Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Silver-catalyzed acylative annulation of *N*-propargylated indoles with α-keto acids: Access to acylated pyrrolo[1,2-*a*]indoles

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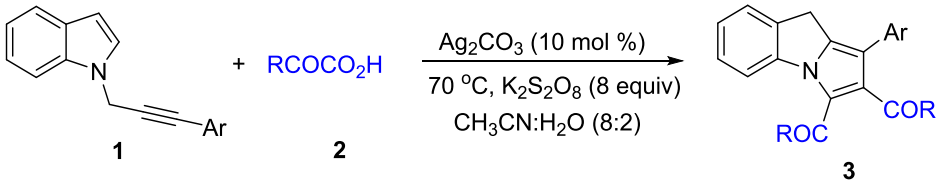
1. General Experimental:

All the reactions were carried out under inert atmosphere with oven-dried glassware. Commercially available reagents and solvents were used without further purification, unless otherwise stated. All reactions were magnetically stirred and monitored by thin-layer chromatography carried out on silica plates using UV-light, anisaldehyde and ninhydrin for visualization. Column chromatography was performed on silica gel (60–120 and 100-200 mesh) using hexanes, ethyl acetate and methanol as eluent. Evaporation of solvents was conducted under reduced pressure at temperatures less than 45 °C. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent on a 300 MHz, 400 MHz and 500 MHz NMR spectrometer. Chemical shifts δ and coupling constants J are given in ppm (parts per million) and Hz (hertz) respectively. Chemical shifts are reported relative to residual solvent as an internal standard for ^{1}H and ^{13}C ($CDCl_3$: δ 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C). FTIR spectra were recorded on alpha (Bruker) infrared spectrometer. High resolution spectra (HRMS) [ESI^{+}] were obtain using either a TOF or a double focusing spectrometer. Substituted *N*-propargylic indole (**1**) are prepared from known procedures in literature.[1]

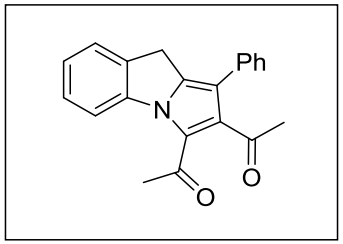
2. Experimental procedures and characterization data

2.1 General procedure for the synthesis of diacylated-9*H*-pyrrolo[1,2-*a*]indoles (3)



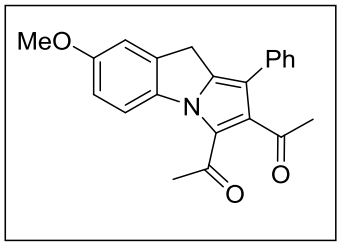
A 5 mL reaction vial equipped with a magnetic stirring bar was charged with Ag_2CO_3 (0.04 mmol), potassium persulfate (3.2 mmol), substituted *N*-propargyl indole **1** (0.4 mmol), *α*-keto acid **2** (1.2 mmol) and 3 mL of CH_3CN/H_2O (v1/v2 = 8:2). After that reaction mixture was allowed to stir at 70 °C for 6-9 h. The reaction was monitored by TLC, after completion of starting material reaction mixture was diluted with water and extracted with ethyl acetate (2 times). The organic layers were combined and dried over sodium sulphate and solvent was removed in vacuo. The obtained crude product was purified by column chromatography on silica gel (10% EtOAc in hexane) to afford the corresponding compounds **3**.

1,1'-(1-Phenyl-9*H*-pyrrolo[1,2-*a*]indole-2,3-diyl)bis(ethan-1-one) (3a)



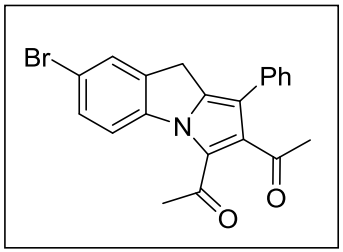
Following the general procedure compound **3a** obtained as a yellow solid, yield: 102 mg, 80%; mp 168-170 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (d, J = 8.2 Hz, 1H), 7.45 – 7.40 (m, 3H), 7.39 – 7.34 (m, 4H), 7.22 (t, J = 7.5 Hz, 1H), 3.95 (s, 2H), 2.50 (s, 3H), 2.24 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 201.3, 190.7, 141.2, 139.0, 134.6, 134.3, 133.6, 128.9, 128.4, 128.1, 127.4, 126.1, 125.3, 125.2, 117.7, 116.1, 32.4, 30.02, 29.1; **IR (KBr)** ν_{max} = 2926, 1700, 1465,760 cm^{-1}; **HRMS (ESI):** m/z calcd for $C_{21}H_{18}NO_2$ $(M+H)^+$: 316.1338, found: 316.1331.

1'-(7-Methoxy-1-phenyl-9*H*-pyrrolo[1,2-*a*]indole-2,3-diyl)bis(ethan-1-one) (3b)



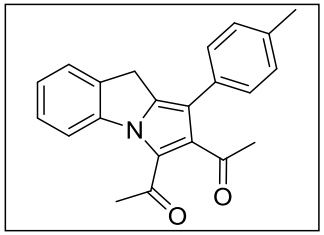
Following the general procedure compound **3b** obtained as a yellow solid, yield: 107 mg, 78%; mp 140-142 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, J = 9.0 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.39 – 7.32 (m, 3H), 6.96 (d, J = 2.5 Hz, 1H), 6.86 (dd, J = 9.0, 2.6 Hz, 1H), 3.91 (s, 2H), 3.83 (s, 3H), 2.48 (s, 3H), 2.24 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.5, 190.5, 157.6, 138.8, 136.1, 135.1, 134.0, 133.6, 128.9, 128.4, 127.4, 125.7, 117.8, 116.9, 112.4, 111.7, 55.7, 32.4, 29.9, 29.3; **IR (KBr) ν_{max}** = 2920, 1703, 1470, 764 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{22}H_{20}NO_3$ $(M+H)^+$: 346.1443, found: 346.1440.

1,1'-(7-Bromo-1-phenyl-9*H*-pyrrolo[1,2-*a*]indole-2,3-diyl)bis(ethan-1-one) (3c)



Following the general procedure compound **3c** obtained as a pale yellow solid, yield: 117 mg, 75%; mp 184-186^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.7 Hz, 1H), 7.53 (d, J= 1.7 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.39 – 7.34(m,3H), 3.94 (s, 2H), 2.48 (s, 3H), 2.25 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.5, 190.1, 140.4, 138.8, 136.5, 135.3, 133.1, 131.0, 129.2, 129.0, 128.4, 128.3, 127.6, 125.8, 118.4, 117.8, 32.5, 29.8, 29.0; **IR (KBr) ν_{max}** = 2910, 1704, 1462, 763 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{21}H_{17}NO_2Br$ $(M+H)^+$: 394.0443, found: 394.0443.

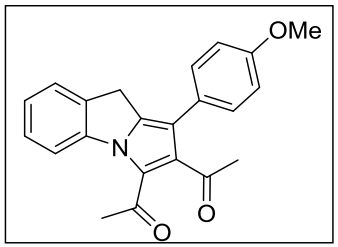
1,1'-(1-(*p*-Tolyl)-9*H*-pyrrolo[1,2-*a*]indole-2,3-diyl)bis(ethan-1-one) (3d)



Following the general procedure compound **3d** obtained as a yellow semisolid, yield: 103 mg, 79%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, J= 8.2 Hz, 1H), 7.43 – 7.32 (m, 2H), 7.29 – 7.18 (m, 5H), 3.92 (s, 2H), 2.50 (s, 3H), 2.40 (s, 3H), 2.25 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.5, 190.6, 141.2, 138.9, 137.2, 134.6, 134.4, 130.5, 129.6, 128.3, 128.0, 125.9, 125.3, 125.2, 117.7, 116.1, 32.4, 30.0, 29.0, 21.2; **IR (KBr) ν_{max}** = 2927, 1705, 1464, 759 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{22}H_{20}NO_2$ $(M+H)^+$:

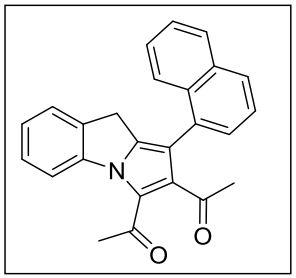
330.1494, found: 330.1496.

1,1'-(1-(4-Methoxyphenyl)-9*H*-pyrrolo[1,2-*a*]indole-2,3-diyl)bis(ethan-1-one) (3e)



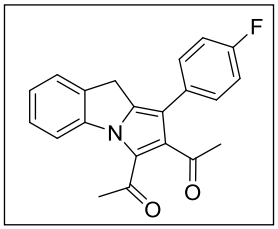
Following the general procedure compound **3e** obtained as a yellow solid, yield: 112 mg, 81%; mp 160-162 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (d, J = 8.2 Hz, 1H), 7.43 – 7.33 (m, 2H), 7.29 (d, J = 8.7 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 8.7 Hz, 2H), 3.91 (s, 2H), 3.86 (s, 3H), 2.50 (s, 3H), 2.24 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.5, 190.6, 159.0, 141.2, 138.9, 134.4, 131.6, 129.6, 128.0, 125.9, 125.7, 125.3, 125.2, 117.4, 116.1, 114.4, 55.3, 32.4, 29.9, 29.0; **IR (KBr)** ν_{max} = 2920, 1710, 1466, 760 cm^{-1};**HRMS (ESI)**: m/z calcd for $C_{22}H_{20}NO_3$ $(M+H)^+$:346.1443, found: 346.1447.

1,1'-(1-(Naphthalen-1-yl)-9*H*-pyrrolo[1,2-*a*]indole-2,3-diyl)bis(ethan-1-one) (3f)



Following the general procedure compound **3f** obtained as a yellow solid, yield: 109 mg, 75%; mp 156-158 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.2 Hz, 1H), 7.93 (t, J = 8.3 Hz, 2H), 7.77 (d, J= 8.4 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.49 – 7.45 (m, 2H), 7.39 – 7.33 (m, 2H), 7.21 (td, J = 7.5, 0.8 Hz, 1H), 3.76 – 3.61 (m, 2H), 2.59 (s, 3H), 1.88 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.8, 193.1, 140.9, 139.0, 134.8, 134.3, 133.8, 132.2, 131.4, 128.6, 128.5, 128.1, 127.3, 126.7, 126.3, 125.6, 125.5, 125.4, 116.0, 115.5, 30.8, 30.4, 28.8; **IR (KBr)** ν_{max}= 2910, 1702, 1467, 764 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{25}H_{20}NO_2$ $(M+H)^+$: 366.1494, found: 366.1488.

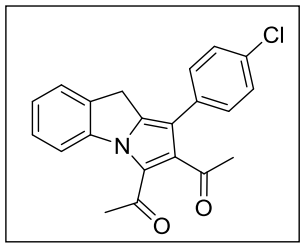
1,1'-(1-(4-Fluorophenyl)-9*H*-pyrrolo[1,2-*a*]indole-2,3-diyl)bis(ethan-1-one) (3g)



Following the general procedure compound **3g** obtained as a yellow solid, yield: 102 mg, 77%; mp 162-164 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, J= 8.2 Hz, 1H), 7.43 – 7.32 (m, 4H), 7.22 (td, J = 7.5, 0.9 Hz, 1H), 7.17 – 7.11 (m, 2H), 3.91 (s, 2H), 2.50 (s, 3H), 2.23 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.97,

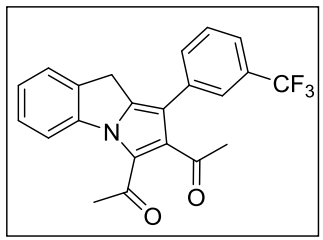
190.75,162.18 (d, *J* = 247.4 Hz), 141.1, 138.9, 134.4, 134.2, 130.1 (d, *J* = 8.1 Hz), 129.6, 128.1, 126.1, 125.3 (d, *J* = 3.1 Hz),116.6, 116.1, 116.1, 115.8, 32.4, 30.0, 28.9; **IR (KBr)** ν_{max} = 2920, 1709, 1465, 757 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{21}H_{17}NO_2F$ $(M+H)^+$: 334.1243, found: 334.1237.

1,1'-(1-(4-Chlorophenyl)-9*H*-pyrrolo[1,2-*a*]indole-2,3-diyl)bis(ethan-1-one) (3h)



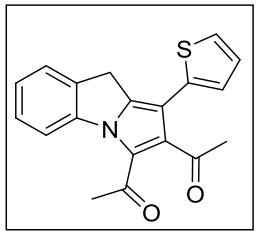
Following the general procedure compound **3h** obtained as a yellow solid, yield: 106 mg, 77%; mp 174-176 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J*= 8.2 Hz, 1H), 7.44 – 7.29 (m, 6H), 7.23 (td, *J* = 7.5, 0.8 Hz, 1H), 3.92 (s, 2H), 2.50 (s, 3H), 2.26 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.0, 190.6, 141.1, 139.0, 134.3, 134.2, 133.4, 132.1, 129.7, 129.2, 128.1, 126.2, 125.4, 116.4, 116.1, 32.5, 30.0, 29.0; **IR (KBr)** ν_{max} = 2926, 1700, 1465, 760 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{21}H_{17}NO_2Cl$ $(M+H)^+$: 350.0948, found: 350.0948.

1,1'-(1-(3-(Trifluoromethyl)phenyl)-9*H*-pyrrolo[1,2-*a*]indole-2,3-diyl)bis(ethan-1-one) (3i)



Following the general procedure compound **3i** obtained as a yellow solid, yield: 119 mg, 78%; mp 136-138 ^oC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.2 Hz, 1H), 7.67 (s, 1H), 7.64 – 7.54 (m, 3H), 7.43 (d, J = 7.4 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.24 (td, *J* = 7.5, 0.9 Hz, 1H), 3.95 (s, 2H), 2.52 (s, 3H), 2.25 (s, 3H); **^{13}C NMR** (126 MHz,$CDCl_3$) δ 200.5, 190.9, 140.9, 139.1, 134.5, 134.1, 131.8,131.4 (q, *J* = 32.4 Hz), 129.5, 128.2, 126.5, 125.5, 125.4, 125.0, 124.2,121.8 (q, *J* = 272.5 Hz), 116.1, 116.1, 32.4, 30.1, 29.0; **IR (KBr)** ν_{max} = 2916, 1704, 1460, 757 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{22}H_{17}NO_2F_3$ $(M+H)^+$: 384.1211, found: 384.1206.

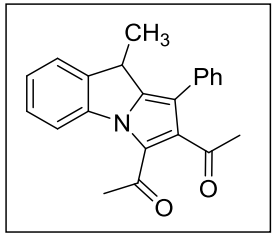
1,1'-(1-(Thiophen-2-yl)-9*H*-pyrrolo[1,2-*a*]indole-2,3-diyl)bis(ethan-1-one) (3j)



Following the general procedure compound **3j** obtained as a yellow solid, yield: 101 mg, 79%; mp 130-132^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J*= 7.5 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.23 (td, *J*

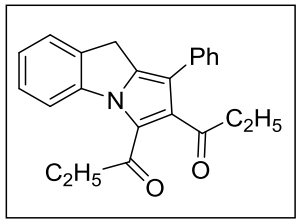
= 7.6, 1.0 Hz, 1H), 7.12 – 7.08 (m, 1H), 7.02 (dd,*J* = 3.5, 1.1 Hz, 1H), 3.99 (s, 2H), 2.49 (s, 3H), 2.42 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.5, 189.9, 141.2, 139.8, 134.3, 133.0, 128.1, 127.7, 126.0, 125.3, 125.0, 122.3, 116.3, 110.5, 106.4, 97.4, 32.5, 29.8, 29.5; **IR (KBr)** ν_{max} = 2900, 1703, 1467, 758 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{19}H_{16}NO_2S$ $(M+H)^+$: 322.0902, found: 322.0914.

1,1'-(9-Methyl-1-phenyl-9*H*-pyrrolo[1,2-*a*]indole-2,3-diyl)bis(ethan-1-one) (3k)



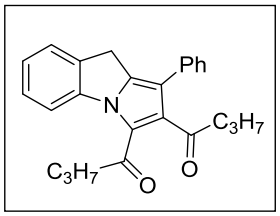
Following the general procedure compound **3k** obtained as a yellow semisolid, Yield: 99 mg, 76%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J*= 8.1 Hz, 1H), 7.47 – 7.30 (m, 7H), 7.22 (td, *J* = 7.5, 1.0 Hz, 1H), 4.20 (q, *J* = 7.3 Hz, 1H), 2.51 (s, 3H), 2.16 (s, 3H), 1.27 (d, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.6, 191.5, 143.5, 140.6, 140.1, 134.5, 133.4, 129.1, 128.8, 128.1, 127.6, 125.8, 125.4, 124.2, 118.1, 115.8, 35.5, 32.09, 3.14, 17.20; **IR (KBr)** ν_{max} = 2927, 1710, 1459, 759 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{22}H_{20}NO_2$ $(M+H)^+$: 330.1494, found: 330.1490.

1,1'-(1-Phenyl-9*H*-pyrrolo[1,2-*a*]indole-2,3-diyl)bis(propan-1-one) (3l)



Following the general procedure compound **3l** obtained as a yellow solid, yield: 104 mg, 75%; mp 148-150 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.2 Hz, 1H), 7.46 – 7.39 (m, 3H), 7.39 – 7.32 (m, 4H), 7.21 (td, *J* = 7.5, 0.9 Hz, 1H), 3.95 (s, 2H), 2.74 (q, *J* = 7.2 Hz, 2H), 2.49 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.3 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$)δ 204.9, 194.1, 141.2, 138.9, 134.3, 133.9, 133.7, 128.9, 128.3, 128.0, 127.3, 125.9, 125.3, 125.1, 117.4, 116.0, 38.2, 34.9, 29.2, 8.8, 8.3; **IR (KBr)** ν_{max} = 2979, 1700, 1466, 764 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{23}H_{22}NO_2$ $(M+H)^+$: 344.1651, found: 344.1649.

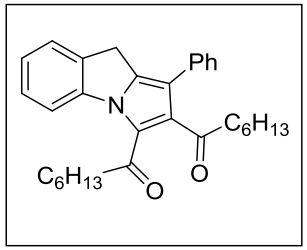
1,1'-(1-Phenyl-9*H*-pyrrolo[1,2-*a*]indole-2,3-diyl)bis(butan-1-one) (3m)



Following the general procedure compound **3m** obtained as a yellow solid, yield: 117 mg, 78%; mp 124-126 ^oC; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.11 (d, *J*= 8.1 Hz, 1H), 7.47 – 7.30 (m, 7H), 7.21 (t, *J* = 7.4 Hz, 1H),

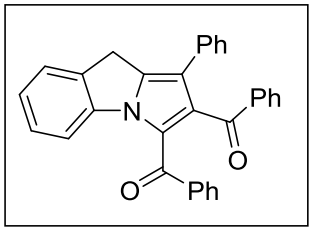
3.94 (s, 2H), 2.71 (t, *J* = 7.3 Hz, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 1.89 – 1.73 (m, 2H), 1.64 – 1.48 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.79 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 203.9, 193.9, 141.2, 138.8, 134.4, 133.9, 133.7, 128.8, 128.4, 128.0, 127.3, 126.2, 125.4, 125.1, 117.4, 115.8, 46.7, 43.7, 29.1, 18.4, 17.5, 13.8, 13.6; **IR (KBr)** $\boldsymbol{\nu}_{\mathbf{max}}$ = 2971, 1710, 1465, 762 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{25}H_{26}NO_2$ $(M+H)^+$: 372.1964, found: 372.1960.

1,1'-(1-Phenyl-9*H*-pyrrolo[1,2-*a*]indole-2,3-diyl)bis(heptan-1-one) (3n)



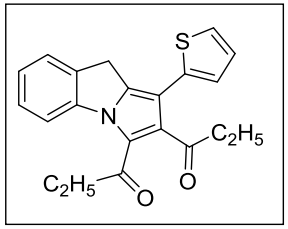
Following the general procedure compound **3n** obtained as a yellow semisolid, yield: 134 mg, 73%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J*= 8.2 Hz, 1H), 7.45 – 7.38 (m, 3H), 7.38 – 7.31 (m, 4H), 7.20 (td, *J* = 7.5, 1.0 Hz, 1H), 3.94 (s, 2H), 2.72 (t, *J* = 9.3, 5.7 Hz, 2H), 2.45 (t, *J* = 9.7, 5.1 Hz, 2H), 1.79 – 1.71 (m, 2H), 1.57 – 1.49 (m, 2H), 1.36 – 1.29 (m, *J* = 7.1, 6.3 Hz, 6H), 1.18 – 1.09 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.82 (t, *J* = 8.3, 6.0 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 204.1, 194.1, 141.2, 138.8, 134.4, 133.9, 133.7, 128.8, 128.4, 128.0, 127.3, 126.2, 125.3, 125.1, 117.4, 115.8, 44.8, 41.9, 31.7, 31.5, 29.1, 28.9, 28.7, 25.0, 24.0, 22.5, 22.4, 14.1, 14.0; **IR (KBr)** $\boldsymbol{\nu}_{\mathbf{max}}$ = 2931, 1712, 1462, 756 cm^{-1}; **HRMS (ESI)**: $C_{31}H_{38}NO_2$ $(M+H)^+$: 456.2903, found: 456.2904.

(1-Phenyl-9H-pyrrolo[1,2-*a*]indole-2,3-diyl)bis(phenylmethanone) (3o)



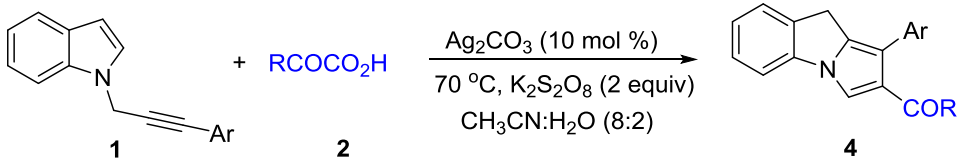
Following the general procedure, reaction was completed in 12 h and corresponding compound was purified by using preparative HPLC (phenomenex C8 column, eluent methanol/0.1% formic acid with water 70/30, wavelength= 306, 15 ml/min) to obtain the **3o** as a yellow semisolid, yield: 49 mg, 28% (along with mono compound **4j** in 11%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 1H), 7.50 (d, *J* = 7.3 Hz, 1H), 7.48 – 7.45 (m, 2H), 7.42 – 7.39 (m, 2H), 7.38 – 7.32 (m, 5H), 7.31 – 7.26 (m, 3H), 7.25 – 7.21 (m, 1H), 7.18 – 7.11 (m, 4H), 4.14 (s, 2H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.2, 187.2, 140.8, 139.7, 139.6, 139.4, 134.5, 133.1, 132.7, 132.5, 132.5, 129.6, 128.9, 128.7, 128.5, 128.1, 128.0, 126.9, 126.4, 125.6, 125.3, 119.9, 119.9, 115.4, 29.7; **IR (KBr)** $\boldsymbol{\nu}_{\mathbf{max}}$ = 1731, 1646, 1464, 761 cm^{-1}; **HRMS (ESI)**: *m/z* calcd for $C_{31}H_{22}NO_2$ $(M+H)^+$: 440.1651, found: 440.1643.

1,1'-(1-(Thiophen-2-yl)-9*H*-pyrrolo[1,2-*a*]indole-2,3-diyl)bis(propan-1-one) (3p)



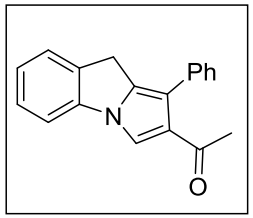
Following the general procedure compound **3o** obtained as a yellow semisolid, yield: 101 mg, 73%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.32 (dd, *J* = 5.2, 1.0 Hz, 1H), 7.23 (td, *J* = 7.5, 0.8 Hz, 1H), 7.10 – 7.06 (m, 1H), 6.98 (dd, *J* = 3.5, 1.0 Hz, 1H), 4.00 (s, 2H), 2.75 – 2.65 (m, *J* = 12.4, 7.2 Hz, 4H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.9, 193.2, 141.3, 139.6, 134.7, 134.3, 133.8, 128.1, 127.7, 125.6, 125.5, 125.4, 125.2, 124.8, 116.2, 110.4, 38.6, 34.8, 29.7, 8.8, 8.3; **IR (KBr)** $\boldsymbol{\nu_{max}}$ = 2930, 1705, 1467, 756 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{21}H_{20}NO_2S$ $(M+H)^+$: 350.1215, found: 350.1208.

2.2 General procedure for the synthesis of monoacylated-9*H*-pyrrolo[1,2-a]indoles (4)



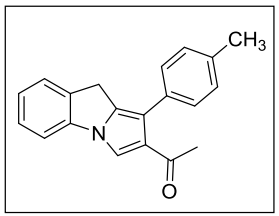
A 5 mL reaction vial equipped with a magnetic stirring bar was charged with Ag_2CO_3(0.04 mmol), potassium persulfate (0.8 mmol), substituted *N*-propargyl indole **1** (0.4 mmol), *α*-keto acid (**2**) (1.2 mmol) and 3 mL of CH_3CN/H_2O (v1/v2 = 8:2). After that, the mixture was allowed to stir at 70 °C for 2- 4 h. The reaction was monitored by TLC, after completion of starting material reaction mixture was diluted with water and extracted with ethyl acetate (2 times). The organic layers were combined and dried over sodium sulphate and solvent was removed in vacuo. The obtained crude product was purified by column chromatography on silica gel (15% EtOAc in hexane) to afford the corresponding compounds **4.**

1-(1-Phenyl-9*H*-pyrrolo[1,2-*a*]indol-2-yl)ethan-1-one (4a)



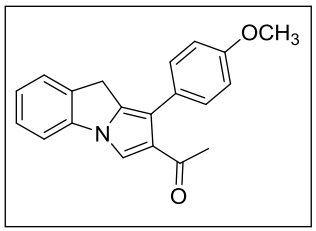
Following the general procedure compound **4a** obtained as a yellow semisolid, yield: 76 mg, 69%; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.78 (s, 1H), 7.50 – 7.46 (m, 2H), 7.45 – 7.36 (m, 5H), 7.33 – 7.27 (m, 1H), 7.21 (td, *J* = 7.3, 1.6 Hz, 1H), 3.92 (s, 2H), 2.37 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.1, 139.8, 135.1, 134.8, 134.6, 129.3, 128.1, 127.9, 127.7, 126.7, 126.2, 124.9, 118.9, 116.1, 110.7, 29.2, 28.7; **IR (KBr)** ν_{max} = 2925, 1713, 1498, 760 cm^{-1}; **HRMS (ESI)**: *m/z* calcd for $C_{19}H_{16}NO$ $(M+H)^+$: 274.1232, found: 274.1225.

1-(1-(*p*-Tolyl)-9*H*-pyrrolo[1,2-*a*]indol-2-yl)ethan-1-one (4b)



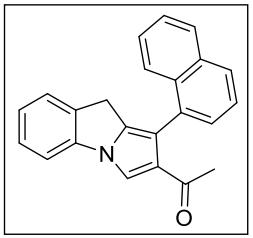
Following the general procedure compound **4b** obtained as a yellow semisolid, yield: 73 mg, 64%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.45 – 7.35 (m, 5H), 7.23 – 7.20 (m, 3H), 3.91 (s, 2H), 2.39 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.2, 139.8, 136.3, 134.9, 134.6, 131.7, 129.1, 128.8, 127.8, 127.6, 126.2, 124.8, 118.9, 115.9, 110.6, 29.0, 28.7, 21.3; **IR (KBr)** ν_{max} = 2923, 1716, 1497, 754 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{20}H_{18}NO$ $(M+H)^+$: 288.1388, found: 288.1391.

1-(1-(4-Methoxyphenyl)-9*H*-pyrrolo[1,2-*a*]indol-2-yl)ethan-1-one (4c)



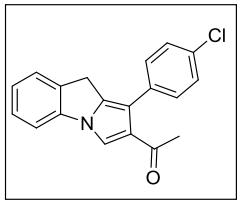
Following the general procedure compound **4c** obtained as a yellow semisolid, yield: 75 mg, 62%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.42 – 7.34 (m, 5H), 7.22 – 7.16 (m, 1H), 6.96 – 6.91 (m, 2H), 3.87 (s, 2H), 3.84 (s, 3H), 2.36 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 194.1, 158.4, 139.7, 134.7, 134.6, 130.4, 127.8, 127.4, 127.0, 126.1, 124.8, 118.6, 116.1, 113.5, 110.6, 55.3, 29.0, 28.6; **IR (KBr)** ν_{max} = 2920, 1703, 1502, 756 cm^{-1}; **HRMS (ESI)**: *m/z* calcd for $C_{20}H_{18}NO_2$ $(M+H)^+$: 304.1338, found: 304.1332.

1-(1-(Naphthalen-1-yl)-9*H*-pyrrolo[1,2-*a*]indol-2-yl)ethan-1-one (4d)



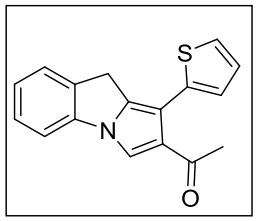
Following the general procedure compound **4d** obtained as a yellow semisolid, yield: 79 mg, 62%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.93 – 7.86 (m, 2H), 7.76 (d, J = 8.1 Hz, 1H), 7.56 – 7.45 (m, 4H), 7.43 – 7.36 (m, 3H), 7.20 (td, J = 7.5, 1.1 Hz, 1H), 3.82 – 3.58 (m, 2H), 2.02 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.6, 140.0, 135.7, 134.89, 133.7, 133.0, 132.7, 129.7, 128.4, 127.9, 127.8, 127.7, 126.3, 126.1, 125.9, 125.8, 125.5, 124.9, 116.6, 115.1, 110.9, 28.8, 28.5; **IR (KBr)** $\boldsymbol{\nu}_{\mathbf{max}}$ = 2924, 1712, 1493, 752 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{23}H_{18}NO$ $(M+H)^+$: 324.1388, found: 324.1384.

1-(1-(4-Chlorophenyl)-9*H*-pyrrolo[1,2-*a*]indol-2-yl)ethan-1-one (4e)



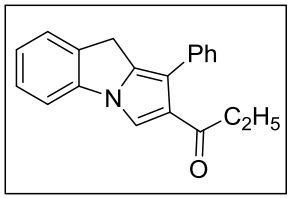
Following the general procedure compound **4e** obtained as a yellow solid, yield: 74 mg, 61%; mp 72-74 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.46 – 7.38 (m, 5H), 7.37 – 7.34 (m, 2H), 7.25 – 7.20 (m, 1H), 3.91 (s, 2H), 2.42 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.7, 139.7, 135.3, 134.4, 133.2, 132.3, 130.5, 128.2, 127.9, 127.1, 126.2, 125.1, 117.8, 116.6, 110.7, 29.1, 28.5; **IR (KBr)** $\boldsymbol{\nu}_{\mathbf{max}}$ = 2915, 1710, 1500, 759 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{19}H_{15}NOCl$ $(M+H)^+$: 308.0842, found: 308.0848.

1-(1-(Thiophen-2-yl)-9*H*-pyrrolo[1,2-*a*]indol-2-yl)ethan-1-one (4f)



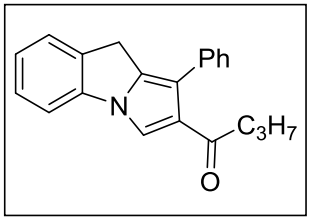
Following the general procedure compound **4f** obtained as a yellow solid, yield: 70 mg, 63%; mp 116-118 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.54 (dd, J = 3.6, 1.1 Hz, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.28 (dd, J = 5.2, 1.1 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.11 – 7.07 (m, 1H), 4.00 (s, 2H), 2.47 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.6, 139.5, 136.1, 135.5, 134.6, 127.9, 127.1, 127.0, 126.8, 126.2, 125.1, 124.0, 116.8, 112.1, 110.7, 30.3, 28.5; **IR (KBr)** $\boldsymbol{\nu}_{\mathbf{max}}$ = 2927, 1716, 1505, 760 cm^{-1}; **HRMS (ESI):** m/z calcd for $C_{17}H_{14}NOS$ $(M+H)^+$: 280.0796, found: 280.0802.

1-(1-Phenyl-9*H*-pyrrolo[1,2-*a*]indol-2-yl)propan-1-one (4g)



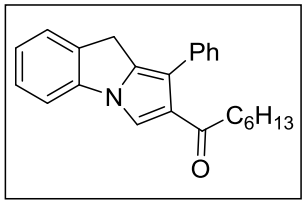
Following the general procedure compound **4g** obtained as a yellow semisolid, yield: 68 mg, 59%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.50 – 7.45 (m, 2H), 7.44 – 7.35 (m, 5H), 7.32 – 7.26 (m, 1H), 7.22 – 7.16 (m, 1H), 3.91 (s, 2H), 2.75 (q, *J* = 7.4 Hz, 2H), 1.15 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.3, 139.8, 135.0, 134.9, 134.6, 129.2, 128.0, 127.8, 126.9, 126.6, 126.2, 124.8, 118.9, 115.5, 110.6, 33.66, 29.1, 8.8; **IR (KBr)** $\boldsymbol{\nu_{max}}$ = 2924, 1705, 1497, 754 cm^{-1}; **HRMS (ESI)**: m/z calcd forC_{20} $H_{18}NO$ $(M+H)^+$: 288.1388, found: 288.1382.

1-(1-Phenyl-9*H*-pyrrolo[1,2-*a*]indol-2-yl)butan-1-one (4h)



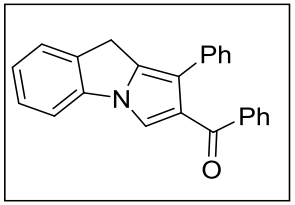
Following the general procedure compound **4h** obtained as a yellow semisolid, yield: 73 mg, 60%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.50 – 7.46 (m, 2H), 7.45 – 7.36 (m, 5H), 7.31 – 7.28 (m, 1H), 7.20 (td, *J* = 7.3, 1.4 Hz, 1H), 3.93 (s, 2H), 2.70 (t, *J* = 7.4 Hz, 2H), 1.76 – 1.67 (m, *J* = 14.8, 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.9, 139.9, 135.1, 134.9, 134.6, 129.2, 128.0, 127.8, 127.3, 126.6, 126.2, 124.8, 118.9, 115.6, 110.6, 42.5, 29.1, 18.4, 14.0; **IR (KBr)** $\boldsymbol{\nu_{max}}$ = 2920, 1714, 1501, 758 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{21}H_{20}NO$ $(M+H)^+$:302.1545, found: 302.1539.

1-(1-Phenyl-9*H*-pyrrolo[1,2-*a*]indol-2-yl)heptan-1-one (4i)



Following the general procedure compound **4i** obtained as a yellow semisolid, yield: 86 mg, 62%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.49 – 7.45 (m, 2H), 7.44 – 7.36 (m, 5H), 7.31 – 7.26 (m, 1H), 7.20 (td, *J* = 7.2, 1.7 Hz, 1H), 3.93 (s, 2H), 2.70 (t, *J* = 7.4 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.32 – 1.23 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.1, 139.9, 135.1, 134.9, 134.6, 129.2, 128.0, 127.8, 127.3, 126.6, 126.2, 124.8, 118.9, 115.6, 110.6, 40.7, 31.7, 29.1, 29.1, 25.0, 22.6, 14.1; **IR (KBr)** $\boldsymbol{\nu_{max}}$ = 2926, 1710, 1497, 755 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{24}H_{26}NO(M+H)^+$: 344.2014, found: 344.2014.

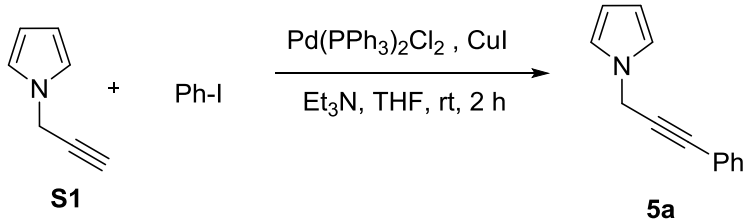
Phenyl(1-phenyl-9H-pyrrolo[1,2-*a*]indol-2-yl)methanone (4j)



Following the general procedure, reaction was completed in 2 h and corresponding compound was purified by using preparative HPLC (phenomenex C8 column, eluent methanol/0.1% formic acid with water 70/30, wavelength= 306, 15 ml/min) to obtain the **4j** as a yellow semisolid, yield: 68 mg, 51%; (along with di compound **3o** in 5%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 2H), 7.55 (s, 1H), 7.52 – 7.43 (m, 4H), 7.42 – 7.35 (m, 4H), 7.34 – 7.29 (m, 2H), 7.24 – 7.19 (m, 2H), 4.06 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.5, 139.9, 139.8, 134.8, 134.6, 134.4, 131.7, 129.6, 128.7, 128.5, 128.1, 128.0, 127.9, 126.2, 126.1, 124.9, 119.8, 118.0, 110.7, 29.4; **IR (KBr)** ν_{max} = 2925, 1735, 1638, 1500, 727 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{24}H_{18}NO$ $(M+H)^+$: 336.1388, found: 336.1379.

