

Supporting Information
For
**Total Synthesis of (+)-Heabethoxazole via an Iron-Mediated
Pauson-Khand [2+2+1] Carbocyclization**

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<u>Table of Contents</u>	<u>Page</u>
General information.....	S-2
Experimental procedures and characterization data.....	S-4
¹ H, ¹³ C NMR and 2D NMR spectra.....	S-48

General Information:

Unless otherwise noted, all reactions were performed in flame-dried or oven-dried glassware under argon atmosphere. Non-aqueous reagents were transferred using syringe techniques under argon atmosphere. Bulk grade hexanes, pentane, diethyl ether and ethyl acetate for chromatography were distilled prior to use. Tetrahydrofuran (THF), dimethylformamide (DMF), toluene, acetonitrile (AcCN) and dichloromethane (DCM) were obtained anhydrous by degassing with argon and then passing through activated alumina columns to remove water and oxygen.¹ Commercial reagents were used as obtained unless otherwise specified. Air-sensitive reagents were handled inside glovebox facility.

Reactions were monitored by standard thin-layer chromatography (TLC) techniques using EMD silica gel 60 F₂₅₄ pre-coated plates (0.25 mm thickness). Following the run, TLC plates were visualized under UV light and/or by appropriate stains (*p*-anisaldehyde or ceric ammonium nitrate or potassium permanganate). Flash column chromatography was performed with Silica-P Flash Silica Gel (ultra-pure 40–63 μ m) from Silicycle Chemical Division (Quebec QC, Canada).²

Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on Varian VXR 400 (400 MHz), Varian INOVA 400 (400 MHz) or Varian 500 (500 MHz) instruments. Carbon nuclear magnetic resonance (¹³C NMR) spectra were measured using Varian VXR 400 (101 MHz), Varian INOVA 400 (101 MHz) or Varian 500 (125 MHz) instruments. NMR coupling constants and signal patterns are reported as *J* values in Hz and δ values in parts per million (ppm). ¹H and ¹³C NMR spectra are internally referenced to residual protio solvent signals (CDCl₃ referenced to δ 7.26 and 77.23 ppm respectively, d₈-CH₂Cl₂ referenced to 5.32 ppm and 53.84 ppm respectively, Note: ileabethoxazole **1** is referenced relative to tetramethylsilane using CDCl₃ as in internal standard set to δ 7.26 ppm for ¹H and δ 77.00 ppm for ¹³C NMR spectra). The following abbreviations were used to indicate the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High resolution mass measurements (HRMS) were obtained on Thermo Electron Corporation MAT 95XP (EI/CI) or Agilent 1200 HPLC-6130 MSD (ESI). Optical rotation data were obtained on Perkin Elmer Model

343 polarimeter and are reported in terms of degree of rotation of plane-polarized light. IR spectra were recorded on a XYZ spectrometer and are reported in terms of frequency of absorption (cm^{-1}).

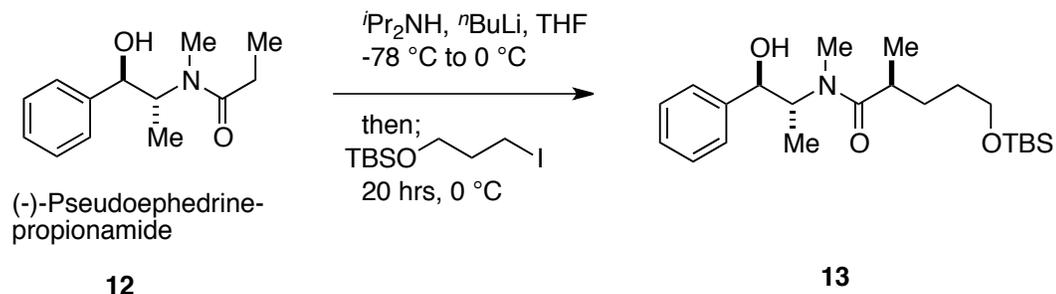
Freshly Prepared Solutions of LDA in THF.

Solutions of lithium diisopropylamide (LDA) in anhydrous THF are freshly prepared according to the following description. A round-bottom flask, equipped with a stir bar, is flame dried under vacuum and placed under an argon atmosphere. After cooling to 0 °C, freshly distilled diisopropylamine (1.1 equiv.) is introduced via syringe followed by the dropwise addition of titrated $n\text{BuLi}$ in hexanes (1.0 equiv.) with continuous stirring. A thick white precipitate forms, and stirring is continued for an additional 30–60 minutes. The excess diisopropylamine and hexanes are removed *in vacuo* at rt to yield a white solid, and a volume of precooled, anhydrous THF is introduced by cannulation into the flask which is cooled by a -78 °C bath. The assumption of 100% conversion to LDA from the solution of titrated $n\text{BuLi}$, and the use of a known volume of THF establishes the molarity of the stock solution. Small aliquots of this stock solution are utilized in small-scale reactions based on the calculated molarity.

¹Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

²Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

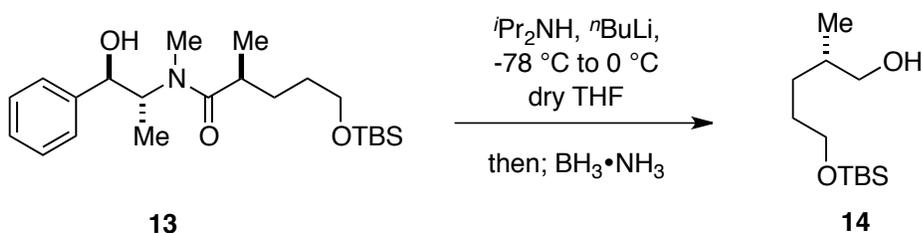
Experimental Procedures:



(*S*)-5-((*tert*-butyldimethylsilyl)oxy)-*N*-((1*R*,2*R*)-1-hydroxy-1-phenylpropan-2-yl)-*N*,2-

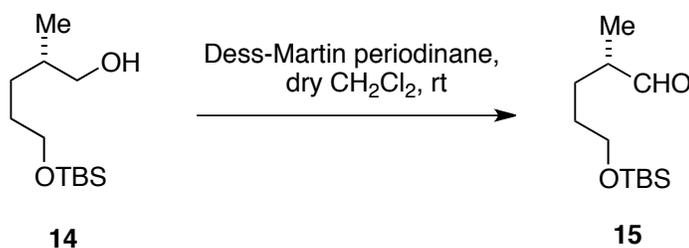
dimethylpentanamide (13): To a stirred solution of vacuum-dried LiCl (11.11 g, 262.20 mmol) in dry THF (50 mL) was added distilled $i\text{Pr}_2\text{NH}$ (14.12 mL, 99.93 mmol). The solution was cooled to $-78\text{ }^\circ\text{C}$ and $t\text{BuLi}$ (39.01 mL, 2.5M in hexanes, 97.53 mmol) was added dropwise. After stirring for 5 min at $-78\text{ }^\circ\text{C}$, solution was then stirred at $0\text{ }^\circ\text{C}$ briefly (~ 10 min) and cooled to $-78\text{ }^\circ\text{C}$. To this solution was then added pre-cooled solution of propionamide **12** (9.82 g, 44.36 mmol) in dry THF (134 mL) dropwise over 20 min. The resulting reaction mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 hour, then 15 min at $0\text{ }^\circ\text{C}$ and 5 min at rt. The reaction mixture was then cooled to $0\text{ }^\circ\text{C}$ and a solution of iodide (12.0 g, 39.97 mmol) in dry THF (24 mL) was added dropwise over 10 min. The reaction mixture was stirred at $0\text{ }^\circ\text{C}$ for 18 h and then quenched with half-saturated aqueous NH_4Cl solution (75 mL). Organic layer was separated and aqueous layer was extracted in EtOAc (2×75 mL). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 15% EtOAc in hexanes to 40% EtOAc in hexanes) to yield 14.7 g (94% yield, $>25:1$ dr) of the product as light yellow gel. $R_f = 0.47$ (SiO_2 , 50% EtOAc in hexanes); $[\alpha]_D^{20} -44.2^\circ$ (c 0.7, CHCl_3); IR (film) ν_{max} 3385 (br), 3063, 3029, 2930, 1614, 1471, 1255, 1101, 939 cm^{-1} ; ^1H NMR ($\text{DMSO}-d_6$, $117\text{ }^\circ\text{C}$, 500 MHz) δ 7.36 (2H, d, $J = 7.3$ Hz), 7.31 (2H, t, $J = 7.5$ Hz), 7.24 (1H, t, $J = 7.5$ Hz), 4.86 (1H, br s), 4.61 (1H, d, $J = 7.3$ Hz), 3.63–3.53 (2H, m), 2.84 (3H, s), 2.72 (1H, dd, $J = 13.0, 6.4$ Hz), 1.62 (1H, td, $J = 14.2, 7.2$ Hz), 1.47–1.40 (2H, m), 1.32 (1H, td, $J = 14.0, 7.1$ Hz), 1.00 (3H, d, $J = 6.8$ Hz), 0.96 (3H, d, $J = 6.7$ Hz), 0.91 (9H,

s), 0.05 (6H, s); ^{13}C NMR (DMSO- d_6 , 101 MHz, 1:1 rotamer ratio) δ 175.7, 175.5, 143.6, 128.0, 127.8, 127.3, 126.9, 126.8, 126.7, 73.85, 73.78, 62.8, 62.5, 56.8, 34.6, 34.4, 30.1, 30.0, 29.9, 29.8, 27.1, 25.9, 25.8, 18.1, 18.0, 17.9, 17.3, 15.6, 14.1, -5.33, -5.29; HRMS m/e calcd. for $\text{C}_{22}\text{H}_{39}\text{NO}_3\text{SiNa}$ (M+Na) $^+$ 416.2597 found 416.2582.

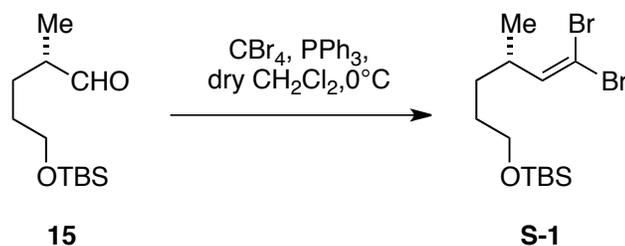


(S)-5-((tert-butyldimethylsilyloxy)-2-methylpentan-1-ol (14): To a stirred solution of $i\text{Pr}_2\text{NH}$ (21.90 mL, 157.13 mmol) in dry THF (157 mL) was added $^n\text{BuLi}$ (58.36 mL, 2.5M in hexanes, 145.90 mmol) dropwise at $-78\text{ }^\circ\text{C}$. After stirring for 10 min at $-78\text{ }^\circ\text{C}$, solution was stirred at $0\text{ }^\circ\text{C}$ for 10 min. The mixture was then treated with $\text{BH}_3\cdot\text{NH}_3$ (4.62 g, 149.64 mmol) by careful addition in one portion. The resulting solution was stirred at $0\text{ }^\circ\text{C}$ for additional 20 min and then 15 min at rt. The reaction mixture was then cooled to $0\text{ }^\circ\text{C}$ and a solution of **13** (14.74 g, 37.41 mmol) in dry THF (125 mL) was added dropwise over 15 min. The solution was then warmed to rt by removing ice-bath and stirred for 2 hr. The reaction mixture was then cooled to $0\text{ }^\circ\text{C}$, carefully quenched with saturated aqueous NH_4Cl solution (75 mL) and stirred for additional 10 min at $0\text{ }^\circ\text{C}$. The crude mixture was then extracted in diethyl ether ($3 \times 75\text{ mL}$). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 15% ethyl acetate in hexanes to 40% ethyl acetate in hexanes) to yield 7.5 g (87% yield, 95% ee) of the product as colorless oil. $R_f = 0.64$ (SiO_2 , 50% ethyl acetate in hexanes); $[\alpha]_D^{20} -9.6^\circ$ (c 1.2, CHCl_3); IR (film) ν_{max} 3354, 2930, 1472, 1255, 1098, 836 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 3.56 (2H, t, $J = 7.2\text{ Hz}$), 3.39 (2H, ddd, $J = 32.7, 10.5, 6.2\text{ Hz}$), 2.44 (1H, br s), 1.63–1.32 (4H, m), 1.18–1.05 (1H, m), 0.87 (3H, d, $J = 6.4\text{ Hz}$), 0.85 (9H, s), 0.00 (6H, s); ^{13}C NMR (CDCl_3 ,

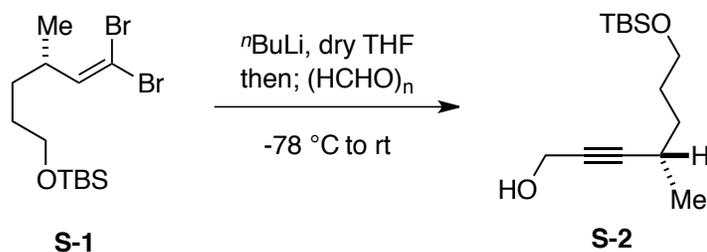
101 MHz) δ 68.1, 63.7, 35.6, 30.3, 29.4, 26.1, 18.5, 16.8, -5.2; HRMS m/e calcd. for $C_{12}H_{29}O_2Si$ $(M+H)^+$ 233.1931 found 233.1932.



(S)-5-((tert-butyldimethylsilyl)oxy)-2-methylpentanal (15): To a stirred solution of alcohol **14** (3.5 g, 15.15 mmol) in dry CH_2Cl_2 (56 mL) was added DMP (9.0 g, 21.21 mmol) followed by $NaHCO_3$ (2.80 g, 33.33 mmol) at rt. After stirring for 6 h at rt, reaction was quenched with saturated $NaHCO_3$ solution (50 mL) and $Na_2S_2O_3$ solution (50 mL) carefully. The crude mixture was then extracted in diethyl ether (3 \times 25 mL). The combined organic layers were dried over $MgSO_4$ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 5% ethyl acetate in hexanes to 20% ethyl acetate in hexanes) to yield 3.10 g (87% yield, 95% ee) of the product as colorless oil. R_f = 0.71 (SiO_2 , 25% ethyl acetate in hexanes); $[\alpha]_D^{20} +11.8^\circ$ (c 0.7, $CHCl_3$); IR (film) ν_{max} 2931, 2854, 1726, 1426, 1108 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 9.60 (1H, d, J = 1.8 Hz), 3.60 (2H, t, J = 6.4 Hz), 2.34 (1H, sextet of doublets, J = 6.9, 1.8 Hz), 1.75 (1H, ddd, J = 19.6, 12.0, 6.6 Hz), 1.59–1.47 (2H, m), 1.45–1.35 (1H, m), 1.08 (3H, d, J = 7.2 Hz), 0.87 (9H, s), 0.02 (6H, s); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 205.2, 62.9, 46.2, 30.2, 27.0, 26.1, 18.5, 13.5, -5.2; HRMS m/e calcd. for $C_{12}H_{27}O_2Si$ $(M+H)^+$ 231.1775 found 231.1769.

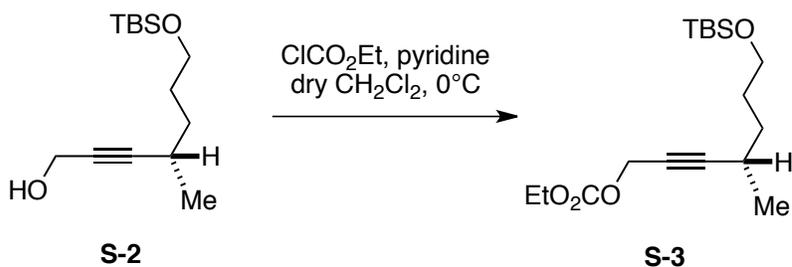


(S)-tert-butyl((6,6-dibromo-4-methylhex-5-en-1-yl)oxy)dimethylsilane (S-1): To a stirred solution of aldehyde **15** (3.5 g, 15.22 mmol) in dry CH₂Cl₂ (76 mL) was added CBr₄ (7.57 g, 22.83 mmol) followed by PPh₃ (11.98 g, 45.66 mmol) at 0 °C and then stirred at 0 °C. After stirring for 3 hr, the reaction mixture was diluted with hexanes (100 mL). After stirring for additional 10 min, the insoluble solid was filtered off and subsequently washed with hexanes (50 mL). The combined organic layers were evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 100% hexanes to 15% diethyl ether in hexanes) to yield 4.50 g (77% yield) of the product as yellow oil. $R_f = 0.67$ (SiO₂, 5% diethyl ether in hexanes); $[\alpha]_D^{20} +0.7^\circ$ (c 2.4, CHCl₃); IR (film) ν_{\max} 2929, 2856, 1471, 1255, 1102, 835, 776 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 6.17 (1H, d, $J = 8.8$ Hz), 3.60 (2H, t, $J = 6.4$ Hz), 2.52–2.41 (1H, m), 1.55–1.47 (2H, m), 1.46–1.32 (2H, m), 1.01 (3H, d, $J = 6.8$ Hz), 0.94 (9H, s), 0.05 (6H, s); ¹³C NMR (CDCl₃, 101 MHz) δ 144.4, 87.7, 63.1, 38.3, 32.5, 30.6, 26.2, 19.5, 18.6, -5.1; HRMS m/e calcd. for C₁₃H₂₇OBr₂Si (M+H)⁺ 387.0172 found 387.0160.



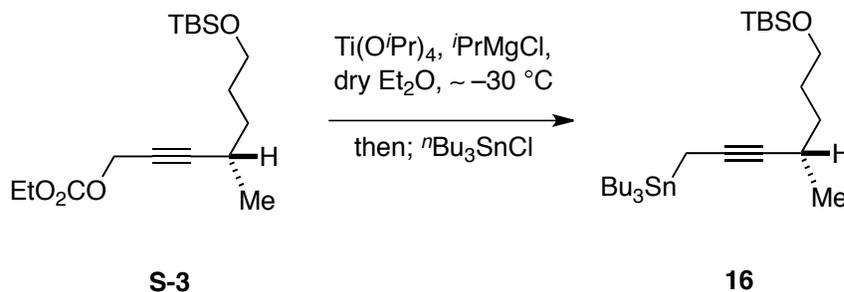
(S)-7-((tert-butyldimethylsilyl)oxy)-4-methylhept-2-yn-1-ol (S-2): To a stirred solution of **S-1** (3.17 g, 8.21 mmol) in dry THF (41 mL) was added ⁿBuLi (9.85 mL, 24.64 mmol) at -78 °C and stirred for 2 hours at -78 °C. Paraformaldehyde (370.0 mg, 12.32 mmol) was then added to the above solution

at $-78\text{ }^{\circ}\text{C}$ and reaction mixture was then allowed to slowly warm to rt. After stirring for 12 hr, reaction was quenched with saturated aqueous NH_4Cl solution (30 mL). The crude mixture was then extracted in diethyl ether ($3 \times 25\text{ mL}$). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 5% diethyl ether in hexanes to 20% diethyl ether in hexanes) to yield 1.90 g (90% yield) of the product as colorless oil. $R_f = 0.55$ (SiO_2 , 30% diethyl ether in hexanes); $[\alpha]_D^{20} +11.9^{\circ}$ (c 1.33, CHCl_3); IR (film) ν_{max} 3356 (br), 2929, 1472, 1255, 1102 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 4.24 (2H, d, $J = 1.5\text{ Hz}$), 3.62 (2H, t, $J = 6.3\text{ Hz}$), 2.50–2.43 (1H, m), 1.73–1.65 (2H, m), 1.63–1.55 (1H, m), 1.52–1.39 (2H, m), 1.16 (3H, d, $J = 7.0\text{ Hz}$), 0.89 (9H, s), 0.04 (6H, s); ^{13}C NMR (CDCl_3 , 125 MHz) δ 90.0, 78.9, 63.2, 51.6, 33.3, 30.8, 26.2, 25.9, 21.2, 18.6, -5.1 ; HRMS m/e calcd. for $\text{C}_{14}\text{H}_{29}\text{O}_2\text{Si}$ ($\text{M}+\text{H}$) $^+$ 257.1931 found 257.1936.



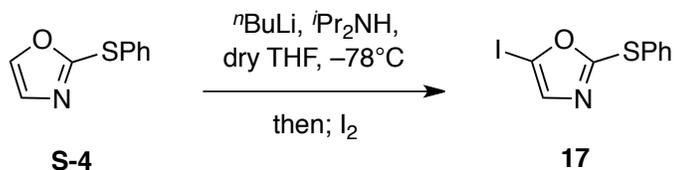
(S)-7-((tert-butyldimethylsilyloxy)-4-methylhept-2-yn-1-yl) ethyl carbonate (S-3): To a stirred solution of **S-2** (4.42 g, 17.27 mmol) in dry CH_2Cl_2 (50 mL) was added pyridine (3.49 mL, 43.18 mmol) dropwise at $0\text{ }^{\circ}\text{C}$. Ethyl chloroformate (2.95 mL, 31.09 mmol) was then added dropwise at $0\text{ }^{\circ}\text{C}$. After stirring for 2 h at $0\text{ }^{\circ}\text{C}$, reaction was quenched with saturated aqueous NH_4Cl solution (40 mL). The crude mixture was then extracted in dichloromethane ($5 \times 50\text{ mL}$). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 5% diethyl ether in hexanes to 30% diethyl ether in hexanes) to yield 5.41 g (95% yield) of the product as pale yellow oil. $R_f = 0.61$ (SiO_2 , 10% ethyl acetate in hexanes); $[\alpha]_D^{20} +10.2^{\circ}$ (c 1.73, CHCl_3); IR (film) ν_{max} 2931, 2858, 1752, 1472, 1256,

1100, 776 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 4.72 (2H, d, $J = 2.0$ Hz), 4.21 (2H, q, $J = 7.0$ Hz), 3.61 (2H, t, $J = 6.5$ Hz), 2.56–2.40 (1H, m), 1.69–1.64 (1H, m), 1.61–1.55 (1H, m), 1.53–1.42 (2H, m), 1.31 (3H, t, $J = 7.0$ Hz), 1.16 (3H, d, $J = 6.5$ Hz), 0.89 (9H, s), 0.04 (6H, s); ^{13}C NMR (CDCl_3 , 125 MHz) δ 154.9, 92.7, 73.9, 64.5, 63.1, 56.3, 33.1, 30.7, 26.2, 26.0, 21.0, 18.6, 14.5, –5.1; HRMS m/e calcd. for $\text{C}_{13}\text{H}_{23}\text{O}_4\text{Si}$ ($\text{M}-\text{C}_4\text{H}_9$) $^+$ 271.1360 found 271.1371.

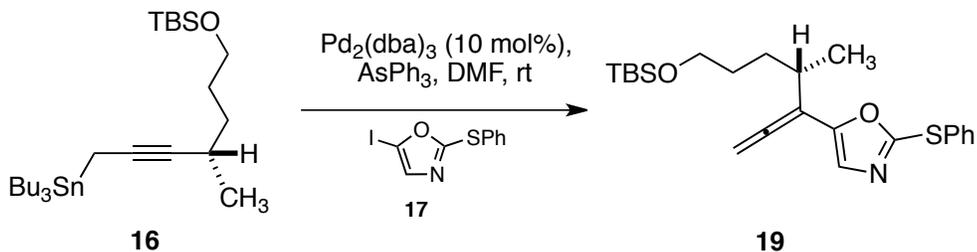


(S)-tert-butyl dimethyl((4-methyl-7-(tributylstannyl)hept-5-yn-1-yl)oxy)silane (16): To a stirred solution of **S-3** (3.10 g, 9.44 mmol) in dry diethyl ether (63 mL) was added distilled $\text{Ti}(\text{O}^i\text{Pr})_4$ (2.85 mL, 9.63 mmol) dropwise at $-50\text{ }^\circ\text{C}$ followed immediately by the addition of $^i\text{PrMgCl}$ (14.16 mL, 28.32 mmol) dropwise at $-50\text{ }^\circ\text{C}$. The resulting yellow solution was stirred for 2 h at $-30\text{ }^\circ\text{C}$. During this period, the solution turned to yellow-brown in color. The reaction mixture was then cooled to $-78\text{ }^\circ\text{C}$ and $^t\text{Bu}_3\text{SnCl}$ (2.69 mL, 9.91 mmol) was added to the mixture dropwise. The solution was warmed to rt over 3 h and was quenched with saturated aqueous NaHCO_3 (50 mL). The insoluble solid was filtered off and filtrate was extracted with diethyl ether (5×50 mL). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (100% hexanes containing 3% Et_3N ; Note: Prior to chromatography, silica gel was neutralized using hexanes containing 5% Et_3N) to yield 4.50 g (90% yield) as colorless oil. $R_f = 0.19$ (SiO_2 , 100% hexanes); $[\alpha]_D^{20} +8.6^\circ$ (c 3.15, CHCl_3); IR (film) ν_{max} 2956, 2927, 2856, 1463, 1255, 1101, 836 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 3.61 (2H, td, $J = 6.4, 1.7$ Hz), 2.42–2.33 (1H, m), 1.75–1.62 (1H, m), 1.62–1.48 (9H, m), 1.46–1.40 (2H, m), 1.38–1.23 (6H, m), 1.11 (3H, d, $J = 6.9$ Hz), 0.95 (6H, t, $J = 7.5$ Hz), 0.91–0.87 (18H, m), 0.04 (6H, s); ^{13}C NMR (CDCl_3 , 125 MHz) δ

82.6, 80.5, 63.4, 34.2, 31.1, 29.2, 27.5, 26.3, 26.2, 22.1, 18.6, 13.9, 9.9, -4.1, -5.1; HRMS *m/e* calcd. for C₂₂H₄₅OSiSn (M-C₄H₉)⁺ 473.2256 found 473.2249.

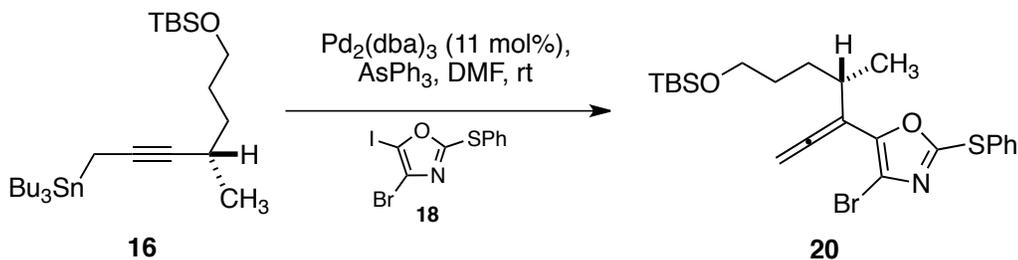


5-iodo-2-(phenylthio)oxazole (17): To a stirred solution **S-4** (500 mg, 2.89 mmol) in dry THF (14.5 mL) was added ⁿBuLi (1.27 mL, 2.5M in hexane, 3.18 mmol) at -78 °C and stirred for 40 min at -40 °C. A solution of I₂ (808 mg, 3.18 mmol) in dry THF (5.3 mL) was then added dropwise at -78 °C. After stirring for 90 min at -78 °C, the reaction was quenched with saturated aqueous NH₄Cl solution (10 mL) at -78 °C. The crude mixture was extracted in diethyl ether (3 × 40 mL). The combined organic layers were dried over MgSO₄ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 100% hexanes to 10% diethyl ether in hexanes) to yield 700 mg (80% yield) of the product as pale yellow solid. *R_f* = 0.53 (SiO₂, 10% ethyl acetate in hexanes); IR (film) ν_{max} 3061, 2925, 1582, 1510, 1478, 1069, 945 745 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz,) δ 7.63–7.55 (2H, m), 7.46–7.37 (3H, m), 7.14 (1H, s); ¹³C NMR (CDCl₃, 101 MHz) δ 163.1, 137.6, 133.5, 129.8, 129.6, 128.7, 87.8; HRMS *m/e* calcd. for C₉H₇ONSI (M)⁺ 303.9288 found 303.9273.



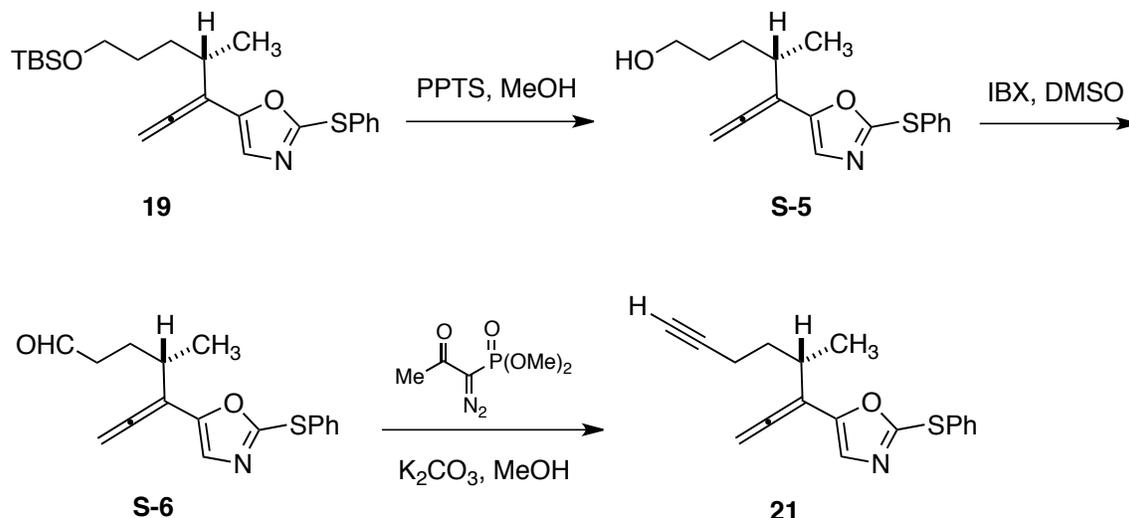
(S)-5-(7-((*tert*-butyldimethylsilyl)oxy)-4-methylhepta-1,2-dien-3-yl)-2-(phenylthio) oxazole (19):

To a stirred solution of **17** (620 mg, 2.04 mmol) in dry DMF (6.8 mL) was added propargyl stannane **16** (1.30 g, 2.46 mmol), $\text{Pd}_2(\text{dba})_3$ (187 mg, 0.21 mmol) and AsPh_3 (250 mg, 0.82 mmol) at rt. After stirring for 18 h at rt, the reaction was quenched with saturated aqueous NaHCO_3 solution (15 mL). The crude mixture was extracted in ethyl acetate (3 \times 30 mL). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 100% hexanes to 15% diethyl ether in hexanes containing 3% Et_3N) to yield 500 mg (59% yield) of the desired product as colorless oil. $R_f = 0.82$ (SiO_2 , 30% ethyl acetate in hexanes); $[\alpha]_D^{20} +11.0^\circ$ (c 1.67, CHCl_3); IR (film) ν_{max} 2928, 2856, 1939, 1582, 1472, 1255, 1098, 1024, 835 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.61–7.51 (2H, m), 7.45–7.31 (3H, m), 6.92 (1H, s), 5.17 (2H, s), 3.58 (2H, t, $J = 6.0$ Hz), 2.43–2.30 (1H, m), 1.61–1.35 (4H, m), 1.12 (3H, d, $J = 6.8$ Hz), 0.88 (9H, s), 0.03 (6H, s); ^{13}C NMR (CDCl_3 , 101 MHz) δ 206.8, 157.7, 150.3, 133.0, 129.60, 129.57, 129.1, 124.8, 101.1, 81.0, 63.3, 33.2, 32.3, 30.7, 26.2, 20.3, 18.5, -5.1 ; HRMS m/e calcd. for $\text{C}_{23}\text{H}_{33}\text{O}_2\text{NSSi}$ (M) $^+$ 415.1996 found 415.2004.



(S)-4-bromo-5-(7-((tert-butyldimethylsilyl)oxy)-4-methylhepta-1,2-dien-3-yl)-2-

(phenylthio)oxazole (20): To a stirred solution of **18** (500 mg, 1.31 mmol) in dry DMF (8.7 mL) was added propargyl stannane **16** (904 mg, 1.71 mmol), $\text{Pd}_2(\text{dba})_3$ (132 mg, 0.14 mmol) and AsPh_3 (177 mg, 0.58 mmol) at rt. After stirring for 15 h at rt, the reaction was quenched with saturated aqueous NaHCO_3 solution (20 mL). The crude mixture was extracted in ethyl acetate (4 × 20 mL). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 100% hexanes to 20% diethyl ether in hexanes containing 3% Et_3N) to yield 530 mg (82% yield) of the desired product as colorless oil. $R_f = 0.65$ (SiO_2 , 15% ethyl acetate in hexanes); $[\alpha]_D^{20} +3.0^\circ$ (c 0.50, CHCl_3); IR (film) ν_{max} 2928, 1583, 1471, 1255, 1096, 835 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz), δ 7.61–7.53 (2H, m), 7.45–7.36 (3H, m), 5.14 (2H, d, $J = 2.1$ Hz), 3.54 (2H, t, $J = 6.2$ Hz), 2.58–2.47 (1H, m), 1.52–1.41 (2H, m), 1.38–1.25 (2H, m), 1.04 (3H, d, $J = 6.8$ Hz), 0.89 (9H, s), 0.03 (6H, s); ^{13}C NMR (CDCl_3 , 101 MHz) δ 207.8, 157.4, 145.6, 133.5, 129.7, 129.5, 128.7, 113.6, 100.0, 81.2, 63.4, 33.4, 32.1, 30.6, 26.2, 19.9, 18.6, -5.5 ; HRMS m/e calcd. for $\text{C}_{23}\text{H}_{32}\text{O}_2\text{NBrSSi}$ (M) $^+$ 493.1101 found 493.1102.

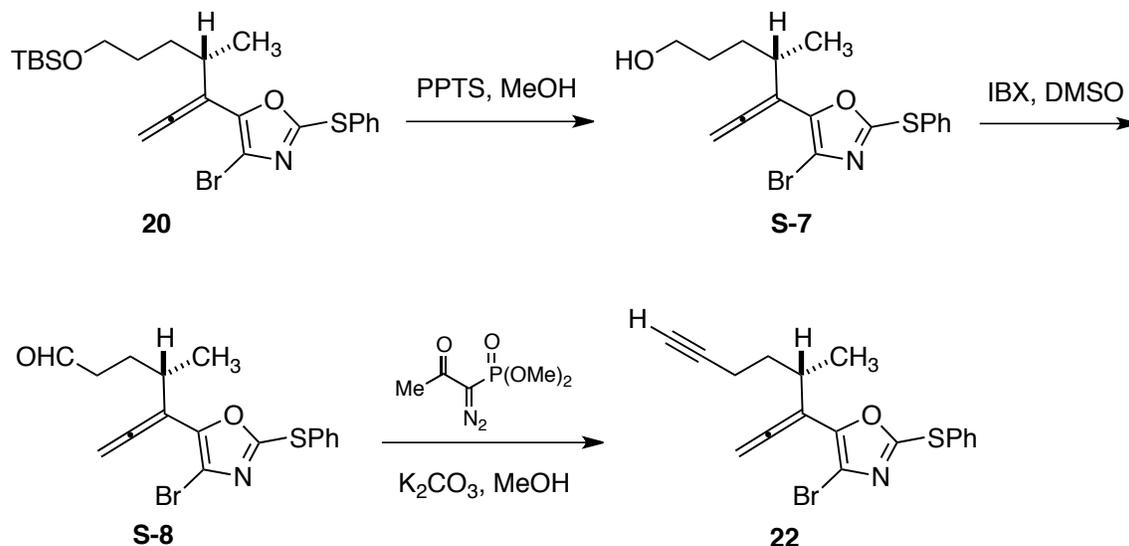


(S)-4-methyl-5-(2-(phenylthio)oxazol-5-yl)hepta-5,6-dien-1-ol (S-5): To a stirred solution of **19** (450 mg, 1.08 mmol) in anhydrous MeOH (3.6 mL) was added pyridinium *p*-toluenesulfonate (625 mg, 2.49 mmol) at rt. After stirring for 3 h at rt, the reaction was quenched with saturated aqueous NaHCO₃ solution (5 mL). The crude mixture was then extracted in ethyl acetate (3 × 30 mL). The combined organic layers were dried over MgSO₄ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 10% ethyl acetate in hexanes to 50% ethyl acetate in hexanes) to yield 219 mg (91% yield) of **S-5** as yellow oil. *R_f* = 0.16 (SiO₂, 30% ethyl acetate in hexanes); $[\alpha]_D^{20} +16.2^\circ$ (c 3.25, CHCl₃); IR (film) ν_{\max} 3261 (br), 2933, 2871, 1938, 1681, 1475, 1067, 748, 689 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz), δ 7.58–7.55 (2H, m), 7.46–7.30 (3H, m), 6.92 (1H, s), 5.18 (2H, s), 3.60 (2H, t, *J* = 5.7 Hz), 2.41–2.36 (1H, m), 1.66–1.51 (3H, m), 1.48–1.38 (1H, m), 1.33 (1H, br s), 1.14 (3H, d, *J* = 6.8 Hz); ¹³C NMR (CDCl₃, 101 MHz) δ 206.7, 157.7, 150.2, 133.1, 129.6, 129.5, 129.1, 124.8, 100.9, 81.1, 63.0, 33.1, 32.1, 30.5, 20.2; HRMS *m/e* calcd. for C₁₇H₁₉O₂NS (M)⁺ 301.1131 found 301.1132.

(S)-4-methyl-5-(2-(phenylthio)oxazol-5-yl)hepta-5,6-dienal (S-6): To a stirred solution of **S-5** (275 mg, 0.91 mmol) in anhydrous DMSO (5.0 mL) was added IBX (332.5 mg, 1.21 mmol) at rt. After stirring for 3 h at rt, the reaction was quenched with saturated aqueous NaHCO₃ solution (5 mL). The

crude mixture was then extracted in ethyl acetate (3 × 30 mL). The combined organic layers were dried over MgSO₄ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 100% hexanes to 20% ethyl acetate in hexanes containing 3% Et₃N) to yield 200 mg (73% yield) of **S-6** as colorless oil. *R_f* = 0.39 (SiO₂, 30% ethyl acetate in hexanes); [α]_D²⁰ +26.2° (c 1.17, CHCl₃); IR (film) *v*_{max} 2964, 1723, 1581, 1475, 1114, 747 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 9.73 (1H, s), 7.57 (2H, dd, *J* = 6.3, 3.0 Hz), 7.43–7.32 (3H, m), 6.93 (1H, s), 5.20 (2H, d, *J* = 1.2 Hz), 2.45 (2H, t, *J* = 7.5 Hz), 2.42–2.36 (1H, m), 1.90–1.67 (2H, m), 1.13 (3H, d, *J* = 6.8 Hz); ¹³C NMR (CDCl₃, 101 MHz) δ 206.6, 202.1, 158.1, 149.7, 133.3, 129.6, 129.31, 129.25, 125.0, 100.3, 81.6, 41.7, 32.7, 28.0, 20.5; HRMS *m/e* calcd. for C₁₇H₁₇O₂NS (M)⁺ 299.0975 found 299.0973.

(S)-5-(4-methylocta-1,2-dien-7-yn-3-yl)-2-(phenylthio)oxazole (21): To a stirred solution of **S-6** (200 mg, 0.67 mmol) in anhydrous MeOH (3.4 mL) was added K₂CO₃ (278 mg, 2.01 mmol) followed by Bestmann–Ohira reagent (200 μL, 1.34 mmol) at 0 °C. The reaction mixture was warmed to rt after 10 min and stirred for additional 2 h at rt. The reaction was quenched with saturated aqueous NaHCO₃ solution (10 mL). The crude mixture was then extracted in ethyl acetate (3 × 20 mL). The combined organic layers were dried over MgSO₄ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 100% hexanes to 20% diethyl ether in hexanes) to yield 160 mg (81% yield) of **21** as colorless oil. *R_f* = 0.86 (SiO₂, 30% ethyl acetate in hexanes); [α]_D²⁰ +21.3° (c 0.10, CHCl₃); IR (film) *v*_{max} 3298, 2929, 1525, 1468 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.61–7.54 (2H, m), 7.42–7.34 (3H, m), 6.98 (1H, s), 5.20 (2H, app t, *J* = 12.8 Hz), 2.60–2.49 (1H, m), 2.21 (2H, td, *J* = 7.2, 2.6 Hz), 1.94 (1H, t, *J* = 2.6 Hz), 1.77 (1H, dq, A of AB, *J* = 14.3, 7.2 Hz), 1.59 (1H, td, B of AB, *J* = 13.9, 7.0 Hz), 1.13 (3H, d, *J* = 6.8 Hz); ¹³C NMR (CDCl₃, 101 MHz) δ 206.6, 157.9, 149.9, 133.2, 129.6, 129.4, 129.2, 125.0, 100.5, 84.1, 81.4, 68.9, 34.6, 32.2, 19.8, 16.5; HRMS *m/e* calcd. for C₁₈H₁₇ONS (M)⁺ 295.1025 found 295.1027.

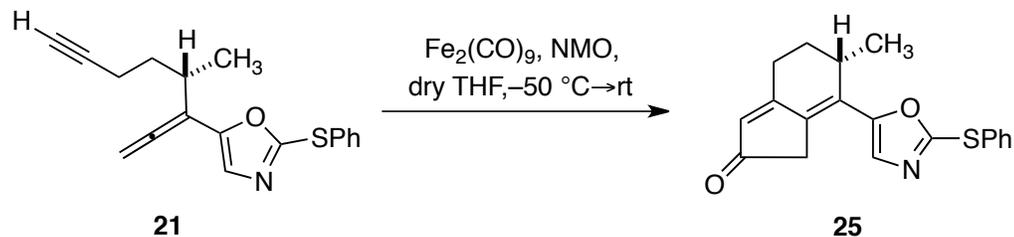


(S)-5-(4-bromo-2-(phenylthio)oxazol-5-yl)-4-methylhepta-5,6-dien-1-ol (S-7): To a stirred solution of **20** (318 mg, 0.64 mmol) in anhydrous MeOH (4.5 mL) was added pyridinium *p*-toluenesulfonate (406 mg, 1.62 mmol) at rt. After stirring for 5 h at rt, the reaction was quenched with saturated aqueous NaHCO₃ solution (5 mL). The crude mixture was then extracted in ethyl acetate (4 × 30 mL). The combined organic layers were dried over MgSO₄ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 20% ethyl acetate in hexanes to 80% ethyl acetate in hexanes) to yield 219 mg (90% yield) of **S-7** as colorless oil. $R_f = 0.12$ (SiO₂, 15% ethyl acetate in hexanes); $[\alpha]_D^{20} +7.9^\circ$ (c 0.75, CHCl₃); IR (film) ν_{\max} 3250 (br), 2932, 1731, 1470, 1068, 749 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz), δ 7.61–7.54 (2H, m), 7.42–7.36 (3H, m), 5.15 (2H, d, $J = 2.0$ Hz), 3.56 (2H, t, $J = 6.2$ Hz), 2.62–2.47 (1H, m), 1.60–1.19 (4H, m), 1.05 (3H, d, $J = 6.8$ Hz); ¹³C NMR (CDCl₃, 101 MHz) δ 207.8, 157.4, 145.4, 133.5, 129.7, 129.5, 128.5, 113.6, 99.8, 81.3, 63.1, 33.4, 31.9, 30.4, 19.8; HRMS *m/e* calcd. for C₁₇H₁₈O₂NBrS (M)⁺ 379.0236 found 379.0240.

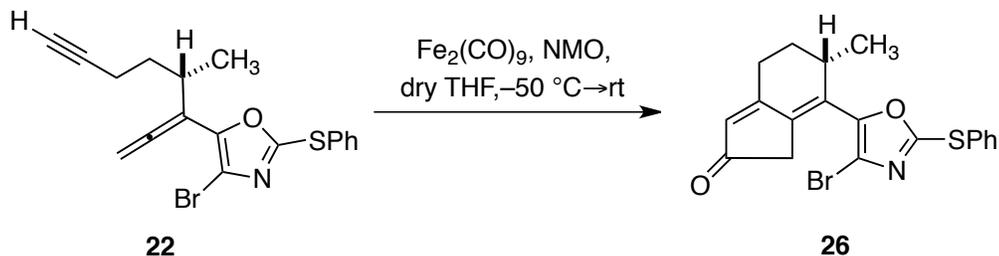
(S)-5-(4-bromo-2-(phenylthio)oxazol-5-yl)-4-methylhepta-5,6-dienal (S-8): To a stirred solution of **S-7** (140 mg, 0.37 mmol) in anhydrous DMSO (1.8 mL) was added IBX (135 mg, 0.48 mmol) at rt. After stirring for 2 h at rt, the reaction was quenched with saturated aqueous NaHCO₃ solution (2

mL). The crude mixture was then extracted in ethyl acetate (4 × 10 mL). The combined organic layers were dried over MgSO₄ and evaporated *in vacuo*. The crude mixture was quickly passed through a plug of silica gel (eluted with 10% ethyl acetate in hexanes) to yield 120 mg (86% yield) of **S-8** as colorless oil. The product was immediately used in the next step without further purification. $R_f = 0.42$ (SiO₂, 10% ethyl acetate in hexanes); ¹H NMR (CDCl₃, 400 MHz, δ) 9.69 (1H, s), 7.64–7.53 (2H, m), 7.43–7.36 (3H, m), 5.18 (2H, d, $J = 1.2$ Hz), 2.64–2.48 (1H, m), 2.39 (2H, t, $J = 7.6$ Hz), 1.79–1.59 (2H, m), 1.05 (3H, d, $J = 6.8$ Hz).

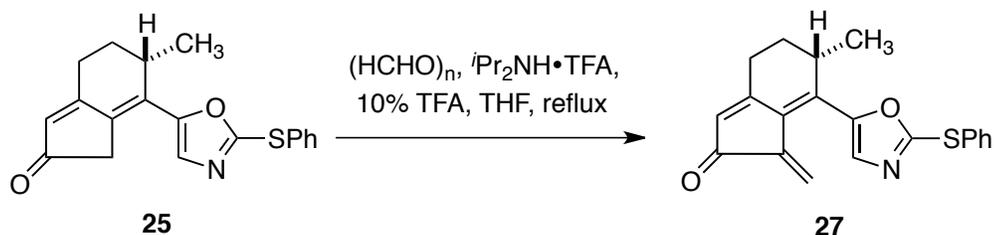
(S)-4-bromo-5-(4-methylocta-1,2-dien-7-yn-3-yl)-2-(phenylthio)oxazole (22): To a stirred solution of **S-8** (120 mg, 0.32 mmol) in anhydrous MeOH (2.5 mL) was added K₂CO₃ (87.6 mg, 0.63 mmol) followed by Bestmann–Ohira reagent (85.8 μ L, 0.57 mmol) at 0 °C. The reaction mixture was warmed to rt after 10 min and stirred for additional 1 h at rt. The reaction was quenched with saturated aqueous NaHCO₃ solution (10 mL). The crude mixture was then extracted in ethyl acetate (3 × 20 mL). The combined organic layers were dried over MgSO₄ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 100% hexanes to 20% diethyl ether in hexanes) to yield 110 mg (92% yield) of **22** as colorless oil. $R_f = 0.65$ (SiO₂, 10% ethyl acetate in hexanes); $[\alpha]_D^{20} +14.2^\circ$ (c 0.50, CHCl₃); IR (film) ν_{\max} 3300, 2927, 1680, 1470 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz, δ) 7.61–7.54 (2H, m), 7.39–7.37 (3H, m), 5.17 (2H, d, $J = 2.0$ Hz), 2.73–2.62 (1H, m), 2.15 (2H, td, $J = 7.4, 2.6$ Hz), 1.91 (1H, t, $J = 2.6$ Hz), 1.68 (1H, td, $J = 14.5, 7.3$ Hz), 1.52 (1H, td, $J = 14.3, 7.4$ Hz), 1.05 (3H, d, $J = 6.8$ Hz); ¹³C NMR (CDCl₃, 101 MHz) δ 207.7, 157.5, 145.1, 133.6, 129.7, 129.5, 128.4, 113.8, 99.2, 84.0, 81.5, 68.7, 34.4, 32.7, 19.5, 16.4; HRMS m/e calcd. for C₁₈H₁₆ONBrS (M)⁺ 373.0130 found 373.0124.



(S)-6-methyl-7-(2-(phenylthio)oxazol-5-yl)-5,6-dihydro-1H-inden-2(4H)-one (25): To a stirred solution of **21** (220 mg, 0.75 mmol) in dry THF (25.6 mL) was added N-methylmorpholine oxide (281 mg, 2.40 mmol) followed by iron nonacarbonyl (436 mg, 1.20 mmol) at $-50\text{ }^{\circ}\text{C}$ and stirred for 5 min. The reaction mixture was then warmed to rt immediately and stirred for additional 90 min. The reaction was then diluted with hexanes (30 mL). The insoluble solid was removed by passing through a plug of Florisil® and eluted with additional ethyl acetate ($2 \times 20\text{ mL}$). The combined organic layers were evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 20% ethyl acetate in hexanes to 60% ethyl acetate in hexanes) to yield 125 mg (52% yield) of the desired product as yellow oil. $R_f = 0.18$ (SiO_2 , 30% ethyl acetate in hexanes); $[\alpha]_D^{20} -40.0^{\circ}$ (c 0.50, CHCl_3); IR (film) ν_{max} 2925, 1682, 1582, 1460 1222 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz,) δ 7.64 (2H, dd, $J = 7.4, 2.0\text{ Hz}$), 7.52–7.42 (3H, m), 7.17 (1H, s), 5.97 (1H, s), 2.88 (2H, d, $J = 2.0\text{ Hz}$), 2.85–2.79 (1H, m) 2.78–2.64 (2H, m), 1.92 (1H, ddd, $J = 11.4, 9.6, 5.1\text{ Hz}$), 1.85–1.77 (1H, m), 1.22 (3H, d, $J = 7.1\text{ Hz}$); $^{13}\text{C NMR}$ (CDCl_3 , 101 MHz) δ 204.8, 170.1, 160.5, 152.8, 134.5, 131.6, 130.1, 129.9, 128.5, 128.3, 127.8, 127.1, 40.0, 29.5, 28.5, 21.5, 19.2; HRMS m/e calcd. for $\text{C}_{19}\text{H}_{17}\text{O}_2\text{NS}$ (M) $^+$ 323.0975 found 323.0960.

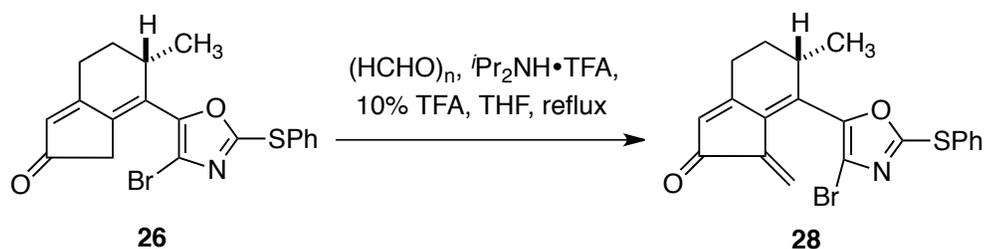


(S)-7-(4-bromo-2-(phenylthio)oxazol-5-yl)-6-methyl-5,6-dihydro-1H-inden-2(4H)-one (26): To a stirred solution of **22** (60 mg, 0.16 mmol) in dry THF (8.0 mL) was added N-methylmorpholine oxide (94.0 mg, 0.80 mmol) followed by iron nonacarbonyl (145.0 mg, 0.40 mmol) at $-50\text{ }^\circ\text{C}$ and stirred for 5 min. The reaction mixture was then warmed to rt immediately and stirred for additional 80 min. The reaction was then diluted with hexanes (10 mL). The insoluble solid was removed by passing through a plug of Florisil® and eluted with additional ethyl acetate ($2 \times 10\text{ mL}$). The combined organic layers were evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 10% ethyl acetate in hexanes to 40% ethyl acetate in hexanes) to yield 33 mg (52% yield) of the desired product as yellow solid. $R_f = 0.51$ (SiO_2 , 25% ethyl acetate in hexanes); $[\alpha]_D^{20} +28.7^\circ$ (c 0.12, CHCl_3); IR (film) ν_{max} 2925, 1683, 1583, 1468 1224, 1035 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz,) δ 7.66–7.62 (2H, m), 7.56–7.45 (3H, m), 5.97 (1H, s), 3.43–3.33 (1H, m), 2.75–2.66 (3H, m) 2.61 (1H, B of AB, $J = 21.7\text{ Hz}$), 1.97–1.86 (1H, m), 1.81–1.75 (1H, m), 1.17 (3H, d, $J = 7.0\text{ Hz}$); ^{13}C NMR (CDCl_3 , 101 MHz) δ 204.7, 169.9, 160.2, 148.0, 135.0, 134.2, 130.7, 130.1, 129.1, 127.2, 126.6, 115.8, 40.3, 28.7, 28.3, 21.8, 19.4; HRMS m/e calcd. for $\text{C}_{19}\text{H}_{16}\text{O}_2\text{NBrS}$ (M^+) 401.0080 found 401.0081.

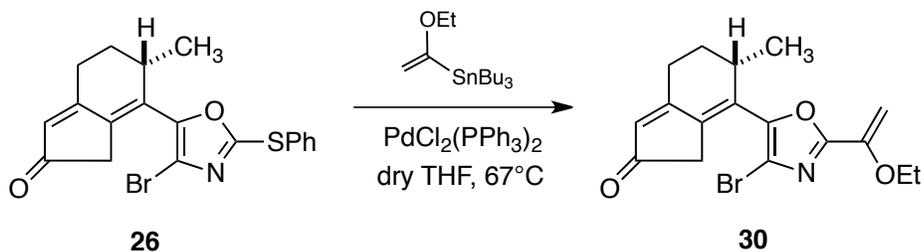


(S)-6-methyl-1-methylene-7-(2-(phenylthio)oxazol-5-yl)-5,6-dihydro-1H-inden-2(4H)-one (27):

To a stirred solution of **25** (15.0 mg, 46.4 μmol) in dry THF (310 μL) was added paraformaldehyde (2.8 mg, 92.9 μmol), $i\text{Pr}_2\text{NH}\cdot\text{TFA}$ (9.9 mg, 46.4) and TFA (0.4 μL , 4.6 μmol) sequentially at rt. The reaction was refluxed (67 $^\circ\text{C}$) for 120 min. The reaction was cooled to rt and additional paraformaldehyde (2.8 mg, 92.9 μmol) was added. After refluxing for 6 hr, reaction was cooled to rt and quenched with saturated aqueous NH_4Cl solution (1 mL). The crude mixture was then extracted in ethyl acetate (3 \times 10 mL) and washed successively with 1N aqueous HCl solution (3 mL) and 1N aqueous NaOH solution (3 mL). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 20% ethyl acetate in hexanes to 60% ethyl acetate in hexanes) to yield 13.0 mg (84% yield) of the desired product as yellow solid. $R_f = 0.46$ (SiO_2 , 50% ethyl acetate in hexanes); $[\alpha]_D^{20} -22.5^\circ$ (c 0.10, CHCl_3); IR (film) ν_{max} 2924, 1700, 1459 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.67–7.61 (2H, m), 7.47–7.40 (3H, m), 7.27 (1H, s), 6.08 (1H, s), 5.94 (1H, s), 5.63 (1H, s), 2.98–2.86 (1H, m), 2.77 (2H, dd, $J = 10.6, 3.1$ Hz), 1.99–1.89 (1H, m), 1.86–1.77 (1H, m), 1.17 (3H, d, $J = 7.1$ Hz); $^{13}\text{C NMR}$ (CDCl_3 , 101 MHz) δ 216.8, 193.7, 167.4, 160.4, 151.6, 137.9, 134.5, 130.4, 130.1, 130.0, 128.2, 128.0, 126.4, 118.4, 32.5, 27.9, 22.1, 19.2; HRMS m/e calcd. for $\text{C}_{20}\text{H}_{17}\text{O}_2\text{NS}$ (M) $^+$ 335.0975 found 335.0962.

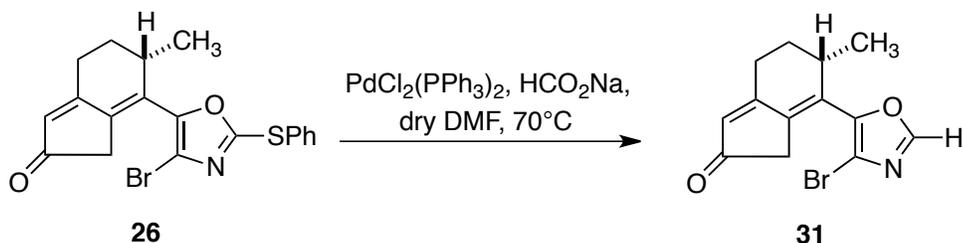


(S)-7-(4-bromo-2-(phenylthio)oxazol-5-yl)-6-methyl-1-methylene-5,6-dihydro-1H-inden-2(4H)-one (28): To a stirred solution of **26** (20.0 mg, 49.8 μmol) in dry THF (500 μL) was added paraformaldehyde (3.0 mg, 99.5 μmol), $i\text{Pr}_2\text{NH}\cdot\text{TFA}$ (11.0 mg, 49.8) and TFA (0.4 μL , 4.9 μmol) sequentially at rt. The reaction was refluxed (67 $^\circ\text{C}$) for 100 min. The reaction was cooled to rt and additional paraformaldehyde (3.0 mg, 99.5 μmol) was added. After refluxing for 6 hr, reaction was cooled to 22 $^\circ\text{C}$ quenched with saturated aqueous NH_4Cl solution (1 mL). The crude mixture was then extracted in ethyl acetate (3 \times 15 mL) and washed successively with 1N aqueous HCl solution (5 mL) and 1N aqueous NaOH solution (5 mL). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 20% ethyl acetate in hexanes to 60% ethyl acetate in hexanes) to yield 16.0 mg (78% yield) of the desired product as yellow solid. $R_f = 0.56$ (SiO_2 , 50% ethyl acetate in hexanes); $[\alpha]_D^{20} +17.3^\circ$ (c 0.08, CHCl_3); IR (film) ν_{max} 2924, 1698, 1457 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz,) δ 7.64–7.59 (2H, m), 7.45–7.37 (3H, m), 6.14 (1H, s), 6.04 (1H, s), 5.11 (1H, s), 2.96–2.87 (1H, m), 2.80–2.73 (2H, m), 2.05–1.93 (1H, m), 1.81–1.74 (1H, m), 1.05 (3H, d, $J = 7.1$ Hz); ^{13}C NMR (CDCl_3 , 101 MHz) δ 193.5, 166.2, 160.2, 147.7, 137.2, 134.6, 134.1, 130.1, 129.8, 127.7, 127.6, 126.9, 118.0, 117.3, 33.0, 28.4, 22.6, 18.4; HRMS m/e calcd. for $\text{C}_{20}\text{H}_{16}\text{O}_2\text{NBrS}$ (M) $^+$ 413.0080 found 413.0080.

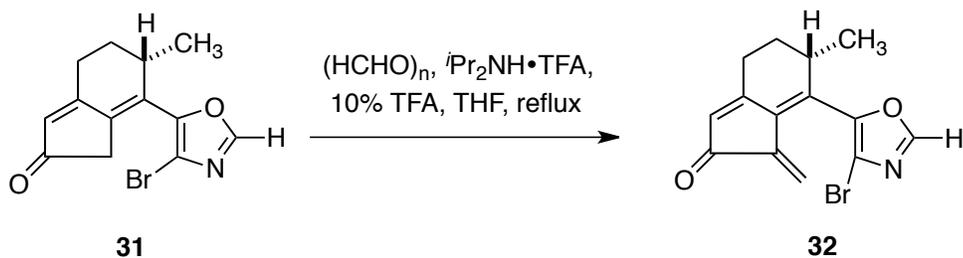


(S)-7-(4-bromo-2-(1-ethoxyvinyl)oxazol-5-yl)-6-methyl-5,6-dihydro-1H-inden-2(4H)-one (30):

To a stirred solution of **26** (8.0 mg, 19.9 μmol) in dry THF (1.60 mL) was added tributyl(1-ethoxyvinyl)tin (13.5 μL , 39.8 μmol) and $\text{PdCl}_2(\text{PPh}_3)_2$ (2.8 mg, 3.9 μmol) sequentially at rt. The reaction was refluxed (67°C) for 4 hr. The reaction was then cooled to rt and 5% HCl (1 mL) was added. After stirring for 15 min, layers were separated. An aqueous layer was extracted with ethyl acetate (3 \times 10 mL). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 100% hexanes to 30% diethyl ether in hexanes) to yield 6.0 mg (83% yield) of the product as yellow oil. $R_f = 0.46$ (SiO_2 , 25% ethyl acetate in hexanes); $[\alpha]_D^{20} +51.0^\circ$ (c 0.10, CHCl_3); IR (film) ν_{max} 2925, 1682, 1583, 1456 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz,) δ 6.07 (1H, s), 5.20 (1H, d, $J = 3.2$ Hz), 4.61 (1H, d, $J = 3.2$ Hz), 3.97 (2H, q, $J = 7.0$ Hz), 3.48 (1H, br s), 3.37 (1H, A of AB, $J = 21.5$ Hz), 3.13 (1H, B of AB, $J = 21.5$ Hz), 2.80–2.75 (2H, m), 2.06–1.92 (1H, m), 1.91–1.78 (1H, m), 1.45 (3H, t, $J = 7.0$ Hz), 1.21 (3H, d, $J = 7.0$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 204.9, 170.2, 158.1, 148.4, 146.1, 135.1, 129.3, 127.7, 115.9, 90.3, 64.5, 40.7, 29.0, 28.4, 21.9, 9.4, 14.5; HRMS m/e calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_3\text{NBr}$ (M) $^+$ 363.0465 found 363.0461.

