SUPPORTING INFORMATION

A Rh-Catalyzed Cycloisomerization/Diels-Alder Cascade Reaction of 1,5-Bisallenes for the Synthesis of Polycyclic Heterocycles

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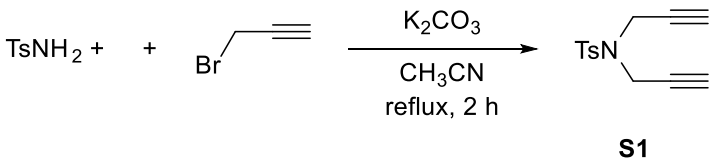
General materials and methods

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. CH_2Cl_2 and THF were dried under nitrogen by passing through solvent purification columns (MBraun, SPS-800). Reaction progress during the preparation of all compounds was monitored using thin layer chromatography on Macherey-Nagel Xtra SIL G/UV254 silica gel plates. Solvents were removed under reduced pressure with a rotary evaporator. Reaction mixtures were chromatographed on silica gel. All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ASCEND 400 spectrometer equipped with a 5 mm BBFO probe using $CDCl_3$ as a deuterated solvent. Chemical shifts for ^{1}H and ^{13}C NMR are reported in ppm (δ) relative to residual solvent signals. Coupling constants are given in Hertz (Hz). ^{1}H and ^{13}C NMR signals were assigned based on 2D-NMR HSQC, HMBC, COSY and NOESY experiments. Mass spectrometry analyses were recorded on a Bruker micrOTOF-Q II mass spectrometer (high resolution), equipped with electrospray ion source. The instrument was operated in the positive ESI (+) ion mode. IR spectra were recorded on an Agilent Cary 630 FT-IR spectrometer equipped with an ATR sampling accessory. The X-ray intensity data were measured on a three-circle diffractometer system equipped with a Ceramic x-ray tube (Mo Kα, λ = 0.71073 Å) and a doubly curved silicon crystal Bruker Triumph monochromator. Melting points were measured in a SMP10 apparatus from Stuart without any correction. High performance liquid chromatography (HPLC) was performed using a CHIRALPAK IA column (4.6 x 250 mm, 5 µm) on an Agilent Technologies 1260 Infinity instrument, equipped with a quaternary pump G1311C, an auto sampler G1329B, a thermostatic column compartment G1316A and a variable wavelength UV-Vis detector G1314F.

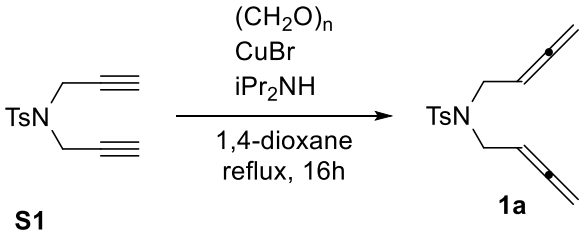
Scheme S1. Synthesis of diyne S1



In a 100 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer, a mixture of 4-methylbenzenesulfonamide (1 g, 5.84 mmol), K_2CO_3 (4.80 g, 34.73 mmol) and propargyl bromide (1.45 mL, 80 % in toluene, 1.60 mg, 13.42 mmol) in acetonitrile (60 mL) was stirred at 80 °C for 2 h until completion (TLC monitoring). The reaction mixture was allowed to cool to room temperature, the solids were filtered off and the filtrate was concentrated under reduced pressure to provide a yellowish oil which was purified by column chromatography (SiO_2, 40–60 μm, Hexanes/CH_2Cl_2 1:1 v/v) to afford diyne **S1** (1.33 g, 92% yield), as a colourless solid.

MW ($C_{13}H_{13}NO_2S$): 247.3 g/mol; **Rf**: 0.33 (Hexanes/CH_2Cl_2 1:1); **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm)**: 2.14 (t, *J* = 2.4 Hz, 2H), 2.41 (s, 3H), 4.15 (d, *J* = 2.4 Hz, 4H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 21.67, 36.27, 74.17, 76.24, 127.96, 129.67, 135.22, 144.11.; **ESI-MS (m/z):** $[M+H]^+$ = 248.0. Spectral data in accordance with literature values.[1]

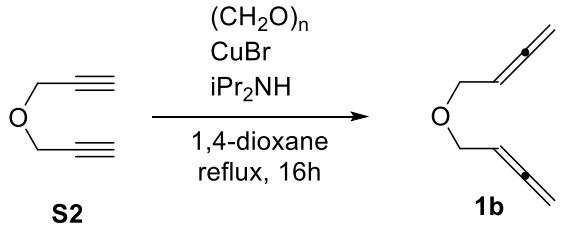
Scheme S2. Synthesis of bisallenes 1a-b



In a 250 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer, a suspension of diyne **S1** (6 g, 24.26 mmol), paraformaldehyde (3.64 g, 121.3 mmol) and CuBr (3.48 g, 24.26 mmol) in 1,4-dioxane (100 mL) was stirred and heated at reflux. Diisopropylamine (13.60 mL, 9.82 g, 97.04 mmol) was then added and the resulting mixture was stirred at reflux for 16 h until completion (TLC monitoring). The reaction mixture was allowed to cool to room temperature, filtered through a Celite pad and concentrated under reduced pressure. The resulting brown oil was mixed with Et_2O (200 mL) and water (100 mL) and the mixture was acidified to pH=2 with HCl 6M. The Et_2O/water layers were decanted from solid residues, the Et_2O layer was separated and the water layer was extracted with Et_2O (3 x 100 mL). The combined organic extracts were washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure.

The crude product was purified by column chromatography (SiO_2, 40–60 μm, Hexanes/EtOAc 95:5 v/v) to afford bisallene **1a** (4.10 g, 61% yield) as a colourless solid.

MW ($C_{15}H_{17}NO_2S$): 275.4 g/mol; **Rf**: 0.50 (hexanes/EtOAc 8:2); **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm)**: 2.41 (s, 3H), 3.89 (dt, *J* = 6.8, 2.4 Hz, 4H), 4.70 (dt, *J* = 6.8, 2.4 Hz, 4H), 4.93 (p, *J* = 6.8 Hz, 2H), 7.29 (d, *J* = 8.4, 2H), 7.69 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 21.61, 45.77, 76.27, 85.75, 127.27, 129.79, 137.66, 143.40, 209.78; **ESI-MS (m/z):** $[M+Na]^+$: 298.0. Spectral data in accordance with literature values.[2]

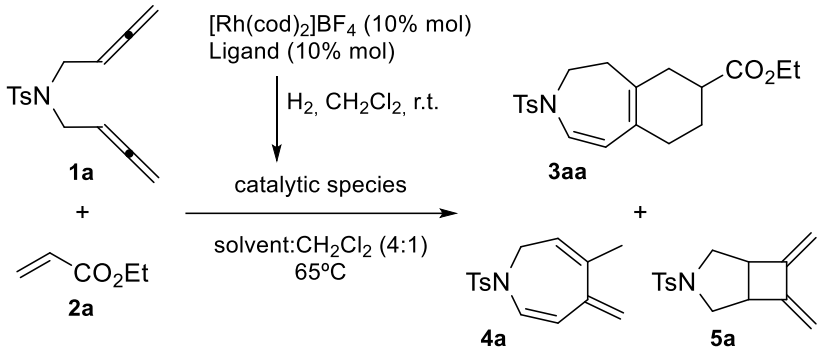


S2 **1b**

In a round-bottom flask equipped with a reflux condenser and a magnetic stirrer, a suspension of commercially available diyne **S2** (1.50 g, 15.96 mmol), paraformaldehyde (2.40 g, 80 mmol) and CuBr (2.30 g, 16.03 mmol) in 1,4-dioxane (60 mL) was stirred and heated at reflux. Diisopropylamine (9 mL, 6.48 g, 64 mmol) was then added and the resulting mixture was stirred for 16 h at reflux until completion (TLC monitoring). The reaction mixture was allowed to cool to room temperature, filtered through a Celite pad and concentrated under reduced pressure. The resulting brown oil was mixed with Et_2O (120 mL) and water (60 mL) and the mixture was acidified to pH=2 with HCl 6M. The Et_2O/water layers were decanted from any residues, the Et_2O layer was separated and the water layer was extracted with Et_2O (3 x 60 mL). The combined organic extracts were washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, 40–60 μm, Hexanes/EtOAc 95:5 v/v) to provide bisallene **1b**[1] (394 mg, 20% yield) as a yellowish oil.

MW ($C_8H_{10}O$): 122.2 g/mol; **Rf**: 0.67 (hexanes/EtOAc 8:2); **IR (ATR) ν (cm^{-1})**: 2920, 2854, 1953, 1450, 1357, 1318, 1251, 1077; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm)**: 4.03 (dt, *J* = 6.8, 2.4 Hz, 4H), 4.78 (dt, *J* = 6.8, 2.4 Hz, 4H), 5.23 (quint, *J* = 6.8 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 67.68, 75.78, 87.67, 209.49.

Table S1. Optimization of the rhodium(I)-catalyzed cycloaddition of bisallene 1a with alkene 2a



Entry	Ligand	Solvent	[1a] (mM)	Temperature (ºC)	**1a**:**2a** ratio	Yield of **3aa** / **4a** / **5a** (%)
1	(*R*)-BINAP	Toluene	18	65	1:10	30 / 29 / -
2	(*R*)-BINAP	DCE	18	65	1:10	- / - / -
3	(*R*)-BINAP	Acetonitrile	18	65	1:10	29 / 18 / -
4	(*R*)-BINAP	1,4-Dioxane	18	65	1:10	42 / 53 / -
5	(*R*)-BINAP	EtOH	18	65	1:10	18 / 24 / -
6	(*R*)-BINAP	THF	18	65	1:10	46 / 39 / -
7	(*R*)-BINAP	THF	18	65	1:50	45 / 45 / -
8	(*R*)-BINAP	THF	9	65	1:10	46 / 52 / -
9	(*R*)-BINAP	THF	9	65	1:50	49 / 45 / -
10	(*R*)-Tol-BINAP	THF	9	65	1:50	54 / 44 / -
11	(*R*)-H_8-BINAP	THF	9	65	1:50	54 / 38 / -
12	(*R*)-Monophos	THF	9	65	1:50	26 / 18 / -
13	BIPHEP	THF	9	65	1:50	- / 37 / -
14	(*R*)-DTBM-Segphos	THF	9	65	1:50	65 / 5 / 15
15	(*R*)-DTBM-Segphos	THF	9	40	1:50	60 / - / 15
16[b]	(*R*)-DTBM-Segphos	THF	9	40	1:50	44 / - / 15
17[c]	-	THF	9	40	1:50	- / - / -
18	-	THF	9	40	1:50	- / - / -

[a] Reaction conditions: 0.09 mmol of **1a,** 10-50 equivalents of **2a**, 10% mol of Rh catalyst in 10-20 mL of solvent:CH_2Cl_2 (4:1) at 65ºC for 4h or 40ºC for 16h. The 10% mol mixture of $[Rh(cod)_2]BF_4$ and phosphine was treated with hydrogen in dichloromethane (CH_2Cl_2) solution for catalyst activation prior to substrate addition. [b] The reaction was run with 5% mol of $[Rh(cod)_2]BF_4$ and 5% mol of ligand. [c] The reaction was run without $[Rh(cod)_2]BF_4$.

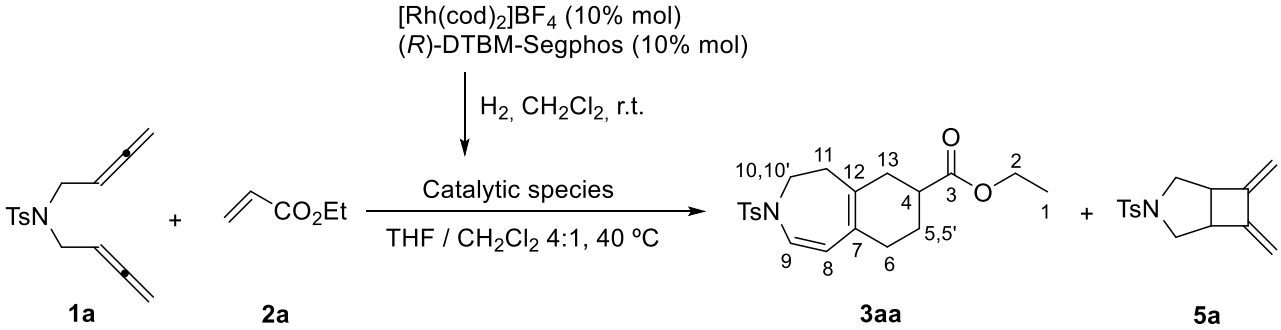
We started by studying the cycloaddition of *N*-tosyl-tethered bisallene **1a** and ethyl acrylate **2a** using 10% mol of cationic rhodium complex $[Rh(cod)_2]BF_4$ with (*R*)-BINAP in mixtures of solvents with 4:1 ratio (varying solvents: CH_2Cl_2) at 65°C (entries 1-6). With a **1a**:**2a** ratio of 1:10 and a 18 mM concentration of bisallene (**1a**), two different compounds, **3aa** and **4a**, were obtained in varying quantities in all cases except when 1,2-dichloroethane (DCE) was used as co-solvent (entry 2). The best results were obtained with THF, which improved both the yield of **3aa** and its selectivity towards **4a** (entry 6). After a complete NMR analysis (see SI) of compound **3aa**, it was possible to determine the structure of the cycloadduct, confirming that a 4-aza-bicyclo[5.4.0]undeca-1(7),2-diene skeleton had been forged, purportedly originating from the oxidative coupling of the two external double bonds of **1a** and double bond isomerization. The seven-membered cross-conjugated triene **4a** was generated alongside **3aa** by cycloisomerization of the starting bisallene without participation of the alkene in an outcome that is complementary to the selectivity observed by Ma and Mukai.[3–5]

We next examined the effect of various reaction parameters on the efficiency of the process, focusing on improving the selectivity towards **3**. We varied two further parameters: first, the excess of the alkene was increased to 50 equiv. (entry 7) and, second, the concentration of the bisallene was reduced to 9 mM (entry 8). An additive effect was observed when the two factors were combined ([**1a**] = 9 mM and 50 equiv. of **2a**, entry 9). We then resorted to a combination of a cationic rhodium complex $[Rh(cod)_2]BF_4$ with several phosphines as ligands: (*R*)-Tol-BINAP (entry 10), (*R*)-H_8-BINAP (entry 11), (*R*)-Monophos (entry 12), BIPHEP (entry 13) and (*R*)-DTBM-Segphos (entry 14). Intriguingly, only triene **4a** was obtained in 37% yield using BIPHEP as the phosphine and the desired product - **3aa** - was not observed. When the bulky phosphine DTBM-Segphos was used, the yield of **3aa** was improved to 65%, and the yield of triene **4a** was reduced to 5%. However, another by-product **5a**, originating also from the cycloisomerization of the bisallene, was obtained in 15% yield. Lowering the temperature to 40°C avoided the formation of **4a**, resulting in our optimized set of conditions (entry 15). An attempt to reduce the catalyst loading from 10% to 5% was detrimental for the yield of **3aa**, and we therefore decided to work with a 10% mol of rhodium throughout our study.

Two control experiments were run. First, in the absence of the Rh catalyst (entry 17) and, second, in the presence of $[Rh(cod)_2]BF_4$ and without the bisphosphine (entry 18). Starting bisallene **1a** was recovered in both cases, revealing the essential role of the two components in this transformation.

Synthesis of compounds 3aa-3bj

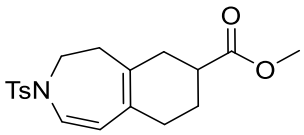
Scheme S3. General procedure for the synthesis of product 3aa



In a 10 mL capped vial, a mixture of $[Rh(cod)_2]BF_4$ (7.4 mg, 0.018 mmol) and (*R*)-DTBM-Segphos (23.6 mg, 0.020 mmol) was purged with nitrogen and dissolved in anhydrous CH_2Cl_2 (4 mL). Hydrogen gas was bubbled into the catalyst solution and the mixture was stirred for 30 min. The resulting mixture was concentrated to dryness under a stream of nitrogen, dissolved again in anhydrous CH_2Cl_2 (4 mL) and transferred via syringe into a solution of bisallene **1a** (50 mg, 0.18 mmol, 1 equiv.) and ethyl acrylate **2a** (1.0 mL, 9.00 mmol, 50 equiv.) in anhydrous THF (16 mL) preheated to 40 °C and under inert atmosphere. The resulting mixture was stirred at 40 ºC for 16h. The solvent was removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel using hexane/EtOAc mixtures as the eluent (98:2 to 95:5 v/v). Concentration under reduced pressure afforded compound **5a** (7.7 mg, 15% yield) as a colourless solid, and **3aa** (40.2 mg, 60% yield) as a pale yellow oil (in order of elution).

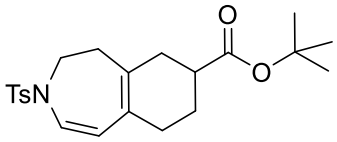
3aa: **MW** ($C_{20}H_{25}NO_4S$): 375.48 g/mol; **Rf**: 0.49 (Hexane/EtOAc 8:2); **IR (ATR) ν (cm^{-1})**: 2924, 1724, 1344, 1161; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 1.22 (t, *J* = 7.1, 3H, H**1**), 1.51 - 1.62 (m, 1H, H**5/5'**), 1.90 - 1.97 (m, 1H, H**5/**H**5'**), 2.05 - 2.13 (m, 2H, H**11**), 2.10 - 2.17 (m, 2H, H**6**), 2.15 - 2.33 (m, 2H, H**13**), 2.38 - 2.47 (m, 1H, H**4**), 2.42 (s, 3H, CH_3-**Ar**), 3.47 (ddd, *J* = 13.4, 6.1, 3.0 Hz, 1H, H**10/10'**), 3.64 - 3.71 (m, 1H, H**10/**H**10'**), 4.11 (q, *J* = 7.1 Hz, 2H, H**2**), 4.86 (d, *J* = 10.3 Hz, 1H, H**8**), 6.66 (d, *J* = 10.3 Hz, 1H, H**9**), 7.30 (d, *J* = 8.2 Hz, 2H, CH-**Ar**), 7.66 (d, *J* = 8.2 Hz, 2H, CH-**Ar**); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm):** 14.35 (C**1**), 21.70 (CH_3-**Ar**), 25.41 (C**5**), 30.91 (C**6**), 34.59 (C**13**), 36.32 (C**11**), 39.52 (C**4**), 47.08 (C**10**), 60.49 (C**2**), 110.58 (C**8**), 124.74 (C**9**), 126.11 (C**7**), 127.18 (CH-**Ar**), 130.01 (CH-**Ar**), 133.54 (C**12**), 135.72 (C-**Ar**), 143.96 (C-**Ar)**, 175.57 (C**3**); **ESI-HRMS (*m/z*)** calcd for $[M+Na]^+$ = 398.1397; found 398.1405.

5a: **MW** ($C_{15}H_{17}NO_2S$): 275.4 g/mol; **Rf**: 0.35 (Hexane/EtOAc 8:2); **^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm):** 2.43 (s, 3H), 2.75 (dd, *J* = 9.6, 6.0 Hz, 2H), 3.28 - 3.34 (m, 2H), 3.62 (d, *J* = 9.6 Hz, 2H), 4.80 (s, 2H), 5.22 (s, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm):** 21.68, 44.81, 53.49, 105.69, 128.24, 129.61, 132.28, 143.68, 149.15; **ESI-MS (*m/z*)** $[M+H]^+$ = 275.1. Spectral data in accordance with literature values.[2]



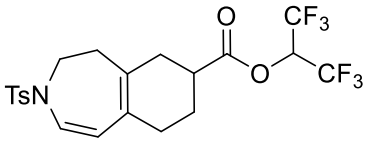
Compound 3ab was obtained from bisallene **1a** (52 mg, 0.19 mmol) and methyl acrylate (0.84 mL, 9.3 mmol), following the general procedure. Purification by column chromatography (silica gel, 40–63 µm, Hexanes/EtOAc) provided **5a** (7.7 mg, 15% yield) as a colourless solid and **3ab** (36 mg, 53% yield) as a yellow oil.

MW ($C_{19}H_{23}NO_4S$): 361.46 g/mol **Rf**: 0.31 (Hexane/EtOAc 8:2); **IR (ATR) ν (cm^{-1})**: 2924, 1727, 1341, 1158; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 1.51 - 1.63 (m, 1H), 1.91 - 1.98 (m, 1H), 2.06 - 2.33 (m, 6H), 2.40 - 2.50 (m, 1H), 2.42 (s, 3H), 3.48 (ddd, *J* = 13.4, 6.2, 3.0 Hz, 1H), 3.66 (s, 3H), 3.63 - 3.71 (m, 1H), 4.86 (d, *J* = 10.3 Hz, 1H), 6.66 (d, *J* = 10.3 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 21.70, 25.40, 30.90, 34.58, 36.33, 39.42, 47.08, 51.82, 110.52, 124.82, 126.15, 127.20, 130.02, 133.44, 135.76, 143.97, 176.00; **ESI-HRMS (*m/z*)** calcd for $[M+Na]^+$ = 384.1240; found 384.1236.



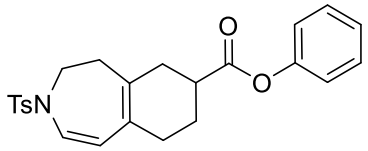
Compound 3ac was obtained from bisallene **1a** (49.6 mg, 0.18 mmol) and tert-butyl acrylate (1.36 mL, 98%, 9.1 mmol), following the general procedure. Purification by column chromatography (silica gel, 40–63 µm, Hexanes/EtOAc) provided **5a** (7.1 mg, 14 %yield) as a colourless solid and **3ac** (36.6 mg, 50% yield) as a pale yellow oil.

MW ($C_{22}H_{29}NO_4S$): 403.54 g/mol; **Rf**: 0.36 (Hexane/EtOAc 9:1); **IR (ATR) ν (cm^{-1})**: 2924, 1719, 1343, 1149; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 1.41 (s, 9H), 1.48 - 1.59 (m, 1H), 1.85 - 1.94 (m, 1H), 2.08 - 2.27 (m, 6H), 2.29 - 2.38 (m, 1H), 2.42 (s, 3H), 3.48 (ddd, J = 13.4, 6.1, 2.9 Hz, 1H), 3.63 - 3.71 (m, 1H), 4.86 (d, J = 10.3 Hz, 1H), 6.66 (d, J = 10.3 Hz, 1H), 7.30 (d, J = 8.4, 2H), 7.66 (d, J = 8.4 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 21.72, 25.48, 28.20, 30.95, 34.74, 36.35, 40.43, 47.12, 80.24, 110.73, 124.65, 126.09, 127.21, 130.02, 133.82, 135.78, 143.95, 174.99; **ESI-HRMS (*m/z*)** calcd for $[M+Na]^+$ = 426.1710; found 426.1712.



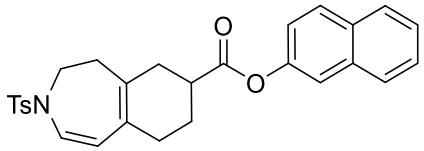
Compound 3ad was obtained from bisallene **1a** (51.8 mg, 0.19 mmol) and 1,1,1,3,3,3-hexafluoroisopropyl acrylate (1.55 mL, 99%, 9.2 mmol), following the general procedure. Purification by column chromatography (silica gel, 40–63 µm, Hexanes/EtOAc) provided **3ad** (49.3 mg, 53% yield) as a yellowish oil and **5a** (4.3 mg, 8% yield) as a colourless solid.

MW ($C_{21}H_{21}F_6NO_4S$): 497.45 g/mol; **Rf**: 0.40 (Hexane/EtOAc 9:1); **IR (ATR) ν (cm^{-1})**: 2926, 1772, 1349, 1197, 1163; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 1.65 - 1.77 (m, 1H), 1.98 - 2.06 (m, 1H), 2.11 - 2.40 (m, 6H), 2.45 (s, 3H), 2.67 - 2.76 (m, 1H), 3.52 (ddd, *J* = 13.6, 6.4, 2.9 Hz, 1H), 3.66 - 3.74 (m, 1H), 4.88 (d, *J* = 10.3 Hz, 1H), 5.76 (hept, $^3J_{H\text{-}F}$ = 6.1 Hz, 1H), 6.72 (d, *J* = 10.3 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 21.71, 24.92, 30.28, 33.89, 36.21, 38.89, 47.00, 66.51 (quint, $^2J_{C\text{-}F}$ = 34.7), 110.11, 120.53 (q, $^1J_{C\text{-}F}$ = 283.3) 125.27, 126.37, 127.22, 130.06, 132.29, 135.66, 144.08, 172.16; **ESI-HRMS (*m/z*)** calcd for $[M+Na]^+$ = 520.0988; found 520.1001.



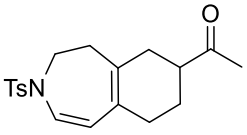
Compound 3ae was obtained from bis(allene) **1a** (50.2 mg, 0.18 mmol) and phenyl acrylate (1.25 mL, 9.1 mmol), following the general procedure. Purification by column chromatography (silica gel, 40–63 µm, Hexanes/EtOAc 98:2 to 90:10) provided **3ae** (50.4 mg, 65% yield) as a pale yellow oil.

MW ($C_{24}H_{25}NO_4S$): 423.53 g/mol; **Rf**: 0.24 (Hexane/EtOAc 9:1); **IR (ATR) ν (cm^{-1})**: 2923, 1748, 1340, 1157; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 1.69 - 1.80 (m, 1H), 2.07 - 2.18 (m, 3H), 2.19 - 2.27 (m, 2H), 2.30 - 2.49 (m, 2H), 2.42 (s, 3H), 2.68 - 2.77 (m, 1H), 3.51 (ddd, *J* = 13.4, 6.2, 2.9 Hz, 1H), 3.67 - 3.74 (m, 1H), 4.90 (d, *J* = 10.3 Hz, 1H), 6.70 (d, *J* = 10.3 Hz, 1H), 7.04 (dd, *J* = 8.6, 1.2 Hz, 2H), 7.19 - 7.24 (m, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.32 - 7.41 (m, 2H), 7.67 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 21.72, 25.39, 30.78, 34.45, 36.35, 39.61, 47.09, 110.45, 121.58, 124.97, 125.92, 126.26, 127.21, 129.55, 130.05, 133.21, 135.73, 144.02, 150.86, 174.04; **ESI-HRMS (*m/z*)** calcd for $[M+Na]^+$ = 446.1397; found 446.1397.



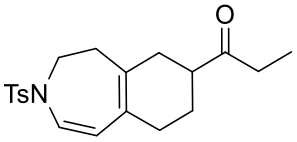
Compound 3af was obtained from bisallene **1a** (49.9 mg, 0.18 mmol) and naphtyl acrylate (909 mg, 4.6 mmol), following the general procedure. Purification by column chromatography (silica gel, 40–63 µm, Hexanes/EtOAc 98:2 to 90:10) provided **3af** (58 mg, 68% yield) as a pale yellow solid.

MW ($C_{28}H_{27}NO_4S$): 473.59 g/mol; **Rf**: 0.34 (Hexane/EtOAc 8:2); **MP (°C):** 144 - 146 (Hexane/EtOAc 9:1); **IR (ATR) ν (cm^{-1})**: 2921, 1745, 1345, 1161; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 1.73 - 1.86 (m, 1H), 2.12 - 2.30 (m, 5H), 2.34 - 2.54 (m, 2H), 2.42 (s, 3H), 2.74 - 2.82 (m, 1H), 3.53 (ddd, *J* = 13.4, 6.3, 2.9 Hz, 1H), 3.68 - 3.76 (m, 1H), 4.91 (d, *J* = 10.3 Hz, 1H), 6.71 (d, *J* = 10.3 Hz, 1H), 7.18 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.43 - 7.53 (m, 3H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.79 (dd, *J* = 7.1, 2.1 Hz, 1H), 7.82 - 7.86 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 21.72, 25.45, 30.83, 34.50, 36.37, 39.70, 47.10, 110.44, 118.53, 121.15, 125.01, 125.83, 126.29, 126.72, 127.21, 127.72, 127.90, 129.53, 130.05, 131.55, 133.20, 133.87, 135.73, 144.02, 148.50, 174.21; **ESI-HRMS (*m/z*)** calcd for $[M+Na]^+$ = 496.1553; found 496.1547.



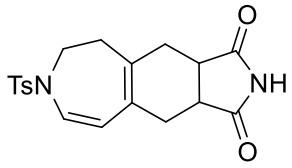
Compound 3ag was obtained from bisallene **1a** (49.5 mg, 0.18 mmol) and 3-buten-2-one (0.74 mL, 99%, 9.0 mmol), following the general procedure. Purification by column chromatography (silica gel, 40–63 µm, Hexanes/EtOAc 98:2 to 90:10) provided **5a** (5.8 mg, 12% yield) as a colourless solid and **3ag** (45 mg, 72% yield) as a yellowish oil.

MW ($C_{19}H_{23}NO_3S$): 345.46 g/mol; **Rf**: 0.17 (Hexane/EtOAc 8:2); **IR (ATR) ν (cm^{-1})**: 2921, 1703, 1342, 1160; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 1.41 - 1.50 (m, 1H), 1.89 - 1.96 (m, 1H), 2.04 - 2.27 (m, 6H), 2.14 (s, 3H), 2.41 (s, 3H), 2.44 - 2.53 (m, 1H), 3.46 (ddd, *J* = 13.5, 6.8, 2.3 Hz, 1H), 3.64 - 3.72 (m, 1H), 4.85 (d, *J* = 10.3 Hz, 1H), 6.66 (d, *J* = 10.3 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 21.69, 25.04, 28.16, 31.20, 33.77, 36.40, 47.05, 47.39, 110.46, 124.78, 126.10, 127.17, 130.01, 133.61, 135.70, 143.98, 211.19; **ESI-HRMS (*m/z*)** calcd for $[M+Na]^+$ = 368.1291; found 368.1294.



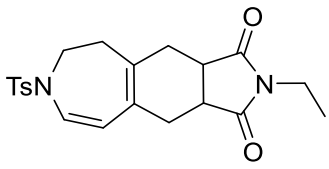
Compound 3ah was obtained from bisallene **1a** (50 mg, 0.18 mmol) and 1-penten-3-one (0.93 mL, 97%, 9.1 mmol), following the general procedure. Purification by column chromatography (silica gel, 40–63 µm, Hexanes/EtOAc 98:2 to 90:10) provided **3ah** (48.8 mg, 75% yield) as a yellowish oil.

MW ($C_{20}H_{25}NO_3S$): 359.48 g/mol; **Rf**: 0.29 (Hexane/EtOAc 8:2); **IR (ATR) ν (cm^{-1})**: 2924, 1704, 1342, 1160; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 1.03 (t, *J* = 7.3 Hz, 3H), 1.40 - 1.52 (m, 1H), 1.83 - 1.93 (m, 1H), 2.01 - 2.30 (m, 6H), 2.37 - 2.56 (m, 3H), 2.42 (s, 3H), 3.47 (ddd, *J* = 13.4, 7.1, 2.2 Hz, 1H), 3.65 – 3.74 (m, 1H), 4.86 (d, *J* = 10.3 Hz, 1H), 6.66 (d, *J* = 10.3 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 7.91, 21.72, 25.30, 31.30, 34.08, 34.10, 36.45, 46.47, 47.08, 110.53, 124.78, 126.08, 127.21, 130.03, 133.82, 135.76, 143.99, 213.86; **ESI-HRMS (*m/z*)** calcd for $[M+Na]^+$ = 382.1447; found 382.1447.



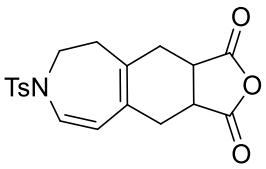
Compound 3ai was obtained from bisallene **1a** (50 mg, 0.18 mmol) and maleimide (88 mg, 0.91 mmol), following the general procedure. Purification by column chromatography (silica gel, 40–63 µm, hexanes/EtOAc 8:2 to 1:1) provided **3ai** (51 mg, 76% yield) as a pale yellow solid.

MW ($C_{19}H_{20}N_2O_4S$): 372.44 g/mol; **Rf**: 0.24 (Hexane/EtOAc 1:1); **MP (°C)**: 221 - 223 (Hexane/EtOAc 1:1); **IR (ATR) ν (cm^{-1})**: 3220, 2924, 1775, 1699, 1331, 1157; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 2.25 - 2.35 (m, 4H), 2.42 (s, 3H), 2.44 - 2.56 (m, 2H), 3.02 - 3.12 (m, 2H), 3.41 - 3.57 (m, 2H), 4.97 (d, *J* = 9.9 Hz, 1H), 6.65 (d, *J* = 9.9 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 8.06 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 21.72, 31.95, 32.17, 38.10, 40.89, 41.00, 46.51, 110.13, 126.84, 127.18, 127.42, 130.10, 135.16, 135.66, 144.22, 179.60, 179.78; **ESI-HRMS (*m/z*)** calcd for $[M+Na]^+$ = 395.1036; found 395.1043.



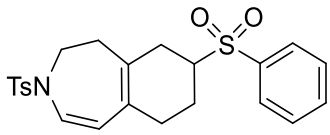
Compound 3aj was obtained from bisallene **1a** (49.8 mg, 0.18 mmol) and N-ethylmaleimide (603 mg, 4.8 mmol), following the general procedure. Purification by column chromatography (silica gel, 40–63 µm, Hexanes/EtOAc 8:2 to 1:1) provided **3aj** (46.5 mg, 64% yield) as a pale yellow solid.

MW ($C_{21}H_{24}N_2O_4S$): 400.49 g/mol; **Rf**: 0.37 (Hexane/EtOAc 1:1); **MP (°C):** 140 - 141 (Hexane/EtOAc 1:1); **IR (ATR) ν (cm^{-1})**: 2913, 1764, 1687, 1334, 1160; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 0.90 (t, *J* = 7.2 Hz, 3H), 2.14 - 2.36 (m, 4H), 2.41 (s, 3H), 2.47 - 2.58 (m, 2H), 2.94 - 3.04 (m, 2H), 3.39 (d, *J* = 7.2 Hz, 2H), 3.38 - 3.45 (m, 1H), 3.51 (ddd, *J* = 13.7, 6.9, 1.7 Hz, 1H), 4.96 (d, *J* = 10.0 Hz, 1H), 6.63 (d, *J* = 10.0 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 13.24, 21.69, 32.30, 32.55, 33.81, 37.94, 39.63, 39.71, 46.39, 110.14, 126.55, 127.14, 127.44, 130.04, 135.18, 135.59, 144.11, 179.43, 179.74; **ESI-HRMS (*m/z*)** calcd for $[M+Na]^+$ = 423.1349; found 423.1348.



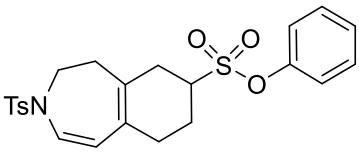
Compound 3ak was obtained from bisallene **1a** (49.6 mg, 0.18 mmol) and maleic anhydride (446 mg, 4.5 mmol), following the general procedure. Purification by column chromatography (silica gel, 40–63 µm, Hexanes/EtOAc 8:2 to 1:1) provided **3ak** (54.8 mg, 81% yield) as a yellow solid.

MW ($C_{19}H_{19}NO_5S$): 373.42 g/mol; **Rf**: 0.46 (Hexane/EtOAc 1:1); **MP (°C):** 156 - 157 (Hexane/EtOAc 1:1); **IR (ATR) ν (cm^{-1})**: 2919, 1841, 1769, 1348, 1159; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 2.17 - 2.26 (m, 1H), 2.31 - 2.41 (m, 3H), 2.44 (s, 3H), 2.50 - 2.62 (m, 2H), 3.27 - 3.38 (m, 2H), 3.49 - 3.55 (m, 2H), 4.98 (d, *J* = 10 Hz, 1H), 6.71 (d, *J* = 10 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 21.73, 32.07, 32.20, 37.97, 40.26, 40.33, 46.30, 109.70, 127.09, 127.67, 127.76, 130.22, 134.93, 135.51, 144.49, 173.80, 174.09; **ESI-HRMS (*m/z*)** calcd for $[M+Na]^+$ = 396.0876; found 396.0876.



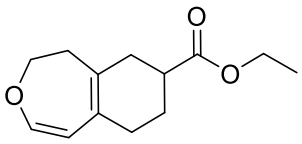
Compound 3al was obtained from bisallene **1a** (50.1 mg, 0.18 mmol) and phenyl vinyl sulfone (828 mg, 4.9 mmol), following the general procedure. Purification by column chromatography (silica gel, 40–63 µm, Hexanes/EtOAc 98:2 to 90:10) provided **3al** (24.7 mg, 31% yield) as a pale yellow solid.

MW ($C_{23}H_{25}NO_4S_2$): 443.58 g/mol; **Rf**: 0.29 (Hexane/EtOAc 7:3); **MP (°C):** 104 - 109 (dec.), (Hexane/EtOAc 9:1); **IR (ATR) ν (cm^{-1})**: 2923, 1343, 1302, 1160, 1143; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 1.37 - 1.50 (m, 1H), 1.92 - 2.15 (m, 6H), 2.20 - 2.28 (m, 1H), 2.32 (s, 3H), 2.91 - 3.01 (m, 1H), 3.34 (ddd, *J* = 13.6, 7.0, 2.3 Hz, 1H), 3.50 - 3.57 (m, 1H), 4.71 (d, *J* = 10.3 Hz, 1H), 6.57 (d, *J* = 10.3 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.43 - 7.50 (m, 2H), 7.51 - 7.59 (m, 3H), 7.72 – 7.81 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 21.73, 22.19, 30.83, 31.29, 36.21, 46.87, 60.18, 109.54, 125.61, 126.45, 127.20, 129.08, 129.32, 130.09, 131.46, 133.93, 135.56, 137.27, 144.16; **ESI-HRMS (*m/z*)** calcd for $[M+Na]^+$ = 466.1117; found 466.1117.



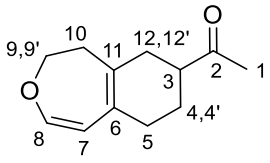
Compound 3am was obtained from bisallene **1a** (50.3 mg, 0.18 mmol) and phenyl vinyl sulfonate (1,0 g 5.4 mmol), following the general procedure. Purification by column chromatography (silica gel, 40–63 µm, Hexanes/EtOAc 98:2 to 90:10) provided **3am** (50.2 mg, 60% yield) as a colourless solid.

MW ($C_{23}H_{25}NO_5S_2$): 459.57 g/mol; **Rf**: 0.48 (Hexane/EtOAc 7:3); **MP (°C):** 125 - 126 (Hexane/EtOAc 9:1); **IR (ATR) ν (cm^{-1})**: 2919, 1364, 1341, 1159, 1143; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 1.78 - 1.92 (m, 1H), 2.08 - 2.24 (m, 2H), 2.30 (d, *J* = 7.6 Hz, 2H), 2.34 - 2.41 (m, 1H), 2.43 (s, 3H), 2.47 - 2.55 (m, 1H), 2.58 - 2.69 (m, 1H), 3.29 - 3.40 (m, 1H), 3.49 (ddd, *J* = 13.6, 7.0, 2.3 Hz, 1H), 3.67 - 3.75 (m, 1H), 4.87 (d, *J* = 10.3 Hz, 1H), 6.73 (d, *J* = 10.3 Hz, 1H), 7.21 -7.25 (m, 2H), 7.27 - 7.30 (m, 1H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.36 - 7.42 (m, 2H), 7.66 (d, *J* = 8.3 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 21.74, 23.21, 30.59, 32.10, 36.18, 46.89, 56.81, 109.39, 122.09, 125.88, 126.55, 127.22, 127.25, 130.09, 130.12, 131.06, 135.56, 144.21, 149.05; **ESI-HRMS (*m/z*)** calcd for $[M+Na]^+$ = 482.1066; found 482.1078.



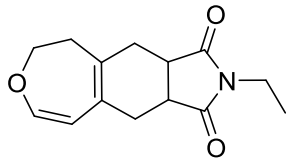
Compound 3ba was obtained from bisallene **1b** (23.4 mg, 0.19 mmol) and ethyl acrylate (1.0 mL, 99%, 9.1 mmol), following the general procedure. Purification by column chromatography (silica gel, 40–63 µm, Hexanes/EtOAc 99:1) provided **3ba** (7.2 mg, 17% yield) as a pale yellow oil.

MW ($C_{13}H_{18}O_3$): 222.28 g/mol; **Rf**: 0.61(Hexane/EtOAc 9:1); **IR (ATR) ν (cm^{-1})**: 2924, 1729; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 1.26 (t, *J* = 7.1 Hz, 3H), 1.57 - 1.69 (m, 1H), 1.95 - 2.02 (m, 1H), 2.08 - 2.20 (m, 2H), 2.22 - 2.44 (m, 3H), 2.45 - 2.54 (m, 2H), 4.07 - 4.22 (m, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.57 (d, *J* = 7.9 Hz, 1H), 6.26 (d, *J* = 7.9 Hz, 1H) ; **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 14.40, 25.54, 30.72, 34.27, 38.90, 39.77, 60.49, 70.09, 105.83, 126.20, 131.98, 145.02, 175.86; **ESI-HRMS (*m/z*)** calcd for $[M+Na]^+$ = 245.1148; found 245.1146.



Compound 3bg was obtained from bisallene **1b** (23.4 mg, 0.19 mmol) and 3-buten-2-one (0.74, 99%, mL, 9.0 mmol), following the general procedure. Purification by column chromatography (silica gel, 40–63 µm, Hexanes/EtOAc 98:2) provided **3bg** (10.0 mg, 27% yield) as a pale yellow oil.

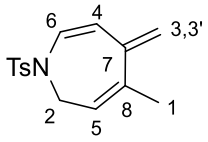
MW ($C_{12}H_{16}O_2$): 192.26 g/mol; **Rf**: 0.49 (Hexane/EtOAc 8:2); **IR (ATR) ν (cm^{-1})**: 2923, 1704; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 1.44 - 1.57 (m, 1H, H**4**/H**4'**), 1.92 - 2.01 (m, 1H, H**4**/H**4'**), 2.09 - 2.22 (m, 3H, H**5**, H**12**/H**12'**), 2.18 (s, 3H, H**1**), 2.23 - 2.34 (m, 1H, H**12**/H**12'**), 2.36 - 2.50 (m, 2H, H**10**), 2.50 - 2.60 (m, 1H, H**3**), 4.11 (ddd, *J* = 10.9, 6.8, 1.6 Hz, 1H, H**9**/H**9'**), 4.18 (ddd, *J* = 10.9, 5.9, 2.0 Hz, 1H, H**9**/H**9'**), 4.57 (d, *J* = 7.8 Hz, 1H, H**7**), 6.26 (d, *J* = 7.8 Hz, 1H, H**8**) ; **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 25.13 (C**4**), 28.21 (C**1**), 31.00 (C**5**), 33.51 (C**12**), 38.96 (C**10**), 47.70 (C**3**), 70.05 (C**9**), 105.73 (C**7**), 126.23 (C**6**), 132.01 (C**11**), 145.08 (C**8**), 211.52 (C**2**); **ESI-HRMS (*m/z*)** calcd for $[M+Na]^+$ = 215.1043; found 215.1037.



Compound 3bj was obtained from bisallene **1b** (23.4 mg, 0.19 mmol) and N-ethylmaleimide (580 mg, 4.6 mmol), following the general procedure. Purification by column chromatography (silica gel, 40–63 µm, Hexanes/EtOAc 95:5 to 80:20) provided **3bj** (15.0 mg, 32% yield) as a pale yellow oil.

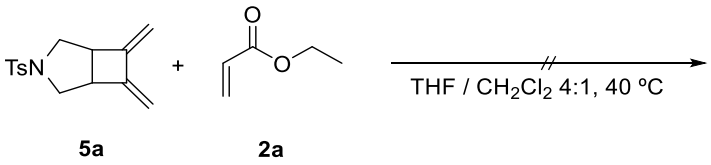
MW ($C_{14}H_{17}NO_3$): 247.29 g/mol; **Rf**: 0.21(Hexane/EtOAc 8:2); **IR (ATR) ν (cm^{-1})**: 2922, 1763, 1684; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 1.07 (t, *J* = 7.2 Hz, 3H), 2.27 - 2.38 (m, 2H), 2.47 - 2.63 (m, 4H), 2.99 - 3.06 (m, 2H), 3.48 (q, *J* = 7.2 Hz, 2H), 4.00 (ddd, *J* = 11.2, 6.2, 2.1 Hz, 1H), 4.09 (ddd, *J* = 11.2, 6.1, 2.2 Hz, 1H), 4.68 (d, *J* = 7.6 Hz, 1H), 6.25 (d, *J* = 7.6 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 13.34, 31.83, 31.89, 33.90, 39.76, 39.79, 40.00, 69.63, 105.85, 127.48, 133.53, 147.04, 179.71, 180.02; **ESI-HRMS (*m/z*)** calcd for $[M+Na]^+$ = 270.1101; found 270.1107.

Compound 4a



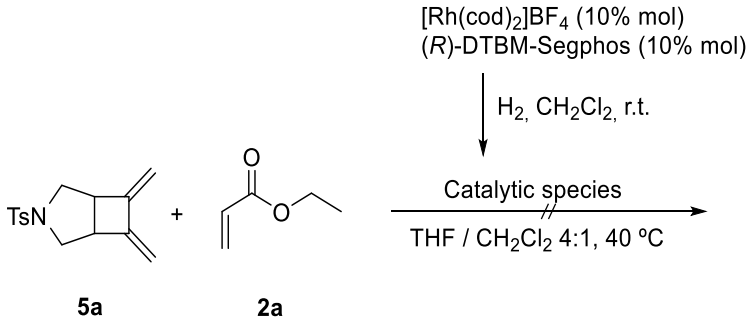
MW ($C_{15}H_{17}NO_2S$): 275.4 g/mol; **Rf**: 0.50 (Hexanes/EtOAc 8:2); **IR (ATR) ν (cm^{-1})**: 2921, 2852, 1456, 1337, 1158, 1090; **^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm):** 1.76 (s, 3H, H**1**), 2.41 (s, 3H, CH_3-**Ar**), 3.95 (d, *J* = 7.2 Hz, 2H, H**2**), 5.02 (s, 1H, H**3**/H**3'**), 5.09 (s, 1H, H**3**/H**3'**), 5.37 (d, *J* = 10.4 Hz, 1H, H**4**), 5.55 (t, *J* = 7.2 Hz, 1H, H**5**), 6.52 (d, *J* = 10.4, 1H, H**6**), 7.28 (d, *J* = 8.4 Hz, 2H, H-**Ar**), 7.66 (d, *J* = 8.4, 2H, H-**Ar**); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 21.64 (CH_3-**Ar**), 23.01 (C**1**), 45.60 (C**2**), 113.72 (C**4**), 117.68 (C**3**), 120.91 (C**5**), 127.01 (C**6**),127.13 (CH-**Ar**), 129.83 (CH-**Ar**), 136.24 (C-**Ar**), 142.06 (C**7**), 143.46 (C**8**), 143.90 (C-**Ar**); **ESI-HRMS (*m/z*)** calcd for $[M+Na]^+$ = 298.0872; found: 298.0875.

Scheme S4. Mechanistic experiments using compound 5a and ethyl acrylate 2a



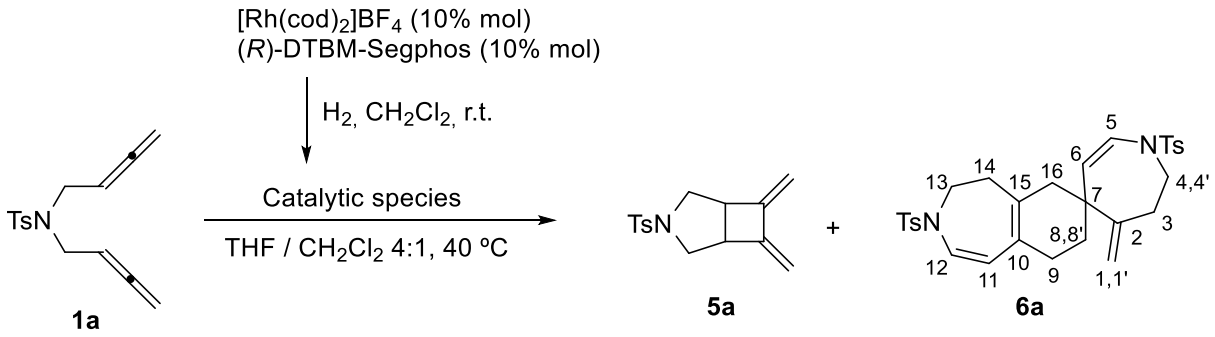
In a 25 mL round-bottom flask equipped with a magnetic stirrer and an inert atmosphere, a solution of **5a** (15 mg, 0.055 mmol) and ethyl acrylate **2a** (0.3 mL, 275 mg, 2.75 mmol) in a 4:1 mixture of THF/CH_2Cl_2 (6 mL) was stirred at 40 °C for 16h. The solvent and ethyl acrylate **2a** were removed under reduced pressure. ^{1}H NMR analysis of the crude product revealed the presence of unaltered starting material **5a**.

Scheme S5. Mechanistic experiments using compound 5a, ethyl acrylate 2a and Rh(I) catalyst



In a 10 mL capped vial, a mixture of $[Rh(cod)_2]BF_4$ (4.26 mg, 0.010 mmol) and *(R)*-DTBM-Segphos (12.4 mg, 0.011 mmol) was purged with nitrogen and dissolved in anhydrous CH_2Cl_2 (4 mL). Hydrogen gas was bubbled into the catalyst solution for 30 min. The resulting mixture was concentrated to dryness, dissolved again in anhydrous CH_2Cl_2 (2 mL) and transferred via syringe into a 40 °C preheated solution of **5a** (29 mg, 0.11 mmol) and ethyl acrylate **2a** (0.6 mL, 550 mg, 5.33 mmol) in anhydrous THF (10 mL) and under inert atmosphere. The resulting mixture was stirred at 40 °C for 16h. The solvent and ethyl acrylate **2a** were removed under reduced pressure and the crude reaction mixture was filtered through a short silica gel pad (Hexanes/EtOAc 8:2 v/v). ^{1}H NMR analysis of the crude product revealed the presence of unaltered starting material **5a**.

Scheme S6. Mechanistic experiments using compound 1a and Rh(I) catalyst

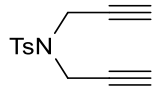


In a 10 mL capped vial, a mixture of $[Rh(cod)_2]BF_4$ (7.4 mg, 0.018 mmol) and *(R)*-DTBM-Segphos (23.6 mg, 0.020 mmol) was purged with nitrogen and dissolved in anhydrous CH_2Cl_2 (4 mL). Hydrogen gas was bubbled into the catalyst solution and the mixture was stirred for 30 min. The resulting mixture was concentrated to dryness, dissolved again in anhydrous CH_2Cl_2 (4 mL) and transferred via syringe into a preheated solution to 40 °C of bisallene **1a** (48.4 mg, 0.18 mmol) in anhydrous THF (16 mL) and under inert atmosphere. The resulting mixture was stirred at 40 °C for 16 h. The solvent was removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel using hexane/EtOAc mixtures as the eluent (95:5 to 90:10 v/v), affording first, compound **5a** (5.5 mg, 12% yield) as a colourless solid, and second, **6a** (28.3 mg, 58% yield) as a pale yellow solid.

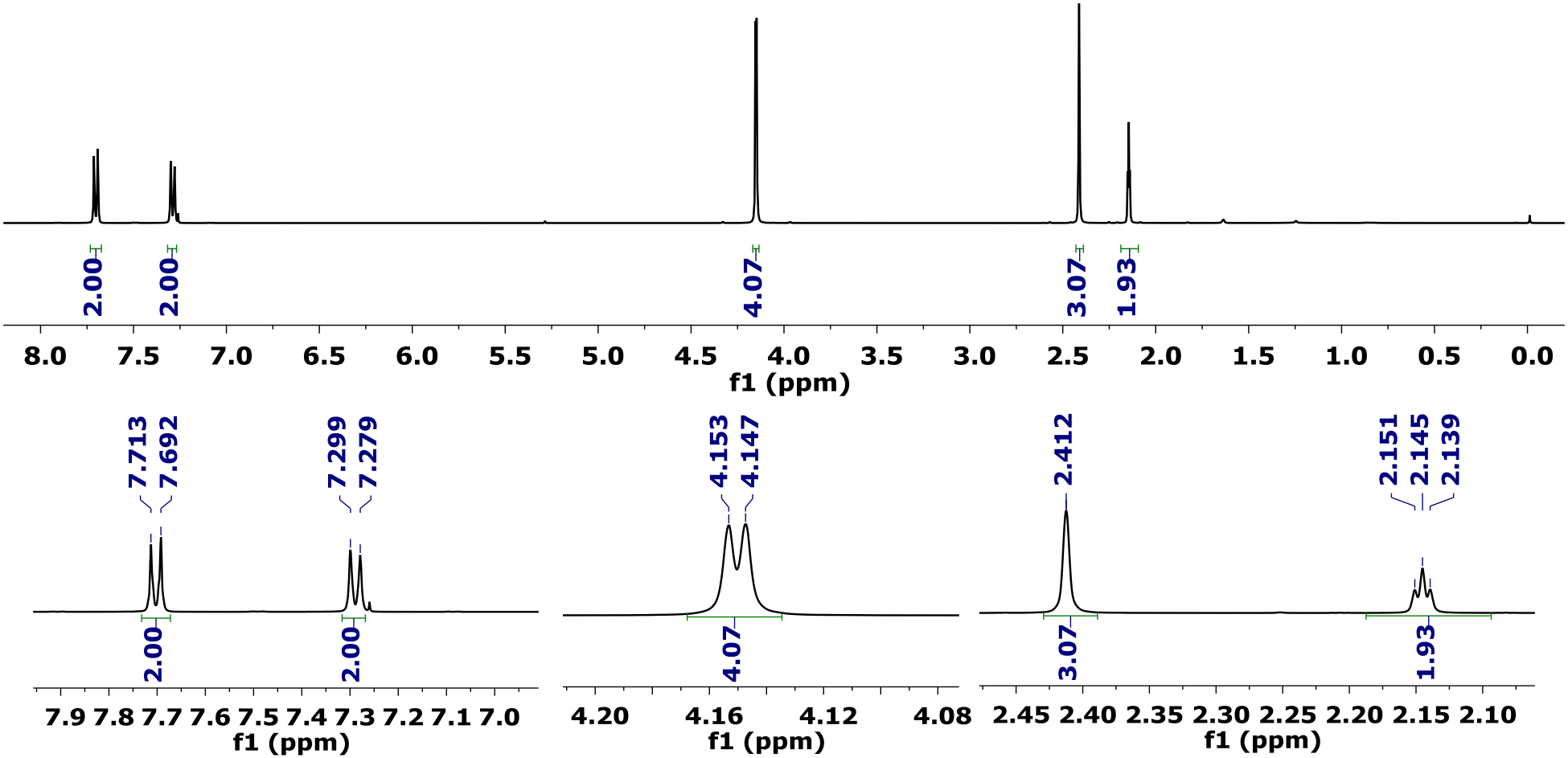
6a: **MW** ($C_{30}H_{34}N_2O_4S_2$): 550.73 g/mol; **Rf**: 0.26 (Hexane/EtOAc 8:2); **MP (°C):** 87-92 (dec); **IR (ATR) ν (cm^{-1})**: 2921, 1336, 1156; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):** 1.46 - 1.55 (m, 1H, H**8**/H**8'**), 1.56 - 1.66 (m, 1H, H**8**/H**8'**), 1.93 - 2.20 (m, 6H, H**9**, H**14**, H**16**), 2.42 (s, 3H, CH_3-**Ar**), 2.42 (s, 3H, CH_3-**Ar**), 2.43 - 2.55 (m, 2H, H**3**), 3.38 - 3.48 (m, 1H, H**4**/H**4'**), 3.49 - 3.66 (m, 3H, H**4**/H**4'**,H**13**), 4.52 (s, 1H, H**1**/H**1'**), 4.63 (s, 1H, H**1**/H**1'**), 4.71 (d, *J* = 9.5 Hz, 1H, H**6**), 4.84 (d, *J* = 10.3 Hz, 1H, H**11**), 6.27 (d, *J* = 9.5 Hz, 1H, H**5**), 6.64 (d, *J* = 10.3 Hz, 1H, H**12**), 7.28 (d, *J* = 8.2 Hz, 2H, CH-**Ar**), 7.31 (d, *J* = 8.2 Hz, 2H, CH-**Ar**), 7.66 (m, 4H, CH-**Ar**); **^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm)**: 21.67 (CH_3-**Ar**), 21.71 (CH_3-**Ar**), 29.10 (C**9**), 32.71 (C**8**), 34.74 (C**3**), 36.69 (C**14**), 42.46 (C**7**), 44.58 (C**16**), 47.03 (C**13**), 50.10 (C**4**), 110.59 (C**11**), 111.82 (C**1**), 122.64 (C**6**), 124.72 (C**12**), 125.67 (C**5**), 125.83 (C**10**), 127.18 (CH-**Ar**), 127.19 (CH-**Ar**), 129.78 (CH-**Ar**), 130.01 (CH-**Ar**), 132.95 (C**15**), 135.83 (C-**Ar**), 136.25 (C-**Ar**), 143.72 (C-**Ar**), 143.97(C-**Ar**), 149.30 (C**2**); **ESI-HRMS (*m/z*)** calcd for $[M+Na]^+$ = 573.1852; found 573.1836.

