Supporting Information for

Rh(III)-Catalyzed Coupling of *N*-Chloroimines with *α*-Diazo-*α*-Phosphonoacetates for the Synthesis of 2*H*-Isoindoles

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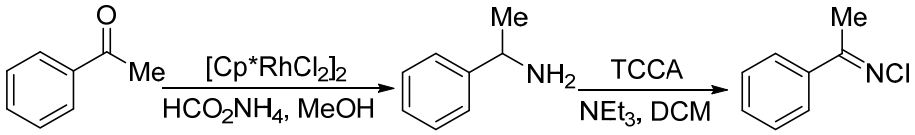
Experimental Procedures

General Information

All reactions were carried out under dry nitrogen atmosphere. All commercial reagents were used without additional purification, unless otherwise stated. Anhydrous solvent was purchased from commercial sources and transferred under N_2 atmosphere. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040-0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm) or iodine. NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz or 500 MHz for ^{1}H NMR, 101 MHz or 126 MHz for ^{13}C NMR and 202 MHz for ^{31}P NMR in $CDCl_3$, DMSO-d_6, CD_3CN, CD_3OCD_3 or CD_2Cl_2 with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; m, multiplet; br, broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High-resolution mass spectrometric data were obtained using Bruker Apex IV RTMS. Column conditions are reported in the experimental section below.

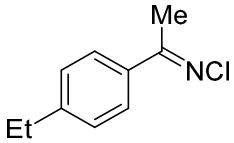
Synthesis and Characterization of Substrates

General procedure for the synthesis of *N*-chloroimines substrates (1a-1o):[1,2]



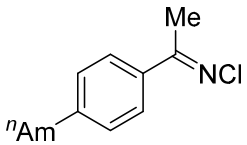
The corresponding ketone (20 mmol, 1.0 equiv) and CH_3OH (20 mL) were added to a 250 mL Schlenk tube containing $[RhCp^*Cl_2]_2$ (61.8 mg, 100 μmol, 0.5 mmol %) and HCO_2NH_4 (6.4 g, 100 mmol, 5.0 equiv). The brown mixture was frozen, and the whole system was evacuated. The system was closed and then stirred at 70 °C for 7 h. After the dark green resulting solution was cooled to room temperature, 1 M aqueous HCl solution (38.4 mL) was added, and the mixture was washed twice with CH_2Cl_2 (5 mL) to remove the neutral compounds. After addition of a cold 12 M aqueous NaOH solution (3.6 mL) to the aqueous layer, the mixture was extracted six times with CH_2Cl_2 (12 mL). The combined organic layers were dried over anhydrous Na_2SO_4. Filtration and evaporation under reduced pressure gave crude amine, which was used without purification. All the crude corresponding amine was dissolved in dichloromethane (50 mL), and TCCA (trichloroisocyanuric acid) (3.2 g, 14 mmol) was added in a 250 mL round-bottom flask at 0°C. Then, the mixture was stirred at ambient temperature during 1 h. Triethylamine (6.0 g) dissolved in dichloromethane (50 mL) was added, and the resulting mixture was washed with water (200 mL) and hydrochloric acid (1 M, 200 mL) successively. The organic layer was dried over anhydrous sodium sulfate. After concentration under reduced pressure, purification by column chromatography on silica gel (*n*-hexane/EtOAc = 40/1) afforded pure product.

***N*-Chloro-1-(4-ethylphenyl)ethan-1-imine (1c):**



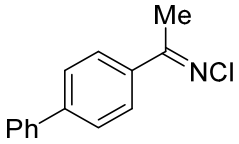
The title compound was obtained as transparent liquid in 61% yield (2.2 g). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.71 – 7.62 (m, 2H), 7.27 (d, J = 8.3 Hz, 2H), 2.72 (q, J = 7.6 Hz, 2H), 2.61 (s, 3H), 1.29 (t, J = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 176.90, 147.45, 134.65, 128.15, 127.02, 28.76, 20.55, 15.36. **HRMS (EI)** calcd. for $C_{10}H_{12}ClN$: $[M]^+$, 181.0658. Found: m/z 181.0657.

***N*-Chloro-1-(4-pentylphenyl)ethan-1-imine (1d):**



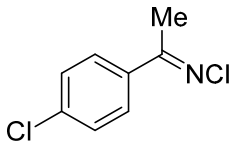
The title compound was obtained as transparent liquid in 76% yield (3.4 g). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.65 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 2.68 – 2.63 (m, 2H), 2.61 (s, 3H), 1.65 (dt, J = 15.0, 7.6 Hz, 2H), 1.41 – 1.28 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 176.93, 146.20, 134.61, 128.67, 126.90, 35.75, 31.44, 30.90, 22.53, 20.57, 14.04. **HRMS (EI)** calcd. for $C_{13}H_{18}ClN$: $[M]^+$, 223.1128. Found: m/z 223.1135.

1-([1,1'-biphenyl]-4-yl)-N-chloroethan-1-imine (1e):



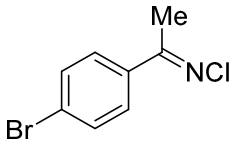
The title compound was obtained as white solid in 72% yield (3.3 g). **Melting point**: 110-111 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 – 7.76 (m, 2H), 7.66 – 7.59 (m, 4H), 7.49 – 7.43 (m, 2H), 7.41 – 7.35 (m, 1H), 2.63 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.66, 143.58, 140.00, 135.96, 128.92, 127.96, 127.43, 127.25, 127.13, 20.54. **HRMS (EI)** calcd. for $C_{14}H_{12}ClN$: $[M]^+$, 229.0658. Found: m/z 229.0662.

***N*-Chloro-1-(4-chlorophenyl)ethan-1-imine (1h):**



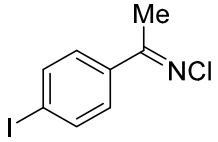
The title compound was obtained as white crystal in 71% yield (2.6 g). **Melting point**: 31-33 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 – 7.63 (m, 2H), 7.42 – 7.35 (m, 2H), 2.58 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.96, 137.11, 135.52, 128.89, 128.27, 20.44. **HRMS (EI)** calcd. for $C_8H_7Cl_2N$: $[M]^+$, 186.9956. Found: m/z 186.9952.

1-(4-Bromophenyl)-*N*-chloroethan-1-imine (1i):



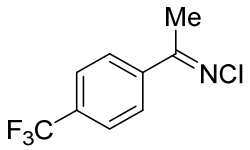
The title compound was obtained as white crystal in 84% yield (3.9 g). **Melting point**: 35-37 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 – 7.49 (m, 4H), 2.57 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.07, 135.96, 131.86, 128.48, 125.54, 20.40. **HRMS (EI)** calcd. for C_8H_7BrClN: $[M]^+$, 230.9450. Found: m/z 230.9445.

***N*-Chloro-1-(4-iodophenyl)ethan-1-imine (1j):**



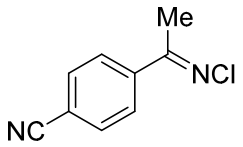
The title compound was obtained as brown crystal in 54% yield (3.0 g). **Melting point**: 42-44 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 – 7.72 (m, 2H), 7.48 – 7.38 (m, 2H), 2.56 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.25, 137.83, 136.56, 128.49, 97.68, 20.32. **HRMS (EI)** calcd. for $C_8H_7ICl N$: $[M]^+$, 278.9312. Found: m/z 278.9320.

***N*-Chloro-1-(4-(trifluoromethyl)phenyl)ethan-1-imine (1k):**



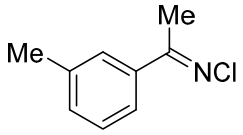
The title compound was obtained as white crystal in 34% yield (1.5 g). **Melting point**: 30-32 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 2.62 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.04, 140.31, 132.50 (q, *J* = 32.8 Hz), 125.62 (q, *J* = 3.8 Hz), 123.75 (q, *J* = 272.5 Hz), 20.58. **HRMS (EI)** calcd. for $C_9H_7BrClF_3N$: $[M]^+$, 221.0219. Found: m/z 221.0221.

4-(1-(Chloroimino)ethyl)benzonitrile (1l):



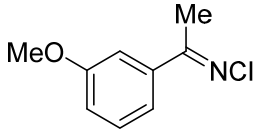
The title compound was obtained as white crystal in 59% yield (2.1 g). **Melting point**: 82-84 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 – 7.79 (m, 2H), 7.75 – 7.69 (m, 2H), 2.61 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.62, 140.93, 132.42, 127.57, 118.11, 114.41, 20.40. **HRMS (EI)** calcd. for $C_9H_7ClN_2$: $[M]^+$, 178.0298. Found: m/z 178.0296.

***N*-Chloro-1-(m-tolyl)ethan-1-imine (1m):**



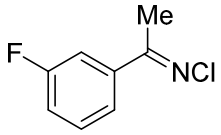
The title compound was obtained as transparent liquid in 57% yield (1.9 g). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 (s, 1H), 7.47 (d, *J* = 7.1 Hz, 1H), 7.32 – 7.23 (m, 2H), 2.58 (s, 3H), 2.38 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.32, 138.41, 137.20, 131.58, 128.50, 127.55, 124.12, 21.40, 20.75. **HRMS (ESI)** calcd. for $C_9H_{11}ClN$: $[M+H]^+$, 168.0575. Found: m/z 168.0574.

***N*-chloro-1-(3-methoxyphenyl)ethan-1-imine (1n):**



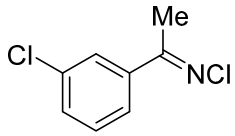
The title compound was obtained as transparent liquid in 49% yield (1.8 g). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 – 7.22 (m, 3H), 7.00 (ddd, *J* = 8.1, 2.6, 1.1 Hz, 1H), 3.83 (s, 3H), 2.58 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.96, 159.67, 138.44, 129.57, 119.47, 116.99, 111.87, 55.39, 20.72. **HRMS (EI)** calcd. for $C_9H_{10}ClNO$: $[M]^+$, 183.0451. Found: m/z 183.0450.

***N*-chloro-1-(3-fluorophenyl)ethan-1-imine (1o):**



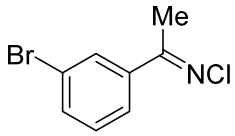
The title compound was obtained as transparent liquid in 67% yield (2.3 g). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 – 7.33 (m, 3H), 7.15 (tdd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 2.58 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.93 (d, *J* = 2.5 Hz), 162.70 (d, *J* = 247.0 Hz), 139.11 (d, *J* = 7.5 Hz), 130.19 (d, *J* = 8.1 Hz), 122.70 (d, *J* = 3.1 Hz), 117.78 (d, *J* = 21.2 Hz), 113.90, 20.50. **HRMS (EI)** calcd. for C_8H_7ClFN: $[M]^+$, 171.0251. Found: m/z 171.0253.

***N*-Chloro-1-(3-Chlorophenyl)ethan-1-imine (1p):**



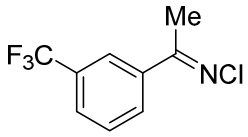
The title compound was obtained as transparent liquid in 54% yield (2.0 g). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 (t, *J* = 1.9 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.42 (ddd, *J* = 8.0, 2.0, 1.1 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 2.57 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.88, 138.72, 134.75, 130.81, 129.88, 127.12, 125.09, 20.49. **HRMS (EI)** calcd. for $C_8H_7Cl_2N$: $[M]^+$, 186.9956. Found: m/z 186.9953.

1-(3-Bromophenyl)-*N*-chloroethan-1-imine (1q):



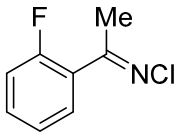
The title compound was obtained as transparent liquid in 47% yield (2.2 g). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (s, 1H), 7.60 (dd, *J* = 16.5, 7.9 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 1H), 2.56 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.79, 138.94, 133.74, 130.14, 130.01, 125.54, 122.82, 20.50. **HRMS (EI)** calcd. for C_8H_7BrClN: $[M]^+$, 230.9450. Found: m/z 230.9455.

***N*-chloro-1-(3-(trifluoromethyl)phenyl)ethan-1-imine (1r):**



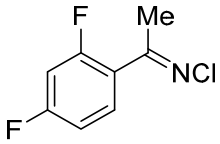
The title compound was obtained as transparent liquid in 56% yield (2.5 g). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 2.62 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.04, 140.31, 140.31, 132.50 (q, *J* = 32.8 Hz), 127.35, 126.45, 125.62 (q, *J* = 3.8 Hz), 123.75 (q, *J* = 272.5 Hz), 20.58. **HRMS (EI)** calcd. for $C_9H_7BrClF_3N$: $[M]^+$, 221.0219. Found: m/z 221.0223.

***N*-Chloro-1-(2-fluorophenyl)ethan-1-imine (1s):**



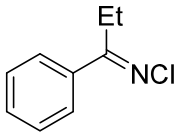
The title compound was obtained as transparent liquid in 35% yield (1.2 g). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.54 (td, *J* = 7.6, 1.8 Hz, 1H), 7.45 (dddd, *J* = 8.3, 7.2, 5.2, 1.8 Hz, 1H), 7.21 (td, *J* = 7.6, 1.1 Hz, 1H), 7.14 (ddd, *J* = 10.9, 8.3, 0.9 Hz, 1H), 2.61 (d, *J* = 2.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 176.18, 159.83 (d, *J* = 251.4 Hz), 132.19 (d, *J* = 8.6 Hz), 129.79 (d, *J* = 2.8 Hz), 126.18 (d, *J* = 12.6 Hz), 124.43 (d, *J* = 3.5 Hz), 116.28 (d, *J* = 21.8 Hz), 23.10 (d, *J* = 5.3 Hz). **HRMS (EI)** calcd. for C_8H_7ClFN: $[M]^+$, 171.0251. Found: m/z 171.0249.

***N*-Chloro-1-(2,4-difluorophenyl)ethan-1-imine (1t):**



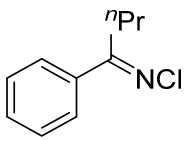
The title compound was obtained as transparent liquid in 37% yield (1.4 g). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.57 (td, *J* = 8.5, 6.4 Hz, 1H), 6.98 – 6.86 (m, 2H), 2.59 (d, *J* = 3.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 175.16 (d, *J* = 1.7 Hz), 164.29 (dd, *J* = 253.6, 12.1 Hz), 160.29 (dd, *J* = 254.3, 12.3 Hz), 131.09 (dd, *J* = 10.0, 4.4 Hz), 122.53 (d, *J* = 12.8 Hz), 111.91 (dd, *J* = 21.4, 3.5 Hz), 104.68 (t, *J* = 25.7 Hz), 22.93 (d, *J* = 5.5 Hz). **HRMS (EI)** calcd. for $C_{10}H_{12}ClN$: $[M]^+$, 189.0157. Found: m/z 189.0162.

***N*-Chloro-1-phenylpropan-1-imine (1u):**



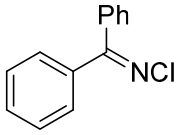
The title compound was obtained as transparent liquid in 63% yield (2.1 g). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.75 – 7.69 (m, 2H), 7.46 (ddd, *J* = 13.1, 7.9, 6.4 Hz, 3H), 3.09 (q, *J* = 7.7 Hz, 2H), 1.26 (t, *J* = 7.7 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 181.31, 136.10, 130.77, 128.70, 127.12, 27.41, 10.51. **HRMS (EI)** calcd. for $C_9H_{10}ClN$: $[M]^+$, 167.0502. Found: m/z 167.0496.

***N*-Chloro-1-phenylbutan-1-imine (1v):**



The title compound was obtained as transparent liquid in 63% yield (2.3 g). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.72 – 7.67 (m, 2H), 7.52 – 7.40 (m, 3H), 3.08 – 3.03 (m, 2H), 1.73 – 1.64 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 180.45, 136.45, 130.72, 128.68, 127.13, 35.77, 19.71, 14.08. **HRMS (EI)** calcd. for $C_{10}H_{12}ClN$: $[M]^+$, 181.0658. Found: m/z 181.0657.

***N*-Chloro-1,1-diphenylmethanimine (1w):**

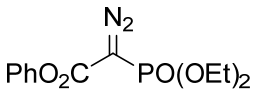


The title compound was obtained as transparent liquid in 30% yield (1.3 g). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 – 7.40 (m, 6H), 7.38 – 7.26 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.64, 137.01, 136.30, 131.31, 129.70, 128.89, 128.49, 127.78. **HRMS (EI)** calcd. for $C_{10}H_{12}ClN$: $[M]^+$, 215.0502. Found: m/z 215.0498.

General procedure for the synthesis of *α*-diazo-*α*-phosphonoacetate substrates[3]

To a cooled solution (0 °C) of *p*-acetamidobenzolsulfonyl azide (2.6 g, 10.8 mmol) and substituted 2-(diethoxyphosphoryl)acetate (10.3 mmol) in acetonitrile (42 mL) was slowly added NEt_3 (4.3 mL, 30.9 mmol). Thereafter the mixture was warmed to room temperature and stirred overnight. The solvent was removed in vacuo and the residue purified by flash chromatography (petroleum ether/EtOAc, 1:1). The *α*-diazo-*α*-phosphonoacetate substrates was obtained as a yellow liquid.

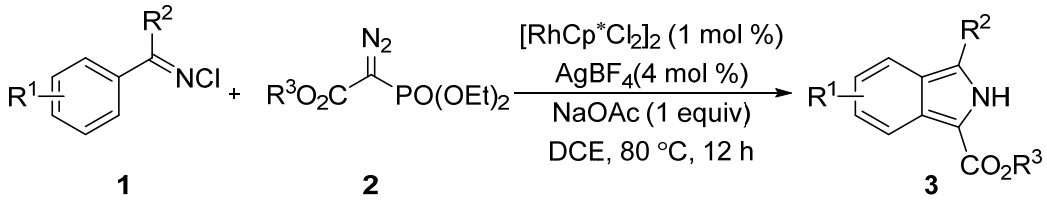
Phenyl 2-diazo-2-(diethoxyphosphoryl)acetate (2d):



The title compound was obtained as yellow oil in 81% yield (2.5 g). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.40 – 7.33 (m, 2H), 7.22 (s, 1H), 7.14 – 7.09 (m, 2H), 4.30 – 4.17 (m, 4H), 1.37 (t, J = 7.2 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.91 (d, J = 12.7 Hz), 150.06, 129.48, 126.18, 121.39, 63.98, 63.93, 16.19, 16.14. **^{31}P NMR (202 MHz, $CDCl_3$)** δ 8.92. **HRMS (EI)** calcd. for $C_{12}H_{16}N_2O_5P$: $[M+H]^+$, 299.0791. Found: m/z 299.0791.

Synthesis and Characterization of Products

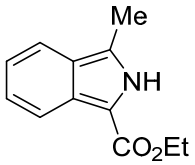
Synthesis of *2H*-isoindoles



1 **2** **3**

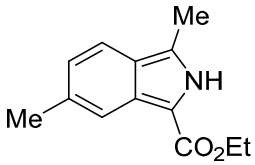
To a 13 × 150 mm test tube equipped with magnetic stir bar were added $[Cp^*RhCl_2]_2$ (1.2 mg, 1 mol %), $AgBF_4$ (1.6 mg, 4 mol %) and NaOAc (16.4 mg, 0.2 mmol, 1. equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1a-1x** (0.2 mmol, 1 equiv) and **2a-2d** (0.3 mmol, 1.5 equiv) in DCE (2 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 °C) for 12 h. Then the reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 5/1).

Ethyl 3-methyl-2*H*-isoindole-1-carboxylate (3aa):



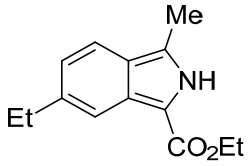
The title compound was obtained as off-white solid in 91% yield (37.1 mg). **Melting point**: 162-163 °C. **^{1}H NMR (500 MHz, DMSO)** δ 13.05 (s, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.24 – 7.17 (m, 1H), 7.03 – 6.96 (m, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.59 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 161.10, 128.13, 127.97, 125.62, 123.96, 121.07, 120.73, 120.45, 108.20, 59.34, 15.16, 11.24. **HRMS (ESI)** calcd. for $C_{12}H_{14}NO_2$: $[M+H]^+$, 204.1019. Found: m/z 204.1020.

Ethyl 3,6-dimethyl-2*H*-isoindole-1-carboxylate (3ba):



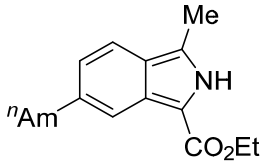
The title compound was obtained as off-white solid in 98% yield (42.6 mg). **Melting point**: 166-167 °C. **^{1}H NMR (500 MHz, DMSO)** δ 12.86 (s, 1H), 7.68 (s, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.55 (s, 3H), 2.38 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 161.08, 134.72, 128.75, 127.96, 123.40, 122.66, 120.83, 119.08, 107.53, 59.20, 22.43, 15.21, 11.25. **HRMS (ESI)** calcd. for $C_{13}H_{16}NO_2$: $[M+H]^+$, 218.1176. Found: m/z 218.1176.

Ethyl 6-ethyl-3-methyl-2*H*-isoindole-1-carboxylate (3ca):



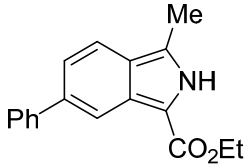
The title compound was obtained as white solid in 52% yield (24.0 mg). **Melting point**: 168-170 °C. **^{1}H NMR (500 MHz, DMSO)** δ 12.86 (s, 1H), 7.69 (s, 1H), 7.57 (d, *J* = 8.6 Hz, 1H), 6.88 (dd, *J* = 8.6, 1.3 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.67 (q, *J* = 7.5 Hz, 2H), 2.55 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 161.05, 141.15, 128.76, 127.90, 122.84, 122.41, 120.96, 117.74, 107.72, 59.21, 29.43, 16.10, 15.20, 11.27. **HRMS (ESI)** calcd. for $C_{14}H_{18}NO_2$: $[M+H]^+$, 232.1332. Found: m/z 232.1334.

Ethyl 3-methyl-6-pentyl-2*H*-isoindole-1-carboxylate (3da):



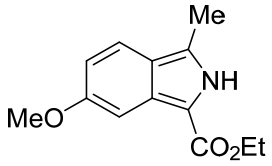
The title compound was obtained as white solid in 83% yield (45.4 mg). **Melting point**: 135-137 °C. **^{1}H NMR (500 MHz, DMSO)** δ 12.86 (s, 1H), 7.68 (s, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 6.85 (dd, *J* = 8.6, 1.3 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.55 (s, 3H), 1.64 – 1.56 (m, 2H), 1.36 (d, *J* = 7.1 Hz, 3H), 1.28 (ddt, *J* = 12.8, 8.3, 6.2 Hz, 4H), 0.86 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 161.03, 139.65, 128.78, 127.86, 122.85, 122.68, 120.85, 118.51, 107.65, 59.17, 36.37, 31.38, 31.07, 22.48, 15.18, 14.38, 11.24. **HRMS (ESI)** calcd. for $C_{14}H_{18}NO_2$: $[M+H]^+$, 247.1802. Found: m/z 247.1804.

Ethyl 3-methyl-6-phenyl-2*H*-isoindole-1-carboxylate (3ea):



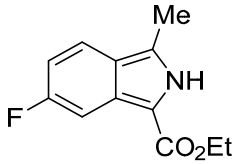
The title compound was obtained as white solid in 95% yield (53.1 mg). **Melting point**: 236-238 °C. **^{1}H NMR (500 MHz, DMSO)** δ 13.09 (s, 1H), 8.14 (s, 1H), 7.76 (d, *J* = 0.7 Hz, 1H), 7.71 – 7.67 (m, 2H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.32 (dd, *J* = 8.7, 1.5 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.61 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 161.01, 141.79, 137.67, 129.42, 128.58, 128.06, 127.60, 127.28, 123.25, 121.86, 120.72, 118.04, 108.86, 59.43, 15.20, 11.31. **HRMS (ESI)** calcd. for $C_{13}H_{16}NO_2$: $[M+H]^+$, 280.1332. Found: m/z 280.1332.

Ethyl 6-methoxy-3-methyl-2*H*-isoindole-1-carboxylate (3fa):



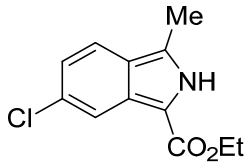
The title compound was obtained as white solid in 56% yield (26.1 mg). **Melting point**: 186-187 °C. **^{1}H NMR (500 MHz, DMSO)** δ 12.70 (s, 1H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.22 (s, 1H), 6.66 (dd, *J* = 9.0, 2.3 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.53 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 160.96, 158.28, 129.56, 128.57, 122.55, 119.96, 114.80, 107.65, 98.00, 59.13, 55.19, 15.18, 11.29. **HRMS (ESI)** calcd. for $C_{13}H_{16}NO_3$: $[M+H]^+$, 234.1125. Found: m/z 24.1125.

Ethyl 6-fluoro-3-methyl-2H-isoindole-1-carboxylate (3ga):



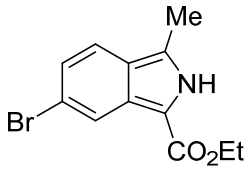
The title compound was obtained as white solid in 95% yield (42.0 mg). **Melting point**: 169-170 °C. **^{1}H NMR (500 MHz, DMSO)** δ 13.13 (s, 1H), 7.74 (dd, *J* = 9.1, 5.3 Hz, 1H), 7.48 (dd, *J* = 10.7, 1.8 Hz, 1H), 6.88 (td, *J* = 9.2, 2.3 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.58 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 161.31 (d, *J* = 240.2 Hz), 160.93, 129.05, 127.91, 124.02 (d, *J* = 10.6 Hz), 121.36, 111.54 (d, *J* = 27.7 Hz), 108.57 (d, *J* = 7.1 Hz), 103.21 (d, *J* = 24.0 Hz), 59.47, 15.09, 11.26. **HRMS (ESI)** calcd. for $C_{12}H_{13}FNO_2$: $[M+H]^+$, 222.0925. Found: m/z 222.0925. CCDC# at the Cambridge Crystallographic Data Center: 1858032.

Ethyl 6-chloro-3-methyl-2*H*-isoindole-1-carboxylate (3ha):



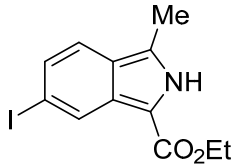
The title compound was obtained as white solid in 84% yield (39.9 mg). **Melting point**: 186-188 °C. **^{1}H NMR (500 MHz, DMSO)** δ 13.24 (s, 1H), 7.86 (d, *J* = 1.2 Hz, 1H), 7.73 (dd, *J* = 8.8, 0.5 Hz, 1H), 6.97 (dd, *J* = 8.9, 1.9 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 1H), 2.58 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 160.80, 130.74, 128.90, 128.06, 123.49, 122.24, 121.43, 119.00, 108.19, 59.64, 15.12, 11.23. **HRMS (ESI)** calcd. for $C_{12}H_{13}ClNO_2$: $[M+H]^+$, 238.0629. Found: m/z 238.0630.

Ethyl 6-bromo-3-methyl-2*H*-isoindole-1-carboxylate (3ia):



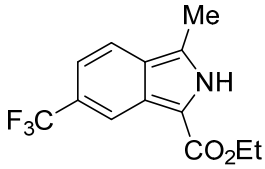
The title compound was obtained as white solid in 87% yield (49.1 mg). **Melting point**: 188-190 °C. **^{1}H NMR (500 MHz, DMSO)** δ 13.24 (s, 1H), 8.04 (s, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.08 (dd, *J* = 8.8, 1.7 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.58 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 160.78, 128.89, 128.67, 123.74, 123.58, 122.31, 122.29, 119.53, 108.06, 59.65, 15.12, 11.20. **HRMS (ESI)** calcd. for $C_{12}H_{13}BrNO_2$: $[M+H]^+$, 282.0124. Found: m/z 282.0125.

Ethyl 6-iodo-3-methyl-2*H*-isoindole-1-carboxylate (3ja):



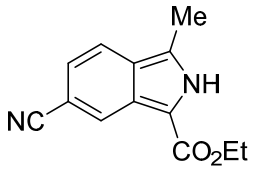
The title compound was obtained as brown solid in 86% yield (56.6 mg). **Melting point**: 216-217 °C. **^{1}H NMR (500 MHz, DMSO)** δ 13.18 (s, 1H), 8.30 (s, 1H), 7.52 (d, *J* = 8.7 Hz, 1H), 7.23 (dd, *J* = 8.7, 1.4 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.57 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 160.75, 129.52, 129.00, 128.80, 125.63, 123.45, 122.38, 107.55, 92.50, 59.63, 15.13, 11.18. **HRMS (ESI)** calcd. for $C_{12}H_{13}INO_2$: $[M+H]^+$, 329.9985. Found: m/z 329.9984.

Ethyl 3-methyl-6-(trifluoromethyl)-2*H*-isoindole-1-carboxylate (3ka):



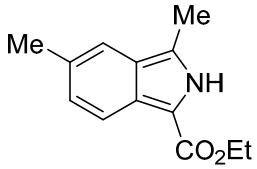
The title compound was obtained as white solid in 76% yield (41.2 mg). **Melting point**: 225-227 °C. **^{1}H NMR (500 MHz, DMSO)** δ 13.54 (s, 1H), 8.25 (s, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.17 (dd, *J* = 8.8, 1.4 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.62 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 160.65, 128.51, 126.53, 125.81, 125.80 (q, *J* = 30.7 Hz), 124.39, 122.98, 118.47 (q, *J* = 5.0 Hz), 115.82 (d, *J* = 2.9 Hz), 110.19, 59.88, 15.00, 11.19. **HRMS (ESI)** calcd. for $C_{13}H_{14}F_3NO_2$: $[M+H]^+$, 272.0893. Found: m/z 272.0895.

Ethyl 6-cyano-3-methyl-2*H*-isoindole-1-carboxylate (3la):



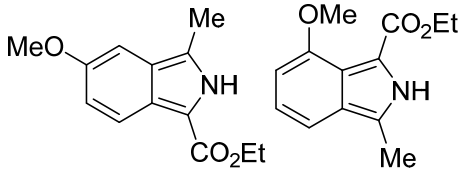
The title compound was obtained as white solid in 68% yield (31.0 mg). **Melting point**: 231-233 °C. **^{1}H NMR (500 MHz, DMSO)** δ 13.68 (s, 1H), 8.35 (s, 1H), 7.89 (dd, *J* = 8.6, 0.8 Hz, 1H), 7.20 (dd, *J* = 8.7, 1.3 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.61 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 160.57, 128.85, 127.59, 125.70, 123.99, 123.12, 120.75, 120.63, 110.22, 107.61, 60.09, 15.04, 11.14. **HRMS (ESI)** calcd. for $C_{13}H_{13}N_2O_2$: $[M+H]^+$, 229.0972. Found: m/z 229.0972.

Ethyl 3,5-dimethyl-2*H*-isoindole-1-carboxylate (3ma):



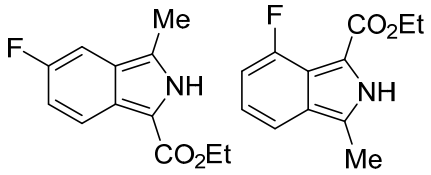
The title compound was obtained as white solid in 85% yield (36.9 mg). **Melting point**: 164-166 °C. **^{1}H NMR (500 MHz, DMSO)** δ 12.90 (s, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.41 (s, 1H), 7.05 (dd, *J* = 8.7, 1.2 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.54 (s, 3H), 2.35 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 160.97, 129.37, 128.29, 126.94, 126.83, 124.29, 120.32, 119.38, 108.10, 59.27, 21.80, 15.18, 11.19. **HRMS (ESI)** calcd. for $C_{13}H_{16}NO_2$: $[M+H]^+$, 218.1176. Found: m/z 218.1176.

Ethyl 5-methoxy-3-methyl-2*H*-isoindole-1-carboxylate (3naI), Ethyl 7-methoxy-3-methyl-2*H*-isoindole-1-carboxylate (3naII):



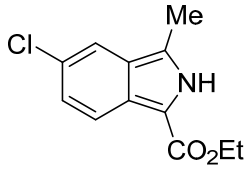
The title compounds were not separated (1:0.44) obtained as white solid in 86% yield (40.2 mg). **Melting point**: 149-151 °C. **^{1}H NMR (500 MHz, DMSO)** δ 12.82 (s, 1Hx1), 12.76 (s, 1Hx0.44), 7.79 (d, *J* = 9.1 Hz, 1Hx0.44), 7.18 (d, *J* = 8.2 Hz, 1Hx1), 6.98 (d, *J* = 2.0 Hz, 1Hx0.44), 6.93 – 6.84 (m, 1Hx1+1Hx0.44), 6.55 (d, *J* = 7.3 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 3Hx0.44), 4.24 (q, *J* = 7.1 Hz, 3H), 3.81 (s, 3Hx1), 3.78 (s, 3Hx0.44), 2.54 (s, 3Hx1+3Hx0.44), 1.34 (dt, *J* = 13.1, 6.5 Hz, 3Hx1+3Hx0.44). **^{13}C NMR (126 MHz, DMSO)** δ 160.68, 154.38, 153.17, 126.76, 126.38, 123.98, 121.78, 121.45, 119.75, 119.35, 113.07, 108.78, 103.80, 98.27, 59.49, 59.32, 55.36, 15.15, 15.00, 11.27, 11.18. **HRMS (ESI)** calcd. for $C_{13}H_{16}NO_3$: $[M+H]^+$, 234.1125. Found: m/z 24.1125.

Ethyl 5-fluoro-3-methyl-2*H*-isoindole-1-carboxylate (3oaI), Ethyl 7-fluoro-3-methyl-2*H*-isoindole-1-carboxylate (3oaII):



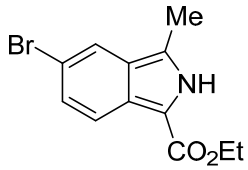
The title compounds were not separated (1:0.1) obtained as white solid in 68% yield (30.1 mg). **Melting point**: 166-168 ºC. **^{1}H NMR (500 MHz, DMSO)** δ 13.20 (s, 1Hx1+1Hx0.1), 7.93 (dd, *J* = 9.2, 5.2 Hz, 1Hx0.1), 7.48 (d, *J* = 8.1 Hz, 1Hx1), 7.42 (dd, *J* = 10.2, 2.1 Hz, 1Hx0.1), 7.10 (td, *J* = 9.2, 2.3 Hz, 1Hx0.1), 6.97 – 6.87 (m, 2Hx1), 4.30 (dq, *J* = 14.2, 7.1 Hz, 2Hx1+2Hx0.1)), 2.59 (s, 3Hx1), 2.55 (s, 3Hx0.1), 1.34 (dt, *J* = 14.2, 7.1 Hz, 3Hx1+3Hx0.1)). **^{13}C NMR (126 MHz, DMSO)** δ 160.83, 160.33, 157.78 (d, *J* = 236.0 Hz), 155.19 (d, *J* = 253.3 Hz), 128.19 (d, *J* = 1.8 Hz), 127.48 (d, *J* = 7.8 Hz), 125.26, 123.11 (d, *J* = 10.2 Hz), 122.80 (d, *J* = 9.3 Hz), 120.74 (d, *J* = 6.3 Hz), 117.19 (d, *J* = 4.4 Hz), 116.95 (d, *J* = 18.5 Hz), 116.29 (d, *J* = 27.4 Hz), 109.38 (d, *J* = 20.2 Hz), 108.87, 107.37 (d, *J* = 4.9 Hz), 103.69 (d, *J* = 22.2 Hz), 59.74, 59.53, 15.03, 14.89, 11.12. **HRMS (ESI)** calcd. for $C_{12}H_{13}FNO_2$: $[M+H]^+$, 222.0925. Found: m/z 222.0925.

Ethyl 5-chloro-3-methyl-2H-isoindole-1-carboxylate (3pa):



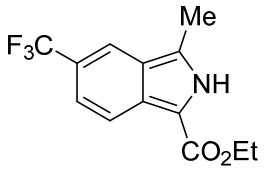
The title compound was obtained as white solid in 51% yield (24.3 mg). **Melting point**: 167-168 ºC. **^{1}H NMR (500 MHz, DMSO)** δ 13.24 (s, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.78 (d, *J* = 1.4 Hz, 1H), 7.17 (dd, *J* = 9.0, 1.9 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.56 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 160.81, 127.71, 126.17, 126.05, 125.36, 124.17, 122.46, 120.04, 108.93, 59.65, 15.10, 11.17. **HRMS (ESI)** calcd. for $C_{12}H_{13}ClNO_2$: $[M+H]^+$, 238.0629. Found: m/z 238.0629.

Ethyl 5-bromo-3-methyl-2H-isoindole-1-carboxylate (3qa):



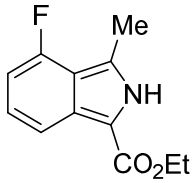
The title compound was obtained as white solid in78% yield (44.0 mg). **Melting point**: 171-173 ºC. **^{1}H NMR (500 MHz, DMSO)** δ 13.24 (s, 1H), 7.94 (d, *J* = 1.2 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.27 (dd, *J* = 9.0, 1.7 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.56 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 160.81, 128.44, 127.68, 126.11, 124.94, 123.36, 122.66, 113.57, 108.93, 59.66, 15.10, 11.17. **HRMS (ESI)** calcd. for $C_{12}H_{11}BrNO_2$: $[M-H]^-$, 279.9979. Found: m/z 279.9977.

Ethyl 3-methyl-5-(trifluoromethyl)-2*H*-isoindole-1-carboxylate (3ra):



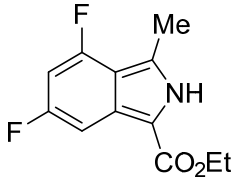
The title compound was obtained as white solid in 28% yield (15.2 mg). **Melting point**: 203-205 °C. **^{1}H NMR (500 MHz, DMSO)** δ 13.49 (s, 1H), 8.16 (s, 1H), 8.06 (d, *J* = 8.9 Hz, 1H), 7.38 (dd, *J* = 8.9, 1.3 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.65 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 160.86, 130.63, 128.47 – 128.01 (m), 128.23, 125.61 (q, *J* = 271.3 Hz), 122.14, 121.78, 121.22 (q, *J* = 31.1 Hz), 120.71 (d, *J* = 2.9 Hz), 120.12 (q, *J* = 4.8 Hz), 59.79, 15.06, 11.22. **HRMS (ESI)** calcd. for $C_{13}H_{14}F_3NO_2$: $[M+H]^+$, 272.0893. Found: m/z 272.0894.

Ethyl 4-fluoro-3-methyl-2*H*-isoindole-1-carboxylate (3sa):



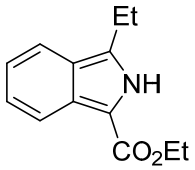
The title compound was obtained as white solid in 71% yield (31.4 mg). **Melting point**: 187-189 °C. **^{1}H NMR (500 MHz, DMSO)** δ 13.23 (s, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.17 – 7.08 (m, 1H), 6.69 (dd, *J* = 12.0, 7.4 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.68 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 160.95, 157.92 (d, *J* = 250.4 Hz), 130.72, 126.07 (d, *J* = 3.6 Hz), 125.95 (d, *J* = 7.2 Hz), 116.85 (d, *J* = 4.0 Hz), 114.02 (d, *J* = 17.7 Hz), 109.44, 104.01 (d, *J* = 17.6 Hz), 59.70, 15.07, 13.11 (d, *J* = 2.3 Hz).**HRMS (ESI)** calcd. for $C_{12}H_{13}FNO_2$: $[M+H]^+$, 222.0925. Found: m/z 222.0925.

Ethyl 4,6-difluoro-3-methyl-2*H*-isoindole-1-carboxylate (3ta):



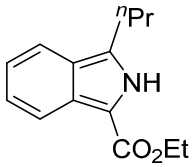
The title compound was obtained as white solid in 46% yield (21.8 mg). **Melting point**: 208-209 °C. **^{1}H NMR (500 MHz, DMSO)** δ 13.32 (s, 1H), 7.32 (dd, *J* = 10.1, 1.9 Hz, 1H), 6.79 (ddd, *J* = 11.6, 9.8, 1.9 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.65 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 160.83, 160.24 (dd, *J* = 241.4, 11.1 Hz), 158.23 (dd, *J* = 254.4, 15.3 Hz), 128.73, 127.19, 111.46 (d, *J* = 17.2 Hz), 110.18, 99.77 (dd, *J* = 24.1, 4.6 Hz), 96.74 (dd, *J* = 32.1, 22.4 Hz), 59.82, 15.02, 12.98 (d, *J* = 2.2 Hz). **HRMS (ESI)** calcd. for $C_{12}H_{12}F_2NO_2$: $[M+H]^+$, 240.0831. Found: m/z 240.0833.

Ethyl 3-ethyl-2*H*-isoindole-1-carboxylate (3ua):



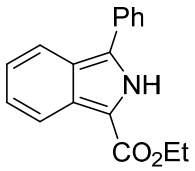
The title compound was obtained as white solid in 74% yield (32.2 mg). **Melting point**: 110-111 °C. **^{1}H NMR (500 MHz, DMSO)** δ 13.03 (s, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.20 (ddd, *J* = 8.4, 6.6, 0.7 Hz, 1H), 7.03 – 6.97 (m, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.01 (q, *J* = 7.6 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 161.12, 133.92, 128.17, 125.58, 123.07, 121.03, 120.81, 120.55, 108.24, 59.48, 19.22, 15.24, 15.18. **HRMS (ESI)** calcd. for $C_{13}H_{16}NO_2$: $[M+H]^+$, 218.1176. Found: m/z 218.1176.

Ethyl 3-propyl-2*H*-isoindole-1-carboxylate (3va):



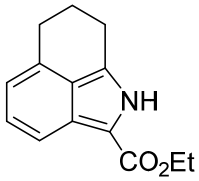
The title compound was obtained as white solid in 53% yield (24.5 mg). **Melting point**: 113-114 °C. **^{1}H NMR (500 MHz, DMSO)** δ 13.03 (s, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.23 – 7.16 (m, 1H), 7.02 – 6.95 (m, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.97 (t, *J* = 7.4 Hz, 2H), 1.75 – 1.65 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, DMSO**) δ 161.12, 132.46, 128.09, 125.54, 123.71, 121.09, 120.82, 120.55, 108.36, 59.38, 27.59, 23.54, 15.17, 14.10. **HRMS (ESI)** calcd. for $C_{14}H_{18}NO_2$: $[M+H]^+$, 232.1332. Found: m/z 232.1334.

Ethyl 3-phenyl-2*H*-isoindole-1-carboxylate (3wa):



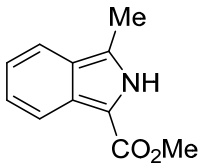
The title compound was obtained as white crystal in 72% yield (38.2 mg). **Melting point**: 136-138 °C. **^{1}H NMR (500 MHz, DMSO)** δ 13.46 (s, 1H), 8.07 (d, *J* = 8.6 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.90 – 7.84 (m, 2H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.33 – 7.25 (m, 1H), 7.15 (ddd, *J* = 8.3, 6.6, 0.7 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 161.21, 131.42, 129.35, 129.28, 128.57, 128.48, 128.17, 125.74, 123.09, 123.01, 121.24, 121.07, 59.88, 15.10. **HRMS (ESI)** calcd. for $C_{17}H_{16}NO_2$: $[M+H]^+$, 266.1176. Found: m/z 266.1175.

Ethyl 1,6,7,8-tetrahydrobenzo[*cd*]indole-2-carboxylate (3xa):



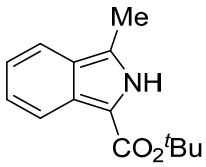
The title compound was obtained as white solid in 44% yield (20.2 mg). **Melting point**: 143-144 °C. **^{1}H NMR (500 MHz, DMSO)** δ 12.88 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.12 (dd, *J* = 8.4, 6.6 Hz, 1H), 6.67 (d, *J* = 6.5 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.97 (t, *J* = 6.0 Hz, 2H), 2.86 (t, *J* = 5.8 Hz, 2H), 2.13 – 2.01 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 161.38, 134.39, 131.53, 127.23, 126.12, 124.01, 117.44, 115.97, 108.27, 59.21, 26.88, 24.21, 22.95, 15.18. **HRMS (ESI)** calcd. for $C_{14}H_{16}NO_2$: $[M+H]^+$, 230.1176. Found: m/z 230.1176.

Methyl 3-methyl-2*H*-isoindole-1-carboxylate (3ab):



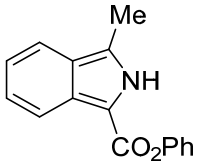
The title compound was obtained as white solid in 82% yield (31.1 mg). **Melting point**: 180-182 °C. **^{1}H NMR (500 MHz, DMSO)** δ 13.10 (s, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.27 – 7.17 (m, 1H), 7.04 – 6.95 (m, 1H), 3.84 (s, 3H), 2.58 (s, 2H). **^{13}C NMR (126 MHz, DMSO)** δ 161.38, 128.26, 128.14, 125.69, 123.97, 121.11, 120.77, 120.36, 107.92, 51.01, 11.25. **HRMS (ESI)** calcd. for $C_{11}H_{12}NO_2$: $[M+H]^+$, 190.0836. Found: m/z 190.0836.

Tert-butyl 3-methyl-2*H*-isoindole-1-carboxylate (3ac):



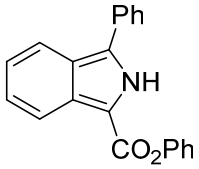
The title compound was obtained as brown solid in 63% yield (29.2 mg). **Melting point**: 161-162 °C. **^{1}H NMR (500 MHz, DMSO)** δ 12.85 (s, 1H), 7.84 (t, *J* = 11.5 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.21 – 7.13 (m, 1H), 7.01 – 6.93 (m, 1H), 2.58 (s, 3H), 1.59 (s, 9H). **^{13}C NMR (126 MHz, DMSO)** δ 160.88, 127.55, 127.03, 125.32, 123.81, 120.98, 120.55, 109.59, 79.33, 28.83, 11.08. **HRMS (ESI)** calcd. for $C_{14}H_{18}NO_2$: $[M+H]^+$, 232.1332. Found: m/z 232.1333.

Phenyl 3-methyl-2*H*-isoindole-1-carboxylate (3ad):



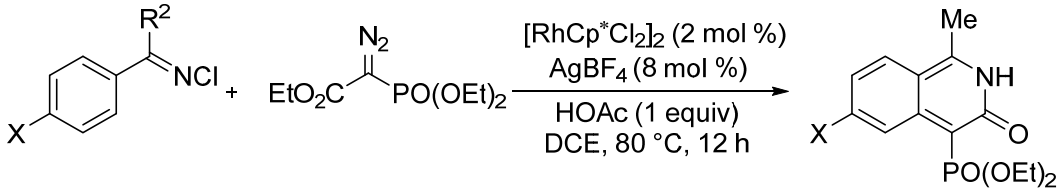
The title compound was obtained as brown solid in 78% yield (39.2 mg). **Melting point**: 165-167 °C. **^{1}H NMR (500 MHz, DMSO)** δ 13.38 (s, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.42 (m, 2H), 7.36 – 7.22 (m, 4H), 7.12 – 7.00 (m, 1H), 2.65 (s, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 158.78, 151.29, 129.86, 126.46, 125.70, 124.53, 122.70, 121.40, 121.24, 120.39, 11.40. **HRMS (ESI)** calcd. for $C_{16}H_{14}NO_2$: $[M+H]^+$, 252.1019. Found: m/z 252.1018.

phenyl 3-phenyl-2H-isoindole-1-carboxylate (3wd):



The title compound was obtained as brown solid in 66% yield (41.4 mg). **Melting point**: 110-112 °C. **^{1}H NMR (500 MHz, DMSO)** δ 13.75 (s, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.6 Hz, 1H), 7.93 – 7.89 (m, 2H), 7.57 (t, *J* = 7.7 Hz, 2H), 7.53 – 7.44 (m, 3H), 7.39 – 7.29 (m, 4H), 7.25 – 7.20 (m, 1H). **^{13}C NMR (126 MHz, DMSO)** δ 159.16, 151.15, 131.16, 131.13, 129.93, 129.80, 129.35, 128.71, 128.60, 126.51, 125.93, 123.50, 123.37, 122.68, 121.56, 120.95, 110.23. **HRMS (ESI)** calcd. for $C_{21}H_{17}NO_2$: $[M+H]^+$, 314.1176. Found: m/z 314.1173.

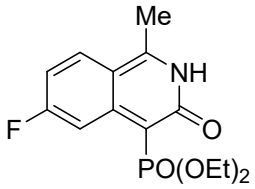
Synthesis of isoquinolin-3(*2H*)-ones



1g, 1h **2a** **3ga', 3ha'**

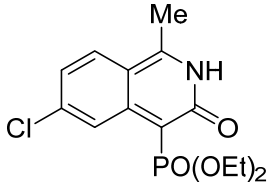
To a 13 × 150 mm test tube equipped with magnetic stir bar were added $[Cp^*RhCl_2]_2$ (2.5 mg, 2 mol %), $AgBF_4$ (3.2 mg, 8 mol %) and HOAc (12.0 mg, 0.2 mmol,1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1g** or **1h** (0.2 mmol, 1 equiv) and **2a** (75.0 mg, 0.3 mmol, 3 equiv) in DCE (2 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80℃) for 12 h. Then the reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 1/1).

Diethyl (6-fluoro-1-methyl-3-oxo-2,3-dihydroisoquinolin-4-yl)phosphonate(3ga'):



The title compound was obtained as yellow solid in 51% yield (32.0 mg). **Melting point**: 83-85 °C. **^{1}H NMR (500 MHz, DMSO)** δ 12.41 (s, 1H), 8.22 (t, *J* = 6.5 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 4.12 – 4.04 (m, 2H), 4.03 – 3.94 (m, 1H), 2.84 (s, 3H), 1.21 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 175.26 (d, *J* = 4.9 Hz), 166.23, 165.73 (d, *J* = 10.5 Hz), 164.52 (d, *J* = 253.5 Hz), 140.37 (dd, *J* = 11.6, 7.1 Hz), 129.77 (d, *J* = 10.6 Hz), 120.51 (d, *J* = 9.0 Hz), 114.55, 114.35, 108.84 (dd, *J* = 23.6, 4.7 Hz), 63.00 (d, *J* = 4.7 Hz), 22.82, 16.14 (d, *J* = 6.7 Hz). **^{31}P NMR (202 MHz, $CDCl_3$)** δ 23.17. **HRMS (ESI)** calcd. for $C_{14}H_{18}FNO_4P$: $[M+H]^+$, 314.0952. Found: m/z 314.0951.

Diethyl (6-chloro-1-methyl-3-oxo-2,3-dihydroisoquinolin-4-yl)phosphonate (3ha'):



The title compound was obtained as yellow solid in 52% yield (34.3 mg). **Melting point**: 108-110 °C. **^{1}H NMR (400 MHz, DMSO)** δ 12.43 (s, 1H), 8.56 (s, 1H), 8.15 (d, *J* = 8.9 Hz, 1H), 7.37 (d, *J* = 8.9 Hz, 1H), 4.15 – 4.05 (m, 2H), 4.05 – 3.95 (m, 2H), 2.85 (s, 3H), 1.21 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR (101 MHz, DMSO)** δ 164.90, 163.38, 142.14, 138.33, 130.25, 124.09, 123.18, 123.15, 119.63, 62.53, 62.48, 21.49, 16.60, 16.54. **^{31}P NMR (202 MHz, DMSO)** δ 20.18. **HRMS (ESI)** calcd. for $C_{14}H_{18}ClNO_4P$: $[M+H]^+$, 330.0656. Found: m/z 330.0654.

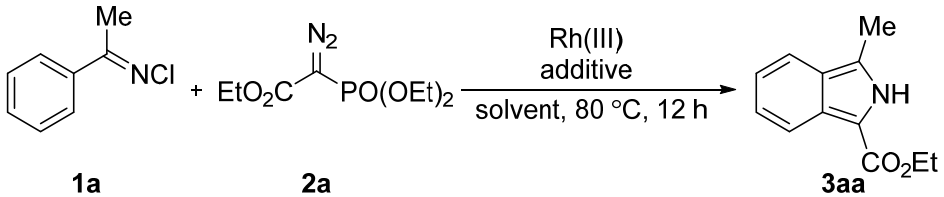
Synthesis of 3aa on a 1 mmol Scale

To a 50 mL pressure tube equipped with magnetic stir bar were added $[Cp^*RhCl_2]_2$ (6.2 mg, 1 mol %), $AgBF_4$ (7.8 mg, 4 mol %) and NaOAc (82.0 mg, 1 mmol, 1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1a** (153.6 mg, 1 mmol, 1 equiv) and **2a** (375.0 mg, 3 mmol, 1.5 equiv) in DCE (10 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. Then the reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 5/1). Off-white solid was obtained **3aa** (184.9 mg, 91%)

Results and Discussion

Optimization of Reaction Conditions

Table S1. Optimization of Reaction Conditions[a,b]



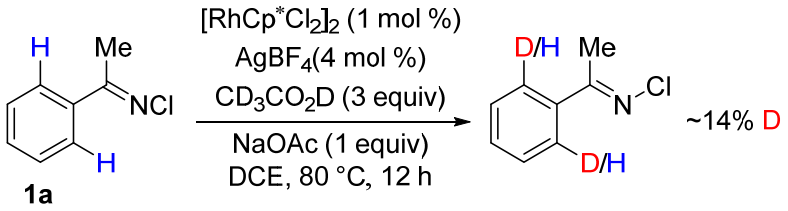
1a **2a** **3aa**

entry	Rh (III) (mol %)	Ag Salt (mol %)/ additive (equiv)	solvent	yield (%)
1	$[RhCp^*Cl_2]_2$ (2)	$AgSbF_6$ (8) /HOAc (1)	DCE	0
2	$[RhCp^*Cl_2]_2$ (2)	$AgSbF_6$ (8) /NaOAc (1)	DCE	64
3	$[RhCp^*Cl_2]_2$ (2)	$AgSbF_6$ (8) /AgOAc (1)	DCE	0
4	$[RhCp^*Cl_2]_2$ (2)	NaOAc (1)	DCE	0
5	$[RhCp^*Cl_2]_2$ (2)	$AgSbF_6$ (8)	DCE	trace
6	$[RhCp^*Cl_2]_2$ (2)	$AgSbF_6$ (8) /NaOAc (0.5)	DCE	trace
7	$[RhCp^*Cl_2]_2$ (2)	$AgSbF_6$ (8) /NaOAc (2)	DCE	39
8	$[RhCp^*Cl_2]_2$ (2)	$AgSbF_6$ (8) /LiOAc (1)	DCE	trace
9	$[RhCp^*Cl_2]_2$ (2)	$AgSbF_6$ (8) /CsOAc (1)	DCE	trace
10	$[RhCp^*Cl_2]_2$ (2)	$AgSbF_6$ (8) /KOAc (1)	DCE	20
11	$[RhCp^*Cl_2]_2$ (2)	$AgSbF_6$ (8) /NaOAc (1)	MeOH	0
12	$[RhCp^*Cl_2]_2$ (2)	$AgSbF_6$ (8) /NaOAc (1)	MeCN	0
13	$[RhCp^*Cl_2]_2$ (2)	$AgSbF_6$ (8) /NaOAc (1)	THF	34
14	$[RhCp^*Cl_2]_2$ (2)	$AgSbF_6$ (8) /NaOAc (1)	TFE	trace
15	$[RhCp^*Cl_2]_2$ (2)	$AgSbF_6$ (8) /NaOAc (1)	1,4-dioxane	0
16	$[RhCp^*Cl_2]_2$ (2)	$AgBF_4$ (8) /NaOAc (1)	DCE	84
17	$[RhCp^*Cl_2]_2$ (2)	AgO_2CCF_3 (8) /NaOAc (1)	DCE	0
18	$[RhCp^*(OAc)_2]_2$ (2)	NaOAc (1)	DCE	0
19	$[RhCp^*(MeCN)_3](SbF_6)_2$ (4)	NaOAc (1)	DCE	79
20	-	$AgBF_4$ (8) /NaOAc (1)	DCE	0
21	$[RhCp^*Cl_2]_2$ (1)	$AgBF_4$ (4) /NaOAc (1)	DCE	91
22	$[RhCp^*Cl_2]_2$ (0.5)	$AgBF_4$ (2) /NaOAc (1)	DCE	71

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), solvent (2 mL).

[b] Isolated yields.

Hydrogen-Deuterium Scrambling Experiments



To a 13 × 150 mm test tube equipped with magnetic stir bar were added $[Cp^*RhCl_2]_2$ (1.2 mg, 1 mol %), $AgBF_4$ (1.6 mg, 4 mol %) and NaOAc (16.4 mg, 0.2 mol, 1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1a** (31.7 mg, 0.2 mmol, 1 equiv) and CD_3CO_2D (37.2 mg, 0.6 mmol, 3 equiv) in DCE (2 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 °C) for 12 h. Then the reaction mixture was cooled to room temperature and isolated on silica gel (*n*-hexane/EtOAc = 40/1) to give **1a** as transparent liquid (25.9 mg, 82%).

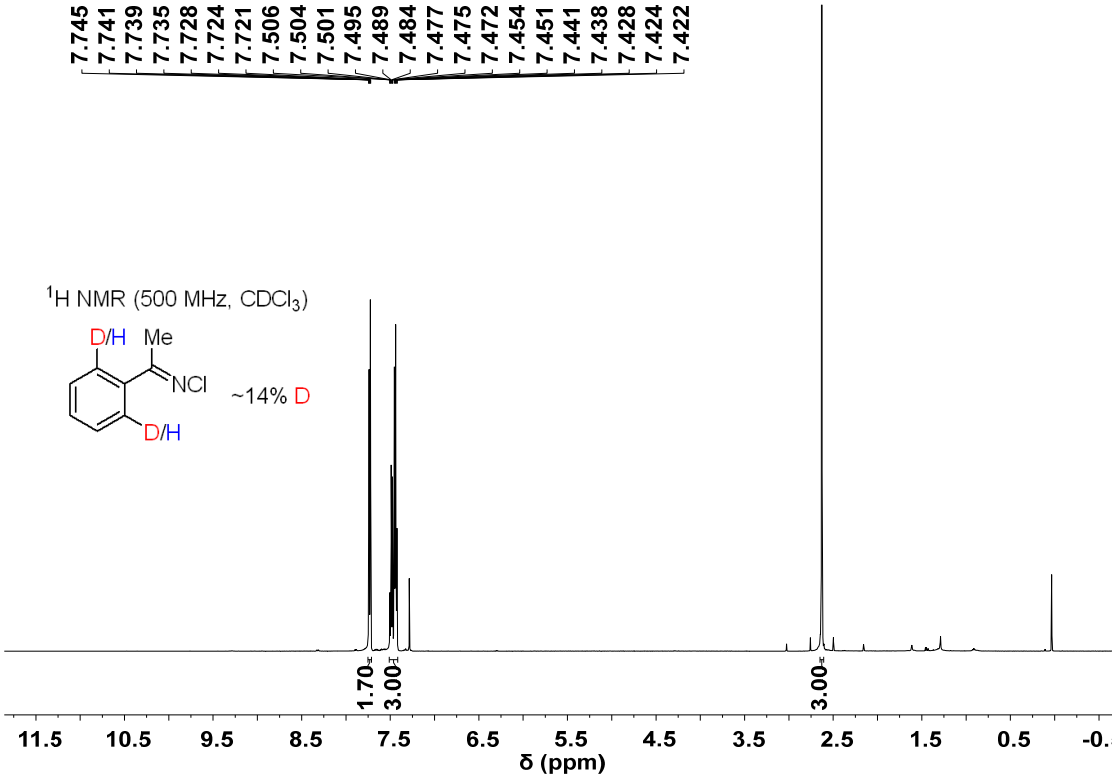
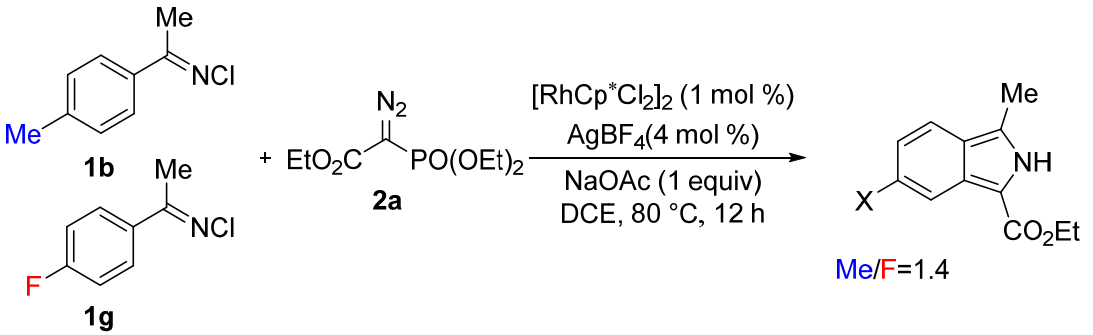


Figure S1.^{1}H NMR (500 MHz, $CDCl_3$) spectrum for the products of equation above.

Competition Experiment



To a 13 × 150 mm test tube equipped with magnetic stir bar were added [Cp*$RhCl_2$]$_2$ (1.2 mg, 1 mol %), $AgBF_4$ (1.6 mg, 4 mol %) and NaOAc (16.4 mg, 0.2 mol, 1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1b** (33.5 mg, 0.2 mmol, 1 equiv), **1g** (34.3 mg, 0.2 mmol, 1 equiv) and **2a** (50.0 mg, 0.2 mmol, 1.5 equiv) in DCE (2 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 °C) for 12 h. Then the reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 5/1). The mixture product was subjected to ^{1}H NMR.

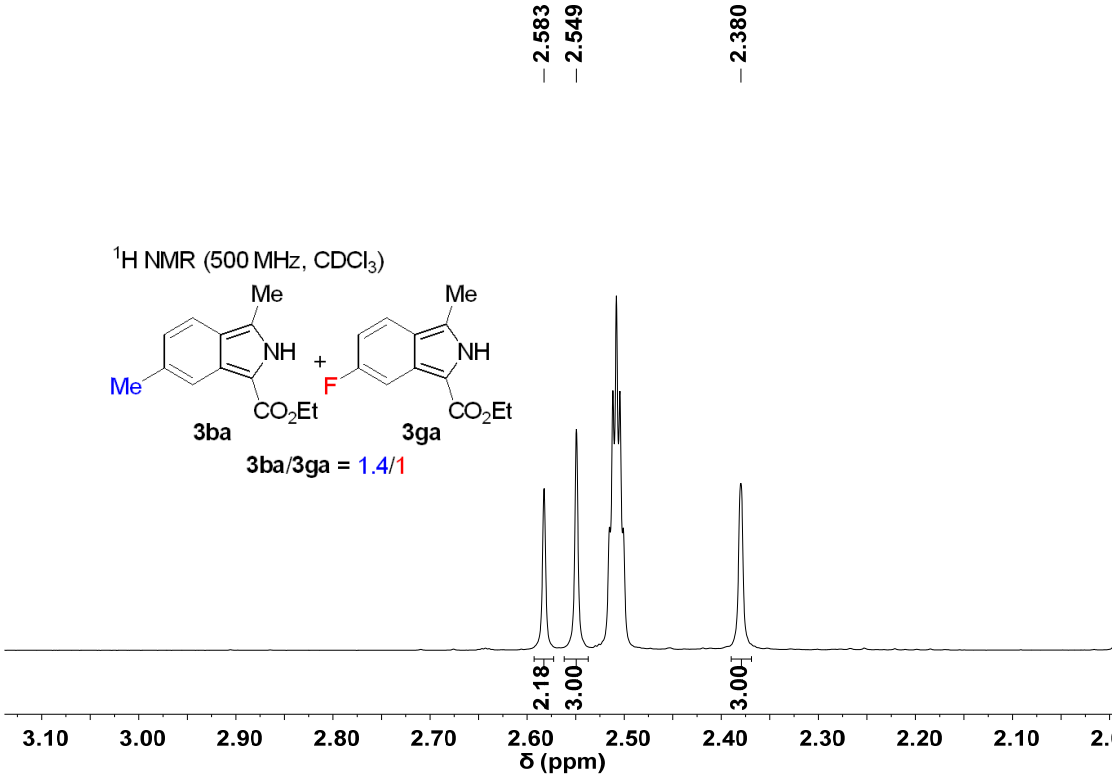
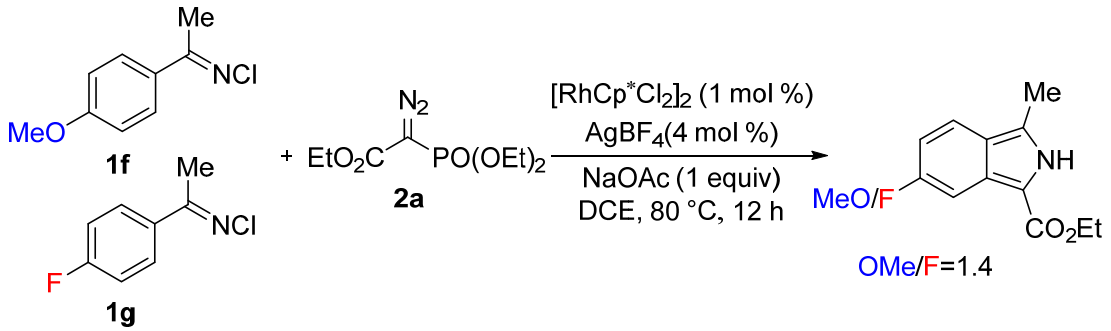


Figure S2. ^{1}H NMR (500 MHz, DMSO) spectrum for the mixture products of the equation above.



To a 13 × 150 mm test tube equipped with magnetic stir bar were added $[Cp^*RhCl_2]_2$ (1.2 mg, 1 mol %), $AgBF_4$ (1.6 mg, 4 mol %) and NaOAc (16.4 mg, 0.2 mmol, 1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1f** (36.7 mg, 0.2 mmol, 1 equiv), **1g** (34.3 mg, 0.2 mmol, 1 equiv) and **2a** (50.0 mg, 0.2 mmol, 1 equiv) in DCE (2 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 °C) for 12 h. Then the reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 5/1). The mixture product was subjected to ^{1}H NMR.

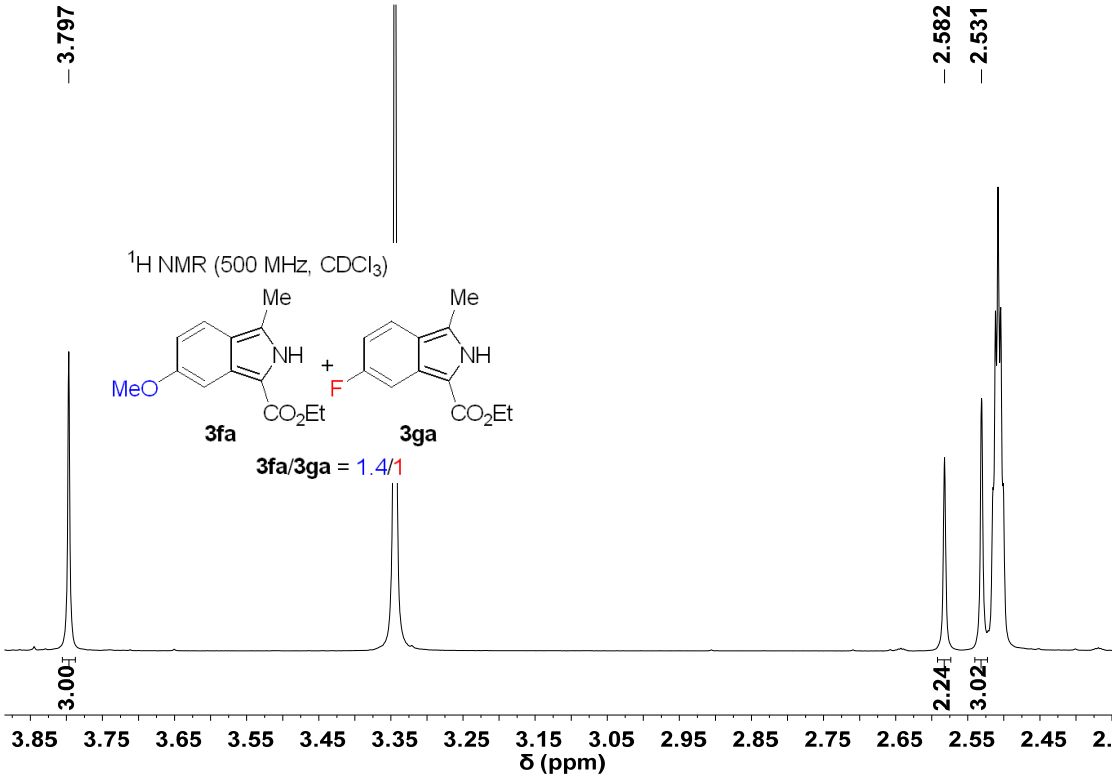
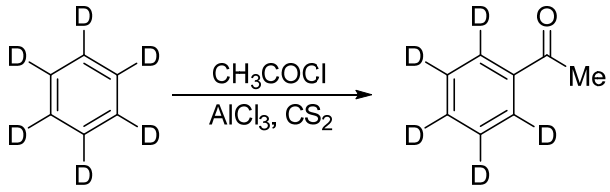
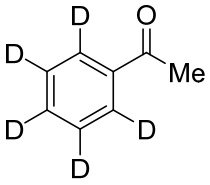


Figure S3. ^{1}H NMR (500 MHz, DMSO) spectrum for the mixture products of the equation above.

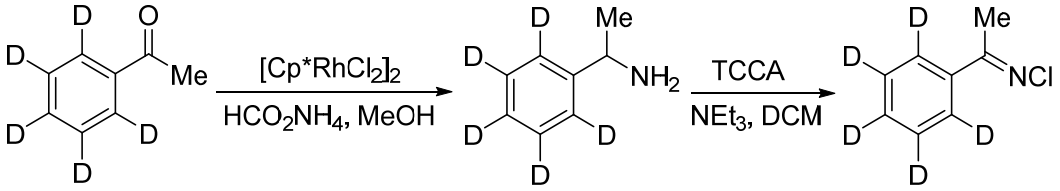
Kinetic Isotope Effect Experiments

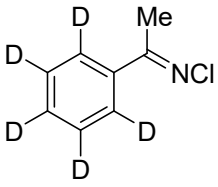
Preparation of 1-(phenyl-*d*$_5$)ethan-1-one substrate:





1-(phenyl-*d*$_5$)ethan-1-one: The title compound was synthesized according to a literature-reported procedure.[4] A solution of anhydrous CS_2 (10 mL) containing $[D]_6$-Benzene (2.4 ml, 25.6 mmol) and $AlCl_3$ (4.3 g, 32 mmol) were added to a 50 mL flask under N_2 atmosphere. To the mixture was dropwise added a solution of acetyl chloride (2.5 g, 32 mmol) in anhydrous CS_2 (10 mL) at 0 ℃. The resulting mixture was allowed to warm up to ambient temperature and was stirred for 5 h. Then the mixture was heated to 50 ℃ for 3 h. After cooling to ambient temperature, the resulting mixture was poured into ice water and extracted with CH_2Cl_2 (10 × 30 mL). The organic layer was washed with saturated aqueous Na_2CO_3 (60 mL) and brine (40 mL), and then dried over Na_2SO_4. After concentration under reduced pressure, purification by column chromatography on silica gel (*n*-hexane/EtOAc = 20/1) afforded 1-(phenyl-*d*$_5$)ethan-1-one (2.5 g, 78%) as colorless oil.

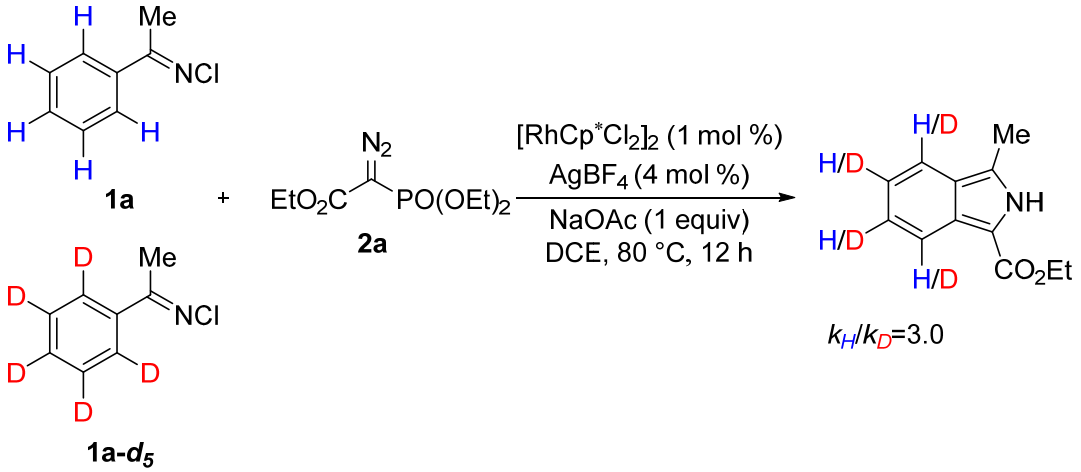




***N*-chloro-1-(phenyl-*d*$_5$)ethan-1-imine (1a-*d*$_5$):** The title compound was synthesized according to a literature-reported procedure. [1,2] Acetophenone (2.5 g, 20 mmol) and CH_3OH (20 mL) were added to a 250 mL Schlenk tube containing $[RhCp^*Cl_2]_2$ (61.8 mg, 100 μmol) and HCO_2NH_4 (6.4 g, 100 mmol). The brown mixture was frozen, and the whole system was evacuated. The system was closed and then stirred at 70 °C for 7 h. After the dark green resulting solution was cooled to room temperature, 1 M aqueous HCl solution (38.4 mL) was added, and the mixture was washed twice with CH_2Cl_2 (5 mL) to remove the neutral compounds. After addition of a cold 12 M aqueous NaOH solution (3.6 mL) to the aqueous layer, the mixture was extracted six times with CH_2Cl_2 (12 mL). The combined organic layers were dried over anhydrous Na_2SO_4. Filtration and evaporation under reduced pressure gave crude 1-(phenyl-*d5*)ethan-1-amine, which was used without purification. All the crude 1-(phenyl-*d5*)ethan-1-amine was dissolved in dichloromethane (50 mL), and TCCA (trichloroisocyanuric acid) (3.2 g, 14 mmol) was added in a 250 mL round-bottom flask at 0°C. Then, the mixture was stirred at ambient temperature during 1 h. Triethylamine (6.0 g, 0.06 mol) dissolved in dichloromethane (50 mL) was added, and the resulting mixture was washed with water (200 mL) and hydrochloric acid (1 M, 200 mL) successively. The organic layer was dried over anhydrous sodium sulfate. After concentration under reduced pressure, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 40/1) afforded **1a-*d*$_5$** (2.5g, 79%) as transparent liquid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 2.63 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ

177.11, 137.04, 130.39 (dd, J = 43.4, 18.3 Hz), 128.20 (dd, J = 42.6, 18.2 Hz), 126.62 (dd, J = 42.3, 17.8 Hz), 20.68. **HRMS (EI)** calcd. for $C_8H_3D_5ClN$: $[M]^+$, 158.0659. Found: m/z 158.0657.

Determination of intermolecular kinetic isotope effect:



To a 13 × 150 mm test tube equipped with magnetic stir bar were added $[Cp^*RhCl_2]_2$ (1.2 mg, 1 mol %), $AgBF_4$ (1.6 mg, 4 mol %) and NaOAc (16.4 mg, 0.2mmol, 1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1a** (30.7 mg, 0.2 mmol, 1 equiv), **1a-*d*$_5$** (31.7 mg, 0.2 mmol, 1 equiv) and **2a** (50.0 mg, 0.2 mmol, 1 equiv) in DCE (2 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. Then the reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 5/1). The mixture product was subjected to ^{1}H NMR.