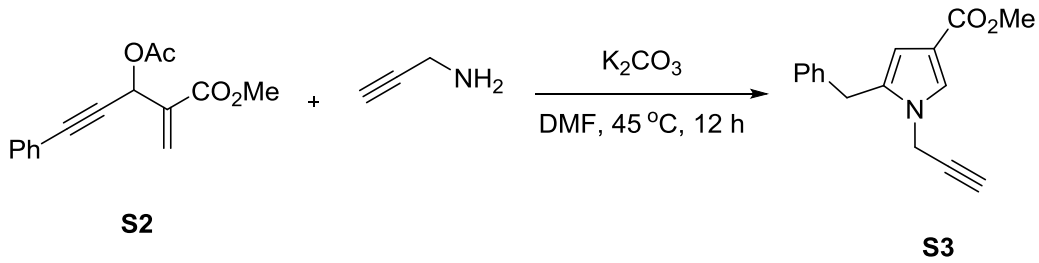
3.0 General procedure for the preparation *N*-propargylated pyrroles

3.1 Preparation of 1-(3-phenylprop-2-yn-1-yl)-1*H*-pyrrole (5a)



To a magnetically stirred solution of terminal alkyne **S1**[2] (1.0 gm, 9.52 mmol) in THF (10 mL) and Et_3N (5 mL) was added iodobenzene (1.17 mL, 10.47 mmol), $Pd(PPh_3)_2Cl_2$ (333 mg, 5 mol%) and CuI (18 mg, 1 mol%) under nitrogen atmosphere at room temperature. The reaction mixture was stirred 2 h at room temperature. Then the reaction mixture was filtered through celite and the filtrate was concentrated under reduced pressure. Purification of the crude residue on a silica gel column chromatography using EtOAc/Pet ether as eluent, furnished the product **5a** (1.38 gm, 80%) as a light yellow semisolid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 2H), 7.35 – 7.29 (m, 3H), 6.88 – 6.81 (m, 2H), 6.23 – 6.17 (m, 2H), 4.90 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.8, 128.7, 128.4, 122.4, 120.5, 108.8, 85.3, 83.4, 39.5; **IR (KBr)** ν_{max} = 3097, 2909, 1277, 721 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{13}H_{12}N$ $(M+H)^+$: 182.0970, found: 182.0966.

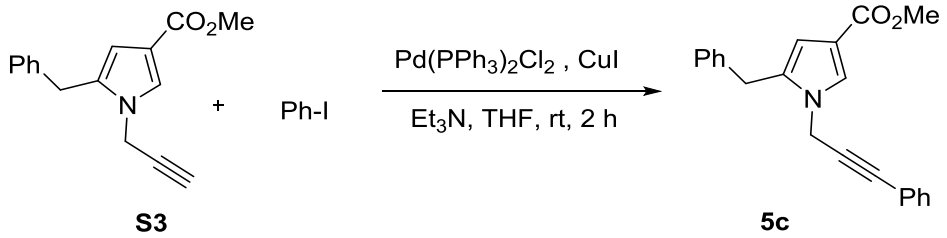
3.2 Preparation of methyl 5-benzyl-1-(prop-2-yn-1-yl)-1*H*-pyrrole-3-carboxylate (S3)[3]



S2 **S3**

To a solution of MBH acetate **S2** (1.3 gm, 5.0 mmol) and propargylamine (0.32 mL, 5.0 mmol) in 10 mL of dimethylformamide was added potassium carbonate (695 mg, 5.0 mmol) at room temperature. Then, the temperature was raised to 45 ^{o}C. The reaction mixture was stirred at the same temperature for 12 h. After the completion of reaction, the mixture was diluted with water (10 mL) and extracted with ethyl acetate three times. The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : hexanes) to afford the corresponding product (**S3**) (822 mg, 65%) as yellow oil ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 2H), 7.39 – 7.33 (m, 4H), 6.99 (s, 1H), 3.85 (s, 2H), 3.82 (s, 3H), 3.47 (d, J = 2.4 Hz, 2H), 2.20 (t, J = 2.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 139.4, 131.9, 129.4, 128.5, 122.6, 122.3, 102.6, 85.2, 82.2, 71.5, 52.3, 46.3, 37.5; **IR (KBr)** $\boldsymbol{\nu_{max}}$ = 3297, 2948, 2196, 1709, 1217, 760 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{16}H_{16}NO_2$ $(M+H)^+$: 254.1181, found: 254.1170.

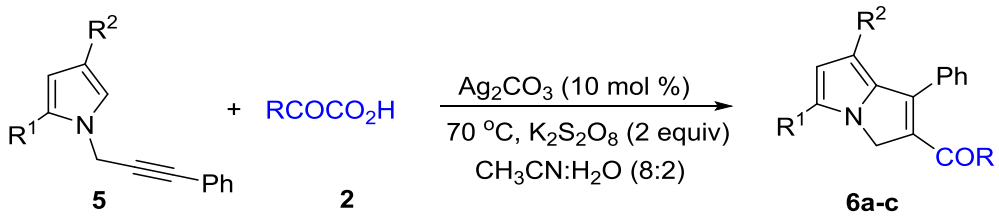
3.3 Preparation of methyl 5-benzyl-1-(3-phenylprop-2-yn-1-yl)-1*H*-pyrrole-3-carboxylate (5c)



S3 **5c**

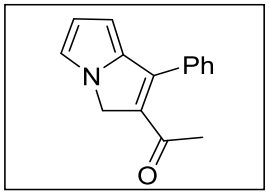
To a magnetically stirred solution of terminal alkyne **S3** (800 mg, 3.16 mmol) in THF (10 mL) and Et_3N (5 mL) was added iodobenzene (0.6 mL, 3.79 mmol), $Pd(PPh_3)_2Cl_2$ (110 mg, 5 mol%) and CuI (6 mg, 1 mol%) under nitrogen atmosphere at room temperature. The reaction mixture was stirred 2 h at room temperature. Then the reaction mixture was filtrated through celite and the filtrate was concentrated under reduced pressure. Purification of the crude residue on a silica gel column chromatography using EtOAc/Pet ether as eluent, furnished the product **5c** (811 mg, 78%) as a yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, J = 1.9 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.35 – 7.28 (m, 5H), 7.25 – 7.22 (m, 1H), 7.21 – 7.17 (m, 2H), 6.41 – 6.38 (m, 1H), 4.65 (s, 2H), 4.04 (s, 2H), 3.79 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3, 138.0, 132.3, 131.8, 128.9, 128.7, 128.51, 128.4, 126.7, 126.4, 121.9, 114.8, 110.1, 86.0, 82.2, 51.06, 37.8, 32.7; **IR (KBr)** ν_{max} = 3026, 2948, 1707, 1215, 760 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{22}H_{20}NO_2$ $(M+H)^+$: 330.1494, found: 330.1485.

4.0 General procedure for the synthesis of acylated-3*H*-pyrrolizines (6a-c)



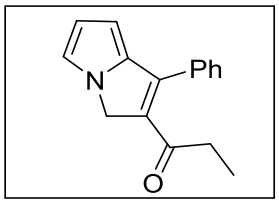
A 5 mL reaction vial equipped with a magnetic stirring bar was charged with Ag_2CO_3 (0.04 mmol), potassium persulfate (3.2 mmol), substituted *N*-propargyl pyrrole **5** (0.4 mmol), α-keto acid **2** (1.2 mmol) and 3 mL of CH_3CN/H_2O (v1/v2 = 8:2). After that reaction mixture was allowed to stir at 70 °C for 12 h. The reaction was monitored by TLC, after completion of starting material reaction mixture was diluted with water and extracted with ethyl acetate (2 times). The organic layers were combined and dried over sodium sulphate and solvent was removed in vacuo. The obtained crude product was purified by column chromatography on silica gel (10% EtOAc in hexane) to afford the corresponding compounds **6**.

1-(1-Phenyl-3*H*-pyrrolizin-2-yl)ethan-1-one (6a)



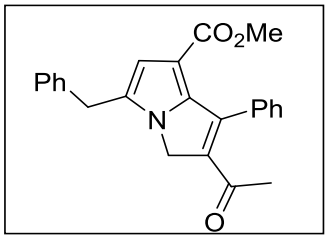
Following the general procedure compound **6a** obtained as a light yellow semisolid, yield: 70 mg, 79%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.32 (m, 4H), 7.01 (dd, J = 4.0, 1.7 Hz, 1H), 6.21 (dd, J = 4.0, 2.6 Hz, 1H), 5.44 (s, 2H), 2.46 (s, 3H) ; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.7, 131.8, 130.1, 129.2, 128.6, 128.3, 122.4, 120.5, 108.5, 85.8, 83.5, 39.7, 27.2; **IR (KBr)** $\boldsymbol{\nu}_{\mathbf{max}}$ = 2924, 1740, 1650, 1409,748 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{15}H_{14}NO$ $(M+H)^+$: 224.1075, found: 224.1065.

1-(1-Phenyl-3*H*-pyrrolizin-2-yl)propan-1-one (6b)



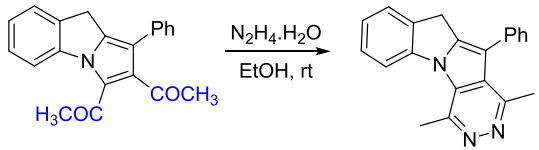
Following the general procedure compound **6b.** obtained as a light yellow semisolid, yield: 74 mg, 78%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.27 – 7.21 (m, 4H), 6.94 (dd, J = 4.0, 1.7 Hz, 1H), 6.13 (dd, J = 4.0, 2.6 Hz, 1H), 5.38 (s, 2H), 2.76 (q, J = 7.4 Hz, 2H), 1.13 (t, J = 7.4 Hz, 3H) ; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.2, 130.8, 128.7, 127.9, 127.5, 127.3, 121.4, 118.4, 107.3, 84.7, 82.5, 38.6, 31.2, 8.0; **IR (KBr)** $\boldsymbol{\nu}_{\mathbf{max}}$ = 2927, 1741, 1651, 1413, 744 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{16}H_{16}NO$ $(M+H)^+$: 238.1232, found: 238.1222.

Methyl 2-acetyl-5-benzyl-1-phenyl-3*H*-pyrrolizine-7-carboxylate (6c)



Following the general procedure compound **6c** obtained as a light yellow semisolid, yield: 102 mg, 69%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 3H), 7.34 – 7.29 (m, 4H), 7.26 – 7.23 (m, 3H), 6.64 (s, 1H), 4.52 (s, 2H), 3.97 (s, 2H), 3.19 (s, 3H), 1.77 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.7, 164.1, 145.4, 142.1, 139.4, 136.3, 134.2, 132.1, 128.8, 128.7, 128.5, 128.3, 128.1, 126.9, 115.0, 111.3, 50.7, 33.3, 29.7, 29.3; **IR (KBr)** $\boldsymbol{\nu}_{\mathbf{max}}$ = 2928, 1711, 1642, 1442, 1223 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{24}H_{22}NO_3$ $(M+H)^+$: 372.1600, found: 372.1591.

5. General procedure for the preparation of 1,4-dimethyl-11-phenyl-10*H*-pyridazino[4',5':4,5]pyrrolo[1,2-*a*]indole (7)



3a **5**

To a stirred solution of compound **3a** (100 mg, 0.317mmol) in ethanol (2 mL) was added solution of hydrazine hydrate (0.018 mL, 0.38 mmol) in 1 mL ethanol dropwise at 0 ^{o}C over a period of 5 min under nitrogen. After that reaction mixture was warmed to room temperature and stirred for 2 h. After completion of reaction, it was concentrated in *vacuo* and crude product was purified by column chromatography on silica gel (10% MeOH in EtOAc) to afford the compound **5** as a green solid, yield: 79 mg, 80%; mp 86-88 ^{o}C; **^{1}H NMR** (400 MHz, DMSO) δ 8.25 (d, J = 8.2 Hz, 1H), 7.64 – 7.48 (m, 7H), 7.36 – 7.31 (m, 1H), 4.20 (s, 2H), 3.30 (s, 3H), 2.47 (s, 3H); **^{13}C NMR** (101 MHz, DMSO) δ 151.8, 145.3, 143.6, 140.5, 134.8, 133.8, 130.7, 128.8, 128.6, 127.9, 127.1, 125.6, 125.2, 115.7, 114.0, 111.4, 28.4, 24.7, 21.4; **IR (KBr)** $\boldsymbol{\nu_{max}}$ = 2929, 1468, 759 cm^{-1}; **HRMS (ESI)**: m/z calcd for $C_{21}H_{18}N_3$ $(M+H)^+$: 312.1501, found: 312.1495.

6. References:

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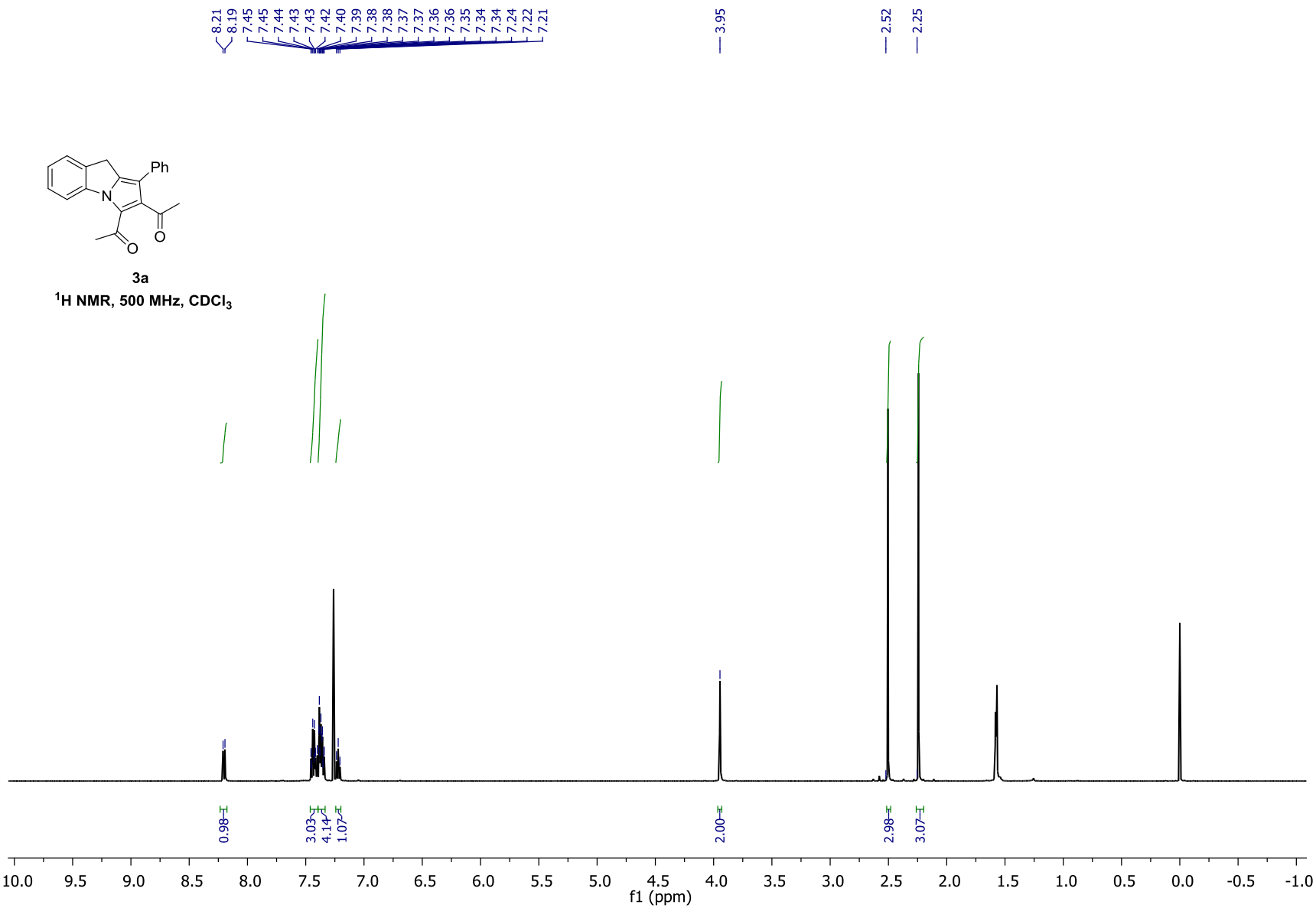
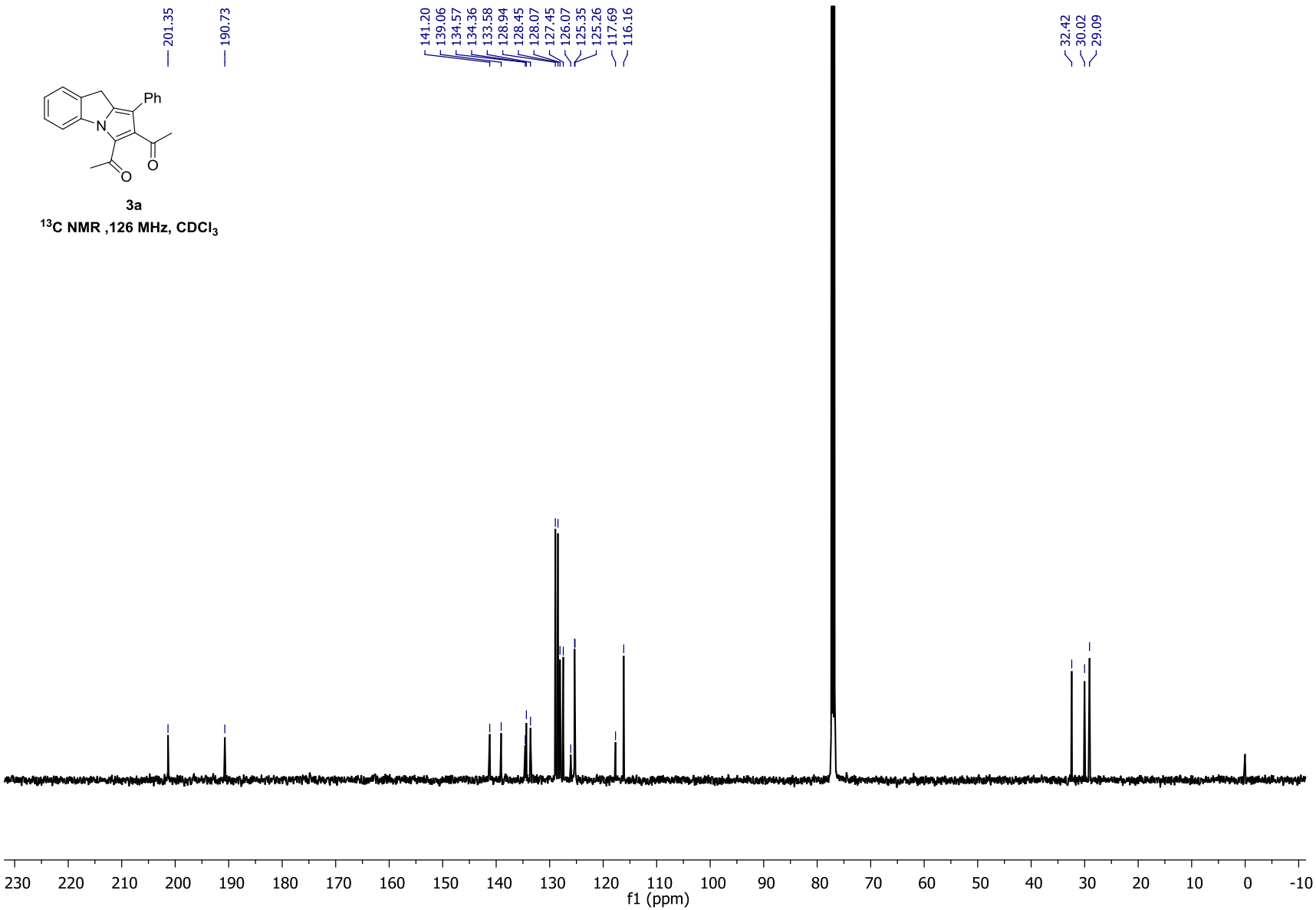
2. M. A. Galindo, J. Hannant, R. W. Harrington, W. Clegg, B. R. Horrocks, A. R. Pikea and A. Houlton, *Org. Biomol. Chem.*, 2011, **9**, 1555–1564.
3. C. R. Reddy, M. D. Reddy, B. Srikanth and K. R. Prasad, *Org. Biomol. Chem.*, 2011, **9**, 6027–6033.



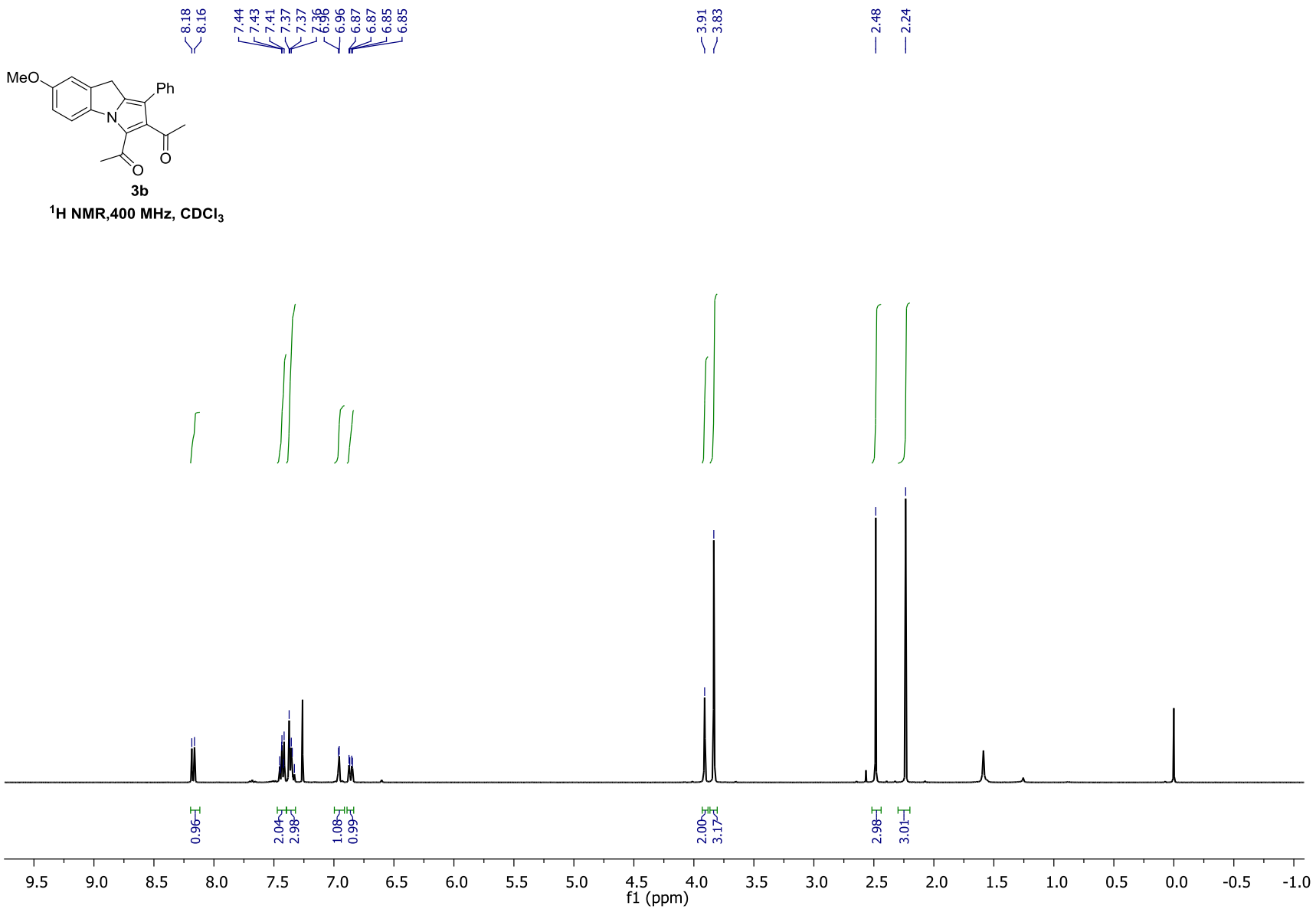
3a

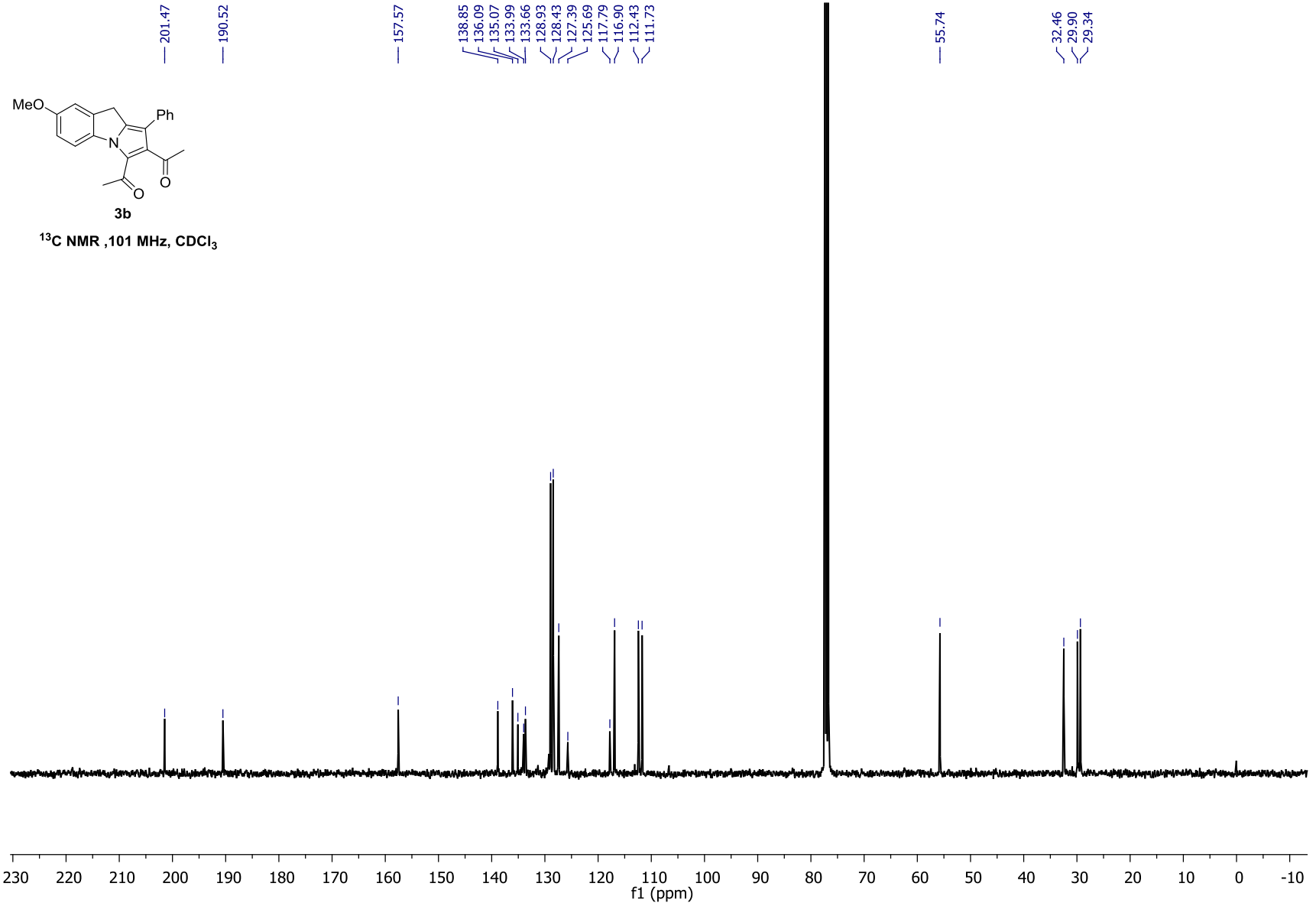
^{1}H NMR, 500 MHz, $CDCl_3$

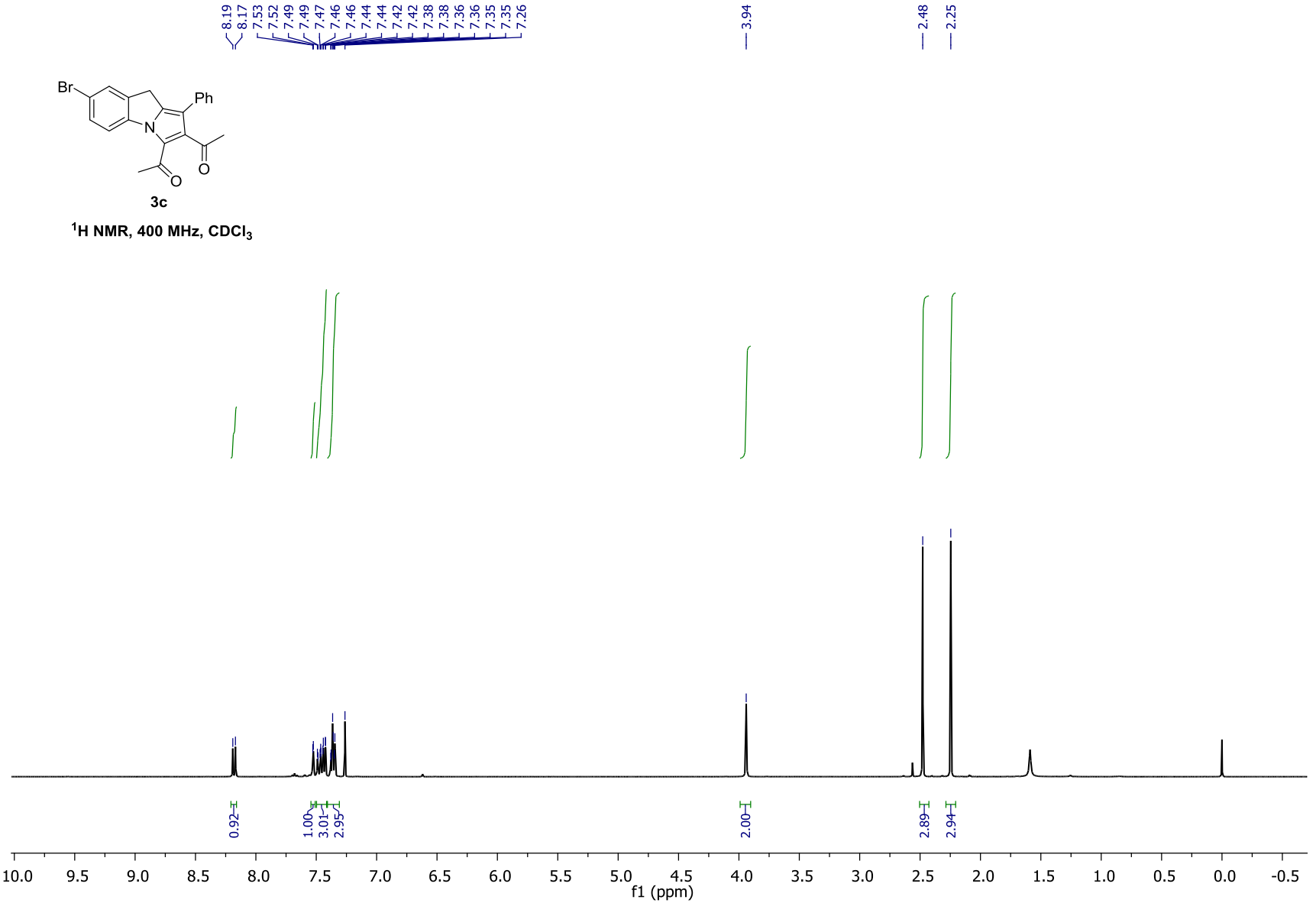


3a

^{13}C NMR ,126 MHz, $CDCl_3$

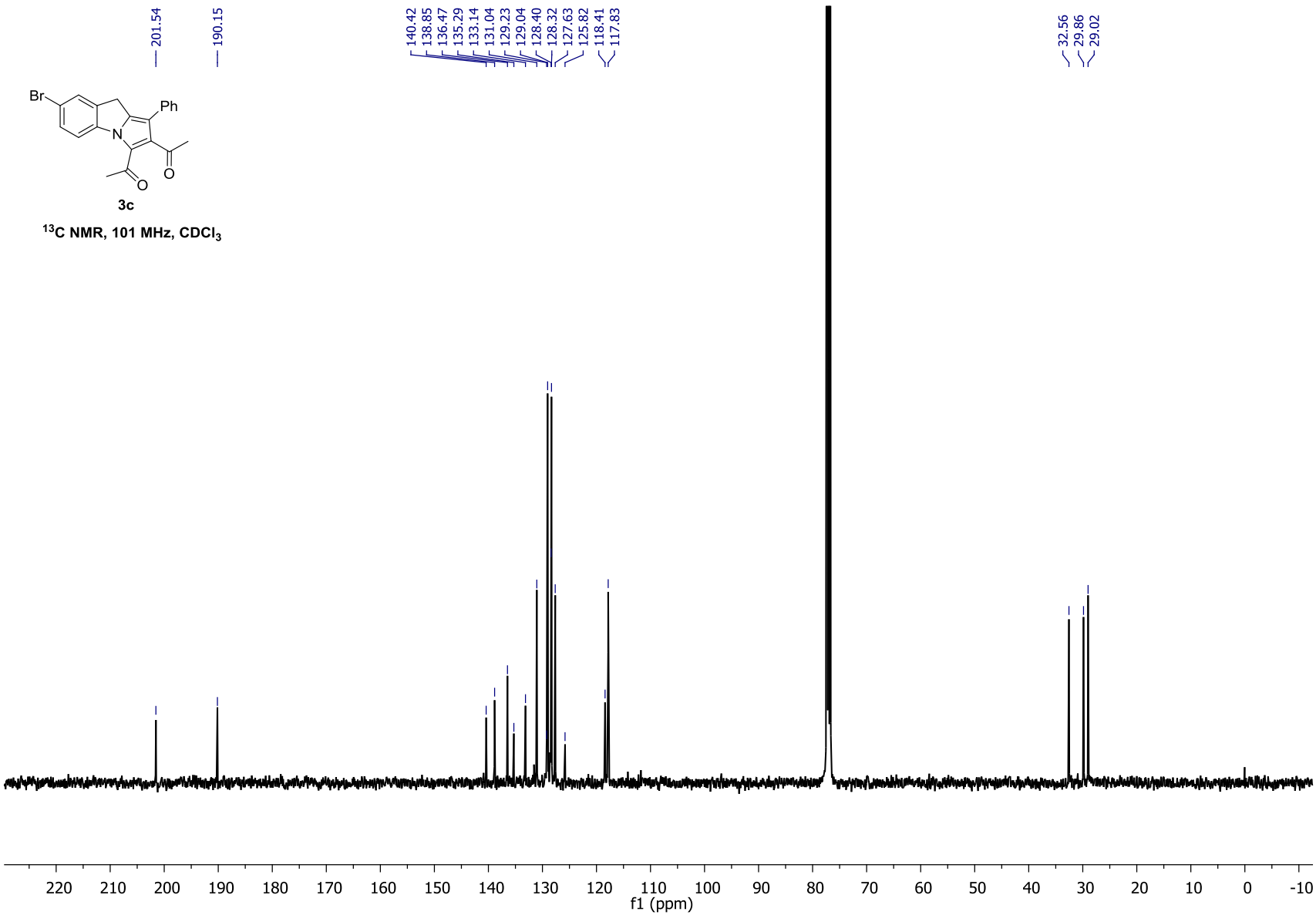

8.18
8.16
7.44
7.43
7.41
7.37
7.37
7.36
6.96
6.87
6.87
6.85
6.85
3.91
3.83
2.48
2.24
MeO
Ph
N
O
O
3b
^{1}H NMR,400 MHz, CDCl$_3$
0.96
2.04
2.98
1.08
0.99
2.00
3.17
2.98
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

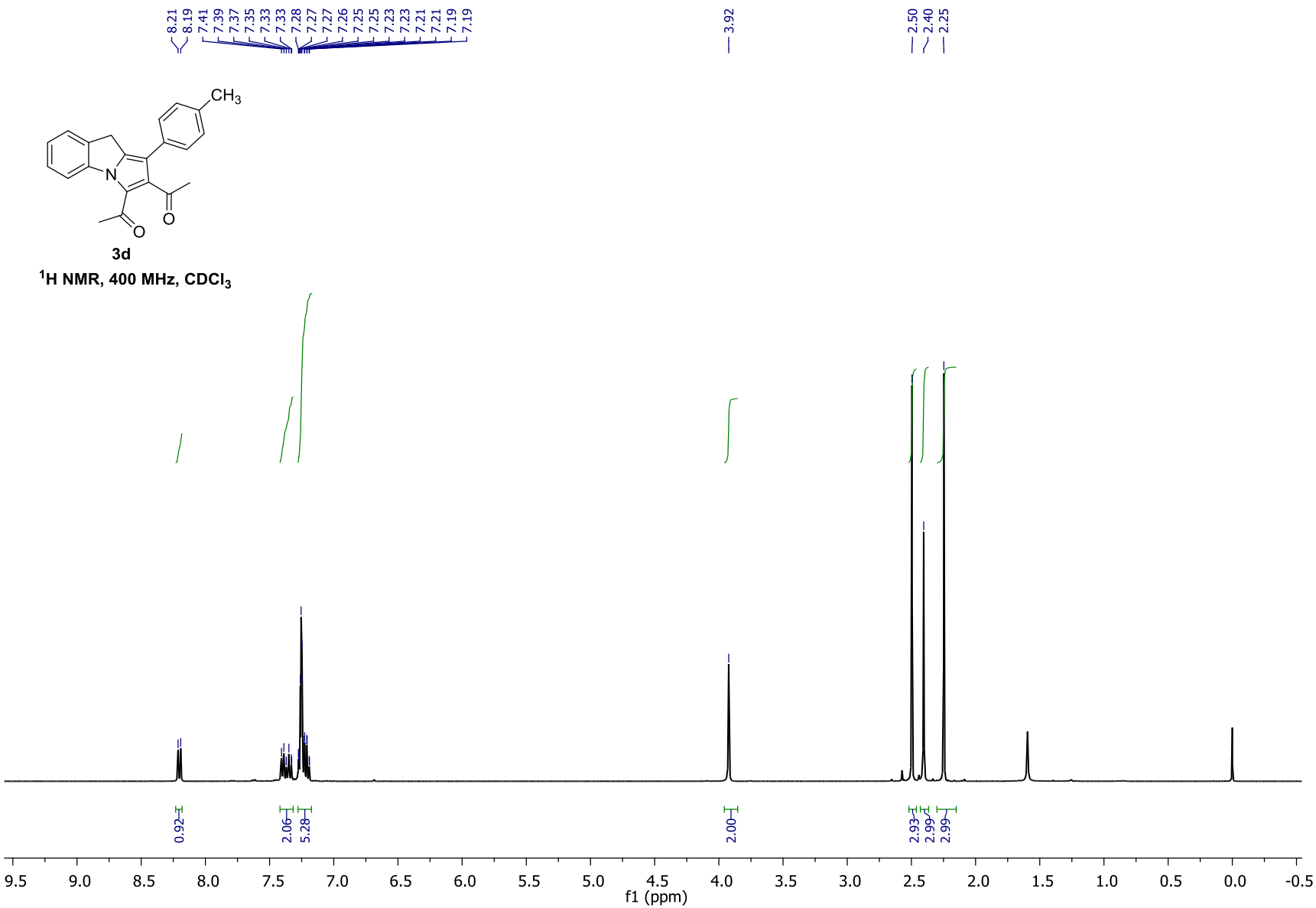

201.47
190.52
157.57
138.85
136.09
135.07
133.99
133.66
128.93
128.43
127.39
125.69
117.79
116.90
112.43
111.73
55.74
32.46
29.90
29.34
MeO
Ph
N
O
O
3b
13C NMR ,101 MHz, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3c