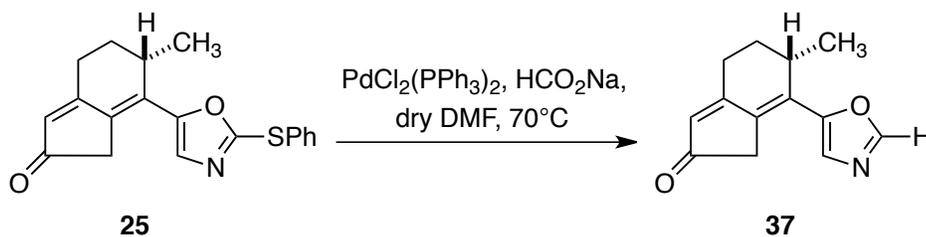


(S)-7-(4-bromooxazol-5-yl)-6-methyl-5,6-dihydro-1H-inden-2(4H)-one (31): To a stirred solution of **26** (32.0 mg, 79.6 μmol) in dry THF (4.0 mL) was added sodium formate (32.6 mg, 0.48 mmol) and $\text{PdCl}_2(\text{PPh}_3)_2$ (11.2 mg, 15.9 μmol) sequentially at rt. The reaction was stirred at 70°C for 5 hr. The reaction was then cooled to rt and quenched with saturated aqueous NaHCO_3 solution (3 mL). The crude mixture was then extracted in ethyl acetate (3 \times 30 mL). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 10% ethyl acetate in hexanes to 50% ethyl acetate in hexanes) to yield 17.0 mg (73% yield) of the desired product as yellow solid. $R_f = 0.19$ (SiO_2 , 25% ethyl acetate in hexanes); $[\alpha]_D^{20} -1.5^\circ$ (c 0.13, CHCl_3); IR (film) ν_{max} 2925, 1683, 1584 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz,) δ 7.87 (1H, s), 6.07 (1H, s), 3.44–3.34 (1H, m), 3.34 (1H, A of AB, $J = 21.5$ Hz), 3.06 (1H, B of AB, $J = 21.4$ Hz), 2.78 (2H, dd, $J = 8.4, 3.9$ Hz), 2.06–1.96 (1H, m), 1.83 (1H, dq, $J = 13.2, 4.0$ Hz), 1.18 (3H, d, $J = 7.0$ Hz); ^{13}C NMR (CDCl_3 , 101 MHz) δ 204.7, 169.9, 150.9, 146.6, 135.8, 129.6, 127.6, 114.6, 40.4, 29.5, 28.5, 22.0, 19.3; HRMS m/e calcd. for $\text{C}_{13}\text{H}_{13}\text{O}_2\text{NBr}$ ($\text{M}+\text{H}$) $^+$ 294.0124 found 294.0111.



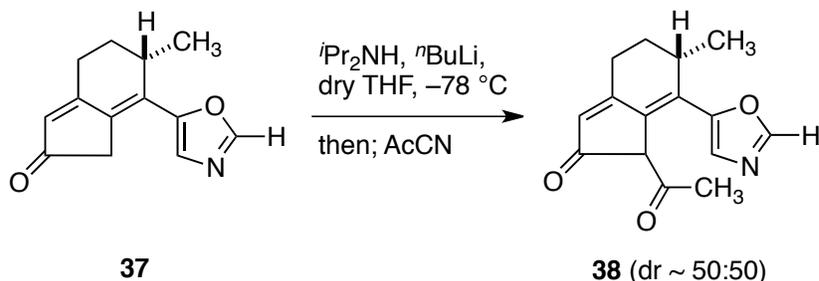
(S)-7-(4-bromooxazol-5-yl)-6-methyl-1-methylene-5,6-dihydro-1H-inden-2(4H)-one (32): To a stirred solution of **31** (10.0 mg, 34.0 μmol) in dry THF (1.7 mL) was added paraformaldehyde (2.1

mg, 68.0 μmol), $i\text{Pr}_2\text{NH}\cdot\text{TFA}$ (7.3 mg, 34.0) and TFA (0.5 μL , 6.8 μmol) sequentially at rt. The reaction was refluxed (67 $^\circ\text{C}$) for 90 min. The reaction was cooled to rt and additional paraformaldehyde (2.1 mg, 68.0 μmol) was added. After refluxing for 4 hr, reaction was cooled to 22 $^\circ\text{C}$ and quenched with saturated aqueous NH_4Cl solution (2 mL). The crude mixture was then extracted in ethyl acetate (3 \times 15 mL) and washed with 5% aqueous HCl solution (5 mL). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 10% ethyl acetate in hexanes to 30% ethyl acetate in hexanes) to yield 7.0 mg (68% yield) of the desired product as white solid. $R_f = 0.30$ (SiO_2 , 25% ethyl acetate in hexanes); IR (film) ν_{max} 2925, 1694, 1455, 1014 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.93 (1H, s), 6.19 (1H, s), 6.10 (1H, s), 5.04 (1H, s), 2.98 (1H, qd, $J = 11.6, 7.1$ Hz), 2.87–2.79 (2H, m), 2.12–2.00 (1H, m), 1.82 (1H, dq, $J = 13.2, 4.8$ Hz), 1.08 (3H, d, $J = 7.1$ Hz); ^{13}C NMR (CDCl_3 , 101 MHz) δ 193.5, 166.1, 151.3, 145.9, 137.3, 135.3, 127.9, 127.1, 117.8, 116.0, 33.3, 28.6, 22.7, 18.4; HRMS m/e calcd. for $\text{C}_{14}\text{H}_{13}\text{O}_2\text{NBr}$ ($\text{M}+\text{H}$) $^+$ 306.0124 found 306.0129.



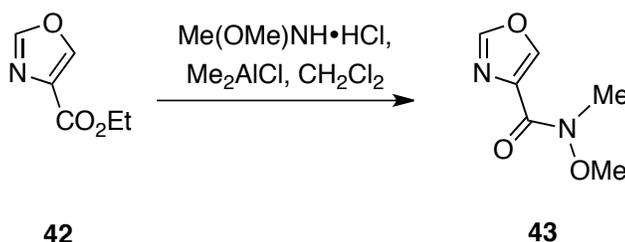
(S)-6-methyl-7-(oxazol-5-yl)-5,6-dihydro-1H-inden-2(4H)-one (37): To a stirred solution of **25** (15.0 mg, 46.4 μmol) in dry THF (3.0 mL) was added sodium formate (18.9 mg, 0.28 mmol) and $\text{PdCl}_2(\text{PPh}_3)_2$ (6.5 mg, 9.2 μmol) sequentially at rt. The reaction was stirred at 70 $^\circ\text{C}$ for 4 hr. The reaction was then cooled to rt and quenched with saturated aqueous NaHCO_3 solution (2 mL). The crude mixture was then extracted in ethyl acetate (3 \times 20 mL). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 10% ethyl acetate in hexanes to 50% ethyl acetate in hexanes) to yield 6.5 mg (65% yield) of the desired product as yellow solid. $R_f = 0.20$ (SiO_2 , 30% ethyl acetate

in hexanes); IR (film) ν_{\max} 2927, 1684, 1584 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.95 (1H, s), 7.22 (1H, s), 6.04 (1H, s), 3.27 (1H, A of AB, $J = 21.3$ Hz), 3.19 (1H, B of AB, $J = 21.3$ Hz), 3.03–2.93 (1H, m), 2.83–2.72 (2H, m), 2.06–1.93 (1H, m), 1.92–1.81 (1H, m), 1.28 (3H, d, $J = 7.1$ Hz); ^{13}C NMR (CDCl_3 , 101 MHz) δ 204.8, 170.3, 151.6, 151.1, 132.4, 128.8, 127.7, 126.3, 40.2, 29.8, 28.6, 21.6, 19.2; HRMS m/e calcd. for $\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}$ (M) $^+$ 215.0941 found 215.0936.

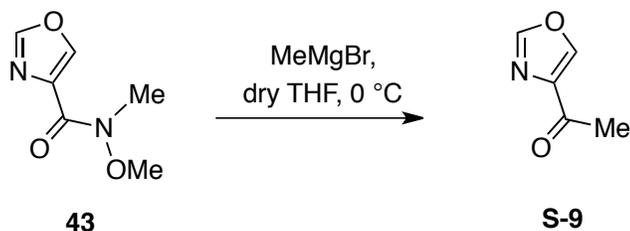


(6S)-1-acetyl-6-methyl-7-(oxazol-5-yl)-5,6-dihydro-1H-inden-2(4H)-one (38): To a stirred solution of freshly generated lithium diisopropylamine solution (203.4 μL , 0.37M in THF, 74.8 μmol) was added **37** (8.0 mg, 37.3 μmol) in dry THF (148 μL) at -78 $^{\circ}\text{C}$. After stirring for 45 min at -78 $^{\circ}\text{C}$, reaction was transferred to ice-bath (0 $^{\circ}\text{C}$) and stirred for additional 15 min. A solution of AcCN (5.5 μL , 78.3 μmol) in dry THF (150 μL) was then added at -78 $^{\circ}\text{C}$ and stirred for 70 min at -78 $^{\circ}\text{C}$. The reaction was then quenched with saturated aqueous NaHCO_3 solution (1.0 mL) at -78 $^{\circ}\text{C}$. The crude mixture was extracted in ethyl acetate (3×5 mL). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 100% hexanes to 30% ethyl acetate in hexanes) to yield 5.0 mg (52% yield) of the desired product (colorless oil) as 1:1 mixture of inseparable diastereomers. $R_f = 0.14$ (SiO_2 , 50% ethyl acetate in hexanes); $[\alpha]_D^{20} +10.5^{\circ}$ (c 0.20, CHCl_3); IR (film) ν_{\max} 2923, 1698, 1012, 980 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, asterisk denotes minor diastereomer) δ 7.89 (1H, s), 7.25 (1H, s), 5.98 (1H, s), 4.53 (1H, s), 4.47* (1H, s), 3.01 (1H, dd, $J = 13.0, 6.2$ Hz), 2.98–2.91* (1H, m), 2.91–2.70 (2H, m), 2.39 (3H, s), 2.38* (3H, s), 2.18–1.81 (2H, m), 1.37 (3H, d, $J = 7.1$ Hz), 1.27 (3H, d, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , 101 MHz, asterisk denotes minor diastereomer) δ 200.3,

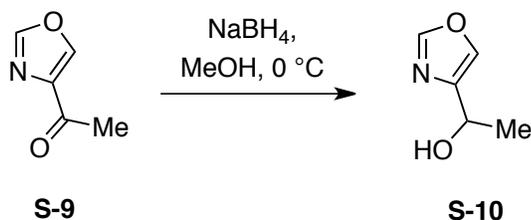
198.5*, 198.4, 172.6, 172.1*, 152.5, 152.3*, 133.3*, 133.2, 131.3, 131.2*, 130.0, 129.77*, 129.75, 129.2, 129.0, 128.6, 128.5*, 126.4, 126.3, 64.6, 64.3*, 30.6*, 30.5, 29.9, 29.7*, 28.7, 27.9*, 21.7, 21.6*, 19.7, 19.3*; HRMS m/e calcd. for $C_{15}H_{15}O_3N$ (M)⁺ 257.1046 found 257.1043.



***N*-methoxy-*N*-methyloxazole-4-carboxamide (43):** To a stirred solution of *N,O*-Dimethylhydroxylamine hydrochloride (20.74 g, 212.60 mmol) in dry CH₂Cl₂ (330 mL) was added Me₂AlCl (212.6 mL, 1.0 M solution, 212.60 mmol) dropwise at 0 °C. The reaction mixture was then warmed to rt and stirred at rt for additional 90 min. A solution of **42** (6.0 g, 42.52 mmol) in dry CH₂Cl₂ (106 mL) was then added dropwise to above reaction mixture at rt. After stirring for additional 90 min at rt, reaction was carefully quenched with pH=7 buffer followed by 2N aq. NaOH solution at cold. Extraction was then performed in dichloromethane (3 × 75 mL). The combined organic layers were dried over MgSO₄ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (50% ethyl acetate in hexanes) to yield 6.05 g (91% yield) of the desired product as white solid. R_f = 0.21 (SiO₂, 75% EtOAc in hexanes); IR (film) ν_{\max} 3140, 3111, 1652, 1547, 1427, 1094, 957, 761 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.17 (1H, s), 7.89 (1H, s), 3.71 (3H, s), 3.33 (3H, s); ¹³C NMR (CDCl₃, 101 MHz) δ 160.9, 150.7, 142.9, 133.4, 61.5, 33.3; HRMS m/e calcd. for C₆H₉O₃N₂ (M+H)⁺ 157.0608 found 157.0601.

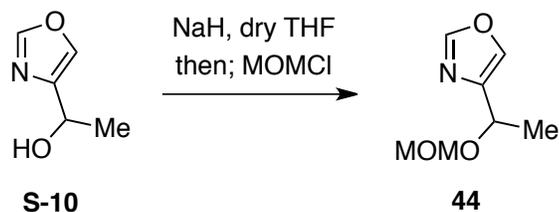


1-(oxazol-4-yl)ethanone (S-9): To a stirred solution of **43** (8.92 g, 57.18 mmol) in dry THF (239 mL) was added MeMgBr (42.0 mL, 125.80 mmol) dropwise at 0 °C. After stirring for 1 h at 0 °C, reaction was quenched with saturated aqueous NH₄Cl solution (70 mL) at 0 °C. The crude mixture was then extracted in ethyl acetate (4 × 70 mL). The combined organic layers were dried over MgSO₄ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 20% ethyl acetate in hexanes to 60% ethyl acetate in hexanes) to yield 5.50 g (87% yield) of **S-9** as white solid. *R_f* = 0.39 (SiO₂, 50% ethyl acetate in hexanes); IR (film) ν_{max} 2922, 1728, 1461, 1262 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.21 (1H, s), 7.89 (1H, s), 2.50 (3H, s); ¹³C NMR (CDCl₃, 101 MHz) δ 192.7, 151.2, 142.4, 140.6, 27.5; HRMS *m/e* calcd. for C₅H₆O₂N (M+H)⁺ 112.0393 found 112.0389.

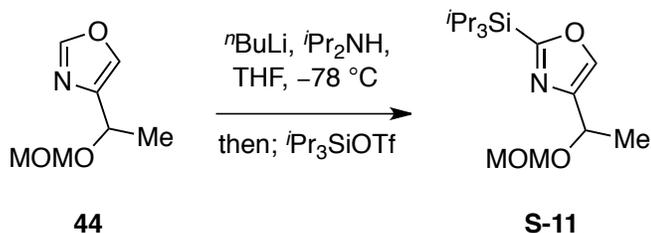


1-(oxazol-4-yl)ethanol (S-10): To a stirred solution of **S-9** (5.16 g, 46.49 mmol) in anhydrous MeOH (116 mL) was added NaBH₄ (3.52 g, 92.97 mmol) at 0 °C. After stirring for 1 h at 0 °C, reaction was quenched with 5% aqueous Na₂CO₃ solution (27 mL) and concentrated by evaporating solvent *in vacuo*. The crude mixture was then diluted with H₂O (50 mL) and extracted in ethyl acetate (5 × 75 mL). The combined organic layers were dried over MgSO₄ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 20% ethyl

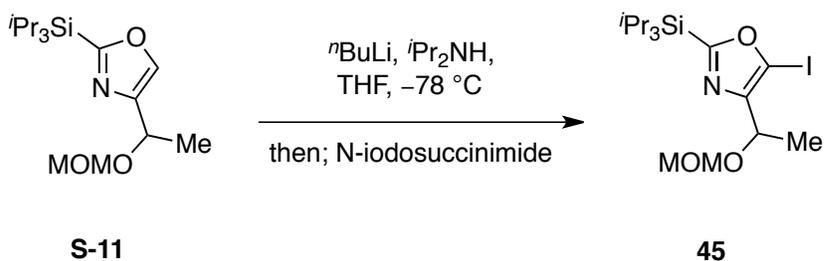
acetate in hexanes to 70% ethyl acetate in hexanes) to yield 4.75 g (90% yield) of **S-10** as colorless oil. $R_f = 0.18$ (SiO₂, 50% ethyl acetate in hexanes); IR (film) ν_{\max} 3355, 3133, 2979, 2933, 1514, 1101, 1062, 917 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.83 (1H, s), 7.55 (1H, s), 4.84 (1H, q, $J = 6.4$ Hz), 3.55 (1H, br s), 1.50 (3H, d, $J = 6.5$ Hz); ¹³C NMR (CDCl₃, 101 MHz) δ 151.4, 144.6, 134.2, 62.9, 22.2; HRMS m/e calcd. for C₅H₈O₂N (M+H)⁺ 114.0550 found 114.0554.



4-(1-(methoxymethoxy)ethyl)oxazole (44): To a stirred solution of **S-10** (4.75 g, 42.04 mmol) in dry THF (105 mL) was added NaH (5.04 g, 60% in mineral oil, 126.11 mmol) at 0 °C and stirred at 0 °C for additional 10 min. The reaction mixture was then warmed to rt immediately. After stirring at rt for additional 50 min, reaction mixture was cooled to 0 °C and MOMCl (9.48 g, 117.71 mmol) was added. After 10 min, reaction mixture was warmed to rt and stirred for 4 hr. The reaction was then cooled to 0 °C and carefully quenched with saturated aqueous NaHCO₃ solution (40 mL). The crude mixture was then extracted in ethyl acetate (5 × 80 mL). The combined organic layers were dried over MgSO₄ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 10% ethyl acetate in hexanes to 40% ethyl acetate in hexanes) to yield 4.0 g (61% yield) of the desired product as yellow oil. $R_f = 0.45$ (SiO₂, 50% ethyl acetate in hexanes); IR (film) ν_{\max} 1708, 1447, 1035 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.80 (1H, s), 7.54 (1H, s), 4.74 (1H, app dd, $J = 12.9, 6.4$ Hz), 4.62 (1H, A of AB, $J = 6.8$ Hz), 4.60 (1H, B of AB, $J = 6.8$ Hz), 3.32 (3H, s), 1.46 (3H, d, $J = 6.6$ Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 151.2, 141.6, 134.8, 93.8, 66.4, 54.6, 19.8; HRMS m/e calcd. for C₇H₁₁O₃N (M)⁺ 157.0733 found 157.0730.

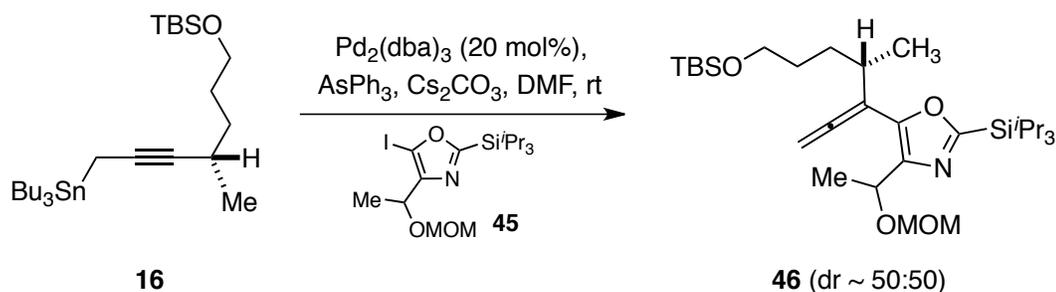


4-(1-(methoxymethoxy)ethyl)-2-(triisopropylsilyl)oxazole (S-11): To a stirred solution of **44** (2.34 g, 14.90 mmol) in dry THF (50 mL) was added freshly generated lithium diisopropylamine solution (46.26 mL, 0.48 M in THF, 22.36 mmol) dropwise at $-78\text{ }^\circ\text{C}$ and stirred at the same temperature for 75 min. A neat $i\text{-Pr}_3\text{SiOTf}$ (6.03 mL, 22.36 mmol) was added dropwise at $-78\text{ }^\circ\text{C}$. After stirring for additional 2 h at $-78\text{ }^\circ\text{C}$, reaction was quenched with saturated aqueous NaHCO_3 solution (30 mL) at $-78\text{ }^\circ\text{C}$. The crude mixture was then extracted in diethyl ether ($3 \times 50\text{ mL}$). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 100% hexanes to 20% diethyl ether in hexanes containing 3% Et_3N) to yield 4.50 g (97% yield) of **S-11** as yellow oil. ($R_f = 0.55$ (SiO_2 , 20% ethyl acetate in hexanes); IR (film) ν_{max} 2945, 2868, 1465, 1038, 883 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.65 (1H, d, $J = 0.5\text{ Hz}$), 4.79 (1H, q, $J = 6.4\text{ Hz}$), 4.69 (1H, A of AB, $J = 6.7\text{ Hz}$), 4.62 (1H, B of AB, $J = 6.7\text{ Hz}$), 3.34 (3H, s), 1.49 (3H, d, $J = 6.4\text{ Hz}$), 1.42–1.30 (3H, m), 1.10 (9H, d, $J = 2.0\text{ Hz}$), 1.08 (9H, d, $J = 1.9\text{ Hz}$); ^{13}C NMR (CDCl_3 , 101 MHz) δ 168.8, 142.5, 136.9, 94.6, 67.5, 55.4, 20.8, 18.5, 11.1; HRMS m/e calcd. for $\text{C}_{16}\text{H}_{31}\text{O}_3\text{NSiNa}$ ($\text{M}+\text{Na}$) $^+$ 336.1971 found 336.1958.



5-iodo-4-(1-(methoxymethoxy)ethyl)-2-(triisopropylsilyl)oxazole (45): To a freshly generated lithium diisopropylamine solution (119.7 mL, 0.44M in THF, 52.75 mmol) was added a solution of **S-**

11 (5.16 g, 16.49 mmol) in dry THF (33 mL) dropwise at $-78\text{ }^{\circ}\text{C}$ and stirred for additional 90 min at the same temperature. A solution of N-iodosuccinimide (11.87 g, 52.75 mmol) in dry THF (66 mL) was then added to the reaction mixture at $-78\text{ }^{\circ}\text{C}$. After stirring for additional 70 min at $-78\text{ }^{\circ}\text{C}$, reaction was quenched with saturated aqueous NaHCO_3 solution (40 mL) at $-78\text{ }^{\circ}\text{C}$. The crude mixture was then extracted in diethyl ether ($3 \times 50\text{ mL}$). The combined organic layers were washed with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution, dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 100% hexanes to 20% diethyl ether in hexanes containing 3% Et_3N) to yield 7.15 g (99% yield) of the desired product as dark yellow oil. $R_f = 0.60$ (SiO_2 , 20% ethyl acetate in hexanes); IR (film) ν_{max} 2944, 2867, 1464, 1040, 883 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 4.72 (1H, q, $J = 6.6\text{ Hz}$), 4.58 (1H, A of AB, $J = 6.8\text{ Hz}$), 4.53 (1H, B of AB, $J = 6.8\text{ Hz}$), 3.33 (3H, s), 1.51 (3H, d, $J = 6.6\text{ Hz}$), 1.44–1.31 (3H, m), 1.11 (9H, d, $J = 5.4\text{ Hz}$), 1.09 (9H, d, $J = 5.4\text{ Hz}$); ^{13}C NMR (CDCl_3 , 101 MHz) δ 174.6, 145.2, 94.4, 89.5, 66.4, 55.5, 20.3, 18.5, 11.1; HRMS *m/e* calcd. for $\text{C}_{16}\text{H}_{30}\text{O}_3\text{NSiINa}$ ($\text{M}+\text{Na}$) $^+$ 462.0937 found 462.0948.



5-((S)-7-((tert-butyldimethylsilyl)oxy)-4-methylhepta-1,2-dien-3-yl)-4-(1-

(methoxymethoxy)ethyl)-2-(triisopropylsilyl)oxazole (46): To a stirred solution of iodide **45** (2.00 g, 4.56 mmol) in dry DMF (30 mL) was added stannane **16** (3.14 g, 5.92 mmol), $\text{Pd}_2(\text{dba})_3$ (835 mg, 0.91 mmol), AsPh_3 (1.12 g, 3.65 mmol) and Cs_2CO_3 (10.41 g, 31.92 mmol) at rt. After stirring for 17 h at rt, the reaction was quenched with saturated aqueous NaHCO_3 solution (20 mL). The insoluble solid was filtered off and washed with ethyl acetate (50 mL). The crude mixture was then extracted in

(4S)-5-(4-(1-(methoxymethoxy)ethyl)oxazol-5-yl)-4-methylhepta-5,6-dien-1-ol (S-12): To a stirred solution of **46** (1.91 g, 3.46 mmol) in anhydrous MeOH (23 mL) was added pyridinium *p*-toluenesulfonate (6.96 g, 27.68 mmol) at rt. After stirring for 20 h at rt, the reaction was quenched with saturated aqueous NaHCO₃ solution (20 mL). The crude mixture was then extracted in ethyl acetate (4 × 40 mL). The combined organic layers were dried over MgSO₄ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 20% ethyl acetate in hexanes to 80% ethyl acetate in hexanes) to yield 760 mg (78% yield) of the **S-12** (colorless oil) as separable 1:1 mixture of diastereomers.

Diastereomer #1: $R_f = 0.18$ (SiO₂, 50% ethyl acetate in hexanes); $[\alpha]_D^{20} -1.9^\circ$ (c 2.00, CHCl₃); IR (film) ν_{\max} 3393, 2933, 1726, 1514, 1453, 1374, 1158, 1029, 919 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.80 (1H, s), 5.10 (2H, qd, $J = 12.2, 2.2$ Hz), 4.91 (1H, q, $J = 6.5$ Hz), 4.53 (1H, A of AB, $J = 6.9$ Hz), 4.47 (1H, B of AB, $J = 6.9$ Hz), 3.63–3.47 (2H, m), 3.31 (3H, s), 2.69–2.58 (1H, m), 2.15 (1H, br s), 1.59–1.47 (3H, m), 1.45 (3H, d, $J = 6.6$ Hz), 1.43–1.37 (1H, m), 1.10 (3H, d, $J = 6.9$ Hz); ¹³C NMR (CDCl₃, 101 MHz) δ 208.4, 150.2, 143.7, 136.1, 100.1, 93.9, 79.6, 65.3, 62.9, 55.4, 33.6, 31.8, 29.9, 20.3, 19.3; HRMS *m/e* calcd. for C₁₅H₂₄O₄N (M+H)⁺ 282.1700 found 282.1700.

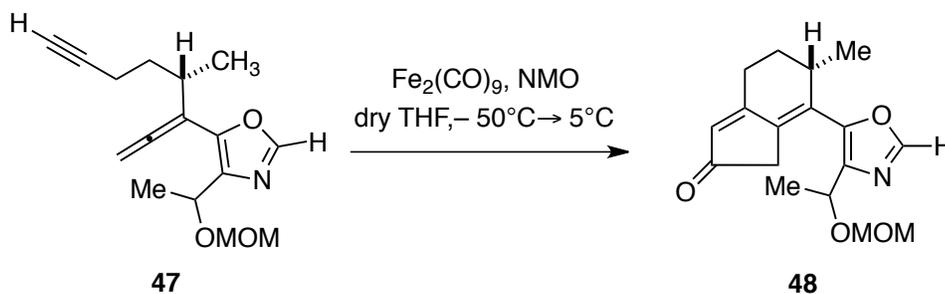
Diastereomer #2: $R_f = 0.17$ (SiO₂, 50% ethyl acetate in hexanes); $[\alpha]_D^{20} +55.8^\circ$ (c 2.00, CHCl₃); ¹H NMR (CDCl₃, 400 MHz) δ 7.78 (1H, s), 5.14–5.04 (2H, m), 4.91 (1H, q, $J = 6.5$ Hz), 4.52 (1H, A of AB, $J = 6.8$ Hz), 4.48 (1H, B of AB, $J = 6.8$ Hz), 3.61–3.51 (2H, m), 3.29 (3H, s), 2.61–2.47 (1H, m), 2.16 (1H, br s), 1.64–1.47 (3H, m), 1.43 (3H, d, $J = 6.5$ Hz), 1.40–1.32 (1H, m), 1.08 (3H, d, $J = 6.8$ Hz); ¹³C NMR (CDCl₃, 101 MHz) δ 208.1, 150.1, 143.3, 136.3, 100.2, 94.0, 79.5, 65.3, 62.8, 55.4, 34.3, 31.7, 30.6, 20.2, 20.1.

(4S)-5-(4-(1-(methoxymethoxy)ethyl)oxazol-5-yl)-4-methylhepta-5,6-dienal (S-13): To a stirred solution of **S-12** (690 mg, 2.45 mmol) in anhydrous DMSO (14.5 mL) was added IBX (993 mg, 3.55 mmol) at rt. After stirring for 3 h at rt, the reaction was quenched with saturated aqueous NaHCO₃

solution (10 mL). The crude mixture was then extracted in ethyl acetate (4 × 30 mL). The combined organic layers were dried over MgSO₄ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 10% ethyl acetate in hexanes to 50% ethyl acetate in hexanes) to yield 550 mg (81% yield) of **S-13** (colorless oil) as inseparable 1:1 mixture of diastereomers. $R_f = 0.42$ (SiO₂, 50% ethyl acetate in hexanes); $[\alpha]_D^{20} +23.5^\circ$ (c 2.15, CHCl₃); IR (film) ν_{\max} 2933, 1724, 1515, 1454, 1375, 1301, 1100, 1030, 919 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz, asterisk denotes other diastereomer signals) δ 9.71 (1H, s), 9.69* (1H, s), 7.78 (1H, s), 7.77* (1H, s), 5.16–5.09 (2H, m), 5.12* (2H, qd, $J = 12.4, 2.0$ Hz), 4.90 (1H, q, $J = 6.5$ Hz), 4.51 (1H, A of AB, $J = 6.8$ Hz), 4.49* (1H, A of AB, $J = 6.8$ Hz), 4.46 (1H, B of AB, $J = 6.8$ Hz), 4.44* (1H, B of AB, $J = 6.8$ Hz), 3.27 (3H, s), 3.26* (3H, s), 2.68–2.53 (1H, m), 2.49–2.34 (2H, m), 1.85–1.62 (2H, m), 1.43 (3H, d, $J = 6.5$ Hz), 1.08 (3H, d, $J = 6.5$ Hz), 1.07* (3H, d, $J = 7.0$ Hz); ¹³C NMR (CDCl₃, 125 MHz, asterisk denotes other diastereomer signals) δ 208.0, 207.8*, 202.2, 202.1*, 150.1, 150.0*, 142.9, 142.8*, 136.6, 136.5*, 99.6, 99.5*, 94.09, 94.07*, 80.2, 80.0*, 65.19, 65.15*, 55.3, 41.8, 41.3*, 33.7, 33.5*, 27.7, 27.6*, 20.1, 19.9, 19.4*; HRMS m/e calcd. for C₁₅H₂₂O₄N (M+H)⁺ 280.1543 found 280.1535.

4-(1-(methoxymethoxy)ethyl)-5-((S)-4-methylocta-1,2-dien-7-yn-3-yl)oxazole (47): To a stirred solution of **S-13** (510 mg, 1.83 mmol) in anhydrous MeOH (18.0 mL) was added K₂CO₃ (481 mg, 3.48 mmol) followed by Bestmann–Ohira reagent (466 μ L, 3.11 mmol) at 0 °C. The reaction mixture was warmed to rt after 10 min and stirred for additional 2 h at rt. The reaction was quenched with saturated aqueous NaHCO₃ solution (10 mL) at 22 °C. The crude mixture was then extracted in ethyl acetate (3 × 30 mL). The combined organic layers were dried over MgSO₄ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 5% ethyl acetate in hexanes to 20% ethyl acetate in hexanes) to yield 430 mg (85% yield) of **47** (colorless oil) as inseparable 1:1 mixture of diastereomers. $R_f = 0.67$ (SiO₂, 50% ethyl acetate in hexanes); $[\alpha]_D^{20} +39.4^\circ$ (c 2.28, CHCl₃); IR (film) ν_{\max} 3296, 2933, 1682, 1514, 1452, 1158, 1099, 1028 cm⁻¹; ¹H

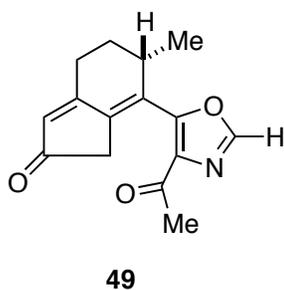
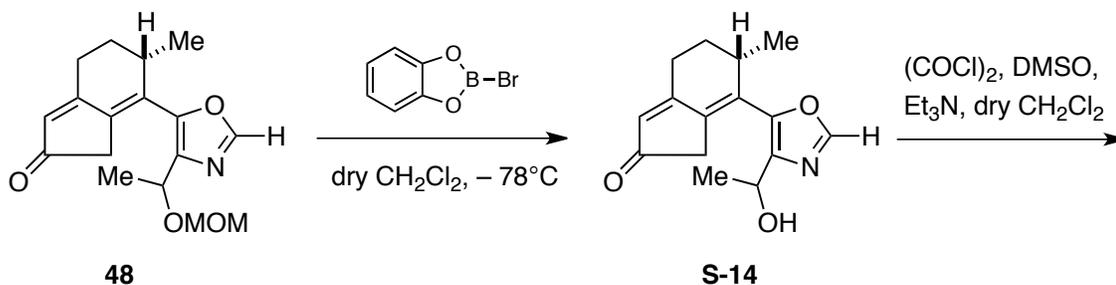
NMR (CDCl₃, 500 MHz, asterisk denotes other diastereomer signals) δ 7.79 (1H, s), 5.18–5.02 (2H, m), 4.94 (1H, q, J = 6.5 Hz), 4.93* (1H, q, J = 6.5 Hz), 4.53 (1H, A of AB, J = 6.8 Hz), 4.49 (1H, B of AB, J = 6.8 Hz), 4.48* (1H, B of AB, J = 6.5 Hz), 3.29 (3H, s), 2.76–2.67 (1H, m), 2.20 (2H, qd, J = 7.3, 2.6 Hz), 1.92 (1H, t, J = 2.6 Hz), 1.90* (1H, t, J = 2.6 Hz), 1.79–1.69 (1H, m), 1.60–1.50 (1H, m), 1.45 (3H, d, J = 6.6 Hz), 1.09 (3H, d, J = 6.9 Hz), 1.07* (3H, d, J = 6.9 Hz); ¹³C NMR (CDCl₃, 125 MHz, asterisk denotes other diastereomer signals) δ 208.0, 207.8*, 150.0, 142.99, 142.97*, 136.6, 136.5*, 99.8, 99.7*, 94.17, 94.15*, 84.05, 84.03*, 80.03, 80.00*, 68.7, 65.3, 65.2*, 55.4, 34.4, 34.1*, 33.28, 33.27*, 20.2, 19.7, 19.4*, 16.4, 16.3*; HRMS m/e calcd. for C₁₆H₂₁O₃NNa (M+Na)⁺ 298.1419 found 298.1406.



(6S)-7-(4-(1-(methoxymethoxy)ethyl)oxazol-5-yl)-6-methyl-5,6-dihydro-1H-inden-2(4H)-one

(48): To a stirred solution of **47** (715 mg, 2.60 mmol) in dry THF (74.0 mL) was added N-methylmorpholine oxide (1.58 g, 13.52 mmol) followed by Fe₂(CO)₉ (2.45 g, 6.76 mmol) at -50°C and stirred for 5 min. The reaction mixture was then transferred to ice-cold bath (0°C) and stirred for additional 50 min. The reaction was then diluted with hexanes (50 mL). The insoluble solid was filtered off and washed with ethyl acetate (2×30 mL). The combined organic layers were evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 25% ethyl acetate in hexanes to 80% ethyl acetate in hexanes) to yield 480 mg (61% yield) of the desired product (yellow oil) as inseparable 1:1 mixture of diastereomers. R_f = 0.16 (SiO₂, 50% ethyl acetate in hexanes); $[\alpha]_D^{20}$ -64.4° (c 1.70, CHCl₃); IR (film) ν_{max} 2933, 1706, 1584, 1447, 1099, 1037 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz, 46°C , asterisk denotes other diastereomer signals) δ 7.84

(1H, s), 7.83* (1H,s), 6.01 (1H, s), 4.85 (1H, q, $J = 6.4$ Hz), 4.62 (1H, A of AB, $J = 6.9$ Hz), 4.55 (1H, B of AB, $J = 6.9$ Hz), 4.47* (1H, B of AB, $J = 6.8$ Hz), 3.33 (3H, s), 3.29* (3H, s), 3.18 (1H, A of AB, $J = 21.2$ Hz), 3.15* (1H, A of AB, $J = 21.3$ Hz), 3.03 (1H, br m), 2.91* (1H, br m), 2.90 (1H, B of AB, $J = 20.9$ Hz), 2.85* (1H, B of AB, $J = 21.3$ Hz), 2.79–2.68 (2H, m), 2.08–1.95 (1H, m), 1.84–1.71 (1H, m), 1.57 (3H, d, $J = 6.4$ Hz), 1.50* (3H, d, $J = 6.5$ Hz), 1.13 (3H, d, $J = 7.0$ Hz), 1.09* (3H, d, $J = 7.0$ Hz); ^{13}C NMR (CDCl_3 , 101 MHz, 46 °C, asterisk denotes other diastereomer signals) δ 204.30, 204.28*, 169.7, 169.5*, 150.81*, 150.77, 145.9*, 145.3, 138.8*, 138.4, 136.8*, 136.5, 129.44*, 129.36, 94.4, 94.1*, 66.9, 66.1*, 55.7, 55.5*, 39.8, 39.5*, 31.8, 31.3*, 29.2, 29.1*, 22.4*, 22.3, 21.1, 20.1, 19.1*, 19.0; HRMS m/e calcd. for $\text{C}_{17}\text{H}_{22}\text{O}_4\text{N}$ ($\text{M}+\text{H}$) $^+$ 304.1543 found 304.1550.

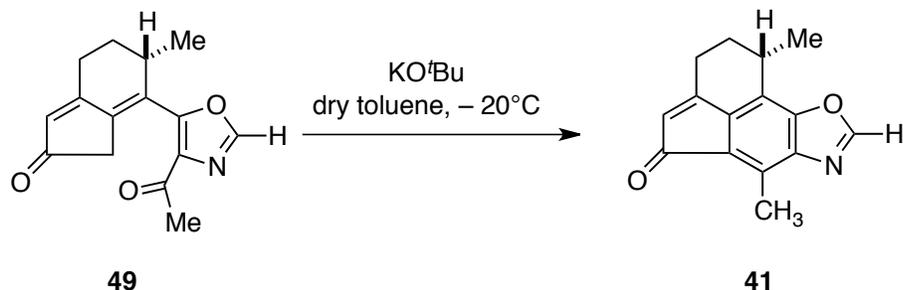


(6S)-7-(4-(1-hydroxyethyl)oxazol-5-yl)-6-methyl-5,6-dihydro-1H-inden-2(4H)-one (S-14): To a stirred solution of **48** (300 mg, 0.99 mmol) in dry CH_2Cl_2 (13.0 mL) was added a solution of B-bromocatecholborane (394 mg, 1.98 mmol) in dry CH_2Cl_2 (5.0 mL) at -78 °C and stirred for 30 min. The reaction was quenched with saturated aqueous NaHCO_3 solution (10 mL) at -78 °C. The crude mixture was then extracted in dichloromethane (4 \times 20 mL). The combined organic layers were

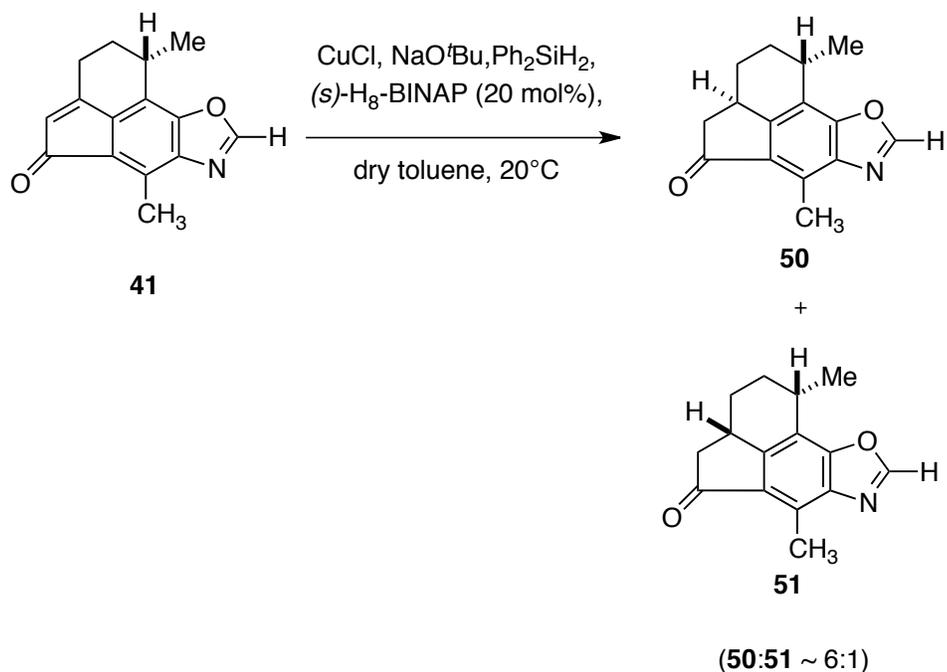
washed with 0.2 M aqueous NaOH solution (2 × 10 mL), dried over MgSO₄ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 50% ethyl acetate in hexanes to 100% ethyl acetate) to yield 218 mg (85% yield) of the **S-14** (yellow oil) as inseparable 1:1 mixture of diastereomers. $R_f = 0.33$ (SiO₂, 100% ethyl acetate in hexanes); $[\alpha]_D^{20} -42.3^\circ$ (c 1.55, CHCl₃); IR (film) ν_{\max} 3393 (br), 2939, 1708, 1440, 1037 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz, asterisk denotes other diastereomer signals) δ 7.86 (1H, s), 6.02 (1H, s), 5.02–4.81 (1H, m), 3.26* (1H, A of AB, $J = 21.4$ Hz), 3.17 (1H, A of AB, $J = 21.3$ Hz), 3.00 (1H, br m), 2.97 (1H, B of AB, $J = 21.3$ Hz), 2.95* (1H, B of AB, $J = 21.4$ Hz), 2.84–2.62 (2H, m), 2.12–1.93 (1H, m), 1.84–1.76 (1H, m), 1.58 (3H, d, $J = 6.4$ Hz), 1.51* (3H, d, $J = 6.3$ Hz), 1.14* (3H, d, $J = 7.2$ Hz), 1.13 (3H, d, $J = 7.2$ Hz); ¹³C NMR (CDCl₃, 125 MHz, asterisk denotes other diastereomer signals) δ 204.8, 170.0, 169.9*, 150.7, 144.5, 143.9*, 141.0*, 140.9, 135.8*, 135.7, 129.3*, 129.24, 129.17, 129.0*, 63.0, 39.9, 39.8*, 30.94, 30.89*, 28.8*, 28.7, 24.0*, 23.2, 22.1*, 22.0, 19.14, 19.10*; HRMS *m/e* calcd. for C₁₅H₁₇O₃N (M)⁺ 259.1203 found 259.1191.

(S)-7-(4-acetyloxazol-5-yl)-6-methyl-5,6-dihydro-1H-inden-2(4H)-one (49): To a stirred solution of oxalyl chloride (107 μ L, 1.25 mmol) in dry CH₂Cl₂ (13.0 mL) was added DMSO (178 μ L, 2.50 mmol) at –78 °C and stirred for 15 min at the same temperature. A solution of **S-14** (230 mg, 0.89 mmol) in dry CH₂Cl₂ (9.0 mL) was then added to above solution at –78 °C and stirred for 45 min. Et₃N (0.55 mL, 3.92 mmol) was then added at –78 °C and reaction mixture was warmed to –30 °C. After stirring for additional 1 h at –30 °C, the reaction was quenched with saturated aqueous Na₂CO₃ solution (15 mL) at that temperature. The crude mixture was then extracted in ethyl acetate (4 × 30 mL). The combined organic layers were dried over MgSO₄ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 10% ethyl acetate in hexanes to 40% ethyl acetate in hexanes) to yield 185 mg (81% yield) of **49** as yellow oil. $R_f = 0.55$ (SiO₂, 80% ethyl acetate in hexanes); $[\alpha]_D^{20} +65.5^\circ$ (c 1.25, CHCl₃); IR (film) ν_{\max} 2931, 1708 (sh), 1687 (sh), 1588, 1366, 1088, 949 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 7.85 (1H, s), 6.06

(1H, s), 3.17–3.11 (1H, m), 3.08 (1H, A of AB, $J = 21.0$ Hz), 2.84–2.76 (1H, m), 2.72 (1H, dt, $J = 17.5, 5.5$ Hz), 2.66 (1H, B of AB, $J = 21.0$ Hz), 2.58 (3H, s), 2.07 (1H, ddd, $J = 18.2, 10.1, 4.9$ Hz), 1.74 (1H, dt, $J = 11.2, 5.3$ Hz), 0.99 (3H, d, $J = 7.1$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz, 50 °C) δ 203.8, 193.9, 168.9, 152.2, 149.3, 140.2, 136.2, 130.4, 129.0, 38.9, 31.5, 29.6, 28.5, 22.9, 19.1; HRMS m/e calcd. for $\text{C}_{15}\text{H}_{16}\text{O}_3\text{N}$ ($\text{M}+\text{H}$) $^+$ 258.1125 found 258.1122.



(S)-1,6-dimethyl-2,3-dihydroacenaphtho[4,5-d]oxazol-5(1H)-one (41): To a stirred solution of **49** (113 mg, 0.44 mmol) in dry toluene (44.0 mL) was added KO^tBu (118 mg, 1.06 mmol) at -30°C and stirred at approximately -20°C for 1 hr. The reaction was quenched with saturated aqueous NH_4Cl solution (20 mL) at -20°C . The crude mixture was then extracted in ethyl acetate (3×30 mL). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 100% hexanes to 30% diethyl ether in hexanes) to yield 98 mg (93% yield) of the desired product as yellow amorphous solid. $R_f = 0.53$ (SiO_2 , 25% ethyl acetate in hexanes); melting point $120\text{--}127^\circ\text{C}$; $[\alpha]_{\text{D}}^{20} +9.3^\circ$ (c 0.60, CHCl_3); IR (film) ν_{max} 2925, 2850, 1697 (sh), 1583, 1062 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 8.00 (1H, s), 5.52 (1H, s), 3.23–3.14 (1H, m), 2.82 (1H, ddd, A of AB, $J = 9.5, 4.5, 1.5$ Hz), 2.71 (3H, s), 2.67 (1H, ddd, B of AB, $J = 9.5, 4.5, 1.5$ Hz), 2.07 (1H, qd, $J = 8.8, 4.6$ Hz), 1.79–1.71 (1H, m), 1.46 (3H, d, $J = 7.1$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 198.1, 160.2, 151.9, 150.5, 141.8, 140.1, 129.6, 124.3, 121.1, 120.8, 30.5, 27.9, 23.2, 19.6, 11.7; HRMS m/e calcd. for $\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}$ (M) $^+$ 239.0941 found 239.0952.



(1*S*,3*aR*)-1,6-dimethyl-2,3,3*a*,4-tetrahydroacenaphtho[4,5-*d*]oxazol-5(1*H*)-one (50):

Preparation of a chiral copper hydride solution: A chiral bis-phosphine (*s*)-H₈-BINAP (25.2 mg, 40.2 μmol) was dissolved in dry toluene (2.0 mL) in an over-dried vial. The vial was transferred inside a glovebox. In the glovebox, CuCl (4.0 mg, 40.2 μmol) and NaO^{*t*}Bu (3.9 mg, 40.2 μmol) were weighed in a vial and subsequently dissolved in a toluene solution of (*s*)-H₈-BINAP. The vial was removed from the glovebox, stirred at rt for 20 min and Ph₂SiH₂ (19.7 μL, 0.11 mmol) was then added dropwise at rt. After stirring for 25 min, the solution was observed to be orange in color. This solution served as reductant toward chiral conjugate reduction of **41**.

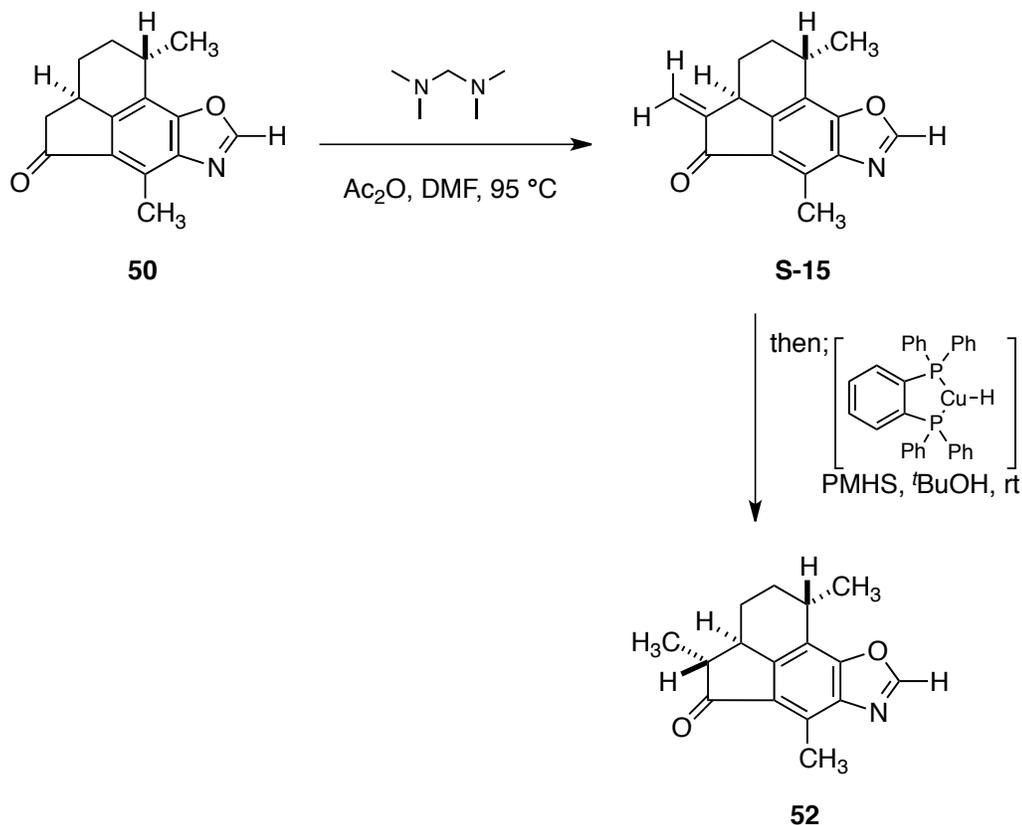
To a stirred solution of **41** (48 mg, 0.20 mmol) in dry toluene (6.0 mL) was added freshly generated chiral copper hydride solution at 20 °C. After stirring for 2 h at 20 °C, reaction was quenched with H₂O (4 mL). The crude mixture was then extracted in ethyl acetate (3 × 20 mL). The combined organic layers were dried over MgSO₄ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 100% hexanes to 10% diethyl ether in

hexanes) to yield 38 mg (79% yield) of (white crystalline solid) inseparable 6:1 mixture of **50** and **51** diastereomers.

50: $R_f = 0.41$ (SiO₂, 25% ethyl acetate in hexanes); $[\alpha]_D^{20} -1.0^\circ$ (c 0.20, CHCl₃); IR (film) ν_{\max} 2928, 1700 (sh), 1595, 1286, 1054 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 8.08 (1H, s), 3.27–3.11 (2H, m), 2.91 (1H, dd, $J = 17.3, 7.0$ Hz), 2.85 (3H, s), 2.36 (1H, dd, $J = 17.3, 7.0$ Hz), 2.34–2.29 (1H, m), 2.25–2.19 (1H, m), 1.61 (1H, tdd, $J = 13.5, 10.6, 3.0$ Hz), 1.54 (3H, d, $J = 6.9$ Hz), 1.41 (1H, ddd, $J = 14.9, 12.8, 2.6$ Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 205.7, 153.9, 152.4, 151.7, 140.4, 129.8, 129.6, 120.7, 46.8, 36.4, 33.2, 29.42, 29.37, 21.1, 12.4; HRMS m/e calcd. for C₁₅H₁₆O₂N (M+H)⁺ 242.1176 found 242.1173

51: $[\alpha]_D^{20} -21.5^\circ$ (c 0.20, CHCl₃); ¹H NMR (CDCl₃, 500 MHz) δ 8.07 (1H, s), 3.43 (1H, p, $J = 7.0$ Hz), 3.14 (1H, td, $J = 11.9, 7.1$ Hz), 2.93 (1H, dd, $J = 17.1, 7.0$ Hz), 2.86 (3H, s), 2.41 (1H, dd, $J = 17.1, 7.4$ Hz), 2.24–2.07 (2H, m), 1.94–1.89 (1H, m), 1.55 (1H, qd, $J = 12.4, 2.6$ Hz), 1.34 (3H, d, $J = 7.2$ Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 205.6, 153.1, 152.4, 151.4, 140.3, 129.8, 129.6, 121.3, 47.0, 36.8, 30.9, 27.1, 24.7, 21.9, 12.4

Separation of diastereomers **50** and **51**: Diastereomer **50** may be enriched by repeated flash chromatography or by preparative HPLC techniques. In order to effect the complete separation of the diastereomers **50** and **51**, these ketones are reduced to give two alcohols (one alcohol from each ketone). These alcohols are completely separated by flash chromatography to give pure samples for oxidation to provide pure **50** and pure **51**. The mixture of diastereomers was subjected to reduction using NaBH₄ to afford the corresponding alcohol as 6:1 mixture of diastereomers. At this stage, major and minor diastereomers were separated by flash silica gel column chromatography (gradient elution from 100% hexanes to 20% ethyl acetate in hexanes). Each diastereomer was then oxidized separately to provide corresponding pure ketone **50** (major and desired) and **51**.

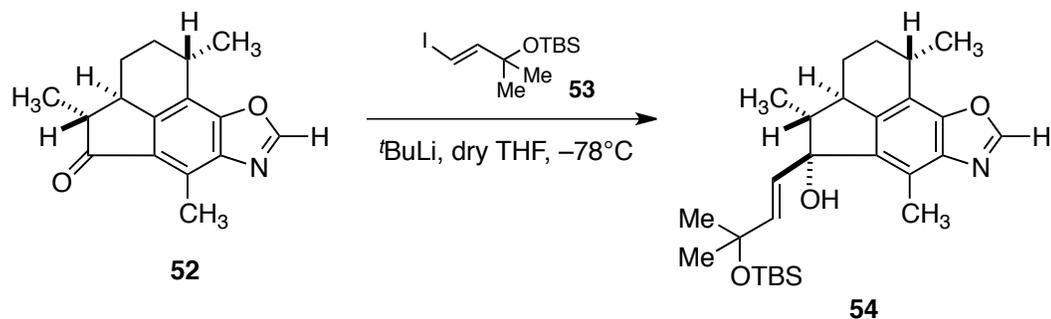


(1*S*,3*aR*,4*R*)-1,4,6-trimethyl-2,3,3*a*,4-tetrahydroacenaphtho[4,5-*d*]oxazol-5(1*H*)-one (52): To a stirred solution of **50** (19 mg, 79.1 μmol) in dry DMF (1.40 mL) was added *N,N,N',N'*-tetramethyldiaminomethane (0.80 mL, 5.93 mmol) and acetic anhydride (0.81 mL, 8.61 mmol) at rt and stirred at 95 $^\circ\text{C}$ for 2 hr. The reaction was then cooled to rt and quenched with saturated aqueous NaHCO_3 solution (3 mL). The crude mixture was then extracted in diethyl ether (6 \times 10 mL). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was passed through a plug of silica-gel (eluted using 10% diethyl ether in hexanes) to obtain pure α -methylenation intermediate **S-15** as a white solid and used in next step without further purification. $R_f = 0.50$ (SiO_2 , 25% ethyl acetate in hexanes); $[\alpha]_D^{20} +22.2^\circ$ (c 0.09, CHCl_3); IR (film) ν_{max} 2927, 1719 (sh), 1260, 1169, 1076 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz), δ 8.10 (1H, s), 6.20 (1H, d, $J = 2.5$ Hz), 5.45 (1H, d, $J = 1.8$ Hz), 3.63 (1H, d, $J = 9.8$ Hz), 3.27–3.18 (1H, m), 2.94 (3H, s), 2.47–2.33 (2H, m), 1.76–1.64 (1H, m), 1.57 (3H, d, $J = 6.8$ Hz), 1.49–1.38 (1H, m); ^{13}C NMR (CDCl_3 , 101

MHz) δ 193.9, 152.5, 151.9, 150.2, 150.0, 140.5, 130.9, 130.4, 120.6, 115.7, 40.4, 32.8, 29.9, 27.4, 21.3, 12.6; HRMS m/e calcd. for $C_{16}H_{16}O_2N$ (M+H)⁺ 254.1176 found 254.1185

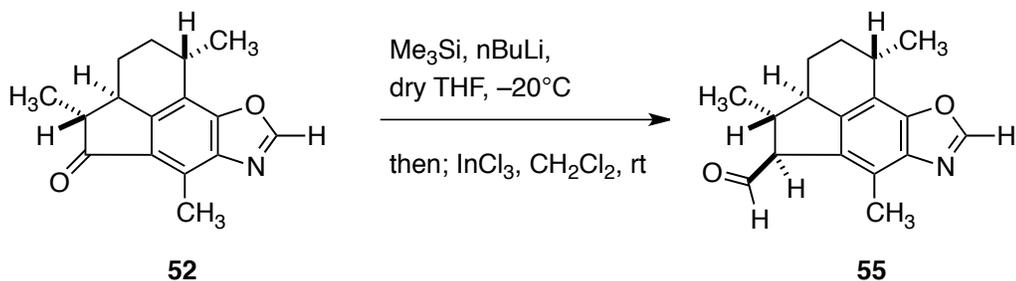
Preparation of a copper hydride solution for reduction of S-15: To a stirred solution of $Cu(OAc)_2 \cdot H_2O$ (3.2 mg, 15.8 μ mol) and bis(diphenylphosphino)benzene (7.9 μ mol) in dry toluene (527 μ L) was added degassed ^tBuOH (21.58 μ L, 0.24 mmol) at rt. The resulting blue solution was stirred for 20 min at rt. PMHS (15.8 μ L, 0.24 mmol) was added at rt and stirred for additional 25 min during which solution changed color from blue to yellow. This solution served as a reductant toward conjugate reduction of S-15.

