Supporting Information

MHAT-Enabled Cascade Radical Annulation to Access *N*-Fused Indoles and Pyrroles

Santosh J. Gharpure,* Simran R. Narang, Rupali S. Chavan
Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400076, India.
Fax: +91-22-2576 7152; Tel: +91-22-2576 7171; E-mail: sjgharpure@iitb.ac.in

Table of Contents

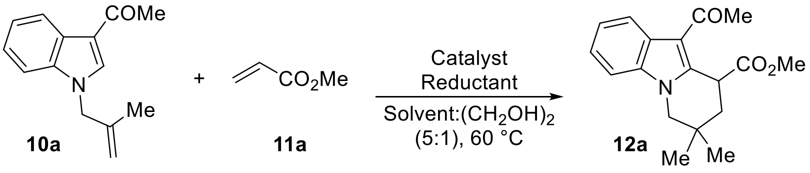
General experimental:

Melting points are recorded using sigma melting point apparatus in capillary tubes and are uncorrected. IR spectra were recorded on Nicolet 6700 spectrophotometer. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker Avance 400 spectrometer. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on Bruker Avance 500 spectrometer. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in the standard fashion with reference to residual $CHCl_3$ (7.26 ppm for ^{1}H) or the central line (77.16 ppm) of $CDCl_3$ (for ^{13}C). In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.

High resolution mass measurements were carried out using Maxis impact (brucker) instrument using direct inlet mode. X-ray diffraction studies were carried out using Bruker Single Crystal Kappa Apex II. For crystal growth, compound was added to a 5 mL glass vial and dissolved in DCM. Then, the glass vial was placed in a dry, ventilated place at room temperature. Analytical thin-layer chromatographies (TLC) were performed on glass plates (7.5 × 2.5 and 9 × 5.0 cm) coated with Merck or Acme's silica gel G containing 13% calcium sulfate as binder or on pre-coated 0.2 mm thick Merck 60 F_{245} silica plates and various combinations of ethyl acetate and hexanes were used as eluent. Visualization of spots was accomplished by either exposure to iodine vapour, vanillin or $KMnO_4$ stain. All small-scale dry reactions were carried out using standard syringe septum technique. Dry ethanol was prepared by refluxing over magnesium and distillation on to molecular sieves. Dry dichloromethane was prepared by refluxing over anhydrous $CaCl_2$ and distillation on to calcium hydride. Dry THF was prepared by refluxing over anhydrous P_2O_5 and distillation over sodium-benzophenone ketyl. All other acceptors, $Fe(acac)_3$, phenyl silane and ethylene glycol are commercial reagents and were used as such without further purification.

Optimization Table

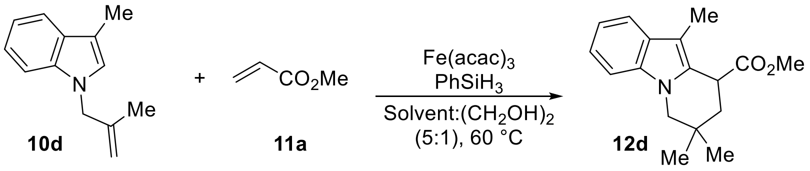
Table S1. Optimisation of MHAT Radical Cyclisation for the Synthesis of Tetrahydropyrido[1,2-*a*]indole **12a**



Entry	**Catalyst (equiv.)**	**Reductant (equiv.)**	**Solvent**	**Yield (%)[b] 12a**	**Yield (%)[b] 10a**
1	Fe(acac)$_3$ (0.3)	PhSiH$_3$ (1.5)	EtOH	32	38
2	Fe(dibm)$_3$ (0.3)	PhSiH$_3$ (1.5)	EtOH	6	83
3	Mn(dpm)$_3$ (0.3)	PhSiH$_3$ (1.5)	EtOH	-	97
4	Fe(acac)$_3$ (1.0)	PhSiH$_3$ (1.5)	EtOH	64 (61)[c]	-
5	Fe(acac)$_3$ (1.0)	PhSiH$_3$ (1.2)	EtOH	48	7
6	Fe(acac)$_3$ (1.0)	PhSiH$_3$ (2.0)	EtOH	50	-
7	Fe(acac)$_3$ (1.0)	TMDS (3.0)	EtOH	21	62
8	Fe(acac)$_3$ (1.5)	PhSiH$_3$ (1.5)	EtOH	59 (57)[c]	-
9	Fe(acac)$_3$ **(1.5)**	PhSiH$_3$ **(2.5)**	**EtOH**	**60 (58)[c]**	-
10	Fe(acac)$_3$ (1.5)	PhSiH$_3$ (1.5)	EtOH	14[d]	9
11	Fe(acac)$_3$ (1.5)	PhSiH$_3$ (1.5)	HFIP	50[d]	20
12	Fe(acac)$_3$ (1.5)	PhSiH$_3$ (1.5)	TFE	54[d]	10
13	Fe(acac)$_3$ (1.5)	PhSiH$_3$ (1.5)	THF	54[e]	7
14	Fe(acac)$_3$ (1.5)	PhSiH$_3$ (2.5)	EtOH	35[f]	40

[a]all reactions were carried out using indole **10a** (0.25 mmol), **11a** (0.75 mmol), solvent (2 mL), $(CH_2OH)_2$ (0.4 mL) at 60 °C for 12h. [b]NMR yield using trimethoxybenzene as internal standard. [c]isolated yield. [d]reaction at rt. [e]2.0 equiv of EtOH was used instead of $(CH_2OH)_2$. [f]without $(CH_2OH)_2$.

Table S2. Optimisation of MHAT Radical Cyclisation for the Synthesis of Tetrahydropyrido[1,2-*a*]indole **12d**



Entry[a]	Fe(acac)$_3$ (equiv.)	PhSiH$_3$ (equiv.)	Solvent	Yield (%)[b] **12d**	Yield (%)[b] **10d**
1	1.0	1.5	EtOH	40	15
2	**1.5**	**2.5**	**EtOH**	**62**	-

[a]all reactions were carried out using indole **10d** (0.25 mmol), **11a** (0.75 mmol), solvent (2 mL), $(CH_2OH)_2$ (0.4 mL) at 60 °C for 12h. [b]isolated yield.

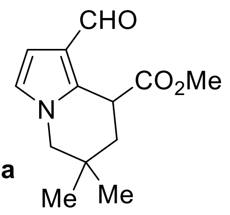
Experimental and Characterization of Compounds:

General procedure for the *N*-alkylation of indole/pyrrole[1]:

To an oven-dried round bottom flask was added NaH (60% in dispersion) (6.280 mmol, 2.5 equiv) and dry DMF under N_2 atmosphere. The round bottom flask was further cooled to 0 ^oC, and then the corresponding indole/pyrrole substrate (3.140 mmol, 1.0 equiv) was added to this solution. The mixture was stirred for 30 min at 0 °C, and subsequently, respective allyl chloride (4.711 mmol, 1.5 equiv) was added dropwise. After the addition was complete, the solution was kept stirring by gradually increasing to room temperature and was stirred for 12 h. After the reaction completion, the reaction was diluted with EtOAc and organic layer was washed with cold water and brine and dried over Na_2SO_4. Concentrate under reduced pressure and purification of residue over a silica gel column using EtOAc-petroleum ether (1.0:9.0) as eluent furnished *N*-alkylated indole /pyrrole derivative.

Representative procedure for the synthesis of *N*-fused pyrrole 14a (gram scale synthesis):

To a magnetically stirred solution of the pyrrole derivative **13a** (1.0 g, 6.703 mmol), methyl acrylate (1.8 mL, 20.108 mmol), $Fe(acac)_3$ (3.6 g, 10.054 mmol), in ethanol (18 mL) and ethylene glycol (3.6 mL) was added $PhSiH_3$ (2.1 mL, 16.767 mmol) under nitrogen atmosphere. The resulting mixture was stirred overnight at 60 ^oC in oil bath. After completion of reaction (TLC control), concentration of reaction mixture under reduced pressure and then diluted with EtOAc. The organic layer was washed with 2N HCl, water and brine and dried over Na_2SO_4 and concentrated under reduced pressure and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydroindolizine derivative **14a** (1.1 g, 72%).



14a

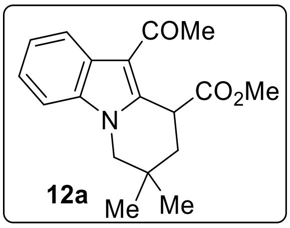
Experimental Procedure:

General procedure for the radical cyclisation reaction:

methyl 10-acetyl-7,7-dimethyl-6,7,8,9-tetrahydropyrido[1,2-a]indole-9-carboxylate (12a):

To a magnetically stirred solution of the indole derivative **10a** (60 mg, 0.281 mmol), methyl acrylate (77 µL, 0.844 mmol), $Fe(acac)_3$ (149 mg, 0.422 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added $PhSiH_3$ (87 µL, 0.703 mmol) under nitrogen atmosphere. The resulting mixture was stirred overnight at 60 ^oC in oil bath. After completion of reaction (TLC control), concentration of reaction mixture under reduced pressure and then diluted with EtOAc. The organic layer was washed with 2N HCl, water and brine and dried over Na_2SO_4

and concentrated under reduced pressure and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydropyrido[1,2-*a*]indole derivative **12a** (49 mg, 58%).



Physical appearance: yellow solid.

Melting point: 132-135 °C.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 2953, 1739, 1639, 1505, 1438, 1263, 1163, 1034, 965, 745 cm^{-1}.

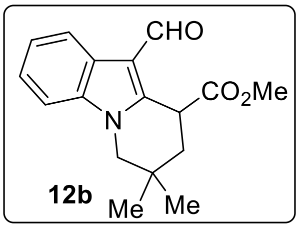
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.93-7.91 (m, 1H), 7.37-7.28 (m, 3H), 4.39 (dd, *J* = 10.4, 7.6 Hz, 1H), 3.89-3.75 (m, 5H), 2.69 (s, 3H), 2.20-2.14 (m, 1H), 1.90 (dd, *J* = 13.2, 10.0 Hz, 1H), 1.22 (s, 3H), 0.98 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, DEPT): δ 194.1 (C), 173.5 (C), 140.7 (C), 136.3 (C), 126.3 (C), 122.6 (CH), 122.2 (CH), 120.6 (CH), 113.8 (C), 110.0 (CH), 53.6 (CH$_2$), 52.3 (CH$_3$), 41.1 (CH), 37.8 (CH$_2$), 31.2 (CH$_3$), 30.5 (C), 27.8 (CH$_3$), 24.1 (CH$_3$).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{18}H_{22}NO_3$ is 300.1594 and was found to be 300.1606.

methyl 10-formyl-7,7-dimethyl-6,7-dihydropyrido[1,2-a]indole-9-carboxylate (12b):

To a magnetically stirred solution of the indole derivative **10b** (60 mg, 0.301 mmol), methyl acrylate (82 μL, 0.903 mmol), Fe(acac)$_3$ (159 mg, 0.452 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added PhSiH$_3$ (93 μL, 0.753 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydropyrido[1,2-*a*]indole derivative **12b** (49 mg, 57%).



Physical appearance: colourless liquid.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 2955, 1737, 1658, 1521, 1445, 1393, 1252, 1170, 1057, 917, 844, 749 cm^{-1}.

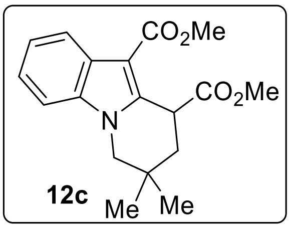
^{1}H NMR (400 MHz, CDCl$_3$): δ 10.20 (s, 1H), 8.12-8.11 (m, 1H), 7.35-7.29 (m, 3H), 4.42-4.38 (m, 1H), 3.87-3.79 (m, 2H), 3.76 (s, 3H), 2.18-2.13 (m, 1H), 2.05-1.99 (m, 1H), 1.22 (s, 3H), 1.01 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, DEPT): δ 184.1 (CH), 173.0 (C), 140.5 (C), 136.1 (C), 126.9 (C), 123.2 (CH), 123.1 (CH), 119.5 (CH), 113.5 (C), 109.8 (CH), 53.5 (CH$_2$), 52.7 (CH$_3$), 39.6 (CH), 37.5 (CH$_2$), 30.5 (C), 27.5 (CH$_3$), 24.3 (CH$_3$).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{17}H_{20}NO_3$ is 286.1438 and was found to be 286.1450.

dimethyl 7,7-dimethyl-6,7,8,9-tetrahydropyrido[1,2-a]indole-9,10-dicarboxylate (12c):

To a magnetically stirred solution of the indole derivative **10c** (60 mg, 0.262 mmol), methyl acrylate (71 µL g, 0.785 mmol), Fe(acac)$_3$ (138 mg, 0.392 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added PhSiH$_3$ (81 µL, 0.654 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydropyrido[1,2-*a*]indole derivative **12c** (33 mg, 40%).



12c

Physical appearance: colourless liquid.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 2953, 1731, 1698, 1536, 1455, 1260, 1215, 1143, 1028, 930, 753 cm^{-1}.

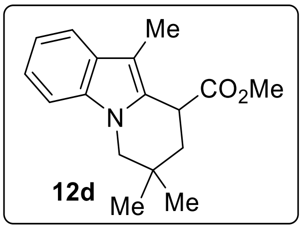
^{1}H NMR (400 MHz, CDCl$_3$): δ 8.16-8.14 (m, 1H), 7.33-7.27 (m, 3H), 4.42-4.38 (m, 1H), 3.95-3.85 (m, 4H), 3.84-3.68 (m, 4H), 2.20-2.04 (m, 1H), 1.95-1.89 (m, 1H), 1.22 (s, 3H), 0.99 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, DEPT): δ 173.9 (C), 166.0 (C), 139.9 (C), 136.0 (C), 126.7 (C), 122.42 (CH), 122.38 (CH), 121.7 (CH), 109.4 (CH), 104.3 (C), 53.6 (CH$_2$), 52.4 (CH$_3$), 50.9 (CH), 40.4 (CH$_3$), 38.0 (CH$_2$), 30.6 (C), 27.7 (CH$_3$), 24.1 (CH$_3$).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{18}H_{22}NO_4$ is 316.1543 and was found to be 316.1560.

methyl 7,7,10-trimethyl-6,7,8,9-tetrahydropyrido[1,2-a]indole-9-carboxylate (12d):

To a magnetically stirred solution of the indole derivative **10d** (60 mg, 0.324 mmol), methyl acrylate (88 µL, 0.971 mmol), Fe(acac)$_3$ (171 mg, 0.486 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added PhSiH$_3$ (100 µL, 0.810 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (0.5:9.5) as eluent furnished tetrahydropyrido[1,2-*a*]indole derivative **12d** (55 mg, 62%).



12d

Physical appearance: colourless liquid.

R*f*: 0.3 (1:9 EtOAc:Petroleum ether).

IR (neat): 2922, 1732, 1578, 1462, 1377, 1191, 739, 699 cm^{-1}.

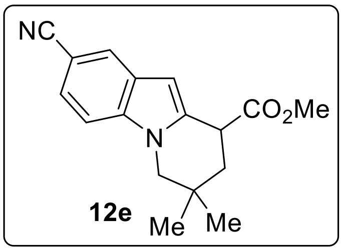
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.27-7.25 (m, 1H), 7.21-7.17 (m, 1H), 7.14-7.10 (m, 1H), 4.08 (t, *J* = 8.4 Hz, 1H), 3.83-3.70 (m, 5H), 2.19 (s, 3H), 2.05 (d, *J* = 8.4 Hz, 2H), 1.20 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, DEPT): δ 174.3 (C), 135.7 (C), 128.7 (C), 127.5 (C), 121.0 (CH), 119.2 (CH), 118.3 (CH), 108.7 (CH), 107.4 (C), 53.5 (CH$_2$), 52.4 (CH), 38.8 (CH$_3$), 38.6 (CH$_2$), 30.8 (C), 27.8 (CH$_3$), 24.4 (CH$_3$), 8.7 (CH$_3$).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{17}H_{22}NO_2$ is 272.1645 and was found to be 272.1644.

methyl 2-cyano-7,7-dimethyl-6,7-dihydropyrido[1,2-a]indole-9-carboxylate (12e):

To a magnetically stirred solution of the indole derivative **10e** (60 mg, 0.305 mmol), methyl acrylate (83 µL, 0.917 mmol), $Fe(acac)_3$ (162 mg, 0.457 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added $PhSiH_3$ (94 µL, 0.762 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydropyrido[1,2-*a*]indole derivative **12e** (20 mg, 23%).



12e

Physical appearance: colourless liquid.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 3431, 2922, 2223, 1732, 1618, 1462, 1378, 1251, 1129, 904, 755 cm^{-1}.

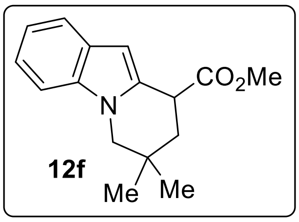
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.40-7.38 (m, 1H), 7.30-7.26 (m, 1H), 6.52 (s, 1H), 4.13-4.08 (m, 1H), 3.91-3.88 (m, 1H), 3.82 (s, 3H), 3.72-3.64 (m, 1H), 2.10-1.96 (m, 2H), 1.23 (s, 3H), 1.06 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 172.7 (C), 137.8 (C), 134.4 (C), 128.0 (C), 125.8 (CH), 124.1 (CH), 121.0 (C), 109.8 (CH), 102.9 (C), 100.4 (CH), 53.7 (CH_2), 52.7 (CH_3), 38.9 (CH), 37.0 (CH_2), 30.4 (C), 28.5 (CH_3), 24.0 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{17}H_{19}N_2O_2$ is 283.1441 and was found to be 283.1442.

methyl 7,7-dimethyl-6,7,8,9-tetrahydropyrido[1,2-a]indole-9-carboxylate (12f):

To a magnetically stirred solution of the indole derivative **10f** (60 mg, 0.350 mmol), methyl acrylate (95 µL, 1.050 mmol), $Fe(acac)_3$ (185 mg, 0.525 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added $PhSiH_3$ (108 µL, 0.875 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydropyrido[1,2-*a*]indole derivative **12f** (45 mg, 50%).



12f

Physical appearance: colourless liquid.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).

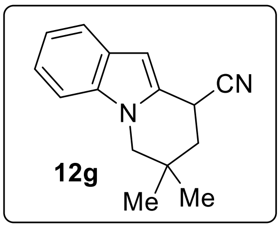
IR (neat): 2955, 1737, 1614, 1459, 1347, 1257, 1165, 1084, 1033, 890, 759, 666 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.22-7.18 (m, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.47 (s, 1H), 4.16-4.12 (m, 1H), 3.92 (dd, *J* = 11.6, 1.6 Hz, 1H), 3.84 (s, 3H), 3.64 (d, *J* = 11.6 Hz, 1H), 2.13-1.95 (m, 2H), 1.25 (s, 3H), 1.09 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, DEPT): δ 173.2 (C), 136.3 (C), 131.7 (C), 128.3 (C), 121.0 (CH), 120.3 (CH), 119.9 (CH), 109.0 (CH), 99.2 (CH), 53.5 (CH$_2$), 52.5 (CH), 39.1 (CH), 37.3 (CH$_2$), 30.4 (C), 28.7 (CH$_3$), 24.0 (CH$_3$).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{16}H_{20}NO_2$ is 258.1488 and was found to be 258.1489.

7,7-dimethyl-6,7,8,9-tetrahydropyrido[1,2-a]indole-9-carbonitrile (12g):



12g

To a magnetically stirred solution of the indole derivative **10f** (60 mg, 0.350 mmol), acrylonitrile (69 μL, 1.05 mmol), Fe(acac)$_3$ (185 mg, 0.525 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added PhSiH$_3$ (108 μL, 0.875 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydropyrido[1,2-*a*]indole derivative **12g** (43 mg, 55%).

Physical appearance: colourless liquid.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 2823, 2196, 1527, 1466, 1377, 1213, 1159, 751 cm^{-1}.

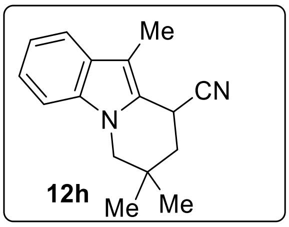
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.62 (d, J = 8.0 Hz, 1H), 7.30-7.22 (m, 2H), 7.19-7.17 (m, 1H), 6.65 (s, 1H), 4.29-4.25 (m, 1H), 3.86 (dd, J = 11.6, 1.2 Hz, 1H), 3.59 (d, J = 12.0 Hz, 1H), 2.14-2.10 (m, 1H), 2.03-1.97 (m, 1H), 1.26 (s, 3H), 1.12 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, DEPT): δ 136.8 (C), 128.1 (C), 128.0 (C), 121.9 (CH), 120.8 (CH), 120.6 (CH), 120.1 (C), 109.2 (CH), 100.6 (CH), 53.3 (CH$_2$), 38.4 (CH$_2$), 30.7 (C), 28.0 (CH), 24.7 (CH$_3$), 24.1 (CH$_3$).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{15}H_{17}N_2$ is 225.1385 and was found to be 225.1386.

7,7,10-trimethyl-6,7,8,9-tetrahydropyrido[1,2-a]indole-9-carbonitrile (12h):

To a magnetically stirred solution of the indole derivative **10d** (60 mg, 0.324 mmol), acrylonitrile (64 μL, 0.971 mmol), Fe(acac)$_3$ (171 mg, 0.486 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added PhSiH$_3$ (100 μL, 0.810 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydropyrido[1,2-*a*]indole derivative **12h** (46 mg, 60%).



12h

Physical appearance: colourless liquid.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 2959, 2924, 2240, 1460, 1371, 1237, 1216, 1143, 1015, 926, 759, 667 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.59 (d, J = 8.0 Hz, 1H), 7.27-7.22 (m, 2H), 7.18-7.14 (m, 1H), 4.24 (t, J = 7.2 Hz, 1H), 3.73-3.72 (m, 2H), 2.43 (s, 3H), 2.13-2.10 (m, 2H), 1.28 (s, 3H), 1.10 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, DEPT): δ 136.0 (C), 128.4 (2 × C), 122.0 (C), 121.9 (CH), 119.7 (CH), 119.5 (C), 118.7 (CH), 108.9 (CH), 53.2 (CH$_2$), 38.2 (CH$_2$), 30.8 (C), 26.7 (CH), 25.2 (CH$_3$), 23.0 (CH$_3$), 8.8 (CH$_3$).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{16}H_{19}N_2$ is 239.1543 and was found to be 239.1552.

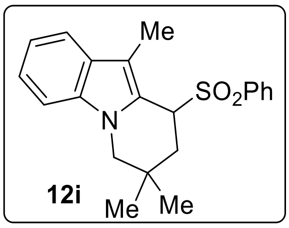
7,7,10-trimethyl-9-(phenylsulfonyl)-6,7,8,9-tetrahydropyrido[1,2-a]indole (12i):

To a magnetically stirred solution of the indole derivative **10d** (60 mg, 0.324 mmol), vinyl sulphone (163 mg, 0.971 mmol), Fe(acac)$_3$ (171 mg, 0.486 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added PhSiH$_3$ (100 µL, 0.810 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydropyrido[1,2-*a*]indole derivative **12i** (34 mg, 30%).

Physical appearance: colourless solid.

Melting point: 138°C-140°C.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).



12i

IR (neat): 2923, 2855, 1643, 1456, 1082, 986, 910, 736, 630 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.62-7.58 (m, 1H), 7.53-7.48 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.22-7.08 (m, 3H), 4.76 (dd, *J* = 10.8, 4.4 Hz, 1H), 3.71 (dd, *J* = 12.0, 2.4 Hz, 1H), 3.45 (d, *J* = 12.0 Hz, 1H), 2.50-2.45 (m, 1H), 2.16-2.09 (m, 1H), 1.81 (s, 3H), 1.18 (s, 3H), 0.45 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, DEPT): δ 137.2 (C), 136.5 (C), 134.0 (CH), 129.7 (2 × CH), 129.0 (2 × CH), 127.9 (C), 122.3 (CH), 122.1 (C), 119.2 (CH), 119.1 (CH), 112.4 (C), 108.9 (CH), 58.6 (CH), 52.4 (CH$_2$), 33.7 (CH$_2$), 33.2 (C), 28.1 (CH$_3$), 25.5 (CH$_3$), 8.5 (CH$_3$).

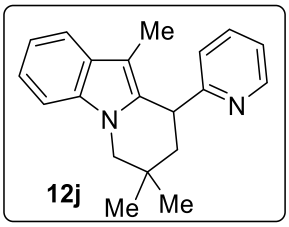
HRMS (ESI, M+H$^+$): m/z calcd. $C_{21}H_{24}NO_2S$ is 354.1522 and was found t o be 354.1521.

7,7,10-trimethyl-9-(pyridin-2-yl)-6,7,8,9-tetrahydropyrido[1,2-a]indole (12j):

To a magnetically stirred solution of the indole derivative **10d** (60 mg, 0.324 mmol), vinyl pyridine (104 µL, 0.971 mmol), Fe(acac)$_3$ (171 mg, 0.486 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added PhSiH$_3$ (100 µL, 0.810 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydropyrido[1,2-*a*]indole derivative **12j** (28 mg, 28%).

Physical appearance: colourless liquid.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).



12j

IR (neat): 2925, 1595, 1462, 1373, 1283, 1216, 1134, 1095, 759, 699, 668 cm^{-1}.

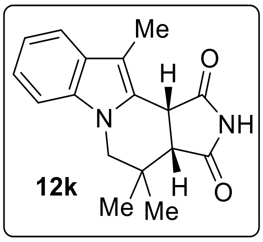
^{1}H NMR (400 MHz, CDCl$_3$): δ 8.58-8.56 (m, 1H), 7.62-7.58 (m, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.20-7.15 (m, 3H), 7.12-7.08 (m, 1H), 4.55 (dd, *J* = 11.2, 6.8 Hz, 1H), 3.96-3.93 (m, 1H), 3.74 (d, *J* = 11.6 Hz, 1H), 2.19-2.13 (m, 1H), 1.88-1.82 (m, 1H), 1.73 (s, 3H), 1.17 (s, 3H), 1.10 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 164.5 (C), 149.1 (CH), 137.0 (CH), 135.8 (C), 132.1 (C), 129.0 (C), 122.6 (CH), 121.6 (CH), 120.7 (CH), 119.0 (CH), 118.1 (CH), 108.7 (CH), 106.9 (C), 53.9 (CH_2), 44.5 (CH_2), 41.7 (CH), 31.2 (C), 28.6 (CH_3), 23.9 (CH_3), 9.2 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{20}H_{23}N_2$ is 291.1855 and was found to be 291.1861.

(3aS*,11bR*)-4,4,11-trimethyl-3a,4,5,11b-tetrahydro-1H-pyrrolo[3',4':3,4]pyrido[1,2-a]indole-1,3(2H)-dione (12k):

To a magnetically stirred solution of the indole derivative **10d** (60 mg, 0.213 mmol), maleimide (62 mg, 0.638 mmol), Fe(acac)$_3$ (113 mg, 0.319 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added $PhSiH_3$ (66 μL, 0.532 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydropyrido[1,2-*a*]indole derivative **12k** (49 mg, 54%).



Physical appearance: colourless liquid.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 2254, 2127, 1715, 1655, 1048, 1023, 999, 823, 761, 609 cm^{-1}.

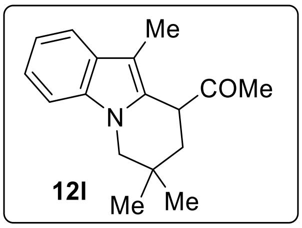
^{1}H NMR (400 MHz, DMSO): δ 11.37 (s, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.12-7.08 (m, 1H), 7.04-7.00 (m, 1H), 4.62 (d, *J* = 8.4 Hz, 1H), 3.91 (d, *J* = 12.2 Hz, 1H), 3.64 (d, *J* = 12.2 Hz, 1H), 3.07 (d, *J* = 8.0 Hz, 1H), 2.35 (s, 3H), 1.09 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (100 MHz, DMSO, DEPT): δ 178.2 (C), 177.0 (C), 135.8 (C), 128.4 (C), 125.3 (C), 121.0 (CH), 119.1 (CH), 118.2 (CH), 109.4 (CH), 108.4 (C), 51.3 (CH_2), 49.0 (CH), 40.3 (CH), 33.7 (C), 25.7 (CH_3), 21.9 (CH_3), 9.5 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{17}H_{19}N_2O_2$ is 283.1441 and was found to be 283.1446.

1-(7,7,10-trimethyl-6,7,8,9-tetrahydropyrido[1,2-a]indol-9-yl)ethan-1-one (12l):

To a magnetically stirred solution of the indole derivative **10d** (57 mg, 0.308 mmol), methyl vinyl ketone (77 μL, 0.924 mmol), Fe(acac)$_3$ (163 mg, 0.461 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added $PhSiH_3$ (95 μL, 0.769 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2:8) as eluent furnished tetrahydropyrido[1,2-*a*]indole derivative **12l** (51 mg, 69%).



Physical appearance: white solid.

Melting point: 108-110°C.

R_f: 0.4 (3:7EtOAc:Petroleum ether).

IR (neat): 2926, 2350, 1707, 1612, 1527, 1464, 1355, 1239, 1162, 1015, 745 cm^{-1}.

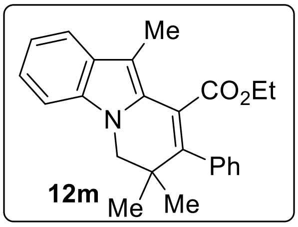
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.29-7.26 (m, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 4.03 (dd, *J* = 10.4, 8.0 Hz, 1H), 3.88 (dd, *J* = 12.0, 1.6 Hz, 1H), 3.69 (d, *J* = 11.6 Hz, 1H), 2.18 (s, 3H), 2.13 (s, 3H), 1.99-1.94 (m, 1H), 1.86-1.81 (m, 1H), 1.23 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 208.9 (C), 136.0 (C), 128.7 (C), 128.0 (C), 121.2 (CH), 119.3 (CH), 118.4 (CH), 108.8 (CH), 107.4 (C), 53.5 (CH_2), 47.5 (CH), 37.6 (CH_2), 31.1 (C), 28.4 (CH_3), 26.4 (CH_3), 24.0 (CH_3), 9.0 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{17}H_{22}NO$ is 256.1695 and was found to be 256.1711.

ethyl 7,7,10-trimethyl-8-phenyl-6,7-dihydropyrido[1,2-a]indole-9-carboxylate (12m):

To a magnetically stirred solution of the indole derivative **10d** (60 mg, 0.324 mmol), alkyne (99 μL, 0.388 mmol), $Fe(acac)_3$ (171 mg, 0.486 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added $PhSiH_3$ (99 μL, 0.807 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydropyrido[1,2-*a*]indole derivative **12m** (65 mg, 56%).



12m

Physical appearance: colourless liquid.

R_f: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 2934, 1706, 1669, 1471, 1079, 741 cm^{-1}.

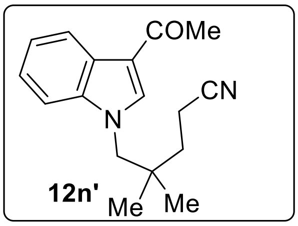
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.49 (m, 1H), 7.39-7.36 (m, 3H), 7.30-7.26 (m, 4H), 7.09-7.05 (m, 1H), 3.93-3.88 (m, 4H), 1.59 (s, 3H), 1.33 (s, 6H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 168.7 (C), 138.3 (C), 136.4 (C), 134.8 (C), 133.9 (C), 129.54 (C), 129.46 (C), 129.1 (2 × CH), 128.4 (2 × CH), 127.9 (CH), 123.3 (CH), 119.4 (CH), 119.1 (CH), 112.2 (C), 108.6 (CH), 60.4 (CH_2), 53.0 (CH_2), 35.8 (C), 24.8 (2 × CH_3), 13.8 (CH_3), 9.7 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{24}H_{26}NO_2$ is 360.1958 and was found to be 360.1964.

5-(3-acetyl-1H-indol-1-yl)-4,4-dimethylpentanenitrile (12n'):

To a magnetically stirred solution of the indole derivative **10a** (60 mg, 0.281 mmol), acrylonitrile (55 μL, 0.844 mmol), $Fe(acac)_3$ (149 mg, 0.422 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added $PhSiH_3$ (76 μL, 0.703 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydropyrido[1,2-*a*]indole derivative **12n'** (38 mg, 51%).



12n'

Physical appearance: colourless liquid.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 2918, 2855, 2232, 1732, 1460, 1381, 1146, 771, 538 cm^{-1}.

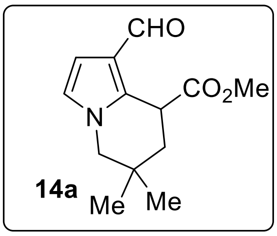
^{1}H NMR (500 MHz, CDCl$_3$): δ 8.38-8.36 (m, 1H), 7.67 (s, 1H), 7.34-7.26 (m, 3H), 3.98 (s, 2H), 2.53 (s, 3H), 2.32 (t, *J* = 8.0 Hz, 2H), 1.74 (t, *J* = 8.0 Hz, 2H), 1.03 (s, 6H).

^{13}C NMR (125 MHz, CDCl$_3$, DEPT): δ 193.2 (C), 138.1 (C), 136.0 (CH), 125.9 (C), 123.6 (CH), 122.6 (2 × CH), 119.8 (C), 117.4 (C), 110.4 (CH), 57.2 (CH$_2$), 36.6 (C), 35.7 (CH$_2$), 27.8 (CH), 24.7 (2 × CH$_3$), 12.4 (CH$_2$).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{17}H_{21}N_2O$ is 269.1648 and was found to be 269.1650.

methyl 1-formyl-6,6-dimethyl-5,6,7,8-tetrahydroindolizine-8-carboxylate (14a):

To a magnetically stirred solution of the pyrrole derivative **13a** (60 mg, 0.402 mmol), methyl acrylate (109 μL, 1.206 mmol), Fe(acac)$_3$ (213 mg, 0.603 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added PhSiH$_3$ (124 μL, 1.005 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydroindolizine derivative **14a** (76 mg, 80%).



Physical appearance: colourless liquid.

R*f*: 0.5 (1:9 EtOAc:Petroleum ether).

IR (neat): 2923, 1742, 1665, 1540, 1503, 1298, 1273, 1170, 1085, 771, 735 cm^{-1}.

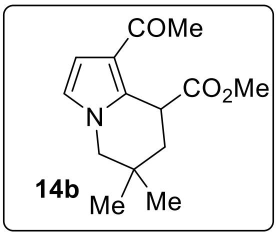
^{1}H NMR (500 MHz, CDCl$_3$): δ 9.72 (s, 1H), 6.61 (d, *J* = 3.0 Hz, 1H), 6.51 (d, *J* = 3.0 Hz, 1H), 4.13-4.10 (m, 1H), 3.73 (s, 3H), 3.72-3.69 (m, 1H), 3.61-3.59 (m, 1H), 2.08-2.03 (m, 1H), 1.86-1.81 (m, 1H), 1.12 (s, 3H), 0.96 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$, DEPT): δ 186.2 (CH), 173.7 (C), 130.9 (C), 122.0 (C), 121.2 (CH), 111.4 (CH), 56.7 (CH$_2$), 52.5 (CH$_3$), 39.4 (CH), 37.8 (CH$_2$), 31.0 (C), 27.5 (CH$_3$), 23.8 (CH$_3$).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{13}H_{18}NO_3$ is 236.1281 and was found to be 236.1285.

methyl 1-acetyl-6,6-dimethyl-5,6,7,8-tetrahydroindolizine-8-carboxylate (14b):

To a magnetically stirred solution of the pyrrole derivative **13b** (60 mg, 0.367 mmol), methyl acrylate (100 μL, 1.103 mmol), Fe(acac)$_3$ (195 mg, 0.551 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added PhSiH$_3$ (113 μL, 0.919 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydroindolizine derivative derivative **14b** (77 mg, 84%).



Physical appearance: colourless solid.

Melting point: 98-100 °C.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 2955, 1743, 1651, 1536, 1499, 1462, 1248, 1197, 1168, 1026, 929, 734, 623, 489 cm^{-1}.

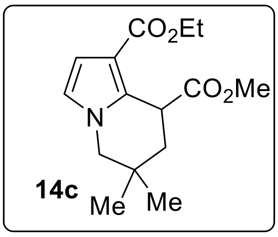
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.54 (d, *J* = 3.0 Hz, 1H), 6.46 (d, *J* = 3.0 Hz, 1H), 4.10-4.07 (m, 1H), 3.73 (s, 3H), 3.70-3.68 (m, 1H), 3.59-3.56 (m, 1H), 2.35 (s, 3H), 2.06-2.02 (m, 1H), 1.76-1.72 (m, 1H), 1.10 (s, 3H), 0.92 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 194.4 (C), 174.1 (C), 130.6 (C), 121.2 (C), 120.1 (CH), 110.7 (CH), 56.8 (CH_2), 52.2 (CH_3), 40.1 (CH), 37.9 (CH_2), 30.9 (C), 27.7 (CH_3), 27.6 (CH_3), 23.5 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{14}H_{20}NO_3$ is 250.1437 and was found to be 250.1441.

1-ethyl 8-methyl 6,6-dimethyl-5,6,7,8-tetrahydroindolizine-1,8-dicarboxylate (14c):

To a magnetically stirred solution of the pyrrole derivative **13c** (60 mg, 0.310 mmol), methyl acrylate (84 μL, 0.931 mmol), Fe(acac)$_3$ (164 mg, 0.465 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added $PhSiH_3$ (96 μL, 0.776 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydroindolizine derivative **14c** (72 mg, 83%).



14c

Physical appearance: colourless liquid.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 2955, 1739, 1696, 1550, 1503, 1465, 1372, 1244, 1197, 1140, 1054, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.60 (d, *J* = 2.8 Hz, 1H), 6.45 (d, *J* = 2.8 Hz, 1H), 4.24-4.18 (m, 2H), 4.14-4.10 (m, 1H), 3.69 (s, 3H), 3.66-3.55 (m, 2H), 2.08-2.03 (m, 1H), 1.79-1.73 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.09 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 174.5 (C), 165.0 (C), 130.7 (C), 120.1 (CH), 112.6 (C), 110.3 (CH), 59.5 (CH_2), 56.9 (CH_2), 52.2 (CH_3), 39.6 (CH), 38.3 (CH_2), 30.9 (C), 27.3 (CH_3), 23.6 (CH_3), 14.6 (CH_3).

