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SUPPLEMENTARY INFORMATION

Diastereoselective intramolecular cyclization/Povarov reaction cascade for the one-pot synthesis of polycyclic quinolines

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General methods

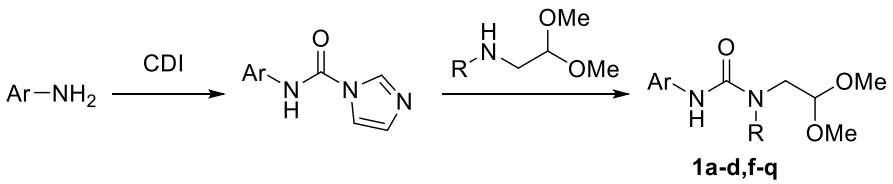
^{1}H spectra were recorded on a Bruker MSL 400 (400 MHz), Bruker Avance 500 (500 MHz) or Bruker Avance 600 (600 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker Avance 600 (151 MHz), Bruker Avance 500 (126 MHz) or Bruker MSL 400 (100 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference (proton, $CDCl_3$ δ 7.28, $(CD_3)_2SO$ δ 2.50; carbon, $CDCl_3$ δ 77.7, $(CD_3)_2SO$ δ 40.0). ^{31}P spectra were recorded on a Bruker MSL 400 (162 MHz) spectrometer using 85% H_3PO_4 as an external reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), td (triplet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). The IR spectra were recorded on a Vector 22 Fourier spectrometer by Bruker in the range of 400-4000 cm^{-1}. Crystalline samples were studied as a suspension in vaseline oil. The melting points were determined in glass capillaries on a Stuart SMP 10 instrument. Elemental analysis of the compounds was carried out on a high-temperature 2-reactor C, H, Nanalyzer of EuroVector brand EA 3000. The halogen content was determined by the Schöniger method. MALDI-TOF mass spectra were recorded on a Bruker ULTRAFLEX III TOF/TOF instrument (with 2,5-dihydroxybenzoic acid matrix). All commercially available reagents were used as received for the reactions without any purification. All solvents were purified and dried according to standard procedures.

Synthesis of starting compounds

Synthesis of ureas 1

The ureas **1a-d,f-q** were obtained as described below. The urea **1e** was not isolated and the final compound ***endo*-2h** was obtained in one-pot manner directly from *p*-isopropylaniline and 2,2-dimethoxy-*N*-methylethan-1-amine (see page S13). The urea **1j** was obtained as described on page S7.

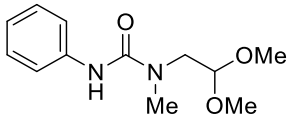
General method for synthesis of ureas 1a-d,f-q



1a-d,f-q

To a 25 mL flask a substituted aniline (5.4 mmol, 1.0 equiv.), chloroform (10 mL) and CDI (6.5 mmol, 1.2 equiv.) were added. The reaction mixture was allowed to stir at room temperature for 10 h. Then, 2,2-dimethoxy-*N*-methylethan-1-amine (0.94 g, 5.4 mmol, 1.0 equiv.) or 2,2-dimethoxyethan-1-amine (0.57 g, 5.4 mmol, 1.0 equiv.) was added and the reaction mixture was refluxed for 10 h. The mixture was subsequently cooled to room temperature, and distilled water (10 mL) was added. The mixture was transferred to a separatory funnel and the organic layer was separated. The aqueous layer was washed with chloroform (3 x 10 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude compound **1** as an off-white solid, which was used in next steps without further purification.

1-(2,2-dimethoxyethyl)-1-methyl-3-phenylurea (1a)[1]

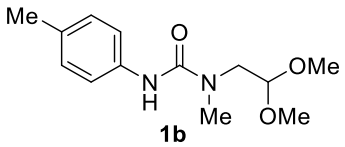


1a

1.701 g, yield 65%, white solid, mp 66-68 °C; ^{1}H NMR (400 MHz, $CHCl_3$) δ 3.06 (s, 3H, CH_3), 3.46 (d, 2H, *J* = 5.0 Hz, CH_2), 3.53 (s, 6H, CH_3), 4.51 (t, 1H, *J* = 5.0 Hz, CH), 6.99-7.04 (m, 1H, ArH), 7.26-7.32 (m, 2H, ArH), 7.32-

7.37 (m, 2H, ArH), 7.61 (br s, 1H, NH). ^{13}C NMR (151 MHz, $CHCl_3$) δ 36.56, 53.25, 55.98, 104.85, 119.90, 122.95, 129.29, 140.21, 157.17. MS (EI) *m/z* calcd for 238.3; found 261.5 $[M+Na]^+$.

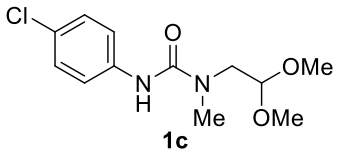
1-(2,2-Dimethoxyethyl)-1-methyl-3-(*p*-tolyl)urea (1b)[2]



1b

2.498 g, yield 90%, white solid, mp 65-69 °C; ^{1}H NMR (400 MHz, $CHCl_3$) δ 2.29 (s, 3H, CH_3), 3.03 (s, 3H, CH_3), 3.43 (d, 2H, *J* = 5.0 Hz, CH_2), 3.50 (s, 6H, CH_3), 4.48 (t, 1H, *J* = 5.0 Hz, CH), 7.07 (d, 2H, *J* = 8.0 Hz, ArH), 7.22 (d, 2H, *J* = 8.2 Hz, ArH), 7.47 (br s, 1H, NH); ^{13}C NMR (151 MHz, $CHCl_3$) δ 20.72, 36.06, 52.75, 55.45, 104.39, 119.55, 129.30, 131.92, 137.07, 156.76. MS (EI) *m/z* calcd for 252.3; found 273.1 $[M+Na]^+$, found 291.1 $[M+K]^+$.

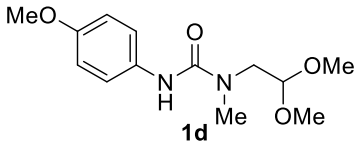
3-(4-Chlorophenyl)-1-(2,2-dimethoxyethyl)-1-methylurea (1c)[2]



1c

2.730 g, yield 91%, white solid, mp 68-72 °C; ^{1}H NMR (400 MHz, $CHCl_3$,) δ 3.03 (s, 3H, CH_3), 3.43 (d, 2H, *J* = 5.0 Hz, CH_2), 3.51 (s, 6H, CH_3), 4.48 (t, 1H, *J* = 5.0 Hz, CH), 7.20-7.24 (m, 2H, ArH), 7.25-7.30 (m, 2H, ArH), 7.69 (br s, 1H, NH); ^{13}C NMR (151 MHz, $CHCl_3$) δ 35.55, 52.29, 55.04, 103.81, 119.95, 126.72, 128.20, 137.83, 155.97. MS (EI) *m/z* calcd for 272.7; found 273.4 $[M+H]^+$.

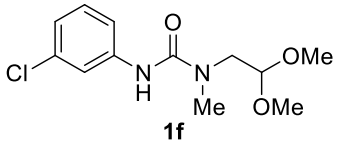
1-(2,2-Dimethoxyethyl)-3-(4-methoxyphenyl)-1-methylurea (1d)[2]



1d

2.833 g, yield 96%, white solid, mp 50-54 °C; ^{1}H NMR (400 MHz, $CHCl_3$) δ 3.00 (s, 3H, CH_3), 3.40 (d, 2H, *J* = 5.0 Hz, CH_2), 3.47 (s, 6H, CH_3), 3.75 (s, 3H, CH_3), 4.46 (t, 1H, *J* = 5.0 Hz, CH), 6.80 (d, 2H, *J* = 9.0 Hz, ArH), 7.21 (d, 2H, *J* = 8.9 Hz, ArH), 7.36 (br s, 1H, NH); ^{13}C NMR (151 MHz, $CHCl_3$) δ 36.05, 52.61, 55.38, 55.51, 104.34, 114.08, 121.53, 132.78, 155.42, 157.00. MS (EI) *m/z* calcd for 268.3; found 268.9 $[M]^+$, found 306.9 $[M+K]^+$.

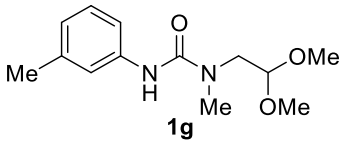
3-(3-Chlorophenyl)-1-(2,2-dimethoxyethyl)-1-methylurea (1f)[2]



1f

2.393 g, yield 80%, white solid, mp 85-89 °C; ^{1}H NMR (400 MHz, $CHCl_3$, δ ppm) 3.03 (s, 3H, CH_3), 3.42 (d, 2H, *J* = 5.0 Hz, CH_2), 3.31 (s, 6H, CH_3), 4.48 (t, 1H, *J* = 4.9 Hz, CH), 6.93–6.98 (m, 1H, ArH), 7.147.21 (m, 2H, ArH), 7.43 (s, 1H, ArH), 7.75 (br s, 1H, NH); ^{13}C NMR (151 MHz, $CHCl_3$, δ ppm) 36.09, 52.82, 55.59, 104.31, 117.24, 119.28, 122.36, 129.73, 134.42, 140.99, 156.37. MS (EI) *m/z* calcd for 272.7; found 272.0 $[M]^+$, found 295.0 $[M+Na]^+$.

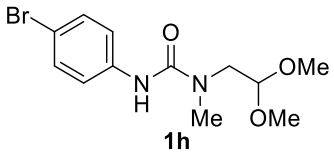
1-(2,2-Dimethoxyethyl)-1-methyl-3-(*m*-tolyl)urea (1g)[2]



1g

2.198 g, yield 79%, white solid, mp 71-75 °C; ^{1}H NMR (400 MHz, $CHCl_3$) δ 2.32 (s, 3H, CH_3), 3.03 (s, 3H, CH_3), 3.43 (d, 2H, *J* = 4.7 Hz, CH_2), 3.50 (s, 6H, CH_3), 4.48 (t, 1H, *J* = 4.7 Hz, CH), 6.81 (d, 1H, *J* = 7.4 Hz, ArH), 7.02-7.11 (m, 1H, ArH), 7.12-7.17 (m, 1H, ArH), 7.21 (s, 1H, ArH), 7.53 (br s, 1H, NH); ^{13}C NMR (151 MHz, $CHCl_3$) δ 21.50, 36.05, 52.76, 55.47, 104.37, 116.46, 120.10, 123.30, 128.60, 138.60, 139.58, 156.67. MS (EI) *m/z* calcd for 252.3; found 253.1 $[M+H]^+$, found 275.1 $[M+Na]^+$.

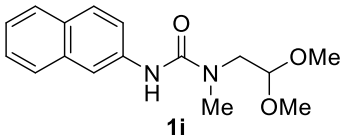
3-(4-Bromophenyl)-1-(2,2-dimethoxyethyl)-1-methylurea (1h)



1h

2.426 g, 45% yield, white solid, mp 61-65 °C; IR 1591, 1644, 2836, 2919. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.99 (s, 3H, CH_3), 3.31 (s, 6H, OCH_3), 3.40 (d, 2H, *J* = 5.3 Hz, CH_2), 4.50 (t, 1H, *J* = 5.3 Hz, CH), 7.37-7.42 (m, 2H, ArH), 7.44-7.47 (m, 2H, ArH), 8.39 (br s, 1H, NH). ^{13}C NMR (151 MHz, DMSO-d_6) δ 36.31, 50.55, 54.29, 103.15, 113.65, 122.03, 131.45, 140.46, 155.75. Anal. Calcd for $C_{12}H_{17}BrN_2O_3$: C, 45.44; H, 5.40; Br, 25.19; N, 8.83. Found: C, 45.54; H, 5.35; Br, 25.28; N, 8.76. MS (EI) *m/z* calcd for 317.1; found 317.1 $[M]^+$.

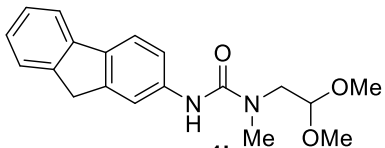
1-(2,2-Dimethoxyethyl)-1-methyl-3-(naphthalen-2-yl)urea (1i)



1i

2.462 g, 61% yield, white solid, mp 61-65 °C; IR 1544, 1642, 2831, 2940. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.07 (s, 3H, CH_3), 3.49 (d, 2H, *J* = 5.0 Hz, CH_2), 3.53 (s, 6H, OCH_3), 4.51 (t, 1H, *J* = 5.0 Hz, CH), 7.31-7.43 (m, 3H, ArH), 7.71-7.76 (m, 3H, ArH), 7.84 (br s, 1H, NH), 7.93 (s, 1H, ArH). ^{13}C NMR (151 MHz, $CDCl_3$) δ 36.64, 53.32, 56.06, 104.90, 115.65, 120.85, 124.65, 126.73, 127.80, 128.03, 128.97, 130.39, 134.71, 137.82, 157.27. Anal. Calcd for $C_{16}H_{20}N_2O_3$: C, 66.65; H, 6.99; N, 9.72. Found: C, 66.46; H, 7.15; N, 9.95. MS (EI) *m/z* calcd for 288.3; found 311.3 $[M+Na]^+$.

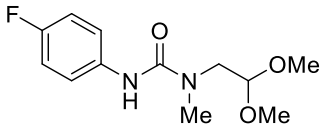
1-(2,2-Dimethoxyethyl)-3-(9*H*-fluoren-2-yl)-1-methylurea (1k)



1j

718 mg, 40% yield, yellow oil; IR 1560, 1641, 2854, 2962. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.07 (s, 3H, CH_3), 3.47 (d, 2H, *J* = 5.0 Hz, CH_2), 3.52 (s, 6H, CH_3), 3.86 (s, 2H, CH_2), 4.51 (t, 1H, *J* = 5.0 Hz, CH), 7.19-7.28 (m, 2H, ArH), 7.35 (t, 1H, *J* = 7.5 Hz, ArH), 7.51 (d, 1H, *J* = 7.4 Hz, ArH), 7.64-7.72 (m, 3H, ArH), 7.79 (br s, 1H, NH). ^{13}C NMR (151 MHz, $CDCl_3$) δ 36.13, 37.00, 52.80, 55.52, 104.36, 116.47, 118.29, 119.25, 120.00, 121.65, 124.90, 125.88, 126.68, 136.51, 138.59, 143.01, 144.32, 156.87. Anal. Calcd for $C_{19}H_{22}N_2O_3$: C, 69.92; H, 6.79; N, 8.58. Found: C, 69.95; H, 6.84; N, 8.44. MS (EI) *m/z* calcd for 326.4; found 327.8 $[M+H]^+$.

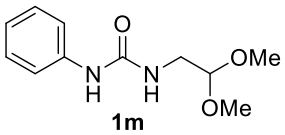
1-(2,2-Dimethoxyethyl)-3-(4-fluorophenyl)-1-methylurea (1l)



1k

1.528 g, 67% yield, dark crystalline solid, mp 125 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.03 (s, 3H, CH_3), 3.44 (d, 2H, *J* = 5.0 Hz, CH_2), 3.50 (s, 6H, CH_3), 4.48 (t, 1H, *J* = 5.0 Hz, CH), 6.92-6.97 (m, 2H, ArH), 7.23-7.27 (m, 2H, ArH), 7.62 (br s, 1H, NH). ^{13}C NMR (151 MHz, $CDCl_3$) δ 36.11, 52.74, 55.51, 104.34, 115.36 (d, *J* = 11.0 Hz), 120.79, 121.39, 135.58, 156.98, 158.60 (d, *J* = 241.0 Hz). Anal. Calcd for $C_{12}H_{17}FN_2O_3$: C, 56.24; H, 6.69; N, 10.93. Found: C, 56.35; H, 6.54; N, 11.05. MS (EI) *m/z* calcd for 256.3; found 295.1 $[M+K]^+$.

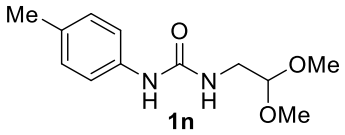
1-(2,2-Dimethoxyethyl)-3-phenylurea (1m)[3]



1m

2.020 g, yield 82%, white solid, mp 66-70 °C; ^{1}H NMR (400 MHz, $CHCl_3$) δ 3.41-3.45 (m, 2H, CH_2), 3.43 (s, 6H, CH_3), 4.44 (t, 1H, *J* = 5.1 Hz, CH), 5.37 (s, 1H, NH), 7.02-7.10 (m, 2H, ArH), 7.30 (s, 1H, NH), 7.30-7.33 (m, 3H, ArH). ^{13}C NMR (126 MHz, $CDCl_3$) δ 41.86, 54.54, 103.58, 120.25, 123.19, 129.04, 138.92, 156.45. MS (EI) *m/z* calcd for 224.2; found 247.4 $[M+Na]^+$.

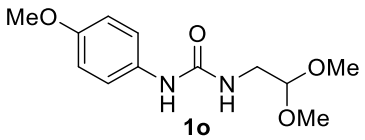
1-(2,2-Dimethoxyethyl)-3-(*p*-tolyl)urea (1n)[4]



1n

2.359 g, yield 90%, white solid, mp 69-73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H, CH_3), 3.38 (s, 6H, CH_3), 3.34-3.40 (m, 2H, CH_2), 4.39 (t, 1H, *J* = 5.2 Hz, CH), 5.52 (br s, 1H, NH), 7.06 (d, 2H, *J* = 8.2 Hz, ArH), 7.15 (br s, 1H, NH), 7.16 (d, 2H, *J* = 8.4 Hz, ArH). ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.27, 42.41, 55.06, 104.10, 121.59, 130.20, 133.74, 136.59, 157.02. MS (EI) *m/z* calcd for 238.3; found 239.5 $[M+H]^+$, found 261.2 $[M+Na]^+$.

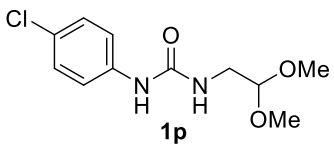
1-(2,2-Dimethoxyethyl)-3-(4-methoxyphenyl)urea (1o)[2]



1o

2.713 g, yield 97%, white solid, mp 68-72 °C; ^{1}H NMR (400 MHz, $CHCl_3$) δ 3.39 (s, 6H, CH_3), 3.32-3.44 (m, 2H, CH_2), 3.77 (s, 3H, CH_3), 4.40 (t, 1H, *J* = 5.0 Hz, CH), 5.44 (br s, 1H, NH), 6.82 (d, 2H, *J* = 9.0 Hz, ArH), 7.08 (br s, 1H, NH), 7.19 (d, 2H, *J* = 9.1 Hz, ArH); ^{13}C NMR (151 MHz, $CHCl_3$) δ 41.90, 54.53, 55.51, 103.56, 114.45, 123.49, 131.47, 156.43, 156.83. MS (EI) *m/z* calcd for 254.3; found 277.5 $[M+Na]^+$.

1-(4-Chlorophenyl)-3-(2,2-dimethoxyethyl)urea (1p)[2]

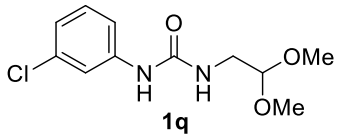


1p

2.703 g, 95% yield, white crystalline solid, mp 73-77 °C; ^{1}H NMR (400 MHz, $CHCl_3$) δ 3.41 (s, 6H, CH_3), 3.36-3.45 (m, 2H, CH_2), 4.40 (t, 1H, *J* = 4.7 Hz, CH), 5.68 (br s, 1H, NH), 7.17-7.25 (m, 4H, ArH), 7.48 (br s, 1H, NH); ^{13}C

NMR (151 MHz, $CHCl_3$) δ 41.87, 54.73, 103.69, 121.24, 128.18, 128.98, 137.52, 156.12. MS (EI) *m/z* calcd for 258.7; found 259.0 $[M+H]^+$.

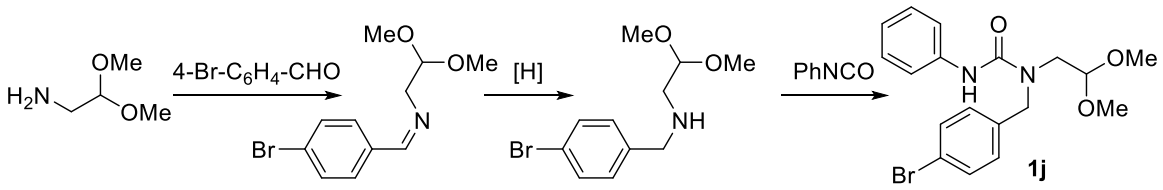
1-(3-Chlorophenyl)-3-(2,2-dimethoxyethyl)urea (1q)[2]



1q

2.333 g, yield 82%, white solid, mp 60-65 °C; ^{1}H NMR (400 MHz, $CHCl_3$) δ 3.42 (s, 6H, CH_3), 3.37-3.46 (m, 2H, CH_2), 4.41 (t, 1H, *J* = 4.9 Hz, CH), 5.77 (br s, 1H, NH), 6.96 (d, 1H, *J* = 7.4 Hz, ArH), 7.10–7.19 (m, 2H, ArH), 7.39 (s, 1H, ArH), 7.65 (br s, 1H, NH); ^{13}C-NMR (151 MHz, $CHCl_3$, δ ppm) 41.86, 54.69, 103.66, 117.59, 119.62, 122.84, 129.92, 134.56, 140.37, 155.98. MS (EI) *m/z* calcd for 258.7; found 281.2 $[M+Na]^+$.

Synthesis of 1-(4-bromobenzyl)-1-(2,2-dimethoxyethyl)-3-phenylurea (1j)

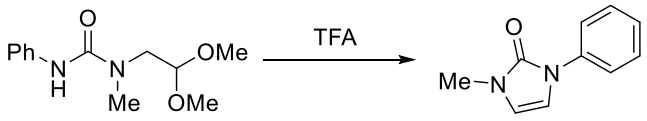


1j

A 4-bromobenzaldehyde (3.5 g, 19 mmol, 1.0 equiv.), 2,2-dimethoxyethan-1-amine (2.0 g, 19 mmol, 1.0 equiv.) and DCM (10 mL) were placed in 25 mL flask. The reaction mixture was allowed to stir at room temperature for 10 h and then cooled to 0°C. $NaBH_4$ (1.0 g, 28.5 mmol, 1.5 eqiuv.) was added slowly. The mixture was subsequently warmed to room temperature and allowed to stir for 4 h. An ice-cold distilled water was added and the organic layer was separated. The aqueous layer was extracted with DCM (3 x 10 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The yellowish gummy residue was dissolved in benzene (10 mL) and a phenylisocyanate (2.30 g, 19 mmol, 1.0 equiv.) was added slowly at room temperature. The mixture was allowed to stir for 6 h, the volatiles were removed in vacuum to give the crude **1j** as white solid (3.964 g, 72% yield), which was used without further purification.

Mp 110 °C; IR 1538, 1653, 2946, 3308. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.41 (d, 2H, *J* = 5.0 Hz, CH_2), 3.45 (s, 6H, OCH_3), 4.27 (t, 1H, *J* = 4.9 Hz, CH), 4.58 (s, 2H, CH_2), 7.03 (t, 1H, *J* = 7.3 Hz, ArH), 7.23 (d, 2H, *J* = 8.4 Hz, ArH), 7.27-7.32 (m, 2H, ArH), 7.36-7.39 (m, 2H, ArH), 7.48 (d, 2H, *J* = 8.4 Hz, ArH), 8.07 (br s, 1H, NH). ^{13}C NMR (151 MHz, $CDCl_3$) δ 50.77, 51.04, 55.56, 104.64, 119.37, 121.36, 122.59, 128.82, 129.74, 131.73, 137.23, 139.57, 156.80. Anal. Calcd for $C_{18}H_{21}BrN_2O_3$: C, 45.44; H, 5.40; Br, 25.19; N, 8.83. Found: C, 45.55; H, 5.36; Br, 25.12; N, 9.14. MS (EI) *m/z* calcd for for 393.3; found 417.0 $[M+Na]^+$.

Synthesis of imidazolin-2-one 3a

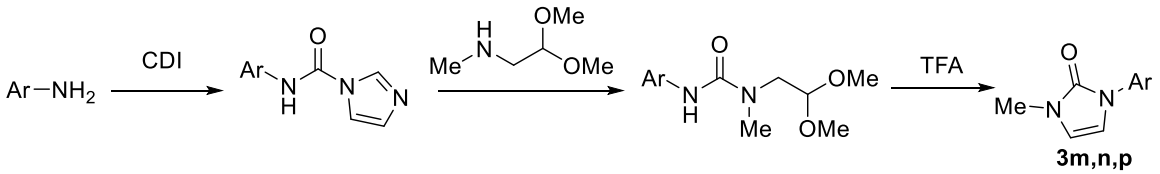


1a **3a**

To a 25 mL flask a urea **1a** (0.50 g, 2.1 mmol, 1.0 equiv.), chloroform (10 mL) and TFA (0.28 mL, 0.353 g, 3.1 mmol, 1.5 equiv.) was added. The reaction mixture was allowed to stir at room temperature for 6 h and concentrated under reduced pressure. To the resulting yellow oily residue distilled water (15 mL) and Na_2CO_3 (0.45 g, 4.2 mmol, 2 equiv.) was added. The precipitate was filtered off and dried under reduced pressure to give the compound **3a** as yellowish solid (329 mg, yield 90%), which was used without further purification.

Mp 103-107 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.20 (s, 3H, CH_3), 6.69 (d, 1H, *J* = 3.0 Hz, CH), 6.97 (d, 1H, *J* = 3.1 Hz, CH), 7.18-7.24 (m, 1H, ArH), 7.38-7.44 (m, 2H, ArH), 7.66-7.35 (m, 2H, ArH). ^{13}C NMR (151 MHz, DMSO-d_6) δ 30.34, 109.14, 113.99, 114.06, 116.93, 120.99, 125.49, 129.40, 137.93, 151.86. Anal. Calcd for $C_{10}H_{10}N_2O$: C, 68.95; H, 5.79; N, 16.08. Found: C, 68.80; H, 5.63; N, 16.13. MS (EI) *m/z* calcd for 174.2; found 175.1 $[M+H]^+$, 197.5 $[M+Na]^+$.

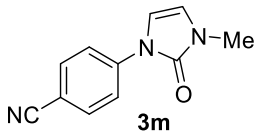
Synthesis of imidazolin-2-ones 3m,n,p



3m,n,p

To a 25 mL flask a substituted aniline (5.4 mmol, 1.0 equiv.), chloroform (10 mL) and CDI (6.5 mmol, 1.2 equiv.) were added. The reaction mixture was allowed to stir at room temperature for 10 h. Then, 2,2-dimethoxy-*N*-methylethan-1-amine (0.94 g, 5.4 mmol, 1.0 equiv.) was added and the reaction mixture was refluxed for 10 h. The mixture was subsequently cooled to room temperature, and distilled water (10 mL) was added. The mixture was transferred to a separatory funnel and the organic layer was separated. The aqueous layer was washed with chloroform (3 x 10 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was dissolved in ethanol (10 mL) and the concentrated hydrochloric acid (39% wt., 2 mL) was added. The reaction mixture was allowed to stir at room temperature for 3 h and then concentrated under reduced pressure to give target compound **3**, which was used without further purification.

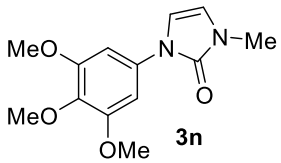
4-(3-Methyl-2-oxo-2,3-dihydro-1*H*-imidazol-1-yl)benzonitrile (3m)



3m

468 mg, 28% yield, white solid, mp 168-172 °C; IR 1620, 1692, 2891, 2978. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.32 (s, 3H, CH_3), 6.40 (d, 1H, *J* = 3.2 Hz, CH), 6.63 (d, 1H, *J* = 3.2 Hz, CH), 7.68-7.71 (m, 2H, ArH), 7.81-7.84 (m, 2H, ArH). ^{13}C NMR (151 MHz, $CDCl_3$) δ 30.38, 107.53, 108.35, 114.06, 118.38, 120.42, 133.13, 140.95, 151.64. Anal. Calcd for $C_{11}H_9N_3O$: C, 66.32; H, 4.55; N, 21.09. Found: C, 66.25; H, 4.72; N, 21.15. MS (EI) *m/z* calcd for 199.2; found 238.5 $[M+K]^+$.

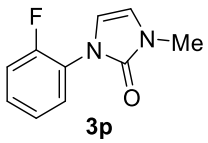
1-Methyl-3-(3,4,5-trimethoxyphenyl)-1,3-dihydro-2*H*-imidazol-2-one (3n)



3n

910 mg, 63% yield, white solid, mp 144-148 °C; IR 1510, 1706, 2874, 2950. ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.19 (s, 3H, CH_3), 3.66 (s, 3H, OCH_3), 3.79 (s, 6H, OCH_3), 6.71 (d, 1H, *J* = 3.1 Hz, CH), 7.02 (s, 2H, ArH), 7.04 (d, 1H, *J* = 3.1 Hz, CH). ^{13}C NMR (151 MHz, DMSO-d_6) δ 30.92, 57.00, 61.09, 99.68, 110.16, 114.20, 134.41, 135.94, 152.33, 153.97. Anal. Calcd for $C_{13}H_{16}N_2O_4$: C, 59.08; H, 6.10; N, 10.60. Found: C, 59.19; H, 6.18; N, 10.74. MS (EI) *m/z* calcd for 264.3; found 265.7 $[M+H]^+$.

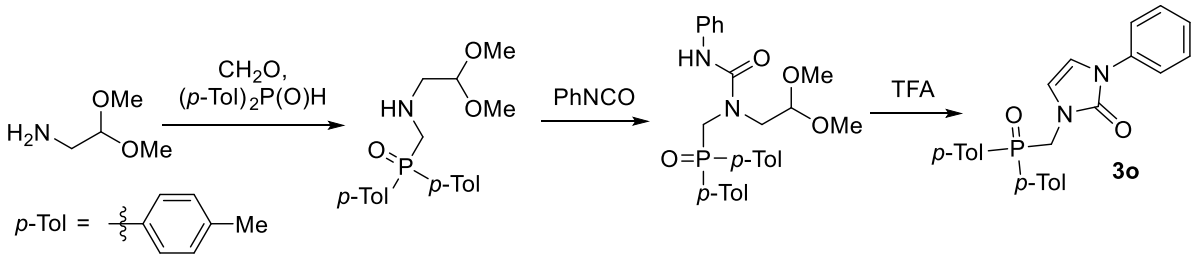
1-(2-Fluorophenyl)-3-methyl-1,3-dihydro-2*H*-imidazol-2-one (3p)



3p

325 mg, 65% yield, brown oil; IR 1318, 1470, 1682, 2881, 2985. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.42 (s, 3H, CH_3), 6.45 (d, 1H, *J* = 2.9 Hz, CH), 6.55 (d, 1H, *J* = 2.4 Hz, CH), 7.19-7.25 (m, 2H, ArH), 7.35-7.39 (m, 1H, ArH), 7.49-7.53 (m, 1H, ArH). ^{13}C NMR (151 MHz, $CDCl_3$) δ 31.26, 112.83, 113.59, 116.95 (d, *J* = 19.6 Hz), 123.31, 124.79, 124.87 (*J* = 4.1 Hz), 128.04, 130.08 (d, *J* = 7.7 Hz), 156.74 (d, *J* = 251.9 Hz). Anal. Calcd for $C_{10}H_9FN_2O$: C, 62.49; H, 4.72; N, 14.58. Found: C, 62.53; H, 4.82; N, 14.50. MS (EI) *m/z* calcd for 192.2; found 215.7 $[M+Na]^+$.

Synthesis of imidazolin-2-one 3o



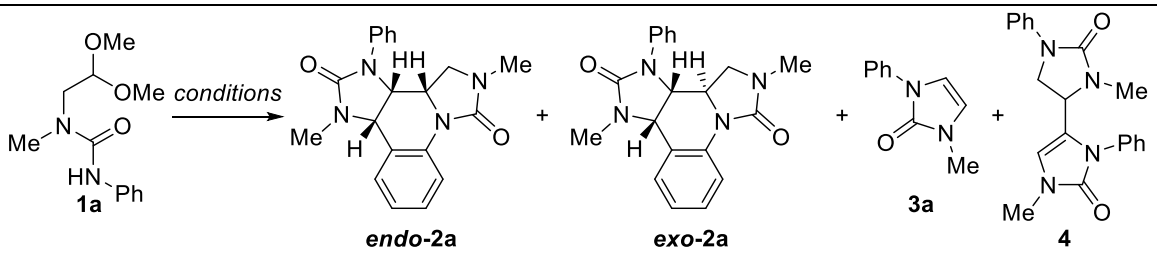
To a 100 mL flask a 2,2-dimethoxyethan-1-amine (1.0 g, 9.5 mmol, 1.0 equiv.), di-*p*-tolylphosphine oxide (1.0 g, 9.5 mmol, 1.0 eqiuiv.), parafom (0.3 g, 9.5 mmol, 1.0 equiv.), *p*-toluenesulfonic acid (0.082 g, 0.475 mmol, 0.05 equiv.) and benzene (30 mL) were added. The mixture was refluxed with Dean-Stark apparatus for 14 h, allowed to cool to room temperature and washed with saturated $NaHCO_3$ solution (3 x 10 mL). The organic layer was separated, dried over $MgSO_4$ and concentrated under reduced pressure. The resulting yellow oil was dissolved in benzene (10 mL), a phenylisocyanate (1.10 g, 9.5 mmol, 1.0 equiv.) was added and the reaction mixture was allowed to stir at room temperature for 10 h. Then, a TFA (1.09 mL, 1.62 g, 14.25 mmol, 1.5 equiv.) was added and the reaction mixture was allowed to stir at room temperature for additional 6 h. The volatiles were removed in vacuum to give the crude compound **3d** as brown oil (2.49 g, 65% yield), which was used without further purification.

IR 1120, 1554, 1673, 2958, 3023. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 6H, CH_3), 4.73 (d, 2H, *J* = 5.4 Hz, CH_2), 6.55 (d, 1H, *J* = 2.2 Hz, CH), 6.89 (d, 1H, *J* = 3.1 Hz, CH), 7.32-7.41 (m, 8H, ArH), 7.68-7.79 (m, 5H, ArH). ^{31}P NMR (161.5 MHz, $CDCl_3$) δ 35.04. ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.57, 43.06 (d, *J* = 76.2 Hz), 111.28, 112.63, 122.46, 129.91 (d, *J* = 12.8 Hz), 131.25 (d, *J* = 10.7 Hz), 136.37, 144.23, 151.43. ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.32. Anal. Calcd for $C_{24}H_{23}N_2O_2P$: C, 71.63; H, 5.76; N, 6.96; P, 7.70. Found: C, 71.77; H, 5.64; N, 7.03; P, 7.71. MS (EI) *m/z* calcd for 402.4; found 403.5 $[M+H]^+$.

Reaction conditions optimization

The reaction conditions were screened using various Lewis and Bronsted acid catalysts and solvents. $AlCl_3$ was found to completely unsuitable for this reaction (Table S1, entries 2,3). Boron trifluoride provided the desired compounds **2a** in 40% yield at the room temperature (Table S1, entry 9). However, the yield lowered to 6% upon refluxing the reaction mixture (Table S1, entry 8). Among the Bronsted acids, the triflic acid in refluxing *o*-xylene performed the best, providing the desired octahydro-diimidazoquinolines ***endo*-2a** and ***exo*-2a** in 98% yield and 85 : 15 *dr* (Table S1, entry 7). Interestingly, lower reaction temperatures improved the *dr* up to 95 : 5. However, a lot of unidentified byproducts were formed and the yield dropped to 27% (Table S1, entry 6). The same *dr* was achieved when the acetic acid was used as solvent, albeit the yield was only 35% (Table S1, entry 14). Chiral (1*S*)-(+)-10-camphorsulfonic and (1*R*)-(−)-10-camphorsulfonic acids provided the octahydro-diimidazoquinolines ***endo*-2a** and ***exo*-2a** in low yields and almost identical *dr* (Table S1, entries 10,12).

Table S1. Reaction conditions optimization[a]



endo-2a *exo*-2a

№	catalyst	solvent	ratio (*endo*-2a+*exo*-2a) / 3a / 4, %[b]	*dr*[b] (*endo* : *exo*)
1	HCl(conc)	-	5 / 81 / 13	1 : 1
2	$AlCl_3$	toluene	0 / 0 / 0	-
3	$AlCl_3$	water	0 / 0 / 0	-
4	TFA	toluene	0 / 98/ 0	-
5	TFA	water	0 / 0 / 0	-
6	TfOH	toluene	27 / 0 / 0[c]	> 95 : 5
7	**TfOH**	***o*-xylene**	**98 / 0 / 0**	**85 : 15**
8	BF_3*Et_2O	toluene	6 / 53 / 40	67 : 33
9	BF_3*Et_2O	toluene[d]	40 / 0 / 0[c]	85 : 15
10	+CSA	toluene	6 / 75 / 18	84 : 16
11	+CSA	water	0 / 93 / 6	-
12	-CSA	toluene	6 / 75 / 18	85 : 15
13	-CSA	water	0 / 94 / 5	-
14	AcOH	-	35 / 47 / 17	> 95 : 5

*[a] Reaction conditions: urea **1a** (2.1 mmol), catalyst (10% mol.), solvent (5 mL), reflux, 10 h; [b] According to 1H NMR data; [c] A lot of unidentified products were observed; [d] Reaction was carried out at rt*

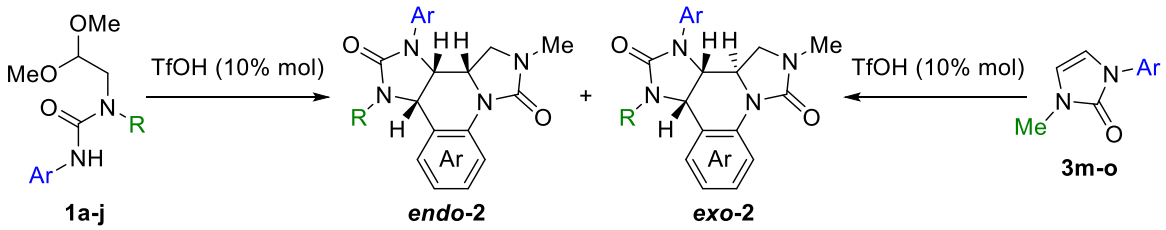
Isolation of the 4,4'-bi(imidazole-2-one) 4

Compound **4** was isolated from the reaction mixture (Table S1, entry 1) as follows. First, the solvent was removed in vacuum. The dark residue was thoroughly washed with cold acetone and the precipitate of ***exo*-2a** and ***endo*-2a** was filtered off. The filtrate was evaporated and washed multiple times with distilled water and diethyl ether to give **4** as white crystalline solid with 3% isolated yield. Alternative synthesis of this compound was achieved after multiple attempts starting from urea **1a** (see page S20).

Synthesis of octahydro-diimidazoquinolines 2

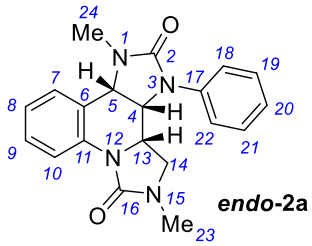
The compounds **2a-i,m-o** were obtained as described below. In case of compound ***endo*-2e**, the intermediate urea **1e** was not isolated and the reaction was carried in one-pot manner starting from *p*-isopropylaniline and 2,2-dimethoxy-*N*-methylethan-1-amine (see page S13). In case of ureas **1l** and **1k** the reaction resulted in imidazolinones **3l** and **3k**.

General method for synthesis of octahydro-diimidazoquinolines 2a-i,m-o



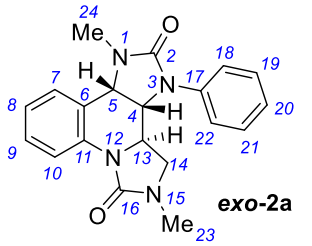
To a 10 mL flask a 1-(2,2-dimethoxyethyl)urea **1a-d,f-l** (2.1 mmol, 1.0 equiv.) or imidazolin-2-one **3m-p** (2.1 mmol, 1.0 equiv.), *o*-xylene (5 mL) and triflic acid (31.53 mg, 0.21 mmol, 0.1 equiv.) were added. The reaction mixture was refluxed for 10 h and cooled to room temperature. The volatiles were removed in vacuum. The resulting dark residue was washed with diethyl ether (2 x 10 mL) and recrystallized multiple times from dry acetone to give the compounds **2** as a pure *exo*- or *endo*-diastereomer.

(3a*R*,3b*R*,11b*R*)-1,5-Dimethyl-3-phenyl-1,3a,3b,4,5,11b-hexahydro-2*H*-diimidazo[1,5-a:4',5'-c]quinoline-2,6(3*H*)-dione (*endo*-2a)



259 mg, 74% yield, white solid, mp 124-128 °C; IR 1492, 1701, 2889, 2929. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.459 (s, 3H, H^{24}), 2.509 (s, 3H, H^{23}), 2.758 (dd, *J* = 8.8 Hz, *J* = 9.1 Hz, 1H, H^{14} (*trans* to H^{13})), 3.278 (dd, *J* = 8.8 Hz, *J* = 9.0 Hz, 1H, H^{14} (*cis* to H^{13}), 3.985 (dd, *J* = 4.3 Hz, *J* = 9.1 Hz, 1H, H^{13}), 4.890 (d, *J* = 9.5 Hz, 1H, H^{5}), 5.277 (dd, *J* = 4.3 Hz, *J* = 9.5 Hz, 1H, H^{4}), 7.106 (t, *J* = 7.6 Hz 1H, H^{8}), 7.136 (m, 1H, H^{20}), 7.362 (t, *J* = 7.6 Hz 1H, H^{9}), 7.434 (d, *J* = 7.5 Hz, 2H, H$^{19/21}$), 7.440 (td, *J* = 1.4 Hz, *J* = 7.6 Hz, 1H, H^{7}), 7.554 (d, *J* = 7.7 Hz, 2H, H$^{18/22}$), 7.982 (dd, *J* = 1.4 Hz, *J* = 7.6 Hz, 1H, H^{10}). ^{13}C NMR (126 MHz, DMSO-d_6) δ 28.3 (C^{23}), 30.1 (C^{24}), 45.6 (C^{14}), 54.8 (C^{13}), 55.5 (C^{5}), 56.2 (C^{4}), 117.8 (C^{10}), 120.4 (C$^{18/22}$), 122.2 (C^{8}), 123.5 (C^{20}), 123.6 (C^{6}), 128.7 (C$^{19/21}$), 128.8 (C^{9}), 130.5 (C^{7}), 139.3 (C^{11}), 140.6 (C^{17}), 156.2 (C^{16}), 157.6 (C^{2}). ^{15}N NMR (51 MHz, DMSO-d_6) δ 102.6 (N^{12}), 102.0 (N^{3}), 87.1 (N^{1}), 77.5 (N^{15}). Anal. Calcd for $C_{20}H_{20}N_4O_2$: C, 68.95; H, 5.79; N, 16.08. Found: C, 68.86; H, 5.90; N, 15.86. MS (EI) *m/z* calcd for 348.4; found 349.6 [M+H]$^{+}$.

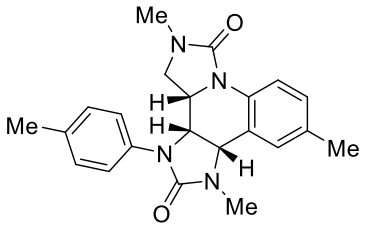
(3a*S*,3b*R*,11b*S*)-1,5-Dimethyl-3-phenyl-3,3a,4,5-tetrahydro-1*H*-diimidazo[1,5-a:4',5'-c]quinoline-2,6(3b*H*,11b*H*)-dione (*exo*-2a)



54 mg, 15% yield, white solid, mp 158-162 °C; IR 1492, 1702, 2876, 2913. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.590 (s, 3H, H^{23}), 2.785 (s, 3H, H^{24}), 2.863 (dd, *J* = 8.6 Hz, *J* = 8.8 Hz, 1H, H^{14} (*trans* to H^{13})), 2.892 (dd, *J* = 8.6 Hz, *J* = 9.0 Hz, 1H, H^{14} (*cis* to H^{13})), 3.993 (m, *J* = 9.9 Hz, *J* = 8.9 Hz, 1H, H^{13}), 4.610 (d, *J* = 6.8 Hz, 1H, H^{5}), 4.782 (dd, *J* = 6.8 Hz, *J* = 9.9 Hz, 1H, H^{4}), 7.081 (td, *J* = 7.7 Hz, *J* = 1.2 Hz, 1H, H^{8}), 7.184 (t, *J* = 7.5 Hz, 1H, H^{20}), 7.372 (m, 1H, H^{9}), 7.389 (t, *J* = 7.5 Hz, 2H, H$^{19/21}$), 7.477 (td, *J* = 7.7 Hz, *J* = 1.4 Hz, 1H, H^{7}), 7.604 (d, *J* = 7.5 Hz, 2H, H$^{18/22}$), 8.328 (dd, *J* = 7.7 Hz, *J* = 1.4 Hz, 1H, H^{10}). ^{13}C NMR (126 MHz, DMSO-d_6) δ 29.3 (C^{23}), 30.4 (C^{24}), 48.1

(C^{14}), 51.0 (C^{13}), 54.5 (C^{4}), 55.5 (C^{5}), 117.1 (C^{10}), 119.0 (C^{6}), 121.3 (C^{8}), 122.7 ($C^{18/22}$), 124.6 (C^{20}), 128.8 ($C^{19/21}$), 129.0 (C^{9}), 131.5 (C^{7}), 136.9 (C^{11}), 138.5 (C^{17}), 156.1 (C^{16}), 157.2 (C^{2}). ^{15}N NMR (51 MHz, DMSO-d_6) δ 106.6 (N^{3}), 101.6 (N^{12}), 91.9 (N^{1}), 76.6 (N^{15}). Anal. Calcd for $C_{20}H_{20}N_4O_2$: C, 68.95; H, 5.79; N, 16.08. Found: C, 68.87; H, 5.88; N, 15.86. MS (EI) *m/z* calcd for 348.4; found 387.4 $[M+K]^+$.

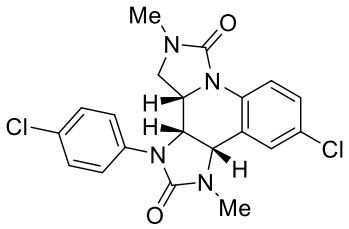
(3a*S*,3b*S*,11b*S*)-1,5,10-Trimethyl-3-(*p*-tolyl)-3,3a,4,5-tetrahydro-1*H*-diimidazo[1,5-a:4',5'-c]quinoline-2,6(3bH,11b*H*)-dione (*endo*-2b)



***endo*-2b**

79 mg, 20% yield, white solid, mp 176-180 °C; IR 1511, 1694, 2866, 2920. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.29 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 2.51 (s, 3H, CH_3), 2.71-2.77 (m, 1H, CH_2), 3.20-3.26 (m, 1H, CH_2), 3.90-3.96 (m, 1H, CH), 4.82 (d, 1H, *J* = 9.5 Hz, CH), 4.78 (dd, 1H, 1H, *J* = 9.5 Hz, *J* = 4.2 Hz, CH), 7.13-7.19 (m, 3H, ArH), 7.24 (s, 1H, ArH), 7.41 (d, 2H, *J* = 8.2 Hz, ArH), 7.84 (d, 1H, *J* = 8.3 Hz, ArH). ^{13}C NMR (126 MHz, DMSO-d_6) δ 20.86, 20.92, 28.87, 30.72, 46.10, 55.41, 56.11, 56.78, 118.24, 121.15, 123.99, 129.71, 129.79, 131.26, 131.72, 133.11, 137.26, 138.66, 156.86, 158.31. Anal. Calcd for $C_{22}H_{24}N_4O_2$: C, 70.19; H, 6.43; N, 14.88. Found: C, 70.30; H, 6.58; N, 14.88. MS (EI) *m/z* calcd for 376.5; found 399.5 $[M+Na]^+$.

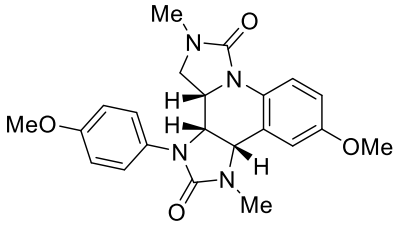
(3a*S*,3b*S*,11b*S*)-10-Chloro-3-(4-chlorophenyl)-1,5-dimethyl-3,3a,4,5-tetrahydro-1*H*-diimidazo[1,5-a:4',5'-c]quinoline-2,6(3b*H*,11b*H*)-dione (*endo*-2c)



***endo*-2c**

109 mg, 25% yield, white solid, mp 174-178 °C; IR 1595, 1713, 2880, 2958. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.49 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 2.71-2.79 (m, 1H, CH_2), 3.26-3.31 (m, 1H, CH_2), 3.95-4.03 (m, 1H, CH), 4.91 (d, 1H, *J* = 9.5 Hz, CH), 5.28 (dd, 1H, 1H, *J* = 9.5 Hz, *J* = 4.3 Hz, CH), 7.41-7.45 (m, 3H, ArH), 7.58-7.62 (m, 3H, ArH), 8.02 (d, 1H, *J* = 8.8 Hz, ArH). ^{13}C NMR (151 MHz, DMSO-d_6) δ 28.81, 30.68, 46.10, 55.33, 55.54, 56.53, 119.88, 122.27, 126.05, 126.49, 127.83, 129.11, 129.29, 130.52, 138.81, 139.91, 156.58, 157.79. Anal. Calcd for $C_{20}H_{18}Cl_2N_4O_2$: C, 57.57; H, 4.35; Cl, 16.99; N, 13.43. Found: C, 57.75; H, 4.64; Cl, 17.09; N, 13.26. MS (EI) *m/z* calcd for 417.3; found 439.1 $[M+Na]^+$.

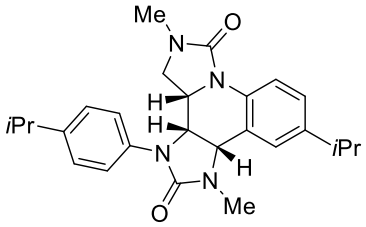
(3a*R*,3b*R*,11b*R*)-10-Methoxy-3-(4-methoxyphenyl)-1,5-dimethyl-1,3a,3b,4,5,11b-hexahydro-2*H*-diimidazo[1,5-a:4',5'-c]quinoline-2,6(3*H*)-dione (*endo*-2d)



***endo*-2d**

150 mg, 35% yield, white solid, mp 204-208 °C; IR 1508, 1692, 2838, 2934. ^{1}H NMR (600 MHz, DMSO-d_6) δ 2.47 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 2.68-2.74 (m, 1H, CH_2), 3.89-3.97 (m, 1H, CH_2), 4.54-4.58 (m, 1H, CH), 4.86 (d, 1H, *J* = 9.4 Hz, CH), 5.11 (dd, 1H, *J* = 9.7, *J* = 3.4 Hz, CH), 6.98-6.91 (m, 4H, ArH), 7.36 (d, 2H, *J* = 8.7 Hz, ArH), 7.82 (d, 1H, *J* = 8.9 Hz, ArH). ^{13}C NMR (151 MHz, DMSO-d_6) δ 29.06, 30.63, 45.73, 54.90, 55.75, 55.79, 55.93, 56.04, 57.41, 114.44, 114.66, 115.90, 119.94, 124.34, 125.40, 125.92, 132.55, 134.13, 154.86, 156.67, 156.85, 158.73. Anal. Calcd for $C_{22}H_{24}N_4O_4$: C, 64.69; H, 5.92; N, 13.72; O, 15.67. Found: C, 64.75; H, 6.08; N, 13.85; O, 15.32. MS (EI) *m/z* calcd for 408.4; found 408.2 $[M]^+$.

(3a*S*,3b*S*,11b*S*)-10-Isopropyl-3-(4-isopropylphenyl)-1,5-dimethyl-3,3a,4,5-tetrahydro-1*H*-diimidazo[1,5-a:4',5'-c]quinoline-2,6(3b*H*,11b*H*)-dione (*endo*-2e)

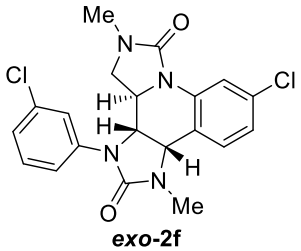


***endo*-2e**

To a 25 mL flask a *p*-isopropylaniline (0.32 g, 2.4 mmol, 1 equiv.) and DCM (10 mL) was added. Then, a CDI (0.42 g, 2.6 mmol, 1.08 equiv.) was slowly added and the reaction mixture was allowed to stir at room temperature for 10 h. Next, 2,2-dimethoxy-*N*-methylethan-1-amine (0.29 g, 2.4 mmol, 1 equiv.) was added dropwise and the reaction mixture was refluxed for 14 h. The solvent was removed under reduced pressure. The resulting white residue was dissolved in ethanol (15 mL) and concentrated hydrochloric acid (39% wt., 15 mL) was added. The reaction mixture was refluxed for 72 h. The dark brown precipitate was filtered off, washed with distilled water (3 x 15 mL) and recrystallized multiple times from anhydrous DMF to give the compound ***endo*-2e** (240 mg, 46% yield) as white solid.

Mp 180-184 °C; IR 1513, 1702, 2959, 3312. ^{1}H NMR (600 MHz, DMSO-d_6) δ 1.20-1.24 (m, 12H, CH_3), 2.46 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 2.71-2.76 (m, 1H, CH_2), 2.86-2.93 (m, 2H, CH), 3.23-3.29 (m, 1H, CH_2), 3.95-4.02 (m, 1H, CH), 4.87 (d, 1H, *J* = 9.4 Hz, CH), 5.16 (dd, 1H, 1H, *J* = 9.6 Hz, *J* = 3.8 Hz, CH), 7.20-7.27 (m, 3H, ArH), 7.29 (s, 1H, ArH), 7.40 (d, 2H, *J* = 8.5 Hz, ArH), 7.83 (d, 1H, *J* = 8.3 Hz, ArH). ^{13}C NMR (151 MHz, DMSO-d_6) δ 24.33, 24.36, 24.47, 24.54, 28.86, 30.54, 33.28, 33.36, 45.94, 54.90, 56.18, 57.14, 118.54, 121.83, 123.97, 126.94, 127.10, 128.55, 137.18, 138.86, 142.80, 144.50, 156.71, 158.46. Anal. Calcd for $C_{26}H_{32}N_4O_2$: C, 72.19; H, 7.46; N, 12.95. Found: C, 80.19; H, 7.68; N, 12.75. MS (EI) *m/z* calcd for 432.6; found 433.2 $[M+H]^+$.

(3a*S*,3b*S*,11b*R*)-9-Chloro-3-(3-chlorophenyl)-1,5-dimethyl-1,3a,3b,4,5,11b-hexahydro-2*H*-imidazo[4,5-c]pyrrolo[1,2-a]quinoline-2,6(3*H*)-dione (*exo*-2f)

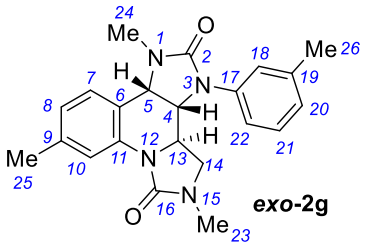


***exo*-2f**

114 mg, 26% yield, white solid, mp 144-148 °C; IR 1595, 1713, 2878, 2915. ^{1}H NMR (600 MHz, DMSO-d_6) δ 2.44 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 2.75-2.80 (m, 1H, CH_2), 3.31-3.32 (m, 1H, CH_2), 4.00-4.03 (m, 1H, CH), 4.92 (d, 1H, *J* = 9.4 Hz, CH), 5.30 (dd, *J* = 9.5, *J* = 4.5 Hz, 1H), 7.14-7.18 (m, 2H, ArH), 7.36-7.40 (m, 1H, ArH), 7.43-7.46 (m, 1H, ArH), 8.06 (d, 1H, *J* = 2.1 Hz, ArH), 7.82 (s, 1H, ArH), 8.07 (s, 1H, ArH). ^{13}C NMR (151 MHz, DMSO-d_6) δ 28.73, 30.68, 31.16, 46.19, 55.51, 56.37, 117.79, 118.54, 119.93, 122.58, 122.78, 123.54, 130.84, 132.73,

133.84, 134.10, 141.20, 142.49, 156.55, 157.71. Anal. Calcd for $C_{20}H_{18}Cl_2N_4O_2$: C, 57.57; H, 4.35; Cl, 16.99; N, 13.43. Found: C, 57.62; H, 4.15; Cl, 17.15; N, 13.26. MS (EI) *m/z* calcd for 417.3; found 440.7 $[M+Na]^+$.

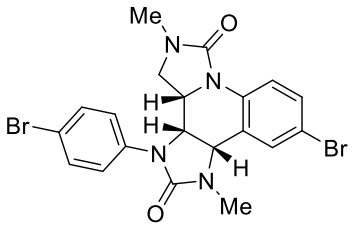
(3a*R*,3b*S*,11b*R*)-1,5,9-Trimethyl-3-(*m*-tolyl)-1,3a,3b,4,5,11b-hexahydro-2*H*-diimidazo[1,5-a:4',5'-c]quinoline-2,6(3*H*)-dione (*exo*-2g)



***exo*-2g**

162 mg, 41% yield, white solid, mp 134-138 °C; IR 1494, 1671, 2923, 3033. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.304 (s, 3H, H^{25}), 2.315 (s, 3H, H^{26}), 2.592 (s, 3H, H^{23}), 2.758 (s, 3H, H^{24}), 2.87 (dd, *J* = 8.9 Hz, *J* = 9.0 Hz, 1H, H^{14} (*tans* to H^{13})), 3.984 (dd, *J* = 8.5 Hz, *J* = 9.0 Hz, 1H, H^{14} (*cis* to H^{13})), 3.932 (dd, *J* = 9.0 Hz, *J* = 9.9 Hz, 1H, H^{13}), 4.545 (d, *J* = 6.8 Hz, 1H, H^5), 4.720 (dd, *J* = 6.8 Hz, *J* = 9.9 Hz, 1H, H^4), 6.901 (dd, *J* = 7.8 Hz, *J* = 1.5 Hz, 1H, H^8), 6.983 (d, *J* = 7.5 Hz, 1H, H^{20}), 7.258 (t, *J* = 7.5 Hz, 1H, H^{21}), 7.346 (d, *J* = 7.8 Hz 1H, H^7), 7.361 (d, *J* = 7.5 Hz, 1H, H^{22}), 7.454 (m, 1H, H^{18}), 8.158 (d, *J* = 1.4 Hz, 1H, H^{10}). ^{13}C NMR (126 MHz, DMSO-d_6) δ 21.1 (C^{26}), 21.2 (C^{25}), 29.2 (C^{24}), 30.4 (C^{23}), 48.0 (C^{14}), 51.1 (C^{13}), 54.6 (C^4), 54.9 (C^5), 116.3 (C^6), 117.4 (C^{10}), 119.8 (C^{22}), 122.2 (C^8), 123.3 (C^{18}), 125.2 (C^{20}), 128.6 (C^{21}), 131.3 (C^7), 136.8 (C^{11}), 138.1 (C^{19}), 138.4 (C^9), 138.4 (C^{17}), 156.1 (C^{16}), 157.1 (C^2). ^{15}N NMR (51 MHz, DMSO-d_6) δ 101.8 (N^{12}), 101.0 (N^3), 92.1 (N^1), 76.3 (N^{15}). Anal. Calcd for $C_{22}H_{24}N_4O_2$: C, 70.19; H, 6.43; N, 14.88. Found: C, 70.30; H, 6.58; N, 14.88. MS (EI) *m/z* calcd for 376.5; found 377.2 $[M+H]^+$.

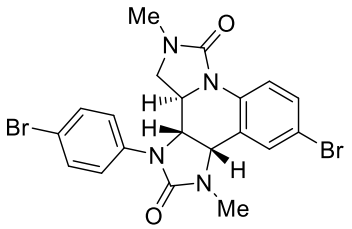
(3a*R*,3b*R*,11b*R*)-9-Bromo-3-(4-bromophenyl)-1,5-dimethyl-1,3a,3b,4,5,11b-hexahydro-2*H*-diimidazo[1,5-a:4',5'-c]quinoline-2,6(3*H*)-dione (*endo*-2h)



***endo*-2h**

202 mg, 38% yield, white solid, mp 127-131 °C; IR 1493, 1703, 2952, 3067. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.46 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 2.72-2.77 (m, 1H, CH_2), 3.30-3.33 (m, 1H, CH_2), 3.94-4.00 (m, 1H, CH), 4.90 (d, 1H, *J* = 9.4 Hz, CH), 5.27 (dd, 1H, *J* = 9.5, *J* = 4.4 Hz, CH), 7.53-7.55 (m, 4H, ArH), 7.55-7.57 (m, 1H, ArH), 7.70 (d, 1H, *J* = 2.4 Hz, ArH), 7.96 (d, 1H, *J* = 8.8 Hz, ArH). ^{13}C NMR (151 MHz, DMSO-d_6) δ 28.25, 30.16, 45.61, 54.81, 54.93, 55.93, 113.84, 115.26, 119.66, 121.88, 125.90, 131.48, 131.58, 131.67, 132.83, 138.77, 139.82, 156.03, 157.18. Anal. Calcd for $C_{20}H_{18}Br_2N_4O_2$: C, 47.46; H, 3.58; Br, 31.57; N, 11.07. Found: C, 47.55; H, 3.70; Br, 31.35; N, 11.05. MS (EI) *m/z* calcd for 506.2; found 529.3 $[M+Na]^+$.

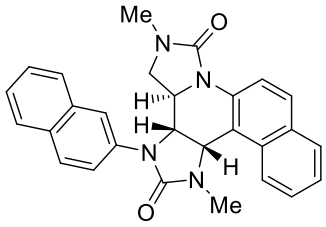
(3a*R*,3b*S*,11b*R*)-9-Bromo-3-(4-bromophenyl)-1,5-dimethyl-1,3a,3b,4,5,11b-hexahydro-2*H*-diimidazo[1,5-a:4',5'-c]quinoline-2,6(3*H*)-dione (*exo*-2h)



***exo*-2h**

111 mg, 21% yield, white solid, mp 126-129 °C; IR 1514, 1715, 2961, 3052. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.81 (s, 3H, CH_3), 2.86 (s, 3H, CH_3), 3.61-3.67 (m, 2H, CH_2), 4.09-4.14 (m, 1H, CH), 4.26 (d, 1H, *J* = 8.3 Hz, CH), 5.73 (d, 1H, *J* = 8.3 Hz, CH), 6.89 (d, 1H, *J* = 2.3 Hz, ArH), 7.29-7.34 (m, 2H, ArH), 7.52-7.59 (m, 3H, ArH), 7.76-7.80 (m, 1H, ArH). ^{13}C NMR (151 MHz, DMSO-d_6) δ 31.37, 33.06, 46.39, 53.04, 54.69, 59.43, 114.31, 117.83, 121.54, 127.14, 127.46, 131.81, 132.26, 132.65, 137.80, 138.58, 157.06, 159.44. Anal. Calcd for $C_{20}H_{18}Br_2N_4O_2$: C, 47.46; H, 3.58; Br, 31.57; N, 11.07. Found: C, 47.38; H, 3.72; Br, 31.22; N, 11.15. MS (EI) *m/z* calcd for 506.2; found 529.7 $[M+Na]^+$.

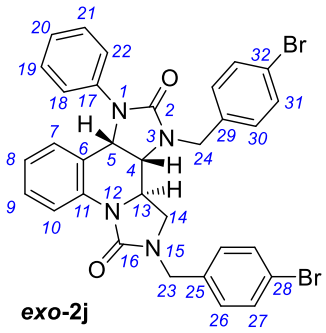
(3a*R*,3b*S*,13b*R*)-1,5-Dimethyl-3-(naphthalen-2-yl)-1,3a,3b,4,5,13b-hexahydro-2*H*-benzo[g]diimidazo[1,5-a:4',5'-c]quinoline-2,6(3*H*)-dione (*exo*-2i)



***exo*-2i**

113 mg, 51% yield, white solid, mp <250 °C; IR 1474, 1691, 2874, 2992. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.61 (s, 3H, CH_3), 2.66 (s, 3H, CH_3), 2.98-3.04 (m, 1H, CH_2), 3.08-3.13 (m, 1H, CH_2), 4.23-4.31 (m, 1H, CH), 5.00 (dd, 1H, *J* = 9.9, *J* = 5.9 Hz, CH), 5.65 (d, 1H, *J* = 6.0 Hz, CH), 7.43-7.62 (m, 5H, ArH), 7.86 (d, 1H, *J* = 8.6 Hz, ArH), 7.90-7.99 (m, 6H, ArH), 8.24 (d, 1H, *J* = 1.9 Hz, ArH), 8.32 (d, 1H, *J* = 8.6 Hz, ArH), 8.71 (d, 1H, *J* = 9.1 Hz, ArH). ^{13}C NMR (151 MHz, DMSO-d_6) δ 30.30, 30.97, 48.23, 50.93, 51.33, 54.77, 111.32, 117.96, 119.02, 121.98, 123.93, 124.50, 125.59, 127.02, 127.34, 127.84, 128.02, 129.02, 129.08, 129.45, 130.24, 130.49, 133.62, 133.83, 136.68, 137.08, 156.72, 157.50. Anal. Calcd for $C_{28}H_{24}N_4O_2$: C, 74.98; H, 5.39; N, 12.49. Found: C, 75.08; H, 5.45; N, 12.38. MS (EI) *m/z* calcd for 448.5; found 449.5 $[M+H]^+$; found 471.5 $[M+H]^+$.

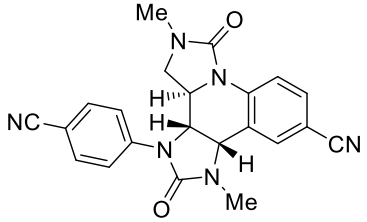
(3a*S*,3b*R*,11b*S*)-3,5-bis(4-bromobenzyl)-1-phenyl-1,3a,3b,4,5,11b-hexahydro-2*H*-diimidazo[1,5-a:4',5'-c]quinoline-2,6(3*H*)-dione (*exo*-2j)



***exo*-2j**

138 mg, 20% yield, white solid, mp <250 °C; IR 1498, 1696, 2875, 2924. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.84 (dd, *J* = 7.9 Hz, *J* = 7.8 Hz, 1H, H^{14} (*trans* to H^{13})), 3.03 (dd, *J* = 8.6 Hz, *J* = 8.7 Hz, 1H, H^{14} (*cis* to H^{13})), 4.20 (m, *J* = 9.8 Hz, *J* = 8.7 Hz, 1H, H^{13}), 4.19 (d, *J* = 16.9 Hz, 1H, H^{23}), 4.28 (d, *J* = 16.9 Hz, 1H, H^{23}), 4.39 (d, *J* = 16.8 Hz, 1H, H^{24}), 4.68 (d, *J* = 16.8 Hz, 1H, H^{24}), 4.82 (d, *J* = 6.6 Hz, 1H, H^{5}), 4.88 (dd, *J* = 6.7 Hz, *J* = 9.8 Hz, 1H, H^{4}), 6.97 (t, *J* = 7.5 Hz, 1H, H^{8}), 7.10-7.18 (m, 1H, H^{20}), 7.10-7.18 (m, 4H, H^{26}, H^{30}), 7.21 (d, *J* = 7.8 Hz, 1H, H^{7}), 7.31 (t, *J* = 7.6 Hz, 2H, $H^{19/21}$), 7.26-7.38 (m, 1H, H^{9}), 7.49 (d, *J* = 8.1 Hz, 2H, H^{27}), 7.52 (d, *J* = 8.0 Hz, 2H, H^{31}), 7.59 (d, *J* = 8.0 Hz, 2H, $H^{18/22}$), 8.19 (d, *J* = 8.4 Hz, 1H, H^{10}). ^{13}C NMR (100 MHz, DMSO-d_6) δ 44.7 (C^{24}), 45.5 (C^{14}), 46.4 (C^{23}), 51.6 (C^{13}), 53.6 (C^{5}), 54.5 (C^{4}), 118.5 (C^{10}), 119.6 (C^{6}), 120.3 (C^{32}), 120.8 (C^{28}), 122.3 (C^{8}), 122.8 ($C^{18/22}$), 124.9 (C^{20}), 129.3 ($C^{19/21}$), 129.5 (C^{9}), 129.7 (C^{26}), 130.2 (C^{30}), 131.7 (C^{7}), 131.8 (C^{31}), 131.9 (C^{27}), 136.7 (C^{11}), 137.1 (C^{29}), 138.9 (C^{25}), 138.9 (C^{17}), 156.3 (C^{16}), 157.6 (C^{2}). Anal. Calcd for $C_{32}H_{26}Br_2N_4O_2$: C, 58.38; H, 3.98; Br, 24.27; N, 8.51. Found: C, 58.44; H, 4.06; Br, 24.21; N, 8.56. MS (EI) *m/z* calcd for 658.4; found 681.3 $[M+Na]^+$.

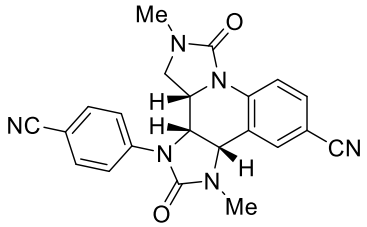
(3a*S*,3b*S*,11b*R*)-10-cyano-3-(4-cyanophenyl)-1,5-dimethyl-1,3a,3b,4,5,11b-hexahydro-2*H*-imidazo[4,5-c]pyrrolo[1,2-a]quinoline-2,6(3*H*)-dione (*exo*-2m)



***exo*-2m**

The compound ***exo*-2m** was obtained from imidazolinone **3m**. 87 mg, 21% yield, white solid, mp <250 °C; IR 1507, 1711, 2224, 2917. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.68 (s, 3H, CH_3), 2.81 (s, 3H, CH_3), 3.12-3.22 (m, 2H, CH_2), 4.05-4.11 (m, 1H, CH), 4.73 (d, 1H, *J* = 6.5 Hz, CH), 5.09 (dd, *J* = 9.9, *J* = 6.6 Hz, 1H), 7.82-7.86 (m, 3H, ArH), 7.90-7.93 (m, 2H, ArH), 8.01 (d, 1H, *J* = 8.8 Hz, ArH), 8.58 (d, 1H, *J* = 8.8 Hz, ArH). ^{13}C NMR (126 MHz, DMSO-d_6) δ 28.78, 30.36, 47.73, 52.48, 50.97, 54.17, 102.92, 105.35, 116.91, 118.87, 119.02, 120.53, 133.21, 136.01, 141.19, 142.84, 155.53, 156.09. Anal. Calcd for $C_{22}H_{18}N_6O_2$: C, 66.32; H, 4.55; N, 21.09. Found: C, 66.43; H, 4.58; N, 21.15. MS (EI) *m/z* calcd for 398.4; found 421.4 $[M+Na]^+$.

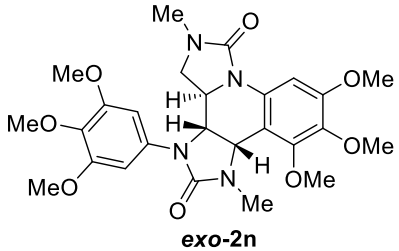
(3a*S*,3b*S*,11b*S*)-10-Isocyano-3-(4-isocyanophenyl)-1,5-dimethyl-1,3a,3b,4,5,11b-hexahydro-2*H*-imidazo[4,5-c]pyrrolo[1,2-a]quinoline-2,6(3*H*)-dione (*endo*-2m)



***endo*-2m**

The compound ***endo*-2m** was obtained from imidazolinone **3m**. 65 mg, 15% yield, white solid, mp <250 °C; IR 1510 1722, 2251, 2964. ^{1}H NMR (600 MHz, DMSO-d_6) δ 2.28 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.69-2.74 (m, 1H, CH_2), 3.21-3.25 (m, 1H, CH_2), 3.87-3.94 (m, 1H, CH), 4.82 (d, 1H, *J* = 9.5 Hz, CH), 5.19 (dd, 1H, *J* = 9.5, *J* = 4.3 Hz, CH), 7.13-7.18 (m, 4H, ArH), 7.40 (d, 2H, *J* = 8.1 Hz, ArH), 7.82 (d, 1H, *J* = 8.3 Hz, ArH). ^{13}C NMR (151 MHz, DMSO-d_6) δ 20.33, 20.39, 28.34, 30.17, 45.55, 54.86, 55.57, 56.26, 117.73, 120.67, 123.46, 129.19, 129.27, 130.73, 131.21, 132.63, 136.71, 138.11, 156.35, 157.81. Anal. Calcd for $C_{22}H_{18}N_6O_2$: C, 66.32; H, 4.55; N, 21.09. Found: C, 66.20; H, 4.35; N, 21.09. MS (EI) *m/z* calcd for 398.4; found 400.1 $[M+H]^+$.

(3a*S*,3b*S*,11b*R*)-9,10,11-Trimethoxy-1,5-dimethyl-3-(3,4,5-trimethoxyphenyl)-1,3a,3b,4,5,11b-hexahydro-2*H*-imidazo[4,5-c]pyrrolo[1,2-a]quinoline-2,6(3*H*)-dione (*exo*-2n)

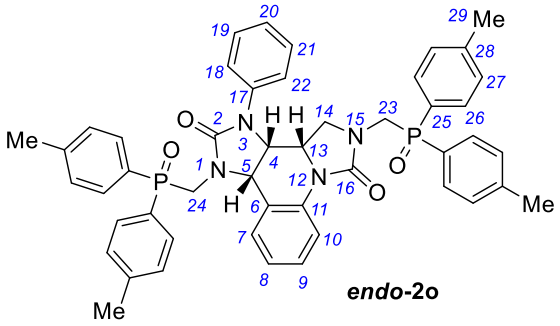


***exo*-2n**

The compound ***exo*-2n** was obtained from imidazolinone **3n**. 110 mg, 20% yield, white solid, mp <250 °C; IR 1521, 1688, 2841, 2954. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.63 (s, 3H, CH_3), 2.68 (s, 3H, CH_3), 2.92-2.98 (m, 1H, CH), 3.08-3.15 (m, 1H, CH_2), 3.66 (s, 3H, CH_3), 3.74 (s, 3H, CH_3), 3.77 (s, 6H, CH_3), 3.78 (s, 3H, CH_3), 3.89 (s, 3H, CH_3), 3.93-4.01 (m, 1H, CH), 4.60-4.67 (m, 1H, CH), 4.75 (d, 1H, *J* = 6.1 Hz, CH), 6.95 (s, 2H, ArH), 7.94 (s, 1H, ArH). ^{13}C NMR (151 MHz, DMSO-d_6) δ 29.82, 30.96, 48.36, 51.04, 51.29, 55.08, 56.13, 56.48, 60.66, 61.04,

61.32, 97.00, 100.98, 104.96, 134.07, 134.81, 135.17, 136.25, 153.29, 154.27, 156.85, 157.56. Anal. Calcd for $C_{26}H_{32}N_4O_8$: C, 59.08; H, 6.10; N, 10.60. Found: C, 59.20; H, 6.16; N, 10.75. MS (EI) *m/z* calcd for 527.6; found 527.4 $[M]^+$.

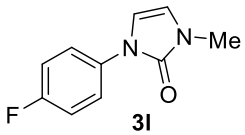
(3a*R*,3b*R*,11b*R*)-1,5-Bis((di-*p*-tolylphosphoryl)methyl)-3-phenyl-1,3a,3b,4,5,11b-hexahydro-2*H*-diimidazo[1,5-a:4',5'-c]quinoline-2,6(3*H*)-dione (*endo*-2o)



***endo*-2o**

The compound ***endo*-2o** was obtained from imidazolinone **3o**. 186 mg, 22% yield, white solid, mp 173-177°C; IR 1443, 1697, 2870, 2919. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.287, 2.315, 2.338 and 2.368 (s, 12H, CH^{29}), 2.799 (dd, *J* = 8.8 Hz, *J* = 9.0 Hz, 1H, H^{14} (*tans* to H^{13})), 3.394 (dd, *J* = 8.9 Hz, *J* = 9.0 Hz, 1H, H^{14} (*cis* to H^{13})), 3.068, 4.433 (m, 2H, H^{24}), 3.396, 4.361 (m, 2H, H^{23}), 3.868 (dd, *J* = 8.8 Hz, *J* = 3.8 Hz, 1H, H^{13}), 5.065 (dd, *J* = 9.4 Hz, *J* = 3.8 Hz, 1H, H^4), 5.441 (d, *J* = 9.4 Hz, 1H, H^5), 7.008 (td, *J* = 7.5 Hz, *J* = 1.1 Hz, 1H, H^8), 7.153 (t, *J* = 7.5 Hz, 1H, H^{20}), 7.260 (t, *J* = 7.5 Hz, 1H, $H^{19/21}$), 7.287 -7.374 (m, 8H, H^{27}), 7.325 (m, 1H, H^9), 7.470 (d, *J* = 7.5 1H, H^7), 7.507 -7.570 (m, 8H, H^{26}), 7.574 (d, *J* = 7.5 Hz, 1H, $H^{18/22}$), 7.835 (d, *J* = 7.5 1H, H^{10}). ^{13}C NMR (126 MHz, DMSO-d_6) δ 21.0 (C^{29}), 40.6 (d, *J*(CP) = 80.3 Hz, C^{24}), 43.3 (d, *J*(CP) = 81.5 Hz, C^{23}), 44.7 (C^{14}), 53.7 (C^{13}), 53.6 (C^5), 55.0 (C^4), 117.8 (C^{10}), 120.9 ($C^{18/22}$), 122.4 (C^8), 122.6 (C^6), 124.1 (C4-Ar), 128.4 (d, *J*(CP) = 98.4 Hz, C^{25}), 129.0 ($C^{19/21}$), 129.1 (C^9), 130.9, 130.4 (d, *J*(CP) = 4.4 Hz, C^{26}), 130.9, 130.4 (d, *J*(CP) = 9.8 Hz, C^{26}), 131.0 (C^7), 138.8 (C^{11}), 140.1 (C^{17}), 142.2, 142.0 (C^{28}), 155.6 (C^{16}), 156.6 (C^2). ^{31}P NMR (161.5 MHz, DMSO-d_6) δ 25.83, 28.05. Anal. Calcd for $C_{48}H_{46}N_4O_4P_2$: C, 71.63; H, 5.76; N, 6.96; P, 7.70. Found: C, 71.72; H, 5.82; N, 6.76; P, 7.78. MS (EI) *m/z* calcd for 804.8; found 827.4 $[M+Na]^+$.

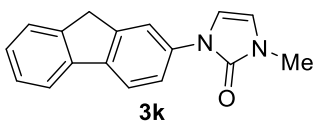
1-(4-Fluorophenyl)-3-Methyl-1,3-dihydro-2*H*-imidazol-2-one (3l)



3l

350 mg, 70% yield, brown oil; IR 1320, 458, 1690, 2863, 2990. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (s, 3H, CH_3), 6.42 (d, 1H, *J* = 2.9 Hz, CH), 6.57 (d, 1H, *J* = 2.9 Hz, CH), 7.11-7.17 (m, 2H, ArH), 7.47-7.52 (m, 2H, ArH). ^{13}C NMR (151 MHz, $CDCl_3$) δ 30.95, 110.76, 113,33, 161.21 (d, *J* = 247.2 Hz), 124.74 (d, *J* = 8.5 Hz), 127.79, 132.57, 132.57, 152.10, 161.21 (d, *J* = 247.2 Hz). Anal. Calcd for $C_{10}H_9FN_2O$: C, 62.49; H, 4.72; N, 14.58. Found: C, 62.36; H, 4.85; N, 14.62. MS (EI) *m/z* calcd for 192.2; found 193.6 $[M+H]^+$.

1-(9*H*-Fluoren-2-yl)-3-methyl-1,3-dihydro-2*H*-imidazol-2-one (3k)

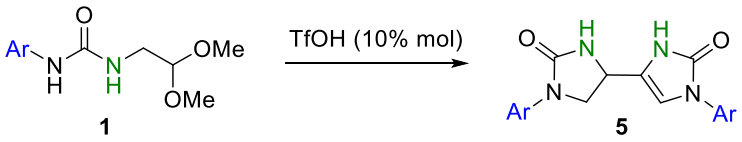


3k

410 mg, 60% yield, mp 148-152 °C; IR 1525, 1761, 2870, 2943. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.22 (s, 3H, CH_3), 3.96 (s, 2H, CH_2), 6.75 (d, 1H, *J* = 3.0 Hz, CH), 7.07 (d, 1H, *J* = 3.1 Hz, CH), 7.29-7.32 (m, 1H, ArH), 7.36-7.40 (m, 1H, ArH), 7.59 (d, 1H, *J* = 7.4 Hz, ArH), 7.71-7.74 (m, 1H, ArH), 7.89 (d, 1H, *J* = 7.5 Hz, ArH), 7.94 (d, 1H, *J* = 8.3 Hz, ArH), 7.95 (s, 1H, ArH). ^{13}C NMR (151 MHz, DMSO-d_6) δ 31.03, 37.57, 109.97, 114.56, 118.50, 120.33,

120.90, 121.31, 126.11, 127.58, 127.82, 137.34, 139.07, 141.57, 144.05, 144.91, 152.45. Anal. Calcd for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.90; H, 5.33; N, 10.72. MS (EI) *m/z* calcd for 262.3; found 263.3 $[M+H]^+$.

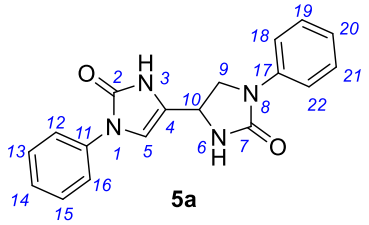
Synthesis of the 4,4'-bi(imidazole-2-one) derivatives 5



1 5

To a 10 mL flask a 1-(2,2-dimethoxyethyl)urea **1m-q** (2.2 mmol, 1.0 equiv.), *o*-xylene (5 mL) and triflic acid (32.99 mg, 0.22 mmol, 0.1 equiv.) were added. The reaction mixture was refluxed for 10 h and cooled to room temperature. The volatiles were removed in vacuum. The resulting dark residue was washed with diethyl ether (2 x 10 mL) and recrystallized from dry acetone to give the compounds **5**.

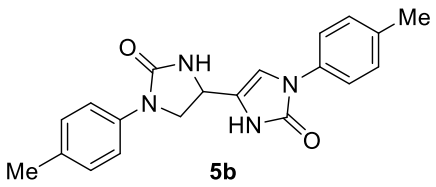
4-(2-Oxo-1-phenylimidazolidin-4-yl)-1-phenyl-1,3-dihydro-2*H*-imidazol-2-one (5a)



5a

256 mg, 80% yield, white solid, mp <250 °C; IR 1578, 1680, 2891, 2994. ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.827 (dd, *J* = 7.8 Hz, *J* = 9.4 Hz, 1H, H^9 (*cis* to H^{10})), 4.092 (dd, *J* = 8.6 Hz, *J* = 9.4 Hz, 1H, H9 (*trans* to H^{10})), 4.708 (dd, *J* = 7.8 Hz, *J* = 8.6 Hz, 1H, H^{10}), 7.00 (tr, *J* = 7.3 Hz 1H, H^{20}), 7.036 (m, 1H, H^5), 7.211 (tr, *J* = 7.7 Hz, 1H, H^{14}), 7.315 (tr, *J* = 7.3 Hz 2H, $H^{21/19}$), 7.382 (s, 1H, NH^6), 7.211 (tr, *J* = 7.7 Hz, 2H, $H^{13/15}$), 7.577 (d, *J* = 7.3 Hz 2H, $H^{22/18}$), 7.690 (d, *J* = 7.7 Hz, 2H, $H^{12/16}$), 10.64 (s, 1H, NH^3). ^{13}C NMR (126 MHz, DMSO-d_6) δ 44.5 (C^{10}), 49.0 (C^9), 107.6 (C^5), 117.2 ($C^{18/22}$), 120.3 ($C^{12/16}$), 121.7 (C^{20}), 122.2 (C^4), 124.9 (C^{14}), 128.5 ($C^{19/21}$), 129.0 ($C^{13/15}$), 137.2(C^{11}), 140.4 (C^{17}), 152.2 (C^2), 157.8 (C^7). ^{15}N NMR (51 MHz, DMSO-d_6) δ 143.5 (N^1), 128.8 (N^3), 101.0 (N^8), 92.0 (N^6). Anal. Calcd for $C_{18}H_{16}N_4O_2$: C, 67.49; H, 5.03; N, 17.49. Found: C, 67.65; H, 5.14; N, 17.67. MS (EI) *m/z* calcd for 320.1; found 342.8 $[M+Na]^+$.

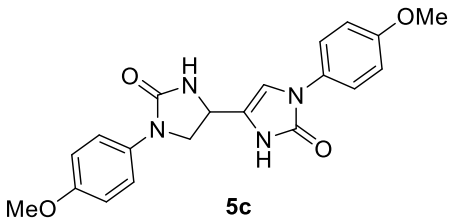
4-(2-Oxo-1-(*p*-tolyl)imidazolidin-4-yl)-1-(*p*-tolyl)-1,3-dihydro-2*H*-imidazol-2-one (5b)



5b

178 mg, 46% yield, white solid, mp 90-94 °C; IR 1643, 1699, 2873, 2968. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.25 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.74-3.83 (m, 1H, CH_2), 3.99-4.09 (m, 1H, CH_2), 4.64-4.72 (m, 1H, CH), 7.12 (d, 2H, *J* = 8.3 Hz, ArH), 7.22 (d, 2H, *J* = 8.2 Hz, ArH), 7.28 (s, 1H, CH), 7.50 (d, 2H, *J* = 8.3 Hz, ArH), 7.56 (d, 2H, *J* = 8.3 Hz, ArH), 10.58 (s, NH), 10.81 (s, NH). ^{13}C NMR (151 MHz, DMSO-d_6) δ 20.74, 20.89, 45.04, 49.59, 108.16, 106.17, 117.78, 120.81, 121.02, 129.39, 129.87, 135.29, 135.96, 138.42, 152.69, 158.37. Anal. Calcd for $C_{20}H_{20}N_4O_2$: C, 68.95; H, 5.79; N, 16.08. Found: C, 69.15; H, 5.98; N, 15.85. MS (EI) *m/z* calcd for 348.1; found 387.5 $[M+K]^+$.

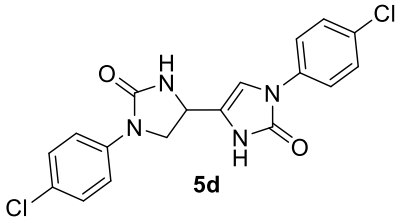
1-(4-Methoxyphenyl)-4-(1-(4-methoxyphenyl)-2-oxoimidazolidin-4-yl)-1*H*-imidazol-2(3*H*)-one (5c)



5c

209 mg, 50% yield, white solid, mp 92-96 °C; IR 1670, 1692, 2757, 2920. ^{1}H NMR (600 MHz, DMSO-d_6) δ 3.32 (s, 3H, CH_3), 3.45-3.50 (m, 1H, CH_2), 3.74 (s, 3H, CH_3), 3.99-4.03 (m, 1H, CH_2), 4.35-4.40 (m, 1H, CH), 5.49-5.53 (m, 1H, CH), 6.12 (d, 1H, *J* = 2.9 Hz, ArH), 6.72-6.76 (m, 1H, ArH), 6.92 (d, 2H, *J* = 8.9 Hz, ArH), 7.10-7.17 (m, 3H, ArH), 7.82 (s, 1H, NH). ^{13}C NMR (151 MHz, DMSO) δ 39.09, 53.13, 54.70, 55.17, 55.81, 56.80, 113.83, 114.47, 114.73, 120.08, 125.66, 127.55, 130.94, 131.49, 153.83, 157.07, 158.61, 159.48. Anal. Calcd for $C_{20}H_{20}N_4O_4$: C, 63.15; H, 5.30; N, 14.73. Found: C, 63.22; H, 5.27; N, 14.88. MS (EI) *m/z* calcd for 380.4; found 381.4 $[M+H]^+$.