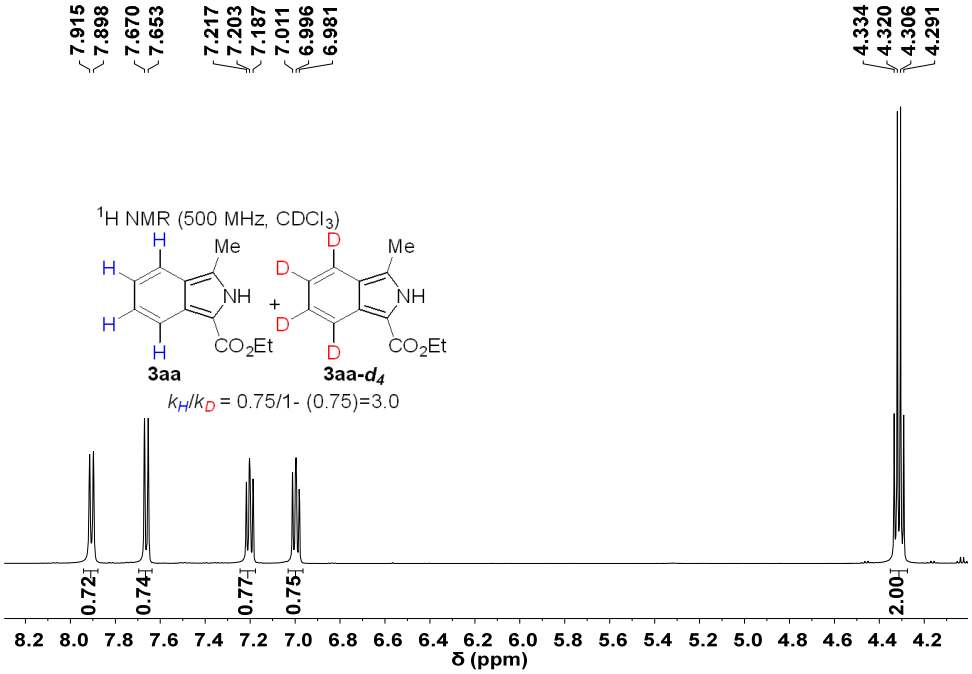
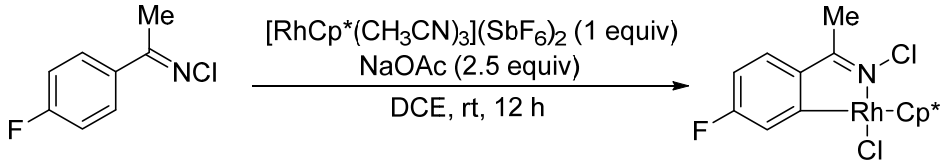


Figure S4. ^{1}H NMR (500 MHz, DMSO) spectrum for the mixture products of the equation above.

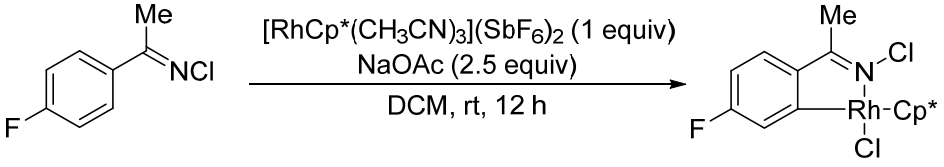
Synthesis and Characterization of Rh(III) Intermediates

Synthesis of 1g-Rh-Cl:



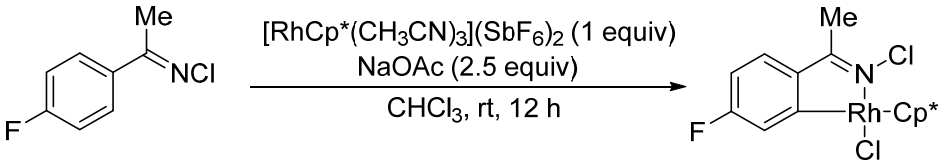
1g **1g-Rh-Cl**

To a 13 × 150 mm test tube equipped with magnetic stir bar were added $[RhCp^*(CH_3CN)_3](SbF6)_2$ (166.4 mg, 0.2 mmol, 1 equiv), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1g** (34.3 mg, 0.2 mmol, 1 equiv) in DCE (2 mL) was injected into the test tube via syringe. The reaction mixture was placed at ambient temperature for 12 h. Then the reaction mixture was isolated on silica gel to give **1g-Rh-Cl** as yellow solid (38.9 mg, 44%).



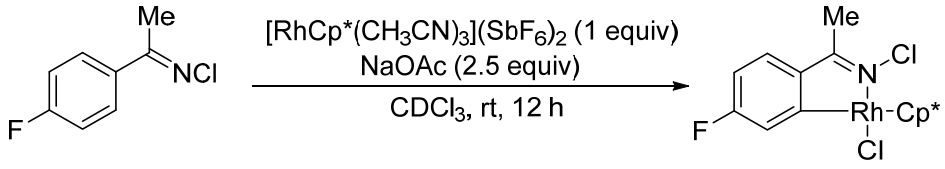
1g **1g-Rh-Cl**

To a 13 × 150 mm test tube equipped with magnetic stir bar were added $[RhCp^*(CH_3CN)_3](SbF6)_2$ (166.4 mg, 0.2 mmol, 1 equiv), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1g** (34.3 mg, 0.2 mmol, 1 equiv) in DCM (2 mL) was injected into the test tube via syringe. The reaction mixture was placed at ambient temperature for 12 h. Then the reaction mixture was isolated on silica gel to give **1g-Rh-Cl** as yellow solid (39.6 mg, 45%).



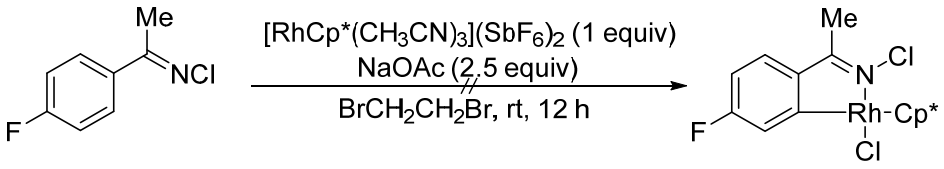
1g **1g-Rh-Cl**

To a 13 × 150 mm test tube equipped with magnetic stir bar were added $[RhCp^*(CH_3CN)_3](SbF6)_2$ (166.4 mg, 0.2 mmol, 1 equiv), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1g** (34.3 mg, 0.2 mmol, 1 equiv) in $CHCl_3$ (2 mL) was injected into the test tube via syringe. The reaction mixture was placed at ambient temperature for 12 h. Then the reaction mixture was isolated on silica gel to give **1g-Rh-Cl** as yellow solid (39.8 mg, 45%).



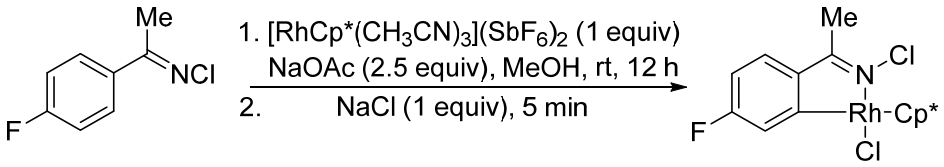
1g **1g-Rh-Cl**

To a 13 × 150 mm test tube equipped with magnetic stir bar were added $[RhCp^*(CH_3CN)_3](SbF6)_2$ (166.4 mg, 0.2 mmol, 1 equiv), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1g** (34.3 mg, 0.2 mmol, 1 equiv) in $CDCl_3$ (2 mL) was injected into the test tube via syringe. The reaction mixture was placed at ambient temperature for 12 h. Then the reaction mixture was isolated on silica gel to give **1g-Rh-Cl** as yellow solid (40.2 mg, 45%).



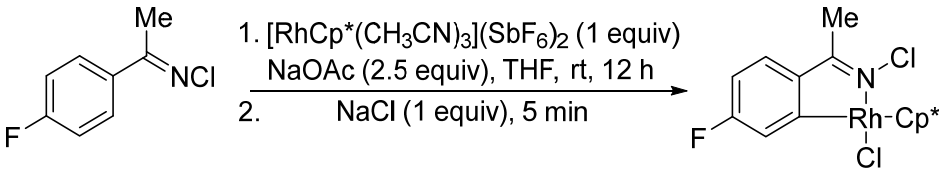
1g **1g-Rh-Cl**

To a 13 × 150 mm test tube equipped with magnetic stir bar were added $[RhCp^*(CH_3CN)_3](SbF6)_2$ (166.4 mg, 0.2 mmol, 1 equiv), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1g** (34.3 mg, 0.2 mmol, 1 equiv) in $BrCH_2CH_2Br$ (2 mL) was injected into the test tube via syringe. The reaction mixture was placed at ambient temperature for 12 h. There was no **1g-Rh-Cl** observed.



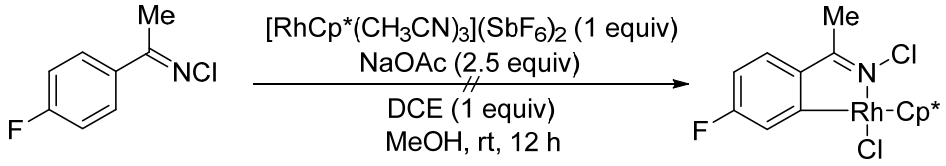
1g **1g-Rh-Cl**

To a 13 × 150 mm test tube equipped with magnetic stir bar were added $[RhCp^*(CH_3CN)_3](SbF6)_2$ (166.4 mg, 0.2 mmol, 1 equiv), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1g** (34.3 mg, 0.2 mmol, 1 equiv) in MeOH (2 mL) was injected into the test tube via syringe. The reaction mixture was placed at ambient temperature for 12 h. Then to the test tube containing the reaction mixture was added with NaCl (11.7 mg, 0.2 mmol, 1 equiv). The reaction mixture was stirred for additional 5 min. Then the reaction mixture was isolated on silica gel to give **1g-Rh-Cl** as yellow solid (24.7 mg, 28%).



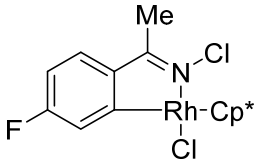
1g **1g-Rh-Cl**

To a 13 × 150 mm test tube equipped with magnetic stir bar were added $[RhCp^*(CH_3CN)_3](SbF_6)_2$ (166.4 mg, 0.2 mmol, 1 equiv), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1g** (34.3 mg, 0.2 mmol, 1 equiv) in THF (2 mL) was injected into the test tube via syringe. The reaction mixture was placed at ambient temperature for 12 h. Then to the test tube containing the reaction mixture was added with NaCl (11.7 mg, 0.2 mmol, 1 equiv). The reaction mixture was stirred for additional 5 min. Then the reaction mixture was isolated on silica gel to give **1g-Rh-Cl** as yellow solid (33.6 mg, 38%).



1g **1g-Rh-Cl**

To a 13 × 150 mm test tube equipped with magnetic stir bar were added $[RhCp^*(CH_3CN)_3](SbF6)_2$ (166.4 mg, 0.2 mmol, 1 equiv), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1g** (34.3 mg, 0.2 mmol, 1 equiv) in MeOH (2 mL) and equivalent DCE (19.8 mg, 0.2 mmol, 1 equiv) was injected into the test tube via syringe. The reaction mixture was placed at ambient temperature for 12 h. There was no **1g-Rh-Cl** observed.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.45 (dd, *J* = 8.5, 5.3 Hz, 1H), 6.80 – 6.74 (m, 1H), 2.64 (s, 3H), 1.71 (s, 15H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 185.61 (dd, *J* = 33.1, 5.0 Hz), 184.14 (d, *J* = 2.6 Hz), 163.51 (dd, *J* = 258.4, 1.6 Hz), 138.11, 129.17 (d, *J* = 9.2 Hz), 122.34 (d, *J* = 18.1 Hz), 110.21 (d, *J* = 23.4 Hz), 97.17 (d, *J* = 6.4 Hz), 18.68, 9.28. **HRMS (MALDI-TOF, positive)** calcd. for $C_{18}H_{21}ClFNRh$: $[M\text{-}Cl]^+$, 408.0380. Found: m/z 408.0490.

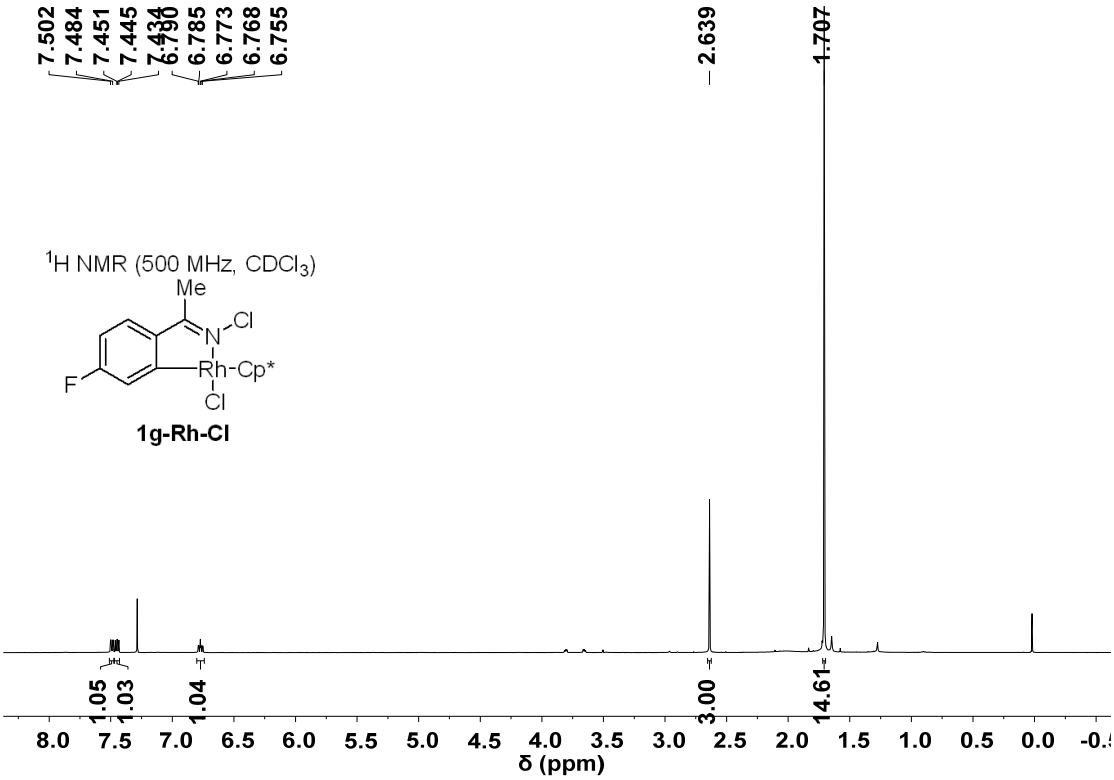


Figure S5 ^{1}H NMR spectrum for **1g-Rh-Cl**.

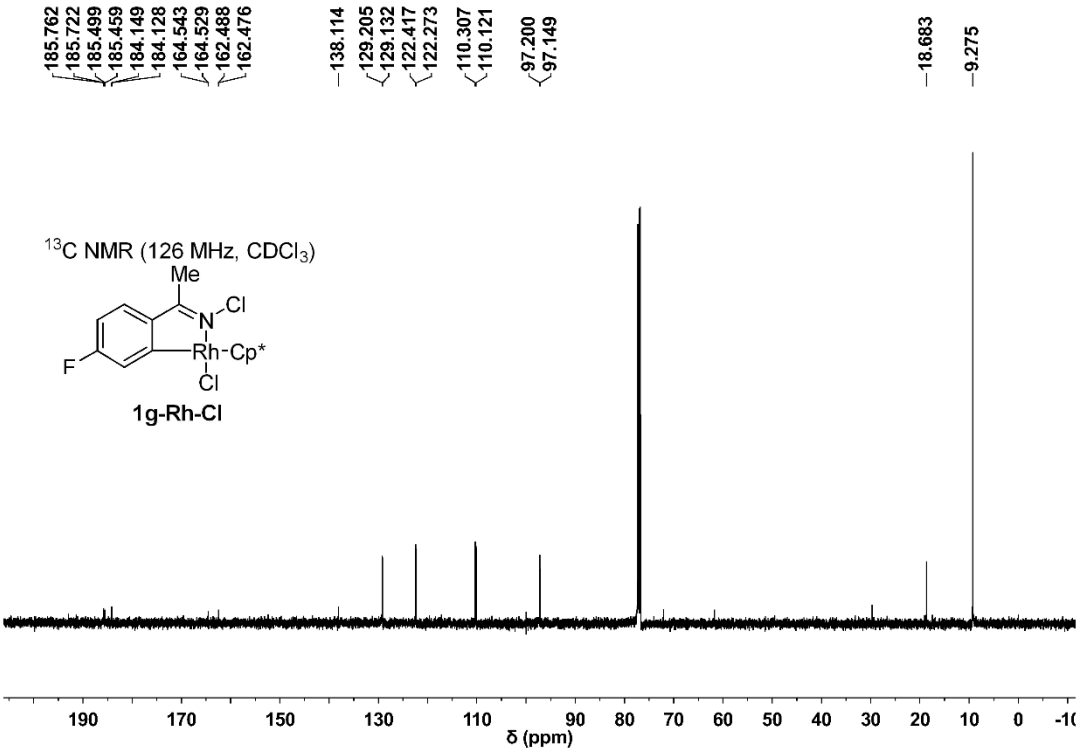


Figure S6 ^{13}C NMR spectrum for **1g-Rh-Cl**.

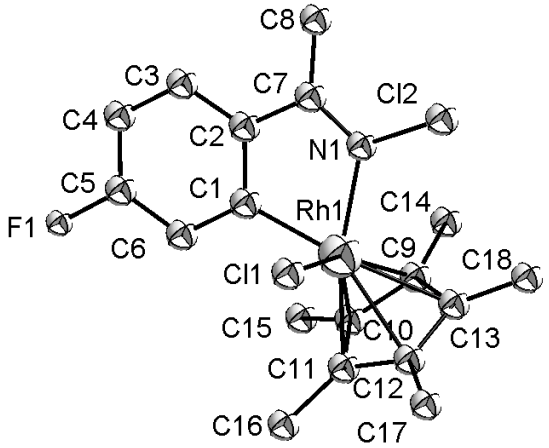
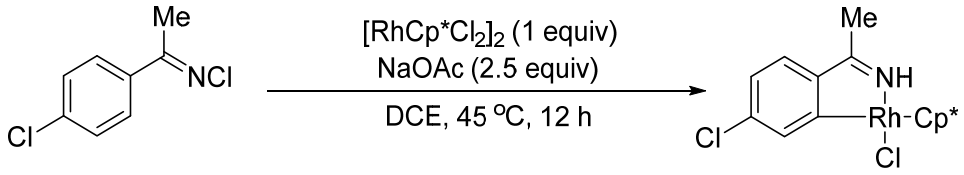


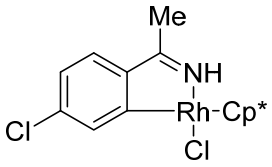
Figure S7 ORTEP drawing of **1g-Rh-Cl** showing 30% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity. CCDC# at the Cambridge Crystallographic Data Center: 1858042.

Synthesis of 1h-Rh-Cl:



1h **1h'-Rh-Cl**

To a 13 × 150 mm test tube equipped with magnetic stir bar were added $[RhCp^*Cl_2]_2$ (61.8 mg, 0.1 mmol, 0.5 equiv), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1h** (37.6 mg, 0.2 mmol, 1 equiv) in DCE (2 mL) was injected into the test tube via syringe. The reaction mixture was placed at 45 °C for 12 h. Then the reaction mixture was isolated on silica gel (EtOAc) to give **1h'-Rh-Cl** as yellow solid (21.2 mg, 25%). The breaking of N-Cl bond is likely due to the presence of Rh-bound Cl^- ligand in $[RhCp^*Cl_2]_2$.



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.74 (s, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.00 (dd, *J* = 8.1, 1.8 Hz, 1H), 2.46 (s, 3H), 1.68 (s, 15H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 185.63, 185.37, 183.83, 144.25, 136.92, 135.91, 128.42, 122.65, 95.80, 95.75, 22.53 (d, *J* = 1.9 Hz), 9.33. **HRMS (MALDI-TOF, positive)** calcd. for $C_{18}H_{22}ClNRh$: $[M\text{-}Cl]^+$, 390.0500. Found: m/z 390.0490.

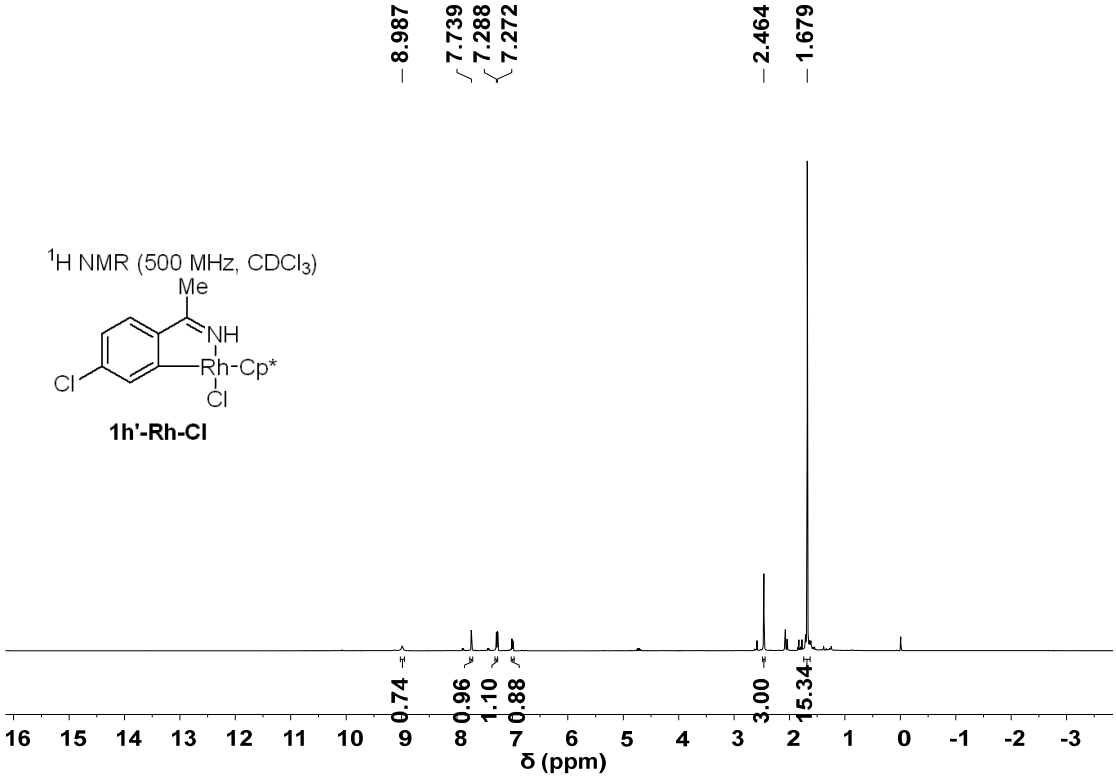


Figure S8 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **1h'-Rh-Cl**.

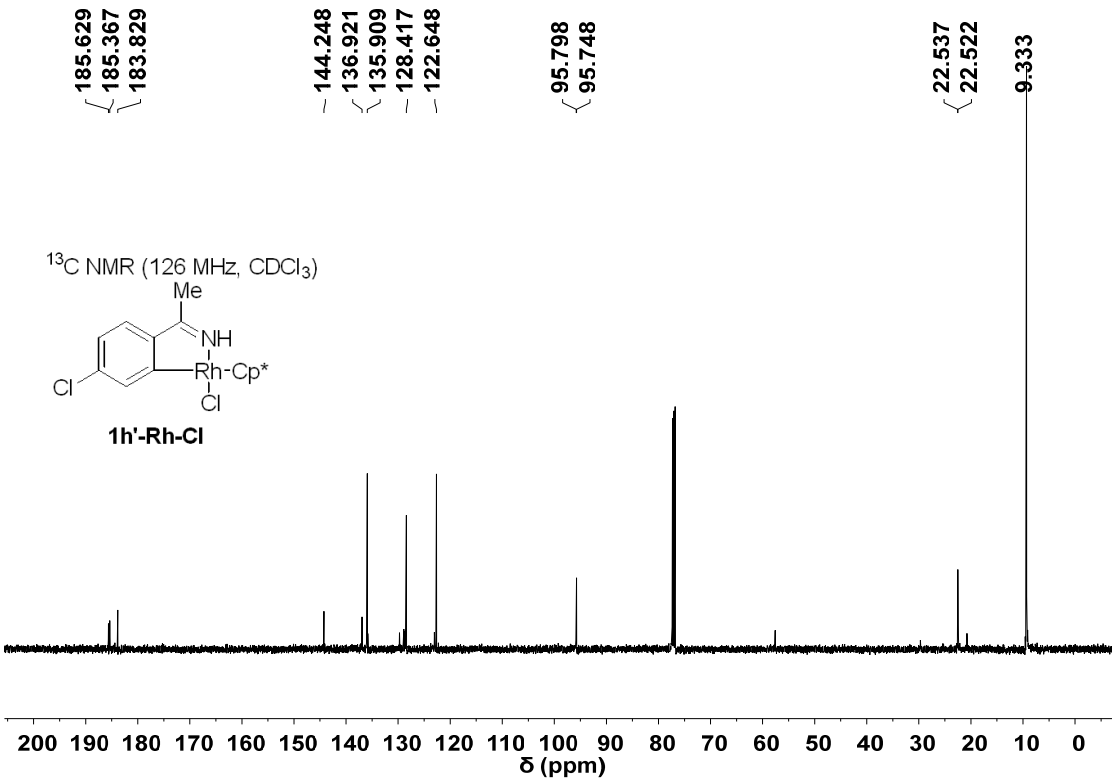


Figure S9 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum for **1h'-Rh-Cl**.

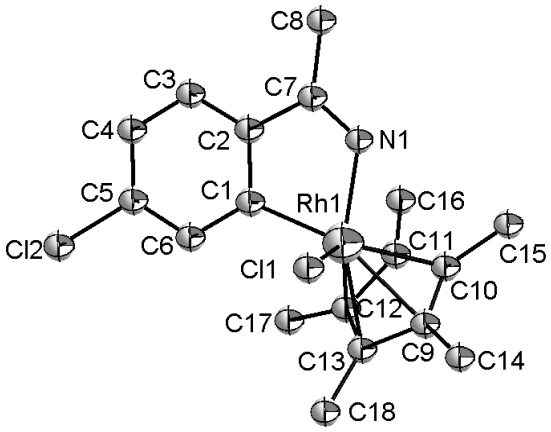
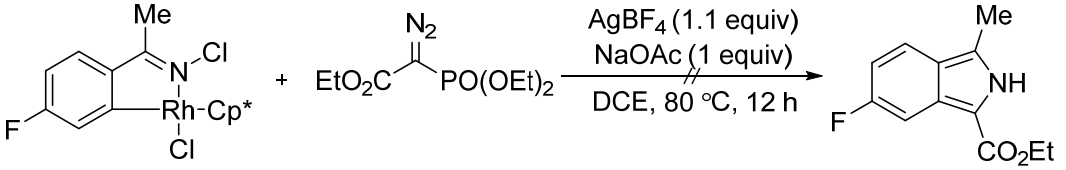


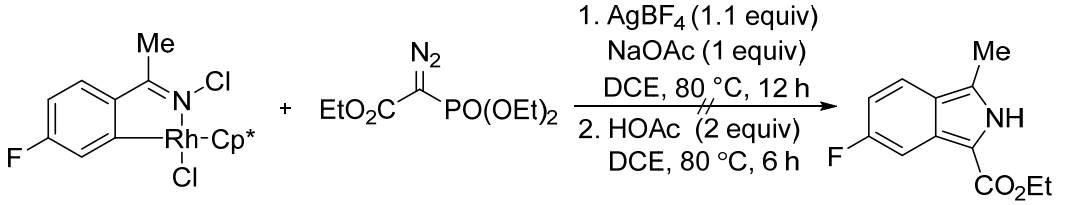
Figure S10 ORTEP drawing of **1h'-Rh-Cl** showing 30% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity. CCDC# at the Cambridge Crystallographic Data Center: 1858398.

Mechanism Experiments



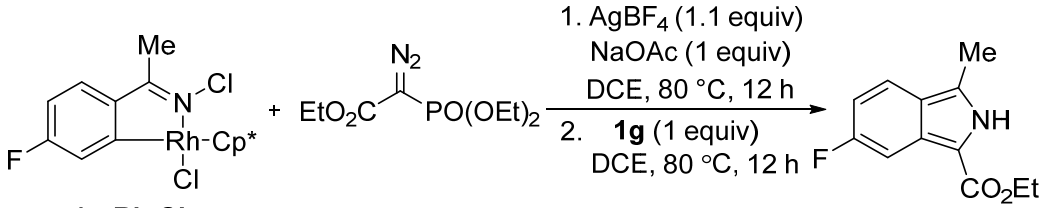
1g-Rh-Cl **2a** **3ga**: trace

To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1g-Rh-Cl** (22.1 mg, 0.05 mmol, 1 equiv), $AgBF_4$ (10.7 mg, 0.055 mmol, 1.1 equiv) and NaOAc (4.1 mg, 0.05 mmol, 1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **2a** (18.7 mg, 0.075 mmol, 1.5 equiv) in DCE (1 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. Only minimal amounts of **3ga** was observed.



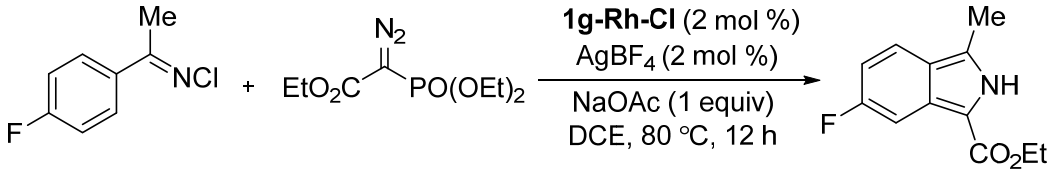
1g-Rh-Cl **2a** **3ga**: trace

To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1g-Rh-Cl** (22.1 mg, 0.05 mmol, 1 equiv), $AgBF_4$ (10.7 mg, 0.055 mmol, 1.1 equiv) and NaOAc (4.1 mg, 0.05 mmol, 1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **2a** (18.7 mg, 0.075 mmol, 1.5 equiv) in DCE (1 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. Added HOAc (6.0 mg, 0.1 mmol, 2 equiv) into the test tube, the mixture was stirred at 80 ℃ for 6 h. Only minimal amounts of **3ga** was observed.



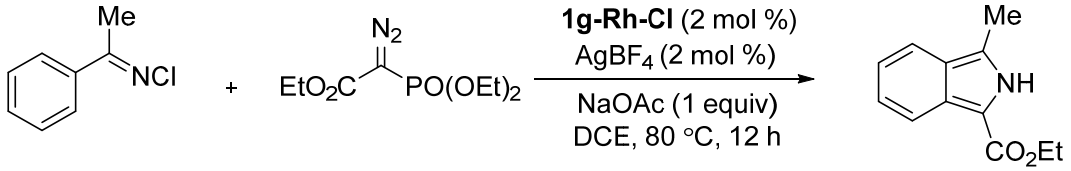
1g-Rh-Cl **2a** **3ga**: trace

To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1g-Rh-Cl** (22.1 mg, 0.05 mmol, 1 equiv), $AgBF_4$ (10.7 mg, 0.055 mmol, 1.1 equiv) and NaOAc (4.1 mg, 0.05 mmol, 1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **2a** (18.7 mg, 0.075 mmol, 1.5 equiv) in DCE (1 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. Added **1g** (8.6 mg, 0.05 mmol, 1 equiv) into the test tube, the mixture was stirred at 80 ℃ for 12 h. Only minimal amounts of **3ga** was observed



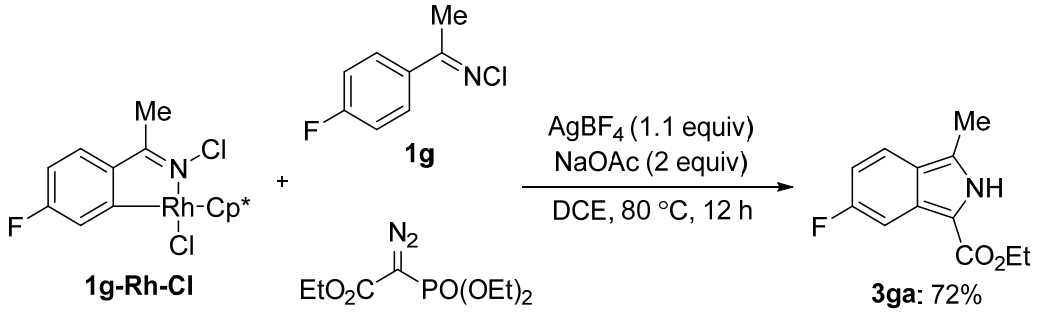
1g **2a** **3ga**: 54%

To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1g** (34.3 mg, 0.2 mmol, 1 equiv), **1g-Rh-Cl** (1.8 mg, 2 mol %), $AgBF_4$ (0.8 mg, 2 mol %) and NaOAc (16.4 mg, 0.2 mmol,1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **2a** (75.0 mg, 0.3 mmol, 1.5 equiv) in DCE (2 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 °C) for 12 h. Then the reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 5/1) to give the **3ga** (29 mg) in 54% as white solid.



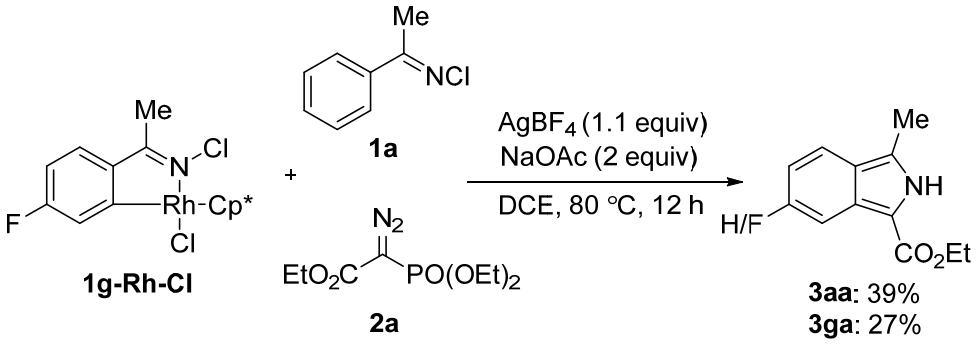
1a **2a** **3aa**: 79%

To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1a** (31.7 mg, 0.2 mmol, 1 equiv), **1g-Rh-Cl** (1.8 mg, 2 mol %), $AgBF_4$ (0.8 mg, 2 mol %) and NaOAc (16.4 mg, 0.2 mmol,1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **2a** (75.0 mg, 0.3 mmol, 1.5 equiv) in DCE (2 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 °C) for 12 h. Then the reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 5/1) to give the products **3aa** (32.1 mg) in 79% as white solid.

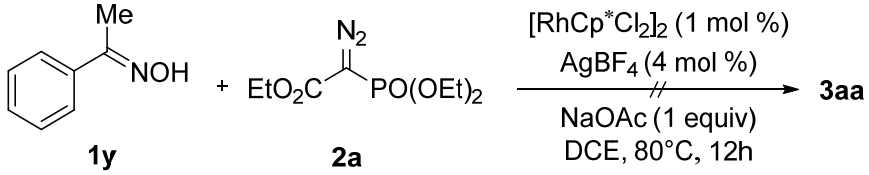


3ga: 72%

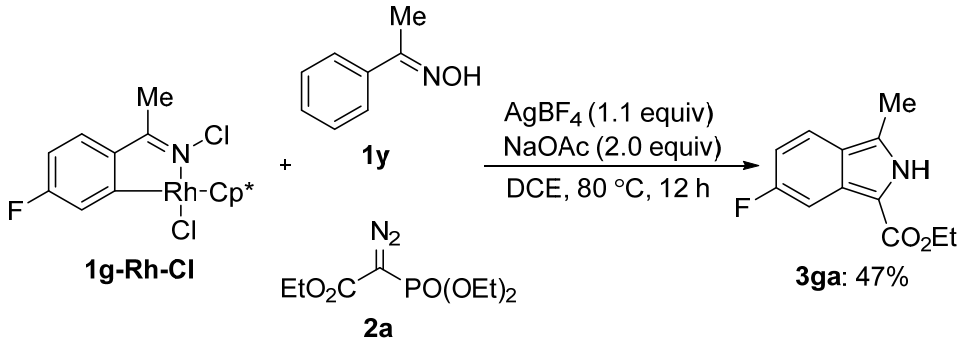
To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1g-Rh-Cl** (22.1 mg, 0.05 mmol, 1 equiv), $AgBF_4$ (10.7 mg, 0.055 mmol, 1.1 equiv) and NaOAc (8.2 mg, 0.1 mmol, 2 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1g** (8.6 mg, 0.05 mmol, 1 equiv) and **2a** (37.5 mg, 0.15 mmol, 3.0 equiv) in DCE (1 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 °C) for 12 h. Then the reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 5/1) to give the products (**3ga**, 8.0 mg) in 72% as white solid.



To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1g-Rh-Cl** (22.1 mg, 0.05 mmol, 1 equiv), $AgBF_4$ (10.7 mg, 0.055 mmol, 1.1 equiv) and NaOAc (8.2 mg, 0.1 mmol,2 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1a** (7.9 mg,0.05 mmol, 1 equiv) and **2a** (37.5 mg, 0.15 mmol, 3.0 equiv) in DCE (1 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. Then the reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 5/1) to give the products (**3aa**, 4.0 mg; **3ga**, 3.1 mg) in 39% and 27% as white solid, respectively.

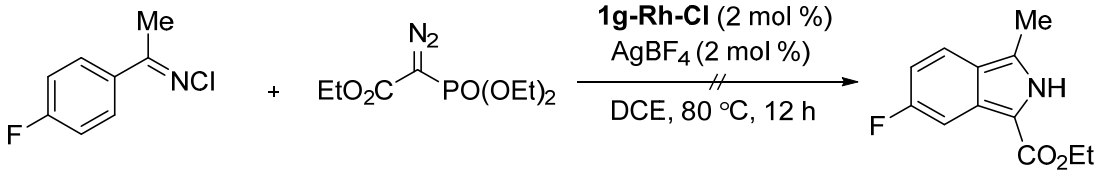


To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1y** (27.0 mg, 0.2 mmol, 1 equiv), $[Cp^*RhCl_2]_2$ (1.2 mg, 1 mol %), $AgBF_4$ (1.6 mg, 4 mol %) and NaOAc (16.4 mg, 0.2 mmol,1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **2a** (75.0 mg, 0.30 mmol, 1.5 equiv) in DCE (2 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. There is no reaction between **1y** and **2a** under the conditions.



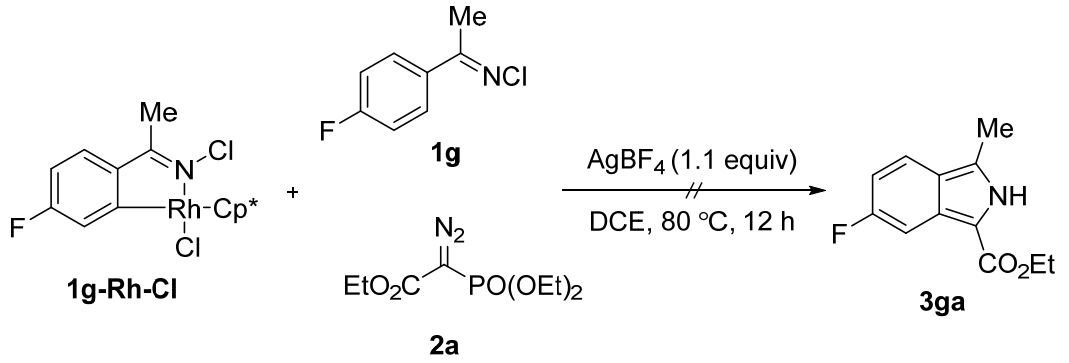
To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1y** (6.8 mg, 0.05 mmol, 1 equiv), **1g-Rh-Cl** (22.1 mg, 0.055 mmol, 1 equiv), $AgBF_4$ (10.7 mg, 0.55 mmol, 1.1 equiv) and NaOAc (8.2 mg, 0.1 mmol, 2 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **2a** (37.5 mg, 0.15 mmol, 3.0 equiv) in DCE (1 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. Then the reaction mixture was concentrated in vacuo, the residue was dissolved in methylene

chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 5/1) to give the products (**3ga**, 5.3 mg) in 47% as white solid.

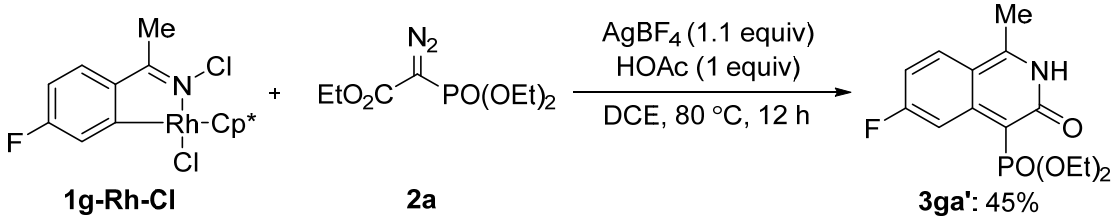


1g **2a** **3ga**

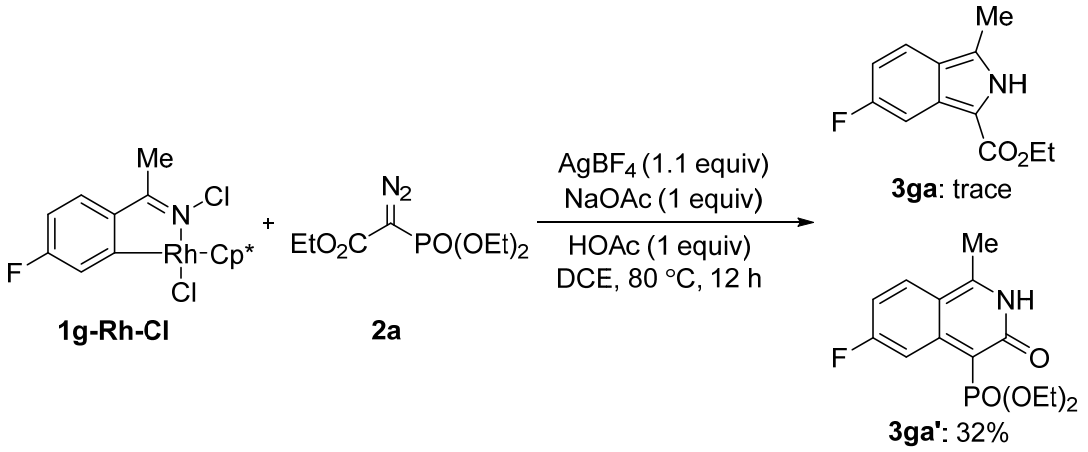
To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1g** (34.3 mg, 0.2 mmol, 1 equiv), **1g-Rh-Cl** (1.8 mg, 2 mol %) and $AgBF_4$ (0.8 mg, 2 mol %). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **2a** (75.0 mg, 0.3 mmol, 1.5 equiv) in DCE (2 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. There was no **3ga** observed.



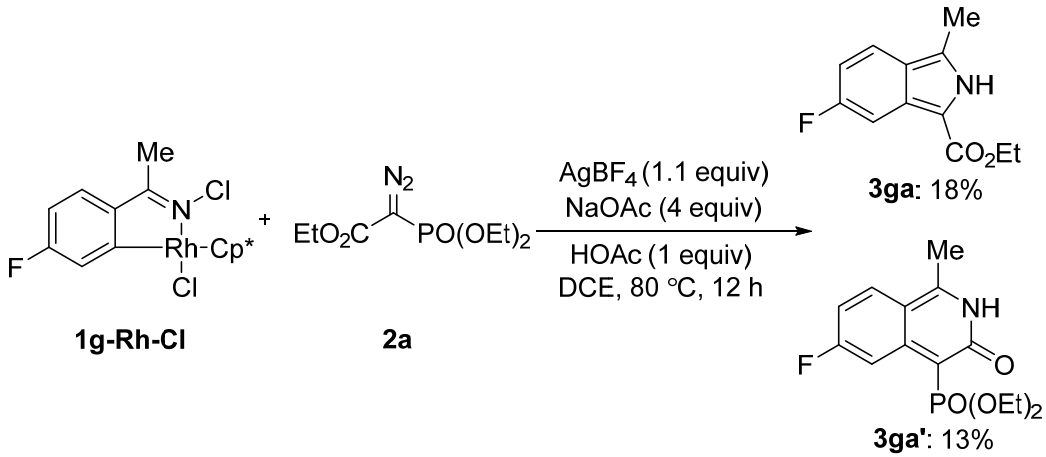
To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1g-Rh-Cl** (22.1 mg, 0.05 mmol, 1 equiv) and $AgBF_4$ (10.7 mg, 0.055 mmol, 1.1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **1g** (8.6 mg, 0.05 mmol, 1 equiv) and **2a** (37.5 mg, 0.15 mmol, 3.0 equiv) in DCE (1 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. There was no **3ga** observed.



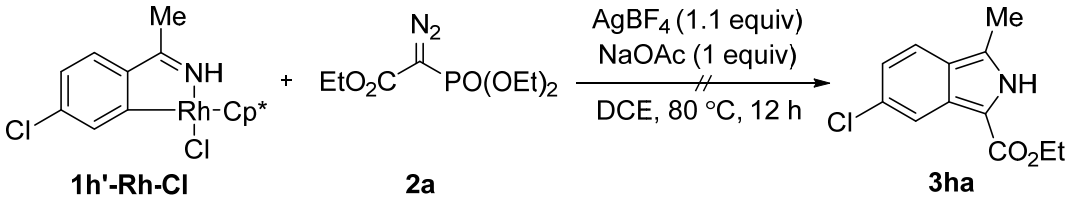
To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1g-Rh-Cl** (22.1 mg, 0.05 mmol, 1 equiv), $AgBF_4$ (10.7 mg, 0.055 mmol, 1.1 equiv) and HOAc (3.0 mg, 0.05 mmol, 1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **2a** (18.7 mg, 0.075 mmol, 1.5 equiv) in DCE (1 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. Then the reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 1/1) to give the products (**3ga'**, 7.2 mg) in 45% as white solid.



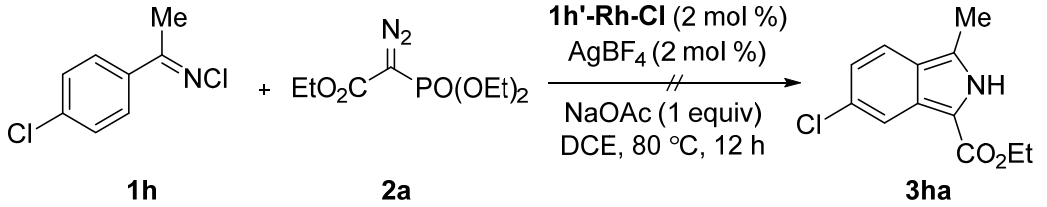
To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1g-Rh-Cl** (22.1 mg, 0.05 mmol, 1 equiv), $AgBF_4$ (10.7 mg, 0.055 mmol, 1.1 equiv), NaOAc (4.1 mg, 0.05 mmol, 1 equiv) and HOAc (3.0 mg, 0.05 mmol, 1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **2a** (18.7 mg, 0.075 mmol, 1.5 equiv) in DCE (1 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. Then the reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 1/1) to give the products (**3ga'**, 5.1 mg) in 32% as yellow solid and only minimal amounts of **3ga** was observed.



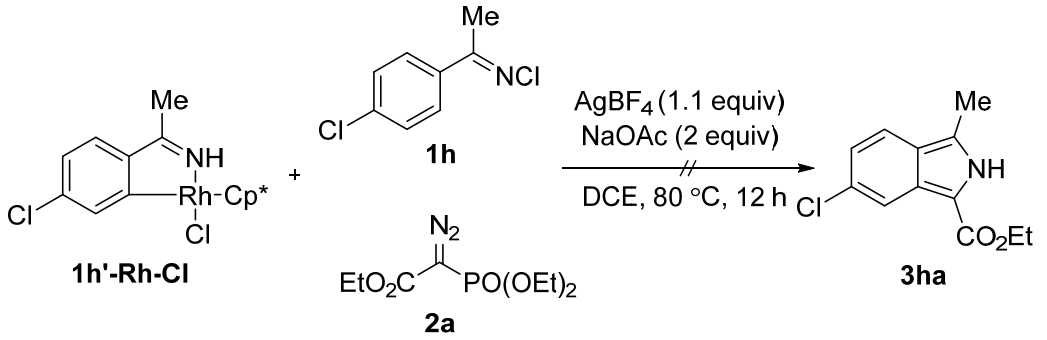
To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1g-Rh-Cl** (22.1 mg, 0.05 mmol, 1 equiv), $AgBF_4$ (10.7 mg, 0.055 mmol, 1.1 equiv), NaOAc (16.4 mg, 0.2 mmol, 4 equiv) and HOAc (3.0 mg, 0.05 mmol, 1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **2a** (18.7 mg, 0.075 mmol, 1.5 equiv) in DCE (1 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. Then the reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 5/1) to give the **3ga** (2.0 mg) in 18% as white solid and (silica gel, *n*-hexane/EtOAc = 1/1) to give the **3ga'** (2.0 mg) in 13% as yellow solid.



To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1h'-Rh-Cl** (21.2 mg, 0.05mmol), $AgBF_4$ (10.7 mg, 0.055 mmol, 1.1 equiv) and NaOAc (4.1 mg, 0.05 mmol,1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of and **2a** (18.7 mg, 0.30 mmol, 1 equiv) in DCE (2 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. There was no **3ha** observed.

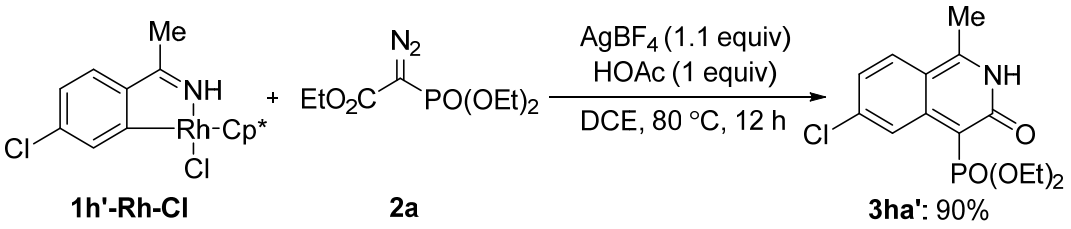


To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1h** (37.6 mg, 0.2 mmol, 1 equiv), **1h'-Rh-Cl** (1.6 mg, 2 mol %), $AgBF_4$ (0.8 mg, 2 mol %) and NaOAc (16.4 mg, 0.2 mmol, 1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **2a** (75.0 mg, 0.3 mmol, 1.5 equiv) in DCE (2 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. There was no **3ha** observed.



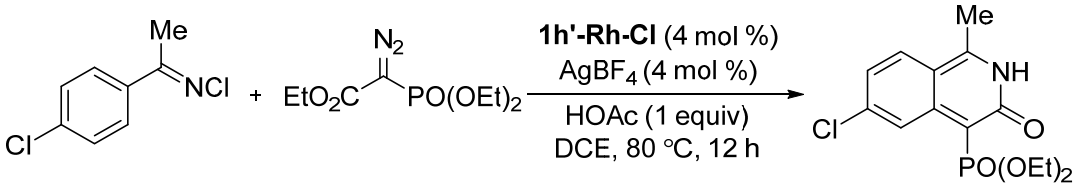
To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1h** (9.4 mg, 0.05 mmol, 1 equiv), **1h'-Rh-Cl** (21.2 mg, 0.05 mmol, 1 equiv), $AgBF_4$ (10.7 mg, 0.055 mmol, 1.1 equiv) and NaOAc (8.2 mg, 0.1 mmol, 2 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **2a** (37.5 mg, 0.15 mmol, 3.0 equiv) in DCE (1 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. There was no **3ha** observed.

Molecular Weight: 329.72



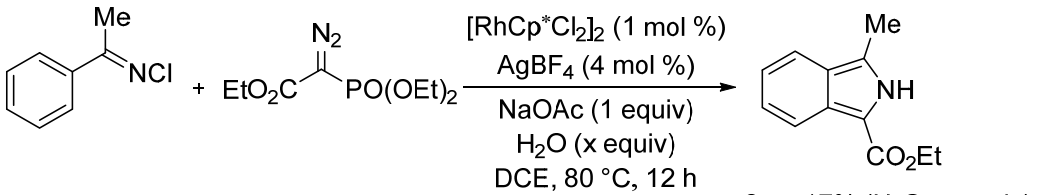
1h'-Rh-Cl **2a** **3ha'**: 90%

To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1h'-Rh-Cl** (21.2 mg, 0.05 mmol, 1 equiv), $AgBF_4$ (10.7 mg, 0.055 mmol, 1.1 equiv), and HOAc (3.0 mg, 0.05 mmol, 1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **2a** (18.7 mg, 0.075 mmol, 1.5 equiv) in DCE (1 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. Then the reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 1/1) to give the **3ha'** (14.8 mg) in 90% as yellow solid.



1h **2a** **3ha'**: 35%

To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1h** (37.6 mg, 0.2 mmol, 1 equiv), **1h'-Rh-Cl** (1.6 mg, 4 mol %), $AgBF_4$ (0.8 mg, 4 mol %) and NaOAc (16.4 mg, 0.2 mmol, 1 equiv). The test tube was sealed with a rubber septum and removed from the glove-box. The solution of **2a** (75.0 mg, 0.3 mmol, 1.5 equiv) in DCE (2 mL) was injected into the test tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. Then the reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 1/1) to give the **3ha'** (22.9 mg) in 35% as yellow solid



1a **2a**

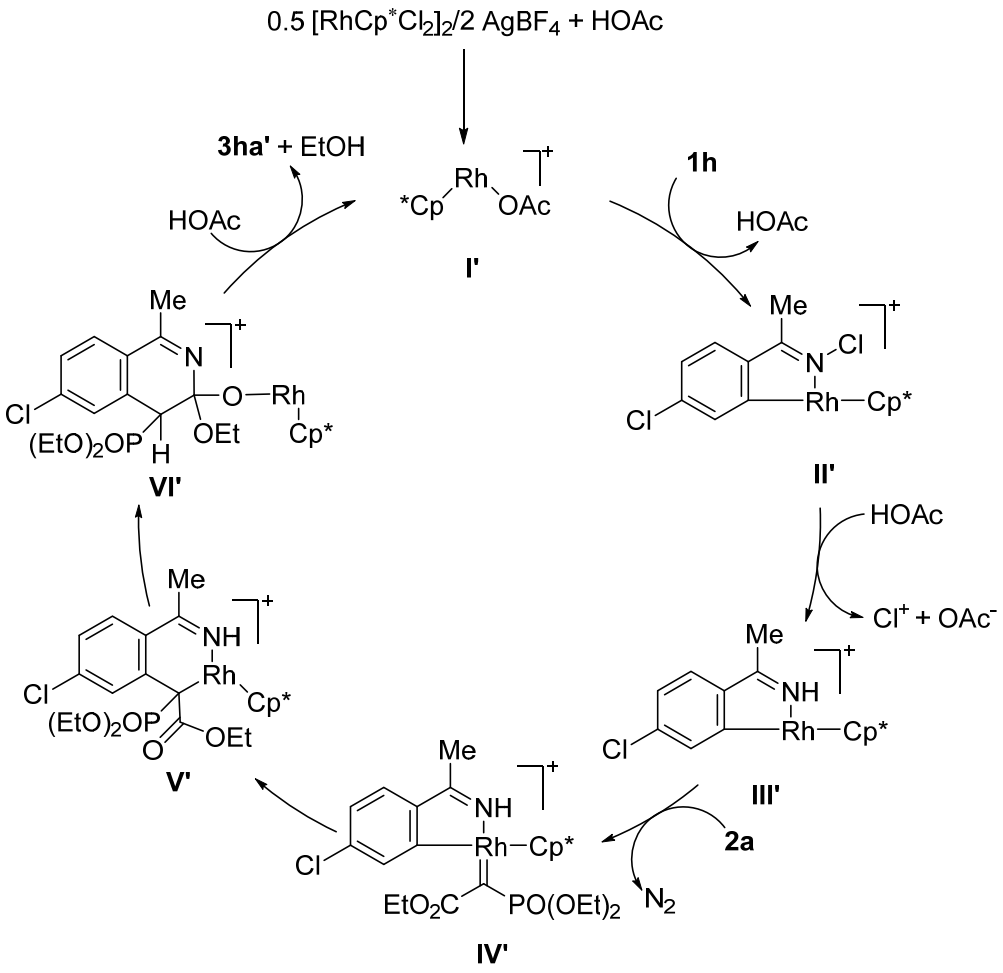
3aa: 17% (H_2O, 1 equiv)
7% (H_2O, 0.5 equiv)
7% (H_2O, 0.25 equiv)

To three 13 × 150 mm test tubes, every tube equipped with magnetic stir bar were added $[Cp^*RhCl_2]_2$ (1.2 mg, 1 mol %), $AgBF_4$ (1.6 mg, 4 mol %) and NaOAc (16.4 mg, 0.2 mmol, 1 equiv). The test tubes were sealed with rubber septums and removed from the glove-box. The H_2O (3.6 mg, 0.2 mmol, 1 equiv), (1.8 mg, 0.1 mmol, 0.5 equiv) and (0.9 mg, 0.05 mmol, 0.25 equiv) was injected into the three test tubes via microsyringe, respectively. The solution of **1a** (31.7 mg, 0.2 mmol, 1equiv), **2a** (75.0 mg, 0.30 mmol, 1.5 equiv) in DCE (2 mL) was injected into every test

tube via syringe. The reaction mixture was placed in a pre-heated oil bath (80 ℃) for 12 h. Then the reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 5/1) offered **3aa** (6.8 mg, 17%), (2.8 mg, 7%), (2.7 mg, 7%), respectively.

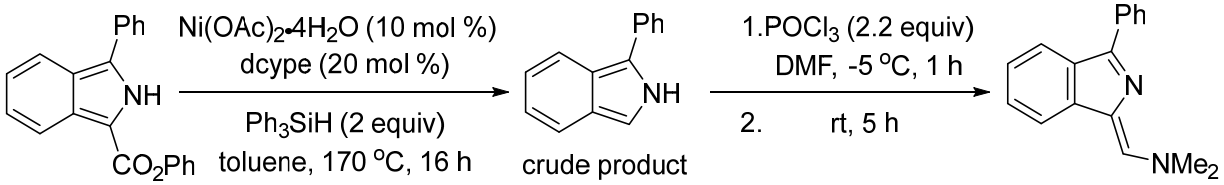
Proposed Reaction Pathway of Isoquinolin-3(*2H*)-ones

First, the reactive cationic Rh(III) species **I'** is generated with the assistance of $AgBF_4$. Subsequently, Rh(III) species **I'** coordinates to substrate **1h**, and C-H bond cleavage forms **II'**. Then proton of HOAc replace the Cl^+ to give the **III'**. The reaction with the diazo compound might then occur to give the metal–carbene intermediate **IV'** by extrusion of N_2. After migratory insertion to provide **V'**, rearrangement and nucleophilic addition to the ester carbonyl group occurs in the presence of Lewis acidic Rh(III) to give **VI'**. Finally, elimination of the ethyoxyl group from **VI'** and proton transfer gives the **3ha'** with regeneration of the catalyst.



Deesterification of 3wd and Exploitation of Reactivity of C3 and N2 Ring Atoms for Attachment of Structurally Distinct Appendages

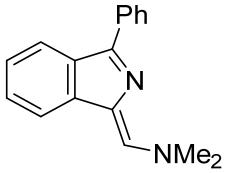
Synthesis of *N,N*-Dimethyl-1-(3-phenyl-*1H*-isoindol-1-ylidene)methanamine[5,6]



3wd **4** **5**

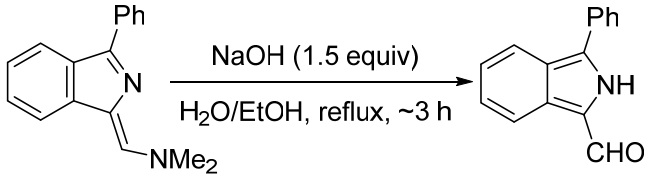
To a 25 mL Schleck tube equipped with magnetic stir bar were added **3wd** (125.3 mg, 0.4 mmol, 1 equiv), $Ni(OAc)_2 \cdot 4H_2O$ (9.6 mg, 10 mol %), dcype (33.8 mg, 20 mol %), Ph_3SiH (208.3 mg, 0.8 mmol, 2 equiv) and exchanged with N_2 three times, then toluene (2 ml) was added. The reaction mixture was placed in a pre-heated oil bath (170 ℃) for 16 h. Then the reaction mixture was evacuated by oil pump and gave the **4** of crude product, the residue was dissolved in dimethylformamide (1 mL). Phosphoryl chloride (100 mg) was added to dimethylformamide (0.5 ml) with stirring (-5 to -10 ℃; N_2). The **4** of crude product in dimethylformamide (1 ml) was added dropwise, and the mixture was stirred at -5 ℃ for 1 h, then at room temperature for 5 h. The mixture was poured into saturated sodium hydrogencarbonate (25 ml) with stirring, washed with water and extracted three times with ethyl acetate (20 mL). The combined organic layers were dried over anhydrous Na_2SO_4. Filtration and evaporation under reduced pressure, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 3/1) to give **5** in 63% yield (62.6 mg) as yellow solid.

***N,N*-Dimethyl-1-(3-phenyl-*1H*-isoindol-1-ylidene)methanamine (5):[6]**



The title compound was obtained as yellow solid in 63% yield (62.6 mg). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.21 – 8.15 (m, 2H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.54 (dd, *J* = 10.7, 4.7 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.31 – 7.25 (m, 1H), 3.88 (s, 3H), 3.17 (S, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 153.97, 142.49, 139.23, 137.13, 131.48, 128.52, 127.92, 127.79, 125.66, 124.81, 122.80, 121.23, 116.25, 46.74, 40.87.

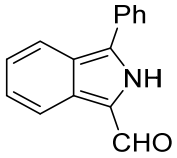
Synthesis of 3-Phenyl-*2H*-isoindole-1-carbaldehyde[6]



5 **6**

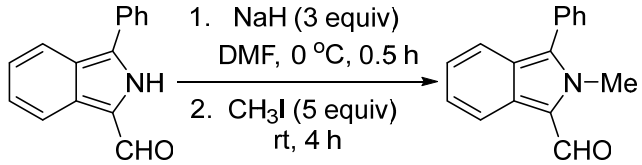
5 (49.7 mg, 0.2 mmol), ethanol (4 mL), and sodium hydroxide (0.3 mL of a 4% aqueous solution) were added into flask and refluxed under N_2 for 3.25 h. The solvent was removed under reduced pressure, the residue being dissolved in dichloromethane (10 mL) and washed with water (2 x 15 mL), the washings being back extracted with dichloromethane. The combined organic solutions were dried Na_2SO_4), and evaporated. The residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 3/1) to give **6** in 70% yield (31.2 mg) as yellow crystal.

3-Phenyl-*2H*-isoindole-1-carbaldehyde (6):[6]



The title compound was obtained as yellow crystal in 70% yield (31.2 mg). **^{1}H NMR (500 MHz, DMSO)** δ 13.81 (s, 1H), 9.96 (s, 1H), 8.21 (s, 1H), 8.02 (d, *J* = 7.1 Hz, 1H), 7.95 – 7.88 (m, 2H), 7.58 (t, *J* = 7.0 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.26 (s, 1H). **^{13}C NMR (126 MHz, CD_2Cl_2)** δ 173.75, 134.29, 132.38, 130.58, 129.24, 129.03, 127.89, 127.28, 123.88, 123.77, 122.11, 121.82, 117.47.

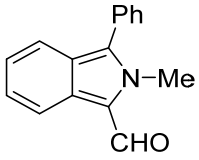
Synthesis of 2-Methyl-3-phenyl-*2H*-Isoindole-1-Carbaldehyde



6 **7**

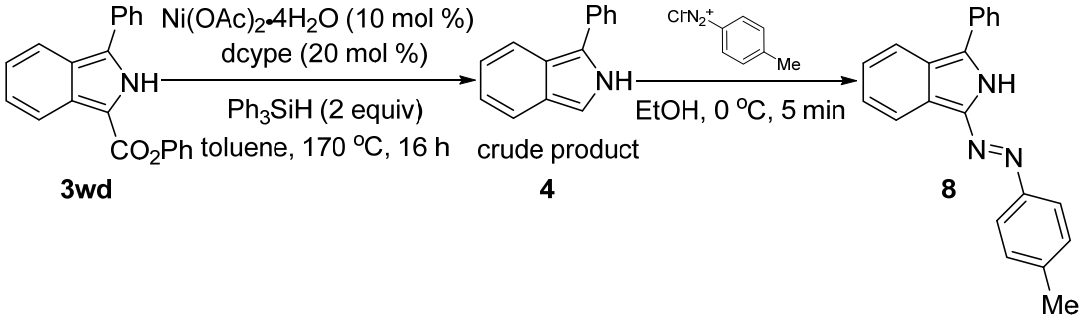
To a 15 mL Schleck tube equipped with magnetic stir bar were **6** (44.3 mg, 0.2 mmol, 1 equiv), NaH (60% dispersion in mineral oil) (0.6 mmol, 3 equiv), and exchanged with N_2 three times, then dimethylformamide (2 mL) was added. The reaction mixture was placed at 0 ℃ for 0.5 h, then added CH_3I (141.9 mg, 1 mmol, 5 equiv) at room temperature for 4 h. The mixture was poured into water (50 mL) and extracted three times with ethyl acetate (20 mLx3). The combined organic layers were dried over anhydrous Na_2SO_4. Filtration and evaporation under reduced pressure, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 3/1) to give **7** in 99% yield (46.7 mg) as yellow solid.

2-Methyl-3-phenyl-*2H*-isoindole-1-carbaldehyde (7):



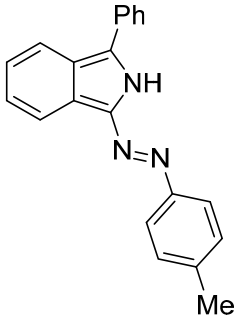
The title compound was obtained as yellow oil in 68% yield (46.7 mg). **Melting point**: 161-163 °C. **^{1}H NMR (500 MHz, CD_3CN)** δ 10.09 (s, 1H), 8.07 (s, 1H), 7.74 – 7.45 (m, 7H), 7.38 – 7.33 (m, 1H), 7.19 – 7.12 (m, 1H), 4.13 (s, 3H). **^{1}H NMR (400 MHz, DMSO)** δ 10.11 (s, 1H), 8.18 (s, 1H), 7.68 – 7.57 (m, 5H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.18 (ddd, *J* = 8.2, 6.7, 0.8 Hz, 1H), 4.17 (s, 3H). **^{13}C NMR (101 MHz, CD_2Cl_2)** δ 174.43, 136.64, 132.78, 130.34, 129.26, 129.17, 128.95, 128.60, 126.76, 124.27, 123.05, 120.79, 116.32, 35.65. **HRMS (ESI)** calcd. for $C_{16}H_{14}ON$: $[M+H]^+$, 236.1070. Found: m/z 236.10660.

Synthesis of 1-Phenyl-3-(*p*-tolyldiazenyl)-*2H*-isoindole[5,7]

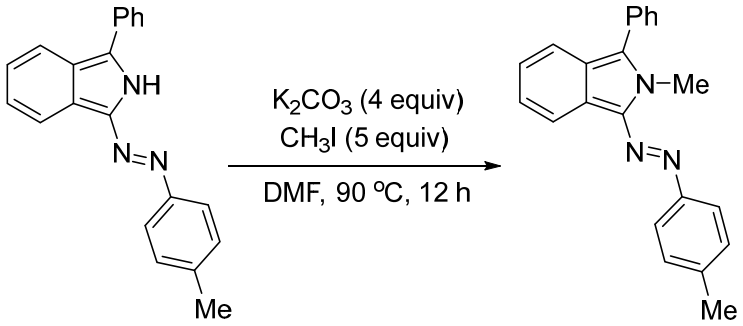


To a 25 mL Schleck tube equipped with magnetic stir bar were added **3wd** (125.3 mg, 0.4 mmol, 1 equiv), $Ni(OAc)_2 \cdot 4H_2O$ (9.6 mg, 10 mol %), dcype (33.8 mg, 20 mol %), Ph_3SiH (208.3 mg, 0.8 mmol, 2 equiv) and exchanged with N_2 three times, then toluene (2 mL) was added. The reaction mixture was placed in a pre-heated oil bath (170 °C) for 16 h. Then the reaction mixture was evacuated by oil pump and gave the **4** of crude product, the crude product was dissolved in ethanol (0.75 mL). *p*-Toluidine (61 mg) was diazotised in the normal way [concentrated HCI (0.25 mL), water (1 mL), $NaNO_2$ of aqueous solution (50 mg in 0.1 mL), 0 °C]. The **4** of crude product in ethanol (0.75 mL) was added to the stirred solution under N_2 for 5 minutes. Then a dark purple precipitate formed. The precipitate was removed by filtration and dissolved in ether (20 mL), the solution being washed with dilute hydrochloric acid (15 mL), then with aqueous sodium hydroxide (2 × 20 mL, solution goes orange), and finally with water. The ethereal solution was dried (Na_2SO_4) and taken to dryness, the oily orange residue dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 20/1) to give **8** in 68% yield (84.7 mg) as orange solid.

1-Phenyl-3-(*p*-tolyldiazenyl)-*2H*-isoindole (8):[7]



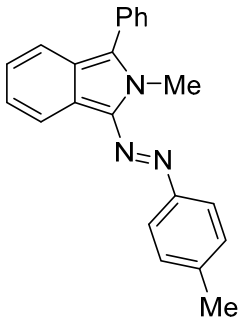
The title compound was obtained as orange solid in 68% yield (84.7 mg). **^{1}H NMR (500 MHz, Acetone)** δ 10.99 (s, 1H), 8.29 – 8.24 (m, 2H), 8.08 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.65 – 7.61 (m, 3H), 7.58 – 7.54 (m, 1H), 7.49 (t, *J* = 8.1 Hz, 3H), 7.21 (d, *J* = 8.2 Hz, 2H), 2.33 (s, 3H). **^{13}C NMR (126 MHz, Acetone)** δ 141.29, 138.74, 136.49, 134.58, 131.27, 130.78, 129.74, 129.12, 129.05, 129.01, 128.95, 128.80, 127.20, 122.88, 119.78, 114.15, 19.92.



8 **9**

To a 15 mL Schleck tube equipped with magnetic stir bar were **8** (62.3mg, 0.2 mmol, 1 equiv), K_2CO_3 (110.6 mg, 0.8 mmol, 4 equiv), and exchanged with N_2 three times, then CH_3I (141.9 mg, 1 mmol, 5 equiv) and dimethylformamide (2 mL) was added. The reaction mixture was placed at 90 °C for 12 h. The mixture was poured into water (50 mL) and extracted three times with ethyl acetate (20 mL). The combined organic layers were dried over anhydrous Na_2SO_4. Filtration and evaporation under reduced pressure, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 20/1) to give **9** in 51% yield (33.1 mg) as orange solid.

2-Methyl-1-phenyl-3-(*p*-tolyldiazenyl)-*2H*-isoindole (9):



The title compound was obtained as orange solid in 51% yield (33.1 mg). **Melting point**: 59-60 ºC. **^{1}H NMR (500 MHz, CD_3CN)** δ 8.21 (dd, *J* = 8.0, 1.6 Hz, 2H), 8.05 – 7.99 (m, 2H), 7.61 – 7.55 (m, 5H), 7.50 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.46 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 4.31 (s, 3H), 2.35 (s, 3H). **^{13}C NMR (126 MHz, CD_3CN)** δ 164.78, 147.04, 145.78, 142.49, 136.03, 135.36, 133.98, 131.22, 130.54, 129.77, 129.48, 129.10, 127.89, 122.91, 121.12, 117.90, 42.18, 20.67. **HRMS (ESI)** calcd. for $C_{22}H_{20}N_3$: $[M+H]^+$, 326.1652. Found: m/z 326.1645.

References

(1) Kitamura, M.; Lee, D.; Hayashi, S.; Tanaka, S.; Yoshimura, M. *J. Org. Chem.***2002**, *67*, 8685.
(2) Xiong, X.; Xu, X.; Zhou, Y.; Weng, C. *Russ. J. Gen. Chem.* **2013**, *83*, 2402.
(3) Müller, S.; Sasse, F.; Maier, M. E.; *Eur. J. Org. Chem.* **2014**, 1025.
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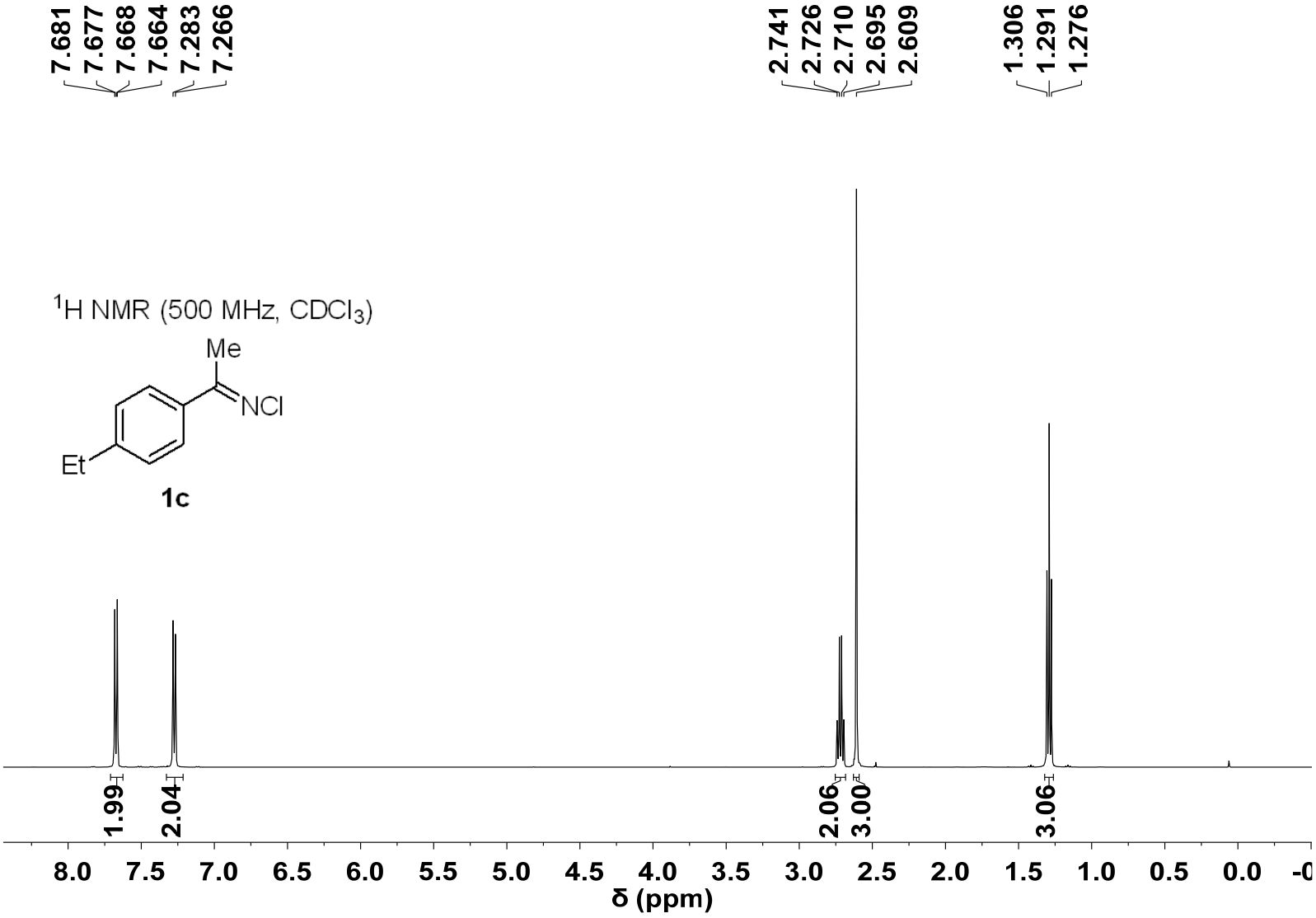
(5) Yue, H.; Guo, L.; Lee, S.-C.; Liu, X.; Rueping, M. *Angew. Chem., Int. Ed.* **2017**, *56*, 3972.
(6) Bonnett, R. M.; Hursthouse, B.; North, S. A.; Trotter, J. *J. Chem. Soc., Perkin Trans. II* **1984**, 833.
(7) Bonnett, R. North, S. A.; Newton, R. F.; Scopes, D. I. C. *Tetrahedron* **1983**, 39, 1401.