To a stirred solution of S-15 (20 mg, 79.1 μ mol) in dry toluene (2.6 mL) was added freshly generated copper hydride solution dropwise at rt. After stirring for 1 h at rt, reaction was quenched with H_2O (3 mL). The crude mixture was then extracted in diethyl ether (4 \times 15 mL). The combined organic layers were dried over $MgSO_4$ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 100% hexanes to 10% diethyl ether in hexanes) to yield 15 mg (76% yield) of **52** as white solid. $R_f = 0.53$ (SiO_2 , 25% ethyl acetate in hexanes); Melting point 142–150 °C; $[\alpha]_D^{20} +4.5^\circ$ (c 0.07, $CHCl_3$); IR (film) ν_{max} 2918, 1698, 1056 cm^{-1} ; ¹H NMR ($CDCl_3$, 500 MHz,) δ 8.09 (1H, s), 3.28–3.16 (1H, m), 2.87 (3H, s), 2.80–2.71 (1H, m), 2.42–2.27 (3H, m), 1.67–1.57 (1H, m), 1.55 (3H, d, $J = 6.9$ Hz), 1.42 (1H, dd, $J = 24.4, 11.5$ Hz), 1.35 (3H, d, $J = 7.0$ Hz); ¹³C NMR ($CDCl_3$, 125 MHz) δ 207.6, 152.3, 151.7, 151.6, 140.3, 129.53, 129.48, 120.5, 52.6, 44.8, 33.2, 29.6, 28.5, 21.1, 13.0, 12.4; HRMS m/e calcd. for $C_{16}H_{18}O_2N$ (M+H)⁺ 256.1332 found 256.1322



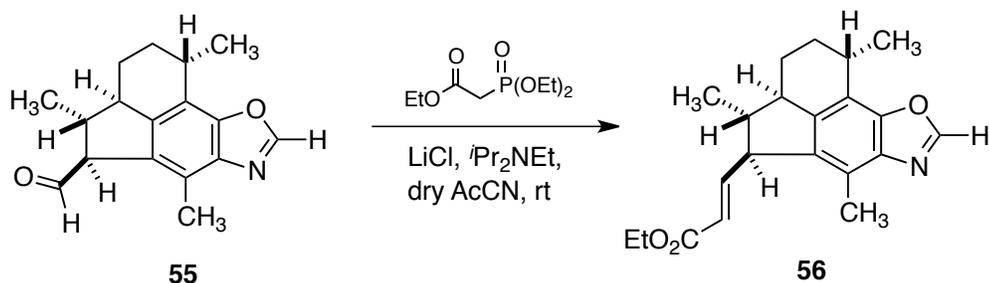
(1*S*,3*aR*,4*R*,5*S*)-5-((*E*)-3-((*tert*-butyldimethylsilyloxy)-3-methylbut-1-en-1-yl)-1,4,6-trimethyl-

1,2,3,3*a*,4,5-hexahydroacenaphtho[4,5-*d*]oxazole (54): To a stirred solution of iodide **53** (102 mg, 0.31 mmol) dry THF (1.25 mL) was added a *t*-BuLi (208 μ L, 0.35 mmol) at -78 °C and stirred for 10 min. The resulting solution was then added to a stirred solution of **52** (10.0 mg, 39.2 μ mol) in dry THF (1.56 mL) at -78 °C. After stirring for 30 min at -78 °C, the reaction was quenched with saturated aqueous NH_4Cl solution (5 mL) at -78 °C. The crude mixture was extracted in diethyl ether (3 \times 30 mL). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 100% hexanes to 10% ethyl acetate in hexanes) to yield 12.0 mg (70% yield) of the desired product as colorless oil. $R_f = 0.33$ (SiO_2 , 25% ethyl acetate in hexanes); $[\alpha]_D^{20} +8.0^\circ$ (c 0.05, CHCl_3); IR (film) ν_{max} 3386 (br), 2923, 1520, 1463, 1081 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz), δ 8.01 (1H, s), 5.73 (1H, d, $J = 15.6$ Hz), 5.56 (1H, d, $J = 15.7$ Hz), 3.19–3.06 (1H, m), 2.59 (3H, s), 2.36 (1H, td, $J = 11.0, 4.1$ Hz), 2.28–2.20 (1H, m), 2.15–2.07 (1H, m), 1.99–1.91 (1H, m), 1.51 (3H, d, $J = 6.9$ Hz), 1.48–1.41 (2H, m), 1.29 (3H, s), 1.26 (3H, s), 1.14 (3H, d, $J = 6.8$ Hz), 0.83 (9H, s), 0.02 (3H, s), 0.00 (3H, s); ^{13}C NMR (CDCl_3 , 125 MHz) δ 151.3, 148.0, 140.6, 139.8, 139.4, 125.2, 125.1, 119.6, 85.8, 73.4, 58.4, 45.1, 33.5, 31.1, 30.8, 29.9, 28.2, 26.0, 21.0, 18.3, 12.1, -1.9 ; HRMS m/e calcd. for $\text{C}_{27}\text{H}_{42}\text{O}_3\text{NSi}$ ($\text{M}+\text{H}$) $^+$ 456.2928 found 456.2940

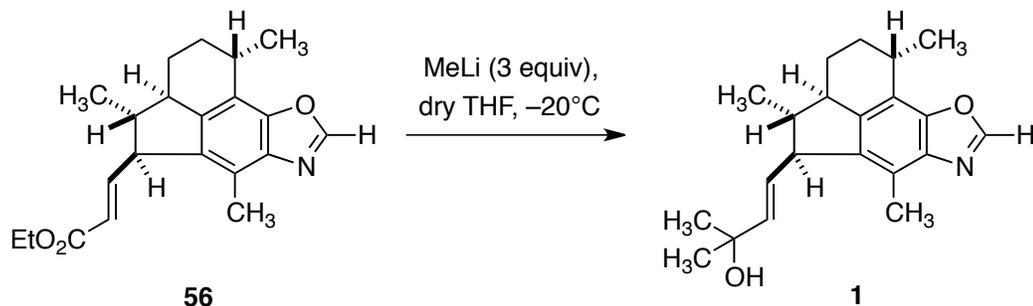


(1S,3aR,4R,5S)-1,4,6-trimethyl-1,2,3,3a,4,5-hexahydroacenaphtho[4,5-d]oxazole-5-carbaldehyde (55): To a stirred suspension of Me_3Si (31.4 mg, 153.7 μmol) in dry THF (1.40 mL) was added $n\text{BuLi}$ (55 μL , 137.3 μmol) dropwise at -30°C and stirred at 0°C for 90 min. The resulting solution of sulfur ylide was then added to a stirred solution of **52** (14 mg, 54.9 μmol) in dry THF (2.46 mL) at -25°C . After stirring for 15 min at -25°C , reaction was quenched with H_2O (3 mL). The crude mixture was then extracted in diethyl ether (4×10 mL). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude epoxide was used without further purification.

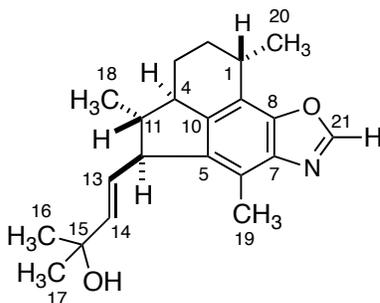
To a stirred solution of epoxide (12 mg, 44.6 μmol) in dry CH_2Cl_2 (2.3 mL) was added InCl_3 (5.9 mg, 26.8 μmol) at rt. After stirring for 10 min at rt, reaction was quenched with saturated aqueous NaHCO_3 solution (2 mL). The crude mixture was then extracted in diethyl ether (3×10 mL). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 100% hexanes to 10% diethyl ether in hexanes) to yield 10.8 mg (90% yield) of **55** as white amorphous solid. $R_f = 0.41$ (SiO_2 , 25% ethyl acetate in hexanes); $[\alpha]_D^{20} +44.0^\circ$ (c 0.08, CHCl_3); IR (film) ν_{max} 2916, 1717, 1078 cm^{-1} ; ^1H NMR (CD_2Cl_2 , 500 MHz) δ 9.53 (1H, d, $J = 5.1$ Hz), 8.02 (1H, s), 3.28–3.16 (1H, m), 3.65 (1H, dd, $J = 9.8, 5.1$ Hz), 3.17–3.07 (1H, m), 2.70 (1H, td, $J = 10.5, 3.7$ Hz), 2.40 (3H, s), 2.32–2.10 (3H, m), 1.50 (3H, d, $J = 6.8$ Hz), 1.49–1.44 (1H, m), 1.36–1.31 (1H, m), 1.25 (3H, d, $J = 6.7$ Hz); ^{13}C NMR (CD_2Cl_2 , 125 MHz) δ 202.0, 167.9, 151.7, 143.3, 133.0, 132.8, 124.7, 120.9, 64.4, 49.0, 45.7, 33.9, 30.1, 29.9, 28.5, 20.8, 14.1; HRMS m/e calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{N}$ ($\text{M}+\text{H}$) $^+$ 270.1494 found 270.1496



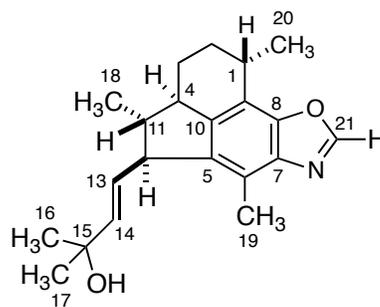
(E)-ethyl-3-((1*S*,3*aR*,4*R*,5*S*)-1,4,6-trimethyl-1,2,3,3*a*,4,5-hexahydroacenaphtho[4,5-*d*]oxazol-5-yl)acrylate (56): To a stirred solution of **55** (7.5 mg, 27.9 μmol) in dry AcCN (2.80 mL) was added LiCl (53.2 mg, 1.26 mmol), triethyl phosphonoacetate (134 μL , 0.67 mmol) and *i*Pr₂NEt (117 μL , 0.67 mmol) sequentially at rt. After stirring for 14 h at rt, reaction was quenched with H₂O (2 mL). The crude mixture was then extracted in ethyl acetate (3 \times 15 mL). The combined organic layers were dried over MgSO₄ and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 100% hexanes to 20% diethyl ether in hexanes) to yield 7 mg (74% yield) of the desired product as colorless oil. $R_f = 0.22$ (SiO₂, 10% ethyl acetate in hexanes); $[\alpha]_D^{20} +28.0^\circ$ (c 0.08, CHCl₃); IR (film) ν_{max} 2927, 1719 (sh), 1650, 1520, 1456, 1261, 1076 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz), δ 8.00 (1H, s), 6.95 (1H, dd, $J = 15.6, 10.1$ Hz), 6.04 (1H, d, $J = 15.6$ Hz), 4.22 (2H, qd, $J = 7.1, 0.9$ Hz), 3.57 (1H, t, $J = 9.9$ Hz), 3.20–3.05 (1H, m), 2.59 (1H, td, $J = 10.7, 2.9$ Hz), 2.47 (3H, s), 2.29–2.23 (1H, m), 2.20–2.15 (1H, m), 1.82–1.73 (1H, m), 1.52–1.43 (1H, m), 1.50 (3H, d, $J = 6.9$ Hz), 1.31 (3H, t, $J = 7.1$ Hz), 1.29–1.21 (1H, m), 1.18 (3H, d, $J = 6.6$ Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 166.7, 151.2, 151.1, 147.7, 142.2, 139.6, 136.9, 124.8, 122.4, 120.0, 60.6, 55.5, 50.9, 48.5, 33.7, 29.7, 28.5, 20.9, 15.5, 14.5, 13.8; HRMS m/e calcd. for C₂₁H₂₆O₃N (M+H)⁺ 340.1907 found 340.1914



(+)-ileabethxazole (1): To a stirred solution of **56** (5.0 mg, 14.8 μmol) in dry THF (1.85 mL) was added MeLi (27.8 μL , 1.6 M in Et_2O , 44.4 μmol) dropwise at -78°C . After stirring for 10 min at -78°C , reaction was quenched with H_2O (2 mL) at -78°C , and allowed to warm to rt. The crude mixture was then extracted in ethyl acetate (4×10 mL). The combined organic layers were dried over MgSO_4 and evaporated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (gradient elution from 10% diethyl ether in hexanes to 60% diethyl ether in hexanes) to yield 4.2 mg (87% yield) of the synthetic sample of ileabethoxazole (**1**) as colorless oil. $R_f = 0.47$ (SiO_2 , 50% ethyl acetate in hexanes); $[\alpha]_D^{20} +9.3^{\circ}$ (c 0.15, CHCl_3); IR (film) ν_{max} 3381 (br), 2923, 2851, 1461, 1078 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 7.99 (1H, s), 5.86 (1H, d, $J = 15.6$ Hz), 5.60 (1H, dd, $J = 15.6, 9.5$ Hz), 3.37 (1H, t, $J = 9.6$ Hz), 3.16–3.05 (1H, m), 2.58–2.41 (1H, m), 2.51 (3H, s), 2.29–2.20 (1H, m), 2.19–2.12 (1H, m), 1.69–1.59 (1H, m), 1.50 (3H, d, $J = 6.9$ Hz), 1.49–1.43 (1H, m), 1.39 (6H, s), 1.33–1.20 (1H, m), 1.16 (3H, d, $J = 6.6$ Hz); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz) δ 150.9, 147.2, 142.1, 139.4, 139.3, 138.0, 129.7, 124.4, 119.5, 70.7, 55.5, 51.3, 48.0, 33.6, 29.9, 29.7, 29.5, 28.3, 20.7, 15.2, 13.5; HRMS m/e calcd. for $\text{C}_{21}\text{H}_{28}\text{O}_2\text{N}$ ($\text{M}+\text{H}$) $^+$ 326.2120 found 326.2110.

Table 1 Comparison of ^1H NMR signals for synthetic and natural (+)-ileabethoxazole (**1**)ileabethoxazole (**1**)

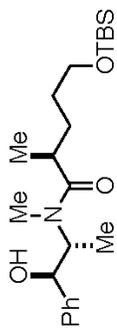
H	Natural	Synthetic
1	3.11 (m)	3.05–3.16 (m)
2 α	2.24 (m)	2.20–2.29 (m)
2 β	1.46 (m)	1.43–1.49 (m)
3 α	2.16 (m)	2.12–2.19 (m)
3 β	1.25 (m)	1.20–1.33 (m)
4	2.50 (m)	2.41–2.58 (m)
11	1.63 (m)	1.59–1.69 (m)
12	3.37 (dd, $J = 9.7, 9.5$ Hz)	3.37 (t, $J = 9.6$ Hz)
13	5.60 (dd, $J = 15.6, 9.5$ Hz)	5.61 (dd, $J = 15.6, 9.5$ Hz)
14	5.86 (d, $J = 15.6$ Hz)	5.86 (d, $J = 15.6$ Hz)
16	1.39 (s)	1.39 (s)
17	1.39 (s)	1.39 (s)
18	1.16 (d, $J = 6.6$ Hz)	1.16 (d, $J = 6.6$ Hz)
19	2.51 (s)	2.51 (s)
20	1.50 (d, $J = 6.9$ Hz)	1.50 (d, $J = 6.9$ Hz)
21	7.99 (s)	7.99 (s)

Table 2 Comparison of ^{13}C NMR signals for synthetic and natural (+)-ilebethoxazole (**1**).ilebethoxazole (**1**)

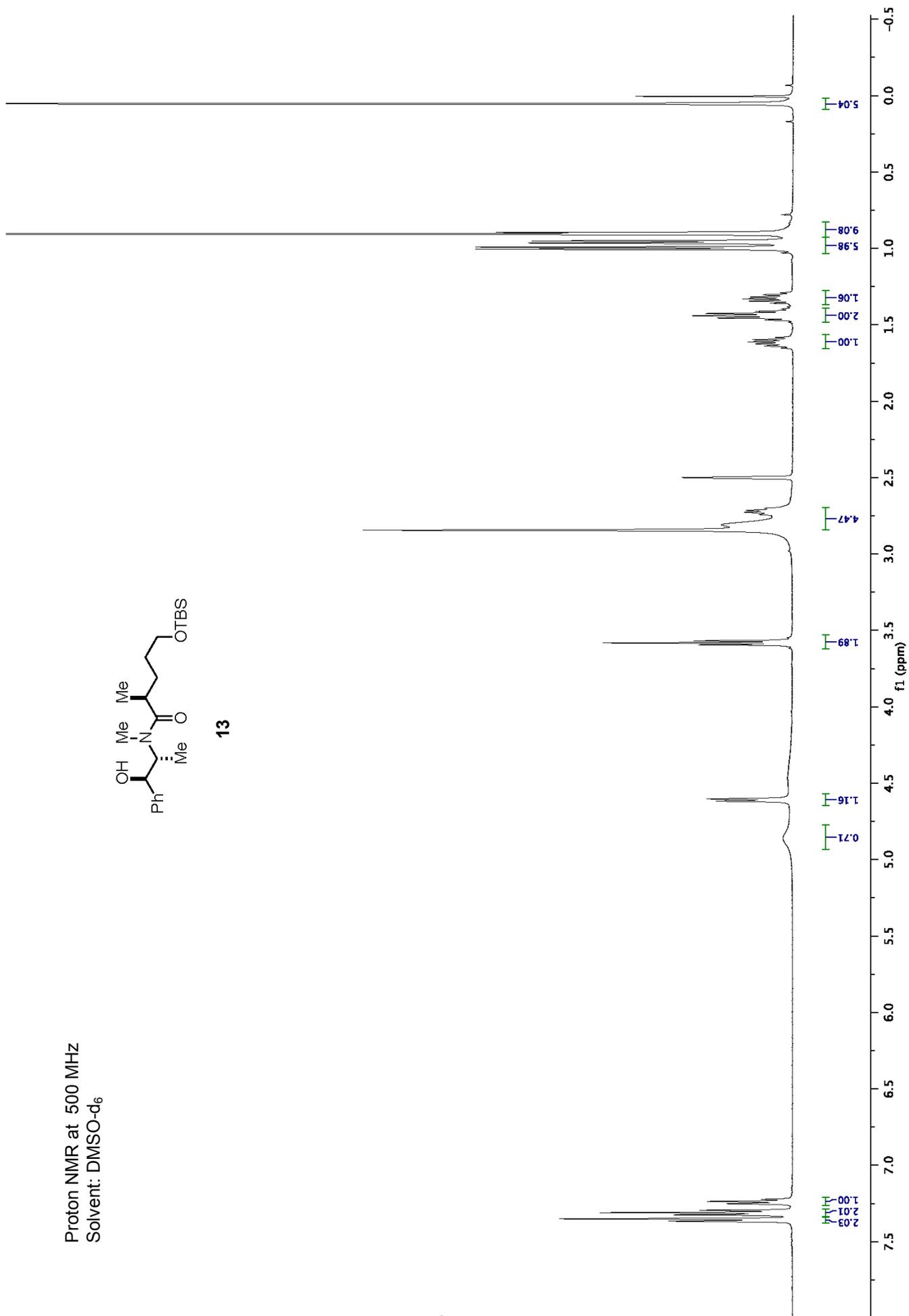
C	Natural	Synthetic	$\Delta(\delta \text{ ppm})$
1	29.5	29.5	0.0
2	33.5	33.6	0.1
3	28.3	28.3	0.0
4	48.0	48.0	0.0
5	138.0	138.0	0.0
6	124.4	124.4	0.0
7	139.2	139.3	0.1
8	147.2	147.2	0.0
9	119.5	119.5	0.0
10	142.1	142.1	0.0
11	51.2	51.2	0.0
12	55.5	55.5	0.0
13	129.6	129.7	0.1
14	139.4	139.4	0.0
15	70.8	70.7	0.1
16	29.7	29.7	0.0
17	29.8	29.9	0.1
18	15.2	15.2	0.0

19	13.5	13.5	0.0
20	20.7	20.7	0.0
21	150.9	150.9	0.0

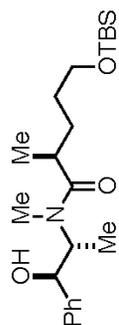
Proton NMR at 500 MHz
Solvent: DMSO-d₆



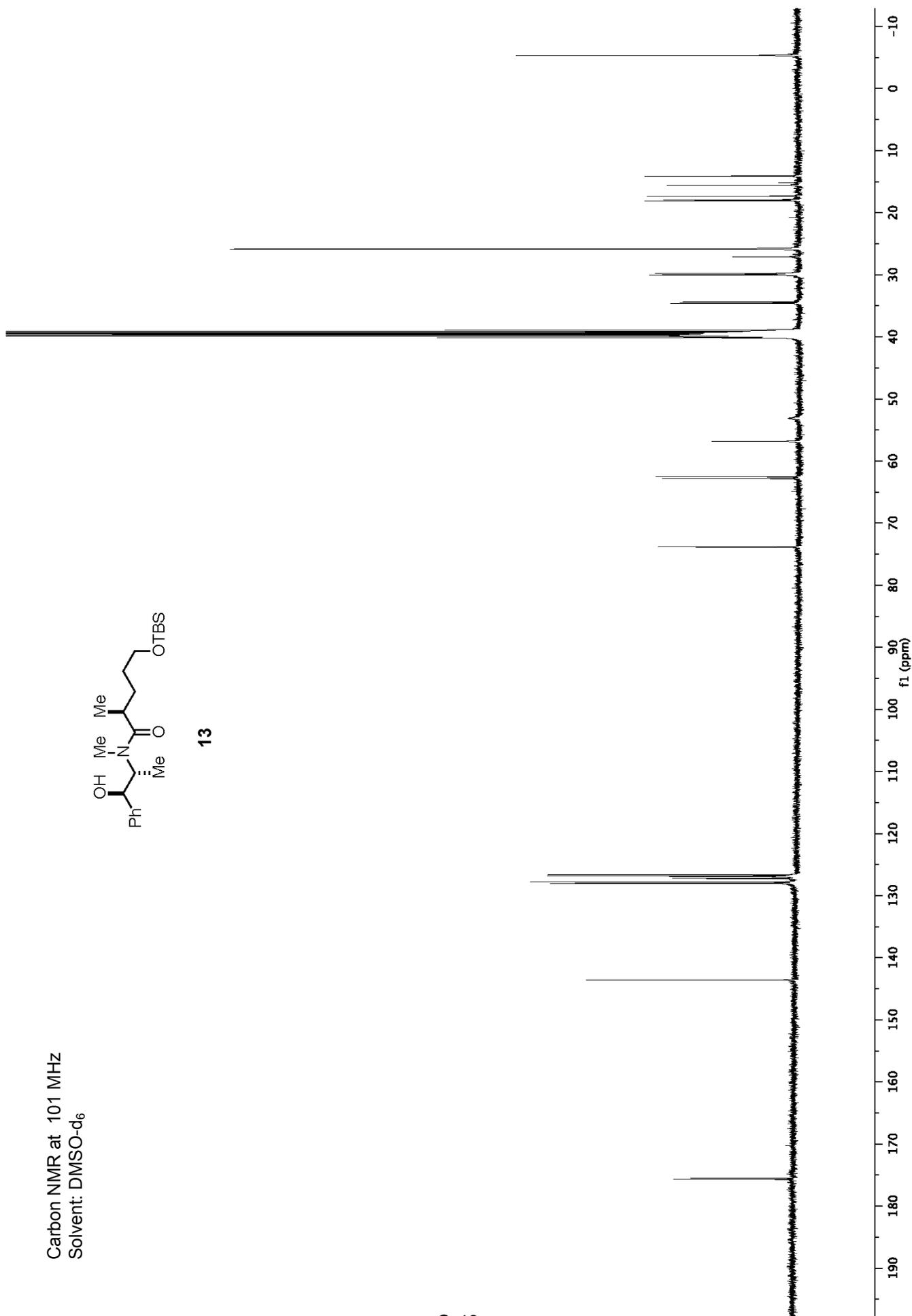
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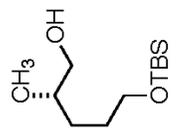
Carbon NMR at 101 MHz
Solvent: DMSO-d₆



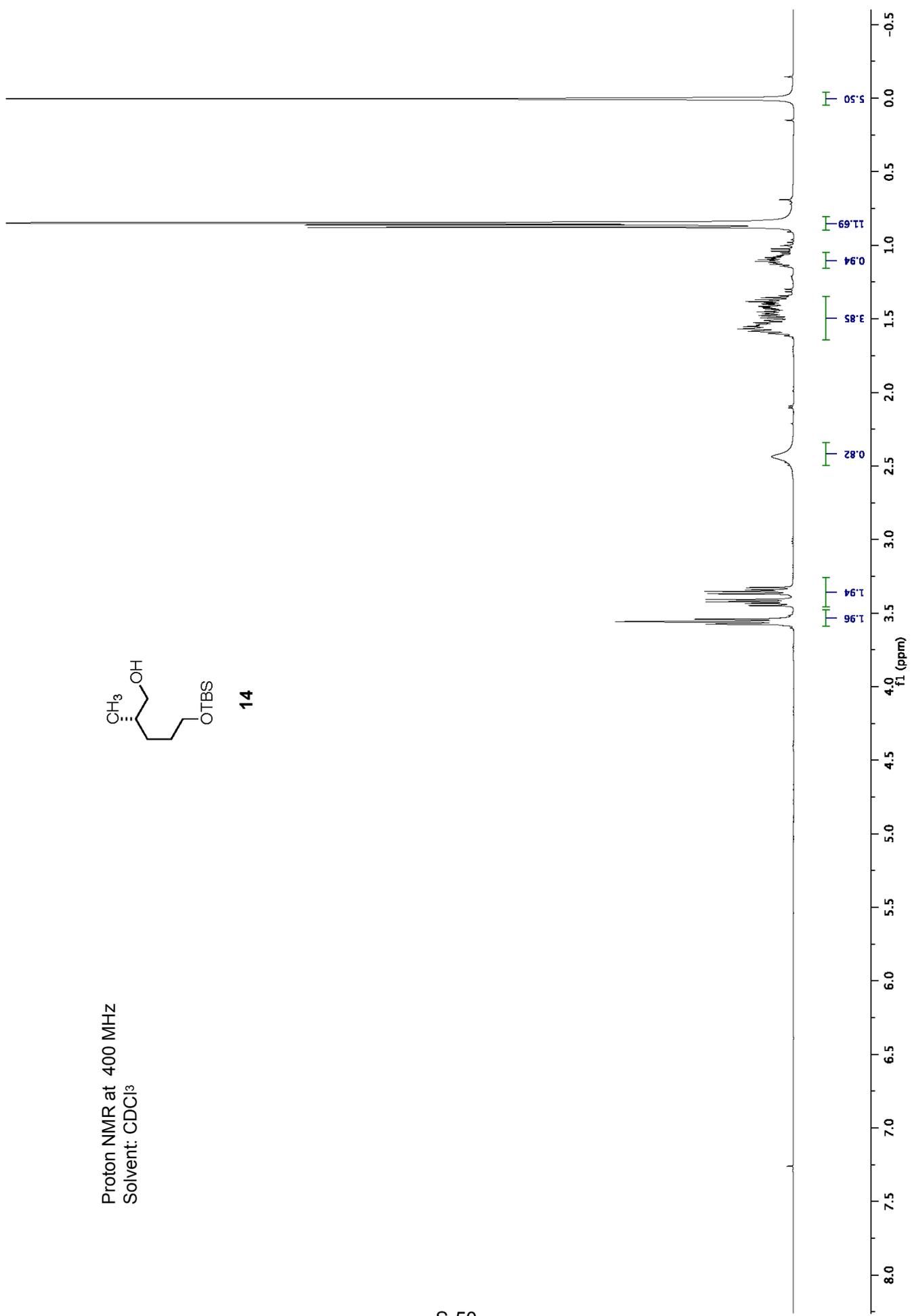
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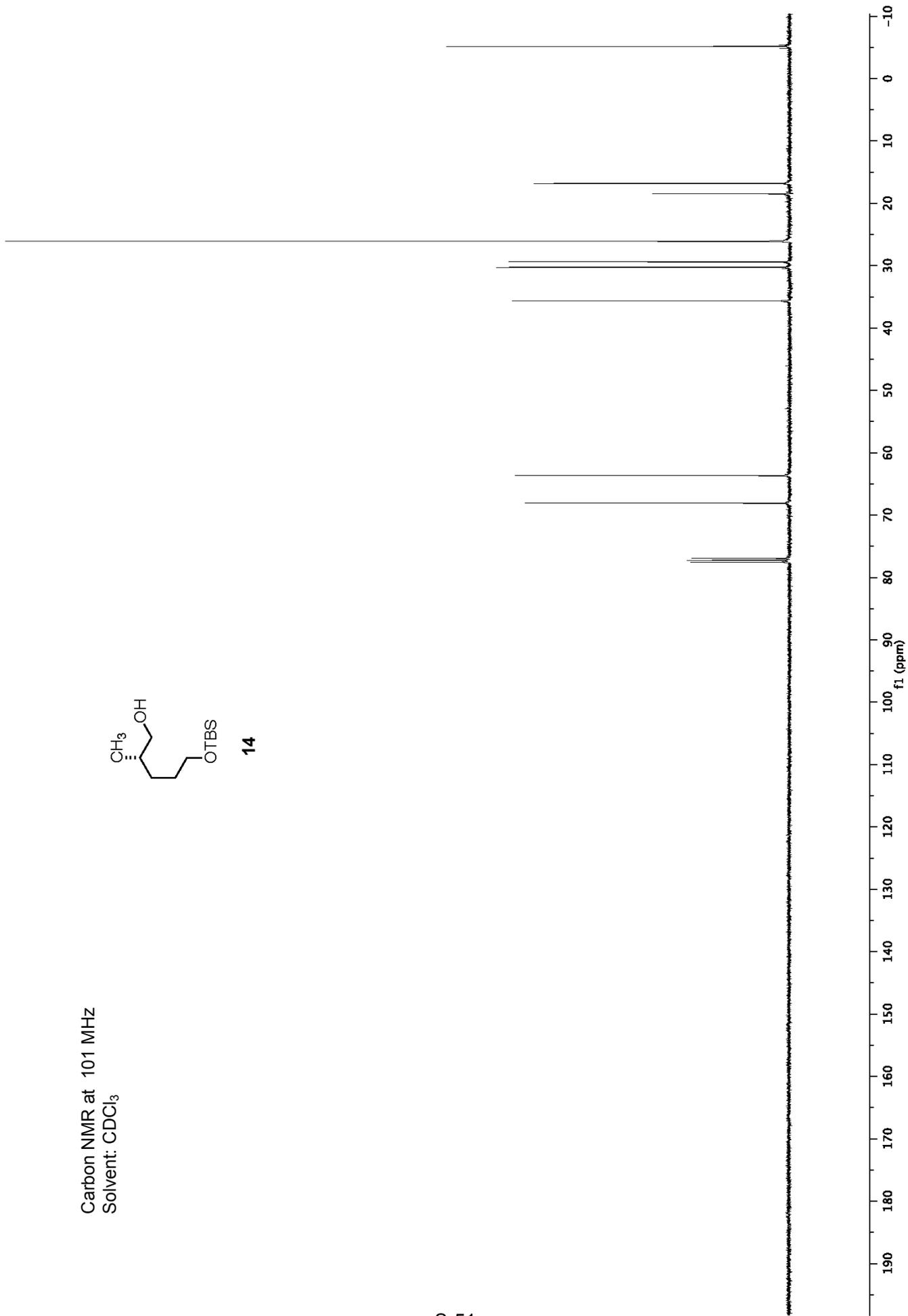
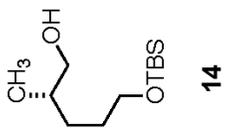
Proton NMR at 400 MHz
Solvent: CDCl₃



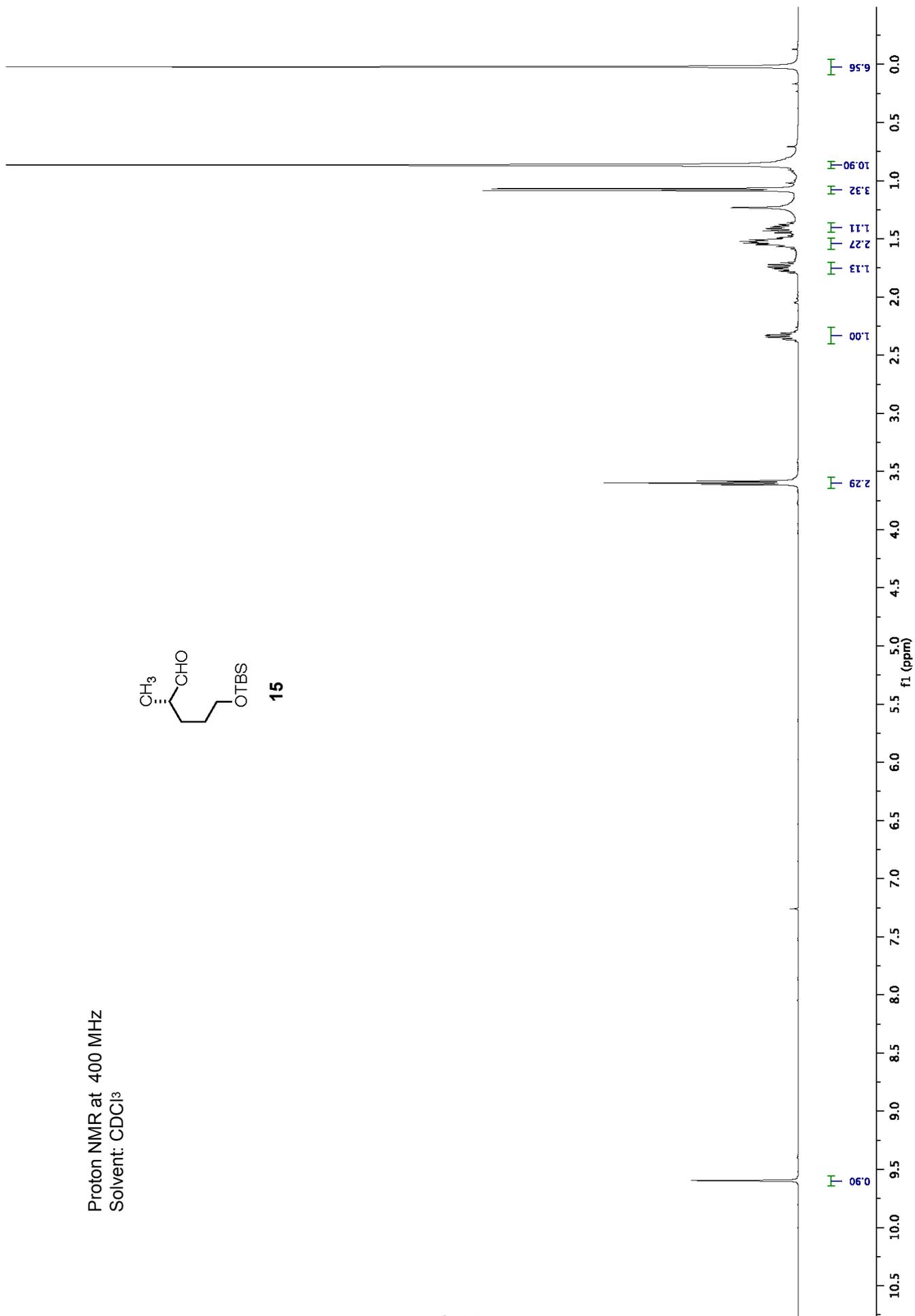
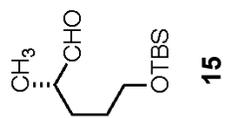
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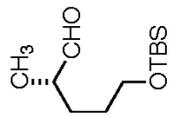
Carbon NMR at 101 MHz
Solvent: CDCl₃



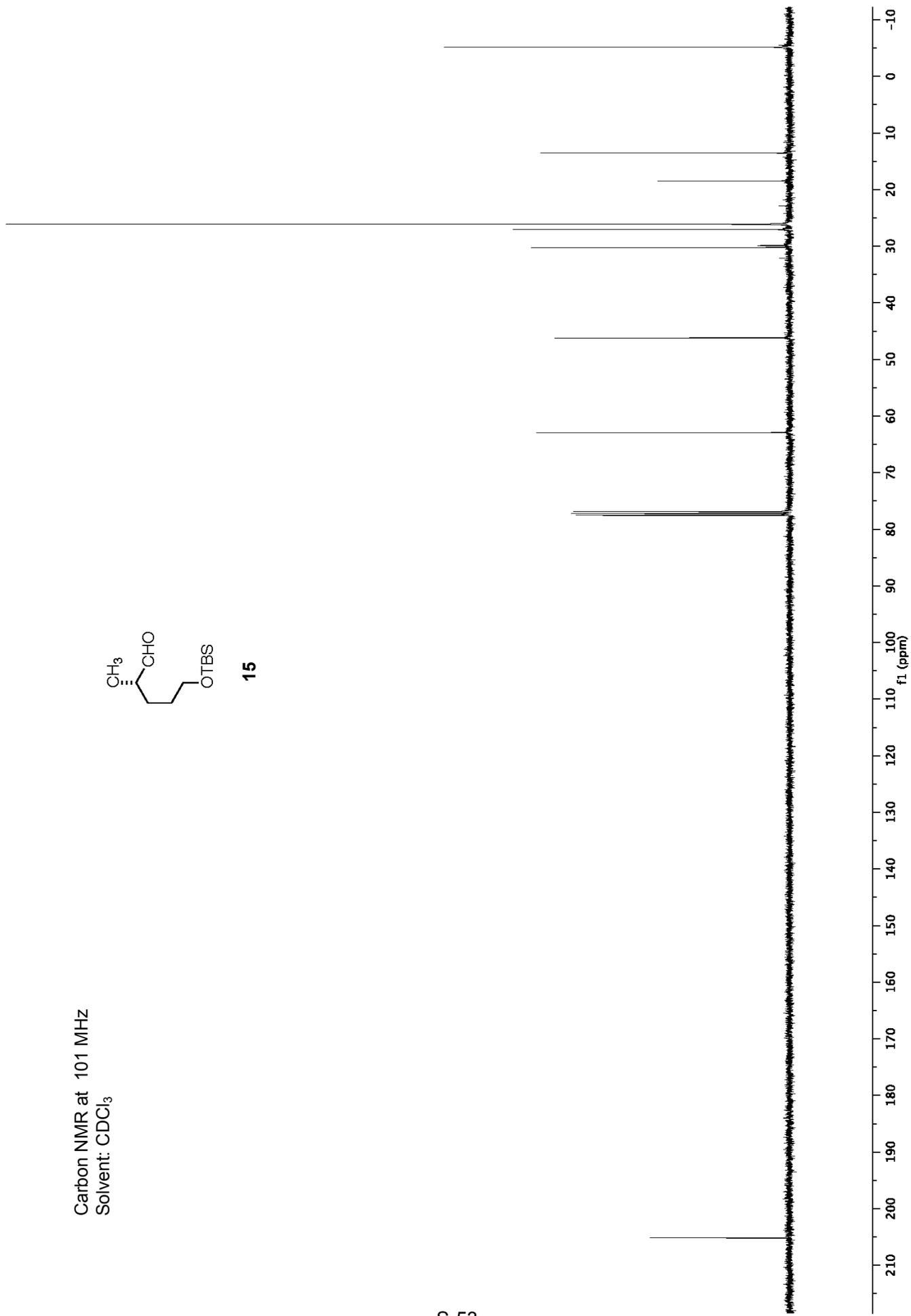
Proton NMR at 400 MHz
Solvent: CDCl₃



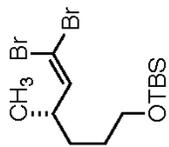
Carbon NMR at 101 MHz
Solvent: CDCl₃



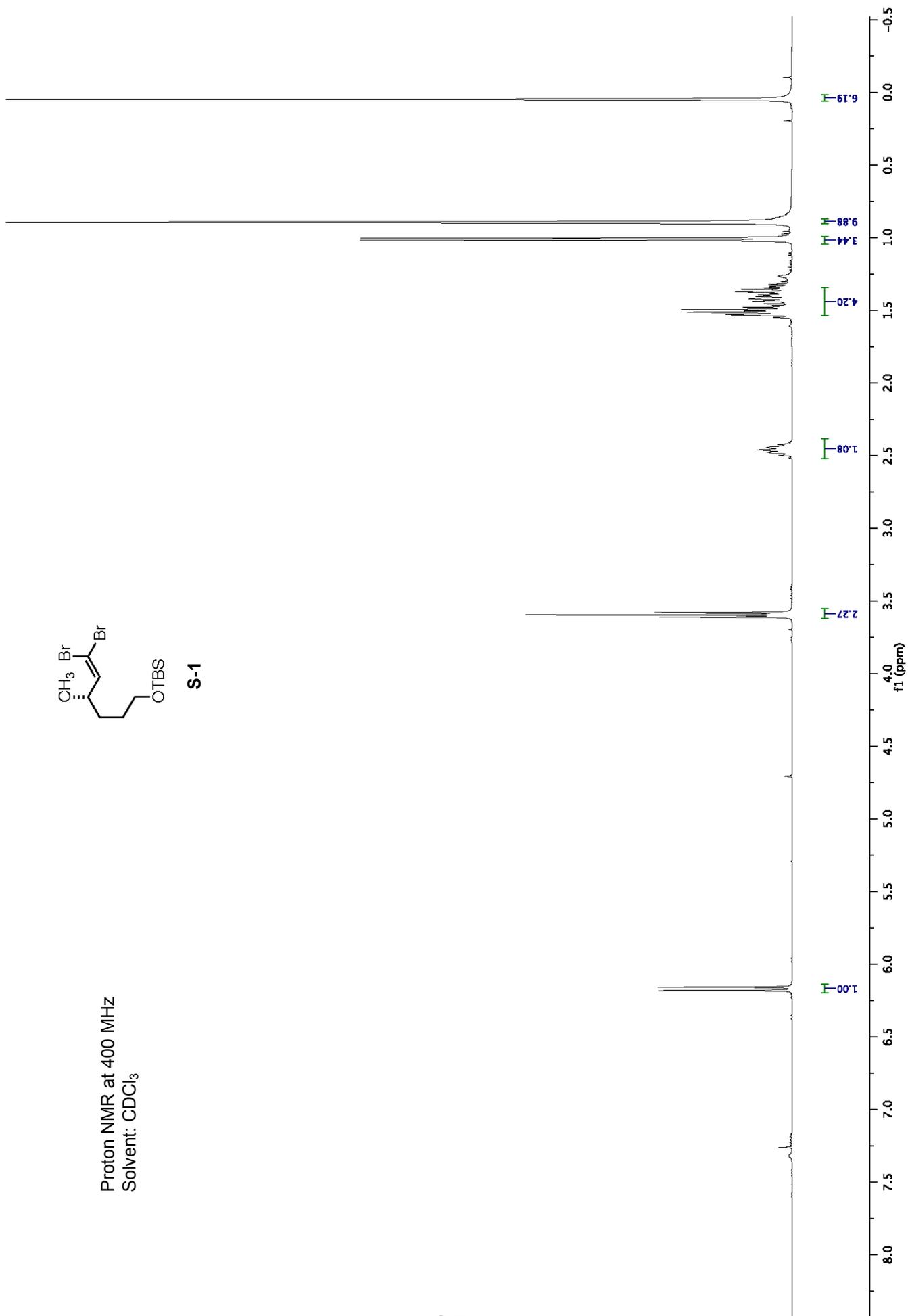
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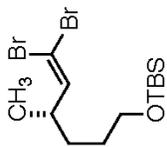
Proton NMR at 400 MHz
Solvent: CDCl₃



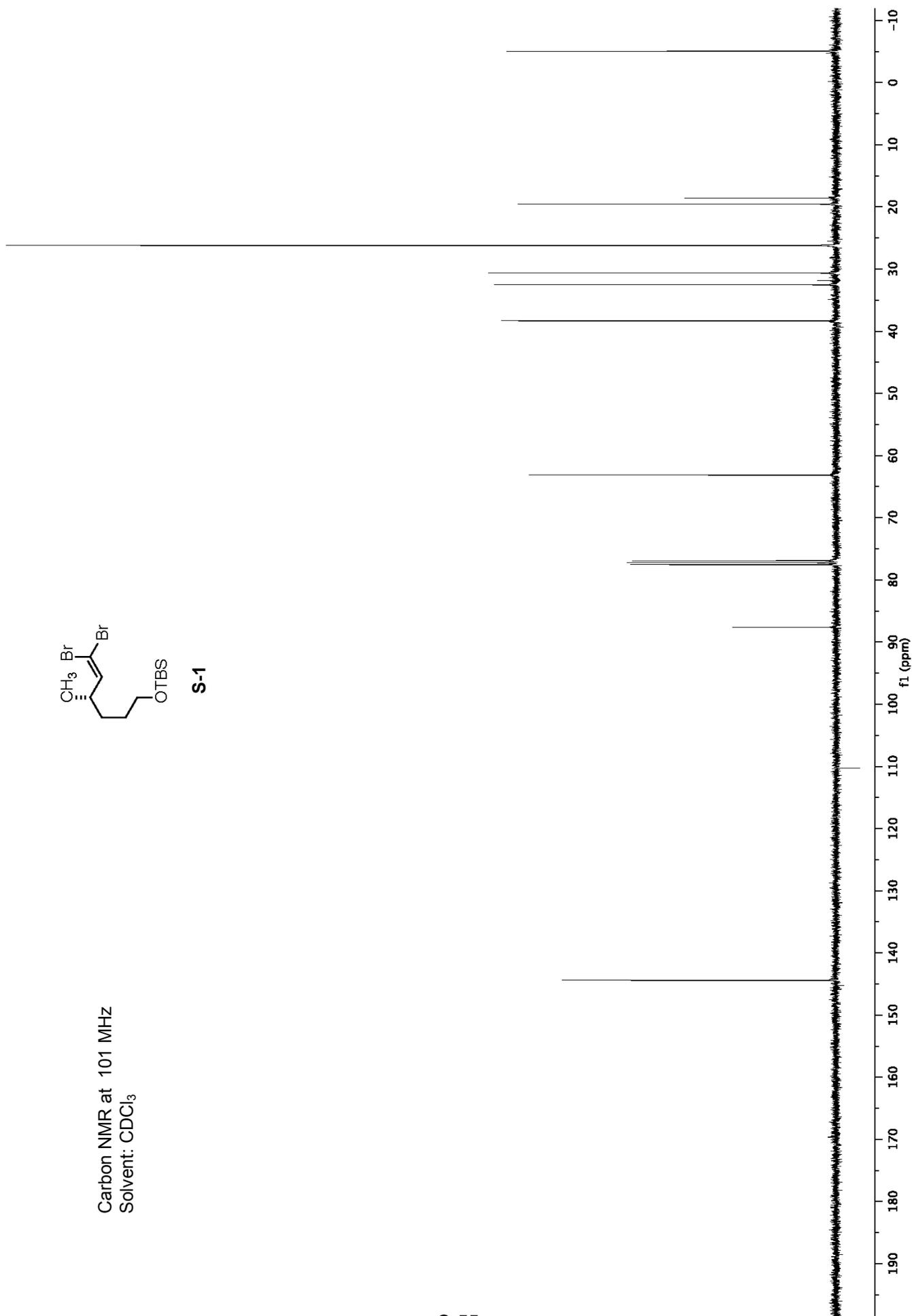
S-1

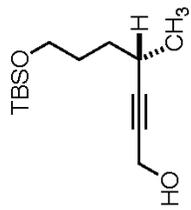


Carbon NMR at 101 MHz
Solvent: CDCl₃



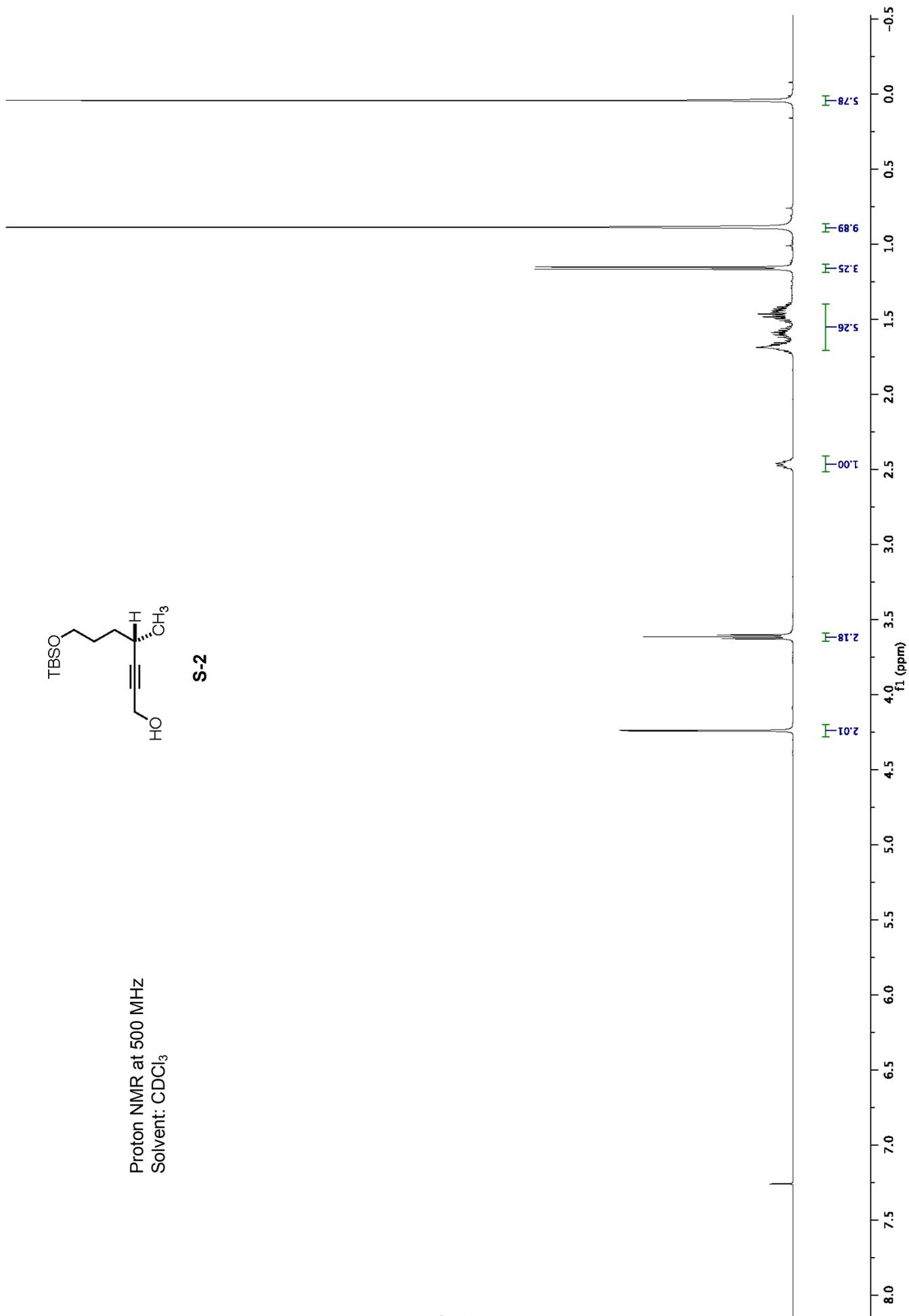
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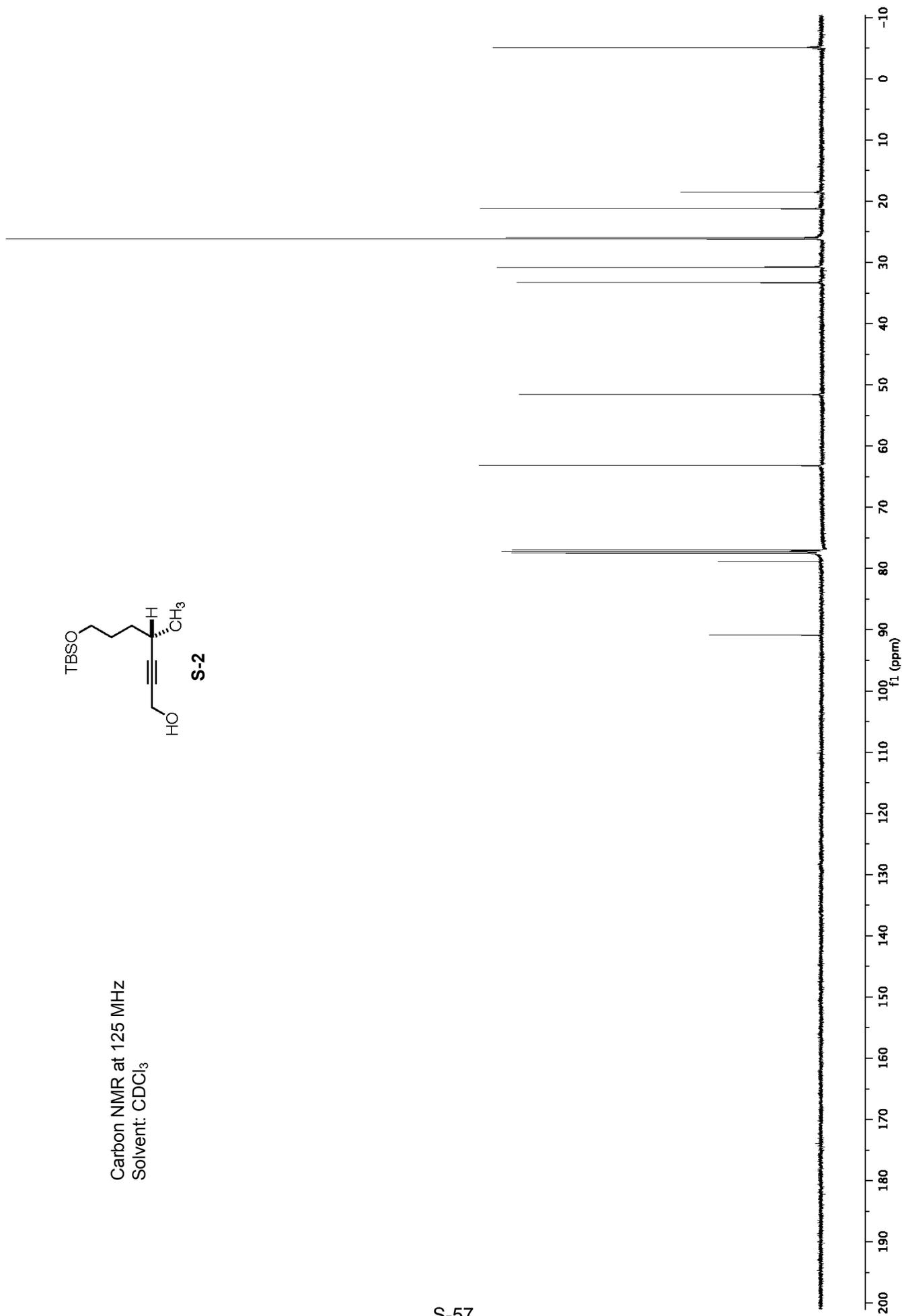
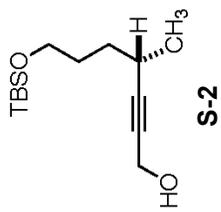


S-2

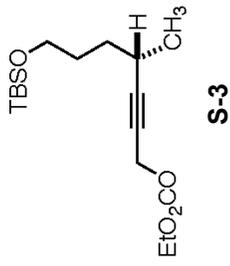
Proton NMR at 500 MHz
Solvent: CDCl₃



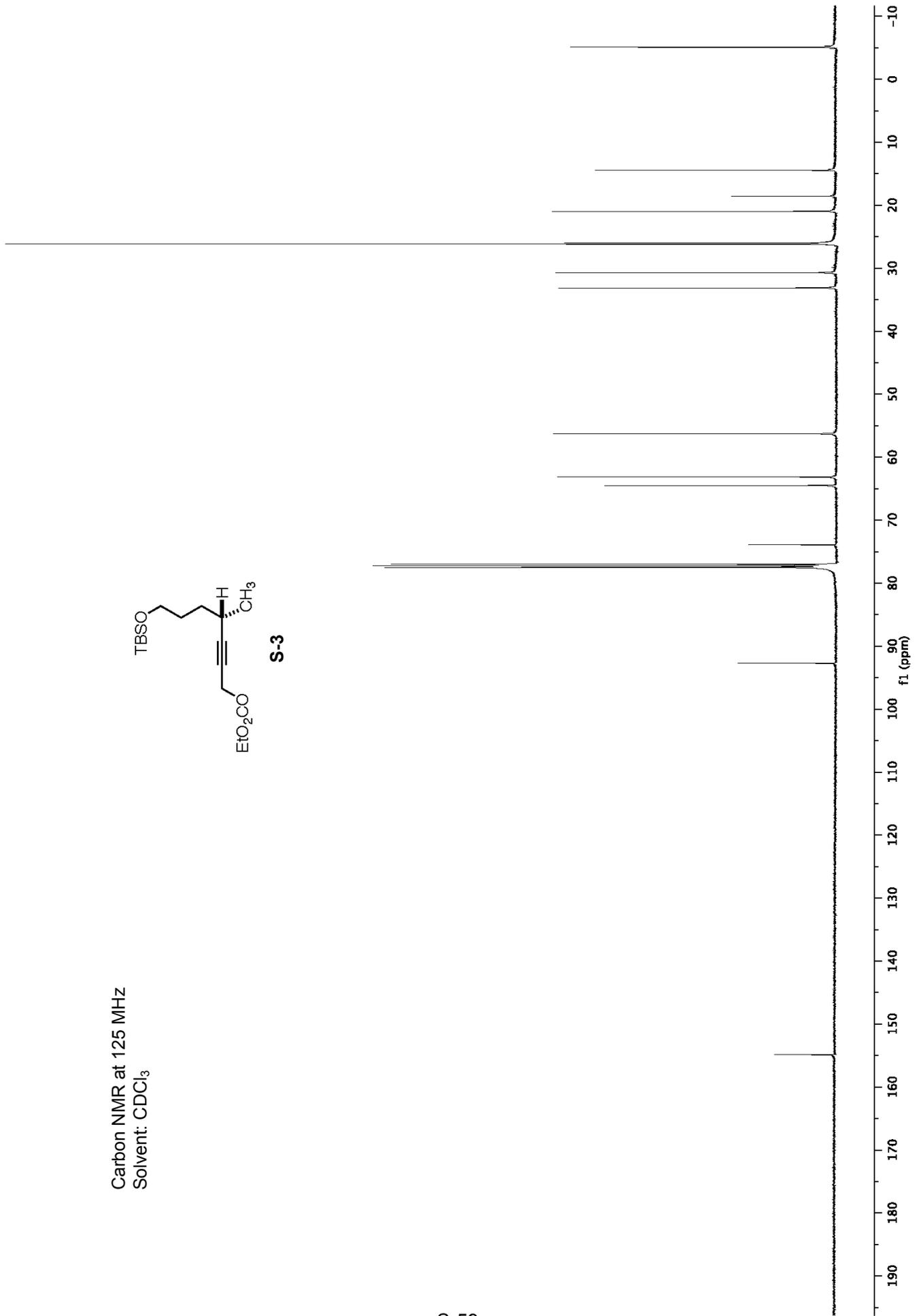
Carbon NMR at 125 MHz
Solvent: CDCl₃



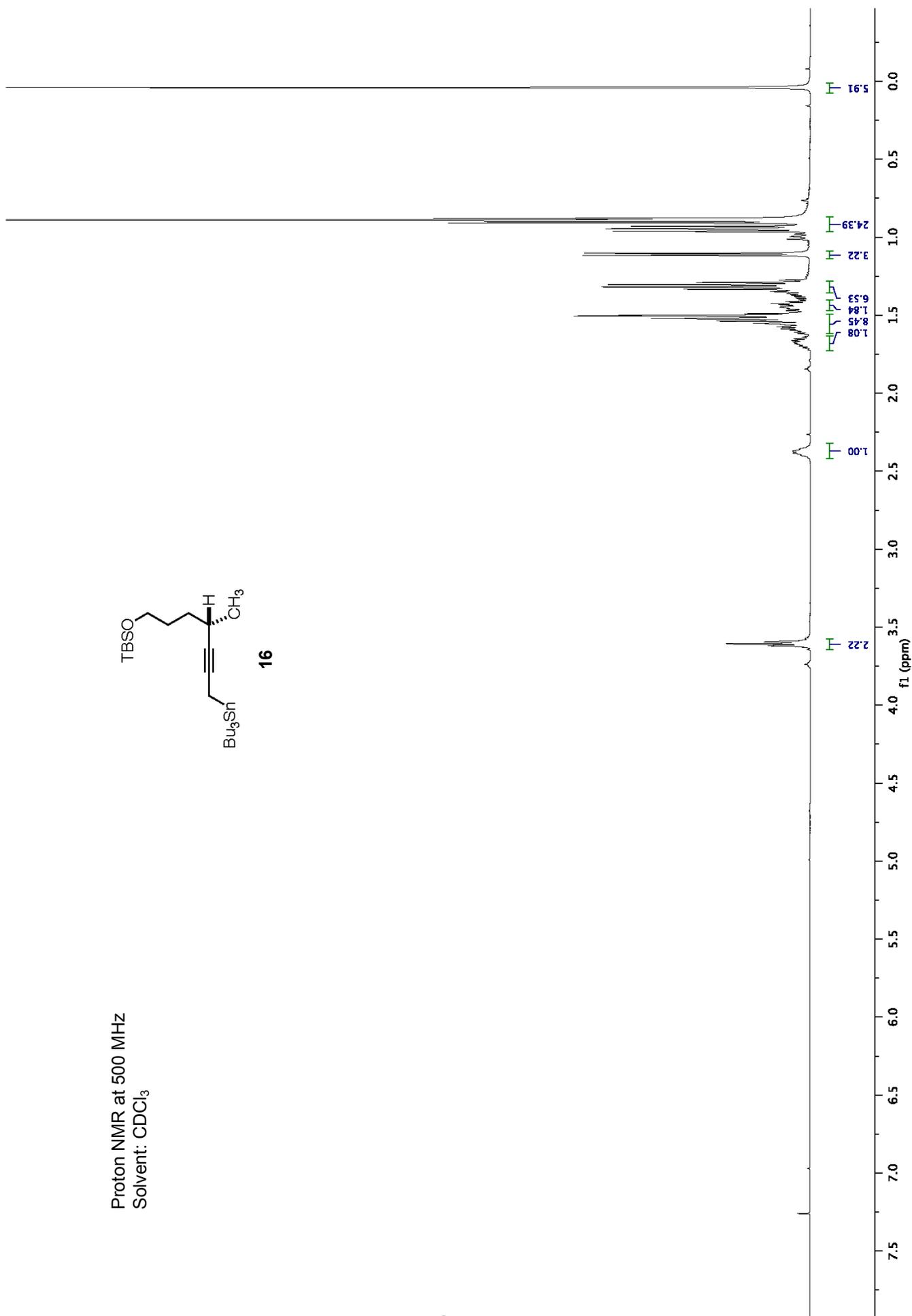
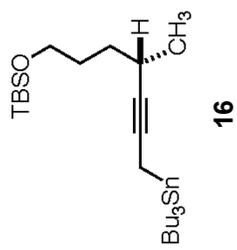
Carbon NMR at 125 MHz
Solvent: CDCl₃



