

Supporting Information

Construction of Polyfunctionalized 6-5-5 Fused Tricyclic Carbocycles via One-pot Sequential Semipinacol Rearrangement/Michael Addition/Henry Reaction

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1. General information

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. All solvents were purified and dried by standard techniques, and distilled prior to use. Reactions were monitored by thin-layer chromatography (TLC).

¹H NMR and **¹³C NMR** (400 and 100 MHz, respectively) spectra were recorded on Bruker AM-400 MHz instruments in CDCl₃ or DMSO-d₆. **¹H NMR** chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CDCl₃ at 7.27 ppm, DMSO-d₆ at 2.50 ppm). **¹³C NMR** chemical shifts were internally referenced to the solvent signal from CDCl₃ (δ 77.00) and DMSO-d₆ (δ 39.50). The following descriptors were used to denote coupling patterns: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplicity). Signals that have singlet multiplicity and are deemed as broad are prefixed with “brs”. Fourier-transform infrared (**FT-IR**) spectra were recorded on a FT-170SX spectrometer. The **MS** data were obtained with EI (70 eV). High-resolution mass spectra (**HRMS**) data were measured by means of the ESI technique on Fourier transform ion cyclotron resonance mass nanalyzer. The X-ray single-crystal determination was performed on an Agilent SuperNova single crystal X-ray diffractometer. Melting points were recorded on a melting point apparatus and uncorrected.

Starting materials **S1-S5** are known compounds. Substrates **2a**, **2u**¹, and all nitroalkene² are known compounds.

2. Optimization of the One-pot Reaction Conditions

Table S1. Screening of the reaction temperature^a

entry	temperature (°C)	yield (%) ^b	dr (6a: 6a') ^c
1	0	58	1:1.7
2	-10	63	1:1.5
3	-20	64	1:1.5
4	-30	64	1:1.4
5	-40	64	1:1.2
6	-50	52	1:1
7	-60	<5	n.d. ^d
8	-70	0	-

^aReactions were carried out: **2a** (0.20 mmol), **4a** (0.24 mmol), and 1.1 equiv of AlCl₃ in 2.0 mL of CH₂Cl₂ at the corresponding temperature for 1h. ^bCombined isolated yields of products **6** and **6'** were reported. ^cDr values were determined by ¹H NMR analysis of the crude products. ^dn.d. = not detected.

When AlCl_3 was selected as a Lewis acid, the influence of reaction temperature was investigated (Table S1). The lower temperature ($0\text{ }^\circ\text{C}$ – $-40\text{ }^\circ\text{C}$) provided a good yield with a decreasing dr value (entries 1–5). While the temperature was decreased to $-50\text{ }^\circ\text{C}$, both the yield and the dr value of the reaction were reduced. Then, by decreasing temperature to $-60\text{ }^\circ\text{C}$, only gave a trace amount of the product (entry 7). When the temperature was further decreased to $-70\text{ }^\circ\text{C}$, the targeted product was not obtained.

Subsequently, different solvents were also screened (Table S2). The results showed that CH_2Cl_2 is the optimal choice.

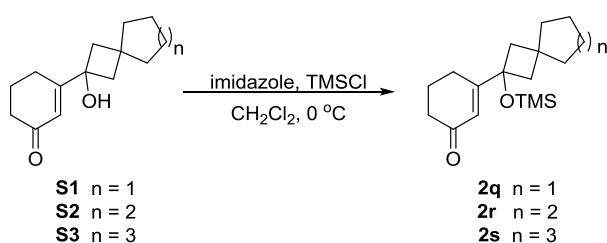
Table S2. Screening of solvents^a

entry	solvent	yield (%) ^b	dr (6a : 6a') ^c
1	CH_2Cl_2	58	1:1.7
2	CHCl_3	57	1.4:1
3	CCl_4	14	n.d. ^d
4	$\text{ClCH}_2\text{CH}_2\text{Cl}$	60	1.2:1
5	THF	0	-
6	Et_2O	23	1:1.2
7	toluene	18	1:1.5
8	acetone	0	-

^aReactions were carried out: **2a** (0.20 mmol), **4a** (0.24 mmol), and 1.1 equiv of AlCl_3 in solvent (2.0 mL) at $0\text{ }^\circ\text{C}$ for 1h. ^bCombined isolated yields of products **6** and **6'** were reported. ^cDr values were determined by ^1H NMR analysis of the crude products. ^dn.d. = not detected.

3. Preparation of substrates and spectroscopic data of new compounds.

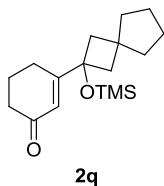
3.1 Preparation of substrates **2q–2s**:



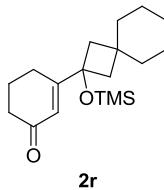
To a stirred solution of compound **S1**³ (406.0 mg, 1.85 mmol) in CH_2Cl_2 (20 mL) was added imidazole (313.7 mg, 4.61 mmol) and trimethyl chlorosilane (TMSCl) (352 μL , 2.78 mmol) successively at $0\text{ }^\circ\text{C}$. The reaction mixture was allowed to warm to room temperature and stirred for 0.5 h. The reaction was quenched with water (5 mL). The aqueous layer was extracted with CH_2Cl_2

and the combined organic layer was washed brine, and dried over Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by flash column chromatography to afford substrate **2q** (79% yield, 427 mg) as a colourless oil.

The similar procedure was used for preparation of substrates **2r** and **2s** from starting materials **S2** and **S3**, respectively.

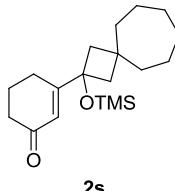


$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ 6.03 (s, 1H), 2.41-2.30 (m, 6H), 2.18-2.15 (m, 2H), 2.03-1.96 (m, 2H), 1.75-1.68 (m, 2H), 1.57-1.43 (m, 6H), 0.08 (s, 9H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3): δ 200.5, 167.7, 123.3, 74.7, 46.0 (2C), 41.3, 39.4, 37.9, 37.7, 24.5, 24.0, 23.6, 22.9, 1.8 (3C). **IR** (KBr) 2954, 2868, 1676, 1251, 841 cm^{-1} ; **MS (EI)** m/z (%) 292 (11), 236 (22), 207 (28), 167 (65), 96 (30), 73 (100); **HRMS (ESI)** calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{17}\text{H}_{28}\text{N}_2\text{O}_2\text{SiNa}$: 315.1751, found: 315.1747.



2r was synthesized under the similar procedure from compound **S2** (211.8 mg, 0.91 mmol), imidazole (153.7 mg, 2.26 mmol), and TMSCl (172 μL , 1.36 mmol). Colourless oil, 83% yield (230 mg).

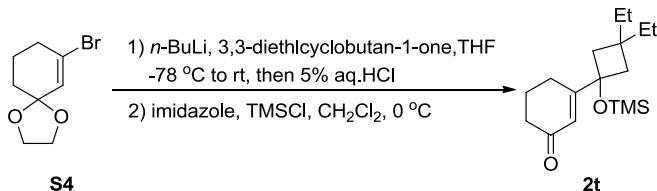
$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ 6.00 (s, 1H), 2.41-2.35 (m, 4H), 2.19-2.16 (m, 2H), 2.03-1.98 (m, 4H), 1.60-1.57 (m, 2H), 1.41-1.32 (m, 8H), 0.08 (s, 9H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3): δ 200.7, 168.5, 123.0, 74.6, 45.1, 39.7, 38.2, 37.6, 31.4, 25.7, 24.4, 22.9(2C), 22.7, 1.8(3C). **IR** (KBr) 3051, 2945, 2849, 1672, 1449, 839 cm^{-1} ; **MS (EI)** m/z (%) 306 (10), 278 (9), 250 (11), 167 (83), 57 (100); **HRMS (ESI)** calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{18}\text{H}_{30}\text{O}_2\text{SiNa}$: 329.1907, found: 323.1907.



2s was synthesized under the similar procedure from compound **S3** (664.5 mg, 2.68 mmol), imidazole (454.2 mg, 6.69 mmol), and TMSCl (510 μL , 4.02 mmol). Colourless oil, 92% yield (789 mg).

¹H NMR (400 MHz, CDCl₃, ppm): δ 5.98 (s, 1H), 2.38-2.33 (m, 4H), 2.21-2.18 (m, 2H), 2.04-1.94 (m, 4H), 1.76-1.74 (m, 2H), 1.47-1.35 (m, 10H), 0.06 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 200.5, 168.3, 123.0, 74.3, 46.1 (2C), 43.0, 41.5, 37.6, 34.0, 27.5, 27.4, 24.3, 22.9, 22.8, 22.8, 1.7 (3C). **IR** (film) 2925, 2855, 1676, 1459, 841 cm⁻¹; **MS (EI)** *m/z* (%) 320 (100), 305 (27), 264 (16), 211 (19), 182 (62), 167 (28); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₉H₃₂O₂SiNa: 343.2064, found: 343.2058.

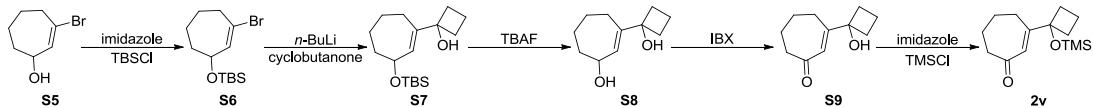
3.2 Preparation of substrate 2t:



Under Ar atmosphere, to a -78 °C solution of compound **S4**⁴ (397 mg, 1.81 mmol, 1.0 equiv) in 18 mL dry THF was added dropwise 2.5 M *n*-butyllithium in hexane (1.59 mL, 3.98 mmol, 2.2 equiv). The resulting solution was stirred at -78 °C for 0.5 h. The diethylcyclobutanone (274 mg, 2.17 mmol, 1.2 equiv) was added, and the reaction mixture was stirred at -78 °C for 1 h. The reaction mixture was poured into 5% HCl (10 mL) and extracted with ethyl acetate. The combined organic layer was washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography to afford vinylogous α-ketol mixed with a small quantity of impurity. The crude compound was dissolved in dry CH₂Cl₂ cooled to 0 °C. Then imidazole (135 mg, 1.99 mmol, 2.5 equiv.) and TMSCl (160 μL, 1.26 mmol, 1.2 equiv.) were added. The reaction mixture was stirred at room temperature for 0.5 h. The reaction mixture was quenched with water, extracted with CH₂Cl₂, and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography to afford desired substrate **2t** (41% yield, 217 mg, two steps) as a colourless oil.

¹H NMR (400 MHz, CDCl₃, ppm): δ 5.99 (s, 1H), 2.40-2.34 (m, 4H), 2.15-2.11 (m, 2H), 2.02-1.95 (m, 4H), 1.57 (q, *J* = 7.2 Hz, 2H), 1.29 (q, *J* = 7.5 Hz, 2H), 0.77 (t, *J* = 7.4 Hz, 3H), 0.68 (t, *J* = 7.4 Hz, 3H), 0.07 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 200.6, 168.4, 123.0, 74.3, 43.7(2C), 37.6, 33.7, 30.7, 29.8, 24.3, 22.9, 8.0, 7.9, 1.7 (3C). **IR** (film) 3049, 2961, 2875, 1677, 1458, 841 cm⁻¹; **MS (EI)** *m/z* (%) 294 (10), 266 (9), 237 (8), 222 (4), 167 (100); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₇H₃₀O₂SiNa: 317.1907, found: 317.1903.

3.3 Preparation of substrate 2v:



A solution of the known compound **S5**⁵ (2.500 g, 13 mmol) in CH₂Cl₂ (25 mL) was treated with imidazole (1.945 g, 29 mmol, 2.2 equiv) and *tert*-Butyldimethylsilyl chloride (TBSCl, 2.159 g, 14 mmol, 1.1 equiv) at room temperature, and the reaction mixture was stirred for 0.5 h. The reaction mixture was quenched with water, extracted with CH₂Cl₂, and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography to afford desired compound **S6** (96% yield, 8.190 g) as a colourless oil.

¹H NMR (400 MHz, CDCl₃, ppm): δ 6.15 (d, *J* = 4.0 Hz, 1H), 4.29-4.23 (m, 1H), 2.66-2.64 (m, 2H), 1.94-1.87 (m, 1H), 1.75-1.70 (m, 2H), 1.66-1.64 (m, 1H), 1.62-1.54 (m, 2H), 0.90 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 139.6, 124.4, 71.8, 40.4, 35.9, 25.9, 25.8, 25.8 (3C), 18.1, -4.8, -4.8. **IR** (film) 2929, 2857, 1642, 837 cm⁻¹; **MS (EI)** *m/z* (%) 304 (1), 247 (38), 225 (100), 139 (27); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₃H₂₅BrOSiNa: 327.0750, found: 327.0763.

Under Ar atmosphere, 2.5 M *t*-BuLi (17.0 mL, 22 mmol, 2.2 equiv) was added dropwise to the solution of **S6** (3.050 g, 10 mmol, 1.0 equiv) in dry THF (100 mL) at -78 °C. The reaction mixture was stirred at -78 °C for 0.5 h and then was added dropwise cyclobutanone (1.5 mL, 20 mmol, 2.0 equiv). The above mixture was stirred at the same temperature for another 0.5 h. The reaction mixture was quenched with saturated ammonium chloride solution, extracted with ethyl acetate, and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography to afford desired compound **S7** (43% yield, 1.277 g) as a colourless oil.

¹H NMR (400 MHz, CDCl₃, ppm): δ 5.78 (s, 1H), 4.41-4.39 (m, 1H), 2.34-2.21 (m, 3H), 2.05-1.92 (m, 4H), 1.89-1.80 (m, 1H), 1.79-1.70 (m, 2H), 1.67-1.56 (m, 3H), 1.53-1.45 (m, 1H), 1.25-1.16 (m, 1H), 0.91 (s, 9H), 0.08 (s, 3H), 0.08 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 142.2, 133.4, 78.8, 72.7, 36.9, 33.8, 33.7, 28.3, 28.2, 27.0, 25.9 (3C), 18.3, 12.6, -4.6, -4.7. **IR** (film) 3356, 2927, 2856, 1665, 836 cm⁻¹; **MS (EI)** *m/z* (%) 296 (1), 182 (30), 167 (18), 147 (23), 75 (100); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₇H₃₂O₂SiNa: 319.2064, found: 319.2064.

A solution of compound **S7** (1.76 g, 6 mmol, 2.0 equiv) in THF (60 mL) was treated with (Bu)₄NF•3H₂O (3.132 g, 12 mmol, 2.0 equiv) at room temperature, and the reaction was monitored by TLC. After completion of the reaction, water (12 mL) was added and the aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography to afford desired compound **S8** (80% yield, 862 mg) as a colourless oil.

¹H NMR (400 MHz, CDCl₃, ppm): δ 5.74 (s, 1H), 4.41-4.39 (m, 1H), 3.20 (brs, 1H), 2.89 (brs, 1H), 2.28-2.20 (m, 3H), 2.03-1.92 (m, 4H), 1.87-1.79 (m, 2H), 1.72-1.68 (m, 1H), 1.61-1.44 (m, 3H), 1.23-1.15 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 143.1, 131.5, 78.6, 71.7, 36.4, 33.6, 33.5, 28.2, 28.1, 26.7, 12.7. **IR** (film) 3350, 2927, 2852, 1446, 842, 738 cm⁻¹; **MS (EI)** m/z (%) 164 (9), 146 (12), 111 (95), 84 (100); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₁H₁₈O₂Na: 205.1199, found: 205.1207.

To a suspension of **S8** (862 mg, 4.74 mmol, 1.5 equiv) in ethyl acetate (50 mL) was added 2-Iodoxybenzoic acid (IBX) (1.960 g, 7 mmol, 1.5 equiv), and the resulting solution was heated at 85 °C (oil bath temperature). The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature and filtered through a short pad of celite. The solvent was removed under reduced pressure and the crude reaction mixture was directly purified through flash column chromatography on silica gel to afford the desired compound **S9** (98% yield, 836 mg) as a colourless oil.

¹H NMR (400 MHz, CDCl₃, ppm): δ 5.97 (s, 1H), 3.63 (brs, 1H), 2.51-2.42 (m, 4H), 2.28-2.21 (m, 2H), 2.10-2.03 (m, 2H), 1.95-1.86 (m, 1H), 1.72-1.71 (m, 4H), 1.56-1.48 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 205.8, 162.6, 126.1, 78.6, 41.7, 33.9(2C), 26.9, 25.4, 20.9, 13.0. **IR** (film) 3401, 2942, 2868, 1655, 888 cm⁻¹; **MS (EI)** m/z (%) 180 (10), 162 (2), 123 (63), 109 (84), 81 (100); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₁H₁₆O₂Na: 203.1043, found: 203.1046.

To a stirred solution of substrate **S9** (836 mg, 4.64 mmol, 1.0 equiv) in CH₂Cl₂ (50 mL) was added imidazole (790 mg, 11.61 mmol, 2.5 equiv) and TMSCl (883 μL, 6.96 mmol, 1.5 equiv) successively at 0 °C. The cool bath was removed and the reation mixture was stirred at room temperature for 0.5 h. The reaction was quenched with water and extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated under vacuum. The crude mixture was purified through flash column chromatography on silica gel to afford product **2v** (90% yield, 1.05 g) as a colourless oil.

¹H NMR (400 MHz, CDCl₃, ppm): δ 6.05 (s, 1H), 2.57-2.54 (m, 2H), 2.46-2.44 (m, 2H), 2.26-2.14 (m, 4H), 1.76-1.68 (m, 5H), 1.49-1.37 (m, 1H), 0.04 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 204.9, 161.5, 126.0, 79.7, 41.6, 35.0 (2C), 26.8, 25.5, 20.9, 12.7, 1.56(3C). **IR** (film) 2950, 2868, 1666, 1456, 841 cm⁻¹; **MS (EI)** m/z (%) 252 (1), 236 (8), 195 (13), 181 (26), 59 (100); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₄H₂₄O₂SiNa: 275.1438, found: 275.1430.

4. General procedure of the semipinacol rearrangement/Michael addition/Henry reaction.

General procedure A for Table 1 (entries 1-2), Table S1, and Table S2: The substrate **2a** (47.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)- β -nitroalkene **4a** (35.8 mg, 0.24 mmol, 1.2 equiv) were mixed

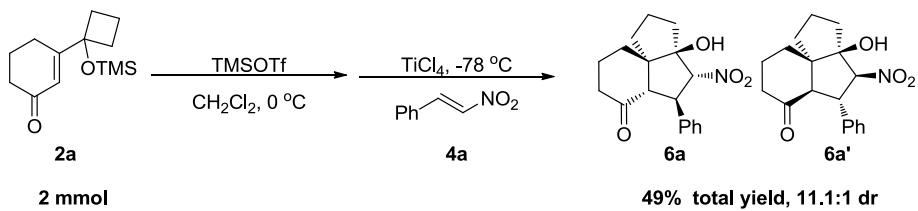
in dry solvent (2.0 mL). Then AlCl_3 (29.3 mg, 0.22 mmol, 1.1 equiv) was added at the indicated temperature and stirred for 1 h. The reaction was quenched carefully with saturated NaHCO_3 at 0 °C, and stirred at room temperature for 2 h. The mixture was extracted with CH_2Cl_2 , and the combined organic phase washed with brine, dried over Na_2SO_4 , and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate =10:1-2:1) to afford products **6a** and **6a'**.

General procedure B for entries 3-12 of Table 1: A mixture of **2a** (47.6 mg, 0.20 mmol, 1.0 equiv), **4a** (35.8 mg, 0.24 mmol, 1.2 equiv), and 1.1 equiv of the first Lewis acid in 2.0 mL CH_2Cl_2 was stirred at 0 °C for 10 min; after that, the second Lewis acid (the indicated equivalent in the Table 1) was added at the indicated temperature and stirred for a further 1 h. The reaction was quenched carefully with saturated NaHCO_3 at 0 °C, and stirred at room temperature for 2 h. The mixture was extracted with CH_2Cl_2 , and the combined organic phase washed with brine, dried over Na_2SO_4 , and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate =10:1-2:1) to afford products **6a** and **6a'**.

General procedure C for entries 13-15 of Table 1: A mixture of **2a** (47.6 mg, 0.20 mmol, 1.0 equiv) and TMSOTf (the indicated equivalent in the Table 1) in 2.0 mL CH_2Cl_2 was stirred for 10 min at 0 °C, and then, TiCl_4 and **4a** (35.8 mg, 0.24 mmol, 1.2 equiv) were added successively at -78 °C. The resulting mixture was allowed to stir for an additional 1 hour at -78 °C. The reaction was quenched carefully with saturated NaHCO_3 at 0 °C, and stirred at room temperature for 2 h. The mixture was extracted with CH_2Cl_2 , and the combined organic phase washed with brine, dried over Na_2SO_4 , and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate =10:1-2:1) to afford products **6a** and **6a'**.

General procedure D: The substrate **2** (0.20 mmol, 1.0 equiv) and TMSOTf (55 μL , 0.30 mmol, 1.5 equiv) were mixed in dry CH_2Cl_2 (2.0 mL) at 0 °C. After stirring of the mixture for 10 min, the reaction mixture was cooled to -78 °C, and TiCl_4 (1 M in CH_2Cl_2 , 440 μL , 0.44 mmol, 2.2 equiv) and nitroalkene **4** (0.24 mmol, 1.2 equiv) was added successively at -78 °C. The resulting mixture was allowed to stir for an additional 1 hour at -78 °C. The reaction was quenched carefully with saturated NaHCO_3 at 0 °C, and stirred at room temperature for 2 h. The mixture was extracted with CH_2Cl_2 , and the combined organic phase was washed with brine, dried over Na_2SO_4 , and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate =10:1-2:1) to afford products **6** and **6'**.

5. 2 mmol-scale model reaction.

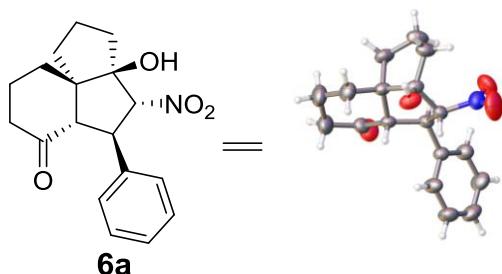


The substrate **2a** (476.0 mg, 2.0 mmol, 1.0 equiv) and TMSOTf (542 μL , 3.0 mmol, 1.5 equiv) were mixed in dry CH_2Cl_2 (20 mL) at 0 °C. After stirring of the mixture for 10 min, the reaction

mixture was cooled to -78 °C, and TiCl₄ (1 M in CH₂Cl₂, 4.4 mL, 4.4 mmol, 2.2 equiv) and (*E*)- β -nitrostyrene **4a** (357.6 mg, 2.4 mmol, 1.2 equiv) was added successively at -78 °C. The resulting mixture was allowed to stir for an additional 1 hour at -78 °C. The reaction was quenched carefully with saturated NaHCO₃ at 0 °C, and stirred at room temperature for 2 h. The mixture was extracted with CH₂Cl₂, and the combined organic phase was washed with brine, dried over Na₂SO₄, and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate =10:1-3:1) to afford product **6a** (284.2 mg) as a white solid and **6a'** (25.6 mg) as a white solid; 49% total yield, 11.1:1 dr value was determined by the mass of isolated **6a** and **6a'**.

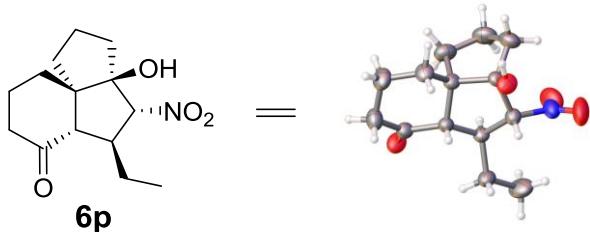
6. X-ray crystal structure and data.

6.1 X-ray crystal structure and data of compound 6a (CCDC 1962897).



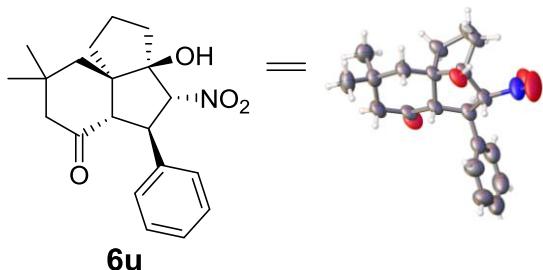
Identification code	compound 6a
Empirical formula	C ₁₈ H ₂₁ NO ₄
Formula weight	315.36
Temperature/K	293.38(10)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	8.6036(7)
b/Å	12.8834(12)
c/Å	14.9608(10)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å ³	1658.3(2)
Z	4
ρ _{calc} g/cm ³	1.263
μ/mm ⁻¹	0.089
F(000)	672.0
Crystal size/mm ³	0.23 × 0.21 × 0.17
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	7.22 to 52.02
Index ranges	-10 ≤ h ≤ 6, -8 ≤ k ≤ 15, -18 ≤ l ≤ 11
Reflections collected	4218
Independent reflections	2971 [R _{int} = 0.0311, R _{sigma} = 0.0778]
Data/restraints/parameters	2971/0/209
Goodness-of-fit on F ²	1.047
Final R indexes [I>=2σ (I)]	R ₁ = 0.0612, wR ₂ = 0.1177
Final R indexes [all data]	R ₁ = 0.1040, wR ₂ = 0.1441
Largest diff. peak/hole / e Å ⁻³	0.18/-0.22
Flack parameter	0(2)

6.2 X-ray crystal structure of data of compound **6p (CCDC 1962898).**



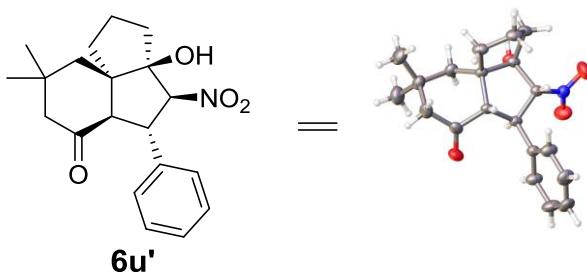
Identification code	compound 6p
Empirical formula	$\text{C}_{14}\text{H}_{21}\text{NO}_4$
Formula weight	267.32
Temperature/K	296.15
Crystal system	monoclinic
Space group	$\text{P}2_1/\text{n}$
a/ \AA	7.6167(10)
b/ \AA	9.9108(13)
c/ \AA	18.091(3)
$\alpha/^\circ$	90
$\beta/^\circ$	95.497(2)
$\gamma/^\circ$	90
Volume/ \AA^3	1359.3(3)
Z	4
$\rho_{\text{calc}} \text{g/cm}^3$	1.306
μ/mm^{-1}	0.095
F(000)	576.0
Crystal size/ mm^3	0.3 \times 0.2 \times 0.2
Radiation	$\text{MoK}\alpha (\lambda = 0.71073)$
2 Θ range for data collection/ $^\circ$	4.524 to 54.478
Index ranges	-9 \leq h \leq 9, -12 \leq k \leq 11, -19 \leq l \leq 23
Reflections collected	8036
Independent reflections	3032 [$\text{R}_{\text{int}} = 0.0271$, $\text{R}_{\text{sigma}} = 0.0329$]
Data/restraints/parameters	3032/0/174
Goodness-of-fit on F^2	0.999
Final R indexes [$I \geq 2\sigma(I)$]	$\text{R}_1 = 0.0706$, $\text{wR}_2 = 0.2101$
Final R indexes [all data]	$\text{R}_1 = 0.0877$, $\text{wR}_2 = 0.2225$
Largest diff. peak/hole / e \AA^{-3}	0.44/-0.27

6.3 X-ray crystal structure of data of compound **6u (CCDC 1962905).**



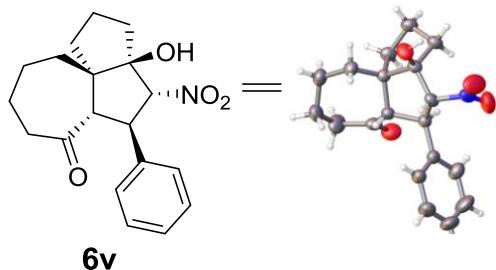
Identification code	compound 6u
Empirical formula	C ₂₀ H ₂₅ NO ₄
Formula weight	343.41
Temperature/K	292.77(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	12.2676(14)
b/Å	19.2472(18)
c/Å	16.3321(13)
α/°	90
β/°	110.838(11)
γ/°	90
Volume/Å ³	3604.0(6)
Z	8
ρ _{calc} g/cm ³	1.266
μ/mm ⁻¹	0.711
F(000)	1472.0
Crystal size/mm ³	0.19 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.978 to 133.128
Index ranges	-11 ≤ h ≤ 14, -20 ≤ k ≤ 22, -19 ≤ l ≤ 19
Reflections collected	12201
Independent reflections	3189 [R _{int} = 0.0348, R _{sigma} = 0.0281]
Data/restraints/parameters	3189/0/229
Goodness-of-fit on F ²	1.066
Final R indexes [I>=2σ (I)]	R ₁ = 0.0579, wR ₂ = 0.1587
Final R indexes [all data]	R ₁ = 0.0702, wR ₂ = 0.1724
Largest diff. peak/hole / e Å ⁻³	0.26/-0.26

6.4 X-ray crystal structure of data of compound **6u' (CCDC 1962899).**



Identification code	compound 6u'
Empirical formula	C ₂₀ H ₂₅ NO ₄
Formula weight	343.41
Temperature/K	294.49(10)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	11.6804(3)
b/Å	13.8086(3)
c/Å	11.9718(3)
α/°	90
β/°	115.551(4)
γ/°	90
Volume/Å ³	1742.09(9)
Z	4
ρ _{calc} g/cm ³	1.309
μ/mm ⁻¹	0.736
F(000)	736.0
Crystal size/mm ³	0.19 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.398 to 133.198
Index ranges	-11 ≤ h ≤ 13, -16 ≤ k ≤ 14, -14 ≤ l ≤ 8
Reflections collected	5575
Independent reflections	2932 [R _{int} = 0.0186, R _{sigma} = 0.0231]
Data/restraints/parameters	2932/0/229
Goodness-of-fit on F ²	1.070
Final R indexes [I>=2σ (I)]	R ₁ = 0.0482, wR ₂ = 0.1223
Final R indexes [all data]	R ₁ = 0.0518, wR ₂ = 0.1261
Largest diff. peak/hole / e Å ⁻³	0.32/-0.33

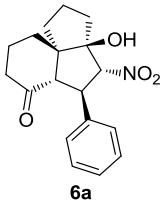
6.5 X-ray crystal structure and data of compound **6v (CCDC 1962903).**



Identification code	compound 6v
Empirical formula	C ₁₉ H ₂₃ NO ₄
Formula weight	329.38
Temperature/K	296.15
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	12.493(2)
b/Å	5.9360(10)
c/Å	22.661(4)
α/°	90
β/°	99.959(3)
γ/°	90
Volume/Å ³	1655.2(5)
Z	4
ρ _{calc} g/cm ³	1.322
μ/mm ⁻¹	0.092
F(000)	704.0
Crystal size/mm ³	0.3 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.31 to 52.576
Index ranges	-15 ≤ h ≤ 13, -7 ≤ k ≤ 7, -28 ≤ l ≤ 25
Reflections collected	8864
Independent reflections	3348 [R _{int} = 0.0278, R _{sigma} = 0.0354]
Data/restraints/parameters	3348/19/218
Goodness-of-fit on F ²	1.001
Final R indexes [I>=2σ (I)]	R ₁ = 0.0445, wR ₂ = 0.1229
Final R indexes [all data]	R ₁ = 0.0628, wR ₂ = 0.1385
Largest diff. peak/hole / e Å ⁻³	0.20/-0.20

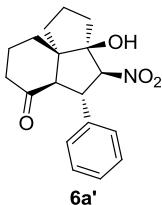
7. Characterization data for products

Prepared by general procedure D from **2a** (47.6 mg, 0.20 mmol) and **4a** (35.8 mg, 0.24 mmol), and gave the desired products **6a** and **6a'**: 72% total yield; 11.4 : 1 dr value analyzed by ¹H NMR.



3a-hydroxy-4-nitro-5-phenyloctahydro-1*H*-cyclopenta[*c*]inden-6(*7H*)-one (**6a**)

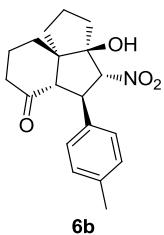
White solid; m.p. 175-176 °C; ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7.33-7.27 (m, 4H), 7.25-7.21 (m, 1H), 5.01 (d, *J* = 11.2 Hz, 1H), 3.93 (dd, *J* = 11.4, 11.2 Hz, 1H), 3.18 (d, *J* = 12.4 Hz, 1H), 2.93 (d, *J* = 16.0 Hz, 1H), 2.32-2.27 (m, 2H), 2.20-2.14 (m, 1H), 2.05-1.92 (m, 1H), 1.91-1.79 (m, 3H), 1.76-1.61 (m, 4H), 1.58-1.50 (m, 1H); ¹³**C NMR** (100 MHz, CDCl₃): δ 208.0, 137.5, 128.7(2C), 127.6, 127.4(2C), 102.9, 90.2, 60.3, 58.7, 45.0, 41.2, 37.1, 32.6, 32.3, 24.0, 22.2. **IR** (KBr) 3415, 2968, 1704, 1541, 1365, 1107, 759, 703 cm⁻¹; **MS (EI)** *m/z* (%) 315 (1), 268 (100), 251 (15), 91 (86); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₈H₂₁NO₄Na: 338.1368, found: 338.1365.



3a-hydroxy-4-nitro-5-phenyloctahydro-1*H*-cyclopenta[*c*]inden-6(*7H*)-one (**6a'**)

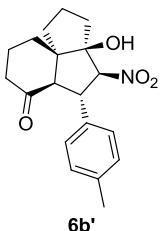
White solid; m.p. 170-171 °C; ¹**H NMR** (400 MHz, CDCl₃, ppm): δ 7.34-7.31 (m, 2H), 7.28-7.26 (m, 1H), 7.24-7.22 (m, 2H), 4.83 (d, *J* = 11.2 Hz, 1H), 4.34 (t, *J* = 11.8 Hz, 1H), 2.59 (d, *J* = 12.4 Hz, 1H), 2.52-2.47 (m, 1H), 2.41-2.35 (m, 2H), 2.30 (s, 1H), 2.17-2.10 (m, 2H), 2.00-1.97 (m, 1H), 1.90-1.84 (m, 2H), 1.83-1.77 (m, 2H), 1.73-1.68 (m, 1H), 1.63-1.59 (m, 1H); ¹³**C NMR** (100 MHz, CDCl₃): δ 210.3, 136.6, 128.9 (2C), 127.9, 127.2 (2C), 97.1, 88.4, 60.8, 58.4, 49.3, 39.8, 38.7, 37.8, 28.8, 22.6, 21.9. **IR** (KBr) 3373, 2949, 1690, 1546, 1366, 1099, 698 cm⁻¹; **MS (EI)** *m/z* (%) 315 (1), 268 (42), 251 (19), 226 (100), 91 (35); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₈H₂₁NO₄Na: 338.1368, found: 338.1365.

Prepared by general procedure D from **2a** (47.6 mg, 0.20 mmol) and **4b** (39.1 mg, 0.24 mmol), and gave the desired products **6b** and **6b'**: 62% total yield; 10.6 : 1 dr value analyzed by ¹H NMR.



3a-hydroxy-4-nitro-5-(*p*-tolyl)octahydro-1*H*-cyclopenta[*c*]inden-6(7*H*)-one (6b)

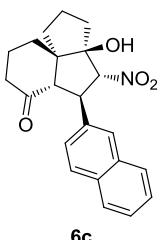
White solid; m.p. 186-188 °C; **1H NMR** (400 MHz, CDCl₃, ppm): δ 7.20 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 4.99 (d, *J* = 10.8 Hz, 1H), 3.91 (t, *J* = 11.8 Hz, 1H), 3.14 (d, *J* = 12.4 Hz, 1H), 2.62 (s, 1H), 2.30-2.27 (m, 5H), 2.21-2.15 (m, 1H), 2.07-1.99 (m, 1H), 1.96-1.77 (m, 3H), 1.74-1.52 (m, 5H); **13C NMR** (100 MHz, CDCl₃): δ 207.7, 137.2, 134.5, 129.4 (2C), 127.3 (2C), 103.0, 90.2, 60.4, 58.8, 44.8, 41.2, 37.2, 32.6, 32.3, 24.0, 22.2, 21.0. **IR** (KBr) 3379, 2951, 1698, 1543, 1367, 1100, 839, 520 cm⁻¹; **MS (EI)** *m/z* (%) 329 (6), 282 (100), 265 (19), 226 (49), 105 (73), 91 (44); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₉H₂₃NO₄Na: 352.1525, found: 352.1531.



3a-hydroxy-4-nitro-5-(*p*-tolyl)octahydro-1*H*-cyclopenta[*c*]inden-6(7*H*)-one (6b')

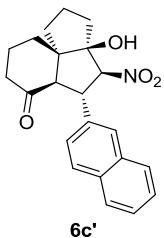
White solid; m.p. 168-169 °C; **1H NMR** (400 MHz, CDCl₃, ppm): δ 7.14-7.09 (m, 4H), 4.80 (d, *J* = 10.8 Hz, 1H), 4.31 (dd, *J* = 12.0, 10.8 Hz, 1H), 2.56 (d, *J* = 12.4 Hz, 1H), 2.51-2.46 (m, 1H), 2.41 (s, 1H), 2.38-2.33 (m, 2H), 2.30 (s, 3H), 2.17-2.09 (m, 2H), 1.98-1.95 (m, 1H), 1.89-1.83 (m, 2H), 1.82-1.76 (m, 2H), 1.71-1.64 (m, 1H), 1.61-1.57 (m, 1H); **13C NMR** (100 MHz, CDCl₃): δ 209.9, 137.7, 133.5, 129.6 (2C), 127.0 (2C), 97.4, 88.4, 61.0, 58.5, 49.3, 40.2, 38.7, 37.9, 28.8, 22.8, 22.1, 21.0. **IR** (KBr) 3406, 2948, 1693, 1548, 1365, 1097, 812 cm⁻¹; **MS (EI)** *m/z* (%) 282 (49), 265 (16), 105 (36), 91 (30); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₉H₂₃NO₄Na: 352.1525, found: 352.1526.

Prepared by general procedure D from **2a** (47.6 mg, 0.20 mmol) and **4c** (47.8 mg, 0.24 mmol), and gave the desired products **6c** and **6c'**: 73% total yield; 15.0:1 dr value analyzed by ¹H NMR.



3a-hydroxy-5-(naphthalen-2-yl)-4-nitrooctahydro-1*H*-cyclopenta[*c*]inden-6(7*H*)-one (6c).

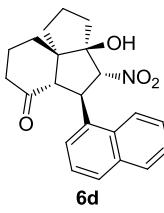
White solid; m.p. 164-166 °C; **1H NMR** (400 MHz, CDCl₃, ppm): δ 7.81-7.78 (m, 4H), 7.49-7.42 (m, 3H), 5.13 (d, *J* = 10.8 Hz, 1H), 4.10 (dd, *J* = 12.4, 11.6 Hz, 1H), 3.27 (d, *J* = 12.4 Hz, 1H), 3.08 (brs, 1H), 2.28-2.23 (m, 2H), 2.13-2.08 (m, 1H), 2.02-1.94 (m, 1H), 1.93-1.75 (m, 3H), 1.73-1.64 (m, 2H), 1.60-1.54 (m, 3H); **13C NMR** (100 MHz, CDCl₃): δ 208.1, 135.0, 133.3, 132.8, 128.5, 127.7, 127.5, 126.6, 126.2, 125.9, 125.2, 102.9, 90.3, 60.4, 58.9, 45.2, 41.1, 37.0, 32.5, 32.2, 23.9, 22.1. **IR** (KBr) 3415, 2956, 1701, 1544, 1365, 1099, 746, 478 cm⁻¹; **MS (EI)** *m/z* (%) 365 (63), 318 (100), 301 (22), 141 (49), 128 (22); **HRMS (ESI)** calcd for [M+Na]⁺ C₂₂H₂₃NO₄Na: 388.1525, found: 388.1521.



3a-hydroxy-5-(naphthalen-2-yl)-4-nitrooctahydro-1*H*-cyclopenta[c]inden-6(7*H*)-one (6c').

White solid; m.p. 106-107 °C; **1H NMR** (400 MHz, CDCl₃, ppm): δ 7.84-7.79 (m, 3H), 7.71 (d, *J* = 1.6 Hz, 1H), 7.49-7.46 (m, 2H), 7.34 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.93 (d, *J* = 11.2 Hz, 1H), 4.52 (t, *J* = 11.6 Hz, 1H), 2.70 (d, *J* = 12.4 Hz, 1H), 2.54-2.48 (m, 2H), 2.40-2.33 (m, 2H), 2.17-2.10 (m, 2H), 1.96-1.76 (m, 5H), 1.72-1.67 (m, 1H), 1.60-1.57 (m, 1H); **13C NMR** (100 MHz, CDCl₃): δ 210.0, 134.0, 133.3, 132.9, 128.9, 127.8, 127.6, 126.8, 126.4, 126.1, 124.4, 97.1, 88.5, 60.9, 58.5, 49.6, 40.0, 38.7, 37.9, 28.8, 22.6, 22.0. **IR** (KBr) 3400, 2949, 1690, 1548, 1366, 1096, 816, 747, 477 cm⁻¹; **MS (EI)** *m/z* (%) 365 (4), 318 (87), 301 (17), 276 (100), 141 (31), 128 (31); **HRMS (ESI)** calcd for [M+Na]⁺ C₂₂H₂₃NO₄Na: 388.1525, found: 388.1524.

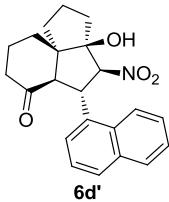
Prepared by general procedure D from **2a** (47.6 mg, 0.20 mmol) and **4d** (47.8 mg, 0.24 mmol), and gave the desired products **6d** and **6d'**: 55% total yield; 12.0:1 dr value analyzed by ¹H NMR.



3a-hydroxy-5-(naphthalen-1-yl)-4-nitrooctahydro-1*H*-cyclopenta[c]inden-6(7*H*)-one (6d).

White solid; m.p. 140-142 °C; **1H NMR** (400 MHz, DMSO-d₆, ppm): δ 8.41 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.20 Hz, 1H), 7.62 (td, *J* = 7.2, 1.2 Hz, 1H), 7.55-7.48 (m, 2H), 6.09 (s, 1H), 5.23 (d, *J* = 10.8 Hz, 1H), 4.64 (t, *J* = 11.6 Hz, 1H), 3.57 (d, *J* = 12.0 Hz, 1H), 2.43-2.34 (m, 1H), 2.10-2.05 (m, 1H), 2.02-1.96 (m, 2H), 1.88-1.60 (m, 8H); **13C NMR** (100 MHz, DMSO-d₆): δ 208.0, 135.3, 133.4, 131.7, 128.4, 127.5, 126.0, 125.7, 125.5,

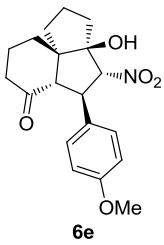
123.7, 123.5, 104.7, 90.1, 61.0, 58.7, 40.5, 39.7, 35.8, 32.4, 32.2, 23.6, 22.0. **IR** (KBr) 3331, 2925, 1696, 1543, 775 cm⁻¹; **MS (EI)** *m/z* (%) 365 (100), 318 (27), 301 (36), 141 (89), 128 (53); **HRMS (ESI)** calcd for [M+Na]⁺ C₂₂H₂₃NO₄Na: 388.1525, found: 388.1515.



3a-hydroxy-5-(naphthalen-1-yl)-4-nitrooctahydro-1*H*-cyclopenta[c]inden-6(7*H*)-one (6d').

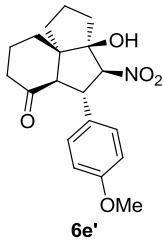
White solid; m.p. 196-198 °C; **1H NMR** (400 MHz, DMSO-d₆, ppm): δ 8.40 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.52-7.46 (m, 2H), 5.71 (s, 1H), 5.34 (d, *J* = 11.2 Hz, 1H), 5.10 (t, *J* = 11.8 Hz, 1H), 2.57-2.40 (m, 3H), 2.22-2.18 (m, 1H), 2.14-2.10 (m, 1H), 2.04-2.02 (m, 1H), 1.93-1.90 (m, 1H), 1.83-1.67 (m, 4H), 1.57-1.45 (m, 2H); **13C NMR** (100 MHz, DMSO-d₆): δ 209.7, 134.5, 133.3, 131.8, 128.5, 127.4, 126.1, 125.5, 125.4, 124.2, 123.2, 96.3, 88.3, 62.0, 57.1, 41.7, 38.7, 38.3, 38.0, 29.5, 21.7, 21.0. **IR** (KBr) 3372, 2934, 1693, 1549, 1371, 1087, 808, 781 cm⁻¹; **MS (EI)** *m/z* (%) 365 (13), 318 (93), 301 (37), 276 (100), 141 (47), 128 (99); **HRMS (ESI)** calcd for [M+Na]⁺ C₂₂H₂₃NO₄Na: 388.1525, found: 388.1521.

Prepared by general procedure D from **2a** (47.6 mg, 0.20 mmol) and **4e** (43.0 mg, 0.24 mmol), and gave the desired products **6e** and **6e'**: 57% total yield; 4.4:1 dr value analyzed by ¹H NMR.



3a-hydroxy-5-(4-methoxyphenyl)-4-nitrooctahydro-1*H*-cyclopenta[c]inden-6(7*H*)-one (6e).

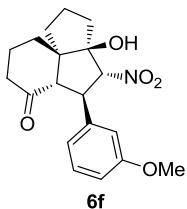
White solid; m.p. 148-150 °C; **1H NMR** (400 MHz, CDCl₃, ppm): δ 7.23 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.96 (d, *J* = 11.2 Hz, 1H), 3.89 (t, *J* = 11.8 Hz, 1H), 3.76 (s, 3H), 3.11 (d, *J* = 12.4 Hz, 1H), 2.72 (s, 1H), 2.31-2.27 (m, 2H), 2.20-2.15 (m, 1H), 2.05-1.98 (m, 1H), 1.94-1.86 (m, 2H), 1.84-1.78 (m, 1H), 1.76-1.68 (m, 2H), 1.65-1.61 (m, 2H), 1.59-1.54 (m, 1H); **13C NMR** (100 MHz, CDCl₃): δ 207.7, 158.9, 129.5, 128.4 (2C), 114.2 (2C), 103.1, 90.1, 60.4, 58.8, 55.2, 44.4, 41.2, 37.2, 32.6, 32.3, 24.0, 22.2. **IR** (KBr) 3411, 2961, 1700, 1543, 1249, 1040, 840 cm⁻¹; **MS (EI)** *m/z* (%) 345 (30), 298 (100), 281 (25), 121(66), 91 (35); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₉H₂₃NO₅Na: 368.1474, found: 368.1469.



3a-hydroxy-5-(4-methoxyphenyl)-4-nitrooctahydro-1*H*-cyclopenta[c]inden-6(7*H*)-one (6e').

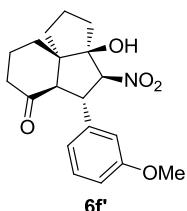
White solid; m.p. 146-147 °C; **1H NMR** (400 MHz, CDCl₃, ppm): δ 7.14 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.75 (d, *J* = 10.8 Hz, 1H), 4.28 (dd, *J* = 12.4, 10.8 Hz, 1H), 3.77 (s, 3H), 2.54 (d, *J* = 12.4 Hz, 1H), 2.50-2.45 (m, 2H), 2.37-2.32 (m, 2H), 2.16-2.09 (m, 2H), 1.97-1.93 (m, 1H), 1.90-1.72 (m, 4H), 1.69-1.65 (m, 1H), 1.60-1.57 (m, 1H); **13C NMR** (100 MHz, CDCl₃): δ 210.0, 159.2, 128.4, 128.3 (2C), 114.3 (2C), 97.5, 88.2, 61.0, 58.4, 55.2, 49.0, 40.2, 38.7, 37.9, 28.8, 22.8, 22.1. **IR** (KBr) 3406, 2960, 1688, 1543, 1255, 831 cm⁻¹; **MS (EI)** *m/z* (%) 345 (1), 298 (63), 281 (17), 256 (100), 121 (32), 107 (27), 91 (19); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₉H₂₃NO₅Na: 368.1474, found: 368.1464.

Prepared by general procedure D from **2a** (47.6 mg, 0.20 mmol) and **4f** (43.0 mg, 0.24 mmol), and gave the desired products **6f** and **6f'**: 68% total yield; 9.2:1 dr value analyzed by ¹H NMR.



3a-hydroxy-5-(3-methoxyphenyl)-4-nitrooctahydro-1*H*-cyclopenta[c]inden-6(7*H*)-one (6f).

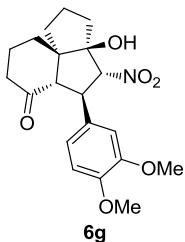
White solid; m.p. 134-136 °C; **1H NMR** (400 MHz, CDCl₃, ppm): δ 7.21 (t, *J* = 7.8 Hz, 1H), 6.90-6.87 (m, 2H), 6.78-6.76 (m, 1H), 5.00 (d, *J* = 11.2 Hz, 1H), 3.92 (dd, *J* = 12.4, 11.6 Hz, 1H), 3.79 (s, 3H), 3.16 (d, *J* = 12.4 Hz, 1H), 2.71 (s, 1H), 2.36-2.24 (m, 2H), 2.21-2.15 (m, 1H), 2.06-1.96 (m, 1H), 1.95-1.85 (m, 2H), 1.83-1.69 (m, 3H), 1.66-1.62 (m, 2H), 1.60-1.54 (m, 1H); **13C NMR** (100 MHz, CDCl₃): δ 207.9, 159.7, 139.2, 129.7, 119.5, 113.8, 112.6, 102.9, 90.2, 60.3, 58.9, 55.2, 45.0, 41.2, 37.1, 32.6, 32.2, 24.0, 22.1. **IR** (KBr) 3484, 2959, 1704, 1545, 1261, 1032, 700 cm⁻¹; **MS (EI)** *m/z* (%) 345 (100), 298 (96), 281 (27), 121 (44), 91 (39); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₉H₂₃NO₅Na: 368.1474, found: 368.1466.



3a-hydroxy-5-(3-methoxyphenyl)-4-nitrooctahydro-1*H*-cyclopenta[c]inden-6(7*H*)-one (6f'**).**

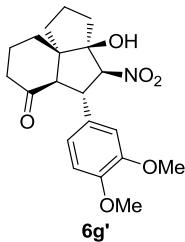
White solid; m.p. 143-144 °C; **1H NMR** (400 MHz, CDCl₃, ppm): δ 7.23 (t, *J* = 8.0 Hz, 1H), 6.81-6.75 (m, 3H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.34 (t, *J* = 11.4 Hz, 1H), 3.78 (s, 3H), 2.58 (d, *J* = 12.4 Hz, 1H), 2.55-2.46 (m, 1H), 2.41-2.33 (m, 2H), 2.21-2.20 (m, 1H), 2.18-2.07 (m, 2H), 2.01-1.94 (m, 1H), 1.91-1.68 (m, 5H), 1.62-1.61 (m, 1H); **13C NMR** (100 MHz, CDCl₃): δ 209.5, 159.9, 138.5, 130.1, 119.2, 113.7, 112.8, 97.2, 88.5, 61.0, 58.6, 55.2, 49.4, 40.0, 38.6, 37.8, 28.7, 22.7, 22.0. **IR** (KBr) 3447, 2947, 1702, 1549, 1266, 698 cm⁻¹; **MS (EI)** *m/z* (%) 345 (2), 298 (71), 281 (24), 256 (100), 121 (27), 91 (25); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₉H₂₃NO₅Na: 368.1474, found: 368.1472.

Prepared by general procedure D from **2a** (47.6 mg, 0.20 mmol) and **4g** (50.2 mg, 0.24 mmol), and gave the desired products **6g** and **6g'**: 57% total yield; 2.7:1 dr value analyzed by ¹H NMR.



5-(3,4-dimethoxyphenyl)-3a-hydroxy-4-nitrooctahydro-1*H*-cyclopenta[c]inden-6(7*H*)-one (6g**).**

White solid; m.p. 180-181 °C; **1H NMR** (400 MHz, DMSO-d₆, ppm): δ 6.90-6.81 (m, 3H), 5.92 (s, 1H), 4.98 (d, *J* = 11.2 Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 3.59 (t, *J* = 11.8 Hz, 1H), 3.35 (d, *J* = 12.4 Hz, 1H), 2.46-2.38 (m, 1H), 2.09-1.90 (m, 3H), 1.81-1.72 (m, 2H), 1.61-1.52 (m, 4H), 1.47-1.41 (m, 2H); **13C NMR** (100 MHz, DMSO-d₆): δ 208.2, 148.6, 148.0, 130.7, 119.8, 111.7, 110.9, 103.5, 89.7, 58.8, 58.3, 55.5, 55.4, 45.0, 40.7, 35.9, 32.5, 32.3, 23.7, 21.8. **IR** (KBr) 3388, 2933, 1716, 1546, 1277, 1002 cm⁻¹; **MS (EI)** *m/z* (%) 375 (85), 328 (91), 311 (23), 151 (57), 138 (44); **HRMS (ESI)** calcd for [M+Na]⁺ C₂₀H₂₅NO₆Na: 398.1580, found: 398.1564.

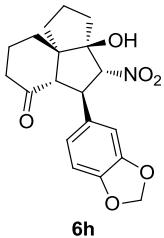


5-(3,4-dimethoxyphenyl)-3a-hydroxy-4-nitrooctahydro-1*H*-cyclopenta[c]inden-6(7*H*)-one (6g'**).**

White solid; m.p. 185-186 °C; **1H NMR** (400 MHz, CDCl₃, ppm): δ 6.81-6.75 (m, 2H), 6.71 (d, *J* = 1.6 Hz, 1H), 4.76 (d, *J* = 11.2 Hz, 1H), 4.31 (t, *J* = 11.6 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 2.56 (d, *J* = 12.4 Hz, 1H), 2.51-2.33 (m, 4H), 2.16-2.08 (m, 2H), 1.99-1.94 (m, 1H), 1.90-1.78 (m, 4H),

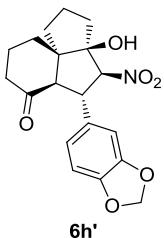
1.72-1.67 (m, 1H), 1.60-1.57 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 210.0, 149.1, 148.7, 129.1, 119.0, 111.4, 110.7, 97.6, 88.3, 60.7, 58.5, 55.9, 55.8, 49.2, 40.1, 38.7, 37.8, 28.8, 22.8, 22.1. **IR** (KBr) 3526, 2922, 1701, 1518, 1255, 1023, 807 cm⁻¹; **MS (EI)** *m/z* (%) 375 (4), 328 (63), 311 (12), 286 (100), 151 (16), 138 (44); **HRMS (ESI)** calcd for [M+Na]⁺ C₂₀H₂₅NO₆Na: 398.1580, found: 398.1567.