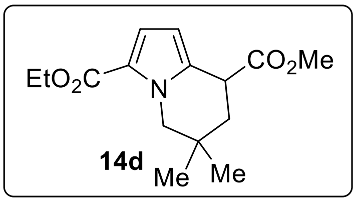
HRMS (ESI, M+Na$^+$): m/z calcd. $C_{15}H_{21}NNaO_4$ is 302.1362 and was found to be 302.1362.

3-ethyl 8-methyl 6,6-dimethyl-5,6,7,8-tetrahydroindolizine-3,8-dicarboxylate (14d):

To a magnetically stirred solution of the pyrrole derivative **13d** (60 mg, 0.310 mmol), methyl acrylate (84 μL, 0.9314 mmol), Fe(acac)$_3$ (164 mg, 0.465 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added $PhSiH_3$ (96 μL, 0.776 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (1.0:9.0) as eluent furnished tetrahydroindolizine derivative **14d** (50 mg, 57%)**.**

Physical appearance: colourless liquid.

R*f*: 0.5 (1:9 EtOAc:Petroleum ether).



14d

IR (neat): 2936, 1744, 1703, 1487, 1467, 1324, 1277, 1240, 1169, 1133, 1048, 976, 756, 663 493 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94 (d, *J* = 4.0 Hz, 1H), 6.07 (d, *J* = 4.0 Hz, 1H), 4.44 (dd, *J* = 13.6 Hz, 1.6 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.92-3.88 (m, 1H), 3.76-3.71 (m, 4H), 1.96-1.86 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.13 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 173.2 (C), 161.4 (C), 131.5 (C), 121.7 (C), 117.8 (CH), 107.2 (CH), 59.7 (CH_2), 56.1 (CH_2), 52.5 (CH), 39.1 (CH_3), 36.5 (CH_2), 30.3 (C), 28.4 (CH_3), 23.8 (CH_3), 14.6 (CH_3).

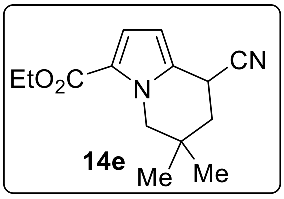
HRMS (ESI, M+H$^+$): m/z calcd. $C_{15}H_{22}NO_4$ is 280.1543 and was found to be 280.1548.

ethyl 8-cyano-6,6-dimethyl-5,6,7,8-tetrahydroindolizine-3-carboxylate (14e):

To a magnetically stirred solution of the pyrrole derivative **13d** (60 mg, 0.310 mmol), acrylonitrile (61 μL, 0.9314 mmol), Fe(acac)$_3$ (164 mg, 0.465 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added $PhSiH_3$ (96 μL, 0.776 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydroindolizine derivative **14e** (46 mg, 60%).

Physical appearance: colourless sticky liquid.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).



14e

IR (neat): 2963, 1700, 1487, 1433, 1389, 1302, 1241, 1179, 1135, 1051, 934, 793, 755, 541 cm^{-1}.

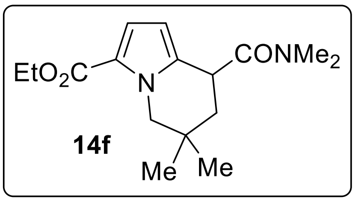
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.97 (d, *J* = 4.0 Hz,, 1H), 6.27 (d, *J* = 4.0 Hz,, 1H), 4.35 (d, *J* = 15.0 Hz, 1H), 4.25 (q, *J* = 7.0 Hz, 2H), 4.10-4.07 (m, 1H), 3.81 (d, *J* = 15.0 Hz, 1H), 2.05-2.01 (m, 1H), 1.94-1.90 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.17 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 161.2 (C), 127.3 (C), 122.8 (C), 119.8 (C), 117.9 (CH), 107.8 (CH), 60.0 (CH_2), 55.9 (CH_2), 37.2 (CH_2), 30.4 (C), 27.7 (CH), 24.5 (CH_3), 24.0 (CH_3),14.5 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{14}H_{19}N_2O_2$ is 247.1441 and was found to be 247.1446.

ethyl 8-(dimethylcarbamoyl)-6,6-dimethyl-5,6,7,8-tetrahydroindolizine-3-carboxylate (14f):

To a magnetically stirred solution of the pyrrole derivative **13d** (60 mg, 0.310 mmol), *N*,*N*-dimethylacrylamide (38 µL, 0.372 mmol), Fe(acac)$_3$ (164 mg, 0.465 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added PhSiH$_3$ (96 µL, 0.776 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (1:1) as eluent furnished tetrahydroindolizine derivative **14f** (58 mg, 64%).



14f

Physical appearance: colourless liquid.

R*f*: 0.5 (1:1 EtOAc:Petroleum ether).

IR (neat): 2958, 1698, 1650, 1485, 1240, 1132, 754 cm^{-1}.

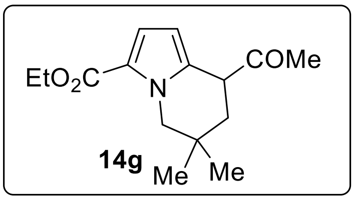
^{1}H NMR (400 MHz, CDCl$_3$): δ 6.93 (d, *J* = 4.0 Hz, 1H), 5.83 (d, *J* = 4.0 Hz, 1H), 4.49 (dd, *J* = 13.6 Hz, 1.6 Hz, 1H), 4.23 (q, *J* = 6.8 Hz, 2H), 4.11 (dd, *J* = 11.6, 6.0, 1H), 3.71 (d, *J* = 13.6 Hz, 1H), 3.11 (s, 3H), 3.01 (s, 3H), 1.98 (t, *J* = 13.2 Hz, 1H), 1.71-1.66 (m, 1H), 3.75 1.32 (t, *J* = 6.8 Hz, 3H), 1.13 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, DEPT): δ 172.4 (C), 161.4 (C), 133.2 (C), 121.7 (C), 118.0 (CH), 106.0 (CH), 59.7 (CH$_2$), 56.1 (CH$_2$), 37.9 (CH), 36.9 (CH$_2$), 36.6 (CH$_3$), 36.3 (CH$_3$), 30.3 (C), 28.9 (CH$_3$), 24.1 (CH$_3$), 14.6 (CH$_3$).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{16}H_{25}N_2O_3$ is 293.1859 and was found to be 293.1864.

ethyl 8-acetyl-6,6-dimethyl-5,6,7,8-tetrahydroindolizine-3-carboxylate (14g):

To a magnetically stirred solution of the pyrrole derivative **13d** (60 mg, 0.310 mmol), methyl vinyl ketone (78 µL, 0.930 mmol), Fe(acac)$_3$ (164 mg, 0.465 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added PhSiH$_3$ (96 µL, 0.776 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2:8) as eluent furnished tetrahydroindolizine derivative **14g** (54 mg, 66%).



14g

Physical appearance: colourless liquid.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 2960, 1701, 1485, 1243, 1138, 1034, 758 cm^{-1}.

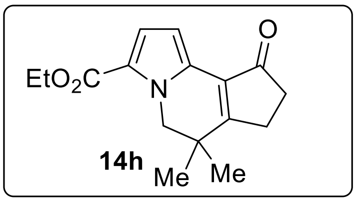
^{1}H NMR (400 MHz, CDCl$_3$): δ 6.95 (d, *J* = 4.0 Hz, 1H), 5.93 (d, *J* = 4.0 Hz, 1H), 4.47 (dd, *J* = 13.6 Hz, 1.6 Hz, 1H), 4.28-4.22 (m, 2H), 3.87 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.71 (d, *J* = 14.0 Hz, 1H), 2.16 (s, 3H), 1.84-1.70 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.14 (s, 3H), 0.95 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, DEPT): δ 207.6 (C), 161.4 (C), 131.8 (C), 122.0 (C), 117.9 (CH), 107.3 (CH), 59.8 (CH$_2$), 56.1 (CH$_2$), 47.8 (CH), 36.4 (CH$_2$), 30.6 (C), 28.6 (CH$_3$), 27.3 (CH$_3$), 23.7 (CH$_3$), 14.6 (CH$_3$).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{15}H_{22}NO_3$ is 264.1594 and was found to be 264.1593.

Ethyl6,6-dimethyl-9-oxo-6,7,8,9-tetrahydro-5H-cyclopenta[g]indolizine-3-carboxylate (14h):

To a magnetically stirred solution of the pyrrole derivative **13d** (60 mg, 0.310 mmol), cyclopentenone (78 µL, 0.931 mmol), Fe(acac)$_3$ (164 mg, 0.465 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added PhSiH$_3$ (96 µL, 0.776 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (3.0:7.0) as eluent furnished tetrahydroindolizine derivative **14h** (30 mg, 35%).



14h

Physical appearance: yellow solid.

Melting point: 102-104 °C.

R*f*: 0.5 (3:7 EtOAc:Petroleum ether).

IR (neat): 2915, 1697, 1491, 1404, 1339, 1256, 1128, 1036, 759 cm^{-1}.

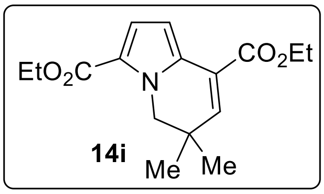
^{1}H NMR (400 MHz, CDCl$_3$): δ 6.98 (d, J = 4.0 Hz, 1H), 6.68 (d, J = 3.6 Hz, 1H), 4.34 (s, 2H), 4.28 (q, J = 7.2 Hz, 2H), 2.71-2.69 (m, 2H), 2.57-2.55 (m, 2H), 1.36 (t, J = 7.2 Hz, 3H), 1.23 (s, 6H).

^{13}C NMR (100 MHz, CDCl$_3$, DEPT): δ 204.3 (C), 174.8 (C), 161.7 (C), 129.7 (2 × C), 122.8 (C), 118.3 (CH), 106.3 (CH), 60.1 (CH$_2$), 54.0 (CH$_2$), 36.0 (C), 35.5 (CH$_2$), 25.2 (CH$_2$), 23.9 (2 × CH$_3$), 14.5 (CH$_3$).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{16}H_{20}NO_3$ is 274.1437 and was found to be 274.1448.

diethyl 6,6-dimethyl-5,6-dihydroindolizine-3,8-dicarboxylate (14i) & diethyl 6,6-dimethyl-5,6,7,8-tetrahydroindolizine-3,8-dicarboxylate (14i'):

To a magnetically stirred solution of the pyrrole derivative **13d** (60 mg, 0.310 mmol), vinyl pyridine (100 µL, 0.931 mmol), Fe(acac)$_3$ (164 mg, 0.465 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added PhSiH$_3$ (96 µL, 0.776 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished dihydroindolizine derivative derivative **14i** (17 mg, 19%) and tetrahydroindolizine derivative **14i'** (35 mg, 38%).



14i

diethyl 6,6-dimethyl-5,6-dihydroindolizine-3,8-dicarboxylate (14i):

Physical appearance: colourless liquid.

R*f*: 0.5 (1:9 EtOAc:Petroleum ether).

IR (neat): 2924, 1735, 1701, 1468, 1431, 1369, 1241, 1134, 772, 509 cm^{-1}.

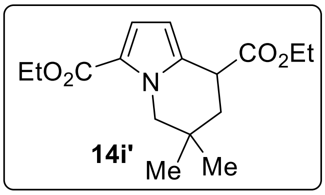
^{1}H NMR (400 MHz, CDCl$_3$): δ 6.95 (d, J = 4.0 Hz, 1H), 6.77 (s, 1H), 6.70 (d, J = 4.1 Hz, 1H), 4.33-4.27 (m, 4H), 4.25 (s, 2H), 1.39-1.25 (m, 6H), 1.15 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 164.8 (C), 161.5 (C), 144.2 (CH), 131.0 (C), 122.8 (2 × C), 117.8 (CH), 109.2 (CH), 61.1 (CH_2), 60.0 (CH_2), 52.9 (CH_2), 33.7 (C), 25.4 (2 × CH_3), 14.5 (CH_3), 14.4 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{16}H_{22}NO_4$ is 292.1543 and was found to be 292.1557.

diethyl 6,6-dimethyl-5,6,7,8-tetrahydroindolizine-3,8-dicarboxylate (14i'):

Physical appearance: colourless liquid.



R_f: 0.5 (1:9 EtOAc:Petroleum ether).

IR (neat): 2960, 1737, 1699, 1485, 1432, 1408, 1387, 1323, 1239, 1176, 1133, 1030, 755 cm^{-1}.

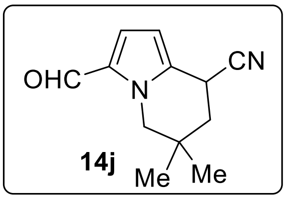
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (d, J = 4.0 Hz, 1H), 6.09 (d, J = 3.6 Hz, 1H), 4.46- 4.42 (m, 1H), 4.31- 4.18 (m, 4H), 3.90-3.85 (m, 1H), 3.73 (d, J = 13.6 Hz, 1H), 1.96- 1.84 (m, 2H), 1.35-1.28 (m, 6H), 1.14 (s, 3H), 0.97 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 172.7 (C), 161.4 (C), 131.7 (C), 121.7 (C), 117.8 (CH), 107.2 (CH), 61.4 (CH_2), 59.7 (CH_2), 56.2 (CH_2), 39.3 (CH_2), 36.4 (CH), 30.3 (C), 28.5 (CH_3), 23.9 (CH_3), 14.6 (CH_3), 14.3 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{16}H_{24}NO_4$ is 294.1710 and was found to be 294.1709.

3-formyl-6,6-dimethyl-5,6,7,8-tetrahydroindolizine-8-carbonitrile (14j):

To a magnetically stirred solution of the pyrrole derivative **13e** (60 mg, 0.402 mmol), acrylonitrile (79 µL, 1.206 mmol), Fe(acac)$_3$ (213 mg, 0.603 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added $PhSiH_3$ (124 µL, 1.005 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydroindolizine derivative **14j** (54 mg, 65%).



Physical appearance: colourless liquid.

R_f: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 2966, 2250, 1661, 1493, 1408, 1261, 1216, 1039, 931, 807, 759, 668 cm^{-1}.

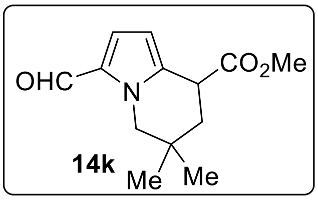
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.49 (s, 1H), 6.95 (d, J = 4.0 Hz, 1H), 6.37 (d, J = 4.0 Hz, 1H), 4.39 (d, J = 16.0 Hz, 1H), 4.29-4.09 (m, 1H), 3.86 (d, J = 12.0 Hz, 1H), 2.09-2.04 (m, 1H), 1.99-1.93 (m, 1H), 1.18 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 179.7 (CH), 132.0 (C), 130.5 (C), 124.6 (CH), 119.3 (C), 109.3 (CH), 56.0 (CH_2), 37.1 (CH_2), 30.3 (C), 27.6 (CH), 24.4 (CH_3), 23.9 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{12}H_{15}N_2O$ is 203.1178 and was found to be 203.1179.

methyl 3-formyl-6,6-dimethyl-5,6,7,8-tetrahydroindolizine-8-carboxylate (14k):

To a magnetically stirred solution of the pyrrole derivative **13e** (60 mg, 0.402 mmol), methyl acrylate (109 µL, 1.206 mmol), Fe(acac)$_3$ (213 mg, 0.603 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added PhSiH$_3$ (124 µL, 1.005 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydroindolizine derivative **14k** (60 mg, 63%).



14k

Physical appearance: yellow liquid.

R*f*: 0.3 (2:8 EtOAc:Petroleum ether).

IR (neat): 2956, 2873, 1741, 1659, 1438, 1322, 1289, 1196, 1170, 1071, 970, 820, 765 cm^{-1}.

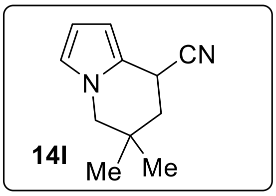
^{1}H NMR (500 MHz, CDCl$_3$): δ 9.43 (s, 1H), 6.89 (d, *J* = 4.0 Hz, 1H), 6.18 (d, *J* = 4.0 Hz, 1H), 4.45 (d, *J* = 13.5 Hz, 1H), 3.93-3.89 (m, 1H), 3.79-3.76 (s, 4H), 1397-1.86 (m, 2H), 1.13 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$, DEPT): δ 179.1 (CH), 172.6 (C), 134.9 (C), 131.3 (C), 124.7 (CH), 109.0 (CH), 56.3 (CH$_2$), 52.6 (CH$_3$), 38.9 (CH), 36.4 (CH$_2$), 30.2 (C), 28.2 (CH$_3$), 23.8 (CH$_3$).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{13}H_{18}NO_3$ is 236.1299 and was found to be 236.1298.

6,6-dimethyl-5,6,7,8-tetrahydroindolizine-8-carbonitrile (14l):

To a magnetically stirred solution of the pyrrole derivative **13f** (60 mg, 0.454 mmol), methyl acrylate (123 µL, 0.136 mmol), Fe(acac)$_3$ (240 mg, 0.681 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added PhSiH$_3$ (140 µL, 1.134 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (1.0:9.0) as eluent furnished tetrahydroindolizine derivative **14l** (39 mg, 45%).



14l

Physical appearance: yellow liquid.

R*f*: 0.5 (1:9 EtOAc:Petroleum ether).

IR (neat): 2956, 2923, 2242, 1463, 1378, 1291, 1217, 1074, 1046, 976, 765, 715 cm^{-1}.

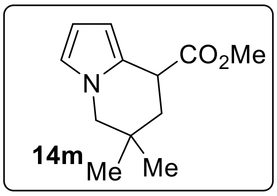
^{1}H NMR (400 MHz, CDCl$_3$): δ 6.55-6.54 (m, 1H), 6.24-6.22 (m, 1H), 6.20-6.18 (m, 1H), 4.10-4.06 (m, 1H), 3.62 (s, 2H), 2.06-1.90 (m, 2H), 1.16 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, DEPT): δ 120.8 (C), 120.7 (C), 120.0 (CH), 108.8 (CH), 106.9 (CH), 56.3 (CH$_2$), 38.5 (CH$_2$), 31.0 (C), 27.4 (CH), 24.0 (CH$_3$), 23.8 (CH$_3$).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{11}H_{15}N_2$ is 175.1242 and was found to be 175.1241.

methyl 6,6-dimethyl-5,6,7,8-tetrahydroindolizine-8-carboxylate (14m):

To a magnetically stirred solution of the pyrrole derivative **13f** (60 mg, 0.454 mmol), methyl acrylate (123 μL, 0.136 mmol), Fe(acac)$_3$ (240 mg, 0.681 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added PhSiH$_3$ (140 μL, 1.134 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (1.0:9.0) as eluent furnished tetrahydroindolizine derivative **14m** (52 mg, 50%).



Physical appearance: colorless liquid.

R*f*: 0.5 (1:9 EtOAc:Petroleum ether).

IR (neat): 2954, 1734, 1631, 1435, 1369, 1288, 1239, 1173, 1113, 701 cm^{-1}.

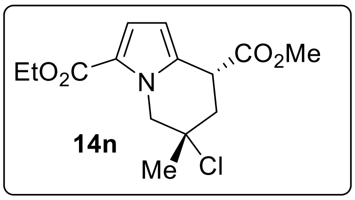
^{1}H NMR (400 MHz, CDCl$_3$): δ 6.50 (s, 1H), 6.15 (t, *J* = 3.6 Hz, 1H), 6.05-6.04 (m, 1H), 3.91-3.86 (m, 1H), 3.76 (s, 3H), 3.67-3.58 (m, 2H), 1.98-1.83 (m, 2H), 1.11 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, DEPT): δ 173.8 (C), 123.9 (C), 119.8 (CH), 108.0 (CH), 105.8 56.7 (CH$_2$), 52.3 (CH$_3$), 38.4 (CH), 37.7 (CH$_2$), 30.8 (C), 28.3 (CH$_3$), 23.6 (CH$_3$).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{12}H_{18}NO_2$ is 208.1332 and was found to be 208.1333.

3-ethyl 8-methyl (6S*,8R*)-6-chloro-6-methyl-5,6,7,8-tetrahydroindolizine-3,8-dicarboxylate (14n):

To a magnetically stirred solution of the pyrrole derivative **13g** (60 mg, 0.281 mmol), methyl acrylate (76 μL, 0.842 mmol), Fe(acac)$_3$ (149 mg, 0.421 mmol), in ethanol (2 mL) and ethylene glycol (0.4 mL) was added PhSiH$_3$ (86 μL, 0.702 mmol) as described in **12a** and purification of residue over a silica gel column using EtOAc-petroleum ether (1:1) as eluent furnished tetrahydroindolizine derivative **14n** as a single diastereomer (43 mg, 51%).



Physical appearance: colourless liquid.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 2253, 1740, 1697, 1439, 1374, 1326, 1240, 1160, 1039, 919, 752, 668 cm^{-1}.

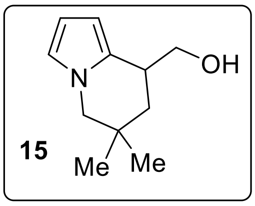
^{1}H NMR (400 MHz, CDCl$_3$): δ 6.98 (d, *J* = 4.0 Hz, 1H), 6.17 (d, *J* = 4.0 Hz, 1H), 5.03 (dd, *J* = 15.2 Hz, 2.4 Hz, 1H), 4.28-4.22 (m, 3H), 4.04 (d, *J* = 15.2 Hz, 1H), 3.80 (s, 3H), 2.45-2.39 (m, 1H), 2.26-2.20 (m, 1H), 1.82 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$, DEPT): δ 172.1 (C), 161.3 (C), 130.6 (C), 122.0 (C), 118.1 (CH), 107.3 (CH), 65.4 (C), 60.0 (CH$_2$), 57.5 (CH$_2$), 52.7 (CH$_3$), 39.4 (CH), 38.0 (CH$_2$), 30.8 (CH$_3$), 14.6 (CH$_3$).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{14}H_{19}ClNO_4$ is 300.0997 and was found to be 300.0999.

(6,6-dimethyl-5,6,7,8-tetrahydroindolizin-8-yl)methanol (15):

To a magnetically stirred solution of the tetrahydroindolizine derivative **14m** (40 mg, 0.193 mmol) in THF, LAH powder (29 mg, 0.772 mmol) was added at 0 °C. After that, the reaction mixture was heated at 80 °C. After the completion of the reaction, it was quenched using sat. Na_2SO_4 solution. Then, the reaction was filtered using ethyl acetate. The purification of residue over a silica gel column using EtOAc-petroleum ether (3:7) as eluent furnished alcohol derivative **15** (28 mg, 82%).


15

Physical appearance: yellow liquid.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 2952, 1445, 1366, 1286, 1169, 1075, 1028, 987, 900, 775, 700 cm^{-1}.

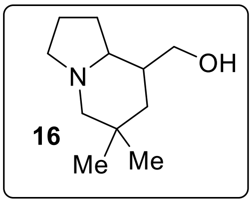
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.52 (s, 1H), 6.17 (t, *J* = 3.2 Hz, 1H), 6.00-5.99 (m, 1H), 3.88-3.78 (m, 2H), 3.64-3.58 (m, 2H), 3.08-3.02 (m, 1H), 1.86 (s, 1H), 1.76-1.12 (m, 1H), 1.55 (t, *J* = 12.0 Hz, 1H), 1.11 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 128.2 (C), 119.6 (CH), 107.9 (CH), 103.4 (CH), 65.9 (CH_2), 56.8 (CH_2), 38.2 (CH_2), 34.5 (CH), 30.8 (C), 28.9 (CH_3), 23.6 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{11}H_{18}NO$ is 180.1382 and was found to be 180.1380.

(6,6-dimethyloctahydroindolizin-8-yl)methanol (16):

To a magnetically stirred solution of the alcohol derivative **15** (26 mg, 0.145 mmol) in EtOAc, Pd /C powder (15 mg, 0.145 mmol) was added at rt. After that, H_2 bladder was attached to the r.b flask for continuous flow of H_2 gas in reaction mixture. After the completion of the reaction, it was filtered through the celite bed and concentrated under reduced pressure to furnish alcohol derivative **16** (23 mg, 88%).


16

Physical appearance: yellow liquid.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 2952, 1286, 1169, 1071, 1056, 925, 965, 775, 700, 559 cm^{-1}.

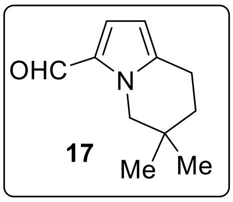
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.57-3.53 (m, 1H), 3.42-3.37 (m, 1H), 3.00-2.96 (m, 1H), 2.67 (d, *J* = 10.8 Hz, 1H), 1.97-1.87 (m, 2H), 1.98-1.86 (m, 3H), 1.82-1.60 (m, 3H), 1.53-1.41 (m, 3H), 1.04 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 67.4 (CH), 65.7 (CH_2), 65.0 (CH_2), 54.3 (CH_2), 41.5 (CH_2), 40.8 (CH), 31.5 (C), 29.9 (CH_3), 28.7 (CH_2), 26.2 (CH_3), 21.1 (CH_2).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{11}H_{22}NO$ is 184.1695 and was found to be 180.1698.

6,6-dimethyl-5,6,7,8-tetrahydroindolizine-3-carbaldehyde (17):

To a magnetically stirred solution of the aldehyde derivative **14k** (31 mg, 0.132 mmol) in DMSO (3 mL) was added LiCl (11 mg, 0.263 mmol). The resulting mixture was stirred at 150 °C in oil bath under nitrogen atmosphere. After completion of reaction (TLC control), diluted with EtOAc and cold water. The organic layer was washed with brine and dried over Na_2SO_4 and concentrated under reduced pressure and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished tetrahydroindolizine derivative **17** (14 mg, 61%).



17

Physical appearance: colourless liquid.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 2930, 1735, 1659, 1438, 1215, 1171, 1044, 928, 872, 758, 669 cm^{-1}.

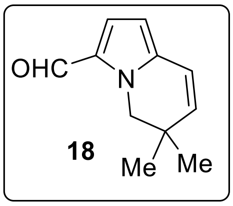
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.38 (s, 1H), 6.88 (d, *J* = 3.6 Hz, 1H), 5.99 (d, *J* = 3.6 Hz, 1H), 4.08 (s, 2H), 2.85 (t, *J* = 6.8 Hz, 2H), 1.61 (t, *J* = 6.8 Hz, 2H), 1.05 (s, 6H)

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 178.3 (CH), 139.5 (C), 130.9 (C), 108.0 (2 × CH), 56.6 (CH_2), 32.9 (CH_2), 29.9 (C), 26.1 (2 × CH_3), 20.8 (CH_2).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{11}H_{16}NO$ is 178.1226 and was found to be 178.1227.

6,6-dimethyl-5,6-dihydroindolizine-3-carbaldehyde (18):

To a magnetically stirred solution of the tetrahydroindolizine derivative **17** (35 mg, 0.298 mmol) in 1,4-dioxane (3 ml), SeO_2 (132 mg, 1.194 mmol) was added at rt. The resulting mixture was then heated at 110 °C in oil bath under nitrogen atmosphere. After the completion of the reaction, concentration of reaction mixture under reduced pressure and then diluted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4 and concentrated under reduced pressure and purification of residue over a silica gel column using EtOAc-petroleum ether (2.0:8.0) as eluent furnished dihydroindolizine derivative **18 (**17 mg, 48%).



18

Physical appearance: colourless liquid.

R*f*: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 2958, 1720, 1466, 1356, 1166, 816, 770, 668, 590, 538 cm^{-1}.

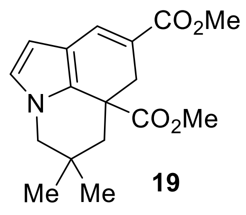
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.48 (s, 1H), 6.87 (d, *J* = 4.0 Hz, 1H), 6.30 (d, *J* = 9.6 Hz, 1H), 6.10 (d, *J* = 4.0 Hz, 1H), 5.81 (d, *J* = 9.6 Hz, 1H), 4.27 (s, 2H), 1.12 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 179.5 (CH), 138.4 (CH), 136.8 (C), 131.6 (C), 124.8 (CH), 116.7 (CH), 108.0 (CH), 54.0 (CH_2), 33.2 (C), 26.2 (2 × CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{11}H_{14}NO$ is 176.1069 and was found to be 176.1069.

Dimethyl 5,5-dimethyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline-6a,8(7H)-dicarboxylate (19):

To a magnetically stirred solution of the pyrrole derivative **14a** (60 mg, 0.255 mmol) in DMF (3 ml) was added NaH (25 mg, 0.637 mmol) at 0 °C. Stir the reaction for 30 minutes at 0 °C then added methyl acrylate (35 µL, 0.382 mmol) in the reaction mixture. After the completion of reaction, quenched it with water and extracted by ethyl acetate (3x5mL) and dried over Na_2SO_4. Then concentrate it under reduced pressure and purification of residue over a silica gel column using EtOAc-petroleum ether (1.0:9.0) as eluent furnished oxazinane derivative **19** (32 mg, 53%).



19

Physical appearance: colourless liquid.

R*f*: 0.5 (1:9 EtOAc:Petroleum ether).

IR (neat): 2925, 1730, 1697, 1597, 1550, 1516, 1435, 1343, 1274, 1242, 1194, 965, 818 cm^{-1}.

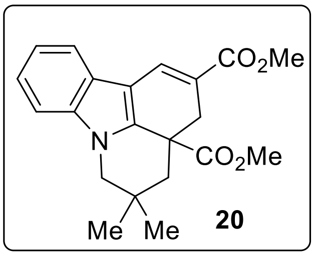
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 2.8 Hz, 1H), 6.56 (d, *J* = 2.8 Hz, 1H), 6.20 (d, *J* = 2.4 Hz, 1H), 3.74-3.69 (m, 4H), 3.58-3.50 (m, 4H), 3.38 (d, *J* = 16.0 Hz, 1H), 2.37 (dd, *J* = 16.4, 3.2 Hz, 1H), 2.30 (d, *J* = 14.0 Hz, 1H), 1.62 (d, *J* = 14.0 Hz, 1H), 1.06 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 175.6 (C), 168.2 (C), 135.0 (CH), 130.2 (C), 121.4 (CH), 119.9 (C), 116.6 (C), 107.0 (CH), 56.3 (CH_2), 52.7 (CH_3), 51.6 (CH_3), 44.9 (CH_2), 41.7 (C), 36.9 (CH_2), 33.2 (C), 28.3 (CH_3), 25.9 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. $C_{17}H_{22}NO_4$ is 304.1543 and was found to be 304.1555.

Dimethyl 5,5-dimethyl-5,6-dihydro-3H-pyrido[3,2,1-jk]carbazole-2,3a(4H)-dicarboxylate (20):

To a magnetically stirred solution of the indole derivative **12b** (60 mg, 0.210 mmol) in DMF (3 ml) was added NaH (21 mg, 0.526 mmol) at 0 °C. Stir the reaction for 30 minutes at 0 °C then added methyl acrylate (30 µL, 0.315 mmol) in the reaction mixture. After the completion of reaction, quenched it with water and extracted by ethyl acetate (3x5mL) and dried over Na_2SO_4. Then concentrate it under reduced pressure and and purification of residue over a silica gel column using EtOAc-petroleum ether (1.0:9.0) as eluent furnished oxazinane derivative **20** (30 mg, 50%).



20

Physical appearance: colourless liquid.

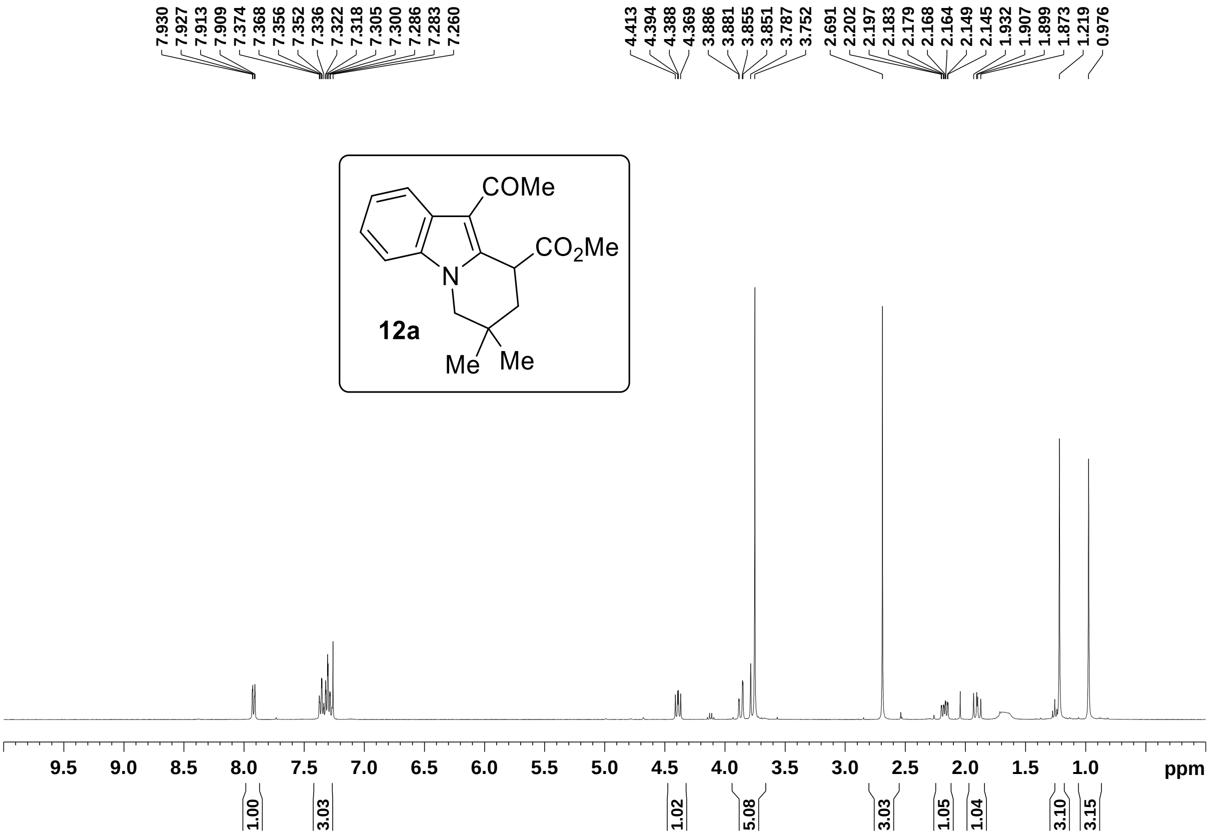
R*f*: 0.5 (2:8 EtOAc:Petroleum ether).

IR (neat): 2923, 1731, 1694, 1599, 1540, 1434, 1391, 1326, 1251, 1193, 1090, 1041, 745 cm^{-1}.

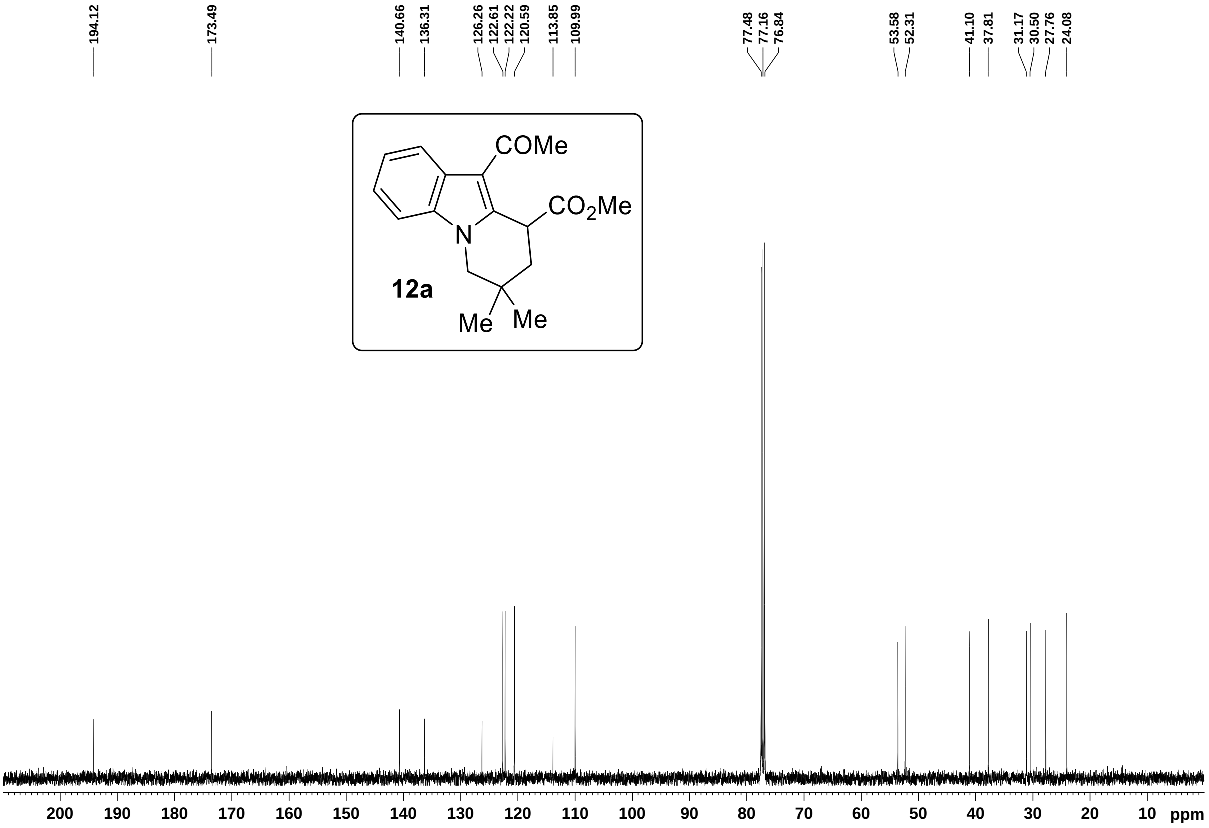
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 2.8 Hz, 1H), 7.69-7.67 (m, 1H), 7.35-7.32 (m, 1H), 7.25-7.19 (m, 2H), 3.94 (d, *J* = 12.0 Hz, 1H), 3.79 (s, 3H), 3.60 (d, *J* = 12.0 Hz, 1H), 3.56 (s, 3H), 3.49 (d, *J* = 16.4 Hz, 1H), 2.51-2.46 (m, 2H), 1.71 (d, *J* = 14.0 Hz, 1H), 1.15 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 174.9 (C), 168.1 (C), 138.2 (C), 138.1 (C), 132.8 (CH), 125.9 (C), 122.0 (CH), 121.5 (CH), 118.8 (CH), 118.8 (C), 110.2 (C), 110.2 (CH), 53.8 (CH_2), 52.8 (CH_3), 51.7 (CH_3), 44.9 (CH_2), 42.6 (C), 37.2 (CH_2), 32.7 (C), 28.9 (CH_3), 25.8 (CH_3).

