Gold-catalyzed *endo*-selective cyclization of alkynylcyclobutanecarboxamides: synthesis of cyclobutane-fused dihydropyridones

M. Soledad Garre,[†] Guillermo G. Otárola,[†] Estíbaliz Merino,[†] David Sucunza,[†] Enrique Aguilar,[‡] M. Teresa Quirós,[†] Juan J. Vaquero, *[†] and Patricia García-García*[†]

[†] Universidad de Alcalá (IRYCIS). Departamento de Química Orgánica y Química Inorgánica, Instituto de Investigación Química "Andrés M. del Río" (IQAR). Campus Científico-Tecnológico, Facultad de Farmacia Autovía A-II, Km 33.1, 28805-Alcalá de Henares, Madrid (Spain)

[‡] Instituto Universitario de Química Organometálica "Enrique Moles", Departamento de Química Orgánica e Inorgánica, Universidad de Oviedo, C/Julián Clavería, 8. 33006, Oviedo, Spain.

Electronic Supplementary Information

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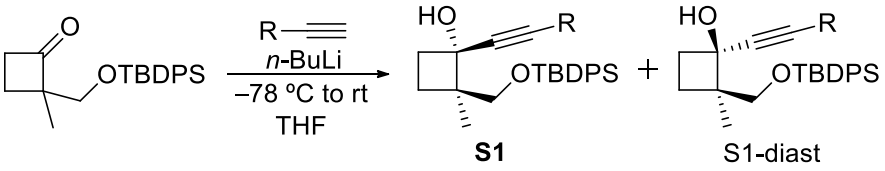
GENERAL EXPERIMENTAL DETAILS

All reactions involving air sensitive compounds were carried out under inert atmosphere (Ar). Starting materials sourced from commercial suppliers were used as received unless otherwise stated. Dry solvents, where necessary, were dried by a MBRAUN MB-SPS-800 apparatus. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60 F254, 70-200 mm) as the stationary phase. All melting points were determined in open capillary tubes on a Stuart Scientific SMP3 melting point apparatus. ^{1}H and ^{13}C spectra were recorded on either a Varian Mercury VX-300, Varian Unity 300, Bruker 400 or Varian Unity 500 MHz spectrometer at room temperature. Chemical shifts are given in ppm (δ) downfield from TMS. Coupling constants (*J*) are in Hertz (Hz) and signals are described as follows: s, singlet; d doublet; t, triplet; bs, broad singlet; dd, double doublet; ddd, double doublet of doublet; dt, double triplet; td, triple doublet; ap t, apparent triplet; ap q, apparent quadruplet; ap dt, apparent double triplet; apparent triple doublet; m, multiplet. High-resolution analysis (HRMS) were performed on an Agilent 6210 time of-flight LC/MS. 2-(1-*tert*-butyldiphenylsilyloxymethyl)-2-methylcyclobutan-1-one[1] and **S3b-d**[2] and **S4a**[2] were prepared as described previously.

EXPERIMENTAL PROCEDURES AND DATA

General procedure for the synthesis of precursors S1

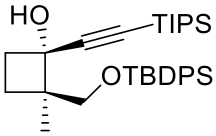


In a round-bottom flask, the corresponding acetylene (3 equiv) was dissolved in dry tetrahydrofuran (THF) (0.7 M) and the resulting mixture was cooled to –78 ºC. Then, *n*-butyllithium (3 equiv) was added dropwise and the reaction mixture was stirred for 30 min at room temperature. The reaction mixture was cooled to –78 ºC and 2-(1-*tert*-butyldiphenylsilyloxymethyl)-2-methylcyclobutan-1-one[1] (1 equiv) in dry THF (0.45 M) was added dropwise. The reaction mixture was stirred at room temperature until the cyclobutanone was completely consumed, which was determined by TLC analysis. Then, the reaction was quenched by addition of H_2O. The mixture was extracted with Et_2O and the combined organic layers were washed with saturated aqueous solution of NH_4Cl and brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue, containing a mixture of **S1** and S1-diast, was purified by flash column chromatography on silica gel to give the corresponding acetylene **S1**.

[1] Yoshida, M.; Sugimoto, K.; Ihara, M. *Org. Lett.,* **2004**, *6*, 1979-1982.

[2] Garre, M. S.; Sucunza, D.; Aguilar, E.; García-García, P.; Vaquero, J. J. *J. Org. Chem.* **2019**, *84*, 5712−5725.

Synthesis of (1*S,2*R**)-2-(((*tert*-butyldiphenylsilyl)oxy)methyl)-2-methyl-1-((triisopropylsilyl)ethynyl)cyclobutanol (S1-TIPS)**



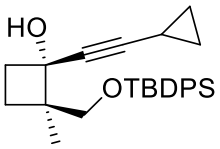
Following the general procedure, using (triisopropylsilyl)acetylene (10.05 mL, 44.80 mmol). Purification by flash column chromatography on silica gel (1 % EtOAc in hexane) gave **S1-TIPS** (2.42 g, 4.52 mmol) as yellow oil in 30 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69–7.60 (m, 4H), 7.45–7.31 (m, 6H), 3.82 (d, *J* = 9.9 Hz, 1H), 3.73 (d, *J* = 9.9 Hz, 1H), 2.31–2.12 (m, 2H), 1.91 (s, 1H), 1.79–1.54 (m, 2H), 1.23 (s, 3H), 1.06 (s, 12H), 0.94 (s, 18H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 135.7 (4xCH), 134.00 (C), 133.95 (C), 129.5 (2xCH), 127.6 (4xCH), 108.6 (C), 86.5 (C), 70.9 (C), 70.2 (CH_2), 48.7 (C), 34.7 (CH_2), 27.2 (3xCH_3), 25.4 (CH_2), 19.7 (C), 18.8 (6xCH_3), 17.8 (CH_3), 11.3 (3xCH).

HRMS (ESI-TOF) m/z calculated for $C_{33}H_{50}NaO_2Si_2$ $[M+]^+$: 557.3242. Found $[M+H]^+$: 557.3253.

Synthesis of (1*R,2*R**)-2-(((*tert*-butyldiphenylsilyl)oxy)methyl)-1-(cyclopropylethynyl)-2-methylcyclobutanol (S1i)**



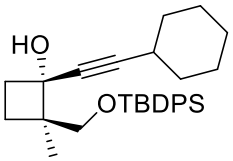
Following the general procedure, using cyclopropylacetylene (1.1 mL, 12.76 mmol). Purification by flash column chromatography on silica gel (1 % EtOAc in hexane) gave **S1i** (0.92 g, 2.21 mmol) as yellow oil in 52 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82–7.73 (m, 4H), 7.51–7.39 (m, 6H), 3.84 (d, *J* = 9.9 Hz, 1H), 3.63 (d, *J* = 9.9 Hz, 1H), 2.33–2.15 (m, 2H), 2.13 (s, 1H), 1.69–1.47 (m, 2H), 1.31 (s, 3H), 1.28–1.16 (m, 1H), 1.14 (s, 9H), 0.77–0.69 (m, 2H), 0.62–0.54 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 135.8 (4xCH), 134.03 (C), 133.96 (C), 129.61 (CH), 129.59 (CH), 127.7 (4xCH), 89.2 (C), 76.9 (C), 71.0 (C), 70.0 (CH_2), 49.0 (C), 34.1 (CH_2), 27.0 (3xCH_3), 24.4 (CH_2), 19.5 (C), 17.8 (CH_3), 8.33 (CH_2), 8.32 (CH_2), –0.4 (CH).

HRMS (ESI-TOF) m/z calculated for $C_{27}H_{35}O_2Si$ $[M+H]^+$: 419.2406. Found $[M+H]^+$: 419.2410.

Synthesis of (1*R,2*R**)-2-(((tert-butyldiphenylsilyl)oxy)methyl)-1-(cyclohexylethynyl)-2-methylcyclobutanol (S1j)**



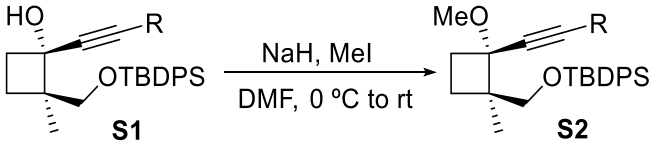
Following the general procedure, using ethynylcyclohexane (0.56 mL, 1.42 mmol). Purification by flash column chromatography on silica gel (5% EtOAc in Hexane) gave **S1j** (0.340 g, 0.74 mmol) as yellow oil in 52 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76–7.67 (m, 4H), 7.47–7.35 (m, 6H), 3.80 (d, *J* = 9.8 Hz, 1H), 3.68 (d, *J* = 9.8 Hz, 1H), 2.35–2.15 (m, 3H), 2.06 (s, 1H), 1.72–1.17 (m, 12H), 1.30 (s, 3H), 1.11 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 135.7 (4xCH), 132.83 (C), 132.75 (C), 129.91 (CH), 129.90 (CH), 127.9 (2xCH), 127.8 (2xCH), 90.6 (C), 81.8 (C), 73.5 (C), 69.1 (CH_2), 47.9 (C), 35.3 (CH_2), 33.0 (2xCH_2), 29.3 (CH), 27.1 (3xCH_3), 26.2 (2xCH_2), 25.1 (CH_2), 24.6 (CH_2), 22.0 (CH_3), 19.9 (C).

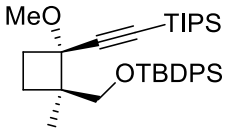
HRMS (ESI-TOF) m/z calculated for $C_{30}H_{41}O_2Si$ $[M+H]^+$: 461.2870. Found $[M+H]^+$: 461.2881.

General procedure for the synthesis of S2



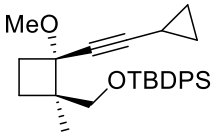
In a round-bottom flask, the corresponding derivative **S1** (1 equiv) was dissolved in dry DMF (0.4 M). Then, sodium hydride (60 % dispersion mineral oil) (1.5 equiv) was added at 0 ºC and the reaction mixture was stirred 1 h at room temperature. Iodomethane (4 equiv) was then added, and the reaction mixture was stirred at room temperature until **S1** derivative was completely consumed, which was determined by TLC analysis. The reaction was quenched by addition of brine and the mixture was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel to give the corresponding derivatives **S2**.

Synthesis of *tert*-butyl(((1*R,2*S**)-2-methoxy-1-methyl-2-((triisopropylsilyl)ethynyl)cyclobutyl)methoxy)diphenylsilane (S2-TIPS)**



Following the general procedure, starting with compound **S1-TIPS** (2.42 g, 4.52 mmol). The resulting residue was filtered over a plug of silica gel eluting with 5 % EtOAc in hexane and was employed in the next step without further purification.

Synthesis of *tert*-butyl(((1R*,2R*)-2-(cyclopropylethynyl)-2-methoxy-1-methylcyclobutyl) methoxy)diphenylsilane (**S2i**)



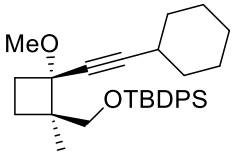
Following the general procedure, starting with compound **S1i** (0.937 g, 2.24 mmol). Purification by flash column chromatography on silica gel (5% EtOAc in Hexane) gave **S2i** (0.242 g, 0.56 mmol) as yellow oil in 25 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78–7.62 (m, 4H), 7.46–7.31 (m, 6H), 3.82 (d, *J* = 10.0 Hz, 1H), 3.42 (d, *J* = 10.0 Hz, 1H), 3.35 (s, 3H), 2.24–2.03 (m, 2H), 1.59–1.19 (m, 3H), 1.25 (s, 3H), 1.06 (s, 9H), 0.78–0.66 (m, 2H), 0.62–0.49 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 135.9 (2xCH), 135.7 (2xCH), 133.9 (C), 133.7 (C), 129.7 (CH), 129.6 (CH), 127.8 (2xCH), 127.7 (2xCH), 91.3 (C), 76.3 (C), 74.2 (C), 69.7 (CH_2), 53.2 (CH_3), 49.2 (C), 32.1 (CH_2), 26.9 (3xCH_3), 23.7 (CH_2), 19.5 (C), 17.7 (CH_3), 8.55 (CH_2), 8.50 (CH_2), –0.25 (CH).

HRMS (ESI-TOF) m/z calculated for $C_{28}H_{37}O_2Si$ $[M+H]^+$: 433.2557. Found $[M+H]^+$: 433.2564.

Synthesis of *tert*-butyl(((1R*,2R*)-2-(cyclohexylethynyl)-2-methoxy-1-methylcyclobutyl) methoxy)diphenylsilane (**S2j**)



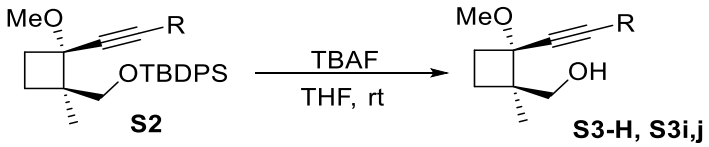
Following the general procedure, starting with compound **S1j** (0.276 g, 0.6 mmol). Purification by flash column chromatography on silica gel (5% EtOAc in Hexane) gave **S2j** (0.257 g, 0.54 mmol) as yellow oil in 90 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76–7.65 (m, 4H), 7.48–7.33 (m, 6H), 3.82 (d, *J* = 9.9 Hz, 1H), 3.53 (d, *J* = 9.9 Hz, 1H), 3.35 (s, 3H), 2.43–2.31 (m, 1H), 2.27–2.06 (m, 2H), 1.76–1.22 (m, 12H) 1.28 (s, 3H), 1.07 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9 (2xCH), 135.9 (2xCH), 134.1 (C), 134.0 (C), 129.64 (CH), 129.60 (CH), 127.7 (2xCH), 127.6 (2xCH), 92.4 (C), 78.8 (C), 76.8 (C), 69.9 (CH_2), 53.1 (CH_3), 49.0 (C), 32.8 (2xCH_2), 32.3 (CH_2), 29.2 (CH), 27.0 (3xCH_3), 26.0 (CH_2), 25.0 (2xCH_2), 24.0 (CH_2), 19.5 (C), 17.7 (CH_3).

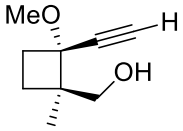
HRMS (ESI-TOF) m/z calculated for $C_{31}H_{42}NaO_2Si$ $[M+Na]^+$: 497.2846. Found $[M+Na]^+$: 497.2859.

General procedure for the synthesis of S3-H and S3i,j



To a solution of the corresponding derivative **S2** (1 equiv) in dry THF (0.45 M) was added tetrabutylammonium fluoride (4 equiv), and the reaction mixture was stirred overnight at room temperature. Then, the mixture was concentrated under reduced pressure and the residue was mixed with brine and extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel to give the corresponding derivatives **4**.

Synthesis of ((1*R,2*R**)-2-ethynyl-2-methoxy-1-methylcyclobutyl)methanol (S3-H)**



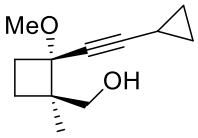
Following the general procedure, starting with compound **S2-TIPS** (1.97 g, 3.59 mmol). Purification by flash column chromatography on silica gel (10 % EtOAc in hexane) gave **S3-H** (0.24 g, 1.54 mmol) as yellow oil in 43 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.83 (d, *J* = 11.5 Hz, 1H), 3.50 (d, *J* = 11.0 Hz, 1H), 3.32 (s, 3H), 2.67 (s, 1H), 2.25–2.18 (m, 2H), 1.95 (bs, 1H), 1.67 (dt, *J* = 11.2, 9.0 Hz, 1H), 1.49 (ddd, J = 11.2, 7.3, 6.5 Hz, 1H), 1.21 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 83.3 (C), 76.0 (C), 75.8 (CH), 69.2 (CH_2), 52.6 (CH_3), 48.7 (C), 30.8 (CH_2), 23.6 (CH_2), 17.6 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_9H_{15}O_2$ [M+H]+: 155.1067. Found $[M+H]^+$: 155.1071.

Synthesis of ((1*R,2*R**)-2-(cyclopropylethynyl)-2-methoxy-1-methylcyclobutyl)methanol (S3i)**



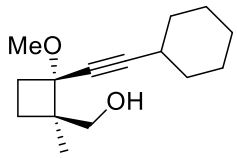
Following the general procedure, starting with compound **S2i** (0.229 g, 0.53 mmol). Purification by flash column chromatography on silica gel (10 % EtOAc in Hexane) gave **S3i** (0.102 g, 0.53 mmol) as yellow oil in 99 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.74 (d, *J* = 11.5 Hz, 1H), 3.45 (d, *J* = 11.5 Hz, 1H), 3.25 (s, 3H), 2.17–2.02 (m, 3H), 1.64 (dt, *J* = 11.1, 8.9 Hz, 1H), 1.48–1.38 (m, 1H), 1.36–1.22 (m, 1H), 1.15 (s, 3H), 0.86–0.76 (m, 2H), 0.73–0.66 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 91.8 (C), 76.0 (C), 74.4 (C), 69.5 (CH_2), 52.2 (CH_3), 48.9 (C), 30.9 (CH_2), 23.5 (CH_2), 17.6 (CH_3), 8.7 (CH_2), 8.6 (CH_2), –0.43 (CH).

HRMS (ESI-TOF) m/z calculated for $C_{12}H_{19}O_2$ $[M+H]^+$: 195.1380. Found $[M+H]^+$: 195.1381.

Synthesis of ((1*R,2*R**)-2-(cyclohexylethynyl)-2-methoxy-1-methylcyclobutyl)methanol (S3j)**



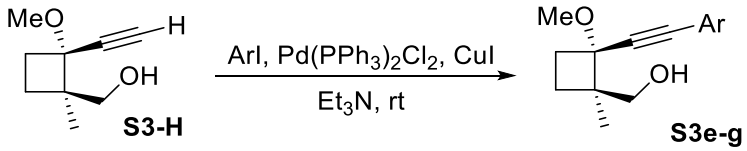
Following the general procedure, starting with compound **S2j** (0.227 g, 0.48 mmol). Purification by flash column chromatography on silica gel (10% EtOAc in Hexane) gave **S3j** (0.112 g, 0.47 mmol) as yellow oil in 99 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.76 (d, *J* = 11.5 Hz, 1H), 3.46 (d, *J* = 11.5 Hz, 1H), 3.27 (s, 3H), 2.54–2.40 (m, 1H), 2.20-2.08 (m, 3H), 1.87–1.76 (m, 2H), 1.75–1.59 (m, 3H), 1.55–1.25 (m, 7H), 1.17 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 92.9 (C), 79.3 (C), 76.0 (C), 69.6 (CH_2), 52.2 (CH_3), 48.9 (C), 32.8 (2xCH_2), 31.0 (CH_2), 29.2 (CH), 25.9 (CH_2), 24.9 (2xCH_2), 23.5 (CH_2), 17.6 (CH_3).

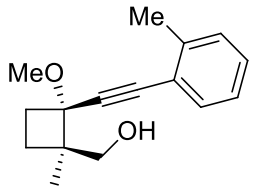
HRMS (ESI-TOF) m/z calculated for $C_{15}H_{25}O_2$ $[M+H]^+$: 237.1849. Found $[M+H]^+$: 237.1836.

General procedure for the synthesis of S3e-g



In a round bottom flask $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (1 mol%) and the corresponding iodoarene (1.2 equiv) were added. Then compound **S3-H** (1 equiv) was added in dry Et_3N (0.13 M) and the reaction was stirred for 4 hours at room temperature. After that, the residue was mixed with brine and extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel to give the corresponding derivatives **S3e-g.**

Synthesis of (1R*,2*R)-2-methoxy-1-methyl-2-(*o*-tolylethynyl)cyclobutyl)methanol (S3e)**



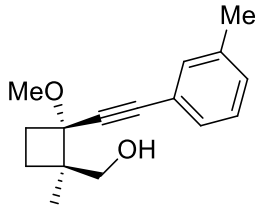
Following the general procedure, using 2-iodotoluene (50 µL, 0.39 mmol). Purification by flash column chromatography on silica gel (20 % EtOAc in hexane) gave **S3e** (26.3 mg, 0.11 mmol) as yellow oil in 33 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.41 (m, 1H), 7.27–7.19 (m, 2H), 7.18–7.12 (m, 1H), 3.91 (d, *J* = 11.4 Hz, 1H), 3.57 (d, *J* = 11.4 Hz, 1H), 3.40 (s, 3H), 2.47 (s, 3H), 2.34–2.29 (m, 2H), 1.97 (bs, 1H), 1.74 (dt, *J* = 11.3, 9.0 Hz, 1H), 1.53 (ddd, J = 11.2, 7.3, 6.5 Hz, 1H), 1.27 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.2 (C), 132.3 (CH), 129.7 (CH), 128.7 (CH), 125.8 (CH), 122.3 (C), 92.3 (C), 86.9 (C), 76.7 (C), 69.5 (CH_2), 52.6 (CH_3), 49.2 (C), 31.3 (CH_2), 23.7 (CH_2), 21.0 (CH_3), 17.6 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{16}H_{21}O_2$ $[M+H]^+$: 245.1536. Found $[M+H]^+$: 245.1540.

Synthesis of (1R*,2*R)-2-methoxy-1-methyl-2-(*m*-tolylethynyl)cyclobutyl)methanol (S3f)**



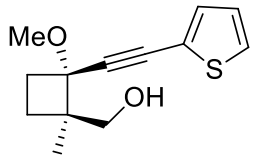
Following the general procedure, using 3-iodotoluene (50 µL, 0.39 mmol). Purification by flash column chromatography on silica gel (20 % EtOAc in hexane) gave **S3f** (26.3 mg, 0.11 mmol) as yellow oil in 52 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.12 (m, 4H), 3.89 (dd, *J* = 11.5, 5.2 Hz, 1H), 3.56 (dd, *J* = 11.5, 6.9 Hz, 1H), 3.38 (s, 3H), 2.34 (s, 3H), 2.38–2.25 (m, 2H), 2.04 (bt, *J* = 6.4 Hz, 1H), 1.73 (dt, *J* = 11.2, 9.0 Hz, 1H), 1.57–1.47 (m, 1H), 1.26 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.2 (C), 132.4 (CH), 129.6 (CH), 128.9 (CH), 128.4 (CH), 122.2 (C), 88.1 (C), 87.9 (C), 76.5 (C), 69.5 (CH_2), 52.6 (CH_3), 49.2 (C), 31.0 (CH_2), 23.6 (CH_2), 21.3 (CH_3), 17.6 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{16}H_{21}O_2$ $[M+H]^+$: 245.1536. Found $[M+H]^+$: 245.1534.

Synthesis of (1*R,2*R**)-2-methoxy-1-methyl-2-(thiophen-2-ylethynyl)cyclobutyl)methanol (S3g)**



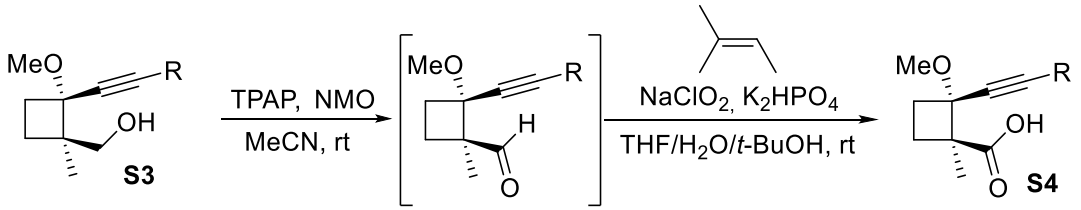
Following the general procedure, using 2-iodothiophene (43.0 µL, 0.39 mmol). Purification by flash column chromatography on silica gel (20 % EtOAc in hexane) gave **S3g** (36.2 mg, 0.15 mmol) as yellow oil in 47 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.22 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.98 (dd, *J* = 5.2, 3.6 Hz, 1H), 3.86 (d, *J* = 11.4 Hz, 1H), 3.55 (d, *J* = 11.4 Hz, 1H), 3.36 (s, 3H), 2.31–2.25 (m, 2H), 1.91 (bs, 1H), 1.71 (dt, *J* = 11.3, 9.1 Hz, 1H), 1.51 (ddd, *J* = 11.3, 8.0, 5.7 Hz, 1H), 1.25 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 132.5 (CH), 127.5 (CH), 127.1 (CH), 122.4 (C), 92.3 (C), 81.0 (C), 76.7 (C), 69.4 (CH_2), 52.7 (CH_3), 49.3 (C), 30.9 (CH_2), 23.7 (CH_2), 17.6 (CH_3).

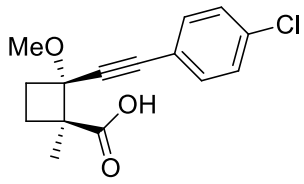
HRMS (ESI-TOF) m/z calculated for $C_{13}H_{17}O_2S$ $[M+H]^+$: 237.0944. Found $[M+H]^+$: 237.0939.

General procedure for the synthesis of carboxylic acids S4



In a round bottom flask, the corresponding alcohol **S3** (1 equiv.), 4-methylmorpholine *N*-oxide (10 equiv) and tetrapropylammonium perruthenate (10 mol%) were dissolved in MeCN (0.25 M), and the resulting mixture was stirred 40 min at room temperature. The residue was concentrated under reduced pressure and without further purification, was dissolved in a mixture of THF/H_2O/tBuOH (3:1:3) (0.06 M). Then, sodium chlorite (3 equiv), dibasic potassium phosphate (3 equiv) and 2-methyl-2-butene (8 equiv) were added and the reaction mixture was stirred overnight at room temperature. The reaction mixture was quenched by the addition of HCl (1 M), and the resulting mixture was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel to give the corresponding derivatives **S4**.

Synthesis of (1*S,2*R**)-2-((4-chlorophenyl)ethynyl)-2-methoxy-1-methylcyclobutanecarboxylic acid (S4b)**



Following the general procedure, starting with compound **S3b**[2] (60.5 mg, 0.23 mmol). Purification by flash column chromatography on silica gel (40 % EtOAc in hexane) gave **S4b** (24.6 mg, 0.09 mmol) as orange solid in 39 **%** yield.

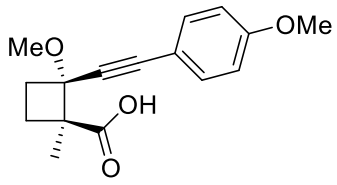
M. p.: 116-118 ^{O}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.24 (m, 2H), 7.22–7.15 (m, 2H), 3.46 (s, 3H), 2.52–2.21 (m, 3H), 1.58 (ddd, *J* = 11.3, 8.7, 3.0 Hz, 1H), 1.48 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.8 (C), 134.7 (C), 133.2 (2xCH), 128.6 (2xCH), 120.9 (C), 88.2 (C), 86.6 (C), 76.1 (C), 55.1 (C), 53.4 (CH_3), 31.6 (CH_2), 22.5 (CH_2), 18.1 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{15}H_{14}ClO_3$ $[M-H]^-$: 277.0637. Found $[M-H]^-$: 277.0638.

Synthesis of (1*S,2*R**)-2-methoxy-2-((4-methoxyphenyl)ethynyl)-1-methylcyclobutanecarboxylic acid (S4c)**



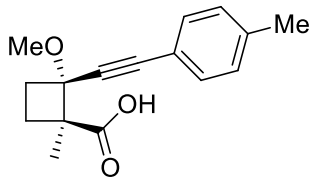
Following the general procedure, starting with compound **S3c**[2] (46.5 mg, 0.18 mmol). Purification by flash column chromatography on silica gel (20 % EtOAc in hexane) gave **9c** (52.3 mg, 0.19 mmol) as yellow oil in >99 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.27 (m, 2H), 6.78–6.71 (m, 2H), 3.77 (s, 3H), 3.46 (s, 3H), 2.47 (td, J = 11.1, 8.4 Hz, 1H), 2.38–2.19 (m, 2H), 1.55 (ddd, *J* = 11.3, 8.9, 2.8 Hz, 1H), 1.48 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.8 (C), 159.7 (C), 133.4 (2xCH), 114.5 (C), 113.9 (2xCH), 87.8 (C), 85.7 (C), 76.2 (C), 55.4 (CH_3), 55.3 (C), 53.4 (CH_3), 31.9 (CH_2), 22.6 (CH_2), 18.3 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{16}H_{17}O_4$ $[M-H]^-$: 273.1132. Found $[M-H]^-$: 273.1133.

Synthesis of (1*S,2*R**)-2-methoxy-1-methyl-2-(*p*-tolylethynyl)cyclobutanecarboxylic acid (S4d)**



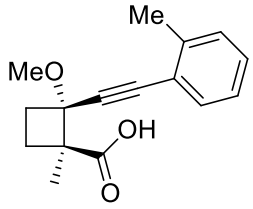
Following the general procedure, starting with compound **S3d**[2] (51.0 mg, 0.21 mmol). Purification by flash column chromatography on silica gel (20 % EtOAc in hexane) gave **S4d** (33.1 mg, 0.13 mmol) as colourless oil 61 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.5 Hz, 2H), 7.04 (d, *J* = 7.5 Hz, 2H), 3.47 (s, 3H), 2.55–2.21 (m, 3H), 2.31 (s, 3H), 1.65–1.51 (m, 1H), 1.50 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 179.8 (C), 138.7 (C), 131.9 (2xCH), 129.1 (2xCH), 119.4 (C), 87.9 (C), 86.4 (C), 76.1 (C), 55.1 (C), 53.4 (CH_3), 31.8 (CH_2), 22.5 (CH_2), 21.6 (CH_3), 18.2 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{16}H_{19}O_3$ $[M+H]^+$: 259.1329. Found $[M+H]^+$: 259.1325.

Synthesis of (1*S,2*R**)-2-methoxy-1-methyl-2-(*o*-tolylethynyl)cyclobutanecarboxylic acid (S4e)**



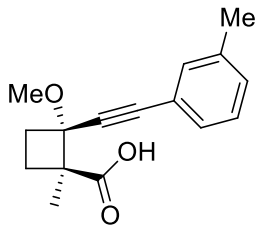
Following the general procedure, starting with compound **S3e** (26.3 mg, 0.11 mmol). Purification by flash column chromatography on silica gel (20 % EtOAc in hexane) gave **S4e** (17.7 mg, 0.07 mmol) as brown oil 64 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.18 (td, *J* = 7.6, 1.4 Hz, 1H), 7.12–7.05 (m, 2H), 3.49 (s, 3H), 2.47 (td, *J* = 11.2, 8.6 Hz, 1H), 2.38 (s, 3H), 2.38–2.25 (m, 2H), 1.57 (ddd, *J* = 11.5, 9.3, 2.6 Hz, 1H), 1.48 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 181.1 (C), 140.4 (C), 132.4 (CH), 129.5 (CH), 128.6 (CH), 125.5 (CH), 122.3 (C), 91.0 (C), 86.4 (C), 76.3 (C), 55.1 (C), 53.5 (CH_3), 32.1 (CH_2), 22.6 (CH_2), 20.7 (CH_3), 18.3 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{16}H_{17}O_3$ $[M-H]^-$: 257.1183. Found $[M-H]^-$: 257.1182.

Synthesis of (1*S,2*R**)-2-methoxy-1-methyl-2-(*m*-tolylethynyl)cyclobutanecarboxylic acid (S4f)**



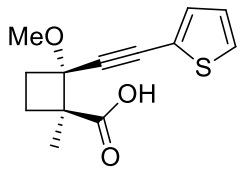
Following the general procedure, starting with compound **S3f** (40.8 mg, 0.17 mmol). Purification by flash column chromatography on silica gel (20 % EtOAc in hexane) gave **S4f** (36.4 mg, 0.14 mmol) as yellow oil 84 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23–7.17 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.10–7.06 (m, 1H), 3.47 (s, 3H), 2.48 (td, *J* = 11.2, 8.7 Hz, 1H), 2.37–2.23 (m, 2H), 2.28 (s, 3H), 1.56 (ddd, *J* = 11.7, 9.5, 2.5 Hz, 1H), 1.47 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 181.1 (C), 137.9 (C), 132.5 (CH), 129.5 (CH), 129.0 (CH), 128.2 (CH), 122.2 (C), 88.0 (C), 86.7 (C), 76.1 (C), 55.2 (C), 53.4 (CH_3), 31.8 (CH_2), 22.5 (CH_2), 21.3 (CH_3), 18.1 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{16}H_{19}O_3$ $[M+H]^+$: 259.1329. Found $[M+H]^+$: 259.1323.

Synthesis of (1*S,2*R**)-2-methoxy-1-methyl-2-(thiophen-2-ylethynyl)cyclobutane carboxylic acid (S4g)**



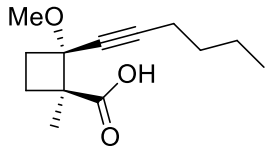
Following the general procedure, starting with compound **S3g** (36.2 mg, 0.15 mmol). Purification by flash column chromatography on silica gel (40 % EtOAc in hexane) gave **S4g** (38.2 mg, 0.15 mmol) as yellow oil in >99 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.15 (dd, *J* = 3.7, 1.1 Hz, 1H), 6.90 (dd, *J* = 5.1, 3.7 Hz, 1H), 3.46 (s, 3H), 2.52–2.20 (m, 3H), 1.57 (ddd, *J* = 11.2, 8.9, 2.7 Hz, 1H), 1.49 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.8 (C), 132.7 (CH), 127.6 (CH), 127.0 (CH), 122.3 (C), 91.1 (C), 81.1 (C), 76.3 (C), 55.2 (C), 53.5 (CH_3), 31.6 (CH_2), 22.5 (CH_2), 18.2 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{13}H_{13}O_3S$ $[M-H]^-$: 249.0580. Found $[M-H]^-$: 249.0591.

Synthesis of (1*S,2*R**)-2-(hex-1-yn-1-yl)-2-methoxy-1-methylcyclobutanecarboxylic acid (S4h)**



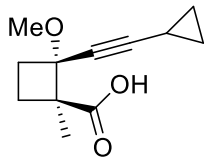
Following the general procedure, starting with compound **S3h**[2] (0.10 g, 0.48 mmol). Purification by flash column chromatography on silica gel (10 % EtOAc in hexane) gave **S4h** (65.4 mg, 0.2918 mmol) as yellow oil 61 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.38 (s, 3H), 2.37 (td, *J* = 11.2, 8.5 Hz, 1H), 2.26–2.13 (m, 4H), 1.55–1.34 (m, 5H), 1.43 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 181.2 (C), 88.5 (C), 78.1 (C), 75.8 (C), 55.0 (C), 53.1 (CH_3), 31.9 (CH_2), 30.8 (CH_2), 22.4 (CH_2), 22.0 (CH_2), 18.5 (CH_2), 18.1 (CH_3), 13.7 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{13}H_{19}O_3$ $[M-H]^-$: 223.1340. Found $[M-H]^-$: 223.1336.

Synthesis of (1*S,2*R**)-2-(cyclopropylethynyl)-2-methoxy-1-methylcyclobutanecarboxylic acid (S4i)**



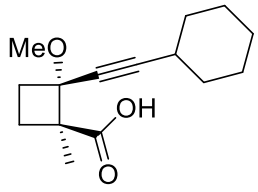
Following the general procedure, starting with compound **S3i** (0.099 g, 0.51 mmol). Purification by flash column chromatography on silica gel (20 % EtOAc in Hexane) gave **S4i** (0.095 g, 0.46 mmol) as yellow oil in 90 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.37 (s, 3H), 2.37 (td, *J* = 11.1, 8.7 Hz, 1H), 2.21–2.10 (m, 2H), 1.55-1.42 (m, 1H), 1.43 (s, 3H), 1.32-1.21 (m, 1H), 0.81-0.73 (m, 2H), 0.70-0.63 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6 (C), 91.9 (C), 75.7 (C), 73.1 (C), 55.0 (C), 53.0 (CH_3), 31.7 (CH_2), 22.4 (CH_2), 18.1 (CH_3), 8.8 (CH_2), 8.6 (CH_2), -0.42 (CH).

HRMS (ESI-TOF) m/z calculated for $C_{12}H_{15}O_3$ $[M-H]^-$: 207.1027. Found $[M+H]^+$: 207.1019.

Synthesis of (1*S,2*R**)-2-(cyclohexylethynyl)-2-methoxy-1-methylcyclobutanecarboxylic acid (S4j)**



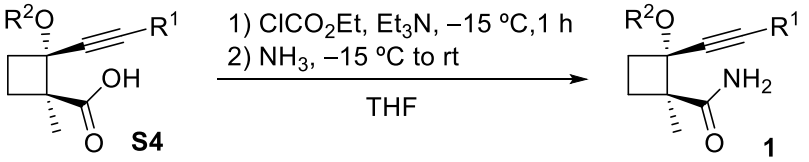
Following the general procedure, starting with compound **S3j** (0.121 g, 0.51 mmol). Purification by flash column chromatography on silica gel (20 % EtOAc in Hexane) gave **S4j** (0.077 g, 0.30 mmol) as yellow oil in 60 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.39 (s, 3H), 2.41–2.31 (m, 1H), 2.22–2.13 (m, 2H), 1.78–1.60 (m, 4H), 1.56-1.19 (m, 8H), 1.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8 (C), 92.4 (C), 78.9 (C), 75.5 (C), 54.8 (CH_3), 52.2 (C), 32.71 (CH_2), 32.69 (CH_2), 31.1 (CH_2), 29.8 (CH), 26.0 (CH_2), 24.8 (2xCH_2), 23.3 (CH_2), 19.7 (CH_3).

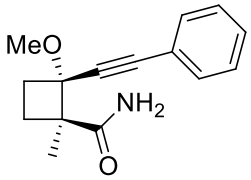
HRMS (ESI-TOF) m/z calculated for $C_{15}H_{23}O_3$ $[M+H]^+$: 251.1647. Found $[M+H]^+$: 251.1642.

General procedure for the synthesis of amides 1



In a round bottom flask, the corresponding alkynylcyclobutane acid **S4** (1 equiv) was dissolved in dry THF (0.07 M) and the solution was stirred at −15 °C. Then Et_3N (1 equiv) and ethyl chloroformate (1 equiv) were added and stirring was maintained for 1 hour at that temperature. Then, the NH_3 (30%, aqueous solution) was added and the stirring was continued for 15 min. After that, the cooling bath was removed, and the mixture was allowed to reach room temperature. Solvent was evaporated under vacuum and the resulting residue was extracted with EtOAc and 5 % sodium bicarbonate solution. The organic layer was sequentially washed with water, 1 M hydrochloric acid, and finally, water. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel to give the corresponding derivatives **1**.

Synthesis of (1*S,2*R**)-2-methoxy-1-methyl-2-(phenylethynyl)cyclobutanecarboxamide (1a)**



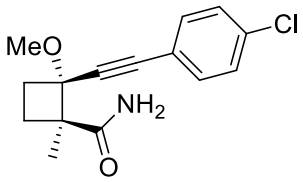
Following the general procedure, starting with compound **S4a**[2] (50.0 mg, 0.20 mmol). Purification by flash column chromatography on silica gel (40 % EtOAc in hexane) gave **1a** (33.0 mg g, 0.14 mmol) as yellow oil in 66 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.41 (m, 2H), 7.32–7.26 (m, 3H), 5.69–5.47 (m, 2H), 3.43 (s, 3H), 2.36–2.19 (m, 3H), 1.67–1.61 (m, 1H), 1.47 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.6 (C), 132.0 (2xCH), 128.7 (CH), 128.4 (2xCH), 122.5 (C), 88.0 (C), 87.5 (C), 75.9 (C), 54.9 (C), 52.6 (CH_3), 30.8 (CH_2), 23.3 (CH_2), 19.7 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{15}H_{18}NO_2$ $[M+H]^+$: 244.1332. Found $[M+H]^+$: 244.1338.

Synthesis of (1*S,2*R**)-2-((4-chlorophenyl)ethynyl)-2-methoxy-1-methylcyclobutane carboxamide (1b)**



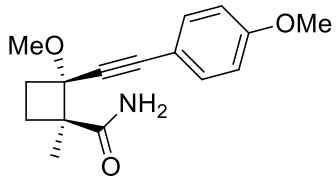
Following the general procedure, starting with compound **S4b** (24.6 mg, 0.09 mmol). Purification by flash column chromatography on silica gel (40 % EtOAc in hexane) gave **1b** (10.5 mg, 0.04 mmol) as yellow oil in 43 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.33 (m, 2H), 7.29–7.24 (m, 2H), 5.51 (bs, 2H), 3.42 (s, 3H), 2.35–2.19 (m, 3H), 1.67–1.61 (m, 1H), 1.47 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.4 (C), 134.7 (C), 133.2 (2xCH), 128.7 (2xCH), 121.0 (C), 89.1 (C), 86.3 (C), 75.9 (C), 54.9 (C), 52.7 (CH_3), 30.8 (CH_2), 23.2 (CH_2), 19.7 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{15}H_{17}NO_2Cl$ $[M+H]^+$: 278.0942. Found $[M+H]^+$: 278.0934.

Synthesis of (1*S,2*R**)-2-methoxy-2-((4-metoxyphenyl)ethynyl)-1-methylcyclobutane carboxamide (1c)**



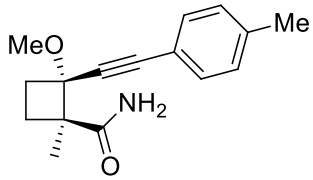
Following the general procedure, starting with compound **S4c** (49.0 mg, 0.18 mmol). Purification by flash column chromatography on silica gel (30 % EtOAc in hexane) gave **1c** (21.8 mg, 0.08 mmol) as yellow oil in 45 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.34 (m, 2H), 6.83–6.78 (m, 2H), 5.68–5.47 (m, 2H), 3.79 (s, 3H), 3.41 (s, 3H), 2.34–2.17 (m, 3H), 1.66–1.60 (m, 1H), 1.46 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.6 (C), 159.9 (C), 133.5 (2xCH), 114.6 (C), 114.0 (2xCH), 87.5 (C), 86.5 (C), 75.9 (C), 55.4 (CH_3), 54.9 (C), 52.5 (CH_3), 30.9 (CH_2), 23.3 (CH_2), 19.7 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{16}H_{20}NO_3$ $[M+H]^+$: 274.1438. Found $[M+H]^+$: 274.1431.

Synthesis of (1*S,2*R**)-2-methoxy-1-methyl-2-(*p*-tolylethynyl)cyclobutanecarboxamide (1d)**



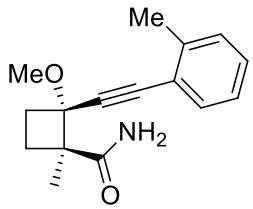
Following the general procedure, starting with compound **S4d** (33.1 mg, 0.13 mmol). Purification by flash column chromatography on silica gel (20 % EtOAc in hexane) gave **1d** (16.4 mg, 0.06 mmol) as yellow oil in 50 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.2 Hz, 2H), 7.09 (d, *J* = 7.2 Hz, 2H), 5.81–5.46 (m, 2H), 3.42 (s, 3H), 2.33 (s, 3H), 2.34–2.18 (m, 3H), 1.66–1.60 (m, 1H), 1.46 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.6 (C), 138.8 (C), 131.9 (2xCH), 129.1 (2xCH), 119.5 (C), 87.7 (C), 87.2 (C), 75.9 (C), 55.0 (C), 52.5 (CH_3), 30.9 (CH_2), 23.3 (CH_2), 21.6 (CH_3), 19.7 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{16}H_{20}NO_2$ $[M+H]^+$: 258.1489. Found $[M+H]^+$: 258.1495.

Synthesis of (1*S,2*R**)-2-methoxy-1-methyl-2-(*o*-tolylethynyl)cyclobutanecarboxamide (1e)**



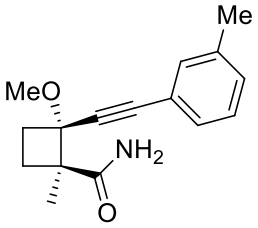
Following the general procedure, starting with compound **S4e** (17.7 mg, 0.07 mmol). Purification by flash column chromatography on silica gel (40 % EtOAc in hexane) gave **1e** (12.2 mg, 0.05 mmol) as yellow oil in 69 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.24–7.15 (m, 2H), 7.14–7.09 (m, 1H), 5.49 (bs, 2H), 3.45 (s, 3H), 2.43 (s, 3H), 2.37–2.21 (m, 3H), 1.68–1.62 (m, 1H), 1.48 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.4 (C), 140.4 (C), 132.4 (CH), 129.6 (CH), 128.7 (CH), 125.6 (CH), 122.4 (C), 91.9 (C), 86.4 (C), 76.1 (C), 54.9 (C), 52.6 (CH_3), 31.2 (CH_2), 23.3 (CH_2), 20.9 (CH_3), 19.8 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{16}H_{20}NO_2$ $[M+H]^+$: 258.1489. Found $[M+H]^+$: 258.1483.

Synthesis of (1*S,2*R**)-2-methoxy-1-methyl-2-(*m*-tolylethynyl)cyclobutanecarboxamide (1f)**



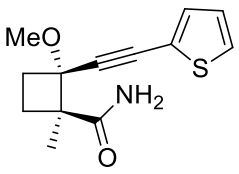
Following the general procedure, starting with compound **S4f** (36.4 mg, 0.14 mmol). Purification by flash column chromatography on silica gel (40 % EtOAc in hexane) gave **1f** (26.6 mg, 0.10 mmol) as yellow oil in 73 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.22 (m, 2H), 7.21–7.15 (m, 1H), 7.14–7.10 (m, 1H), 5.79–5.48 (m, 2H), 3.43 (s, 3H), 2.36–2.19 (m, 3H), 2.31 (s, 3H), 1.67–1.61 (m, 1H), 1.47 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.6 (C), 138.1 (C), 132.5 (CH), 129.5 (CH), 129.1 (CH), 128.3 (CH), 122.3 (C), 87.7 (C), 87.6 (C), 75.9 (C), 54.9 (C), 52.6 (CH_3), 30.9 (CH_2), 23.3 (CH_2), 21.3 (CH_3), 19.7 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{16}H_{20}NO_2$ $[M+H]^+$: 258.1489. Found $[M+H]^+$: 258.1497.

Synthesis of (1*S,2*R**)-2-methoxy-1-methyl-2-(thiophen-2-ylethynyl)cyclobutane carboxamide (1g)**



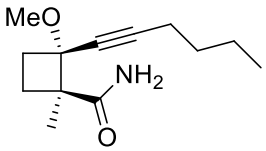
Following the general procedure, starting with compound **S4g** (38.3 mg, 0.15 mmol). Purification by flash column chromatography on silica gel (40 % EtOAc in hexane) gave **1g** (14.4 mg, 0.06 mmol) as yellow solid in 38 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.20 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.95 (dd, *J* = 5.2, 3.6 Hz, 1H), 5.52 (bs, 2H), 3.41 (s, 3H), 2.34–2.19 (m, 3H), 1.67–1.61 (m, 1H), 1.47 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.3 (C), 132.7 (CH), 127.6 (CH), 127.1 (CH), 122.4 (C), 91.9 (C), 80.7 (C), 76.1 (C), 54.9 (C), 52.7 (CH_3), 30.7 (CH_2), 23.3 (CH_2), 19.7 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{13}H_{16}NO_2S$ $[M+H]^+$: 250.0896. Found $[M+H]^+$: 250.0889.

Synthesis of (1*S,2*R**)-2-(hex-1-yn-1-yl)-2-methoxy-1-methylcyclobutanecarboxamide (1h)**



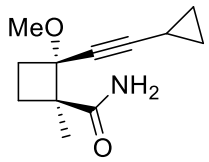
Following the general procedure, starting with compound **S4h** (30.0 mg, 0.13 mmol). Purification by flash column chromatography on silica gel (30 % EtOAc in hexane) gave **1h** (9.4 mg, 0.04 mmol) as yellow oil in 32 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.42 (bs, 2H), 3.32 (s, 3H), 2.27–2.08 (m, 5H), 1.61–1.35 (m, 5H), 1.40 (s, 3H), 0.90 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.8 (C), 88.3 (C), 78.8 (C), 75.6 (C), 54.7 (C), 52.2 (CH_3), 31.0 (CH_2), 30.9 (CH_2), 23.3 (CH_2), 22.0 (CH_2), 19.7 (CH_3), 18.6 (CH_2), 13.7 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{13}H_{22}NO_2$ $[M+H]^+$: 224.1645. Found $[M+H]^+$: 224.1642.

Synthesis of (1*S,2*R**)-2-(cyclopropylethynyl)-2-methoxy-1-methylcyclobutanecarboxylic acid (1i)**



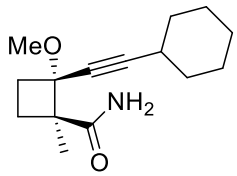
Following the general procedure, starting with compound **S4i** (0.085 g, 0.41 mmol). Purification by flash column chromatography on silica gel (30% EtOAc in Hexane) gave **1i** (0.052 g, 0.25 mmol) as yellow oil in 62 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 (bs, 2H), 3.31 (s, 3H), 2.25–2.15 (m, 1H), 2.12–2.07 (m, 2H), 1.59–1.53 (m, 1H), 1.39 (s, 3H), 1.30–1.20 (m, 1H), 0.81–0.74 (m, 2H), 0.70–0.64 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8 (C), 91.6 (C), 75.5 (C), 73.9 (C), 54.7 (C), 52.2 (CH_3), 30.9 (CH_2), 23.2 (CH_2), 19.7 (CH_3), 8.8 (CH_2), 8.7 (CH_2), -0.4 (CH).

HRMS (ESI-TOF) m/z calculated for $C_{12}H_{18}NO_2$ $[M+H]^+$: 208.1332. Found $[M+H]^+$: 208.1336.

Synthesis of (1*S,2*R**)-2-(cyclohexylethynyl)-2-methoxy-1-methylcyclobutanecarboxylic acid (1j)**



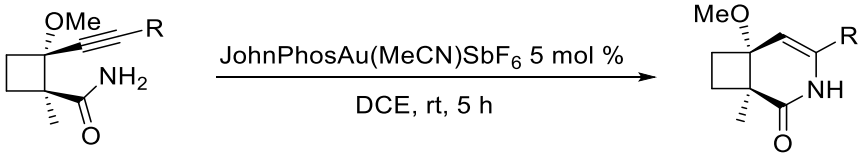
Following the general procedure, starting with compound **S4j** (0.060 g, 0.24 mmol). Purification by flash column chromatography on silica gel (30% EtOAc in Hexane) gave **1j** (0.041 g, 0.16 mmol) as yellow oil in 68 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.54-5.26 (m, 2H), 3.33 (s, 3H), 2.27-2.07 (m, 3H), 1.81-1.20 (m, 12H), 1.41 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 177.8 (C), 92.4 (C), 78.9 (C), 75.5 (C), 54.7 (C), 52.2 (CH_3), 32.7 (2xCH_2), 31.0 (CH_2), 29.7 (CH), 26.0 (CH_2), 24.8 (2xCH_2), 23.3 (CH_2), 19.7 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{15}H_{24}NO_2$ $[M+H]^+$: 250.1802. Found $[M+H]^+$: 250.1806.

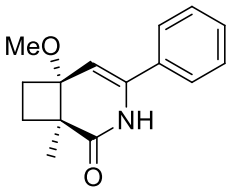
<u>Synthesis of cyclobutane-fused dihydropyridinones 2 by gold-catalyzed 6-*endo*-*dig* cyclization of 1</u>



1 **2**

To a solution of the corresponding compound **1** (1 equiv) in dry DCE (0.1 M) at room temperature was added JohnPhosAu(MeCN)SbF_6 (5 mol%) and the reaction mixture was stirred 5 h. The resulting mixture was filtered over a plug of Celite eluting with CH_2Cl_2, and solvents were removed under reduced pressure. The crude reaction mixture was purified by flash chromatography on silica gel to give the corresponding cyclobutane-fused dihydropyridinones **2**. In some particular cases, the catalyst could not be completely removed, probably due to coordination to the final product. In these cases, residual signals of the catalyst are observed in NMR spectra, mainly those due to the ligand *tert*-butyl groups (1.39 and 1.42 ppm in ^{1}H NMR and 31.0 in ^{13}C NMR)

Synthesis of (1*S,6*R**)-6-methoxy-1-methyl-4-phenyl-3-azabicyclo[4.2.0]oct-4-en-2-one (2a)**



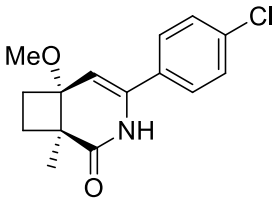
Following the general procedure, starting with compound **1a** (38.5 mg, 0.16 mmol). Purification by flash column chromatography on silica gel (20 % EtOAc in hexane) gave **2a** (34.4 mg, 0.14 mmol) as yellow oil in 89 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.48 (m, 2H), 7.47–7.40 (m, 3H), 7.17 (bs, 1H), 5.25 (s, 1H), 3.19 (s, 3H), 2.51 (td, *J* = 10.8, 9.6 Hz, 1H), 2.17 (ddd, *J* = 11.2, 8.3, 1.8 Hz, 1H), 2.00 (td, *J* = 10.8, 8.3 Hz, 1H), 1.69 (ddd, *J* = 11.2, 9.6, 1.8 Hz, 1H), 1.55 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3 (C), 138.5 (C), 135.1 (C), 129.6 (CH), 129.2 (2xCH), 125.4 (2xCH), 104.2 (CH), 75.8 (C), 51.7 (CH_3), 46.4 (C), 34.9 (CH_2), 26.8 (CH_2), 15.1 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{15}H_{18}NO_2$ $[M+H]^+$: 244.1332. Found $[M+H]^+$: 244.1329.