Prepared by general procedure D from **2a** (47.6 mg, 0.20 mmol) and **4h** (46.3 mg, 0.24 mmol), and gave the desired products **6h** and **6h'**: 58% total yield; 4.9:1 dr value analyzed by ¹H NMR.



5-(benzo[d][1,3]dioxol-5-yl)-3a-hydroxy-4-nitrooctahydro-1*H*-cyclopenta[c]inden-6(7*H*)-one (6h).

White solid; m.p. 107-108 °C; **¹H NMR** (400 MHz, CDCl₃, ppm): δ 6.80-6.72 (m, 3H), 5.92 (s, 2H), 4.93 (d, *J* = 10.8 Hz, 1H), 3.86 (t, *J* = 11.8 Hz, 1H), 3.10 (d, *J* = 12.4 Hz, 1H), 2.55 (s, 1H), 2.37-2.26 (m, 2H), 2.21-2.17 (m, 1H), 2.06-1.99 (m, 1H), 1.95-1.80 (m, 3H), 1.76-1.63 (m, 4H), 1.60-1.50 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 207.8, 147.9, 146.9, 131.3, 120.7, 108.5, 107.7, 103.1, 101.1, 90.1, 60.3, 58.7, 44.9, 41.2, 37.1, 32.6, 32.3, 24.0, 22.1. **IR** (KBr) 3466, 2953, 1712, 1544, 1255, 1041, 930, 739 cm⁻¹; **MS (EI)** *m/z* (%) 359 (82), 312 (100), 295 (27), 135 (72); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₉H₂₁NO₆Na: 382.1267, found: 382.1263.

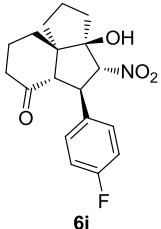


5-(benzo[d][1,3]dioxol-5-yl)-3a-hydroxy-4-nitrooctahydro-1*H*-cyclopenta[c]inden-6(7*H*)-one (6h').

White solid; m.p. 187-188 °C; **¹H NMR** (400 MHz, DMSO-d₆, ppm): δ 7.06 (d, *J* = 1.6 Hz, 1H), 6.83-6.77 (m, 2H), 5.96 (dd, *J* = 6.4, 1.2 Hz, 2H), 5.56 (s, 1H), 5.05 (d, *J* = 11.6 Hz, 1H), 4.11 (t, *J* = 12.0 Hz, 1H), 2.58-2.52 (m, 1H), 2.34-2.27 (m, 2H), 2.15-2.11 (m, 1H), 2.05-1.96 (m, 2H), 1.83-1.81 (m, 1H), 1.71-1.60 (m, 4H), 1.46-1.35 (m, 2H); **¹³C NMR** (100 MHz, DMSO-d₆): δ 210.1, 147.3, 146.3, 131.6, 121.5, 108.0, 107.9, 100.9, 95.4, 60.8, 57.1, 48.0, 38.9, 38.7, 38.4, 38.1, 29.3, 22.1, 21.1. **IR** (KBr) 3357, 2935, 1685, 1548, 1375, 1231, 1037, 817 cm⁻¹; **MS (EI)** *m/z* (%) 359 (2), 312 (45), 295 (14), 270 (100), 135 (25), 122 (38); **HRMS (ESI)** calcd for [M+Na]⁺

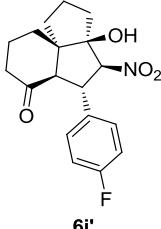
$C_{19}H_{21}NO_6Na$: 382.1267, found: 382.1261.

Prepared by general procedure D from **2a** (47.6 mg, 0.20 mmol) and **4i** (40.1 mg, 0.24 mmol), and gave the desired products **6i** and **6i'**: 67% total yield; 11.5:1 dr value analyzed by 1H NMR.



5-(4-fluorophenyl)-3a-hydroxy-4-nitrooctahydro-1*H*-cyclopenta[c]inden-6(7*H*)-one (6i**).**

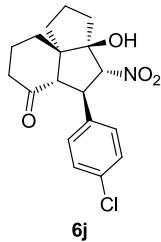
White solid; m.p. 160-162 °C; 1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.29 (dd, J = 7.2, 5.6 Hz, 2H), 6.99 (t, J = 8.0 Hz, 2H), 4.96 (d, J = 11.2 Hz, 1H), 3.92 (t, J = 11.8 Hz, 1H), 3.11 (d, J = 12.4 Hz, 1H), 2.54 (s, 1H), 2.32-2.28 (m, 2H), 2.22-2.18 (m, 1H), 2.07-2.00 (m, 1H), 1.97-1.81 (m, 3H), 1.77-1.63 (m, 4H), 1.60-1.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.7, 162.1 (d, J = 245 Hz), 133.3 (d, J = 3 Hz), 129.0 (d, J = 8 Hz, 2C), 115.6 (d, J = 22 Hz, 2C), 102.9, 90.1, 60.4, 58.7, 44.4, 41.1, 37.1, 32.6, 32.3, 23.9, 22.2. IR (KBr) 3418, 2953, 1709, 1546, 1229, 1103, 738 cm^{-1} ; MS (EI) m/z (%) 333 (2), 286 (100), 269 (16), 109 (90); HRMS (ESI) calcd for $[M+Na]^+$ $C_{18}H_{20}FNO_4Na$: 356.1274, found: 356.1279.



5-(4-fluorophenyl)-3a-hydroxy-4-nitrooctahydro-1*H*-cyclopenta[c]inden-6(7*H*)-one (6i'**).**

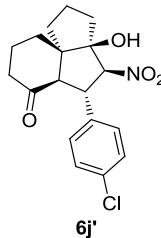
White solid; m.p. 172-174 °C; 1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.23-7.19 (m, 2H), 7.03-6.07 (m, 2H), 4.75 (d, J = 10.8 Hz, 1H), 4.31 (t, J = 11.8 Hz, 1H), 2.54 (d, J = 12.4 Hz, 1H), 2.48-2.43 (m, 1H), 2.42-2.39 (m, 2H), 2.32 (s, 1H), 2.15-2.14 (m, 1H), 2.11-2.07 (m, 1H), 2.00-1.97 (m, 1H), 1.90-1.68 (m, 5H), 1.64-1.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.8, 162.3 (d, J = 245 Hz), 132.5 (d, J = 3 Hz), 129.0 (d, J = 8 Hz, 2C), 115.9 (d, J = 21 Hz, 2C), 97.2, 88.4, 60.8, 58.2, 48.6, 39.9, 38.7, 38.1, 28.9, 22.5, 22.0. IR (KBr) 3409, 2954, 1687, 1552, 1345, 1250, 831 cm^{-1} ; MS (EI) m/z (%) 286 (35), 269 (15), 244 (100), 109 (44); HRMS (ESI) calcd for $[M+Na]^+$ $C_{18}H_{20}FNO_4Na$: 356.1274, found: 356.1277.

Prepared by general procedure D from **2a** (47.6 mg, 0.20 mmol) and **4j** (43.9 mg, 0.24 mmol), and gave the desired products **6j** and **6j'**: 64% total yield; 14.8:1 dr value analyzed by 1H NMR.



5-(4-chlorophenyl)-3a-hydroxy-4-nitrooctahydro-1*H*-cyclopenta[*c*]inden-6(*7H*)-one (6j).

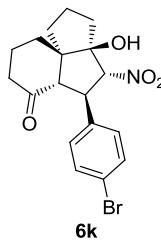
White solid; m.p. 203-204 °C; **1H NMR** (400 MHz, CDCl₃, ppm): δ 7.29-7.24 (m, 4H), 4.95 (d, *J* = 11.2 Hz, 1H), 3.90 (dd, *J* = 12.4, 11.2 Hz, 1H), 3.10 (d, *J* = 12.4 Hz, 1H), 2.59 (s, 1H), 2.31-2.27 (m, 2H), 2.21-2.15 (m, 1H), 2.05-1.98 (m, 1H), 1.96-1.80 (m, 3H), 1.77-1.62 (m, 4H), 1.58-1.49 (m, 1H); **13C NMR** (100 MHz, CDCl₃): δ 207.3, 136.1, 133.5, 129.0 (2C), 128.8 (2C), 102.7, 90.2, 60.4, 58.7, 44.6, 41.1, 37.3, 32.6, 32.4, 23.9, 22.2. **IR** (KBr) 3373, 2968, 1702, 1544, 1367, 1100, 841, 522 cm⁻¹; **MS (EI)** *m/z* (%) 349 (4), 302 (100), 260 (15), 125 (66); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₈H₂₀ClNO₄Na: 372.0979, found: 372.0983.



5-(4-chlorophenyl)-3a-hydroxy-4-nitrooctahydro-1*H*-cyclopenta[*c*]inden-6(*7H*)-one (6j').

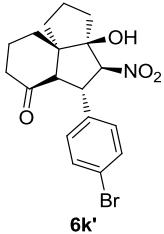
White solid; m.p. 188-190 °C; **1H NMR** (400 MHz, DMSO-d₆, ppm): δ 7.44-7.42 (m, 2H), 7.34-7.32 (m, 2H), 5.62 (s, 1H), 5.14 (d, *J* = 11.6 Hz, 1H), 4.19 (t, *J* = 11.8 Hz, 1H), 2.58-2.51 (m, 1H), 2.36-2.33 (m, 2H), 2.18-2.14 (m, 1H), 2.02-1.96 (m, 2H), 1.88-1.80 (m, 1H), 1.75-1.63 (m, 4H), 1.52-1.47 (m, 1H), 1.40-1.36 (m, 1H); **13C NMR** (100 MHz, DMSO-d₆): δ 210.1, 137.2, 131.7, 129.9 (2C), 128.2 (2C), 95.0, 88.3, 60.5, 56.9, 47.3, 38.6, 38.2, 37.9, 29.2, 21.7, 20.9. **IR** (KBr) 3420, 2951, 1689, 1551, 1368, 1088, 826, 529 cm⁻¹; **MS (EI)** *m/z* (%) 349 (1), 302 (40), 260 (100), 125 (33); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₈H₂₀ClNO₄Na: 372.0979, found: 372.0996.

Prepared by general procedure D from **2a** (47.6 mg, 0.20 mmol) and **4k** (54.5 mg, 0.24 mmol), and gave the desired products **6k** and **6k'**: 64% total yield; 18.0:1 dr value analyzed by ¹H NMR.



5-(4-bromophenyl)-3a-hydroxy-4-nitrooctahydro-1*H*-cyclopenta[*c*]inden-6(*7H*)-one (6k).

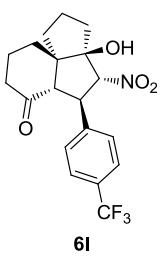
White solid; m.p. 210-212 °C; **1H NMR** (400 MHz, DMSO-d₆, ppm): δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 5.94 (s, 1H), 4.99 (d, *J* = 11.2 Hz, 1H), 3.64 (t, *J* = 11.8 Hz, 1H), 3.59 (d, *J* = 12.4 Hz, 1H), 2.46-2.37 (m, 1H), 2.08-2.00 (m, 2H), 1.96-1.88 (m, 1H), 1.83-1.72 (m, 2H), 1.61-1.52 (m, 4H), 1.45-1.36 (m, 2H); **13C NMR** (100 MHz, DMSO-d₆): δ 207.9, 137.8, 131.3 (2C), 129.8 (2C), 120.3, 102.9, 89.8, 58.7, 58.2, 44.6, 40.5, 35.7, 32.4, 32.2, 23.5, 21.7. **IR** (KBr) 3369, 2924, 1702, 1543, 1366, 1099, 519 cm⁻¹; **MS (EI)** *m/z* (%) 393 (1), 346 (100), 329 (5), 304 (5), 169 (11); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₈H₂₀BrNO₄Na: 416.0473, found: 416.0462.



5-(4-bromophenyl)-3a-hydroxy-4-nitrooctahydro-1*H*-cyclopenta[c]inden-6(7*H*)-one (6k').

White solid; m.p. 186-187 °C; **1H NMR** (400 MHz, DMSO-d₆, ppm): δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 5.61 (s, 1H), 5.13 (d, *J* = 11.2 Hz, 1H), 4.17 (t, *J* = 11.8 Hz, 1H), 2.57-2.52 (m, 1H), 2.35-2.32 (m, 2H), 2.18-2.14 (m, 1H), 2.03-1.96 (m, 2H), 1.89-1.80 (m, 1H), 1.74-1.62 (m, 4H), 1.52-1.45 (m, 1H), 1.40-1.36 (m, 1H); **13C NMR** (100 MHz, DMSO-d₆): δ 210.1, 137.6, 131.1 (2C), 130.3 (2C), 120.3, 94.9, 88.3, 60.5, 56.9, 47.3, 38.6, 38.2, 37.9, 29.2, 21.7, 20.9. **IR** (KBr) 3418, 2949, 1690, 1550, 1367, 1011, 823 cm⁻¹; **MS (EI)** *m/z* (%) 393 (1), 346 (40), 329 (22), 304 (100), 169 (23); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₈H₂₀BrNO₄Na: 416.0473, found: 416.0456.

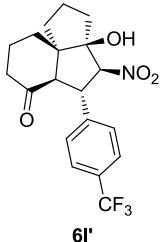
Prepared by general procedure D from **2a** (47.6 mg, 0.20 mmol) and **4l** (52.1 mg, 0.24 mmol), and gave the desired products **6l** and **6l'**: 62% total yield; 16.9:1 dr value analyzed by **1H NMR**.



3a-hydroxy-4-nitro-5-(4-(trifluoromethyl)phenyl)octahydro-1*H*-cyclopenta[c]inden-6(7*H*)-one (6l).

White solid; m.p. 197-198 °C; **1H NMR** (400 MHz, CDCl₃, ppm): δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 5.01 (d, *J* = 11.2 Hz, 1H), 3.99 (t, *J* = 11.6 Hz, 1H), 3.16 (d, *J* = 12.4 Hz, 1H), 2.56 (s, 1H), 2.33-2.29 (m, 2H), 2.24-2.18 (m, 1H), 2.09-2.00 (m, 1H), 1.99-1.94 (m, 1H), 1.92-1.83 (m, 2H), 1.80-1.72 (m, 1H), 1.70-1.65 (m, 3H), 1.59-1.51 (m, 1H); **13C NMR** (100 MHz,

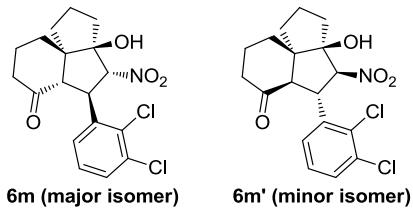
CDCl_3): δ 207.3, 141.7, 130.3 (q, $J = 33$ Hz, 2C), 128.0, 125.8 (q, $J = 4$ Hz, 2C), 123.9 (q, $J = 270$ Hz), 102.5, 90.3, 60.4, 58.8, 45.0, 41.1, 37.2, 32.6, 32.3, 23.8, 22.2. **IR** (KBr) 3390, 2964, 1706, 1545, 1327, 848 cm^{-1} ; **MS (EI)** m/z (%) 336 (100), 319 (26), 294 (13), 159 (54); **HRMS (ESI)** calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{19}\text{H}_{20}\text{F}_3\text{NO}_4\text{Na}$: 406.1242, found: 406.1245.



3a-hydroxy-4-nitro-5-(4-(trifluoromethyl)phenyl)octahydro-1*H*-cyclopenta[c]inden-6(7*H*)-one (6l').

White solid; m.p. 154-156 °C; **$^1\text{H NMR}$** (400 MHz, CDCl_3 , ppm): δ 7.58 (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H), 4.80 (d, $J = 11.2$ Hz, 1H), 4.40 (t, $J = 11.4$ Hz, 1H), 2.58 (d, $J = 12.0$ Hz, 1H), 2.51-2.35 (m, 4H), 2.17-2.12 (m, 1H), 2.08-2.04 (m, 1H), 2.00-1.96 (m, 1H), 1.90-1.73 (m, 5H), 1.62-1.57 (m, 1H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3): δ 209.6, 141.1, 130.2 (q, $J = 32$ Hz, 2C), 127.9, 125.9 (q, $J = 4$ Hz, 2C), 126.7 (q, $J = 293$ Hz), 96.5, 88.7, 60.6, 58.1, 48.6, 39.5, 38.7, 38.2, 28.8, 22.2, 21.8. **IR** (KBr) 3409, 2962, 1695, 1557, 1328, 1111, 828 cm^{-1} ; **MS (EI)** m/z (%) 336 (70), 319 (48), 294 (100), 159 (34); **HRMS (ESI)** calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{19}\text{H}_{20}\text{F}_3\text{NO}_4\text{Na}$: 406.1242, found: 406.1247.

Prepared by general procedure D from **2a** (47.6 mg, 0.20 mmol) and **4m** (52.1 mg, 0.24 mmol), and gave the desired products as a mixture of two diastereoisomers **6m** and **6m'**: 52% total yield; 5.0:1 dr value analyzed by **$^1\text{H NMR}$** .

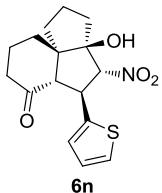


5-(2,3-dichlorophenyl)-3a-hydroxy-4-nitrooctahydro-1*H*-cyclopenta[c]inden-6(7*H*)-one (6m).

White solid; **$^1\text{H NMR}$** (400 MHz, DMSO-d_6 , ppm) (**major isomer**): δ 7.56-7.50 (m, 2H), 7.34 (t, $J = 7.9$ Hz, 1H), 6.02 (s, 1H), 5.11 (d, $J = 11.2$ Hz, 1H), 4.37 (t, $J = 11.8$ Hz, 1H), 3.36 (d, $J = 11.1$ Hz, 1H), 2.40-2.31 (m, 1H), 2.13-1.89 (m, 3H), 1.86-1.73 (m, 2H), 1.70-1.54 (m, 4H), 1.49-1.38 (m, 2H); **$^{13}\text{C NMR}$** (100 MHz, DMSO-d_6) (**major isomer**): δ 207.4, 138.7, 132.3, 132.0, 129.2, 128.2, 126.4, 102.7, 89.8, 60.3, 58.0, 41.7, 40.2, 35.7, 32.4, 32.3, 23.2, 21.9. **MS (EI)** m/z (%) 383 (7), 336 (16), 287 (100), 159 (49), 55 (100); **HRMS (ESI)** calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{18}\text{H}_{19}\text{Cl}_2\text{NO}_4\text{Na}$:

406.0589, found: 406.0574.

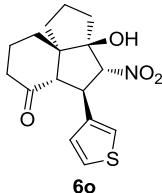
Prepared by general procedure D from **2a** (47.6 mg, 0.20 mmol) and **4n** (37.2 mg, 0.24 mmol), and gave the desired product **6n**: 55% yield; >20:1 dr value analyzed by ¹H NMR.



3a-hydroxy-4-nitro-5-(thiophen-2-yl)octahydro-1H-cyclopenta[c]inden-6(7H)-one (6n).

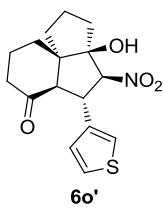
White solid; m.p. 160-161 °C; ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.15 (d, *J* = 5.2 Hz, 1H), 6.96 (d, *J* = 3.2 Hz, 1H), 6.91 (dd, *J* = 4.8, 3.6 Hz, 1H), 4.99 (d, *J* = 10.8 Hz, 1H), 4.25 (t, *J* = 11.6 Hz, 1H), 3.13 (d, *J* = 12.4 Hz, 1H), 2.66 (d, *J* = 10.8 Hz, 1H), 2.41-2.31 (m, 2H), 2.23-2.17 (m, 1H), 2.07-2.00 (m, 1H), 1.95-1.80 (m, 3H), 1.75-1.62 (m, 4H), 1.58-1.48 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 207.5, 140.9, 127.0, 125.3, 124.1, 103.3, 90.1, 61.0, 58.9, 41.2, 40.6, 37.3, 32.6, 32.4, 24.0, 22.2. IR (KBr) 3403, 2971, 1702, 1543, 1362, 1103, 726 cm⁻¹; MS (EI) *m/z* (%) 321 (4), 274 (100), 257 (12), 97 (49); HRMS (ESI) calcd for [M+Na]⁺ C₁₆H₁₉NO₄SNa: 344.0932, found: 344.0934.

Prepared by general procedure D from **2a** (47.6 mg, 0.20 mmol) and **4o** (37.2 mg, 0.24 mmol), and gave the desired products **6o** and **6o'**: 68% total yield; 4.5:1 dr value analyzed by ¹H NMR.



3a-hydroxy-4-nitro-5-(thiophen-3-yl)octahydro-1H-cyclopenta[c]inden-6(7H)-one (6o).

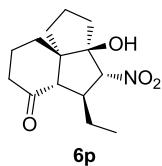
White solid; m.p. 159-161 °C; ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.48-7.45 (m, 1H), 7.33-7.32 (m, 1H), 7.24-7.22 (m, 1H), 5.20 (d, *J* = 10.8 Hz, 1H), 4.28 (t, *J* = 11.6 Hz, 1H), 3.30 (d, *J* = 12.4 Hz, 1H), 3.03 (s, 1H), 2.56-2.50 (m, 2H), 2.43-2.36 (m, 1H), 2.25-2.17 (m, 1H), 2.15-2.09 (m, 2H), 2.03-1.97 (m, 1H), 1.93-1.72 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ 208.0, 138.6, 126.4, 126.2, 121.7, 102.5, 90.2, 60.5, 58.9, 41.3, 40.6, 37.3, 32.7, 32.4, 24.1, 22.2. IR (KBr) 3366, 2949, 1699, 1543, 1314, 1106, 785, 660 cm⁻¹; MS (EI) *m/z* (%) 321 (6), 274 (100), 257 (13), 232 (18), 97 (79); HRMS (ESI) calcd for [M+Na]⁺ C₁₆H₁₉NO₄SNa: 344.0932, found: 344.0931.



3a-hydroxy-4-nitro-5-(thiophen-3-yl)octahydro-1*H*-cyclopenta[*c*]inden-6(7*H*)-one (6o'**).**

White solid; m.p. 159-161 °C; **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.31-7.29 (m, 1H), 7.16-7.15 (m, 1H), 6.96-6.94 (m, 1H), 4.74 (d, *J* = 10.4 Hz, 1H), 4.51 (t, *J* = 11.4 Hz, 1H), 2.59 (d, *J* = 12.4 Hz, 1H), 2.56-2.47 (m, 1H), 2.40-2.30 (m, 2H), 2.27 (s, 1H), 2.20-2.08 (m, 2H), 2.00-1.93 (m, 1H), 1.89-1.68 (m, 5H), 1.63-1.59 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 209.9, 137.9, 126.8, 125.8, 122.2, 97.4, 88.4, 60.5, 58.8, 44.8, 40.3, 38.7, 37.8, 28.7, 22.9, 22.0.. **IR** (KBr) 3361, 2950, 1690, 1546, 1365, 1097, 778 cm⁻¹; **MS (EI)** *m/z* (%) 321 (1), 274 (48), 257 (17), 232 (100), 97 (25); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₆H₁₉NO₄SNa: 344.0932, found: 344.0922.

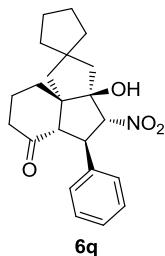
Prepared by general procedure D from **2a** (47.6 mg, 0.20 mmol) and **4p** (24.2 mg, 0.24 mmol), and gave the desired product **6p**: 34% yield; >20:1 dr value analyzed by ¹H NMR.



5-ethyl-3a-hydroxy-4-nitrooctahydro-1*H*-cyclopenta[*c*]inden-6(7*H*)-one (6p**).**

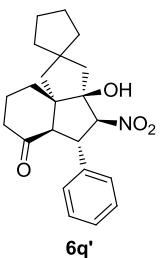
White solid; m.p. 108-110 °C; **¹H NMR** (400 MHz, CDCl₃, ppm): δ 4.58 (d, *J* = 10.4 Hz, 1H), 2.92 (s, 1H), 2.87-2.79 (m, 1H), 2.57 (d, *J* = 12.0 Hz, 1H), 2.33-2.29 (m, 2H), 2.17-2.11 (m, 1H), 1.89-1.74 (m, 4H), 1.71-1.60 (m, 2H), 1.58-1.51 (m, 3H), 1.48-1.36 (m, 2H), 0.83 (t, *J* = 7.6 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 209.2, 101.5, 90.7, 59.0, 58.9, 41.2, 40.5, 36.8, 32.1, 31.7, 24.7, 24.0, 21.8, 10.6. **IR** (KBr) 3467, 2940, 1704, 1546, 1362 cm⁻¹; **MS (EI)** *m/z* (%) 267 (9), 220 (22), 219 (70), 203 (10), 163 (60), 123 (89), 55 (100); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₄H₂₁NO₄Na: 290.1363, found: 290.1372.

Prepared by general procedure D from **2q** (58.4 mg, 0.20 mmol) and **4a** (35.8 mg, 0.24 mmol), and gave the desired products **6q** and **6q'**: 76% total yield; 7.3:1 dr value analyzed by ¹H NMR.



3a-hydroxy-4-nitro-5-phenyloctahydrospiro[cyclopenta[c]indene-2,1'-cyclopentan]-6(1H)-one (6q).

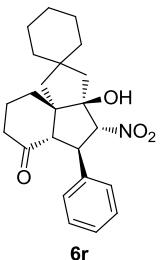
White solid; m.p. 142-144 °C; **1H NMR** (400 MHz, CDCl₃, ppm): δ 7.34-7.26 (m, 4H), 7.24-7.20 (m, 1H), 4.93 (d, *J* = 10.8 Hz, 1H), 4.03 (dd, *J* = 12.4, 10.8 Hz, 1H), 3.04 (d, *J* = 12.4 Hz, 1H), 2.85 (brs, 1H), 2.28-2.19 (m, 3H), 2.07-1.92 (m, 3H), 1.83-1.75 (m, 3H), 1.67-1.40 (m, 9H); **13C NMR** (100 MHz, CDCl₃): δ 207.1, 137.4, 128.7 (2C), 127.6 (2C), 127.5, 102.2, 90.9, 61.3, 60.8, 50.0, 47.7, 43.4, 42.8, 40.9, 40.8, 39.9, 30.8, 24.5, 24.1, 23.4. **IR** (KBr) 3384, 2950, 1697, 1542, 1370, 760, 699 cm⁻¹; **MS (EI)** *m/z* (%) 369 (1), 322 (100), 305 (21), 91 (90); **HRMS (ESI)** calcd for [M+Na]⁺ C₂₂H₂₇NO₄Na: 392.1838, found: 392.1842.



3a-hydroxy-4-nitro-5-phenyloctahydrospiro[cyclopenta[c]indene-2,1'-cyclopentan]-6(1H)-one (6q').

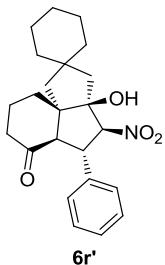
White solid; m.p. 167-168 °C; **1H NMR** (400 MHz, CDCl₃, ppm): δ 7.33-7.30 (m, 2H), 7.27-7.25 (m, 1H), 7.22-7.20 (m, 2H), 4.99 (d, *J* = 10.0 Hz, 1H), 4.57 (t, *J* = 10.8 Hz, 1H), 2.73 (d, *J* = 11.6 Hz, 1H), 2.57-2.48 (m, 1H), 2.36-2.27 (m, 2H), 2.23 (s, 1H), 2.18-2.11 (m, 2H), 1.99 (d, *J* = 14.0 Hz, 1H), 1.88 (d, *J* = 5.2 Hz, 2H), 1.84-1.78 (m, 1H), 1.74-1.64 (m, 9H); **13C NMR** (100 MHz, CDCl₃): δ 209.7, 137.7, 129.1 (2C), 127.9, 127.2 (2C), 97.8, 89.2, 62.6, 60.2, 51.8, 51.0, 50.0, 49.1, 42.5, 42.1, 38.4, 28.4, 23.9, 23.8, 22.7. **IR** (KBr) 3442, 2950, 1691, 1548, 1366, 697 cm⁻¹; **MS (EI)** *m/z* (%) 369 (1), 322 (100), 305 (25), 91 (43); **HRMS (ESI)** calcd for [M+Na]⁺ C₂₂H₂₇NO₄Na: 392.1838, found: 392.1835.

Prepared by general procedure D from **2r** (61.2 mg, 0.20 mmol) and **4a** (35.8 mg, 0.24 mmol), and gave the desired products **6r** and **6r'**: 79% total yield; 2.3:1 dr value analyzed by ¹H NMR.



3a'-hydroxy-4'-nitro-5'-phenyloctahydrospiro[cyclohexane-1,2'-cyclopenta[c]inden]-6'(1'H)-one (6r).

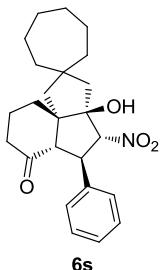
White solid; m.p. 159-162 °C; **1H NMR** (400 MHz, CDCl₃, ppm): δ 7.34-7.26 (m, 4H), 7.24-7.20 (m, 1H), 4.91 (d, *J* = 10.8 Hz, 1H), 3.91 (t, *J* = 11.6 Hz, 1H), 2.98 (d, *J* = 12.4 Hz, 1H), 2.81 (s, 1H), 2.28-2.18 (m, 3H), 2.12-1.92 (m, 3H), 1.81-1.71 (m, 3H), 1.63-1.58 (m, 1H), 1.51-1.26 (m, 10H); **13C NMR** (100 MHz, CDCl₃): δ 206.8, 137.1, 128.7 (2C), 127.6 (3C), 101.8, 90.5, 61.5, 59.8, 49.6 (2C), 43.2, 40.8, 40.6, 39.4, 38.5, 32.3, 25.7, 24.1, 23.7, 23.1. **IR** (KBr) 3497, 2918, 1670, 1542, 1369, 1230, 699 cm⁻¹; **MS (EI)** *m/z* (%) 383 (2), 336 (95), 319 (23), 91 (100); **HRMS (ESI)** calcd for [M+Na]⁺ C₂₃H₂₉NO₄Na: 406.1994, found: 406.1991.



3a'-hydroxy-4'-nitro-5'-phenyloctahydrospiro[cyclohexane-1,2'-cyclopenta[c]inden]-6'(1'H)-one (6r').

White solid; m.p. 192-193 °C; **1H NMR** (400 MHz, DMSO-d₆, ppm): δ 7.30 (d, *J* = 4.4 Hz, 4H), 7.24-7.21 (m, 1H), 5.63 (s, 1H), 5.06 (d, *J* = 10.4 Hz, 1H), 4.50 (t, *J* = 10.6 Hz, 1H), 2.60 (d, *J* = 11.2 Hz, 1H), 2.57-2.52 (m, 1H), 2.23-2.17 (m, 2H), 2.04-1.95 (m, 3H), 1.85 (d, *J* = 14.0 Hz, 1H), 1.81-1.70 (m, 1H), 1.57-1.34 (m, 12H); **13C NMR** (100 MHz, DMSO-d₆): δ 210.3, 138.9, 128.6 (2C), 127.6 (2C), 127.2, 97.6, 89.0, 62.4, 59.4, 50.0, 49.0, 48.7, 41.5, 41.1, 39.9, 38.1, 28.6, 25.3, 23.4, 22.7, 21.9. **IR** (KBr) 3406, 2920, 1690, 1546, 1369, 697 cm⁻¹; **MS (EI)** *m/z* (%) 336 (100), 319 (31), 91 (55); **HRMS (ESI)** calcd for [M+Na]⁺ C₂₃H₂₉NO₄Na: 406.1994, found: 406.1991.

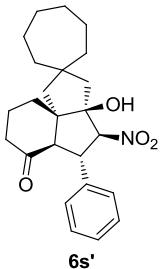
Prepared by general procedure D from **2s** (64.0 mg, 0.20 mmol) and **4a** (35.8 mg, 0.24 mmol), and gave the desired products **6s** and **6s'**: 74% total yield; 2.6:1 dr value analyzed by **1H NMR**.



3a'-hydroxy-4'-nitro-5'-phenyloctahydrospiro[cycloheptane-1,2'-cyclopenta[c]inden]-6'(1'H)-one (6s).

White solid; m.p. 160-162 °C; **1H NMR** (400 MHz, CDCl₃, ppm): δ 7.35-7.29 (m, 4H), 7.25-7.22 (m, 1H), 4.90 (d, *J* = 11.2 Hz, 1H), 3.81 (t, *J* = 11.8 Hz, 1H), 2.96 (d, *J* = 12.0 Hz, 1H), 2.74 (s, 1H), 2.30-2.22 (m, 3H), 2.09-1.96 (m, 3H), 1.85-1.79 (m, 2H), 1.76-1.71 (m, 2H), 1.67-1.57 (m,

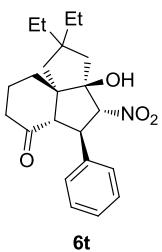
3H), 1.52-1.39 (m, 8H), 1.31-1.27 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.7, 136.8, 128.8 (2C), 127.6, 127.6 (2C), 101.4, 90.0, 61.9, 59.9, 51.9, 44.5, 44.3, 42.9, 42.8, 40.8, 40.4, 32.2, 29.2, 28.8, 24.2 (2C), 23.5. **IR** (KBr) 3522, 2921, 1700, 1584, 1367, 699 cm⁻¹; **MS (EI)** *m/z* (%) 397 (2), 350 (56), 333 (13), 171 (100), 91 (90); **HRMS (ESI)** calcd for [M+Na]⁺ C₂₄H₃₁NO₄Na: 420.2151, found: 420.2140.



3a'-hydroxy-4'-nitro-5'-phenyloctahydrospiro[cycloheptane-1,2'-cyclopenta[c]inden]-6'(1'H)-one (6s').

White solid; m.p. 168-170 °C; **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.34-7.30 (m, 2H), 7.27-7.25 (m, 1H), 7.20-7.18 (m, 2H), 4.96 (d, *J* = 9.6 Hz, 1H), 4.56 (dd, *J* = 12.0, 9.2 Hz, 1H), 2.73 (d, *J* = 12.4 Hz, 1H), 2.61-2.53 (m, 1H), 2.35-2.29 (m, 1H), 2.25 (s, 1H), 2.22-2.13 (m, 3H), 2.04 (d, *J* = 14.0 Hz, 1H), 1.84-1.68 (m, 8H), 1.54-1.47 (m, 8H); **¹³C NMR** (100 MHz, CDCl₃): δ 209.8, 137.4, 129.2 (2C), 128.0, 127.1 (2C), 98.8, 89.2, 63.1, 60.8, 53.9, 51.6, 50.8, 46.1, 45.3, 43.5, 38.2, 29.1, 28.9, 28.2, 24.1, 23.5, 23.4. **IR** (KBr) 3425, 2924, 1688, 1546, 1445, 697 cm⁻¹; **MS (EI)** *m/z* (%) 397 (1), 350 (100), 333 (45), 91 (81); **HRMS (ESI)** calcd for [M+Na]⁺ C₂₄H₃₁NO₄Na: 420.2151, found: 420.2148.

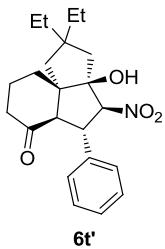
Prepared by general procedure D from **2t** (58.8 mg, 0.20 mmol) and **4a** (35.8 mg, 0.24 mmol), and gave the desired products **6t** and **6t'**: 58% total yield; 3.3:1 dr value analyzed by **¹H NMR**.



2,2-diethyl-3a-hydroxy-4-nitro-5-phenyloctahydro-1*H*-cyclopenta[*c*]inden-6(7*H*)-one (6t).

White solid; m.p. 160-162 °C; **¹H NMR** (400 MHz, CDCl₃, ppm): δ 7.34-7.26 (m, 4H), 7.23-7.20 (m, 1H), 4.90 (d, *J* = 11.6 Hz, 1H), 3.81 (t, *J* = 11.8 Hz, 1H), 2.98-2.95 (m, 2H), 2.27-2.19 (m, 3H), 2.11-1.94 (m, 3H), 1.73-1.64 (m, 3H), 1.58-1.52 (m, 2H), 1.36-1.19 (m, 3H), 0.78-0.73 (m, 6H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.8, 136.8, 128.7 (2C), 127.5 (3C), 101.4, 90.1, 61.6, 59.5, 49.3, 43.6, 42.9, 41.6, 40.7, 32.4, 30.8, 28.7, 24.2, 8.8, 8.5. **IR** (KBr) 3429, 2960, 1700, 1543,

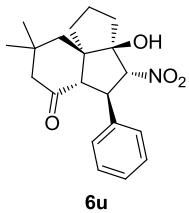
1367, 765, 700 cm^{-1} ; **MS (EI)** m/z (%) 371 (1), 324 (54), 307 (18), 91 (100); **HRMS (ESI)** calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{22}\text{H}_{29}\text{NO}_4\text{Na}$: 394.1994, found: 394.1978.



2,2-diethyl-3a-hydroxy-4-nitro-5-phenyloctahydro-1*H*-cyclopenta[*c*]inden-6(7*H*)-one (6t'**).**

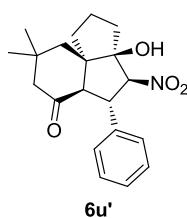
White solid; m.p. 154-155 °C; **¹H NMR** (400 MHz, CDCl_3 , ppm): δ 7.34-7.30 (m, 2H), 7.27-7.25 (m, 1H), 7.19-7.17 (m, 2H), 4.94 (d, $J = 9.6$ Hz, 1H), 4.55 (dd, $J = 12.4, 9.2$ Hz, 1H), 2.73 (d, $J = 12.4$ Hz, 1H), 2.63-2.54 (m, 1H), 2.34-2.26 (m, 2H), 2.23-2.12 (m, 2H), 2.11-2.04 (m, 1H), 1.97-1.94 (m, 1H), 1.80-1.67 (m, 4H), 1.63-1.57 (m, 2H), 1.52-1.46 (m, 2H), 0.84 (t, $J = 7.6$ Hz, 3H), 0.80 (d, $J = 7.2$ Hz, 3H); **¹³C NMR** (100 MHz, CDCl_3): δ 209.8, 137.3, 129.2 (2C), 128.0, 127.0 (2C), 99.1, 89.0, 63.0, 60.8, 51.6, 51.0, 48.6, 45.7, 38.1, 33.0, 31.3, 28.2, 23.5, 9.1, 8.6. **IR** (KBr) 3435, 2979, 1691, 1550, 1372, 1094, 698 cm^{-1} ; **MS (EI)** m/z (%) 371 (1), 324 (100), 307 (33), 91 (59); **HRMS (ESI)** calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{22}\text{H}_{29}\text{NO}_4\text{Na}$: 394.1994, found: 394.1993.

Prepared by general procedure D from **2u** (53.2 mg, 0.20 mmol) and **4a** (35.8 mg, 0.24 mmol), and gave the desired products **6u** and **6u'**: 69% total yield; 4.6:1 dr value analyzed by **¹H NMR**.



3a-hydroxy-8,8-dimethyl-4-nitro-5-phenyloctahydro-1*H*-cyclopenta[*c*]inden-6(7*H*)-one (6u**).**

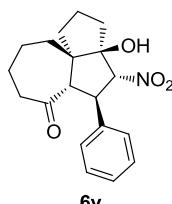
White solid; m.p. 194-196 °C; **¹H NMR** (400 MHz, DMSO-d_6 , ppm): δ 7.34-7.27 (m, 4H), 7.24-7.20 (m, 1H), 5.99 (s, 1H), 4.95 (d, $J = 11.2$ Hz, 1H), 3.60 (t, $J = 11.8$ Hz, 1H), 3.45 (d, $J = 12.4$ Hz, 1H), 2.46 (d, $J = 13.6$ Hz, 1H), 2.09 (d, $J = 13.6$ Hz, 1H), 1.90 (d, $J = 13.2$ Hz, 1H), 1.85-1.72 (m, 2H), 1.60-1.49 (m, 4H), 1.43-1.35 (m, 1H), 1.14 (s, 3H), 1.02 (s, 3H); **¹³C NMR** (100 MHz, DMSO-d_6): δ 207.5, 138.2, 128.5 (2C), 127.5 (2C), 127.2, 103.4, 90.3, 57.5, 56.7, 54.7, 45.7, 44.9, 37.9, 35.5, 34.3, 34.0, 30.1, 22.1. **IR** (KBr) 3357, 2958, 1700, 1545, 1365, 1099, 698 cm^{-1} ; **MS (EI)** m/z (%) 294 (34), 279 (14), 254 (18), 199 (100), 91 (95); **HRMS (ESI)** calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{20}\text{H}_{25}\text{NO}_4\text{Na}$: 366.1681, found: 366.1684.



3a-hydroxy-8,8-dimethyl-4-nitro-5-phenyloctahydro-1*H*-cyclopenta[*c*]inden-6(*7H*)-one (6u'**).**

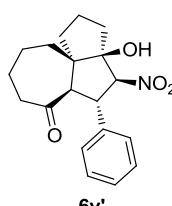
White solid; m.p. 202-204 °C; **1H NMR** (400 MHz, DMSO-d₆, ppm): δ 7.39 (d, *J* = 7.6 Hz, 2H), 7.29-7.24 (m, 2H), 7.22-7.18 (m, 1H), 5.64 (s, 1H), 5.04 (d, *J* = 11.6 Hz, 1H), 4.10 (t, *J* = 12.2 Hz, 1H), 2.72 (d, *J* = 13.2 Hz, 1H), 2.37-2.33 (m, 2H), 2.25 (d, *J* = 13.2 Hz, 1H), 1.86-1.76 (m, 3H), 1.72-1.56 (m, 2H), 1.51-1.44 (m, 1H), 1.23 (d, *J* = 14.8 Hz, 1H), 1.09 (s, 3H), 0.86 (s, 3H); **13C NMR** (100 MHz, DMSO-d₆): δ 210.3, 137.2, 128.3 (2C), 127.7 (2C), 127.3, 95.1, 88.8, 60.2, 55.9, 51.0, 48.6, 42.2, 40.9, 38.4, 36.1, 32.5, 26.4, 21.3. **IR** (KBr) 3399, 2960, 1695, 1547, 1369, 1126, 698 cm⁻¹; **MS (EI)** *m/z* (%) 294 (46), 279 (34), 254 (100), 91 (43); **HRMS (ESI)** calcd for [M+Na]⁺ C₂₀H₂₅NO₄Na: 366.1681, found: 366.1667.

Prepared by general procedure D from **2v** (50.4 mg, 0.20 mmol) and **4a** (35.8 mg, 0.24 mmol), and gave the desired products **6v** and **6v'**: 56% total yield; 2.0:1 dr value analyzed by ¹H NMR.



3a-hydroxy-4-nitro-5-phenyldecahydrocyclopenta[c]azulen-6(*1H*)-one (6v**).**

White solid; m.p. 209-211 °C; **1H NMR** (400 MHz, DMSO-d₆, ppm): δ 7.38-7.35 (m, 2H), 7.29-7.25 (m, 2H), 7.21-7.17 (m, 1H), 5.56 (s, 1H), 5.16 (d, *J* = 12.4 Hz, 1H), 3.71 (t, *J* = 12.1 Hz, 1H), 3.57 (d, *J* = 12.0 Hz, 1H), 2.30-2.25 (m, 1H), 2.14-2.05 (m, 1H), 1.99-1.94 (m, 1H), 1.86-1.70 (m, 3H), 1.68-1.58 (m, 3H), 1.55-1.51 (m, 3H), 1.43-1.33 (m, 1H), 1.26-1.19 (m, 1H); **13C NMR** (100 MHz, DMSO-d₆): δ 208.8, 138.0, 128.3 (2C), 128.0 (2C), 127.1, 99.5, 89.4, 59.8, 53.9, 44.4, 42.4, 37.1, 35.0, 33.5, 25.2, 22.7, 22.2. **IR** (KBr) 3526, 2934, 1692, 1535, 1373, 698 cm⁻¹; **MS (EI)** *m/z* (%) 282 (99), 265 (62), 195 (57), 91 (100), 77 (31); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₉H₂₃NO₄Na: 352.1519, found: 352.1528.



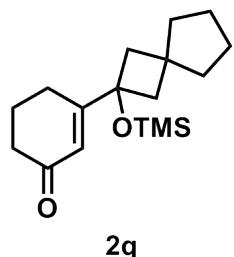
3a-hydroxy-4-nitro-5-phenyldecahydrocyclopenta[c]azulen-6(1H)-one (6v').

White solid; m.p. 160-162 °C; **¹H NMR** (400 MHz, DMSO-d₆, ppm): δ 7.39-7.37 (m, 2H), 7.28-7.24 (m, 2H), 7.19-7.15 (m, 1H), 5.50 (s, 1H), 5.14 (d, *J* = 12.4 Hz, 1H), 4.42 (dd, *J* = 12.4, 10.4 Hz, 1H), 3.00 (d, *J* = 10.4 Hz, 1H), 2.43-2.37 (m, 1H), 2.34-2.29 (m, 1H), 2.22-2.16 (m, 1H), 2.13-1.90 (m, 3H), 1.82-1.70 (m, 2H), 1.67-1.56 (m, 3H), 1.49-1.42 (m, 1H), 1.39-1.32 (m, 1H), 1.30-1.23 (m, 1H); **¹³C NMR** (100 MHz, DMSO-d₆): δ 208.8, 140.1, 128.3 (2C), 128.2 (2C), 126.7, 93.9, 91.0, 65.0, 52.4, 45.3, 41.9, 37.3, 34.0, 29.9, 23.6, 22.8, 20.2. **IR** (KBr) 3385, 2928, 1685, 1547, 1372, 698 cm⁻¹; **MS (EI)** *m/z* (%) 282 (95), 265 (67), 240 (34), 91 (100), 77 (35); **HRMS (ESI)** calcd for [M+Na]⁺ C₁₉H₂₃NO₄Na: 352.1519, found: 352.1504.

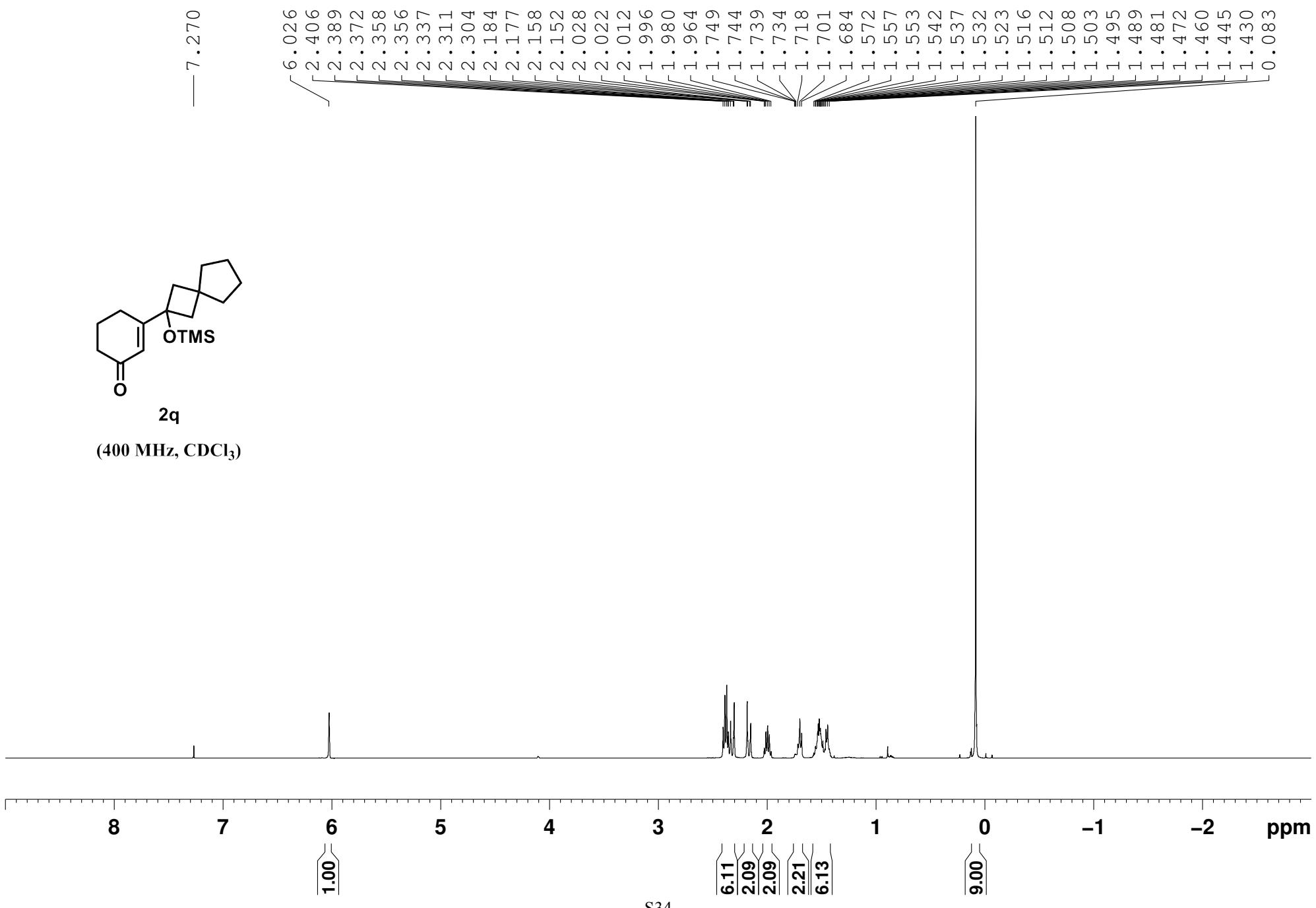
8. References

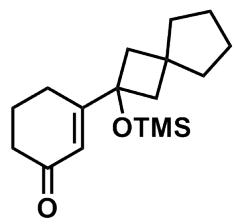
- (1) Yang, M.; Wang, L.; He, Z.-H.; Wang, S.-H.; Zhang, S.-Y.; Tu, Y.-Q.; Zhang, F.-M. Tandem Semipinacol-Type 1,2-Carbon Migration/Aldol Reaction toward the Construction of [5-6-7] All-Carbon Tricyclic Core of Calyciphylline A-Type Alkaloids. *Org. Lett.* **2012**, *14*, 5114–5117.
- (2) Ferraro, A.; Bernardi, L.; Fochia, M. Organocatalytic Enantioselective Transfer Hydrogenation of β-Amino Nitroolefins. *Adv. Synth. Catal.* **2016**, *358*, 1561–1565.
- (3) Zhang, E.; Fan, C.-A.; Tu, Y.-Q.; Zhang, F.-M.; Song, Y.-L. Organocatalytic Asymmetric Vinyllogous α-Ketol Rearrangement: Enantioselective Construction of Chiral All-Carbon Quaternary Stereocenters in Spirocyclic Diketones via Semipinacol-Type 1,2-Carbon Migration. *J. Am. Chem. Soc.* **2009**, *131*, 14626–14627.
- (4) Shih, C.; Swenton, J. S. Use of Protected β-Bromocyclopentenones and β-Bromocyclohexenones as β-Acylvinyl Anion Equivalents. *J. Org. Chem.* **1982**, *47*, 2825–2832.
- (5) Attolini, M.; Iacazio, G.; Peiffer, G.; Maffei, M. Enzymatic Resolution of 3-Bromocyclohept-2-enol: Application to the Determination of the Absolute Configuration of Diethyl (3-hydroxy-cyclohept-1-enyl)phosphonate. *Tetrahedron: Asymmetry* **2003**, *14*, 3857–3860.