^{1}H and ^{13}C NMR spectra

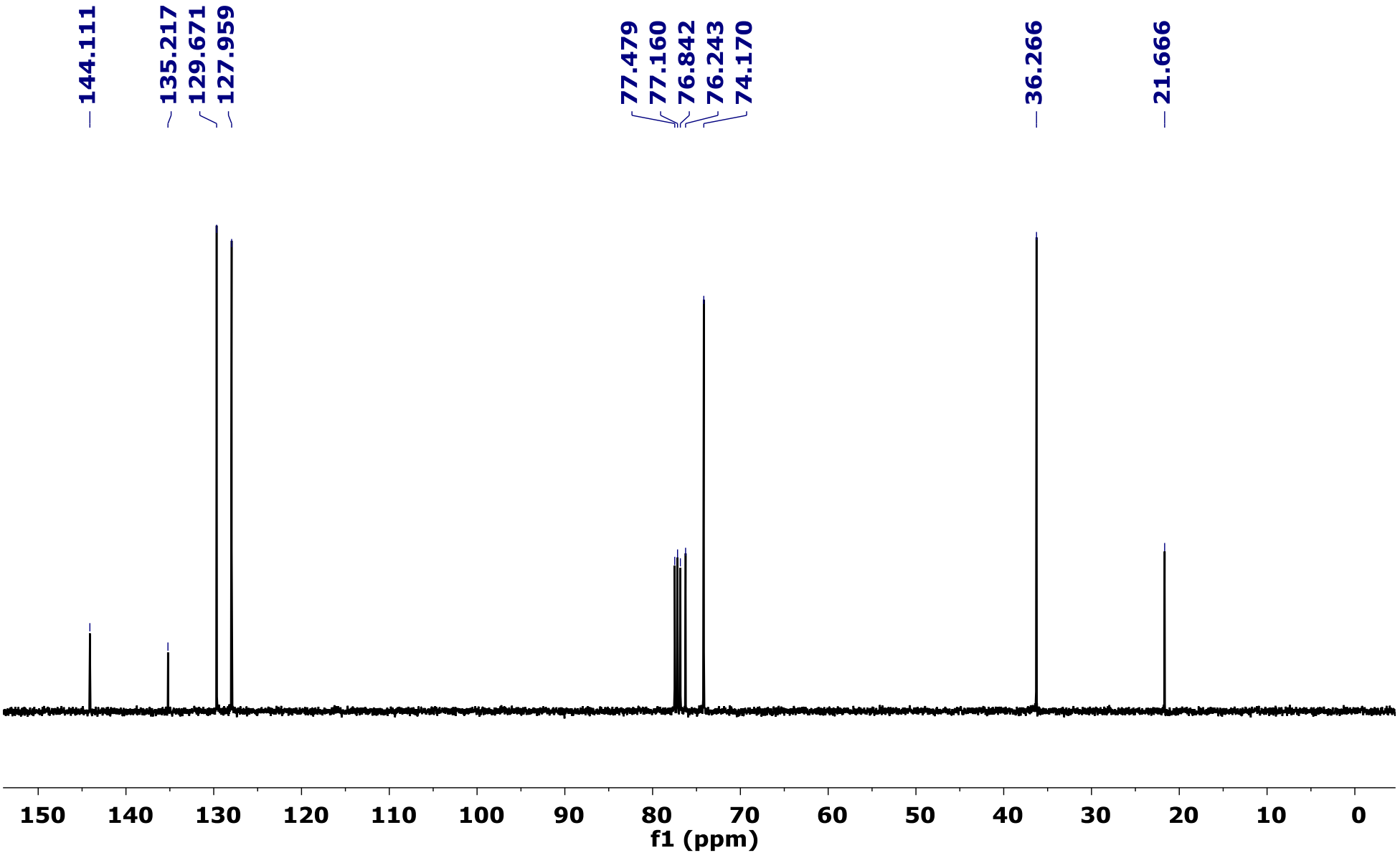
Diyne S1



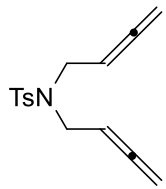
^{1}H NMR (400 MHz, $CDCl_3$)



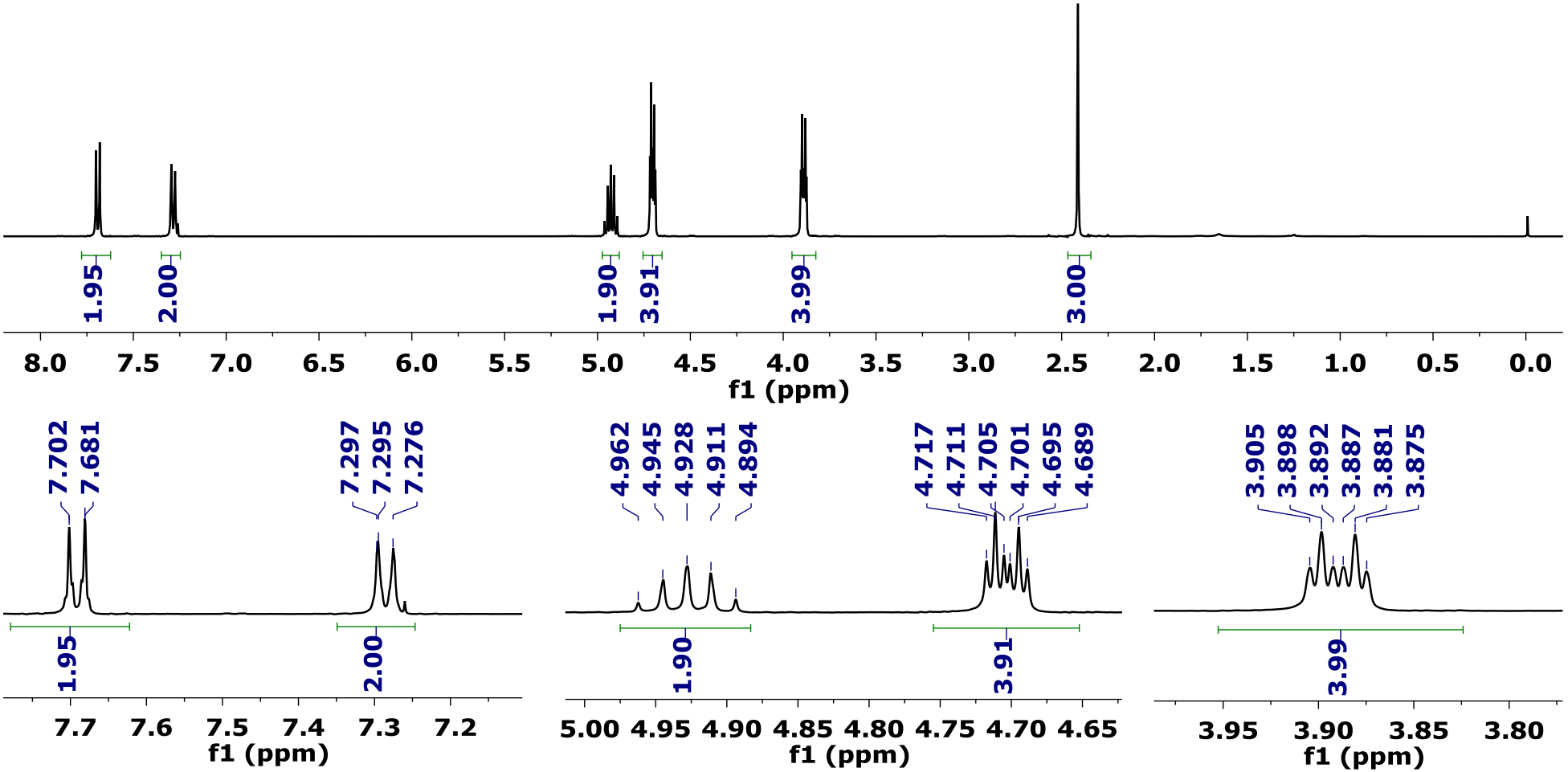
^{13}C NMR (101 MHz, $CDCl_3$)



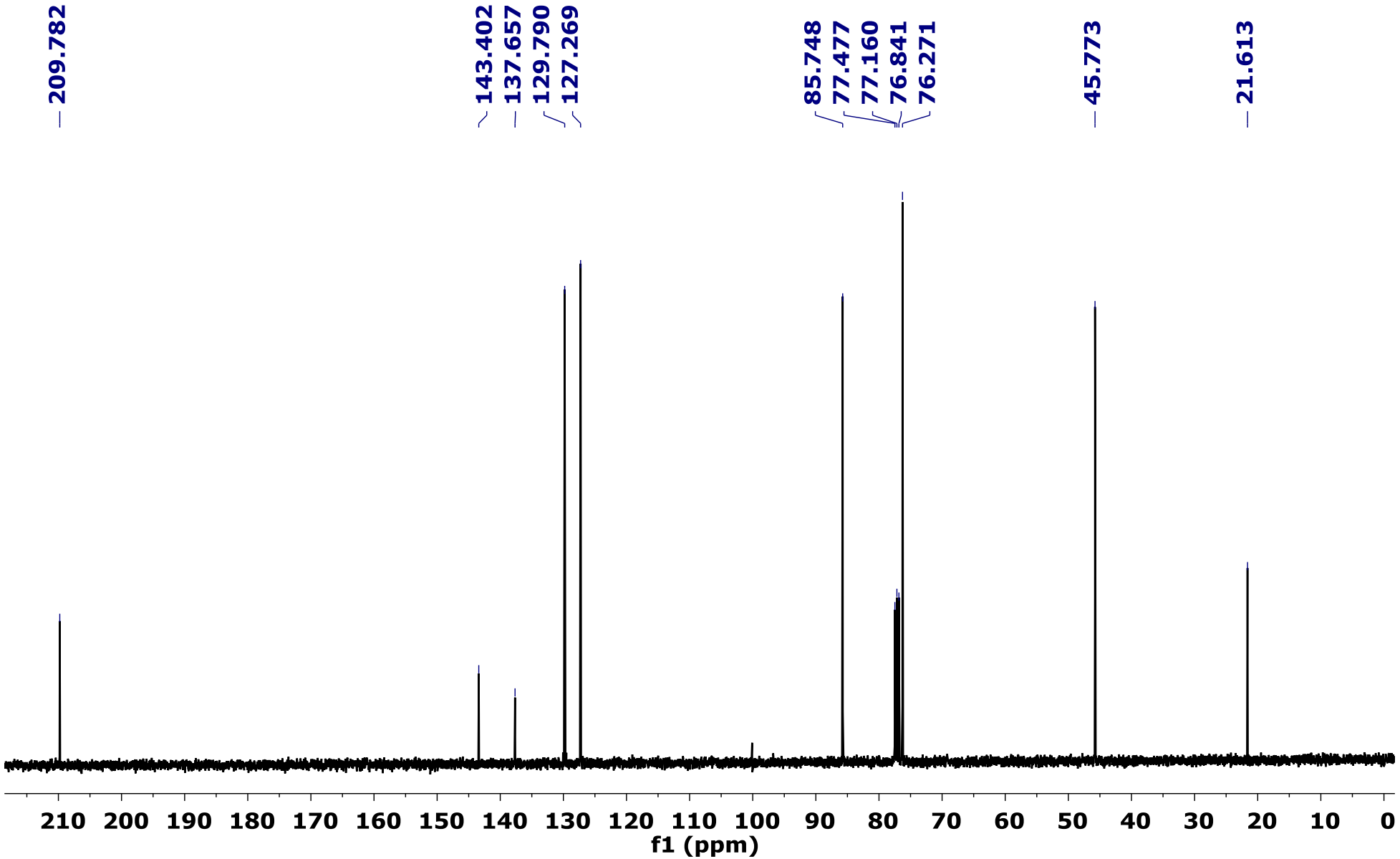
Bisallene 1a



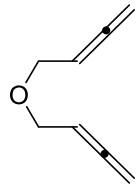
^{1}H NMR (400 MHz, $CDCl_3$)



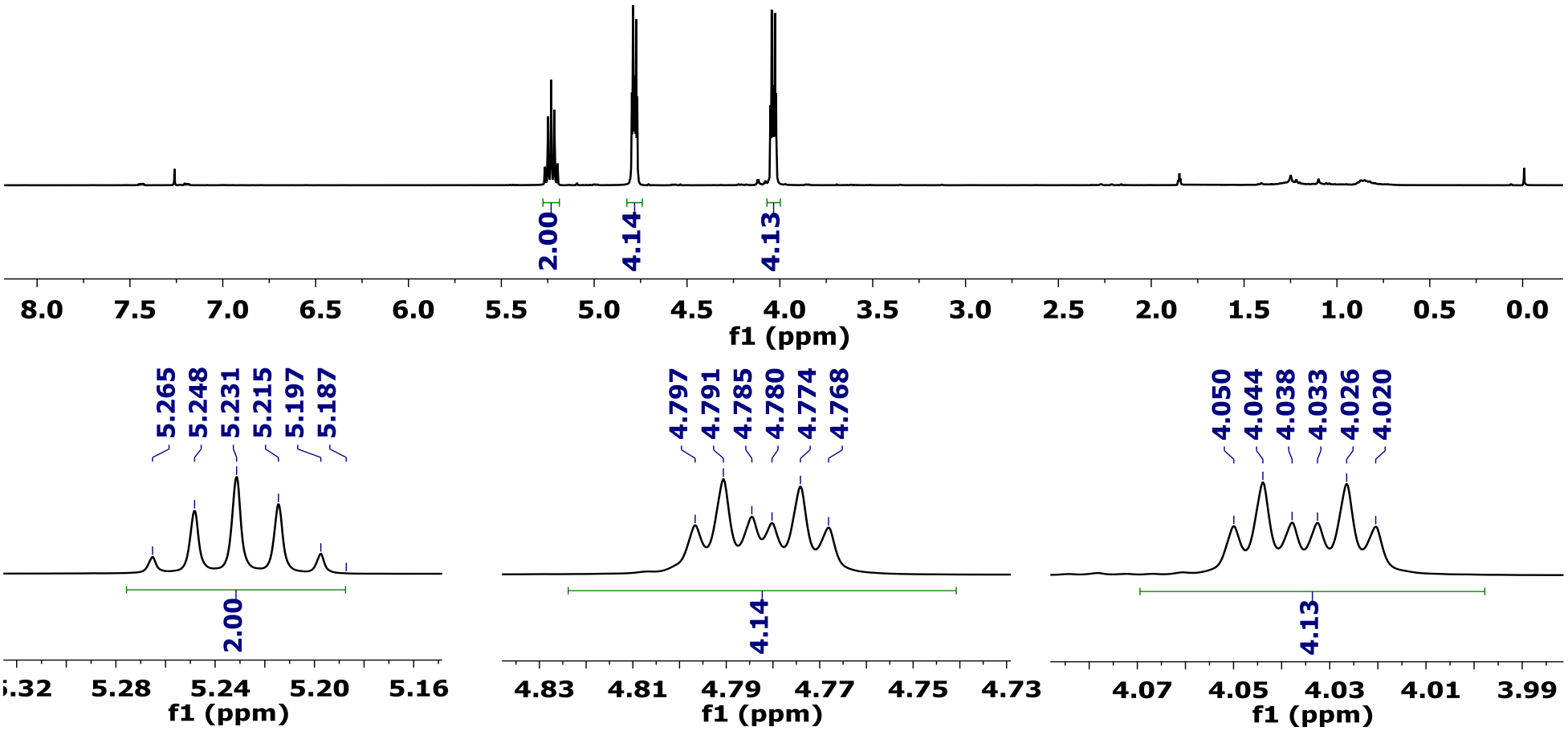
^{13}C NMR (101 MHz, $CDCl_3$)



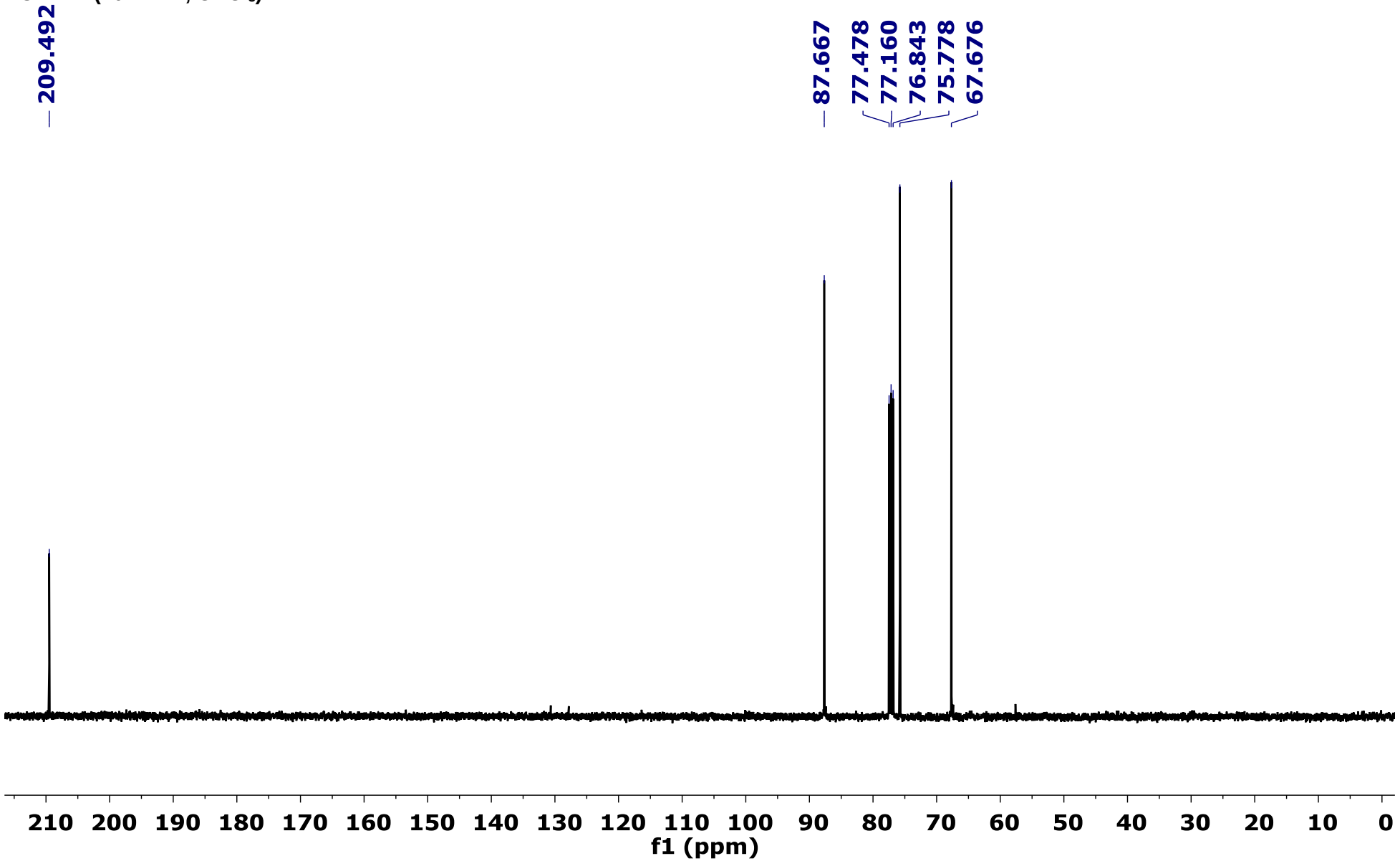
Bisallene 1b



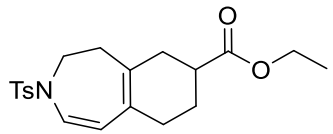
^{1}H NMR (400 MHz, $CDCl_3$)



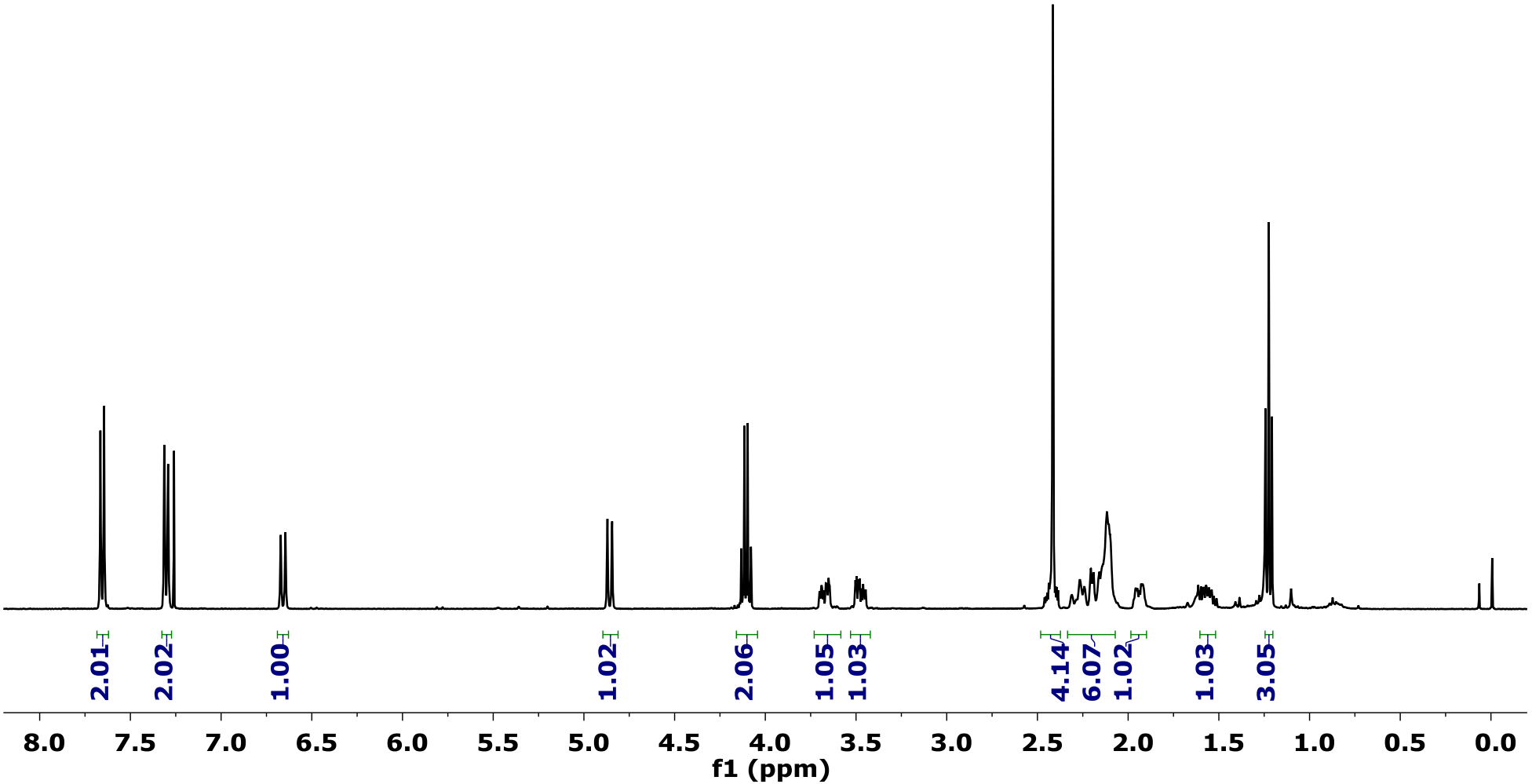
^{13}C NMR (101 MHz, $CDCl_3$)

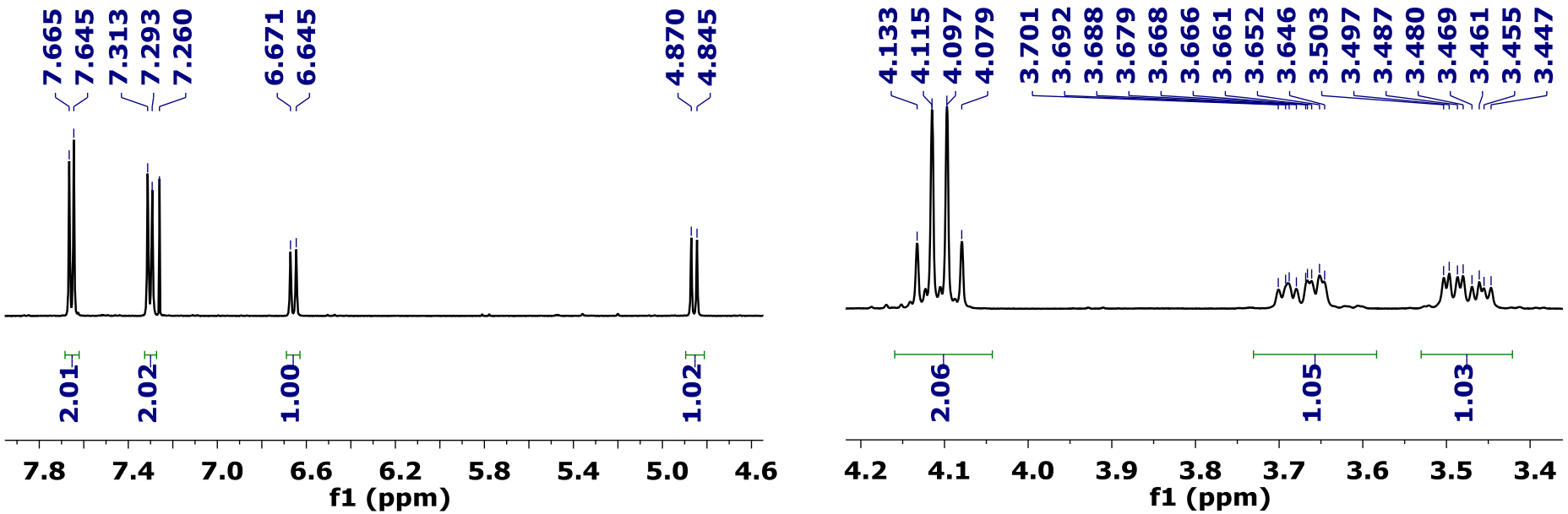


Product 3aa



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

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6.671
6.645
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2.02
1.00
1.02
7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
f1 (ppm)
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4.115
4.097
4.079
3.701
3.692
3.688
3.679
3.668
3.666
3.661
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3.497
3.487
3.480
3.469
3.461
3.455
3.447
2.06
1.05
1.03
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4.1
4.0
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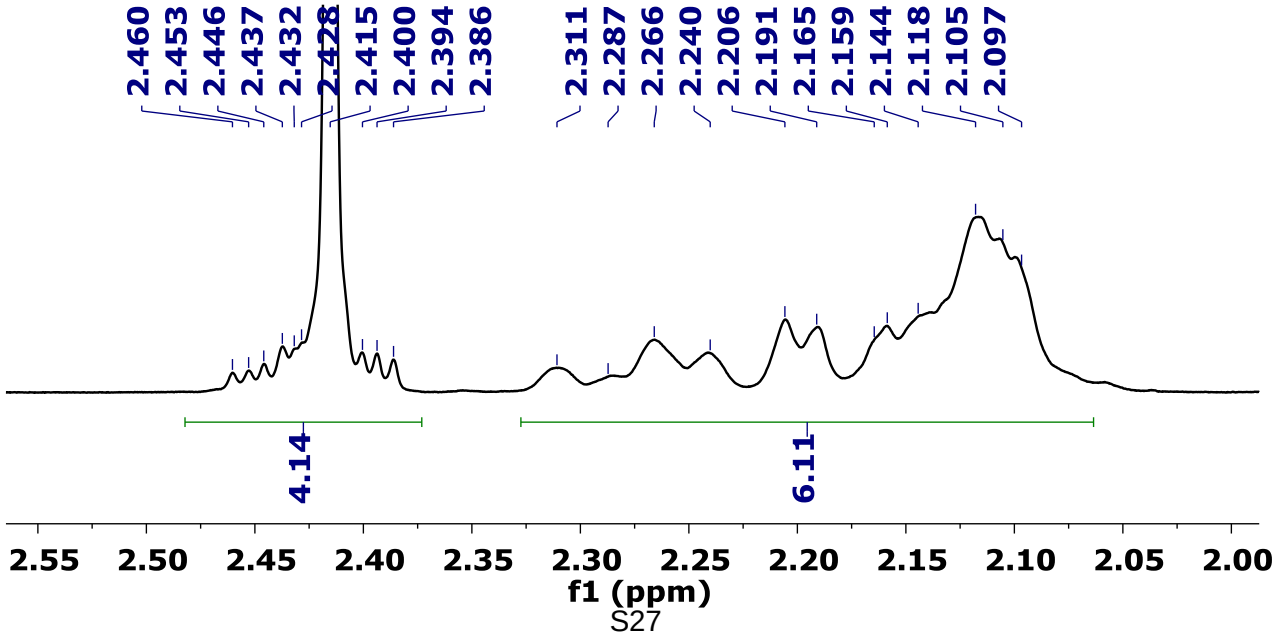
3.6
3.5
3.4
f1 (ppm)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2.118
2.105
2.097
4.14
6.11
2.55
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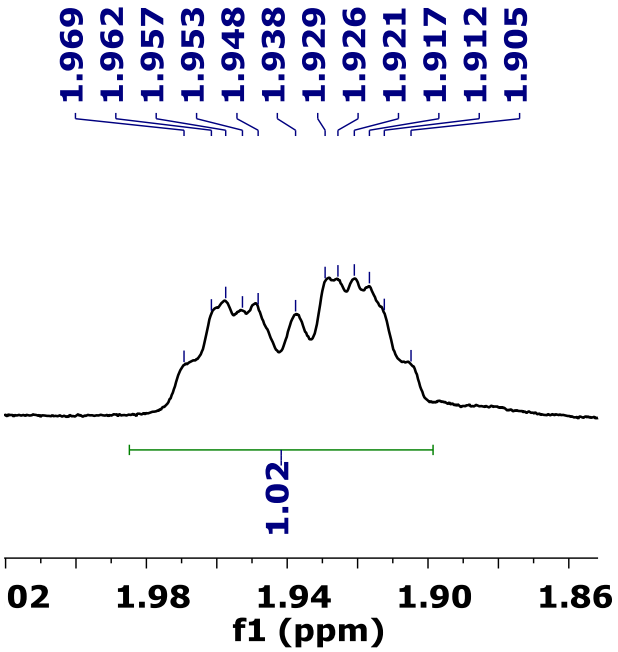
2.00
f1 (ppm)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02
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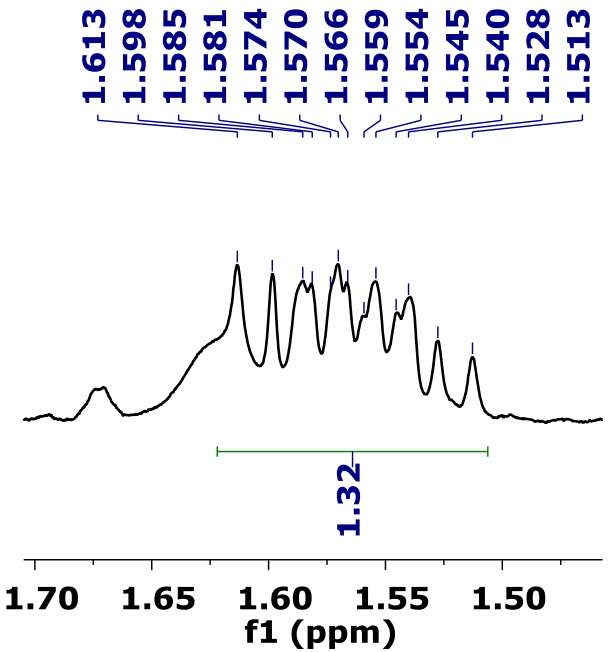
1.86
f1 (ppm)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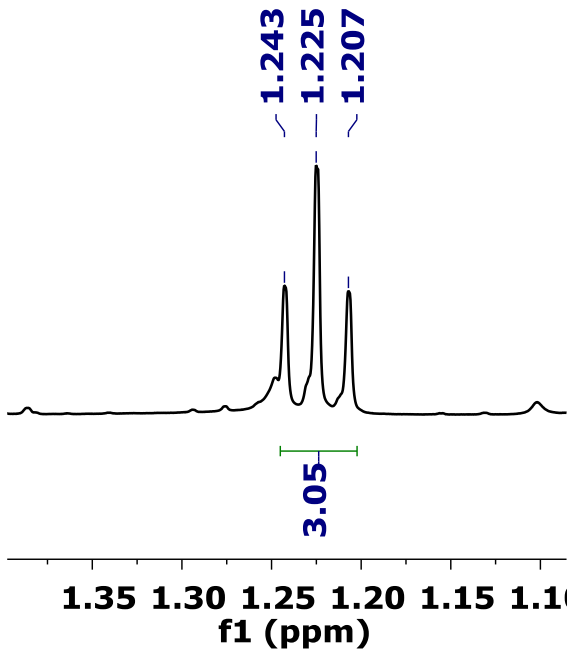
1.65
1.60
1.55
1.50
f1 (ppm)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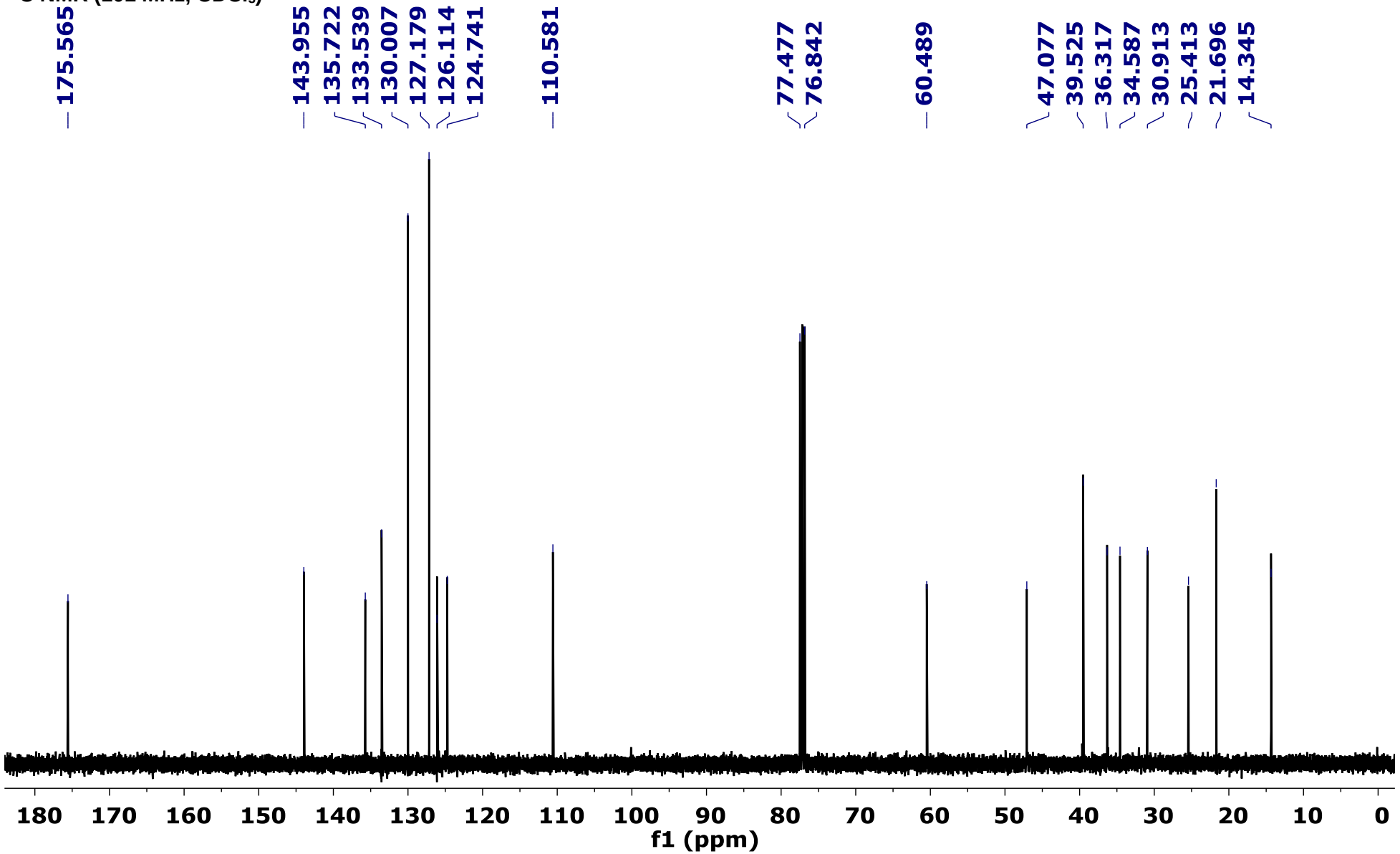
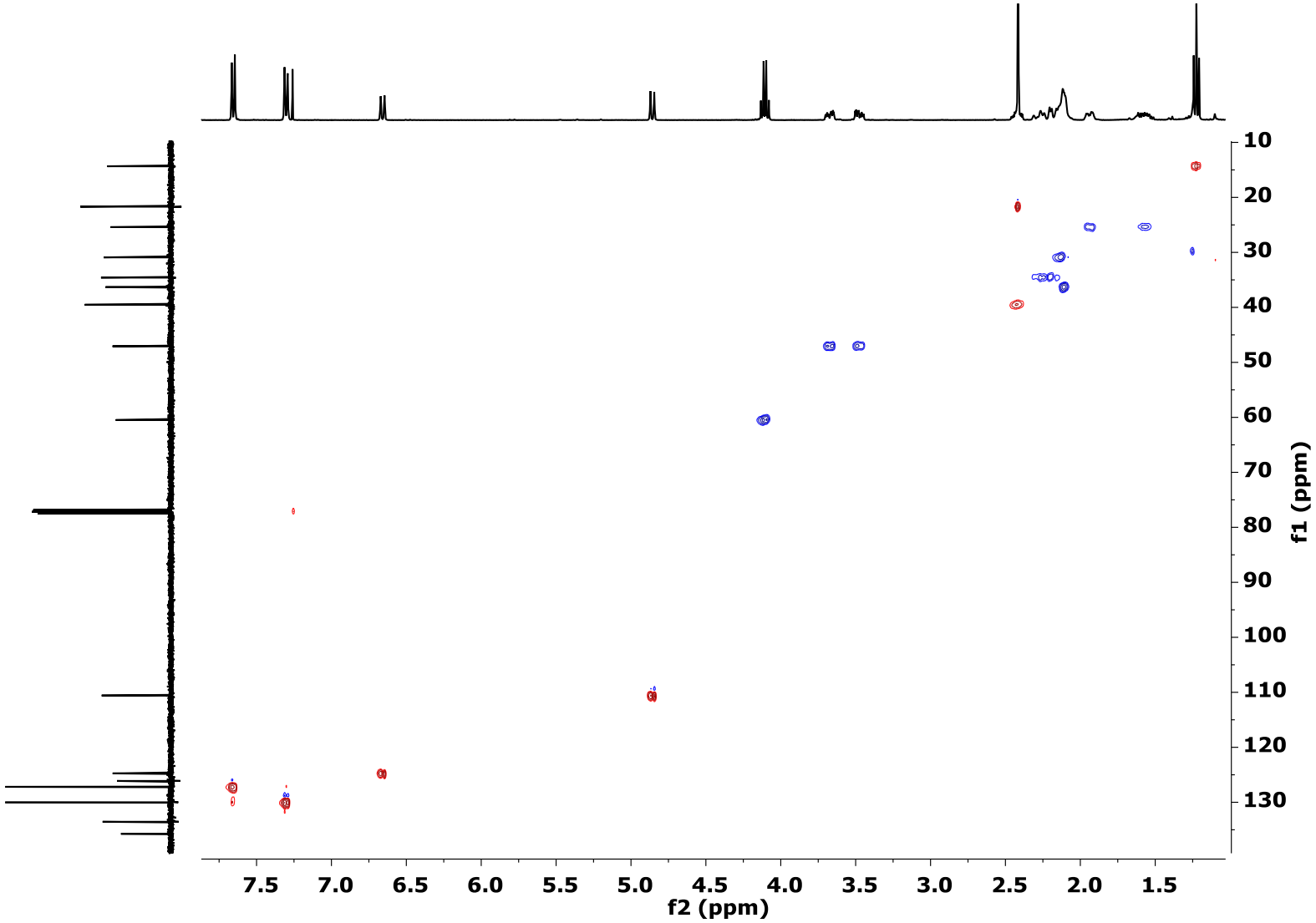
1.20
1.15
f1 (ppm)

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



2D NMR HSQC


10
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30
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50
60
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80
90
100
110
120
130
f1 (ppm)
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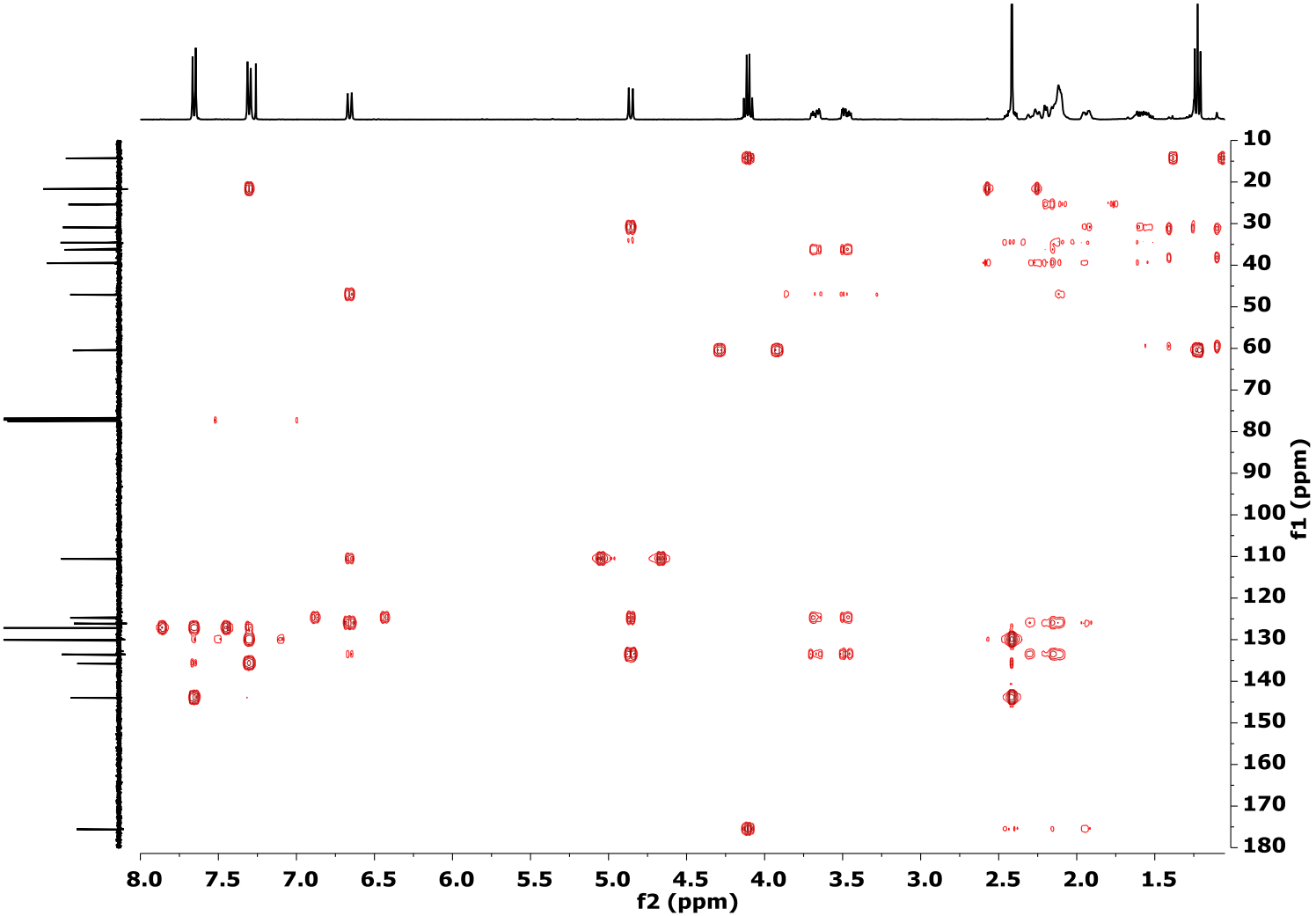
2.5
2.0
1.5
f2 (ppm)

2D NMR HMBC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4.5
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3.0
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1.5
f2 (ppm)
10
20
30
40
50
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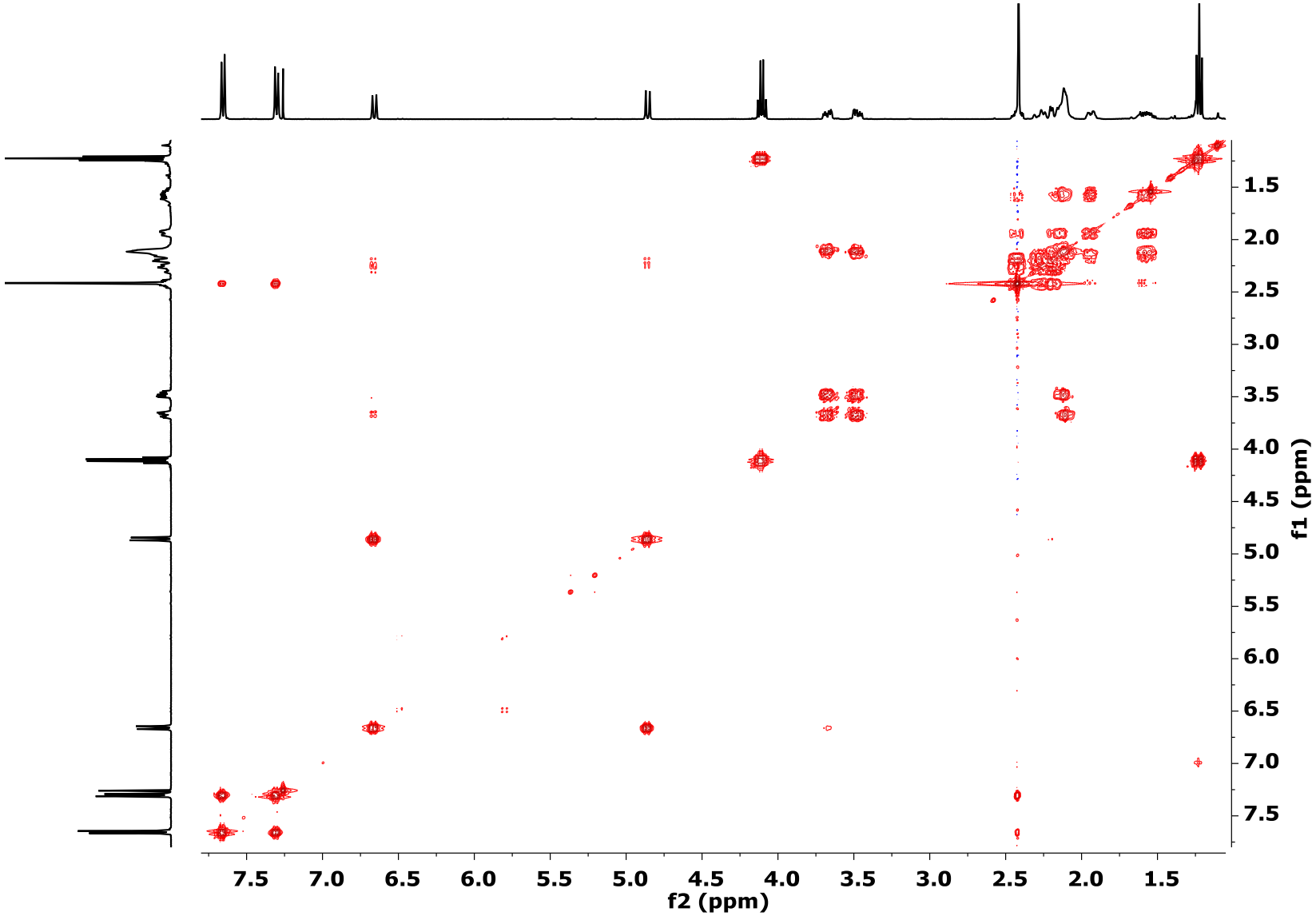
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)