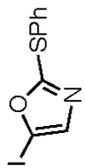
S-3



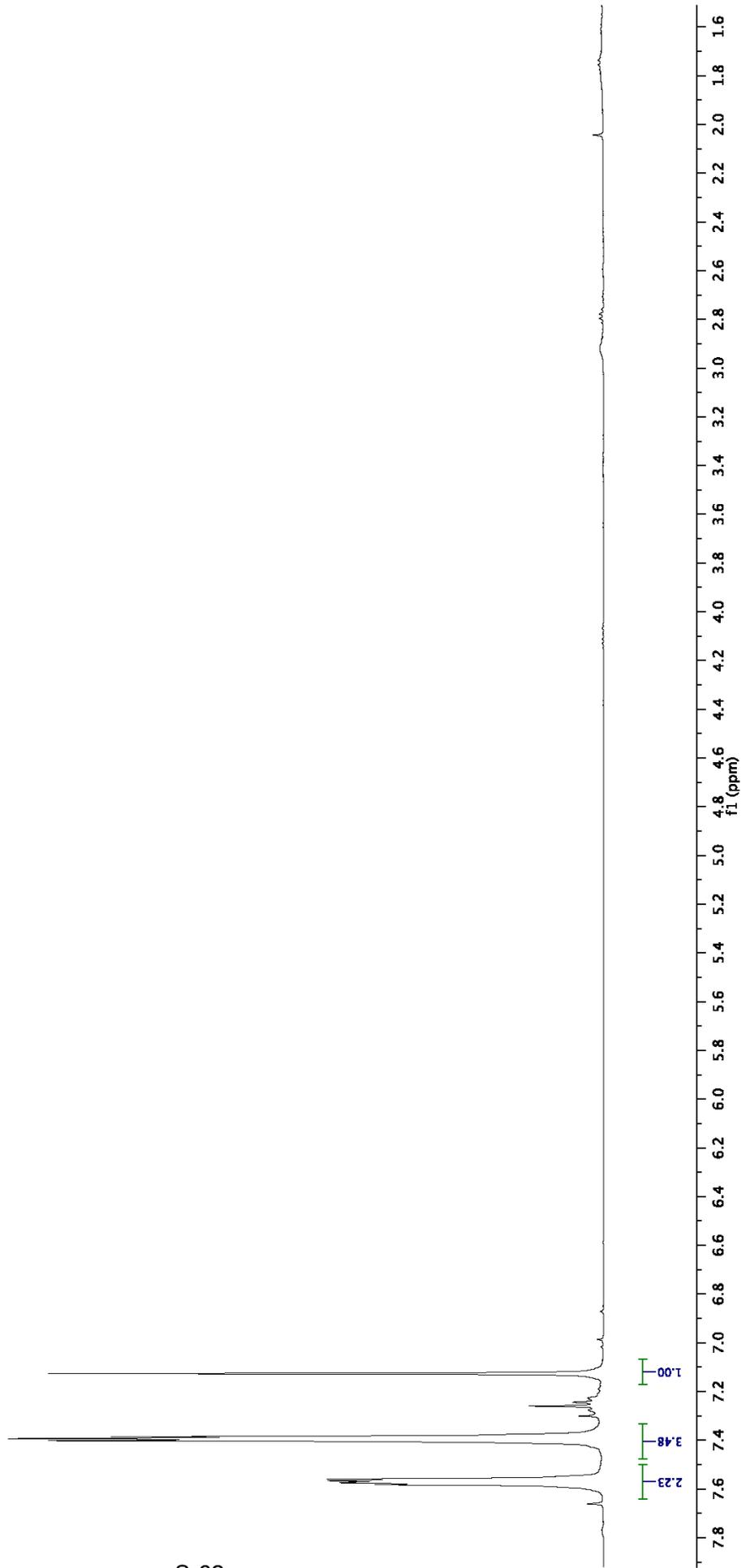
Proton NMR at 500 MHz
Solvent: CDCl₃



Proton NMR at 400 MHz
Solvent: CDCl₃

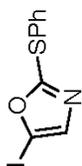


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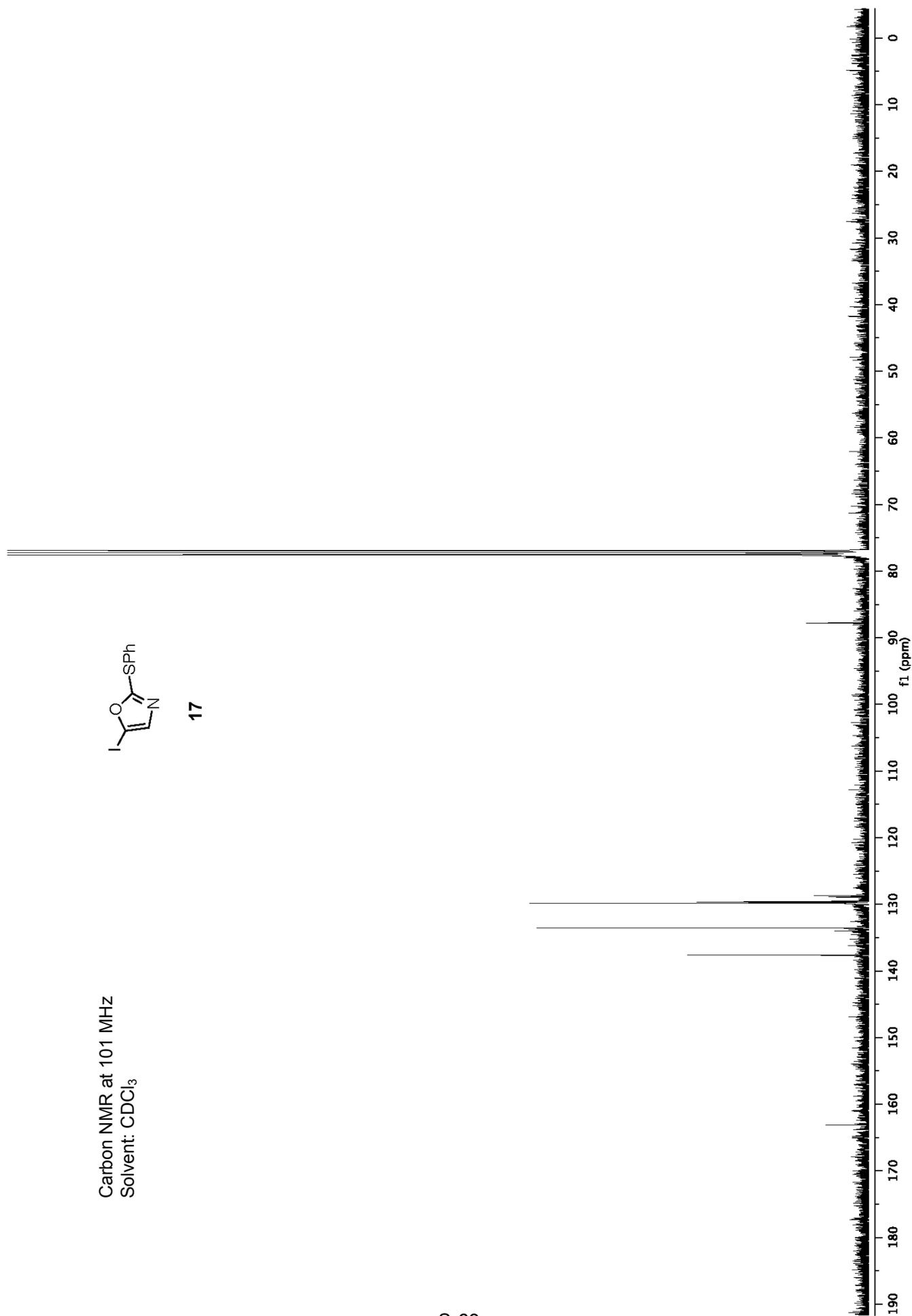


S-62

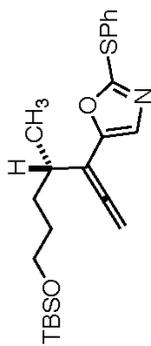
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Solvent: CDCl₃



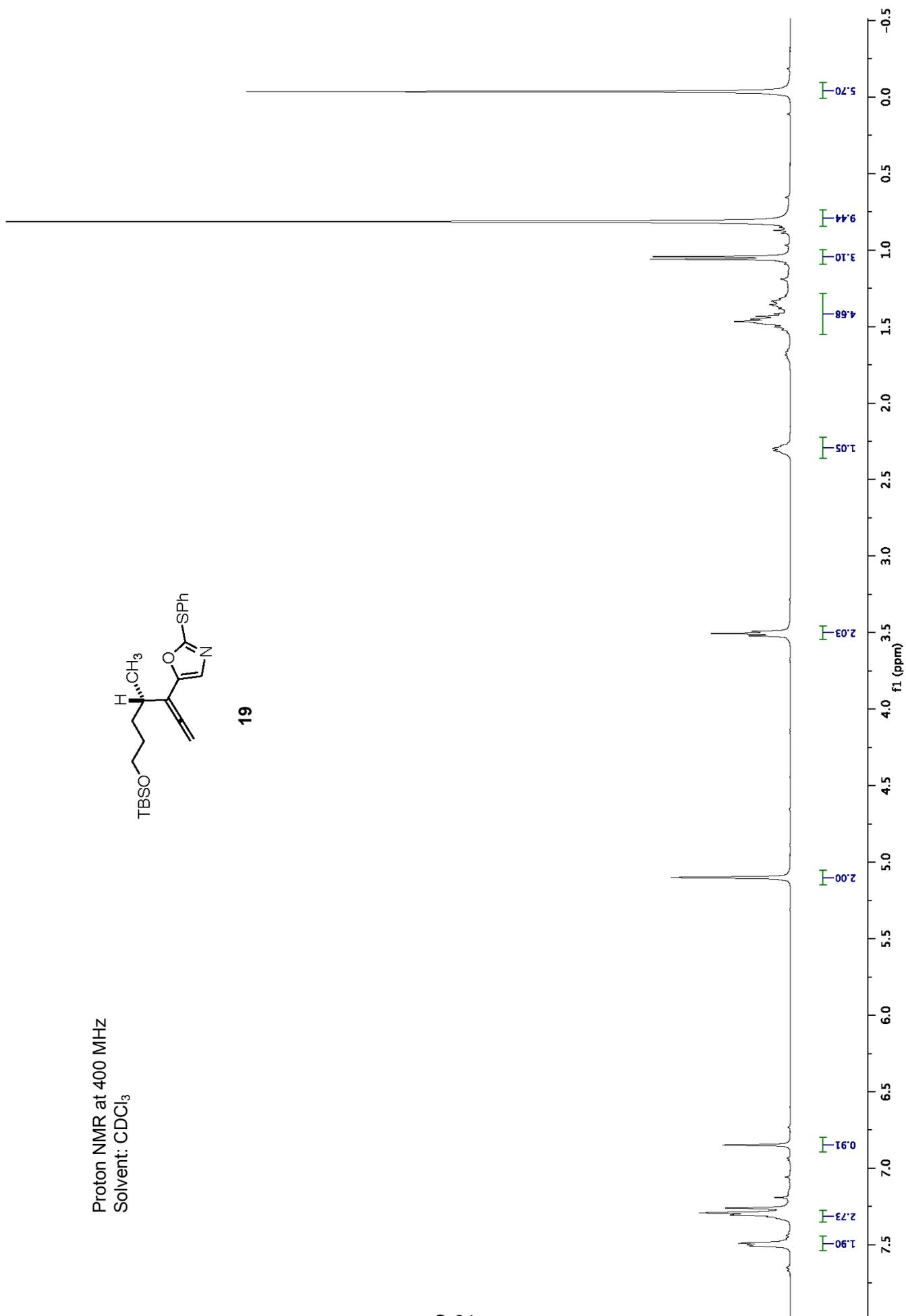
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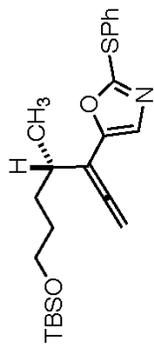
Proton NMR at 400 MHz
Solvent: CDCl₃



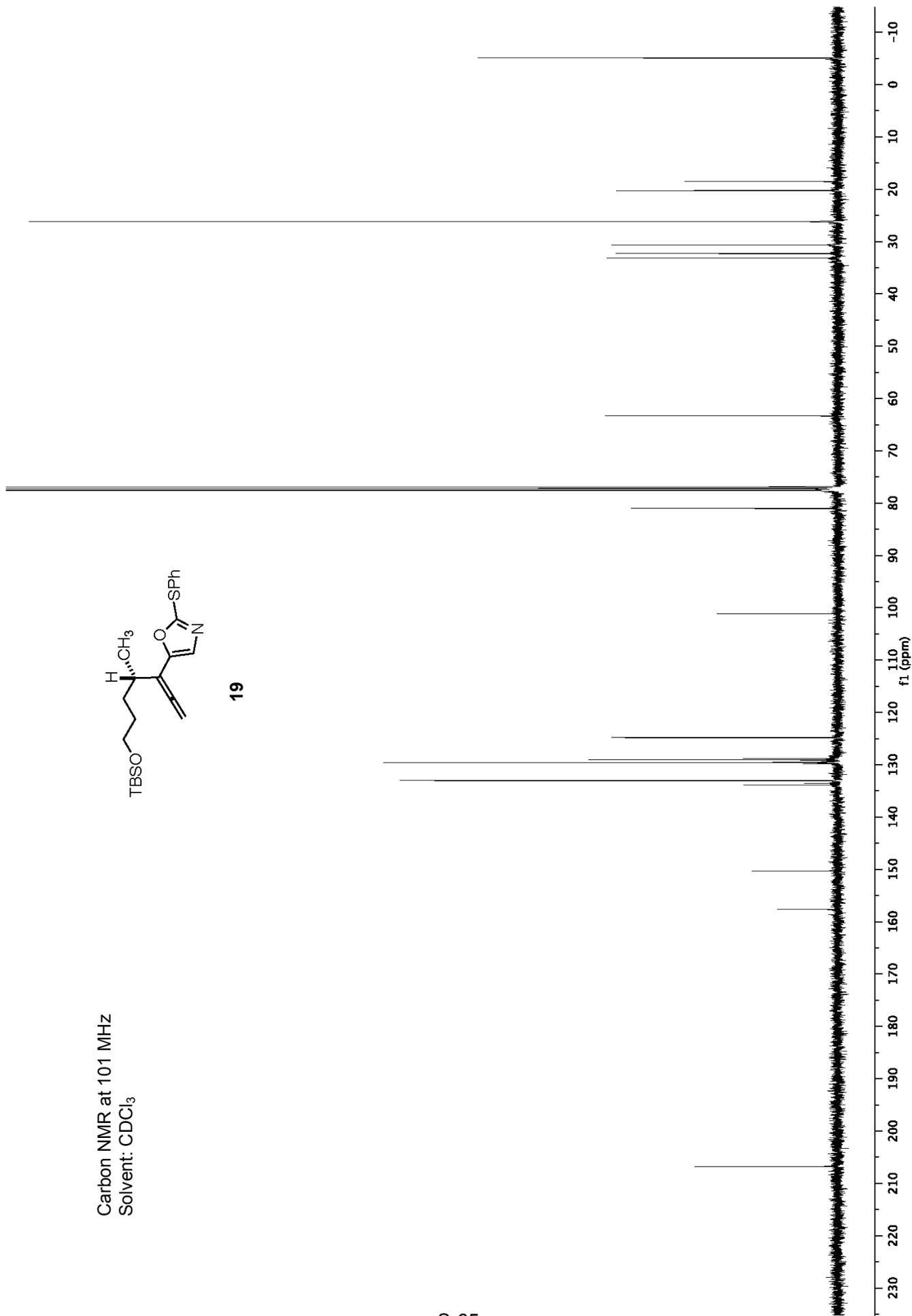
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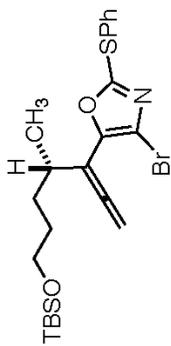
Carbon NMR at 101 MHz
Solvent: CDCl₃



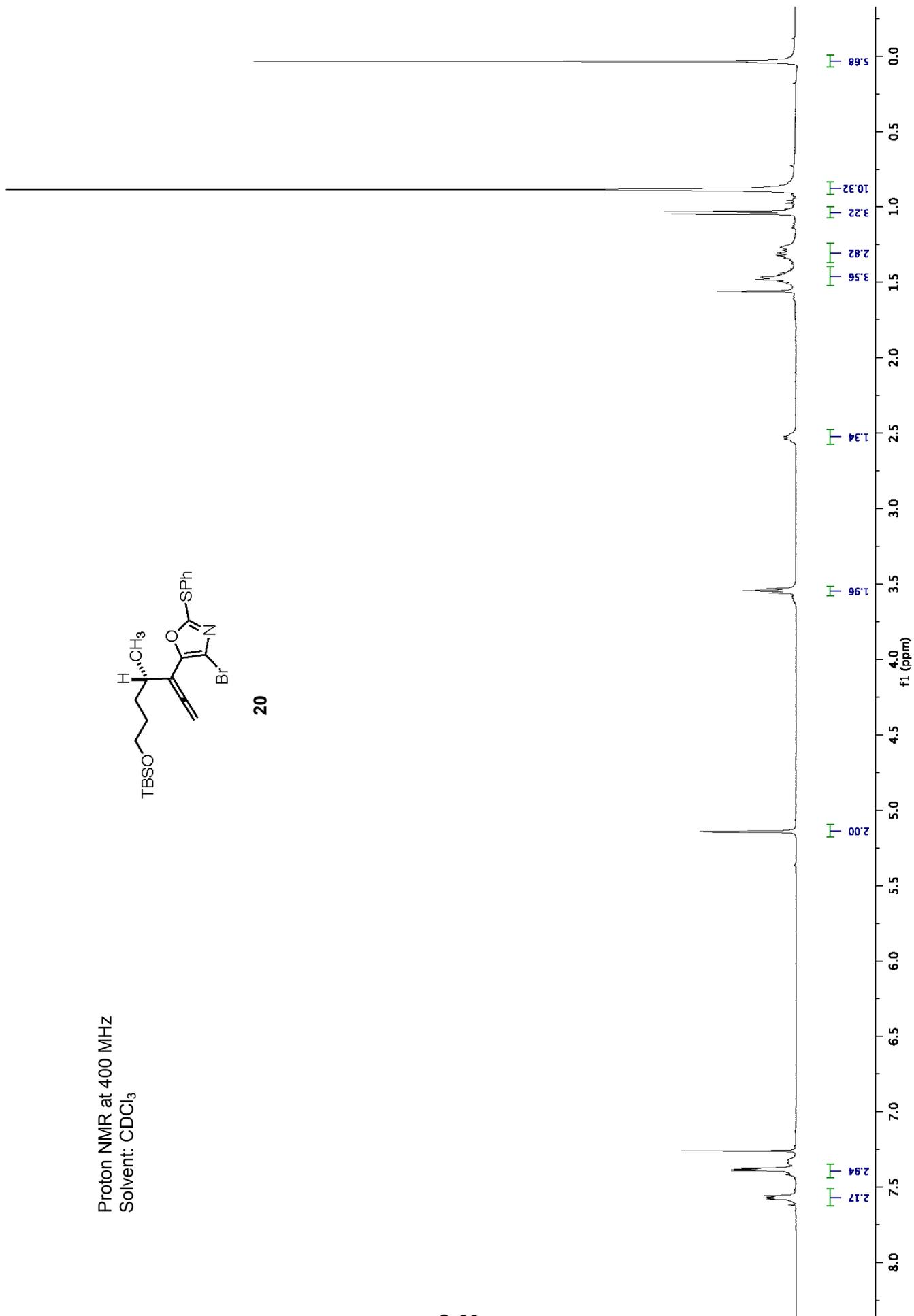
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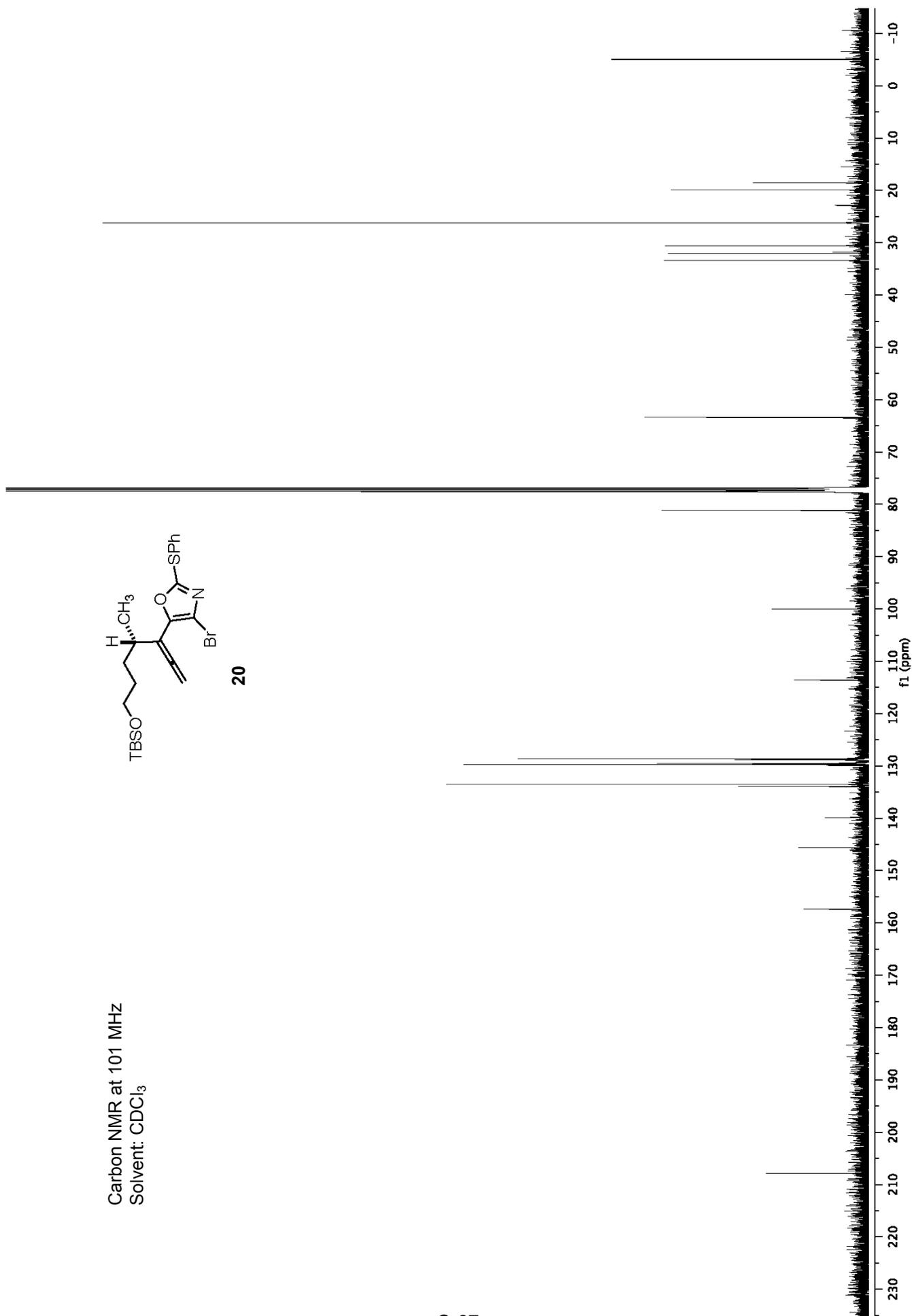
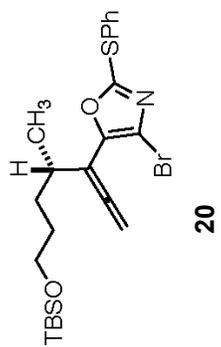
Proton NMR at 400 MHz
Solvent: CDCl₃



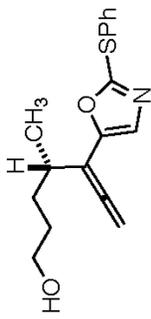
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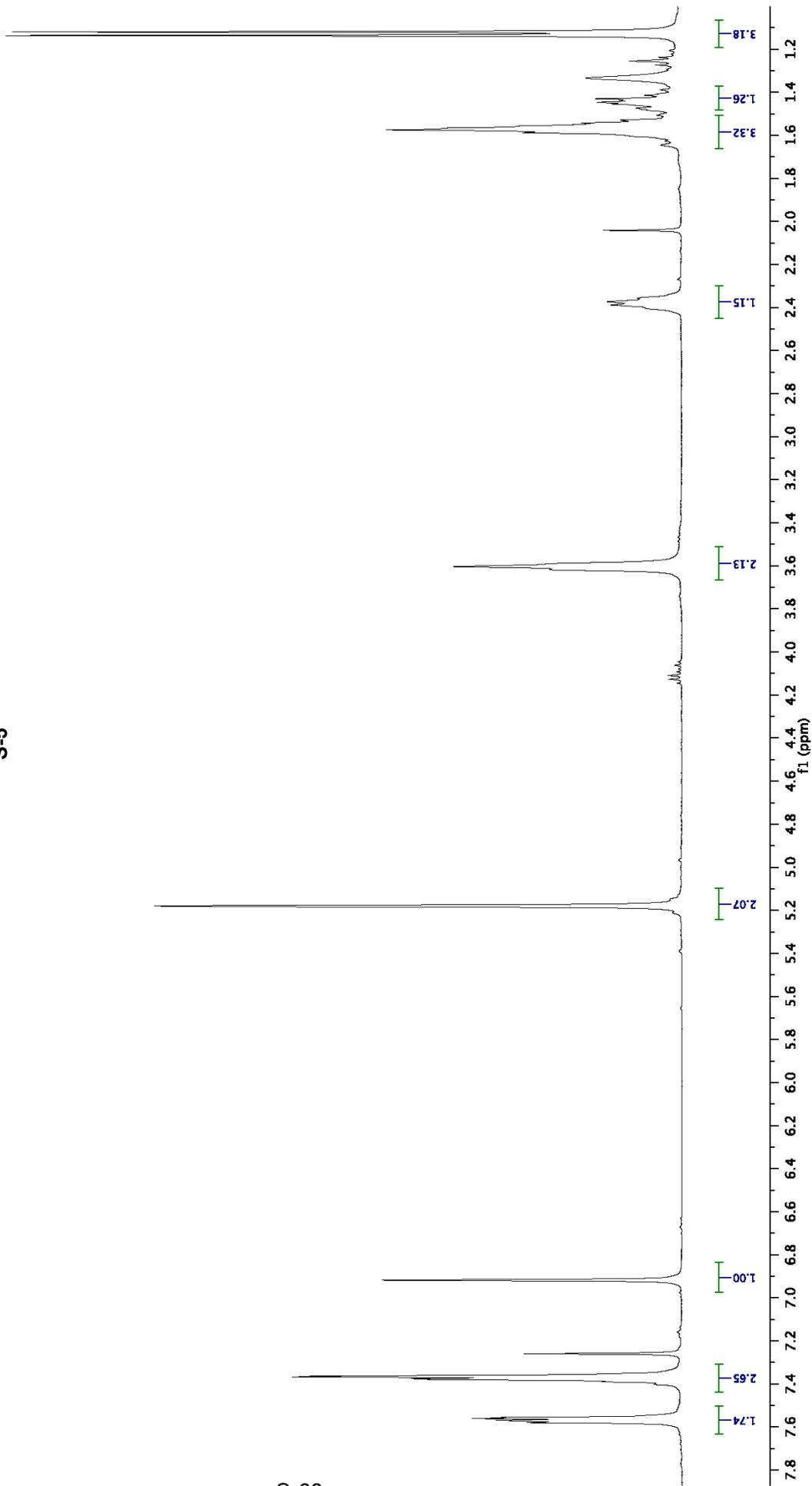
Carbon NMR at 101 MHz
Solvent: CDCl₃



Proton NMR at 400 MHz
Solvent: CDCl₃

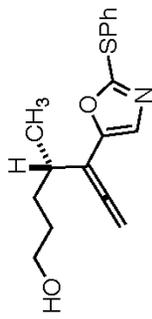


S-5

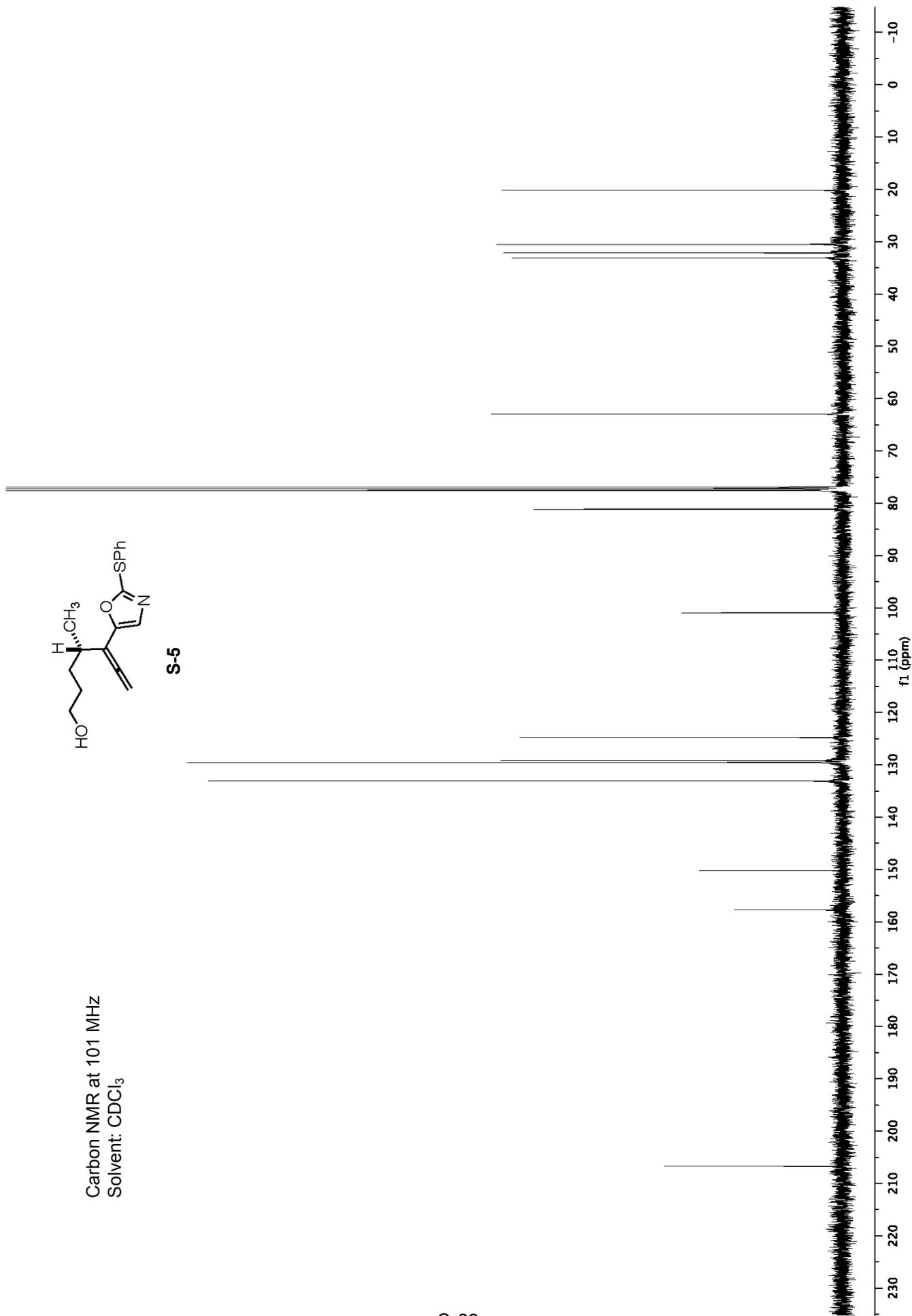


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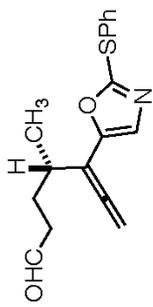
Carbon NMR at 101 MHz
Solvent: CDCl₃



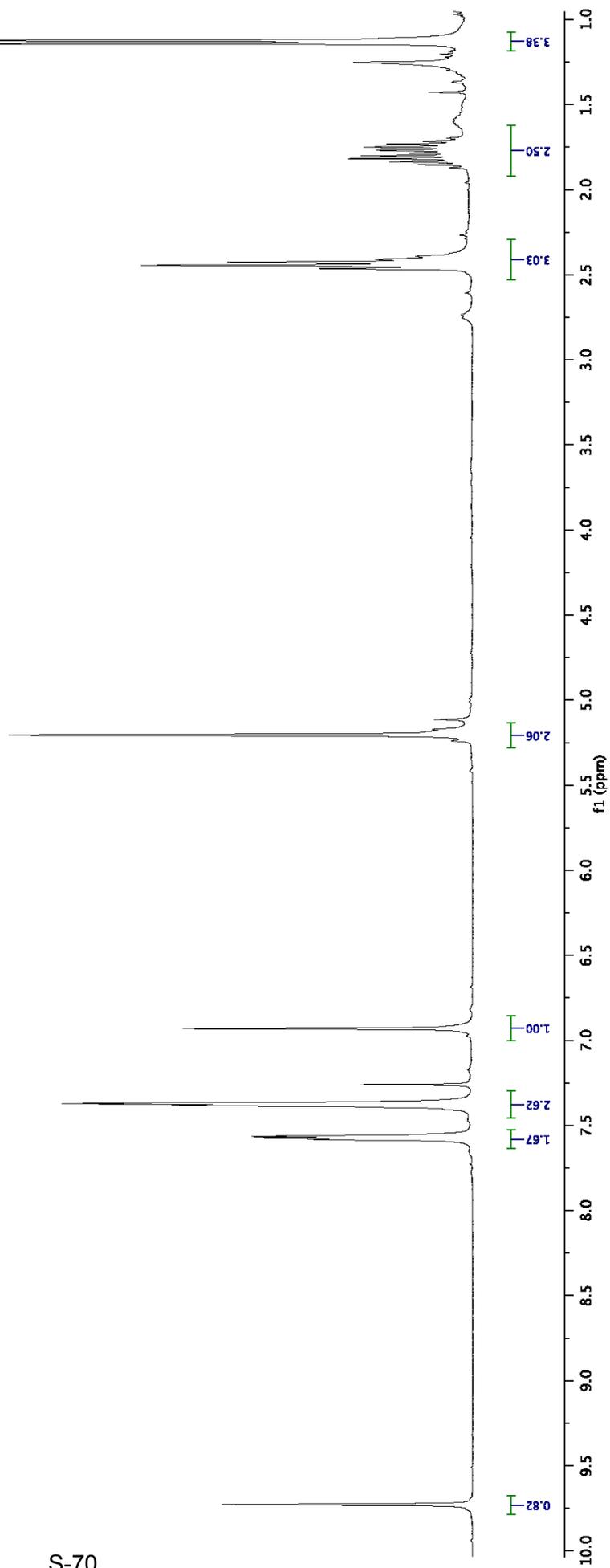
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Proton NMR at 400 MHz
Solvent: CDCl₃

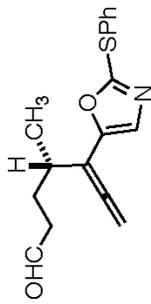


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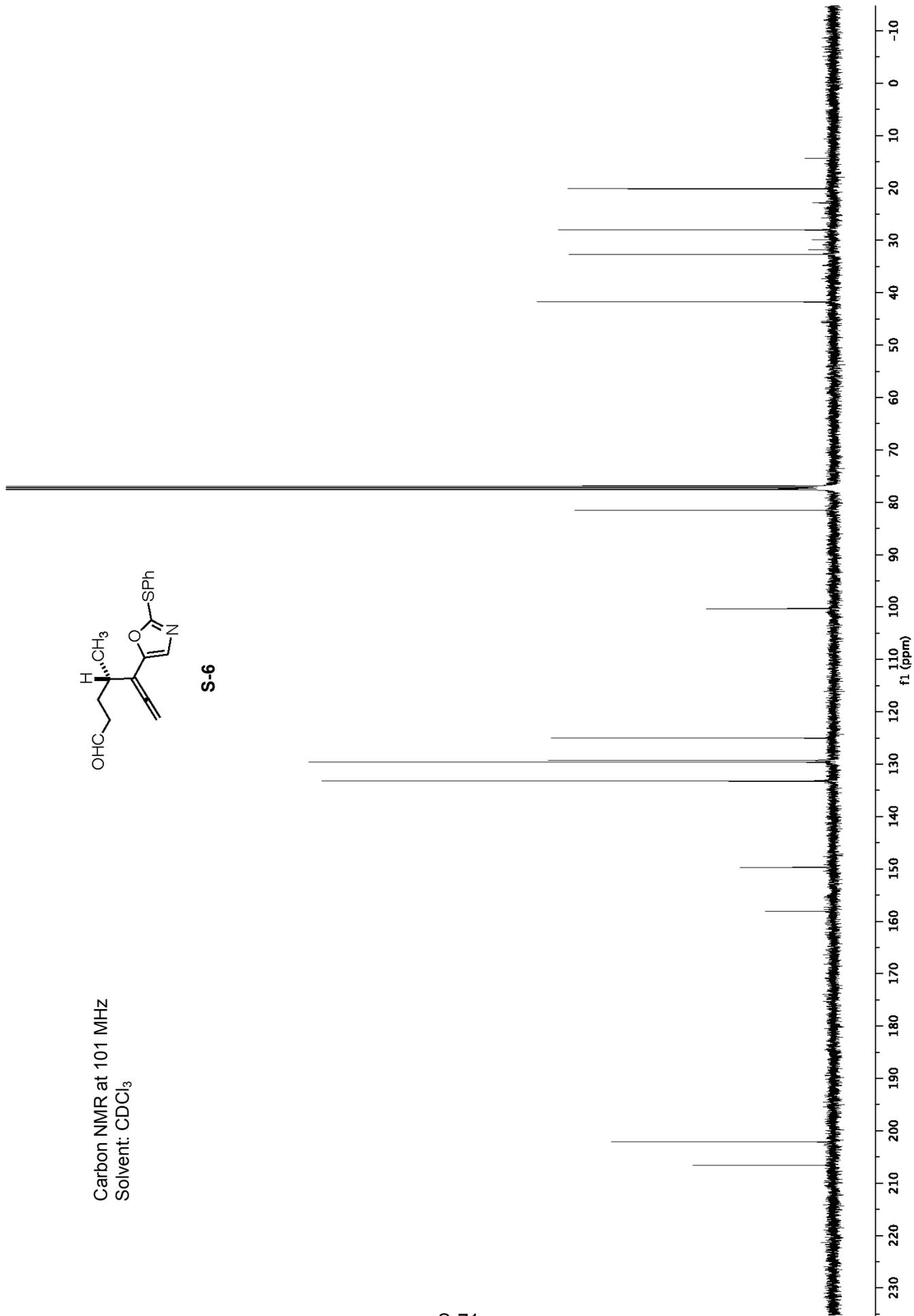


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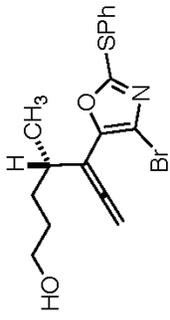
Carbon NMR at 101 MHz
Solvent: CDCl₃



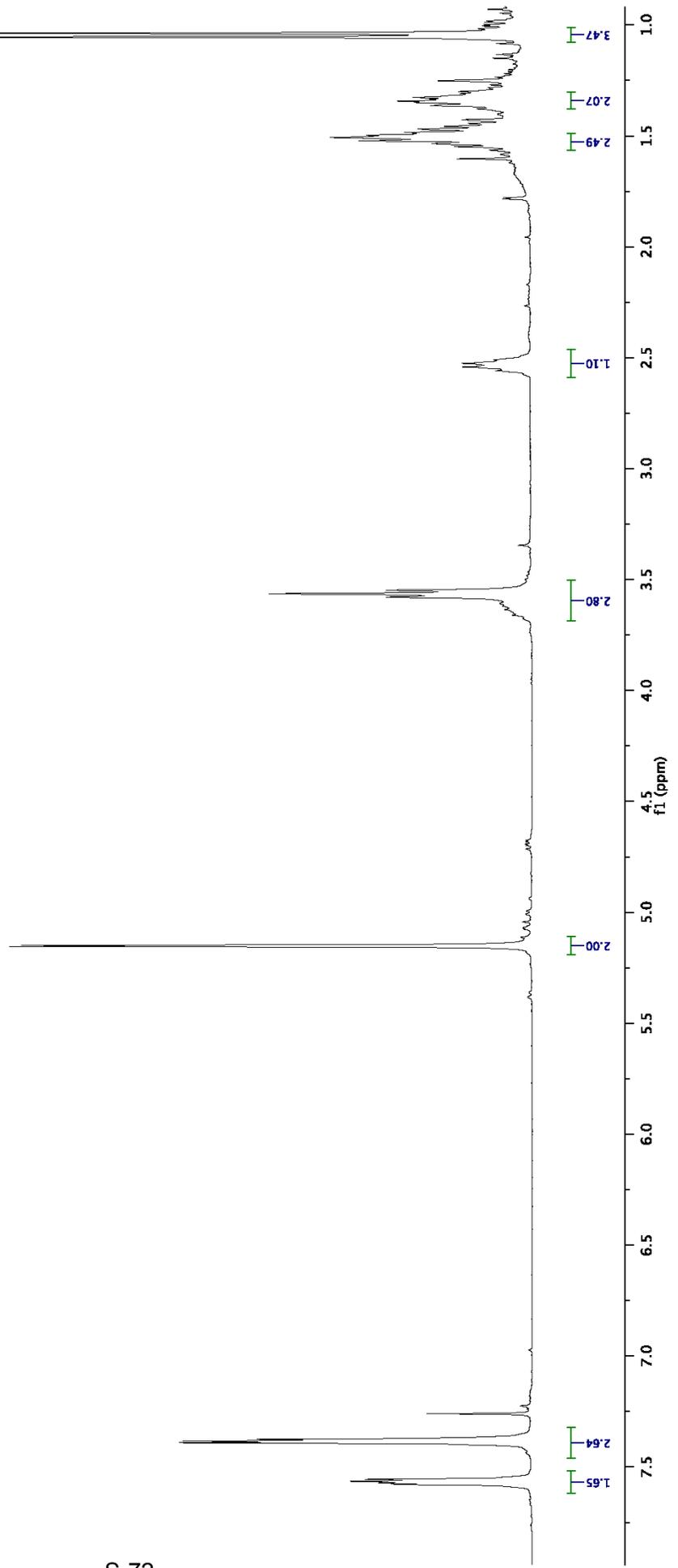
S-6



Proton NMR at 400 MHz
Solvent: CDCl₃

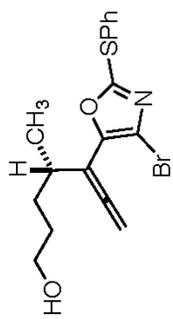


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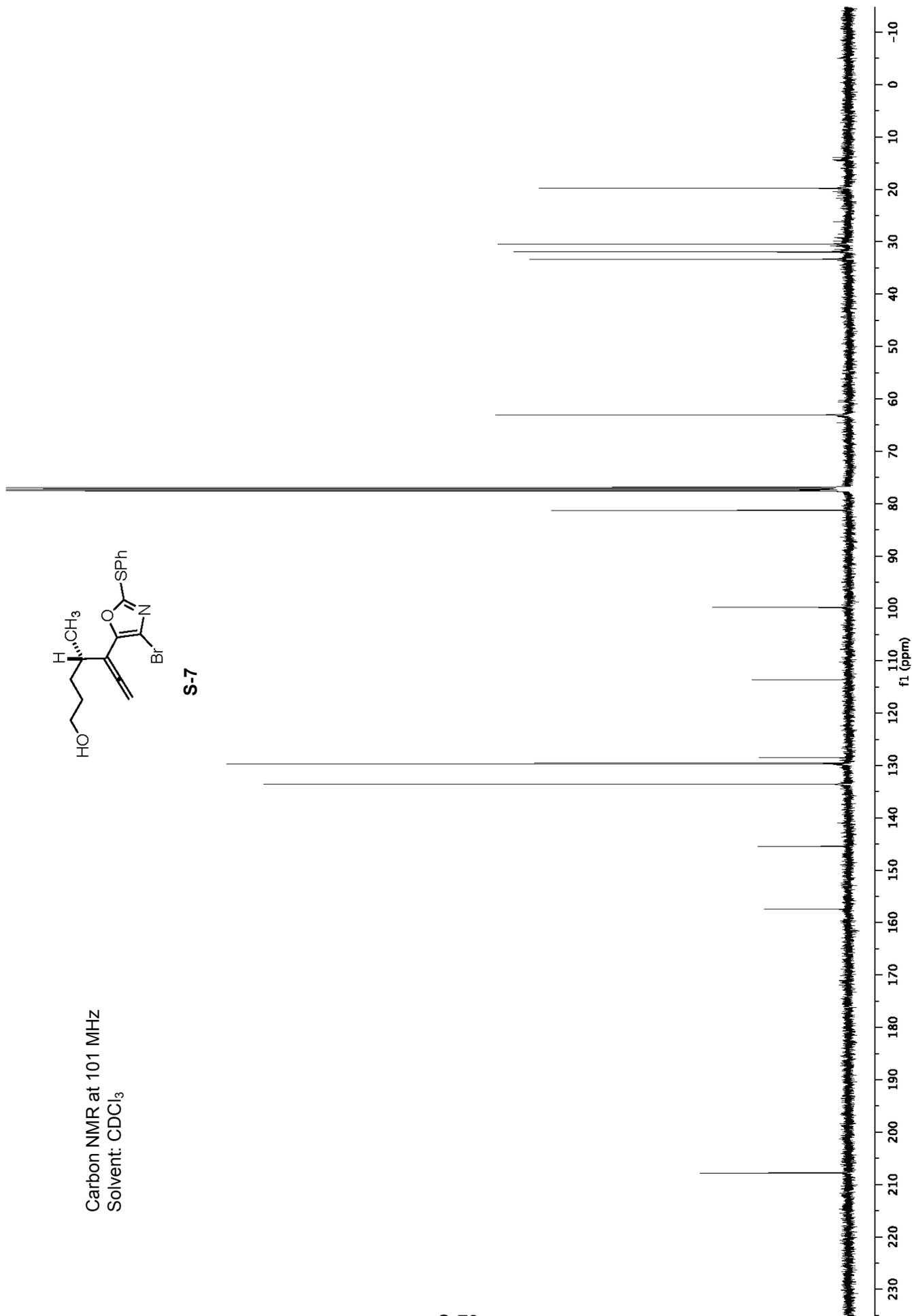


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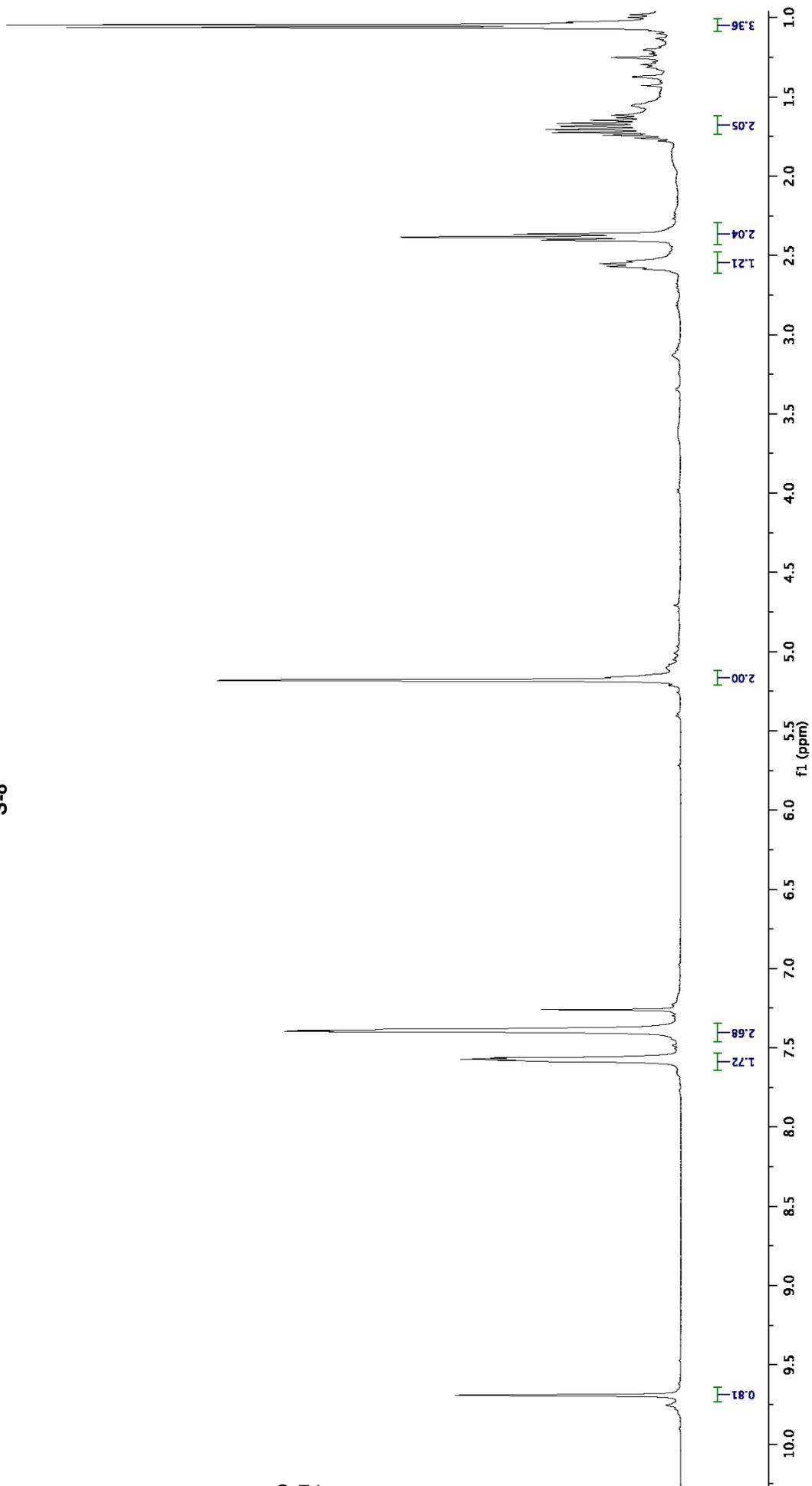
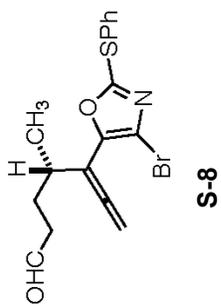
Carbon NMR at 101 MHz
Solvent: CDCl₃



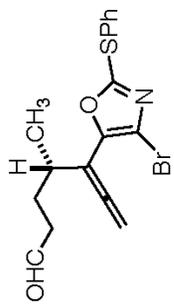
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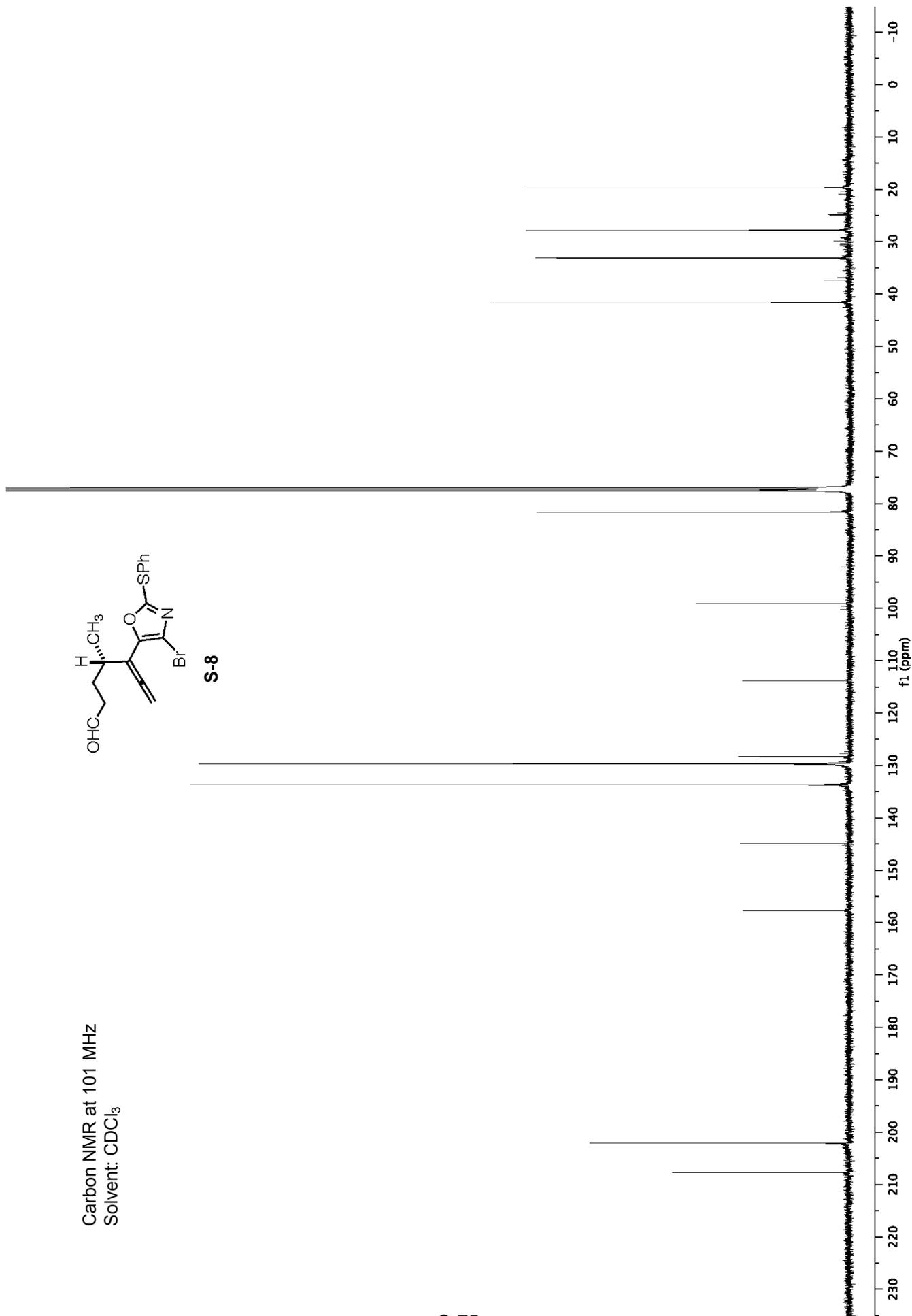
Proton NMR at 400 MHz
Solvent: CDCl₃



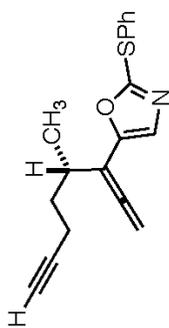
Carbon NMR at 101 MHz
Solvent: CDCl₃



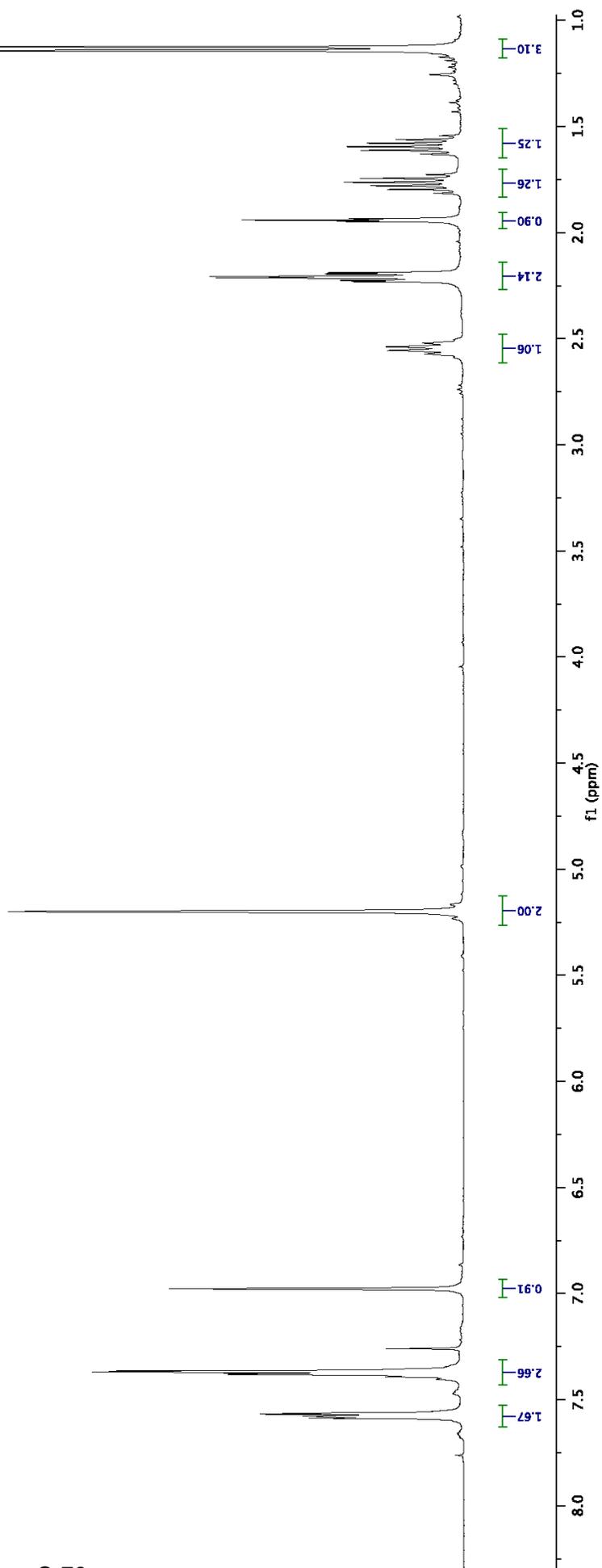
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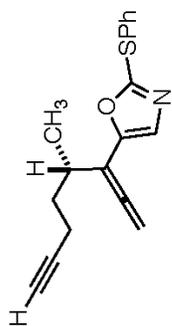
Proton NMR at 400 MHz
Solvent: CDCl₃