Synthesis of (1*S,6*R**)-4-(4-chlorophenyl)-6-methoxy-1-methyl-3-azabicyclo[4.2.0]oct-4-en-2-one (2b)**



Following the general procedure, starting with compound **1b** (10.5 mg, 0.04 mmol). Purification by flash column chromatography on silica gel (20 % EtOAc in hexane) gave **2b** (6.7 mg, 0.02 mmol) as white solid in 64 % yield.

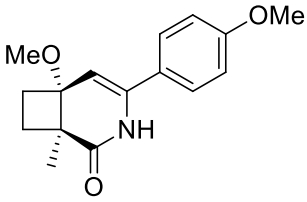
M.p.: 160–162 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.39 (m, 4H), 7.20 (bs, 1H), 5.22 (d, *J* = 1.5 Hz, 1H), 3.18 (s, 3H), 2.51 (td, *J* = 10.9, 9.7 Hz, 1H), 2.16 (ddd, *J* = 11.0, 8.3,1.9 Hz,1H), 2.02–1.94 (m, 1H), 1.69 (ddd, *J* = 11.0, 9.6, 1.9 Hz, 1H), 1.55 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8 (C), 137.6 (C), 135.6 (C), 133.6 (C), 129.5 (2xCH), 126.8 (2xCH), 104.7 (CH), 75.7 (C), 51.8 (CH_3), 46.3 (C), 34.8 (CH_2), 26.8 (CH_2), 15.1 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{15}H_{17}ClNO_2$ $[M+H]^+$: 278.0942. Found $[M+H]^+$: 278.0937.

Synthesis of (1*S,6*R**)-6-methoxy-4-(4-methoxyphenyl)-1-methyl-3-azabicyclo[4.2.0]oct-4-en-2-one (2c)**



Following the general procedure, starting with compound **1c** (21.8 mg, 0.08 mmol). Purification by flash column chromatography on silica gel (20 % EtOAc in hexane) gave **2c** (17.2 mg, 0.06 mmol) as white solid in 79 % yield.

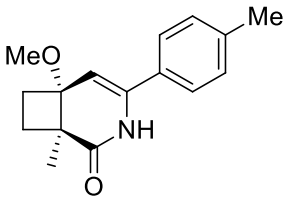
M.p.: 144–145 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.39 (m, 2H), 7.27 (bs, 1H), 6.98–6.91 (m, 2H), 5.15 (d, *J* = 1.4 Hz, 1H), 3.84 (s, 3H), 3.17 (s, 3H), 2.56–2.42 (m, 1H), 2.15 (ddd, *J* = 10.5, 8.2, 1.8 Hz, 1H), 1.98 (td, *J* = 10.5, 8.3 Hz, 1H), 1.72–1.62 (m, 1H), 1.54 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0 (C), 160.6 (C), 138.1 (C), 127.5 (C), 126.7 (2xCH), 114.5 (2xCH), 102.8 (CH), 75.8 (C), 55.6 (CH_3), 51.6 (CH_3), 46.3 (C), 34.9 (CH_2), 26.8 (CH_2), 15.1 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{16}H_{20}NO_3$ $[M+H]^+$: 274.1438. Found $[M+H]^+$: 274.1430.

Synthesis of (1*S,6*R**)-6-methoxy-1-methyl-4-(*p*-tolyl)-3-azabicyclo[4.2.0]oct-4-en-2-one (2d)**



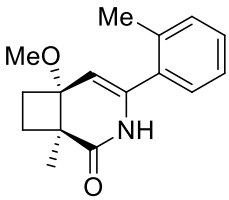
Following the general procedure, starting with compound **1d** (16.4 mg, 0.06 mmol). Purification by flash column chromatography on silica gel (30 % EtOAc in hexane) gave **2d** (16.0 mg, 0.06 mmol) as yellow oil in 98 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.36 (m, 2H), 7.26–7.21 (m, 2H), 7.17 (bs, 1H), 5.20 (d, *J* = 1.4 Hz, 1H), 3.18 (s, 3H), 2.50 (td, *J* = 10.8, 9.6 Hz, 1H), 2.39 (s, 3H), 2.16 (ddd, *J* = 10.8, 8.4, 1.9 Hz, 1H), 2.03–1.95 (m, 1H), 1.68 (ddd, *J* = 11.1, 9.6, 1.8 Hz, 1H), 1.55 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9 (C), 139.7 (C), 138.4 (C), 132.3 (C), 129.9 (2xCH), 125.2 (2xCH), 103.5 (CH), 75.8 (C), 51.7 (CH_3), 46.3 (C), 34.9 (CH_2), 26.8 (CH_2), 21.4 (CH_3), 15.1 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{16}H_{20}NO_2$ $[M+H]^+$: 258.1489. Found $[M+H]^+$: 258.1483.

Synthesis of (1*S,6*R**)-6-methoxy-1-methyl-4-(*o*-tolyl)-3-azabicyclo[4.2.0]oct-4-en-2-one (2e)**



Following the general procedure, starting with compound **1e** (12.2 mg, 0.05 mmol). Purification by flash column chromatography on silica gel (30 % EtOAc in hexane) gave **2e** (9.9 mg, 0.04 mmol) as yellow solid in 81 % yield.

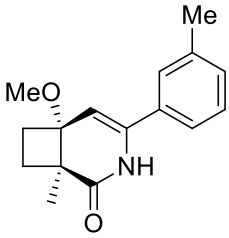
M.p.: 116–117 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.21 (m, 4H), 6.67 (bs, 1H), 4.91 (d, *J* = 1.4 Hz, 1H), 3.24 (s, 3H), 2.51 (td, *J* = 10.8, 9.7 Hz, 1H), 2.41 (s, 3H), 2.18 (ddd, *J* = 10.8, 8.4, 1.8 Hz, 1H), 2.11–2.03 (m, 1H), 1.72 (ddd, *J* = 11.3, 9.7, 1.8 Hz, 1H), 1.56 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2 (C), 138.7 (C), 135.8 (C), 135.6 (C), 131.0 (CH), 129.4 (CH), 128.8 (CH), 126.4 (CH), 105.9 (CH), 75.9 (C), 51.8 (CH_3), 46.5 (C), 34.9 (CH_2), 26.8 (CH_2), 20.0 (CH_3), 15.1 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{16}H_{20}NO_2$ $[M+H]^+$: 258.1489. Found $[M+H]^+$: 258.1484.

Synthesis of (1*S,6*R**)-6-methoxy-1-methyl-4-(*m*-tolyl)-3-azabicyclo[4.2.0]oct-4-en-2-one (2f)**



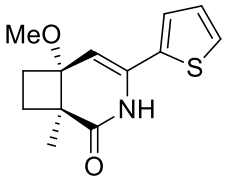
Following the general procedure, starting with compound **1f** (26.6 mg, 0.10 mmol). Purification by flash column chromatography on silica gel (30 % EtOAc in hexane) gave **2f** (16.4 mg, 0.06 mmol) as yellow oil in 62 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.27 (m, 3H), 7.25–7.20 (m, 2H), 5.23 (d, *J* = 1.4 Hz, 1H), 3.19 (s, 3H), 2.50 (td, *J* = 10.8, 9.6 Hz, 1H), 2.40 (s, 3H), 2.16 (ddd, *J* = 10.9, 8.3, 1.9 Hz, 1H), 2.03–1.95 (m, 1H), 1.68 (ddd, *J* = 11.3, 9.6, 1.9 Hz, 1H), 1.55 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9 (C), 139.0 (C), 138.6 (C), 135.1 (C), 130.3 (CH), 129.1 (CH), 126.1 (CH), 122.5 (CH), 104.0 (CH), 75.8 (C), 51.7 (CH_3), 46.4 (C), 34.9 (CH_2), 26.8 (CH_2), 21.6 (CH_3), 15.1 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{16}H_{20}NO_2$ $[M+H]^+$: 258.1489. Found $[M+H]^+$: 258.1496.

Synthesis of (1*S,6*R**)-6-methoxy-1-methyl-4-(thiophen-2-yl)-3-azabicyclo[4.2.0]oct-4-en-2-one (2g)**



Following the general procedure, starting with compound **1g** (14.4 mg, 0.06 mmol). Purification by flash column chromatography on silica gel (20 % EtOAc in hexane) gave **2g** (8.6 mg, 0.03 mmol) as yellow solid in 60 % yield.

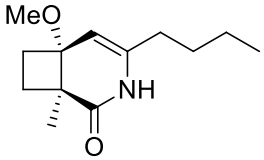
M.p.: 124–126 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (bs, 1H), 7.31 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.22 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.07 (dd, *J* = 5.1, 3.7 Hz, 1H), 5.33 (d, *J* = 1.5 Hz, 1H), 3.17 (s, 3H), 2.50 (td, *J* = 10.8, 9.6 Hz, 1H), 2.22–2.13 (m, 1H), 2.00 (td, *J* = 10.8, 8.3 Hz, 1H), 1.68 (ddd, *J* = 11.2, 9.6, 1.8 Hz, 1H), 1.54 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6 (C), 137.8 (C), 132.7 (C), 127.9 (CH), 126.0 (CH), 123.7 (CH), 103.5 (CH), 75.8 (C), 51.8 (CH_3), 46.5 (C), 34.7 (CH_2), 26.8 (CH_2), 15.1 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{13}H_{16}NO_2S$ $[M+H]^+$: 250.0896. Found $[M+H]^+$: 250.0891.

Synthesis of (1*S,6*R**)-4-butyl-6-methoxy-1-methyl-3-azabicyclo[4.2.0]oct-4-en-2-one (2h)**



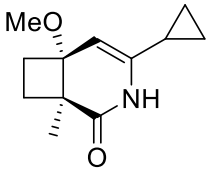
Following the general procedure, starting with compound **1h** (9.4 mg, 0.04 mmol). Purification by flash column chromatography on silica gel (5 % EtOAc in hexane) gave **2h** (8.7 mg, 0.04 mmol) as white oil in 93 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.94 (bs, 1H), 4.68 (bs, 1H), 3.09 (s, 3H), 2.47–2.35 (m, 1H), 2.20–2.11 (m, 2H), 2.05 (ddd, *J* = 10.6, 8.3, 1.8 Hz, 1H), 1.87 (td, *J* = 10.7, 8.3 Hz, 1H), 1.68–1.46 (m, 4H), 1.48 (s, 3H), 1.44–1.31 (m, 1H), 0.94 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 174.1 (C), 138.7 (C), 102.4 (CH), 75.6 (C), 51.4 (CH_3), 46.3 (C), 34.8 (CH_2), 33.4 (CH_2), 29.1 (CH_2), 26.8 (CH_2), 22.1 (CH_2), 15.0 (CH_3), 13.9 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{13}H_{22}NO_2$ $[M+H]^+$: 224.1645. Found $[M+H]^+$: 224.1640.

Synthesis of (1*S,6*R**)-6-methoxy-1-methyl-4-phenyl-3-azabicyclo[4.2.0]oct-4-en-2-one (2i)**



Following the general procedure, starting with compound **1i** (30.0 mg, 0.14 mmol). Purification by flash column chromatography on silica gel (20 % EtOAc in Hexane) gave **2i** (12.0 mg, 0.058 mmol) as a white solid in 40 % yield.

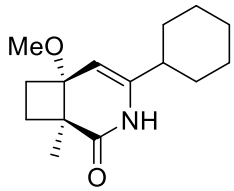
M. p.: 145–149 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.85 (bs, 1H), 4.67 (s, 1H), 3.06 (s, 3H), 2.40 (ap q, *J* = 10.3 Hz, 1H), 2.08–1.99 (m, 1H), 1.92–1.80 (m, 1H), 1.69–1.55 (m, 1H), 1.50–1.36 (m, 1H), 1.47 (s, 3H), 0.83–0.75 (m, 2H), 0.70–0.53 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7 (C), 140.1 (C), 100.9 (CH), 75.5 (C), 51.3 (CH_3), 46.5 (C), 34.8 (CH_2), 26.8 (CH_2), 15.1 (CH_3), 13.7 (CH), 5.6 (CH_2), 4.8 (CH_2).

HRMS (ESI-TOF) m/z calculated for $C_{15}H_{18}NO_2$ $[M+H]^+$: 208.1332. Found $[M+H]^+$: 208.1341.

Synthesis of (1*S,6*R**)-6-methoxy-1-methyl-4-phenyl-3-azabicyclo[4.2.0]oct-4-en-2-one (2j)**



Following the general procedure, starting with compound **1j** (30.0 mg, 0.12 mmol). Purification by flash column chromatography on silica gel (20 % EtOAc in Hexane) gave **2j** (15.3 mg, 0.061 mmol) as a white solid in 51 % yield.

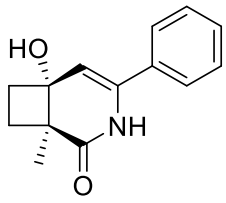
M. p.: 120–124 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (bs, 1H), 4.67 (s, 1H), 3.08 (s, 3H), 2.41 (td, *J* = 10.7, 9.6 Hz, 1H), 2.05 (ddd, *J* = 10.6, 8.3, 1.8 Hz, 1H), 1.99-1.68 (m, 5H), 1.64-1.56 (m, 1H), 1.48 (s, 3H), 1.35-1.21 (m, 7H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0 (C), 143.6 (C), 100.3 (CH), 75.5 (C), 51.3 (CH_3), 46.5 (C), 42.3 (CH), 34.9 (CH_2), 31.5 (CH_2), 31.0 (CH_2), 26.8 (CH_2), 26.3 (CH_2), 26.2 (CH_2), 26.1 (CH_2), 15.1 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{15}H_{24}NO_2$ $[M+H]^+$: 250.1802. Found $[M+H]^+$: 250.1811.

Synthesis of (1S*,6R*)-6-hydroxy-1-methyl-4-phenyl-3-azabicyclo[4.2.0]oct-4-en-2-one (4)



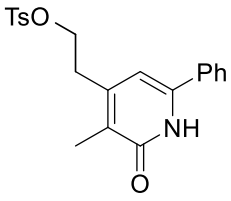
In a round bottom flask, compound **2a** (27 mg, 0.11 mmol) was dissolved in THF (1.1 mL) and hydrochloric acid (1.0M, 1.2 mL) was added. The reaction was stirred at room temperature overnight. After that, the residue was extracted with and the organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Then, the residue was dissolved in CH_2Cl_2 and filtered over a plug of Celite eluting with CH_2Cl_2, and solvent was removed under reduced pressure to give **4** (25 mg, 0.11 mmol) as white oil in 99 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.40 (m, 5H), 7.12 (bs, 1H), 5.34 (d, *J* = 1.5 Hz, 1H), 2.56–2.48 (m, 1H), 2.29 (ddd, *J* = 11.3, 8.5, 2.2 Hz, 1H), 2.00 (m, 2H), 1.73 (ddd, *J* = 11.2, 9.7, 2.2 Hz, 1H), 1.57 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6 (C), 136.6 (C), 135.1 (C), 129.6 (CH), 129.2 (2xCH), 125.5 (2xCH), 105.7 (C), 71.4 (C), 48.0 (C), 36.7 (CH_2), 26.6 (CH_2), 15.3 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{14}H_{16}NO_2$ $[M+H]^+$: 230.1176. Found $[M+H]^+$: 230.1182.

Synthesis of (1S*,6R*)-6-hydroxy-1-methyl-4-phenyl-3-azabicyclo[4.2.0]oct-4-en-2-one (5)



In a round bottom flask, compound **2a** (13.1 mg, 0.054 mmol) and *p*-toluenesulfonic acid (10.3 mg, 0.054 mmol) were dissolved in dry DCE (0.05 M) and the reaction was stirred at 110 ºC for 24 hours. Then, solvent was removed under reduced pressure. Purification of the crude reaction mixture by flash chromatography on silica gel (10 % EtOAc in hexane) gave **5** (16.1 mg, 0.042 mmol) as a yellow oil in 78 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.63 (bs, 1H), 7.71–7.63 (m, 4H), 7.51–7.42 (m, 3H), 7.25–7.21 (m, 2H), 6.23 (s, 1H), 4.25 (t, *J* = 6.7 Hz, 2H), 2.92 (t, *J* = 6.7 Hz, 2H), 2.33 (s, 3H), 2.04 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7 (C), 146.1 (C), 145.2 (C), 142.6 (C), 133.3 (C), 132.7 (C), 129.93 (CH), 129.92 (2xCH), 129.2 (2xCH), 127.9 (2xCH), 126.4 (2xCH), 125.8 (C), 106.7 (CH), 68.6 (CH_2), 33.2 (CH_2), 21.7 (CH_3), 11.9 (CH_3).

HRMS (ESI-TOF) m/z calculated for $C_{21}H_{22}NO_4S$ $[M+H]^+$: 384.1264. Found $[M+H]^+$: 384.1199.

DFT CALCULATIONS

All reported structures were optimized at Density Functional Theory level as implemented in Gaussian 16.[3] The geometry optimizations were performed using B3LYP functional[4] with 6-31G(d,p) basis set for all atoms. Higher level of single point electronic energies for those structures were calculated at M06[5]/6-311++g(d,p) level. Solvent effects were considered in all the calculations applying the polarizable continuum model[6] (IEFPCM) using dichloroethane (for amide) or dimethylformamide (for alcohol and carboxylic acid) as solvent at 298.15 and 223.15 K. Reported energy values correspond to Gibbs Free (G) energies in kcal·mol^{-1}. All structures were optimized without geometrical constraint. Stationary points were characterized by frequency calculations (no negative frequency for minimas and one negative frequency for transition states).

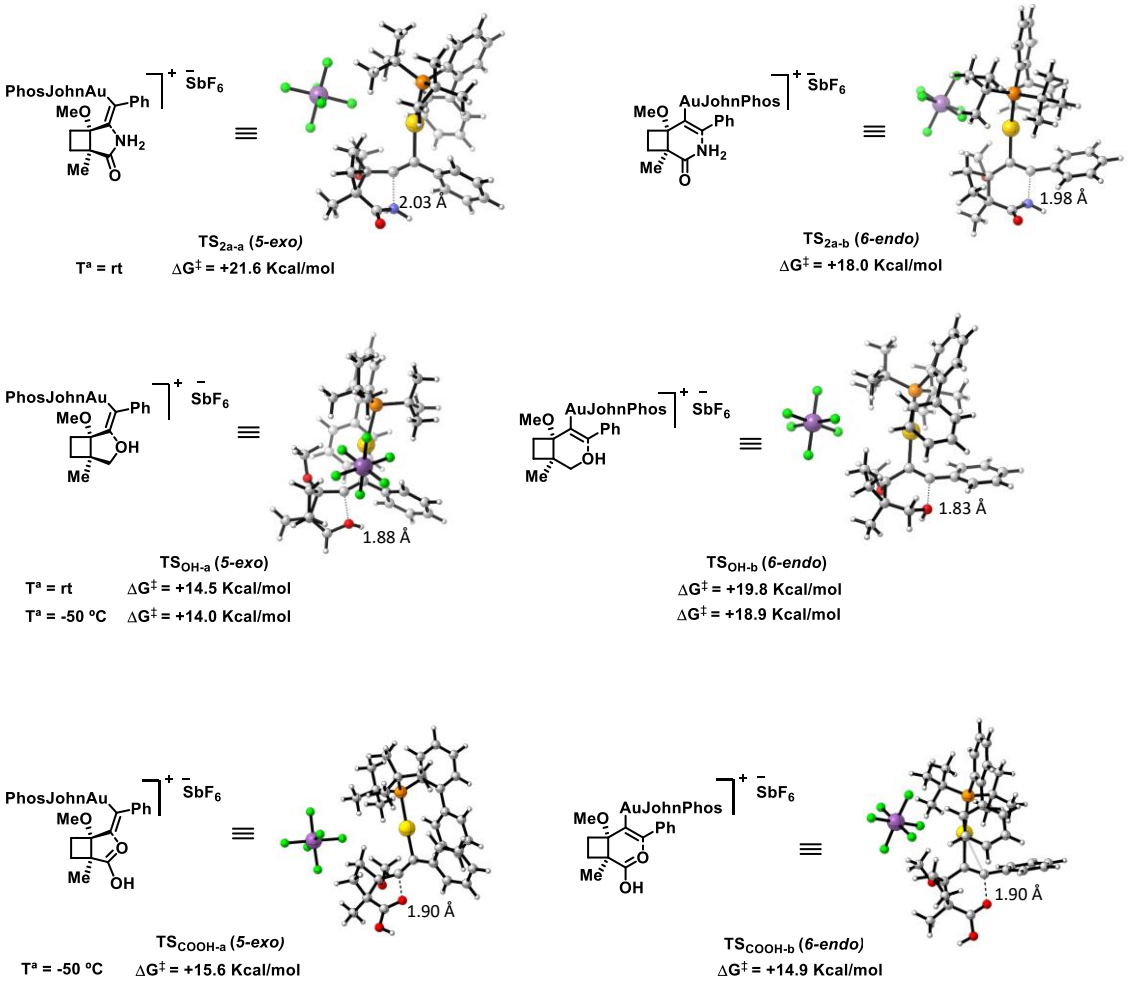


Figure S1.

[3] Gaussian 16, Revision C.01; Frisch, M. J. et al. Gaussian, Inc., Wallingford CT, 2016.

[4] a) Lee, C., Yang, W., & Parr, R. G. *Phys. Rev. B*, **1998**, *37*, 785–789. b) Becke, A. D., *J. Chem. Phys.* **1993**, *98*, 5648–5652. c) Kohn, W., Becke, A. D. & Parr, R. G. *J. Phys. Chem.* **1996**, *100*, 12974–12980.

[5] Zhao, Y. & Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

[6] (a) Cancès, E., Mennucci, B., & Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032–3047. (b) Cossi, M., Barone, V., Mennuci, B., & Tomasi, J. *Chem. Phys. Lett.*, **1998**, *286*, 253–260. (c) Tomasi, J. & Mennucci, B. E. Cancès, *J. Mol. Struct. (Theochem)*, **1999**, *464*, 211–226.

At 298.15 K:

	E (B3LYP)	Correction to G (B3LYP)	G (M02X)	Freq
2a-a	-2646,399293	0,63214	-2645,767153	-
TS_{2a-a} (*5-exo*)	-2646,365382	0,632706	-2645,732676	-370,7072
2a-b	-2646,399282	0,632571	-2645,766711	
TS_{2a-b} (*6-endo*)	-2646,374636	0,636593	-2645,738043	-371,8169
precursor-OH-a	-2592,232172	0,638800	-2591,593372	-
TS_{OH-a} (*5-exo*)	-2592,210709	0,640399	-2591,570310	-231,4537
precursor-OH-b	-2592,234522	0,636716	-2591,597806	-
TS_{OH-b} (*6-endo*)	-2592,207953	0,641626	-2591,566327	-258,7997

At 223.15 K:

	E (B3LYP)	Correction to G (B3LYP)	G (M02X)	Freq
precursor-OH-a	-2592,232172	0,672661	-2591,559511	-
TS_{OH-a} (*5-exo*)	-2592,210712	0,673502	-2591,53721	-231,4603
precursor-OH-b	-2592,234522	0,670996	-2591,563526	
TS_{OH-b} (*6-endo*)	-2592,207953	0,674532	-2591,533421	-258,8009
precursor-COOH-a	-2666,280916	0,655130	-2665,625786	-
TS_{COOH-a}(*5-exo*)	-2666,254910	0,654017	-2665,600893	-261,3451
precursor-COOH-b	-2666,277924	0,654622	-2665,623302	
TS_{COOH-b} (*6-endo*)	-2666,255256	0,655764	-2665,599492	-261,6406

The activation energies to obtain 5-*exo* or 6-*endo* product in this transformation ($\Delta G^{\ddagger}$ = +21.6 and +18.0 kcal·mol^{-1}) reflect the energy cost associated with the formation of the cycle and the notion of a late TS in which a new C–N bond is almost formed ($d_{Csp2\text{-}N}$ = 2.03 Å in TS versus $d_{Csp2\text{-}N}$ = 1.51 Å in the 5-*exo* process and $d_{Csp2\text{-}N}$ = 1.98 Å in TS versus $d_{Csp2\text{-}N}$ = 1.54 Å in the 6-*endo* process) (Fig. S2).

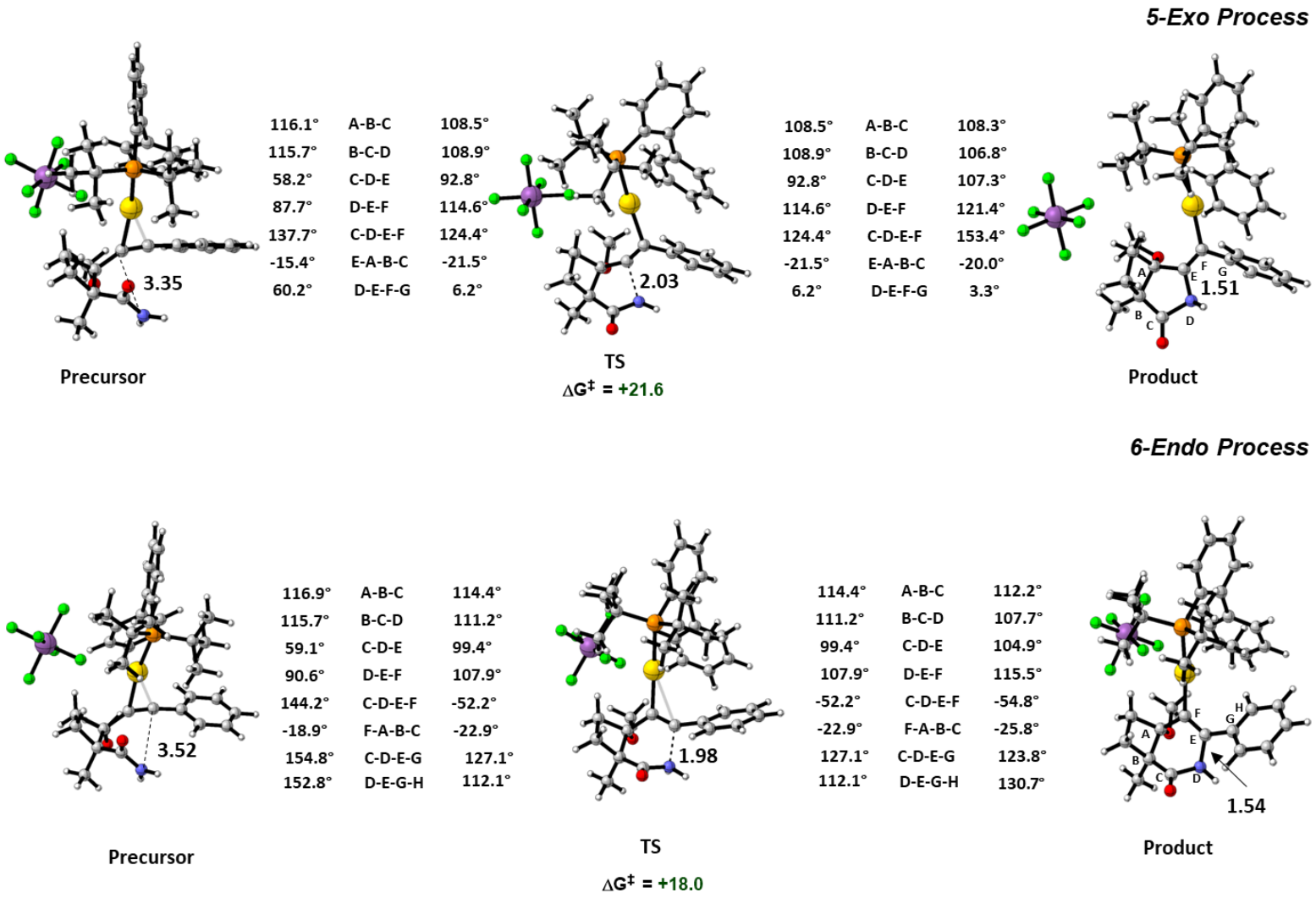
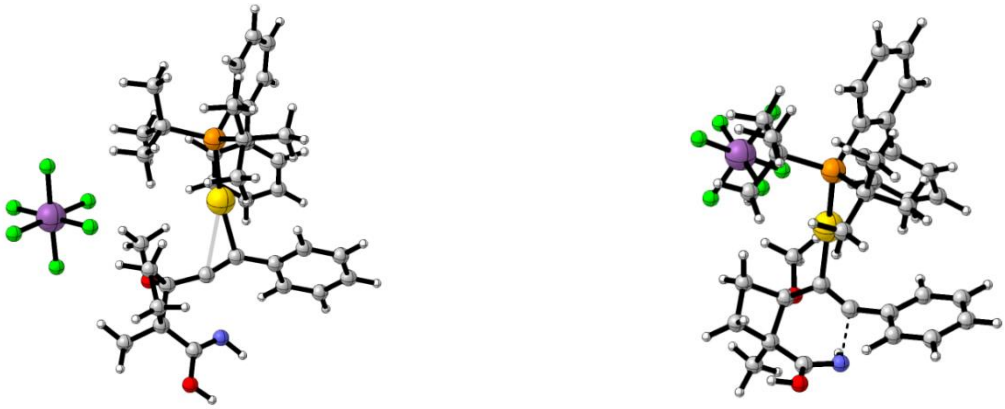


Figure S2. Selected angles and diedrals for precursors, transition states and 5-*exo* and 6-*endo* amide intermediates.

DFT calculations using the enol form of the amide

Based on DFT calculations, the 5-*exo* cyclization of enol amidate would be favored over the 6-*endo* cyclization. Experimentally the formation of 6-*endo* product is observed exclusively which seems to indicate that the transition state goes through the amide form.

On the other hand, the amide intermediate to afford the 6-membered ring is 19 kcal/mol more stable than the corresponding enol amidate.



$\Delta G^{\ddagger}$ = +3.9 kcal/mol

$\Delta G^{\ddagger}$ = +17.4 kcal/mol

Figure S3. Transition states of 5-*exo* (left) and 6-*endo* (right) cyclizations with enol amidate.

Cartesian coordinates of the computed structures:

Precursor OH-a

C	-2.14651400	2.52751100	-2.64107200
C	-1.84876500	3.75449900	-1.73195700
C	-1.90117800	2.76922200	-0.47522600
C	-2.56918000	1.70863900	-1.39969900
H	-2.90385400	2.67953900	-3.41444400
H	-1.24050700	2.13468700	-3.11416400
H	-3.64883400	1.71732100	-1.23729200
H	-2.21739800	0.68439000	-1.31642300
C	-3.01271500	4.75103400	-1.70616800
H	-2.89665300	5.48825400	-0.90675400
H	-3.05670300	5.27745300	-2.66667000
H	-3.97107500	4.25149900	-1.54934500
O	-2.67225800	3.30535000	0.57904100
C	-3.05385600	2.38570100	1.60493300
H	-2.17976900	2.02872900	2.16367000
H	-3.70288100	2.94473900	2.28236900
H	-3.59661300	1.52743700	1.19977900
O	-0.16284100	5.46546200	-1.10259700
C	1.58583200	3.16601700	1.48570400
C	2.03943200	4.45955100	1.15090400
C	2.21139700	2.44825900	2.52173900
C	3.10587400	5.01608100	1.85364100
H	1.54015500	5.00809800	0.35845400
C	3.27891100	3.01749400	3.21188000
H	1.85829300	1.45594900	2.77703400
C	3.72868600	4.29885300	2.87977700
H	3.45255600	6.01298000	1.59891900
H	3.75922000	2.46072600	4.01051500
H	4.56136900	4.73837300	3.42057500
Au	0.73721500	0.54281300	-0.25555600
P	2.00821200	-1.16975000	-1.30250600
C	3.52038800	-0.21647200	-2.05143800
C	0.86268700	-2.00470300	-2.60056000
C	-0.52969800	4.46239300	-2.04675500
H	0.29383900	3.74334900	-2.04975900
H	-0.60130600	4.88319700	-3.06158100
H	-0.77613100	6.20677300	-1.18828600
C	-0.53967900	2.43765300	0.05675200
C	0.46883000	2.62682400	0.75796500
C	4.50511300	0.01347400	-0.88467500
H	5.31291900	0.66640700	-1.23377000
H	4.02283400	0.50786600	-0.03498800
H	4.95387300	-0.91857200	-0.53356500
C	3.04480600	1.16034600	-2.56786400
H	2.31067600	1.07977500	-3.37236600
H	2.61496600	1.77104800	-1.77004400
H	3.91433900	1.69491200	-2.96691700
C	4.25186800	-0.92087700	-3.21106000
H	5.08764200	-0.28226500	-3.51894800
H	4.67874800	-1.88484600	-2.93267500
H	3.61146200	-1.05443400	-4.08587700
C	1.50701500	-3.11137900	-3.45915500
H	0.75491000	-3.45018300	-4.18067400
H	2.37278000	-2.77162400	-4.03014700
H	1.79384200	-3.98001200	-2.86394600
C	0.29762500	-0.91435400	-3.53350400
H	-0.48245500	-1.36235800	-4.15919400
H	-0.15651700	-0.08884300	-2.97755300
H	1.05886000	-0.50683900	-4.20400200
C	-0.28756200	-2.63901700	-1.79320000
H	0.07687600	-3.41543200	-1.11440800
H	-0.85454800	-1.90967900	-1.21607200
H	-0.98485600	-3.11303500	-2.49261000
C	2.73484900	-2.54900100	-0.28853500
C	2.59005600	-2.73401600	1.11226000
C	3.57092600	-3.44271100	-0.99198500
C	3.30356300	-3.78664500	1.72223000
C	4.25604200	-4.48042100	-0.36776800
H	3.70154100	-3.33031400	-2.05762100
C	4.12535500	-4.65090200	1.00799900
H	3.18400500	-3.92896800	2.79137800
H	4.88502600	-5.14091500	-0.95606000
H	4.64992100	-5.45076100	1.52156000
C	1.74037000	-1.94816800	2.06052400
C	2.35231800	-1.33633800	3.17010200
C	0.33897000	-1.96625600	1.99454900
C	1.58511900	-0.76100400	4.18396600
H	3.43612100	-1.32857200	3.24299000
C	-0.42983200	-1.39478500	3.01356000
H	-0.16711300	-2.46383300	1.17607900
C	0.18939800	-0.79266300	4.10988500
H	2.07754400	-0.29982600	5.03537800
H	-1.51079000	-1.43670500	2.94218600
H	-0.40939000	-0.35905600	4.90568500
Sb	-3.62397600	-1.76056100	0.36788700
F	-2.45223400	-3.24616800	0.48977800
F	-5.10310200	-2.91786100	0.19752200
F	-4.76164800	-0.24485600	0.25237700
F	-3.39910600	-1.71542200	-1.51271200
F	-2.11405500	-0.60876400	0.54491000
F	-3.80598600	-1.74729300	2.25543700

$TS_{OH\text{-}a}$ (*5-exo*)

C	3.67470300	1.67475700	-2.32472400
C	3.13804100	3.11677100	-2.08328400
C	1.71028300	2.48314800	-1.88081500
C	2.22739500	1.22266700	-2.64971900
H	4.41674700	1.57242900	-3.11999200
H	4.04828800	1.19670700	-1.41621800
H	2.00233200	1.32198200	-3.71420700
H	1.90731000	0.25014500	-2.28133800
C	3.25315300	4.00326900	-3.32068800
H	2.63911400	4.90253800	-3.22748400
H	4.29742200	4.30564800	-3.45524900
H	2.94181900	3.47220400	-4.22337000
O	0.67667500	3.27792400	-2.42308900
C	-0.48908400	2.58782100	-2.86668400
H	-1.02376900	2.11450900	-2.03585700
H	-1.13569700	3.34192800	-3.31968100

H	-0.24265900	1.83053700	-3.62071500
O	2.99325700	3.11371500	0.26202300
C	1.49899600	2.20354700	-0.42568900
C	0.83156500	1.65773800	0.54161700
C	1.04683200	1.93664600	1.98651500
C	1.47182000	0.93098700	2.87017300
C	0.83182400	3.23523900	2.48641800
C	1.68946900	1.22696400	4.21722700
H	1.65609800	-0.07036100	2.49669700
C	1.04518200	3.52084400	3.83725100
H	0.47117300	4.01232600	1.81846700
C	1.47566000	2.51787300	4.70809800
H	2.02986800	0.44154900	4.88623300
H	0.87234200	4.52808200	4.20512900
H	1.64223600	2.73928100	5.75794700
Au	-0.69283200	0.25212400	0.08860600
P	-2.36166700	-1.43353500	-0.22596100
C	-2.13606800	-2.73893500	1.17668700
C	-2.14395200	-2.16523300	-1.99406800
C	3.57421600	3.85881700	-0.83133800
H	4.66058600	3.86439300	-0.70456200
H	3.19334600	4.88399300	-0.82051900
H	2.72990400	3.68292300	1.00387800
Sb	3.35485000	-2.24834900	0.14075200
F	1.95278100	-1.47732600	-0.89965500
F	4.09374300	-0.51511700	0.37629700
F	4.35759500	-2.48041600	-1.44280100
F	2.53229500	-3.93781400	-0.08721000
F	4.74841500	-3.01352600	1.15809800
F	2.34790500	-2.00228000	1.73641700
C	-0.77855700	-2.87613800	-2.07355500
H	-0.58056100	-3.12644000	-3.12281100
H	0.04363800	-2.25324800	-1.71678700
H	-0.77159300	-3.81442700	-1.51210700
C	-2.13814700	-0.95034700	-2.94717400
H	-3.06537900	-0.37185400	-2.88174000
H	-1.29750700	-0.28314100	-2.74291600
H	-2.04255100	-1.31042200	-3.97814000
C	-3.24192600	-3.13703400	-2.46793600
H	-4.21373300	-2.64998000	-2.56605300
H	-2.95790000	-3.50130600	-3.46208200
H	-3.35035100	-4.01173300	-1.82348300
C	-0.62654200	-2.89614000	1.45353300
H	-0.50003900	-3.60198500	2.28331000
H	-0.06529200	-3.28637600	0.60309300
H	-0.16635200	-1.95187800	1.74925600
C	-2.79714500	-2.14876000	2.44079700
H	-2.58511600	-2.81079300	3.28808200
H	-2.39194100	-1.16120100	2.68487200
H	-3.88212500	-2.06401800	2.34313300
C	-2.72273900	-4.13632600	0.89542600
H	-2.27016800	-4.61094000	0.02186100
H	-2.50322700	-4.77537000	1.75861100
H	-3.80712900	-4.13479600	0.77355300
C	-4.14262600	-0.89057300	-0.14993400
C	-4.58648600	0.45078400	-0.02813000
C	-5.12271500	-1.89796400	-0.27610300
C	-5.96915400	0.71424300	-0.09484300
C	-6.48565800	-1.61883800	-0.31342800
H	-4.82189800	-2.93151000	-0.36023700
C	-6.91428600	-0.29564800	-0.23787800
H	-6.29714800	1.74537500	-0.00766400
H	-7.19905500	-2.43135400	-0.40922800
H	-7.97131800	-0.05065900	-0.27677900
C	-3.74891300	1.66555200	0.22759200
C	-3.24628800	1.92624600	1.51331700
C	-3.64113900	2.66358500	-0.75276500
C	-2.65565200	3.15590300	1.80971700
H	-3.35258100	1.17677900	2.29176500
C	-3.03942700	3.88949700	-0.45911900
H	-4.04730900	2.48310700	-1.74398700
C	-2.55072900	4.14137500	0.82443300
H	-2.28340300	3.34534200	2.81159400
H	-2.96873100	4.65206300	-1.22931500
H	-2.10177600	5.10218500	1.05884900

Precursor OH-b

C	1.40445200	2.83357500	1.91424300
C	0.73543800	3.95508700	1.06672500
C	0.70309100	2.92868400	-0.15457900
C	1.72785500	2.05356500	0.61908500
H	2.25480100	3.13955400	2.52889100
H	0.68185000	2.31088300	2.54846200
H	2.73942900	2.24777000	0.26325400
H	1.56784200	0.97767300	0.62118900
C	1.68991700	5.11948500	0.78354800
H	1.29005000	5.79053300	0.01813700
H	1.84274600	5.69104500	1.70621600
H	2.66464000	4.77209900	0.43442600
O	1.11906800	3.51602600	-1.36994800
C	1.50885100	2.59517100	-2.39071800
H	0.65201800	2.00542700	-2.74288500
H	1.88421200	3.19883700	-3.21944200
H	2.29564100	1.91664500	-2.04504300
O	-1.31535700	5.31232000	0.74198400
C	-3.19100000	2.50788900	-1.12970000
C	-3.83491100	3.63088500	-0.56911800
C	-3.87696700	1.70235200	-2.05771600
C	-5.14775500	3.92445800	-0.93125100
H	-3.29049200	4.26971800	0.11800400
C	-5.18994400	2.00695900	-2.40869300
H	-3.37808900	0.84902600	-2.50180900
C	-5.82938600	3.11383700	-1.84368900
H	-5.63961300	4.79103700	-0.50016000
H	-5.71262100	1.38136800	-3.12536400
H	-6.85350600	3.34735900	-2.11828000
Au	-1.11902400	0.05487800	-0.40266900
P	-1.12650500	-2.31620000	-0.54816300
C	0.68741900	-2.92379000	-0.44520100
C	-2.01420000	-2.73899000	-2.20971400
C	-0.59427100	4.45870300	1.62783900
H	-1.25873700	3.61594300	1.83342400
H	-0.39487100	4.96025800	2.58712500

H	-0.85995300	6.16295300	0.69542600
C	-0.65042200	2.31910800	-0.35759100
C	-1.82616000	2.24694900	-0.75313900
C	1.26092500	-2.32178800	0.85518900
H	2.32866100	-2.55060800	0.90636600
H	1.16656600	-1.23426800	0.88588500
H	0.77082600	-2.73704700	1.74145000
C	1.46142100	-2.37370000	-1.65988500
H	1.20365600	-2.90604300	-2.57955900
H	1.29441800	-1.30443700	-1.81041800
H	2.53085500	-2.50556100	-1.47628800
C	0.87026900	-4.45256900	-0.38081800
H	1.94681000	-4.65554100	-0.35369700
H	0.43528300	-4.88366300	0.52292100
H	0.46425900	-4.97313700	-1.25038900
C	-1.78991400	-4.16988200	-2.73813300
H	-2.32272800	-4.26419200	-3.69121200
H	-0.73700600	-4.38184000	-2.93647700
H	-2.18908700	-4.94000400	-2.07705700
C	-1.53130800	-1.75632700	-3.30044100
H	-2.12327400	-1.93016300	-4.20600100
H	-1.66296500	-0.71171700	-3.00788900
H	-0.48136200	-1.90320700	-3.55967100
C	-3.52212800	-2.51431500	-1.96586300
H	-3.93489600	-3.23498500	-1.25587400
H	-3.73368500	-1.50665400	-1.59442000
H	-4.05255600	-2.63635600	-2.91678000
C	-2.05082100	-3.20499000	0.79194500
C	-2.63501500	-2.58224000	1.92263800
C	-2.17834900	-4.60432100	0.66298000
C	-3.31559800	-3.38436400	2.85787100
C	-2.85849100	-5.37820200	1.59858100
H	-1.73315200	-5.11138400	-0.18066000
C	-3.43431400	-4.76237700	2.70763000
H	-3.75912600	-2.89947500	3.72195500
H	-2.93217100	-6.45178200	1.45706600
H	-3.96900100	-5.34618200	3.45056200
C	-2.61330100	-1.12134000	2.26207100
C	-1.62813000	-0.61103300	3.12246500
C	-3.68631500	-0.29326400	1.89490100
C	-1.71404900	0.69772000	3.60297300
H	-0.80721800	-1.24951100	3.43526200
C	-3.77084500	1.01575300	2.37521800
H	-4.46797500	-0.68577900	1.25094300
C	-2.78824700	1.51245300	3.23497500
H	-0.95323900	1.07160500	4.28196400
H	-4.61065700	1.64096200	2.08762900
H	-2.86520800	2.52272400	3.62557800
Sb	4.85542300	-0.27085500	0.01935800
F	4.56935800	-2.14099400	-0.16603900
F	6.28847600	-0.59168500	1.20855300
F	5.09434900	1.60136000	0.19854900
F	3.65609600	-0.25013300	1.48860100
F	3.42069500	0.05560900	-1.18575000
F	6.04724900	-0.30085300	-1.44733900

$TS_{OH\text{-}b}$ (*6-endo*)

C	1.49301100	3.46391000	1.56081400
C	0.67386000	4.28526000	0.51975400
C	0.63313100	2.99071300	-0.38462700
C	1.76913700	2.38826400	0.48022500
H	2.36304800	3.97189700	1.98458000
H	0.87241500	3.08745600	2.37891800
H	2.74473200	2.51464400	0.01000300
H	1.66123600	1.34528800	0.77635100
C	1.49264300	5.42331400	-0.10089900
H	1.65981500	6.20067500	0.65283500
H	2.46408800	5.07042600	-0.45286200
H	0.98264700	5.88037900	-0.95551200
O	0.92706900	3.31834300	-1.73521100
C	1.35079500	2.24286900	-2.57355700
H	0.53104100	1.54288200	-2.77783300
H	1.66976200	2.69883500	-3.51401300
H	2.18752100	1.69168000	-2.13371300
O	-1.69375000	4.60764700	-0.08102400
C	-0.69738200	2.22289200	-0.35985000
C	-1.85566300	2.81472900	-0.40714700
C	-3.27509000	2.69455200	-0.67770100
C	-4.24538300	3.22084800	0.19659100
C	-3.69137000	2.03423100	-1.85012300
C	-5.59939600	3.06829200	-0.08810900
H	-3.93331400	3.74907900	1.09023400
C	-5.04934500	1.87673400	-2.12326000
H	-2.94404800	1.64991200	-2.53548200
C	-6.00465000	2.39226900	-1.24400000
H	-6.34083100	3.47531700	0.59230500
H	-5.35973000	1.36301000	-3.02772100
H	-7.06197400	2.27533300	-1.46139400
Au	-0.83298300	0.11064000	-0.38892200
P	-1.10473500	-2.25069500	-0.61811100
C	-2.08252900	-2.48593900	-2.27258800
C	0.58900800	-3.14918900	-0.61048600
C	-0.69581200	4.78628400	0.97548500
H	-1.09610800	4.21031700	1.80946400
H	-0.69646800	5.84751300	1.23858500
H	-1.39430000	5.03964500	-0.90074500
C	1.42683900	-2.63643000	-1.79937300
H	1.45792400	-1.54537300	-1.84293000
H	2.45863300	-2.97744900	-1.66889600
H	1.06097500	-3.02291800	-2.75468000
C	1.27661500	-2.74785600	0.71046400
H	2.28685100	-3.16660200	0.72192700
H	1.38132200	-1.66656200	0.81580800
H	0.73406400	-3.14067700	1.57615600
C	0.52363400	-4.68804800	-0.65901000
H	0.03140000	-5.07233200	-1.55402600
H	1.55224700	-5.06697300	-0.66516100
H	0.02954900	-5.10700500	0.22022700
C	-2.01408300	-3.88375900	-2.91949400
H	-2.60978900	-3.85993300	-3.83951100
H	-0.99657600	-4.16098200	-3.20388800
H	-2.43288800	-4.67414900	-2.29519900
C	-1.53631600	-1.47166100	-3.30448800
H	-2.12762400	-1.56070600	-4.22328400

H	-1.61823000	-0.44201400	-2.94749400
H	-0.49213100	-1.65834400	-3.56390100
C	-3.55459600	-2.13035800	-1.97331400
H	-4.03033900	-2.86109600	-1.31514500
H	-3.65084500	-1.13972500	-1.51730600
H	-4.11052500	-2.11589200	-2.91783700
C	-2.12222000	-3.07266800	0.70671200
C	-2.58413400	-2.43735600	1.88944600
C	-2.51379500	-4.40862300	0.47921300
C	-3.43463400	-3.15751000	2.75187600
C	-3.34384100	-5.10590200	1.35217400
H	-2.16814200	-4.92481600	-0.40451500
C	-3.81802600	-4.46997000	2.49722800
H	-3.78402400	-2.66466600	3.65377700
H	-3.61694800	-6.13302200	1.13137600
H	-4.47180000	-4.98979300	3.19092700
C	-2.24898100	-1.05828100	2.37027400
C	-0.97747600	-0.75006600	2.88122800
C	-3.27218100	-0.10418300	2.50068400
C	-0.73560600	0.47893600	3.49941600
H	-0.18335200	-1.48578300	2.82524900
C	-3.02943900	1.12606600	3.11478500
H	-4.26688500	-0.33690700	2.13133600
C	-1.76078800	1.42049000	3.62017300
H	0.25093200	0.69128700	3.90121100
H	-3.83617600	1.84654000	3.21060500
H	-1.57621900	2.36884800	4.11635700
Sb	4.65581700	-0.36426300	0.15797300
F	4.40697100	-2.23153700	-0.07208400
F	3.30092100	-0.03125200	-1.13515300
F	5.94883400	-0.37390500	-1.22041800
F	5.98725400	-0.69740700	1.45669600
F	3.33844500	-0.34570100	1.52764400
F	4.90278800	1.50257800	0.37258800

2a-a

C	-1.62156600	-2.27240900	-2.95072200
C	-2.94970600	-2.41118100	-2.16396100
C	-2.07213700	-2.56004700	-0.83579600
C	-0.85044100	-2.86070500	-1.74602800
H	-1.56913900	-2.82599200	-3.89158400
H	-1.38059600	-1.22640800	-3.13954800
H	-0.73446000	-3.94454900	-1.82609500
H	0.10405300	-2.42598000	-1.46814600
C	-3.69112500	-3.71200500	-2.50887400
H	-4.46659600	-3.96386300	-1.78197000
H	-4.15826400	-3.61104600	-3.49379700
H	-2.99603200	-4.55364500	-2.54736000
O	-2.53795300	-3.59275900	-0.00075500
C	-1.62009200	-4.01617700	1.01323600
H	-1.52420200	-3.25869500	1.80054300
H	-2.04166900	-4.92703300	1.44235500
H	-0.62661800	-4.22523800	0.60396100
C	-3.23697700	0.13703900	1.87738300
C	-3.85778700	1.37893300	1.64003200
C	-3.36917200	-0.48023900	3.13683200
C	-4.59308300	1.99178300	2.65091500
H	-3.75914700	1.84832900	0.66747000
C	-4.11697300	0.13748200	4.13621700
H	-2.89013300	-1.43605800	3.31811300
C	-4.72464600	1.37369400	3.89849300
H	-5.06887100	2.94941800	2.46428700
H	-4.22174300	-0.34469600	5.10302700
H	-5.30229600	1.85332600	4.68266800
C	-2.52046900	-0.54316300	0.83749300
C	-2.03448900	-1.29234600	-0.02584600
Au	-0.74126500	0.56252600	-0.25761700
P	0.52745200	2.37043800	-1.12751100
C	-0.66355500	3.86208800	-1.39892100
C	1.28245400	1.68382100	-2.76490200
C	-3.88150900	-1.19596400	-2.22406300
O	-3.60696500	-0.18801400	-2.87730500
N	-5.03304600	-1.30066700	-1.51267200
H	-5.22609700	-2.08636600	-0.91148900
H	-5.64754200	-0.50081500	-1.46432900
C	1.93731100	0.33885800	-2.38980000
H	2.68751600	0.43487900	-1.60102900
H	1.20088600	-0.39772500	-2.06419800
H	2.43720900	-0.06652000	-3.27687200
C	2.34790700	2.55272700	-3.46194600
H	2.60186400	2.06293000	-4.40888600
H	2.00014500	3.55924700	-3.70463800
H	3.26765800	2.62408100	-2.87937300
C	0.13400300	1.42651100	-3.76324800
H	-0.70800300	0.89367400	-3.31355400
H	-0.23932400	2.35172400	-4.20986000
H	0.52177100	0.80562400	-4.57883800
C	-0.10429500	4.94985400	-2.33582000
H	0.08423200	4.57692900	-3.34521300
H	-0.85200400	5.74683400	-2.42032100
H	0.80847500	5.40849300	-1.95042000
C	-2.00923300	3.36127000	-1.96450200
H	-2.44483100	2.57531300	-1.34227700
H	-2.70935800	4.20435000	-1.98517600
H	-1.92574800	2.97862100	-2.98220700
C	-0.92480100	4.47795100	-0.00867900
H	-1.35986400	3.74903300	0.68093000
H	-0.01575800	4.88547500	0.44091400
H	-1.64145100	5.29937300	-0.12025700
C	1.92891300	3.01514000	-0.09221600
C	2.21420900	2.61219900	1.23852800
C	2.77985200	3.96688600	-0.69391800
C	3.37300400	3.11880300	1.85755100
C	3.90489200	4.47432900	-0.05083700
H	2.57151400	4.32216200	-1.69170600
C	4.21766700	4.02918900	1.23112500
H	3.59141300	2.79523300	2.87040100
H	4.52997300	5.20405500	-0.55584600
H	5.09878400	4.39803100	1.74729900
C	1.37444700	1.74709600	2.13030300
C	0.27333600	2.30002700	2.80683500
C	1.79724700	0.45495200	2.47227000
C	-0.39143900	1.57321600	3.79555800

H	-0.03896700	3.31513500	2.58360500
C	1.12621900	-0.27420300	3.45619000
H	2.64098300	0.01169400	1.95823000
C	0.03574000	0.28396900	4.12480300
H	-1.23631600	2.01721200	4.31373500
H	1.46727000	-1.27829600	3.68565600
H	-0.47778600	-0.27837700	4.89919700
Sb	2.74881200	-2.69192900	0.27681600
F	3.67094200	-1.02936100	0.18916600
F	4.37776800	-3.62652200	0.10669600
F	1.78317700	-4.32147200	0.35141200
F	2.54344100	-2.65810700	-1.60872100
F	2.92398200	-2.67812600	2.16353600
F	1.09360100	-1.75897300	0.45463100