2D NMR COSY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6.5
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5.5
5.0
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3.0
2.5
2.0
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f2 (ppm)
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2.0
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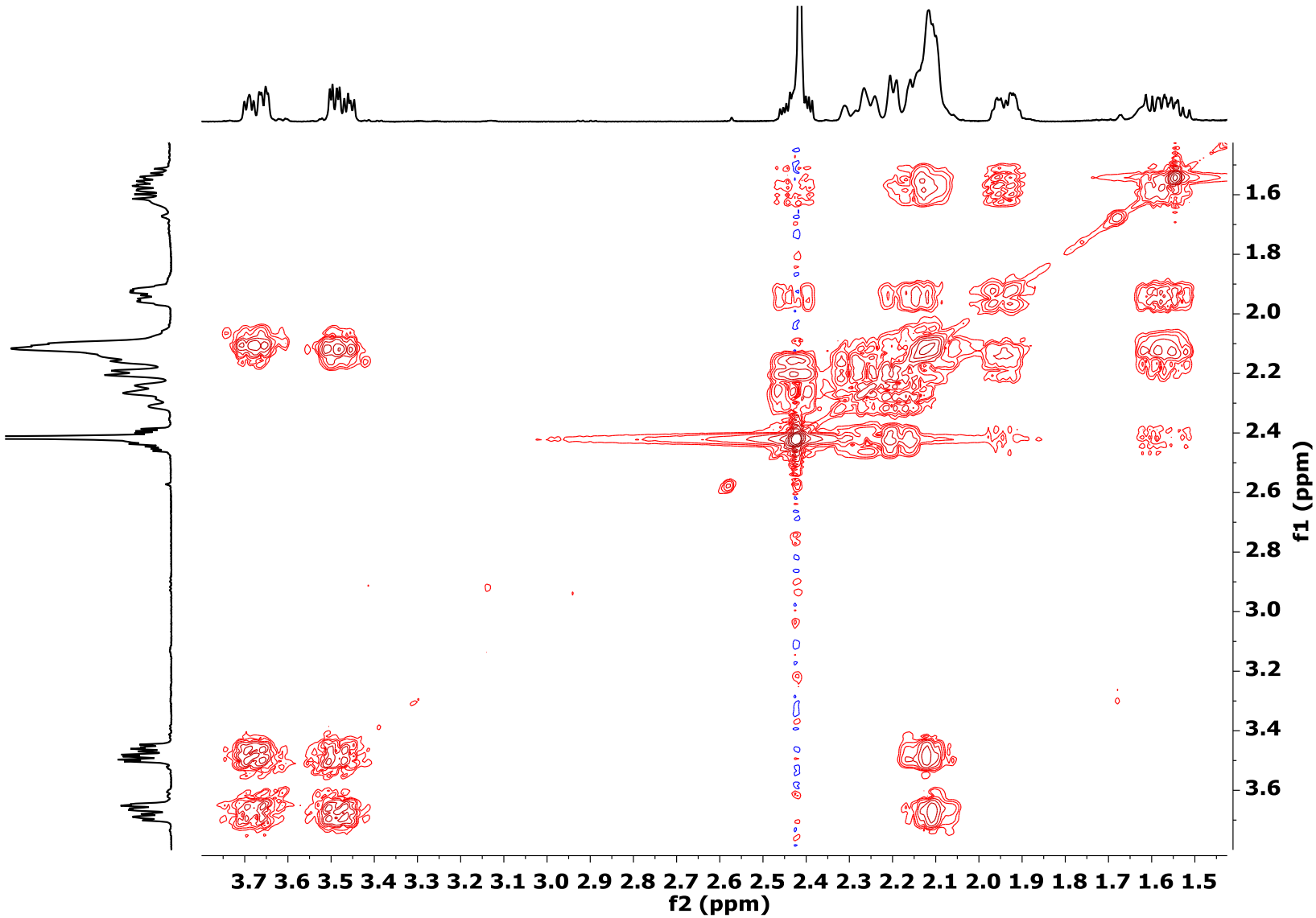
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)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2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
f1 (ppm)
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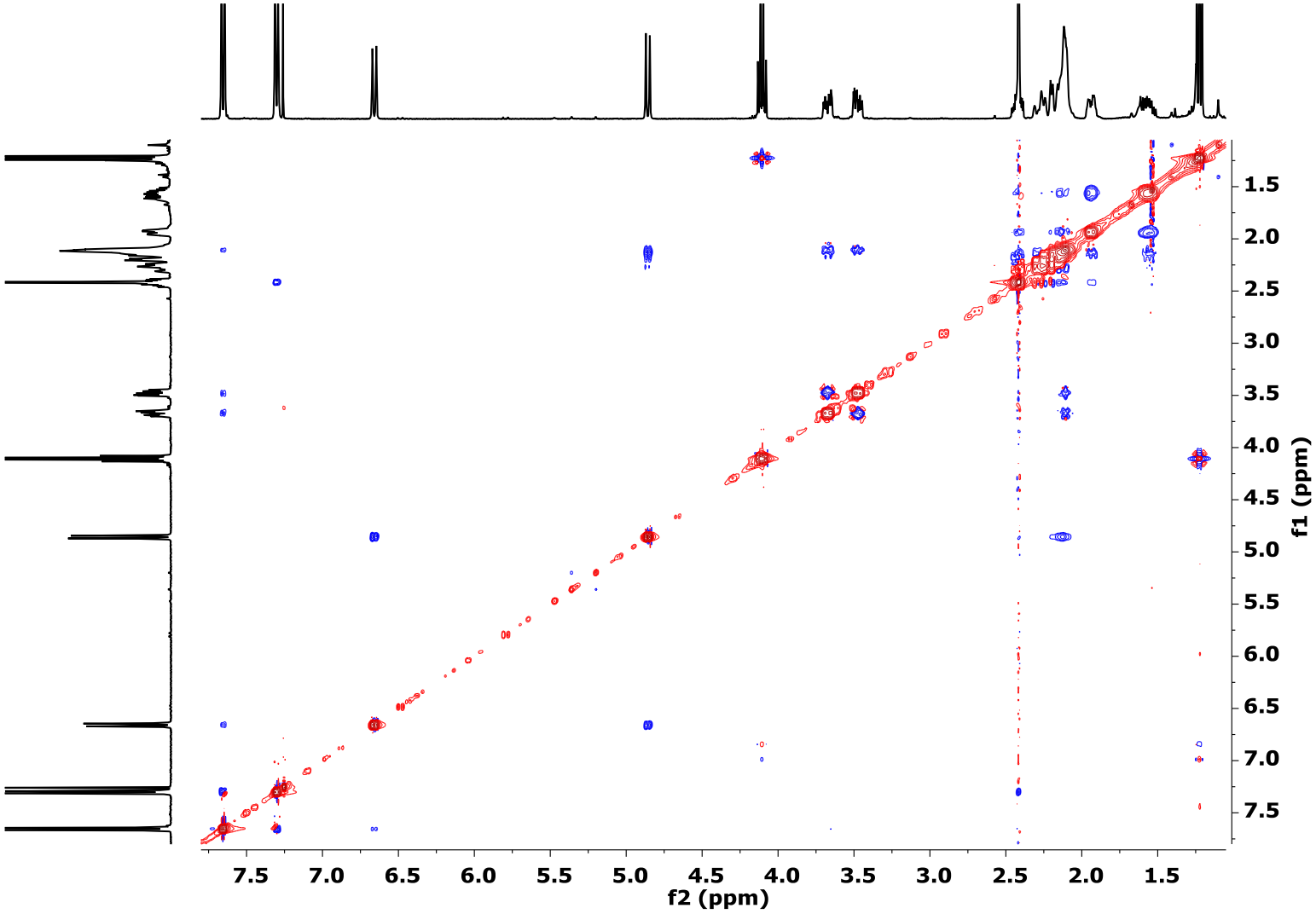
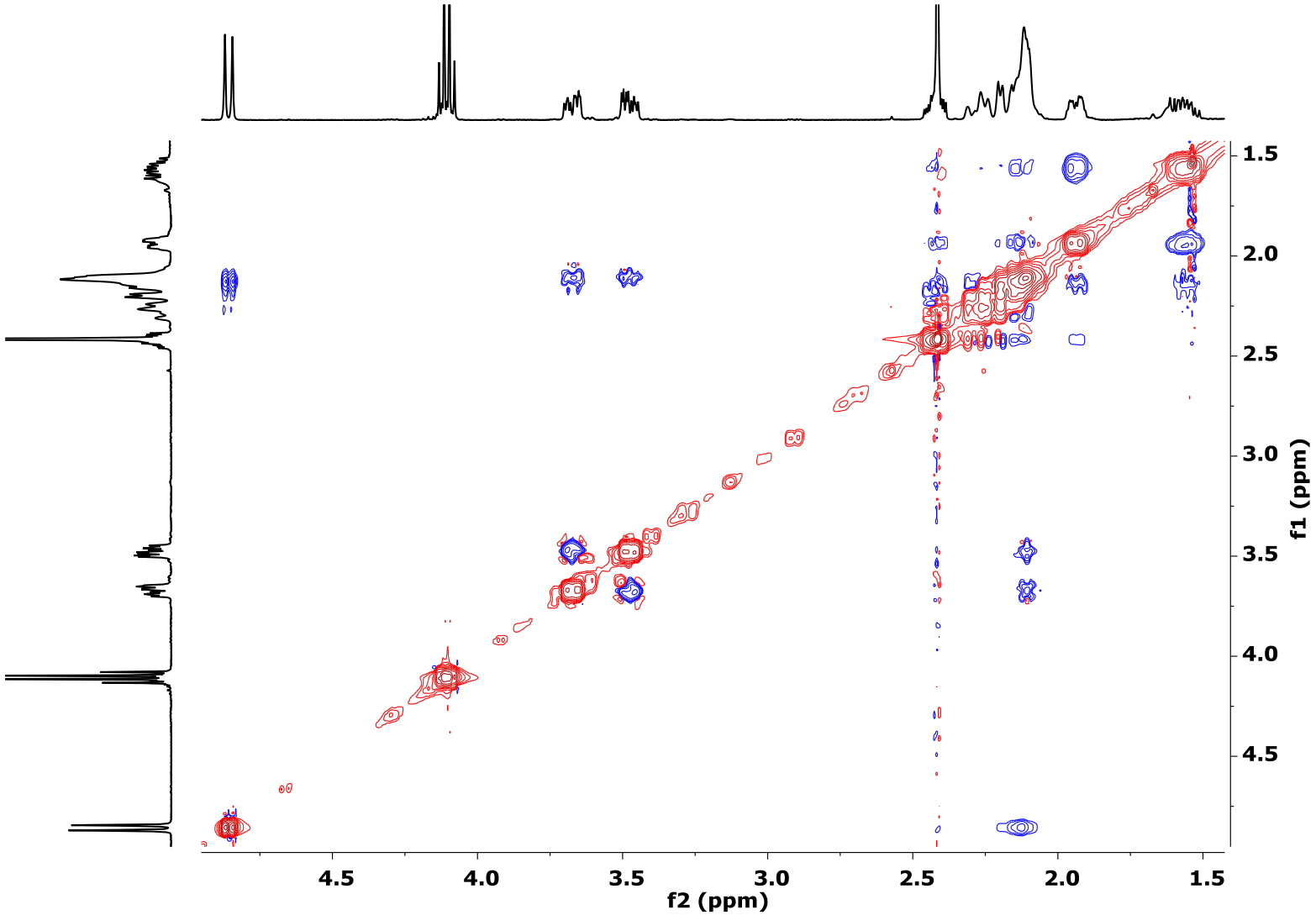
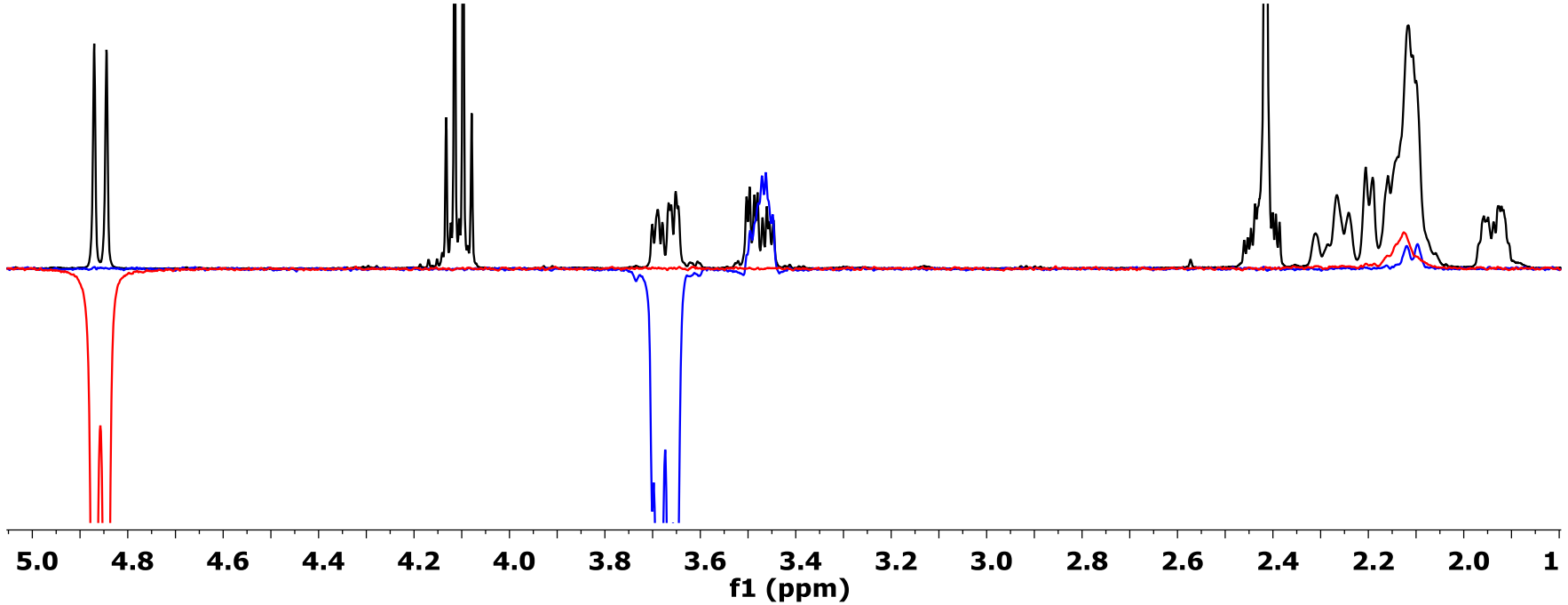
f2 (ppm)

2D NMR NOESY

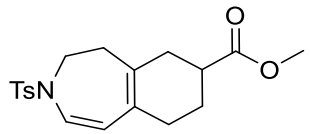

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)


4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
f1 (ppm)

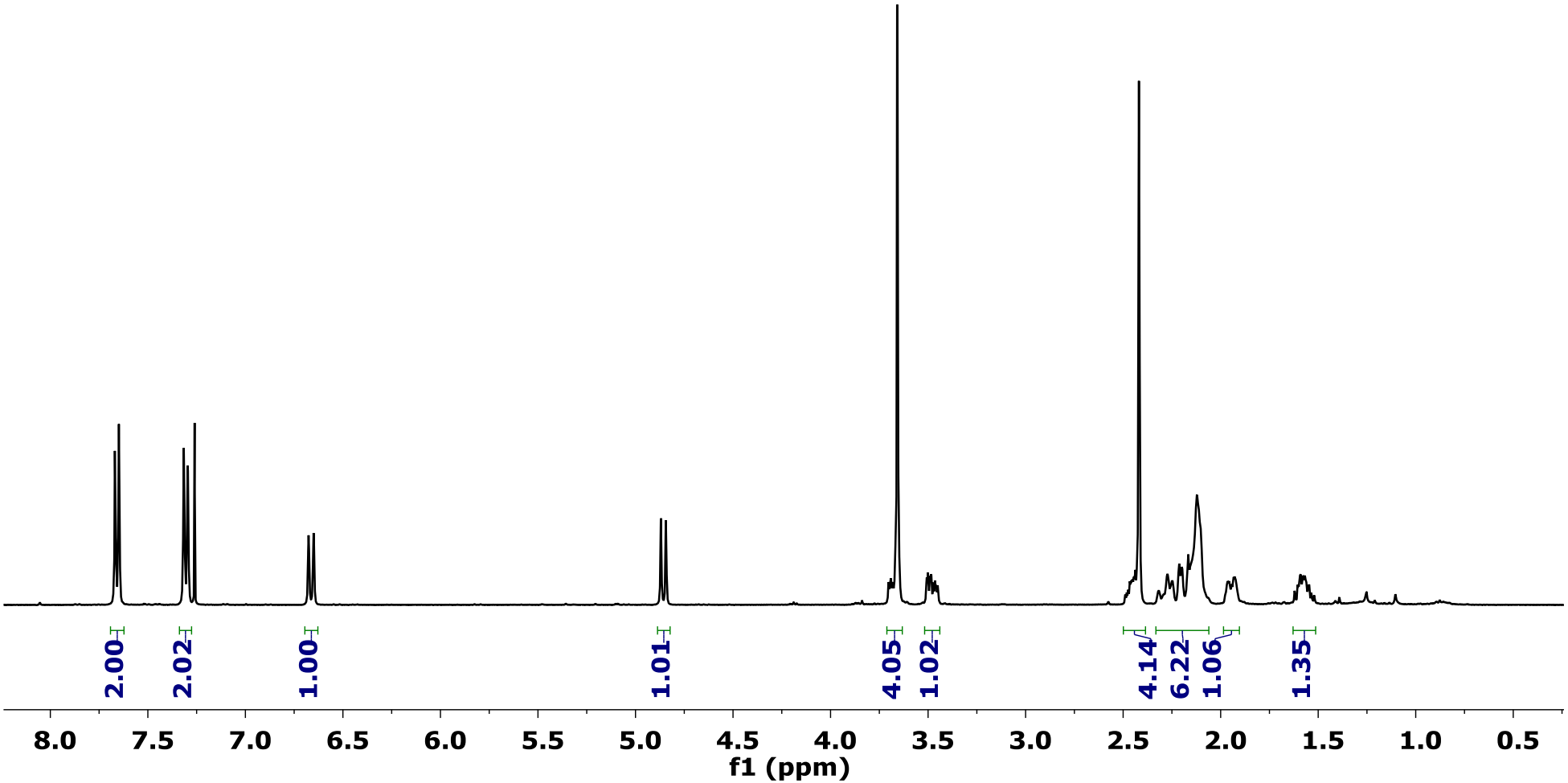
1D NMR SELECTIVE NOESY

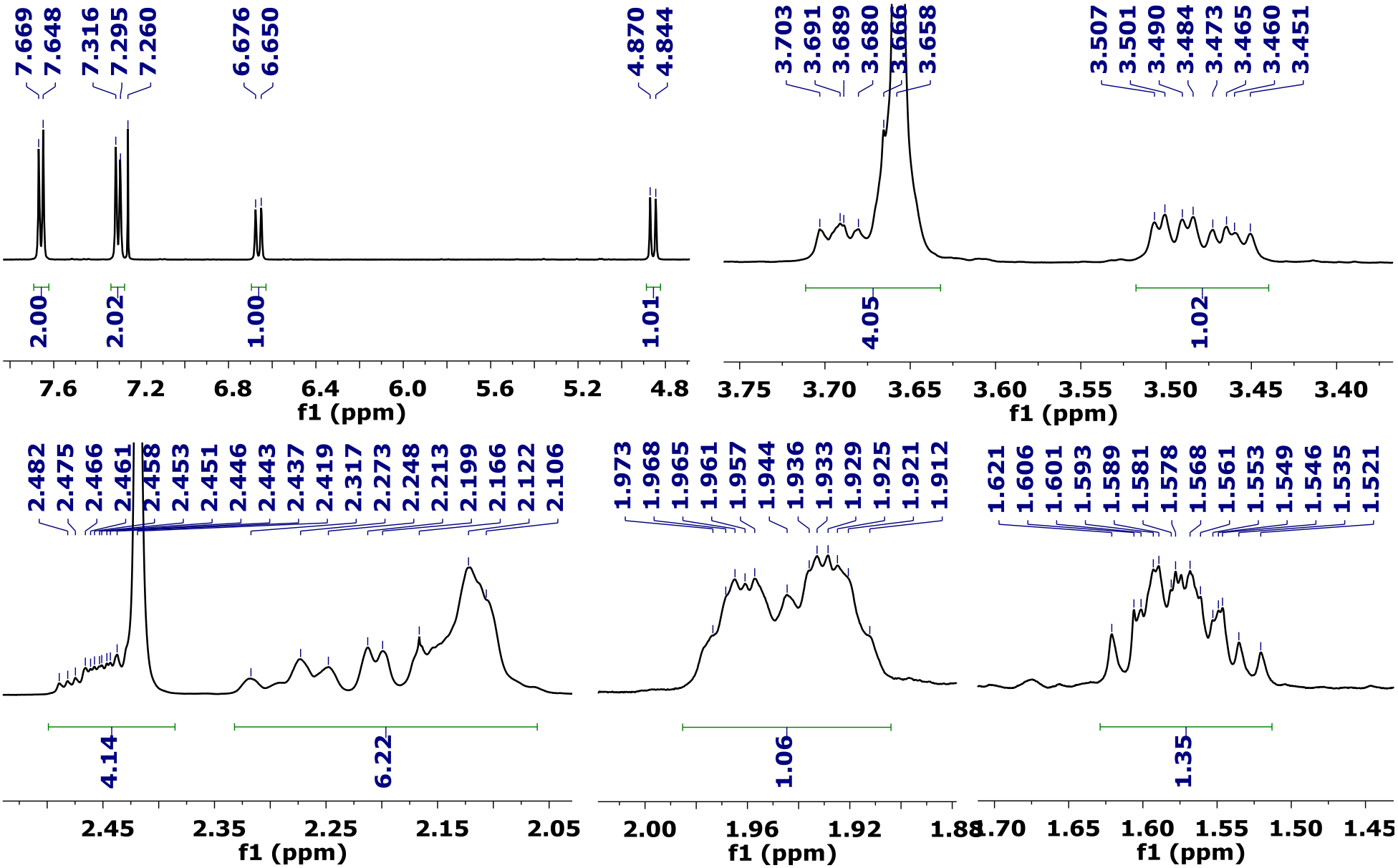


Product 3ab

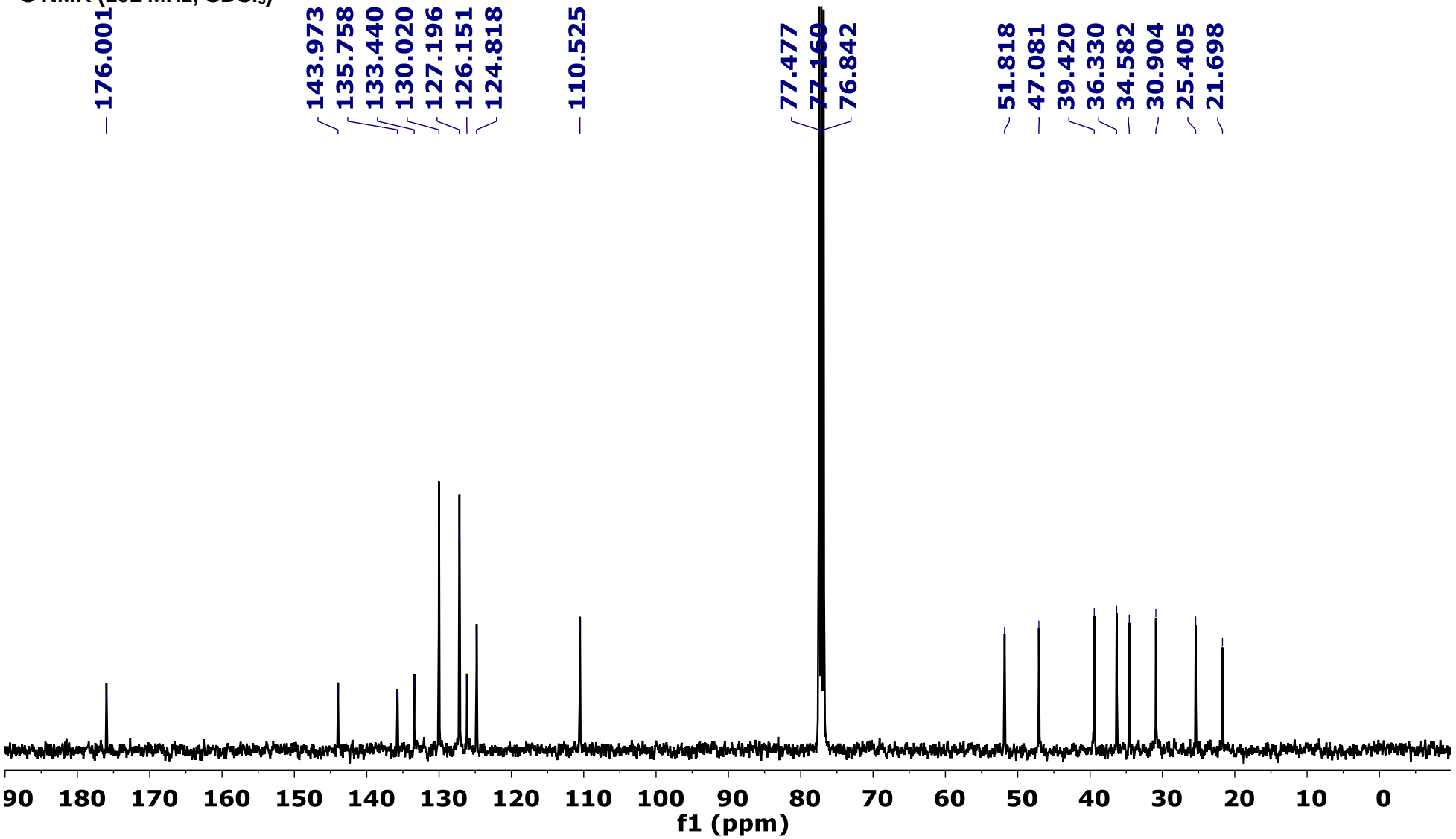


^{1}H NMR (400 MHz, $CDCl_3$)

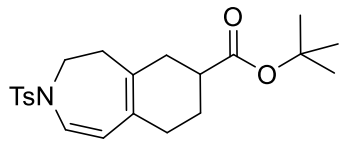



7.669
7.648
7.316
7.295
7.260
6.676
6.650
4.870
4.844
2.00
2.02
1.00
1.01
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
f1 (ppm)
3.703
3.691
3.689
3.680
3.666
3.658
3.507
3.501
3.490
3.484
3.473
3.465
3.460
3.451
4.05
1.02
3.75
3.70
3.65
3.60
3.55
3.50
3.45
3.40
f1 (ppm)
2.482
2.475
2.466
2.461
2.458
2.453
2.451
2.446
2.443
2.437
2.419
2.317
2.273
2.248
2.213
2.199
2.166
2.122
2.106
4.14
6.22
2.45
2.35
2.25
2.15
2.05
f1 (ppm)
1.973
1.968
1.965
1.961
1.957
1.944
1.936
1.933
1.929
1.925
1.921
1.912
1.06
2.00
1.96
1.92
1.88
f1 (ppm)
1.621
1.606
1.601
1.593
1.589
1.581
1.578
1.568
1.561
1.553
1.549
1.546
1.535
1.521
1.35
1.70
1.65
1.60
1.55
1.50
1.45
f1 (ppm)

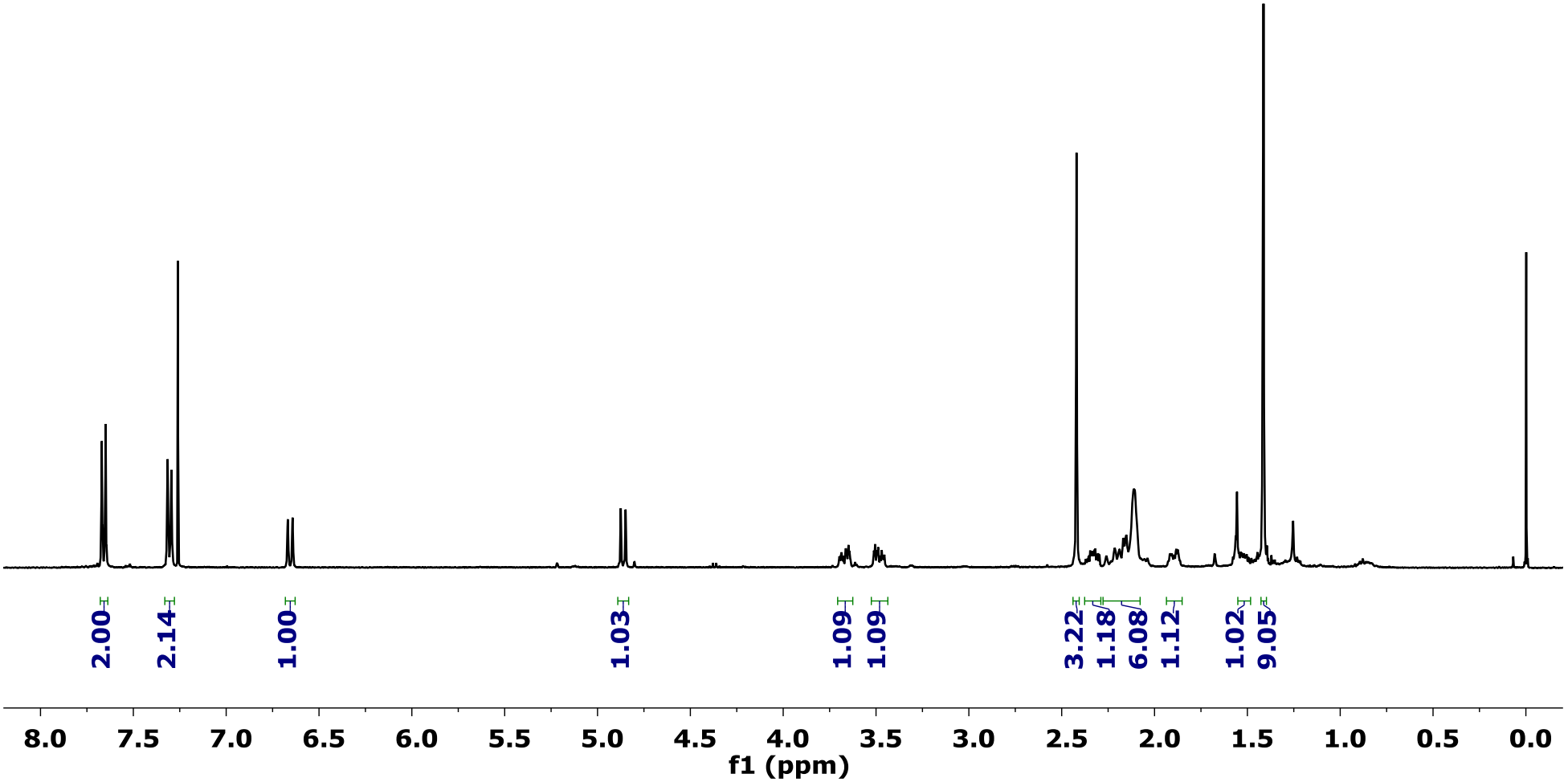
^{13}C NMR (101 MHz, $CDCl_3$)

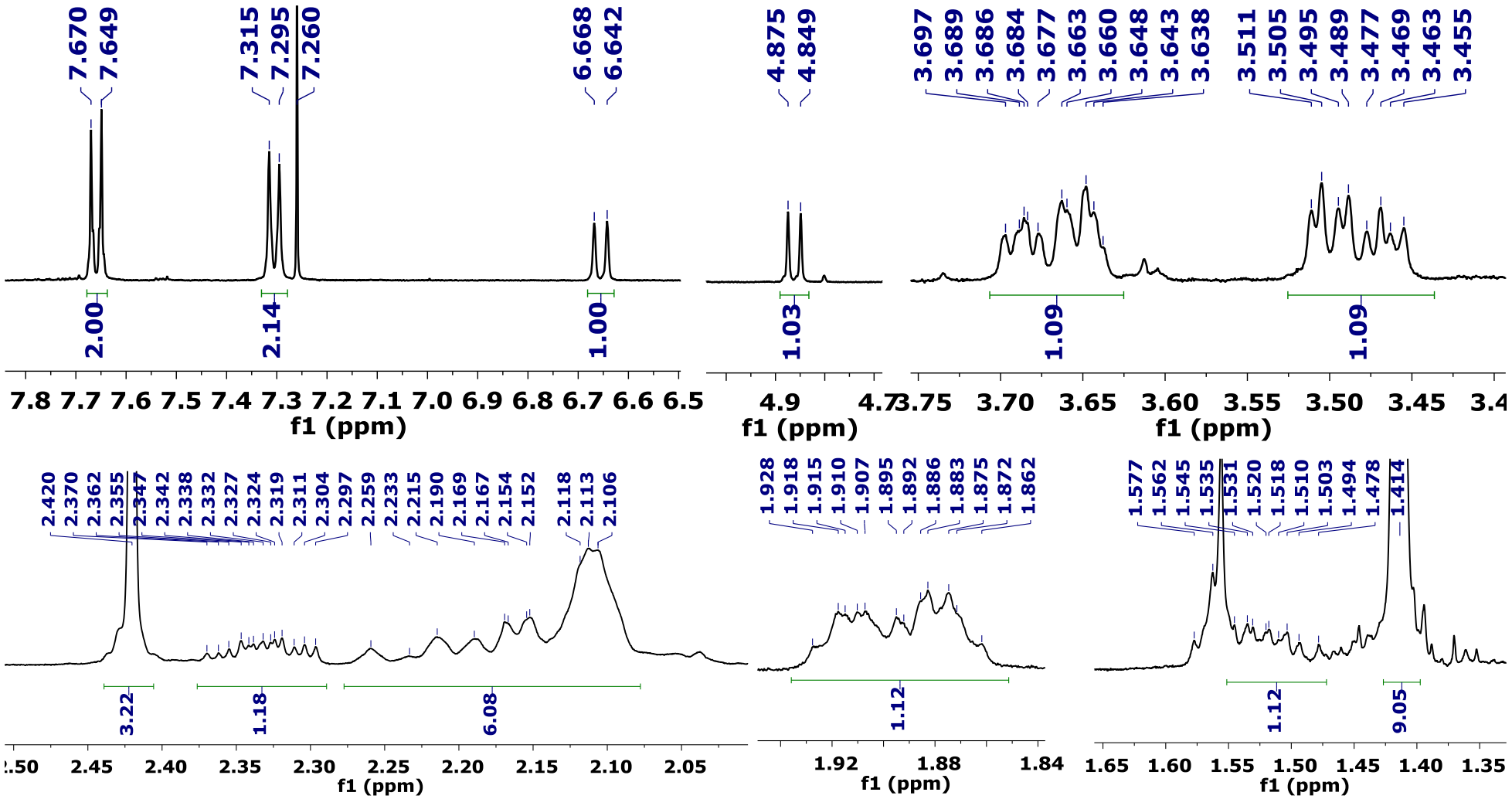


Product 3ac

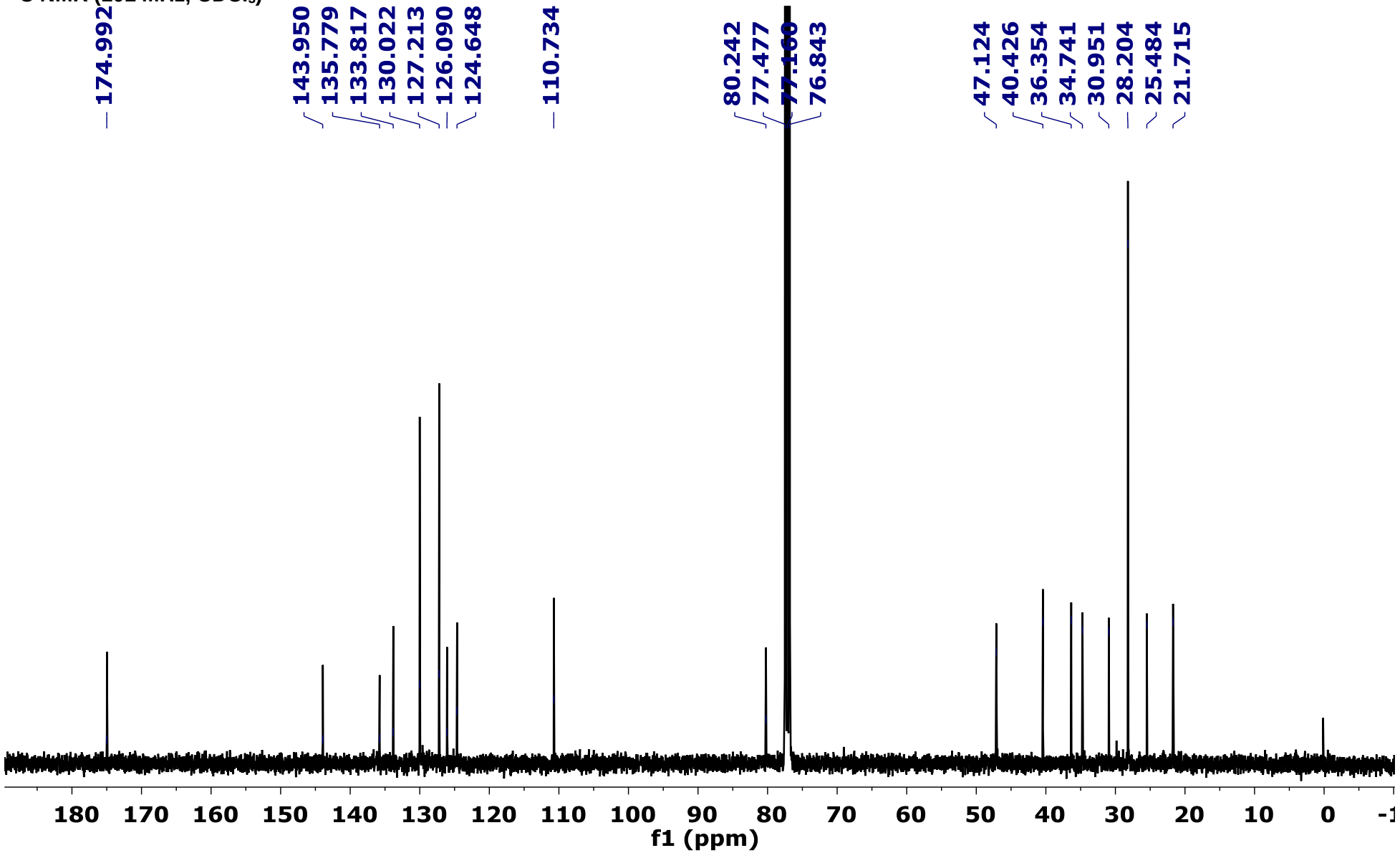


^{1}H NMR (400 MHz, $CDCl_3$)

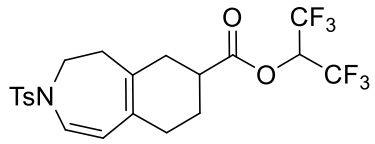



7.670
7.649
7.315
7.295
7.260
6.668
6.642
4.875
4.849
3.697
3.689
3.686
3.684
3.677
3.663
3.660
3.648
3.643
3.638
3.511
3.505
3.495
3.489
3.477
3.469
3.463
3.455
2.00
2.14
1.00
1.03
1.09
1.09
f1 (ppm)
f1 (ppm)
f1 (ppm)
2.420
2.370
2.362
2.355
2.347
2.342
2.338
2.332
2.327
2.324
2.319
2.311
2.304
2.297
2.259
2.233
2.215
2.190
2.169
2.167
2.154
2.152
2.118
2.113
2.106
1.928
1.918
1.915
1.910
1.907
1.895
1.892
1.886
1.883
1.875
1.872
1.862
1.577
1.562
1.545
1.535
1.531
1.520
1.518
1.510
1.503
1.494
1.478
1.414
3.22
1.18
6.08
1.12
1.12
9.05
f1 (ppm)
f1 (ppm)
f1 (ppm)

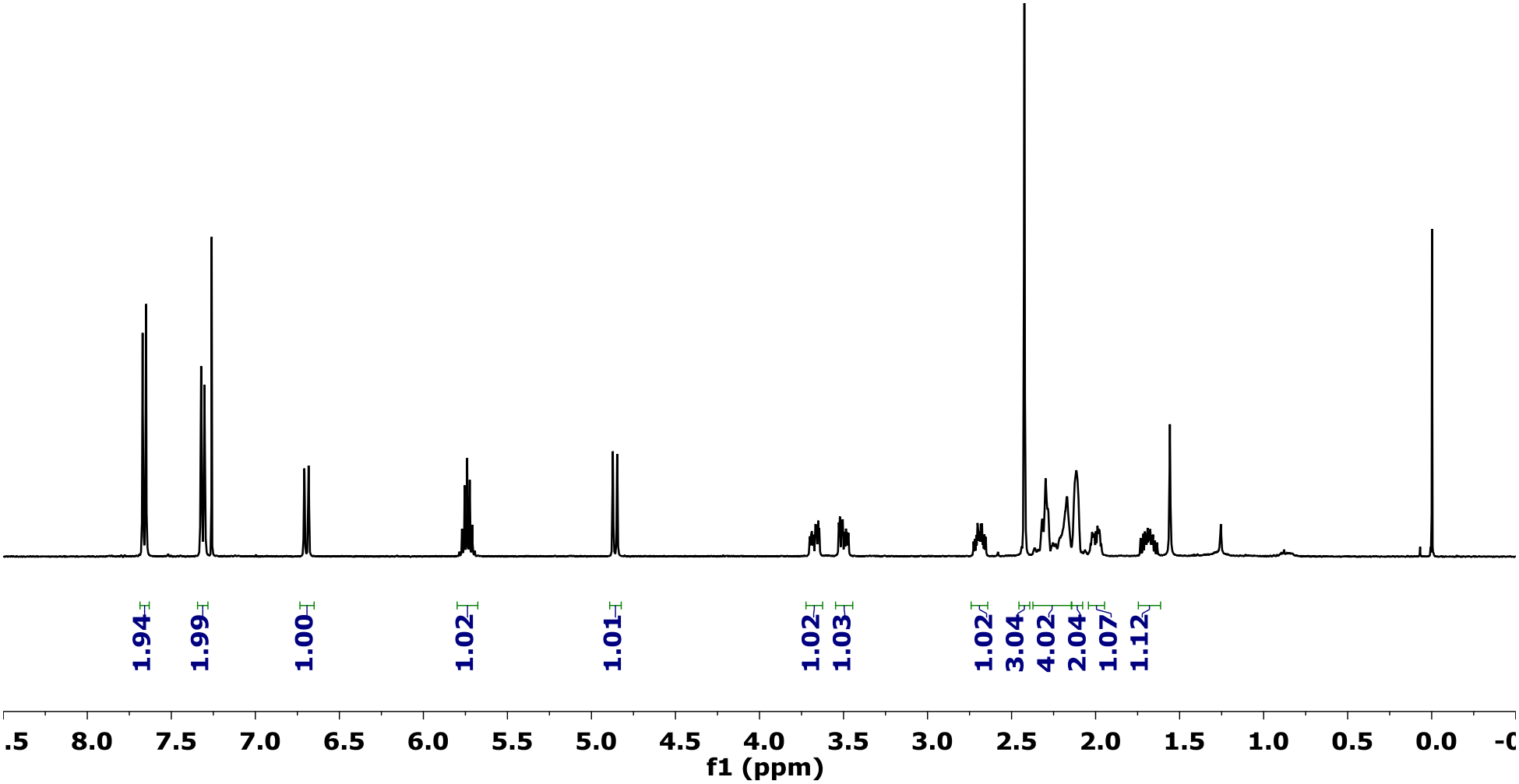
^{13}C NMR (101 MHz, $CDCl_3$)

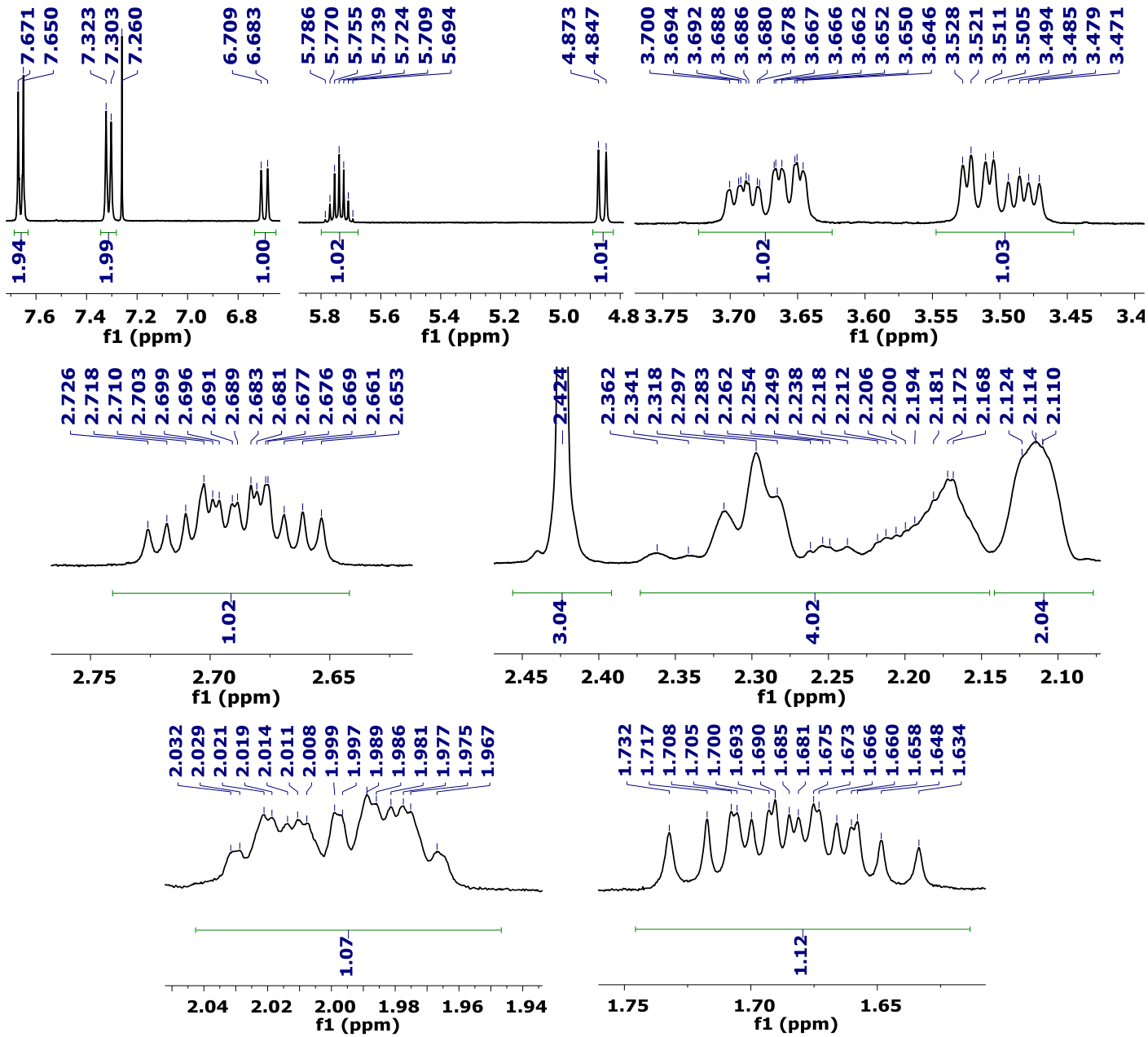


Product 3ad

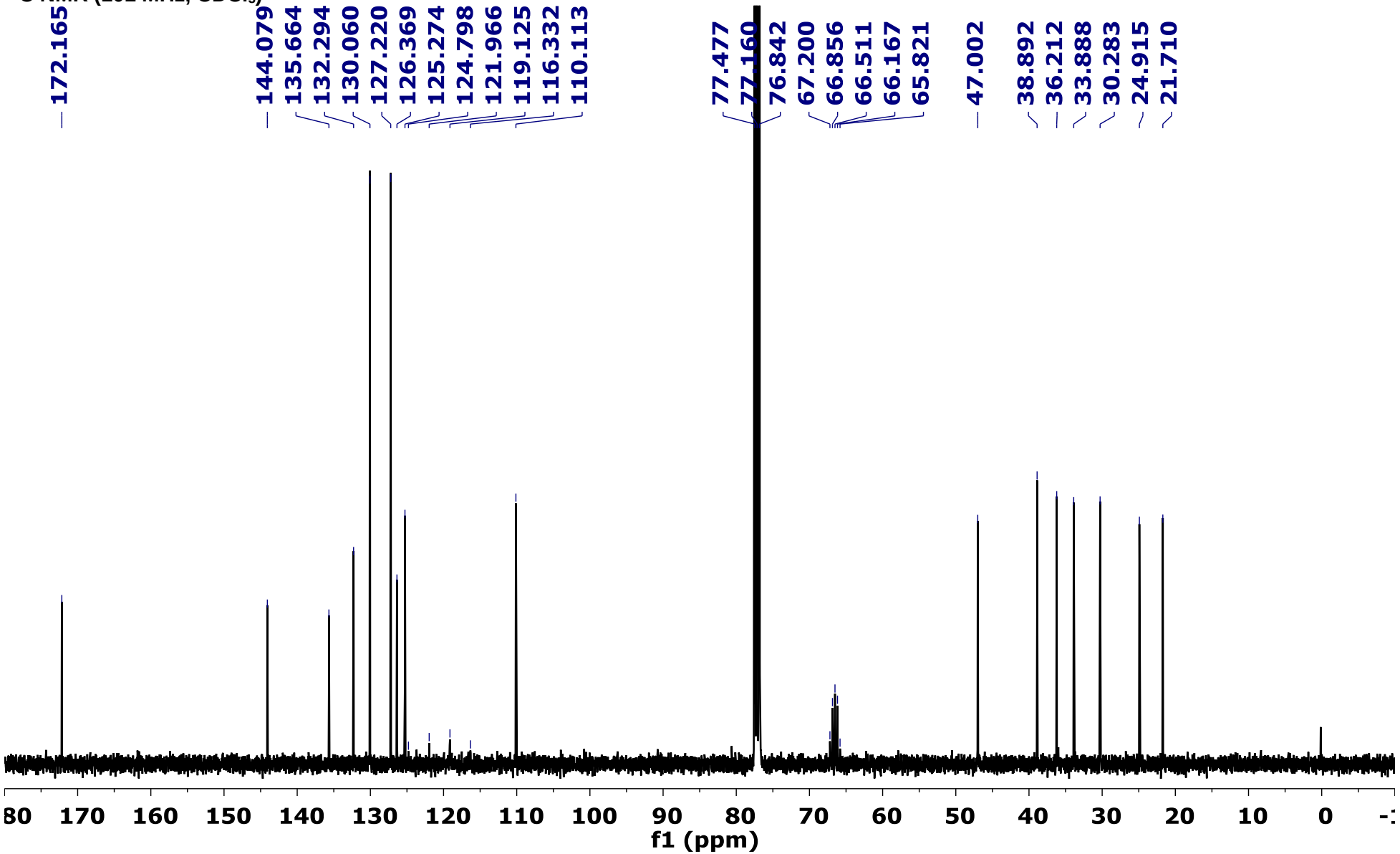


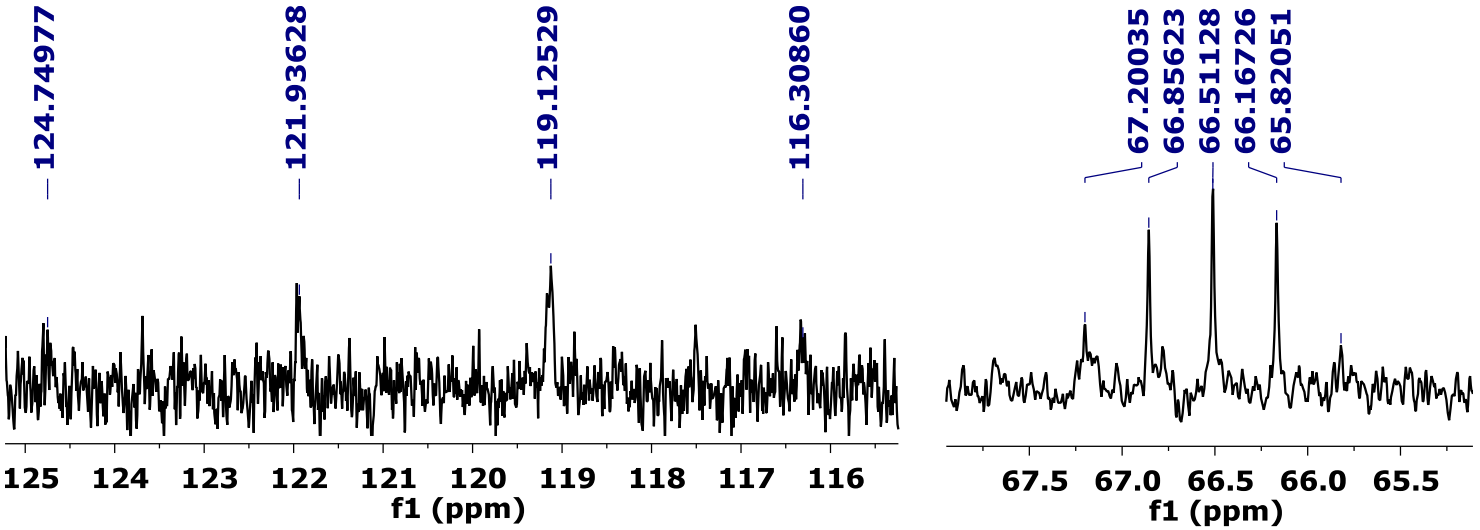
^{1}H NMR (400 MHz, $CDCl_3$)



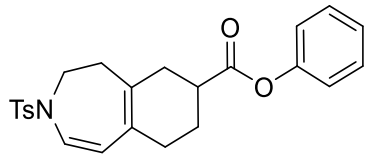

7.671
7.650
7.323
7.303
7.260
6.709
6.683
1.94
1.99
1.00
7.6 7.4 7.2 7.0 6.8
f1 (ppm)
5.786
5.770
5.755
5.739
5.724
5.709
5.694
4.873
4.847
1.02
1.01
5.8 5.6 5.4 5.2 5.0 4.8
f1 (ppm)
3.700
3.694
3.692
3.688
3.686
3.680
3.678
3.667
3.666
3.662
3.652
3.650
3.646
3.528
3.521
3.511
3.505
3.494
3.485
3.479
3.471
1.02
1.03
3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.4
f1 (ppm)
2.726
2.718
2.710
2.703
2.699
2.696
2.691
2.689
2.683
2.681
2.677
2.676
2.669
2.661
2.653
1.02
2.75 2.70 2.65
f1 (ppm)
2.424
2.362
2.341
2.318
2.297
2.283
2.262
2.254
2.249
2.238
2.218
2.212
2.206
2.200
2.194
2.181
2.172
2.168
2.124
2.114
2.110
3.04
4.02
2.04
2.45 2.40 2.35 2.30 2.25 2.20 2.15 2.10
f1 (ppm)
2.032
2.029
2.021
2.019
2.014
2.011
2.008
1.999
1.997
1.989
1.986
1.981
1.977
1.975
1.967
1.07
2.04 2.02 2.00 1.98 1.96 1.94
f1 (ppm)
1.732
1.717
1.708
1.705
1.700
1.693
1.690
1.685
1.681
1.675
1.673
1.666
1.660
1.658
1.648
1.634
1.12
1.75 1.70 1.65
f1 (ppm)