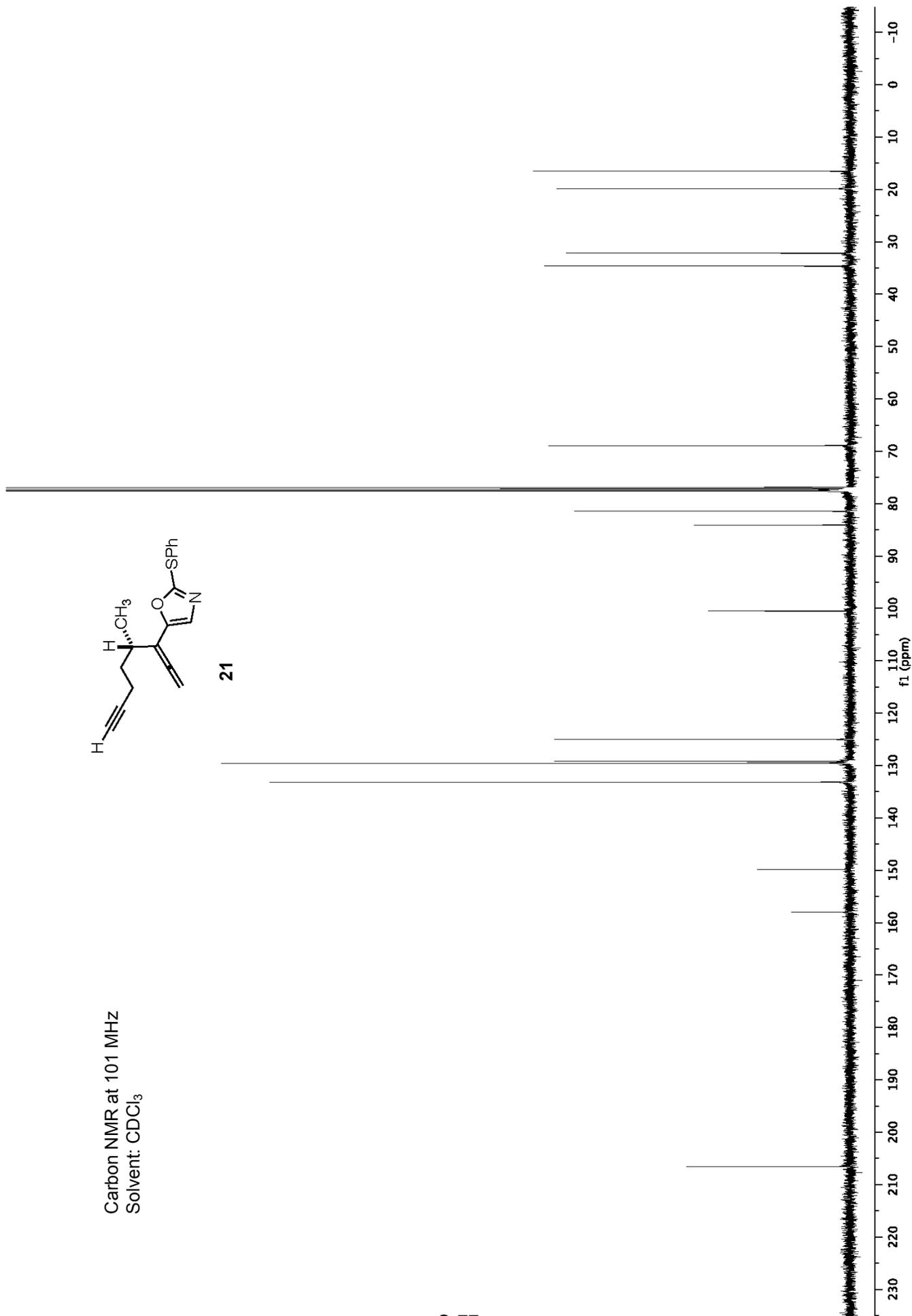
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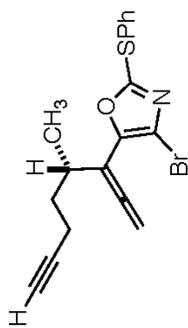
Carbon NMR at 101 MHz
Solvent: CDCl₃



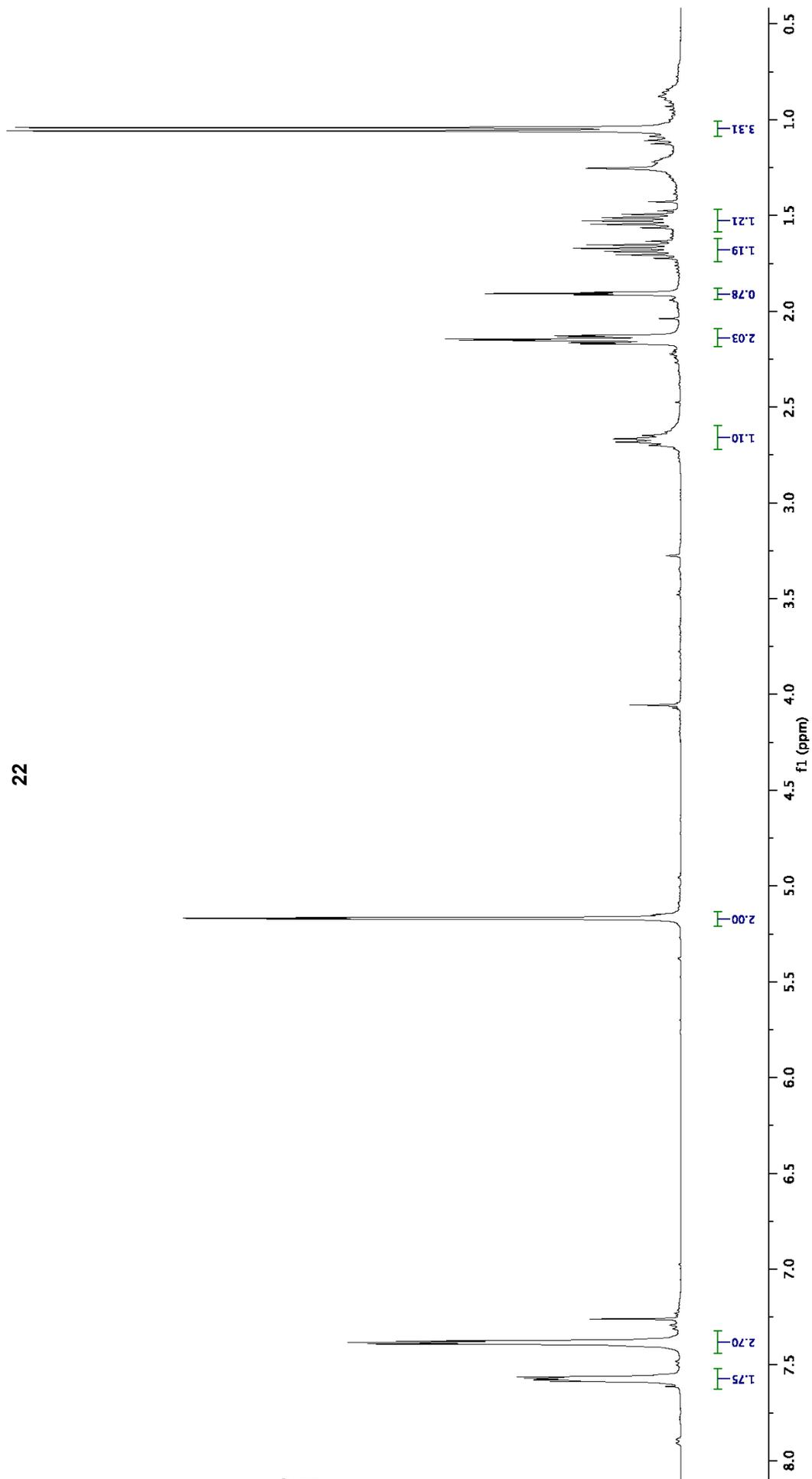
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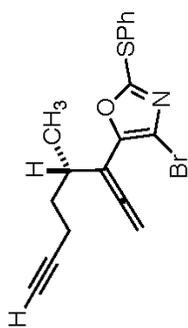
Proton NMR at 400 MHz
Solvent: CDCl₃



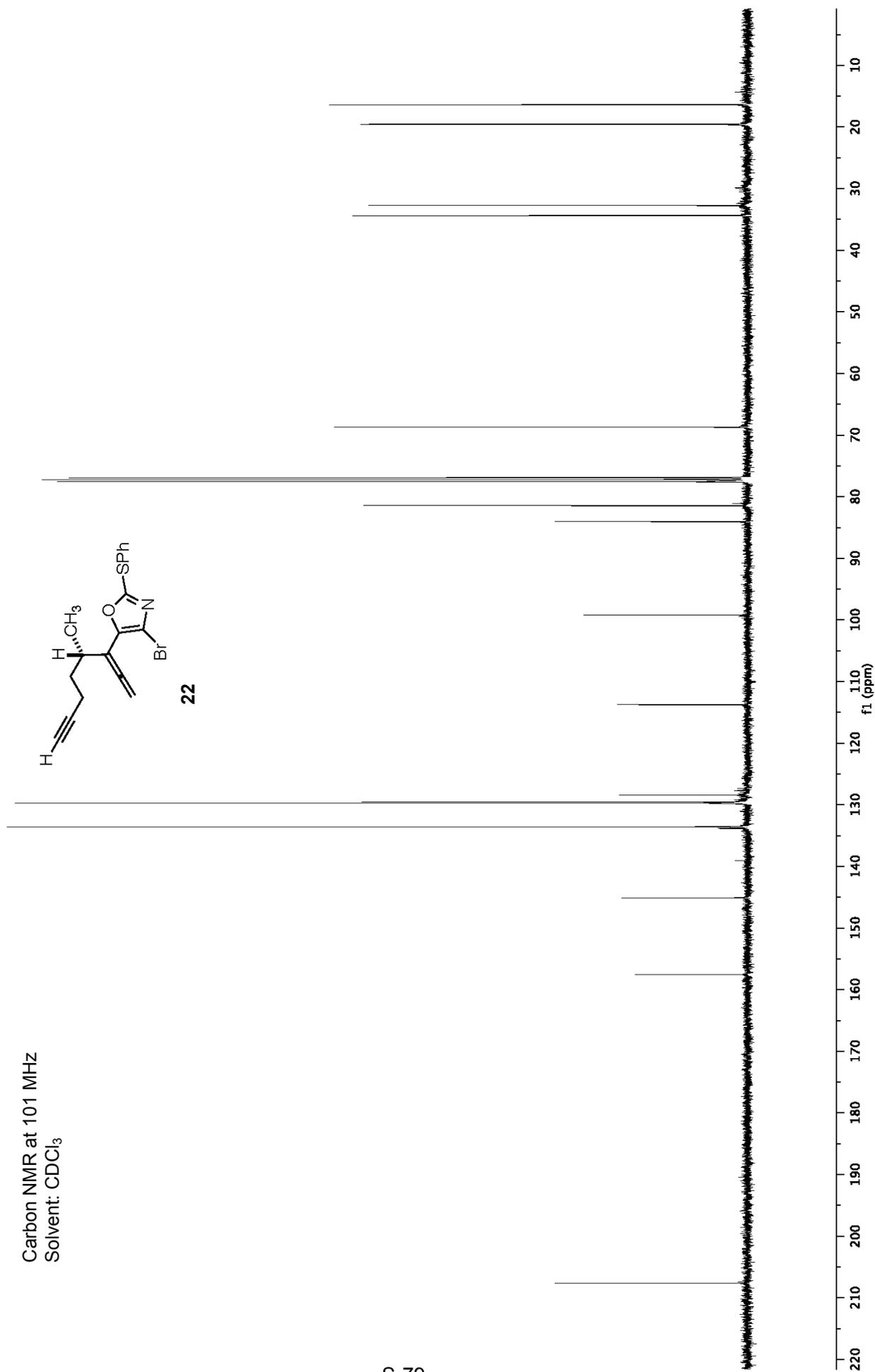
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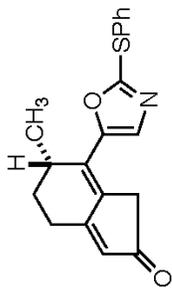
Carbon NMR at 101 MHz
Solvent: CDCl₃



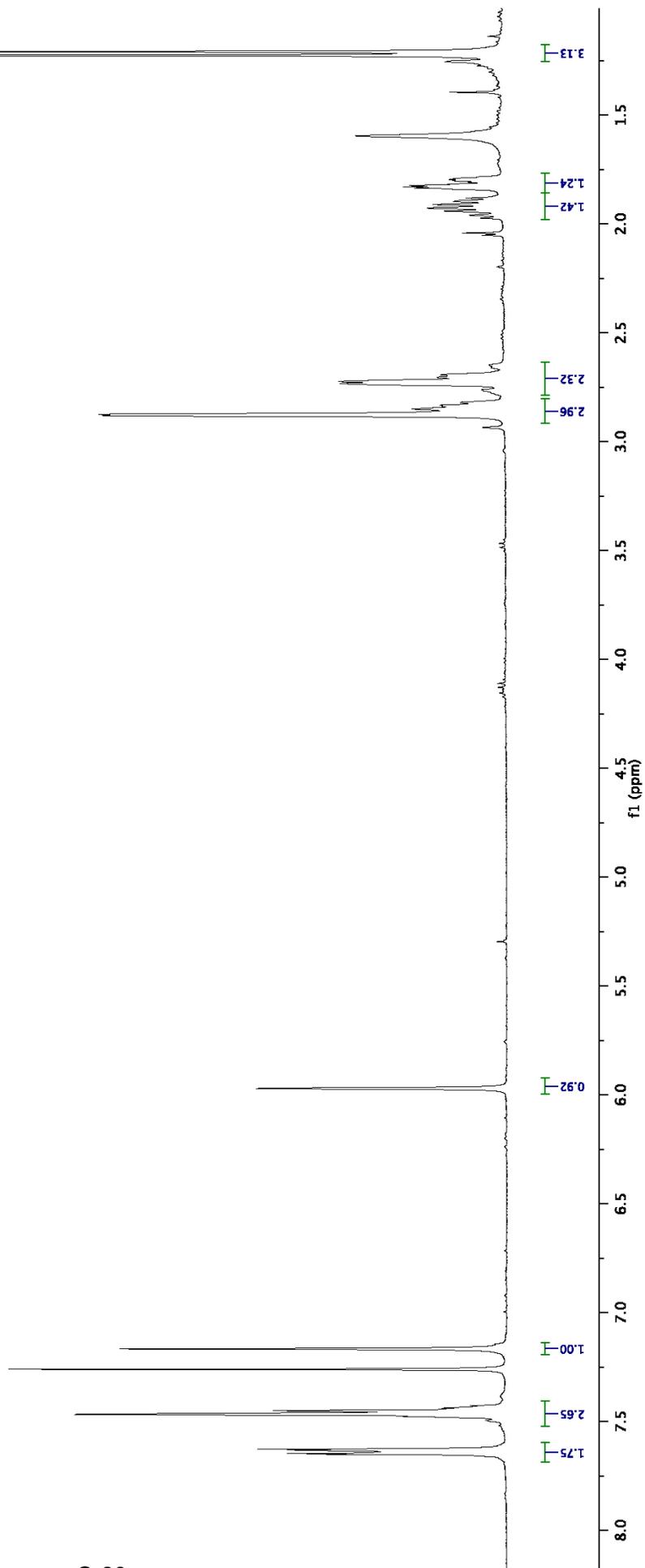
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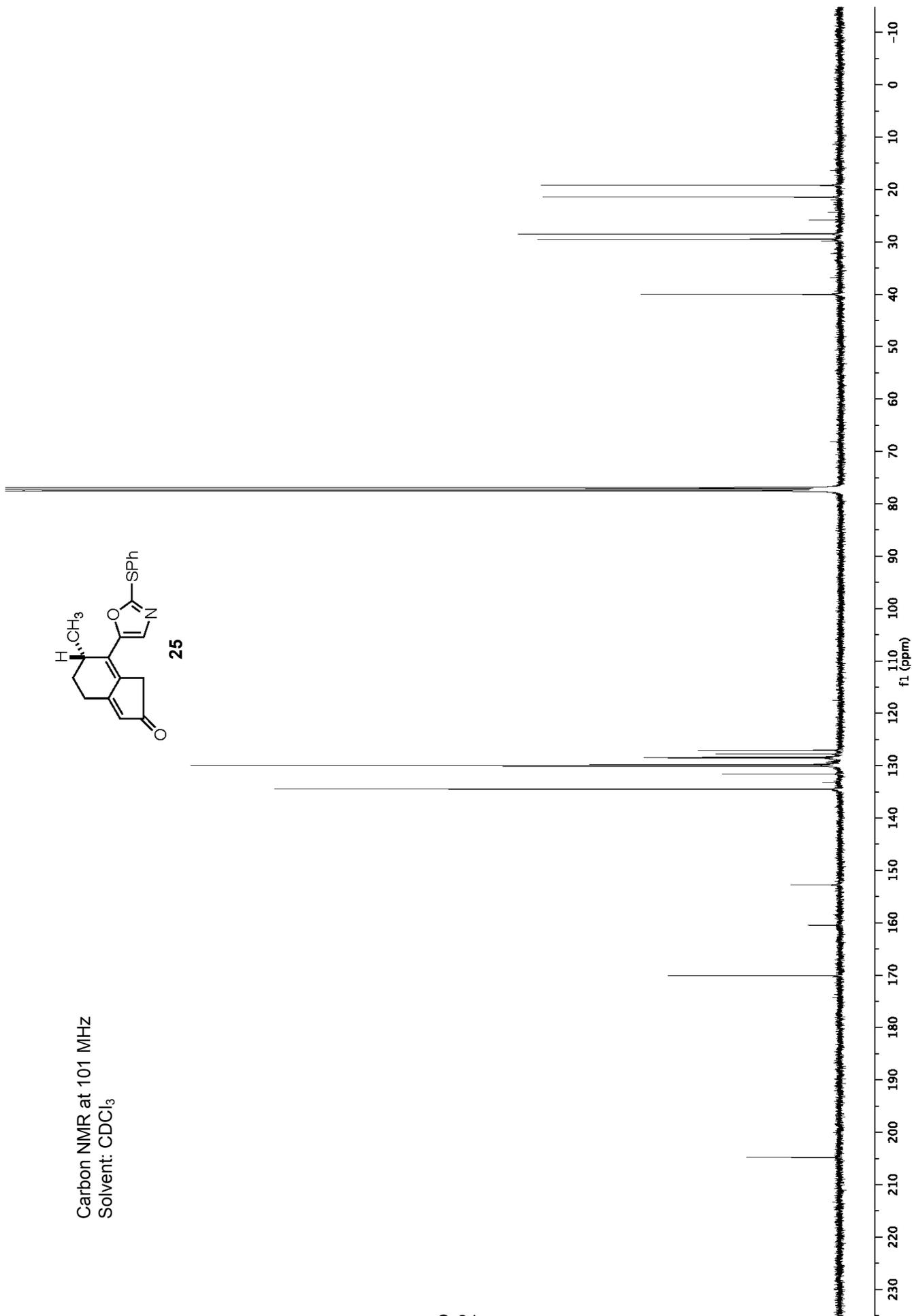
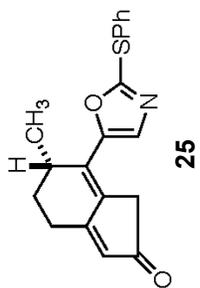
Proton NMR at 400 MHz
Solvent: CDCl₃



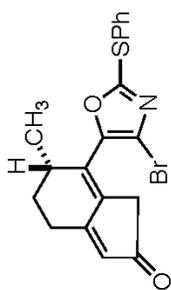
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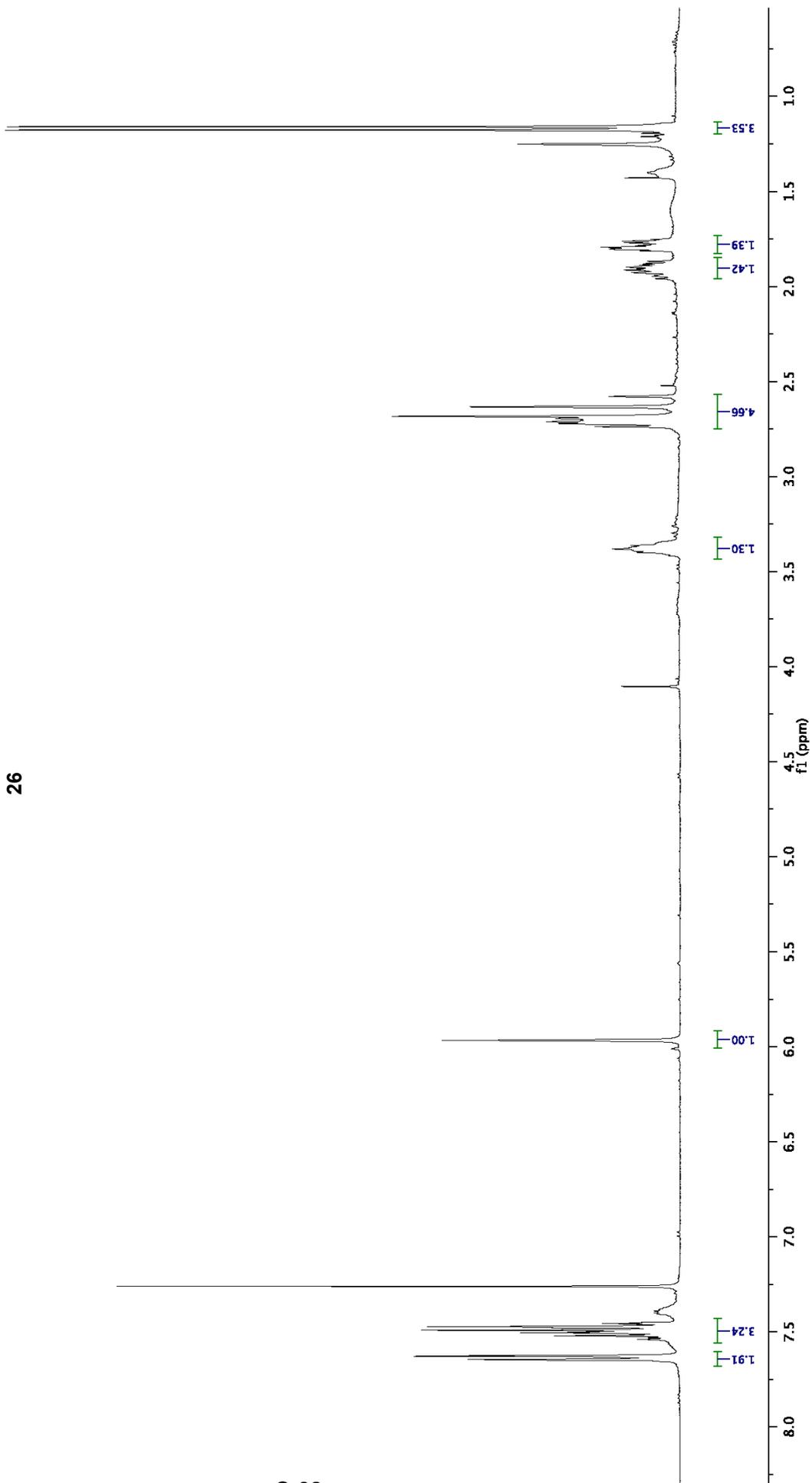
Carbon NMR at 101 MHz
Solvent: CDCl₃



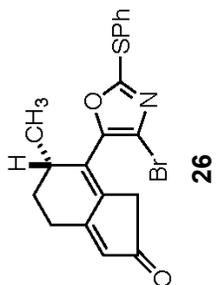
Proton NMR at 400 MHz
Solvent: CDCl₃



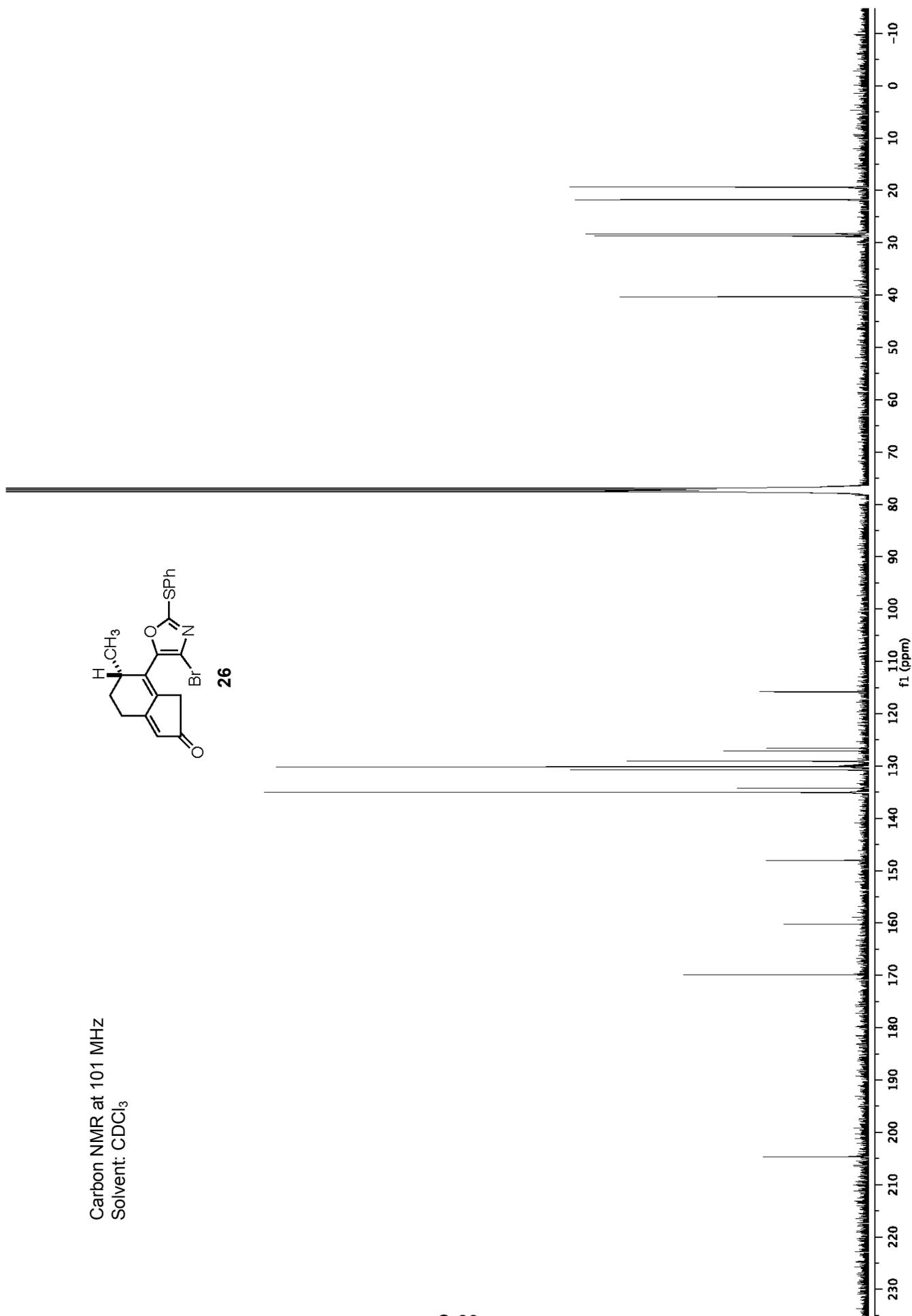
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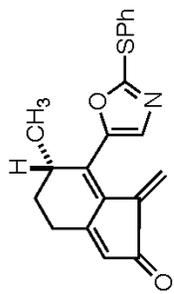


Carbon NMR at 101 MHz
Solvent: CDCl₃



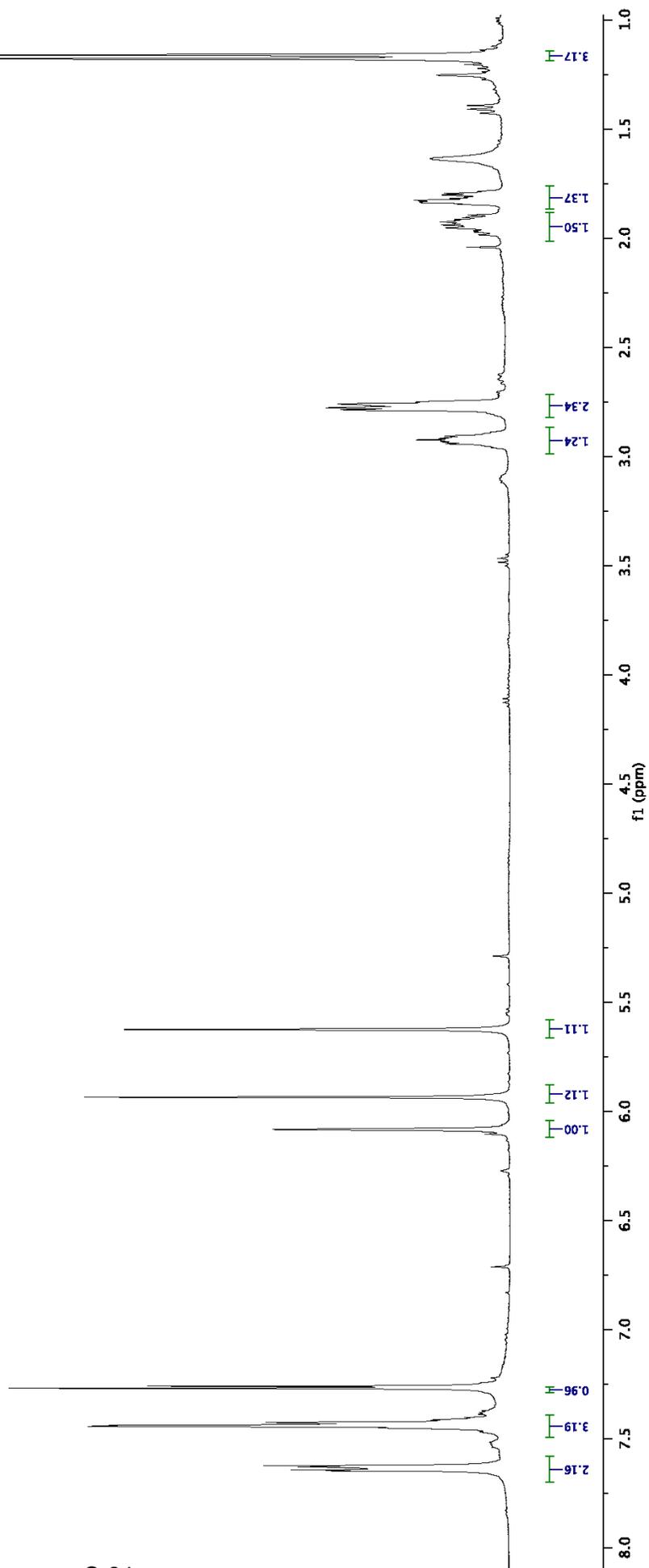
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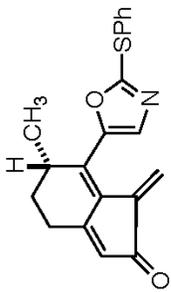
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Proton NMR at 400 MHz
Solvent: CDCl₃

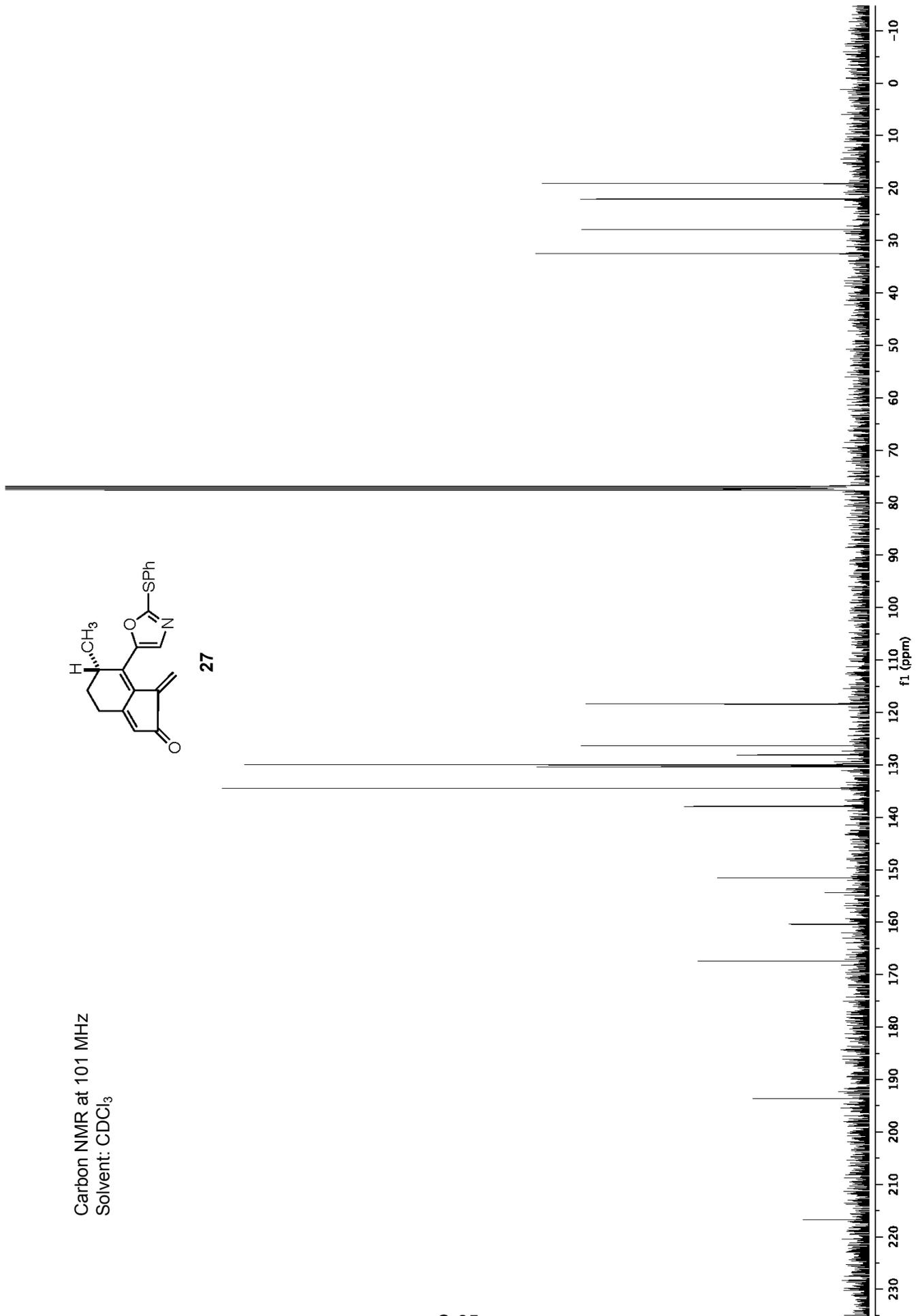


S-84

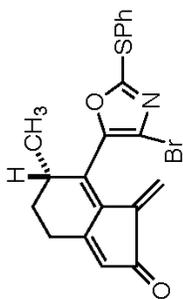
Carbon NMR at 101 MHz
Solvent: CDCl₃



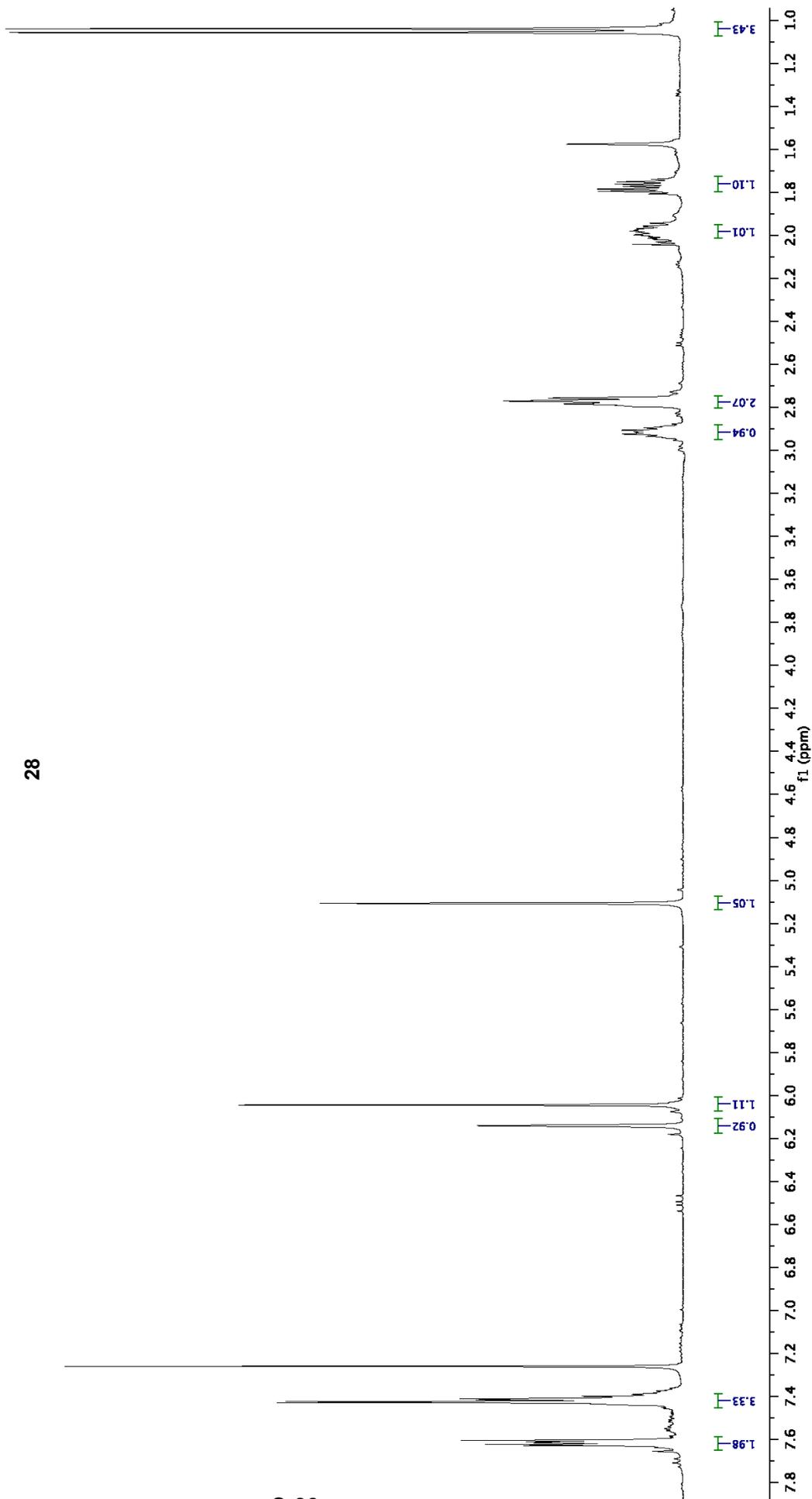
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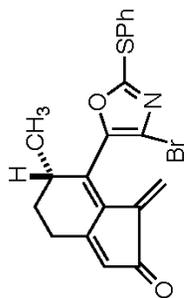
Proton NMR at 400 MHz
Solvent: CDCl₃



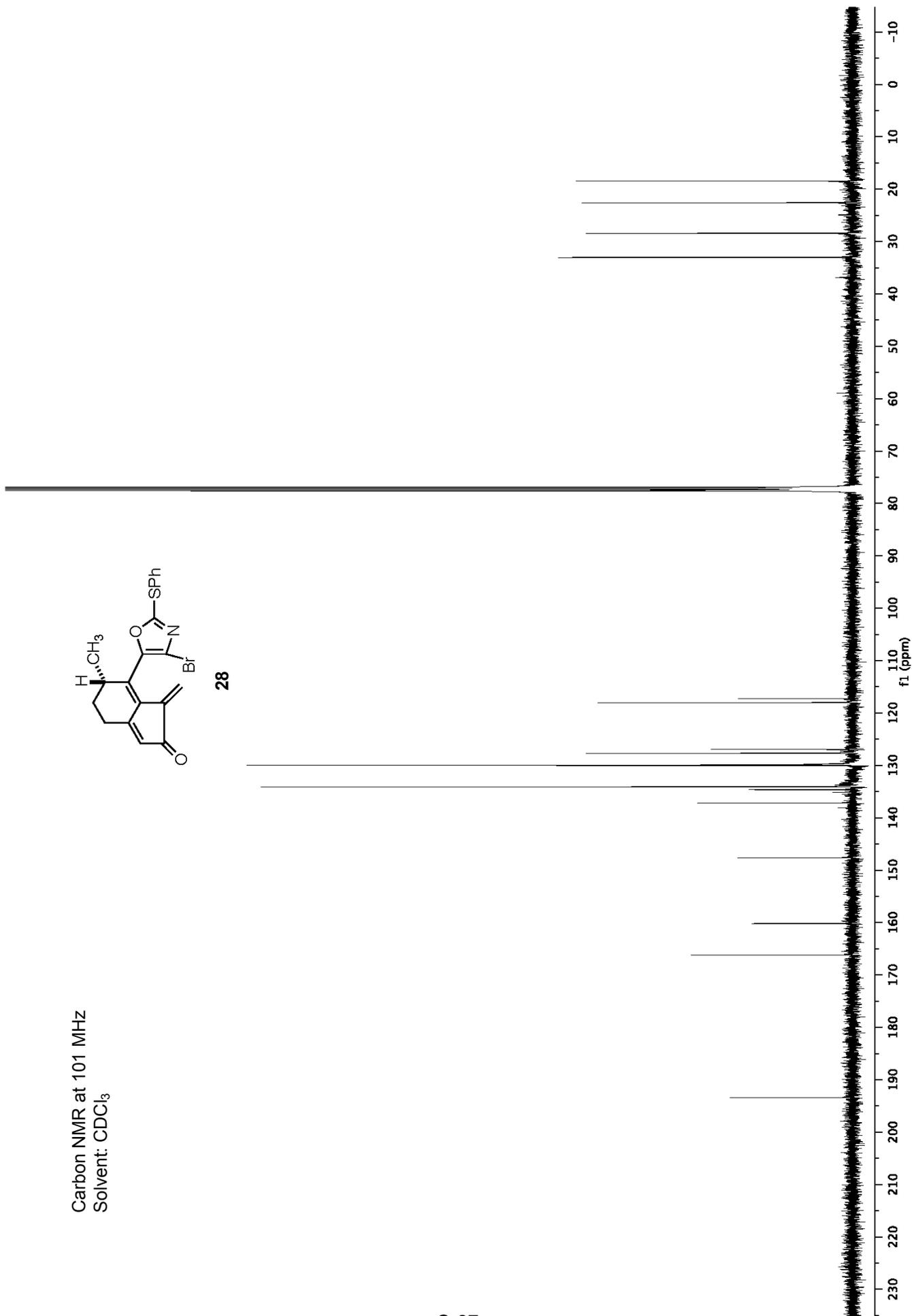
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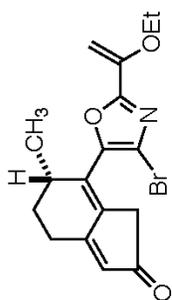
Carbon NMR at 101 MHz
Solvent: CDCl₃



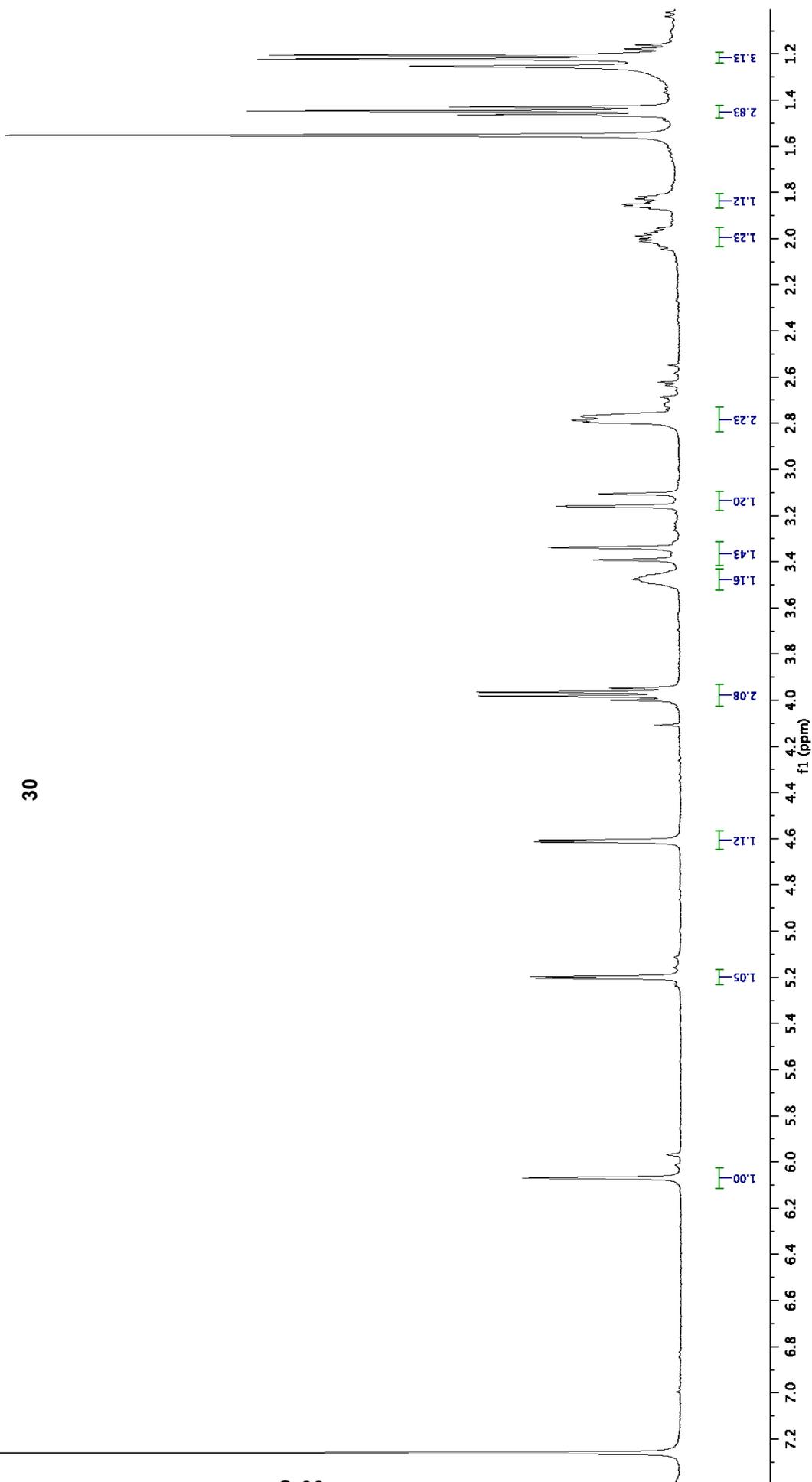
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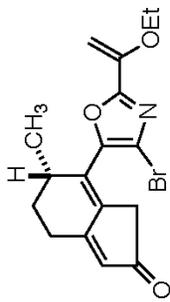
Proton NMR at 400 MHz
Solvent: CDCl₃



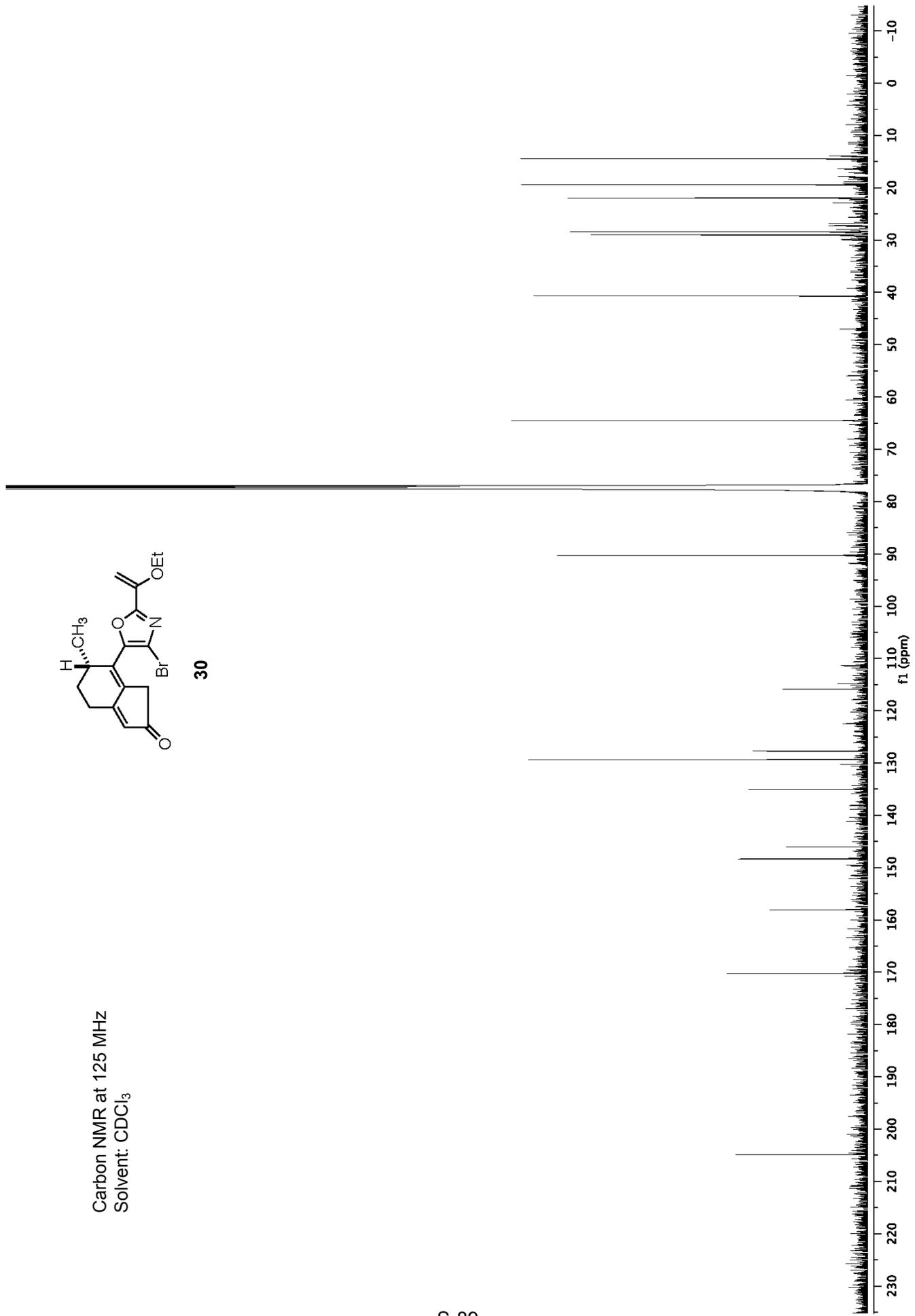
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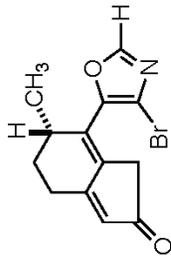
Carbon NMR at 125 MHz
Solvent: CDCl₃



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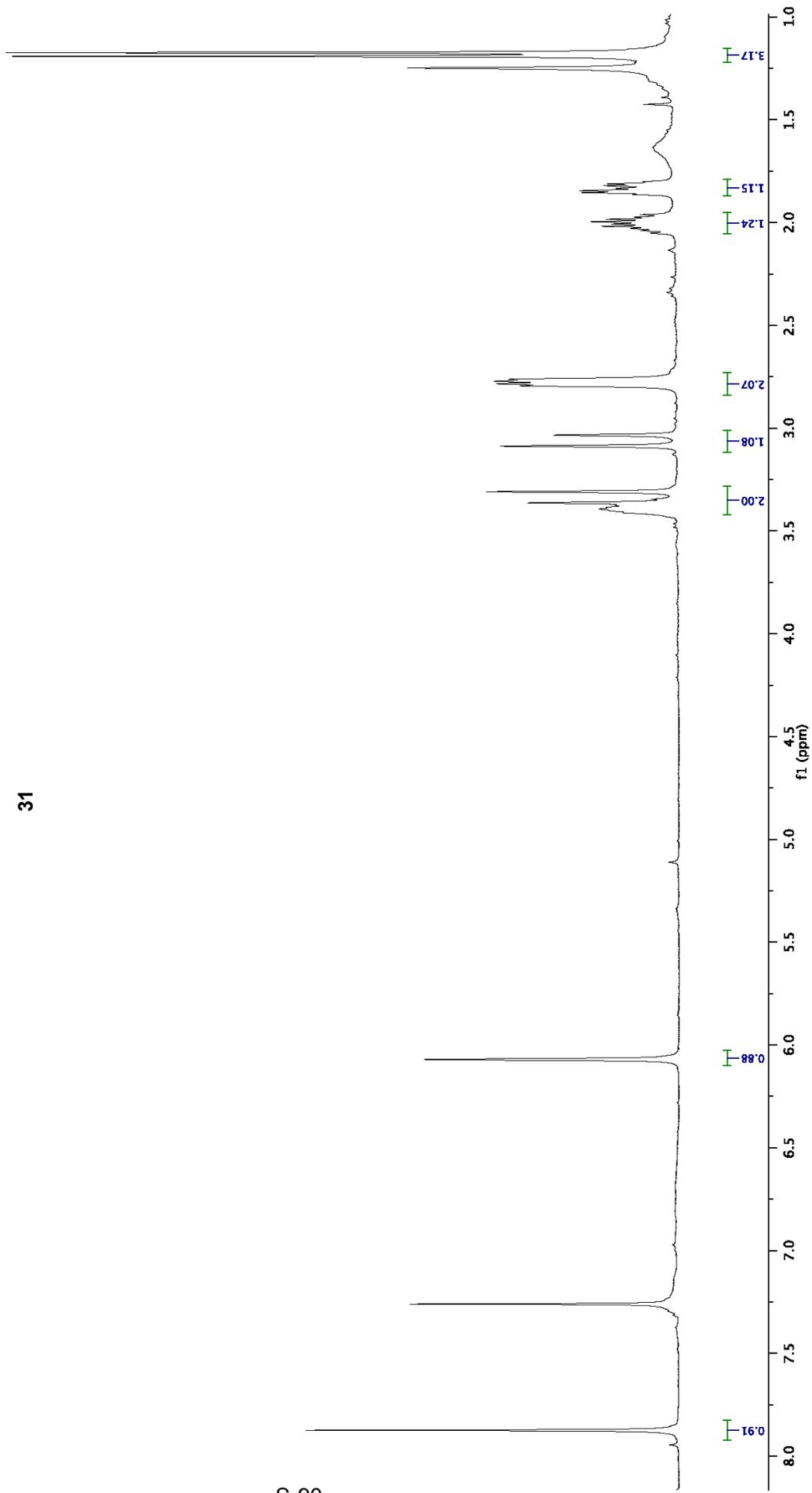


Proton NMR at 400 MHz
Solvent: CDCl₃

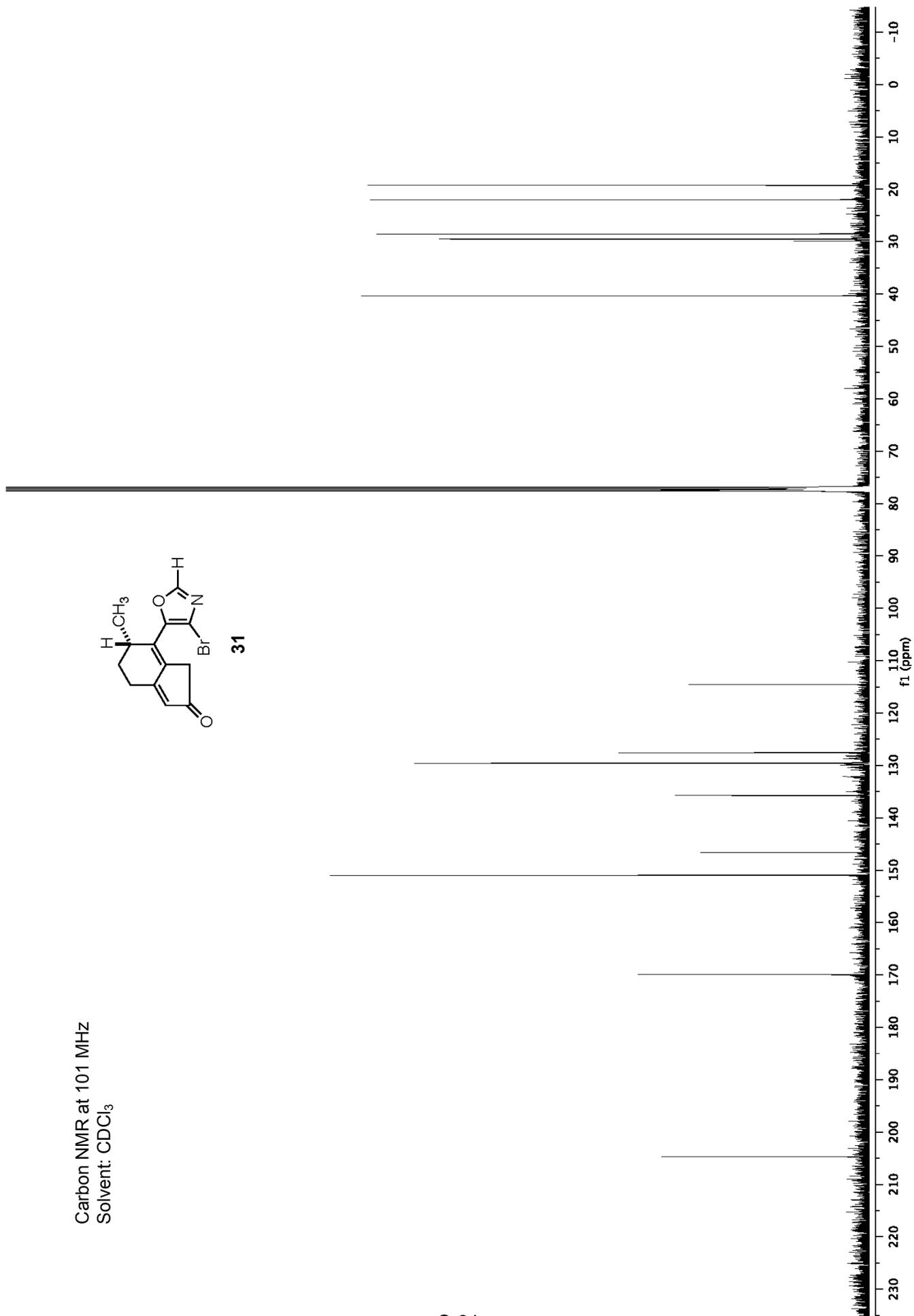
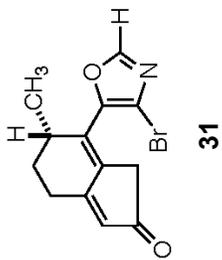


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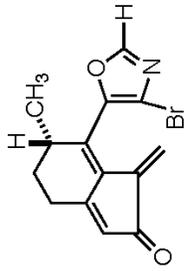
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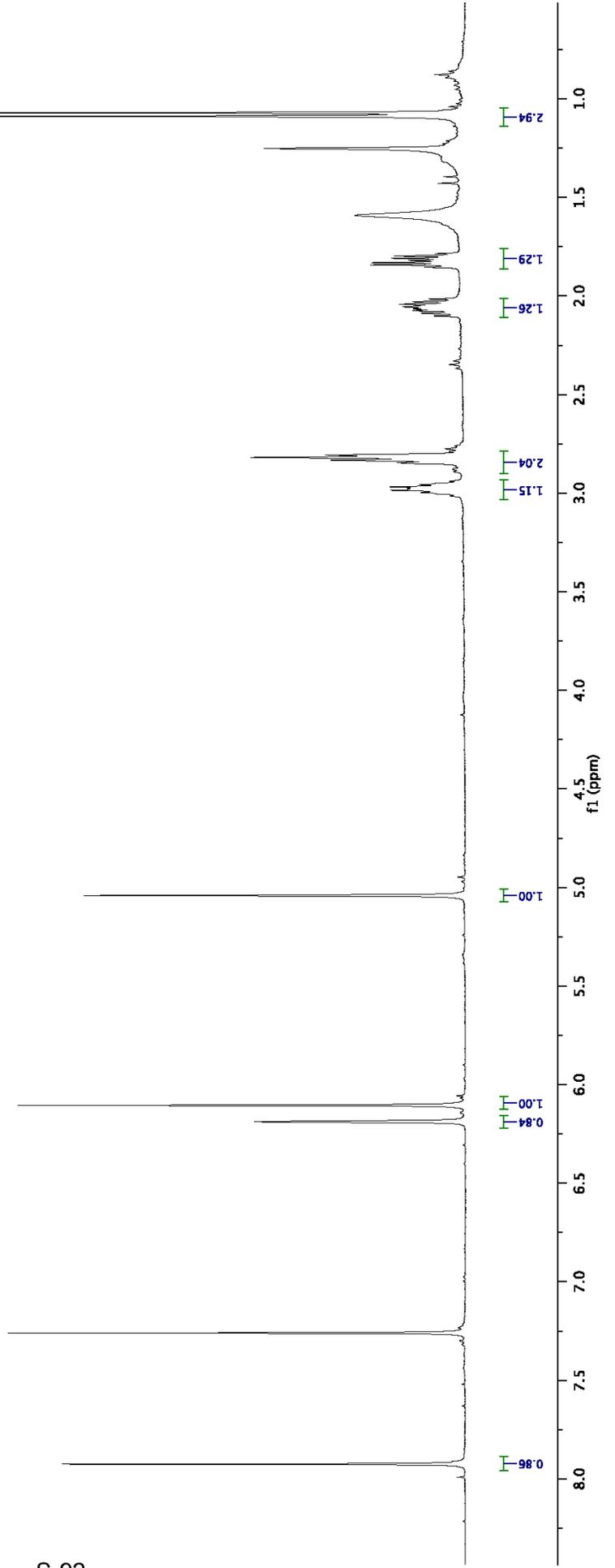
Carbon NMR at 101 MHz
Solvent: CDCl₃