9. Copies of ¹H NMR and ¹³C NMR spectra for compounds.



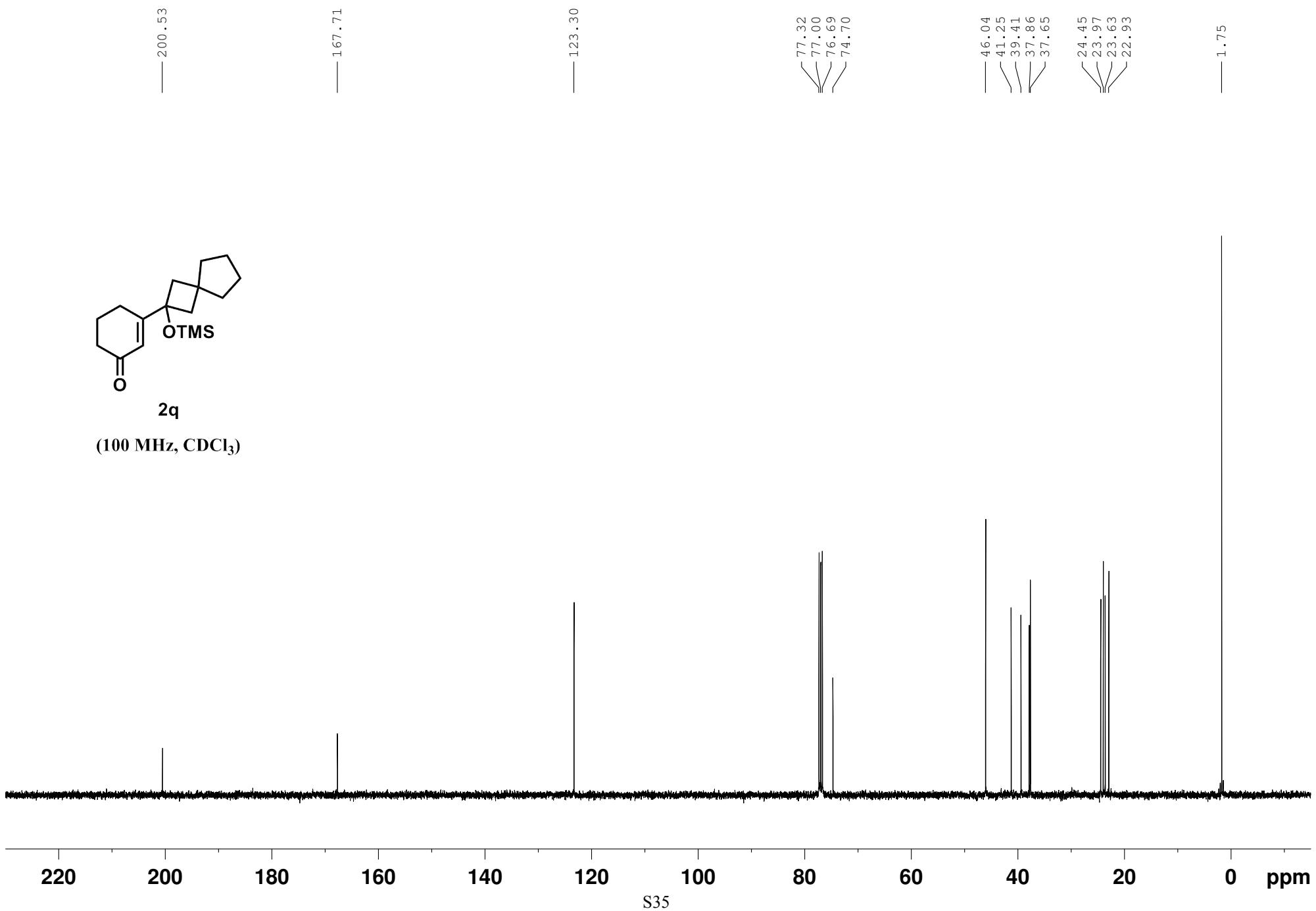
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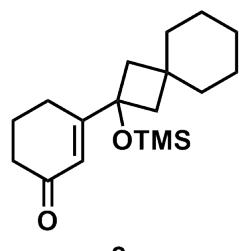




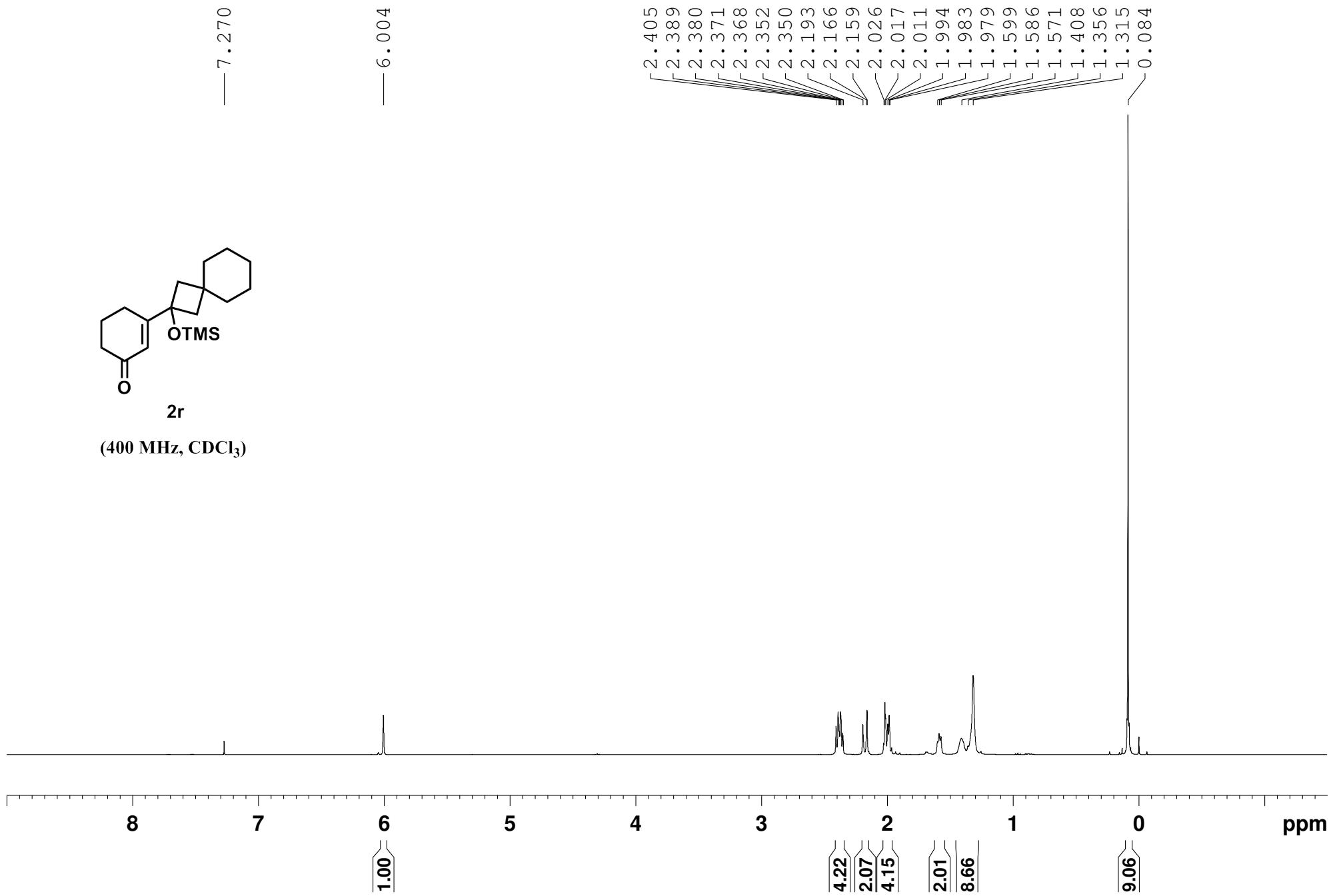
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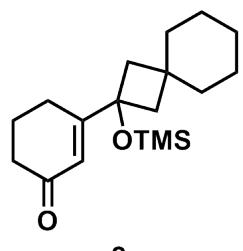
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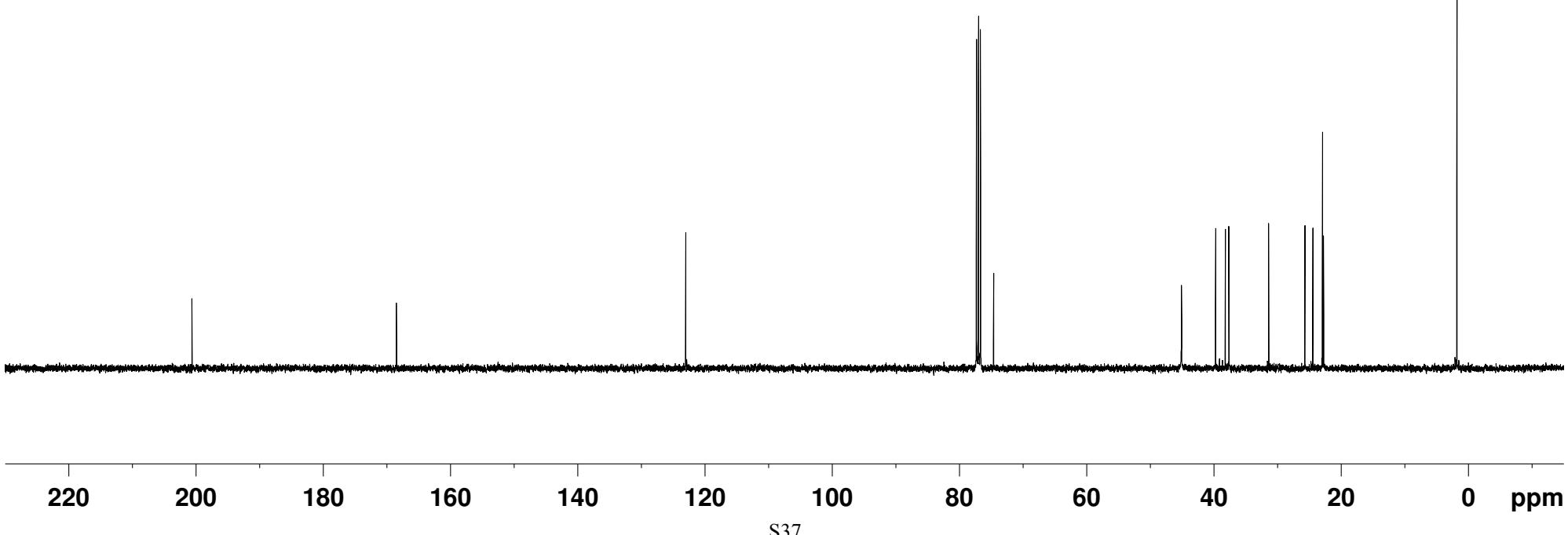
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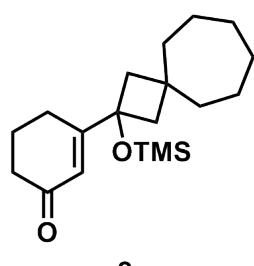




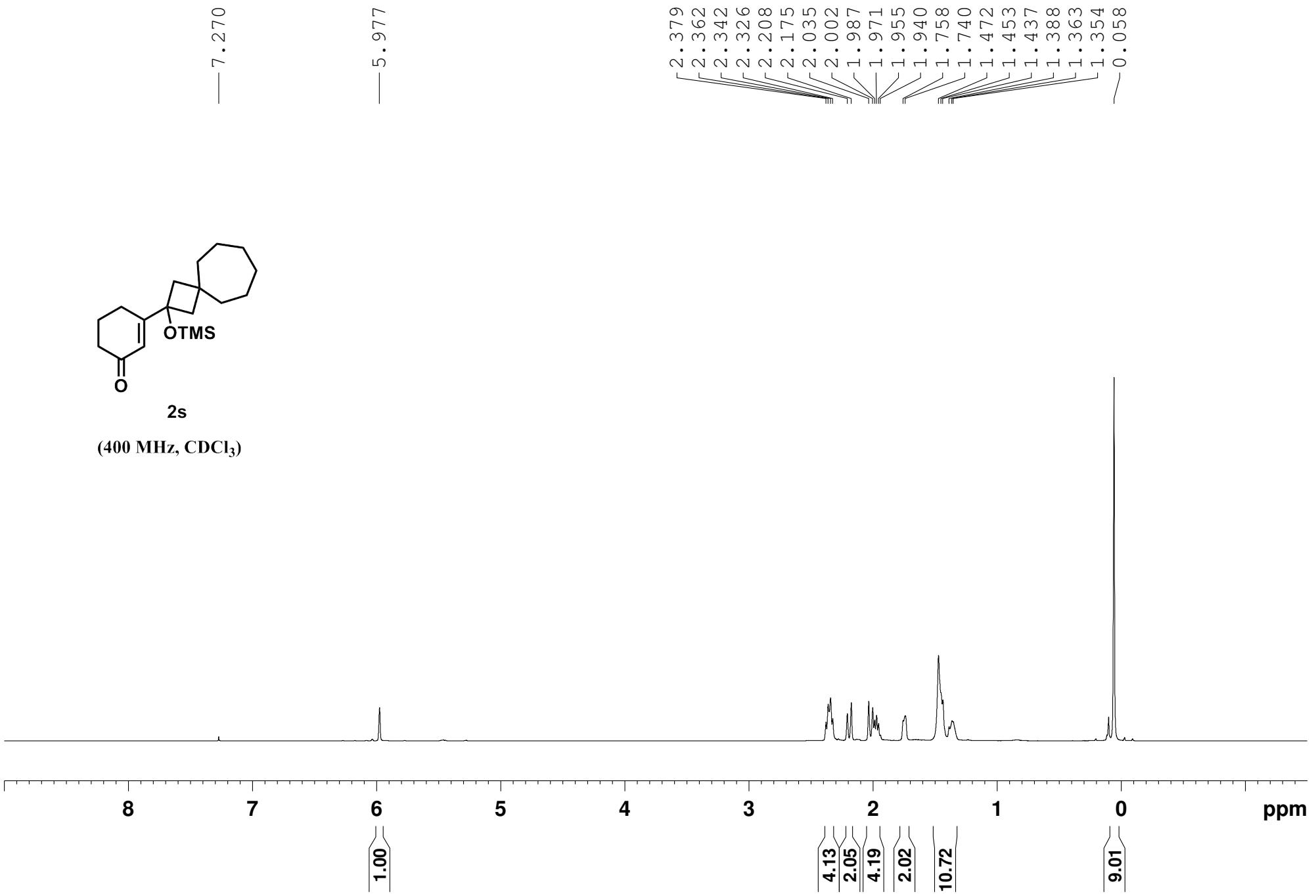
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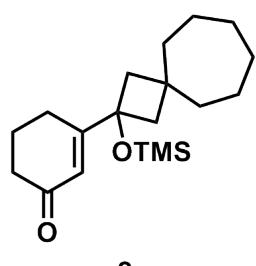
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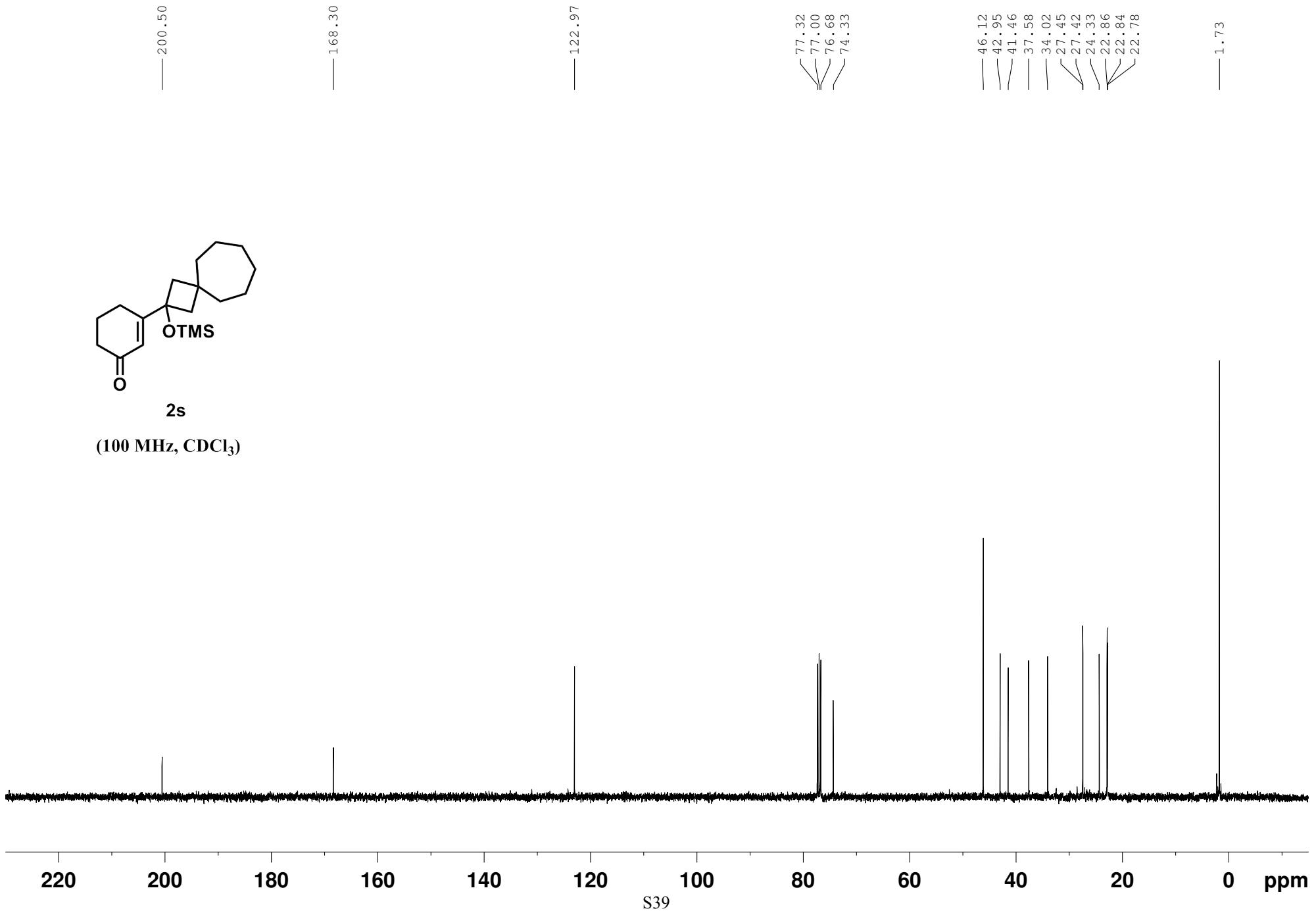
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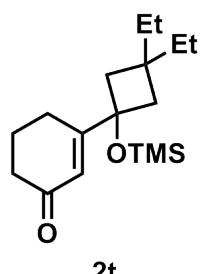




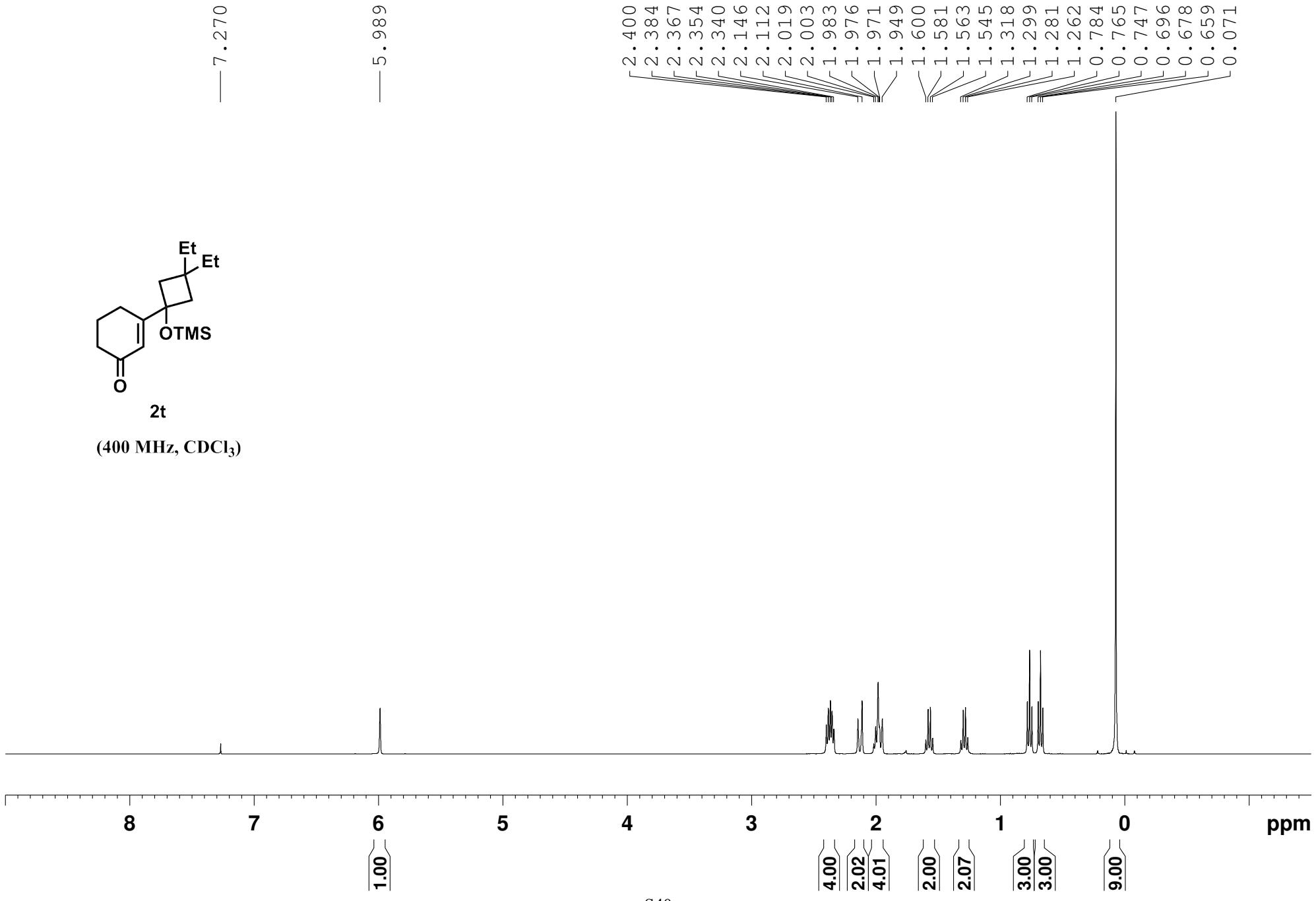
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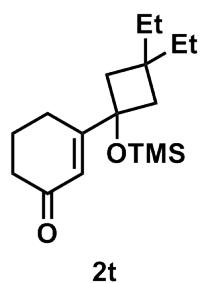
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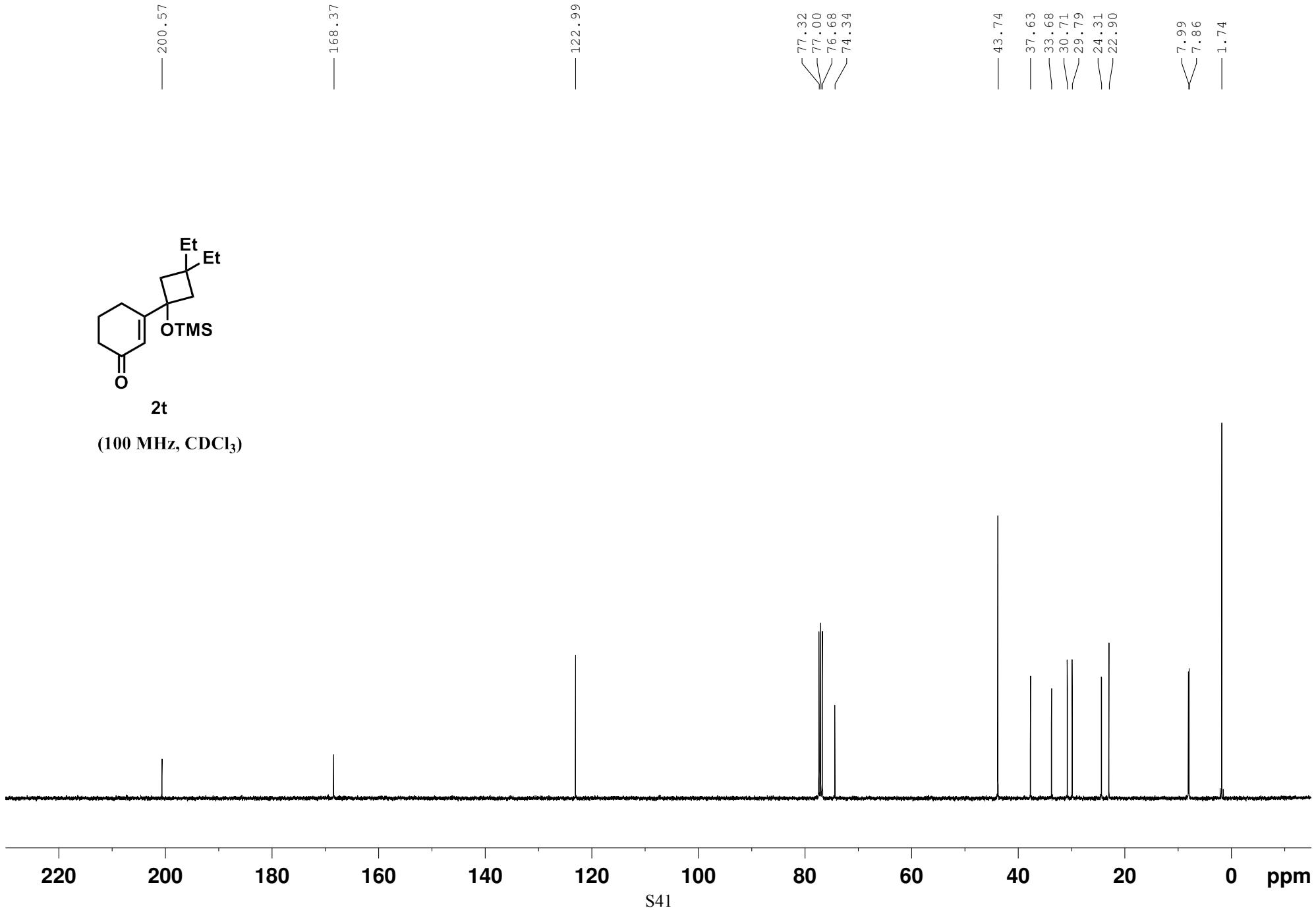
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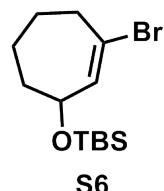




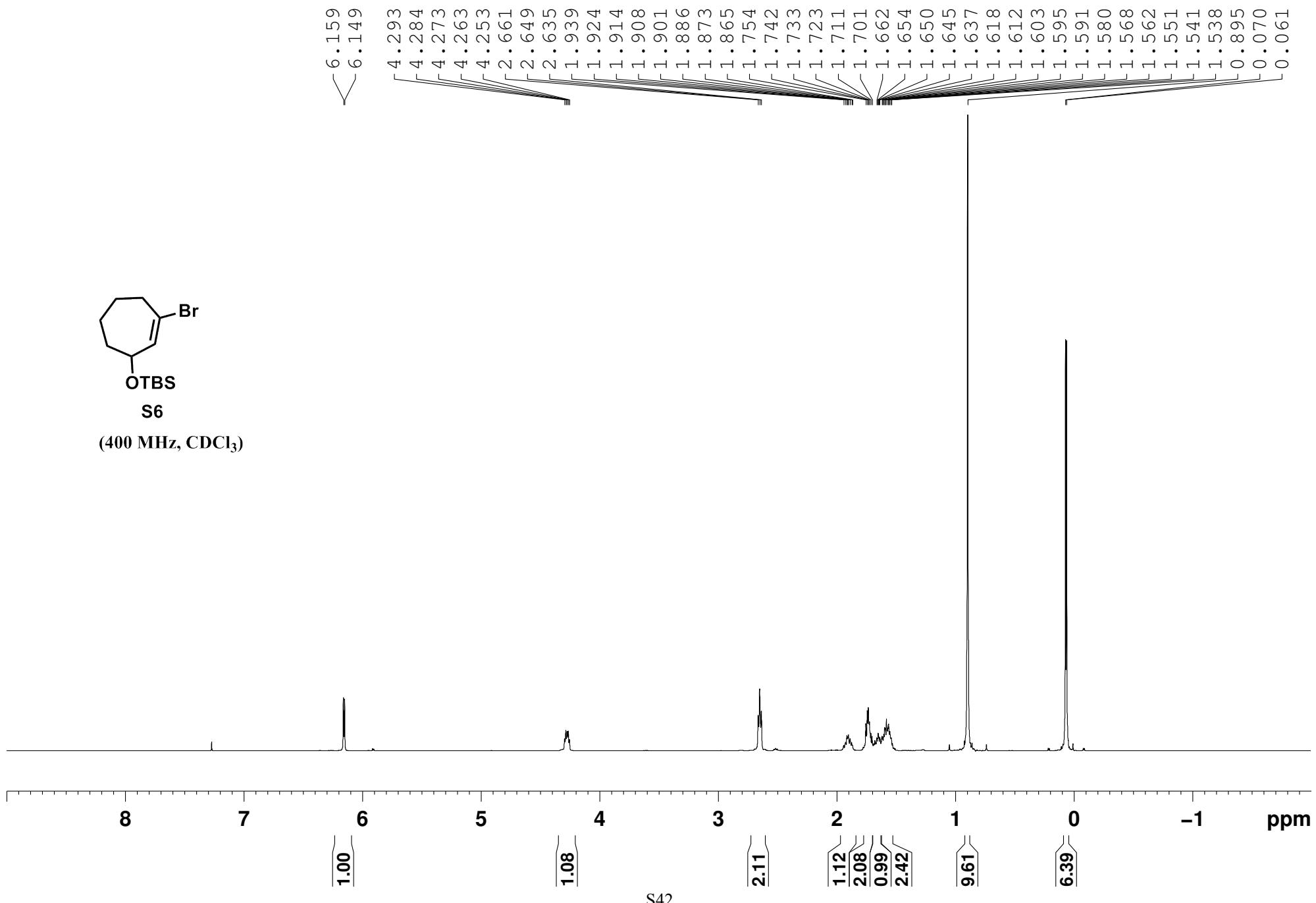
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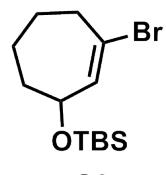
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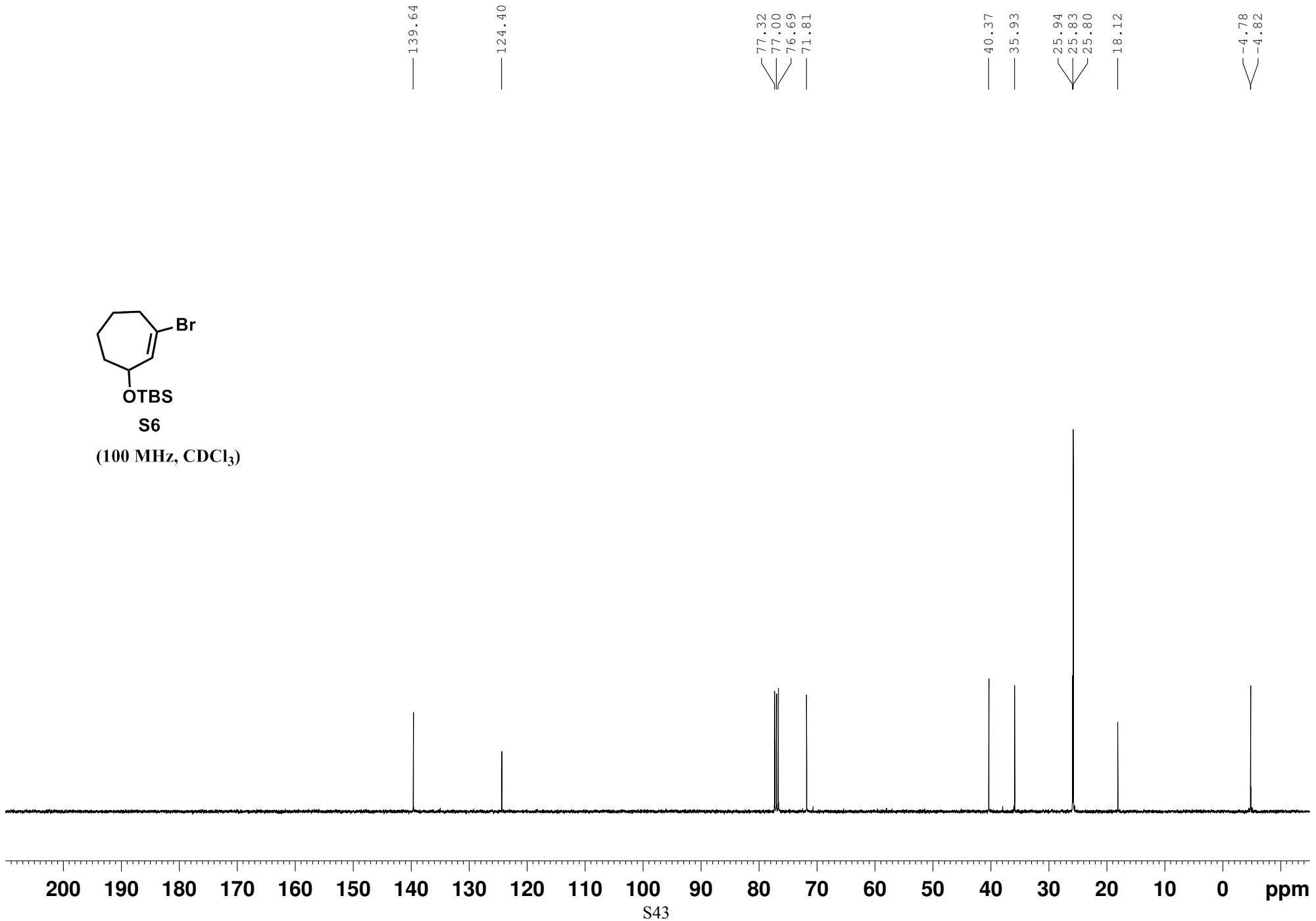
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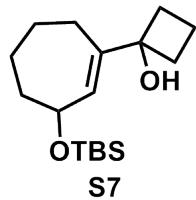




S6

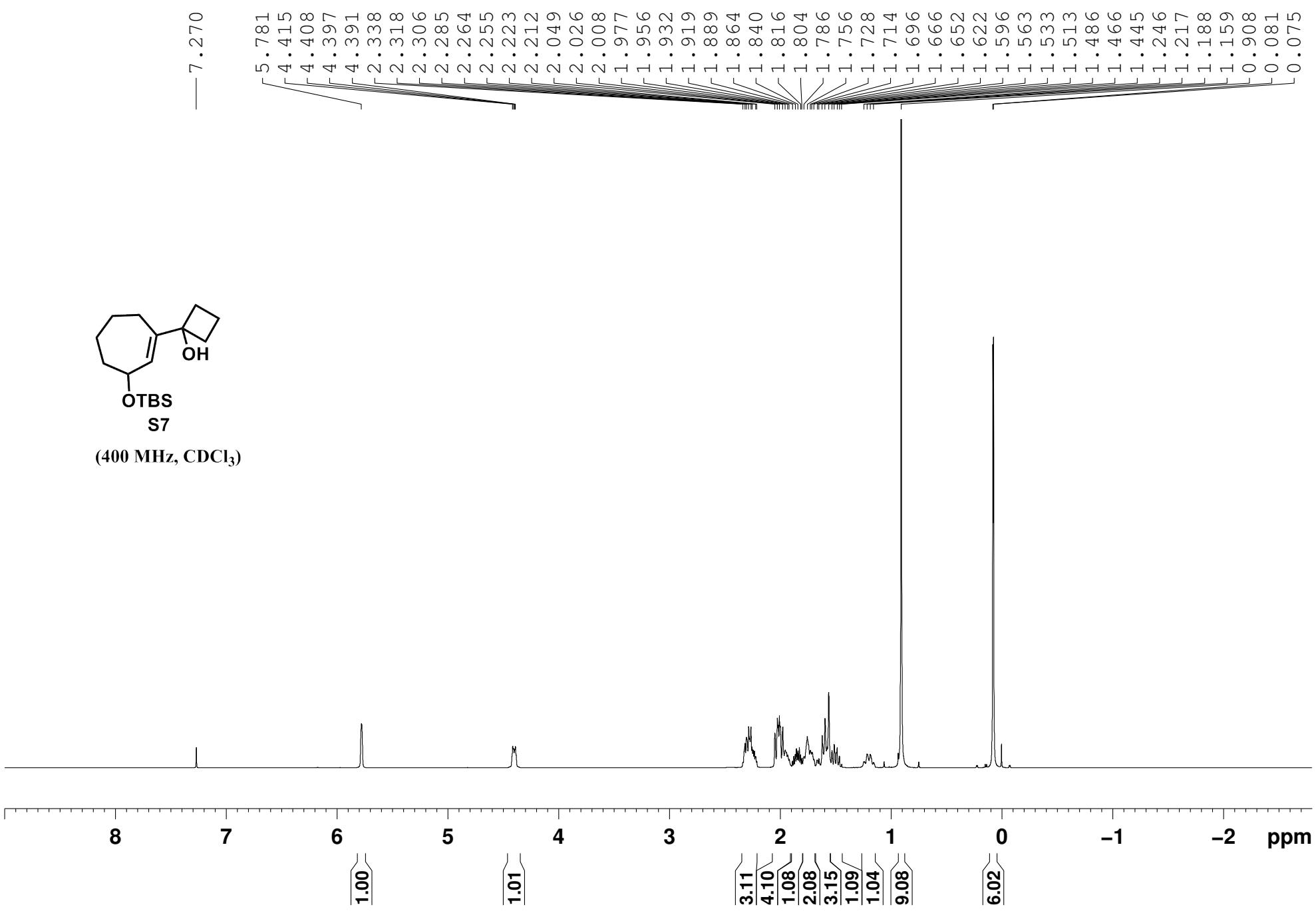
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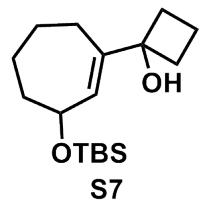




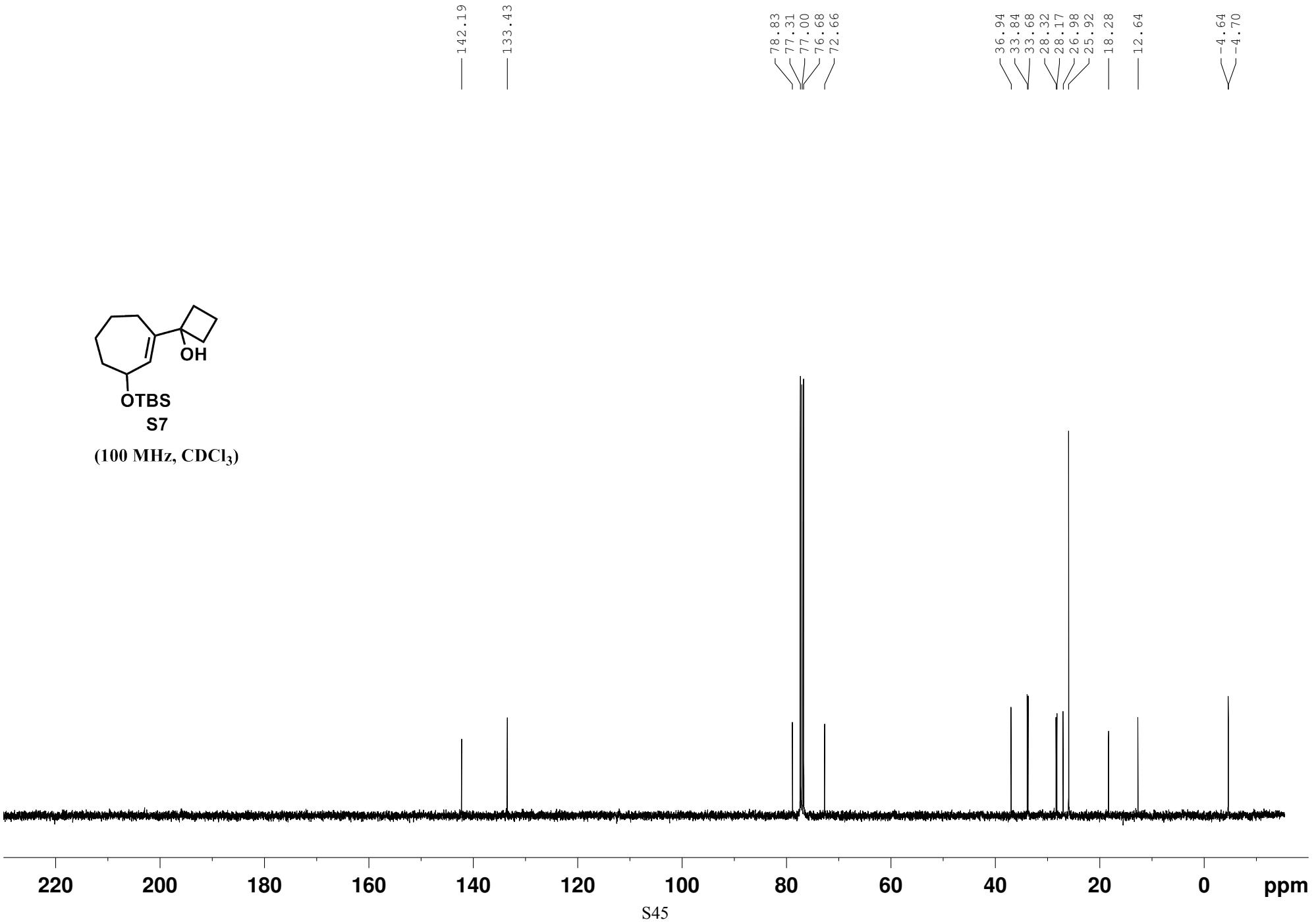
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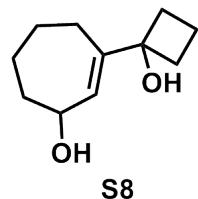
— 7.270



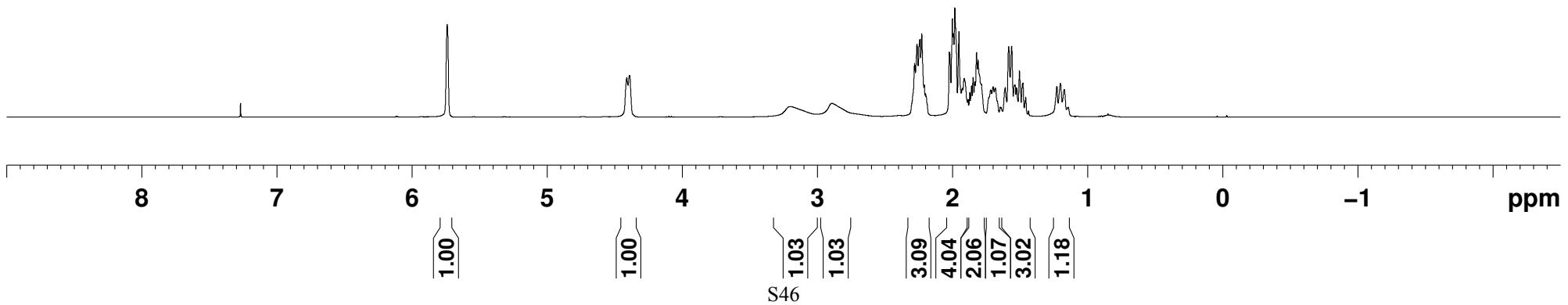


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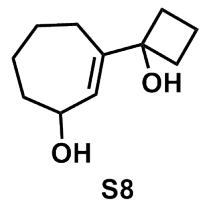




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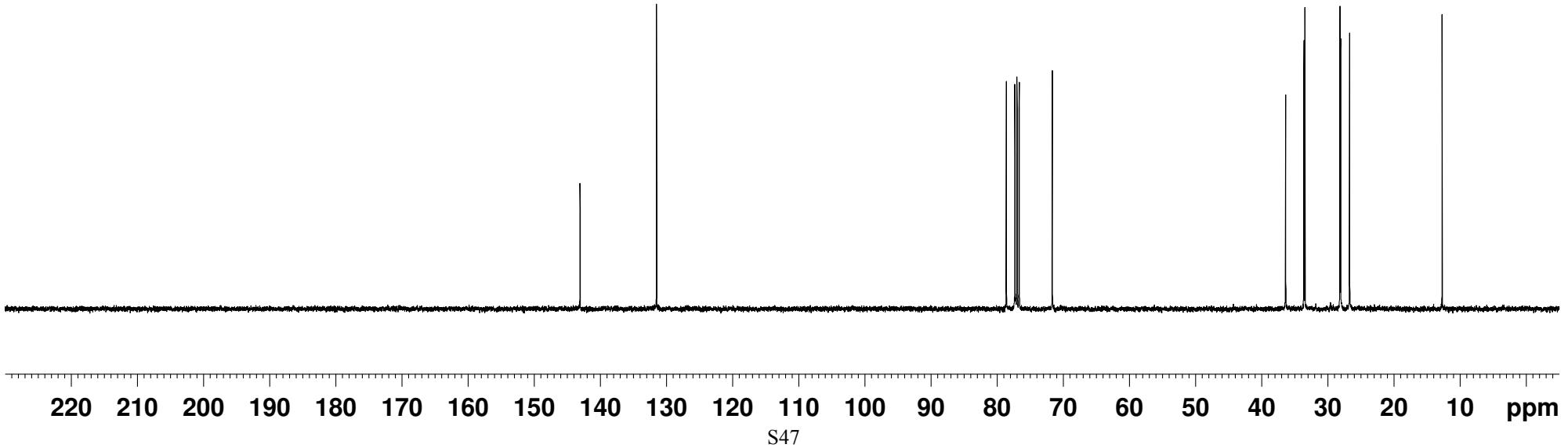


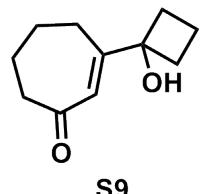
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S8

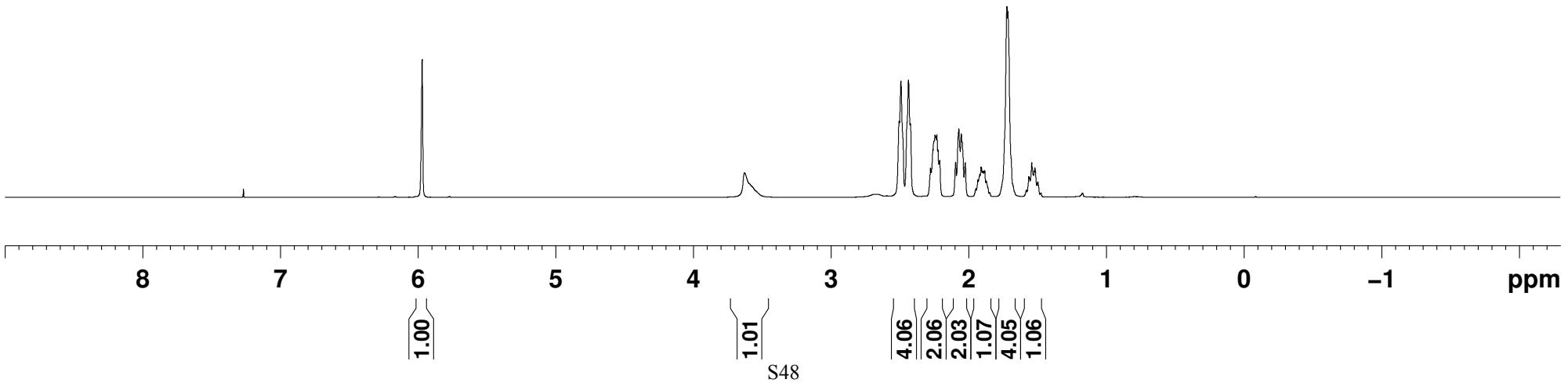
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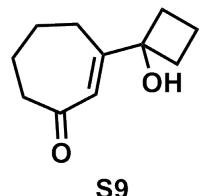




S9

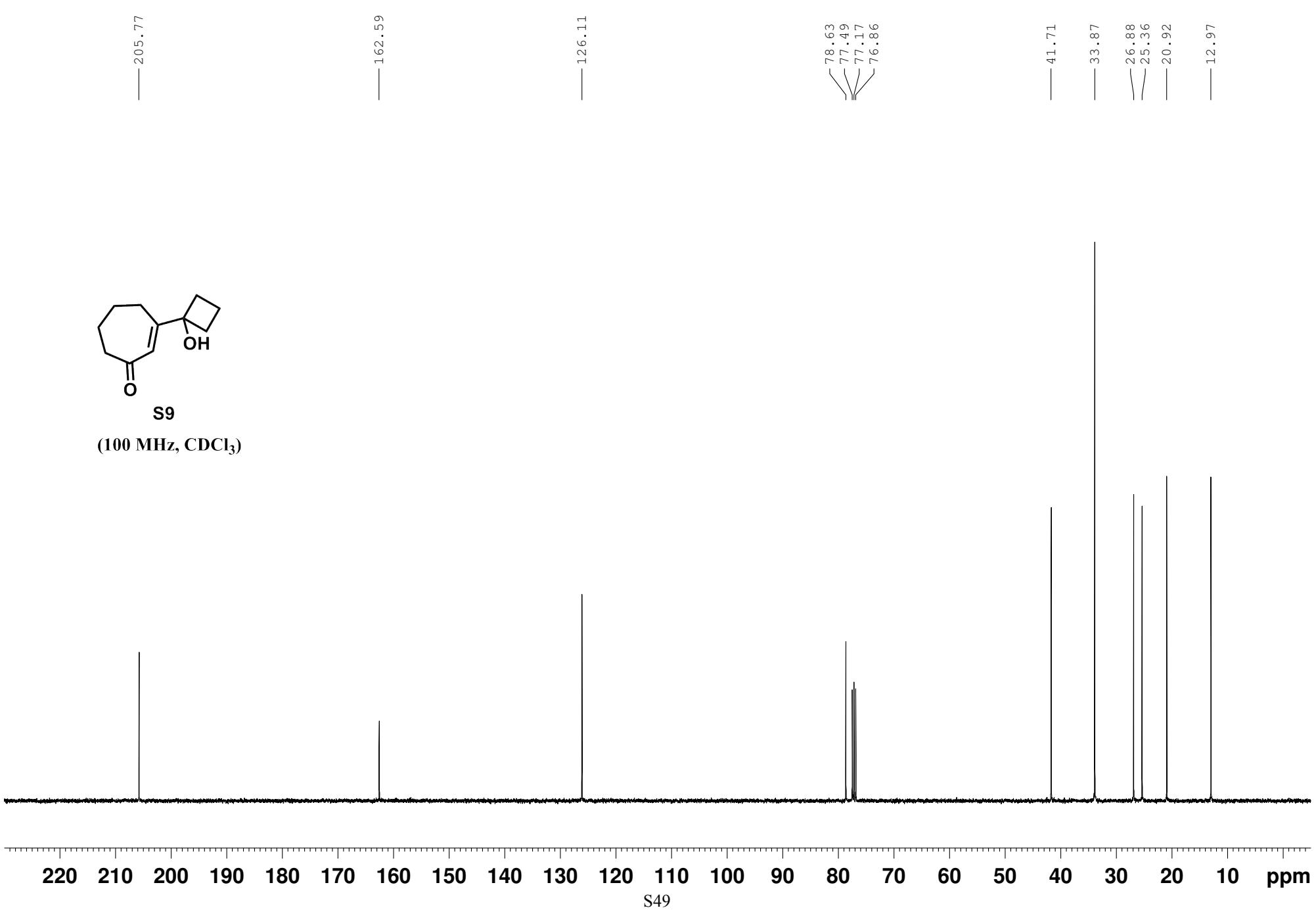
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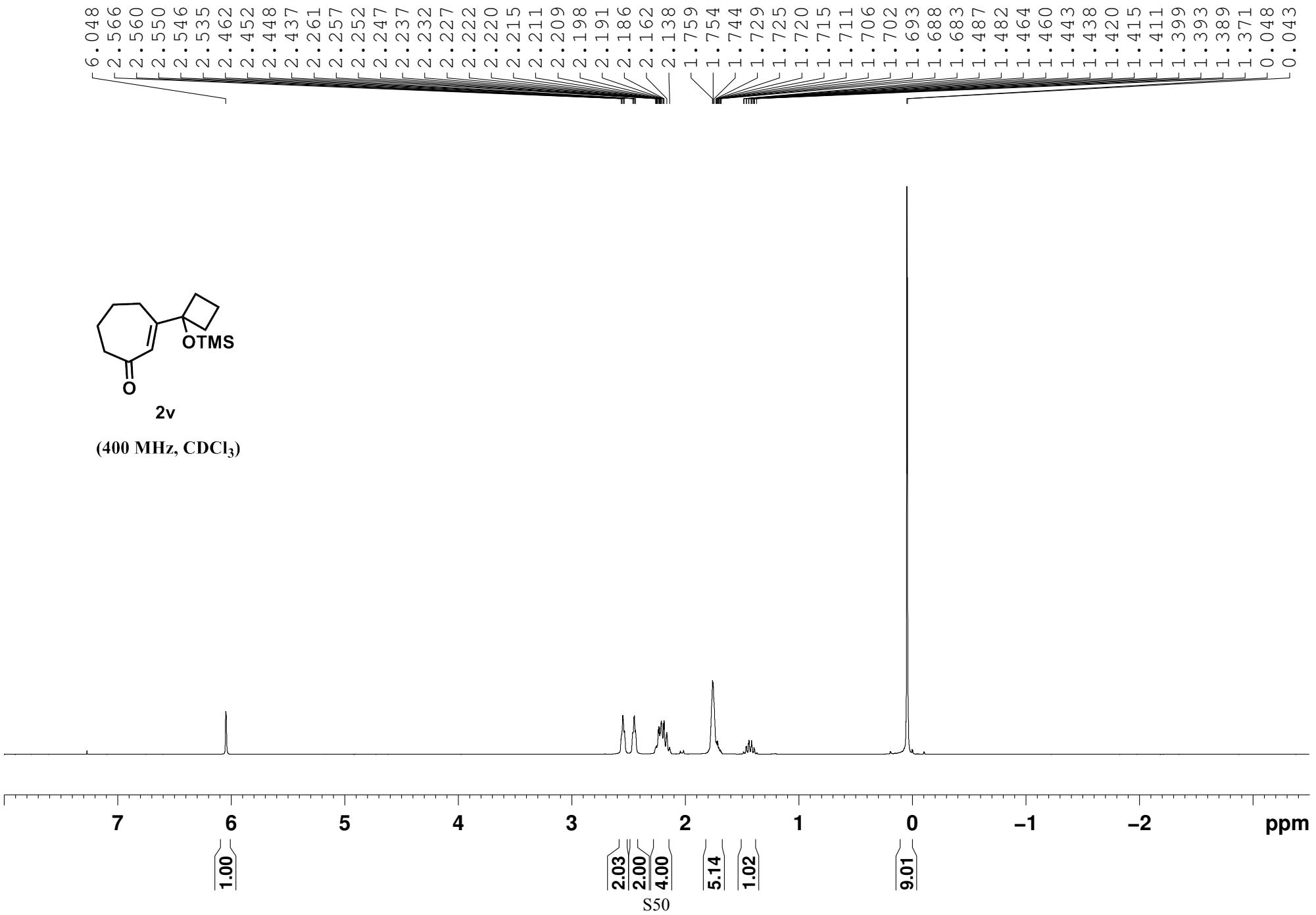


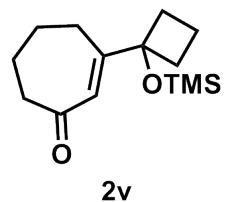


S9

(100 MHz, CDCl₃)