NMR Spectra of Products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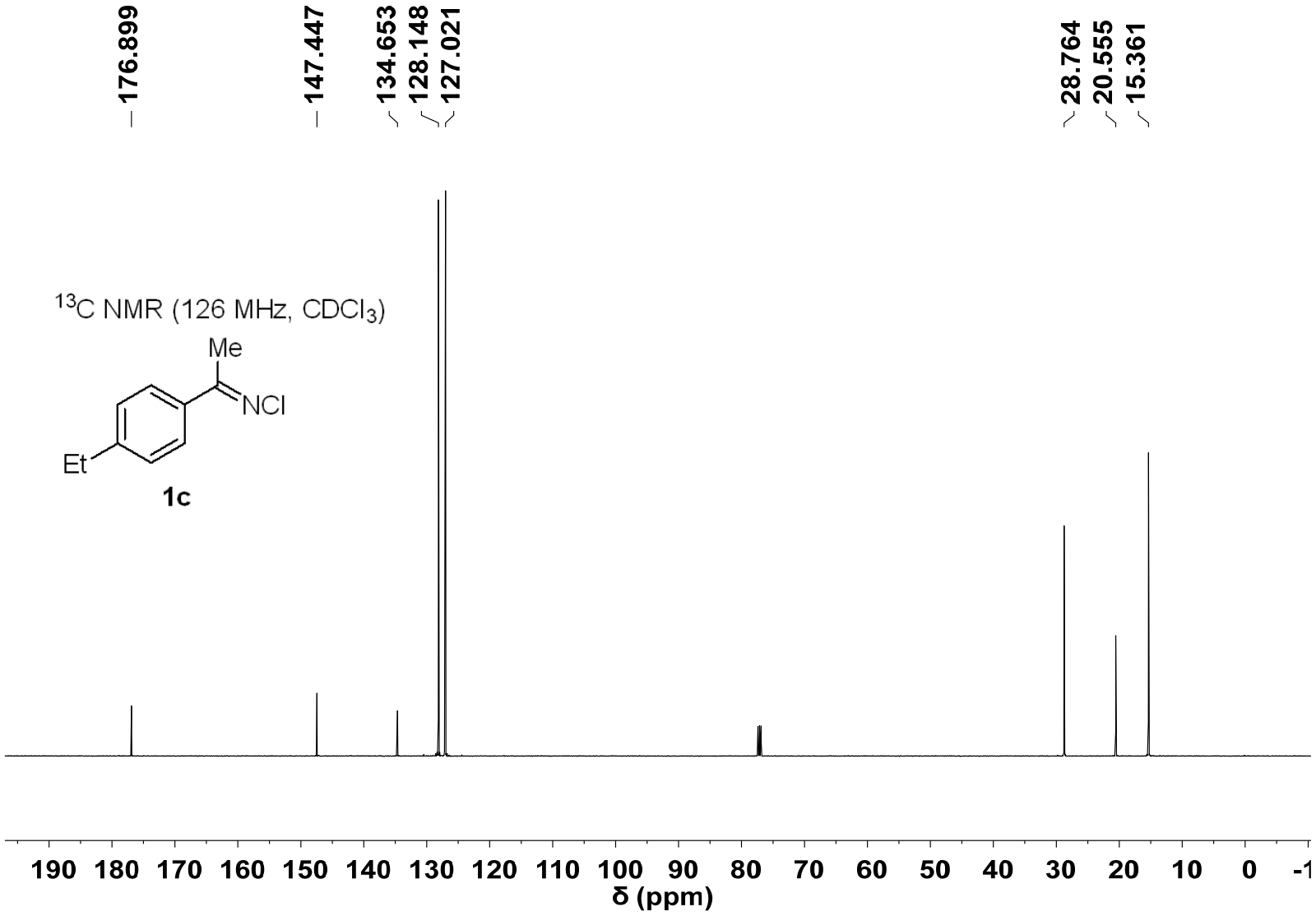
7.677
7.668
7.664
7.283
7.266
2.741
2.726
2.710
2.695
2.609
1.306
1.291
1.276
^{1}H NMR (500 MHz, CDCl$_3$)
Me
NCl
Et
1c
1.99
2.04
2.06
3.00
3.06
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)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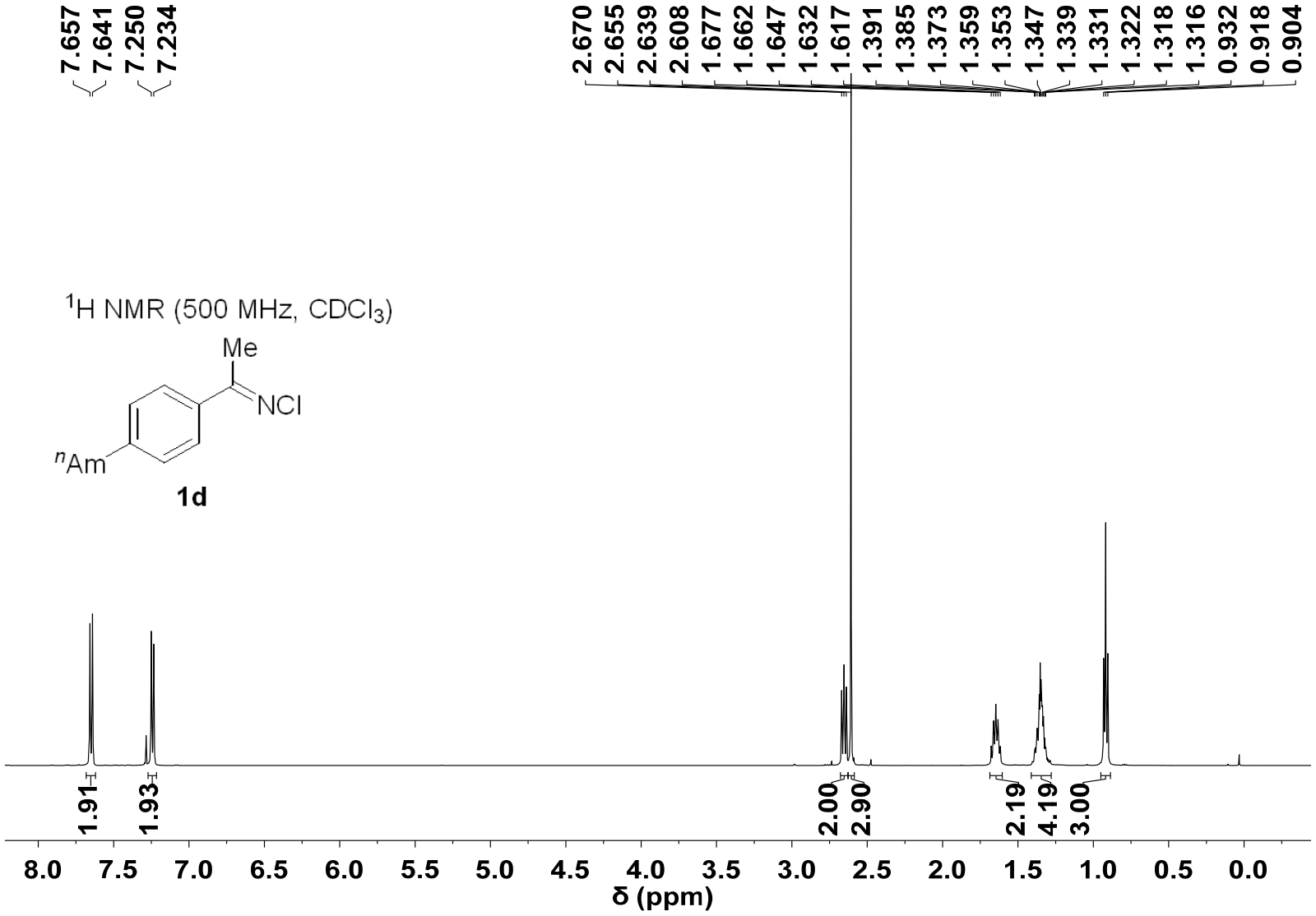
Me
NCl
Et
1c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)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2.655
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2.608
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1.662
1.647
1.632
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1.391
1.385
1.373
1.359
1.353
1.347
1.339
1.331
1.322
1.318
1.316
0.932
0.918
0.904
1H NMR (500 MHz, CDCl3)
Me
NCl
nAm
1d
1.91
1.93
2.00
2.90
2.19
4.19
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.5
2.0
1.5
1.0
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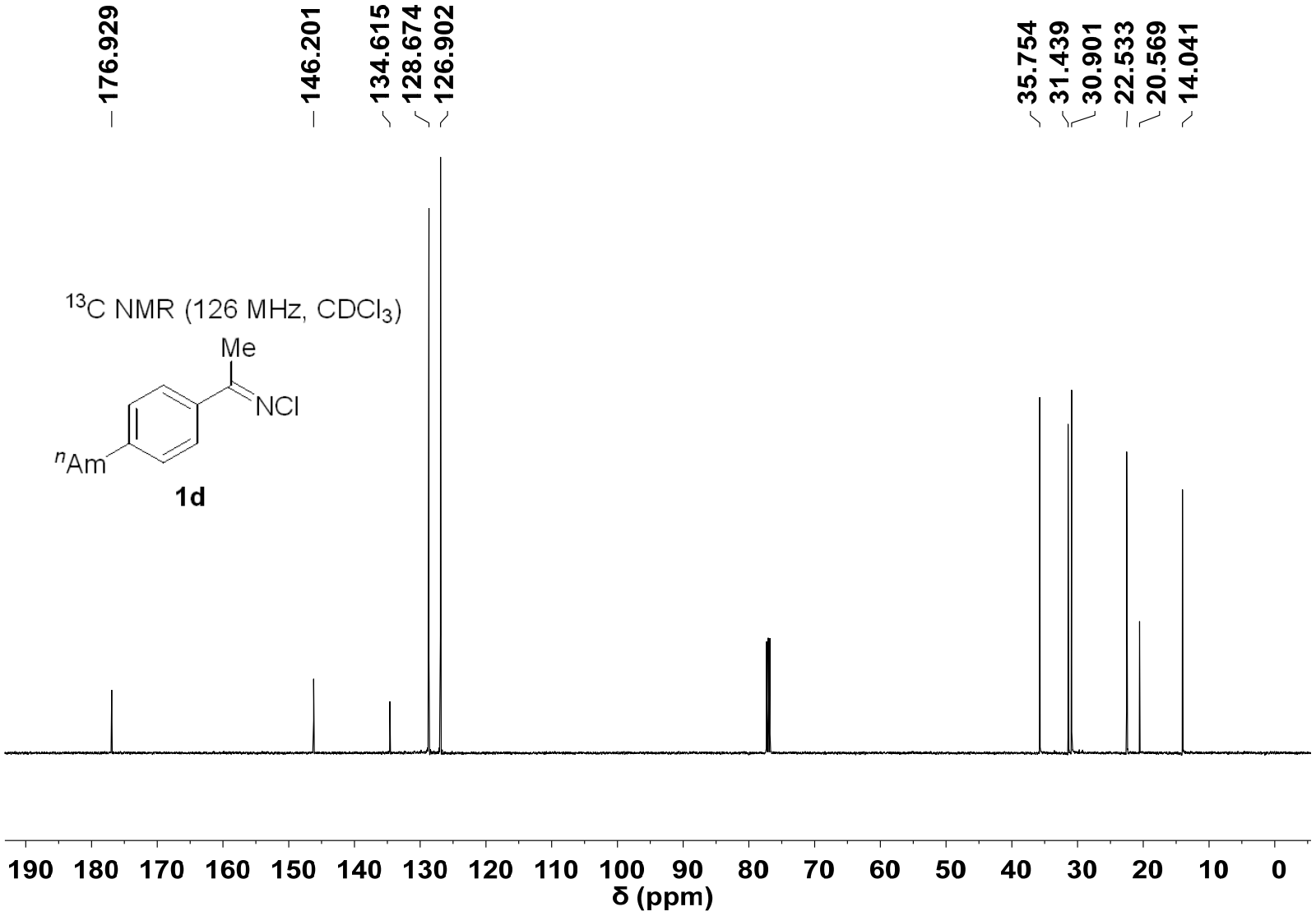
0.0
δ (ppm)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146.201
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128.674
126.902
35.754
31.439
30.901
22.533
20.569
14.041
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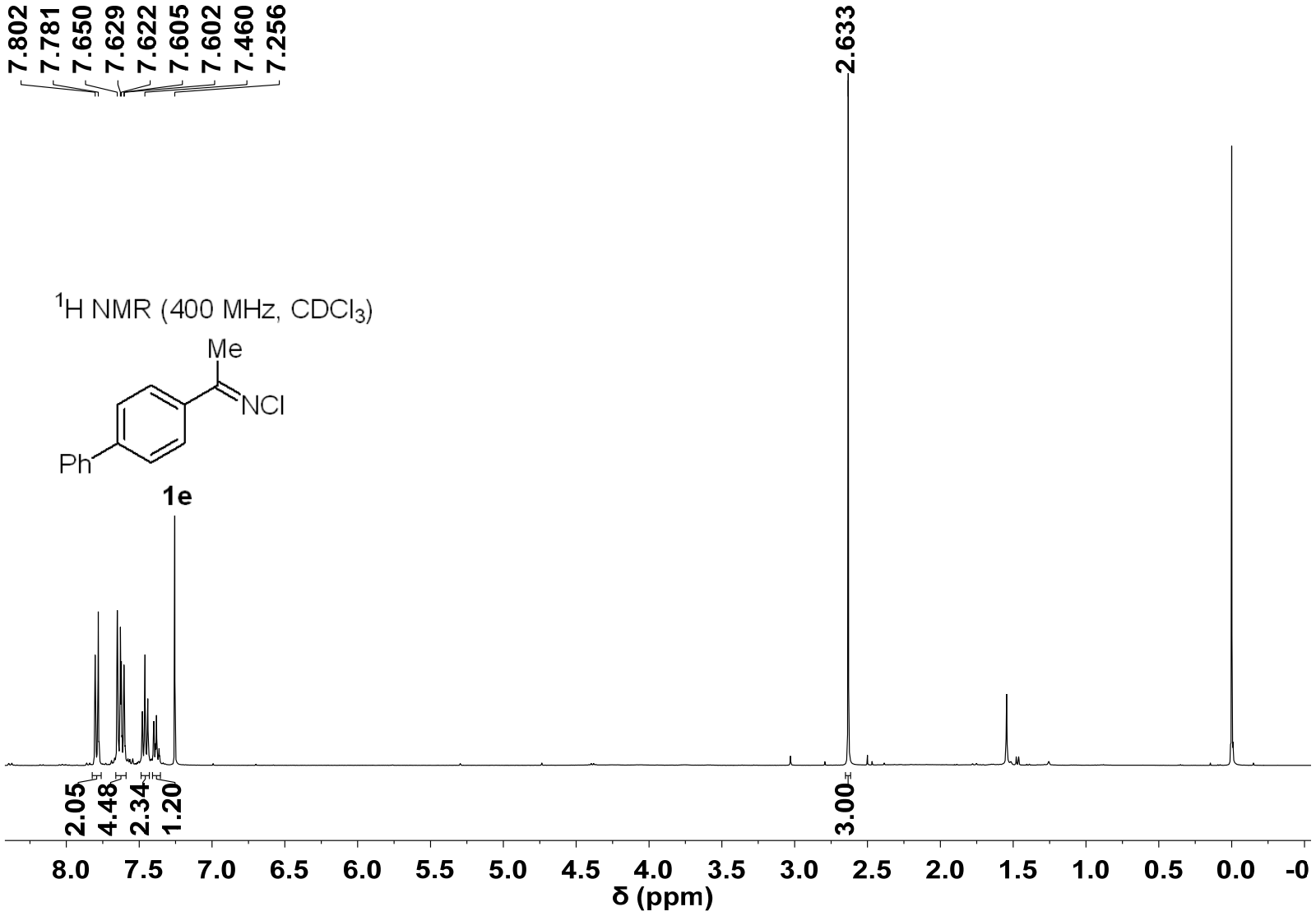
Me
NCl
nAm
1d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)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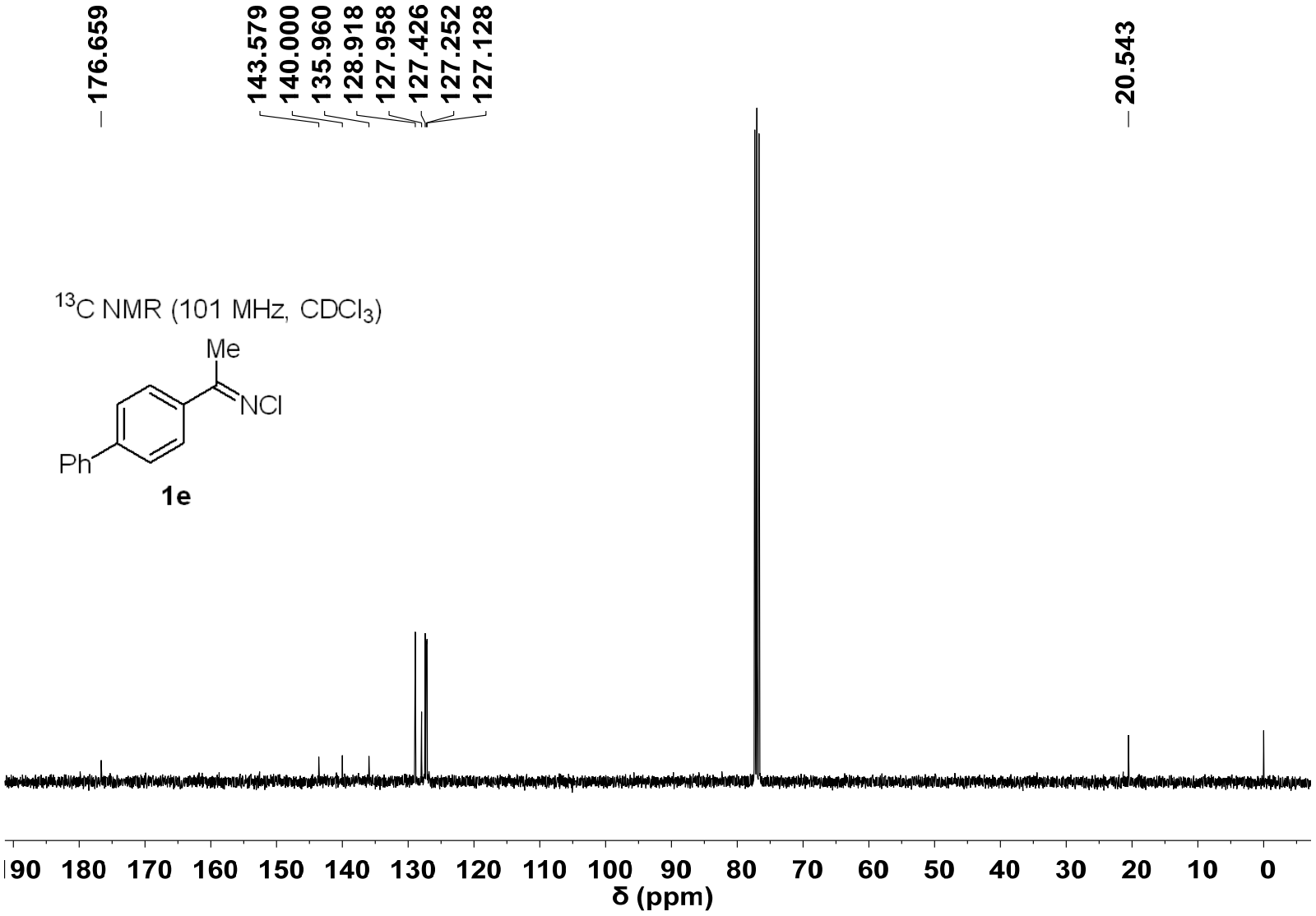
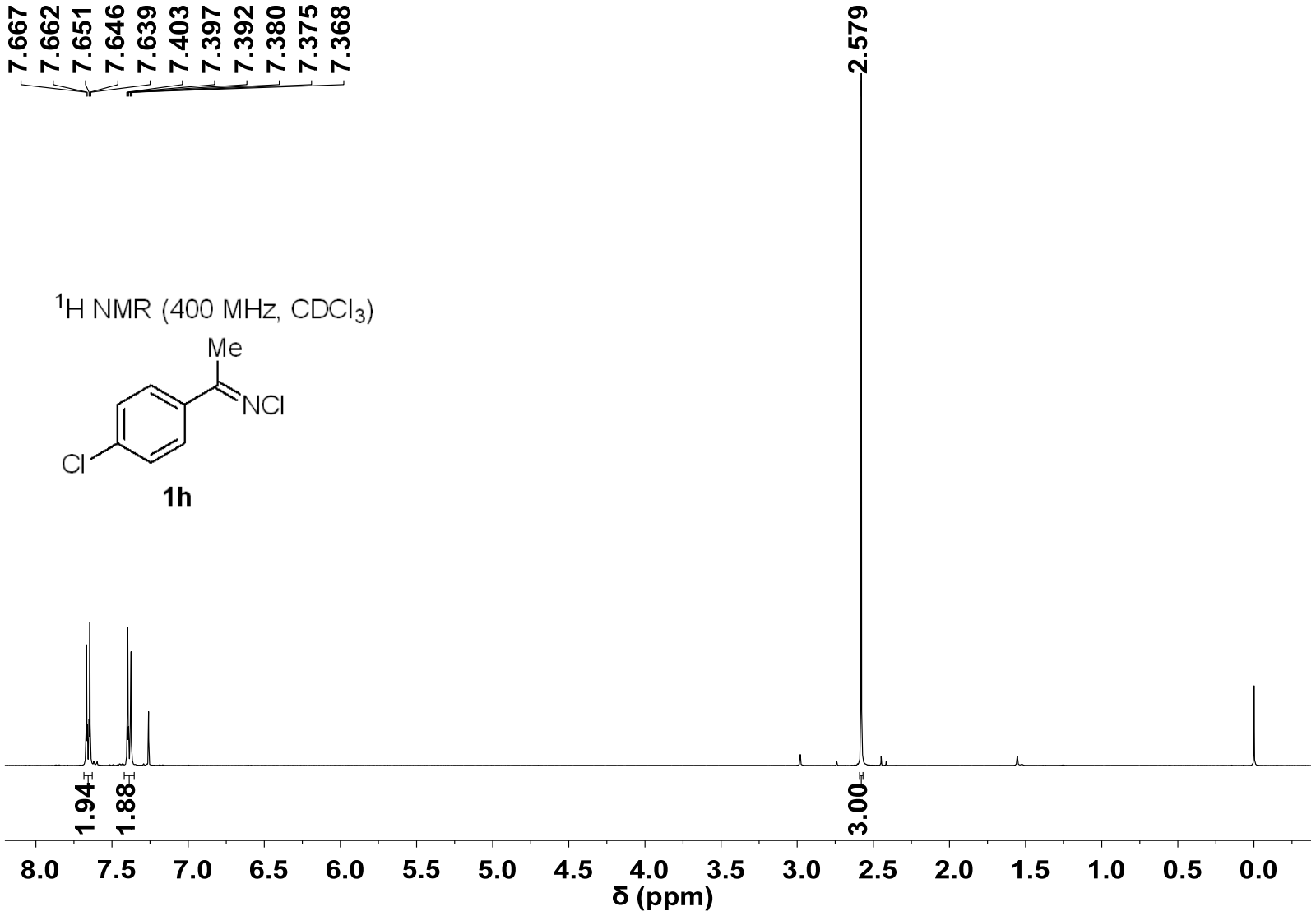
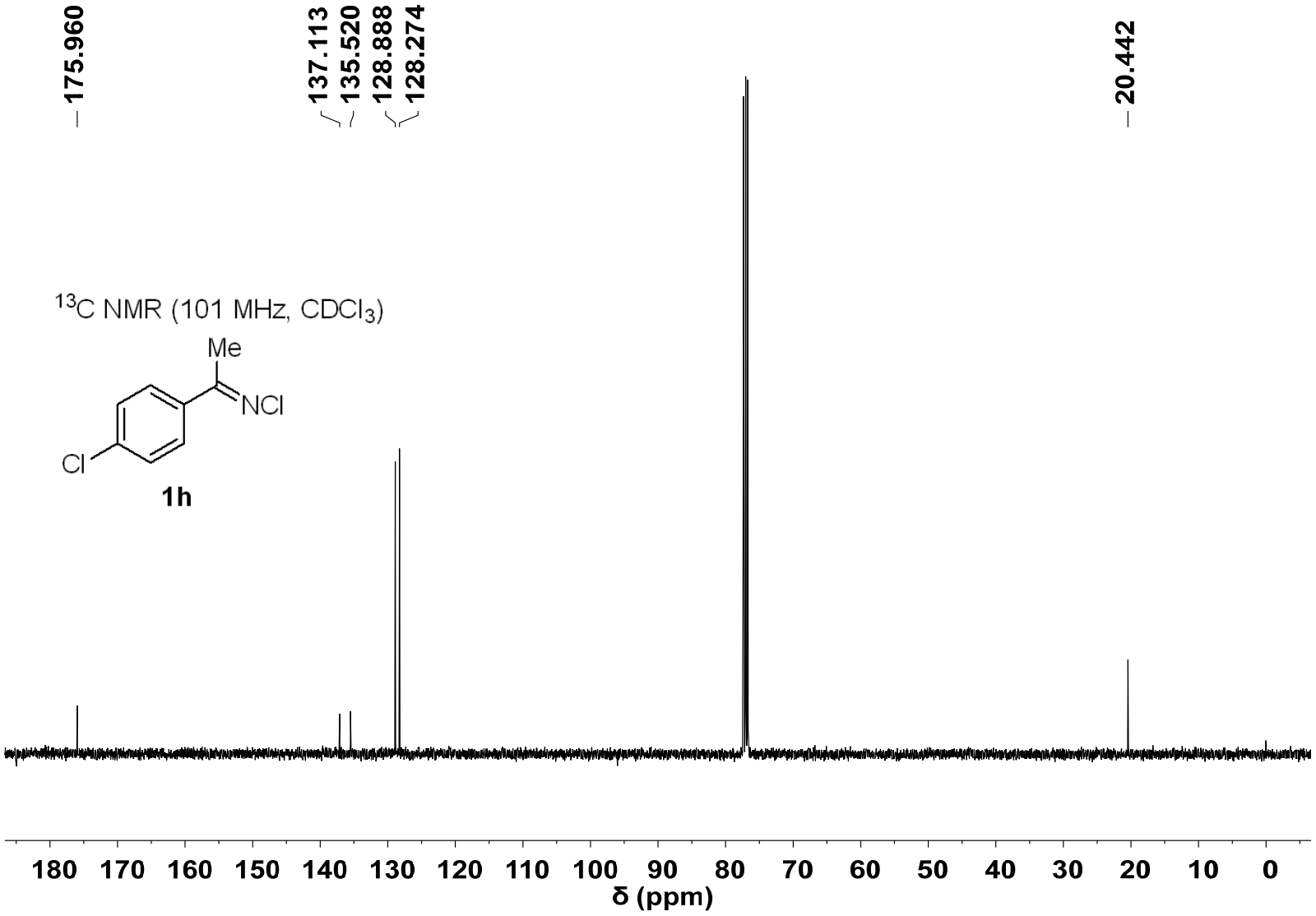
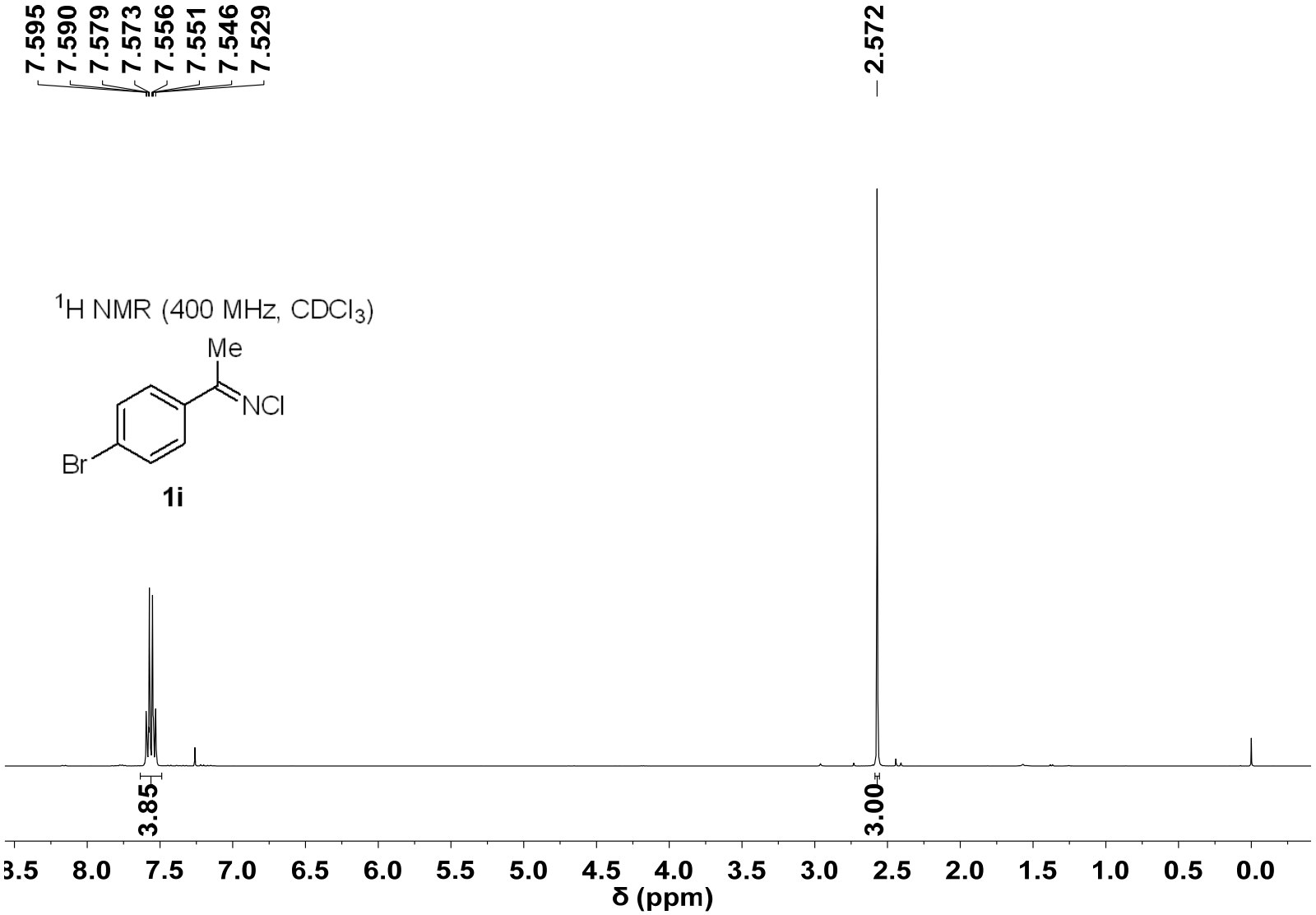
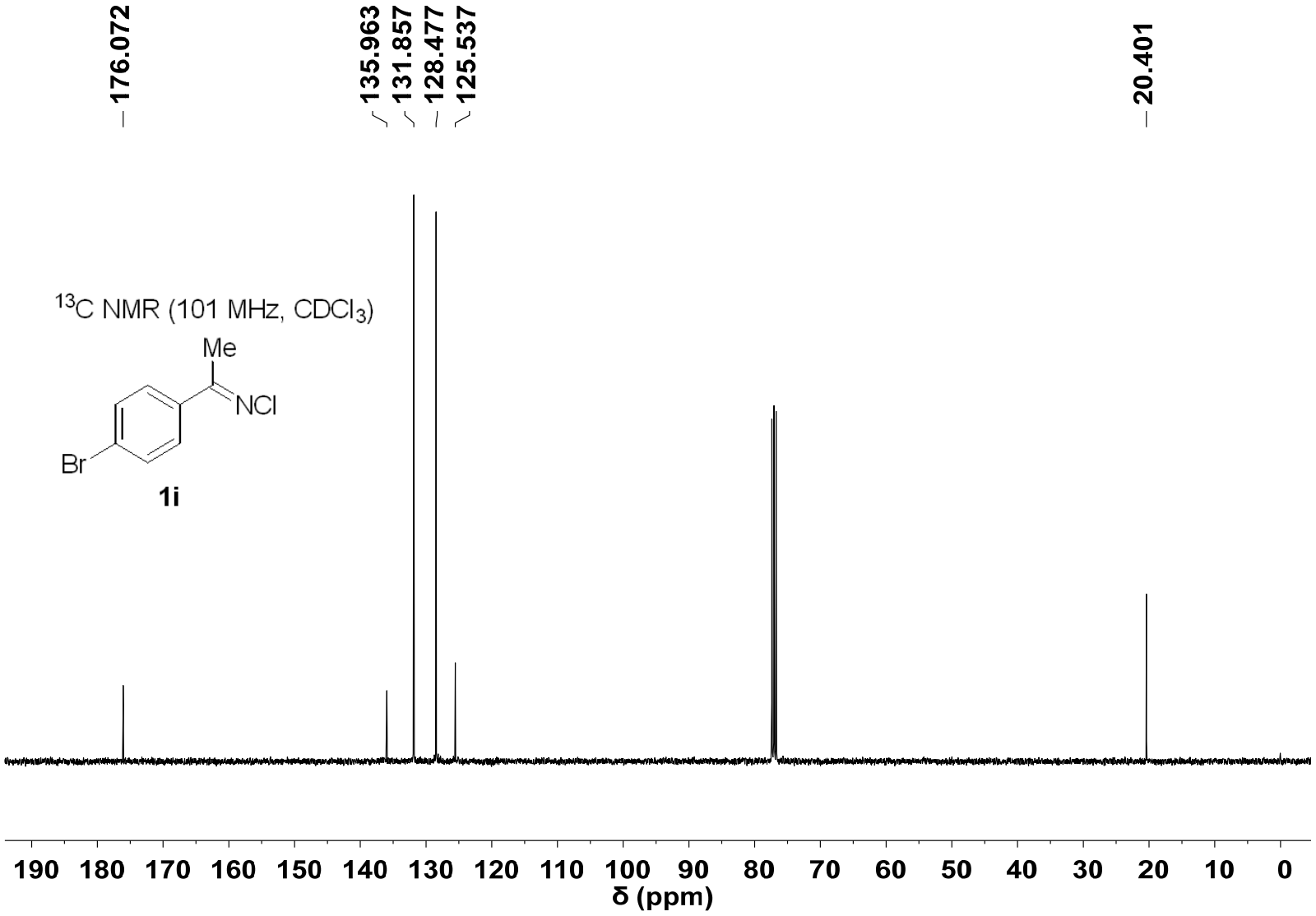
7.605
7.602
7.460
7.256
2.633
^{1}H NMR (400 MHz, CDCl$_3$)
Me
NCl
Ph
1e
2.05
4.48
2.34
1.20
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
δ (ppm)

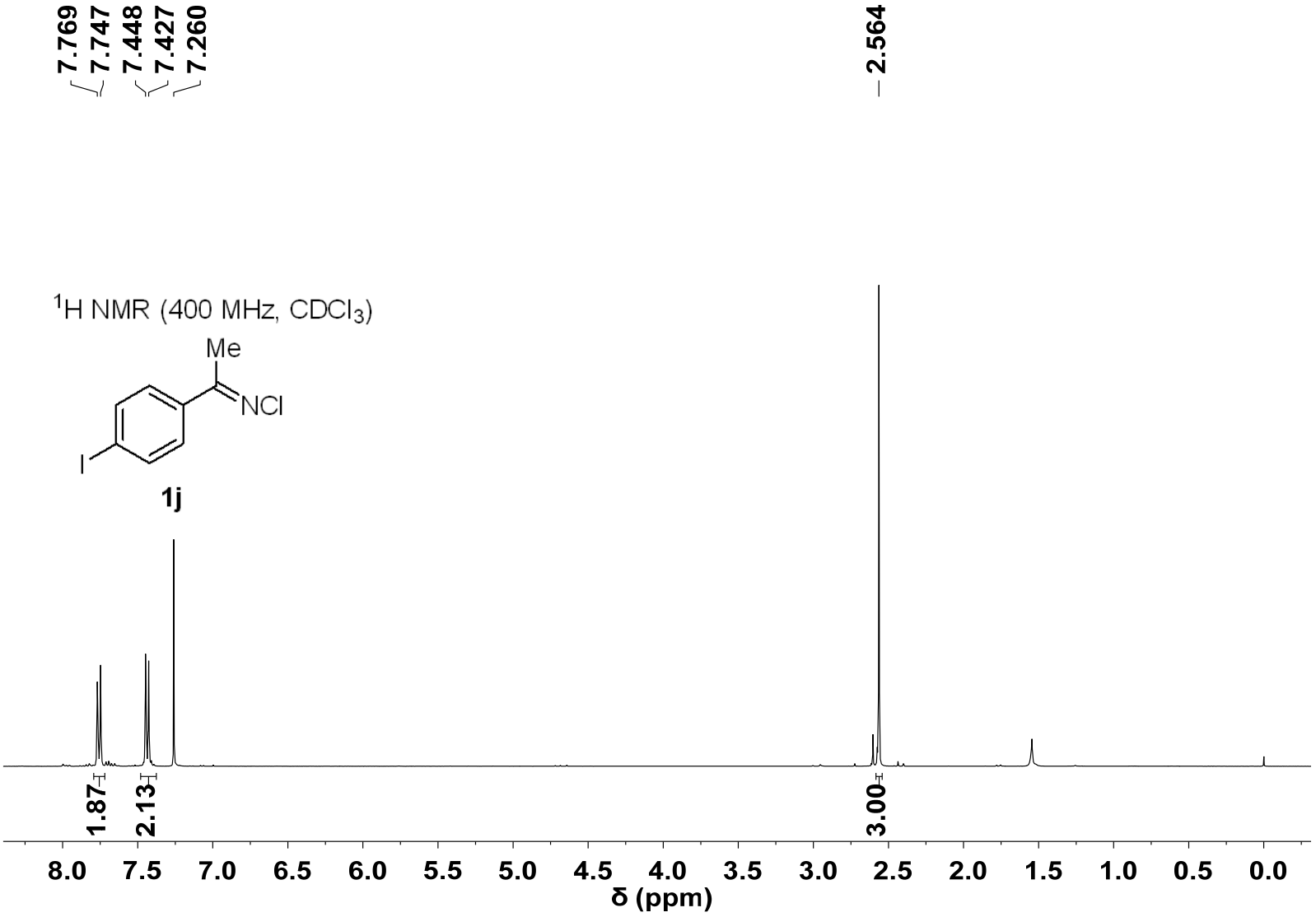

176.659
143.579
140.000
135.960
128.918
127.958
127.426
127.252
127.128
20.543
13C NMR (101 MHz, CDCl3)
Me
NCl
Ph
1e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

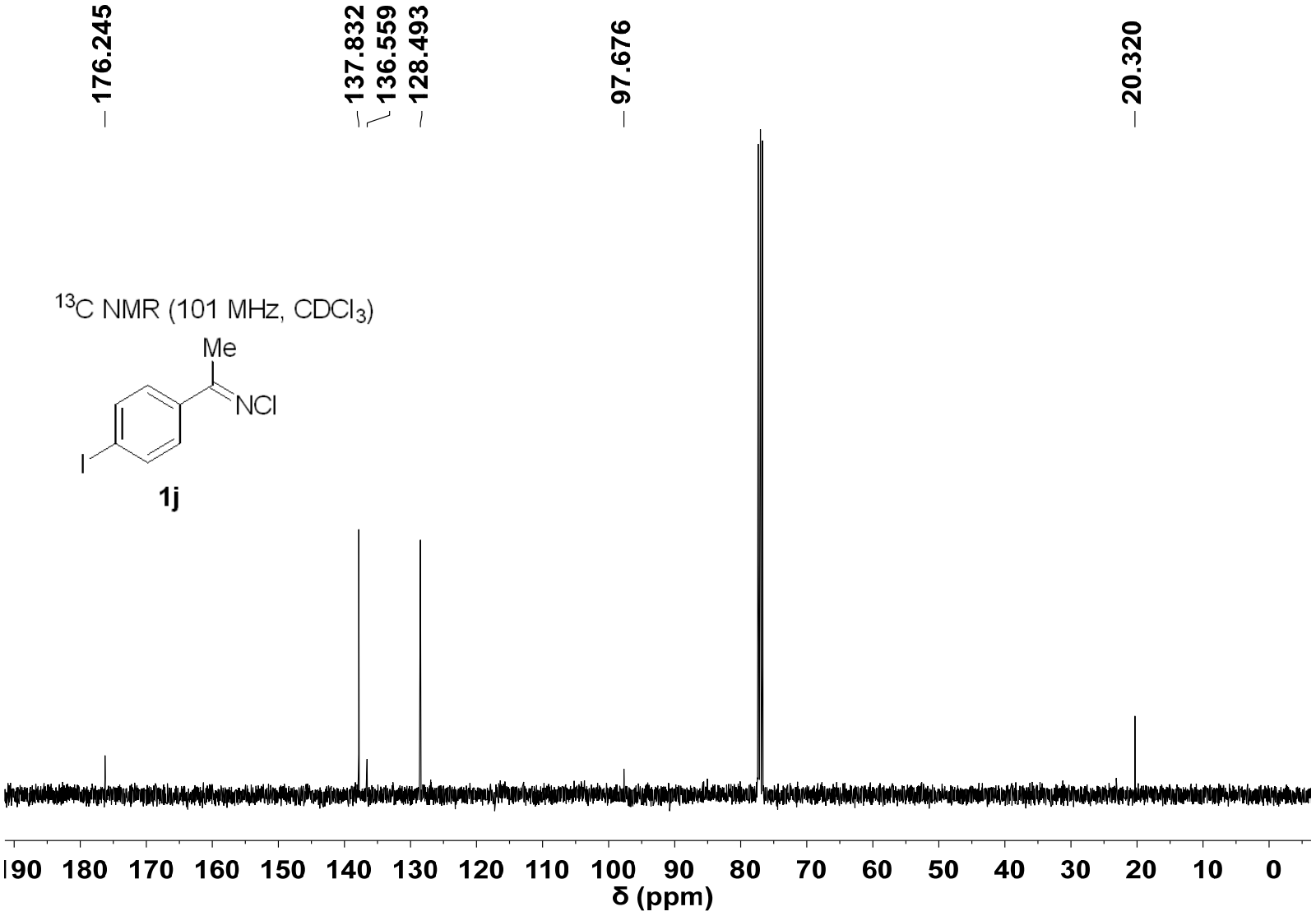

7.667
7.662
7.651
7.646
7.639
7.403
7.397
7.392
7.380
7.375
7.368
2.579
1H NMR (400 MHz, CDCl3)
Me
NCl
Cl
1h
1.94
1.88
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

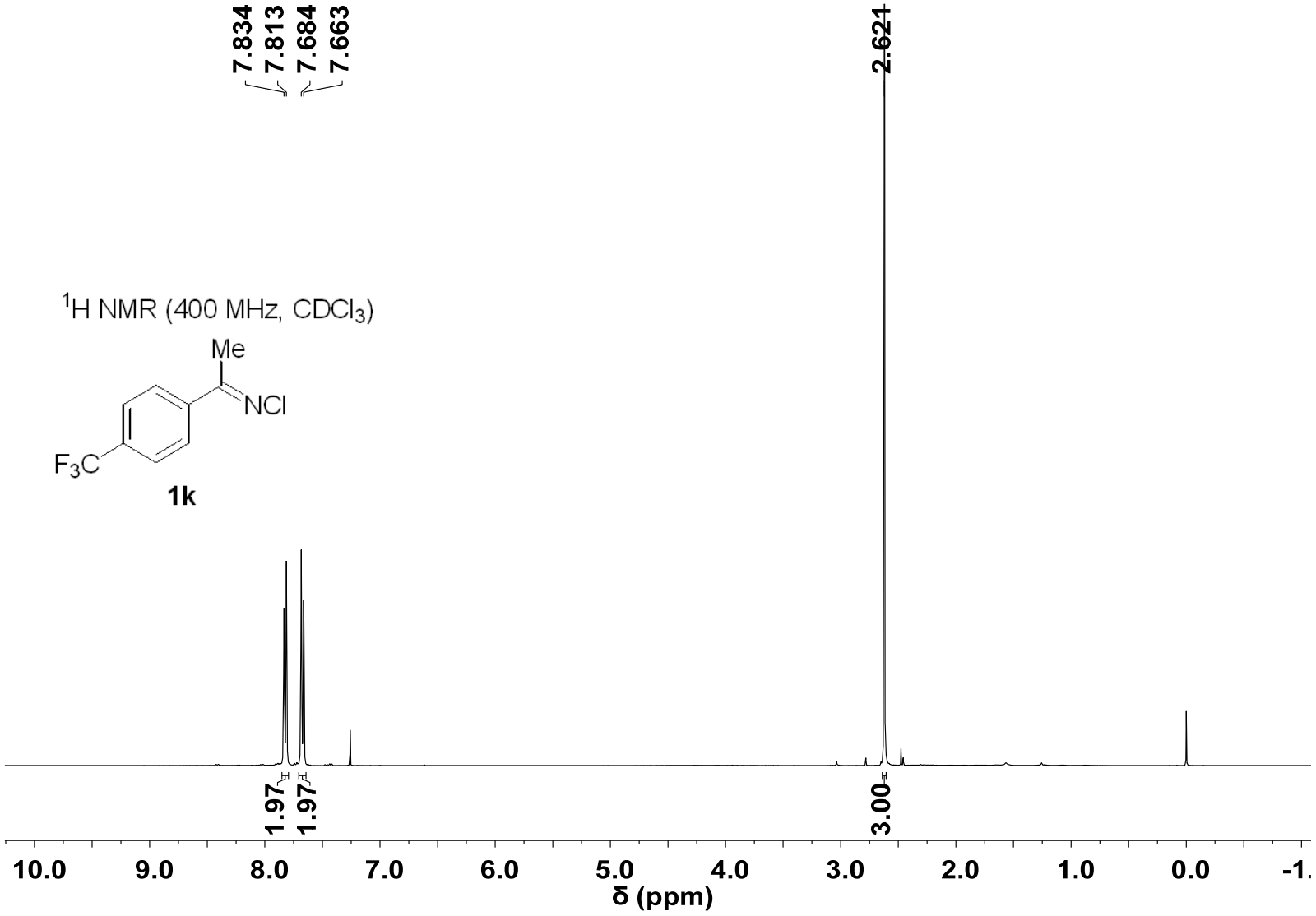

175.960
137.113
135.520
128.888
128.274
20.442
13C NMR (101 MHz, CDCl3)
Me
NCl
Cl
1h
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

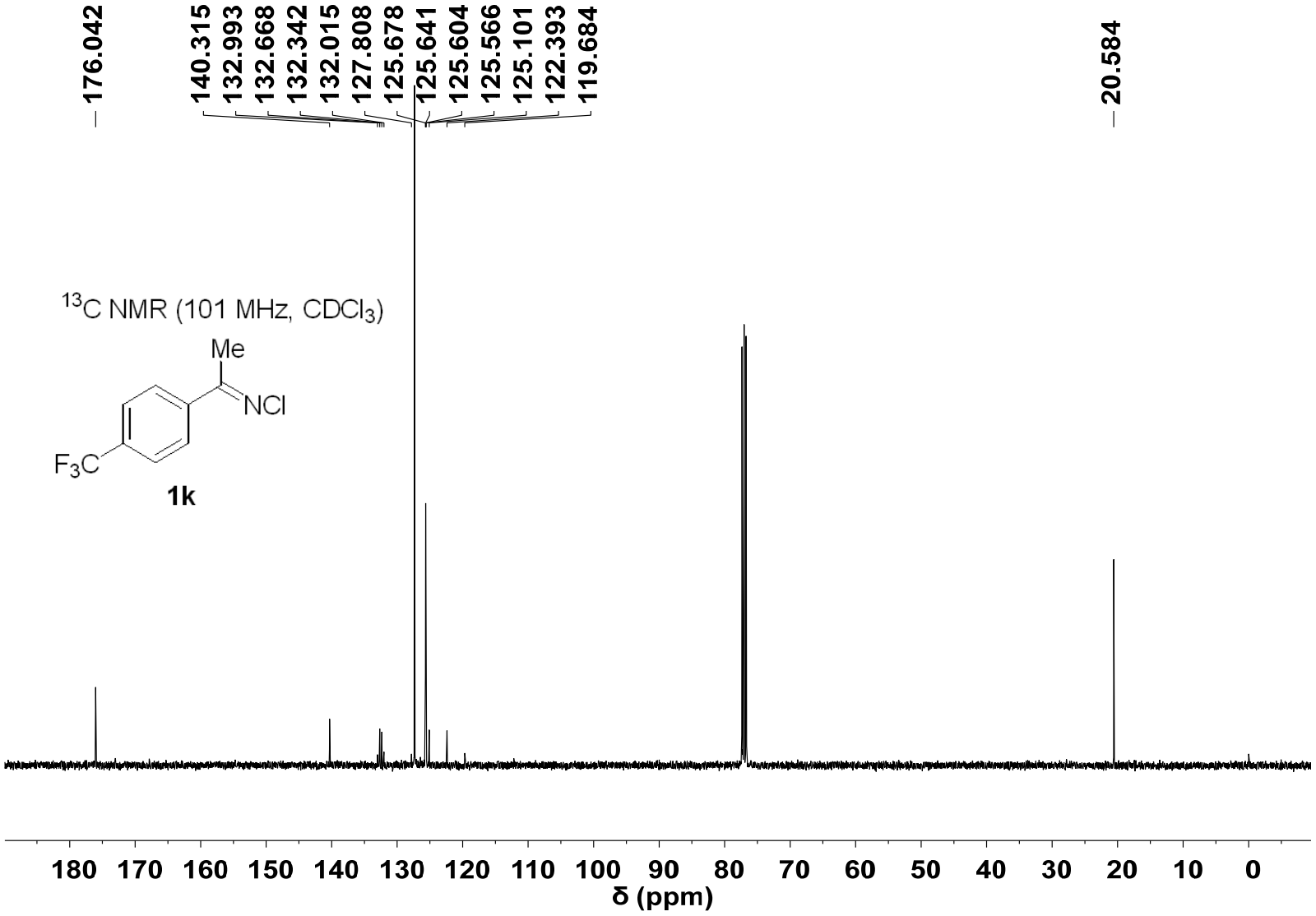

7.595
7.590
7.579
7.573
7.556
7.551
7.546
7.529
2.572
^{1}H NMR (400 MHz, $CDCl_3$)
Me
NCl
Br
1i
3.85
3.00
δ (ppm)

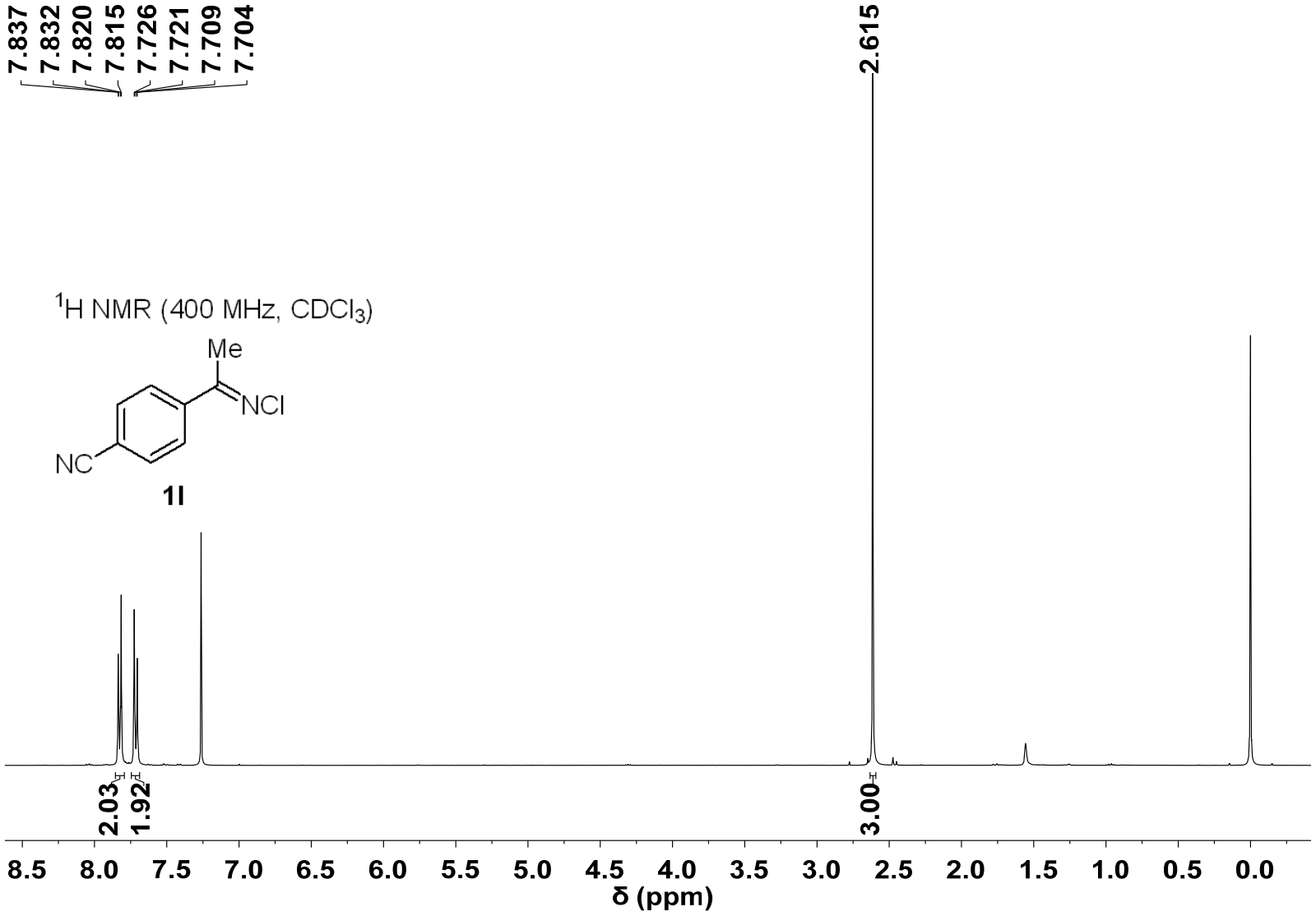

176.072
135.963
131.857
128.477
125.537
20.401
13C NMR (101 MHz, CDCl3)
Me
NCl
Br
1i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

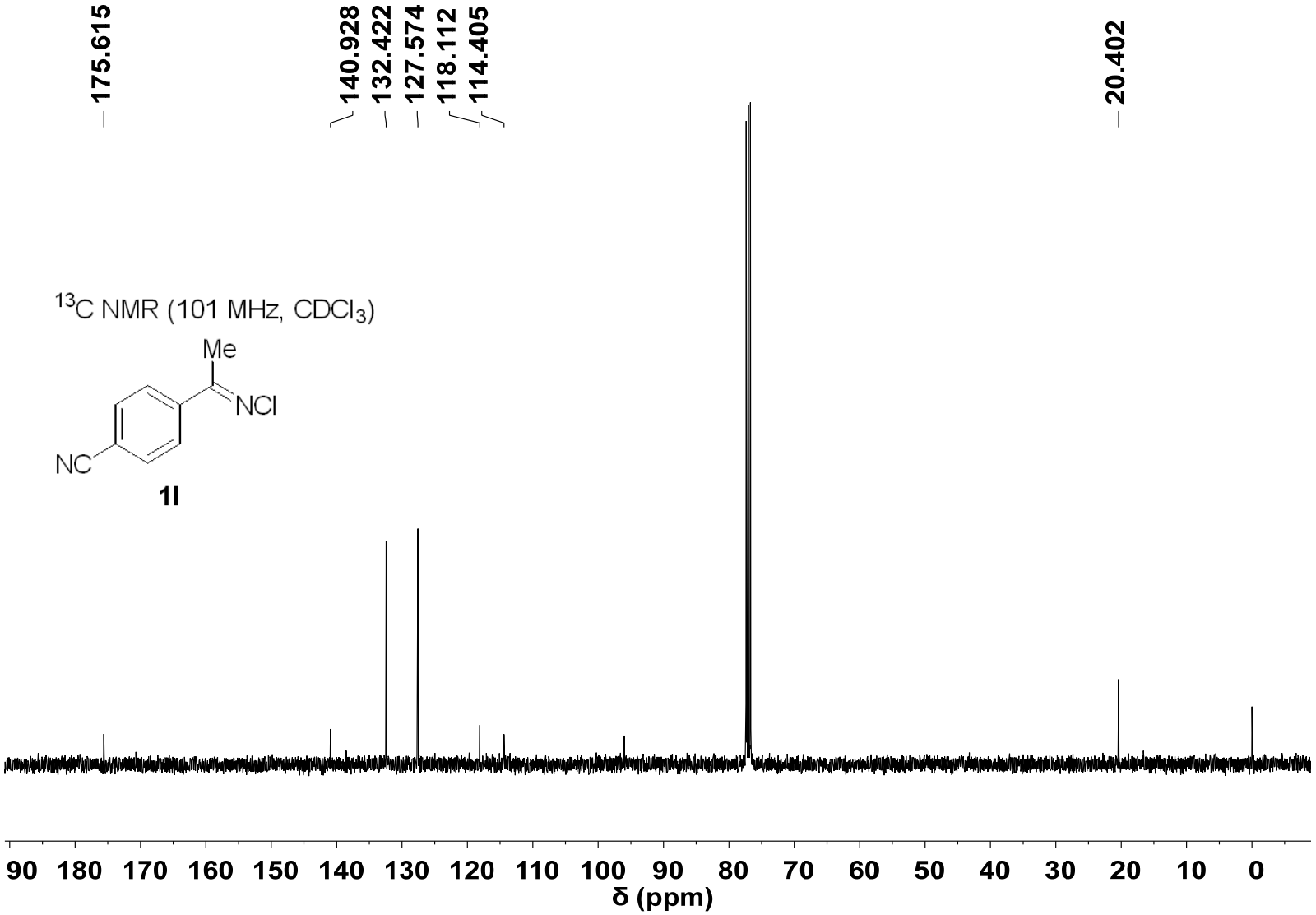

7.769
7.747
7.448
7.427
7.260
2.564
^{1}H NMR (400 MHz, $CDCl_3$)
Me
NCl
I
1j
1.87
2.13
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

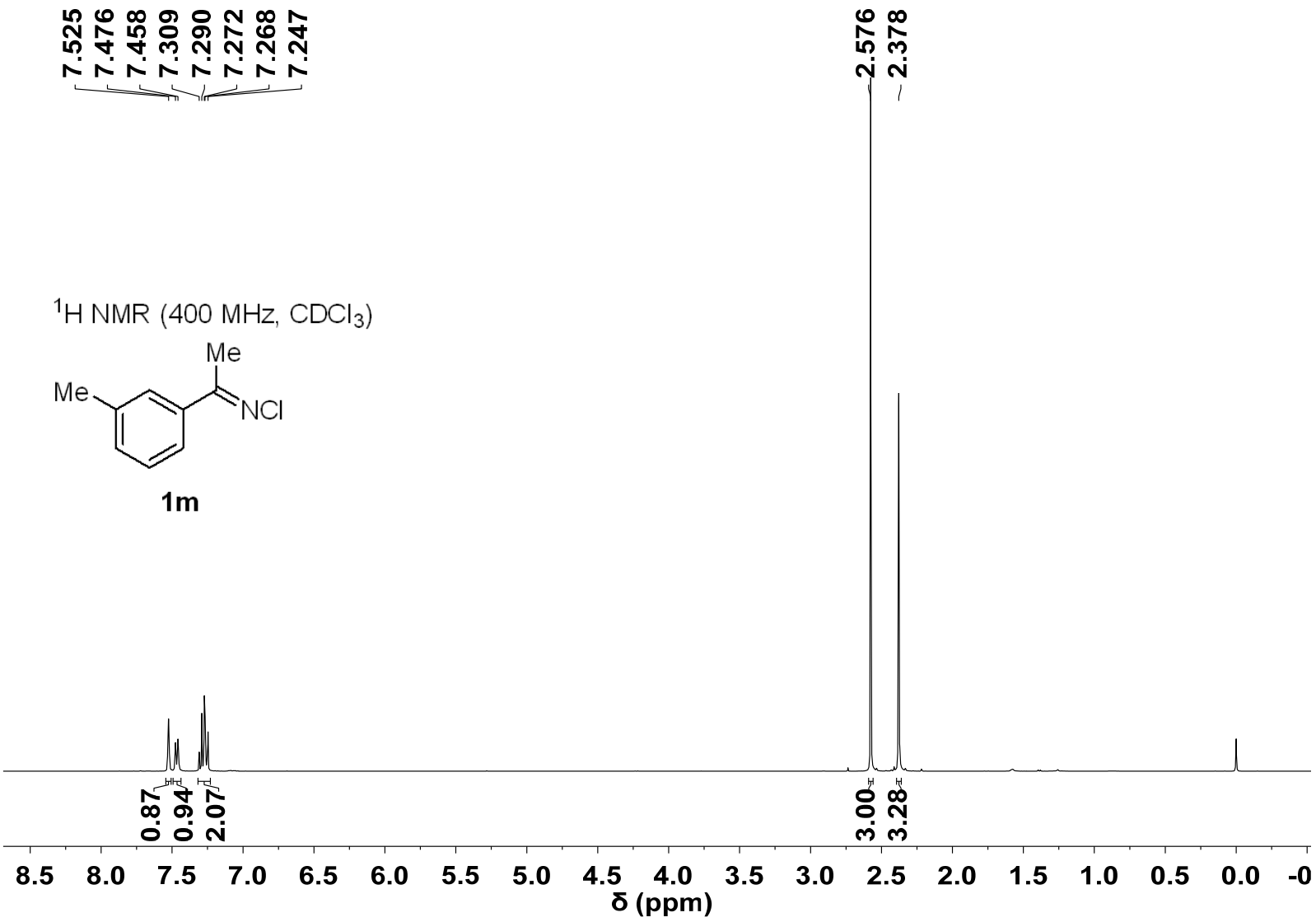

176.245
137.832
136.559
128.493
97.676
20.320
13C NMR (101 MHz, CDCl3)
Me
NCl
I
1j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

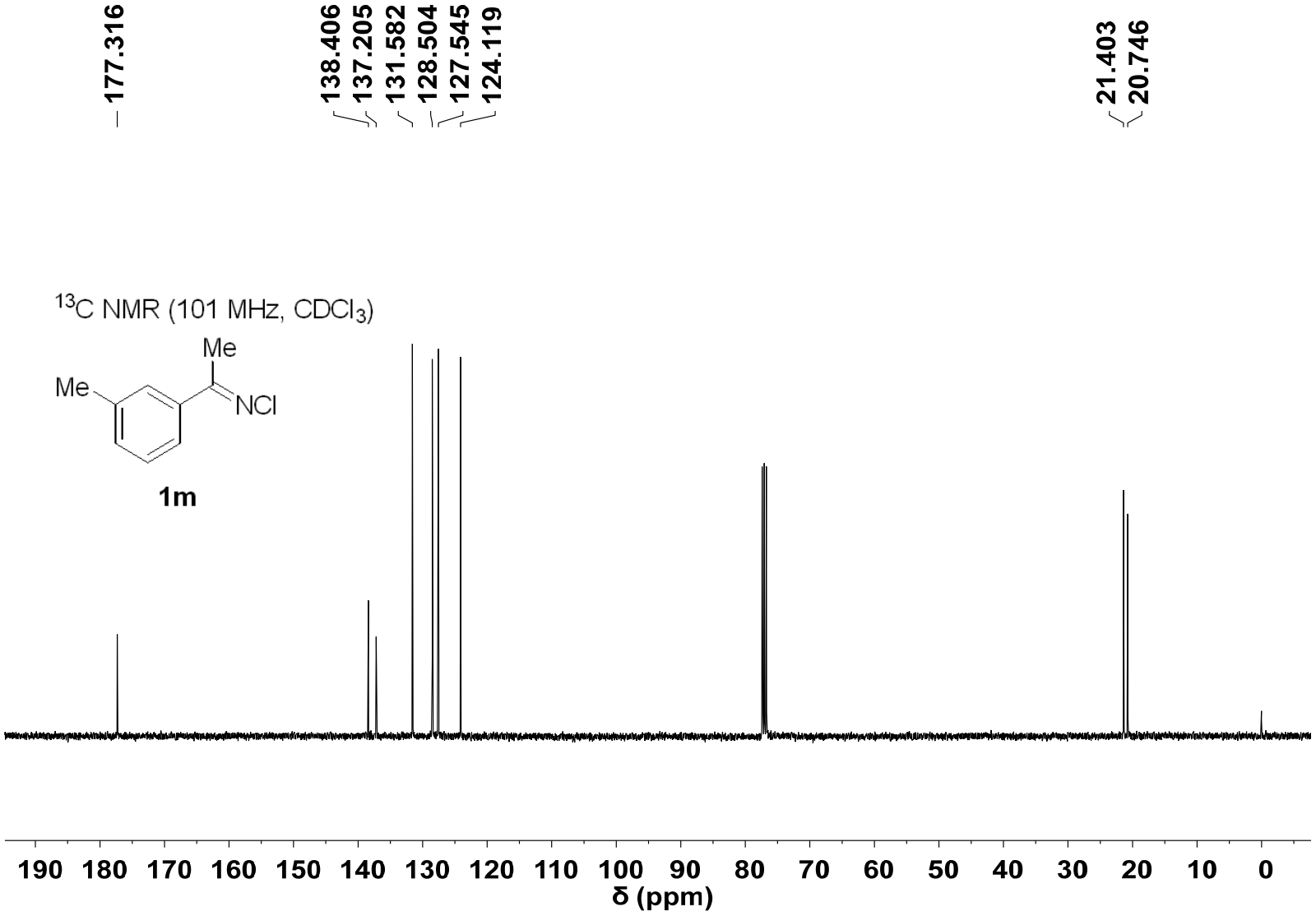

7.834
7.813
7.684
7.663
2.621
^{1}H NMR (400 MHz, $CDCl_3$)
Me
NCl
F_3C
1k
1.97
1.97
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ (ppm)

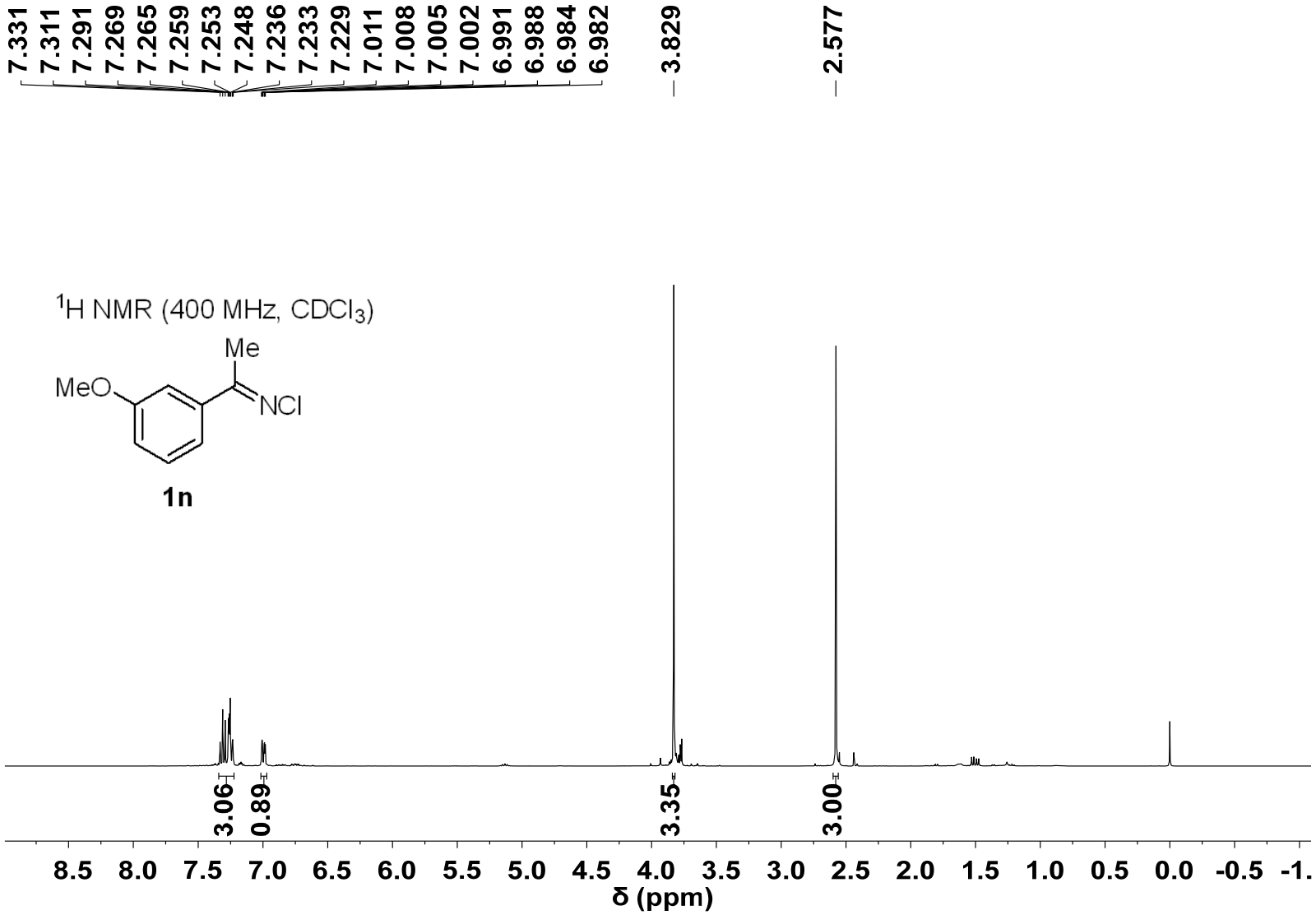

176.042
140.315
132.993
132.668
132.342
132.015
127.808
125.678
125.641
125.604
125.566
125.101
122.393
119.684
20.584
13C NMR (101 MHz, CDCl3)
Me
NCl
F3C
1k
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

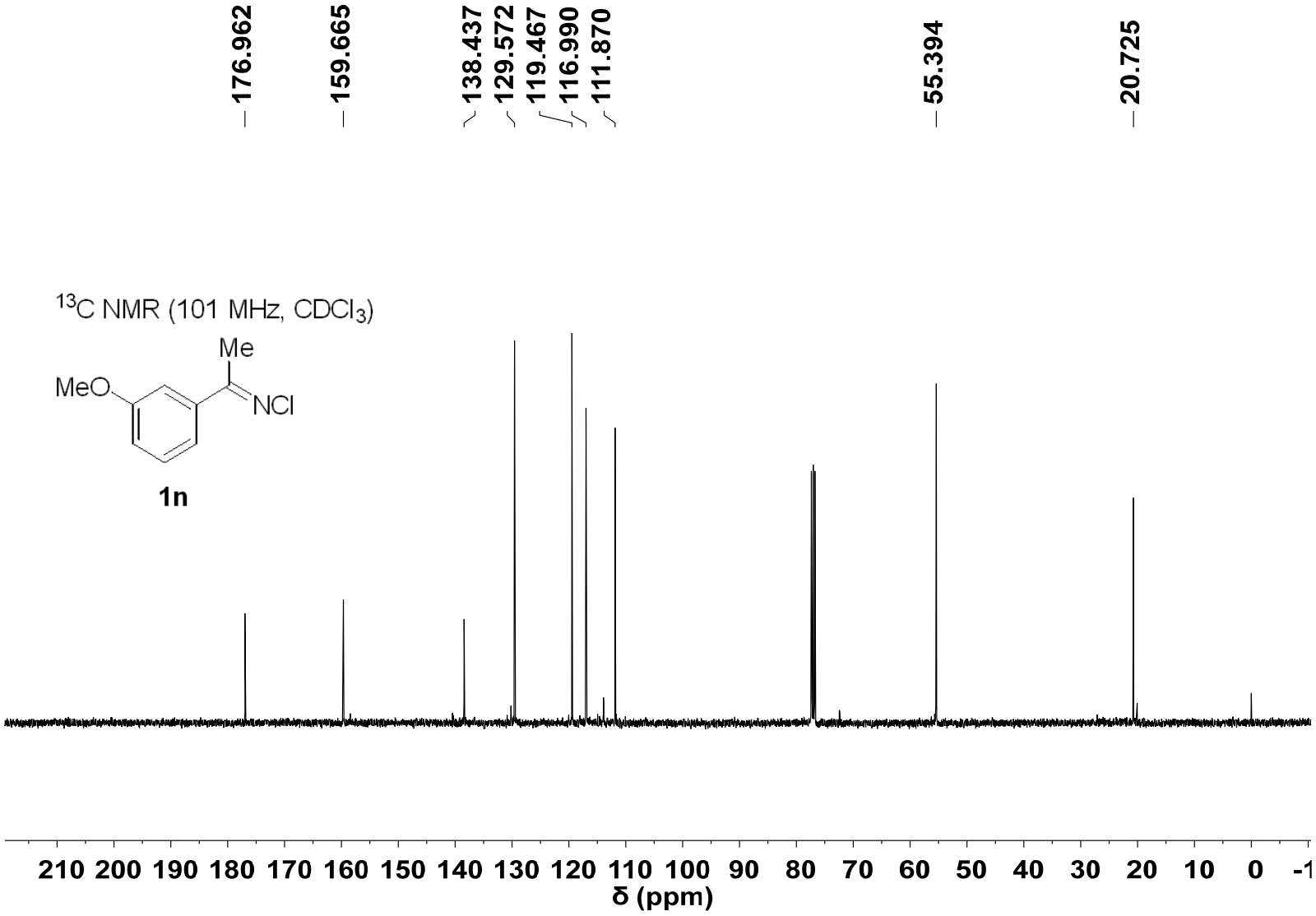

7.837
7.832
7.820
7.815
7.726
7.721
7.709
7.704
2.615
^{1}H NMR (400 MHz, CDCl$_3$)
Me
NCl
NC
1l
2.03
1.92
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