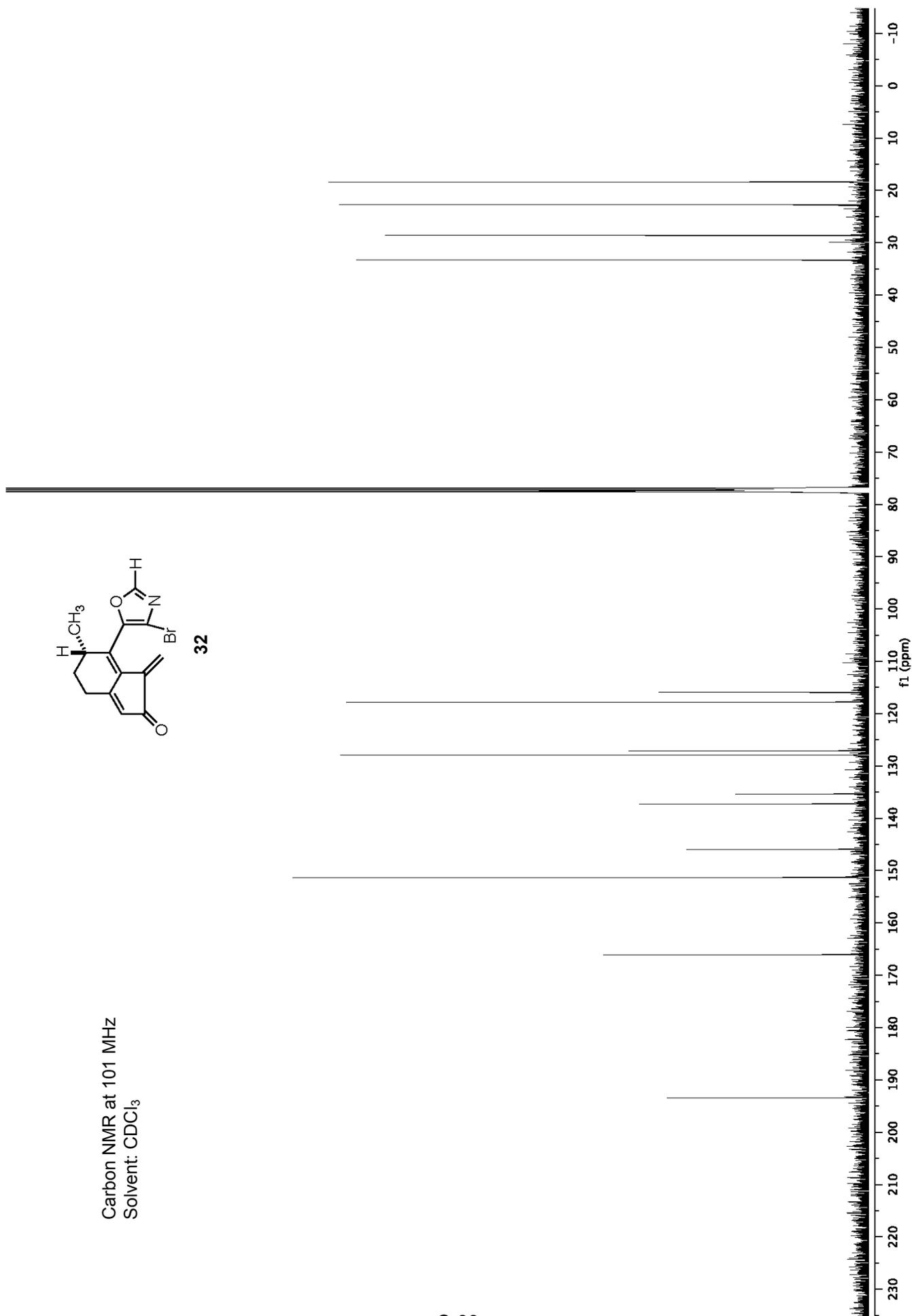
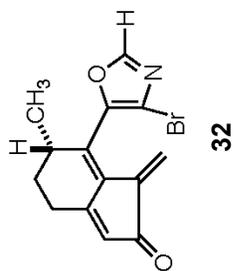
Proton NMR at 400 MHz
Solvent: CDCl₃



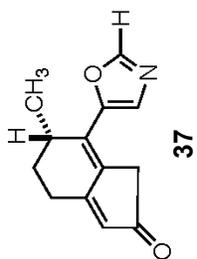
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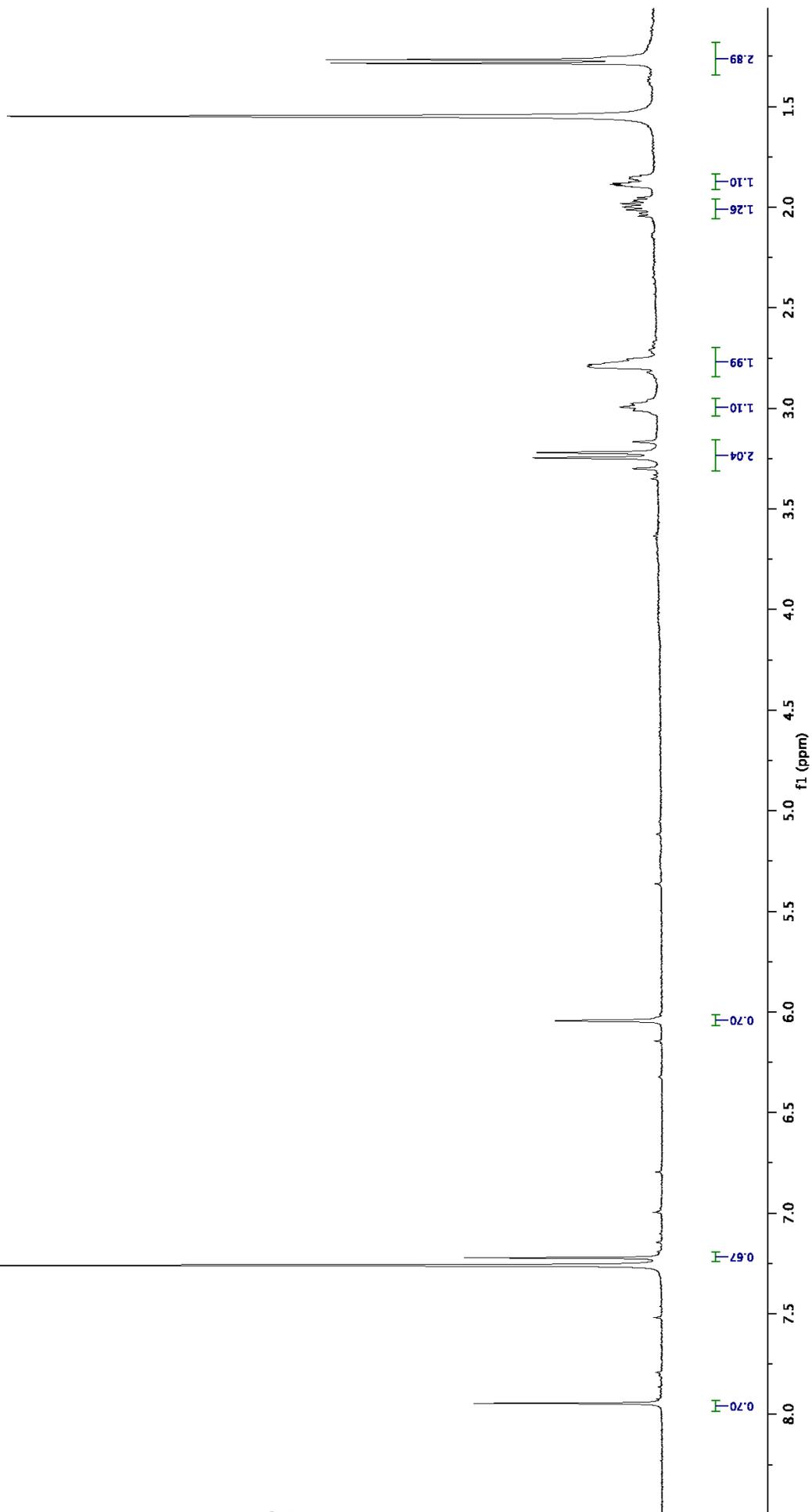
Carbon NMR at 101 MHz
Solvent: CDCl₃



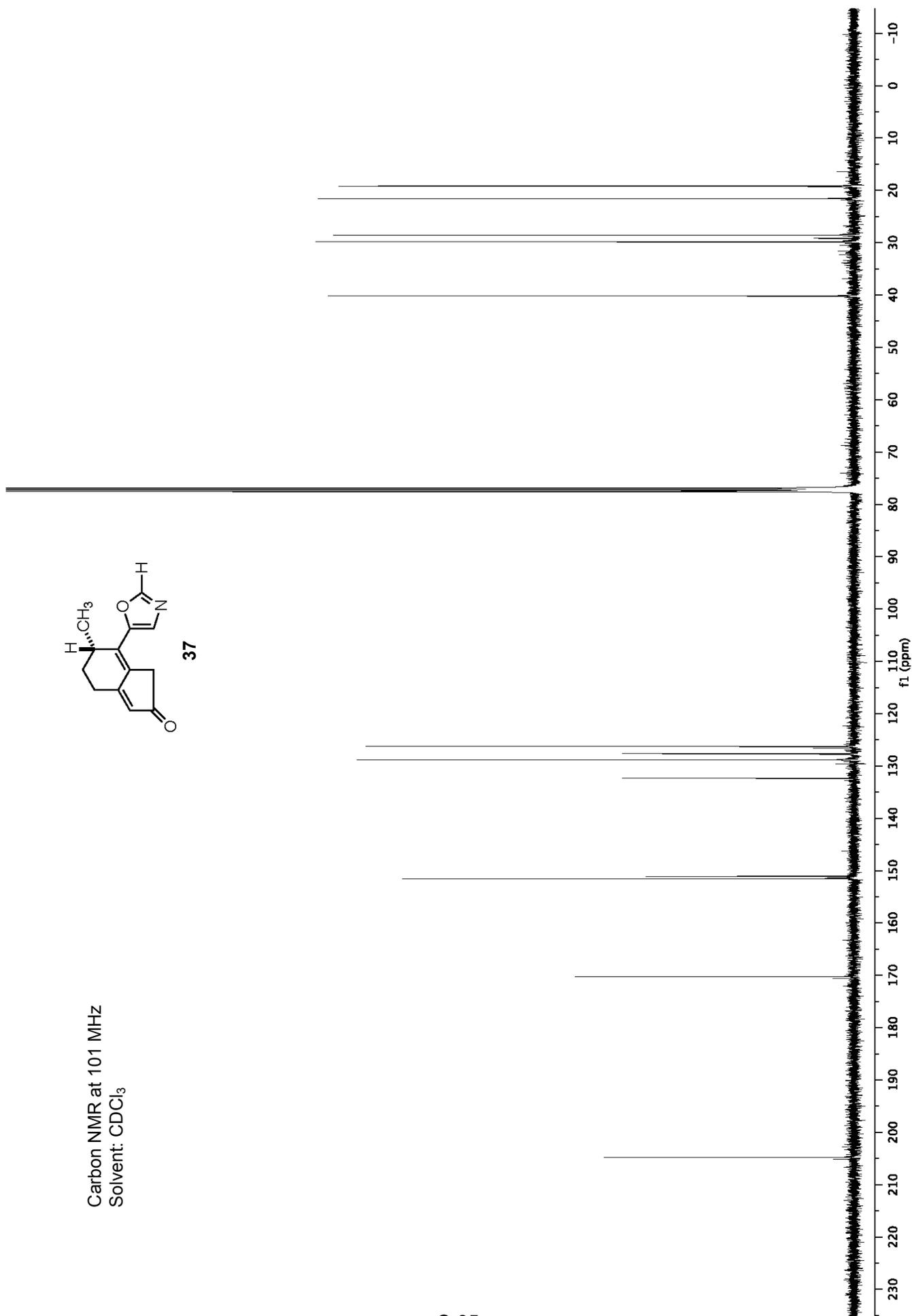
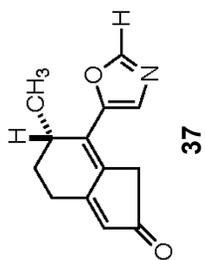
Proton NMR at 101 MHz
Solvent: CDCl₃



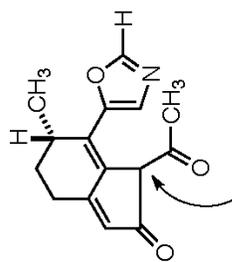
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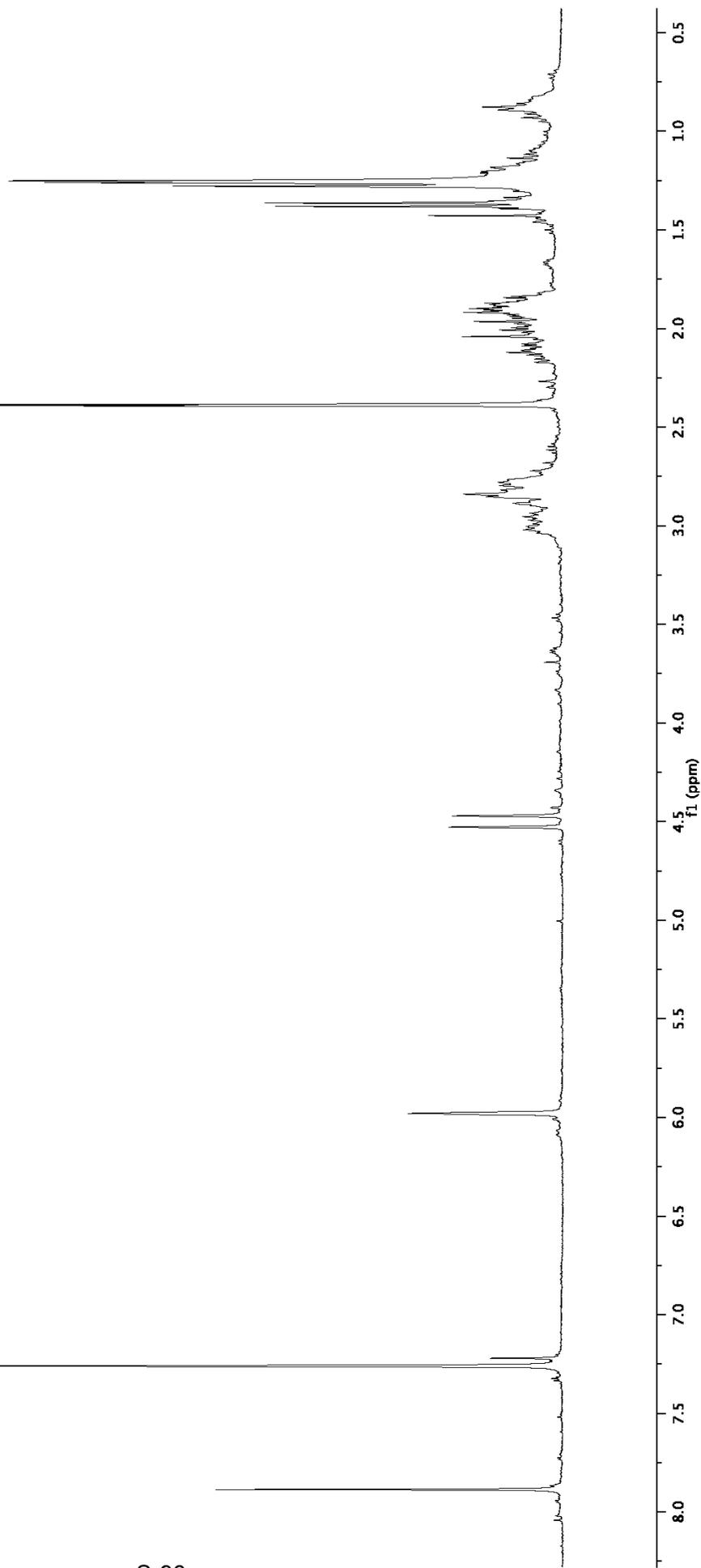
Carbon NMR at 101 MHz
Solvent: CDCl₃



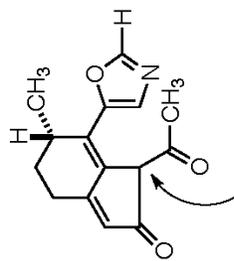
Proton NMR at 400 MHz
Solvent: CDCl₃



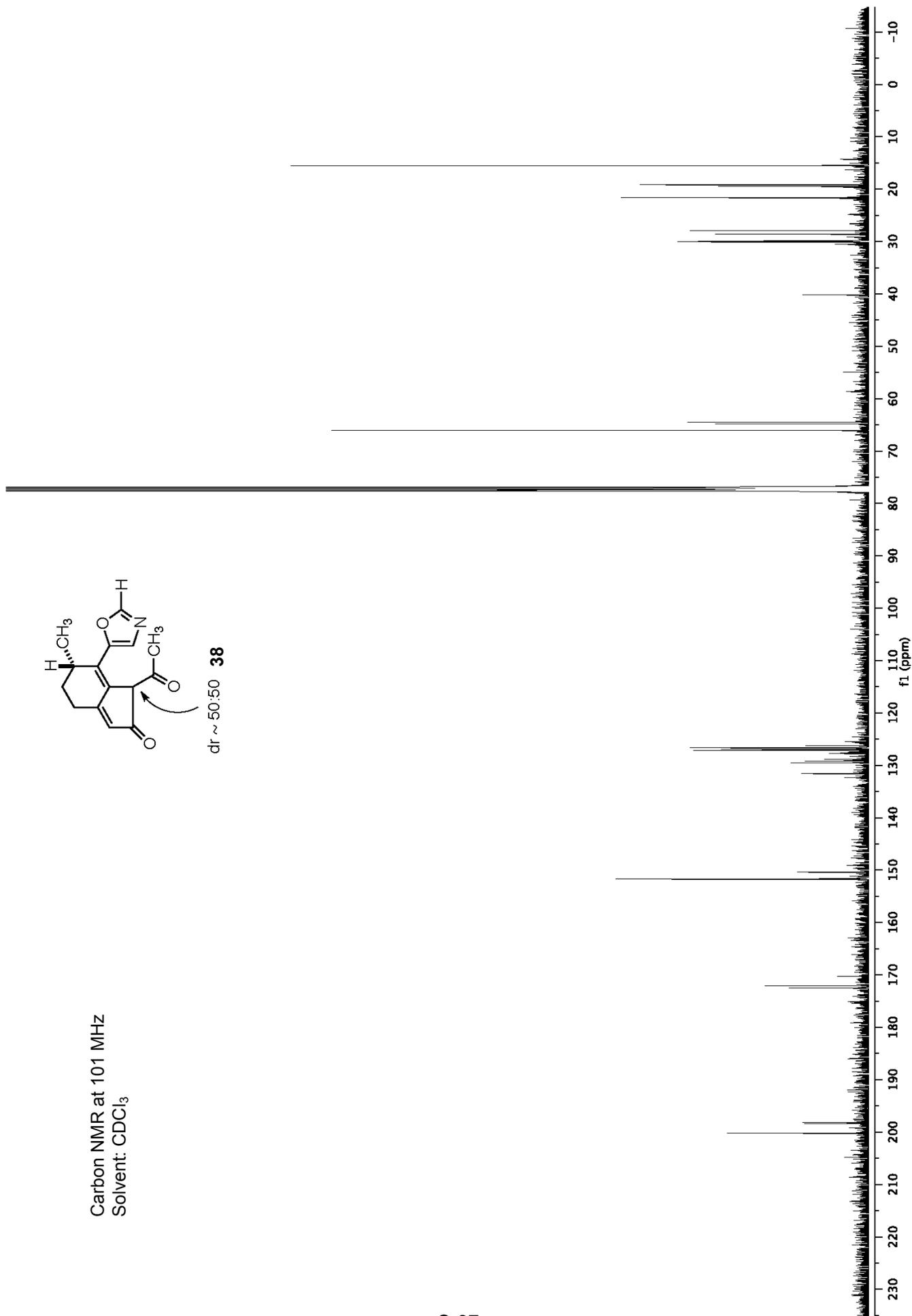
dr ~ 50:50 **38**



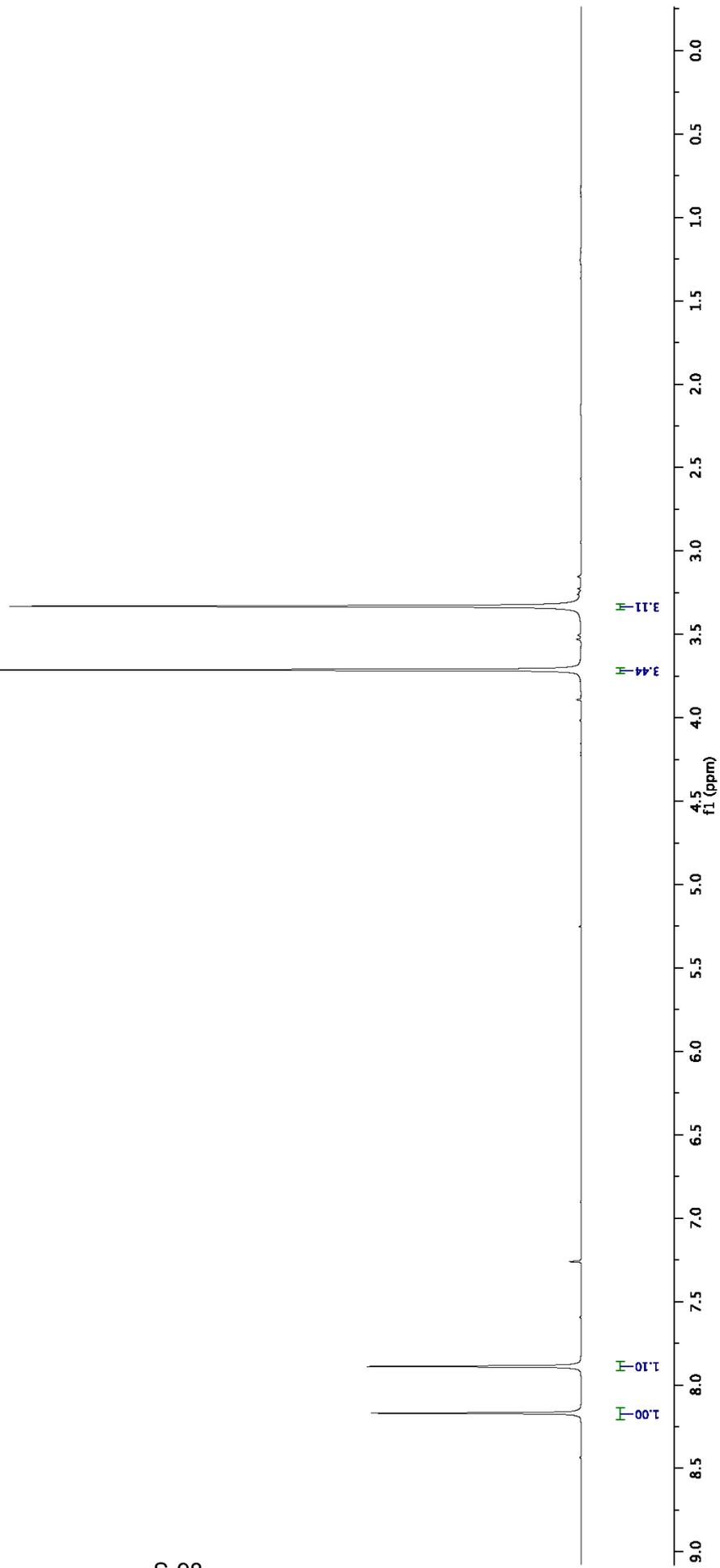
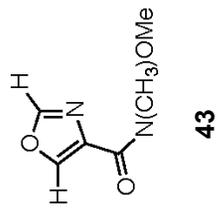
Carbon NMR at 101 MHz
Solvent: CDCl₃



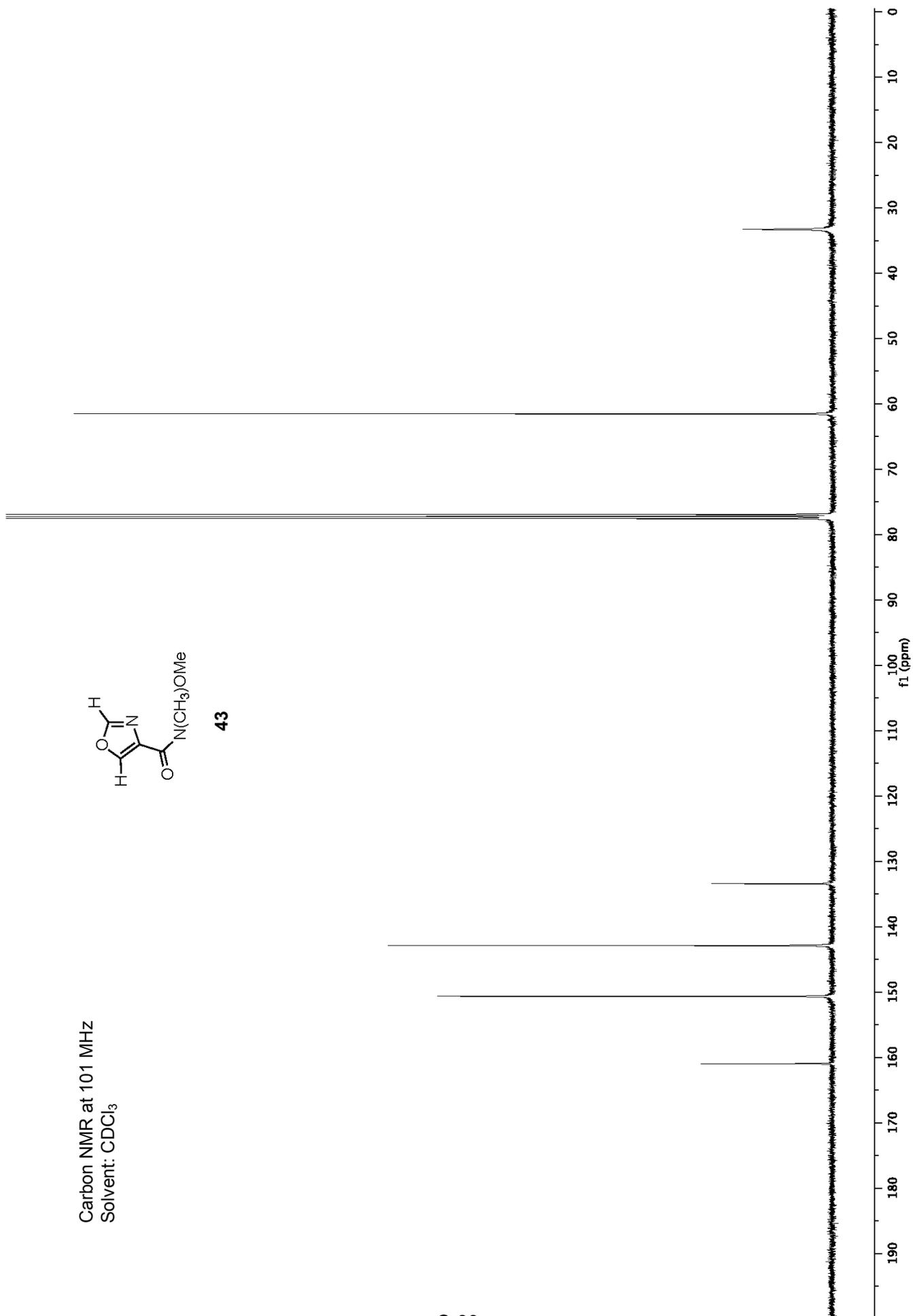
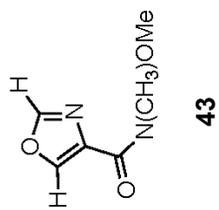
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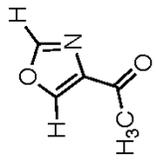
Proton NMR at 400 MHz
Solvent: CDCl₃



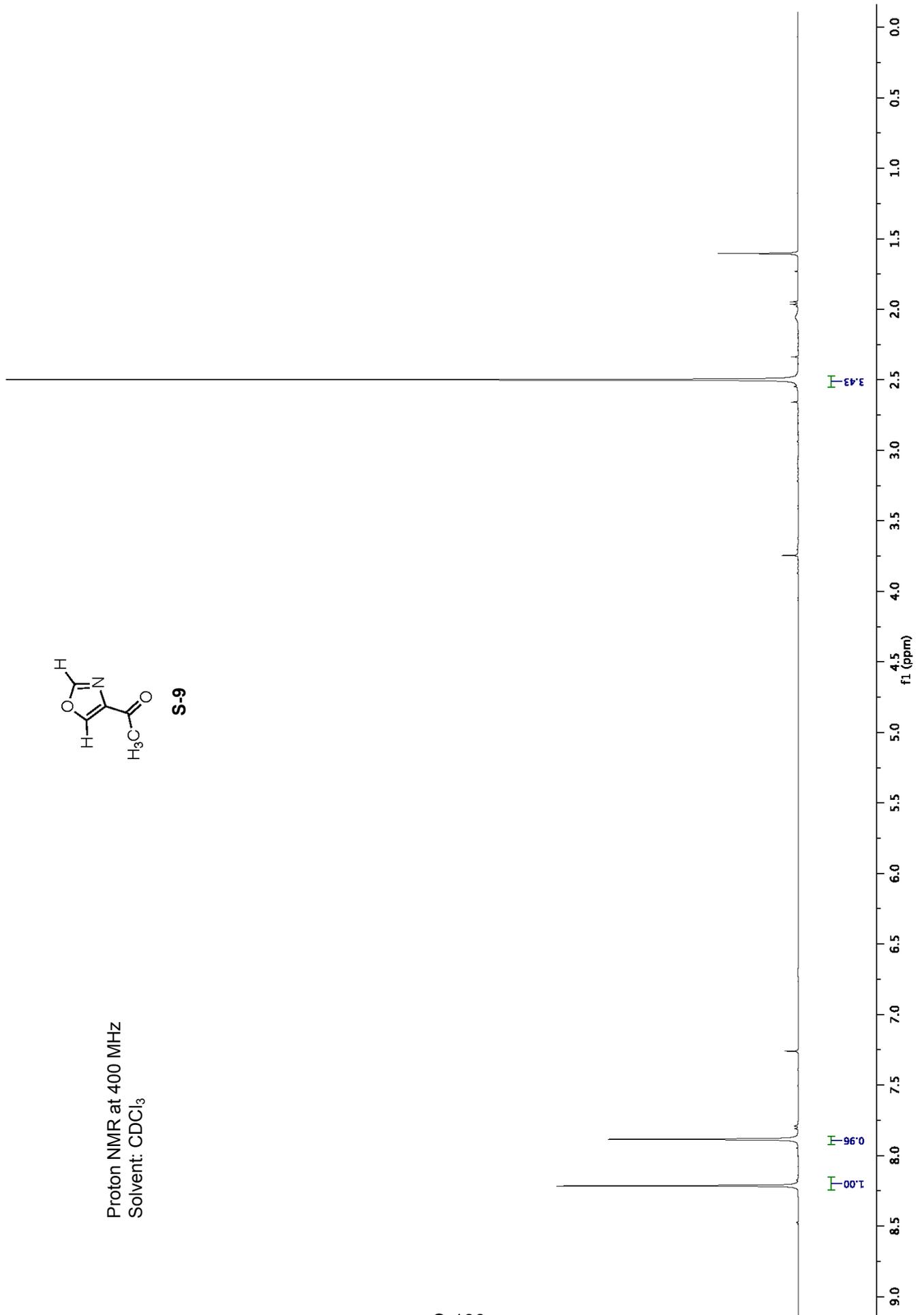
Carbon NMR at 101 MHz
Solvent: CDCl₃



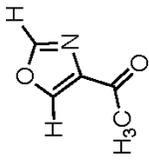
Proton NMR at 400 MHz
Solvent: CDCl₃



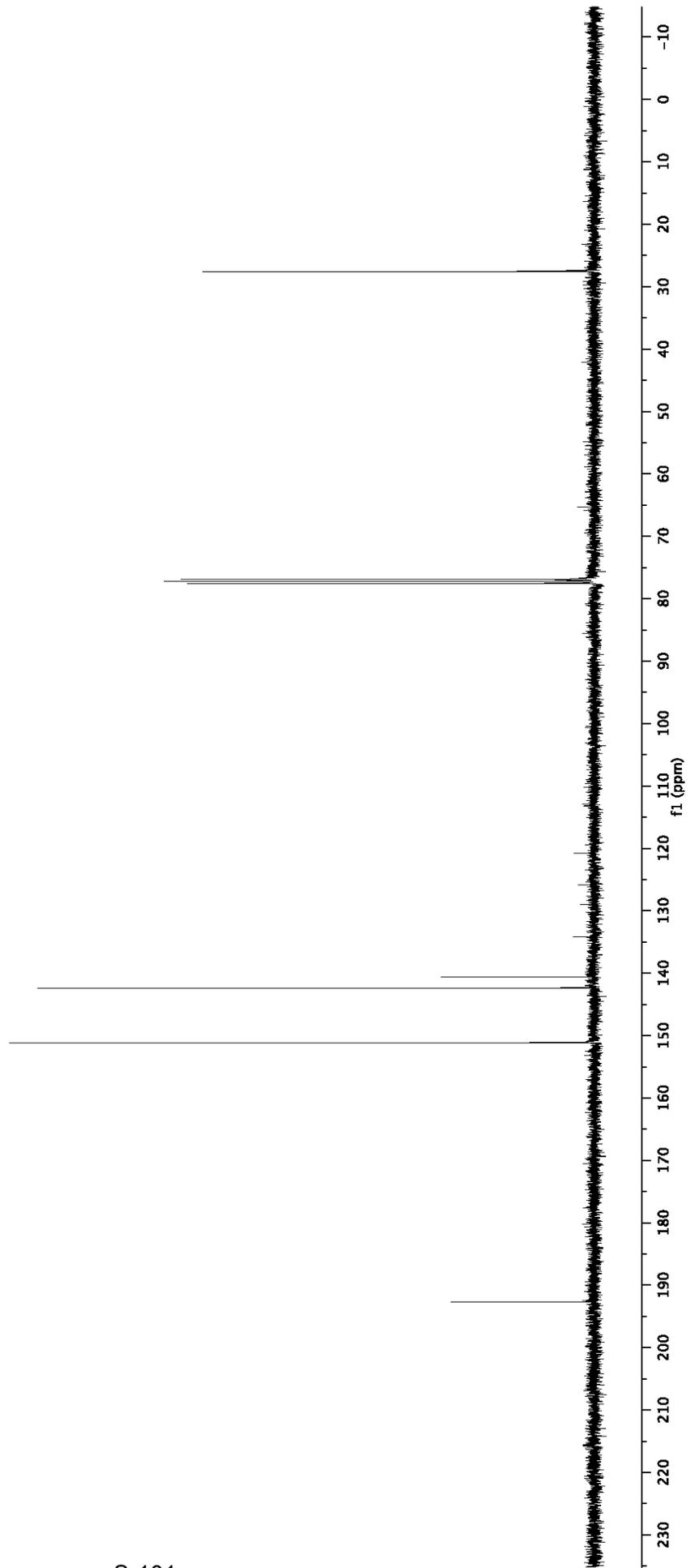
S-9



Carbon NMR at 101 MHz
Solvent: CDCl₃

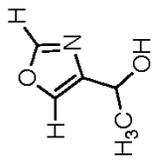


S-9

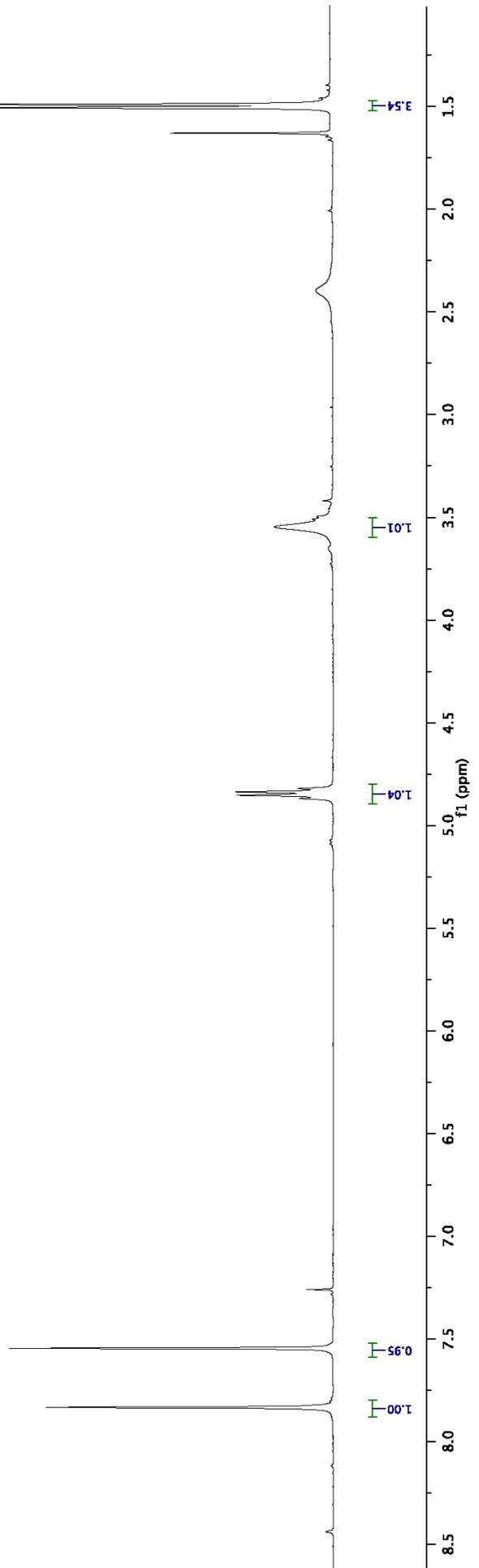


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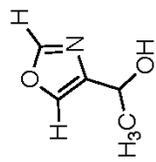
Proton NMR at 400 MHz
Solvent: CDCl₃



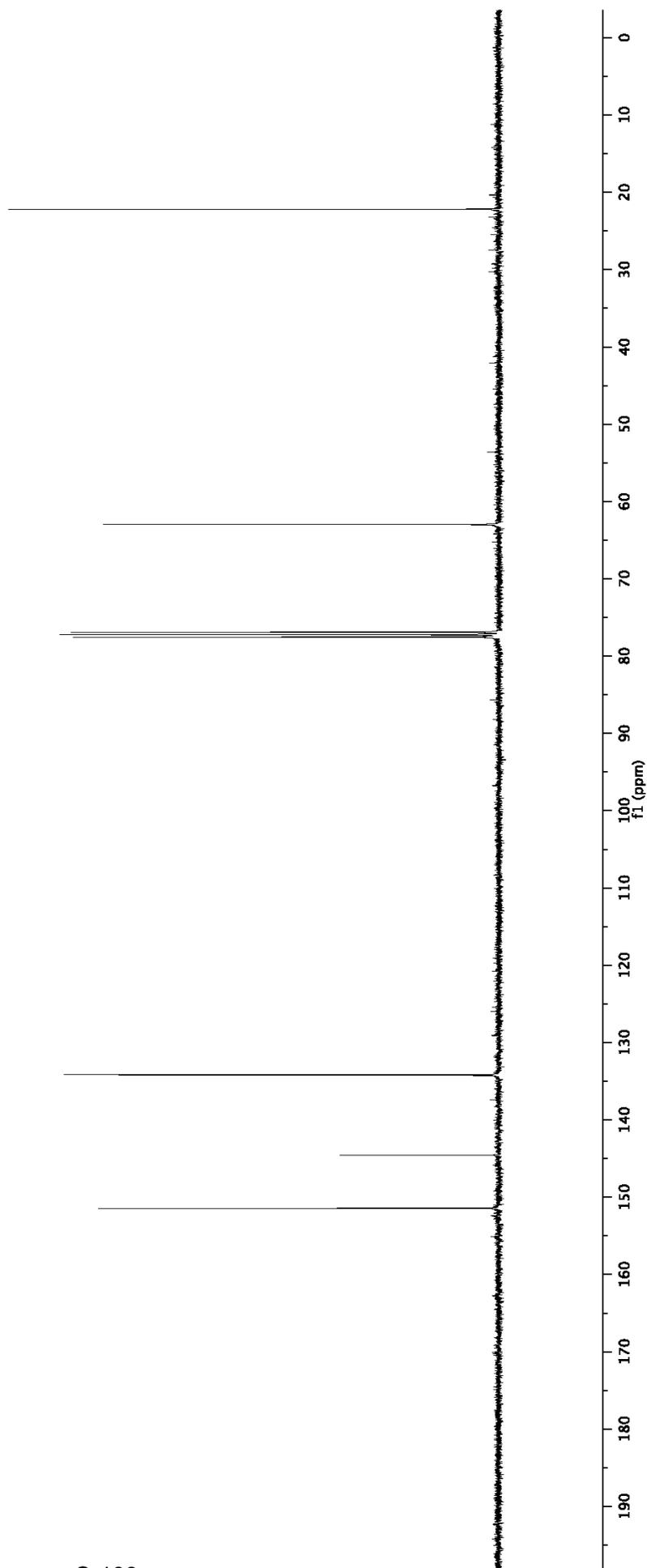
S-10



Carbon NMR at 101 MHz
Solvent: CDCl₃

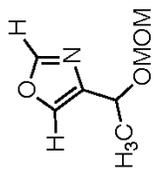


S-10

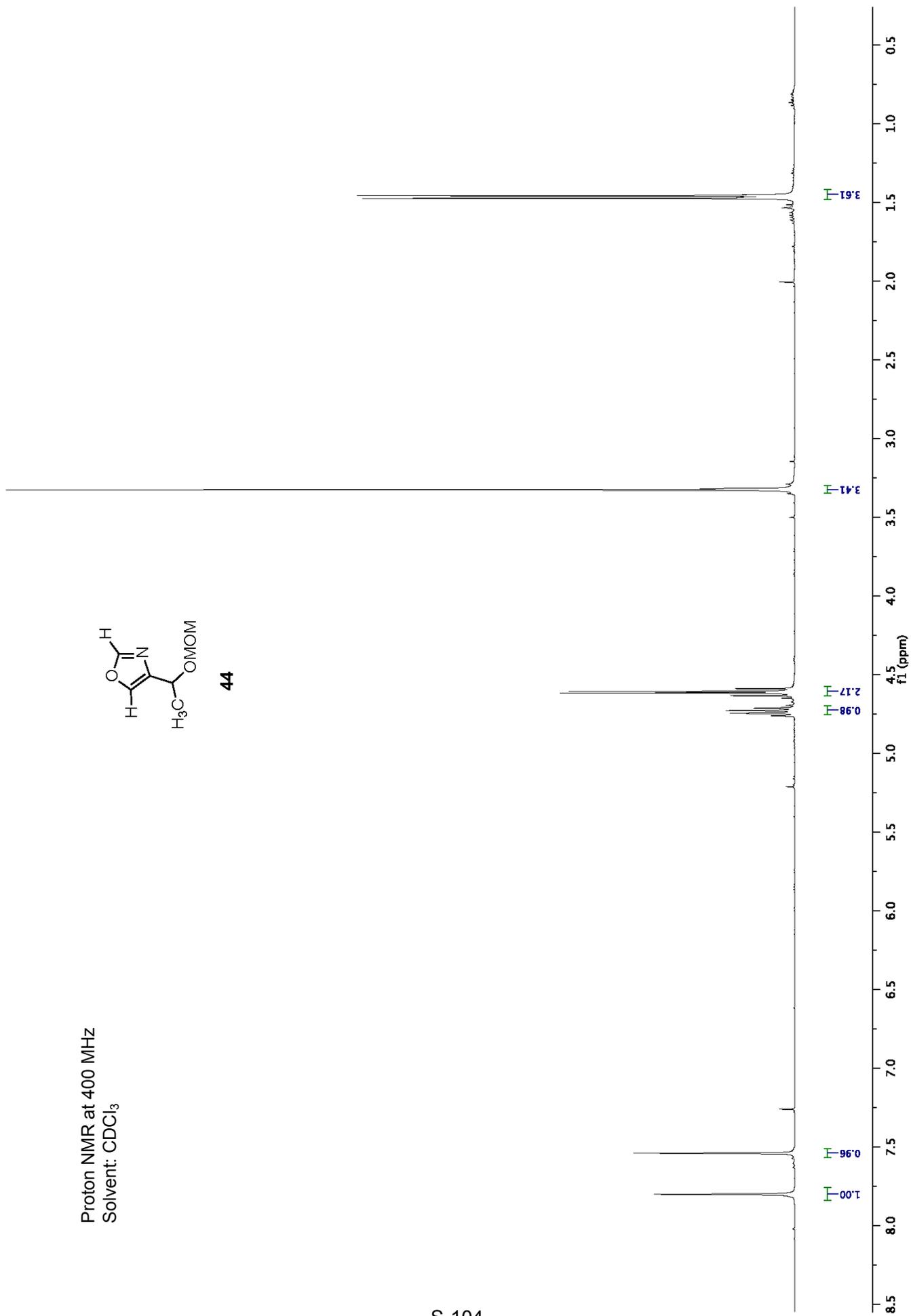


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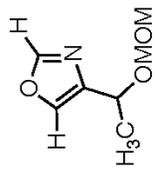
Proton NMR at 400 MHz
Solvent: CDCl₃



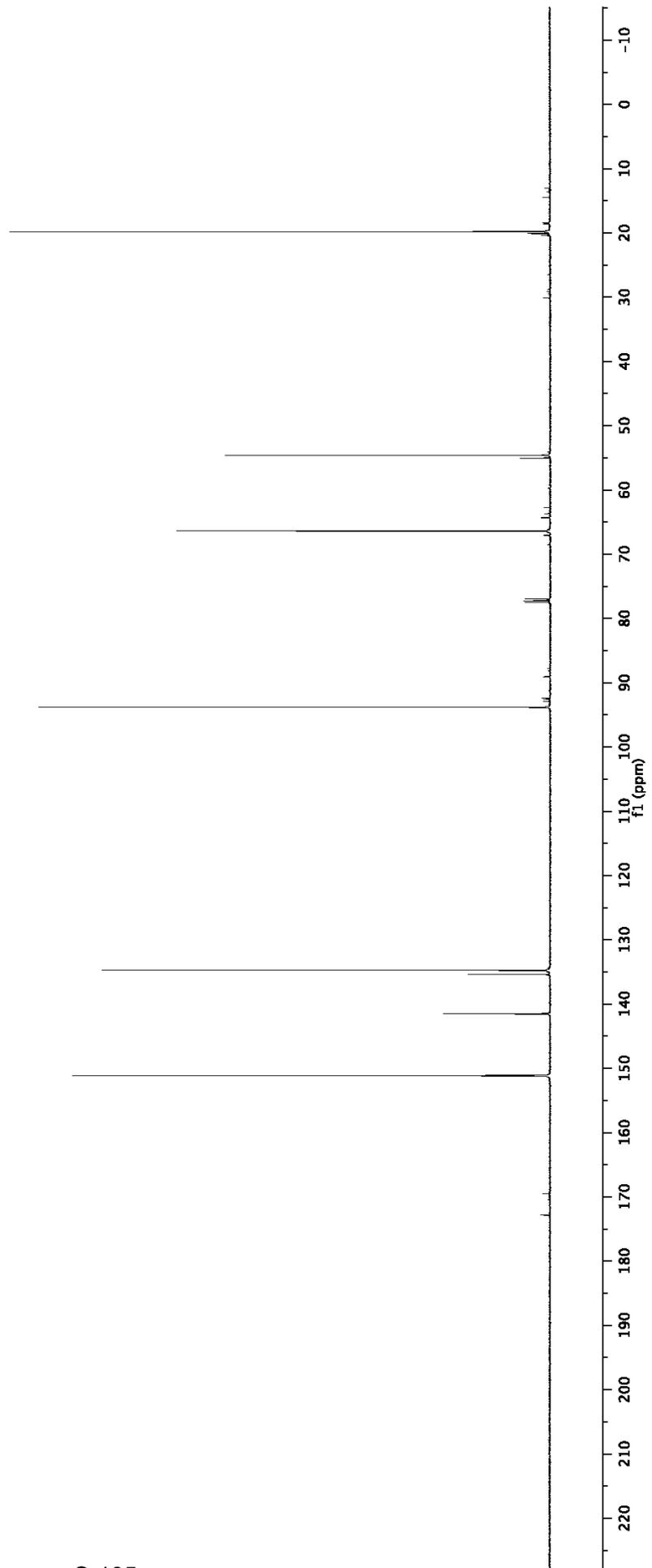
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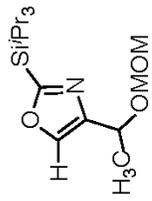
Carbon NMR at 125 MHz
Solvent: CDCl₃



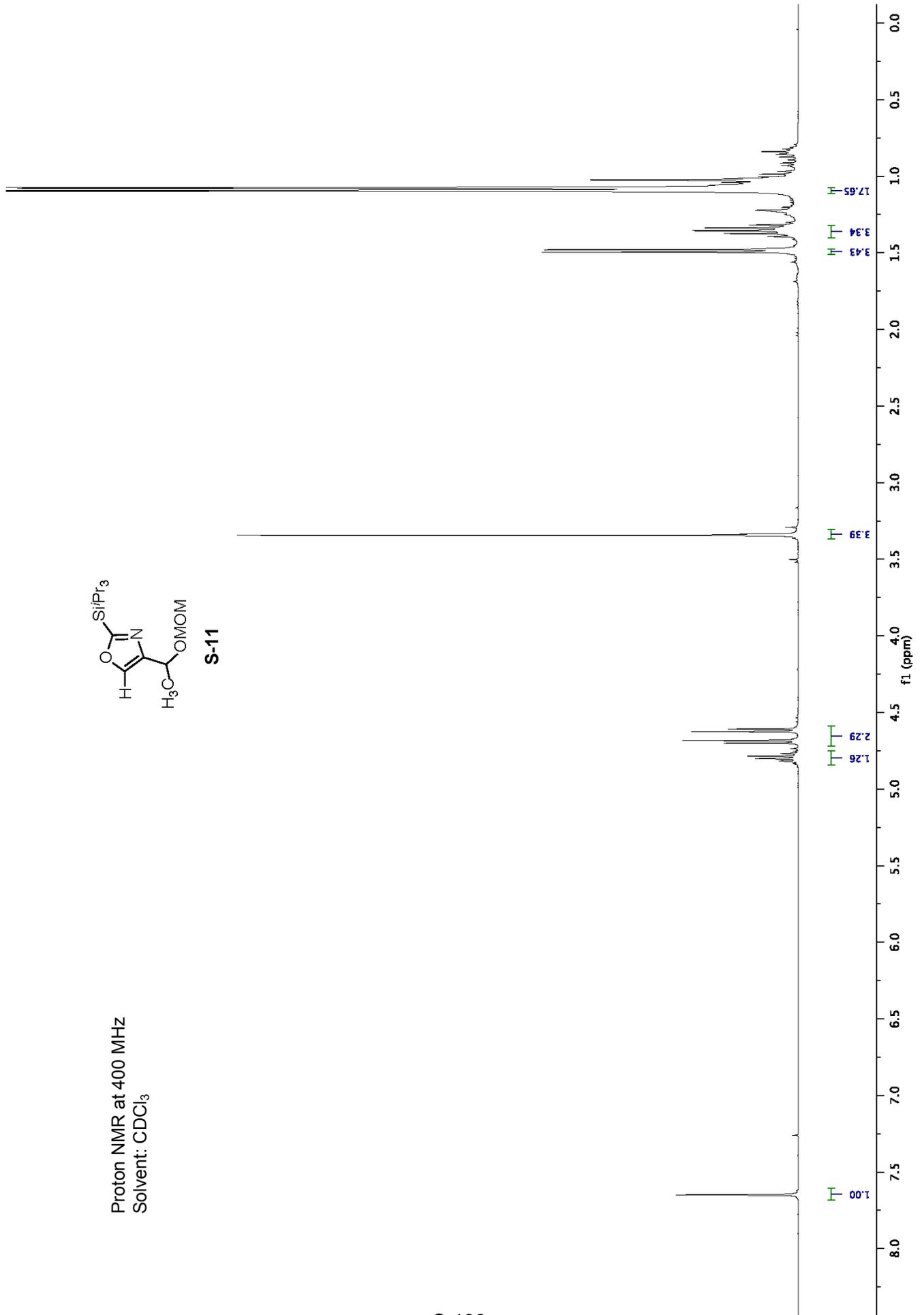
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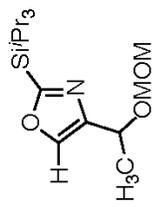
Proton NMR at 400 MHz
Solvent: CDCl₃



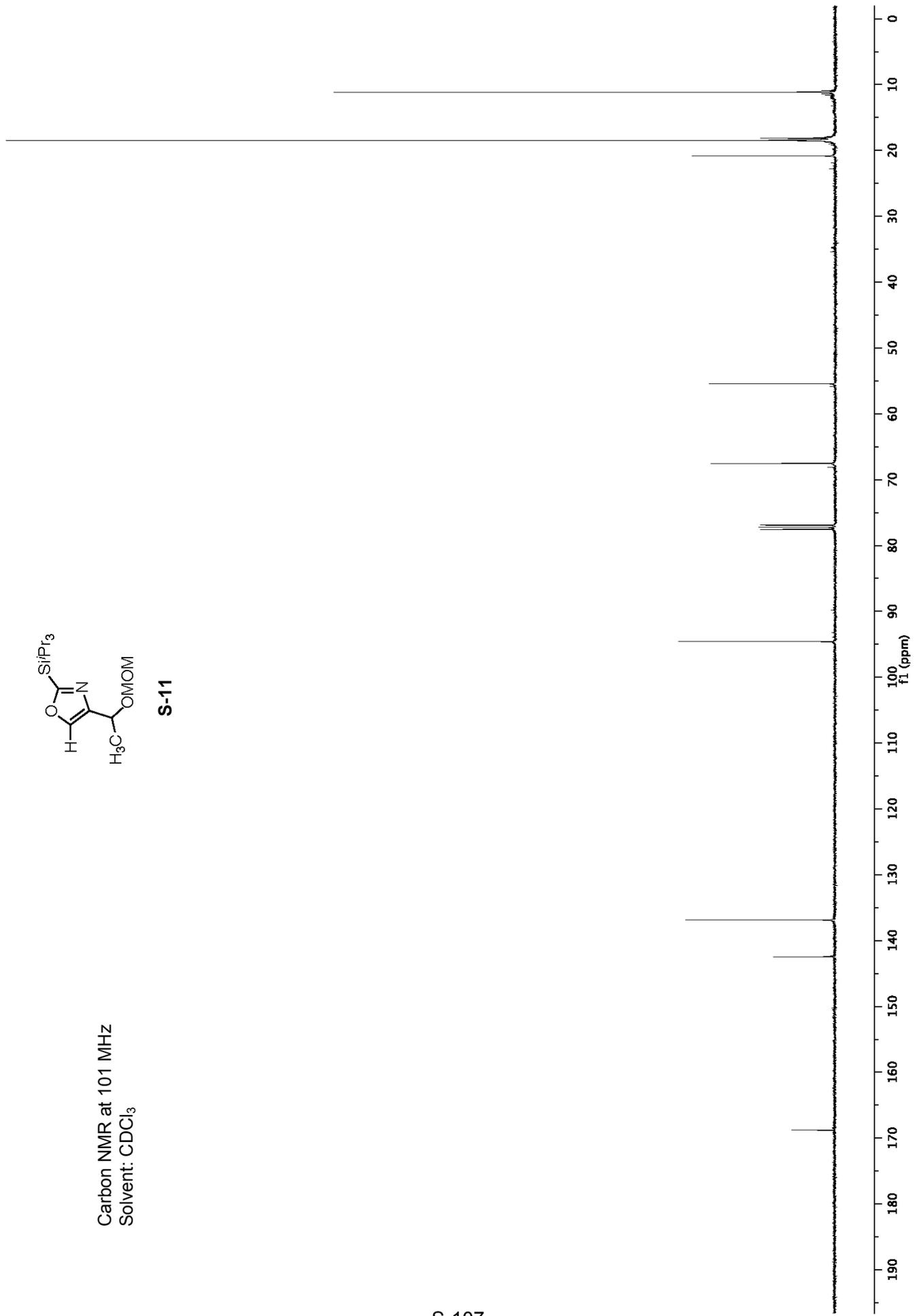
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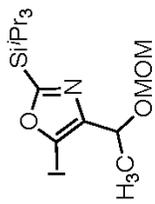
Carbon NMR at 101 MHz
Solvent: CDCl₃



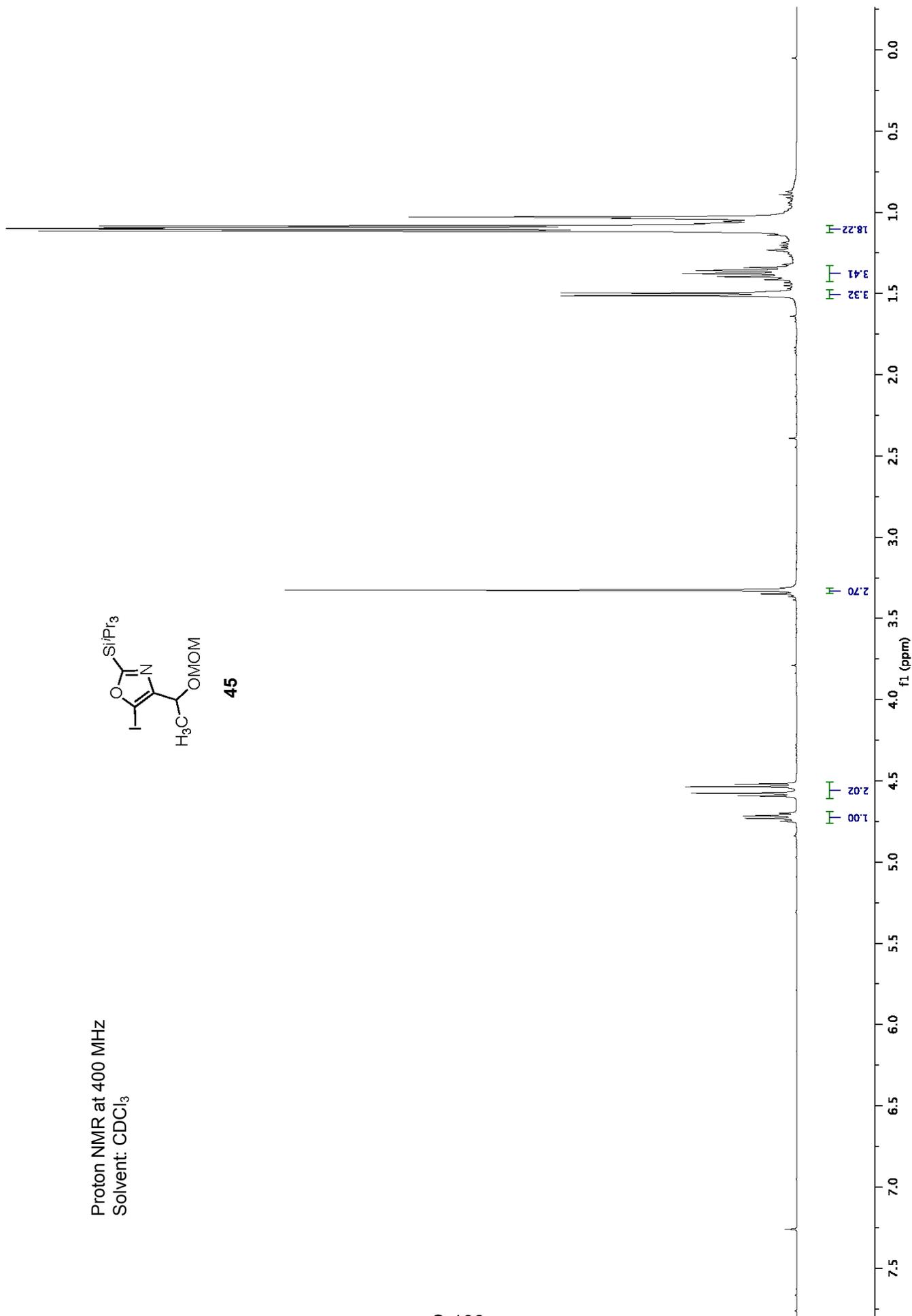
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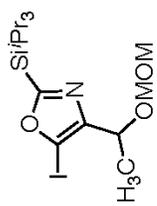
Proton NMR at 400 MHz
Solvent: CDCl₃