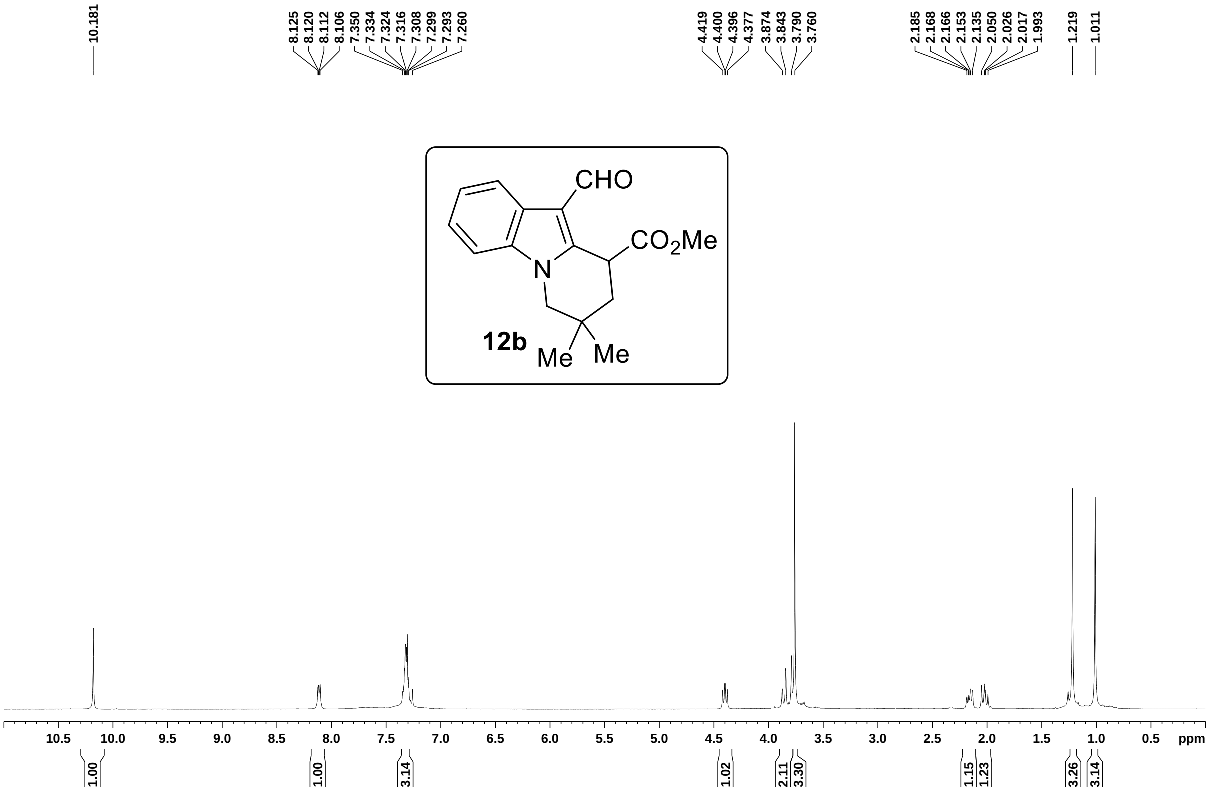
HRMS (ESI, M+H$^+$): m/z calcd. $C_{21}H_{24}NO_4$ is 354.1699 and was found to be 354.1717.



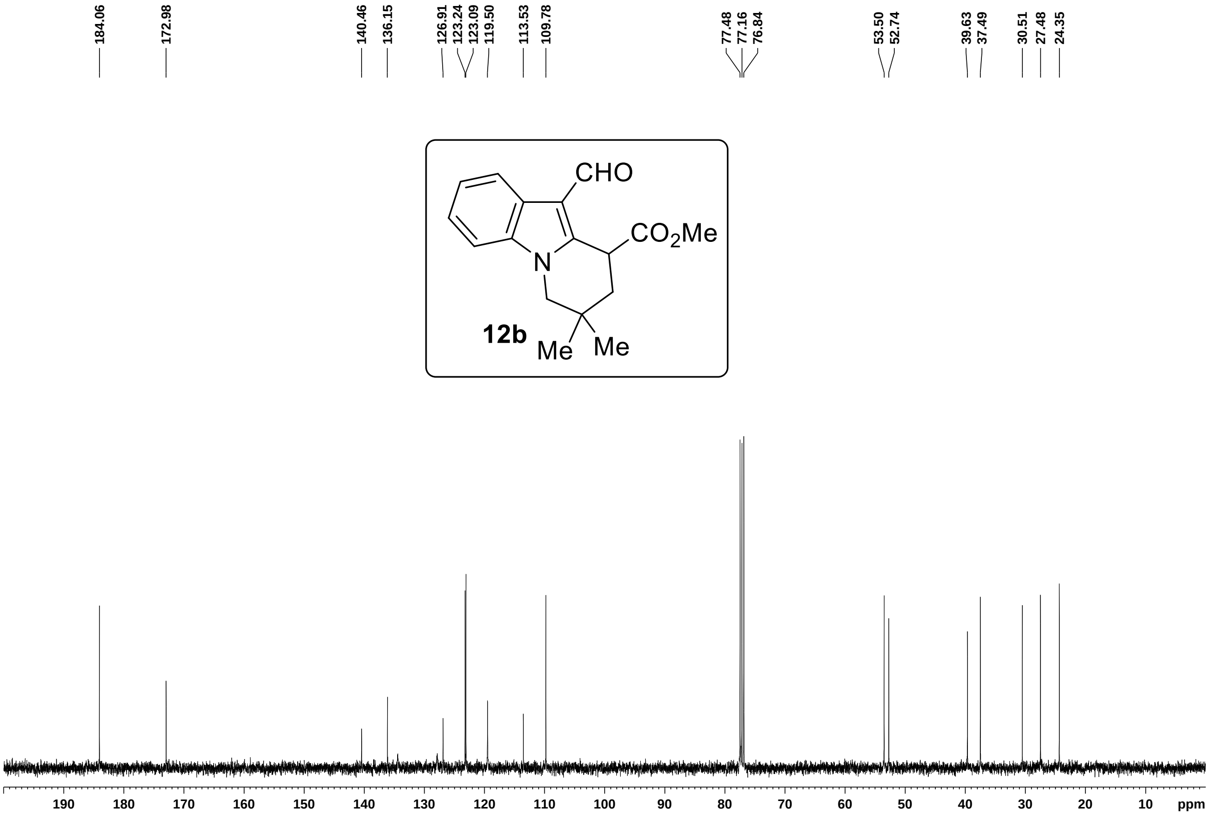
^{1}H NMR spectrum of 12a (400 MHz, CDCl$_3$)



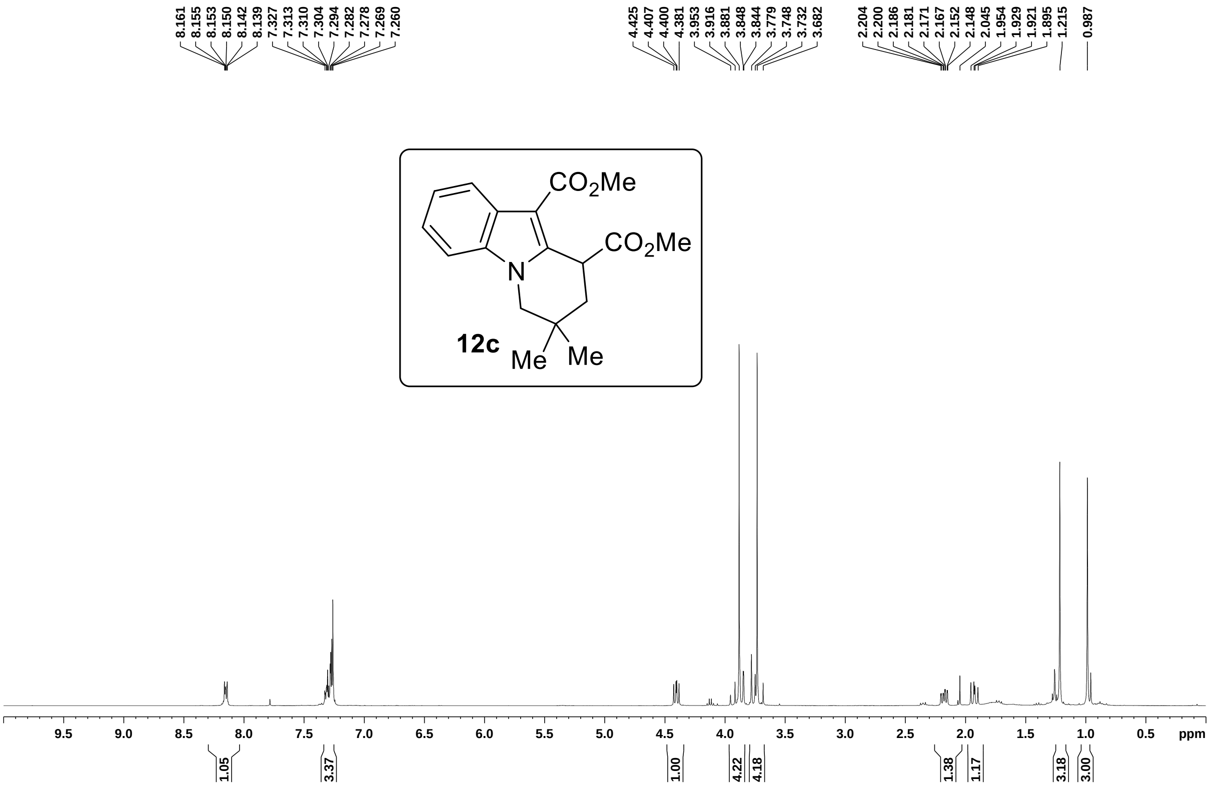
^{13}C NMR spectrum of 12a (100 MHz, CDCl$_3$)



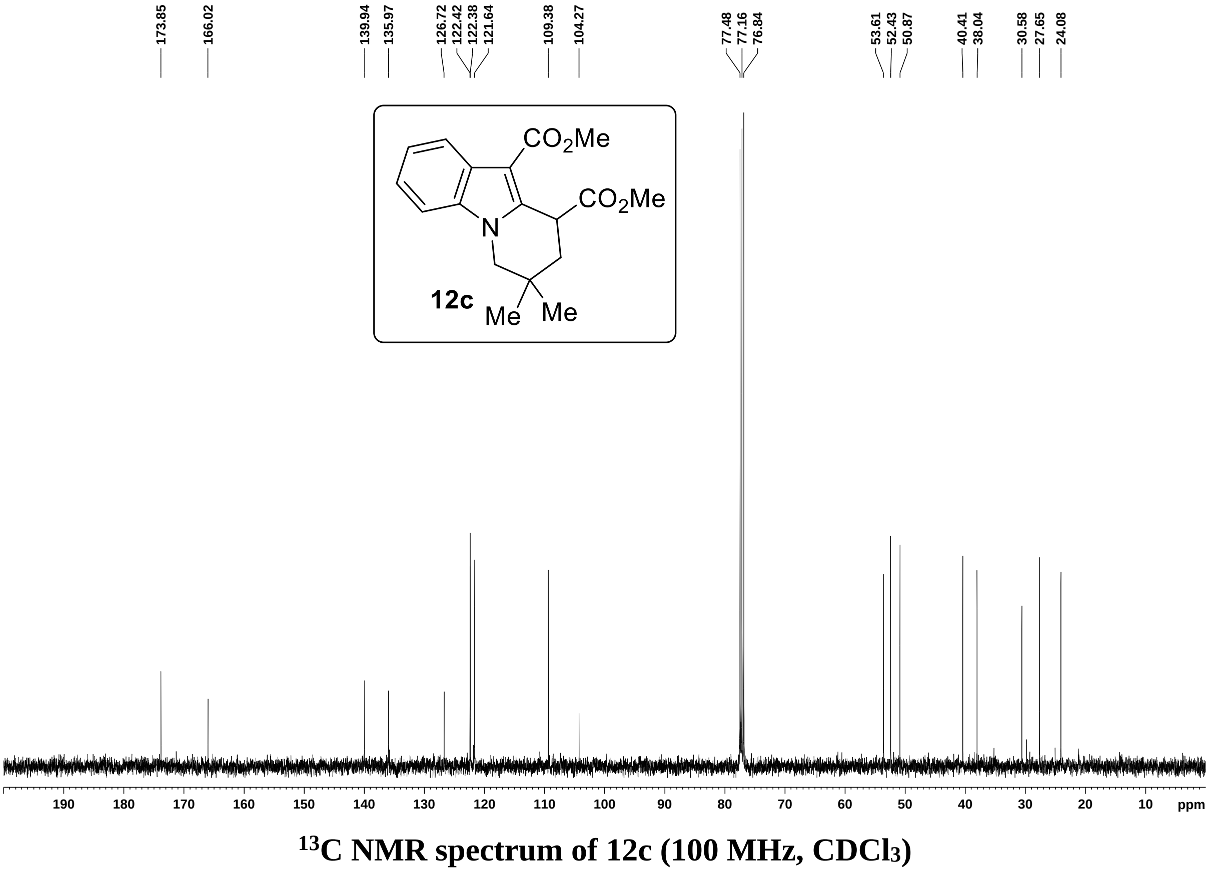
^{1}H NMR spectrum of 12b (400 MHz, $CDCl_3$)



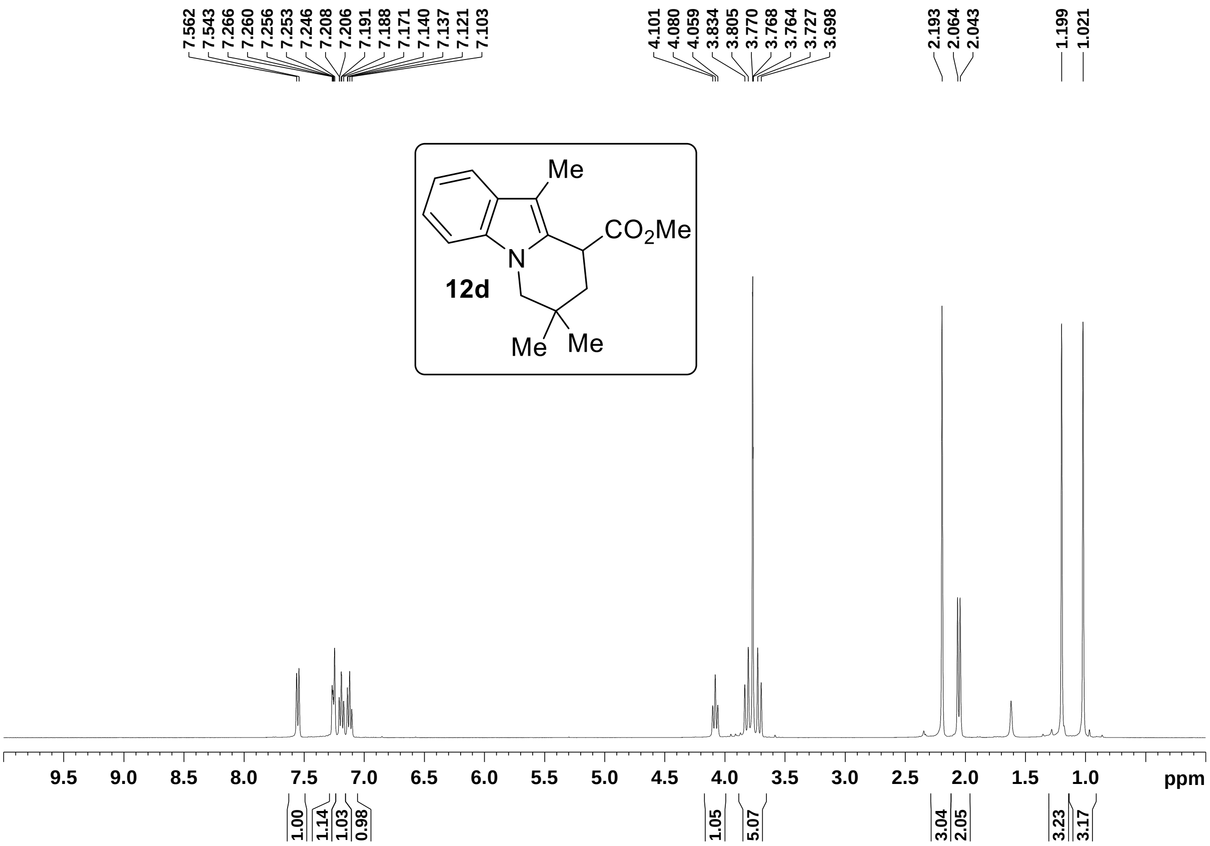
^{13}C NMR spectrum of 12b (100 MHz, $CDCl_3$)



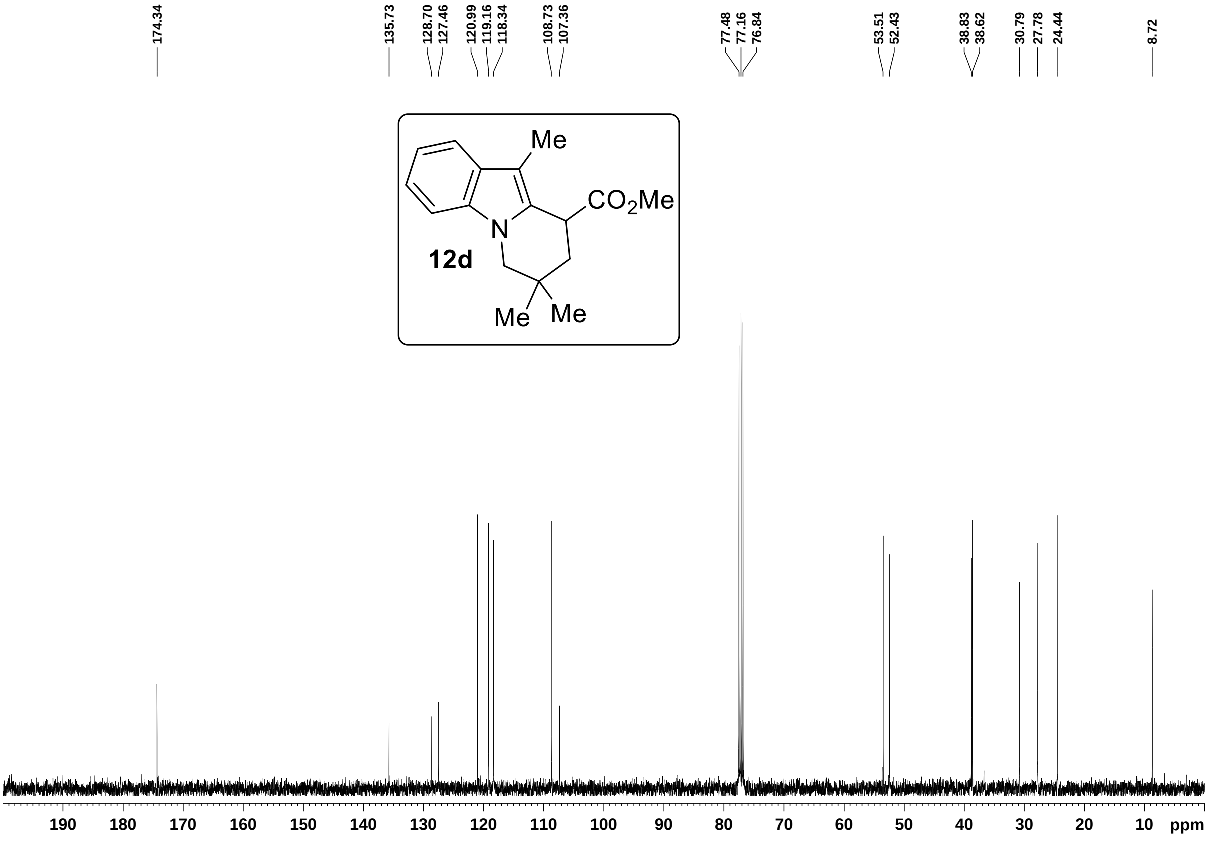
^{1}H NMR spectrum of 12c (400 MHz, CDCl$_3$)



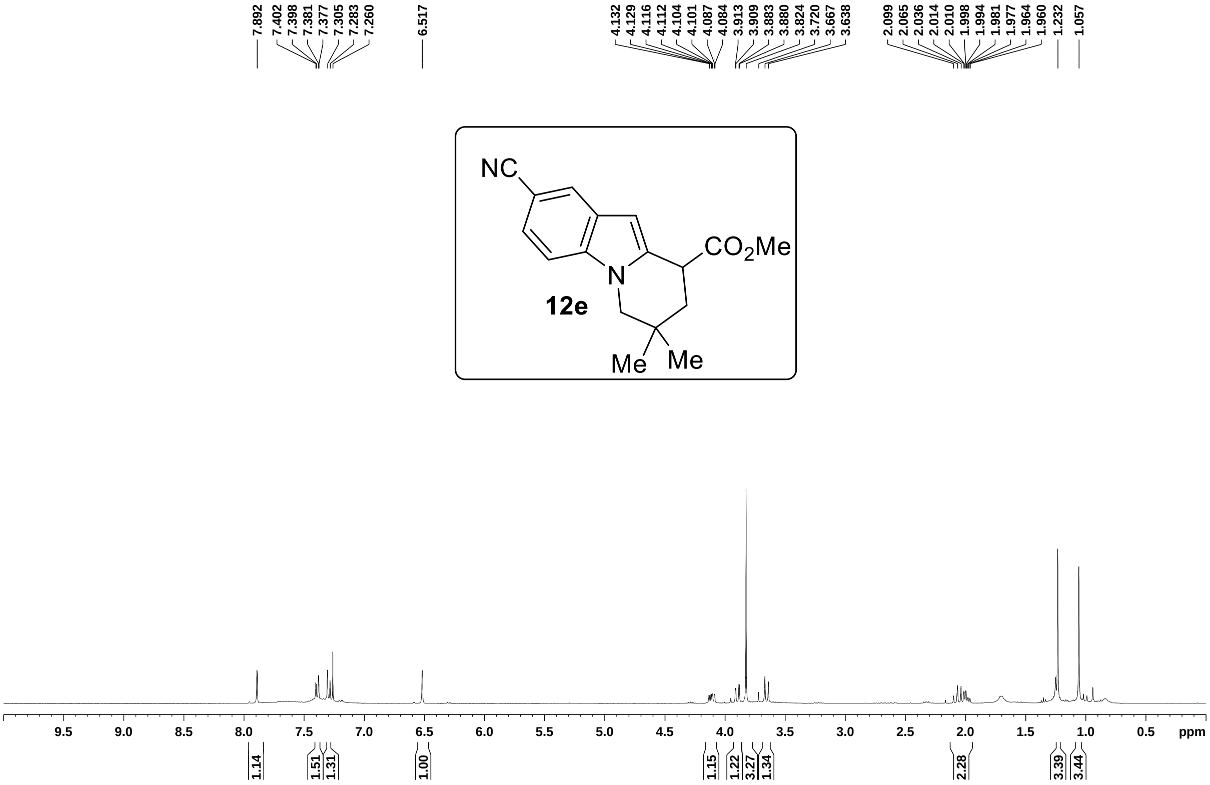
^{13}C NMR spectrum of 12c (100 MHz, CDCl$_3$)



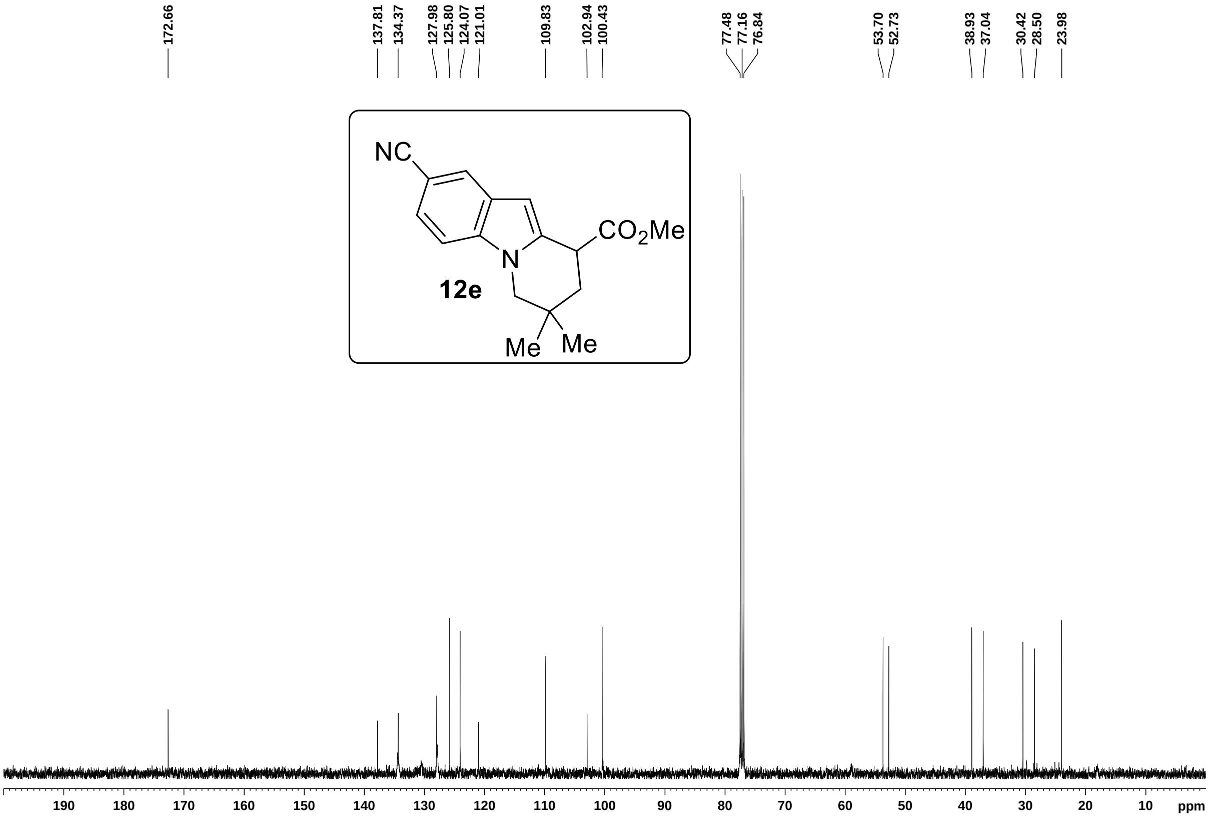
^{1}H NMR spectrum of 12d (400 MHz, $CDCl_3$)



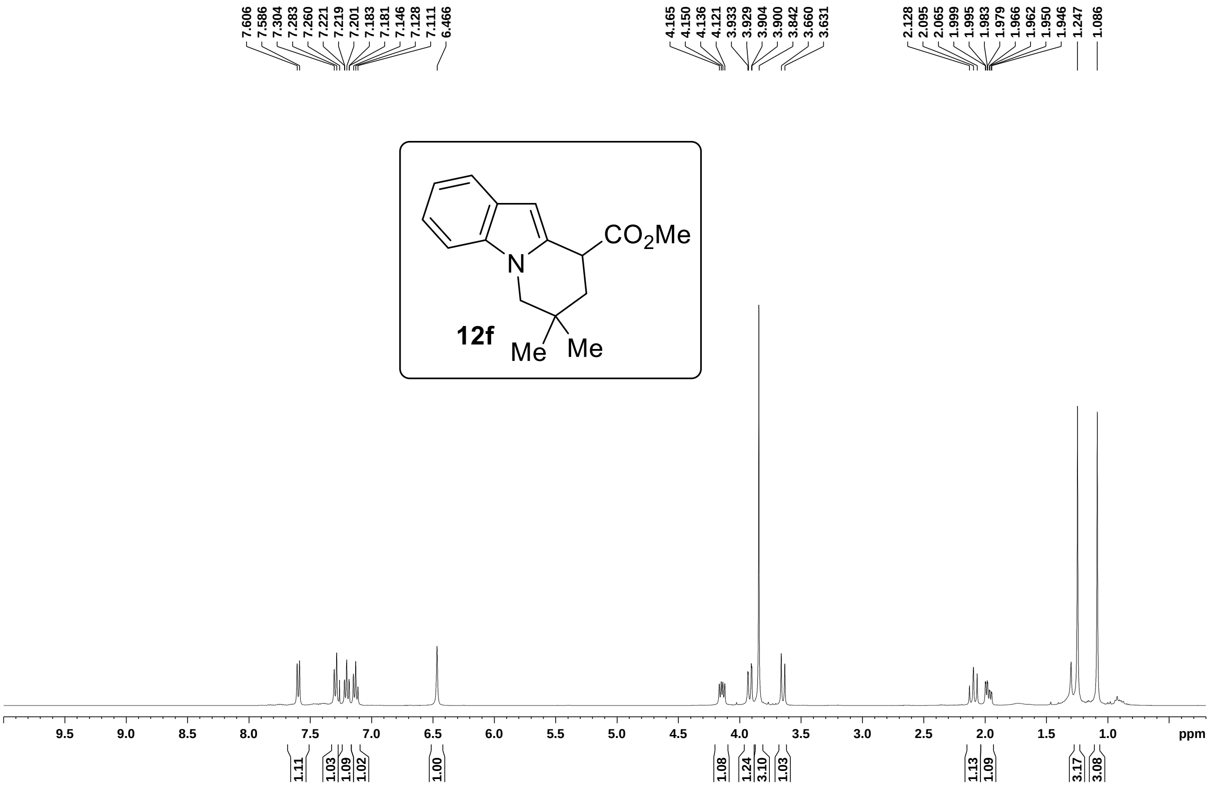
^{13}C NMR spectrum of 12d (100 MHz, $CDCl_3$)



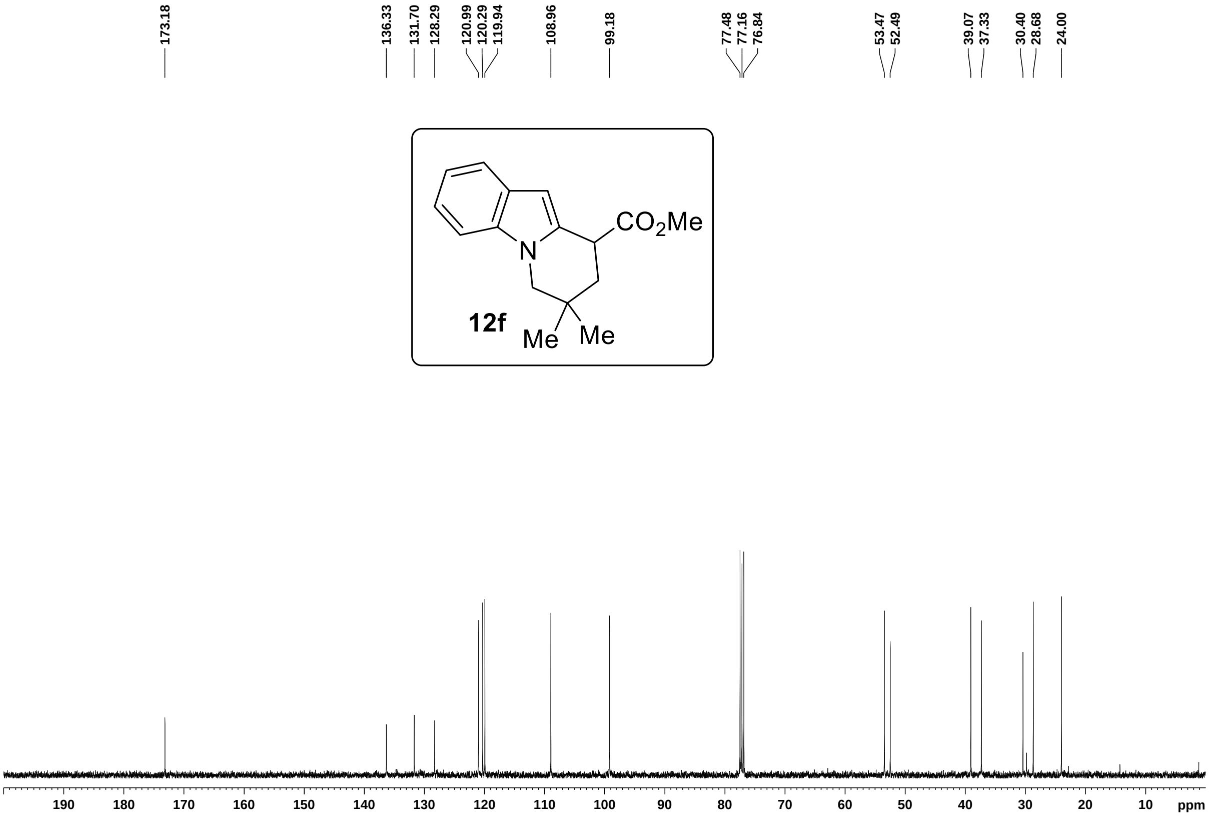
^{1}H NMR spectrum of 12e (400 MHz, CDCl$_3$)



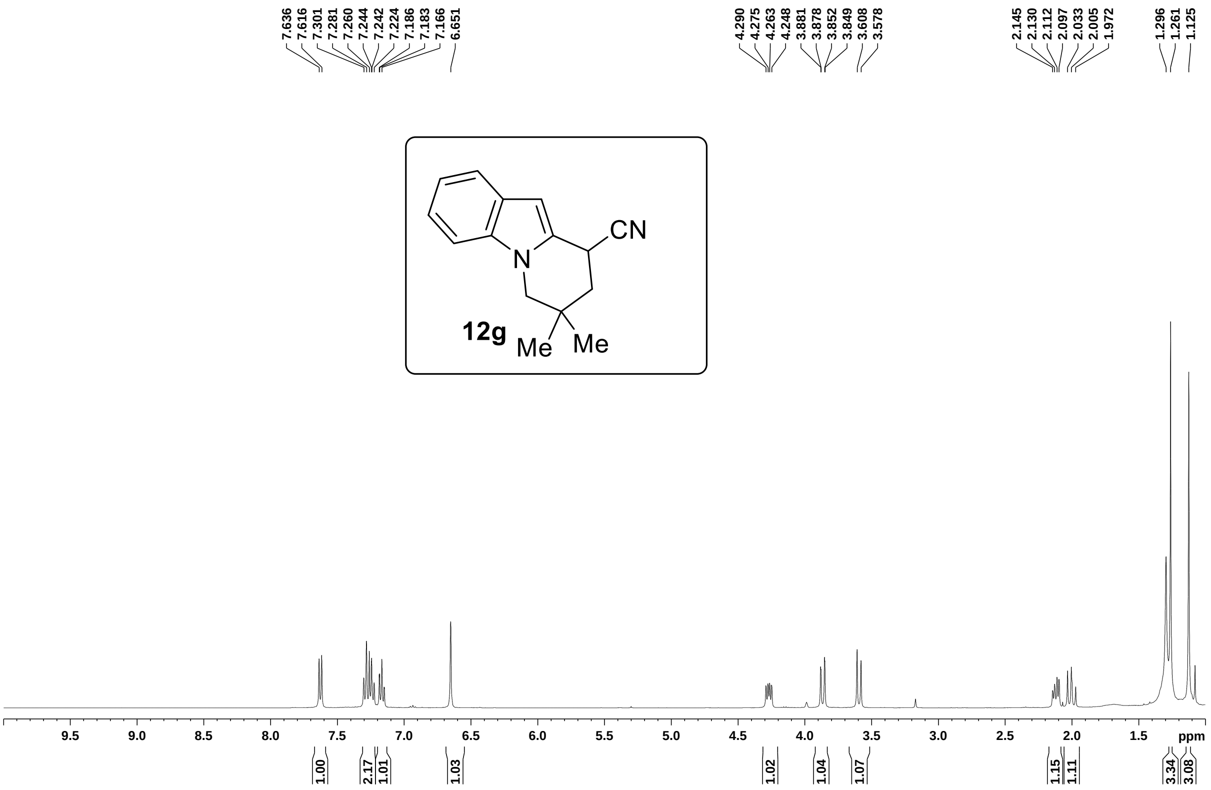
^{13}C NMR spectrum of 12e (100 MHz, CDCl$_3$)



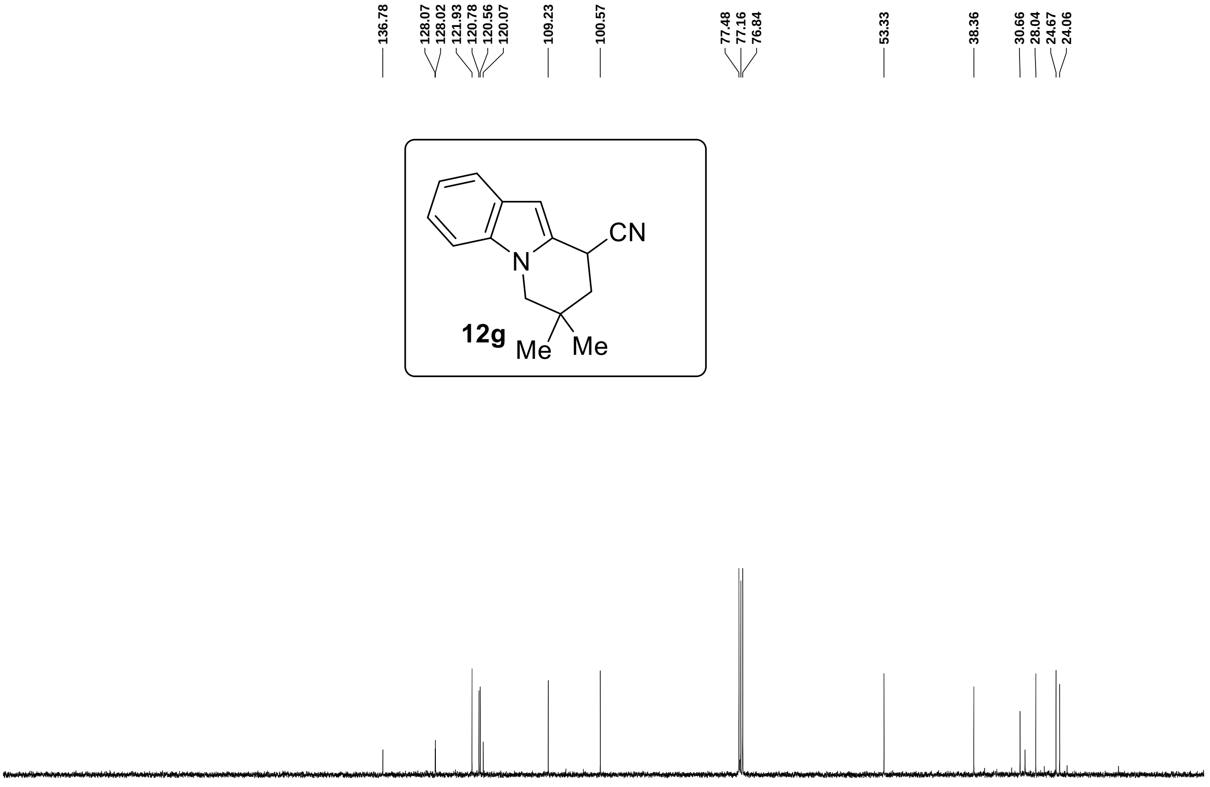
^{1}H NMR spectrum of 12f (400 MHz, CDCl$_3$)