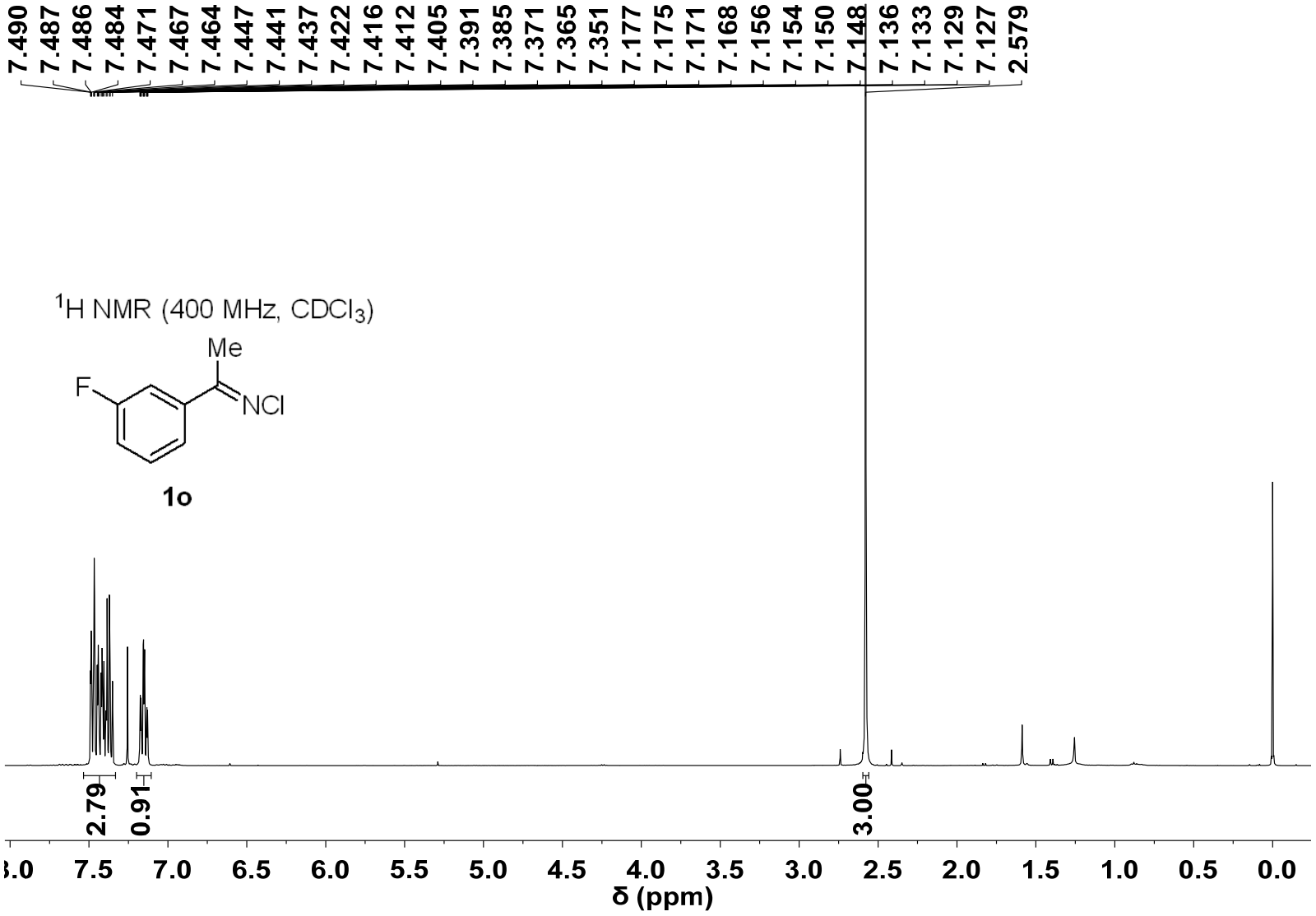

175.615
140.928
132.422
127.574
118.112
114.405
20.402
13C NMR (101 MHz, CDCl3)
Me
NCl
NC
1l
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

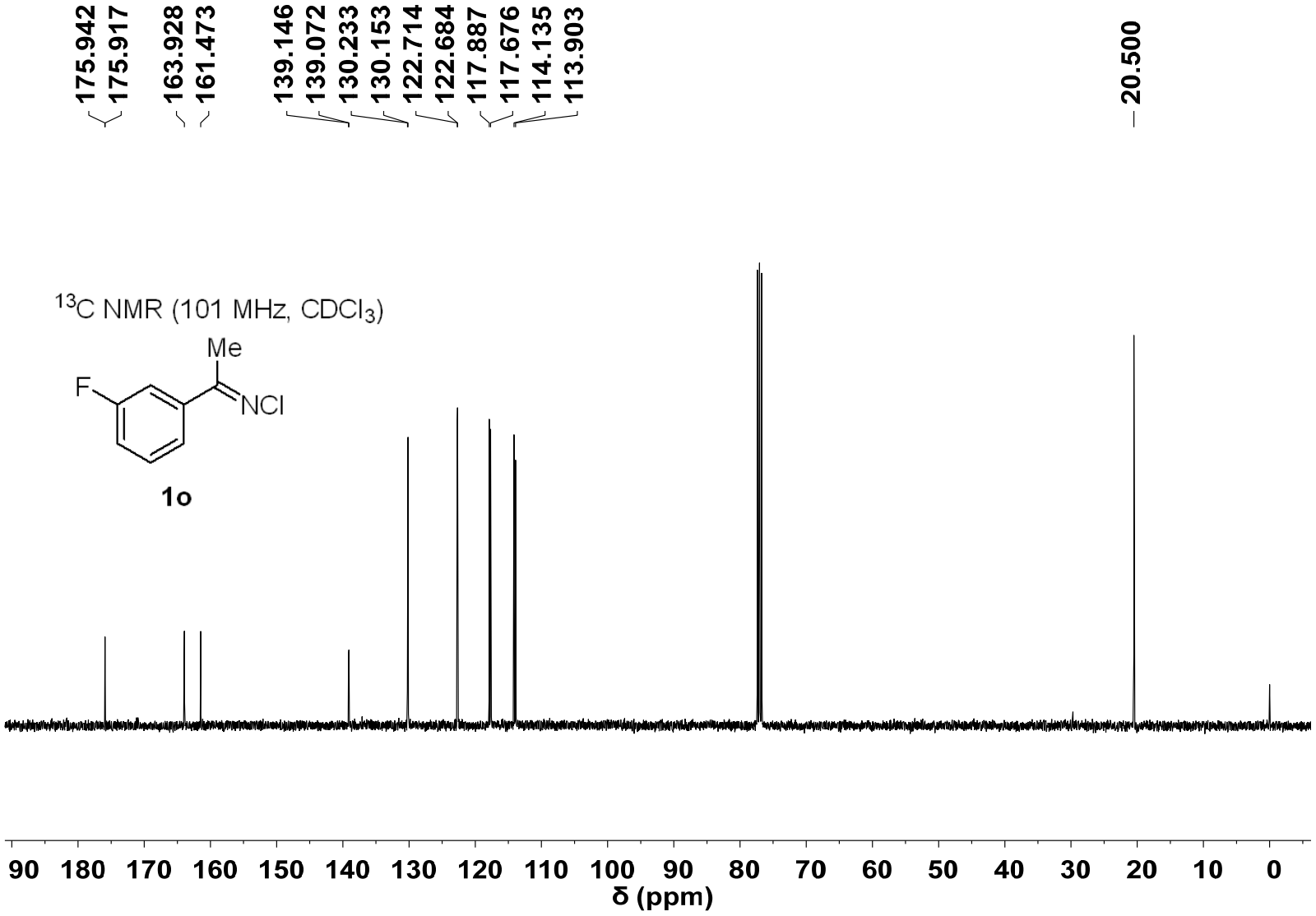

7.525
7.476
7.458
7.309
7.290
7.272
7.268
7.247
2.576
2.378
^{1}H NMR (400 MHz, $CDCl_3$)
Me
Me
NCl
1m
0.87
0.94
2.07
3.00
3.28
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
δ (ppm)

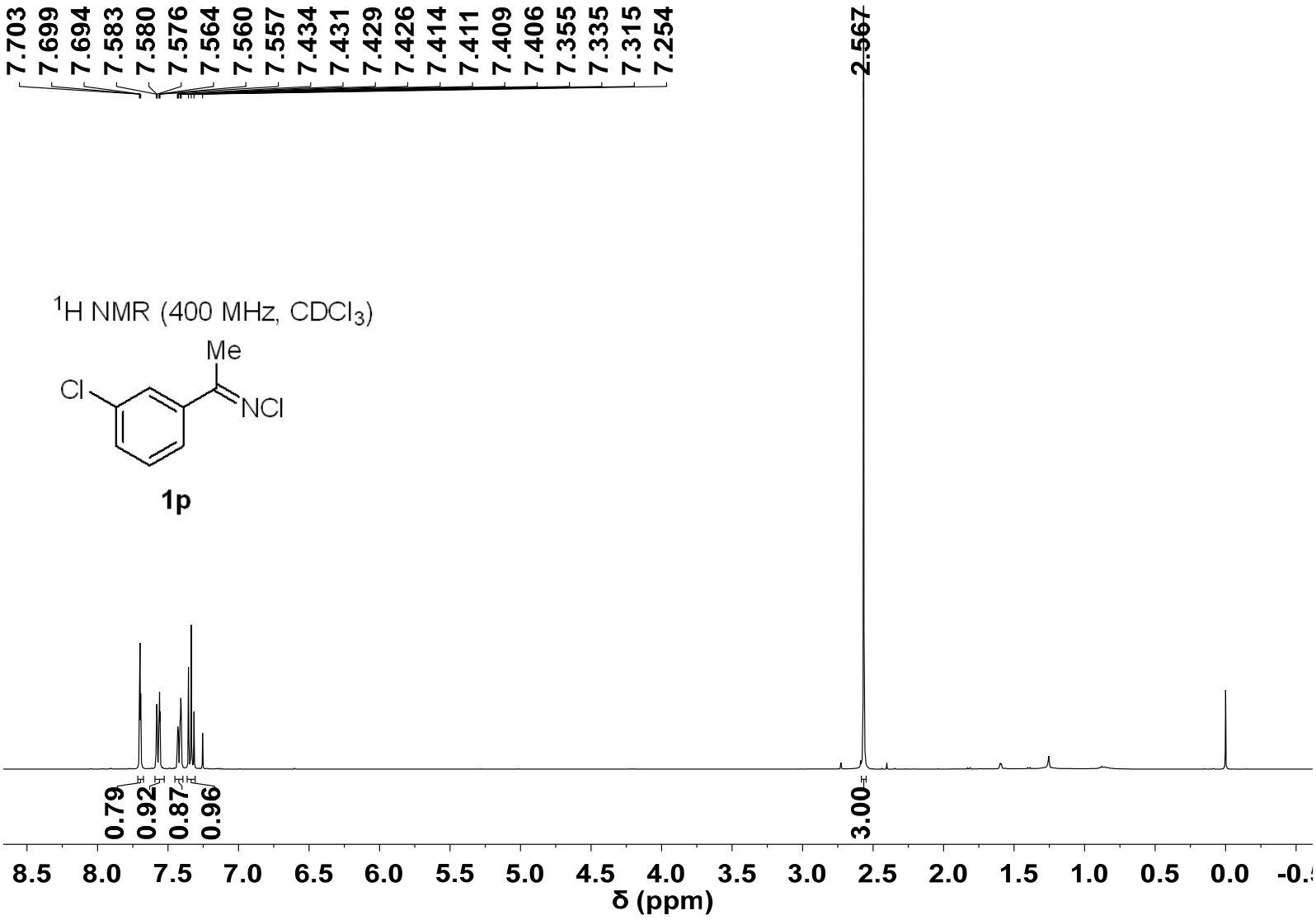

177.316
138.406
137.205
131.582
128.504
127.545
124.119
21.403
20.746
13C NMR (101 MHz, CDCl3)
Me
Me
NCl
1m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

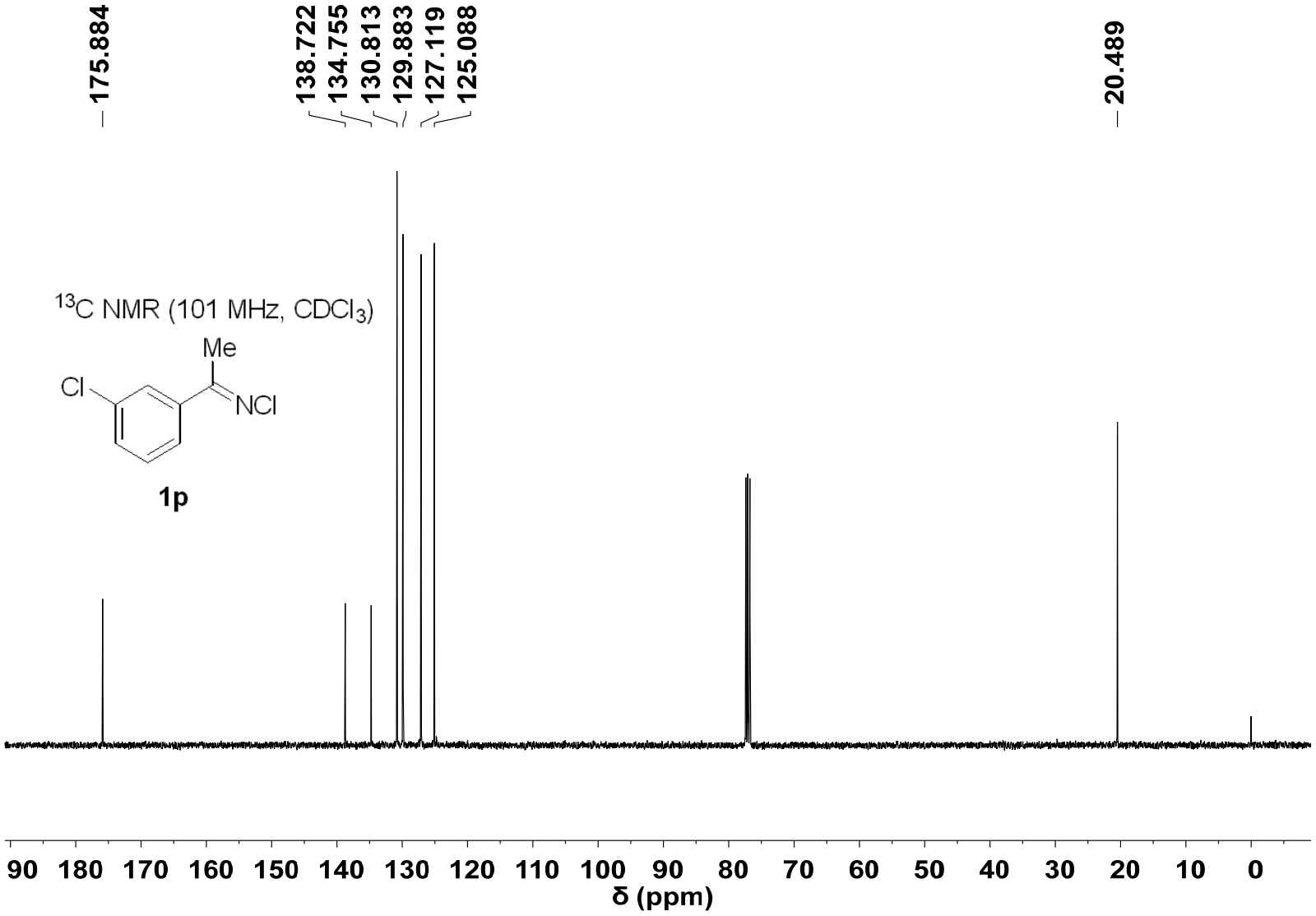

7.331
7.311
7.291
7.269
7.265
7.259
7.253
7.248
7.236
7.233
7.229
7.011
7.008
7.005
7.002
6.991
6.988
6.984
6.982
3.829
2.577
1H NMR (400 MHz, CDCl3)
Me
MeO
NCl
1n
3.06
0.89
3.35
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
δ (ppm)

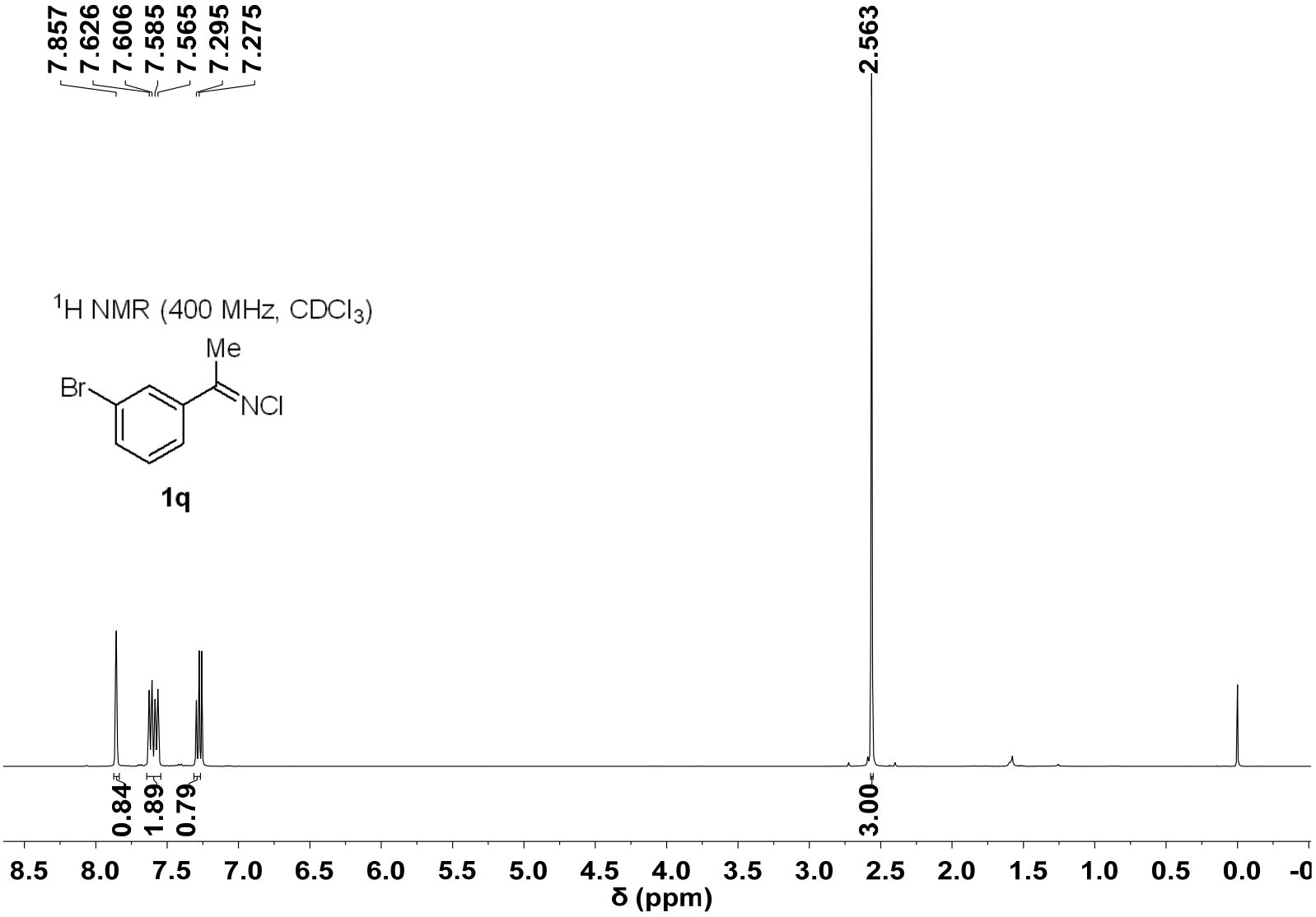

176.962
159.665
138.437
129.572
119.467
116.990
111.870
55.394
20.725
13C NMR (101 MHz, CDCl3)
Me
MeO
NCl
1n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

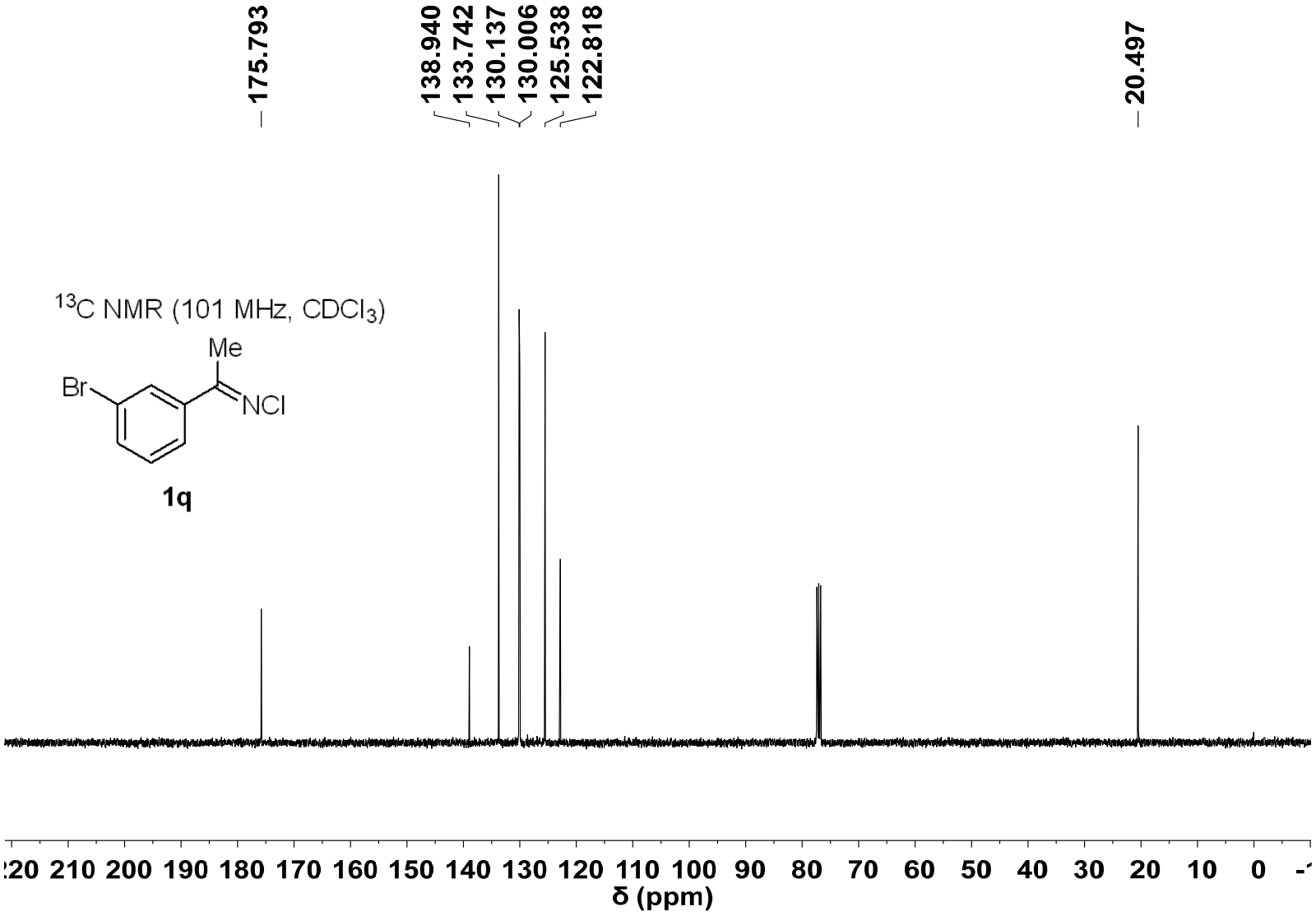

7.490
7.487
7.486
7.484
7.471
7.467
7.464
7.447
7.441
7.437
7.422
7.416
7.412
7.405
7.391
7.385
7.371
7.365
7.351
7.177
7.175
7.171
7.168
7.156
7.154
7.150
7.148
7.136
7.133
7.129
7.127
2.579
1H NMR (400 MHz, CDCl3)
Me
F
NCl
1o
2.79
0.91
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

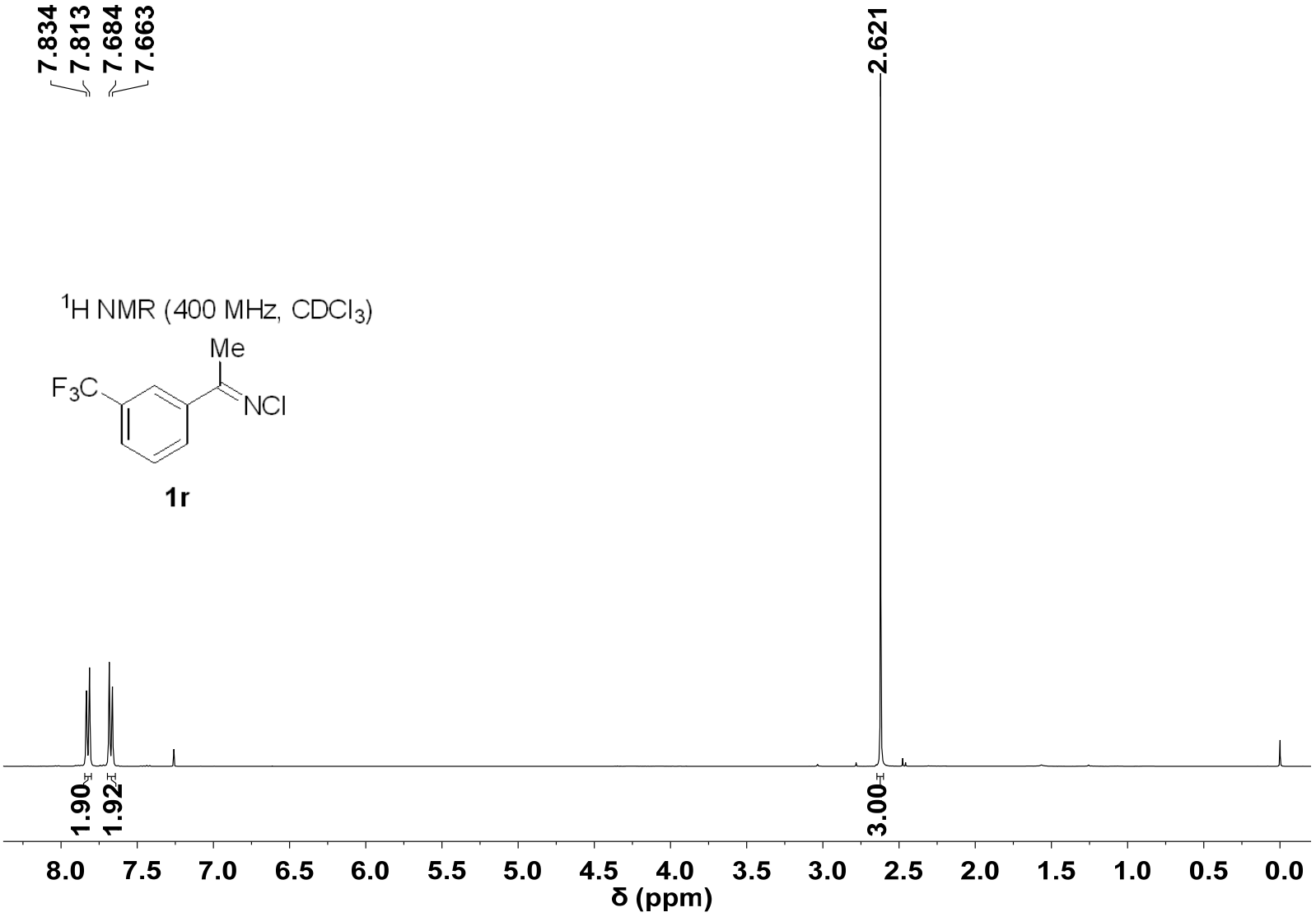

175.942
175.917
163.928
161.473
139.146
139.072
130.233
130.153
122.714
122.684
117.887
117.676
114.135
113.903
20.500
^{13}C NMR (101 MHz, CDCl$_3$)
Me
F
NCl
1o
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

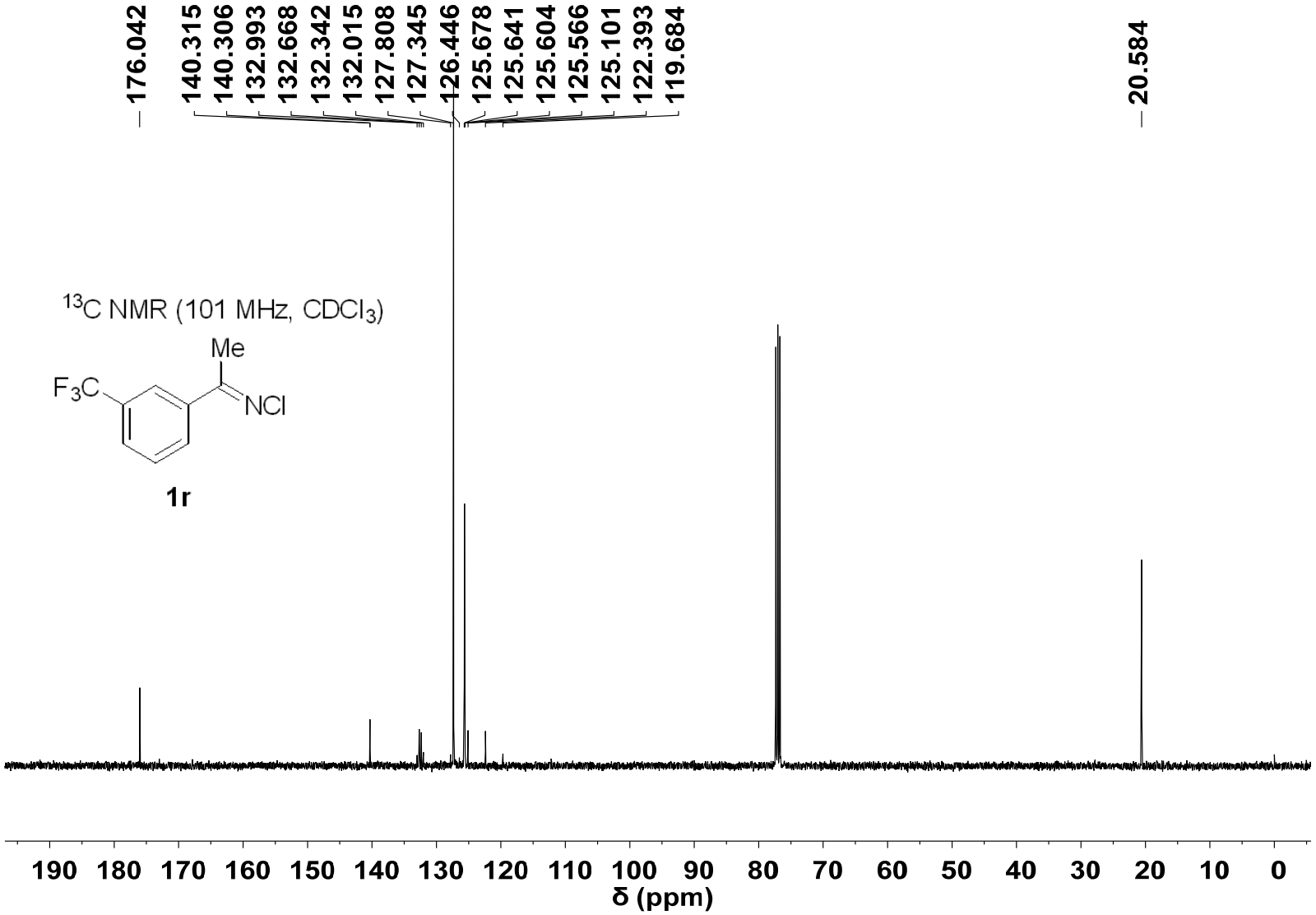

7.703
7.699
7.694
7.583
7.580
7.576
7.564
7.560
7.557
7.434
7.431
7.429
7.426
7.414
7.411
7.409
7.406
7.355
7.335
7.315
7.254
2.567
^{1}H NMR (400 MHz, CDCl$_3$)
Me
Cl
NCl
1p
0.79
0.92
0.87
0.96
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

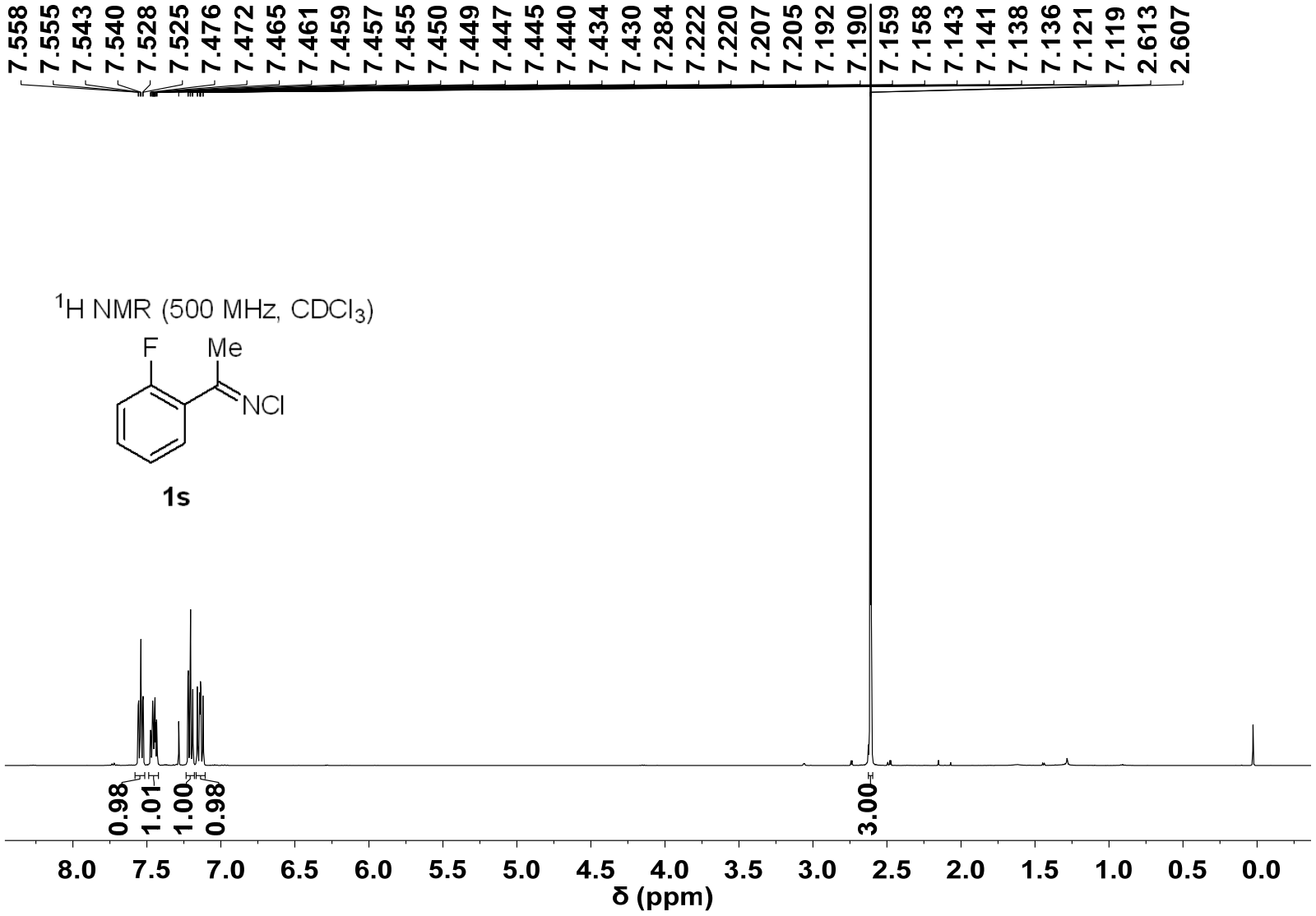

175.884
138.722
134.755
130.813
129.883
127.119
125.088
20.489
13C NMR (101 MHz, CDCl3)
Me
Cl
NCl
1p
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

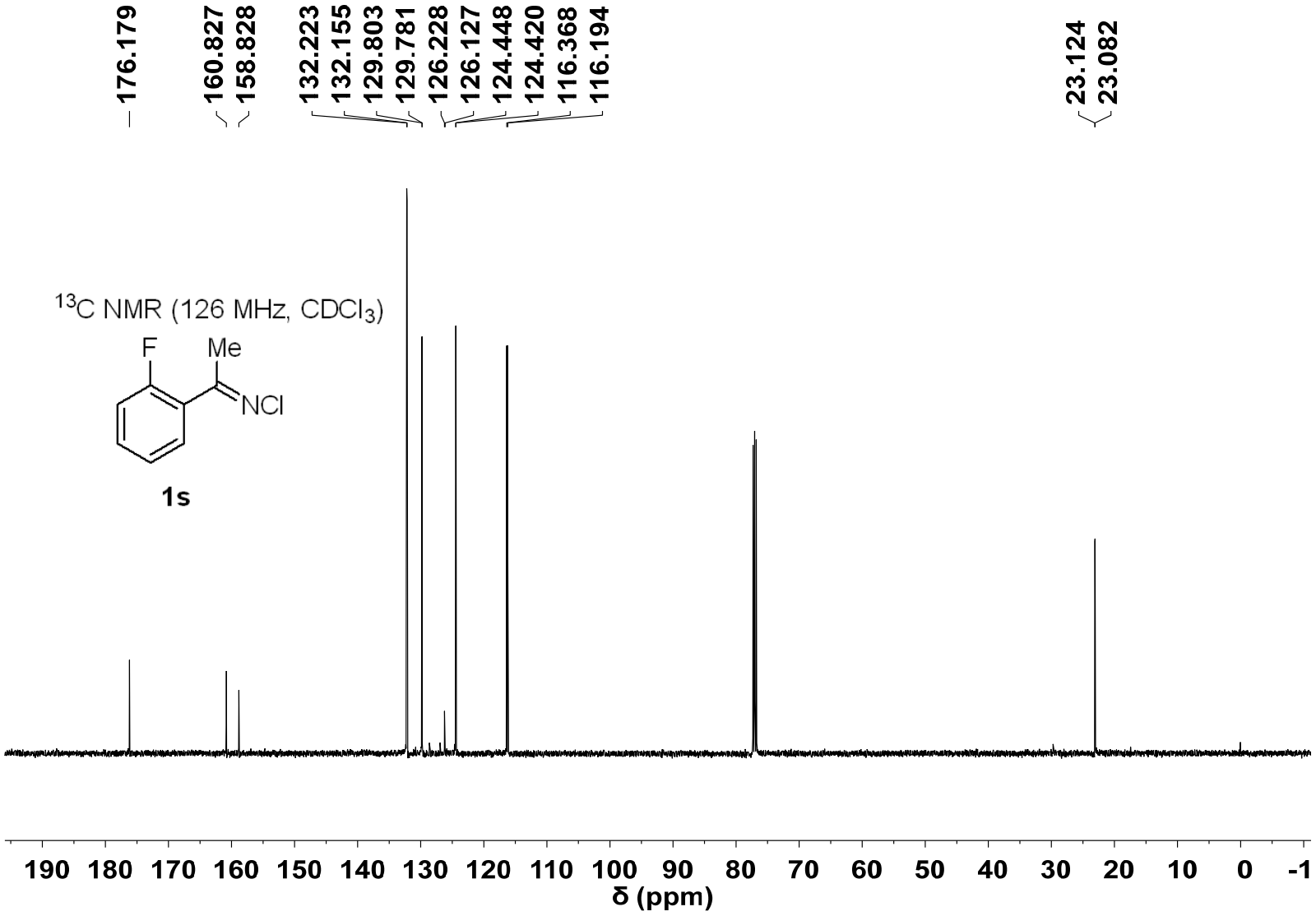

7.857
7.626
7.606
7.585
7.565
7.295
7.275
2.563
^{1}H NMR (400 MHz, $CDCl_3$)
Me
Br
NCl
1q
0.84
1.89
0.79
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

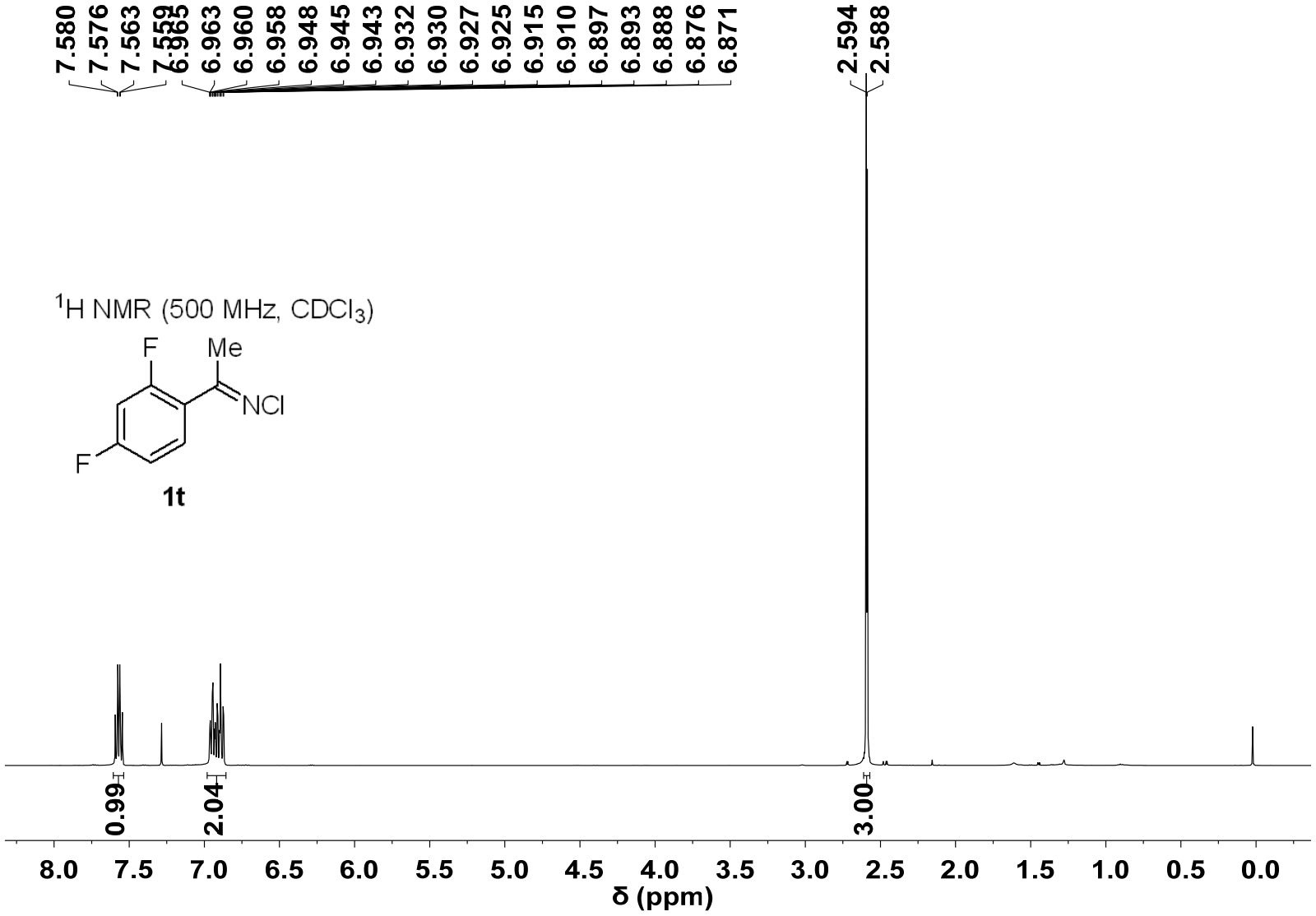

175.793
138.940
133.742
130.137
130.006
125.538
122.818
20.497
13C NMR (101 MHz, CDCl3)
Me
Br
NCl
1q
δ (ppm)

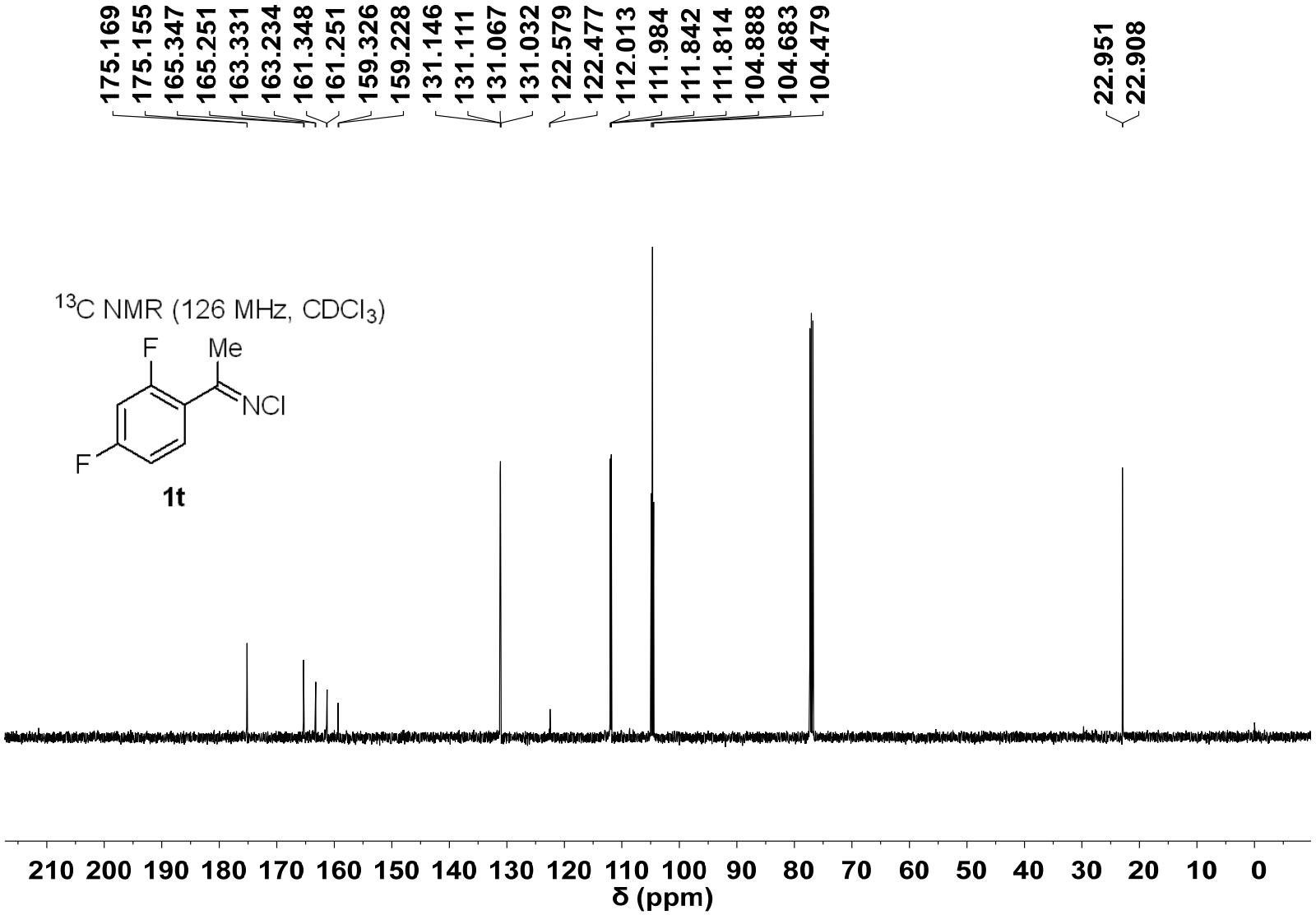

7.834
7.813
7.684
7.663
2.621
^{1}H NMR (400 MHz, $CDCl_3$)
Me
F_3C
NCl
1r
1.90
1.92
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

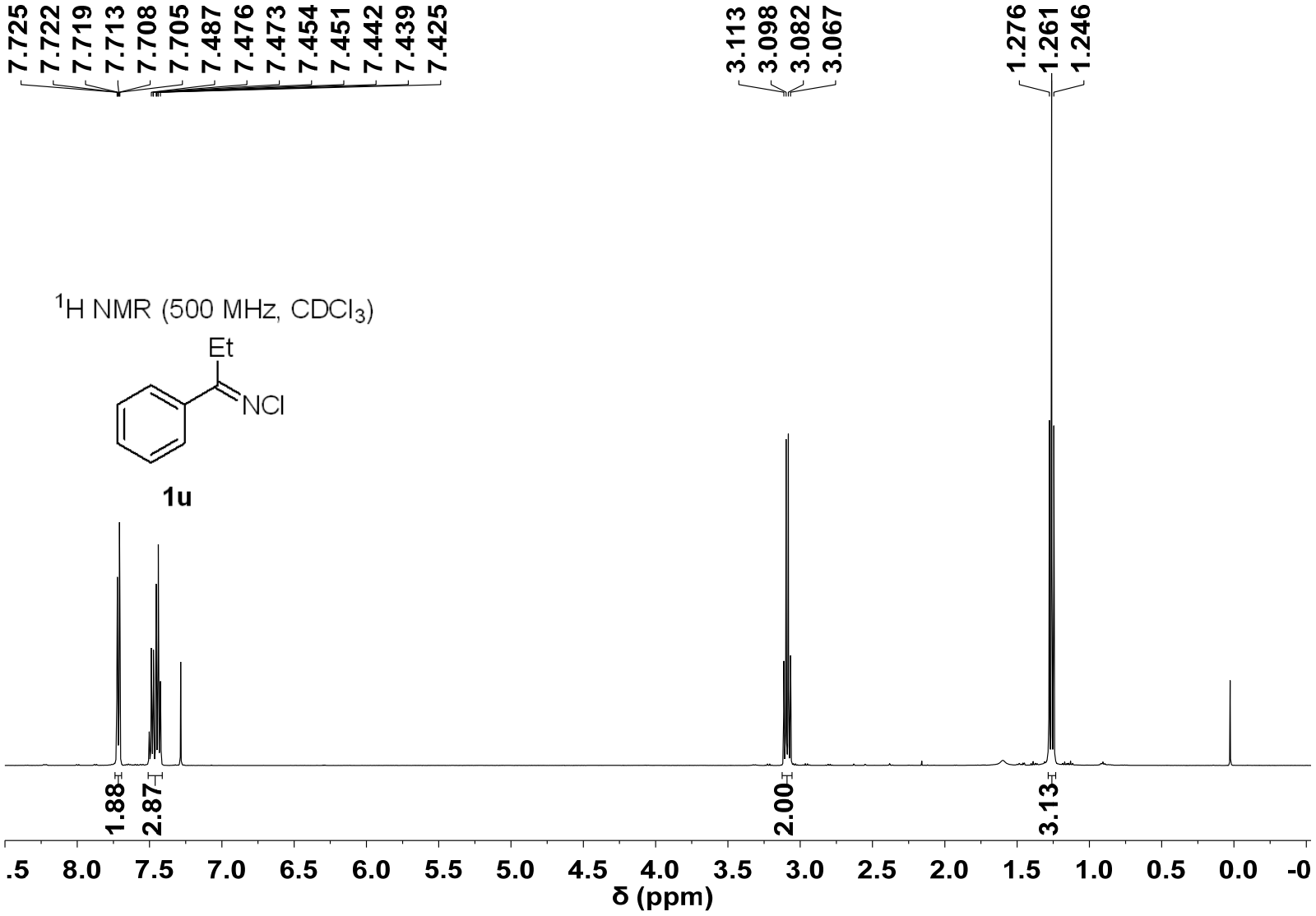

176.042
140.315
140.306
132.993
132.668
132.342
132.015
127.808
127.345
126.446
125.678
125.641
125.604
125.566
125.101
122.393
119.684
20.584
13C NMR (101 MHz, CDCl3)
Me
F3C
NCl
1r
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

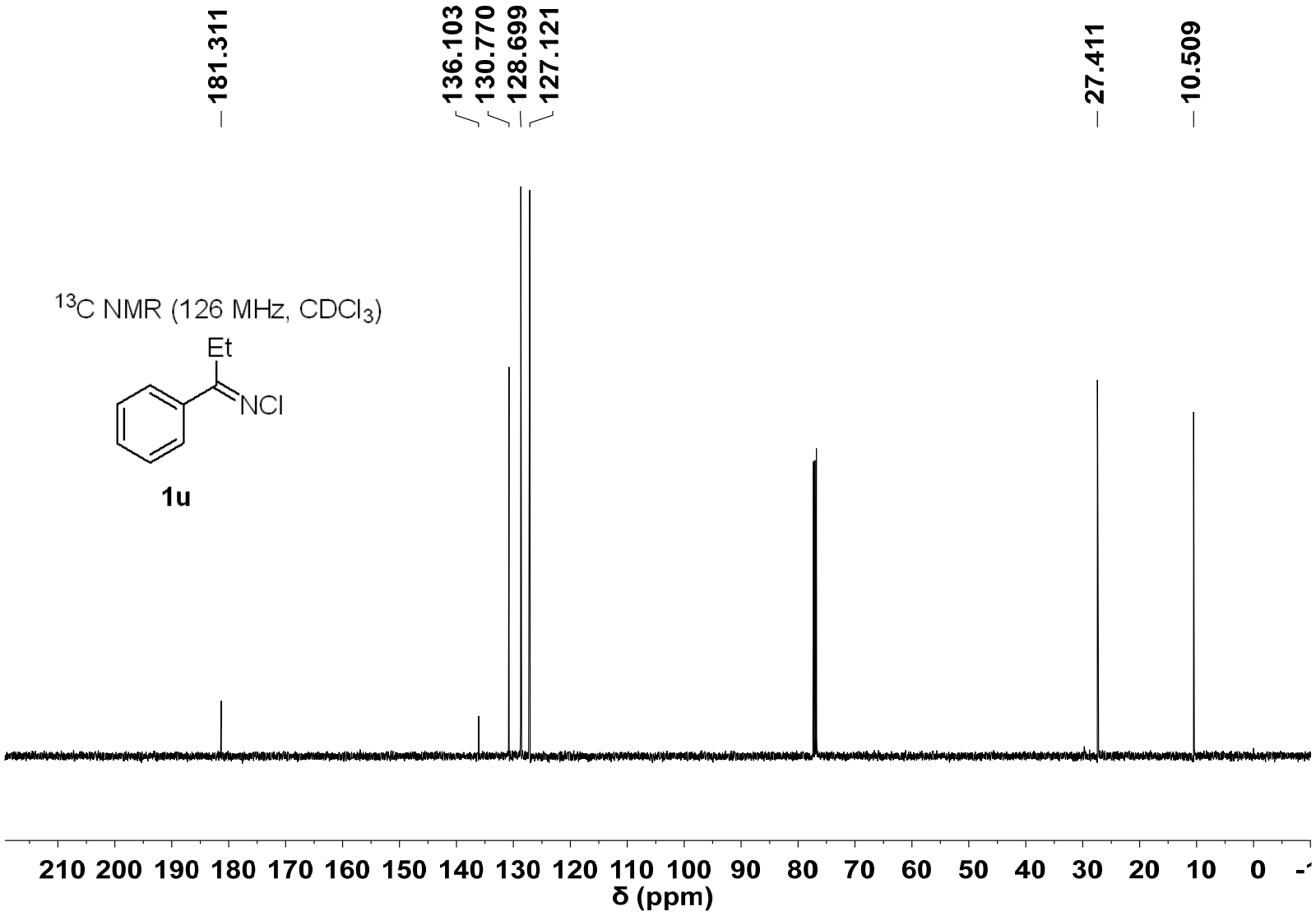

7.558
7.555
7.543
7.540
7.528
7.525
7.476
7.472
7.465
7.461
7.459
7.457
7.455
7.450
7.449
7.447
7.445
7.440
7.434
7.430
7.284
7.222
7.220
7.207
7.205
7.192
7.190
7.159
7.158
7.143
7.141
7.138
7.136
7.121
7.119
2.613
2.607
1H NMR (500 MHz, CDCl3)
F
Me
NCl
1s
0.98
1.01
1.00
0.98
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

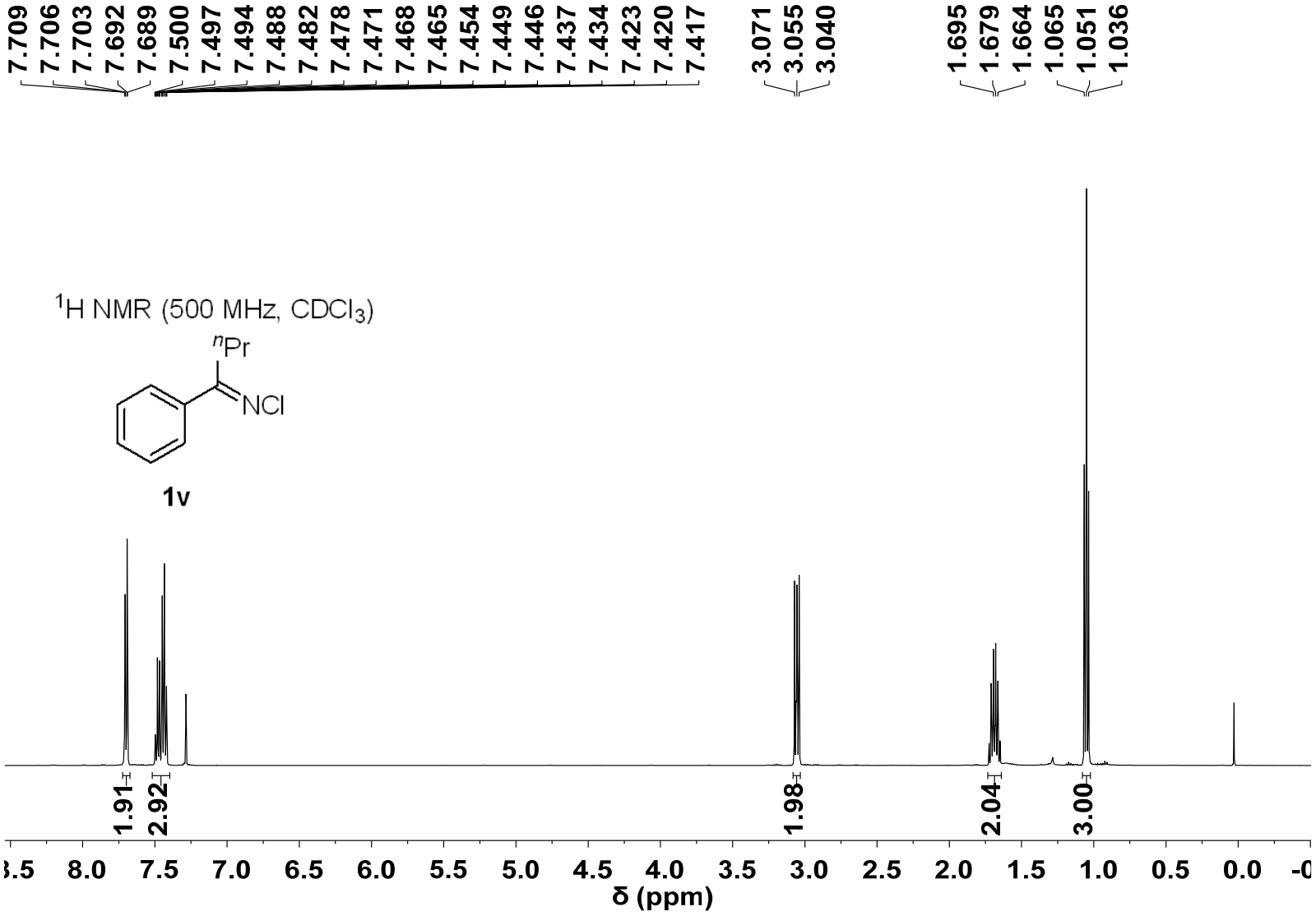

176.179
160.827
158.828
132.223
132.155
129.803
129.781
126.228
126.127
124.448
124.420
116.368
116.194
23.124
23.082
13C NMR (126 MHz, CDCl3)
F
Me
NCl
1s
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

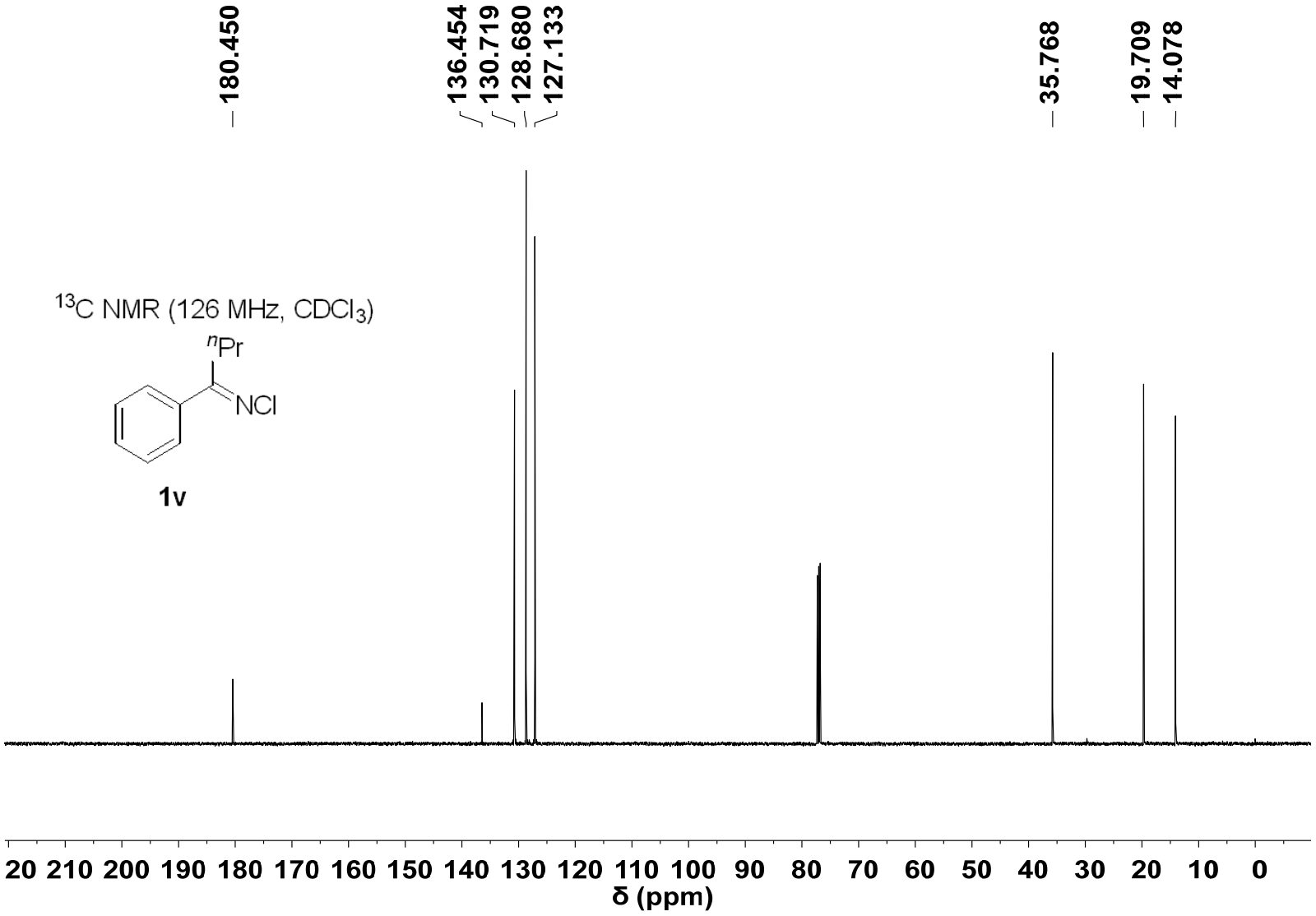

7.580
7.576
7.563
7.559
6.965
6.963
6.960
6.958
6.948
6.945
6.943
6.932
6.930
6.927
6.925
6.915
6.910
6.897
6.893
6.888
6.876
6.871
2.594
2.588
1H NMR (500 MHz, CDCl3)
F
Me
NCl
F
1t
0.99
2.04
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

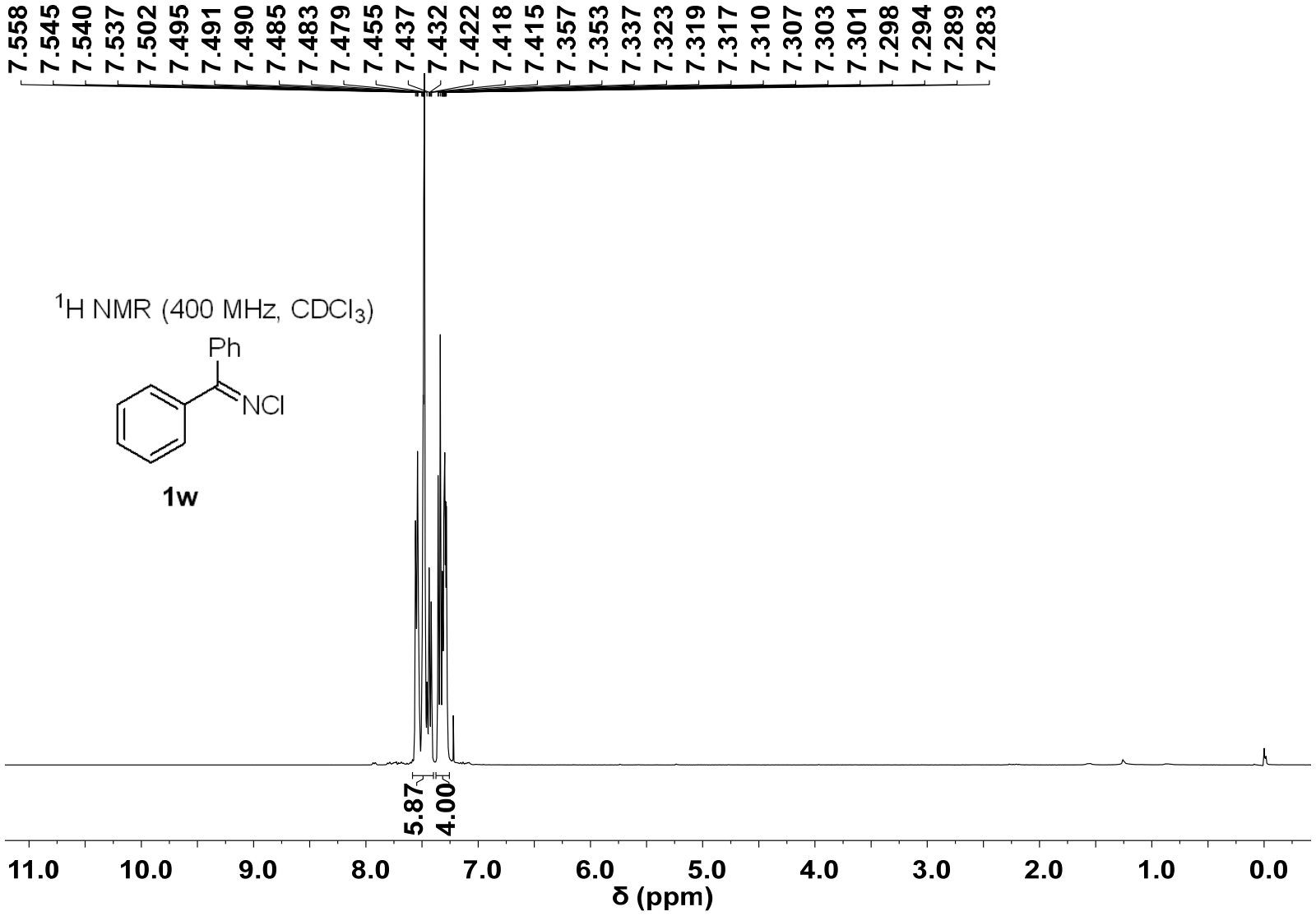

175.169
175.155
165.347
165.251
163.331
163.234
161.348
161.251
159.326
159.228
131.146
131.111
131.067
131.032
122.579
122.477
112.013
111.984
111.842
111.814
104.888
104.683
104.479
22.951
22.908
13C NMR (126 MHz, CDCl3)
F
Me
NCl
F
1t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

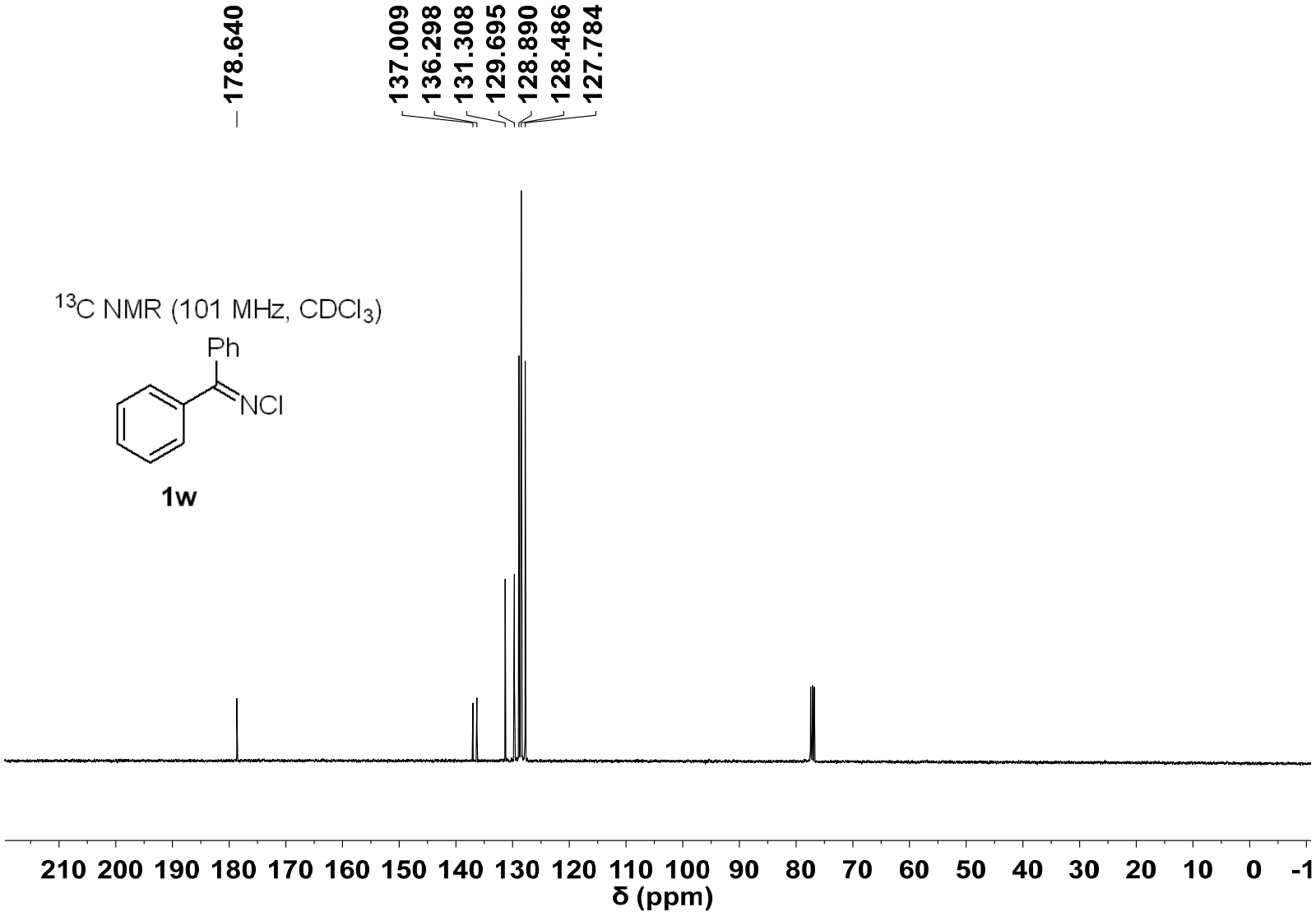

7.725
7.722
7.719
7.713
7.708
7.705
7.487
7.476
7.473
7.454
7.451
7.442
7.439
7.425
3.113
3.098
3.082
3.067
1.276
1.261
1.246
1H NMR (500 MHz, CDCl3)
Et
NCl
1u
1.88
2.87
2.00
3.13
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
δ (ppm)

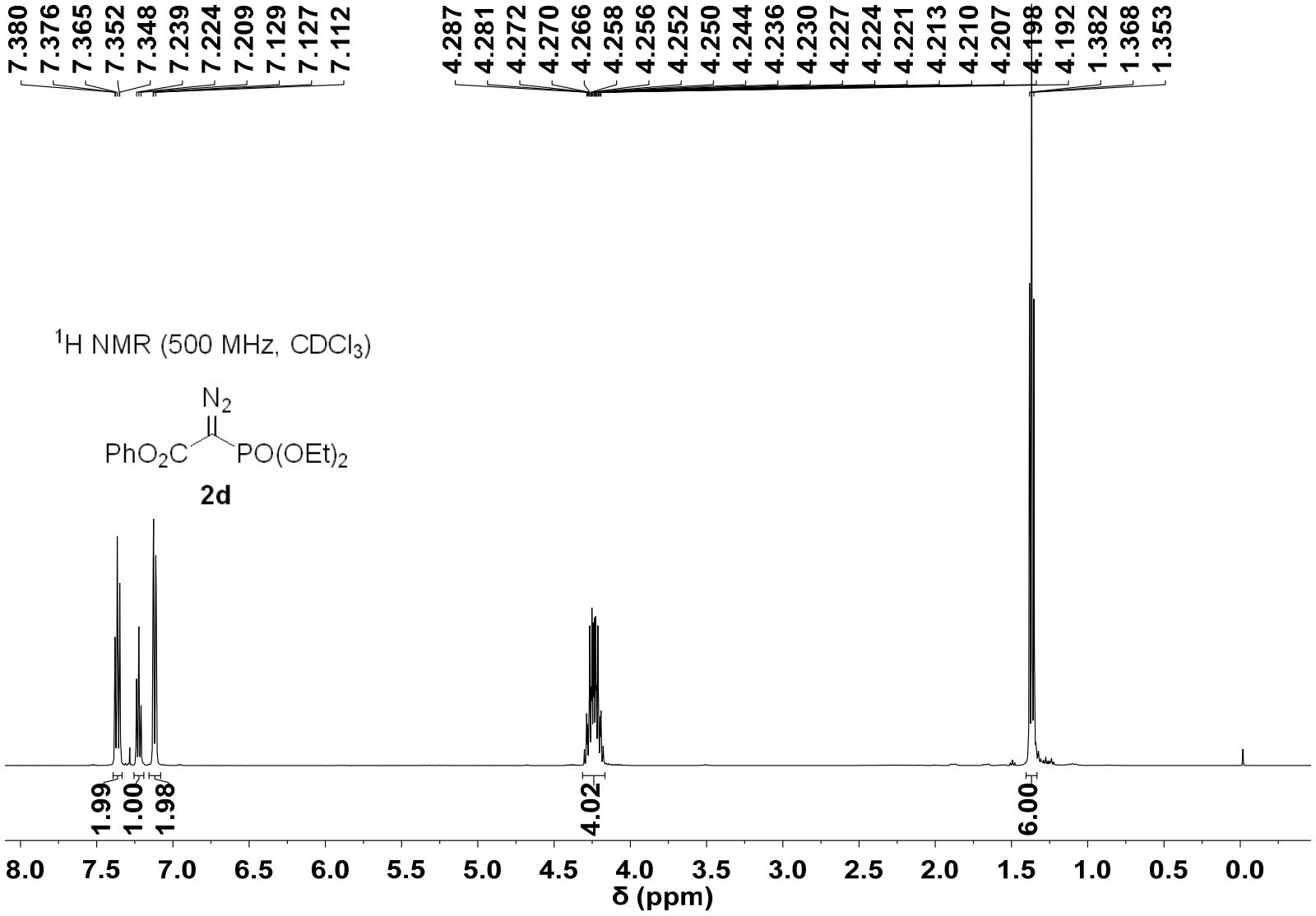

181.311
136.103
130.770
128.699
127.121
27.411
10.509
13C NMR (126 MHz, CDCl3)
Et
NCl
1u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