TS_{2a-a} (*5-exo*)

C	-2.30767200	2.78879200	-2.06536000
C	-2.15531700	3.93723500	-1.01932300
C	-1.65423000	2.86936200	0.01306000
C	-2.25626800	1.76154200	-0.90332400
H	-3.22715000	2.81855900	-2.65283000
H	-1.45407600	2.71693000	-2.74312900
H	-3.24465200	1.48477500	-0.53949300
H	-1.66056400	0.86151300	-1.04507600
C	-3.48017200	4.62331800	-0.67230700
H	-3.79975700	5.23547400	-1.52087000
H	-4.25226200	3.87670500	-0.47272500
H	-3.39339100	5.26247400	0.20985900
O	-2.15918600	3.10715300	1.30530100
C	-2.02531100	2.02680000	2.23739300
H	-2.57560500	1.14739500	1.89687000
H	-0.97217000	1.76334500	2.39448700
H	-2.44744100	2.38797800	3.17720100
C	-1.04531900	4.94012200	-1.24825800
O	-0.80821700	5.57469100	-2.25002100
C	-0.16119700	2.90139700	-0.01011800
C	1.01322600	2.36882500	-0.04794300
C	2.32505400	3.05367100	-0.02826800
C	3.28013000	2.81333900	-1.03082900
C	2.63369100	3.96743700	0.99552800
C	4.49981200	3.49009100	-1.02345300
H	3.05657600	2.10630100	-1.82278500
C	3.86237200	4.62979700	1.00719200
H	1.91679800	4.14092800	1.79180400
C	4.79771800	4.39762400	-0.00362900
H	5.22019900	3.30340600	-1.81442200
H	4.08620700	5.32831000	1.80815100
H	5.75157900	4.91617400	0.00495400
Au	1.08248500	0.23803300	-0.25877600
P	1.54828000	-2.00770100	-0.91382700
C	2.24747100	-1.82300700	-2.71193200
C	0.01108800	-3.14884500	-0.80825900
N	-0.17400200	4.93338300	-0.11236800
H	0.67830700	5.47685200	-0.22432700
C	2.23593800	-3.09194300	-3.58754800
H	1.22280900	-3.44769700	-3.78698800
H	2.68340400	-2.83742400	-4.55539800
H	2.82321100	-3.91394700	-3.17640900
C	1.41269200	-0.74999900	-3.44969900
H	0.36451700	-1.03628700	-3.55989800
H	1.44826600	0.21731700	-2.94209200
H	1.82861000	-0.62037600	-4.45565200
C	3.69611600	-1.30759500	-2.57530400
H	3.75372300	-0.41249800	-1.94739800
H	4.36529900	-2.06286800	-2.15694300
H	4.06901600	-1.04084200	-3.57076000
C	0.25343700	-4.61728500	-1.20988000
H	-0.69812100	-5.15101000	-1.10466200
H	0.57947800	-4.73798000	-2.24386100
H	0.97418300	-5.11028200	-0.55382900
C	-1.10264000	-2.55196400	-1.69060700
H	-2.04004000	-3.07056900	-1.47361800
H	-1.27415400	-1.49463800	-1.47960800
H	-0.88713600	-2.67044500	-2.75637300
C	-0.43338100	-3.13643000	0.66946100
H	0.30616700	-3.62647000	1.31026300
H	-0.62304100	-2.12688300	1.03498500
H	-1.37653700	-3.68544000	0.75045000
C	2.87497500	-2.84485100	0.08524200
C	3.40841800	-4.04402600	-0.43128100
C	3.42273400	-2.33758000	1.29285200
C	4.45451000	-4.72416500	0.18548400
H	3.00459300	-4.46224700	-1.34212500
C	4.48987200	-3.03511300	1.89206800
C	5.00794000	-4.20914400	1.35552900
H	4.83135500	-5.64364500	-0.25140400
H	4.90410300	-2.64057300	2.81465300
H	5.82841100	-4.71815500	1.85212100
C	2.97587800	-1.12279100	2.04778900
C	3.85374200	-0.03498300	2.19068700
C	1.77362300	-1.11339500	2.77365100
C	3.53095000	1.03958300	3.02111500
H	4.79772800	-0.03878800	1.65317600
C	1.45292600	-0.03994800	3.60795600
H	1.10069600	-1.96054100	2.70962900
C	2.32992700	1.03985300	3.73414000
H	4.22104400	1.87247200	3.11410500
H	0.52404200	-0.05841200	4.17065800
H	2.08471000	1.86883200	4.39161300
H	-0.63025800	5.10007200	0.78384000
Sb	-4.36094000	-1.34182300	0.43028400
F	-3.82504400	-3.14051300	0.14644400
F	-4.70580800	-1.72848800	2.24702700
F	-6.13707500	-1.77219500	-0.04096800
F	-3.96651000	-0.93346500	-1.37803400
F	-2.57071700	-0.87880300	0.89614500
F	-4.85933500	0.46938900	0.72088100

2a-b

C	0.90887400	-3.55996200	-1.12496500
C	-0.55144000	-4.07864700	-1.12549500
C	-0.70054400	-3.44916900	0.33117600

C	0.84906500	-3.41795600	0.41420100
H	1.65880500	-4.24351100	-1.52879200
H	0.99714200	-2.59658400	-1.62444900
H	1.19899900	-4.32051400	0.92154000
H	1.32164600	-2.54942100	0.86254100
C	-0.61215600	-5.61503700	-1.09095100
H	-1.59672400	-5.99586600	-0.80985400
H	-0.35839900	-6.00702300	-2.08119200
H	0.10856900	-6.01531600	-0.37450100
O	-1.40137900	-4.29783800	1.21228400
C	-1.21677100	-4.01848200	2.59913300
H	-1.61376000	-3.03190300	2.86762600
H	-1.76776300	-4.78680700	3.14430300
H	-0.15788300	-4.06648700	2.88047400
C	-3.78481800	-0.98357900	0.67074600
C	-4.70448500	-1.02674600	-0.39808100
C	-4.18874300	-0.47528400	1.92174000
C	-6.00519200	-0.56834000	-0.21183700
H	-4.38751100	-1.42446400	-1.35579500
C	-5.49314000	-0.02140300	2.09530800
H	-3.47519500	-0.43813200	2.73720300
C	-6.40039300	-0.06503300	1.03185000
H	-6.71201300	-0.60465700	-1.03471500
H	-5.80368900	0.36733100	3.05993700
H	-7.41604400	0.29187200	1.17257200
C	-2.46343200	-1.49965400	0.48505500
C	-1.38869200	-2.10721300	0.31183300
Au	-0.75087900	-0.01890500	-0.2443360
P	-0.40400600	2.17847200	-1.11753100
C	-2.15260600	2.80288900	-1.62927600
C	0.82443300	2.07899800	-2.60980800
C	-1.46636800	-3.51795100	-2.21862500
O	-1.05581100	-2.76438200	-3.10175600
N	-2.76616800	-3.90961800	-2.15599200
H	-3.11541700	-4.51919500	-1.43349300
H	-3.40844300	-3.58547300	-2.86424800
C	2.25976400	2.26070400	-2.07280800
H	2.46370400	3.29274200	-1.78053100
H	2.47780300	1.61256500	-1.22551900
H	2.95850600	1.99658400	-2.87473100
C	0.57871600	3.09207500	-3.74712300
H	1.35258900	2.93077800	-4.50626800
H	-0.38640800	2.94815700	-4.23762600
H	0.65691700	4.13502400	-3.43442100
C	0.69486800	0.65949100	-3.20775200
H	1.00693000	-0.10388500	-2.49356900
H	-0.32114900	0.43513100	-3.54190300
H	1.35382900	0.59071700	-4.08139500
C	-2.18850500	4.24563600	-2.17088700
H	-1.61987600	4.37517600	-3.09182000
H	-3.23193000	4.49638200	-2.39443200
H	-1.83115500	4.96854900	-1.43434500
C	-2.74068300	1.83717700	-2.67767600
H	-2.73802300	0.80176000	-2.32452000
H	-3.78080500	2.12174200	-2.87384900
H	-2.20639000	1.87689400	-3.63013400
C	-3.02369000	2.75811700	-0.35545000
H	-3.10095400	1.75006000	0.05747100
H	-2.63988700	3.42385200	0.42278000
H	-4.03459900	3.09500800	-0.61217000
C	0.21908600	3.48460400	0.04500700
C	0.24044200	3.37584600	1.45914300
C	0.61917800	4.70615500	-0.53465500
C	0.64529500	4.49579700	2.21146700
C	1.03048900	5.79496700	0.22817800
H	0.60545900	4.81971000	-1.61000300
C	1.03894300	5.69023800	1.61733200
H	0.66069100	4.40532300	3.29309100
H	1.33546600	6.71342300	-0.26339400
H	1.35244000	6.52675400	2.23441700
C	-0.12113600	2.17495200	2.27893900
C	-1.25199100	2.22340300	3.10997100
C	0.74140100	1.07064300	2.37539500
C	-1.52187300	1.18945400	4.00953900
H	-1.91249900	3.08467000	3.06357700
C	0.47269800	0.03979400	3.28067100
H	1.64584600	1.03423700	1.77967900
C	-0.65857400	0.09435400	4.09821800
H	-2.39564300	1.25083400	4.65241000
H	1.16481100	-0.79284100	3.34236400
H	-0.85753400	-0.70155600	4.81030000
Sb	3.82684000	-0.79485000	0.26711600
F	3.72695800	1.03291200	0.78343700
F	4.54532700	-0.28663700	-1.40337100
F	3.84310500	-2.61280400	-0.24945000
F	2.06812100	-0.62025000	-0.47542200
F	5.54566300	-0.94206300	1.02609700
F	3.03224500	-1.27869100	1.92633400

$TS_{2a\text{-}b}$ (*6-endo*)

C	-1.84544200	-3.49590500	-2.29567900
C	-2.66529600	-3.76492100	-1.00641900
C	-1.55563900	-2.97020600	-0.19356000
C	-0.61090700	-3.18923700	-1.40864900
H	-1.76496500	-4.33413500	-2.99089100
H	-2.20526700	-2.61745700	-2.83707200
H	0.01245700	-4.07299700	-1.25171900
H	0.02613300	-2.35295700	-1.68755900
C	-2.72819900	-5.26203200	-0.64783800
H	-3.11411200	-5.43340000	0.36033400
H	-3.37588300	-5.77805500	-1.36307400
H	-1.73159700	-5.70434600	-0.69972500
O	-1.26804500	-3.61527800	1.02524000
C	-0.01121400	-3.28450700	1.62393200
H	0.06891500	-3.90184000	2.52125400
H	0.82420000	-3.50745000	0.95670500
H	0.02843900	-2.22944100	1.90625500
C	-4.04318900	-3.17615300	-0.91514100
O	-4.83746100	-3.00379600	-1.81497300
C	-1.93519200	-1.50208500	0.06036900
C	-3.12038900	-1.11039700	0.41555500
C	-4.01003800	-0.03443100	0.80882600
C	-5.04644200	0.38592700	-0.04856000

C	-3.84645900	0.58992000	2.05885900
C	-5.89360500	1.42102400	0.33769300
H	-5.18160700	-0.10395800	-1.00804800
C	-4.69418400	1.63189200	2.43257900
H	-3.04772600	0.26610400	2.71686900
C	-5.71747200	2.04676300	1.57664900
H	-6.68908000	1.74237200	-0.32726700
H	-4.55785900	2.11639400	3.39435400
H	-6.37920500	2.85456200	1.87401900
Au	-0.68821800	0.19316200	-0.28994200
P	0.28766000	2.18158300	-1.19469000
C	-1.22767100	3.24681900	-1.72723100
C	1.41635300	1.69419600	-2.69201000
N	-4.31145200	-2.69199400	0.40291900
H	-5.27865300	-2.41507600	0.55570000
H	-3.93314800	-3.24869500	1.16755200
Sb	3.54172500	-1.94592500	0.27298100
F	3.99147300	-0.13122900	0.62320800
F	2.74658100	-2.04227100	1.99534600
F	1.87931700	-1.35759400	-0.46112300
F	3.00313800	-3.73035900	-0.07024200
F	5.18493500	-2.52935100	0.99027800
F	4.30272500	-1.80952800	-1.45092100
C	-2.07173700	2.44708800	-2.74066000
H	-2.34688600	1.46268800	-2.34971700
H	-2.99701000	2.99947700	-2.94216400
H	-1.56002800	2.30902800	-3.69650800
C	-2.06381300	3.46854900	-0.44783100
H	-2.95451300	4.05281200	-0.70698200
H	-2.39430600	2.52477400	-0.00611500
H	-1.50753400	4.02942900	0.30887300
C	0.89109000	0.34867100	-3.24450900
H	1.49155300	0.07570700	-4.12060400
H	0.99585600	-0.44653200	-2.50512700
H	-0.15347700	0.40199200	-3.56298400
C	1.45657800	2.69524800	-3.86535000
H	2.13697600	2.29238400	-4.62456400
H	0.48220400	2.82107700	-4.34266300
H	1.83808800	3.68096800	-3.59357600
C	2.84889400	1.47057000	-2.16282600
H	2.88061200	0.79141400	-1.31037000
H	3.44283300	1.01697000	-2.96500800
H	3.33598300	2.40538400	-1.87763300
C	1.27268600	3.33135500	-0.11567500
C	1.30578700	3.28308300	1.30072200
C	1.96905300	4.37520600	-0.75933900
C	2.01386800	4.28628800	1.99189200
C	2.67686500	5.34653000	-0.05785900
H	1.95577500	4.44260900	-1.83817100
C	2.69469700	5.30530400	1.33464000
H	2.03450200	4.24133800	3.07631700
H	3.20211100	6.12735800	-0.59902000
H	3.23603200	6.05398000	1.90509500
C	0.66972300	2.25603300	2.18655000
C	-0.38385000	2.63486100	3.03425900
C	1.22931200	0.97703800	2.33441500
C	-0.87236600	1.75643000	4.00376400
H	-0.80810700	3.63104500	2.94564700
C	0.74998100	0.10560000	3.31633200
H	2.06783400	0.67360800	1.71720400
C	-0.30159200	0.48988000	4.15170400
H	-1.68243700	2.07132400	4.65578600
H	1.22250400	-0.86396800	3.42681300
H	-0.66310200	-0.18600400	4.92165900
C	-0.88454800	4.62909600	-2.31489300
H	-1.82451500	5.14202000	-2.55025700
H	-0.34267000	5.25407200	-1.60180200
H	-0.30620600	4.57265900	-3.23777600

Precursor COOH-a

C	3.97713700	2.07106200	-1.44471700
C	2.89317500	3.17553800	-1.32483800
C	1.79866100	2.05440200	-1.63288400
C	2.96452100	1.17237600	-2.18896800
H	4.88261300	2.35536300	-1.98569100
H	4.25221300	1.64643000	-0.47889800
H	3.02077200	1.29983500	-3.27300000
H	2.95656800	0.11588500	-1.94393300
C	2.97960000	4.21785900	-2.45149700
H	3.86677800	4.84147200	-2.29908400
H	3.06640000	3.73307500	-3.42571300
H	2.09606400	4.85821000	-2.45872600
O	0.82314800	2.50110200	-2.53442300
C	0.13815700	1.48660500	-3.26080400
H	0.83465000	0.83626500	-3.80317200
H	-0.48411500	0.87169100	-2.59797000
H	-0.50807000	1.99976700	-3.97451900
C	2.73733800	3.92431100	-0.01403700
O	1.78703600	4.63388000	0.26060400
C	1.22270600	1.51639200	-0.35017000
C	1.28150800	1.35047500	0.88020100
C	1.43909000	1.32466200	2.30386000
C	1.93738600	0.17649600	2.95319700
C	1.12690000	2.47945700	3.05200100
C	2.11332800	0.19202000	4.33440800
H	2.17651800	-0.70337200	2.36836500
C	1.31135500	2.47939000	4.43190500
H	0.76239400	3.36282500	2.53908700
C	1.80041000	1.33710100	5.07402300
H	2.49742300	-0.69058200	4.83618300
H	1.07613100	3.36968400	5.00649400
H	1.94098200	1.34082300	6.15064700
Au	-0.58726200	0.17644400	0.00698300
P	-2.50842700	-1.21616600	0.16690900
C	-2.63628800	-1.88245700	1.97345500
C	-2.30026700	-2.61435100	-1.14770500
C	-3.48819800	-3.15920400	2.11845300
H	-3.08318300	-4.00229000	1.55524100
H	-3.48817300	-3.44729000	3.17580900
H	-4.53082700	-3.01044600	1.83174900
C	-1.21525900	-2.16596500	2.50284400
H	-0.66239900	-2.88771200	1.90175900
H	-0.62202600	-1.24989200	2.55630400

H	-1.30052000	-2.56706100	3.51967000
C	-3.25360000	-0.76260700	2.83595200
H	-2.65528500	0.15222900	2.79585900
H	-4.27925400	-0.52532300	2.54327000
H	-3.27000700	-1.09834300	3.87894300
C	-3.54351900	-3.48350700	-1.42275300
H	-3.24742400	-4.26264800	-2.13427000
H	-3.92381900	-3.98982700	-0.53314900
H	-4.35486900	-2.91657900	-1.88212000
C	-1.14194200	-3.53714700	-0.71904200
H	-0.90768500	-4.20140900	-1.55865500
H	-0.23186800	-2.99323200	-0.47350600
H	-1.41413500	-4.17244800	0.12773500
C	-1.91975400	-1.90067300	-2.46416200
H	-2.66503500	-1.15521300	-2.76032700
H	-0.94238400	-1.41855300	-2.39199200
H	-1.86405300	-2.64885200	-3.26329700
C	-4.13454500	-0.39062600	-0.19912600
C	-5.28064100	-1.21388600	-0.18616000
C	-4.30521000	0.97898000	-0.52953600
C	-6.54354800	-0.74427700	-0.53452200
H	-5.19402300	-2.25316800	0.09254500
C	-5.58631000	1.42422800	-0.91095400
C	-6.69441000	0.58415800	-0.92509200
H	-7.39433200	-1.41765300	-0.50698900
H	-5.70577400	2.47130500	-1.17081600
H	-7.66615900	0.97042400	-1.21705200
C	-3.28310800	2.06803500	-0.43597200
C	-2.86852100	2.54248200	0.82004200
C	-2.90095500	2.78108300	-1.58331200
C	-2.09141600	3.69751200	0.92376700
H	-3.19447800	2.03064300	1.71911700
C	-2.11463100	3.92991800	-1.47891100
H	-3.23540900	2.44002300	-2.55889600
C	-1.71202000	4.39517300	-0.22527600
H	-1.79733200	4.05953900	1.90462900
H	-1.82623200	4.46669400	-2.37739200
H	-1.10254900	5.28914500	-0.14394400
Sb	2.87703900	-2.53110000	-0.42869700
F	1.71777300	-2.65756700	1.07832200
F	2.19779500	-4.16815500	-1.08595400
F	4.22947000	-3.44239900	0.52078700
F	3.51097300	-0.87556900	0.25667600
F	1.50390300	-1.62585100	-1.40701000
F	4.00316600	-2.33005500	-1.93370300
O	3.77703000	3.74883500	0.82341800
H	3.60483600	4.28583800	1.61711700

$TS_{COOH\text{-}a}$ (*5-exo*)

C	-2.41960400	2.92667500	-1.42699600
C	-2.11057500	3.84832000	-0.18978400
C	-1.29552200	2.66396200	0.41373800
C	-2.05644000	1.70181800	-0.55181800
H	-3.44670100	2.99215800	-1.78867300
H	-1.73009700	3.07919800	-2.26017100
H	-2.93211400	1.28449400	-0.06189500
H	-1.47061700	0.90673800	-1.01074900
C	-3.36201500	4.25966000	0.58087400
H	-3.91834000	5.00447300	0.00531800
H	-4.00539700	3.38994400	0.73337000
H	-3.11193700	4.67991300	1.55736800
O	-1.44999700	2.57190600	1.80691600
C	-1.17955100	1.29495400	2.39182800
H	-1.85748800	0.52991300	2.00130300
H	-0.13963100	0.98984500	2.22815000
H	-1.34796900	1.41488500	3.46409500
C	-1.13536500	4.95622200	-0.42661300
O	0.07869800	4.71274300	-0.31241500
C	0.12993900	2.84072600	-0.00694200
C	1.28762600	2.33259500	-0.27732800
C	2.54861800	3.02794400	-0.61370000
C	3.32325500	2.61922200	-1.71360000
C	3.00505800	4.10249200	0.17078700
C	4.50722100	3.28370500	-2.03520000
H	2.98807000	1.78528100	-2.32215000
C	4.19933400	4.75099800	-0.14234300
H	2.42216500	4.42140400	1.02787000
C	4.95310800	4.34822900	-1.24807000
H	5.08525100	2.96257600	-2.89684500
H	4.53931900	5.57536900	0.47784200
H	5.88077600	4.85734000	-1.49186700
Au	1.31880000	0.19631600	-0.28403300
P	1.48467400	-2.15177600	-0.65312400
C	1.89887000	-2.33399100	-2.53372400
C	-0.14769500	-3.02543800	-0.14326400
C	1.60968300	-3.71164700	-3.16248500
H	0.55030700	-3.97444100	-3.12084000
H	1.88860300	-3.66582400	-4.22159700
H	2.19098100	-4.52139800	-2.71944600
C	1.08325000	-1.28033700	-3.31920900
H	0.00571400	-1.43832800	-3.24113700
H	1.30237800	-0.26210400	-2.98706200
H	1.35380300	-1.35549400	-4.37878800
C	3.39867500	-2.00236000	-2.68961000
H	3.65077300	-1.03441400	-2.24391700
H	4.03911100	-2.76482900	-2.24039200
H	3.63639200	-1.94875000	-3.75806100
C	-0.11998500	-4.56434000	-0.21886300
H	-1.11045500	-4.93135100	0.07384500
H	0.08193000	-4.94271700	-1.22270400
H	0.60518000	-4.99872300	0.47244500
C	-1.29236400	-2.49347800	-1.02646500
H	-2.24881400	-2.83924200	-0.62607600
H	-1.33216100	-1.40272100	-1.04083800
H	-1.21418400	-2.85439200	-2.05572200
C	-0.40067500	-2.62608400	1.32577500
H	0.37431600	-3.02339300	1.98853500
H	-0.45315500	-1.54282700	1.45275800
H	-1.36272000	-3.04137000	1.64242600
C	2.84769800	-3.02281500	0.26427300
C	3.11418600	-4.36107700	-0.09415800
C	3.67205800	-2.42129900	1.24973600
C	4.15686300	-5.09179100	0.46796600

H	2.49739100	-4.85236300	-0.83263200
C	4.72837500	-3.17509000	1.79702100
C	4.97860600	-4.49000400	1.41849600
H	4.32249100	-6.11903200	0.15882300
H	5.35556900	-2.70610900	2.54881700
H	5.80186400	-5.03771000	1.86690300
C	3.54152100	-1.04008400	1.81747400
C	4.51119900	-0.06891000	1.51721300
C	2.58089900	-0.74974800	2.79933400
C	4.51003300	1.16597400	2.16883800
H	5.27650900	-0.29105100	0.77894000
C	2.58431900	0.48345300	3.45584600
H	1.84683400	-1.50138700	3.07064700
C	3.54823400	1.44476800	3.14281900
H	5.26605400	1.90516900	1.92185800
H	1.84213800	0.68500000	4.22276700
H	3.55569400	2.39935100	3.66052700
Sb	-4.90052600	-1.03945400	0.18314400
F	-4.66430900	-2.89195900	-0.13918000
F	-5.81633300	-1.41568000	1.79270300
F	-6.52935600	-1.04554200	-0.77334400
F	-3.96866300	-0.64833900	-1.42127700
F	-3.25817600	-1.02064900	1.14239900
F	-5.07951400	0.82528200	0.51281700
O	-1.59144200	6.14254100	-0.75053500
H	-0.85026400	6.76181100	-0.88778700

Precursor COOH-b

C	1.84917400	-3.79693400	1.26474500
C	2.84598600	-3.66586800	0.07558600
C	1.76498600	-2.75380800	-0.65181200
C	0.70699800	-3.34089300	0.32564500
H	1.76221400	-4.79010000	1.71142400
H	2.02559800	-3.06043700	2.05513300
H	0.19154000	-4.18190200	-0.14080600
H	-0.03317600	-2.65673700	0.72798500
C	3.05188000	-5.00253900	-0.66122300
H	3.64985800	-5.67485400	-0.03720900
H	2.09536900	-5.48712800	-0.86612500
H	3.57119800	-4.84487000	-1.60800800
O	1.66456500	-3.04201500	-2.02154600
C	0.44820200	-2.64915300	-2.66113000
H	0.36953100	-1.55715200	-2.72158400
H	0.49369200	-3.05861000	-3.67211000
H	-0.42936300	-3.04363900	-2.14095000
O	4.74309400	-3.15214000	1.54357500
C	2.03741500	-1.28665700	-0.44089100
C	2.82837500	-0.33975300	-0.28247400
C	3.86278100	0.63981500	-0.14259800
C	4.22968100	1.11585500	1.13168200
C	4.54389000	1.09939700	-1.28812800
C	5.26703000	2.03648200	1.25219300
H	3.69709200	0.76285200	2.00797400
C	5.57801700	2.02116400	-1.15343900
H	4.25875600	0.72578600	-2.26587600
C	5.93993600	2.49060400	0.11346000
H	5.55112500	2.40077900	2.23429500
H	6.10376600	2.37224000	-2.03558400
H	6.74718400	3.20963700	0.21321900
Au	0.60171600	0.47182600	-0.45508700
P	-0.73115700	2.41855900	-0.78761700
C	0.51212700	3.82029500	-1.22910000
C	-2.01295800	2.07053800	-2.19517900
H	4.12186300	-3.58510500	2.14904000
C	-1.40564800	0.98306600	-3.11067700
H	-1.28305300	0.04085900	-2.57374600
H	-2.09457900	0.80758200	-3.94515700
H	-0.44151600	1.27758600	-3.53390000
C	-3.29720000	1.50537300	-1.55299200
H	-3.94067900	1.12652700	-2.35521900
H	-3.09905800	0.67541400	-0.87528500
H	-3.85762800	2.26903400	-1.01002000
C	-2.37722600	3.28251600	-3.07715300
H	-1.52182100	3.66724200	-3.63646600
H	-3.11854800	2.94786600	-3.81171100
H	-2.83047600	4.10792800	-2.52518700
C	-0.12692800	5.20946300	-1.42314100
H	0.67664800	5.92241200	-1.64034400
H	-0.82879400	5.24876400	-2.25622100
H	-0.63429200	5.55667600	-0.52057100
C	1.28468800	3.41948900	-2.50192100
H	2.07218700	4.16008100	-2.68176300
H	1.76403900	2.44171300	-2.39759100
H	0.64786000	3.39915300	-3.38987700
C	1.49903300	3.91798400	-0.04555900
H	0.99337700	4.20276000	0.88150800
H	2.03710000	2.98275600	0.12573000
H	2.23817000	4.69467300	-0.27251300
C	-1.66782400	3.07293300	0.67327600
C	-1.46349000	2.66713100	2.01601500
C	-2.60109700	4.09980000	0.42137700
C	-2.18977500	3.31820800	3.03181400
C	-3.31853500	4.71993500	1.43983100
H	-2.77380500	4.43234000	-0.59311900
C	-3.10697600	4.32831500	2.76022500
H	-2.02748400	3.00388000	4.05813500
H	-4.03019400	5.50302200	1.19822400
H	-3.65156500	4.80051200	3.57213500
C	-0.54237400	1.58941400	2.50399600
C	-0.91666900	0.23713800	2.44483900
C	0.62522900	1.93810400	3.20167100
C	-0.13886600	-0.74011800	3.07275300
H	-1.83019200	-0.05196100	1.93789100
C	1.40742100	0.95867300	3.81838500
H	0.91051400	2.98336400	3.27782300
C	1.02437300	-0.38386800	3.75954300
H	-0.46246900	-1.77426700	3.02858500
H	2.30155800	1.24878800	4.36297100
H	1.61945900	-1.14343600	4.25843800
Sb	-3.15570300	-2.36007300	0.04609800
F	-3.87137200	-0.81168800	0.88370100
F	-1.66924900	-1.30392900	-0.53612000
F	-4.04764100	-1.91702800	-1.55890300

F	-4.62012800	-3.39929600	0.61828300
F	-2.22677200	-2.75264900	1.65565000
F	-2.35358600	-3.86319000	-0.78594300
C	4.22259200	-3.06037800	0.30001400
O	4.87669900	-2.54975700	-0.58530900

$TS_{COOH\text{-}b}$ (*6-endo*)

C	1.36980000	-3.92793700	1.17335500
C	2.28820600	-3.98245300	-0.10020700
C	1.39255600	-2.82107100	-0.69377700
C	0.28649000	-3.22524100	0.32266800
H	1.13103500	-4.90005200	1.60944000
H	1.77455100	-3.27161800	1.94715400
H	-0.42325000	-3.93020100	-0.11364800
H	-0.26800200	-2.41440700	0.78630900
C	2.10285300	-5.30187700	-0.86927400
H	2.41456700	-6.16287200	-0.26512400
H	1.04907800	-5.45642000	-1.10000900
H	2.65164600	-5.30508000	-1.81348400
O	1.18887500	-3.03107200	-2.07303200
C	-0.01612000	-2.52116600	-2.64374200
H	-0.00057700	-1.42736800	-2.68841900
H	-0.05909100	-2.92045600	-3.65964100
H	-0.89997300	-2.84182100	-2.08503400
O	4.59778800	-4.68152900	0.33219600
C	1.90189900	-1.40355400	-0.44554200
C	3.09606000	-1.04986200	-0.11239700
C	4.10148000	-0.02499700	0.06434800
C	4.59232200	0.29526500	1.34307100
C	4.62095900	0.63374700	-1.06564800
C	5.57072900	1.27570500	1.48744700
H	4.19989400	-0.22392700	2.21063400
C	5.59800400	1.61576100	-0.91289700
H	4.24967700	0.37216100	-2.05118100
C	6.07283000	1.93740000	0.36173300
H	5.94376700	1.52408900	2.47612800
H	5.99200600	2.12512000	-1.78673700
H	6.83653700	2.70037400	0.47849200
Au	0.69291900	0.35960300	-0.54648200
P	-0.38669000	2.47591800	-0.82353800
C	1.02870800	3.67901000	-1.33127400
C	-1.77837300	2.34605300	-2.16527800
H	4.16415500	-5.54479700	0.23550100
C	-1.40176300	1.17743000	-3.10334800
H	-1.40342600	0.22893800	-2.56491900
H	-2.15108700	1.11550900	-3.90155600
H	-0.42528300	1.31384000	-3.57626000
C	-3.10422700	1.98817500	-1.45992200
H	-3.84169200	1.73403700	-2.23043200
H	-3.00866200	1.12366300	-0.80227300
H	-3.50384100	2.82353200	-0.88141000
C	-1.99033400	3.60010400	-3.03799000
H	-1.11001300	3.84933600	-3.63442000
H	-2.80451200	3.38506300	-3.73976800
H	-2.28789700	4.48509800	-2.47283300
C	0.61784400	5.15356600	-1.50787500
H	1.51490300	5.72564100	-1.77221200
H	-0.11035500	5.30661900	-2.30487700
H	0.22082200	5.58127200	-0.58476100
C	1.67262900	3.16048100	-2.63363000
H	2.56142500	3.76360200	-2.85237100
H	1.98975700	2.11725500	-2.54142600
H	1.00289200	3.24318300	-3.49362100
C	2.07083300	3.61396400	-0.19318600
H	1.65867700	3.97544100	0.75347000
H	2.45261200	2.60104300	-0.04220600
H	2.91724900	4.25921700	-0.45534900
C	-1.15691500	3.28489900	0.66262700
C	-1.00268200	2.84370600	2.00032600
C	-1.90864600	4.45650700	0.43364300
C	-1.59364300	3.60015700	3.03159400
C	-2.49422300	5.18283600	1.46610000
H	-2.04174100	4.81957500	-0.57601600
C	-2.33177700	4.75213000	2.78128100
H	-1.46882500	3.25597700	4.05365500
H	-3.06709700	6.07653700	1.23922500
H	-2.77582500	5.30350100	3.60452700
C	-0.26312300	1.62878100	2.47621600
C	-0.87377600	0.36480800	2.48013000
C	0.97829600	1.78204800	3.11456600
C	-0.25502800	-0.71696400	3.11283300
H	-1.84156500	0.22496700	2.01154400
C	1.60058200	0.69717300	3.73592800
H	1.44721700	2.76148600	3.14229000
C	0.98159100	-0.55538300	3.74211700
H	-0.75643400	-1.67854600	3.11368100
H	2.55618700	0.83777200	4.23293400
H	1.45319600	-1.39489700	4.24508100
Sb	-3.51492600	-1.92763500	0.14661000
F	-4.03052000	-0.31640400	1.01184200
F	-1.95424800	-1.03421800	-0.48878000
F	-4.42063800	-1.38840500	-1.42219500
F	-5.06415600	-2.80486700	0.76910600
F	-2.58449000	-2.43999600	1.72046900
F	-2.91549500	-3.50813100	-0.71648900
C	3.74072200	-3.68767500	0.15292500
O	4.21653800	-2.54744600	0.24469500

Precursor $TS_{Amidate}$ (*5-exo*)

C	-1.70418500	3.11261600	-2.00812200
C	-1.05553600	4.13199800	-1.02893600
C	-1.00113700	2.95243600	0.04750200
C	-2.05021900	2.19557200	-0.81156300
H	-2.54075400	3.49437900	-2.59854100
H	-0.97378900	2.66133600	-2.68127400
H	-3.05296300	2.36500700	-0.41915800
H	-1.90875000	1.12408400	-0.93229800
C	-2.04320100	5.22687900	-0.60001300
H	-2.21831900	5.90172700	-1.44471400
H	-3.00173400	4.79813700	-0.30001700
H	-1.64001800	5.80537100	0.23168600
O	-1.34300800	3.38116000	1.33837400

C	-1.75154700	2.34903000	2.24166800
H	-2.61931600	1.80410300	1.86255700
H	-0.93344900	1.64261100	2.43060300
H	-2.00930300	2.85251400	3.17554600
C	0.27051700	4.77022800	-1.40331800
O	0.66642600	4.44188600	-2.66402000
C	0.35914400	2.31152500	0.07584100
C	1.60054000	2.33404900	0.08343900
C	3.00650100	2.61198000	0.14097700
C	3.88824800	2.14088700	-0.85001100
C	3.49559100	3.42615900	1.18195900
C	5.23927500	2.47362000	-0.79336700
H	3.50560500	1.52290300	-1.65455800
C	4.84740200	3.75807200	1.22347200
H	2.81218500	3.79426500	1.93889900
C	5.72102700	3.28022100	0.24187600
H	5.91565400	2.10700200	-1.55904000
H	5.21973800	4.38956400	2.02393000
H	6.77467300	3.53871000	0.28186000
Au	0.86795000	0.10305900	-0.21847000
P	1.15229000	-2.14459100	-0.94342400
C	1.93681400	-1.97376700	-2.70718900
C	-0.50501900	-3.10564300	-0.93727800
N	0.88825000	5.51817300	-0.57762800
H	1.77336000	5.86565300	-0.95616500
C	1.77627200	-3.19091000	-3.64061600
H	0.73175300	-3.38084700	-3.89634100
H	2.30077300	-2.96712400	-4.57660000
H	2.21422700	-4.10866700	-3.24621700
C	1.28101000	-0.76468100	-3.41463800
H	0.20324700	-0.88705800	-3.54378100
H	1.45459700	0.17092700	-2.87709200
H	1.72516500	-0.66685500	-4.41185500
C	3.43777900	-1.67617800	-2.50743000
H	3.60342400	-0.84438200	-1.81560700
H	3.98415000	-2.54405700	-2.13187500
H	3.87120900	-1.39672400	-3.47430300
C	-0.40128900	-4.57472900	-1.39405800
H	-1.40706000	-5.00682500	-1.34260000
H	-0.05162400	-4.69002300	-2.42046200
H	0.23805900	-5.16622900	-0.73503300
C	-1.50876700	-2.35429600	-1.83359000
H	-2.50589300	-2.77091900	-1.66923100
H	-1.57047800	-1.29205000	-1.58776500
H	-1.26692300	-2.45733700	-2.89524400
C	-1.00468500	-3.10764200	0.52220000
H	-0.33971600	-3.68904700	1.16805300
H	-1.12041900	-2.10043700	0.92286600
H	-1.99527500	-3.57144200	0.54494100
C	2.33483200	-3.14319400	0.08236800
C	2.76681800	-4.36859800	-0.46667900
C	2.86863900	-2.74562200	1.33648300
C	3.70311000	-5.18093200	0.16582200
H	2.37027200	-4.70220800	-1.41520700
C	3.82512700	-3.57792500	1.95049900
C	4.24495800	-4.77672200	1.38386600
H	4.00483300	-6.11586200	-0.29565100
H	4.22973600	-3.26944200	2.90930700
H	4.98083500	-5.39045300	1.89430500
C	2.51440600	-1.52235800	2.12577500
C	3.50164900	-0.55509400	2.37915500
C	1.27744600	-1.40390300	2.78121300
C	3.25317500	0.50946700	3.24746900
H	4.47190900	-0.64619000	1.89935200
C	1.03038200	-0.33999300	3.65163400
H	0.51706300	-2.16174700	2.63579000
C	2.01653700	0.62102300	3.88674500
H	4.02926900	1.24663200	3.42778300
H	0.07153800	-0.27435800	4.15744500
H	1.82659900	1.44253700	4.57108600
Sb	-4.51205200	-0.64638200	0.39550900
F	-4.23441100	-2.49148100	0.04830400
F	-4.96591600	-1.05136700	2.18390700
F	-6.31517400	-0.79780500	-0.14068400
F	-4.00403500	-0.24253800	-1.38660200
F	-2.68929600	-0.46392500	0.92775400
F	-4.76379900	1.20380500	0.74946100
H	1.50712300	4.88225400	-2.86551100

E(RM06) = -2646.36787593
Zero-point correction= 0.724934 (Hartree/Particle)
Thermal correction to Energy= 0.778867
Thermal correction to Enthalpy= 0.779811
Thermal correction to Gibbs Free Energy= 0.632447
Sum of electronic and zero-point Energies= -2646.424907
Sum of electronic and thermal Energies= -2646.370974
Sum of electronic and thermal Enthalpies= -2646.370030
Sum of electronic and thermal Free Energies= -2646.517395

$TS_{Amidate}$ (*5-exo*)

C	-2.37970600	2.83204000	-1.53945800
C	-2.10293500	3.82975100	-0.36983500
C	-1.30145100	2.68884500	0.35848200
C	-2.05108000	1.67044500	-0.57374000
H	-3.38967800	2.85830700	-1.95265600
H	-1.65370100	2.92437100	-2.35130700
H	-2.93697200	1.29120500	-0.07194900
H	-1.46136500	0.83979400	-0.95935500
C	-3.39047100	4.21280900	0.37006100
H	-3.97447900	4.88894300	-0.26002100
H	-3.99389000	3.32673300	0.57955200
H	-3.17179500	4.71228700	1.31669800
O	-1.53007600	2.68622500	1.74724300
C	-1.27592700	1.45304700	2.42366400
H	-1.91286500	0.64957300	2.04110800
H	-0.22157700	1.16098900	2.34574800
H	-1.51326500	1.63326400	3.47431500
C	-1.25315800	5.03323300	-0.67928200
O	-1.91460700	5.98881700	-1.36077500
C	0.13666300	2.72224400	0.03107400
C	1.32711000	2.37268900	-0.21932800
C	2.61749700	3.02672300	-0.46078000
C	3.49401900	2.56226900	-1.45622300
C	2.98581600	4.14671200	0.30654700

C	4.70360200	3.21527900	-1.69205200
H	3.21721900	1.69652400	-2.04907500
C	4.20336700	4.78567600	0.07590100
H	2.31330300	4.50525800	1.07711900
C	5.06451400	4.32515100	-0.92421500
H	5.36621200	2.85267800	-2.47226600
H	4.47903700	5.64642200	0.67814900
H	6.01086600	4.82692300	-1.10248500
Au	1.27243100	0.19447000	-0.27376700
P	1.47779200	-2.12735600	-0.71741600
C	1.91675400	-2.23464600	-2.59853300
C	-0.14385000	-3.04276100	-0.25383000
N	-0.03778200	5.03960300	-0.29982300
H	0.51049400	5.85821700	-0.56359500
C	1.63723100	-3.59019400	-3.27863600
H	0.57726500	-3.85290800	-3.26324700
H	1.93334300	-3.50780200	-4.33070700
H	2.21070000	-4.41574600	-2.85470100
C	1.10460000	-1.15561300	-3.35242000
H	0.02626800	-1.30855500	-3.27517600
H	1.33222600	-0.14801300	-2.99389400
H	1.37150100	-1.20340500	-4.41446200
C	3.41672500	-1.89362100	-2.72841300
H	3.66393700	-0.94458700	-2.24108100
H	4.05621900	-2.67212400	-2.30652300
H	3.66189600	-1.79481700	-3.79192700
C	-0.08204200	-4.57704700	-0.38621600
H	-1.06626600	-4.97421900	-0.11331700
H	0.13244800	-4.91356200	-1.40214700
H	0.64824300	-5.02132400	0.29343800
C	-1.28842000	-2.49993000	-1.12994000
H	-2.24132000	-2.87827800	-0.75165600
H	-1.35144800	-1.41086800	-1.10318100
H	-1.19294700	-2.82035400	-2.17107700
C	-0.41824000	-2.70434100	1.22647400
H	0.35418900	-3.11903800	1.88148400
H	-0.49104300	-1.62819400	1.39682200
H	-1.37827300	-3.14446000	1.51327400
C	2.85014900	-2.99109400	0.18995100
C	3.15504100	-4.30673500	-0.21803900
C	3.64731600	-2.40689900	1.20794000
C	4.21138600	-5.03135300	0.32570400
H	2.55839400	-4.78378100	-0.98215400
C	4.71907700	-3.15384800	1.73448800
C	5.00826700	-4.44529200	1.30669100
H	4.40695000	-6.04114700	-0.02107600
H	5.32509300	-2.69943100	2.51205300
H	5.84175700	-4.98824000	1.74175400
C	3.47017100	-1.05651000	1.83284700
C	4.44154300	-0.06245400	1.62785200
C	2.45844200	-0.82232100	2.77823700
C	4.39247000	1.14026800	2.33510100
H	5.24458900	-0.24096500	0.91842300
C	2.41518000	0.37769200	3.49179300
H	1.72221100	-1.59324600	2.97894900
C	3.38086800	1.36267000	3.27200000
H	5.14938800	1.89858400	2.15919500
H	1.63505700	0.53432000	4.23093000
H	3.35060200	2.29168700	3.83346100
Sb	-4.81979300	-1.08780400	0.26160600
F	-4.54460700	-2.93904200	-0.04246900
F	-5.63948500	-1.46264800	1.92176100
F	-6.49106200	-1.15585000	-0.61407500
F	-3.97347100	-0.69729500	-1.39039600
F	-3.12944000	-1.00830400	1.13396400
F	-5.03311600	0.77648700	0.57194800
H	-1.32862400	6.73914800	-1.54927600

E(RM06) = -2646.36203643
Zero-point correction= 0.724414 (Hartree/Particle)
Thermal correction to Energy= 0.777504
Thermal correction to Enthalpy= 0.778448
Thermal correction to Gibbs Free Energy= 0.632810
Sum of electronic and zero-point Energies= -2646.419707
Sum of electronic and thermal Energies= -2646.366618
Sum of electronic and thermal Enthalpies= -2646.365674
Sum of electronic and thermal Free Energies= -2646.511312
Frequency: -187.1267

Precursor $TS_{Amidate}$ (*6-endo*)

C	-1.96265500	-3.17635900	-2.25191600
C	-3.01015800	-3.37268800	-1.11225700
C	-1.89408500	-2.84393000	-0.10270100
C	-0.83812500	-3.18925200	-1.18910800
H	-1.93763000	-3.95203700	-3.02071000
H	-2.02422300	-2.19539800	-2.73586500
H	-0.44507800	-4.19214300	-1.01560400
H	-0.00530700	-2.50288900	-1.30753400
C	-3.30598600	-4.86664900	-0.88744100
H	-3.83291400	-5.03298300	0.05410100
H	-3.93124300	-5.23633900	-1.70636900
H	-2.38646900	-5.45470600	-0.86588400
O	-1.88672900	-3.55162700	1.10665500
C	-0.70787200	-3.37981400	1.90142800
H	-0.80773700	-4.06517200	2.74505100
H	0.19754500	-3.62027300	1.33833800
H	-0.63503700	-2.35348300	2.27924700
C	-4.32815900	-2.60769200	-1.13617700
O	-4.65645500	-1.96849600	-2.29041800
C	-2.06436300	-1.36723300	0.16464700
C	-2.75424400	-0.42294300	0.58883800
C	-3.68626700	0.57216900	1.02619100
C	-4.72530800	0.97017900	0.15905100
C	-3.59660800	1.12653600	2.31758500
C	-5.65491300	1.91379600	0.58570900
H	-4.80141300	0.52050900	-0.82457000
C	-4.53440400	2.06899800	2.73088700
H	-2.79269100	0.81973200	2.97669000
C	-5.56046200	2.46515200	1.86776100
H	-6.45749500	2.21597800	-0.07958900
H	-4.46546700	2.49502000	3.72679800
H	-6.28908400	3.20055600	2.19508800
Au	-0.66805500	0.36964200	-0.26054200
P	0.56538700	2.15343100	-1.23670300

C	-0.76871000	3.44333900	-1.74852800
C	1.54696600	1.43183400	-2.74227200
N	-5.15355500	-2.51490100	-0.17129500
H	-4.79568100	-3.02110400	0.63912500
Sb	3.10275200	-2.40538600	0.31125800
F	3.97832200	-0.75944700	0.67102200
F	2.39740500	-2.40587600	2.07295900
F	1.58150900	-1.38652600	-0.26220300
F	2.13274900	-3.99272800	-0.05694500
F	4.60577400	-3.38616000	0.88197200
F	3.73811900	-2.36607000	-1.46738700
C	-1.76810700	2.77637400	-2.71530100
H	-2.19767800	1.86449000	-2.28870800
H	-2.59036900	3.47516100	-2.90695300
H	-1.31859100	2.52931100	-3.68048300
C	-1.51131200	3.83740600	-0.45293100
H	-2.28337100	4.57373100	-0.70389900
H	-2.00360500	2.98174800	0.01626200
H	-0.84021300	4.29675600	0.27845500
C	0.77730600	0.18775700	-3.24368700
H	1.30138200	-0.21368300	-4.11887200
H	0.75001400	-0.59577800	-2.48439800
H	-0.24633500	0.42060700	-3.54922800
C	1.72248300	2.38565300	-3.94239800
H	2.29930800	1.85392200	-4.70766100
H	0.77020200	2.66832100	-4.39647000
H	2.27739200	3.29528000	-3.70642800
C	2.93550900	0.98012800	-2.24086600
H	2.87770900	0.33257600	-1.36571800
H	3.41594500	0.40627400	-3.04144200
H	3.58328500	1.82630100	-2.00352300
C	1.76304800	3.11822900	-0.19865000
C	1.83775800	3.08102500	1.21664400
C	2.60468300	4.01688900	-0.88669200
C	2.73556800	3.95377600	1.86282600
C	3.49548100	4.85852800	-0.22803200
H	2.56386000	4.07175900	-1.96560700
C	3.55788300	4.83040300	1.16343400
H	2.78895300	3.91937000	2.94639100
H	4.12760900	5.52932000	-0.80122100
H	4.24215200	5.47964200	1.70104800
C	1.06441400	2.19521800	2.14472100
C	0.13490200	2.77053400	3.02682300
C	1.38838400	0.83750500	2.29540000
C	-0.46095300	2.00804000	4.03343300
H	-0.10407000	3.82642700	2.93638900
C	0.79645200	0.07784200	3.30851900
H	2.13410200	0.38078400	1.65554700
C	-0.12822900	0.65878400	4.17961700
H	-1.16976000	2.47361100	4.71241800
H	1.08562700	-0.96170100	3.41562700
H	-0.57481500	0.06908700	4.97520700
C	-0.20749200	4.72995000	-2.38449600
H	-1.05148800	5.39024600	-2.61446700
H	0.45179200	5.27003300	-1.70178900
H	0.32751300	4.55020400	-3.31743700
H	-3.99060000	-2.14794500	-2.96808400

E(RM06) = -2646.36884733
Zero-point correction= 0.724932 (Hartree/Particle)
Thermal correction to Energy= 0.778901
Thermal correction to Enthalpy= 0.779845
Thermal correction to Gibbs Free Energy= 0.632661
Sum of electronic and zero-point Energies= -2646.429877
Sum of electronic and thermal Energies= -2646.375908
Sum of electronic and thermal Enthalpies= -2646.374964
Sum of electronic and thermal Free Energies= -2646.522149

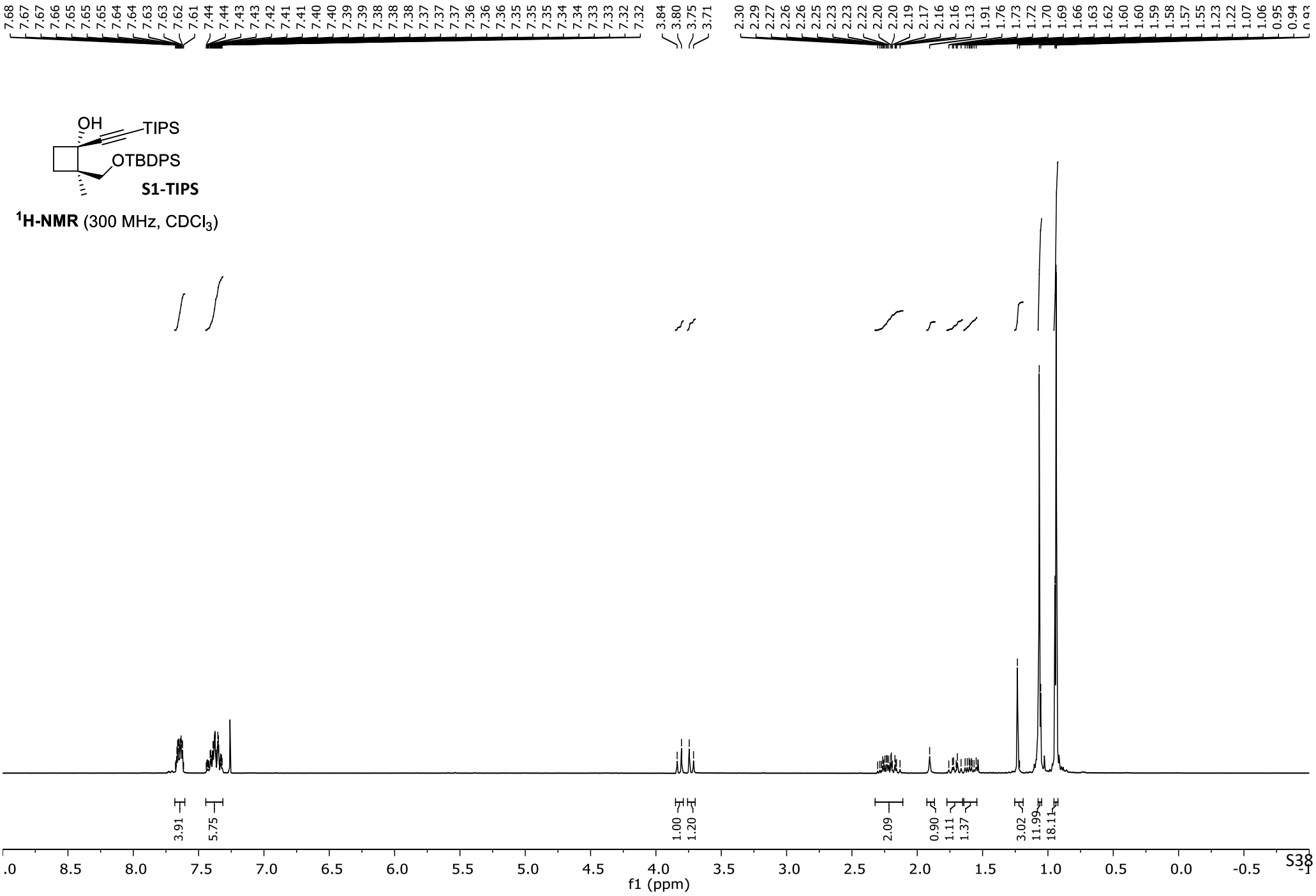
$TS_{Amidate}$ (*6-endo*)