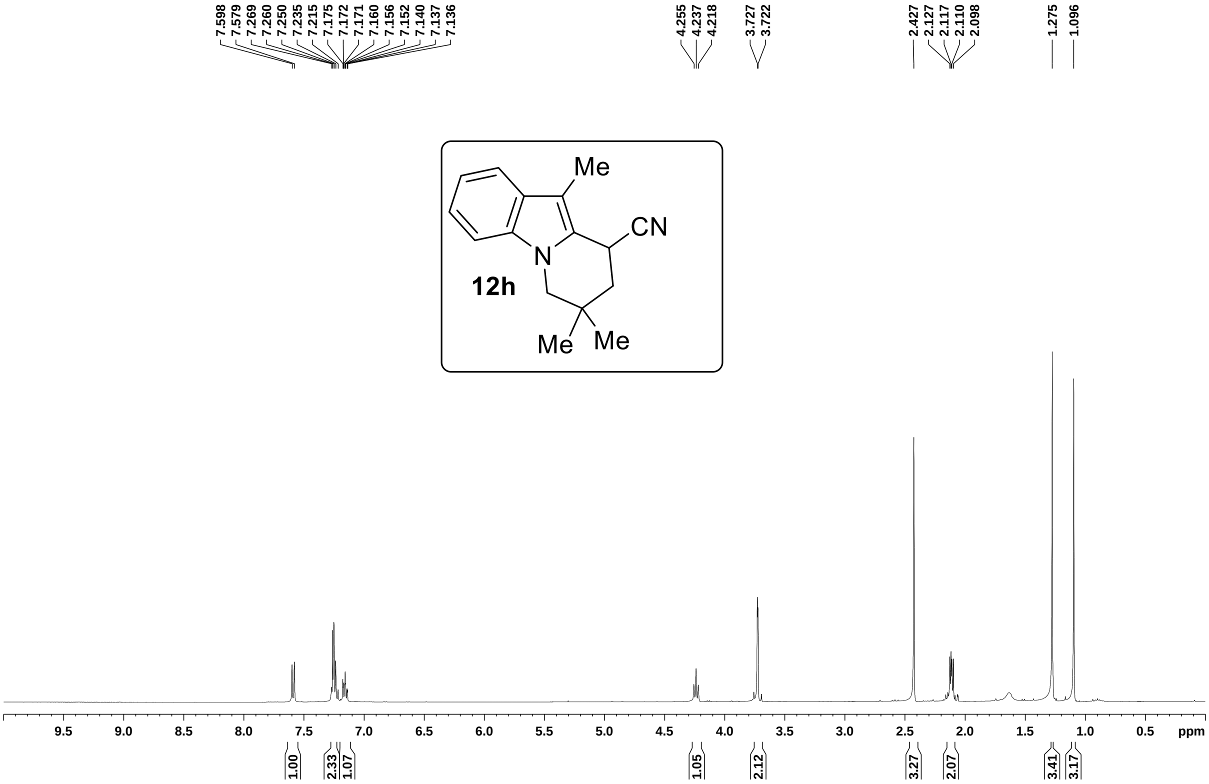
^{13}C NMR spectrum of 12f (100 MHz, CDCl$_3$)



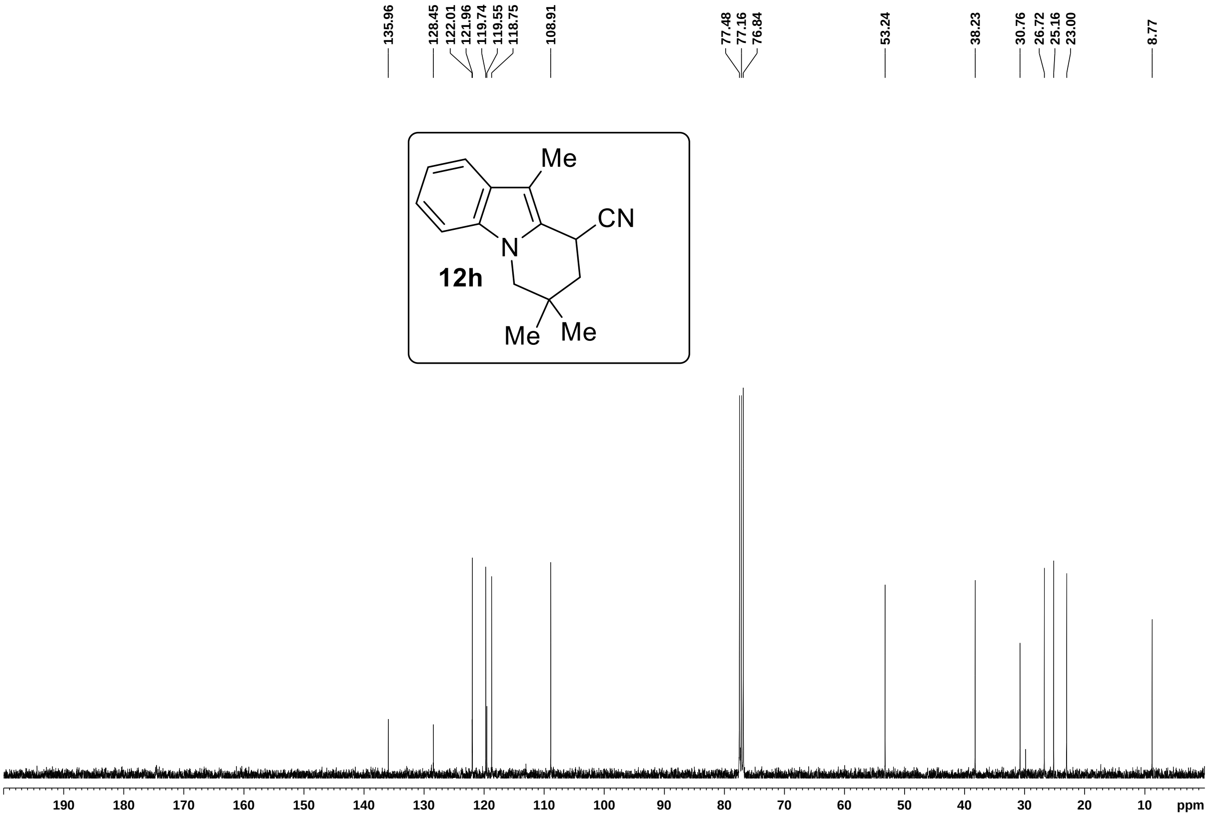
^{1}H NMR spectrum of 12g (400 MHz, CDCl$_3$)



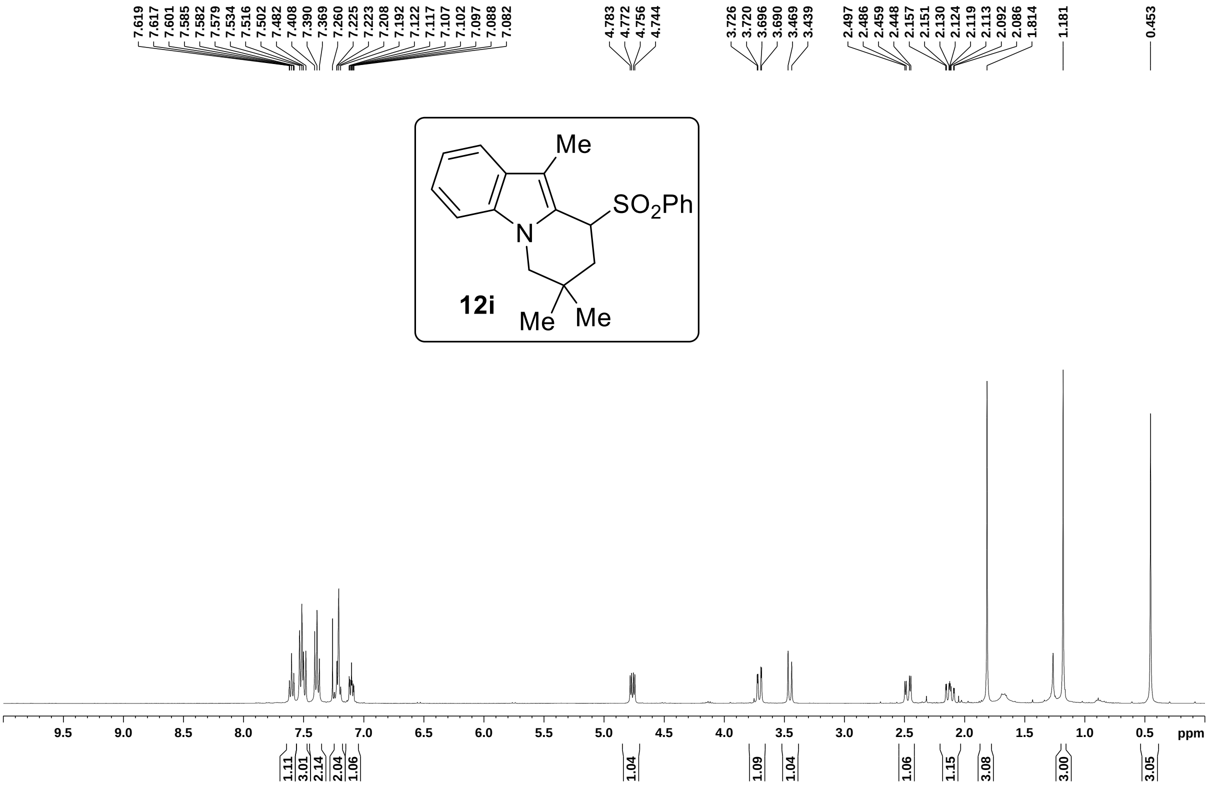
^{13}C NMR spectrum of 12g (100 MHz, CDCl$_3$)



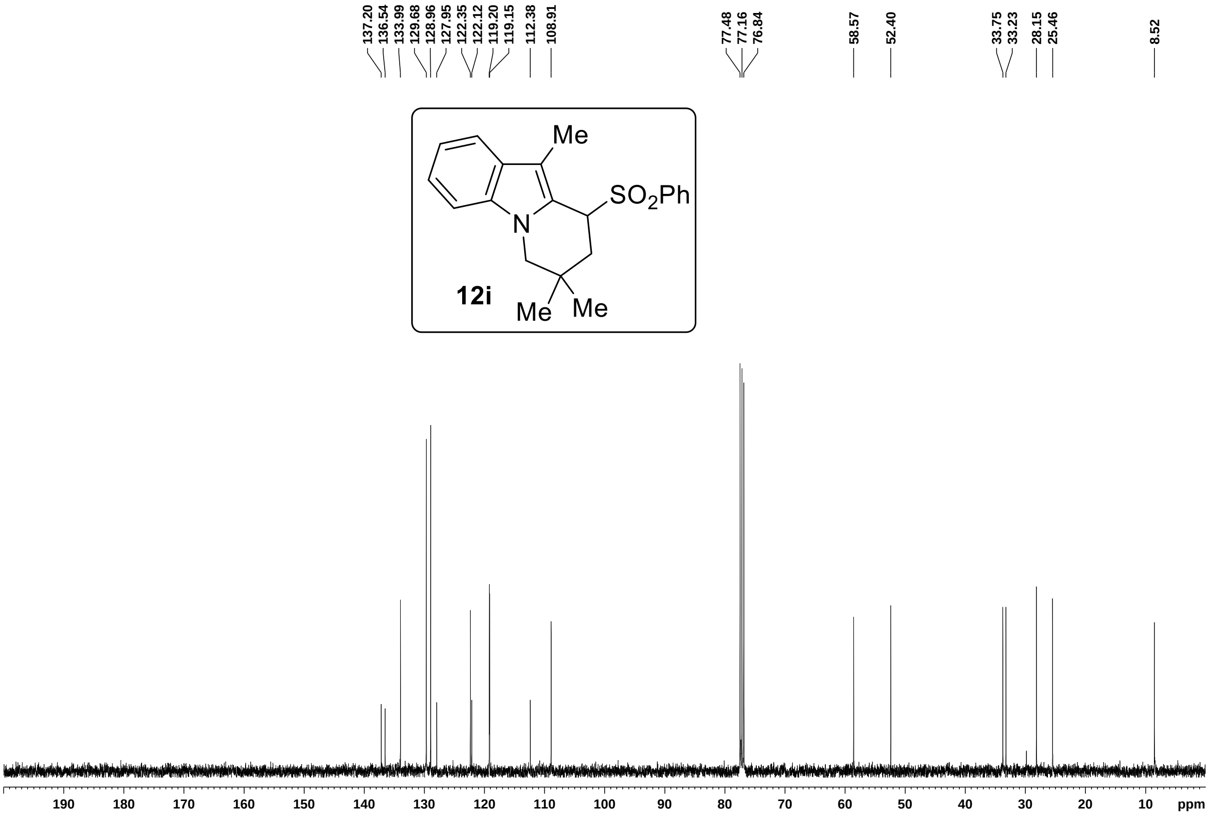
^{1}H NMR spectrum of 12h (400 MHz, CDCl$_3$)



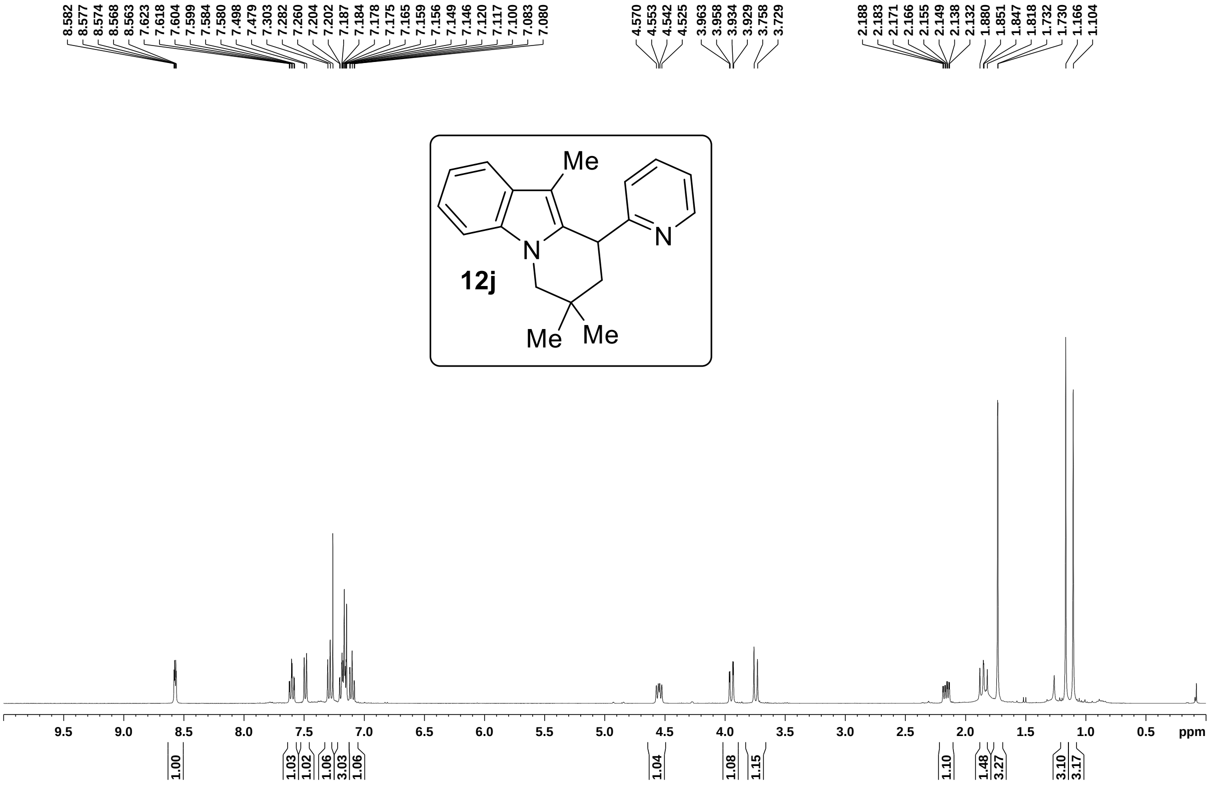
^{13}C NMR spectrum of 12h (100 MHz, CDCl$_3$)



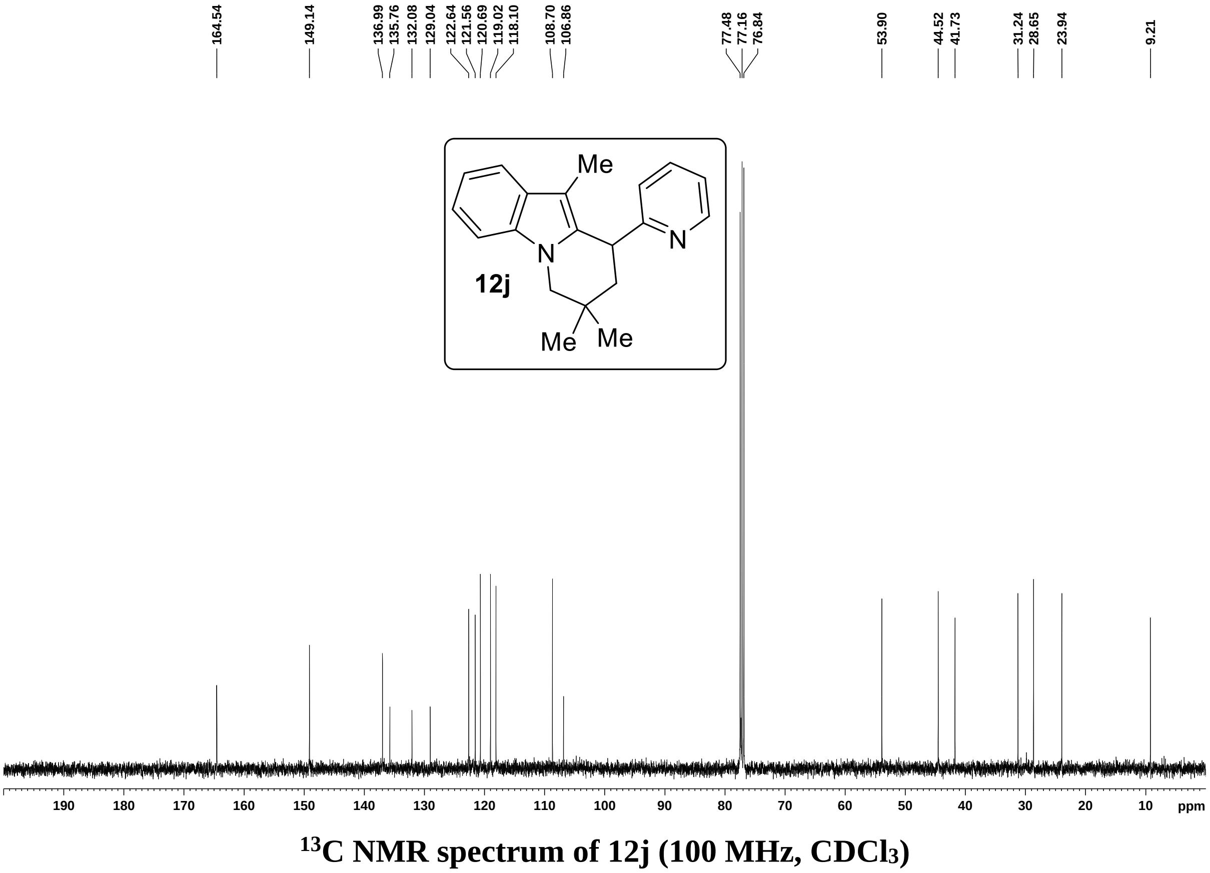
^{1}H NMR spectrum of 12i (400 MHz, CDCl$_3$)



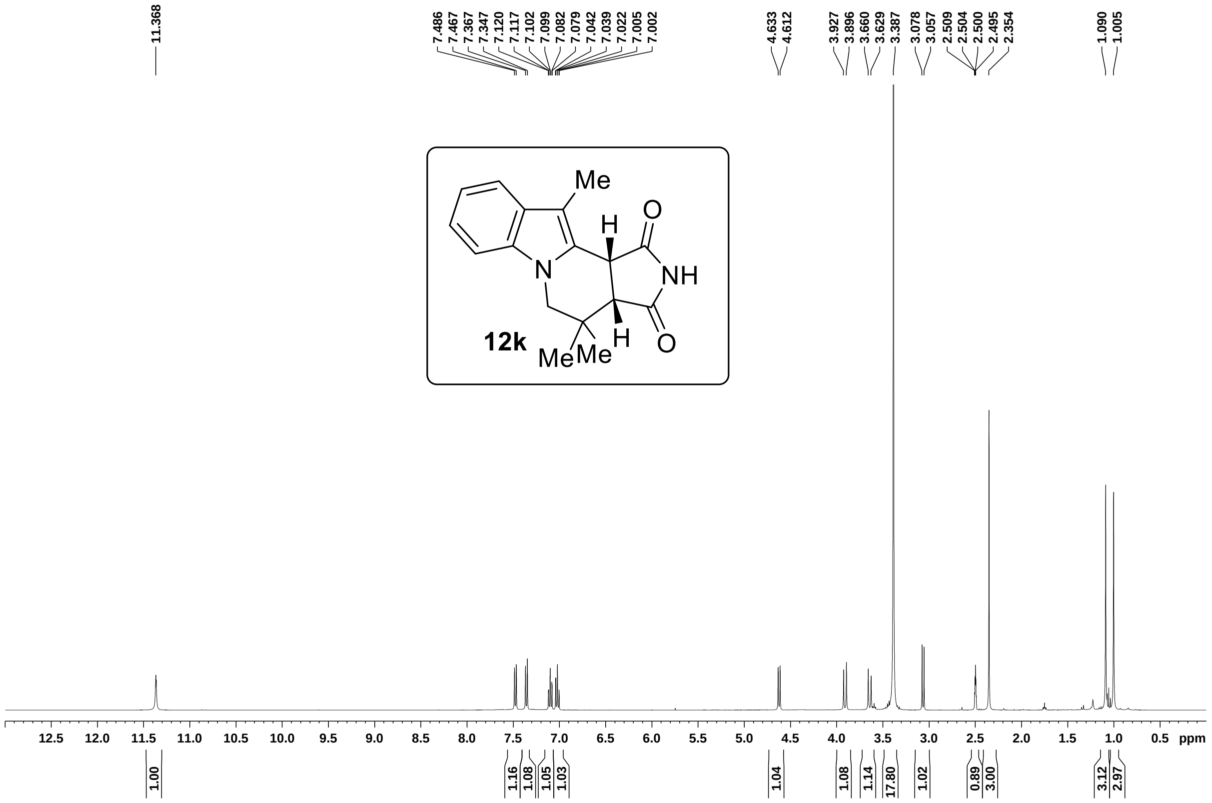
^{13}C NMR spectrum of 12i (100 MHz, CDCl$_3$)



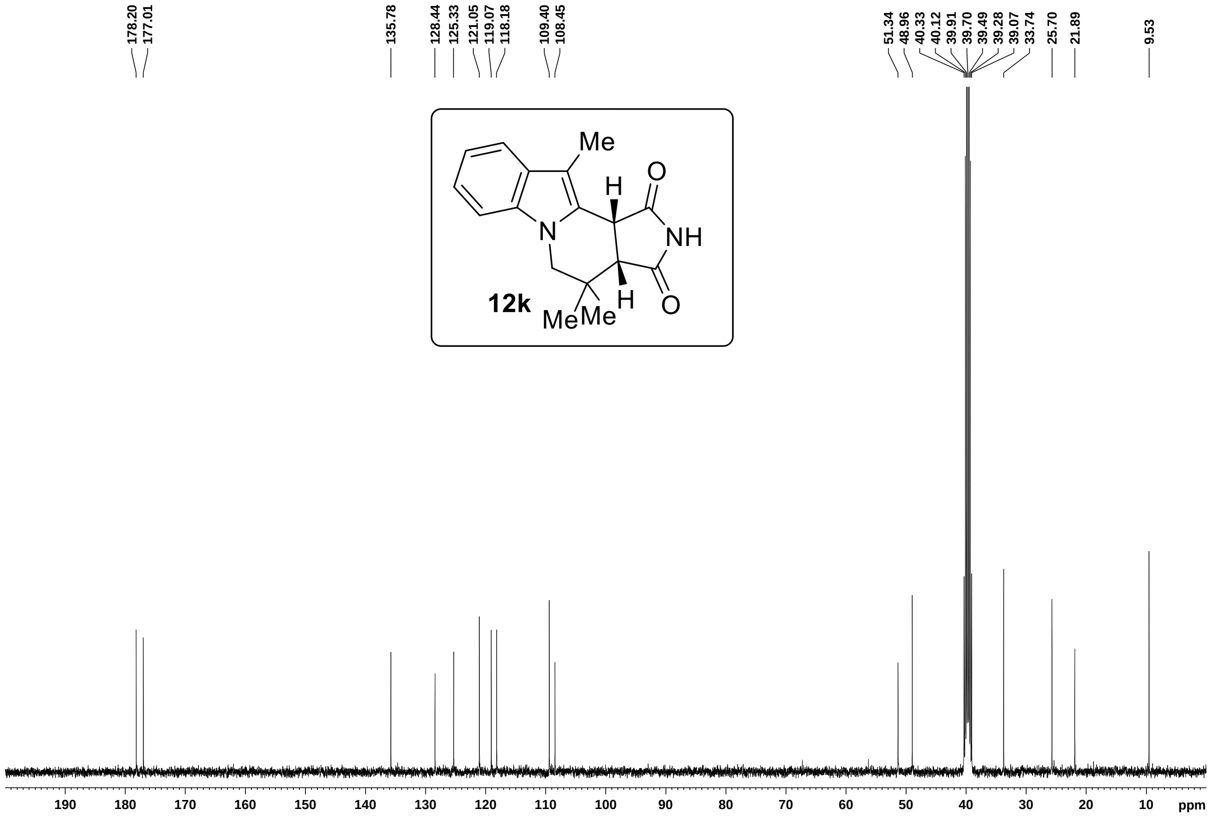
^{1}H NMR spectrum of 12j (400 MHz, CDCl$_3$)



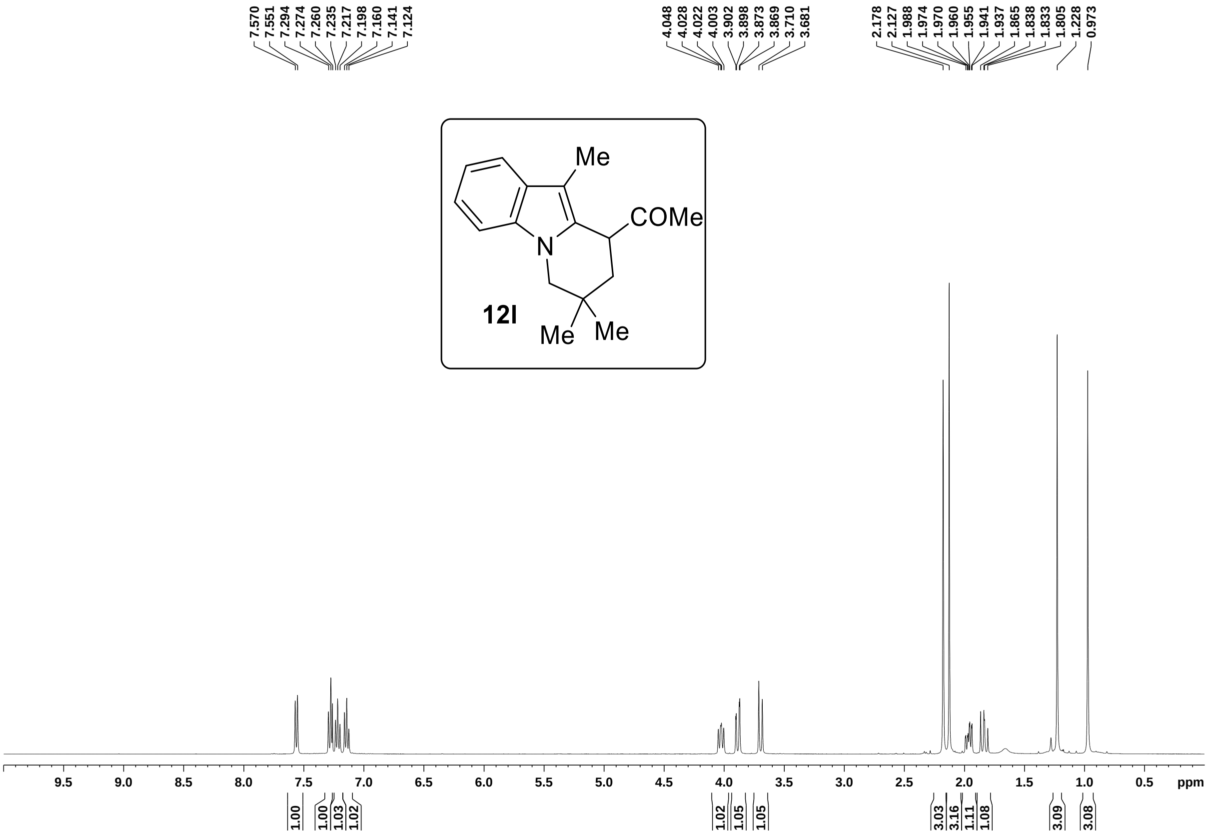
^{13}C NMR spectrum of 12j (100 MHz, CDCl$_3$)



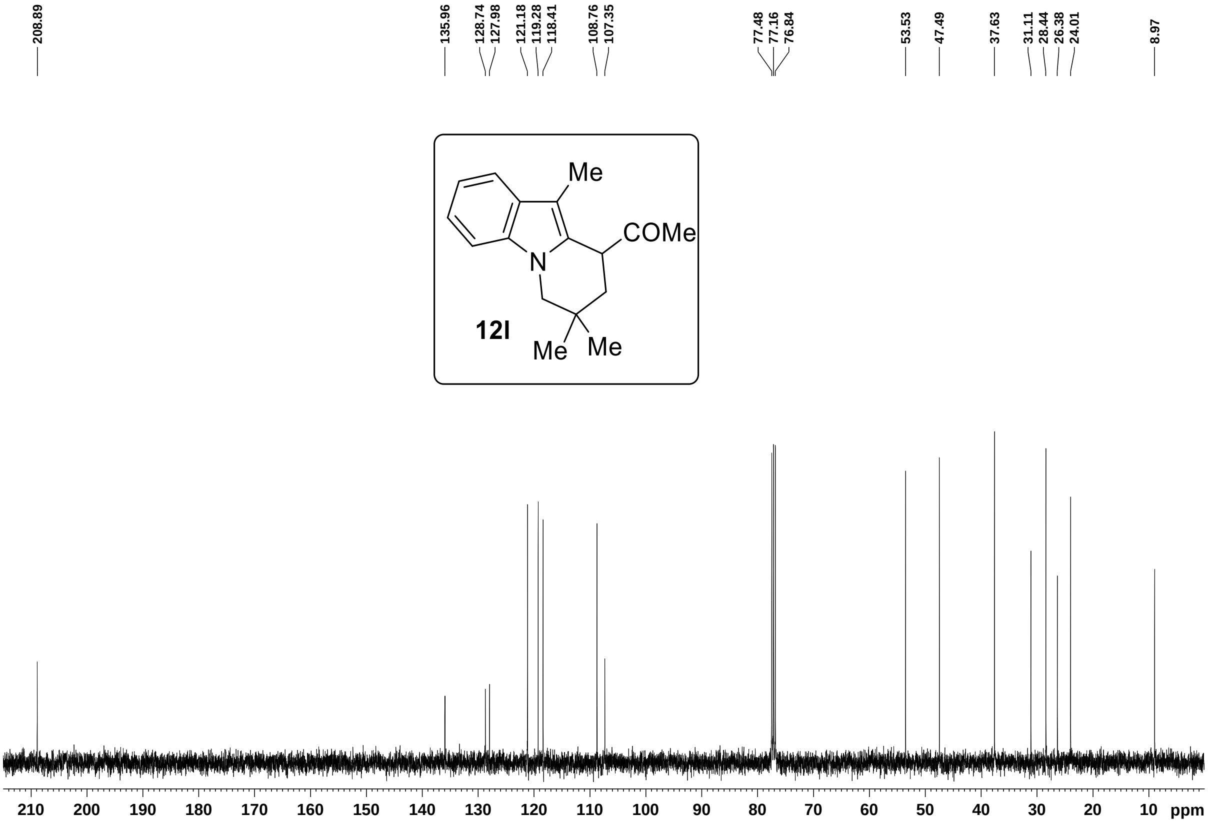
^{1}H NMR spectrum of 12k (400 MHz, DMSO)



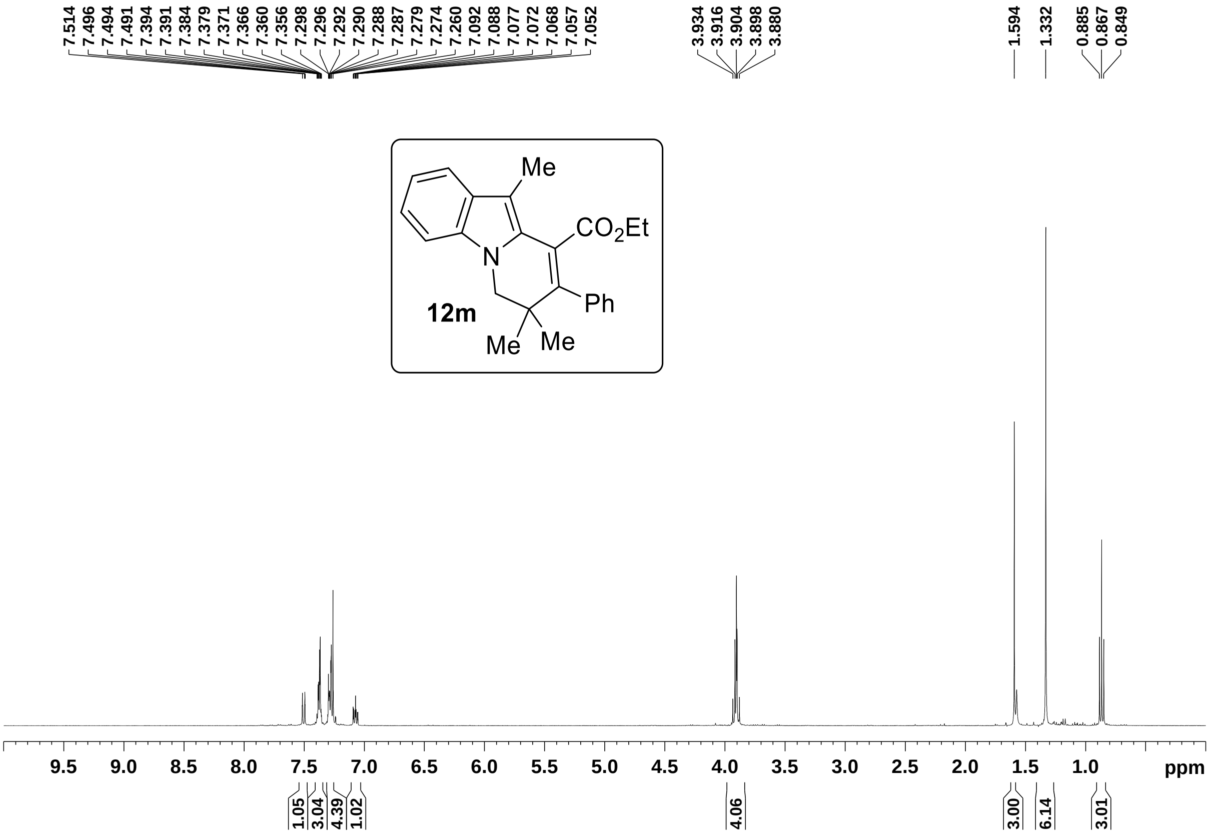
^{13}C NMR spectrum of 12k (100 MHz, DMSO)



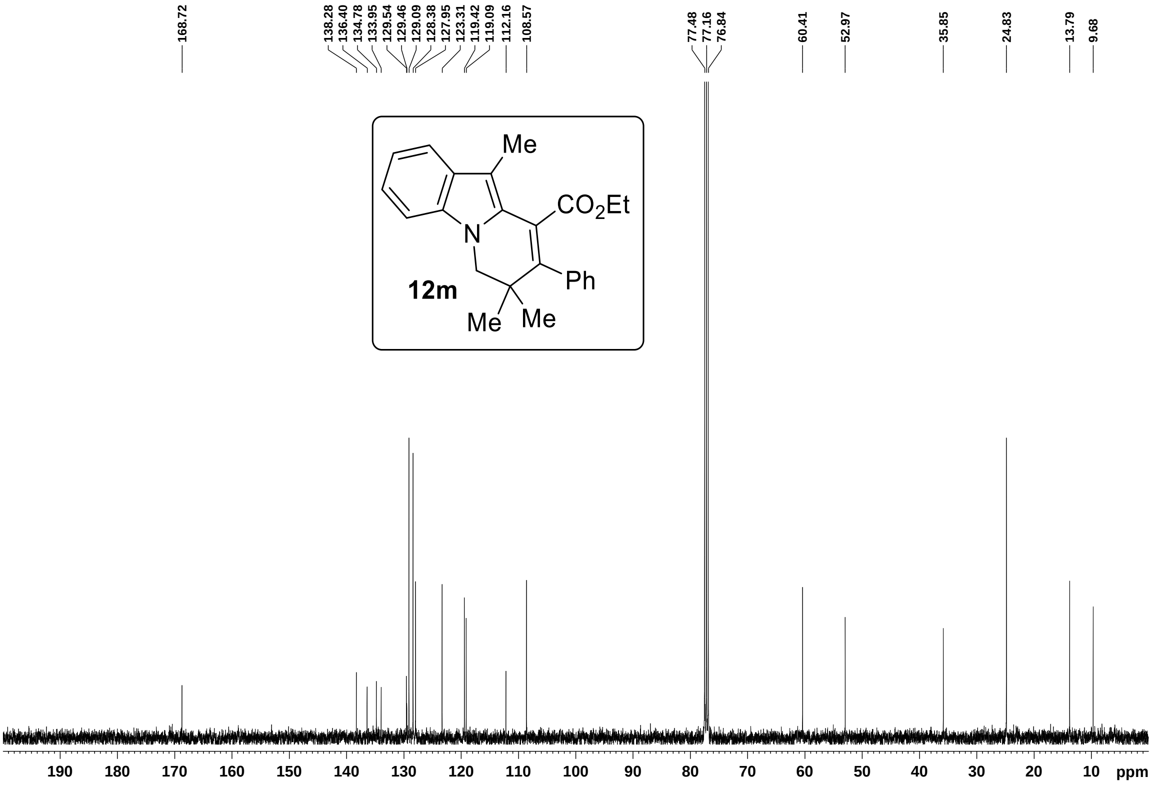
^{1}H NMR spectrum of 12l (400 MHz, CDCl$_3$)