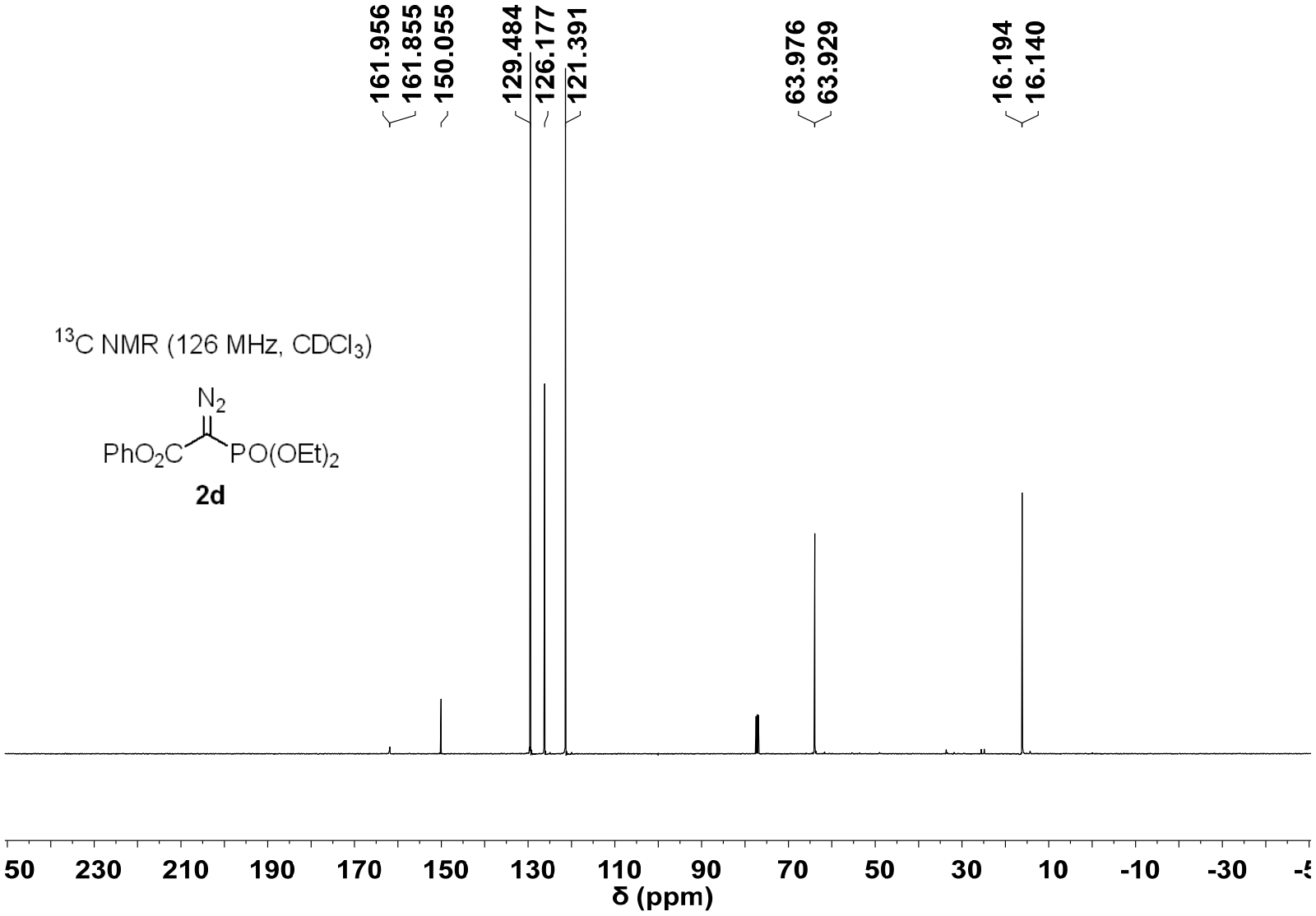

7.709
7.706
7.703
7.692
7.689
7.500
7.497
7.494
7.488
7.482
7.478
7.471
7.468
7.465
7.454
7.449
7.446
7.437
7.434
7.423
7.420
7.417
3.071
3.055
3.040
1.695
1.679
1.664
1.065
1.051
1.036
1H NMR (500 MHz, CDCl3)
nPr
NCl
1v
1.91
2.92
1.98
2.04
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

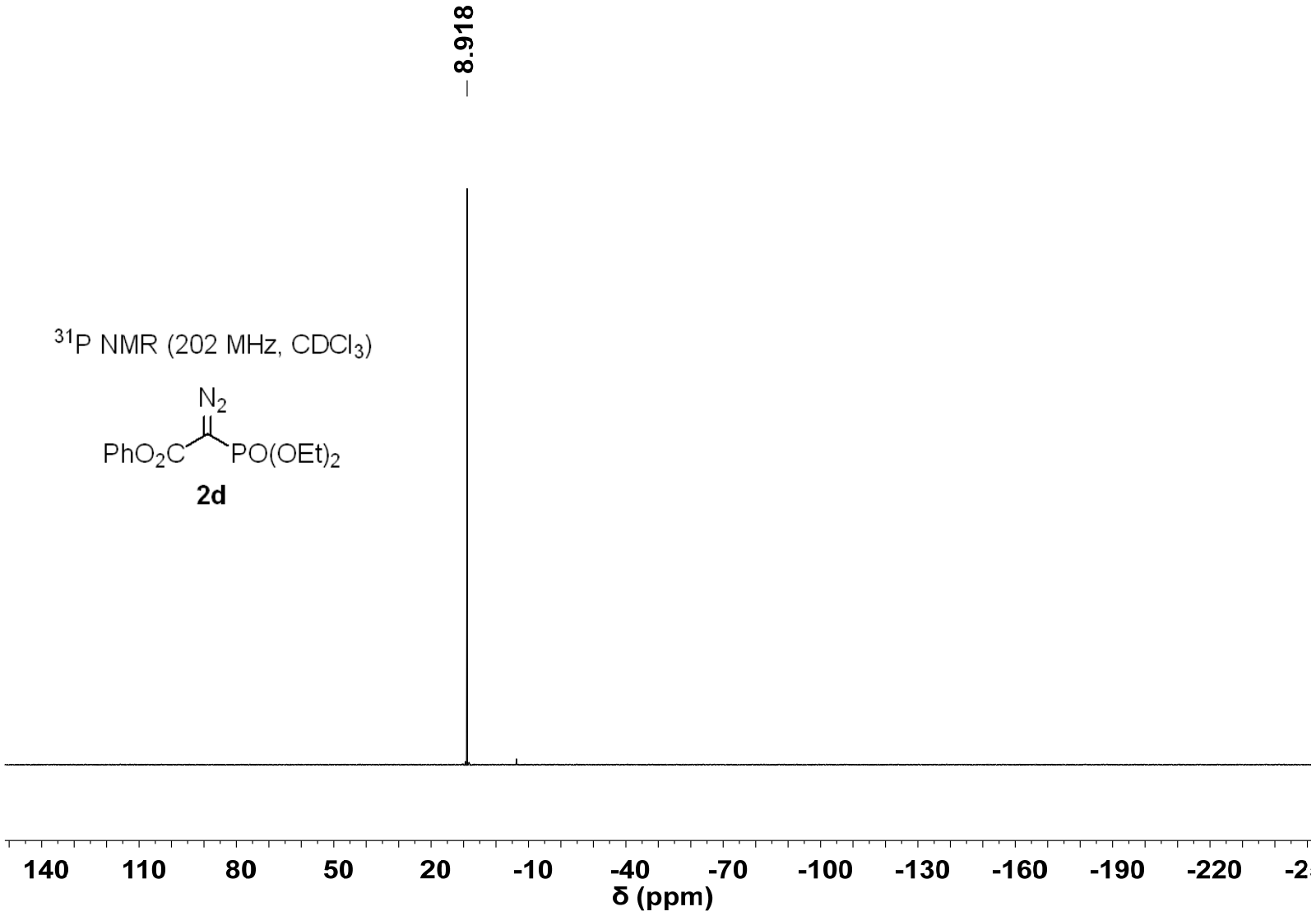

180.450
136.454
130.719
128.680
127.133
35.768
19.709
14.078
13C NMR (126 MHz, CDCl3)
nPr
NCl
1v
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

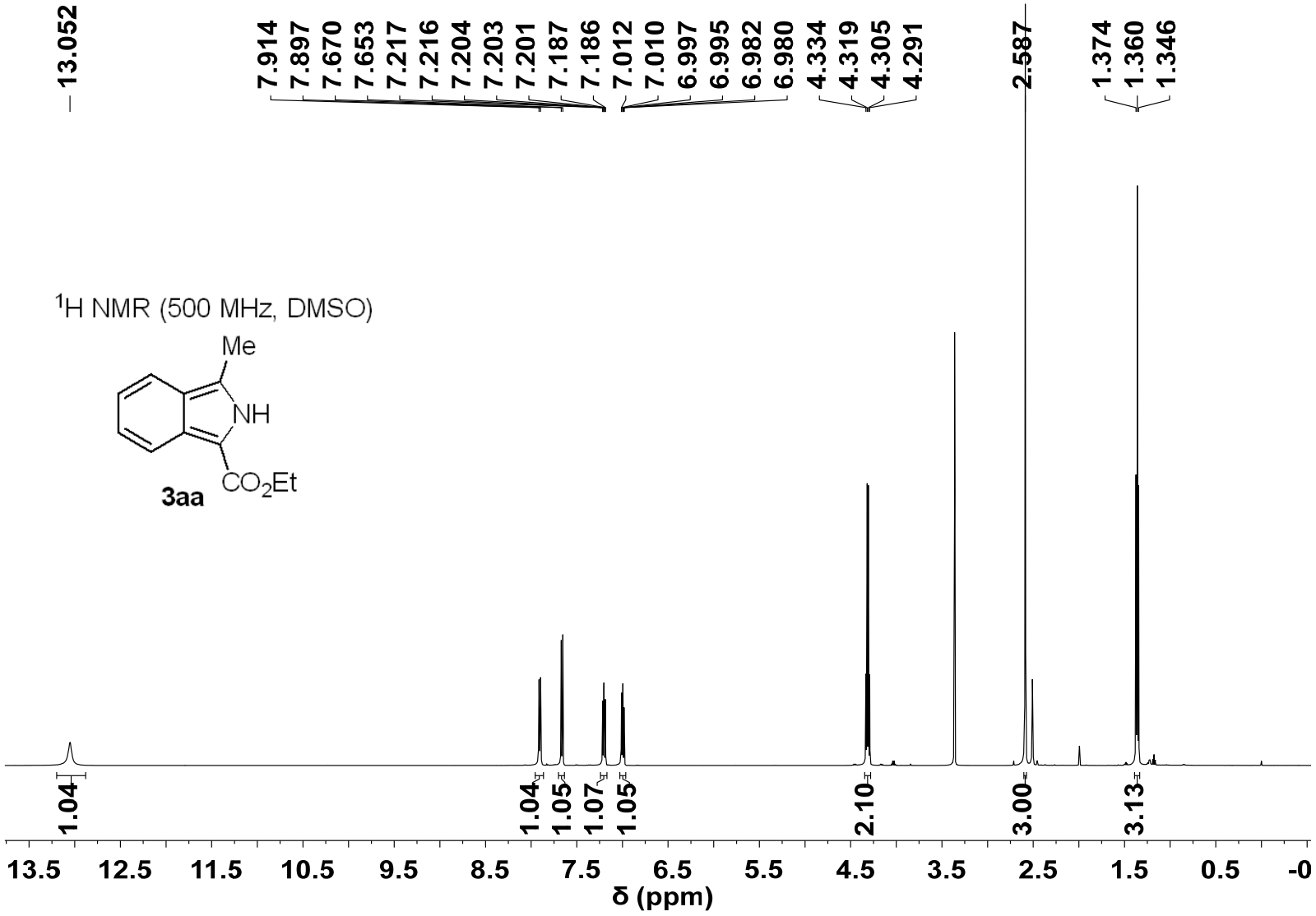

7.558
7.545
7.540
7.537
7.502
7.495
7.491
7.490
7.485
7.483
7.479
7.455
7.437
7.432
7.422
7.418
7.415
7.357
7.353
7.337
7.323
7.319
7.317
7.310
7.307
7.303
7.301
7.298
7.294
7.289
7.283
^{1}H NMR (400 MHz, CDCl$_3$)
Ph
NCl
1w
5.87
4.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ (ppm)

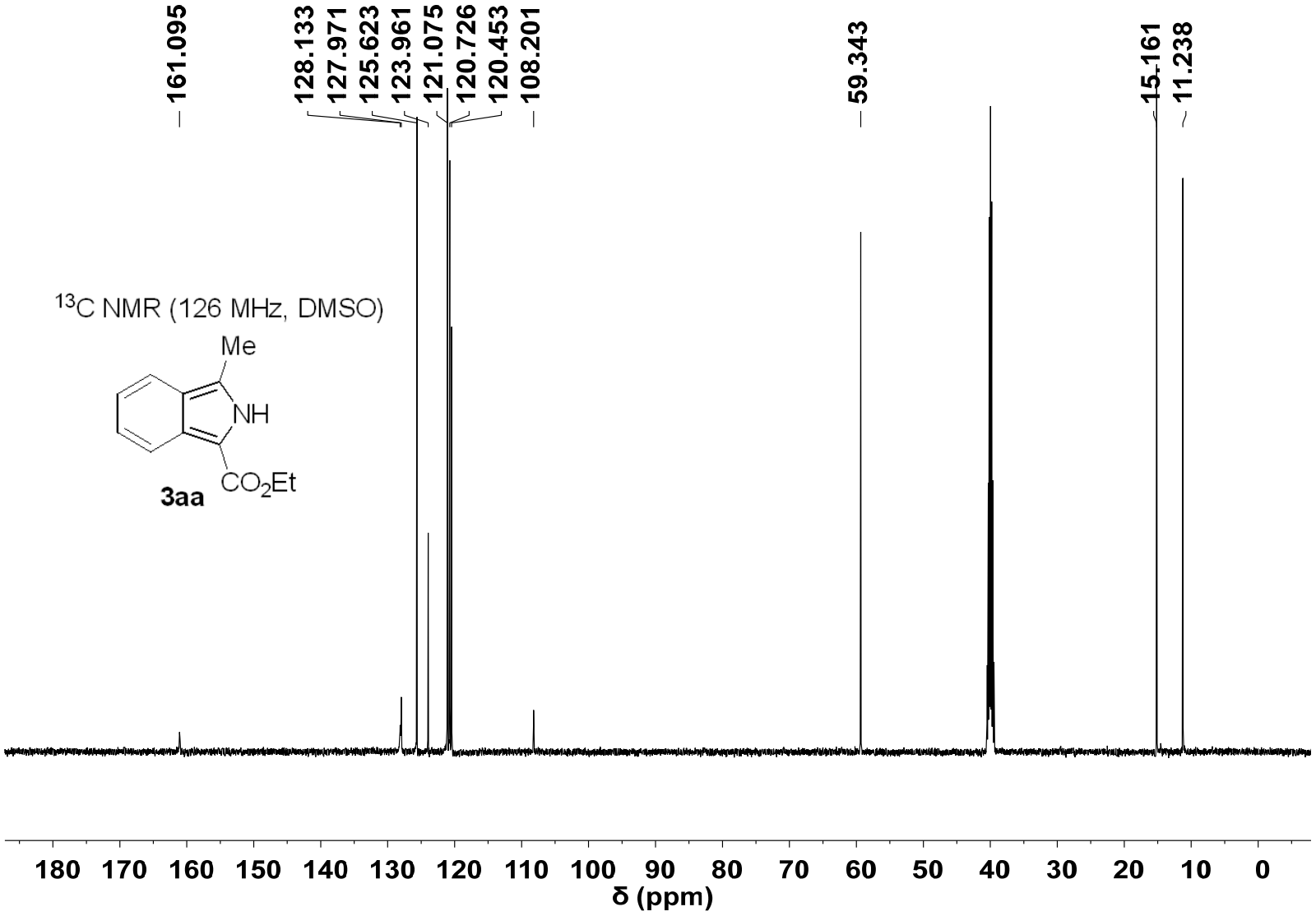

178.640
137.009
136.298
131.308
129.695
128.890
128.486
127.784
13C NMR (101 MHz, CDCl3)
Ph
NCl
1w
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

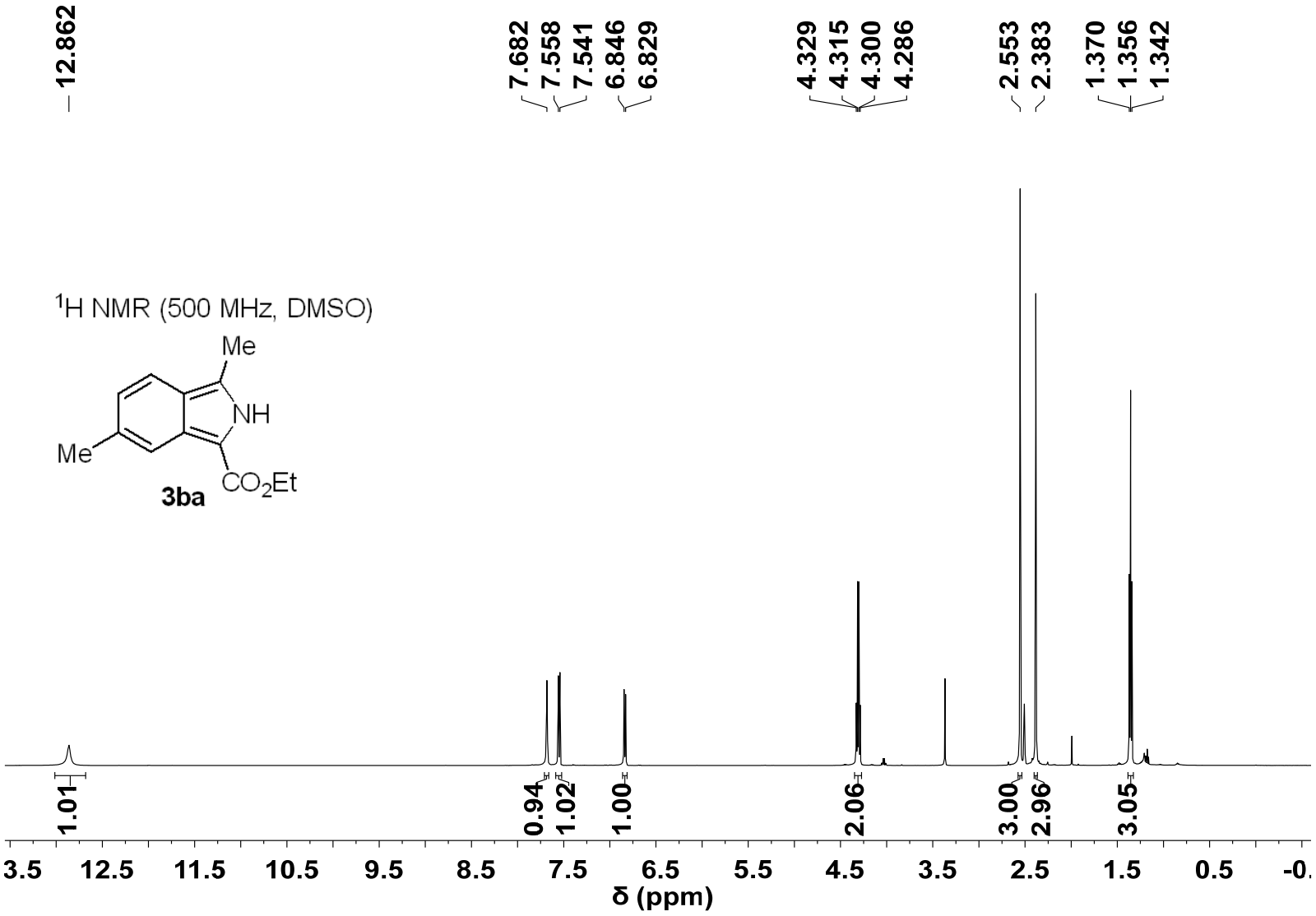

7.380
7.376
7.365
7.352
7.348
7.239
7.224
7.209
7.129
7.127
7.112
4.287
4.281
4.272
4.270
4.266
4.258
4.256
4.252
4.250
4.244
4.236
4.230
4.227
4.224
4.221
4.213
4.210
4.207
4.198
4.192
1.382
1.368
1.353
1H NMR (500 MHz, CDCl3)
N2
PhO2C
PO(OEt)2
2d
1.99
1.00
1.98
4.02
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

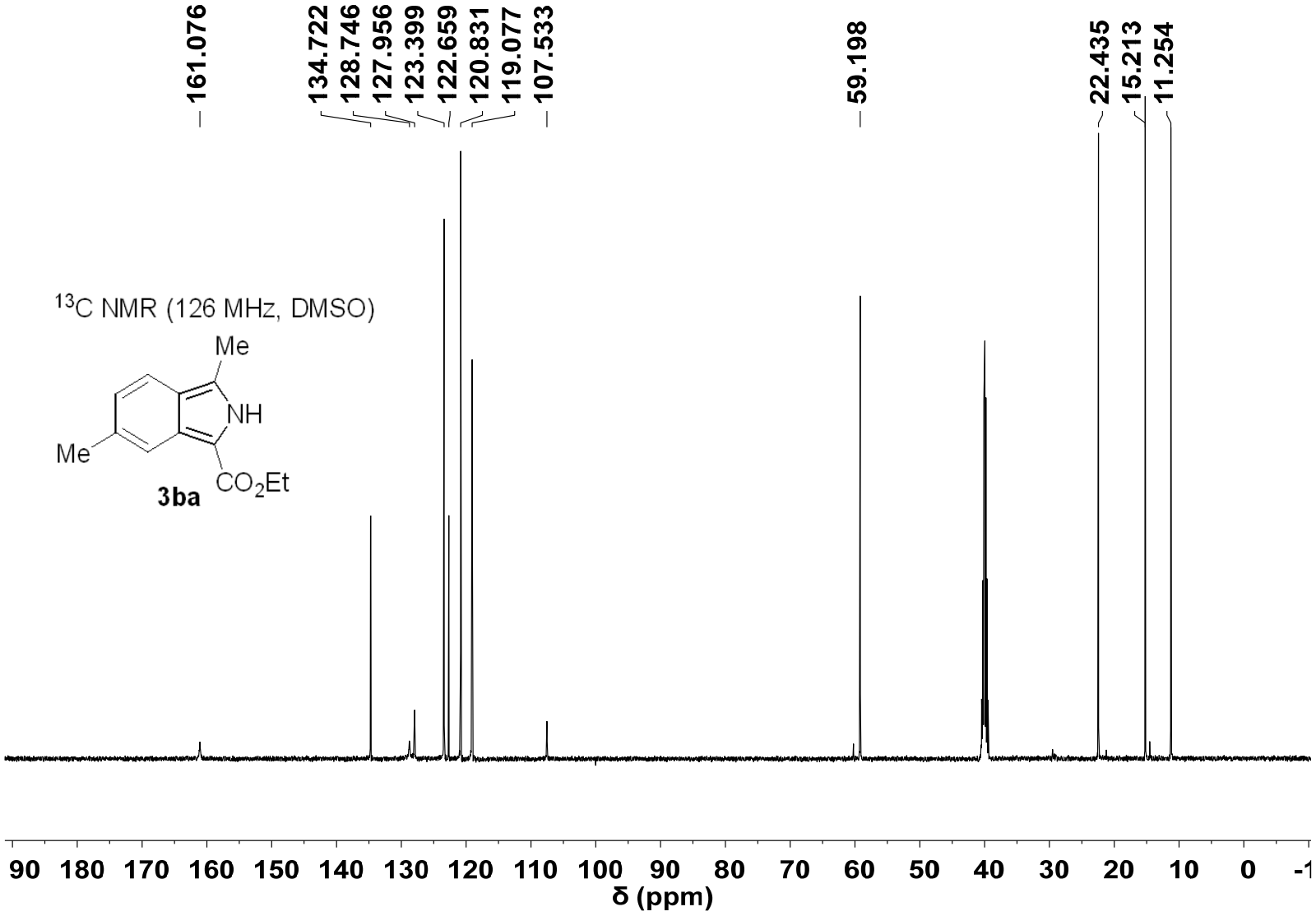

161.956
161.855
150.055
129.484
126.177
121.391
63.976
63.929
16.194
16.140
13C NMR (126 MHz, CDCl3)
N2
PhO2C
PO(OEt)2
2d
50
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
δ (ppm)

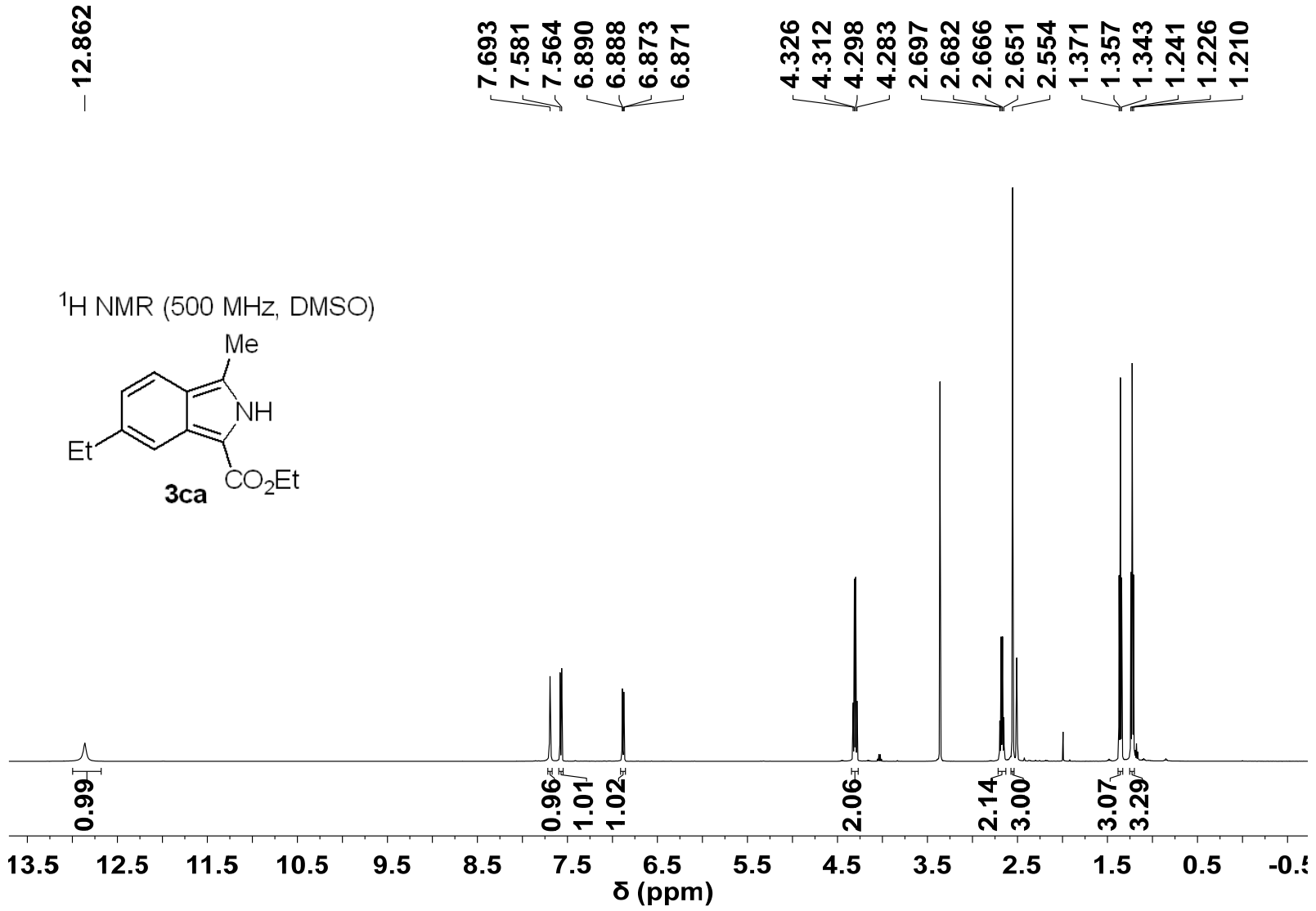

8.918
^{31}P NMR (202 MHz, $CDCl_3$)
N_2
PhO_2C
$PO(OEt)_2$
2d
140
110
80
50
20
-10
-40
-70
-100
-130
-160
-190
-220
δ (ppm)

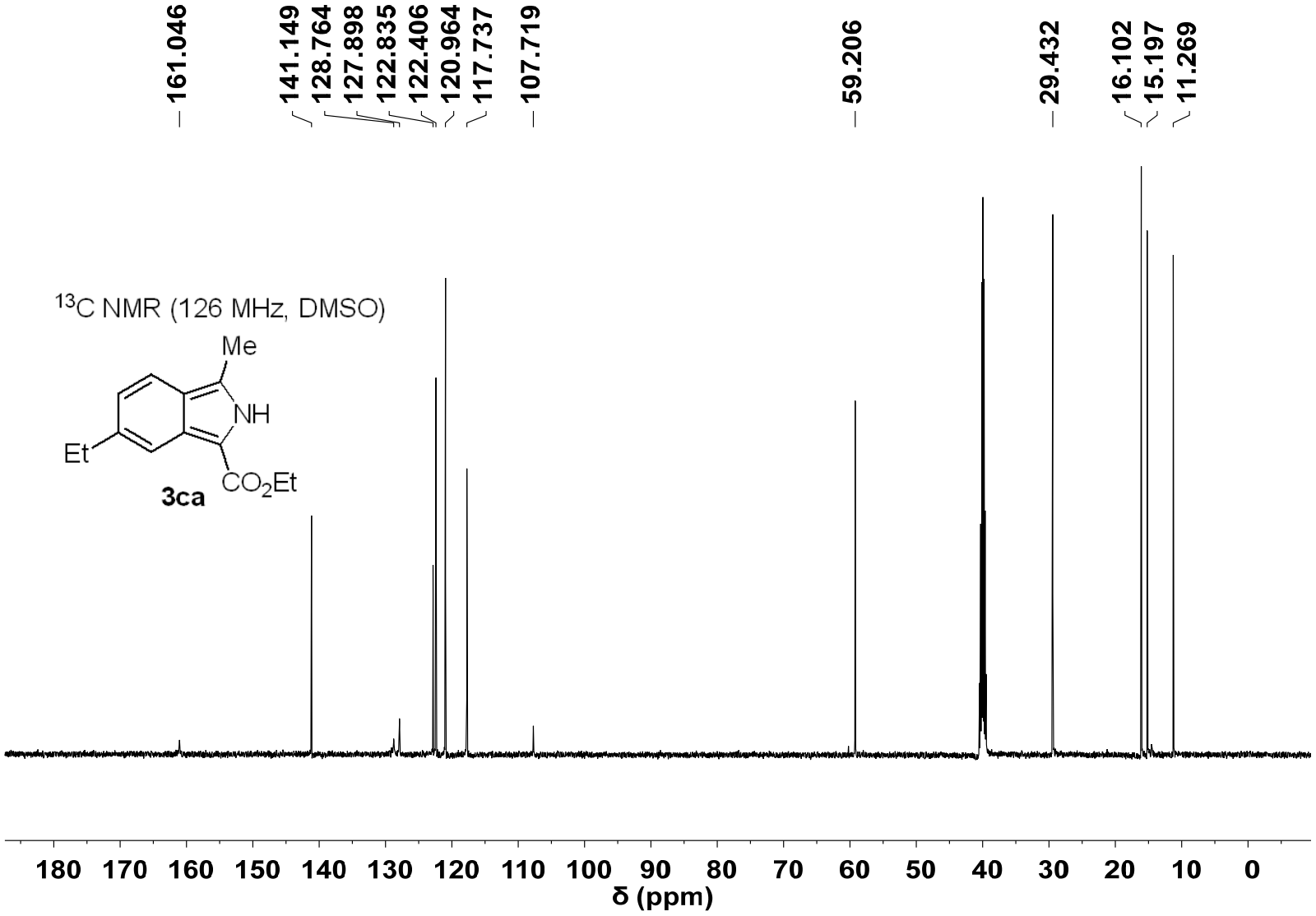

13.052
7.914
7.897
7.670
7.653
7.217
7.216
7.204
7.203
7.201
7.187
7.186
7.012
7.010
6.997
6.995
6.982
6.980
4.334
4.319
4.305
4.291
2.587
1.374
1.360
1.346
1H NMR (500 MHz, DMSO)
Me
NH
CO2Et
3aa
1.04
1.04
1.05
1.07
1.05
2.10
3.00
3.13
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0
δ (ppm)

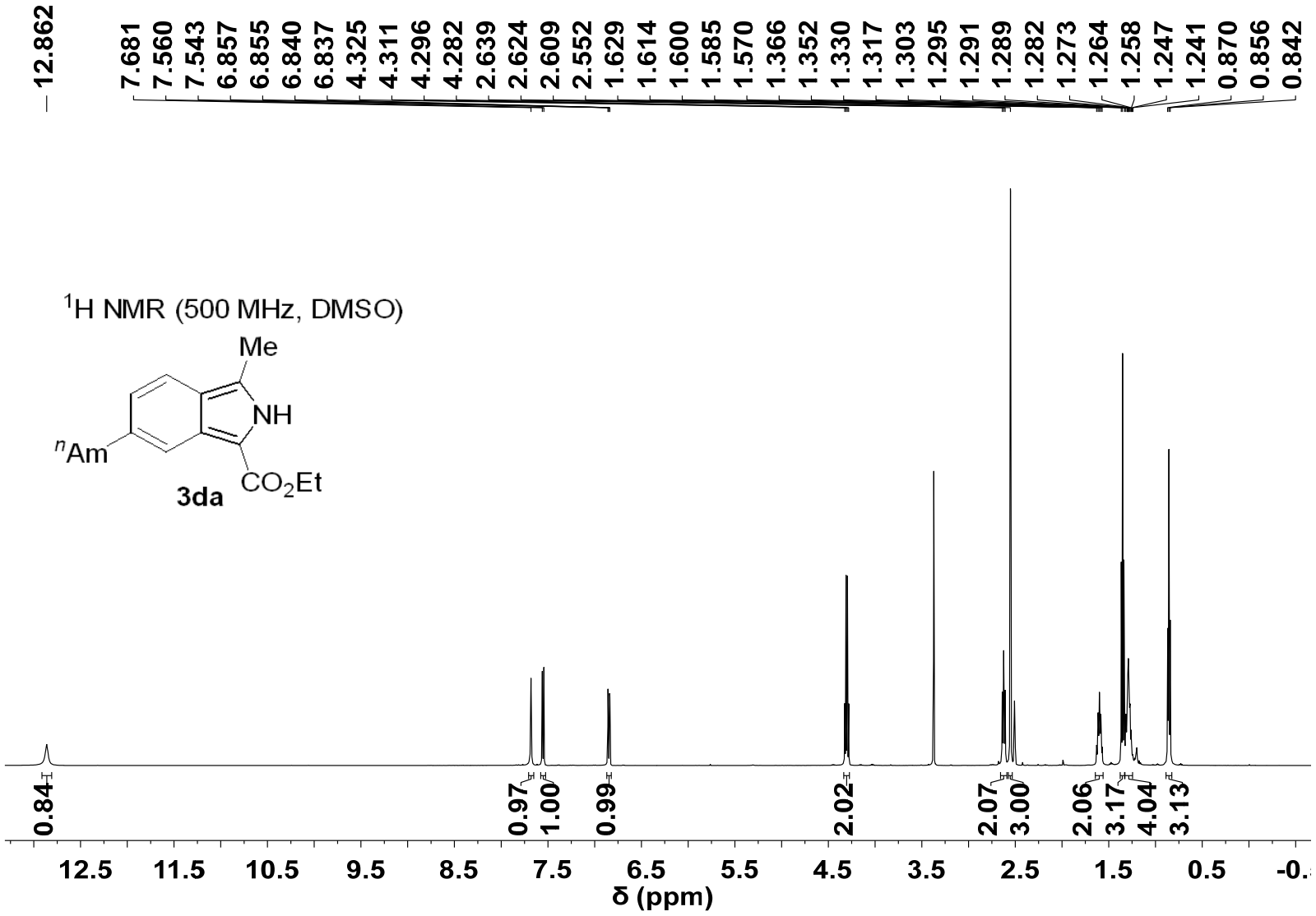

161.095
128.133
127.971
125.623
123.961
121.075
120.726
120.453
108.201
59.343
15.161
11.238
13C NMR (126 MHz, DMSO)
Me
NH
CO2Et
3aa
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

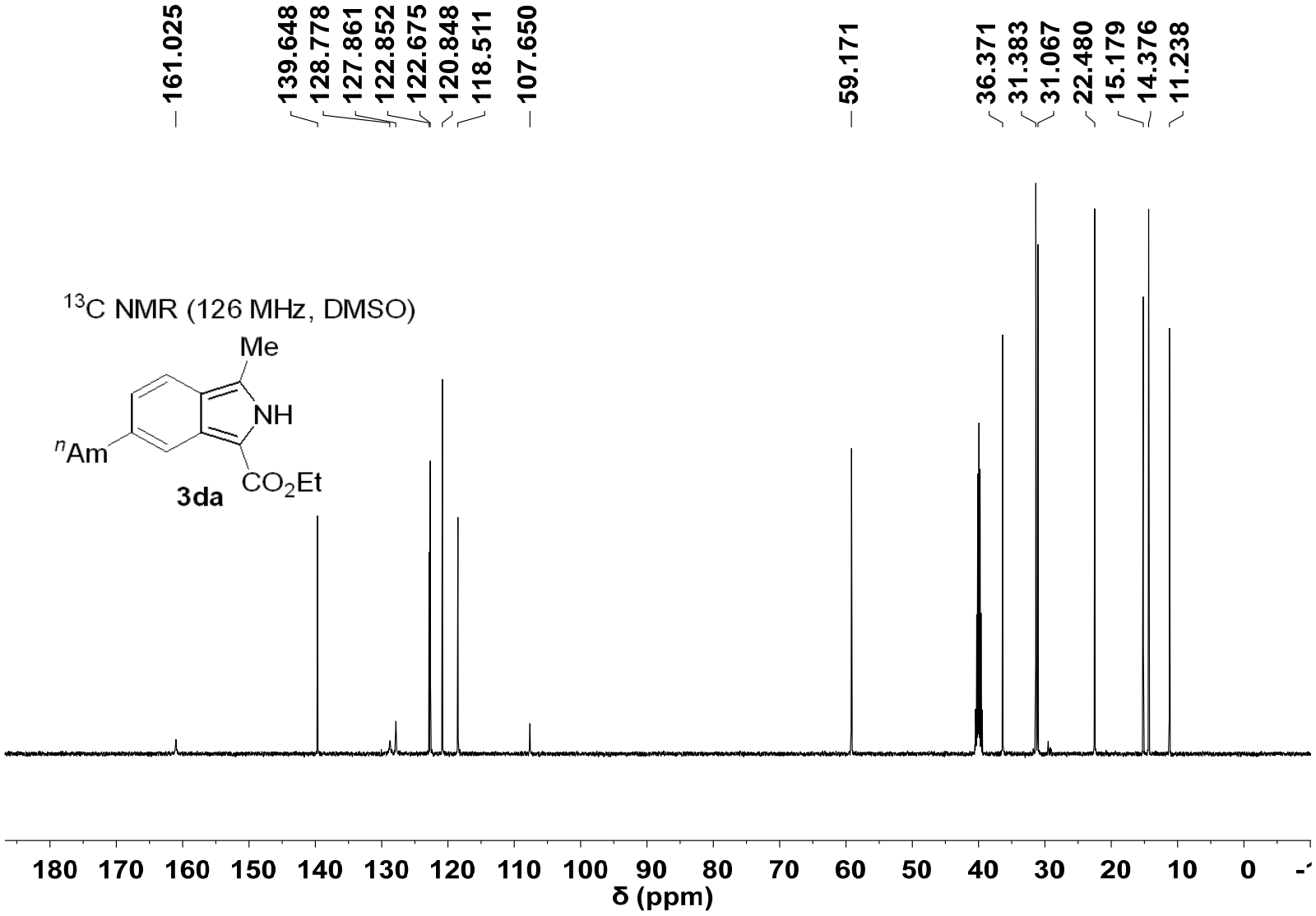

12.862
7.682
7.558
7.541
6.846
6.829
4.329
4.315
4.300
4.286
2.553
2.383
1.370
1.356
1.342
1H NMR (500 MHz, DMSO)
Me
NH
Me
CO2Et
3ba
1.01
0.94
1.02
1.00
2.06
3.00
2.96
3.05
3.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
δ (ppm)

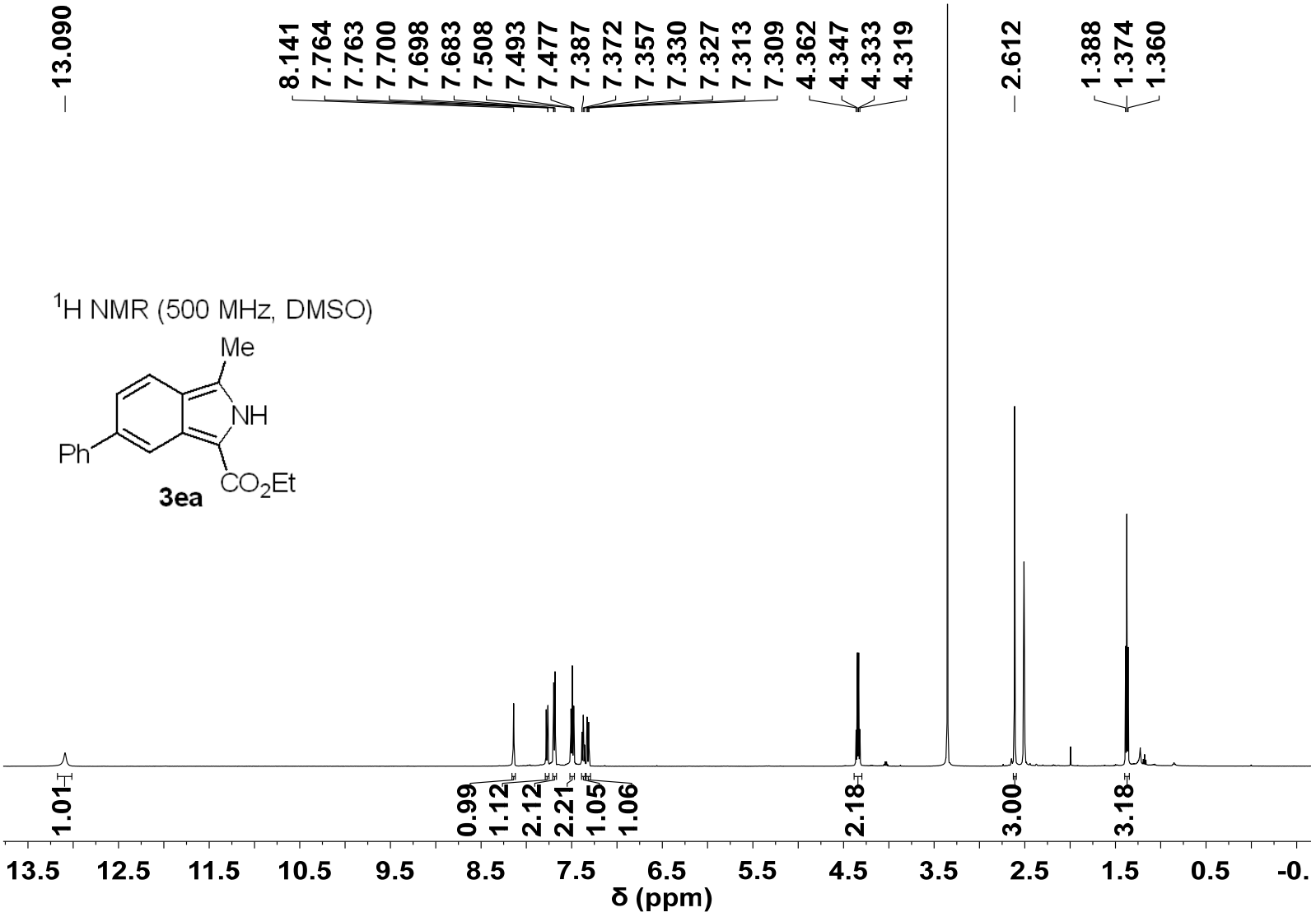

161.076
134.722
128.746
127.956
123.399
122.659
120.831
119.077
107.533
59.198
22.435
15.213
11.254
13C NMR (126 MHz, DMSO)
Me
NH
Me
CO2Et
3ba
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

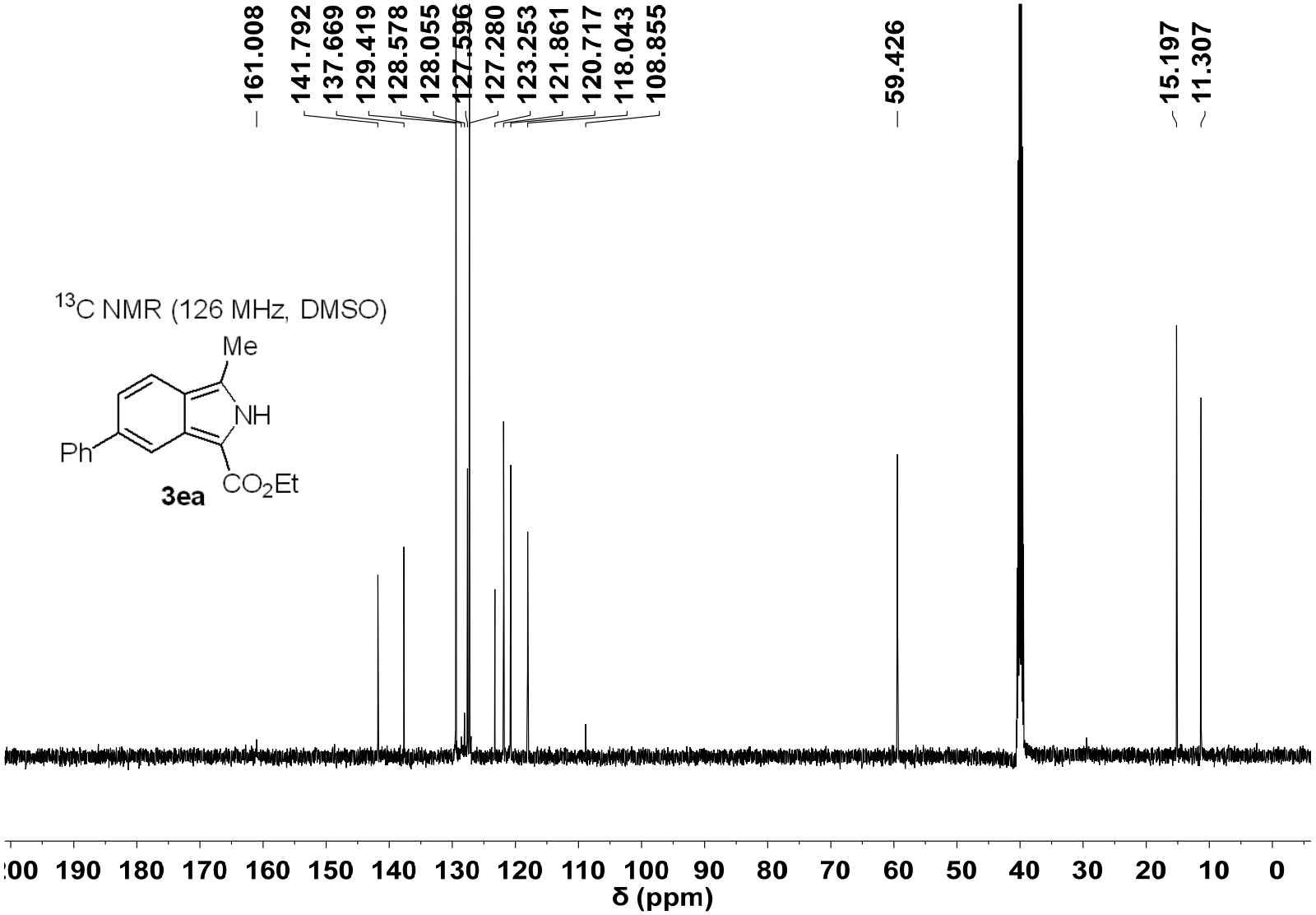

12.862
7.693
7.581
7.564
6.890
6.888
6.873
6.871
4.326
4.312
4.298
4.283
2.697
2.682
2.666
2.651
2.554
1.371
1.357
1.343
1.241
1.226
1.210
1H NMR (500 MHz, DMSO)
Me
NH
Et
CO2Et
3ca
0.99
0.96
1.01
1.02
2.06
2.14
3.00
3.07
3.29
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
δ (ppm)

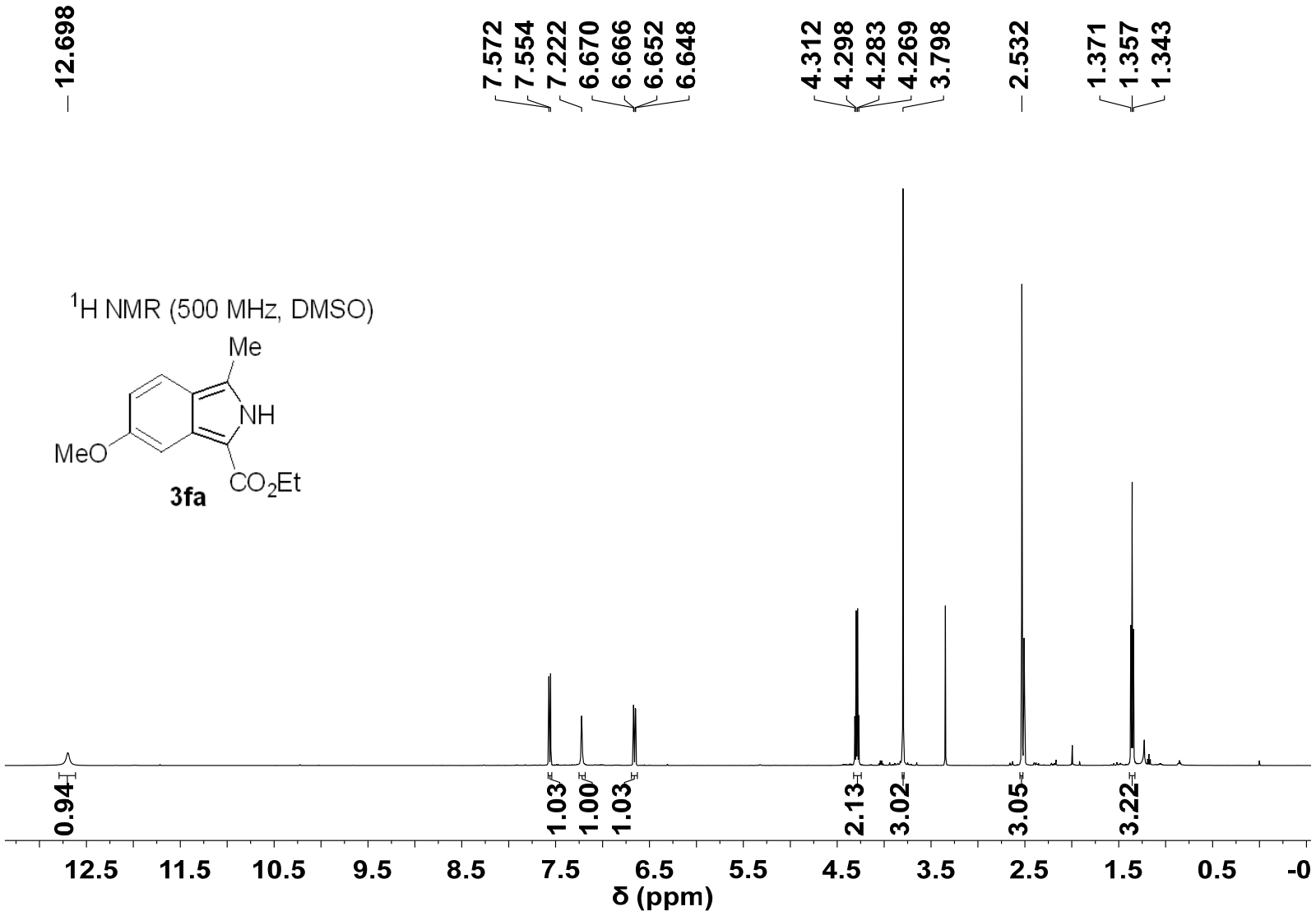

161.046
141.149
128.764
127.898
122.835
122.406
120.964
117.737
107.719
59.206
29.432
16.102
15.197
11.269
13C NMR (126 MHz, DMSO)
Me
NH
Et
CO2Et
3ca
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

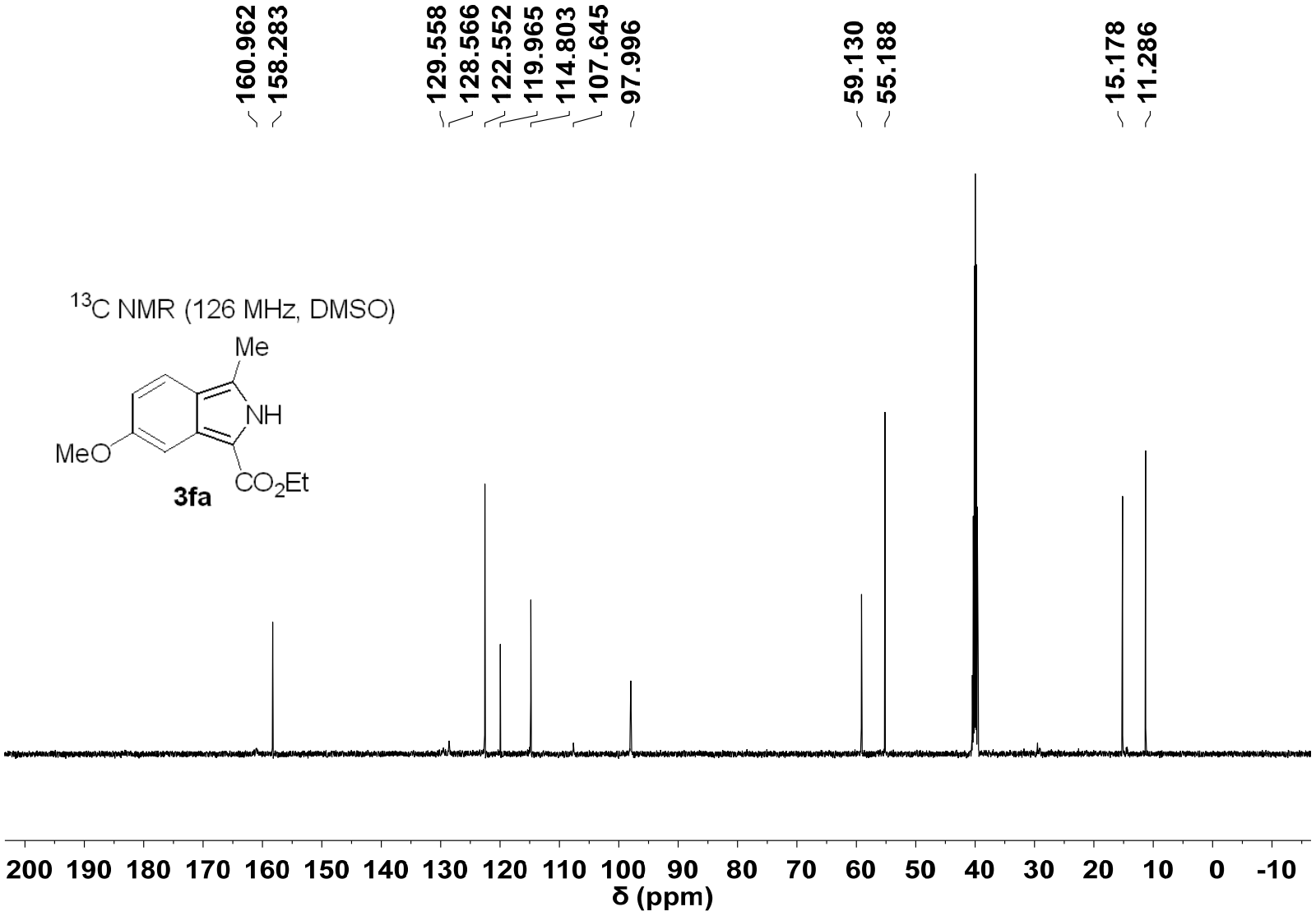

12.862
7.681
7.560
7.543
6.857
6.855
6.840
6.837
4.325
4.311
4.296
4.282
2.639
2.624
2.609
2.552
1.629
1.614
1.600
1.585
1.570
1.366
1.352
1.330
1.317
1.303
1.295
1.291
1.289
1.282
1.273
1.264
1.258
1.247
1.241
0.870
0.856
0.842
1H NMR (500 MHz, DMSO)
Me
NH
nAm
CO2Et
3da
0.84
0.97
1.00
0.99
2.02
2.07
3.00
2.06
3.17
4.04
3.13
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
δ (ppm)

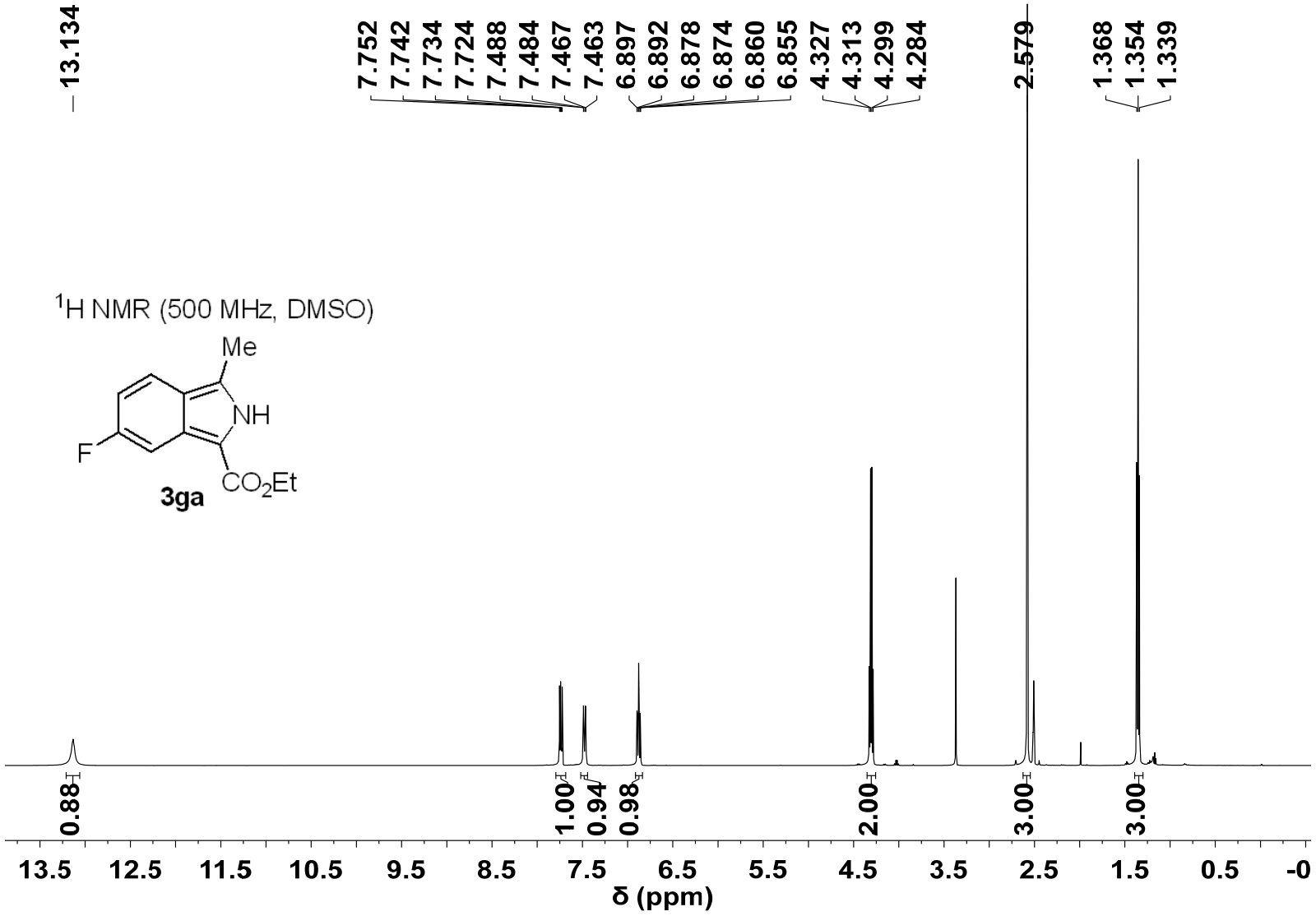

161.025
139.648
128.778
127.861
122.852
122.675
120.848
118.511
107.650
59.171
36.371
31.383
31.067
22.480
15.179
14.376
11.238
13C NMR (126 MHz, DMSO)
Me
NH
nAm
CO2Et
3da
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

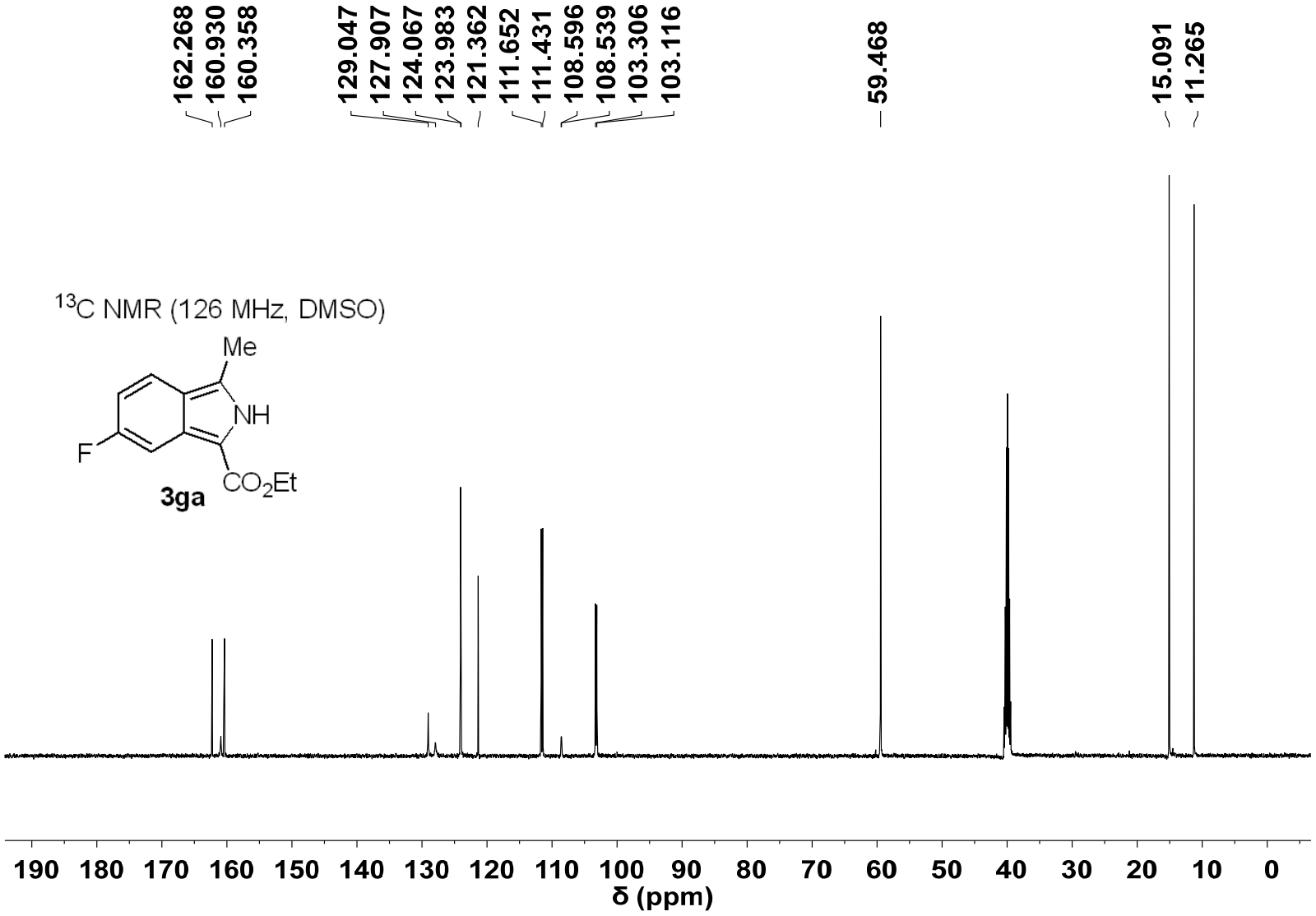

13.090
8.141
7.764
7.763
7.700
7.698
7.683
7.508
7.493
7.477
7.387
7.372
7.357
7.330
7.327
7.313
7.309
4.362
4.347
4.333
4.319
2.612
1.388
1.374
1.360
1H NMR (500 MHz, DMSO)
Me
NH
Ph
CO2Et
3ea
1.01
0.99
1.12
2.12
2.21
1.05
1.06
2.18
3.00
3.18
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.
δ (ppm)

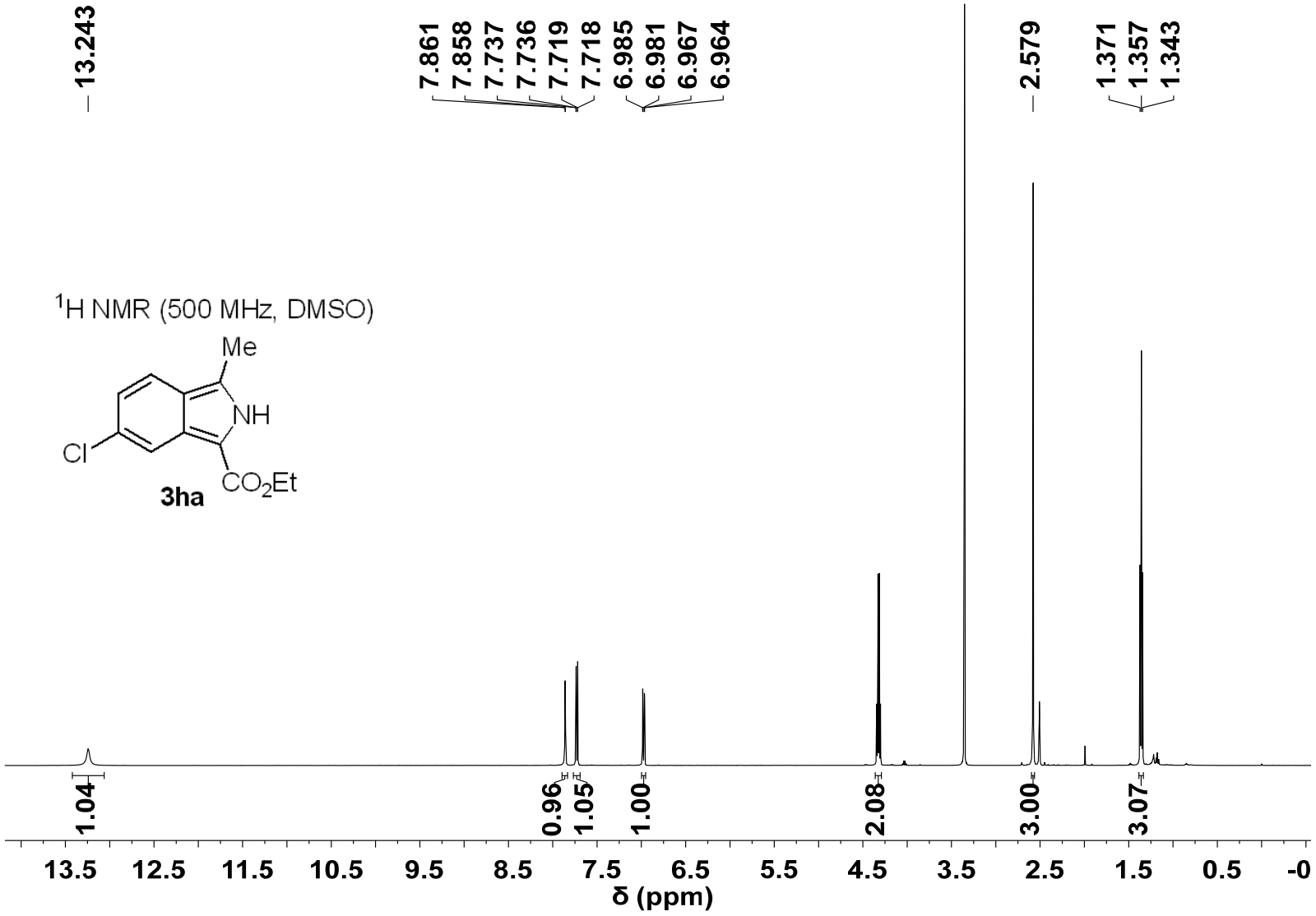

161.008
141.792
137.669
129.419
128.578
128.055
127.596
127.280
123.253
121.861
120.717
118.043
108.855
59.426
15.197
11.307
13C NMR (126 MHz, DMSO)
Me
NH
Ph
CO2Et
3ea
δ (ppm)

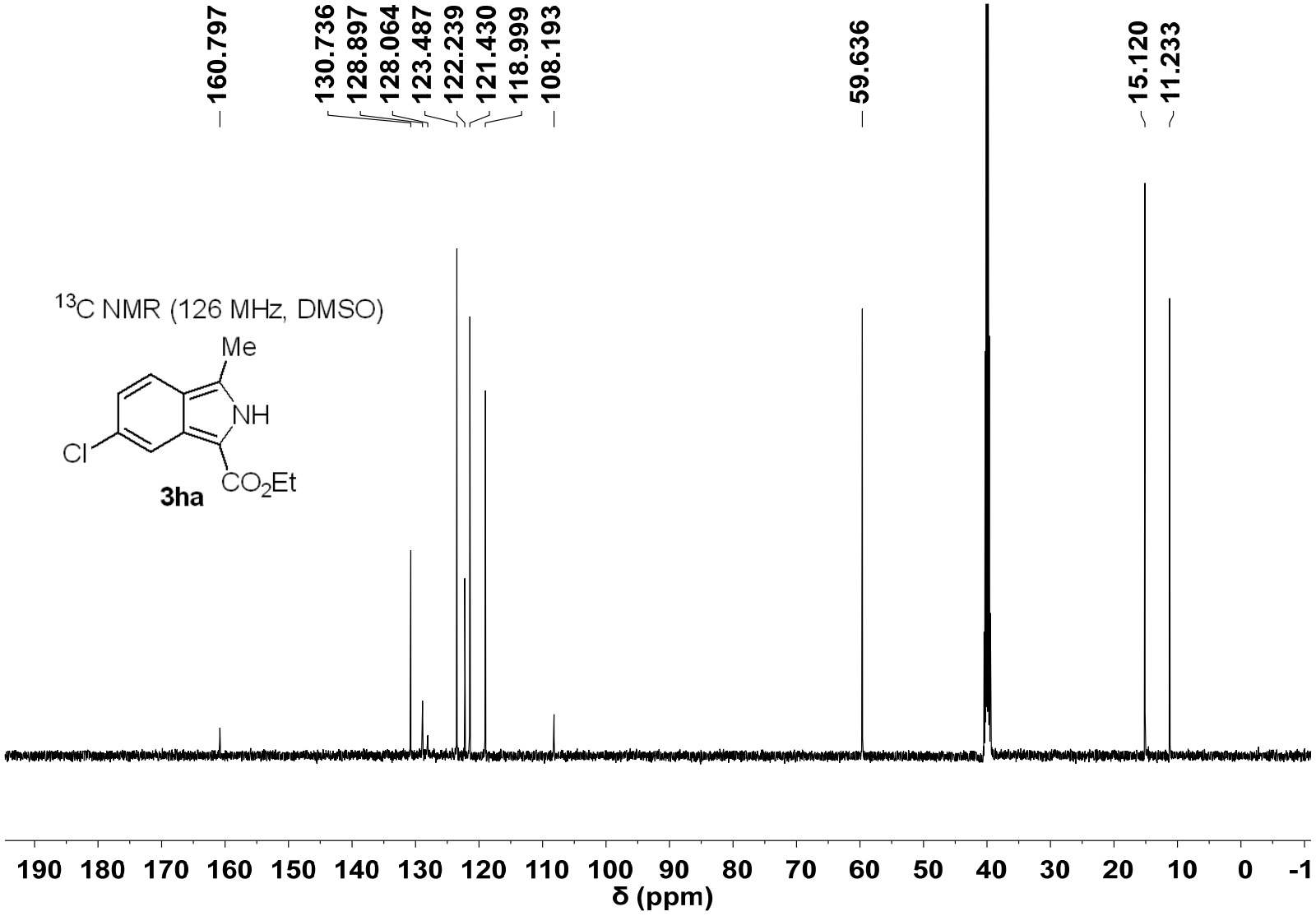

12.698
7.572
7.554
7.222
6.670
6.666
6.652
6.648
4.312
4.298
4.283
4.269
3.798
2.532
1.371
1.357
1.343
1H NMR (500 MHz, DMSO)
Me
NH
MeO
CO2Et
3fa
0.94
1.03
1.00
1.03
2.13
3.02
3.05
3.22
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0
δ (ppm)

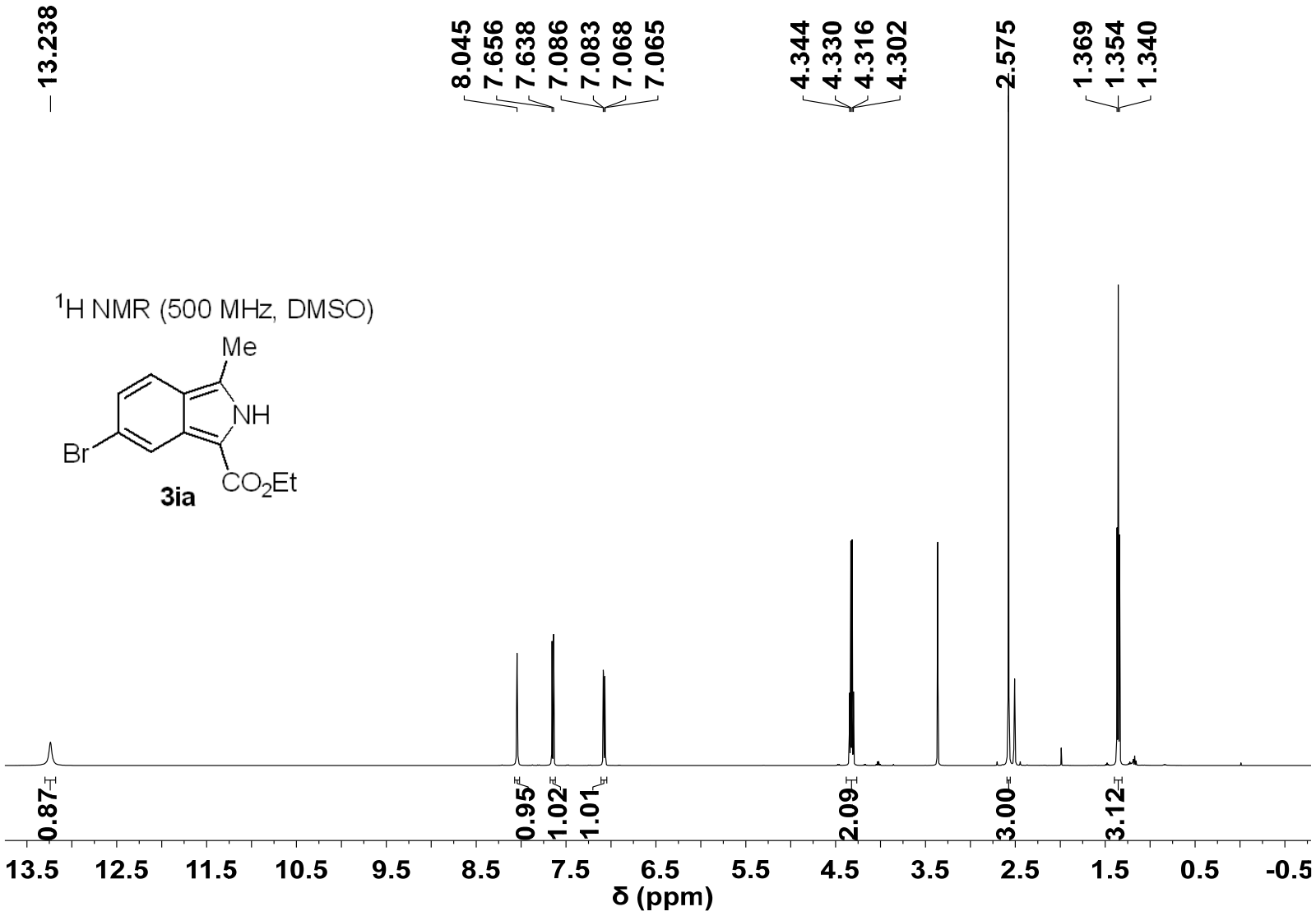

160.962
158.283
129.558
128.566
122.552
119.965
114.803
107.645
97.996
59.130
55.188
15.178
11.286
^{13}C NMR (126 MHz, DMSO)
Me
NH
MeO
CO_2Et
3fa
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