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

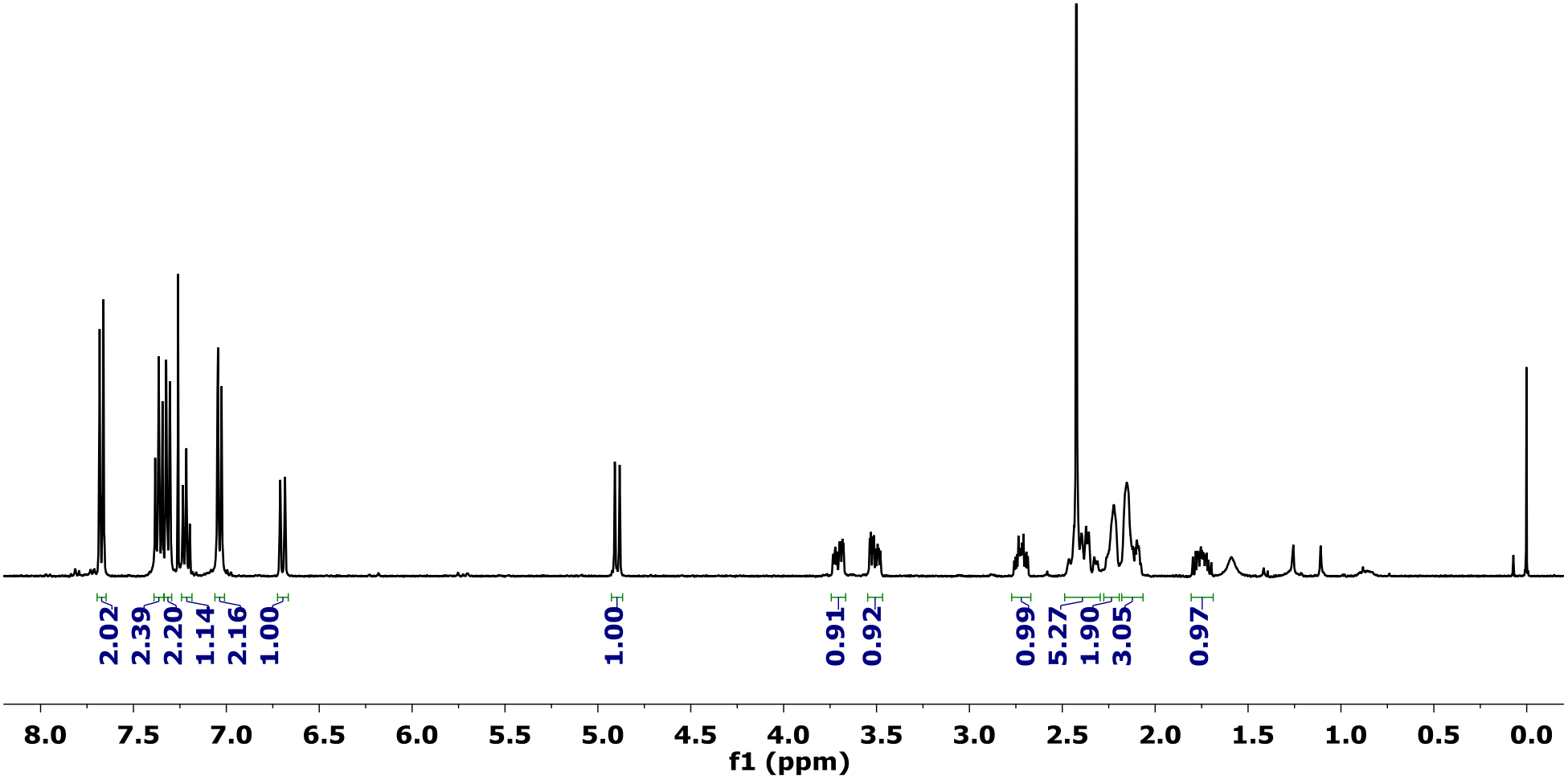


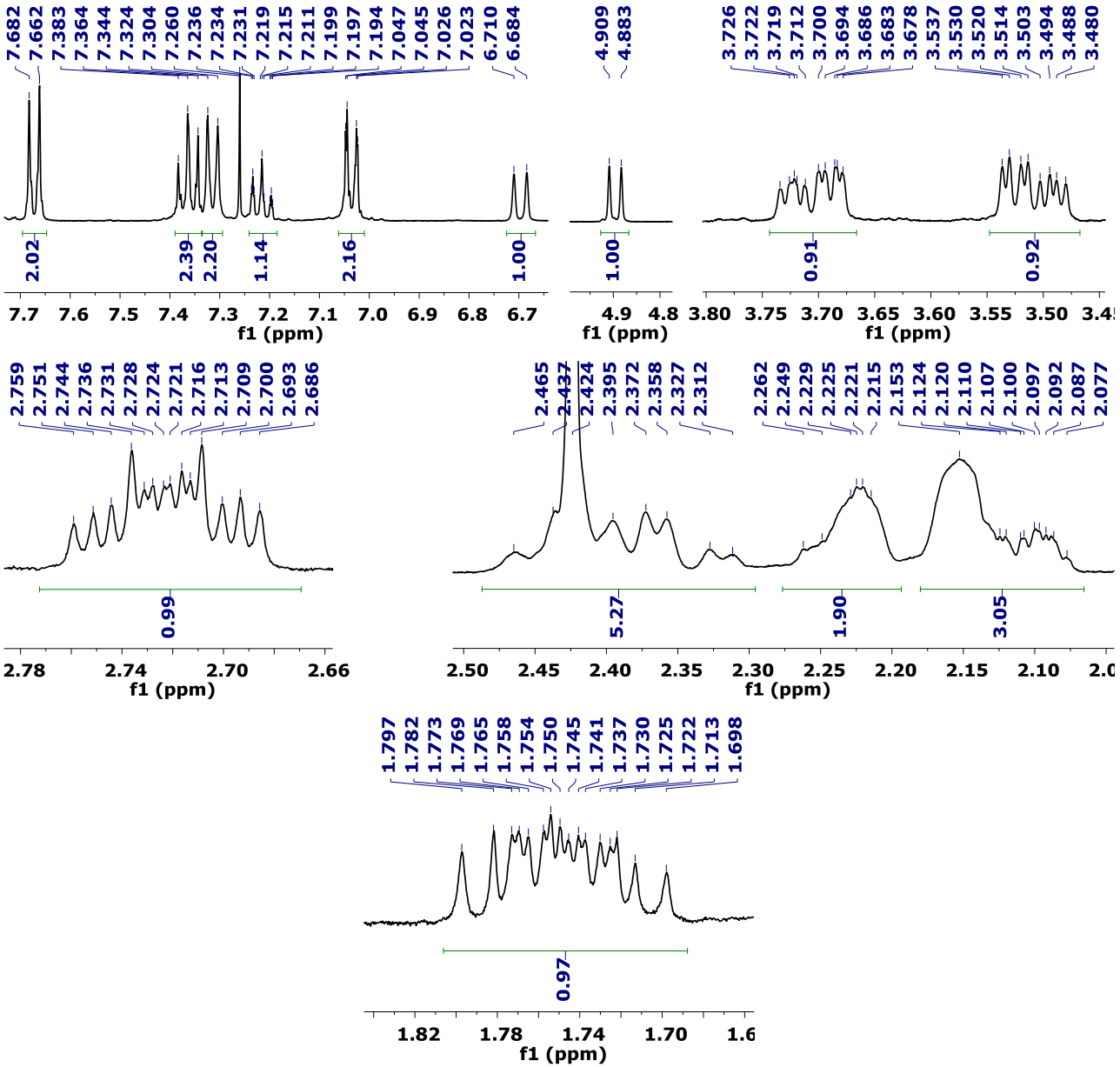

124.74977
121.93628
119.12529
116.30860
125
124
123
122
121
120
119
118
117
116
f1 (ppm)
67.20035
66.85623
66.51128
66.16726
65.82051
67.5
67.0
66.5
66.0
65.5
f1 (ppm)

Product 3ae

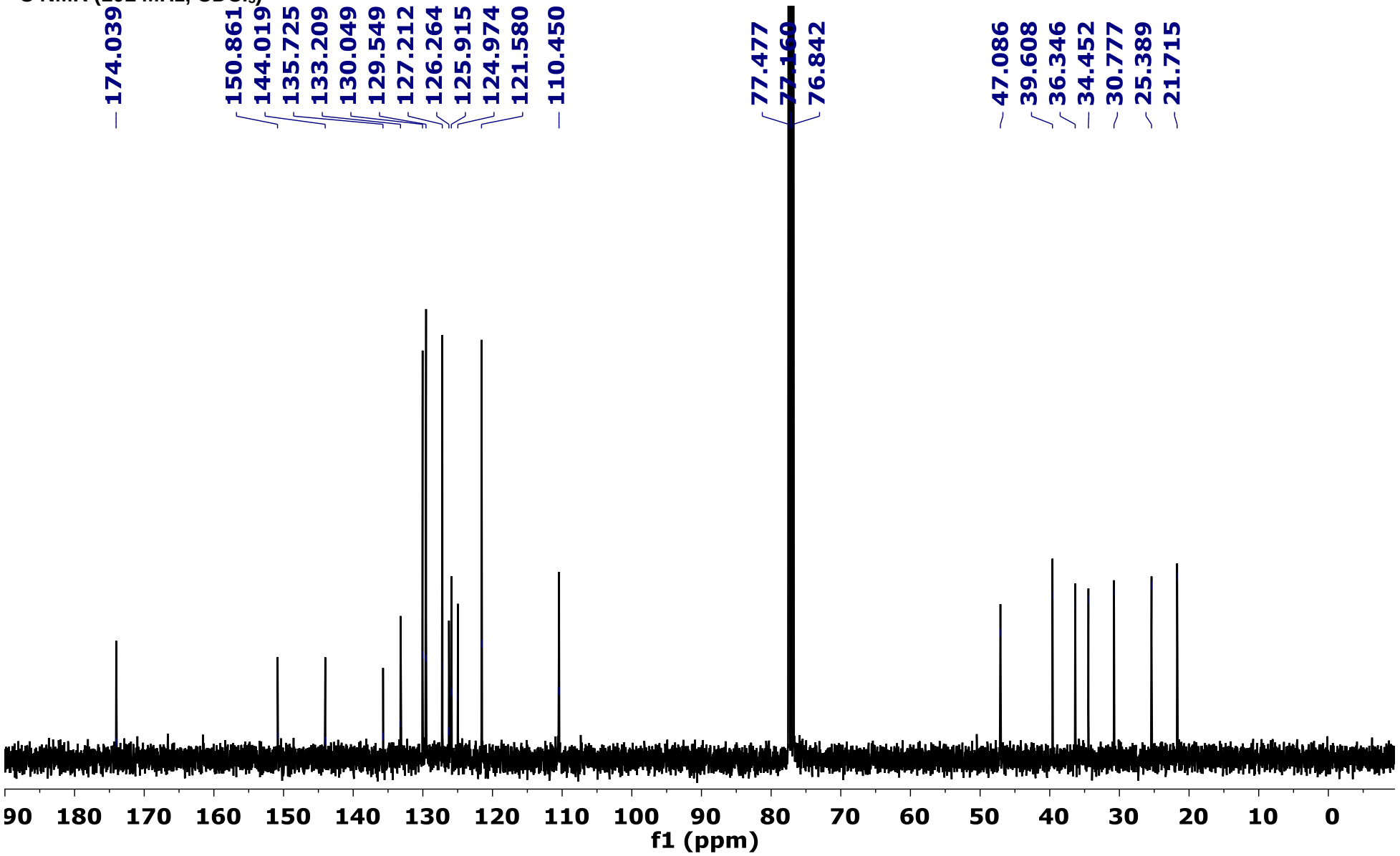


^{1}H NMR (400 MHz, $CDCl_3$)

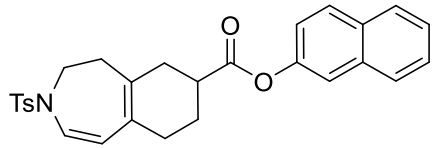



7.682
7.662
7.383
7.364
7.344
7.324
7.304
7.260
7.236
7.234
7.231
7.219
7.215
7.211
7.199
7.197
7.194
7.047
7.045
7.026
7.023
6.710
6.684
4.909
4.883
3.726
3.722
3.719
3.712
3.700
3.694
3.686
3.683
3.678
3.537
3.530
3.520
3.514
3.503
3.494
3.488
3.480
2.02
2.39
2.20
1.14
2.16
1.00
1.00
0.91
0.92
f1 (ppm)
2.759
2.751
2.744
2.736
2.731
2.728
2.724
2.721
2.716
2.713
2.709
2.700
2.693
2.686
2.465
2.437
2.424
2.395
2.372
2.358
2.327
2.312
2.262
2.249
2.229
2.225
2.221
2.215
2.153
2.124
2.120
2.110
2.107
2.100
2.097
2.092
2.087
2.077
0.99
5.27
1.90
3.05
f1 (ppm)
1.797
1.782
1.773
1.769
1.765
1.758
1.754
1.750
1.745
1.741
1.737
1.730
1.725
1.722
1.713
1.698
0.97
f1 (ppm)

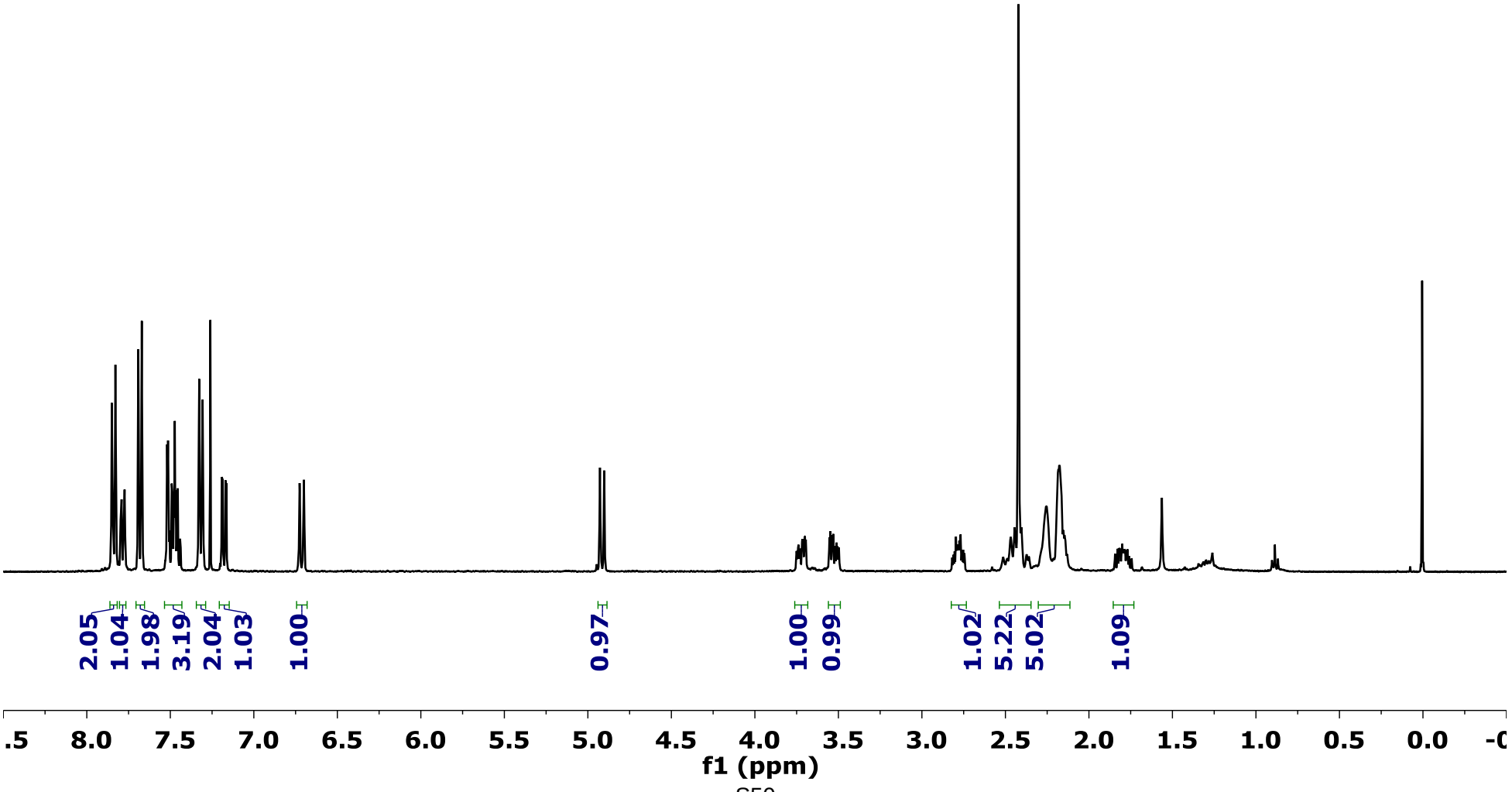
^{13}C NMR (101 MHz, $CDCl_3$)

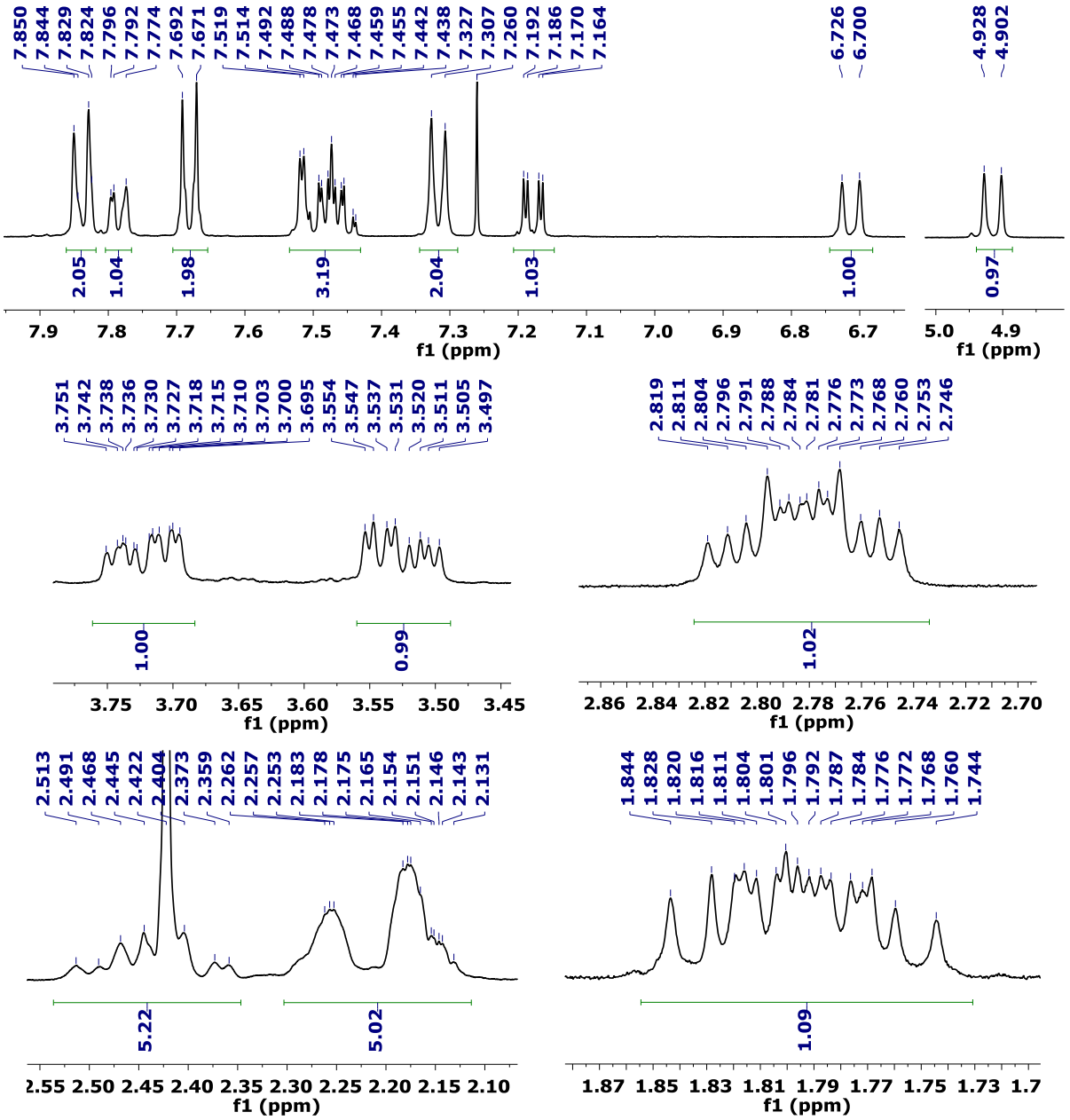


Product 3af

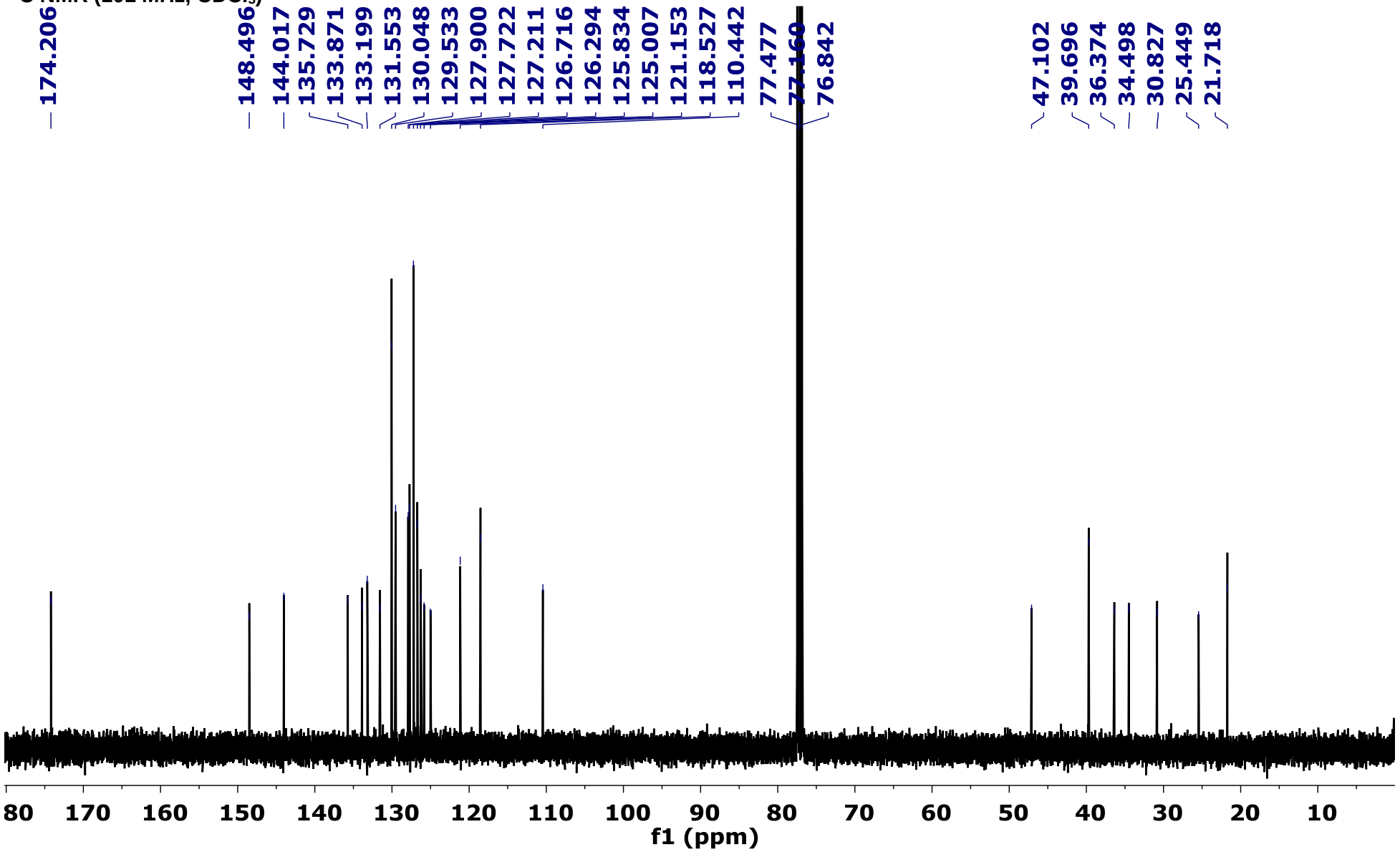


^{1}H NMR (400 MHz, $CDCl_3$)

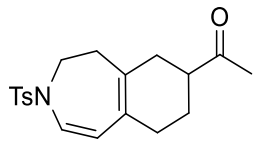



7.850
7.844
7.829
7.824
7.796
7.792
7.774
7.692
7.671
7.519
7.514
7.492
7.488
7.478
7.473
7.468
7.459
7.455
7.442
7.438
7.327
7.307
7.260
7.192
7.186
7.170
7.164
6.726
6.700
4.928
4.902
2.05
1.04
1.98
3.19
2.04
1.03
1.00
0.97
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
5.0 4.9
f1 (ppm)
3.751
3.742
3.738
3.736
3.730
3.727
3.718
3.715
3.710
3.703
3.700
3.695
3.554
3.547
3.537
3.531
3.520
3.511
3.505
3.497
1.00
0.99
3.75 3.70 3.65 3.60 3.55 3.50 3.45
f1 (ppm)
2.819
2.811
2.804
2.796
2.791
2.788
2.784
2.781
2.776
2.773
2.768
2.760
2.753
2.746
1.02
2.86 2.84 2.82 2.80 2.78 2.76 2.74 2.72 2.70
f1 (ppm)
2.513
2.491
2.468
2.445
2.422
2.404
2.373
2.359
2.262
2.257
2.253
2.183
2.178
2.175
2.165
2.154
2.151
2.146
2.143
2.131
5.22
5.02
2.55 2.50 2.45 2.40 2.35 2.30 2.25 2.20 2.15 2.10
f1 (ppm)
1.844
1.828
1.820
1.816
1.811
1.804
1.801
1.796
1.792
1.787
1.784
1.776
1.772
1.768
1.760
1.744
1.09
1.87 1.85 1.83 1.81 1.79 1.77 1.75 1.73 1.7
f1 (ppm)

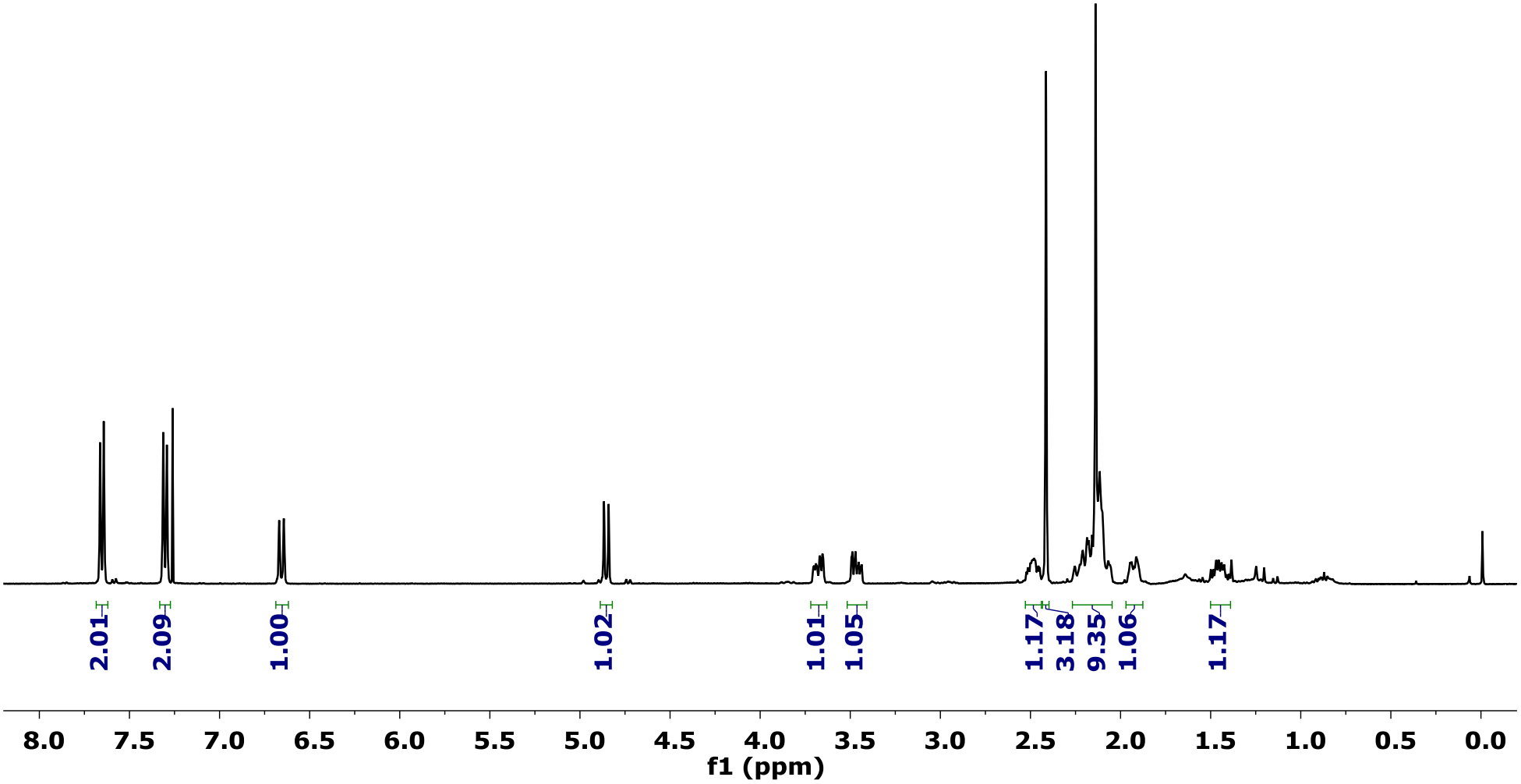
^{13}C NMR (101 MHz, $CDCl_3$)

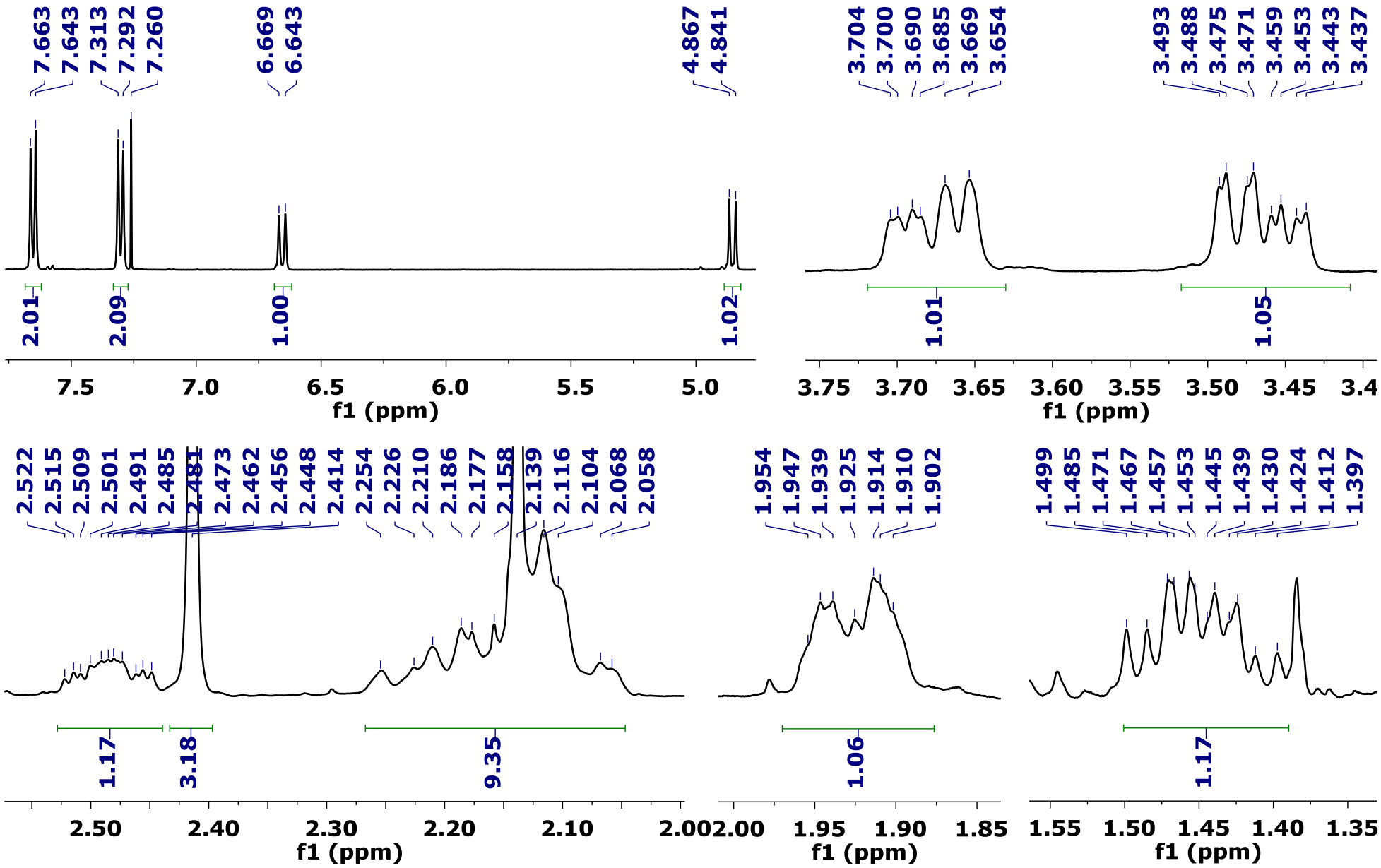


Product 3ag

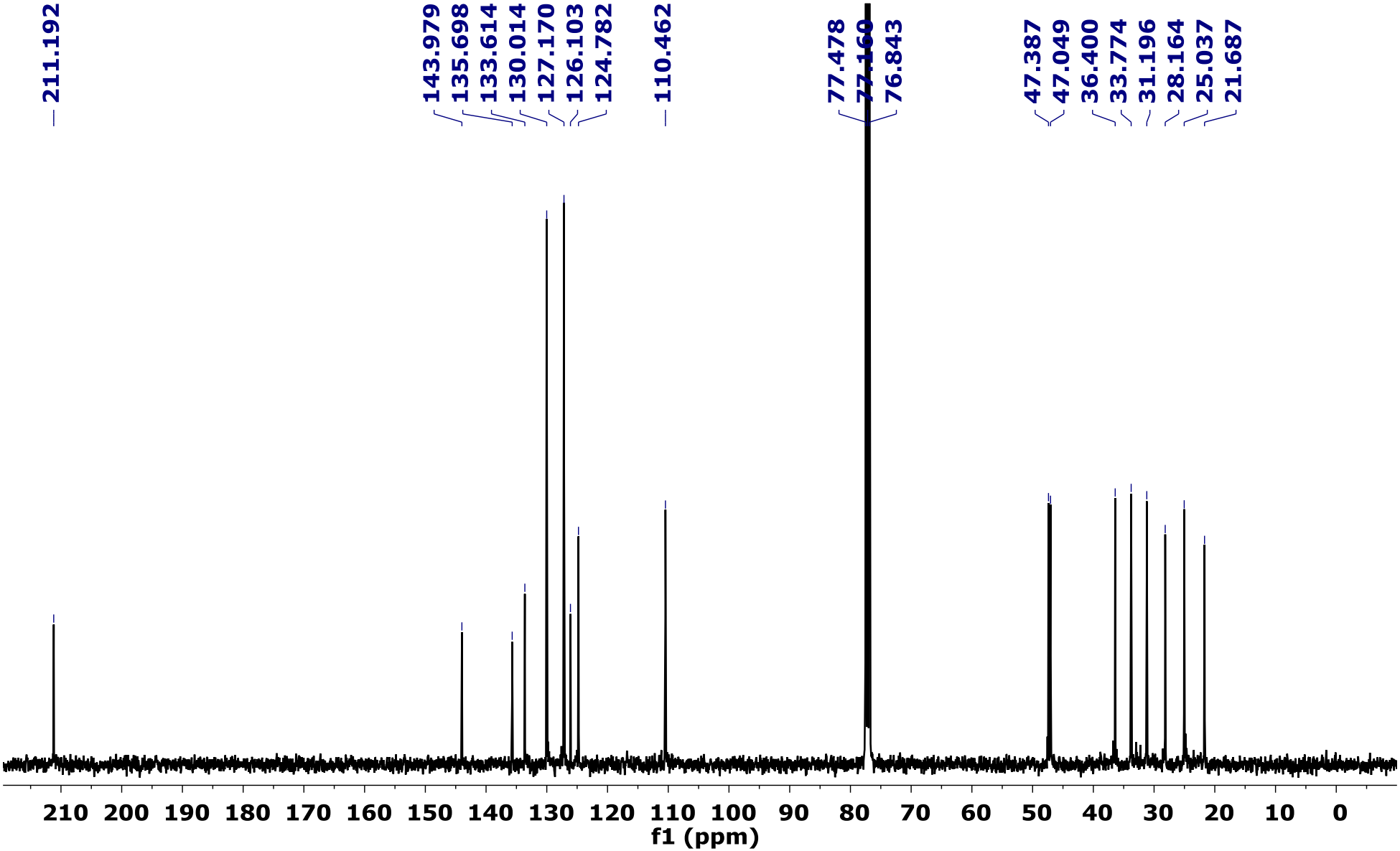


^{1}H NMR (400 MHz, $CDCl_3$)

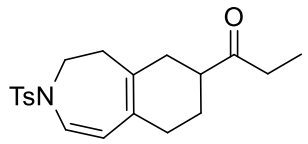



7.663
7.643
7.313
7.292
7.260
6.669
6.643
4.867
4.841
2.01
2.09
1.00
1.02
7.5
7.0
6.5
6.0
5.5
5.0
f1 (ppm)
3.704
3.700
3.690
3.685
3.669
3.654
3.493
3.488
3.475
3.471
3.459
3.453
3.443
3.437
1.01
1.05
3.75
3.70
3.65
3.60
3.55
3.50
3.45
3.4
f1 (ppm)
2.522
2.515
2.509
2.501
2.491
2.485
2.481
2.473
2.462
2.456
2.448
2.414
2.254
2.226
2.210
2.186
2.177
2.158
2.139
2.116
2.104
2.068
2.058
1.17
3.18
9.35
2.50
2.40
2.30
2.20
2.10
2.00
f1 (ppm)
1.954
1.947
1.939
1.925
1.914
1.910
1.902
1.06
2.00
1.95
1.90
1.85
f1 (ppm)
1.499
1.485
1.471
1.467
1.457
1.453
1.445
1.439
1.430
1.424
1.412
1.397
1.17
1.55
1.50
1.45
1.40
1.35
f1 (ppm)

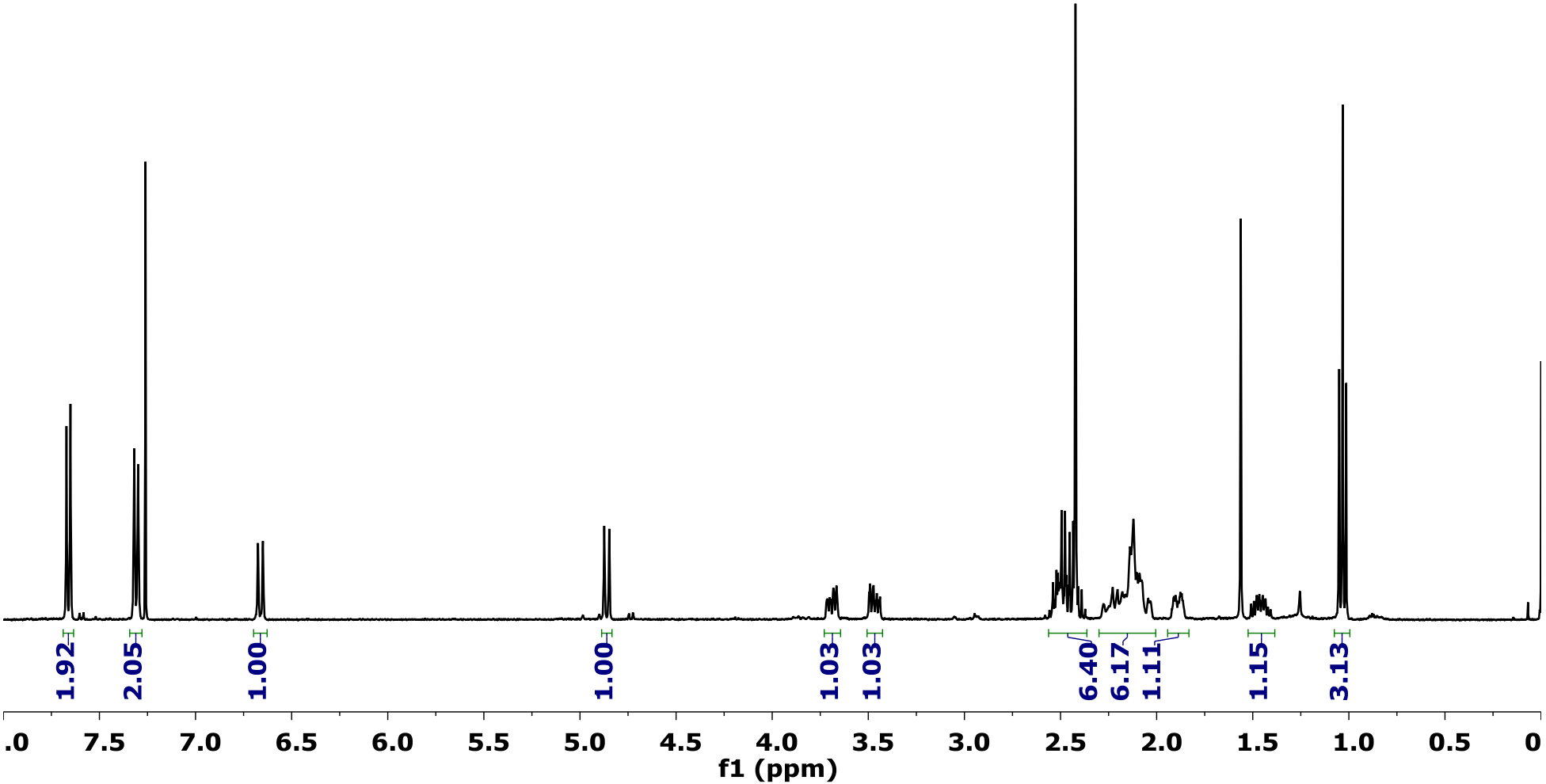
^{13}C NMR (101 MHz, $CDCl_3$)

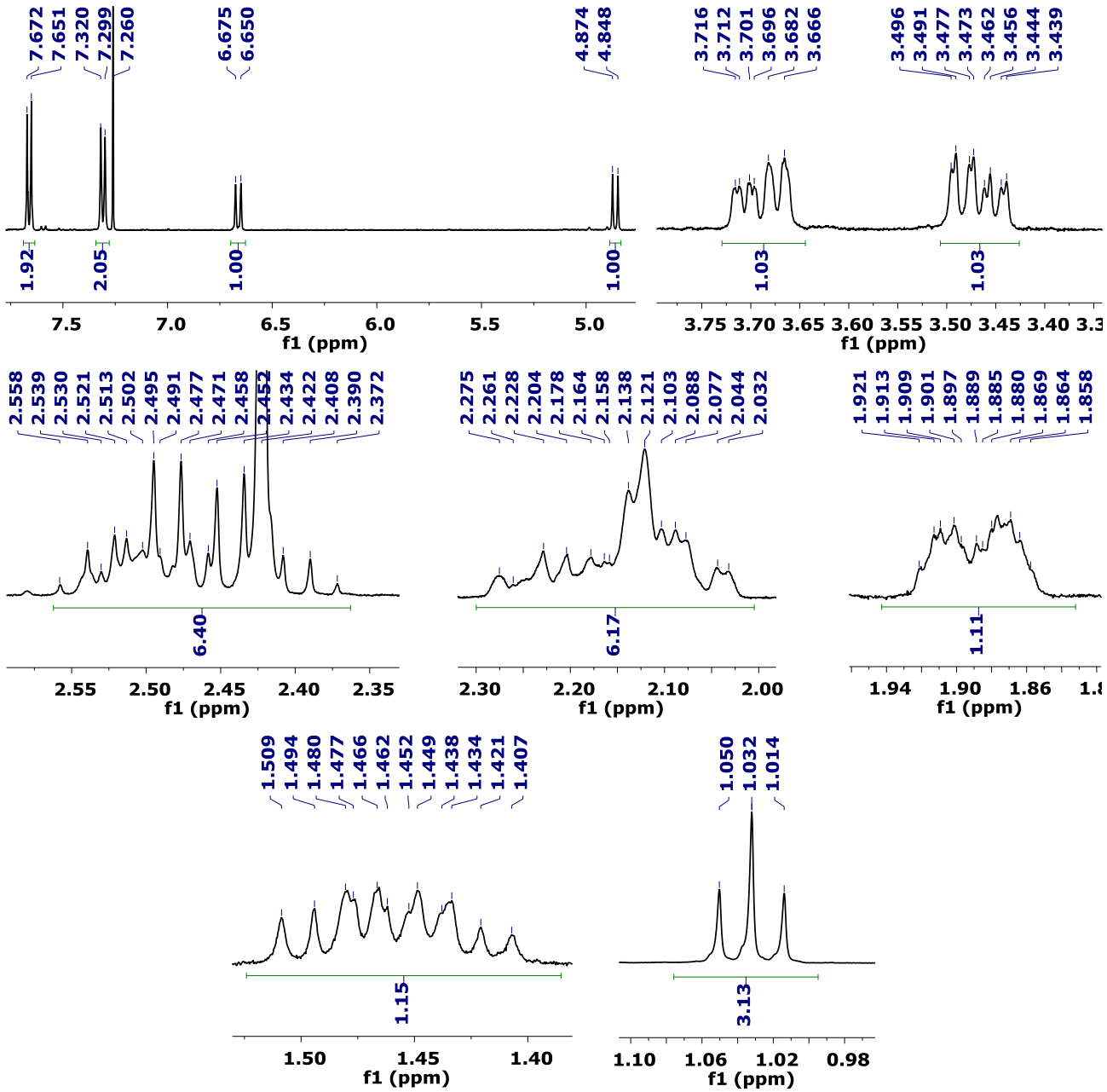


Product 3ah

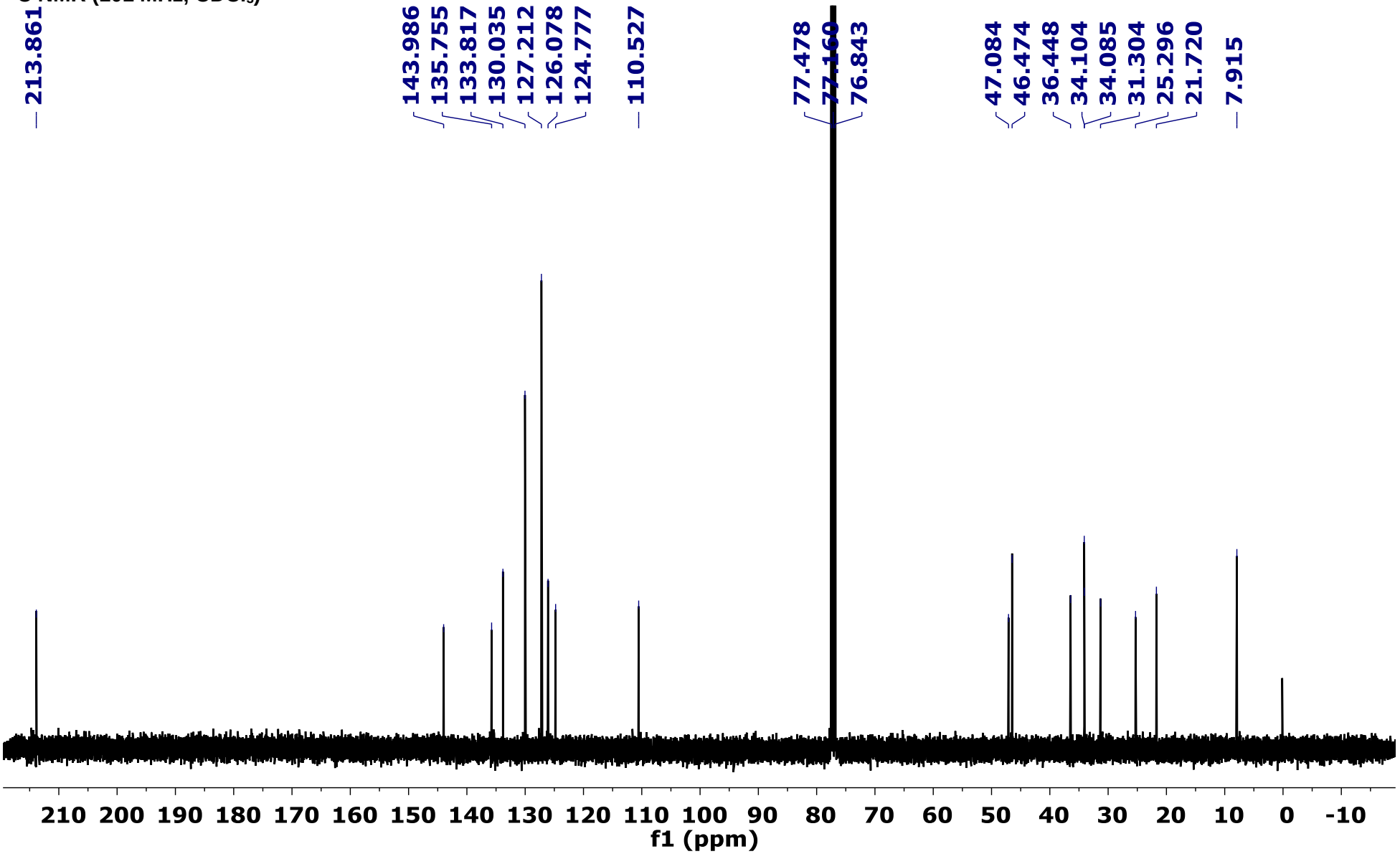


^{1}H NMR (400 MHz, $CDCl_3$)

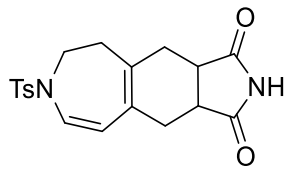



7.672
7.651
7.320
7.299
7.260
6.675
6.650
4.874
4.848
3.716
3.712
3.701
3.696
3.682
3.666
3.496
3.491
3.477
3.473
3.462
3.456
3.444
3.439
1.92
2.05
1.00
1.00
1.03
1.03
f1 (ppm)
2.558
2.539
2.530
2.521
2.513
2.502
2.495
2.491
2.477
2.471
2.458
2.452
2.434
2.422
2.408
2.390
2.372
2.275
2.261
2.228
2.204
2.178
2.164
2.158
2.138
2.121
2.103
2.088
2.077
2.044
2.032
1.921
1.913
1.909
1.901
1.897
1.889
1.885
1.880
1.869
1.864
1.858
6.40
6.17
1.11
f1 (ppm)
1.509
1.494
1.480
1.477
1.466
1.462
1.452
1.449
1.438
1.434
1.421
1.407
1.050
1.032
1.014
1.15
3.13
f1 (ppm)

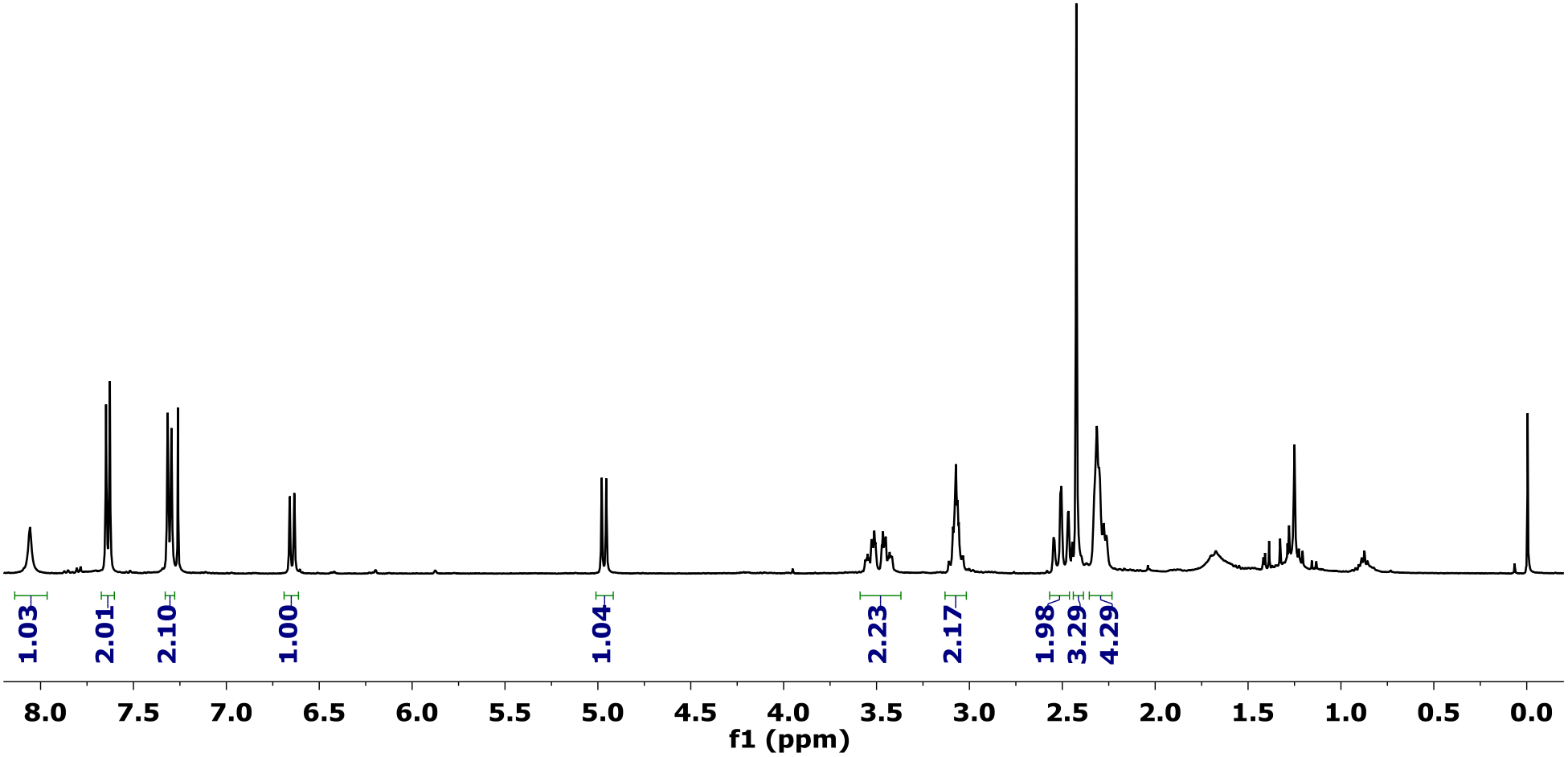
^{13}C NMR (101 MHz, $CDCl_3$)