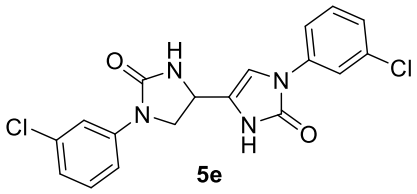
1-(4-Chlorophenyl)-4-(1-(4-chlorophenyl)-2-oxoimidazolidin-4-yl)-1*H*-imidazol-2(3*H*)-one (5d)



5d

231 mg, 54% yield, white solid, mp 92-96 °C; IR 1683, 1698, 2851, 2943. ^{1}H NMR (600 MHz, DMSO-d_6) δ 3.76-3.82 (m, 1H, CH_2), 4.07-4.11 (m, 1H, CH_2), 4.67-4.42 (m, 1H, CH), 7.07-7.09 (m, 1H, CH), 7.34-7.37 (m, 2H, ArH), 7.45-7.49 (m, 2H, ArH), 7.58-7.61 (m, 2H, ArH), 7.74-7.77 (m, 2H, ArH), 10.72 (s, 1H, NH). ^{13}C NMR (151 MHz, DMSO-d_6) δ 44.79, 49.39, 107.89, 119.13, 122.19, 122.99, 125.89, 128.82, 129.28, 129.42, 136.61, 139.82, 152.65, 158.06. Anal. Calcd for $C_{18}H_{14}Cl_2N_4O_2$: C, 55.54; H, 3.63; Cl, 18.22; N, 14.39; O, 8.22. Found: C, 55.65; H, 3.52; Cl, 18.36; N, 14.55; O, 7.92. MS (EI) *m/z* calcd for 389.2 found 389.0 $[M]^+$.

1-(3-Chlorophenyl)-4-(1-(3-chlorophenyl)-2-oxoimidazolidin-4-yl)-1*H*-imidazol-2(3*H*)-one (5e)

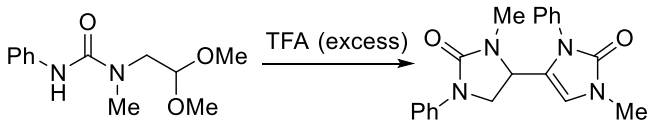


5e

196 mg, 46% yield, white solid, mp 83-87 °C; IR 1664, 1688, 2872, 2998. ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.76-3.86 (m, 1H, CH_2), 4.07-4.15 (m, 1H, CH_2), 4.64-4.76 (m, 1H, CH), 7.05 (d, 1H, *J* = 7.8 Hz, ArH), 7.17 (s, 1H, CH), 7.26 (d, 1H, *J* = 7.7 Hz, ArH), 7.34 (t, 1H, *J* = 8.1 Hz, ArH), 7.41 (d, 1H, *J* = 8.0 Hz, ArH), 7.45 (t, 1H, *J* = 8.0 Hz, ArH), 7.56 (s, 1H, ArH), 7.68 (d, 1H, *J* = 8.3 Hz, ArH), 7.81 (s, 1H, ArH), 7.93 (s, 1H, NH), 10.75 (s, NH). ^{13}C NMR (151 MHz, DMSO-d_6) δ 44.75, 49.30, 107.76, 115.79, 117.28, 118.68, 120.04, 121.76, 123.22, 125.01, 130.65, 131.21, 133.60, 133.95, 139.03, 142.30, 152.67, 157.95. Anal. Calcd for $C_{18}H_{14}Cl_2N_4O_2$: C, 55.54; H, 3.63; Cl, 18.22; N, 14.39. Found: C, 55.71; H, 3.72; Cl, 18.13; N, 14.25. MS (EI) *m/z* calcd for 389.2 found 390.9 $[M+H]^+$.

Mechanistic studies

Synthesis of 4,4'-bi(imidazole-2-one) 4



1a **4**

To a 50 mL flask a 1-(2,2-dimethoxyethyl)urea **1a** (3.99 g, 16.8 mmol, 1 equiv.) and dry chloroform (10 mL) was added. Then a TFA (6.42 mL, 83.9 mmol, 5 equiv.) was added dropwise and the reaction mixture was allowed to stir at room temperature for 10 h. The volatiles were removed under reduced pressure. The residue was washed with distilled water (3 x 10 mL) and triturated in water. The precipitate was filtered off and washed consecutively with distilled water (1 x 10 mL) and diethyl ether (1 x 10 mL) to give the compound **4** as a white solid (1.25 g, 75% yield).

Mp 161°C; IR 1598; 1560. ^{1}H NMR (400 MHz, CD_3OD) δ 2.79 (s, 3H, CH3), 3.33 (s, 3H, CH3), 3.61-3.68 (m, 1H, CH2), 3.91-3.98 (m, 1H, CH2), 4.53-4.60 (m, 1H, CH), 6.77 (s, 1H, CH), 7.00 (tt, 1H, *J* = 6.6 Hz, *J* =1.9 Hz, ArH), 7.22-7.31 37 (m, 6H, ArH), 7.31-7.35 (m, 1H, ArH), 7.36-7.42 (m, 2H, ArH). ^{13}C NMR (151 MHz, CD_3OD) δ 27.91, 29.40, 47.93, 50.76, 113.03, 117.72, 120.66, 122.42, 128.09, 128.17, 128.75, 129.25, 134.47, 139.54, 153.89, 157.21.

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.84 (s, 3H, CH3), 3.34 (s, 3H, CH3), 3.57-3.61 (m, 1H, CH2), 3.81-3.88 (m, 1H, CH2), 4.35-4.43 (m, 1H, CH), 6.35 (s, 1H, CH), 7.02 (t, 1H, *J* = 7.3, ArH), 7.25-7.31 (m, 4H, ArH), 7.33-7.39 (m, 3H, ArH), 7.44 (t, 1H, *J* = 7.8 Hz, ArH).

Anal. Calcd for $C_{20}H_{20}N_4O_2$: C, 68.95; H, 5.79; N, 16.08. Found: C, 68.83; H, 5.69; N, 16.17. MS (EI) *m/z* calcd for 348.4; found 349.11 $[M+H]^+$, 371.06 $[M+Na]^+$.

Synthesis of octahydro-diimidazoquinolines (*exo,endo*)-2a from compound 3a

This reaction was carried out as described on page S11, except the workup procedure, which was modified as follows. After the removal of solvent in vacuum, the residue was washed with diethyl ether (2 x 10 mL) and acetone (15 mL) to afford the mixture of octahydro-diimidazoquinolines ***exo*-2a** and ***endo*-2a** (328 mg, 90% yield) with *dr* 85:15 (according to ^{1}H NMR data). The ^{1}H and ^{13}C NMR spectra of the obtained mixture is consistent with those of compounds ***exo*-2a** and ***endo*-2a**.

Synthesis of octahydro-diimidazoquinolines (*exo,endo*)-2a from compound 4

This reaction was carried out in optimal conditions given in Table S1, entry 7:

To a 10 mL flask the compound **4** (0.5 g, 1.45 mmol, 1 equiv.), *o*-xylene (3.5 mL) and triflic acid (0.0012 g, 0.145 mmol, 0.1 equiv.) was added. The reaction mixture was refluxed for refluxed for 10 h and cooled to room temperature. The volatiles were removed in vacuum. The resulting dark residue was washed with diethyl ether (2 x 10 mL) and acetone (15 mL) to afford the mixture of octahydro-diimidazoquinolines ***exo*-2a** and ***endo*-2a** (435 mg, 87% yield) with *dr* 90:10 (according to ^{1}H NMR data). The ^{1}H and ^{13}C NMR spectra of the obtained mixture is consistent with those of compounds ***exo*-2a** and ***endo*-2a**.

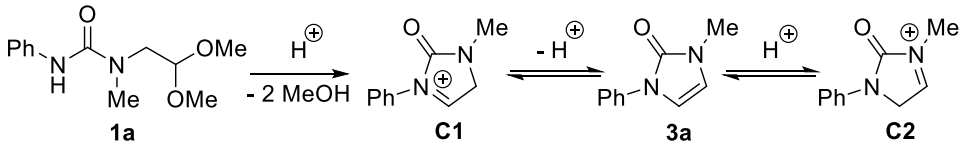
Computational methods

Several works have shown that the B3LYP functional is relatively accurate for kinetic data. In 2004, the Truhlar's group has proposed MPWB1K functional,[5] which improve thermodynamic calculations. Later, it was used by Domingo with coworkers to investigate a mechanism of the Lewis and Bronsted acid-catalysed Povarov reaction of some simple imines.[6] Consequently, DFT computations were carried out using the

MPWB1K exchange-correlation functional, together with the standard 6-31G(d,p) basis set.[7] The optimisations were carried out using the Berny analytical gradient optimisation method.[8] The optimisations of the intermediates were followed by frequency computations in order to verify that they correspond to the true minima. The transition states were accepted if they had one and only one imaginary frequency. The IRC paths[9] were traced in order to check the energy profiles connecting each transition state to the two associated minima of the proposed mechanism using the HPC algorithm.[10] All computations were carried out with the Gaussian 16 suite of programs[11] in gaseous phase.

Mechanism of the formation of octahydro-diimidazoquinolines 2

Our mechanistic proposal includes the intramolecular cyclization of the starting urea **1** to give imidazolin-2-ones **3** through the 2-oxoimidazolium cation **C1** as the first stage of the reaction. The possibility of such a cyclization, as well as the possibility of the subsequent re-protonation of the compound **3** resulting in the isomeric cation **C2** has been demonstrated in our prior work (Scheme S1).[2,12]



Scheme S1. Intramolecular cyclization of the urea **1a**

The subsequent stage involves the Povarov reaction of imidazolium cations **C1** and **C1** with imidazolin-2-one **3**. It is worth noting that the ability of the imidazole-2-ones **3** to serve as the dienophiles in the Povarov reaction was evidenced by Lavilla with coworkers.[13]

In principle, the Povarov reaction may proceed either via concerted [4+2] cycloaddition or the stepwise mechanism. However, most of the data to day suggest that the 2-step nucleophilic addition / intramolecular Friedel-Crafts substitution mechanism is more favourable in case of Lewis or Bronsted acid catalysis.[6,14–17] Taking this into account, a two-step mechanism was also proposed for the formation of the octahydro-diimidazoquinolines **2**, which was further supported by the quantum chemistry data.

The quantum chemistry calculations were performed using the Bronsted acid catalysed cyclization of the imidazolinone **3a** as the model reaction (Scheme S2).* The interaction of the imidazolin-2one **3a** with the cations **C1** and **C2** may result in four regioisomeric intermediates **I11**-**I14**, each of which exists as two diastereomers, giving rise to eight intermediates in total. However, only four of them (**RS-**, **SS-I12** and **RS-**, **SS-I13**) may undergo the intramolecular Friedel-Craft reaction to furnish isomeric octahydro-diimidazoquinolines ***endo*-2a**, ***exo*-2a**, ***endo*-2a**' and ***exo*-2a'**.

Gibbs free energies for all possible intermediates **C1**, **C2**, **I1**-**I14**, **I22**, **I23** and transition states **TS11**-**TS14** and **TS23**, **TS23** were calculated. The obtained results indicate that the intermediates **SS-** and **RS-I14**, as well as the intermediate **SS-I11** have the largest free Gibbs energy barriers for formation (20.81-23.52 kcal/mol). Additionally, the intermediates **SS-I14** and **SS-I11** have the highest free Gibbs energy (12.29 and 6.85 kcal/mol, accordingly). Thus, their formation is both thermodynamically and kinetically disfavored. Although the intermediate **RS-I14** has one of the lowest free energy (4.90 kcal/mol), the highest energy barrier (23.52 kcal/mol) also renders its formation less possible.

The free Gibbs energy of the intermediate **RS-I11** is comparable to that of intermediates **SS-** and **RS-I13** and **SS-I12** (5.16-5.81 kcal/mol). However, it has the lowest formation energy barrier (17.95 kcal/mol) and may be formed under kinetic control. The somewhat lower free energy of the cation **C2** compared to the cation

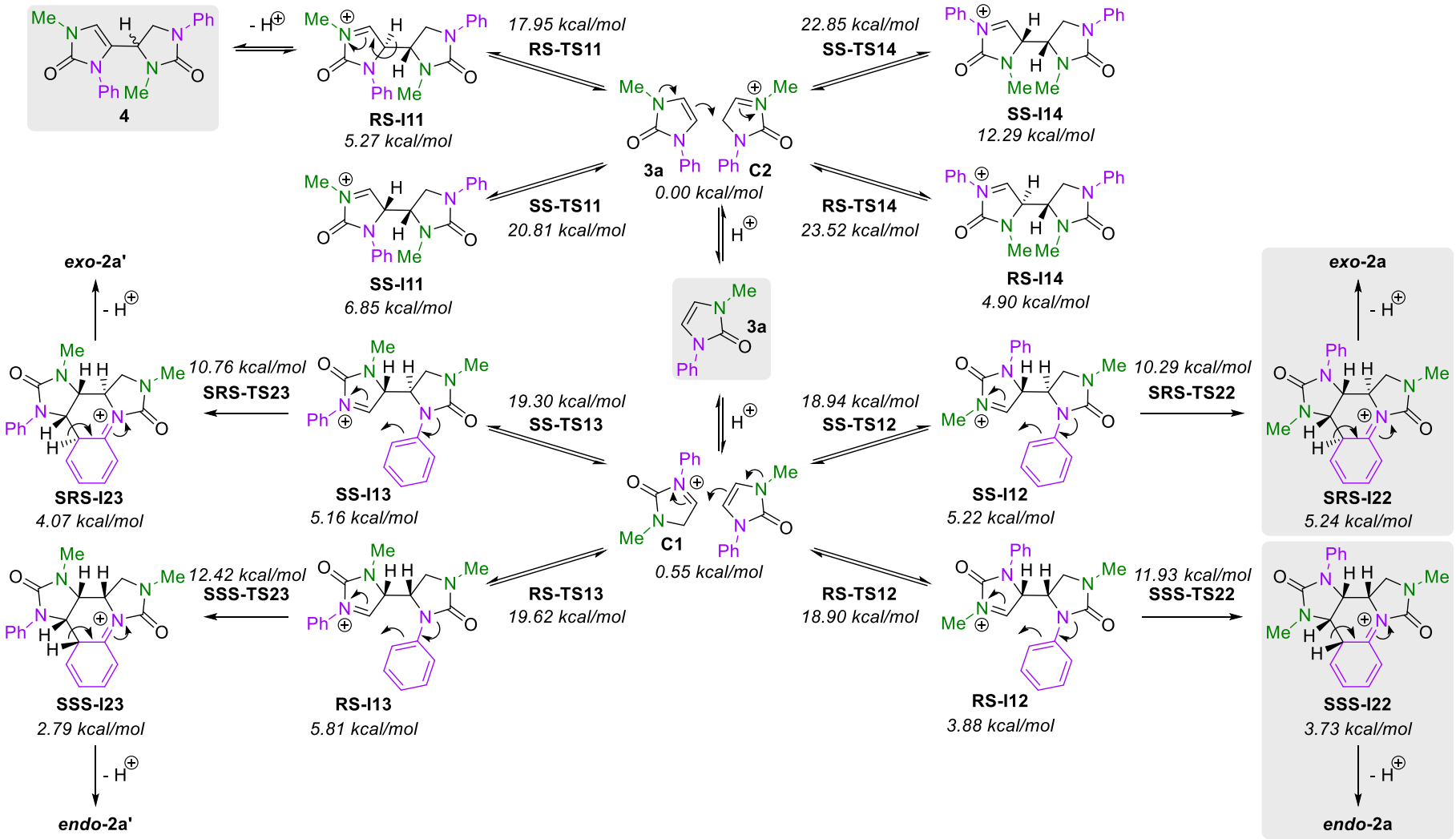
* The formation of the imidazolinone **3a** from urea **1a** was described before[12] and was not modelled.

C1 may also contribute to its formation. The isolation of the compound **4** from the reaction mixtures during optimization studies suggests that this is indeed the case.

As was mentioned before, only four intermediates, namely, **RS-** and **SS-I13** and **RS-**, **SS-I12**, may undergo the intramolecular aromatic electrophilic substitution to give isomeric octahydro-diimidazoquinolines **2a** and **2a'**. In all cases the free energy barrier for the intramolecular substitution is almost two-fold lower than the energy barrier for the formation of the intermediate itself (10.29-12.42 kcal/mol *vs* 18.90-19.62 kcal/mol). Thus, the regio- and diastereomeric composition of the final products is determined by the nucleophilic addition step, rather than intramolecular Friedel-Crafts substitution.

The free energy barriers for the formation of intermediates **SS-** and **RS-I13** are *ca* 0.5 kcal/mol higher than for the intermediates **SS-** and **RS-I12**, so the latter are kinetically favored. We should also note that the difference between free energies of the transition states **RS-TS12** and **SS-TS12** is too small (0.04 kcal/mol) and may be neglected. At the same time, the free energy of the intermediate **RS-I12** is the lowest of all (3.88 kcal/mol) and its formation is thermodynamically preferable.

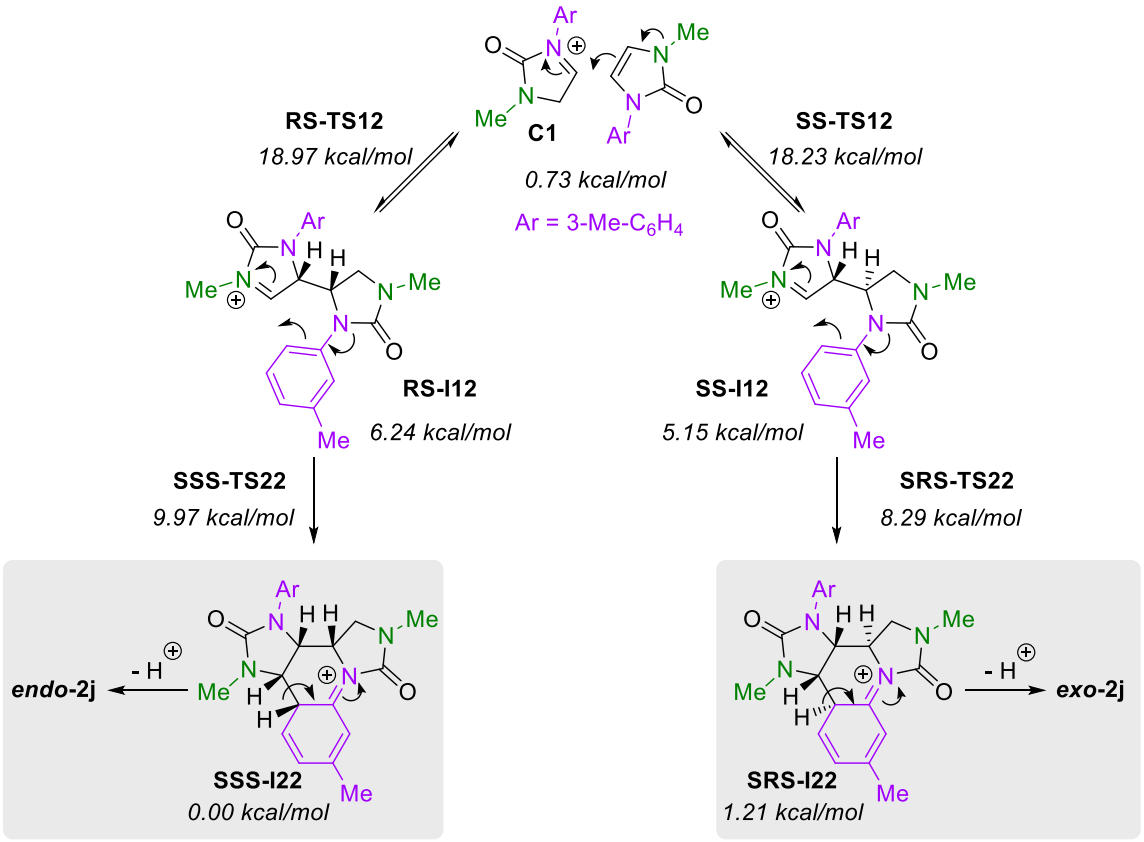
Overall, the presented data suggests that the compound ***endo*-2a** is the most preferable product under thermodynamic control of the reaction, and the compound ***exo*-2a** is the next one. On the other hand, the formation of the compound **4** under kinetic control is also possible. These results are in good agreement with the experimental data. Moreover, the formation of both compounds ***endo*-2a** and ***exo*-2a** (*dr* 95 : 5) from the compound **4** was experimentally observed, which also supports strongly the theoretical calculations.



Scheme S2. Plausible mechanism for the formation of octahydro-diimidazoquinolines and relative free Gibbs energies (kcal/mol) as obtained from quantum chemistry calculations (MPWB1K/6-31G(d,p)).[a]

[a] The cyclization of the urea **1a** was taken as the model reaction

Additional quantum chemistry calculations were performed to explain the preferential formation of the *exo*-diastereomer in case of ureas with 3-substituted phenyl moiety using the urea **1g** as the model compound (Scheme S3). Just as in the case of compounds **(*exo,endo*)-2a**, the formation of the compounds **(*exo,endo*)-2g** is a two-step process with the nucleophilic addition step being a rate-determining one. In contrast to the unsubstituted phenyl ring, the 3-methylphenyl substituent makes the formation of the intermediate **SS-12** more preferable. Not only the free energy barrier is lower by 0.74 kcal/mol in this case, but also the intermediate **SS-12** itself is lower in energy by 1.09 kcal/mol. Thus, the formation of *exo*-isomer is favored by both thermodynamic and kinetic factors and the quantum chemistry data is in good agreement with the experimental results.



Scheme S3. Relative free Gibbs energies (kcal/mol) for the formation of compounds ***exo***- and ***endo*-2g** as obtained from quantum chemistry calculations (MPWB1K/6-31G(d,p))

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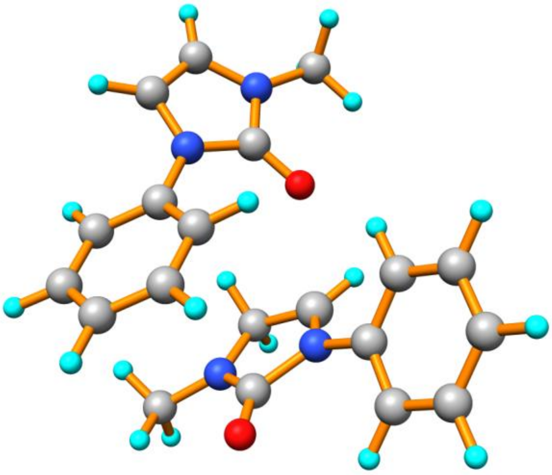
Coordinates of stationary points

Reaction depicted on Scheme S2

Molecule: **C1**



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O				1		1.189
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C	3	1.280	1	110.298	2	178.3
H	5	1.074	3	123.086	1	183.2
C	3	1.422	1	123.242	2	354.8
C	7	1.384	3	119.757	1	41.3
C	7	1.386	3	117.822	1	220.4
C	8	1.381	7	118.142	3	178.6
H	8	1.076	7	120.782	3	358.5
C	9	1.381	7	118.403	3	181.6
H	9	1.081	7	119.998	3	2.9
C	10	1.384	8	120.474	7	0.0
H	10	1.078	8	119.361	7	180.2
H	12	1.078	9	119.583	7	180.2
H	14	1.078	10	119.784	8	179.9
C	4	1.440	1	122.687	2	358.0
H	18	1.085	4	110.007	1	129.1
H	18	1.087	4	110.796	1	250.7
H	18	1.083	4	107.614	1	10.2
C	4	1.427	1	112.782	2	181.8
H	22	1.092	4	112.847	1	118.2
C	13	3.342	9	153.353	7	29.3
O	24	1.235	13	25.537	9	274.2
N	24	1.366	13	115.683	9	37.7
N	24	1.354	13	131.773	9	183.9
C	26	1.386	24	109.484	13	154.7
C	26	1.410	24	124.547	13	334.9
C	29	1.387	26	119.934	24	45.8
C	29	1.385	26	119.471	24	224.2
C	30	1.382	29	119.404	26	178.3
H	30	1.078	29	119.572	26	359.6
C	31	1.384	29	119.490	26	182.4
H	31	1.080	29	119.800	26	1.6
C	34	1.383	31	120.315	29	358.9
H	32	1.079	30	119.596	29	180.0
H	34	1.079	31	119.526	29	178.8
H	36	1.078	34	120.240	31	180.2
C	27	1.438	24	123.208	13	30.9
H	40	1.085	27	110.571	24	240.3
H	40	1.083	27	107.436	24	359.4
H	40	1.086	27	110.730	24	118.8
C	28	1.337	26	107.278	24	359.6
H	22	1.091	4	112.912	1	241.4
H	28	1.071	26	121.672	24	182.0
H	44	1.072	28	130.405	26	181.4

47							
C							1
O					1		1.191
N		1	1.345		2		133.619
N	1	1.459	2	121.292	3	179.2	
C	3	1.437	1	111.401	2	178.9	
H	5	1.090	3	112.091	1	241.2	
C	3	1.417	1	126.175	2	0.5	
C	7	1.388	3	121.137	1	8.8	
C	7	1.387	3	118.453	1	188.3	
C	8	1.382	7	119.000	3	179.7	
H	8	1.075	7	120.693	3	359.7	
C	9	1.381	7	119.715	3	180.5	
H	9	1.078	7	121.216	3	0.8	
C	12	1.382	9	120.402	7	359.9	
H	10	1.078	8	118.861	7	180.0	
H	12	1.078	9	119.257	7	180.0	
H	14	1.078	12	120.272	9	180.0	
C	4	1.445	1	119.377	2	3.3	
H	18	1.082	4	109.169	1	191.1	
H	18	1.083	4	108.191	1	311.9	
H	18	1.086	4	108.538	1	70.3	
C	4	1.275	1	111.039	2	180.2	
H	22	1.074	4	123.986	1	178.2	
C	23	3.233	22	94.509	4	95.9	
O	24	1.237	23	34.400	22	46.0	
N	24	1.365	23	117.560	22	289.0	
N	24	1.353	23	121.951	22	155.9	
C	26	1.386	24	109.448	23	220.3	
C	26	1.409	24	124.923	23	38.6	
C	29	1.385	26	119.273	24	222.8	
C	29	1.387	26	120.169	24	44.5	
C	30	1.384	29	119.615	26	182.3	
H	30	1.079	29	119.821	26	2.3	
C	31	1.383	29	119.337	26	178.5	
H	31	1.078	29	119.491	26	359.4	
C	32	1.383	30	120.240	29	359.0	
H	32	1.078	30	119.538	29	179.3	
H	34	1.078	31	119.614	29	180.2	
H	36	1.078	32	120.201	30	180.1	
C	27	1.437	24	123.343	23	317.2	
H	40	1.083	27	107.478	24	359.1	
H	40	1.086	27	110.718	24	118.6	
H	40	1.085	27	110.570	24	240.0	
C	28	1.336	26	107.336	24	359.5	
H	5	1.089	3	113.327	1	116.8	
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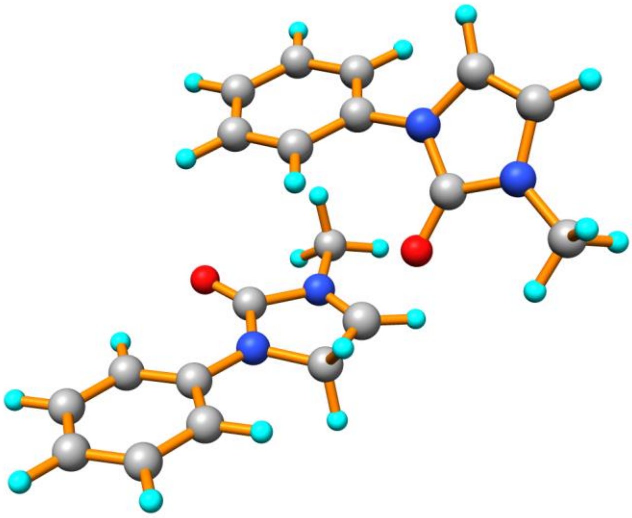
H	28	1.071	26	121.684	24	182.0	

Molecule: **C2**



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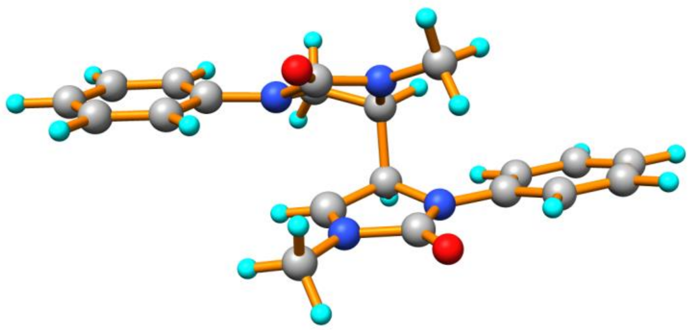
Molecule: **RS-I11**



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O				1		1.201
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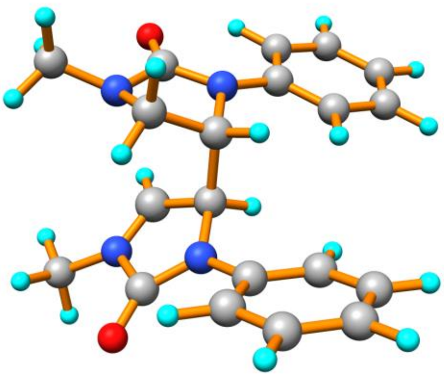
C	3	1.445	1	108.884	2	167.1
H	5	1.090	3	112.148	1	274.4
C	3	1.410	1	124.746	2	9.0
C	7	1.391	3	120.519	1	326.7
C	7	1.388	3	119.373	1	149.7
C	8	1.381	7	119.324	3	182.4
H	8	1.076	7	120.125	3	4.9
C	9	1.383	7	119.838	3	177.3
H	9	1.078	7	120.920	3	355.8
C	12	1.381	9	120.438	7	0.1
H	10	1.078	8	119.075	7	180.9
H	12	1.078	9	119.282	7	179.6
H	14	1.078	12	120.264	9	179.7
C	4	1.443	1	121.529	2	354.1
H	18	1.084	4	109.133	1	202.2
H	18	1.084	4	108.125	1	321.2
H	18	1.088	4	112.847	1	80.9
C	4	1.421	1	110.516	2	168.1
H	22	1.085	4	112.594	1	152.2
C	21	2.634	18	117.249	4	19.4
O	24	1.191	21	81.793	18	186.3
N	24	1.351	21	81.741	18	50.2
N	24	1.452	21	111.834	18	307.1
C	26	1.436	24	110.493	21	260.2
C	26	1.420	24	125.837	21	68.3
C	29	1.388	26	118.656	24	171.9
C	29	1.388	26	121.113	24	351.8
C	30	1.382	29	119.831	26	179.6
H	30	1.079	29	121.335	26	358.3
C	31	1.382	29	119.086	26	180.1
H	31	1.075	29	120.720	26	0.9
C	32	1.382	30	120.365	29	0.3
H	32	1.078	30	119.286	29	179.8
H	34	1.078	31	118.831	29	180.3
H	36	1.078	32	120.264	30	179.8
C	27	1.447	24	119.814	21	265.3
H	40	1.083	27	108.822	24	310.3
H	40	1.085	27	108.010	24	68.9
H	40	1.082	27	108.995	24	188.7
C	27	1.283	24	111.093	21	84.1
H	5	1.088	3	111.294	1	152.1
H	44	1.077	27	123.119	24	172.1
H	28	1.086	26	113.366	24	225.3

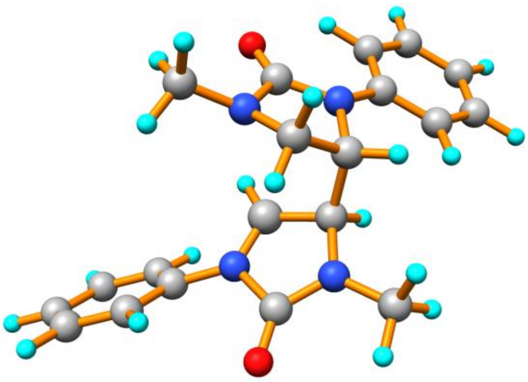
Molecule: **RS-I12**



Energy = -1143.121360 Hartree

47						
C						1
O				1		1.201
N		1	1.383		2	128.512
N	1	1.388	2	124.733	3	184.5
C	3	1.432	1	109.016	2	189.8
H	5	1.084	3	113.636	1	211.7
C	3	1.413	1	126.345	2	353.7
C	7	1.391	3	121.573	1	6.1
C	7	1.391	3	118.928	1	185.8
C	8	1.381	7	119.382	3	180.3
H	8	1.074	7	120.223	3	0.8
C	9	1.383	7	120.214	3	179.6
H	9	1.079	7	121.285	3	357.5
C	12	1.380	9	120.479	7	0.2
H	10	1.078	8	118.671	7	180.2
H	12	1.078	9	119.203	7	179.5
H	14	1.078	12	120.432	9	179.8
C	4	1.442	1	118.555	2	339.2
H	18	1.083	4	108.029	1	32.8
H	18	1.085	4	109.997	1	152.6
H	18	1.089	4	111.316	1	273.5
C	4	1.436	1	109.003	2	194.7
H	22	1.091	4	112.368	1	84.4
C	5	3.447	3	132.449	1	64.0
O	24	1.189	5	152.199	3	207.6
N	24	1.348	5	37.138	3	121.6
N	24	1.458	5	75.571	3	341.0
C	26	1.435	24	112.058	5	323.0
C	26	1.420	24	124.788	5	140.8
C	29	1.386	26	118.835	24	145.3
C	29	1.384	26	120.157	24	324.5
C	30	1.382	29	119.347	26	178.5
H	30	1.080	29	120.732	26	356.8
C	31	1.382	29	118.935	26	180.6
H	31	1.077	29	120.450	26	1.8
C	32	1.383	30	120.198	29	0.8
H	32	1.078	30	119.537	29	179.9
H	34	1.078	31	119.245	29	180.5
H	36	1.078	32	120.046	30	179.5
C	27	1.447	24	119.531	5	200.4
H	40	1.084	27	108.230	24	49.0
H	40	1.082	27	109.320	24	170.0
H	40	1.085	27	108.971	24	291.0
C	27	1.282	24	111.057	5	21.2
H	44	1.077	27	123.377	24	175.8
H	22	1.088	4	112.114	1	207.0
H	28	1.094	26	113.008	24	240.8

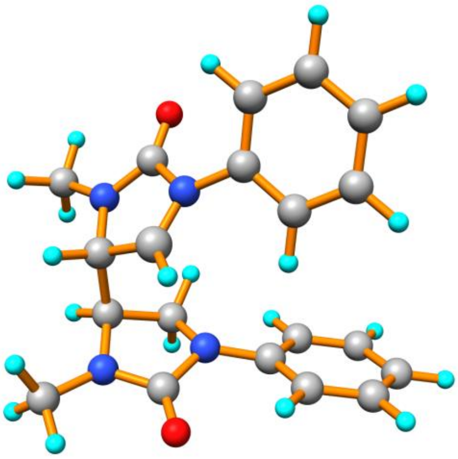
Molecule: **RS-I13**



Energy = -1143.119464 Hartree

47						
C						1
O					1	1.201
N		1	1.384	2		128.362
N	1	1.385	2	124.940	3	184.7
C	3	1.433	1	109.041	2	190.2
H	5	1.084	3	112.619	1	212.3
C	3	1.413	1	126.383	2	355.5
C	7	1.391	3	121.411	1	10.1
C	7	1.391	3	119.162	1	189.4
C	8	1.381	7	119.409	3	179.9
H	8	1.074	7	120.175	3	0.1
C	9	1.383	7	120.291	3	180.1
H	9	1.079	7	121.428	3	358.4
C	12	1.380	9	120.448	7	0.1
H	10	1.078	8	118.660	7	180.2
H	12	1.078	9	119.190	7	179.7
H	14	1.078	12	120.436	9	179.9
C	4	1.441	1	119.197	2	340.8
H	18	1.083	4	107.898	1	29.7
H	18	1.086	4	109.973	1	149.2
H	18	1.089	4	111.311	1	270.3
C	4	1.435	1	109.308	2	194.1
H	22	1.091	4	112.367	1	84.9
C	5	3.470	3	131.782	1	64.2
O	24	1.187	5	152.771	3	201.6
N	24	1.471	5	75.299	3	340.5
N	24	1.343	5	36.212	3	123.3
C	26	1.287	24	110.145	5	21.1
C	26	1.423	24	123.015	5	198.0
C	29	1.384	26	119.436	24	43.7
C	29	1.385	26	118.486	24	223.0
C	30	1.381	29	118.277	26	178.4
H	30	1.076	29	120.737	26	358.1
C	31	1.380	29	118.801	26	181.7
H	31	1.080	29	120.715	26	3.7
C	32	1.384	30	120.480	29	0.1
H	32	1.078	30	119.357	29	180.1
H	34	1.078	31	119.645	29	180.4
H	36	1.078	32	119.833	30	179.7
C	27	1.442	24	122.126	5	147.7
H	40	1.084	27	107.573	24	0.7
H	40	1.086	27	110.391	24	119.7
H	40	1.086	27	111.091	24	241.6
C	27	1.428	24	112.981	5	323.2
H	22	1.088	4	111.956	1	207.6
H	44	1.095	27	112.471	24	242.6
H	28	1.077	26	122.616	24	176.7

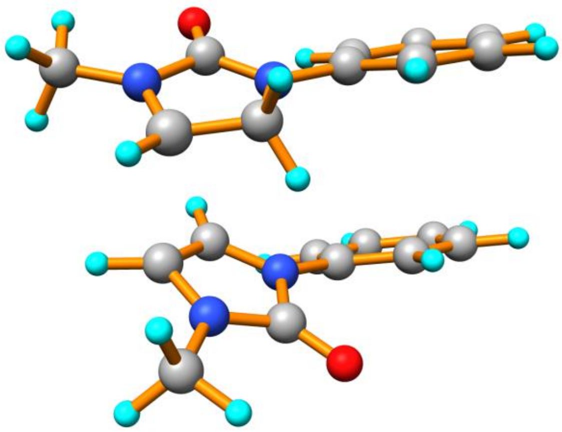
Molecule: **RS-I14**



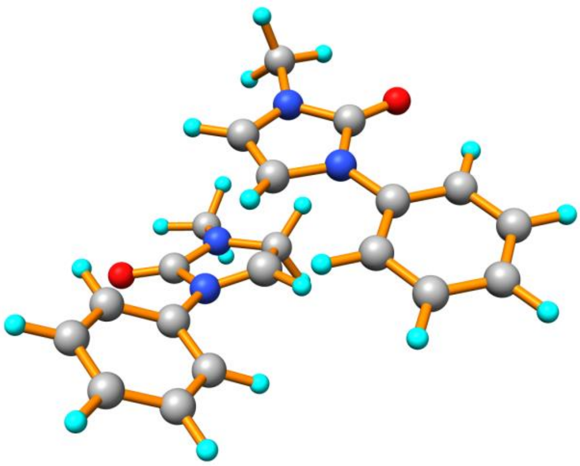
Energy = -1143.120578 Hartree

47

C						1
O				1		1.200
N		1	1.395	2		127.753
N	1	1.371	2	125.818	3	183.5
C	3	1.444	1	108.888	2	168.5
H	5	1.090	3	111.907	1	271.7
C	3	1.412	1	123.768	2	15.4
C	7	1.392	3	120.804	1	327.5
C	7	1.388	3	119.314	1	150.4
C	8	1.381	7	119.361	3	182.4
H	8	1.075	7	120.177	3	4.1
C	9	1.383	7	119.986	3	177.4
H	9	1.078	7	121.031	3	356.6
C	12	1.381	9	120.505	7	0.0
H	10	1.079	8	118.900	7	180.8
H	12	1.078	9	119.214	7	179.7
H	14	1.078	12	120.322	9	179.7
C	4	1.436	1	122.054	2	2.3
H	18	1.084	4	107.195	1	347.2
H	18	1.090	4	112.311	1	106.2
H	18	1.086	4	110.571	1	228.2
C	4	1.420	1	110.801	2	168.5
H	22	1.087	4	112.580	1	148.3
C	22	3.453	4	134.620	1	296.4
O	24	1.187	22	152.054	4	158.9
N	24	1.472	22	75.377	4	21.0
N	24	1.342	22	36.761	4	239.5
C	26	1.286	24	110.156	22	337.2
C	26	1.422	24	122.992	22	156.0
C	29	1.384	26	119.520	24	42.1
C	29	1.385	26	118.162	24	221.2
C	30	1.381	29	118.131	26	178.4
H	30	1.076	29	120.886	26	358.4
C	31	1.380	29	118.605	26	181.6
H	31	1.080	29	120.790	26	4.0
C	34	1.384	31	120.059	29	359.7
H	32	1.078	30	119.342	29	180.3
H	34	1.078	31	119.402	29	180.7
H	36	1.078	34	119.826	31	180.3
C	27	1.443	24	122.131	22	214.8
H	40	1.084	27	107.515	24	357.4
H	40	1.086	27	111.201	24	116.4
H	40	1.086	27	110.371	24	238.3
C	27	1.429	24	112.986	22	37.4
H	5	1.088	3	111.489	1	149.7
H	44	1.093	27	111.894	24	119.0
H	28	1.077	26	122.434	24	184.7

Molecule: **RS-TS11**  Energy = -1143.095350 Hartree Imag. Freq. = -183.2399 cm^{-1}	47 C 1 O 1 1.194 N 1 1.356 2 131.464 N 1 1.430 2 123.041 3 182.0 C 3 1.433 1 111.305 2 177.3 H 5 1.094 3 112.401 1 257.0 C 3 1.415 1 125.777 2 4.1 C 7 1.386 3 120.501 1 330.4 C 7 1.385 3 118.802 1 152.5 C 8 1.381 7 118.994 3 181.7 H 8 1.076 7 120.435 3 2.5 C 9 1.382 7 119.572 3 178.1 H 9 1.079 7 121.008 3 357.3 C 12 1.382 9 120.290 7 0.2 H 10 1.078 8 119.045 7 180.3 H 12 1.078 9 119.367 7 179.6 H 14 1.078 12 120.172 9 179.5 C 4 1.443 1 120.707 2 0.2 H 18 1.087 4 110.630 1 100.9 H 18 1.084 4 110.085 1 222.6 H 18 1.083 4 107.128 1 342.3 C 4 1.315 1 110.453 2 170.9 H 22 1.077 4 121.208 1 167.6 C 5 3.373 3 109.189 1 106.6 O 24 1.198 5 121.748 3 110.1 N 24 1.412 5 68.595 3 348.4 N 24 1.372 5 72.329 3 234.7 C 26 1.342 24 109.683 5 293.5 C 26 1.419 24 124.672 5 115.7 C 29 1.384 26 118.851 24 141.9 C 29 1.384 26 119.789 24 320.3 C 30 1.381 29 119.203 26 177.1 H 30 1.079 29 120.497 26 355.3 C 31 1.381 29 118.759 26 182.3 H 31 1.077 29 120.317 26 2.6 C 32 1.383 30 120.102 29 0.9 H 32 1.078 30 119.569 29 179.7 H 34 1.078 31 119.287 29 179.9 H 36 1.078 32 119.956 30 179.3 C 27 1.441 24 121.818 5 236.9 H 40 1.084 27 107.001 24 2.6 H 40 1.086 27 111.231 24 121.5 H 40 1.086 27 110.737 24 243.6 C 28 1.372 26 108.847 24 3.7 H 5 1.089 3 112.288 1 135.5 H 44 1.075 28 127.295 26 200.6 H 28 1.074 26 121.831 24 181.5

Molecule: **RS-TS12**

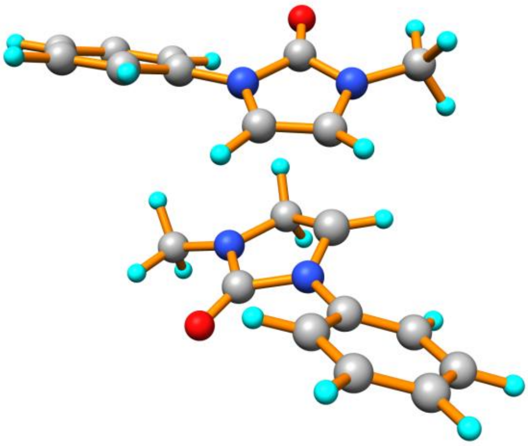


Energy = -1143.096963 Hartree

Imag. Freq. = -202.6069 cm^{-1}

47						
C						1
O					1	1.192
N		1	1.442		2	124.997
N	1	1.351	2	129.753	3	181.2
C	3	1.314	1	109.908	2	184.7
H	5	1.078	3	122.117	1	191.7
C	3	1.419	1	124.588	2	357.6
C	7	1.385	3	120.103	1	326.0
C	7	1.387	3	118.521	1	147.8
C	8	1.382	7	118.637	3	182.2
H	8	1.076	7	120.528	3	3.3
C	9	1.380	7	119.192	3	177.4
H	9	1.080	7	120.629	3	355.2
C	10	1.383	8	120.644	7	0.3
H	10	1.078	8	119.236	7	180.3
H	12	1.078	9	119.603	7	179.4
H	14	1.078	10	119.991	8	180.2
C	4	1.441	1	121.610	2	349.1
H	18	1.083	4	107.700	1	16.9
H	18	1.085	4	110.303	1	136.3
H	18	1.087	4	111.056	1	257.6
C	4	1.428	1	112.028	2	186.2
H	22	1.095	4	112.401	1	102.5
C	22	3.454	4	119.998	1	258.0
O	24	1.202	22	120.664	4	238.6
N	24	1.380	22	72.010	4	111.7
N	24	1.400	22	70.034	4	358.0
C	26	1.391	24	109.238	22	298.3
C	26	1.417	24	126.153	22	114.3
C	29	1.391	26	119.160	24	182.8
C	29	1.388	26	120.949	24	2.5
C	30	1.383	29	119.943	26	179.4
H	30	1.079	29	121.681	26	357.9
C	31	1.382	29	119.236	26	180.5
H	31	1.074	29	120.243	26	0.8
C	32	1.381	30	120.489	29	0.1
H	32	1.078	30	119.190	29	179.5
H	34	1.078	31	118.722	29	180.2
H	36	1.078	32	120.361	30	179.8
C	27	1.443	24	121.276	22	241.4
H	40	1.085	27	110.566	24	254.3
H	40	1.083	27	107.068	24	13.1
H	40	1.085	27	110.306	24	132.8
C	27	1.341	24	110.317	22	65.5
H	44	1.074	27	122.717	24	176.5
H	22	1.090	4	113.458	1	224.6
H	28	1.073	26	122.366	24	199.3

Molecule: **RS-TS13**

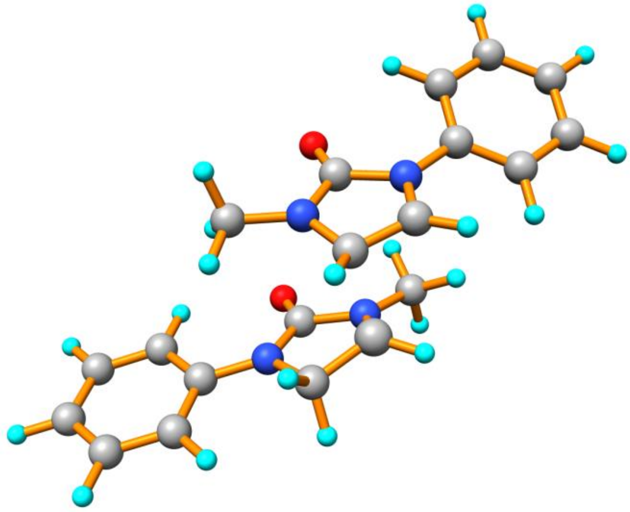


Energy = -1143.096130 Hartree

Imag. Freq. = -208.0142 cm^{-1}

47						
C						1
O					1	1.193
N			1	1.437	2	124.996
N	1	1.352	2	129.673	3	182.0
C	3	1.322	1	109.789	2	186.9
H	5	1.076	3	120.806	1	193.0
C	3	1.419	1	124.448	2	1.0
C	7	1.385	3	120.172	1	322.0
C	7	1.386	3	118.495	1	142.9
C	8	1.382	7	118.661	3	181.6
H	8	1.076	7	120.418	3	2.9
C	9	1.380	7	119.268	3	178.0
H	9	1.080	7	120.457	3	355.7
C	10	1.383	8	120.600	7	0.3
H	10	1.078	8	119.301	7	180.3
H	12	1.078	9	119.650	7	179.6
H	14	1.078	10	119.978	8	180.1
C	4	1.441	1	121.990	2	350.3
H	18	1.085	4	110.098	1	135.8
H	18	1.087	4	110.942	1	257.4
H	18	1.083	4	107.561	1	16.5
C	4	1.428	1	112.002	2	185.7
H	22	1.095	4	112.336	1	100.8
C	22	3.432	4	113.357	1	255.2
O	24	1.199	22	123.069	4	241.6
N	24	1.413	22	66.090	4	1.9
N	24	1.369	22	73.426	4	116.3
C	26	1.344	24	109.666	22	66.3
C	26	1.418	24	124.473	22	246.8
C	29	1.385	26	119.659	24	35.4
C	29	1.384	26	119.192	24	213.9
C	30	1.382	29	118.863	26	177.8
H	30	1.077	29	120.287	26	356.2
C	31	1.382	29	119.279	26	182.8
H	31	1.079	29	120.517	26	4.5
C	34	1.383	31	120.218	29	359.2
H	32	1.078	30	119.297	29	179.5
H	34	1.078	31	119.498	29	180.2
H	36	1.078	34	120.003	31	180.6
C	27	1.440	24	121.931	22	124.9
H	40	1.085	27	110.727	24	117.0
H	40	1.087	27	111.228	24	239.1
H	40	1.084	27	107.039	24	358.0
C	28	1.371	26	108.679	24	356.2
H	22	1.089	4	113.111	1	222.7
H	44	1.075	28	127.275	26	161.0
H	28	1.073	26	122.157	24	178.9

Molecule: **RS-TS14**



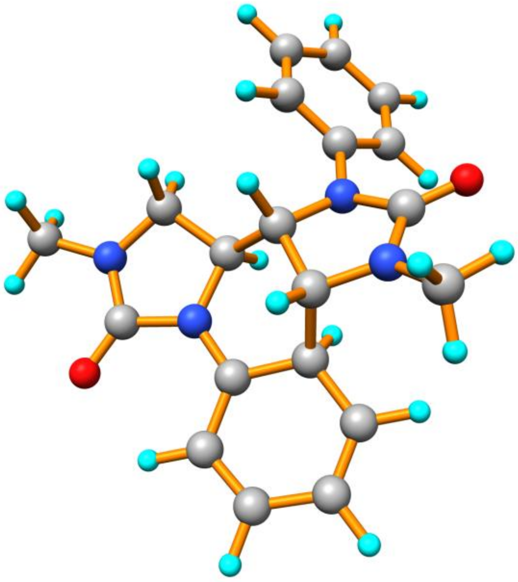
Energy = -1143.092932 Hartree

Imag. Freq. = -317.3563 cm^{-1}

47

C						
O	1	1.195				
N	1	1.359	2	131.134		
N	1	1.418	2	122.790	3	180.6
C	3	1.436	1	110.988	2	177.4
H	5	1.094	3	111.696	1	257.1
C	3	1.411	1	126.506	2	1.0
C	7	1.390	3	121.220	1	346.1
C	7	1.388	3	118.679	1	167.3
C	8	1.381	7	119.150	3	181.3
H	8	1.075	7	120.452	3	2.5
C	9	1.382	7	119.873	3	178.5
H	9	1.078	7	121.130	3	357.3
C	12	1.381	9	120.440	7	0.1
H	10	1.078	8	118.827	7	180.3
H	12	1.078	9	119.237	7	179.7
H	14	1.078	12	120.316	9	179.8
C	4	1.446	1	119.314	2	347.4
H	18	1.085	4	109.195	1	47.8
H	18	1.083	4	109.396	1	168.2
H	18	1.086	4	109.778	1	288.4
C	4	1.333	1	111.139	2	169.6
H	22	1.077	4	119.803	1	157.7
C	19	2.929	18	100.877	4	43.9
O	24	1.195	19	82.347	18	191.2
N	24	1.432	19	77.794	18	60.8
N	24	1.361	19	111.132	18	319.8
C	26	1.325	24	109.190	19	252.0
C	26	1.420	24	124.385	19	71.1
C	29	1.385	26	119.950	24	29.3
C	29	1.387	26	119.026	24	207.9
C	30	1.382	29	118.709	26	178.6
H	30	1.075	29	120.505	26	358.2
C	31	1.380	29	119.504	26	181.9
H	31	1.080	29	120.927	26	2.3
C	32	1.383	30	120.823	29	359.6
H	32	1.078	30	119.069	29	180.0
H	34	1.078	31	119.591	29	180.0
H	36	1.078	32	120.108	30	180.1
C	27	1.446	24	120.800	19	255.5
H	40	1.085	27	109.943	24	289.8
H	40	1.086	27	109.580	24	49.8
H	40	1.083	27	109.331	24	169.4
C	27	1.381	24	110.503	19	75.5
H	5	1.086	3	111.892	1	136.0
H	44	1.076	27	120.947	24	158.4
H	28	1.075	26	122.652	24	183.5

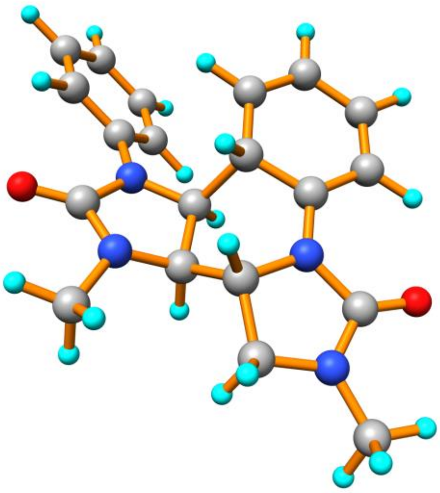
Molecule: **SRS-I22**



Energy = -1143.122346 Hartree

47						
C						1
O				1		1.197
N		1	1.387	2		127.283
N	1	1.375	2	126.463	3	179.2
C	4	1.412	1	111.516	2	185.9
C	3	1.437	1	110.676	2	193.5
H	6	1.093	3	112.342	1	90.5
H	5	1.086	4	112.419	1	217.2
C	3	1.411	1	121.966	2	351.0
C	9	1.386	3	119.191	1	54.3
C	9	1.386	3	120.612	1	233.9
C	10	1.380	9	119.506	3	179.4
H	10	1.077	9	119.534	3	358.1
C	11	1.384	9	119.832	3	181.6
H	11	1.080	9	120.392	3	4.1
C	14	1.382	11	120.163	9	359.0
H	12	1.078	10	119.382	9	179.5
H	14	1.079	11	119.611	9	180.3
H	16	1.078	14	120.119	11	180.5
C	4	1.436	1	122.189	2	12.0
H	20	1.087	4	111.964	1	232.7
H	20	1.084	4	106.915	1	351.9
H	20	1.088	4	111.180	1	111.0
C	6	3.620	3	139.525	1	222.1
O	24	1.198	6	148.332	3	124.0
N	24	1.435	6	29.330	3	76.7
N	24	1.335	6	79.737	3	284.7
C	27	1.435	24	114.377	6	6.7
C	26	1.453	24	111.431	6	327.1
H	29	1.091	26	108.562	24	256.0
H	28	1.085	27	111.578	24	134.8
C	26	1.323	24	126.692	6	153.3
C	32	1.405	26	124.914	24	355.5
C	32	1.474	26	113.854	24	179.7
C	33	1.362	32	118.126	26	182.7
H	33	1.074	32	120.014	26	3.1
C	34	1.467	32	115.873	26	179.0
C	37	1.340	34	121.594	32	357.5
H	35	1.080	33	117.992	32	180.2
H	37	1.078	34	116.816	32	175.8
H	38	1.077	37	121.241	34	179.7
C	27	1.438	24	121.906	6	196.6
H	42	1.086	27	110.164	24	231.6
H	42	1.083	27	107.954	24	351.1
H	42	1.088	27	110.706	24	110.7
H	28	1.091	27	110.491	24	255.2
H	34	1.099	32	109.310	26	301.9

Molecule: **SRS-I23**

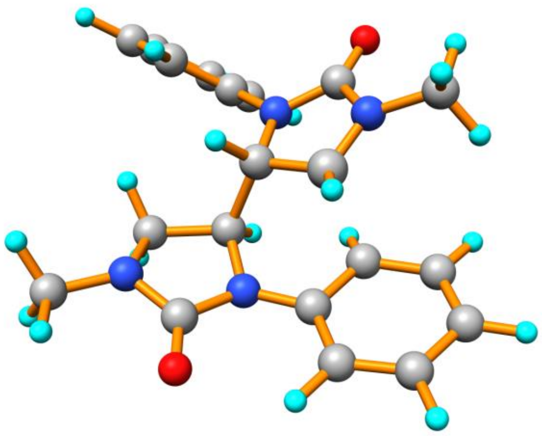


Energy = -1143.125199 Hartree

47

C						
O	1	1.198				
N	1	1.386	2	127.306		
N	1	1.376	2	125.885	3	179.4
C	4	1.426	1	111.436	2	167.6
C	3	1.419	1	111.347	2	177.6
H	6	1.084	3	112.592	1	135.0
H	5	1.094	4	112.038	1	263.3
C	3	1.411	1	124.691	2	357.6
C	9	1.389	3	120.447	1	33.3
C	9	1.389	3	119.552	1	211.7
C	10	1.381	9	119.358	3	178.9
H	10	1.076	9	119.932	3	357.4
C	11	1.382	9	119.954	3	181.8
H	11	1.079	9	120.850	3	3.3
C	14	1.382	11	120.339	9	359.5
H	12	1.078	10	119.055	9	179.4
H	14	1.078	11	119.389	9	180.3
H	16	1.078	14	120.265	11	180.5
C	4	1.437	1	119.906	2	15.8
H	20	1.088	4	110.998	1	219.9
H	20	1.084	4	107.504	1	338.7
H	20	1.091	4	111.526	1	97.9
C	5	3.529	4	143.944	1	142.6
O	24	1.198	5	146.730	4	215.4
N	24	1.431	5	32.482	4	277.7
N	24	1.337	5	79.099	4	62.5
C	27	1.435	24	115.055	5	342.1
C	26	1.445	24	111.937	5	37.2
H	29	1.090	26	108.995	24	115.4
H	28	1.090	27	110.889	24	117.6
C	26	1.326	24	127.390	5	217.4
C	32	1.400	26	124.804	24	358.9
C	32	1.480	26	113.814	24	174.4
C	33	1.366	32	118.105	26	176.9
H	33	1.074	32	120.025	26	356.7
C	34	1.469	32	115.717	26	181.3
C	37	1.342	34	121.393	32	2.6
H	35	1.080	33	117.913	32	179.6
H	37	1.078	34	117.158	32	183.7
H	38	1.077	37	120.956	34	180.0
C	27	1.438	24	122.016	5	160.9
H	42	1.087	27	110.541	24	241.6
H	42	1.083	27	107.890	24	1.1
H	42	1.087	27	110.431	24	120.6
H	28	1.088	27	110.907	24	237.6
H	34	1.097	32	109.611	26	58.2

Molecule: **SRS-TS22**

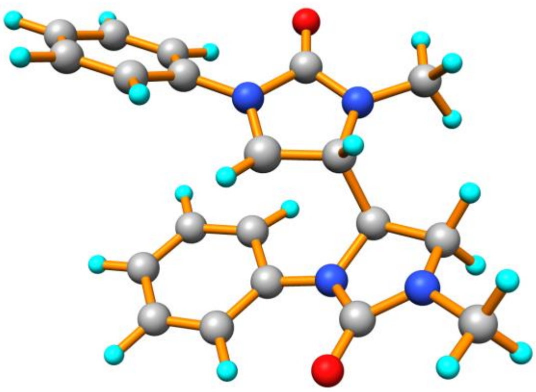


Energy = -1143.112934 Hartree

Imag. Freq. = -267.5081 cm^{-1}

47						
C						1
O				1		1.192
N		1	1.362	2		130.000
N	1	1.417	2	124.592	3	180.3
C	4	1.329	1	111.466	2	186.9
C	3	1.435	1	112.334	2	183.6
H	6	1.096	3	112.336	1	103.2
H	5	1.078	4	119.097	1	201.8
C	3	1.420	1	122.592	2	351.1
C	9	1.383	3	119.473	1	67.3
C	9	1.386	3	119.677	1	248.2
C	10	1.383	9	119.297	3	180.6
H	10	1.078	9	119.748	3	359.4
C	11	1.382	9	119.455	3	180.4
H	11	1.080	9	120.163	3	1.8
C	12	1.383	10	120.239	9	359.3
H	12	1.078	10	119.614	9	179.4
H	14	1.078	11	119.772	9	180.1
H	16	1.078	12	119.963	10	180.3
C	4	1.440	1	121.283	2	1.9
H	20	1.086	4	110.392	1	247.2
H	20	1.083	4	107.070	1	6.5
H	20	1.085	4	110.310	1	126.1
C	7	3.258	6	81.469	3	154.7
O	24	1.199	7	136.464	6	121.2
N	24	1.416	7	61.532	6	8.3
N	24	1.349	7	65.770	6	242.1
C	27	1.435	24	112.449	7	58.4
C	26	1.434	24	110.815	7	315.9
H	29	1.086	26	112.050	24	222.7
H	28	1.091	27	111.529	24	96.5
C	26	1.361	24	126.271	7	115.4
C	32	1.398	26	123.763	24	9.6
C	32	1.420	26	116.184	24	197.2
C	33	1.372	32	118.909	26	186.6
H	33	1.074	32	119.707	26	6.3
C	34	1.415	32	119.168	26	176.9
C	37	1.362	34	120.513	32	354.6
H	35	1.079	33	118.396	32	179.9
H	37	1.079	34	118.659	32	173.2
H	38	1.077	37	120.857	34	181.0
C	27	1.438	24	121.185	7	217.4
H	42	1.089	27	111.084	24	258.7
H	42	1.083	27	107.849	24	18.2
H	42	1.086	27	110.266	24	137.5
H	28	1.086	27	111.902	24	217.8
H	34	1.081	32	119.222	26	331.9

Molecule: **SRS-TS23**

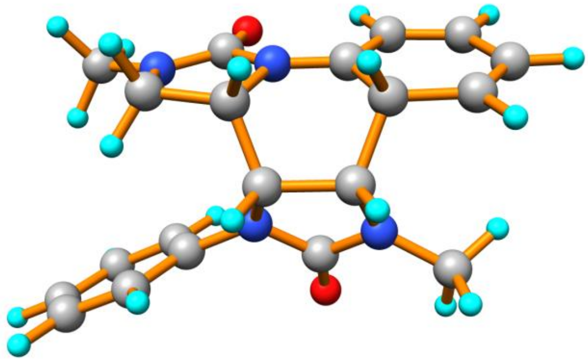


Energy = -1143.113437 Hartree

Imag. Freq. = -241.2620 cm^{-1}

47						
C						1
O					1	1.192
N			1	1.429	2	125.490
N	1	1.354	2	129.052	3	180.3
C	4	1.429	1	112.822	2	175.6
C	3	1.328	1	110.759	2	175.7
H	6	1.076	3	119.781	1	158.9
H	5	1.097	4	112.127	1	255.0
C	3	1.418	1	123.751	2	359.1
C	9	1.385	3	119.725	1	39.5
C	9	1.385	3	118.988	1	218.3
C	10	1.382	9	118.745	3	178.4
H	10	1.076	9	120.338	3	357.2
C	11	1.380	9	119.258	3	182.0
H	11	1.079	9	120.633	3	3.8
C	12	1.383	10	120.547	9	359.7
H	12	1.078	10	119.309	9	179.7
H	14	1.078	11	119.609	9	180.4
H	16	1.078	12	119.990	10	179.9
C	4	1.439	1	121.520	2	8.3
H	20	1.088	4	111.028	1	108.8
H	20	1.087	4	111.073	1	230.9
H	20	1.084	4	107.408	1	349.8
C	8	3.226	5	82.341	4	206.4
O	24	1.199	8	136.360	5	237.5
N	24	1.412	8	62.639	5	351.8
N	24	1.353	8	64.925	5	118.1
C	27	1.433	24	112.077	8	300.2
C	26	1.431	24	110.558	8	43.5
H	29	1.087	26	111.898	24	138.7
H	28	1.088	27	111.536	24	143.2
C	26	1.368	24	126.178	8	245.5
C	32	1.396	26	123.596	24	350.5
C	32	1.417	26	116.452	24	162.9
C	33	1.375	32	118.916	26	172.3
H	33	1.074	32	119.785	26	353.0
C	34	1.410	32	119.603	26	185.6
C	37	1.365	34	120.305	32	3.1
H	35	1.079	33	118.369	32	180.2
H	37	1.078	34	118.864	32	183.0
H	38	1.077	37	120.691	34	178.8
C	27	1.438	24	121.022	8	142.7
H	42	1.086	27	110.255	24	221.1
H	42	1.083	27	107.782	24	340.4
H	42	1.089	27	111.184	24	99.9
H	28	1.091	27	111.689	24	264.5
H	34	1.080	32	119.652	26	26.3

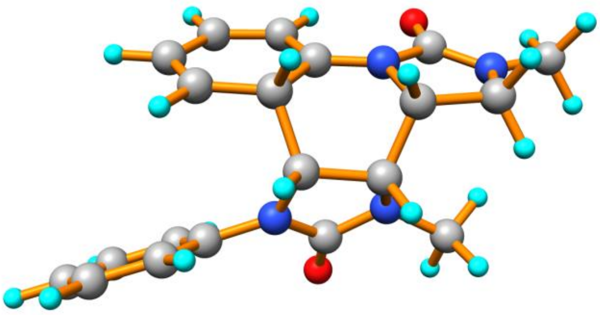
Molecule: **SSS-I22**



Energy = -1143.124440 Hartree

47						
C						1
O				1		1.197
N		1	1.385		2	126.446
N	1	1.373	2	126.164	3	180.1
C	4	1.419	1	112.682	2	183.1
C	3	1.434	1	111.816	2	171.0
H	6	1.090	3	112.763	1	251.6
H	5	1.090	4	111.695	1	123.6
C	3	1.418	1	119.579	2	14.0
C	9	1.384	3	118.639	1	296.2
C	9	1.386	3	121.059	1	115.4
C	10	1.383	9	119.605	3	179.5
H	10	1.078	9	119.318	3	0.7
C	11	1.383	9	119.701	3	179.3
H	11	1.080	9	120.587	3	358.5
C	14	1.383	11	120.221	9	1.4
H	12	1.078	10	119.508	9	181.0
H	14	1.078	11	119.590	9	180.2
H	16	1.078	14	120.051	11	179.2
C	4	1.438	1	120.162	2	344.4
H	20	1.084	4	106.903	1	7.2
H	20	1.085	4	111.989	1	126.2
H	20	1.089	4	110.864	1	248.4
C	3	3.318	1	115.951	2	259.4
O	24	1.197	3	124.736	1	32.6
N	24	1.439	3	58.543	1	280.2
N	24	1.333	3	78.831	1	164.2
C	27	1.435	24	114.895	3	56.9
C	26	1.444	24	111.254	3	299.9
H	29	1.089	26	109.955	24	229.6
H	28	1.089	27	110.762	24	107.2
C	26	1.318	24	126.992	3	105.0
C	32	1.406	26	124.843	24	11.6
C	32	1.481	26	113.697	24	193.2
C	33	1.359	32	117.988	26	178.9
H	33	1.074	32	119.903	26	359.2
C	34	1.473	32	115.373	26	182.1
C	37	1.337	34	121.575	32	358.1
H	35	1.080	33	118.125	32	180.5
H	37	1.080	34	117.120	32	177.4
H	38	1.077	37	121.147	34	179.4
C	27	1.437	24	122.325	3	234.1
H	42	1.087	27	110.489	24	242.1
H	42	1.083	27	107.963	24	1.6
H	42	1.087	27	109.764	24	121.0
H	28	1.086	27	110.767	24	227.8
H	34	1.097	32	107.736	26	301.5

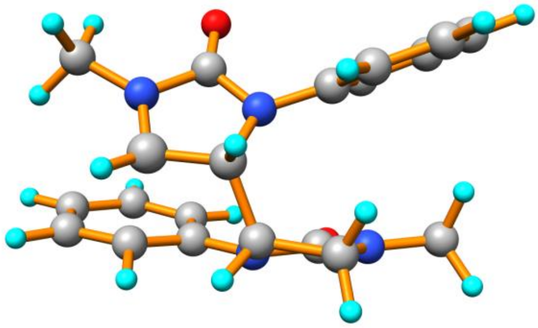
Molecule: **SSS-I23**



Energy = -1143.124451 Hartree

47						
C						1
O				1		1.198
N		1	1.378	2		126.919
N	1	1.381	2	125.745	3	179.9
C	4	1.430	1	111.209	2	191.4
C	3	1.421	1	111.940	2	180.9
H	6	1.086	3	112.282	1	228.5
H	5	1.093	4	112.033	1	101.4
C	3	1.411	1	123.938	2	1.7
C	9	1.387	3	120.218	1	320.0
C	9	1.388	3	119.689	1	140.4
C	10	1.381	9	119.425	3	180.6
H	10	1.076	9	119.729	3	2.0
C	11	1.382	9	119.931	3	178.5
H	11	1.080	9	120.559	3	356.9
C	14	1.382	11	120.191	9	1.0
H	12	1.078	10	119.253	9	180.7
H	14	1.078	11	119.537	9	179.9
H	16	1.078	14	120.164	11	179.3
C	4	1.442	1	117.675	2	340.8
H	20	1.084	4	107.029	1	12.5
H	20	1.086	4	111.718	1	131.0
H	20	1.090	4	111.048	1	253.8
C	22	3.170	20	115.688	4	4.3
O	24	1.197	22	118.133	20	244.0
N	24	1.431	22	91.087	20	15.1
N	24	1.339	22	54.934	20	123.6
C	27	1.435	24	114.626	22	275.2
C	26	1.443	24	111.453	22	49.9
H	29	1.090	26	110.202	24	127.7
H	28	1.088	27	111.338	24	131.2
C	26	1.325	24	126.749	22	245.6
C	32	1.400	26	124.988	24	351.5
C	32	1.481	26	113.749	24	171.0
C	33	1.364	32	118.012	26	181.5
H	33	1.074	32	120.032	26	1.3
C	34	1.473	32	115.623	26	176.9
C	37	1.340	34	121.397	32	2.5
H	35	1.080	33	117.900	32	180.1
H	37	1.078	34	117.339	32	182.9
H	38	1.077	37	121.012	34	179.9
C	27	1.438	24	121.873	22	104.0
H	42	1.087	27	110.327	24	233.2
H	42	1.083	27	107.937	24	352.6
H	42	1.087	27	110.693	24	112.2
H	28	1.089	27	110.877	24	251.4
H	34	1.097	32	106.660	26	58.1

Molecule: **SSS-TS22**



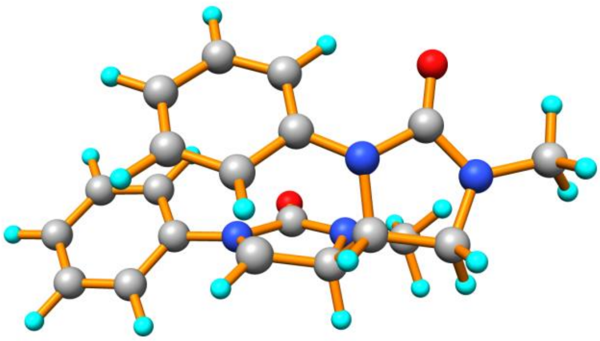
Energy = -1143.112857 Hartree

Imag. Freq. = -286.2390 cm^{-1}

47

C						1
O					1	1.191
N		1	1.369	2	129.586	
N	1	1.413	2	124.346	3	178.2
C	4	1.327	1	111.138	2	175.4
C	3	1.437	1	111.771	2	175.4
H	6	1.094	3	112.431	1	255.3
H	5	1.078	4	119.223	1	155.4
C	3	1.424	1	119.660	2	14.2
C	9	1.384	3	118.791	1	298.8
C	9	1.385	3	120.383	1	116.0
C	10	1.382	9	119.303	3	176.8
H	10	1.078	9	119.719	3	357.4
C	11	1.384	9	119.476	3	182.1
H	11	1.080	9	120.613	3	0.3
C	14	1.384	11	120.131	9	1.3
H	12	1.078	10	119.438	9	180.7
H	14	1.078	11	119.601	9	179.8
H	16	1.078	14	119.990	11	178.9
C	4	1.443	1	121.125	2	352.9
H	20	1.083	4	110.044	1	135.8
H	20	1.086	4	110.339	1	257.3
H	20	1.083	4	107.138	1	16.3
C	3	3.162	1	124.642	2	268.8
O	24	1.202	3	117.039	1	41.6
N	24	1.417	3	63.312	1	283.4
N	24	1.342	3	84.141	1	171.8
C	27	1.429	24	113.744	3	60.0
C	26	1.435	24	109.923	3	299.2
H	29	1.087	26	112.757	24	220.8
H	28	1.090	27	111.569	24	106.2
C	26	1.363	24	125.138	3	89.1
C	32	1.397	26	124.448	24	0.3
C	32	1.419	26	115.847	24	185.7
C	33	1.372	32	118.679	26	184.7
H	33	1.074	32	119.879	26	4.5
C	34	1.415	32	119.596	26	180.4
C	37	1.361	34	120.052	32	352.8
H	35	1.079	33	118.348	32	178.5
H	37	1.079	34	118.956	32	173.3
H	38	1.078	37	120.973	34	182.0
C	27	1.434	24	122.842	3	241.3
H	42	1.087	27	110.933	24	241.6
H	42	1.083	27	107.737	24	1.2
H	42	1.088	27	109.853	24	120.3
H	28	1.087	27	111.121	24	227.2
H	34	1.080	32	117.493	26	333.0

Molecule: **SSS-TS23**



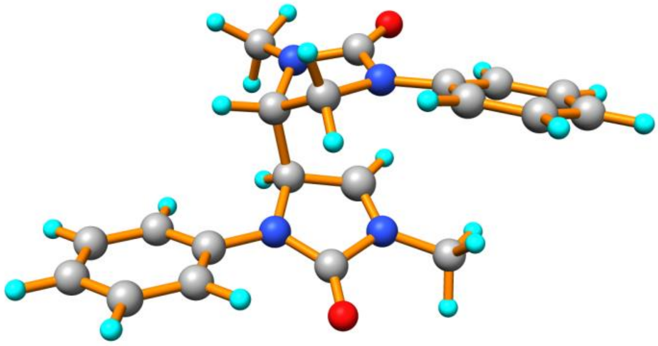
Energy = -1143.111074 Hartree

Imag. Freq. = -287.7437 cm^{-1}

47

C						1
O				1		1.192
N		1	1.425	2		125.223
N	1	1.360	2	128.638	3	178.0
C	4	1.430	1	112.052	2	187.6
C	3	1.329	1	110.267	2	181.9
H	6	1.076	3	119.422	1	203.8
H	5	1.096	4	111.691	1	102.9
C	3	1.418	1	123.917	2	4.0
C	9	1.385	3	119.963	1	320.4
C	9	1.385	3	118.968	1	140.6
C	10	1.380	9	118.858	3	180.6
H	10	1.076	9	120.094	3	0.8
C	11	1.382	9	119.407	3	178.7
H	11	1.080	9	120.799	3	356.4
C	14	1.383	11	120.065	9	0.9
H	12	1.078	10	119.301	9	180.3
H	14	1.078	11	119.598	9	179.8
H	16	1.078	14	119.998	11	179.4
C	4	1.445	1	119.014	2	344.6
H	20	1.084	4	107.087	1	10.6
H	20	1.083	4	111.306	1	129.6
H	20	1.089	4	110.498	1	252.2
C	22	2.899	20	122.153	4	3.8
O	24	1.200	22	112.271	20	240.7
N	24	1.407	22	95.259	20	12.6
N	24	1.351	22	57.939	20	118.9
C	27	1.432	24	113.287	22	270.0
C	26	1.433	24	111.366	22	51.1
H	29	1.089	26	112.424	24	132.3
H	28	1.089	27	111.554	24	133.2
C	26	1.369	24	125.303	22	256.4
C	32	1.393	26	124.210	24	8.2
C	32	1.415	26	115.880	24	182.5
C	33	1.375	32	118.554	26	174.6
H	33	1.075	32	120.064	26	354.7
C	34	1.413	32	119.832	26	181.4
C	37	1.363	34	119.835	32	5.6
H	35	1.079	33	118.343	32	181.3
H	37	1.079	34	119.237	32	184.6
H	38	1.077	37	120.759	34	177.5
C	27	1.436	24	121.897	22	105.0
H	42	1.084	27	107.680	24	347.7
H	42	1.088	27	111.059	24	107.2
H	42	1.087	27	110.617	24	228.4
H	28	1.090	27	111.358	24	253.7
H	34	1.080	32	117.468	26	26.4

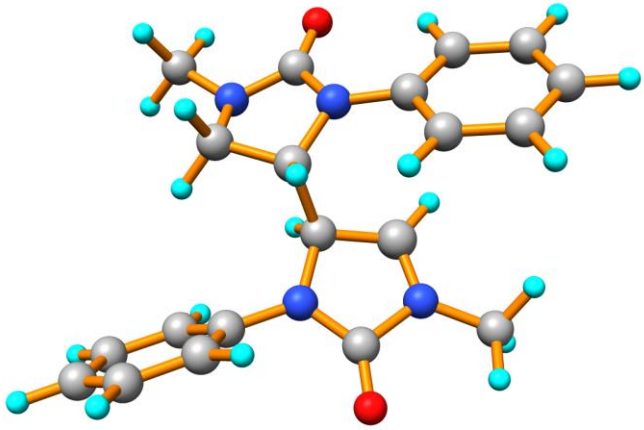
Molecule: **SS-I11**



Energy = -1143.120426 Hartree

47						
C	1					
O	1	1.200				
N	1	1.395	2	127.478		
N	1	1.371	2	126.618	3	185.4
C	3	1.443	1	109.158	2	169.8
H	5	1.089	3	112.420	1	274.7
C	3	1.405	1	126.376	2	0.2
C	7	1.392	3	120.486	1	334.2
C	7	1.389	3	119.203	1	160.1
C	8	1.381	7	119.282	3	186.9
H	8	1.076	7	120.171	3	8.7
C	9	1.383	7	119.821	3	173.0
H	9	1.078	7	120.792	3	351.6
C	12	1.382	9	120.463	7	0.1
H	10	1.079	8	119.028	7	180.5
H	12	1.078	9	119.267	7	179.6
H	14	1.078	12	120.272	9	179.9
C	4	1.438	1	121.658	2	3.7
H	18	1.084	4	107.358	1	342.3
H	18	1.090	4	112.212	1	101.3
H	18	1.085	4	110.428	1	223.2
C	4	1.425	1	109.747	2	163.9
H	22	1.085	4	113.527	1	155.2
C	5	3.403	3	97.030	1	111.0
O	24	1.189	5	132.064	3	113.6
N	24	1.352	5	61.078	3	236.9
N	24	1.453	5	71.403	3	356.8
C	26	1.436	24	111.828	5	55.2
C	26	1.420	24	125.118	5	238.4
C	29	1.386	26	120.488	24	27.4
C	29	1.386	26	118.828	24	206.5
C	30	1.382	29	118.997	26	179.6
H	30	1.076	29	120.565	26	358.4
C	31	1.382	29	119.572	26	181.1
H	31	1.079	29	121.026	26	2.3
C	34	1.382	31	120.253	29	359.4
H	32	1.078	30	119.086	29	179.5
H	34	1.078	31	119.428	29	180.2
H	36	1.078	34	120.125	31	180.5
C	27	1.450	24	120.119	5	129.4
H	40	1.085	27	108.980	24	286.2
H	40	1.083	27	108.260	24	45.3
H	40	1.082	27	108.941	24	166.6
C	27	1.285	24	110.946	5	309.1
H	5	1.086	3	111.217	1	152.0
H	28	1.090	26	112.633	24	122.1
H	44	1.078	27	122.693	24	187.4

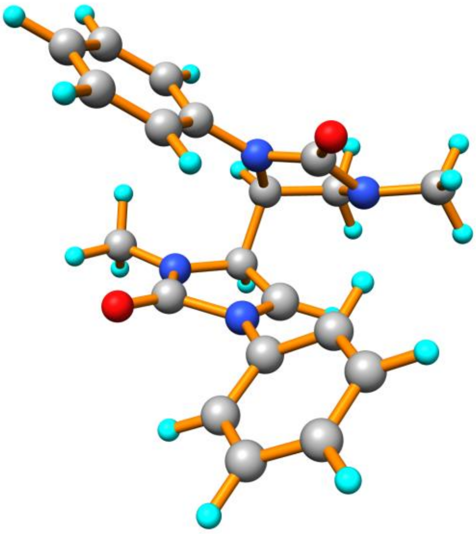
Molecule: **SS-I12**



Energy = -1143.118116 Hartree

47						
C						1
O				1		1.200
N		1	1.401	2		126.660
N	1	1.364	2	126.824	3	181.5
C	3	1.429	1	110.021	2	187.4
H	5	1.084	3	113.541	1	216.8
C	3	1.396	1	126.362	2	352.7
C	7	1.396	3	122.234	1	354.3
C	7	1.397	3	118.595	1	177.9
C	8	1.379	7	119.459	3	183.8
H	8	1.074	7	119.713	3	4.5
C	9	1.388	7	120.467	3	176.3
H	9	1.078	7	120.871	3	352.1
C	12	1.378	9	120.377	7	359.9
H	10	1.079	8	118.627	7	180.4
H	12	1.079	9	119.160	7	178.3
H	14	1.078	12	120.558	9	179.5
C	4	1.439	1	120.003	2	344.4
H	18	1.083	4	107.817	1	26.6
H	18	1.085	4	110.150	1	145.9
H	18	1.089	4	111.439	1	267.2
C	4	1.433	1	110.422	2	194.0
H	22	1.092	4	112.027	1	88.2
C	6	3.372	5	86.434	3	237.8
O	24	1.188	6	134.041	5	195.9
N	24	1.348	6	44.599	5	306.8
N	24	1.455	6	84.197	5	64.5
C	26	1.437	24	112.518	6	62.2
C	26	1.423	24	122.667	6	240.7
C	29	1.382	26	119.567	24	58.2
C	29	1.385	26	119.200	24	239.2
C	30	1.383	29	119.063	26	180.7
H	30	1.078	29	120.030	26	359.5
C	31	1.382	29	119.199	26	180.2
H	31	1.080	29	120.311	26	1.2
C	32	1.383	30	120.247	29	359.3
H	32	1.078	30	119.575	29	179.4
H	34	1.078	31	119.720	29	180.0
H	36	1.078	32	119.932	30	180.3
C	27	1.448	24	120.698	6	141.4
H	40	1.083	27	106.960	24	347.8
H	40	1.084	27	109.859	24	106.7
H	40	1.084	27	109.005	24	227.9
C	27	1.284	24	110.824	6	323.0
H	44	1.077	27	123.034	24	183.8
H	22	1.085	4	112.184	1	210.5
H	28	1.095	26	112.742	24	118.8

Molecule: **SS-I13**

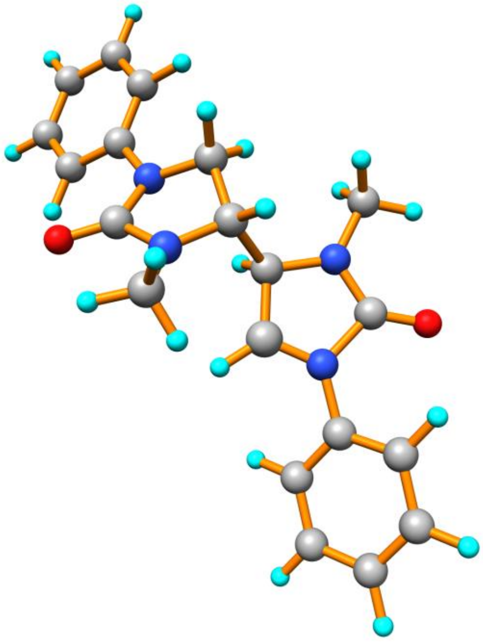


Energy = -1143.121189 Hartree

47

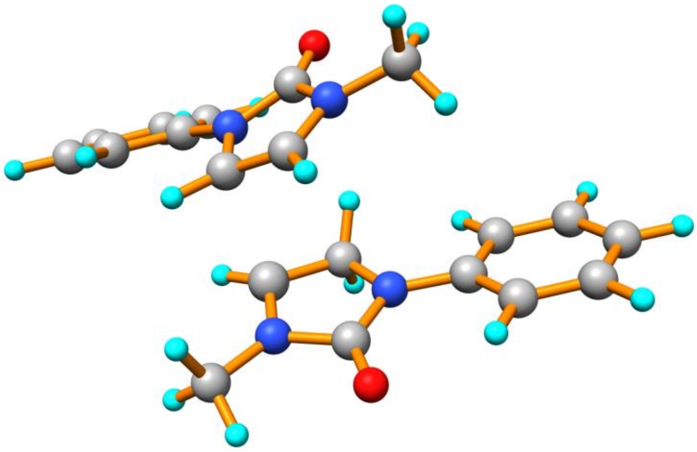
C						1
O				1		1.200
N		1	1.378	2	127.770	
N	1	1.387	2	125.796	3	183.7
C	3	1.428	1	110.294	2	188.5
H	5	1.085	3	112.539	1	213.0
C	3	1.416	1	124.315	2	6.9
C	7	1.385	3	120.245	1	313.2
C	7	1.387	3	119.229	1	132.8
C	8	1.382	7	119.335	3	180.0
H	8	1.078	7	119.860	3	1.4
C	9	1.382	7	119.639	3	179.0
H	9	1.080	7	120.193	3	357.5
C	10	1.383	8	120.488	7	0.8
H	10	1.078	8	119.368	7	180.3
H	12	1.078	9	119.627	7	180.0
H	14	1.078	10	120.099	8	179.6
C	4	1.441	1	118.798	2	339.5
H	18	1.084	4	107.863	1	28.8
H	18	1.086	4	110.498	1	148.7
H	18	1.089	4	111.340	1	269.8
C	4	1.439	1	109.277	2	194.7
H	22	1.091	4	112.023	1	86.2
C	11	3.032	8	94.055	7	293.8
O	24	1.186	11	80.947	8	262.4
N	24	1.477	11	86.957	8	137.8
N	24	1.339	11	104.946	8	33.8
C	26	1.283	24	110.135	11	255.6
C	26	1.421	24	122.928	11	75.4
C	29	1.384	26	119.638	24	44.0
C	29	1.385	26	117.979	24	223.9
C	30	1.380	29	118.111	26	178.8
H	30	1.076	29	120.754	26	358.7
C	31	1.380	29	118.556	26	181.1
H	31	1.079	29	120.451	26	4.5
C	34	1.384	31	120.018	29	359.8
H	32	1.078	30	119.395	29	180.4
H	34	1.078	31	119.650	29	180.9
H	36	1.078	34	119.777	31	180.3
C	27	1.443	24	122.243	11	269.8
H	40	1.083	27	107.363	24	353.0
H	40	1.086	27	110.967	24	111.5
H	40	1.086	27	110.114	24	234.0
C	27	1.428	24	112.646	11	83.6
H	22	1.089	4	111.850	1	208.1
H	28	1.075	26	122.361	24	186.6
H	44	1.090	27	112.530	24	129.9