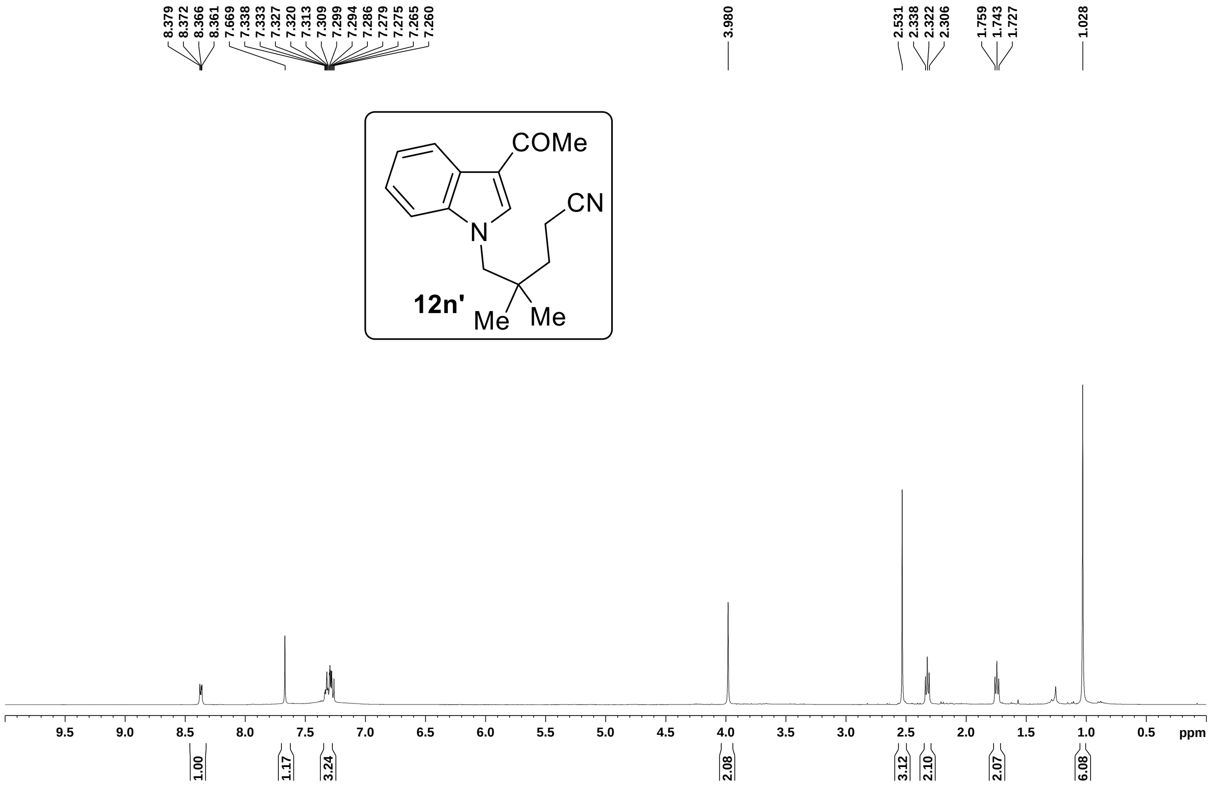
^{13}C NMR spectrum of 12l (100 MHz, CDCl$_3$)



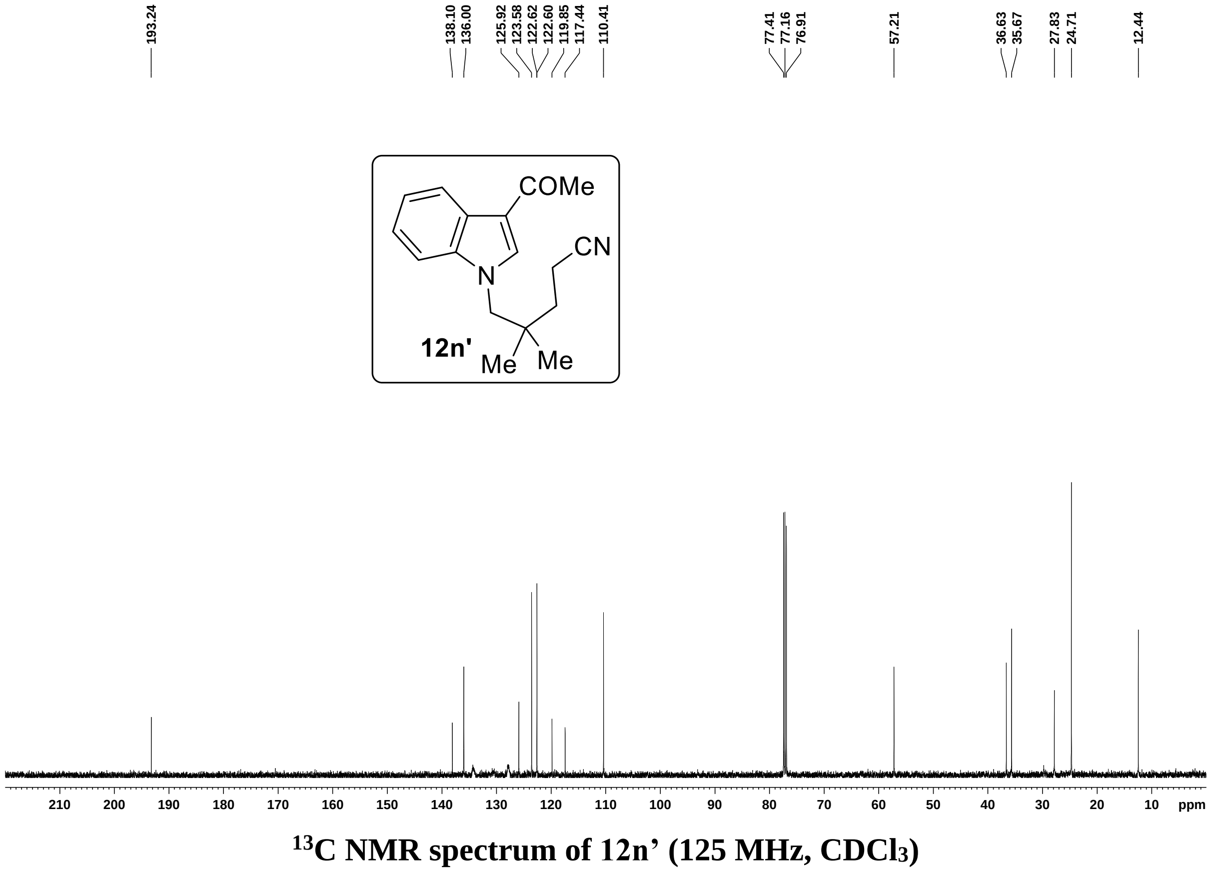
^{1}H NMR spectrum of 12m (400 MHz, CDCl$_3$)



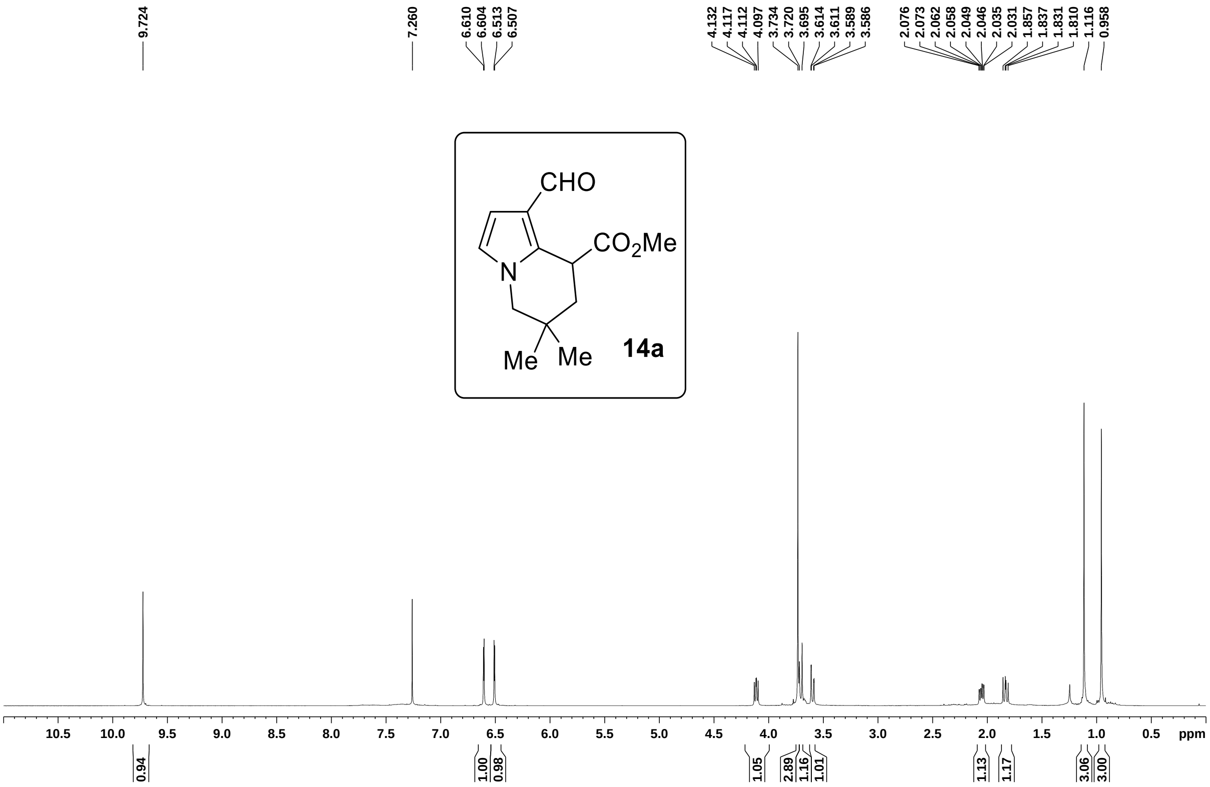
^{13}C NMR spectrum of 12m (100 MHz, CDCl$_3$)



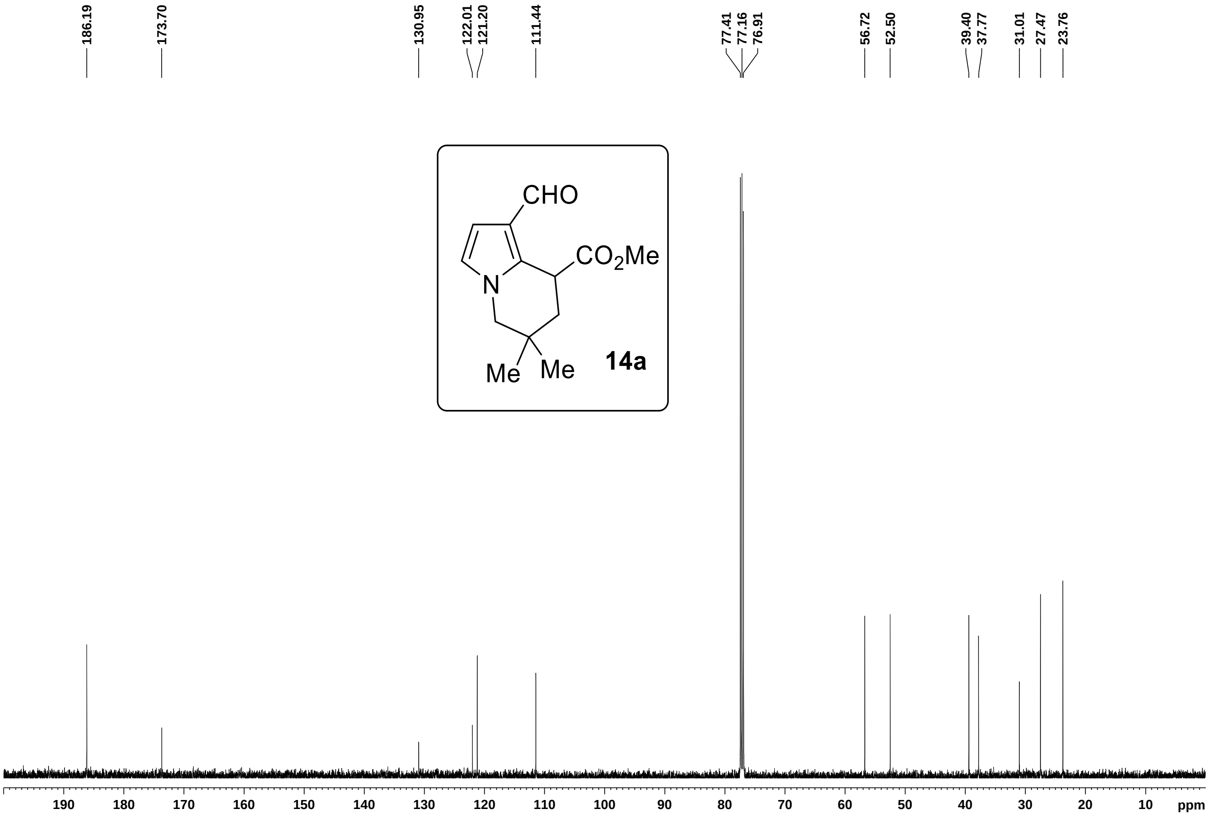
^{1}H NMR spectrum of 12n’ (500 MHz, CDCl$_3$)



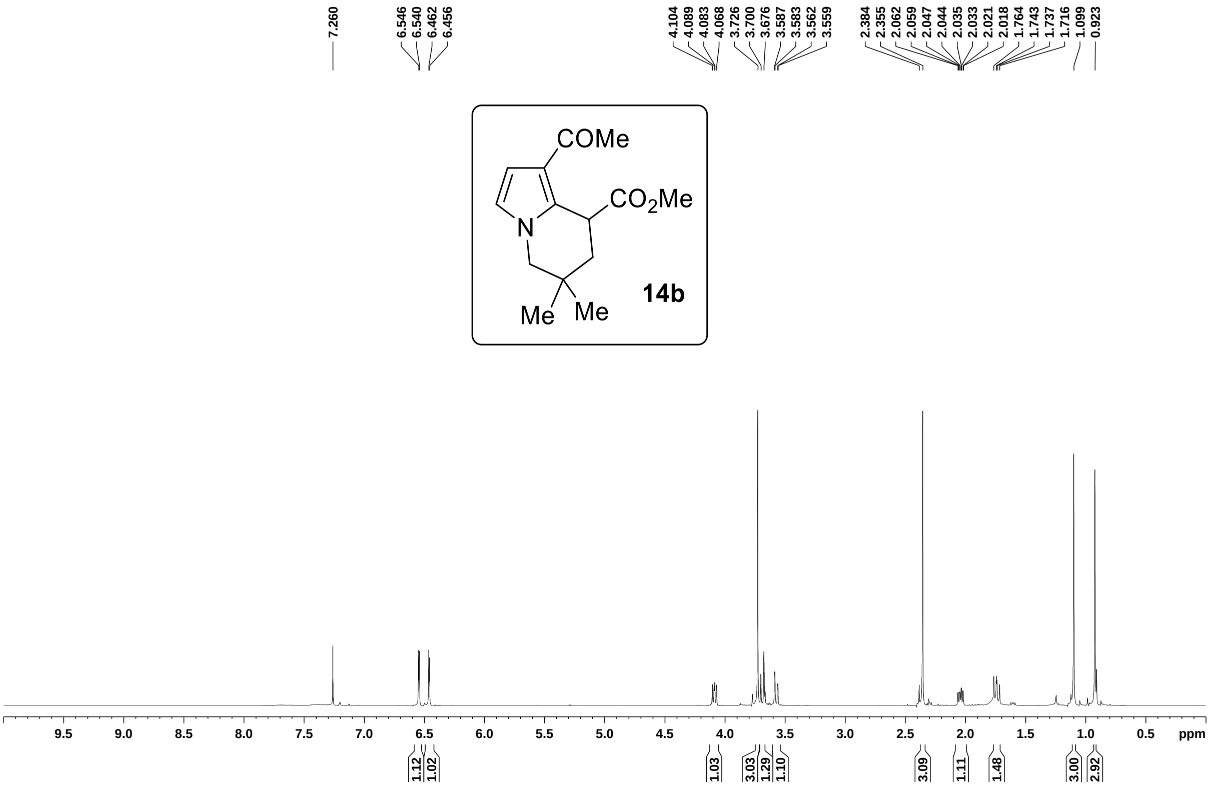
^{13}C NMR spectrum of 12n’ (125 MHz, CDCl$_3$)



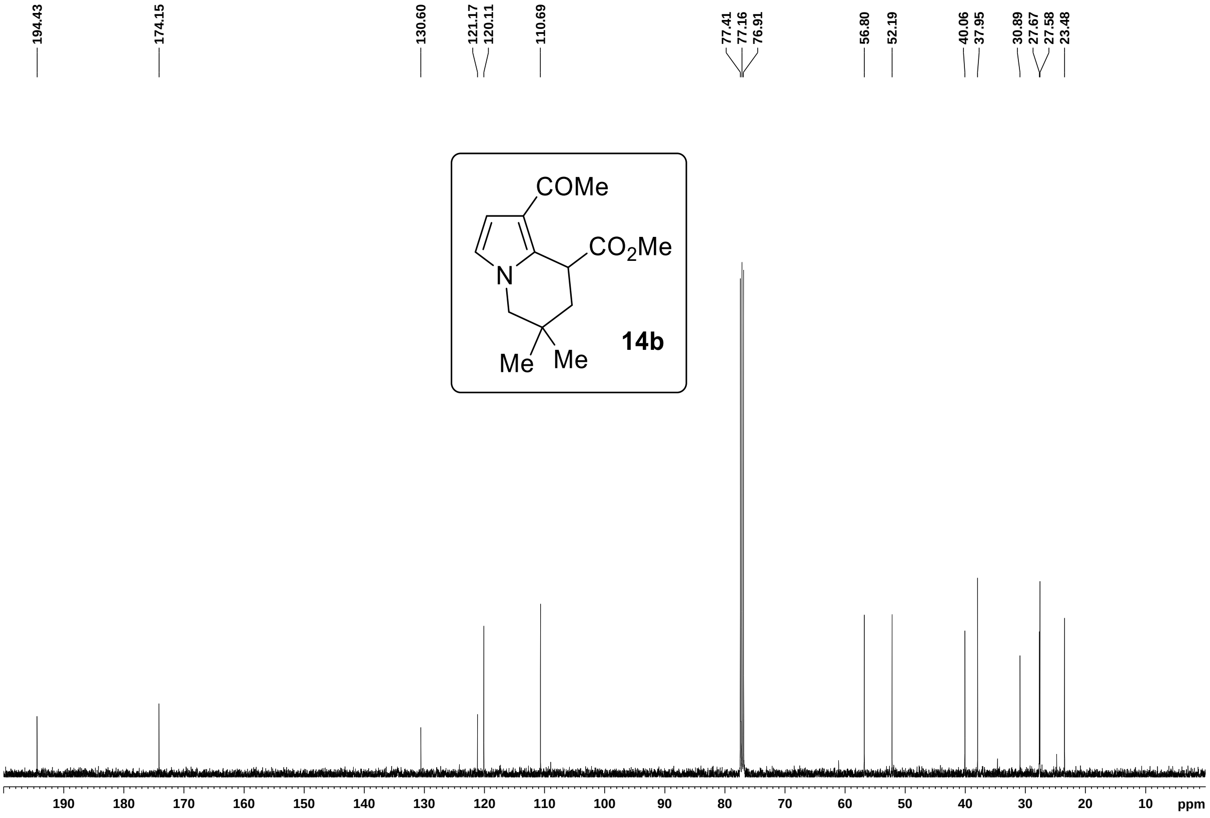
^{1}H NMR spectrum of 14a (500 MHz, CDCl$_3$)



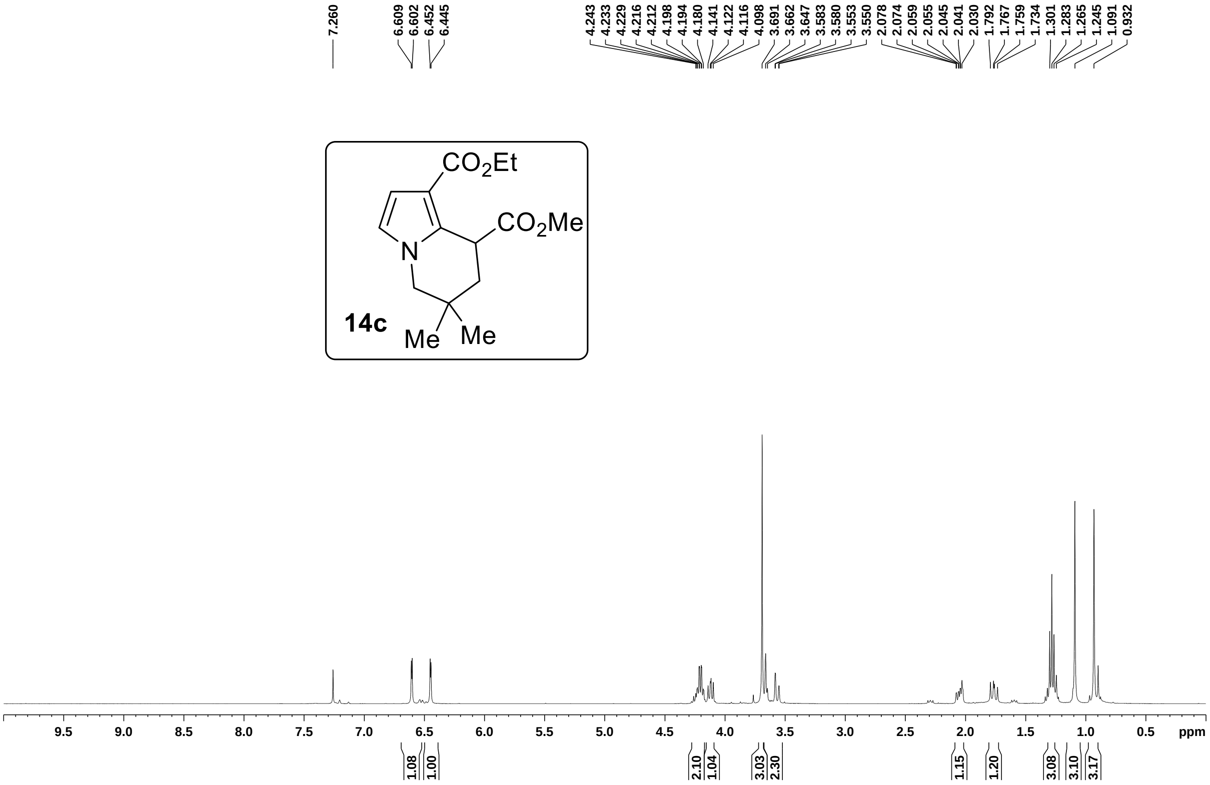
^{13}C NMR spectrum of 14a (125 MHz, CDCl$_3$)



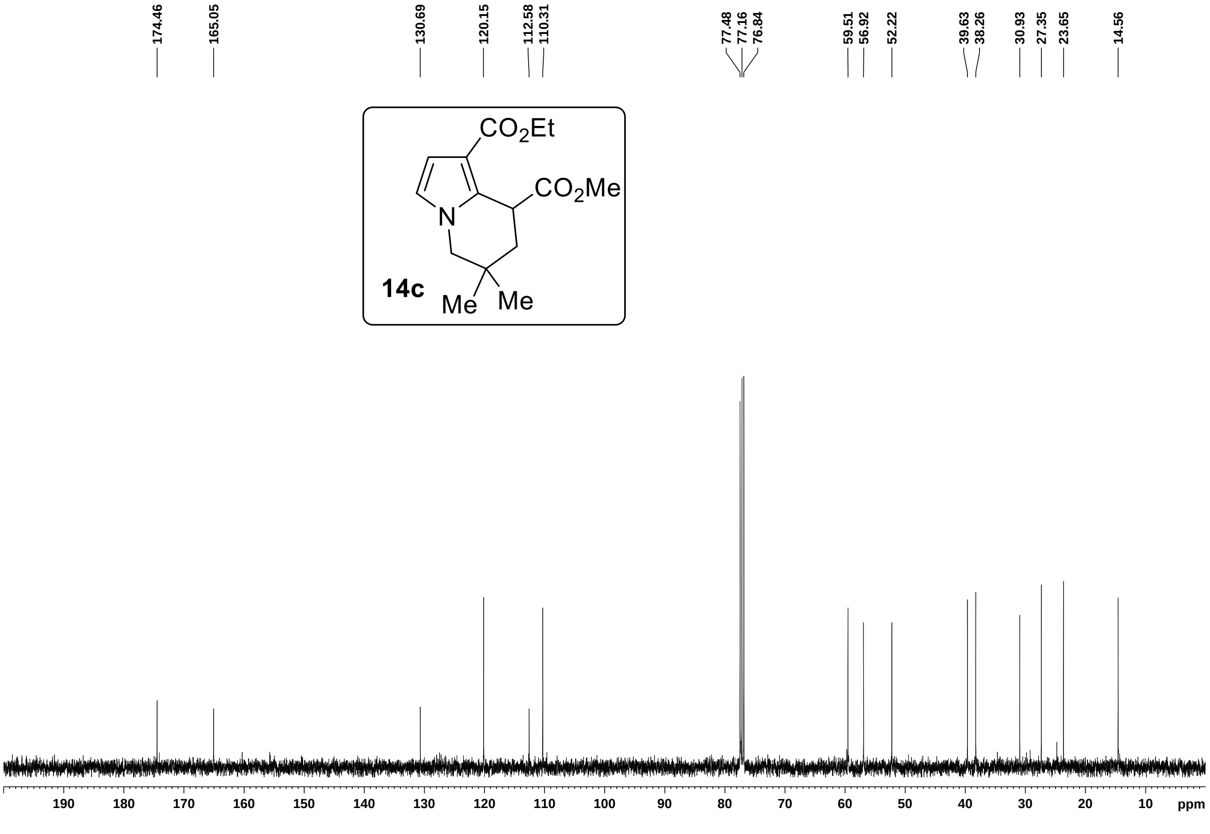
^{1}H NMR spectrum of 14b (500 MHz, CDCl$_3$)



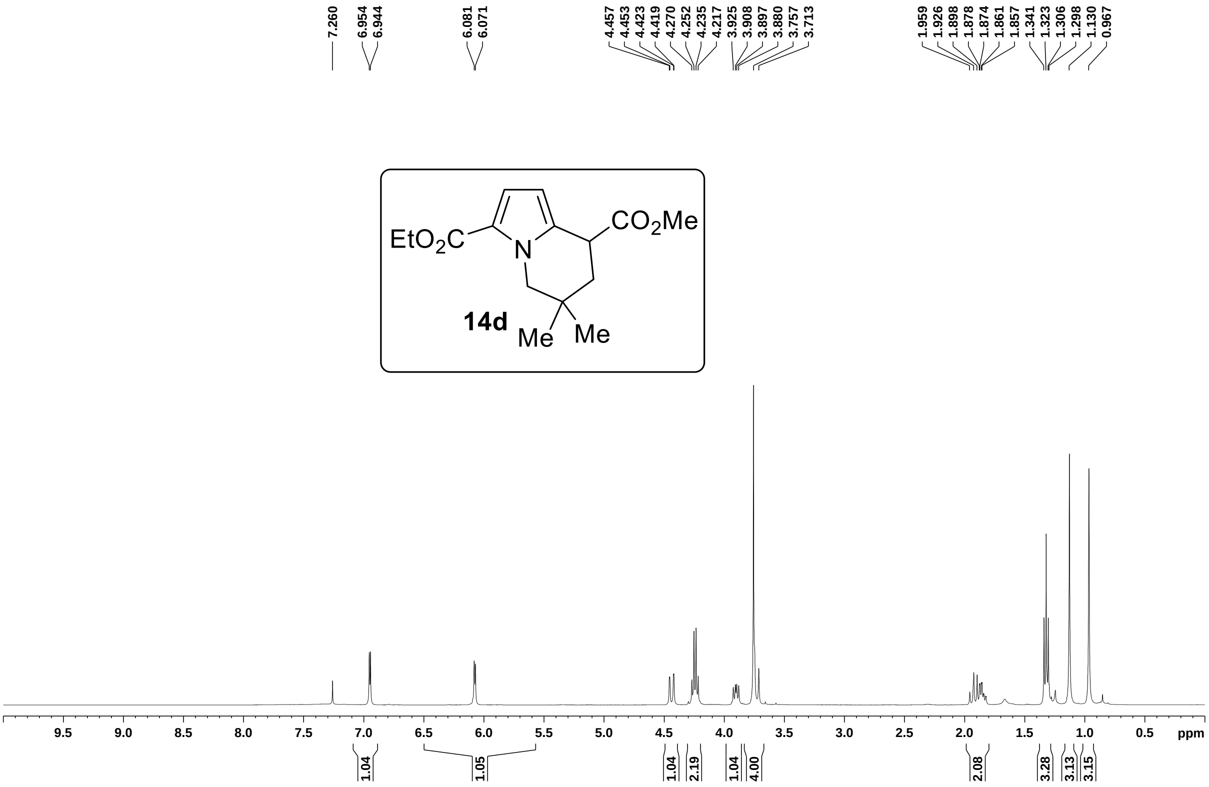
^{13}C NMR spectrum of 14b (125 MHz, CDCl$_3$)



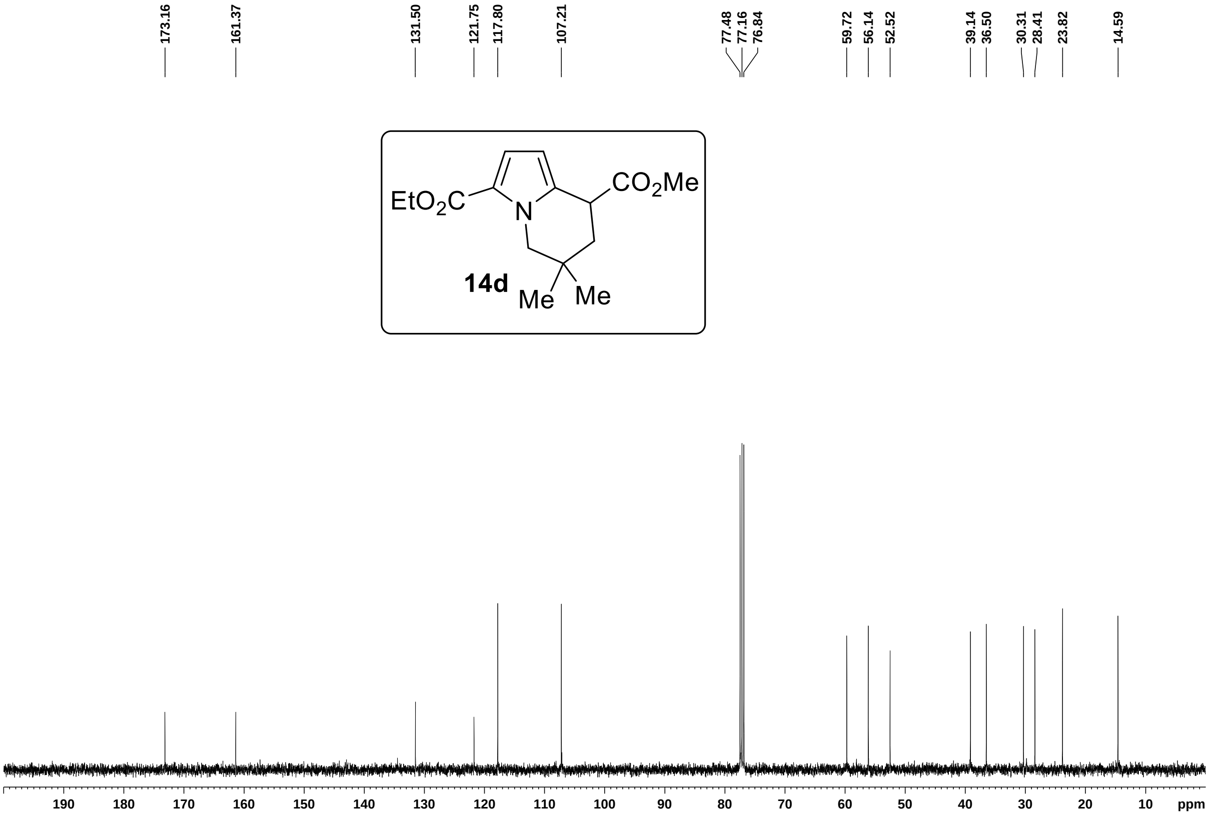
^{1}H NMR spectrum of 14c (400 MHz, CDCl$_3$)



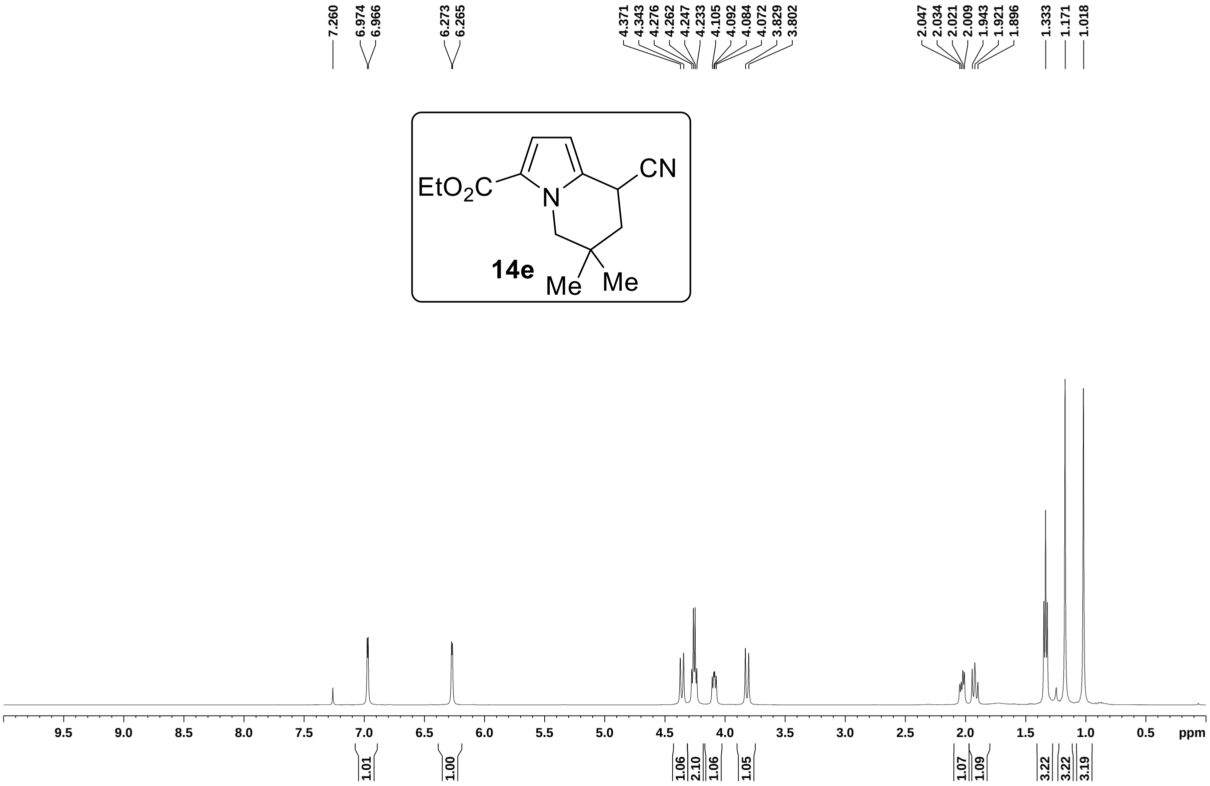
^{13}C NMR spectrum of 14c (100 MHz, CDCl$_3$)



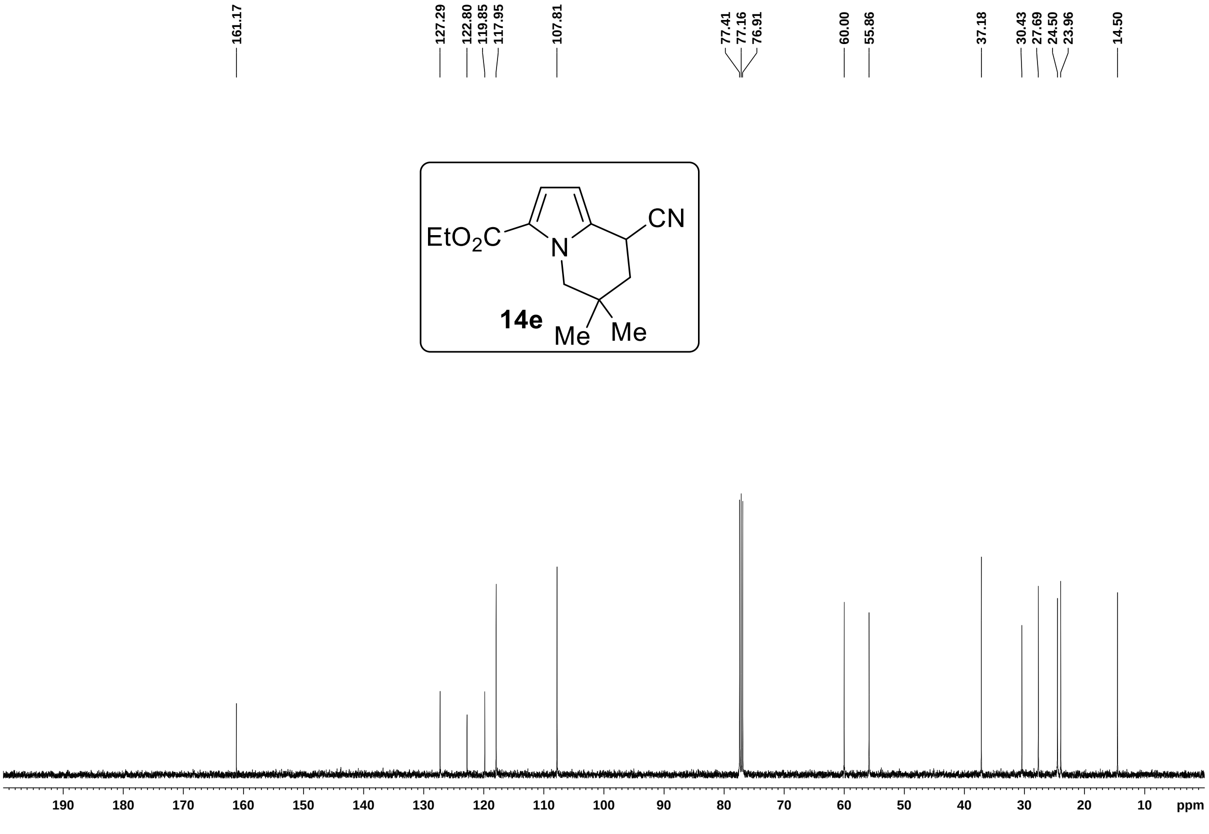
^{1}H NMR spectrum of 14d (400 MHz, CDCl$_3$)