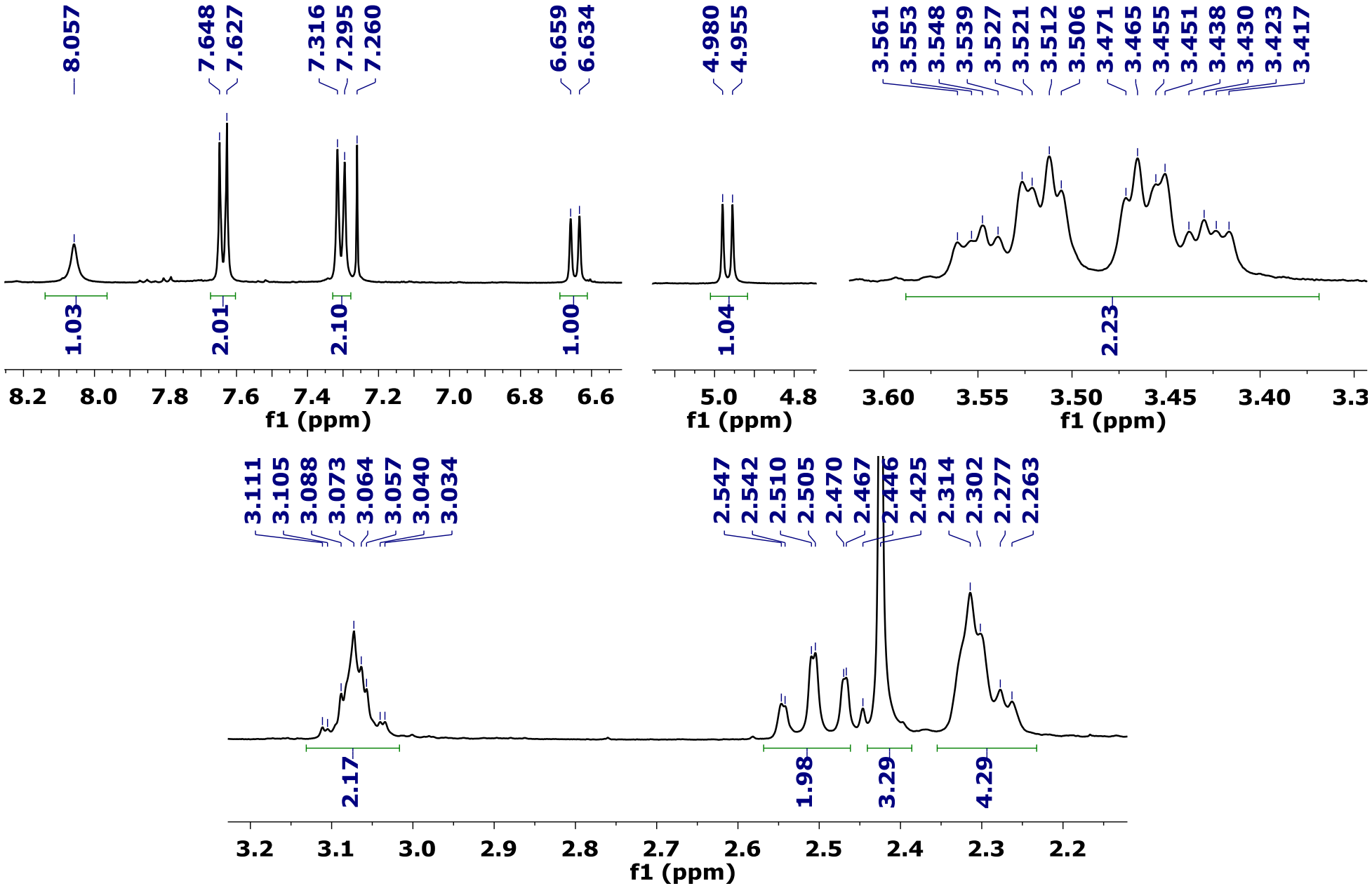


Product 3ai

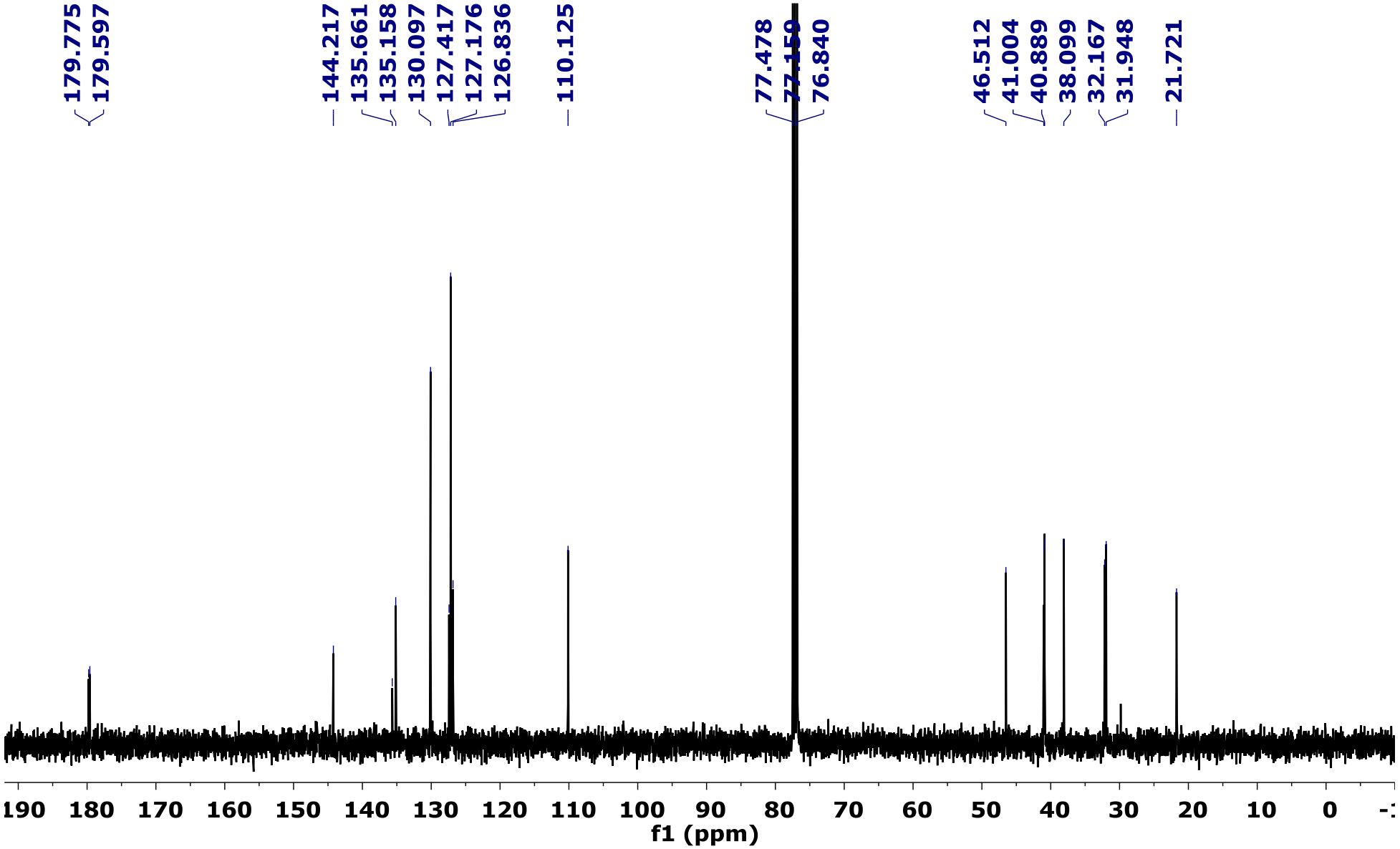


^{1}H NMR (400 MHz, $CDCl_3$)

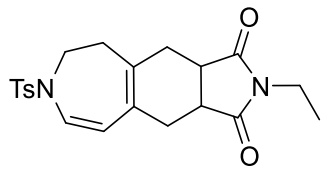



8.057
7.648
7.627
7.316
7.295
7.260
6.659
6.634
4.980
4.955
3.561
3.553
3.548
3.539
3.527
3.521
3.512
3.506
3.471
3.465
3.455
3.451
3.438
3.430
3.423
3.417
1.03
2.01
2.10
1.00
1.04
2.23
f1 (ppm)
3.111
3.105
3.088
3.073
3.064
3.057
3.040
3.034
2.547
2.542
2.510
2.505
2.470
2.467
2.446
2.425
2.314
2.302
2.277
2.263
2.17
1.98
3.29
4.29
f1 (ppm)

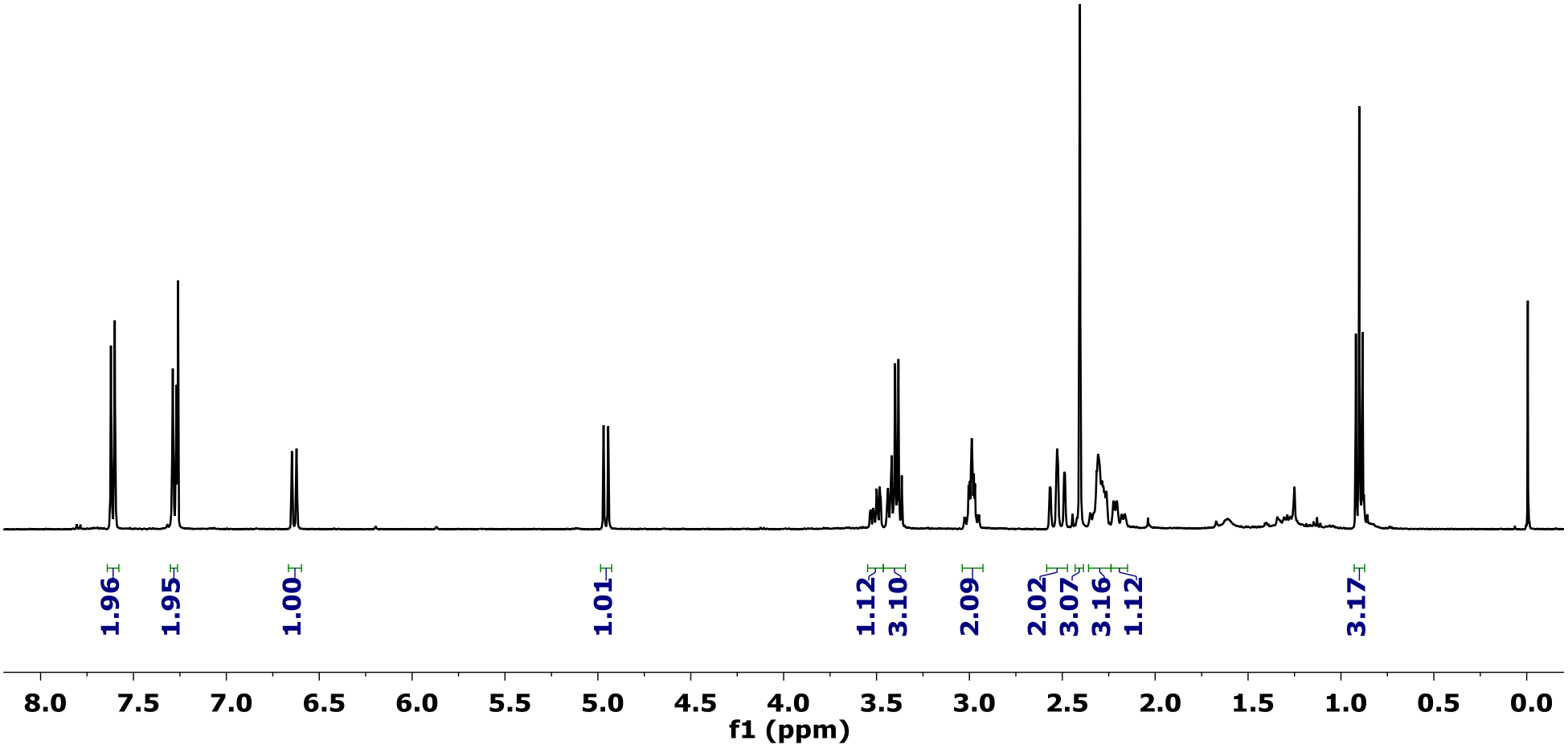
^{13}C NMR (101 MHz, $CDCl_3$)

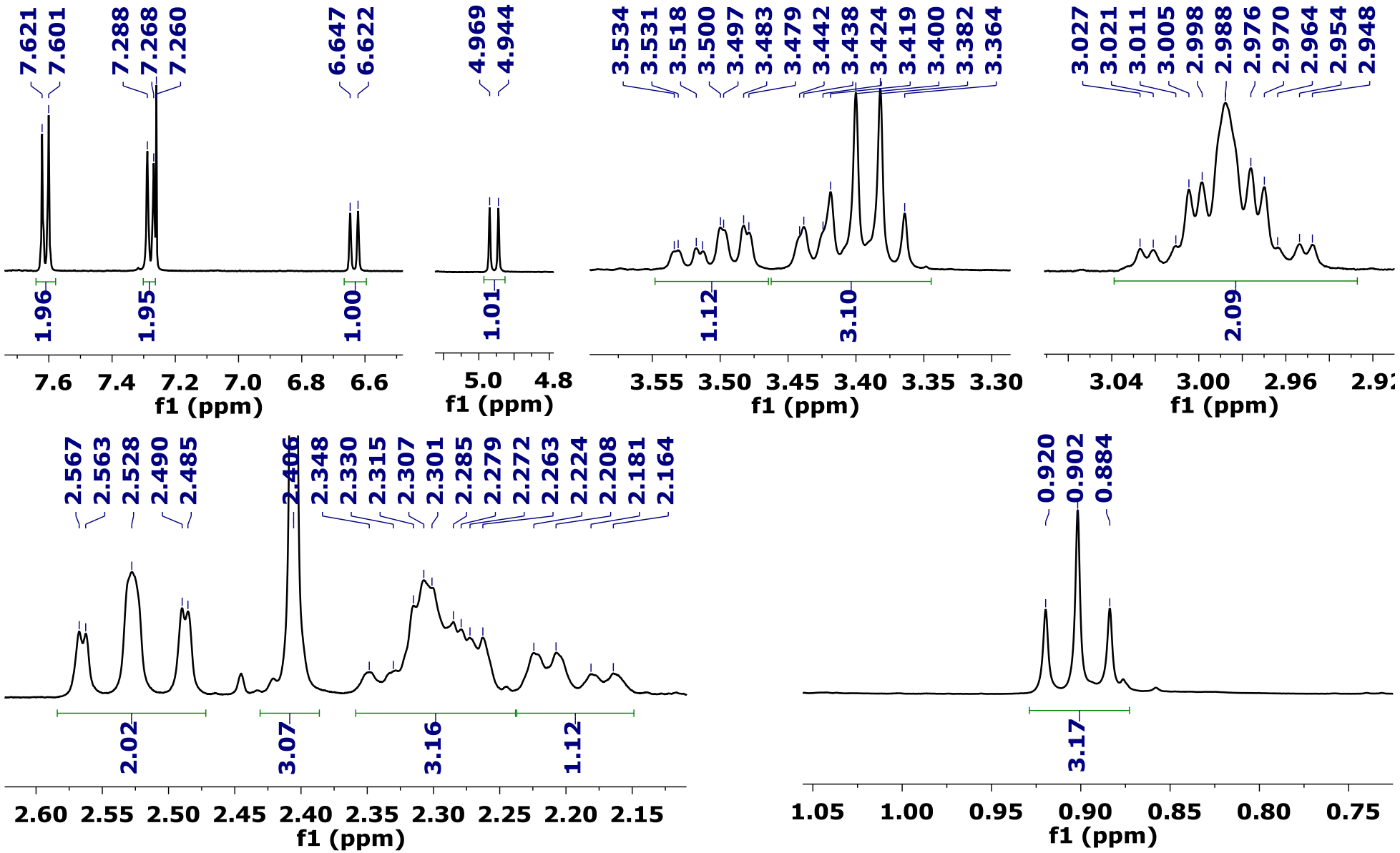


Product 3aj

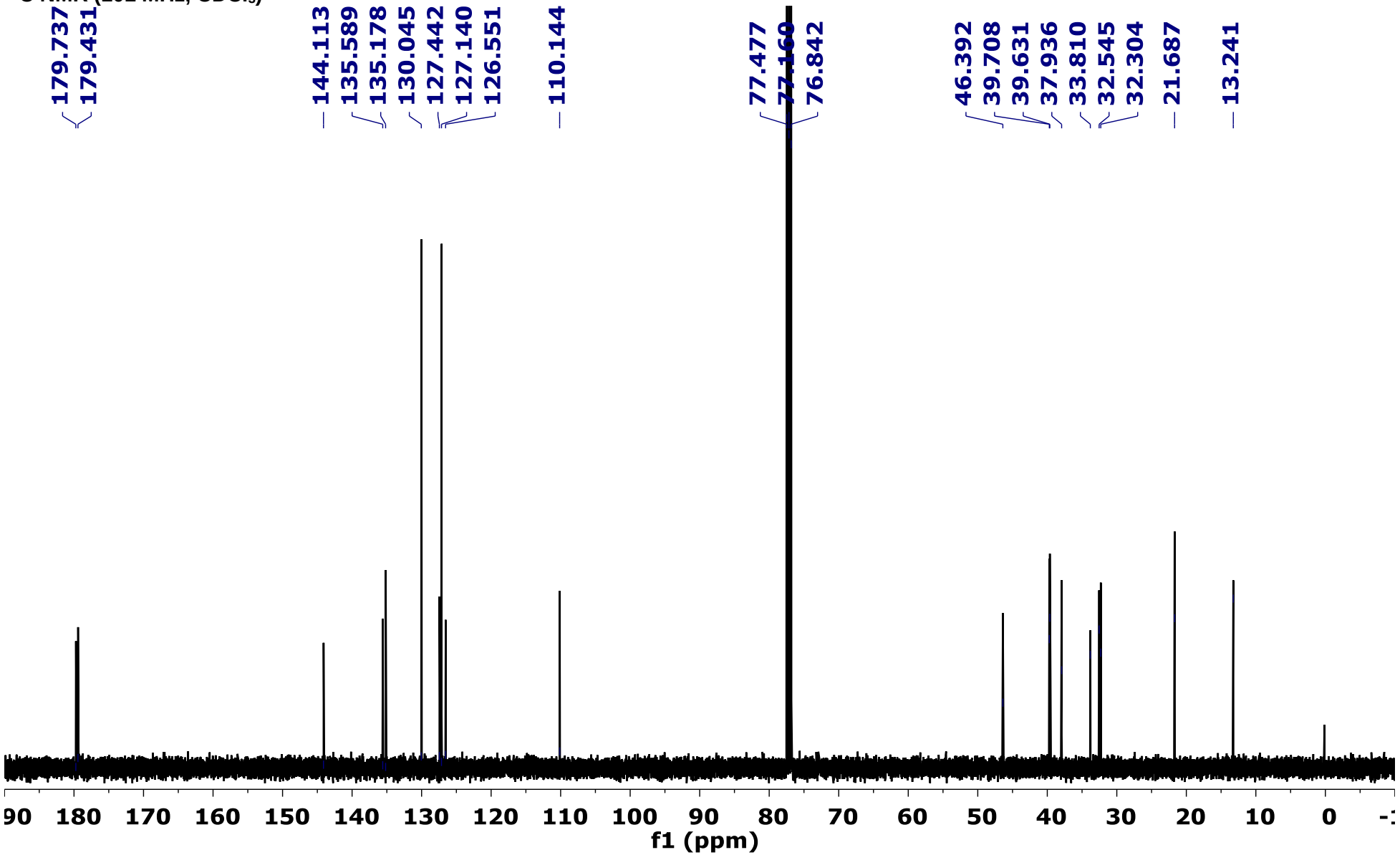


^{1}H NMR (400 MHz, $CDCl_3$)

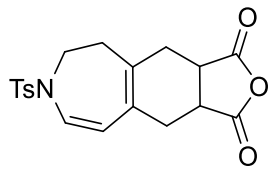



7.621
7.601
7.288
7.268
7.260
6.647
6.622
4.969
4.944
3.534
3.531
3.518
3.500
3.497
3.483
3.479
3.442
3.438
3.424
3.419
3.400
3.382
3.364
3.027
3.021
3.011
3.005
2.998
2.988
2.976
2.970
2.964
2.954
2.948
1.96
1.95
1.00
1.01
1.12
3.10
2.09
7.6 7.4 7.2 7.0 6.8 6.6
5.0 4.8
3.55 3.50 3.45 3.40 3.35 3.30
3.04 3.00 2.96
f1 (ppm)
2.567
2.563
2.528
2.490
2.485
2.406
2.348
2.330
2.315
2.307
2.301
2.285
2.279
2.272
2.263
2.224
2.208
2.181
2.164
2.02
3.07
3.16
1.12
2.60 2.55 2.50 2.45 2.40 2.35 2.30 2.25 2.20 2.15
0.920
0.902
0.884
3.17
1.05 1.00 0.95 0.90 0.85 0.80 0.75
f1 (ppm)

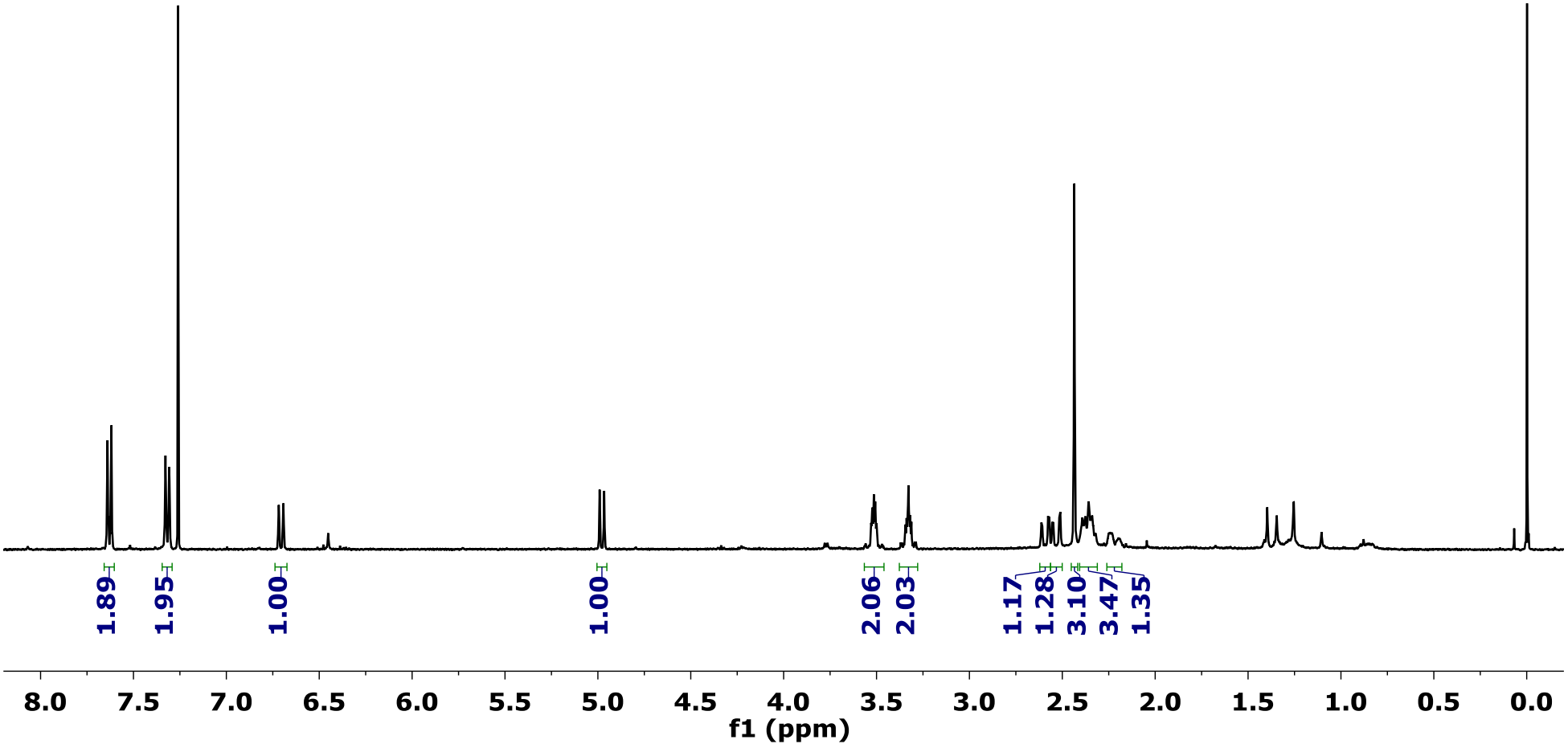
^{13}C NMR (101 MHz, $CDCl_3$)

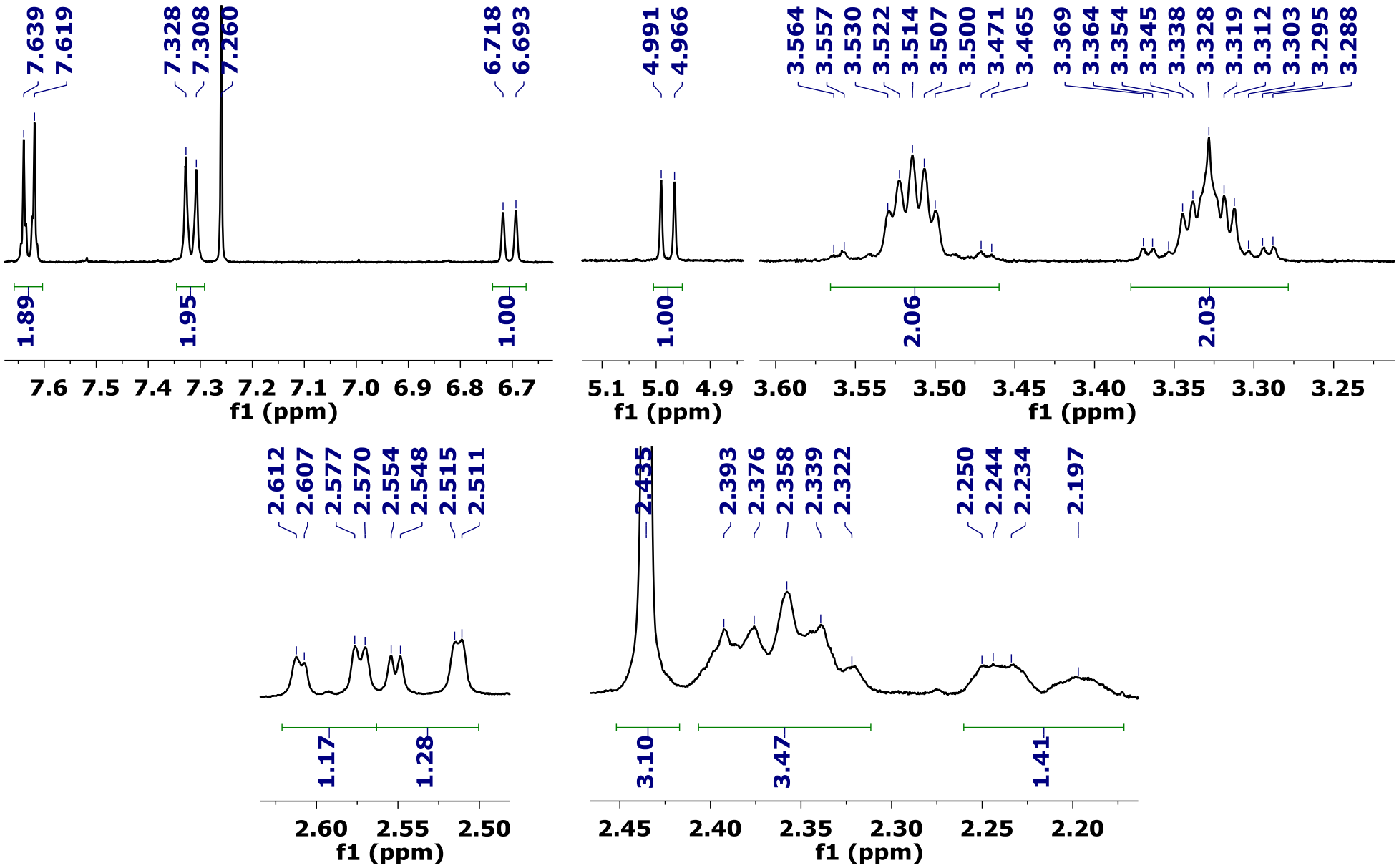


Product 3ak

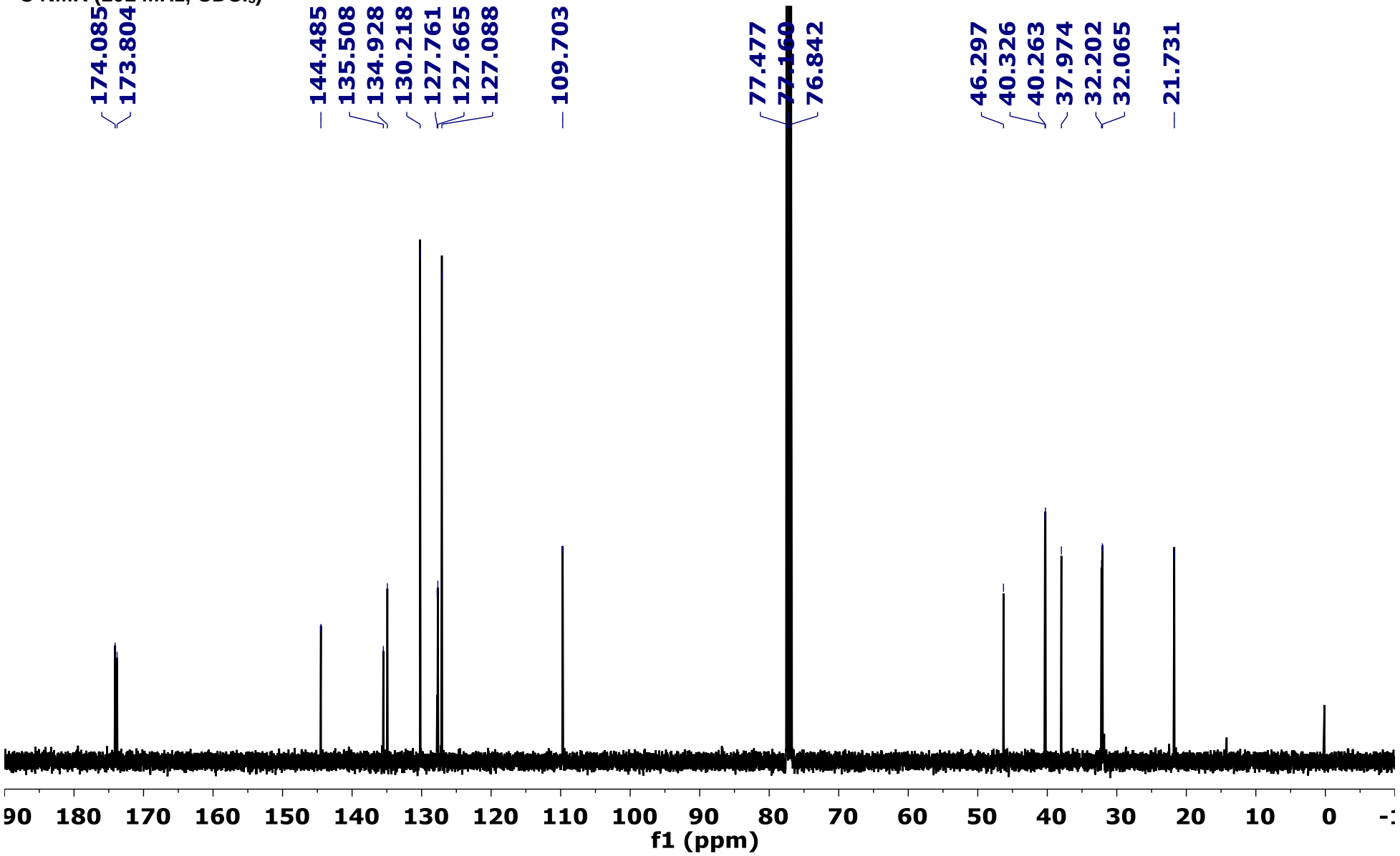


^{1}H NMR (400 MHz, $CDCl_3$)

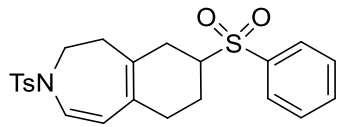



7.639
7.619
7.328
7.308
7.260
6.718
6.693
1.89
1.95
1.00
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
4.991
4.966
1.00
5.1 5.0 4.9
f1 (ppm)
3.564
3.557
3.530
3.522
3.514
3.507
3.500
3.471
3.465
3.369
3.364
3.354
3.345
3.338
3.328
3.319
3.312
3.303
3.295
3.288
2.06
2.03
3.60 3.55 3.50 3.45 3.40 3.35 3.30 3.25
f1 (ppm)
2.612
2.607
2.577
2.570
2.554
2.548
2.515
2.511
1.17
1.28
2.60 2.55 2.50
f1 (ppm)
2.435
2.393
2.376
2.358
2.339
2.322
2.250
2.244
2.234
2.197
3.10
3.47
1.41
2.45 2.40 2.35 2.30 2.25 2.20
f1 (ppm)

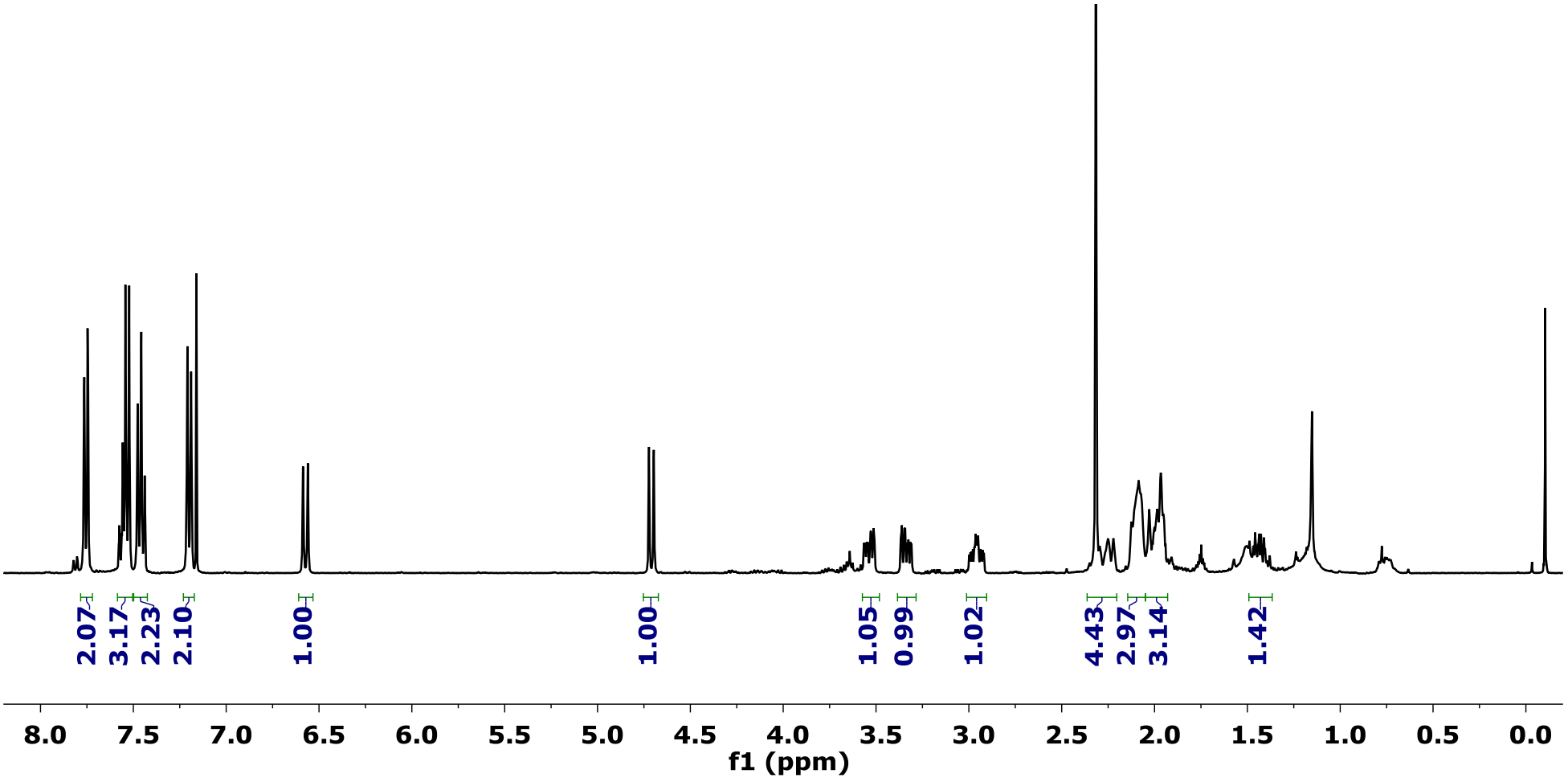
^{13}C NMR (101 MHz, $CDCl_3$)

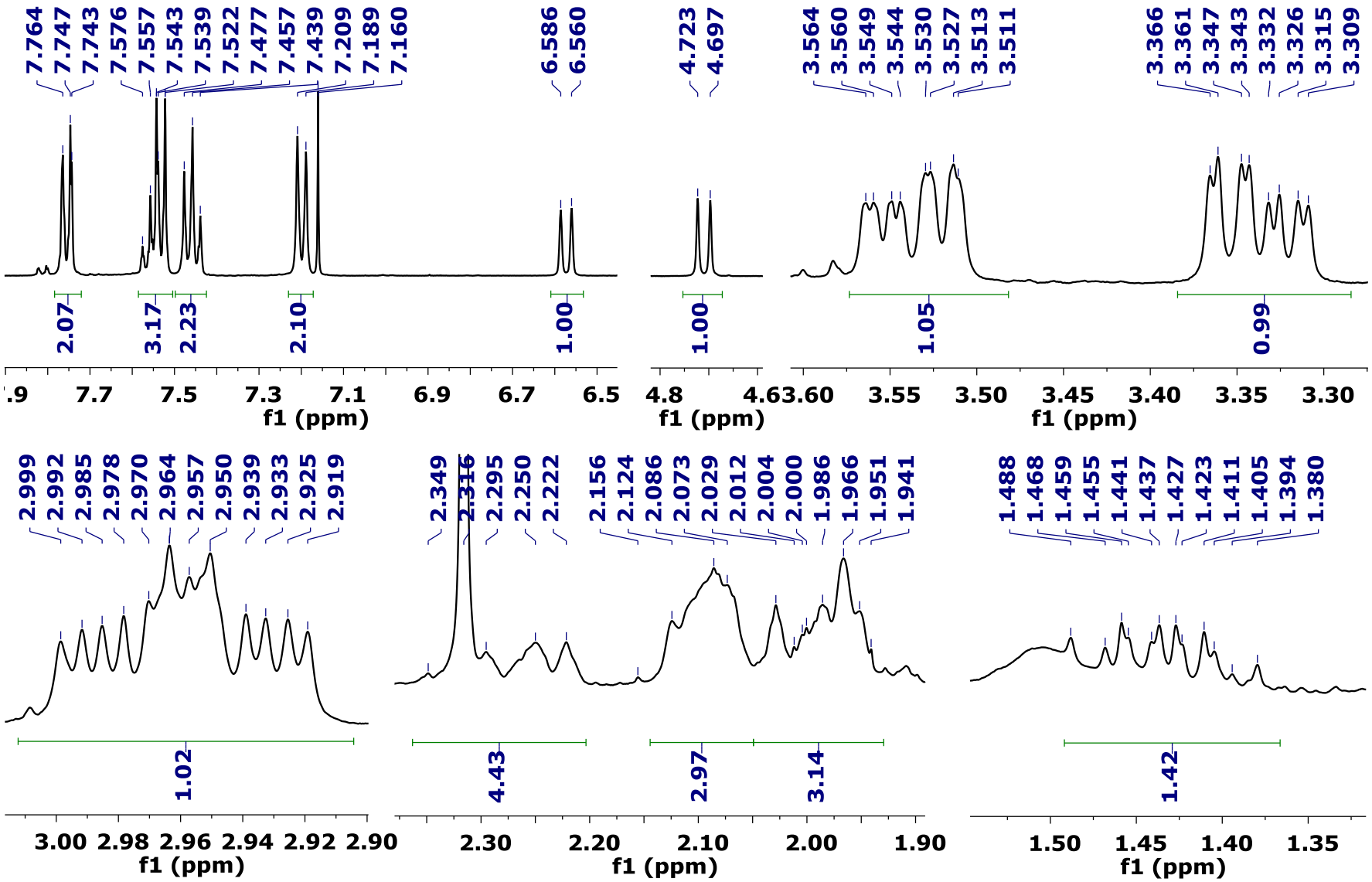


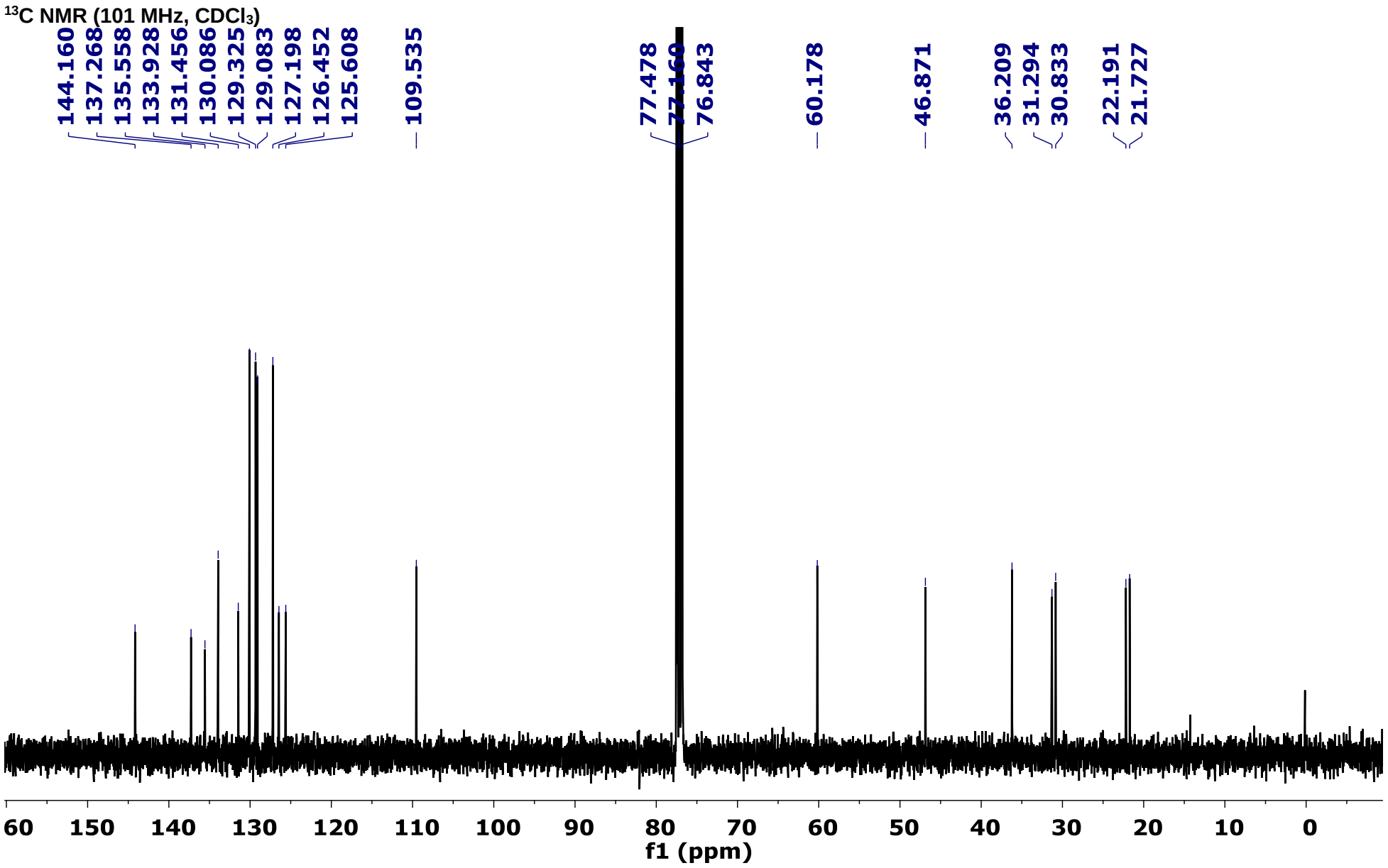
Product 3al



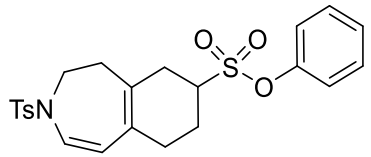
^{1}H NMR (400 MHz, $CDCl_3$)



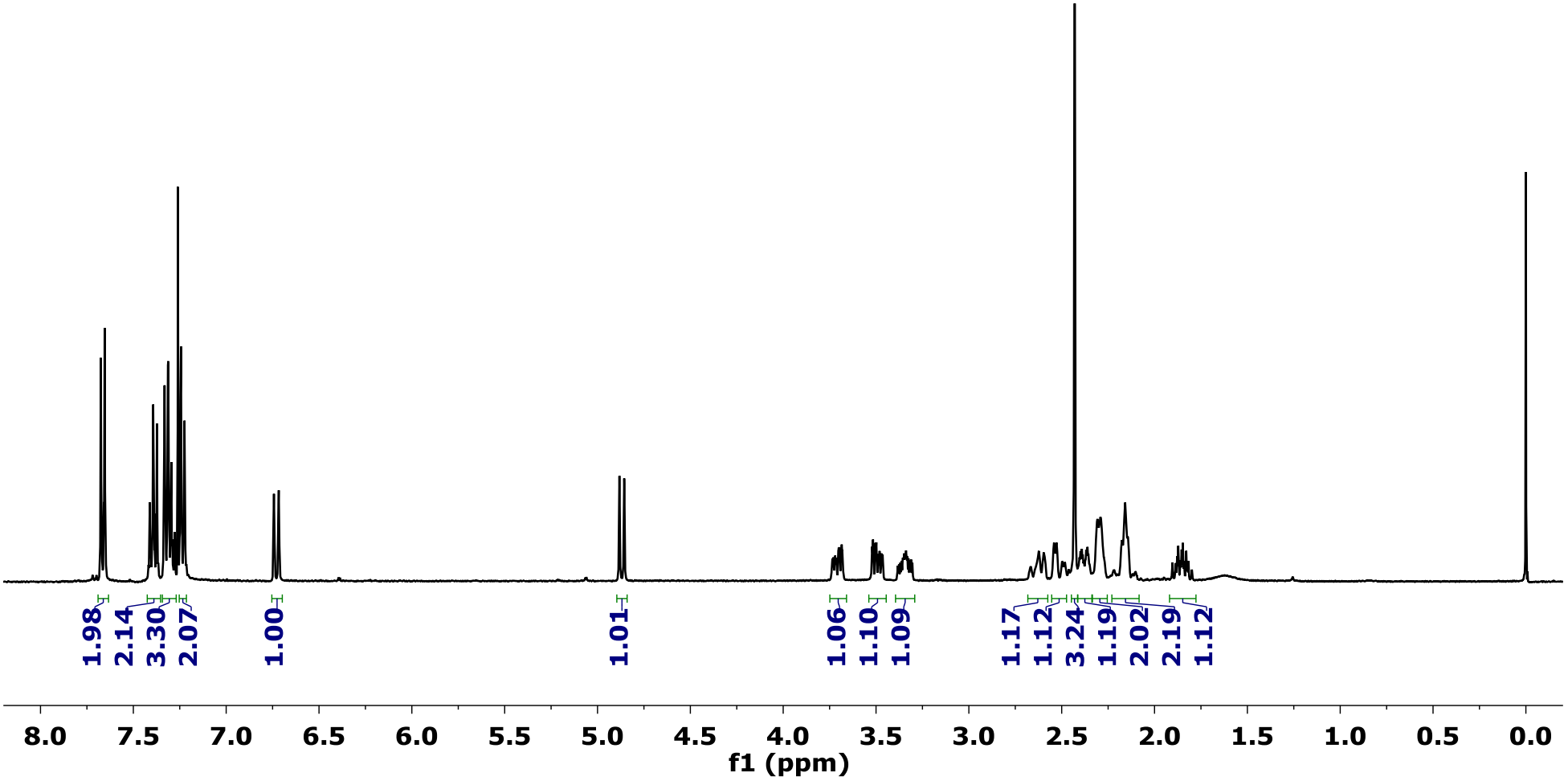

7.764
7.747
7.743
7.576
7.557
7.543
7.539
7.522
7.477
7.457
7.439
7.209
7.189
7.160
6.586
6.560
4.723
4.697
3.564
3.560
3.549
3.544
3.530
3.527
3.513
3.511
3.366
3.361
3.347
3.343
3.332
3.326
3.315
3.309
2.07
3.17
2.23
2.10
1.00
1.00
1.05
0.99
f1 (ppm)
2.999
2.992
2.985
2.978
2.970
2.964
2.957
2.950
2.939
2.933
2.925
2.919
2.349
2.316
2.295
2.250
2.222
2.156
2.124
2.086
2.073
2.029
2.012
2.004
2.000
1.986
1.966
1.951
1.941
1.488
1.468
1.459
1.455
1.441
1.437
1.427
1.423
1.411
1.405
1.394
1.380
1.02
4.43
2.97
3.14
1.42
f1 (ppm)
f1 (ppm)
f1 (ppm)

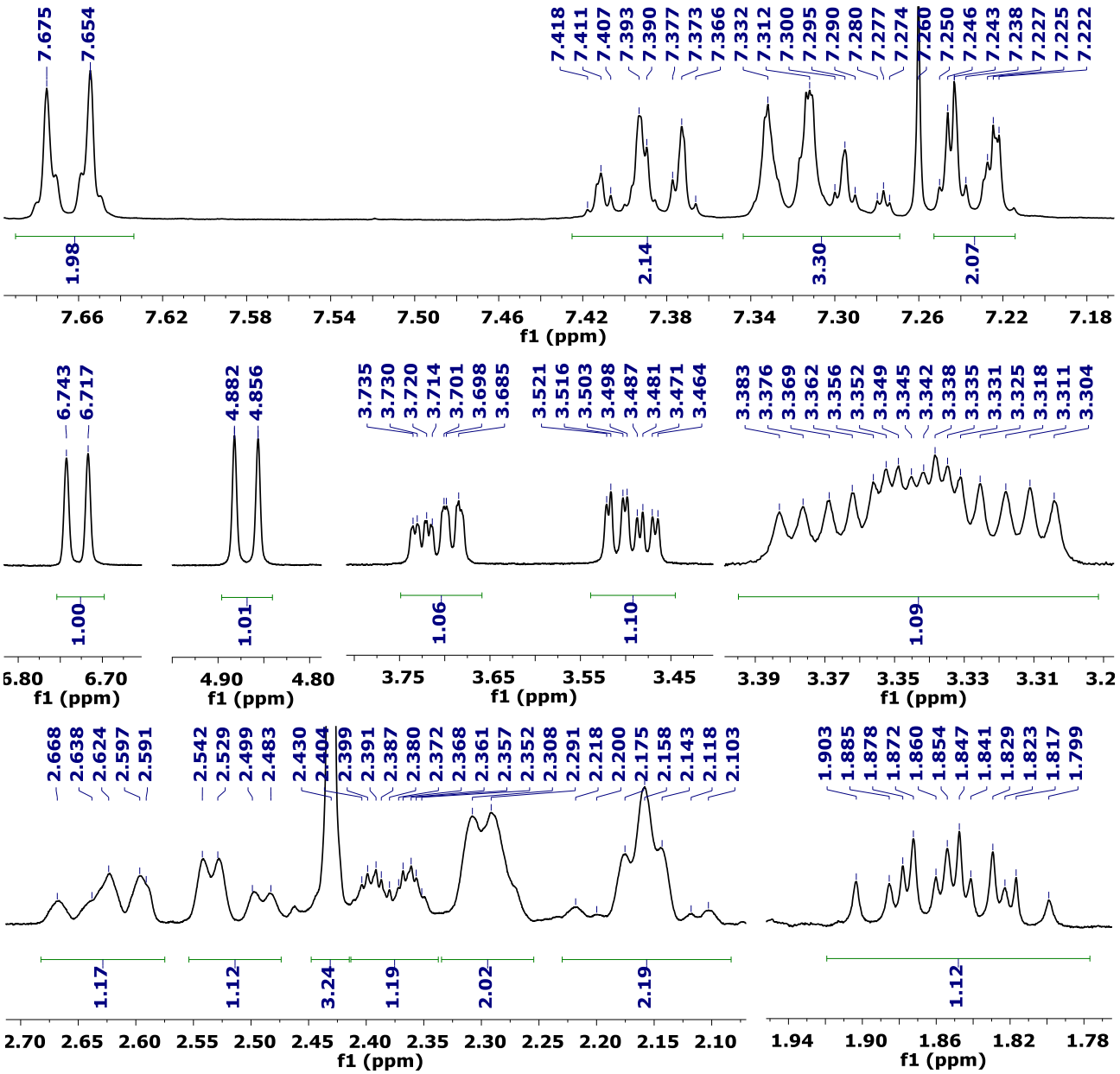

^{13}C NMR (101 MHz, $CDCl_3$)
144.160
137.268
135.558
133.928
131.456
130.086
129.325
129.083
127.198
126.452
125.608
109.535
77.478
77.160
76.843
60.178
46.871
36.209
31.294
30.833
22.191
21.727
60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Product 3am

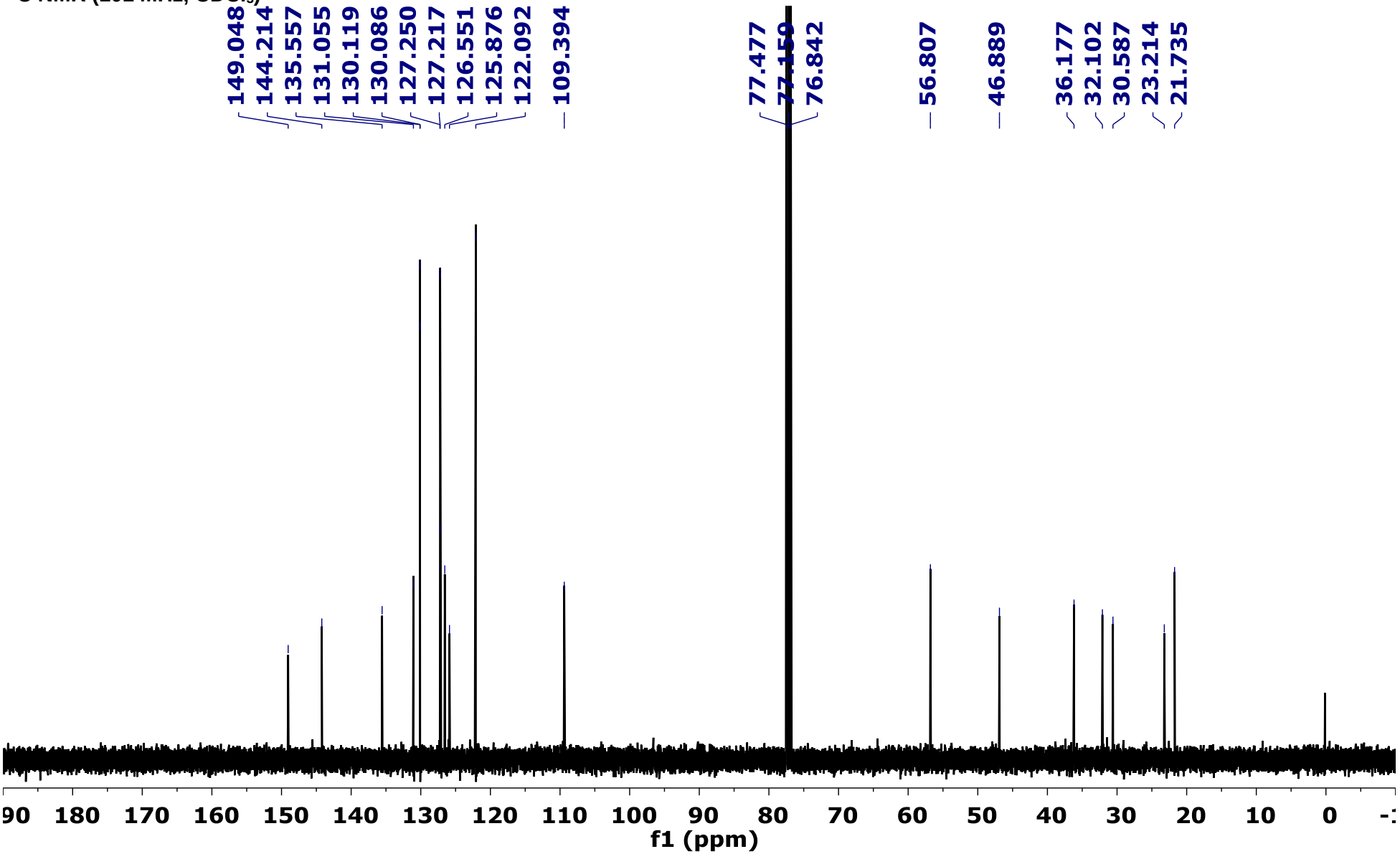


^{1}H NMR (400 MHz, $CDCl_3$)