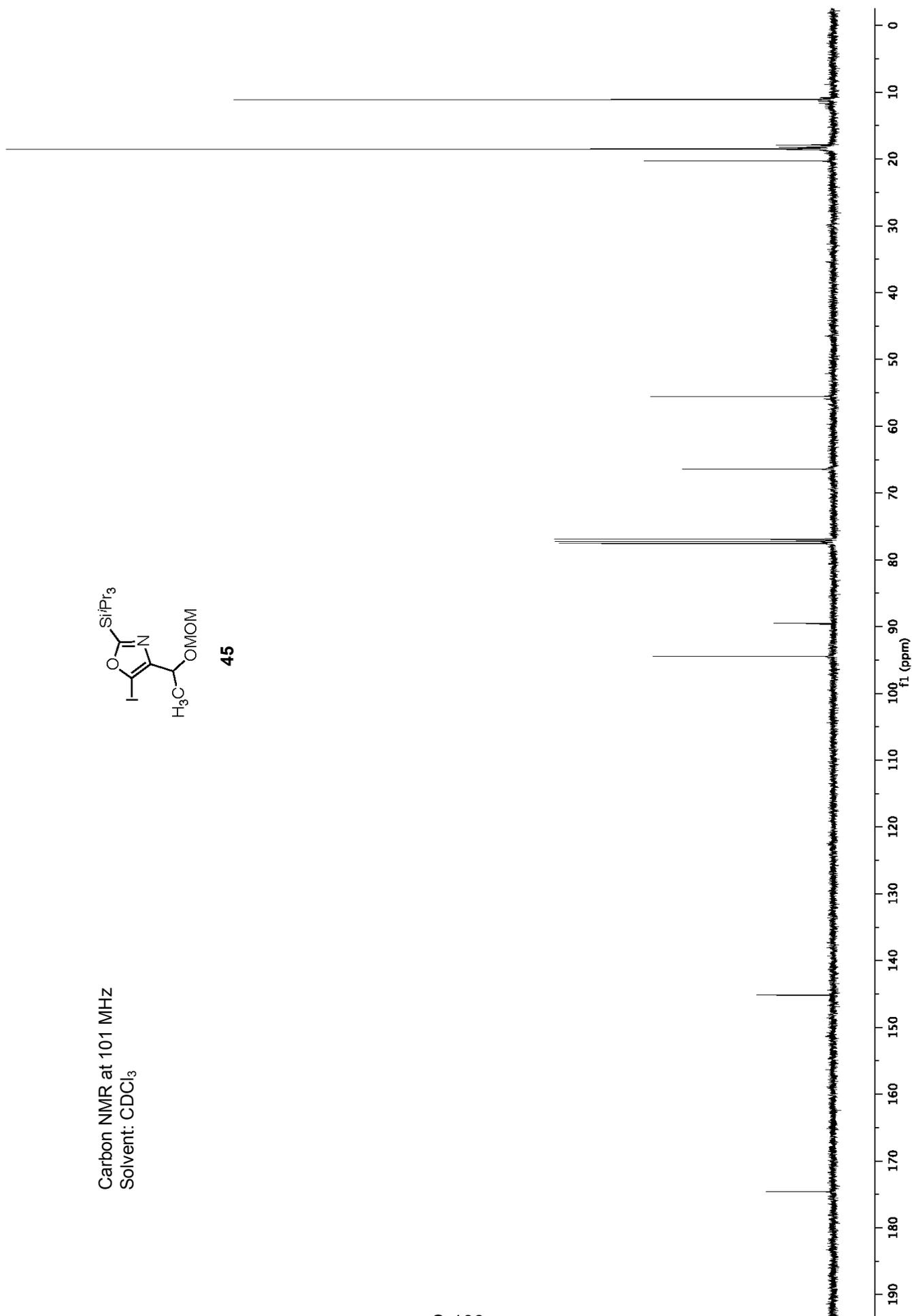
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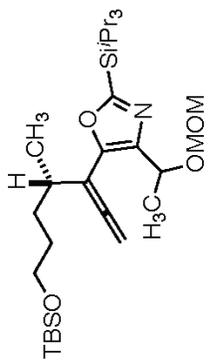
Carbon NMR at 101 MHz
Solvent: CDCl₃



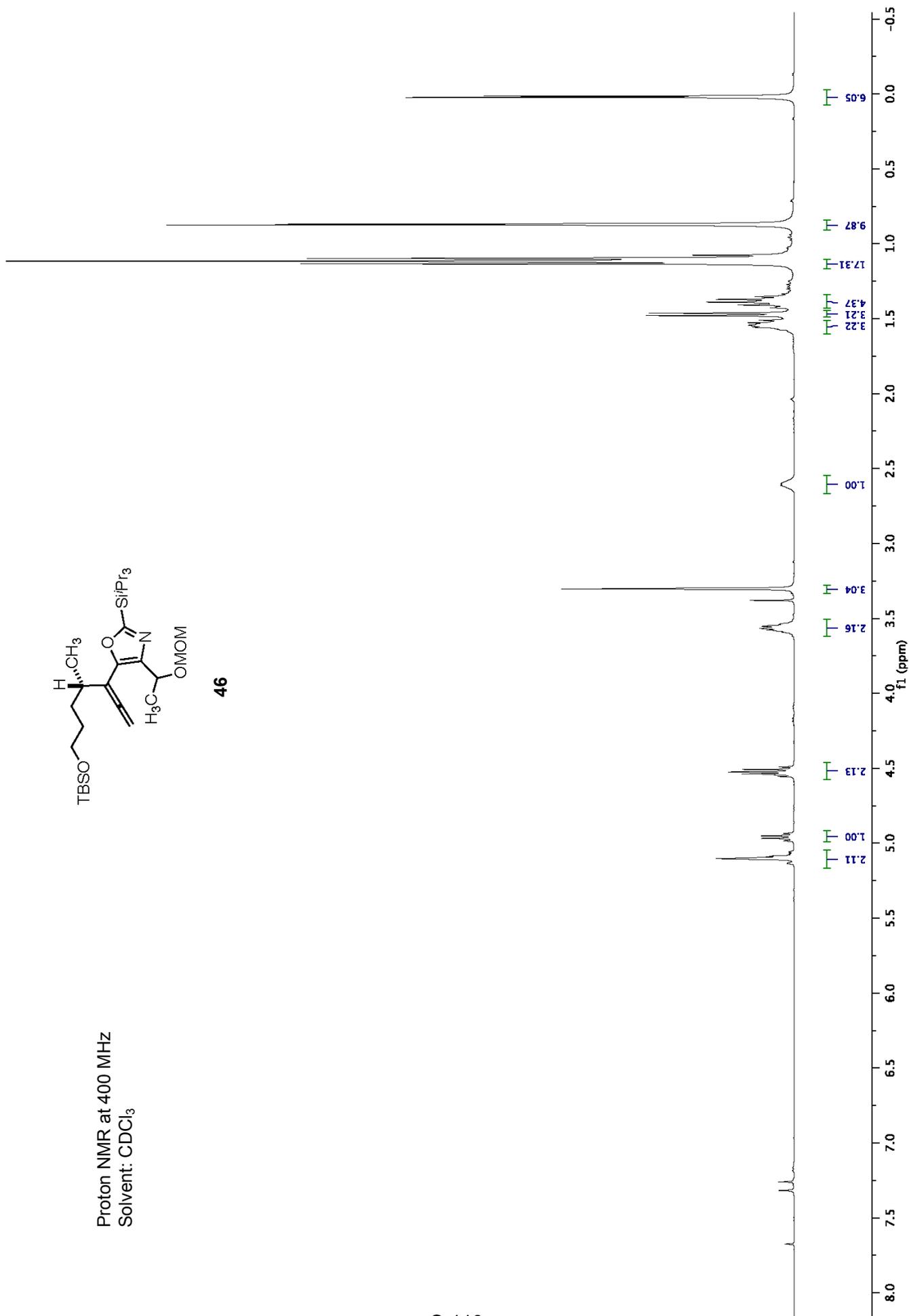
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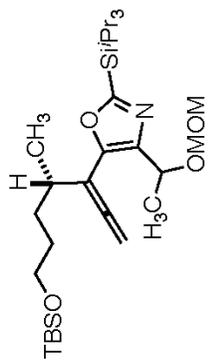
Proton NMR at 400 MHz
Solvent: CDCl₃



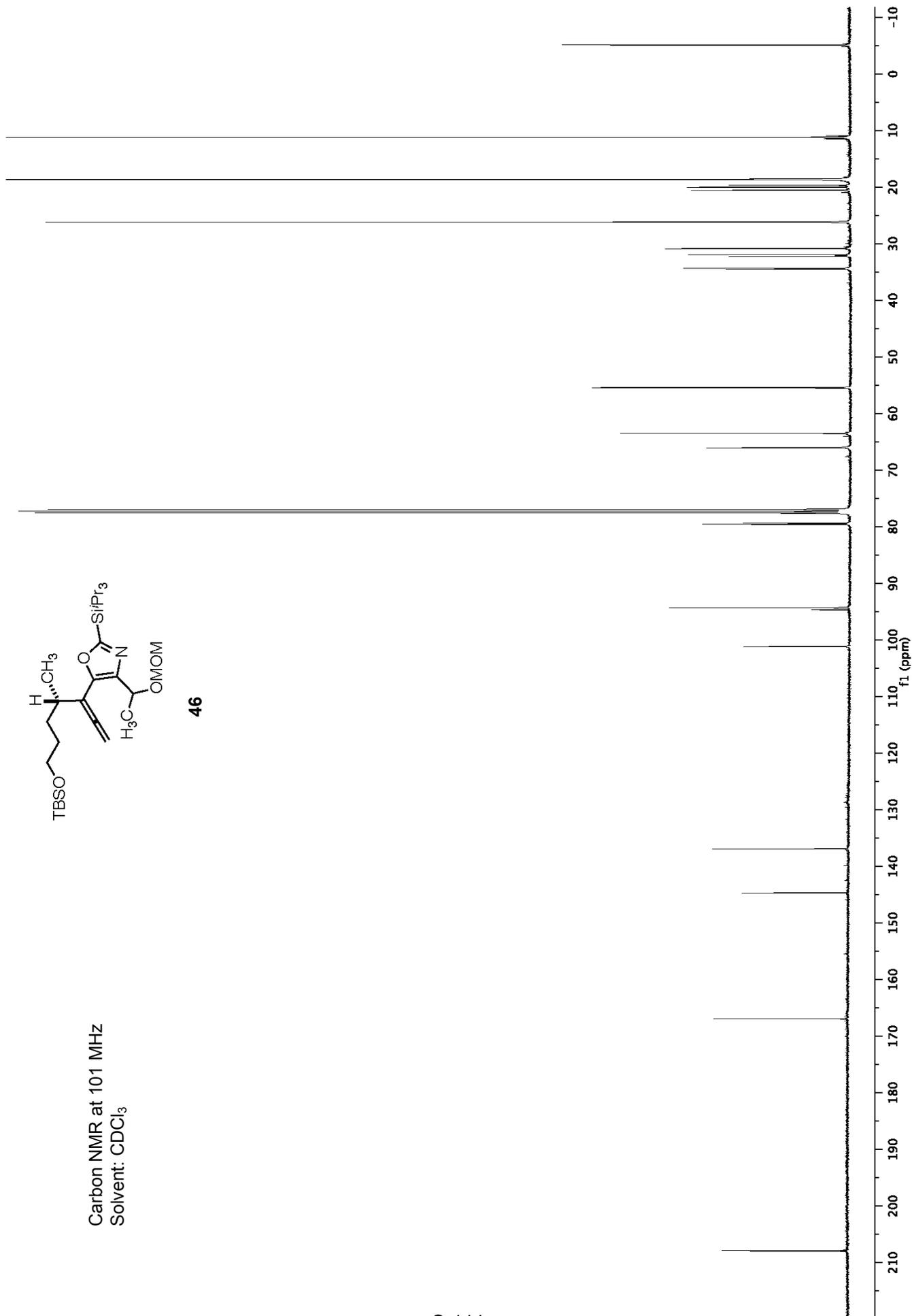
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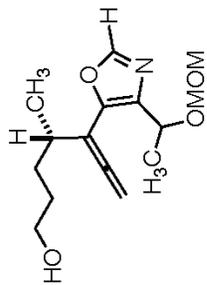
Carbon NMR at 101 MHz
Solvent: CDCl₃



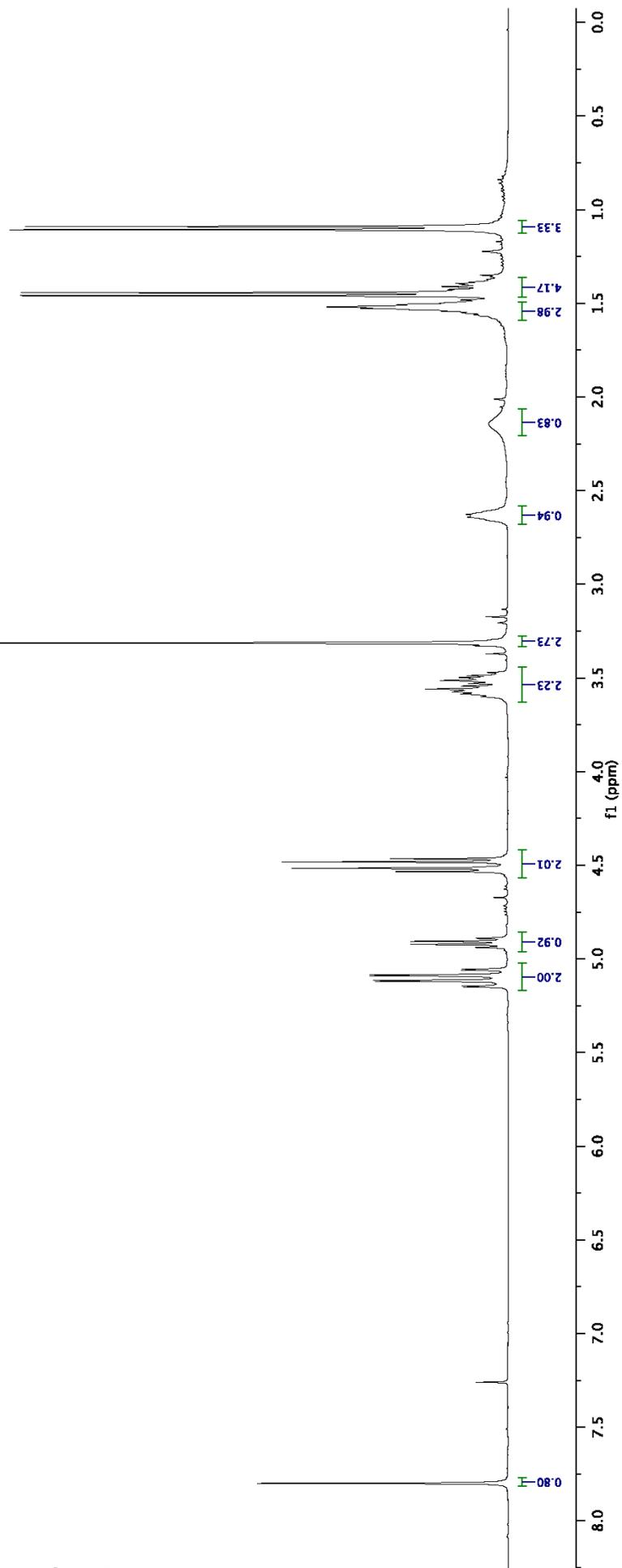
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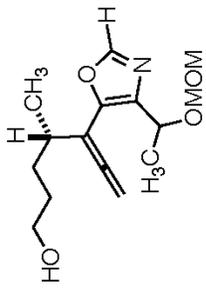
Proton NMR at 400 MHz
Solvent: CDCl₃



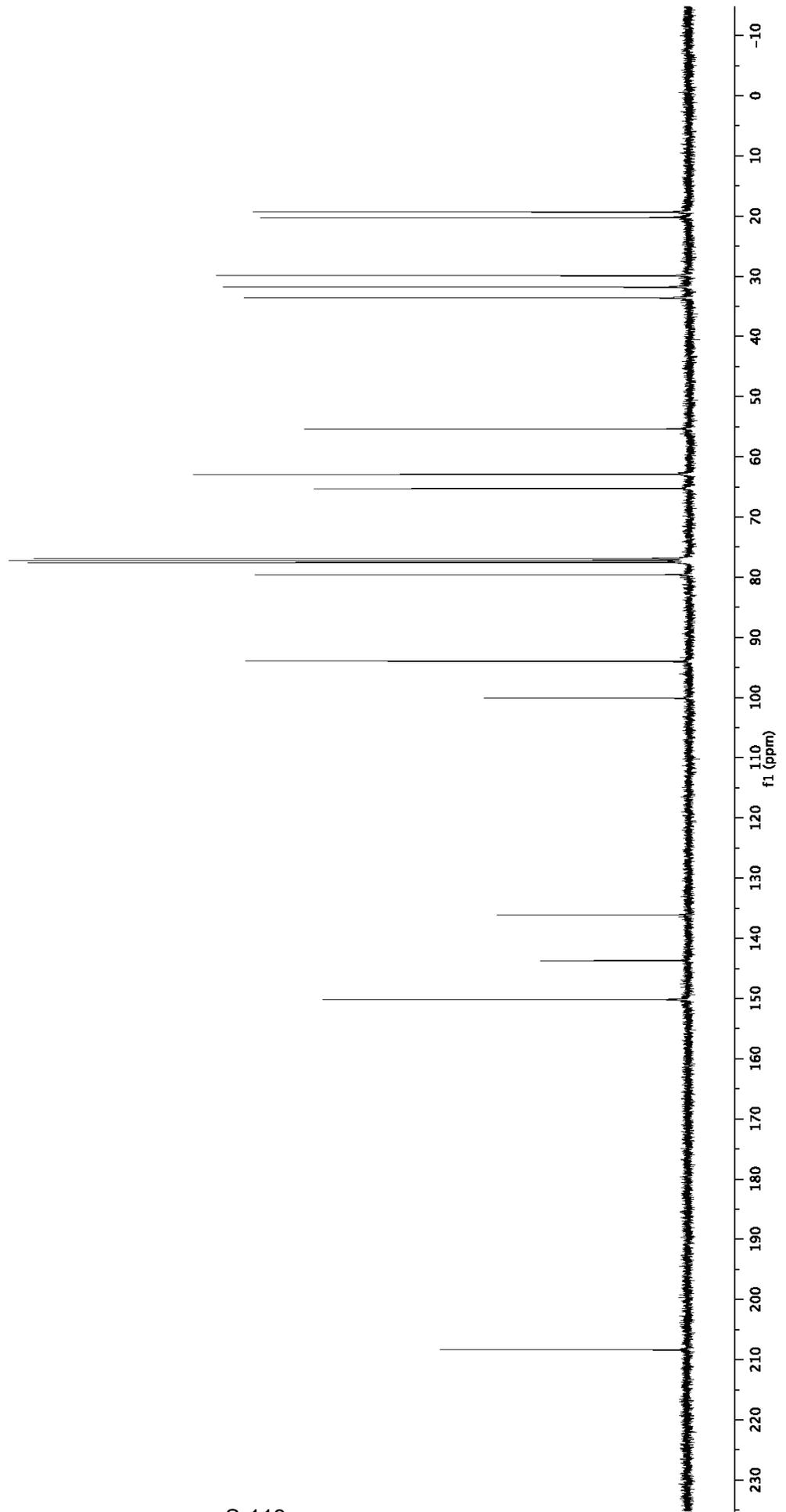
S-12 (diastereomer#1)



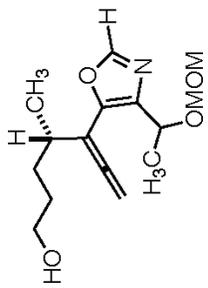
Carbon NMR at 101 MHz
Solvent: CDCl₃



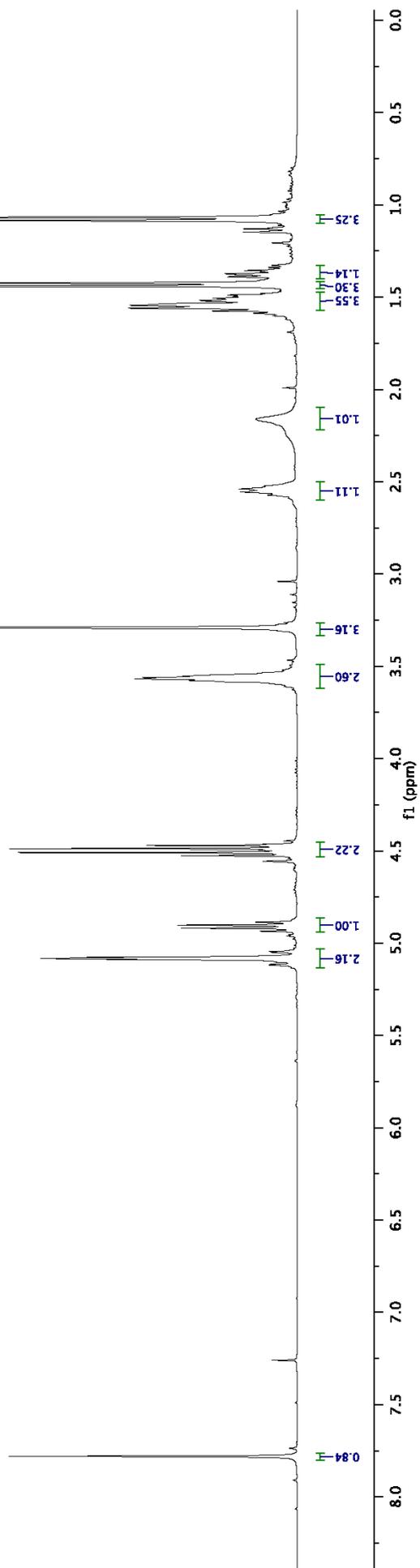
S-12 (diastereomer#1)



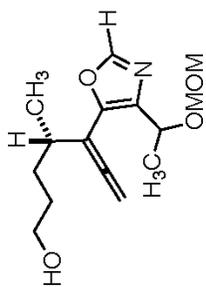
Proton NMR at 400 MHz
Solvent: CDCl₃



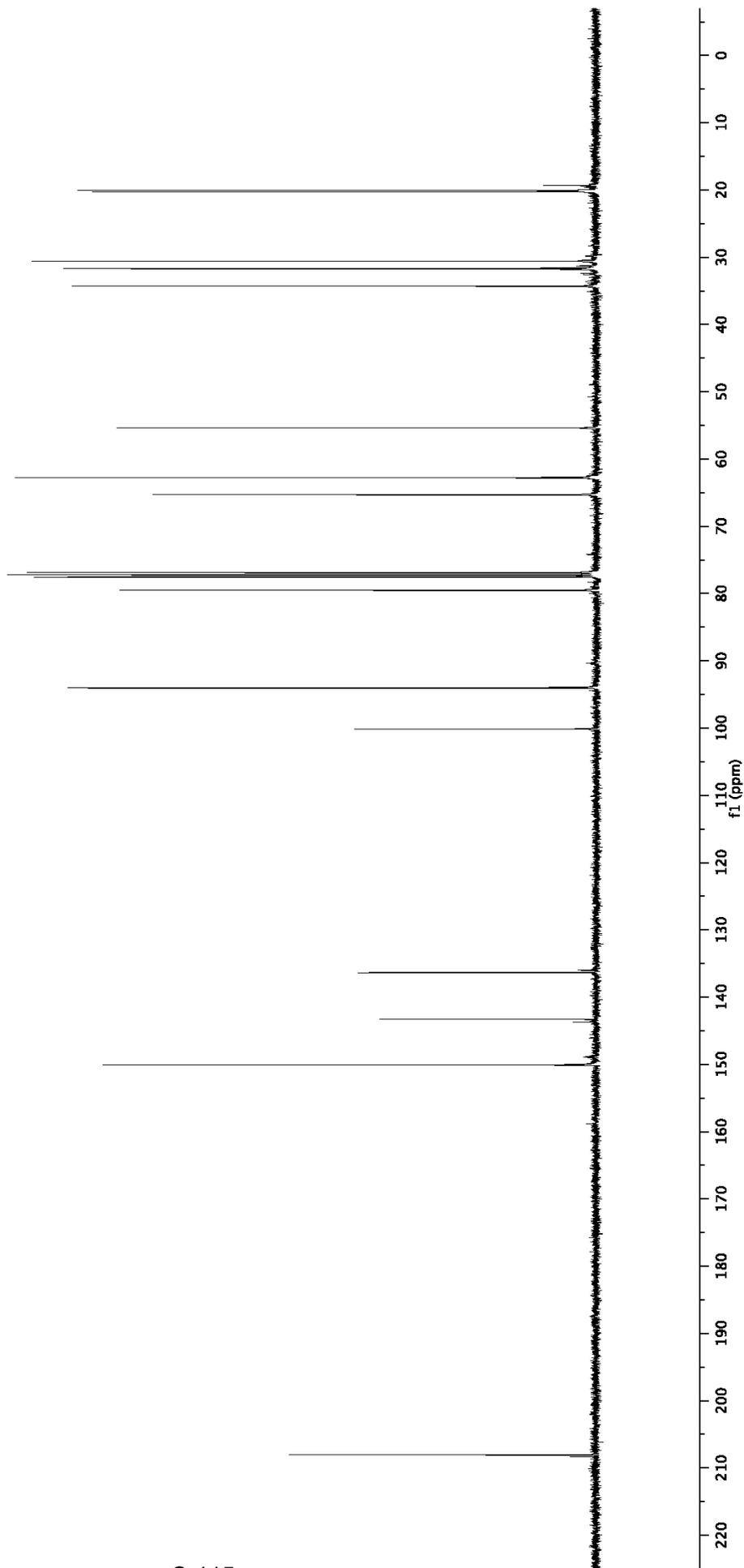
S-12 (diastereomer#2)



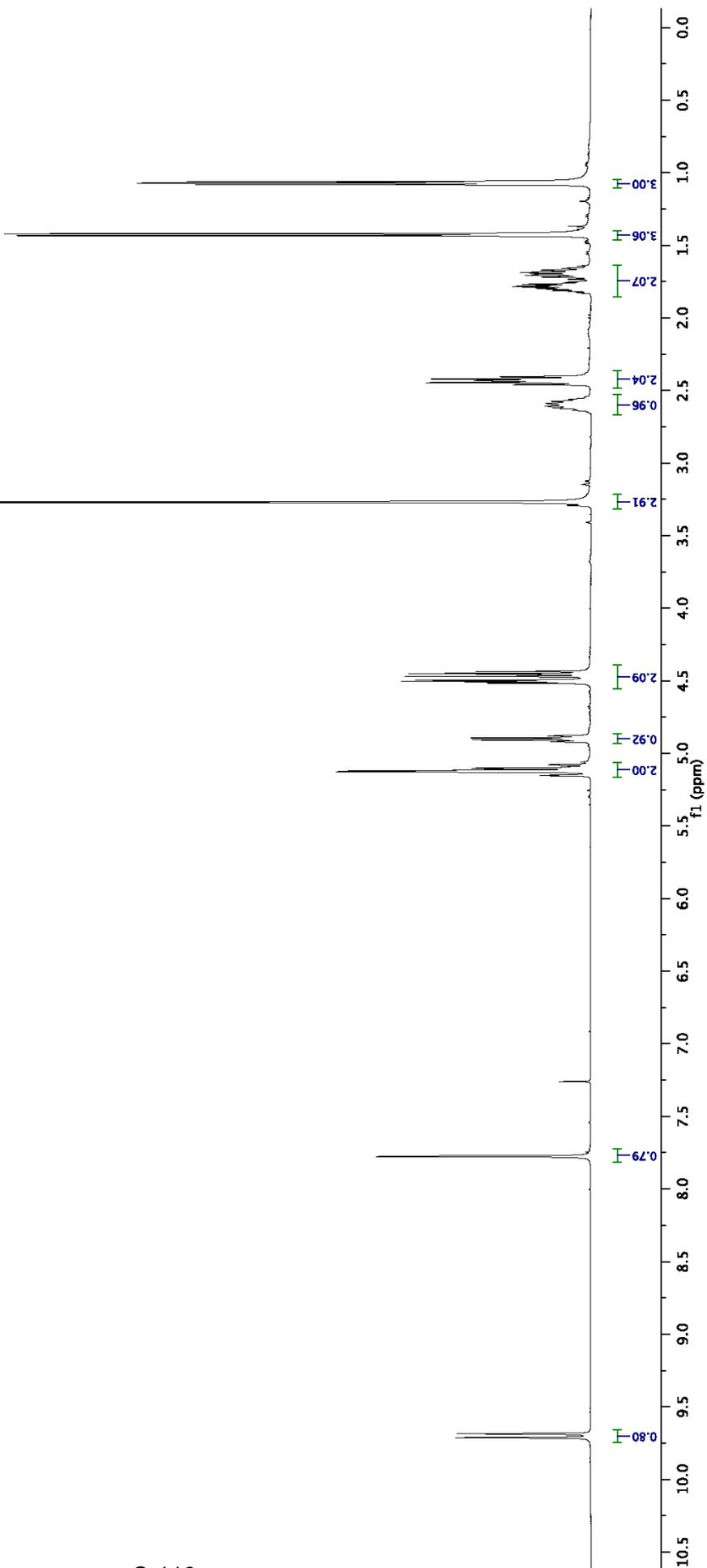
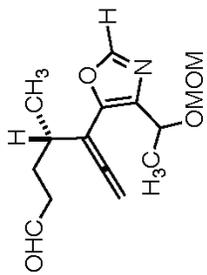
Carbon NMR at 101 MHz
Solvent: CDCl₃



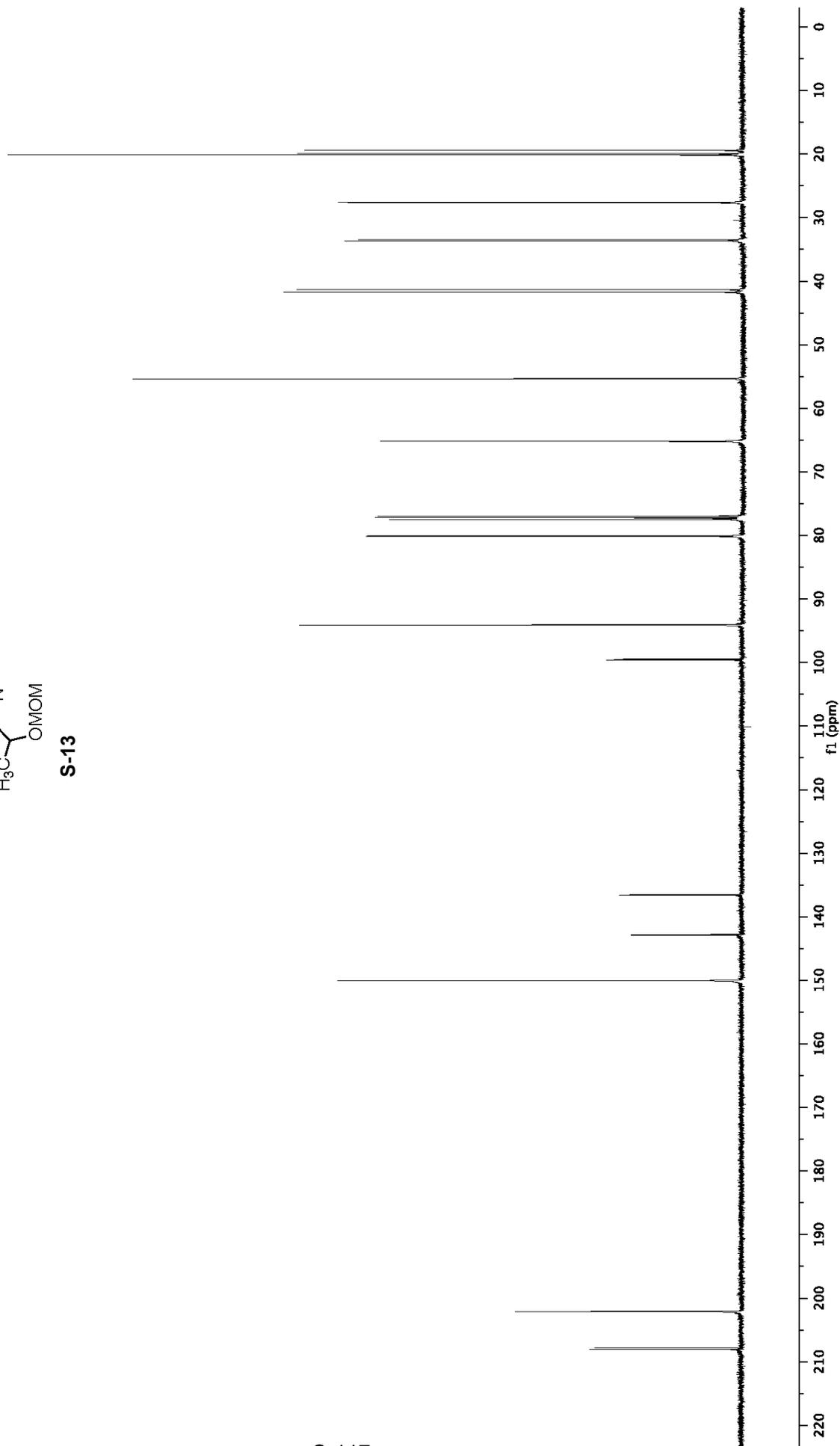
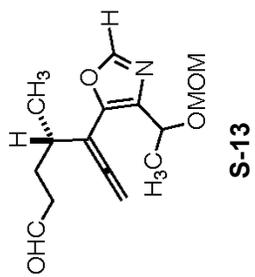
S-12 (diastereomer#2)



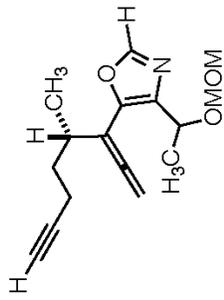
Proton NMR at 500 MHz
Solvent: CDCl₃



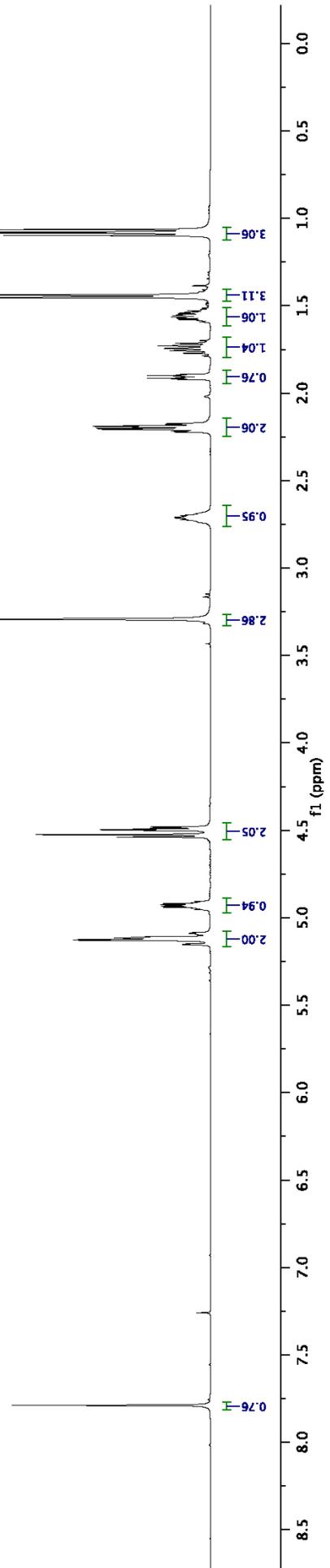
Carbon NMR at 125 MHz
Solvent: CDCl₃



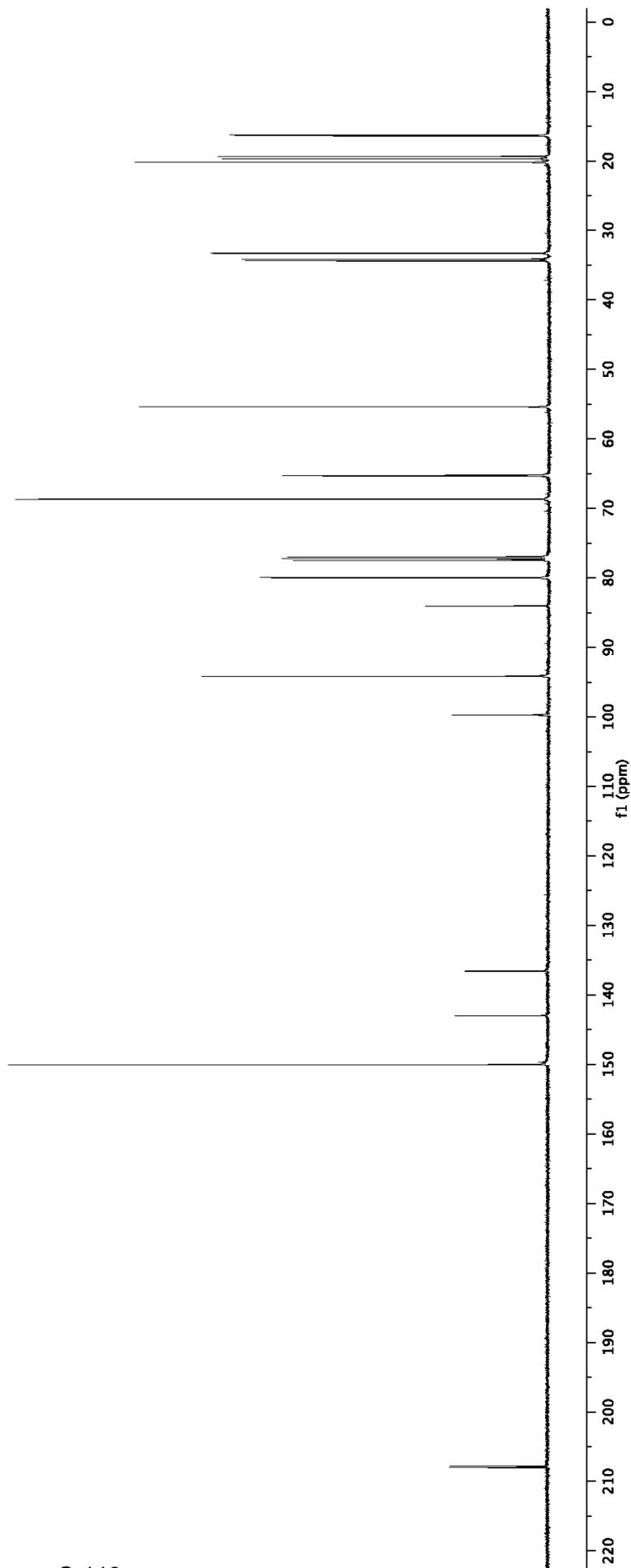
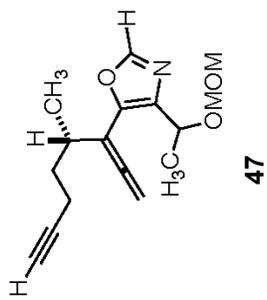
Proton NMR at 500 MHz
Solvent: CDCl₃



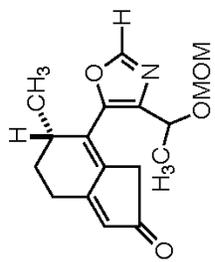
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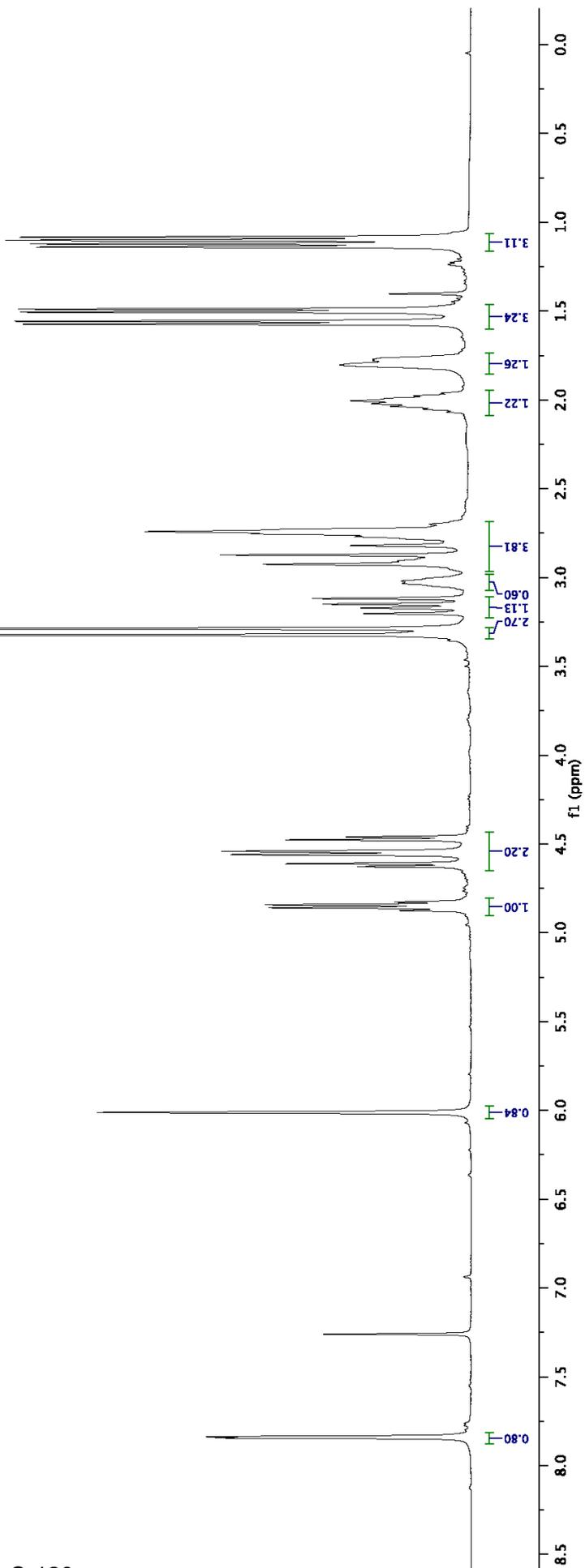
Carbon NMR at 125 MHz
Solvent: CDCl₃



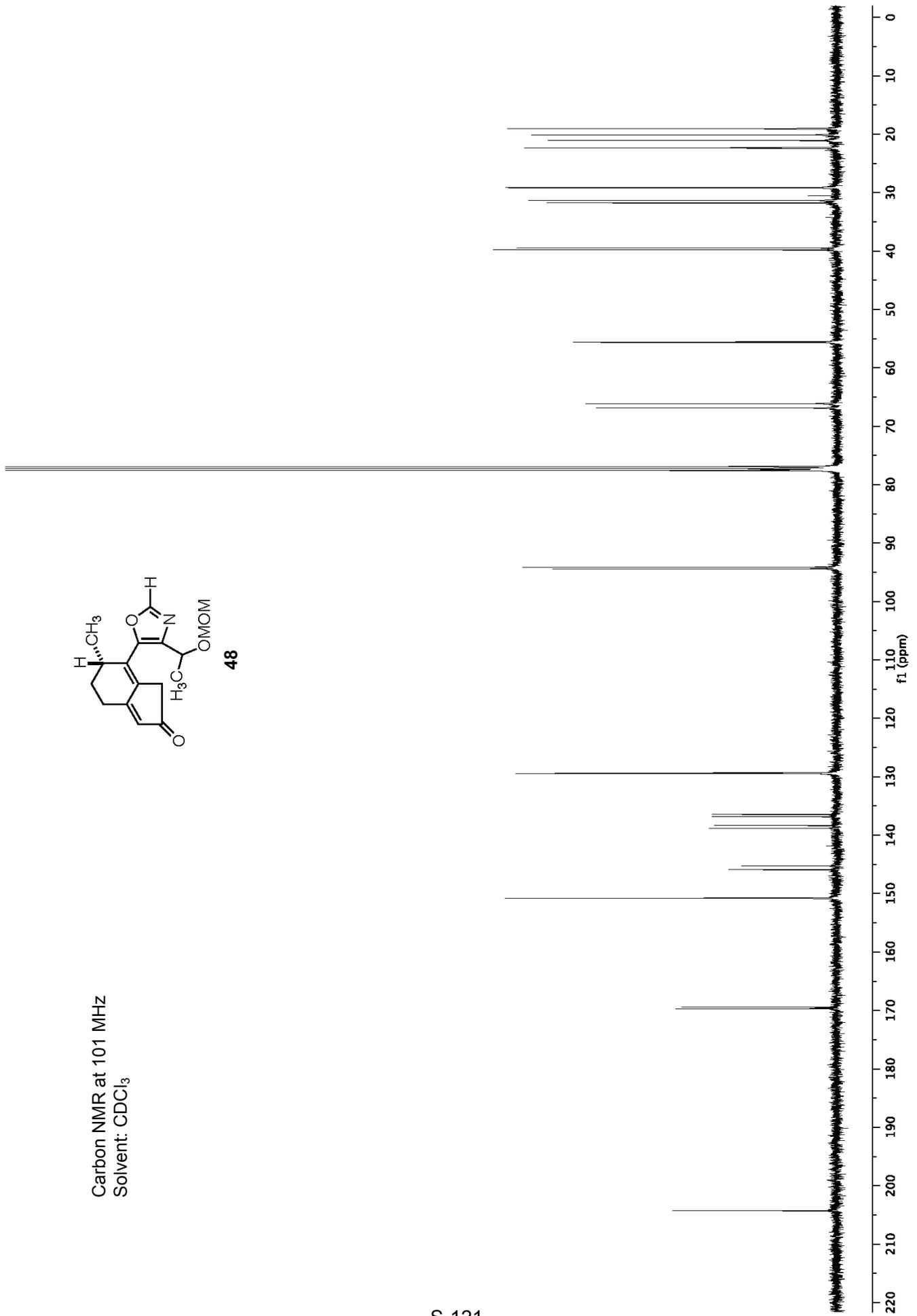
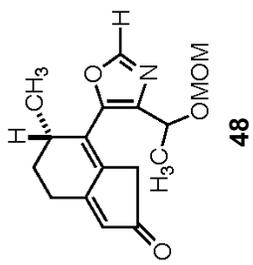
Proton NMR at 400 MHz
Solvent: CDCl₃

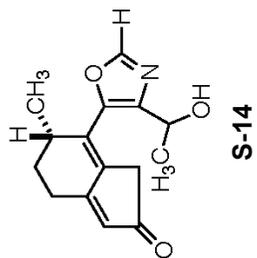


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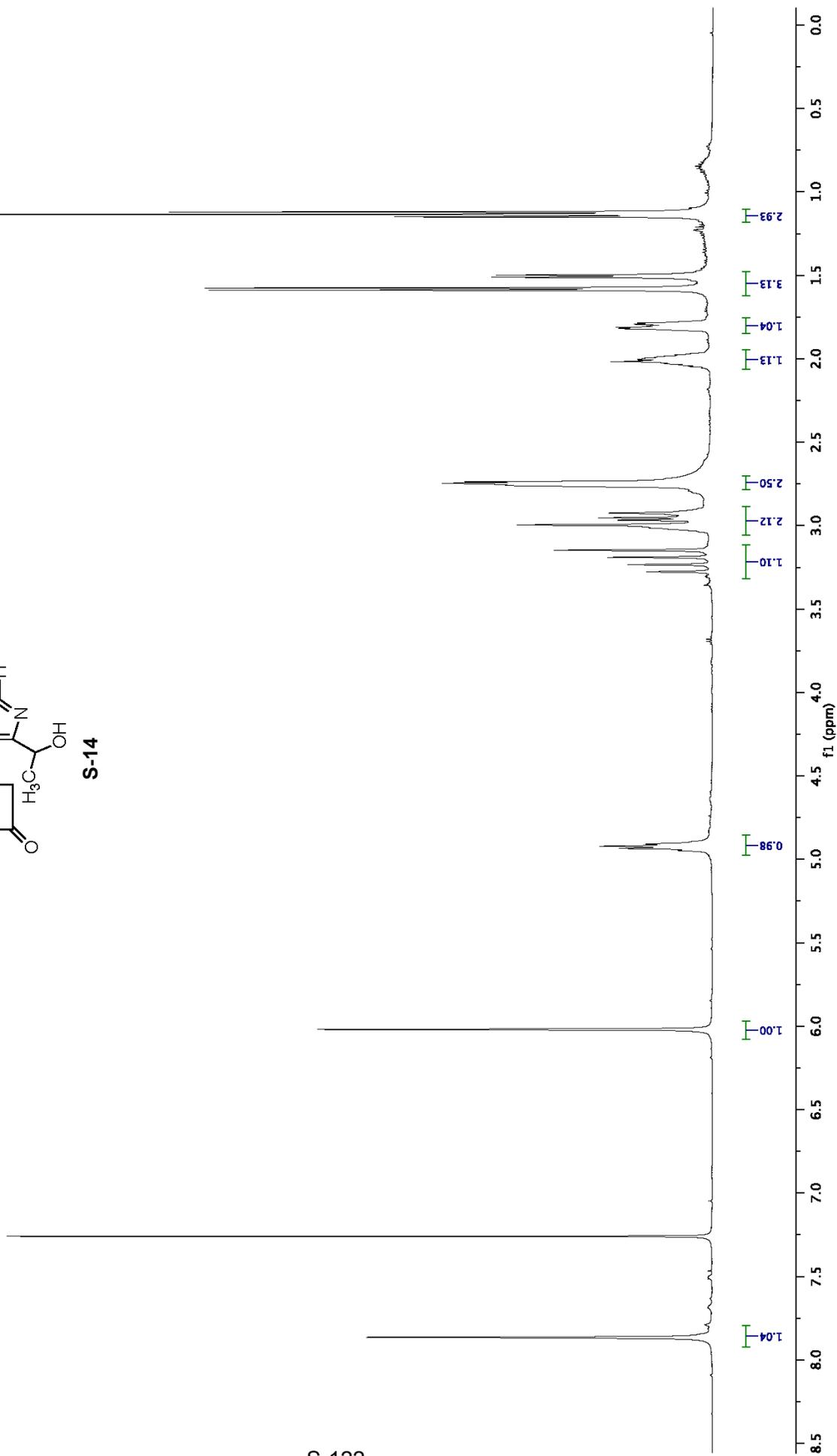


Carbon NMR at 101 MHz
Solvent: CDCl₃

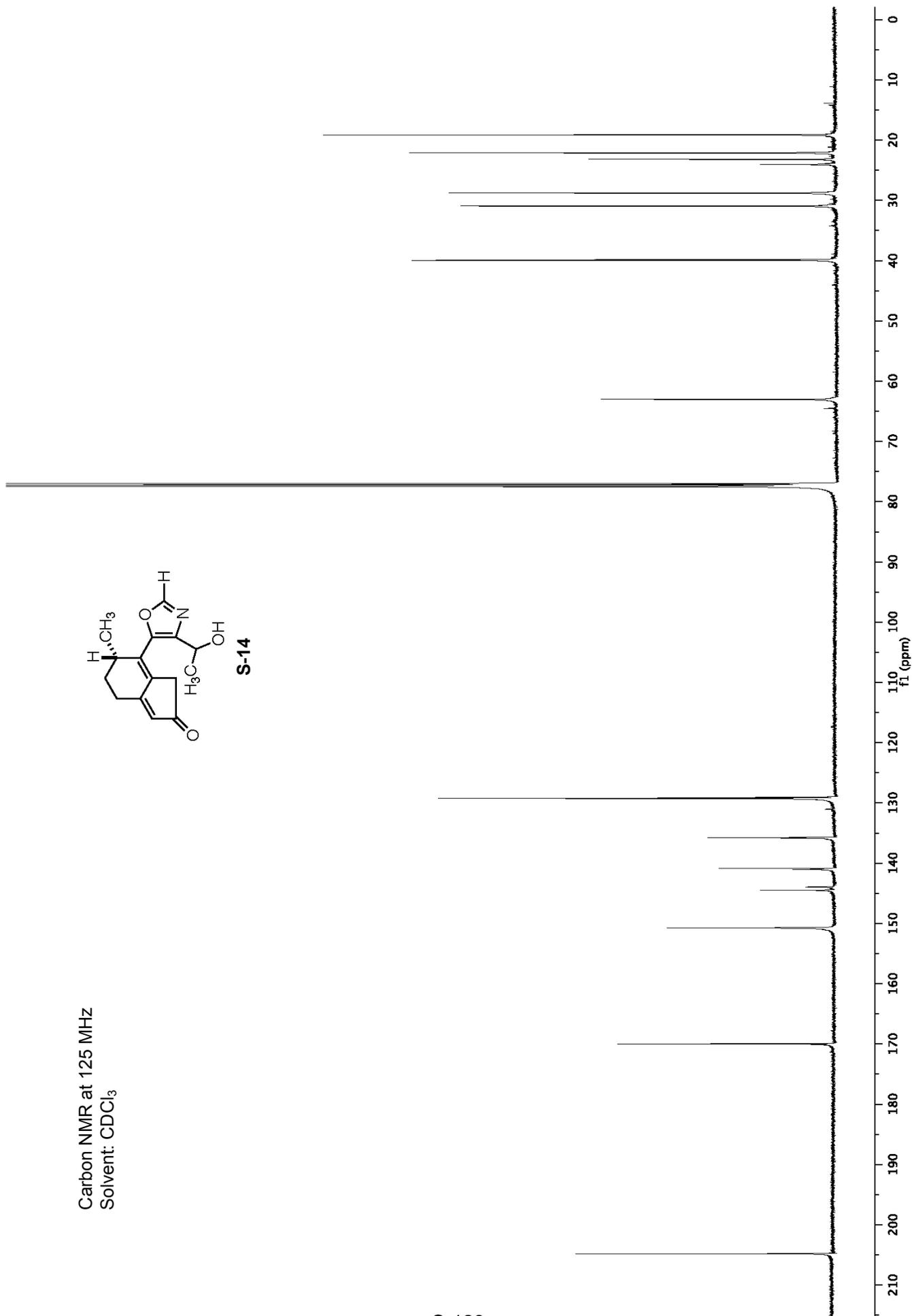
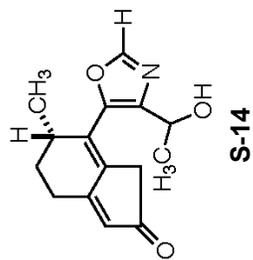




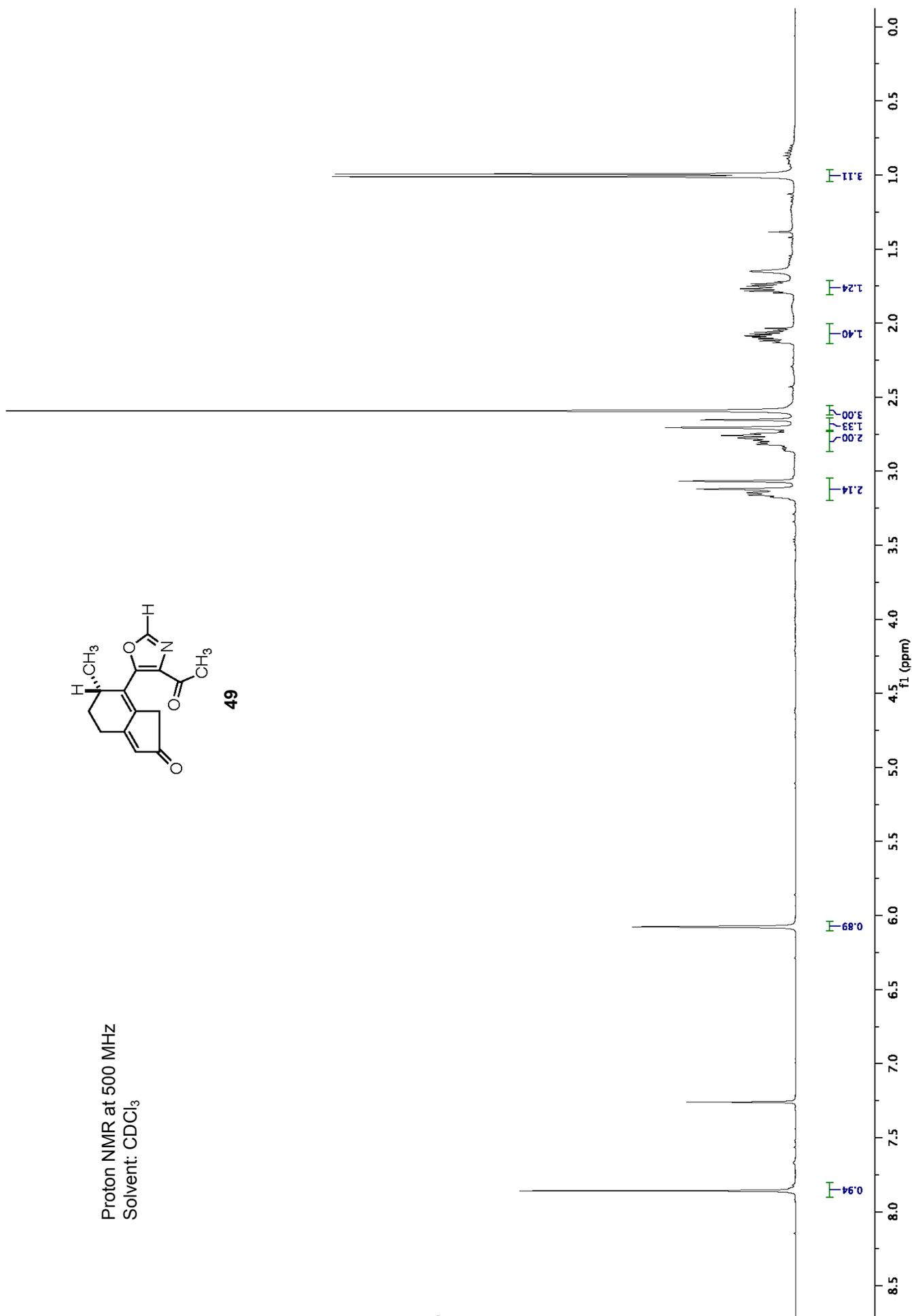
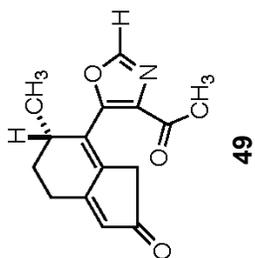
Proton NMR at 500 MHz
Solvent: CDCl₃