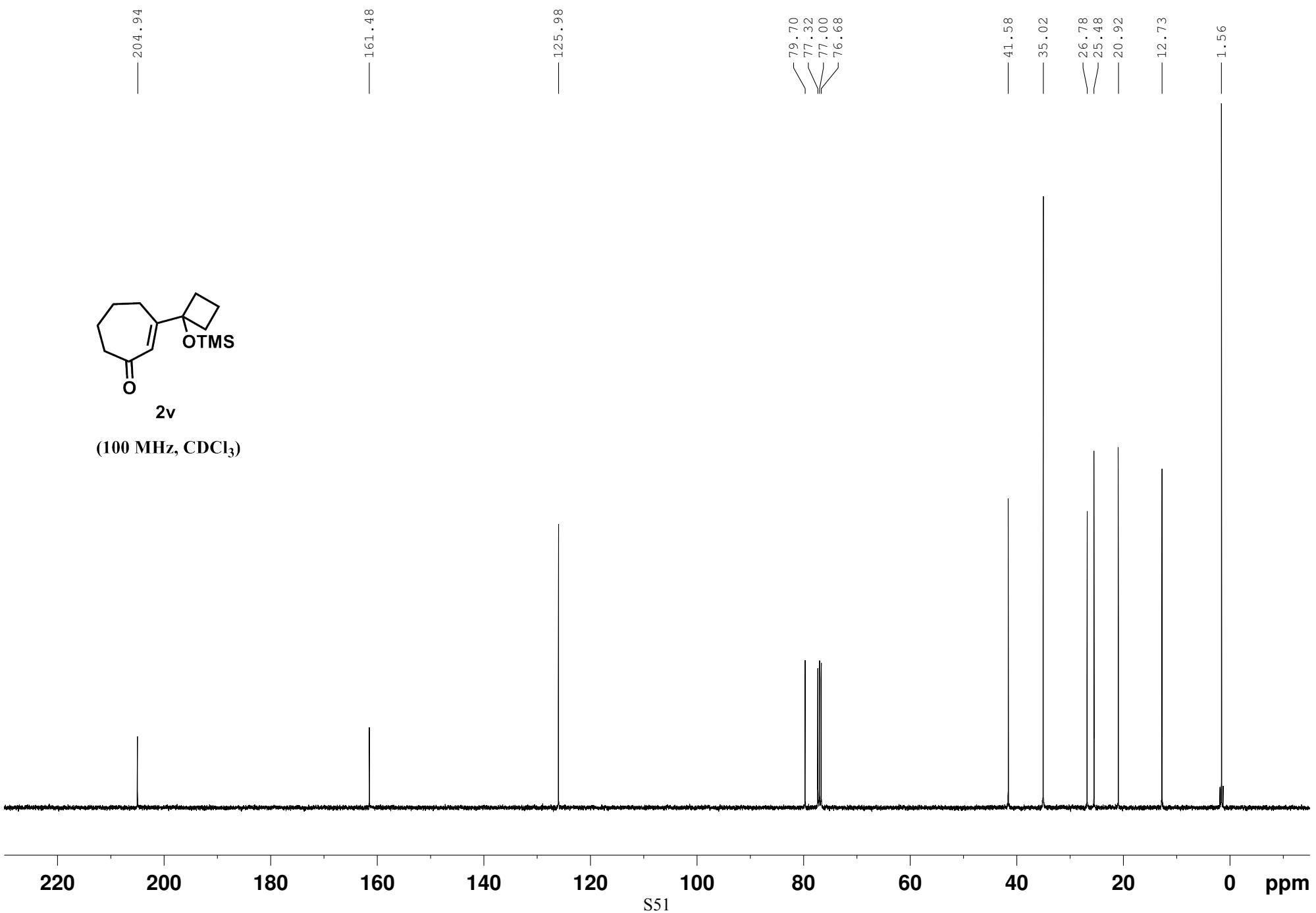




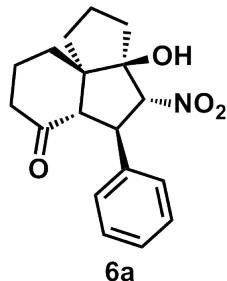


2v

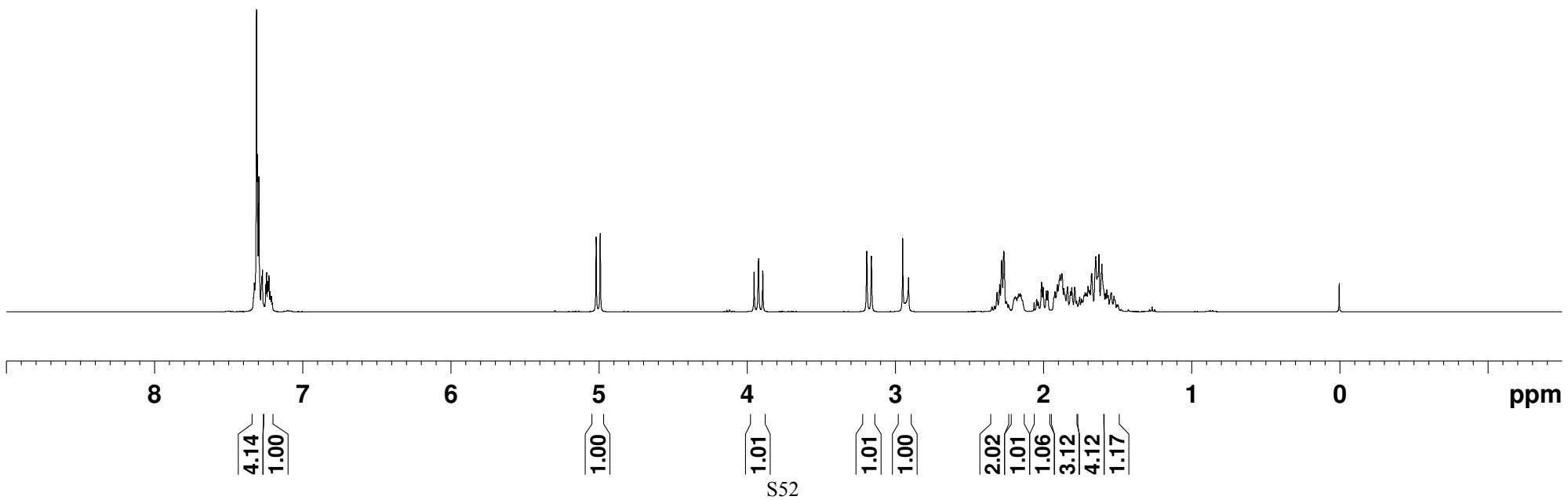
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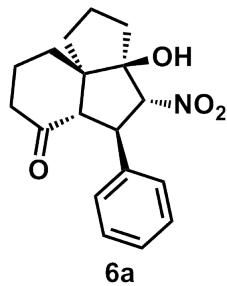


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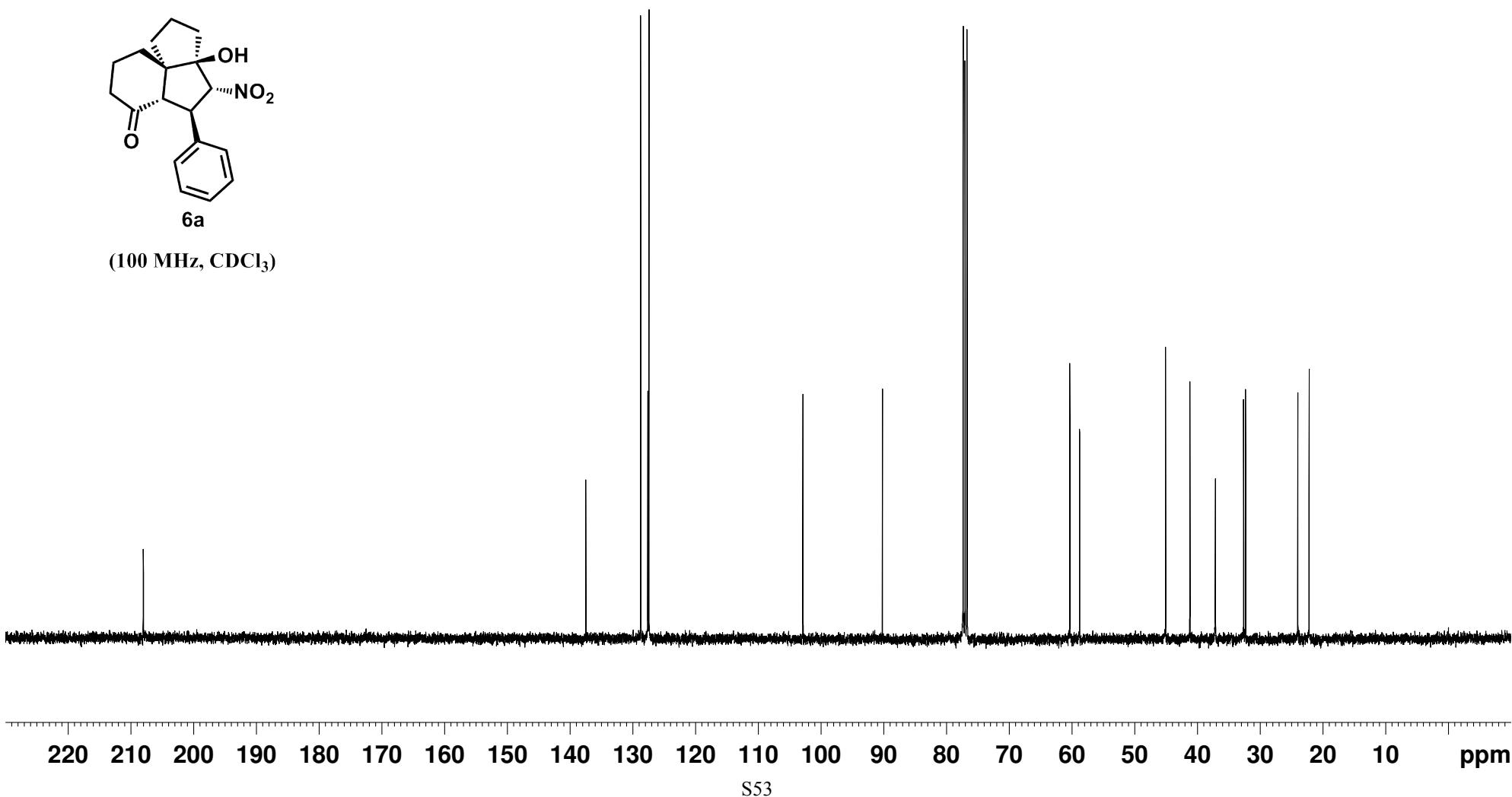
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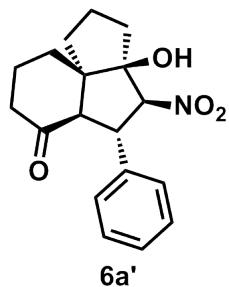


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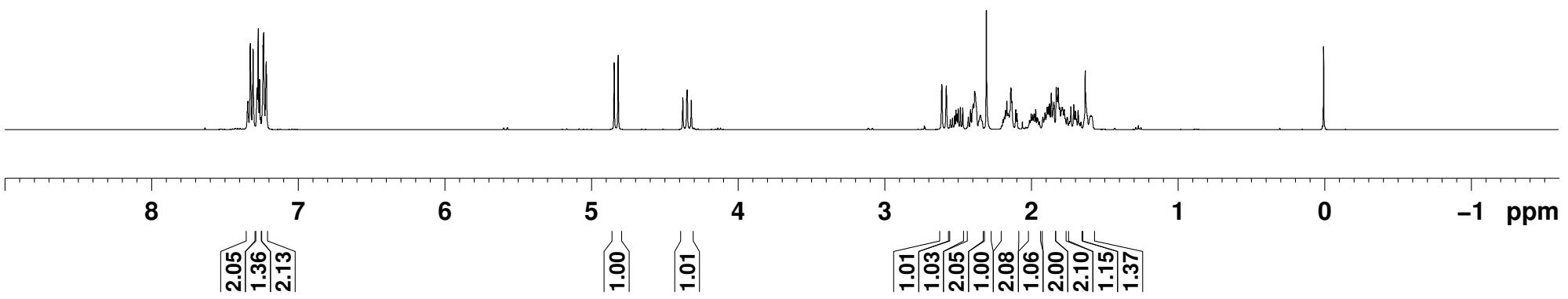
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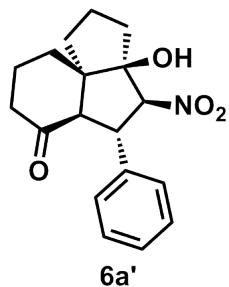
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 2.104
 2.095
 1.998
 1.988
 1.978
 1.969
 1.904
 1.890
 1.827
 1.814
 1.793
 1.786
 1.772
 1.728
 1.708
 1.698
 1.678
 1.630
 1.595
 1.591



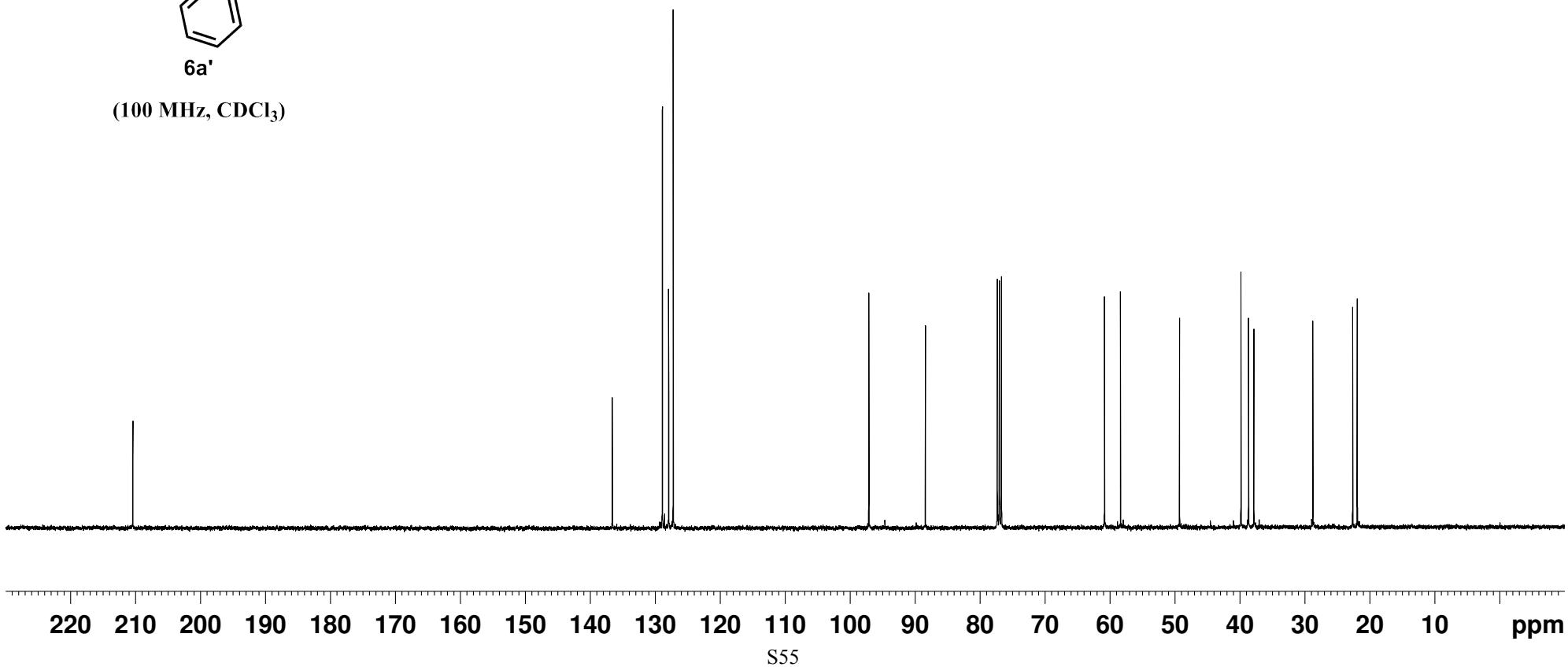
(400 MHz, CDCl₃)

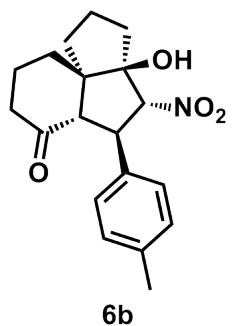
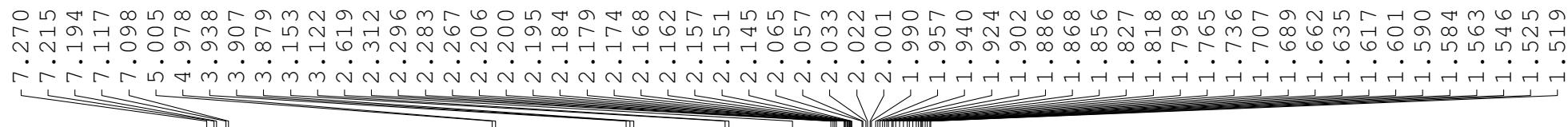


— 210.34
— 136.59
— 128.88
— 127.91
— 127.22
— 97.10
— 88.39
— 77.32
— 77.00
— 76.68
— 60.83
— 58.35
— 49.27
— 39.81
— 38.65
— 37.82
— 28.75
— 22.62
— 21.92

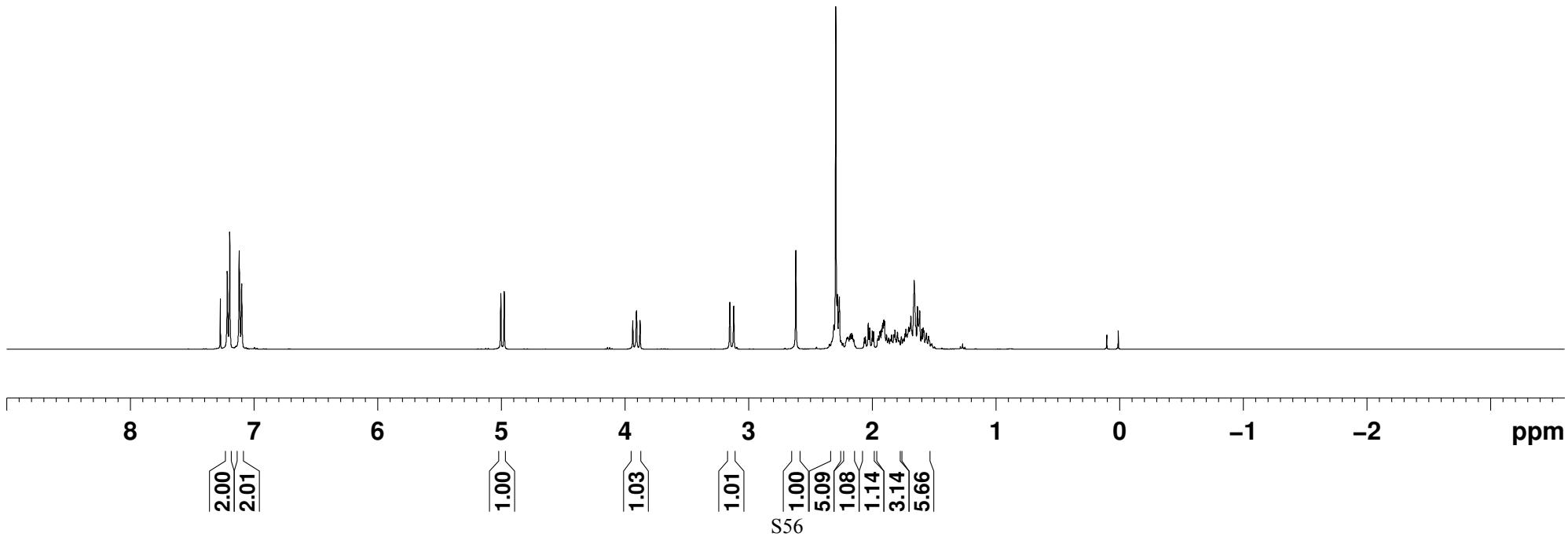


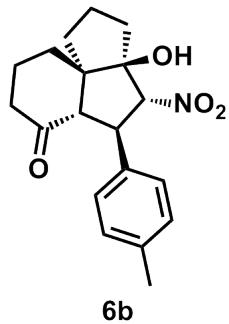
(100 MHz, CDCl₃)



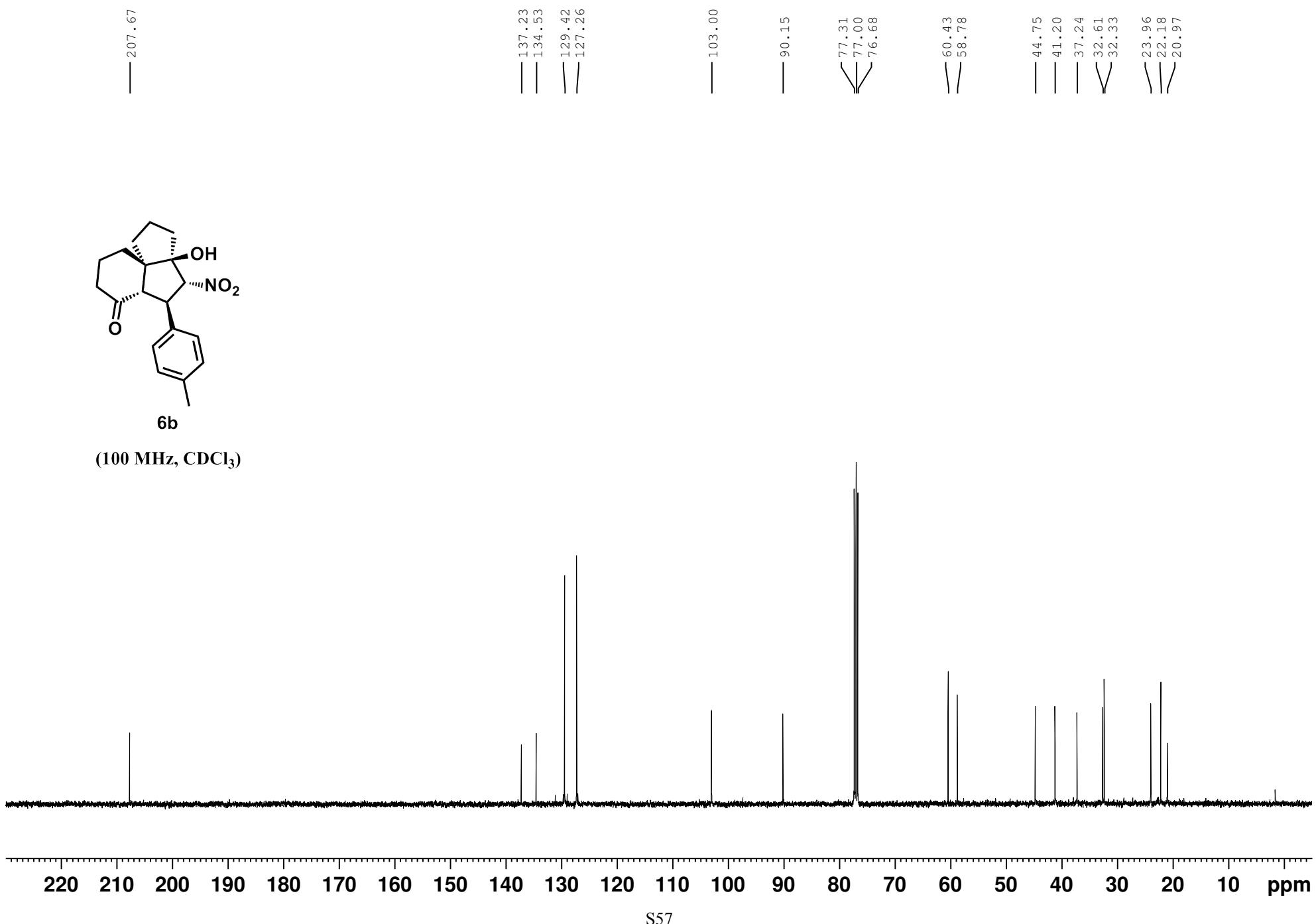


(400 MHz, CDCl_3)

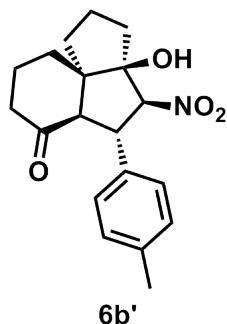




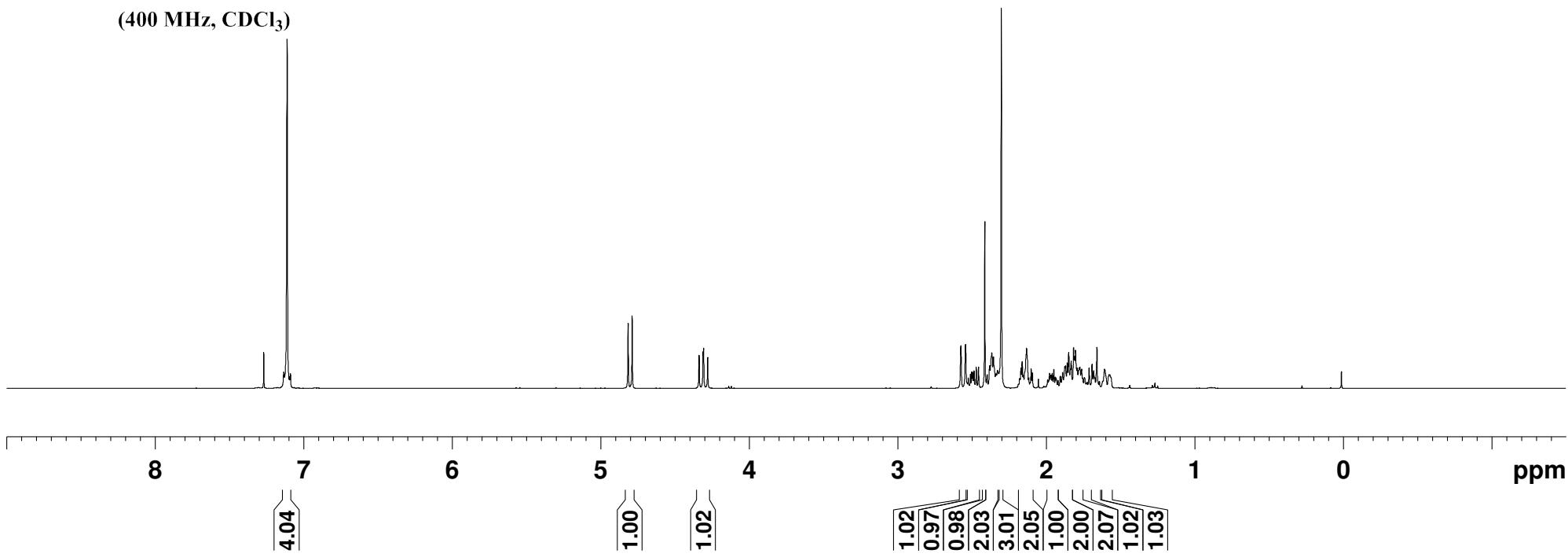
(100 MHz, CDCl₃)

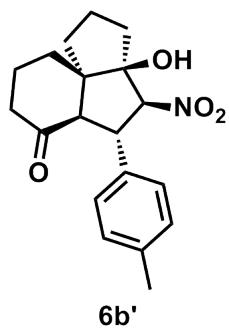


7.136
7.112
7.090
4.816
4.789
4.338
4.311
4.308
4.281
2.575
2.544
2.502
2.511
2.495
2.487
2.472
2.456
2.414
2.382
2.367
2.356
2.356
2.338
2.329
2.326
2.303
2.171
2.162
2.136
2.133
2.102
2.094
2.094
1.978
1.968
1.959
1.949
1.949
1.890
1.876
1.871
1.859
1.849
1.837
1.832
1.816
1.811
1.803
1.792
1.782
1.778
1.774
1.762
1.711
1.692
1.681
1.659
1.608
1.577
1.573

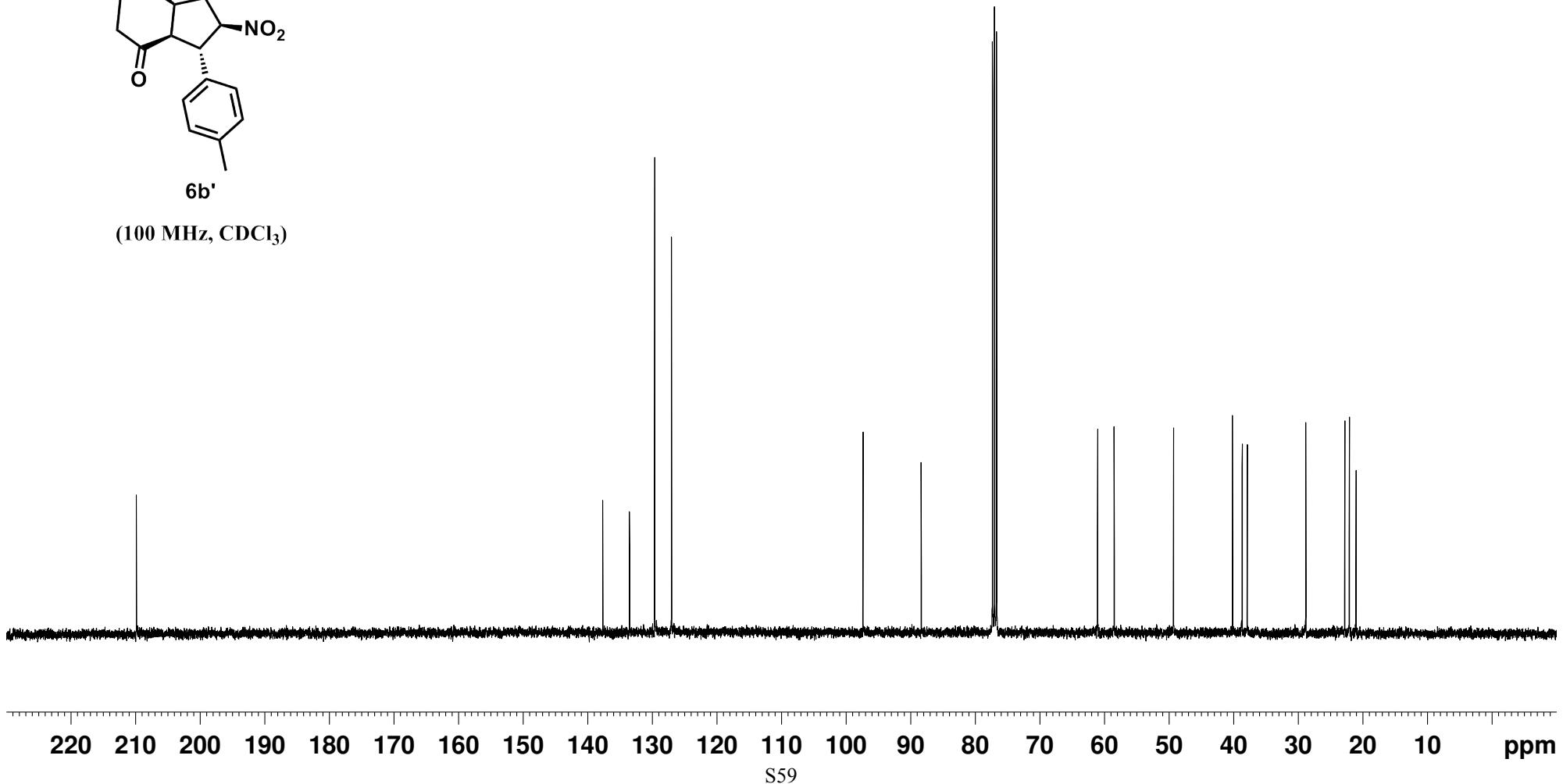


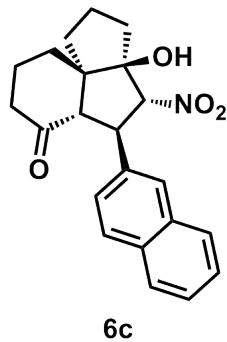
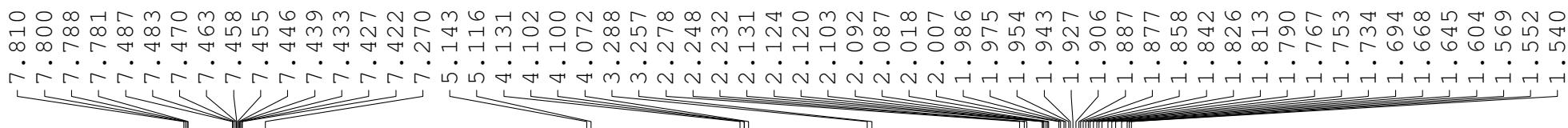
(400 MHz, CDCl₃)



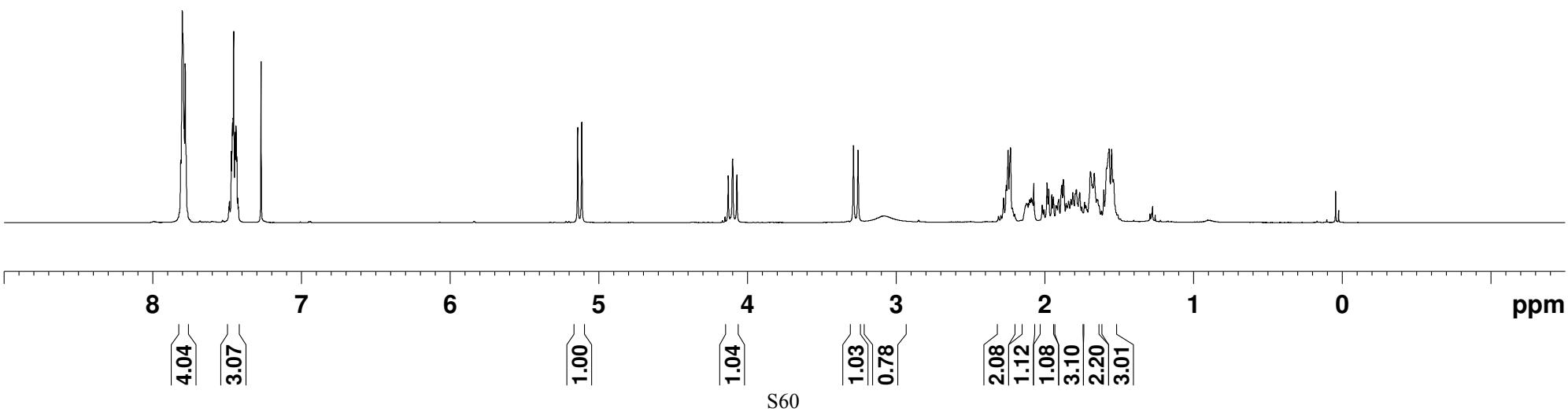


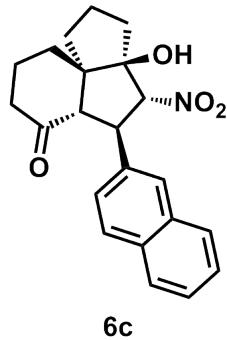
(100 MHz, CDCl₃)



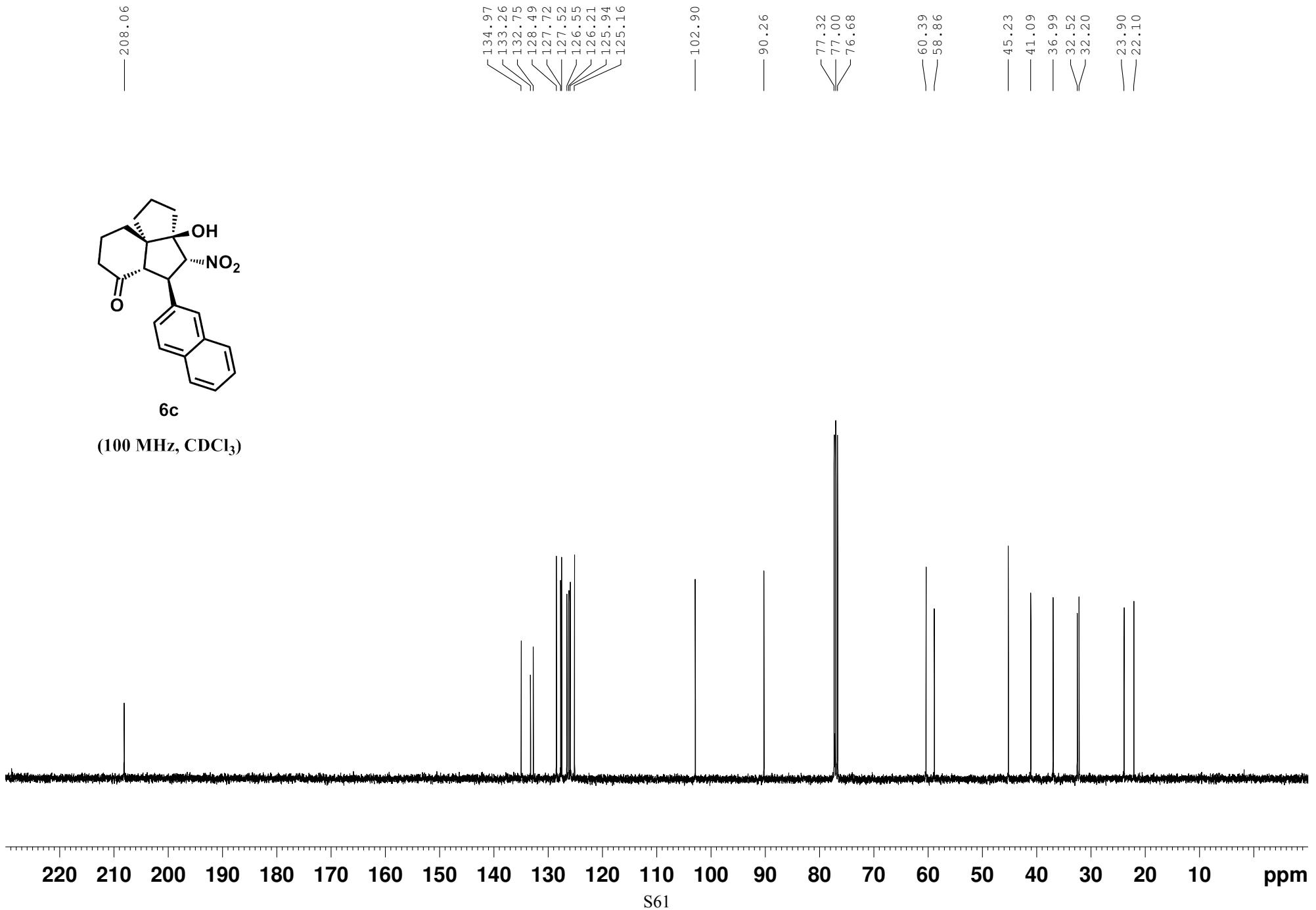


(400 MHz, CDCl₃)

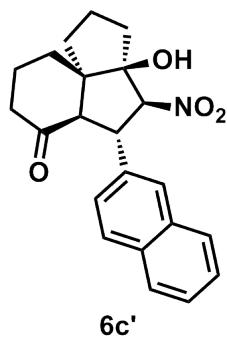




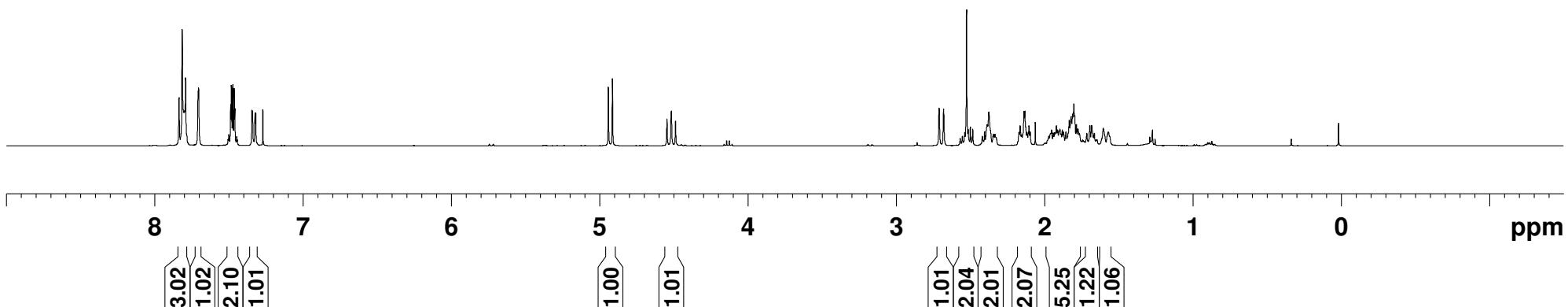
(100 MHz, CDCl₃)

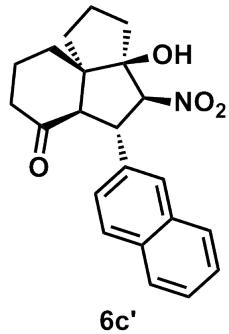


7.835
 7.814
 7.803
 7.799
 7.796
 7.791
 7.707
 7.703
 7.487
 7.473
 7.463
 7.459
 7.422
 7.339
 7.322
 7.318
 7.270
 4.941
 4.913
 4.546
 4.516
 4.516
 4.488
 2.526
 2.515
 2.500
 2.484
 2.403
 2.386
 2.375
 2.345
 2.334
 2.172
 2.139
 2.133
 2.105
 2.097
 1.957
 1.952
 1.932
 1.896
 1.880
 1.872
 1.821
 1.776
 1.764
 1.715
 1.695
 1.682
 1.665
 1.604
 1.570

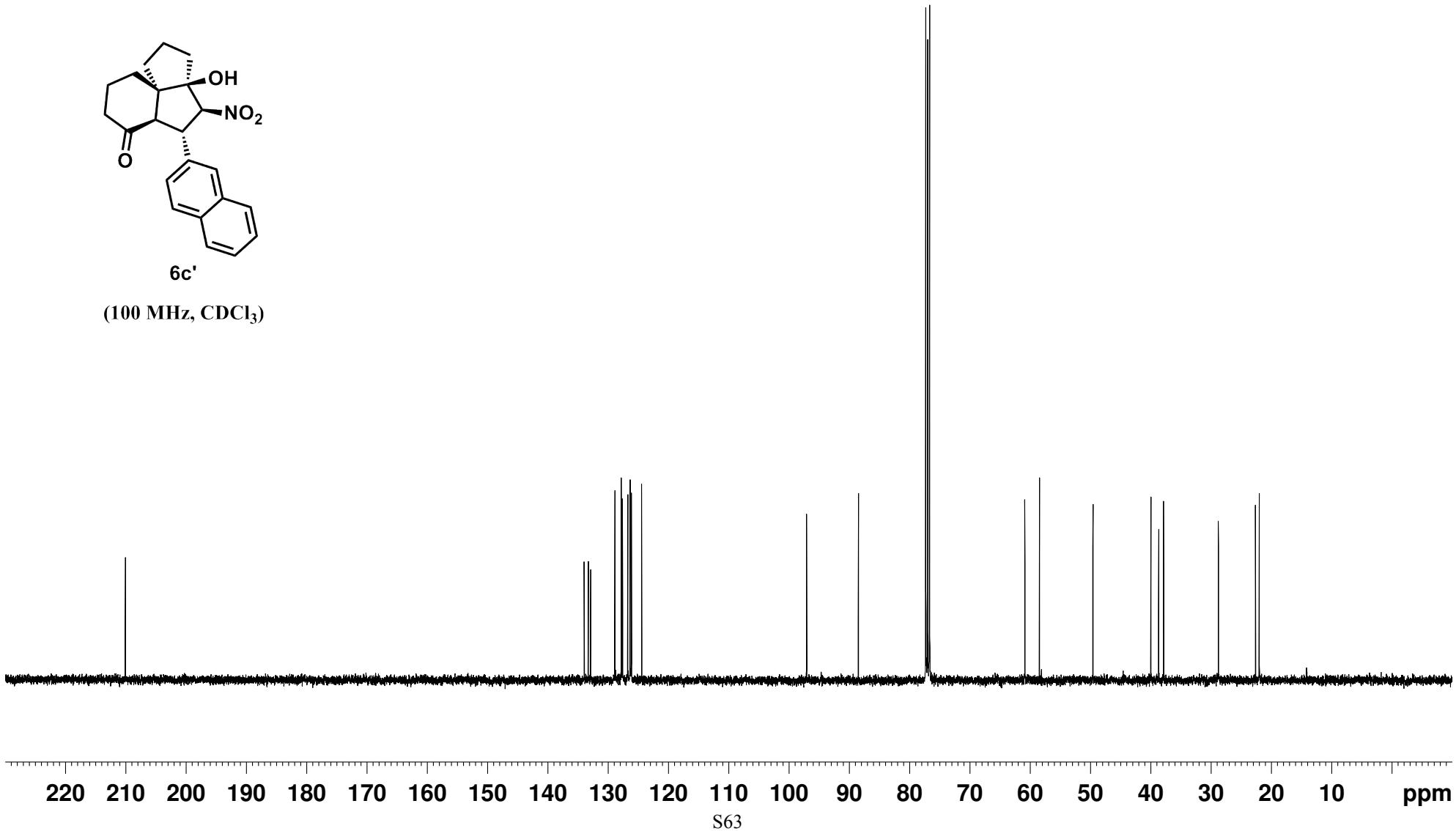
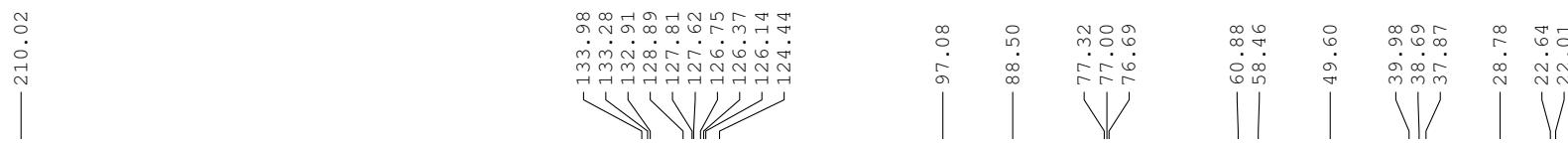


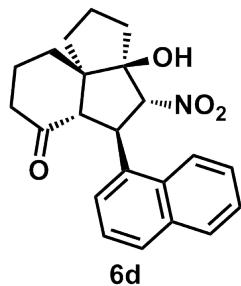
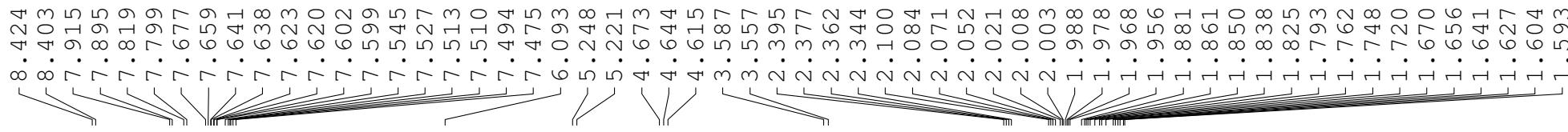
(400 MHz, CDCl₃)



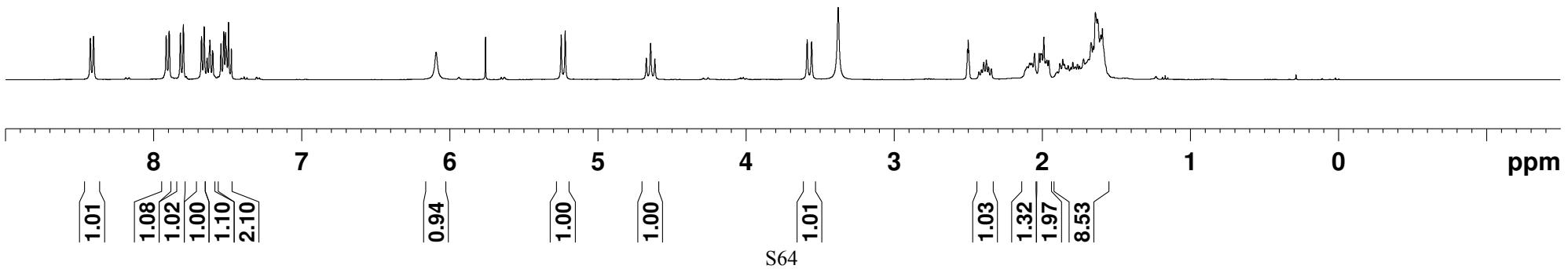


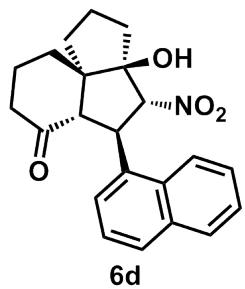
(100 MHz, CDCl₃)



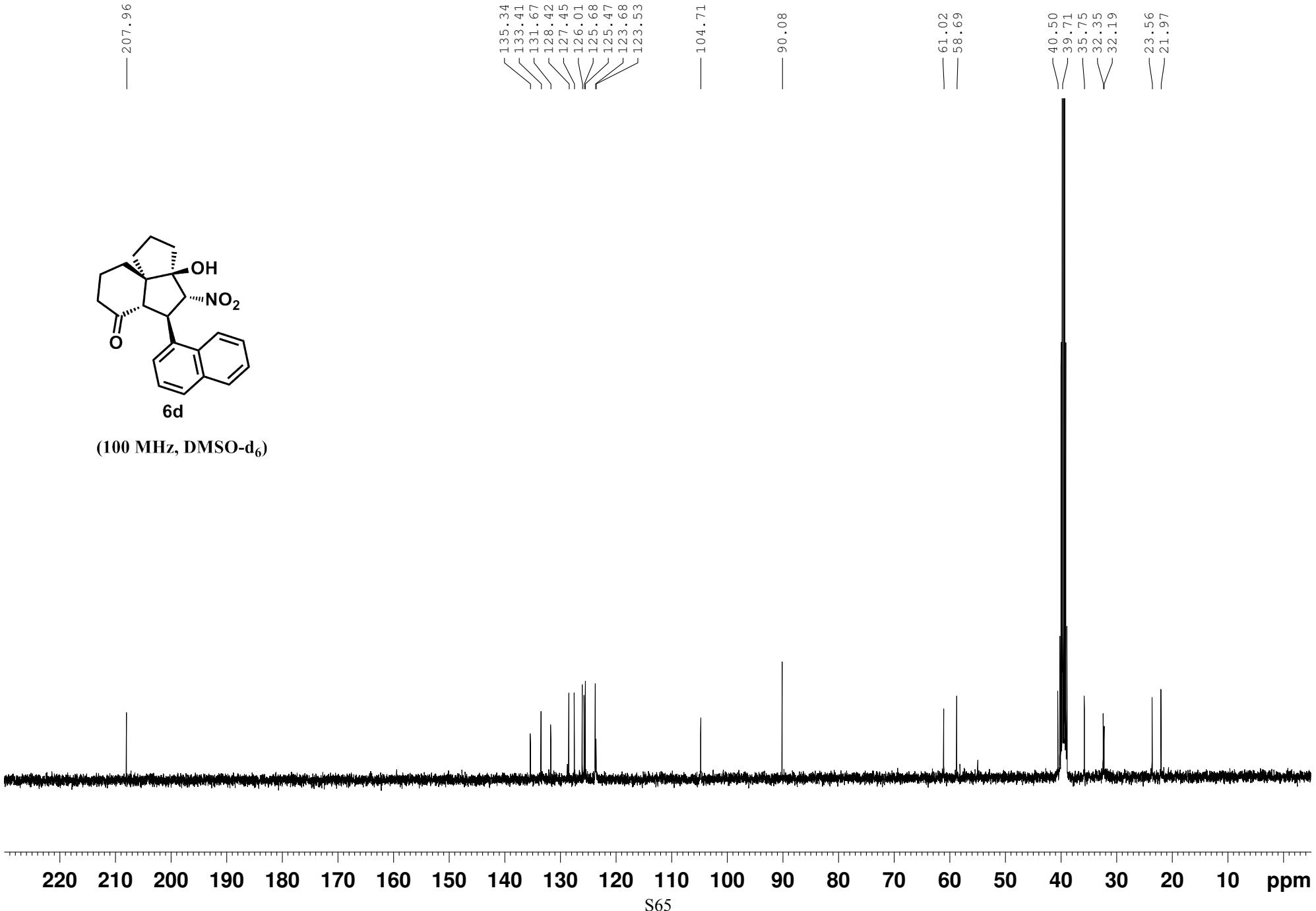


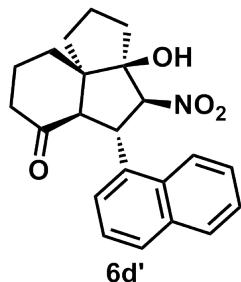
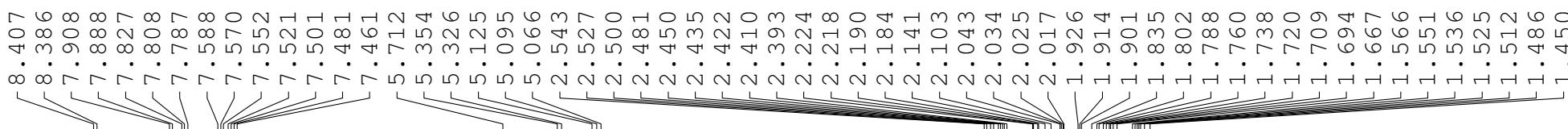
(400 MHz, DMSO-d₆)



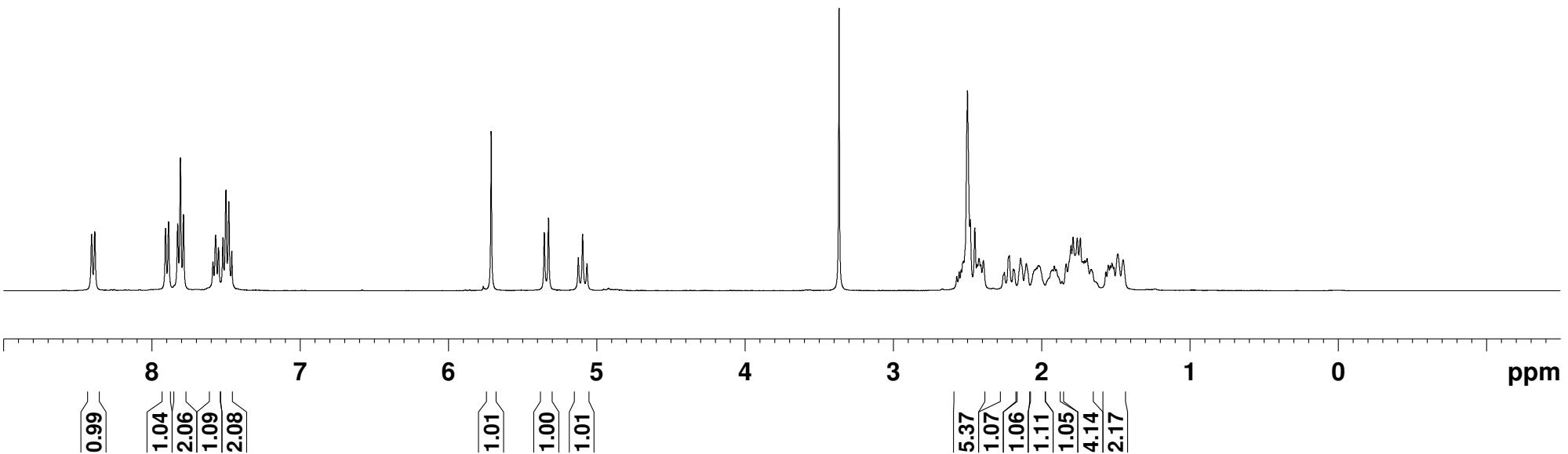


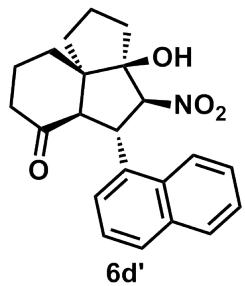
(100 MHz, DMSO-d_6)