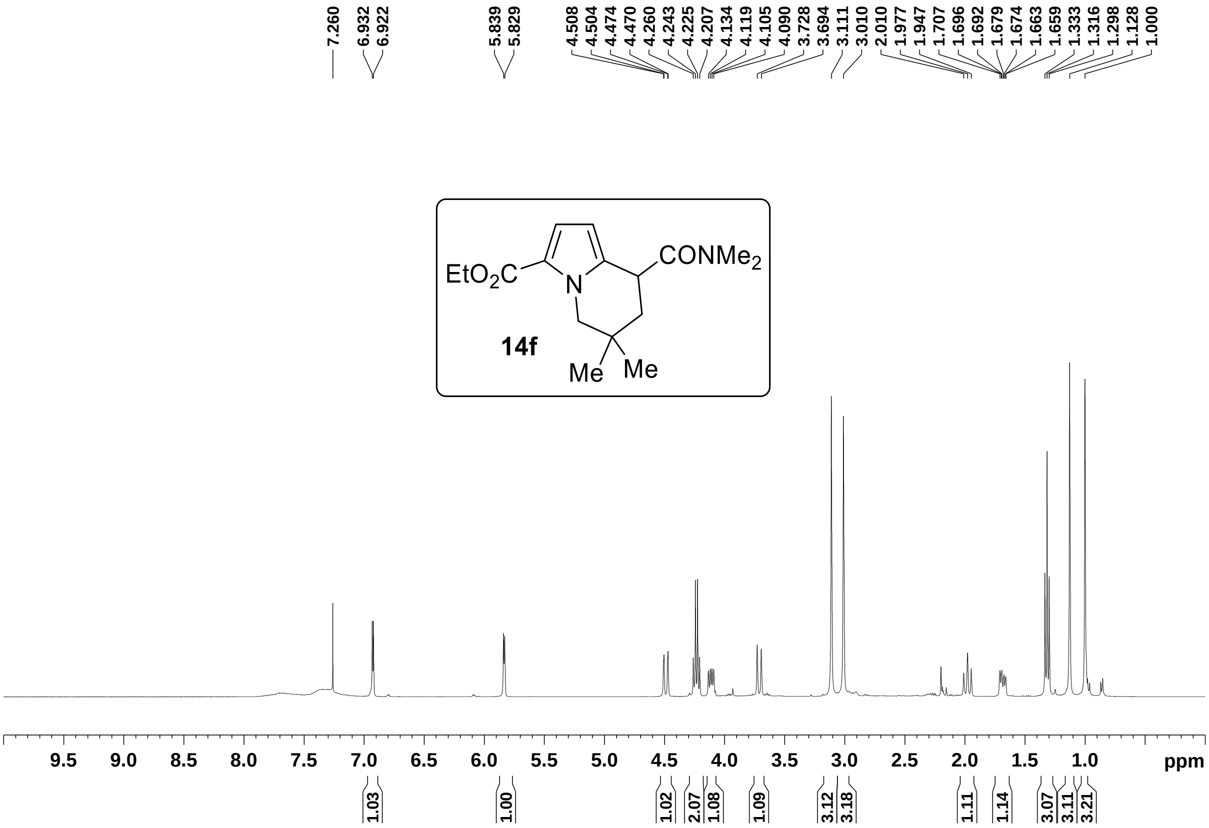
^{1}H NMR spectrum of 14d (100 MHz, CDCl$_3$)



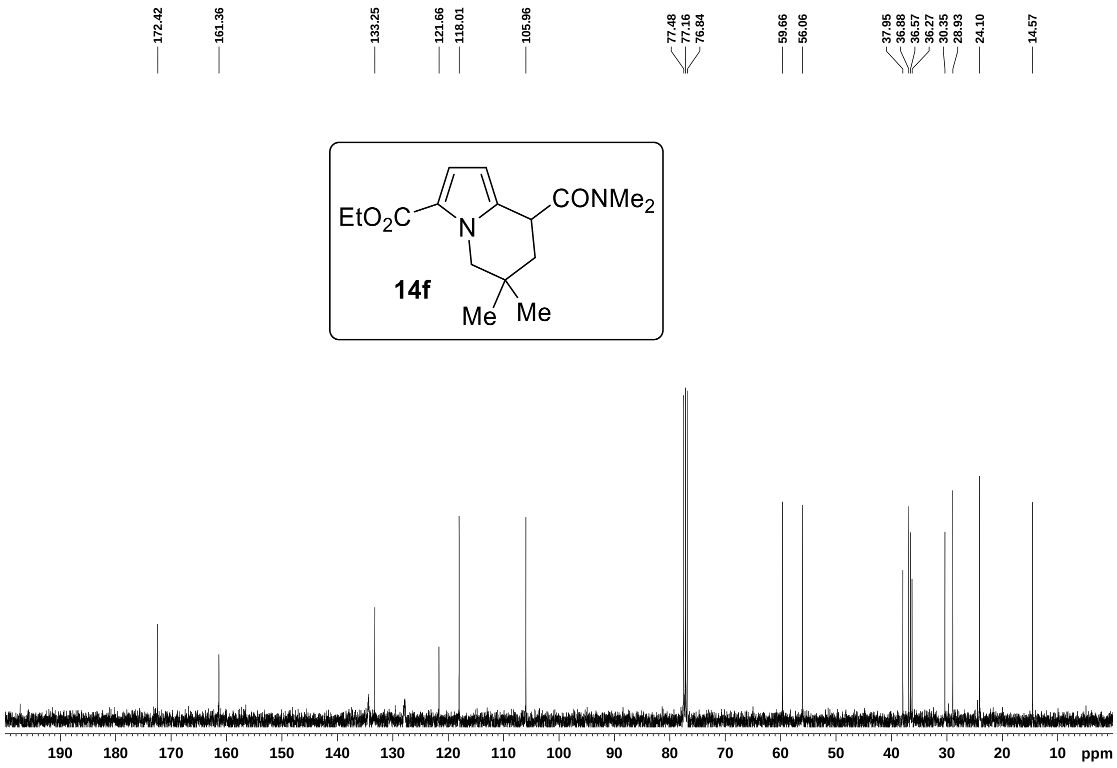
^{1}H NMR spectrum of 14e (500 MHz, CDCl$_3$)



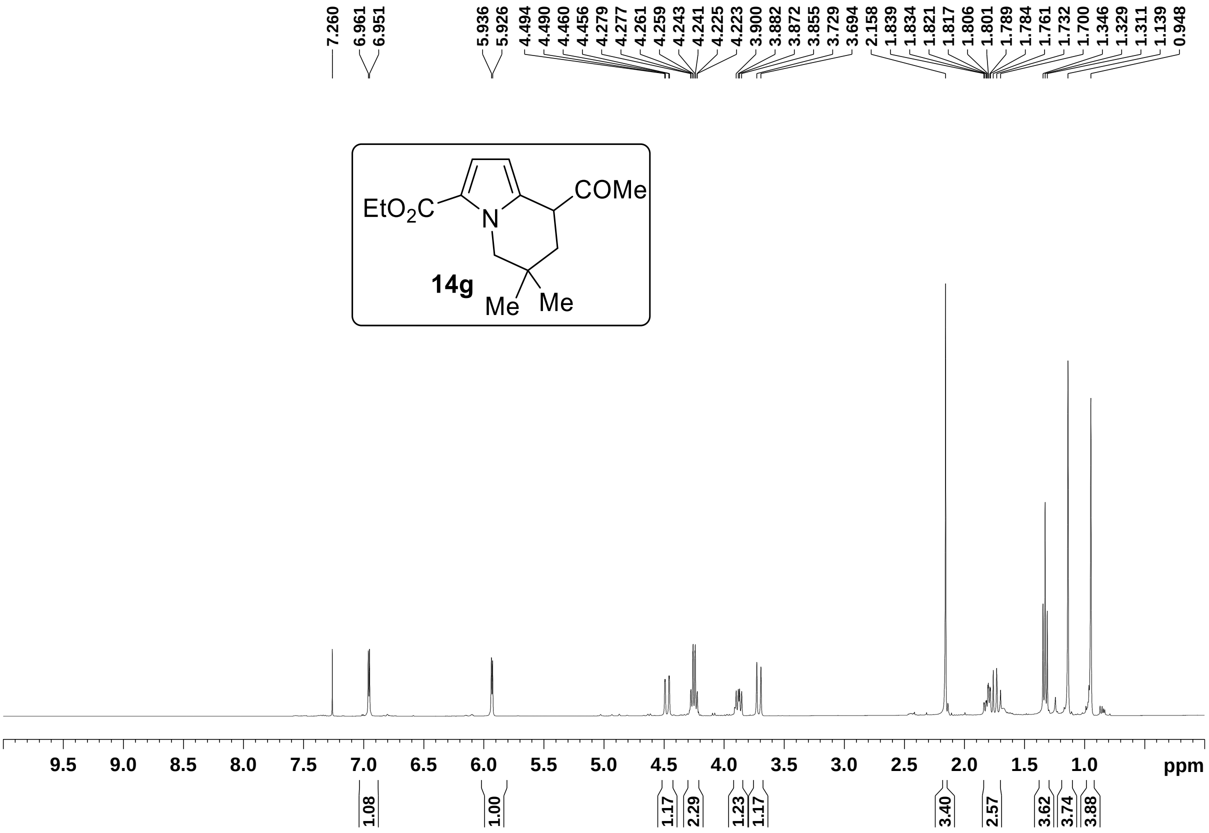
^{13}C NMR spectrum of 14e (125 MHz, CDCl$_3$)



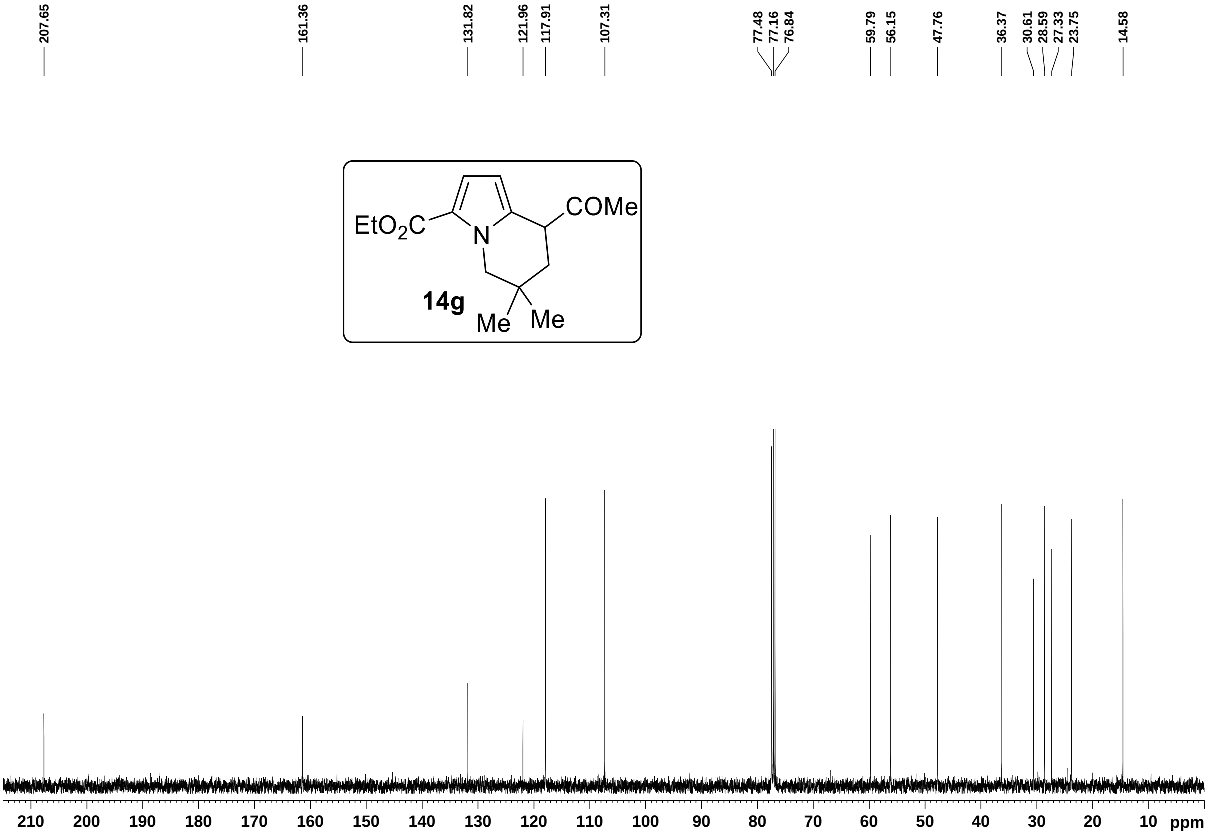
^{1}H NMR spectrum of 14f (400 MHz, CDCl$_3$)



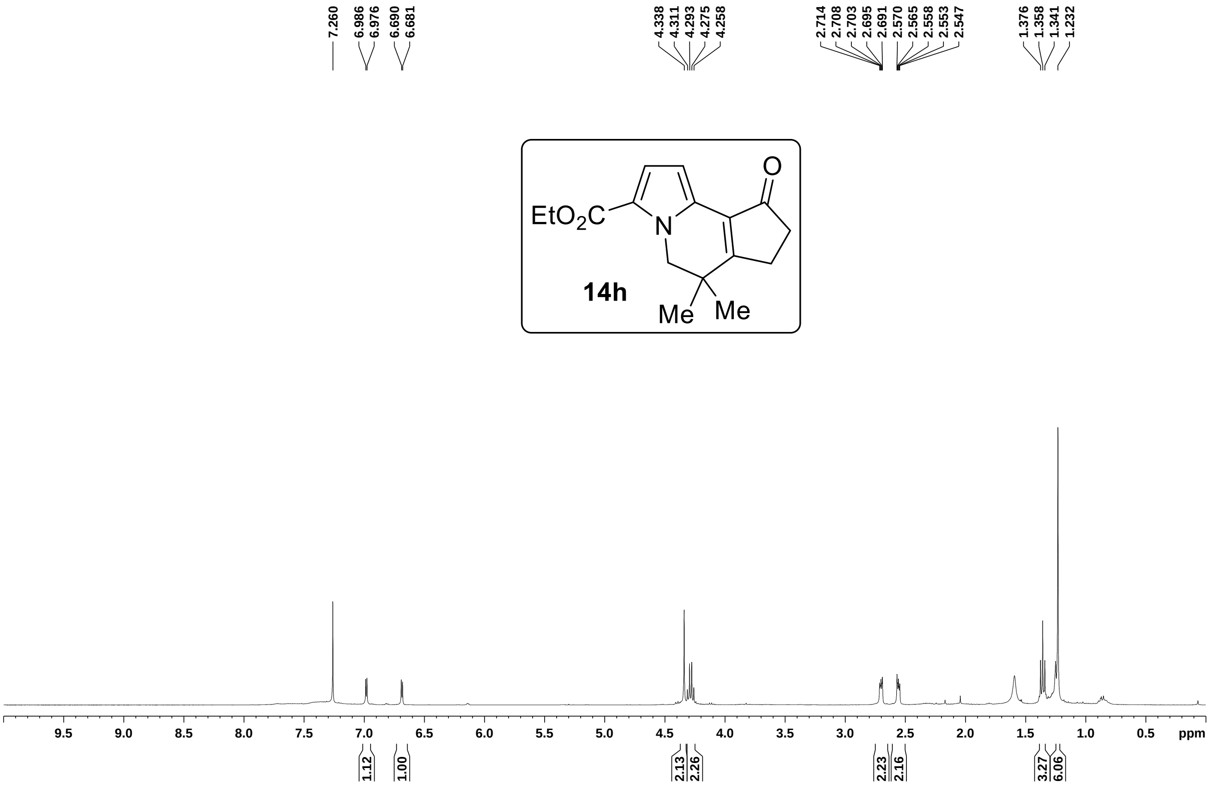
^{13}C NMR spectrum of 14f (100 MHz, CDCl$_3$)



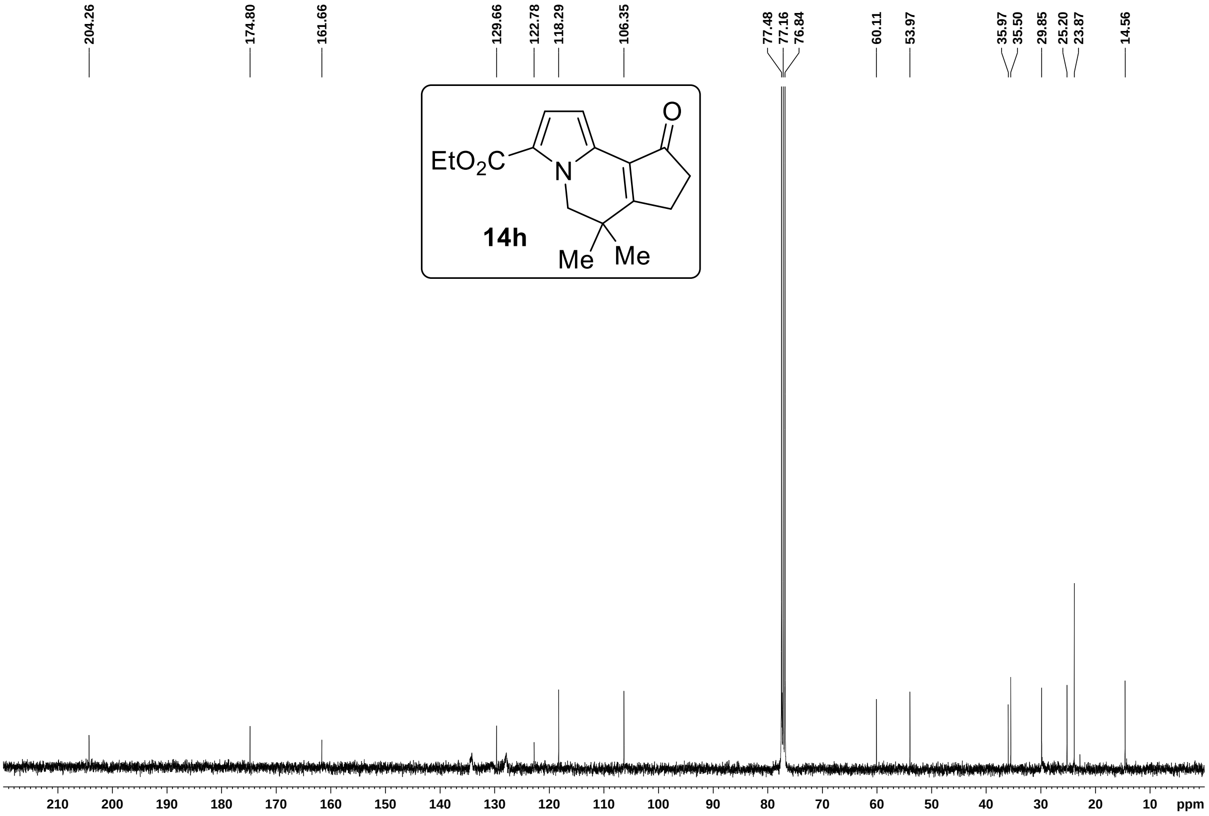
^{1}H NMR spectrum of 14g (400 MHz, $CDCl_3$)



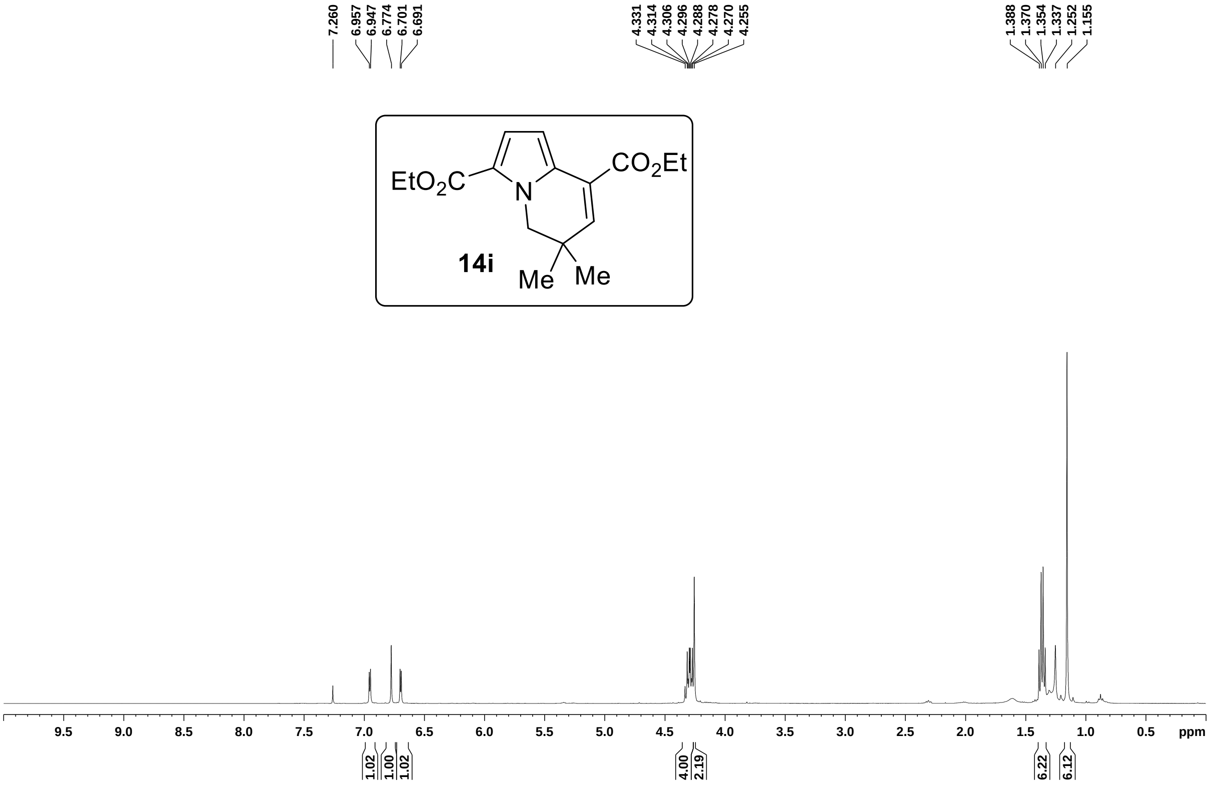
^{13}C NMR spectrum of 14g (100 MHz, $CDCl_3$)



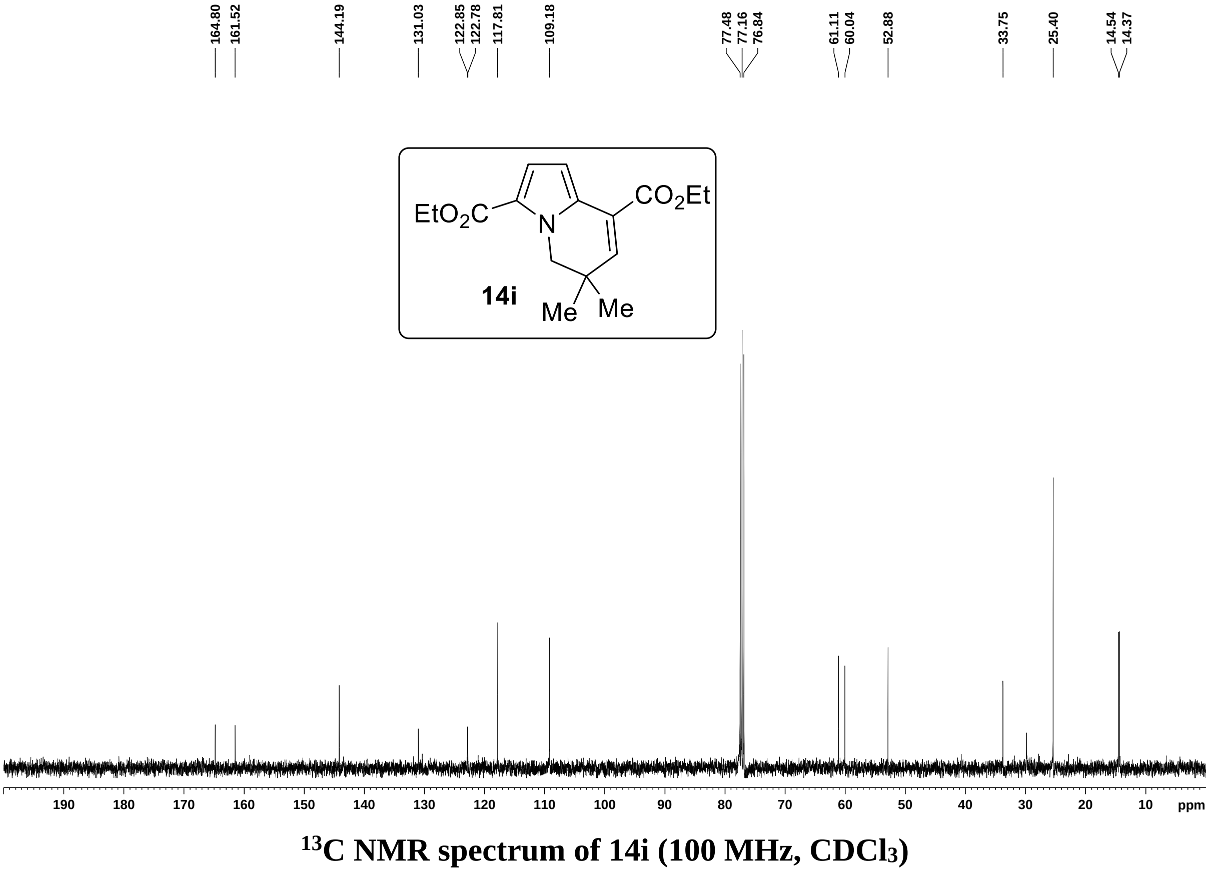
^{1}H NMR spectrum of 14h (400 MHz, $CDCl_3$)



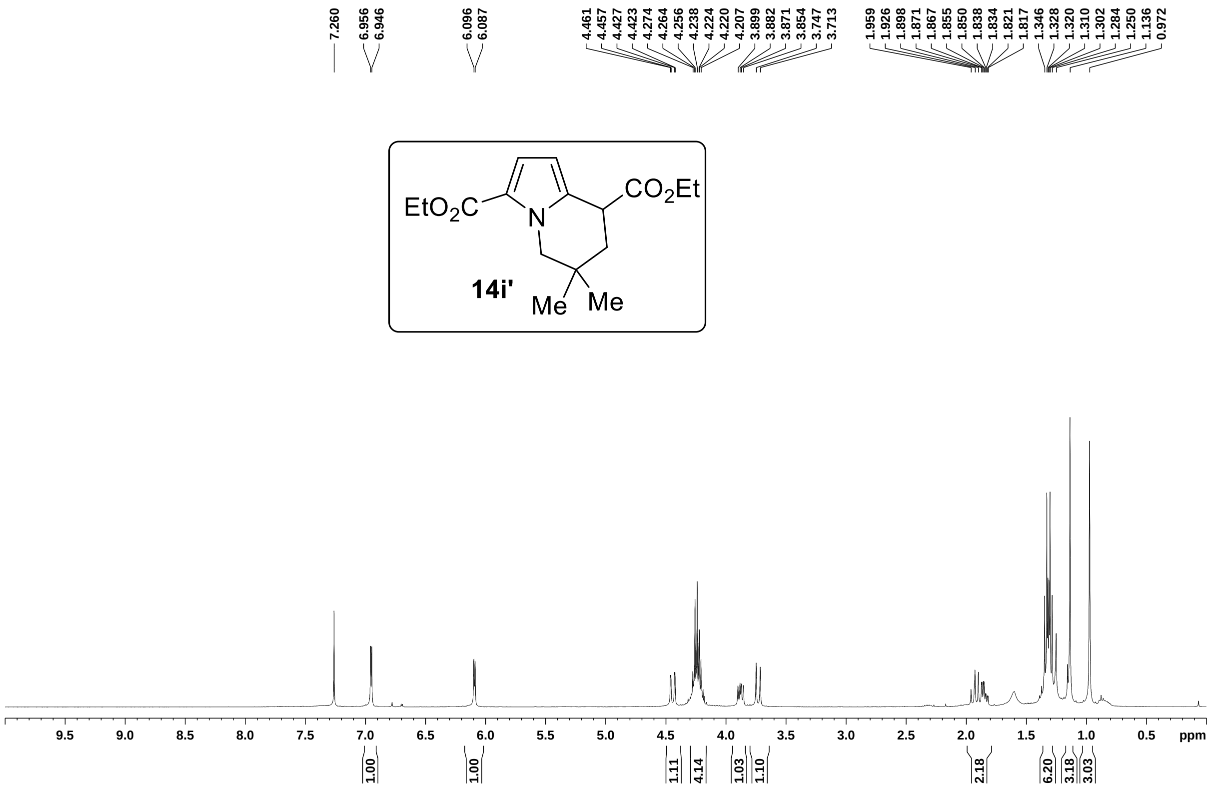
^{13}C NMR spectrum of 14h (100 MHz, $CDCl_3$)



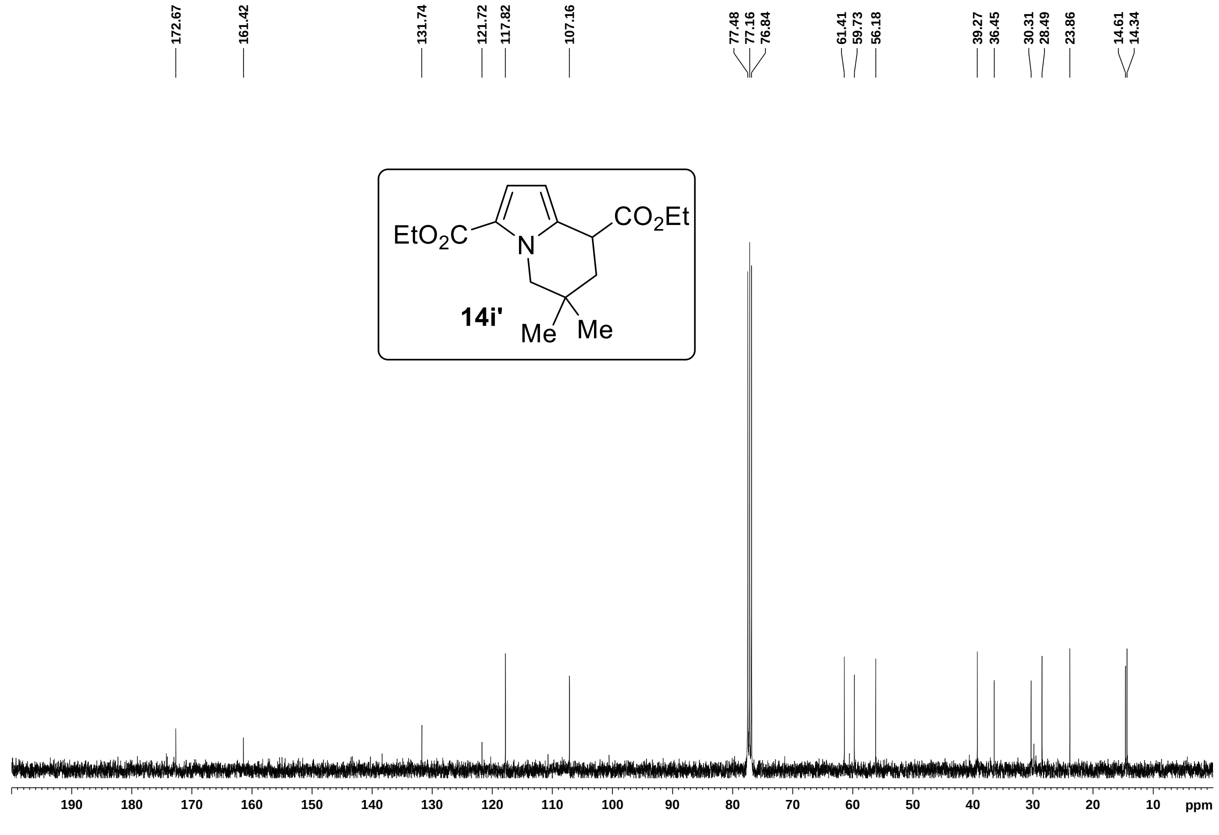
^{1}H NMR spectrum of 14i (400 MHz, CDCl$_3$)



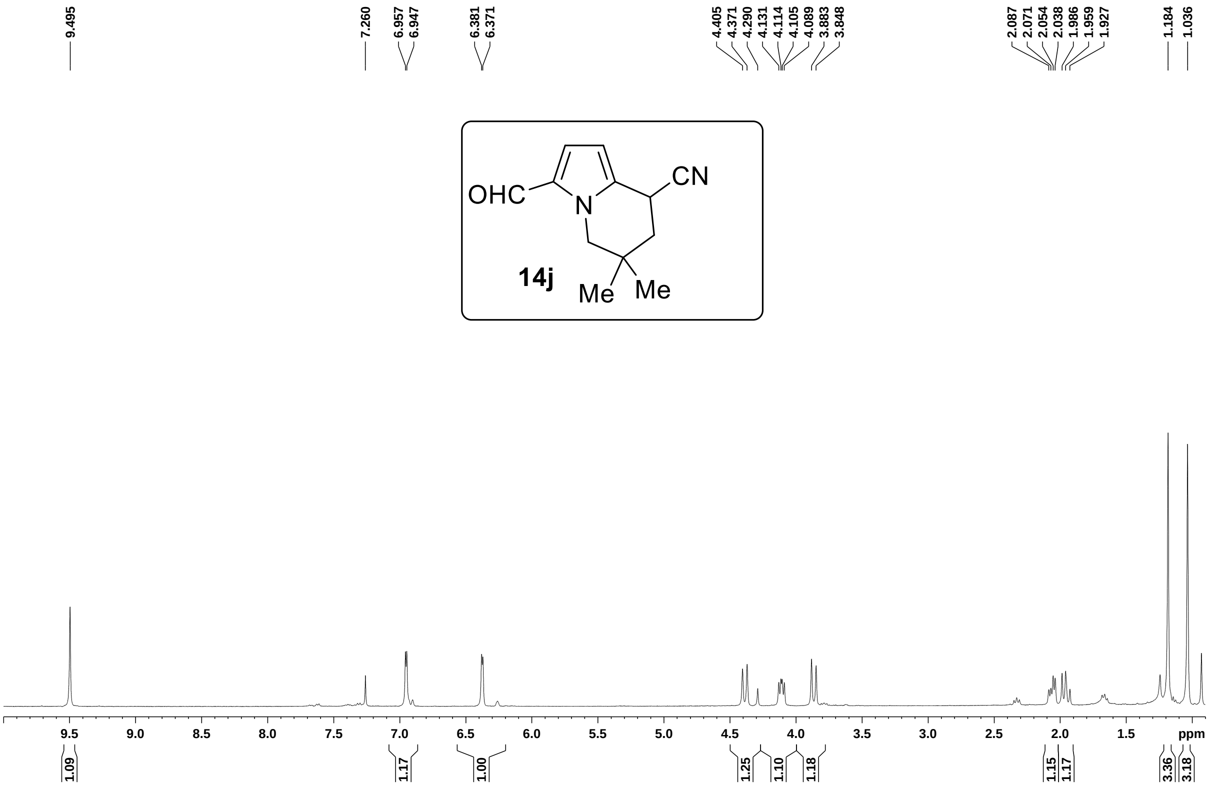
^{13}C NMR spectrum of 14i (100 MHz, CDCl$_3$)