Molecule: **SS-I14**

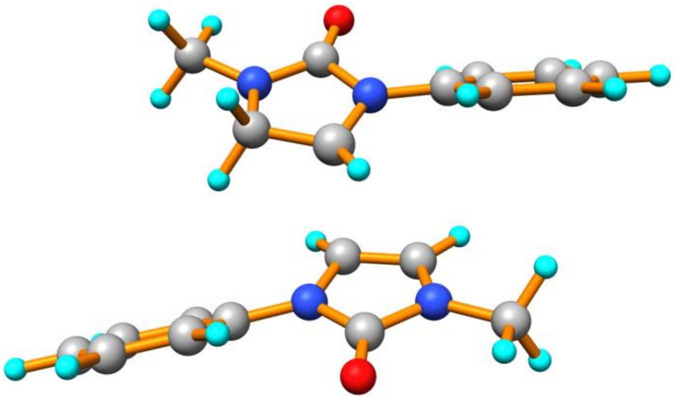


Energy = -1143.107990 Hartree

47						
C						1
O					1	1.199
N		1	1.378	2		128.907
N	1	1.385	2	124.795	3	181.7
C	3	1.439	1	109.574	2	164.2
H	5	1.091	3	112.071	1	271.4
C	3	1.409	1	124.364	2	6.4
C	7	1.389	3	120.471	1	325.9
C	7	1.387	3	119.527	1	147.7
C	8	1.380	7	119.373	3	181.3
H	8	1.075	7	120.076	3	2.4
C	9	1.383	7	119.918	3	178.2
H	9	1.079	7	120.895	3	357.3
C	12	1.381	9	120.412	7	0.3
H	10	1.078	8	119.012	7	180.4
H	12	1.078	9	119.302	7	179.9
H	14	1.078	12	120.313	9	179.7
C	4	1.433	1	121.886	2	344.5
H	18	1.085	4	107.082	1	10.8
H	18	1.091	4	112.200	1	129.9
H	18	1.088	4	111.692	1	251.3
C	4	1.421	1	111.530	2	175.3
H	22	1.087	4	112.918	1	142.5
C	23	3.473	22	83.587	4	124.1
O	24	1.186	23	137.561	22	159.1
N	24	1.479	23	81.795	22	291.4
N	24	1.340	23	43.128	22	52.7
C	26	1.282	24	109.648	23	36.6
C	26	1.421	24	123.118	23	213.9
C	29	1.385	26	119.440	24	41.6
C	29	1.386	26	118.373	24	220.8
C	30	1.381	29	118.165	26	178.3
H	30	1.076	29	120.830	26	358.3
C	31	1.379	29	118.740	26	181.8
H	31	1.080	29	120.738	26	4.1
C	32	1.384	30	120.501	29	0.3
H	32	1.078	30	119.335	29	180.3
H	34	1.078	31	119.673	29	180.6
H	36	1.078	32	119.807	30	179.6
C	27	1.444	24	121.160	23	123.0
H	40	1.084	27	107.430	24	1.7
H	40	1.086	27	110.406	24	120.6
H	40	1.086	27	111.005	24	242.7
C	27	1.431	24	113.076	23	299.1
H	5	1.086	3	110.898	1	149.9
H	28	1.077	26	122.844	24	180.5
H	44	1.098	27	112.342	24	245.1

Molecule: **SS-TS11**  Energy = -1143.097558 Hartree Imag. Freq. = -173.8029 cm^{-1}	47 C 1 O 1 1.194 N 1 1.356 2 132.015 N 1 1.433 2 122.496 3 181.7 C 3 1.435 1 111.037 2 176.7 H 5 1.094 3 112.127 1 256.3 C 3 1.415 1 126.364 2 2.7 C 7 1.388 3 121.102 1 345.7 C 7 1.388 3 118.533 1 167.1 C 8 1.382 7 119.029 3 181.3 H 8 1.075 7 120.578 3 2.1 C 9 1.382 7 119.724 3 178.5 H 9 1.078 7 121.267 3 357.6 C 12 1.382 9 120.404 7 0.1 H 10 1.078 8 118.867 7 180.3 H 12 1.078 9 119.237 7 179.7 H 14 1.078 12 120.261 9 179.7 C 4 1.443 1 120.379 2 1.6 H 18 1.083 4 109.872 1 215.7 H 18 1.083 4 107.364 1 335.7 H 18 1.087 4 110.315 1 94.1 C 4 1.307 1 110.595 2 172.0 H 22 1.079 4 122.449 1 170.6 C 5 3.341 3 115.449 1 106.9 O 24 1.201 5 119.322 3 115.3 N 24 1.378 5 71.418 3 241.2 N 24 1.401 5 71.646 3 354.1 C 26 1.388 24 109.708 5 63.8 C 26 1.416 24 125.454 5 248.0 C 29 1.387 26 120.310 24 28.4 C 29 1.387 26 119.091 24 207.0 C 30 1.382 29 119.073 26 178.4 H 30 1.076 29 120.139 26 356.5 C 31 1.382 29 119.593 26 182.4 H 31 1.079 29 120.708 26 5.0 C 34 1.383 31 120.282 29 359.2 H 32 1.078 30 119.137 29 179.4 H 34 1.078 31 119.431 29 180.4 H 36 1.078 34 120.126 31 180.7 C 27 1.445 24 121.469 5 117.1 H 40 1.084 27 110.273 24 229.3 H 40 1.083 27 106.907 24 348.8 H 40 1.085 27 110.378 24 107.4 C 27 1.341 24 110.380 5 293.9 H 5 1.087 3 112.577 1 134.9 H 28 1.073 26 121.876 24 161.2 H 44 1.074 27 122.424 24 183.4

Molecule: **SS-TS12**

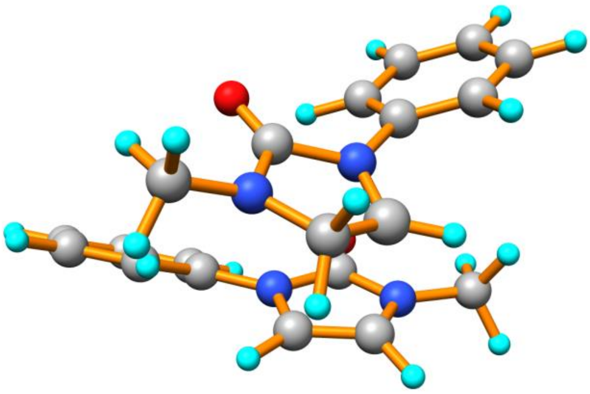


Energy = -1143.097571 Hartree

Imag. Freq. = -228.1080 cm^{-1}

47						
C						1
O					1	1.193
N		1	1.445	2		124.598
N	1	1.345	2	130.204	3	180.7
C	3	1.320	1	110.556	2	184.9
H	5	1.079	3	121.789	1	197.0
C	3	1.414	1	124.260	2	357.9
C	7	1.387	3	120.087	1	325.1
C	7	1.387	3	118.719	1	147.9
C	8	1.382	7	118.745	3	183.2
H	8	1.076	7	120.364	3	4.2
C	9	1.382	7	119.352	3	176.7
H	9	1.080	7	120.503	3	354.0
C	10	1.384	8	120.680	7	0.1
H	10	1.078	8	119.227	7	180.3
H	12	1.078	9	119.620	7	178.8
H	14	1.078	10	120.012	8	180.4
C	4	1.440	1	122.274	2	352.8
H	18	1.083	4	107.636	1	12.8
H	18	1.086	4	110.312	1	132.1
H	18	1.087	4	110.976	1	253.5
C	4	1.429	1	112.307	2	185.8
H	22	1.095	4	112.084	1	102.5
C	6	2.761	5	117.123	3	234.0
O	24	1.200	6	122.753	5	213.5
N	24	1.378	6	68.669	5	337.8
N	24	1.401	6	71.516	5	92.2
C	26	1.389	24	109.734	6	61.0
C	26	1.416	24	124.729	6	238.0
C	29	1.386	26	120.222	24	36.4
C	29	1.387	26	119.034	24	215.6
C	30	1.382	29	119.002	26	179.0
H	30	1.077	29	120.052	26	357.3
C	31	1.382	29	119.511	26	181.8
H	31	1.079	29	120.535	26	4.1
C	34	1.383	31	120.236	29	359.1
H	32	1.078	30	119.183	29	179.3
H	34	1.078	31	119.483	29	180.4
H	36	1.078	34	120.102	31	180.7
C	27	1.443	24	121.509	6	119.7
H	40	1.085	27	110.572	24	107.2
H	40	1.085	27	109.907	24	228.6
H	40	1.083	27	107.038	24	348.3
C	27	1.340	24	110.556	6	297.3
H	44	1.074	27	122.670	24	181.9
H	22	1.087	4	113.159	1	224.3
H	28	1.074	26	121.981	24	165.0

Molecule: **SS-TS13**



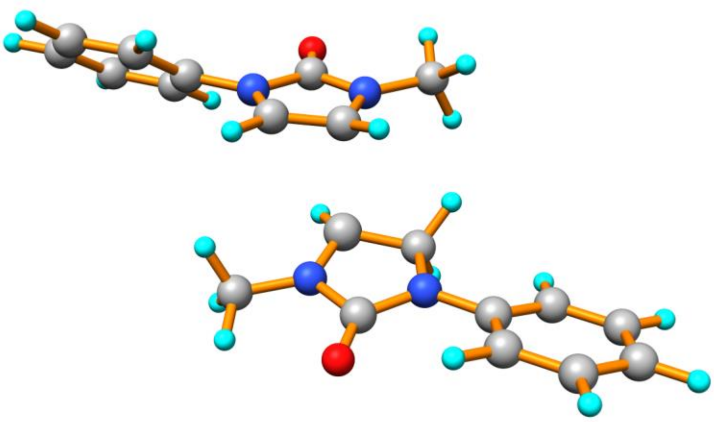
Energy = -1143.099205 Hartree

Imag. Freq. = -170.8280 cm^{-1}

47

C						1
O				1		1.190
N		1	1.445	2		125.174
N	1	1.355	2	129.502	3	180.3
C	3	1.315	1	109.725	2	183.5
H	5	1.076	3	120.569	1	192.7
C	3	1.422	1	123.292	2	10.3
C	7	1.384	3	120.101	1	317.5
C	7	1.388	3	118.417	1	136.5
C	8	1.383	7	118.531	3	179.9
H	8	1.076	7	120.616	3	359.3
C	9	1.379	7	119.168	3	179.6
H	9	1.080	7	120.699	3	357.1
C	10	1.382	8	120.668	7	0.1
H	10	1.078	8	119.102	7	179.6
H	12	1.078	9	119.653	7	179.5
H	14	1.078	10	119.983	8	180.0
C	4	1.441	1	120.984	2	347.9
H	18	1.086	4	110.397	1	139.0
H	18	1.088	4	111.143	1	260.3
H	18	1.084	4	107.578	1	19.5
C	4	1.430	1	111.820	2	188.9
H	22	1.096	4	111.772	1	99.4
C	11	2.910	8	93.204	7	295.8
O	24	1.201	11	66.973	8	265.9
N	24	1.411	11	90.168	8	134.5
N	24	1.366	11	117.027	8	28.0
C	26	1.345	24	109.351	11	239.8
C	26	1.420	24	124.505	11	63.2
C	29	1.386	26	120.270	24	27.4
C	29	1.386	26	118.895	24	205.7
C	30	1.382	29	118.822	26	178.5
H	30	1.075	29	120.414	26	358.2
C	31	1.380	29	119.608	26	182.0
H	31	1.078	29	120.381	26	2.7
C	32	1.383	30	120.864	29	359.5
H	32	1.078	30	119.054	29	180.0
H	34	1.078	31	119.598	29	179.9
H	36	1.078	32	120.167	30	180.2
C	27	1.439	24	122.017	11	279.4
H	40	1.084	27	106.963	24	355.8
H	40	1.088	27	111.036	24	114.1
H	40	1.085	27	110.688	24	236.5
C	28	1.370	26	108.549	24	5.0
H	22	1.086	4	113.207	1	221.4
H	28	1.073	26	122.094	24	186.2
H	44	1.074	28	127.351	26	196.8

Molecule: **SS-TS14**



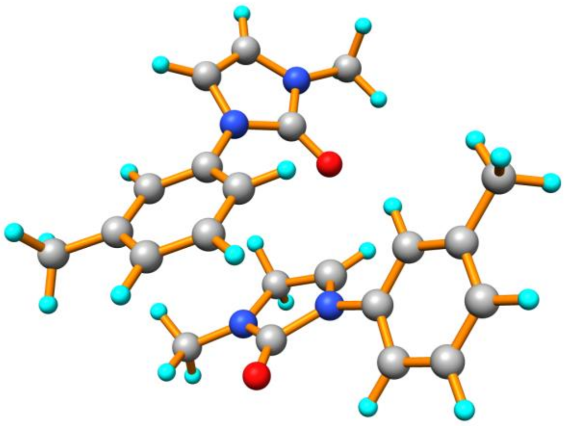
Energy = -1143.089035 Hartree

Imag. Freq. = -231.2093 cm^{-1}

47						
C						1
O				1		1.193
N		1	1.354		2	131.735
N	1	1.432	2	122.771	3	180.6
C	3	1.435	1	110.951	2	174.2
H	5	1.095	3	111.780	1	259.8
C	3	1.415	1	125.831	2	3.8
C	7	1.387	3	120.776	1	336.0
C	7	1.386	3	118.767	1	157.2
C	8	1.381	7	119.029	3	180.9
H	8	1.075	7	120.511	3	1.6
C	9	1.382	7	119.706	3	178.8
H	9	1.079	7	121.101	3	357.9
C	12	1.381	9	120.339	7	0.2
H	10	1.078	8	118.940	7	180.3
H	12	1.078	9	119.338	7	179.8
H	14	1.078	12	120.242	9	179.8
C	4	1.438	1	120.620	2	358.1
H	18	1.088	4	110.595	1	108.1
H	18	1.084	4	110.293	1	229.2
H	18	1.083	4	107.234	1	349.2
C	4	1.318	1	111.482	2	173.0
H	22	1.080	4	121.054	1	162.2
C	23	2.853	22	114.801	4	126.0
O	24	1.197	23	123.652	22	152.1
N	24	1.415	23	74.588	22	277.0
N	24	1.370	23	65.280	22	31.3
C	26	1.338	24	109.550	23	60.7
C	26	1.420	24	124.142	23	236.2
C	29	1.384	26	119.751	24	40.3
C	29	1.385	26	118.879	24	219.9
C	30	1.382	29	118.715	26	178.9
H	30	1.077	29	120.297	26	357.7
C	31	1.381	29	119.193	26	181.7
H	31	1.080	29	120.557	26	3.8
C	32	1.383	30	120.568	29	359.6
H	32	1.078	30	119.314	29	179.7
H	34	1.078	31	119.595	29	180.3
H	36	1.078	32	120.003	30	180.0
C	27	1.442	24	120.956	23	120.8
H	40	1.084	27	107.586	24	23.3
H	40	1.085	27	109.816	24	142.2
H	40	1.087	27	112.062	24	264.7
C	28	1.376	26	109.031	24	355.0
H	5	1.084	3	111.966	1	138.6
H	28	1.073	26	122.218	24	176.3
H	44	1.075	28	126.604	26	160.2

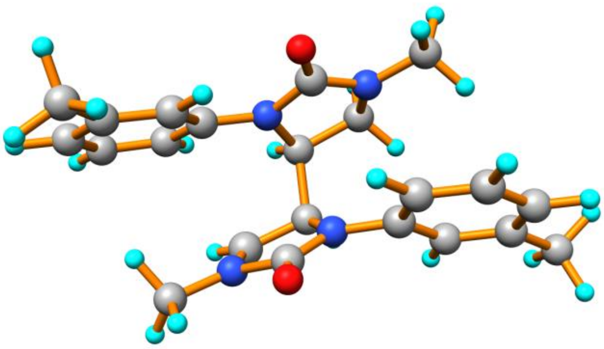
Reaction depicted on Scheme S3

Molecule: **C1**



Energy = -1221.665880 Hartree

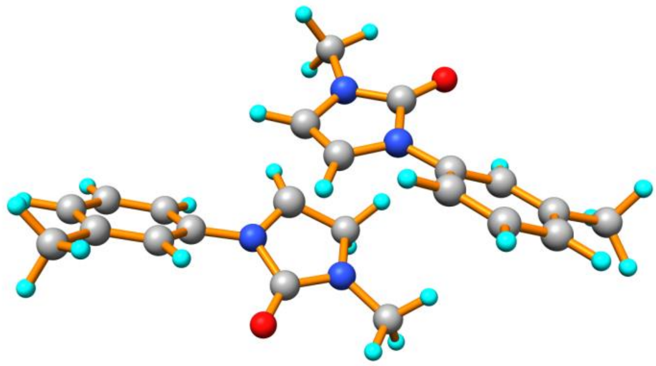
53						
C						1
O				1		1.188
N		1	1.476	2		123.844
N	1	1.337	2	131.694	3	179.0
C	3	1.280	1	110.270	2	178.6
H	5	1.074	3	123.114	1	182.9
C	3	1.422	1	123.292	2	354.6
C	7	1.381	3	119.899	1	40.9
C	7	1.387	3	117.519	1	220.0
C	8	1.382	7	117.507	3	178.6
H	8	1.076	7	121.123	3	358.5
C	9	1.384	7	119.538	3	181.5
H	9	1.082	7	119.689	3	2.9
C	10	1.381	8	120.689	7	0.0
H	10	1.078	8	119.365	7	180.2
H	14	1.080	10	119.390	8	179.8
C	4	1.439	1	122.724	2	359.8
H	17	1.085	4	109.962	1	128.9
H	17	1.087	4	110.874	1	250.5
H	17	1.084	4	107.642	1	10.0
C	4	1.427	1	112.818	2	181.0
H	21	1.092	4	112.972	1	119.6
C	6	3.341	5	90.231	3	248.5
O	23	1.234	6	18.216	5	118.2
N	23	1.367	6	121.444	5	3.6
N	23	1.354	6	128.318	5	211.3
C	25	1.387	23	109.454	6	202.5
C	25	1.410	23	124.593	6	23.1
C	28	1.385	25	120.027	23	44.2
C	28	1.386	25	119.269	23	222.9
C	29	1.382	28	118.814	25	178.6
H	29	1.077	28	119.969	25	359.6
C	30	1.388	28	120.584	25	182.2
H	30	1.081	28	119.448	25	1.7
C	31	1.383	29	120.648	28	359.8
H	31	1.079	29	119.573	28	179.7
H	35	1.079	31	119.639	29	180.0
C	26	1.438	23	123.146	6	335.3
H	38	1.085	26	110.591	23	240.2
H	38	1.083	26	107.410	23	359.3
H	38	1.086	26	110.755	23	118.7
C	27	1.336	25	107.315	23	359.7
H	21	1.091	4	112.679	1	243.0
H	27	1.071	25	121.662	23	182.1
H	42	1.072	27	130.404	25	181.4
C	33	1.495	30	120.749	28	178.4
H	46	1.088	33	110.685	30	257.0
H	46	1.086	33	111.715	30	16.7
H	46	1.087	33	111.355	30	138.0
C	12	1.494	9	121.022	7	180.0
H	50	1.087	12	110.830	9	241.0
H	50	1.085	12	111.503	9	1.4
H	50	1.087	12	110.973	9	122.0

Molecule: **RS-I12-Me**  Energy = -1221.659156 Hartree	(Z-matrix below)

53						
C						1
O					1	1.187
N		1	1.350		2	132.942
N	1	1.458	2	122.208	3	178.3
C	4	1.277	1	110.629	2	180.1
C	3	1.436	1	111.859	2	183.0
H	6	1.091	3	112.947	1	235.7
H	5	1.077	4	122.966	1	178.4
C	3	1.425	1	121.858	2	8.2
C	9	1.381	3	119.249	1	314.2
C	9	1.385	3	119.446	1	132.6
C	10	1.383	9	118.367	3	177.7
H	10	1.077	9	120.503	3	357.3
C	11	1.387	9	120.385	3	181.4
H	11	1.081	9	120.482	3	359.5
C	12	1.381	10	120.723	9	1.1
H	12	1.078	10	119.320	9	180.4
H	16	1.079	12	119.710	10	179.7
C	4	1.447	1	120.722	2	4.9
H	19	1.086	4	107.991	1	103.4
H	19	1.083	4	109.797	1	224.3
H	19	1.083	4	107.162	1	344.6
C	3	3.155	1	106.779	2	269.5
O	23	1.203	3	119.087	1	42.1
N	23	1.403	3	65.461	1	282.6
N	23	1.351	3	79.682	1	168.9
C	26	1.425	23	112.871	3	65.4
C	25	1.424	23	110.113	3	301.2
H	28	1.086	25	113.548	23	219.0
H	27	1.092	26	112.120	23	100.3
C	25	1.401	23	125.976	3	111.4
C	31	1.393	25	121.625	23	340.2
C	31	1.393	25	118.964	23	161.6
C	32	1.387	31	120.665	25	179.5
H	32	1.076	31	119.238	25	2.0
C	33	1.387	31	119.786	25	179.0
C	36	1.378	33	120.577	31	0.8
H	36	1.079	33	119.317	31	178.9
H	37	1.079	36	120.077	33	178.7
C	26	1.431	23	123.125	3	238.3
H	40	1.088	26	111.302	23	250.2
H	40	1.084	26	107.638	23	9.7
H	40	1.088	26	109.958	23	128.7
H	27	1.088	26	111.373	23	222.0
H	33	1.079	31	120.870	25	353.5
C	34	1.494	32	120.024	31	183.3
H	46	1.088	34	110.060	32	93.2
H	46	1.086	34	111.573	32	212.3
H	46	1.085	34	111.608	32	334.0
C	14	1.495	11	120.958	9	179.0
H	50	1.087	14	111.168	11	132.2
H	50	1.088	14	110.678	11	251.2
H	50	1.086	14	111.741	11	11.3

53						
C						1
O				1		1.199
N	1	1.413	2	127.462		
N	1	1.370	2	128.191	3	181.7
C	4	1.380	1	110.616	2	178.2
C	3	1.344	1	109.648	2	179.2
H	6	1.073	3	122.118	1	181.1
H	5	1.075	4	122.029	1	161.4
C	3	1.419	1	124.605	2	358.0
C	9	1.385	3	119.432	1	325.1
C	9	1.383	3	119.197	1	147.1
C	10	1.386	9	119.967	3	182.3
H	10	1.078	9	119.929	3	4.0
C	11	1.382	9	118.618	3	176.8
H	11	1.079	9	120.871	3	355.2
C	14	1.381	11	120.436	9	0.9
H	14	1.078	11	119.527	9	180.0
H	16	1.079	14	119.617	11	179.5
C	4	1.440	1	121.948	2	354.6
H	19	1.085	4	110.747	1	243.2
H	19	1.084	4	107.031	1	2.3
H	19	1.087	4	111.222	1	121.2
C	7	2.870	6	102.359	3	252.2
O	23	1.193	7	105.744	6	183.9
N	23	1.436	7	82.380	6	308.3
N	23	1.352	7	77.200	6	56.0
C	26	1.428	23	111.965	7	274.1
C	25	1.322	23	109.786	7	69.2
H	28	1.076	25	120.742	23	167.0
H	27	1.089	26	113.106	23	137.6
C	25	1.419	23	124.656	7	255.3
C	31	1.385	25	120.017	23	38.1
C	31	1.384	25	118.424	23	216.7
C	32	1.386	31	119.762	25	178.3
H	32	1.077	31	120.019	25	356.9
C	33	1.381	31	118.615	25	182.4
C	36	1.381	33	120.237	31	359.3
H	36	1.078	33	119.677	31	180.2
H	37	1.079	36	119.519	33	180.5
C	26	1.441	23	121.998	7	109.6
H	40	1.083	26	107.553	23	343.2
H	40	1.088	26	110.955	23	102.3
H	40	1.085	26	110.064	23	223.9
H	27	1.095	26	112.331	23	259.5
H	33	1.079	31	120.805	25	4.6
C	12	1.494	10	120.622	9	182.0
H	46	1.085	12	111.651	10	340.3
H	46	1.088	12	110.371	10	99.8
H	46	1.086	12	111.339	10	219.0
C	34	1.494	32	120.693	31	178.5
H	50	1.088	34	110.436	32	256.2
H	50	1.085	34	111.627	32	15.9
H	50	1.086	34	111.234	32	137.1

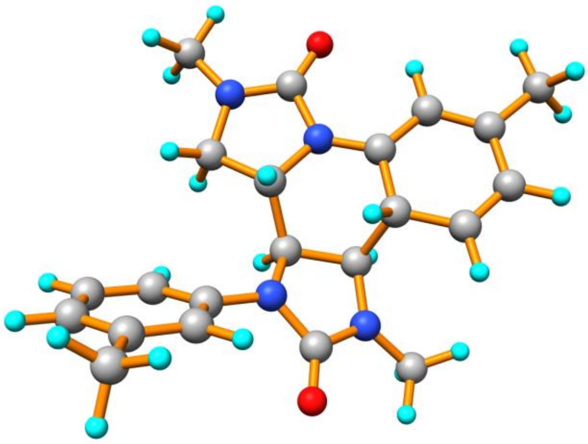
Molecule: **RS-TS12-Me**



Energy = -1221.635863 Hartree

Imag. Freq. = -210.0126 cm^{-1}

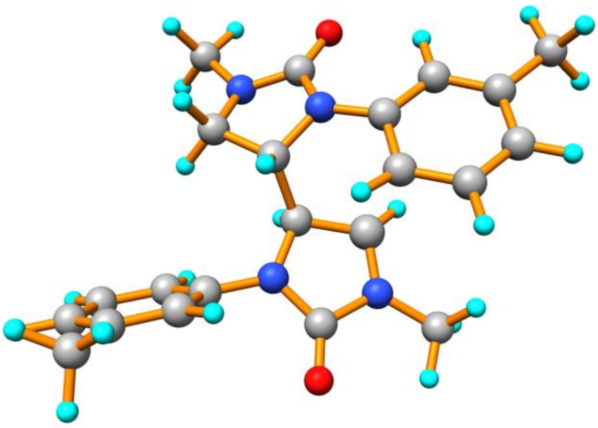
Molecule: **SRS-I22-Me**



Energy = -1221.668627 Hartree

53						
C						1
O				1		1.197
N		1	1.387	2		127.287
N	1	1.375	2	126.366	3	179.2
C	4	1.414	1	111.558	2	185.1
C	3	1.437	1	110.687	2	193.8
H	6	1.093	3	112.318	1	90.8
H	5	1.086	4	112.260	1	218.4
C	3	1.412	1	121.930	2	350.9
C	9	1.386	3	119.002	1	55.1
C	9	1.385	3	120.621	1	234.6
C	10	1.385	9	120.623	3	179.6
H	10	1.078	9	119.122	3	358.2
C	11	1.384	9	119.193	3	181.7
H	11	1.080	9	120.754	3	4.2
C	14	1.380	11	120.373	9	359.0
H	14	1.079	11	119.650	9	180.0
H	16	1.079	14	119.758	11	180.3
C	4	1.436	1	122.044	2	13.3
H	19	1.087	4	112.000	1	231.7
H	19	1.084	4	106.902	1	350.9
H	19	1.088	4	111.241	1	110.0
C	6	3.619	3	139.439	1	221.8
O	23	1.199	6	148.556	3	125.0
N	23	1.432	6	29.279	3	78.2
N	23	1.336	6	79.799	3	285.8
C	26	1.435	23	114.259	6	6.4
C	25	1.453	23	111.395	6	327.3
H	28	1.091	25	108.643	23	256.4
H	27	1.085	26	111.587	23	135.2
C	25	1.327	23	126.714	6	154.2
C	31	1.397	25	124.917	23	355.1
C	31	1.475	25	113.530	23	179.1
C	32	1.371	31	119.380	25	182.5
H	32	1.075	31	119.599	25	2.9
C	33	1.467	31	115.241	25	178.9
C	36	1.336	33	121.764	31	358.0
H	36	1.078	33	116.828	31	176.2
H	37	1.079	36	120.892	33	179.5
C	26	1.437	23	121.945	6	196.7
H	40	1.086	26	110.187	23	231.3
H	40	1.083	26	107.954	23	350.7
H	40	1.088	26	110.754	23	110.3
H	27	1.091	26	110.525	23	255.6
H	33	1.099	31	109.148	25	301.1
C	34	1.481	32	120.508	31	180.4
H	46	1.089	34	109.981	32	238.0
H	46	1.083	34	112.366	32	359.7
H	46	1.089	34	109.817	32	121.1
C	12	1.494	10	120.644	9	177.8
H	50	1.086	12	111.362	10	143.3
H	50	1.088	12	110.409	10	262.6
H	50	1.085	12	111.579	10	22.1

Molecule: **SRS-TS22-Me**

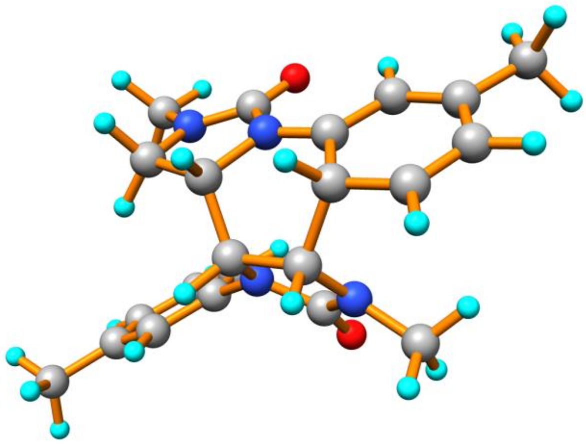


Energy = -1221.655617 Hartree

Imag. Freq. = -223.4549 cm^{-1}

53						
C						1
O				1		1.192
N		1	1.359	2		130.394
N	1	1.422	2	124.279	3	180.3
C	4	1.322	1	111.389	2	186.7
C	3	1.436	1	112.433	2	182.6
H	6	1.096	3	112.243	1	104.8
H	5	1.077	4	119.934	1	199.4
C	3	1.421	1	122.729	2	352.0
C	9	1.382	3	119.221	1	65.9
C	9	1.384	3	119.677	1	246.5
C	10	1.387	9	120.375	3	180.6
H	10	1.079	9	119.380	3	359.3
C	11	1.382	9	118.758	3	180.7
H	11	1.080	9	120.518	3	1.9
C	14	1.382	11	120.254	9	358.8
H	14	1.078	11	119.790	9	179.8
H	16	1.079	14	119.525	11	180.5
C	4	1.440	1	121.172	2	1.4
H	19	1.086	4	110.142	1	247.6
H	19	1.083	4	107.063	1	6.9
H	19	1.085	4	110.269	1	126.5
C	7	3.224	6	82.222	3	154.7
O	23	1.200	7	136.195	6	122.2
N	23	1.412	7	62.538	6	7.9
N	23	1.352	7	65.179	6	241.9
C	26	1.434	23	112.068	7	60.0
C	25	1.433	23	110.613	7	316.3
H	28	1.086	25	112.278	23	221.5
H	27	1.091	26	111.599	23	94.9
C	25	1.367	23	126.313	7	115.3
C	31	1.395	25	123.450	23	9.3
C	31	1.415	25	116.399	23	196.4
C	32	1.379	31	120.188	25	186.0
H	32	1.075	31	119.247	25	5.9
C	33	1.411	31	118.812	25	176.6
C	36	1.362	33	120.656	31	355.6
H	36	1.079	33	118.799	31	174.0
H	37	1.079	36	120.411	33	180.6
C	26	1.437	23	121.005	7	217.3
H	40	1.089	26	111.169	23	260.2
H	40	1.083	26	107.839	23	19.7
H	40	1.086	26	110.256	23	139.1
H	27	1.086	26	112.007	23	216.3
H	33	1.080	31	119.974	25	334.7
C	34	1.490	32	120.398	31	180.4
H	46	1.088	34	110.722	32	237.9
H	46	1.084	34	111.808	32	359.0
H	46	1.088	34	110.253	32	119.7
C	12	1.494	10	120.810	9	177.8
H	50	1.088	12	110.417	10	263.6
H	50	1.085	12	111.624	10	23.2
H	50	1.086	12	111.334	10	144.4

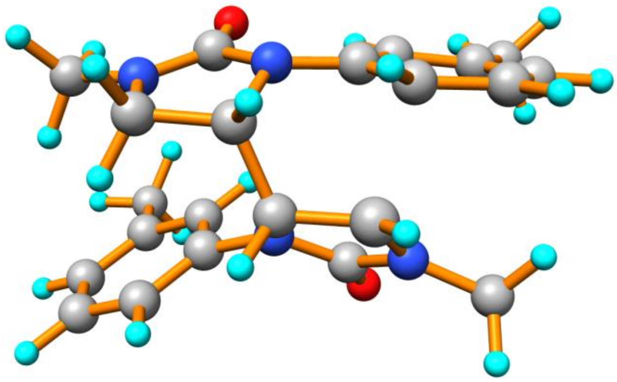
Molecule: **SSS-I22-Me**



Energy = -1221.670394 Hartree

53						
C						1
O					1	1.197
N		1	1.384		2	126.492
N	1	1.374	2	126.017	3	180.1
C	4	1.421	1	112.588	2	183.9
C	3	1.434	1	111.936	2	171.4
H	6	1.090	3	112.646	1	250.3
H	5	1.090	4	111.602	1	121.9
C	3	1.419	1	119.689	2	13.6
C	9	1.382	3	118.715	1	296.5
C	9	1.387	3	120.817	1	115.9
C	10	1.384	9	118.998	3	179.6
H	10	1.078	9	119.622	3	0.8
C	11	1.386	9	120.785	3	179.4
H	11	1.081	9	120.218	3	358.4
C	12	1.381	10	120.571	9	1.0
H	12	1.079	10	119.537	9	180.8
H	16	1.080	12	119.799	10	179.4
C	4	1.438	1	119.794	2	343.1
H	19	1.085	4	111.977	1	128.0
H	19	1.090	4	110.927	1	250.2
H	19	1.084	4	106.887	1	9.0
C	3	3.325	1	114.364	2	258.8
O	23	1.198	3	125.232	1	32.1
N	23	1.436	3	58.741	1	279.6
N	23	1.334	3	78.343	1	163.1
C	26	1.435	23	114.782	3	57.0
C	25	1.444	23	111.272	3	300.4
H	28	1.089	25	109.976	23	229.8
H	27	1.089	26	110.756	23	107.0
C	25	1.322	23	127.049	3	105.8
C	31	1.398	25	124.851	23	11.7
C	31	1.482	25	113.371	23	193.4
C	32	1.368	31	119.269	25	179.1
H	32	1.075	31	119.485	25	359.2
C	33	1.473	31	114.769	25	181.9
C	36	1.334	33	121.728	31	358.3
H	36	1.080	33	117.171	31	177.5
H	37	1.079	36	120.806	33	179.4
C	26	1.437	23	122.382	3	233.8
H	40	1.087	26	110.536	23	242.4
H	40	1.083	26	107.944	23	1.8
H	40	1.087	26	109.783	23	121.2
H	27	1.086	26	110.833	23	227.6
H	33	1.096	31	107.921	25	301.1
C	34	1.481	32	120.669	31	180.3
H	46	1.089	34	109.962	32	121.9
H	46	1.089	34	109.841	32	238.8
H	46	1.083	34	112.323	32	0.2
C	14	1.495	11	120.951	9	179.1
H	50	1.087	14	111.283	11	133.1
H	50	1.088	14	110.676	11	252.2
H	50	1.086	14	111.691	11	12.1

Molecule: **SSS-TS22-Me**



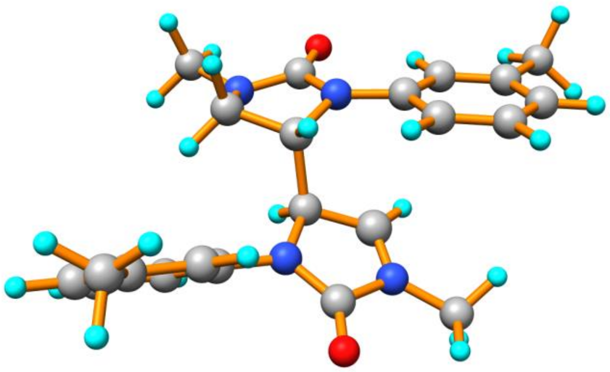
Energy = -1221.655563 Hartree

Imag. Freq. = -250.5242 cm^{-1}

53

C						1
O					1	1.191
N	1	1.366	2	129.995		
N	1	1.417	2	124.031	3	178.3
C	4	1.322	1	110.984	2	175.3
C	3	1.437	1	111.903	2	176.1
H	6	1.095	3	112.348	1	254.5
H	5	1.077	4	119.955	1	157.9
C	3	1.424	1	120.008	2	13.1
C	9	1.382	3	118.563	1	298.2
C	9	1.384	3	120.301	1	115.8
C	10	1.388	9	120.387	3	176.8
H	10	1.079	9	119.256	3	356.8
C	11	1.383	9	118.730	3	182.1
H	11	1.080	9	120.895	3	0.3
C	14	1.383	11	120.337	9	1.1
H	14	1.078	11	119.672	9	179.9
H	16	1.079	14	119.585	11	179.2
C	4	1.444	1	120.928	2	351.8
H	19	1.082	4	109.784	1	144.4
H	19	1.086	4	110.218	1	265.8
H	19	1.083	4	107.448	1	24.7
C	13	3.109	10	91.702	9	298.1
O	23	1.203	13	71.536	10	220.0
N	23	1.414	13	104.772	10	97.0
N	23	1.343	13	97.504	10	347.7
C	26	1.429	23	113.688	13	106.8
C	25	1.435	23	109.880	13	271.8
H	28	1.087	25	112.846	23	220.7
H	27	1.090	26	111.601	23	107.2
C	25	1.370	23	125.054	13	60.3
C	31	1.393	25	124.223	23	356.6
C	31	1.414	25	115.790	23	182.8
C	32	1.380	31	119.904	25	185.7
H	32	1.075	31	119.430	25	5.4
C	33	1.411	31	119.205	25	179.8
C	36	1.360	33	120.105	31	352.6
H	36	1.079	33	119.137	31	173.3
H	37	1.079	36	120.531	33	182.0
C	26	1.433	23	122.863	13	289.3
H	40	1.087	26	110.957	23	240.7
H	40	1.084	26	107.702	23	0.2
H	40	1.088	26	109.927	23	119.3
H	27	1.088	26	111.073	23	228.3
H	33	1.080	31	118.230	25	335.6
C	34	1.489	32	120.337	31	177.7
H	46	1.087	34	110.521	32	127.5
H	46	1.089	34	110.437	32	245.8
H	46	1.084	34	111.769	32	6.3
C	12	1.494	10	120.355	9	181.9
H	50	1.088	12	110.464	10	81.8
H	50	1.085	12	111.409	10	201.4
H	50	1.086	12	111.338	10	322.5

Molecule: **SS-I12-Me**



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53						
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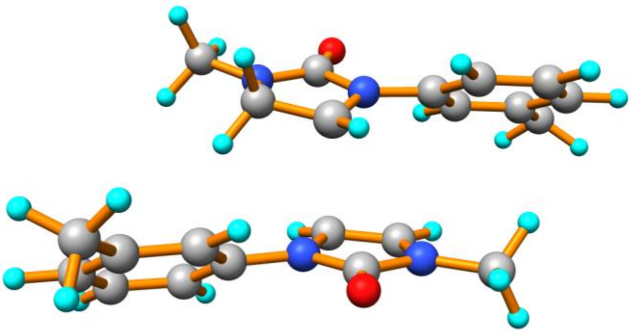
C	4	1.285	1	110.871	2	183.0
C	3	1.437	1	112.517	2	176.8
H	6	1.095	3	112.672	1	118.6
H	5	1.077	4	123.042	1	184.4
C	3	1.423	1	122.796	2	354.9
C	9	1.382	3	119.334	1	58.3
C	9	1.383	3	119.237	1	238.8
C	10	1.387	9	120.175	3	180.5
H	10	1.079	9	119.631	3	359.3
C	11	1.382	9	118.542	3	180.7
H	11	1.080	9	120.660	3	1.5
C	14	1.382	11	120.281	9	358.8
H	14	1.078	11	119.739	9	179.7
H	16	1.079	14	119.487	11	180.5
C	4	1.447	1	120.745	2	1.1
H	19	1.084	4	108.987	1	230.9
H	19	1.083	4	106.933	1	350.7
H	19	1.084	4	109.934	1	109.7
C	7	3.054	6	87.646	3	152.1
O	23	1.201	7	134.545	6	128.8
N	23	1.401	7	66.061	6	10.1
N	23	1.364	7	63.368	6	245.3
C	26	1.433	23	110.462	7	66.8
C	25	1.429	23	109.997	7	316.2
H	28	1.084	25	113.503	23	216.8
H	27	1.092	26	111.992	23	88.2
C	25	1.395	23	126.552	7	121.1
C	31	1.395	25	122.074	23	354.8
C	31	1.396	25	118.508	23	178.7
C	32	1.384	31	120.607	25	183.6
H	32	1.075	31	119.272	25	4.5
C	33	1.389	31	119.774	25	176.2
C	36	1.375	33	120.597	31	359.8
H	36	1.079	33	119.178	31	178.3
H	37	1.079	36	120.159	33	179.6
C	26	1.438	23	120.033	7	217.4
H	40	1.089	26	111.454	23	267.0
H	40	1.083	26	107.819	23	26.5
H	40	1.085	26	110.148	23	145.8
H	27	1.085	26	112.192	23	210.6
H	33	1.078	31	121.215	25	351.5
C	34	1.493	32	120.200	31	181.8
H	46	1.086	34	111.333	32	223.1
H	46	1.085	34	111.625	32	344.6
H	46	1.088	34	110.193	32	104.2
C	12	1.494	10	120.817	9	177.9
H	50	1.086	12	111.292	10	143.1
H	50	1.088	12	110.411	10	262.3
H	50	1.085	12	111.640	10	21.9

Molecule: **SS-TS12-Me**



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53

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C	3	1.320	1	110.589	2	184.8
H	5	1.079	3	121.656	1	196.7
C	3	1.414	1	124.380	2	358.9
C	7	1.386	3	120.056	1	324.2
C	7	1.386	3	118.515	1	146.8
C	8	1.388	7	119.832	3	182.5
H	8	1.077	7	119.947	3	3.8
C	9	1.382	7	118.695	3	177.1
H	9	1.079	7	120.863	3	354.3
C	12	1.382	9	120.275	7	0.1
H	12	1.078	9	119.660	7	179.0
H	14	1.079	12	119.566	9	179.6
C	4	1.439	1	122.231	2	352.6
H	17	1.083	4	107.620	1	12.9
H	17	1.086	4	110.350	1	132.2
H	17	1.087	4	110.987	1	253.6
C	4	1.430	1	112.278	2	185.9
H	21	1.095	4	112.072	1	102.4
C	6	2.749	5	118.360	3	236.1
O	23	1.200	6	122.412	5	210.4
N	23	1.378	6	67.782	5	334.5
N	23	1.400	6	72.798	5	88.6
C	25	1.389	23	109.704	6	62.2
C	25	1.416	23	124.841	6	240.7
C	28	1.385	25	119.950	23	35.1
C	28	1.386	25	119.112	23	213.8
C	29	1.387	28	120.139	25	179.0
H	29	1.077	28	119.689	25	357.2
C	30	1.383	28	118.838	25	182.2
H	30	1.079	28	120.887	25	4.4
C	33	1.381	30	120.476	28	359.0
H	33	1.078	30	119.501	28	180.1
H	35	1.079	33	119.721	30	180.6
C	26	1.443	23	121.523	6	119.8
H	38	1.085	26	110.551	23	109.5
H	38	1.085	26	109.961	23	231.0
H	38	1.083	26	106.957	23	350.7
C	26	1.340	23	110.556	6	297.8
H	42	1.074	26	122.649	23	181.6
H	21	1.087	4	113.212	1	224.2
H	27	1.074	25	122.007	23	164.8
C	10	1.494	8	120.530	7	181.9
H	46	1.085	10	111.633	8	339.0
H	46	1.088	10	110.266	8	98.4
H	46	1.086	10	111.367	8	217.6
C	31	1.494	29	120.425	28	177.6
H	50	1.088	31	110.344	29	262.8
H	50	1.085	31	111.619	29	22.2
H	50	1.086	31	111.385	29	143.6

2D NMR data

All 2D NMR experiments were performed on a Bruker AVANCE-500 spectrometer. The spectrometer was equipped with a z-gradient inverse probe head capable of producing gradients with the strength of 50 G cm^{-1}. All experiments were carried out at 303±0.2 K. The NMR signals were assigned on the basis of COSY, NOESY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC and ^{1}H-^{15}N HSQC, ^{1}H-^{15}N HMBC experiments.

The structure assignment for the octahydro-diimidazoquinolines 2

The structure of the compounds ***endo*-2a** and ***exo*-2a** was confirmed by heteronuclear correlation experiments. The signals of protons, carbon and nitrogen atoms were assigned used the set of 2D homo- and heteronuclear correlation experiments. In the ^{1}H-^{15}N HMBC spectrum the cross-peak is observed between the $H^{18/22}$ protons of the phenyl fragment and N^{3} nitrogen atom (Figure S1, ***endo*-2a** is given as an example). Also, there are cross-peaks between N^{3} nitrogen atom and H^{5} proton of the methyne group and H^{7} proton of the second aromatic ring. Additionally, the cross-peaks between N^{3} nitrogen atom and H^{13} proton of the methyne group, as well as the N^{12} nitrogen atom and the same H^{13} proton are present. The combination of this data, as well as ^{1}H-^{13}C HMBC data indicates the presence of three heterocyclic rings fused with benzene moiety.

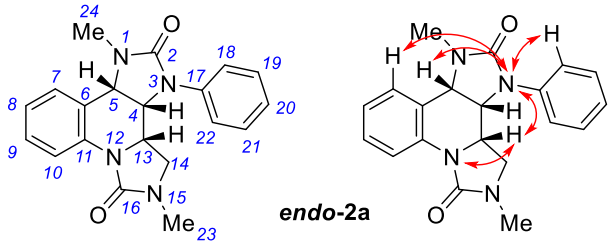


Figure S1 The atom numbering for the compound ***endo*-2a** and the key cross-peaks in the ^{1}H-^{15}N HMBC spectrum

The relative configuration of the *endo*-diastereomer was determined based on the spin-spin coupling constants (Figure S2). For the *exo*-diasteromer $J_{HH}(H^4,H^5)$ = 6.8 Hz and $J_{HH}(H^4,H^{13})$ = 9.9 Hz, whereas for the *endo*-diasteromer $J_{HH}(H^4,H^5)$ = 9.5 Hz and $J_{HH}(H^4,H^{13})$ = 4.3 Hz. According to the Karplus rule, the coupling constant for the vicinal protons in *trans*-configuration is bigger than for protons in *cis*-configuration. Thus, the relative configuration of the H^5-H^4-H^{13} protons is *cis-cis-cis* for the *endo*-diastereomer and *cis-cis-trans* for the *exo*-diastereomer. Additionally, a NOE between H^4 and H^{13} atoms is two times higher for the *endo*-diasteromer than for its *exo*-counterpart, which also supports the above configuration assignment.

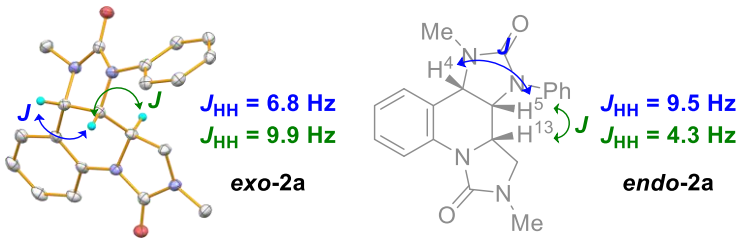


Figure S2 The H-H coupling constants for the compounds ***endo*-2a** and ***exo*-2a**

The structures and relative configurations of the compounds ***endo*-2b**, ***endo*-2m**, ***endo*-2o** and ***exo*-2g** were established similarly using 2D NMR data and the data obtained from the analysis of the compounds ***endo*-2a** and ***exo*-2a**. Additionally, the 2D experiments were carried out for the compound ***exo*-2j** to further check the correctness of the assignments, which were in the agreement with the x-ray data.

For the compound ***exo*-2g**, two regioisomers are possible, namely, ***exo*-2g** and ***exo*-2g'**, which differ in the position of the methyl group in aromatic fragment (Figure S3). Thus, the exact position of the methyl group in the aromatic ring was additionally established by 2D correlation experiments. In the ^{1}H-^{13}C HMBC spectrum

the cross-peak between H^5 proton of the methyne group (4.545 ppm, d, *J* = 6.8 Hz) and C^7 carbon atom (131.3 ppm) of the aromatic ring is present. According to the ^1H-^{13}C HSQC spectrum, the C^7 carbon atom is attached to the H^7 proton (7.346 ppm, d, *J* = 7.8 Hz). In turn, the cross-peak between the H^7 and substituted C^9 carbon atom (138.4 ppm) is also observed in the ^1H-^{13}C HMBC spectrum. At the same time, no cross-peak between substituted aromatic carbon atom and H^5 proton is present. All of these suggest the formation of ***exo*-2g** isomer.

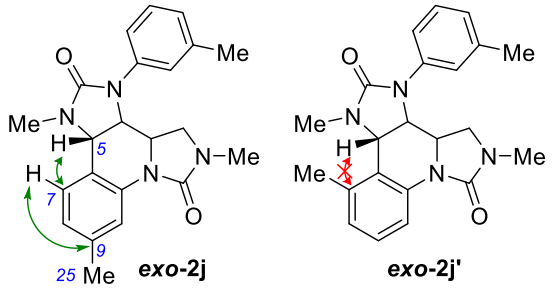


Figure S3 Two possible regioisomers for the compound ***exo*-2j** and the key cross-peaks in the ^1H-^{13}C HMBC spectrum

The structure assignment for the 4,4'-bi(imidazole-2-one) 5a

There are four possible regioisomers for the compound **5a** (Figure S4), so the main question was the determination of the correct substitution pattern for both imidazolinone rings. In the ^1H-^{13}C HMBC spectrum, the cross-peak between H^5 proton of the unsaturated imidazolinone ring (7.036 ppm, m) and C^{11} carbon atom of the phenyl ring (137.2 ppm) is present. Also, the cross-peak is observed between H^{10} proton of the methyne group (4.708 ppm, dd, *J* = 7.8 Hz, *J* = 8.6 Hz) and N^3 nitrogen atom (128.8 ppm) in the ^1H-^{15}N HMBC spectrum. Such interactions are impossible for the regioisomers **5a''** and **5a'''**, thus these regioisomers were ruled out. Additionally, the NOESY spectrum indicates the presence of NOE between H^5 and $H^{12/16}$ protons of the aromatic ring (7.690 ppm, d, *J* = 7.7 Hz), which also supports the formation of either **5a** or **5a'**. The choice between these regioisomers was made based on the NOESY data. The presence of NOE between H^9 proton of the methylene group (4.092 ppm, dd, *J* = 8.6 Hz, *J* = 9.4 Hz, *trans* to H^{10}) and $H^{18/22}$ protons of the phenyl moiety (7.577 ppm, d, *J* = 7.3 Hz) indicates their close proximity. At the same time, no NOE was observed between H^{10} proton and $H^{18/22}$ protons. Thus, the structure **5a** was assigned to the obtained compound.

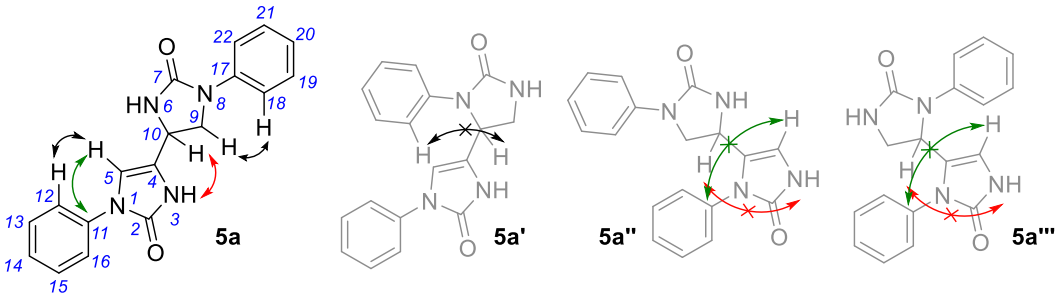


Figure S4 Possible regioisomers and the key cross-peaks in the ^1H-^{13}C HMBC (green), ^1H-^{15}N HMBC (red) and NOESY (black) spectra for the compound **5a**

X-ray data

The X-ray diffraction data for the crystals of ***exo*-2a**, ***endo*-2c**, ***exo*-2n**, ***endo*-2d** were collected on a Bruker D8 Venture automatic diffractometer using graphite monochromated radiation. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELXL97[18] program. All the non-hydrogen atoms were refined with anisotropic atomic displacement parameters. All figures were made using the program OLEX2.[19] X-ray diffraction data for the crystals of **3a**, **4**, ***exo*-2f**, ***endo*-2h**, ***exo*-2i**, ***exo*-2j** were obtained on a Bruker D8 QUEST automated three-circle diffractometer with a PHOTON III area detector and an IμS DIAMOND microfocus X-ray tube at a temperature of 100(2) K: λ(Mo *K*α) = 0.71073 Å, ω/φ scanning mode with a step of 0.5°. Data collection and indexing, determination and refinement of unit cell parameters were carried out using the APEX3 software package. Numerical absorption correction based on the crystal shape, additional spherical absorption correction, and systematic error correction were performed using the SADABS-2016/2 software.[20] Using OLEX2,[19] structures were solved by direct methods using the SHELXT-2018/3 program[21] and refined by full-matrix least-squares on F^2 using the SHELXL-2018/3 program.[22] Nonhydrogen atoms were refined anisotropically. The positions of hydrogen atoms of methyl groups were inserted using the rotation of the group with idealized bond angles; the remaining hydrogen atoms were refined using a riding model. Crystallographic data for the structures reported have been deposited with the Cambridge Crystallographic Data Center (2164569, 2164570, 2161404, 2161405, 2161406, 2161407, 2164571, 2164572, 2164573, 2165308).

Table S2. Crystallographic data for the compounds **3**, **4**, ***exo*-2a**, ***endo*-2c**, ***exo*-2e**, ***endo*-2f**, ***exo*-2i**, ***endo*-2k**, ***exo*-2l**

Compound	**3**	**4**	***exo*-2a**	***endo*-2c**	***exo*-2n**
Empirical formula	$C_{10}H_{10}N_2O$	$C_{20}H_{20}N_4O_2$, 2(H_2O)	$C_{20}H_{20}N_4O_2$	$C_{20}H_{18}Cl_2N_4O_2$	$C_{26}H_{32}N_4O_8$
Formula weight	174.20	384.43	348.40	417.28	528.55
Radiation, wavelength	Mo *K*α, 0.71073 Å	Mo *K*α, 0.71073 Å	Mo *K*α, 0.71073 Å	Mo *K*α, 0.71073 Å	Mo *K*α, 0.71073 Å
Temperature	100(2)	100(2)	100(2)	150(2)	100(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$Pna2_1$ (No. 33)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
Unit cell dimensions	*a* = 6.3685(3) Å, *b* = 7.0657(3) Å, *c* = 18.9967(10) Å, β = 97.181(2)°	*a* = 12.5996(6) Å, *b* = 7.2670(3) Å, *c* = 42.5196(18) Å	*a* = 9.659(3) Å, *b* = 18.266(5) Å, *c* = 10.132(3) Å, β = 113.345(10)°	*a* = 8.8126(4) Å, *b* = 23.7747(9) Å, *c* = 9.4899(4) Å, β = 110.6060(10)°	*a* = 10.678(3) Å, *b* = 9.987(3) Å, *c* = 24.015(7) Å, β = 100.609(15)°
Volume	848.11(7) $Å^3$	3893.1(3) $Å^3$	1641.4(8) $Å^3$	1861.09(14) $Å^3$	2517.0(13) $Å^3$
Z and *Z*′	4 and 1	8 and 2	4 and 1	4 and 1	4 and 1
Calculated density	1.364 g cm^{-3}	1.312 g cm^{-3}	1.333 g cm^{-3}	1.489 g cm^{-3}	1.395 g cm^{-3}
Absorption coefficient	0.091 mm^{-1}	0.093 mm^{-1}	0.094 mm^{-1}	0.374 mm^{-1}	0.104 mm^{-1}

Compound	**3**	**4**	***exo*-2a**	***endo*-2c**	***exo*-2n**
$F(000)$	368	1632	736	864	1120
Crystal size	0.464 x 0.284 x 0.162 mm^3	0.590 x 0.473 x 0.194 mm^3	0.08 x 0.06 x 0.01 mm^3	0.15 x 0.13 x 0.11 mm^3	0.08 x 0.07 x 0.02 mm^3
θ range for data collection	2.161° to 26.991°	1.916° to 27.000°	2.296° to 25.999°	2.448° to 28.998°	1.973° to 24.998°
Index ranges	$-8 \le h \le 8$, $-9 \le k \le 9$, $-24 \le l \le 24$	$-16 \le h \le 16$, $-9 \le k \le 9$, $-54 \le l \le 54$	$-11 \le h \le 11$, $-22 \le k \le 20$, $-12 \le l \le 12$	$-12 \le h \le 12$, $-32 \le k \le 31$, $-12 \le l \le 12$	$-12 \le h \le 11$, $-11 \le k \le 11$, $-28 \le l \le 28$
Reflections collected	22245	44052	11447	19811	13122
Independent reflections	1842	8472	3235	4938	4418
R_{int}	0.0437	0.0695	0.0814	0.0302	0.1967
$R\sigma$	0.0209	0.0537	0.0884	0.0279	0.3270
Observed Data [$I > 2\sigma(I)$]	1663	7806	2043	4271	1343
Completeness to θ = 25.242°	99.7	99.9	99.9	99.8	99.9
Max. and min. transmission	0.7460 and 0.6721	0.7460 and 0.5304	0.7461 and 0.6166	0.7461 and 0.6724	0.7461 and 0.5484
Data / restraints / parameters	1842 / 0 / 119	8472 / 1 / 521	3235 / 0 / 237	4938 / 0 / 255	4418 / 0 / 352
Goodness-of-fit on F^2	1.111	1.098	1.014	1.077	0.954
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0498, $wR2$ = 0.1247	$R1$ = 0.0565, $wR2$ = 0.1406	$R1$ = 0.0509, $wR2$ = 0.1009	$R1$ = 0.0398, $wR2$ = 0.0900	$R1$ = 0.0968, $wR2$ = 0.2035
R indices (all data)	$R1$ = 0.0541, $wR2$ = 0.1272	$R1$ = 0.0615, $wR2$ = 0.1443	$R1$ = 0.0997, $wR2$ = 0.1230	$R1$ = 0.0476, $wR2$ = 0.0943	$R1$ = 0.2888, $wR2$ = 0.2804
Flack parameter	–	0.2(5)	–	–	–
Largest diff. peak and hole	0.323 and –0.264 e $Å^{-3}$	0.563 and –0.248 e $Å^{-3}$	0.258 and –0.303 e $Å^{-3}$	0.367 and –0.308 e $Å^{-3}$	0.579 and –0.308 e $Å^{-3}$
CCDC number	2164569	2164570	2161404	2161405	2161406

Compound	***endo*-2d**	***exo*-2f**	***endo*-2h**	***exo*-2i**	***exo*-2j**
Empirical formula	$C_{22}H_{24}N_4O_4$	$C_{20}H_{18}Cl_2N_4O_2$	$C_{20}H_{18}Br_2N_4O_2$	$C_{28}H_{24}N_4O_2$	$C_{32}H_{26}Br_2N_4O_2$
Formula weight	408.45	417.28	506.20	448.51	658.39
Radiation, wavelength	Mo *K*α, 0.71073 Å	Mo *K*α, 0.71073 Å	Mo *K*α, 0.71073 Å	Mo *K*α, 0.71073 Å	Mo *K*α, 0.71073 Å
Temperature	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Unit cell dimensions	*a* = 9.7783(9) Å, *b* = 11.9953(10) Å, *c* = 17.4364(15) Å, α = 81.427(3)°, β = 83.627(4)°, γ = 70.331(3)°	*a* = 10.8202(9) Å, *b* = 12.3589(10) Å, *c* = 15.5997(14) Å, α = 92.661(3)°, β = 109.964(3)°, γ = 107.892(3)°	*a* = 14.616(3) Å, *b* = 9.5381(15) Å, *c* = 15.044(2) Å, β = 117.626(5)°	*a* = 9.118(4) Å, *b* = 10.799(4) Å, *c* = 10.873(5) Å, α = 90.043(14)°, β = 100.093(12)°, γ = 95.192(12)°	*a* = 9.6635(7) Å, *b* = 11.4629(8) Å, *c* = 14.1743(10) Å, α = 91.874(2)°, β = 106.844(2)°, γ = 112.114(2)°
Volume	1900.3(3) Å^3	1839.0(3) Å^3	1858.2(5) Å^3	1049.5(8) Å^3	1374.29(17) Å^3
Z and *Z*′	4 and 2	12 and 2	4 and 1	2 and 1	2 and 1
Calculated density	1.428 g cm^{-3}	1.507 g cm^{-3}	1.809 g cm^{-3}	1.419 g cm^{-3}	1.591 g cm^{-3}
Absorption coefficient	0.100 mm^{-1}	0.379 mm^{-1}	4.388 mm^{-1}	0.092 mm^{-1}	2.987 mm^{-1}
F(000)	864	864	1008	472	664
Crystal size	0.12 x 0.11 x 0.1 mm^3	0.361 x 0.288 x 0.156 mm^3	0.371 x 0.306 x 0.130 mm^3	0.445 x 0.381 x 0.262 mm^3	0.283 x 0.174 x 0.102 mm^3
θ range for data collection	2.046° to 25.999°	2.058° to 26.999°	2.626° to 26.999°	1.894° to 26.997°	1.521° to 27.943°
Index ranges	–12 ≤ *h* ≤ 11, –13 ≤ *k* ≤ 14, –21 ≤ *l* ≤ 21	–13 ≤ *h* ≤ 13, –15 ≤ *k* ≤ 15, –19 ≤ *l* ≤ 19	–18 ≤ *h* ≤ 18, –12 ≤ *k* ≤ 12, –19 ≤ *l* ≤ 19	–11 ≤ *h* ≤ 11, –13 ≤ *k* ≤ 13, –13 ≤ *l* ≤ 13	–12 ≤ *h* ≤ 12, –15 ≤ *k* ≤ 15, –18 ≤ l ≤ 18
Reflections collected	14765	34578	53022	32526	37004
Independent reflections	7401	8012	4055	4584	6591
R_{int}	0.0493	0.0718	0.0575	0.0931	0.0884
*R*σ	0.0807	0.0698	0.0242	0.0571	0.0661
Observed Data [$I > 2\sigma(I)$]	5288	5302	3519	3305	4984

Compound	***endo*-2d**	***exo*-2f**	***endo*-2h**	***exo*-2i**	***exo*-2j**
Completeness to θ = 25.242°	99.1	100.0	100.0	100.0	100.0
Max. and min. transmission	0.7461 and 0.5450	0.7460 and 0.6775	0.7460 and 0.5824	0.7460 and 0.5828	0.7456 and 0.4725
Data / restraints / parameters	7401 / 0 / 549	8012 / 0 / 509	4055 / 0 / 255	4584 / 0 / 309	6591 / 0 / 361
Goodness-of-fit on F^2	1.030	1.070	1.034	1.029	0.814
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0560, *wR*2 = 0.1241	*R*1 = 0.0445, *wR*2 = 0.0937	*R*1 = 0.0250, *wR*2 = 0.0549	*R*1 = 0.0437, *wR*2 = 0.1021	*R*1 = 0.0466, *wR*2 = 0.1163
R indices (all data)	*R*1 = 0.0850, *wR*2 = 0.1386	*R*1 =0.0858, *wR*2 = 0.1059	*R*1 = 0.0332, *wR*2 = 0.0584	*R*1 = 0.0702, *wR*2 = 0.1154	*R*1 = 0.0714, *wR*2 = 0.1344
Flack parameter	–	–	–	–	–
Largest diff. peak and hole	0.268 and –0.334 e Å^{-3}	0.296 and –0.316 e Å^{-3}	0.362 and –0.357 e Å^{-3}	0.239 and –0.261 e Å^{-3}	1.194 and –0.894 e Å^{-3}
CCDC number	2161407	2164571	2164572	2164573	2165308

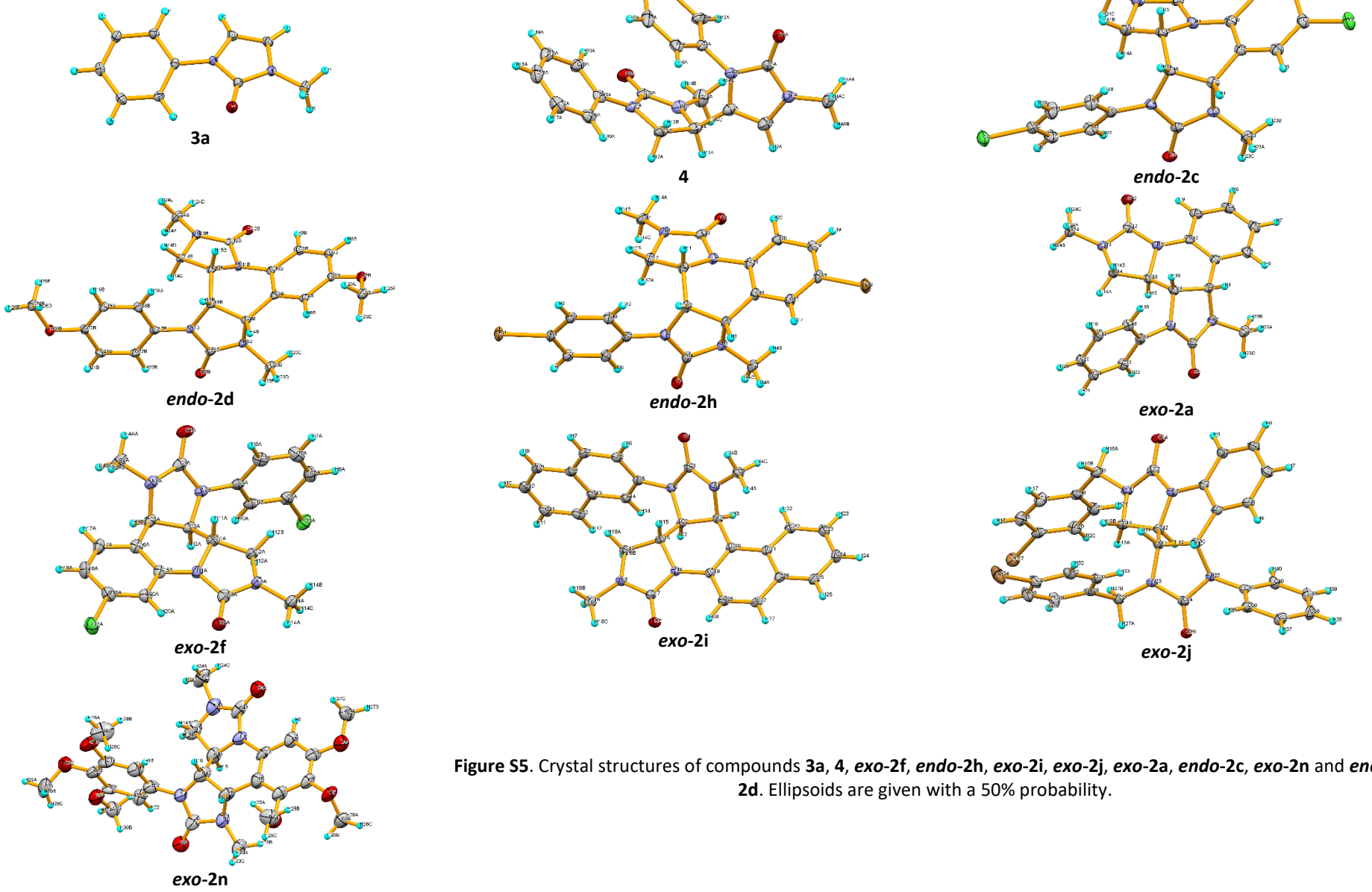
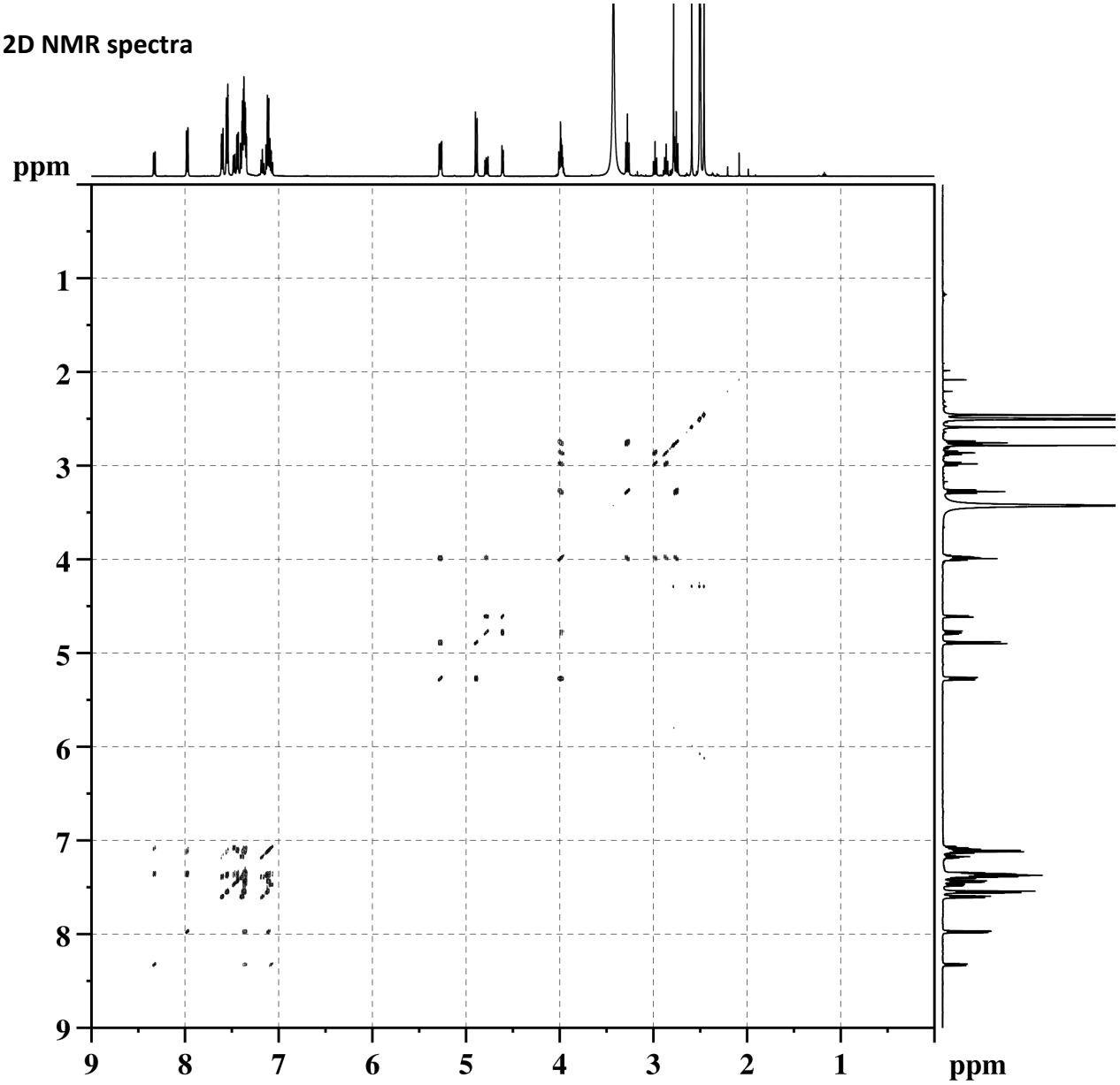
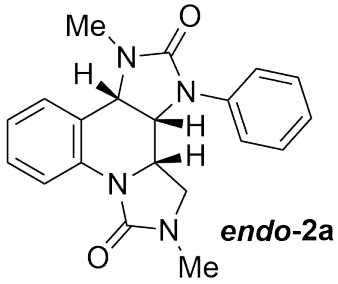


Figure S5. Crystal structures of compounds **3a**, **4**, ***exo*-2f**, ***endo*-2h**, ***exo*-2i**, ***exo*-2j**, ***exo*-2a**, ***endo*-2c**, ***exo*-2n** and ***endo*-2d**. Ellipsoids are given with a 50% probability.

Copies of NMR spectra

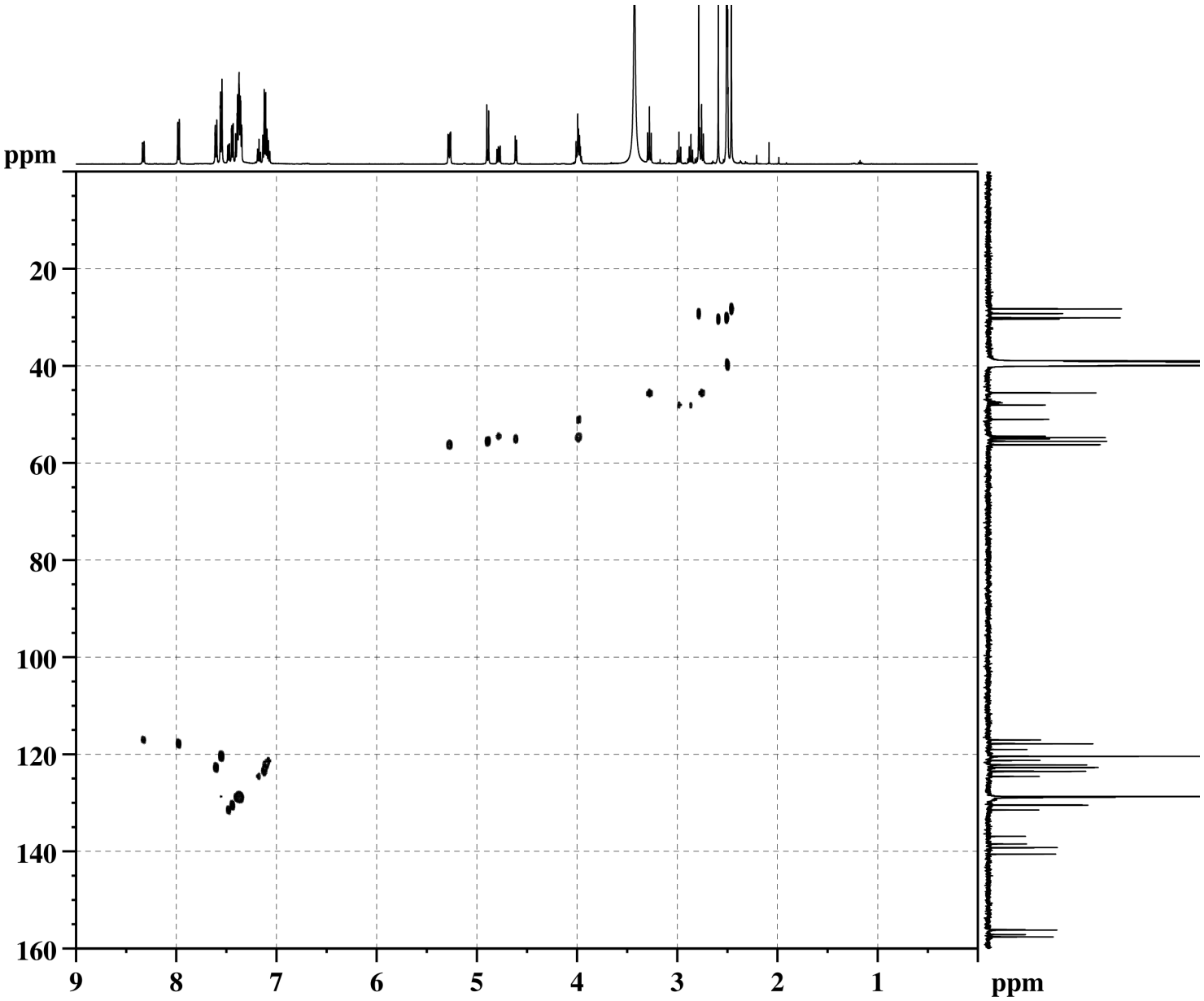
Copies of 2D NMR spectra

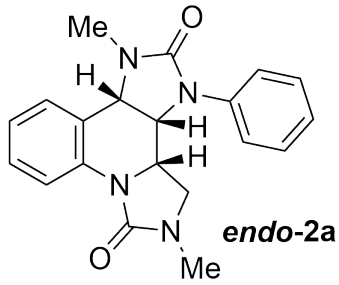




***endo*-2a**

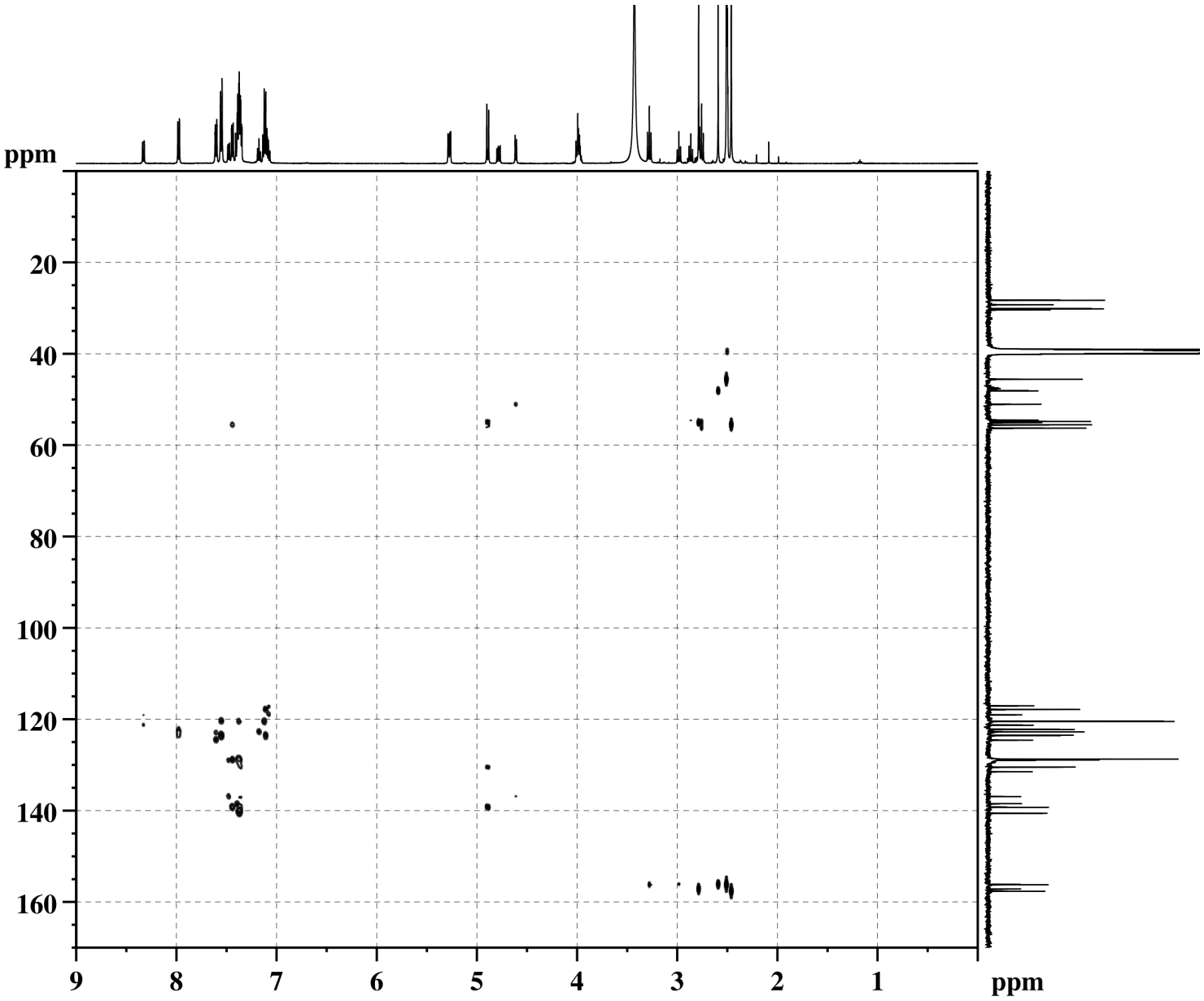
Figure S6. COSY spectrum ($(CD_3)_2SO$, 303 K) of the compound ***endo*-2a**

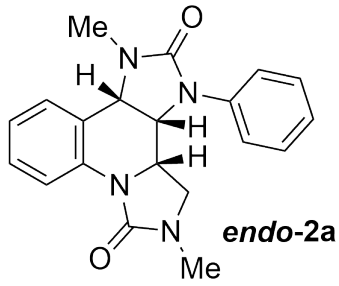




***endo*-2a**

Figure S7. ^{1}H-^{13}C HSQC spectrum ($(CD_3)_2SO$, 303 K) of the compound ***endo*-2a**





***endo*-2a**

Figure S8. ^{1}H-^{13}C HMBC spectrum ($(CD_3)_2SO$, 303 K) of the compound ***endo*-2a**

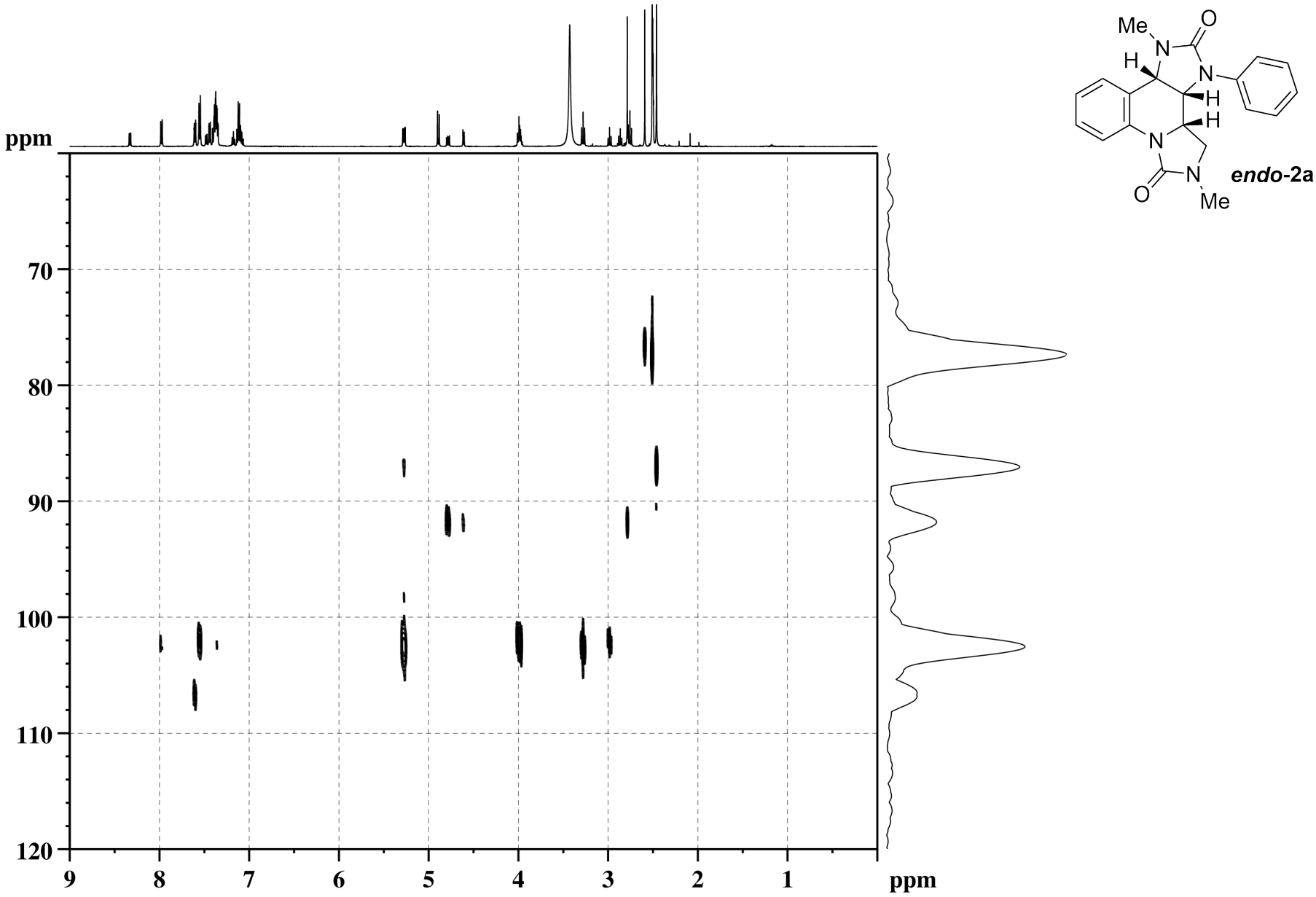


Figure S9. ^{1}H-^{15}N HMBC spectrum ($(CD_3)_2SO$, 303 K) of the compound ***endo*-2a**

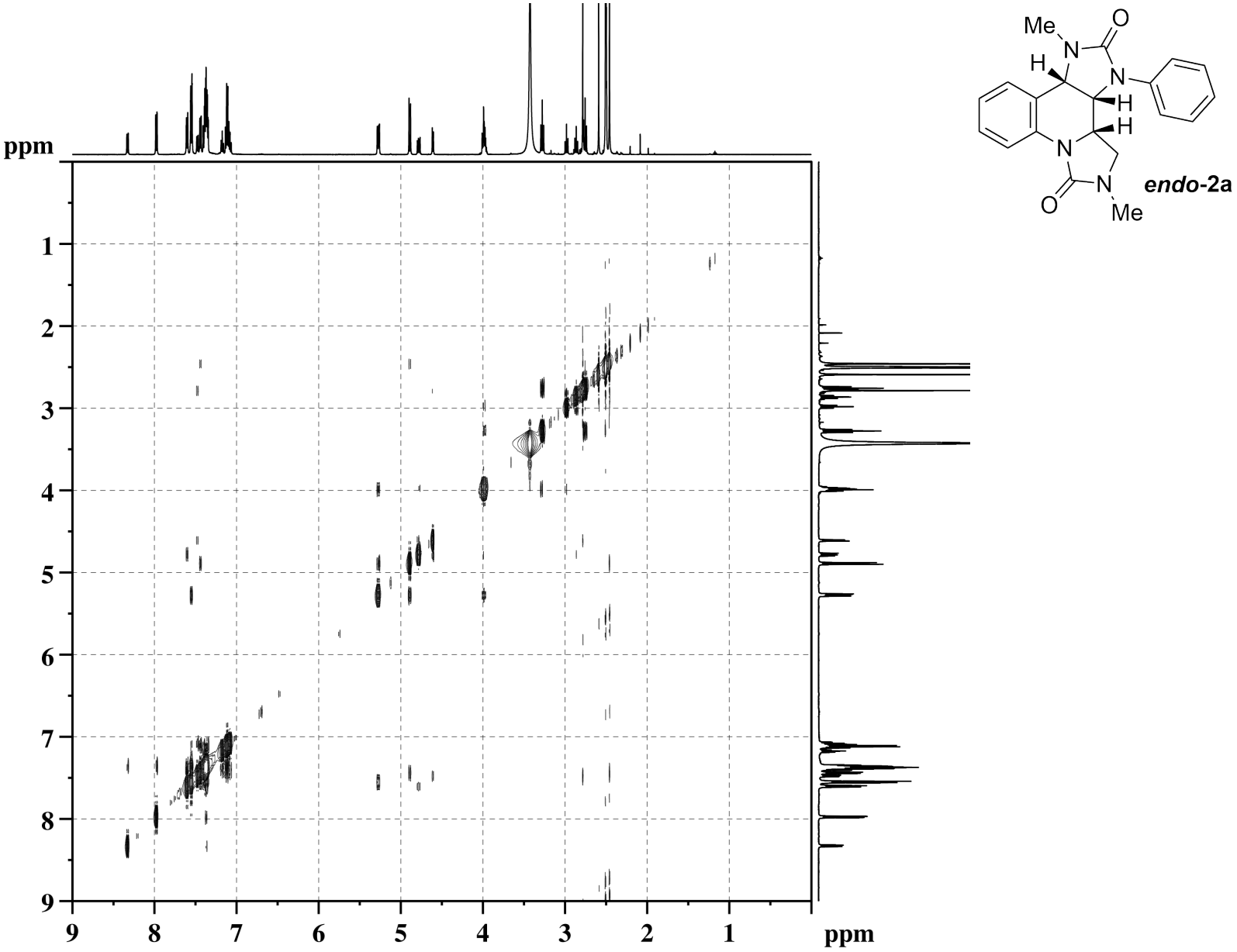


Figure S10. NOESY spectrum ($(CD_3)_2SO$, 303 K) of the compound ***endo*-2a**

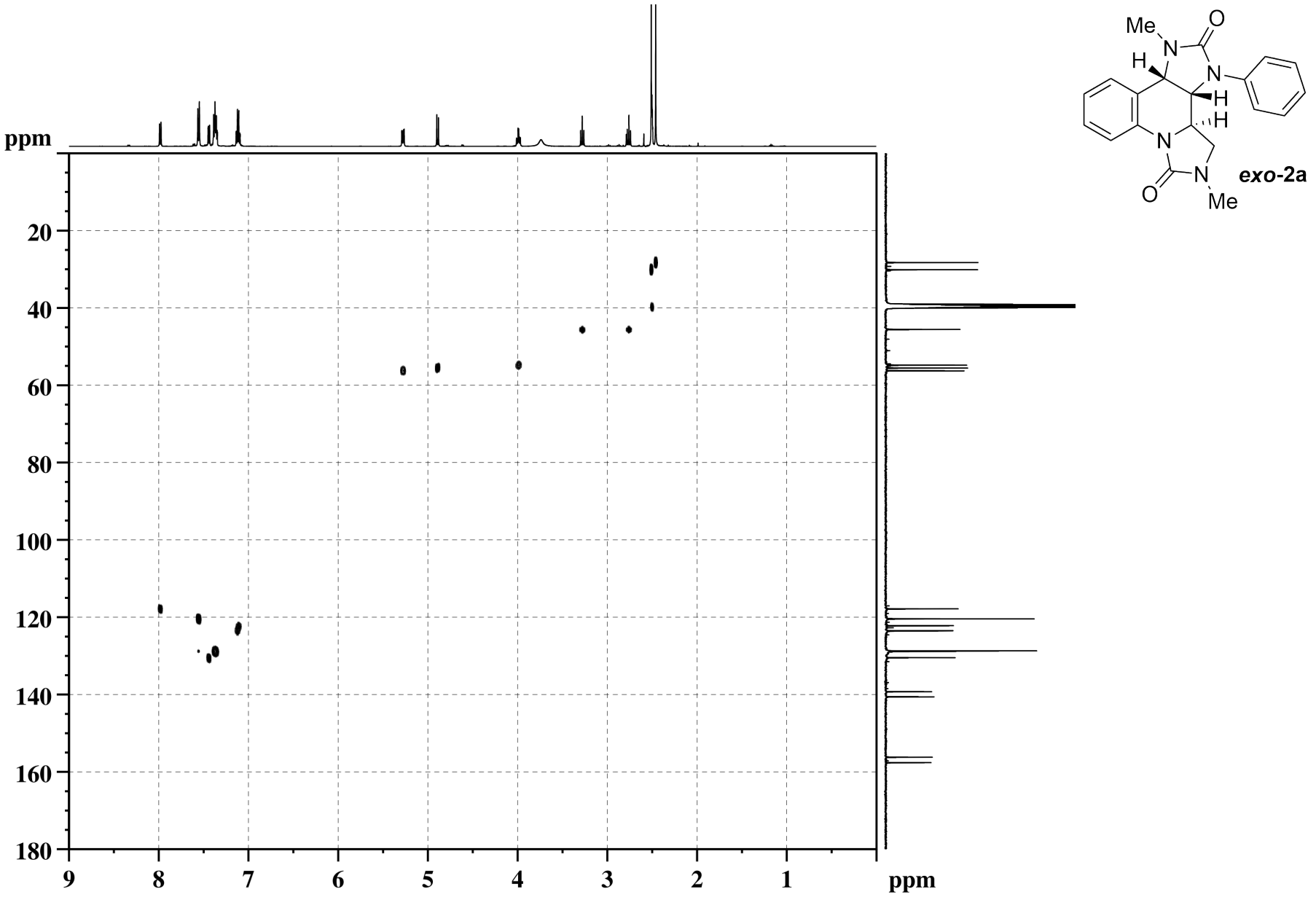


Figure S11. ^{1}H-^{13}C HSQC spectrum ($(CD_3)_2SO$, 303 K) of the compound ***exo*-2a**