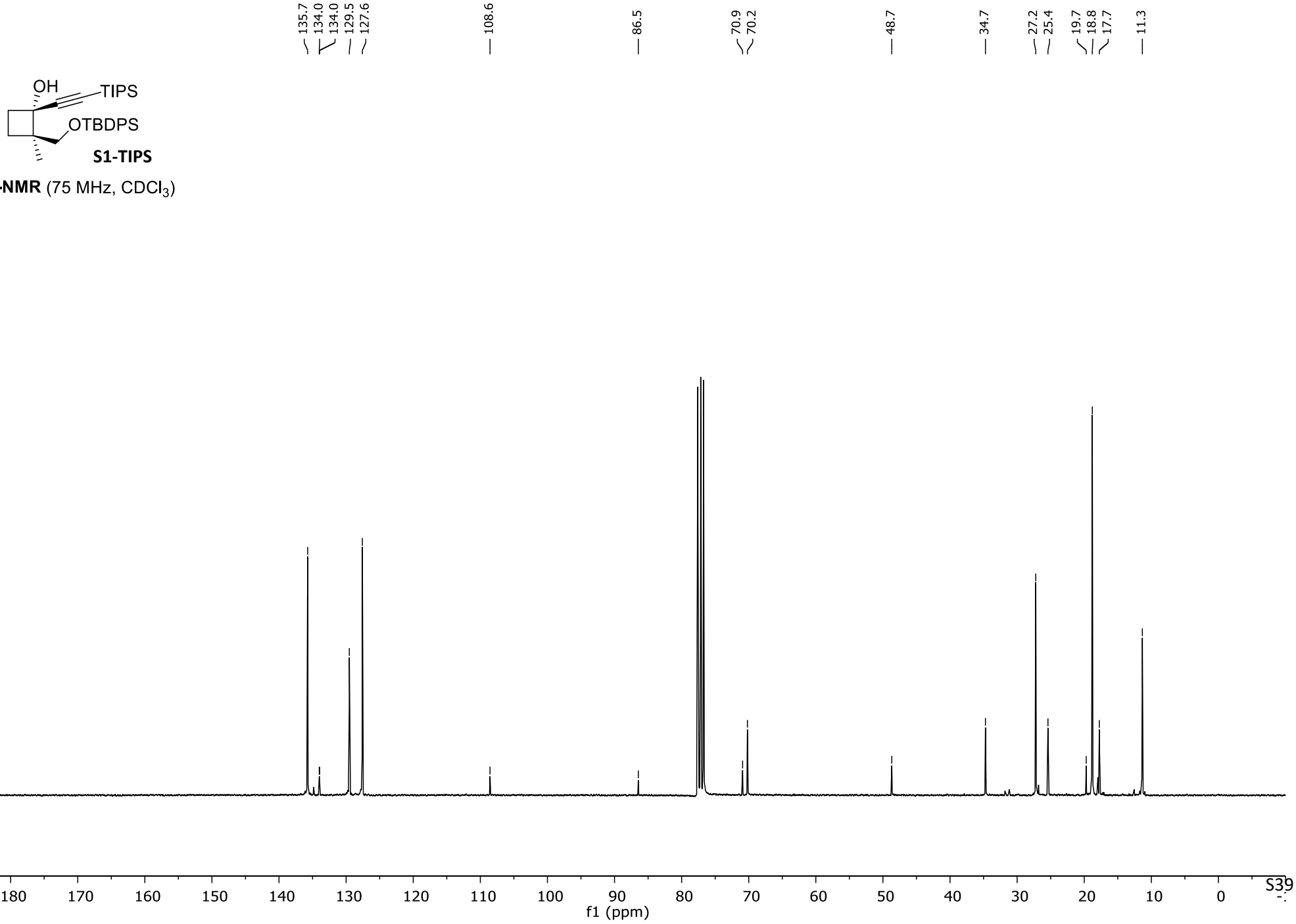
C	-1.67520900	-3.69392400	-2.18477600
C	-2.45729400	-3.94435900	-0.86137900
C	-1.37342500	-3.03384200	-0.10735700
C	-0.45302100	-3.24118700	-1.34352100
H	-1.54123000	-4.56547600	-2.82848400
H	-2.07904800	-2.86894600	-2.78066700
H	0.24785500	-4.05961400	-1.16512200
H	0.10017400	-2.37105500	-1.68931000
C	-2.42736800	-5.41676700	-0.41622000
H	-2.79461200	-5.53963400	0.60483000
H	-3.04793600	-6.01696900	-1.08840900
H	-1.40503900	-5.79682400	-0.45345300
O	-1.00493700	-3.62140800	1.11495900
C	0.25638700	-3.21369600	1.65490700
H	0.39781600	-3.79958800	2.56548700
H	1.07584300	-3.41785300	0.96314800
H	0.25256000	-2.15060900	1.90525500
C	-3.80992300	-3.35234000	-0.67782000
O	-4.59789100	-3.07927300	-1.70557900
C	-1.87197600	-1.60254400	0.10914500
C	-3.10851200	-1.30346800	0.39753400
C	-4.05610900	-0.25038300	0.71602100
C	-5.07466800	0.10749100	-0.18701500
C	-3.96105600	0.41403000	1.95195100
C	-5.96887000	1.12364600	0.13806500
H	-5.16454700	-0.42233400	-1.12922400
C	-4.85720000	1.43545800	2.26662800
H	-3.17771300	0.13499500	2.64831300
C	-5.86140200	1.79103400	1.36334500
H	-6.75177000	1.39607100	-0.56309400
H	-4.77309200	1.94933600	3.21932000
H	-6.56168000	2.58241700	1.61317900
Au	-0.72141800	0.16009700	-0.23322100
P	0.12895300	2.20503500	-1.13993200
C	-1.44971700	3.19868100	-1.62300600
C	1.24293600	1.79335000	-2.67047800
N	-4.20507000	-2.92115800	0.50189300
H	-3.61532000	-3.34080700	1.22261700
Sb	3.65940700	-1.74615000	0.15730600
F	4.05119800	0.07918800	0.52102800
F	2.97452600	-1.90927100	1.92111300
F	1.93233400	-1.22045100	-0.46749400
F	3.17789300	-3.54622400	-0.19393500
F	5.36585500	-2.27314300	0.76167400
F	4.30964000	-1.54416200	-1.60551300

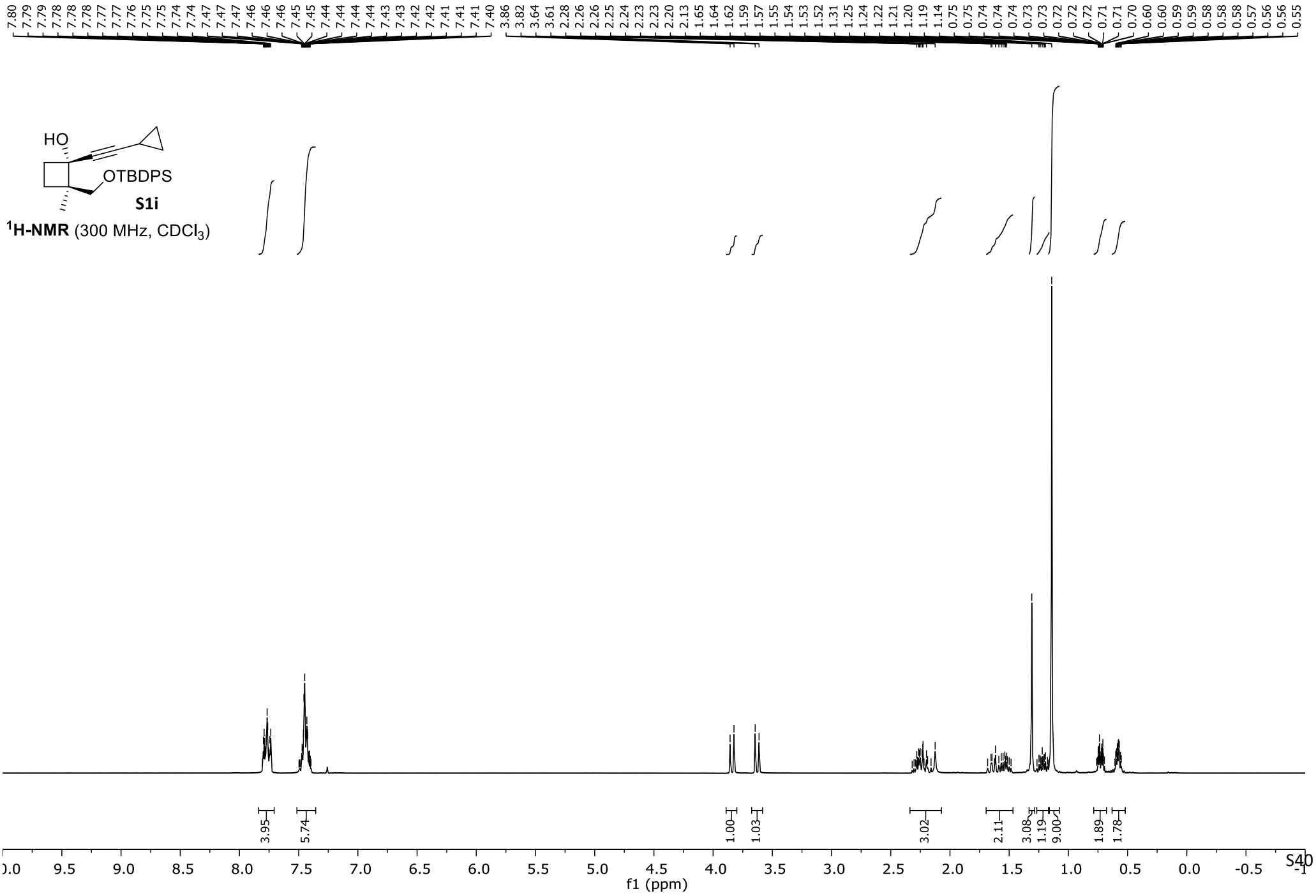
C	-2.28084600	2.36413600	-2.61908100
H	-2.50276400	1.36777300	-2.22449700
H	-3.23433700	2.87500800	-2.79699600
H	-1.78555300	2.25128900	-3.58693400
C	-2.26017500	3.37291500	-0.32030100
H	-3.18895800	3.90676600	-0.55288600
H	-2.52555600	2.41315300	0.13010500
H	-1.71413400	3.96460500	0.42018400
C	0.77719100	0.42660800	-3.22425400
H	1.36813800	0.19513000	-4.11860500
H	0.94434600	-0.36828100	-2.49589400
H	-0.27694800	0.42676500	-3.51479800
C	1.19891400	2.80771400	-3.83200500
H	1.88418200	2.45358100	-4.61094500
H	0.20827600	2.88248900	-4.28611200
H	1.52901900	3.81055700	-3.55529900
C	2.69843100	1.64349200	-2.18006000
H	2.78822500	0.96368600	-1.33261700
H	3.29459800	1.22472500	-2.99925900
H	3.14193100	2.60193800	-1.90250700
C	1.08441400	3.38566600	-0.06981500
C	1.17182300	3.30172000	1.34193700
C	1.70602600	4.47824000	-0.70942600
C	1.85754500	4.31787700	2.03594200
C	2.39184000	5.46375800	-0.00594300
H	1.65223400	4.57170200	-1.78527600
C	2.46410400	5.38587400	1.38339300
H	1.91905400	4.24589400	3.11741700
H	2.85899800	6.28351200	-0.54281800
H	2.99008400	6.14475000	1.95475000
C	0.61366500	2.22211500	2.21950400
C	-0.48969900	2.49851100	3.04246400
C	1.29245100	1.00439300	2.38438500
C	-0.91229800	1.57722100	4.00344800
H	-1.00612100	3.44893100	2.94214400
C	0.87898400	0.09213100	3.35872900
H	2.16378300	0.77957500	1.77873200
C	-0.22380800	0.37299100	4.16885000
H	-1.76379400	1.81185100	4.63622000
H	1.43798200	-0.82897900	3.48076200
H	-0.53621800	-0.33469300	4.93159000
C	-1.19261400	4.59982600	-2.21019400
H	-2.16357800	5.06719300	-2.41227500
H	-0.66067100	5.24627200	-1.50885100
H	-0.64127800	4.57828400	-3.15078500
H	-4.17725000	-3.34425300	-2.53985400

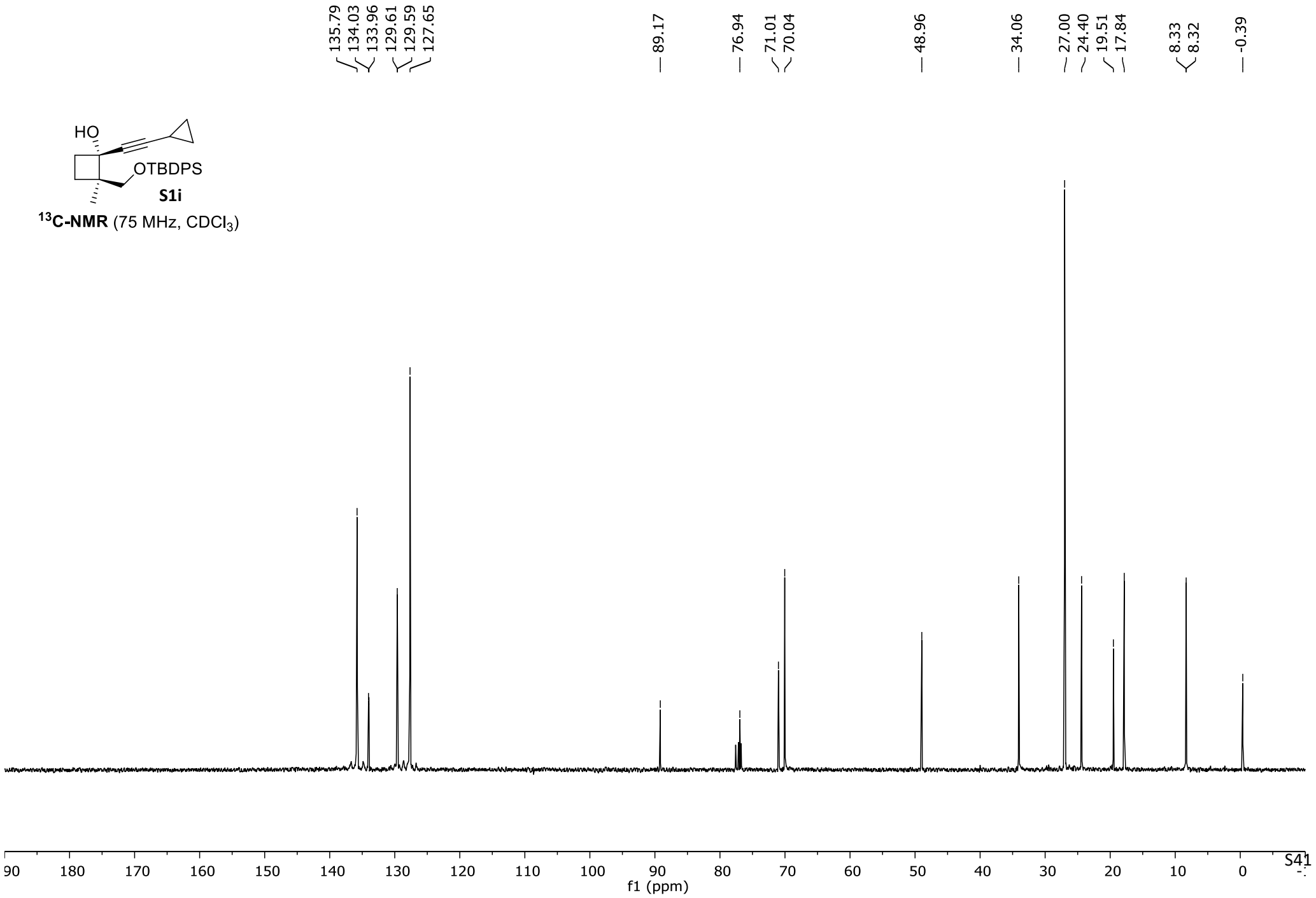
E(RM06) = -2646.34238922
Zero-point correction= 0.724981 (Hartree/Particle)
Thermal correction to Energy= 0.777730
Thermal correction to Enthalpy= 0.778674
Thermal correction to Gibbs Free Energy= 0.633924
Sum of electronic and zero-point Energies= -2646.407735
Sum of electronic and thermal Energies= -2646.354986
Sum of electronic and thermal Enthalpies= -2646.354041
Sum of electronic and thermal Free Energies= -2646.498791
Frequency: -366.9651

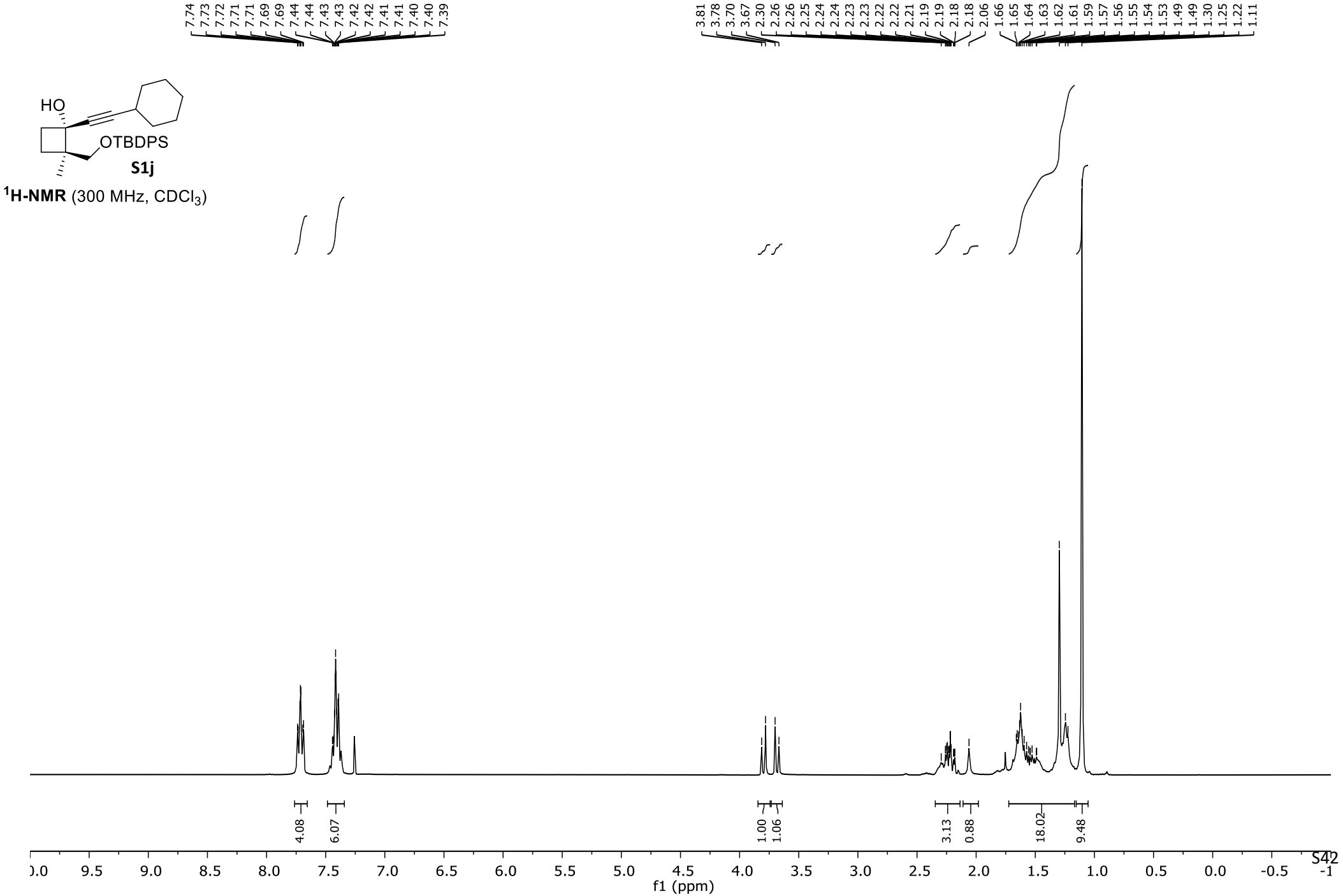
^{1}H and ^{13}C NMR spectra for all new compounds and HMBC spectra for 2a

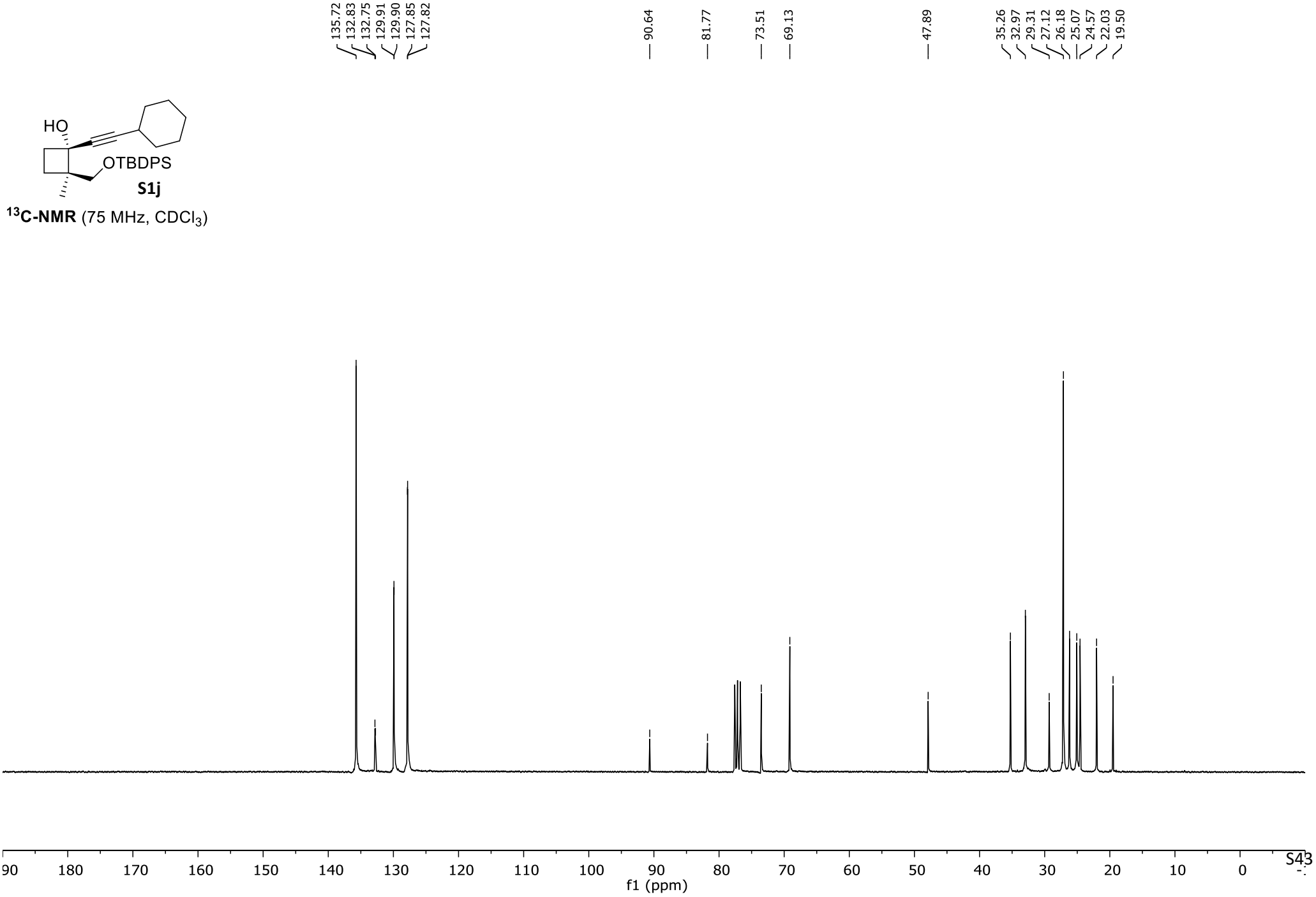

OH
TIPS
OTBDPS
S1-TIPS
1H-NMR (300 MHz, CDCl3)
3.91
5.75
1.00
1.20
2.09
0.90
1.11
1.37
3.02
11.99
18.11
f1 (ppm)


135.7
134.0
134.0
129.5
127.6
108.6
86.5
70.9
70.2
48.7
34.7
27.2
25.4
19.7
18.8
17.7
11.3
OH
TIPS
OTBDPS
S1-TIPS
13C-NMR (75 MHz, CDCl3)
f1 (ppm)

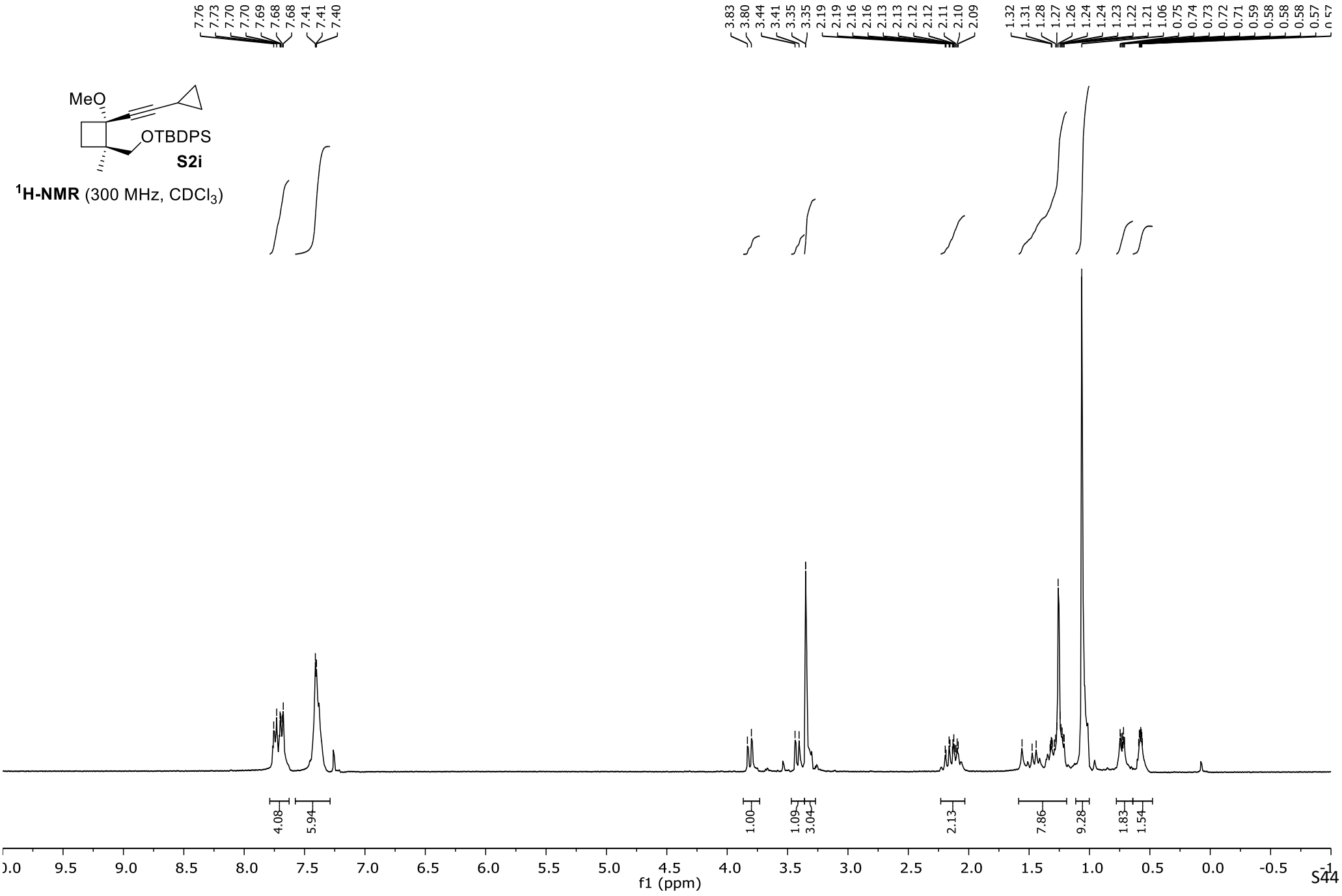

HO
OTBDPS
S1i
1H-NMR (300 MHz, CDCl3)
f1 (ppm)

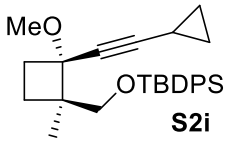

135.79
134.03
133.96
129.61
129.59
127.65
89.17
76.94
71.01
70.04
48.96
34.06
27.00
24.40
19.51
17.84
8.33
8.32
-0.39
HO
OTBDPS
S1i
13C-NMR (75 MHz, CDCl3)
f1 (ppm)


HO
OTBDPS
S1j
1H-NMR (300 MHz, CDCl3)
7.74 7.73 7.72 7.71 7.71 7.69 7.69 7.44 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.40 7.40 7.39
3.81 3.78 3.70 3.67 2.30 2.26 2.26 2.25 2.24 2.24 2.23 2.23 2.22 2.22 2.21 2.19 2.19 2.18 2.18 2.06 1.66 1.65 1.64 1.63 1.62 1.61 1.59 1.57 1.56 1.55 1.54 1.53 1.49 1.49 1.30 1.25 1.22 1.11
4.08
6.07
1.00
1.06
3.13
0.88
18.02
9.48
f1 (ppm)



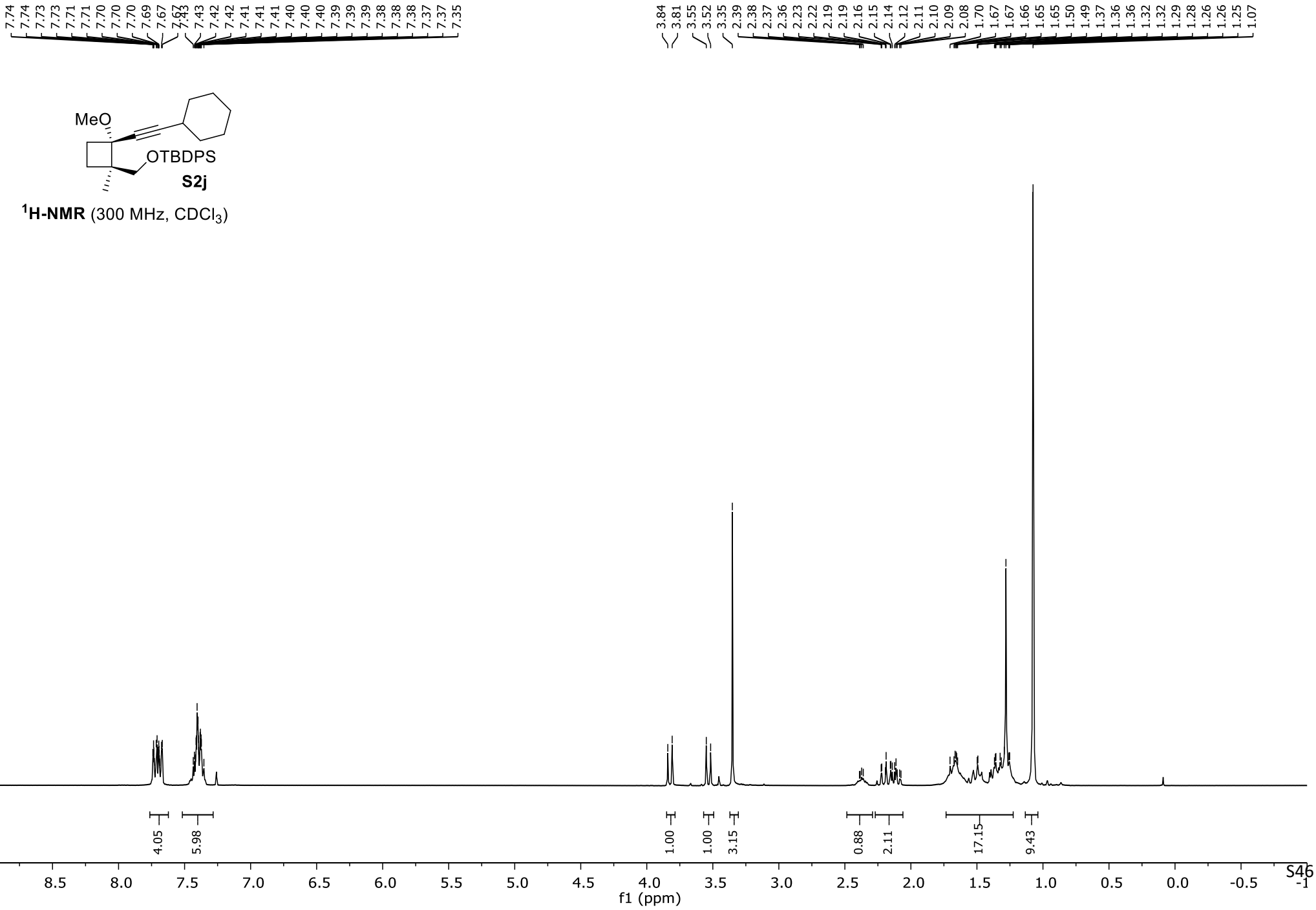
^{13}C-NMR (75 MHz, $CDCl_3$)

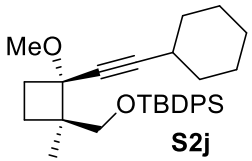

MeO
OTBDPS
S2i
1H-NMR (300 MHz, CDCl3)
7.76 7.73 7.70 7.70 7.69 7.68 7.68 7.41 7.41 7.40
3.83 3.80 3.44 3.41 3.35 3.35 2.19 2.19 2.16 2.16 2.13 2.13 2.12 2.12 2.11 2.10 2.09
1.32 1.31 1.28 1.27 1.26 1.24 1.24 1.23 1.22 1.21 1.06 0.75 0.74 0.73 0.72 0.71 0.59 0.58 0.58 0.58 0.57
4.08 5.94 1.00 1.09 3.04 2.13 7.86 9.28 1.83 1.54
f1 (ppm)



S2i

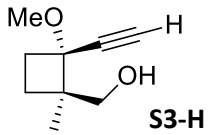
^{13}C-NMR (75 MHz, $CDCl_3$)


7.74 7.74 7.73 7.73 7.71 7.71 7.70 7.70 7.70 7.69 7.67 7.67 7.43 7.43 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.35
3.84 3.81 3.55 3.52 3.35 2.39 2.38 2.37 2.36 2.23 2.22 2.19 2.19 2.16 2.15 2.14 2.12 2.11 2.10 2.09 2.08 1.70 1.67 1.67 1.66 1.65 1.65 1.50 1.49 1.37 1.36 1.36 1.32 1.32 1.29 1.28 1.26 1.26 1.25 1.07
MeO
OTBDPS
S2j
1H-NMR (300 MHz, CDCl3)
4.05
5.98
1.00
1.00
3.15
0.88
2.11
17.15
9.43
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)



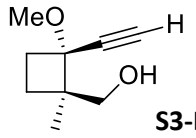
S2j

^{13}C-NMR (100 MHz, $CDCl_3$)



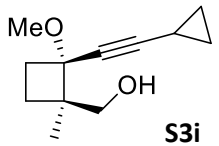
S3-H

^{1}H-NMR (300 MHz, $CDCl_3$)



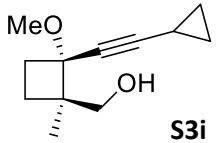
S3-H

^{13}C-NMR (75 MHz, $CDCl_3$)



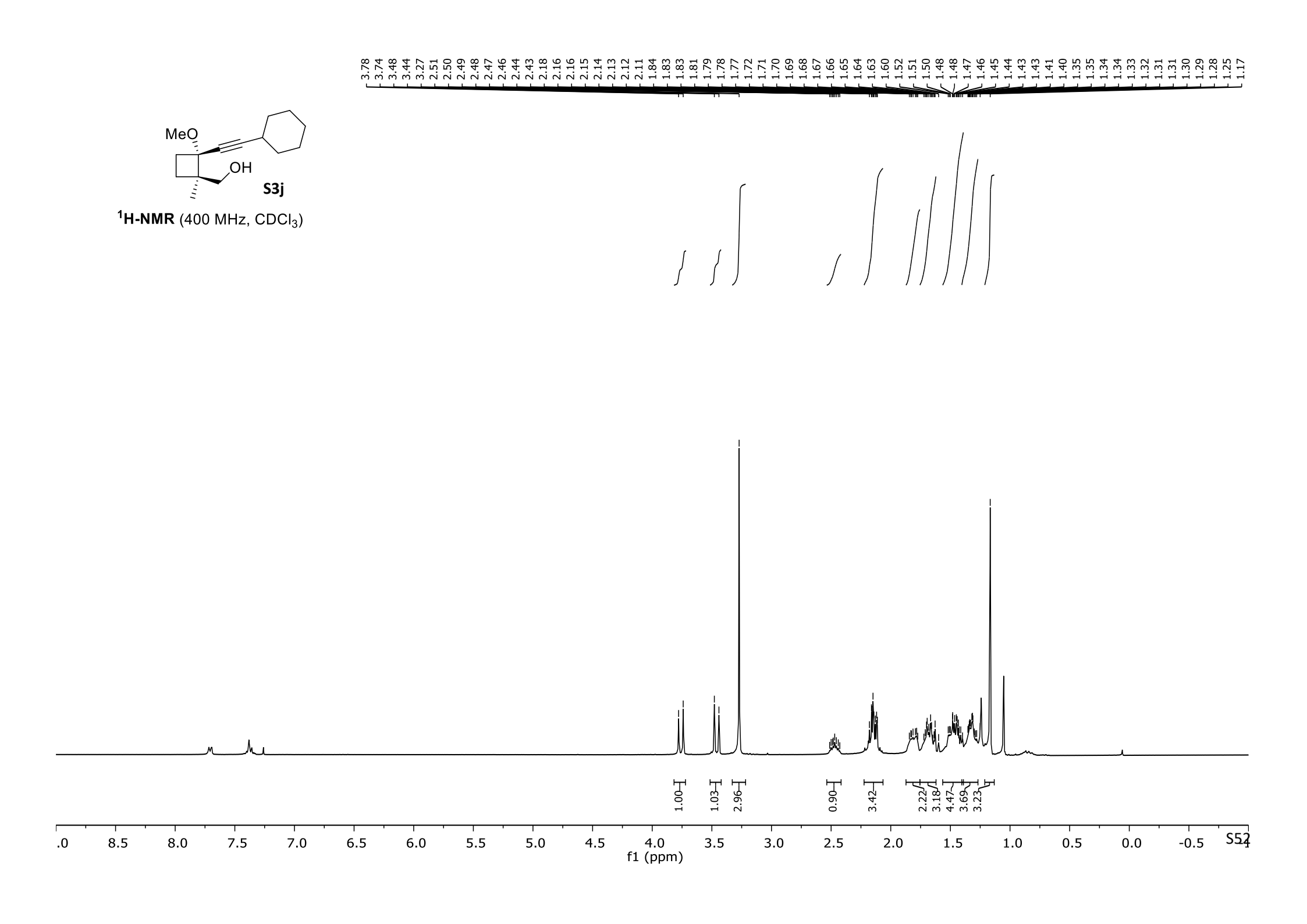
S3i

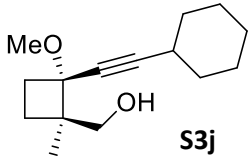
^{1}H-NMR (300 MHz, $CDCl_3$)



S3i

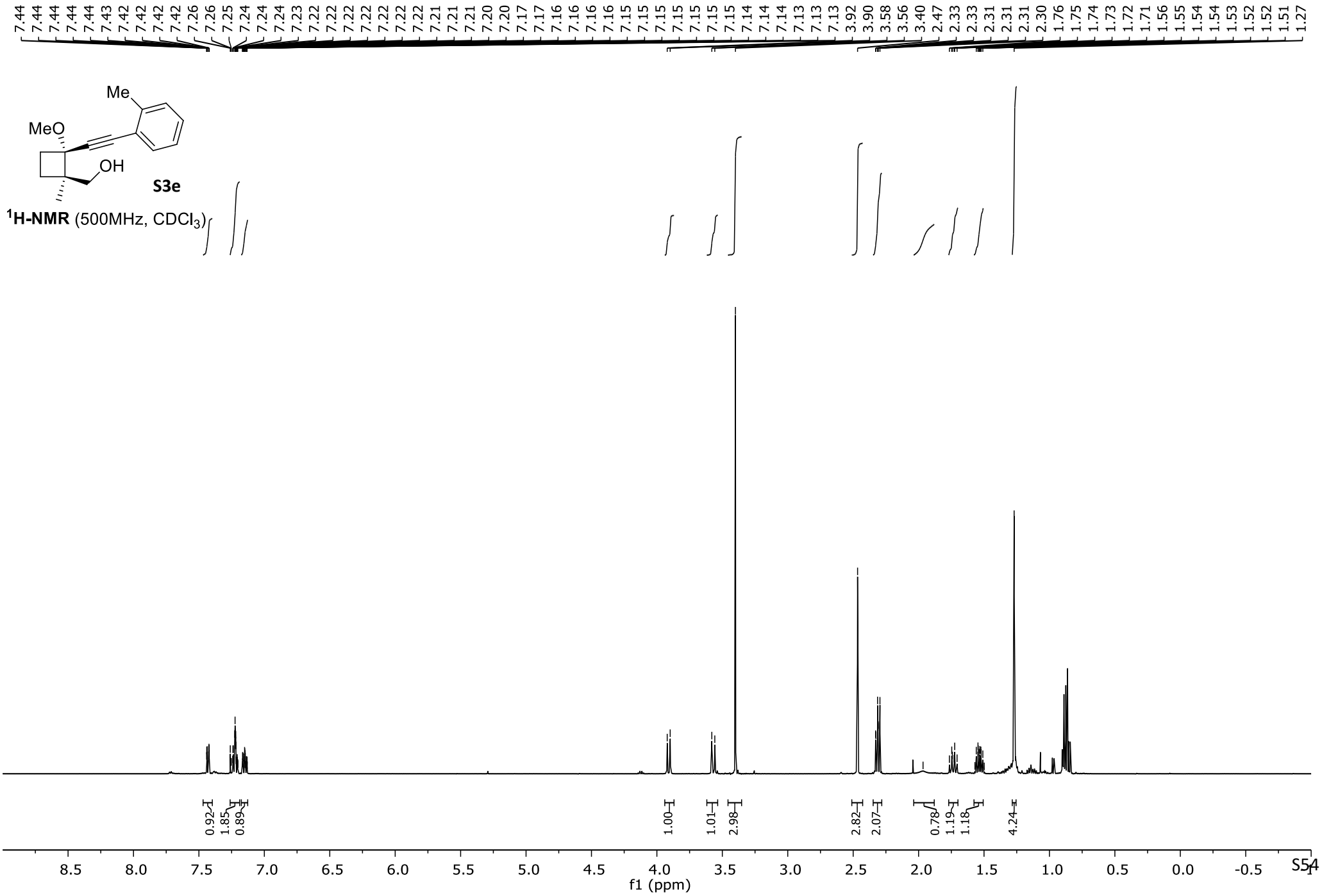
^{13}C-NMR (100 MHz, $CDCl_3$)

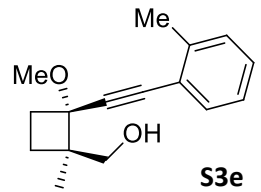

MeO
OH
S3j
1H-NMR (400 MHz, CDCl3)
3.78 3.74 3.48 3.44 3.27 2.51 2.50 2.49 2.48 2.47 2.46 2.44 2.43 2.18 2.16 2.16 2.15 2.14 2.13 2.12 2.11 1.84 1.83 1.83 1.81 1.79 1.78 1.77 1.72 1.71 1.70 1.69 1.68 1.67 1.66 1.65 1.64 1.63 1.60 1.52 1.51 1.50 1.48 1.48 1.47 1.46 1.45 1.44 1.43 1.43 1.41 1.40 1.35 1.35 1.34 1.34 1.33 1.32 1.31 1.31 1.30 1.29 1.28 1.25 1.17
1.00 1.03 2.96 0.90 3.42 2.22 3.18 4.47 3.69 3.23
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



S3j

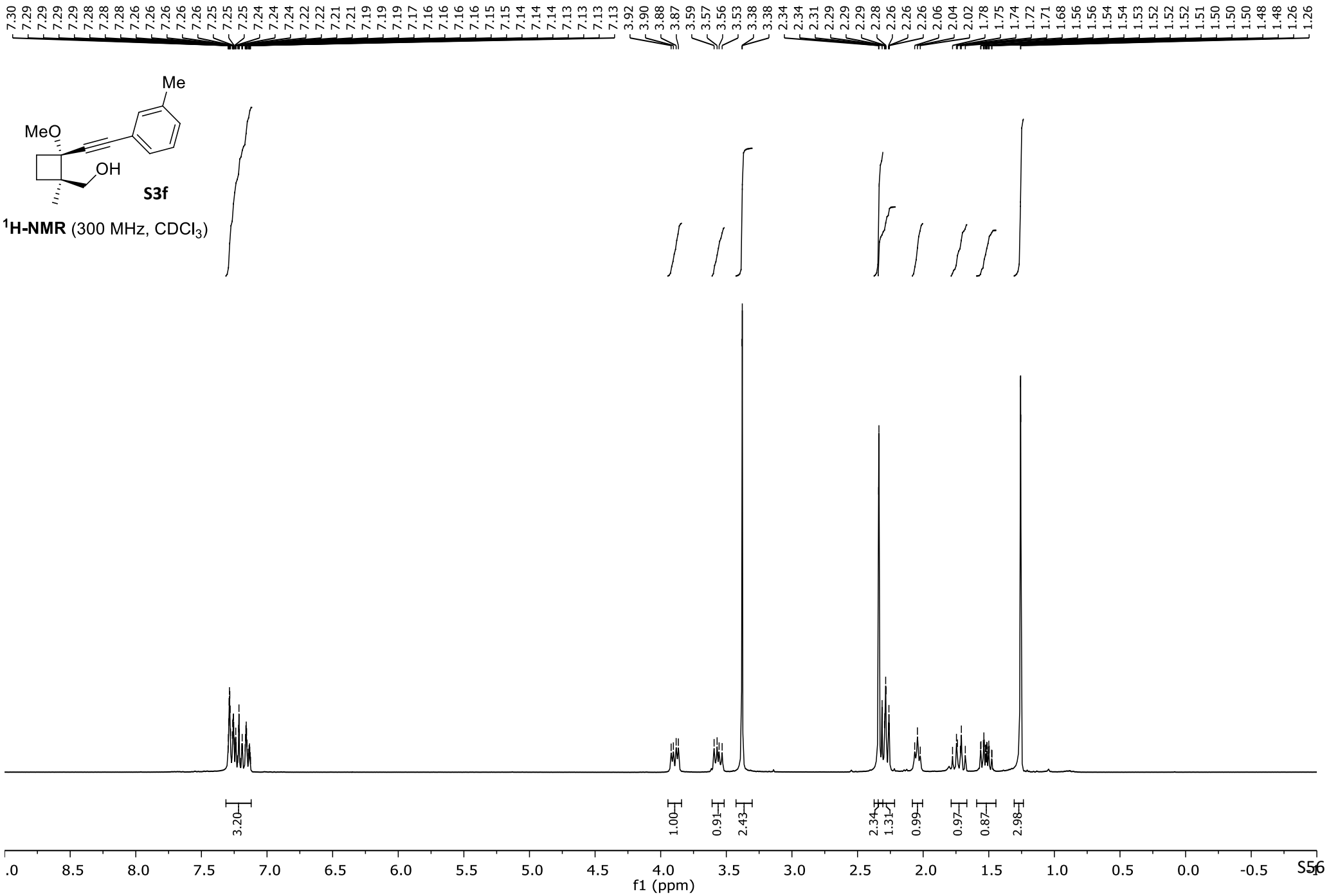
^{1}H-NMR (100 MHz, $CDCl_3$)

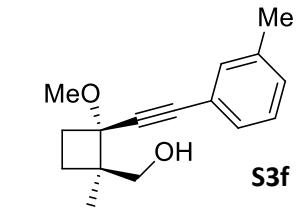

Me
MeO
OH
S3e
1H-NMR (500MHz, CDCl3)
f1 (ppm)



S3e

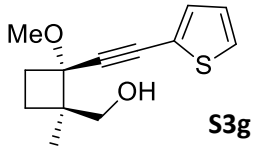
^{13}C-NMR (126MHz, $CDCl_3$)


Me
MeO
OH
S3f
1H-NMR (300 MHz, CDCl3)
f1 (ppm)



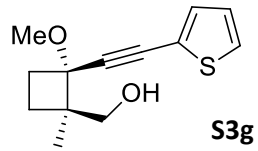
S3f

^{13}C-NMR (75 MHz, $CDCl_3$)



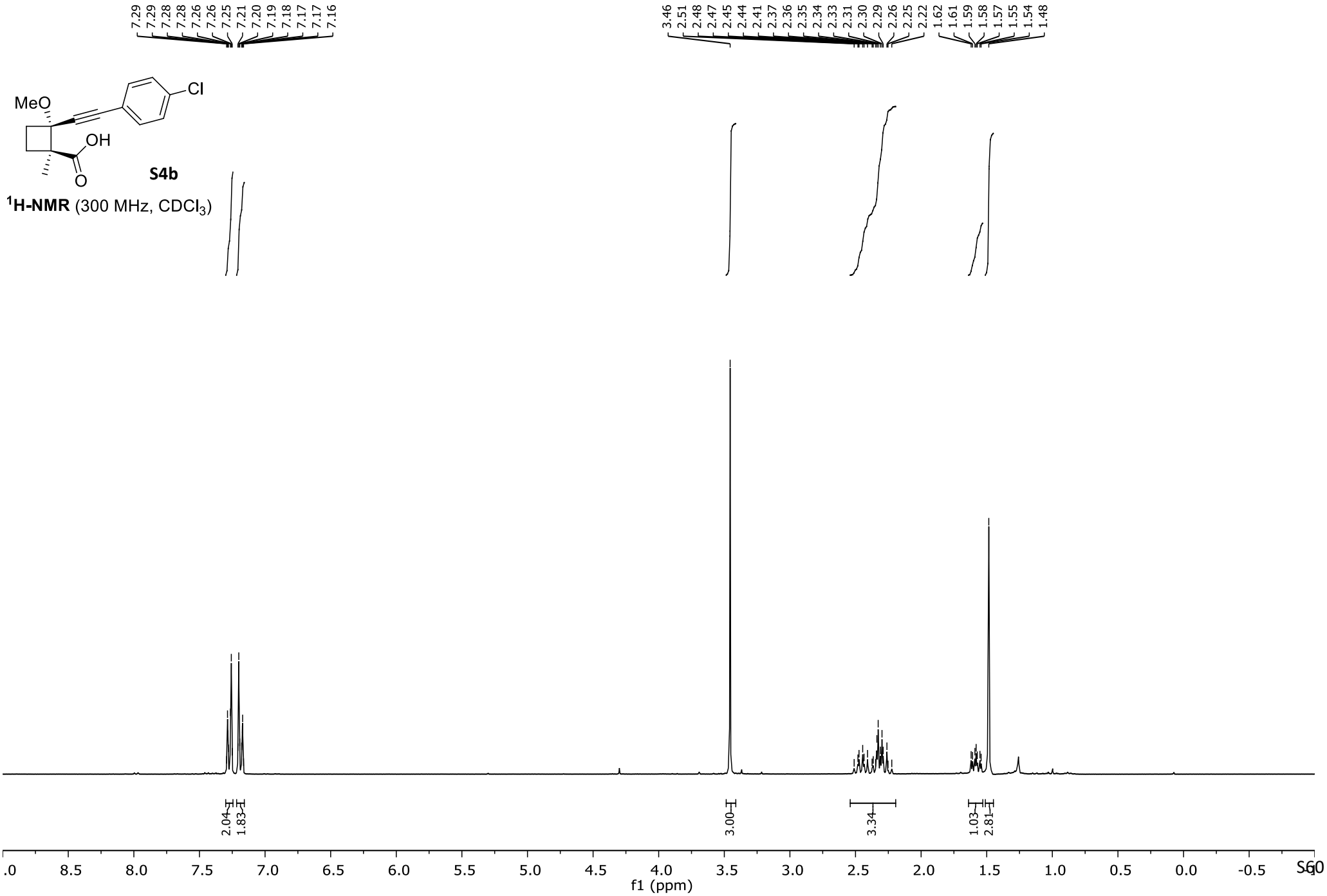
S3g

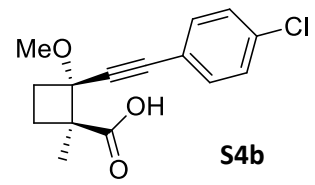
^{1}H-NMR (500MHz, $CDCl_3$)