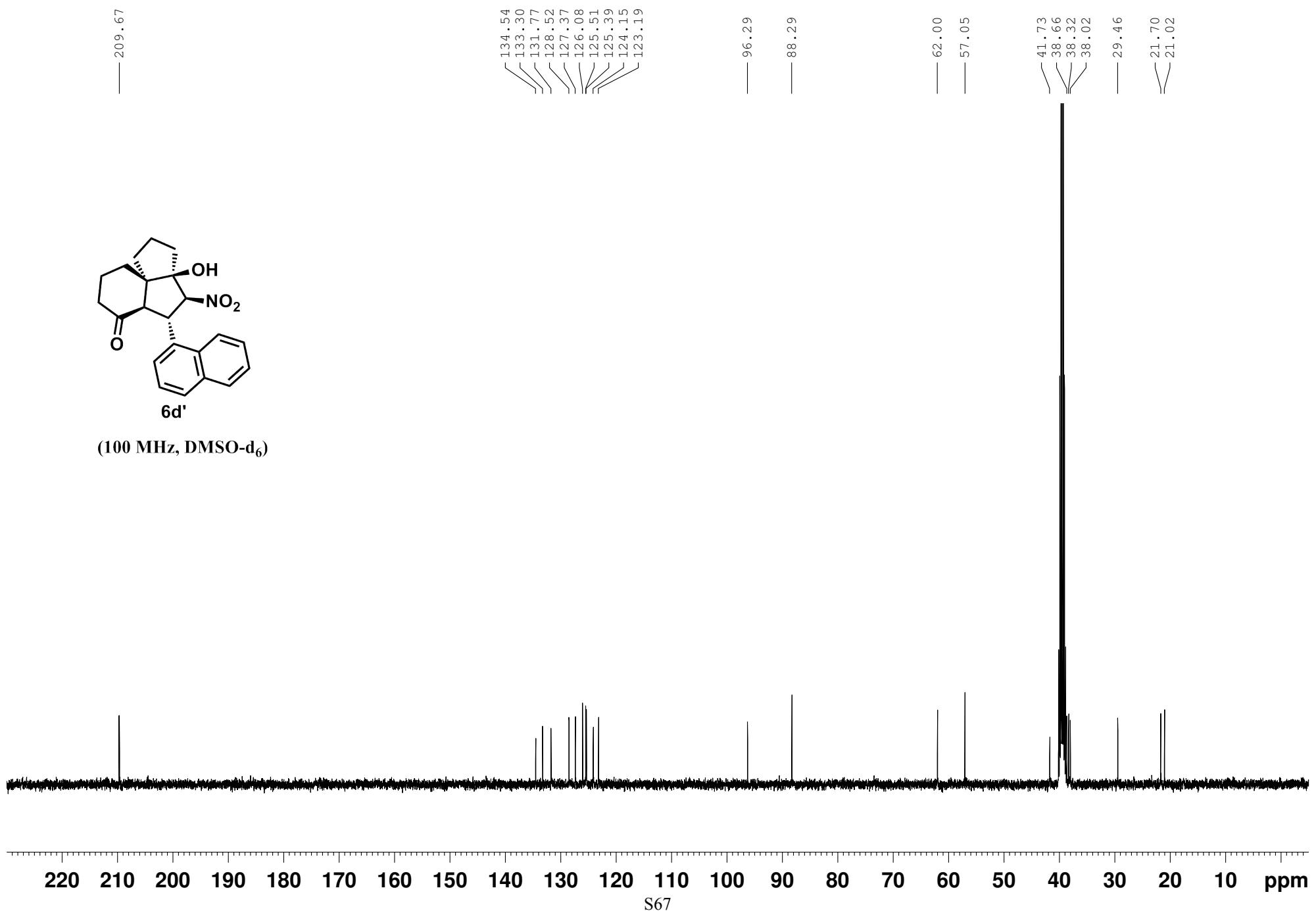


(400 MHz, DMSO-d₆)

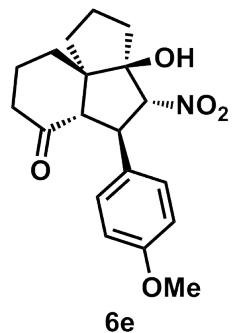




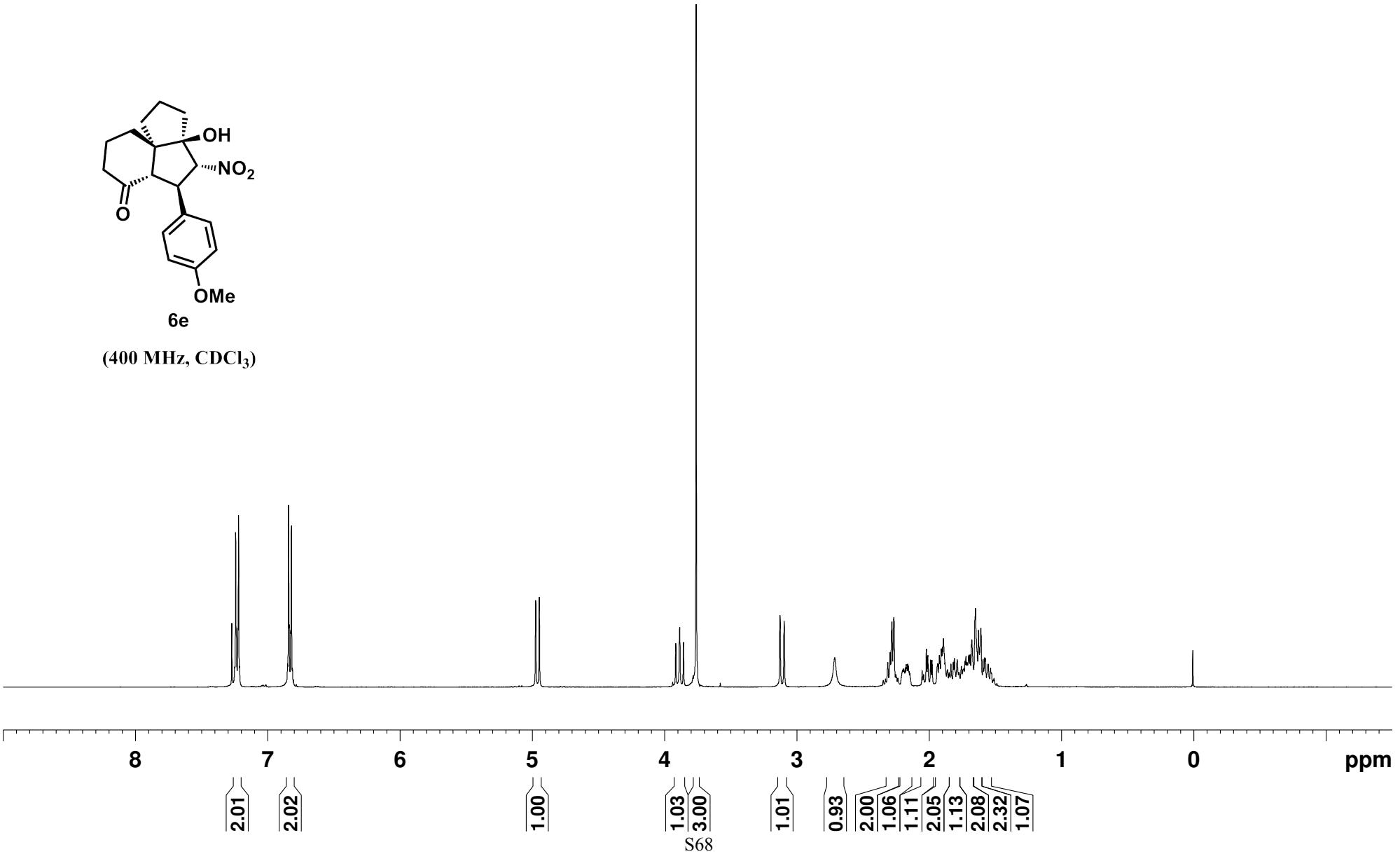
(100 MHz, DMSO-d₆)

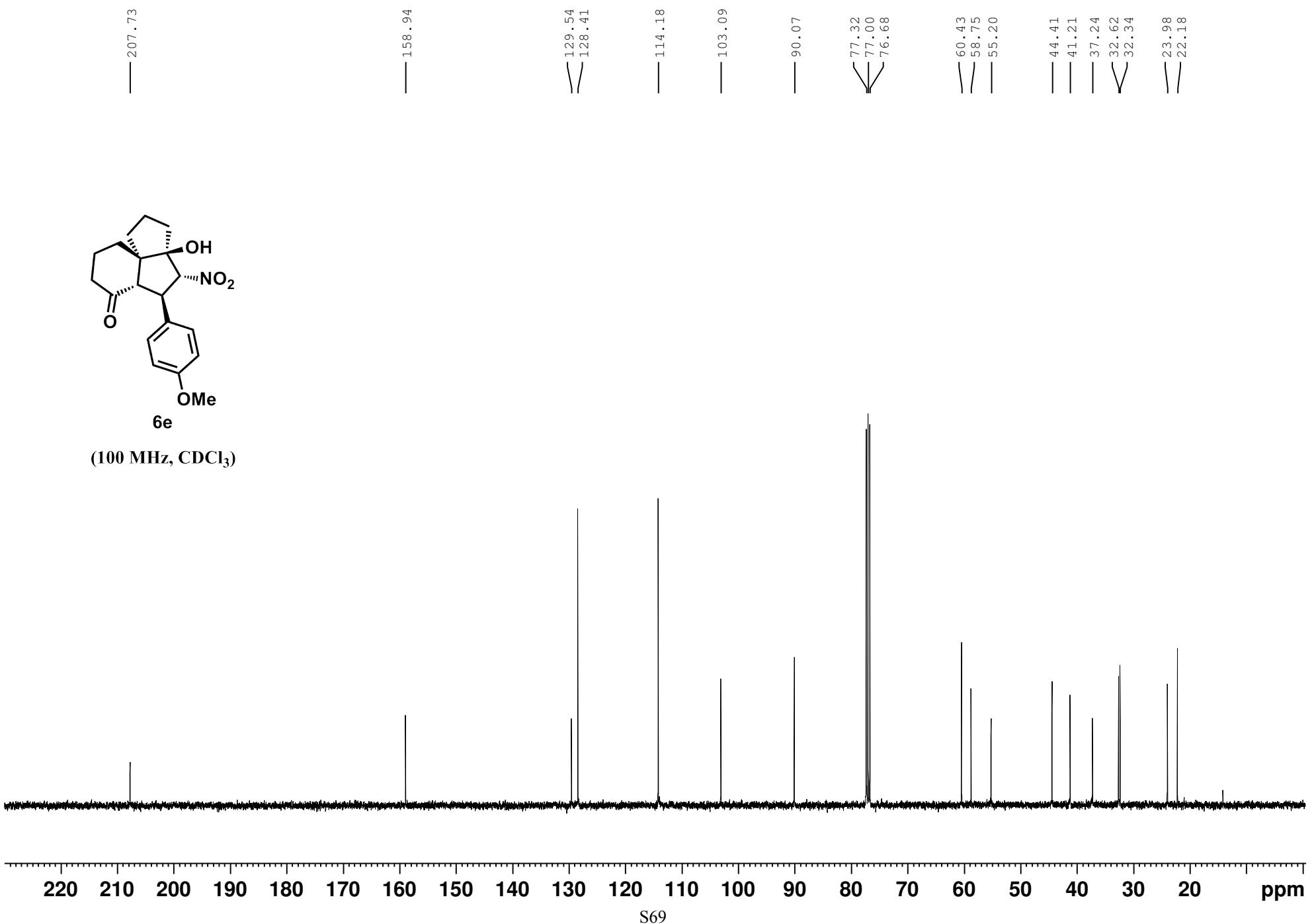


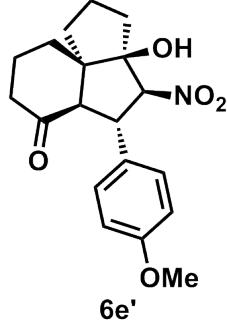
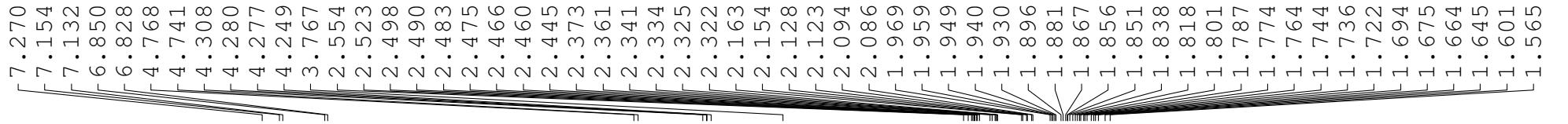
7	2.70
7	2.41
7	2.19
6	8.41
6	8.19
4	9.76
4	9.48
3	9.17
3	8.86
3	8.58
3	8.07
3	7.62
3	1.28
2	2.715
2	3.14
2	2.96
2	2.282
2	2.267
2	2.202
2	1.96
2	1.91
2	1.80
2	1.74
2	1.69
2	1.64
2	1.58
2	1.52
2	0.54
2	0.21
1	9.89
1	9.79
1	9.36
1	9.24
1	9.08
1	8.93
1	8.80
1	8.62
1	8.36
1	8.18
1	8.10
1	7.89
1	7.76
1	7.56
1	7.38
1	7.29
1	7.14
1	7.00
1	6.91
1	6.78
1	6.50
1	6.28
1	6.09
1	5.93
1	5.81
1	5.76
1	5.54
1	5.37



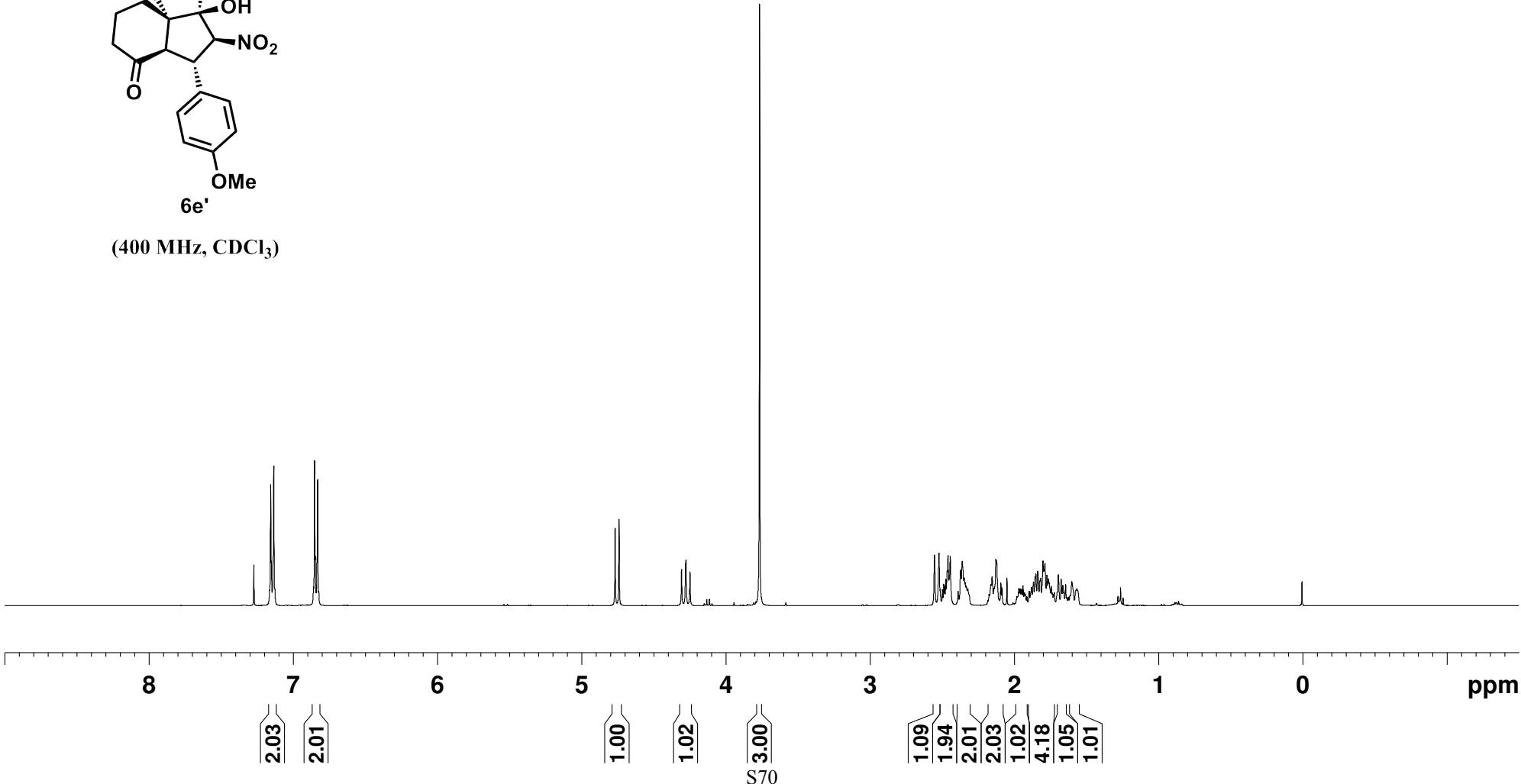
(400 MHz, CDCl₃)

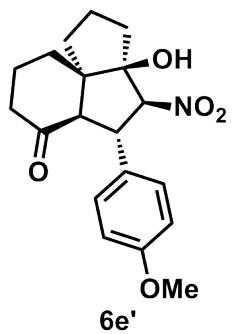




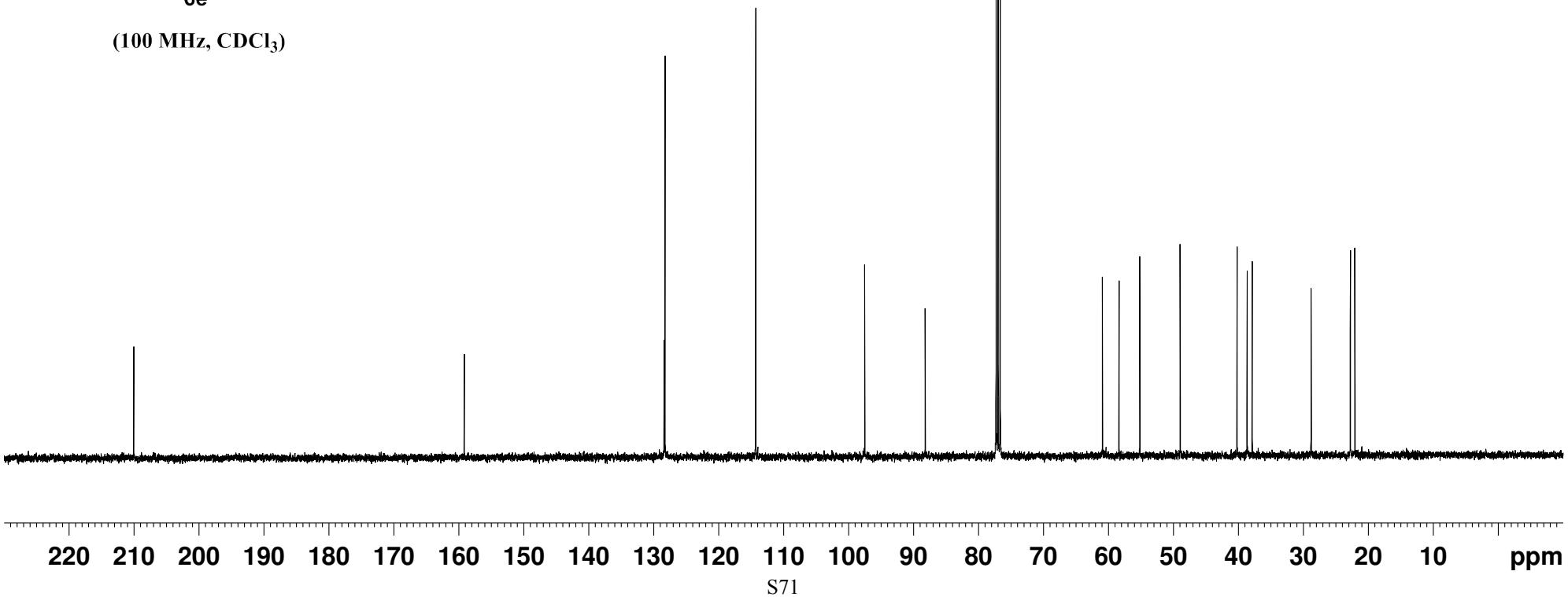


(400 MHz, CDCl₃)

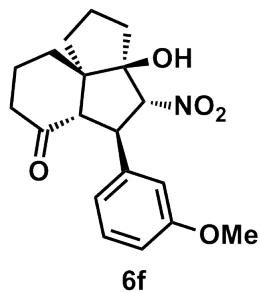




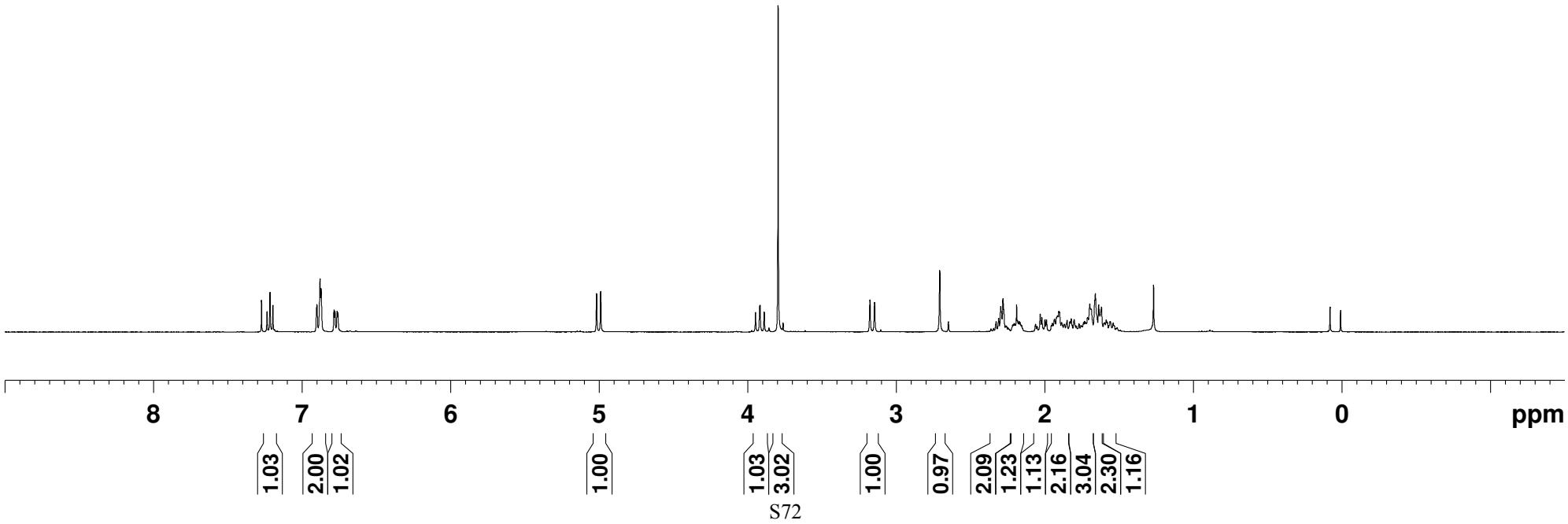
(100 MHz, CDCl₃)

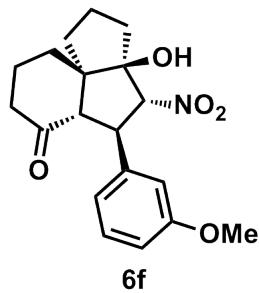


7	2.70
7	2.33
7	2.13
7	1.94
6	8.98
6	8.76
6	8.70
6	7.83
6	7.77
6	7.62
6	7.61
6	7.56
5	0.015
4	9.87
3	9.45
3	9.16
3	9.14
3	8.86
3	7.93
3	1.75
3	1.44
2	7.05
2	3.26
2	3.08
2	2.94
2	2.79
2	1.87
2	1.82
2	1.77
2	1.71
2	1.65
2	0.28
2	0.17
1	9.96
1	9.86
1	9.32
1	9.19
1	9.03
1	8.99
1	8.84
1	8.47
1	8.29
1	8.20
1	8.00
1	7.30
1	7.07
1	6.95
1	6.61
1	6.57
1	6.35
1	6.16
1	5.95
1	5.85
1	5.76
1	5.59
1	5.55
1	5.38

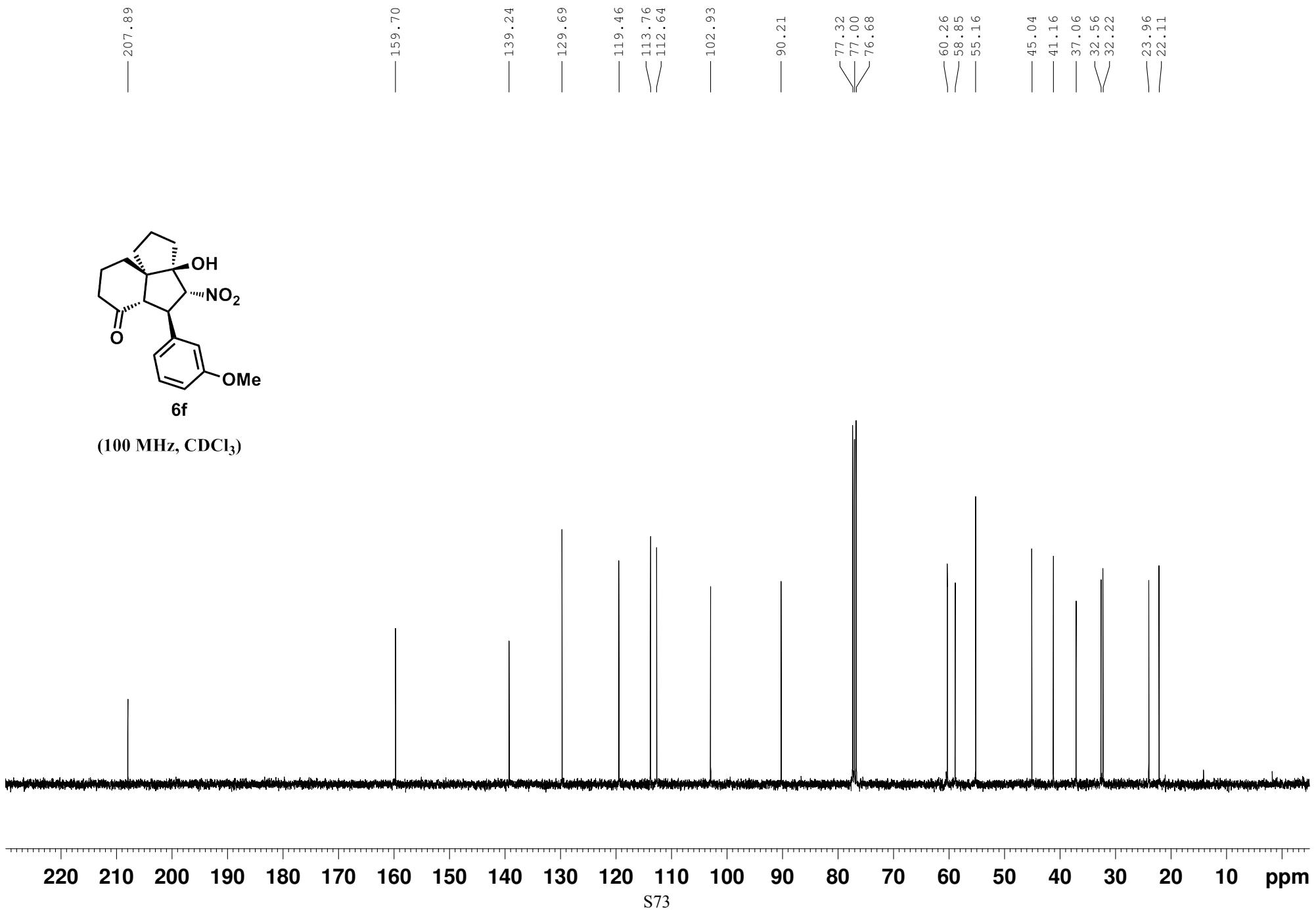


(400 MHz, CDCl₃)

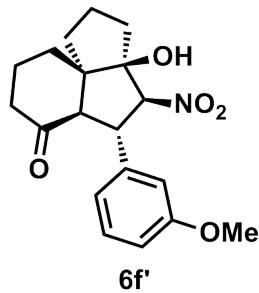




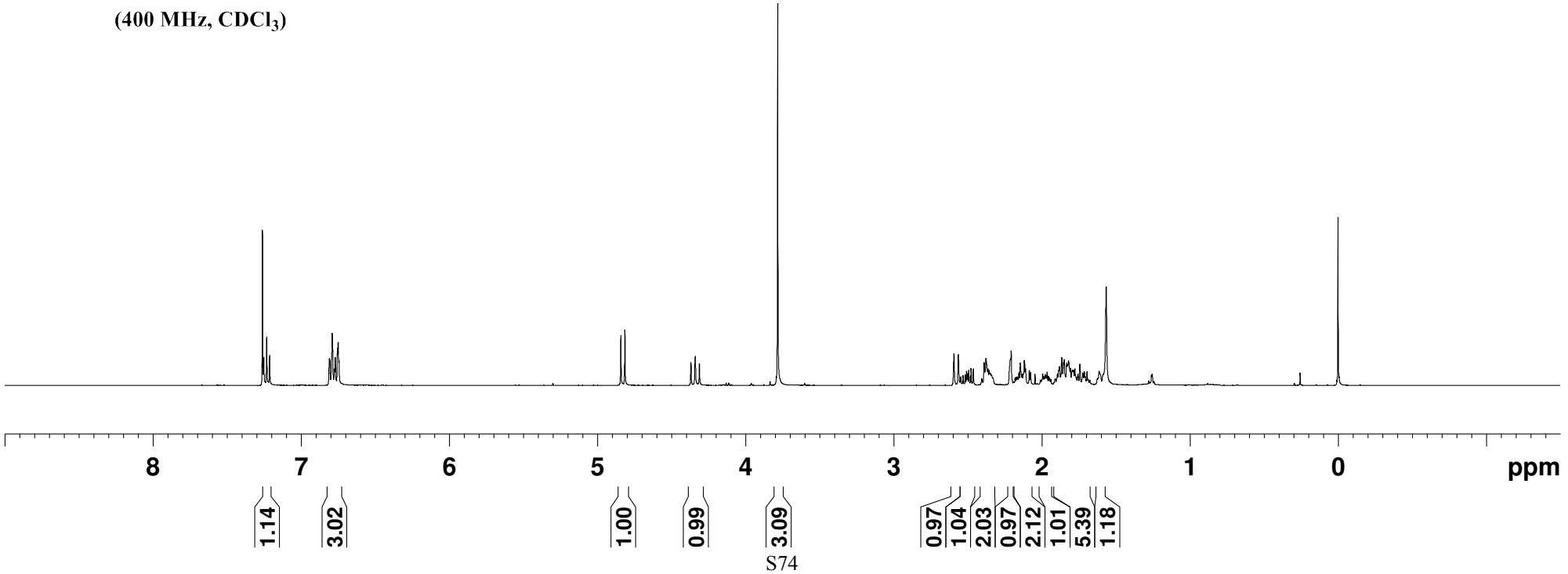
(100 MHz, CDCl₃)

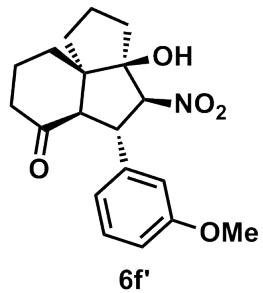


7.262
7.253
7.233
7.213
6.809
6.790
6.777
6.775
6.770
6.755
6.750
6.745
4.842
4.815
4.369
4.339
4.312
3.783
2.594
2.563
2.508
2.493
2.478
2.462
2.390
2.377
2.363
2.355
2.346
2.211
2.207
2.154
2.145
2.118
2.111
2.084
2.076
1.965
1.887
1.881
1.865
1.853
1.849
1.820
1.813
1.832
1.826
1.795
1.790
1.785
1.777
1.743
1.723
1.714
1.695
1.612
1.608

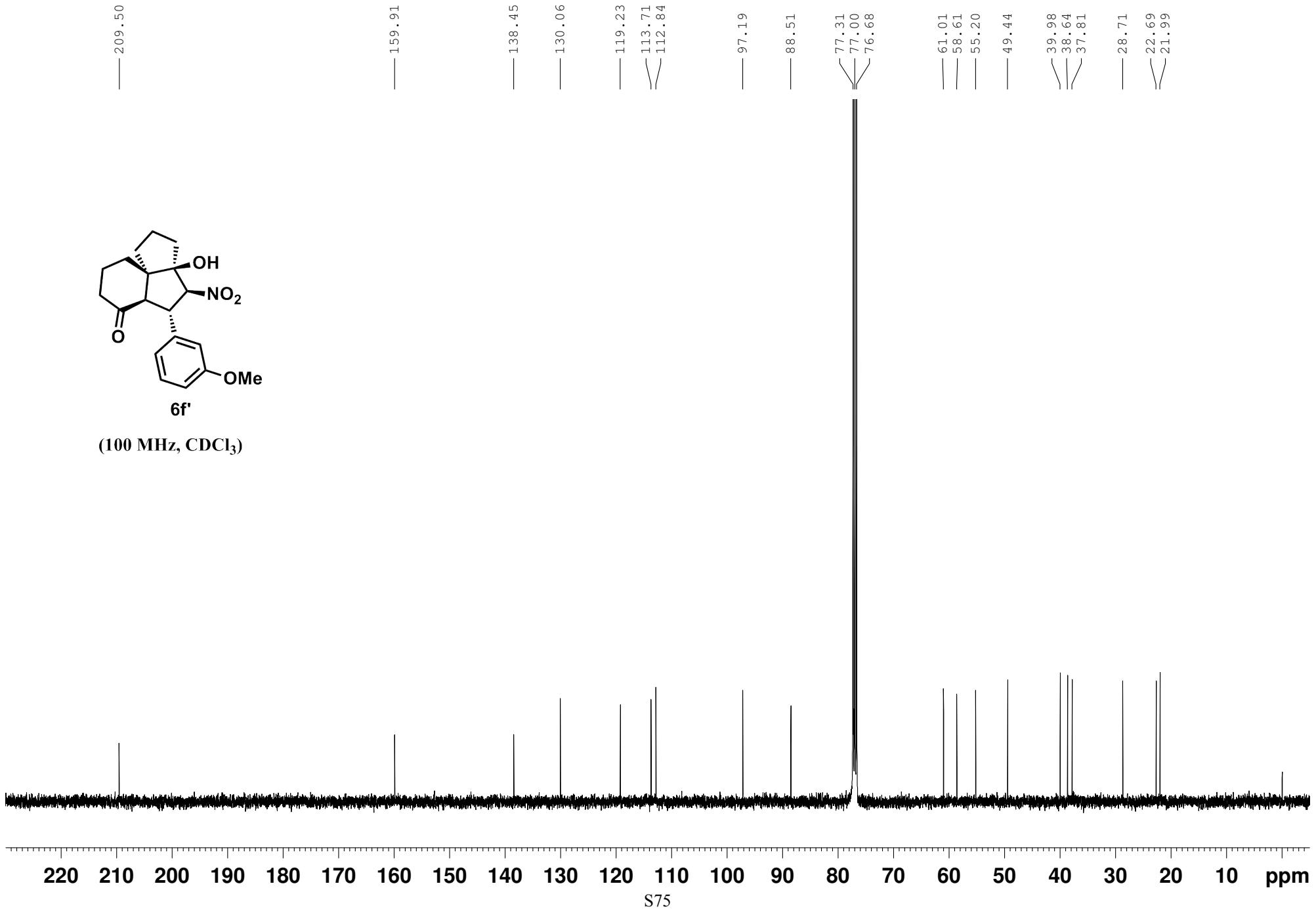


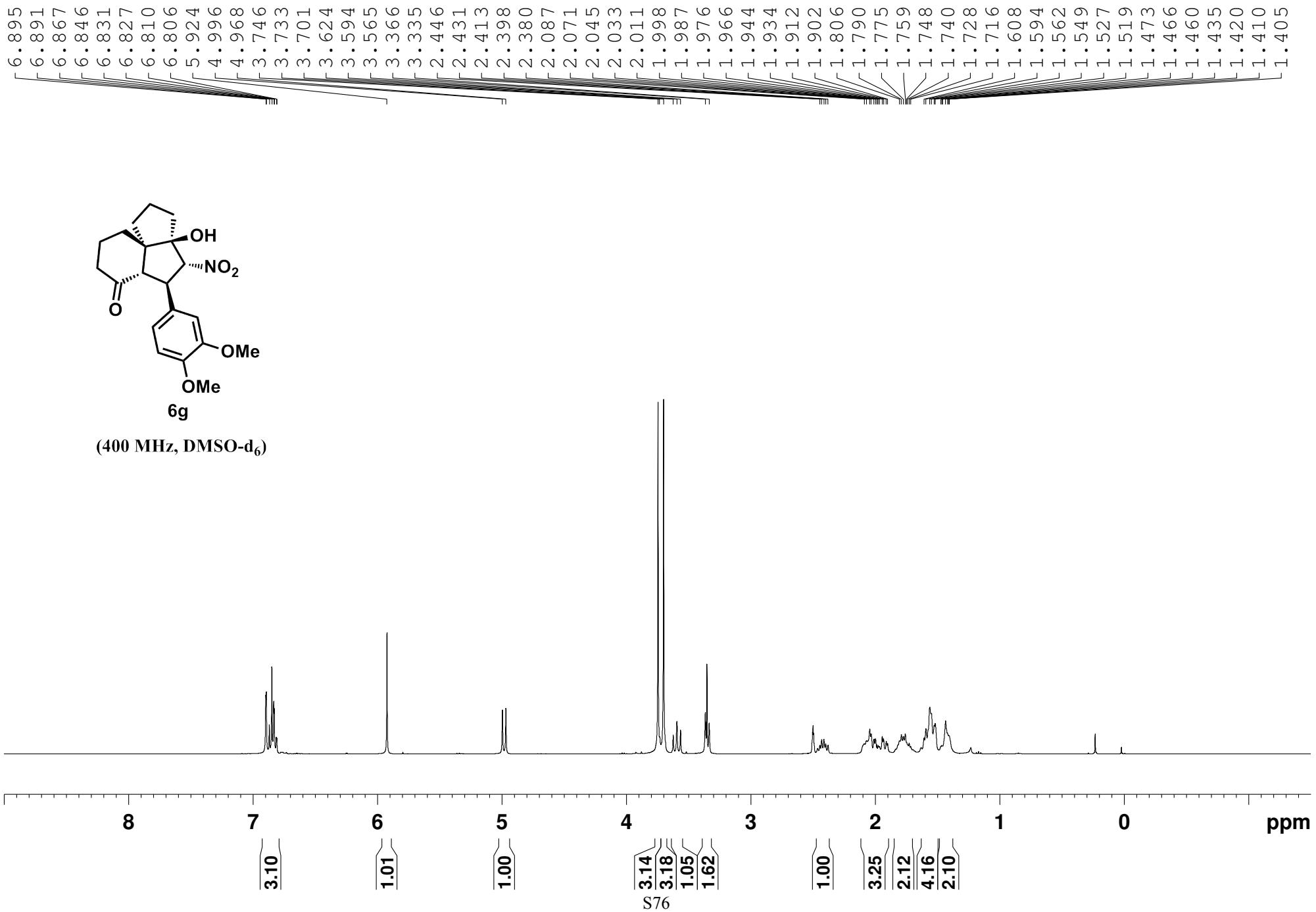
(400 MHz, CDCl₃)

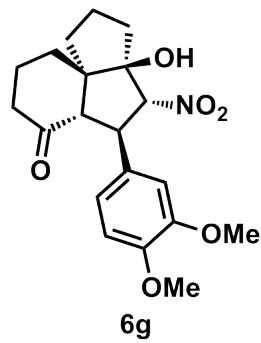




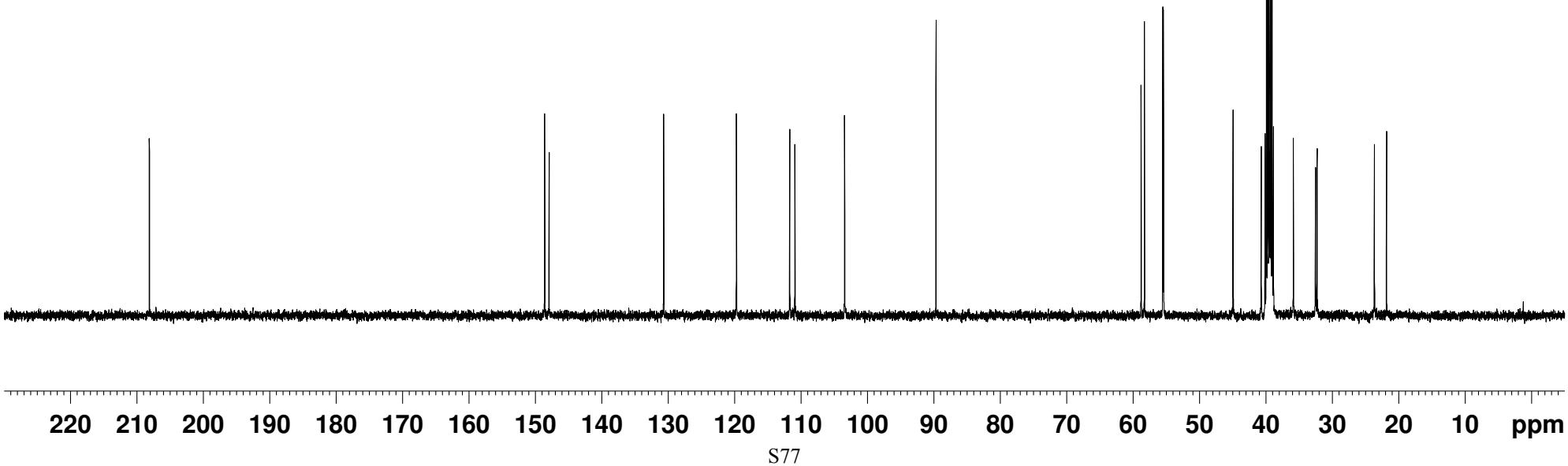
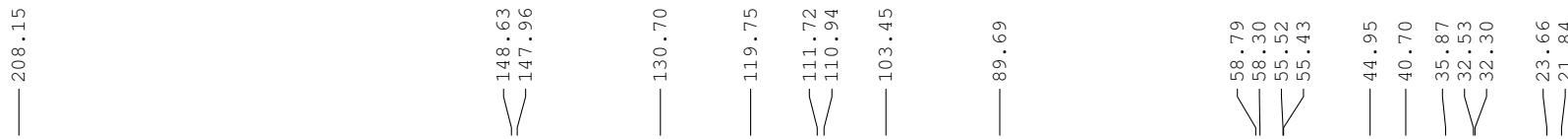
(100 MHz, CDCl₃)



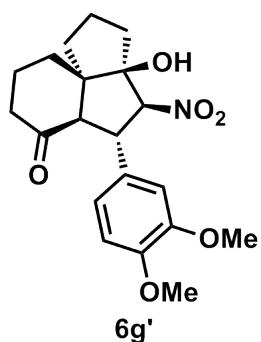




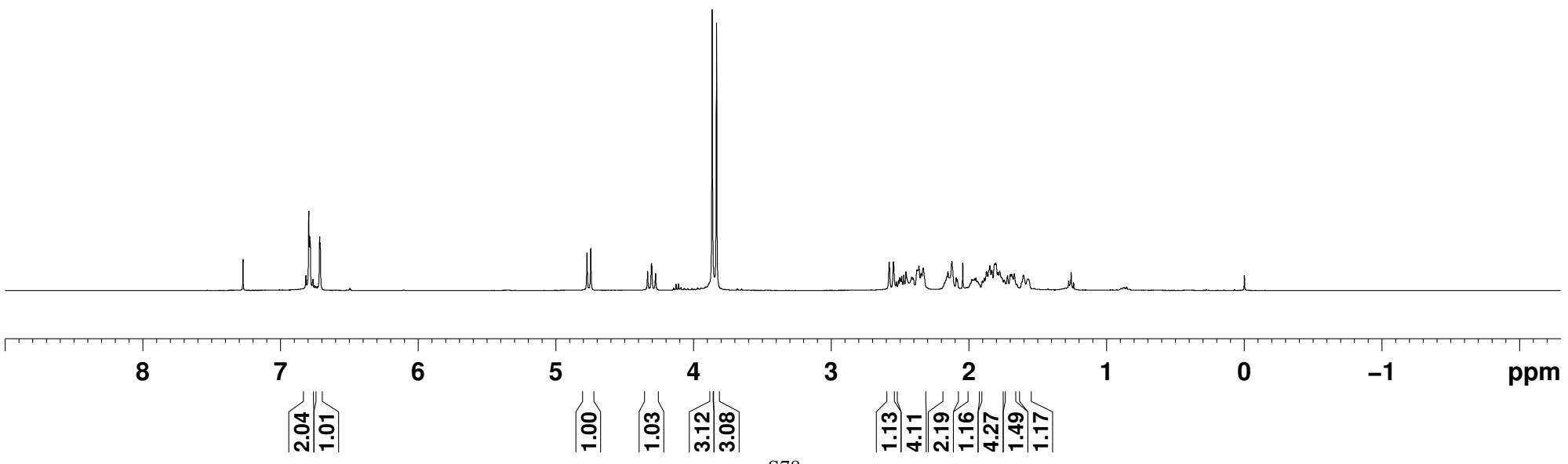
(100 MHz, DMSO-d_6)

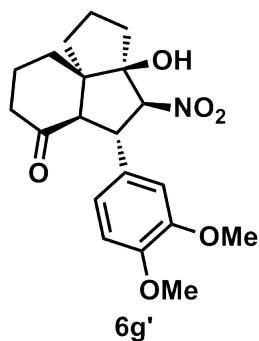


7.270	6.813
6.792	6.786
6.765	6.752
6.761	6.716
6.712	4.774
	4.747
	4.334
	4.305
	4.276
	3.865
	3.833
	2.579
	2.548
	2.512
	2.503
	2.496
	2.488
	2.473
	2.457
	2.413
	2.405
	2.377
	2.347
	2.333
	2.160
	2.152
	2.124
	2.091
	2.083
	1.978
	1.970
	1.960
	1.949
	1.937
	1.902
	1.873
	1.856
	1.847
	1.833
	1.814
	1.804
	1.719
	1.776
	1.699
	1.689
	1.670
	1.604
	1.571

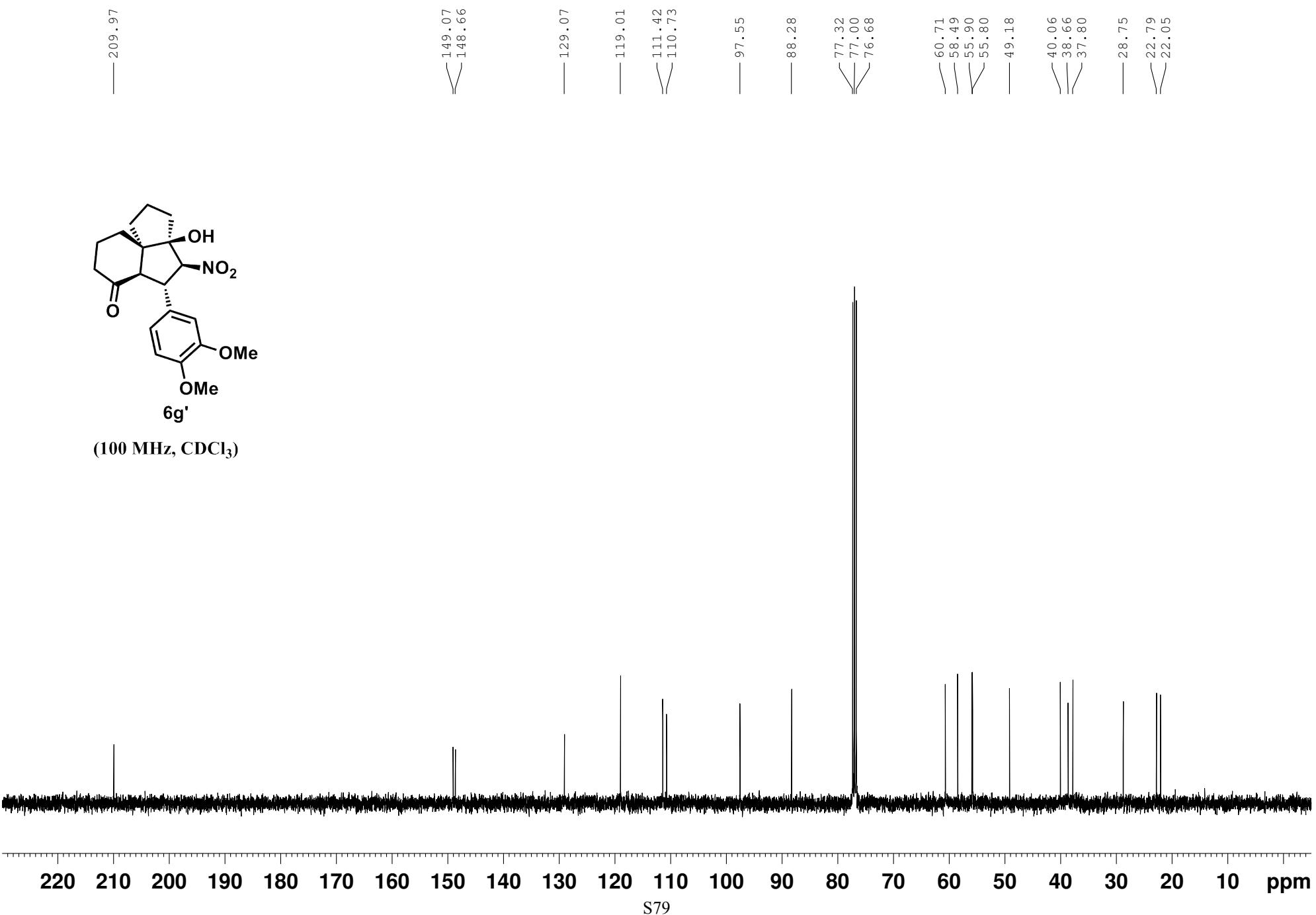


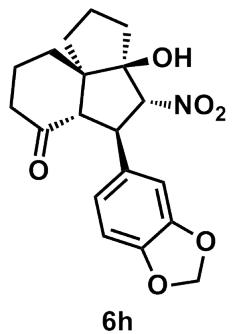
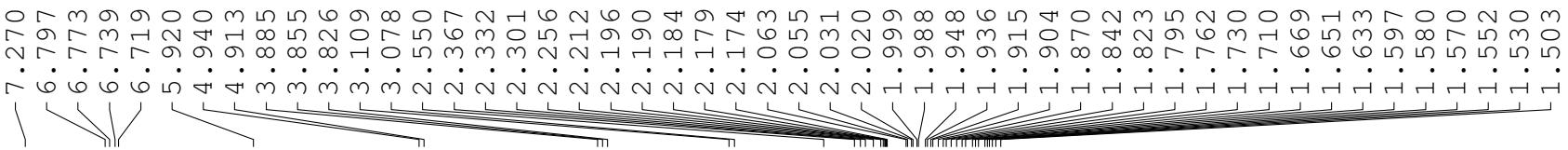
(400 MHz, CDCl₃)



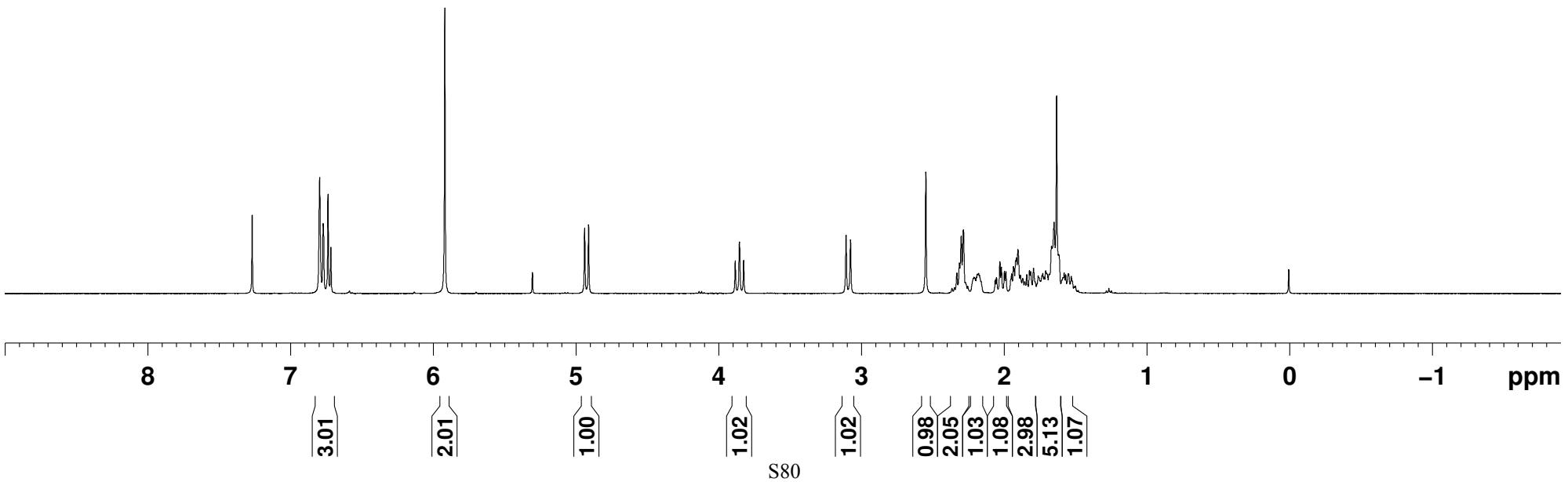


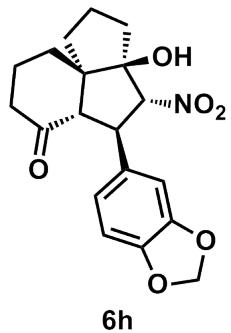
(100 MHz, CDCl₃)





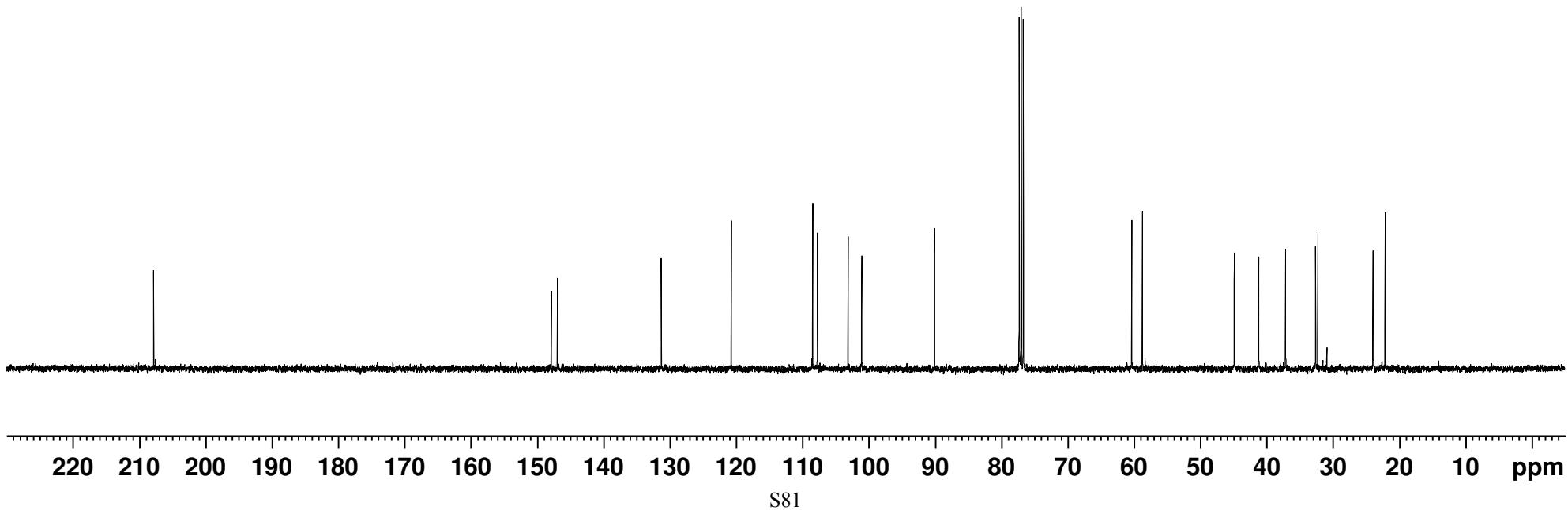
(400 MHz, CDCl₃)