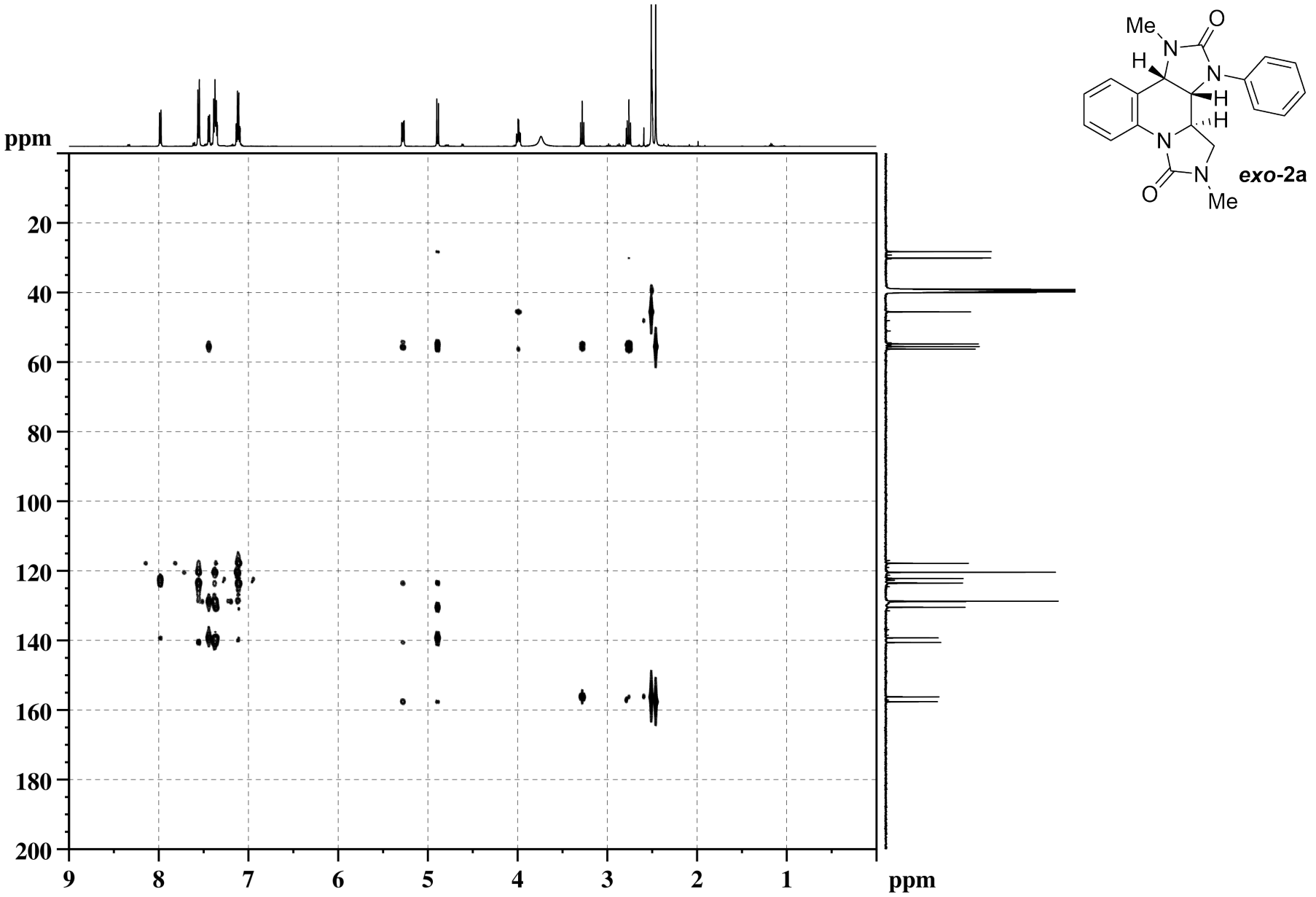
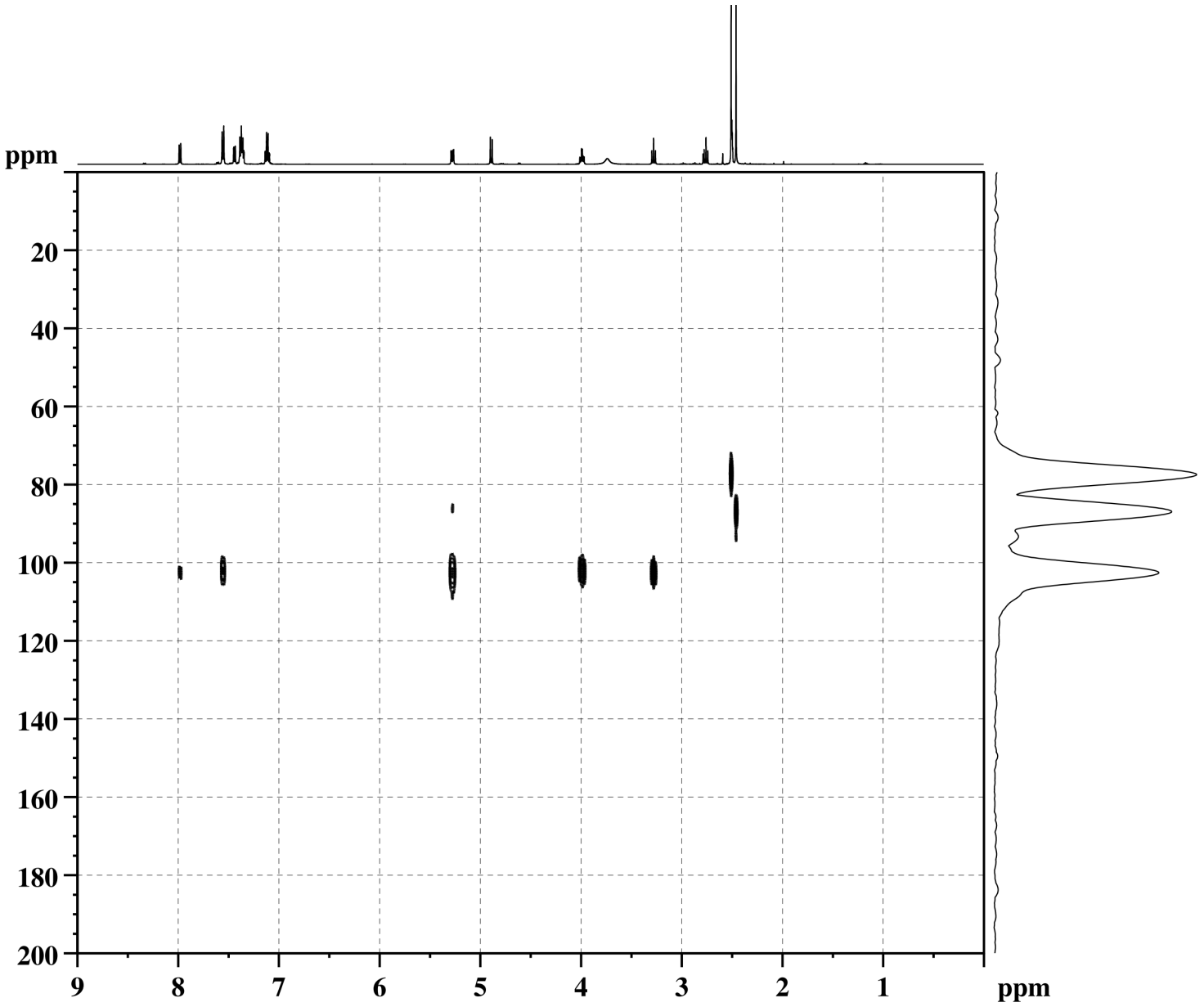
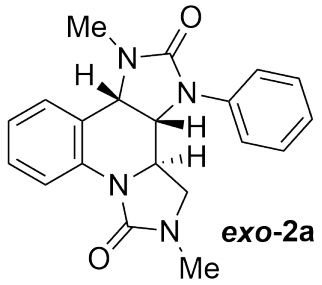


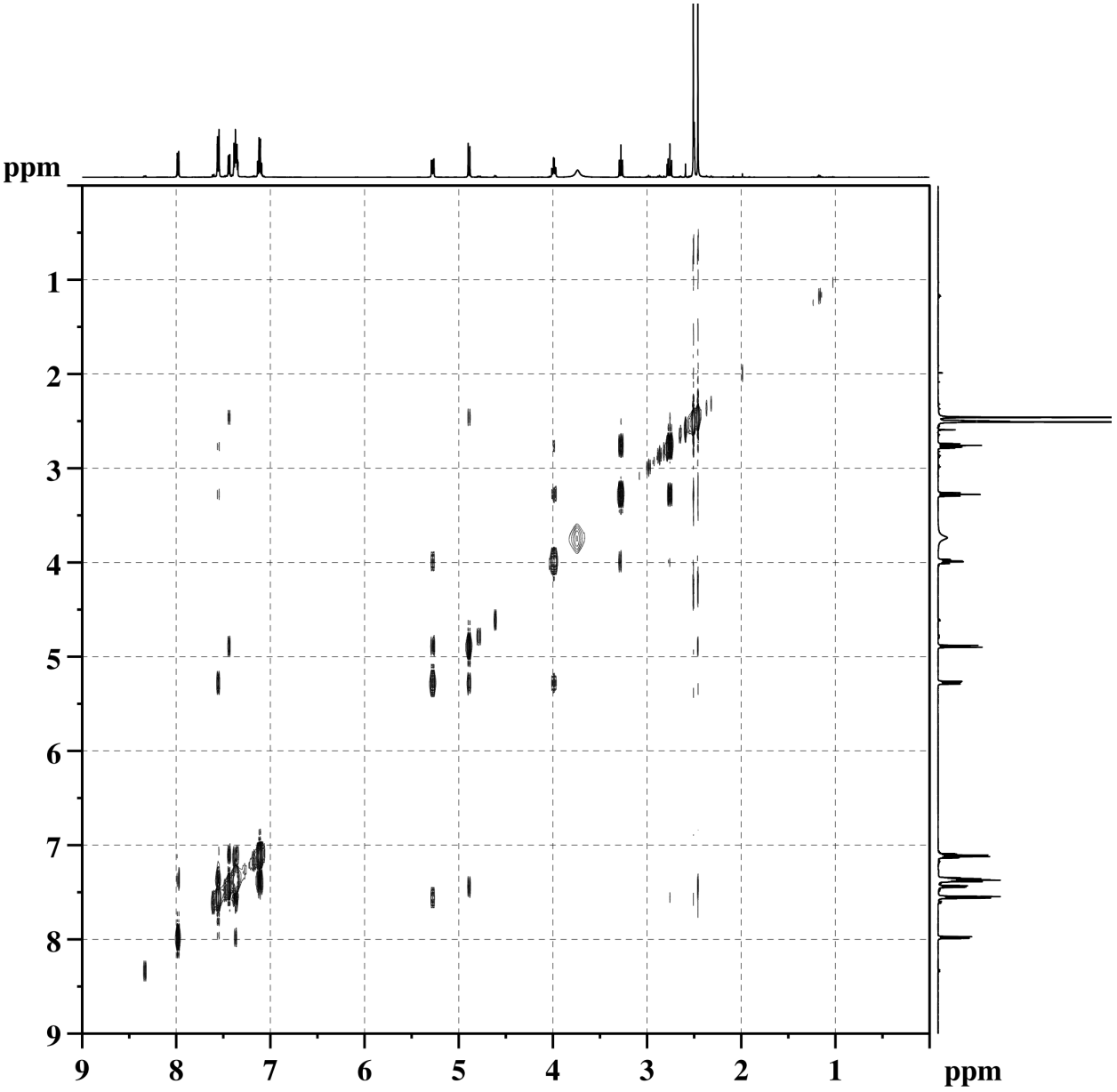
Figure S12. ^{1}H-^{13}C HMBC spectrum ($(CD_3)_2SO$, 303 K) of the compound ***exo*-2a**

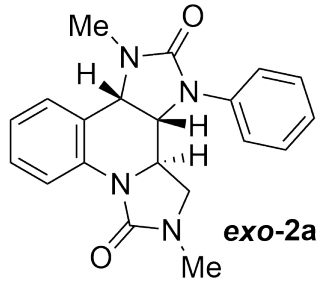




***exo*-2a**

Figure S13. ^{1}H-^{15}N HMBC spectrum ($(CD_3)_2SO$, 303 K) of the compound ***exo*-2a**





***exo*-2a**

Figure S14. NOESY spectrum ($(CD_3)_2SO$, 303 K) of the compound ***exo*-2a**

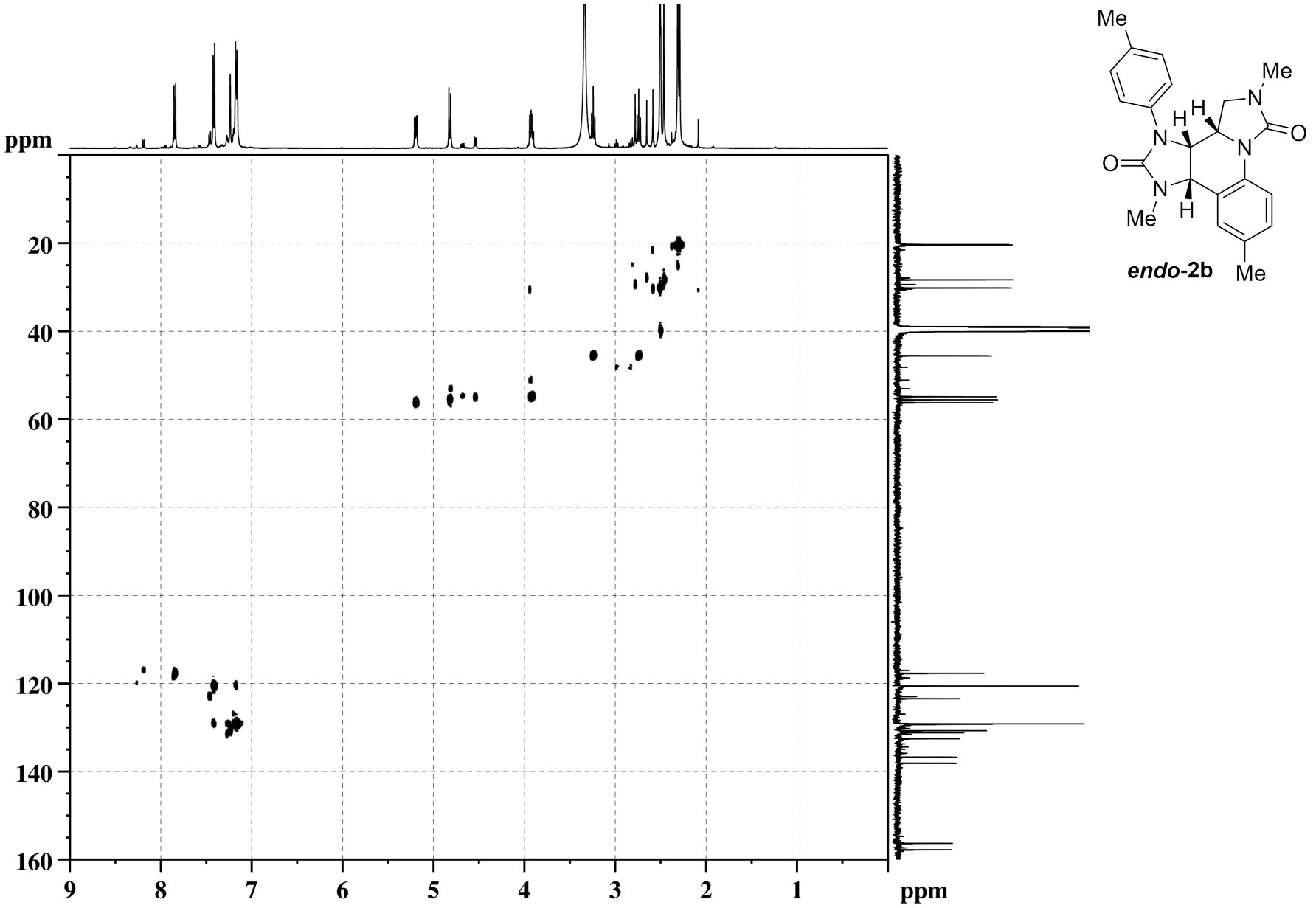


Figure S15. ^{1}H-^{13}C HSQC spectrum ($(CD_3)_2SO$, 303 K) of the compound ***endo*-2b**

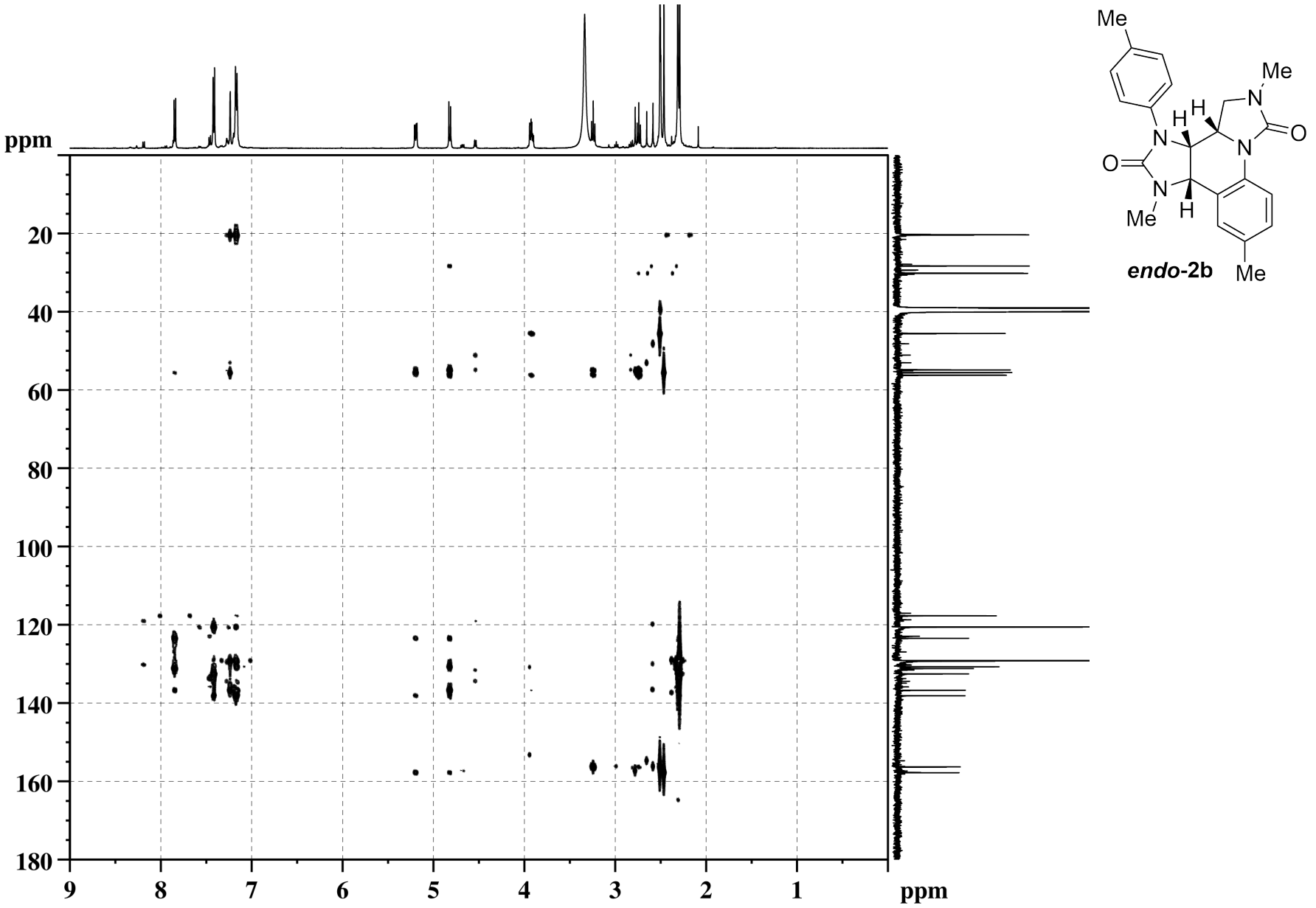
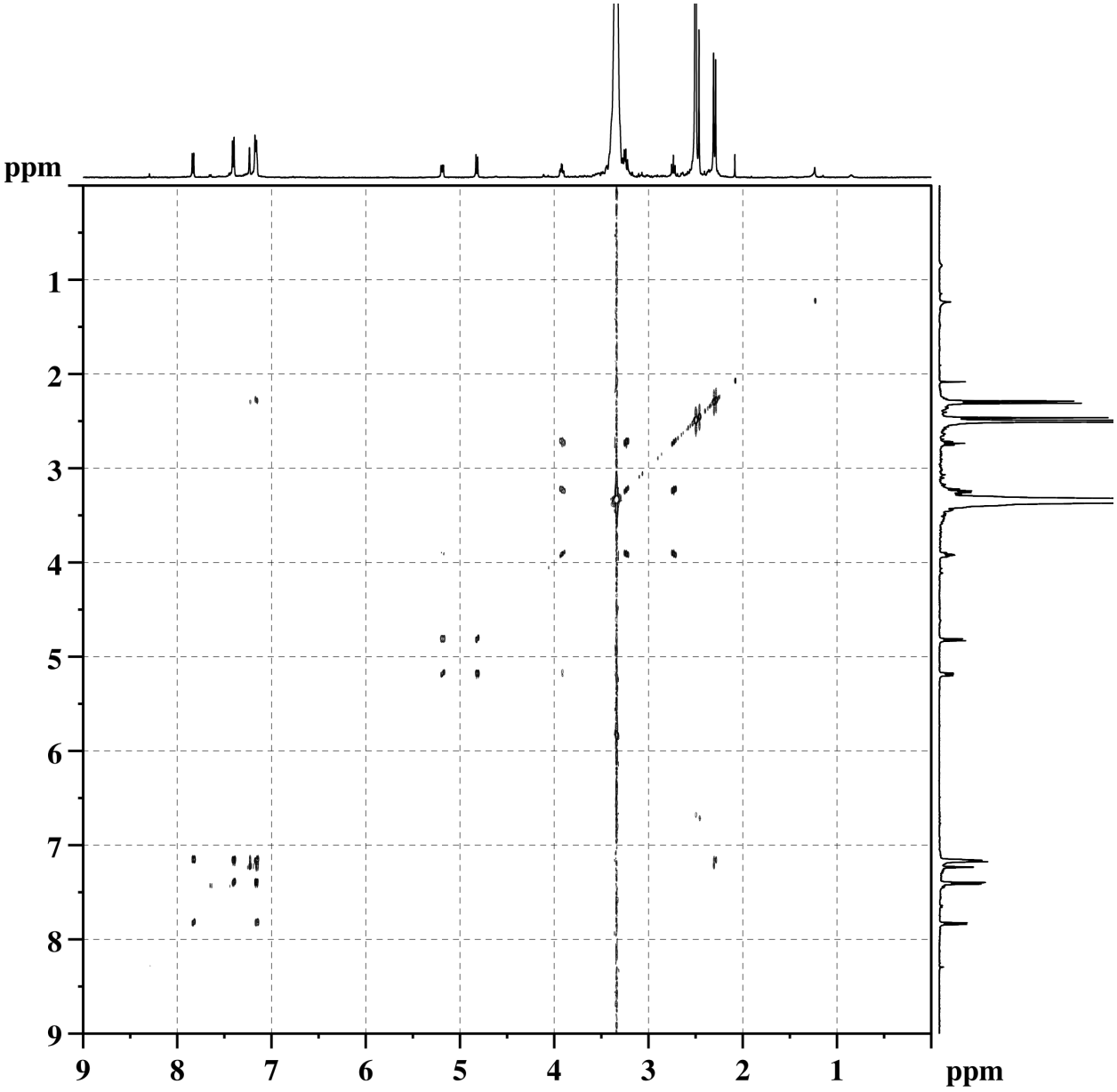
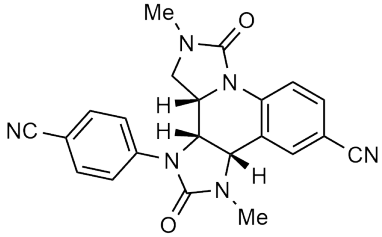


Figure S16. ^{1}H-^{13}C HMBC spectrum ($(CD_3)_2SO$, 303 K) of the compound ***endo*-2b**





***endo*-2m**

Figure S17. COSY spectrum ($(CD_3)_2SO$, 303 K) of the compound ***endo*-2m**

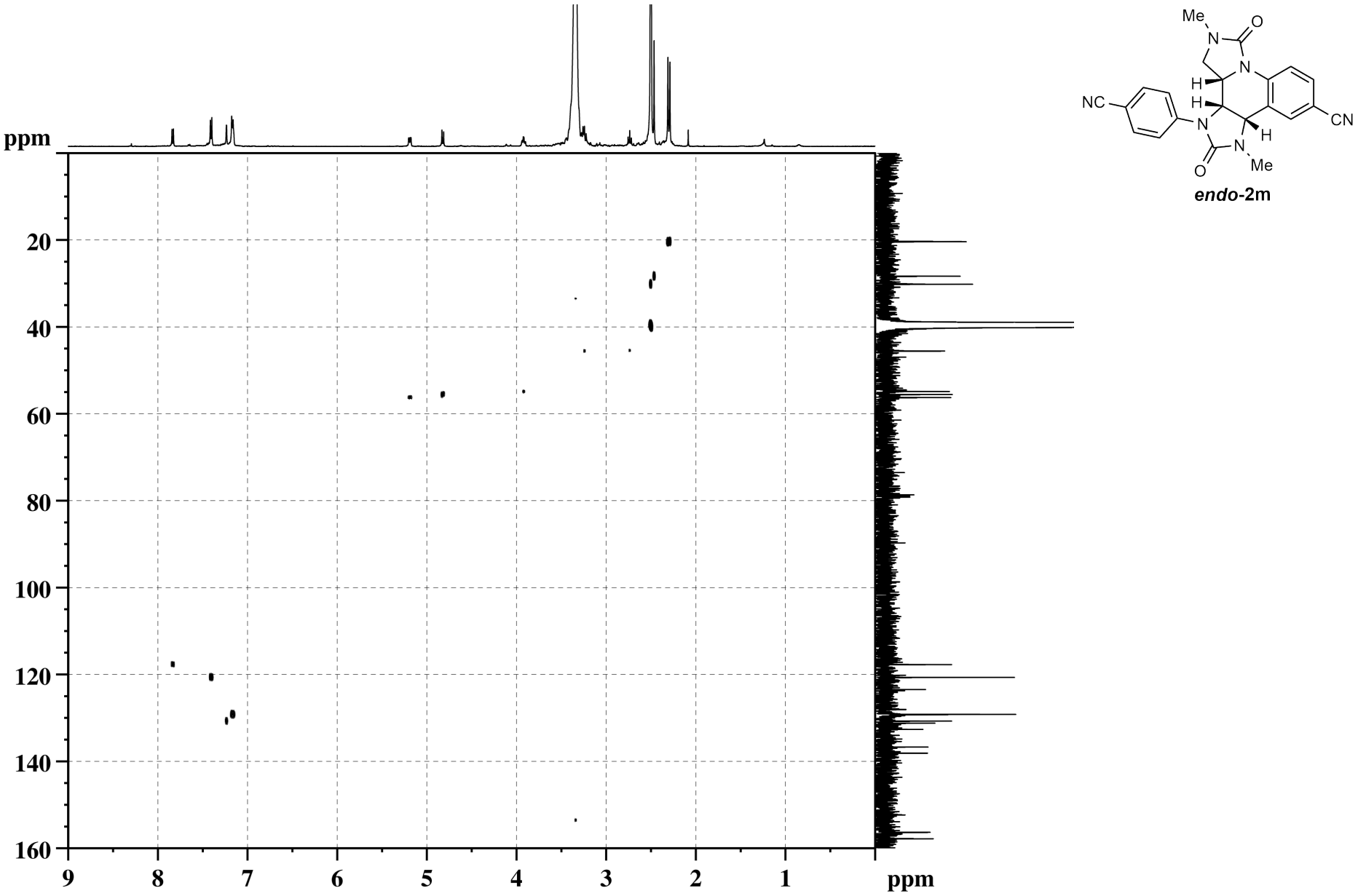
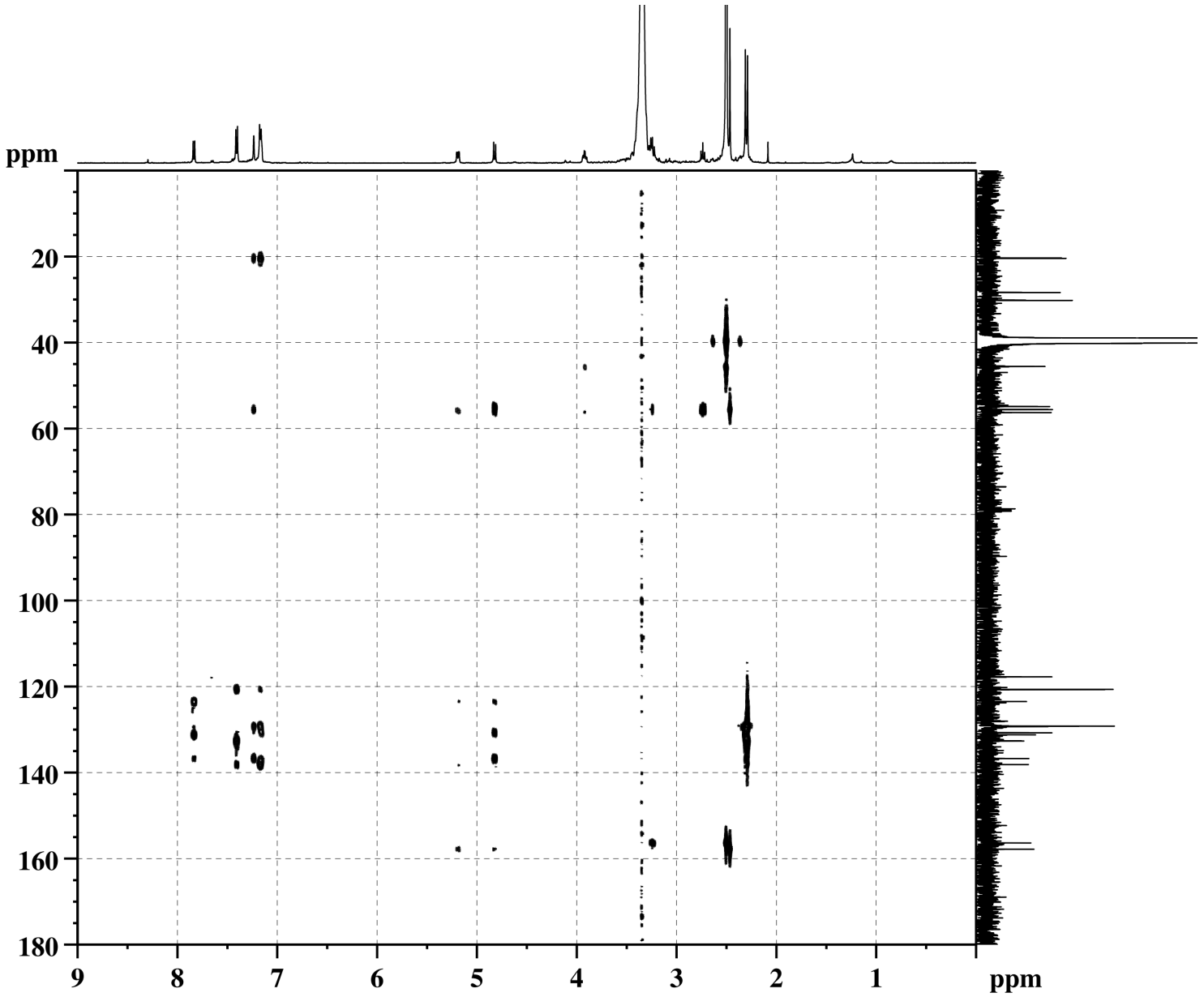
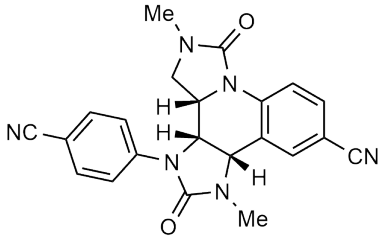


Figure S18. ^{1}H-^{13}C HSQC spectrum ($(CD_3)_2SO$, 303 K) of the compound ***endo*-2m**





***endo*-2m**

Figure S19. ^{1}H-^{13}C HMBC spectrum ($(CD_3)_2SO$, 303 K) of the compound ***endo*-2m**

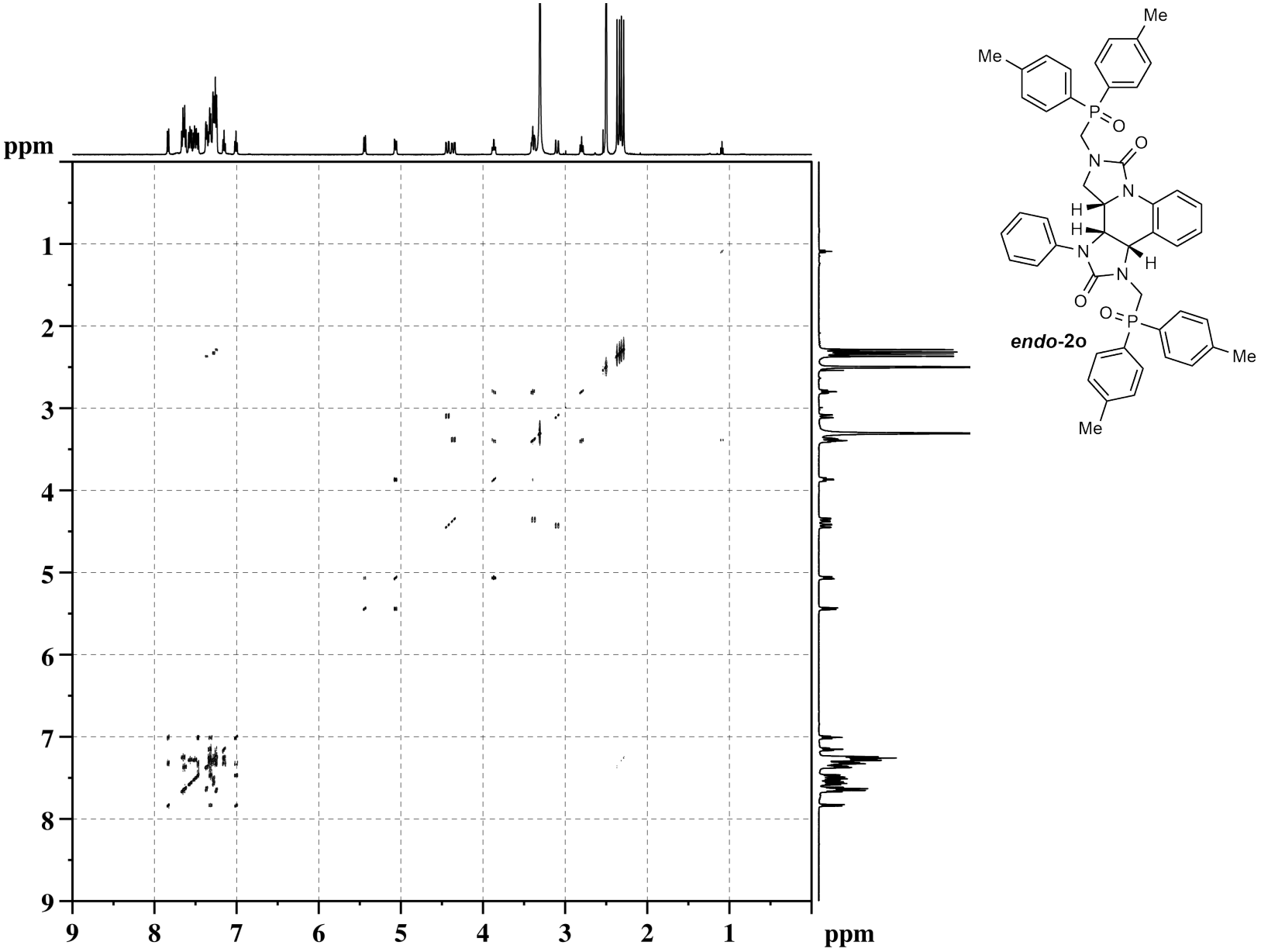


Figure S20. COSY spectrum ($(CD_3)_2SO$, 303 K) of the compound ***endo*-2o**

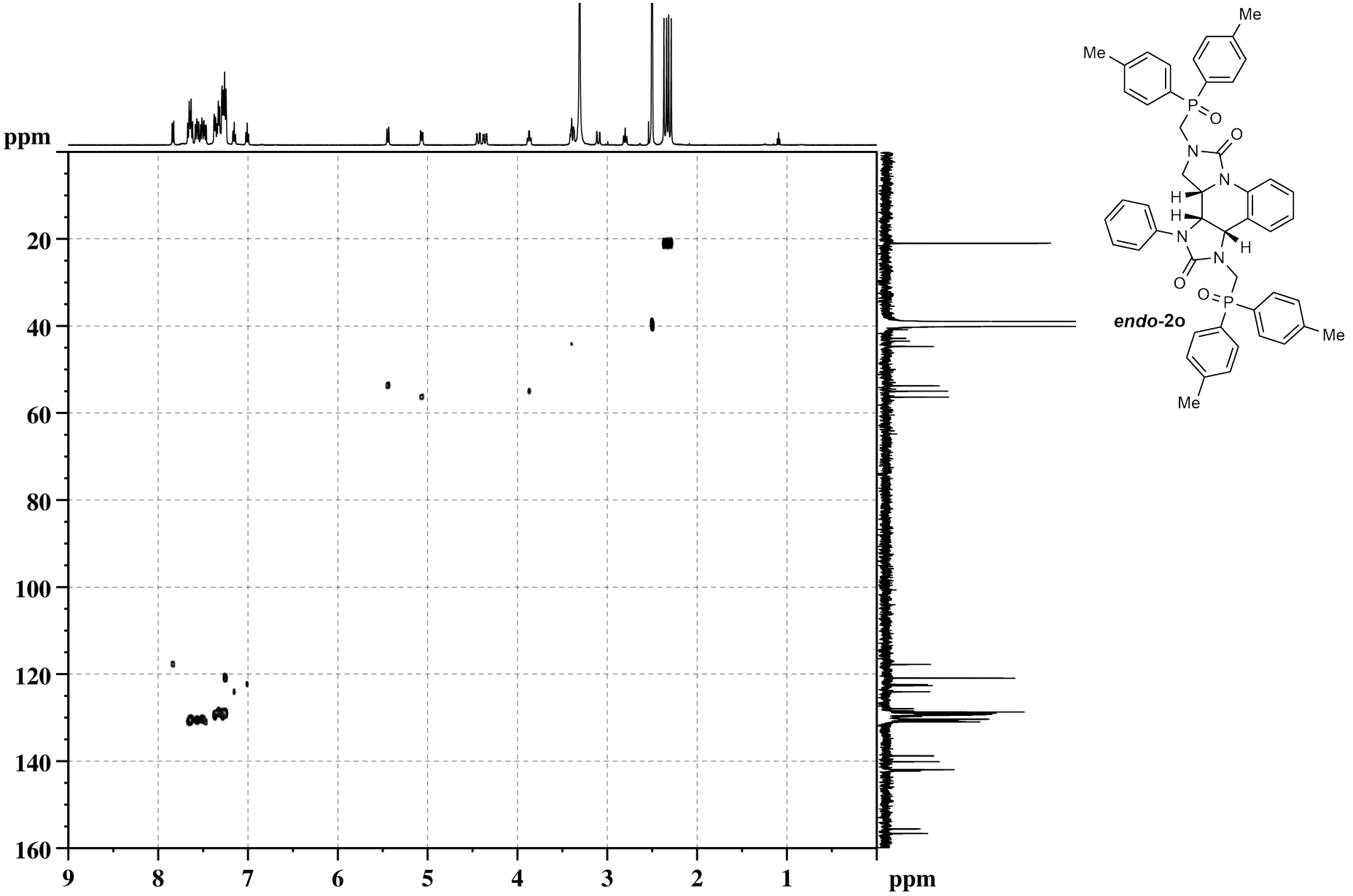


Figure S21. ^{1}H-^{13}C HSQC spectrum ($(CD_3)_2SO$, 303 K) of the compound ***endo*-2o**

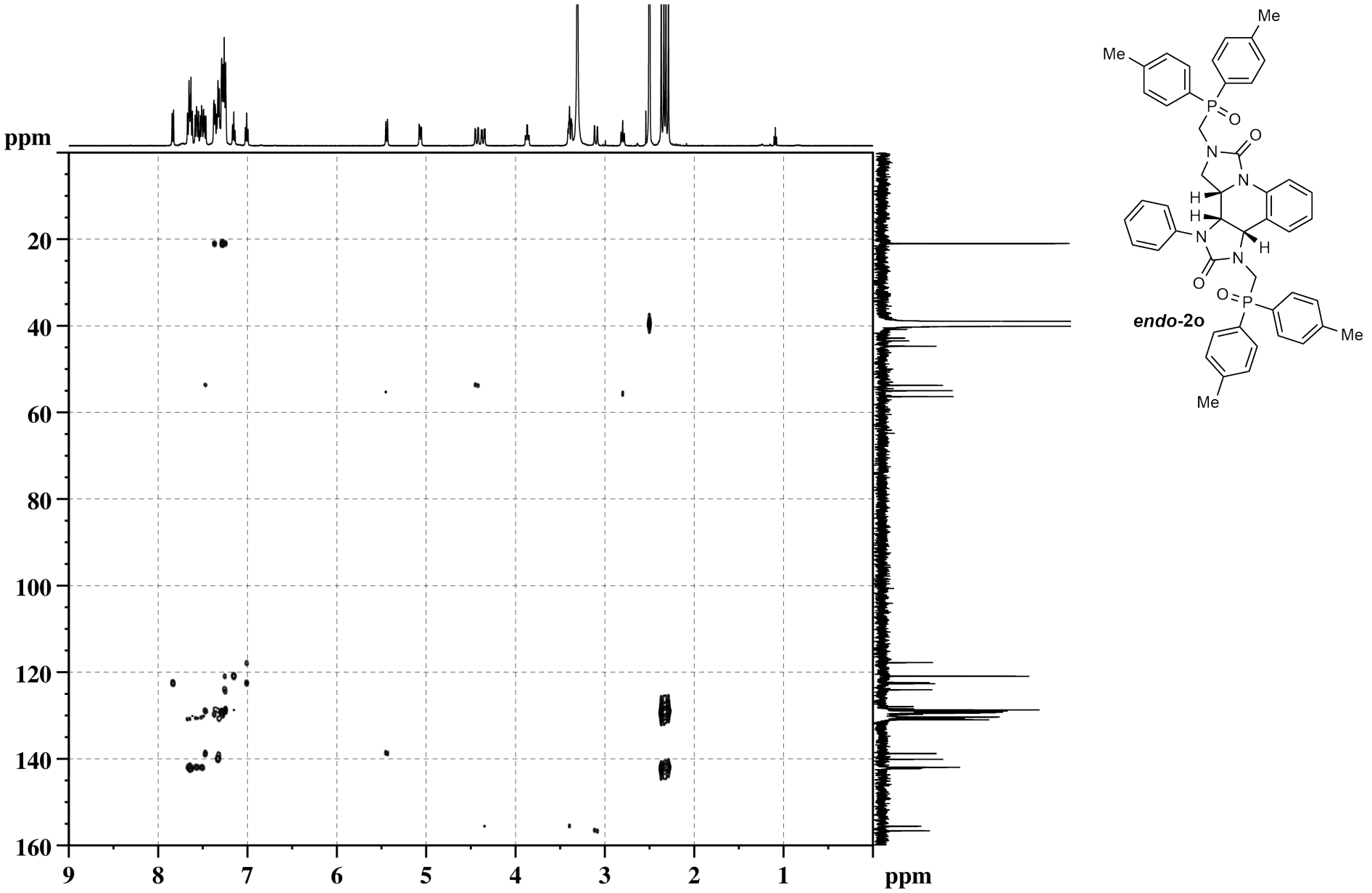
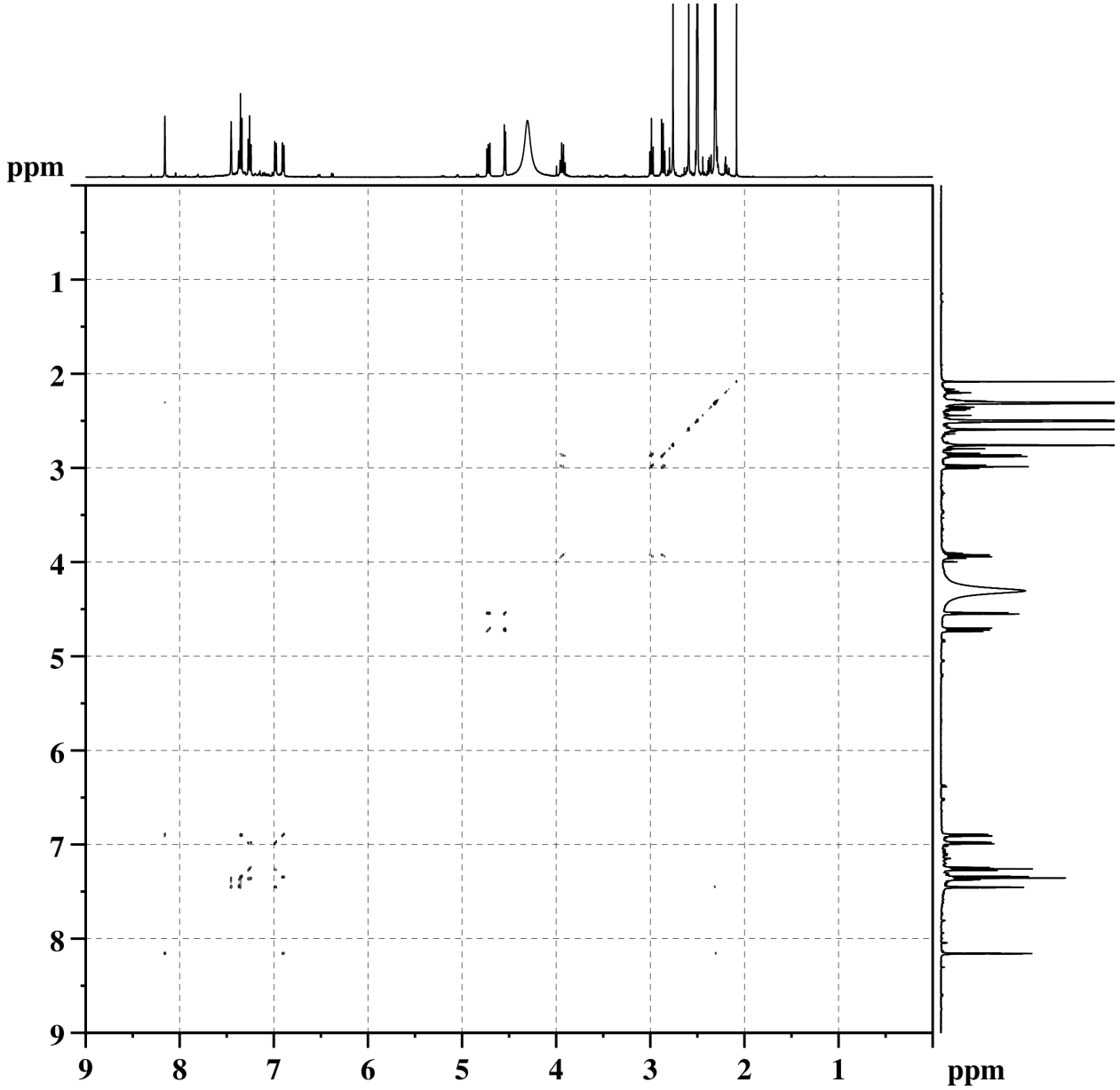
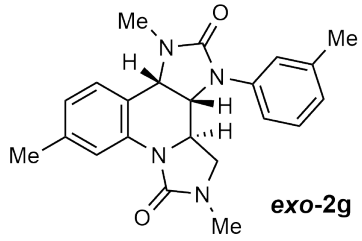


Figure S22. ^{1}H-^{13}C HMBC spectrum ($(CD_3)_2SO$, 303 K) of the compound ***endo*-2o**





***exo*-2g**

Figure S23. COSY spectrum ($(CD_3)_2SO$, 303 K) of the compound ***exo*-2g**

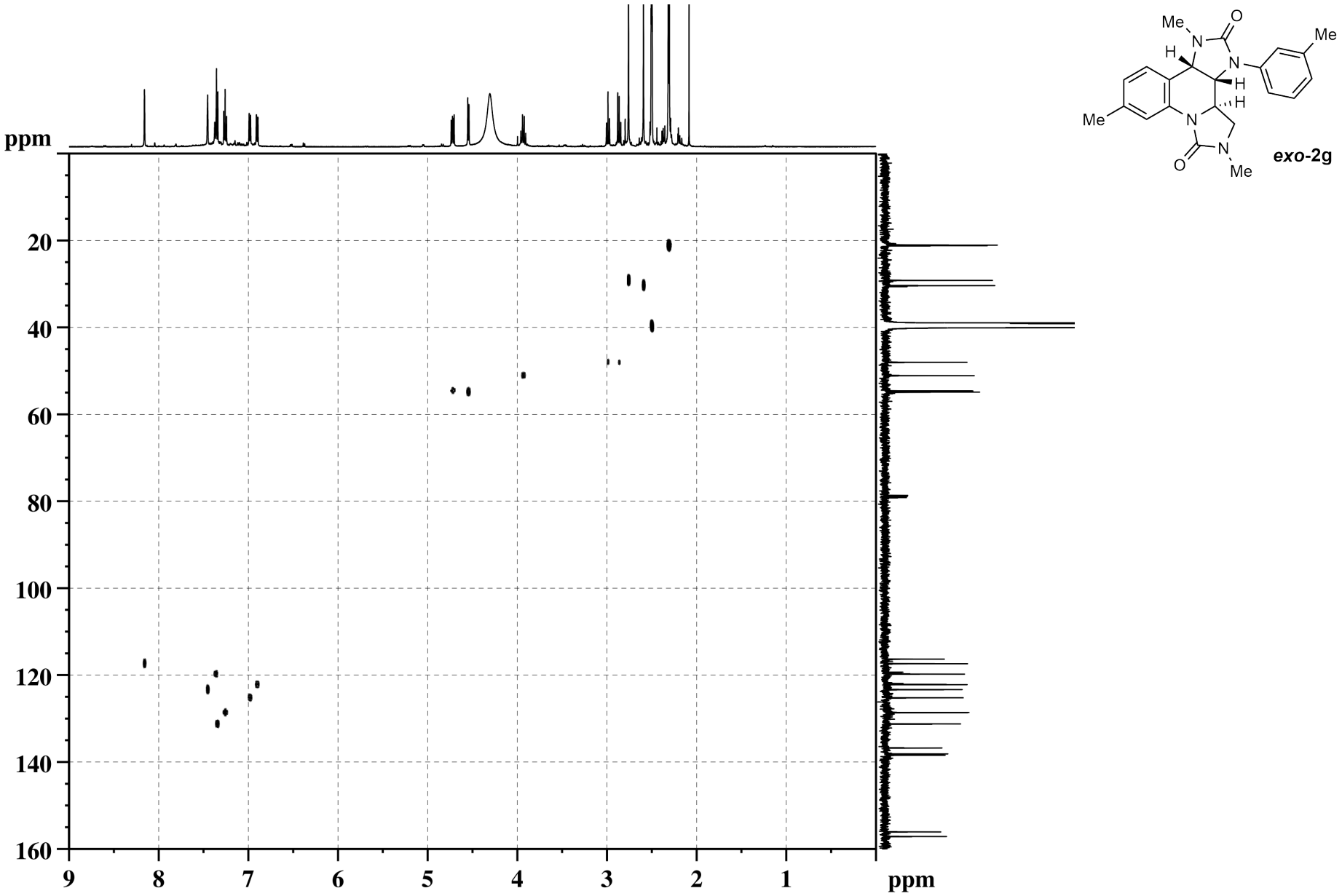
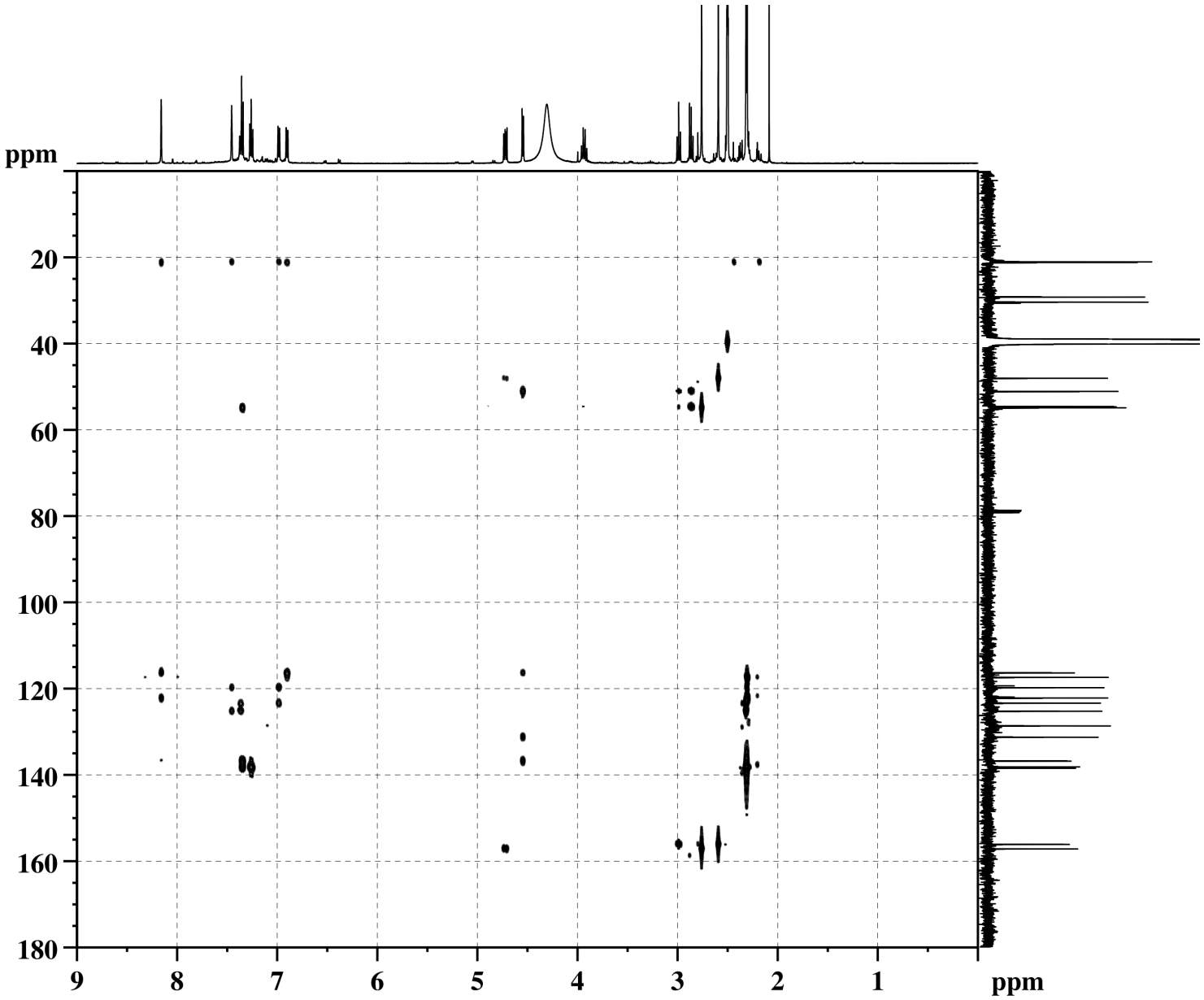
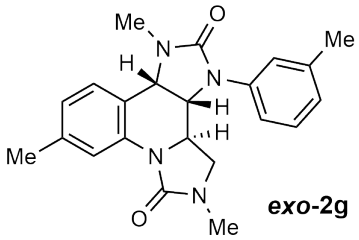


Figure S24. ^{1}H-^{13}C HSQC spectrum ($(CD_3)_2SO$, 303 K) of the compound ***exo*-2g**





***exo*-2g**

Figure S25. ^{1}H-^{13}C HMBC spectrum ($(CD_3)_2SO$, 303 K) of the compound ***exo*-2g**

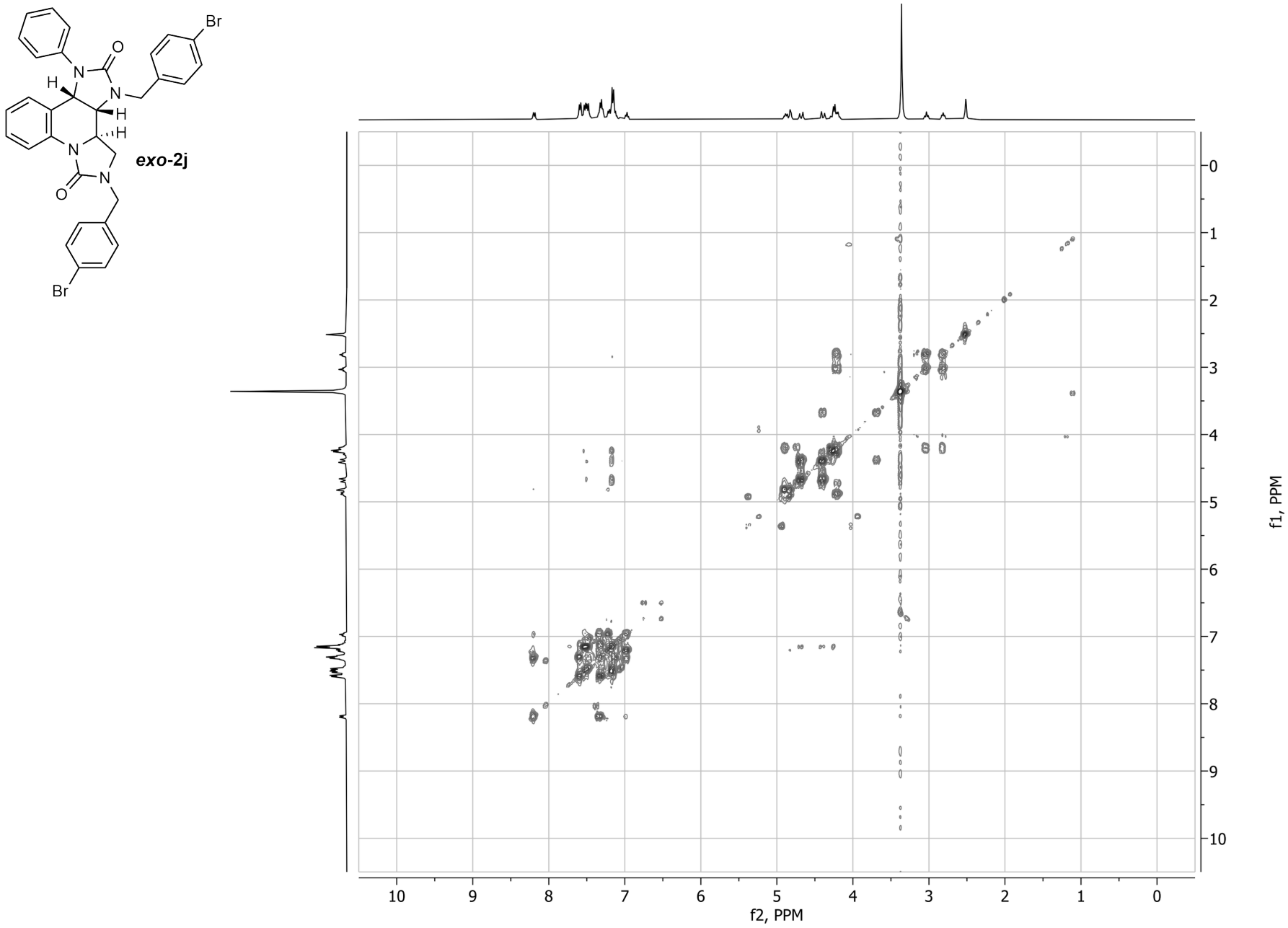


Figure S26. COSY spectrum ($(CD_3)_2SO$, 303 K) of the compound ***exo*-2j**

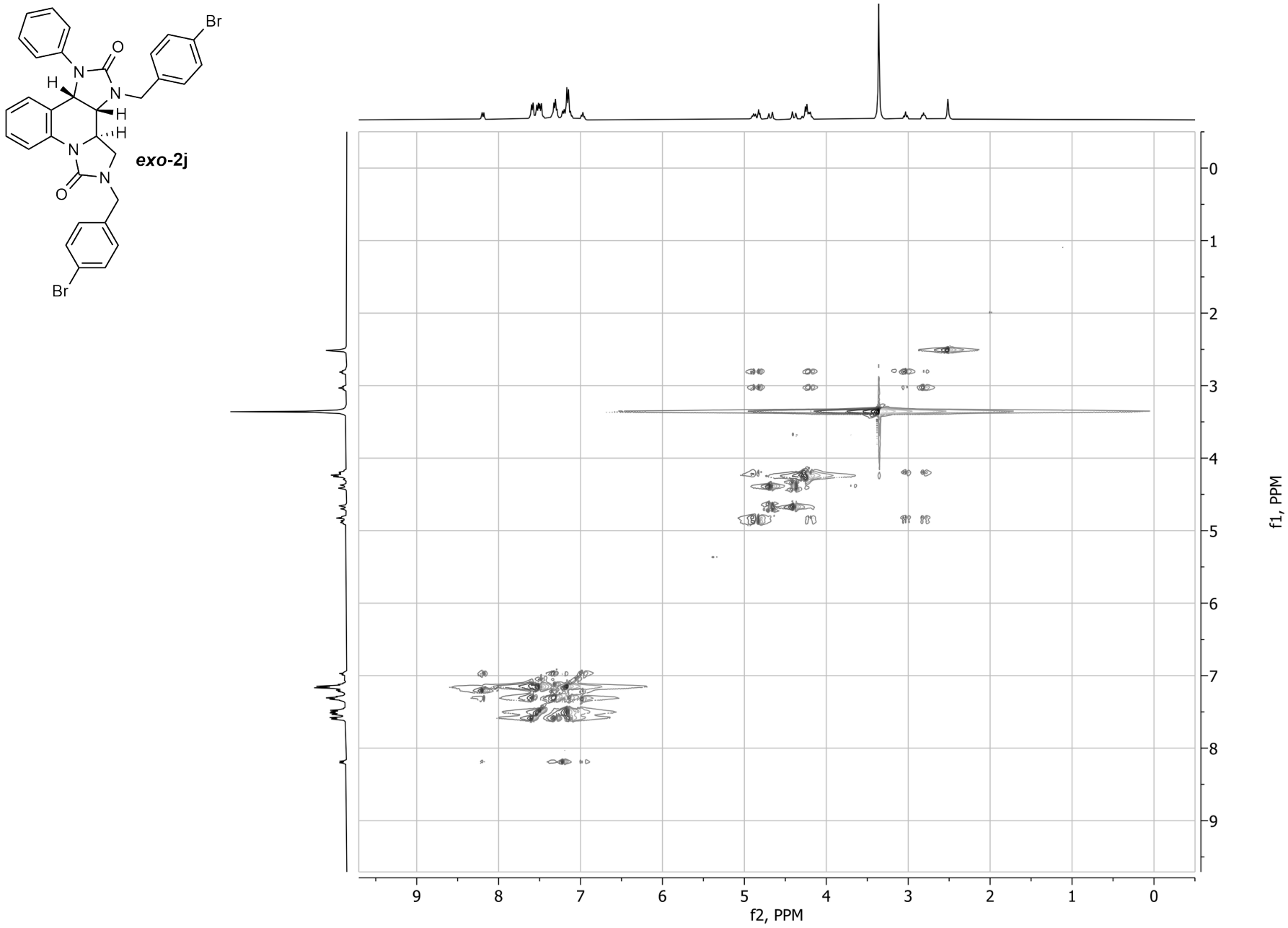


Figure S27. TOCSY spectrum ($(CD_3)_2SO$, 303 K) of the compound ***exo*-2j**

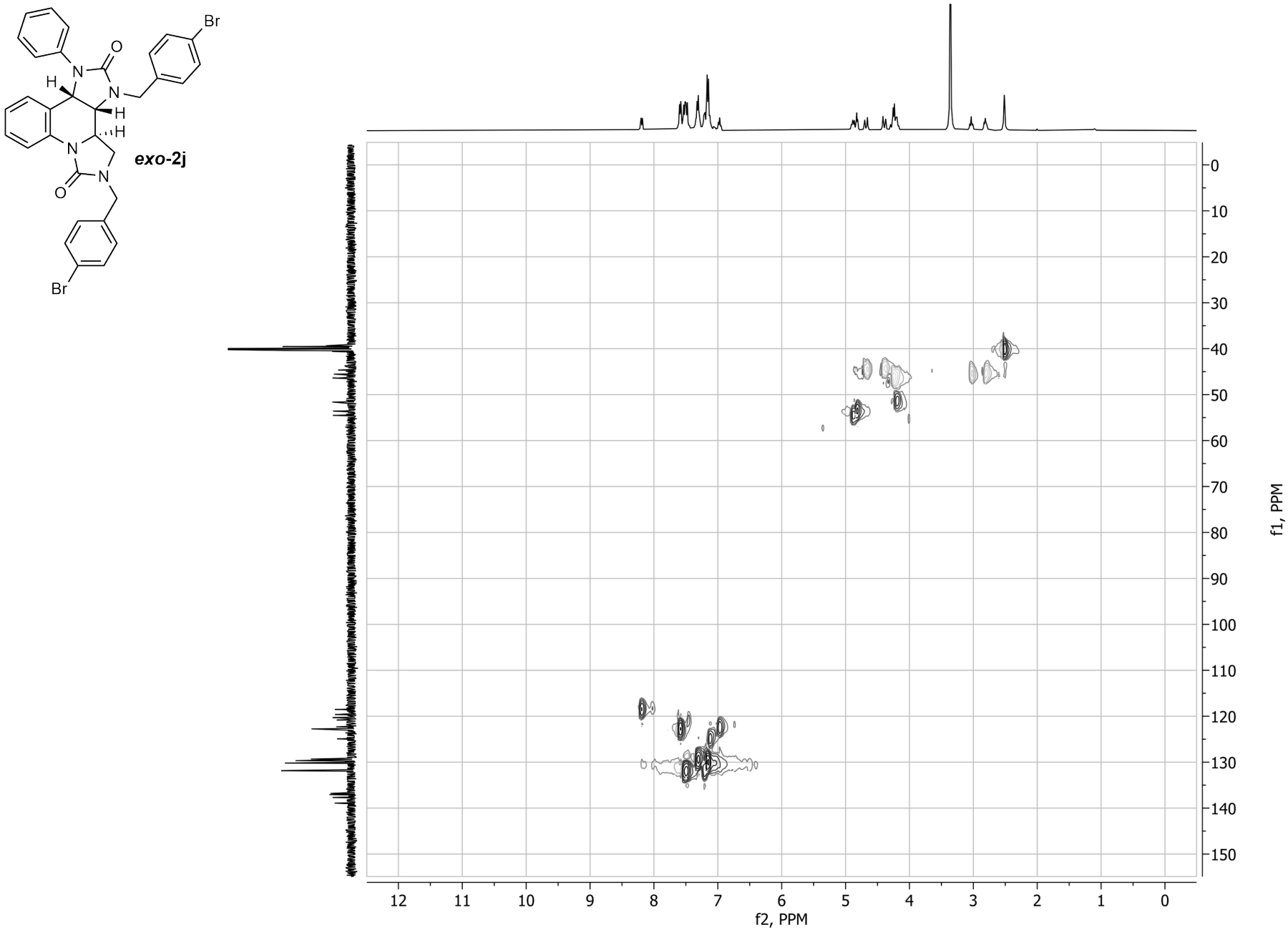


Figure S28. ^{1}H-^{13}C HSQC spectrum ($(CD_3)_2SO$, 303 K) of the compound ***exo*-2j**

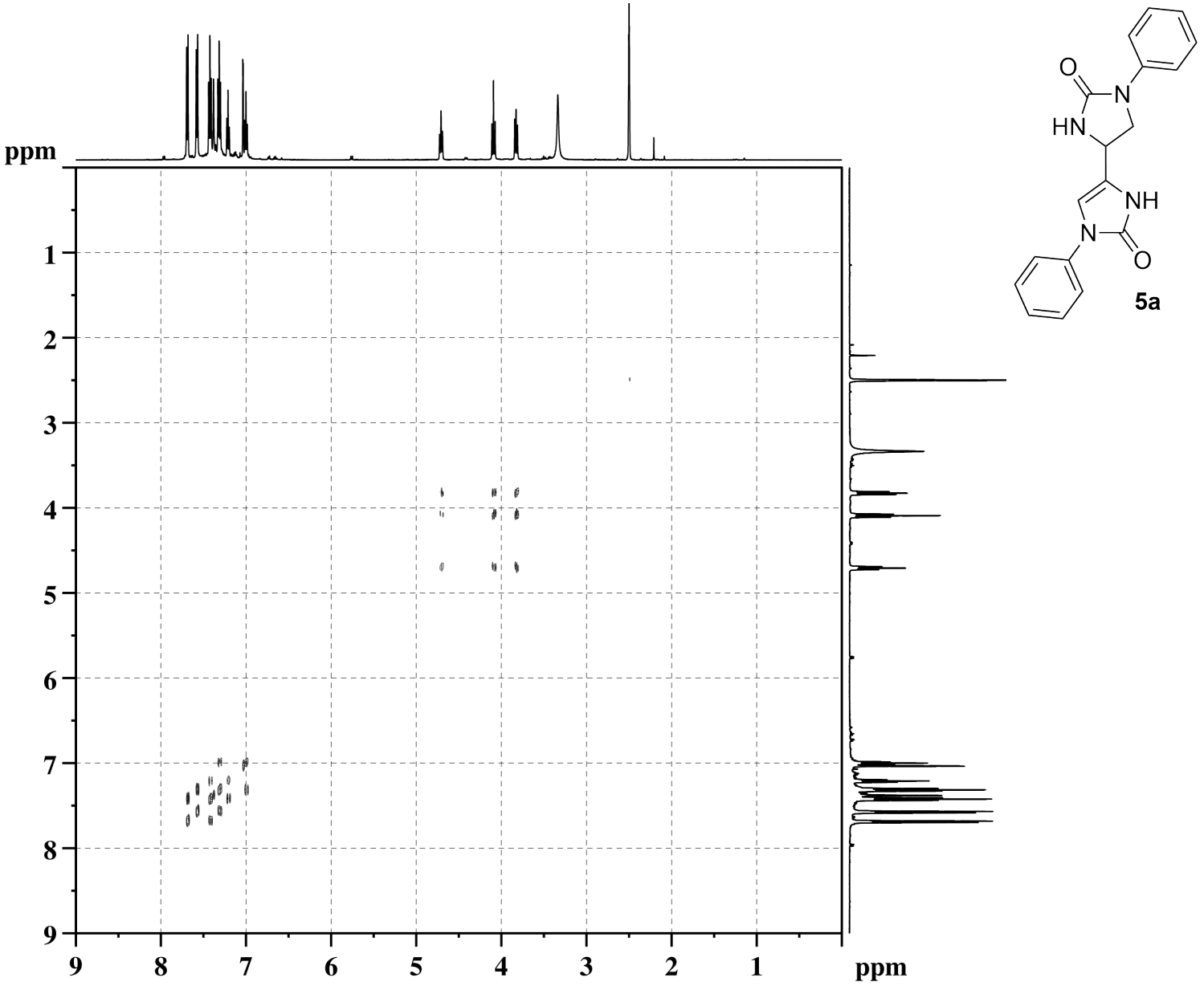


Figure S29. COSY spectrum ($(CD_3)_2SO$, 303 K) of the compound **5a**

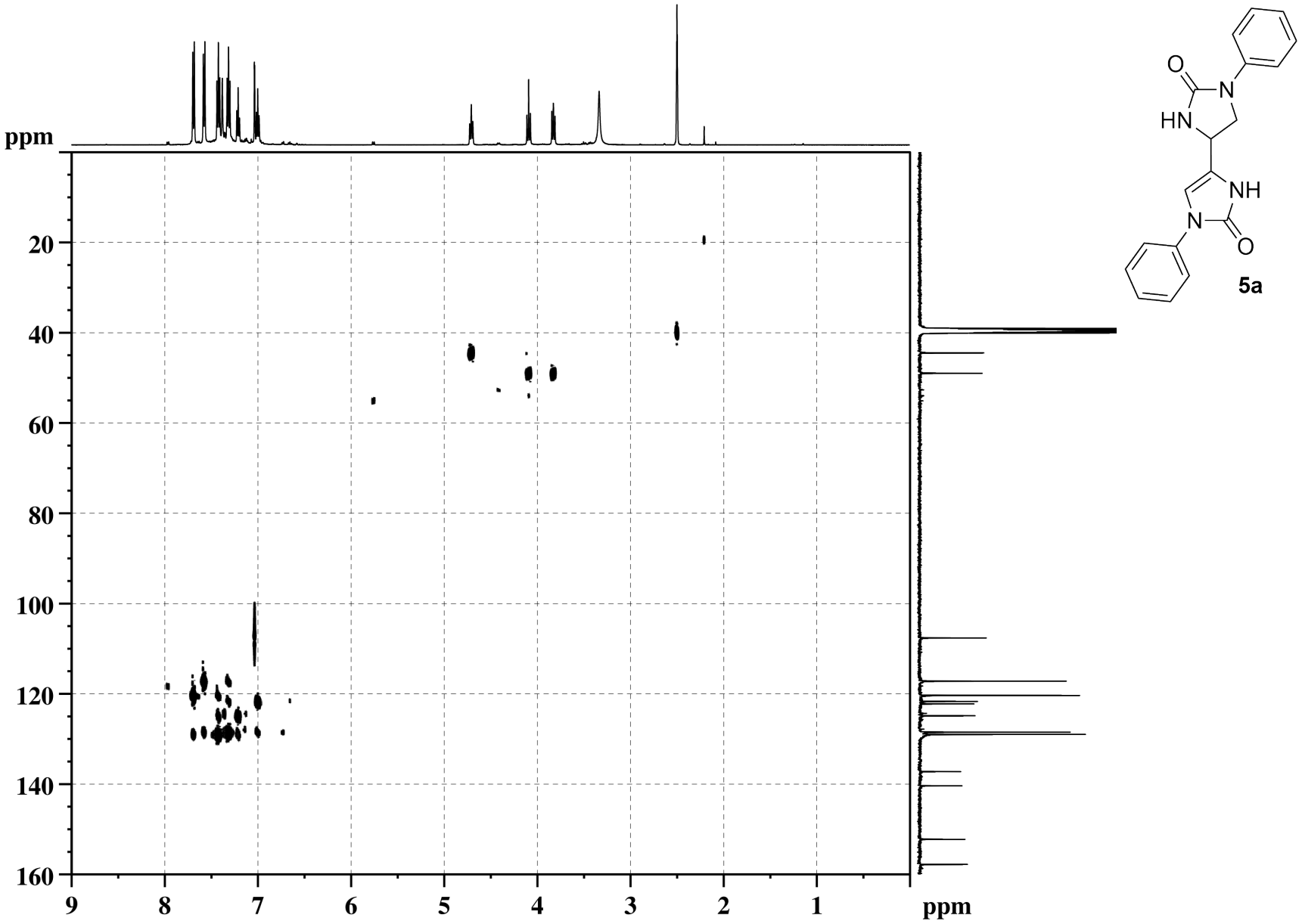


Figure S30. ^{1}H-^{13}C HSQC spectrum ($(CD_3)_2SO$, 303 K) of the compound **5a**

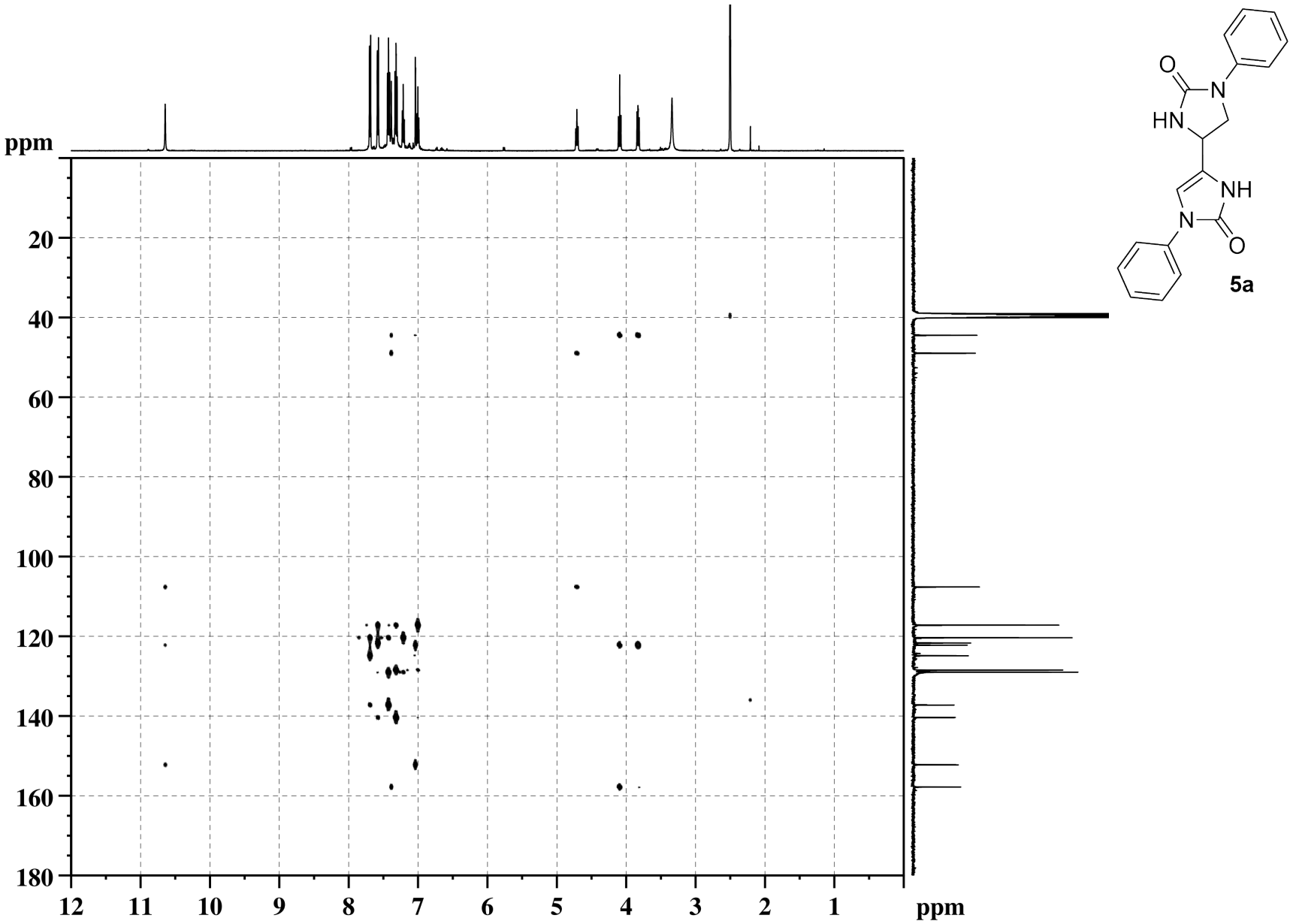


Figure S31. ^{1}H-^{13}C HMBC spectrum ($(CD_3)_2SO$, 303 K) of the compound **5a**

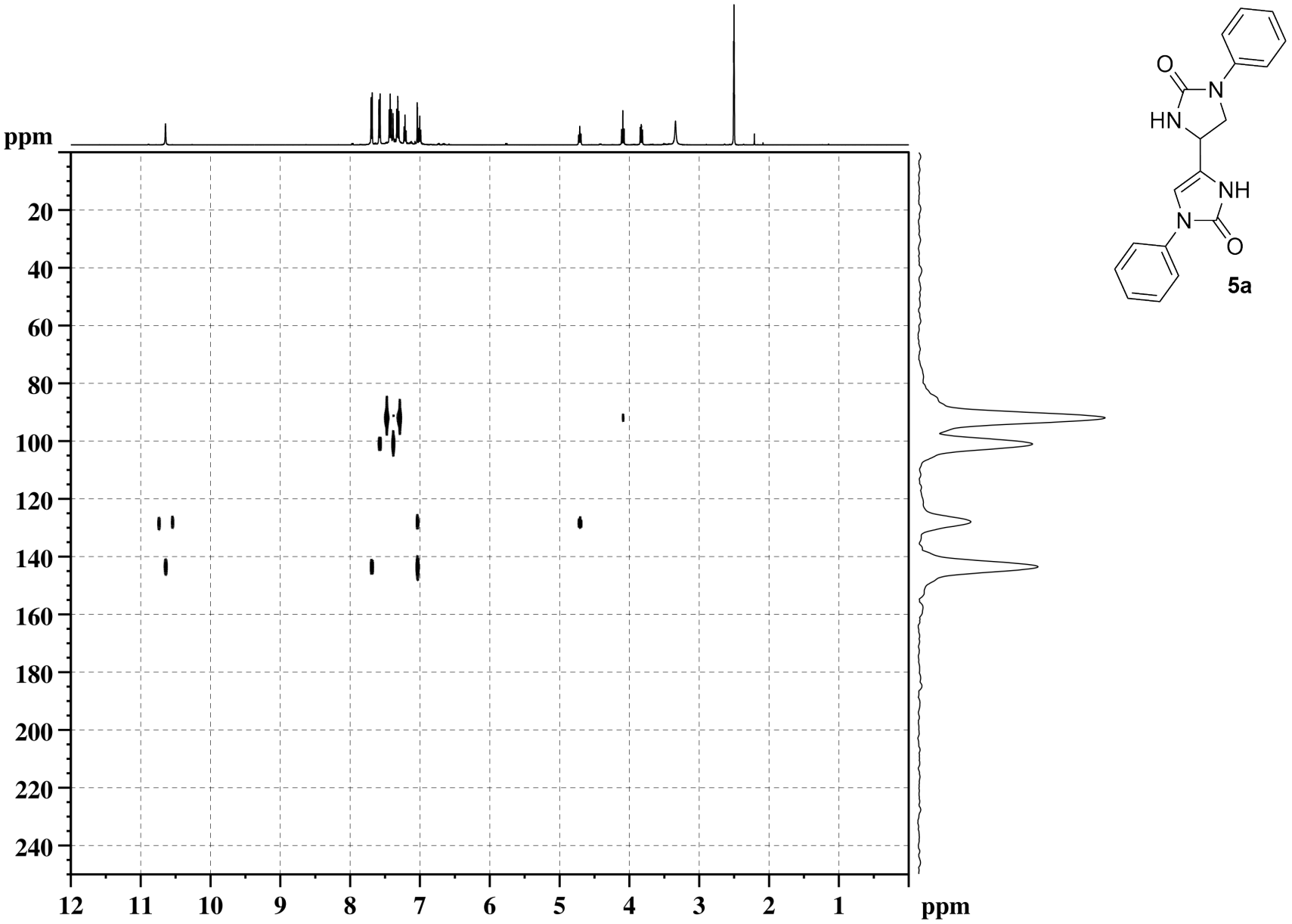


Figure S32. ^{1}H-^{15}N HMBC spectrum ($(CD_3)_2SO$, 303 K) of the compound **5a**