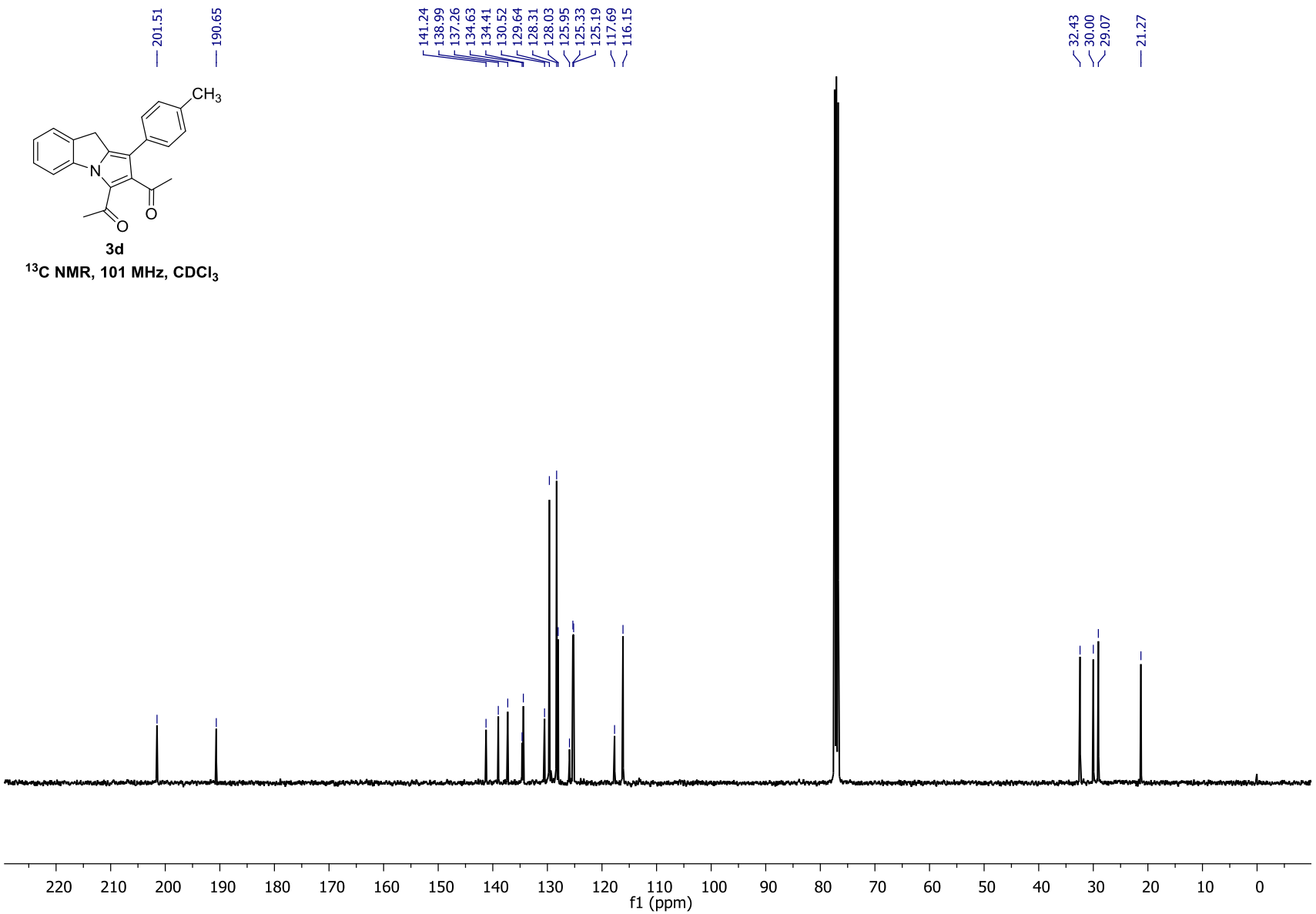
^{1}H NMR, 400 MHz, $CDCl_3$

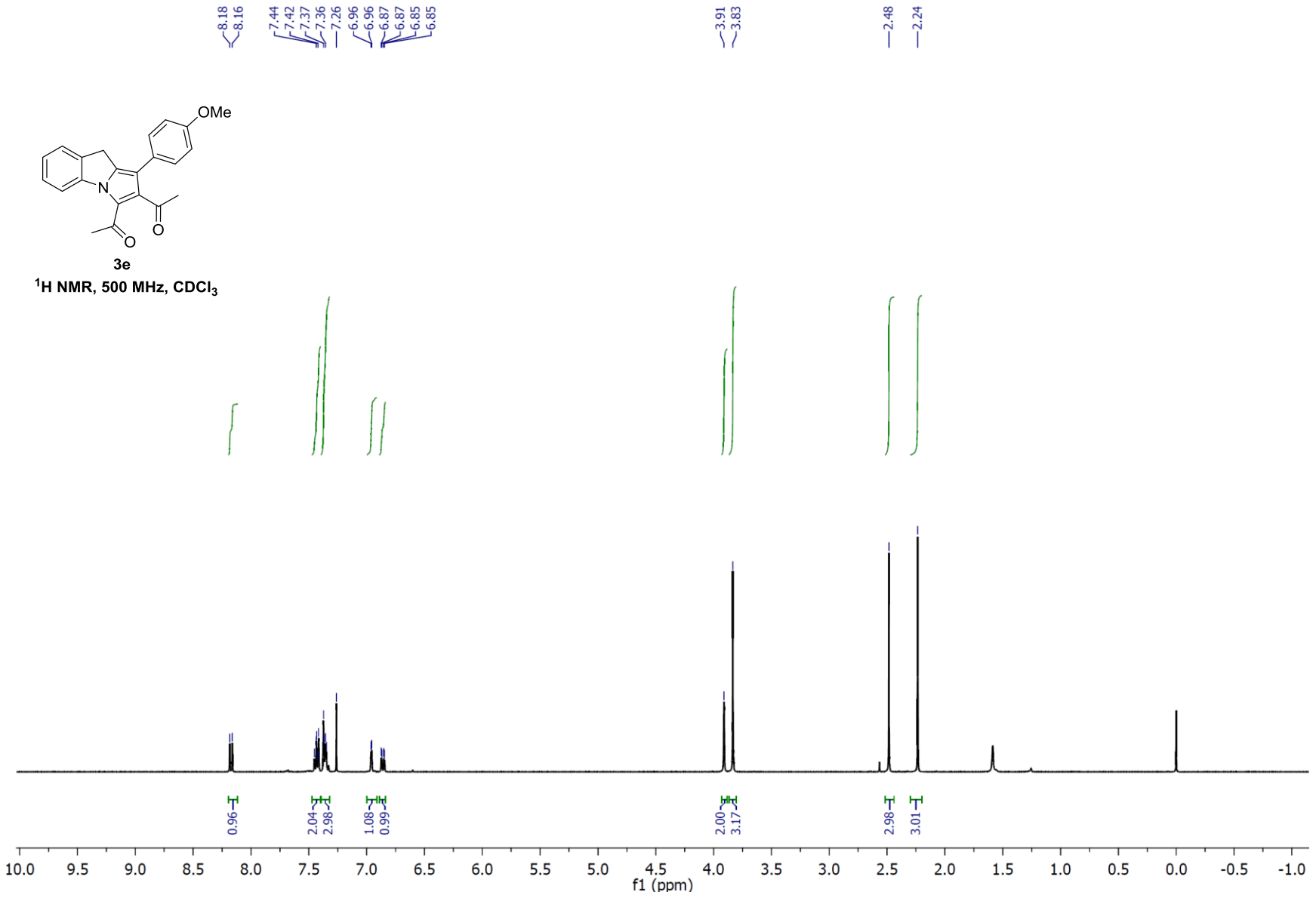

201.54
190.15
140.42
138.85
136.47
135.29
133.14
131.04
129.23
129.04
128.40
128.32
127.63
125.82
118.41
117.83
32.56
29.86
29.02
Br
Ph
N
O
O
3c
13C NMR, 101 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3d

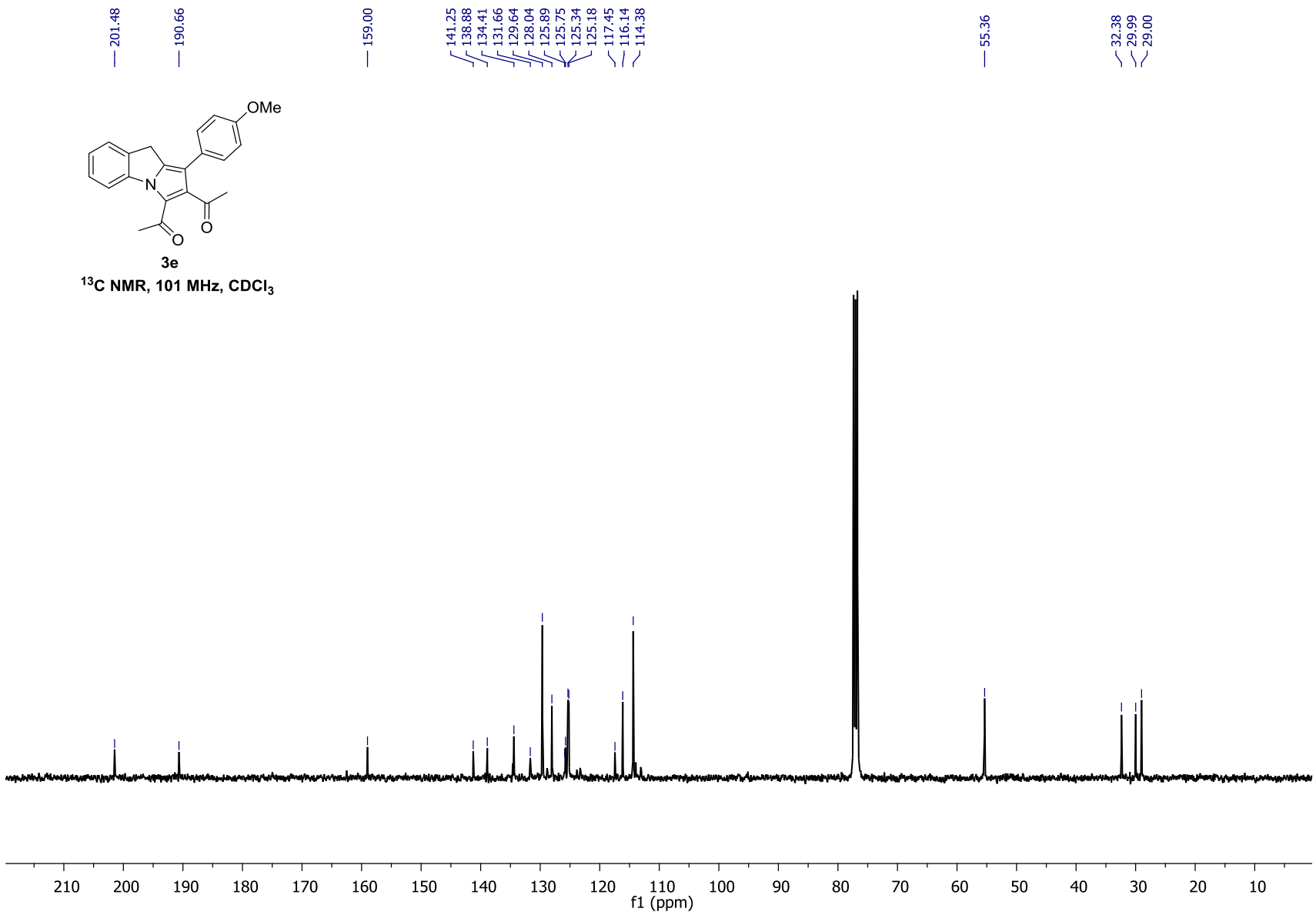
^{1}H NMR, 400 MHz, $CDCl_3$


201.51
190.65
141.24
138.99
137.26
134.63
134.41
130.52
129.64
128.31
128.03
125.95
125.33
125.19
117.69
116.15
32.43
30.00
29.07
21.27
CH3
N
O
O
3d
13C NMR, 101 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



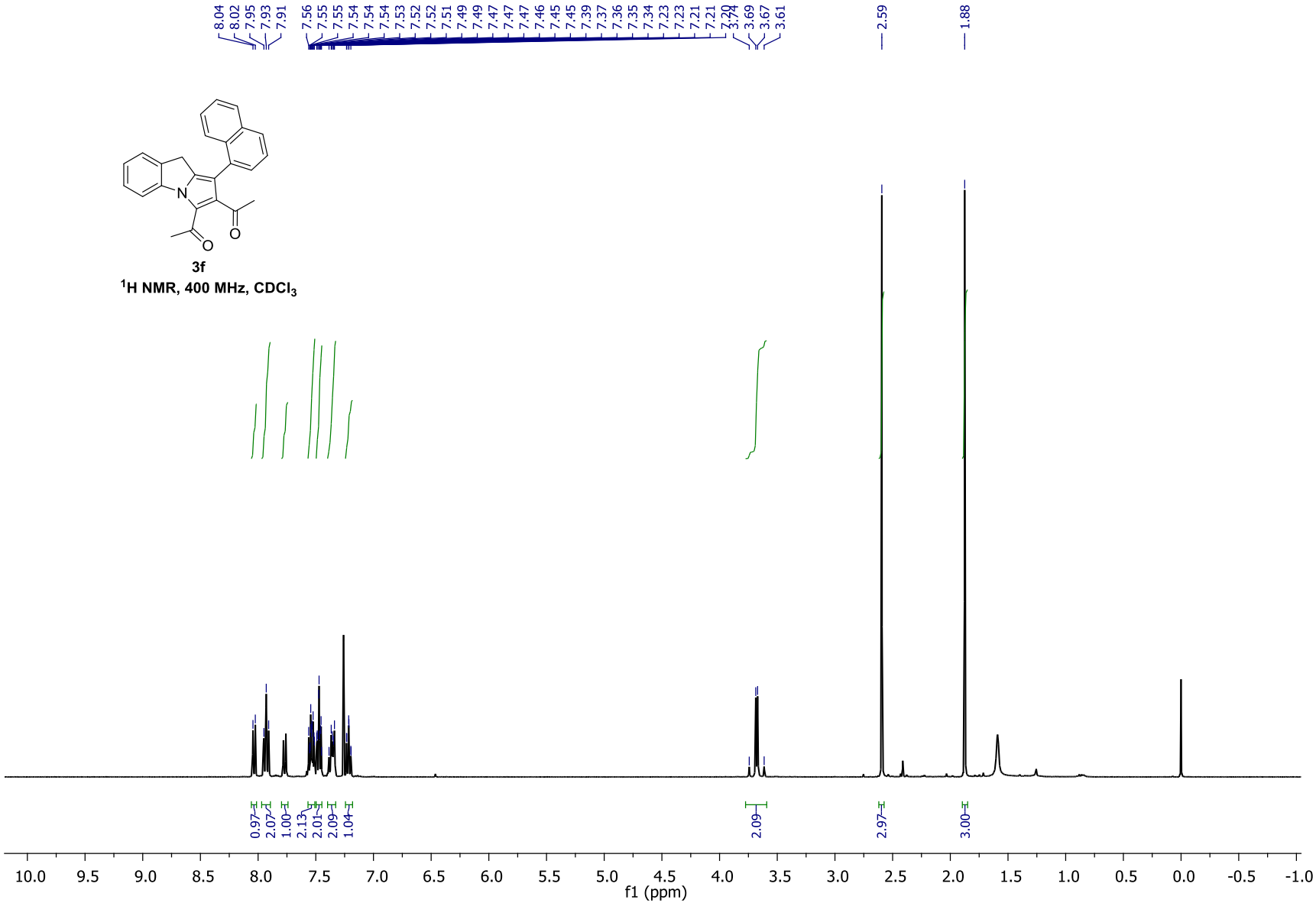
3e

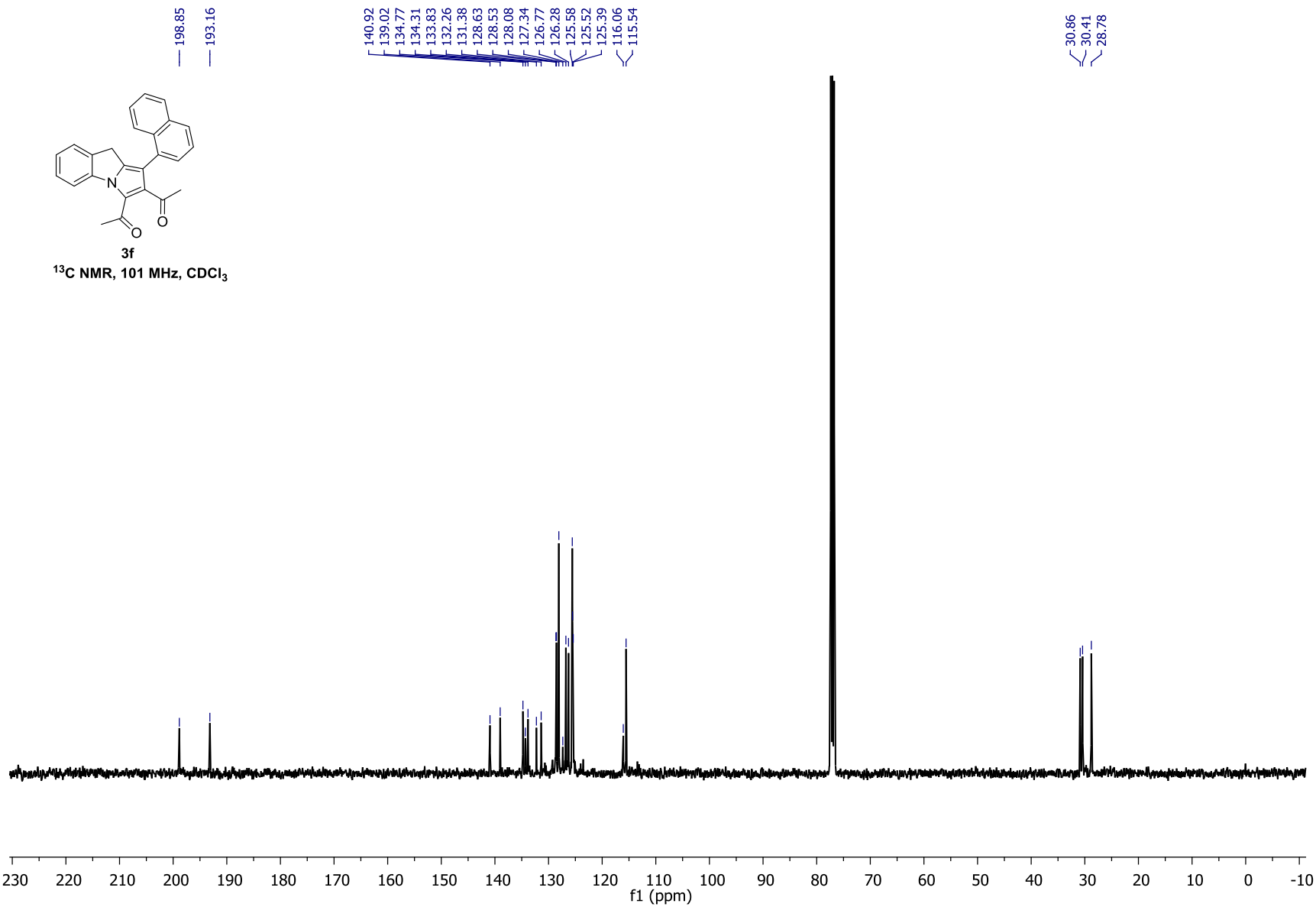
^{1}H NMR, 500 MHz, $CDCl_3$

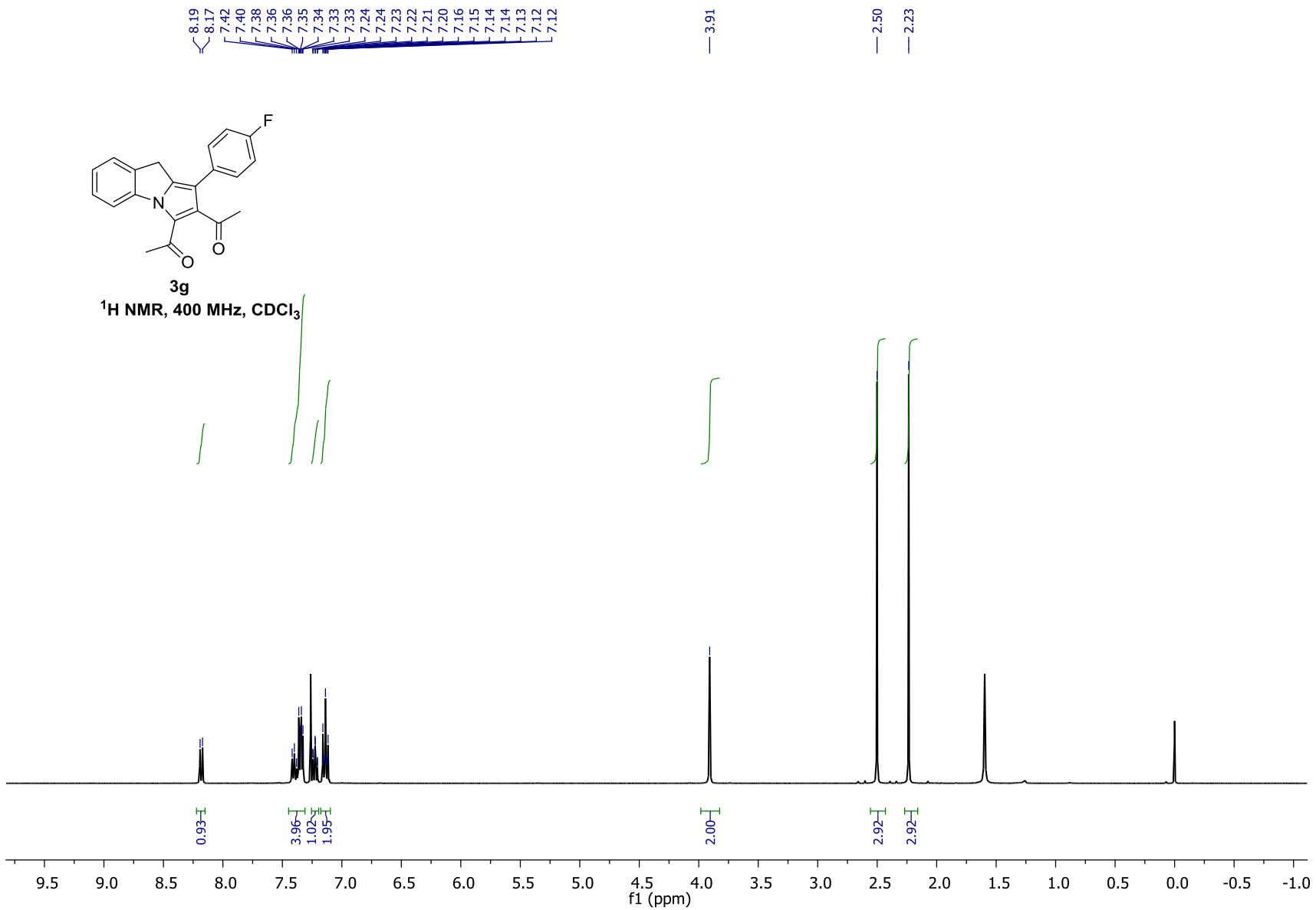


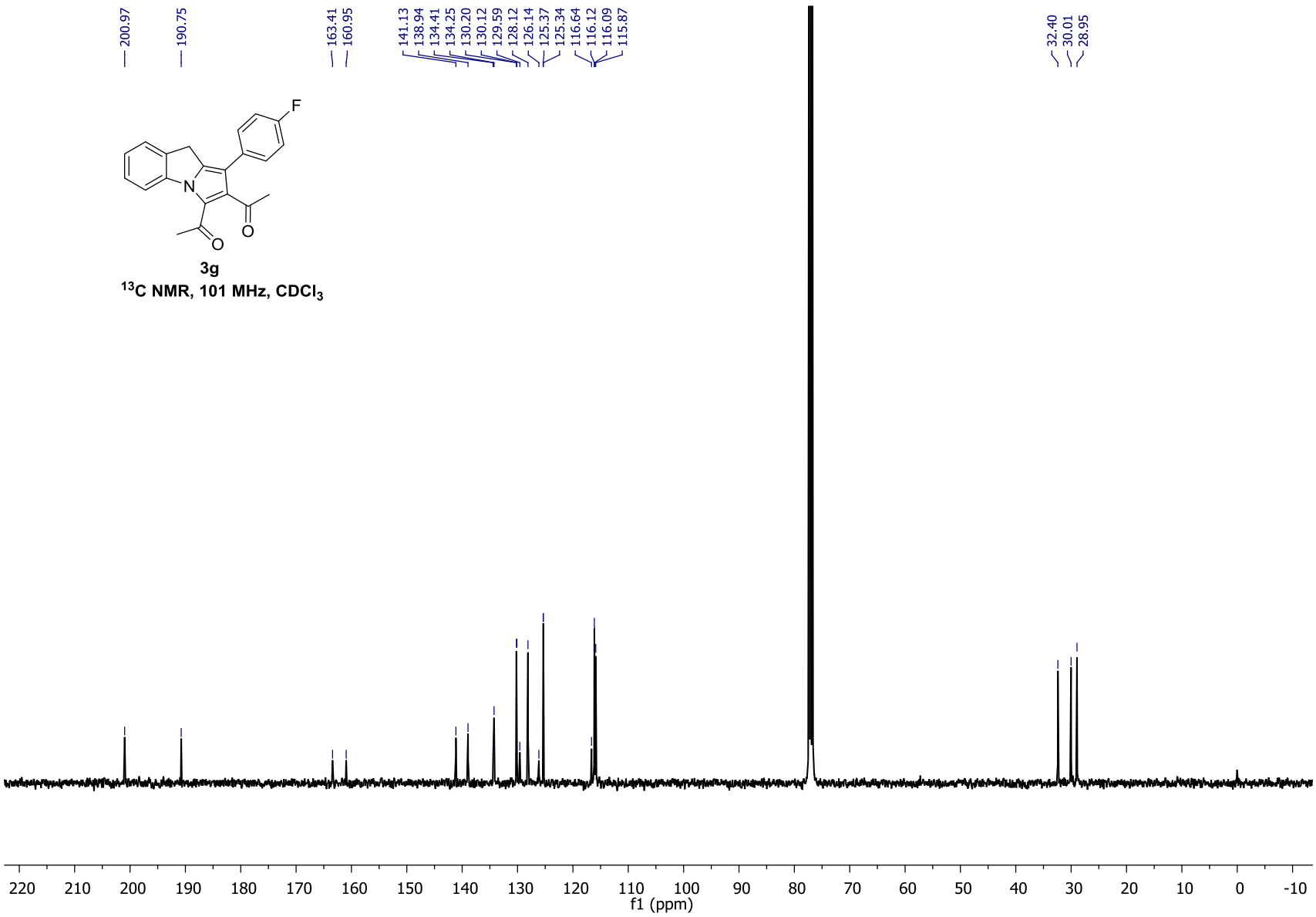
3e

^{13}C NMR, 101 MHz, $CDCl_3$


8.04
8.02
7.95
7.93
7.91
7.56
7.55
7.55
7.54
7.54
7.54
7.53
7.52
7.52
7.51
7.49
7.49
7.47
7.47
7.47
7.46
7.45
7.45
7.39
7.37
7.36
7.35
7.34
7.23
7.23
7.21
7.21
3.69
3.67
3.61
2.59
1.88
N
O
O
3f
1H NMR, 400 MHz, CDCl3
0.97
2.07
1.00
2.13
2.01
2.09
1.04
2.09
2.97
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

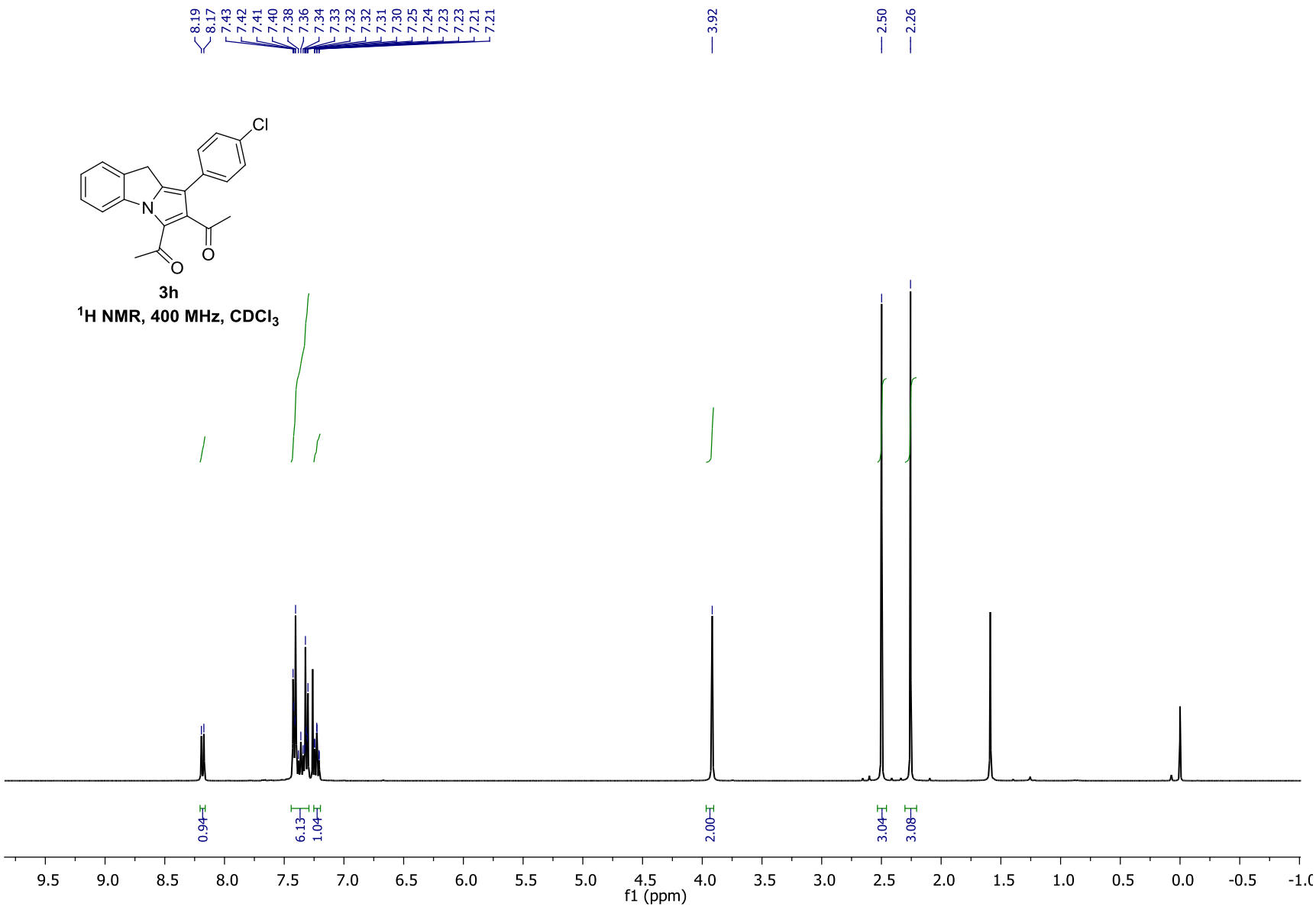

198.85
193.16
140.92
139.02
134.77
134.31
133.83
132.26
131.38
128.63
128.53
128.08
127.34
126.77
126.28
125.58
125.52
125.39
116.06
115.54
30.86
30.41
28.78
N
O
O
3f
13C NMR, 101 MHz, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

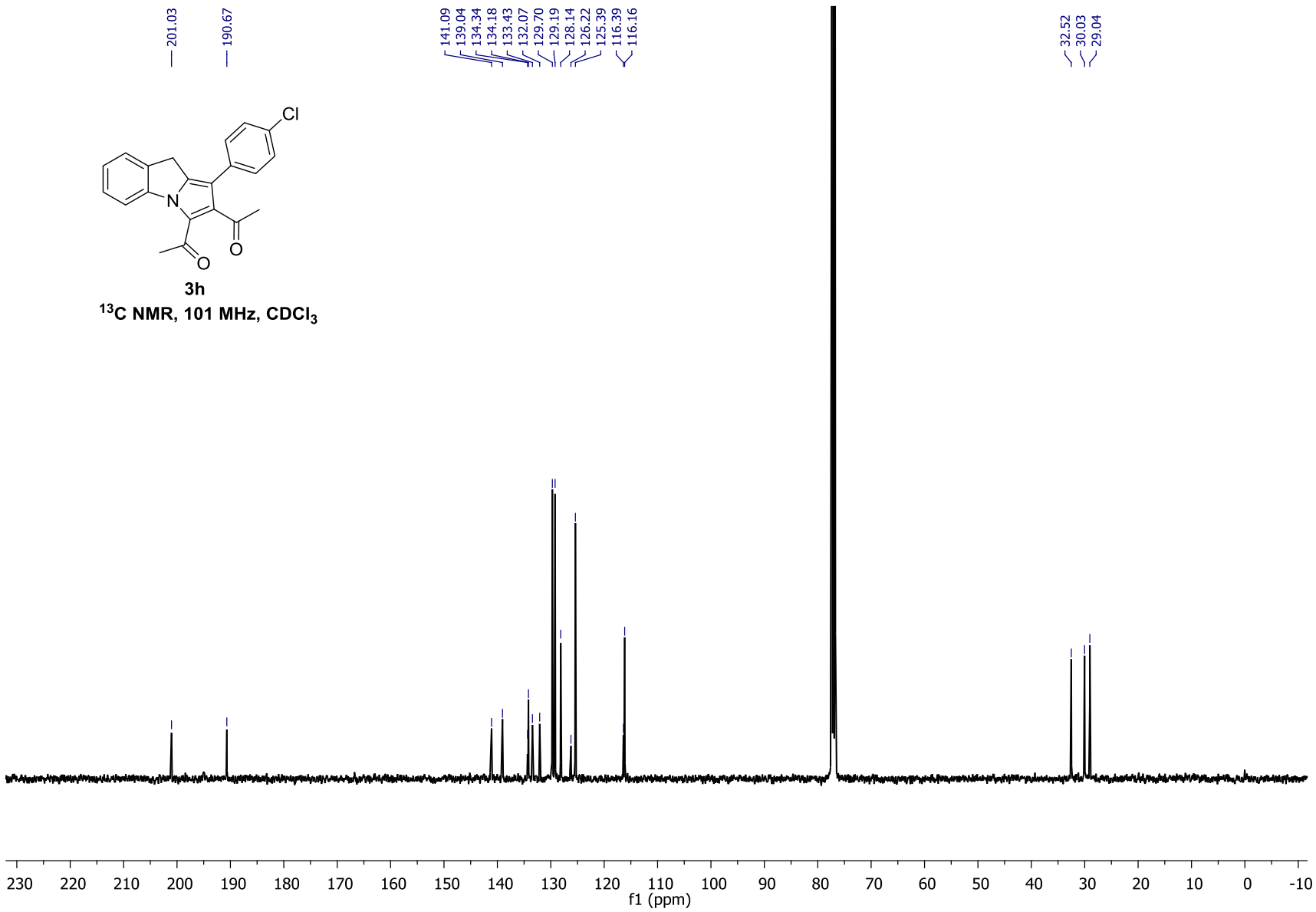

8.19
8.17
7.42
7.40
7.38
7.36
7.36
7.35
7.34
7.33
7.33
7.24
7.24
7.23
7.22
7.21
7.20
7.16
7.15
7.14
7.14
7.13
7.12
7.12
3.91
2.50
2.23
F
N
O
O
3g
^{1}H NMR, 400 MHz, $CDCl_3$
0.93
3.96
1.02
1.95
2.00
2.92
2.92
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