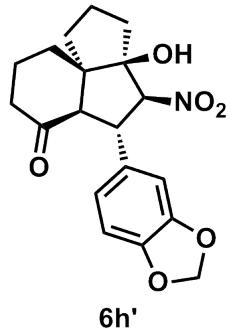


6h

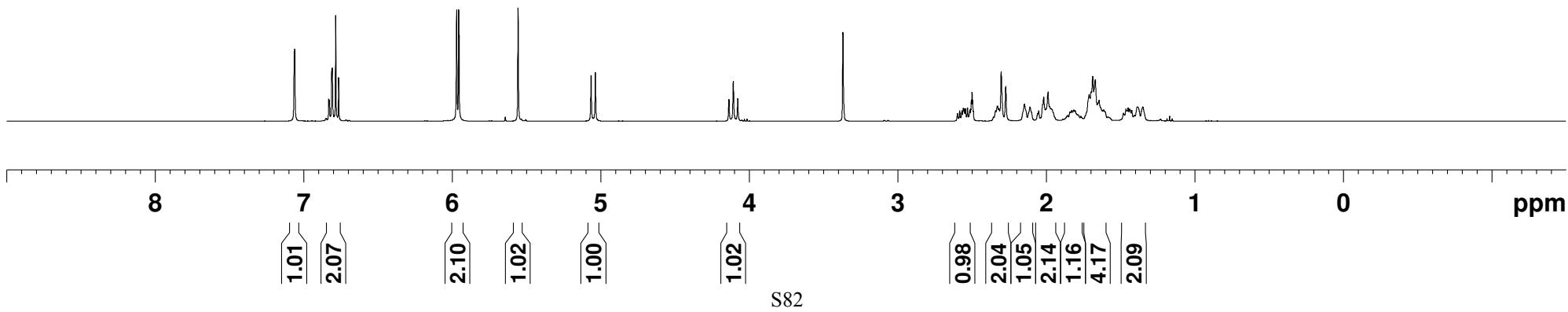
(100 MHz, CDCl_3)

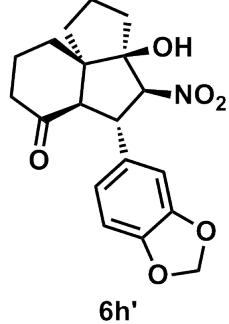


7	0.65
7	0.61
6	0.832
6	0.828
6	0.812
6	0.808
6	0.786
6	0.766
5	0.973
5	0.970
5	0.957
5	0.955
5	0.666
5	0.037
5	0.557
4	4.138
4	4.108
4	4.078
2	5.83
2	5.68
2	5.60
2	5.53
2	5.45
2	5.30
2	5.15
2	3.42
2	3.29
2	3.19
2	3.03
2	2.73
2	2.147
2	2.110
2	2.051
2	2.025
2	2.018
1	9.90
1	9.87
1	9.77
1	9.68
1	9.61
1	8.29
1	8.15
1	8.05
1	7.12
1	6.99
1	6.87
1	6.71
1	6.45
1	6.22
1	6.03
1	4.64
1	4.56
1	4.48
1	4.38
1	4.24
1	3.86
1	3.50

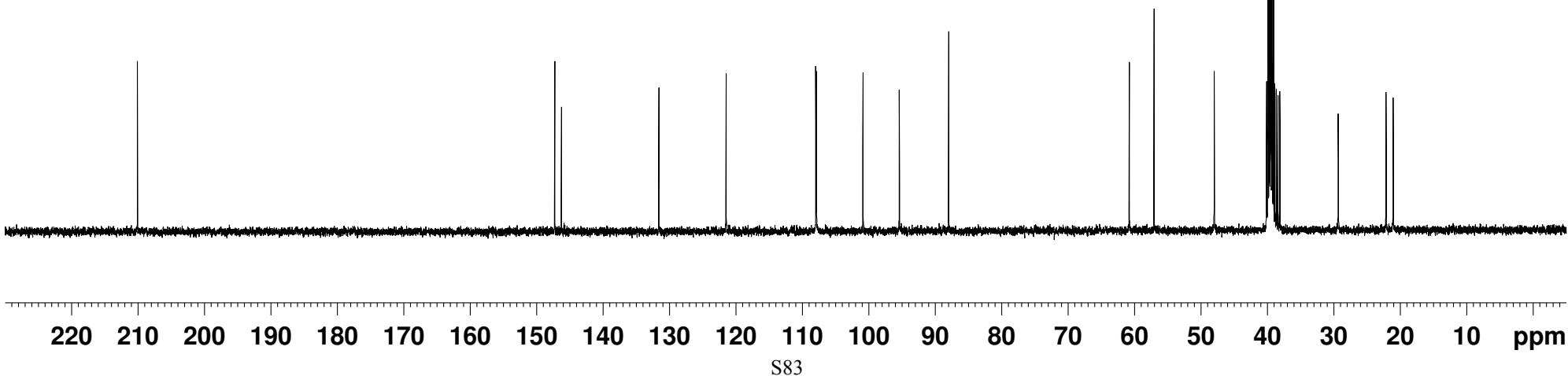
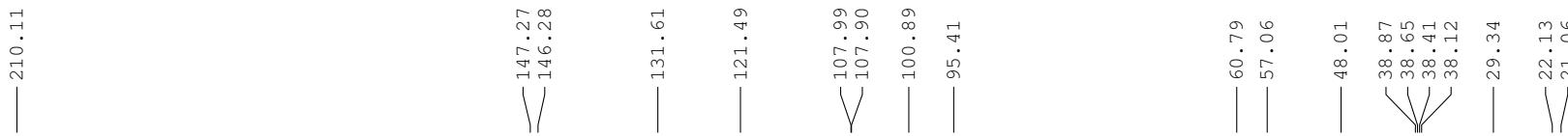


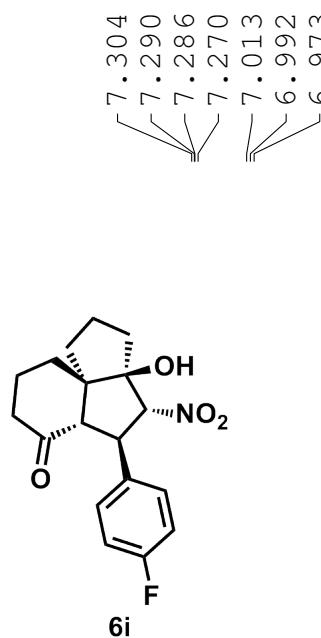
(400 MHz, DMSO-d₆)



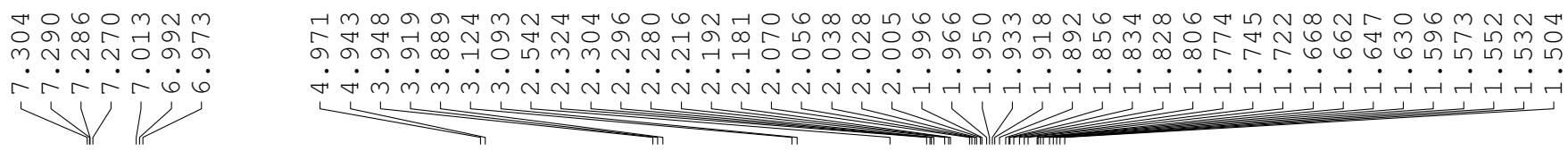
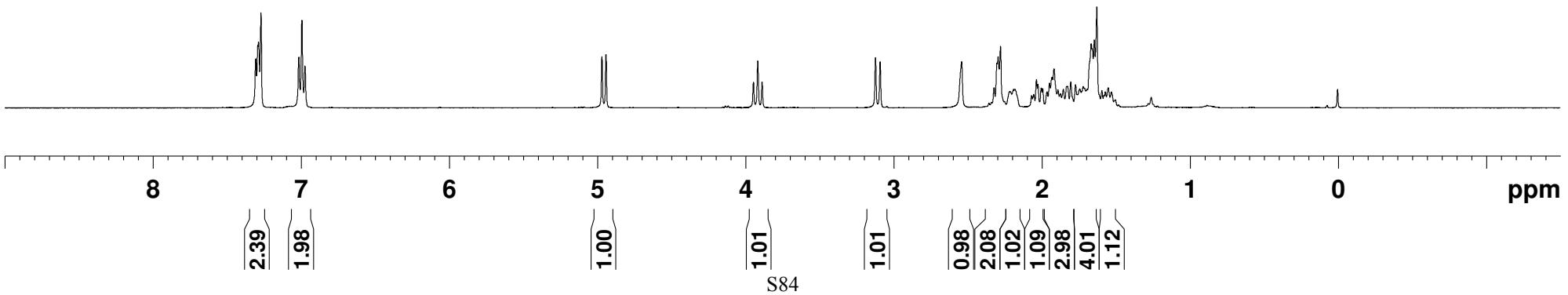


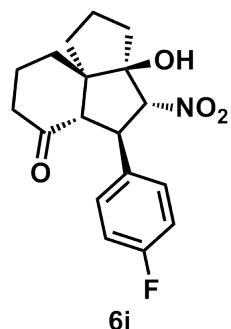
(100 MHz, DMSO-d₆)



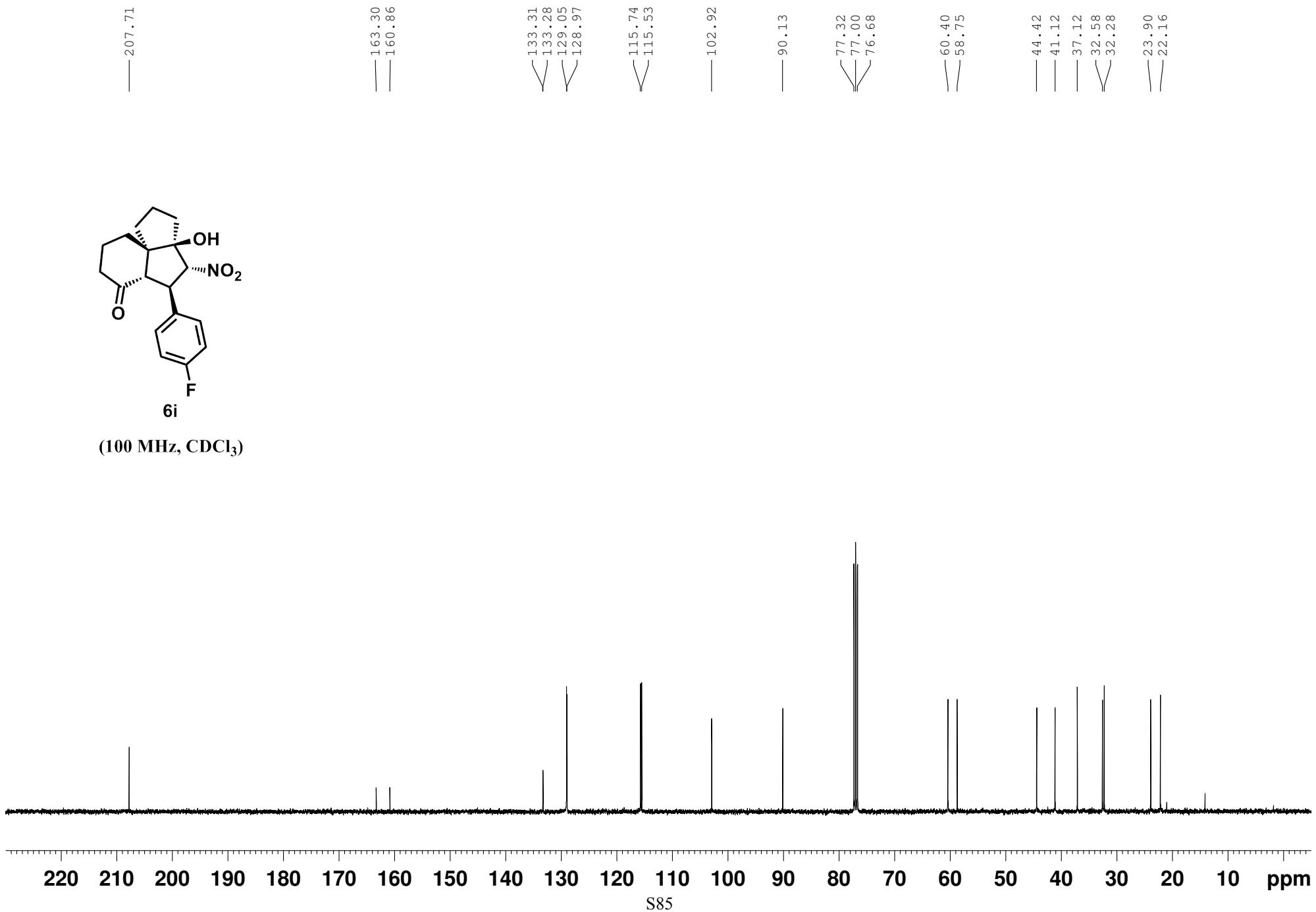


(400 MHz, CDCl₃)

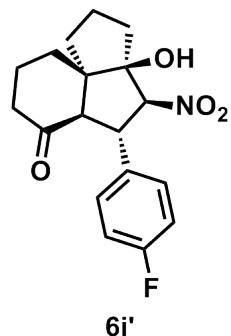




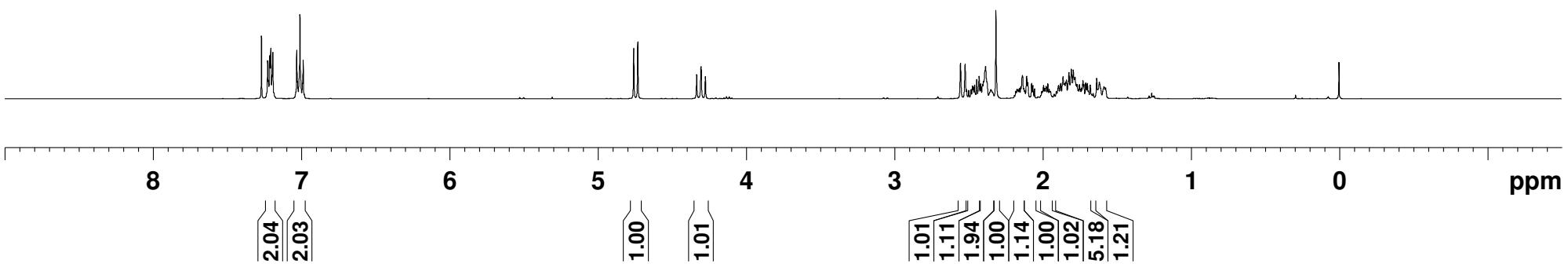
(100 MHz, CDCl₃)

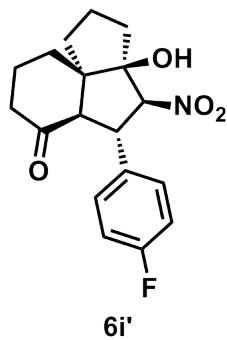


7.270
 7.228
 7.223
 7.215
 7.207
 7.199
 7.194
 7.032
 7.027
 7.011
 6.994
 6.989
 4.759
 4.732
 4.335
 4.305
 4.276
 2.555
 2.524
 2.476
 2.470
 2.460
 2.446
 2.430
 2.420
 2.386
 2.317
 2.149
 2.137
 2.109
 2.102
 2.075
 2.067
 1.995
 1.979
 1.976
 1.967
 1.894
 1.880
 1.864
 1.845
 1.841
 1.824
 1.808
 1.795
 1.783
 1.768
 1.753
 1.739
 1.730
 1.723
 1.711
 1.700
 1.680
 1.637
 1.618
 1.588
 1.577

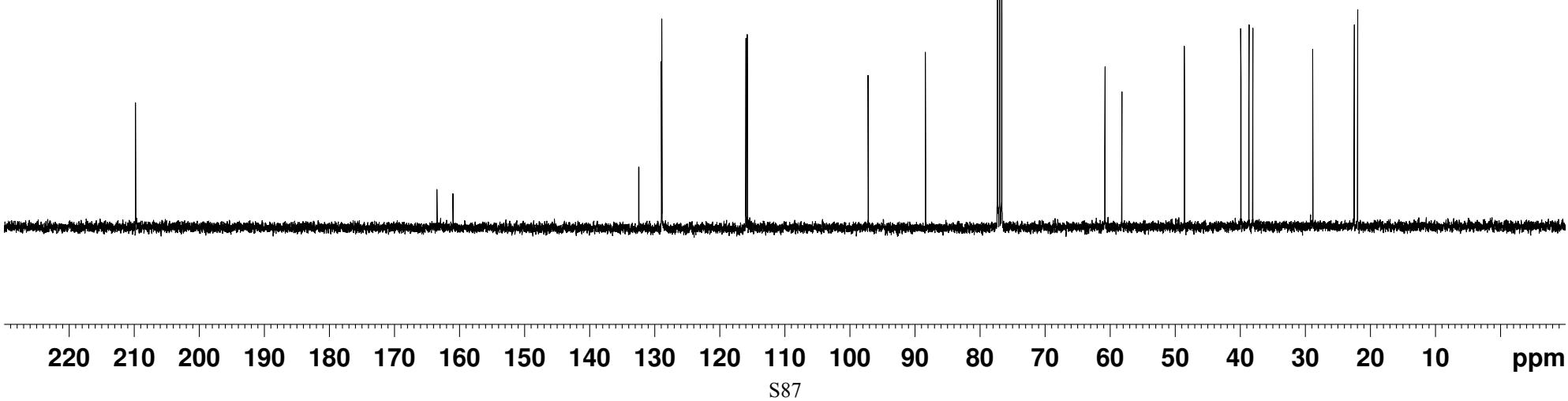


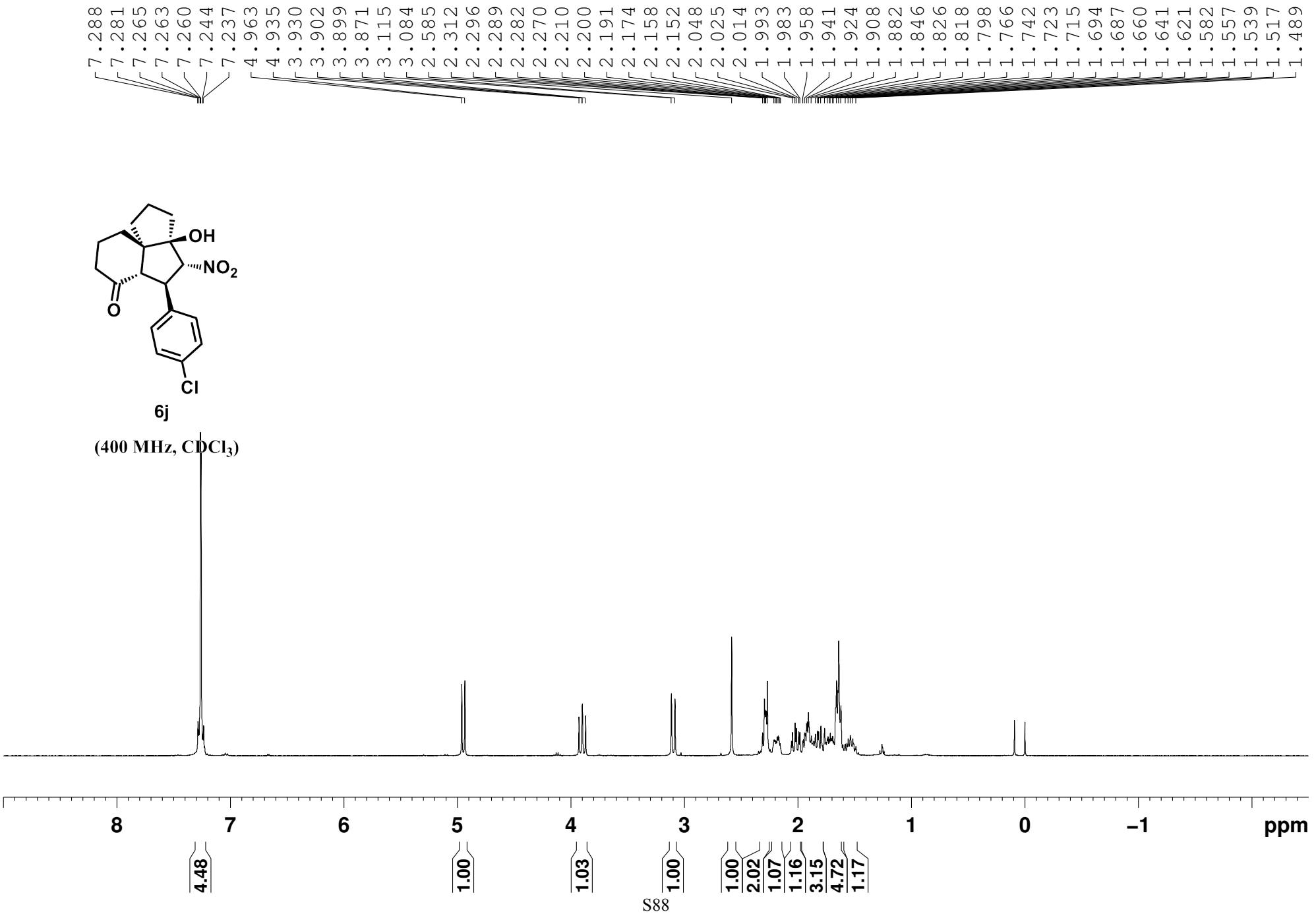
(400 MHz, CDCl₃)

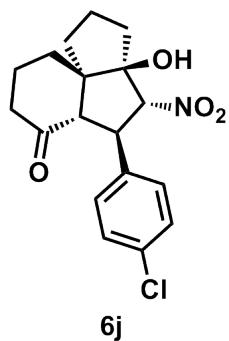




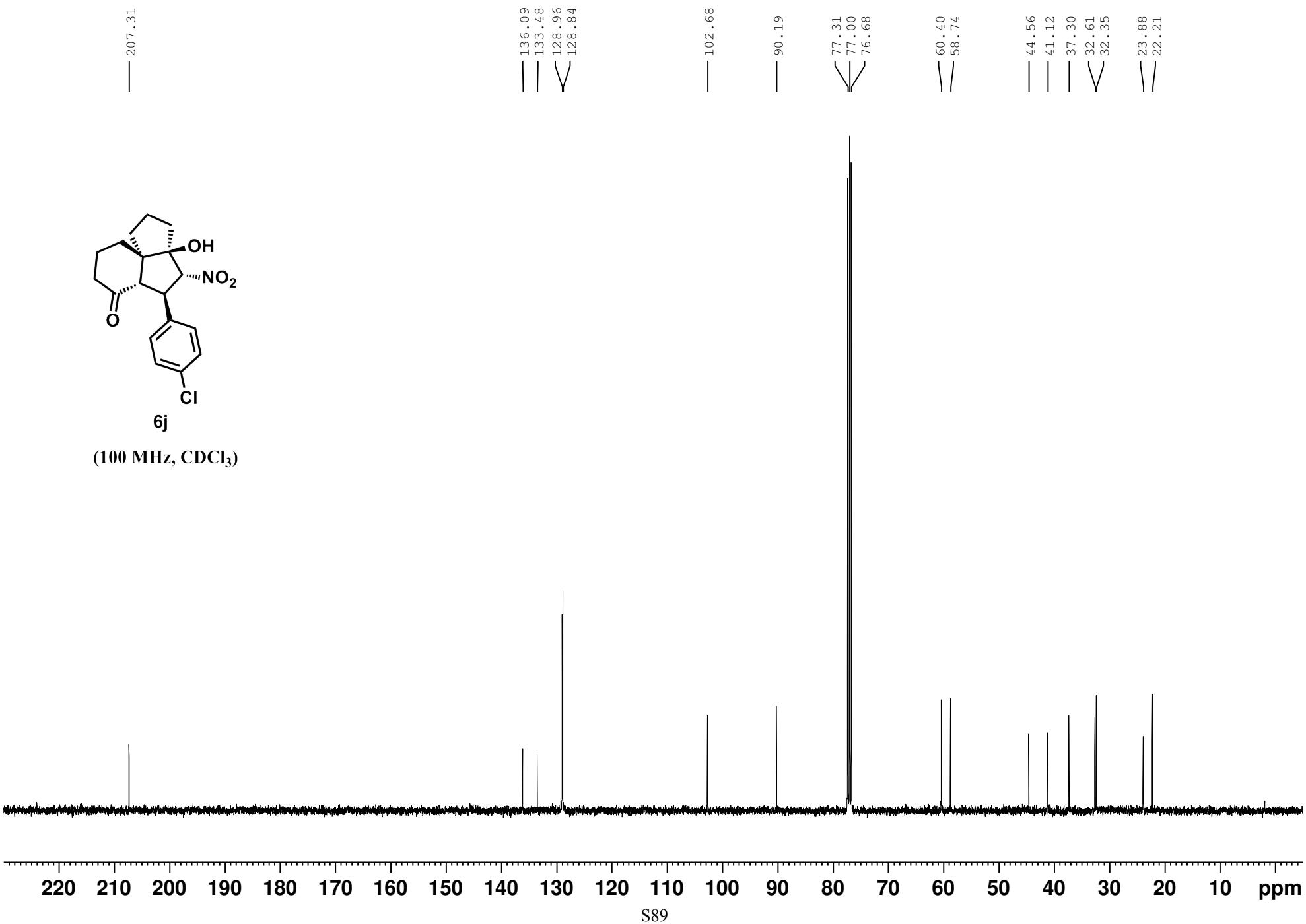
(100 MHz, CDCl₃)

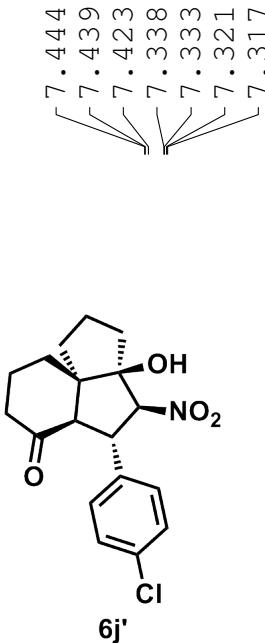




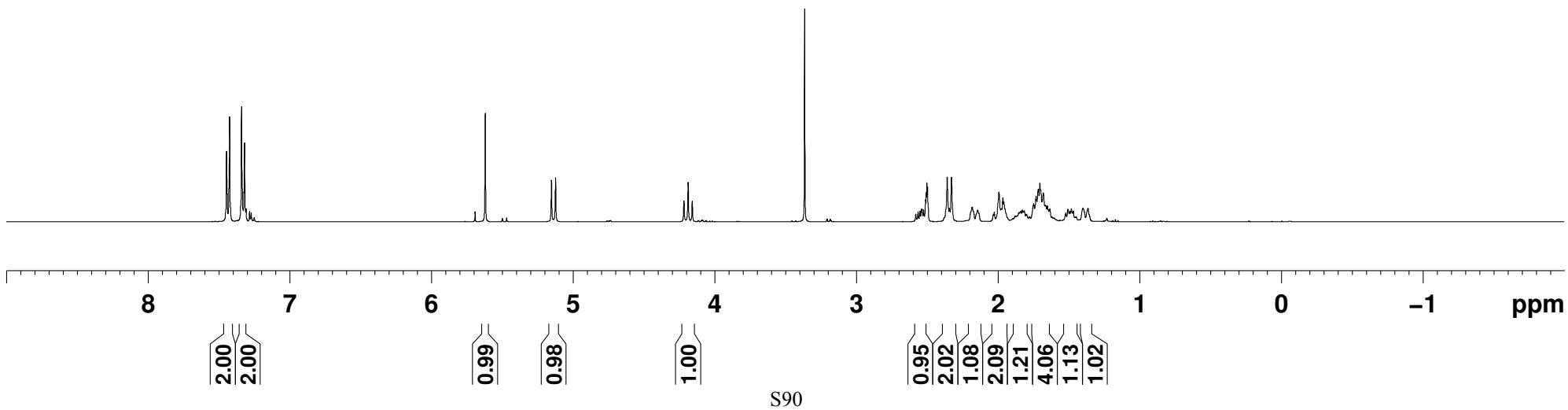


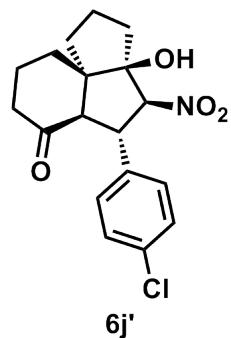
(100 MHz, CDCl_3)



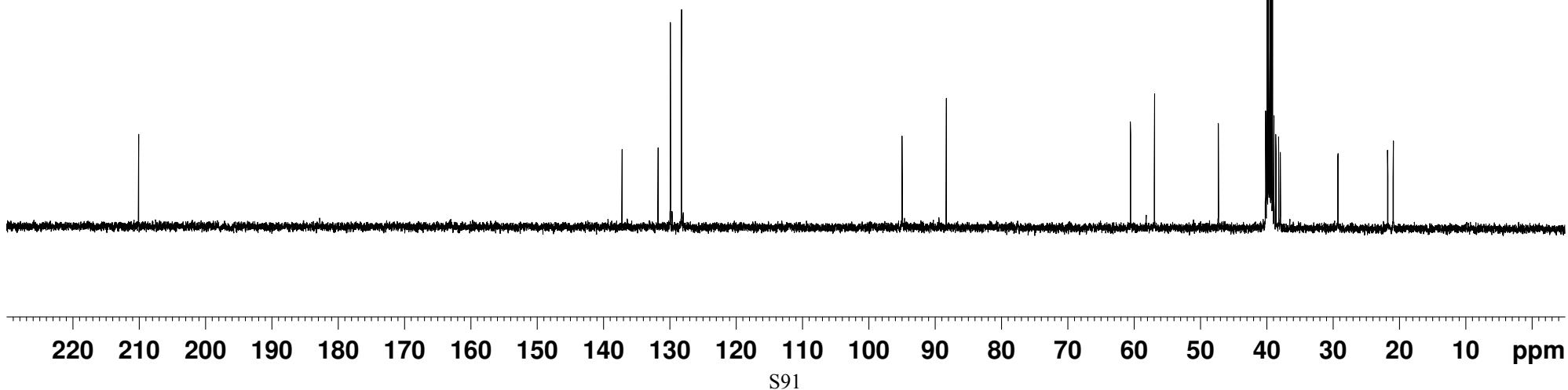


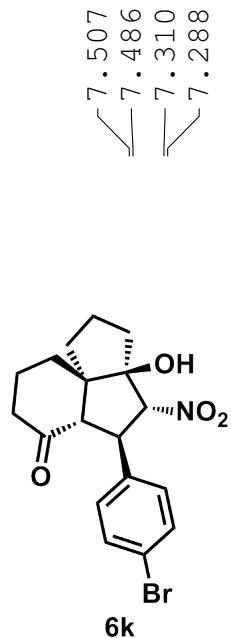
(400 MHz, DMSO-d₆)



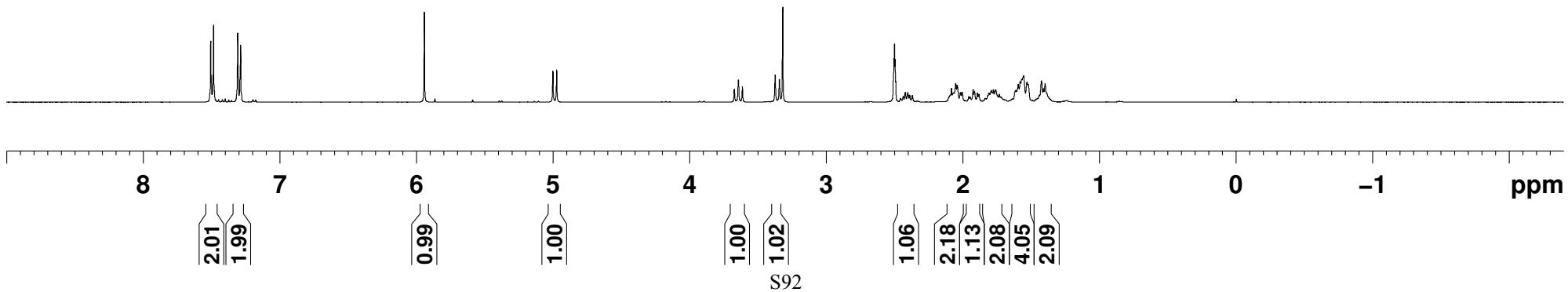


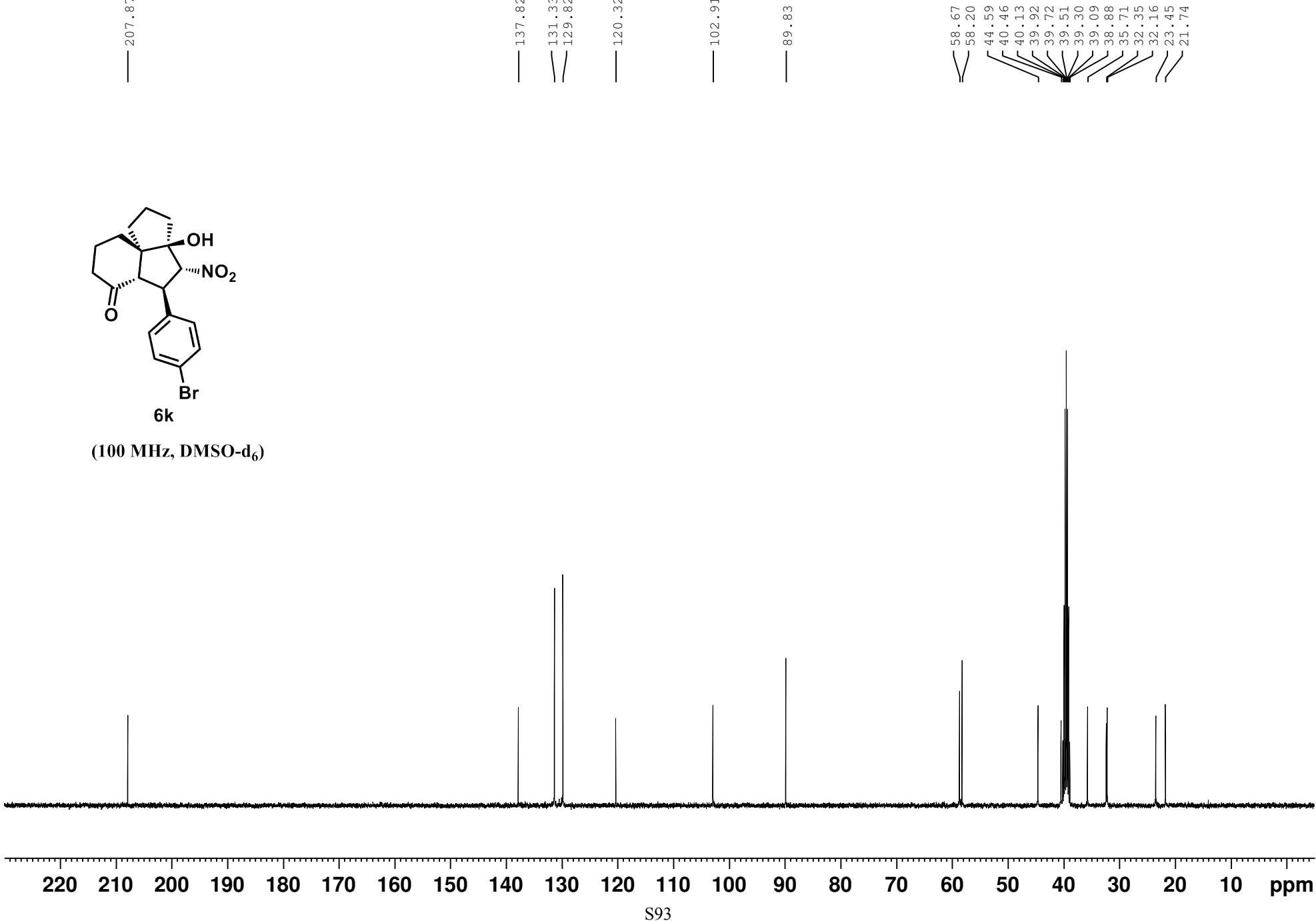
(100 MHz, DMSO-d₆)

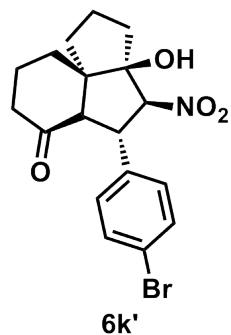




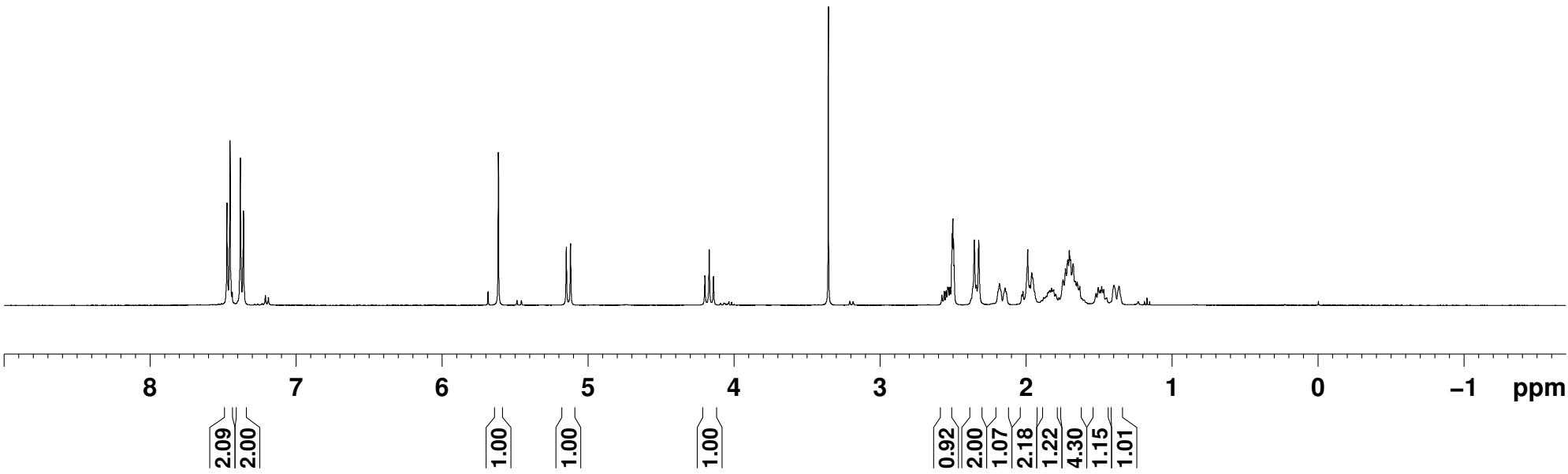
(400 MHz, DMSO-d₆)

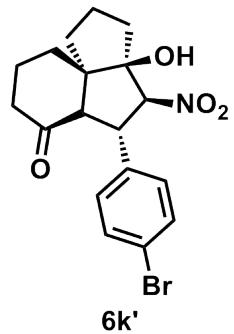




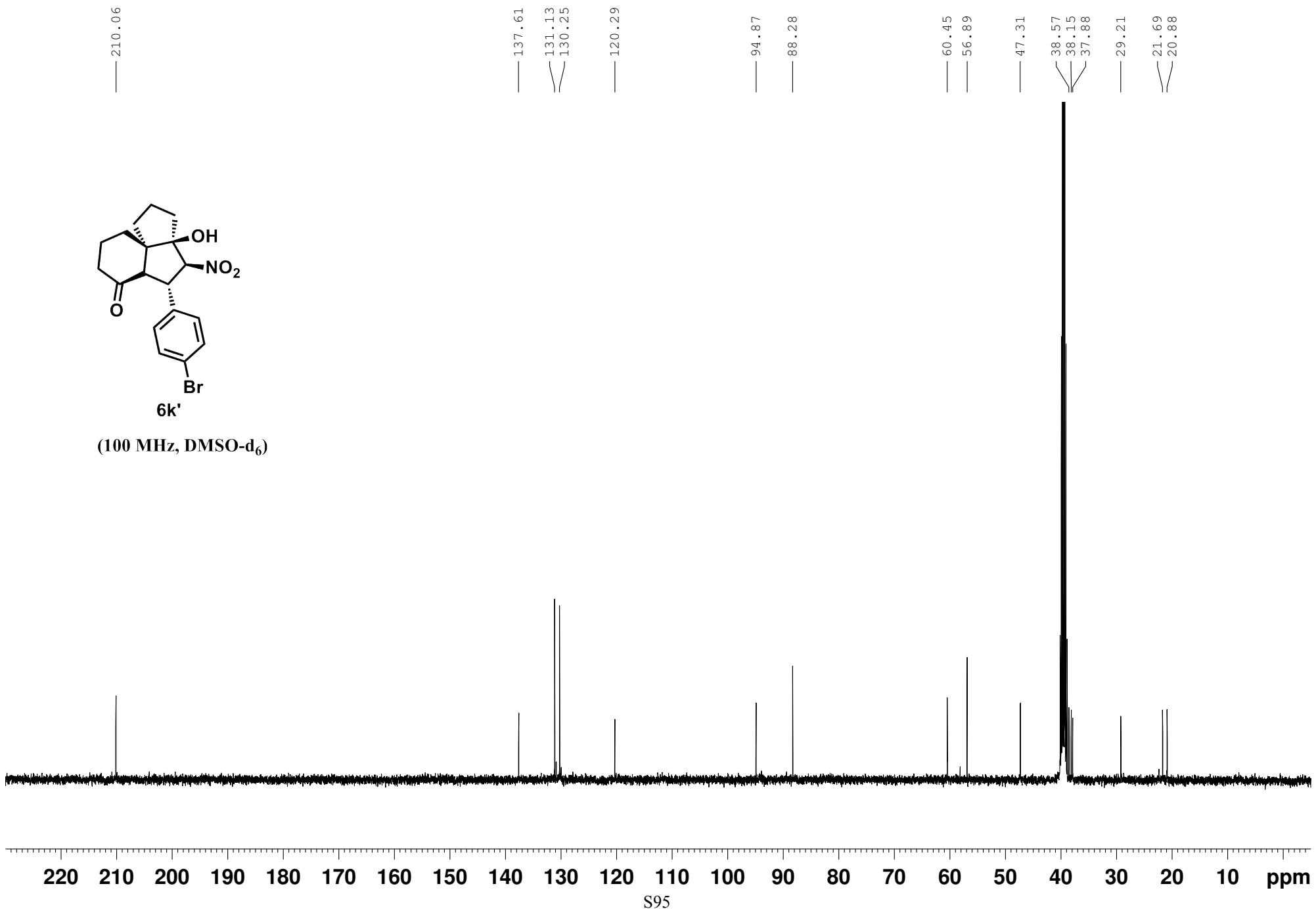


(400 MHz, DMSO-d₆)

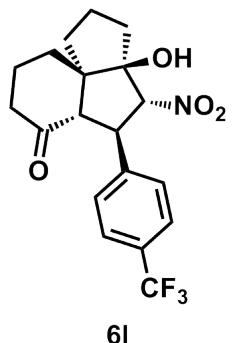




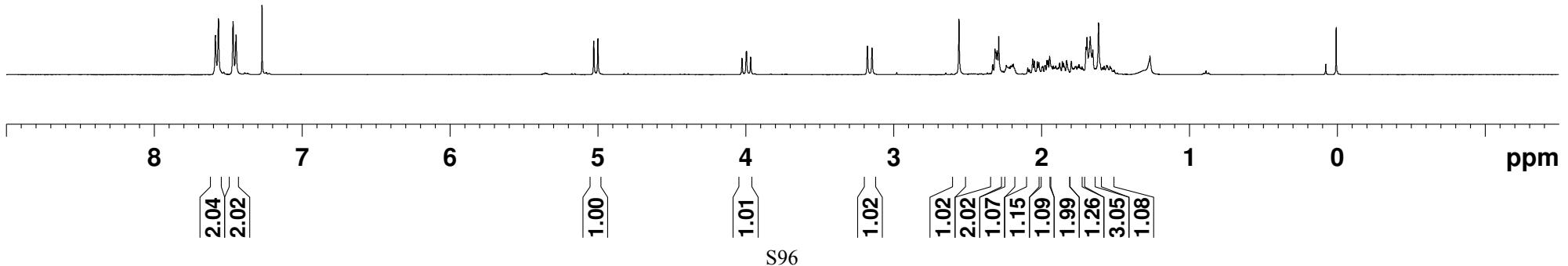
(100 MHz, DMSO-d₆)

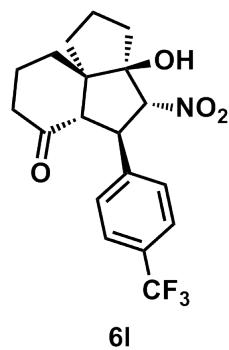


7.585
7.565
7.466
7.446
7.270
5.027
4.999
4.024
3.994
3.966
3.176
3.145
2.557
2.299
2.329
2.314
2.309
2.299
2.288
2.237
2.216
2.209
2.198
2.182
2.189
2.092
2.059
2.049
2.027
2.017
1.996
1.990
1.977
1.974
1.962
1.956
1.945
1.920
1.902
1.877
1.858
1.850
1.829
1.798
1.772
1.745
1.733
1.698
1.692
1.681
1.670
1.652
1.588
1.576
1.558
1.553
1.536

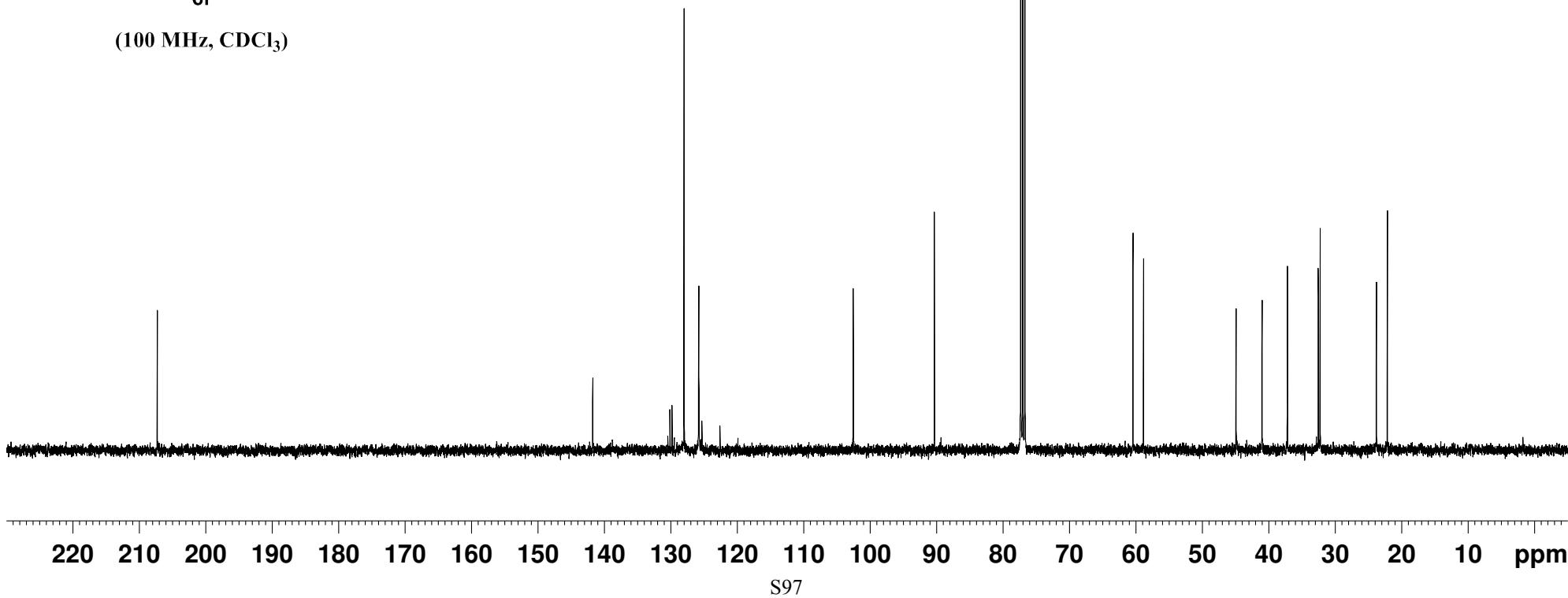
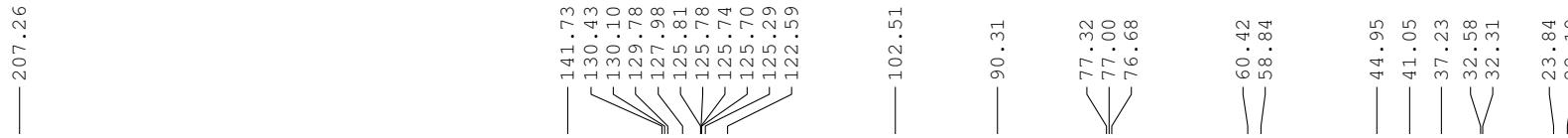


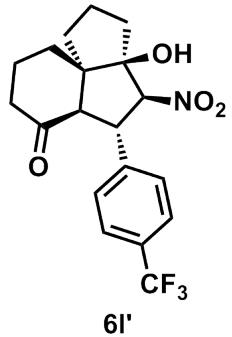
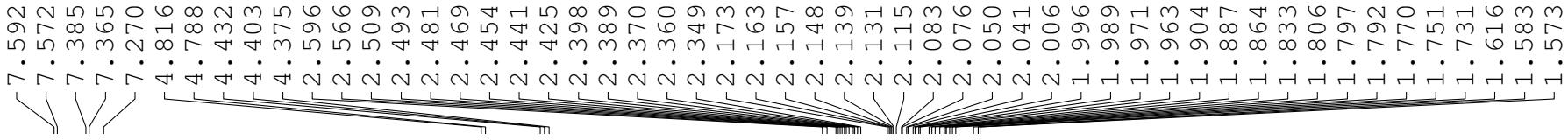
(400 MHz, CDCl₃)



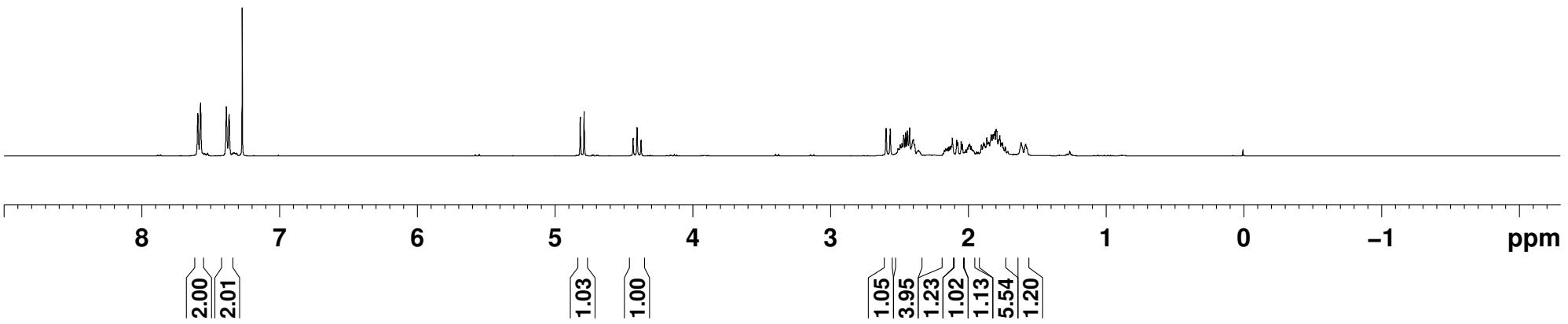


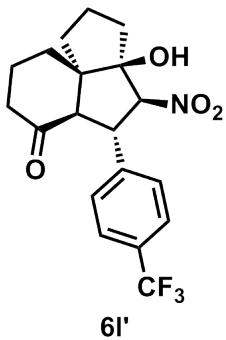
(100 MHz, CDCl_3)





(400 MHz, CDCl_3)





(100 MHz, CDCl_3)

— 209.61

— 141.06
— 131.02
— 130.32
— 130.00
— 129.67
— 128.13
— 127.87
— 125.99
— 125.96
— 125.92
— 125.88
— 125.20
— 122.50