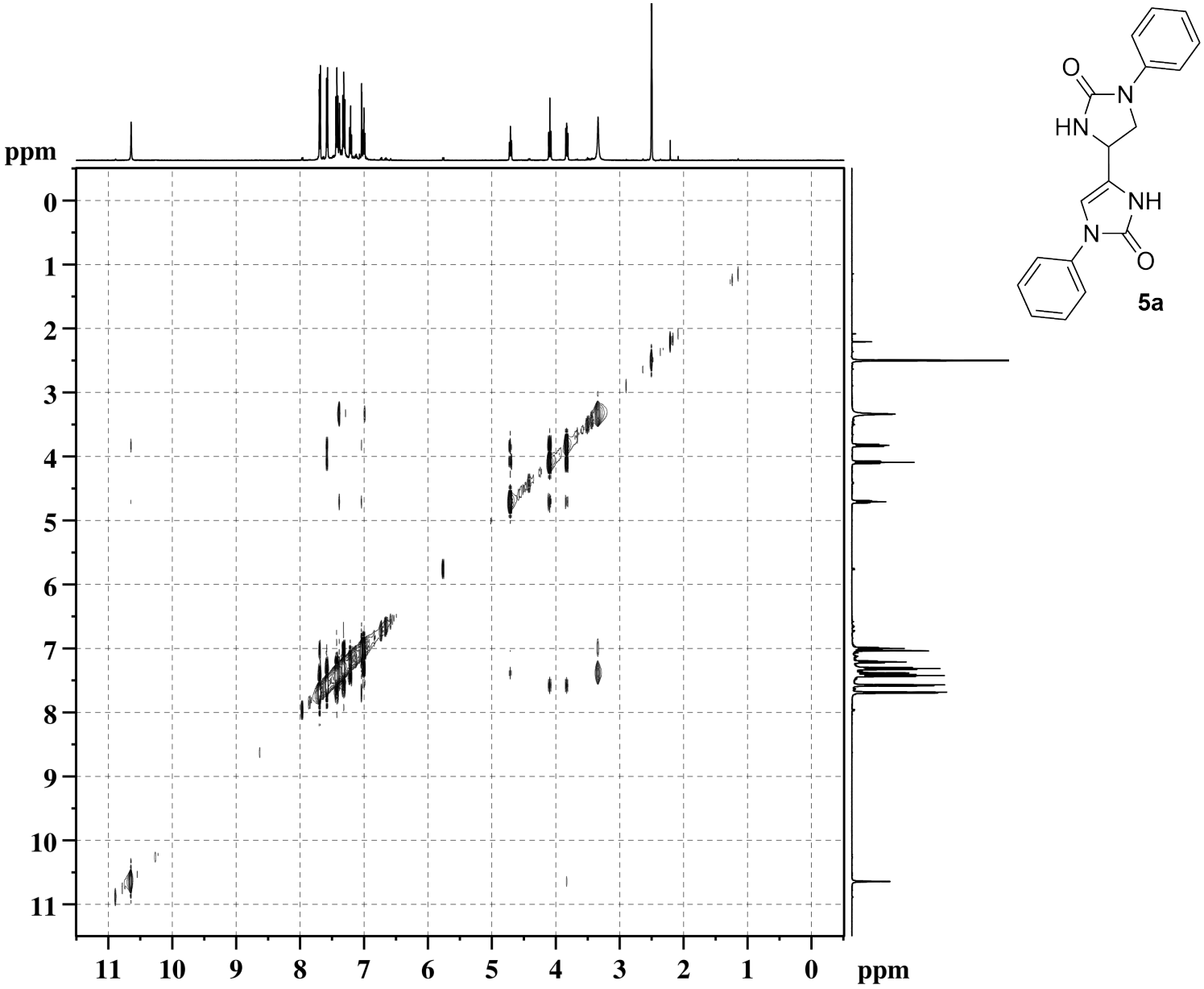


Figure S33. NOESY spectrum ($(CD_3)_2SO$, 303 K) of the compound **5a**

Copies of 1H and 13C NMR spectra

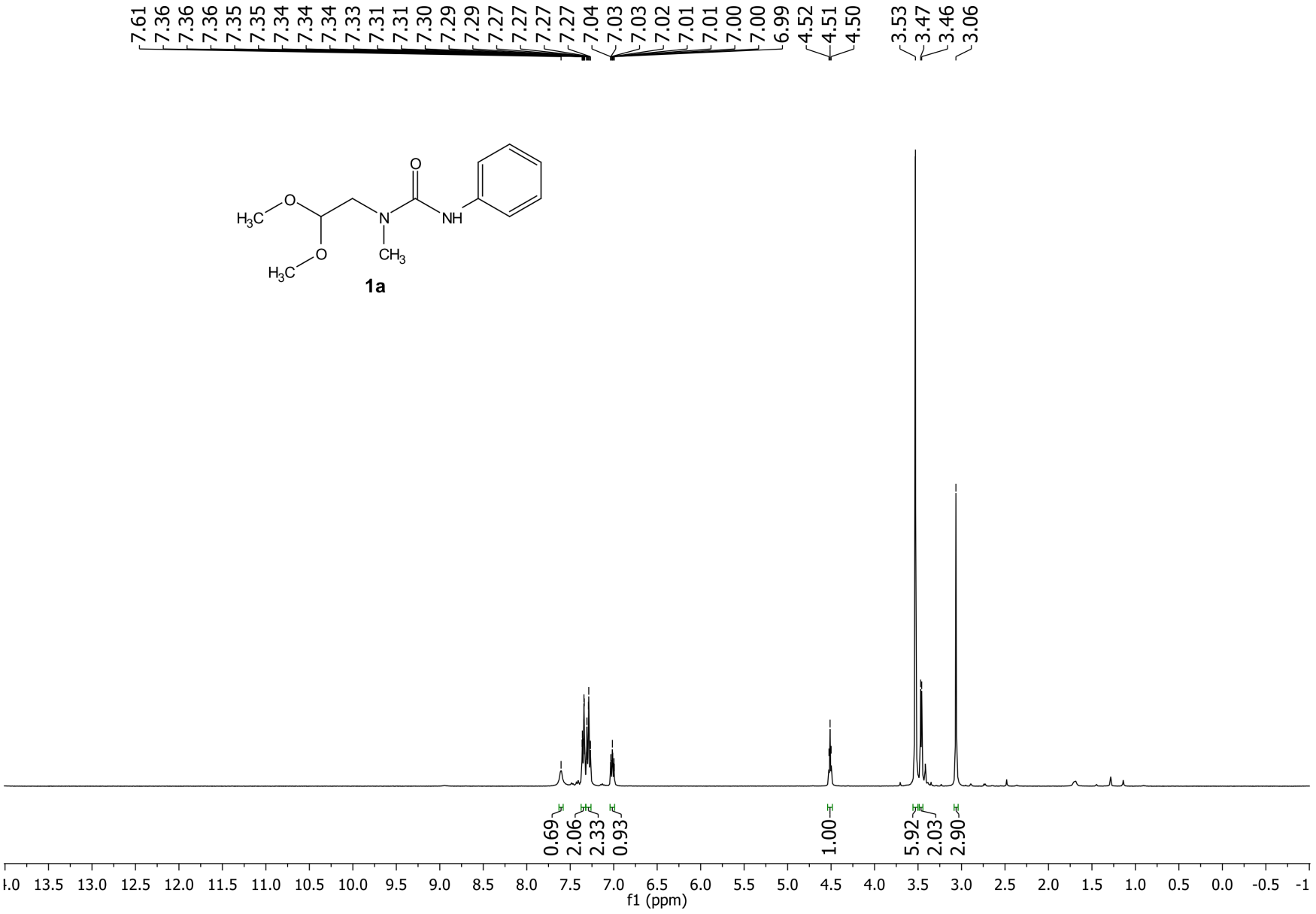


Figure S34. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **1a**

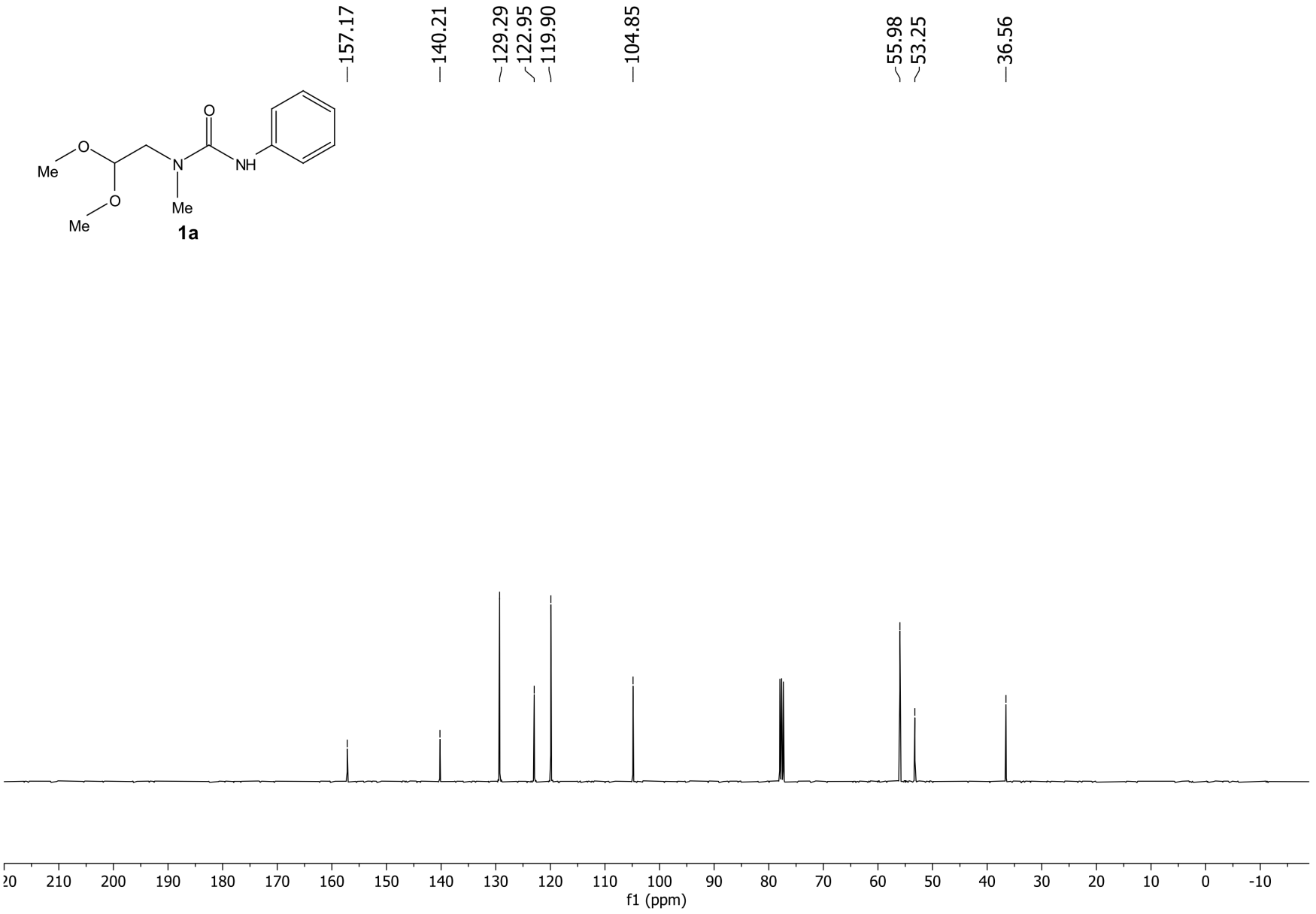


Figure S35. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **1a**

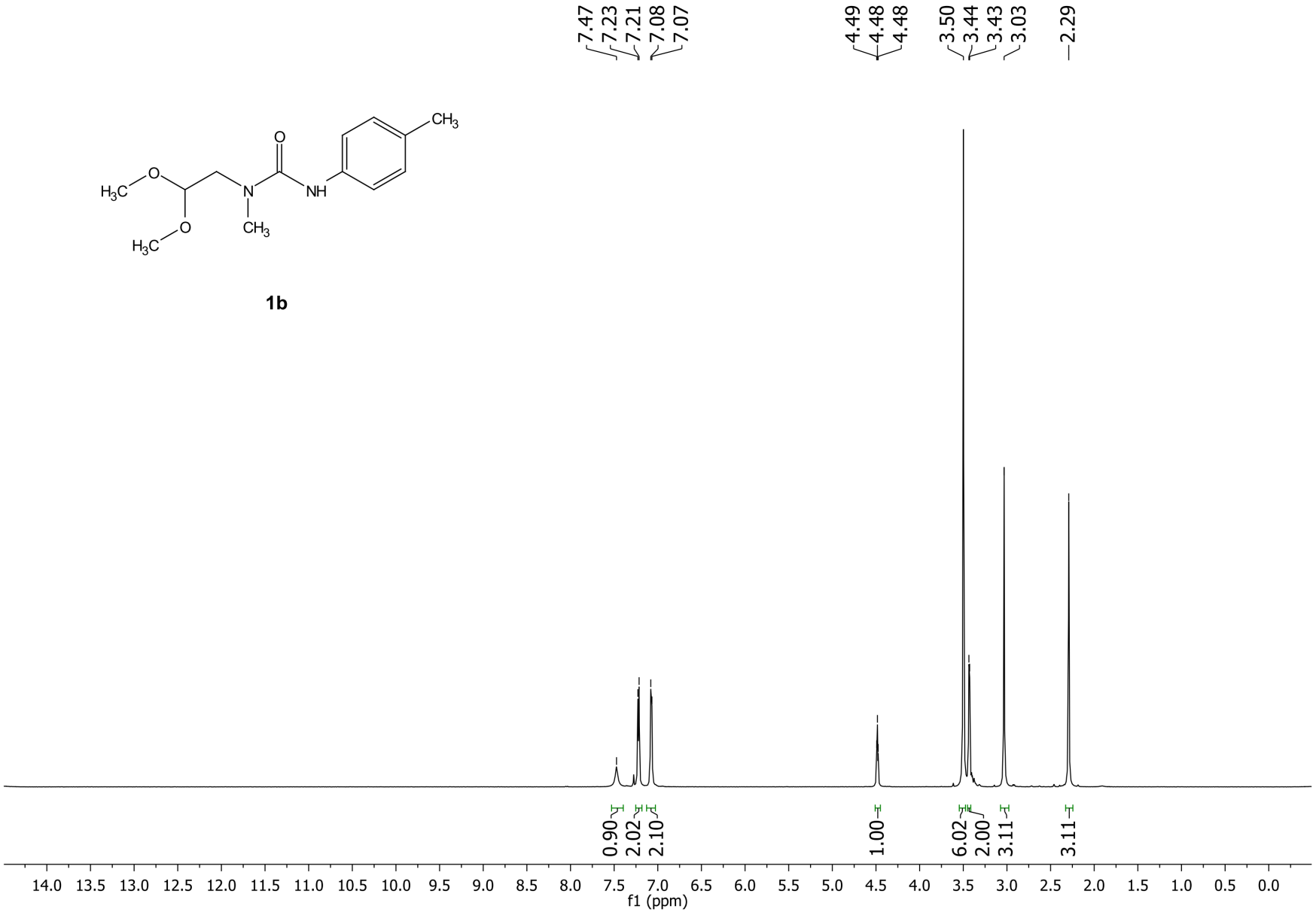


Figure S36. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **1b**

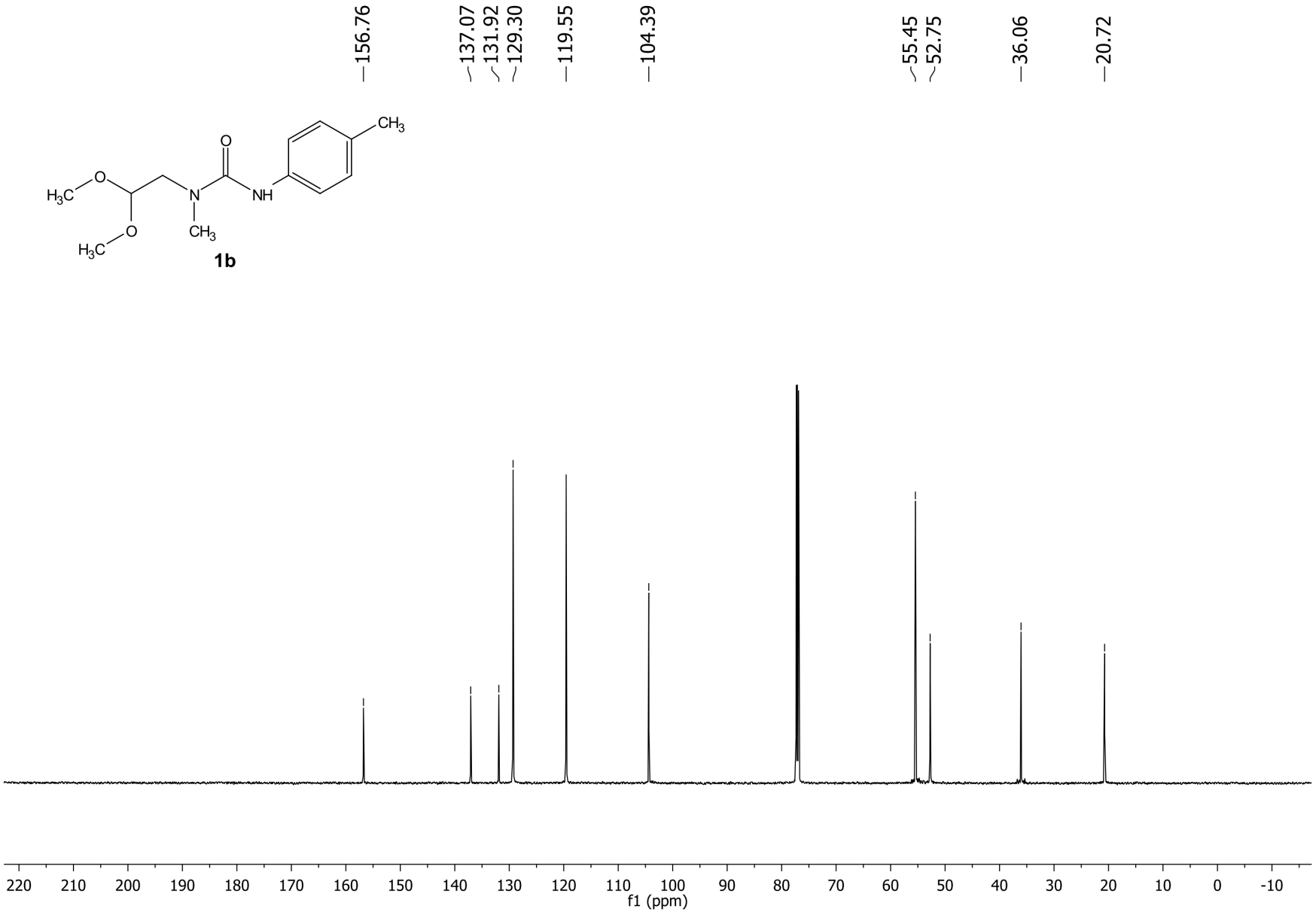


Figure S37. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **1b**

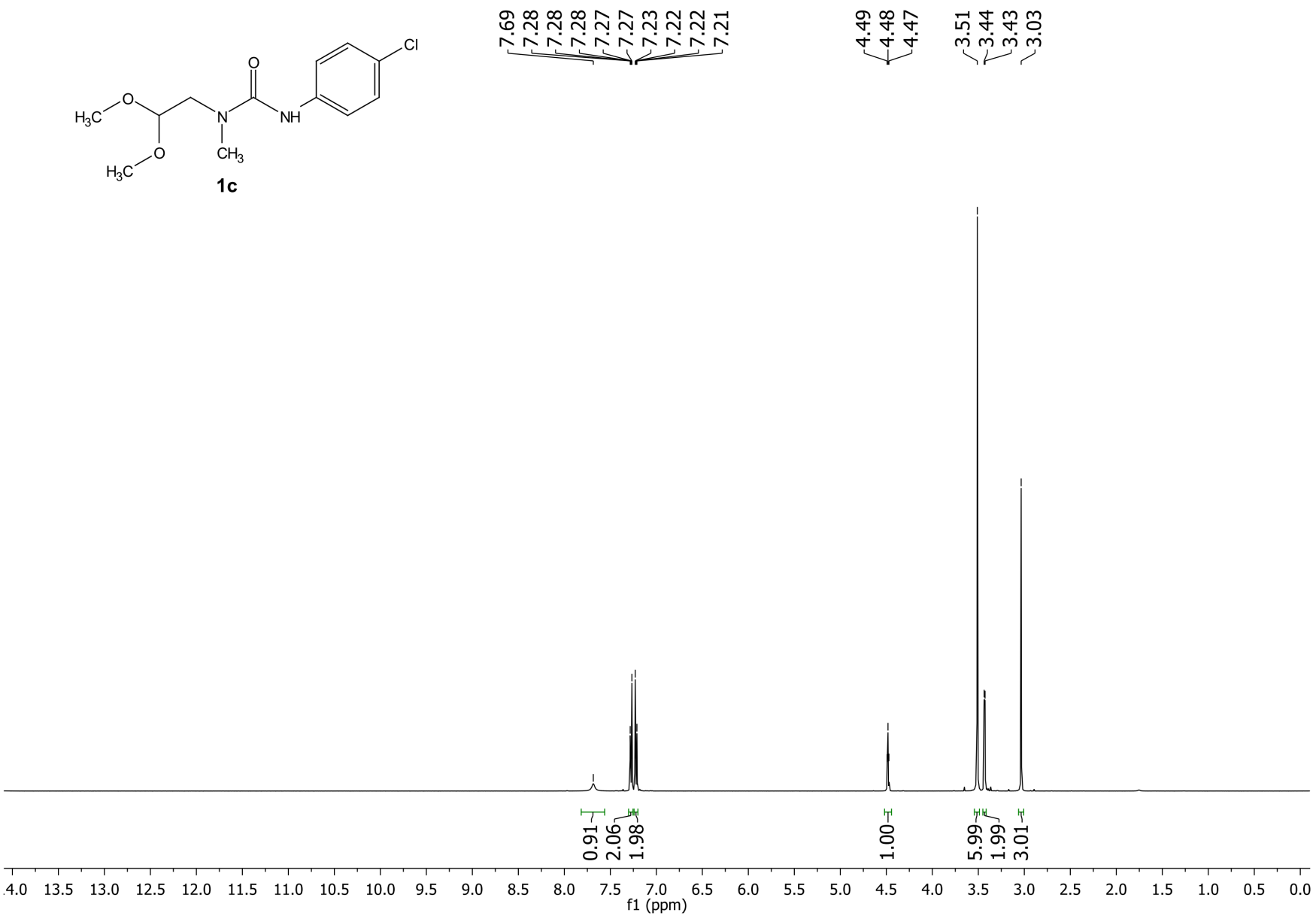


Figure S38. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **1c**

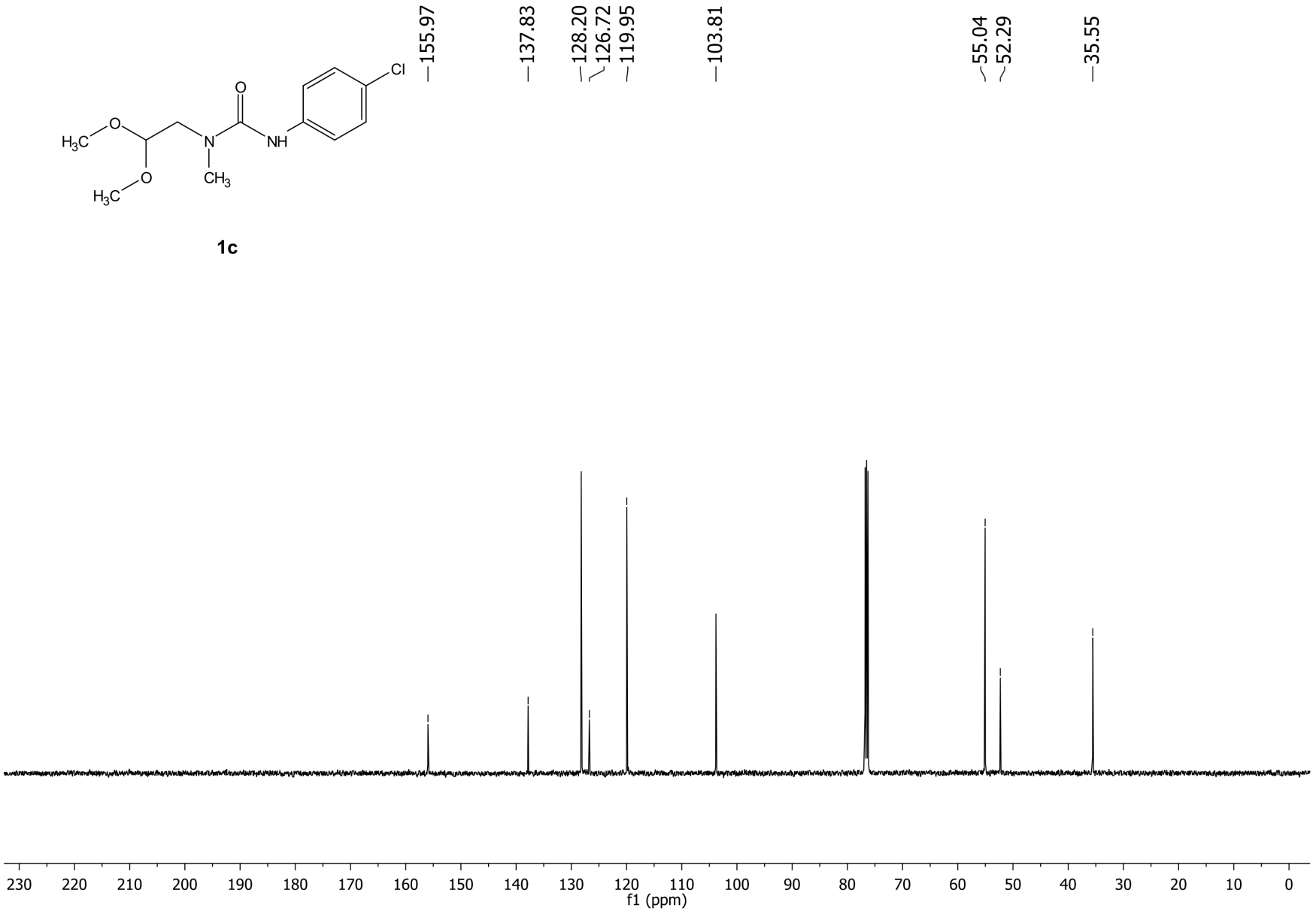
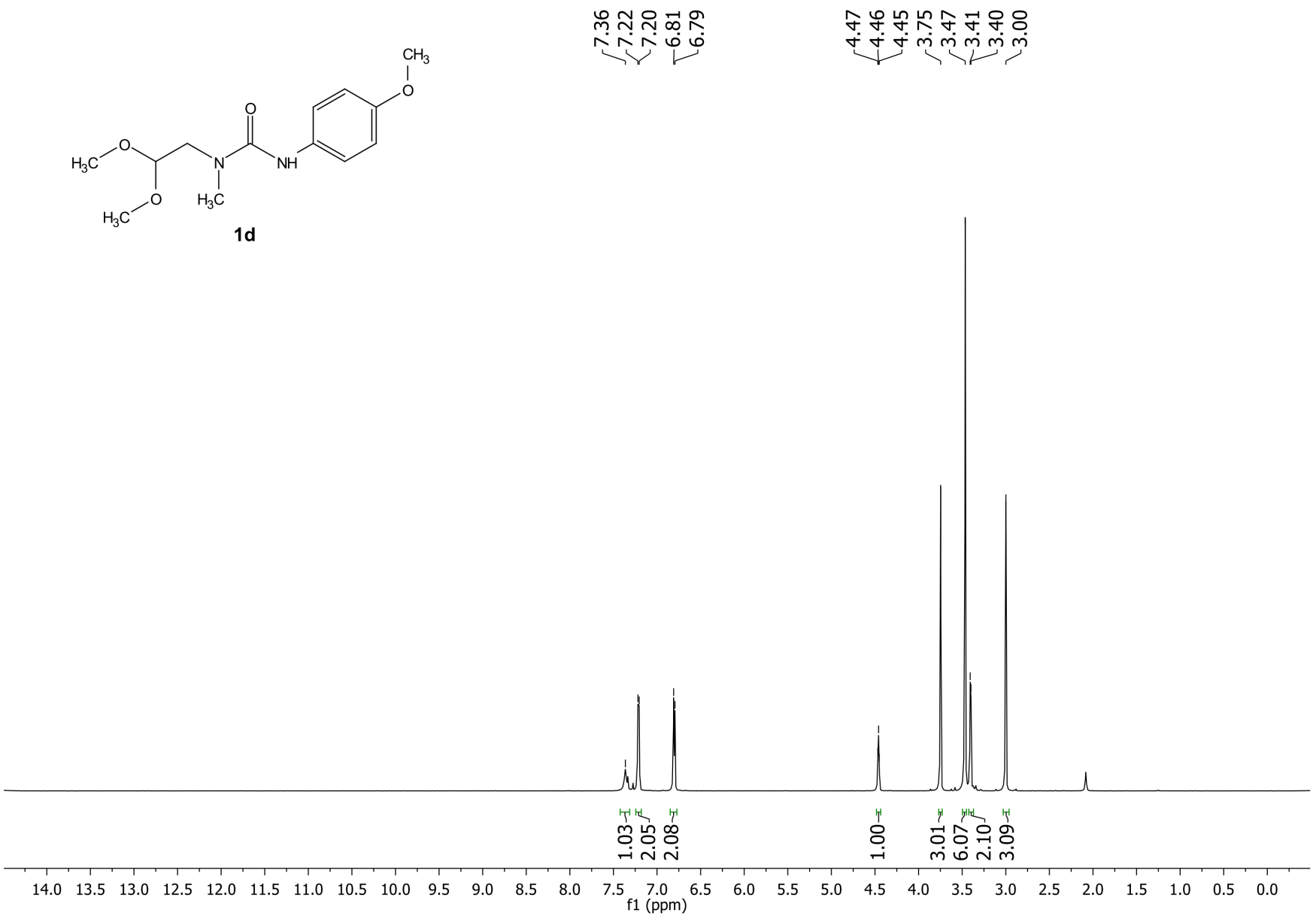