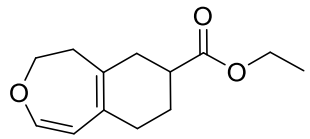



7.675
7.654
7.418
7.411
7.407
7.393
7.390
7.377
7.373
7.366
7.332
7.312
7.300
7.295
7.290
7.280
7.277
7.274
7.260
7.250
7.246
7.243
7.238
7.227
7.225
7.222
1.98
2.14
3.30
2.07
7.66 7.62 7.58 7.54 7.50 7.46 7.42 7.38 7.34 7.30 7.26 7.22 7.18
f1 (ppm)
6.743
6.717
4.882
4.856
3.735
3.730
3.720
3.714
3.701
3.698
3.685
3.521
3.516
3.503
3.498
3.487
3.481
3.471
3.464
3.383
3.376
3.369
3.362
3.356
3.352
3.349
3.345
3.342
3.338
3.335
3.331
3.325
3.318
3.311
3.304
1.00
1.01
1.06
1.10
1.09
6.80 6.70
f1 (ppm)
4.90 4.80
f1 (ppm)
3.75 3.65 3.55 3.45
f1 (ppm)
3.39 3.37 3.35 3.33 3.31 3.2
f1 (ppm)
2.668
2.638
2.624
2.597
2.591
2.542
2.529
2.499
2.483
2.430
2.404
2.399
2.391
2.387
2.380
2.372
2.368
2.361
2.357
2.352
2.308
2.291
2.218
2.200
2.175
2.158
2.143
2.118
2.103
1.903
1.885
1.878
1.872
1.860
1.854
1.847
1.841
1.829
1.823
1.817
1.799
1.17
1.12
3.24
1.19
2.02
2.19
1.12
2.70 2.65 2.60 2.55 2.50 2.45 2.40 2.35 2.30 2.25 2.20 2.15 2.10
f1 (ppm)
1.94 1.90 1.86 1.82 1.78
f1 (ppm)

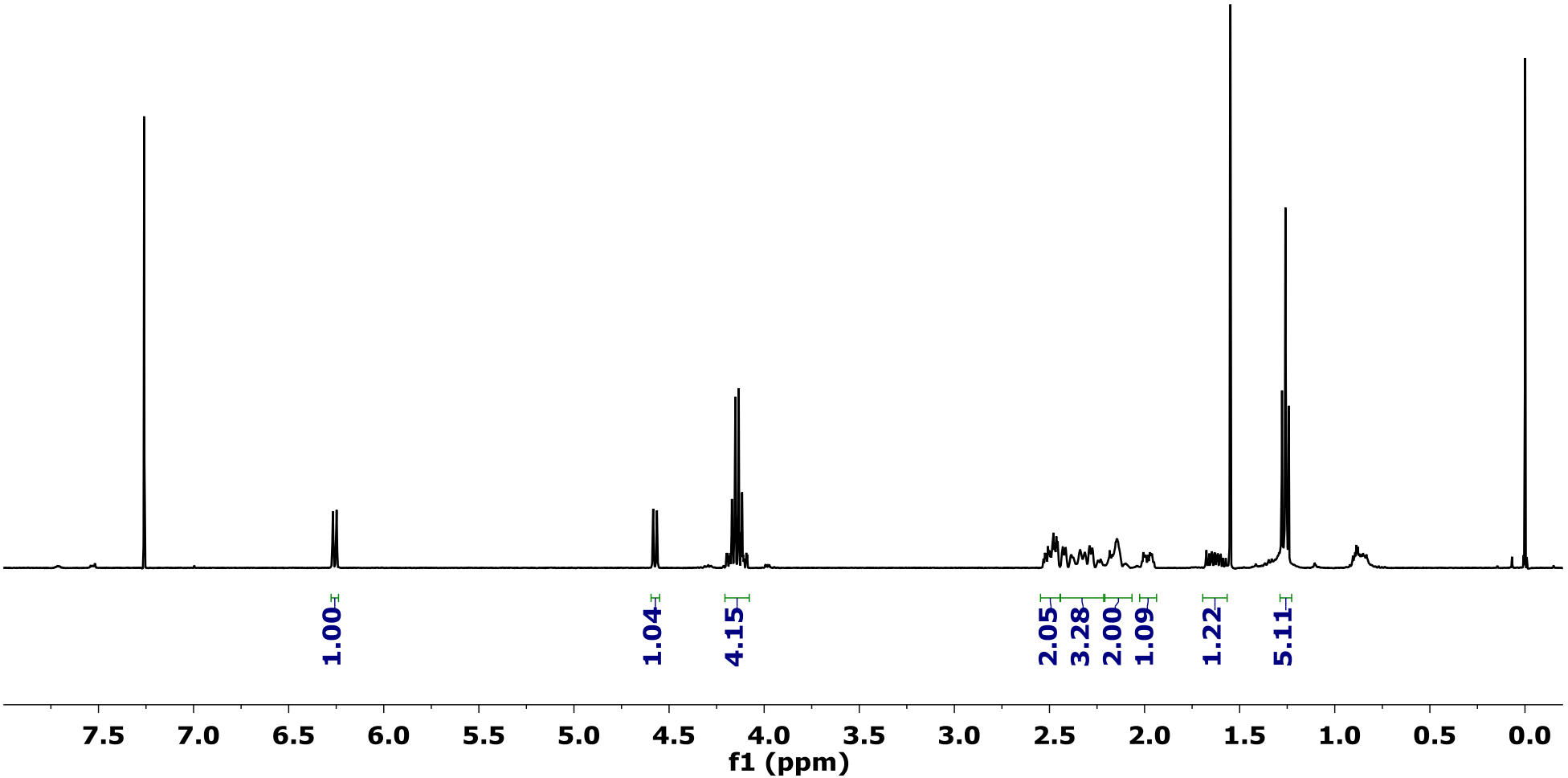
^{13}C NMR (101 MHz, $CDCl_3$)

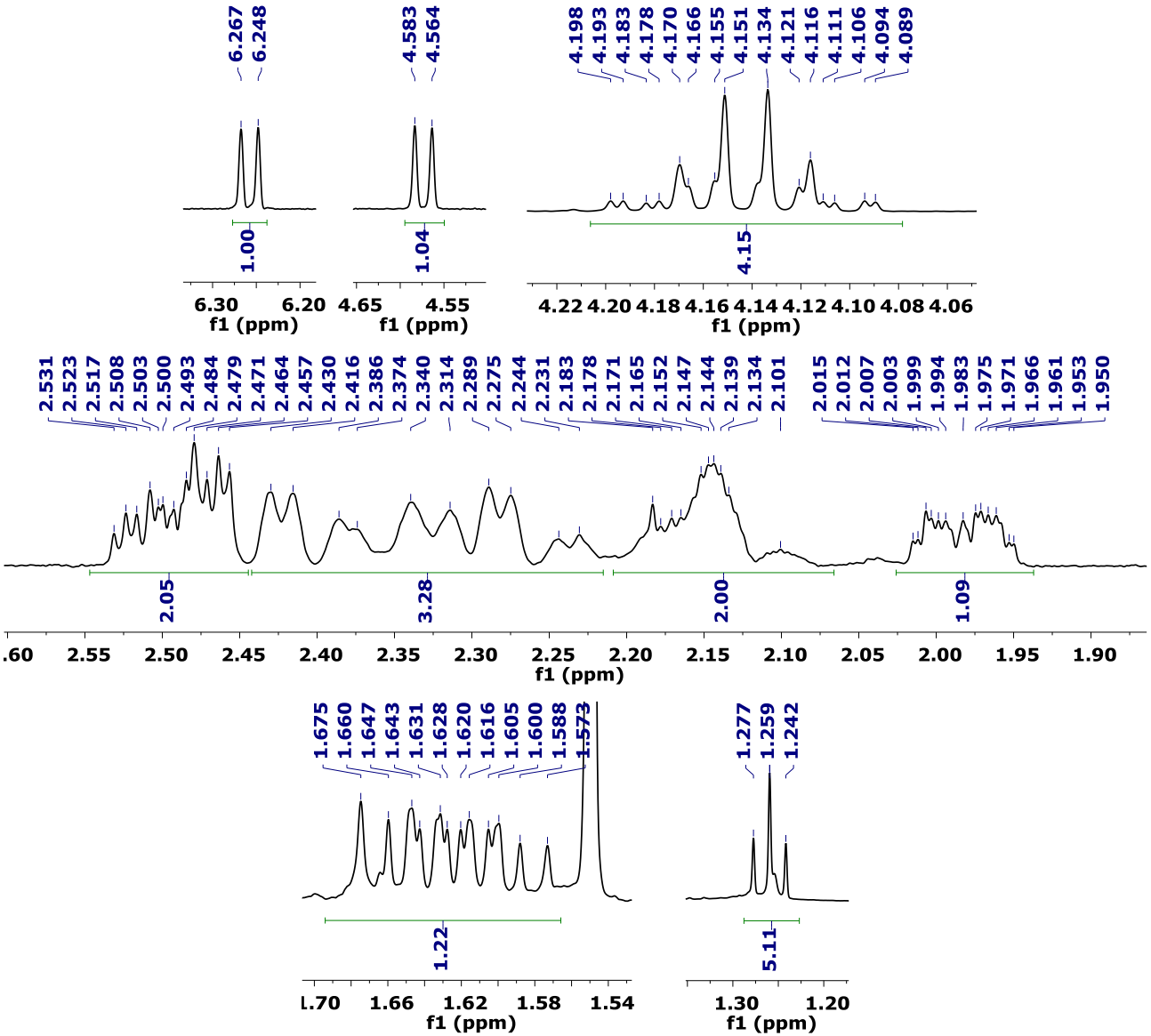


Product 3ba

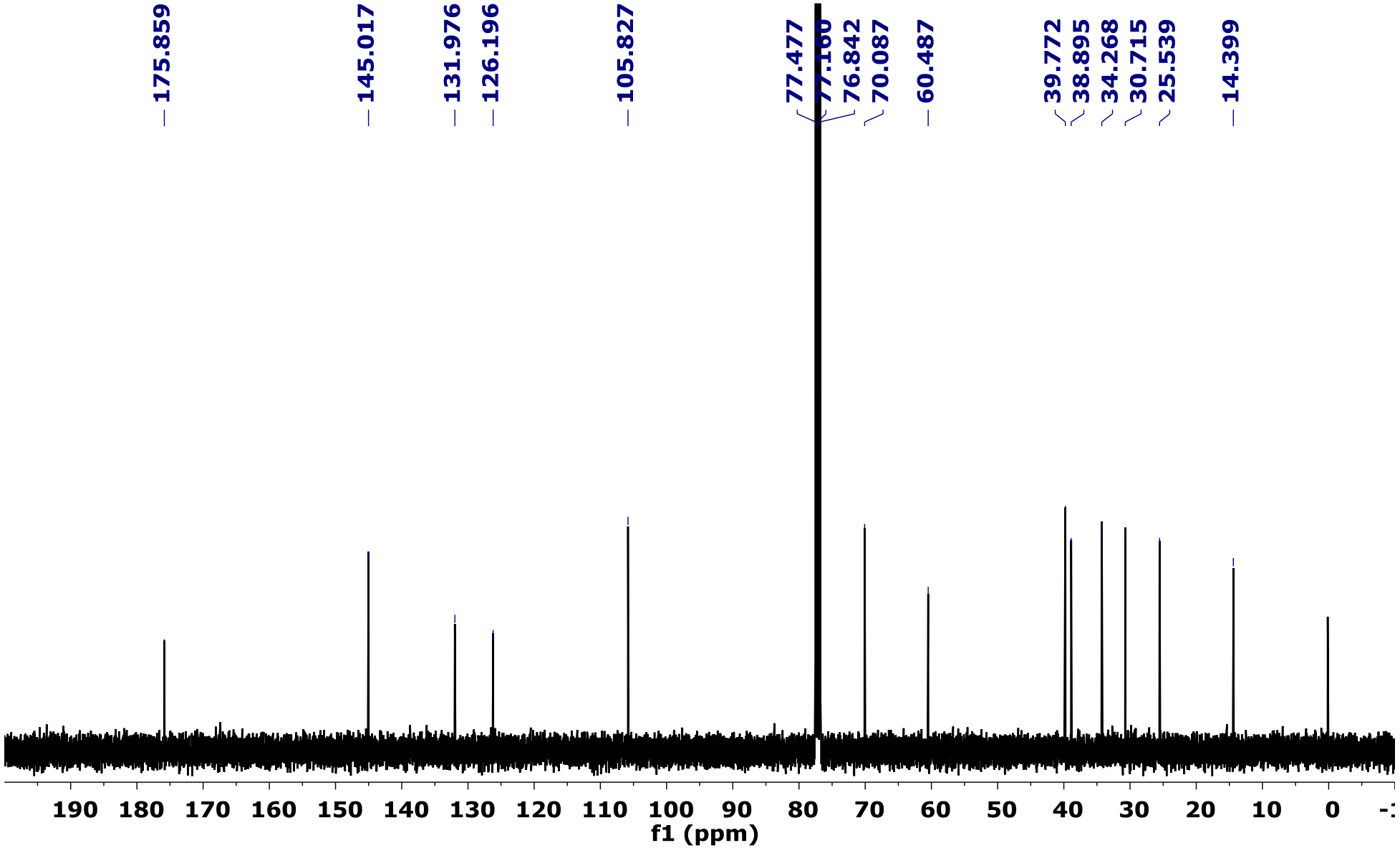


^{1}H NMR (400 MHz, $CDCl_3$)

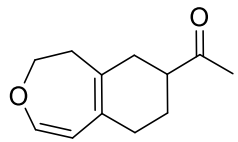



6.267
6.248
4.583
4.564
4.198
4.193
4.183
4.178
4.170
4.166
4.155
4.151
4.134
4.121
4.116
4.111
4.106
4.094
4.089
1.00
1.04
4.15
6.30 6.20
4.65 4.55
4.22 4.20 4.18 4.16 4.14 4.12 4.10 4.08 4.06
f1 (ppm)
2.531
2.523
2.517
2.508
2.503
2.500
2.493
2.484
2.479
2.471
2.464
2.457
2.430
2.416
2.386
2.374
2.340
2.314
2.289
2.275
2.244
2.231
2.183
2.178
2.171
2.165
2.152
2.147
2.144
2.139
2.134
2.101
2.015
2.012
2.007
2.003
1.999
1.994
1.983
1.975
1.971
1.966
1.961
1.953
1.950
2.05
3.28
2.00
1.09
.60 2.55 2.50 2.45 2.40 2.35 2.30 2.25 2.20 2.15 2.10 2.05 2.00 1.95 1.90
f1 (ppm)
1.675
1.660
1.647
1.643
1.631
1.628
1.620
1.616
1.605
1.600
1.588
1.573
1.277
1.259
1.242
1.22
5.11
l.70 1.66 1.62 1.58 1.54
1.30 1.20
f1 (ppm)

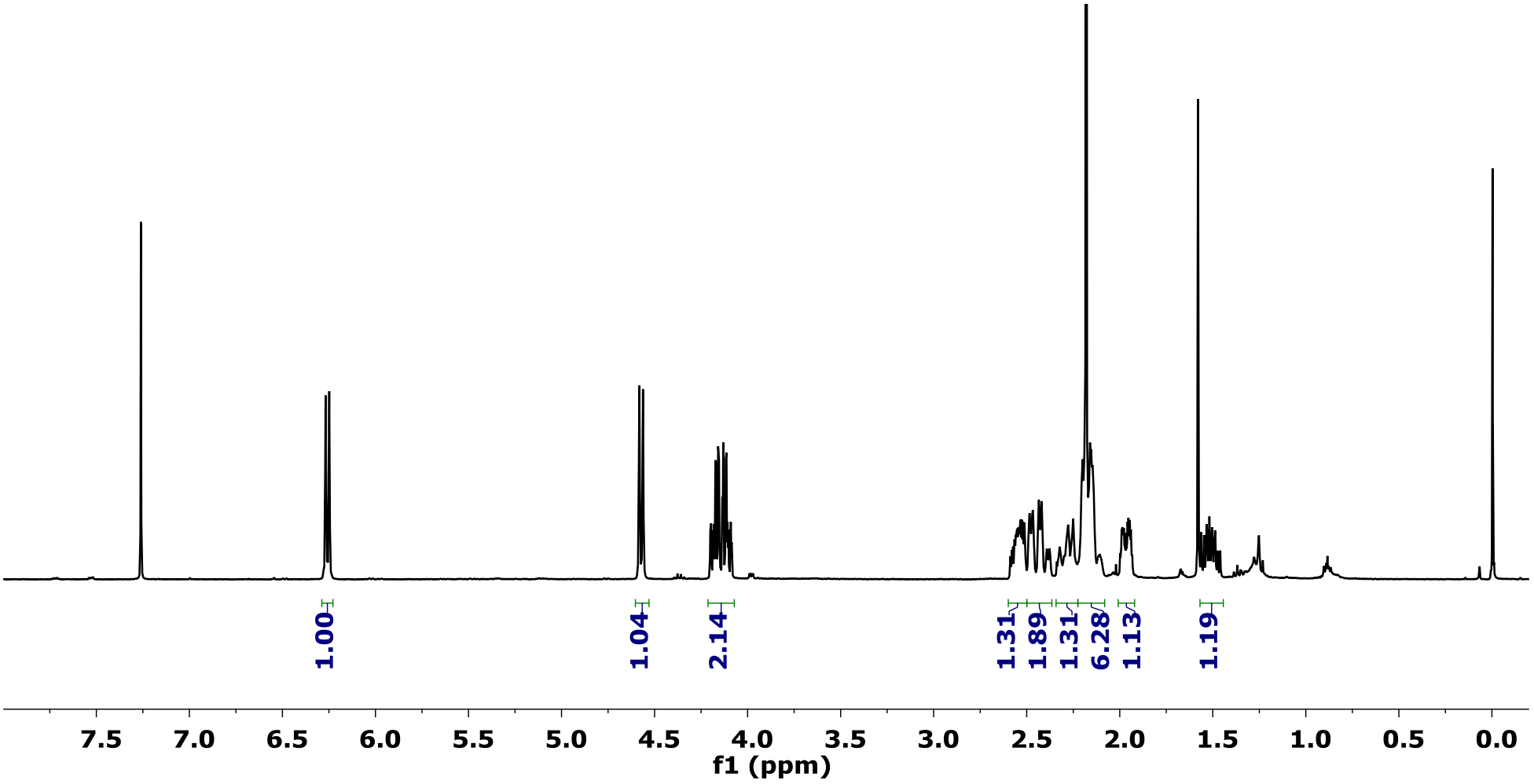
^{13}C NMR (101 MHz, $CDCl_3$)

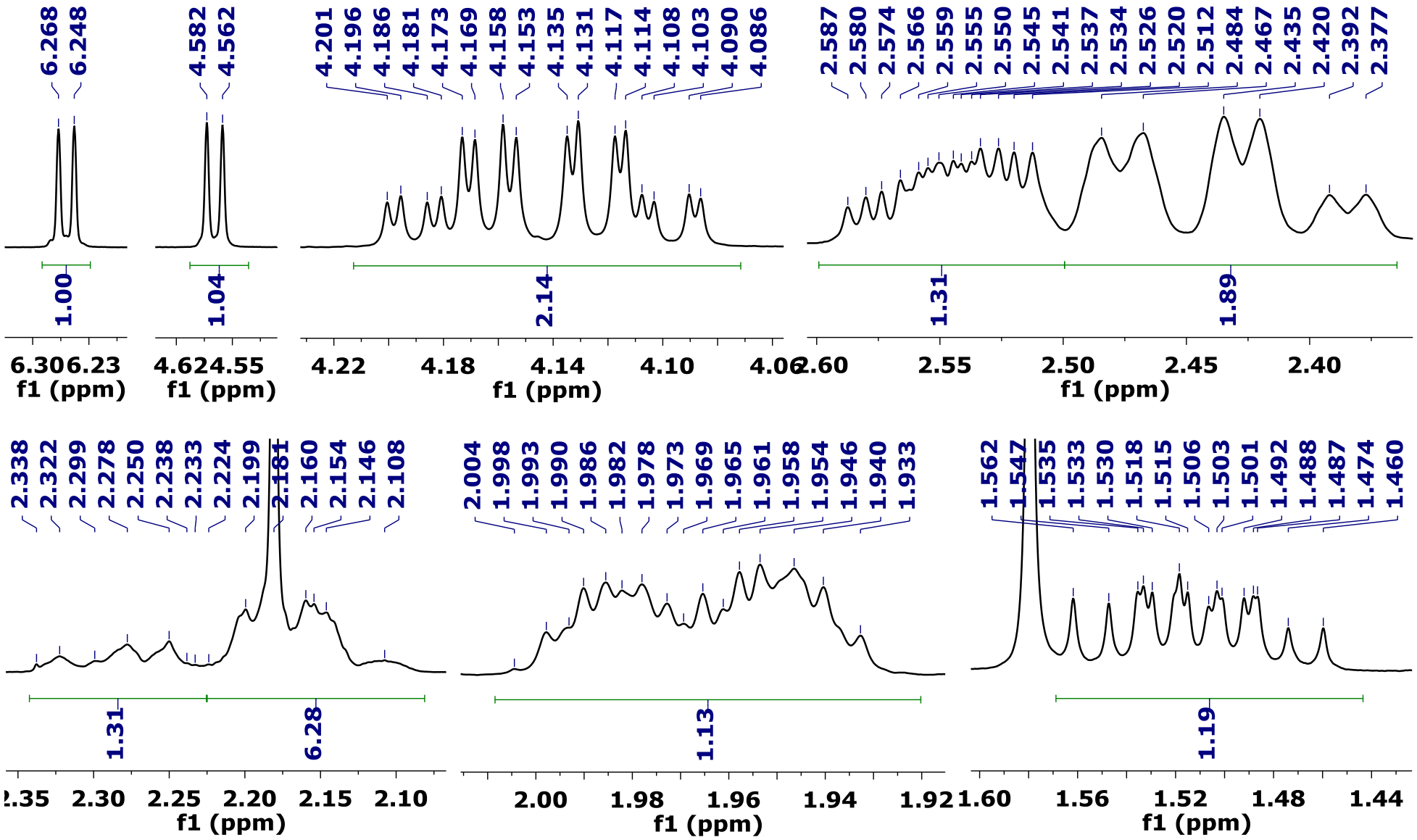


Product 3bg

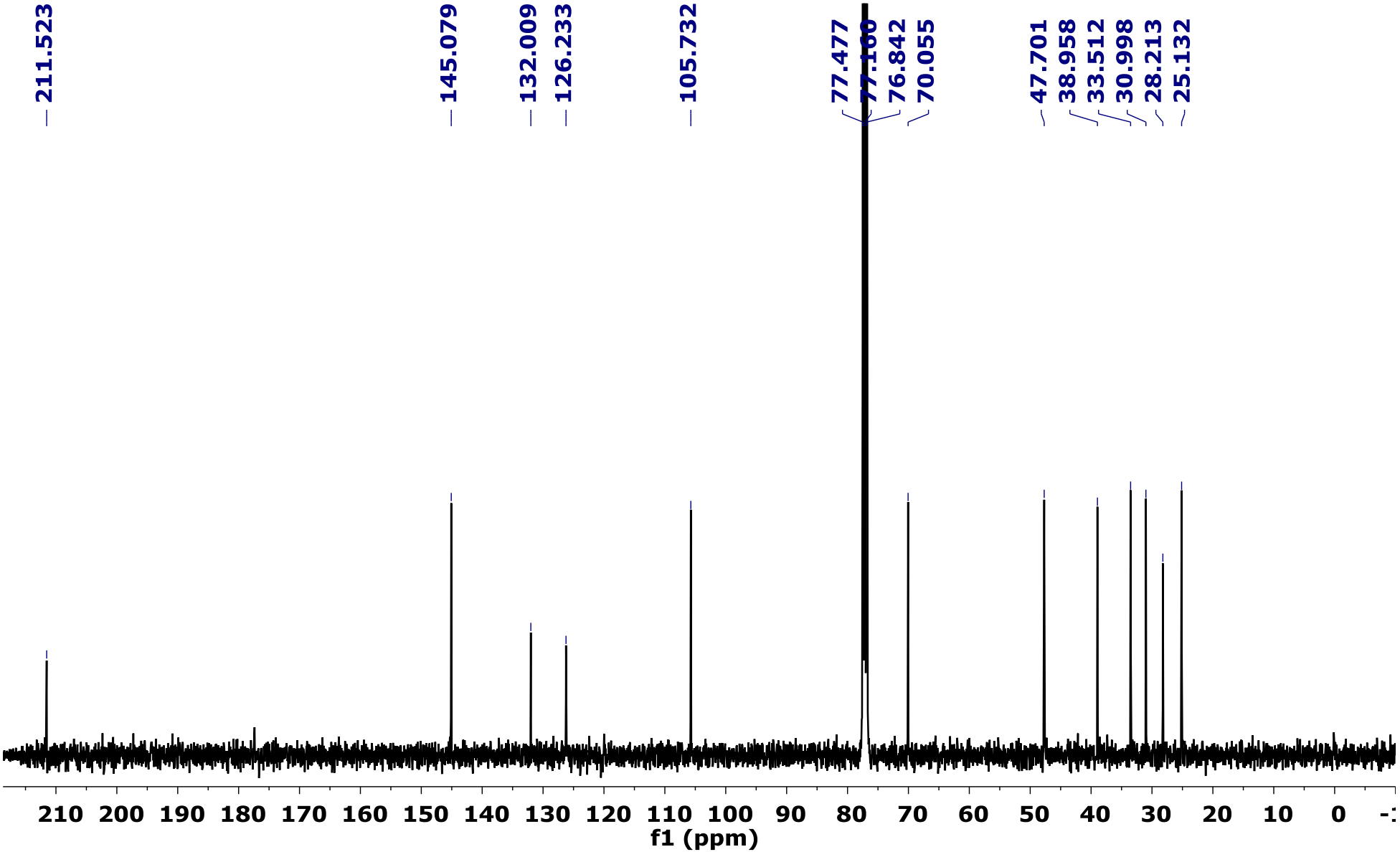


^{1}H NMR (400 MHz, $CDCl_3$)

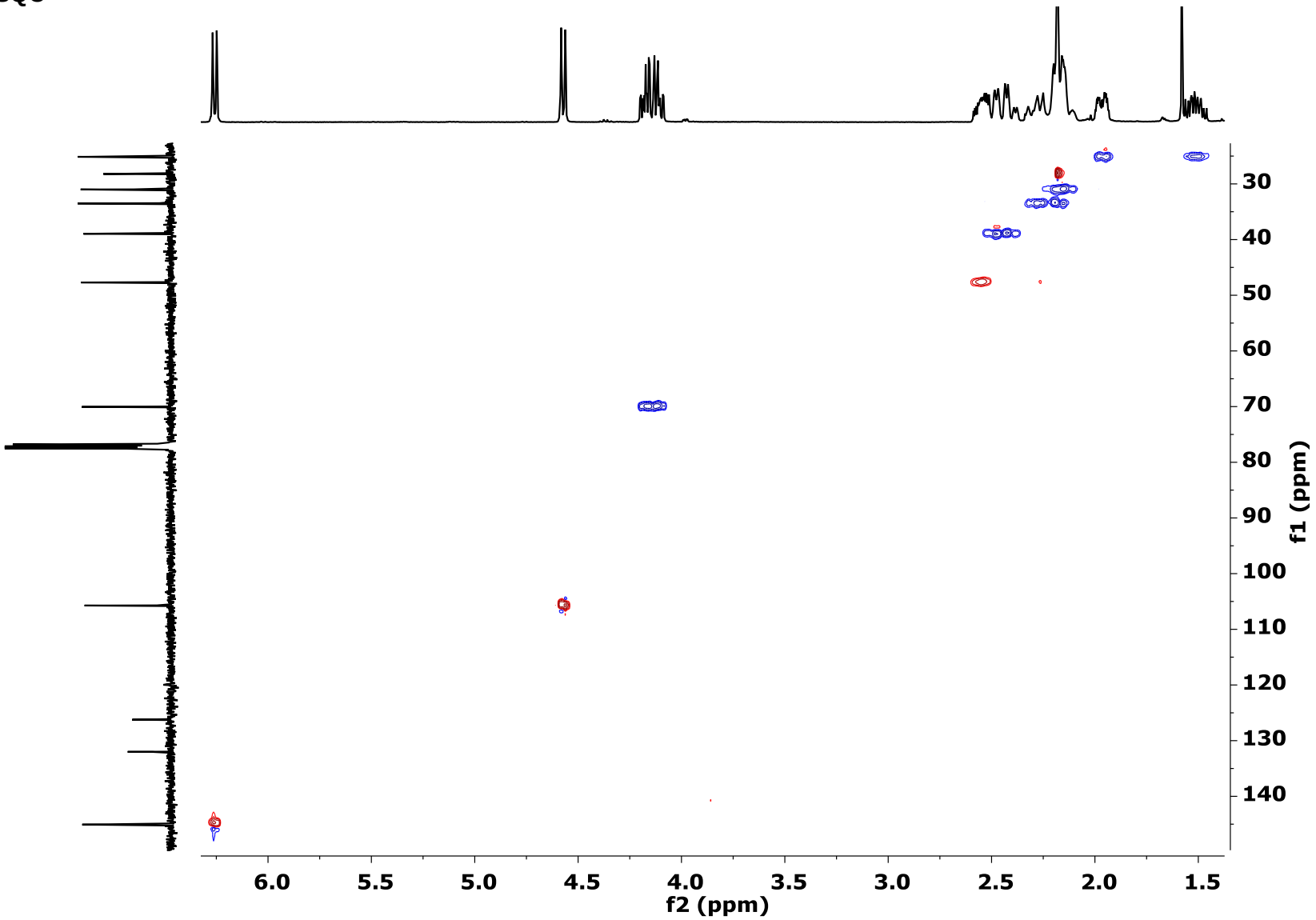



6.268
6.248
4.582
4.562
4.201
4.196
4.186
4.181
4.173
4.169
4.158
4.153
4.135
4.131
4.117
4.114
4.108
4.103
4.090
4.086
2.587
2.580
2.574
2.566
2.559
2.555
2.550
2.545
2.541
2.537
2.534
2.526
2.520
2.512
2.484
2.467
2.435
2.420
2.392
2.377
1.00
1.04
2.14
1.31
1.89
6.306.23
4.624.55
4.22
4.18
4.14
4.10
4.06
2.60
2.55
2.50
2.45
2.40
f1 (ppm)
2.338
2.322
2.299
2.278
2.250
2.238
2.233
2.224
2.199
2.181
2.160
2.154
2.146
2.108
2.004
1.998
1.993
1.990
1.986
1.982
1.978
1.973
1.969
1.965
1.961
1.958
1.954
1.946
1.940
1.933
1.562
1.547
1.535
1.533
1.530
1.518
1.515
1.506
1.503
1.501
1.492
1.488
1.487
1.474
1.460
1.31
6.28
1.13
1.19
2.35
2.30
2.25
2.20
2.15
2.10
2.00
1.98
1.96
1.94
1.92
1.60
1.56
1.52
1.48
1.44
f1 (ppm)

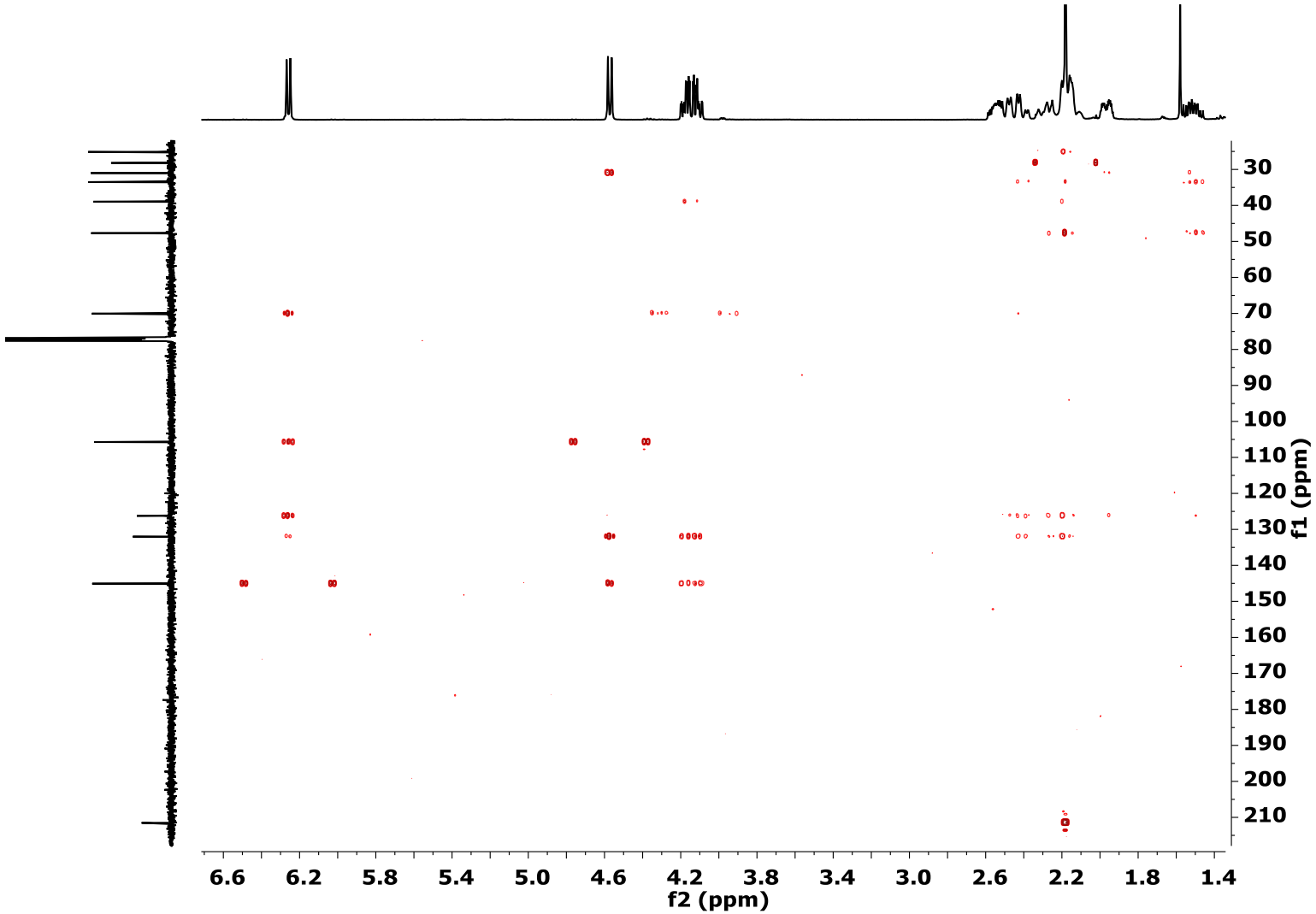
^{13}C NMR (101 MHz, $CDCl_3$)



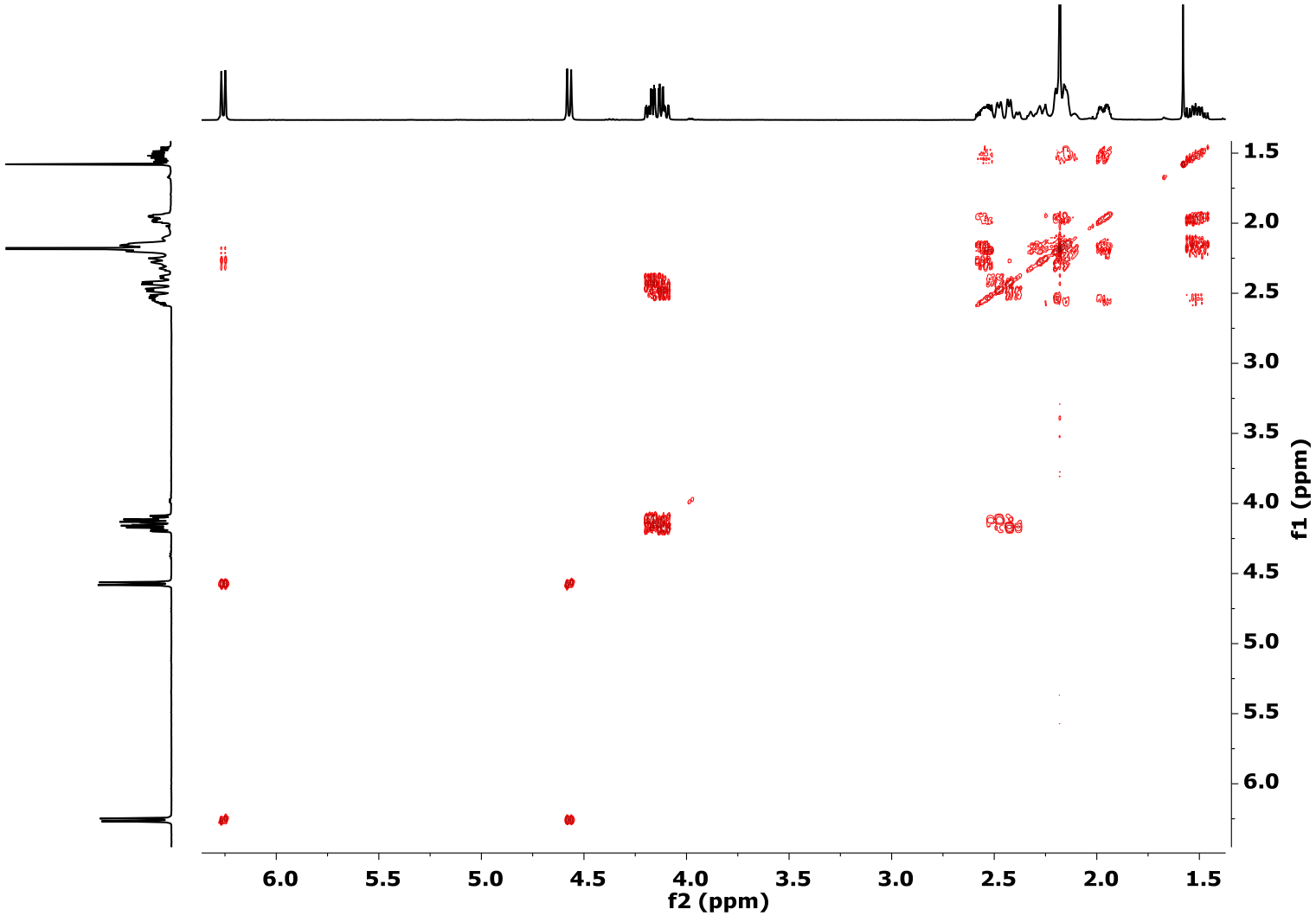
2D NMR HSQC

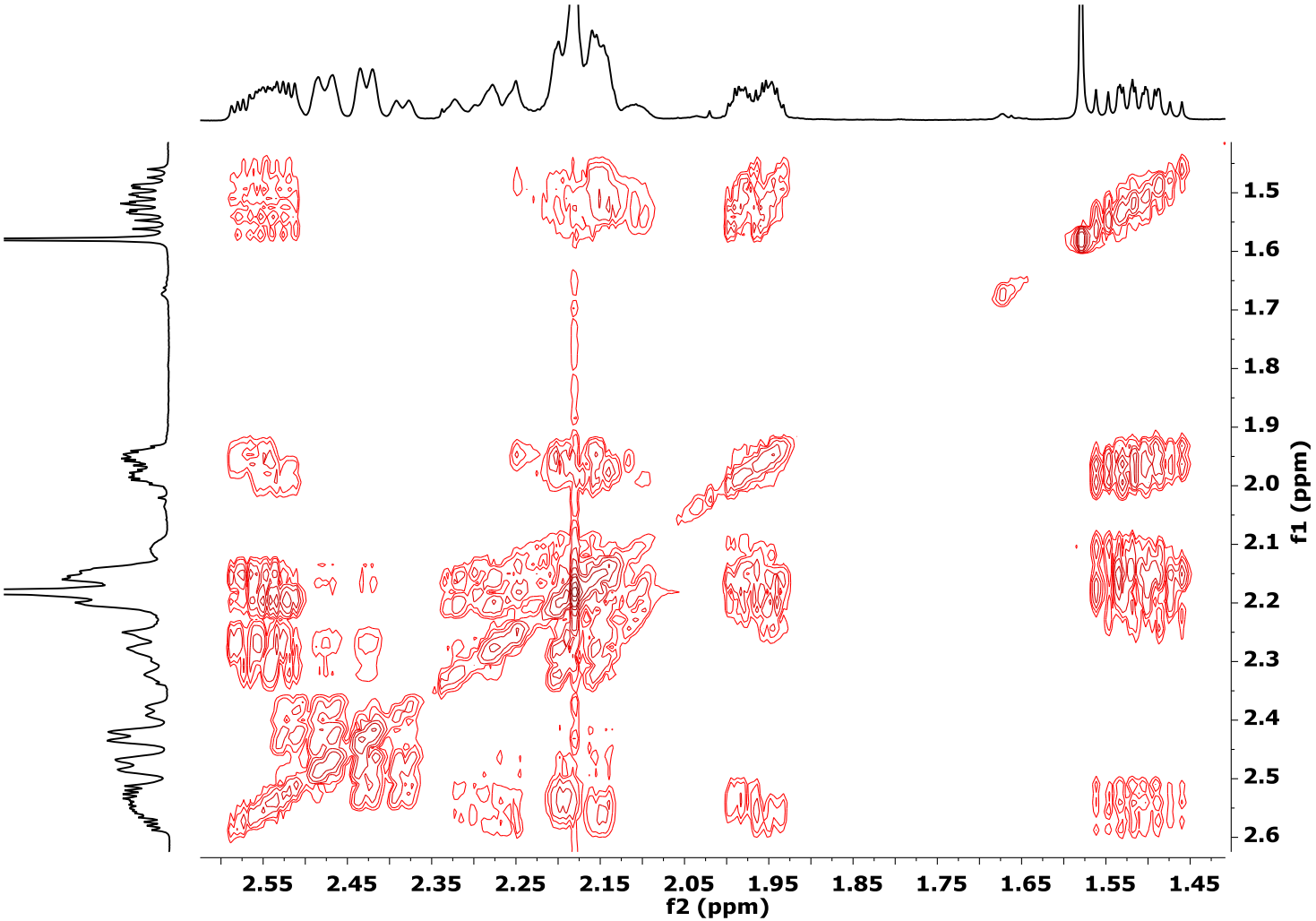

6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)

2D NMR HMBC

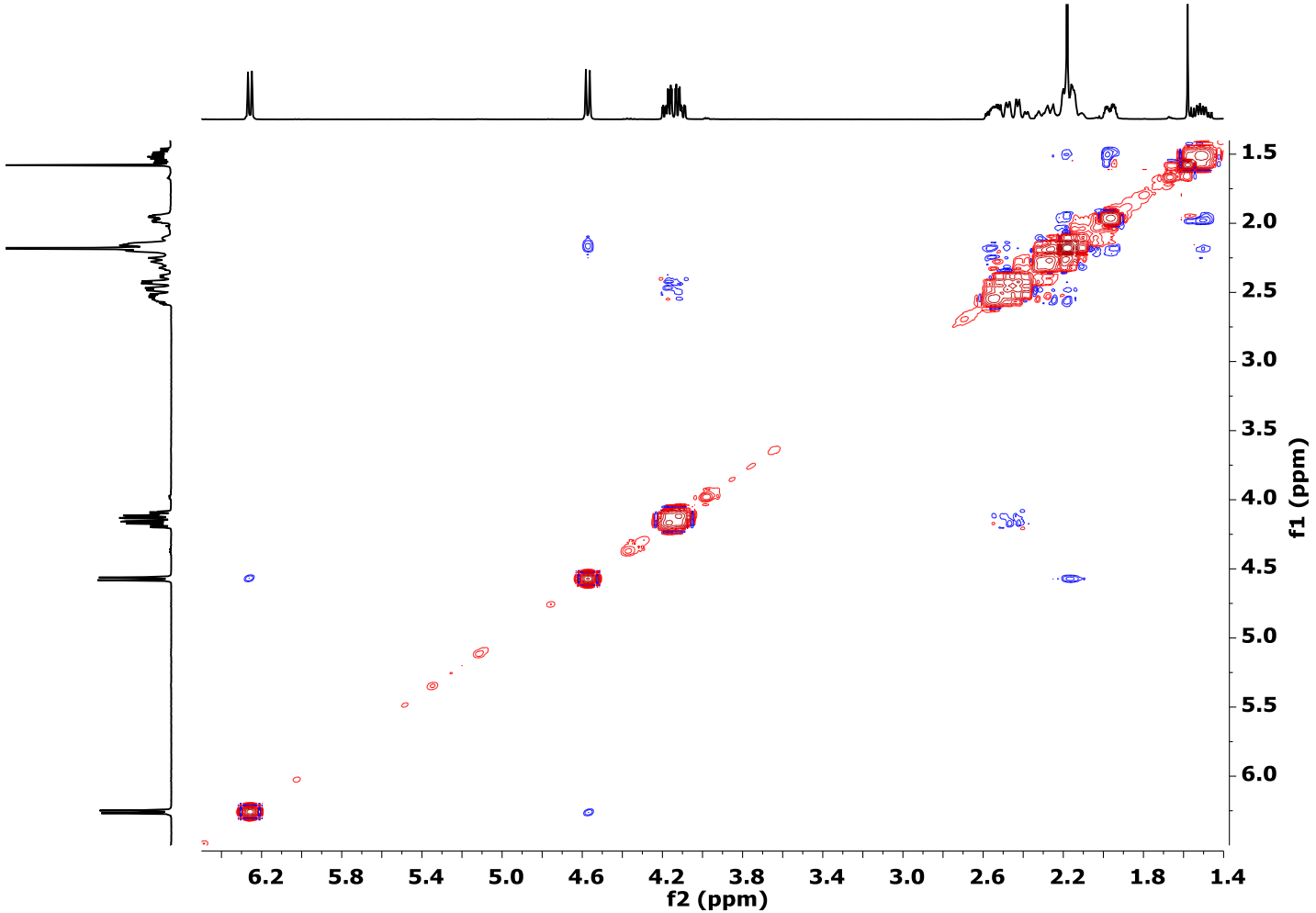

30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
f2 (ppm)

2D NMR COSY

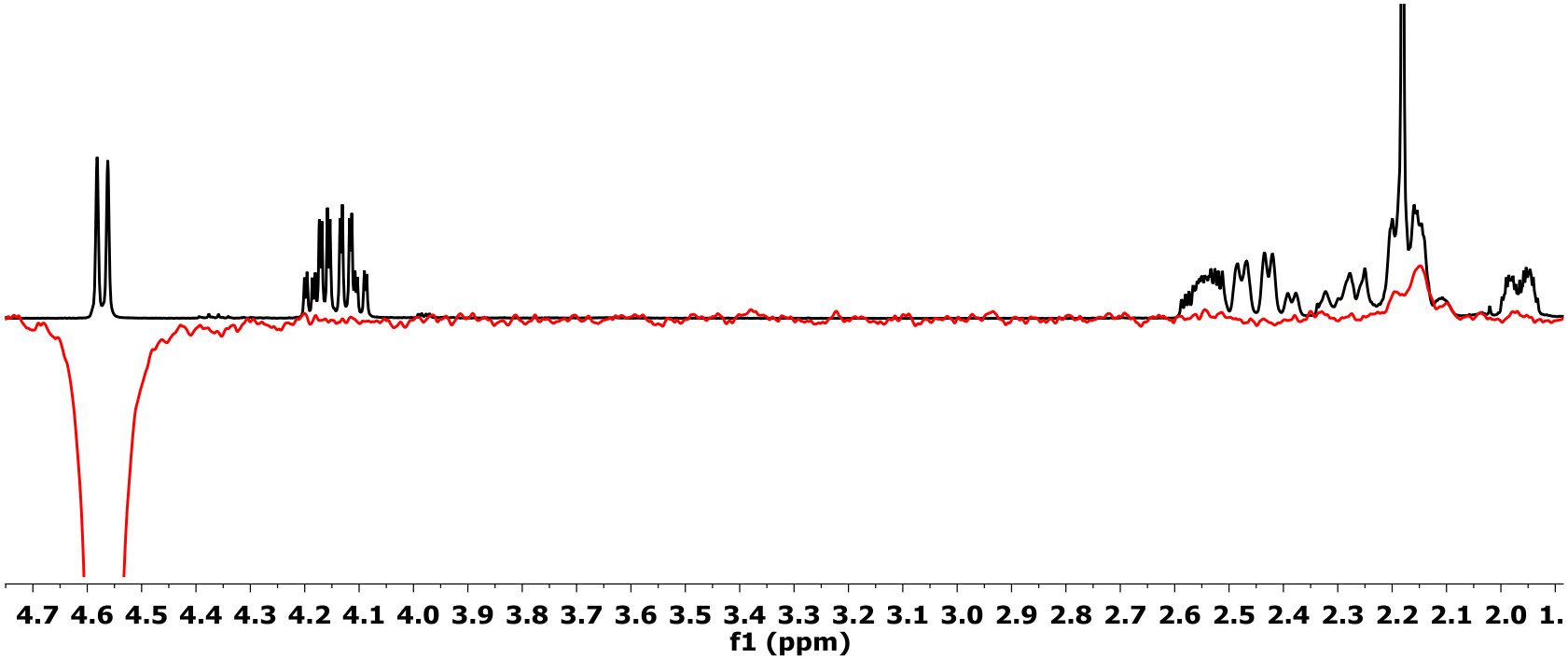

6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
f1 (ppm)


1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
f1 (ppm)
2.55
2.45
2.35
2.25
2.15
2.05
1.95
1.85
1.75
1.65
1.55
1.45
f2 (ppm)

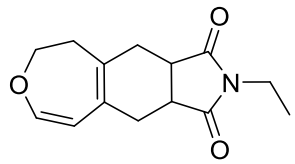
2D NMR NOESY


1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
f1 (ppm)
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
f2 (ppm)