— 96.53

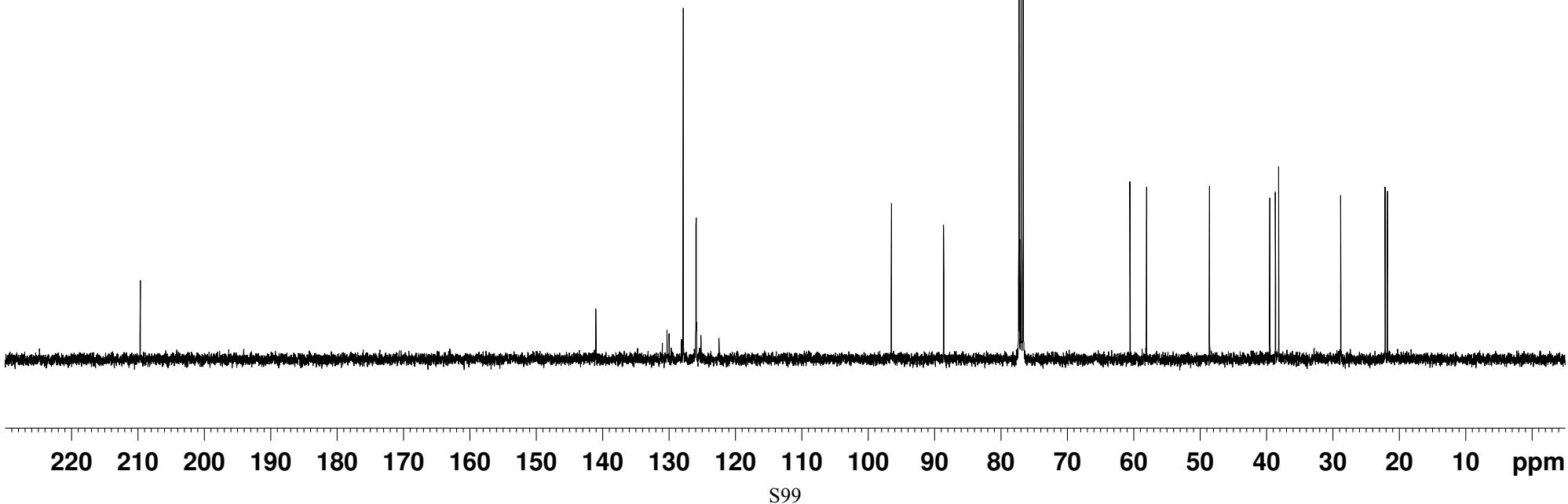
— 88.65

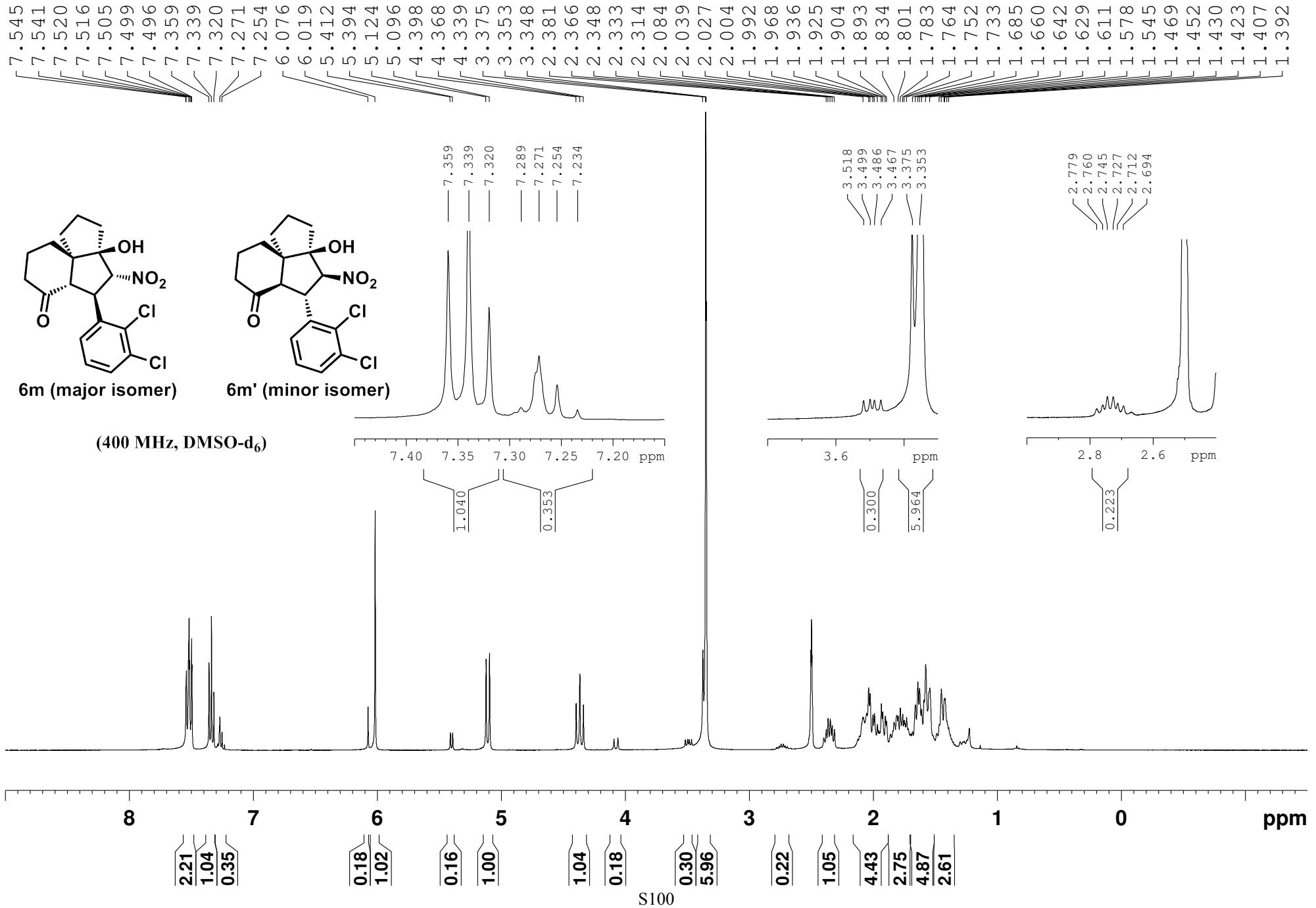
— 77.32
— 77.00
— 76.68

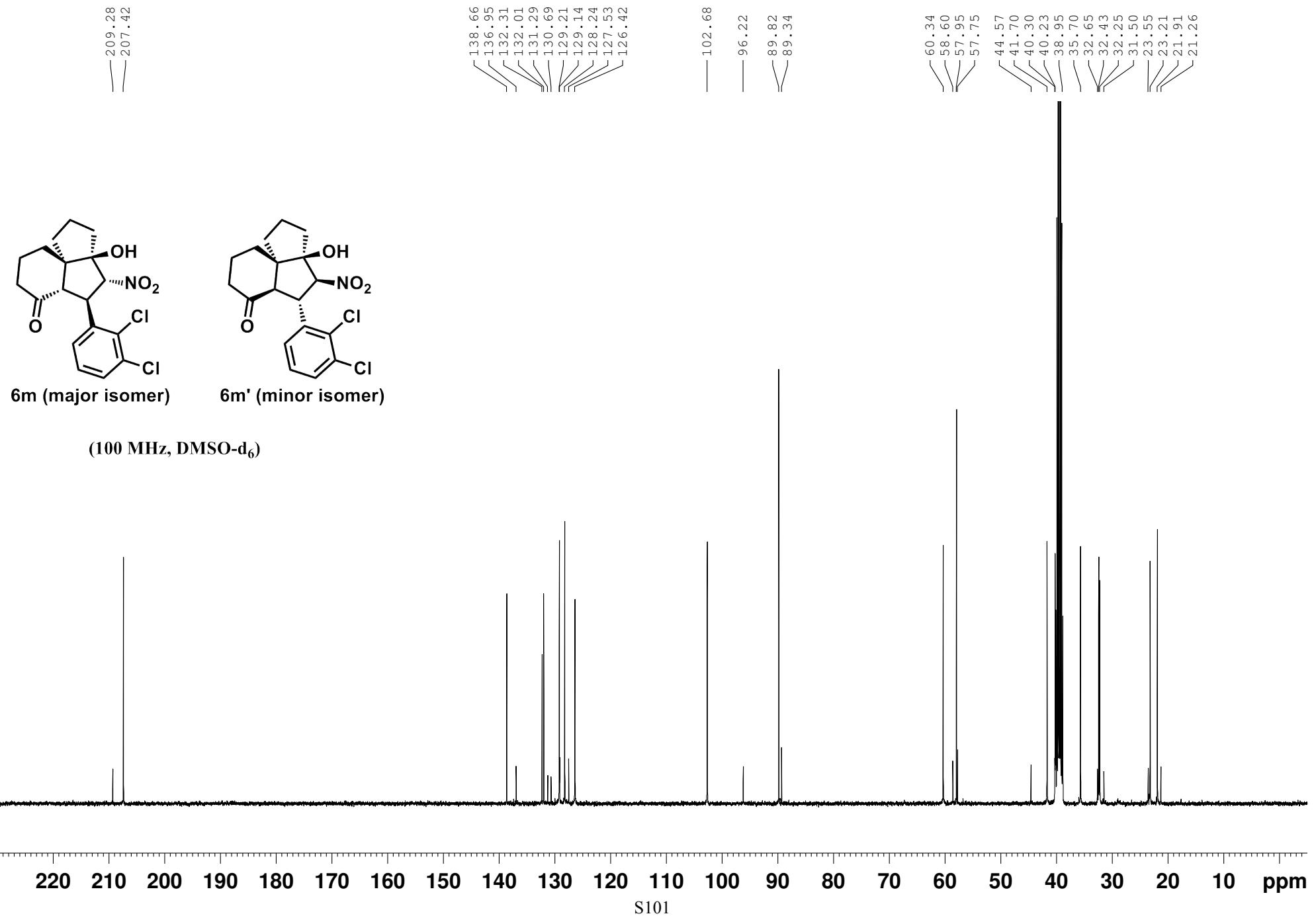
— 60.58
— 58.07

— 48.61
— 39.52
— 38.67
— 38.19

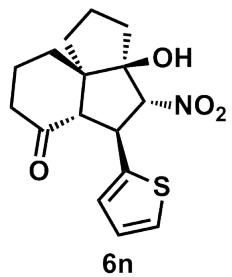
— 28.83
— 22.15
— 21.81



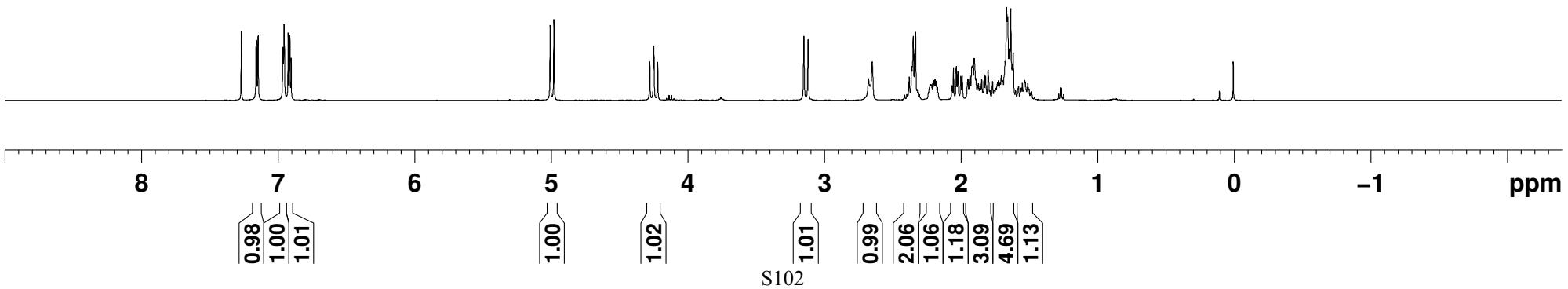


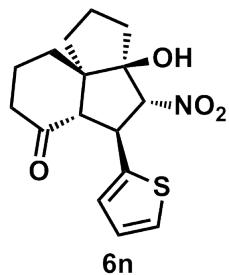


7.270
7.159
7.146
6.964
6.956
6.926
6.917
6.914
6.905
5.008
4.981
4.279
4.249
4.221
3.150
3.119
2.677
2.650
2.413
2.396
2.378
2.349
2.333
2.321
2.315
2.228
2.222
2.195
2.172
2.066
2.055
2.033
2.022
2.001
1.990
1.949
1.933
1.919
1.903
1.849
1.830
1.820
1.801
1.752
1.732
1.725
1.704
1.665
1.617
1.578
1.563
1.551
1.533
1.511
1.483



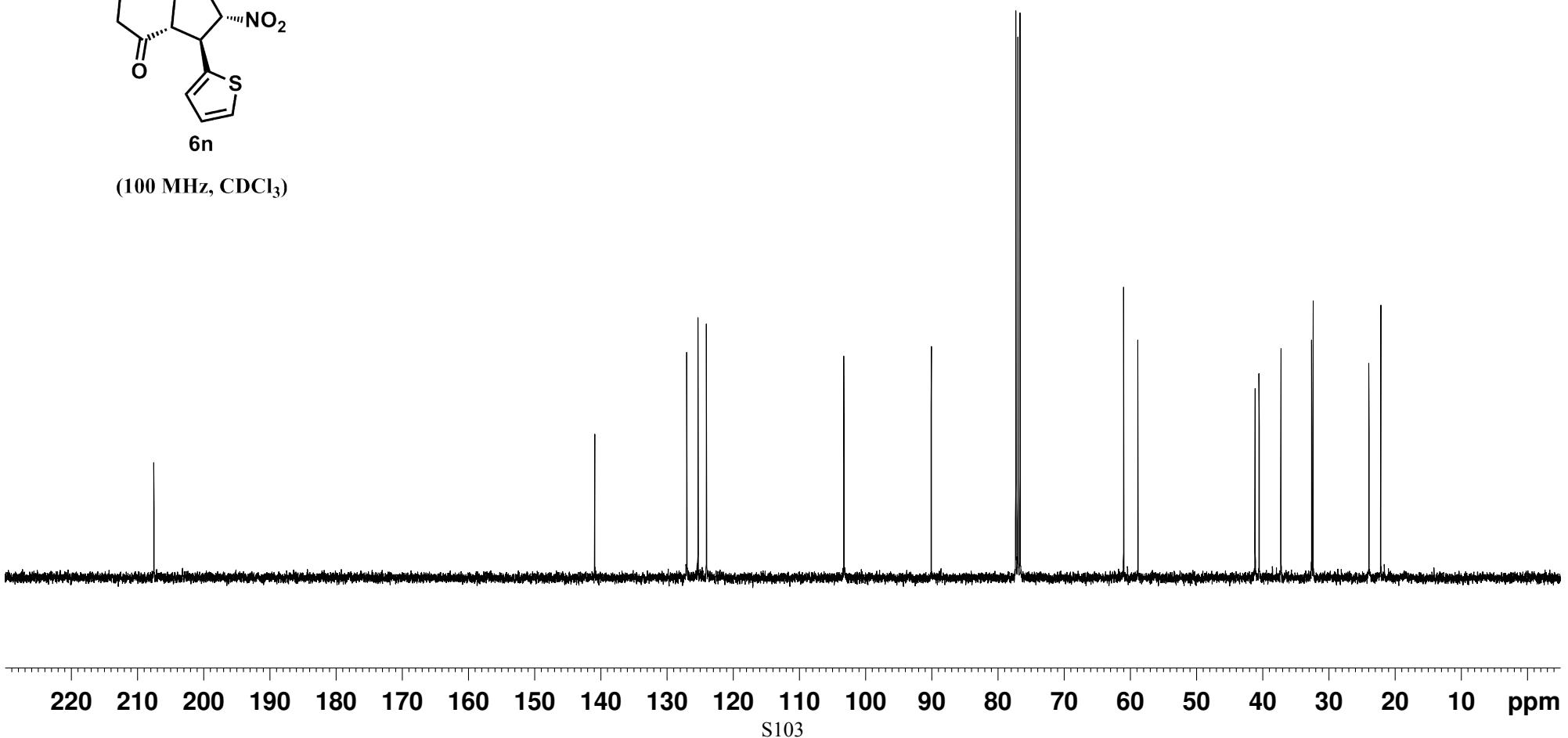
(400 MHz, CDCl₃)



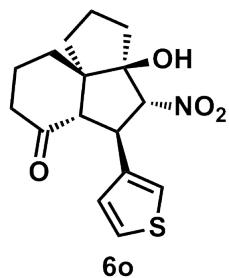


(100 MHz, CDCl_3)

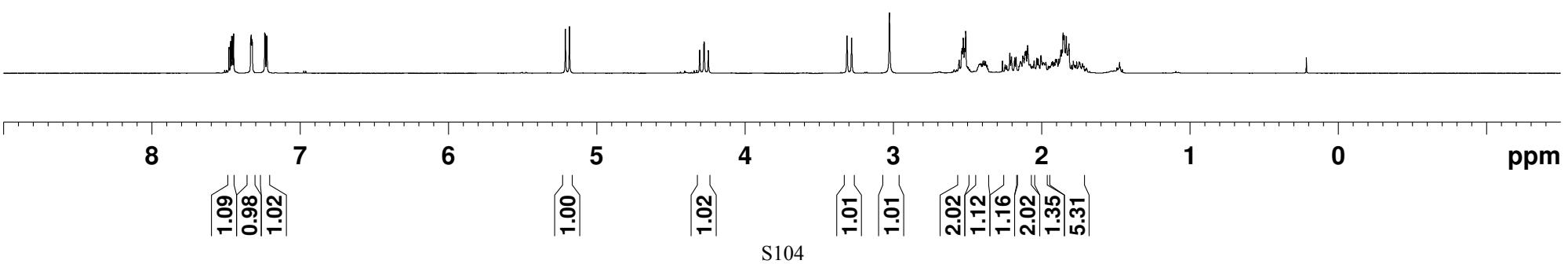
207.48
140.93
127.03
125.34
124.07
103.29
90.09
77.31
77.00
76.68
61.03
58.87
41.17
40.56
37.26
32.62
32.41
23.97
22.18

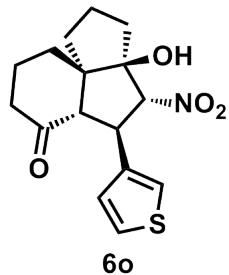


7.481
7.470
7.462
7.457
7.450
7.334
7.332
7.327
7.327
7.324
7.227
7.224
5.211
5.184
4.306
4.276
4.248
3.312
3.281
3.026
2.556
2.538
2.529
2.519
2.512
2.394
2.384
2.378
2.214
2.203
2.182
2.172
2.144
2.126
2.105
2.095
2.032
2.023
2.004
1.990
1.971
1.933
1.926
1.915
1.906
1.897
1.884
1.871
1.855
1.834
1.815
1.787
1.764
1.746
1.724

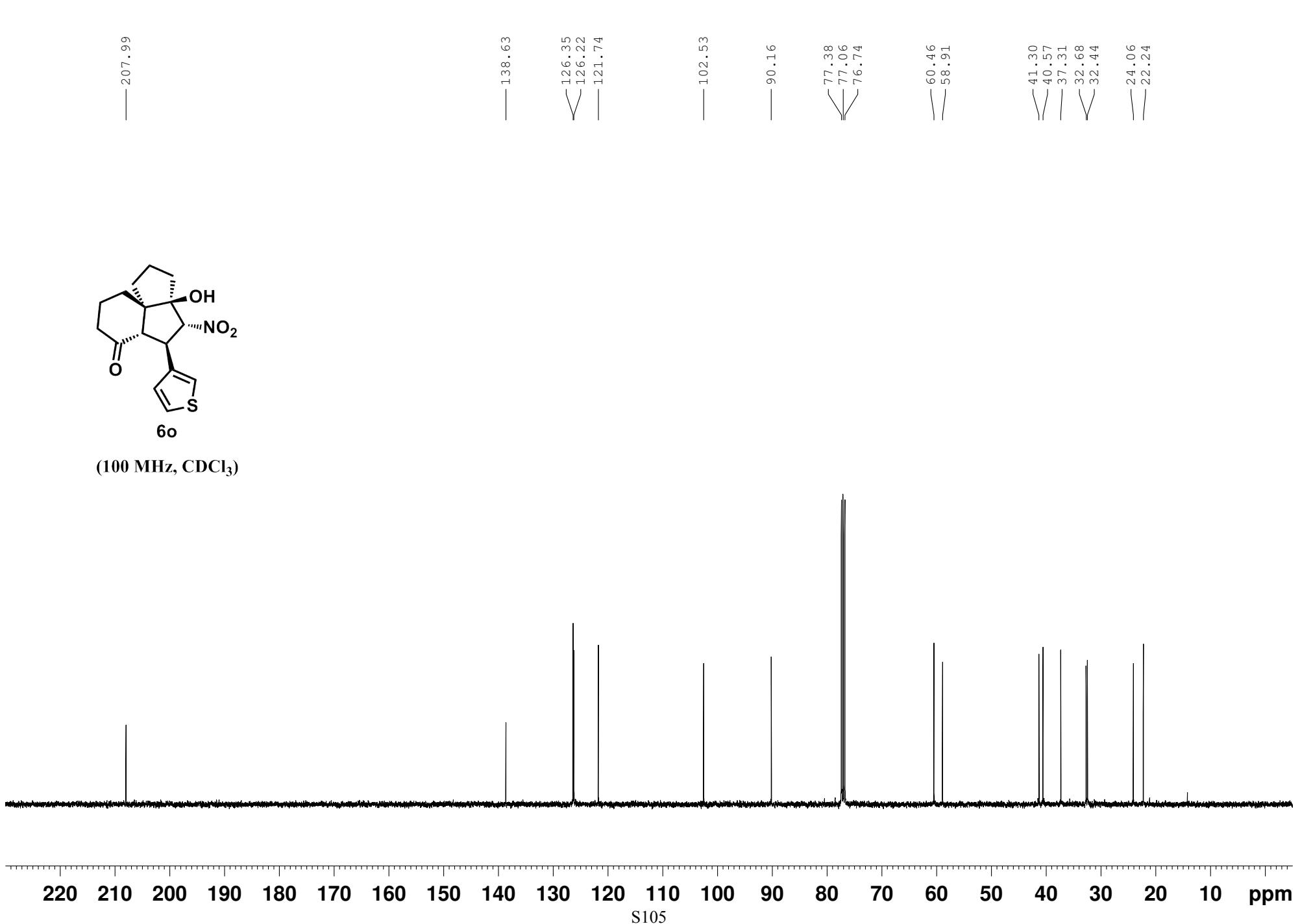


(400 MHz, CDCl₃)

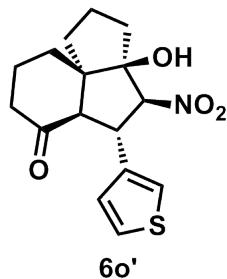




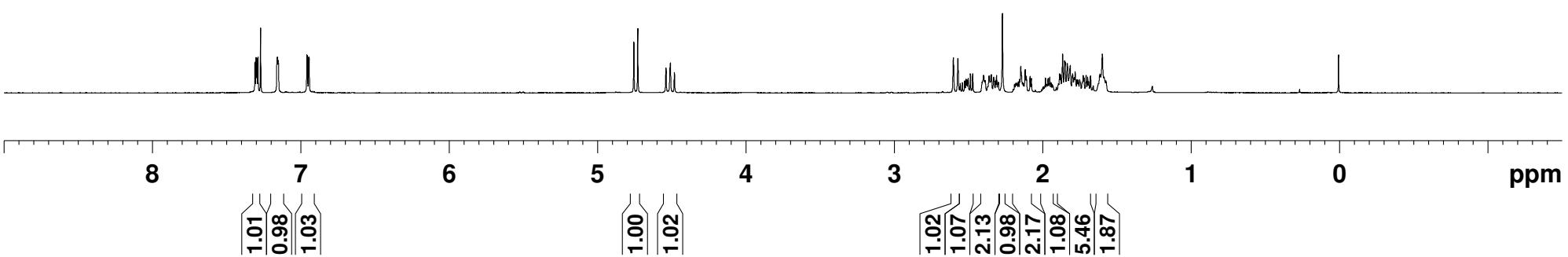
(100 MHz, CDCl_3)

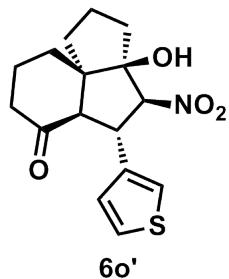


7	308
7	301
7	295
7	288
7	270
7	159
7	157
7	150
7	152
6	958
6	955
6	946
6	943
4	757
4	731
4	541
4	511
4	484
2	604
2	573
2	519
2	504
2	489
2	474
2	402
2	399
2	363
2	349
2	332
2	313
2	273
2	149
2	119
2	113
2	087
2	078
1	983
1	954
1	888
1	881
1	867
1	816
1	801
1	783
1	729
1	723
1	709
1	699
1	680
1	616
1	612
1	600
1	588

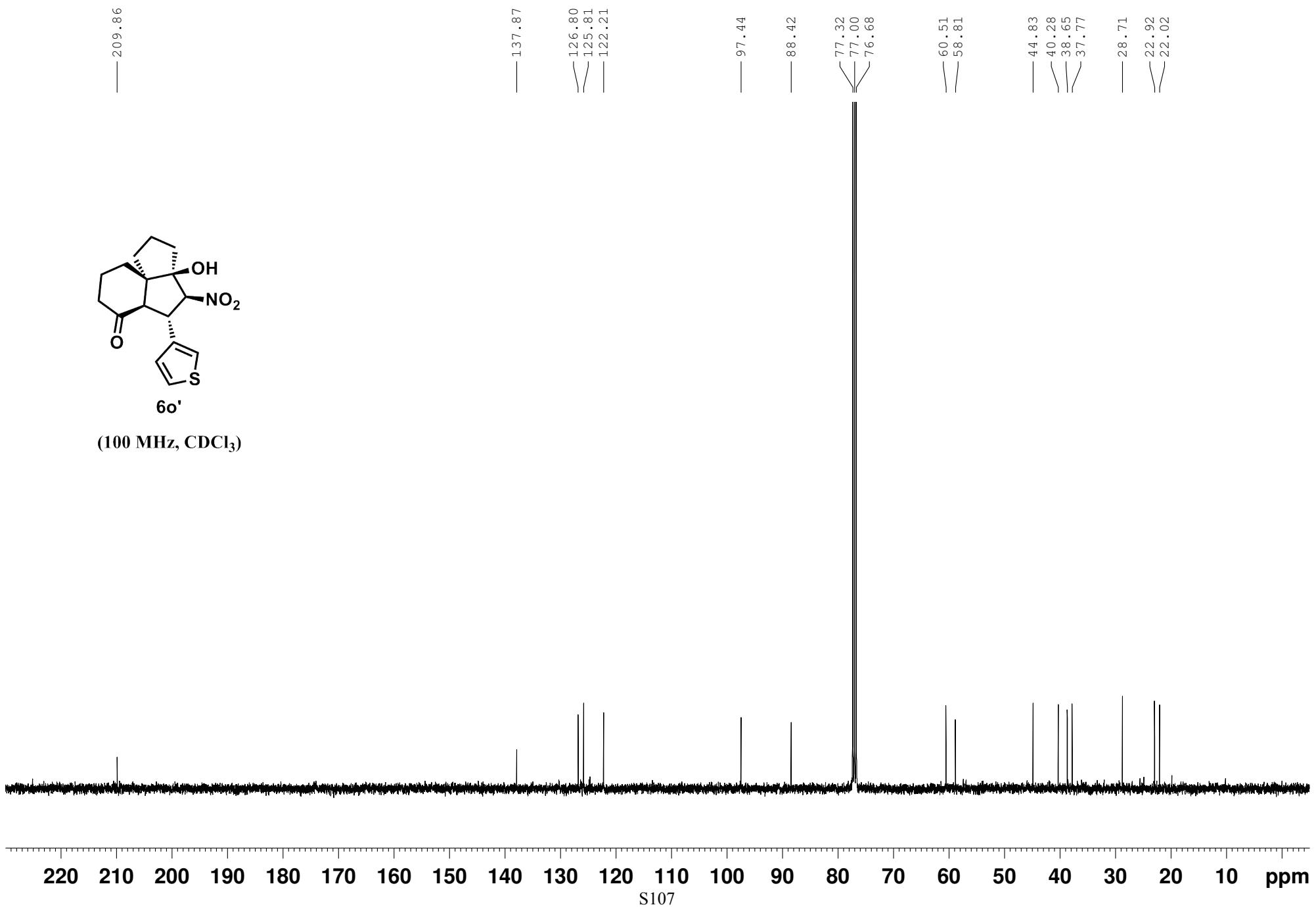


(400 MHz, CDCl₃)

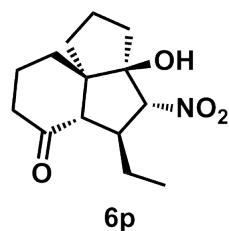




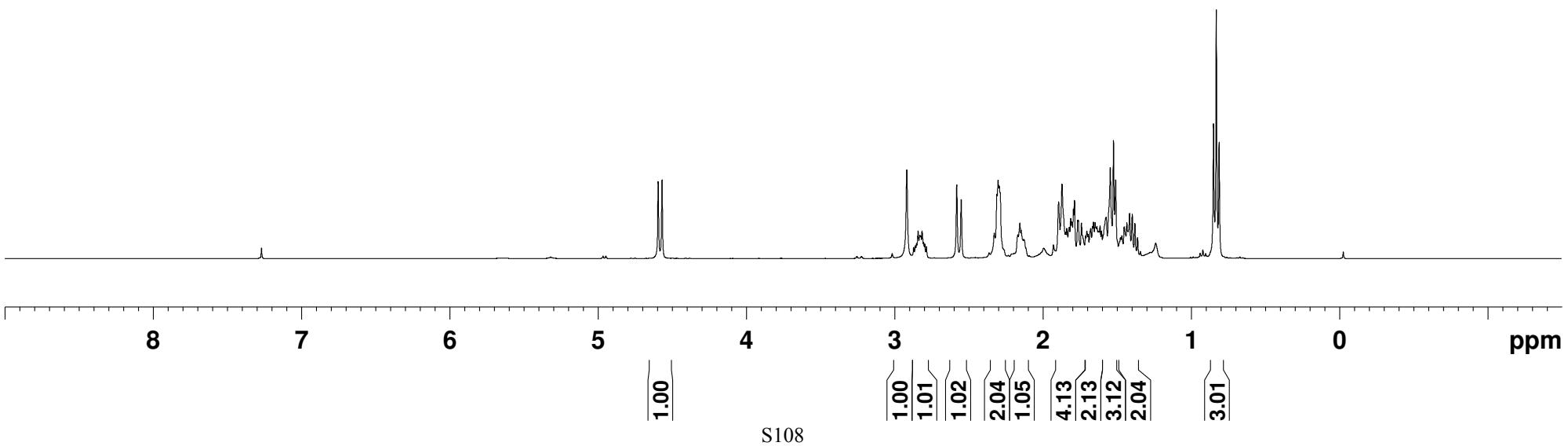
(100 MHz, CDCl₃)

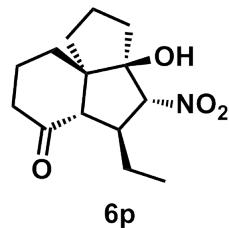


4.595
4.569
2.918
2.841
2.830
2.823
2.815
2.581
2.551
2.328
2.294
2.310
2.302
2.169
2.155
2.146
2.130
1.894
1.871
1.847
1.839
1.821
1.812
1.804
1.794
1.787
1.765
1.761
1.739
1.702
1.694
1.682
1.677
1.665
1.658
1.647
1.635
1.628
1.622
1.614
1.604
1.577
1.573
1.545
1.524
1.509
1.477
1.467
1.451
1.434
1.427
1.415
1.397
1.379
1.361
0.849
0.830
0.811

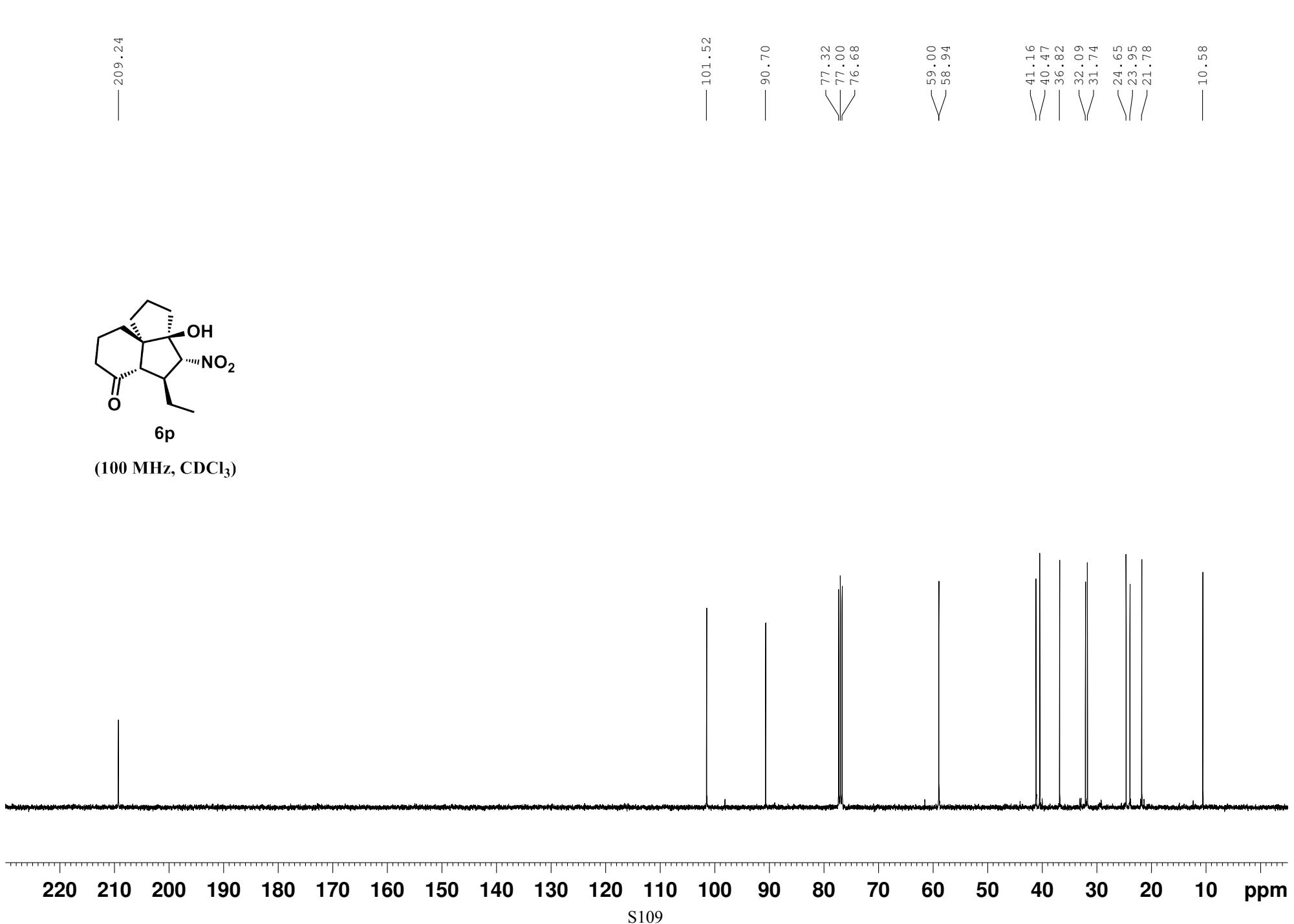


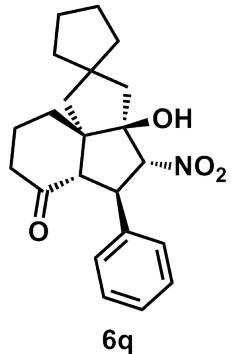
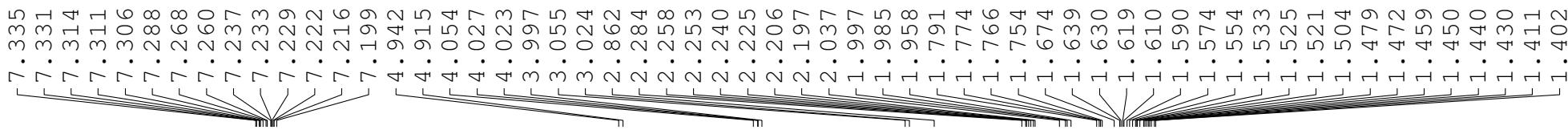
(400 MHz, CDCl₃)



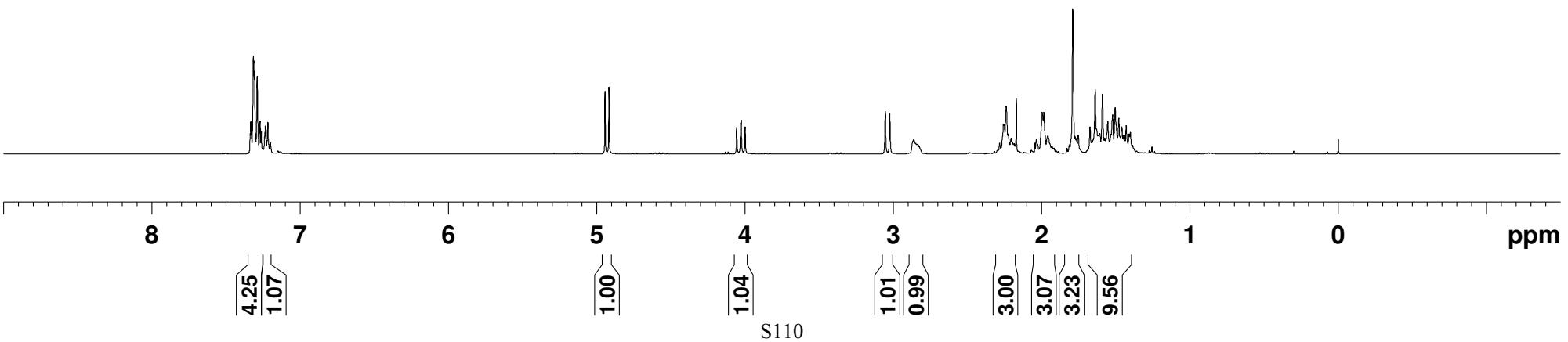


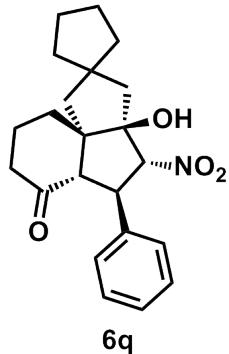
(100 MHz, CDCl₃)





(400 MHz, CDCl₃)





(100 MHz, CDCl_3)

— 207.10

— 137.42

128.72
127.58
127.53

— 102.21

77.31
77.00
76.68

— 90.88

61.33
60.79

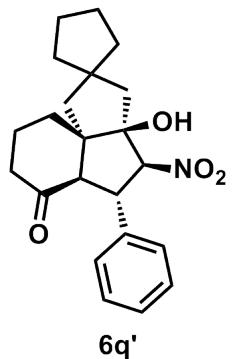
50.00
47.67
43.41
42.81
40.91
40.77
39.93

30.79
24.46
24.12
23.35

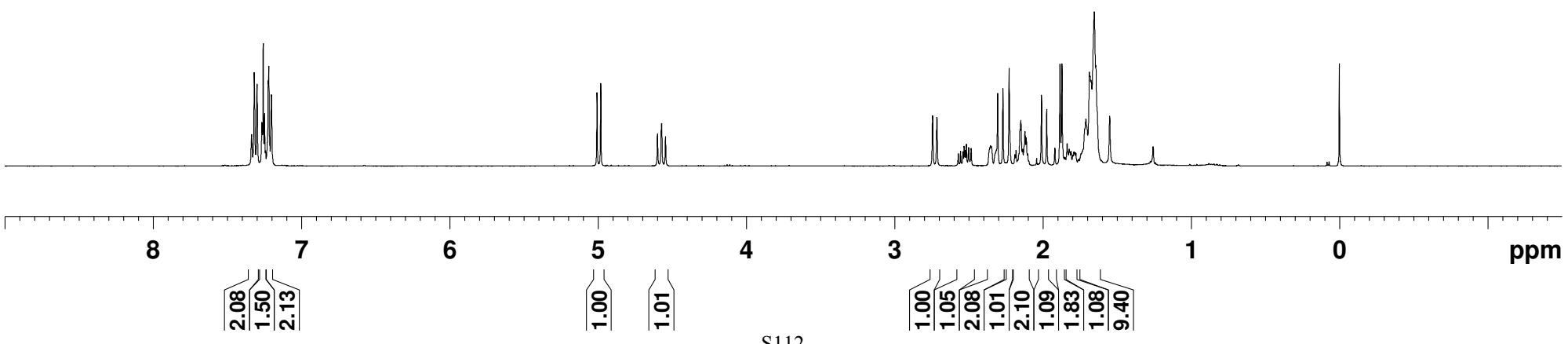
S111

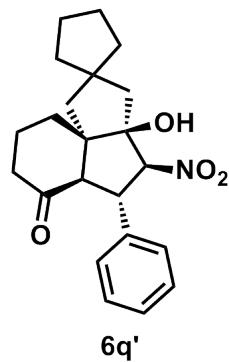
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

7.336
7.319
7.300
7.267
7.264
7.258
7.249
7.224
7.221
7.203
5.007
4.982
4.599
4.571
4.545
2.744
2.715
2.570
2.555
2.539
2.531
2.523
2.515
2.500
2.484
2.360
2.353
2.347
2.321
2.314
2.305
2.269
2.227
2.181
2.154
2.148
2.120
2.112
2.009
1.974
1.884
1.871
1.836
1.822
1.817
1.790
1.786
1.778
1.744
1.710
1.686
1.682
1.676
1.653
1.643

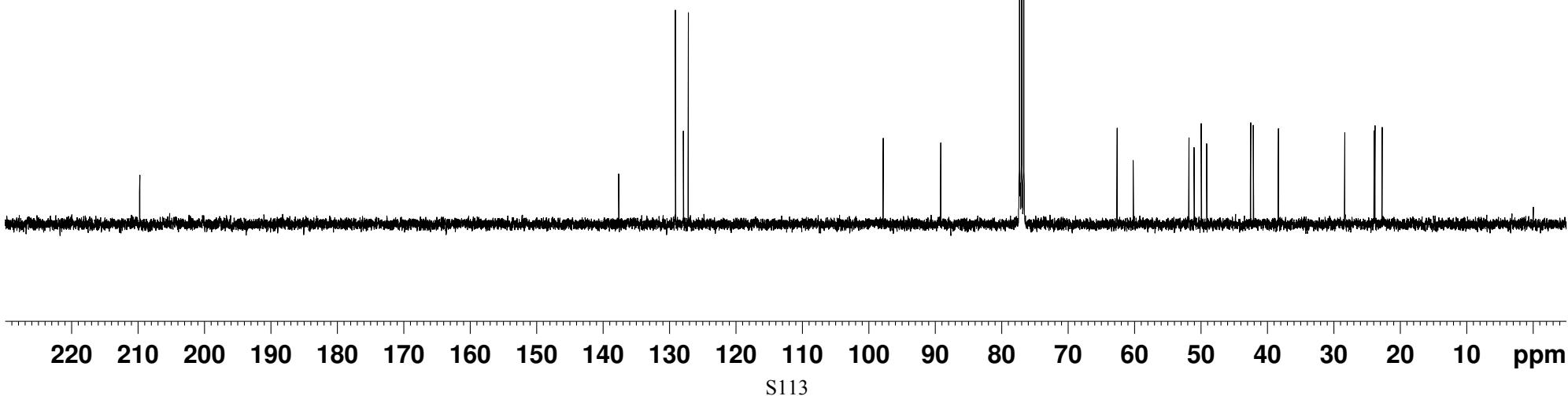


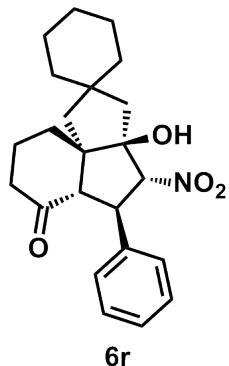
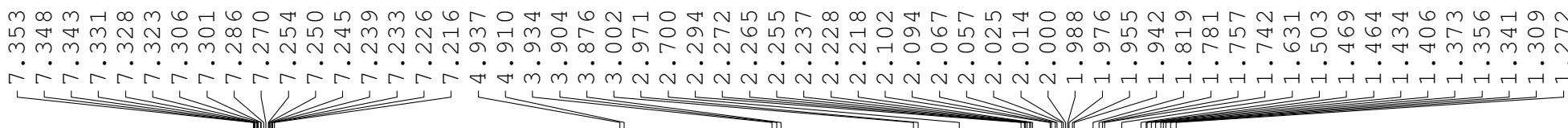
(400 MHz, CDCl₃)



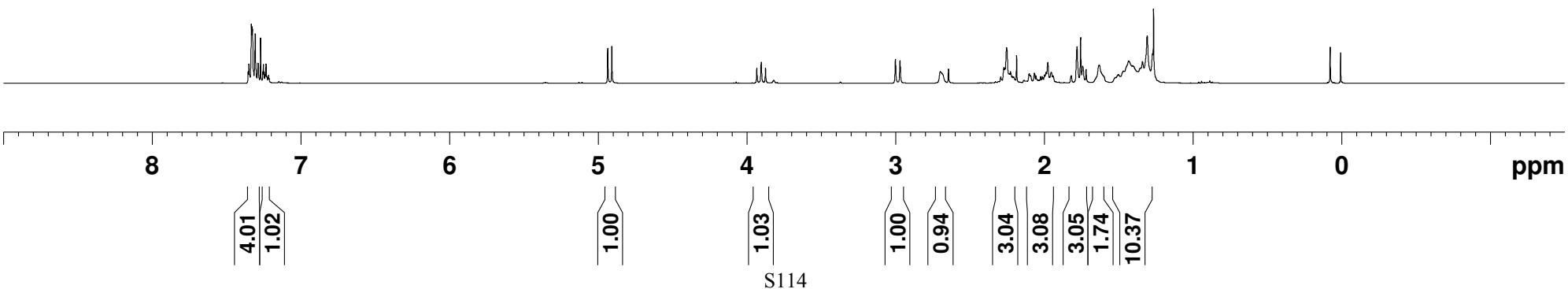


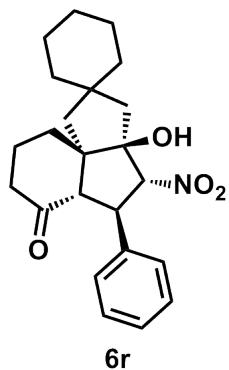
(100 MHz, CDCl₃)



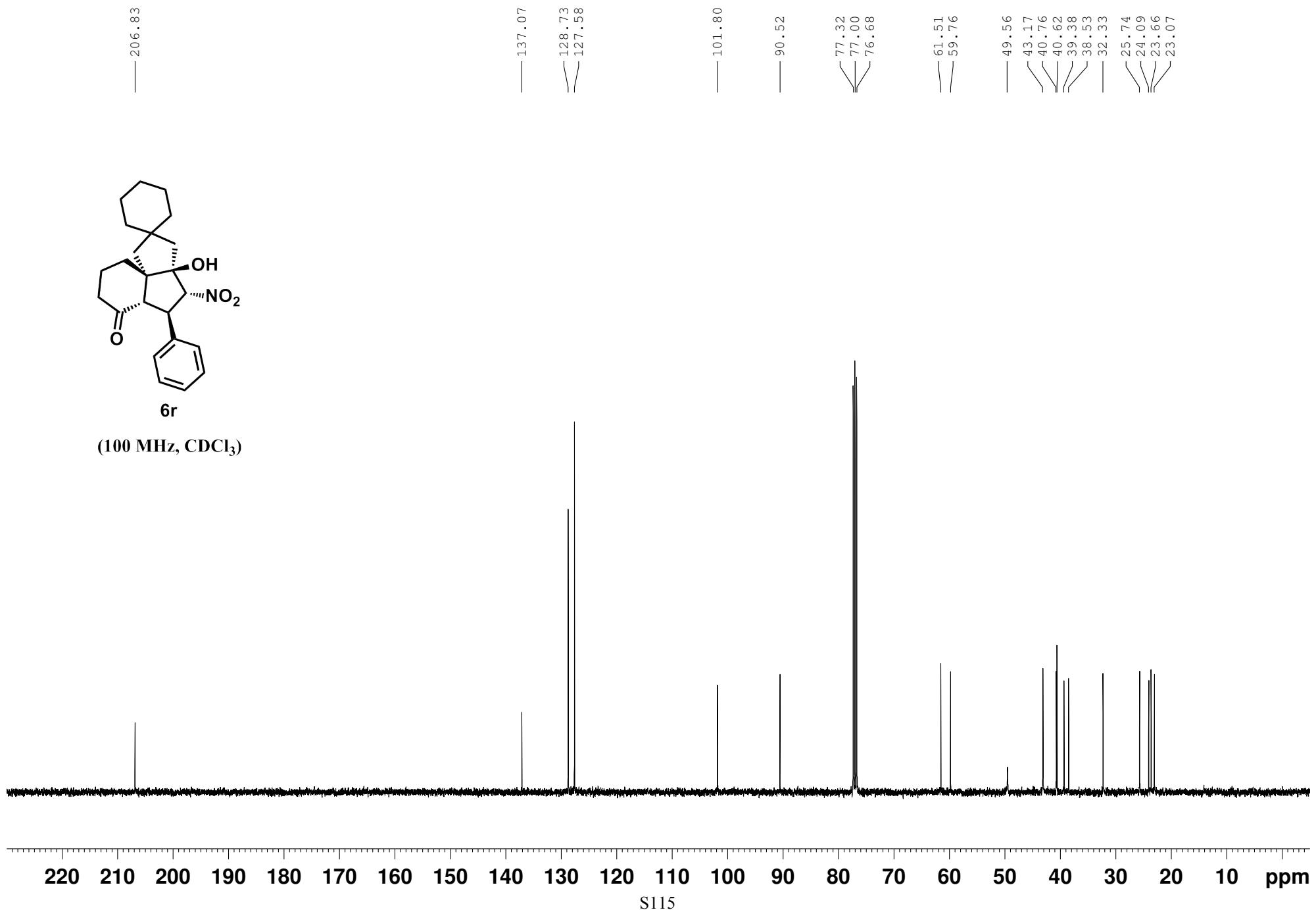


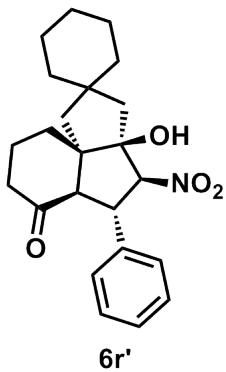
(400 MHz, CDCl₃)



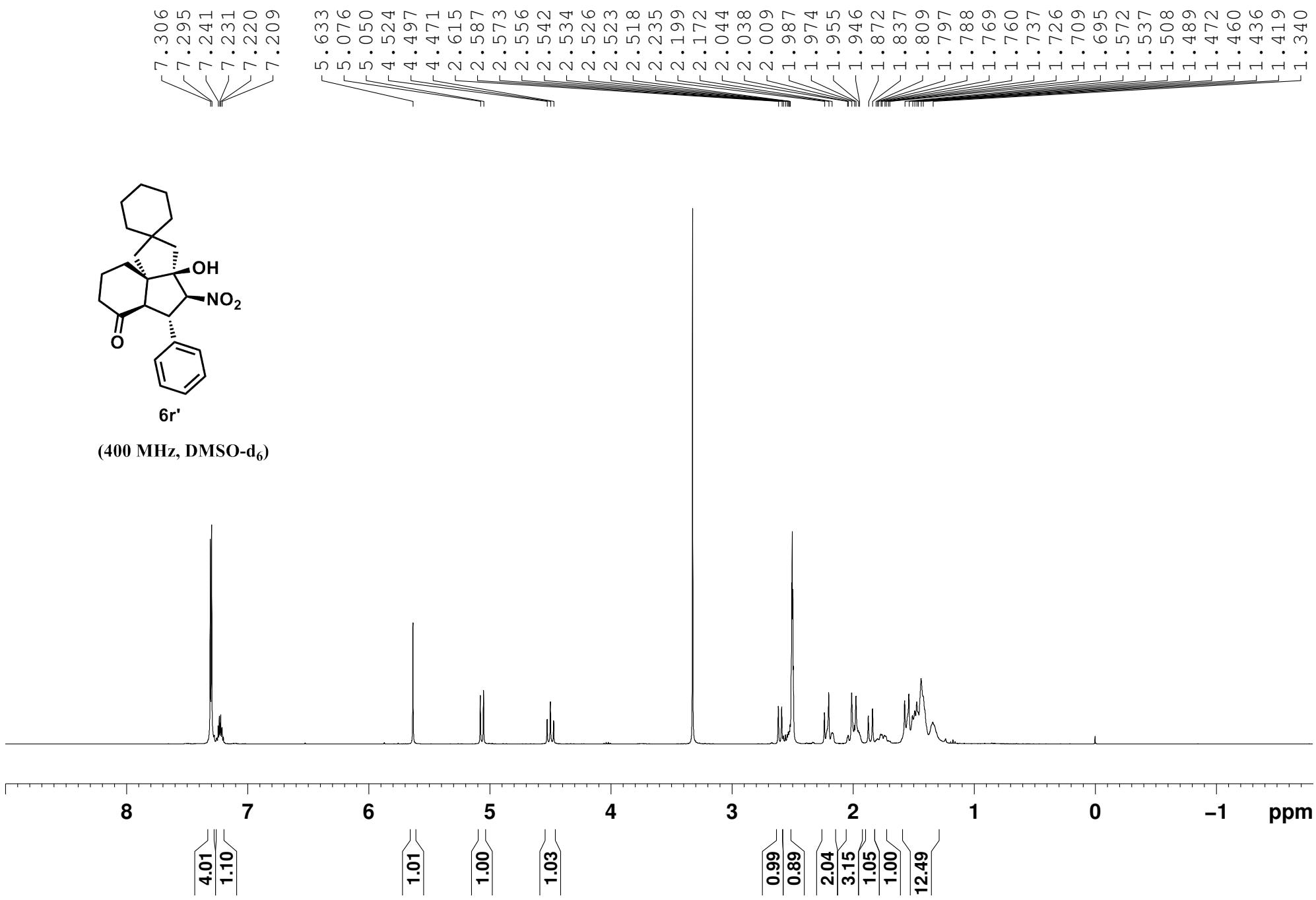


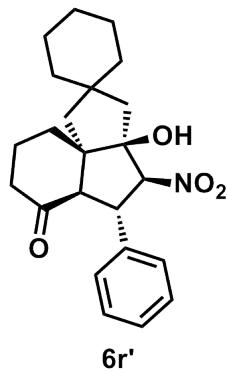
(100 MHz, CDCl₃)



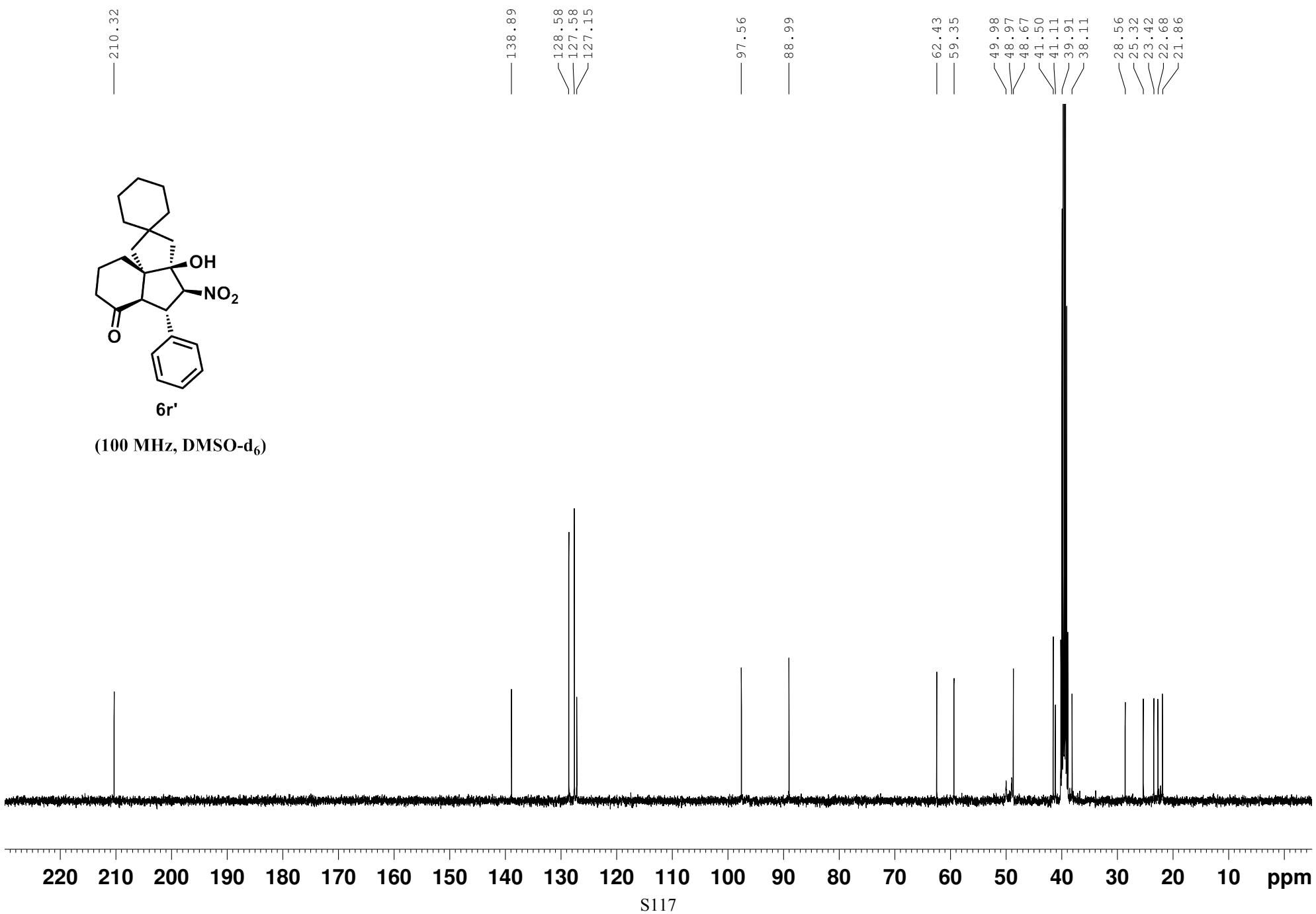


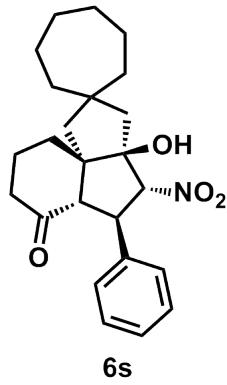
(400 MHz, DMSO-d₆)