S3g

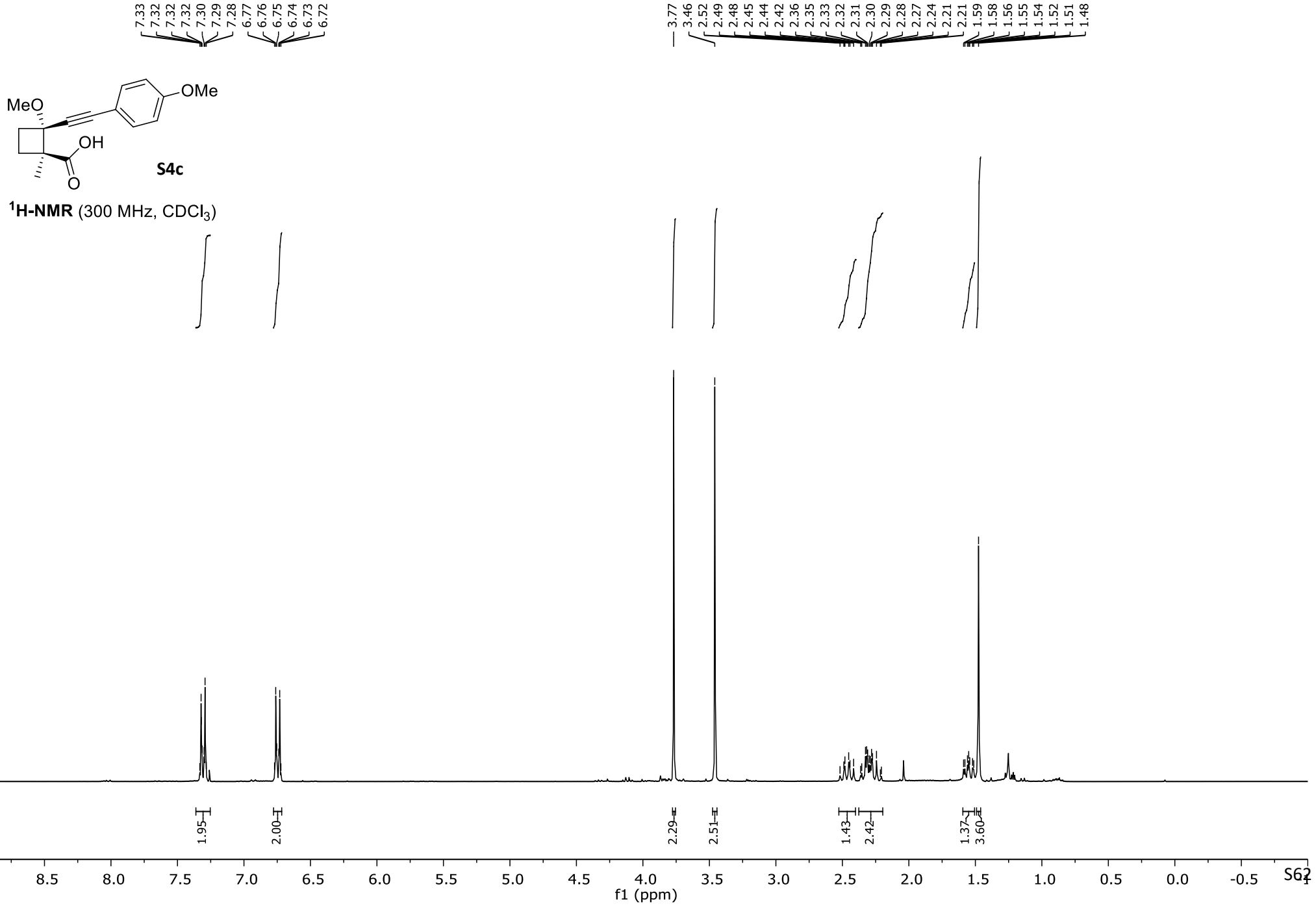
^{13}C-NMR (126MHz, $CDCl_3$)

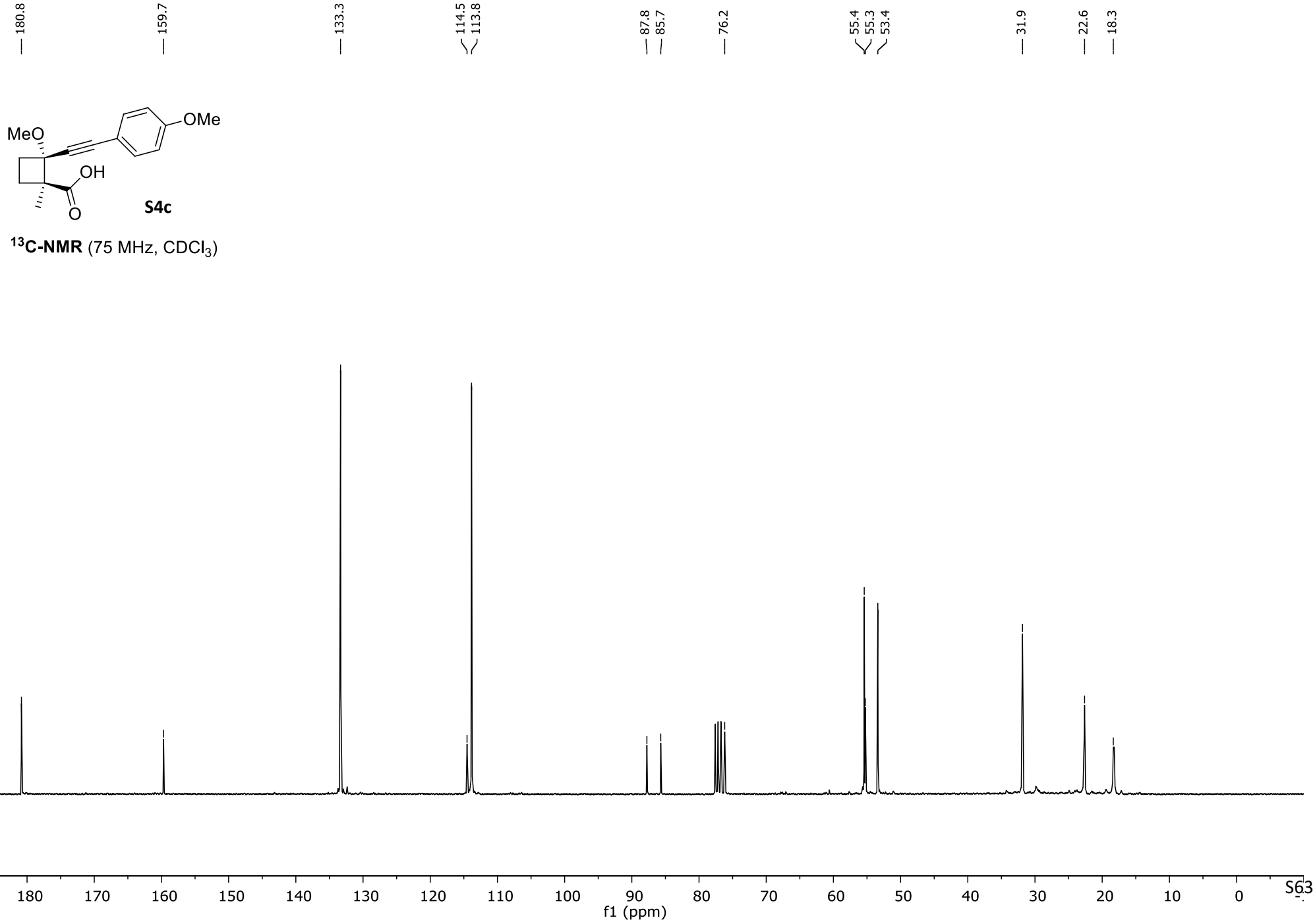

7.29
7.29
7.28
7.28
7.26
7.26
7.25
7.21
7.20
7.19
7.18
7.17
7.17
7.16
3.46
2.51
2.48
2.47
2.45
2.44
2.41
2.37
2.36
2.35
2.34
2.33
2.31
2.30
2.29
2.26
2.25
2.22
1.62
1.61
1.59
1.58
1.57
1.55
1.54
1.48
MeO
Cl
OH
O
S4b
1H-NMR (300 MHz, CDCl3)
2.04
1.83
3.00
3.34
1.03
2.81
f1 (ppm)

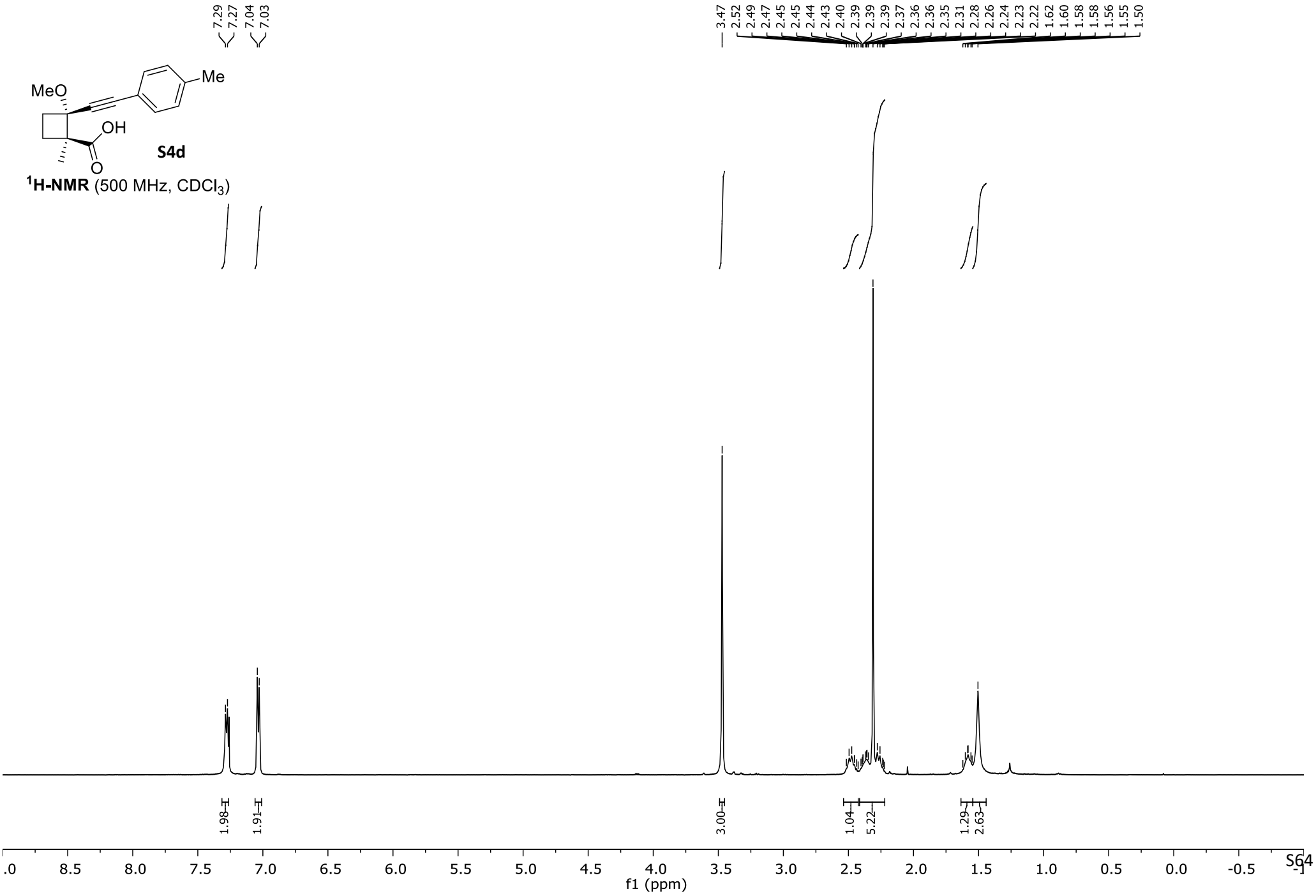


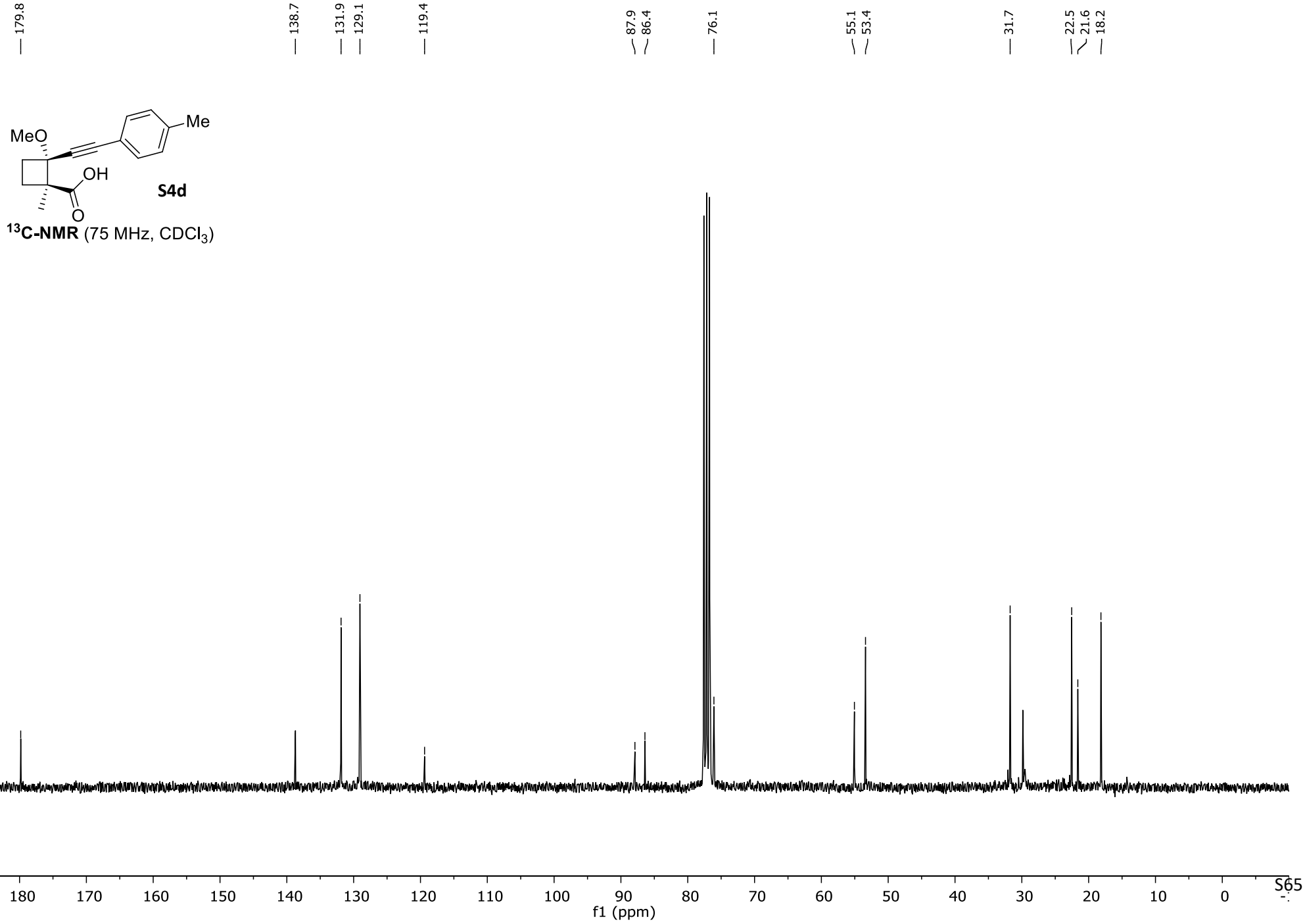
S4b

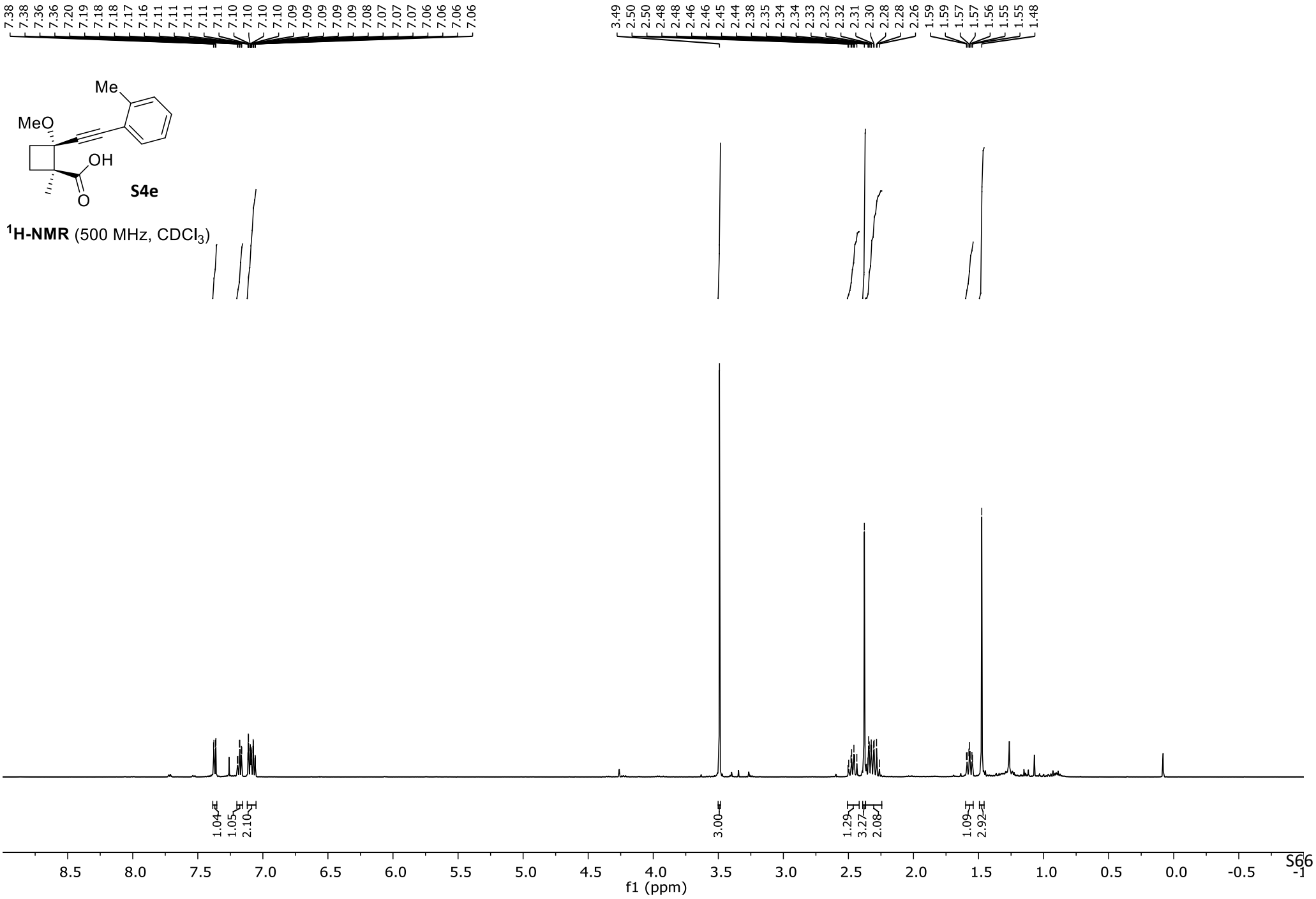
^{13}C-NMR (75 MHz, $CDCl_3$)


7.33
7.32
7.32
7.32
7.30
7.29
7.28
6.77
6.76
6.75
6.74
6.73
6.72
3.77
3.46
2.52
2.49
2.48
2.45
2.44
2.42
2.36
2.35
2.33
2.32
2.31
2.30
2.29
2.28
2.27
2.24
2.21
2.21
1.59
1.58
1.56
1.55
1.54
1.52
1.51
1.48
MeO
OMe
OH
O
S4c
1H-NMR (300 MHz, CDCl3)
1.95
2.00
2.29
2.51
1.43
2.42
1.37
3.60
f1 (ppm)

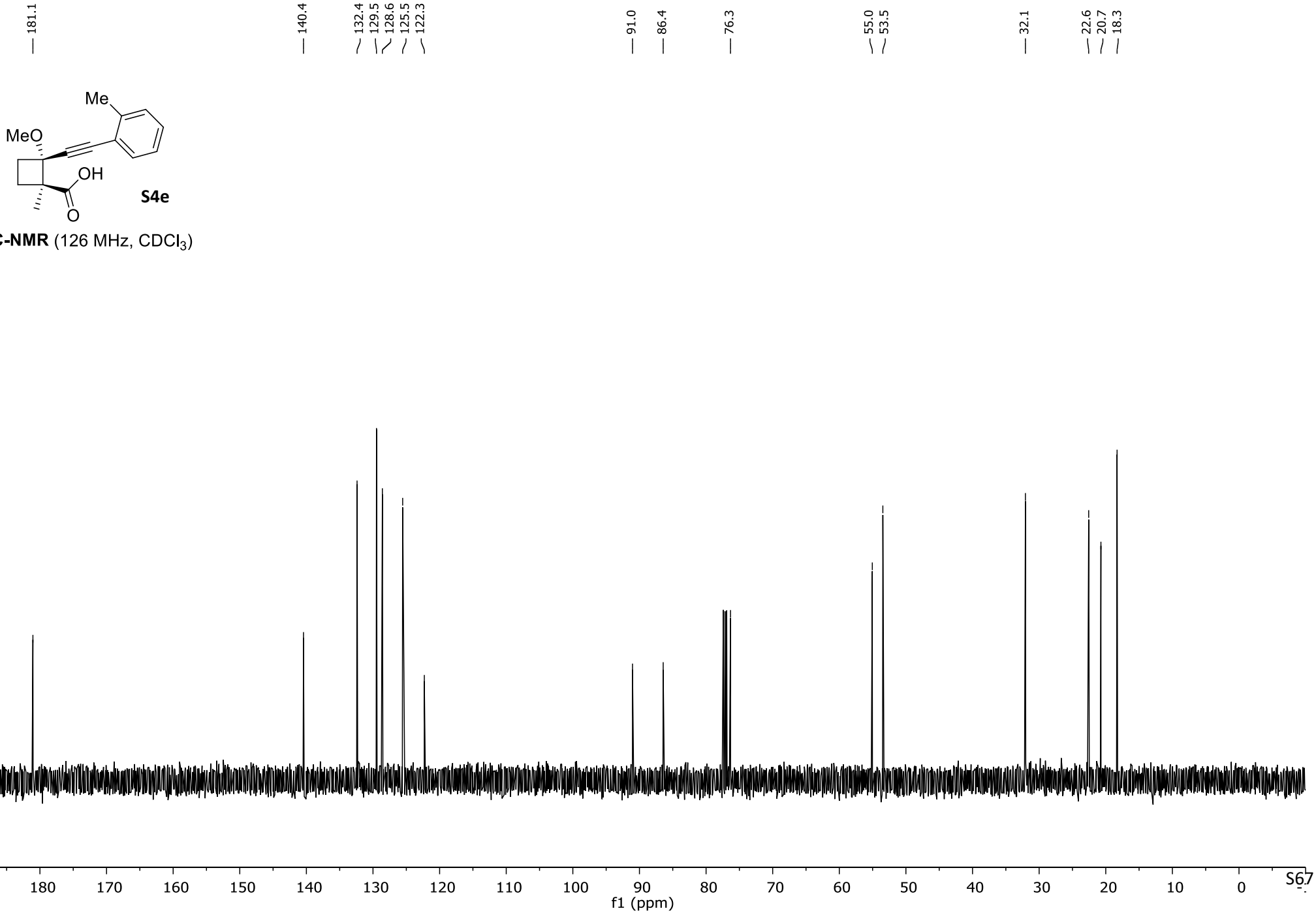

180.8
159.7
133.3
114.5
113.8
87.8
85.7
76.2
55.4
55.3
53.4
31.9
22.6
18.3
MeO
OMe
OH
O
S4c
13C-NMR (75 MHz, CDCl3)
f1 (ppm)


7.29
7.27
7.04
7.03
3.47
2.52
2.49
2.47
2.45
2.45
2.44
2.43
2.40
2.39
2.39
2.39
2.37
2.36
2.36
2.35
2.31
2.28
2.26
2.24
2.23
2.22
1.62
1.60
1.58
1.58
1.56
1.55
1.50
MeO
Me
OH
O
S4d
1H-NMR (500 MHz, CDCl3)
1.98
1.91
3.00
1.04
5.22
1.29
2.63
f1 (ppm)

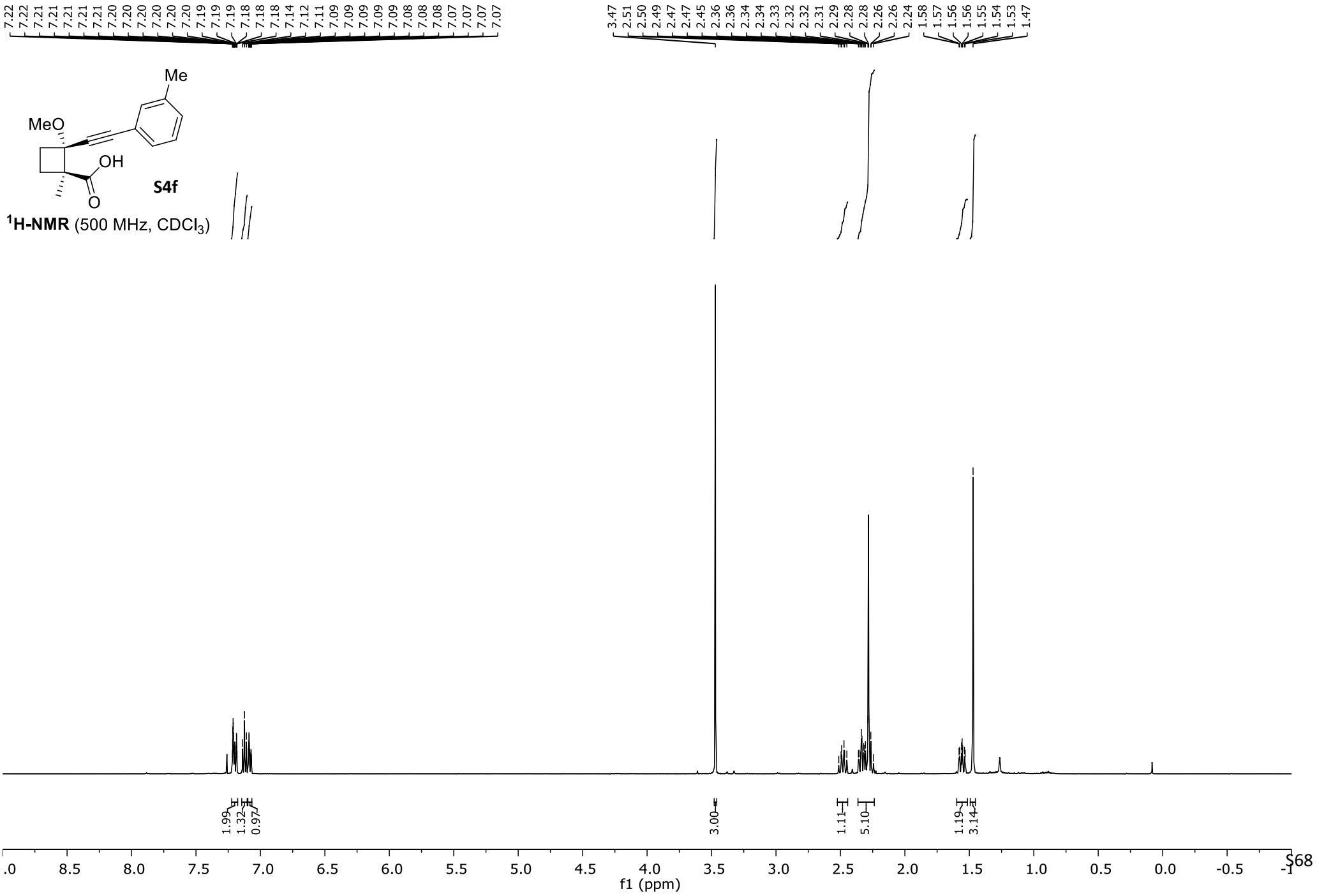

179.8
138.7
131.9
129.1
119.4
87.9
86.4
76.1
55.1
53.4
31.7
22.5
21.6
18.2
MeO
OH
O
Me
S4d
13C-NMR (75 MHz, CDCl3)
f1 (ppm)

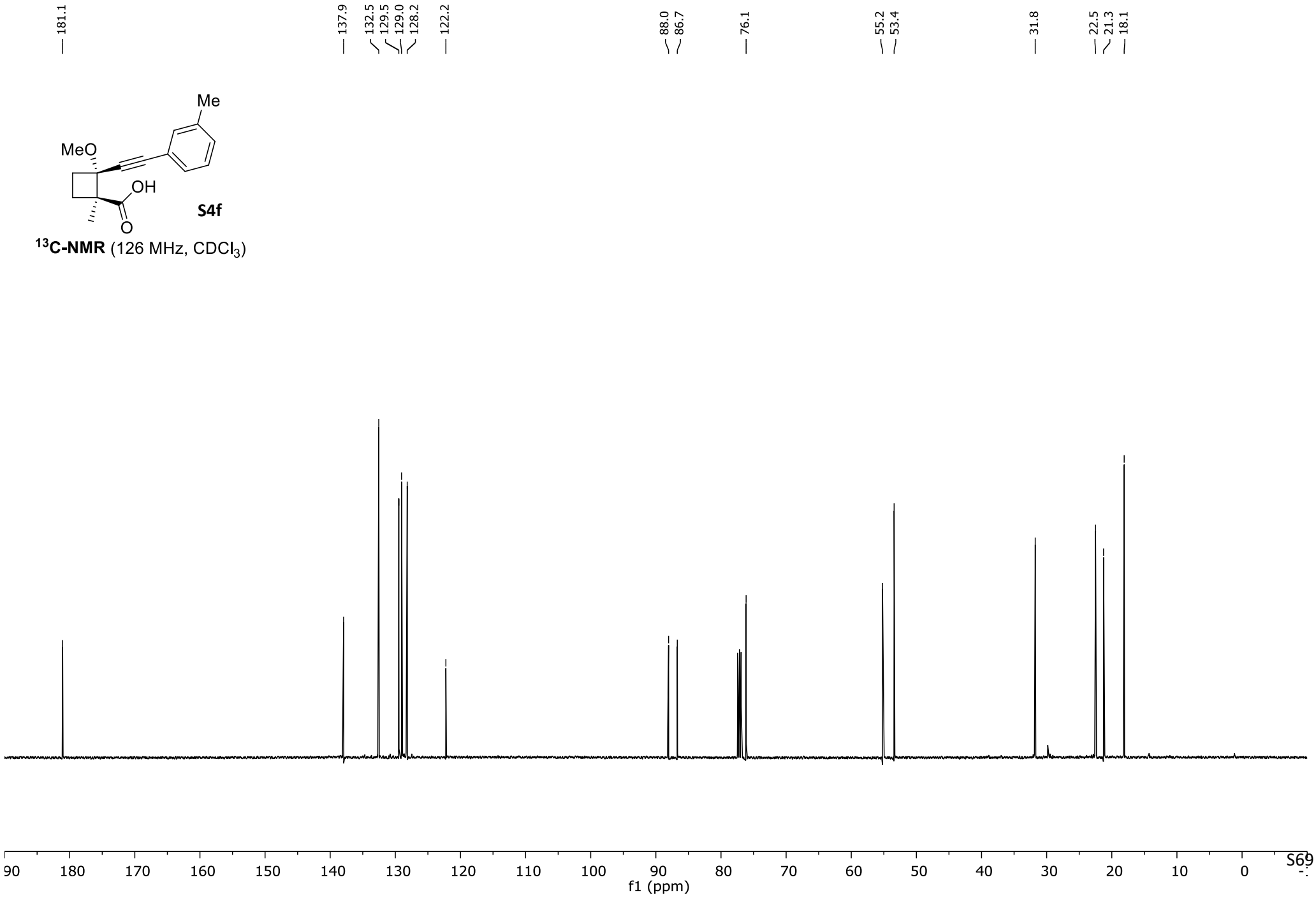


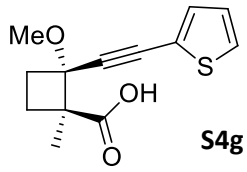
^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (126 MHz, $CDCl_3$)

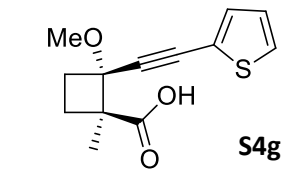

Me
MeO
OH
O
S4f
1H-NMR (500 MHz, CDCl3)
f1 (ppm)


181.1
137.9
132.5
129.5
129.0
128.2
122.2
88.0
86.7
76.1
55.2
53.4
31.8
22.5
21.3
18.1
Me
MeO
OH
O
S4f
13C-NMR (126 MHz, CDCl3)
f1 (ppm)



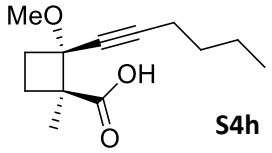
S4g

^{1}H-NMR (300 MHz, $CDCl_3$)



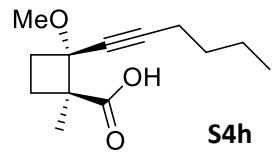
S4g

^{13}C-NMR (75 MHz, $CDCl_3$)



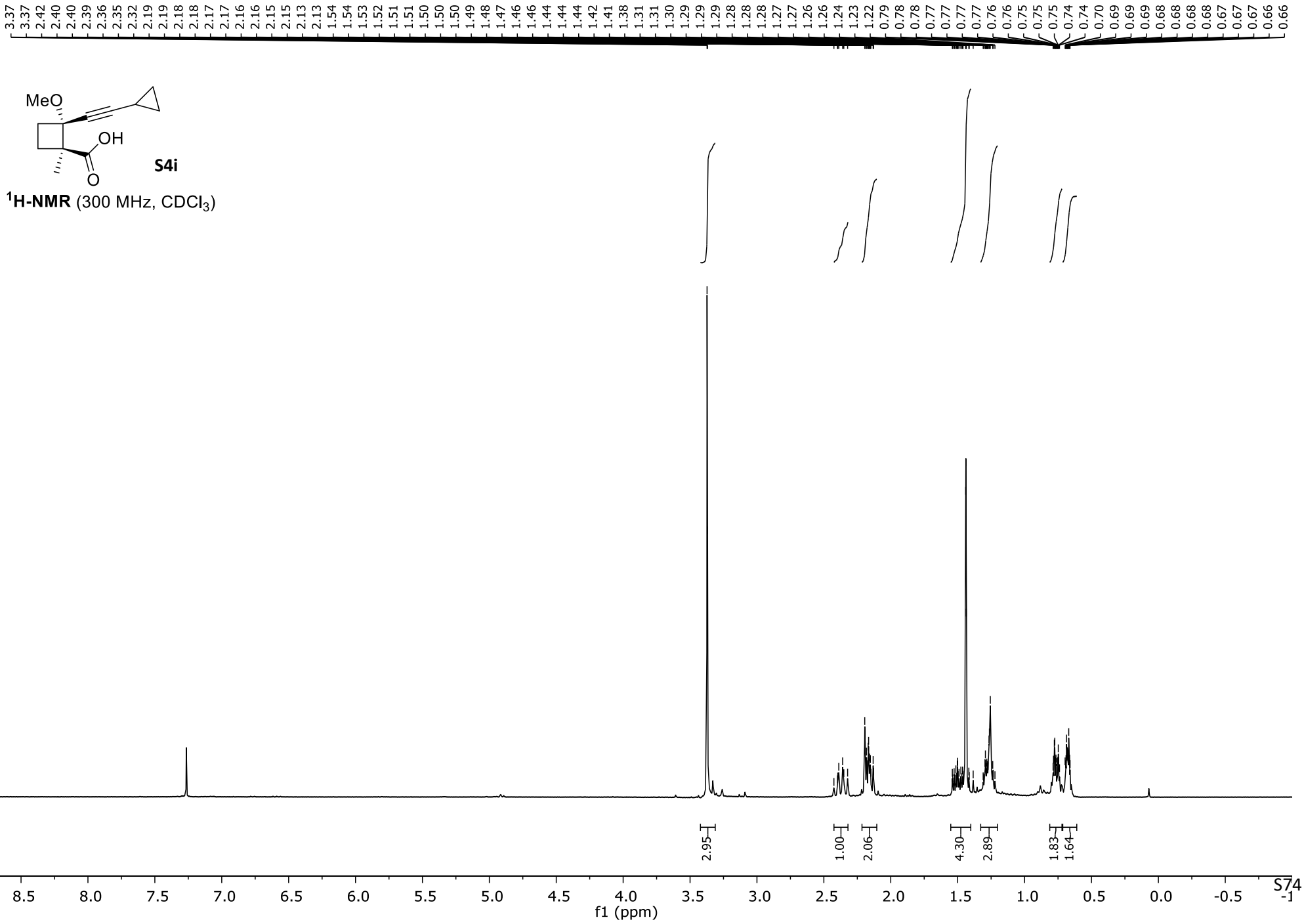
S4h

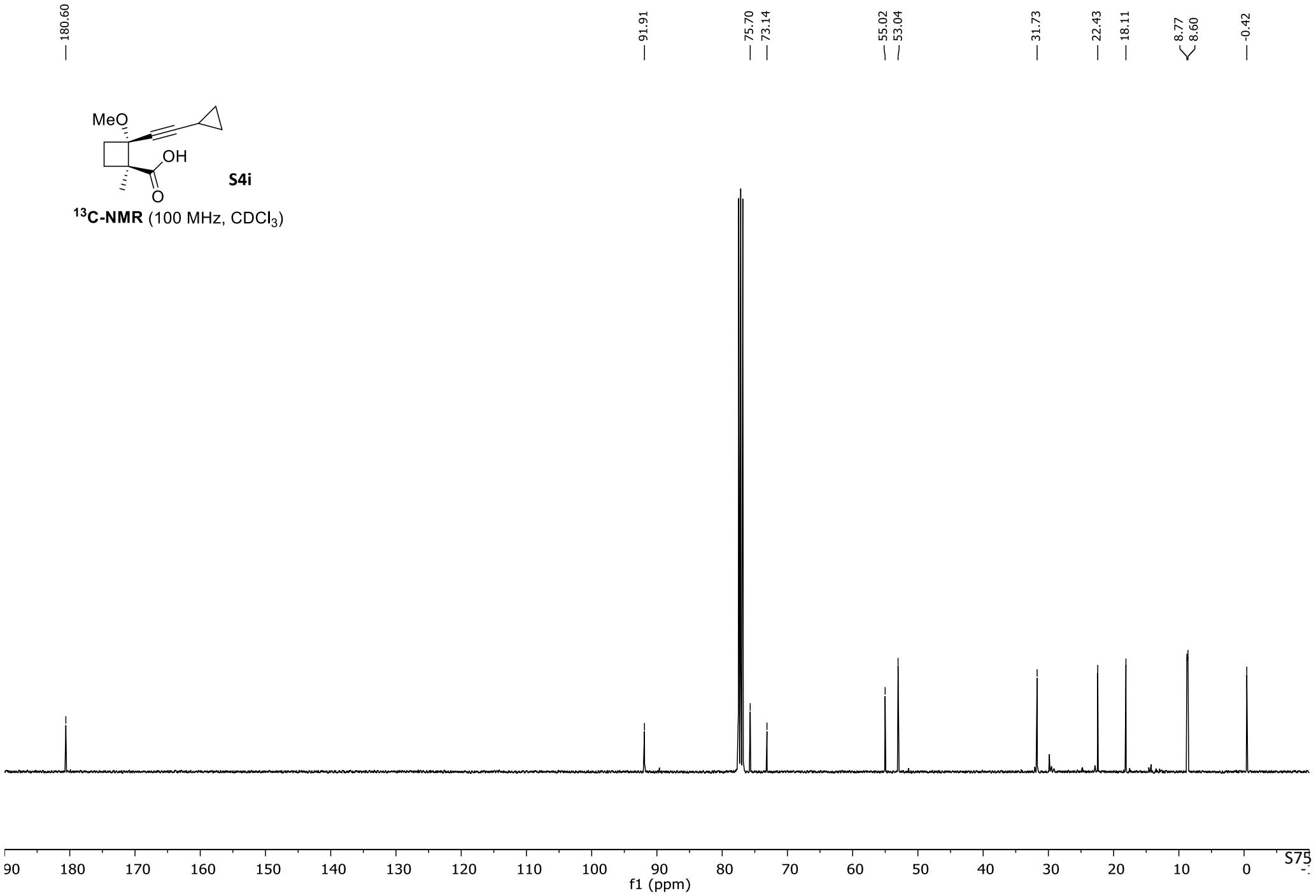
^{1}H-NMR (300 MHz, $CDCl_3$)

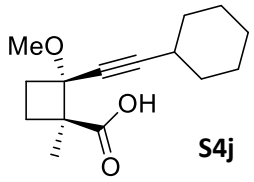


S4h

^{13}C-NMR (75 MHz, $CDCl_3$)

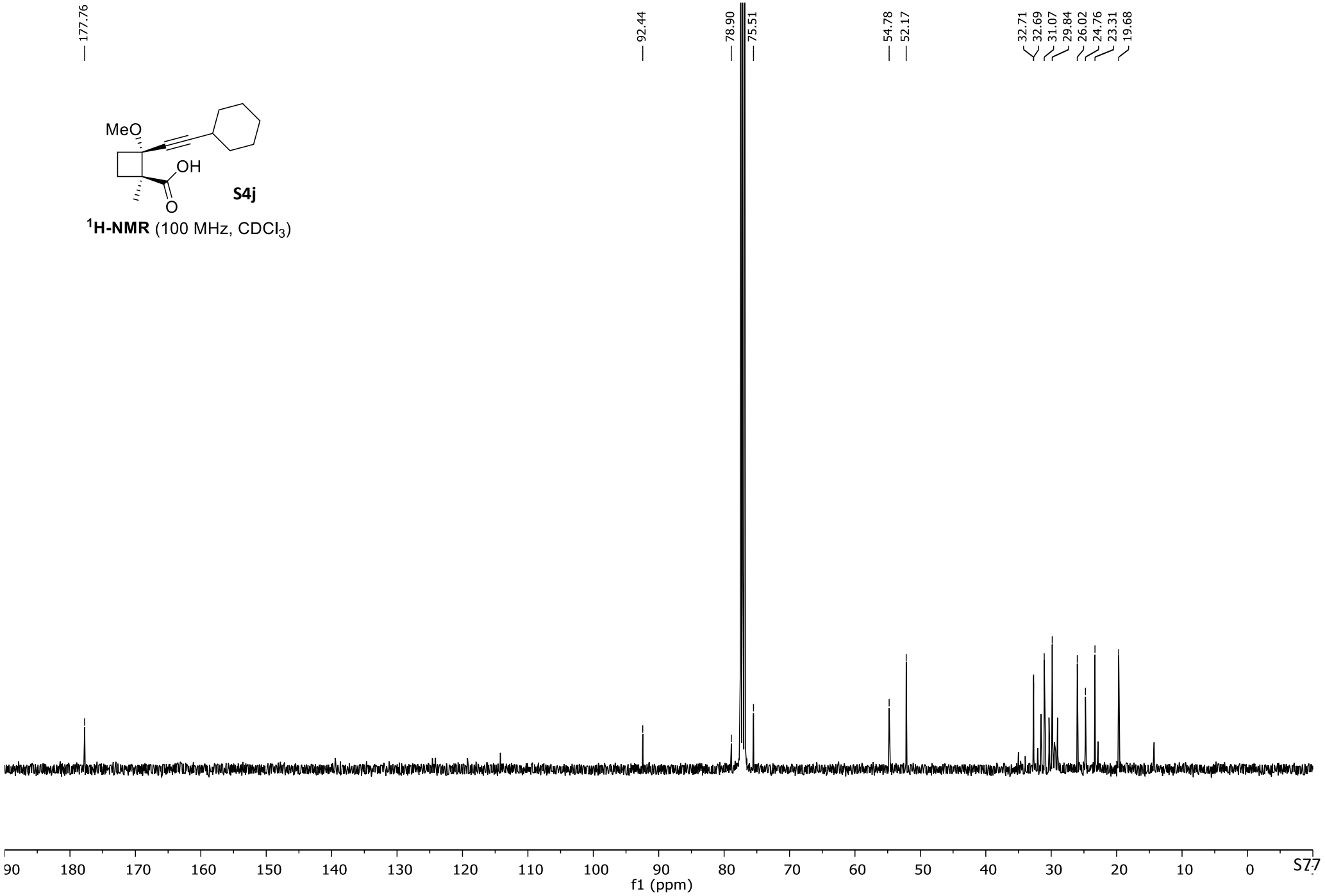

MeO
OH
O
S4i
1H-NMR (300 MHz, CDCl3)
f1 (ppm)

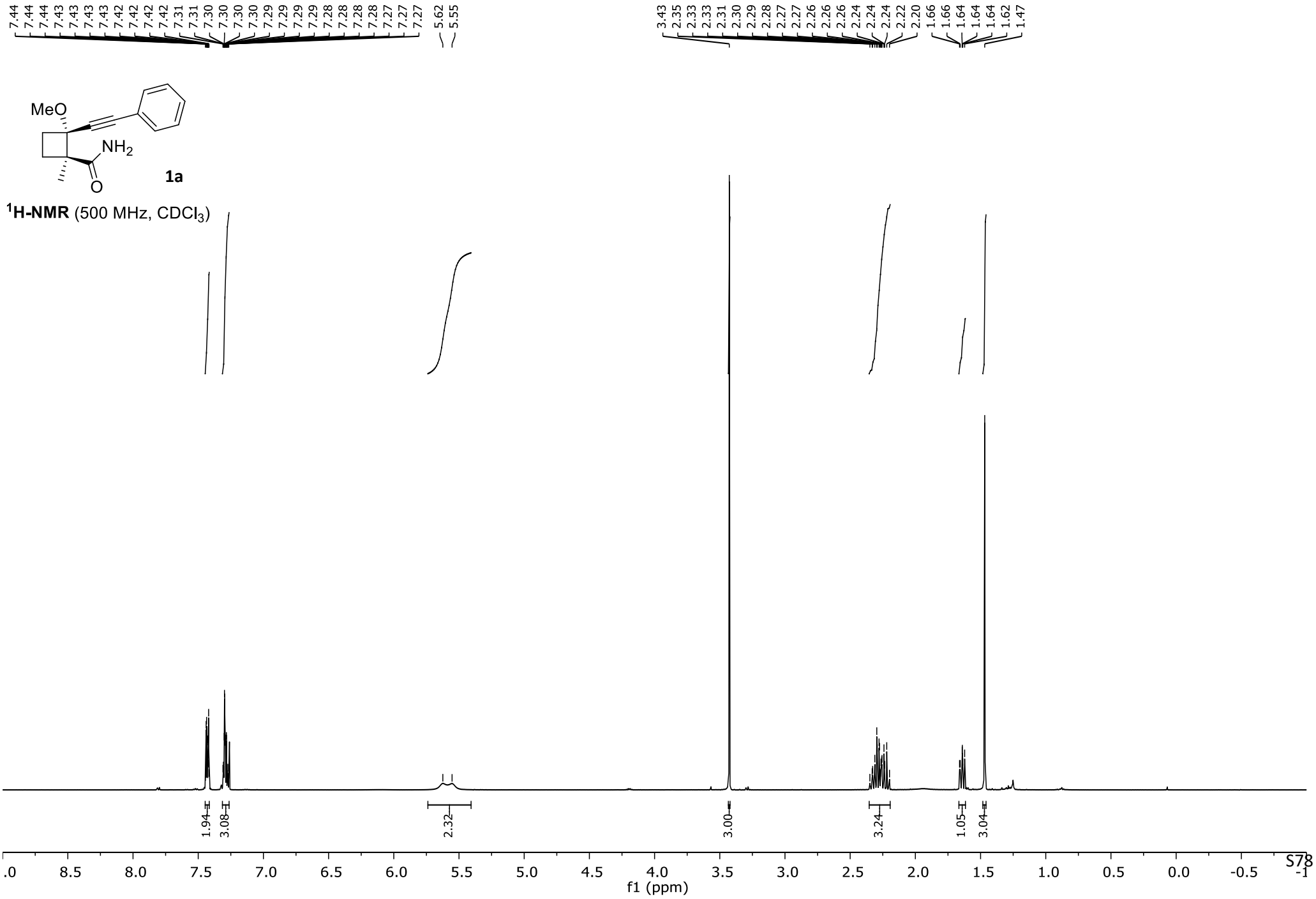

180.60
91.91
75.70
73.14
55.02
53.04
31.73
22.43
18.11
8.77
8.60
-0.42
MeO
OH
O
S4i
13C-NMR (100 MHz, CDCl3)
f1 (ppm)

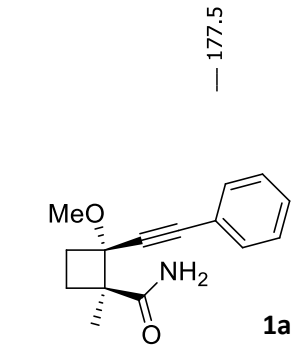


S4j

^{1}H-NMR (300 MHz, $CDCl_3$)

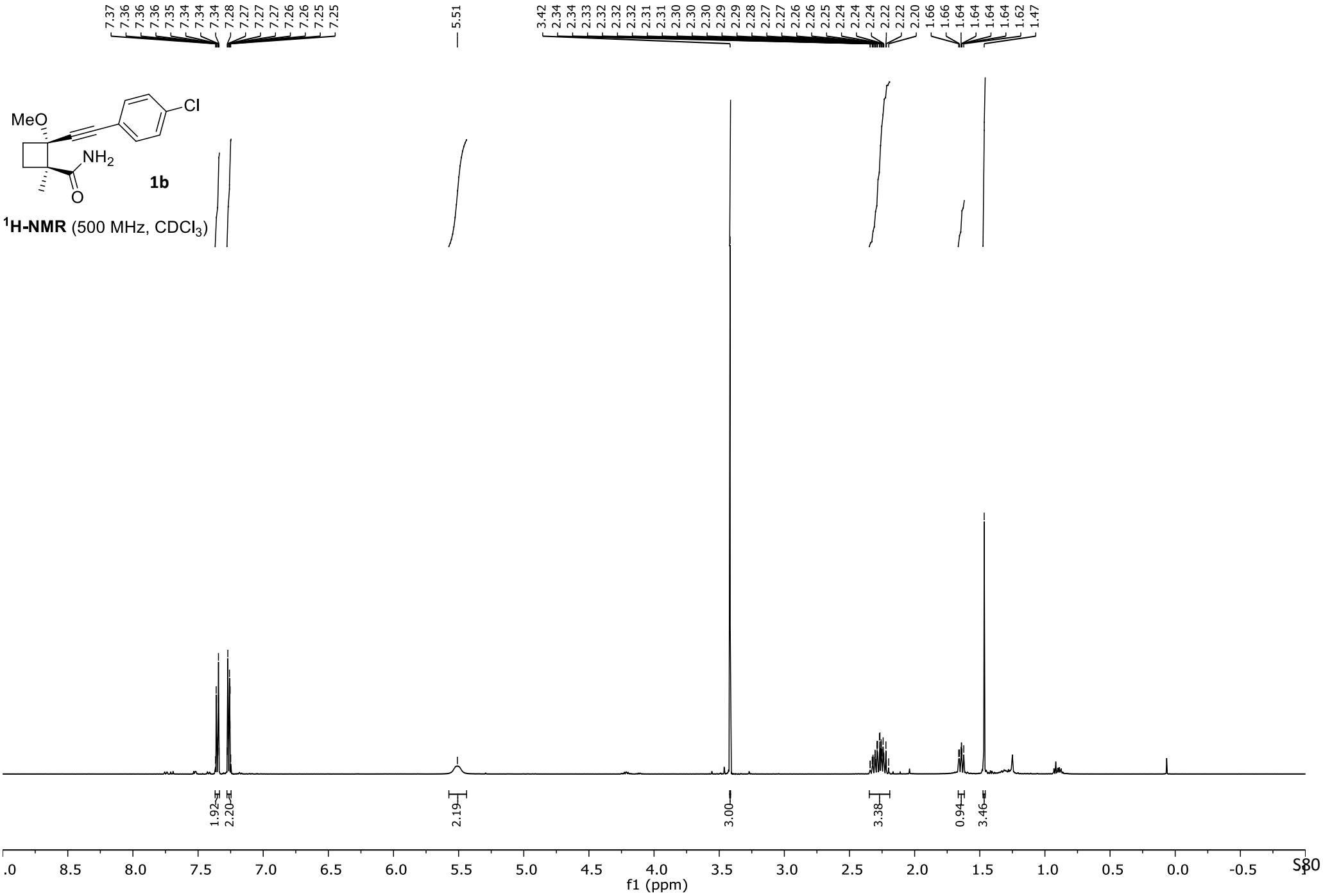

177.76
92.44
78.90
75.51
54.78
52.17
32.71
32.69
31.07
29.84
26.02
24.76
23.31
19.68
MeO
OH
O
S4j
1H-NMR (100 MHz, CDCl3)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