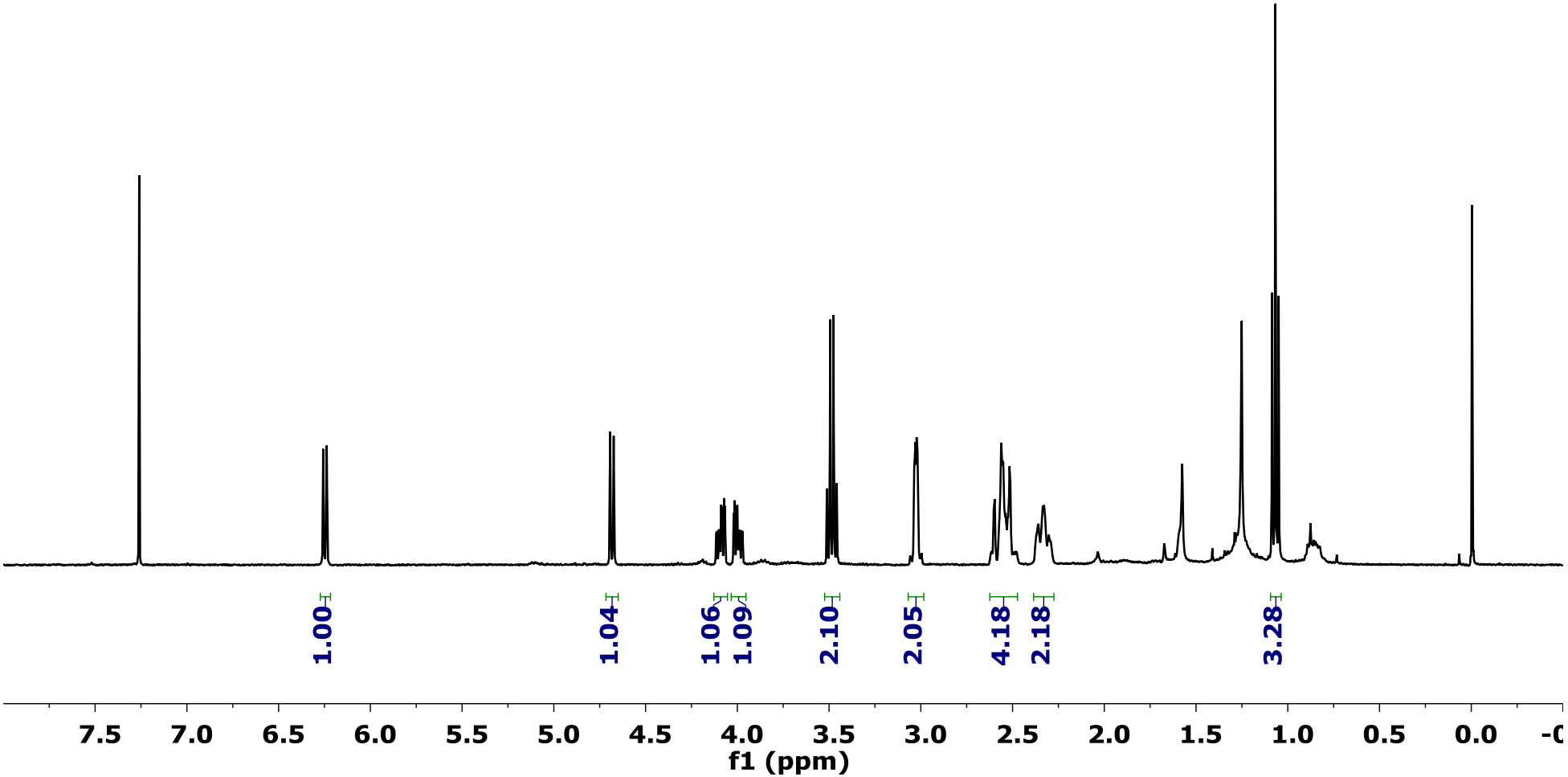
1D NMR SELECTIVE NOESY

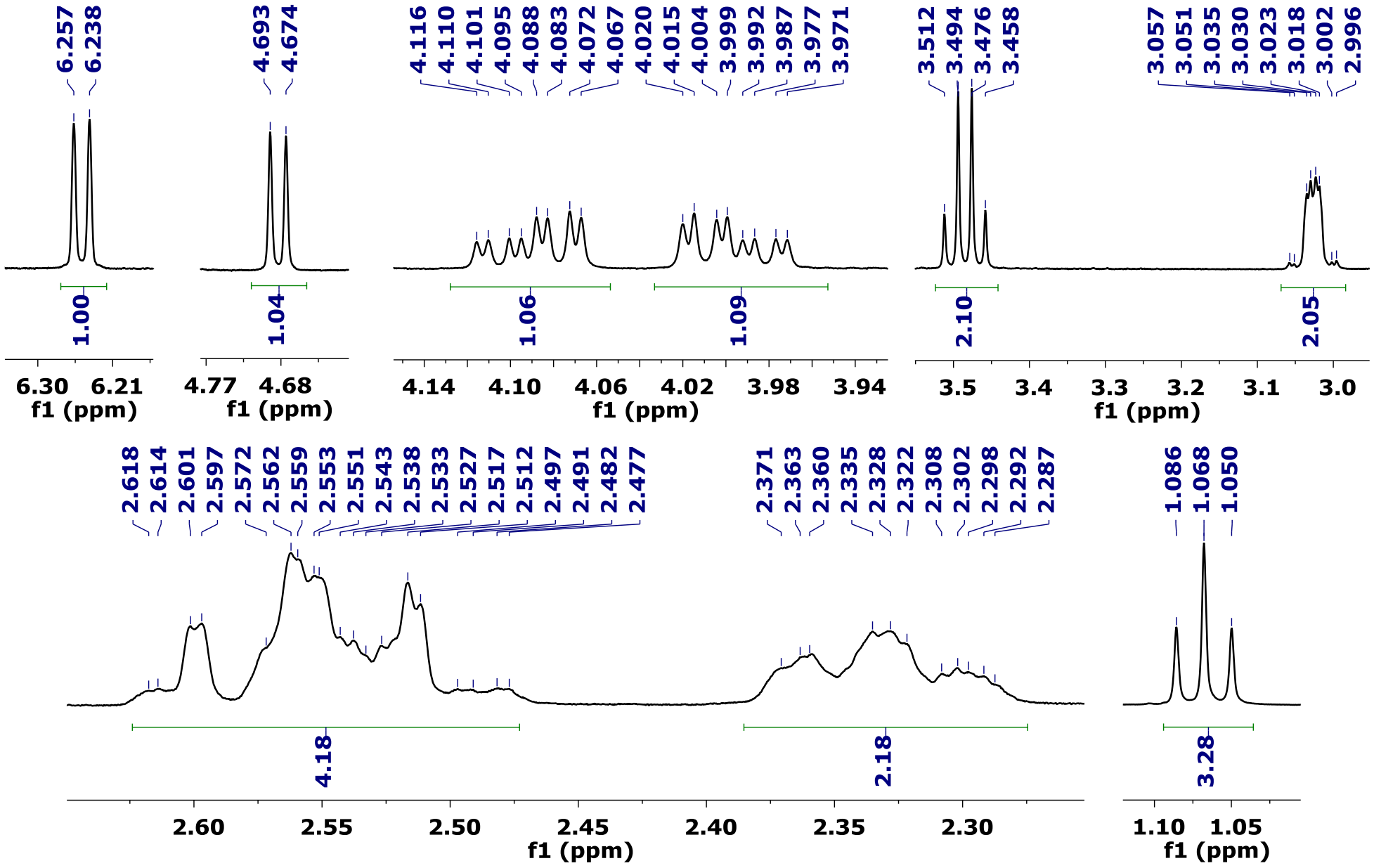


Product 3bj

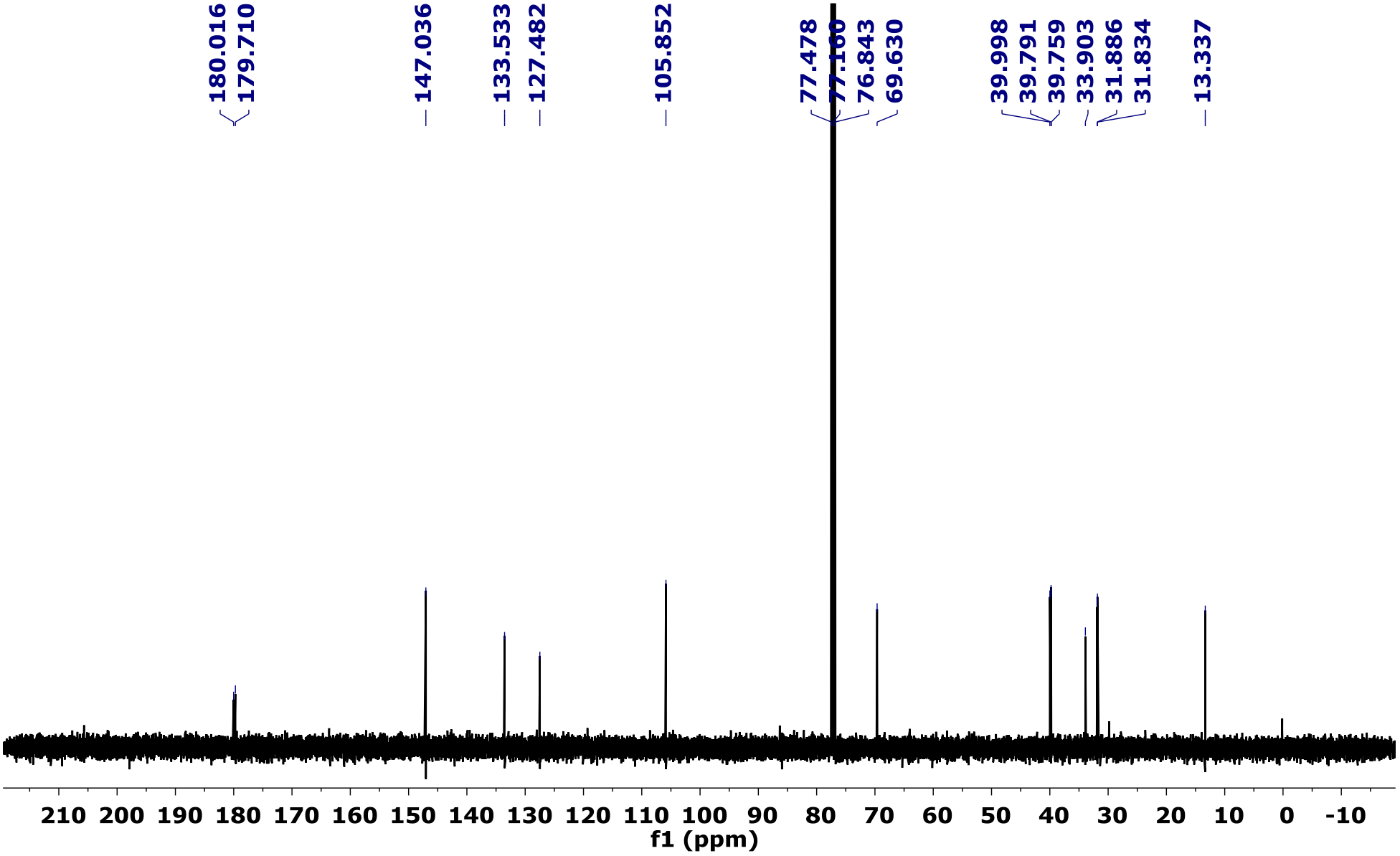


^{1}H NMR (400 MHz, $CDCl_3$)

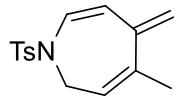



6.257
6.238
4.693
4.674
4.116
4.110
4.101
4.095
4.088
4.083
4.072
4.067
4.020
4.015
4.004
3.999
3.992
3.987
3.977
3.971
3.512
3.494
3.476
3.458
3.057
3.051
3.035
3.030
3.023
3.018
3.002
2.996
1.00
1.04
1.06
1.09
2.10
2.05
6.30
6.21
f1 (ppm)
4.77
4.68
f1 (ppm)
4.14
4.10
4.06
4.02
3.98
3.94
f1 (ppm)
3.5
3.4
3.3
3.2
3.1
3.0
f1 (ppm)
2.618
2.614
2.601
2.597
2.572
2.562
2.559
2.553
2.551
2.543
2.538
2.533
2.527
2.517
2.512
2.497
2.491
2.482
2.477
2.371
2.363
2.360
2.335
2.328
2.322
2.308
2.302
2.298
2.292
2.287
1.086
1.068
1.050
4.18
2.18
3.28
2.60
2.55
2.50
2.45
2.40
2.35
2.30
f1 (ppm)
1.10
1.05
f1 (ppm)

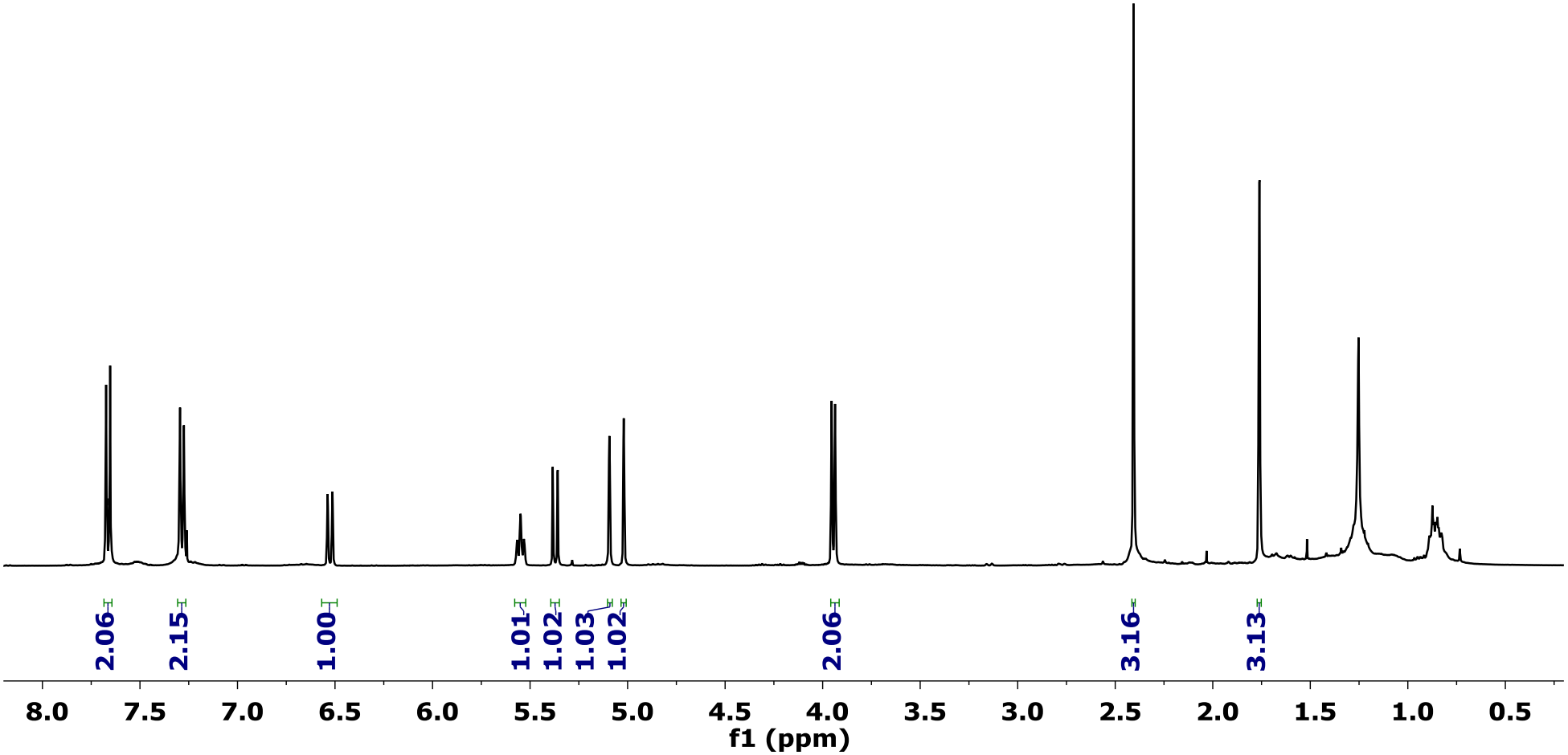
^{13}C NMR (101 MHz, $CDCl_3$)

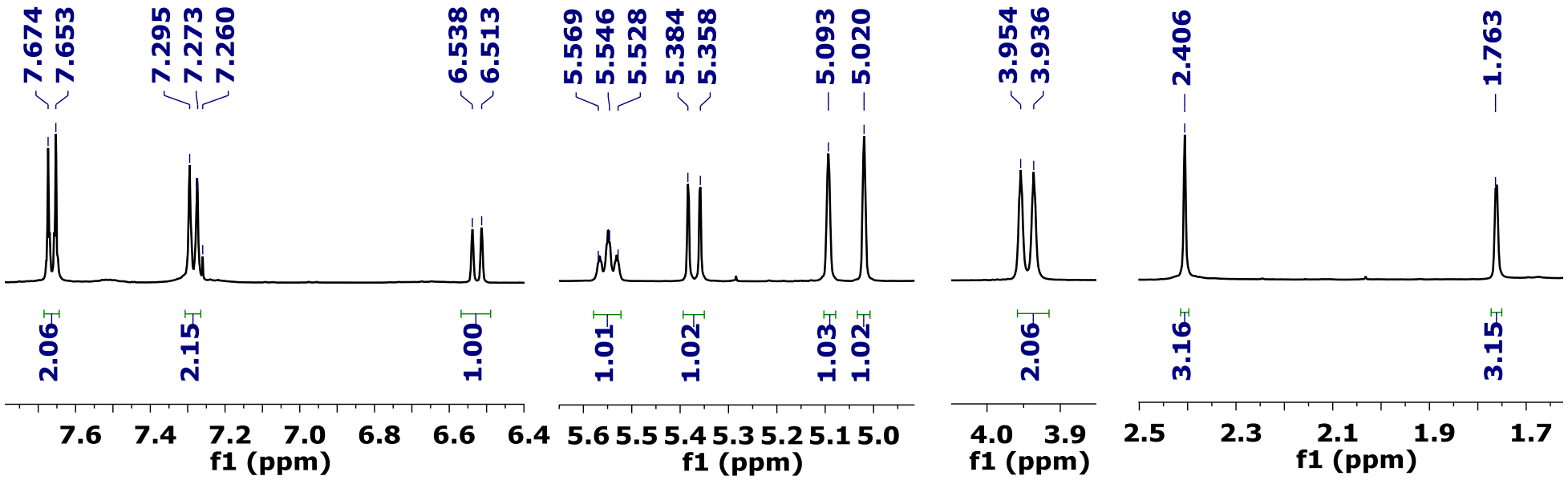


Product 4a

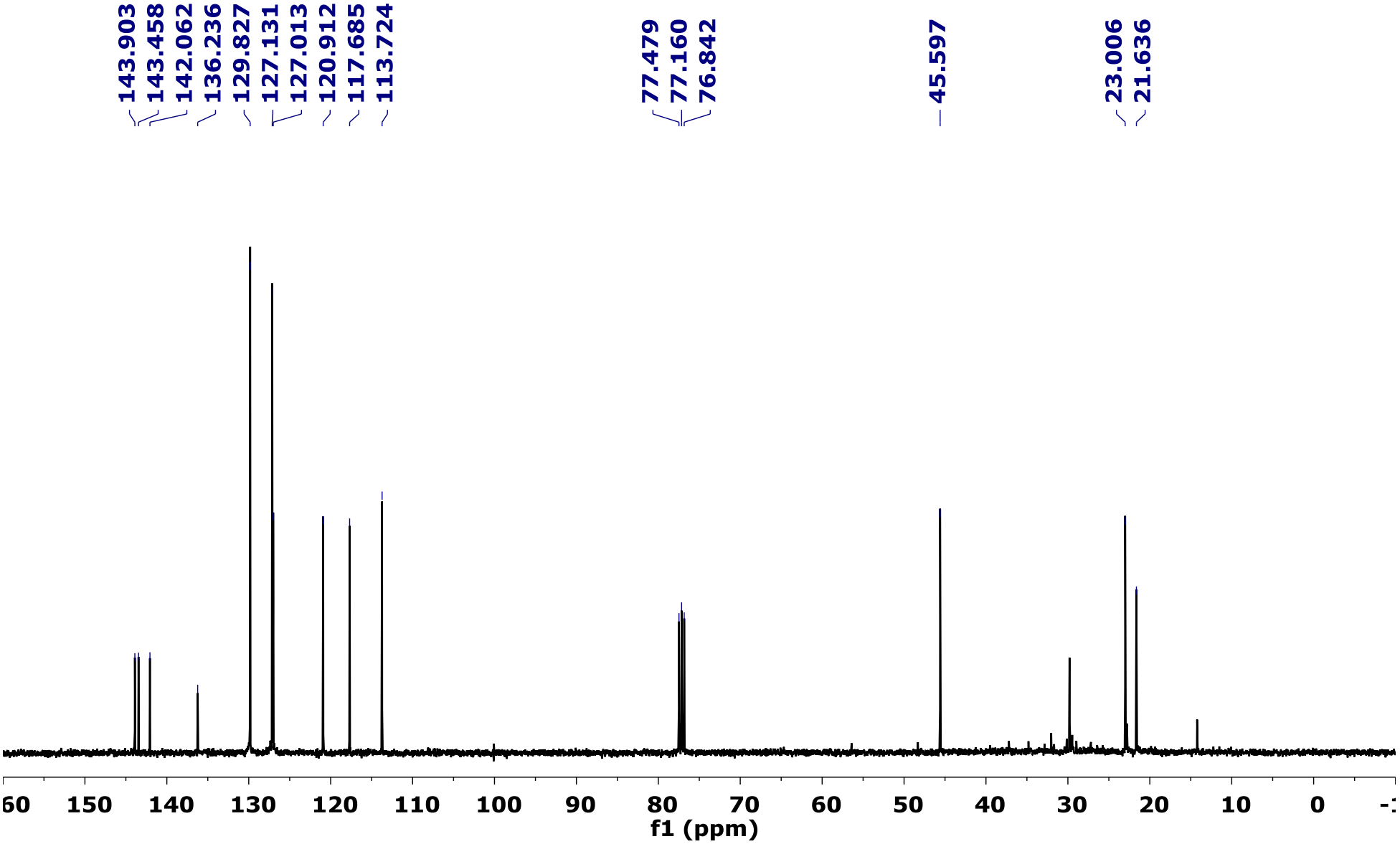


^{1}H NMR (400 MHz, $CDCl_3$)

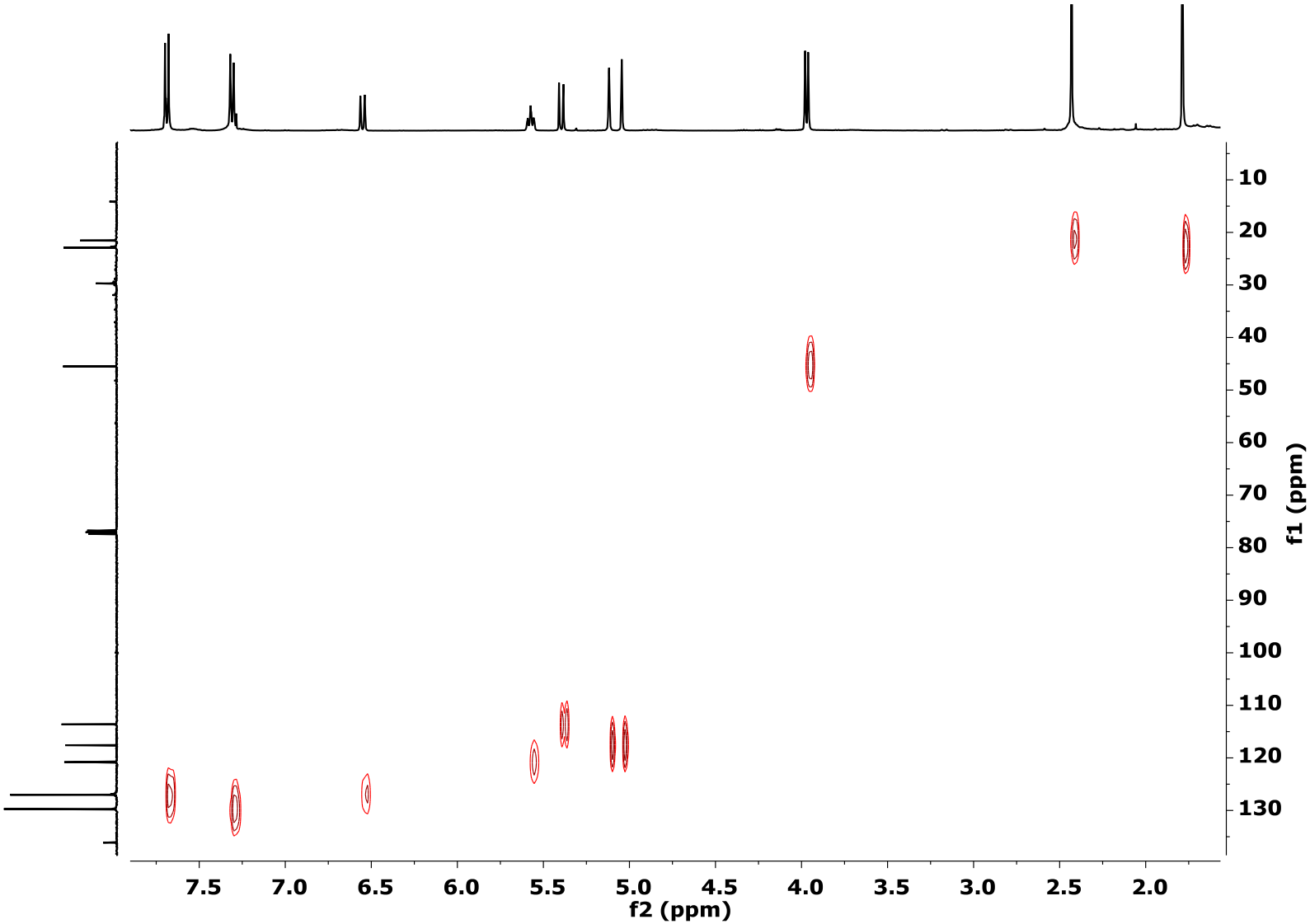



7.674
7.653
7.295
7.273
7.260
6.538
6.513
5.569
5.546
5.528
5.384
5.358
5.093
5.020
3.954
3.936
2.406
1.763
2.06
2.15
1.00
1.01
1.02
1.03
1.02
2.06
3.16
3.15
7.6 7.4 7.2 7.0 6.8 6.6 6.4
5.6 5.5 5.4 5.3 5.2 5.1 5.0
4.0 3.9
2.5 2.3 2.1 1.9 1.7
f1 (ppm)

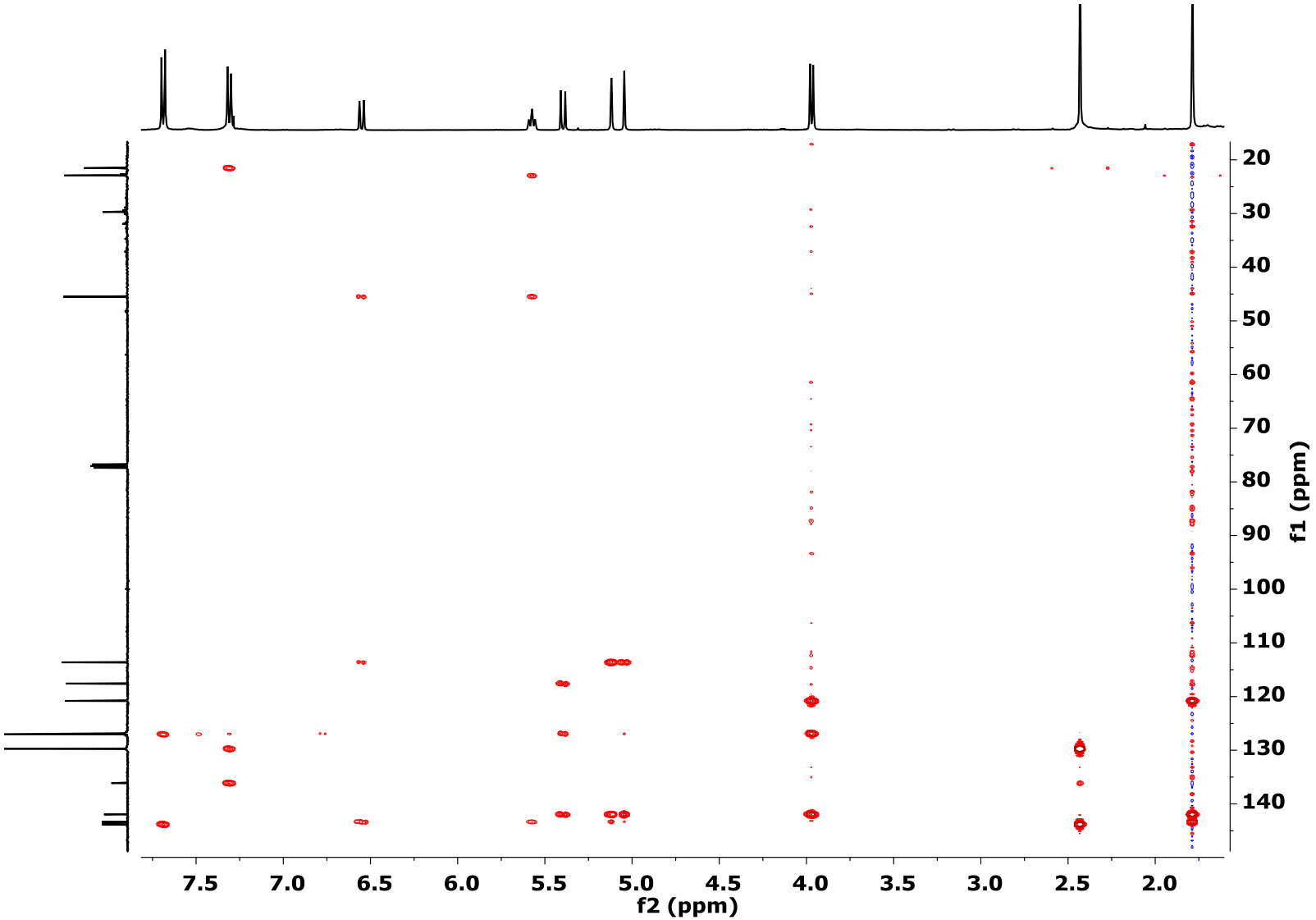
^{13}C NMR (101 MHz, $CDCl_3$)



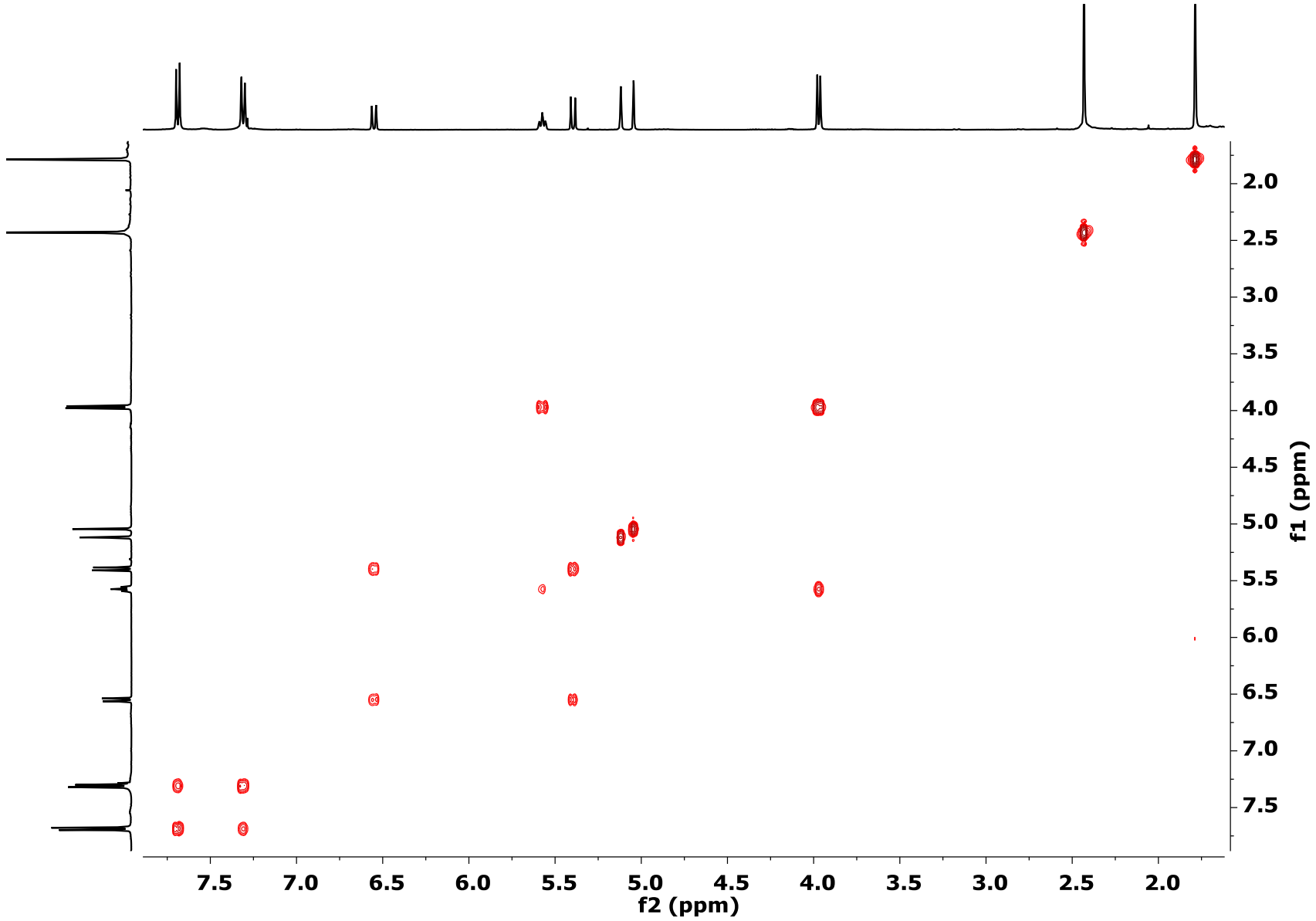
2D NMR HSQC


10
20
30
40
50
60
70
80
90
100
110
120
130
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)

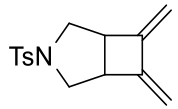
2D NMR HMBC


20
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)

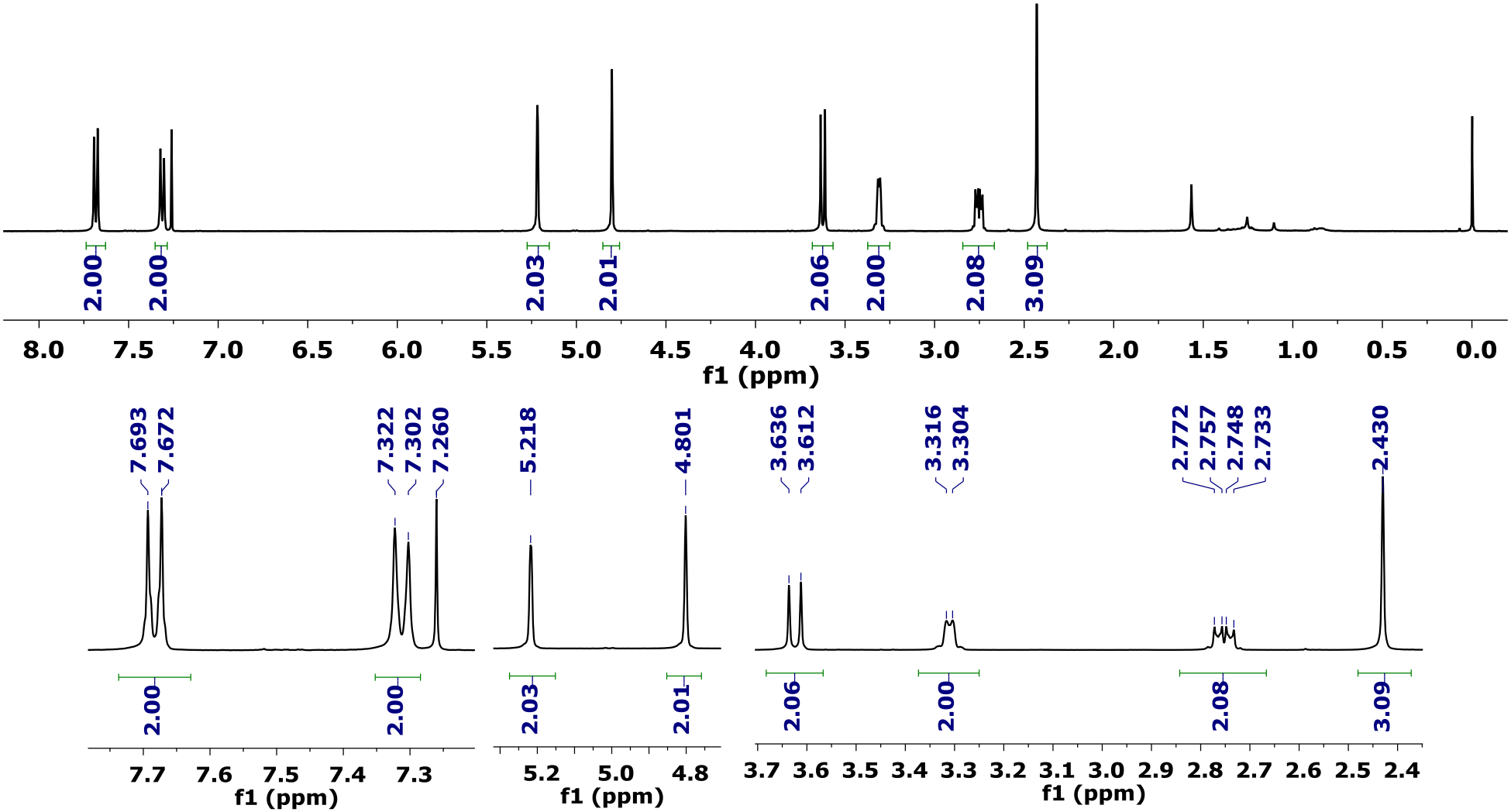
2D NMR COSY

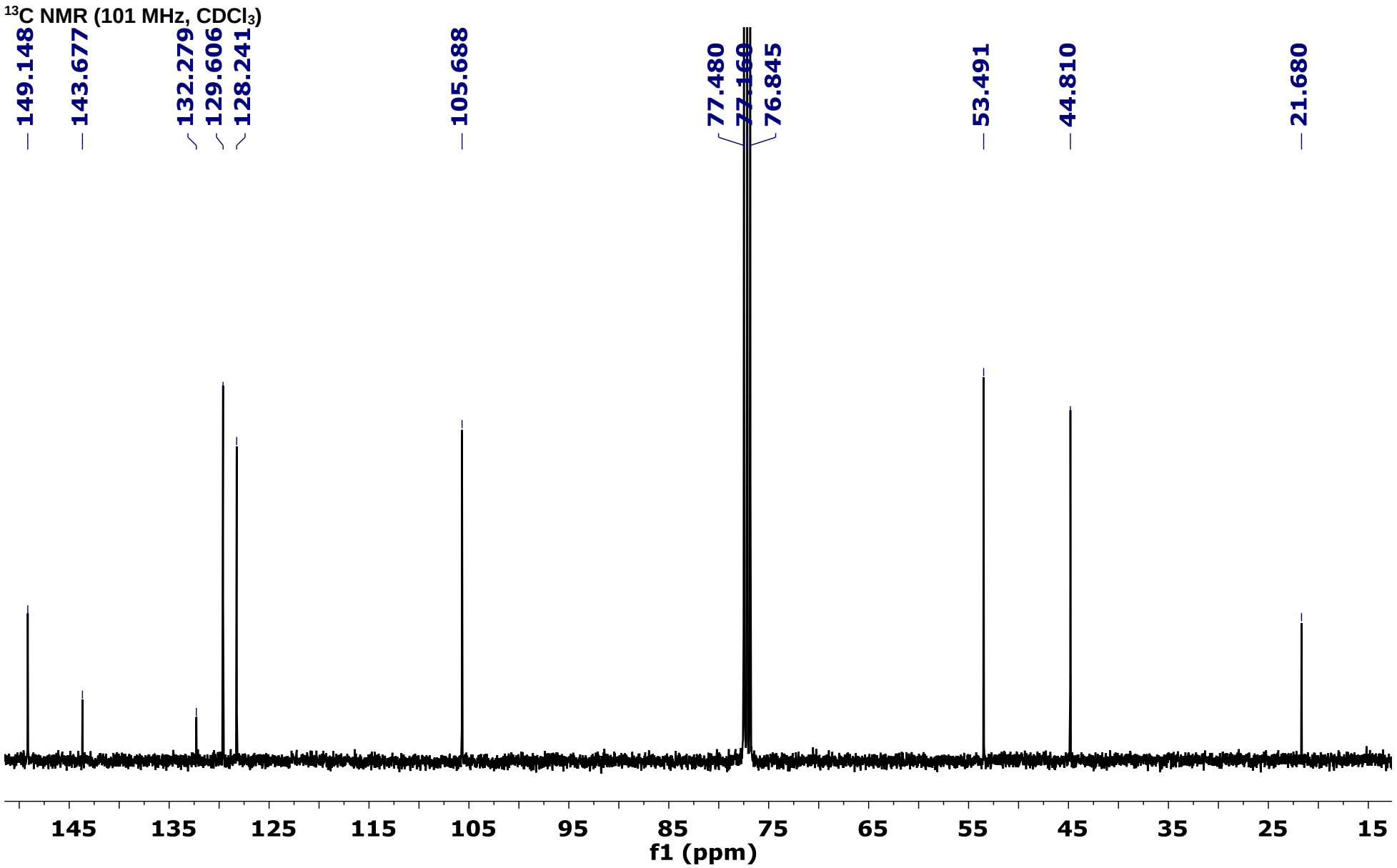

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)

Product 5a

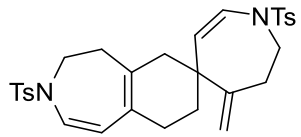


^{1}H NMR (400 MHz, $CDCl_3$)

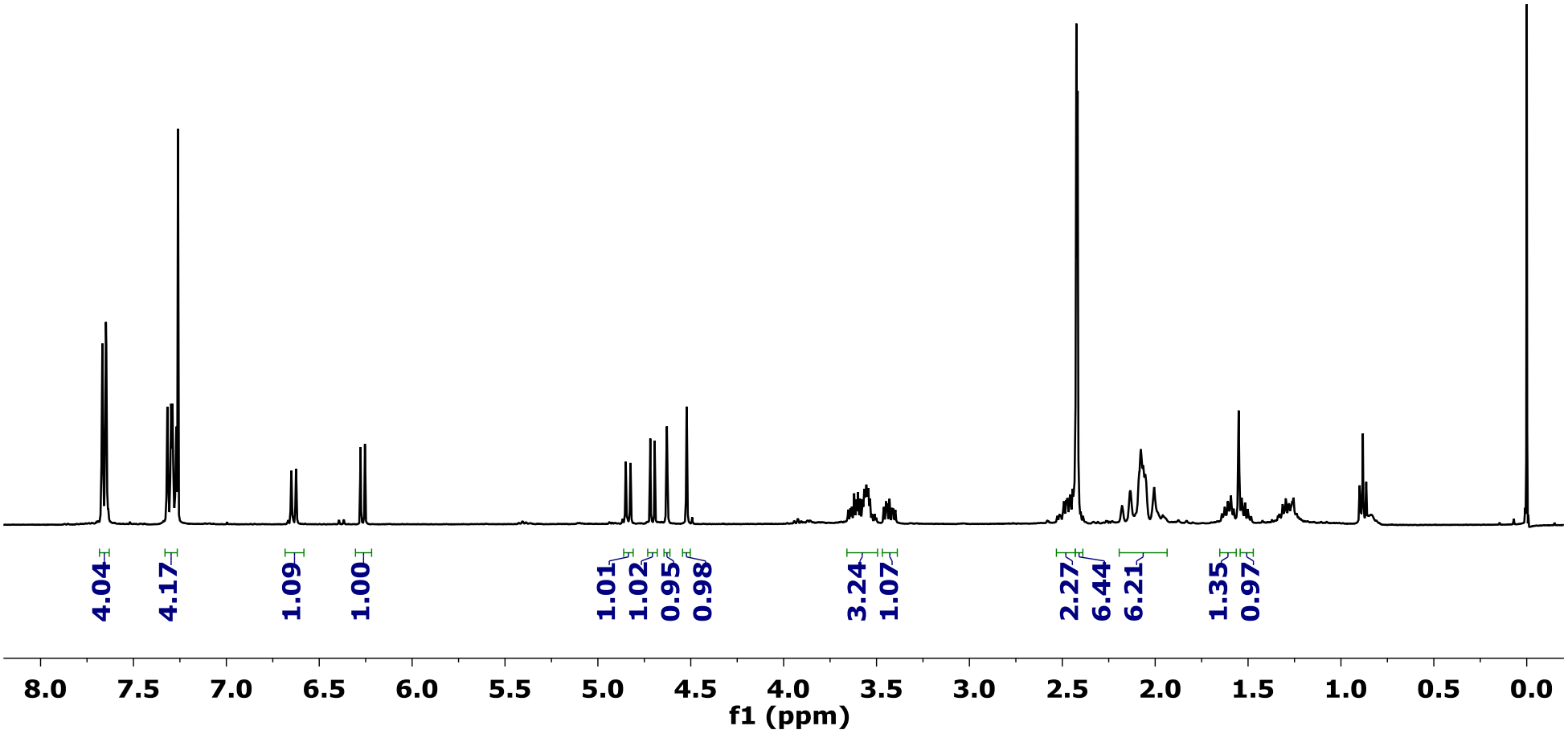


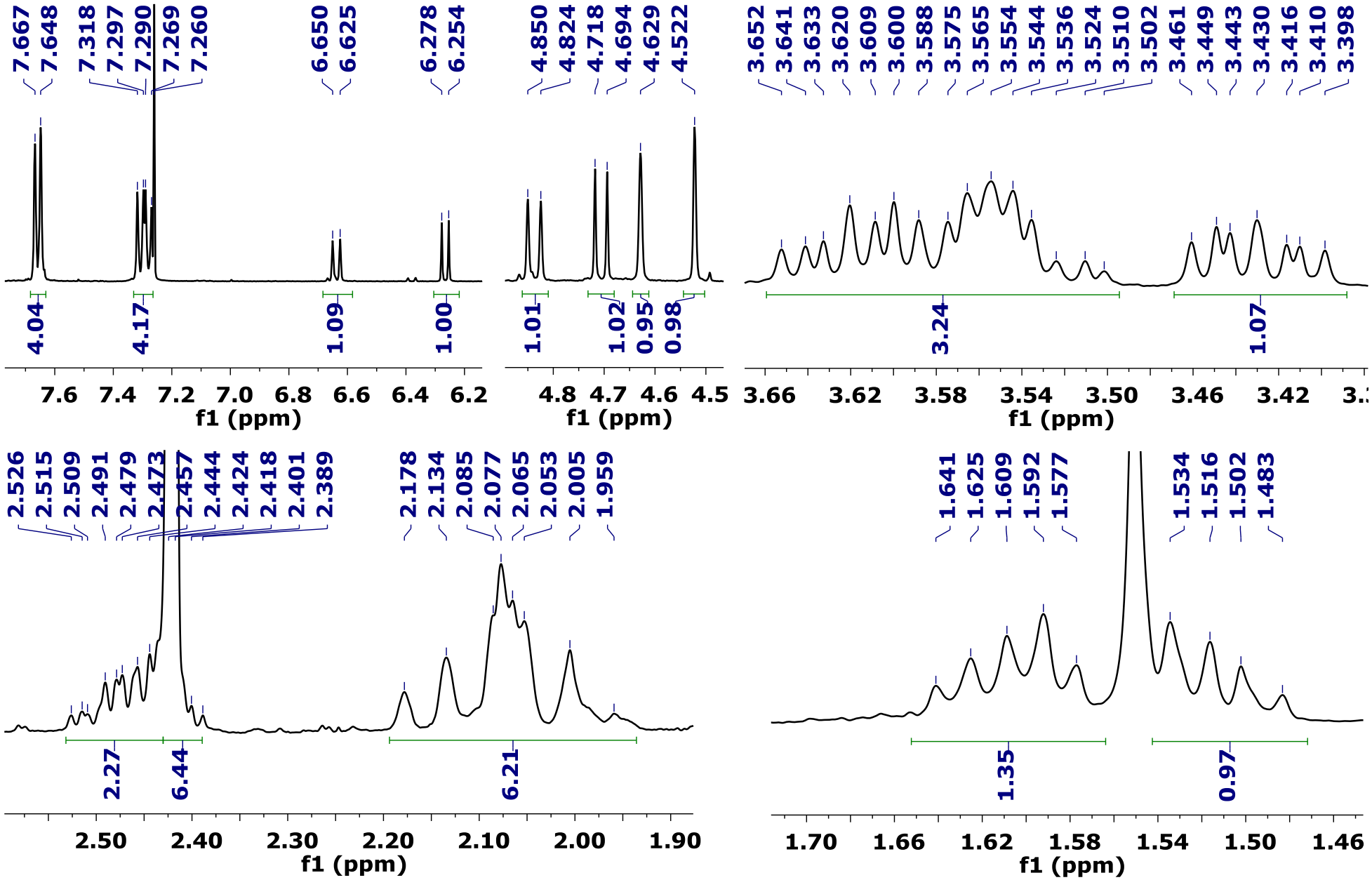

^{13}C NMR (101 MHz, $CDCl_3$)
149.148
143.677
132.279
129.606
128.241
105.688
77.480
77.160
76.845
53.491
44.810
21.680
145
135
125
115
105
95
85
75
65
55
45
35
25
15
f1 (ppm)

Product 6a

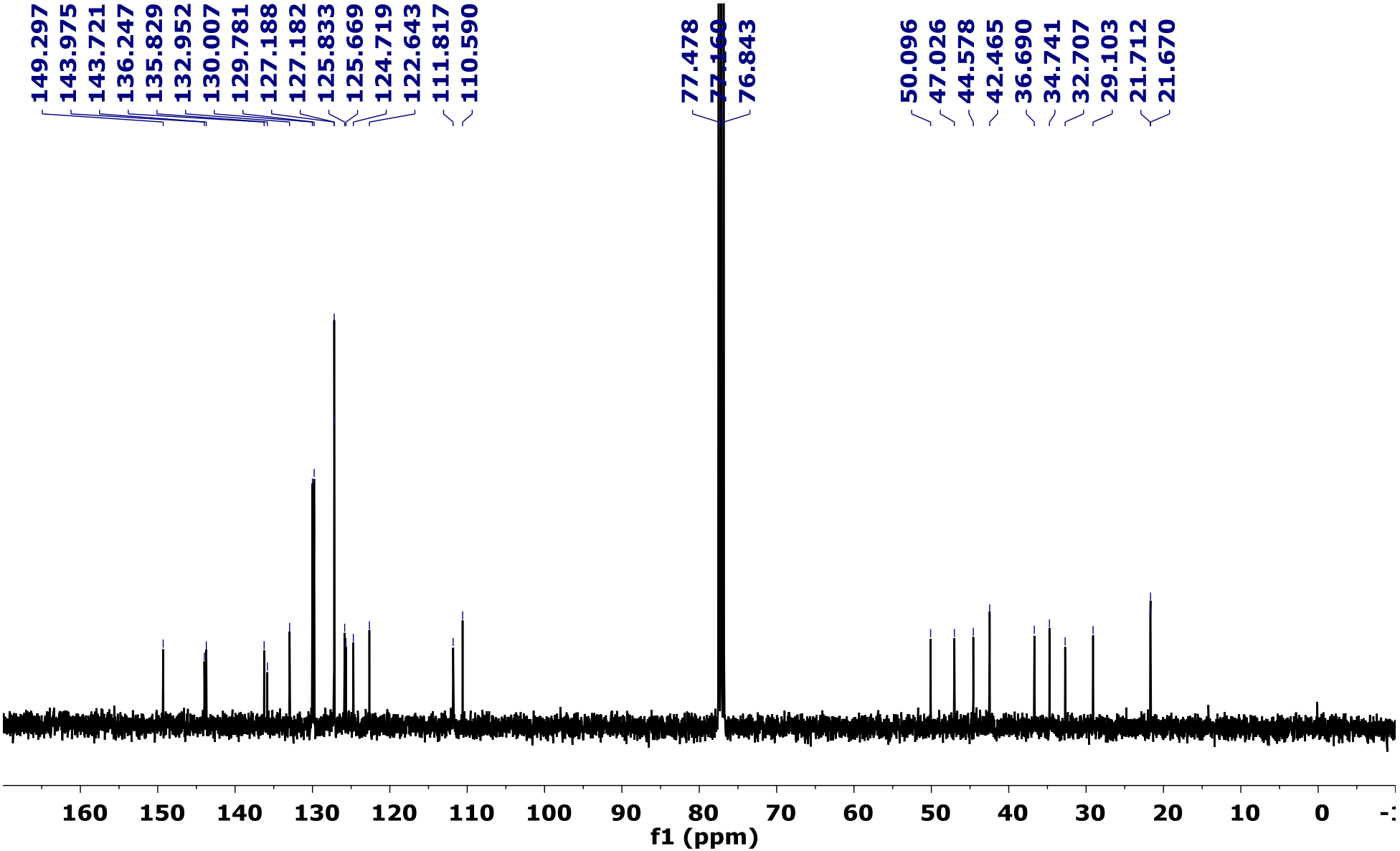


^{1}H NMR (400 MHz, $CDCl_3$)

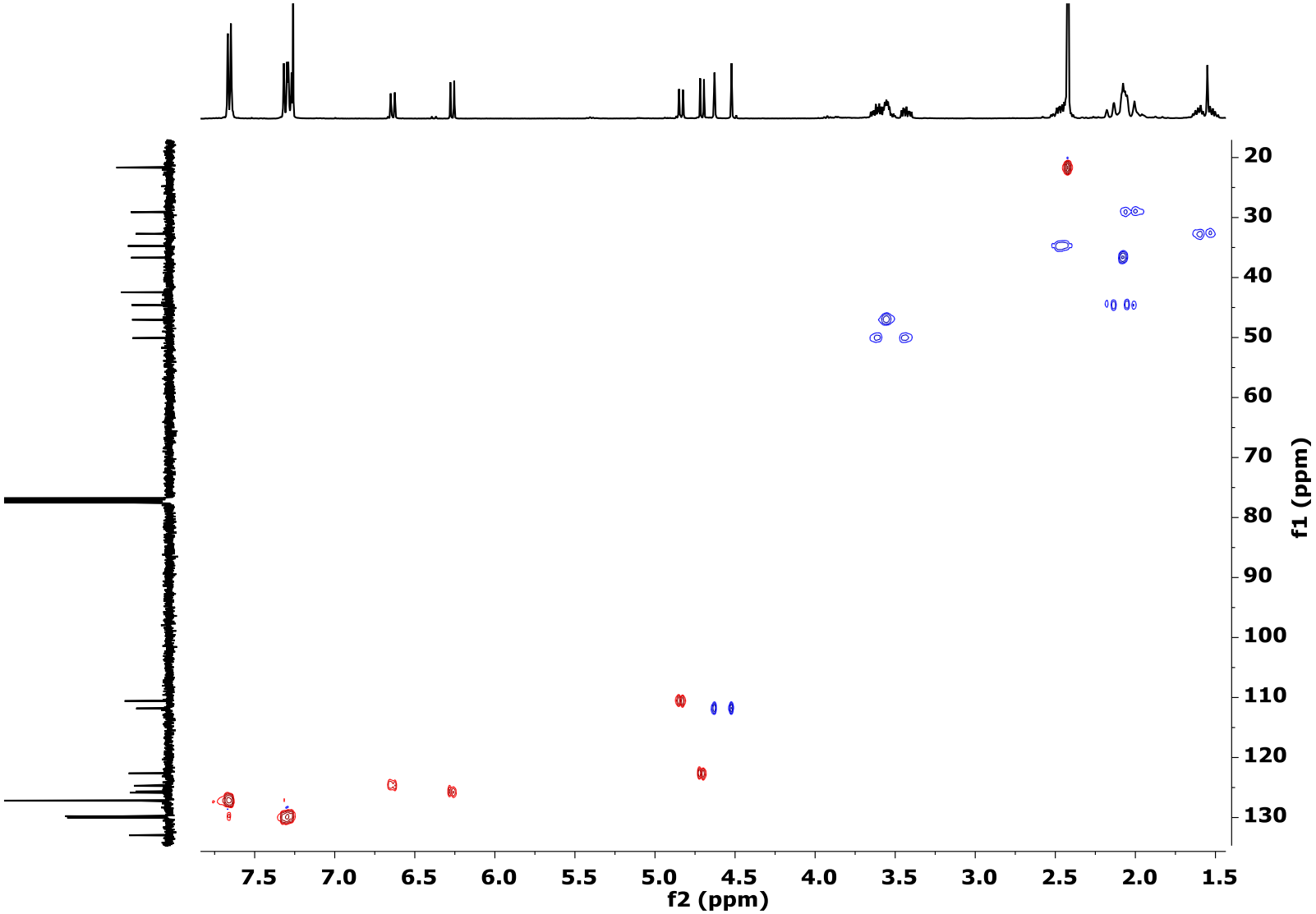



7.667
7.648
7.318
7.297
7.290
7.269
7.260
6.650
6.625
6.278
6.254
4.04
4.17
1.09
1.00
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2
f1 (ppm)
4.850
4.824
4.718
4.694
4.629
4.522
1.01
1.02
0.95
0.98
4.8 4.7 4.6 4.5
f1 (ppm)
3.652
3.641
3.633
3.620
3.609
3.600
3.588
3.575
3.565
3.554
3.544
3.536
3.524
3.510
3.502
3.461
3.449
3.443
3.430
3.416
3.410
3.398
3.24
1.07
3.66 3.62 3.58 3.54 3.50 3.46 3.42
f1 (ppm)
2.526
2.515
2.509
2.491
2.479
2.473
2.457
2.444
2.424
2.418
2.401
2.389
2.178
2.134
2.085
2.077
2.065
2.053
2.005
1.959
2.27
6.44
6.21
2.50 2.40 2.30 2.20 2.10 2.00 1.90
f1 (ppm)
1.641
1.625
1.609
1.592
1.577
1.534
1.516
1.502
1.483
1.35
0.97
1.70 1.66 1.62 1.58 1.54 1.50 1.46
f1 (ppm)