3g

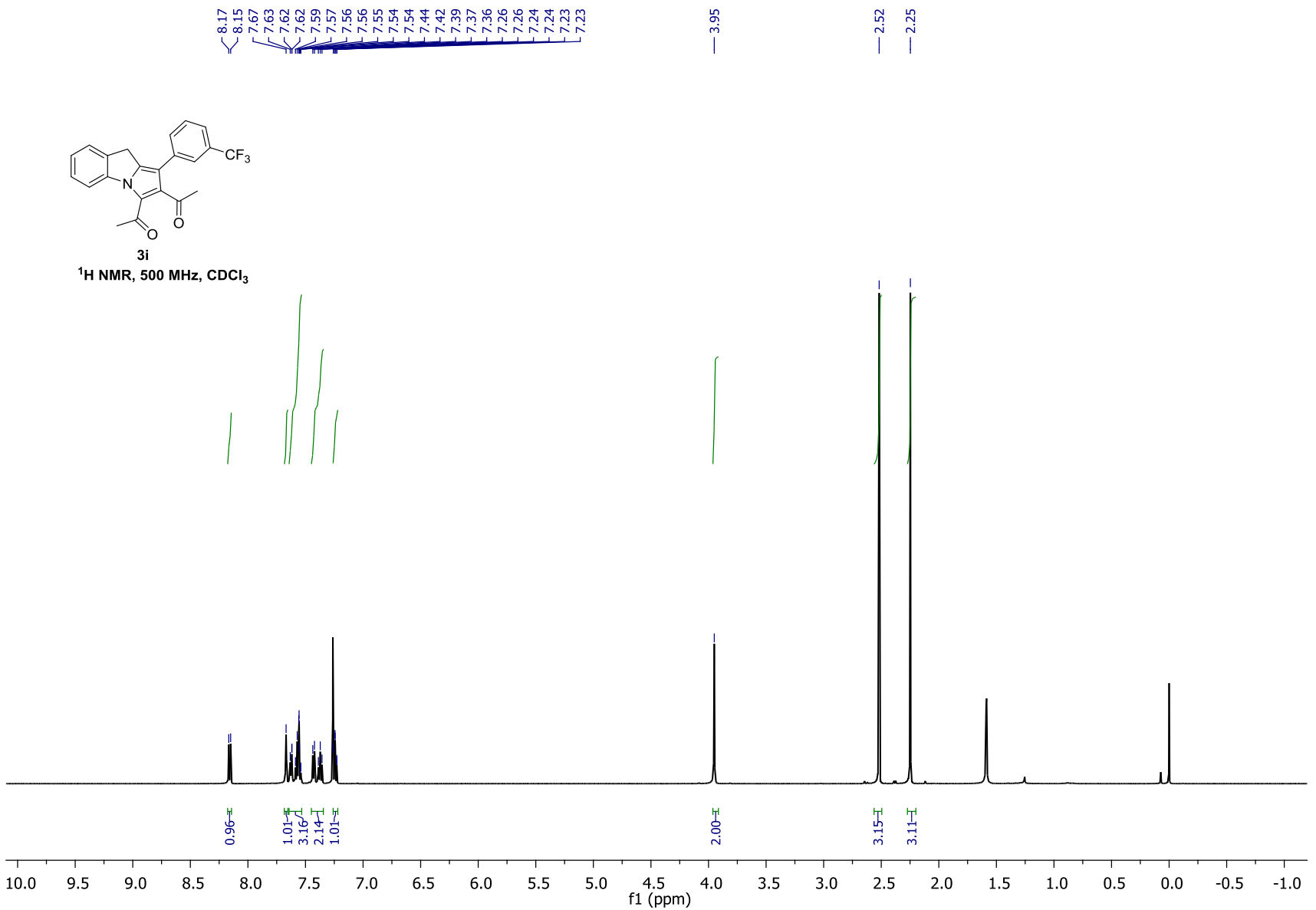
^{13}C NMR, 101 MHz, $CDCl_3$


8.19
8.17
7.43
7.42
7.41
7.40
7.38
7.36
7.34
7.33
7.32
7.32
7.31
7.30
7.25
7.24
7.23
7.23
7.21
7.21
3.92
2.50
2.26
Cl
N
O
O
3h
^{1}H NMR, 400 MHz, CDCl$_3$
0.94
6.13
1.04
2.00
3.04
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



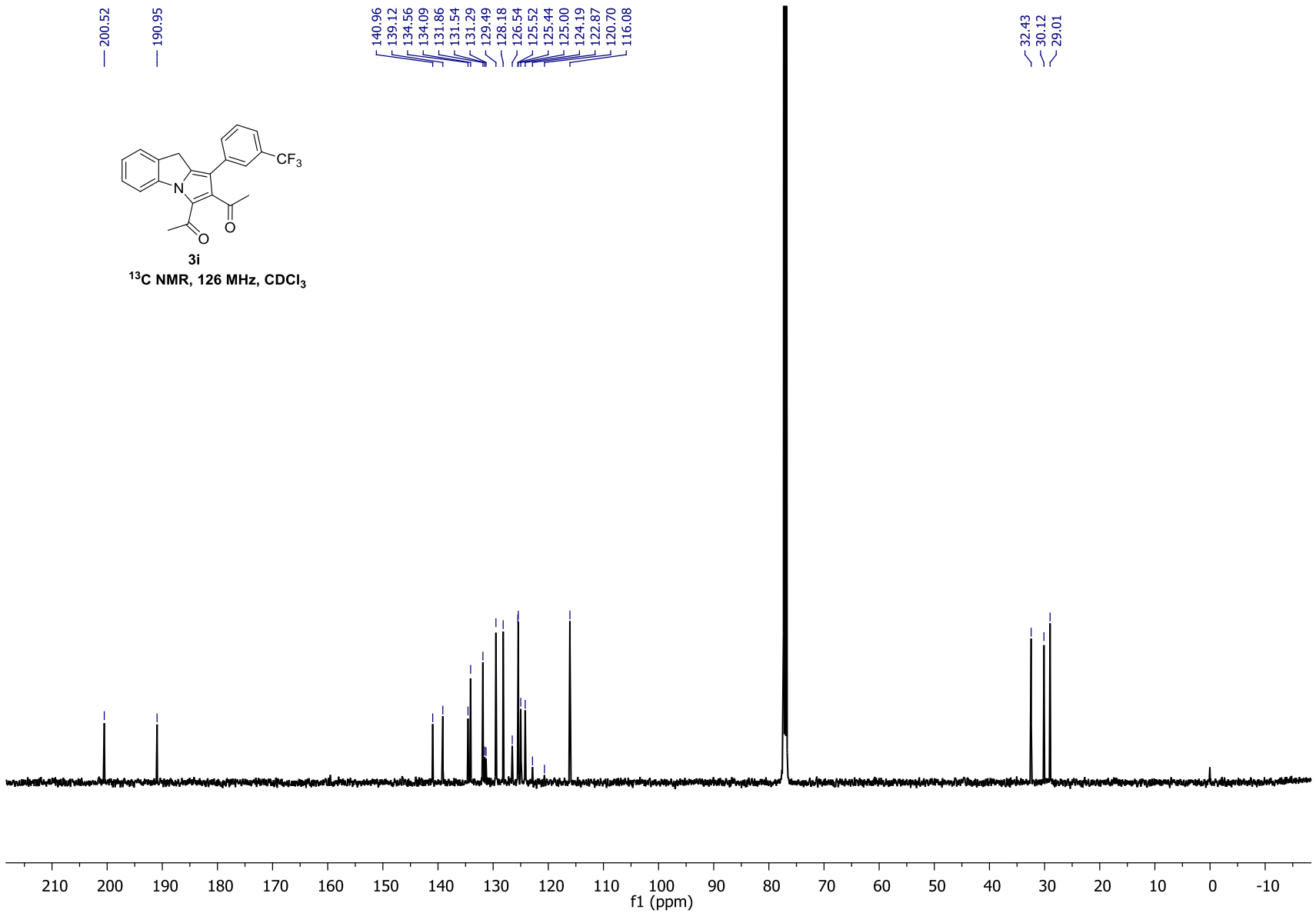
3h

^{13}C NMR, 101 MHz, $CDCl_3$



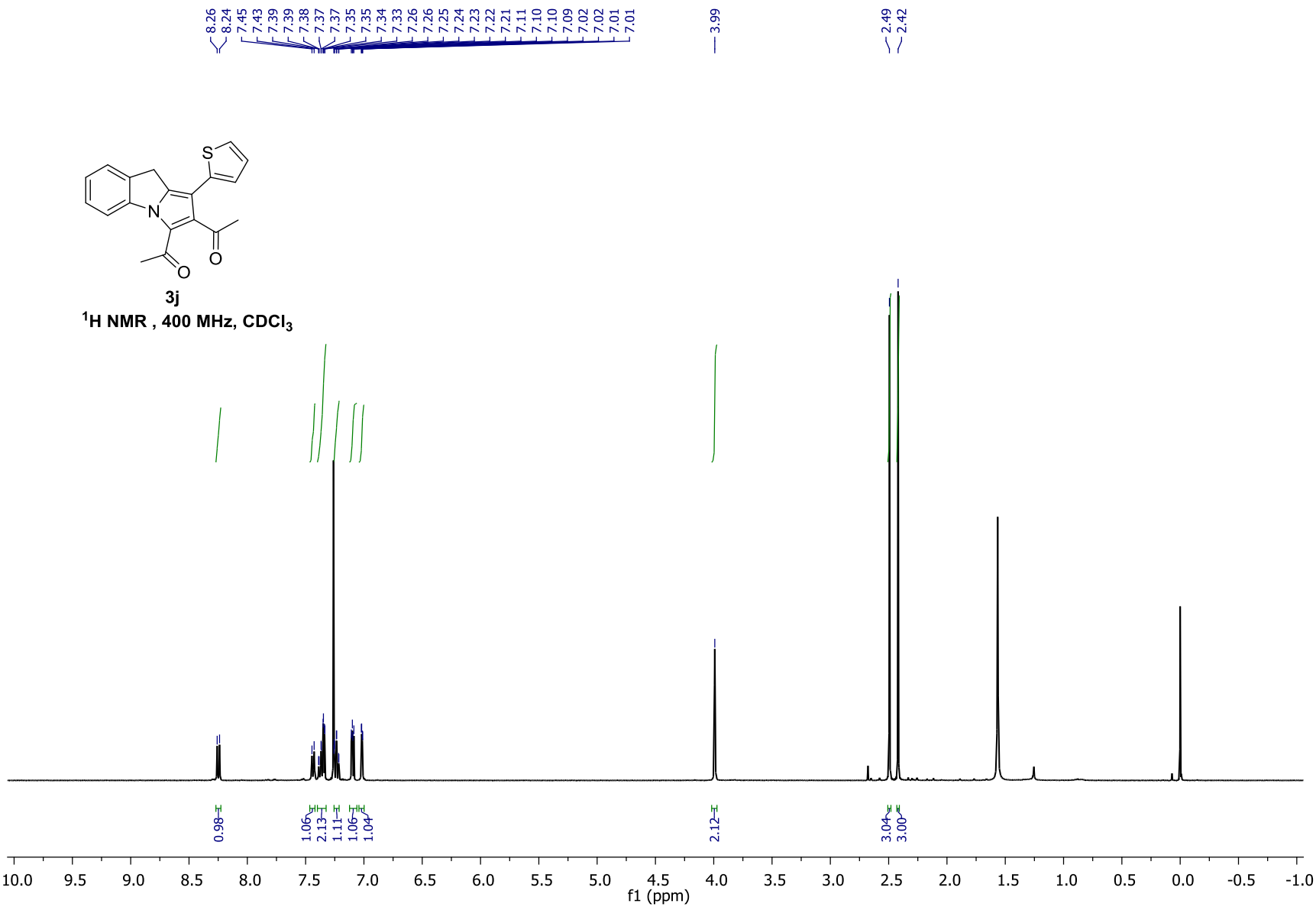
3i

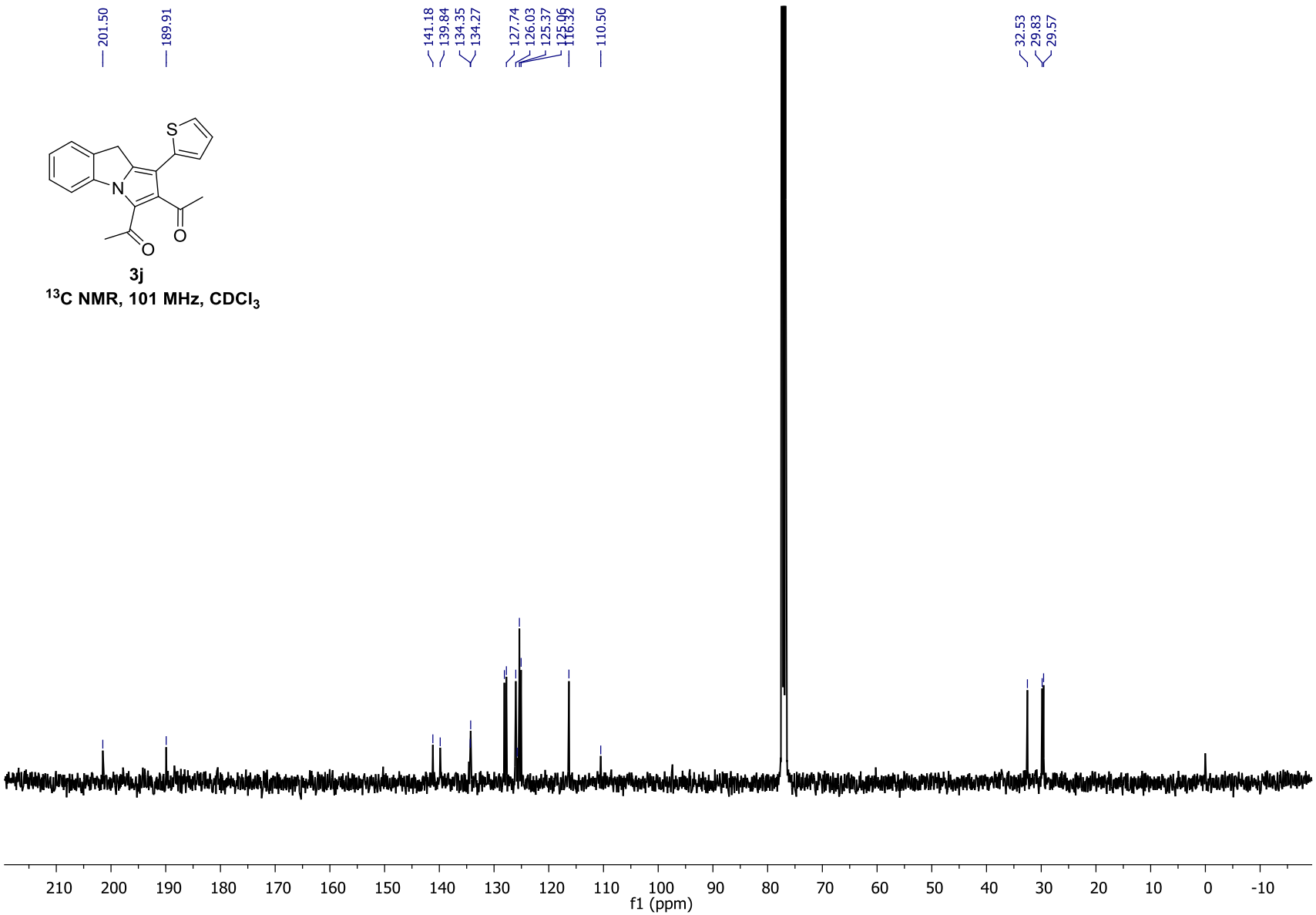
^{1}H NMR, 500 MHz, $CDCl_3$



3i

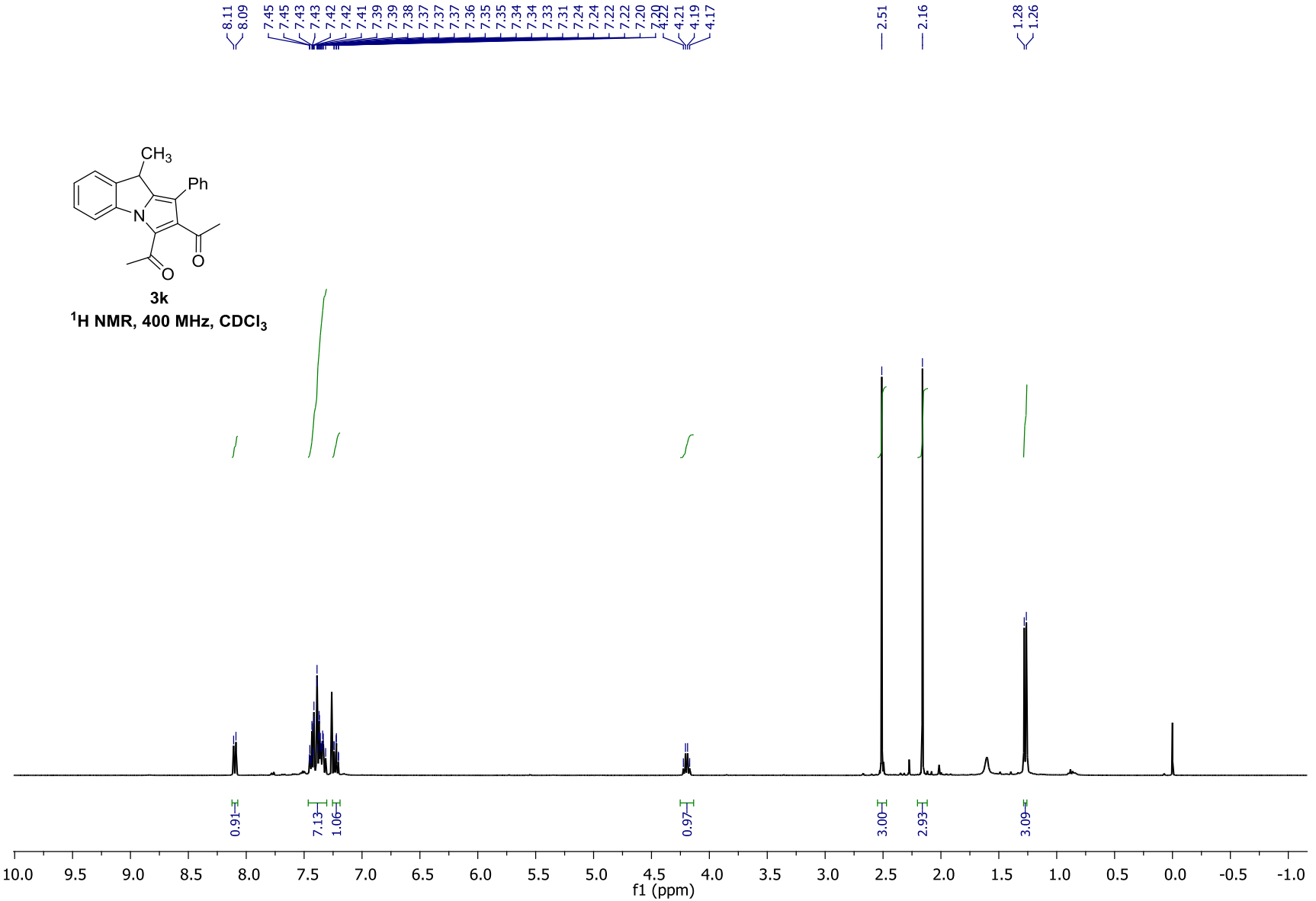
^{13}C NMR, 126 MHz, $CDCl_3$

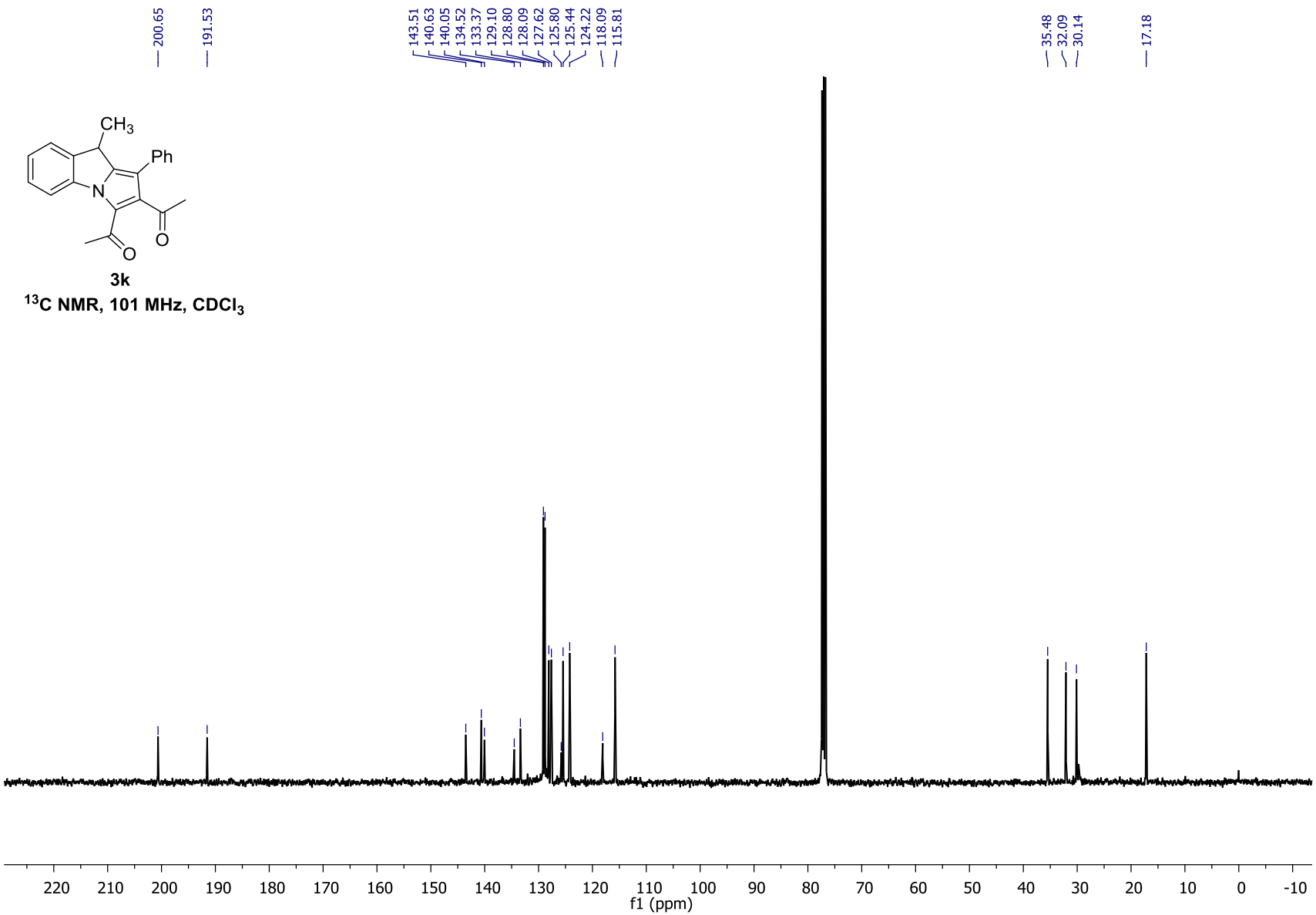

8.26
8.24
7.45
7.43
7.39
7.39
7.38
7.37
7.37
7.35
7.35
7.34
7.33
7.26
7.26
7.25
7.24
7.23
7.22
7.21
7.11
7.10
7.10
7.09
7.02
7.02
7.01
7.01
3.99
2.49
2.42
S
N
O
O
3j
1H NMR , 400 MHz, CDCl3
0.98
1.06
2.13
1.11
1.06
1.04
2.12
3.04
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



3j

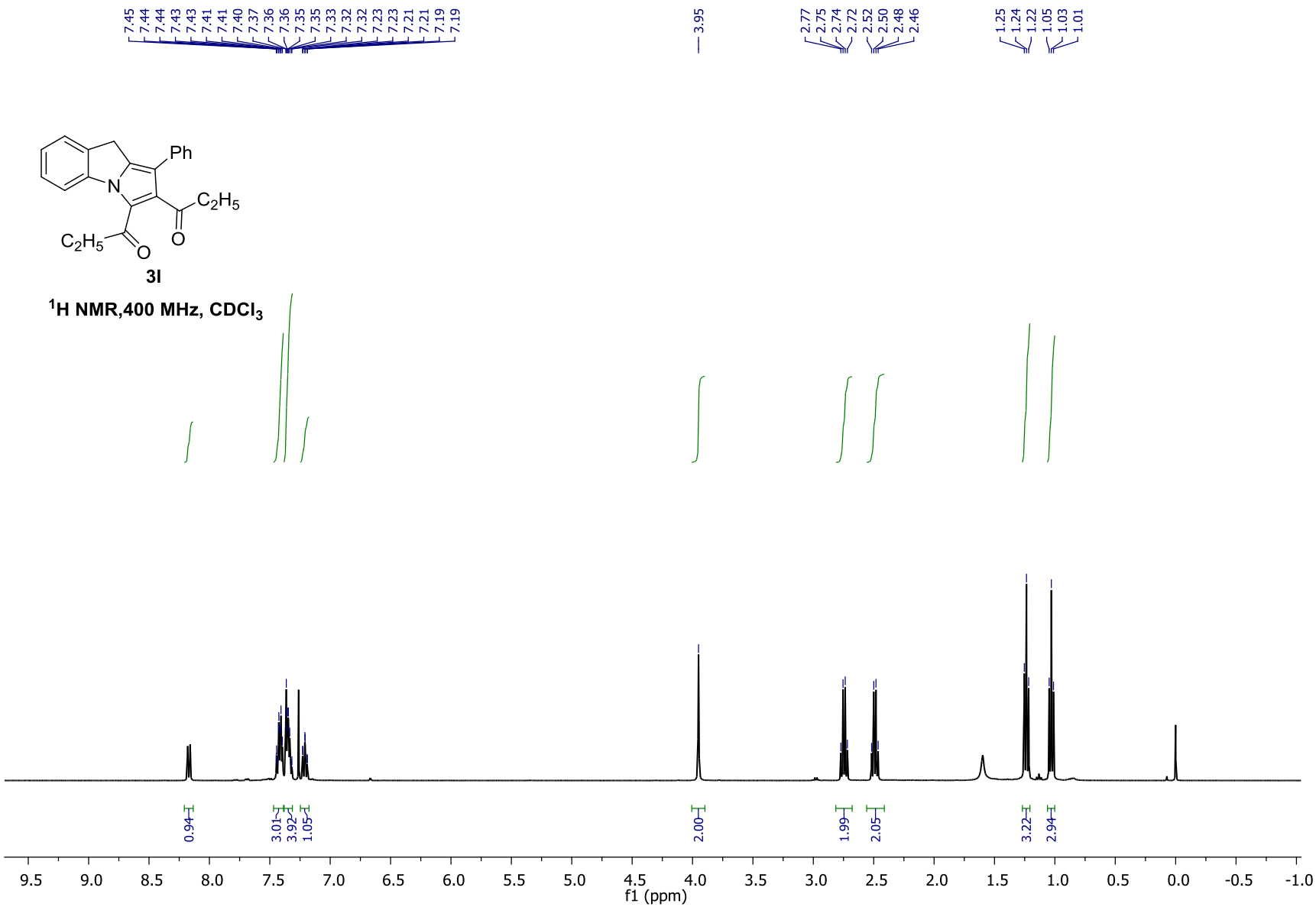
^{13}C NMR, 101 MHz, $CDCl_3$


8.11
8.09
7.45
7.45
7.43
7.43
7.42
7.42
7.41
7.39
7.39
7.38
7.37
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.31
7.24
7.24
7.22
7.22
7.20
4.21
4.19
4.17
2.51
2.16
1.28
1.26
CH3
Ph
N
O
O
3k
1H NMR, 400 MHz, CDCl3
0.91
7.13
1.06
0.97
3.00
2.93
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