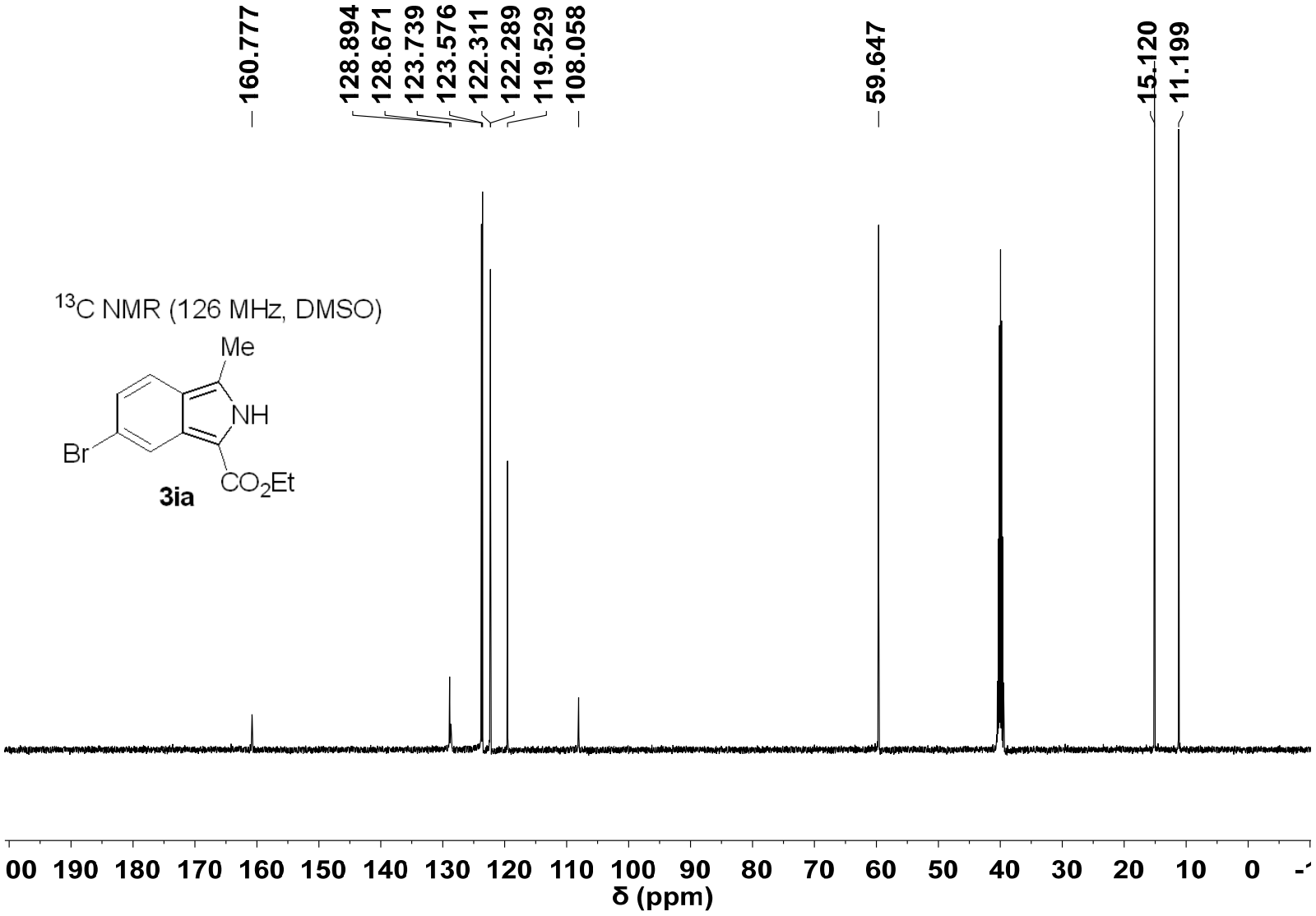

13.134
7.752
7.742
7.734
7.724
7.488
7.484
7.467
7.463
6.897
6.892
6.878
6.874
6.860
6.855
4.327
4.313
4.299
4.284
2.579
1.368
1.354
1.339
1H NMR (500 MHz, DMSO)
Me
NH
F
CO2Et
3ga
0.88
1.00
0.94
0.98
2.00
3.00
3.00
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0
δ (ppm)

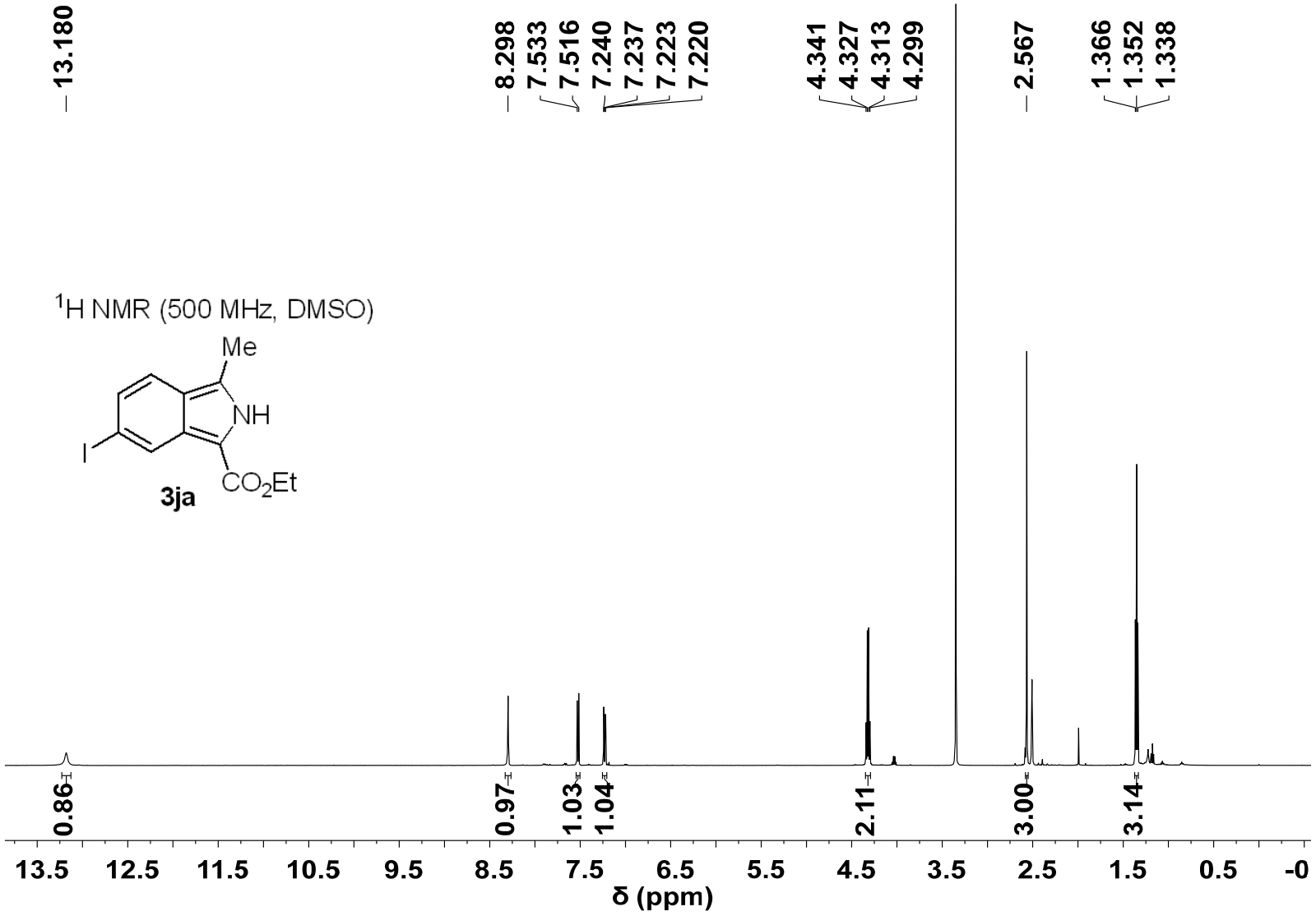

162.268
160.930
160.358
129.047
127.907
124.067
123.983
121.362
111.652
111.431
108.596
108.539
103.306
103.116
59.468
15.091
11.265
13C NMR (126 MHz, DMSO)
Me
NH
F
CO2Et
3ga
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

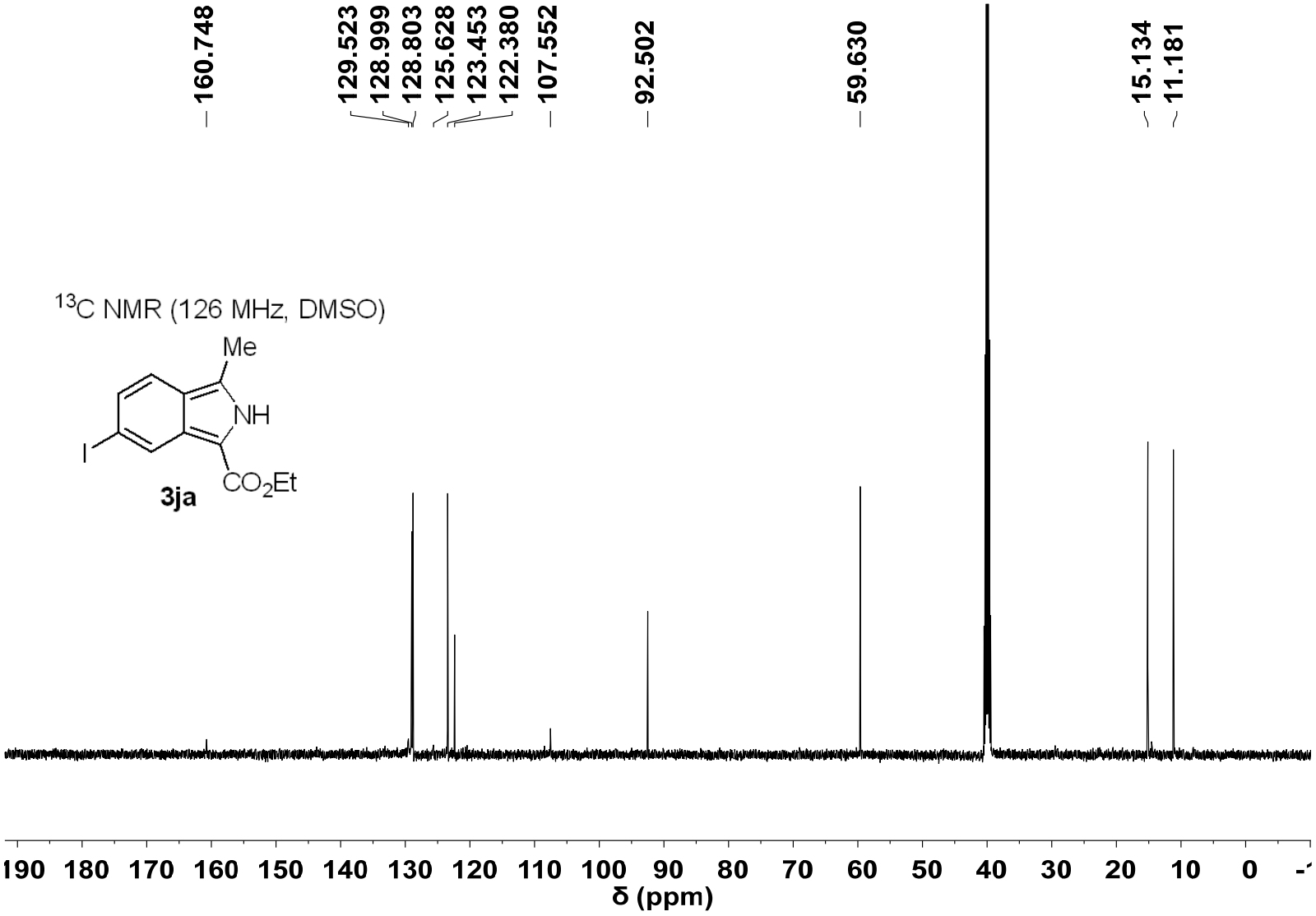

13.243
7.861
7.858
7.737
7.736
7.719
7.718
6.985
6.981
6.967
6.964
2.579
1.371
1.357
1.343
1H NMR (500 MHz, DMSO)
Me
NH
Cl
CO2Et
3ha
1.04
0.96
1.05
1.00
2.08
3.00
3.07
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0
δ (ppm)

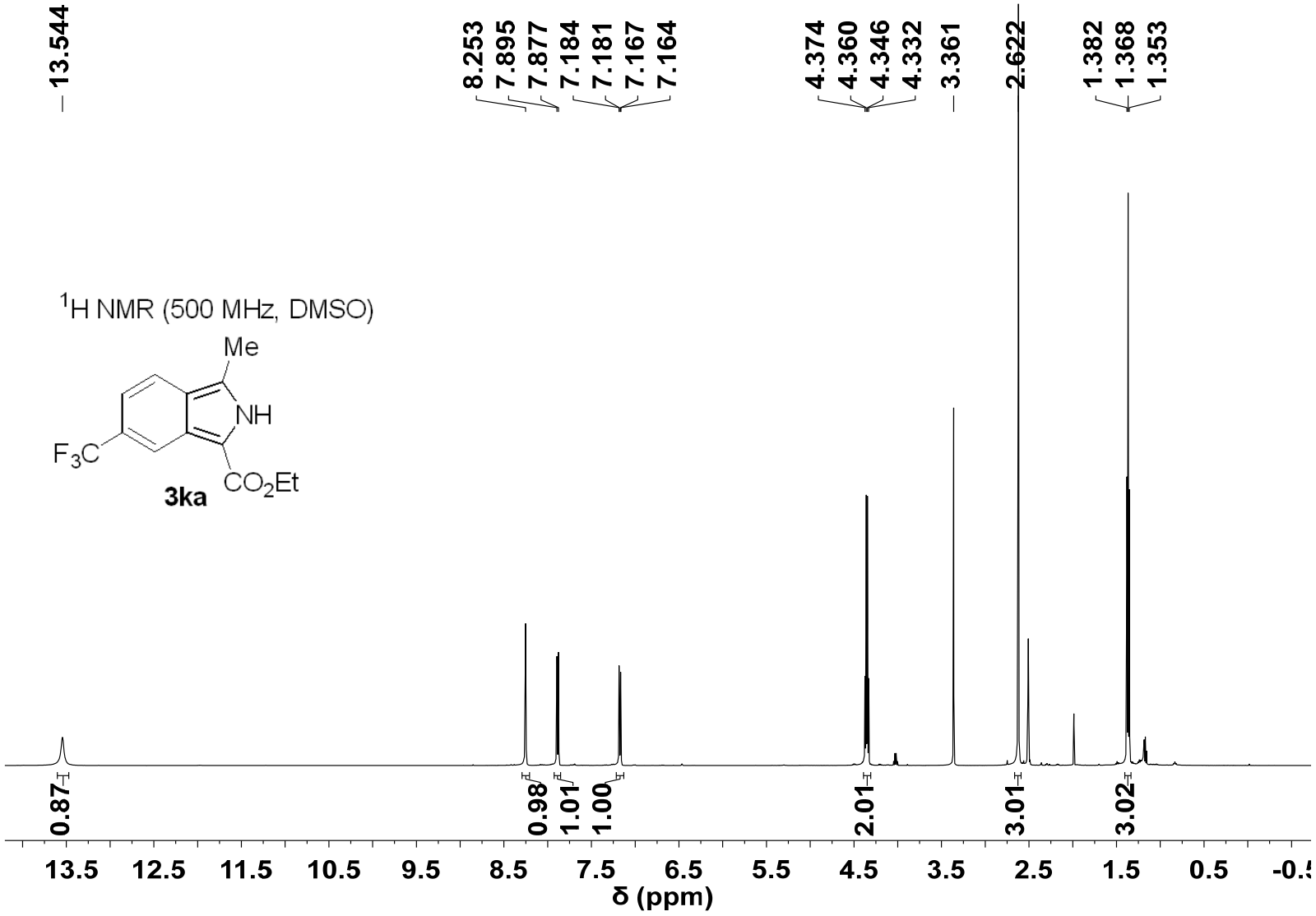

160.797
130.736
128.897
128.064
123.487
122.239
121.430
118.999
108.193
59.636
15.120
11.233
13C NMR (126 MHz, DMSO)
Me
NH
Cl
CO2Et
3ha
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

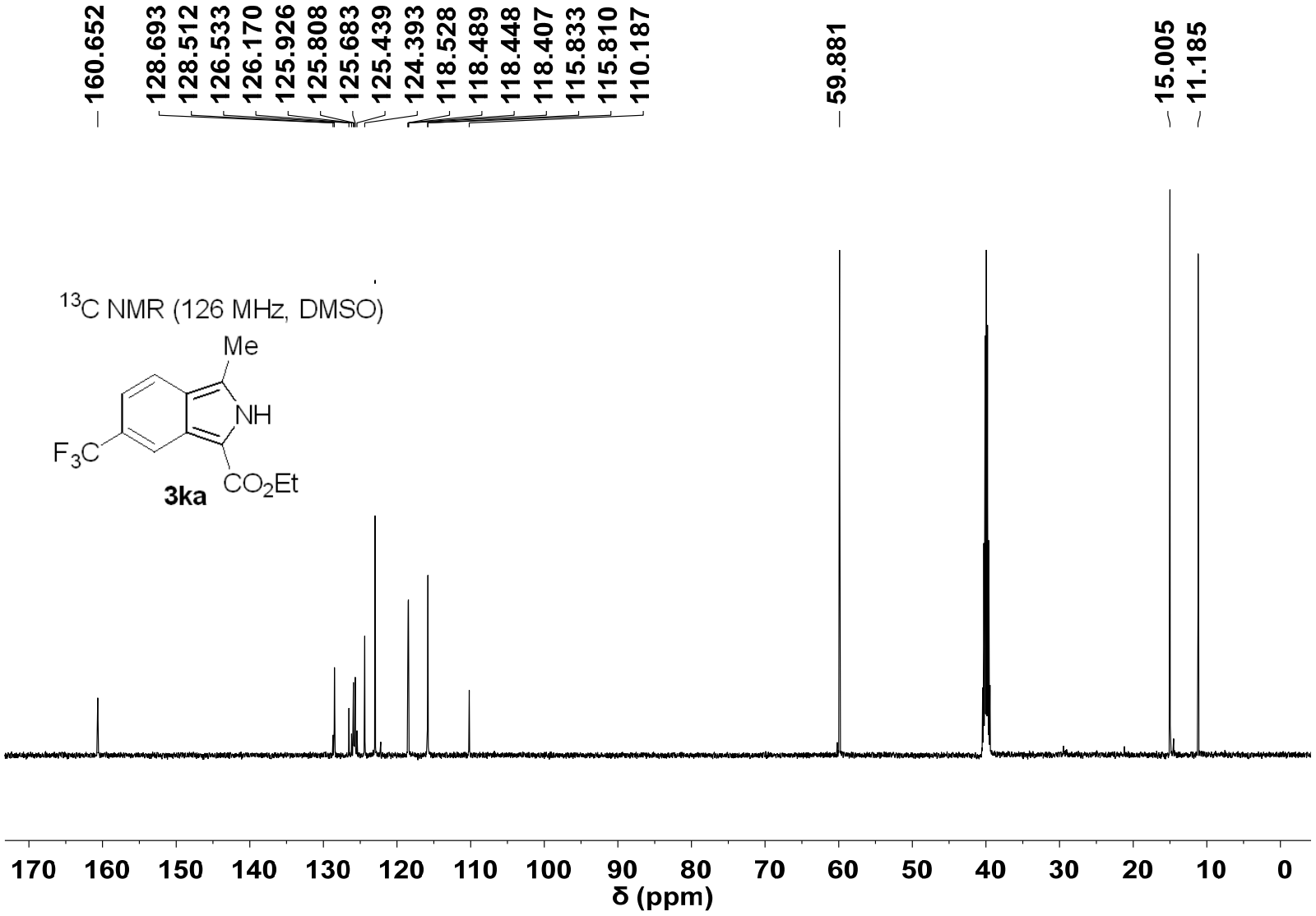

13.238
8.045
7.656
7.638
7.086
7.083
7.068
7.065
4.344
4.330
4.316
4.302
2.575
1.369
1.354
1.340
1H NMR (500 MHz, DMSO)
Me
NH
Br
CO2Et
3ia
0.87
0.95
1.02
1.01
2.09
3.00
3.12
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

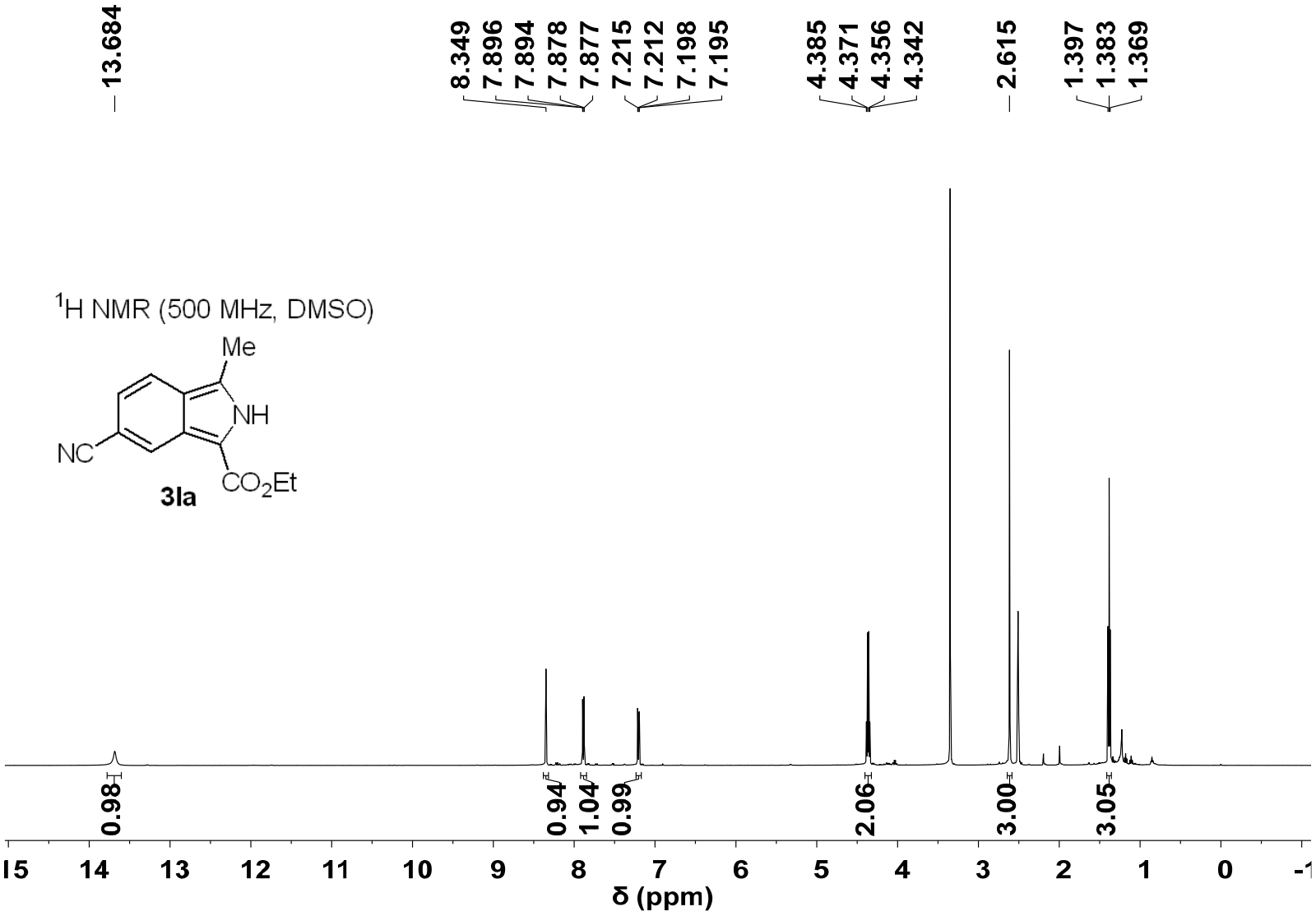

160.777
128.894
128.671
123.739
123.576
122.311
122.289
119.529
108.058
59.647
15.120
11.199
13C NMR (126 MHz, DMSO)
Me
NH
Br
CO2Et
3ia
δ (ppm)

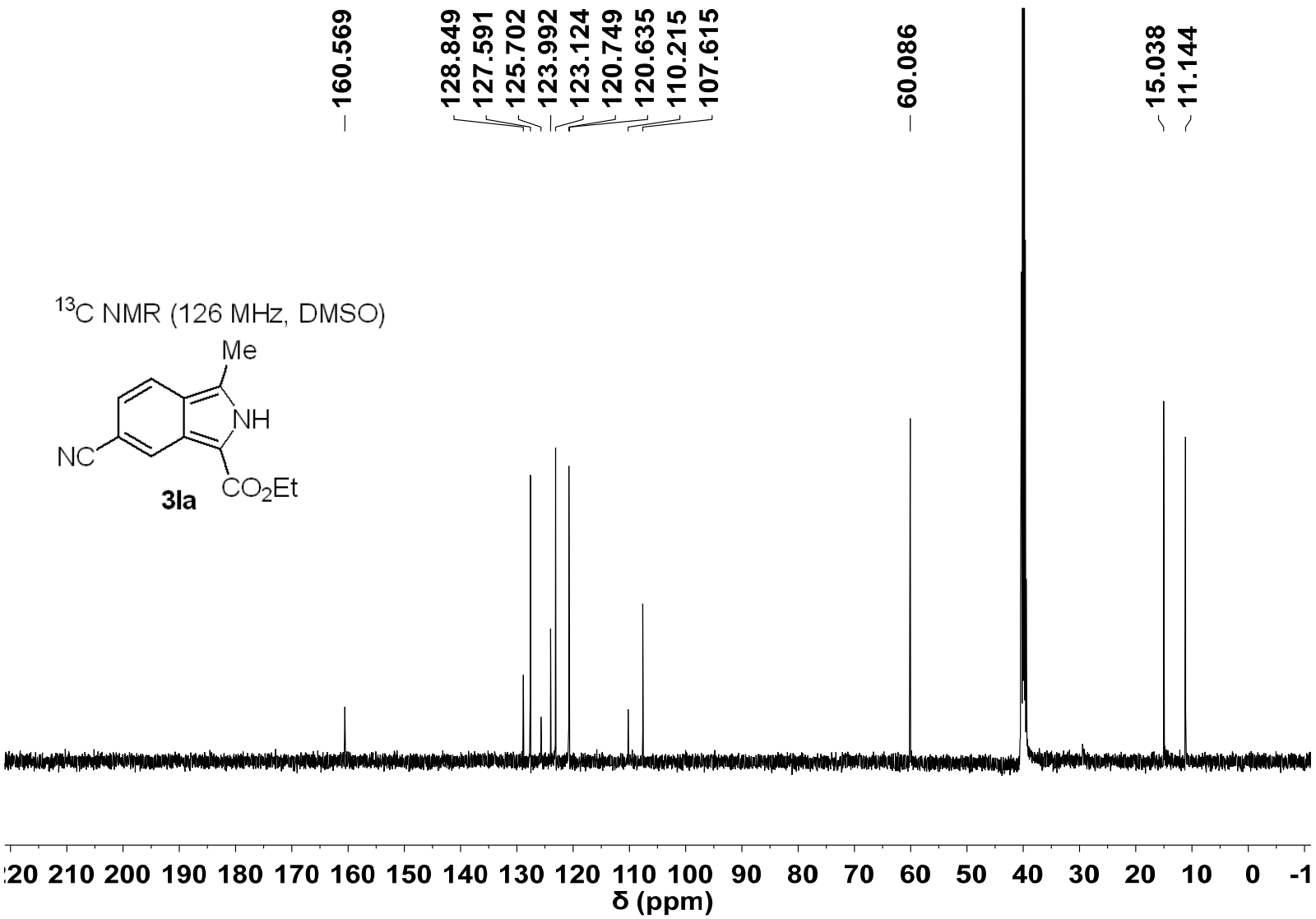

13.180
8.298
7.533
7.516
7.240
7.237
7.223
7.220
4.341
4.327
4.313
4.299
2.567
1.366
1.352
1.338
1H NMR (500 MHz, DMSO)
Me
NH
I
CO2Et
3ja
0.86
0.97
1.03
1.04
2.11
3.00
3.14
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0
δ (ppm)

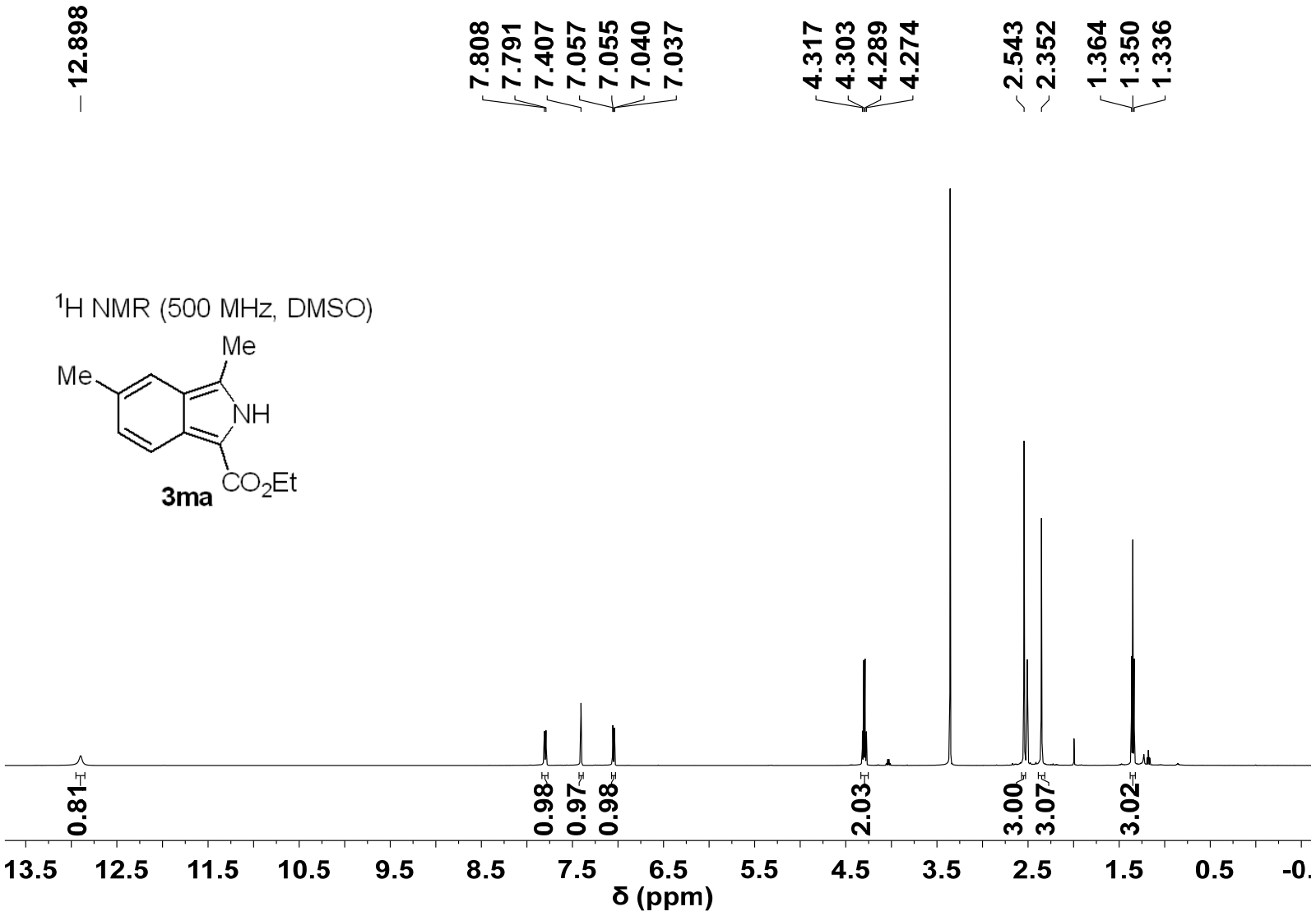

160.748
129.523
128.999
128.803
125.628
123.453
122.380
107.552
92.502
59.630
15.134
11.181
13C NMR (126 MHz, DMSO)
Me
NH
I
CO2Et
3ja
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

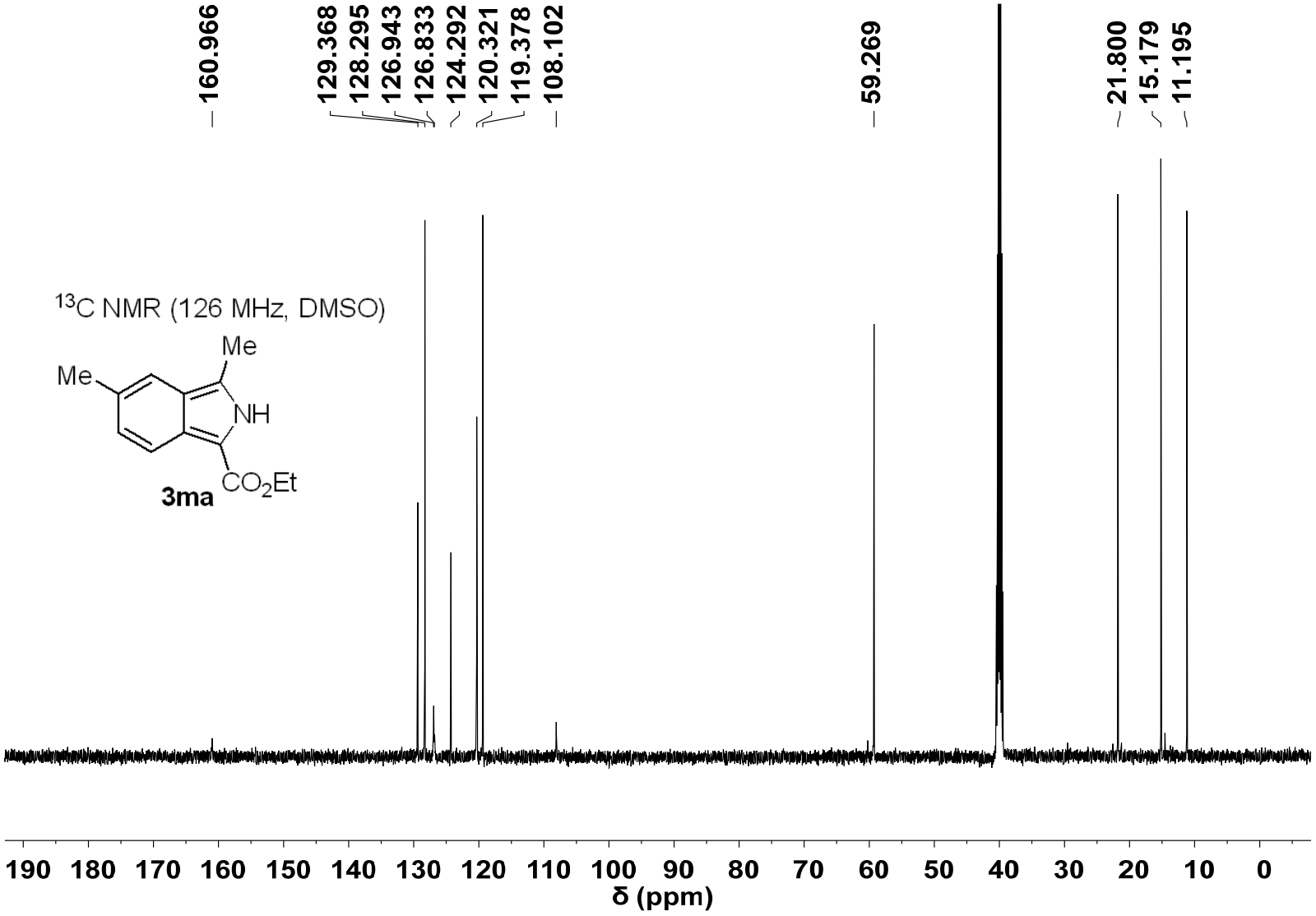

13.544
8.253
7.895
7.877
7.184
7.181
7.167
7.164
4.374
4.360
4.346
4.332
3.361
2.622
1.382
1.368
1.353
1H NMR (500 MHz, DMSO)
Me
NH
F3C
CO2Et
3ka
0.87
0.98
1.01
1.00
2.01
3.01
3.02
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
δ (ppm)

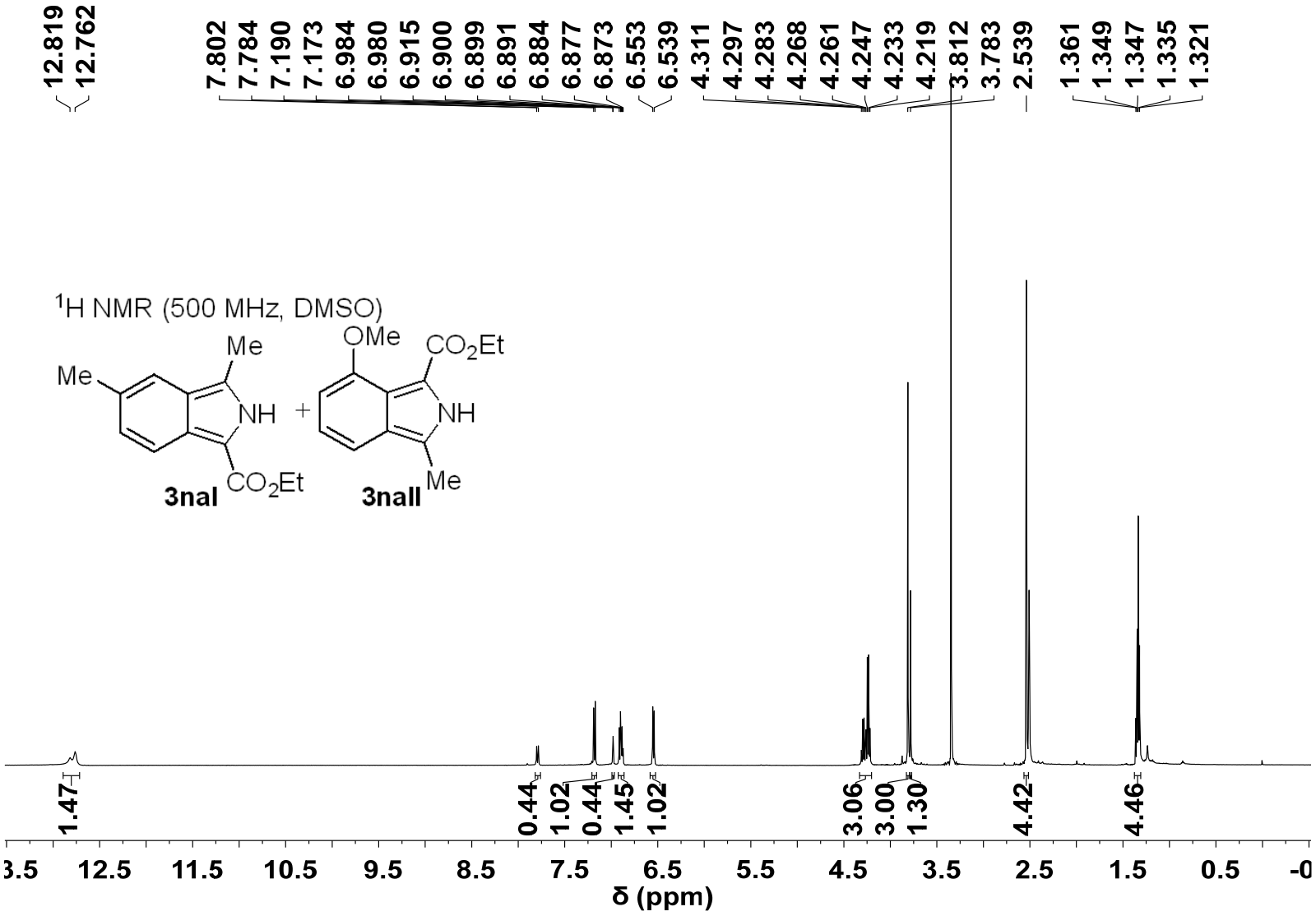

160.652
128.693
128.512
126.533
126.170
125.926
125.808
125.683
125.439
124.393
118.528
118.489
118.448
118.407
115.833
115.810
110.187
59.881
15.005
11.185
13C NMR (126 MHz, DMSO)
Me
NH
F3C
CO2Et
3ka
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

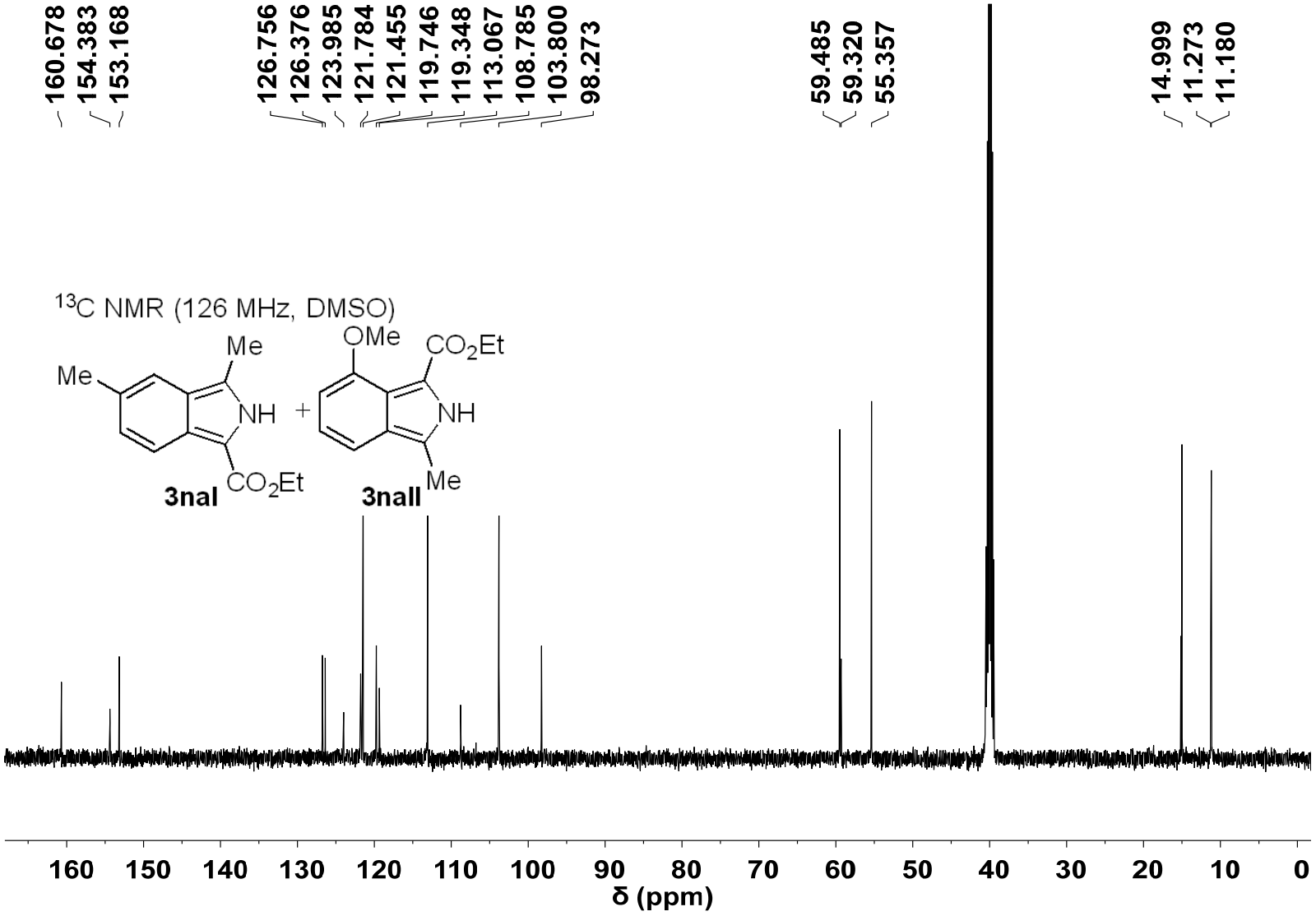

13.684
8.349
7.896
7.894
7.878
7.877
7.215
7.212
7.198
7.195
4.385
4.371
4.356
4.342
2.615
1.397
1.383
1.369
1H NMR (500 MHz, DMSO)
Me
NH
NC
CO2Et
3la
0.98
0.94
1.04
0.99
2.06
3.00
3.05
δ (ppm)

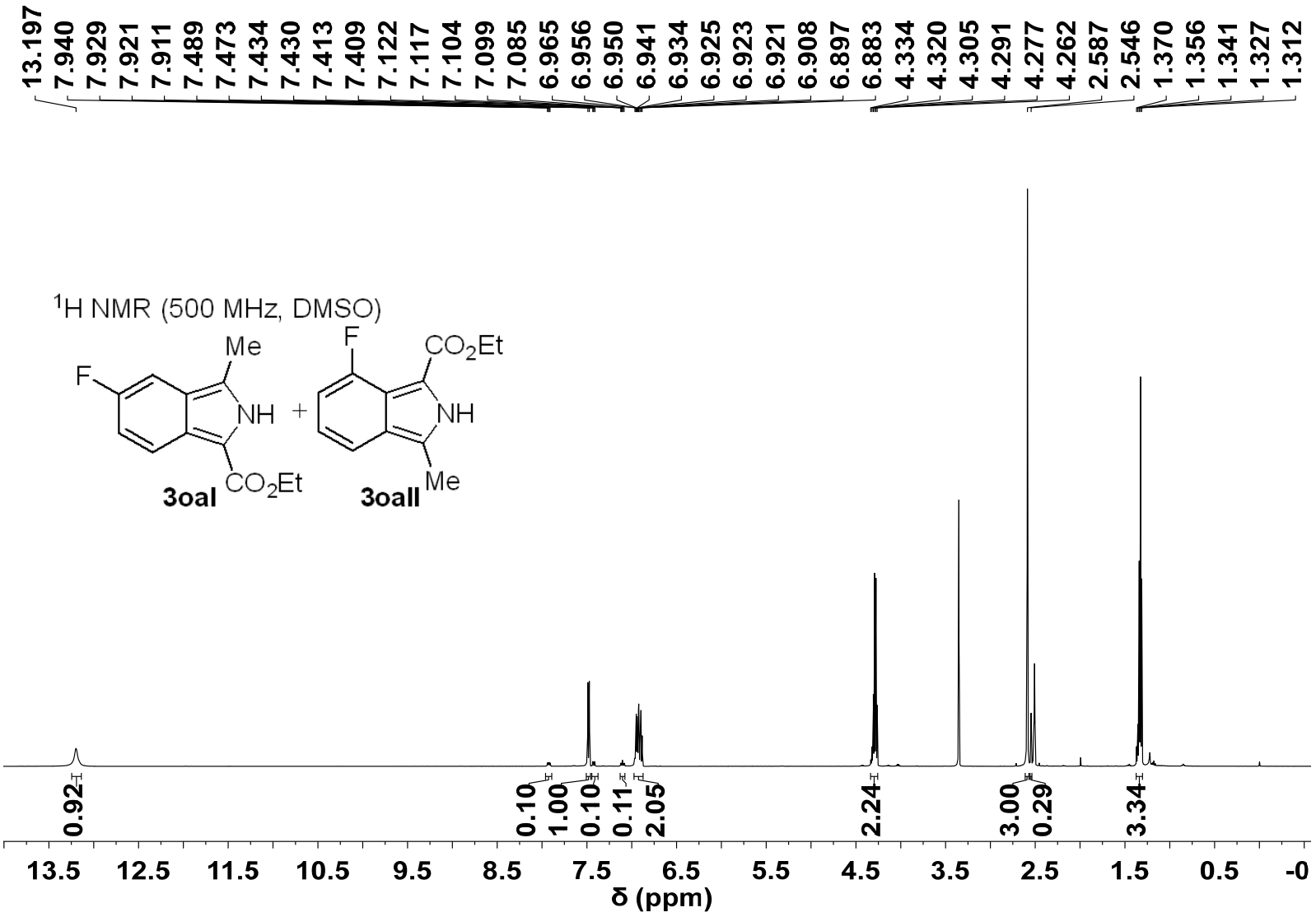

160.569
128.849
127.591
125.702
123.992
123.124
120.749
120.635
110.215
107.615
60.086
15.038
11.144
13C NMR (126 MHz, DMSO)
Me
NH
NC
CO2Et
3la
δ (ppm)

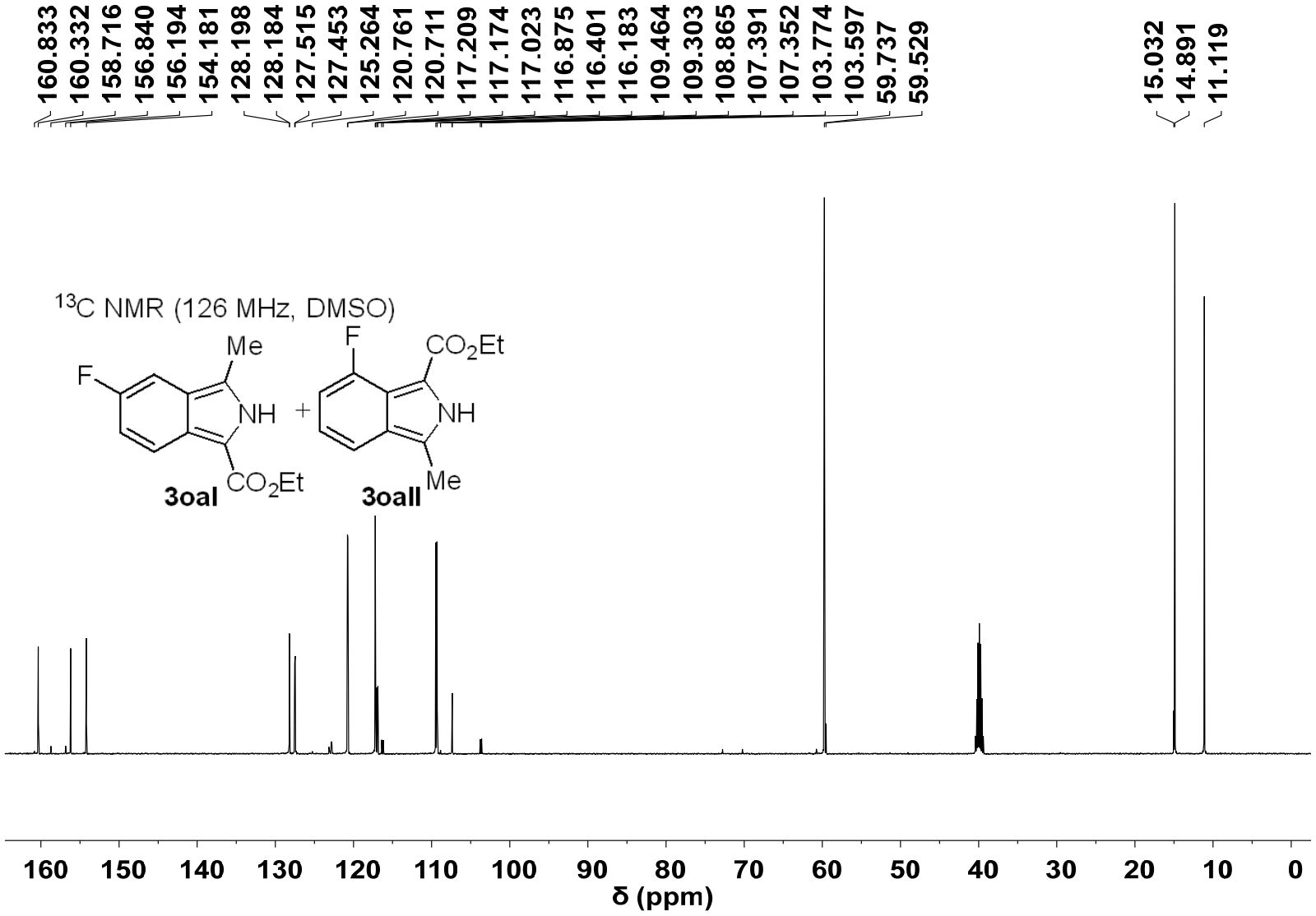

12.898
7.808
7.791
7.407
7.057
7.055
7.040
7.037
4.317
4.303
4.289
4.274
2.543
2.352
1.364
1.350
1.336
1H NMR (500 MHz, DMSO)
Me
Me
NH
CO2Et
3ma
0.81
0.98
0.97
0.98
2.03
3.00
3.07
3.02
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
δ (ppm)

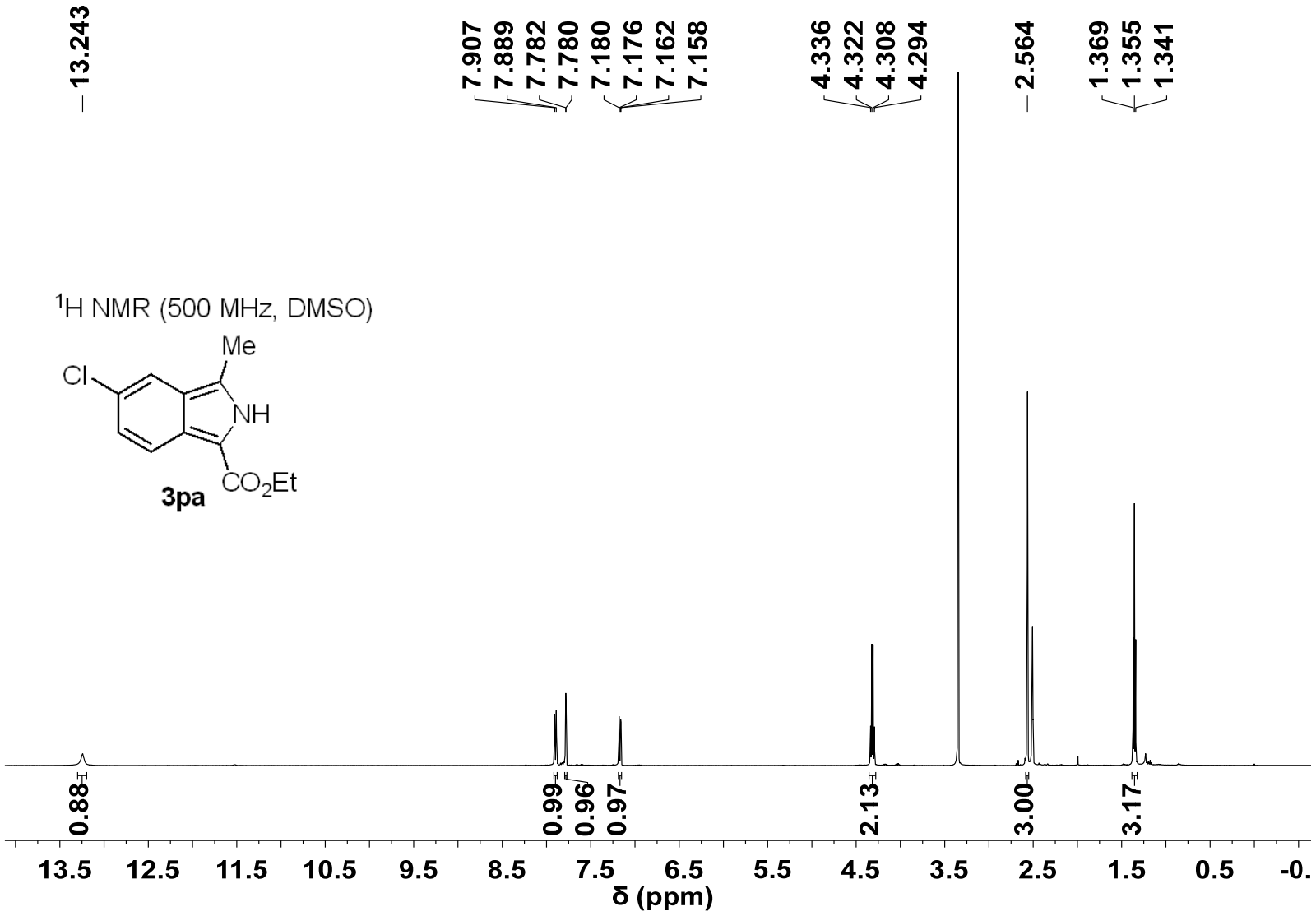

160.966
129.368
128.295
126.943
126.833
124.292
120.321
119.378
108.102
59.269
21.800
15.179
11.195
13C NMR (126 MHz, DMSO)
Me
Me
NH
CO2Et
3ma
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

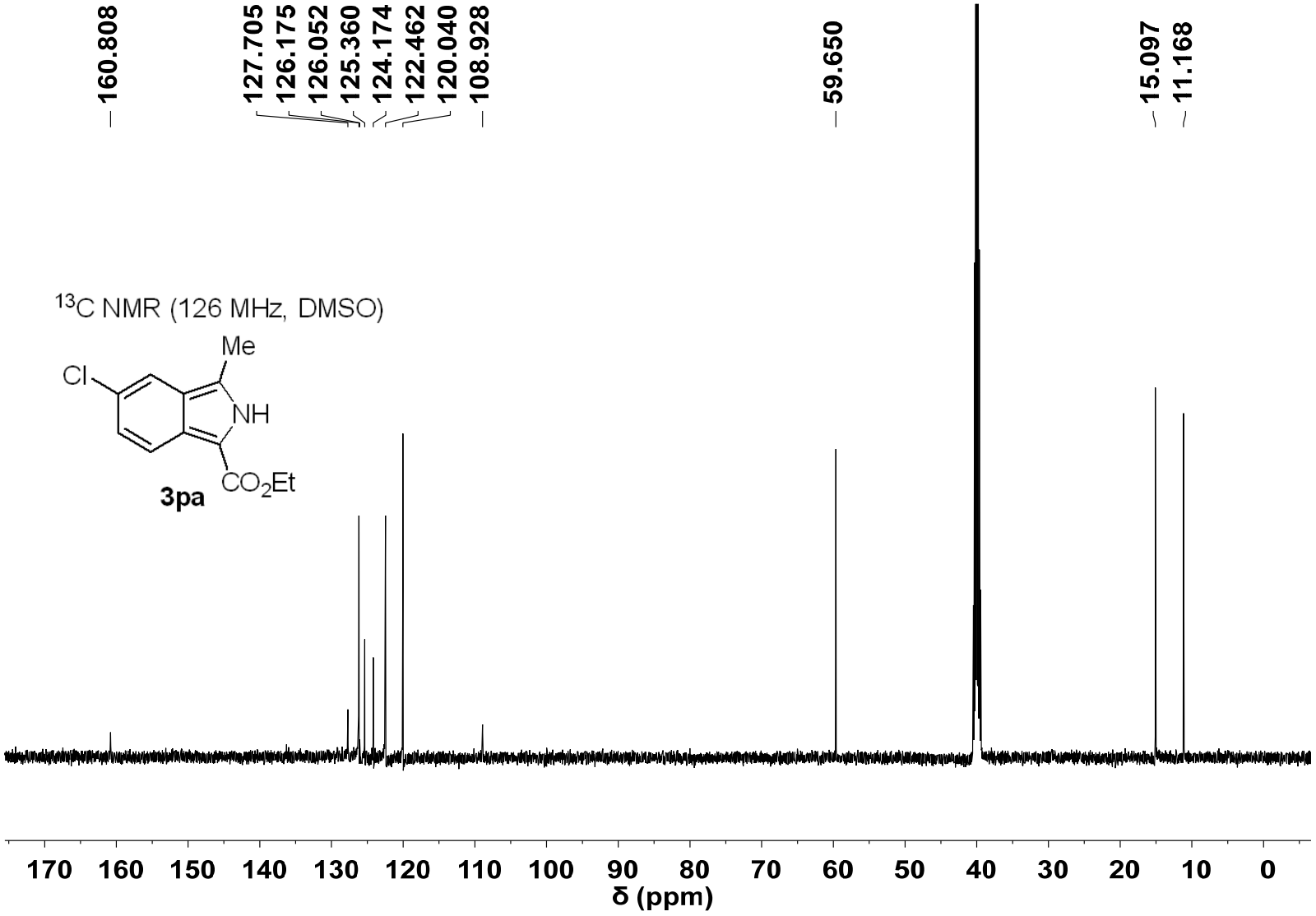

12.819
12.762
7.802
7.784
7.190
7.173
6.984
6.980
6.915
6.900
6.899
6.891
6.884
6.877
6.873
6.553
6.539
4.311
4.297
4.283
4.268
4.261
4.247
4.233
4.219
3.812
3.783
2.539
1.361
1.349
1.347
1.335
1.321
1H NMR (500 MHz, DMSO)
Me
Me
NH
CO2Et
3nal
+
OMe
CO2Et
NH
Me
3nall
1.47
0.44
1.02
0.44
1.45
1.02
3.06
3.00
1.30
4.42
4.46
δ (ppm)

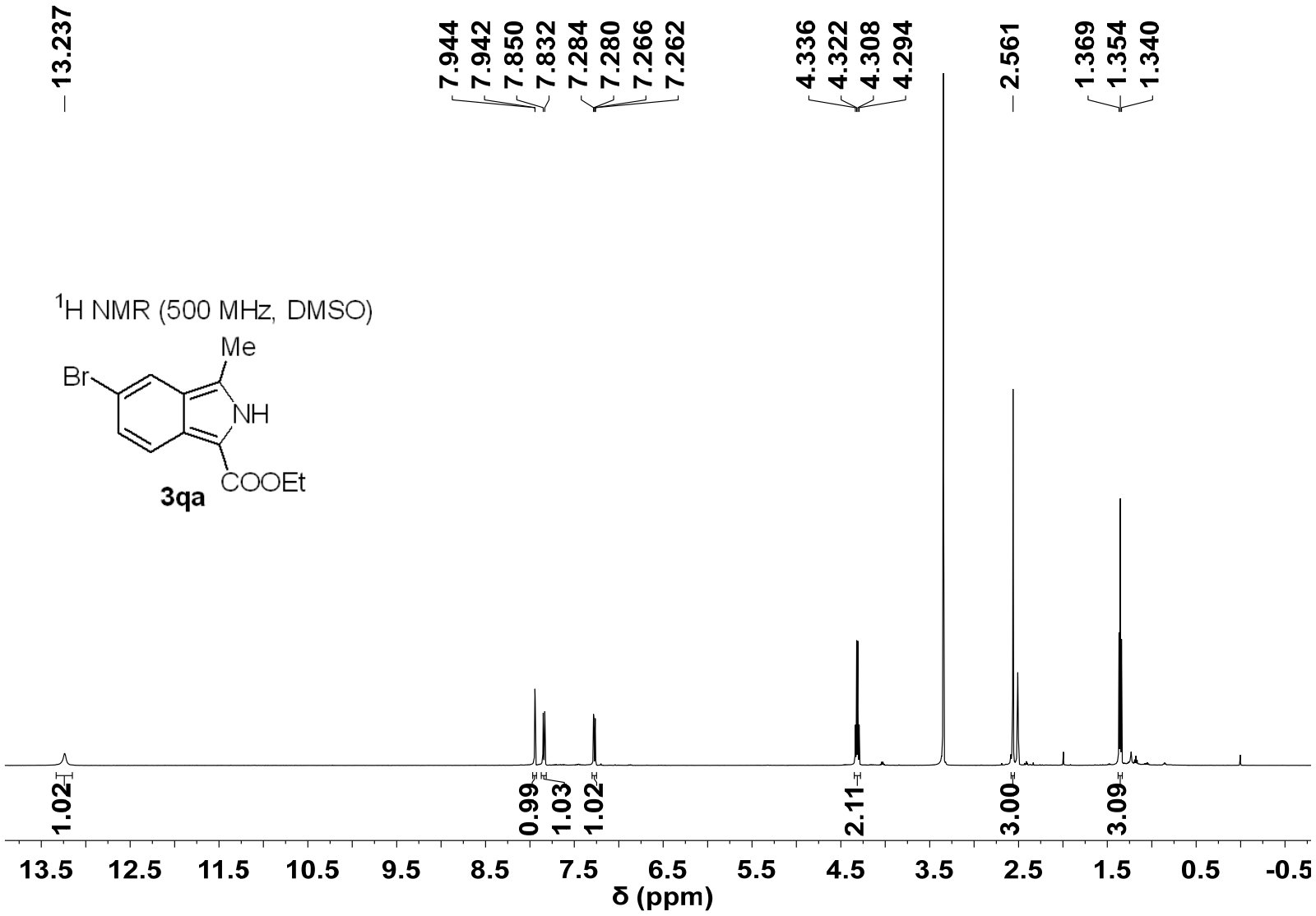

160.678
154.383
153.168
126.756
126.376
123.985
121.784
121.455
119.746
119.348
113.067
108.785
103.800
98.273
59.485
59.320
55.357
14.999
11.273
11.180
13C NMR (126 MHz, DMSO)
Me
Me
NH
CO2Et
3nal
+
OMe
CO2Et
NH
Me
3nall
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

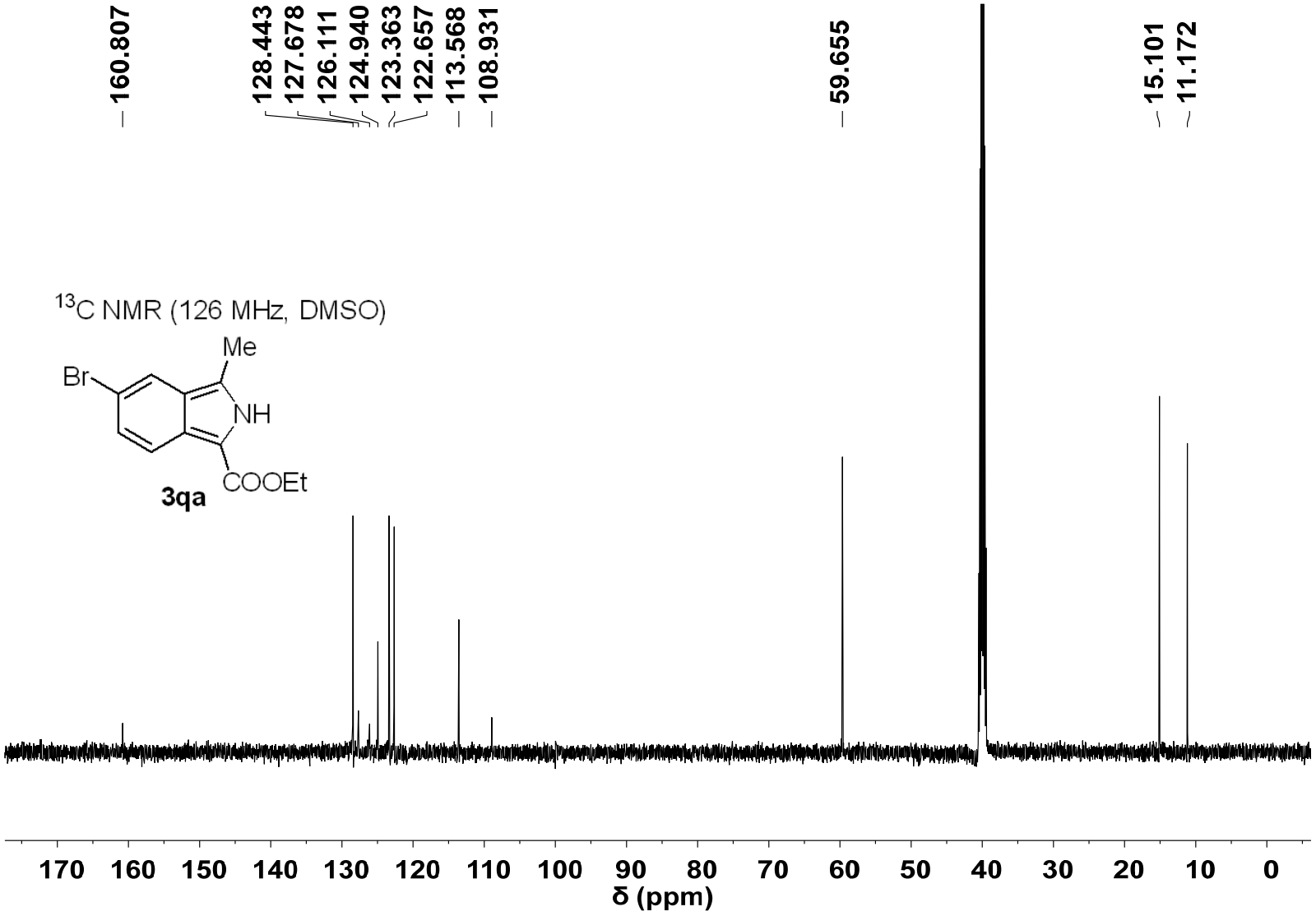

13.197
7.940
7.929
7.921
7.911
7.489
7.473
7.434
7.430
7.413
7.409
7.122
7.117
7.104
7.099
7.085
6.965
6.956
6.950
6.941
6.934
6.925
6.923
6.921
6.908
6.897
6.883
4.334
4.320
4.305
4.291
4.277
4.262
2.587
2.546
1.370
1.356
1.341
1.327
1.312
1H NMR (500 MHz, DMSO)
Me
F
NH
CO2Et
3oal
F
CO2Et
NH
Me
3oall
0.92
0.10
1.00
0.10
0.11
2.05
2.24
3.00
0.29
3.34
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0
δ (ppm)

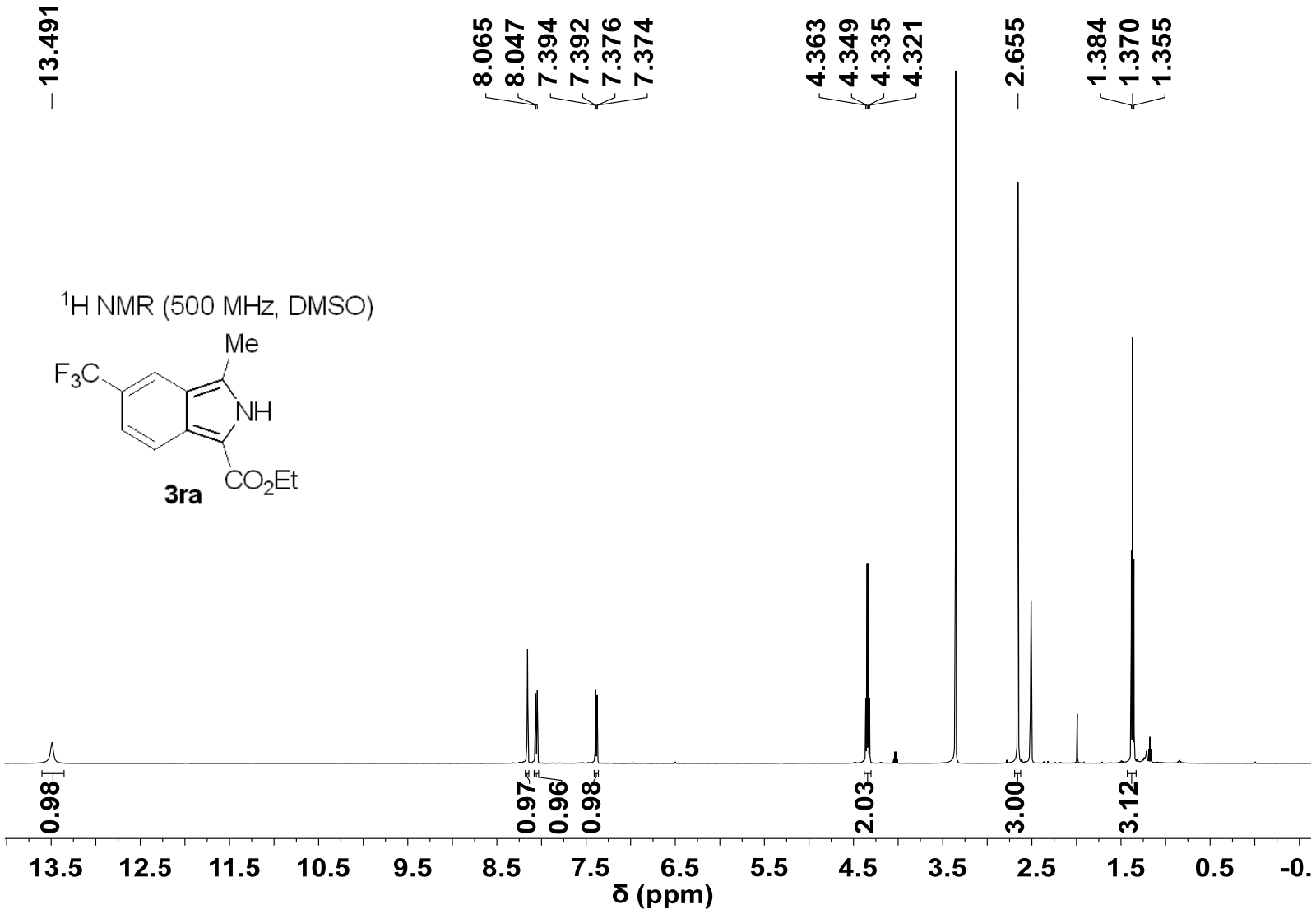

160.833
160.332
158.716
156.840
156.194
154.181
128.198
128.184
127.515
127.453
125.264
120.761
120.711
117.209
117.174
117.023
116.875
116.401
116.183
109.464
109.303
108.865
107.391
107.352
103.774
103.597
59.737
59.529
15.032
14.891
11.119
13C NMR (126 MHz, DMSO)
Me
F
NH
CO2Et
3oal
F
CO2Et
NH
Me
3oall
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

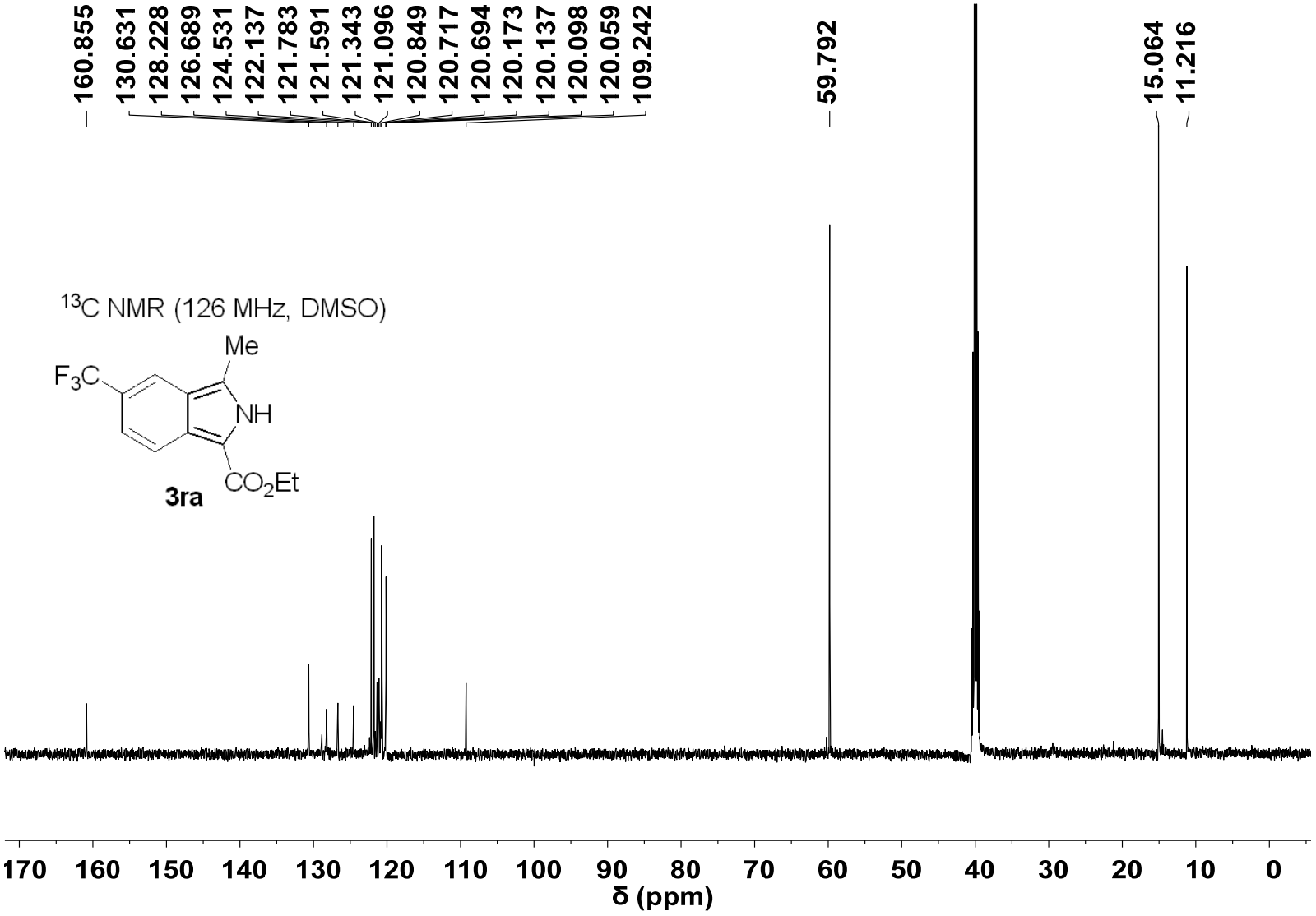

13.243
7.907
7.889
7.782
7.780
7.180
7.176
7.162
7.158
4.336
4.322
4.308
4.294
2.564
1.369
1.355
1.341
1H NMR (500 MHz, DMSO)
Me
Cl
NH
CO2Et
3pa
0.88
0.99
0.96
0.97
2.13
3.00
3.17
13.5 12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.
δ (ppm)