Figure S39. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **1c**



1d

Figure S40. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **1d**

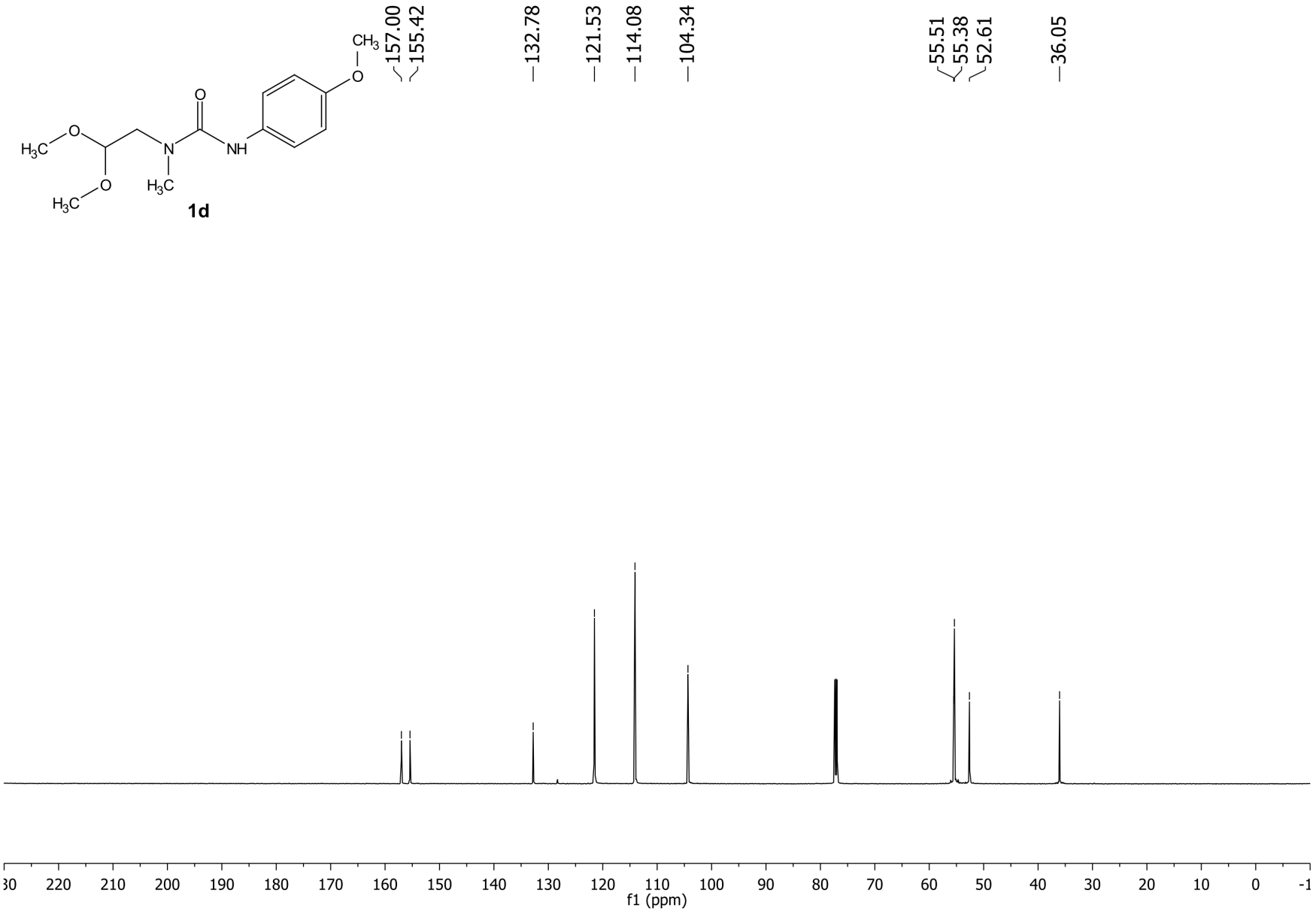


Figure S41. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **1d**

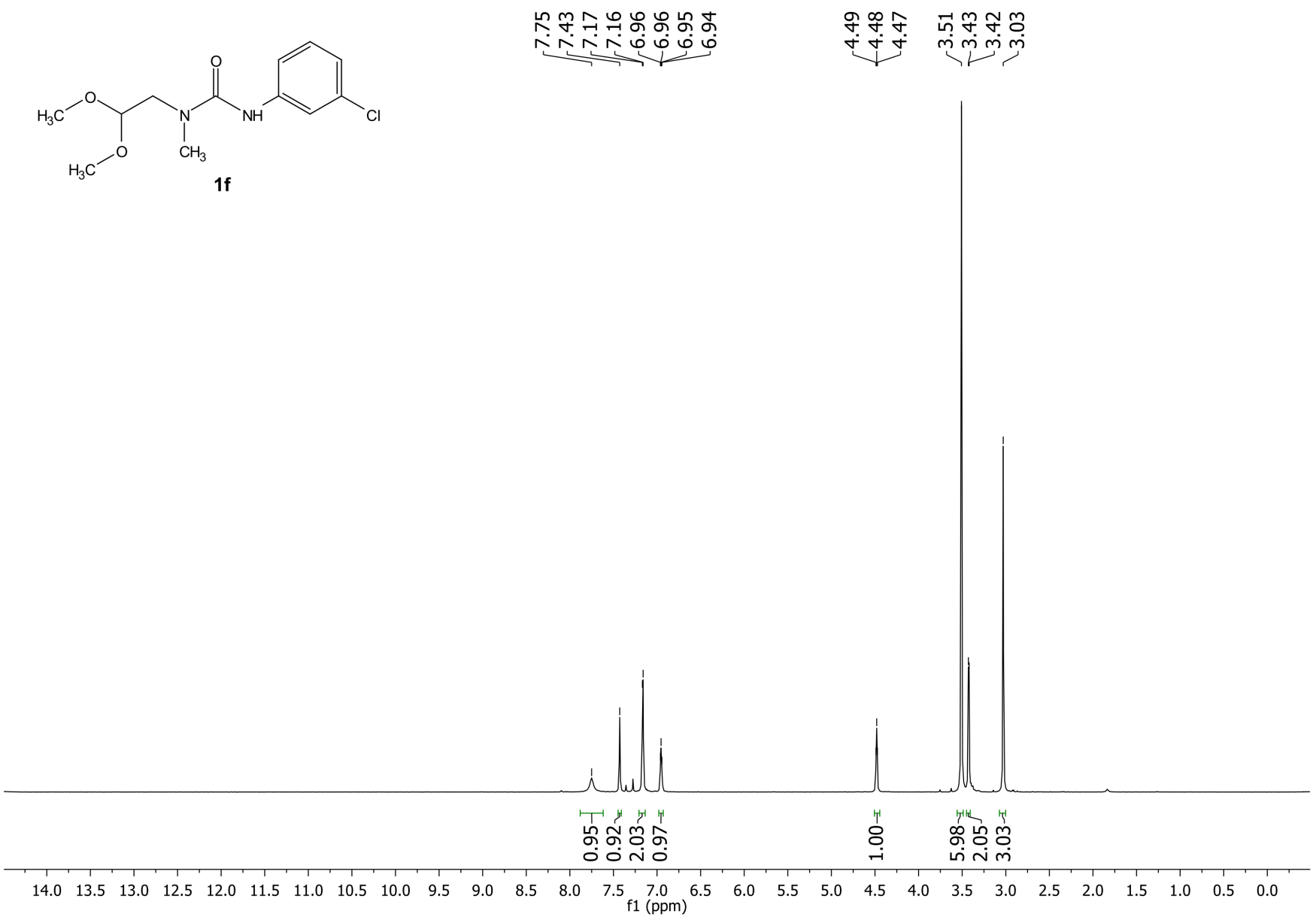


Figure S42. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **1f**

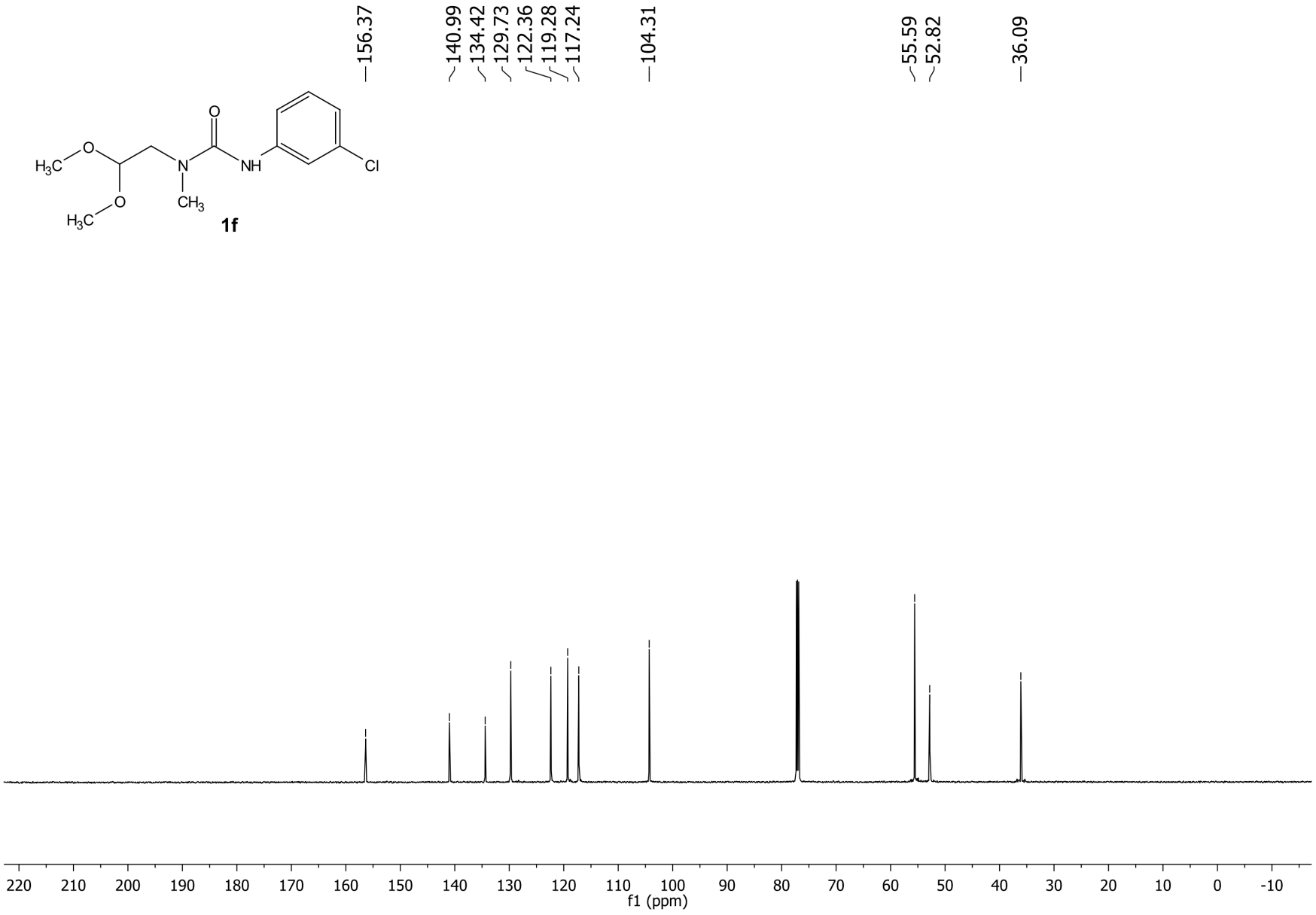


Figure S43. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **1f**

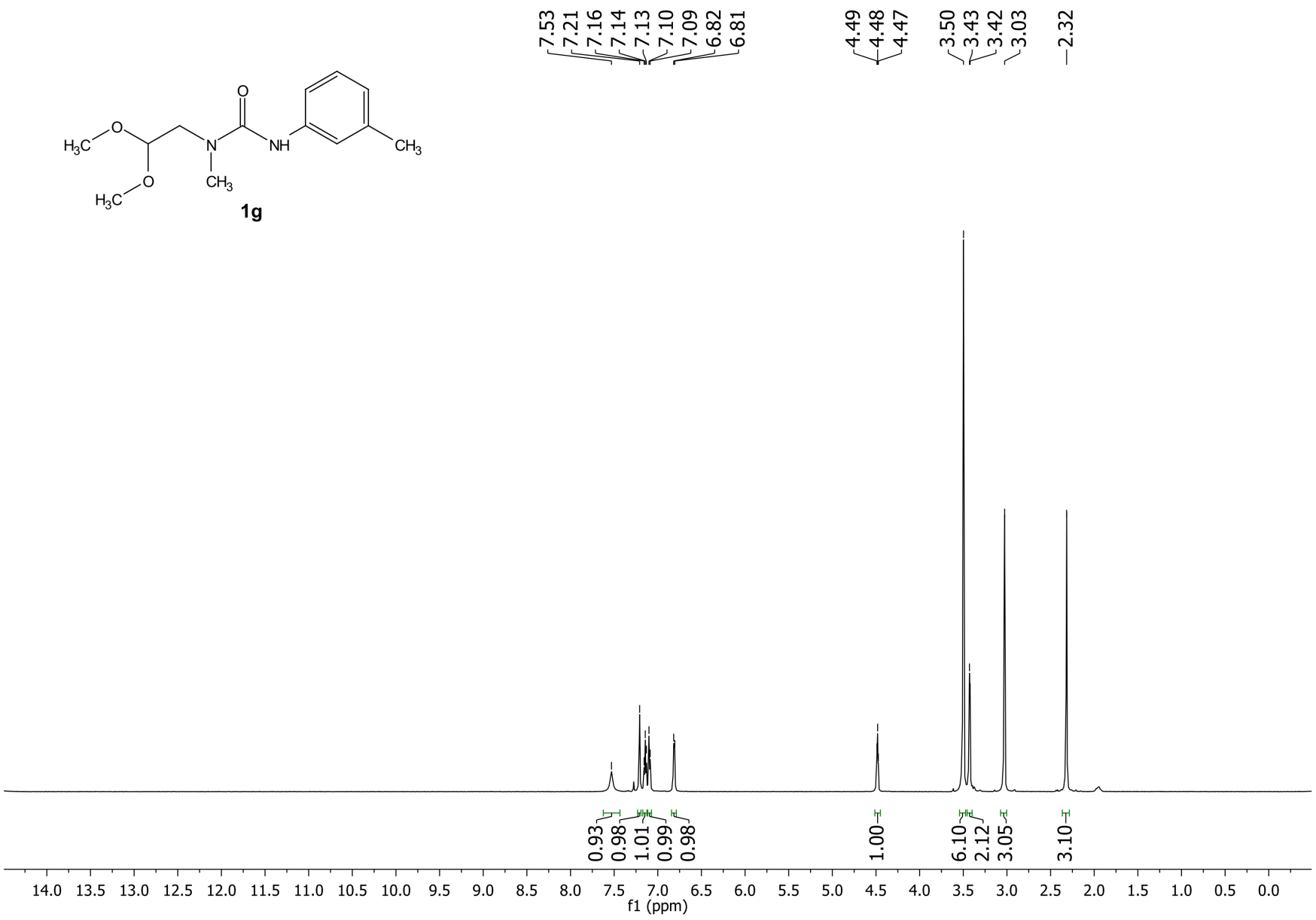


Figure S44. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **1g**

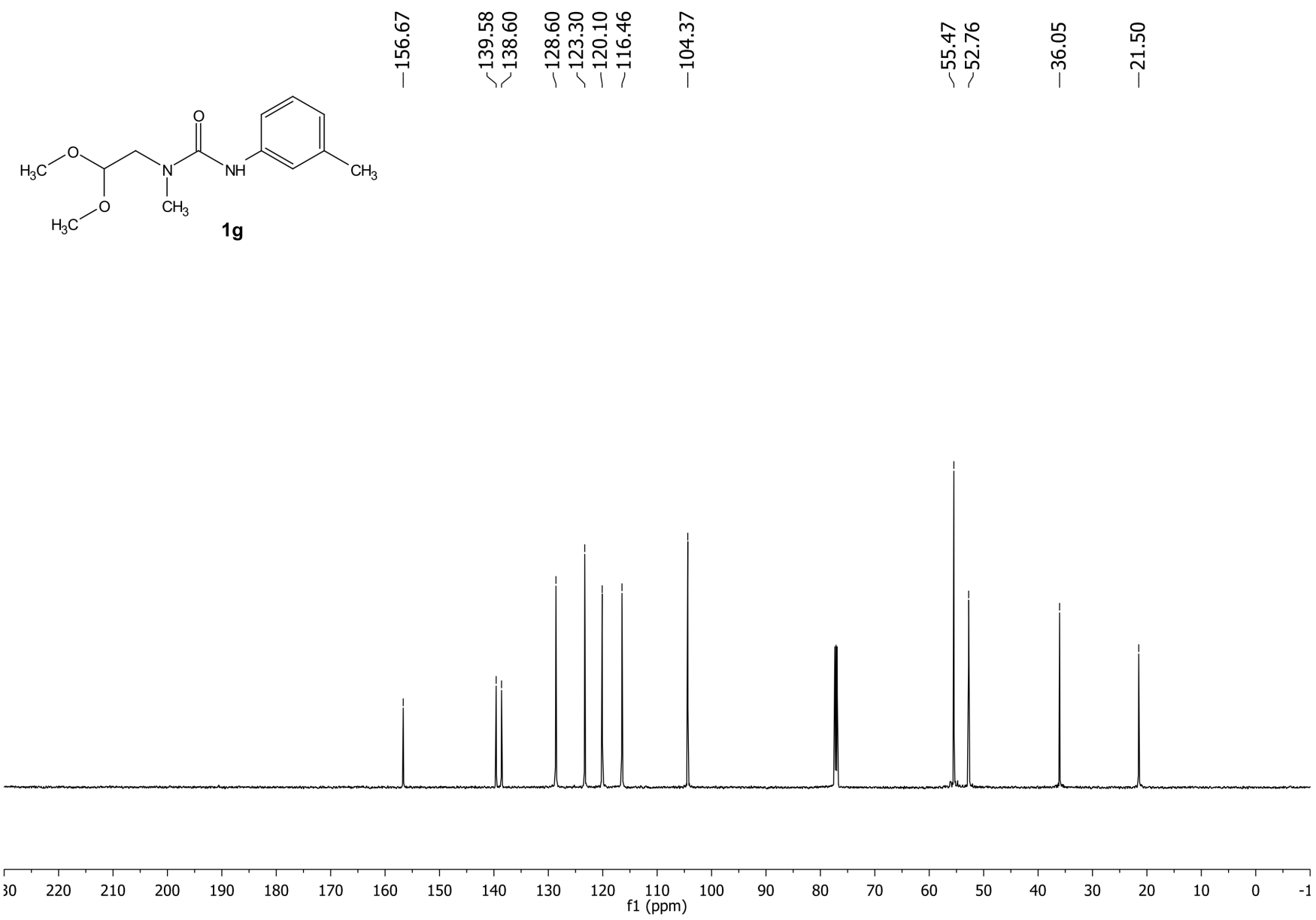


Figure S45. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **1g**

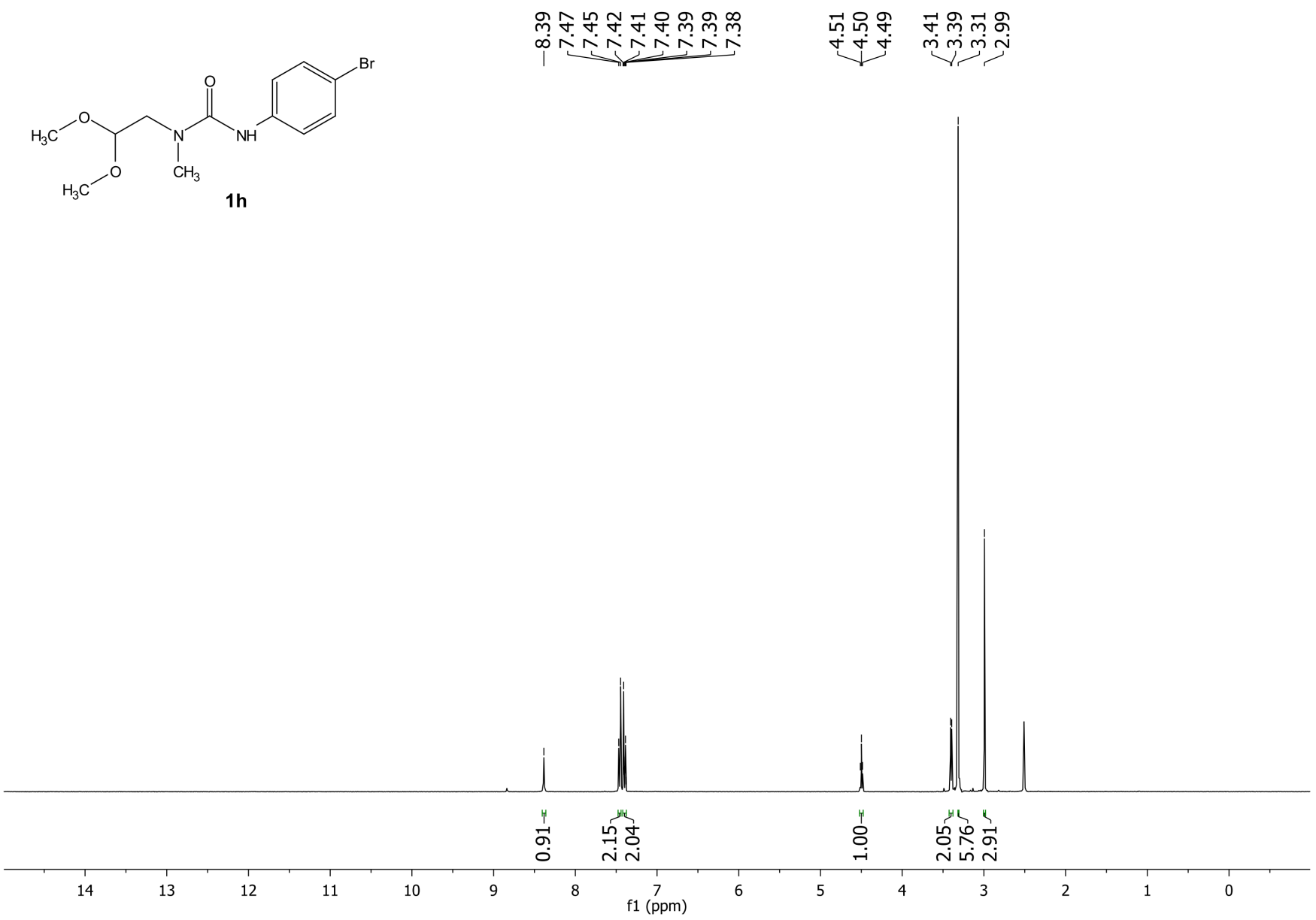


Figure S46. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **1h**

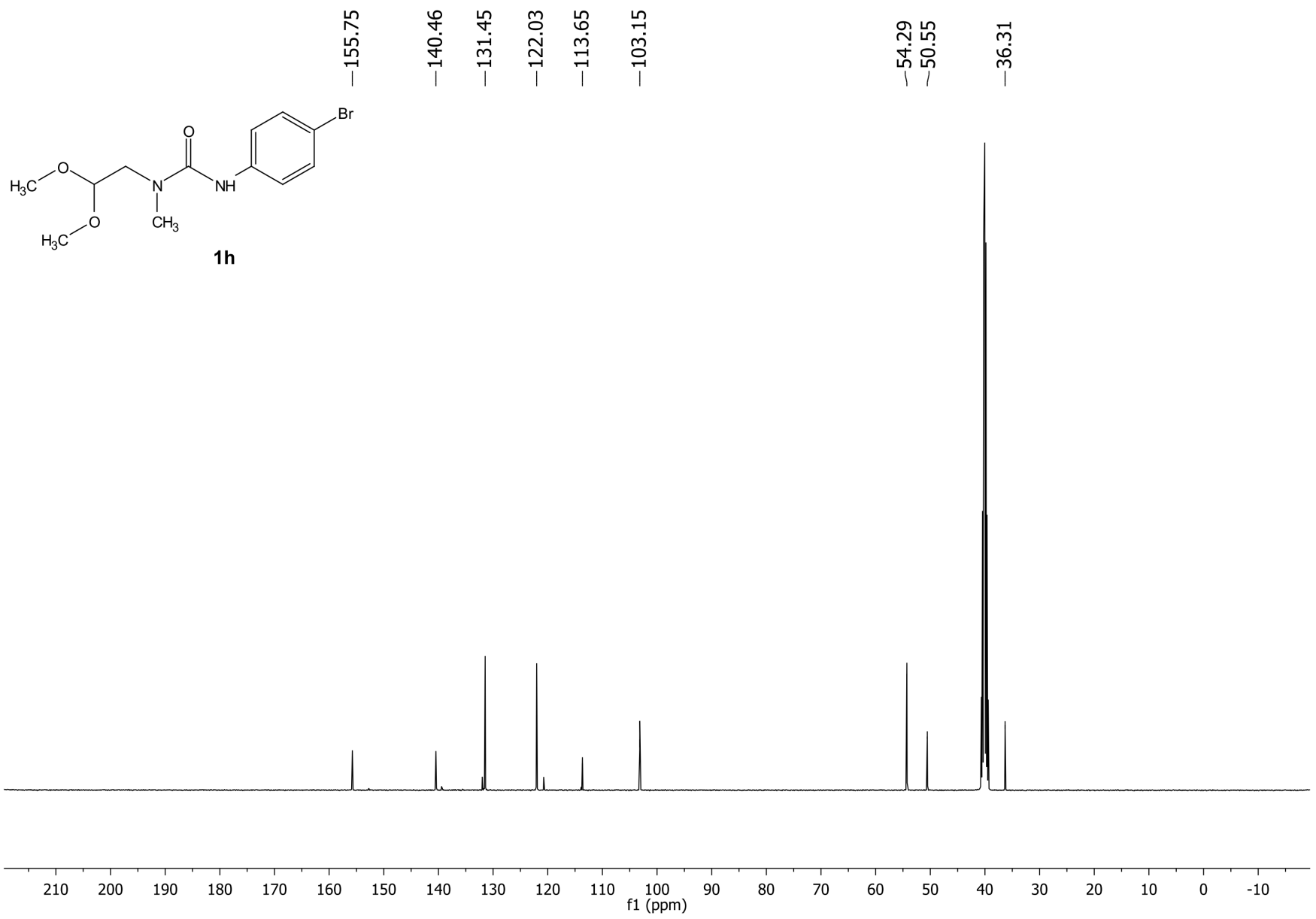


Figure S47. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **1h**

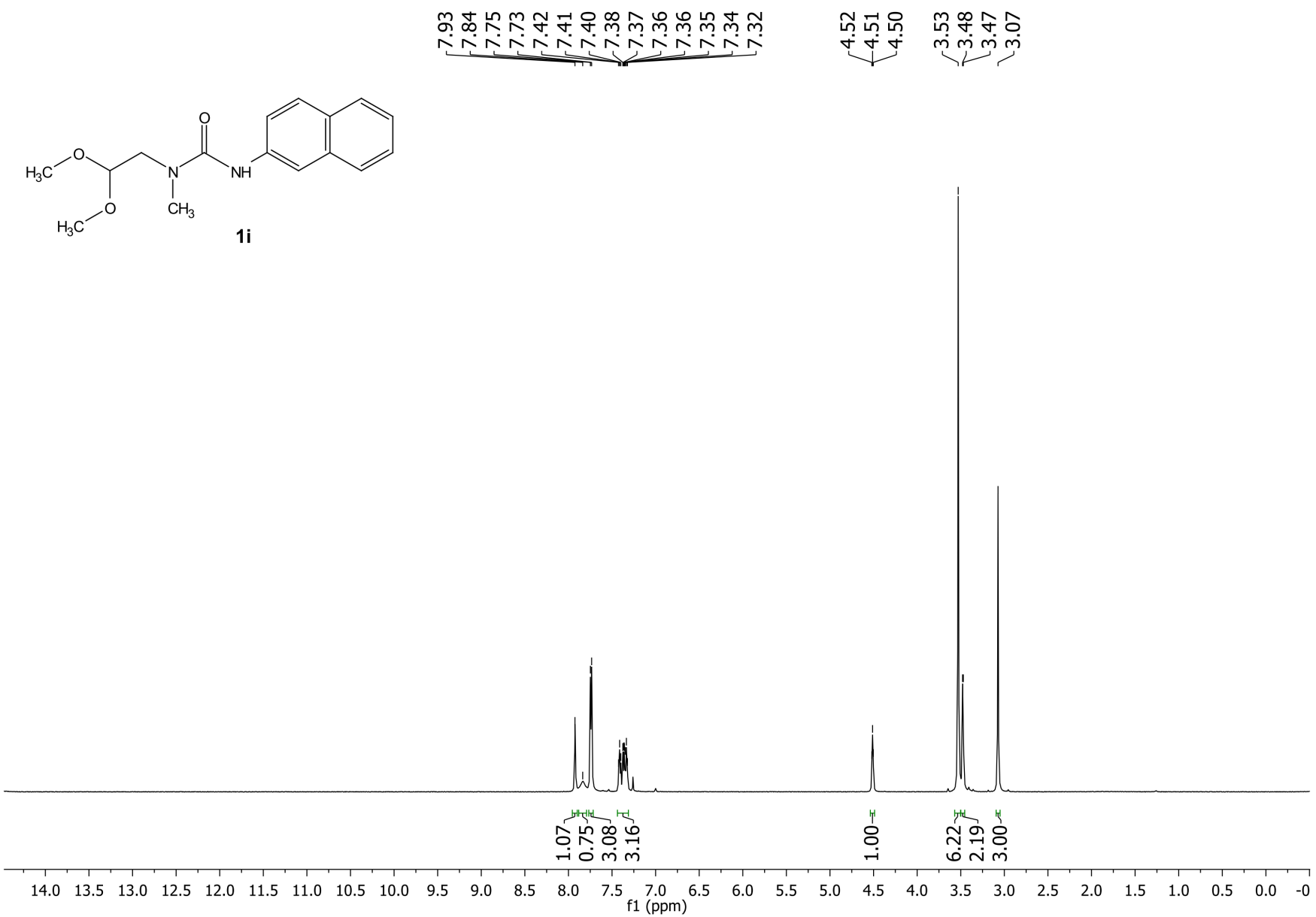


Figure S48. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **1i**

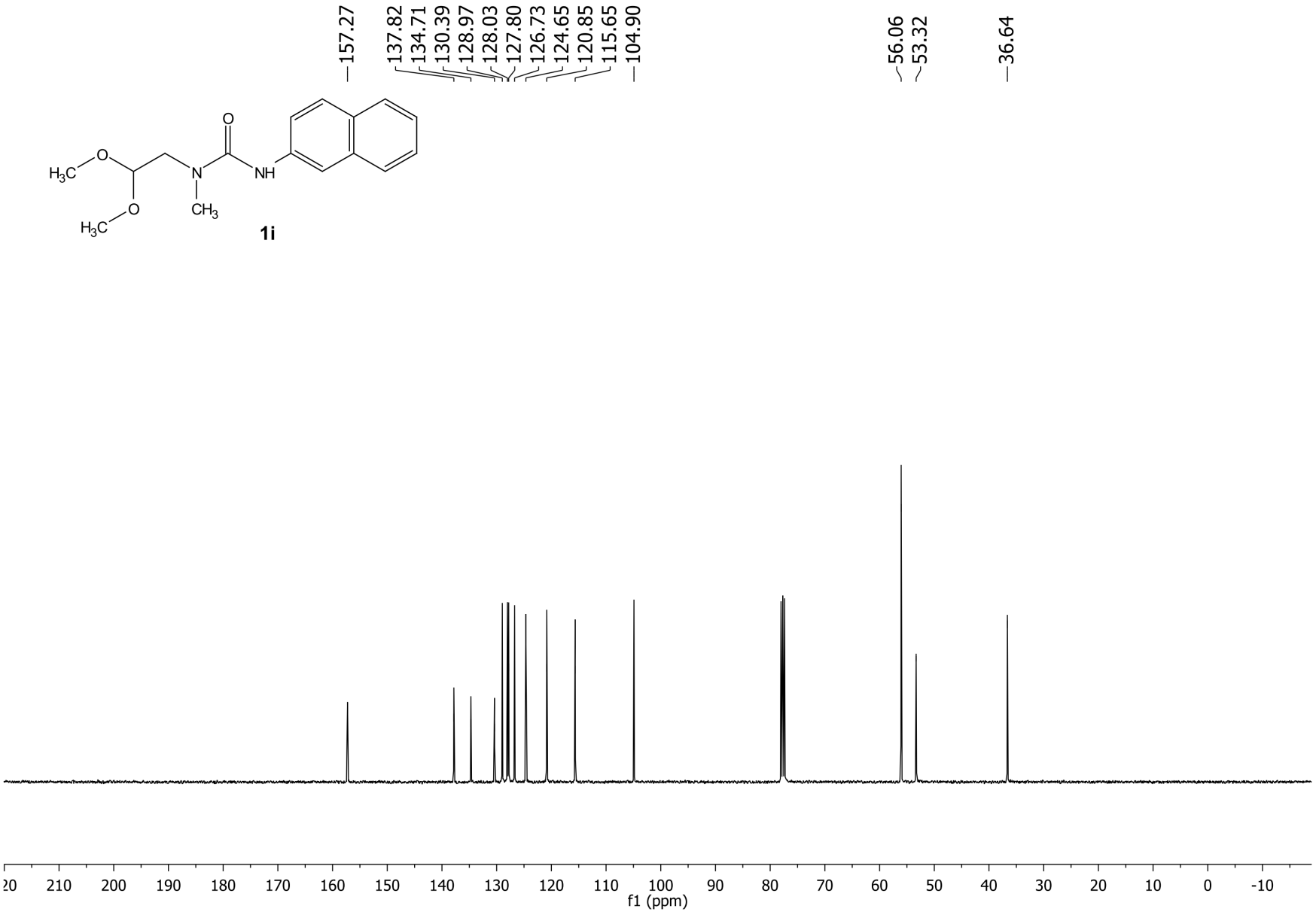


Figure S49. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **1i**

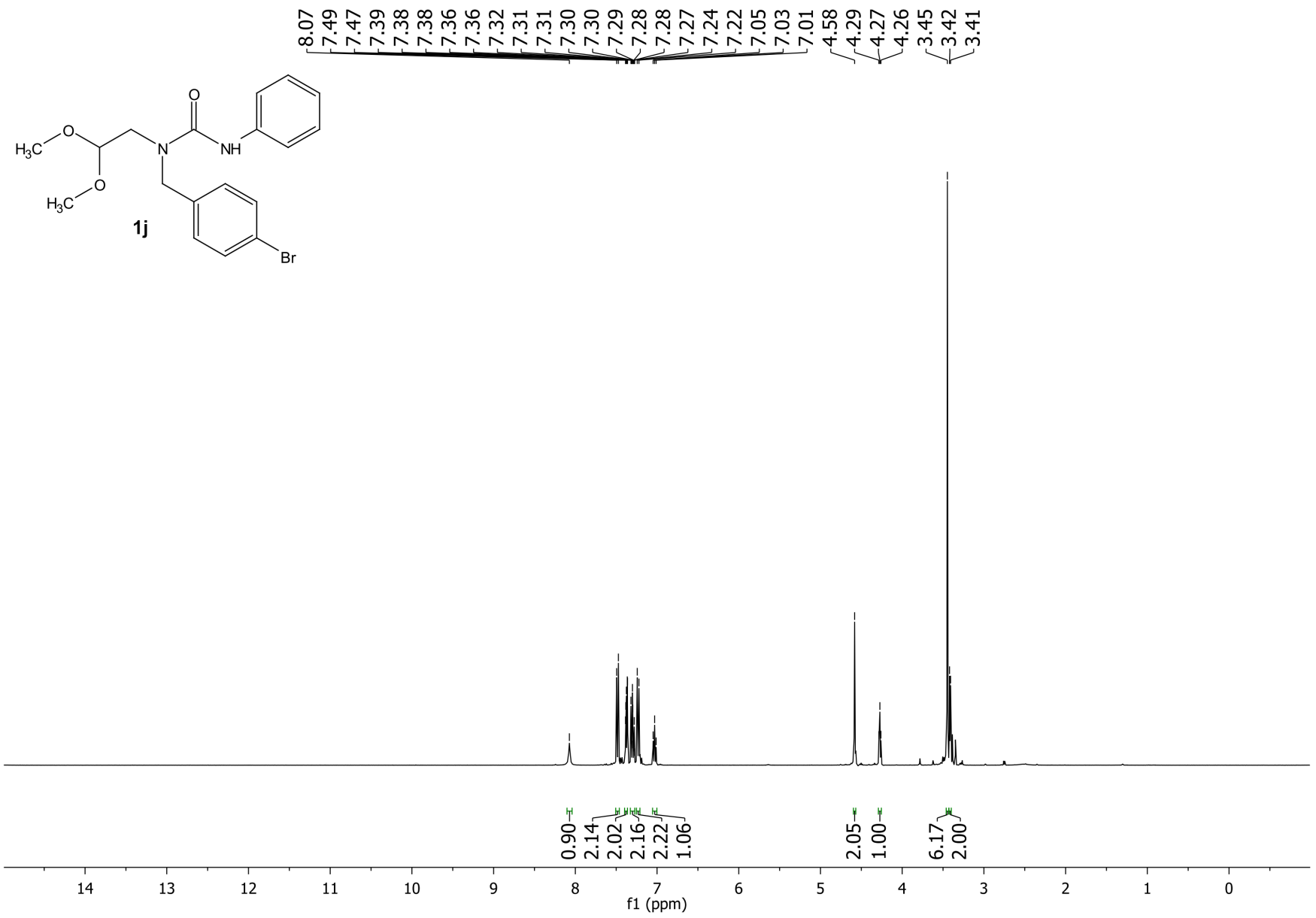


Figure S50. ^{1}H NMR spectrum ($CDCl_3$, 600MHz) of the compound **1j**

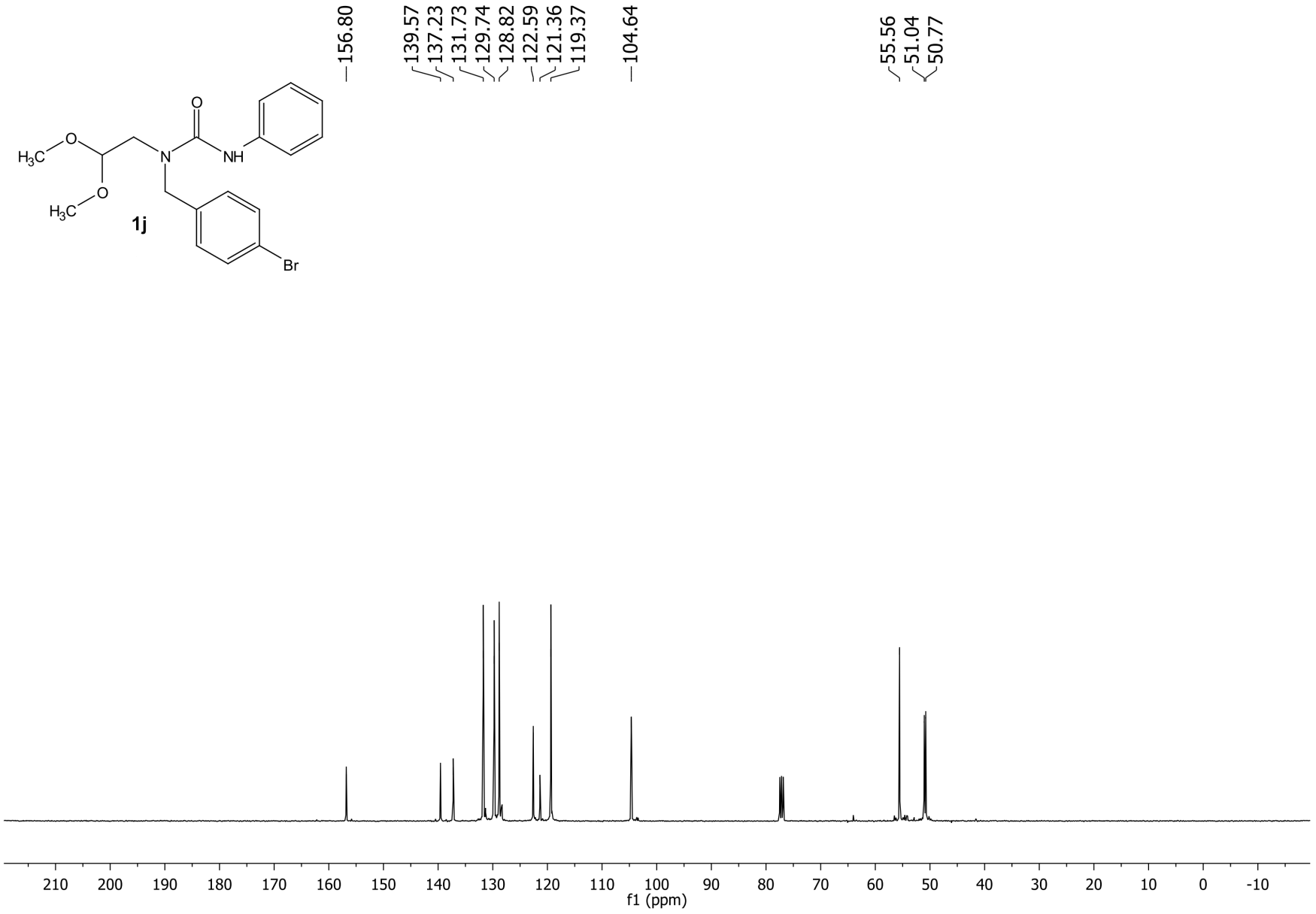


Figure S51. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **1j**

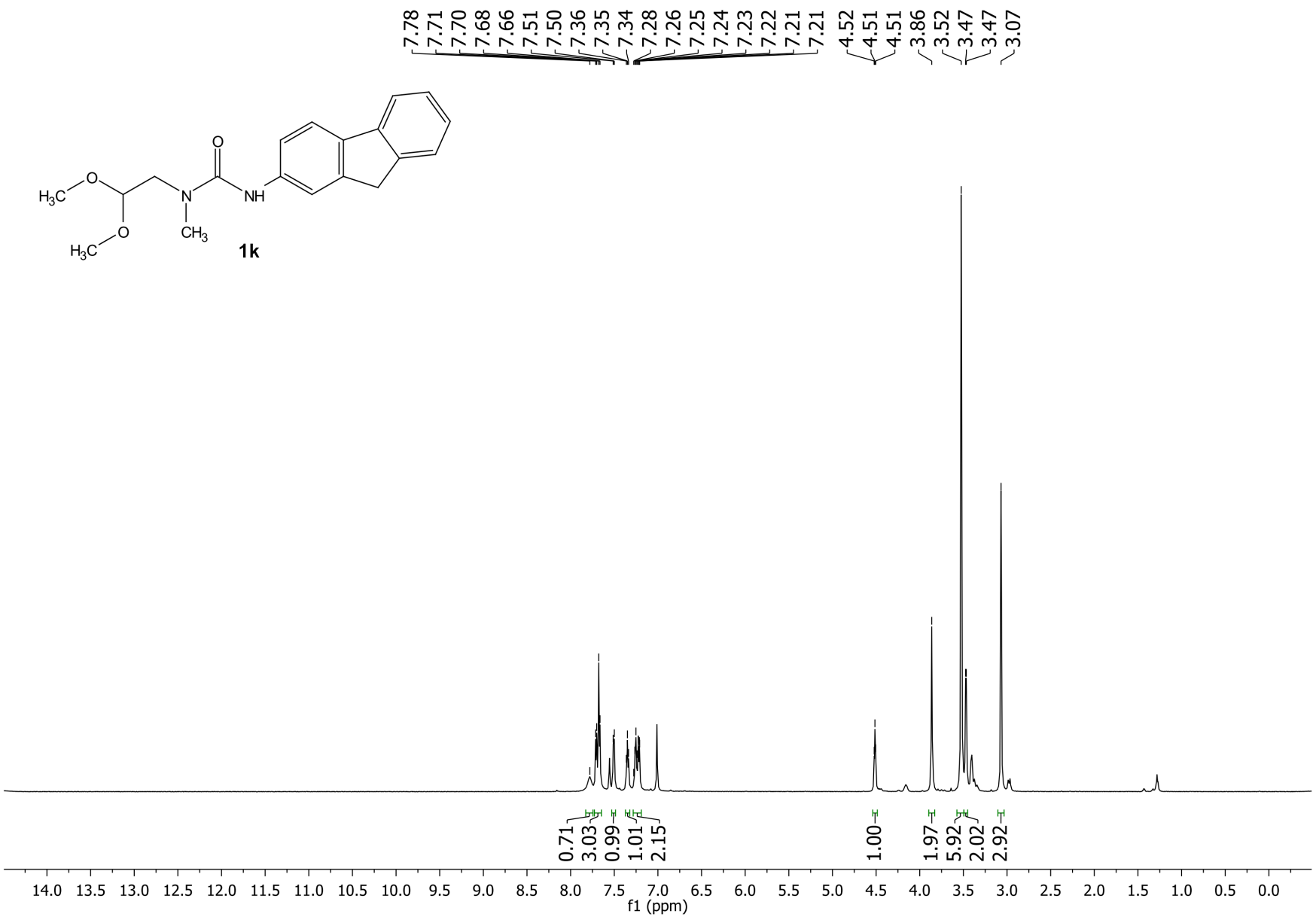


Figure S52. ^{1}H NMR spectrum ($CDCl_3$, 500MHz) of the compound **1k**

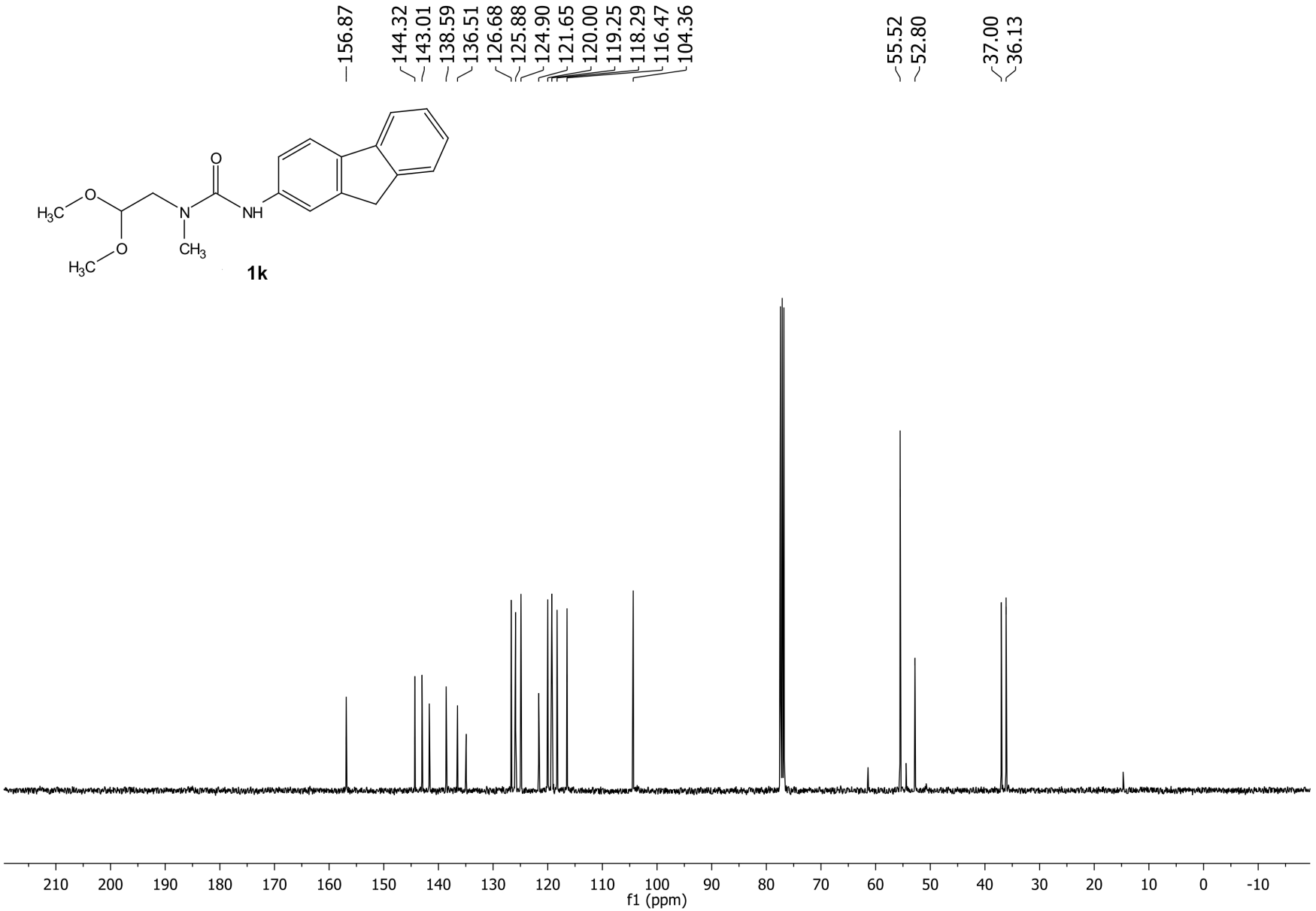


Figure S53. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **1k**

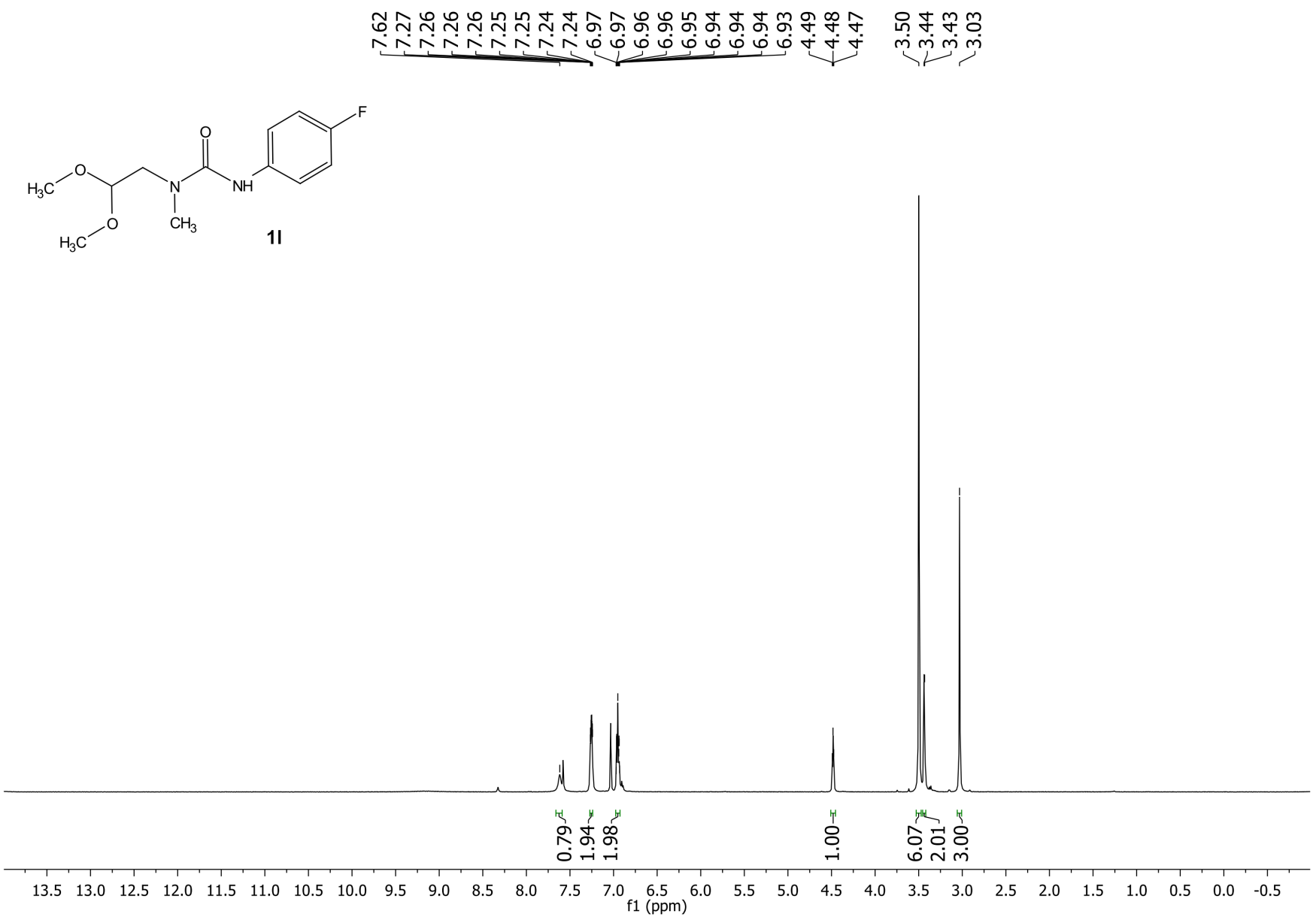


Figure S54. ^{1}H NMR spectrum ($CDCl_3$, 500MHz) of the compound **1l**

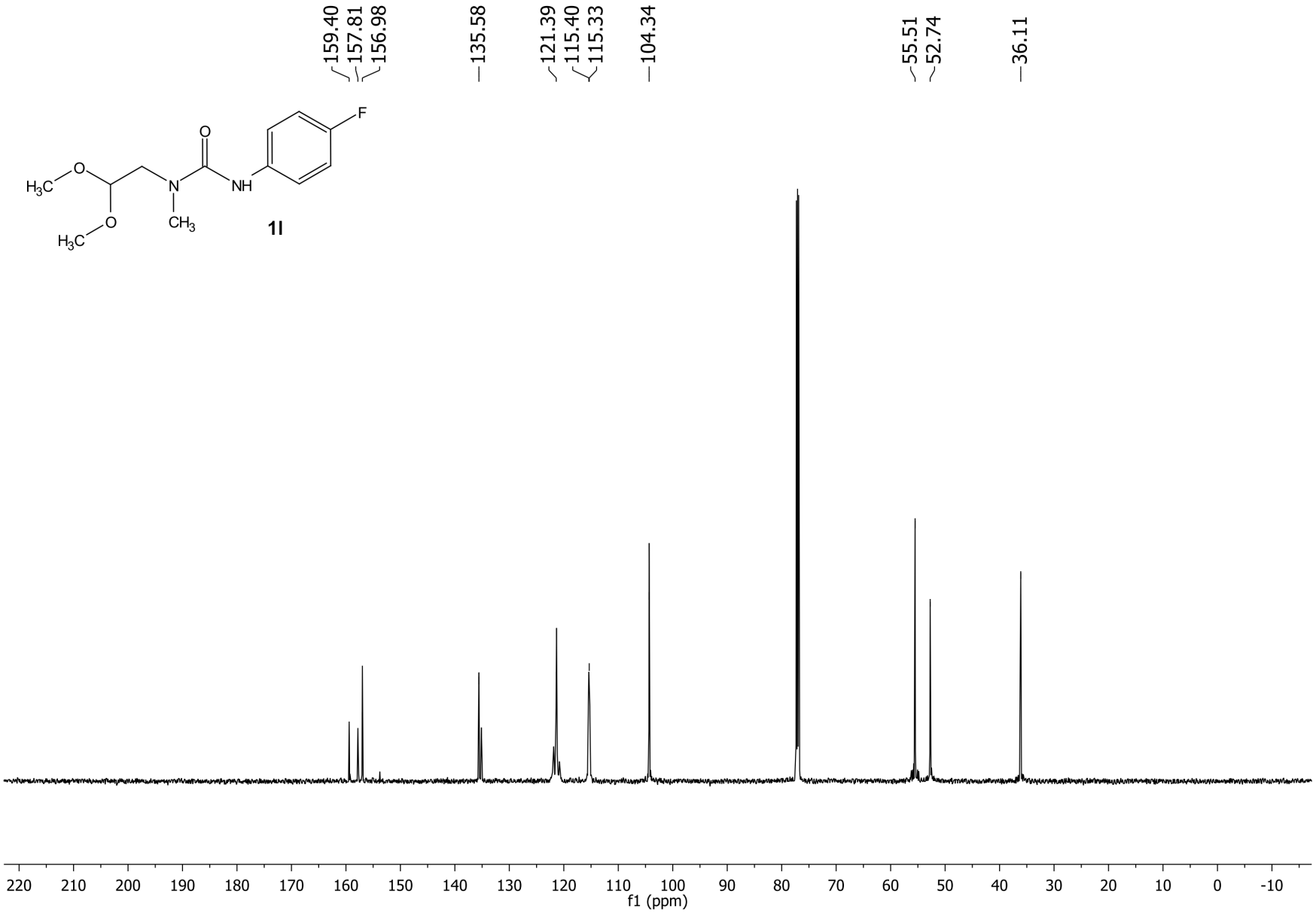


Figure S55. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **1l**

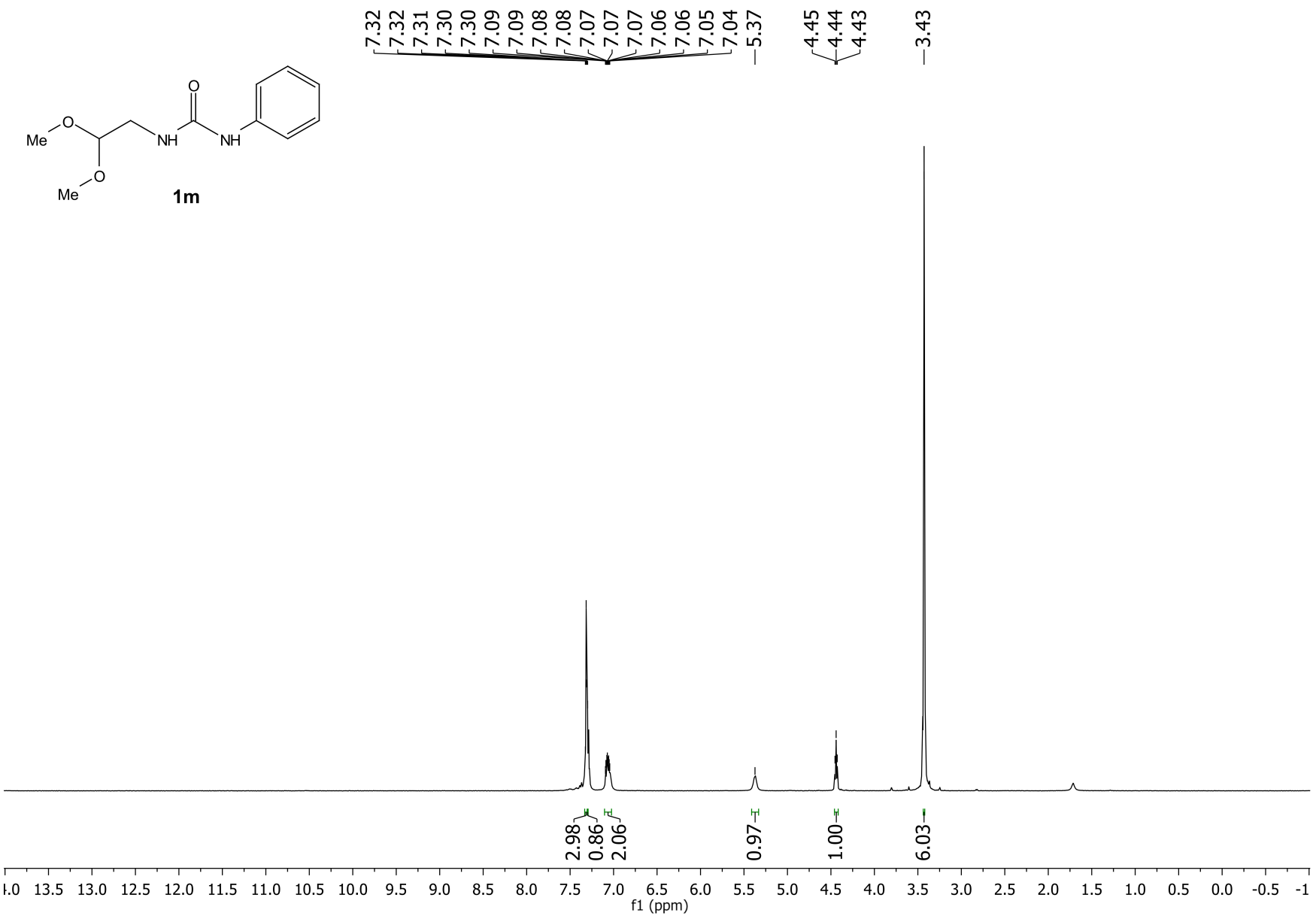


Figure S56. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **1m**

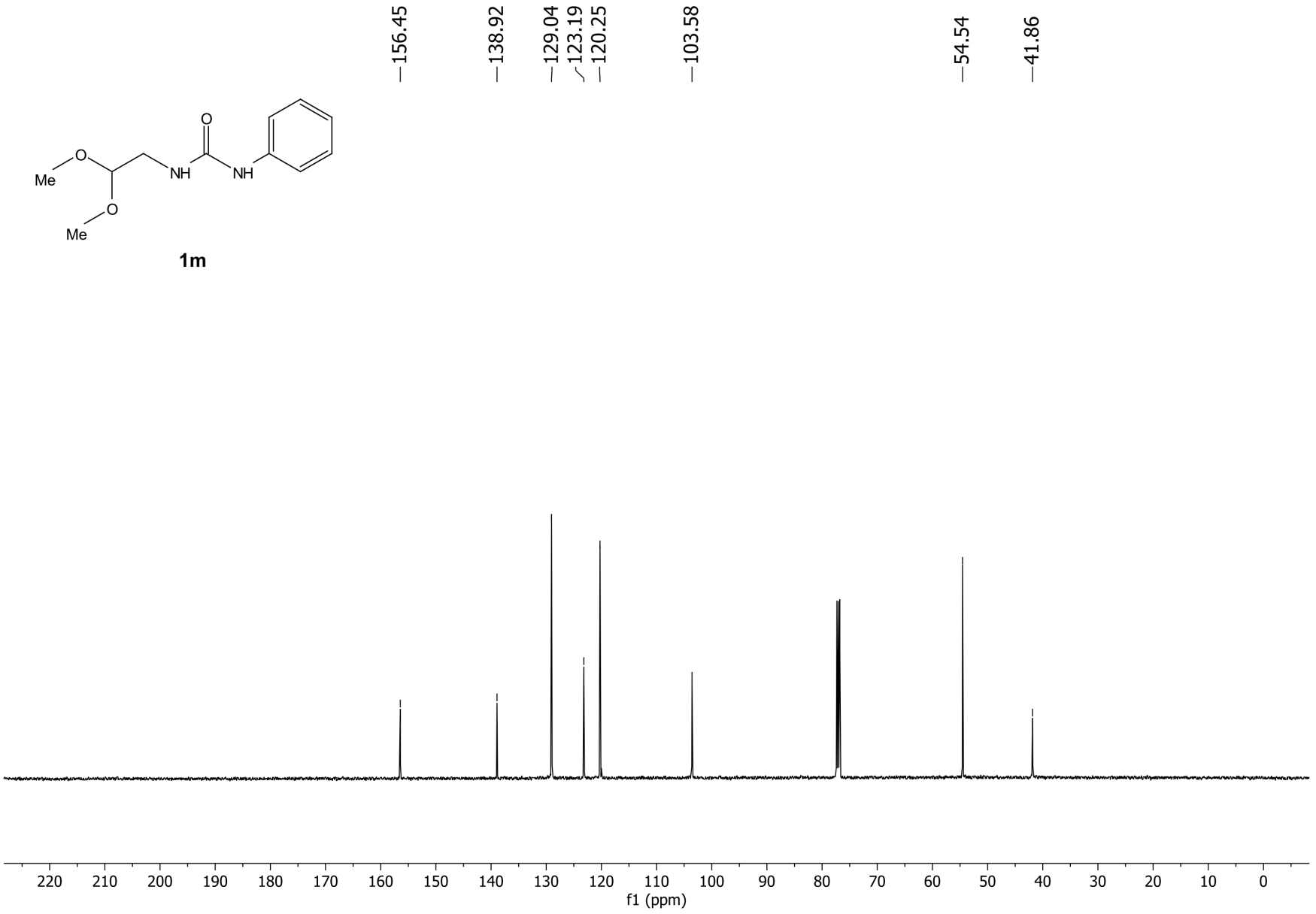


Figure S57. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **1m**

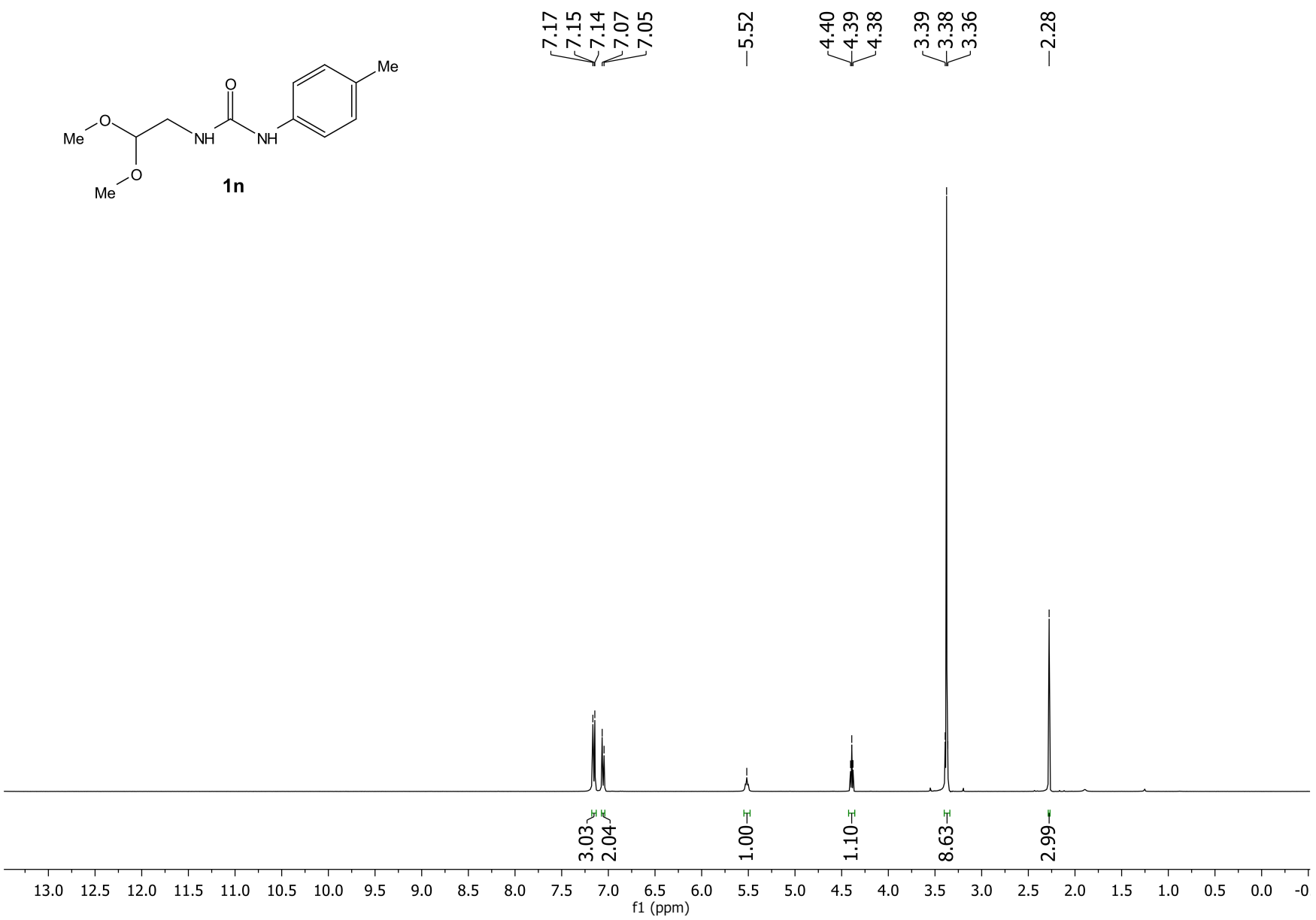


Figure S58. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **1n**

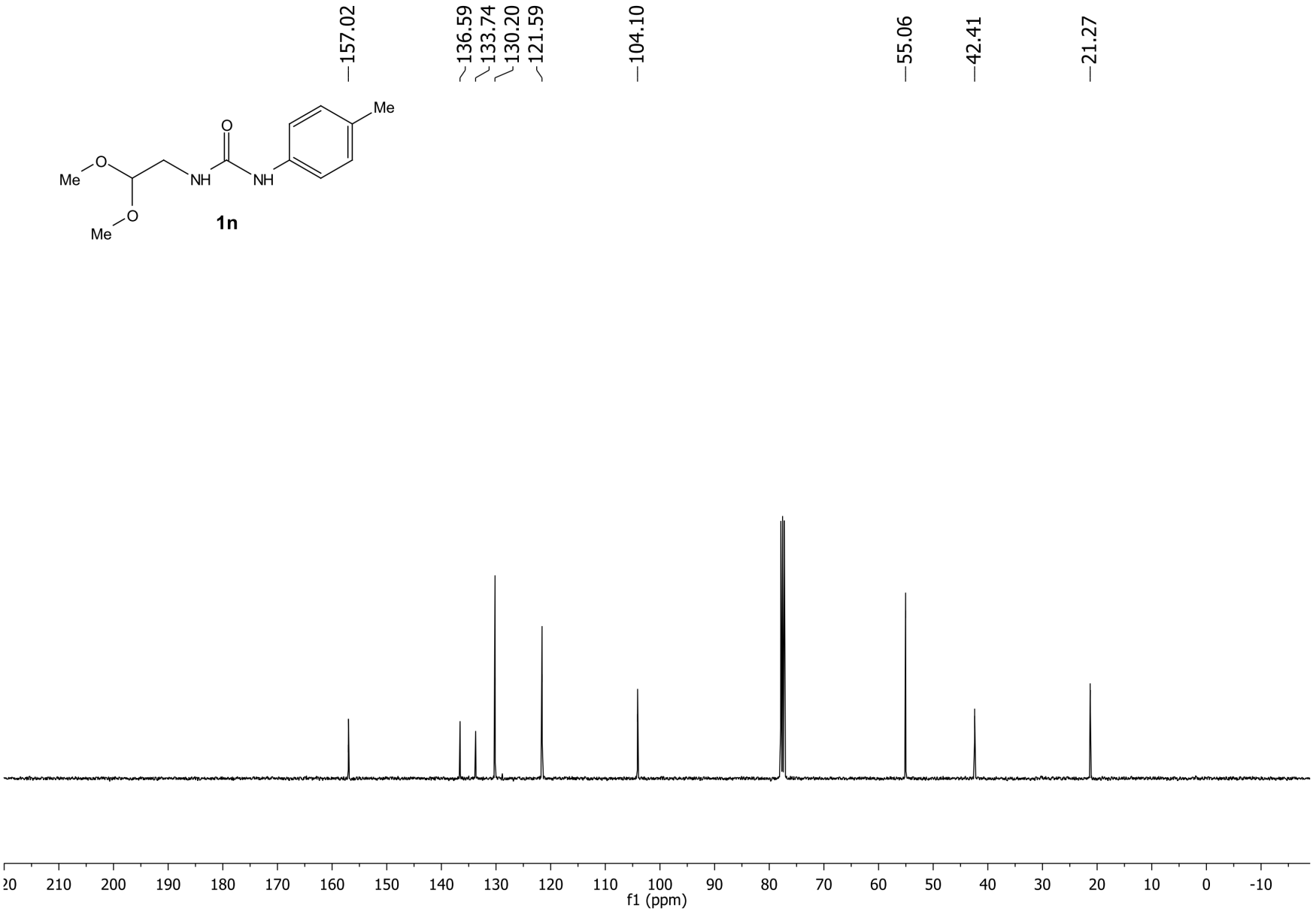


Figure S59. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **1n**

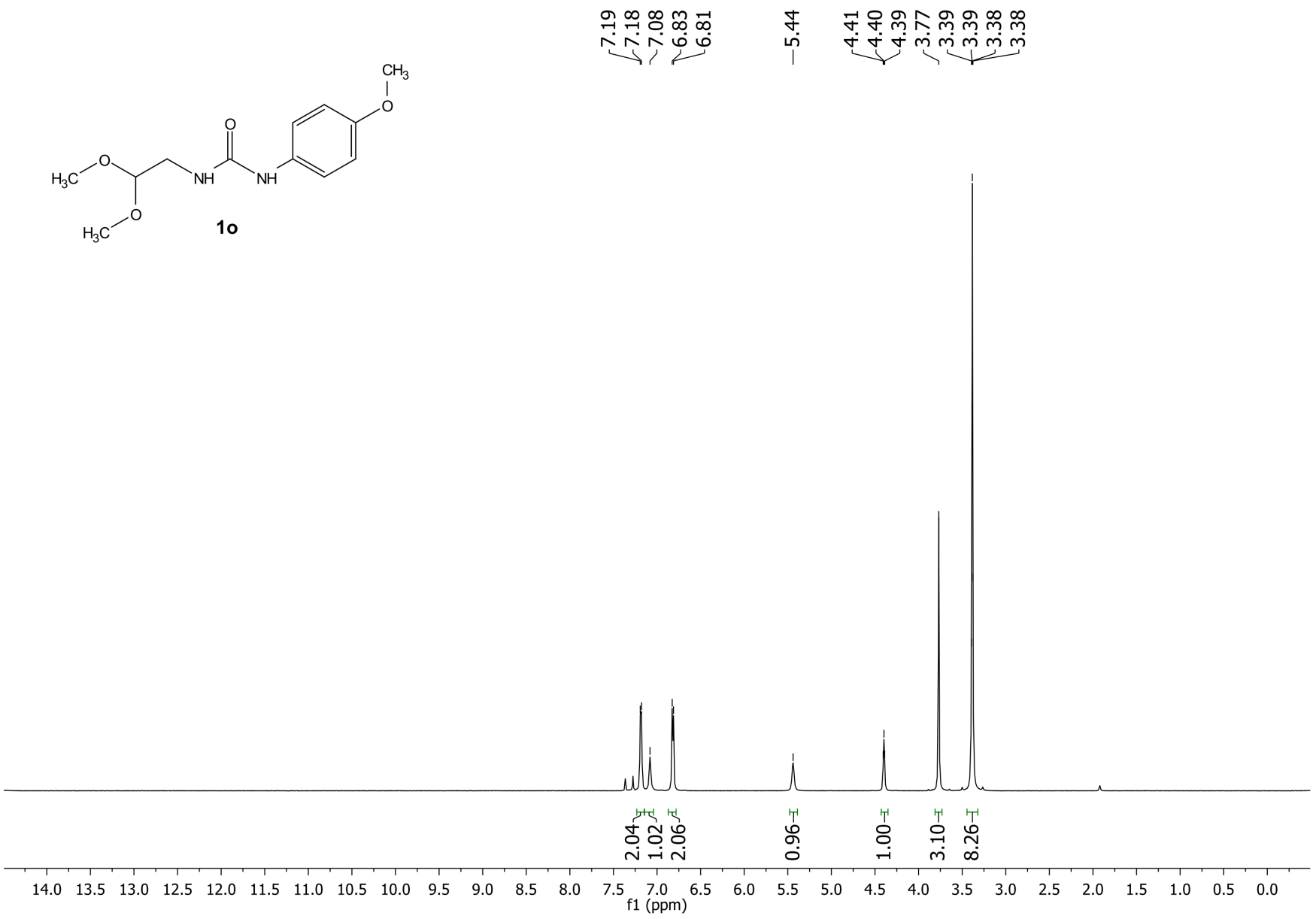


Figure S60. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **1o**

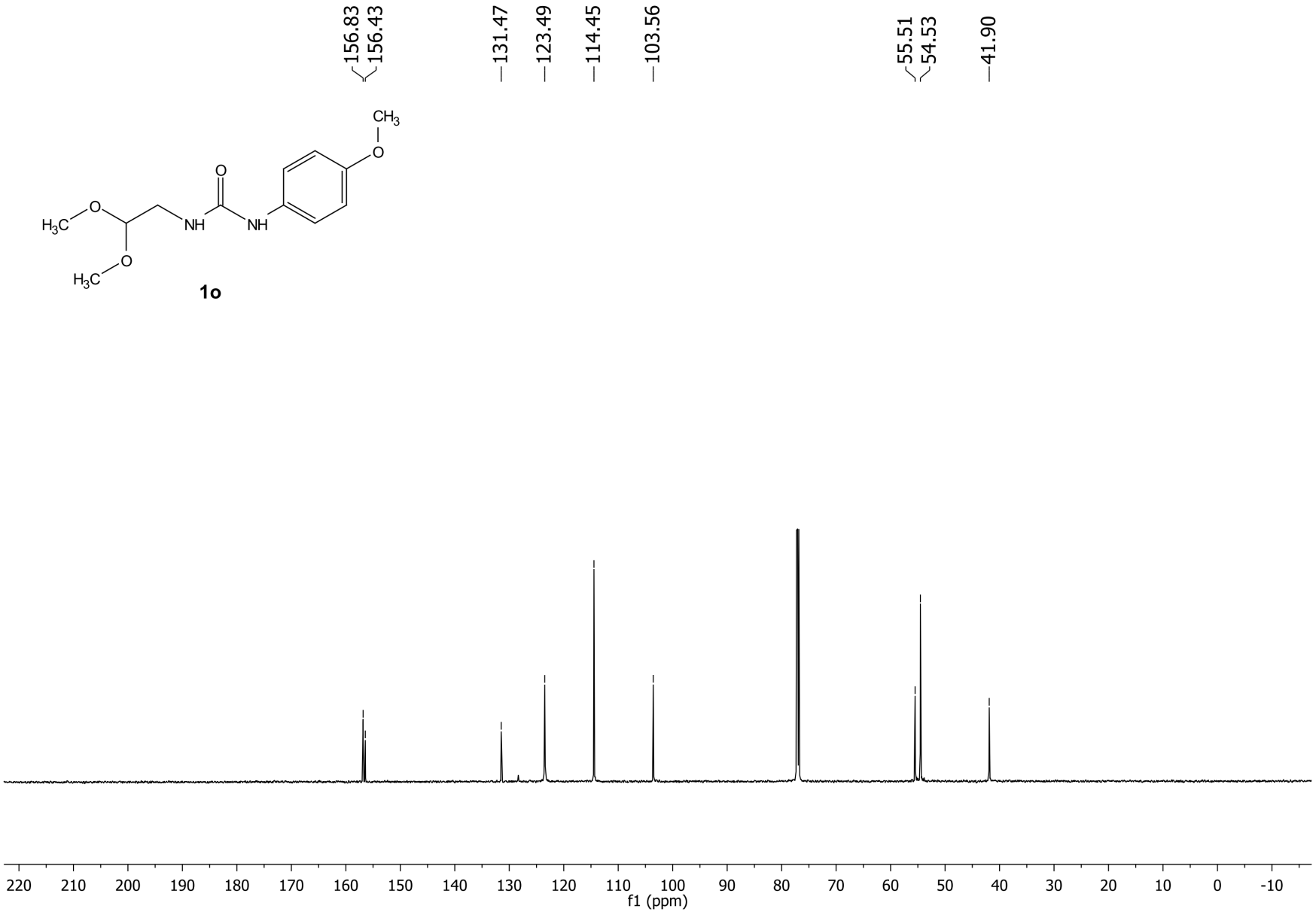


Figure S61. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **1o**

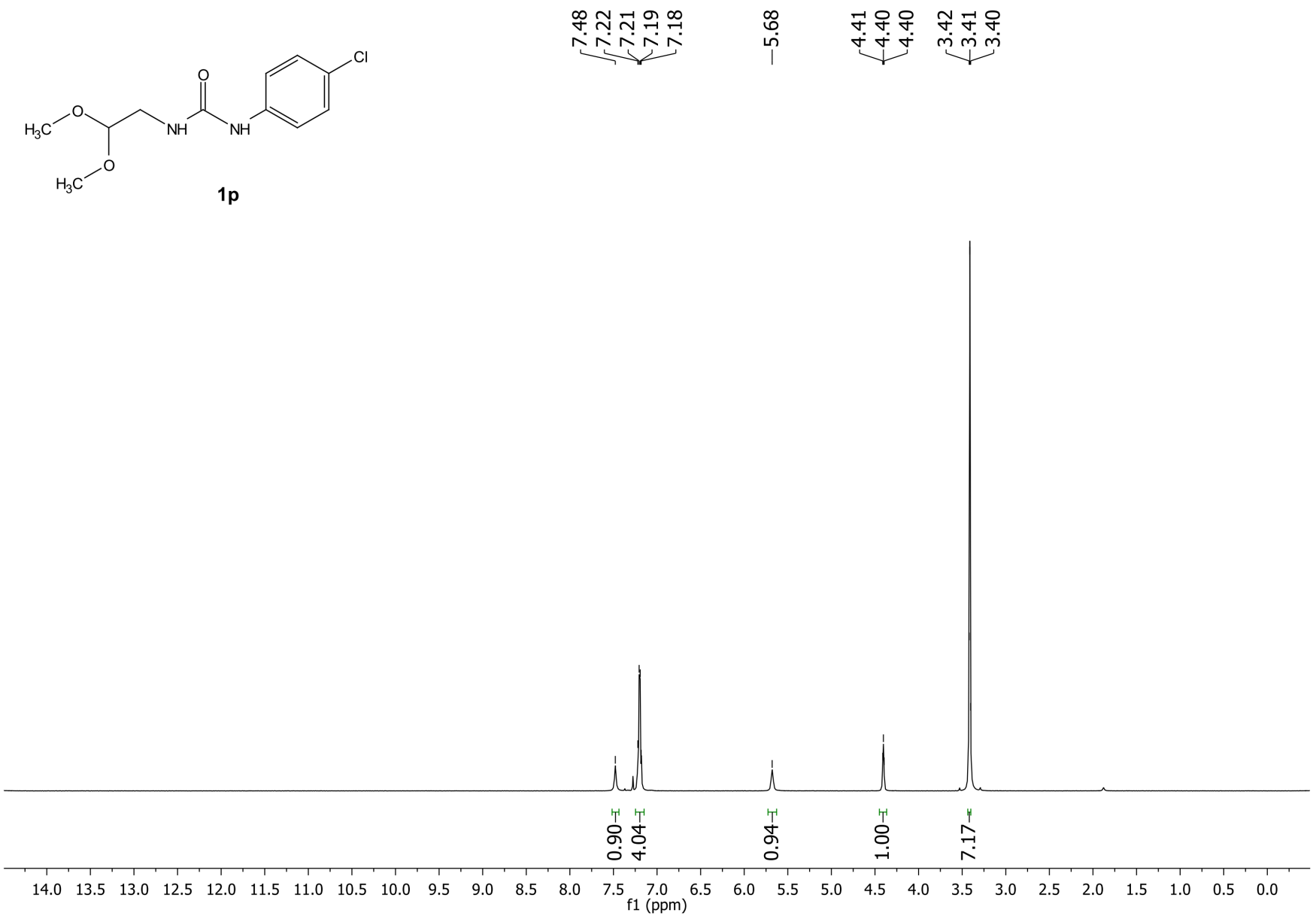


Figure S62. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **1p**

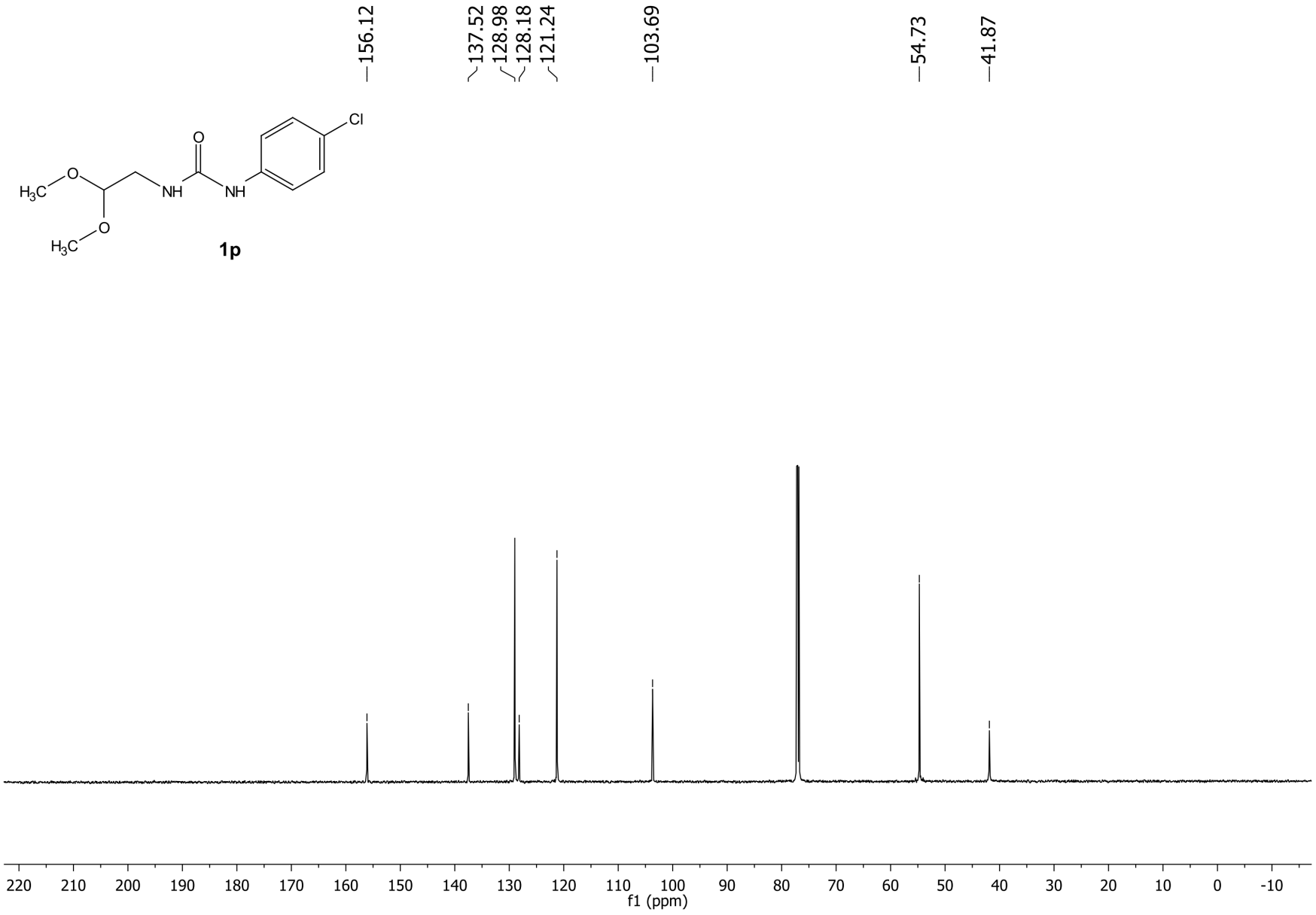


Figure S63. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **1p**

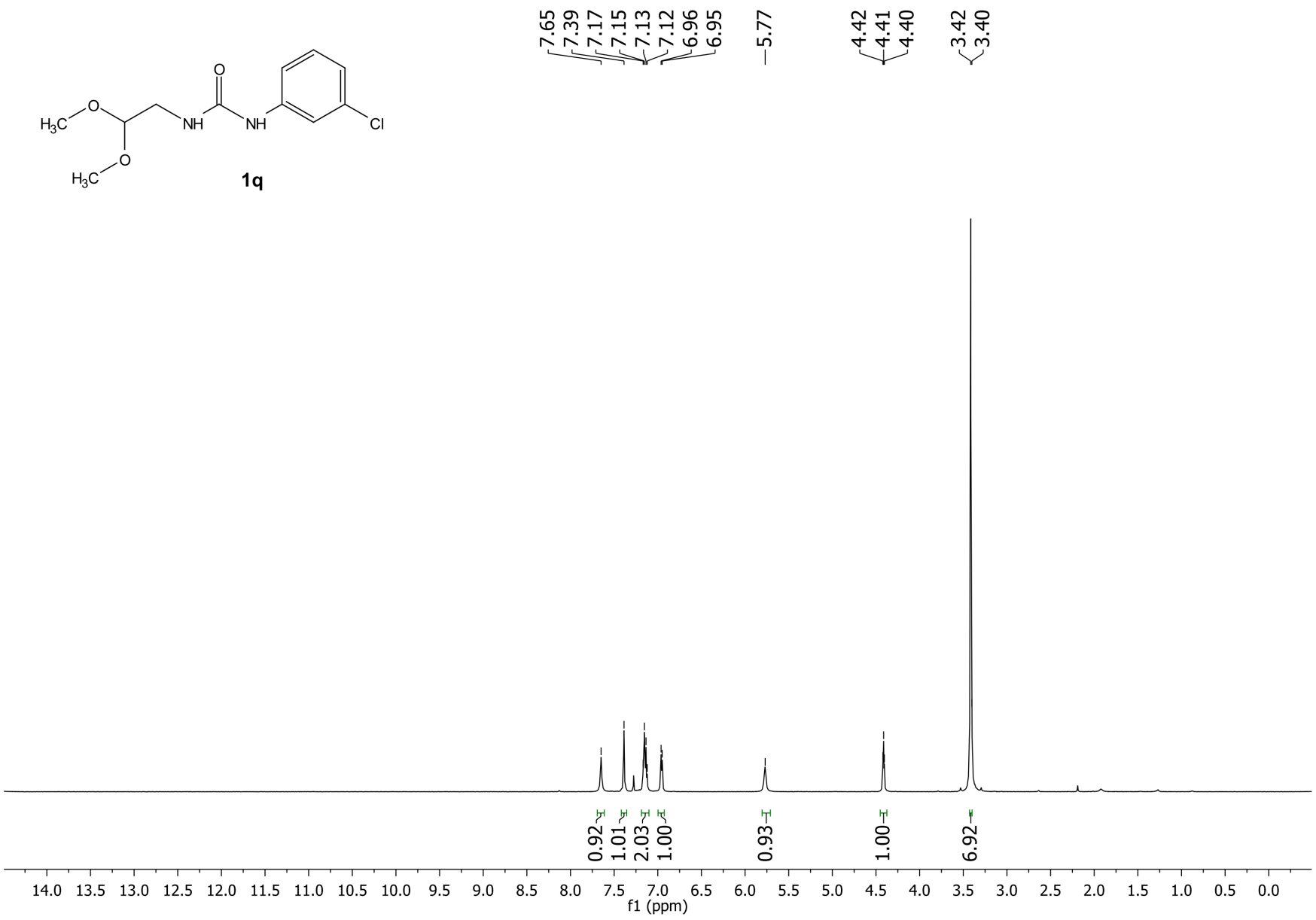


Figure S64. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **1q**

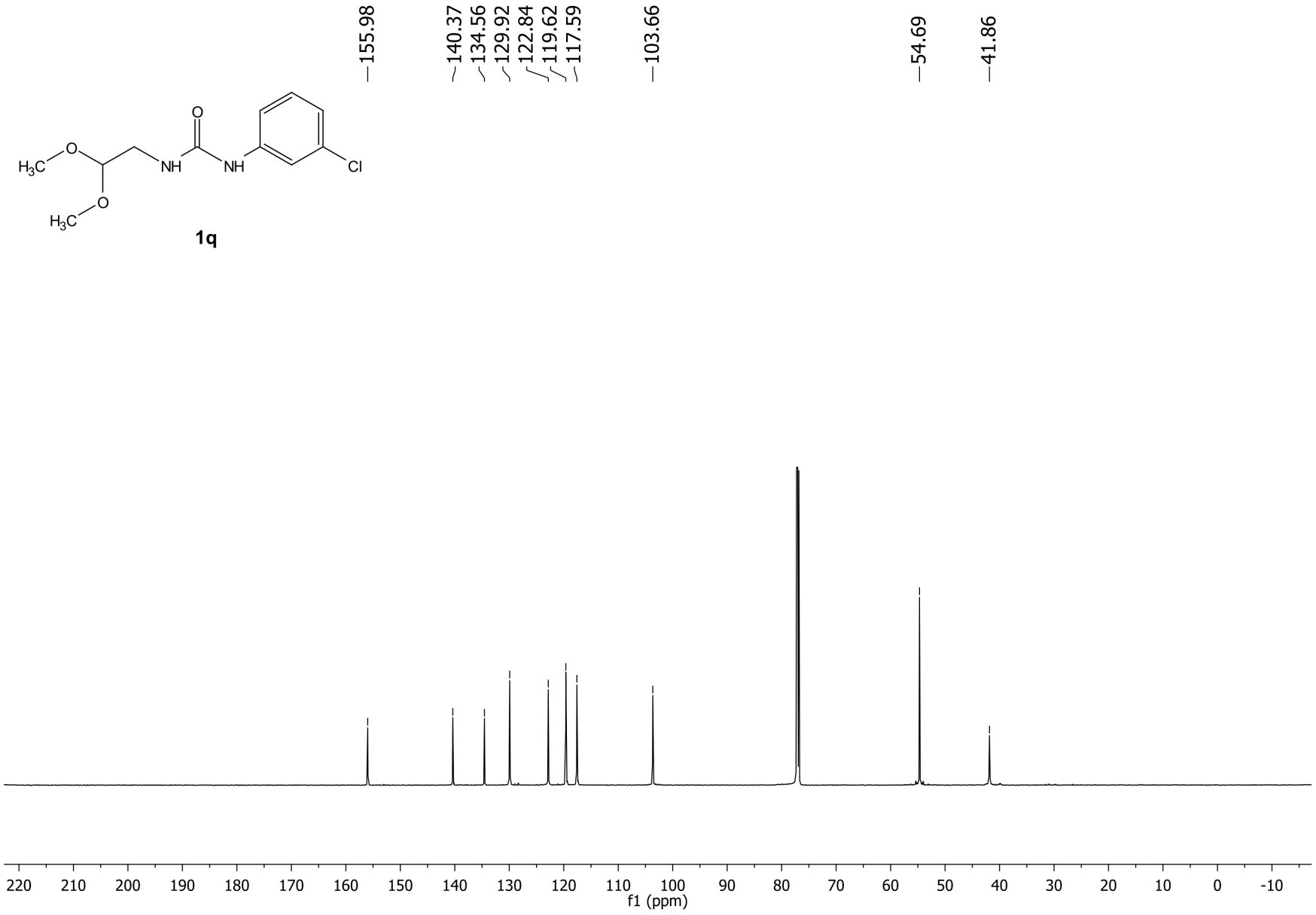


Figure S65. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **1q**

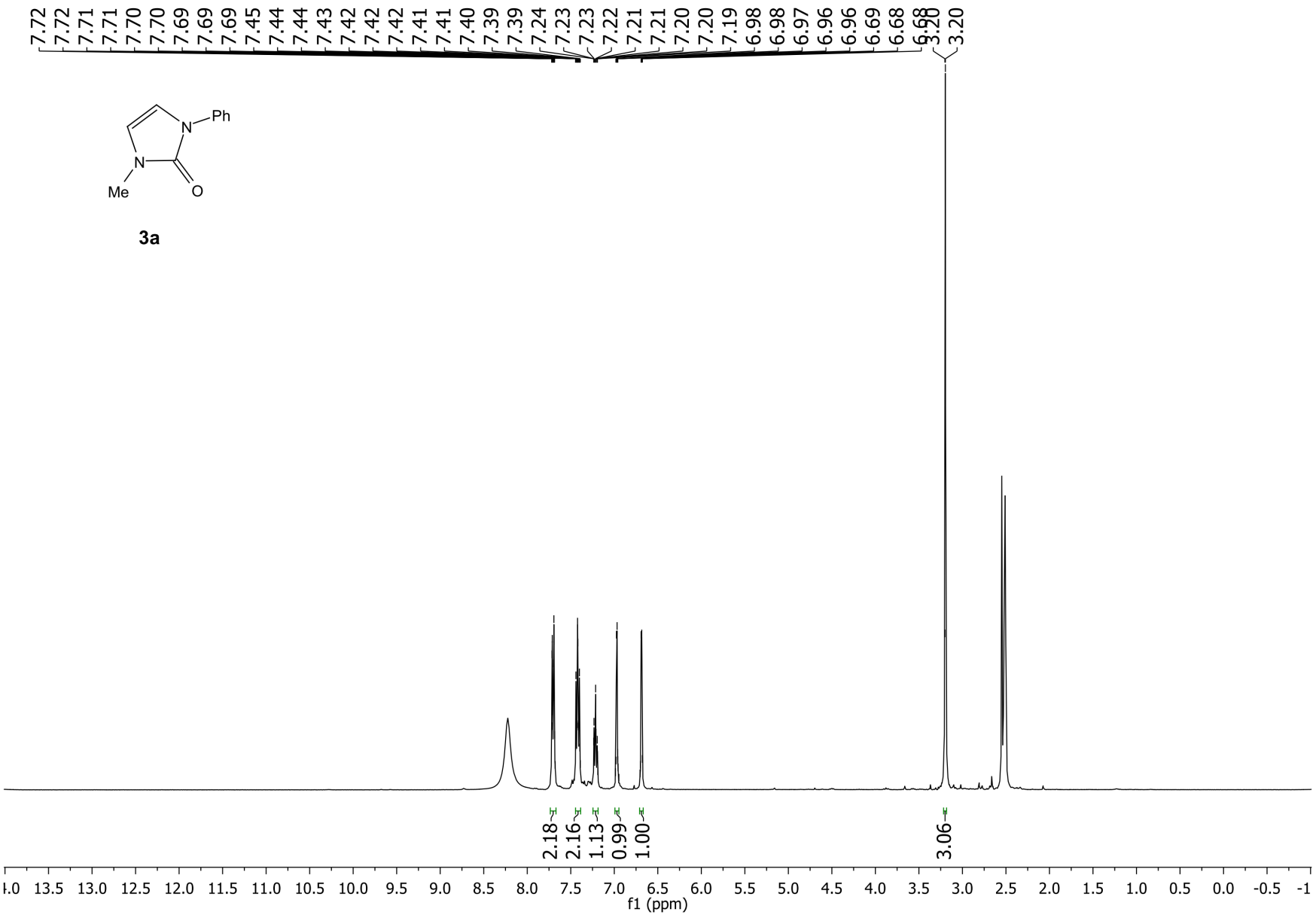


Figure S66. ^{1}H NMR spectrum ($(CD_3)_2SO$, 400MHz) of the compound **3a**

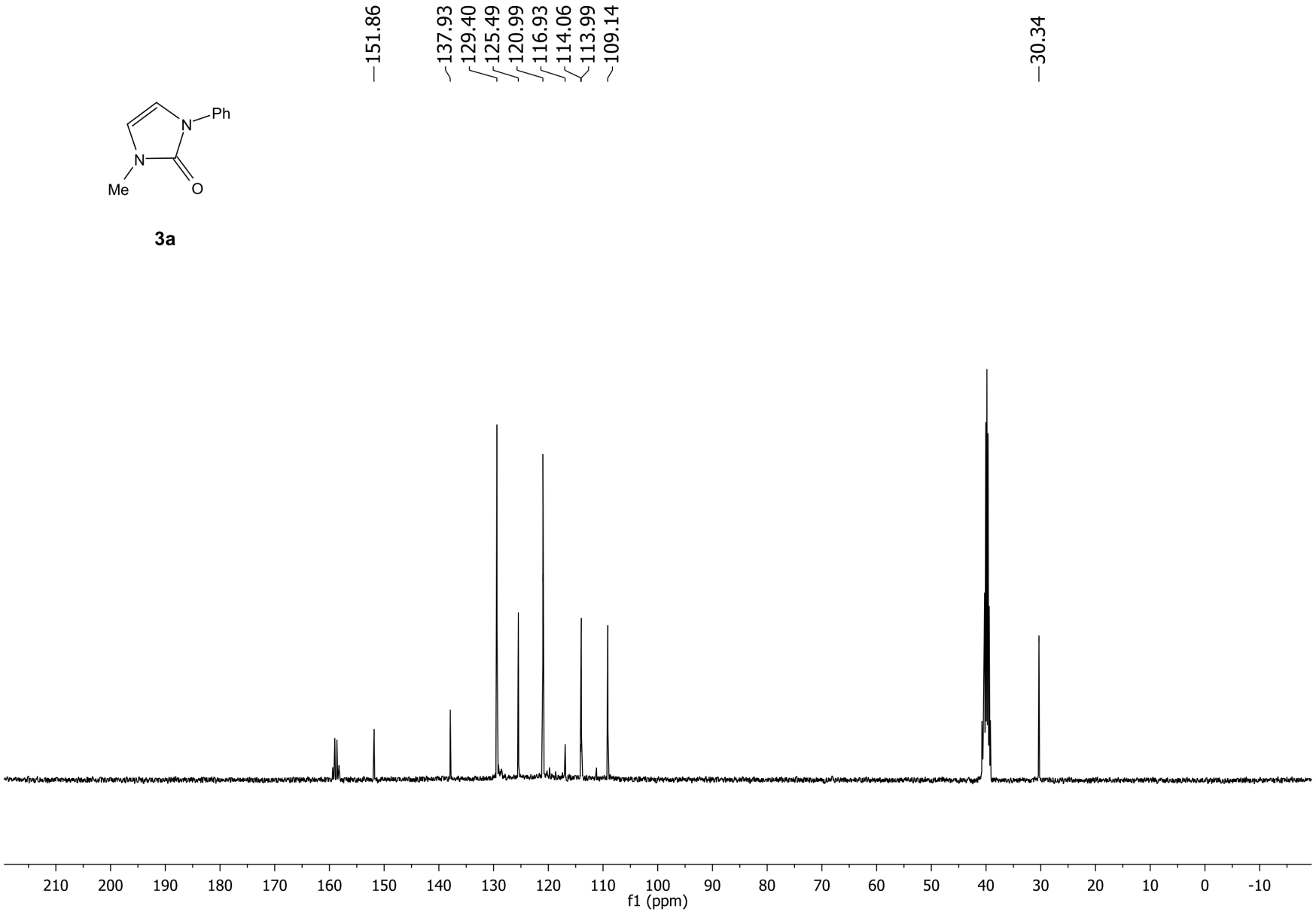


Figure S67. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound **3a**

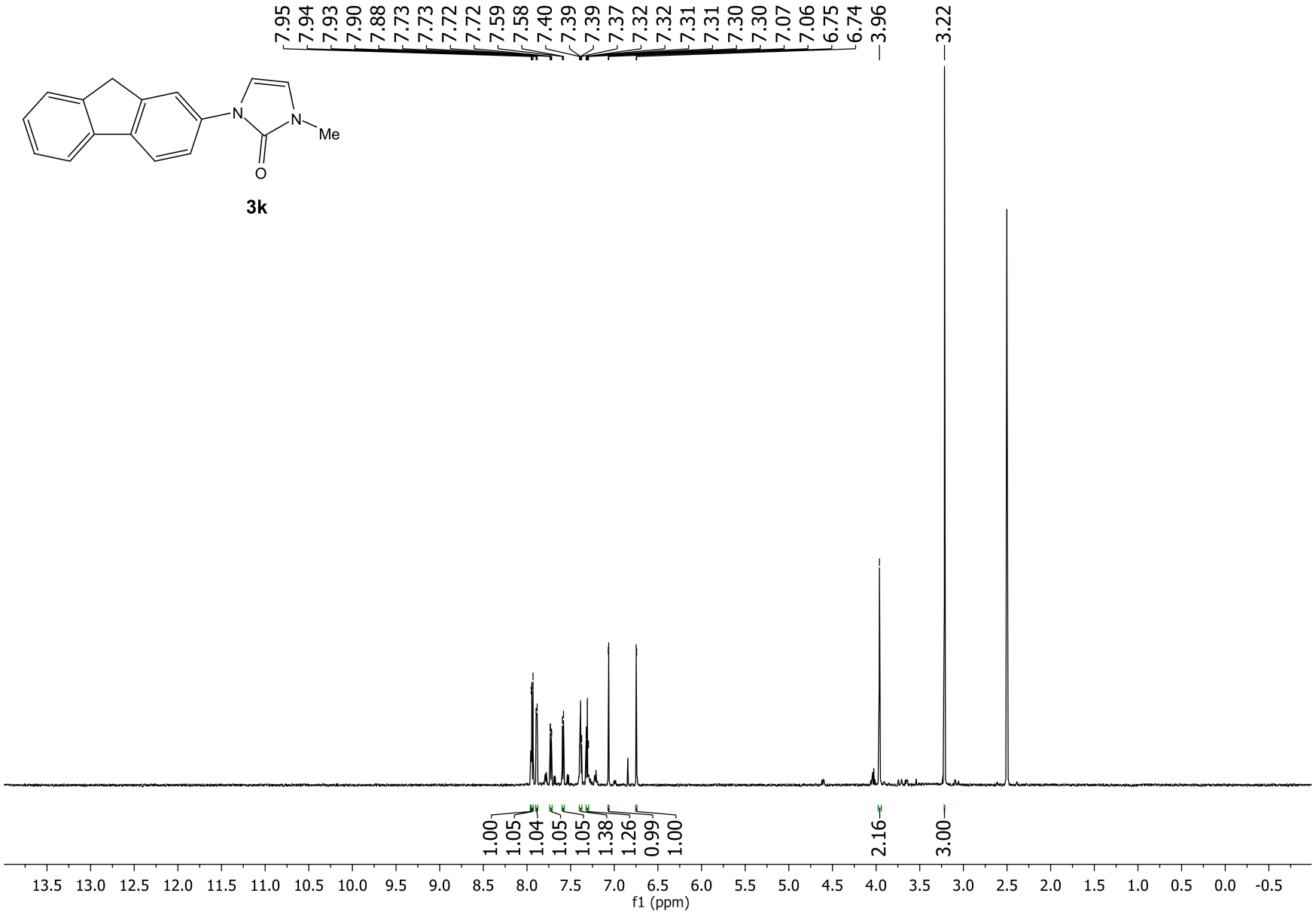


Figure S68. ^{1}H NMR spectrum ($CDCl_3$, 600MHz) of the compound **3k**

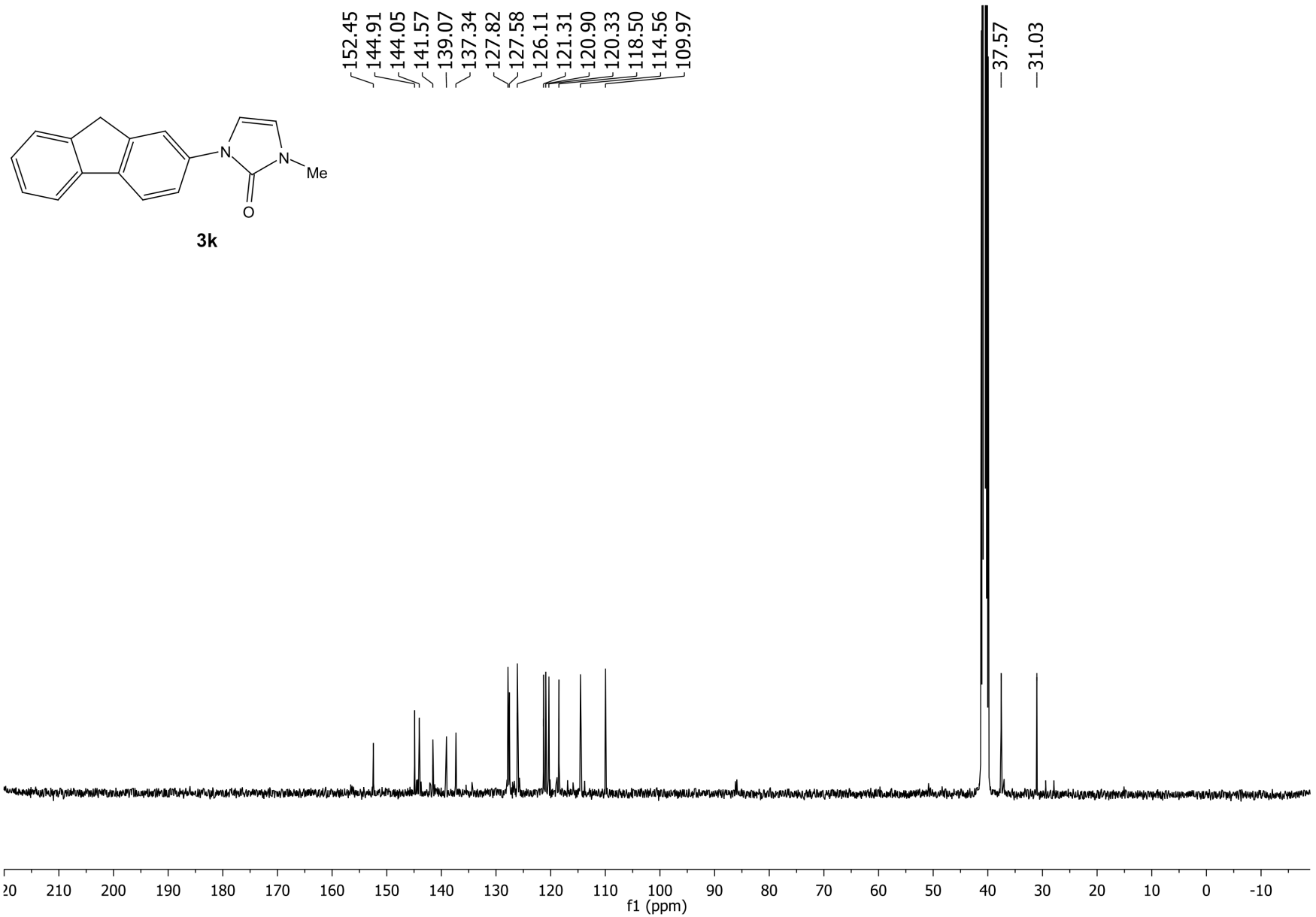


Figure S69. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **3k**

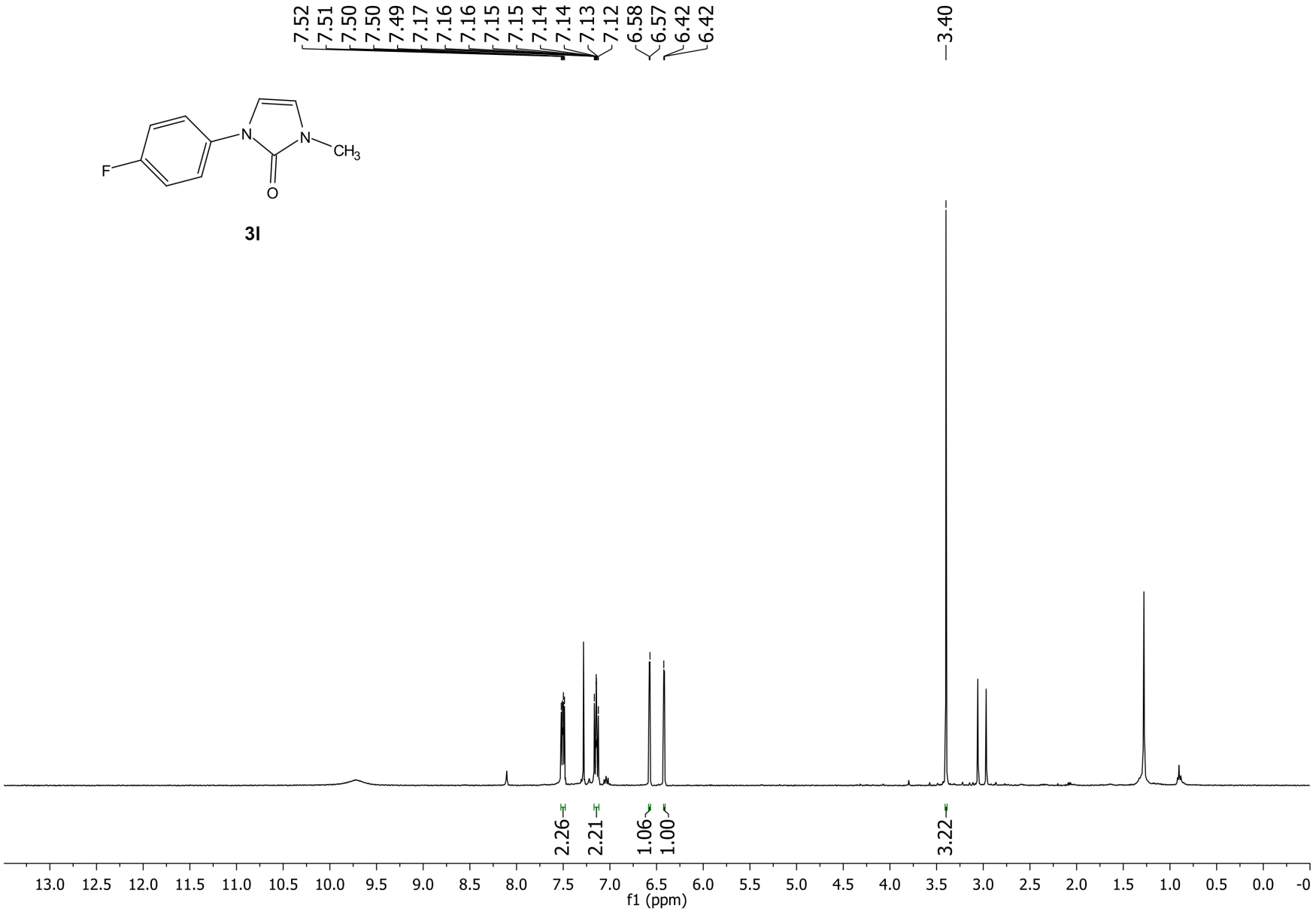


Figure S70. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **3l**

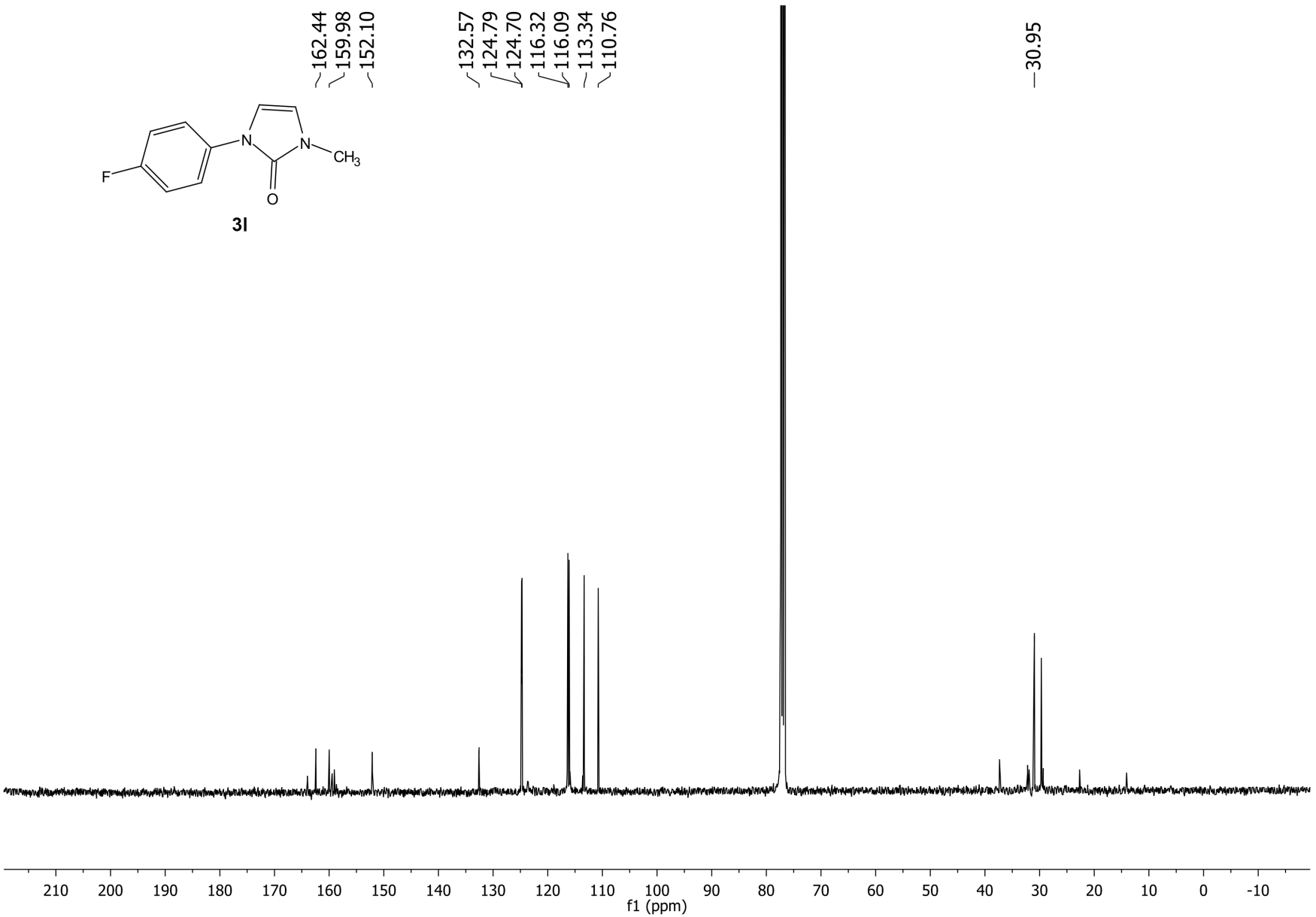


Figure S71. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **3l**

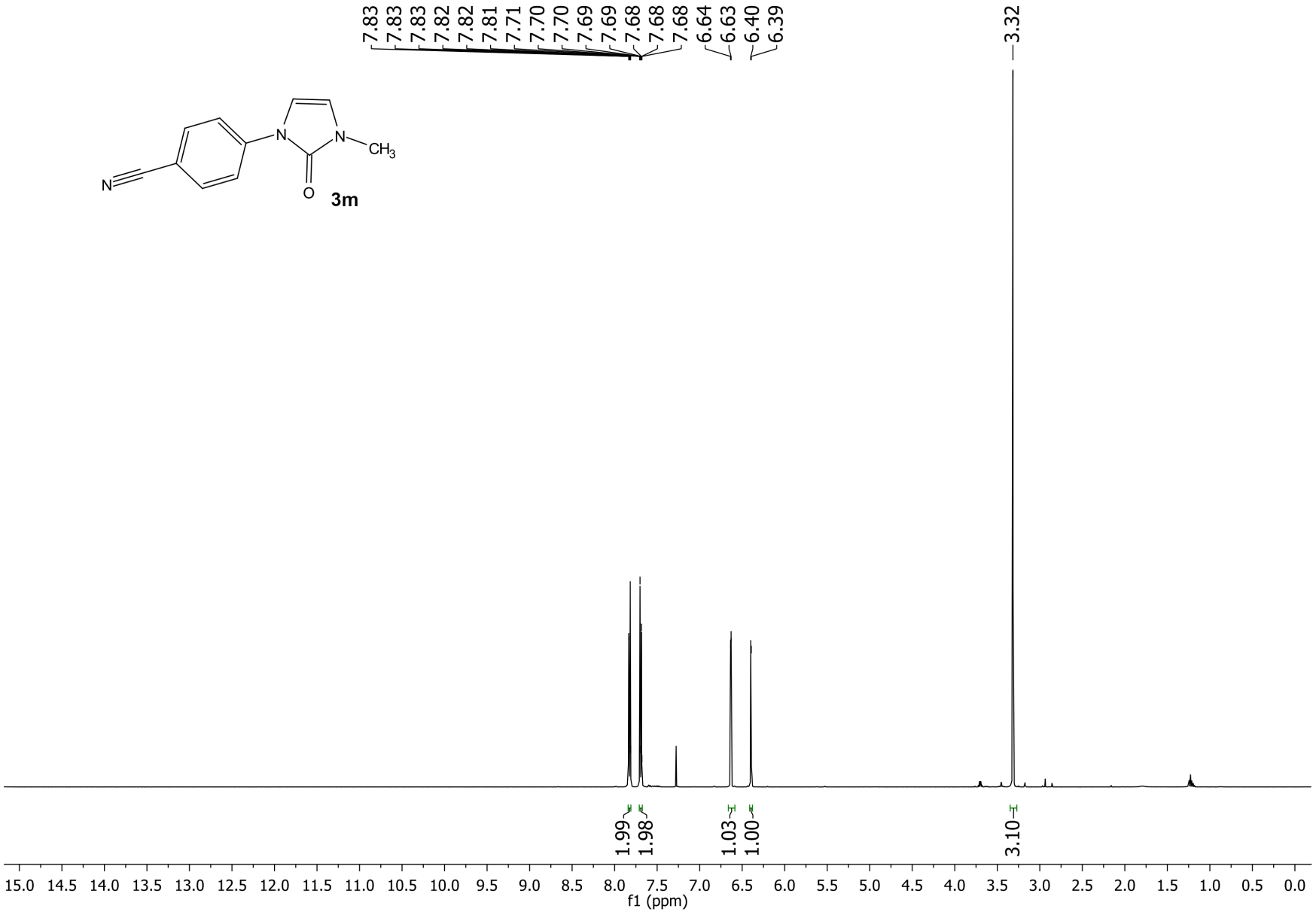


Figure S72. ^{1}H NMR spectrum ($CDCl_3$, 500MHz) of the compound **3m**

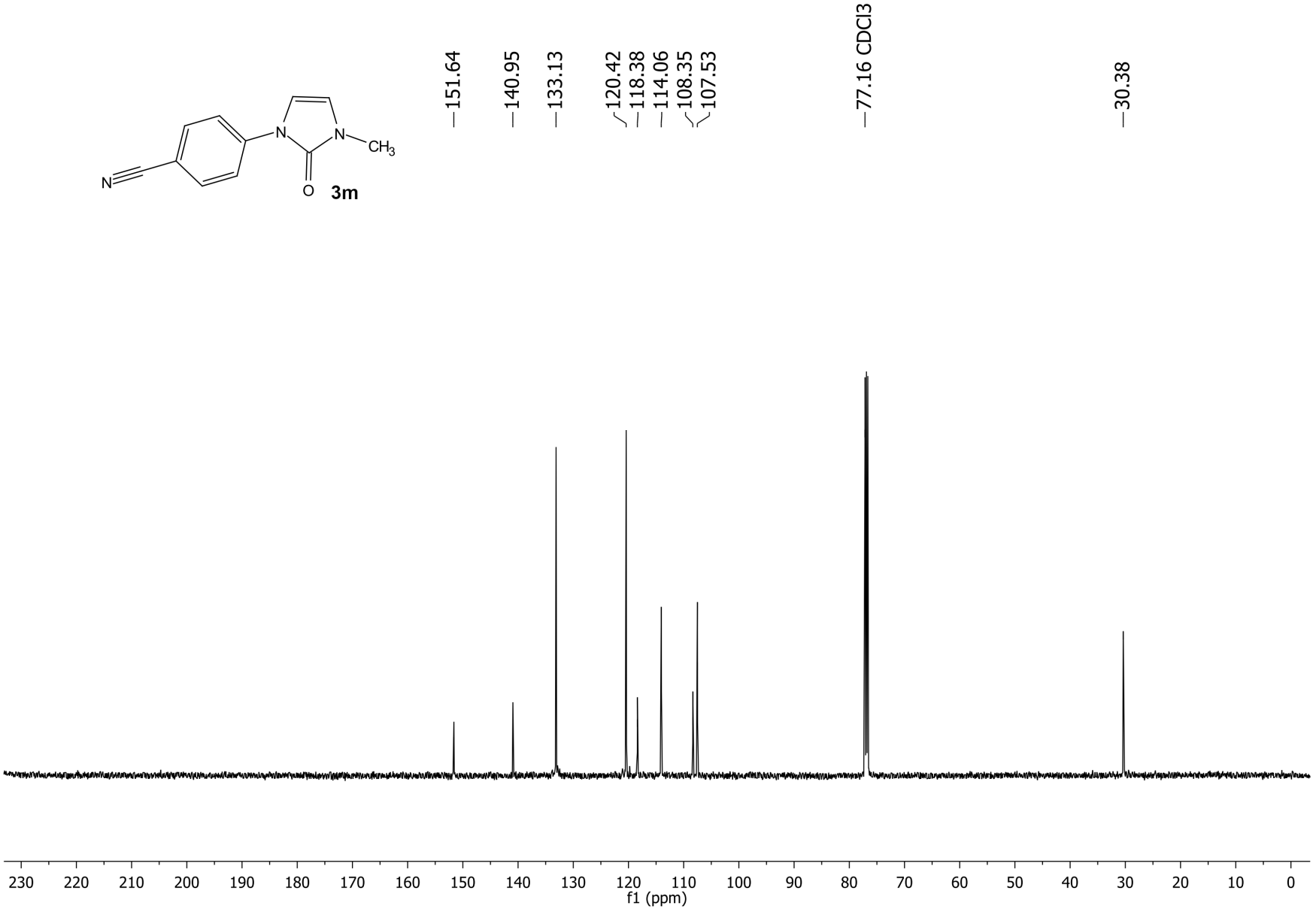


Figure S73. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **3m**

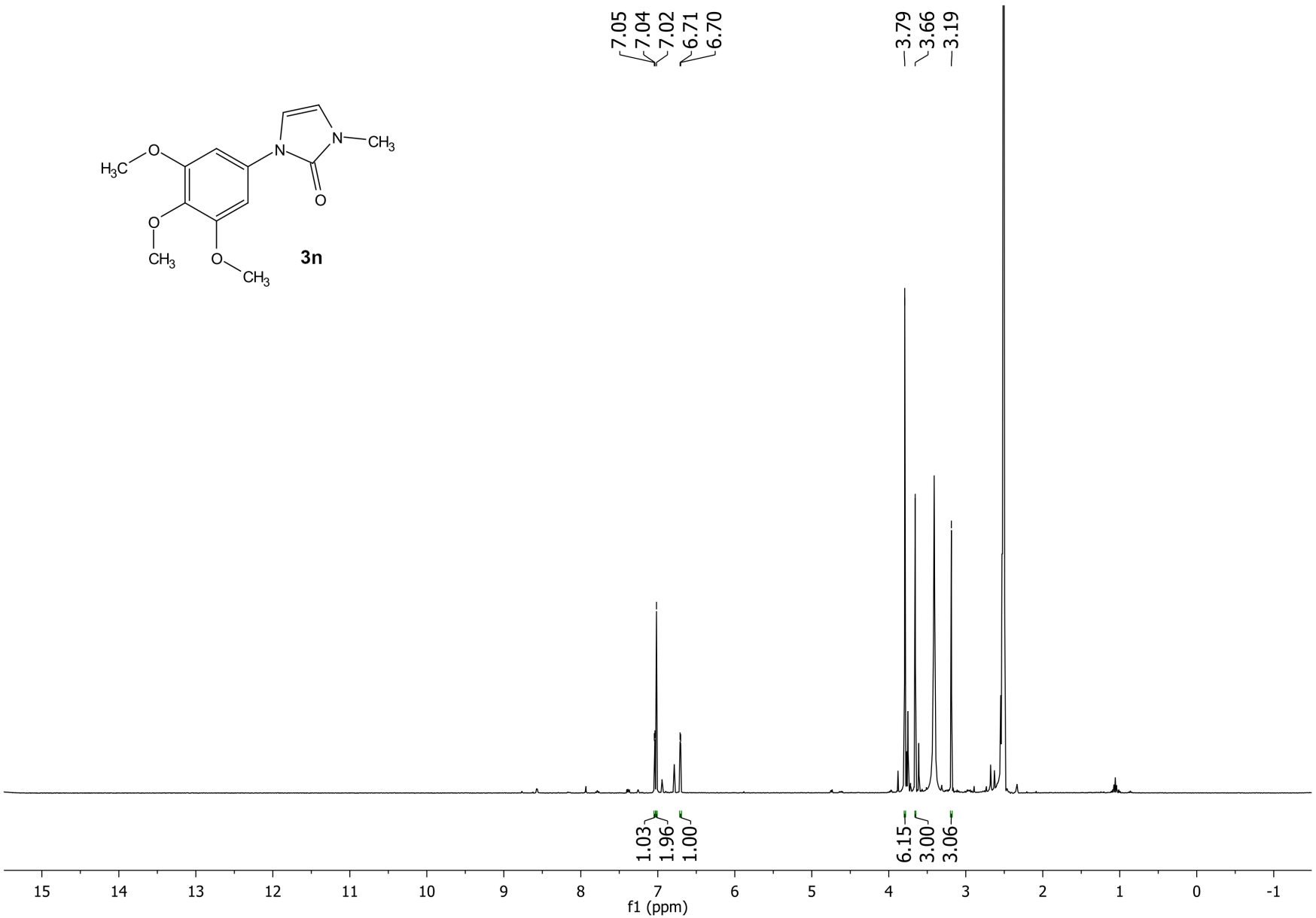


Figure S74. ^{1}H NMR spectrum ($(CD_3)_2SO$, 400MHz) of the compound **3n**

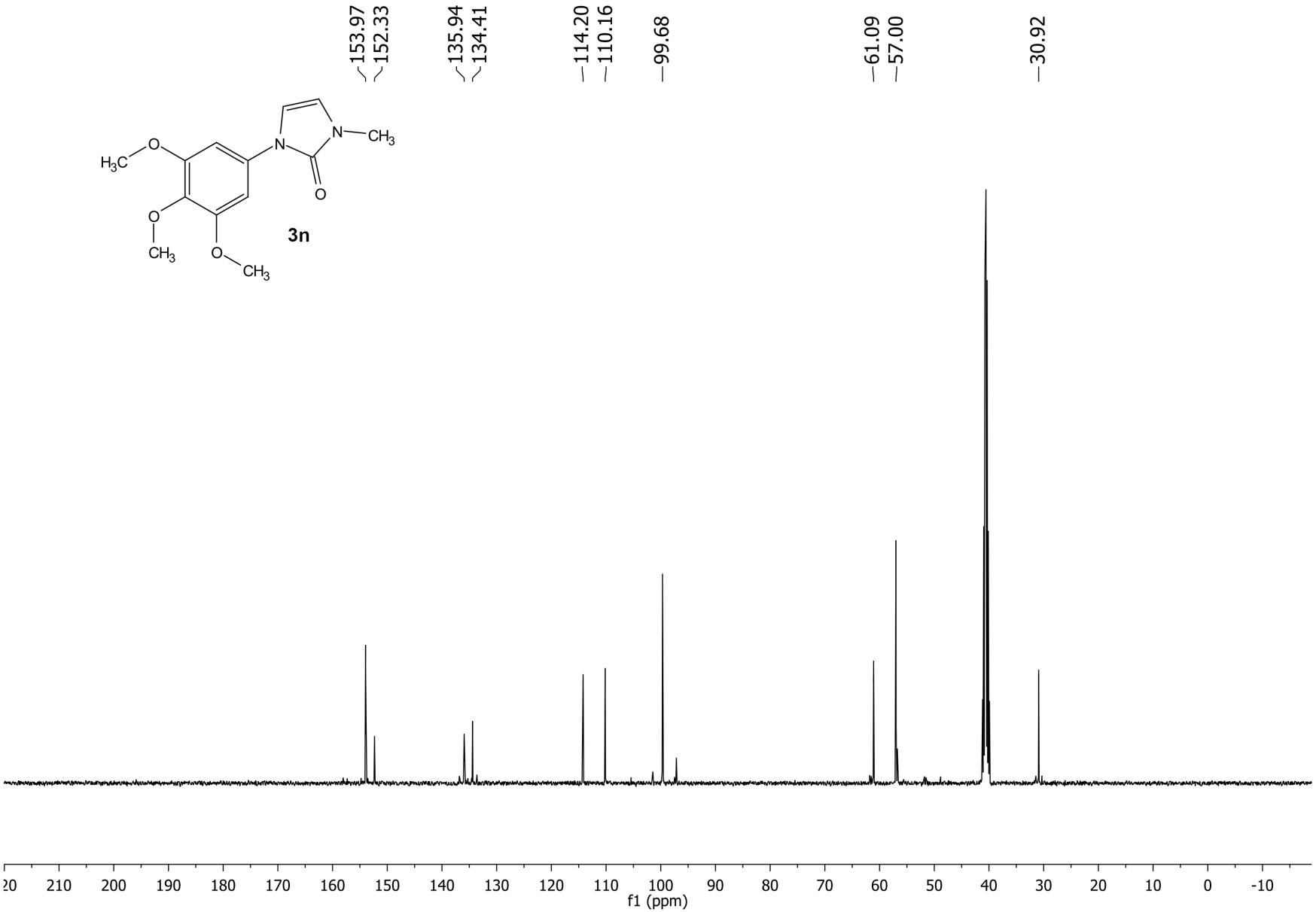


Figure S75. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound **3n**

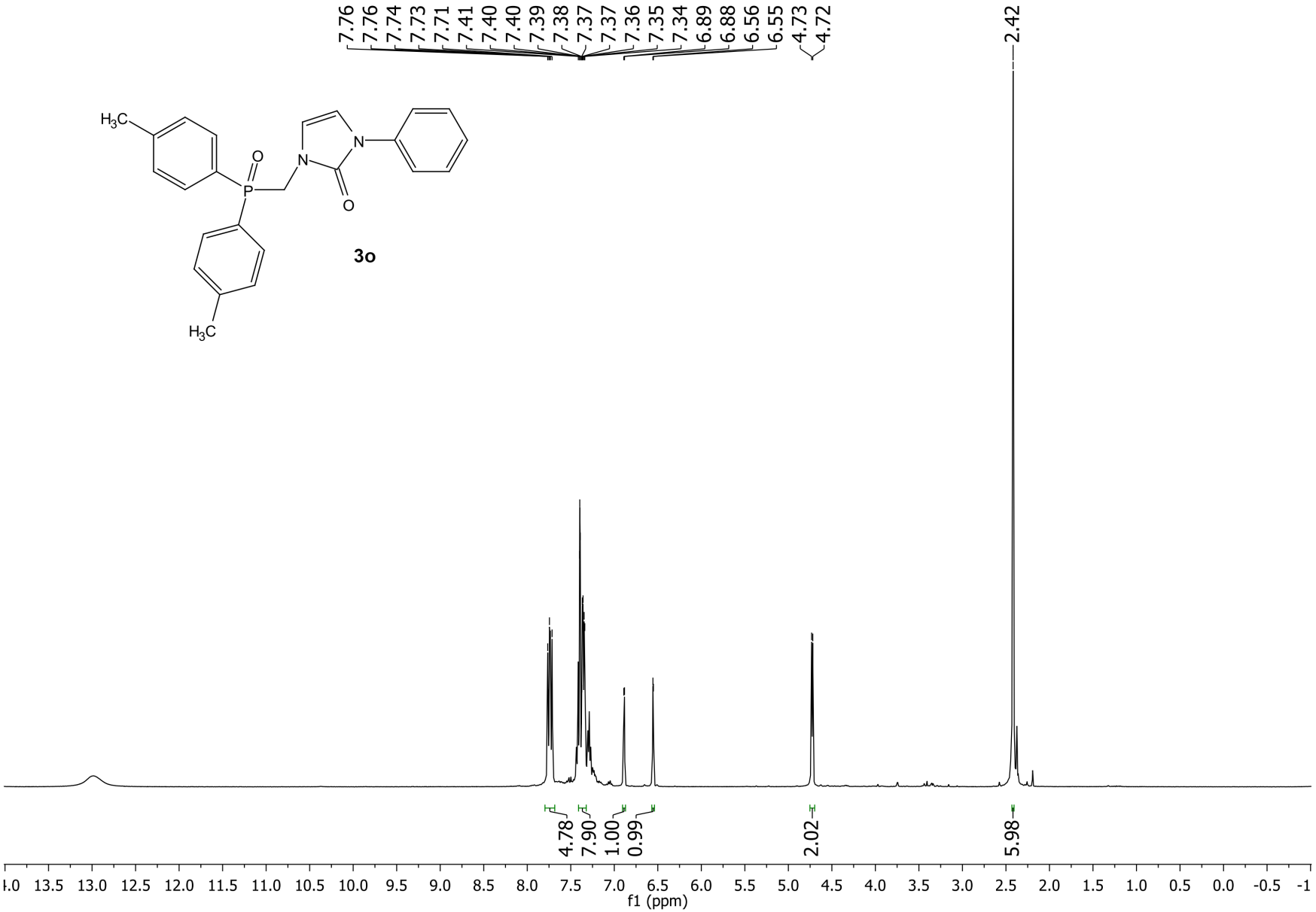


Figure S76. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **3o**

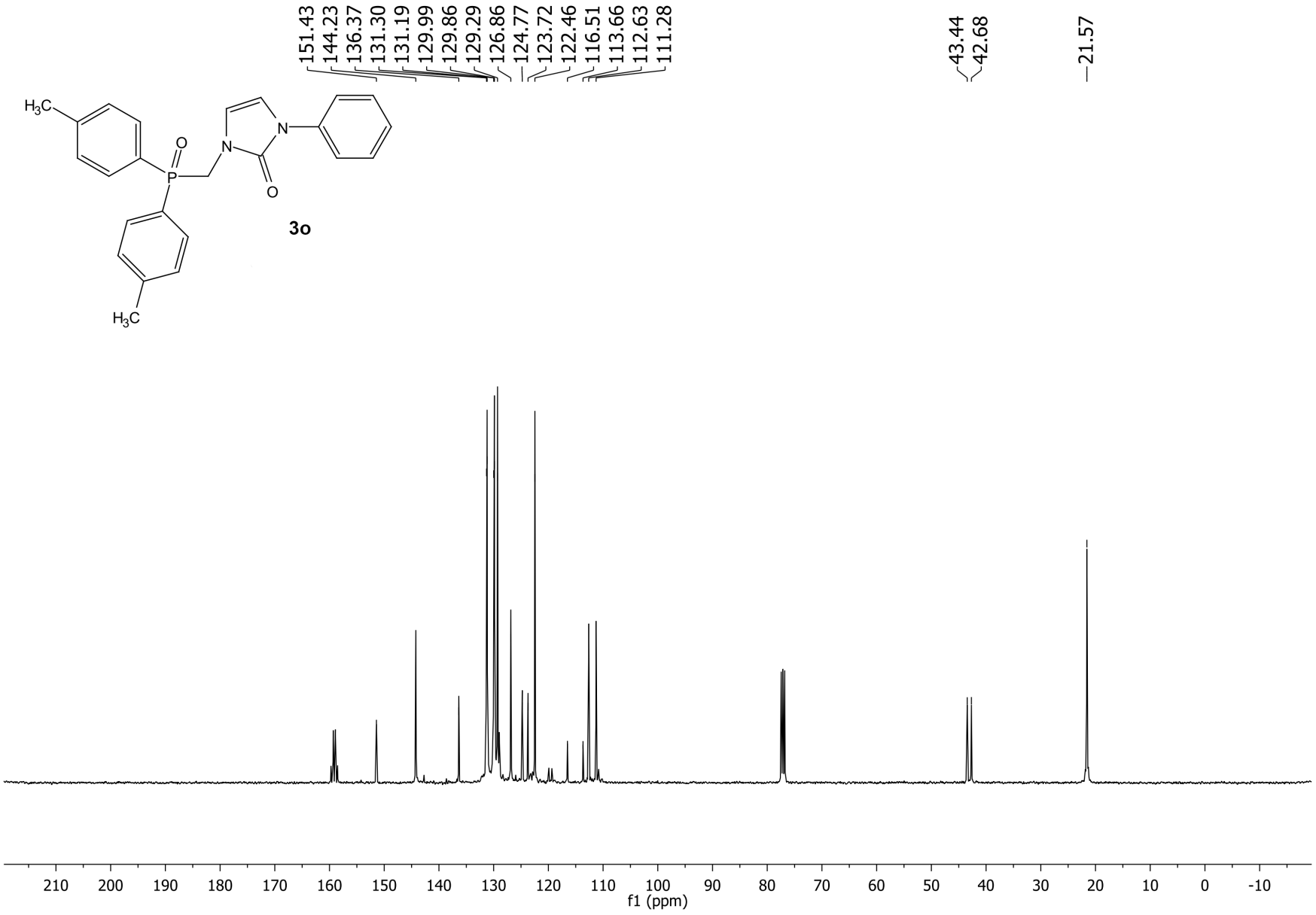


Figure S77. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **3o**

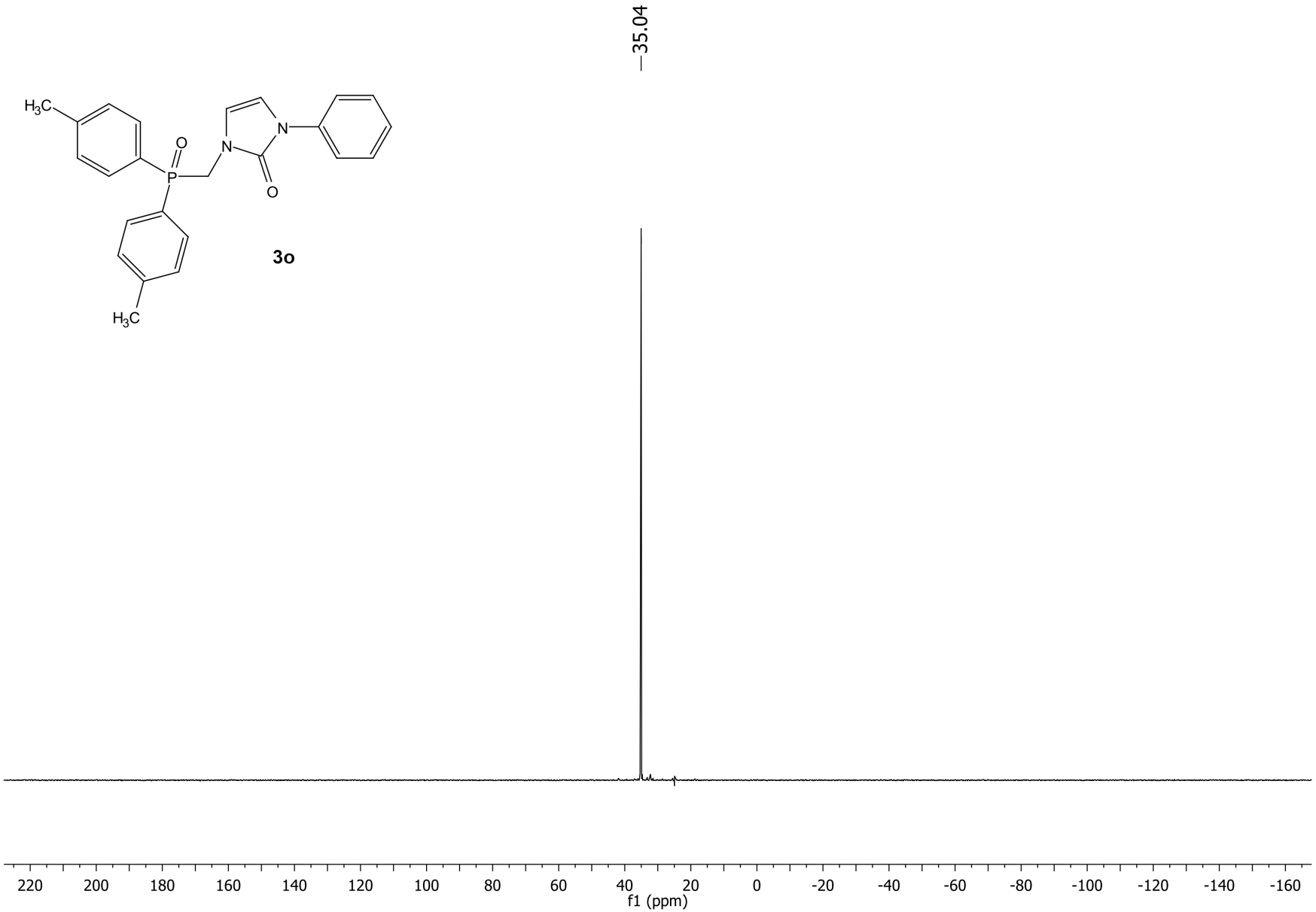


Figure S78. ^{31}P NMR spectrum ($CDCl_3$, 161MHz) of the compound **3o**

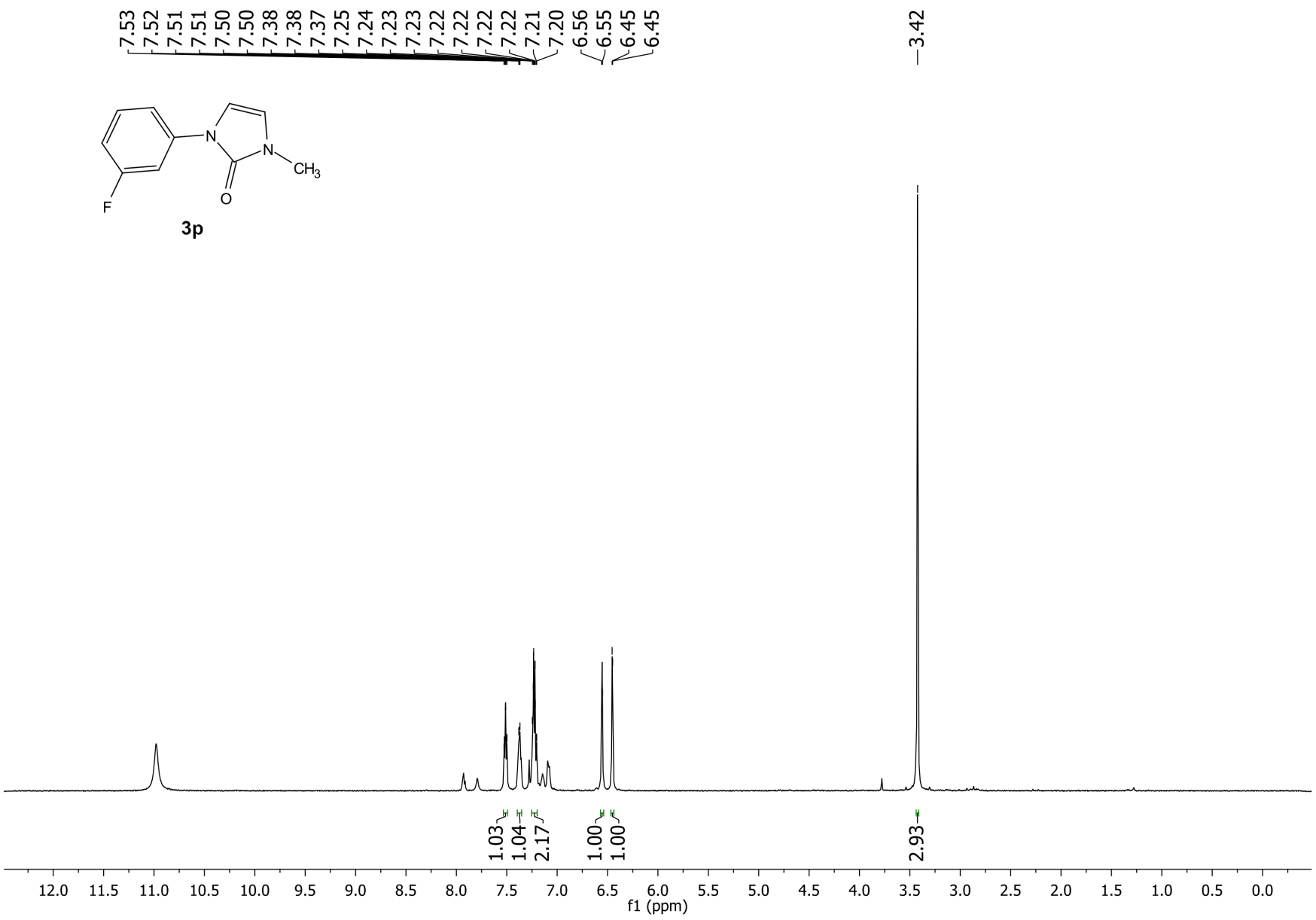


Figure S79. ^{1}H NMR spectrum ($CDCl_3$, 600MHz) of the compound **3p**

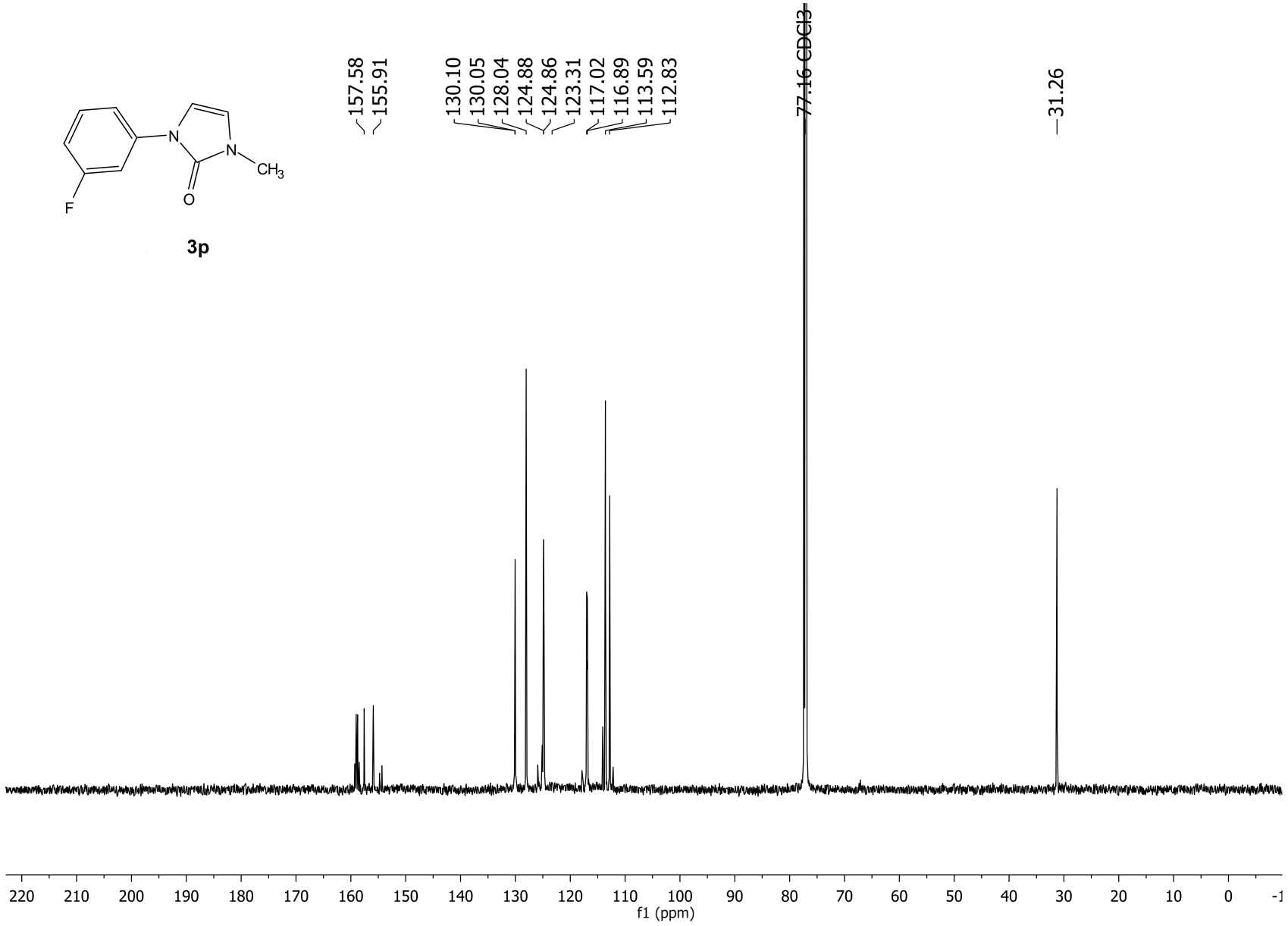


Figure S80. ^{13}C NMR spectrum ($CDCl_3$, 151MHz) of the compound **3p**

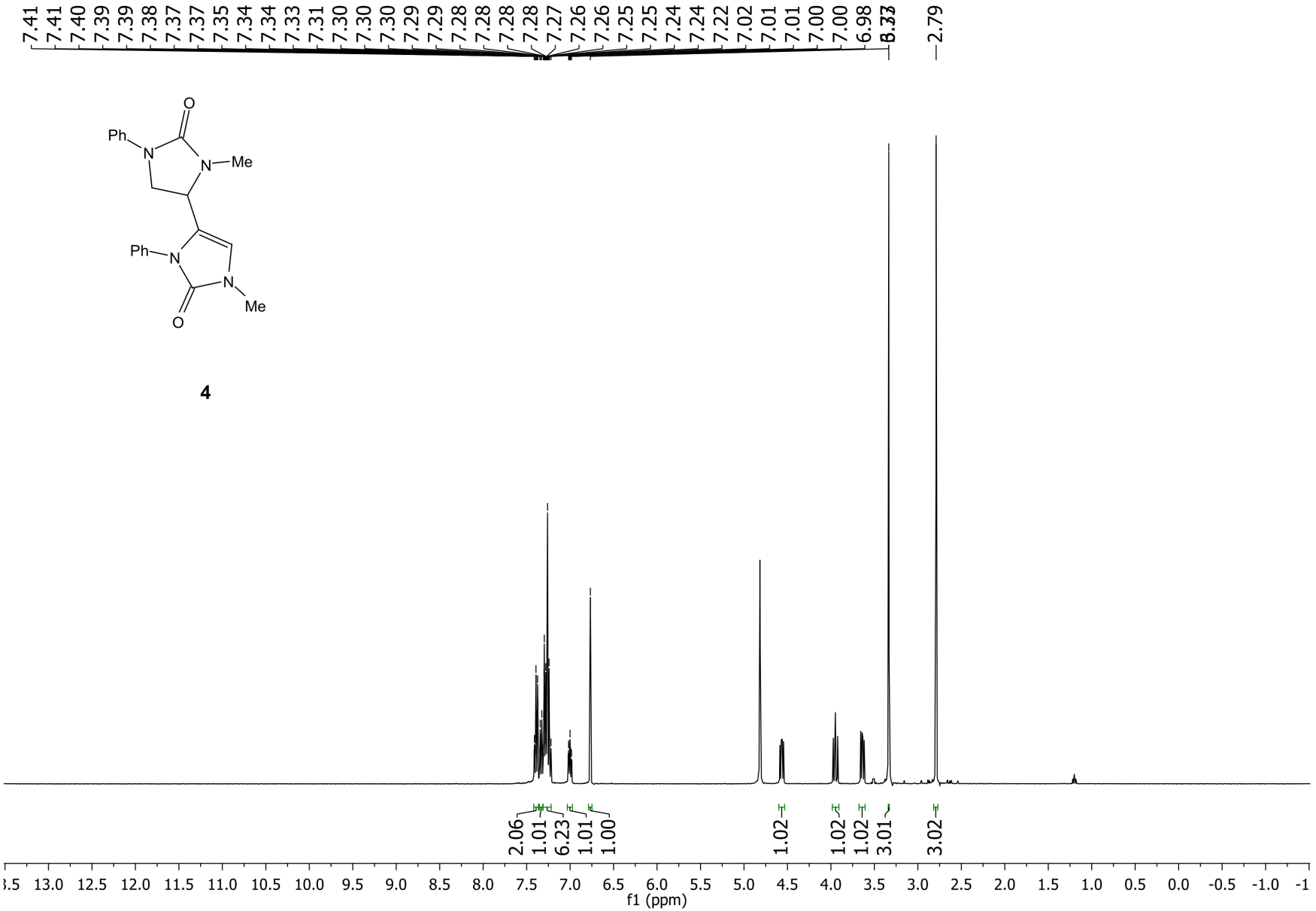


Figure S81. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of the compound **4**