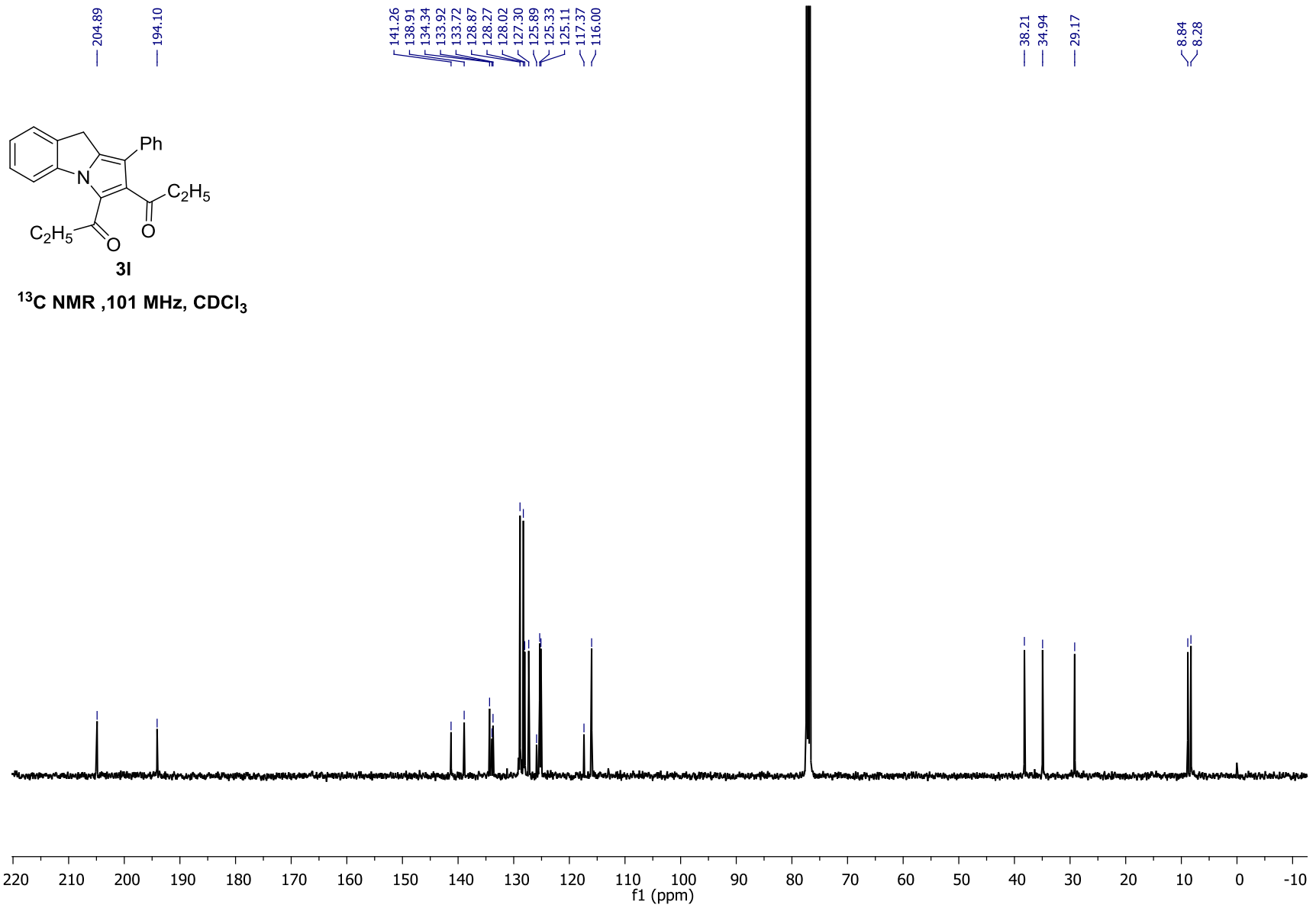
3k

^{13}C NMR, 101 MHz, $CDCl_3$



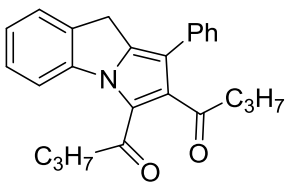
3l

^{1}H NMR,400 MHz, $CDCl_3$



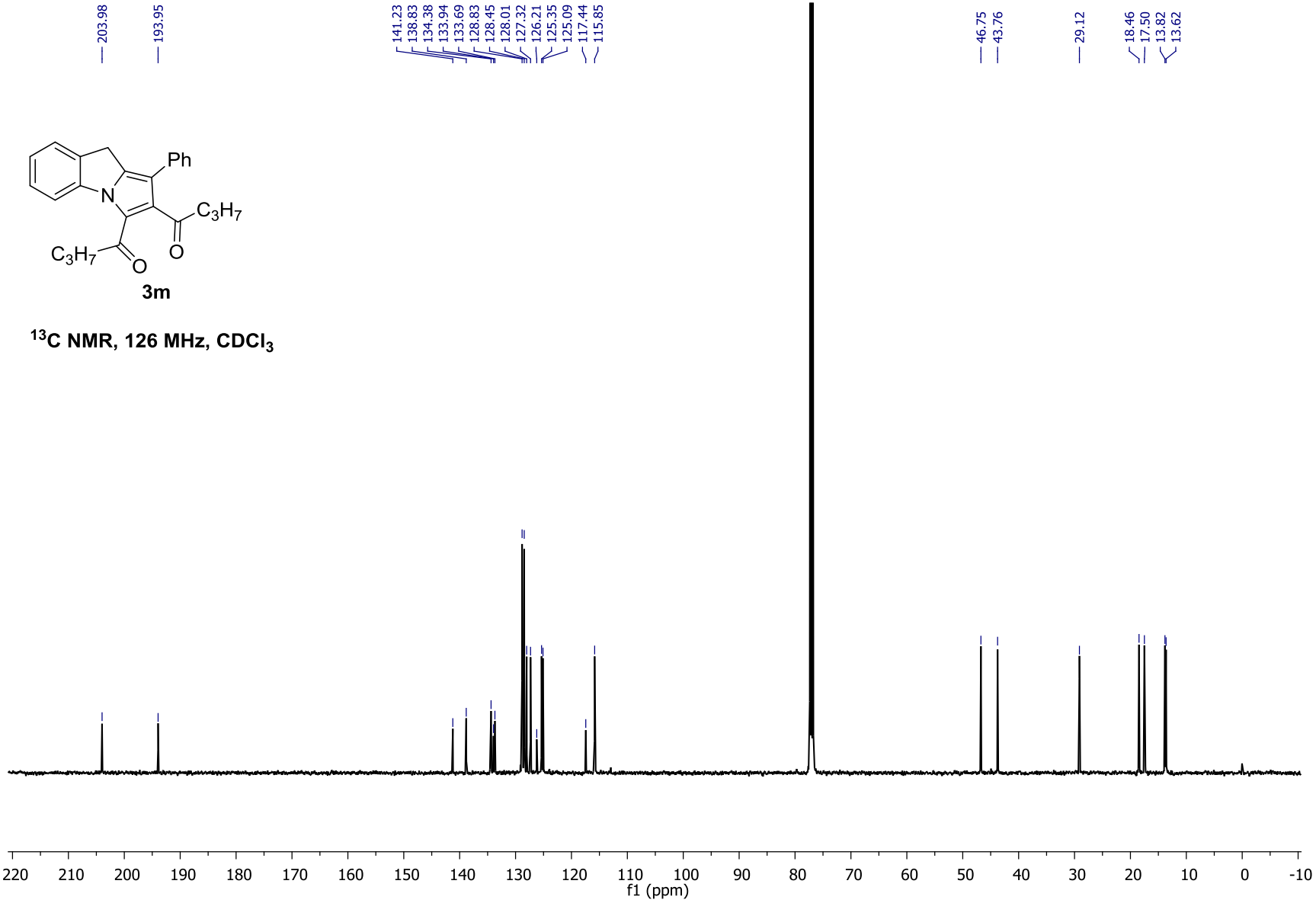
3l

^{13}C NMR ,101 MHz, $CDCl_3$



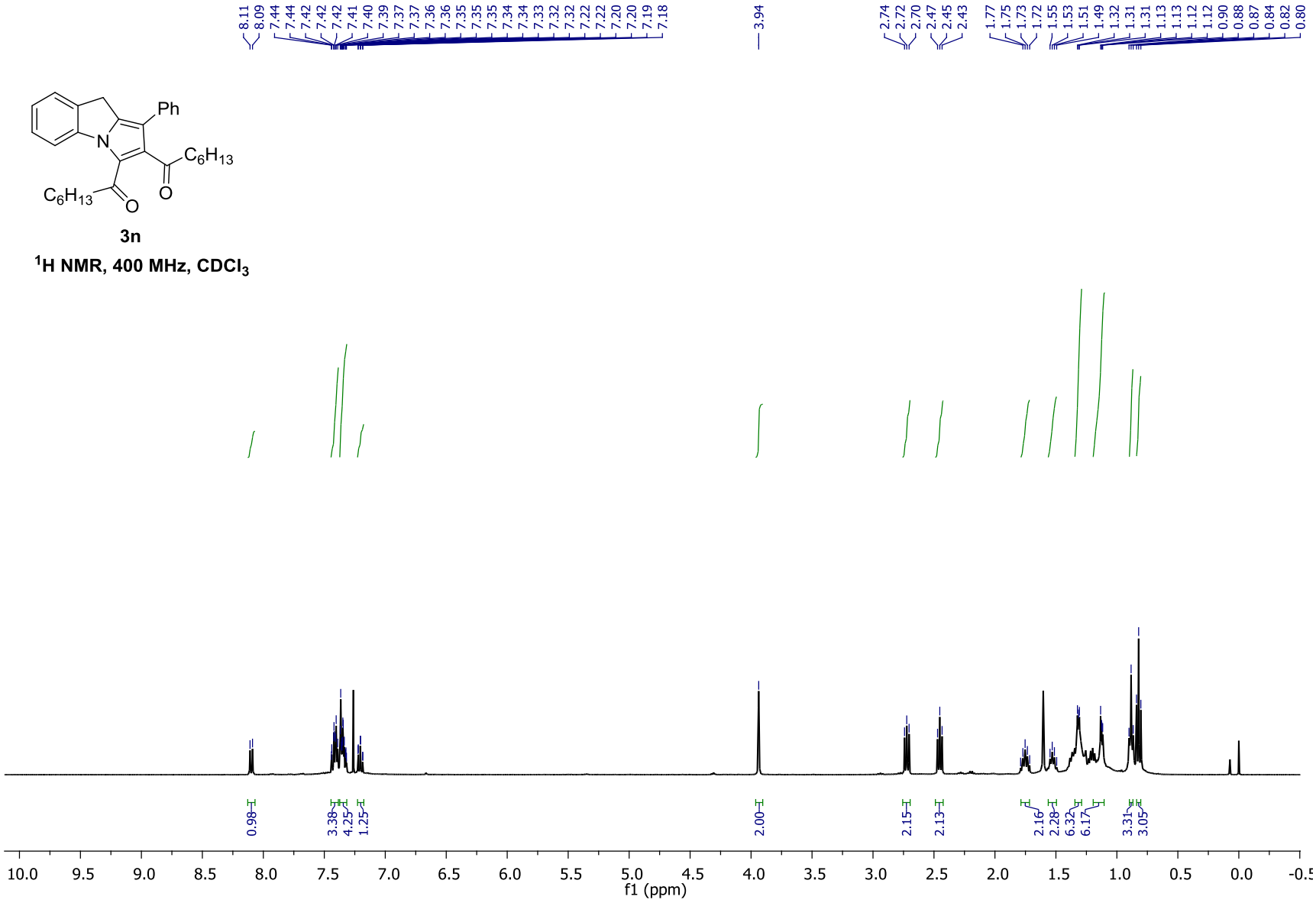
3m

1H NMR, 300 MHz, $CDCl_3$



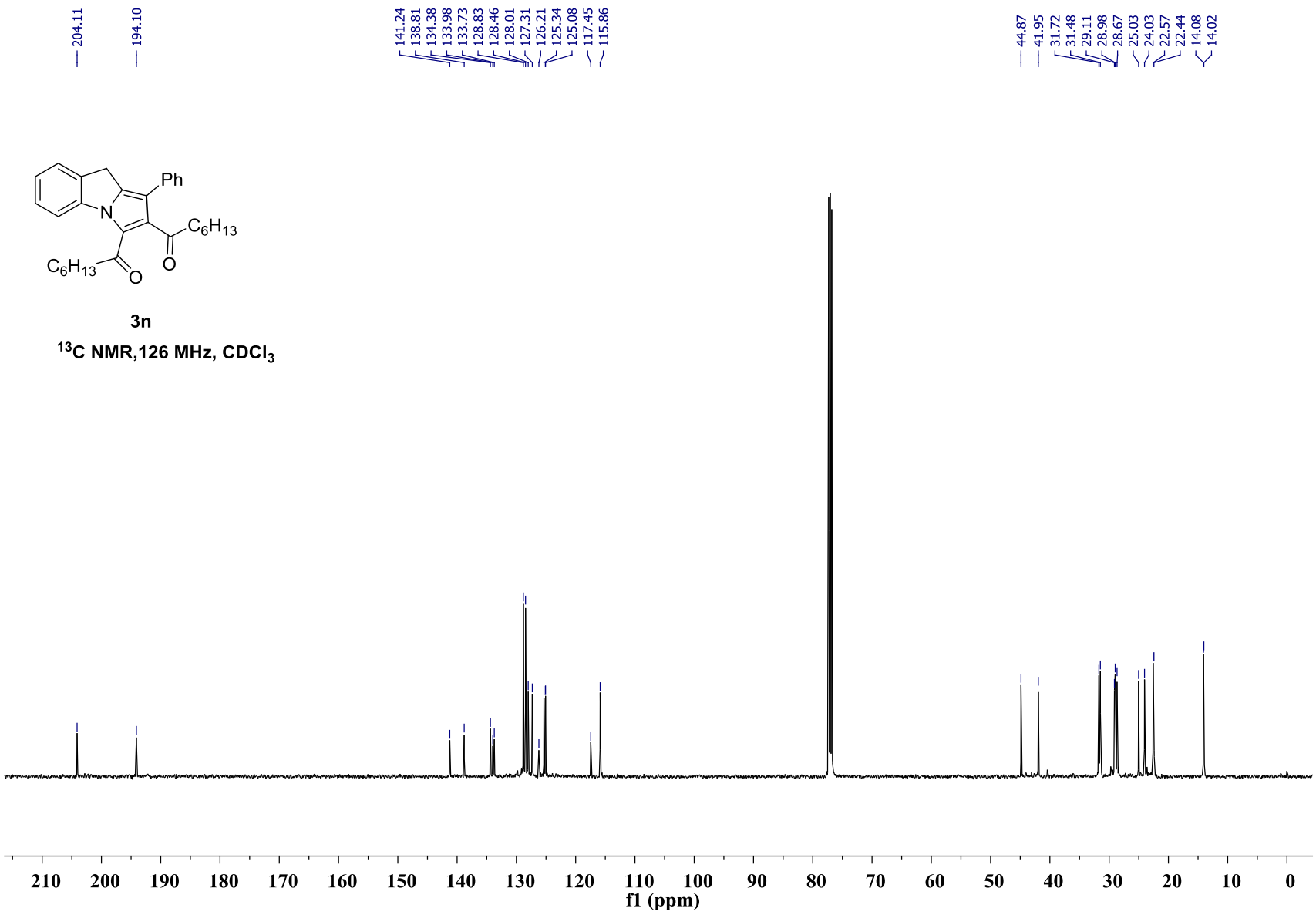
3m

^{13}C NMR, 126 MHz, $CDCl_3$



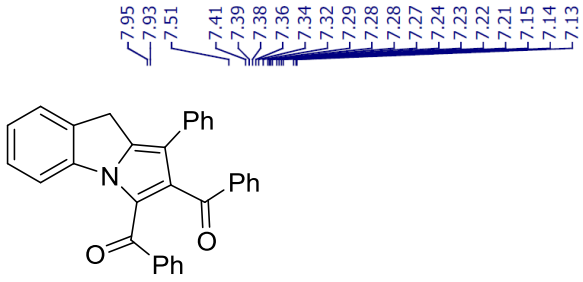
3n

^{1}H NMR, 400 MHz, $CDCl_3$



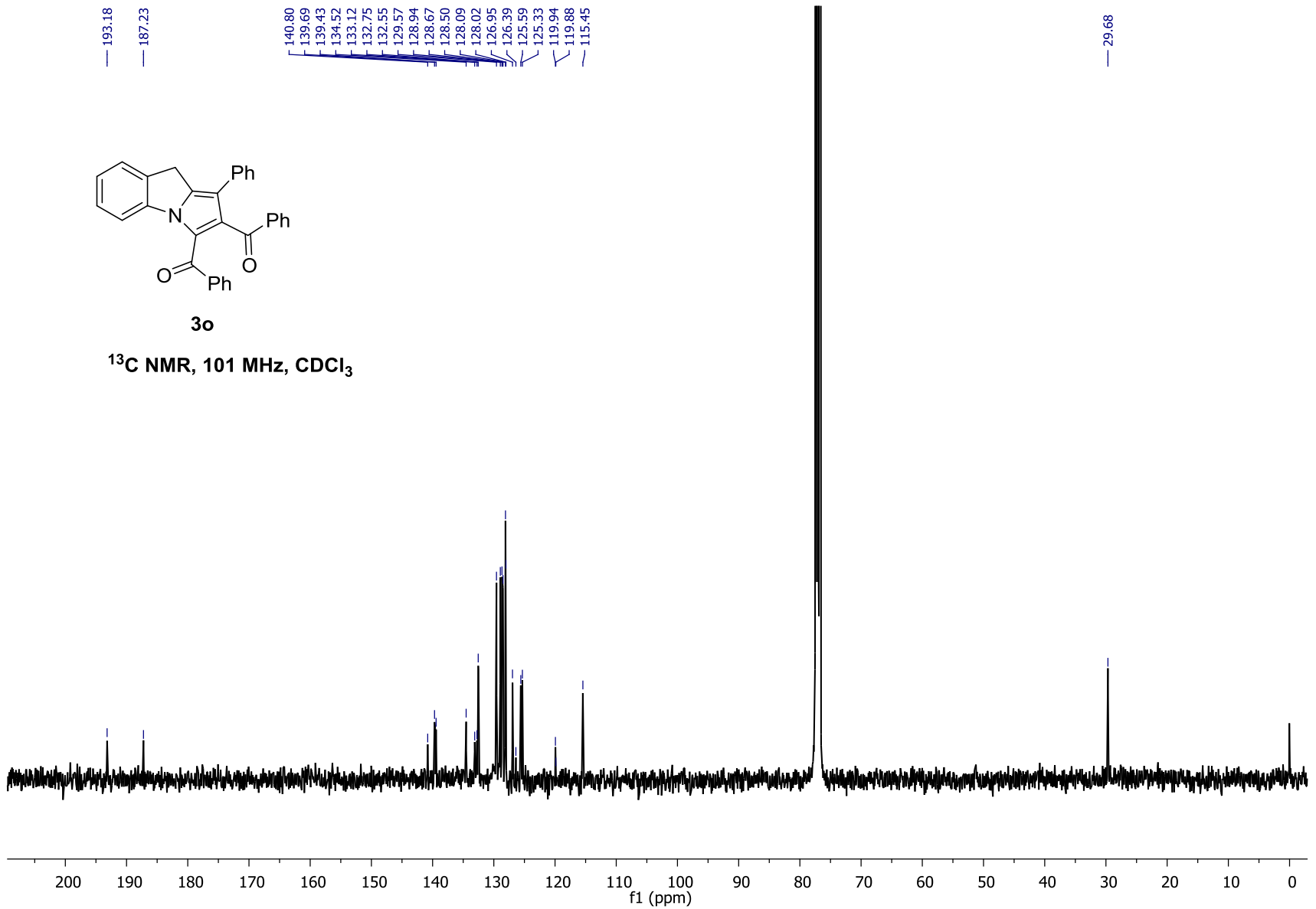
3n

^{13}C NMR,126 MHz, $CDCl_3$



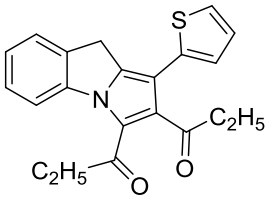
3o

^{1}H NMR, 500 MHz, $CDCl_3$



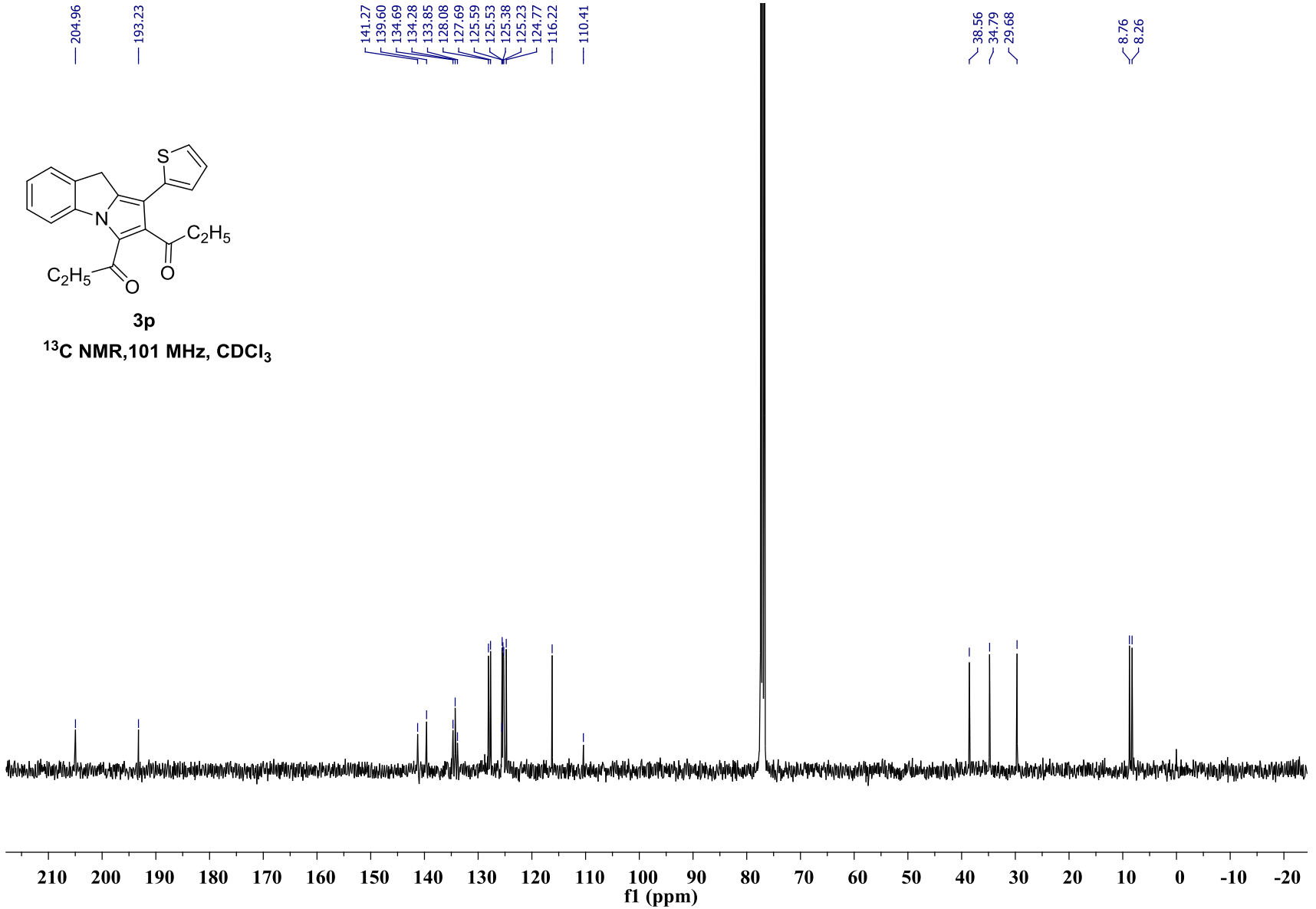
3o

^{13}C NMR, 101 MHz, $CDCl_3$



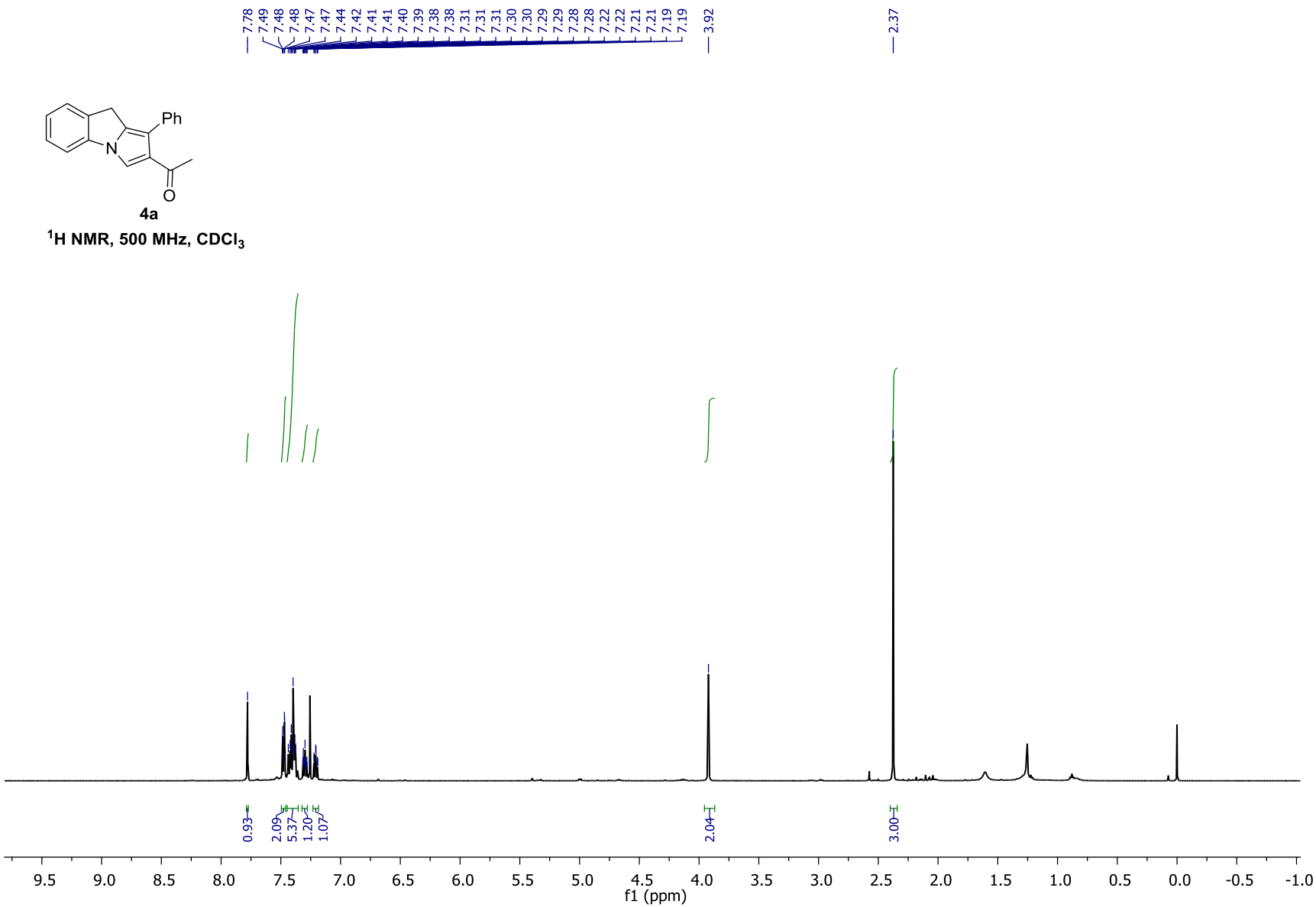
3p

^{1}H NMR, 400 MHz, $CDCl_3$



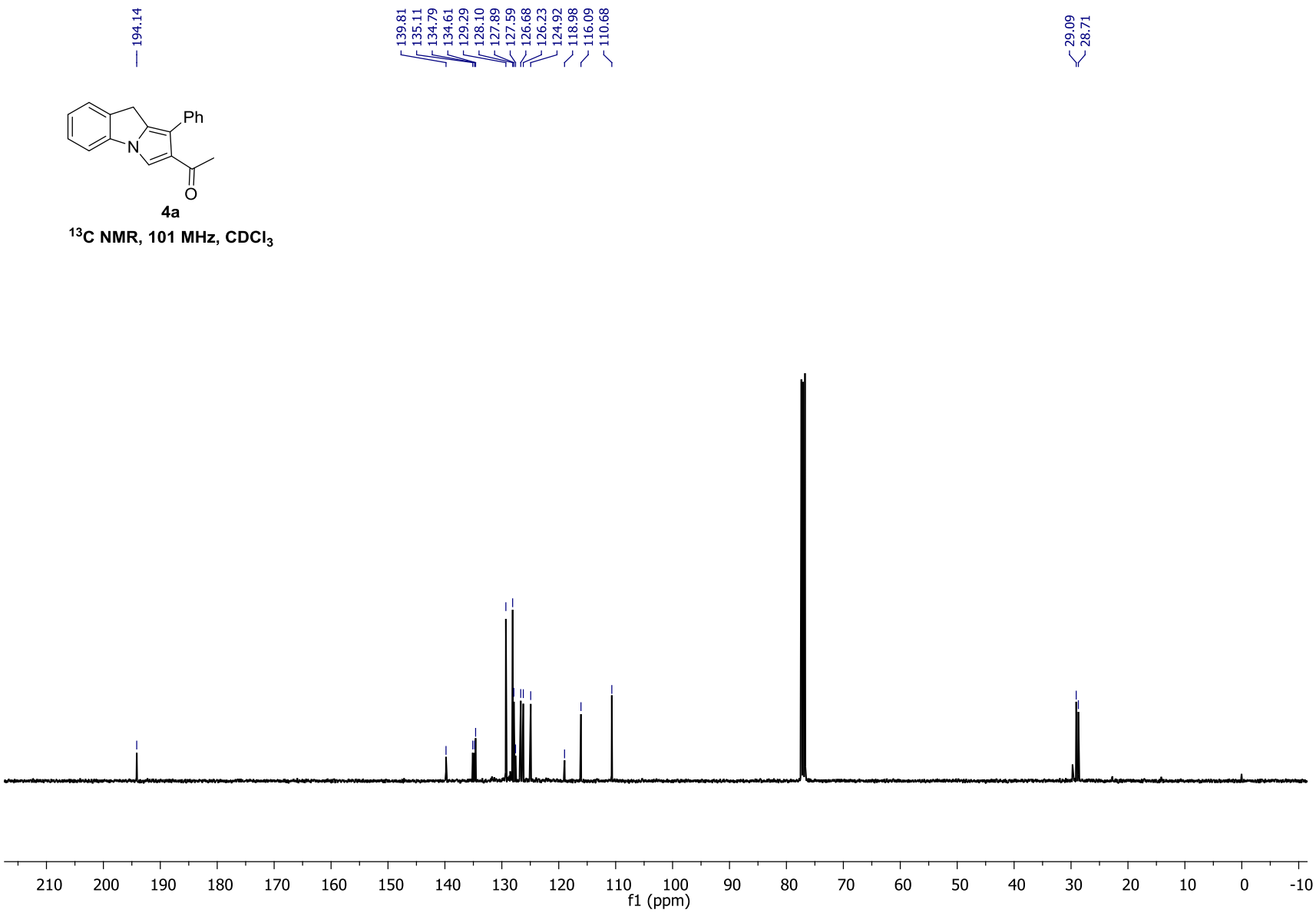
3p

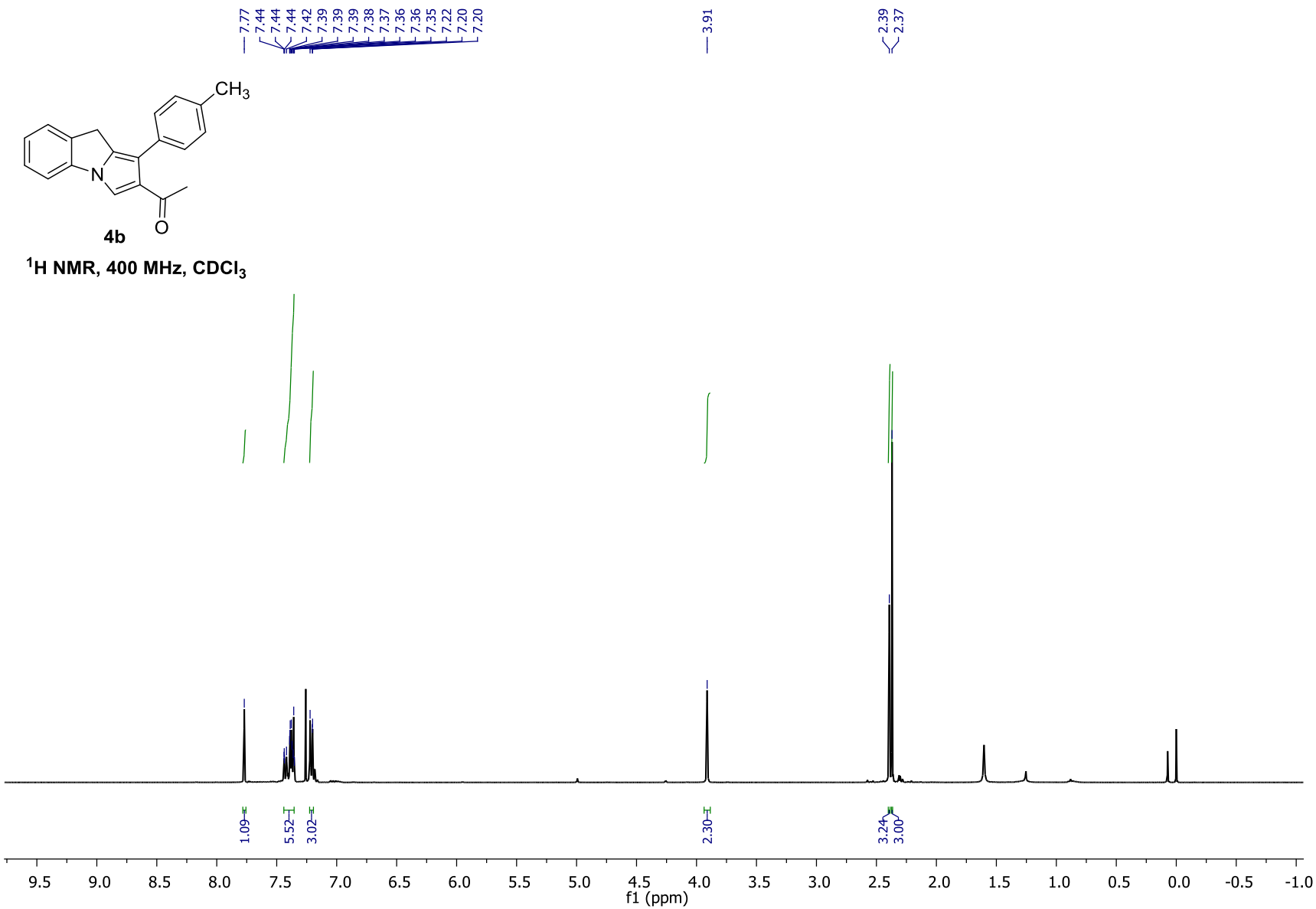
^{13}C NMR,101 MHz, $CDCl_3$

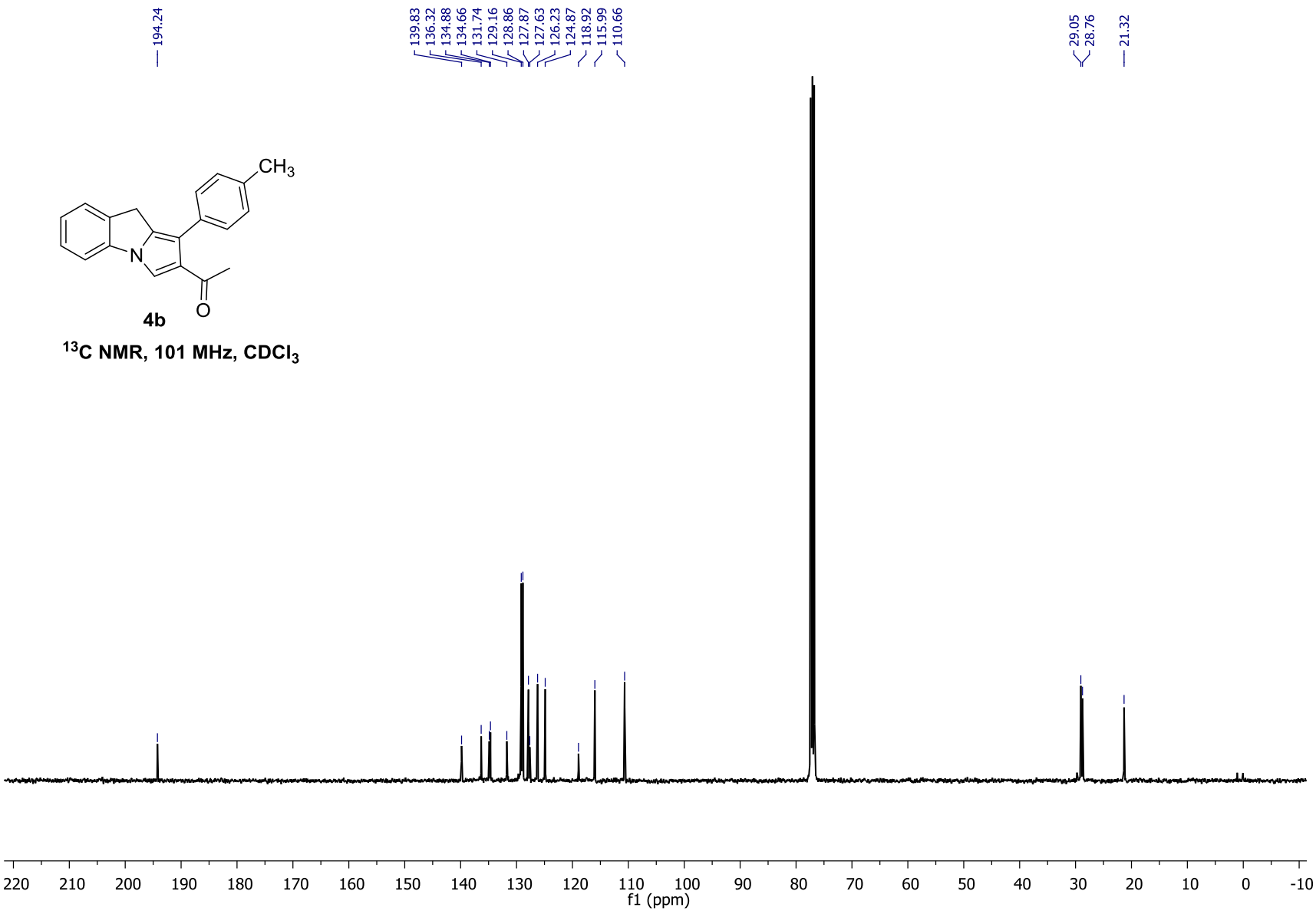


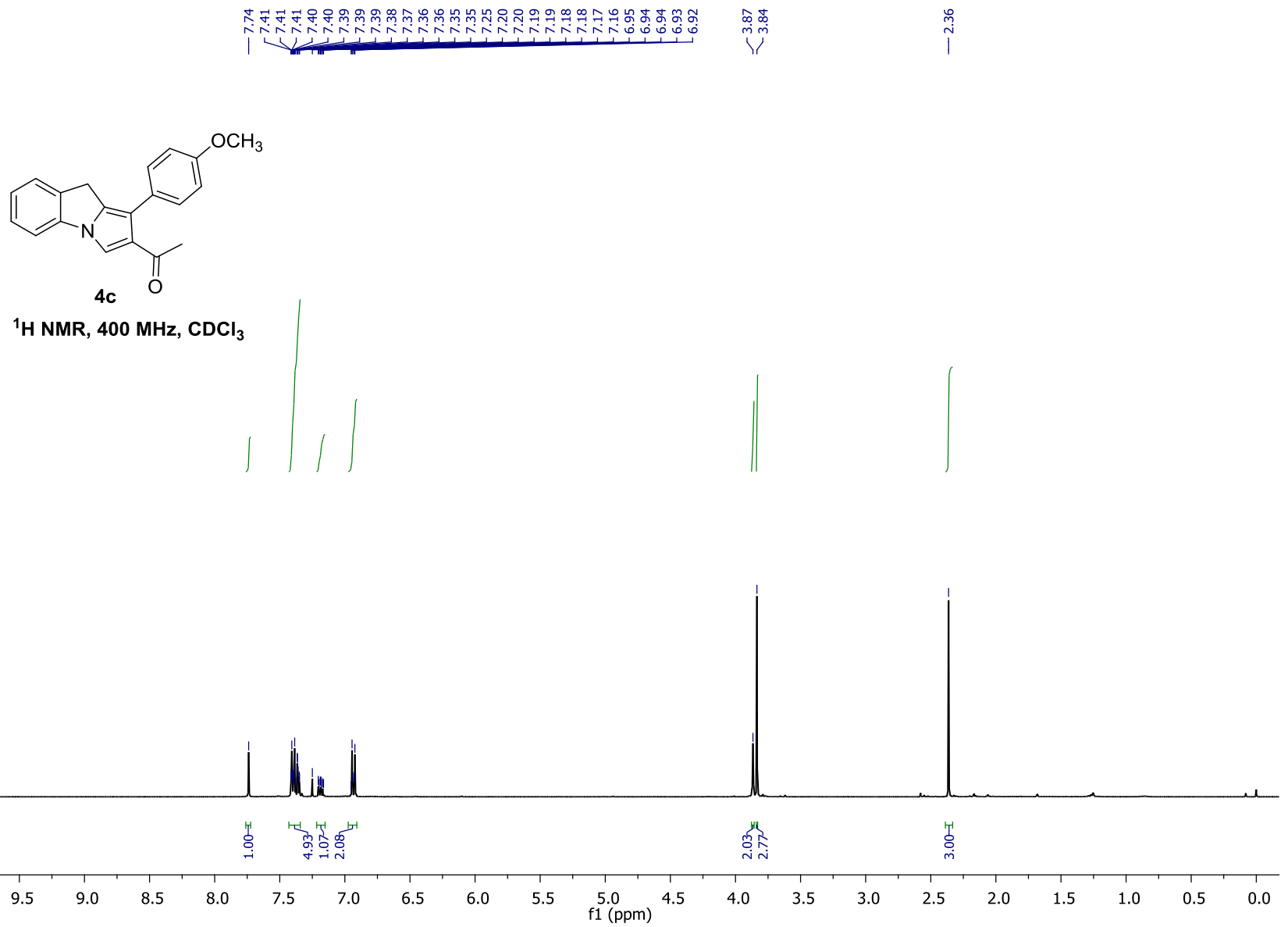
4a

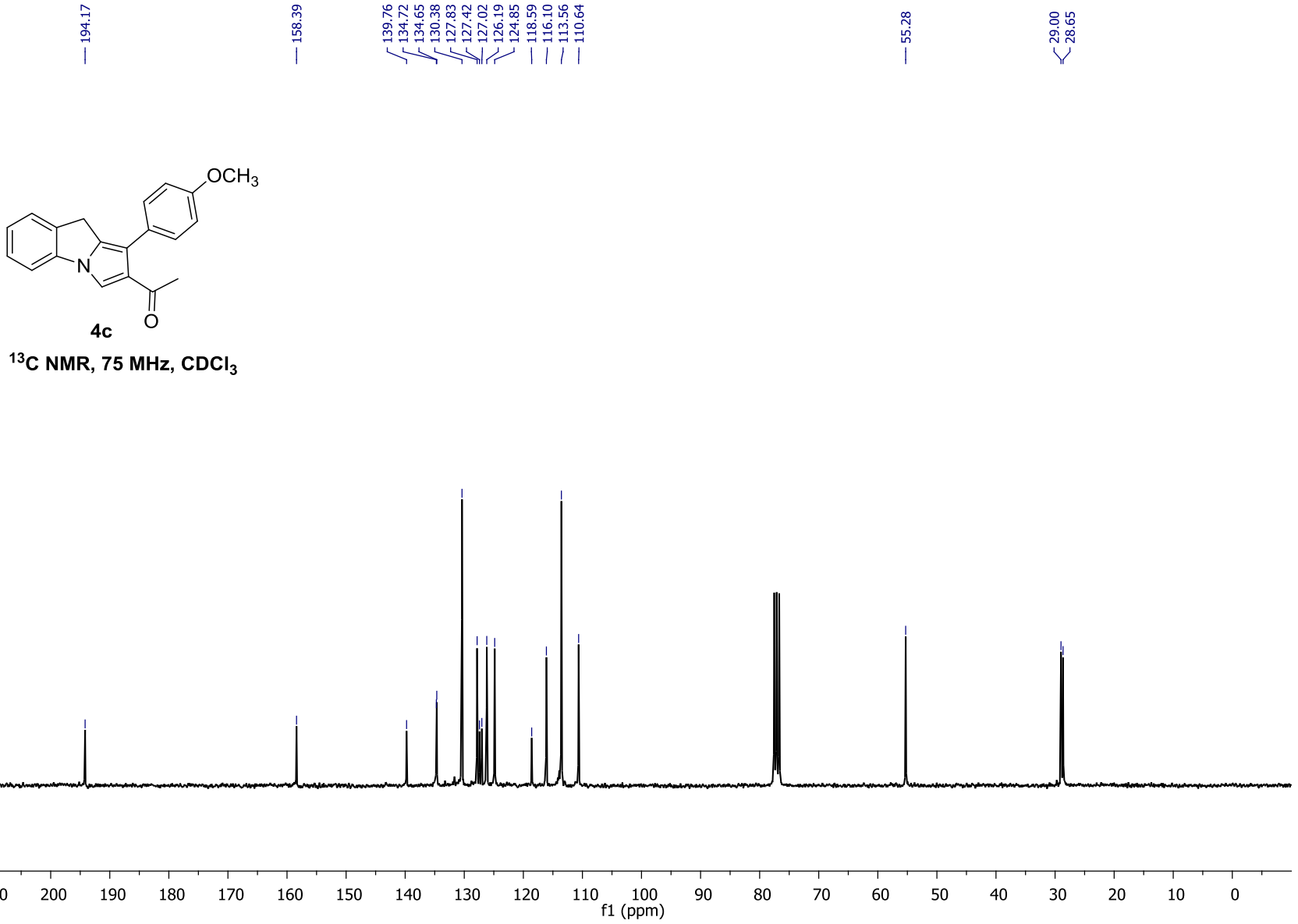
^{1}H NMR, 500 MHz, $CDCl_3$

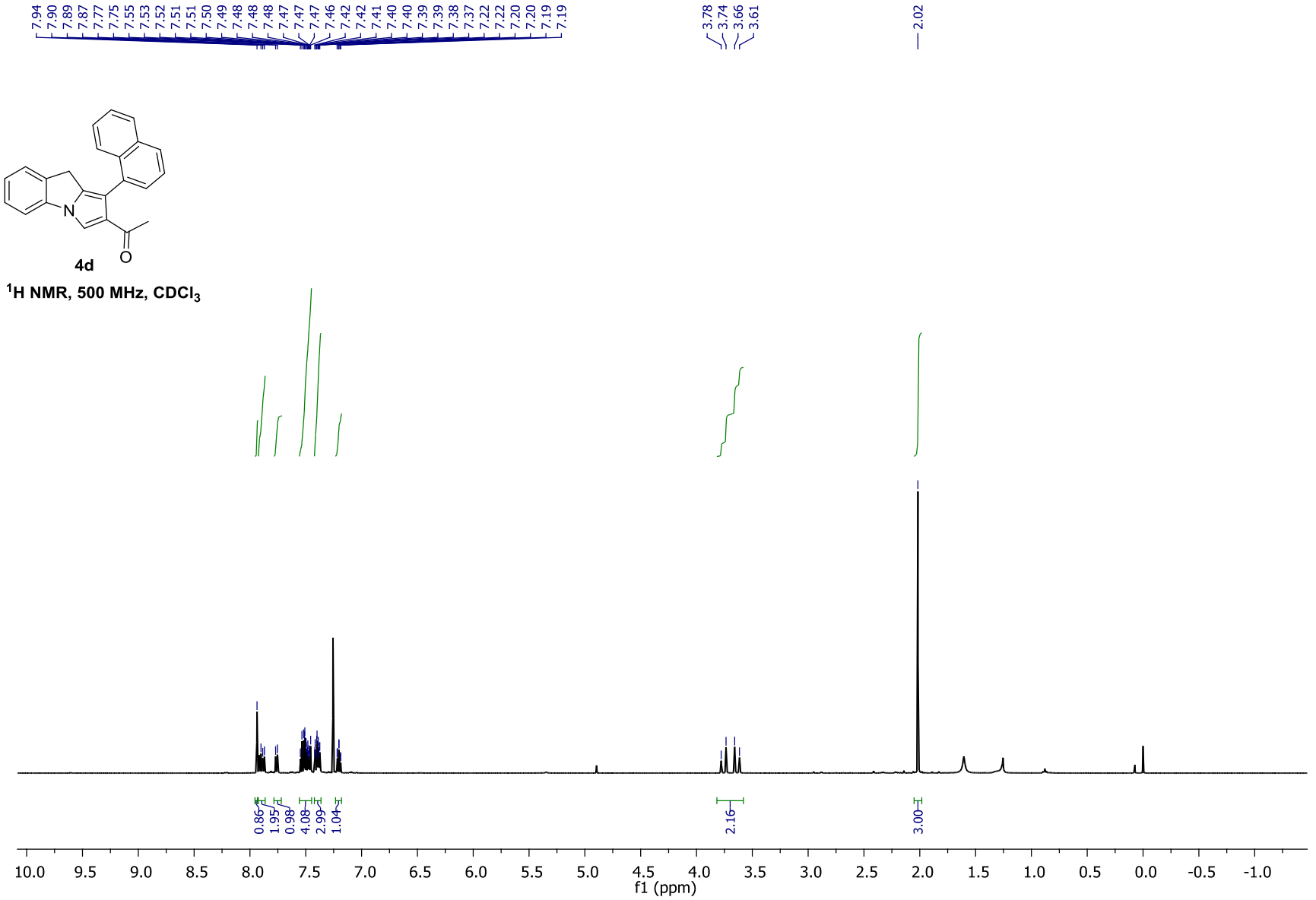

194.14
139.81
135.11
134.79
134.61
129.29
128.10
127.89
127.59
126.68
126.23
124.92
118.98
116.09
110.68
29.09
28.71
Ph
N
O
4a
13C NMR, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