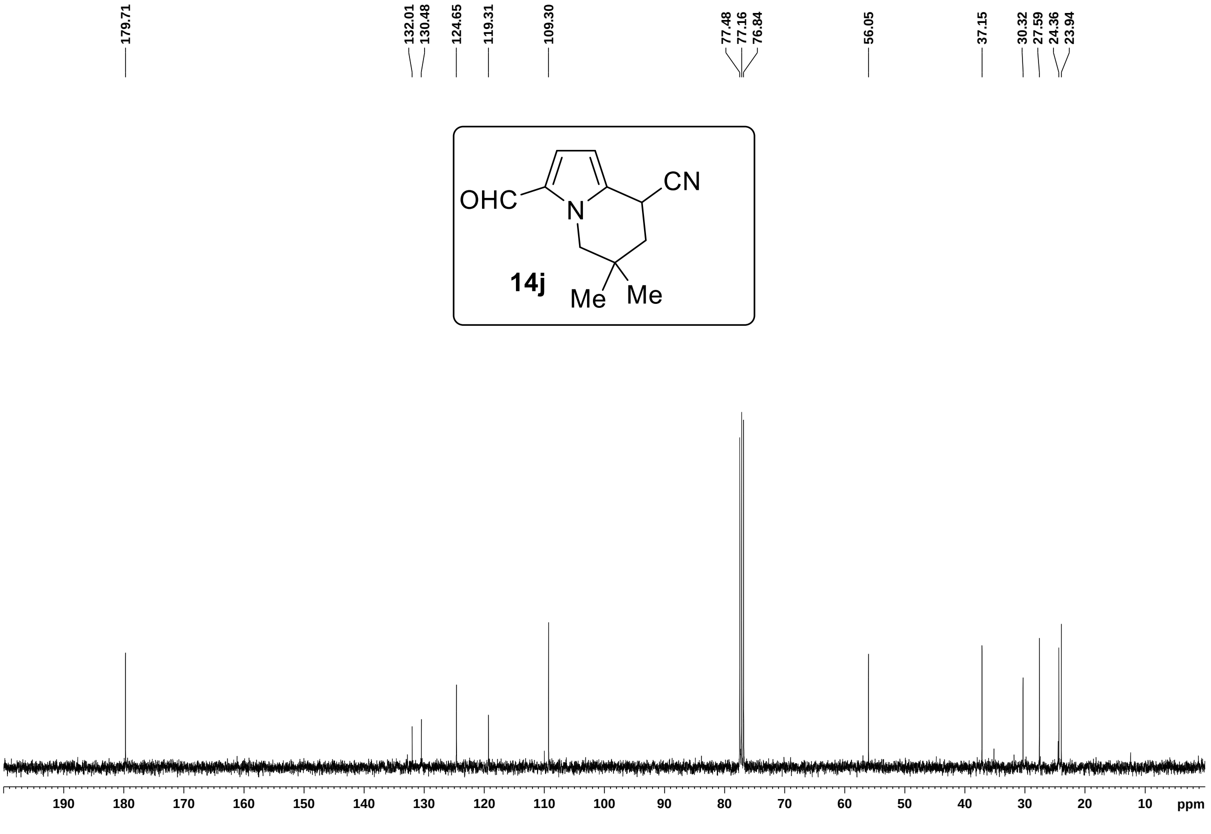
^{1}H NMR spectrum of 14i’ (400 MHz, CDCl$_3$)



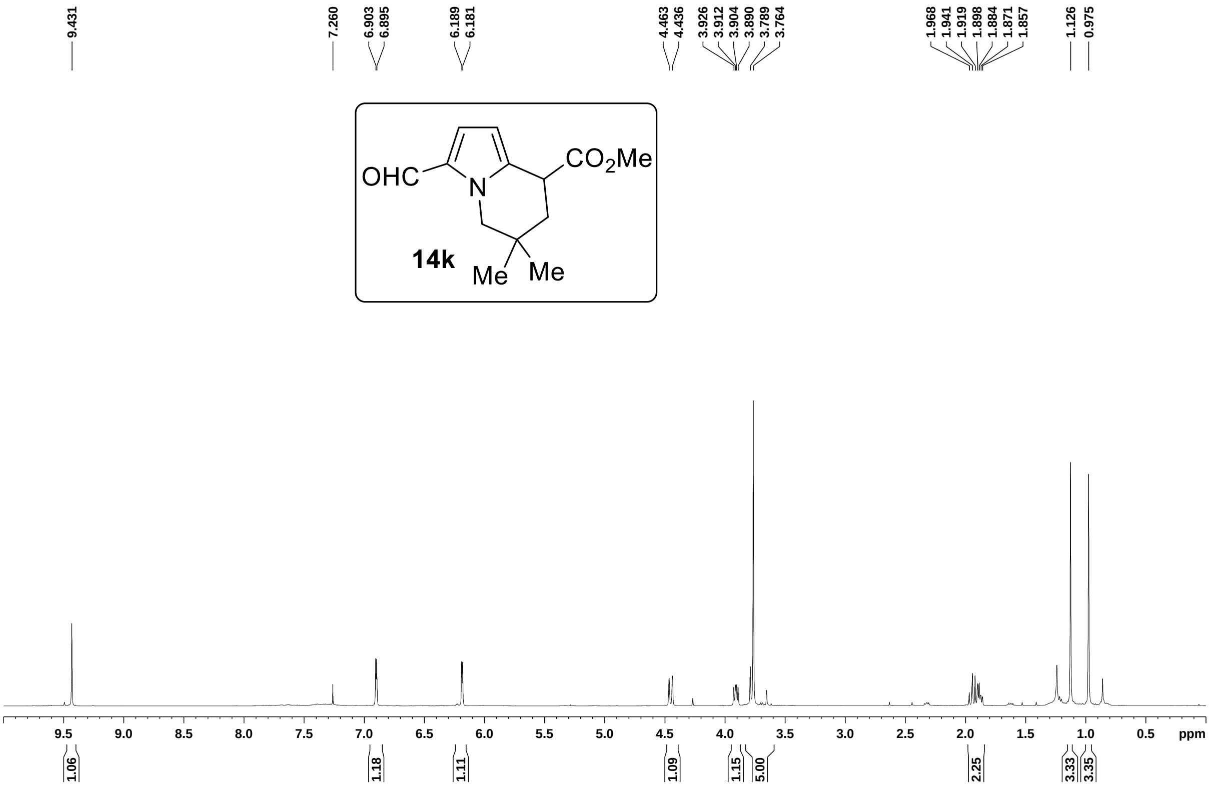
^{13}C NMR spectrum of 14i’ (100 MHz, CDCl$_3$)



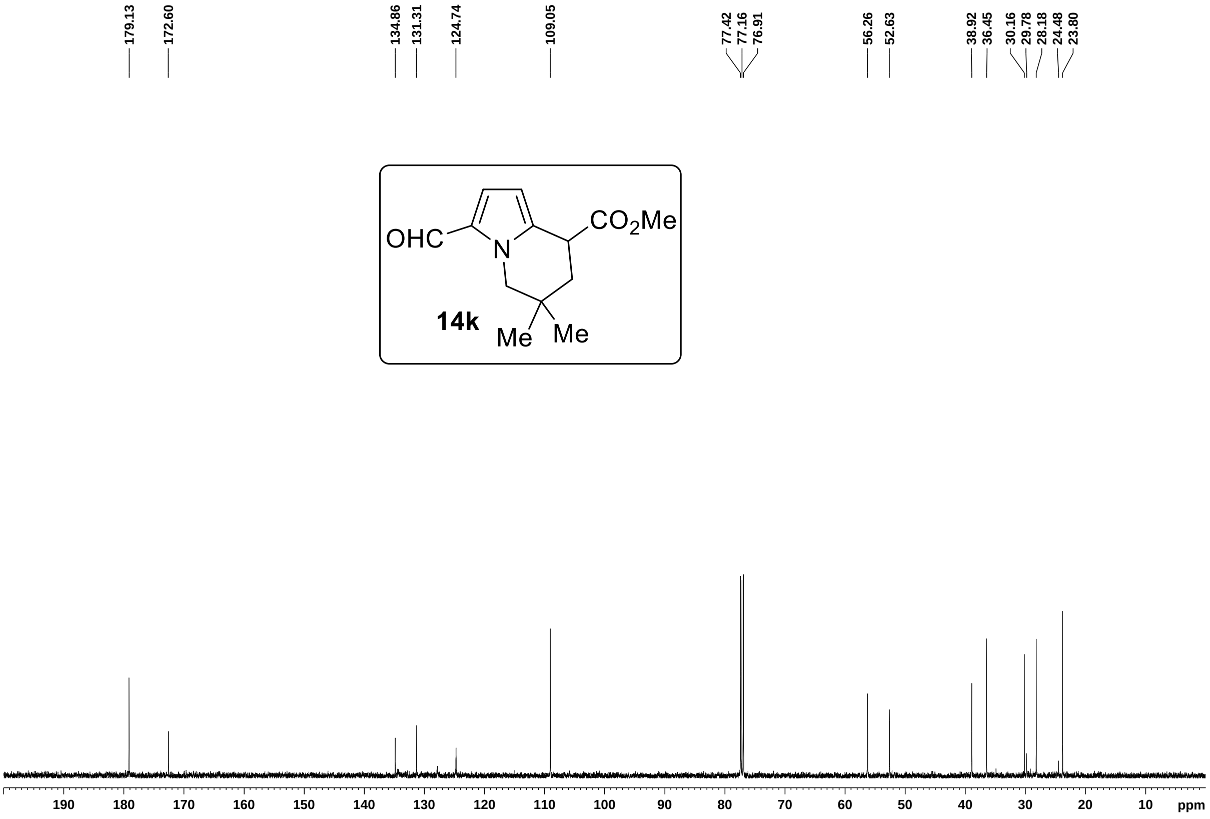
^{1}H NMR spectrum of 14j (400 MHz, CDCl$_3$)



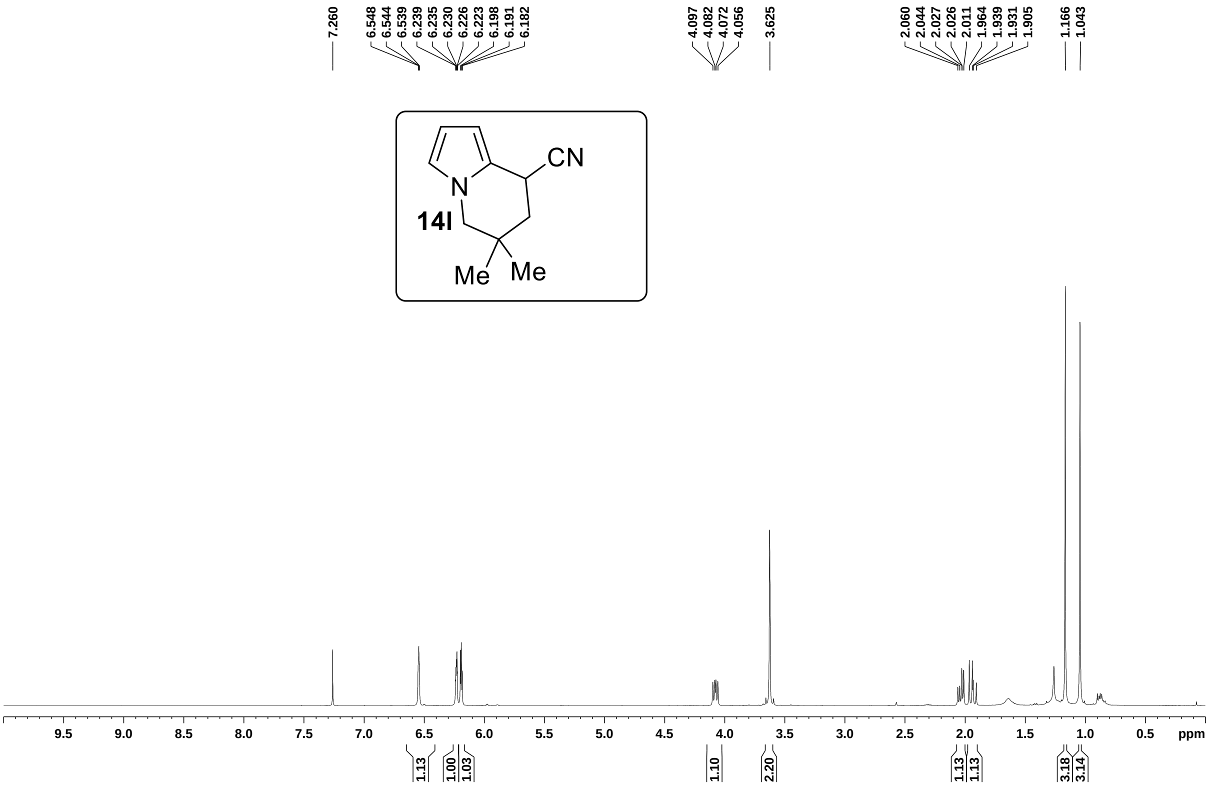
^{13}C NMR spectrum of 14j (100 MHz, CDCl$_3$)



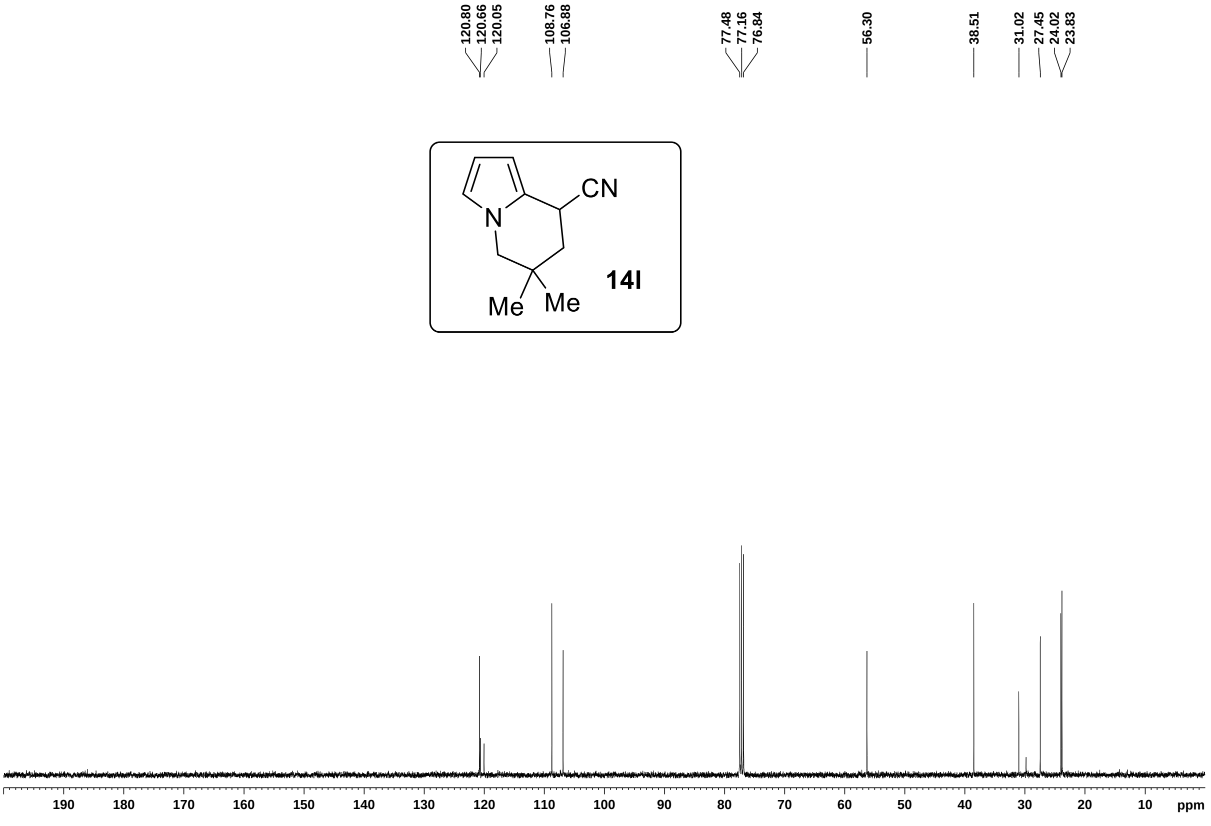
^{1}H NMR spectrum of 14k (500 MHz, $CDCl_3$)



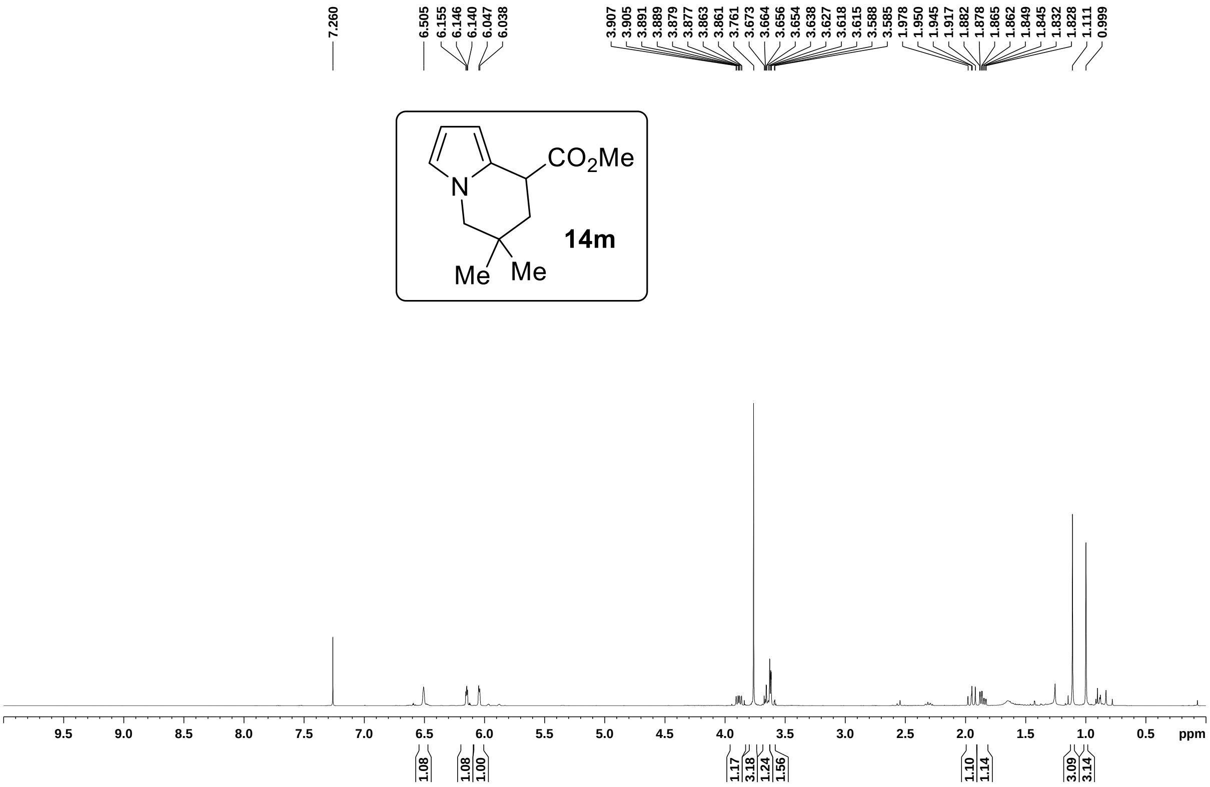
^{13}C NMR spectrum of 14k (125 MHz, $CDCl_3$)



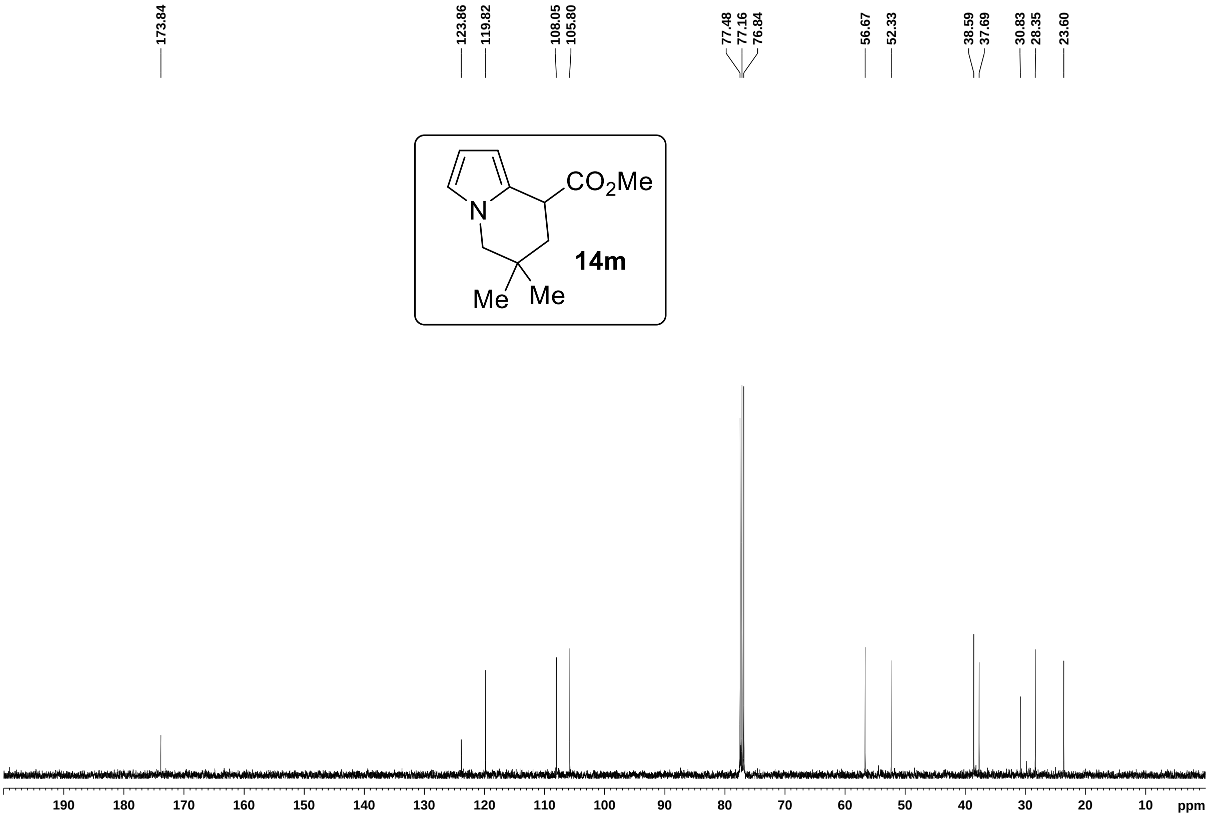
^{1}H NMR spectrum of 14l (400 MHz, $CDCl_3$)



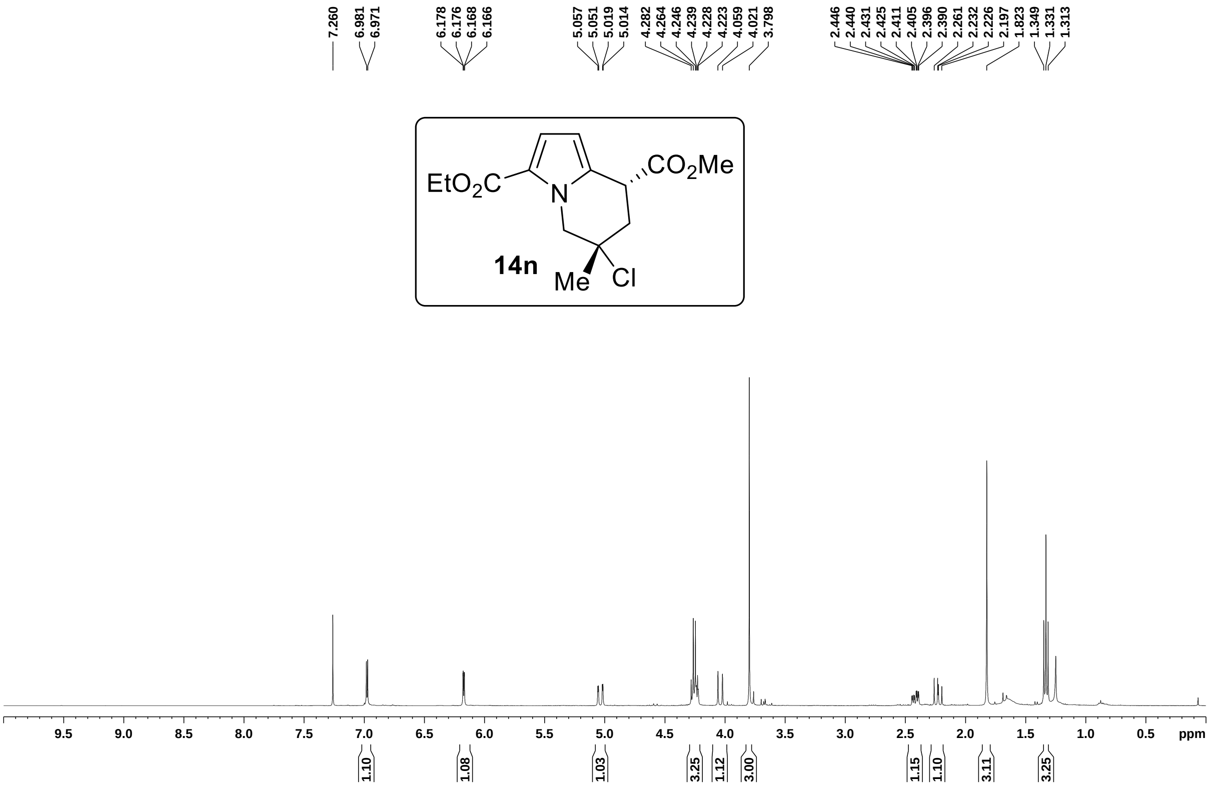
^{13}C NMR spectrum of 14l (100 MHz, $CDCl_3$)



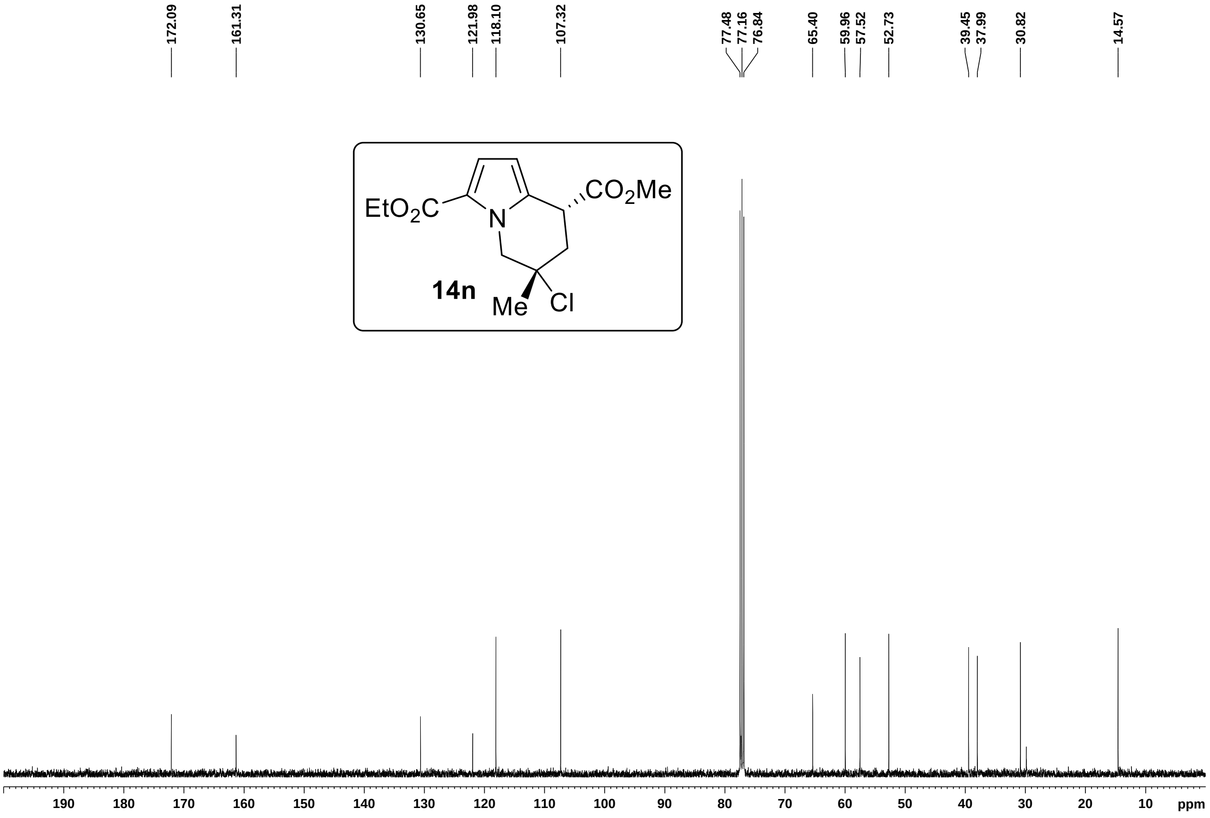
^{1}H NMR spectrum of 14m (400 MHz, CDCl$_3$)



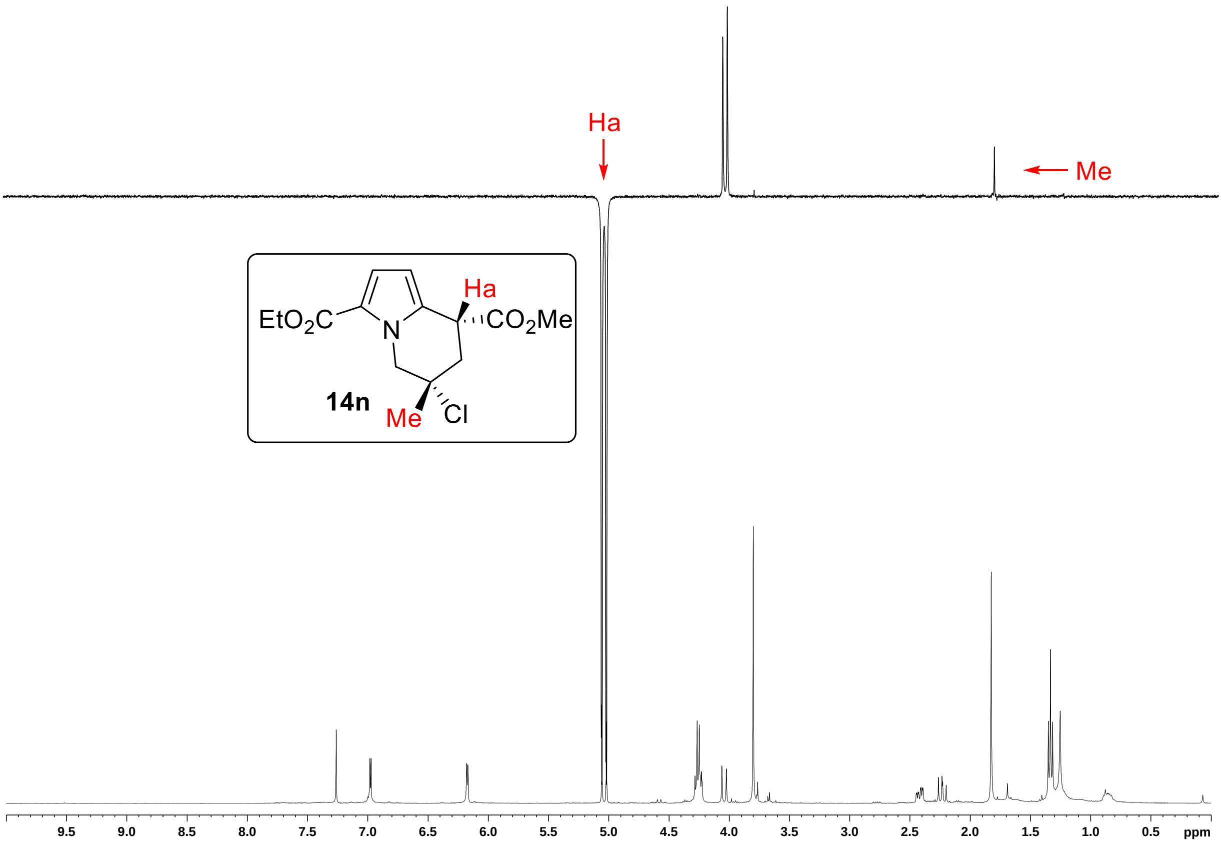
^{13}C NMR spectrum of 14m (100 MHz, CDCl$_3$)



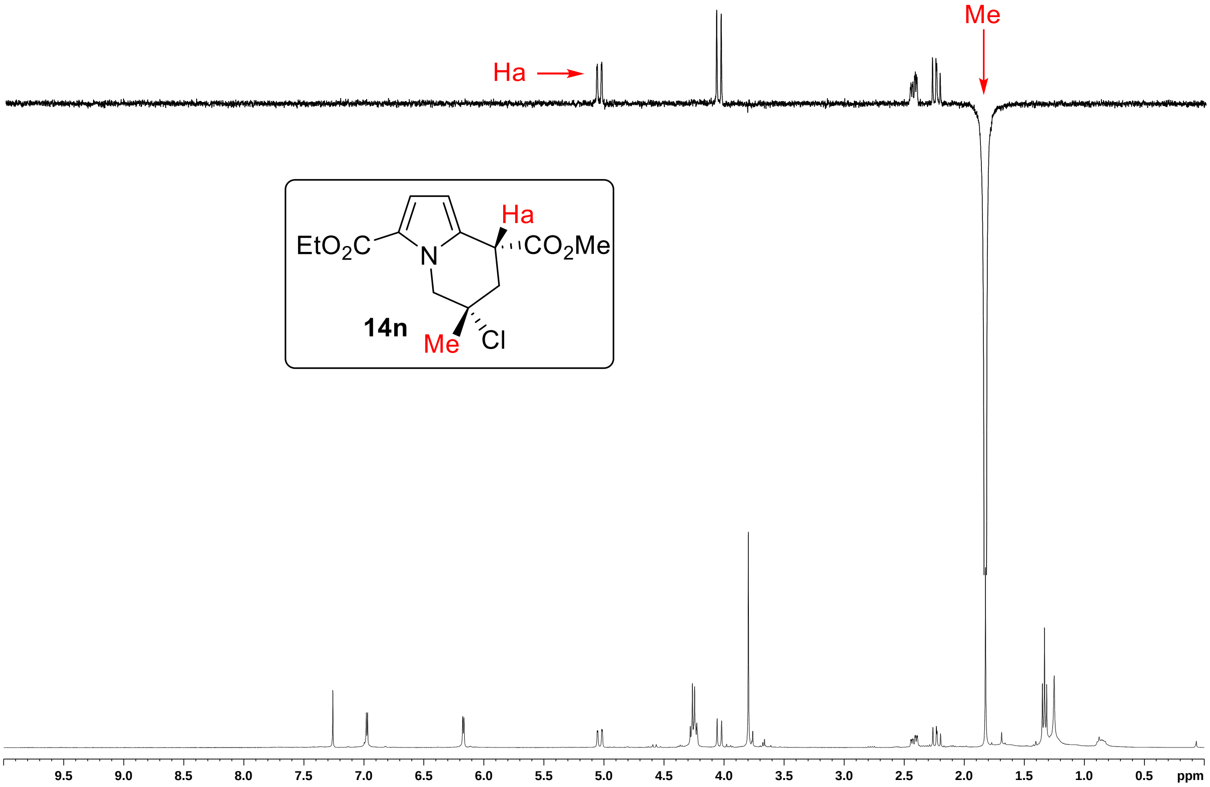
^{1}H NMR spectrum of 14n (400 MHz, CDCl$_3$)



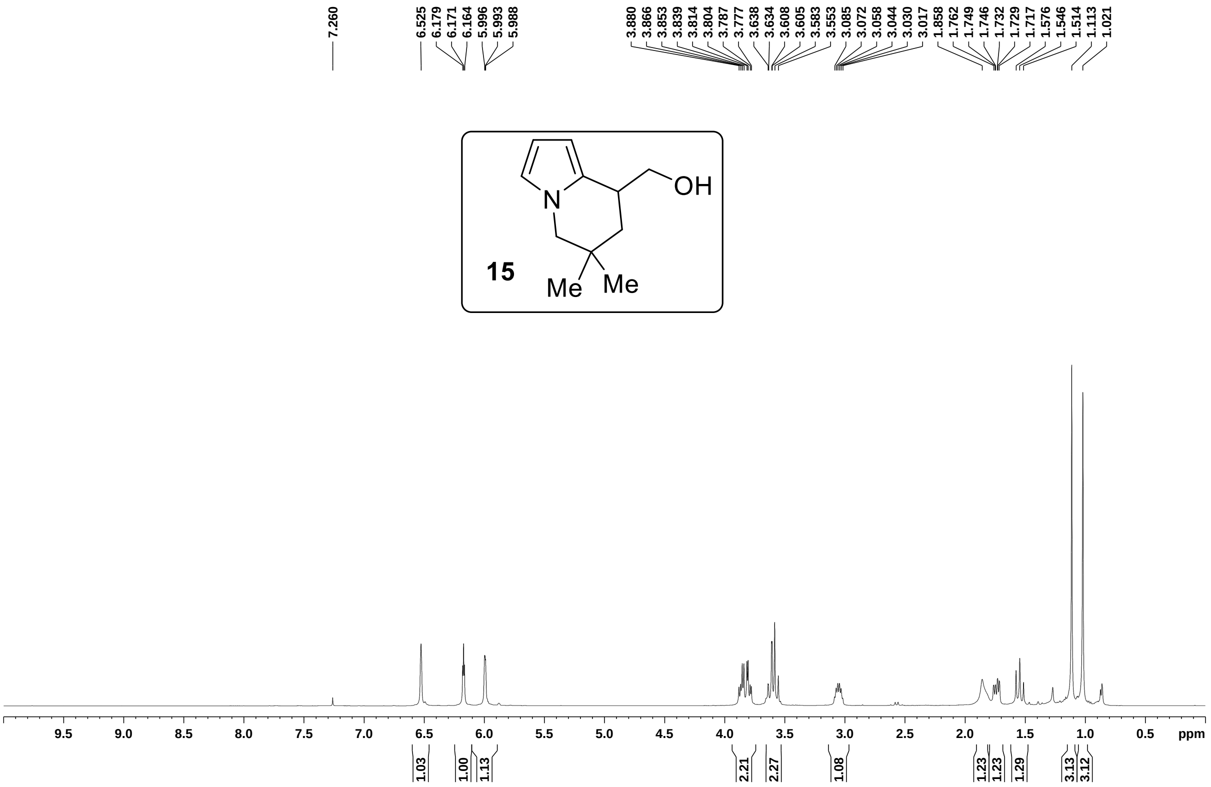
^{13}C NMR spectrum of 14n (100 MHz, CDCl$_3$)