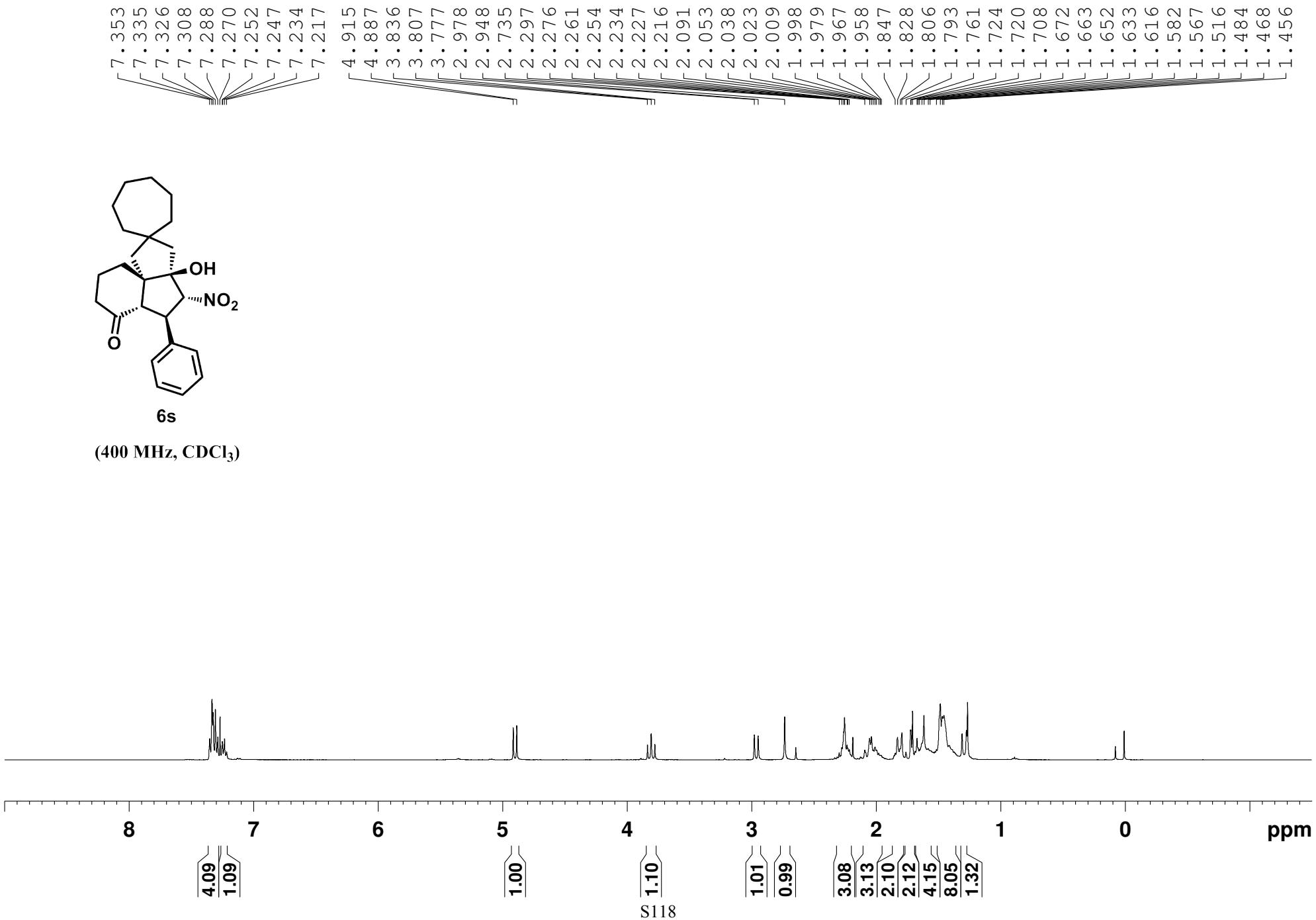


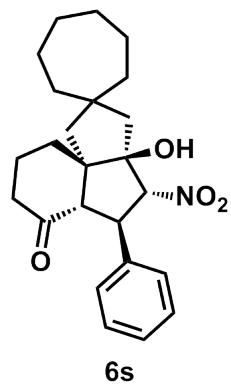
(100 MHz, DMSO-d₆)



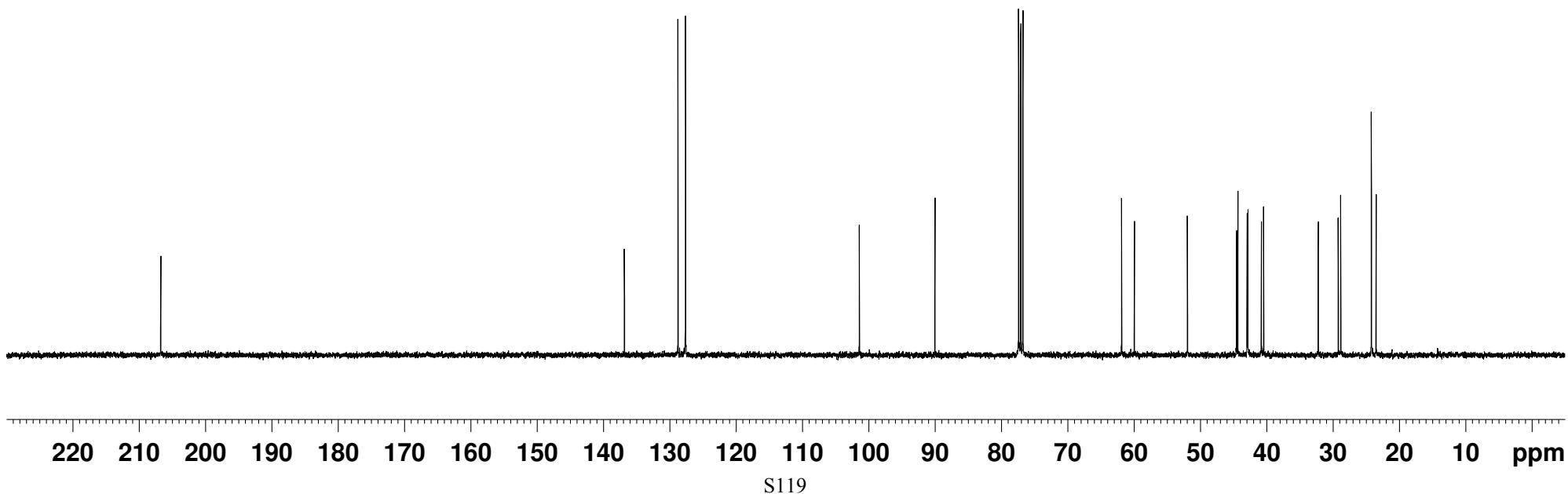


(400 MHz, CDCl₃)

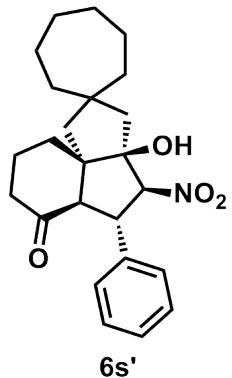




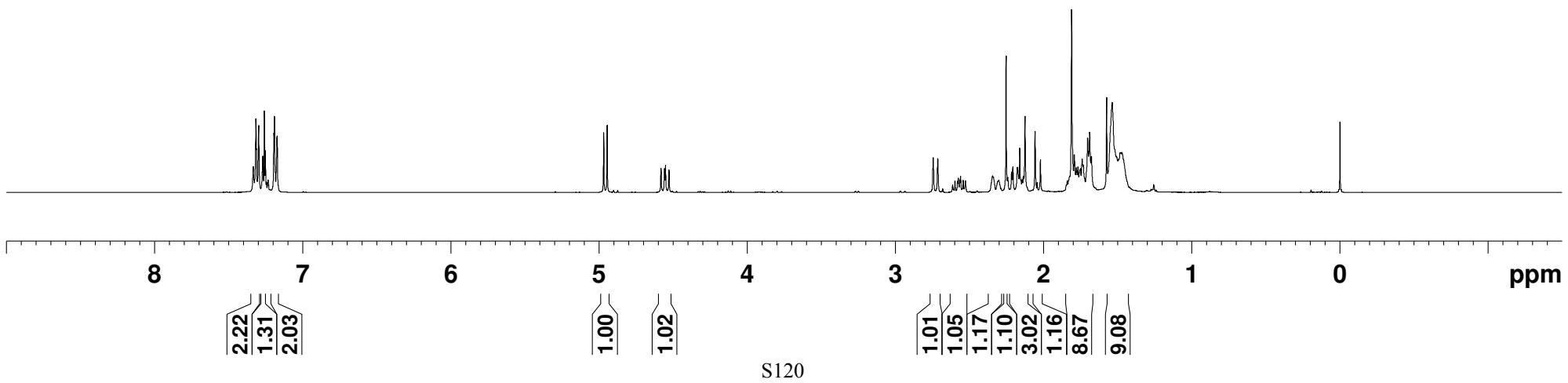
(100 MHz, CDCl_3)

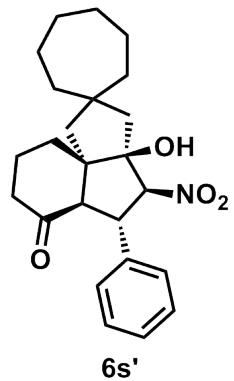


[7.]	335
[7.]	318
[7.]	314
[7.]	299
[7.]	274
[7.]	271
[7.]	268
[7.]	260
[7.]	253
[7.]	253
[7.]	196
[7.]	192
[7.]	175
[4.]	970
[4.]	946
[4.]	583
[4.]	560
[4.]	553
[2.]	715
[2.]	614
[2.]	529
[2.]	746
[2.]	599
[2.]	576
[2.]	561
[2.]	566
[2.]	581
[2.]	543
[2.]	208
[2.]	346
[2.]	303
[2.]	254
[2.]	216
[2.]	178
[2.]	162
[2.]	145
[2.]	137
[2.]	126
[2.]	058
[2.]	022
[1.]	840
[1.]	825
[1.]	812
[1.]	794
[1.]	780
[1.]	769
[1.]	756
[1.]	752
[1.]	741
[1.]	733
[1.]	704
[1.]	690
[1.]	678
[1.]	537
[1.]	508
[1.]	493
[1.]	485
[1.]	473



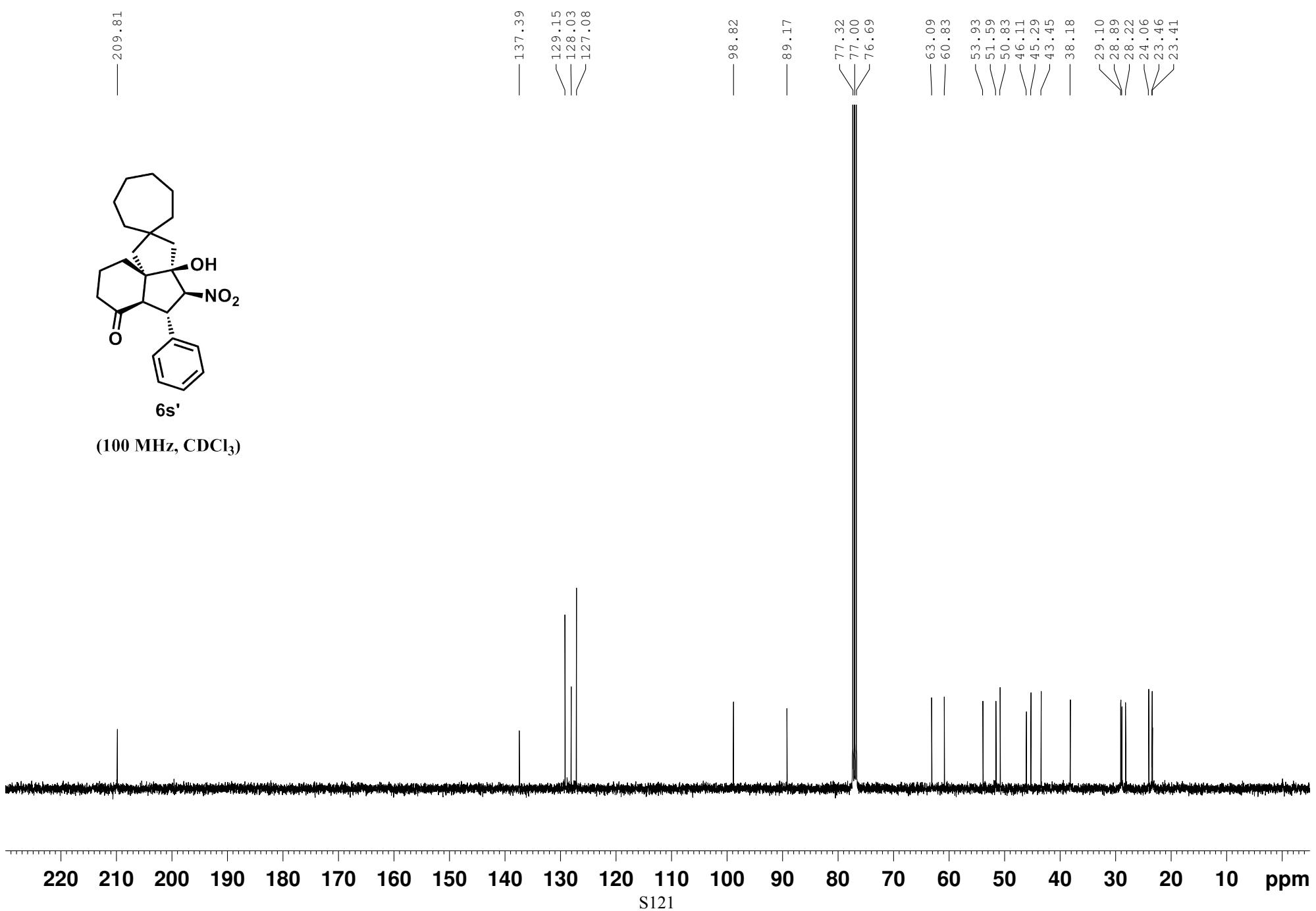
(400 MHz, CDCl₃)





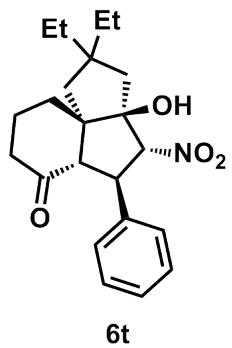
6s'

(100 MHz, CDCl₃)

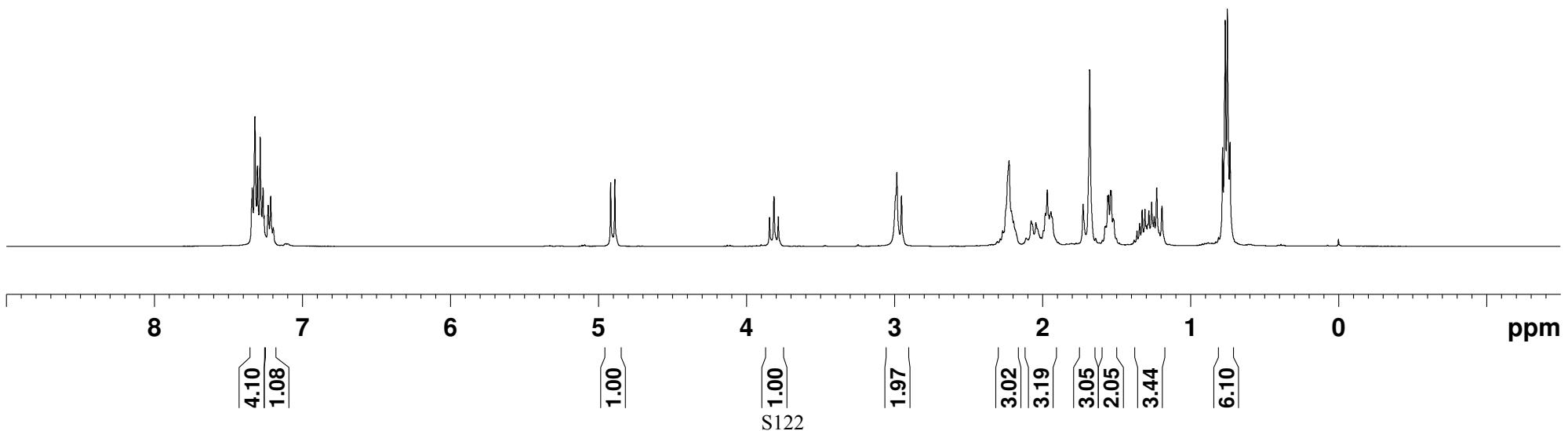


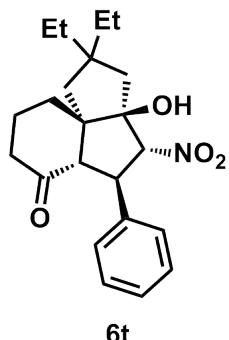
7.338
 7.321
 7.303
 7.285
 7.265
 7.259
 7.231
 7.213
 7.196

4.917
 4.888
 3.843
 3.814
 3.784
 2.983
 2.952
 2.269
 2.225
 2.209
 2.195
 2.110
 2.076
 2.045
 2.011
 1.993
 1.981
 1.968
 1.942
 1.935
 1.725
 1.681
 1.641
 1.577
 1.571
 1.540
 1.535
 1.522
 1.518
 1.361
 1.326
 1.228
 1.193
 1.281
 0.783
 0.765
 0.751
 0.733

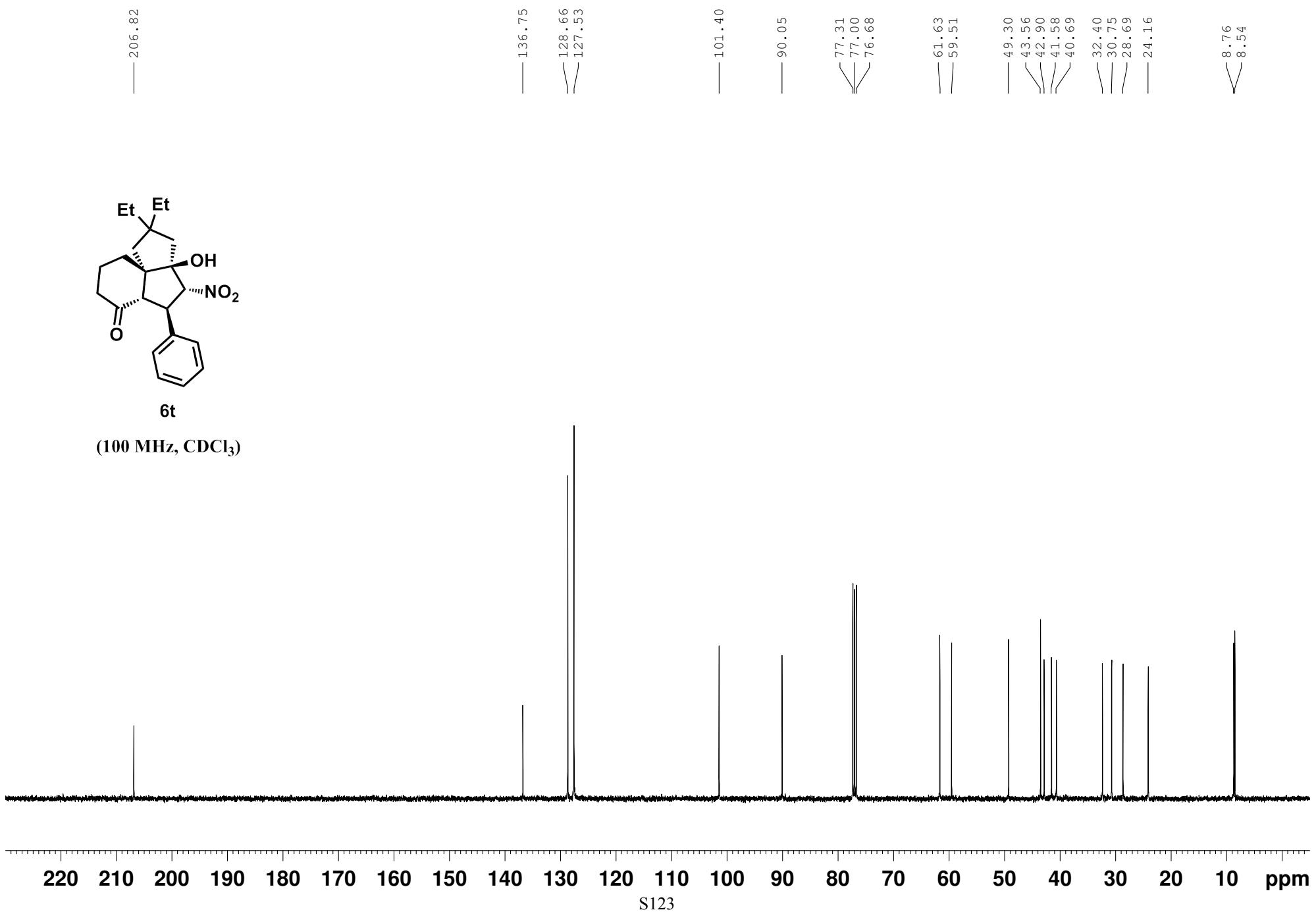


(400 MHz, CDCl₃)

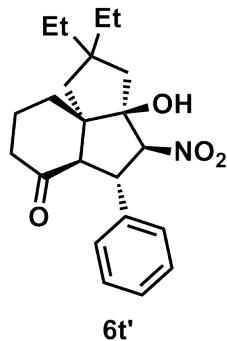




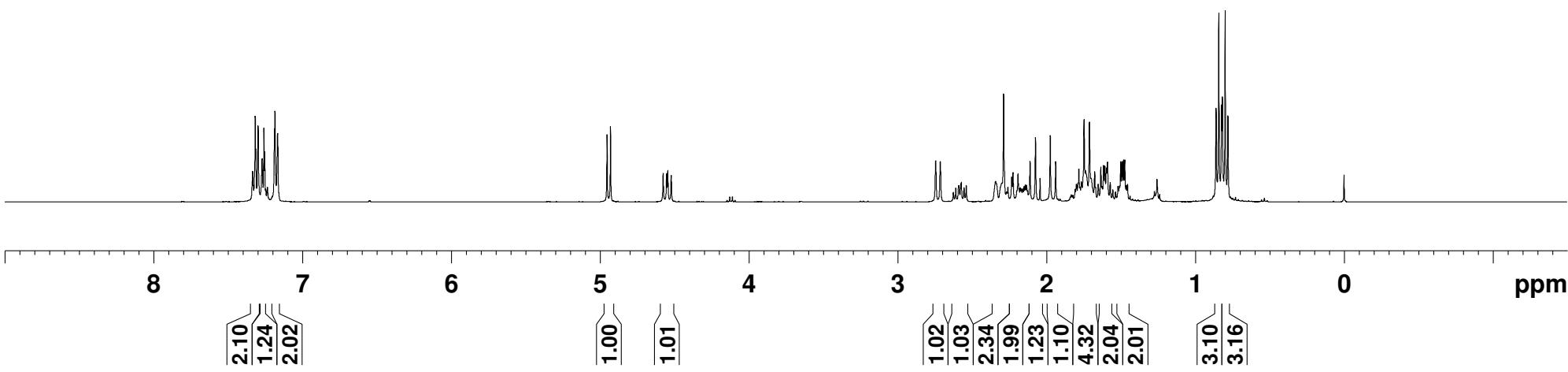
(100 MHz, CDCl₃)

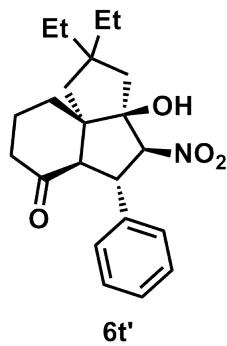


7.335
7.332
7.318
7.315
7.299
7.273
7.260
7.255
7.189
7.185
7.168
4.954
4.930
4.576
4.553
4.545
4.522
2.745
2.714
2.577
2.572
2.539
2.343
2.301
2.288
2.234
2.225
2.192
2.143
2.134
2.111
2.074
2.043
1.975
1.938
1.800
1.789
1.783
1.766
1.747
1.738
1.712
1.635
1.616
1.597
1.572
1.464
1.456
1.608
0.861
0.842
0.823
0.818
0.799
0.781



(400 MHz, CDCl₃)





(100 MHz, CDCl₃)

— 209.84

— 137.26
— 129.15
— 128.04
— 127.04

— 99.07

— 88.96

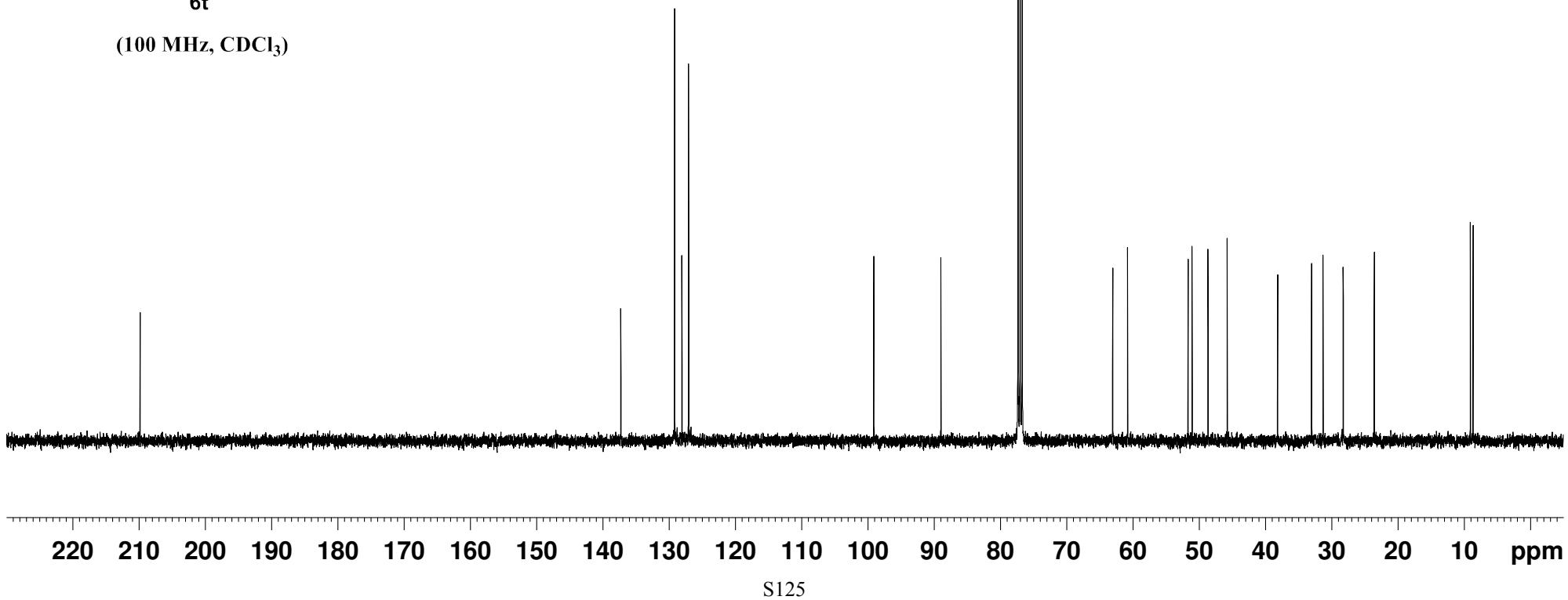
— 77.32
— 77.00
— 76.68

— 63.02
— 60.78

— 51.64
— 51.04
— 48.63
— 45.73

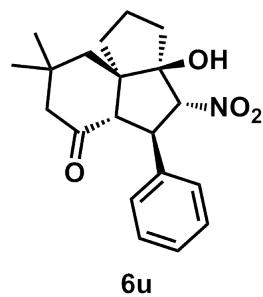
— 38.13
— 33.00
— 31.28
— 28.22
— 23.54

— 9.05
— 8.62

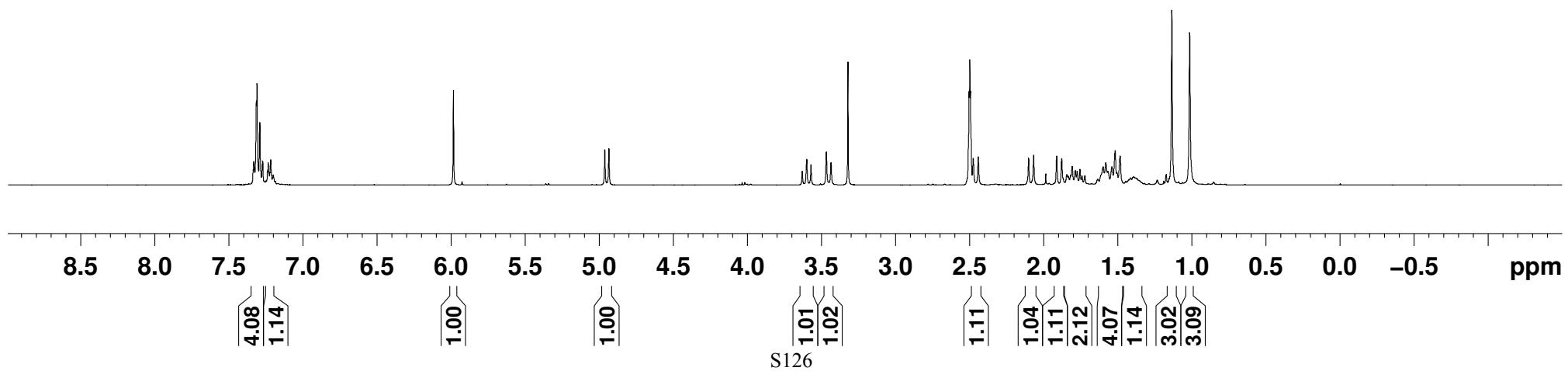


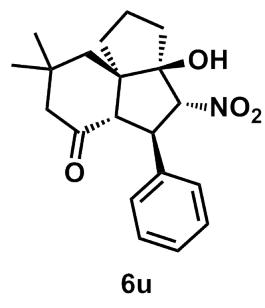
7.338
7.333
7.316
7.293
7.273
7.240
7.226
7.219
7.206
7.202
5.986

4.964
4.936
3.631
3.600
3.572
3.468
3.437
2.477
2.443
2.103
2.069
1.913
1.880
1.845
1.834
1.820
1.809
1.788
1.775
1.756
1.742
1.723
1.600
1.582
1.568
1.540
1.519
1.506
1.485
1.425
1.415
1.378
1.369
1.353
1.136
1.016

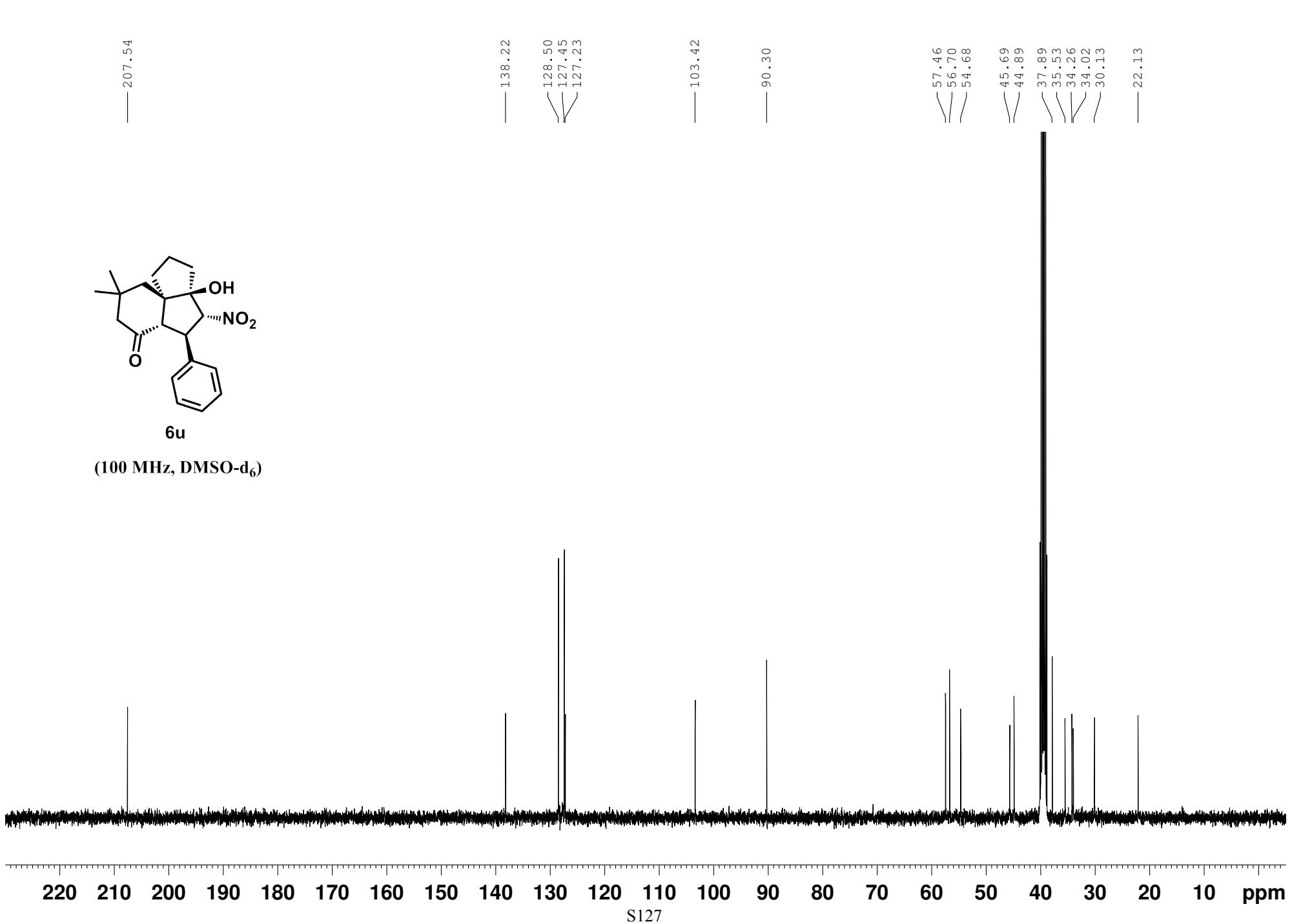


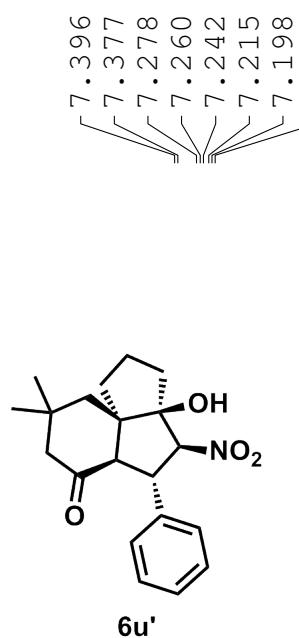
(400 MHz, DMSO-d₆)



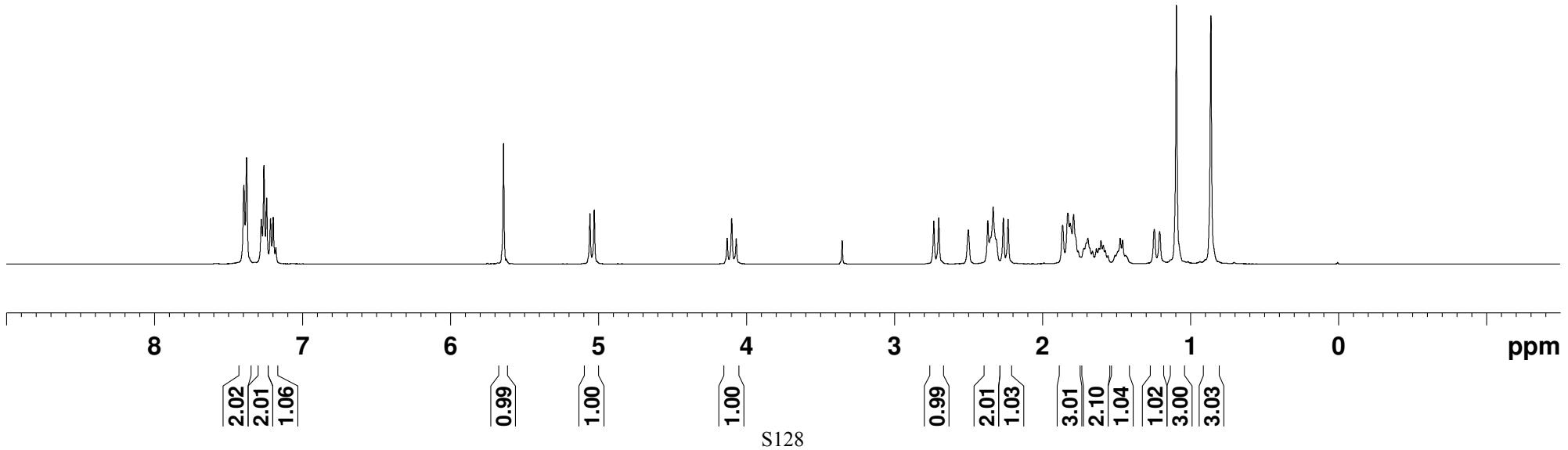


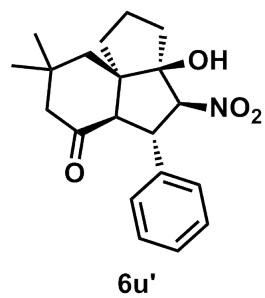
(100 MHz, DMSO-d_6)



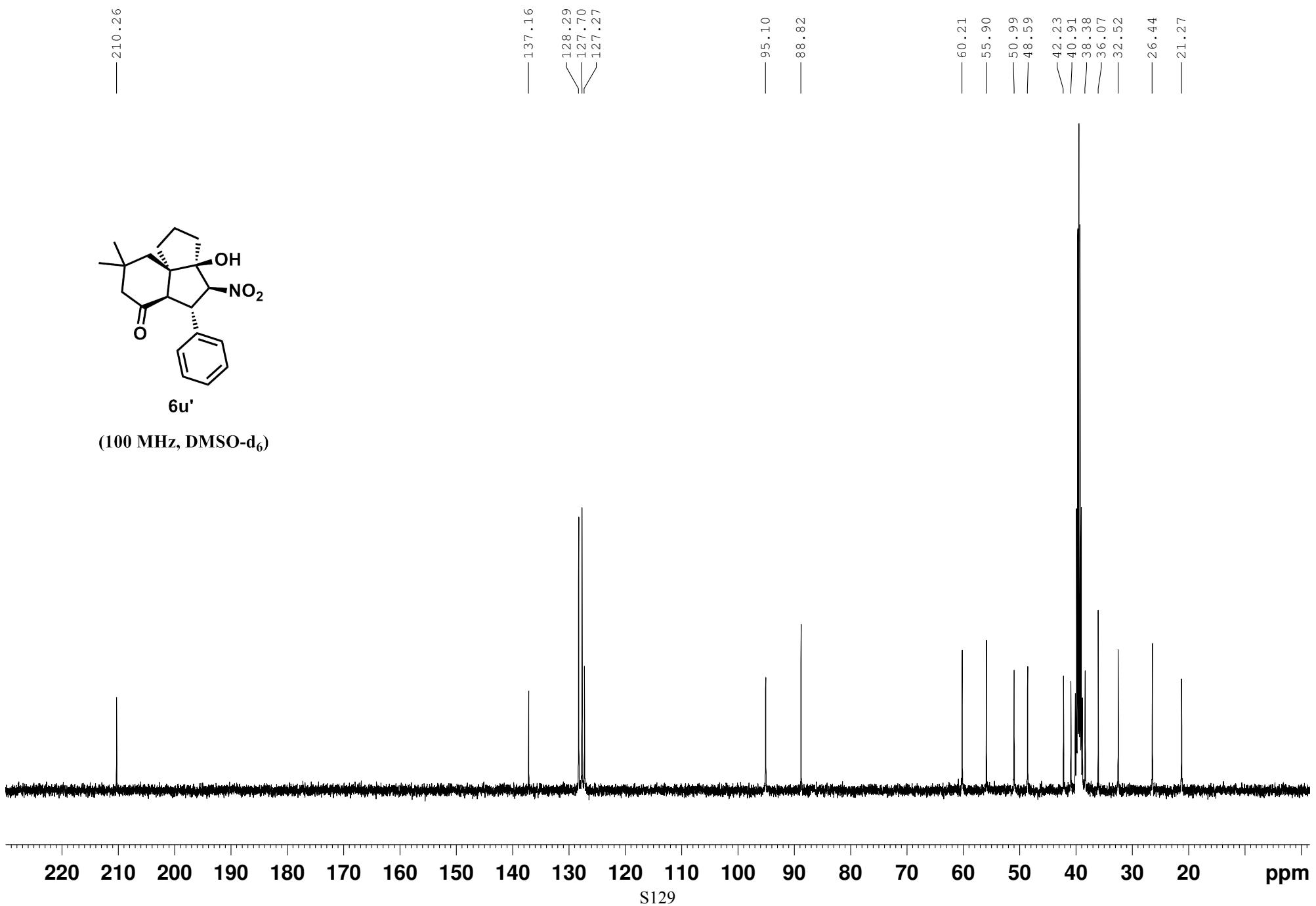


(400 MHz, DMSO-d₆)

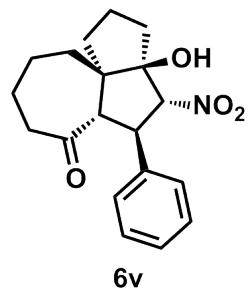




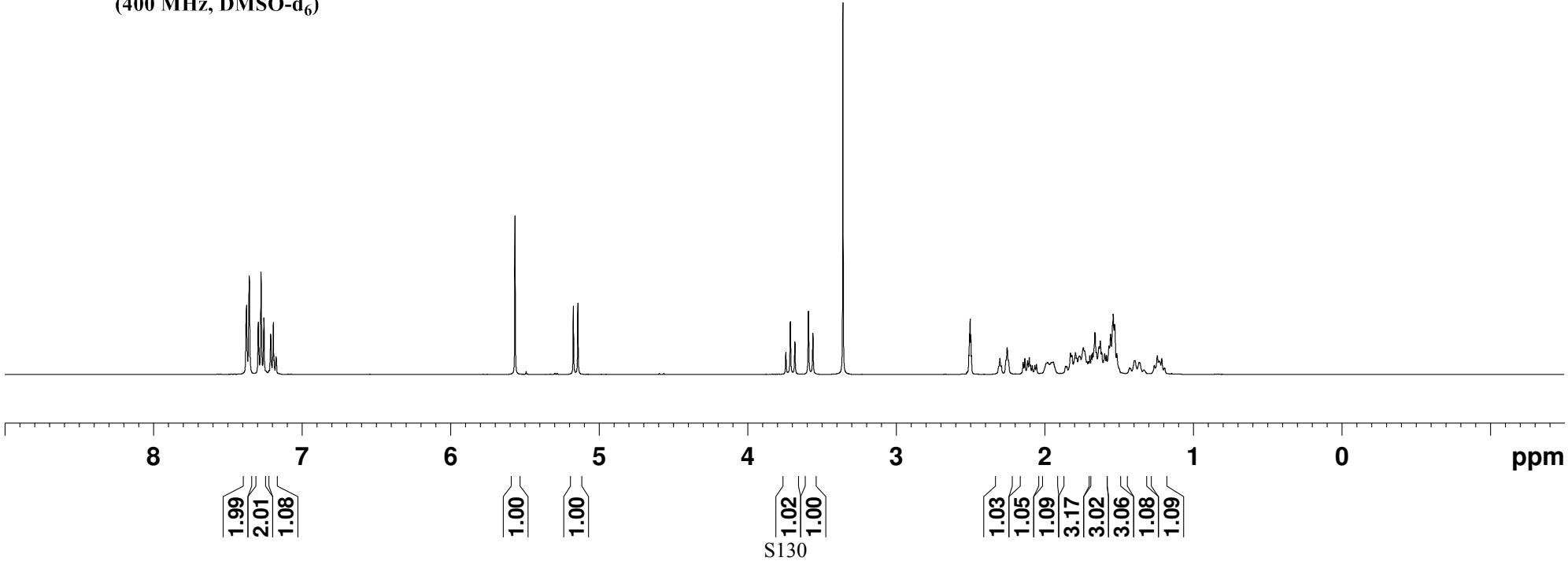
(100 MHz, DMSO-d₆)

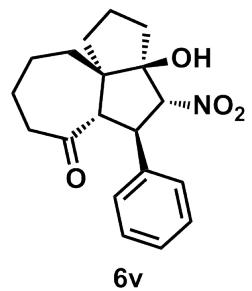


7.375
 7.371
 7.353
 7.292
 7.287
 7.274
 7.254
 7.208
 7.206
 7.196
 7.190
 7.175
 7.172
 7.169
 5.564
 5.171
 5.140
 3.740
 3.710
 3.680
 3.589
 3.559
 2.300
 2.258
 2.251
 2.143
 2.132
 2.114
 2.102
 2.053
 1.986
 1.979
 1.953
 1.942
 1.824
 1.791
 1.764
 1.738
 1.714
 1.704
 1.694
 1.684
 1.594
 1.583
 1.660
 1.624
 1.537
 1.527
 1.513
 1.394
 1.390
 1.362
 1.240
 1.228
 1.210

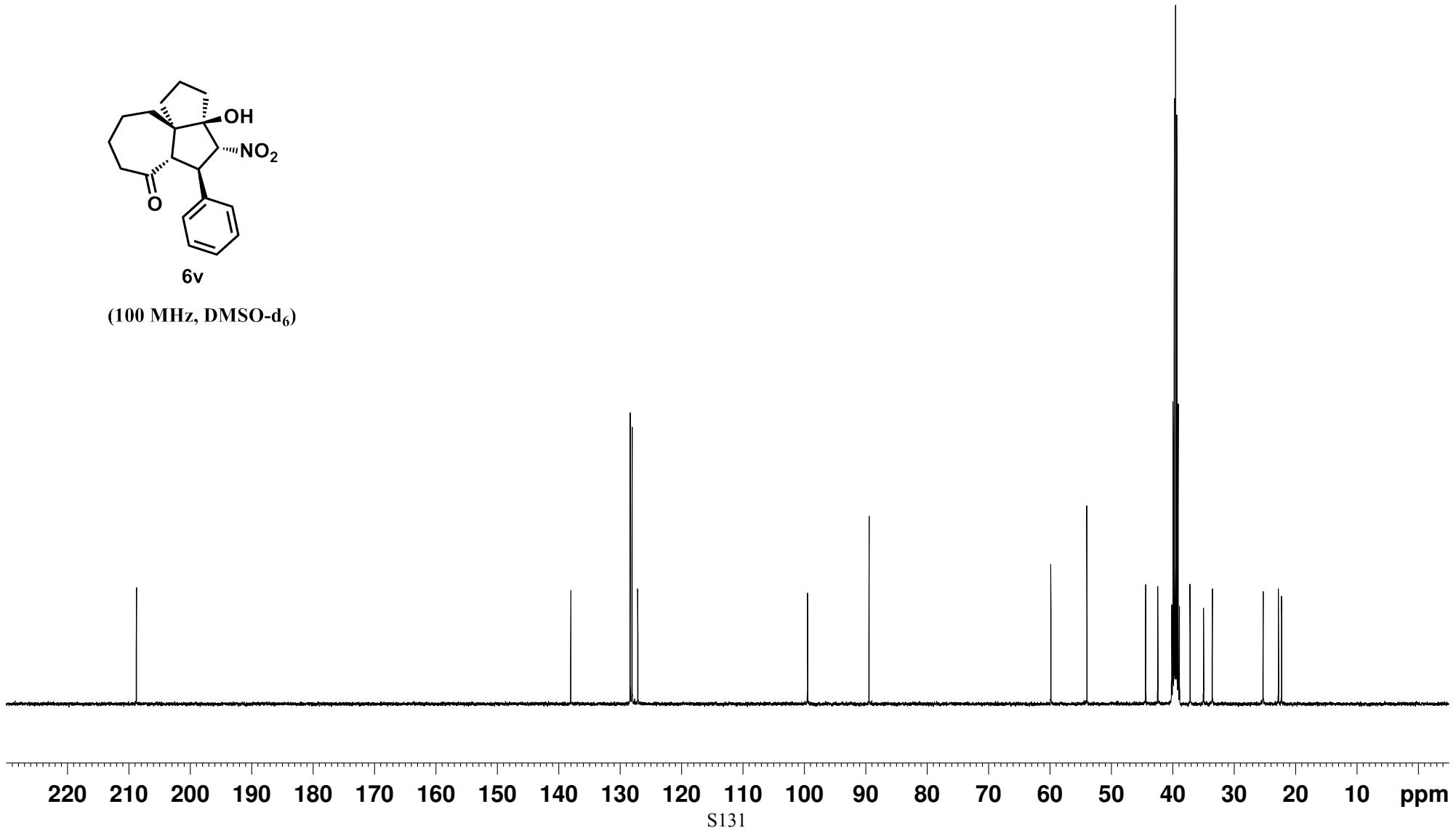


(400 MHz, DMSO-d₆)

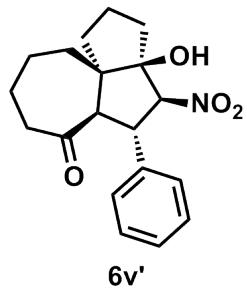




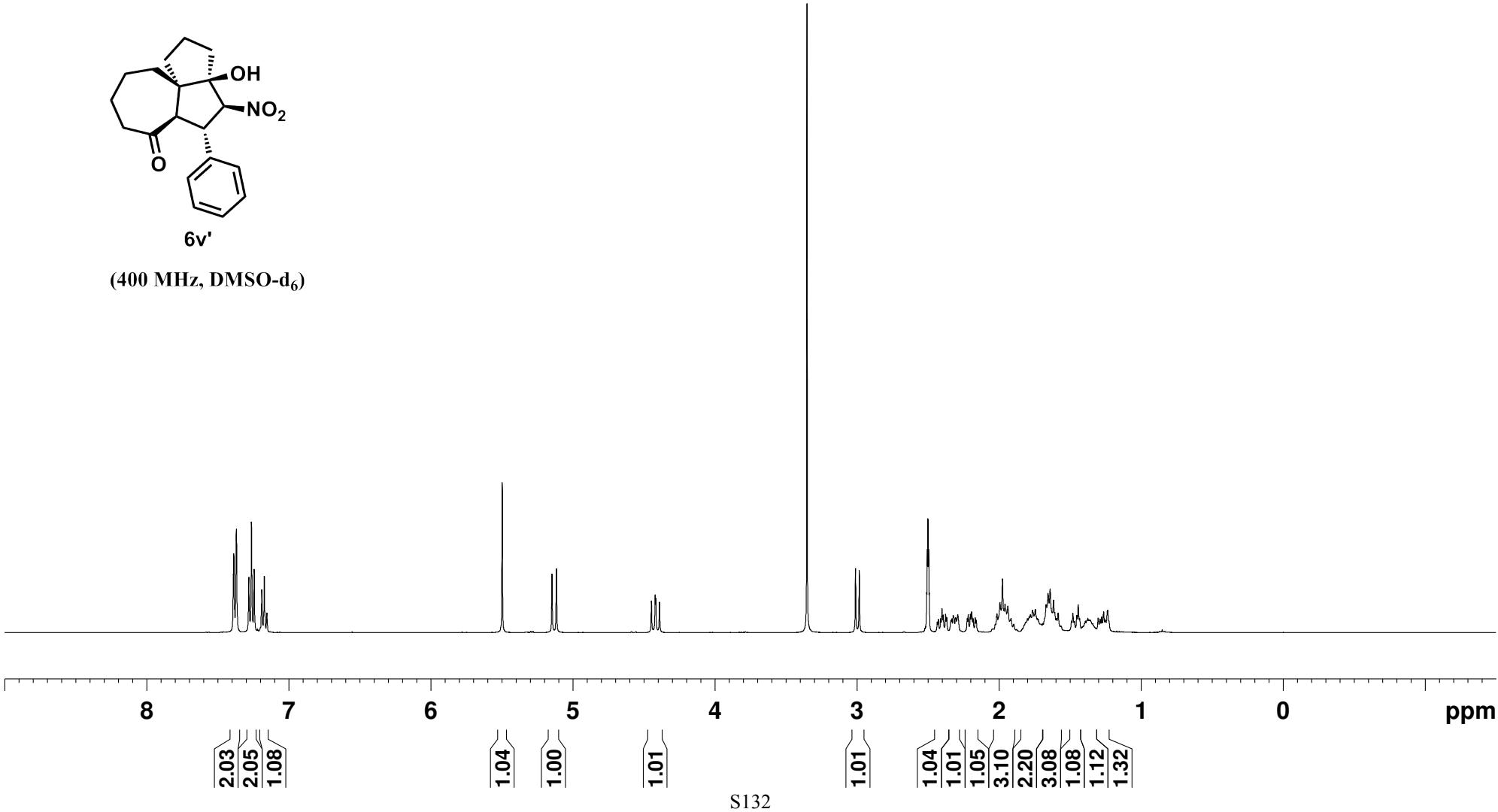
(100 MHz, DMSO-d₆)

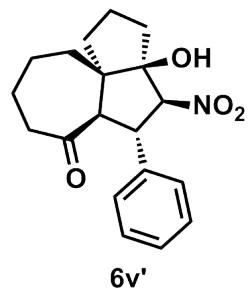


7.391
7.388
7.370
7.281
7.263
7.244
7.191
7.188
7.177
7.172
7.167
7.154
5.498
5.147
5.116
4.447
4.421
4.416
4.390
3.010
2.984
2.393
2.410
2.401
2.376
2.369
2.323
2.318
2.306
2.290
2.216
2.202
2.193
2.182
2.167
2.015
1.993
1.975
1.957
1.938
1.915
1.778
1.764
1.640
1.616
1.583
1.480
1.452
1.442
1.432
1.374
1.302
1.276
1.263
1.235



(400 MHz, DMSO-d₆)





(100 MHz, DMSO-d₆)