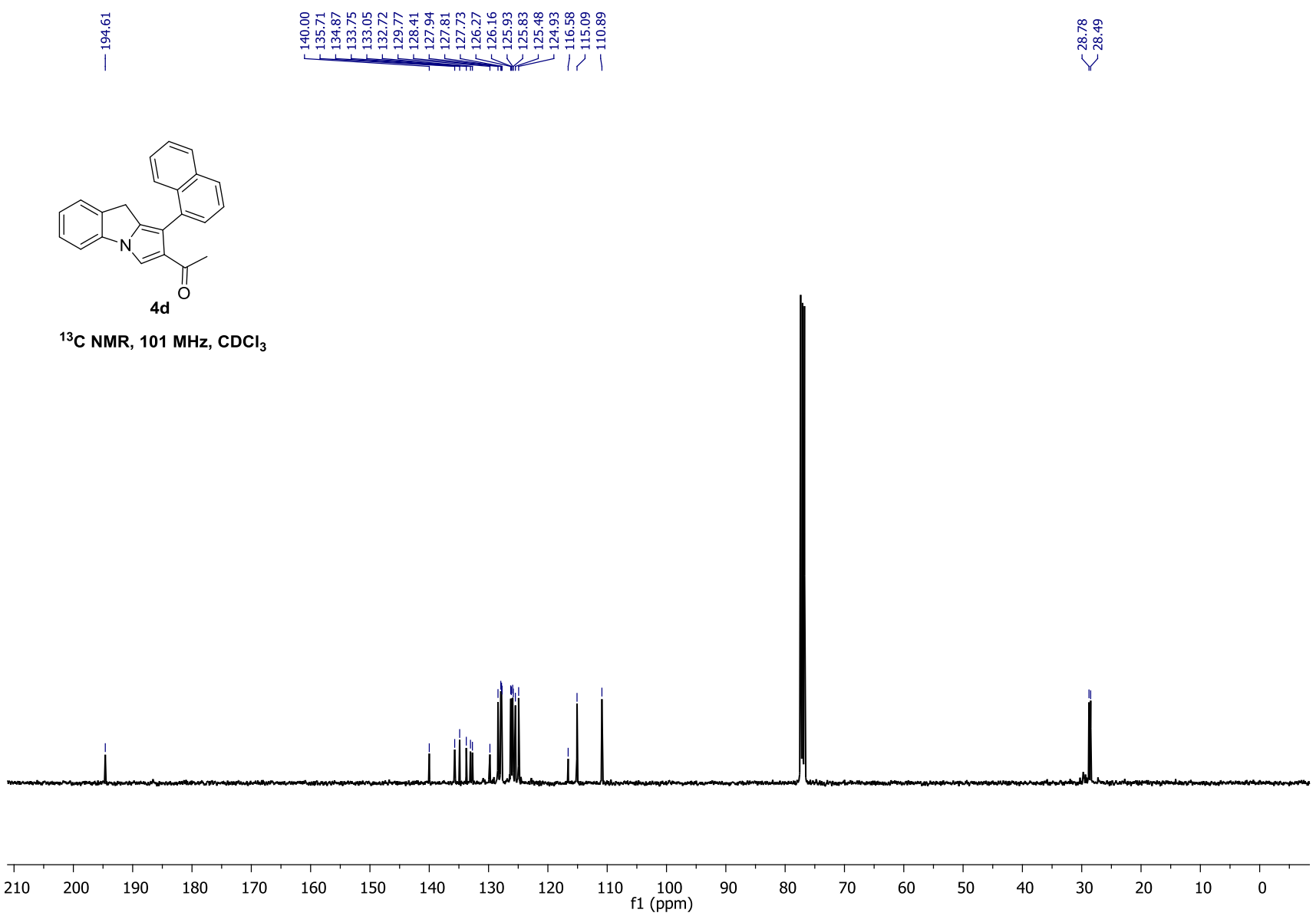

7.77
7.44
7.44
7.44
7.42
7.39
7.39
7.38
7.37
7.36
7.36
7.35
7.22
7.20
7.20
3.91
2.39
2.37
CH3
N
O
4b
1H NMR, 400 MHz, CDCl3
1.09
5.52
3.02
2.30
3.24
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

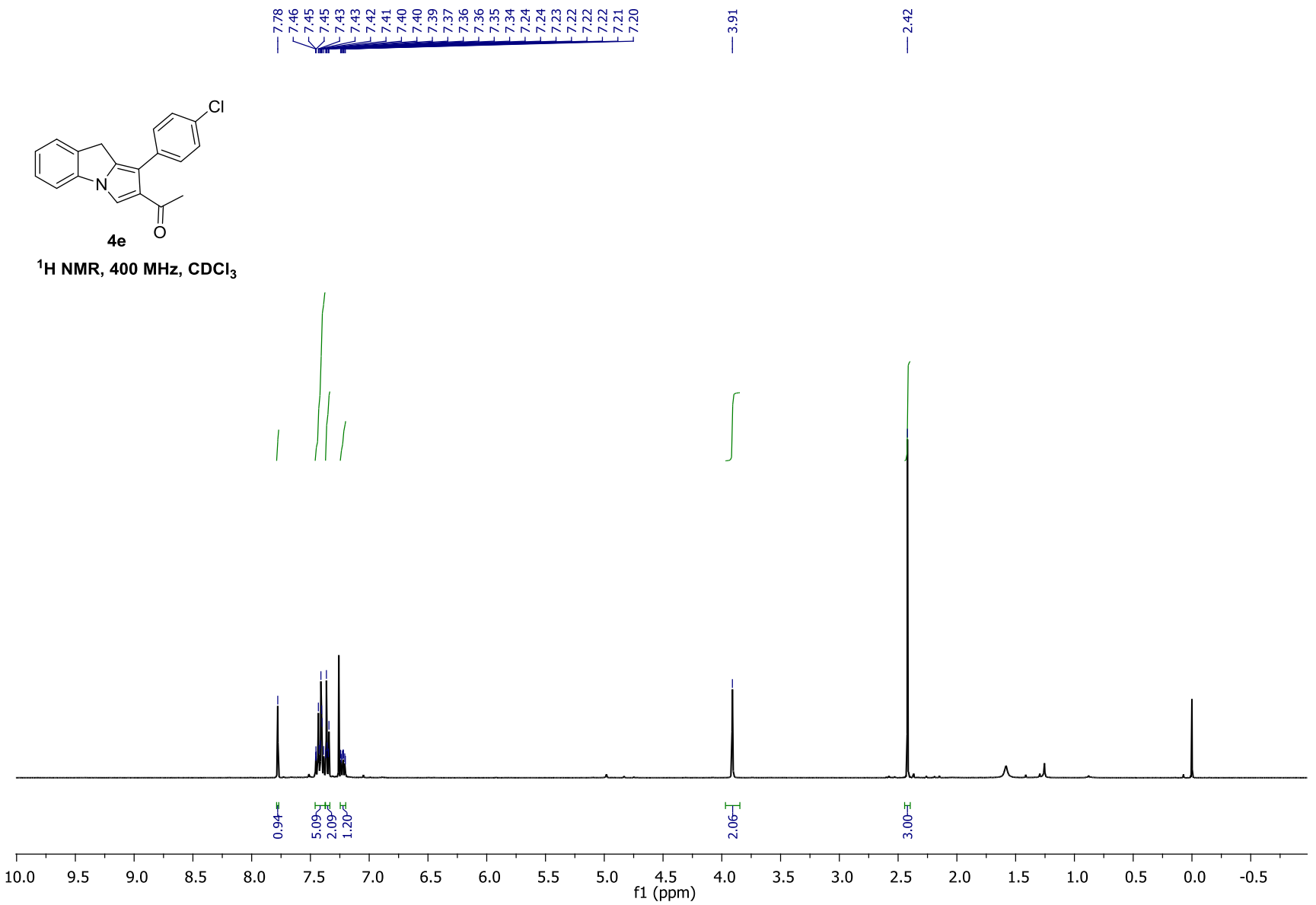

194.24
139.83
136.32
134.88
134.66
131.74
129.16
128.86
127.87
127.63
126.23
124.87
118.92
115.99
110.66
29.05
28.76
21.32
CH3
N
O
4b
13C NMR, 101 MHz, CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

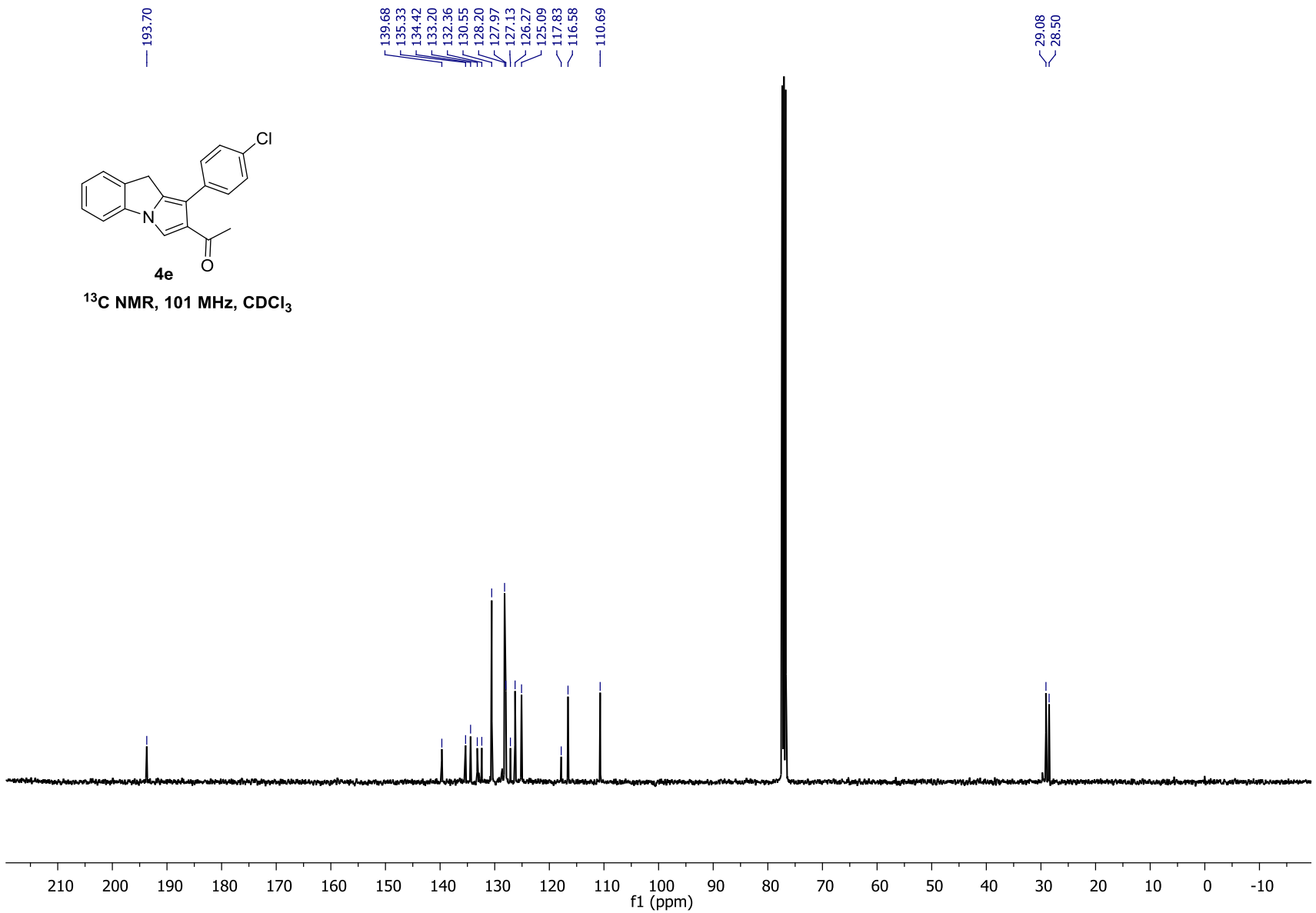

7.74
7.41
7.41
7.41
7.40
7.40
7.39
7.39
7.39
7.38
7.37
7.36
7.36
7.35
7.35
7.25
7.20
7.19
7.19
7.18
7.18
7.17
7.16
6.95
6.94
6.94
6.93
6.92
3.87
3.84
2.36
OCH3
N
O
4c
1H NMR, 400 MHz, CDCl3
1.00
4.93
1.07
2.08
2.03
2.77
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

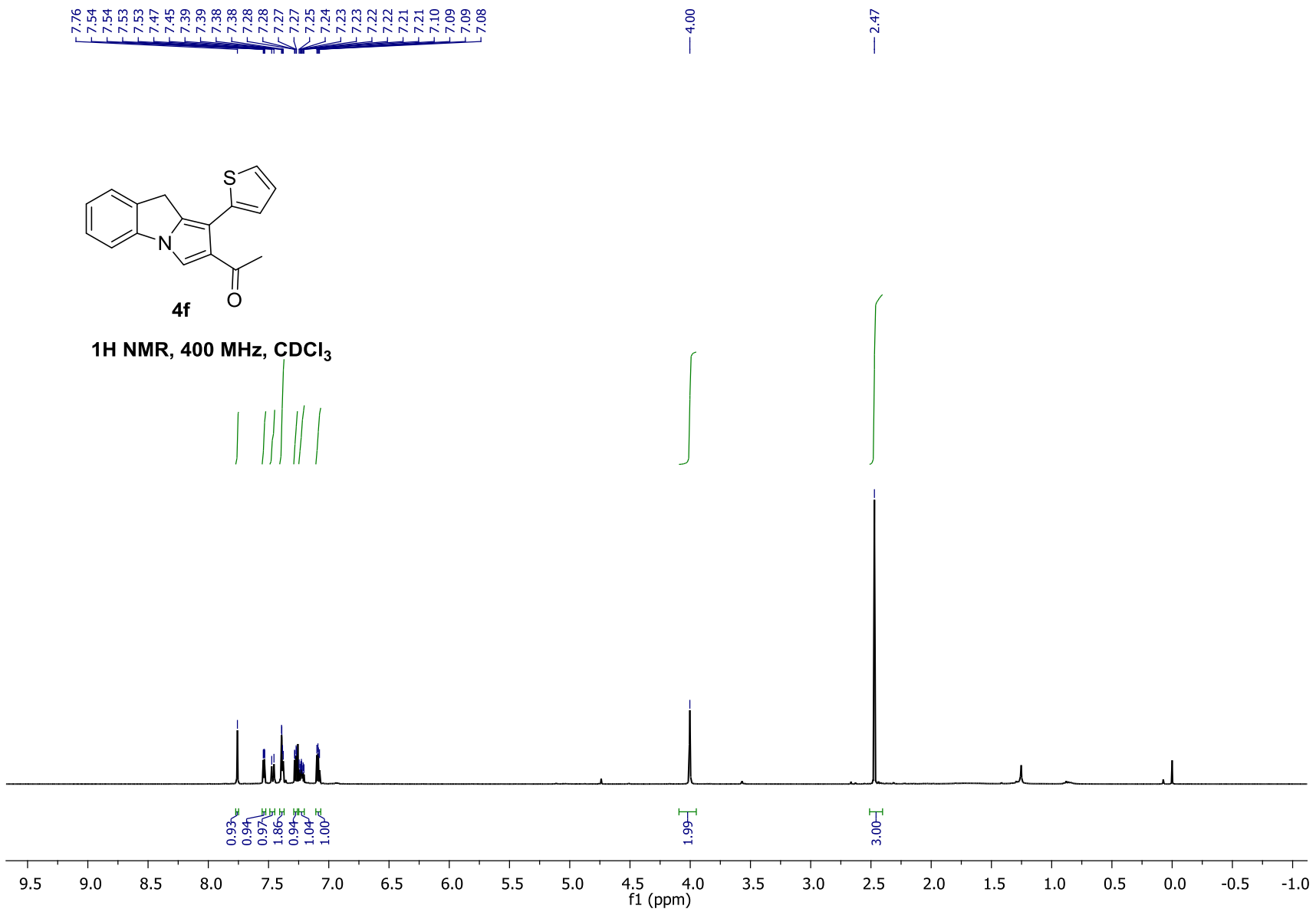

194.17
158.39
139.76
134.72
134.65
130.38
127.83
127.42
127.02
126.19
124.85
118.59
116.10
113.56
110.64
55.28
29.00
28.65
OCH3
N
O
4c
13C NMR, 75 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

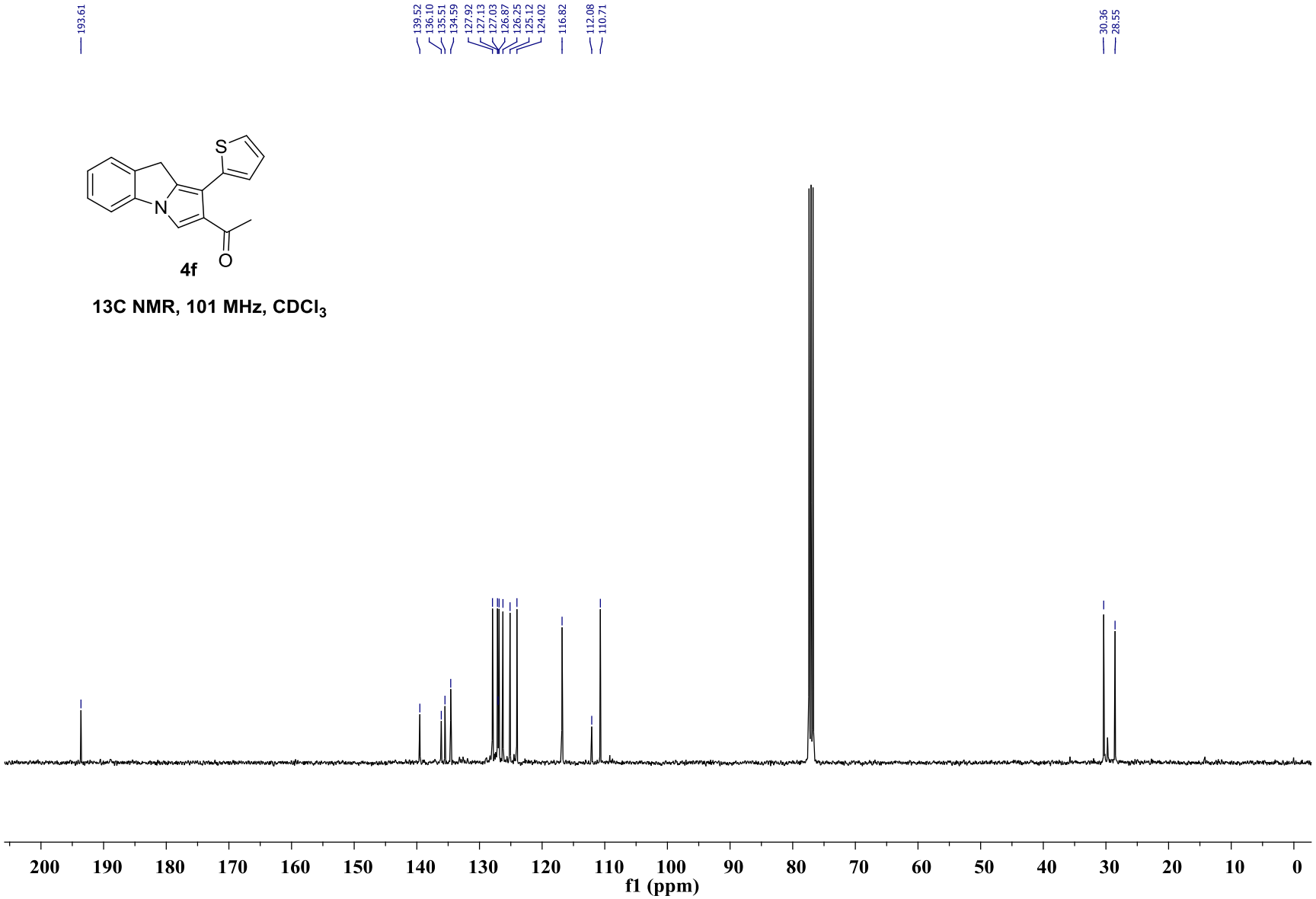

7.94
7.90
7.89
7.87
7.77
7.75
7.55
7.53
7.52
7.51
7.51
7.50
7.49
7.48
7.48
7.48
7.47
7.47
7.47
7.46
7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.38
7.37
7.22
7.22
7.20
7.20
7.19
7.19
3.78
3.74
3.66
3.61
2.02
N
O
4d
1H NMR, 500 MHz, CDCl3
0.86
1.95
0.98
4.08
2.99
1.04
2.16
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


194.61
140.00
135.71
134.87
133.75
133.05
132.72
129.77
128.41
127.94
127.81
127.73
126.27
126.16
125.93
125.83
125.48
124.93
116.58
115.09
110.89
28.78
28.49
N
O
4d
^{13}C NMR, 101 MHz, CDCl$_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

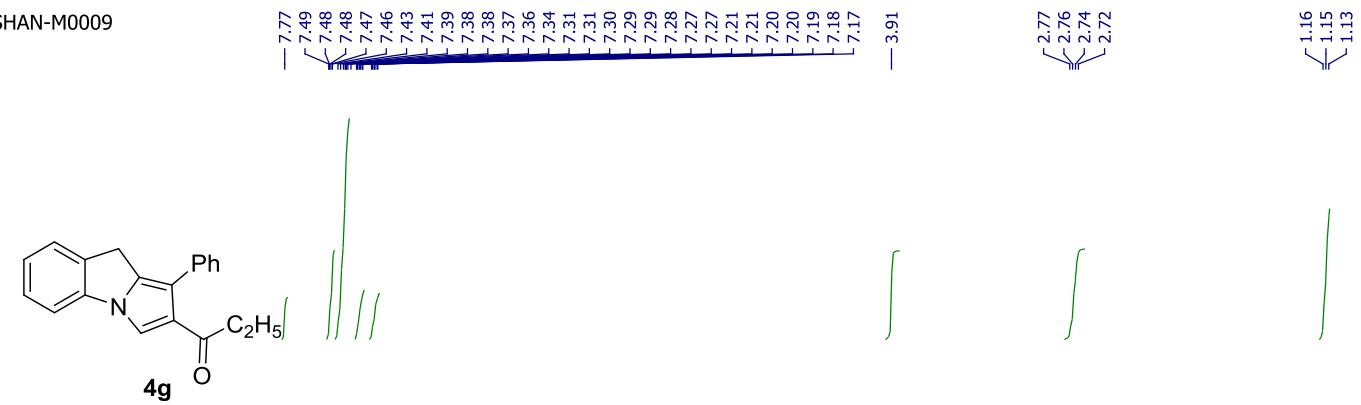

7.78
7.46
7.45
7.45
7.43
7.43
7.42
7.41
7.40
7.40
7.39
7.37
7.36
7.36
7.35
7.34
7.24
7.24
7.23
7.22
7.22
7.22
7.21
7.20
3.91
2.42
Cl
N
O
4e
^{1}H NMR, 400 MHz, CDCl$_3$
0.94
5.09
2.09
1.20
2.06
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


193.70
139.68
135.33
134.42
133.20
132.36
130.55
128.20
127.97
127.13
126.27
125.09
117.83
116.58
110.69
29.08
28.50
Cl
N
O
4e
13C NMR, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.76
7.54
7.54
7.53
7.53
7.47
7.45
7.39
7.39
7.38
7.38
7.28
7.28
7.27
7.27
7.25
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.10
7.09
7.09
7.08
4.00
2.47
S
N
O
4f
1H NMR, 400 MHz, CDCl3
0.93
0.94
0.97
1.86
0.94
1.04
1.00
1.99
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

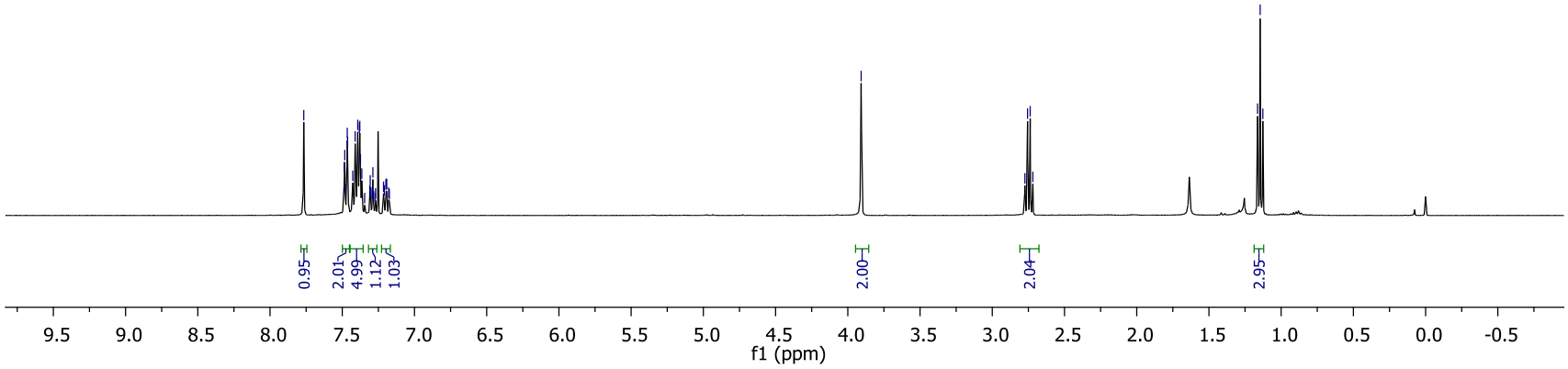

193.61
139.52
136.10
135.51
134.59
127.92
127.13
127.03
126.87
126.25
125.12
124.02
116.82
112.08
110.71
30.36
28.55
S
N
O
4f
13C NMR, 101 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