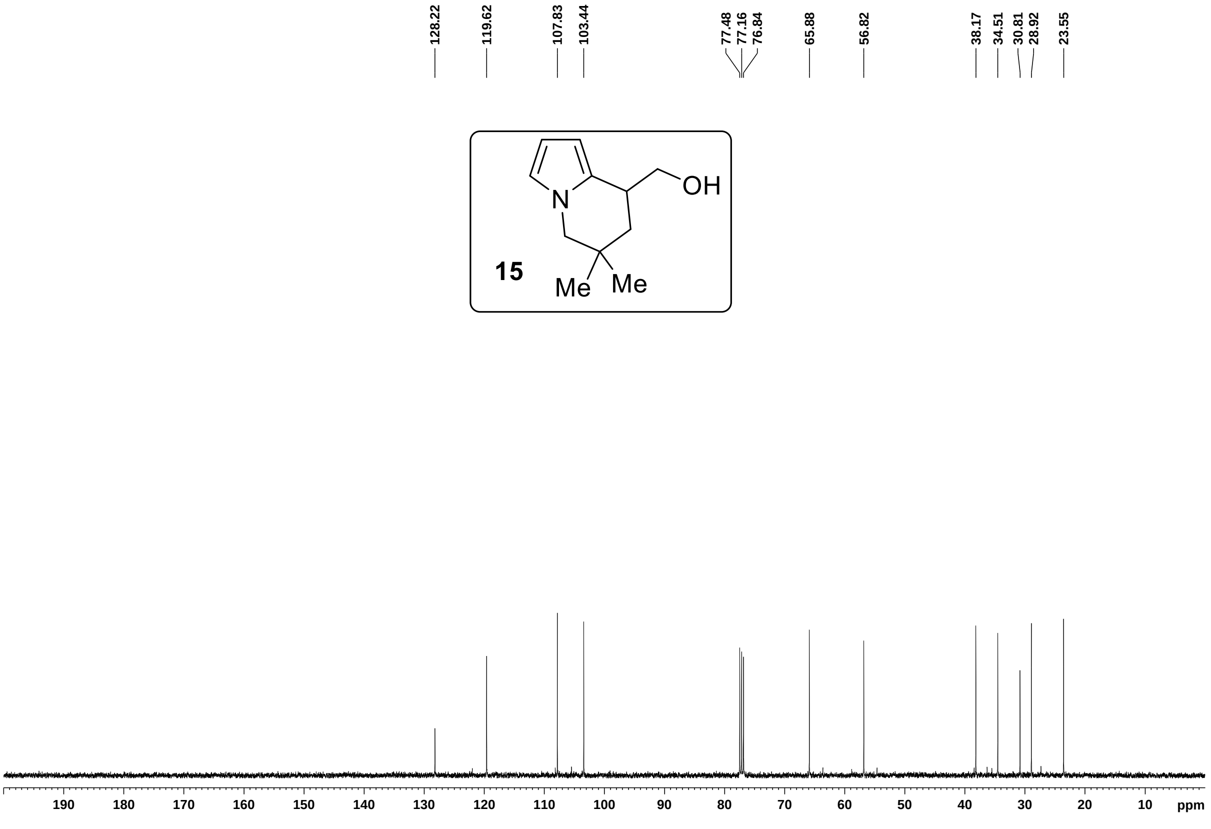
NOE spectrum of 14n with irradiation of Ha



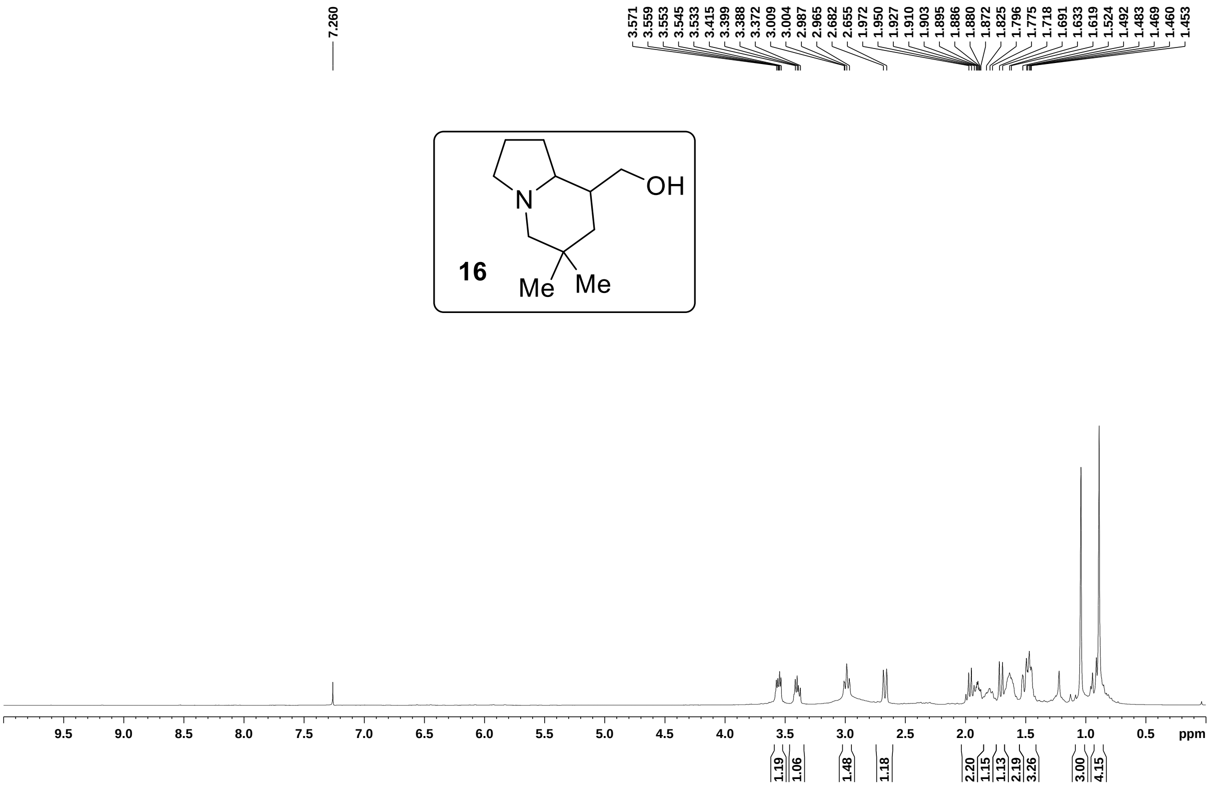
NOE spectrum of 14n with irradiation of Me



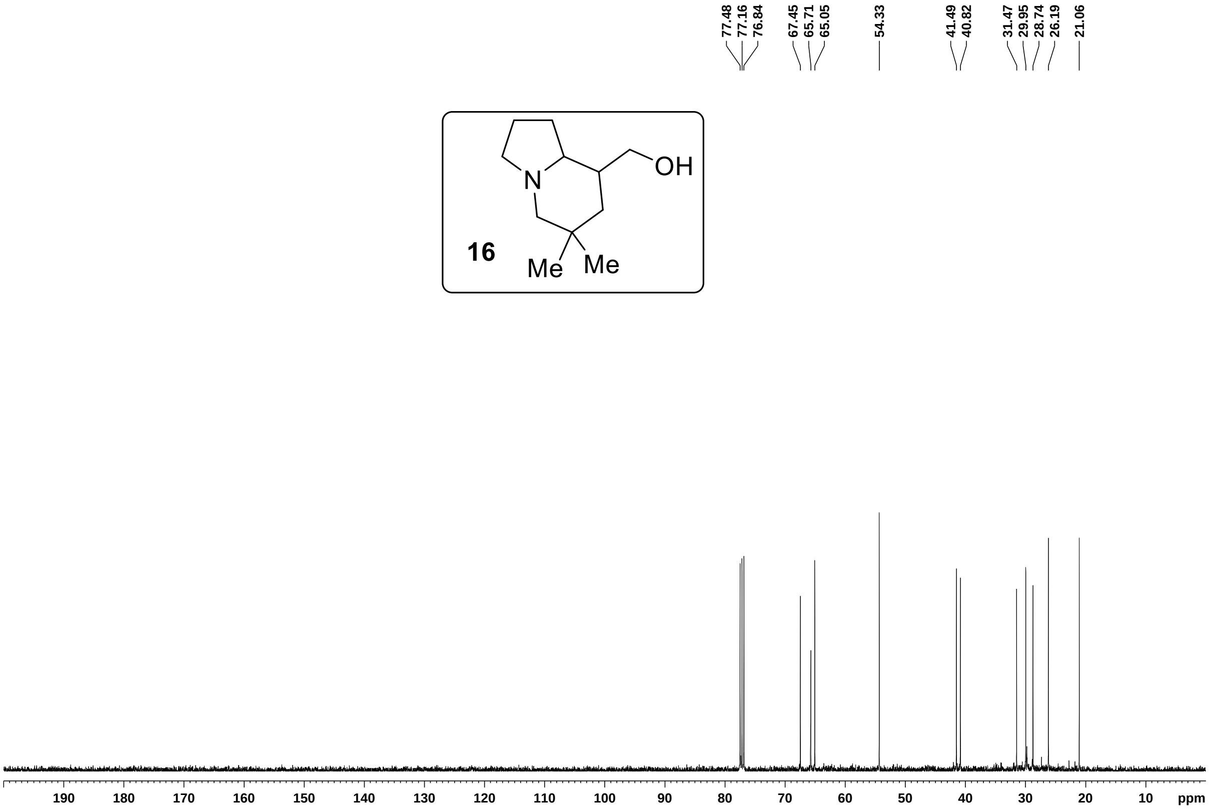
^{1}H NMR spectrum of 15 (400 MHz, $CDCl_3$)



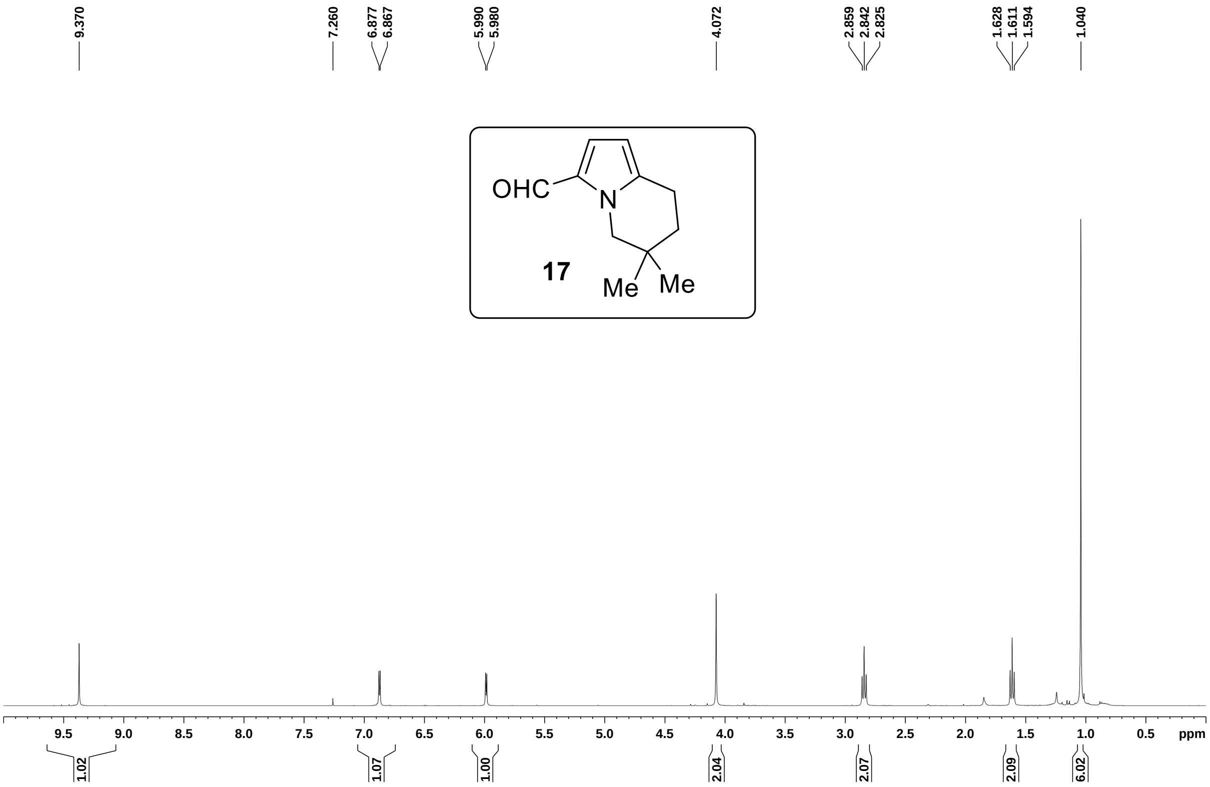
^{13}C NMR spectrum of 15 (100 MHz, $CDCl_3$)



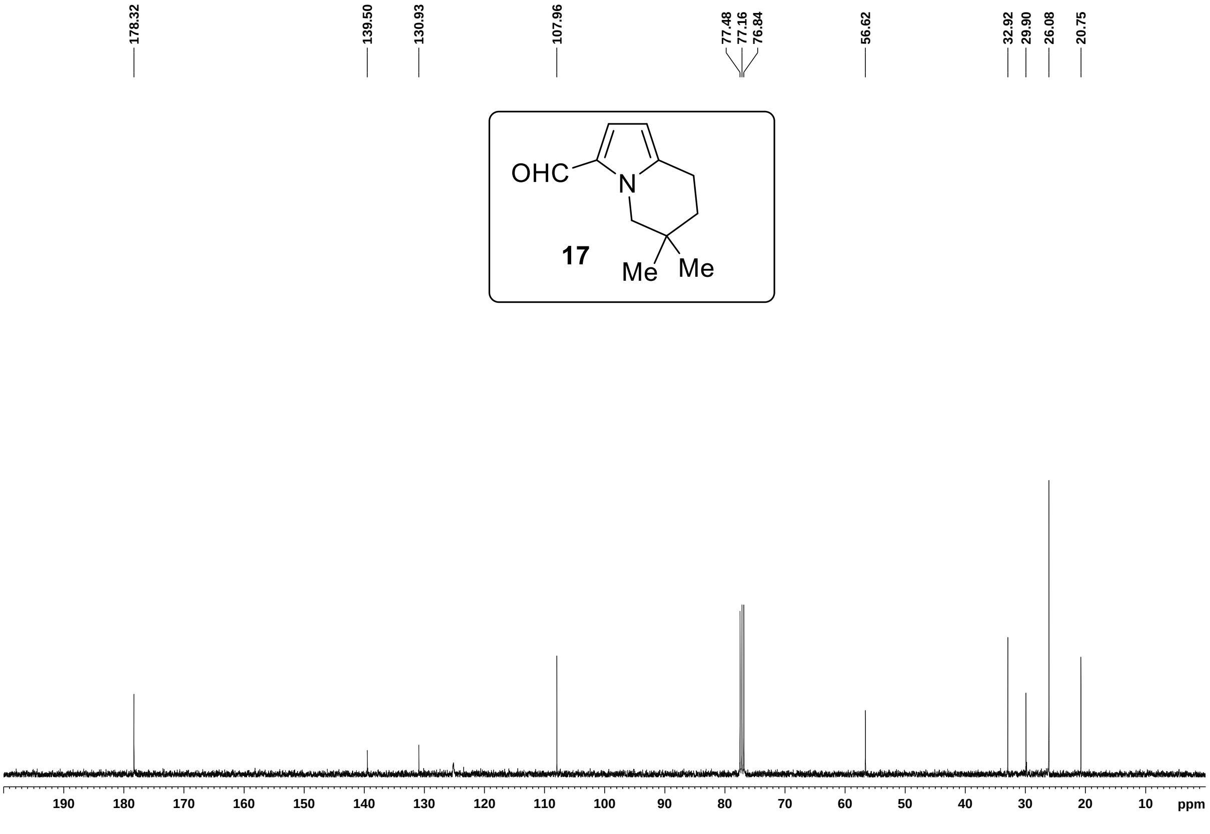
^{1}H NMR spectrum of 16 (400 MHz, CDCl$_3$)



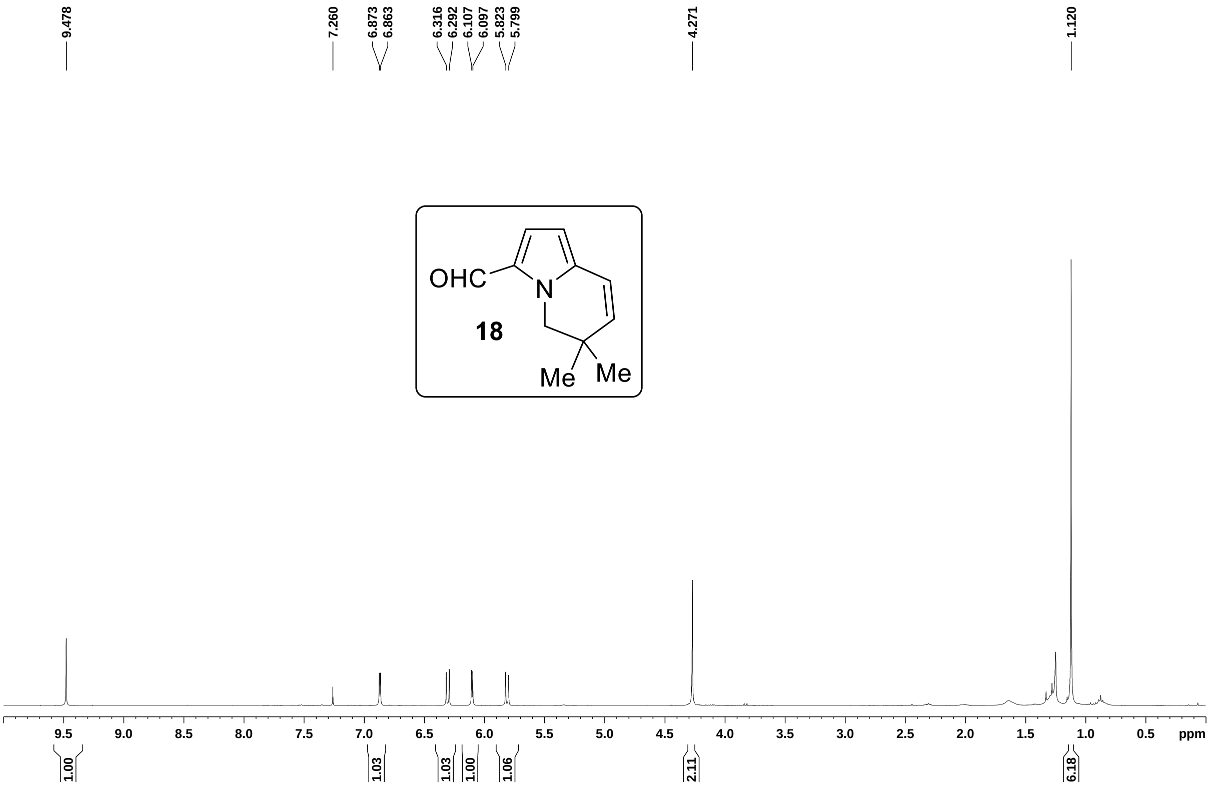
^{13}C NMR spectrum of 16 (100 MHz, CDCl$_3$)



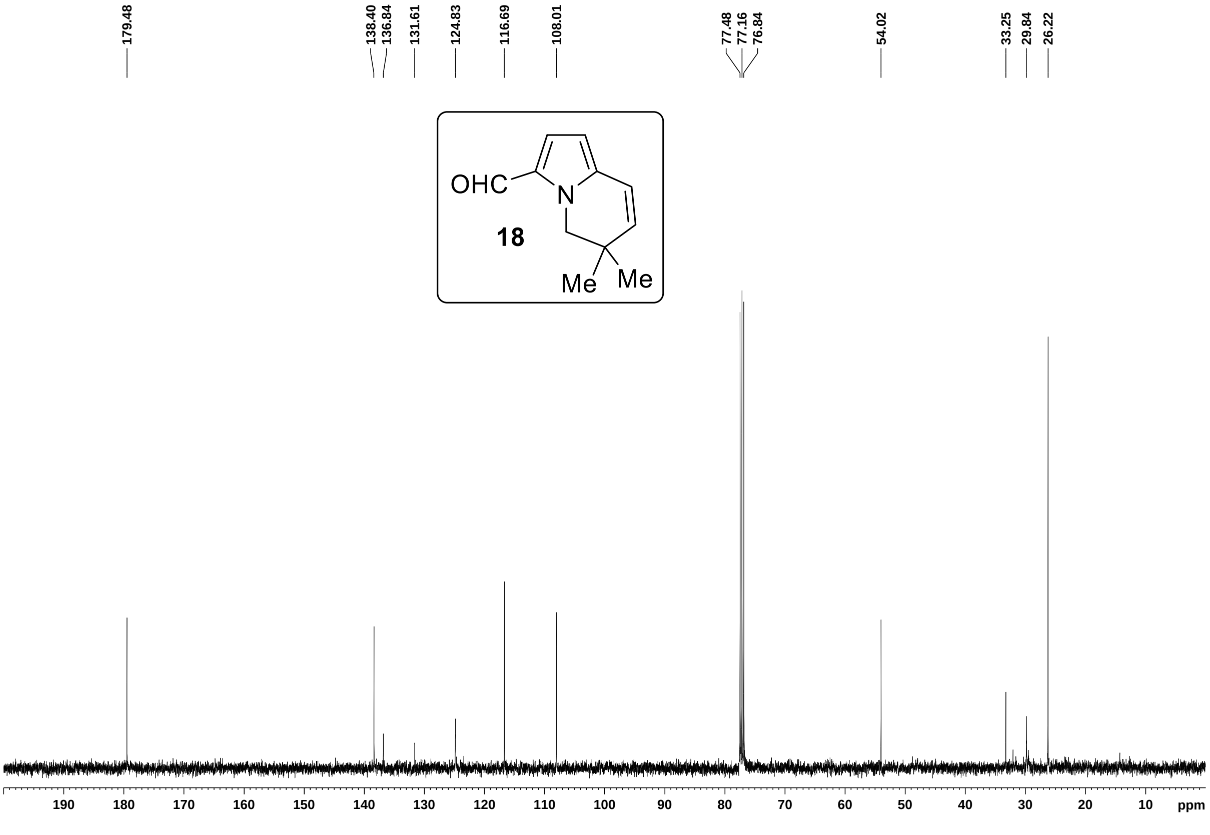
^{1}H NMR spectrum of 17 (400 MHz, CDCl$_3$)



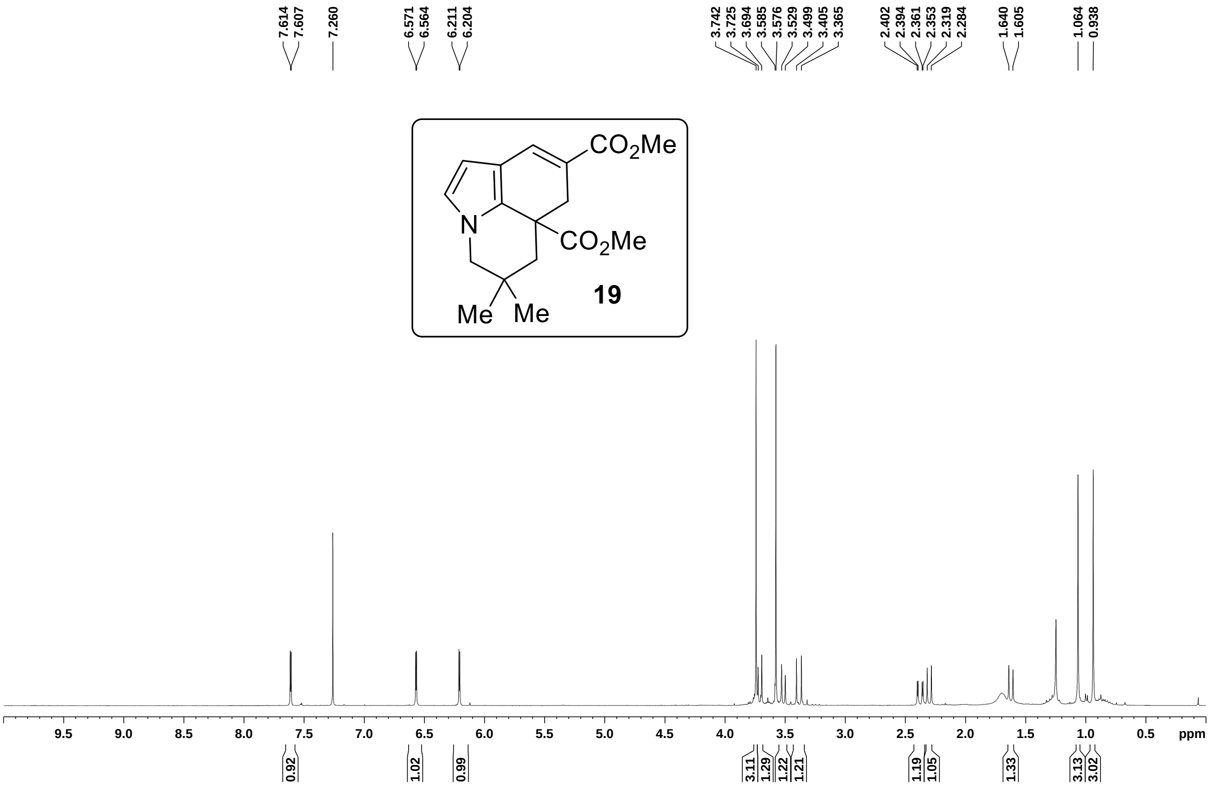
^{13}C NMR spectrum of 17 (100 MHz, CDCl$_3$)



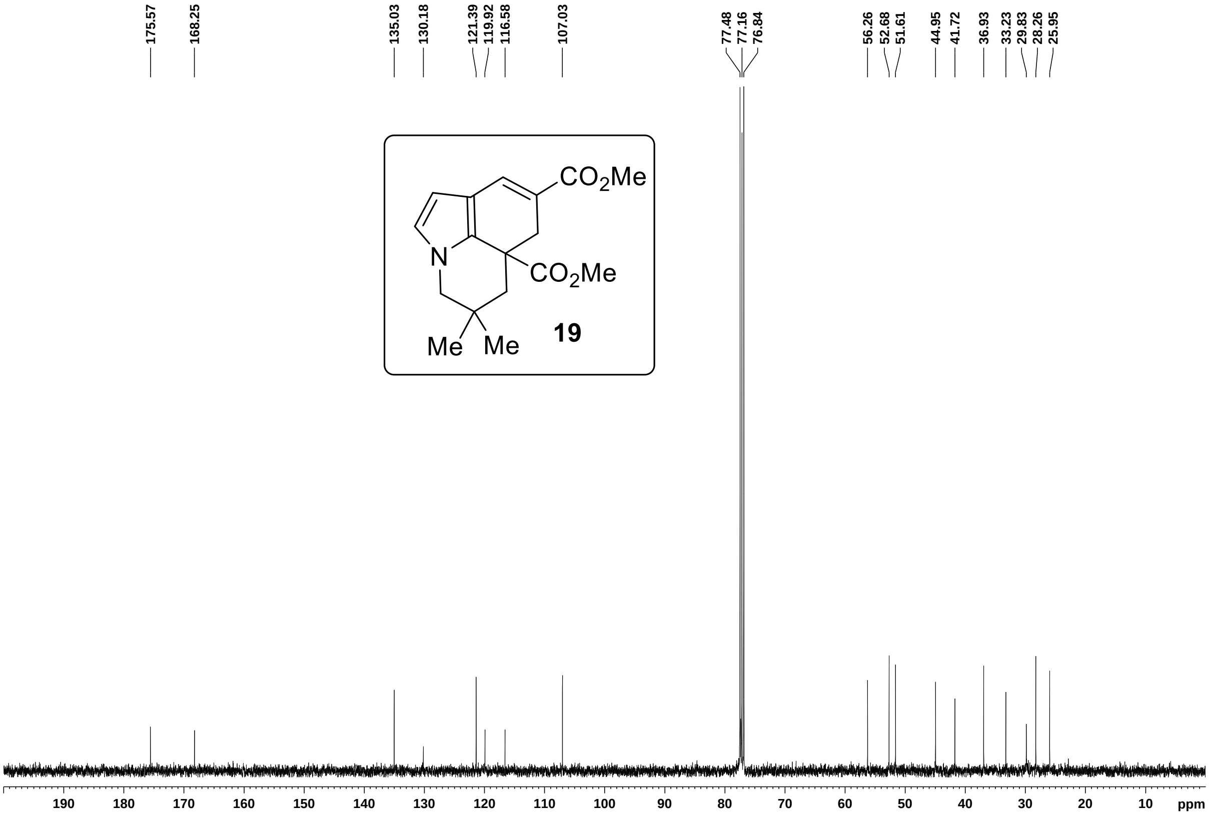
^1H NMR spectrum of 18 (400 MHz, $CDCl_3$)



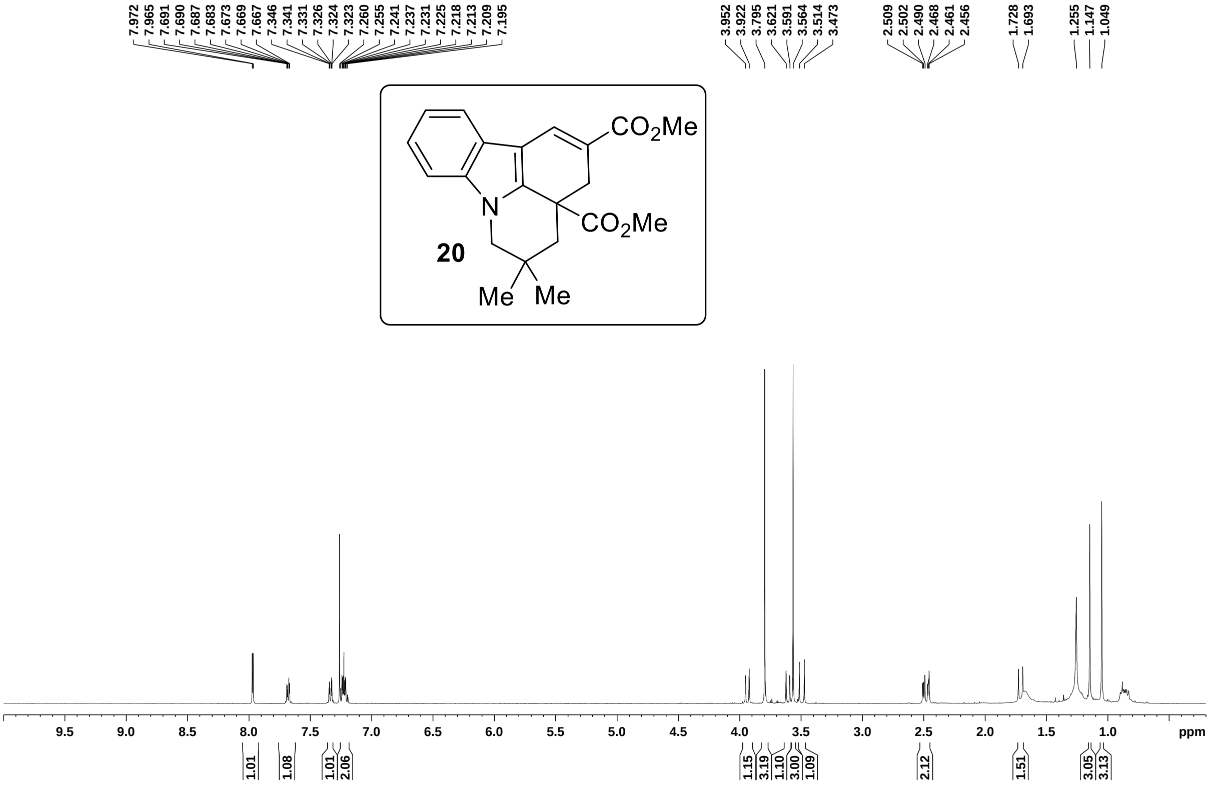
^{13}C NMR spectrum of 18 (100 MHz, $CDCl_3$)



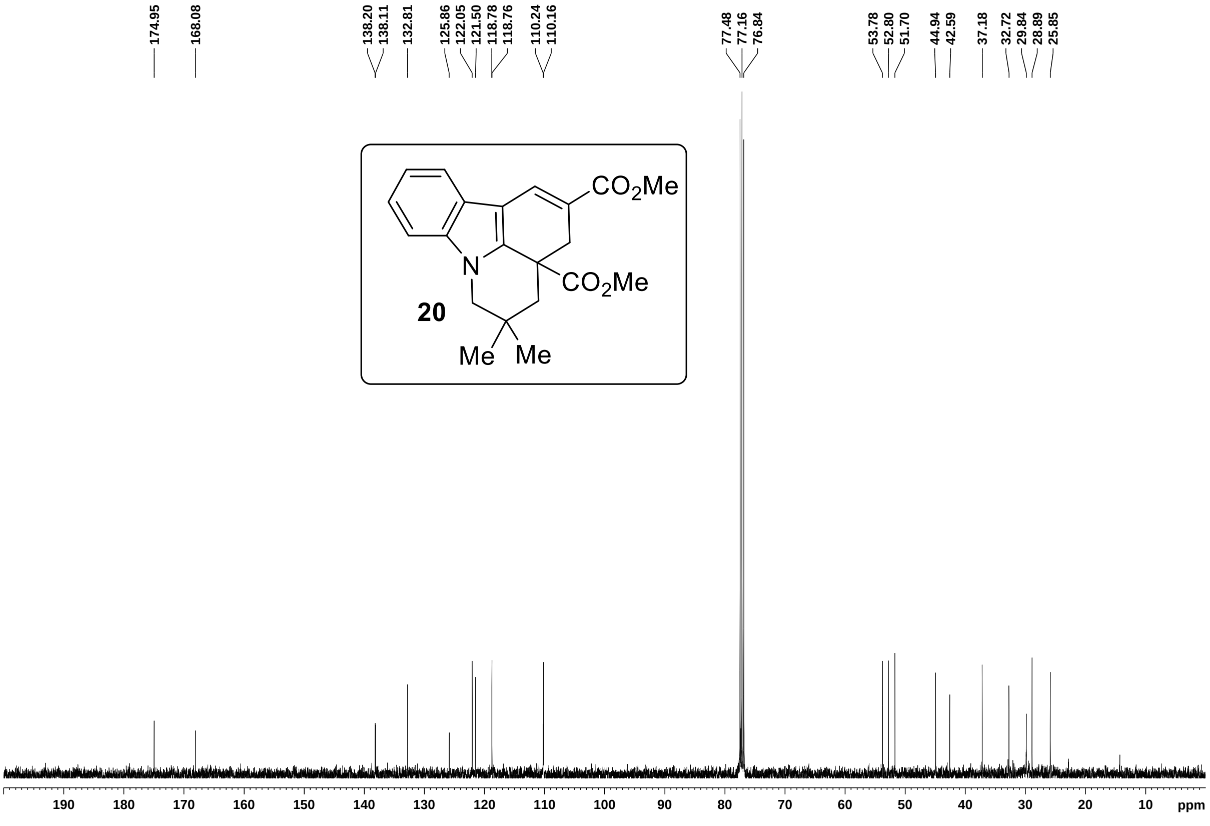
^{1}H NMR spectrum of 19 (400 MHz, CDCl$_3$)



^{13}C NMR spectrum of 19 (100 MHz, CDCl$_3$)



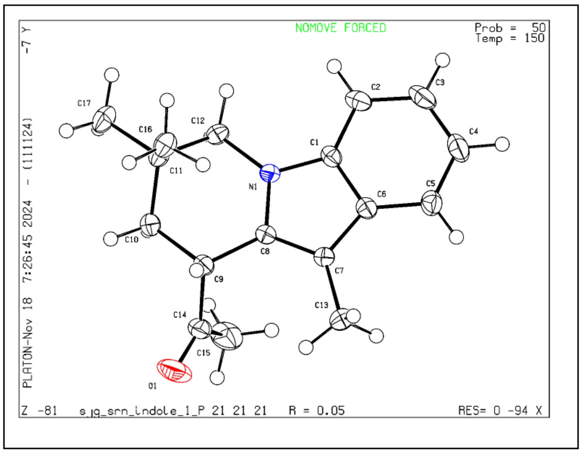
^{1}H NMR spectrum of 20 (400 MHz, CDCl$_3$)



^{13}C NMR spectrum of 20 (100 MHz, CDCl$_3$)

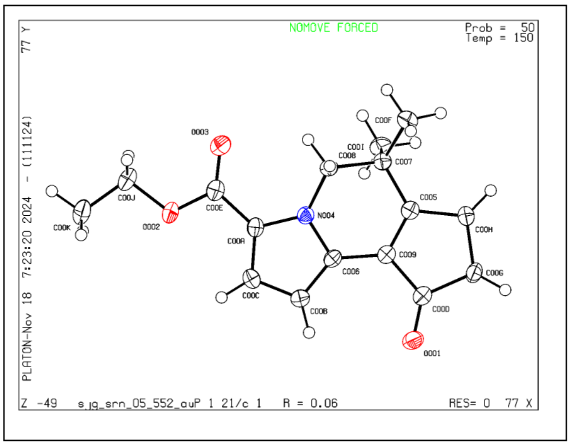
X-Ray crystallographic analysis:

Crystal data and structure refinement for 12l (ellipsoid is drawn at the 50% probability level):



Identification code		**12l**	
Solvent		CH_2Cl_2	
CCDC	2403442		
Bond precision:	C-C = 0.0030 A	Wavelength=0.71073	
Cell:	a= 8.9282(4)	b= 9.5175(5)	c= 16.7953(9)
	alpha=90	beta= 90	gamma=90
Temperature:	150 K		
	Calculated	Reported	
Volume	1427.17(12)	1427.17(12)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C17 H21 N O	C17 H21 N O	
Sum formula	C17 H21 N O	C17 H21 N O	
Mr	255.35	255.35	
Dx, g cm-3	1.188	1.188	
Z	4	4	
Mu (mm-1)	0.073	0.073	
F000	552.0	552.0	
F000’	552.21		
h,k,l max	12,13,23	12,13,23	
Nref	4164[2377]	4036	
Tmin,Tmax	0.995,0.997	0.115,1.000	
Tmin’	0.993		
Correction method =	Numerical		
Data completeness =	1.70/0.97	Theta(max)= 29.991	
R(reflections) =	0.0493(3641)	wR2(reflections)= 0.1206(4036)	
S = 1.046	Npar = 176		

Crystal data and structure refinement for 14h (ellipsoid is drawn at the 50% probability level):



Identification code		**14h**	
Solvent		CH_2Cl_2	
CCDC	2403441		
Bond precision:	C-C = 0.0032 A	Wavelength=0.71073	
Cell:	a= 7.3633(3)	b= 14.6962(6)	c= 12.8105(5)
	alpha=90	beta= 92.627(4)	gamma=90
Temperature:	150 K		
	Calculated	Reported	
Volume	1384.80(10)	1384.80(10)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C16 H17 N O3	C16 H17 N O3	
Sum formula	C16 H17 N O3	C16 H17 N O3	
Mr	271.31	271.30	
Dx, g cm-3	1.301	1.301	
Z	4	4	
Mu (mm-1)	0.090	0.090	
F000	576.0	576.0	
F000’	576.28		
h,k,l max	8,17,15	8,17,15	
Nref	2444	2441	
Tmin,Tmax	0.992,0.996	0.130,1.000	
Tmin’	0.992		
Correction method =	Numerical		
Data completeness =	0.999	Theta(max)= 24.998	
R(reflections) =	0.0593(2108)	wR2(reflections)= 0.1675(2441)	
S = 1.051	Npar = 184		

Reference:

1. J. Diesel, D. Grosheva, S. Kodama, N. Cramer, *Angew. Chem., Int. Ed.* 2019, **58**, 11044.