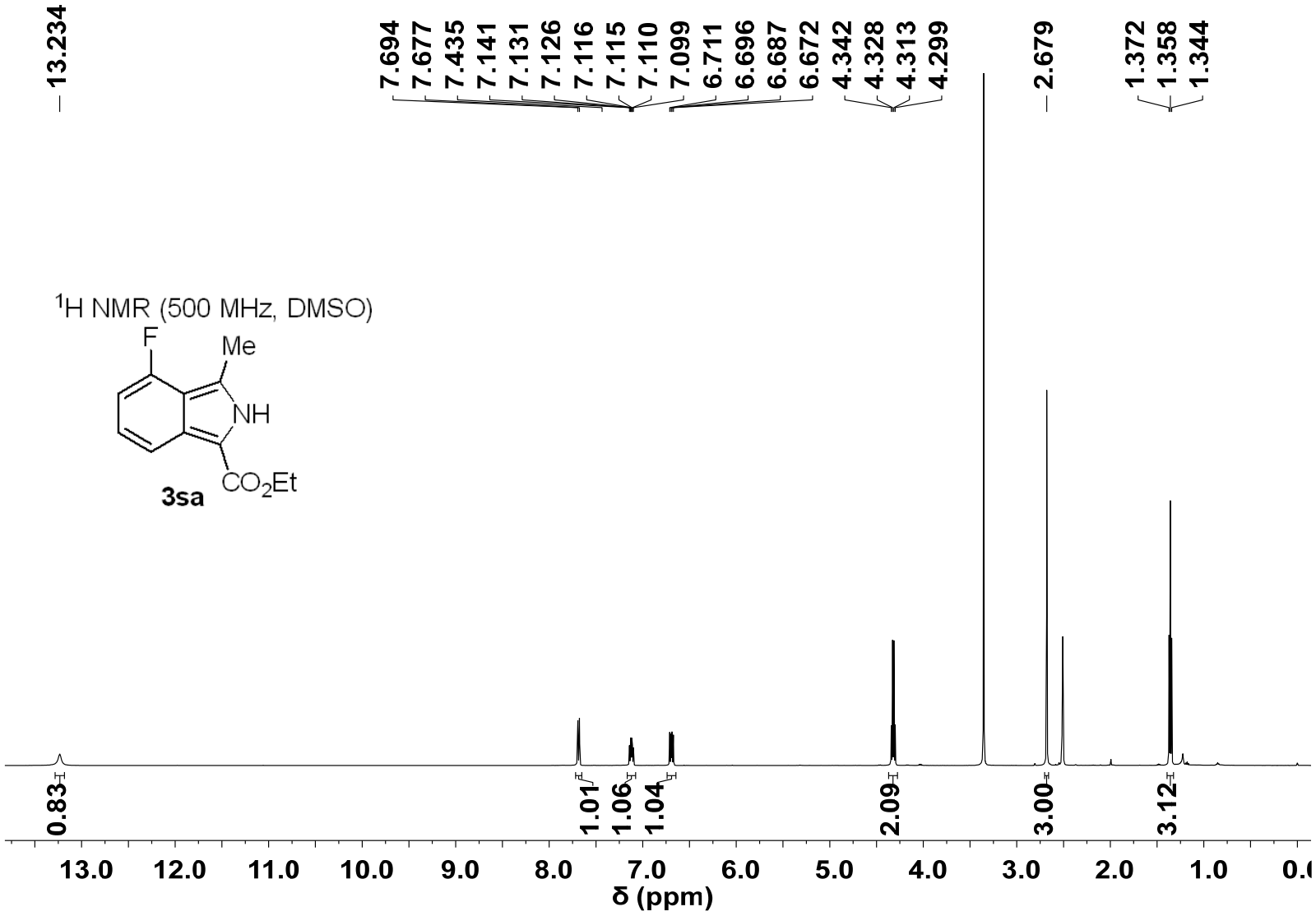

160.808
127.705
126.175
126.052
125.360
124.174
122.462
120.040
108.928
59.650
15.097
11.168
13C NMR (126 MHz, DMSO)
Me
Cl
NH
CO2Et
3pa
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

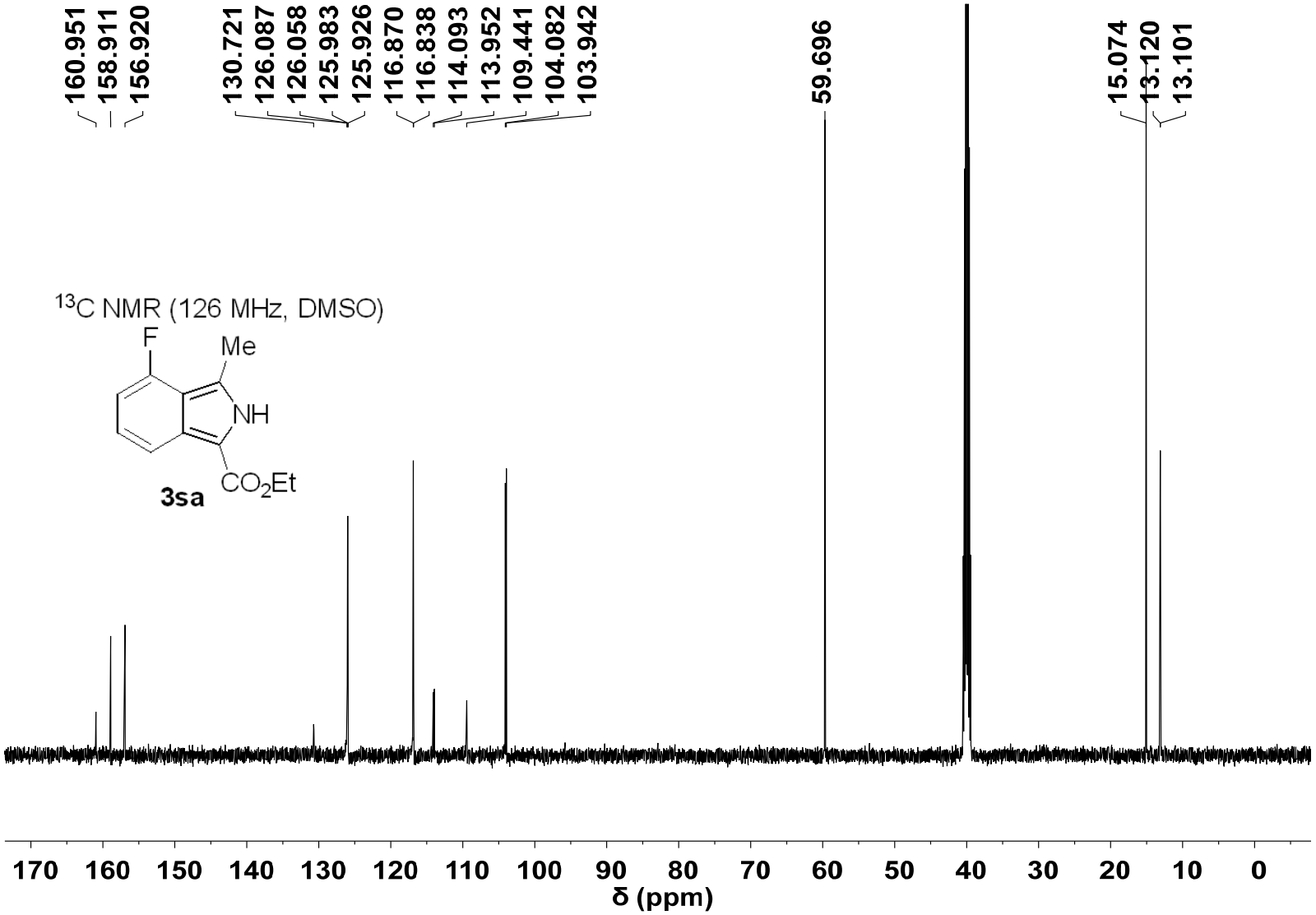

13.237
7.944
7.942
7.850
7.832
7.284
7.280
7.266
7.262
4.336
4.322
4.308
4.294
2.561
1.369
1.354
1.340
1H NMR (500 MHz, DMSO)
Me
Br
NH
COOEt
3qa
1.02
0.99
1.03
1.02
2.11
3.00
3.09
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

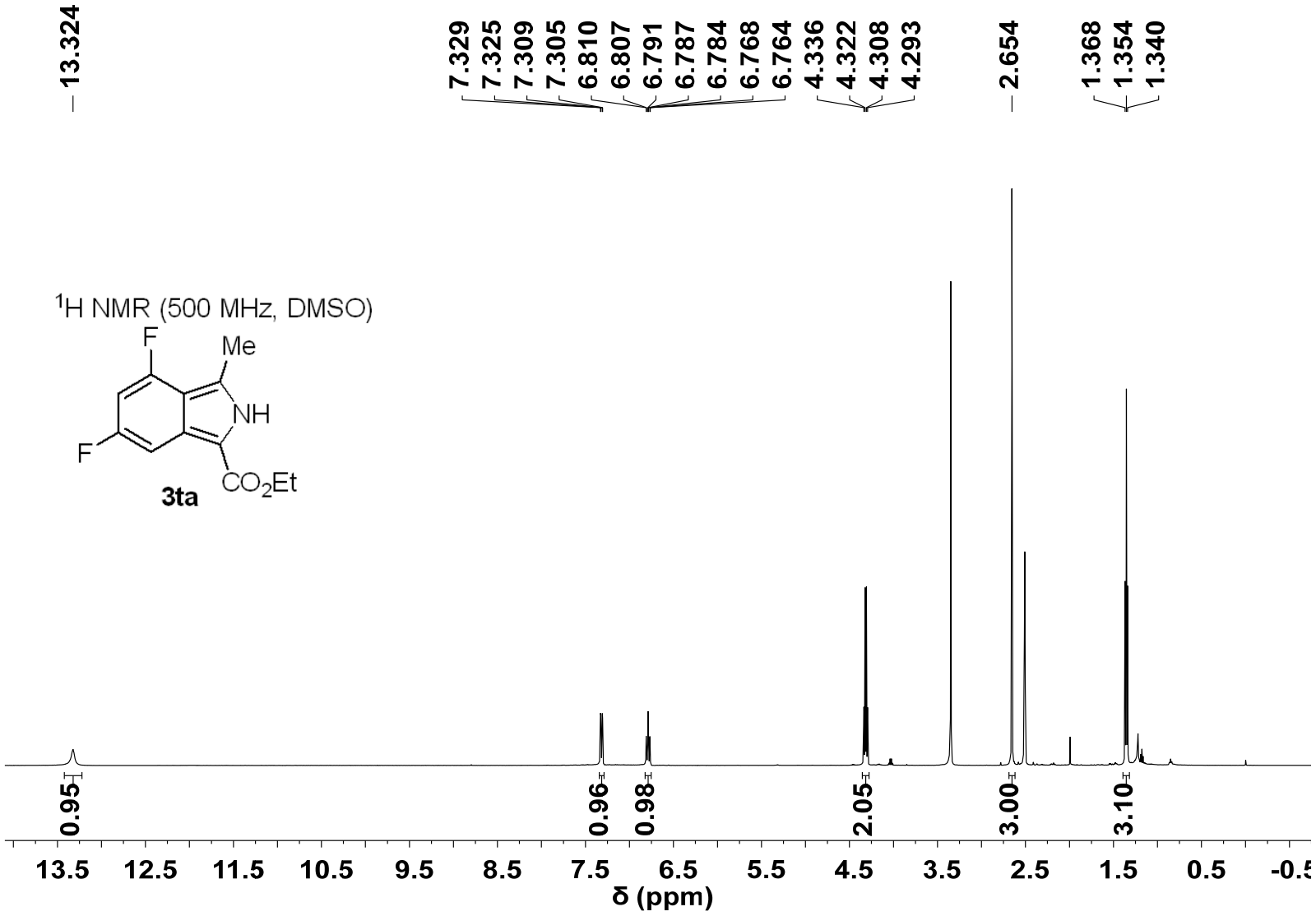

160.807
128.443
127.678
126.111
124.940
123.363
122.657
113.568
108.931
59.655
15.101
11.172
13C NMR (126 MHz, DMSO)
Me
Br
NH
COOEt
3qa
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

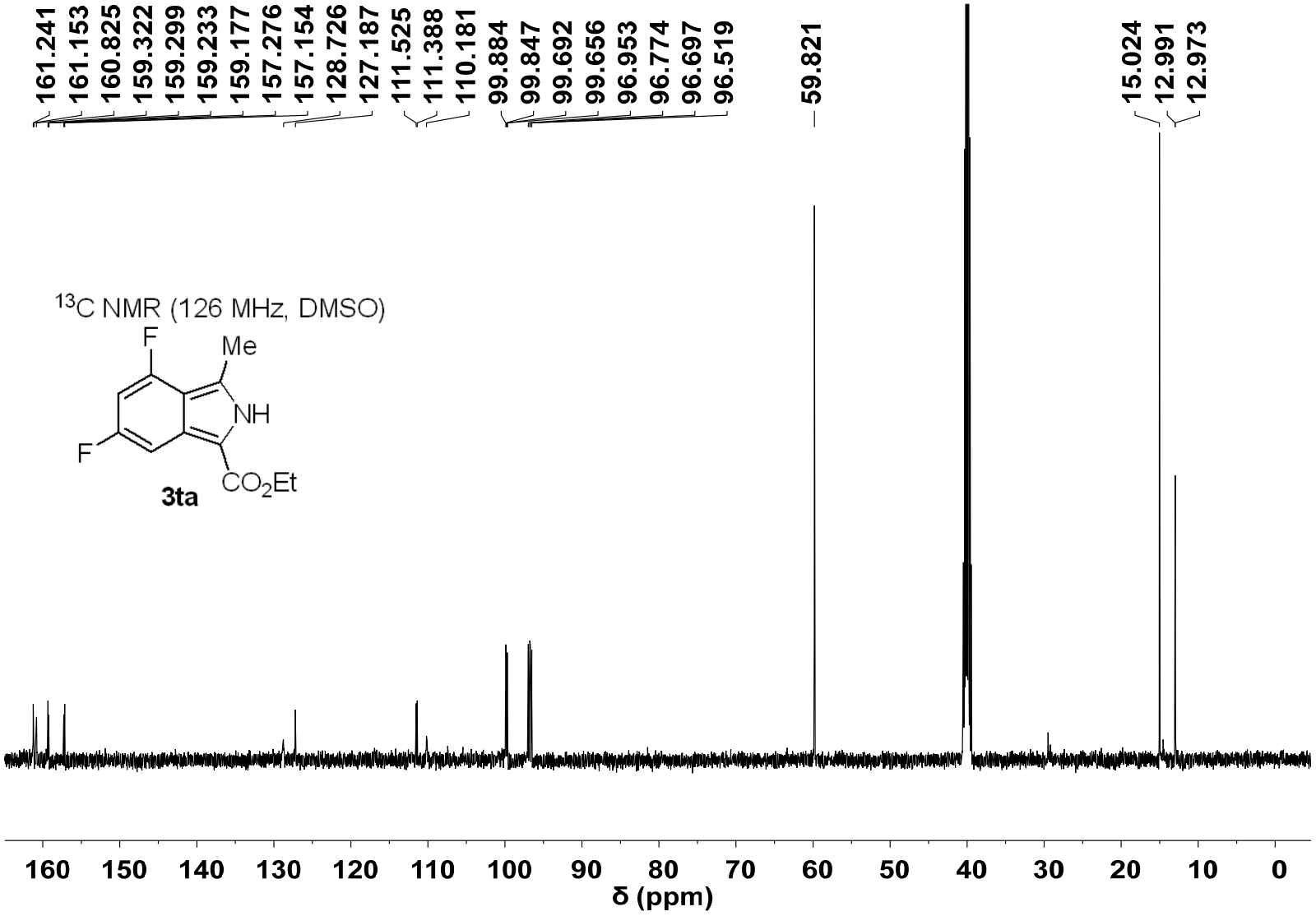

13.491
8.065
8.047
7.394
7.392
7.376
7.374
4.363
4.349
4.335
4.321
2.655
1.384
1.370
1.355
1H NMR (500 MHz, DMSO)
Me
F3C
NH
CO2Et
3ra
0.98
0.97
0.96
0.98
2.03
3.00
3.12
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.
δ (ppm)

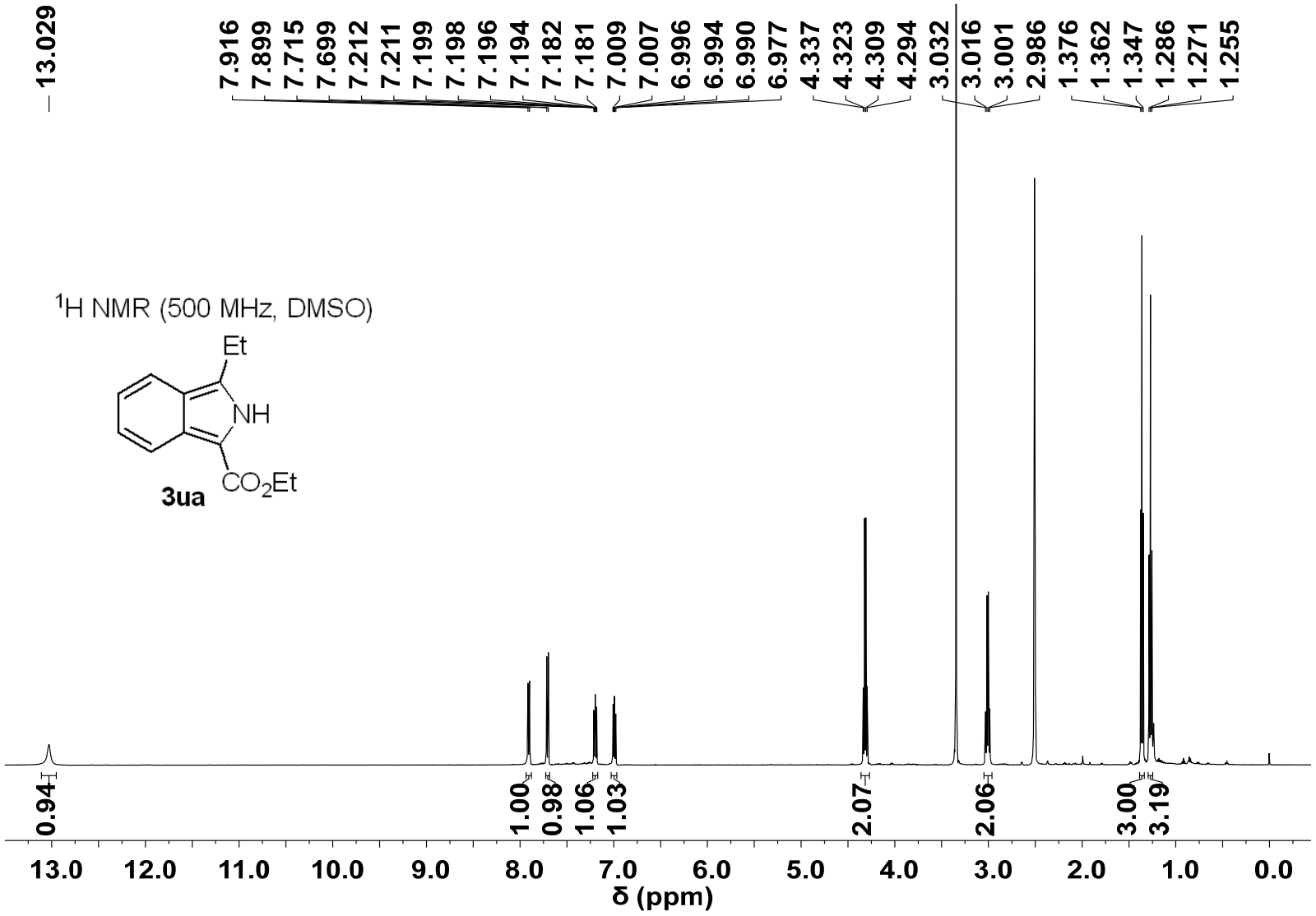

160.855
130.631
128.228
126.689
124.531
122.137
121.783
121.591
121.343
121.096
120.849
120.717
120.694
120.173
120.137
120.098
120.059
109.242
59.792
15.064
11.216
13C NMR (126 MHz, DMSO)
Me
F3C
NH
CO2Et
3ra
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

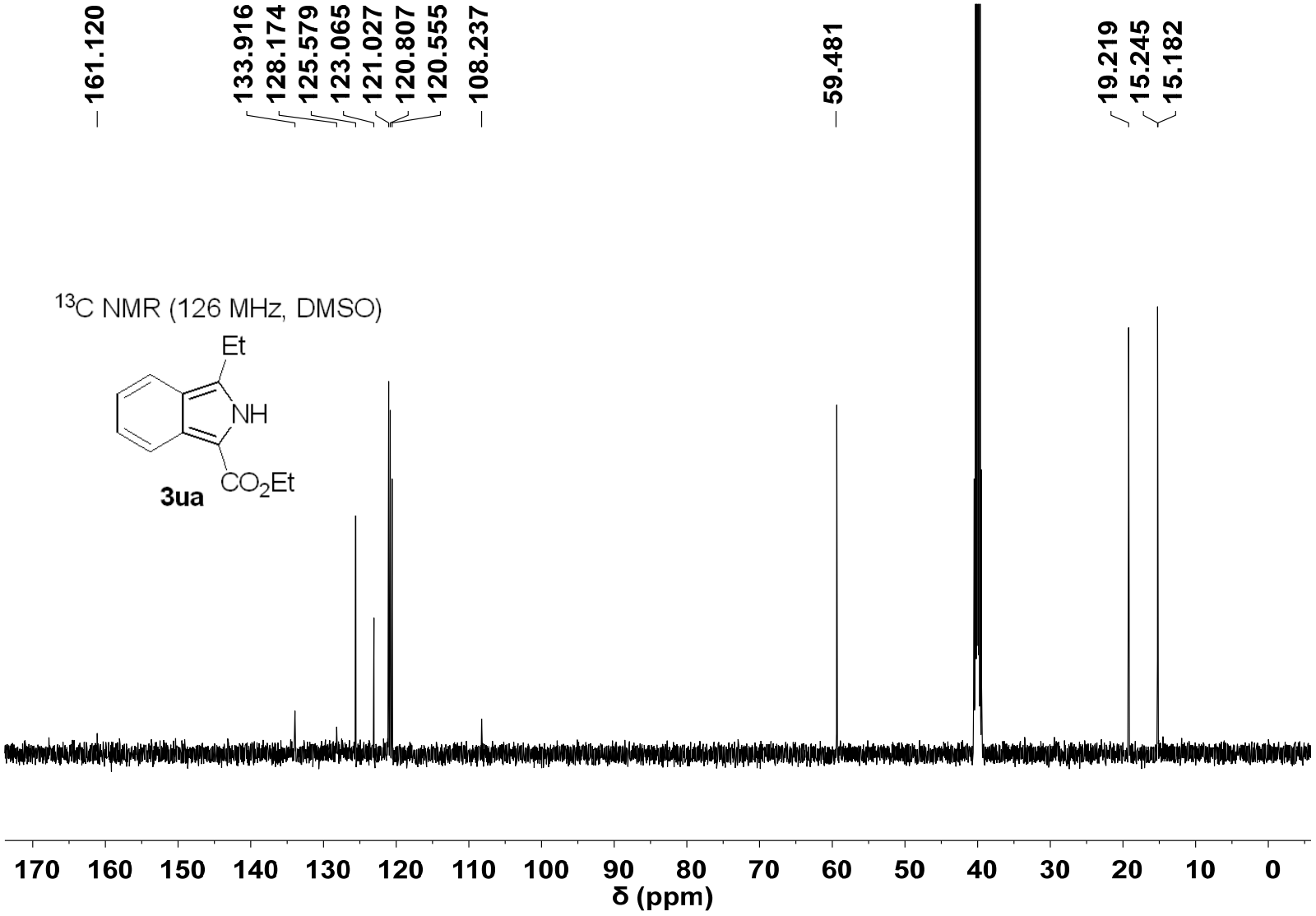

13.234
7.694
7.677
7.435
7.141
7.131
7.126
7.116
7.115
7.110
7.099
6.711
6.696
6.687
6.672
4.342
4.328
4.313
4.299
2.679
1.372
1.358
1.344
1H NMR (500 MHz, DMSO)
F
Me
NH
CO2Et
3sa
0.83
1.01
1.06
1.04
2.09
3.00
3.12
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
δ (ppm)

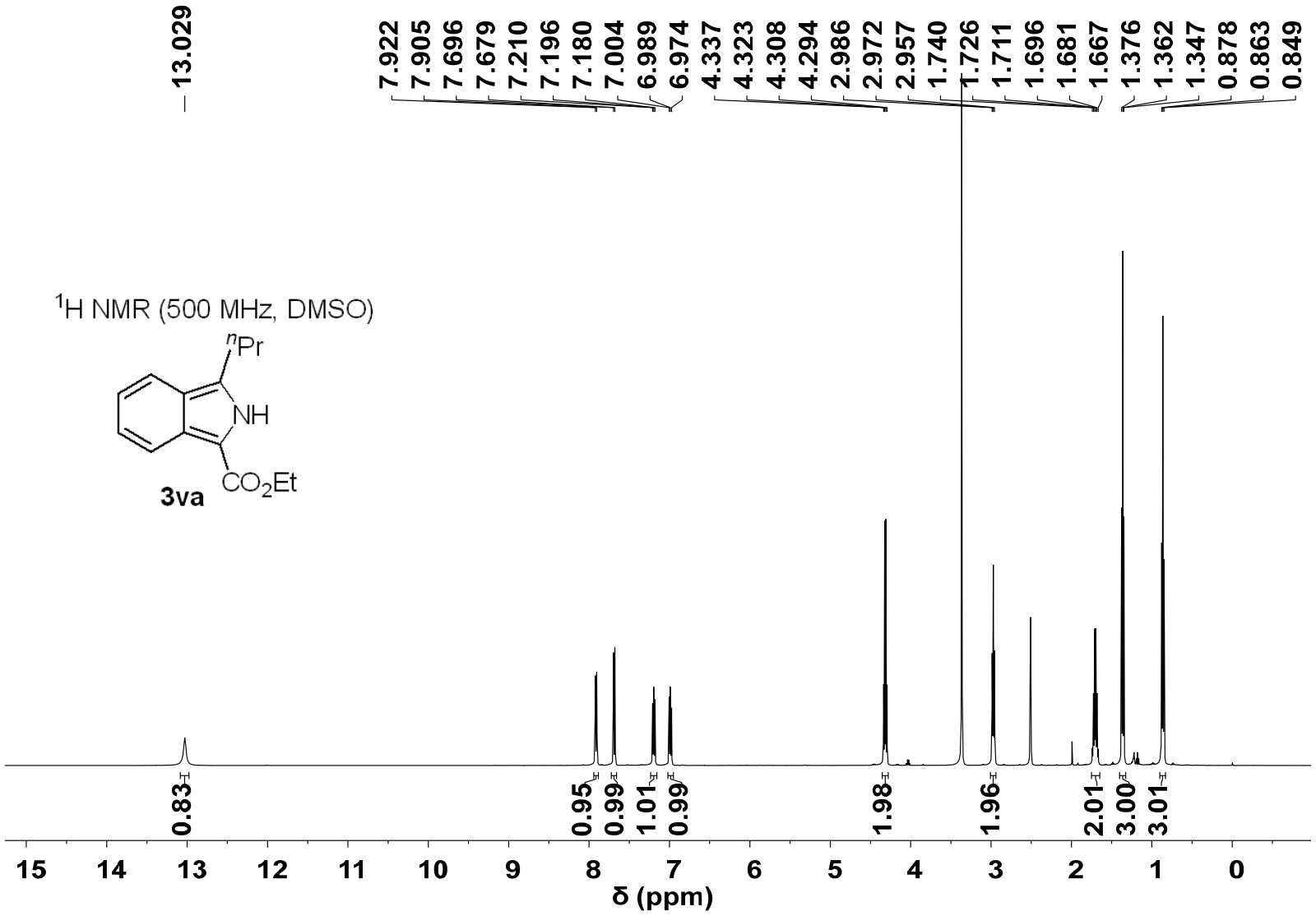

160.951
158.911
156.920
130.721
126.087
126.058
125.983
125.926
116.870
116.838
114.093
113.952
109.441
104.082
103.942
59.696
15.074
13.120
13.101
13C NMR (126 MHz, DMSO)
F
Me
NH
CO2Et
3sa
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

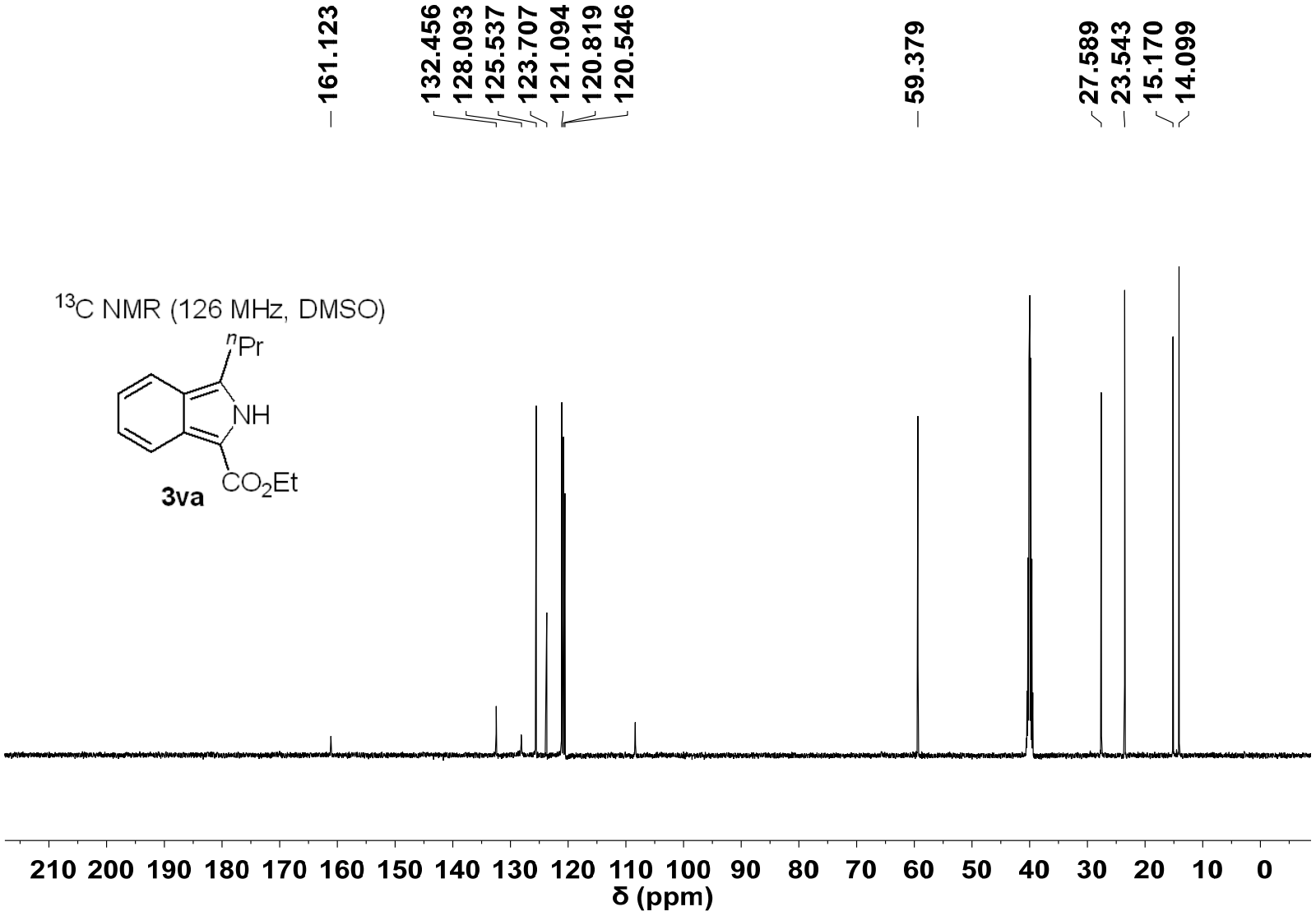

13.324
7.329
7.325
7.309
7.305
6.810
6.807
6.791
6.787
6.784
6.768
6.764
4.336
4.322
4.308
4.293
2.654
1.368
1.354
1.340
1H NMR (500 MHz, DMSO)
F
Me
NH
F
CO2Et
3ta
0.95
0.96
0.98
2.05
3.00
3.10
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
δ (ppm)

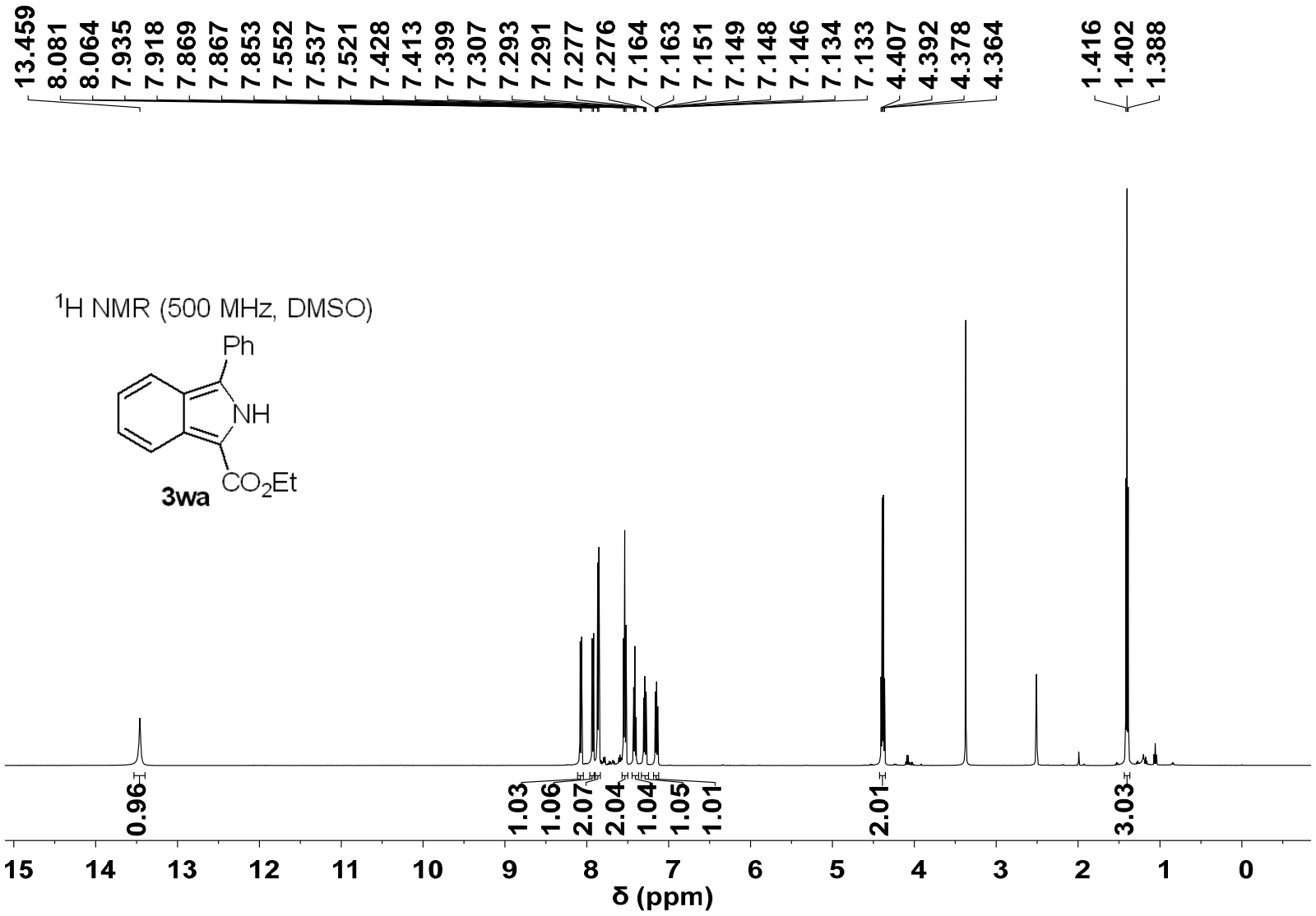

161.241
161.153
160.825
159.322
159.299
159.233
159.177
157.276
157.154
128.726
127.187
111.525
111.388
110.181
99.884
99.847
99.692
99.656
96.953
96.774
96.697
96.519
59.821
15.024
12.991
12.973
13C NMR (126 MHz, DMSO)
F
Me
NH
F
CO2Et
3ta
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

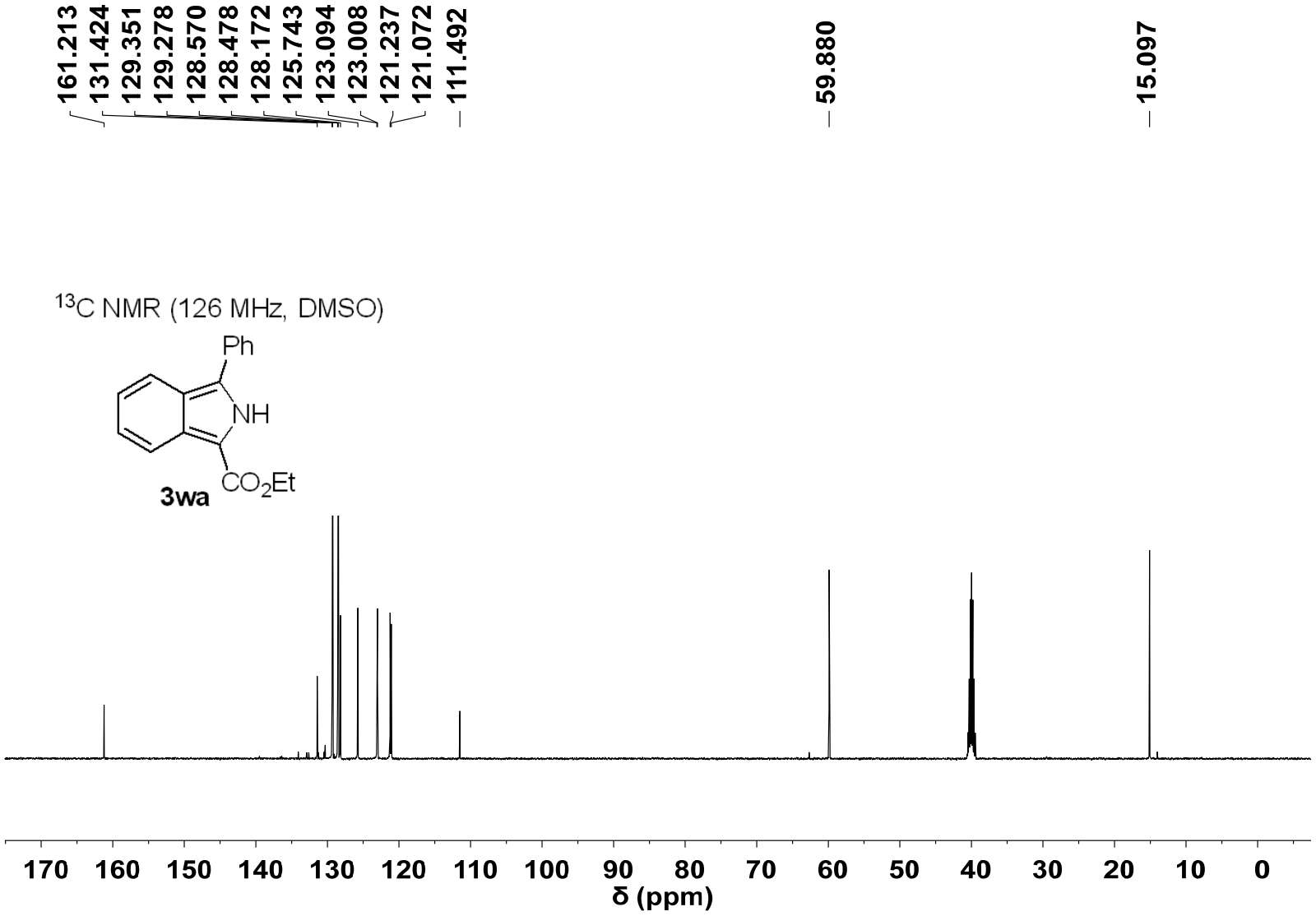

13.029
7.916
7.899
7.715
7.699
7.212
7.211
7.199
7.198
7.196
7.194
7.182
7.181
7.009
7.007
6.996
6.994
6.990
6.977
4.337
4.323
4.309
4.294
3.032
3.016
3.001
2.986
1.376
1.362
1.347
1.286
1.271
1.255
1H NMR (500 MHz, DMSO)
Et
NH
CO2Et
3ua
0.94
1.00
0.98
1.06
1.03
2.07
2.06
3.00
3.19
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ (ppm)

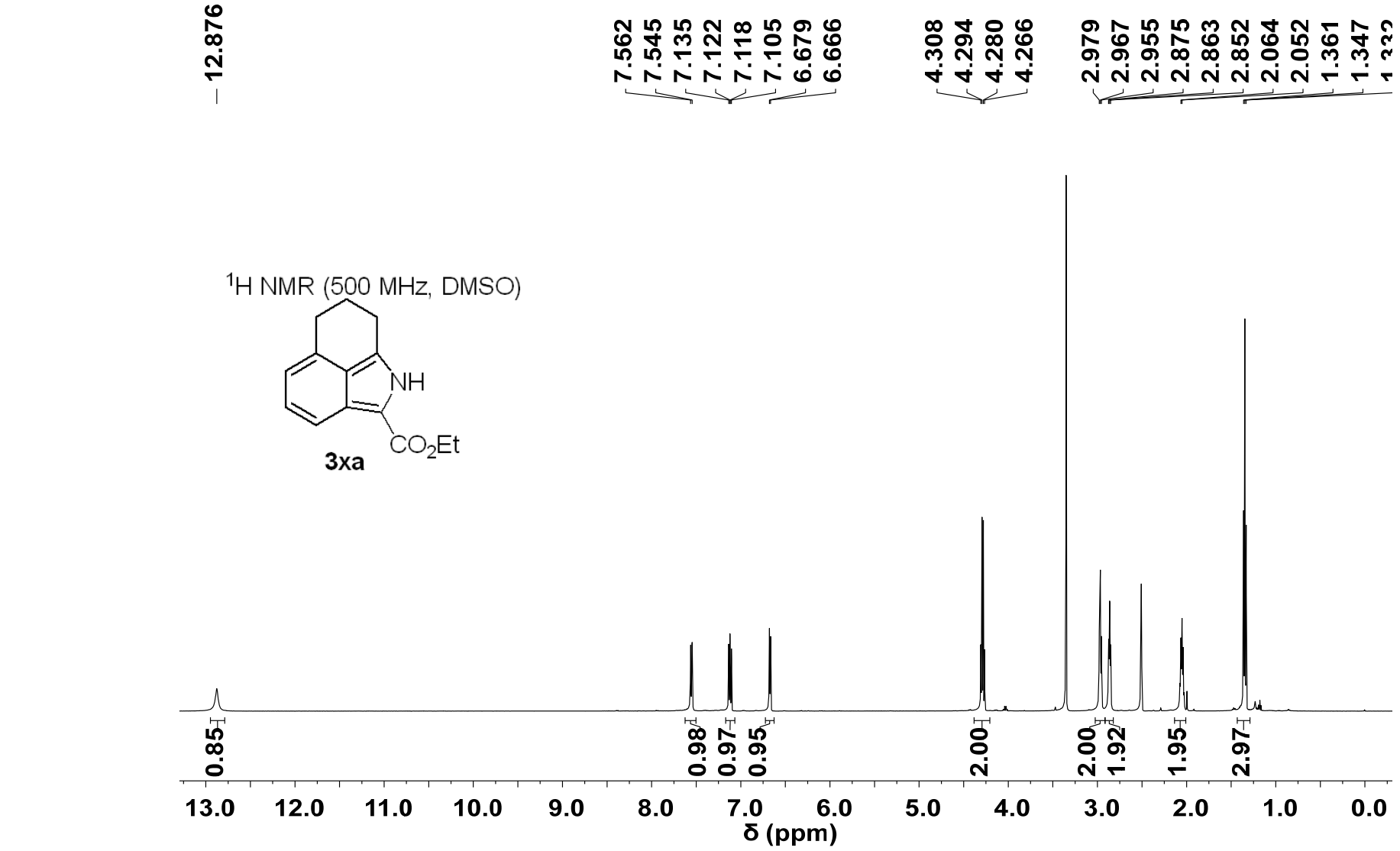

161.120
133.916
128.174
125.579
123.065
121.027
120.807
120.555
108.237
59.481
19.219
15.245
15.182
13C NMR (126 MHz, DMSO)
Et
NH
CO2Et
3ua
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

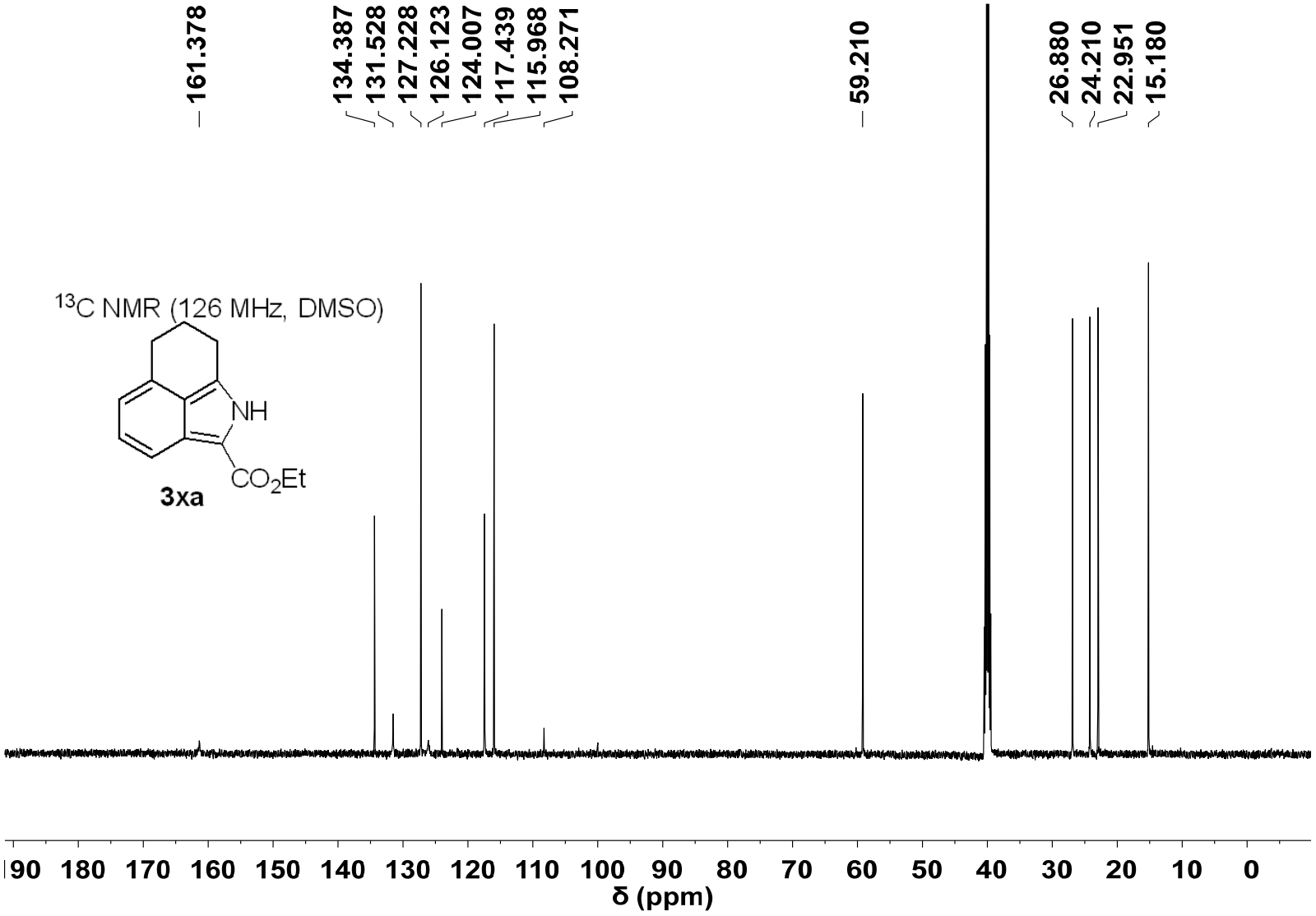

13.029
7.922
7.905
7.696
7.679
7.210
7.196
7.180
7.004
6.989
6.974
4.337
4.323
4.308
4.294
2.986
2.972
2.957
1.740
1.726
1.711
1.696
1.681
1.667
1.376
1.362
1.347
0.878
0.863
0.849
1H NMR (500 MHz, DMSO)
nPr
NH
CO2Et
3va
0.83
0.95
0.99
1.01
0.99
1.98
1.96
2.01
3.00
3.01
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
δ (ppm)

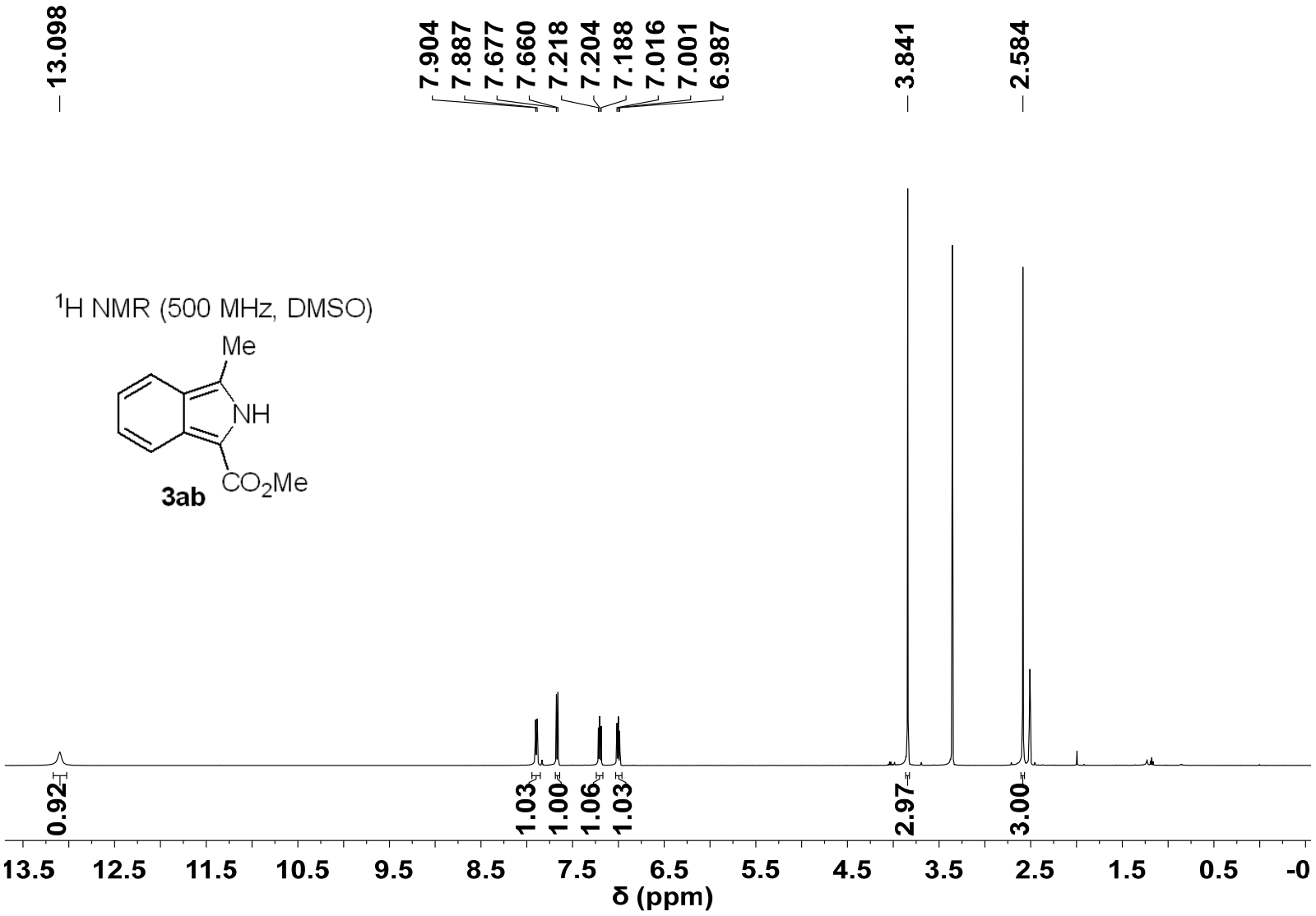

161.123
132.456
128.093
125.537
123.707
121.094
120.819
120.546
59.379
27.589
23.543
15.170
14.099
13C NMR (126 MHz, DMSO)
nPr
NH
CO2Et
3va
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

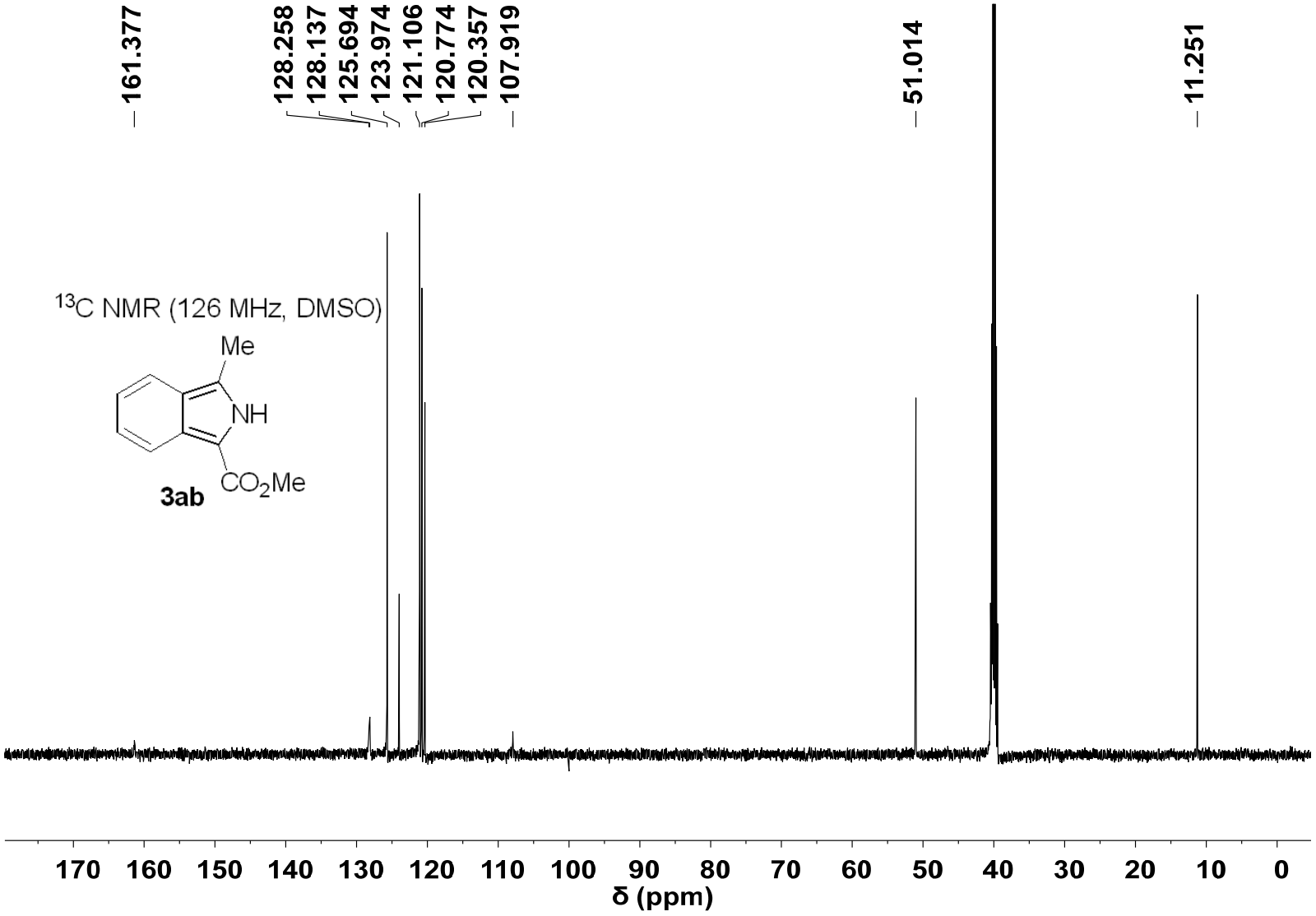

13.459
8.081
8.064
7.935
7.918
7.869
7.867
7.853
7.552
7.537
7.521
7.428
7.413
7.399
7.307
7.293
7.291
7.277
7.276
7.164
7.163
7.151
7.149
7.148
7.146
7.134
7.133
4.407
4.392
4.378
4.364
1.416
1.402
1.388
1H NMR (500 MHz, DMSO)
Ph
NH
CO2Et
3wa
0.96
1.03
1.06
2.07
2.04
1.04
1.05
1.01
2.01
3.03
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

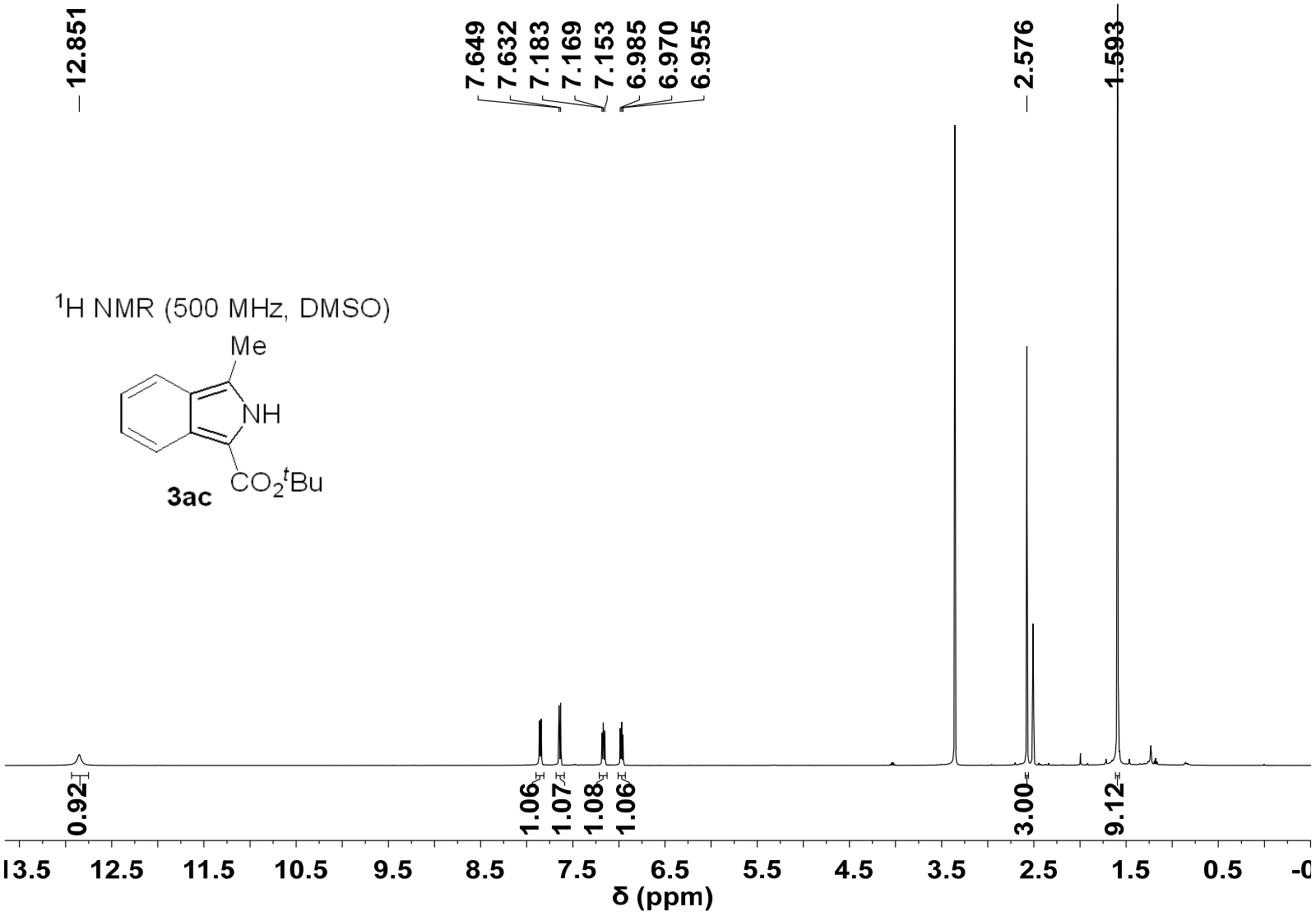

161.213
131.424
129.351
129.278
128.570
128.478
128.172
125.743
123.094
123.008
121.237
121.072
111.492
59.880
15.097
13C NMR (126 MHz, DMSO)
Ph
NH
CO2Et
3wa
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

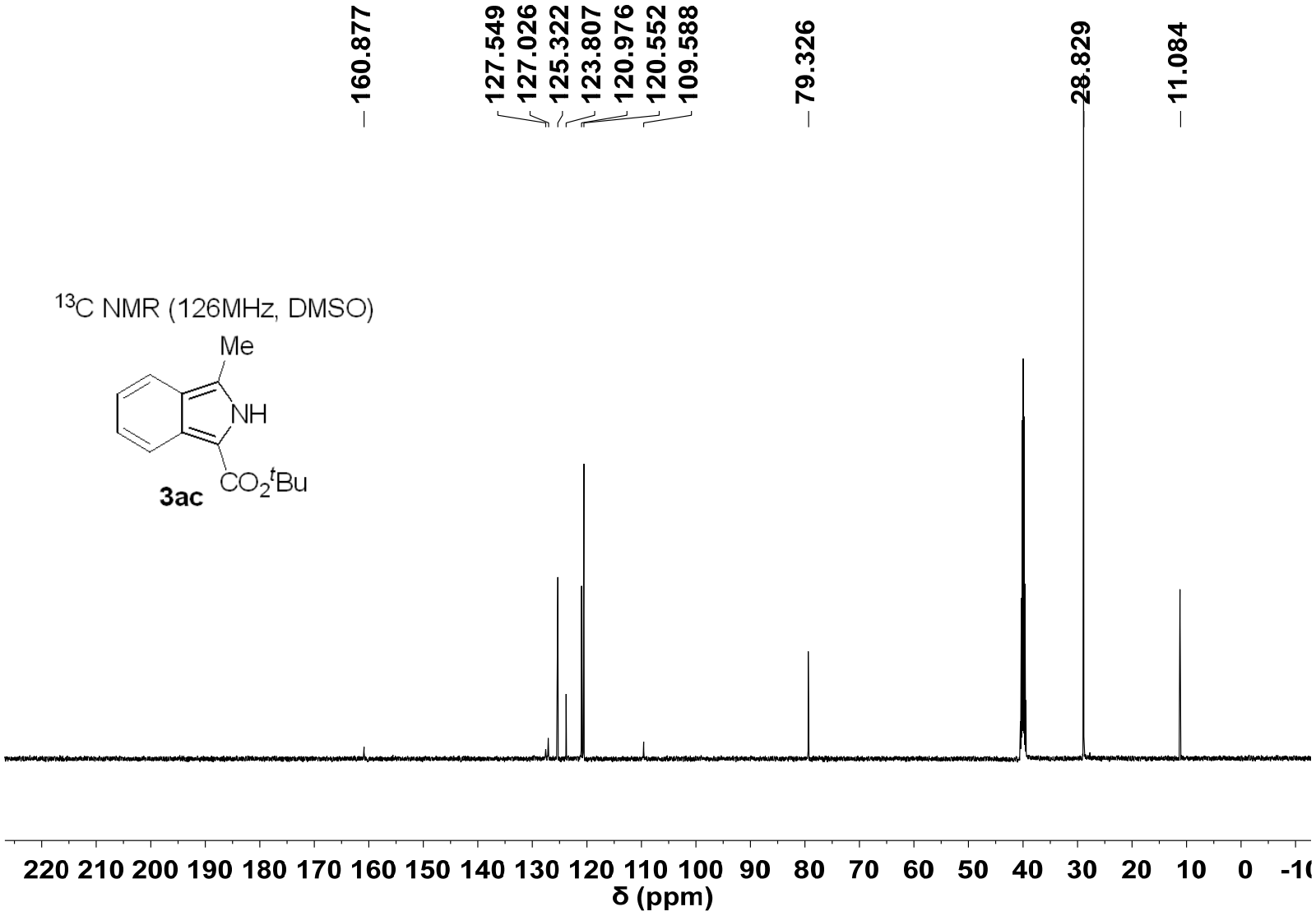

12.876
7.562
7.545
7.135
7.122
7.118
7.105
6.679
6.666
4.308
4.294
4.280
4.266
2.979
2.967
2.955
2.875
2.863
2.852
2.064
2.052
1.361
1.347
^{1}H NMR (500 MHz, DMSO)
NH
CO_2Et
3xa
0.85
0.98
0.97
0.95
2.00
2.00
1.92
1.95
2.97
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ (ppm)

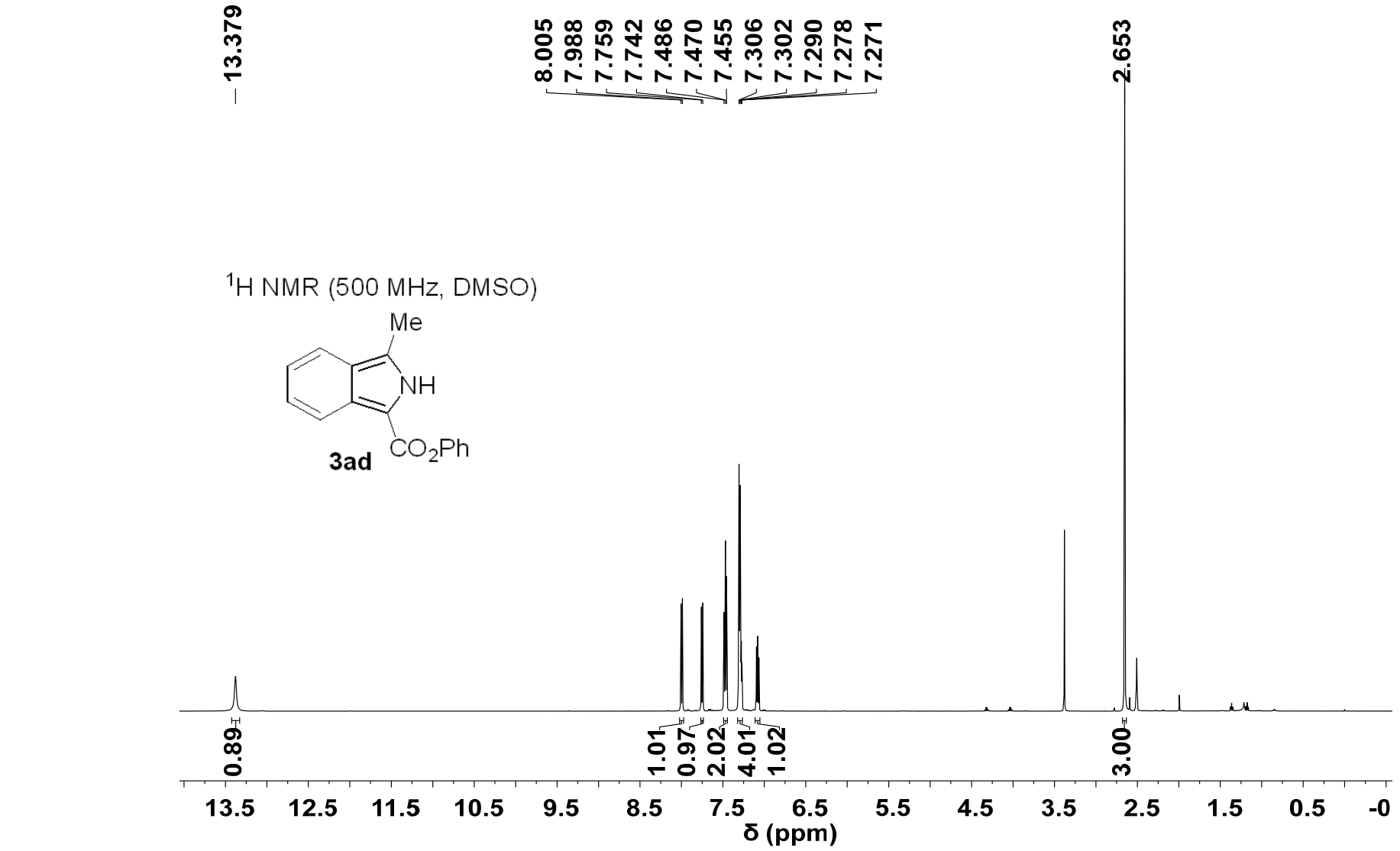

161.378
134.387
131.528
127.228
126.123
124.007
117.439
115.968
108.271
59.210
26.880
24.210
22.951
15.180
13C NMR (126 MHz, DMSO)
NH
CO2Et
3xa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

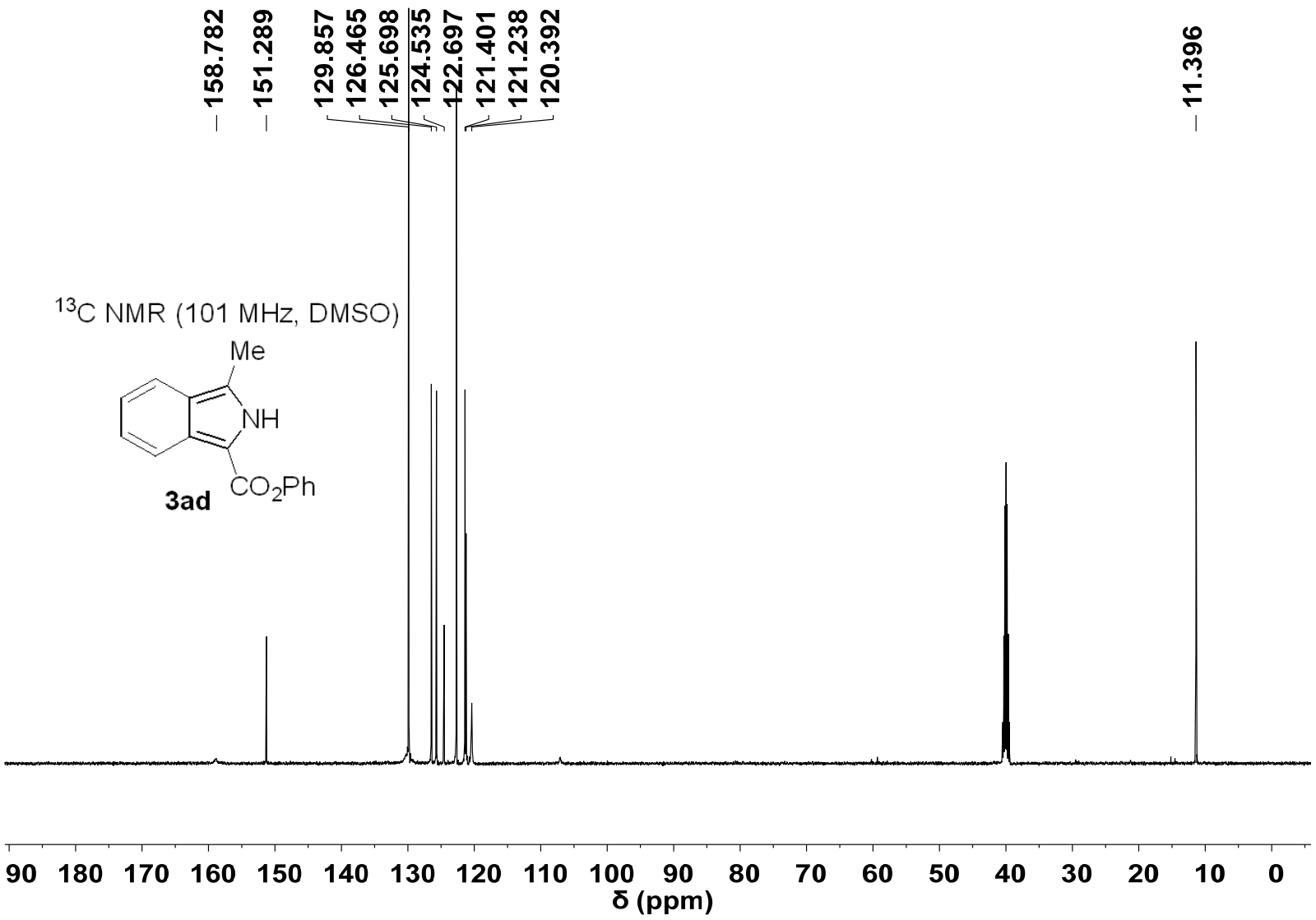

13.098
7.904
7.887
7.677
7.660
7.218
7.204
7.188
7.016
7.001
6.987
3.841
2.584
1H NMR (500 MHz, DMSO)
Me
NH
CO2Me
3ab
0.92
1.03
1.00
1.06
1.03
2.97
3.00
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0
δ (ppm)