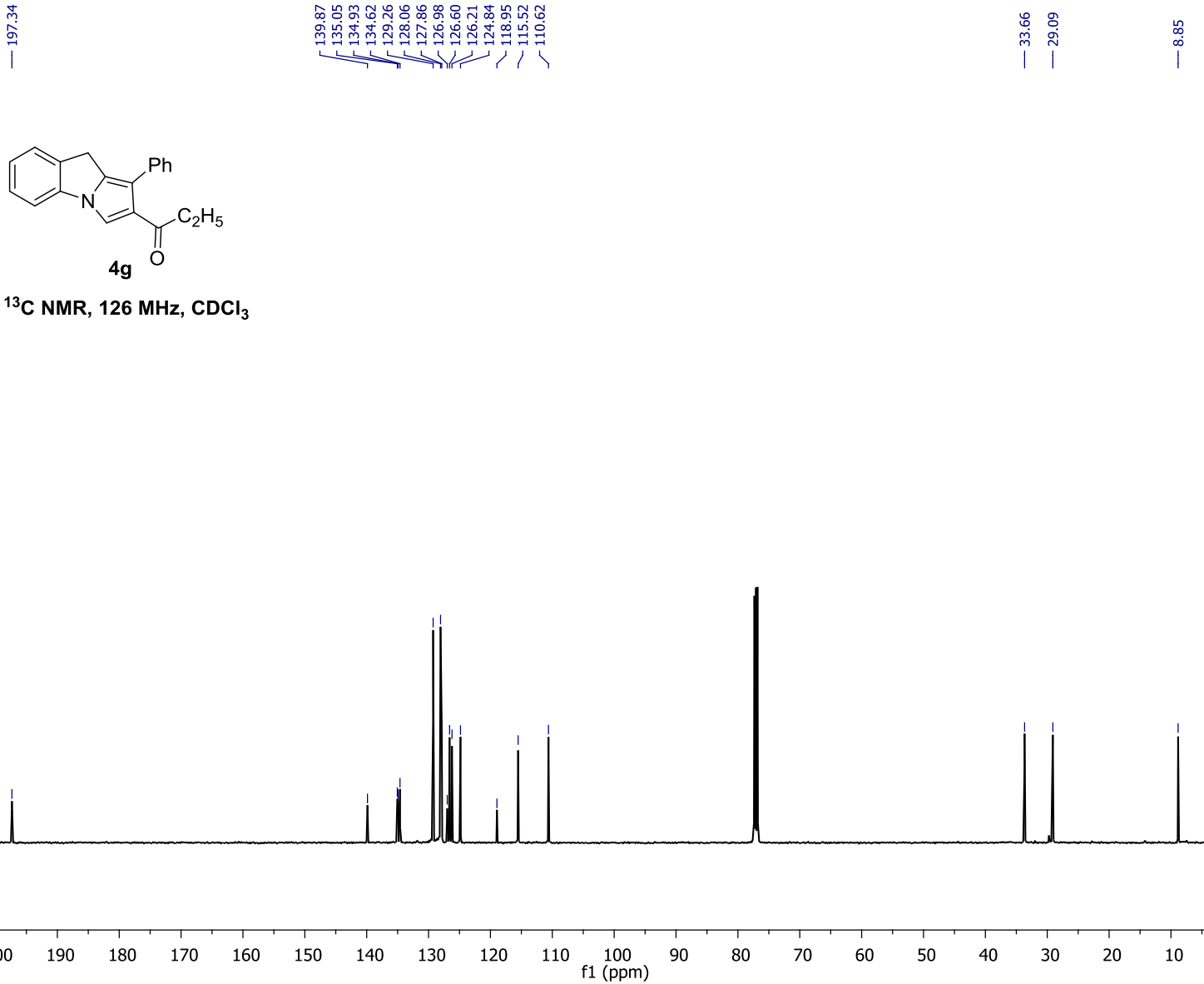
ROSHAN-M0009



4g

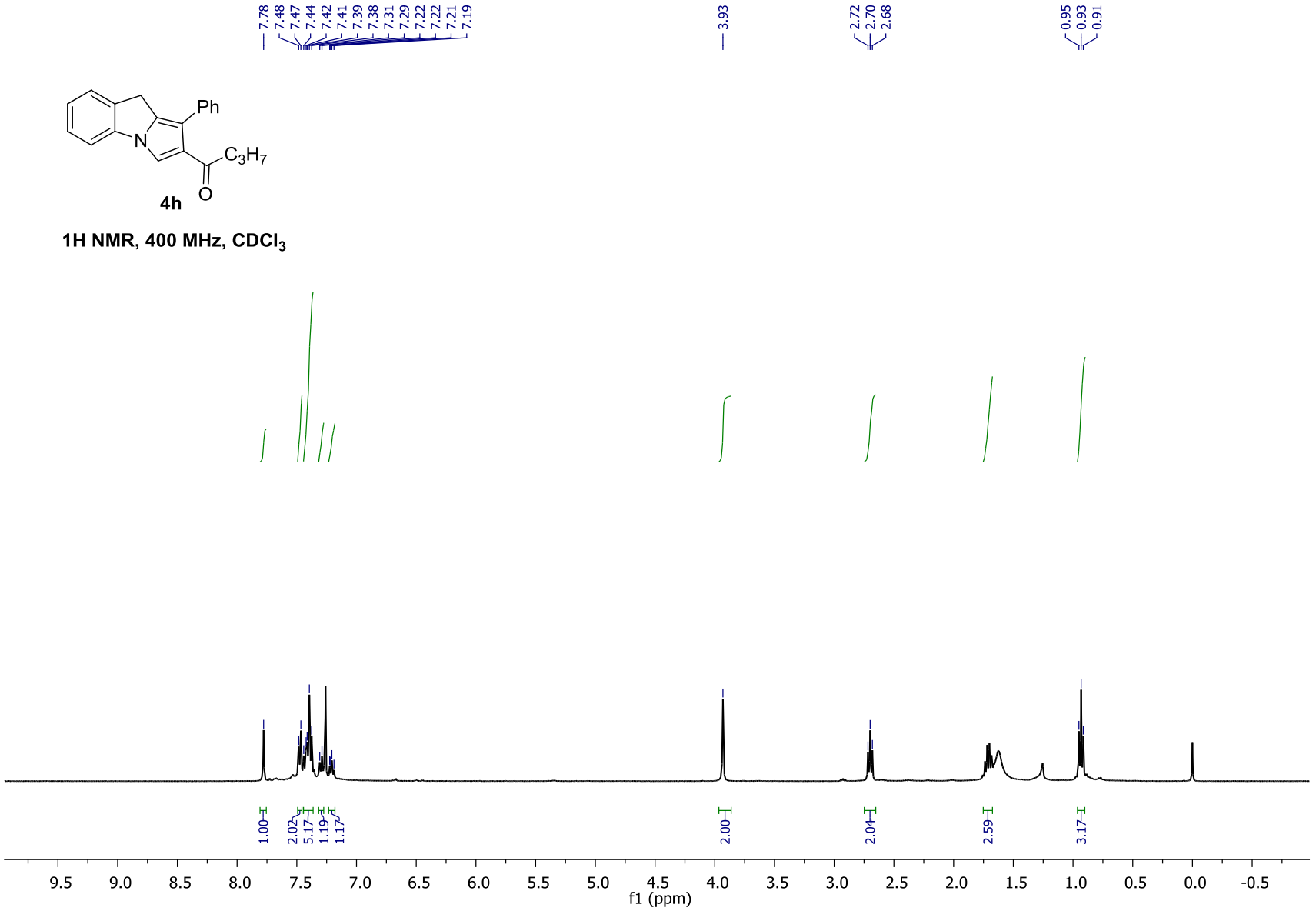
^{1}H NMR, 400 MHz, $CDCl_3$





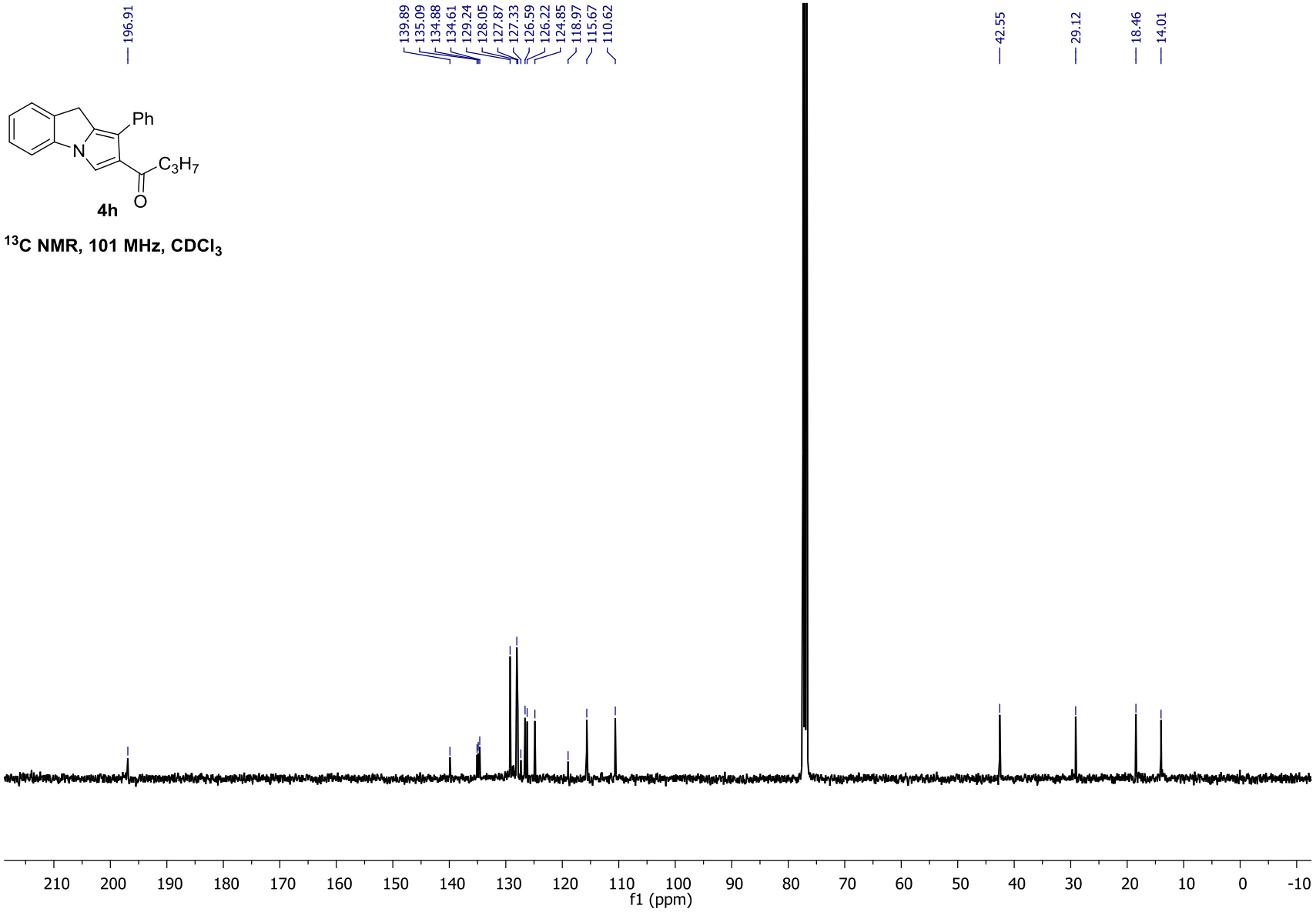
4g

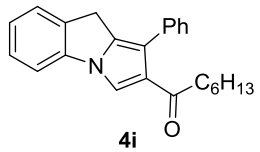
^{13}C NMR, 126 MHz, $CDCl_3$



4h

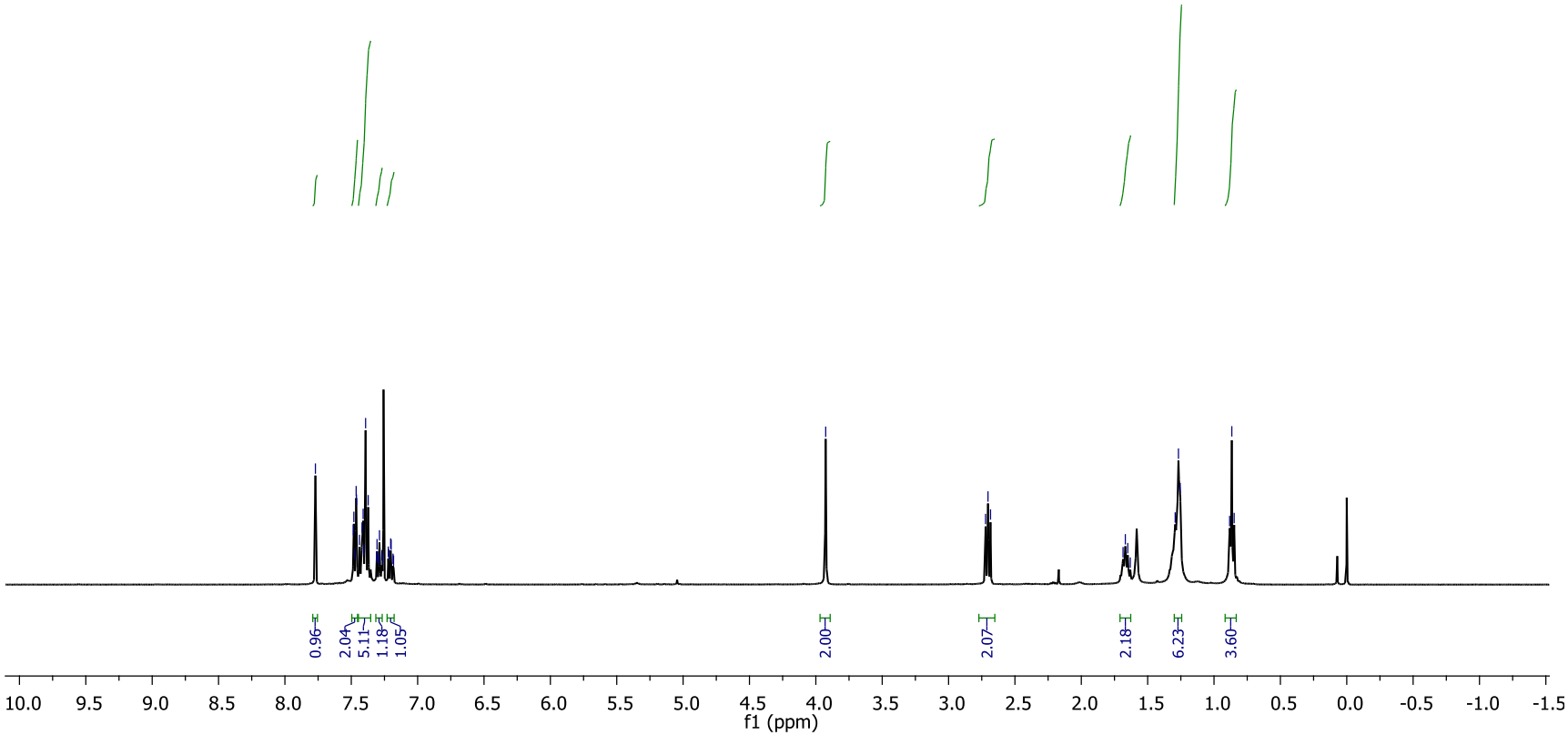
1H NMR, 400 MHz, $CDCl_3$

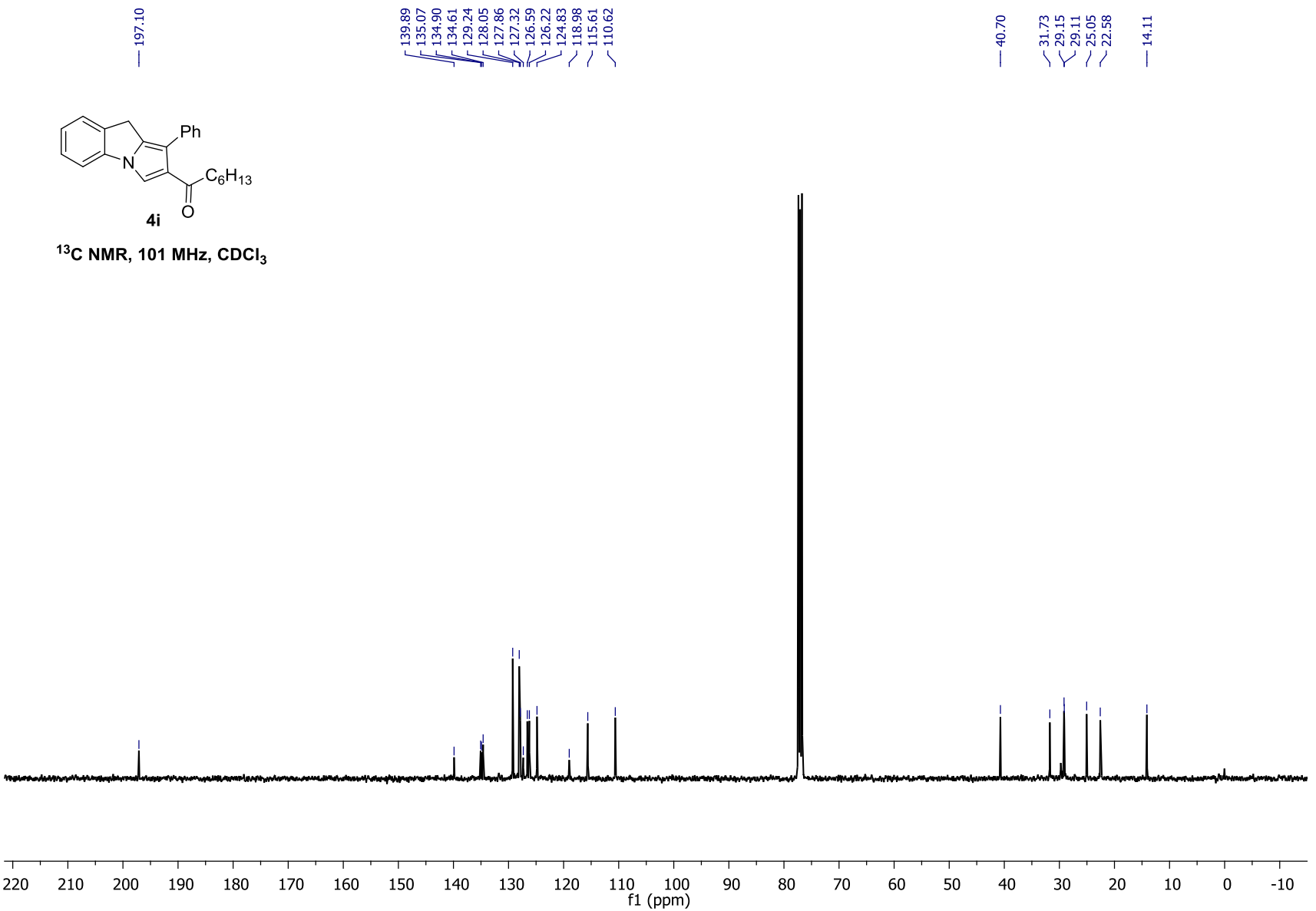

196.91
139.89
135.09
134.88
134.61
129.24
128.05
127.87
127.33
126.59
126.22
124.85
118.97
115.67
110.62
42.55
29.12
18.46
14.01
Ph
N
C3H7
O
4h
13C NMR, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

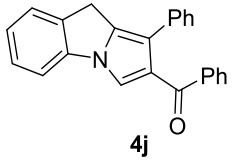


4i

^{1}H NMR, 400 MHz, $CDCl_3$

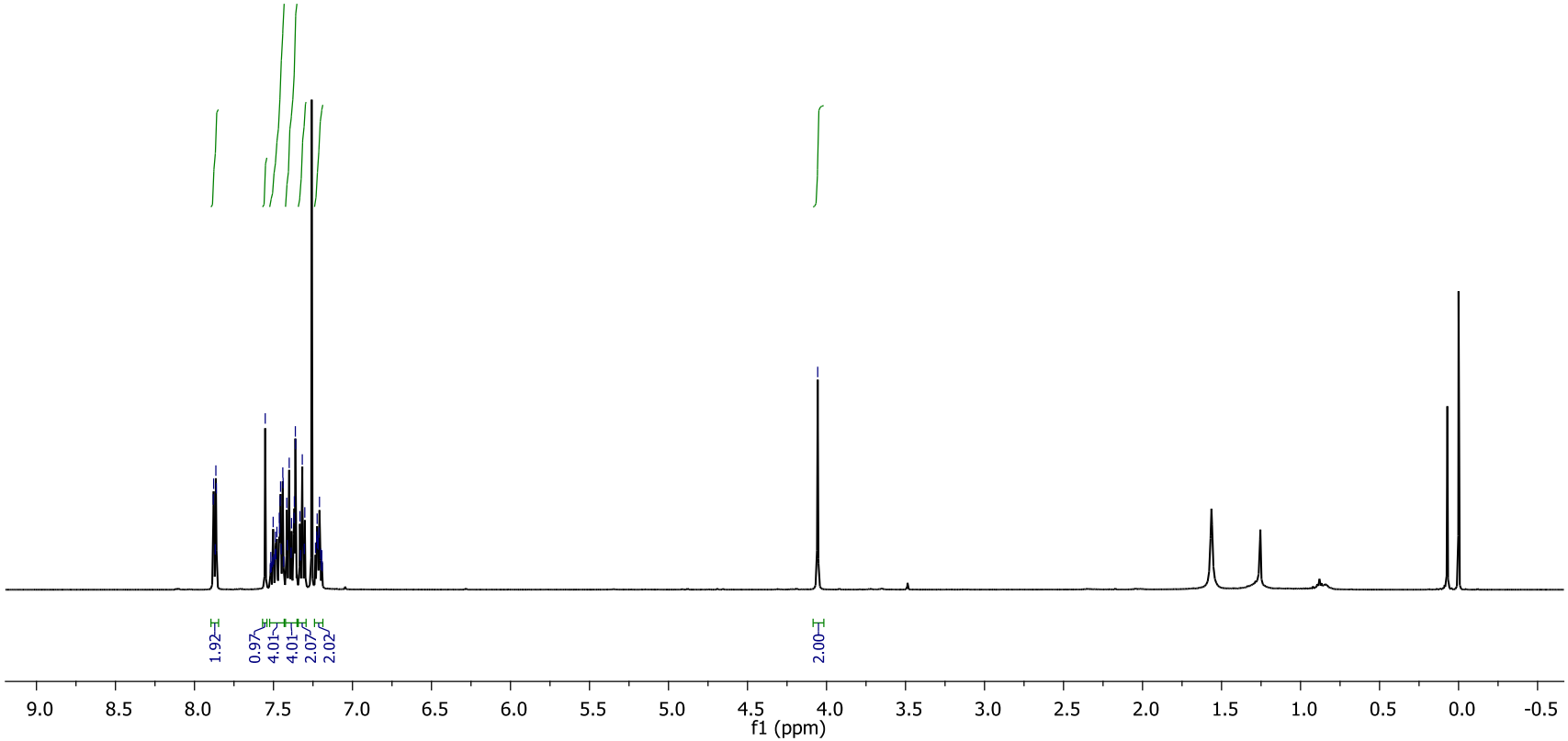


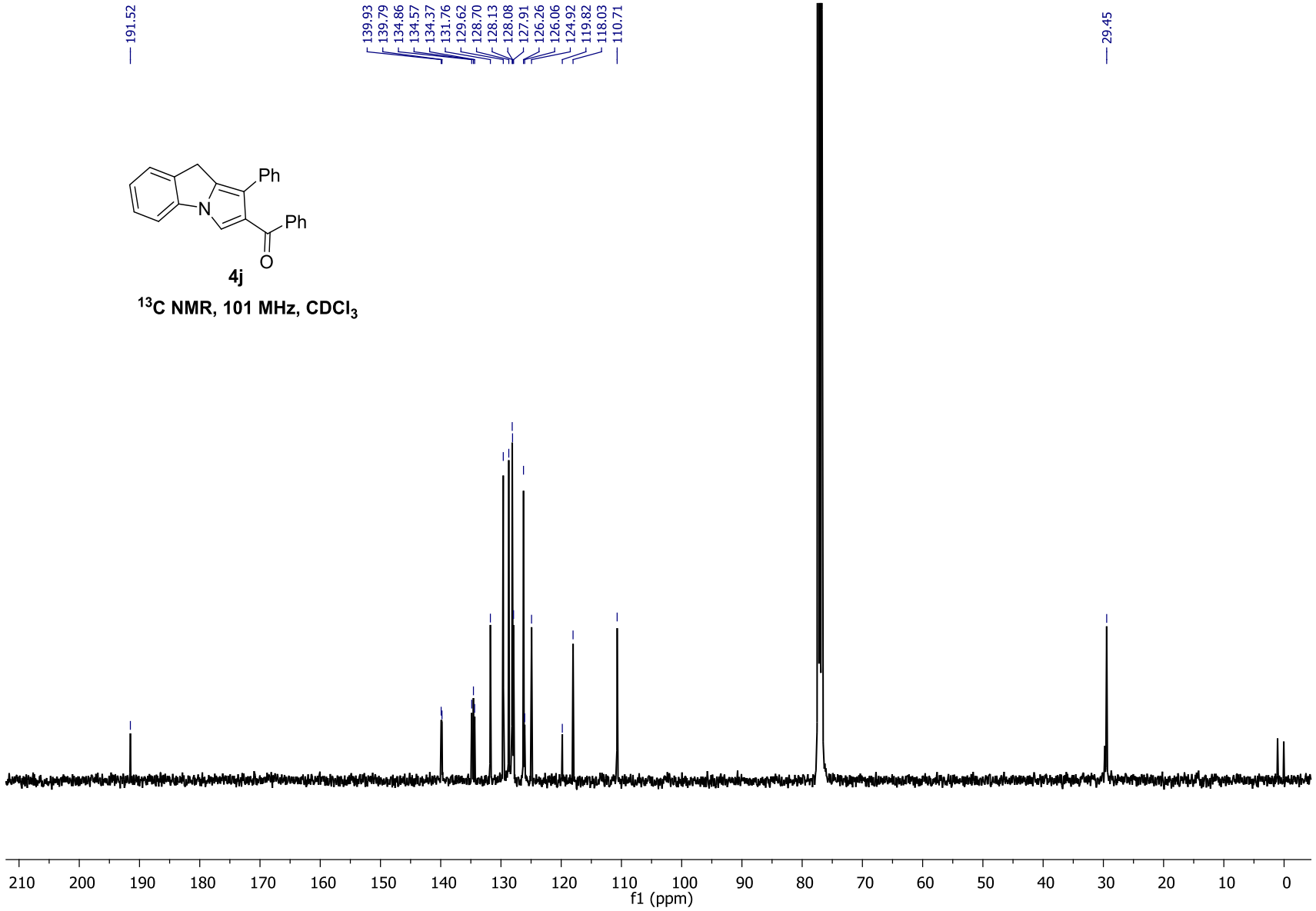

197.10
139.89
135.07
134.90
134.61
129.24
128.05
127.86
127.32
126.59
126.22
124.83
118.98
115.61
110.62
40.70
31.73
29.15
29.11
25.05
22.58
14.11
Ph
N
C6H13
O
4i
13C NMR, 101 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

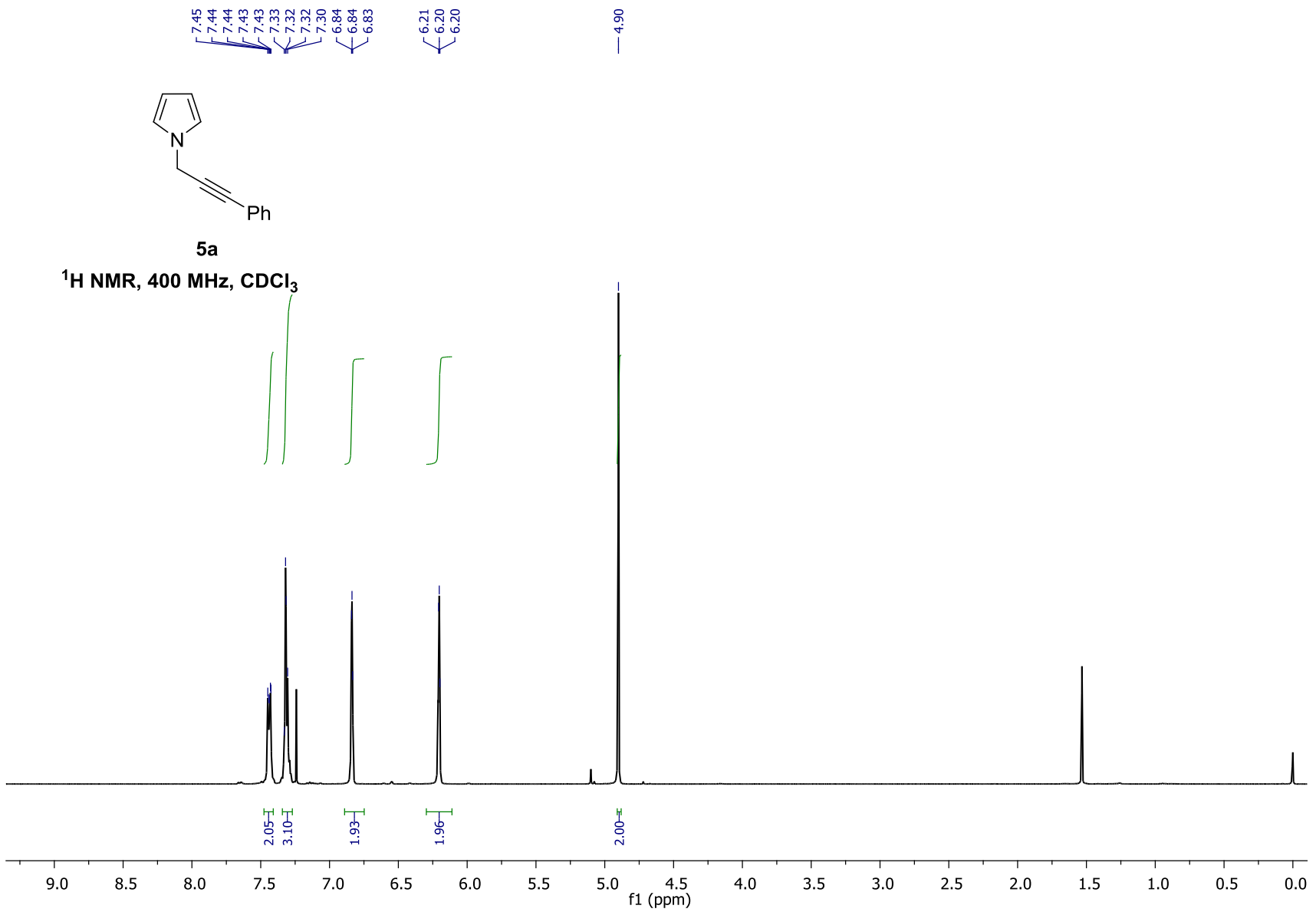


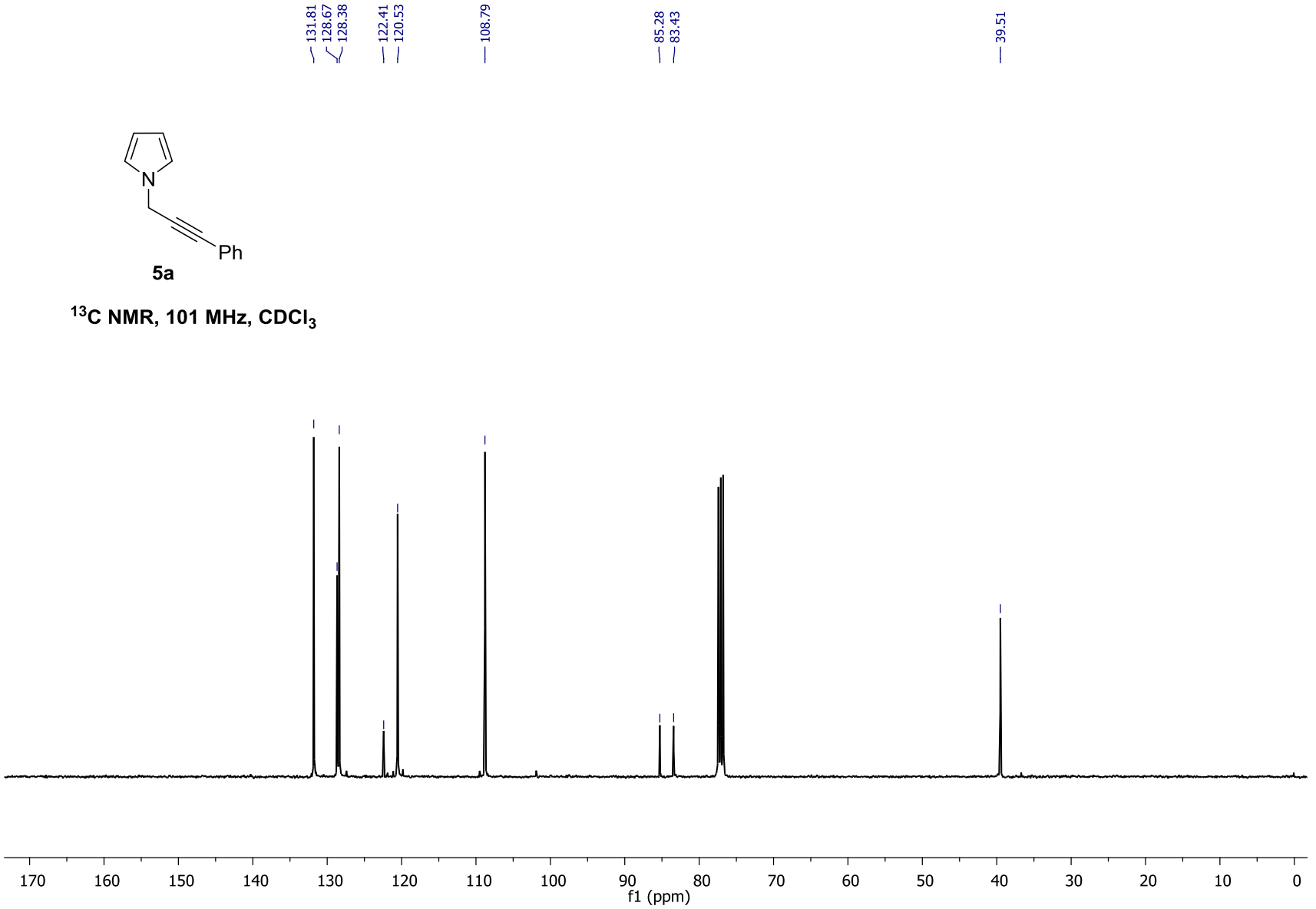
4j

^{1}H NMR, 500 MHz, $CDCl_3$



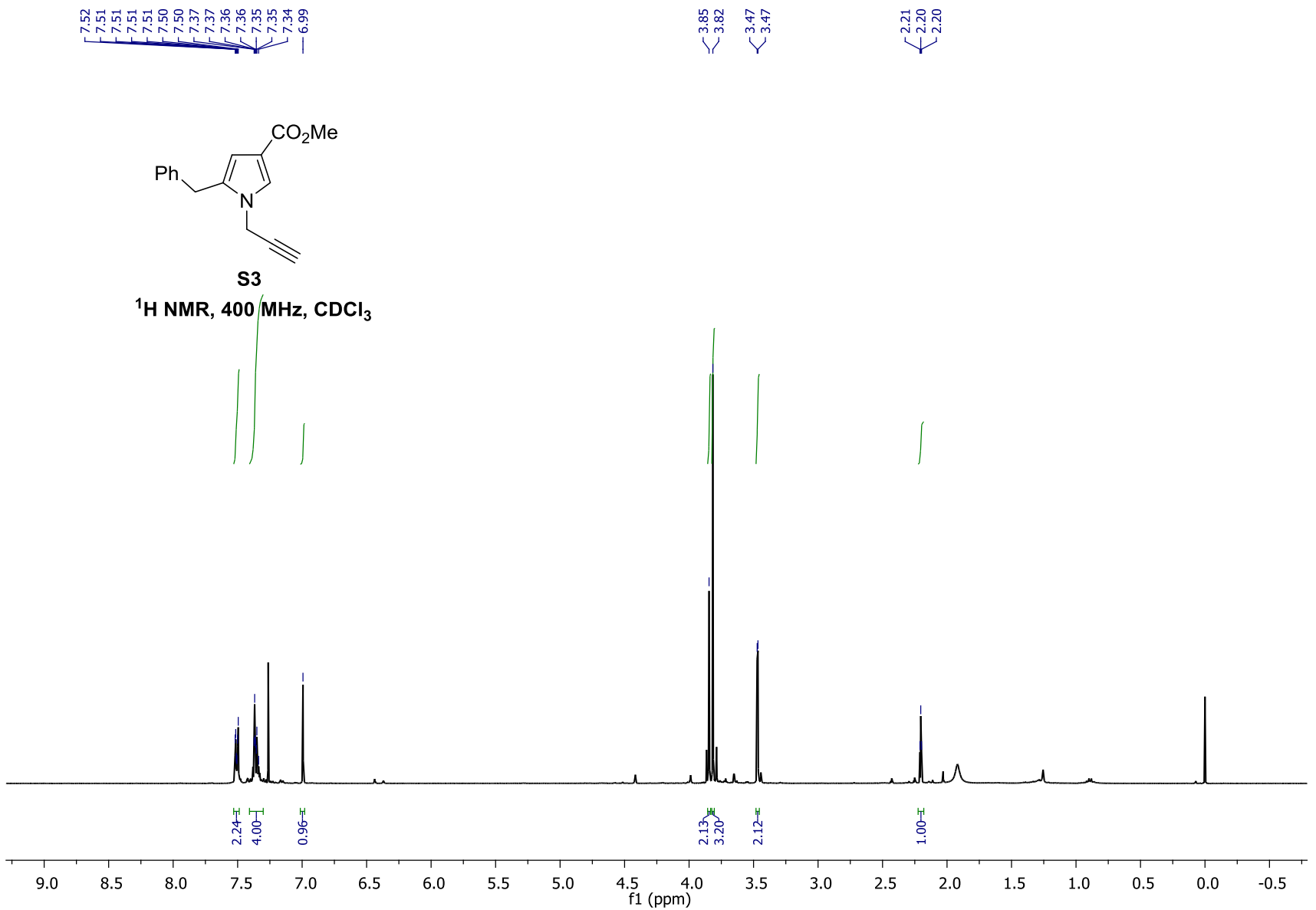

191.52
139.93
139.79
134.86
134.57
134.37
131.76
129.62
128.70
128.13
128.08
127.91
126.26
126.06
124.92
119.82
118.03
110.71
29.45
Ph
Ph
N
O
4j
13C NMR, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.45
7.44
7.44
7.43
7.43
7.33
7.32
7.32
7.30
6.84
6.84
6.83
6.21
6.20
6.20
4.90
N
Ph
5a
1H NMR, 400 MHz, CDCl3
2.05
3.10
1.93
1.96
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