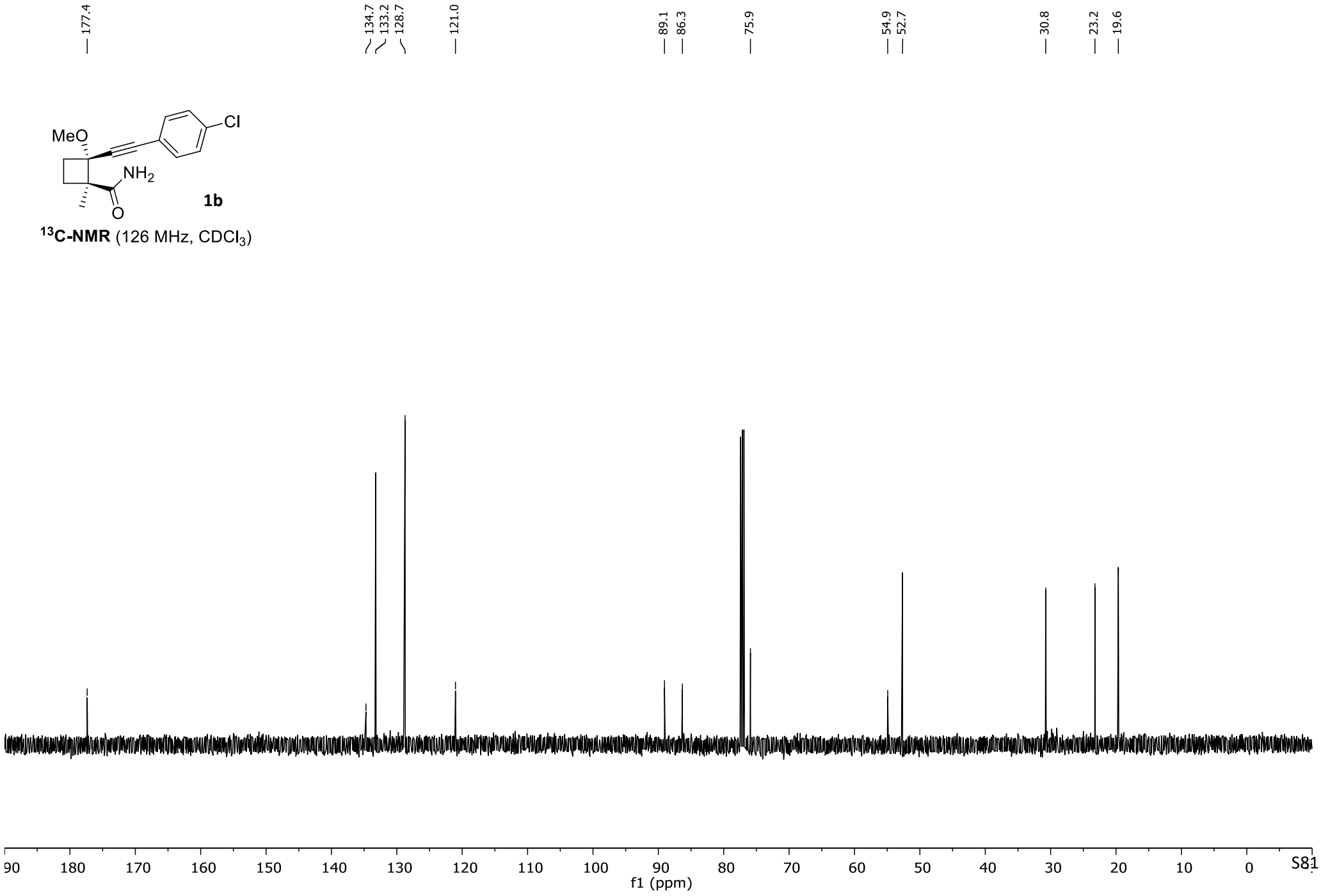

7.44 7.44 7.44 7.43 7.43 7.43 7.43 7.42 7.42 7.42 7.42 7.31 7.31 7.30 7.30 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.28 7.28 7.27 7.27 7.27 5.62 5.55
3.43 2.35 2.33 2.33 2.31 2.30 2.29 2.28 2.27 2.27 2.26 2.26 2.26 2.24 2.24 2.24 2.22 2.20 1.66 1.66 1.64 1.64 1.64 1.62 1.47
MeO
NH2
O
1a
1H-NMR (500 MHz, CDCl3)
1.94
3.08
2.32
3.00
3.24
1.05
3.04
f1 (ppm)

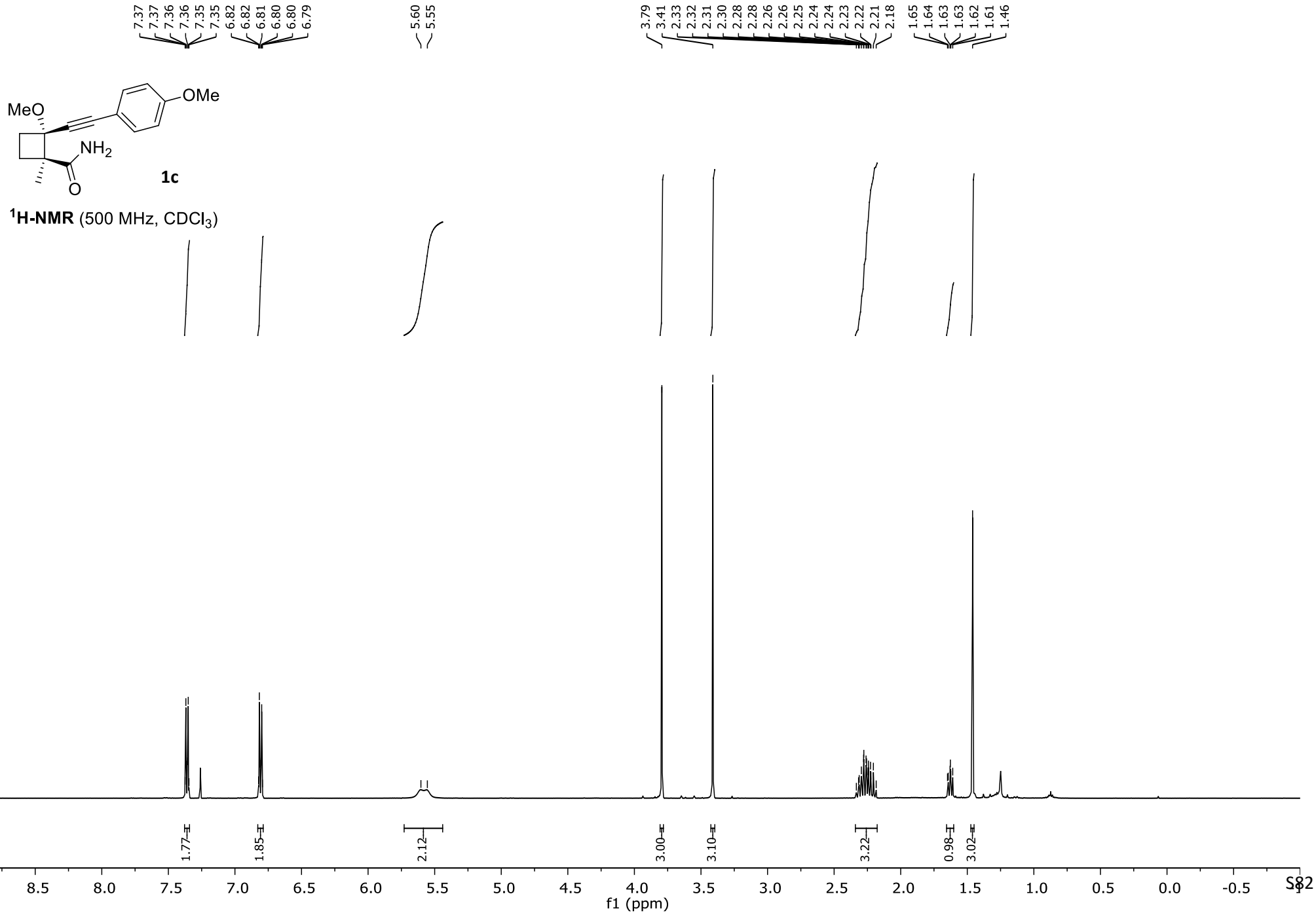


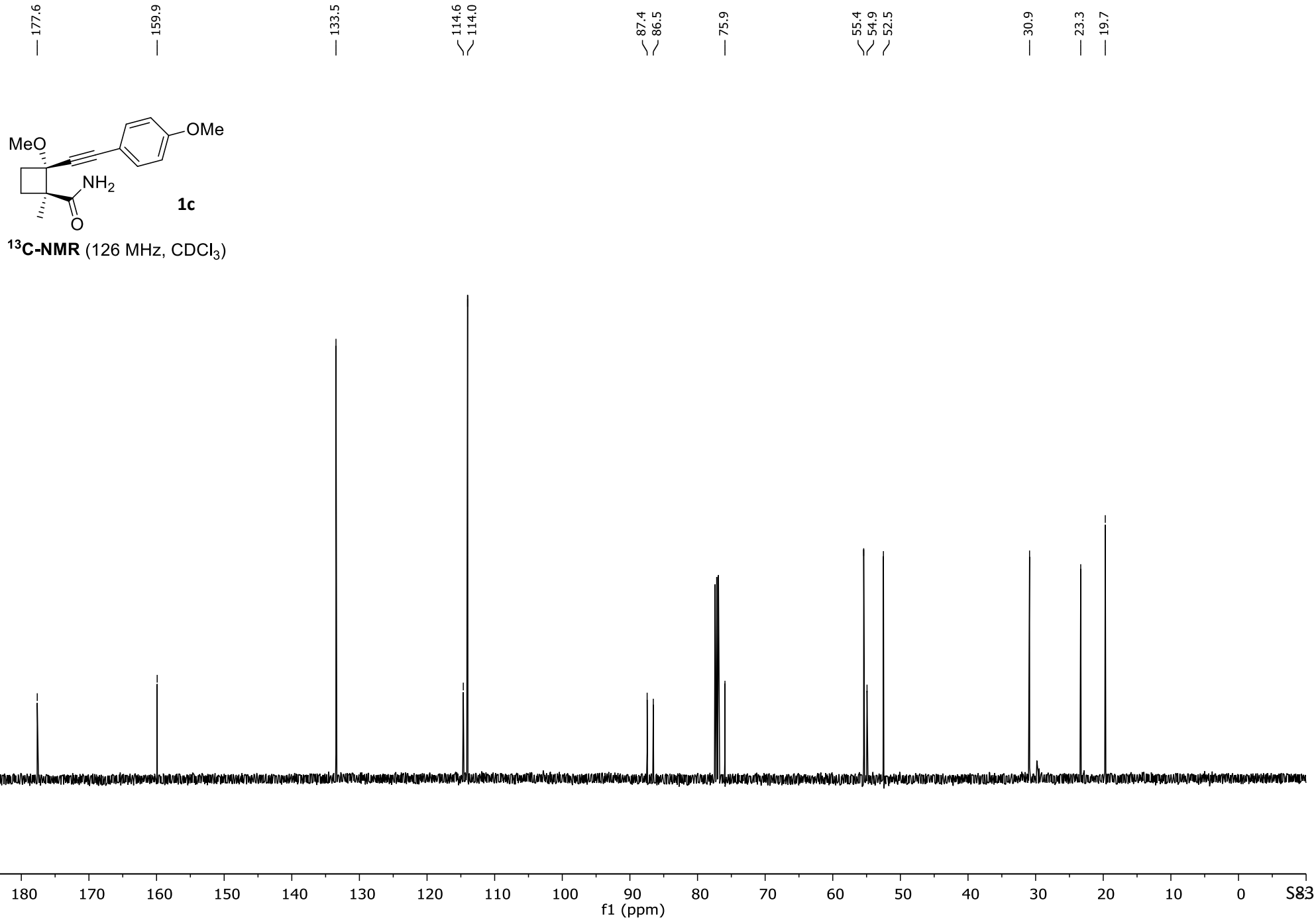
1a

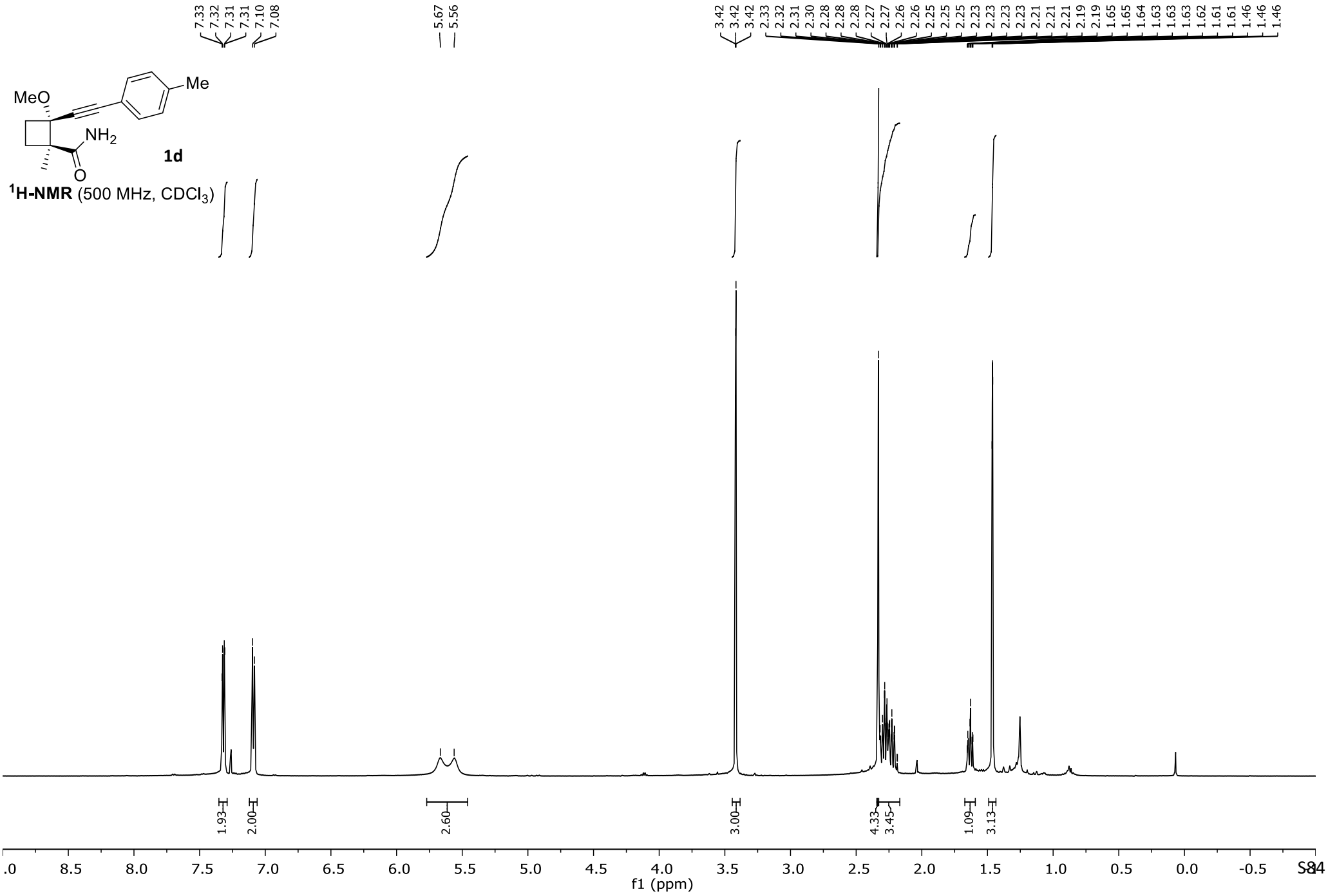
^{13}C-NMR (126 MHz, $CDCl_3$)

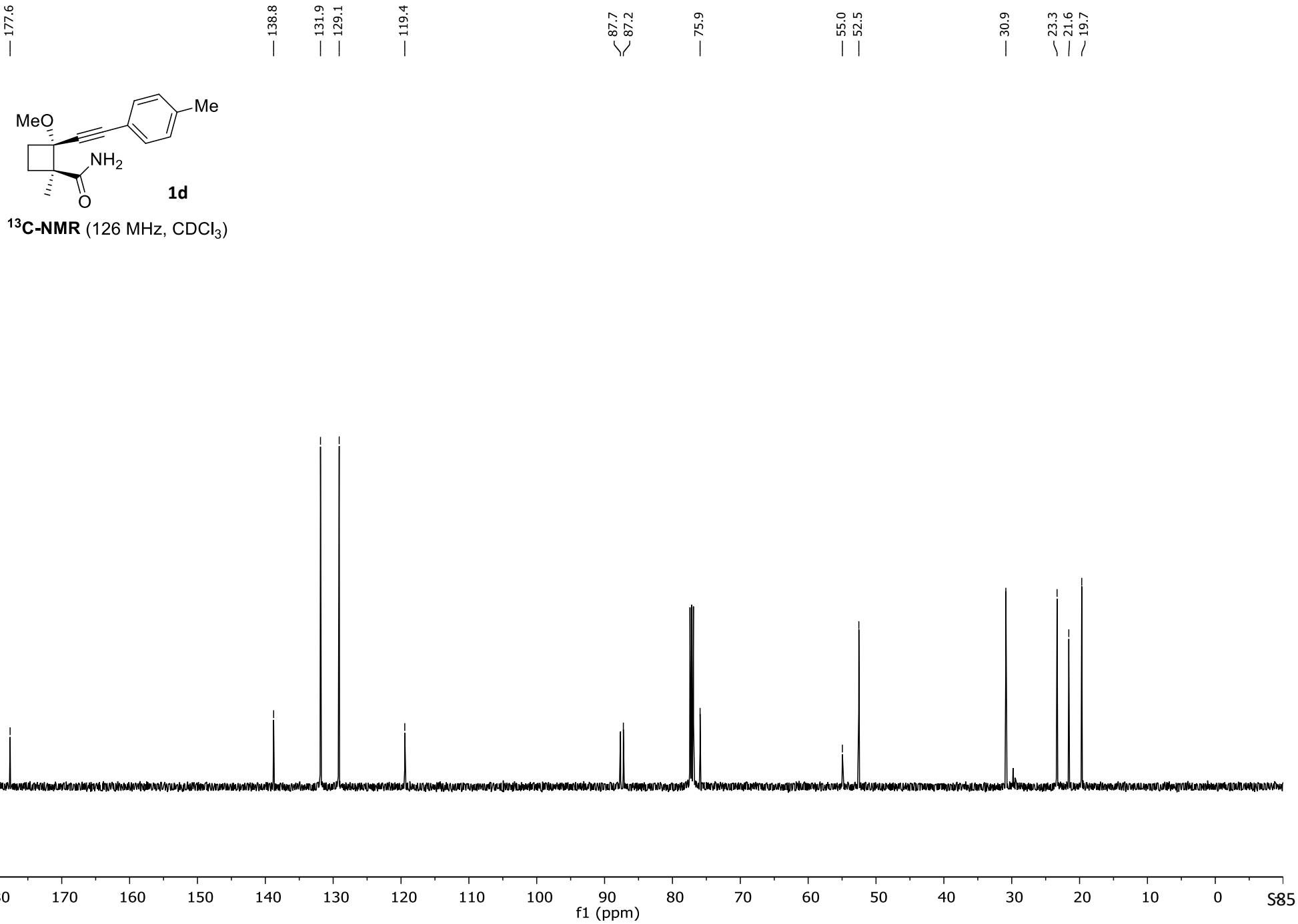

7.37 7.36 7.36 7.36 7.35 7.34 7.34 7.34 7.28 7.27 7.27 7.27 7.26 7.26 7.25 7.25
5.51
3.42 2.34 2.34 2.33 2.32 2.32 2.32 2.31 2.31 2.30 2.30 2.30 2.29 2.29 2.28 2.27 2.27 2.26 2.26 2.25 2.24 2.24 2.24 2.22 2.22 2.20 1.66 1.66 1.64 1.64 1.64 1.64 1.62 1.47
MeO
Cl
NH2
O
1b
1H-NMR (500 MHz, CDCl3)
1.92
2.20
2.19
3.00
3.38
0.94
3.46
f1 (ppm)

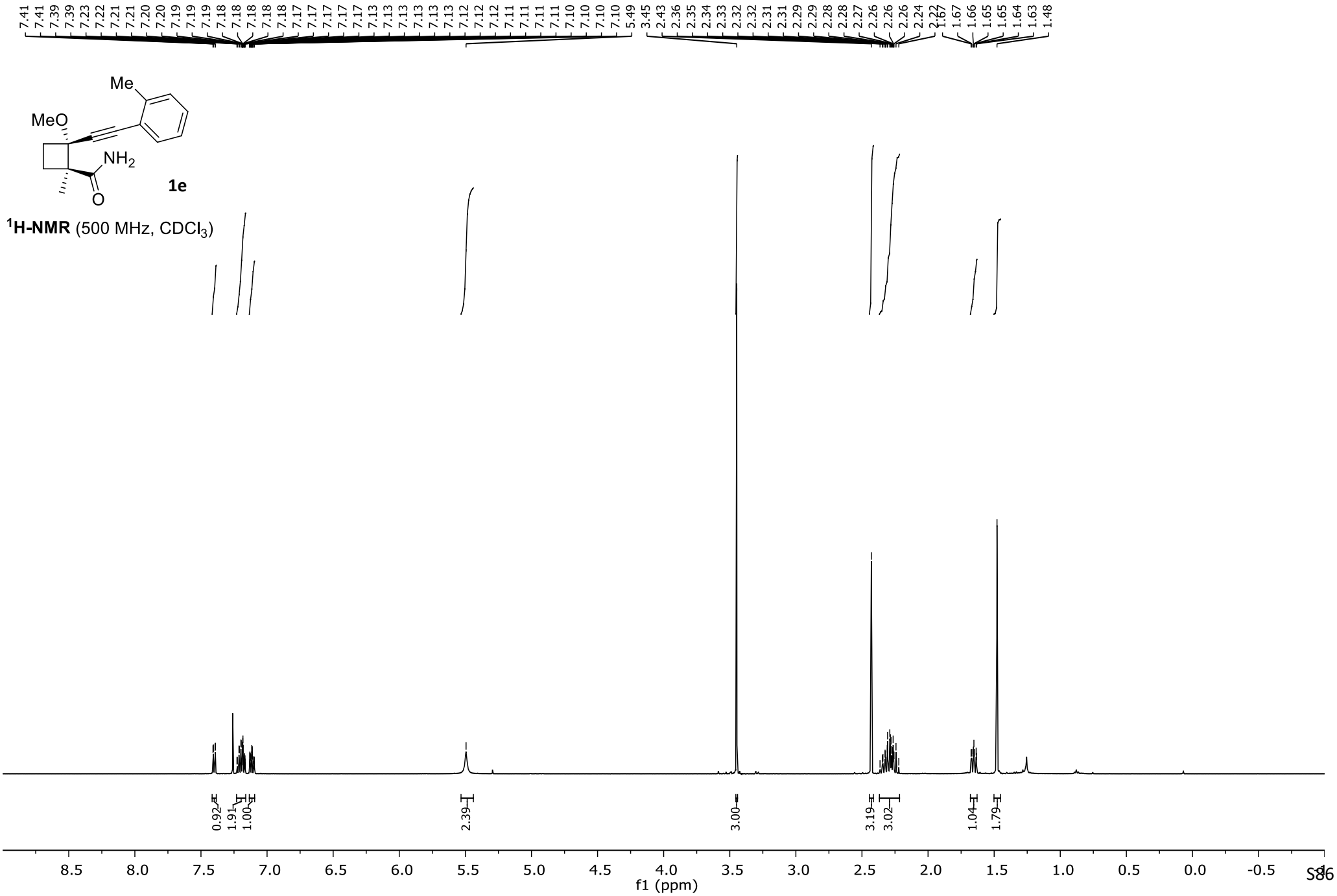

177.4
134.7
133.2
128.7
121.0
89.1
86.3
75.9
54.9
52.7
30.8
23.2
19.6
MeO
Cl
NH2
O
1b
13C-NMR (126 MHz, CDCl3)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

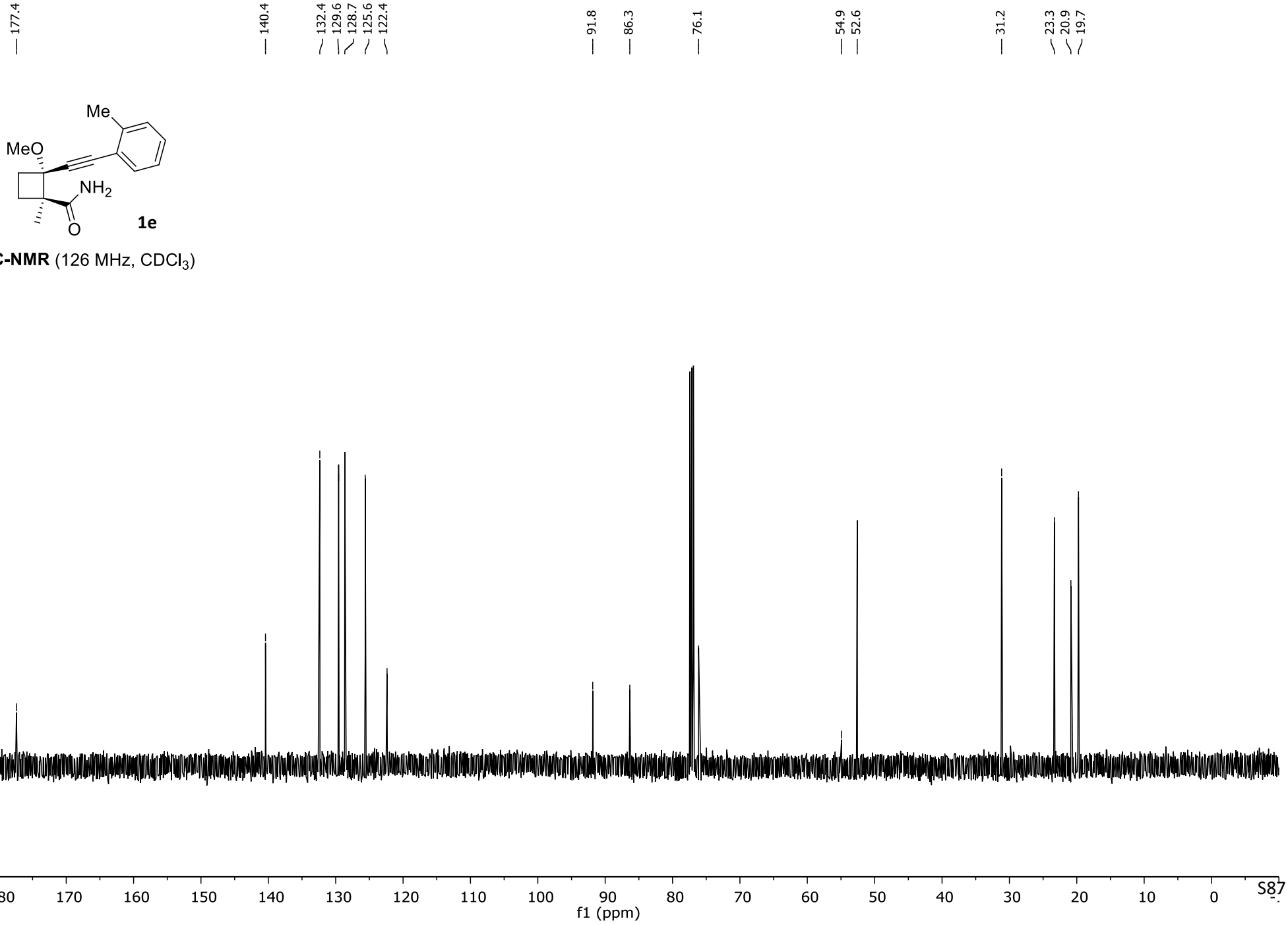

7.37
7.37
7.36
7.36
7.35
7.35
6.82
6.82
6.81
6.80
6.80
6.79
5.60
5.55
3.79
3.41
2.33
2.32
2.31
2.30
2.28
2.28
2.26
2.26
2.25
2.24
2.24
2.23
2.22
2.21
2.18
1.65
1.64
1.63
1.63
1.62
1.61
1.46
MeO
OMe
NH2
O
1c
1H-NMR (500 MHz, CDCl3)
1.77
1.85
2.12
3.00
3.10
3.22
0.98
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

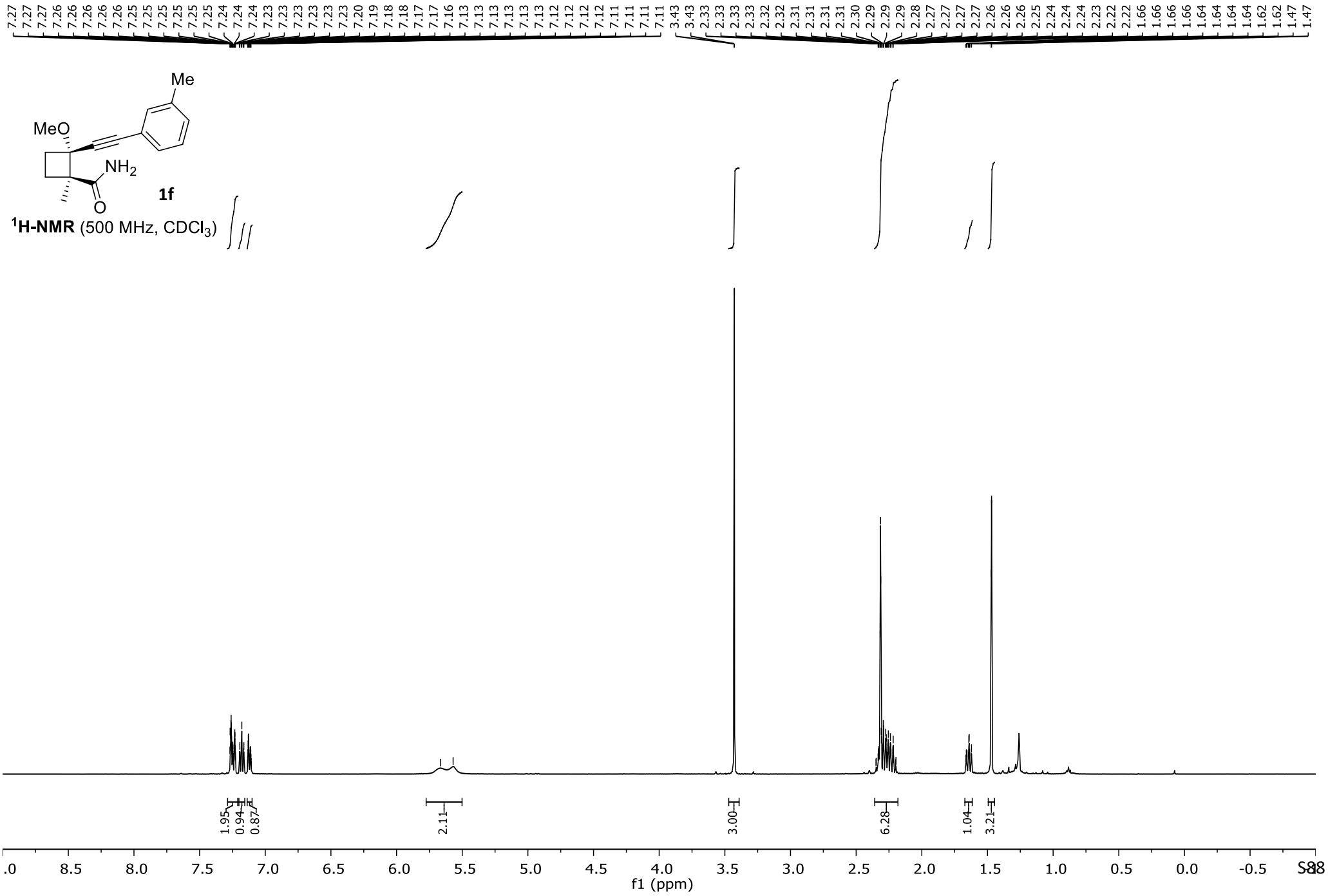

177.6
159.9
133.5
114.6
114.0
87.4
86.5
75.9
55.4
54.9
52.5
30.9
23.3
19.7
MeO
OMe
NH2
O
1c
13C-NMR (126 MHz, CDCl3)
f1 (ppm)

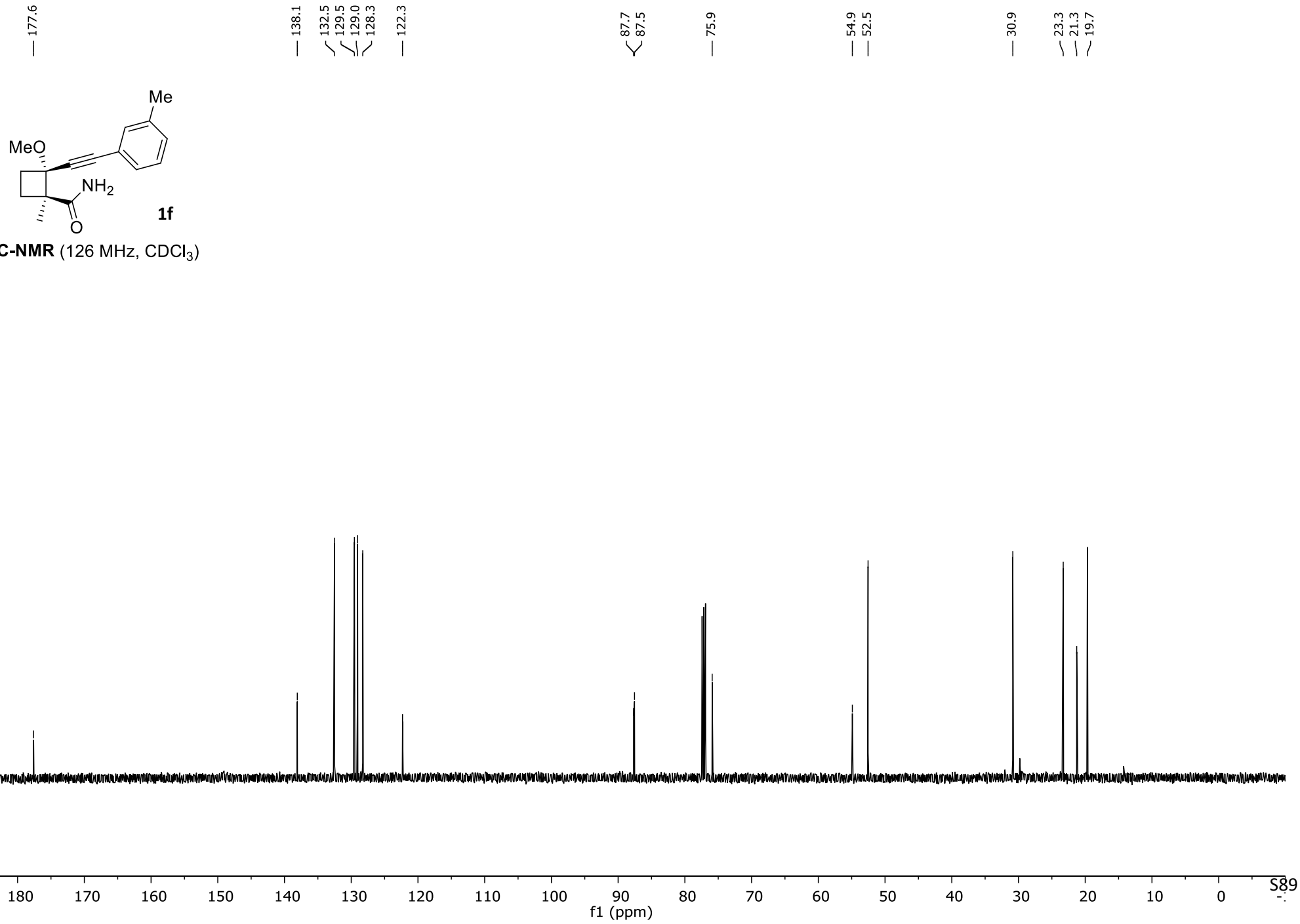

MeO
Me
NH2
O
1d
1H-NMR (500 MHz, CDCl3)
7.33
7.32
7.31
7.31
7.10
7.08
5.67
5.56
3.42
3.42
3.42
2.33
2.32
2.31
2.30
2.28
2.28
2.28
2.27
2.27
2.26
2.26
2.25
2.25
2.25
2.23
2.23
2.23
2.21
2.21
2.21
2.19
1.65
1.65
1.64
1.63
1.63
1.63
1.62
1.61
1.61
1.46
1.46
1.46
1.93
2.00
2.60
3.00
4.33
3.45
1.09
3.13
f1 (ppm)

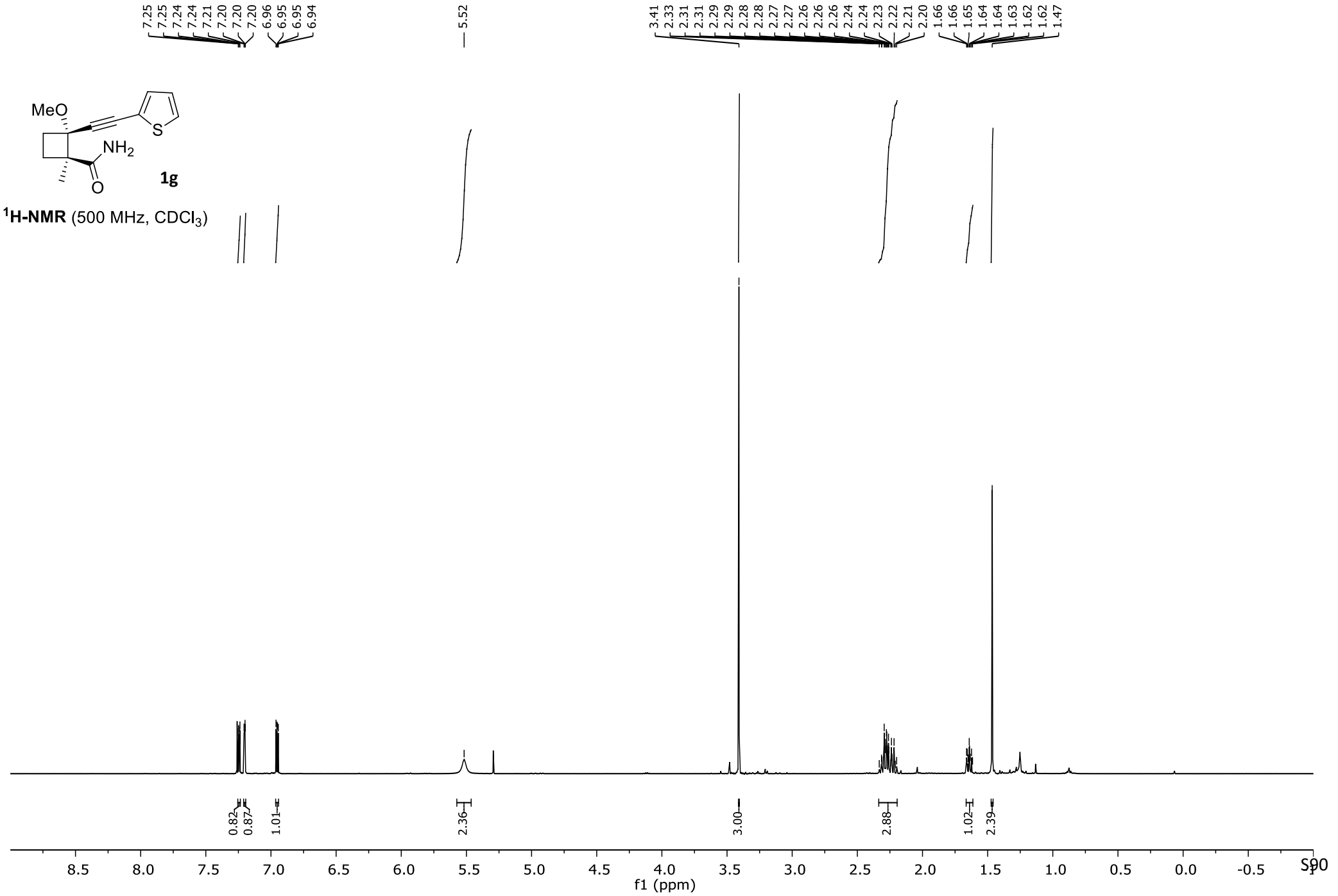

177.6
138.8
131.9
129.1
119.4
87.7
87.2
75.9
55.0
52.5
30.9
23.3
21.6
19.7
MeO
Me
NH2
O
1d
13C-NMR (126 MHz, CDCl3)
f1 (ppm)

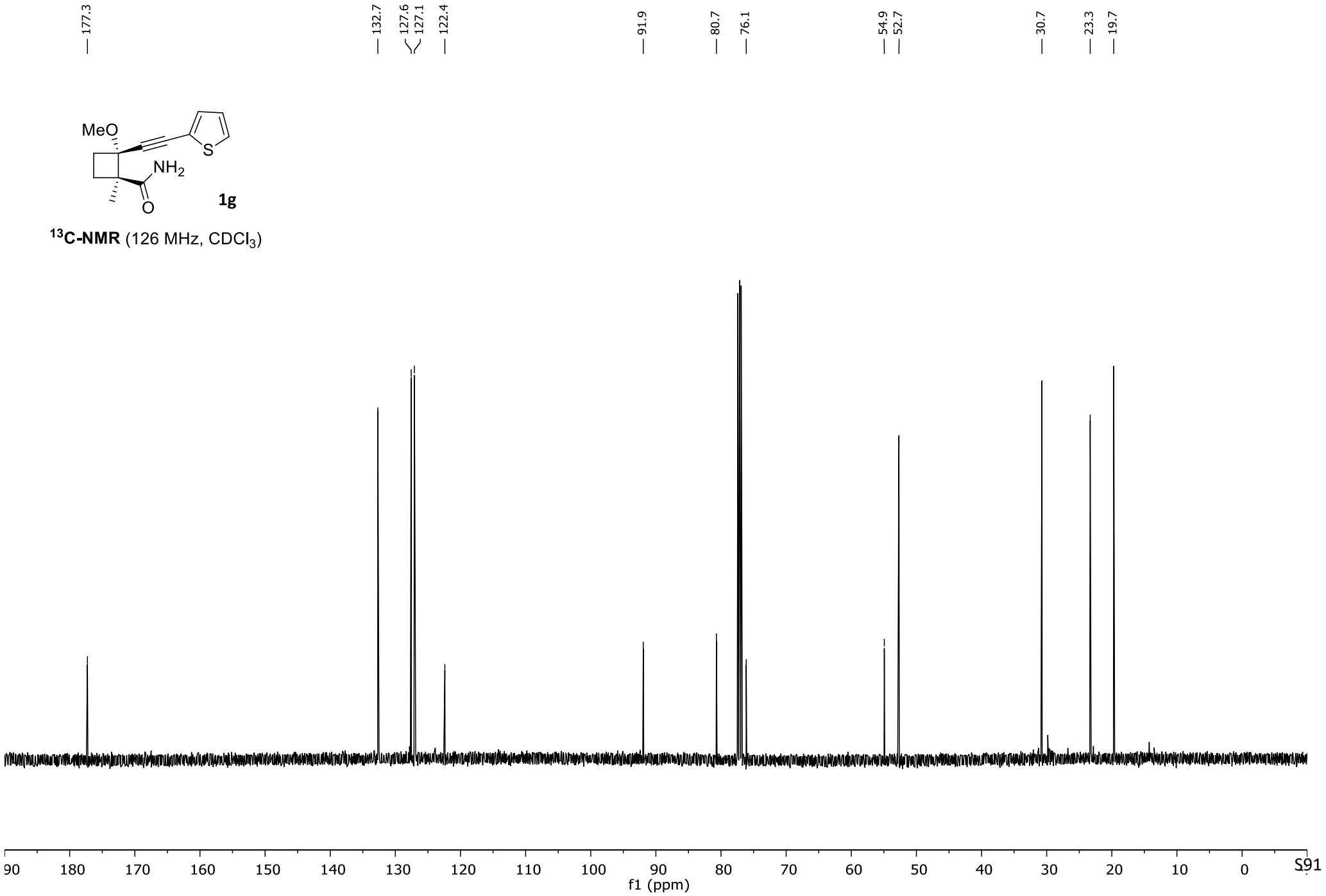

Me
MeO
NH2
O
1e
1H-NMR (500 MHz, CDCl3)
0.92
1.91
1.00
2.39
3.00
3.19
3.02
1.04
1.79
f1 (ppm)

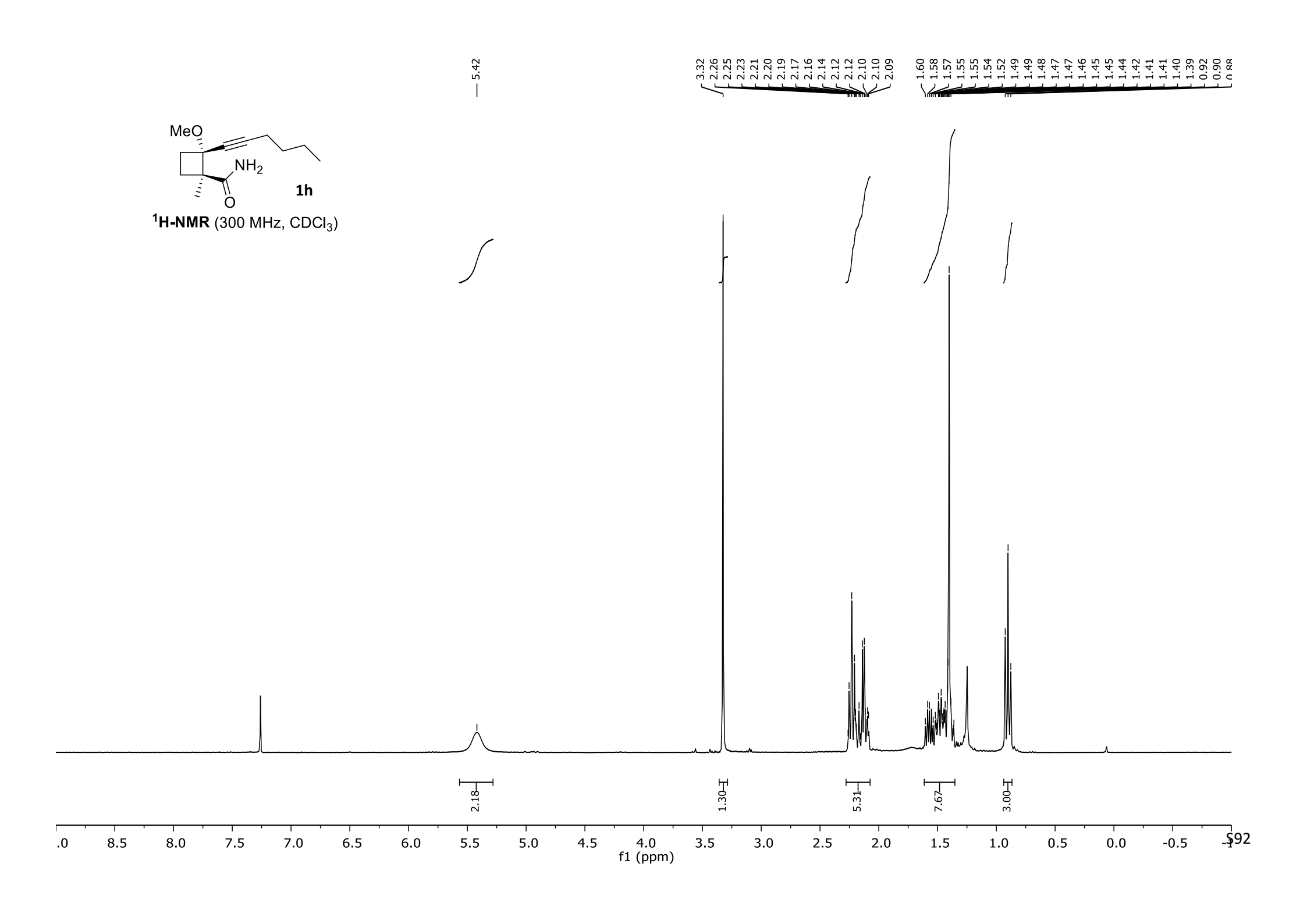

177.4
140.4
132.4
129.6
128.7
125.6
122.4
91.8
86.3
76.1
54.9
52.6
31.2
23.3
20.9
19.7
Me
MeO
NH2
O
1e
13C-NMR (126 MHz, CDCl3)
f1 (ppm)

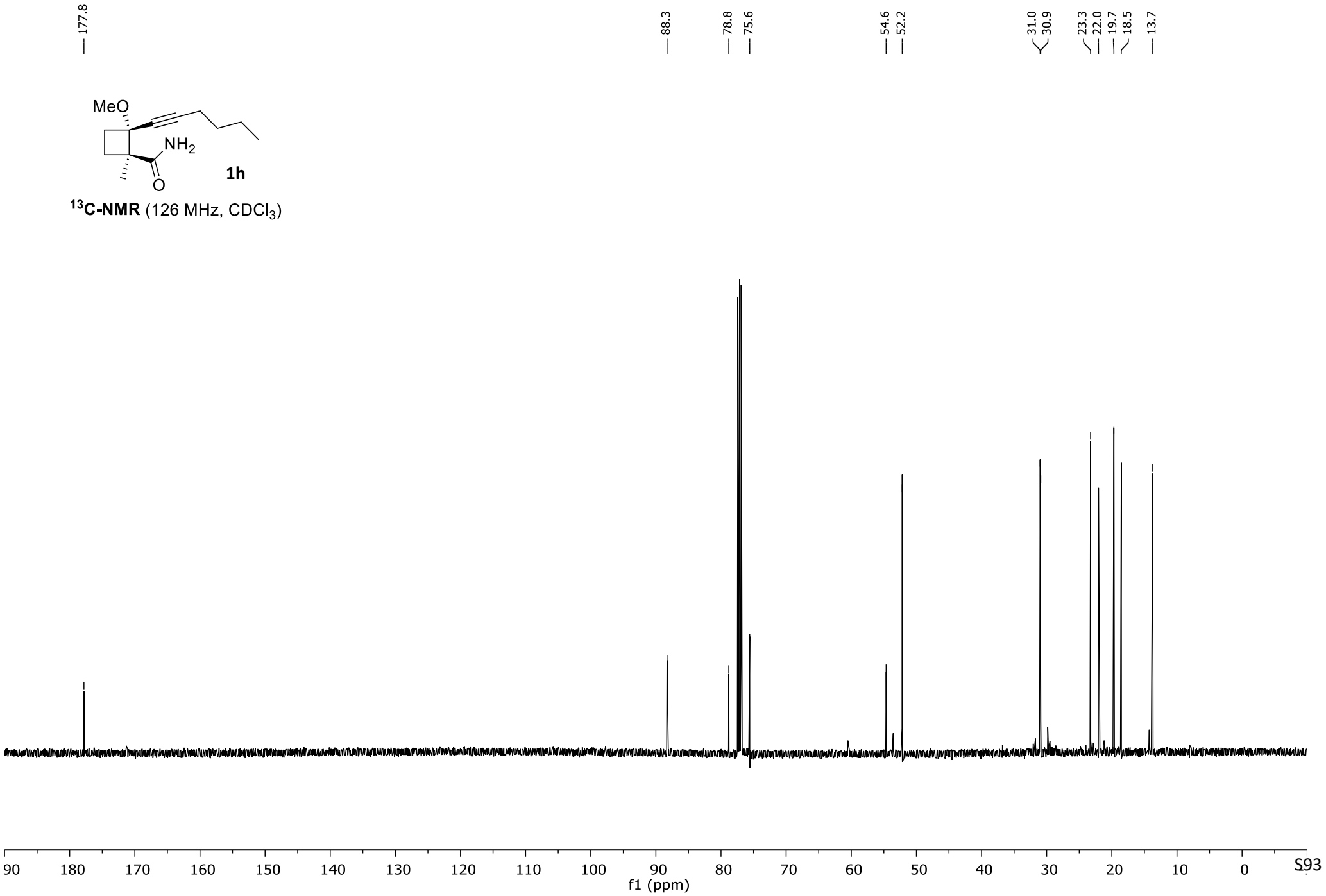

Me
MeO
NH2
O
1f
1H-NMR (500 MHz, CDCl3)
1.95
0.94
0.87
2.11
3.00
6.28
1.04
3.21
f1 (ppm)

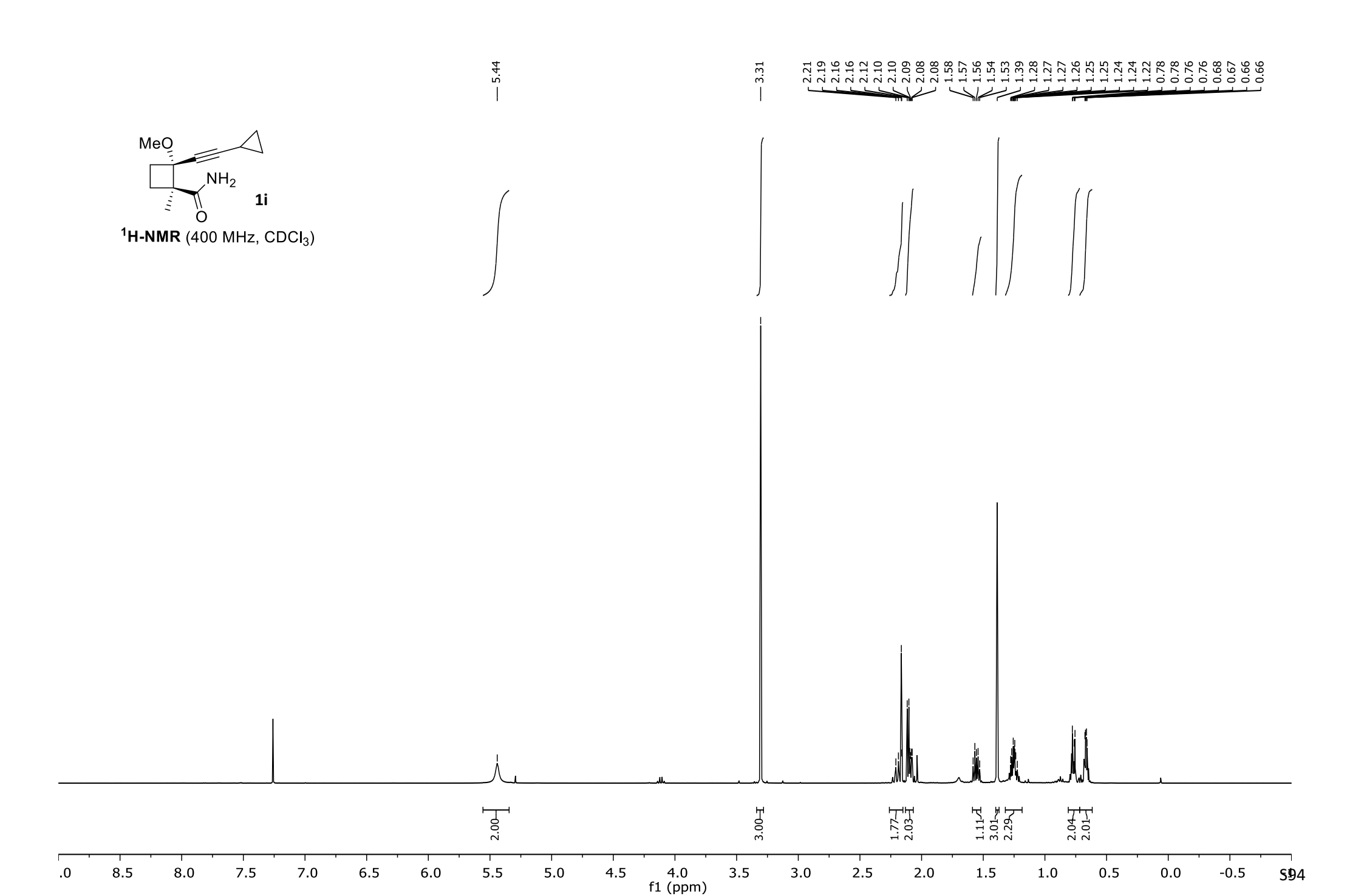

177.6
138.1
132.5
129.5
129.0
128.3
122.3
87.7
87.5
75.9
54.9
52.5
30.9
23.3
21.3
19.7
Me
MeO
NH2
O
1f
13C-NMR (126 MHz, CDCl3)
f1 (ppm)