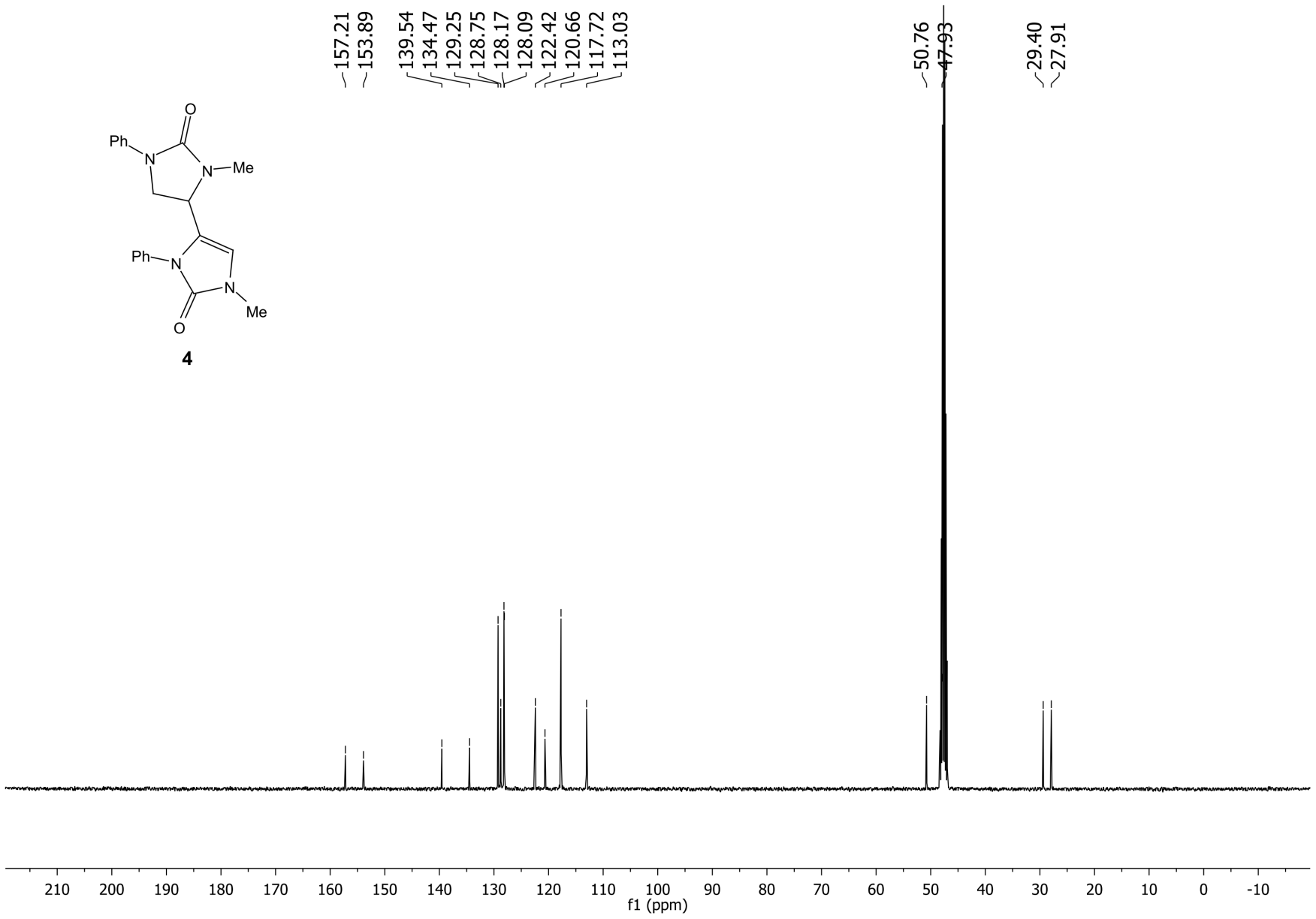
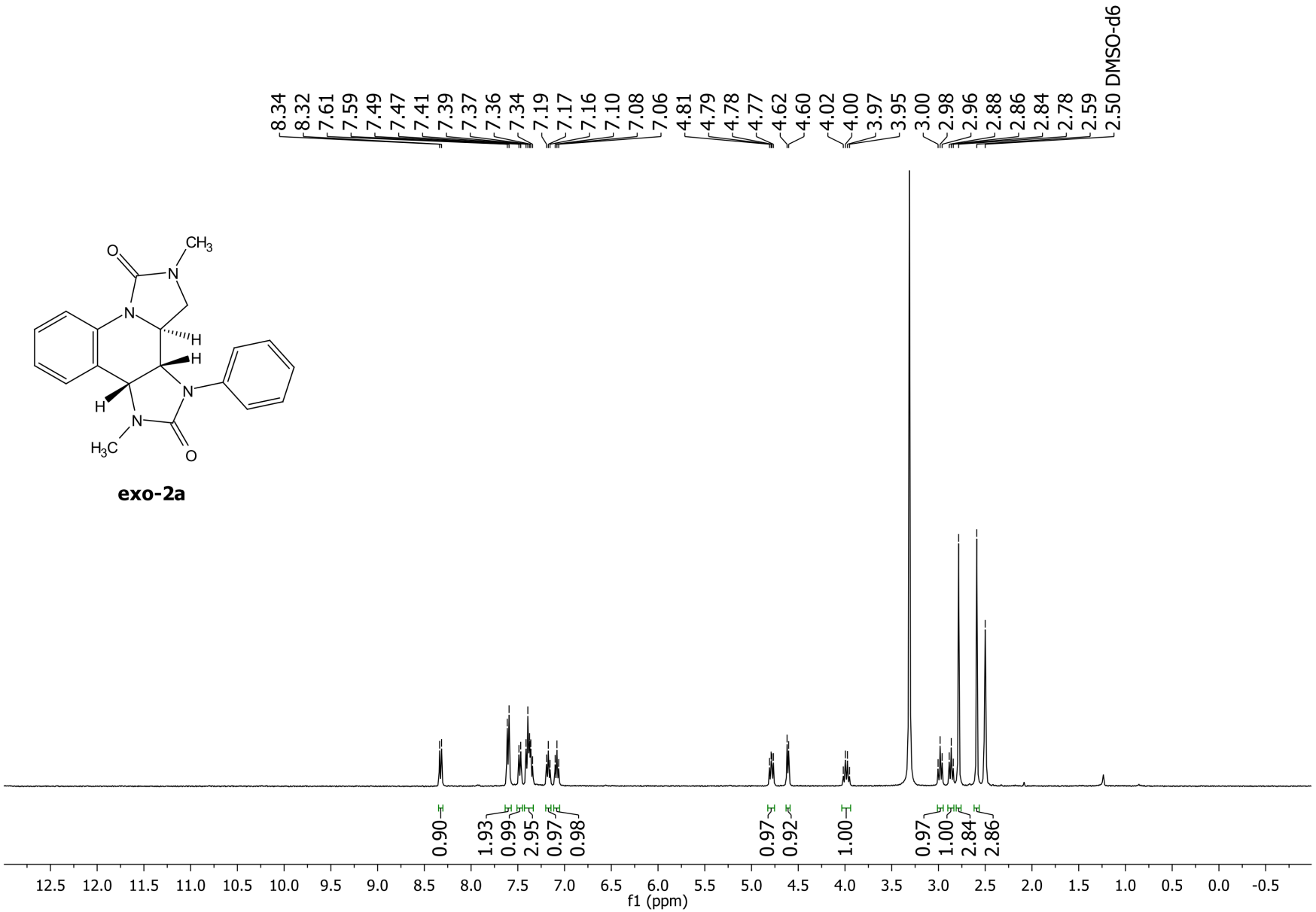


Figure S82. ^{13}C NMR spectrum (CD_3OD, 151MHz) of the compound **4**



exo-2a

Figure S83. ^{1}H NMR spectrum ($(CD_3)_2SO$, 500MHz) of the compound ***exo*-2a**

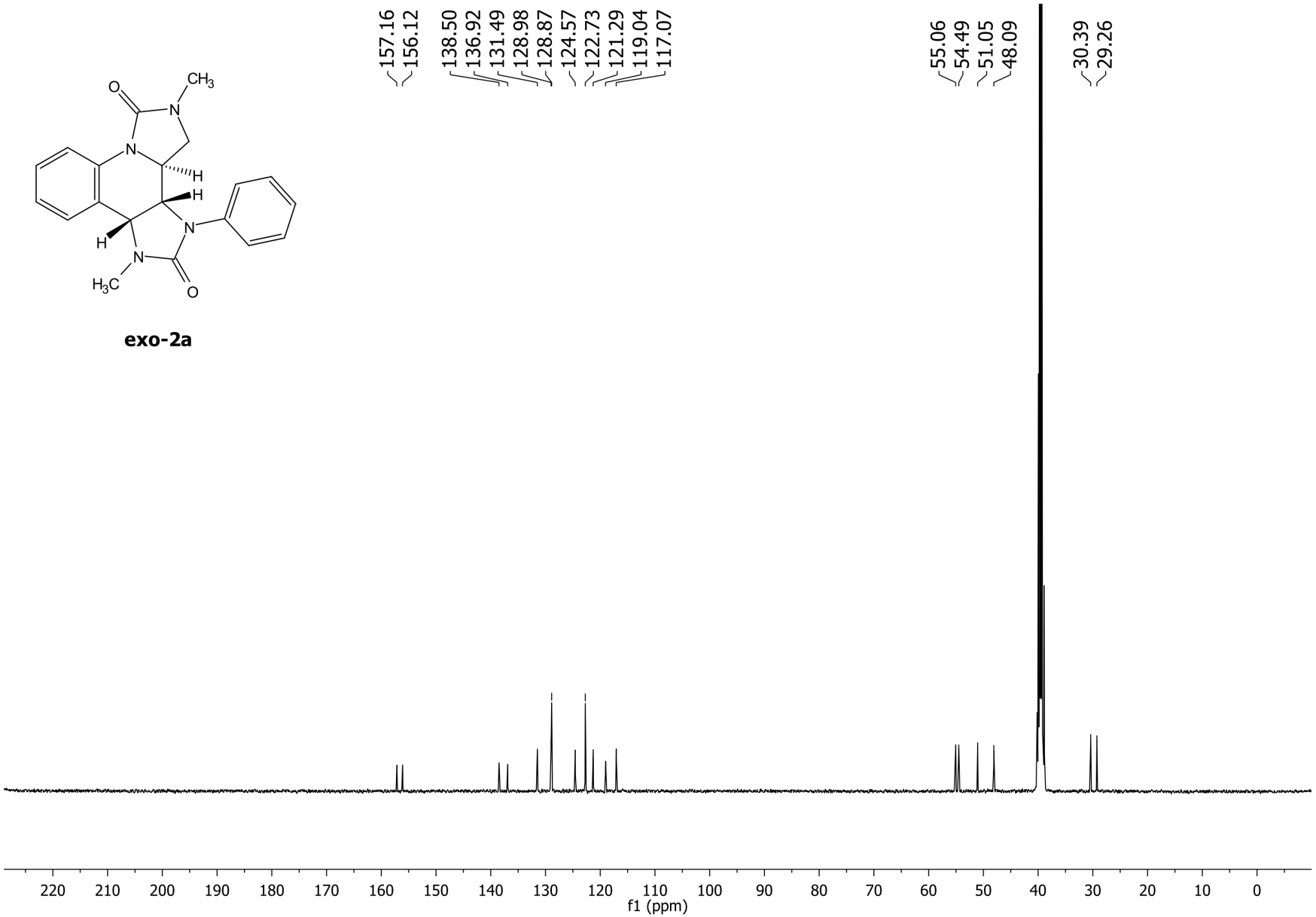


Figure S84. ^{13}C NMR spectrum ($(CD_3)_2SO$, 126MHz) of the compound ***exo*-2a**

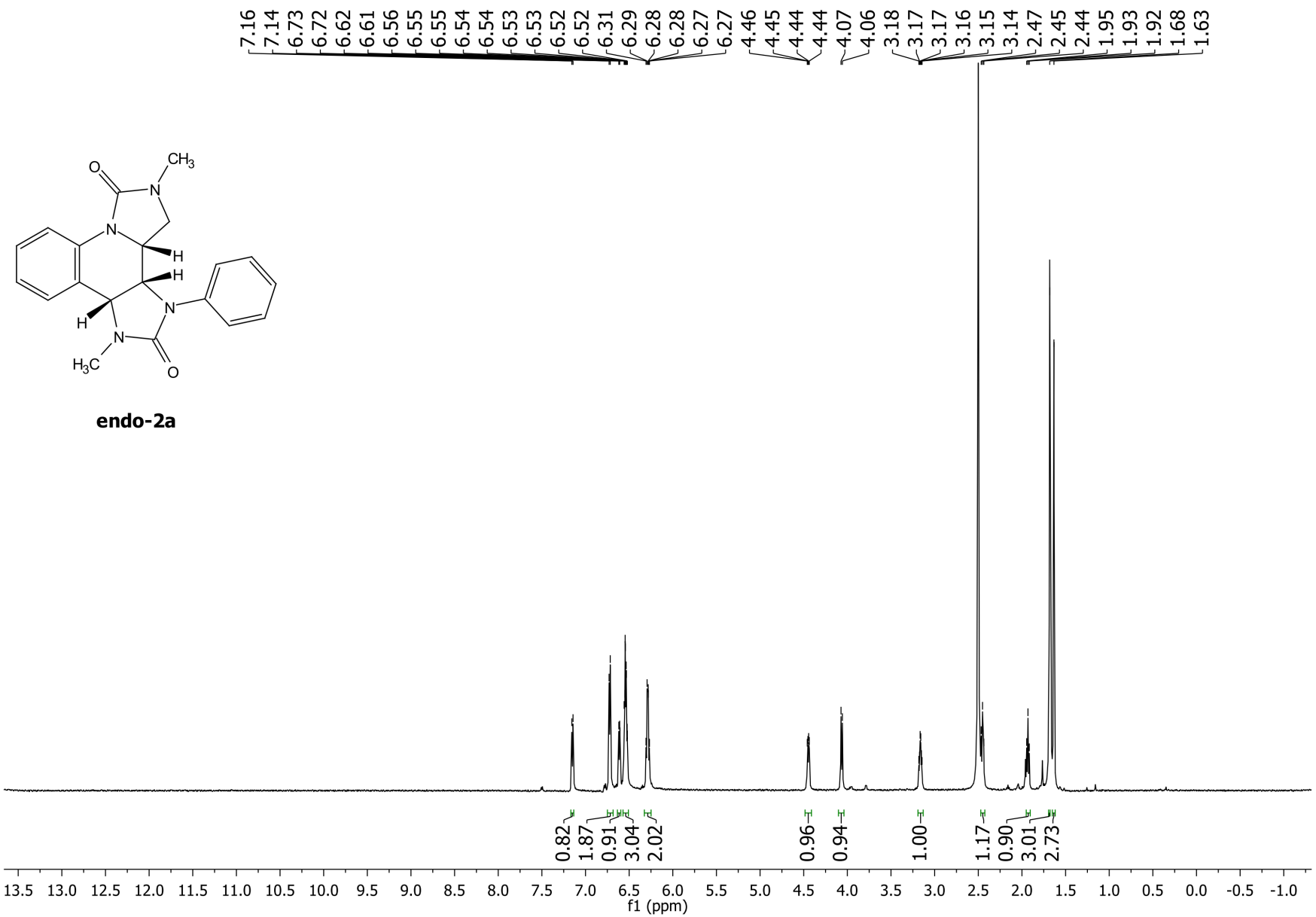


Figure S85. ^{1}H NMR spectrum ($(CD_3)_2SO$, 500MHz) of the compound ***endo*-2a**

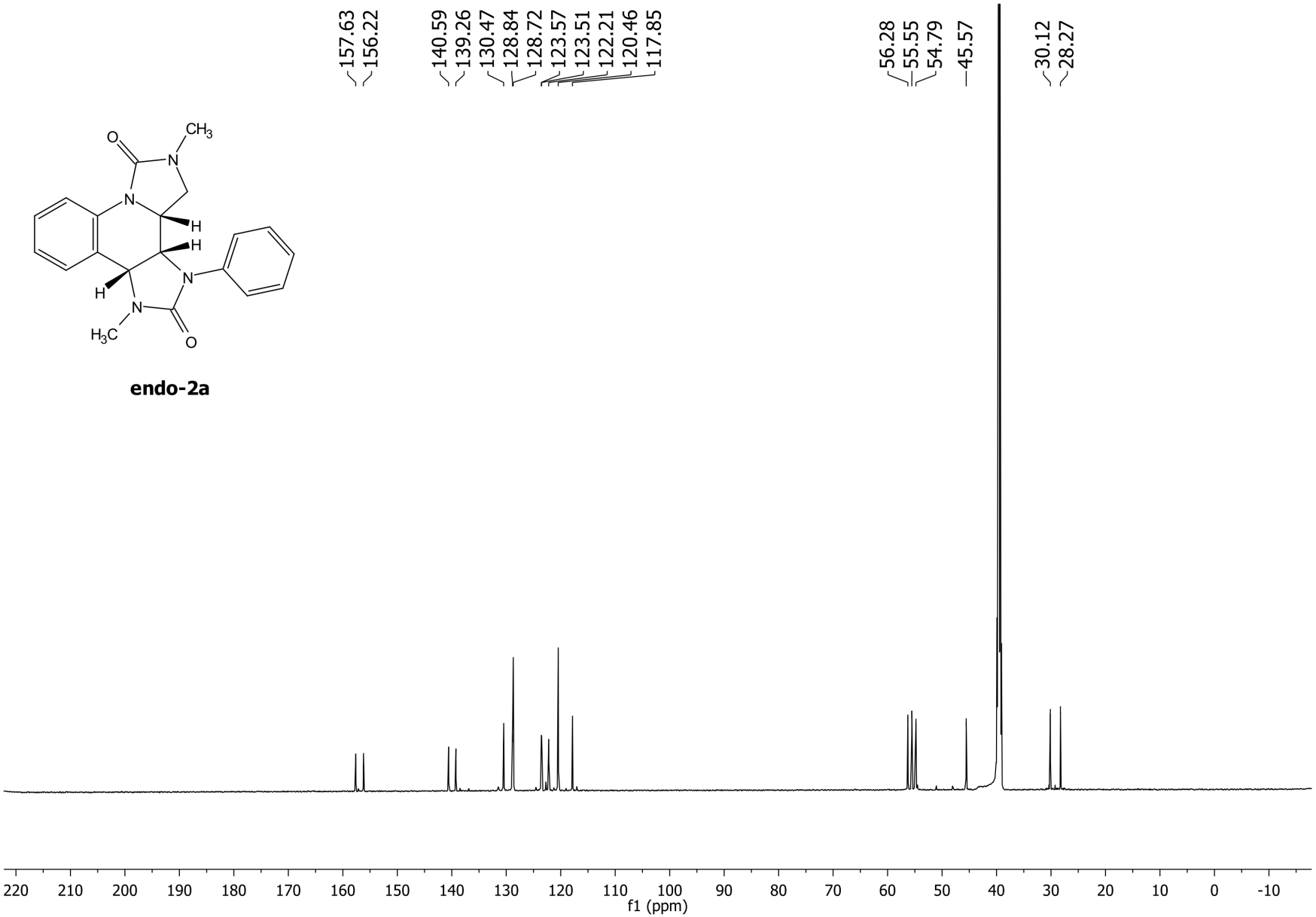


Figure S86. ^{13}C NMR spectrum ($(CD_3)_2SO$, 126MHz) of the compound ***endo*-2a**

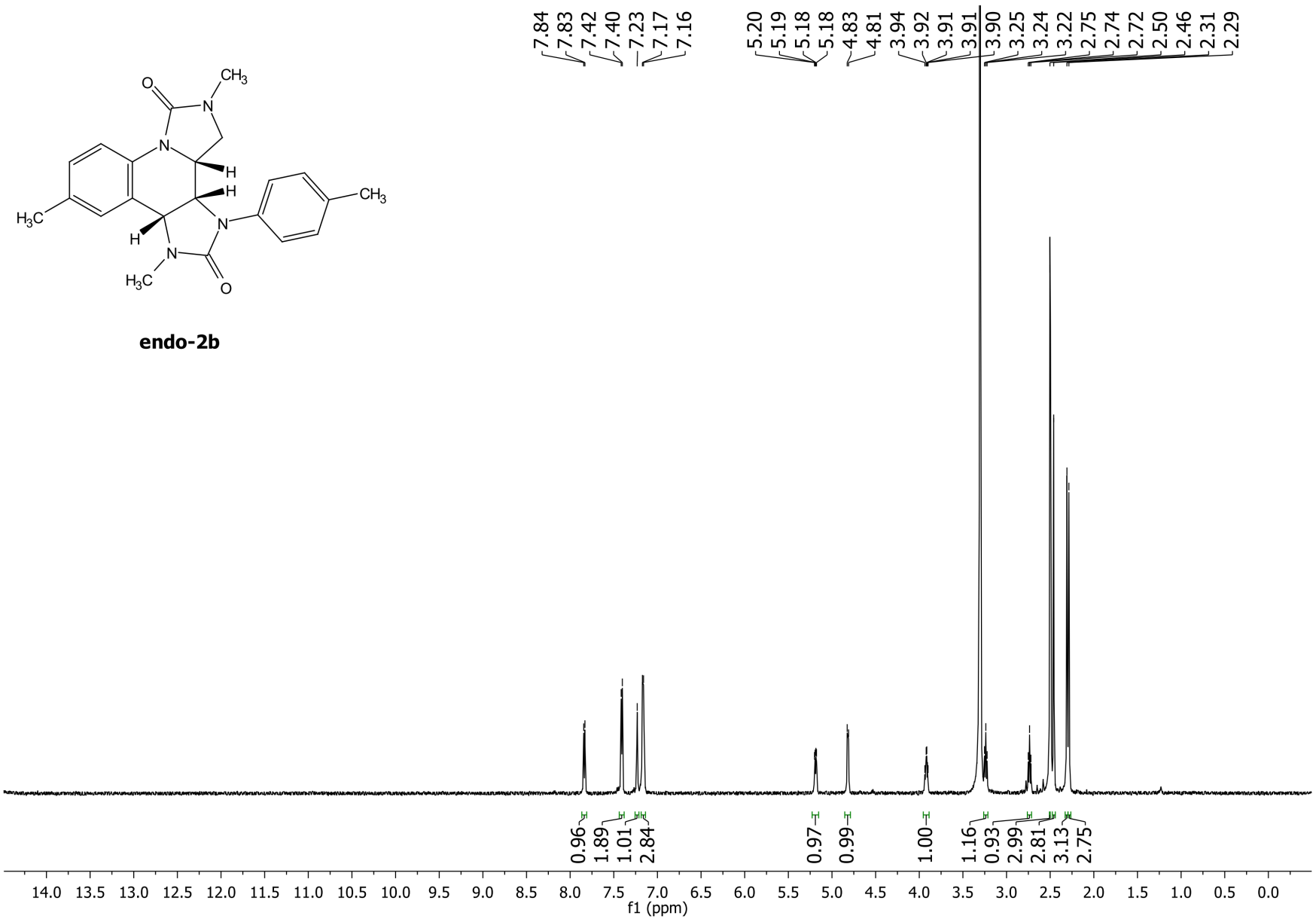


Figure S87. ^{1}H NMR spectrum ($(CD_3)_2SO$, 400MHz) of the compound ***endo*-2b**

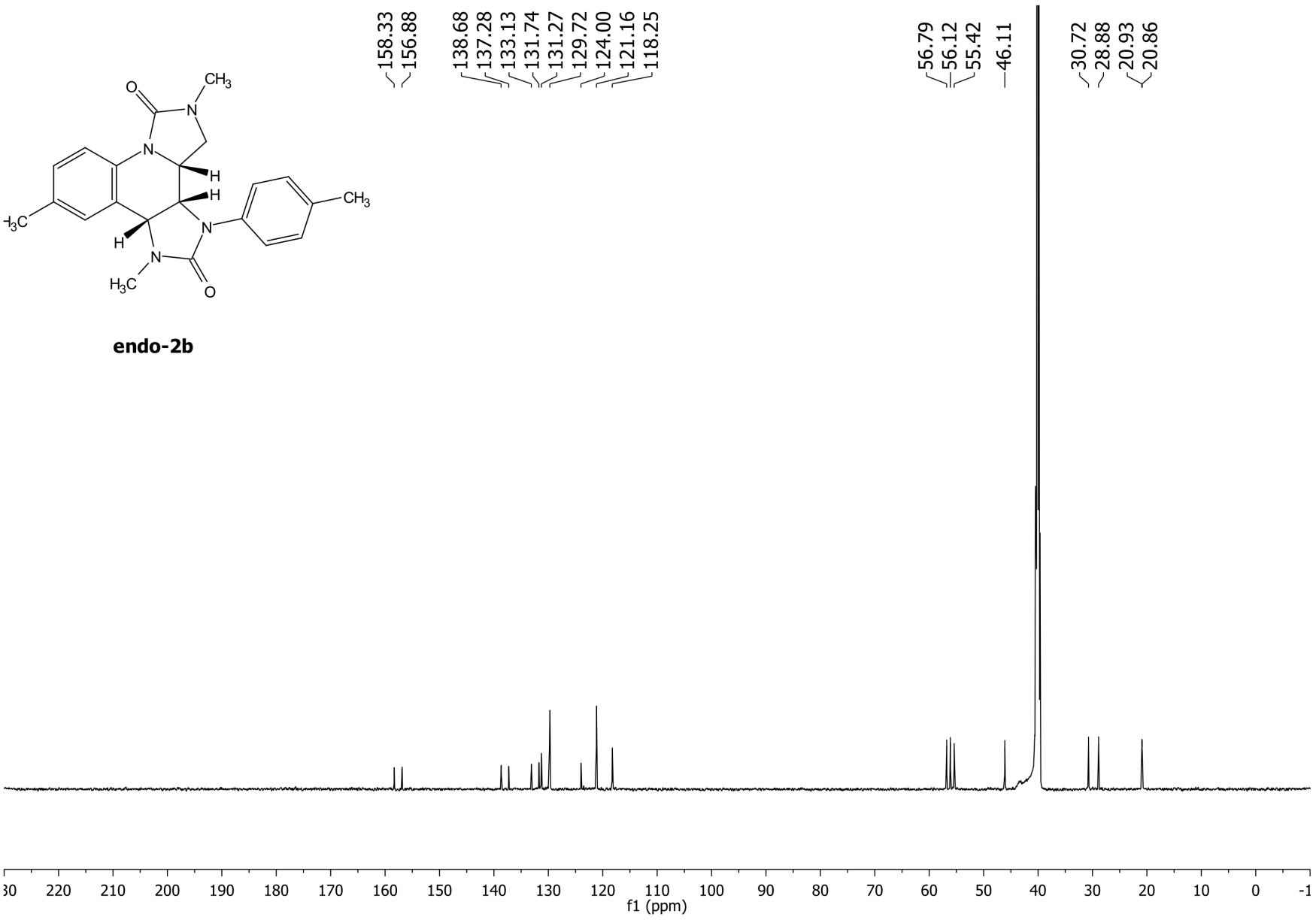


Figure S88. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound ***endo*-2b**

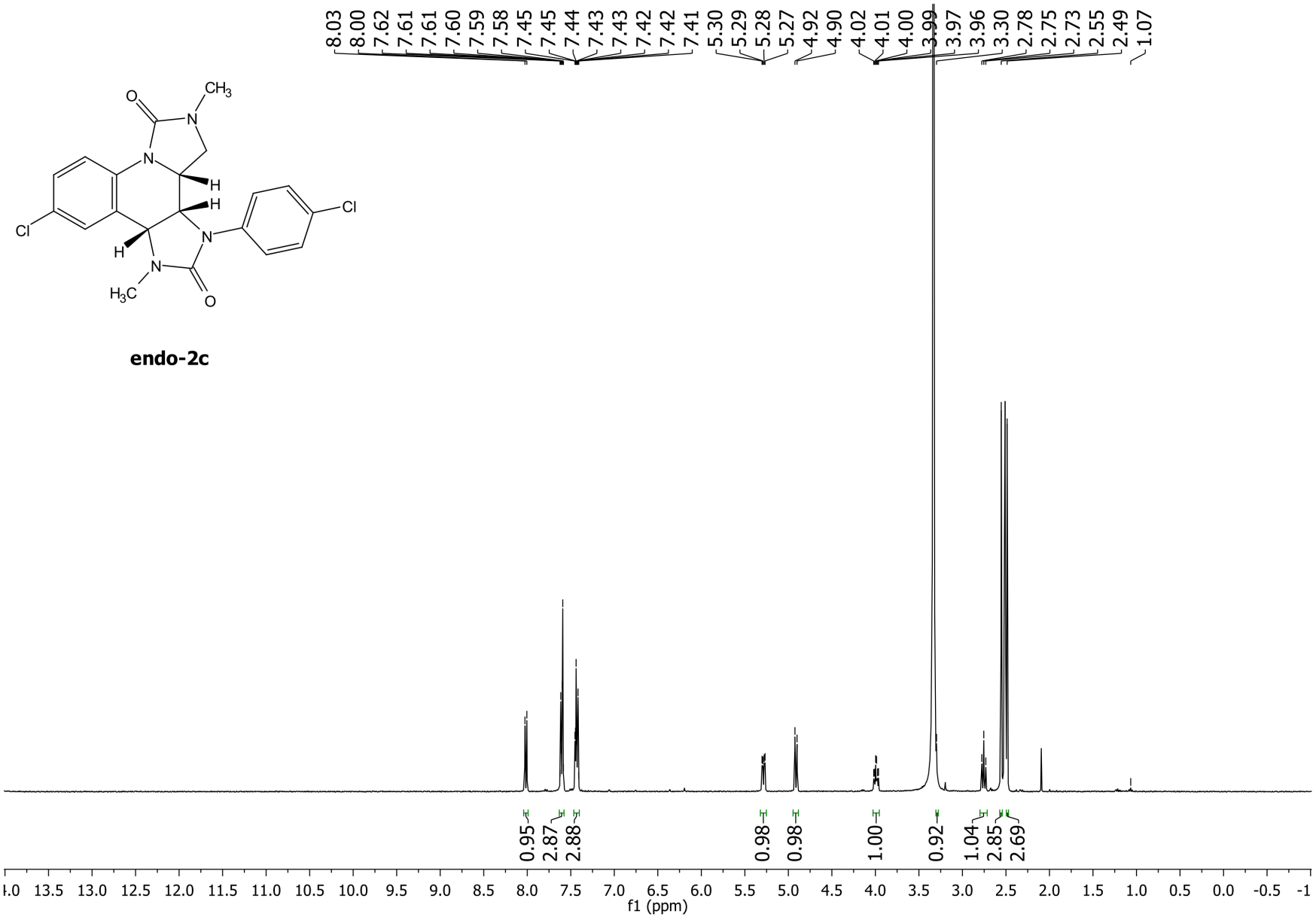


Figure S89. ^{1}H NMR spectrum ($(CD_3)_2SO$, 400MHz) of the compound ***endo*-2c**

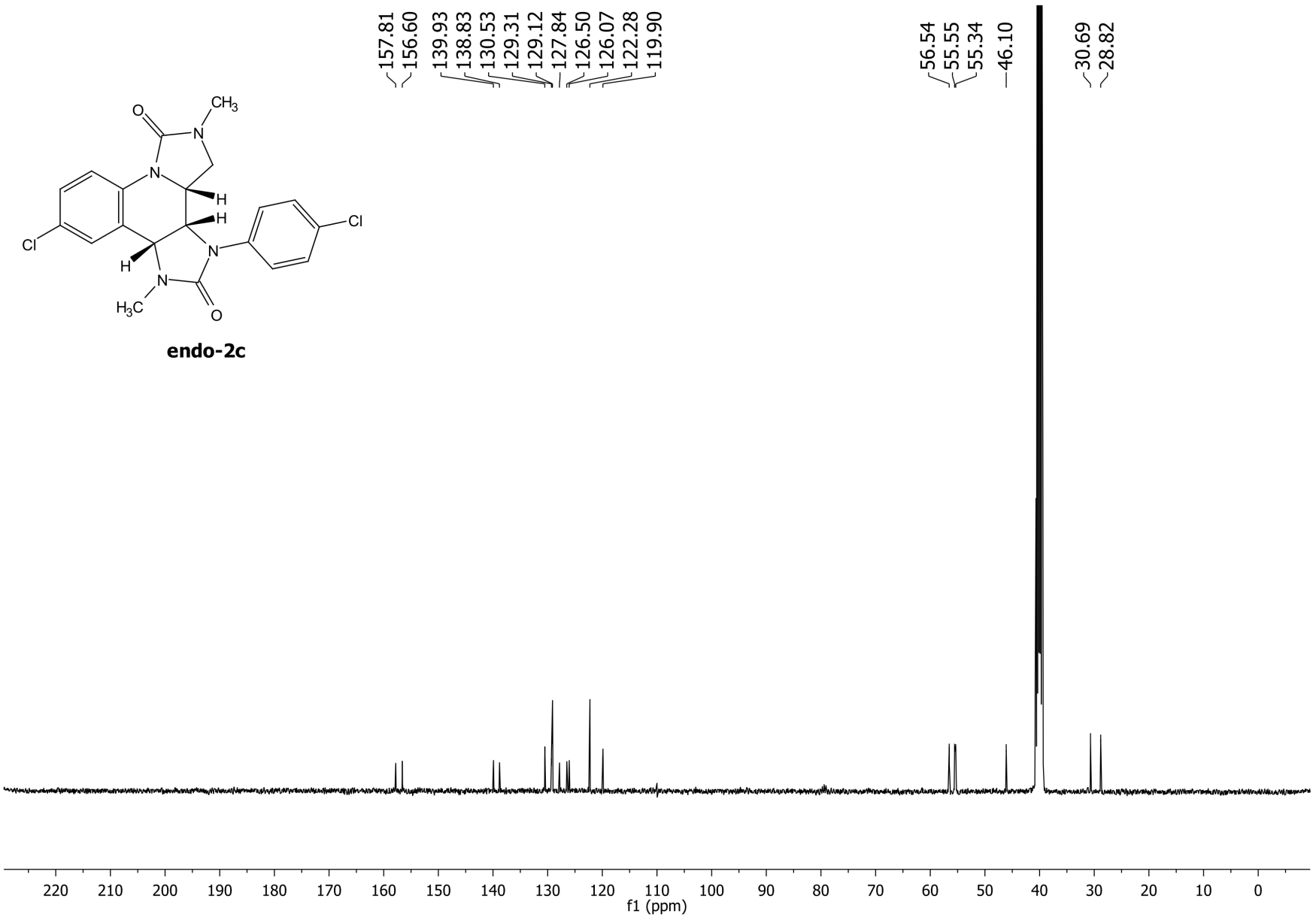


Figure S90. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound ***endo*-2c**

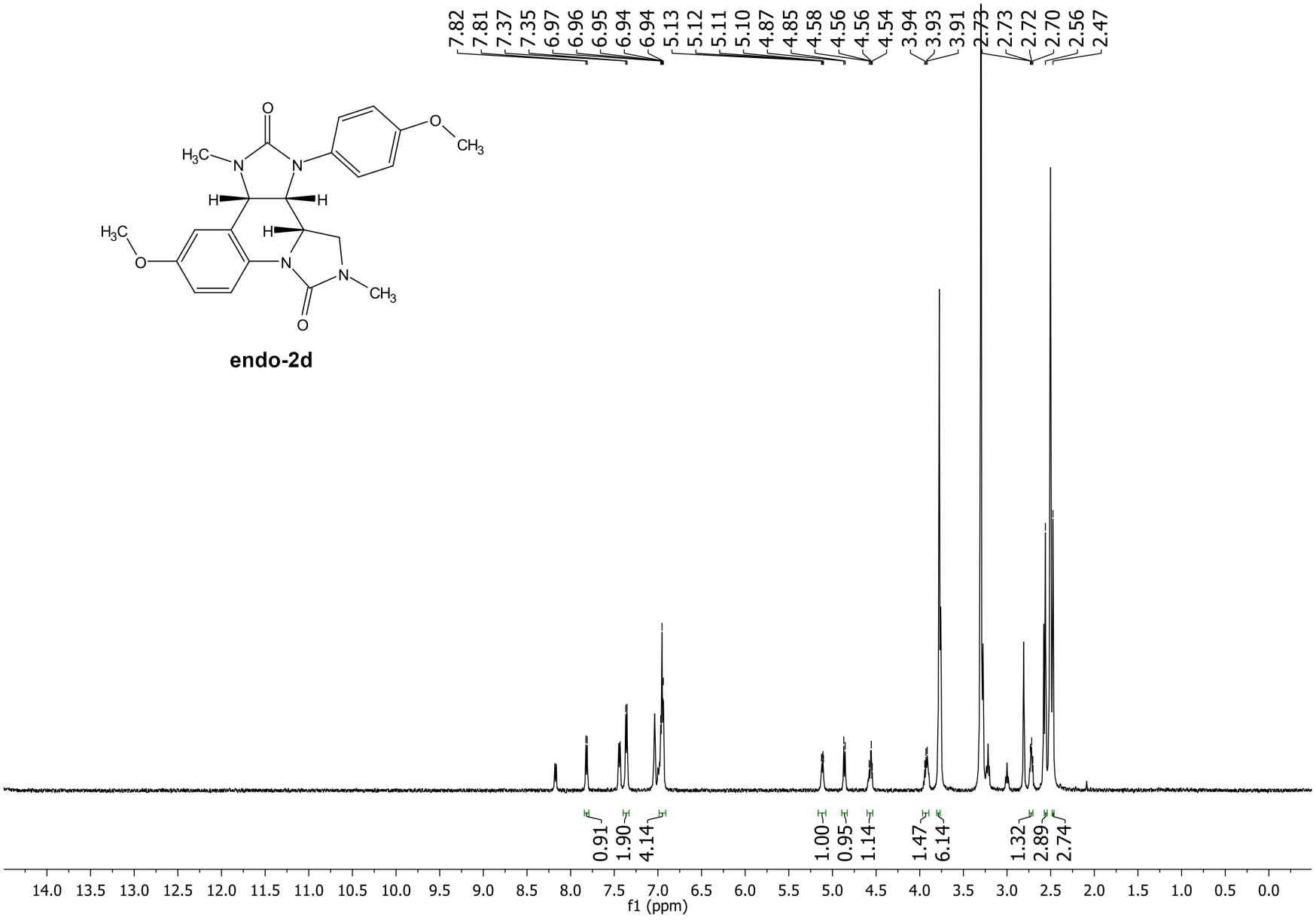


Figure S91. ^{1}H NMR spectrum ($(CD_3)_2SO$, 600MHz) of the compound ***endo*-2d**

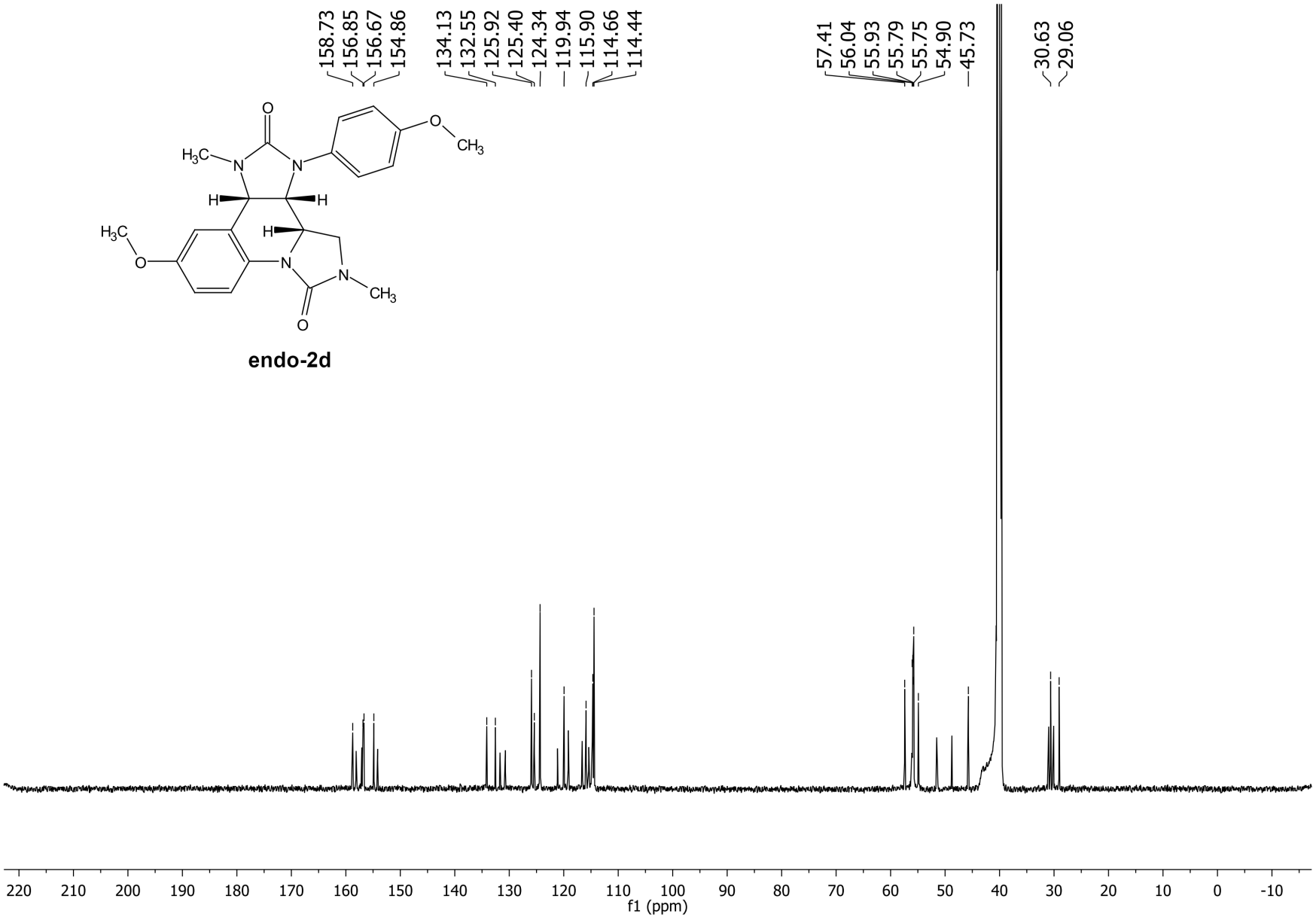


Figure S92. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound ***endo*-2d**

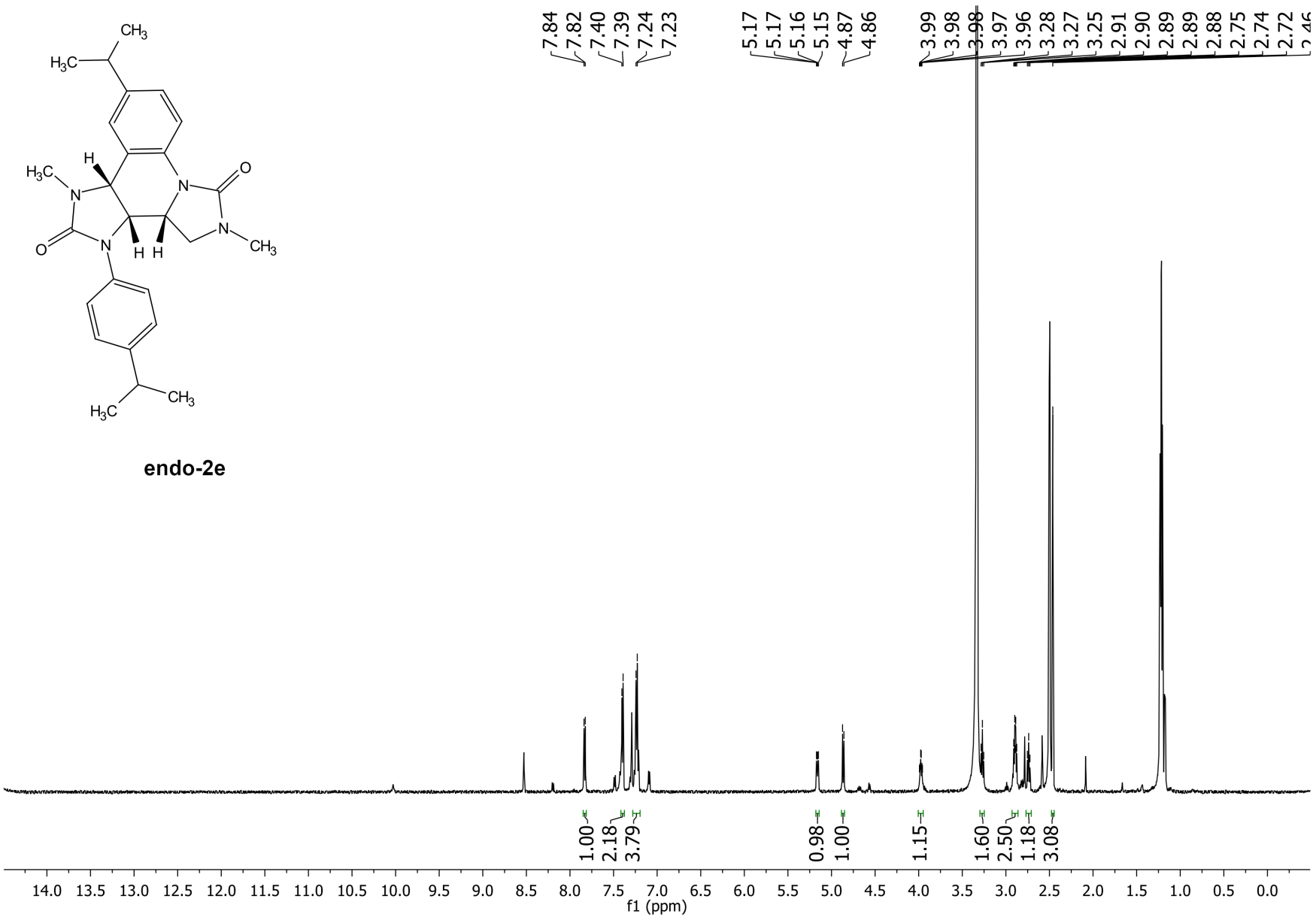


Figure S93. ^{1}H NMR spectrum ($(CD_3)_2SO$, 600MHz) of the compound ***endo*-2e**

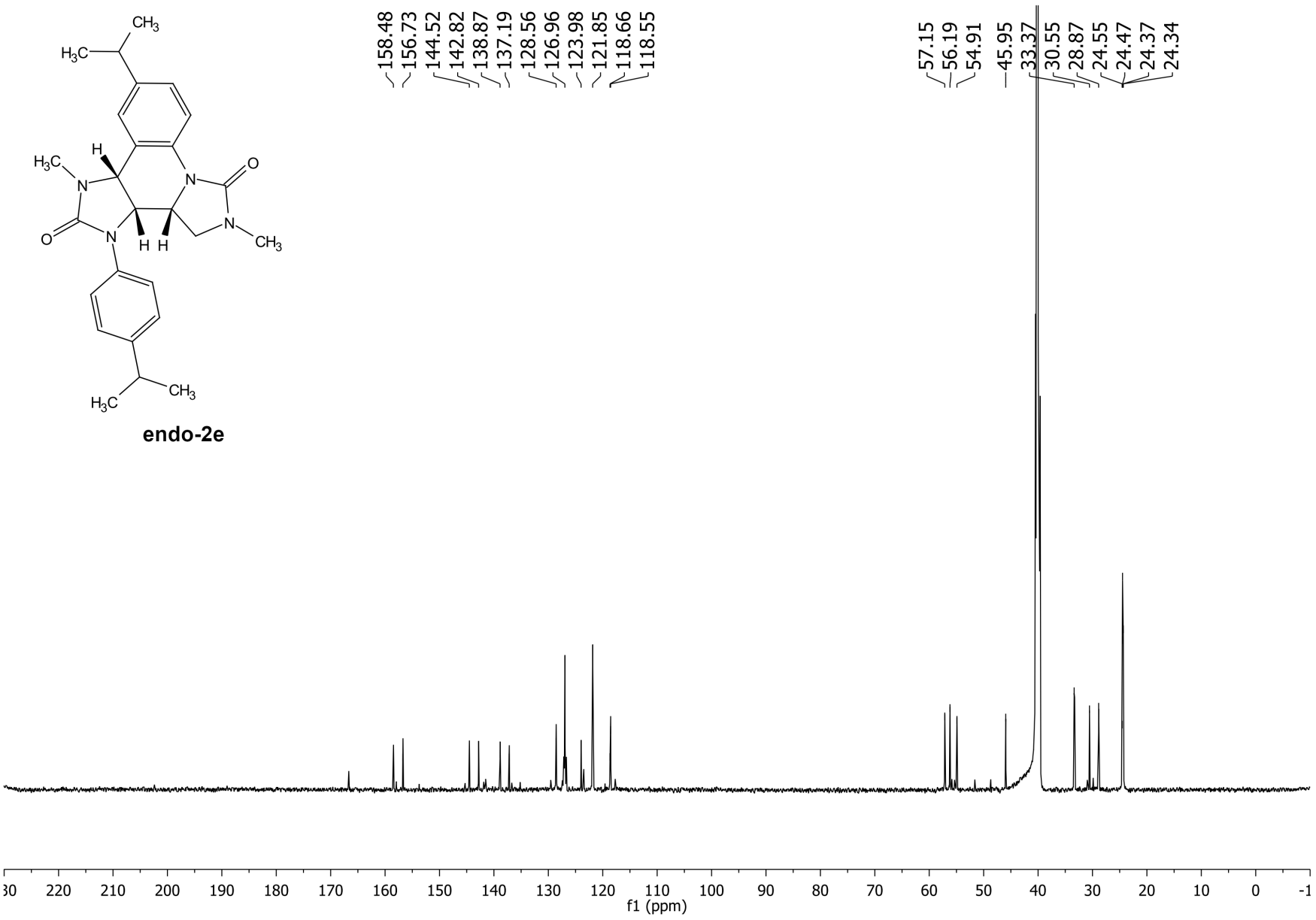


Figure S94. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound ***endo*-2e**

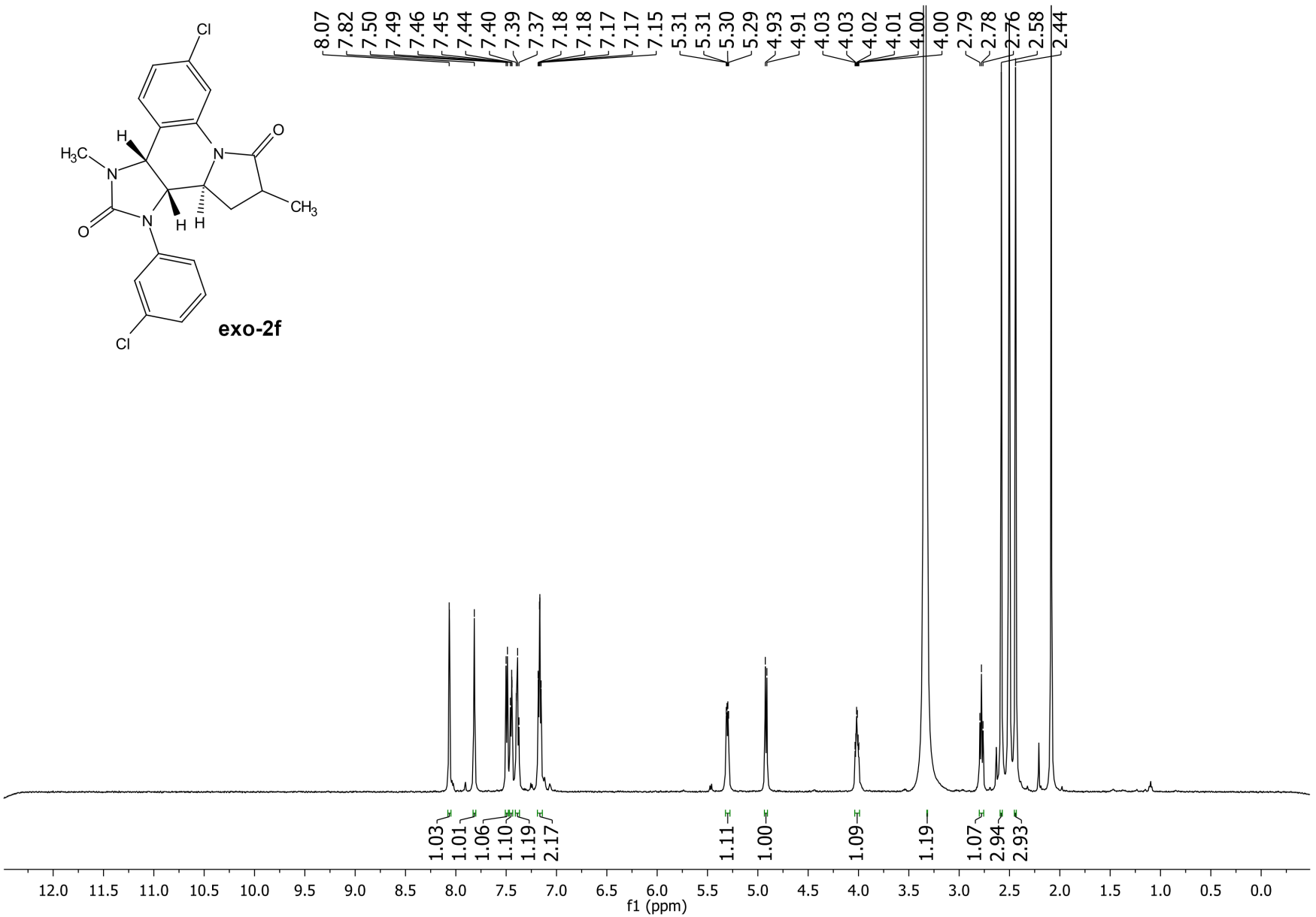


Figure S95. ^{1}H NMR spectrum ($(CD_3)_2SO$, 600MHz) of the compound ***exo*-2f**

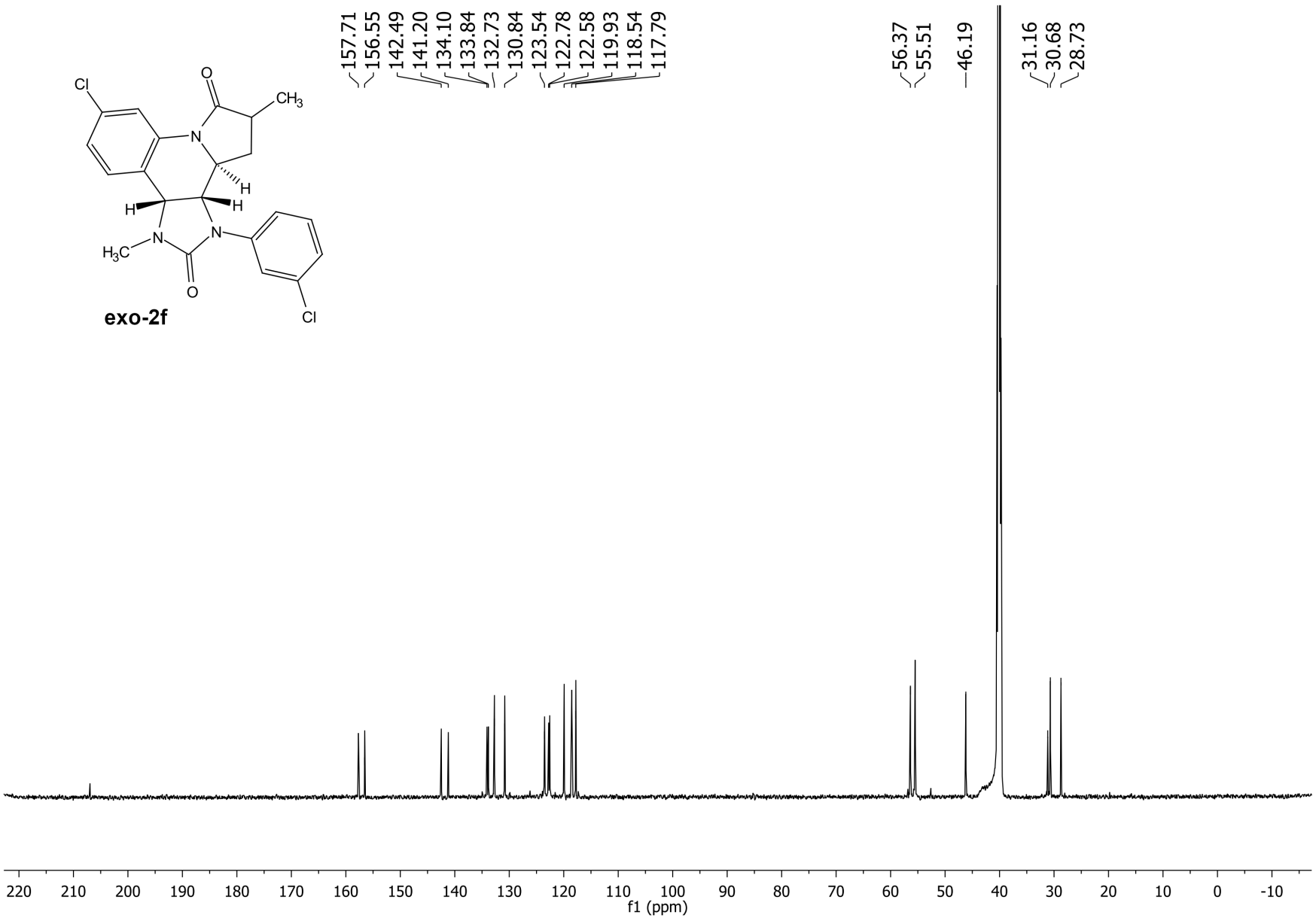


Figure S96. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound ***exo*-2f**

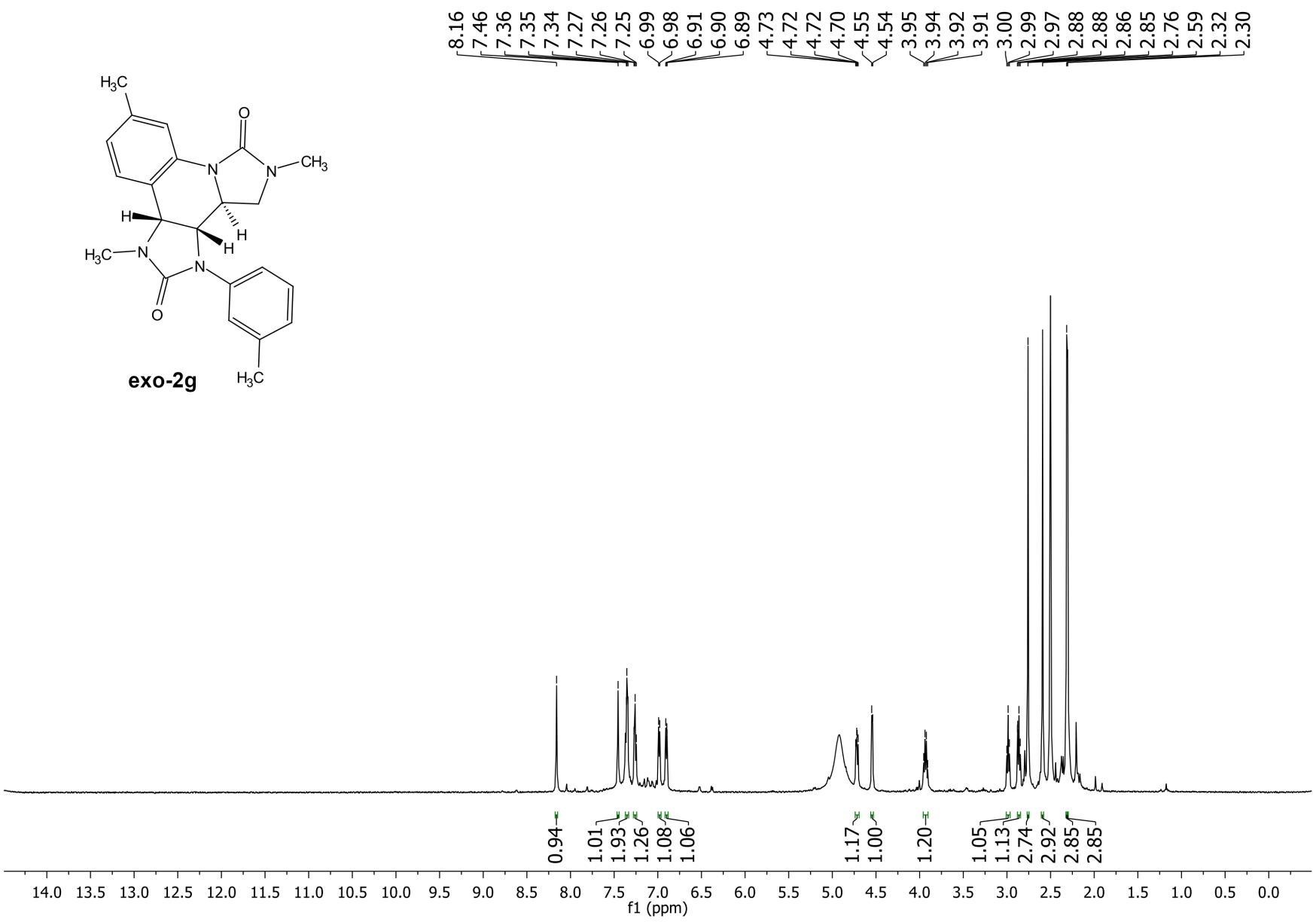


Figure S97. ^{1}H NMR spectrum ($(CD_3)_2SO$, 500MHz) of the compound ***exo*-2g**

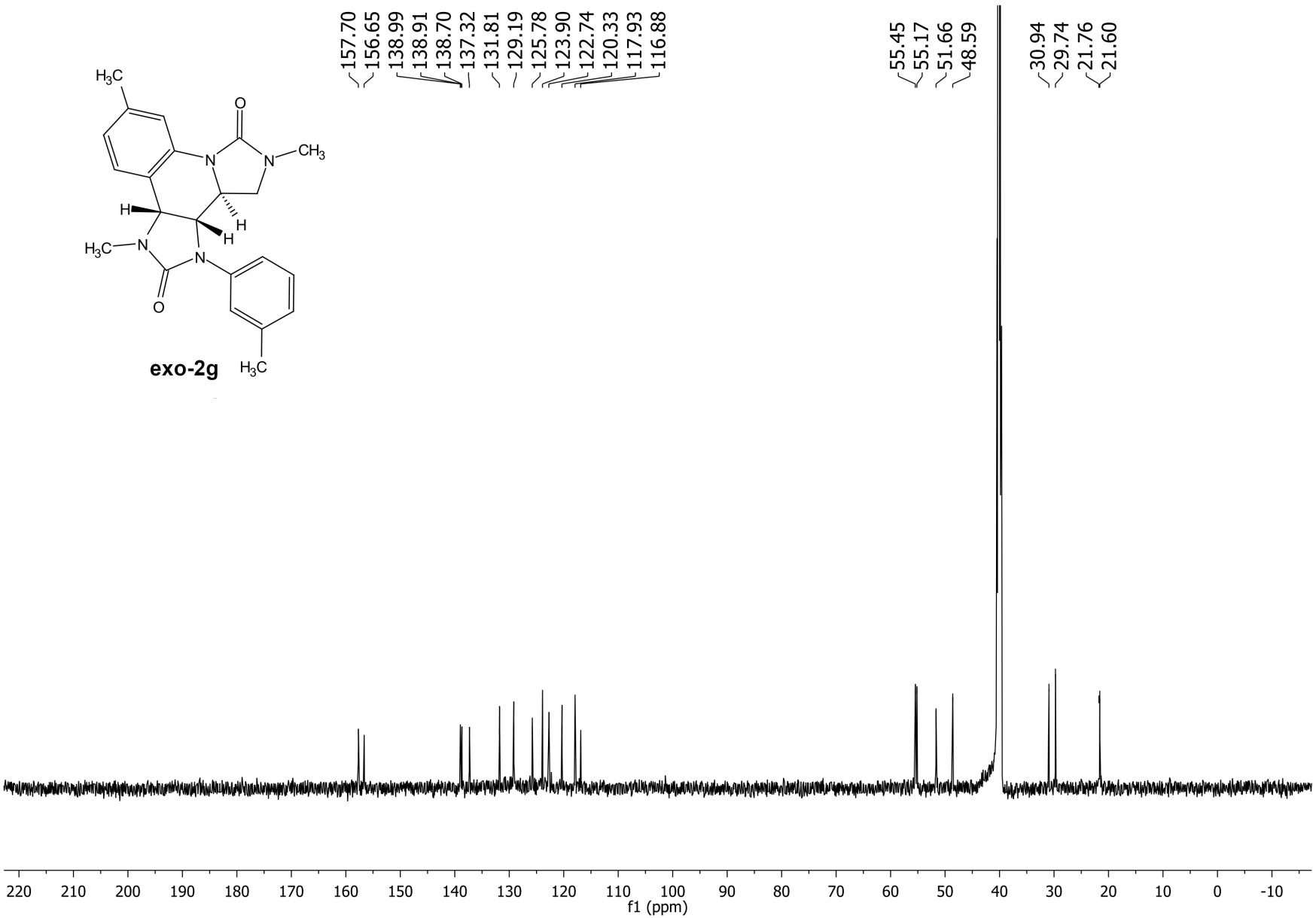


Figure S98. ^{13}C NMR spectrum ($(CD_3)_2SO$, 126MHz) of the compound ***exo*-2g**

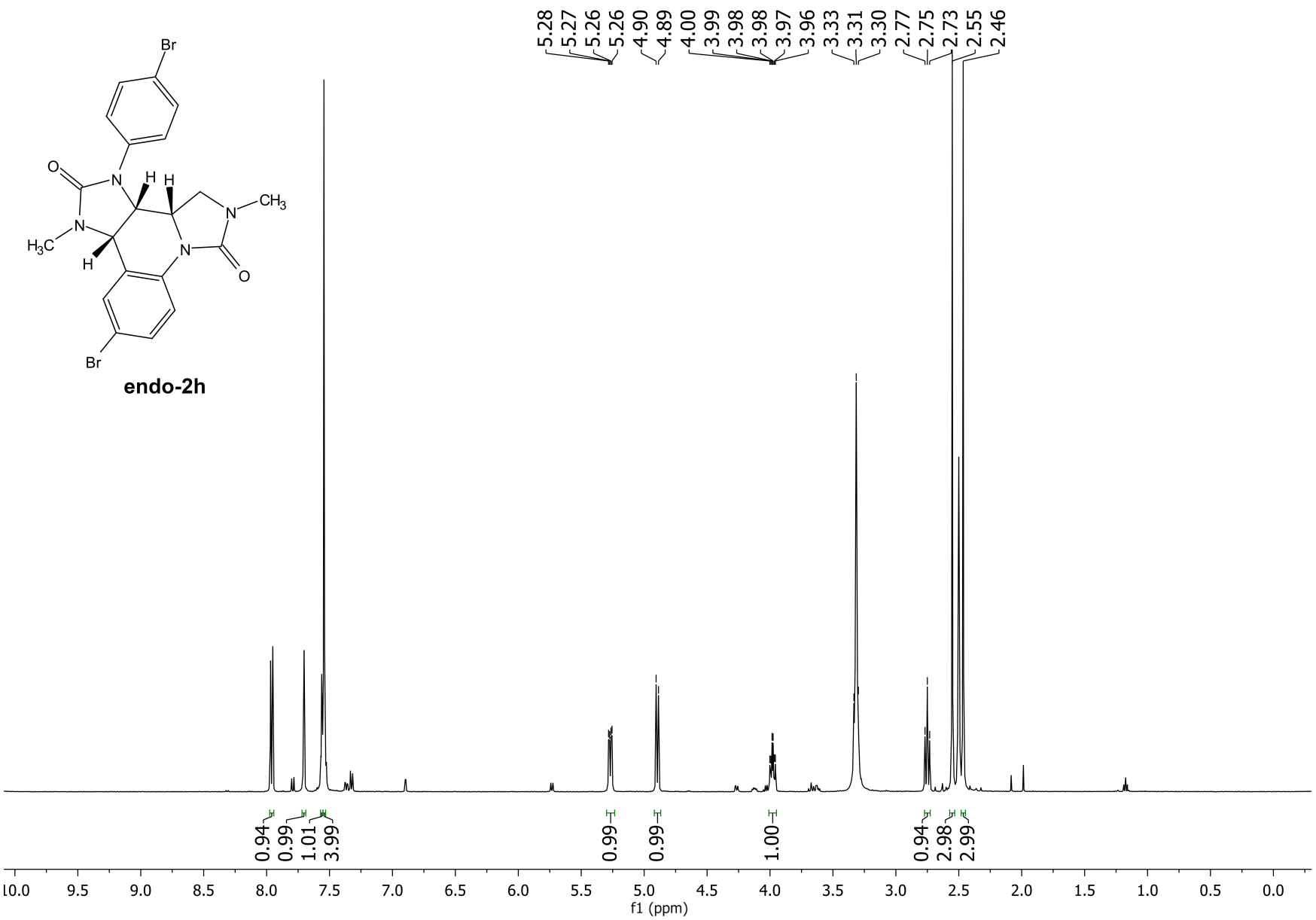


Figure S99. ^{1}H NMR spectrum ($(CD_3)_2SO$, 500MHz) of the compound ***endo*-2h**

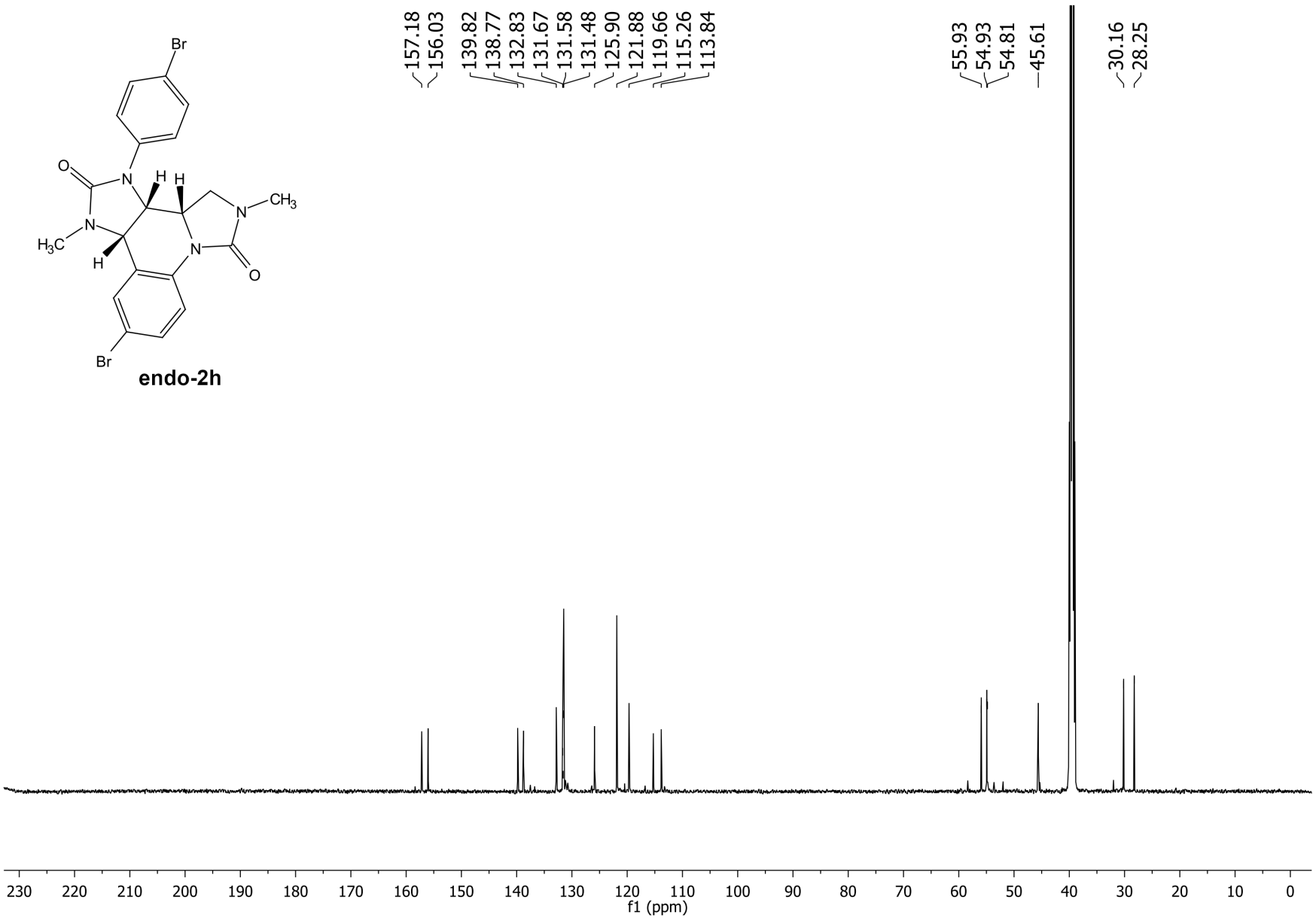


Figure S100. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound ***endo*-2h**

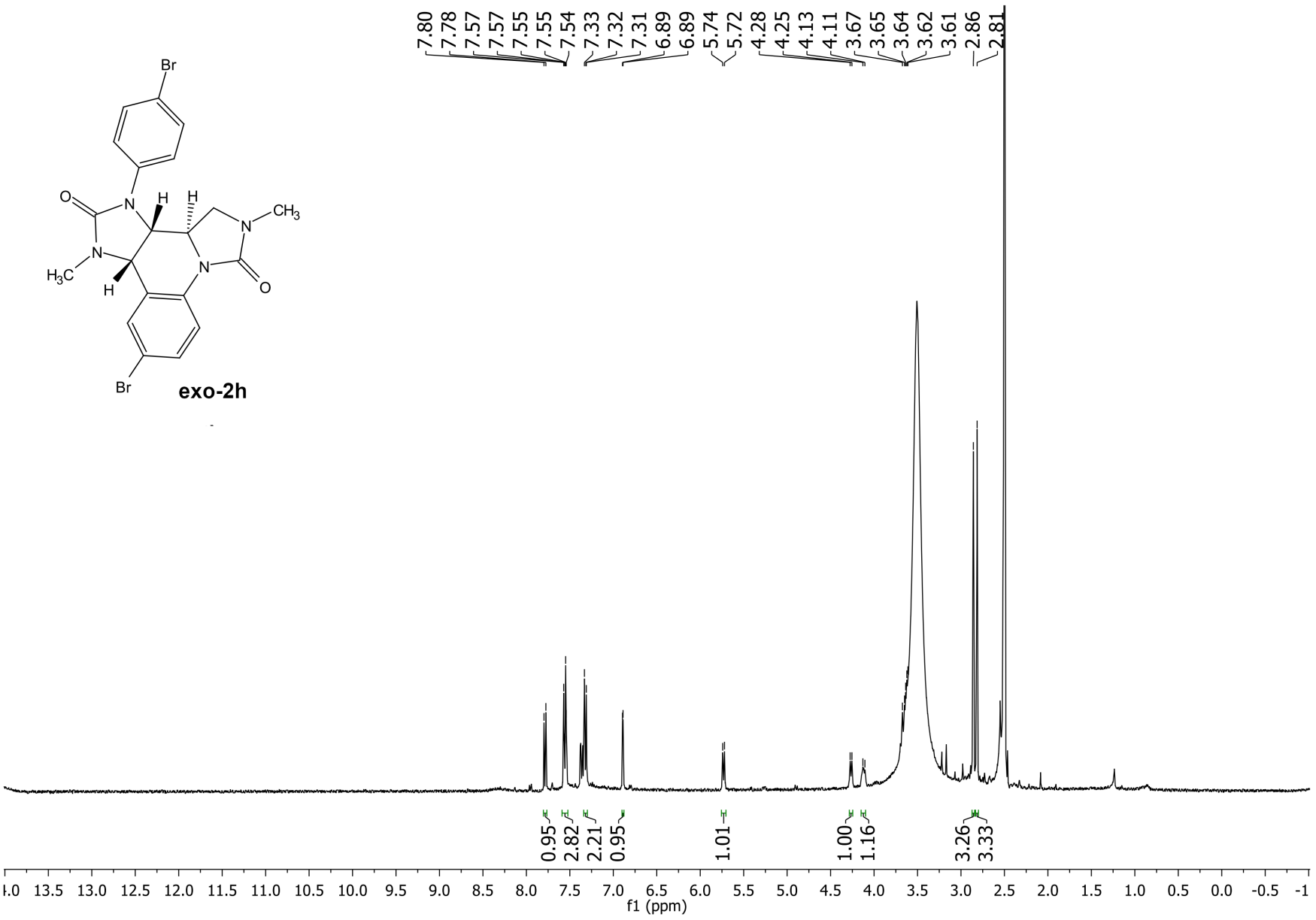


Figure S101. ^{1}H NMR spectrum ($(CD_3)_2SO$, 400MHz) of the compound ***exo*-2h**

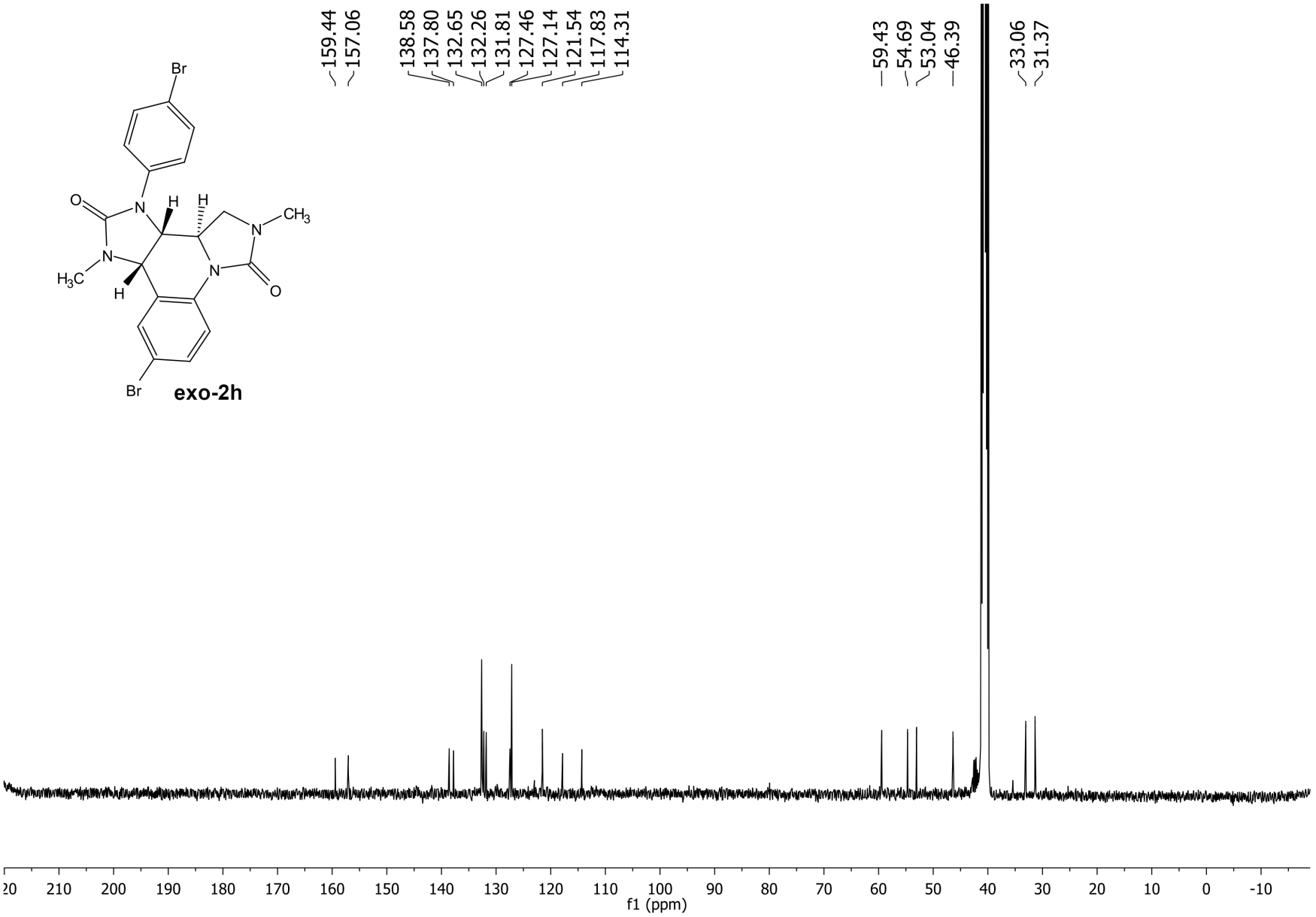


Figure S102. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound ***exo*-2h**