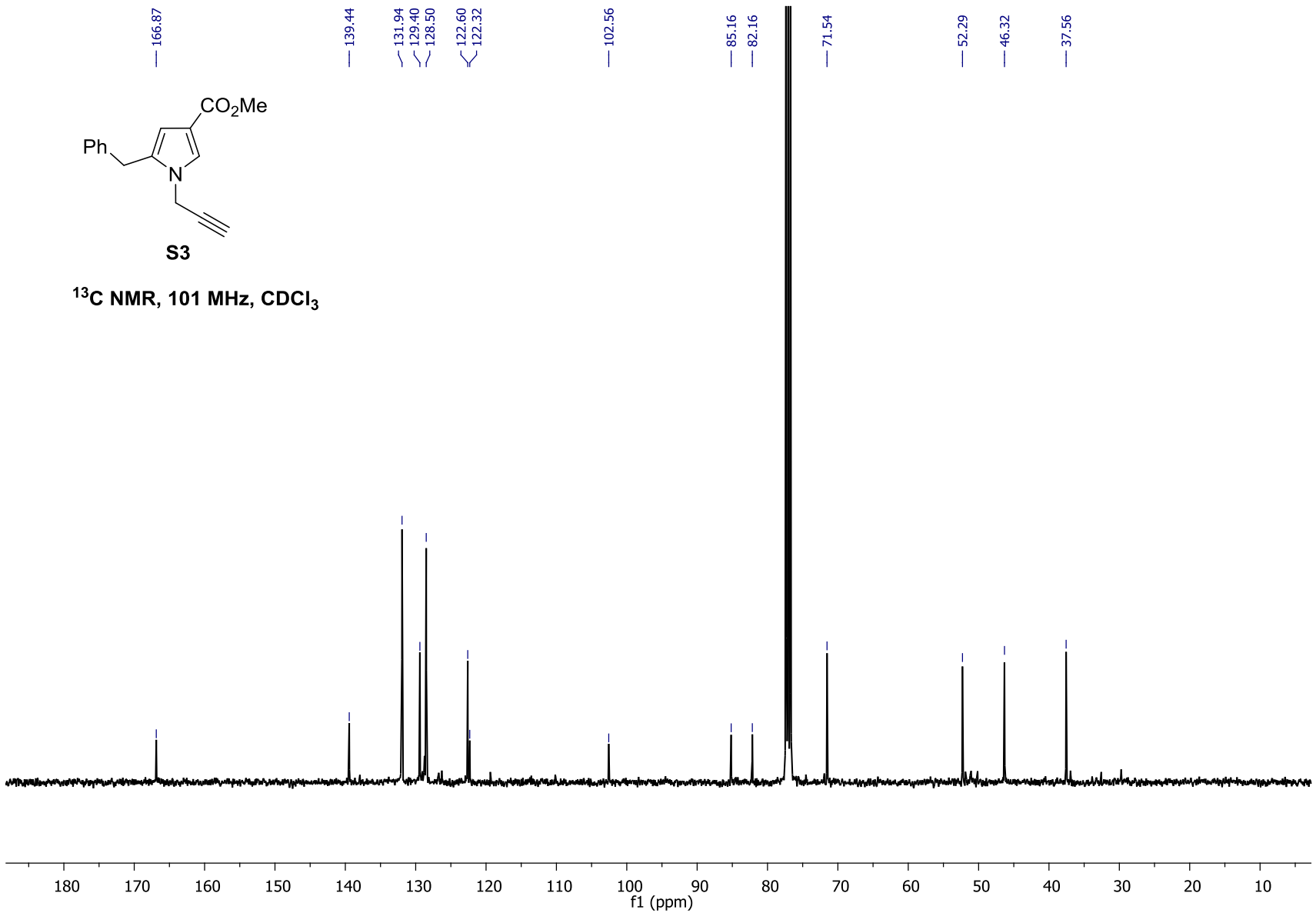
5a

^{13}C NMR, 101 MHz, $CDCl_3$



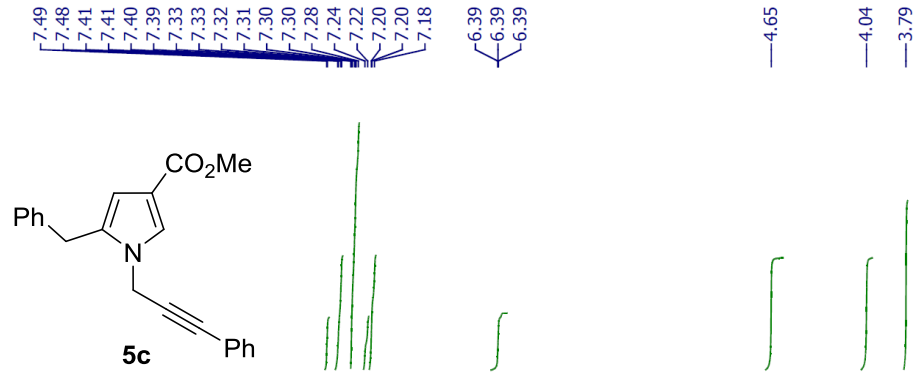
S3

^{1}H NMR, 400 MHz, $CDCl_3$

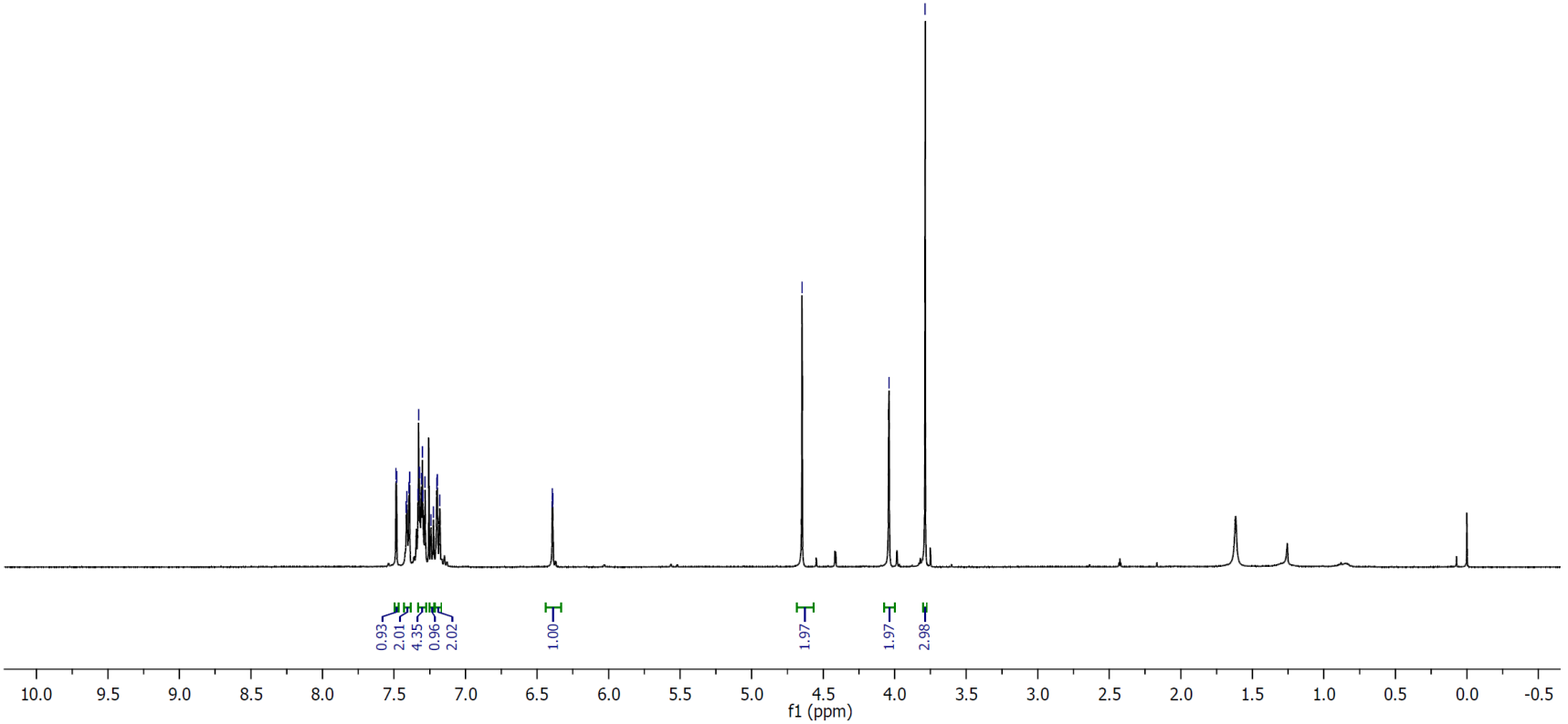


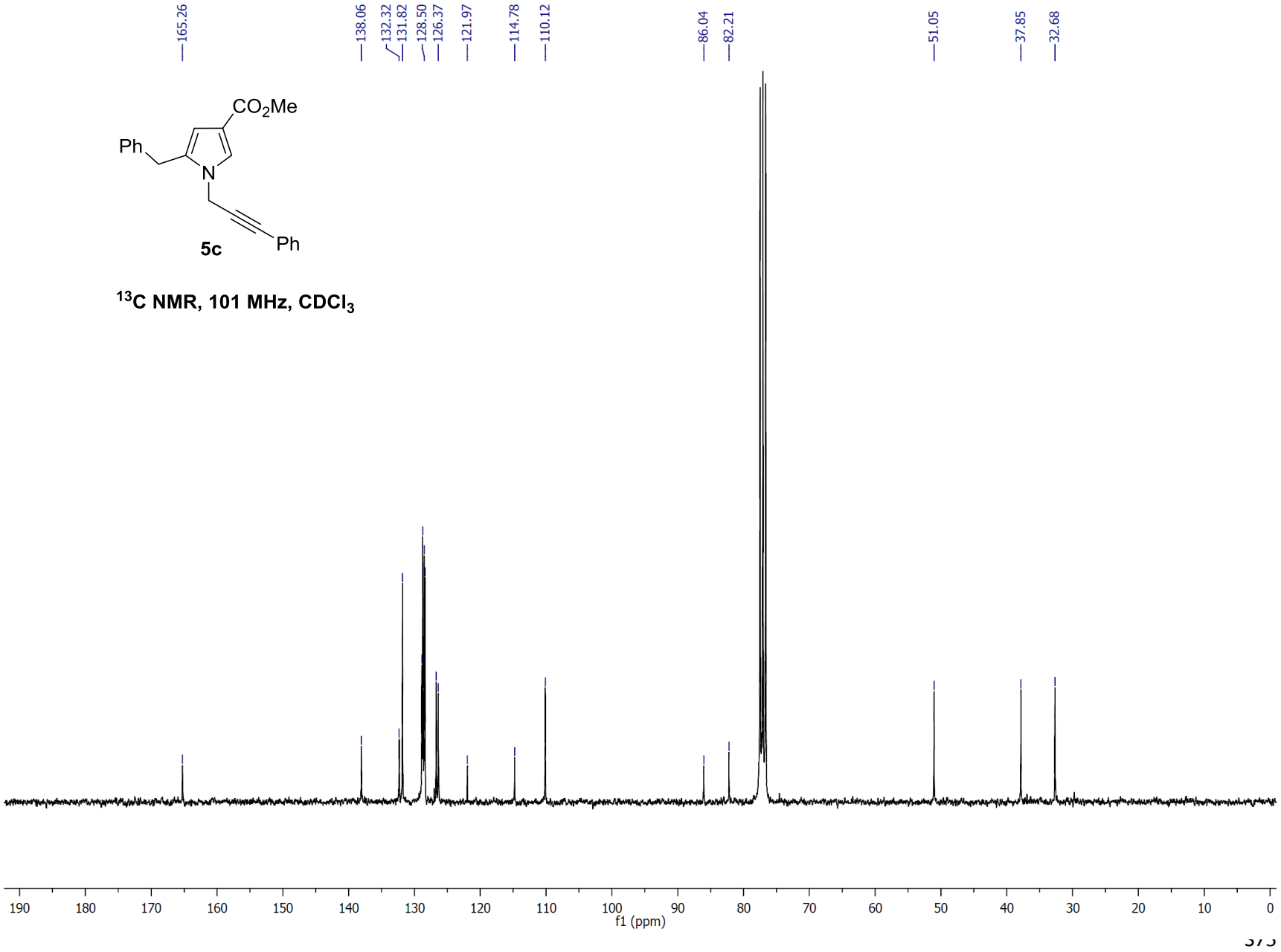
S3

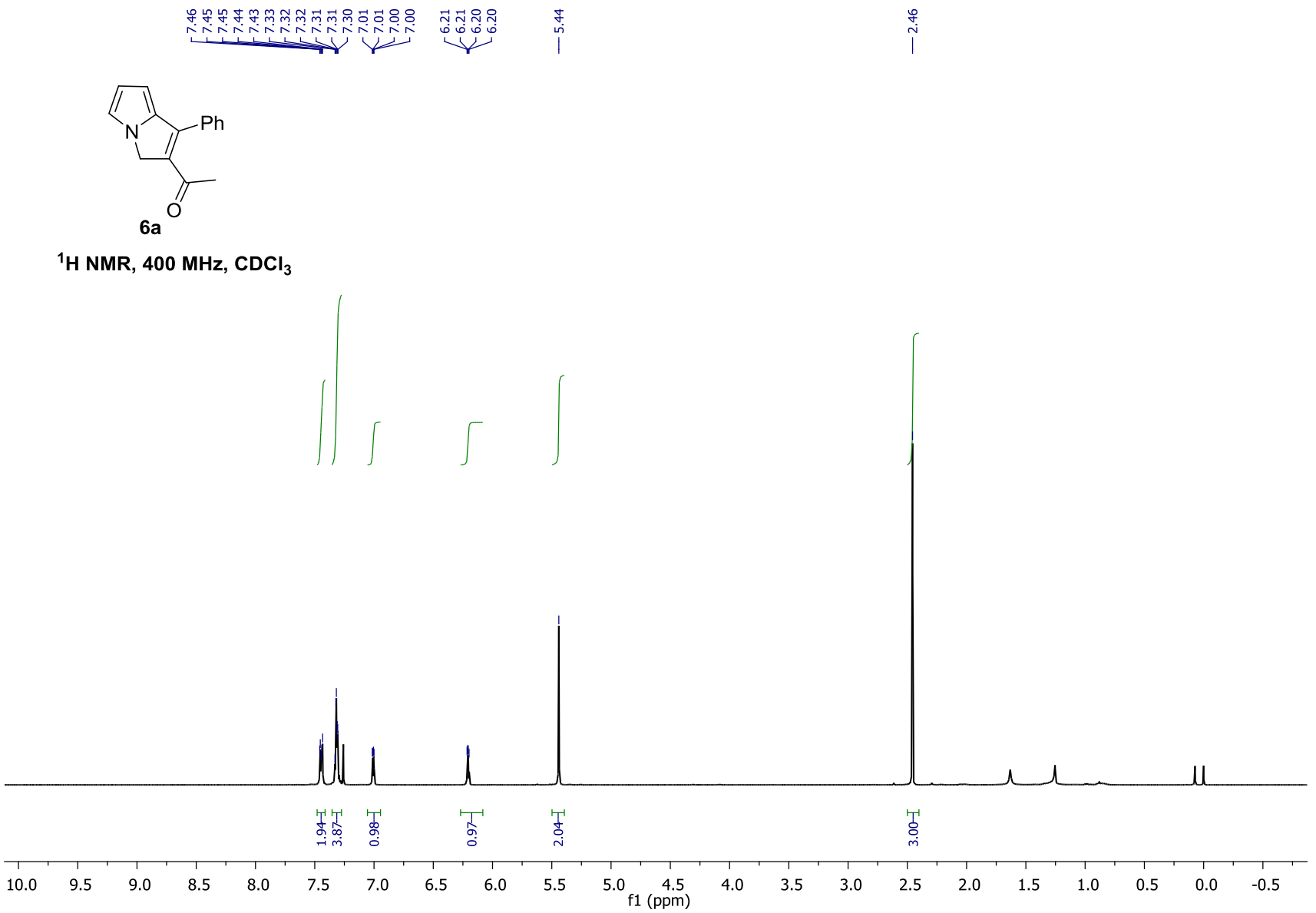
^{13}C NMR, 101 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$

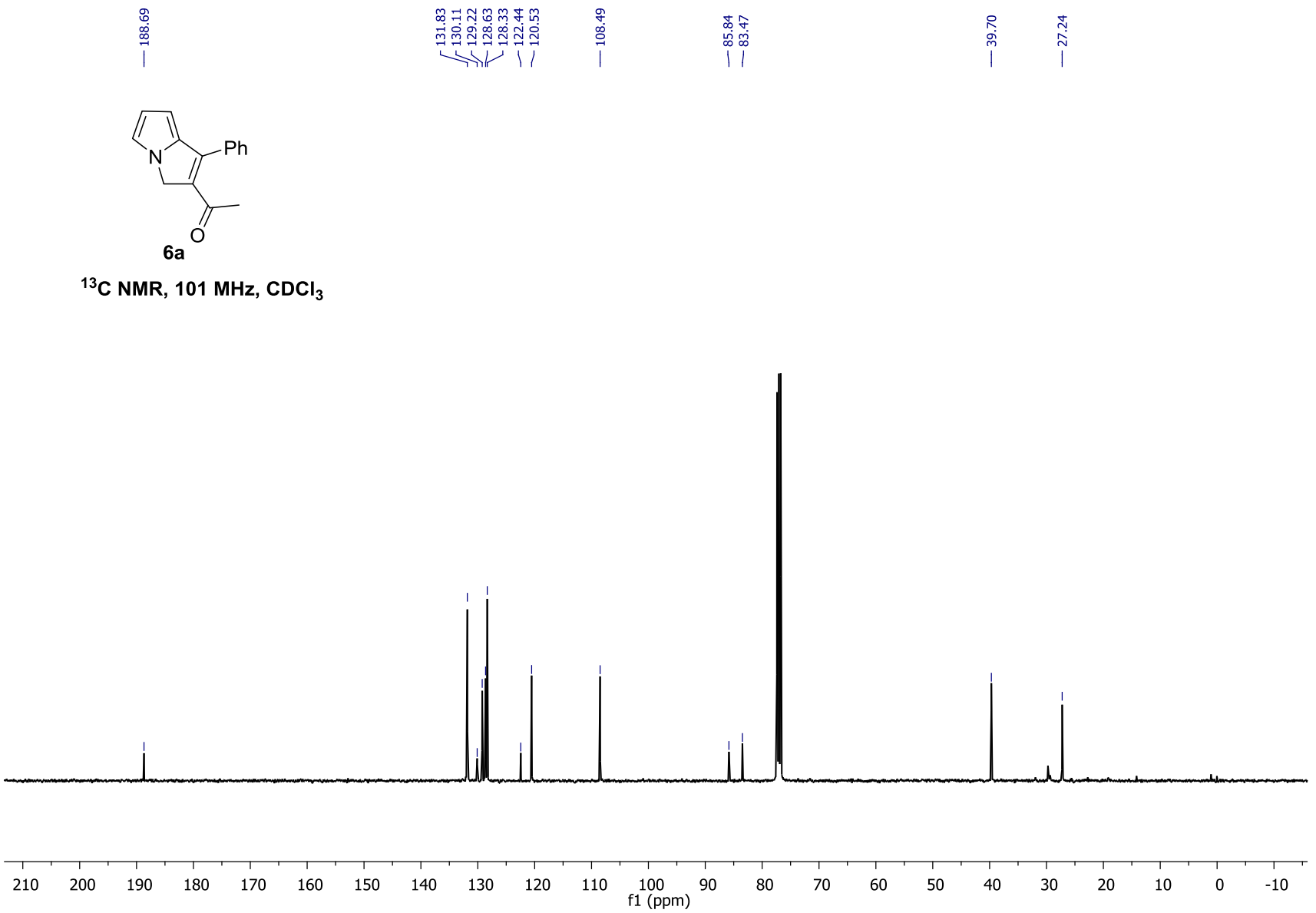


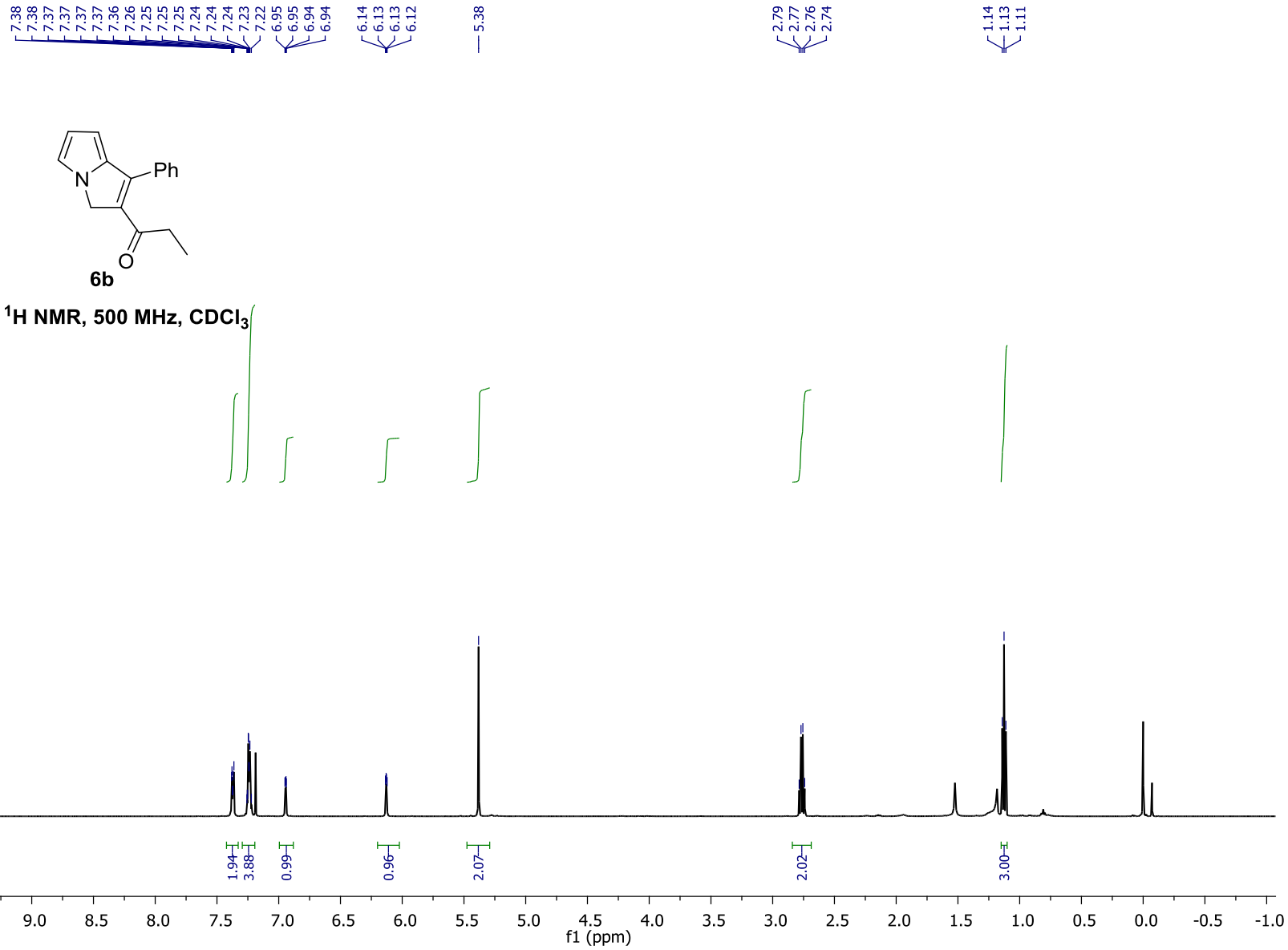

165.26
138.06
132.32
131.82
128.50
126.37
121.97
114.78
110.12
86.04
82.21
51.05
37.85
32.68
CO2Me
Ph
N
Ph
5c
13C NMR, 101 MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

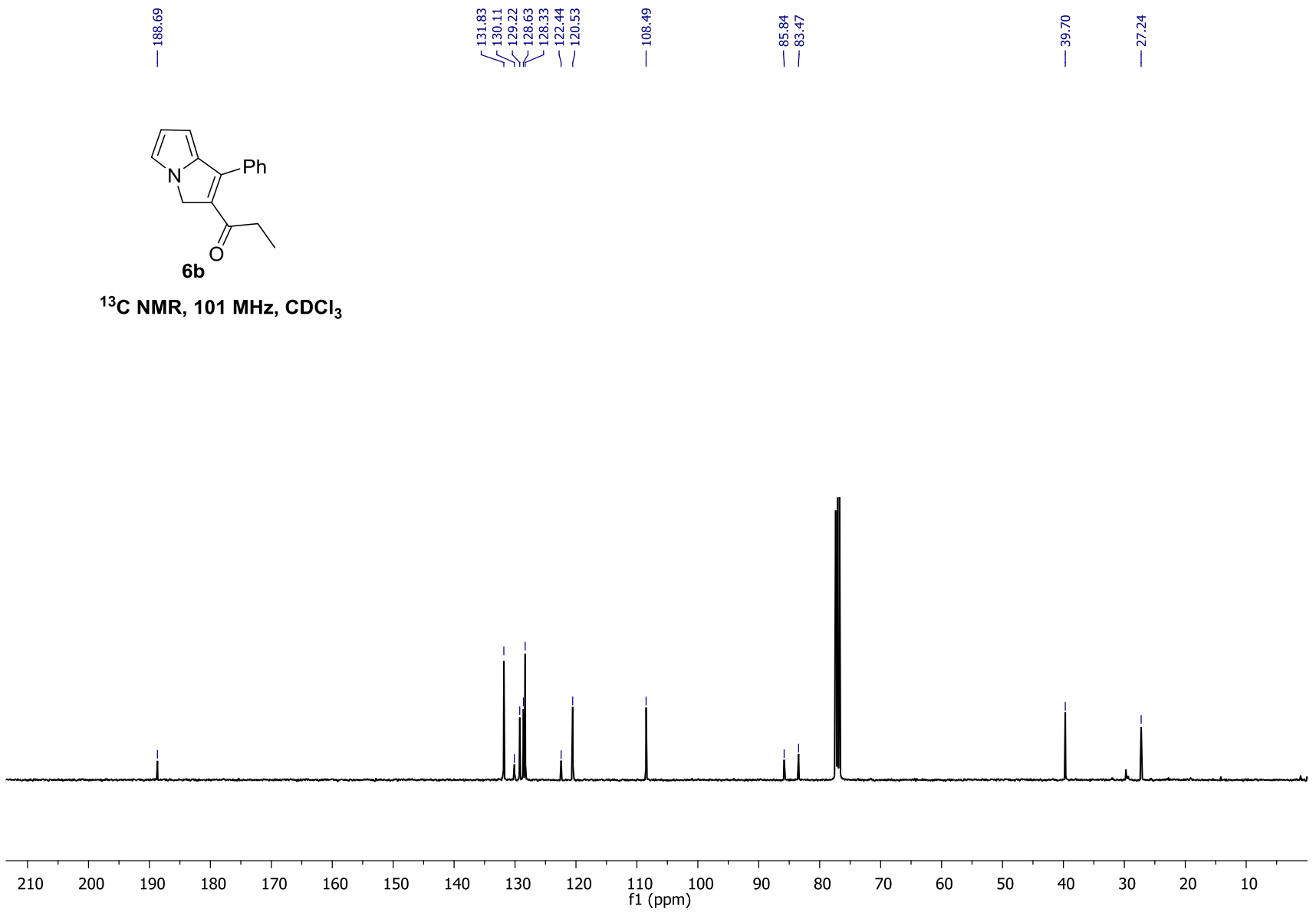


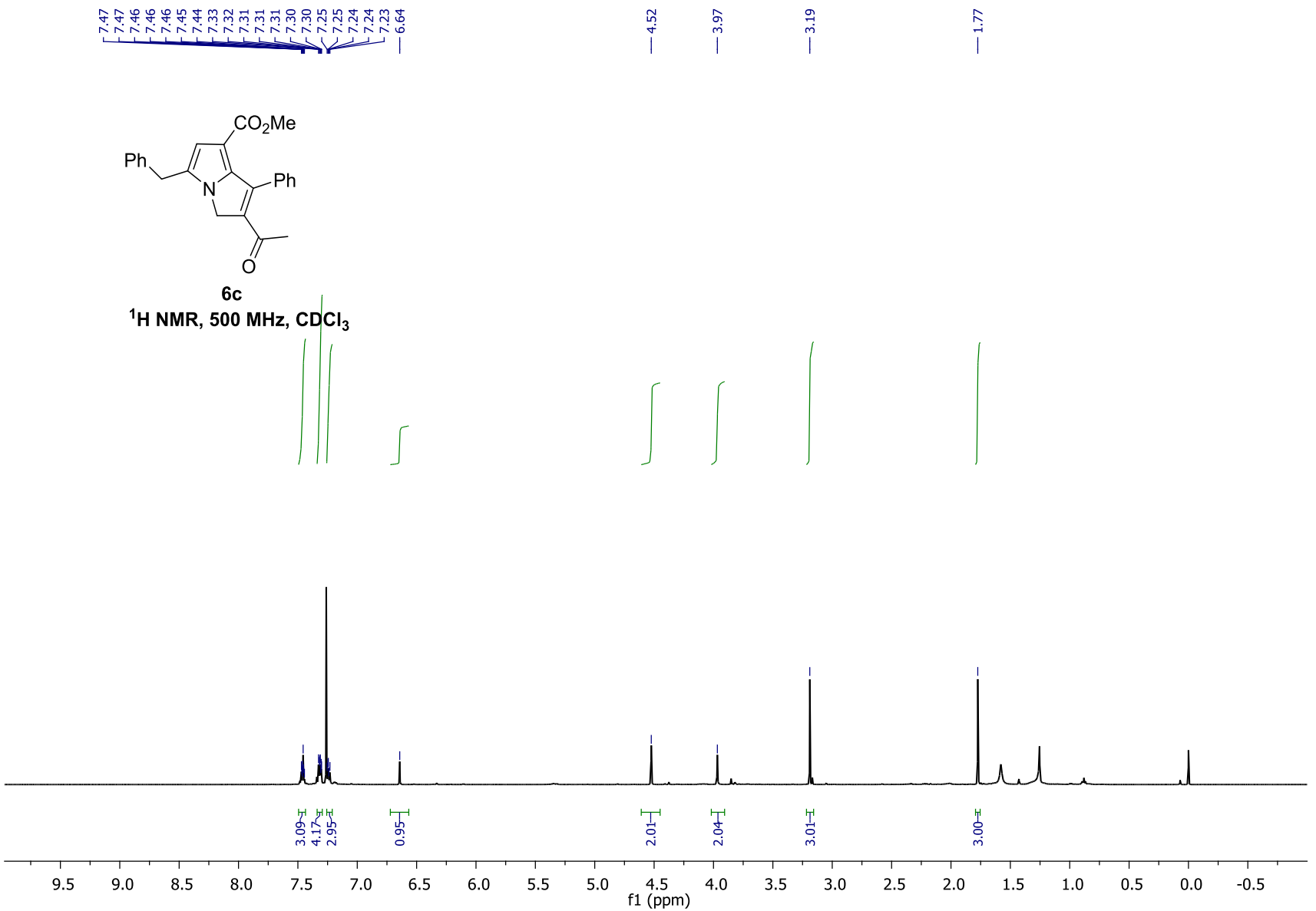
6a

^{1}H NMR, 400 MHz, $CDCl_3$


188.69
131.83
130.11
129.22
128.63
128.33
122.44
120.53
108.49
85.84
83.47
39.70
27.24
N
Ph
O
6a
13C NMR, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

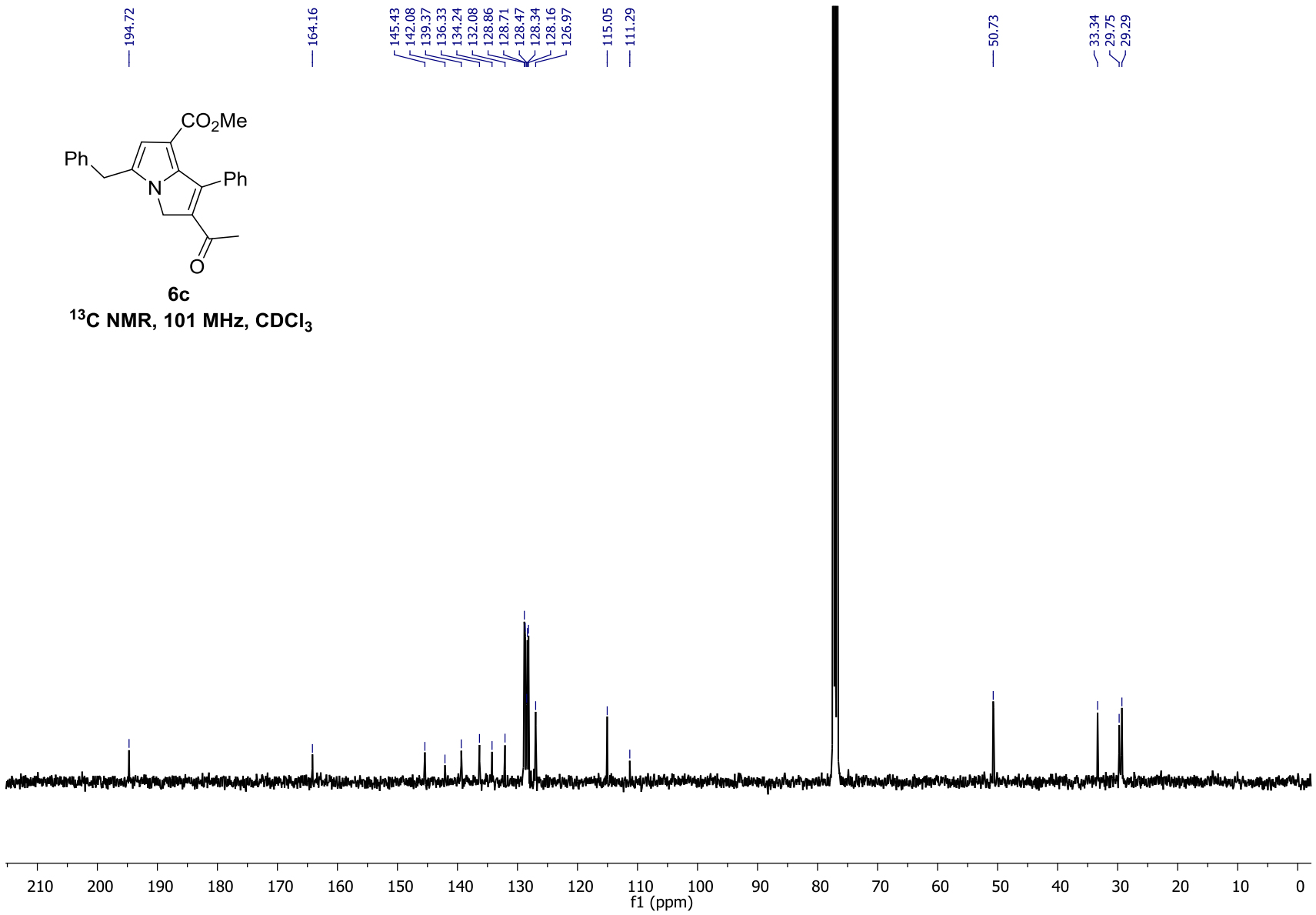

7.38
7.38
7.37
7.37
7.37
7.37
7.36
7.26
7.25
7.25
7.25
7.24
7.24
7.24
7.23
7.22
6.95
6.95
6.94
6.94
6.14
6.13
6.13
6.12
5.38
2.79
2.77
2.76
2.74
1.14
1.13
1.11
N
Ph
O
6b
1H NMR, 500 MHz, CDCl3
1.94
3.88
0.99
0.96
2.07
2.02
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


188.69
131.83
130.11
129.22
128.63
128.33
122.44
120.53
108.49
85.84
83.47
39.70
27.24
N
Ph
O
6b
13C NMR, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



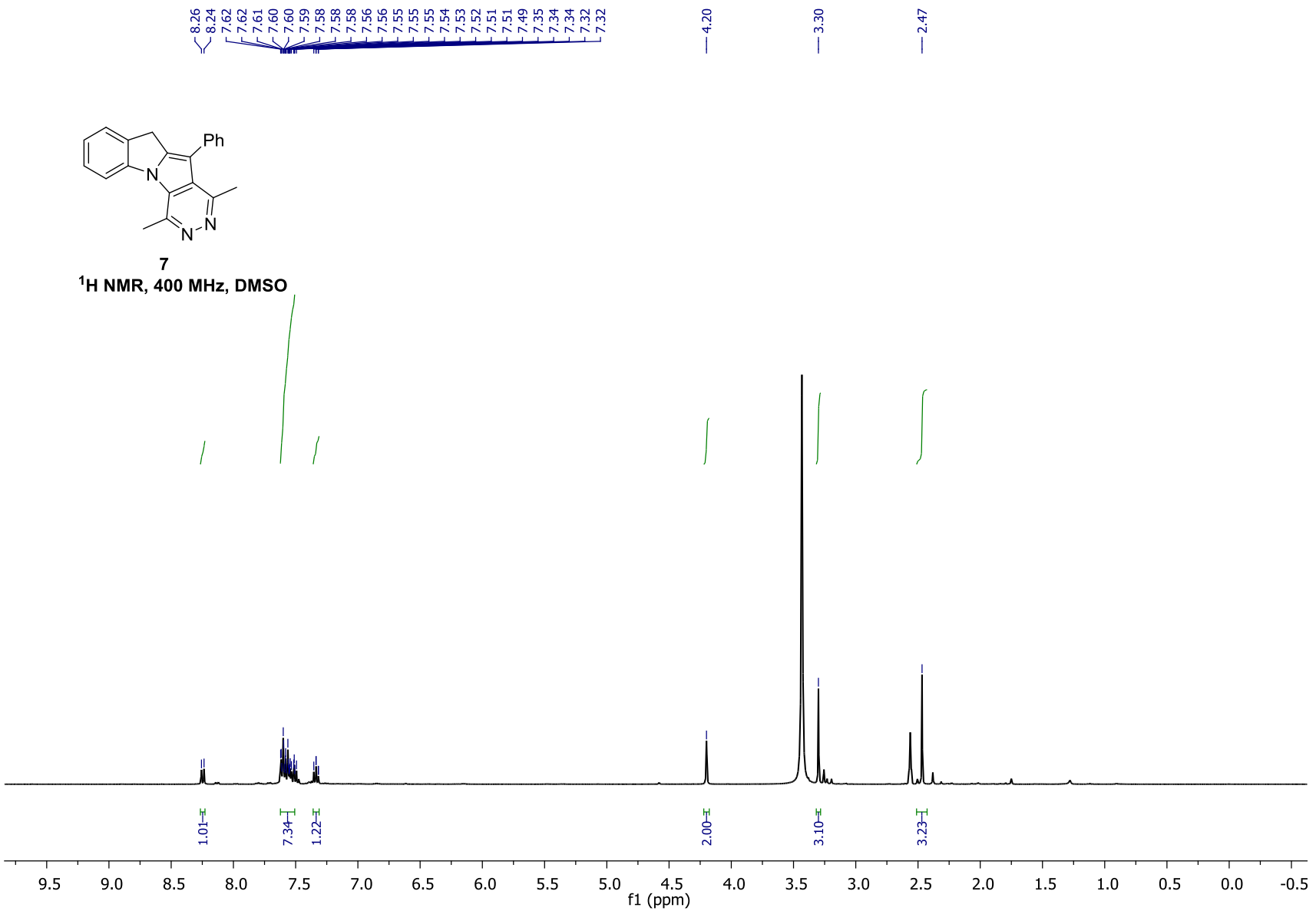
6c

^{1}H NMR, 500 MHz, $CDCl_3$



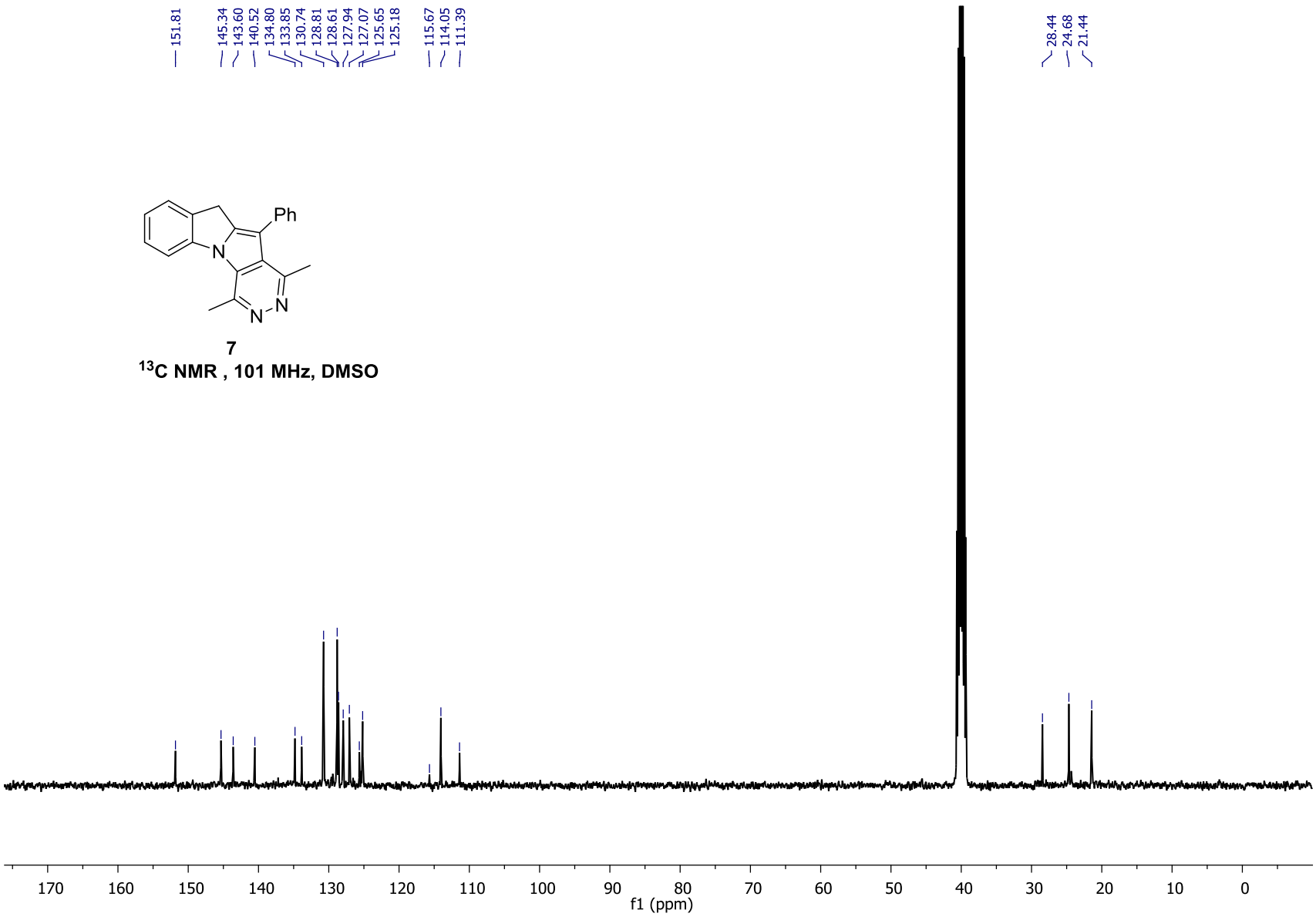
6c

^{13}C NMR, 101 MHz, $CDCl_3$



7

^{1}H NMR, 400 MHz, DMSO


151.81
145.34
143.60
140.52
134.80
133.85
130.74
128.81
128.61
127.94
127.07
125.65
125.18
115.67
114.05
111.39
28.44
24.68
21.44
Ph
N
N
N
7
13C NMR , 101 MHz, DMSO
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)