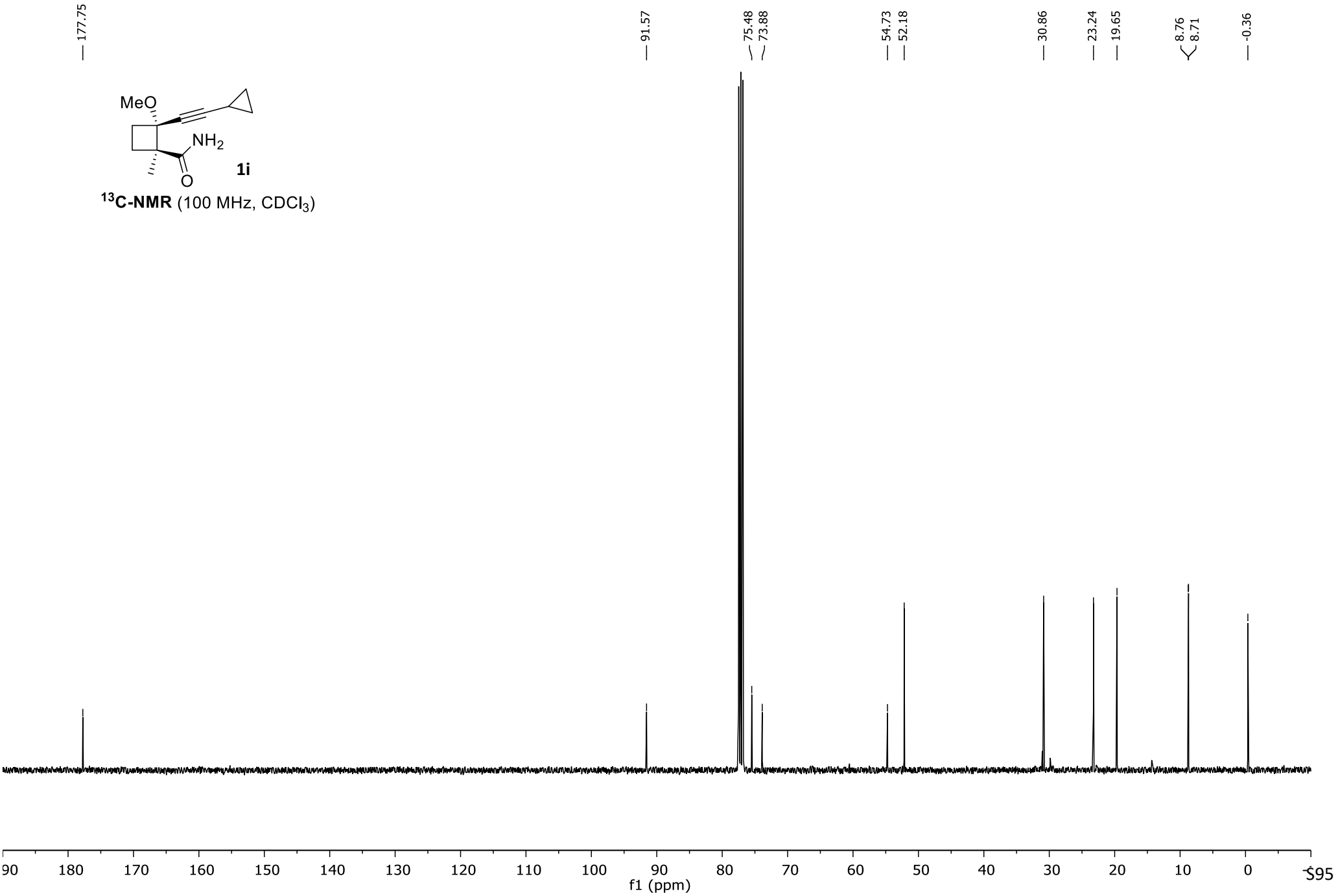

7.25 7.25 7.24 7.24 7.21 7.20 7.20 7.20 6.96 6.95 6.95 6.94
5.52
3.41 2.33 2.31 2.31 2.29 2.29 2.28 2.28 2.27 2.27 2.26 2.26 2.26 2.24 2.24 2.23 2.22 2.21 2.20 1.66 1.66 1.65 1.64 1.64 1.63 1.62 1.62 1.47
MeO
S
NH2
O
1g
1H-NMR (500 MHz, CDCl3)
0.82
0.87
1.01
2.36
3.00
2.88
1.02
2.39
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

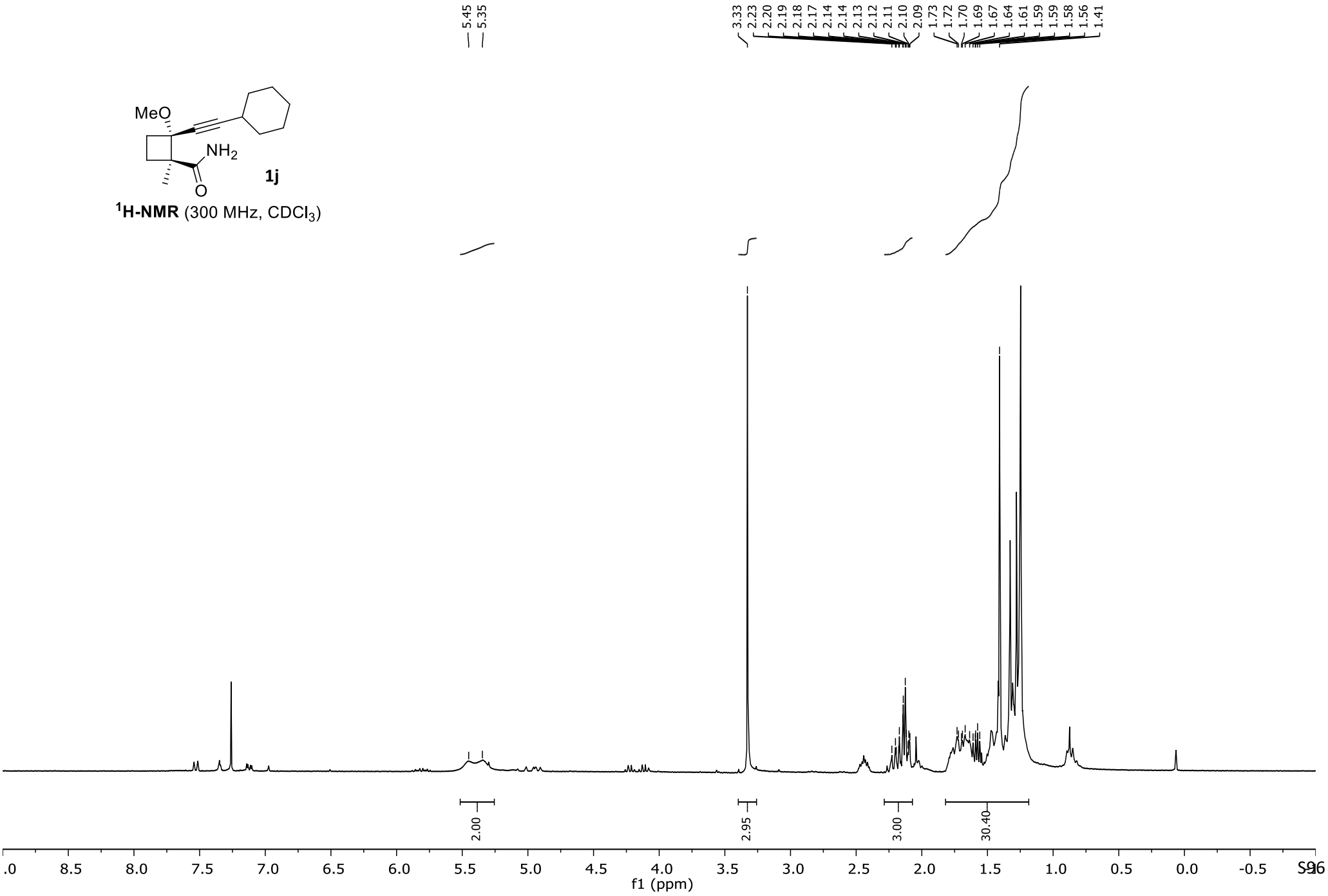

177.3
132.7
127.6
127.1
122.4
91.9
80.7
76.1
54.9
52.7
30.7
23.3
19.7
MeO
NH2
O
S
1g
13C-NMR (126 MHz, CDCl3)
f1 (ppm)

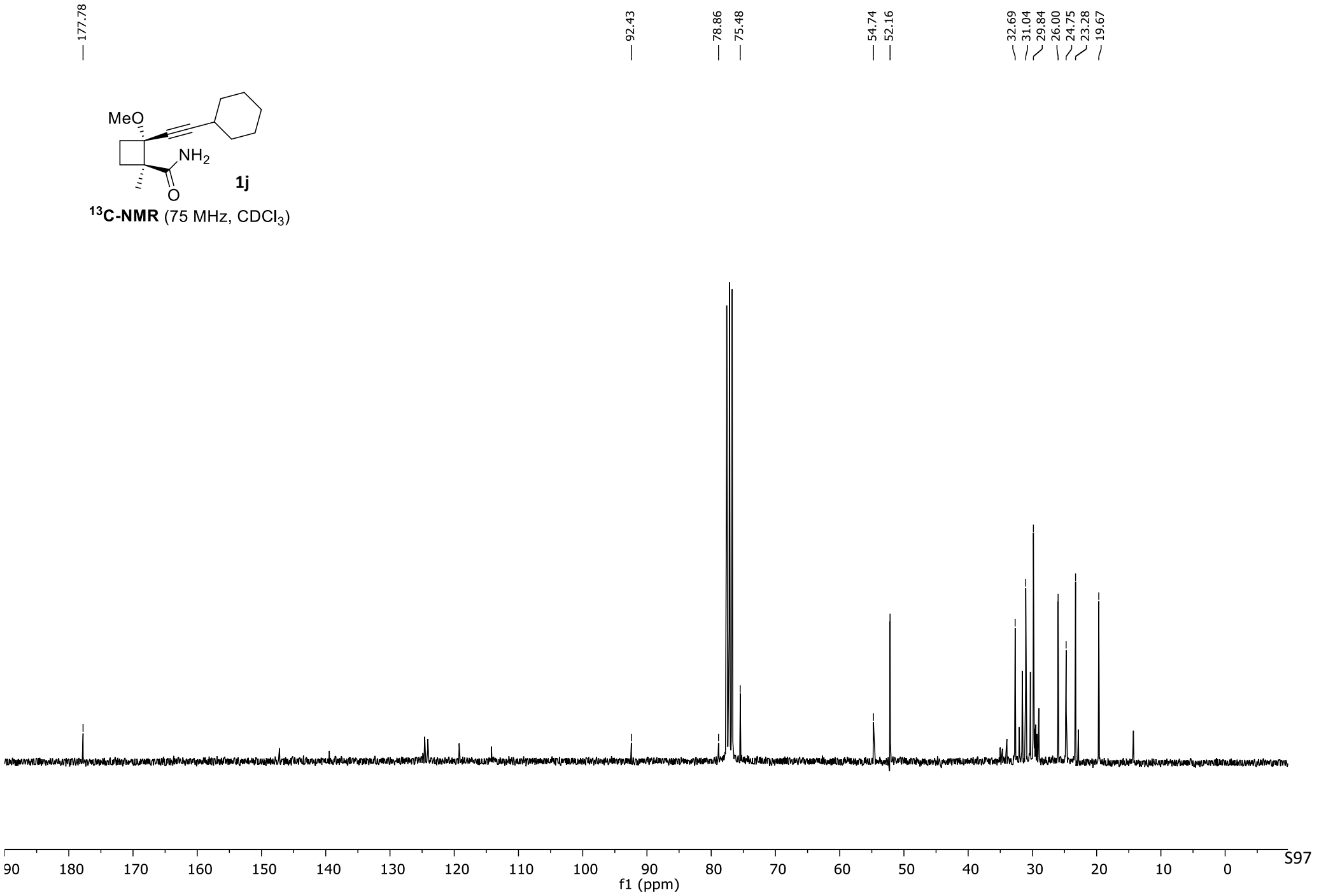

MeO
NH2
O
1h
1H-NMR (300 MHz, CDCl3)
5.42
3.32
2.26
2.25
2.23
2.21
2.20
2.19
2.17
2.16
2.14
2.12
2.12
2.10
2.10
2.09
1.60
1.58
1.57
1.55
1.55
1.54
1.52
1.49
1.49
1.48
1.47
1.47
1.46
1.45
1.45
1.44
1.42
1.41
1.41
1.40
1.39
0.92
0.90
2.18
1.30
5.31
7.67
3.00
f1 (ppm)

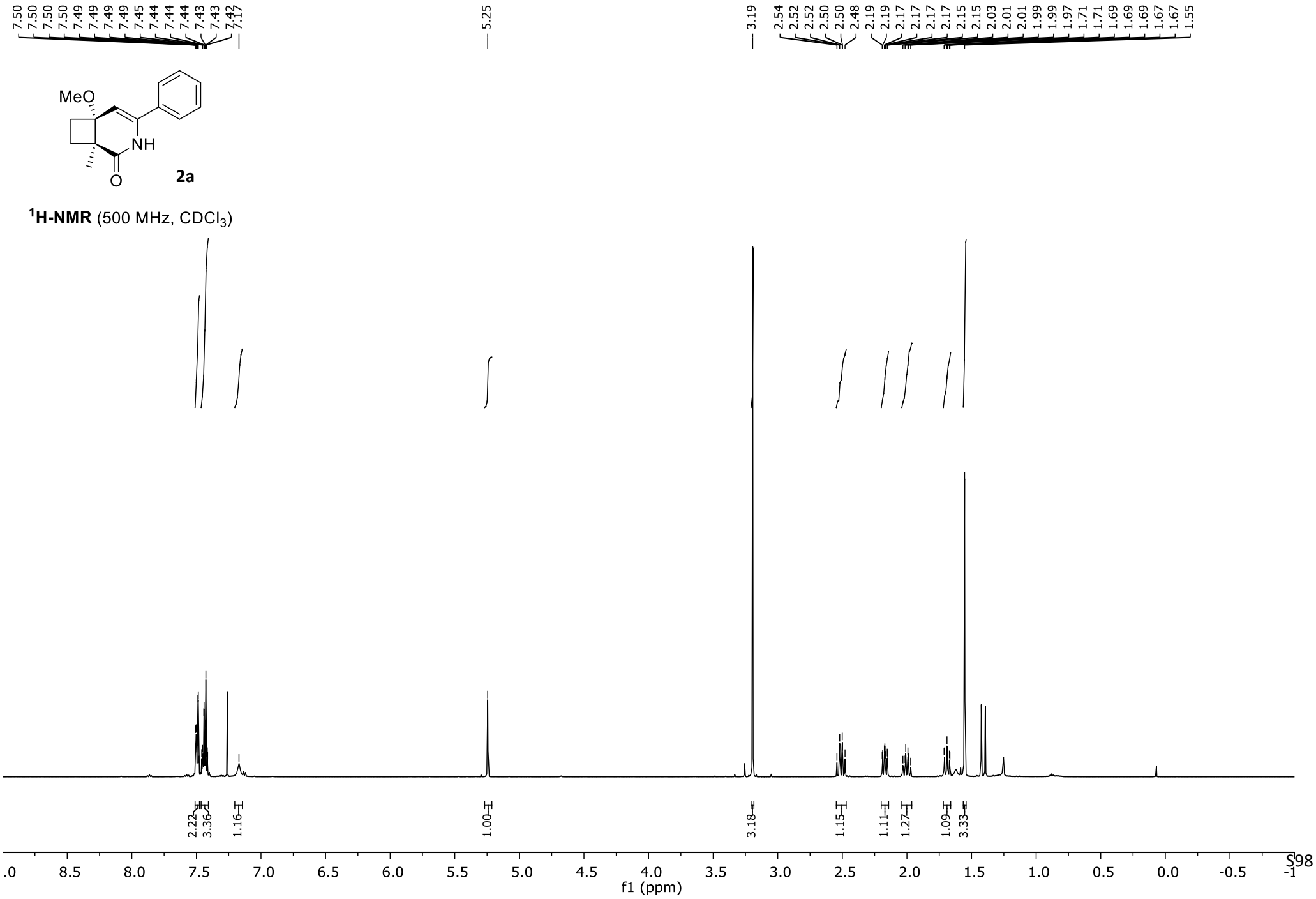

177.8
88.3
78.8
75.6
54.6
52.2
31.0
30.9
23.3
22.0
19.7
18.5
13.7
MeO
NH2
O
1h
13C-NMR (126 MHz, CDCl3)
f1 (ppm)


MeO
NH2
O
1i
1H-NMR (400 MHz, CDCl3)
5.44
3.31
2.21
2.19
2.16
2.16
2.12
2.10
2.10
2.09
2.08
2.08
1.58
1.57
1.56
1.54
1.53
1.39
1.28
1.27
1.27
1.26
1.25
1.25
1.24
1.24
1.22
0.78
0.78
0.76
0.76
0.68
0.67
0.66
0.66
2.00
3.00
1.77
2.03
1.11
3.01
2.29
2.04
2.01
f1 (ppm)

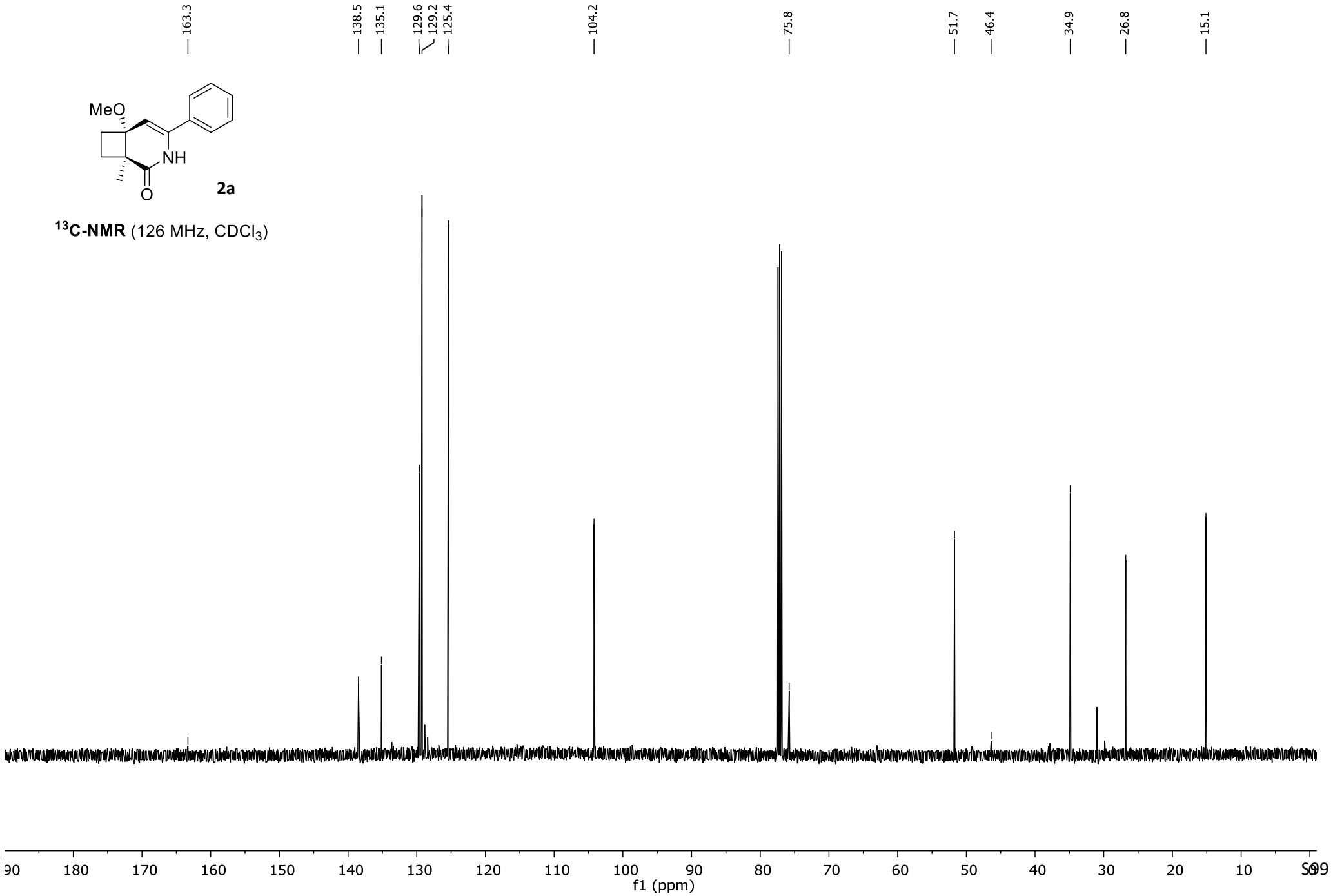

177.75
91.57
75.48
73.88
54.73
52.18
30.86
23.24
19.65
8.76
8.71
-0.36
MeO
NH2
O
1i
13C-NMR (100 MHz, CDCl3)
f1 (ppm)

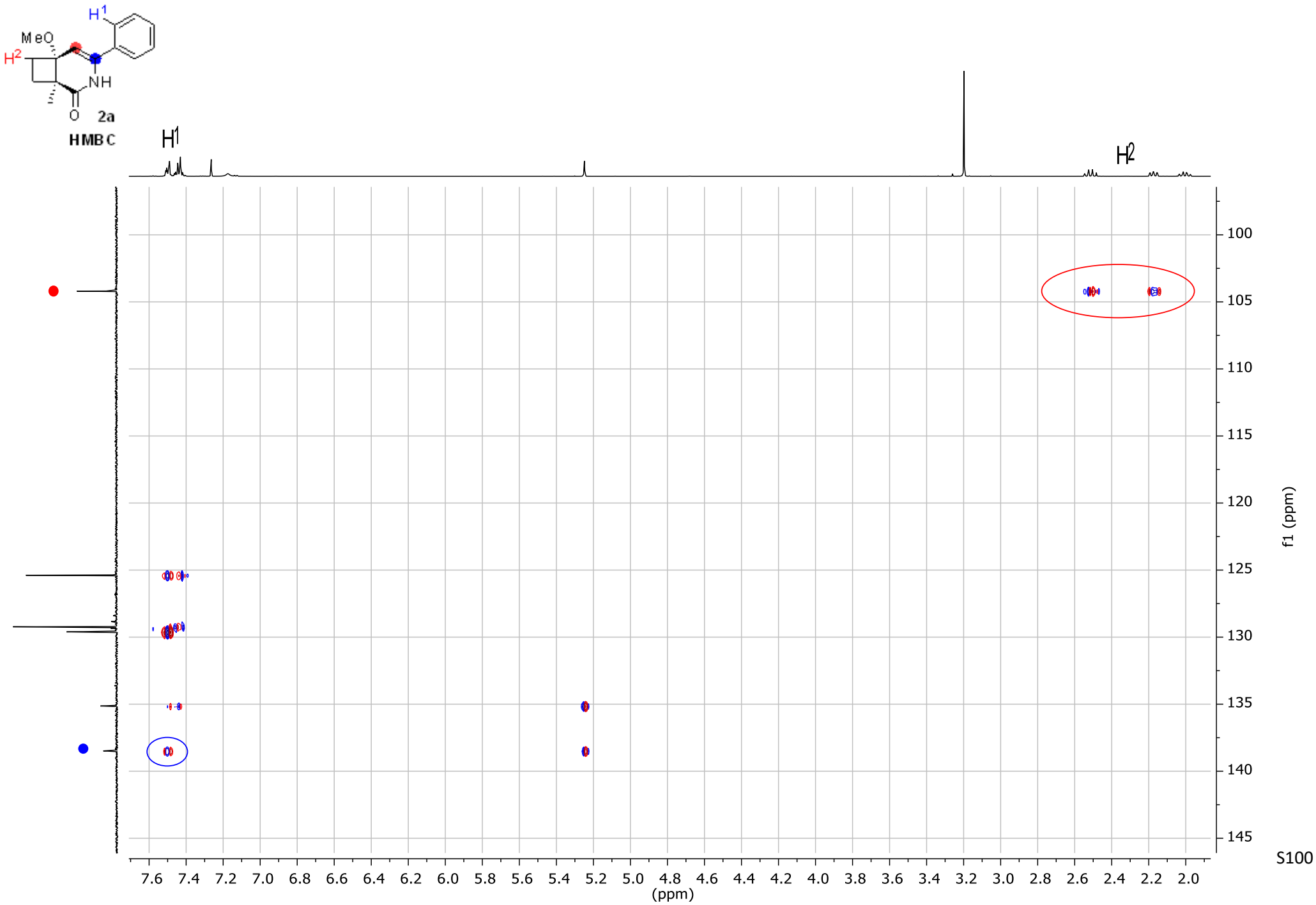

MeO
NH2
O
1j
1H-NMR (300 MHz, CDCl3)
5.45
5.35
3.33
2.23
2.20
2.19
2.18
2.17
2.14
2.14
2.13
2.12
2.11
2.10
2.09
1.73
1.72
1.70
1.69
1.67
1.64
1.61
1.59
1.59
1.58
1.56
1.41
2.00
2.95
3.00
30.40
f1 (ppm)

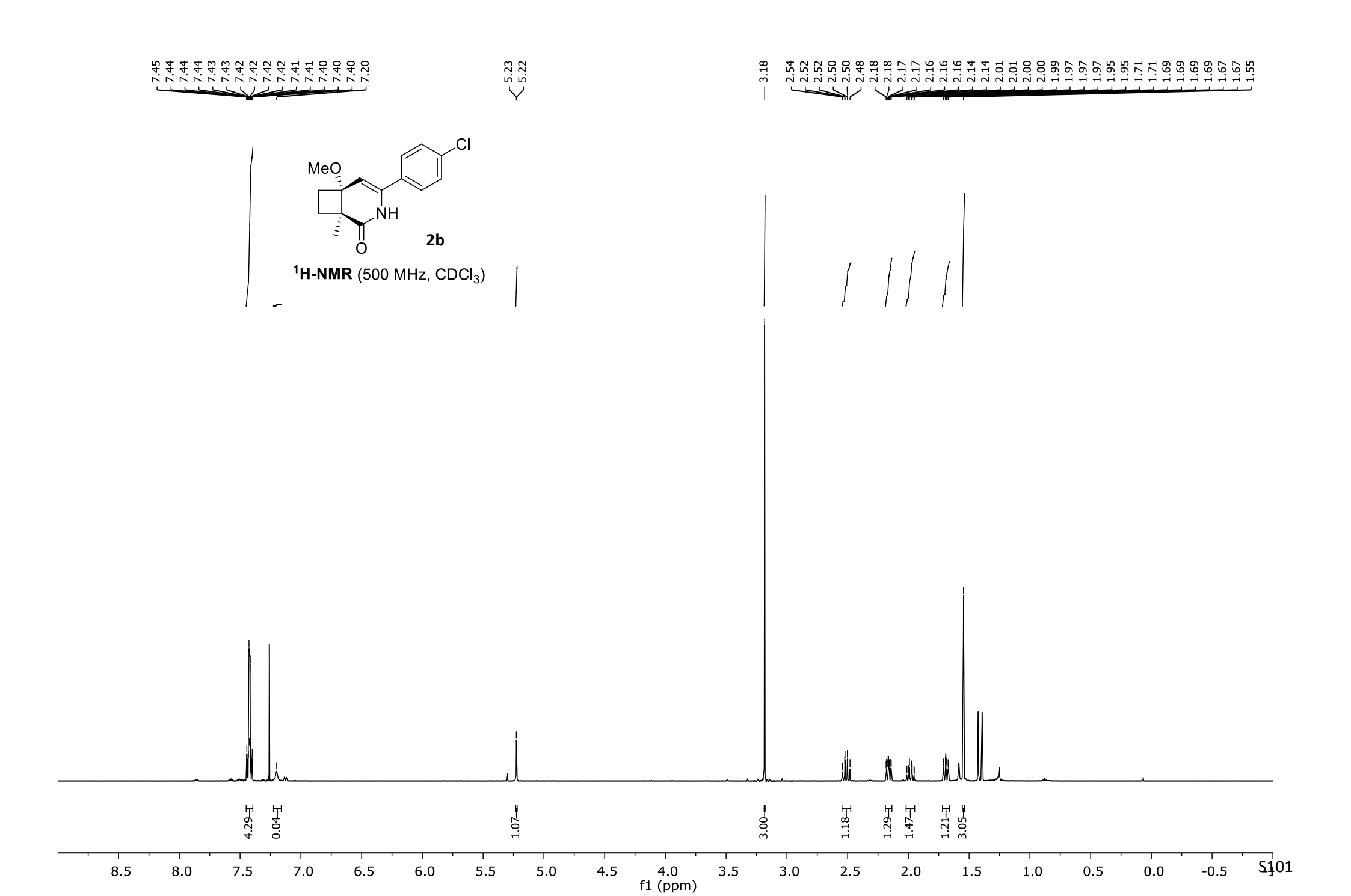

177.78
92.43
78.86
75.48
54.74
52.16
32.69
31.04
29.84
26.00
24.75
23.28
19.67
MeO
NH2
O
1j
13C-NMR (75 MHz, CDCl3)
f1 (ppm)

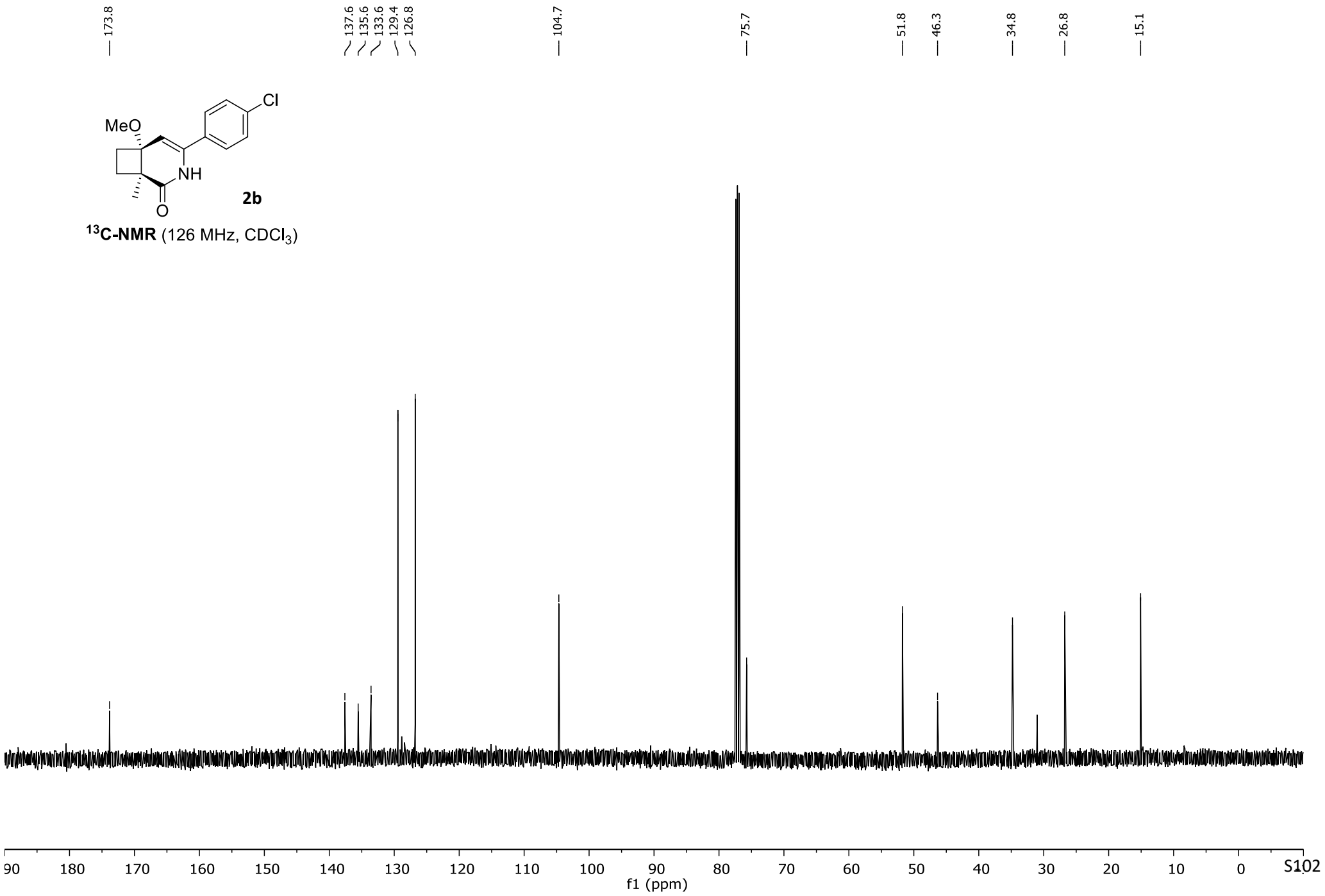


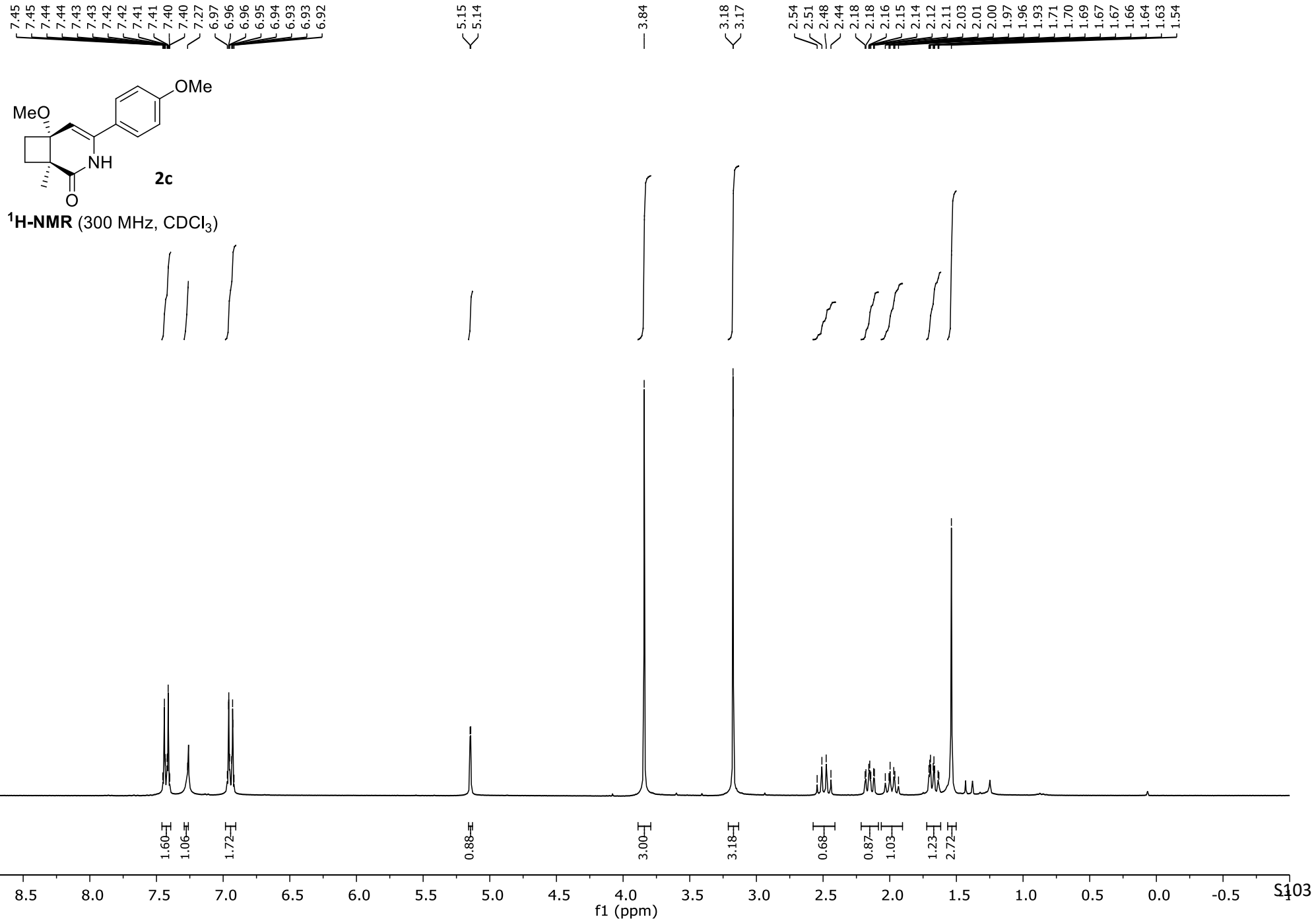
^{1}H-NMR (500 MHz, $CDCl_3$)

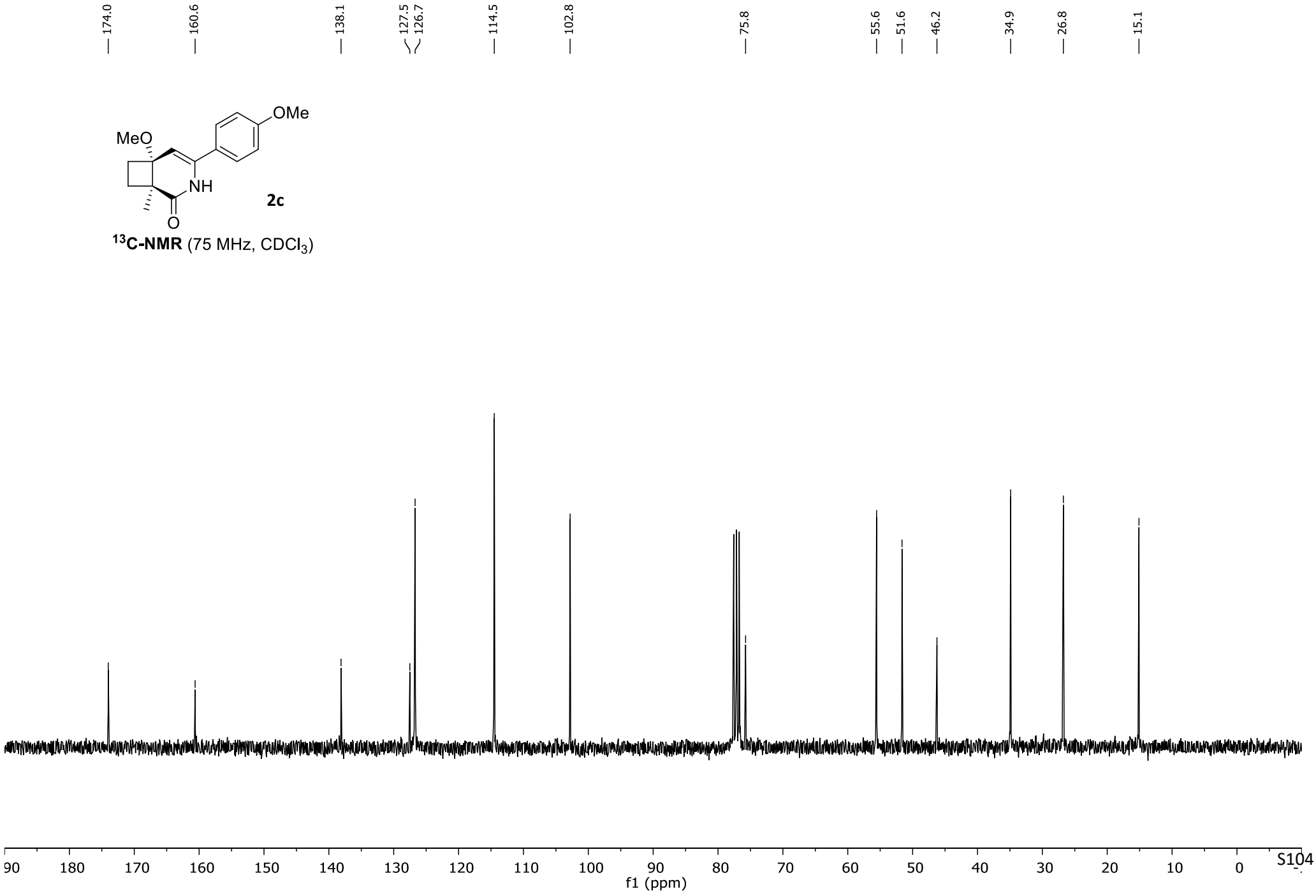

163.3
138.5
135.1
129.6
129.2
125.4
104.2
75.8
51.7
46.4
34.9
26.8
15.1
MeO
NH
O
2a
13C-NMR (126 MHz, CDCl3)
f1 (ppm)

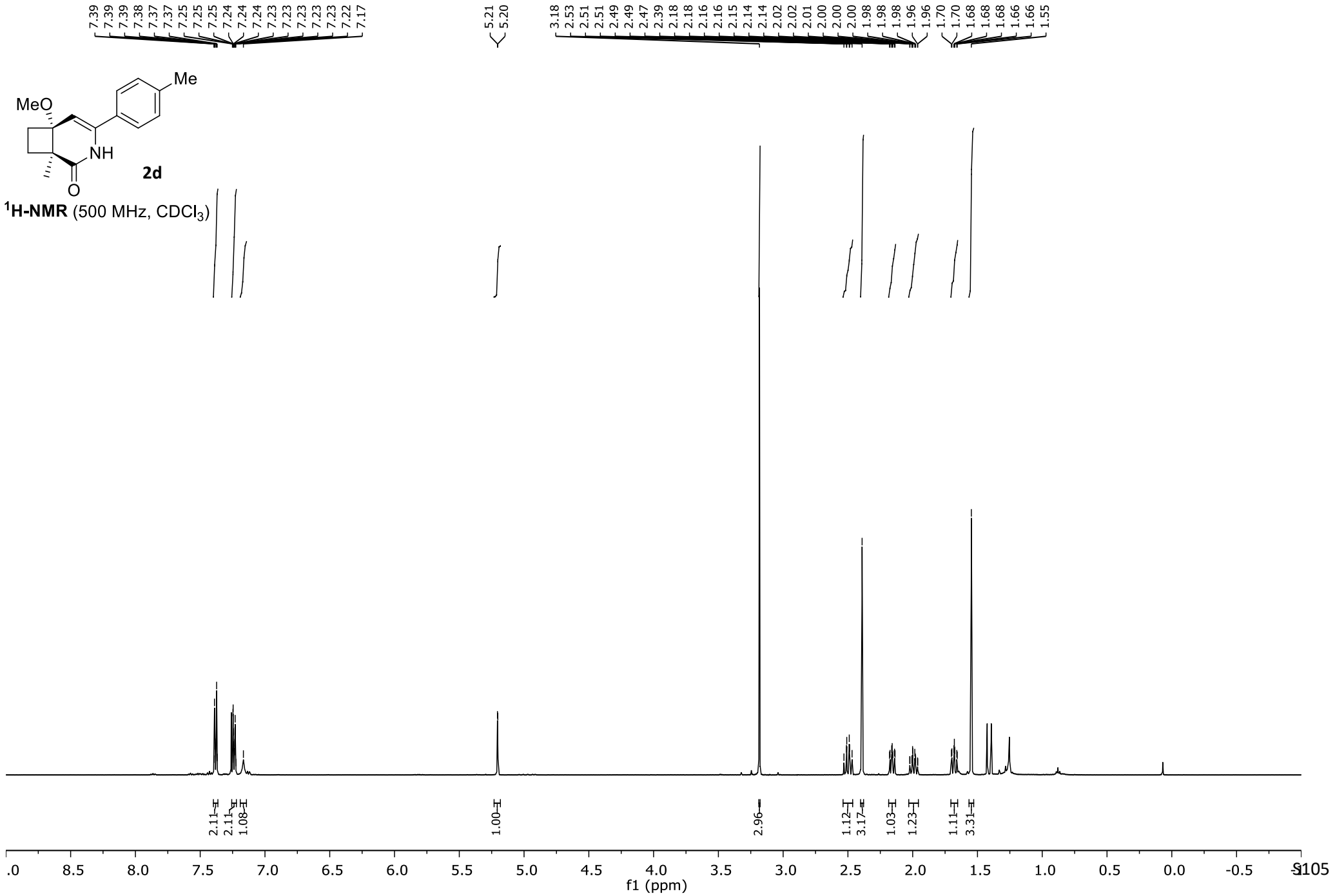

H1
MeO
H2
NH
O
2a
HMBC
H1
H2
100
105
110
115
120
125
130
135
140
145
f1 (ppm)
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
(ppm)

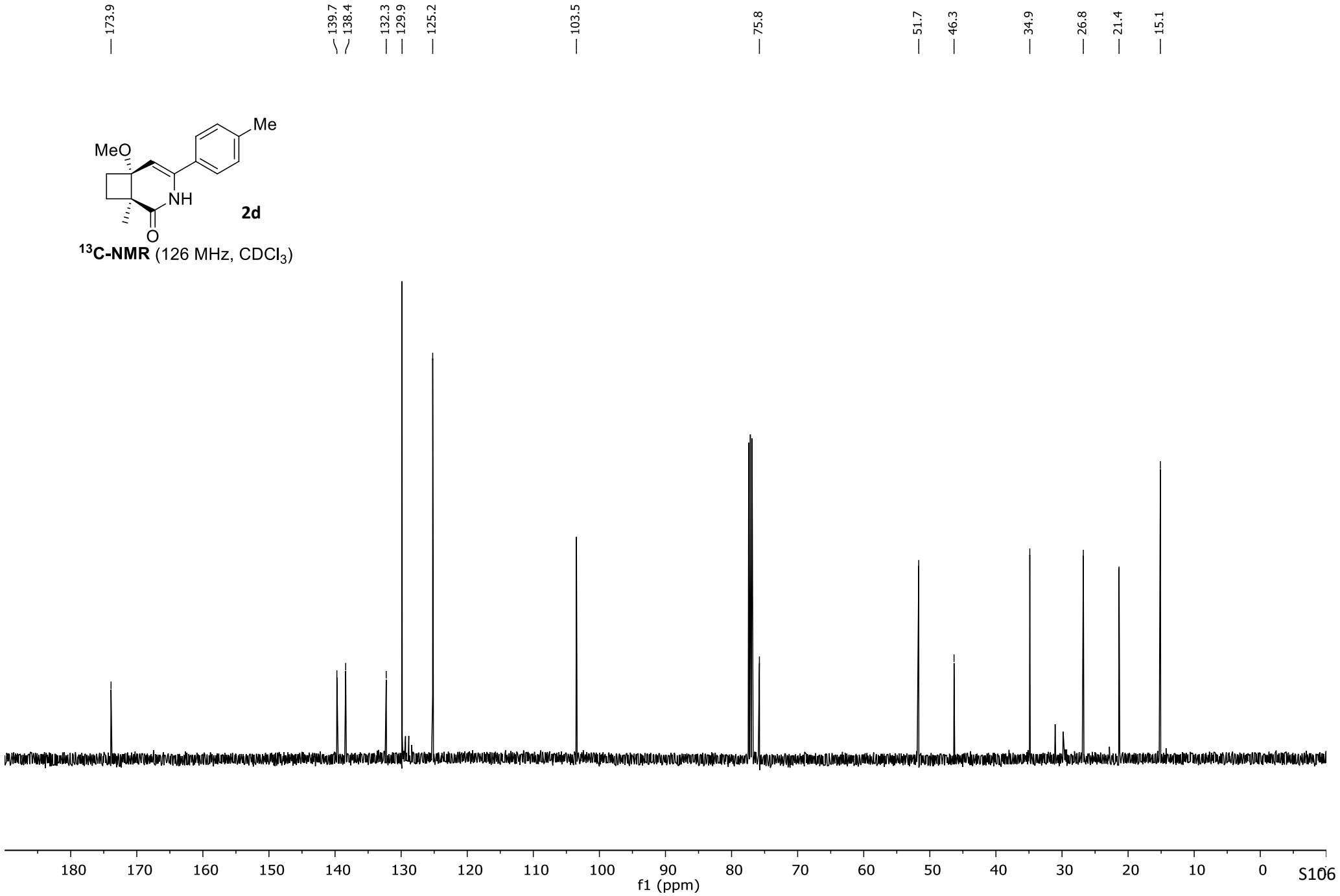

MeO
Cl
NH
O
2b
1H-NMR (500 MHz, CDCl3)
f1 (ppm)

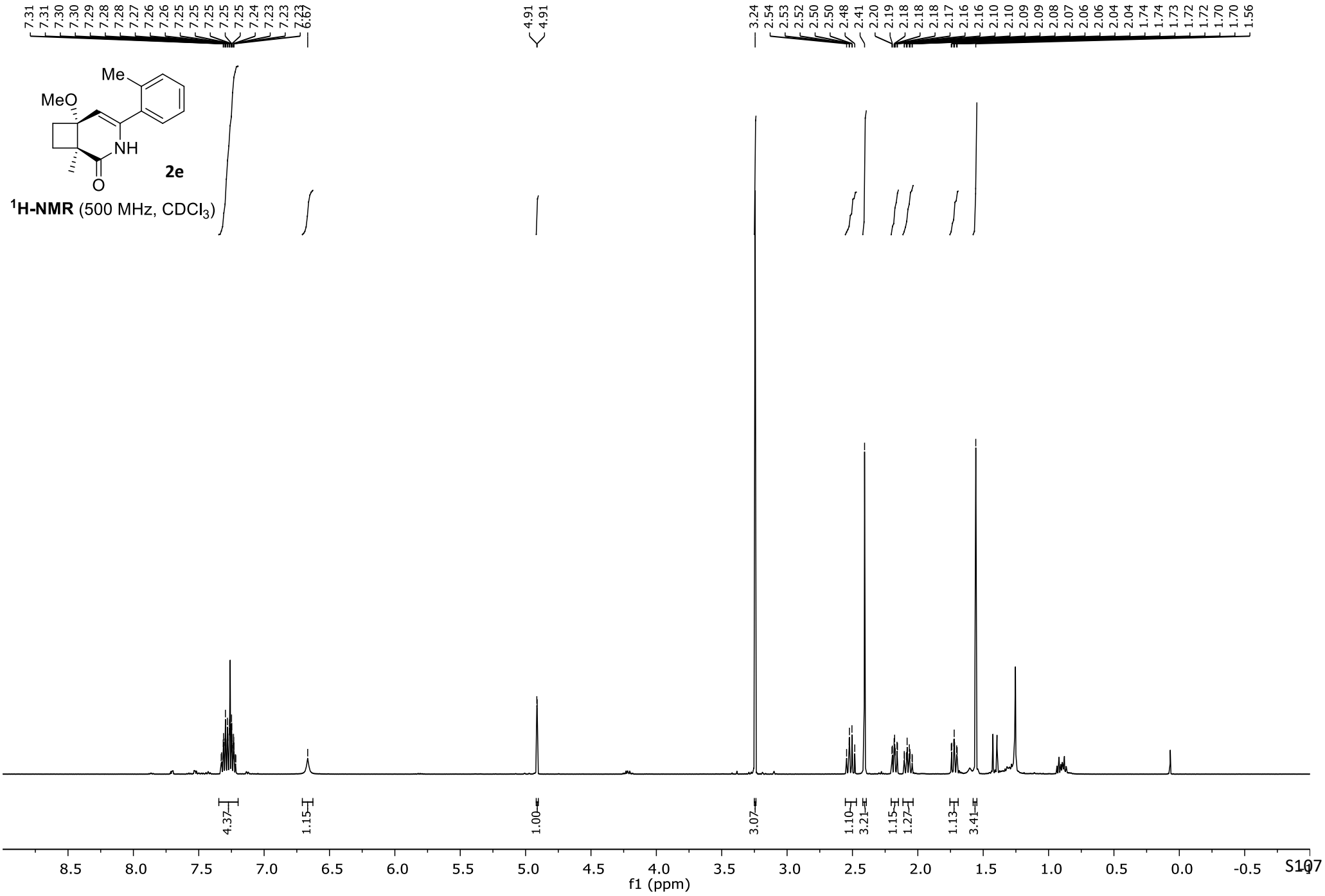

173.8
137.6
135.6
133.6
129.4
126.8
104.7
75.7
51.8
46.3
34.8
26.8
15.1
Cl
MeO
NH
O
2b
13C-NMR (126 MHz, CDCl3)
f1 (ppm)