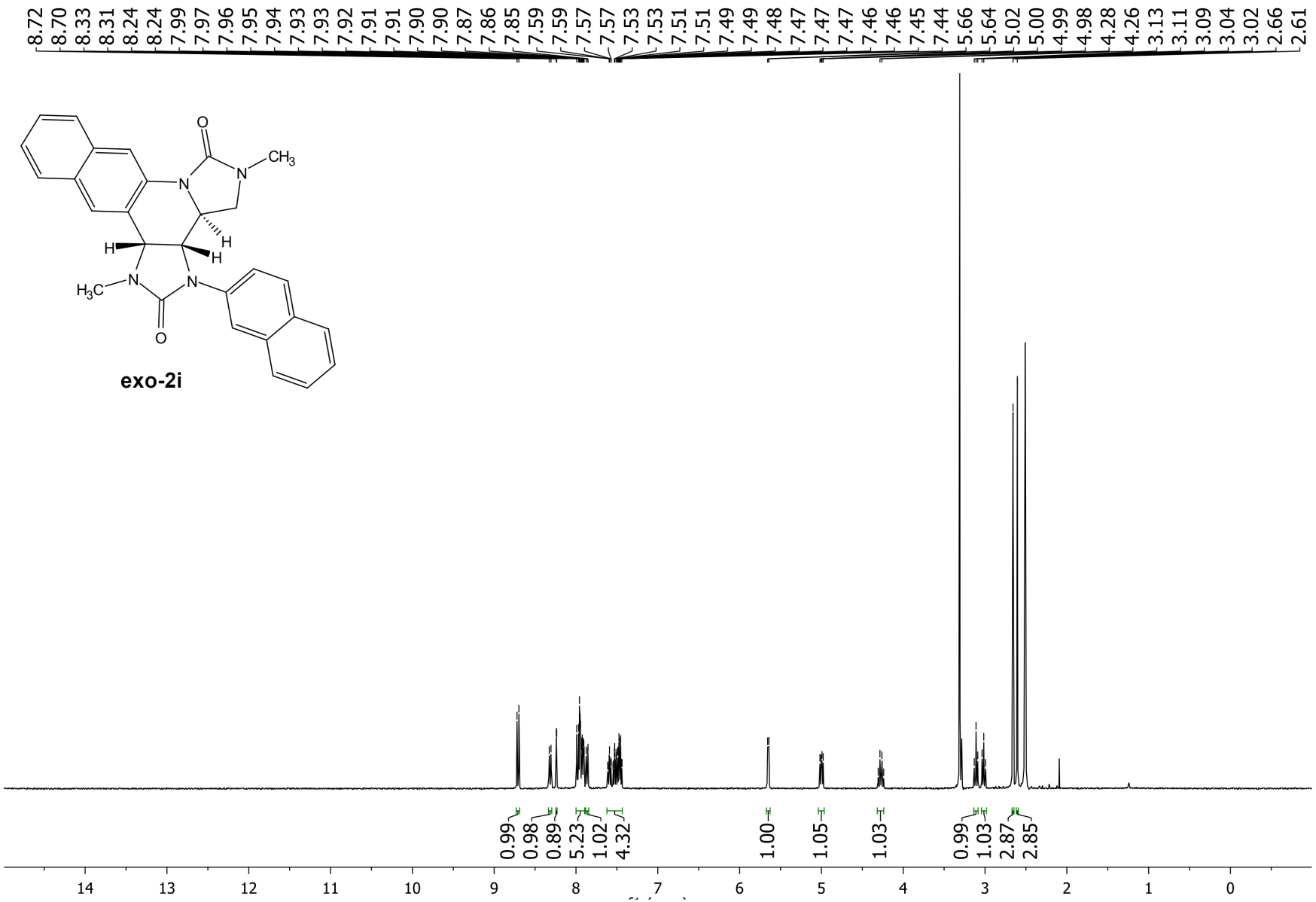


Figure S103. ^{1}H NMR spectrum ($(CD_3)_2SO$, 400MHz) of the compound ***exo*-2i**

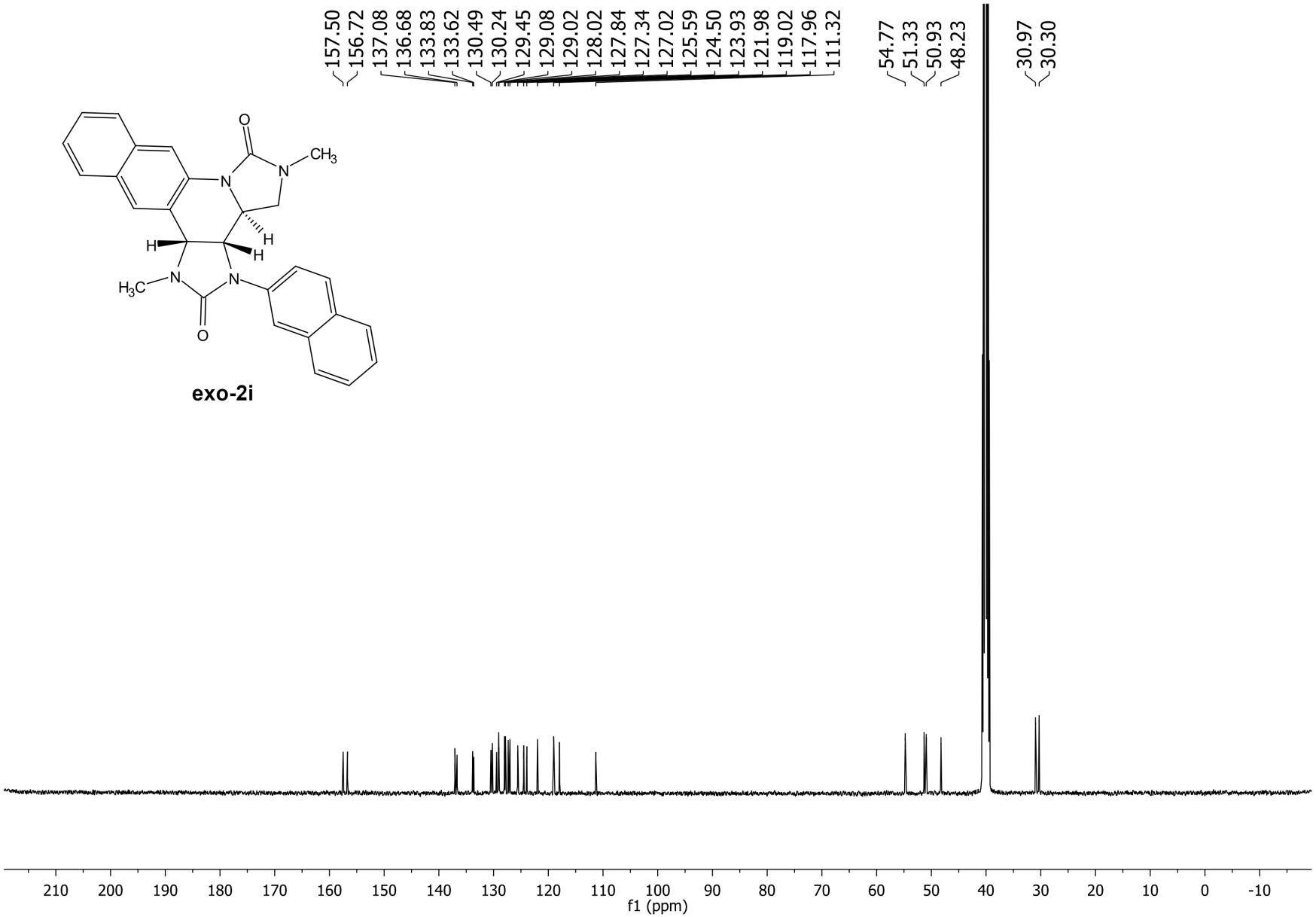


Figure S104. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound ***exo*-2i**

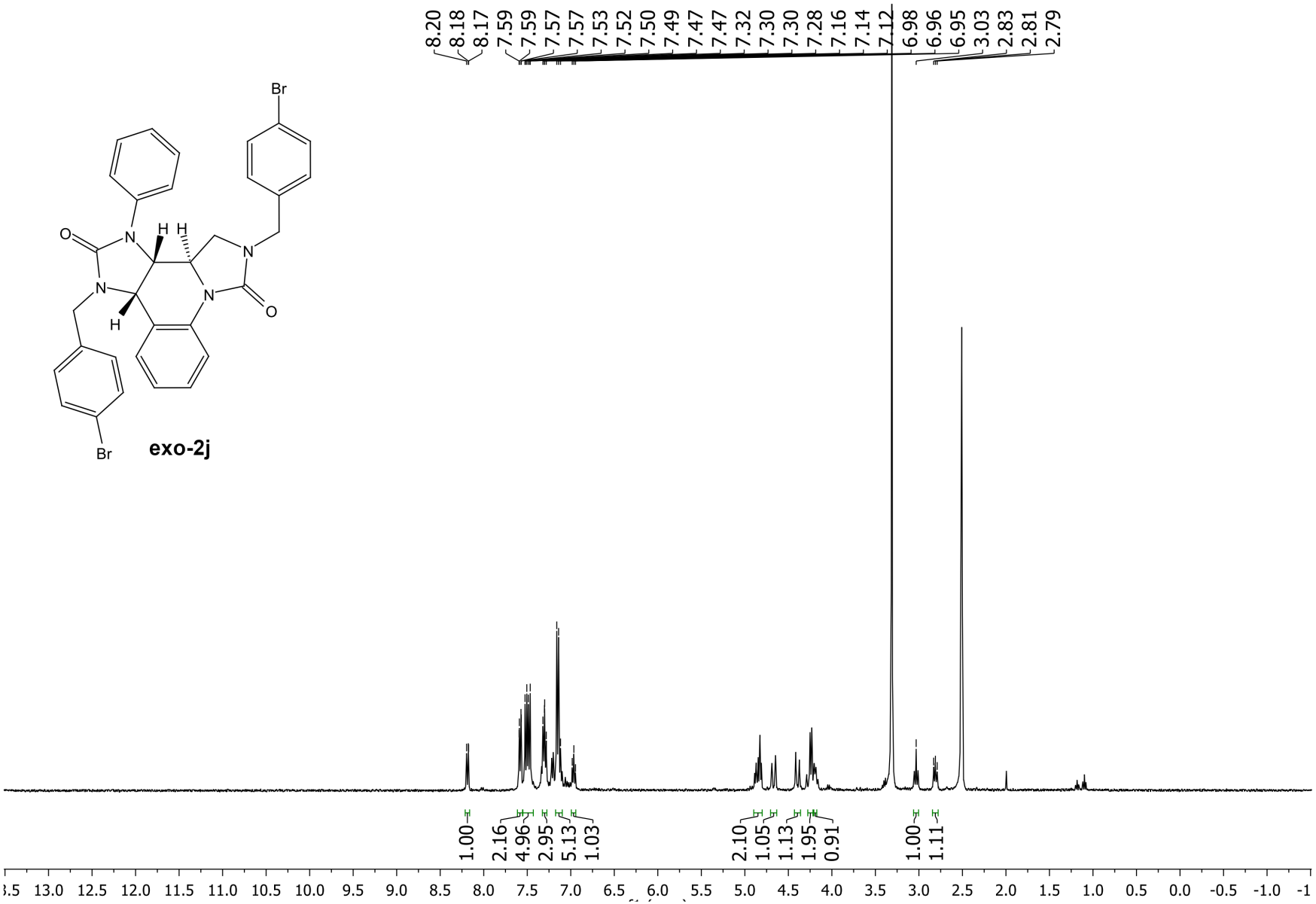


Figure S105. ^{1}H NMR spectrum ($(CD_3)_2SO$, 400MHz) of the compound ***exo*-2j**

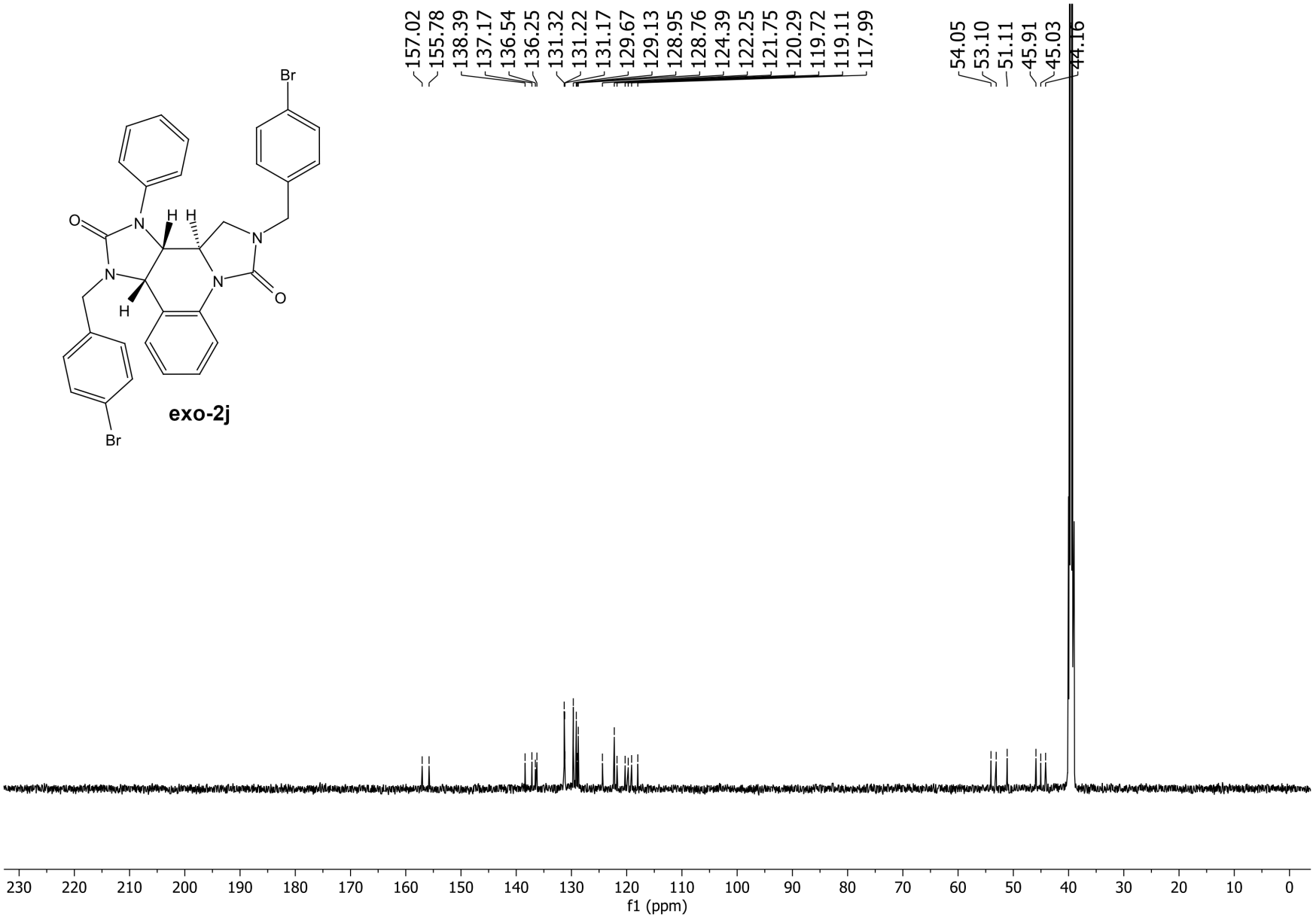


Figure S106. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound ***exo*-2j**

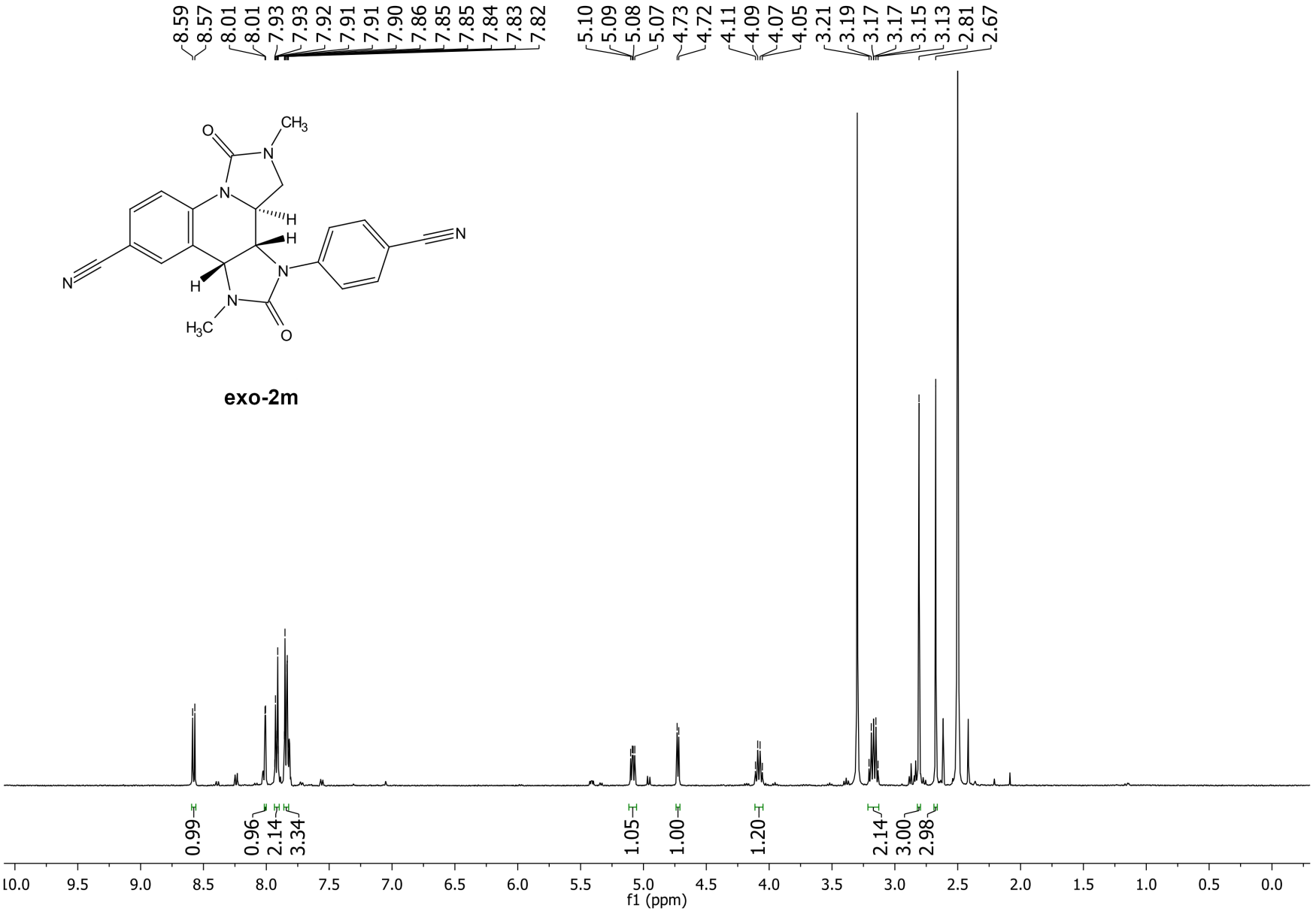


Figure S107. ^{1}H NMR spectrum ($(CD_3)_2SO$, 400MHz) of the compound ***exo*-2m**

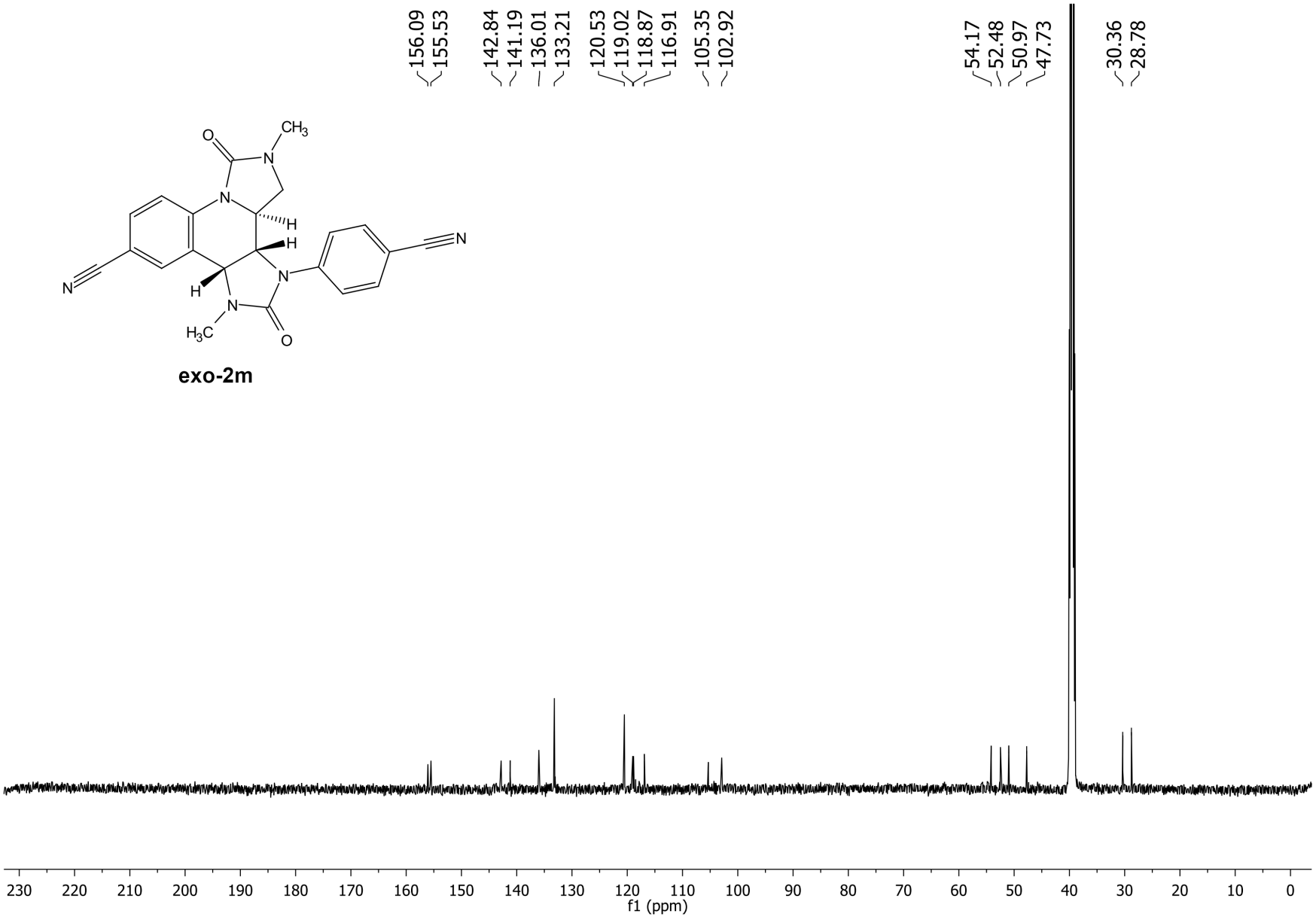


Figure S108. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound ***exo*-2m**

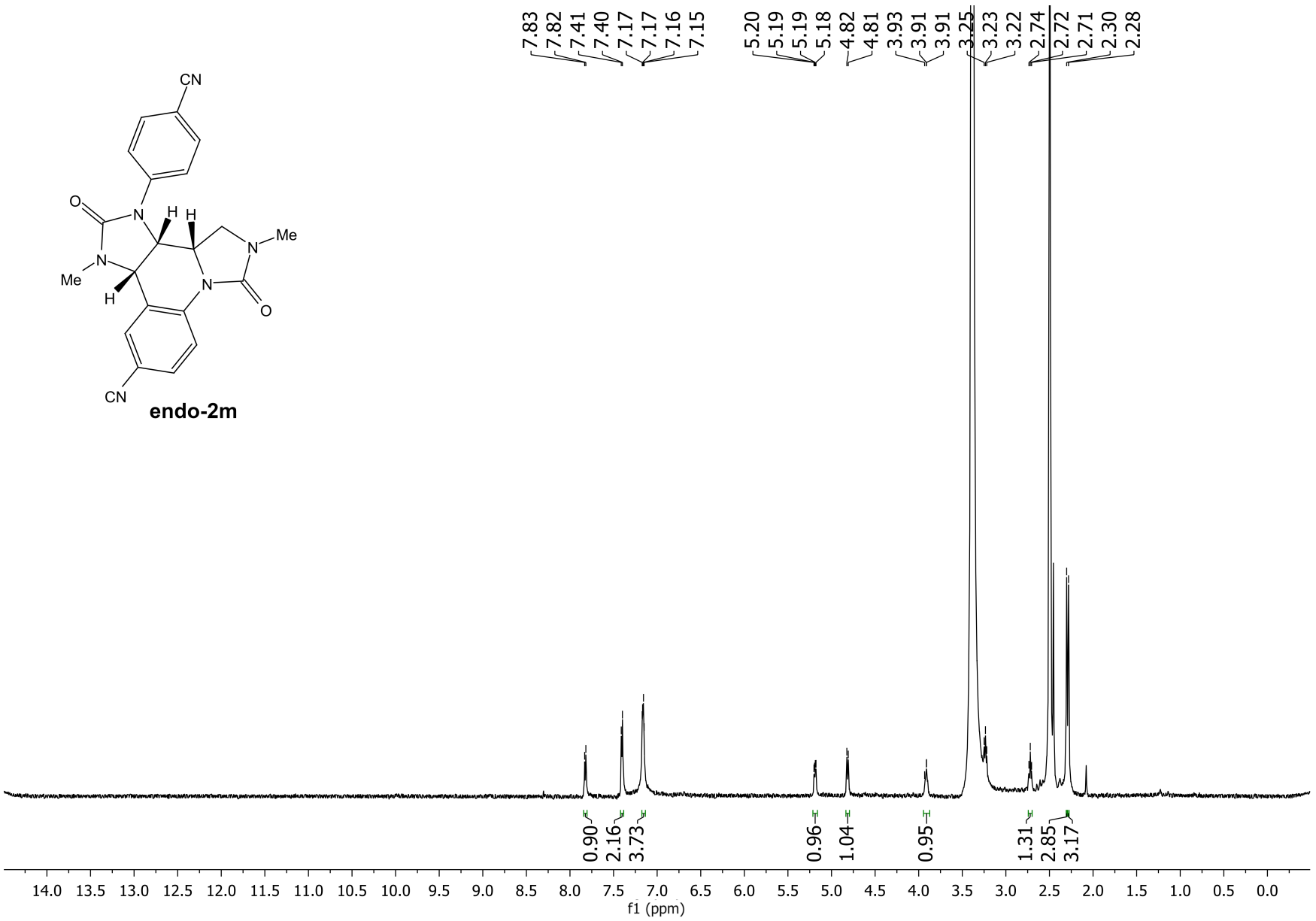


Figure S109. ^{1}H NMR spectrum ($(CD_3)_2SO$, 600MHz) of the compound ***endo*-2m**

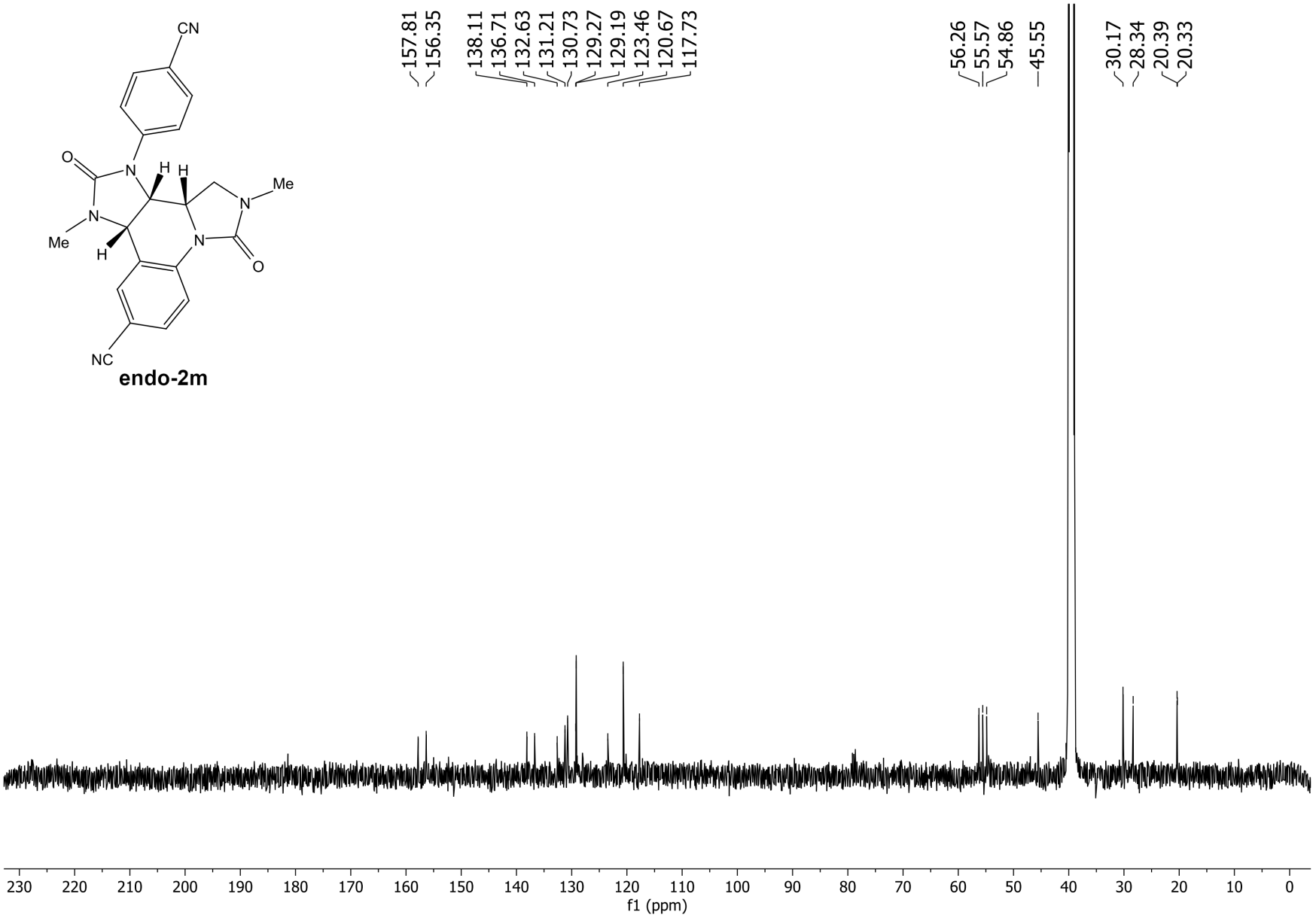


Figure S110. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound ***endo*-2m**

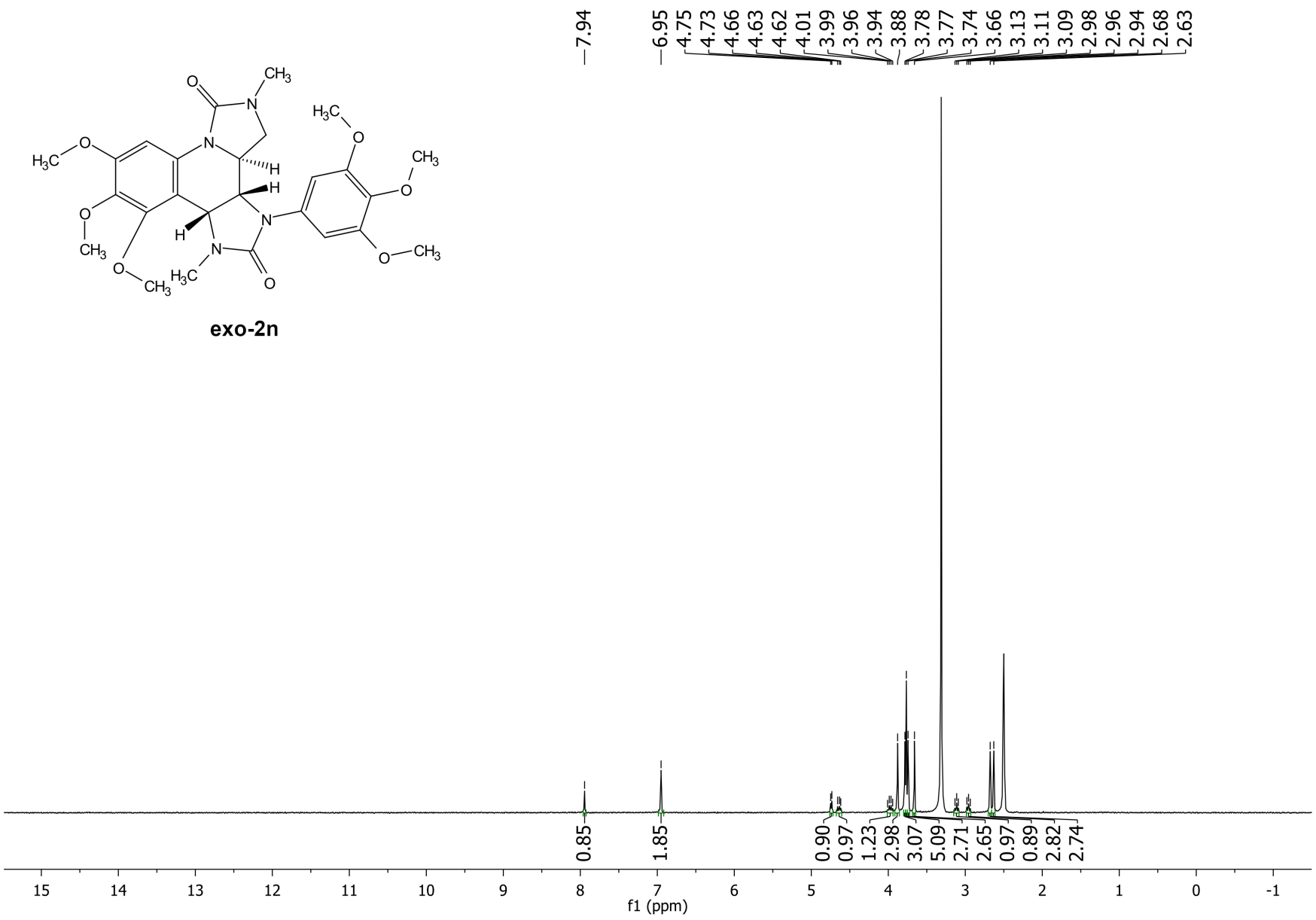


Figure S111. ^{1}H NMR spectrum ($(CD_3)_2SO$, 400MHz) of the compound ***exo*-2n**

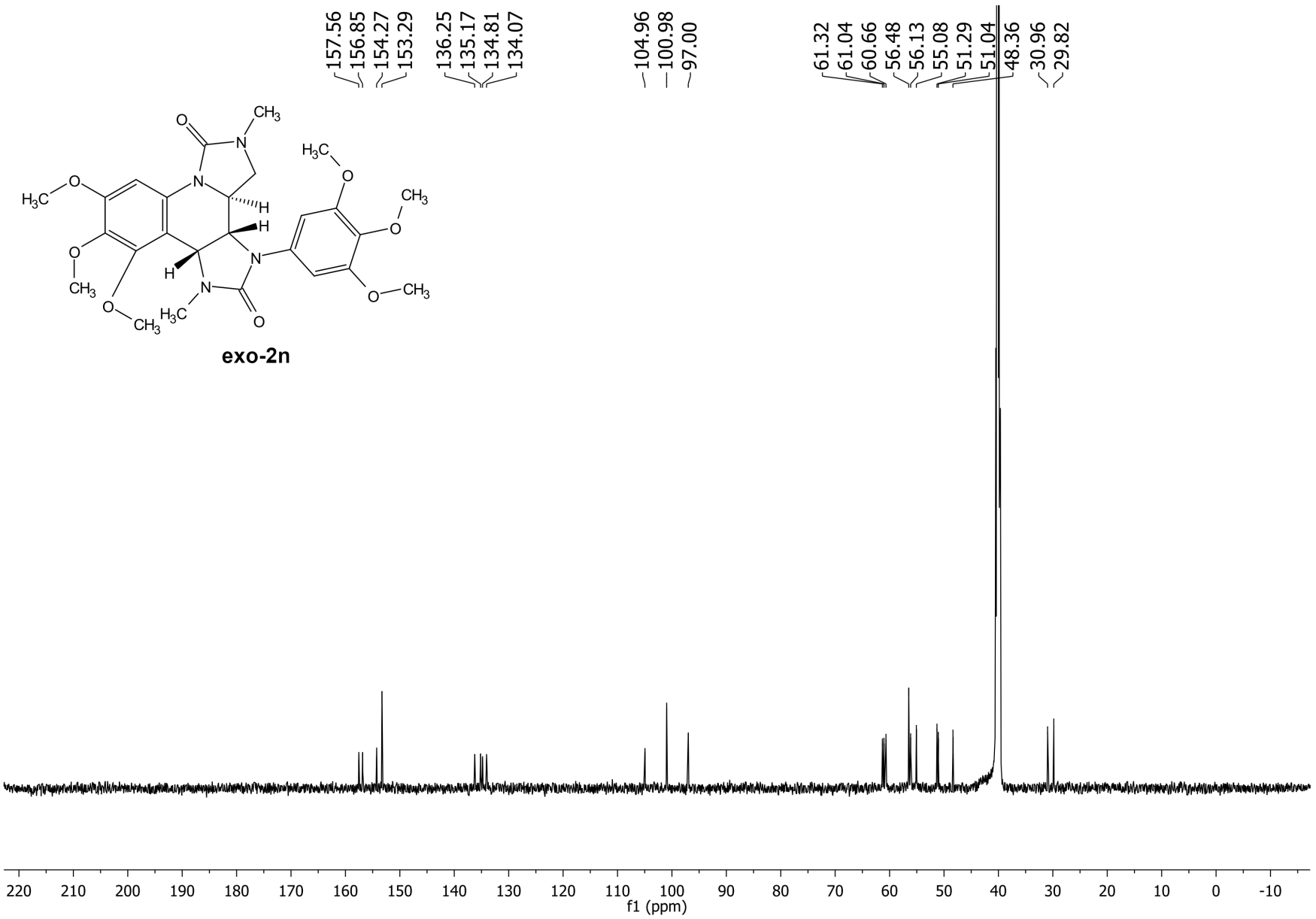


Figure S112. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound ***exo*-2n**

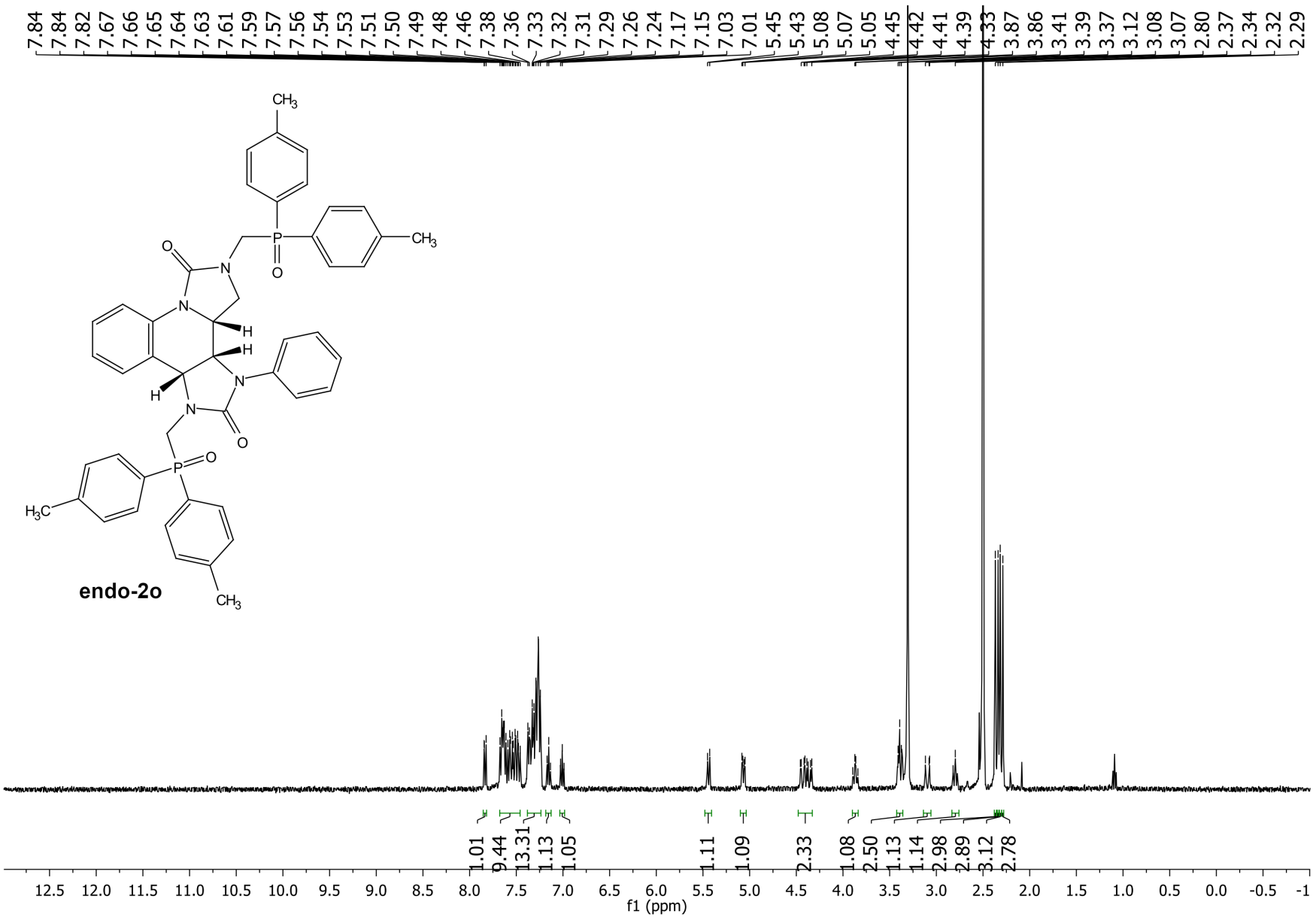


Figure S113. ^{1}H NMR spectrum ($(CD_3)_2SO$, 500MHz) of the compound ***endo*-2o**

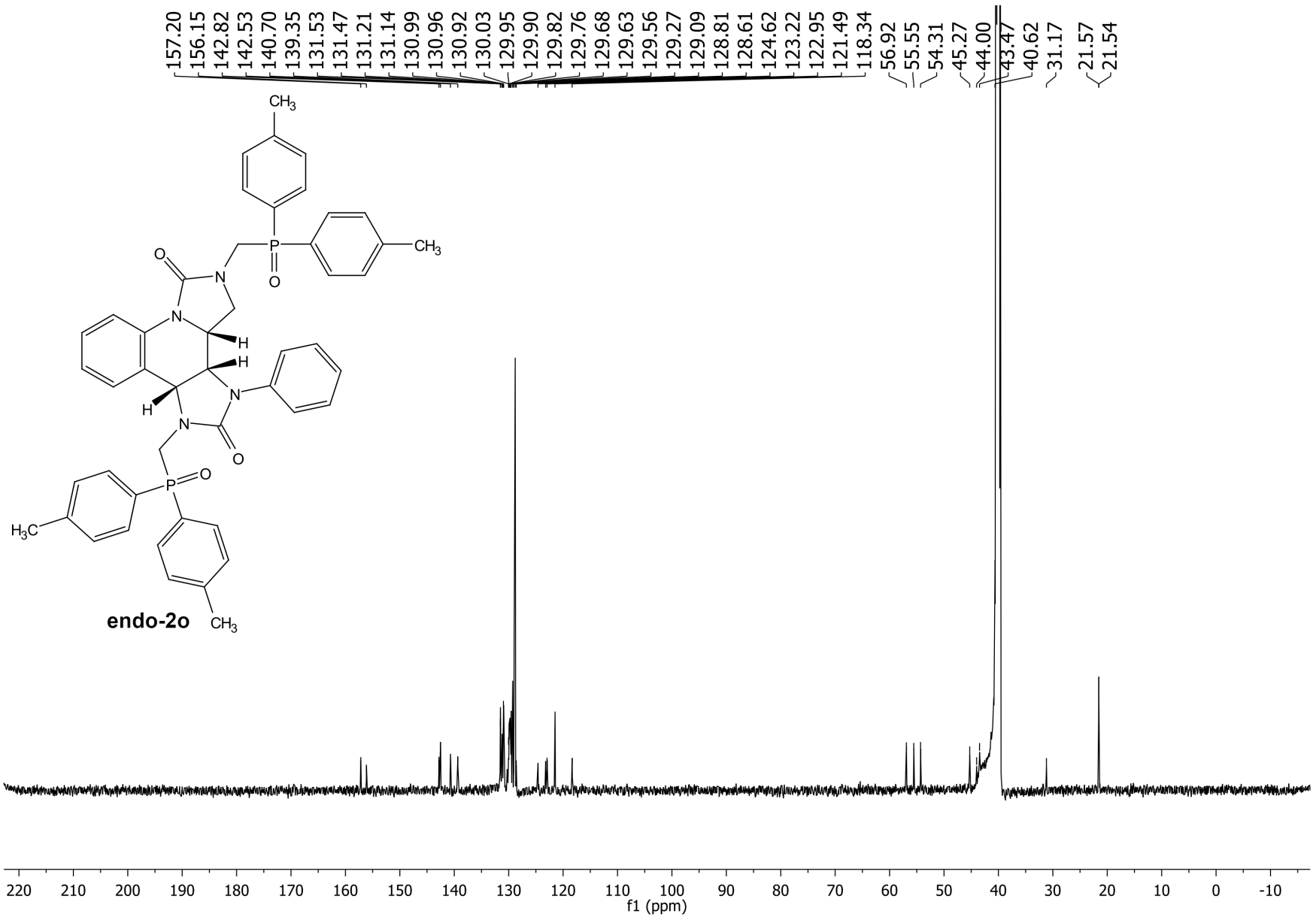


Figure S114. ^{13}C NMR spectrum ($(CD_3)_2SO$, 126MHz) of the compound ***endo*-2o**

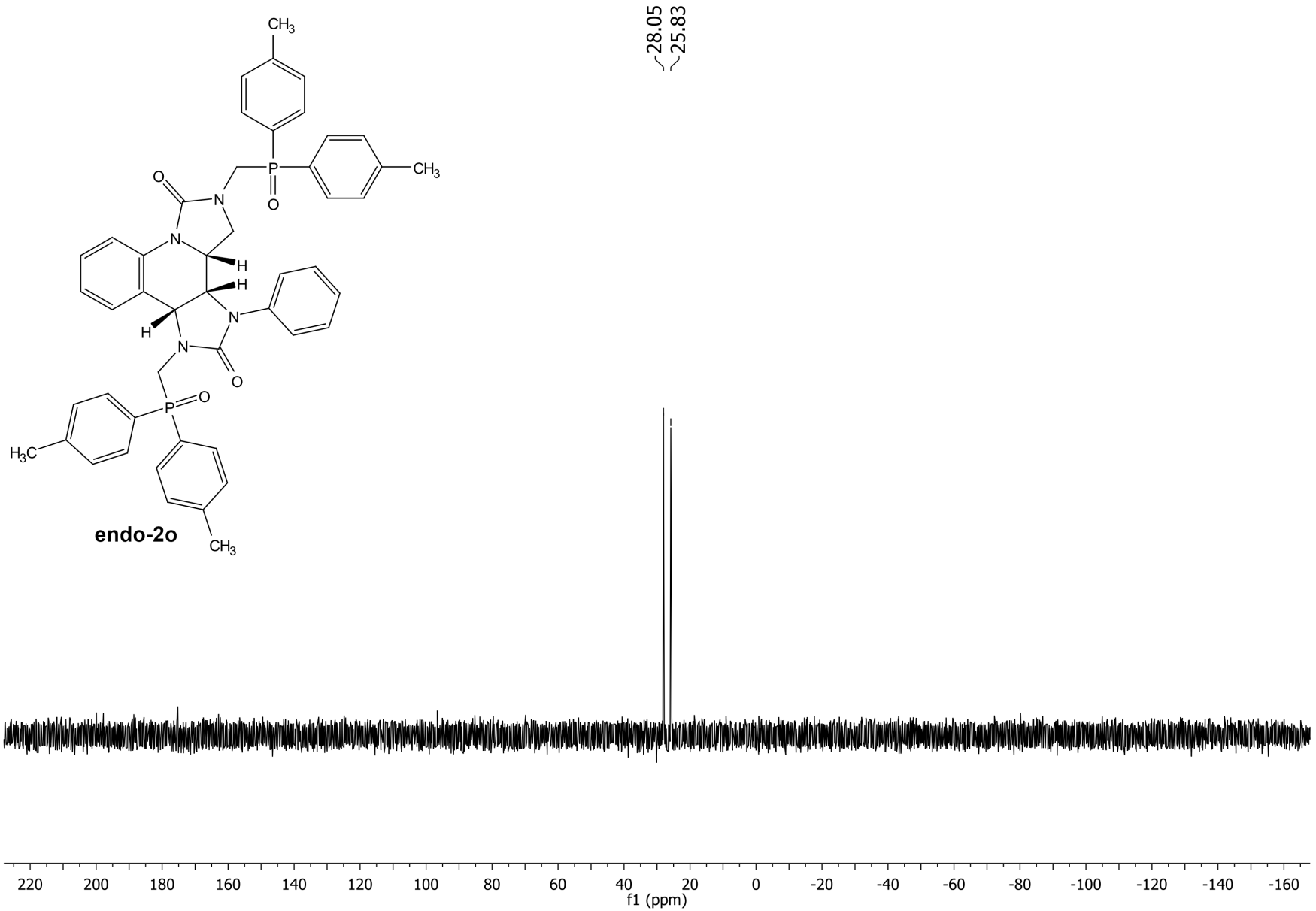


Figure S115. ^{31}P NMR spectrum ($(CD_3)_2SO$, 161MHz) of the compound ***endo*-2o**

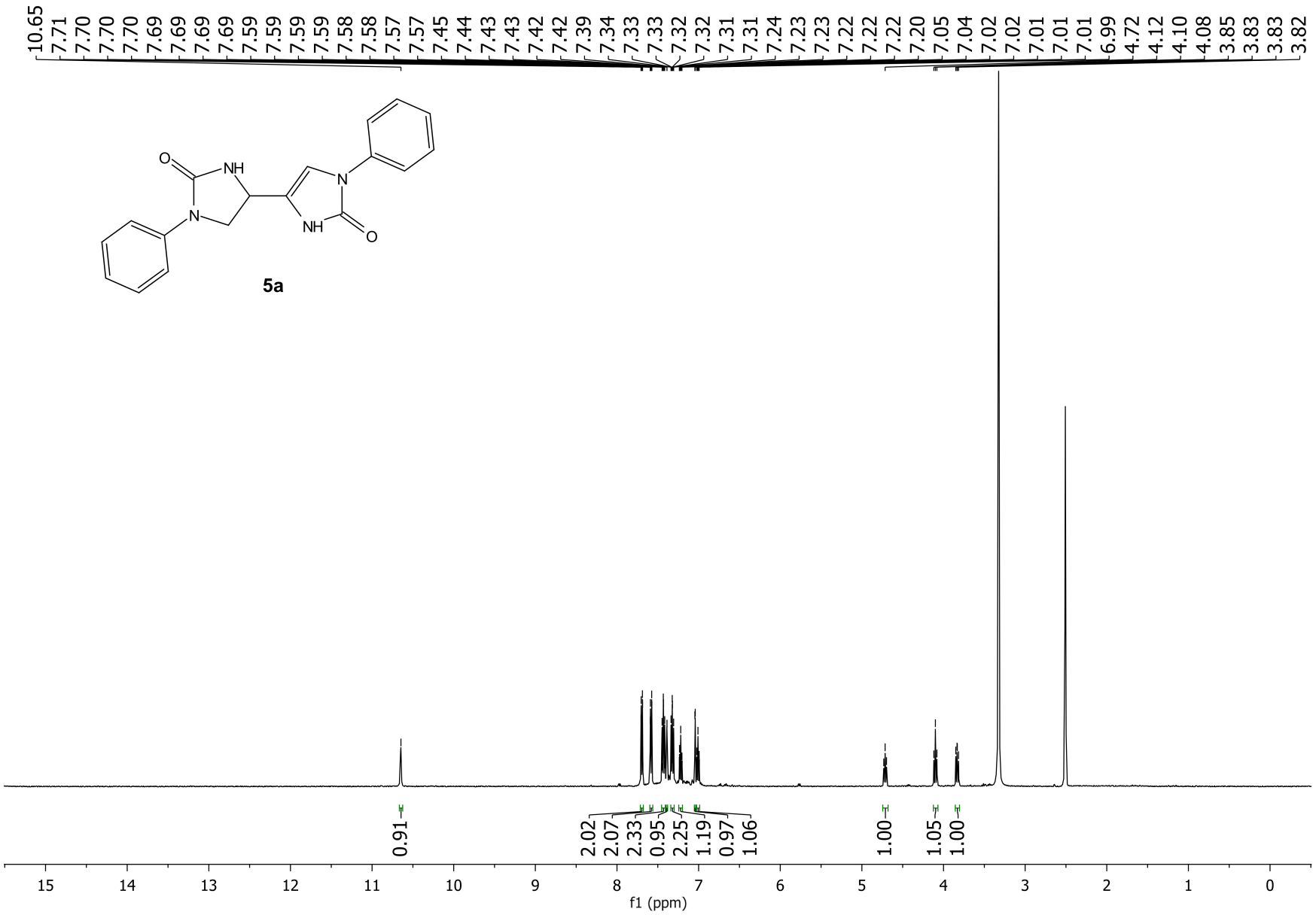


Figure S116. ^{1}H NMR spectrum ($(CD_3)_2SO$, 500MHz) of the compound **5a**

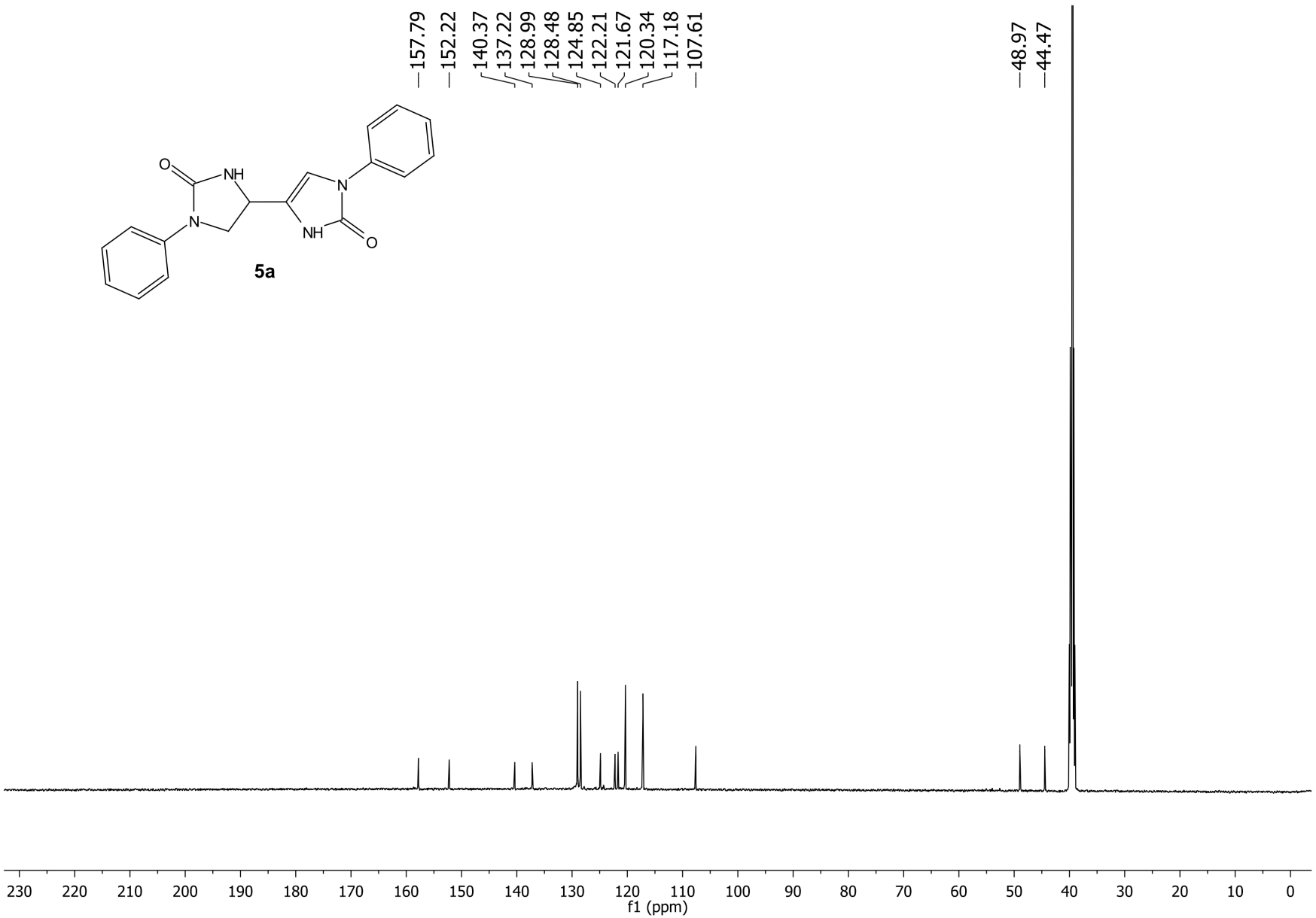


Figure S117. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound **5a**

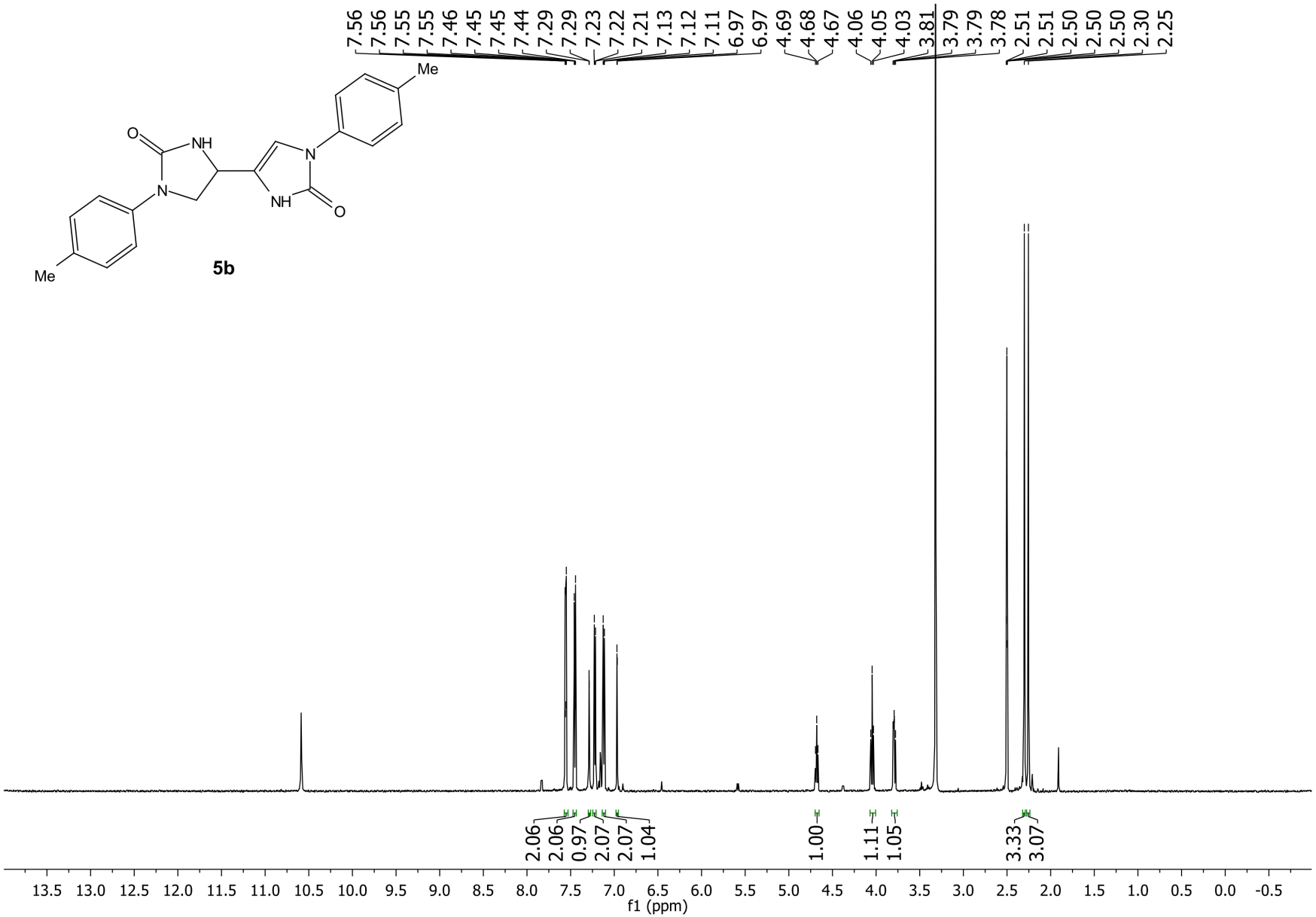


Figure S118. ^{1}H NMR spectrum ($(CD_3)_2SO$, 500MHz) of the compound **5b**

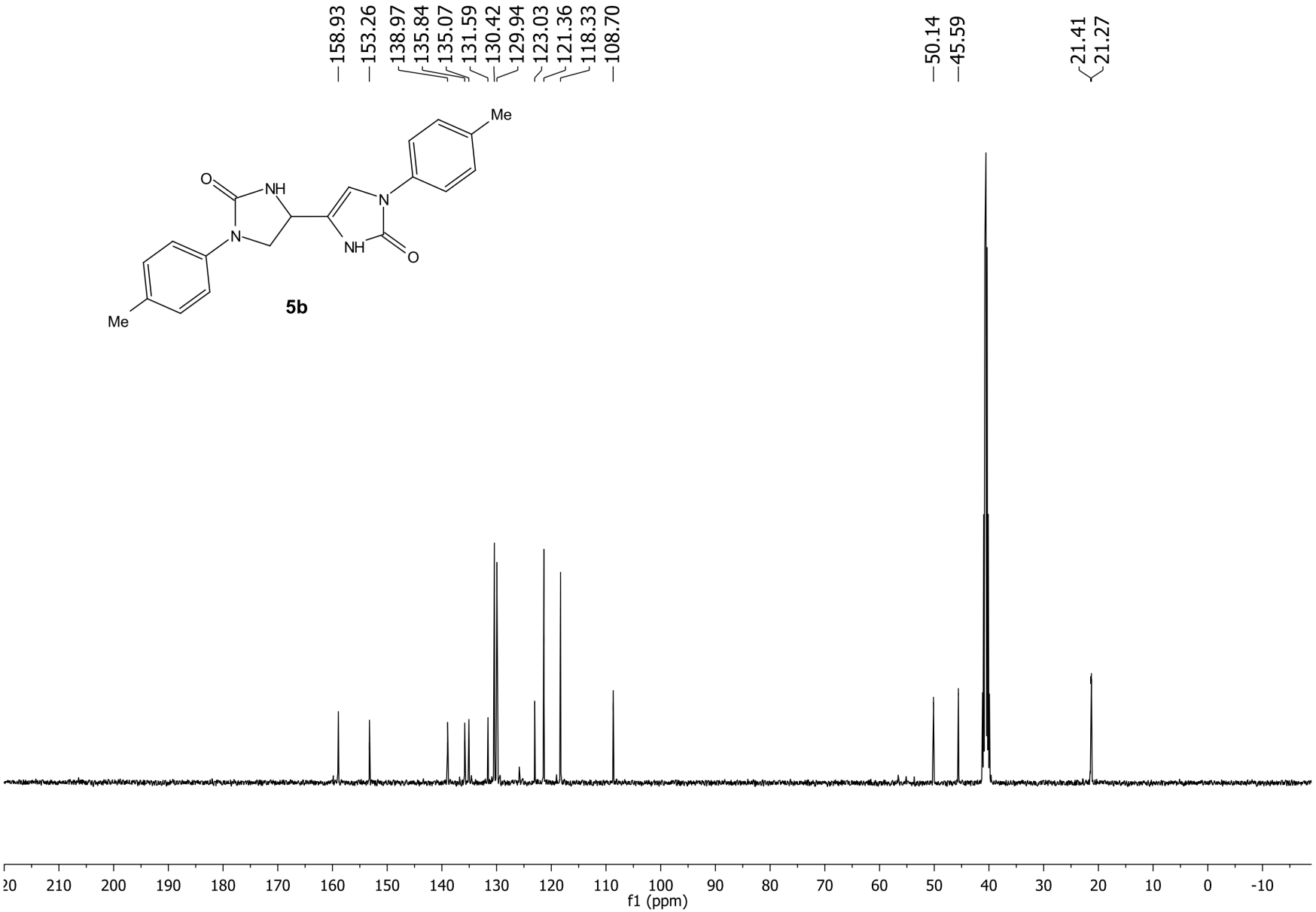


Figure S119. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound **5b**

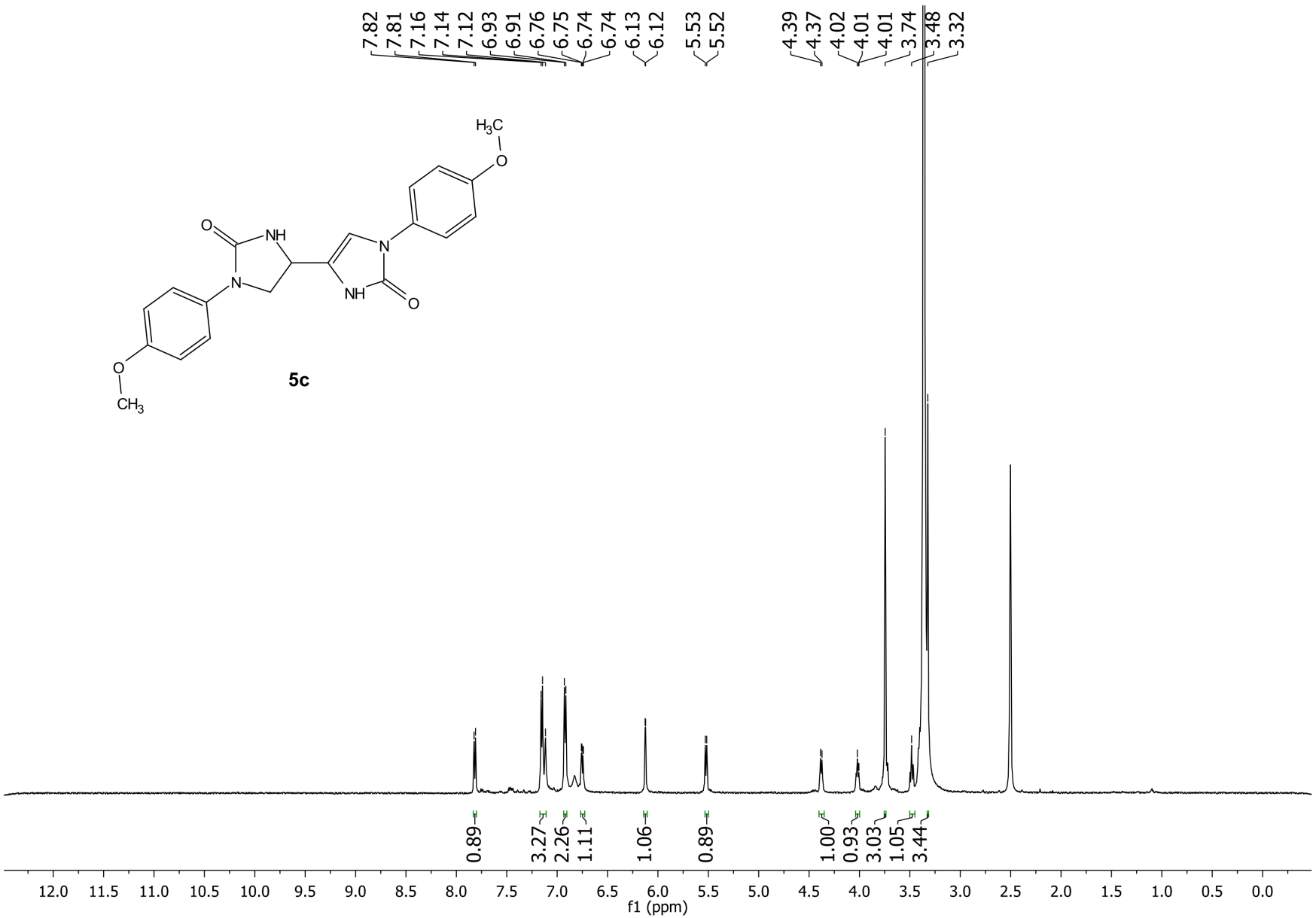


Figure S120. ^{1}H NMR spectrum ($(CD_3)_2SO$, 600MHz) of the compound **5c**

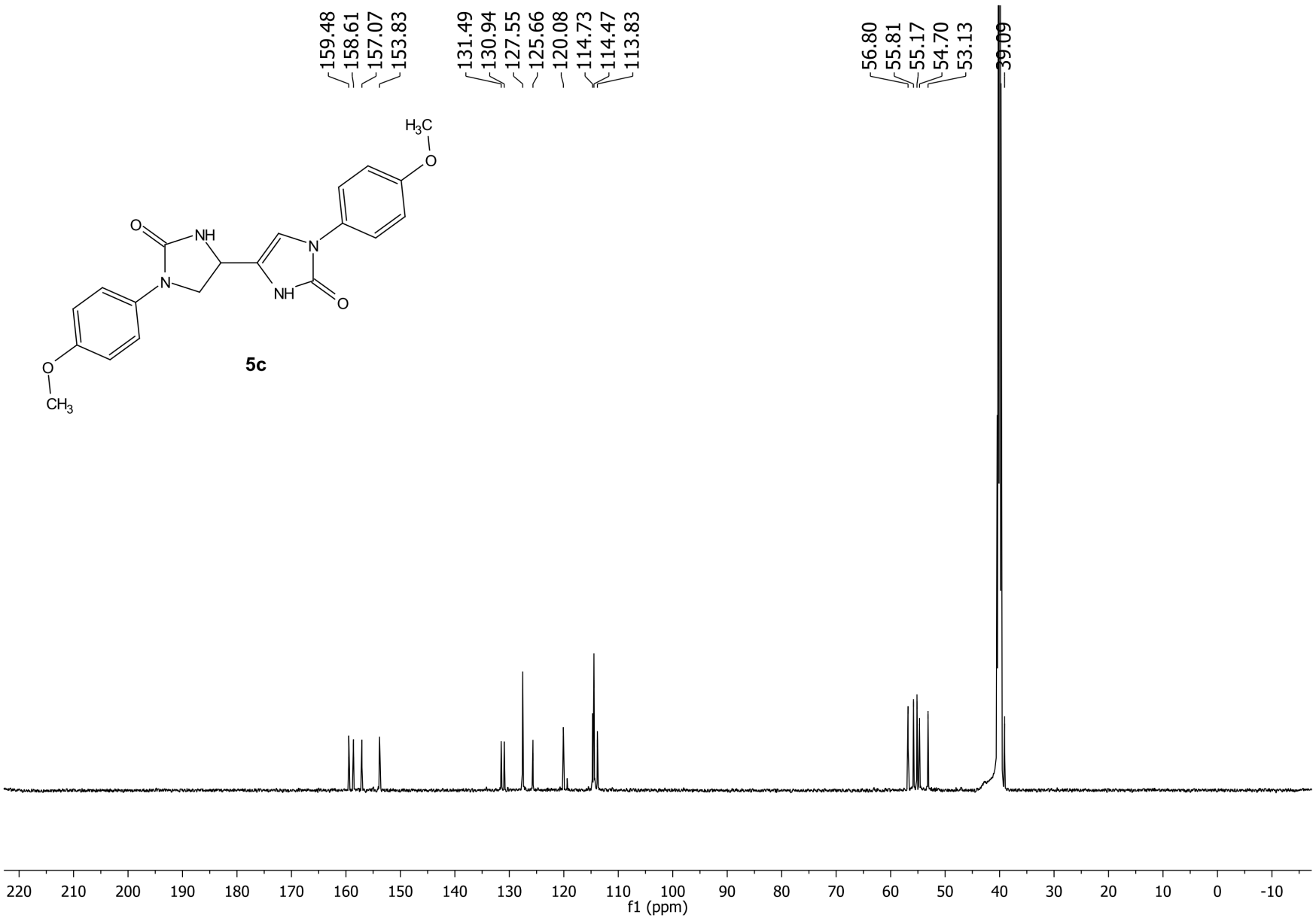


Figure S121. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound **5c**

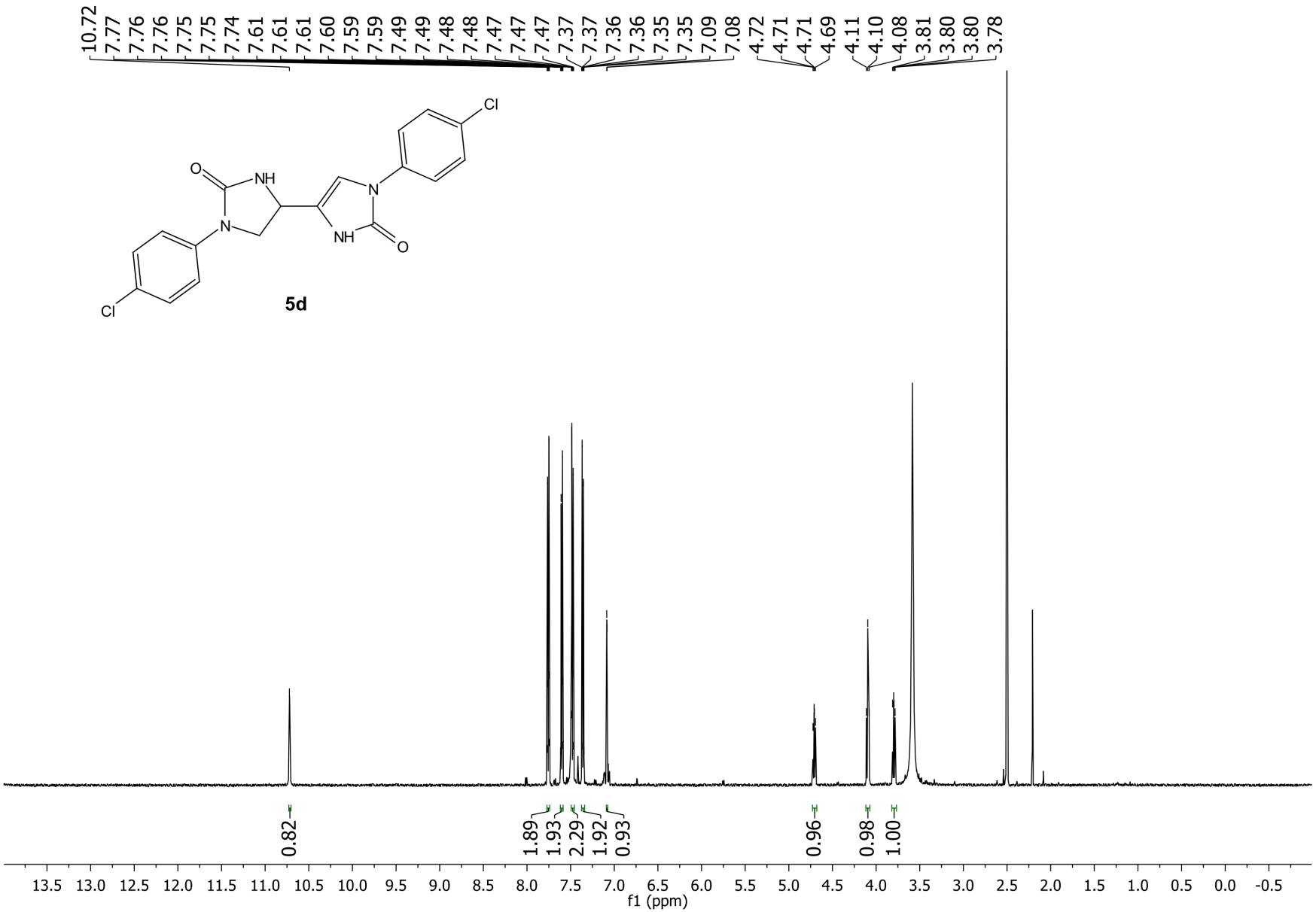


Figure S122. ^{1}H NMR spectrum ($(CD_3)_2SO$, 600MHz) of the compound **5d**

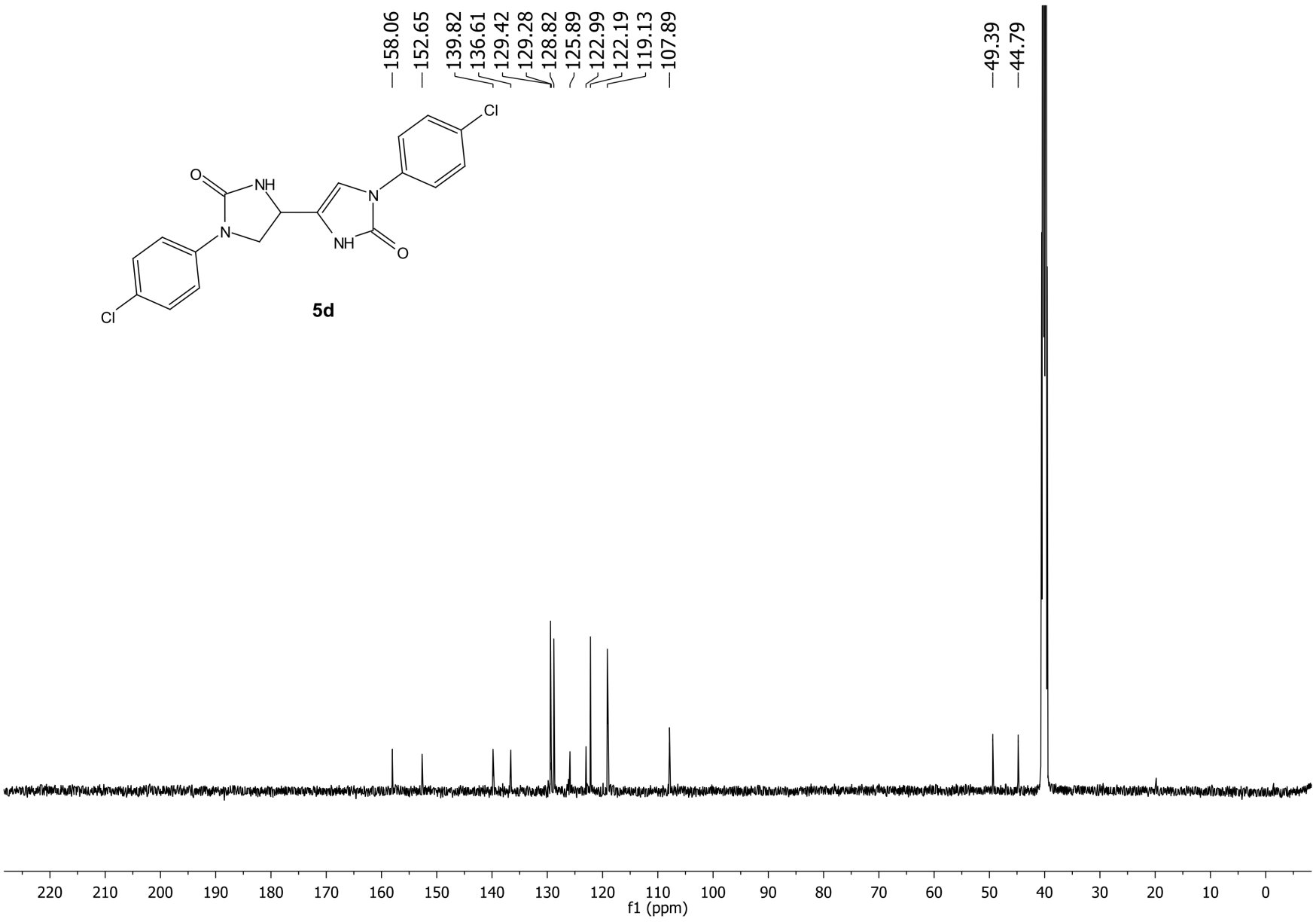


Figure S123. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound **5d**

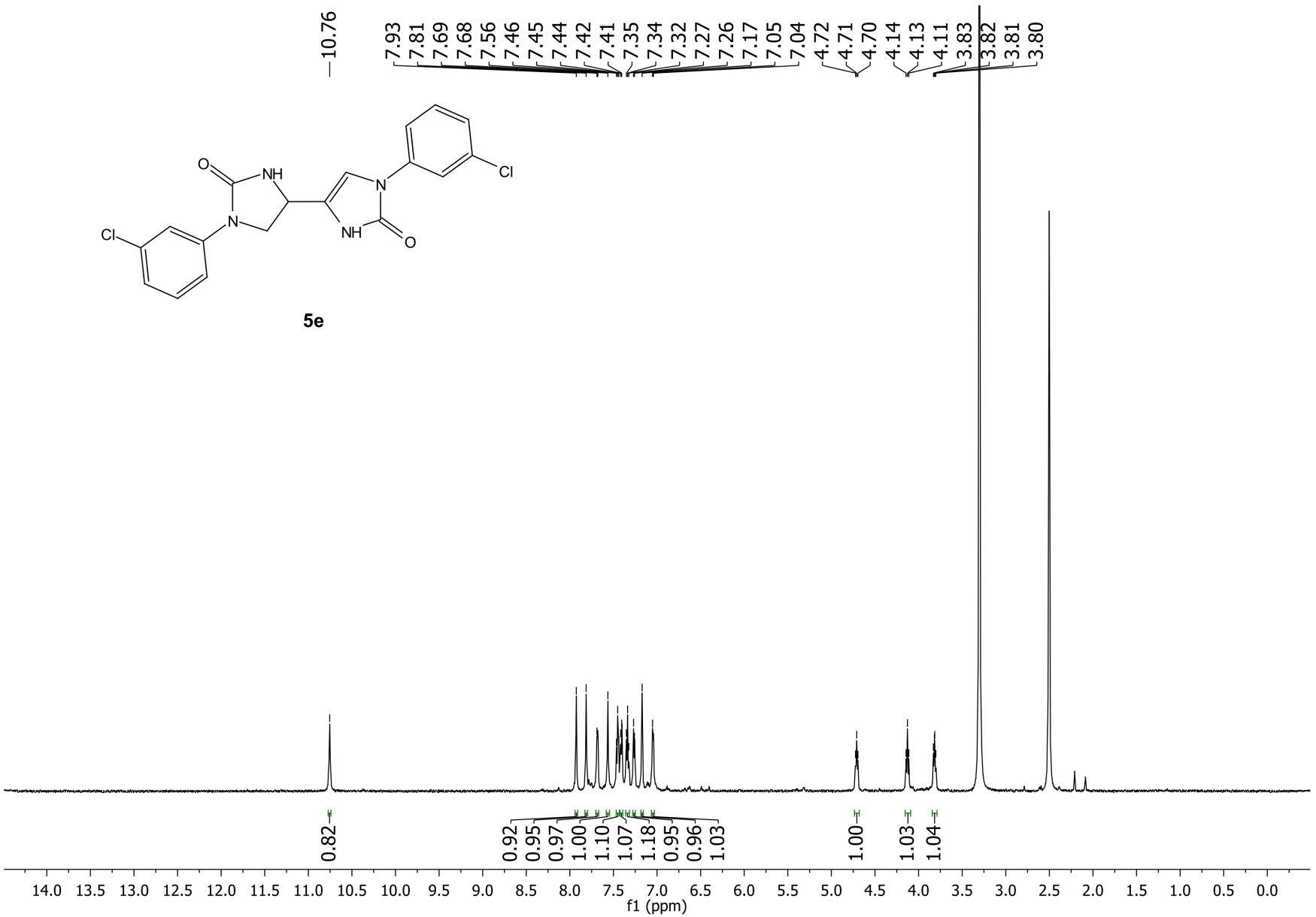


Figure S124. ^{1}H NMR spectrum ($(CD_3)_2SO$, 500MHz) of the compound **5e**

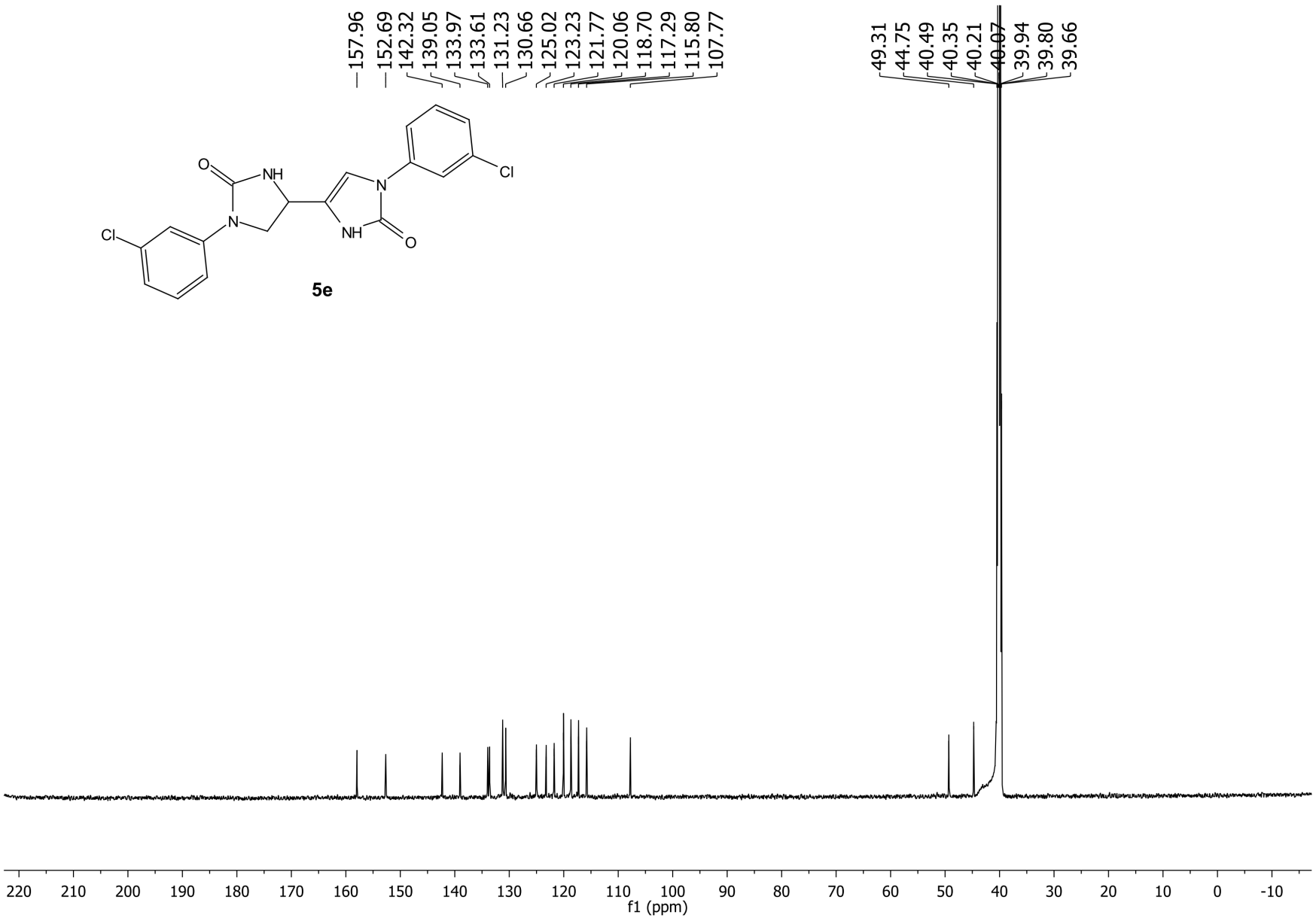


Figure S125. ^{13}C NMR spectrum ($(CD_3)_2SO$, 151MHz) of the compound **5e**