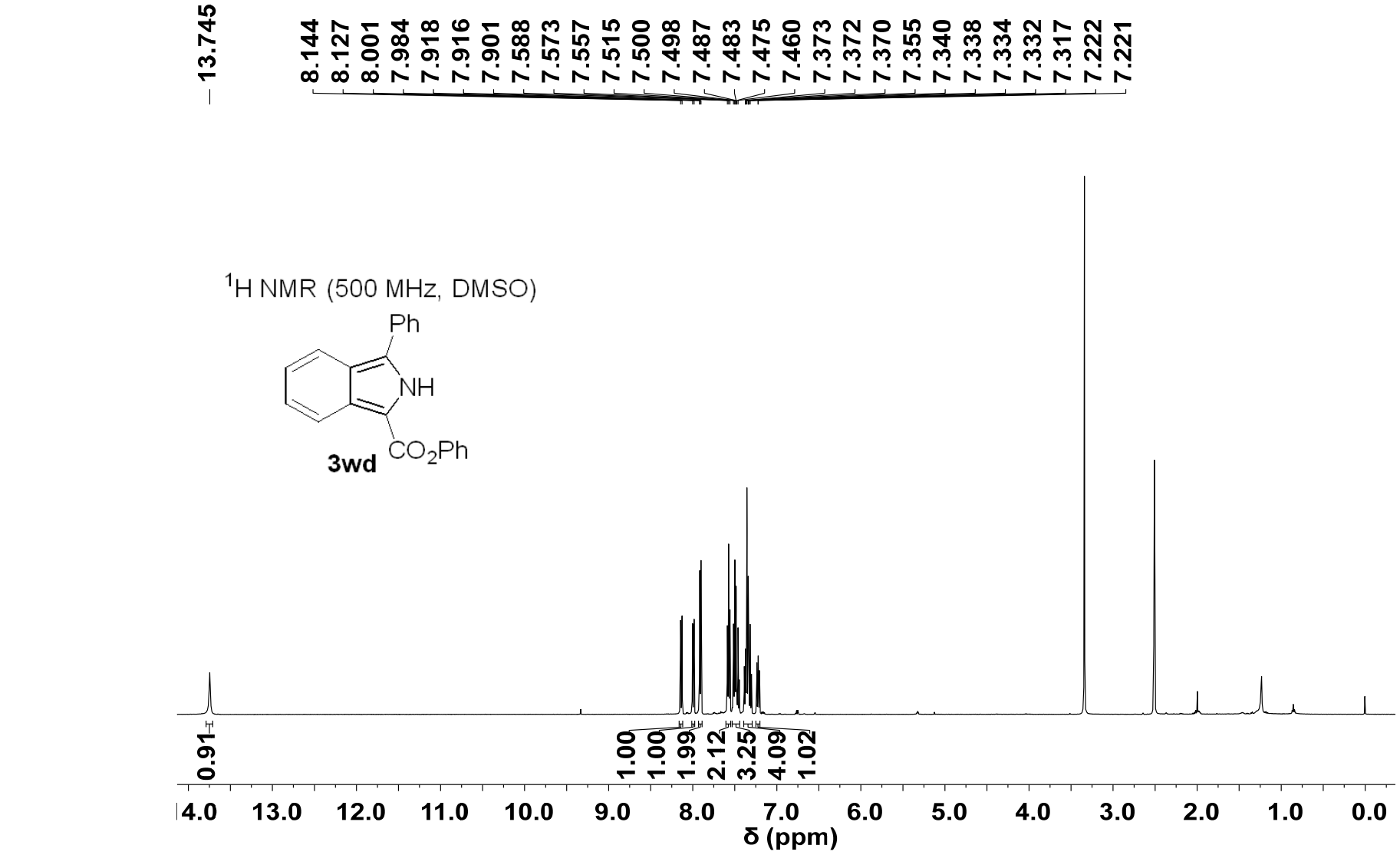

161.377
128.258
128.137
125.694
123.974
121.106
120.774
120.357
107.919
51.014
11.251
^{13}C NMR (126 MHz, DMSO)
Me
NH
CO_2Me
3ab
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

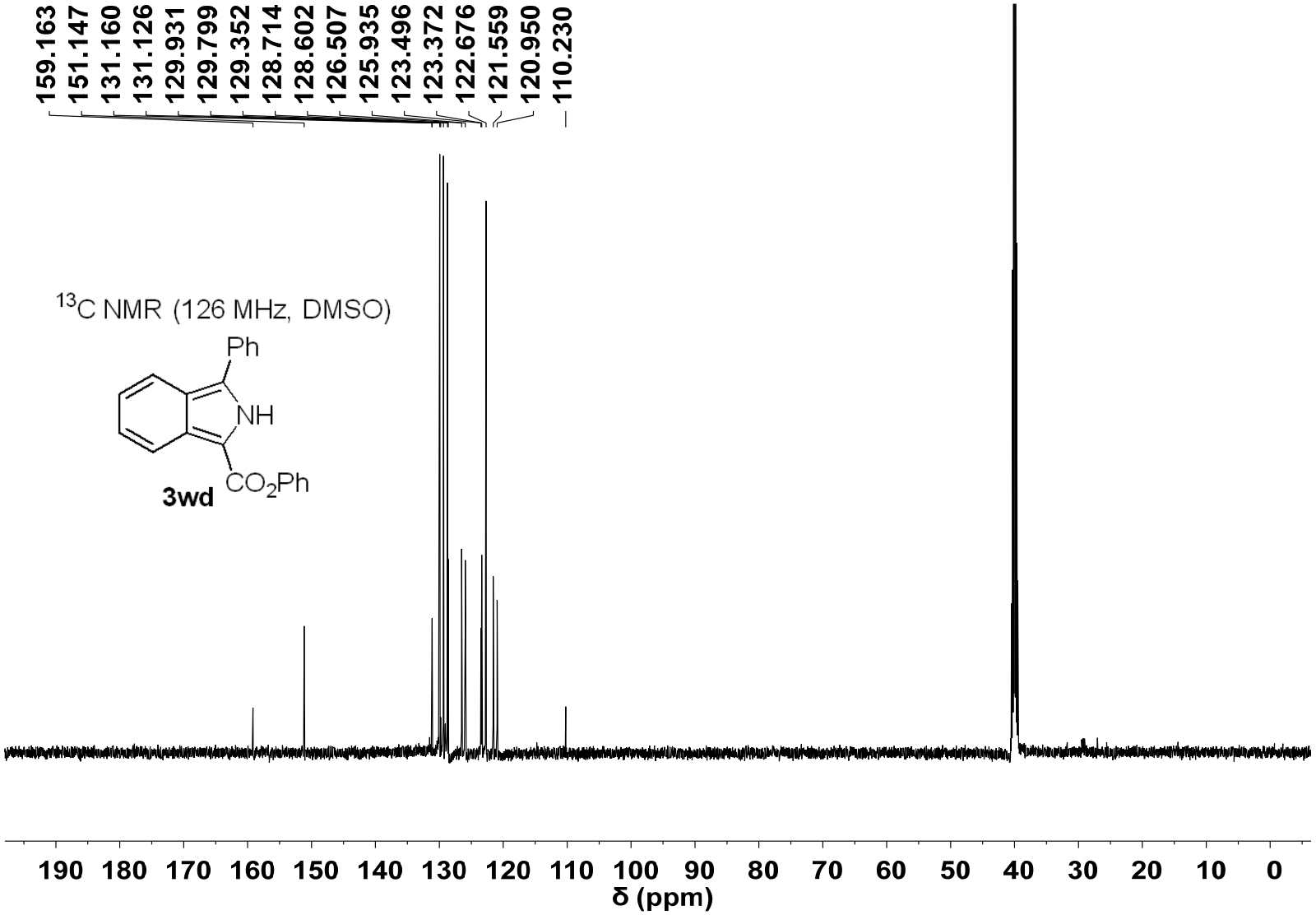

12.851
7.649
7.632
7.183
7.169
7.153
6.985
6.970
6.955
2.576
1.593
^{1}H NMR (500 MHz, DMSO)
Me
NH
$CO_2{}^t$Bu
3ac
0.92
1.06
1.07
1.08
1.06
3.00
9.12
δ (ppm)

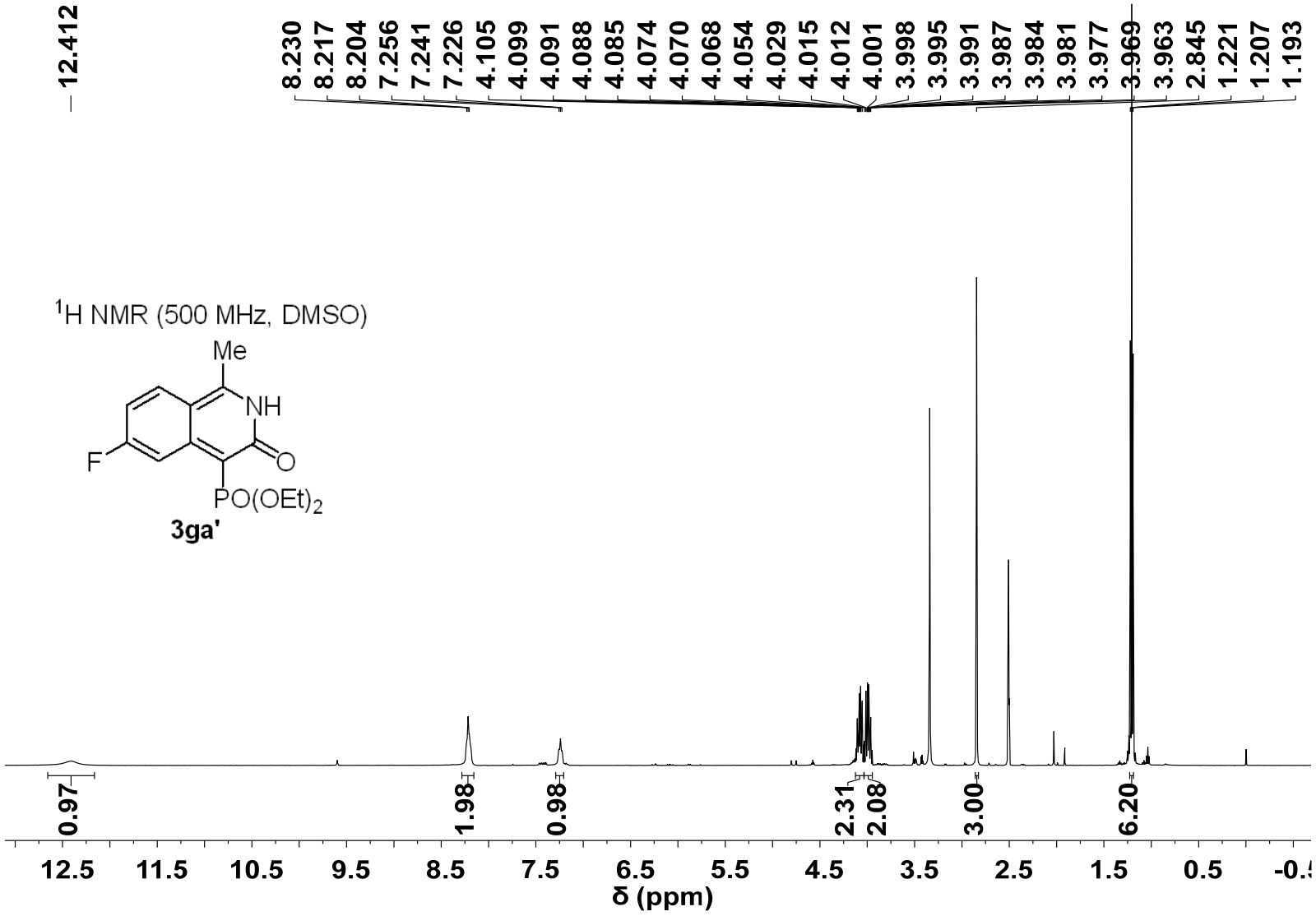

160.877
127.549
127.026
125.322
123.807
120.976
120.552
109.588
79.326
28.829
11.084
13C NMR (126MHz, DMSO)
Me
NH
CO2tBu
3ac
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

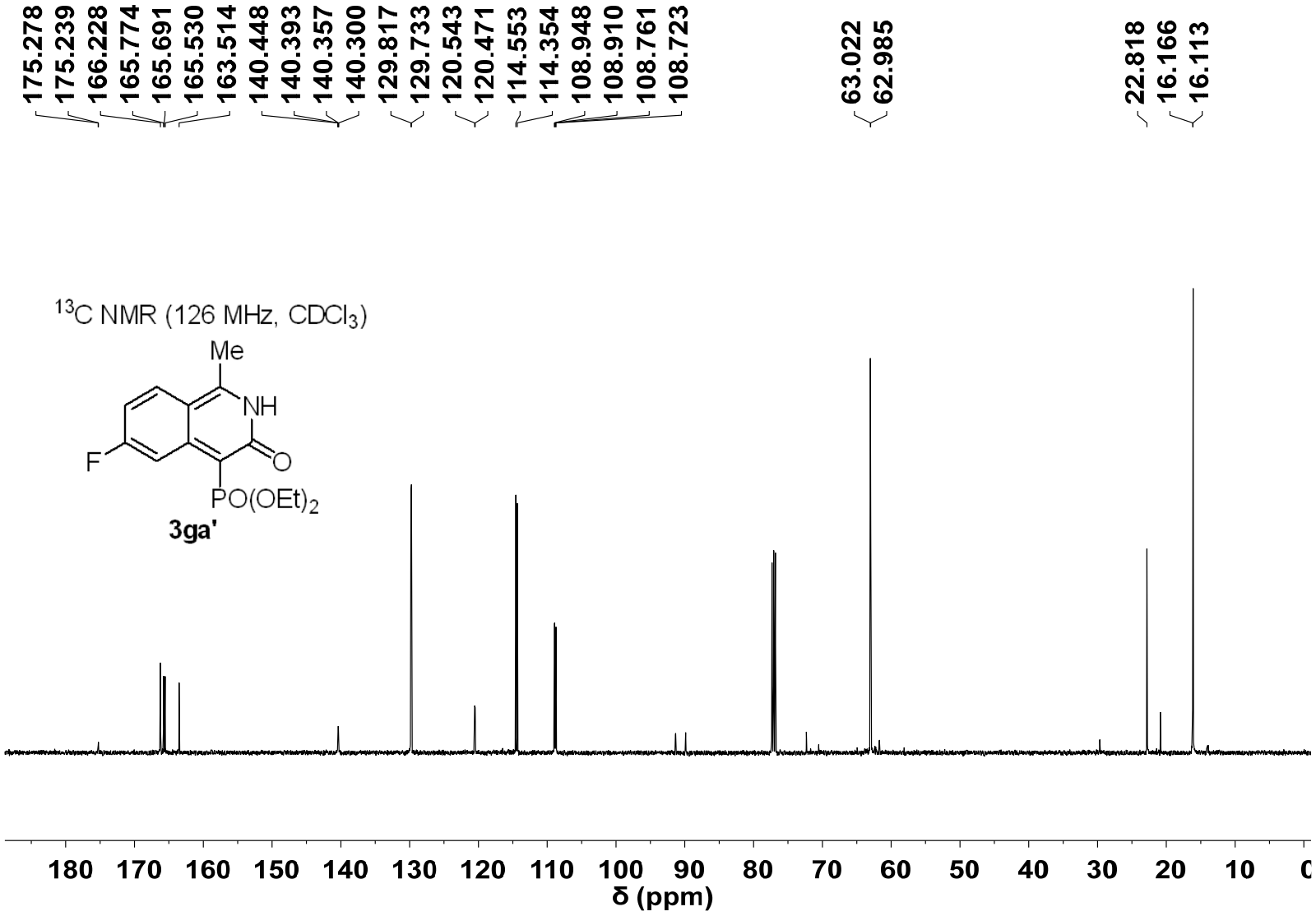

13.379
8.005
7.988
7.759
7.742
7.486
7.470
7.455
7.306
7.302
7.290
7.278
7.271
2.653
1H NMR (500 MHz, DMSO)
Me
NH
CO2Ph
3ad
0.89
1.01
0.97
2.02
4.01
1.02
3.00
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0
δ (ppm)

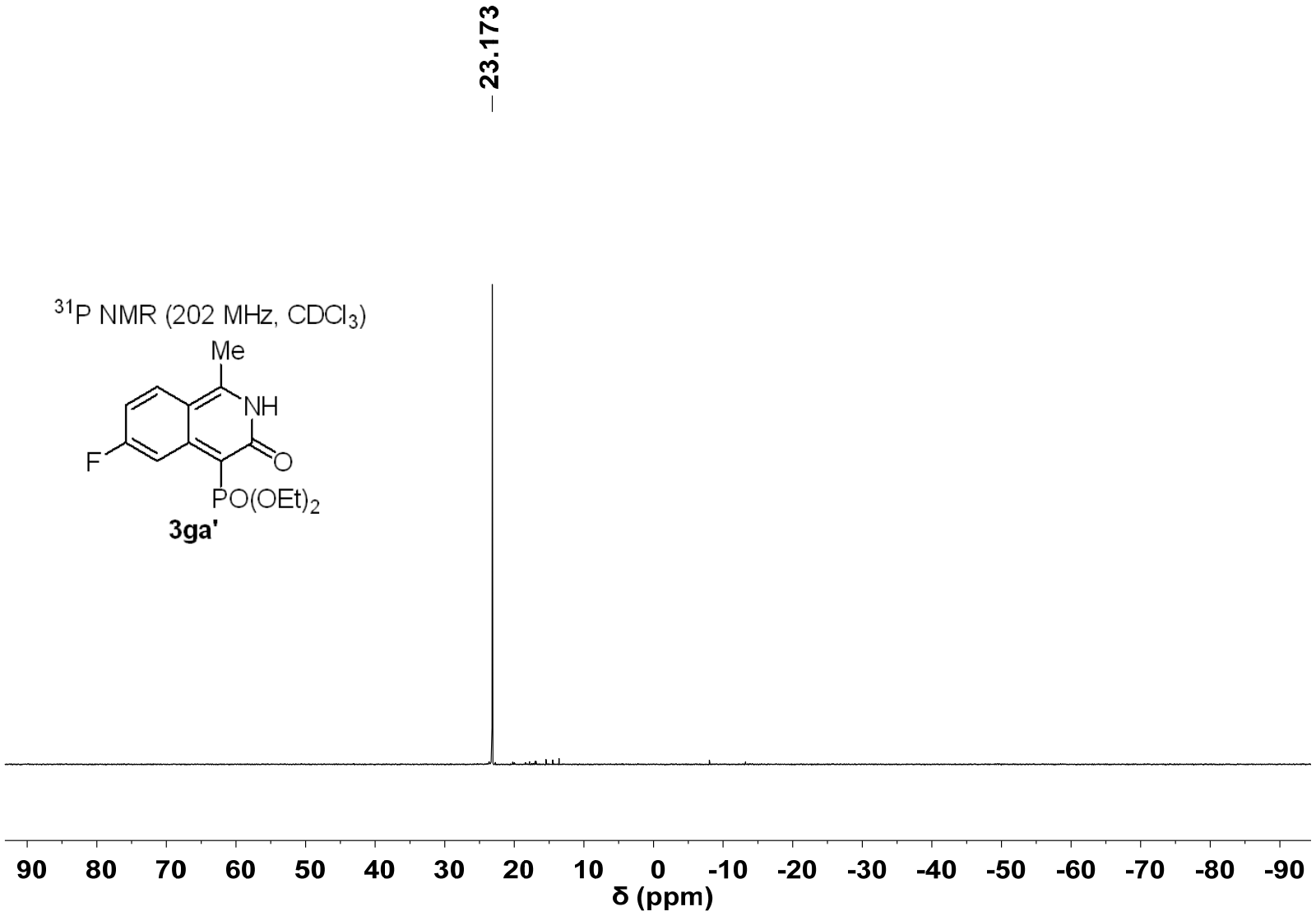

158.782
151.289
129.857
126.465
125.698
124.535
122.697
121.401
121.238
120.392
11.396
13C NMR (101 MHz, DMSO)
Me
NH
CO2Ph
3ad
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

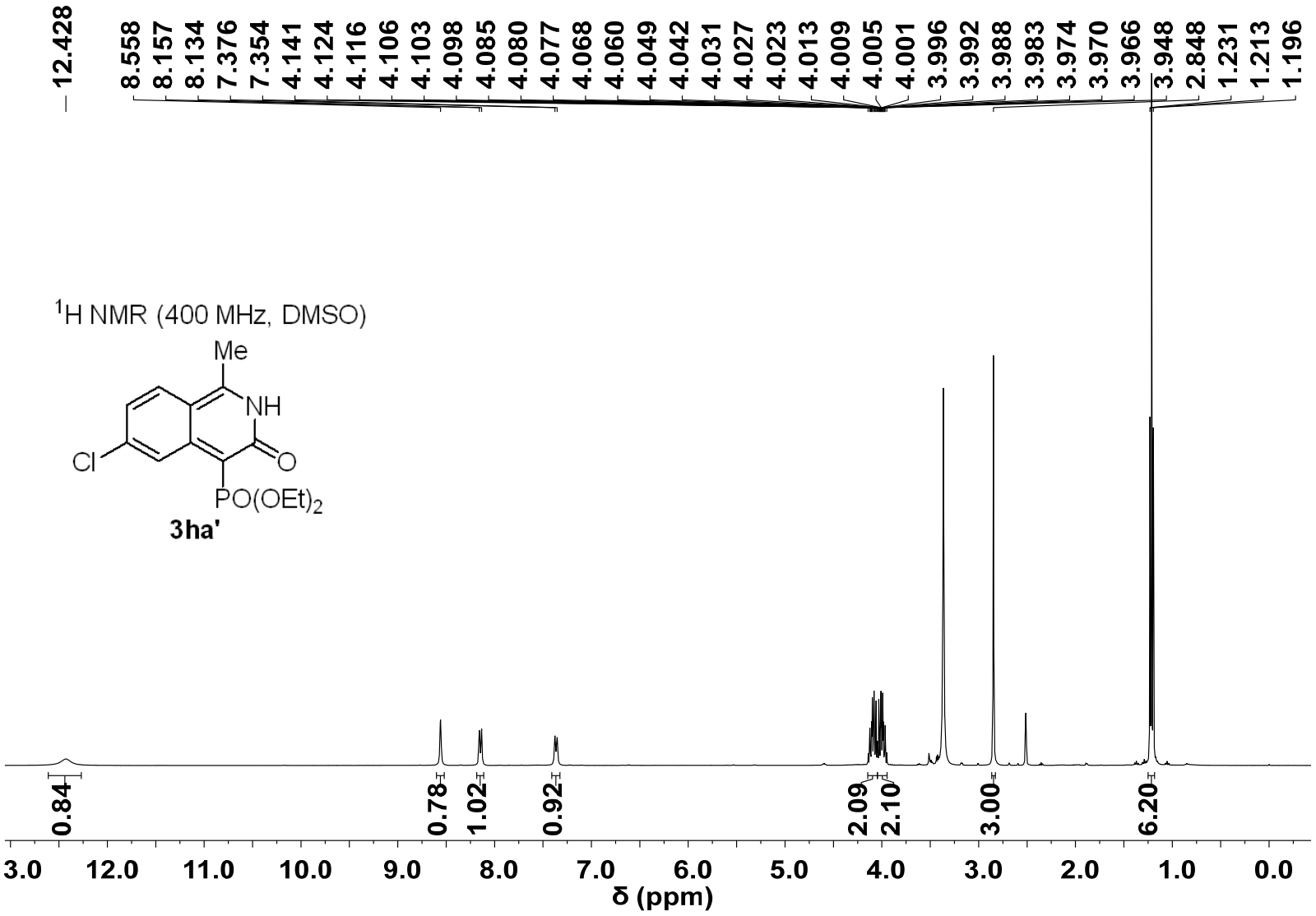

13.745
8.144
8.127
8.001
7.984
7.918
7.916
7.901
7.588
7.573
7.557
7.515
7.500
7.498
7.487
7.483
7.475
7.460
7.373
7.372
7.370
7.355
7.340
7.338
7.334
7.332
7.317
7.222
7.221
1H NMR (500 MHz, DMSO)
Ph
NH
CO2Ph
3wd
0.91
1.00
1.00
1.99
2.12
3.25
4.09
1.02
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ (ppm)

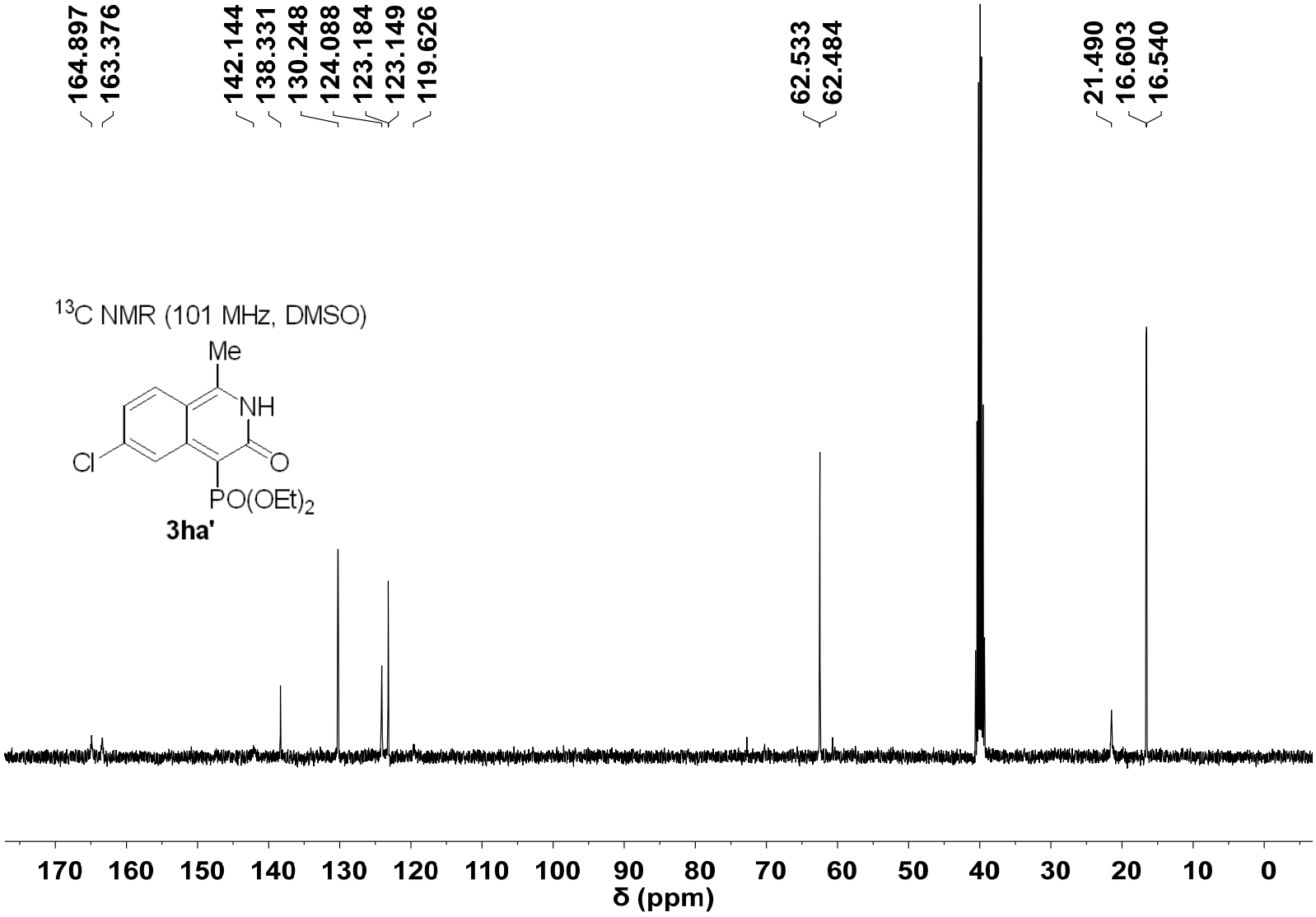

159.163
151.147
131.160
131.126
129.931
129.799
129.352
128.714
128.602
126.507
125.935
123.496
123.372
122.676
121.559
120.950
110.230
13C NMR (126 MHz, DMSO)
Ph
NH
CO2Ph
3wd
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

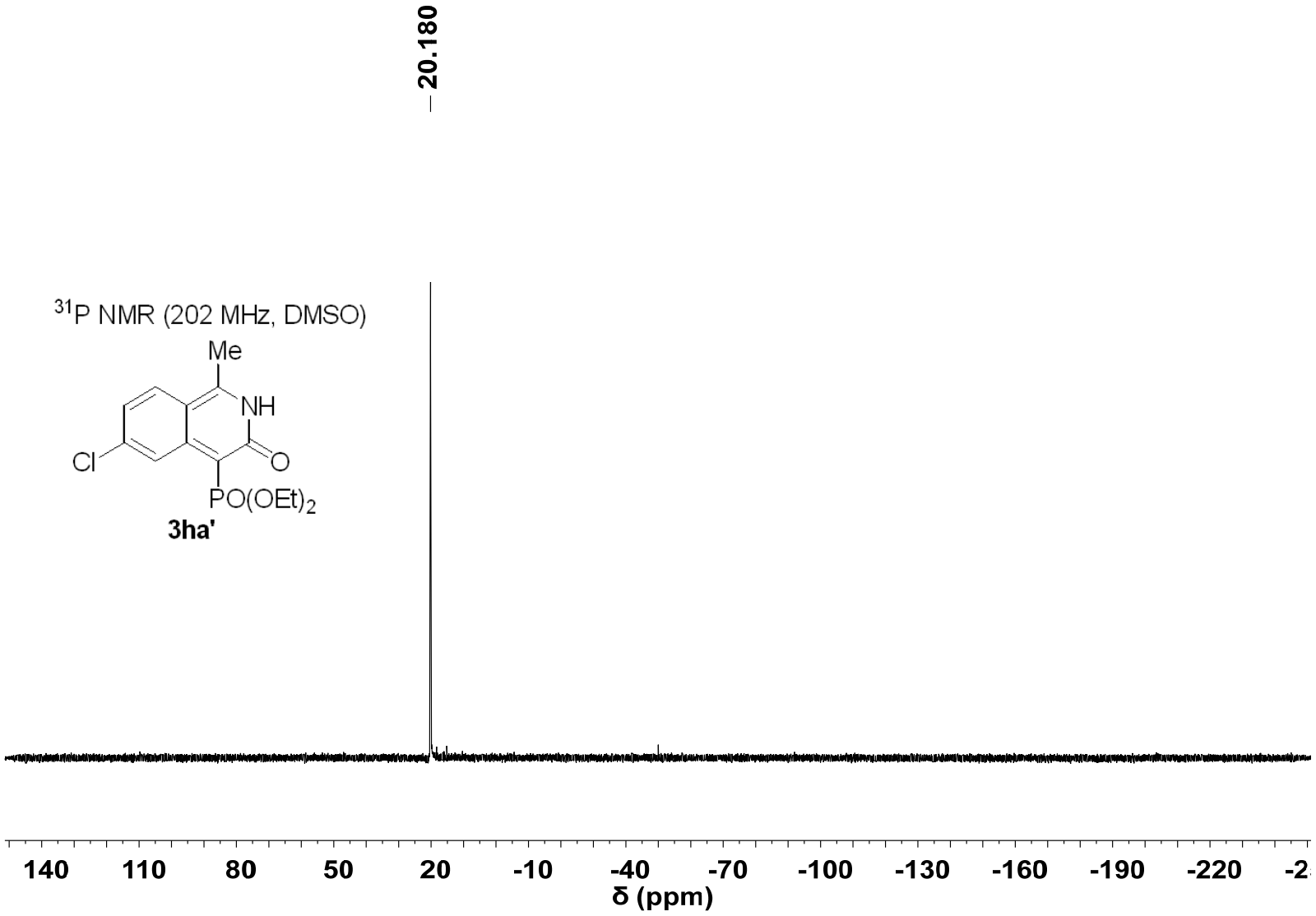

12.412
8.230
8.217
8.204
7.256
7.241
7.226
4.105
4.099
4.091
4.088
4.085
4.074
4.070
4.068
4.054
4.029
4.015
4.012
4.001
3.998
3.995
3.991
3.987
3.984
3.981
3.977
3.969
3.963
2.845
1.221
1.207
1.193
1H NMR (500 MHz, DMSO)
Me
NH
F
O
PO(OEt)2
3ga'
0.97
1.98
0.98
2.31
2.08
3.00
6.20
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
δ (ppm)

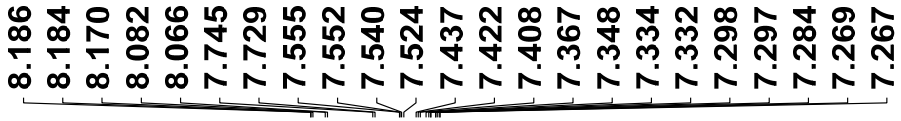

175.278
175.239
166.228
165.774
165.691
165.530
163.514
140.448
140.393
140.357
140.300
129.817
129.733
120.543
120.471
114.553
114.354
108.948
108.910
108.761
108.723
63.022
62.985
22.818
16.166
16.113
13C NMR (126 MHz, CDCl3)
Me
NH
F
O
PO(OEt)2
3ga'
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


23.173
31P NMR (202 MHz, CDCl3)
Me
NH
F
O
PO(OEt)2
3ga'
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
δ (ppm)

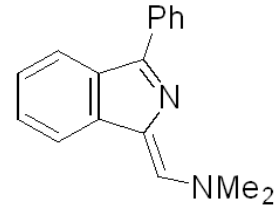

12.428
8.558
8.157
8.134
7.376
7.354
4.141
4.124
4.116
4.106
4.103
4.098
4.085
4.080
4.077
4.068
4.060
4.049
4.042
4.031
4.027
4.023
4.013
4.009
4.005
4.001
3.996
3.992
3.988
3.983
3.974
3.970
3.966
3.948
2.848
1.231
1.213
1.196
1H NMR (400 MHz, DMSO)
Me
NH
Cl
O
PO(OEt)2
3ha'
0.84
0.78
1.02
0.92
2.09
2.10
3.00
6.20
3.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ (ppm)


164.897
163.376
142.144
138.331
130.248
124.088
123.184
123.149
119.626
62.533
62.484
21.490
16.603
16.540
13C NMR (101 MHz, DMSO)
Me
NH
Cl
O
PO(OEt)2
3ha'
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

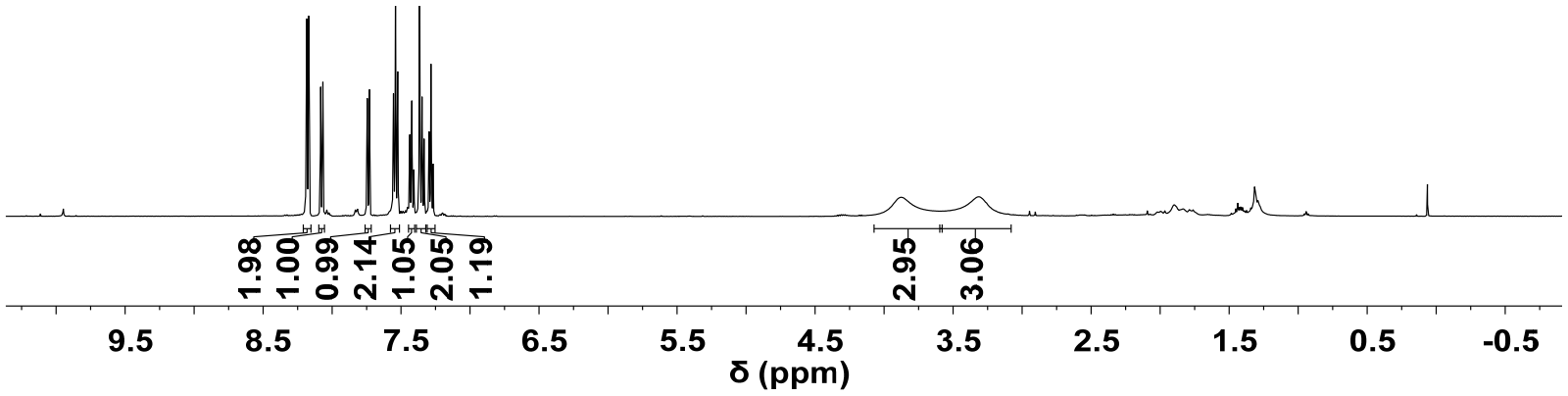

20.180
31P NMR (202 MHz, DMSO)
Me
NH
Cl
O
PO(OEt)2
3ha'
140
110
80
50
20
-10
-40
-70
-100
-130
-160
-190
-220
δ (ppm)

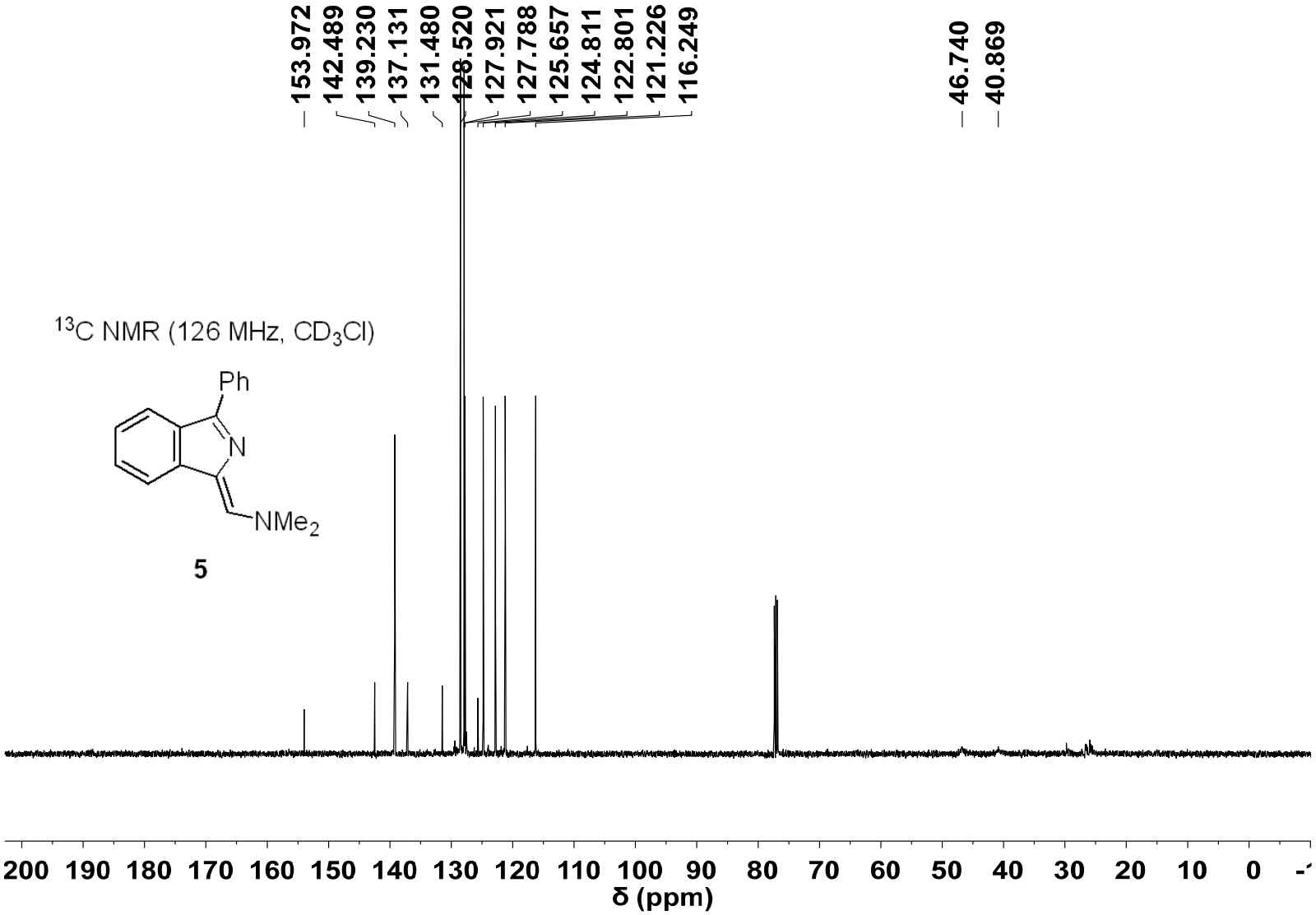


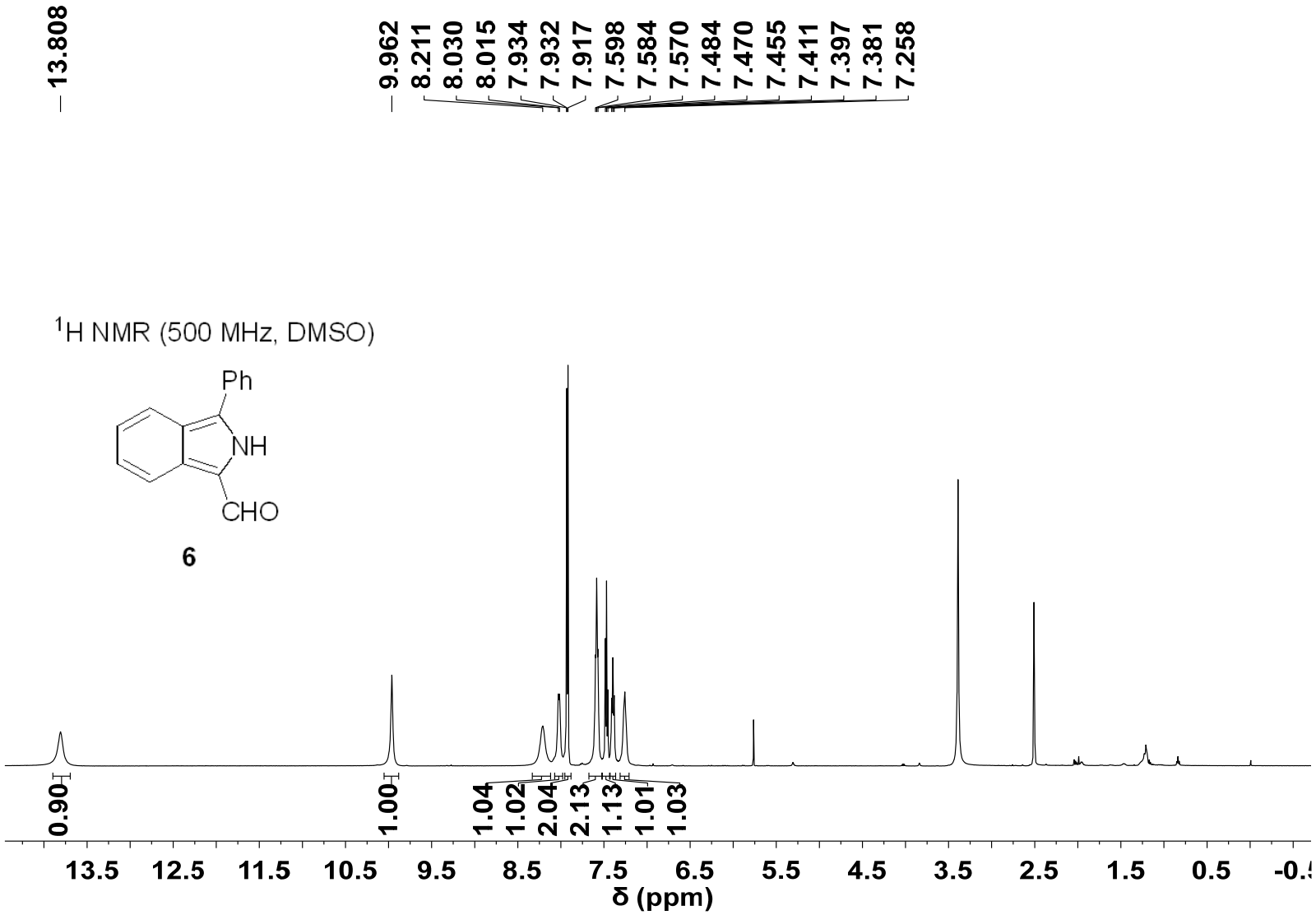
^{1}H NMR (500 MHz, CD_3Cl)

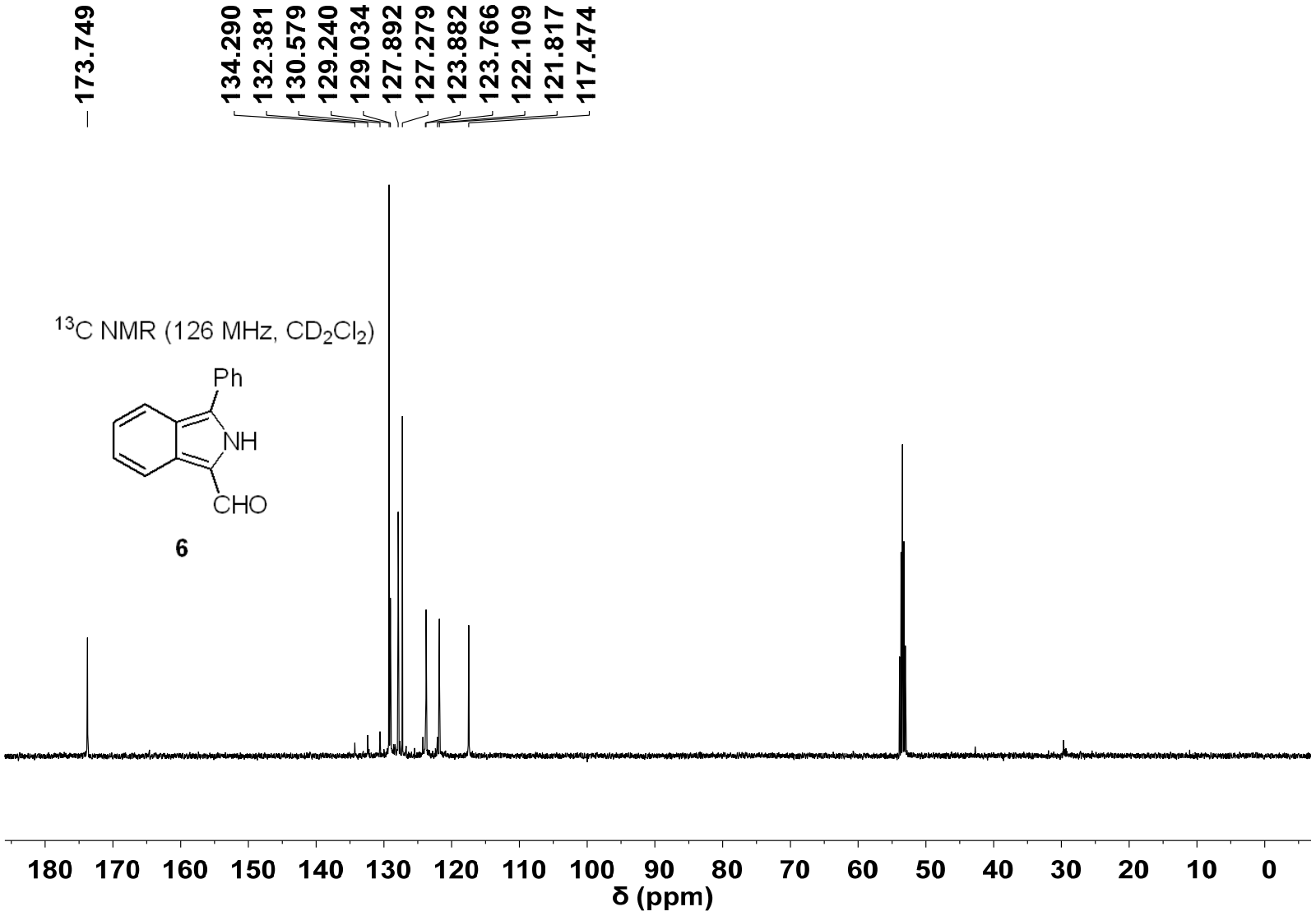


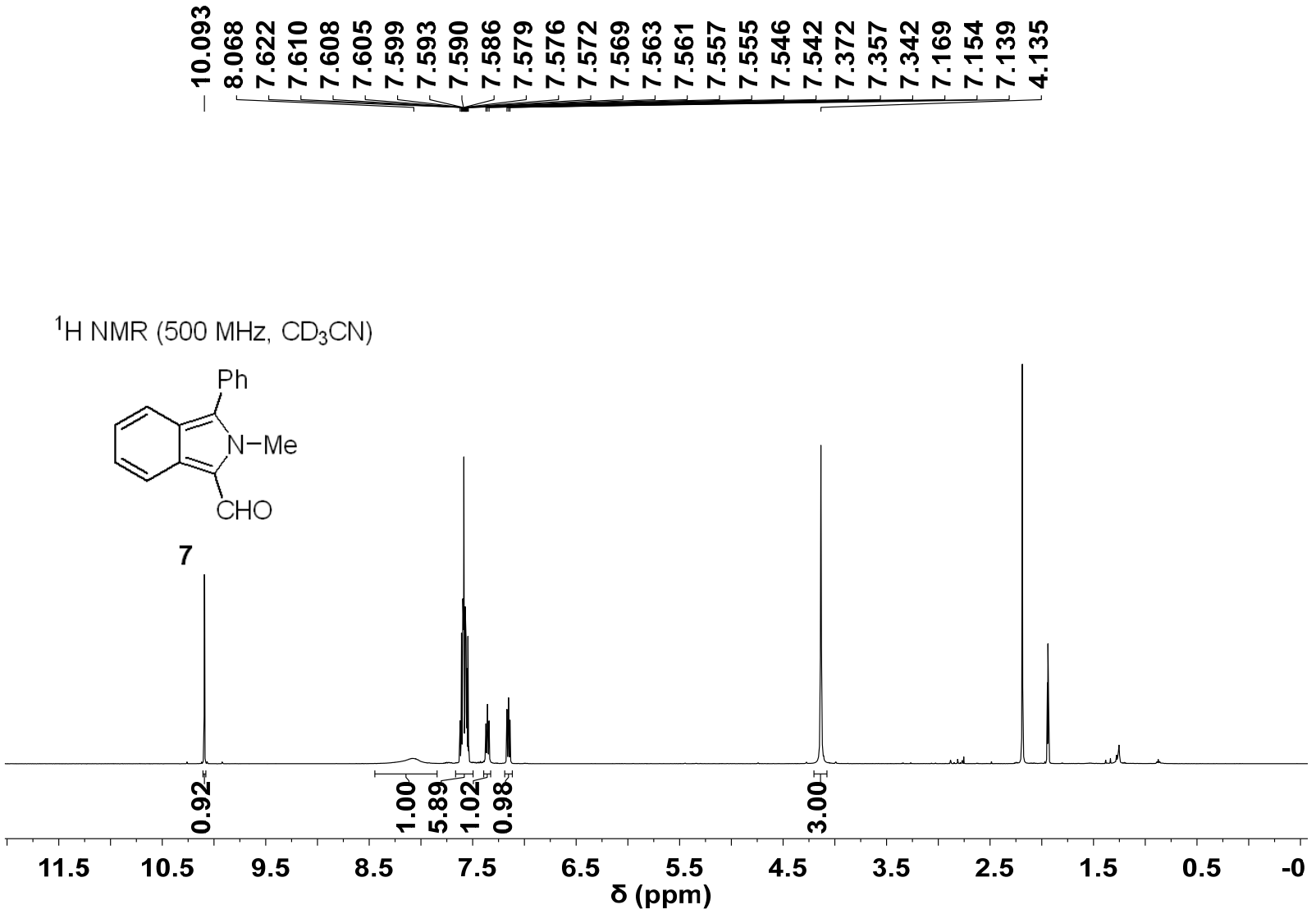
5

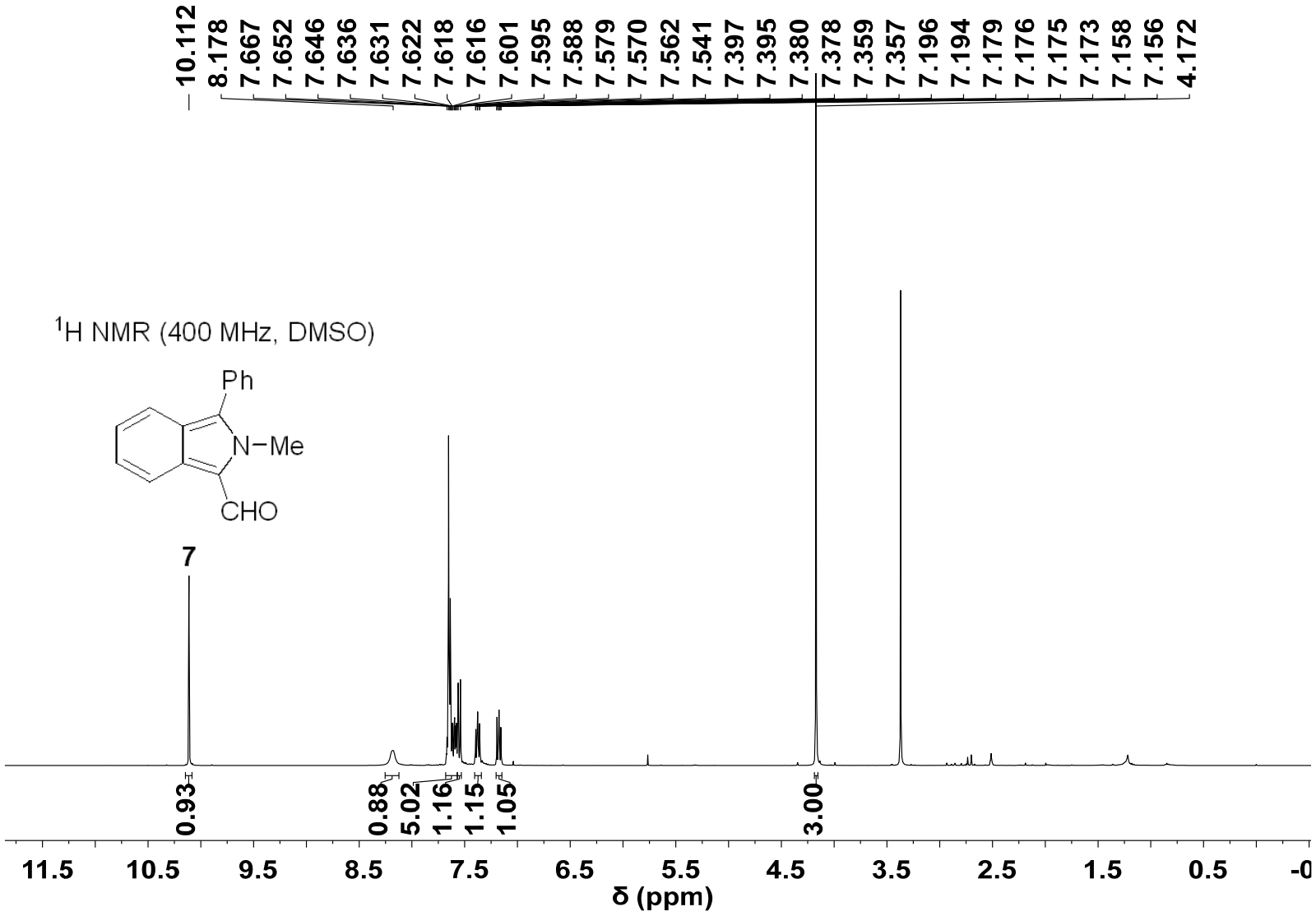


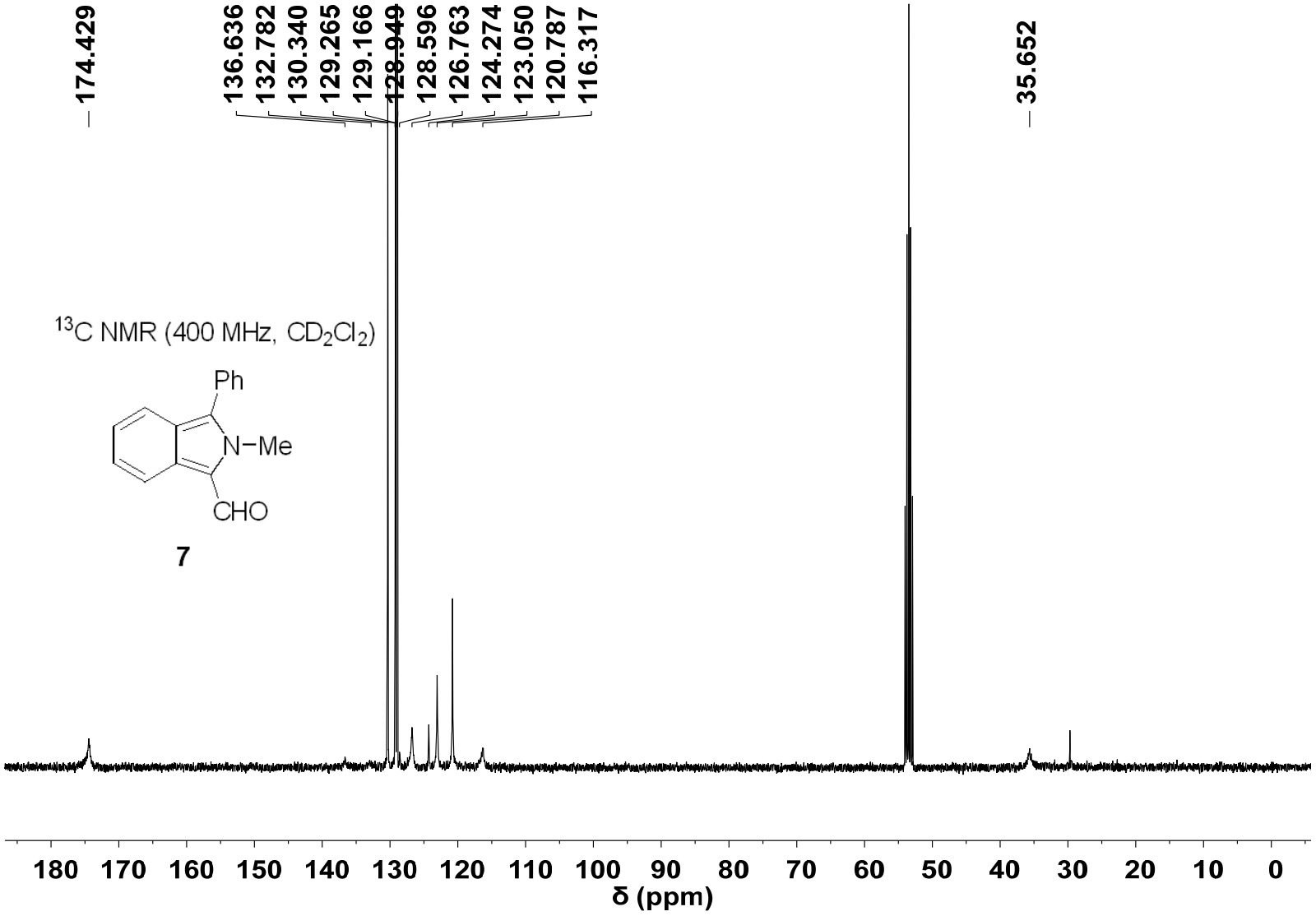

153.972
142.489
139.230
137.131
131.480
128.520
127.921
127.788
125.657
124.811
122.801
121.226
116.249
46.740
40.869
13C NMR (126 MHz, CD3Cl)
Ph
N
NMe2
5
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

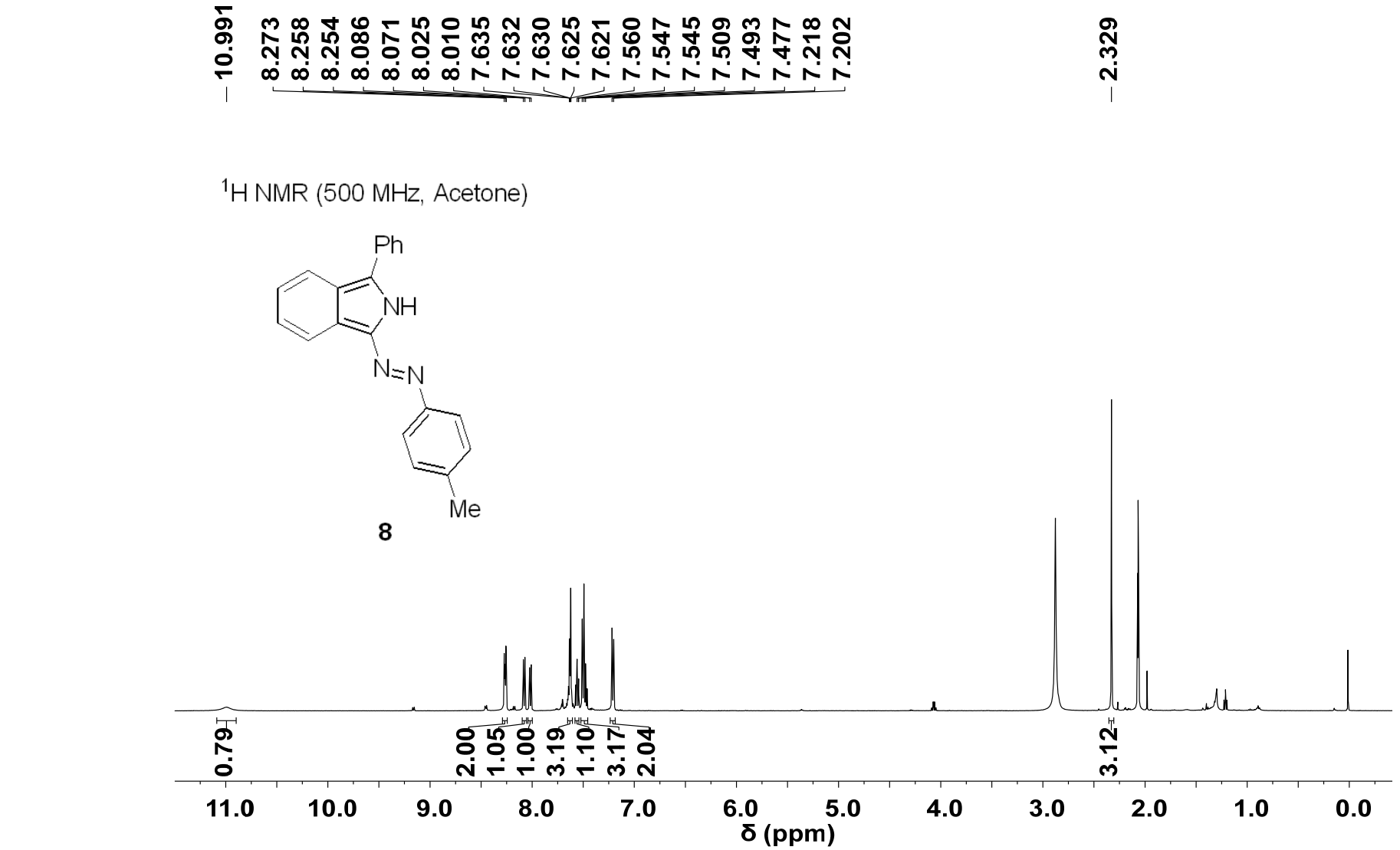

13.808
9.962
8.211
8.030
8.015
7.934
7.932
7.917
7.598
7.584
7.570
7.484
7.470
7.455
7.411
7.397
7.381
7.258
1H NMR (500 MHz, DMSO)
Ph
NH
CHO
6
0.90
1.00
1.04
1.02
2.04
2.13
1.13
1.01
1.03
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
δ (ppm)

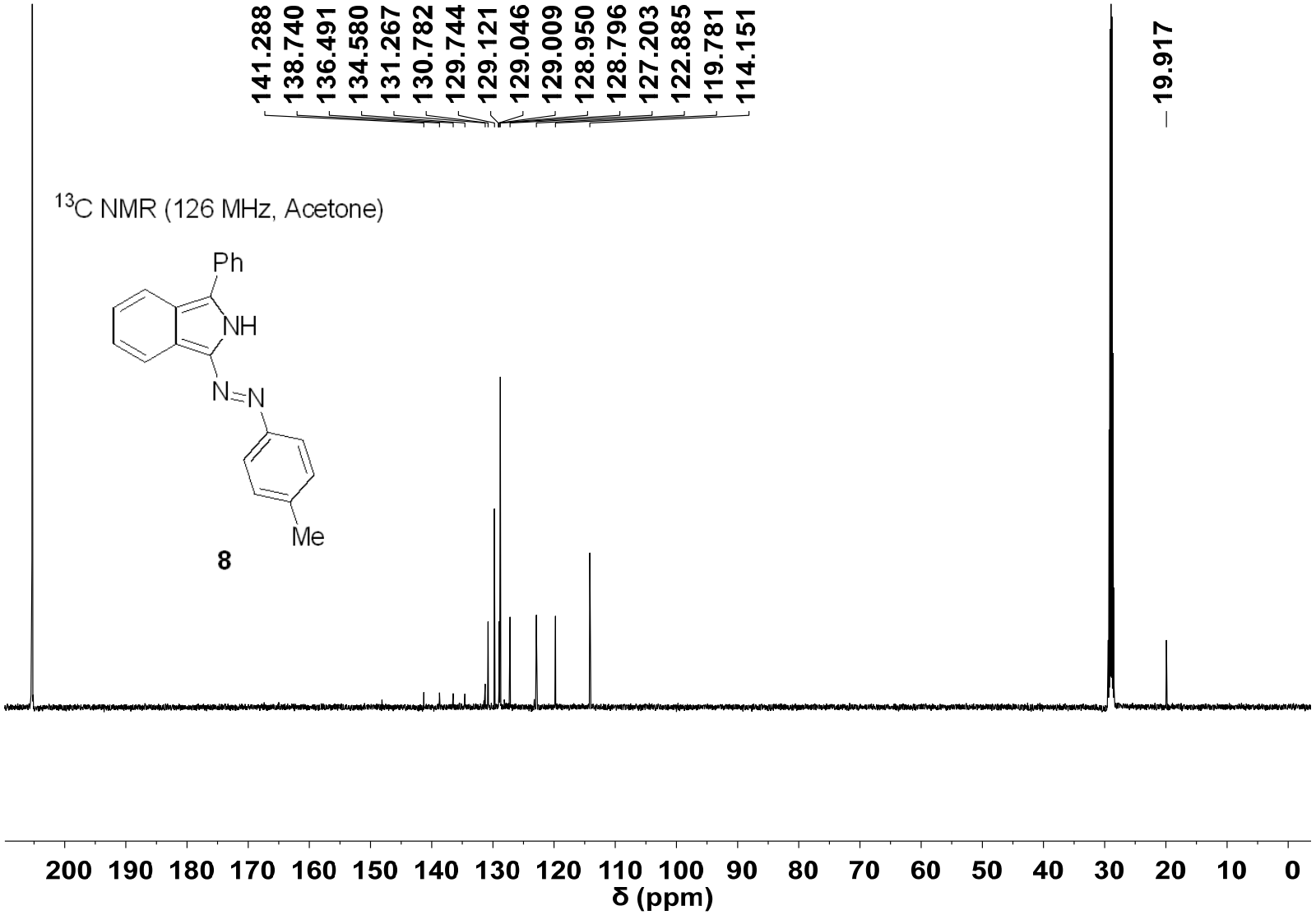

173.749
134.290
132.381
130.579
129.240
129.034
127.892
127.279
123.882
123.766
122.109
121.817
117.474
^{13}C NMR (126 MHz, CD_2Cl_2)
Ph
NH
CHO
6
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

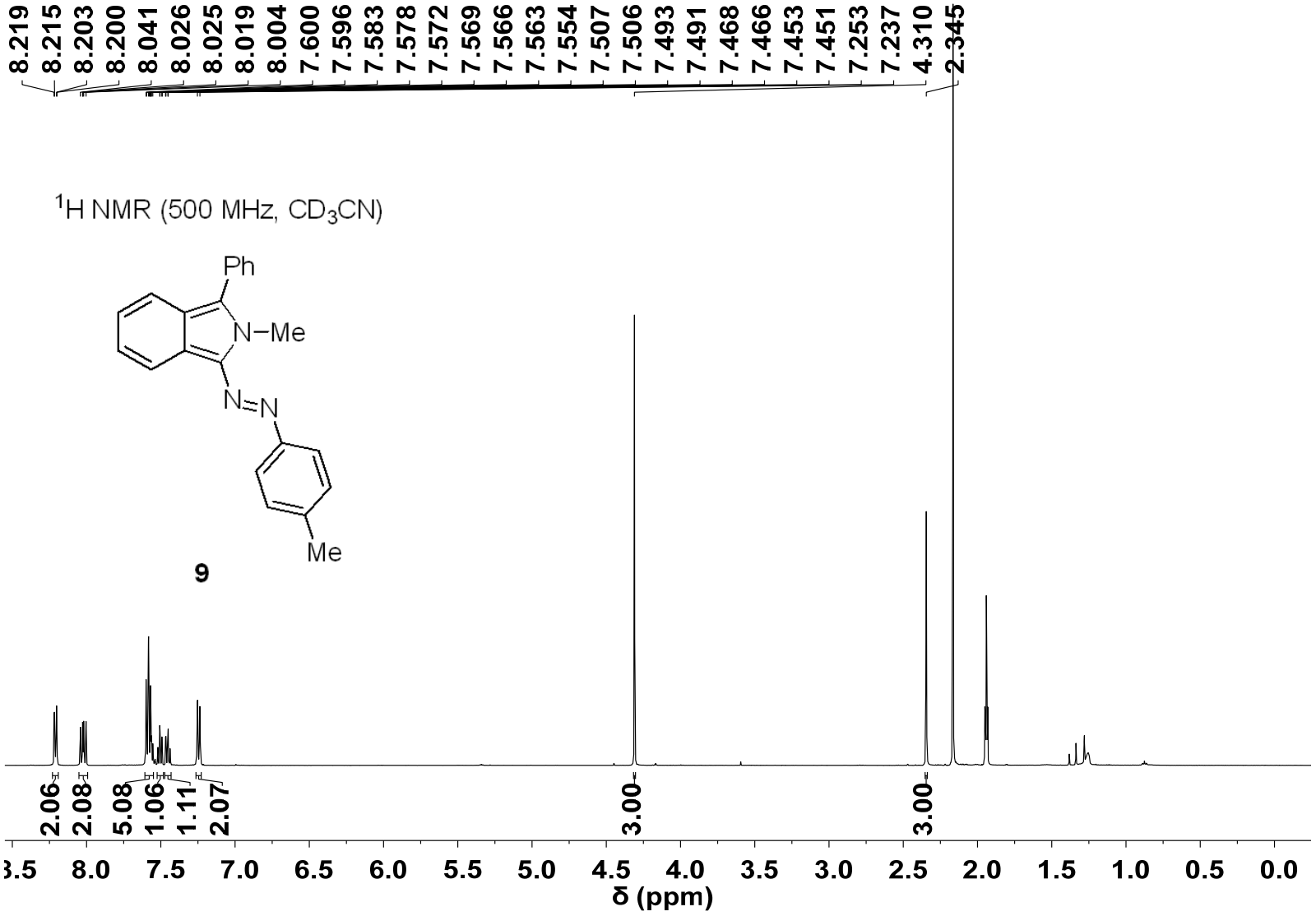

10.093
8.068
7.622
7.610
7.608
7.605
7.599
7.593
7.590
7.586
7.579
7.576
7.572
7.569
7.563
7.561
7.557
7.555
7.546
7.542
7.372
7.357
7.342
7.169
7.154
7.139
4.135
1H NMR (500 MHz, CD3CN)
Ph
N−Me
CHO
7
0.92
1.00
5.89
1.02
0.98
3.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0
δ (ppm)

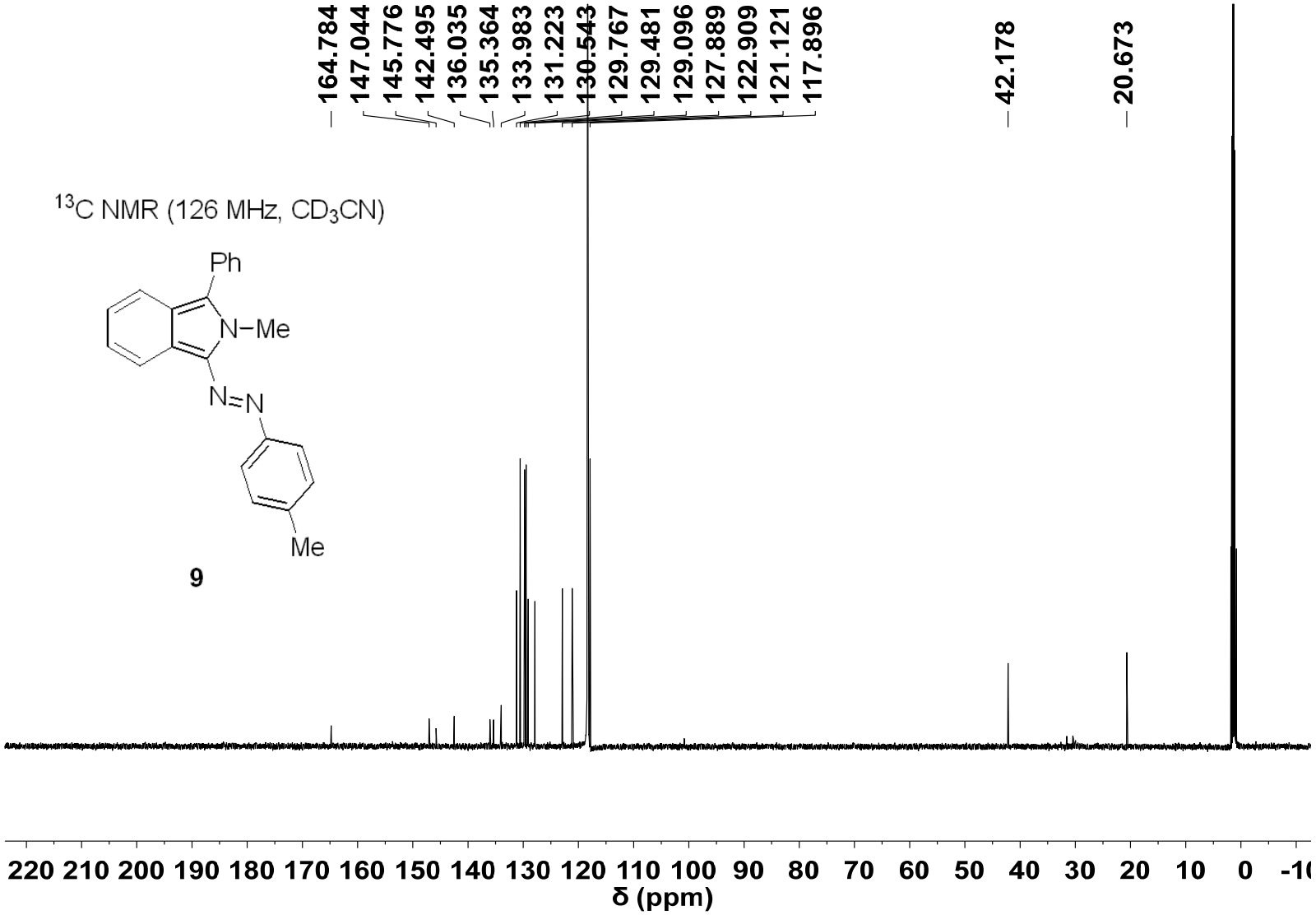

10.112
8.178
7.667
7.652
7.646
7.636
7.631
7.622
7.618
7.616
7.601
7.595
7.588
7.579
7.570
7.562
7.541
7.397
7.395
7.380
7.378
7.359
7.357
7.196
7.194
7.179
7.176
7.175
7.173
7.158
7.156
4.172
1H NMR (400 MHz, DMSO)
Ph
N−Me
CHO
7
0.93
0.88
5.02
1.16
1.15
1.05
3.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
δ (ppm)


174.429
136.636
132.782
130.340
129.265
129.166
128.949
128.596
126.763
124.274
123.050
120.787
116.317
35.652
13C NMR (400 MHz, CD2Cl2)
Ph
N−Me
CHO
7
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


10.991
8.273
8.258
8.254
8.086
8.071
8.025
8.010
7.635
7.632
7.630
7.625
7.621
7.560
7.547
7.545
7.509
7.493
7.477
7.218
7.202
2.329
1H NMR (500 MHz, Acetone)
Ph
NH
N=N
Me
8
0.79
2.00
1.05
1.00
3.19
1.10
3.17
2.04
3.12
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ (ppm)


141.288
138.740
136.491
134.580
131.267
130.782
129.744
129.121
129.046
129.009
128.950
128.796
127.203
122.885
119.781
114.151
19.917
13C NMR (126 MHz, Acetone)
Ph
NH
N=N
Me
8
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


8.219
8.215
8.203
8.200
8.041
8.026
8.025
8.019
8.004
7.600
7.596
7.583
7.578
7.572
7.569
7.566
7.563
7.554
7.507
7.506
7.493
7.491
7.468
7.466
7.453
7.451
7.253
7.237
4.310
2.345
1H NMR (500 MHz, CD3CN)
Ph
N−Me
N=N
Me
9
2.06
2.08
5.08
1.06
1.11
2.07
3.00
3.00
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
δ (ppm)


164.784
147.044
145.776
142.495
136.035
135.364
133.983
131.223
130.543
129.767
129.481
129.096
127.889
122.909
121.121
117.896
42.178
20.673
13C NMR (126 MHz, CD3CN)
Ph
N−Me
N=N
Me
9
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)