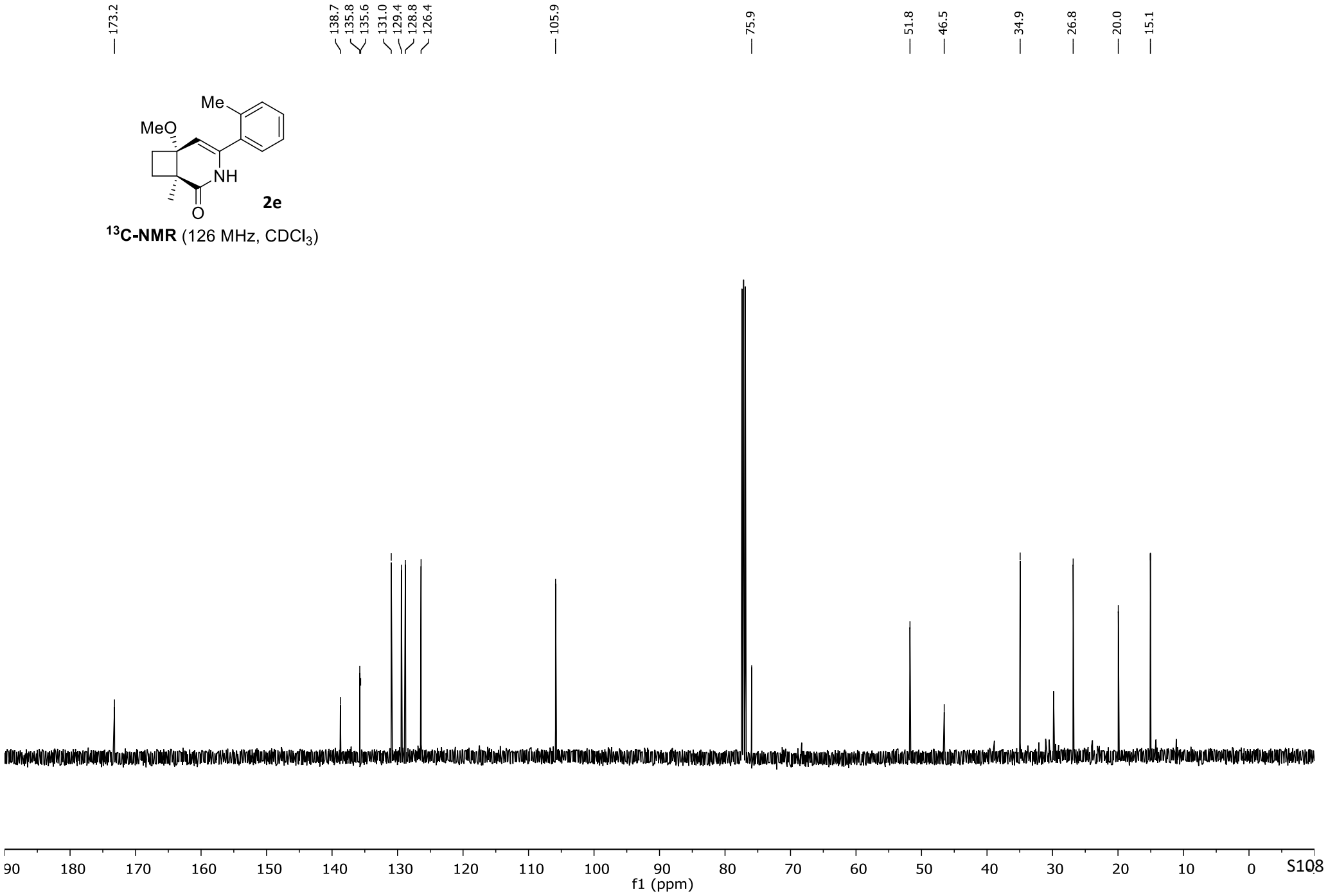

7.45 7.45 7.44 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.40 7.40 7.27 6.97 6.96 6.96 6.95 6.94 6.93 6.93 6.92
5.15 5.14
3.84
3.18 3.17
2.54 2.51 2.48 2.44 2.18 2.18 2.16 2.15 2.14 2.12 2.11 2.03 2.01 2.00 1.97 1.96 1.93 1.71 1.70 1.69 1.67 1.67 1.66 1.64 1.63 1.54
OMe
MeO
NH
O
2c
1H-NMR (300 MHz, CDCl3)
1.60 1.06 1.72 0.88 3.00 3.18 0.68 0.87 1.03 1.23 2.72
f1 (ppm)

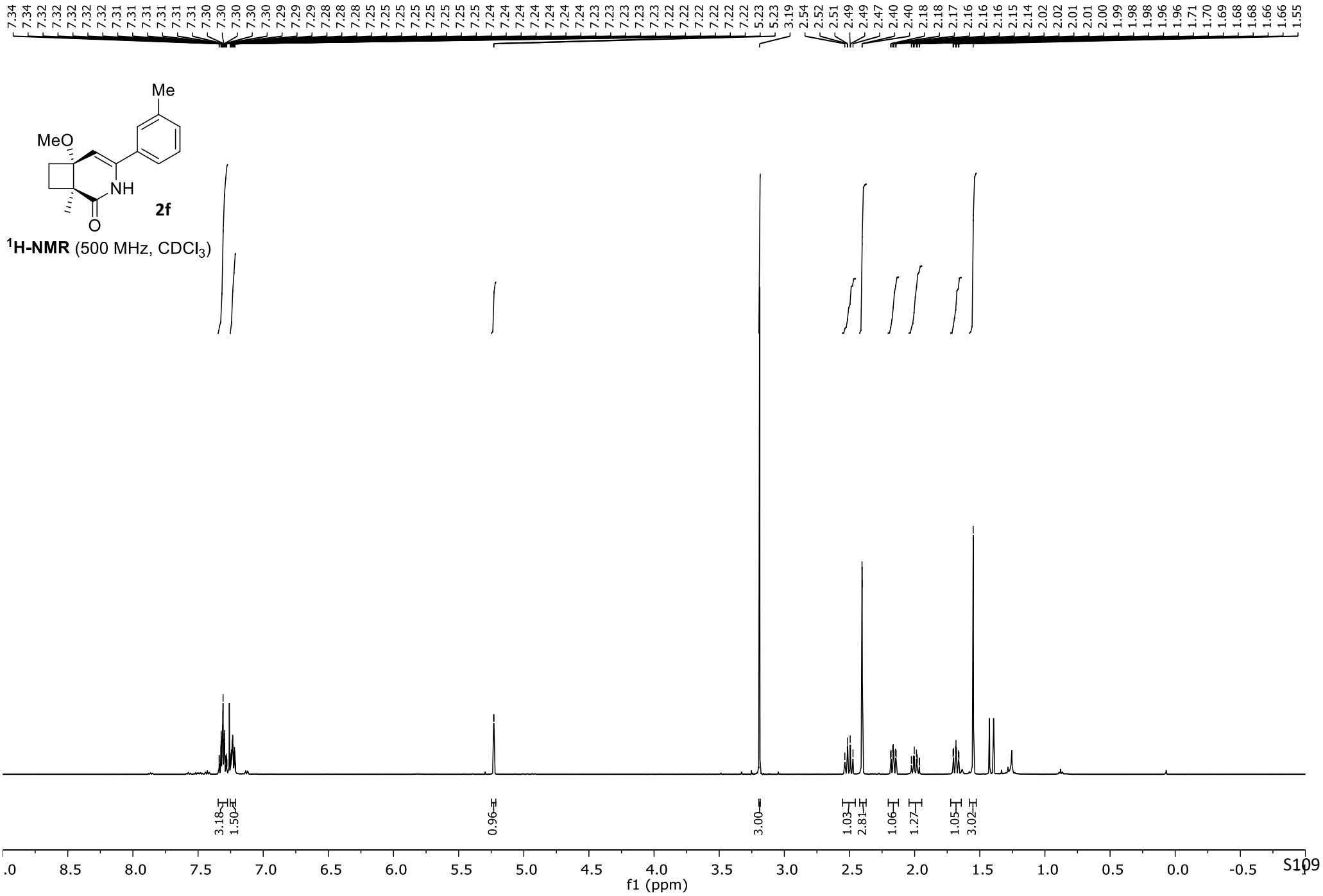

174.0
160.6
138.1
127.5
126.7
114.5
102.8
75.8
55.6
51.6
46.2
34.9
26.8
15.1
OMe
MeO
NH
O
2c
13C-NMR (75 MHz, CDCl3)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

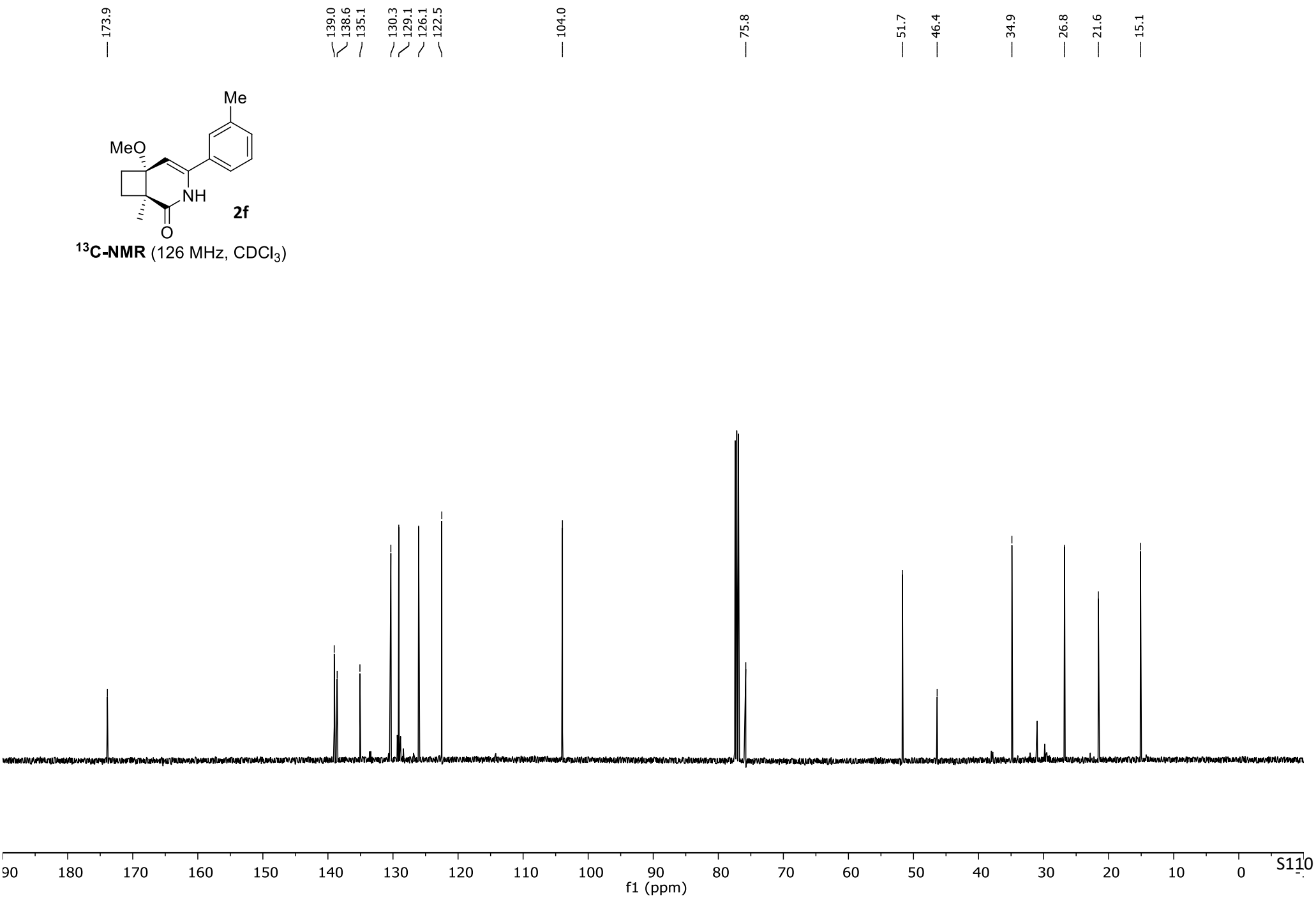

7.39 7.39 7.39 7.38 7.37 7.37 7.25 7.25 7.25 7.24 7.24 7.24 7.23 7.23 7.23 7.23 7.22 7.17
5.21 5.20
3.18 2.53 2.51 2.51 2.49 2.49 2.47 2.39 2.18 2.18 2.16 2.16 2.15 2.14 2.14 2.02 2.02 2.01 2.00 2.00 2.00 1.98 1.98 1.98 1.96 1.96 1.70 1.70 1.68 1.68 1.68 1.66 1.66 1.55
Me
MeO
NH
O
2d
1H-NMR (500 MHz, CDCl3)
2.11 2.11 1.08 1.00 2.96 1.12 3.17 1.03 1.23 1.11 3.31
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

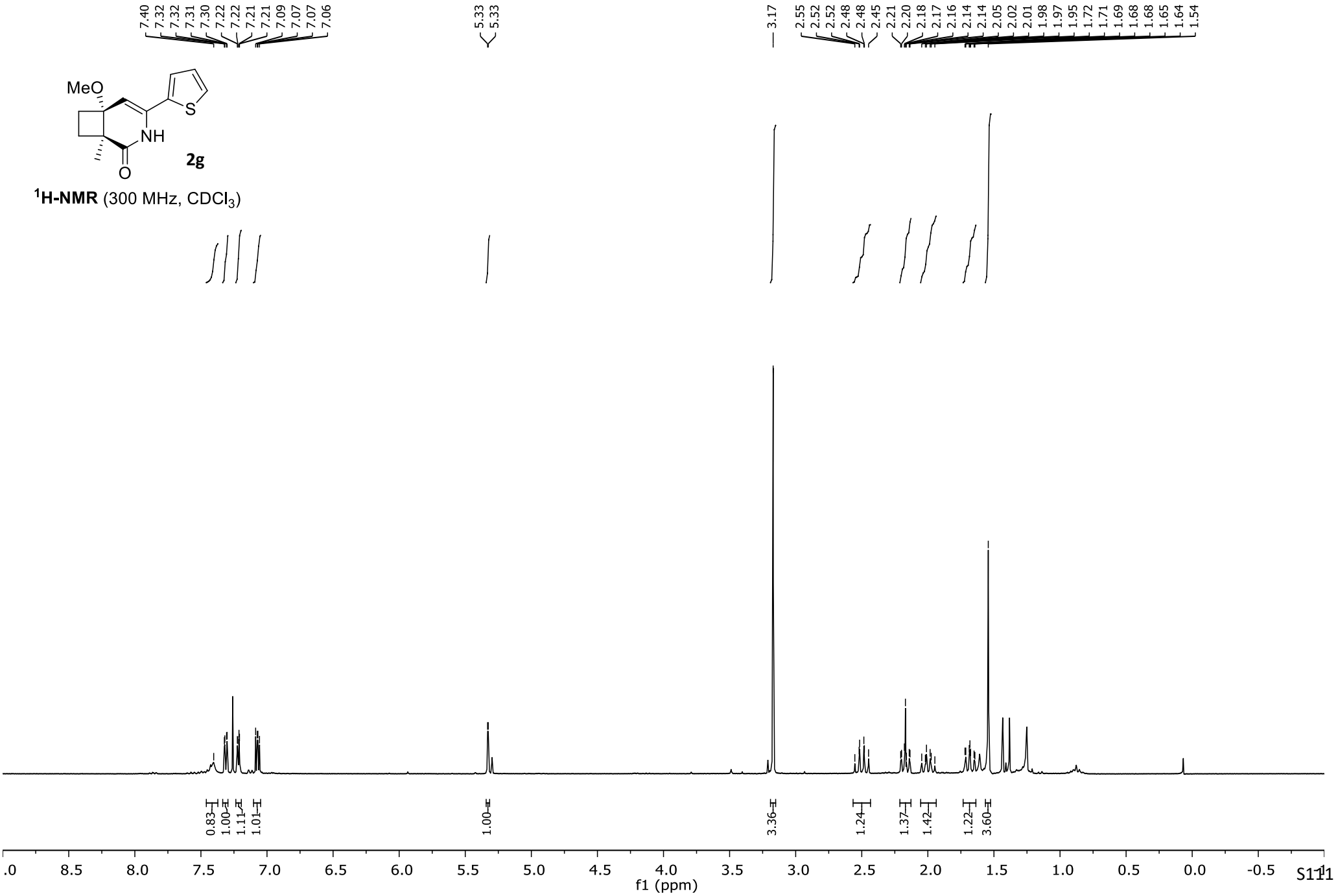

173.9
139.7
138.4
132.3
129.9
125.2
103.5
75.8
51.7
46.3
34.9
26.8
21.4
15.1
MeO
Me
NH
O
2d
13C-NMR (126 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
MeO
NH
O
2e
1H-NMR (500 MHz, CDCl3)
f1 (ppm)

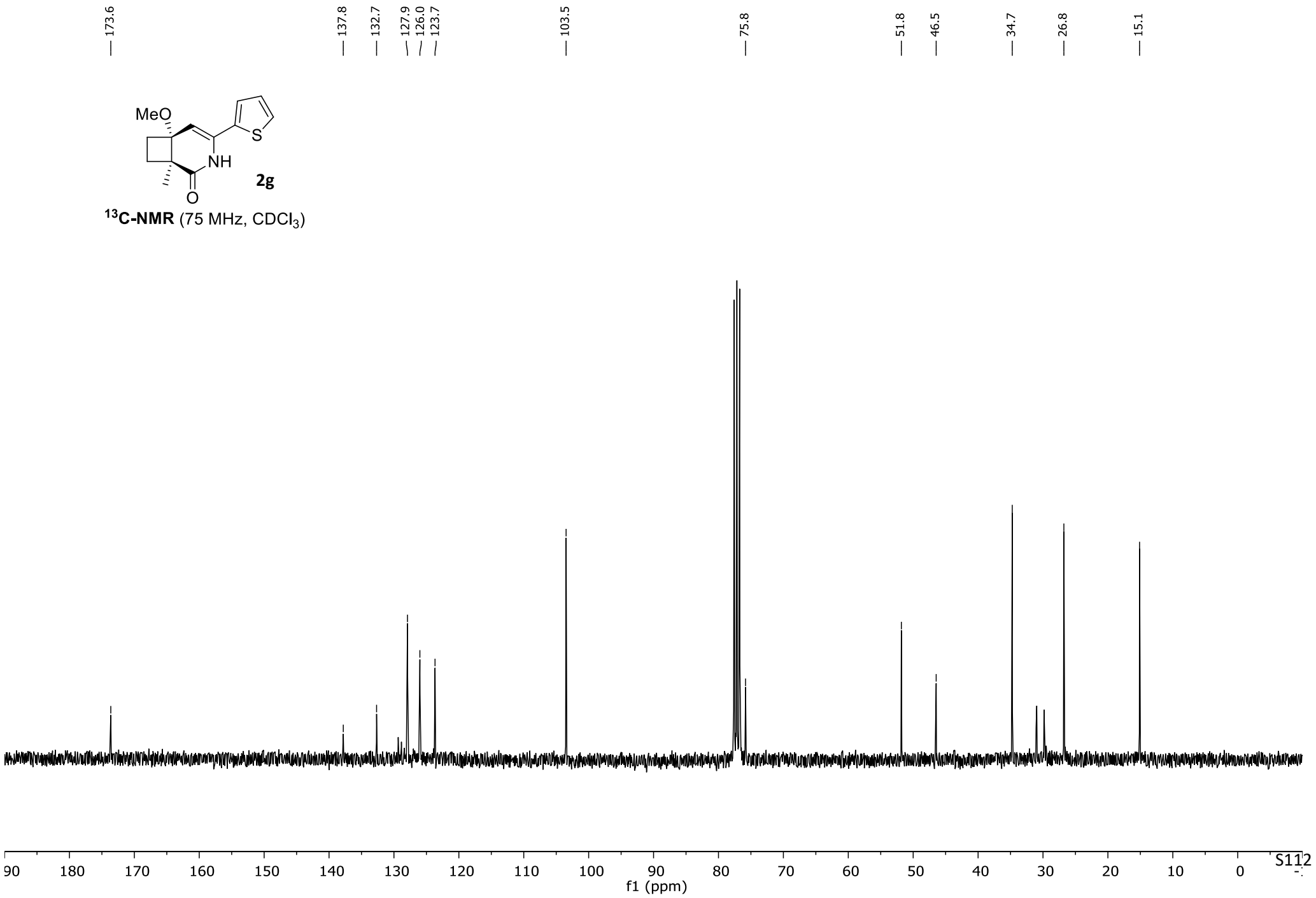

173.2
138.7
135.8
135.6
131.0
129.4
128.8
126.4
105.9
75.9
51.8
46.5
34.9
26.8
20.0
15.1
Me
MeO
NH
O
2e
13C-NMR (126 MHz, CDCl3)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

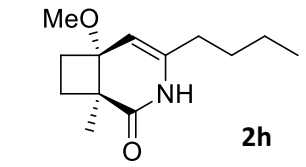

Me
MeO
NH
O
2f
1H-NMR (500 MHz, CDCl3)
f1 (ppm)


173.9
139.0
138.6
135.1
130.3
129.1
126.1
122.5
104.0
75.8
51.7
46.4
34.9
26.8
21.6
15.1
Me
MeO
NH
O
2f
13C-NMR (126 MHz, CDCl3)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



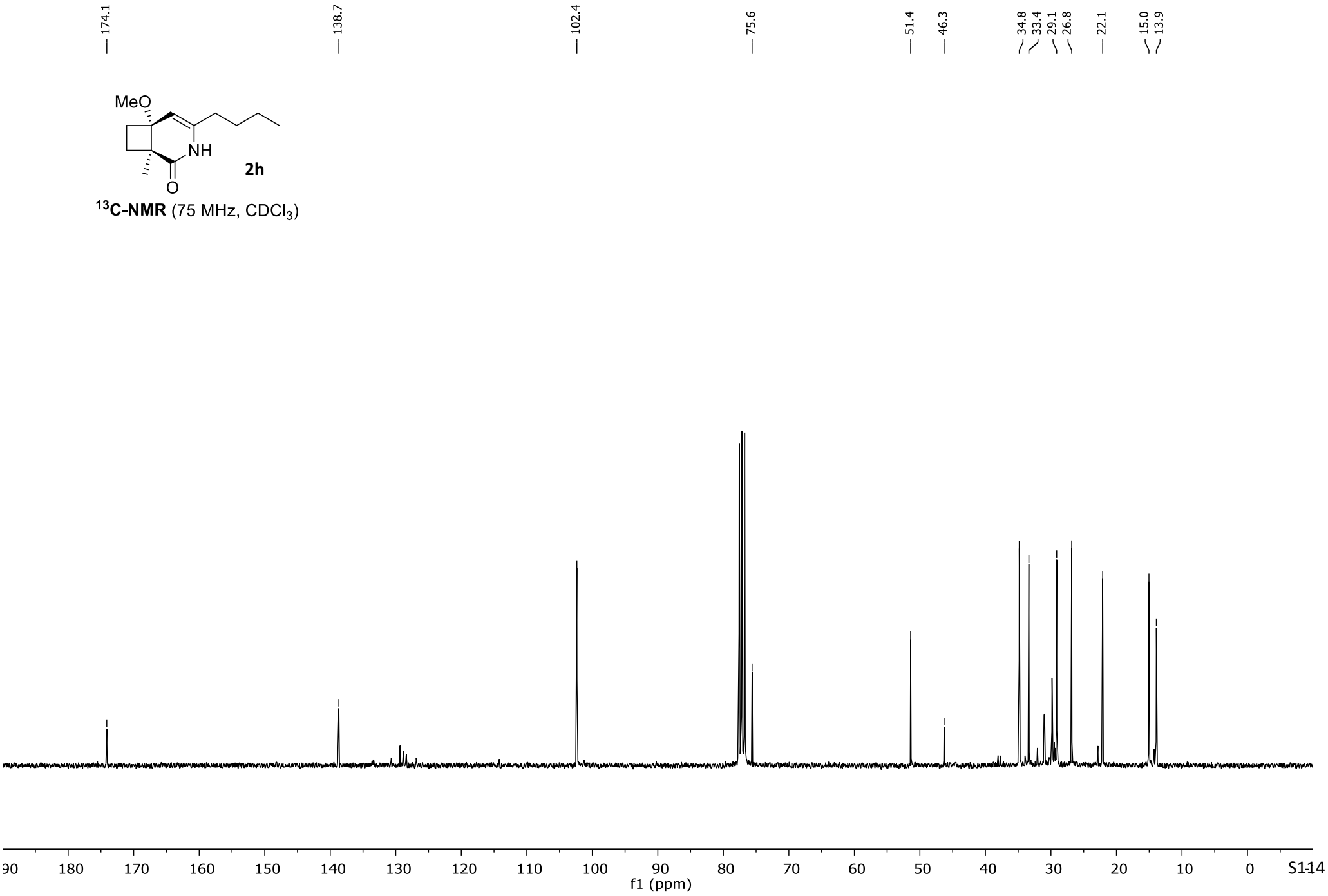
^{1}H-NMR (300 MHz, $CDCl_3$)

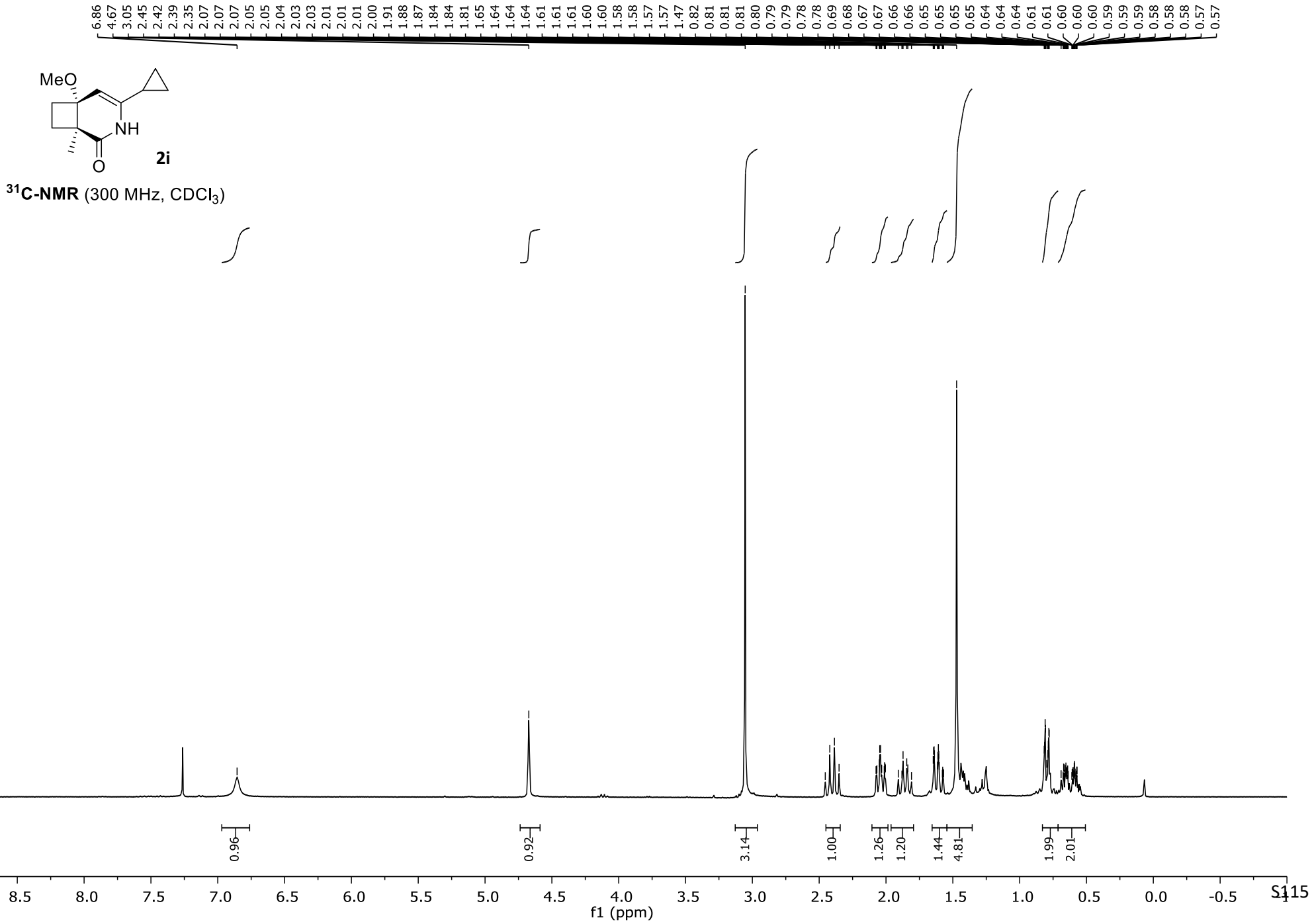

173.6
137.8
132.7
127.9
126.0
123.7
103.5
75.8
51.8
46.5
34.7
26.8
15.1
MeO
S
NH
O
2g
13C-NMR (75 MHz, CDCl3)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

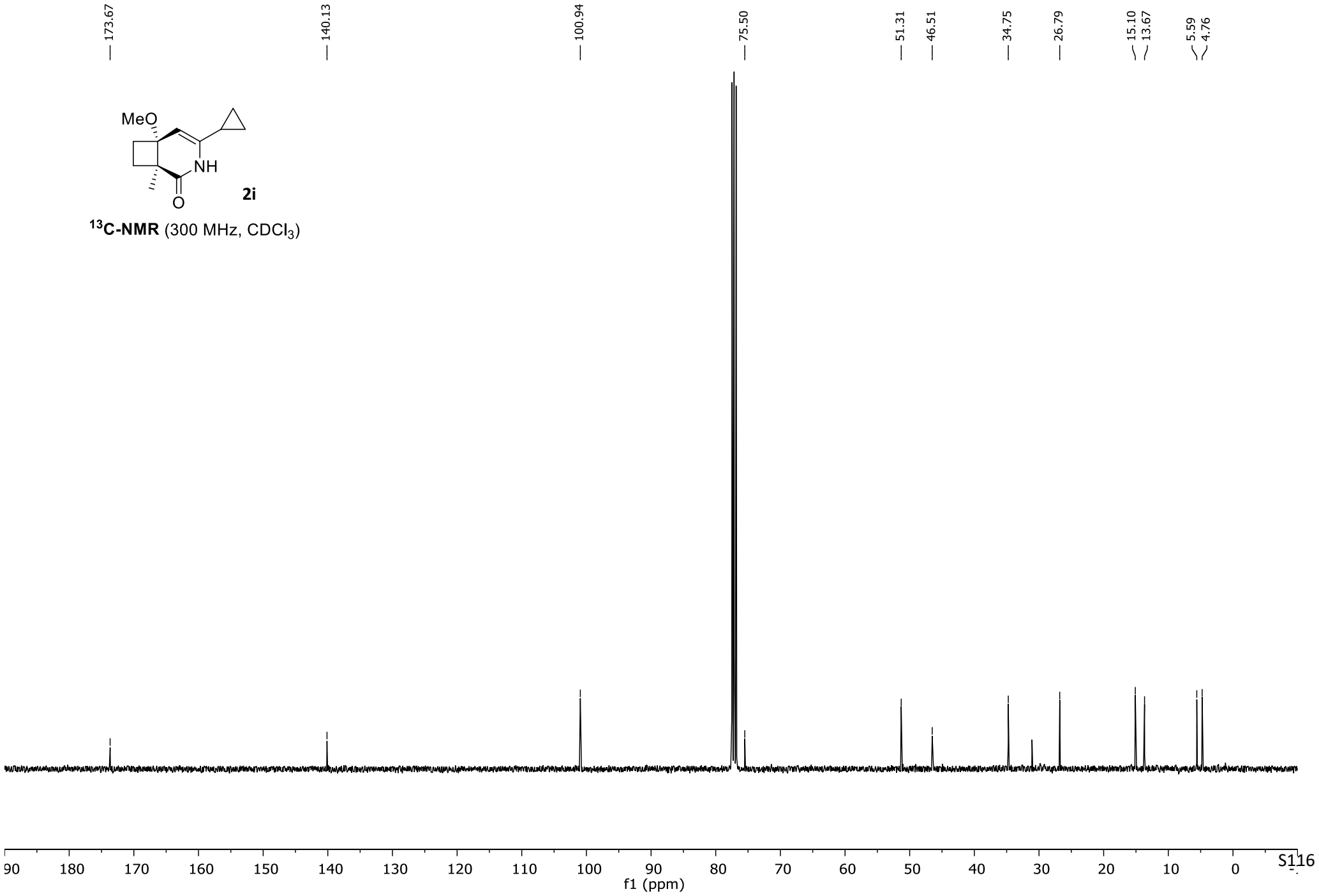


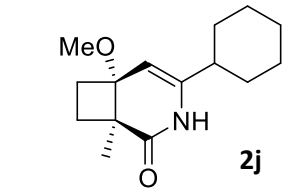
2h

^{1}H-NMR (300 MHz, $CDCl_3$)


174.1
138.7
102.4
75.6
51.4
46.3
34.8
33.4
29.1
26.8
22.1
15.0
13.9
MeO
NH
O
2h
13C-NMR (75 MHz, CDCl3)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

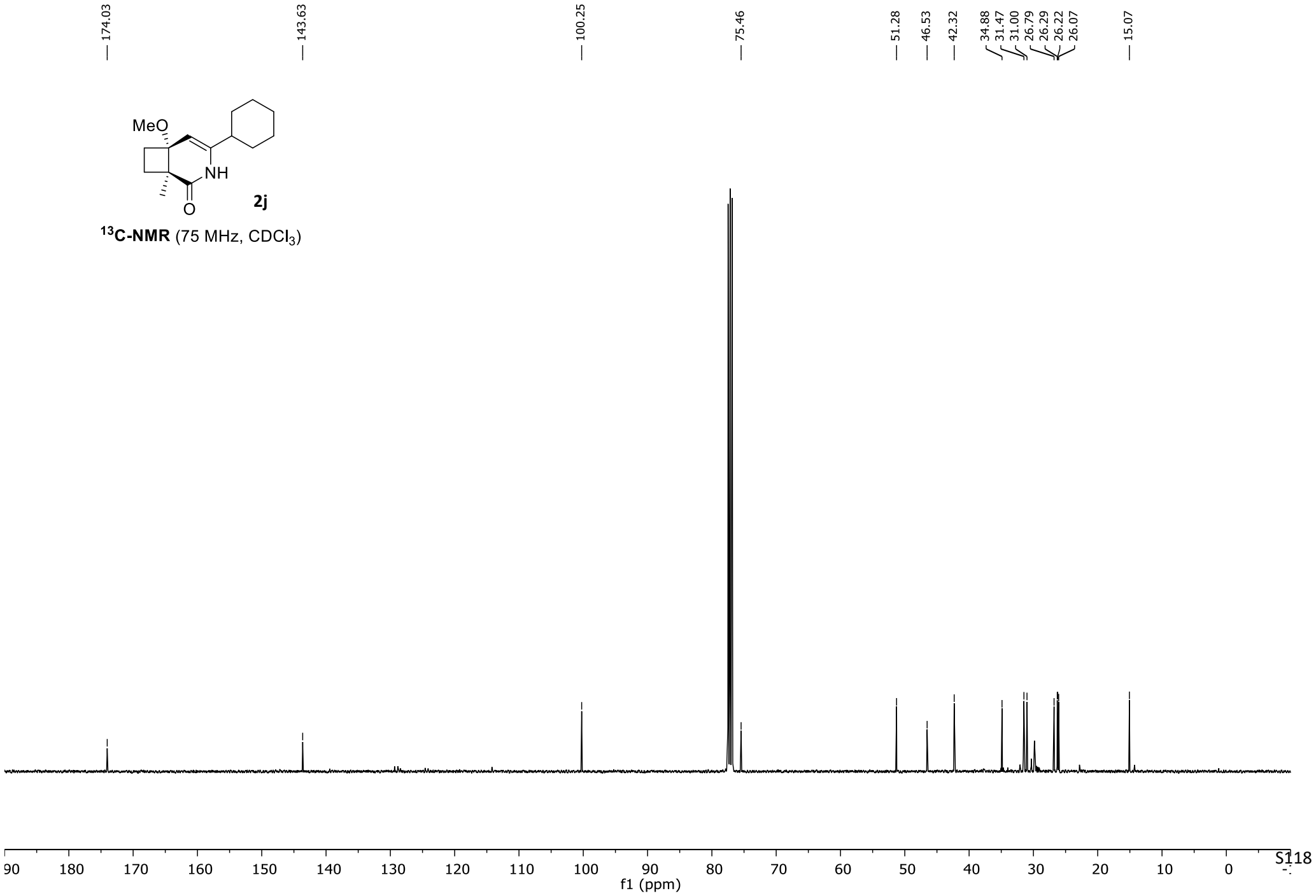

MeO
NH
O
2i
31C-NMR (300 MHz, CDCl3)
f1 (ppm)

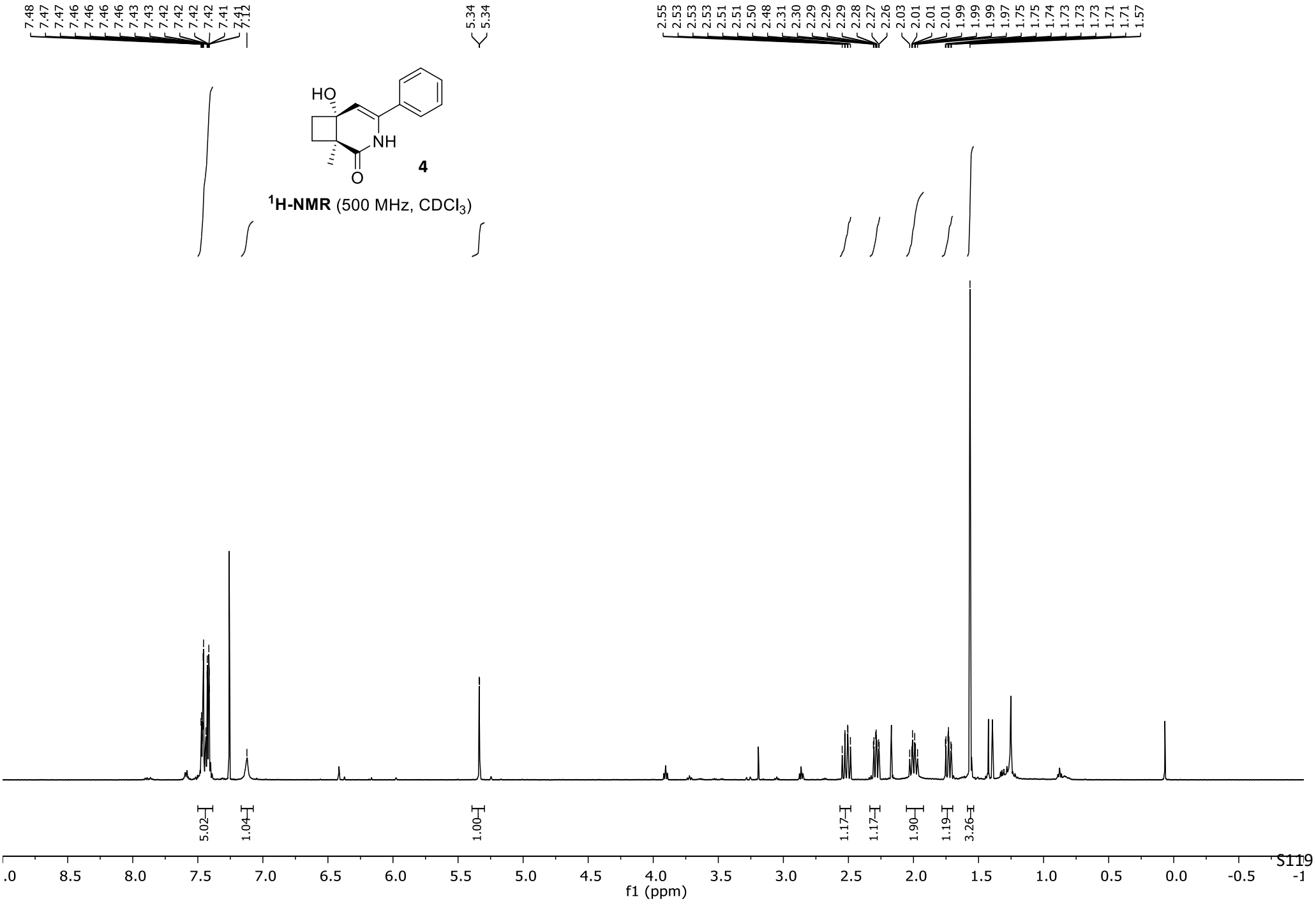

173.67
140.13
100.94
75.50
51.31
46.51
34.75
26.79
15.10
13.67
5.59
4.76
MeO
NH
O
2i
13C-NMR (300 MHz, CDCl3)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

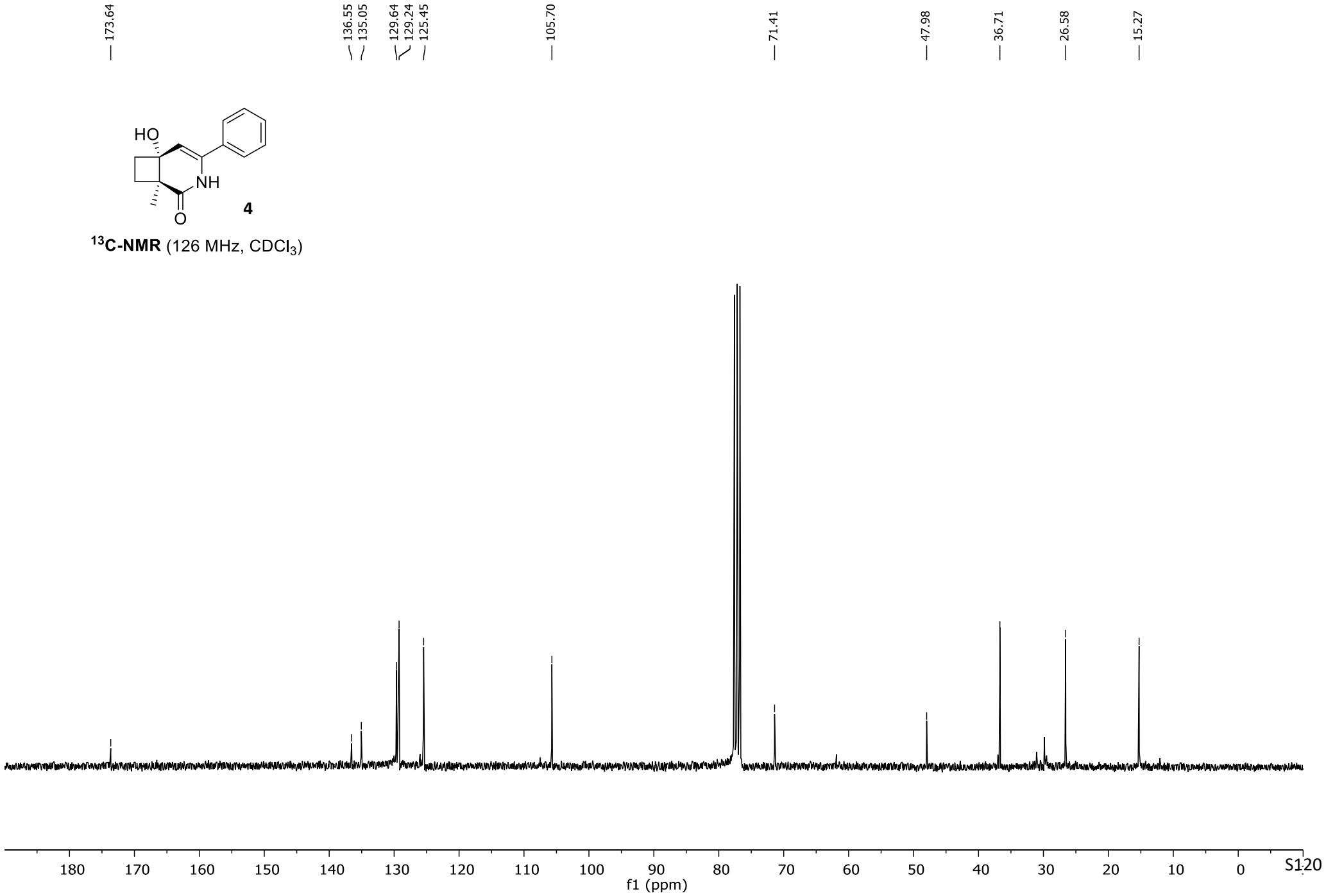


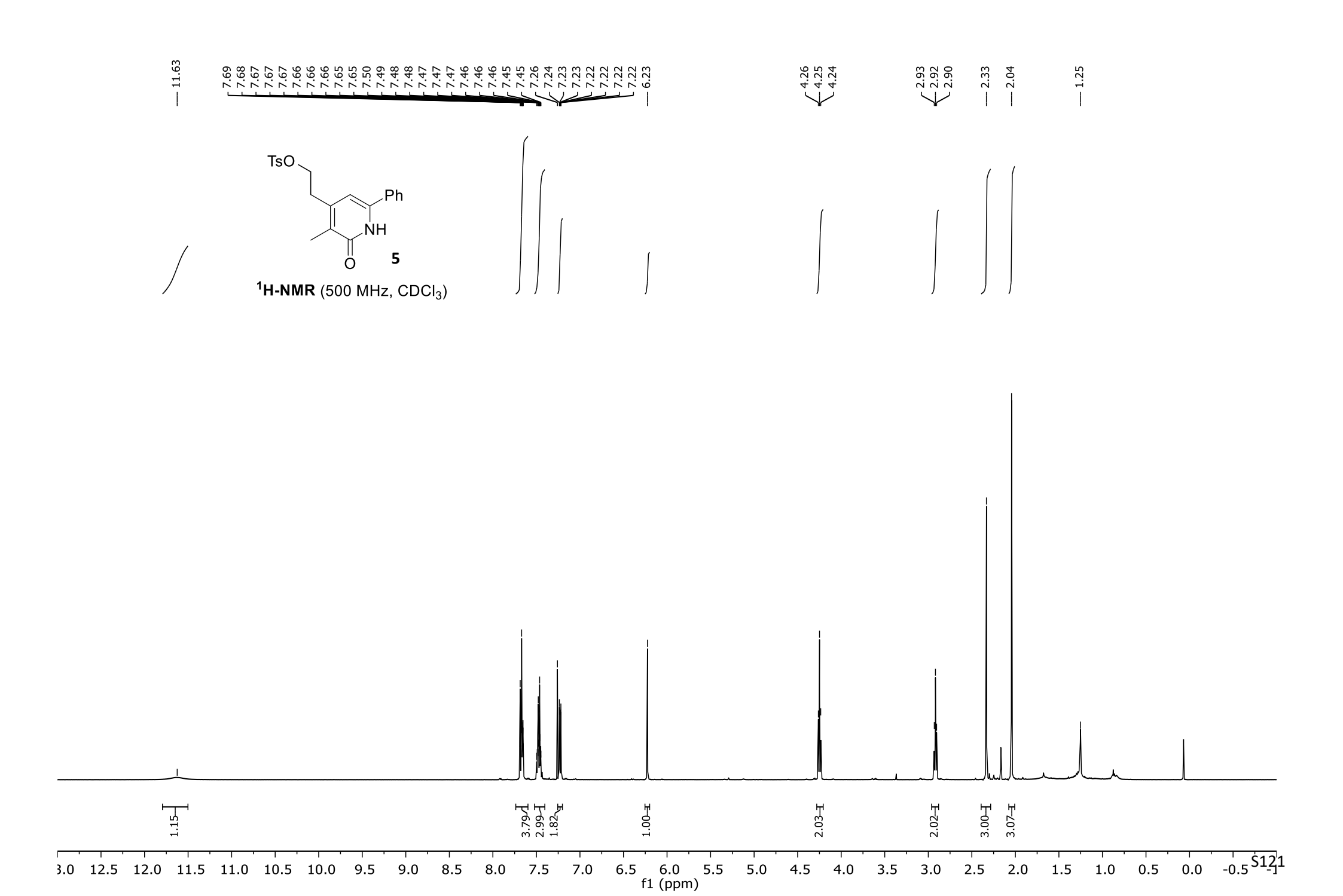
2j

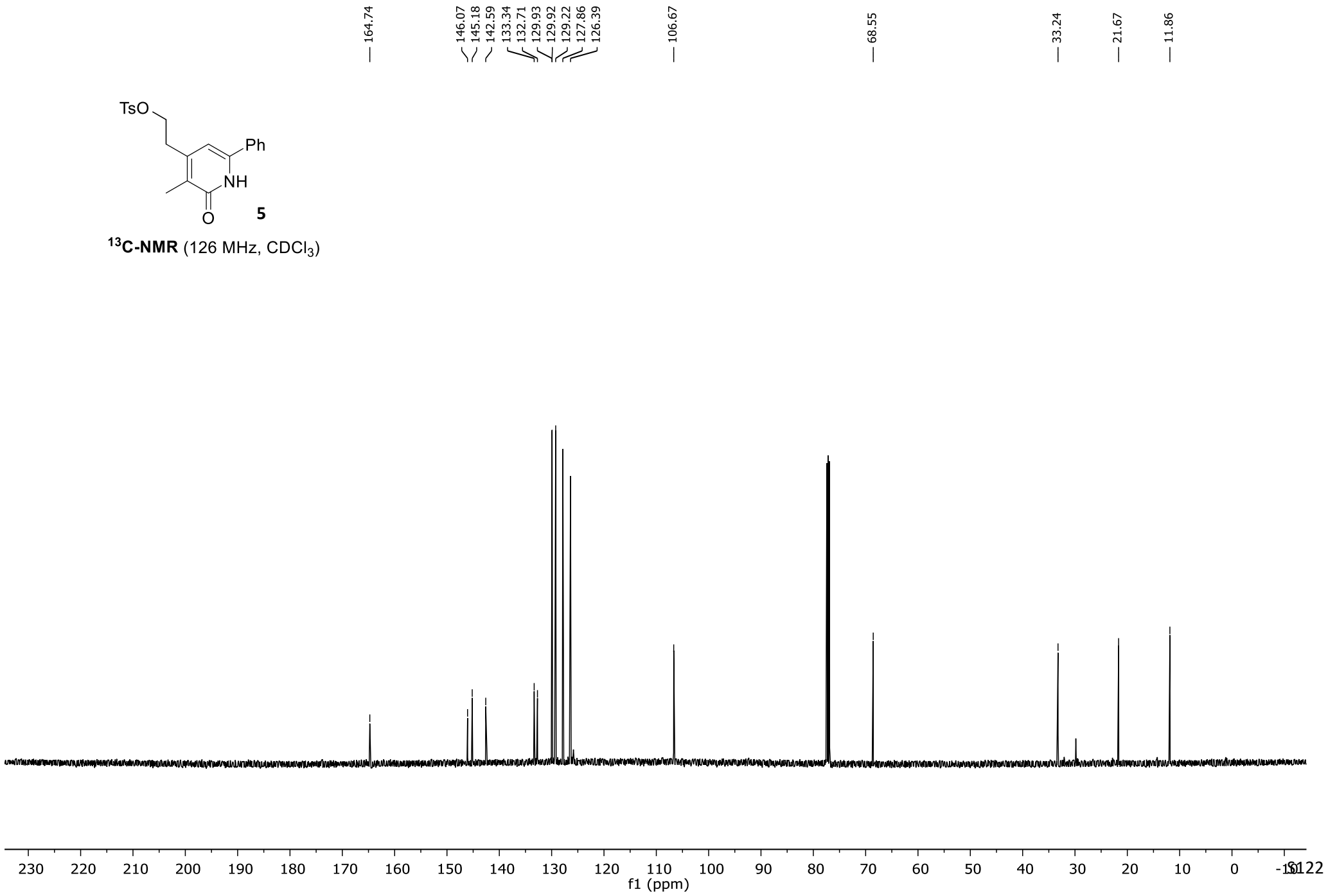
^{1}H-NMR (400 MHz, $CDCl_3$)


174.03
143.63
100.25
75.46
51.28
46.53
42.32
34.88
31.47
31.00
26.79
26.29
26.22
26.07
15.07
MeO
NH
O
2j
13C-NMR (75 MHz, CDCl3)
f1 (ppm)


HO
NH
O
4
1H-NMR (500 MHz, CDCl3)
7.48 7.47 7.47 7.46 7.46 7.46 7.46 7.43 7.43 7.42 7.42 7.42 7.42 7.41 7.41 7.12
5.34 5.34
2.55 2.53 2.53 2.53 2.51 2.51 2.50 2.48 2.31 2.30 2.29 2.29 2.29 2.28 2.27 2.26 2.03 2.01 2.01 2.01 1.99 1.99 1.99 1.97 1.75 1.75 1.74 1.73 1.73 1.73 1.71 1.71 1.57
5.02
1.04
1.00
1.17
1.17
1.90
1.19
3.26
f1 (ppm)


173.64
136.55
135.05
129.64
129.24
125.45
105.70
71.41
47.98
36.71
26.58
15.27
HO
NH
O
4
13C-NMR (126 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


11.63
7.69 7.68 7.67 7.67 7.67 7.66 7.66 7.66 7.65 7.65 7.50 7.49 7.48 7.48 7.47 7.47 7.47 7.46 7.46 7.46 7.45 7.45 7.26 7.24 7.23 7.23 7.22 7.22 7.22 6.23
4.26 4.25 4.24
2.93 2.92 2.90
2.33
2.04
1.25
TsO
Ph
NH
O
5
1H-NMR (500 MHz, CDCl3)
1.15
3.79
2.99
1.82
1.00
2.03
2.02
3.00
3.07
f1 (ppm)



^{13}C-NMR (126 MHz, $CDCl_3$)