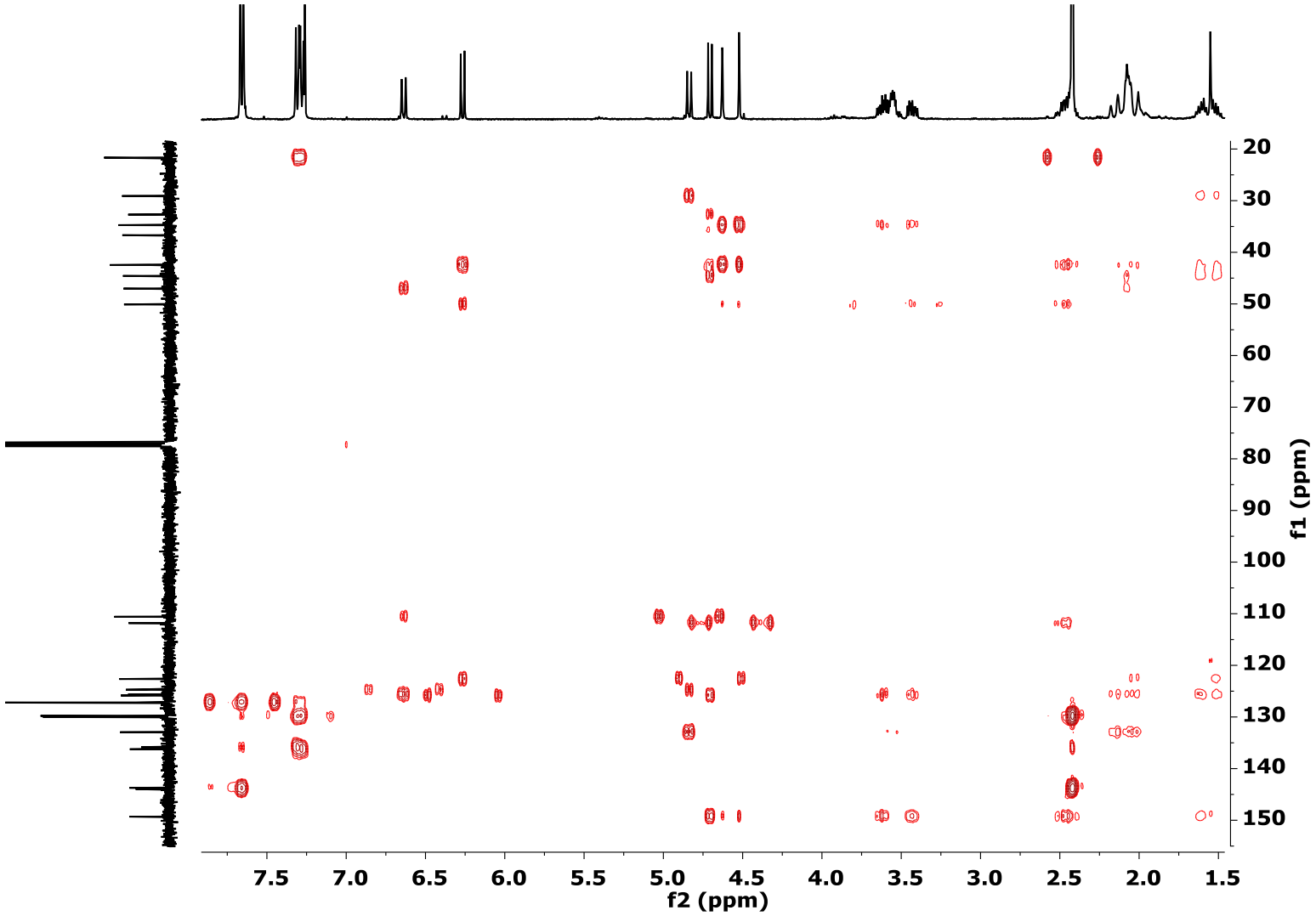
^{13}C NMR (101 MHz, $CDCl_3$)



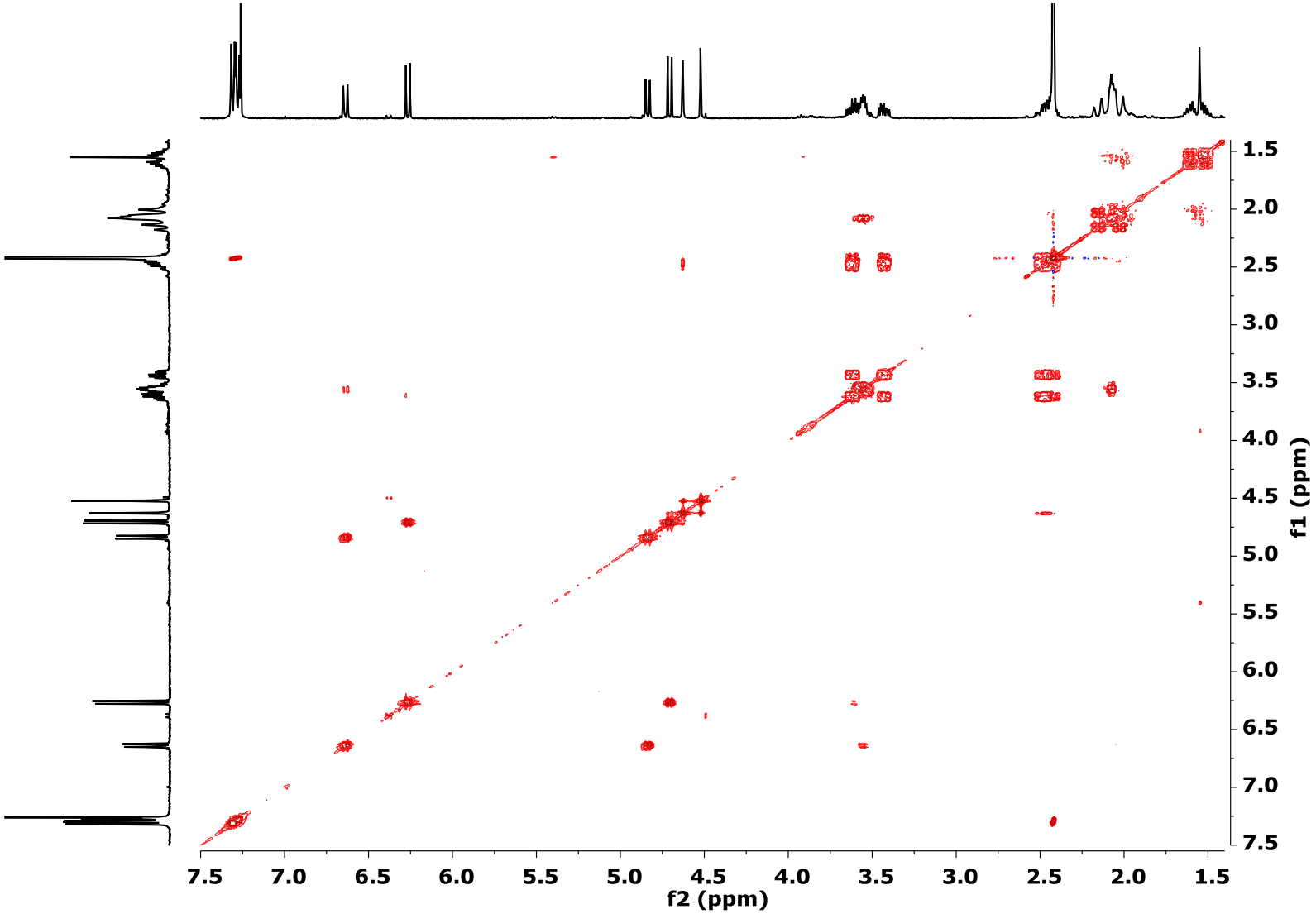
2D NMR HSQC

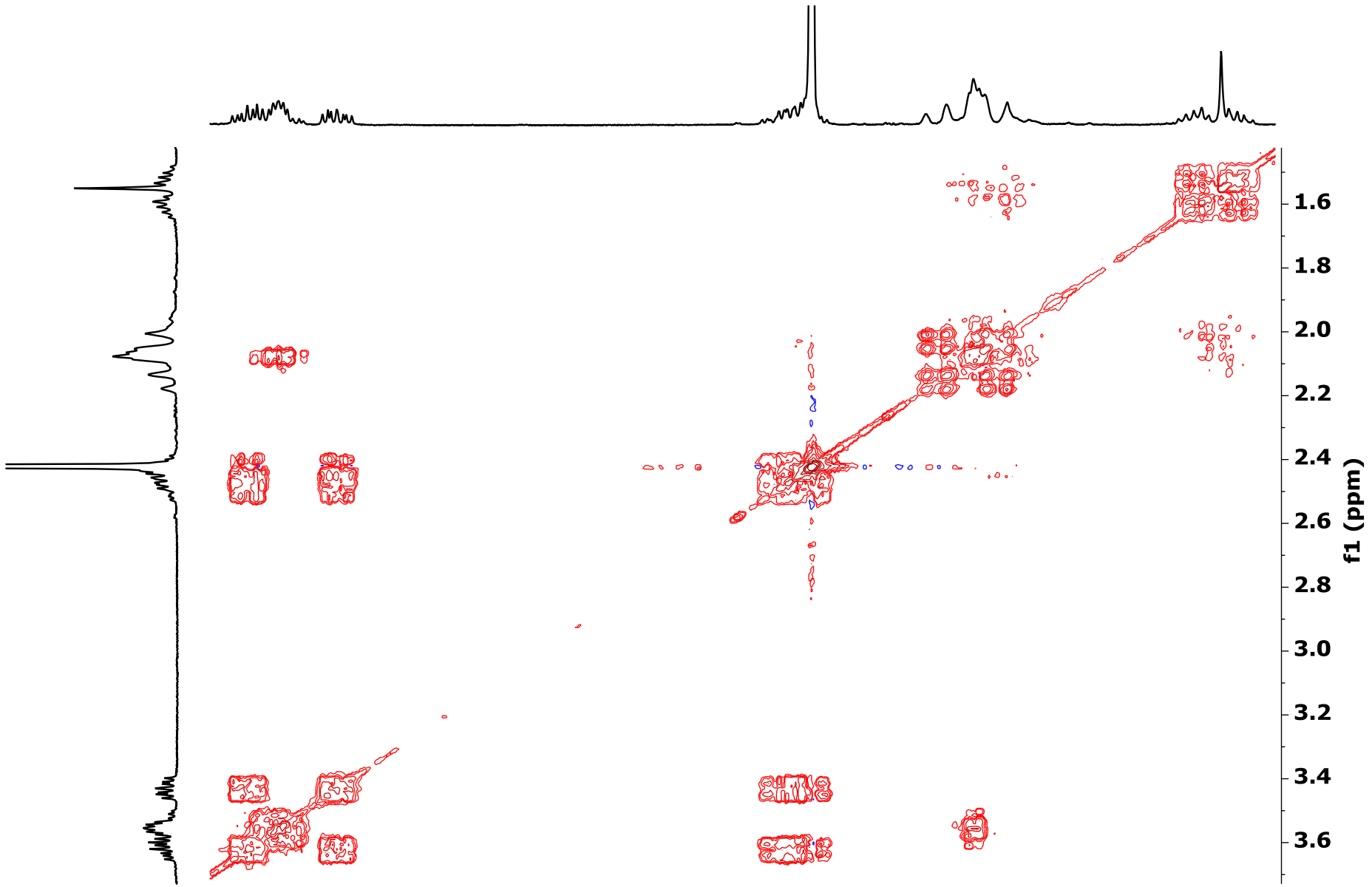

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
120
130
f1 (ppm)

2D NMR HMBC

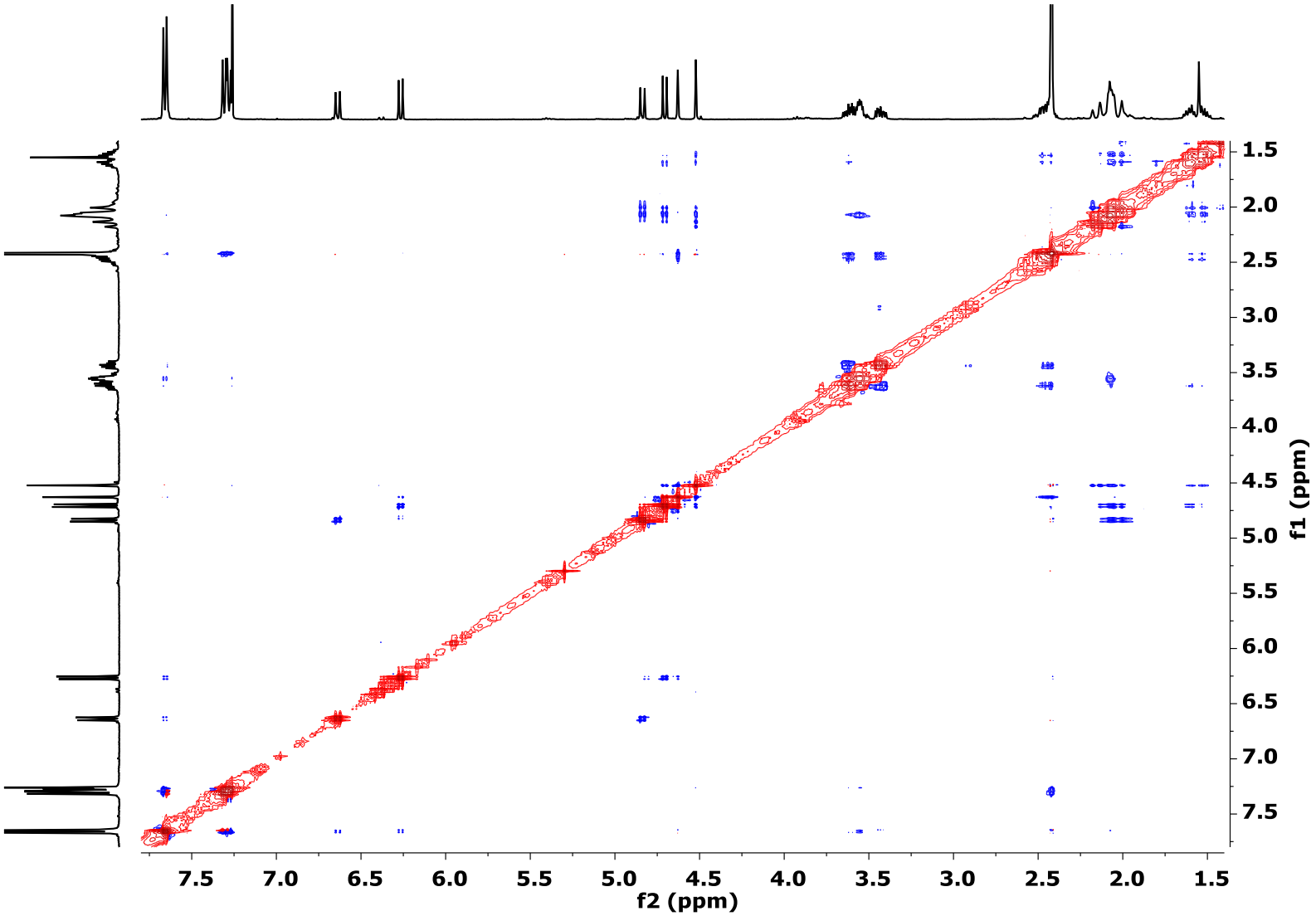

20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)

2D NMR COSY




1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
f1 (ppm)
3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5
f2 (ppm)

2D NMR NOESY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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
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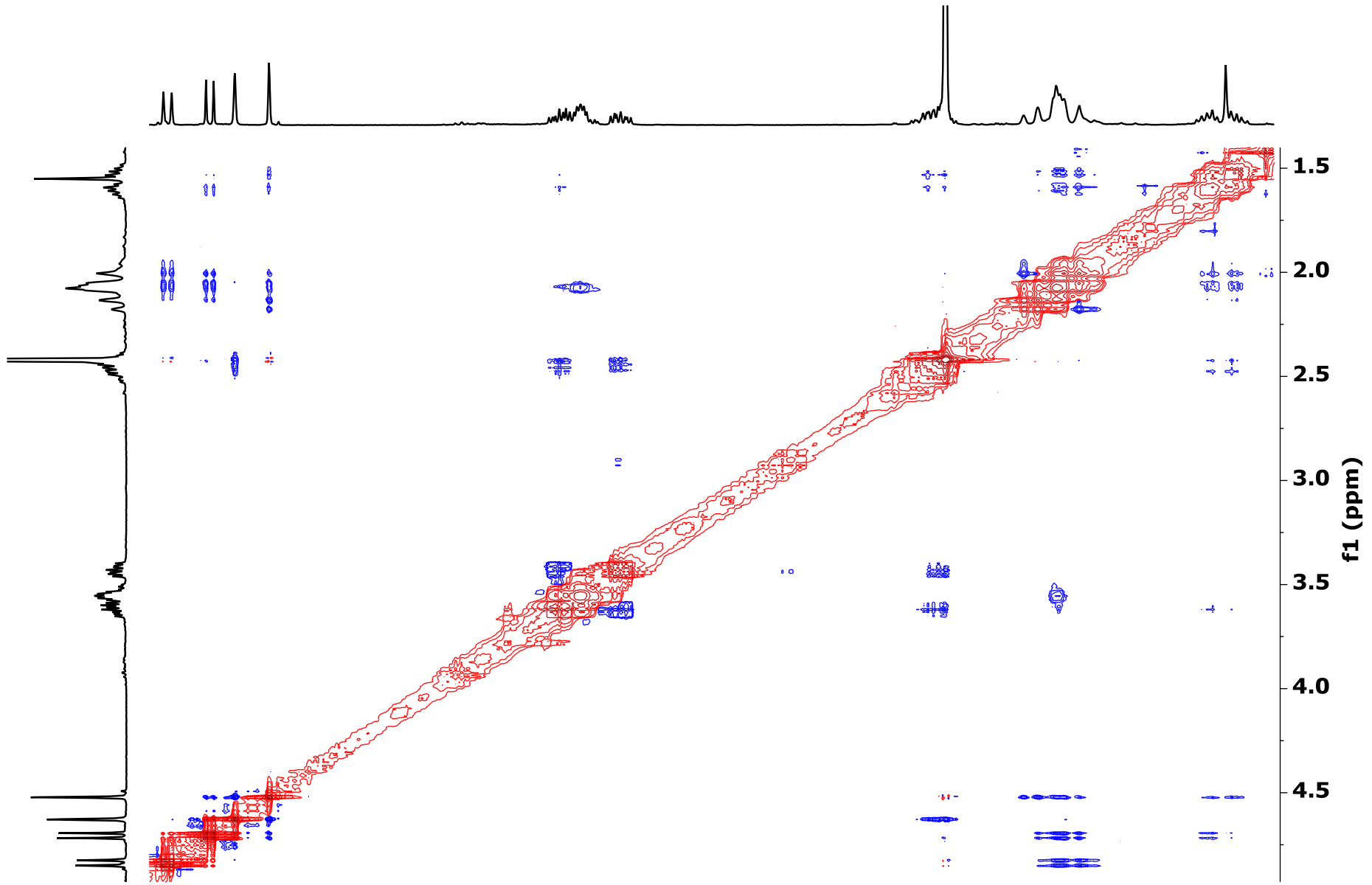
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)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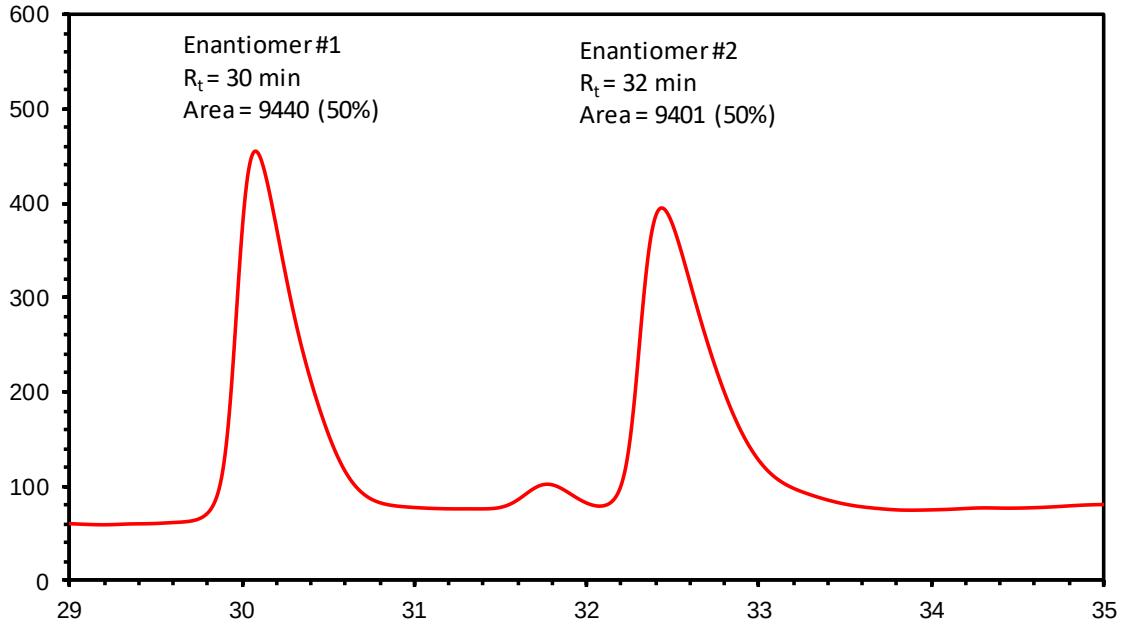
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
f1 (ppm)

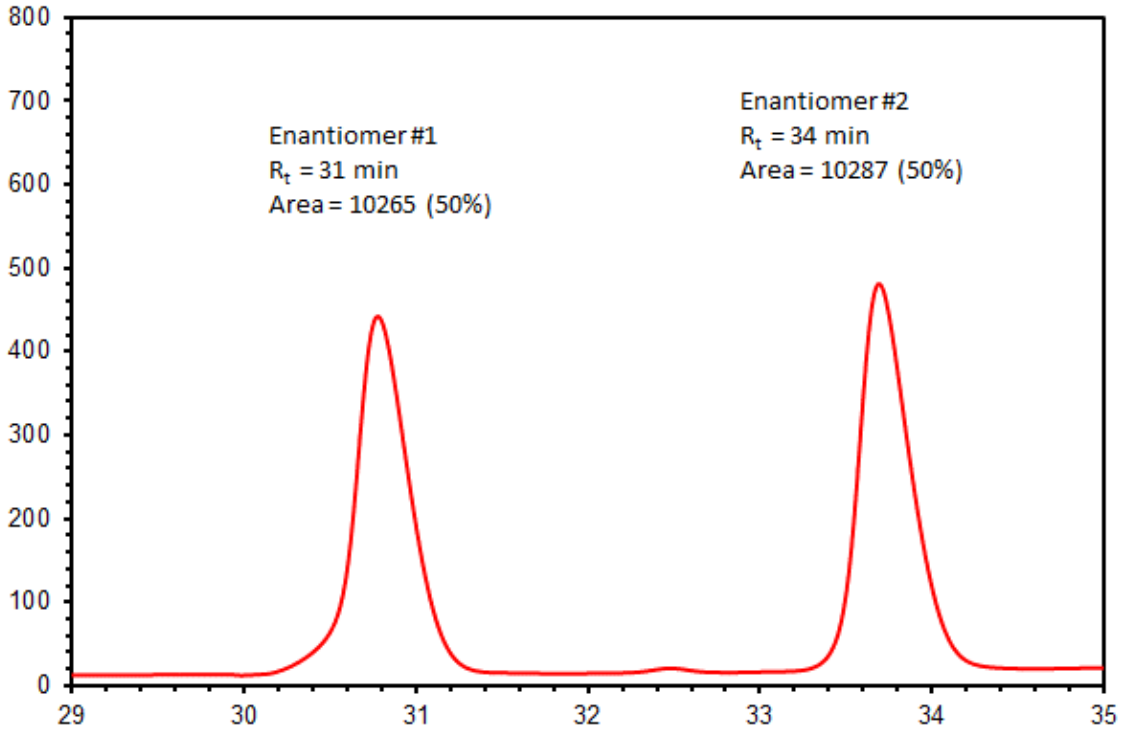
HPLC

Figure S1. HPLC trace of compound 3aa obtained using (±)-BINAP as a phosphine ligand.



Conditions: Chiralpak IA column (4.6 x 250 mm, 5 μm); 1 mL/min flow rate; 100% hexane → 20% 2-propanol in hexane; 40 min.; λ = 254 nm.

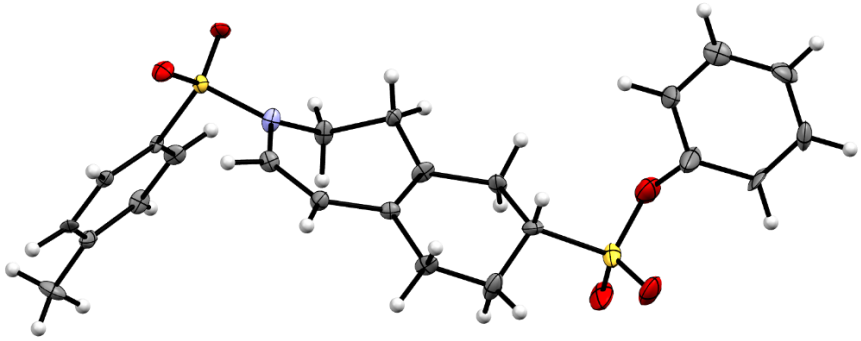
Figure S2. HPLC trace of compound 3aa obtained under optimal conditions, using *(R)*-DTBM-Segphos as a phosphine ligand.



Conditions: Chiralpak IA column (4.6 x 250 mm, 5 μm); 1 mL/min flow rate; 100% hexane → 20% 2-propanol in hexane; 40 min.; λ = 254 nm.

Crystal structure of compound 3am

Figure S3: ORTEP representation of compound 3am with probability level of 30%.



Colourless needle-like crystals of **3am** were grown at 2-6 °C using a layered solution approach. The bottom solution layer, contained within a long straight tube, consisted of the compound **3am** dissolved in CH_2Cl_2. Pentane was carefully placed on top using a syringe. The X-ray intensity data were measured on a three-circle diffractometer system equipped with a Ceramic x-ray tube (Mo Kα, λ = 0.71073 Å) and a doubly curved silicon crystal Bruker Triumph monochromator.

A total of 546 frames were collected. The total exposure time was 9.10 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 15117 reflections to a maximum θ angle of 27.55° (0.77 Å resolution), of which 4959 were independent (average redundancy 3.048, completeness = 98.7%, R_{int} = 4.56%, R_{sig} = 5.51%) and 4430 (89.33%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.7010(15) Å, b = 7.8929(11) Å, c = 11.8094(14) Å, β = 94.717(4)°, volume = 1087.0(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 8874 reflections above 20 σ(I) with 6.214° < 2θ < 54.22°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.619. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9080 and 0.9780.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21 1, with Z = 2 for the formula unit, $C_{23}H_{25}NO_5S_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 270 variables converged at R1 = 12.75%, for the observed data and wR2 = 33.18% for all data. The goodness-of-fit was 1.109. The largest peak in the final difference electron density synthesis was 2.362 $e^-/Å^3$ and the largest hole was -0.894 $e^-/Å^3$ with an RMS deviation of 0.176 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.404 g/cm^3 and F(000), 484 e^-.

Table S2. Sample and crystal data for 3am.

Identification code	vilavadri1_2on	
Chemical formula	$C_{23}H_{25}NO_5S_2$	
Formula weight	459.56 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.080 x 0.100 x 0.350 mm	
Crystal habit	colorless needle	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 11.7010(15) Å	α = 90°
	b = 7.8929(11) Å	β = 94.717(4)°
	c = 11.8094(14) Å	γ = 90°
Volume	1087.0(2) $Å^3$	
Z	2	
Density (calculated)	1.404 g/cm^3	
Absorption coefficient	0.281 mm^{-1}	
F(000)	484	

Table S3. Data collection and structure refinement for 3am.

Diffractometer	Bruker D8 QUEST ECO three-circle diffractometer	
Radiation source	Ceramic x-ray tube (Mo Kα, λ = 0.71073 Å)	
Theta range for data collection	3.11 to 27.55°	
Index ranges	-15<=h<=15, -10<=k<=10, -13<=l<=15	
Reflections collected	15117	
Independent reflections	4959 [R(int) = 0.0456]	
Coverage of independent reflections	98.7%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9780 and 0.9080	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4959 / 1 / 270	
Goodness-of-fit on F^2	1.109	
Final R indices	4430 data; I>2σ(I)	R1 = 0.1275, wR2 = 0.3229
	all data	R1 = 0.1388, wR2 = 0.3318
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1482P)^2+10.0620P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.3(3)	
Largest diff. peak and hole	2.362 and -0.894 $eÅ^{-3}$	

R.M.S. deviation from mean 0.176 eÅ^{-3}

Table S4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for 3am.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
S22	0.7508(2)	0.7786(4)	0.4966(2)	0.0187(5)
S8	0.3208(2)	0.2537(5)	0.9766(2)	0.0328(8)
O7	0.2231(11)	0.3852(16)	0.9631(11)	0.055(3)
O9	0.2747(11)	0.0761(16)	0.9868(11)	0.054(3)
O10	0.3974(10)	0.299(2)	0.0674(9)	0.067(4)
O23	0.6954(7)	0.9390(11)	0.5040(9)	0.033(2)
O24	0.7636(8)	0.7001(12)	0.3889(7)	0.0304(19)
N16	0.6753(9)	0.6437(13)	0.5674(9)	0.026(2)
C1	0.1129(5)	0.3162(18)	0.9130(8)	0.081(9)
C2	0.0361(7)	0.2471(16)	0.9841(6)	0.043(4)
C3	0.9196(6)	0.2440(14)	0.9501(7)	0.041(3)
C4	0.8797(5)	0.3100(14)	0.8451(8)	0.045(4)
C5	0.9565(8)	0.3791(13)	0.7740(6)	0.037(3)
C6	0.0731(7)	0.3822(16)	0.8080(7)	0.050(4)
C11	0.3904(11)	0.272(2)	0.8482(10)	0.035(3)
C12	0.4224(10)	0.4510(14)	0.8256(12)	0.027(2)
C13	0.5061(11)	0.4671(14)	0.7322(10)	0.024(2)
C14	0.5154(10)	0.6445(15)	0.6939(11)	0.025(2)
C15	0.6381(10)	0.7007(14)	0.6792(11)	0.027(2)
C17	0.6890(10)	0.4717(15)	0.5488(10)	0.024(2)
C18	0.6430(11)	0.3379(16)	0.6040(10)	0.026(2)
C19	0.5647(10)	0.3317(14)	0.6954(9)	0.021(2)
C20	0.5449(13)	0.1513(16)	0.7395(11)	0.031(3)
C21	0.4875(14)	0.1507(18)	0.8506(13)	0.041(3)
C25	0.8875(8)	0.7910(13)	0.5702(7)	0.0132(17)
C26	0.9767(10)	0.7015(13)	0.5319(9)	0.021(2)
C27	0.0861(10)	0.7148(15)	0.5913(11)	0.026(2)
C28	0.1024(10)	0.8117(17)	0.6897(11)	0.032(3)
C29	0.0115(10)	0.9051(15)	0.7243(10)	0.025(2)
C30	0.9029(10)	0.8939(14)	0.6667(10)	0.023(2)
C31	0.2176(11)	0.8270(19)	0.7568(12)	0.037(3)

Computational methods

Geometries of all stationary points were optimized without symmetry constraint with the Gaussian 09 program[6] using the DFT B3LYP hybrid exchange-correlation functional.[7–9] The all-electron cc-pVDZ basis set[10,11] was employed for non-metal atoms and the cc-pVDZ-PP basis set[10] containing an effective core relativistic pseudopotential was used for Rh. The electronic energy was improved by performing single point energy calculations with the cc-pVTZ (cc-pVTZ-PP for Rh) basis set and the M06L functional[11] and including solvent effects corrections computed with the solvent model based on density (SMD) continuum solvation.[12] To mimic the experimental solvent mixture with a molar fraction ratio of 76:24 of THF:CH_2Cl_2, the values of the solvent descriptors used in the SMD solvation model were re-defined on the basis of a linear behavior with the molar fraction. Using the "Solvent=(Generic,Read)" options of the Gaussian09 SCRF keyword, the solvent mixture was defined employing the following solvent descriptors: Dynamic Dielectric Constant=1.410; Static Dielectric Constant=1.4085; Abraham's hydrogen bond acidity=0.02424; Abraham's hydrogen bond basicity=0.3758; Surface Tension=39.3697; Carbon Aromaticity=0; Electronegativity Halogenicity=0.1617. The D3 Grimme energy corrections for dispersion[13] with the original damping function were added in all B3LYP/cc-pVDZ-PP and M06L/cc-pVTZ-PP calculations. Analytical Hessians were computed to determine the nature of stationary points (one and zero imaginary frequencies for TSs and minima, respectively) and to calculate unscaled zero-point energies (ZPEs) as well as thermal corrections and entropy effects using the standard statistical-mechanics relationships for an ideal gas.[14] These two latter terms were computed at 313.15 K and 1 atm to provide the reported relative Gibbs energies. As a summary, the reported Gibbs energies contain electronic energies including solvent effects calculated at the M06L-D3/cc-pVTZ-PP//B3LYP-D3/cc-pVDZ-PP level together with gas phase thermal and entropic contributions computed at 313.15 K and 1 atm with the B3LYP-D3/cc-pVDZ-PP method. The catalytic species employed for computational modelling is $[Rh(BINAP)]^+$, noted as **[Rh]** in figures for simplification purposes. All stationary points were unambiguously confirmed by IRC calculations.

Figure S4. Molecular structures of (a) **TS A1A2**, (b) **TS A2A3**, (c) **TS A3A4**, (d) **TS A3'B1**, (e) **TS A5-3aa'** and (f) **TS A5-3aa**. Distances are given in Angstroms (Å). Hydrogen atoms not shown for clarity.

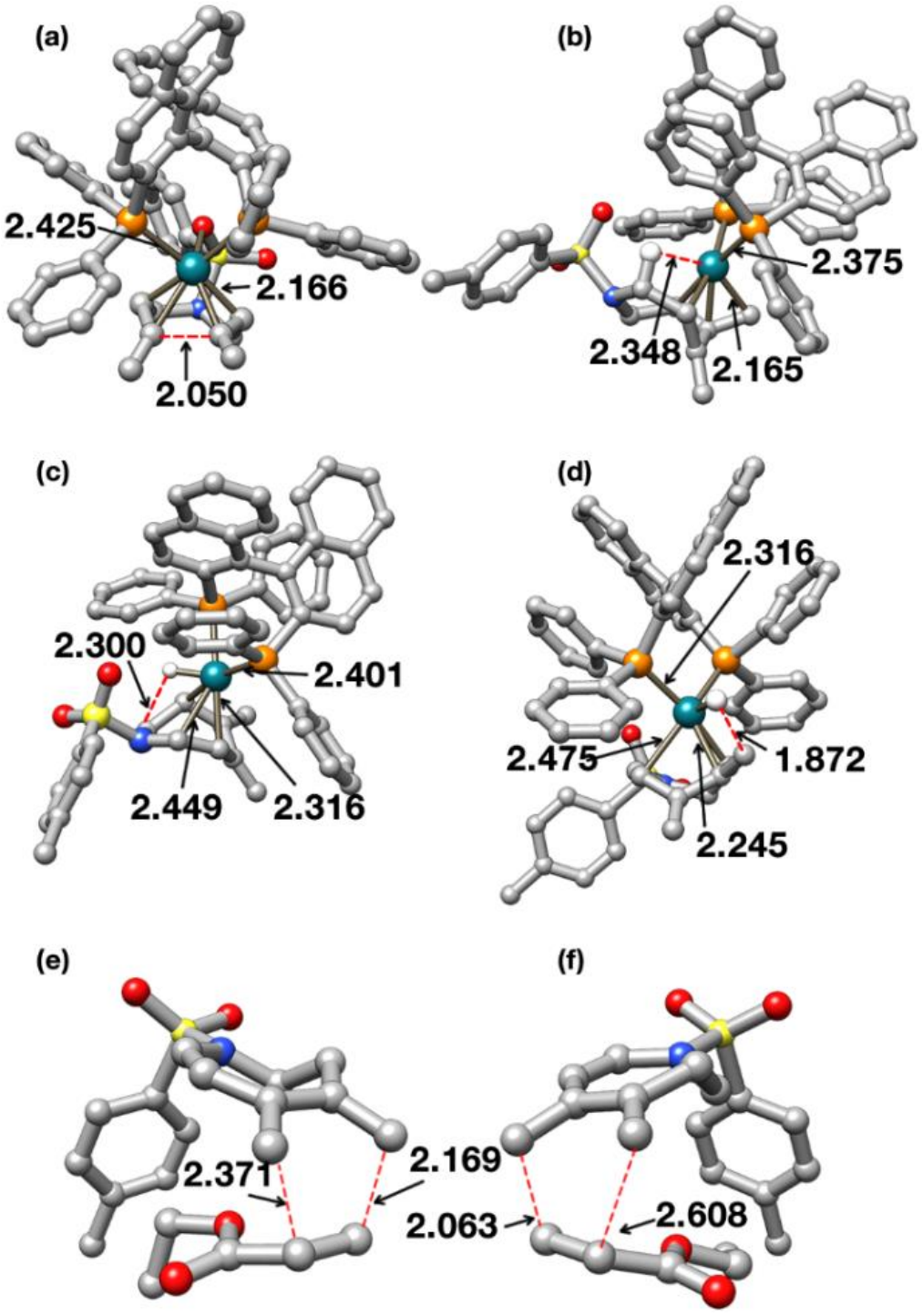


Figure S5. M06L-D3/cc-pVTZ-PP/SMD(76% THF, 24% CH_2Cl_2)//B3LYP-D3/cc-pVDZ-PP Gibbs energy profile for the tandem cycloisomerisation/Diels-Alder cycloaddition of 1,5-bisallene **1a** and ethyl acrylate catalysed by [Rh(BINAP)]$^+$. **Alternative reaction path:** Diels-Alder cycloaddition involving intermediate **A4**.

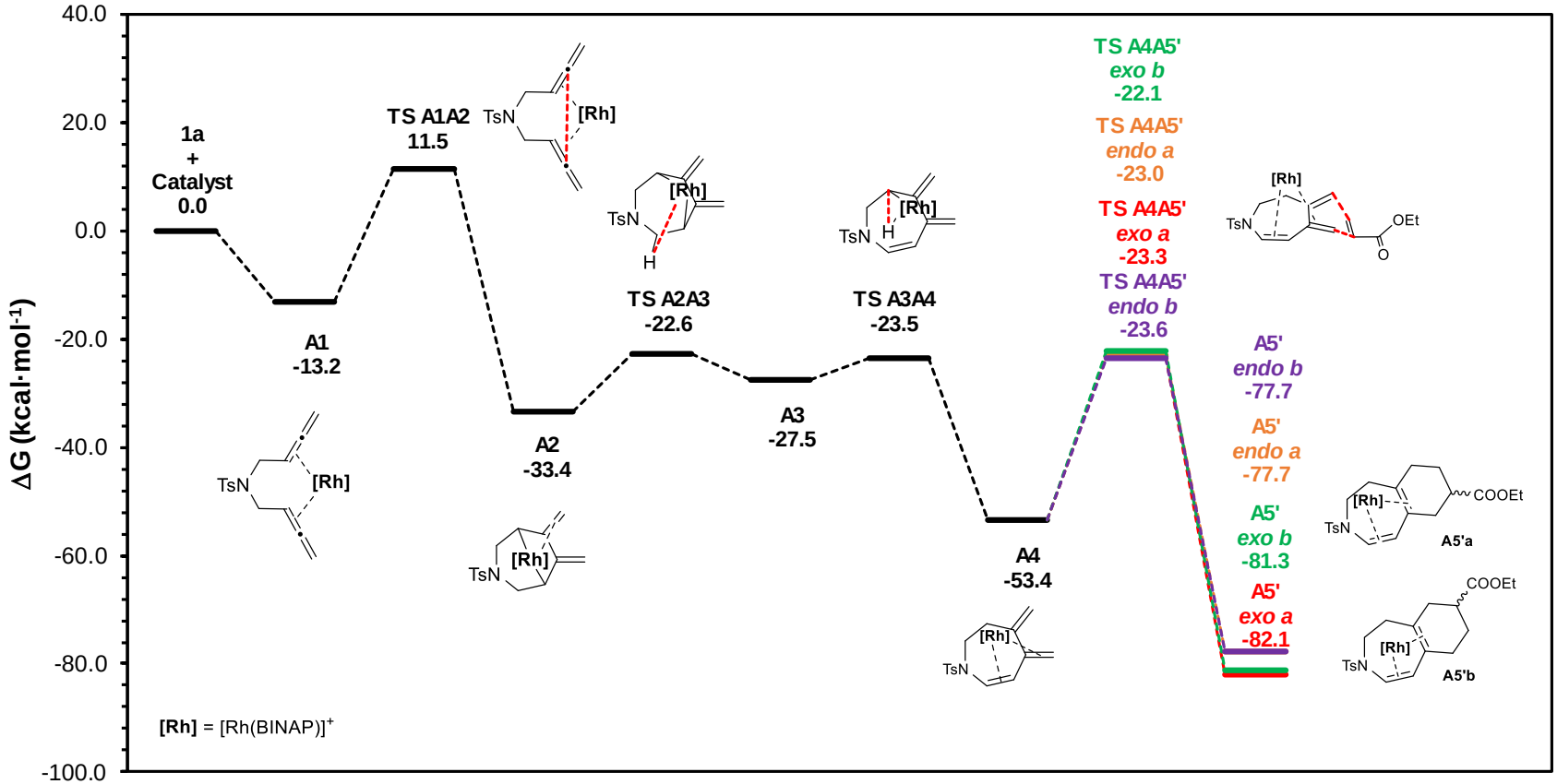


Figure S6. M06L-D3/cc-pVTZ-PP/SMD(76% THF, 24% CH_2Cl_2)//B3LYP-D3/cc-pVDZ-PP Gibbs energy profile for the tandem cycloisomerisation/Diels-Alder cycloaddition of 1,5-bisallene **1a** and ethyl acrylate catalysed by $[Rh(BINAP)]^+$. **Alternative reaction path:** Diels-Alder cycloaddition involving intermediate **A3**.

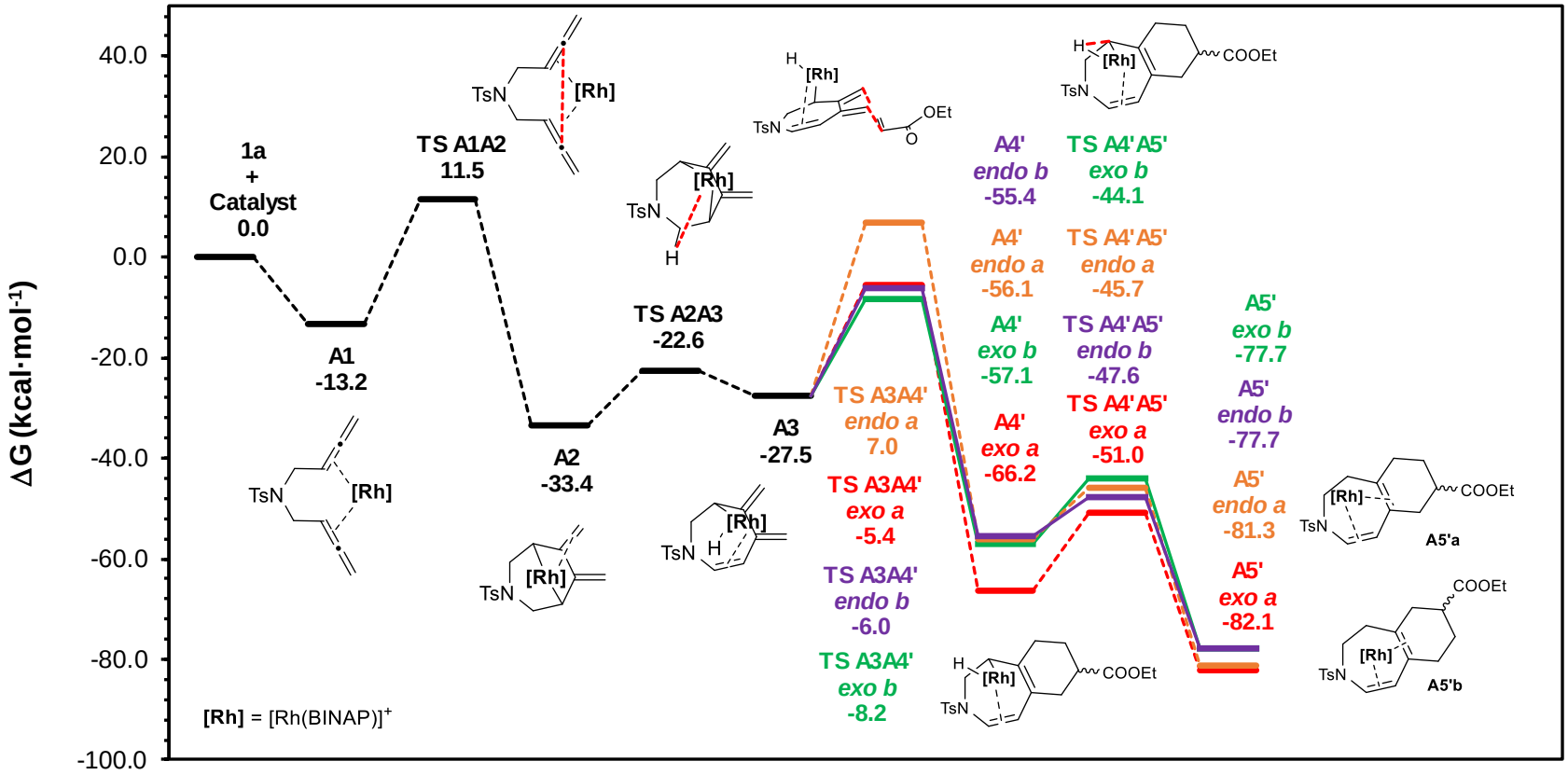


Figure S7. M06L-D3/cc-pVTZ-PP/SMD(76% THF, 24% CH_2Cl_2)//B3LYP-D3/cc-pVDZ-PP Gibbs energy profile for the tandem cycloisomerisation/Diels-Alder cycloaddition of 1,5-bisallene 1a and ethyl acrylate catalysed by $[Rh(BINAP)]^+$. **Alternative reaction path:** Diels-Alder cycloaddition involving intermediate **A2**.

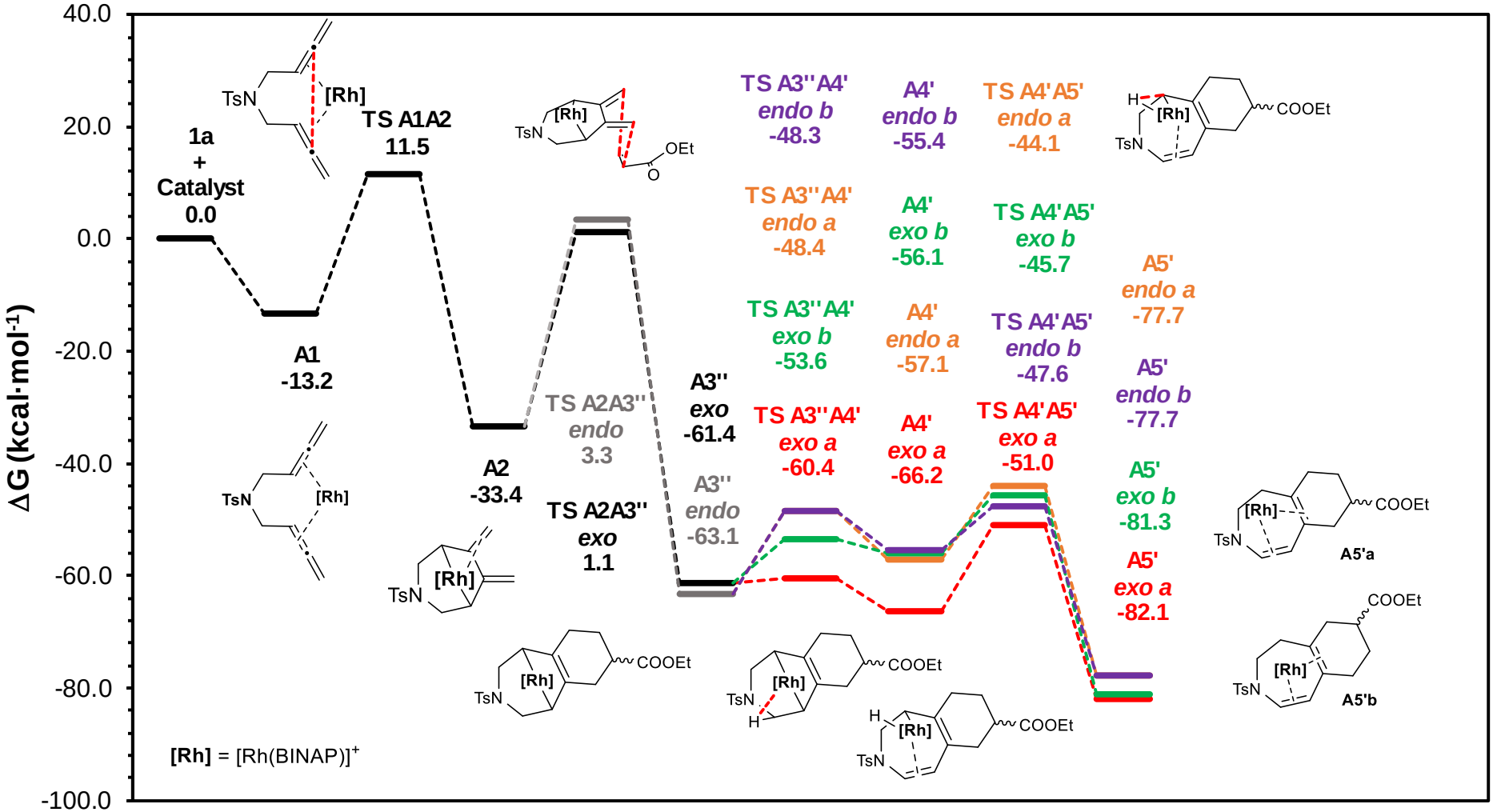
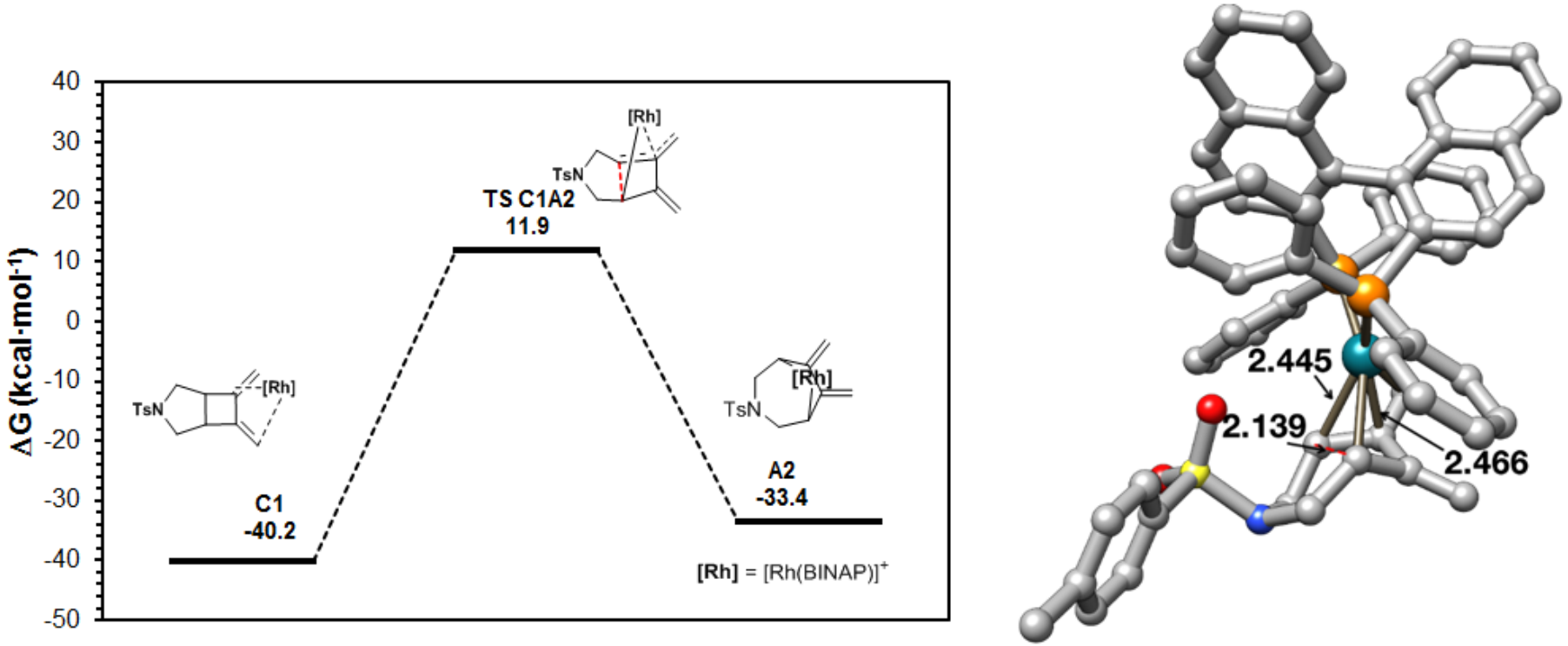


Figure S8. (a) M06L-D3/cc-pVTZ-PP/SMD(76% THF, 24% CH_2Cl_2)//B3LYP-D3/cc-pVDZ-PP Gibbs energy profile for the transformation of intermediate **C1** into intermediate **A2** catalysed by $[Rh(BINAP)]^+$. (b) Molecular structure of **TS C1A2**. Distances are indicated in Angstroms (Å). ΔG relative to **1a** + catalyst. Hydrogen atoms supressed for clarity.



Intermediate **C1** (Chart 1) has to surmount a Gibbs energy barrier of 52.1 kcal/mol (**TSC1A2**) in order to be transformed into **A2**. The backward process is not energetically feasible either (**TS A2C1**, $\Delta G^{\ddagger}$ = 45.3 kcal/mol). Taken together, all these results show that the byproduct **5a** must be formed by a completely independent mechanism involving a Rh(I)-catalyzed [2+2] cycloaddition of the internal C=C bonds of 1,5-bisallene **1a**.[15]

Computational data

All DFT data obtained within this study are provided through the following link:
https://iochem.udg.edu:8443/browse/review-collection/100/660/236d90b68e822f98633662d5

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