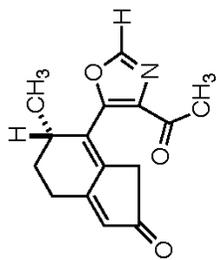
Carbon NMR at 125 MHz
Solvent: CDCl₃



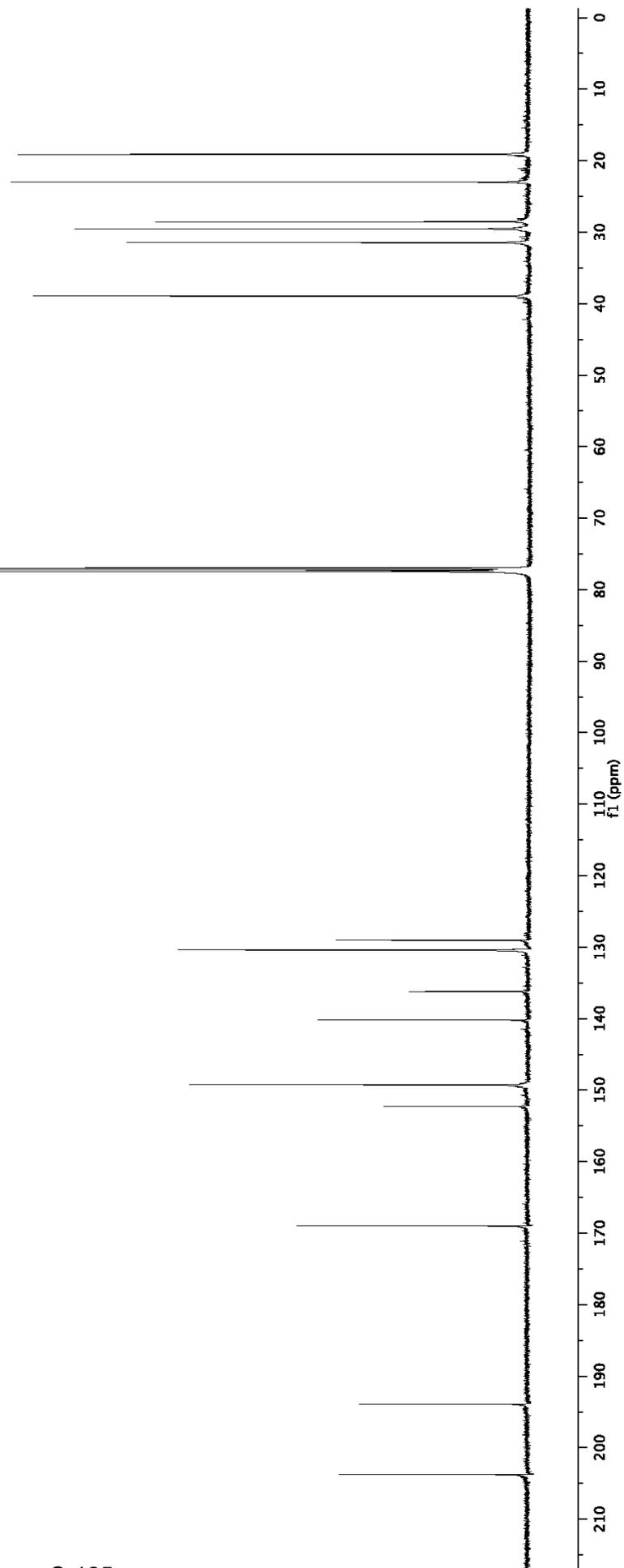
Proton NMR at 500 MHz
Solvent: CDCl₃



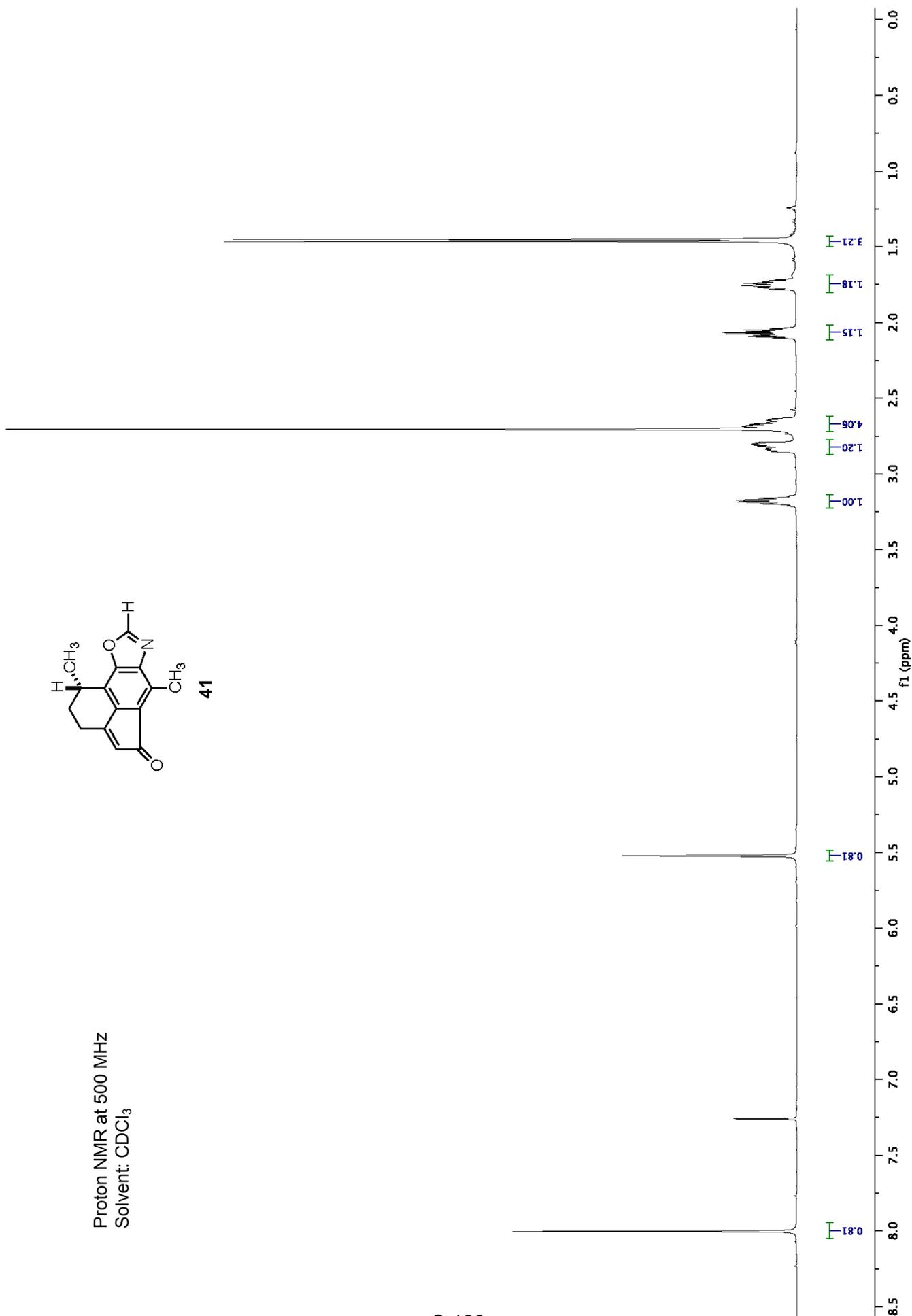
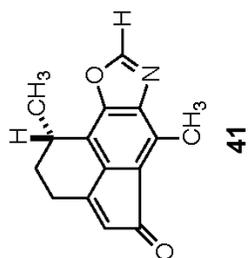
Carbon NMR at 125 MHz
Solvent: CDCl₃



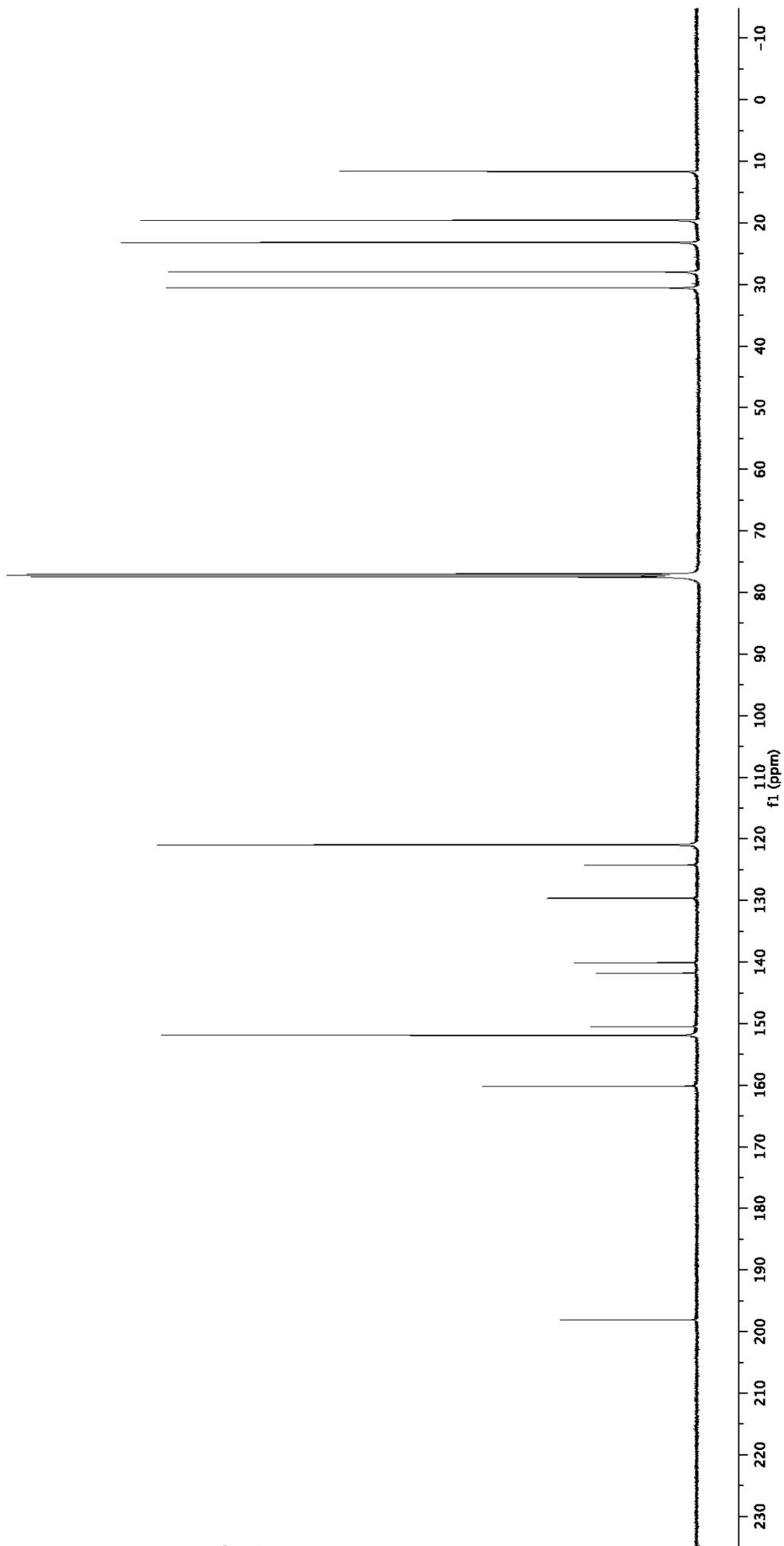
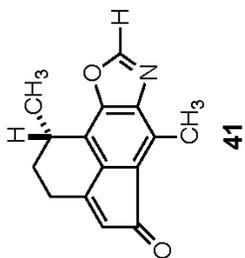
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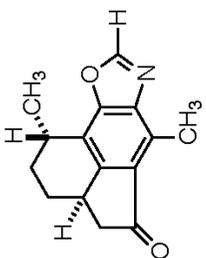
Proton NMR at 500 MHz
Solvent: CDCl₃



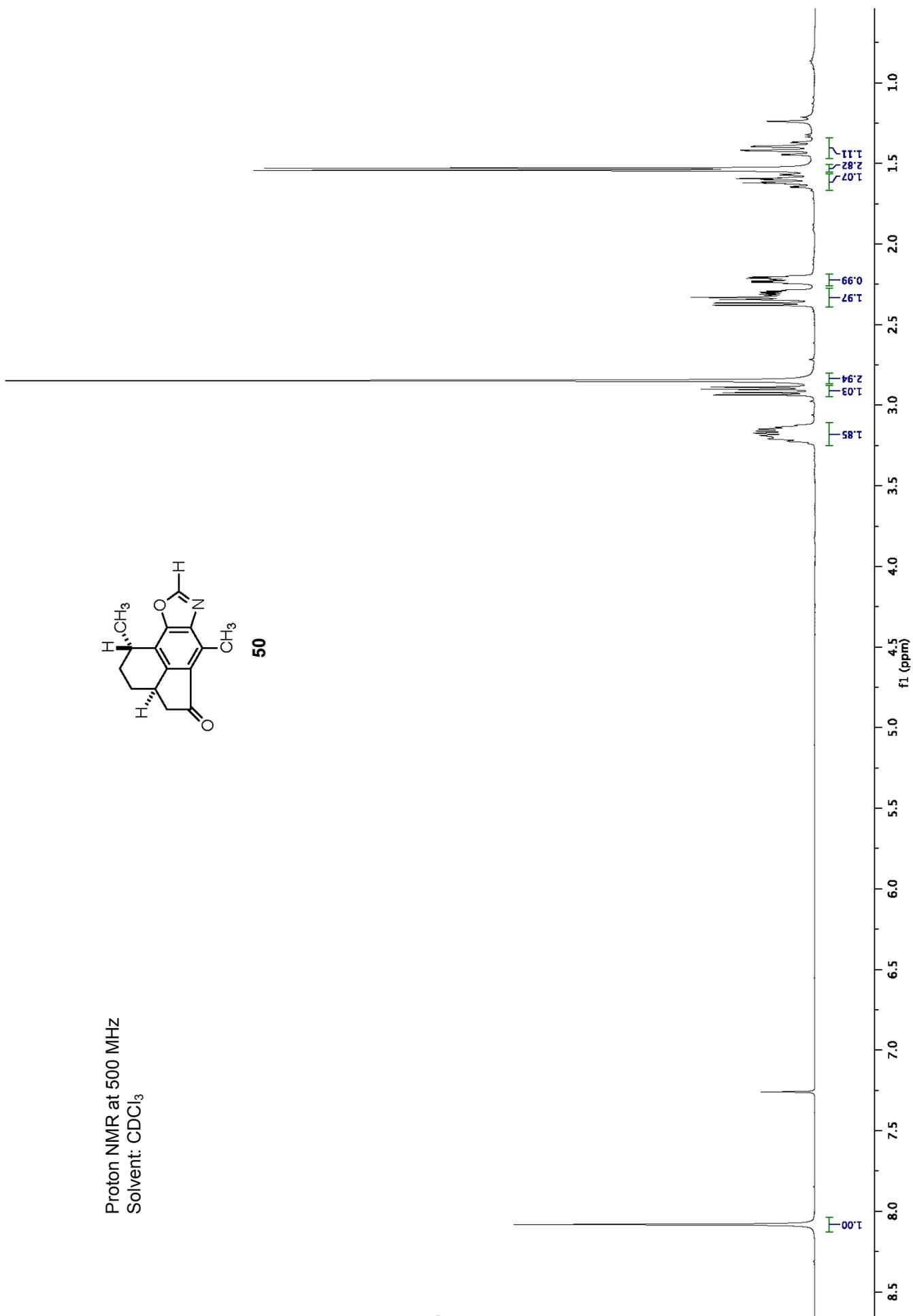
Carbon NMR at 125 MHz
Solvent: CDCl₃



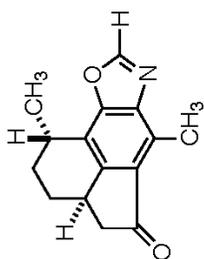
Proton NMR at 500 MHz
Solvent: CDCl₃



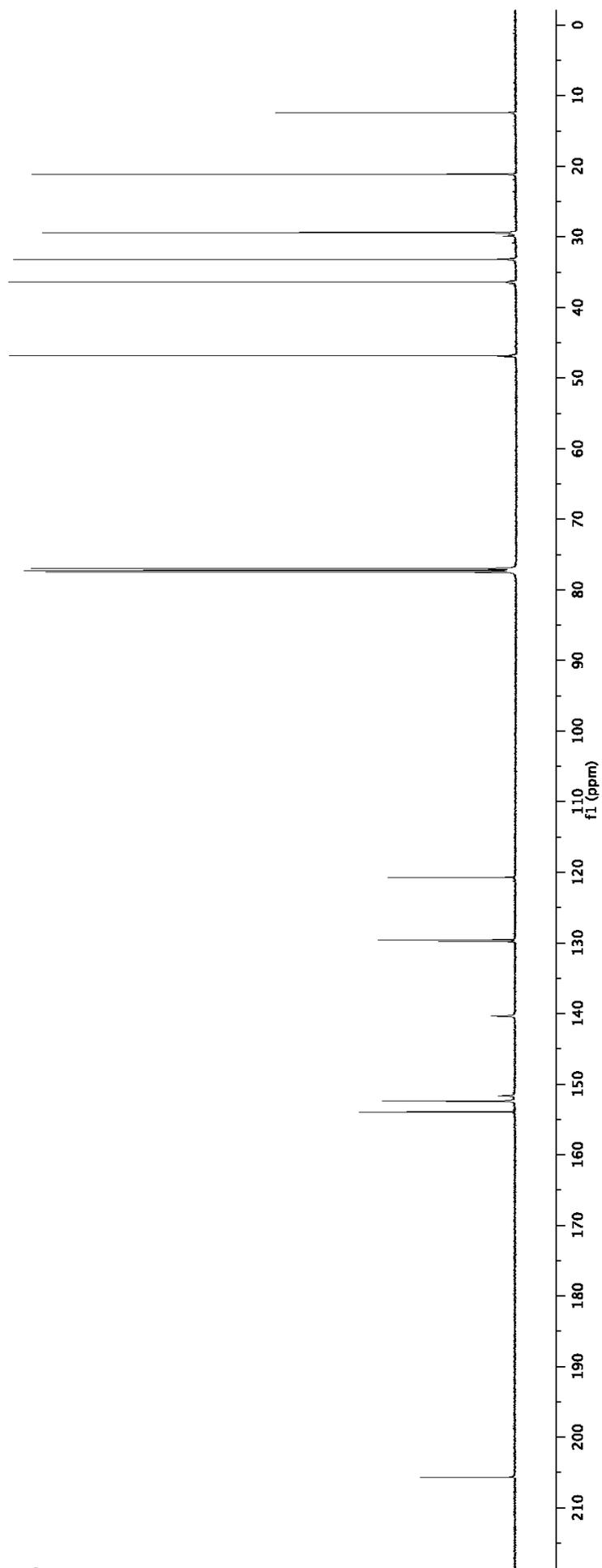
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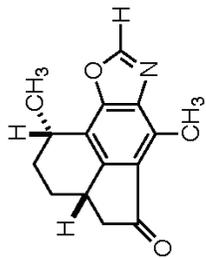
Carbon NMR at 125 MHz
Solvent: CDCl₃



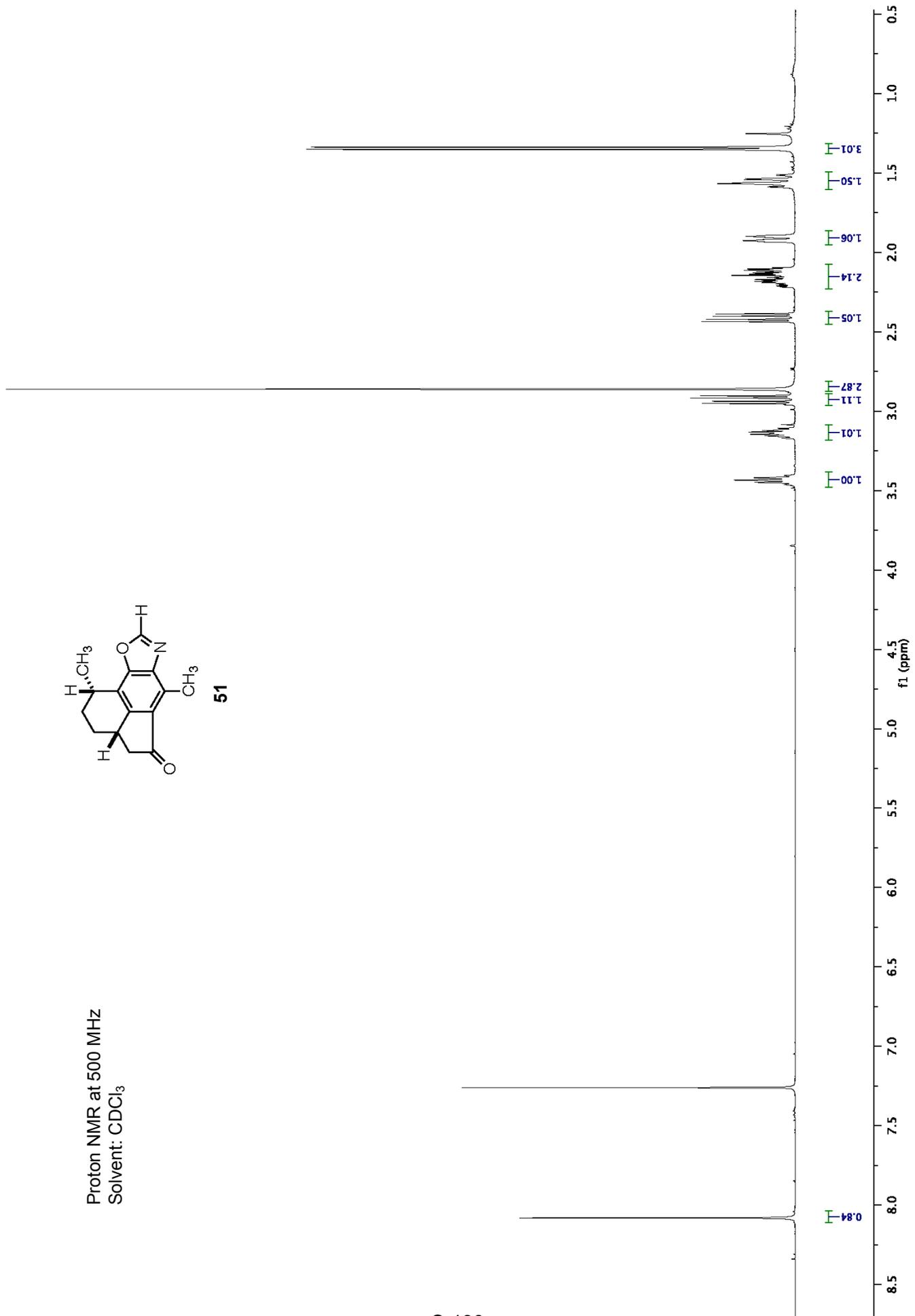
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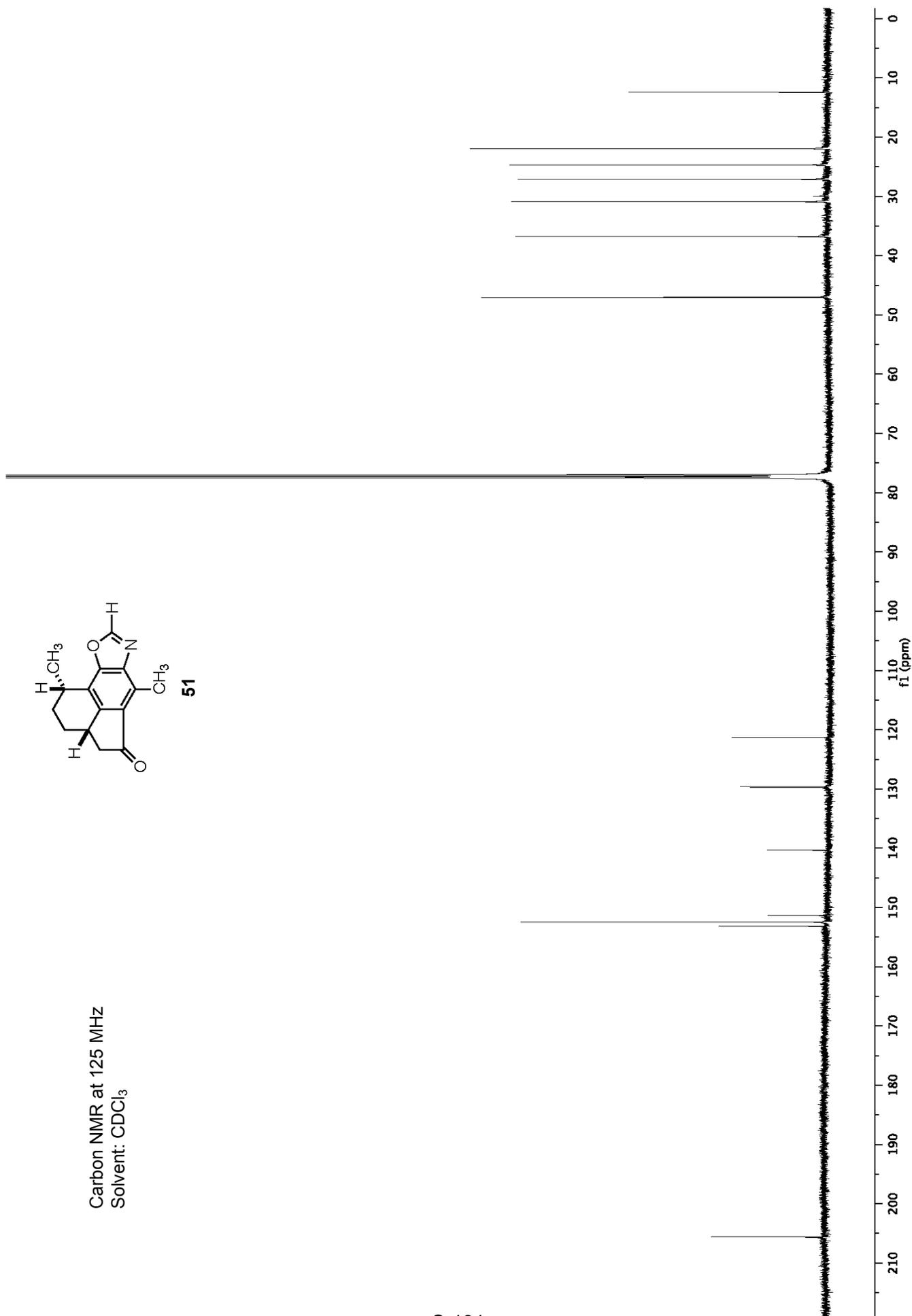
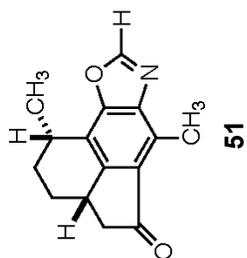
Proton NMR at 500 MHz
Solvent: CDCl₃



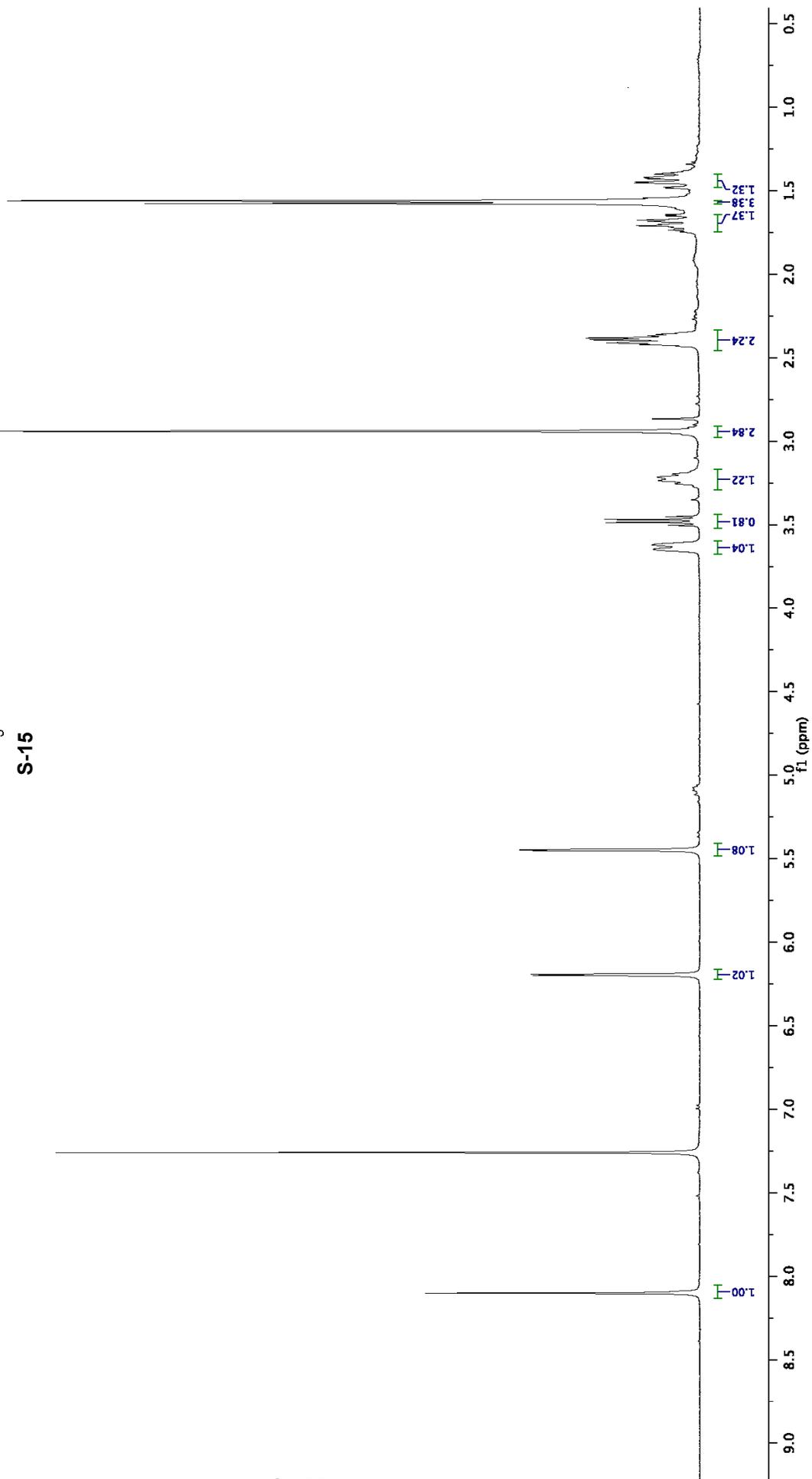
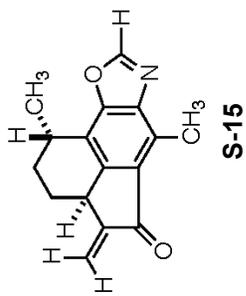
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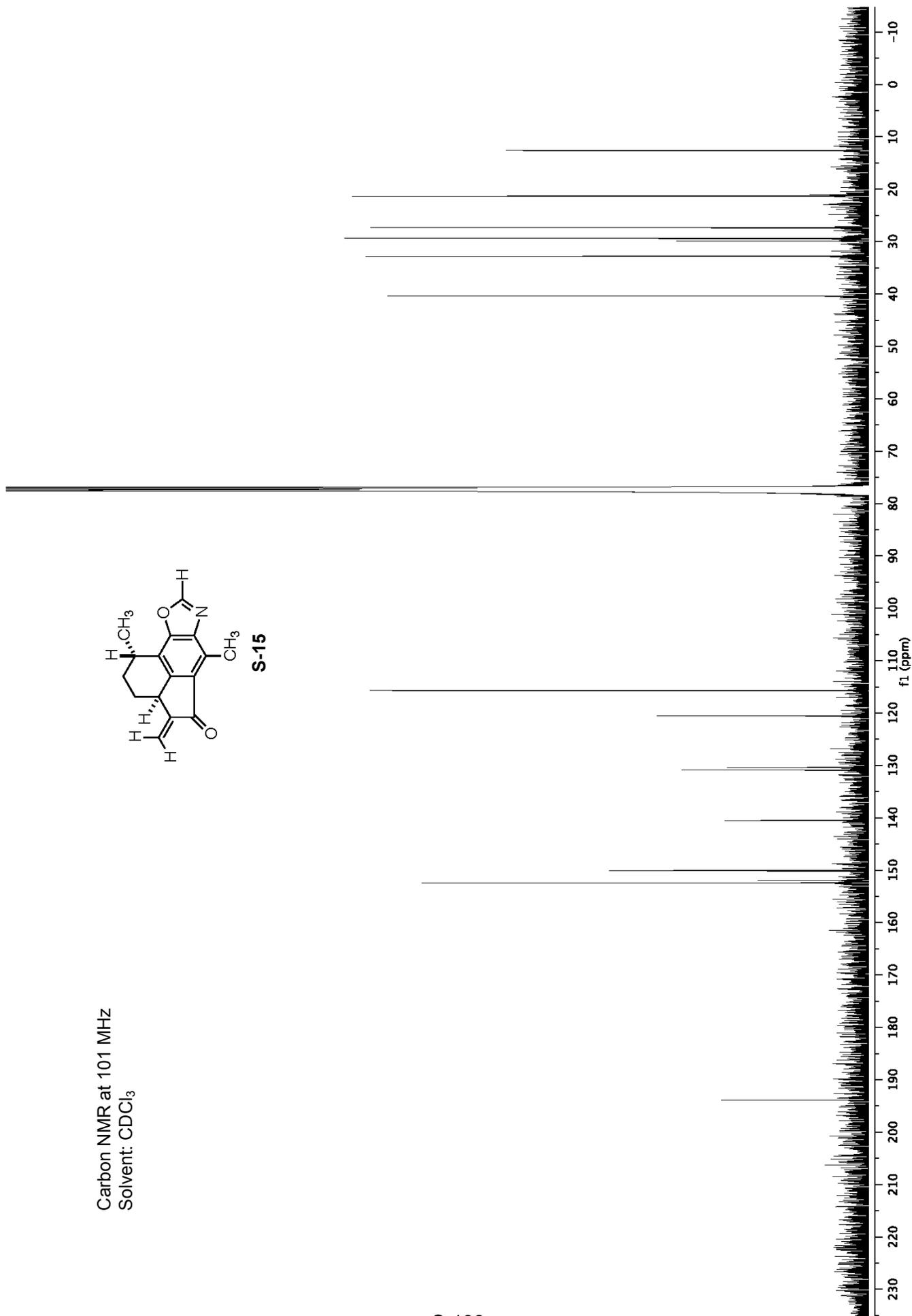
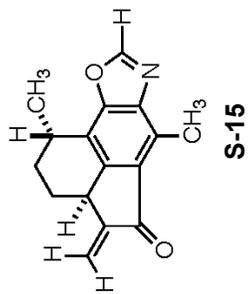
Carbon NMR at 125 MHz
Solvent: CDCl₃



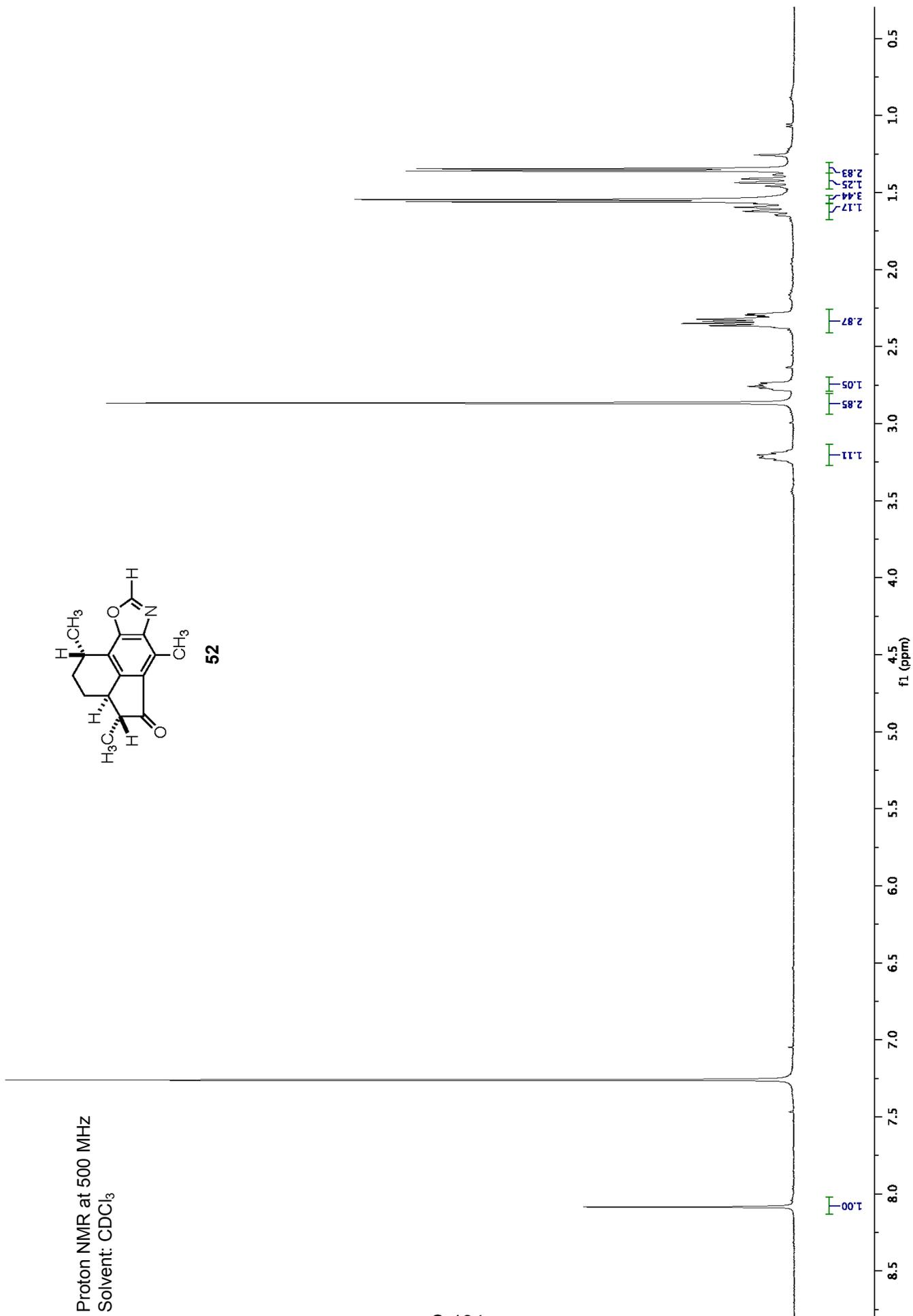
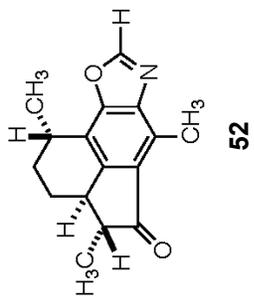
Proton NMR at 400 MHz
Solvent: CDCl₃



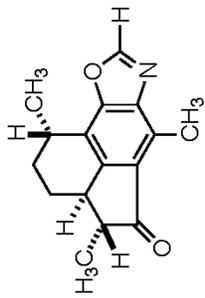
Carbon NMR at 101 MHz
Solvent: CDCl₃



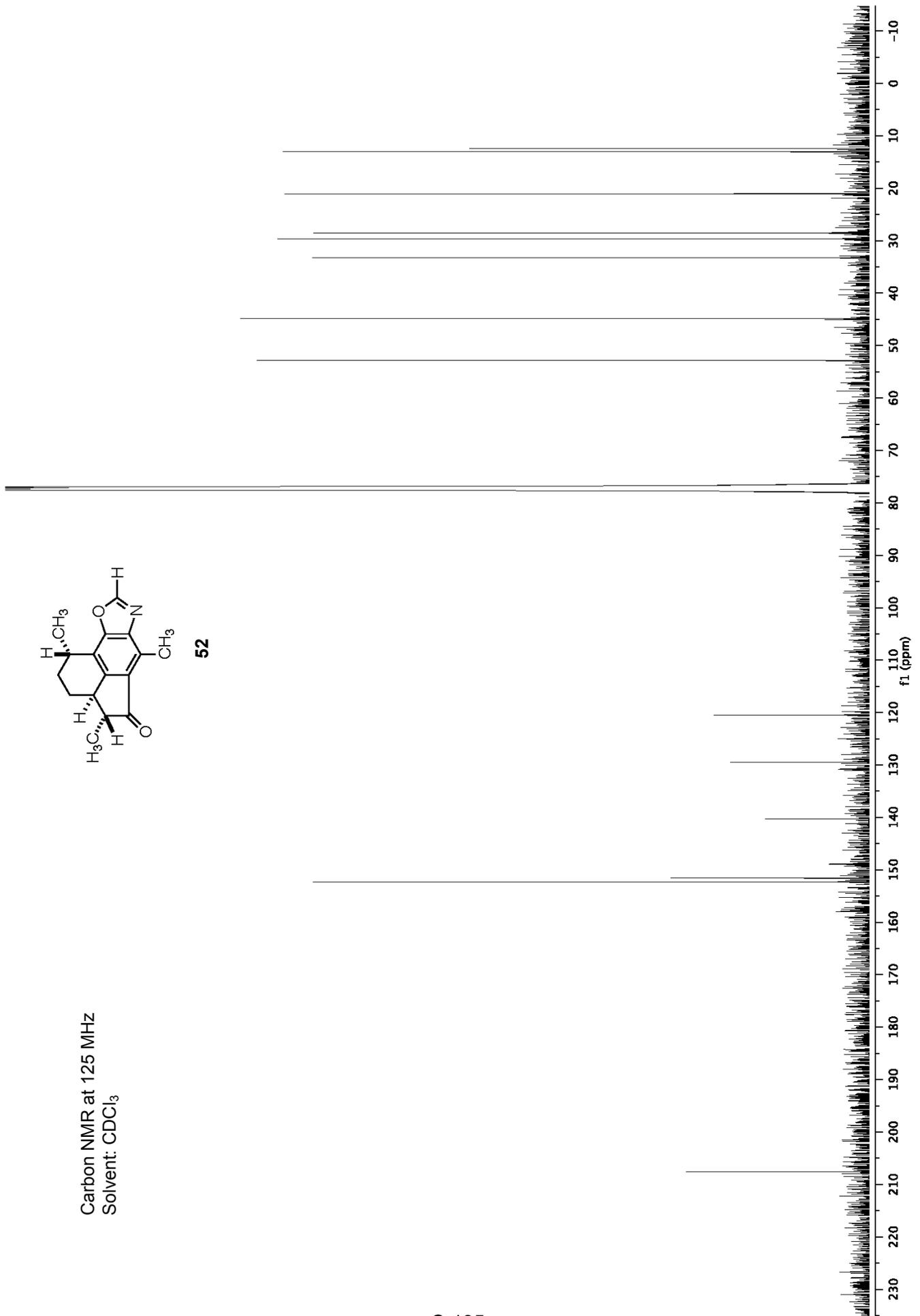
Proton NMR at 500 MHz
Solvent: CDCl₃



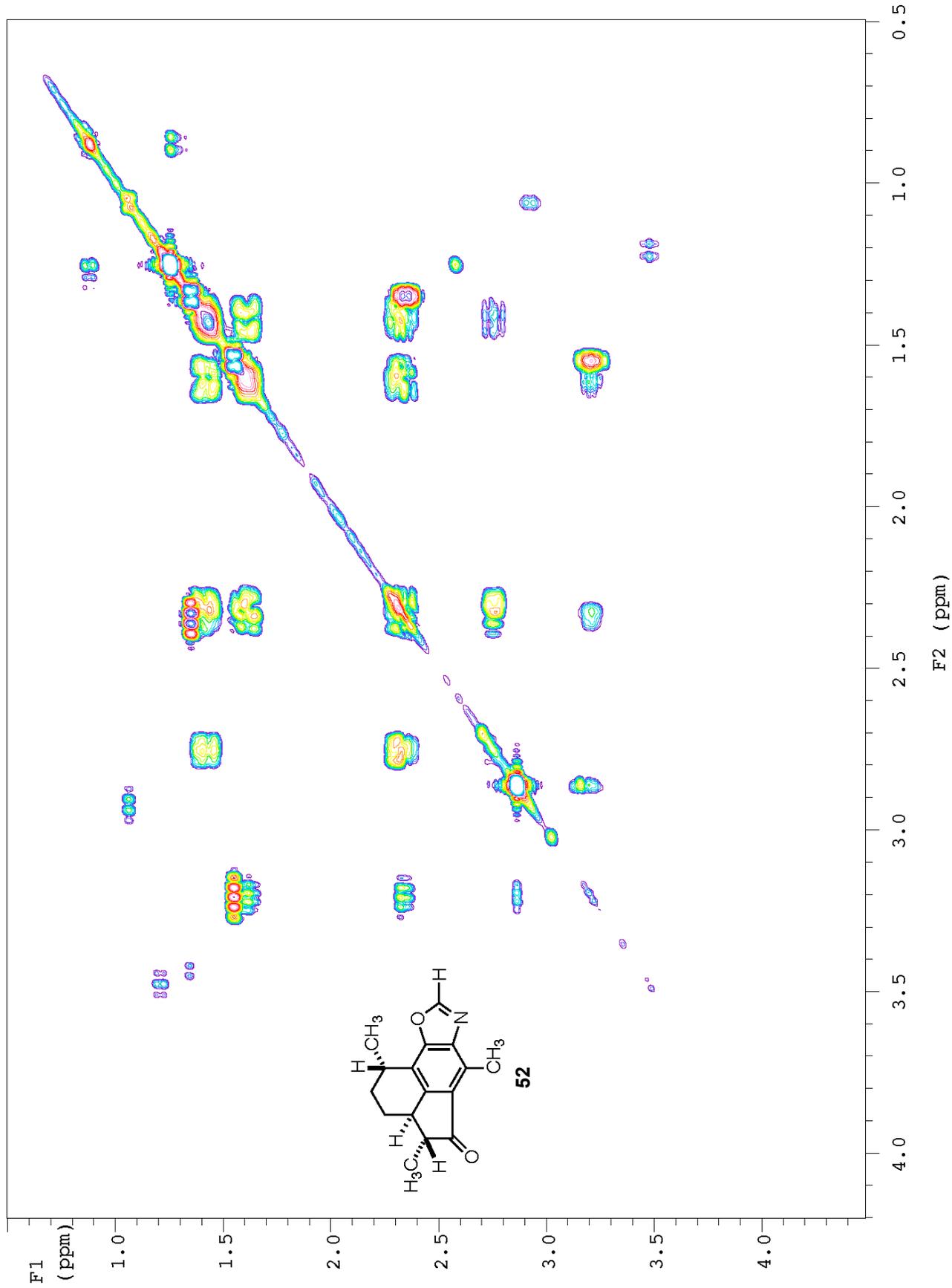
Carbon NMR at 125 MHz
Solvent: CDCl₃



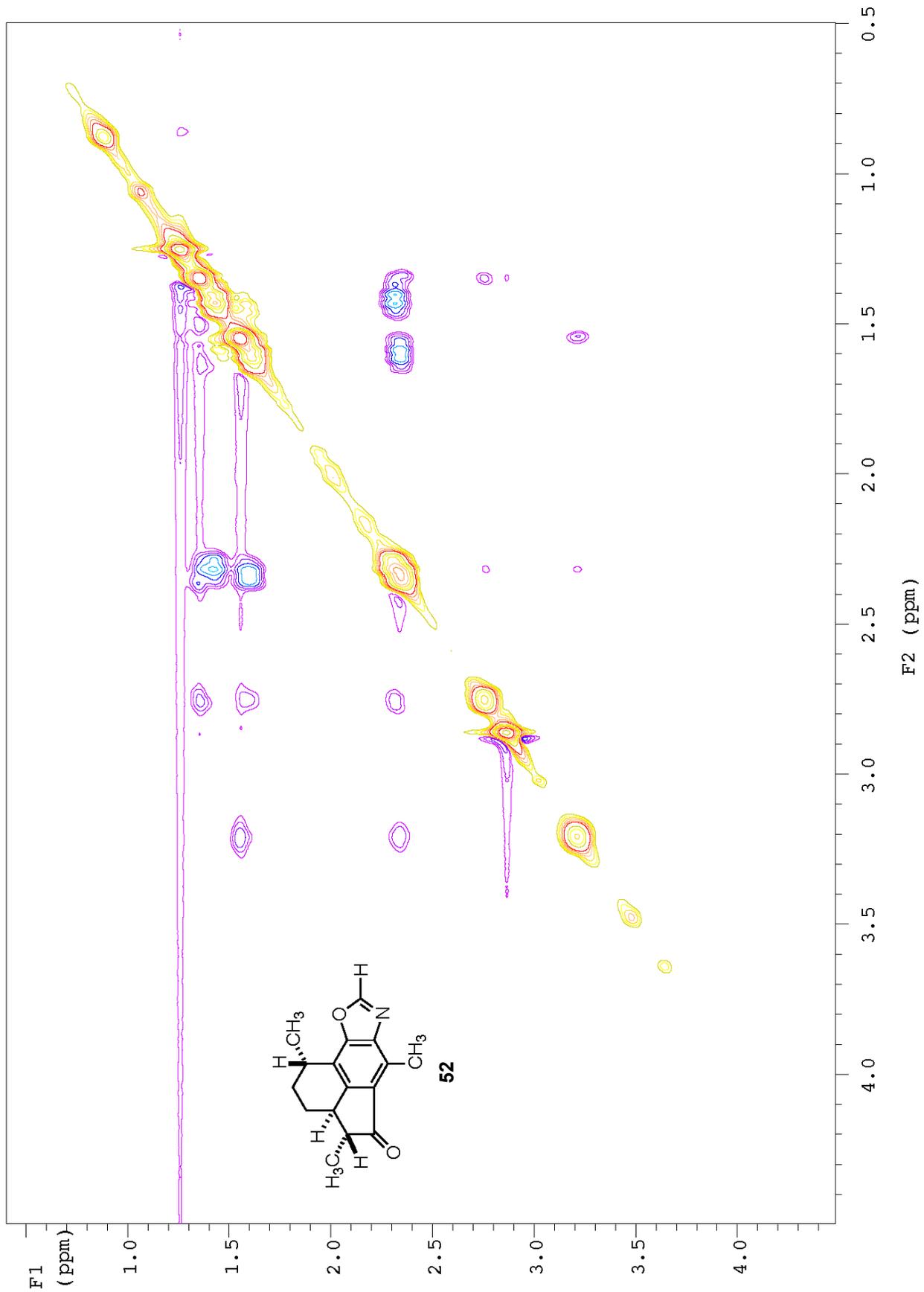
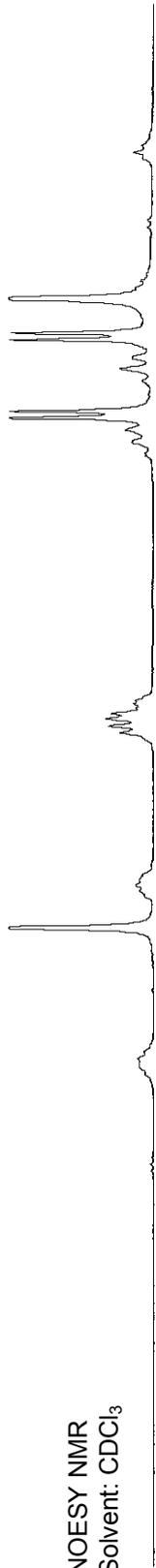
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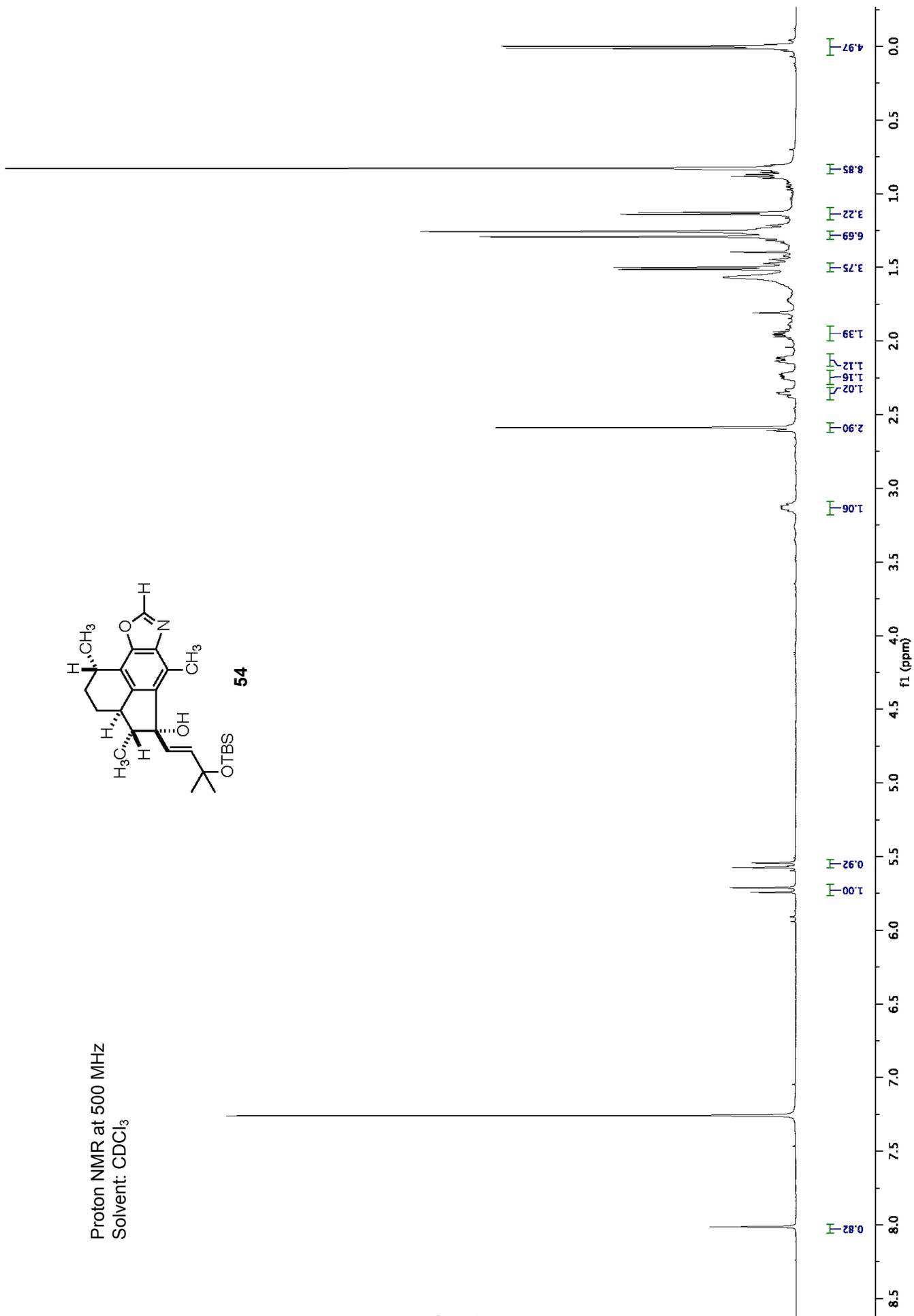
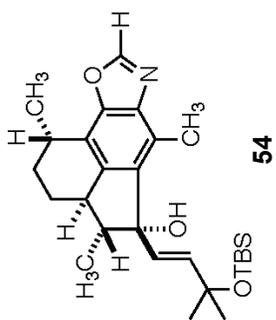
COSY NMR
Solvent: CDCl₃



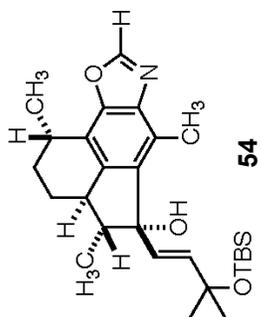
NOESY NMR
Solvent: CDCl₃



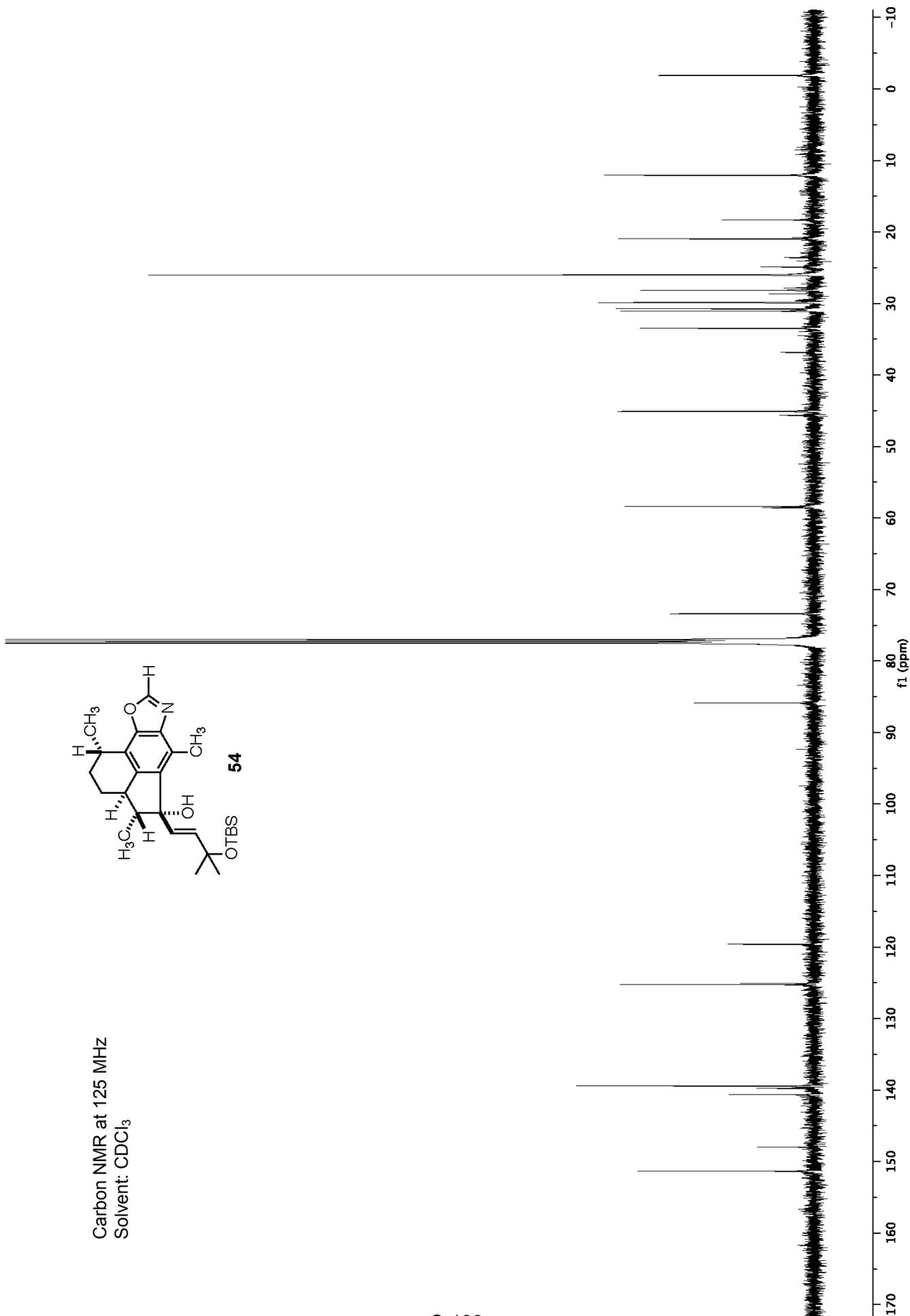
Proton NMR at 500 MHz
Solvent: CDCl₃



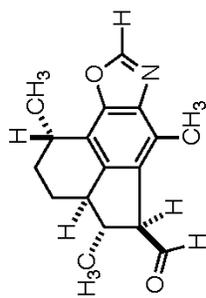
Carbon NMR at 125 MHz
Solvent: CDCl₃



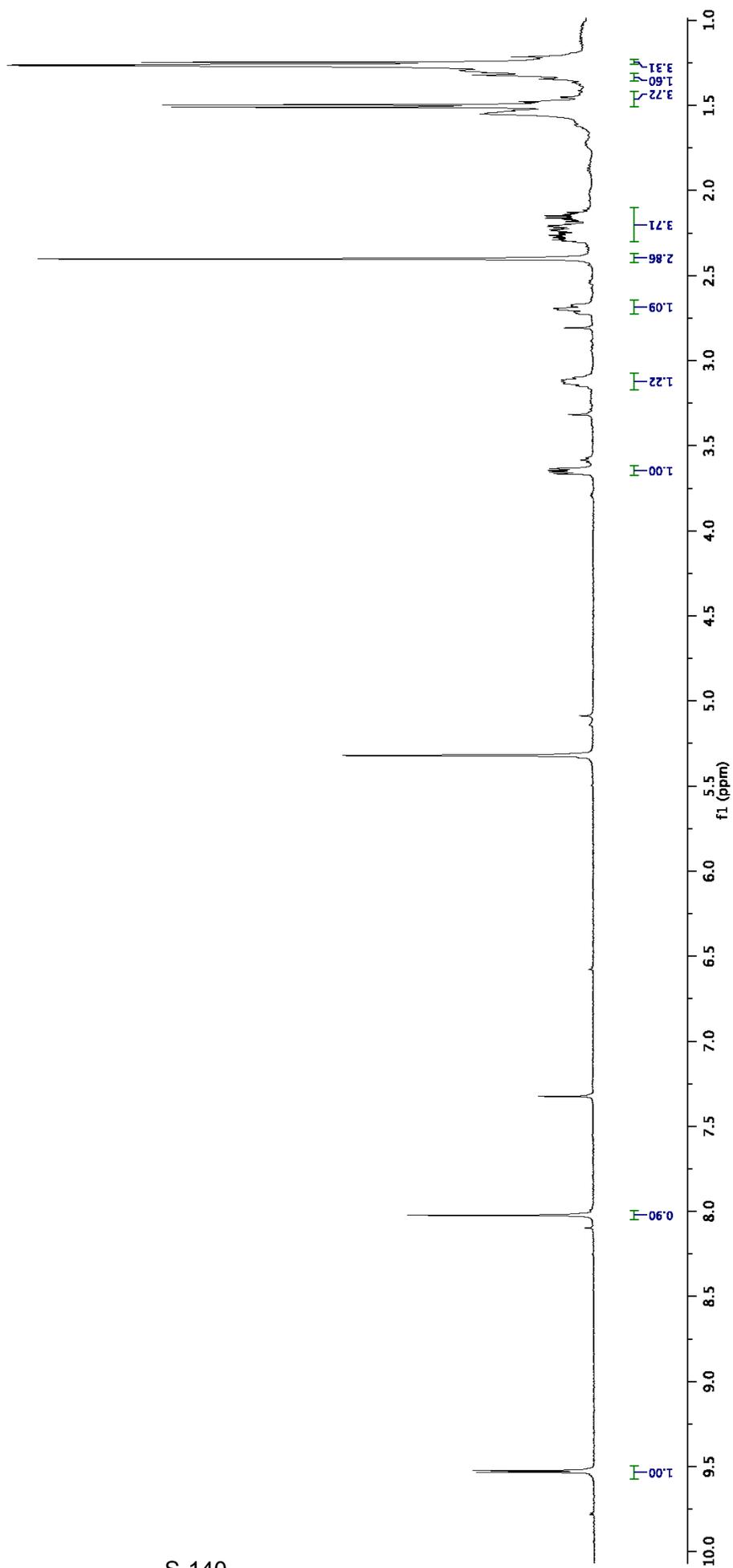
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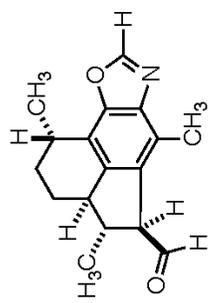
Proton NMR at 500 MHz
Solvent: CD₂Cl₂



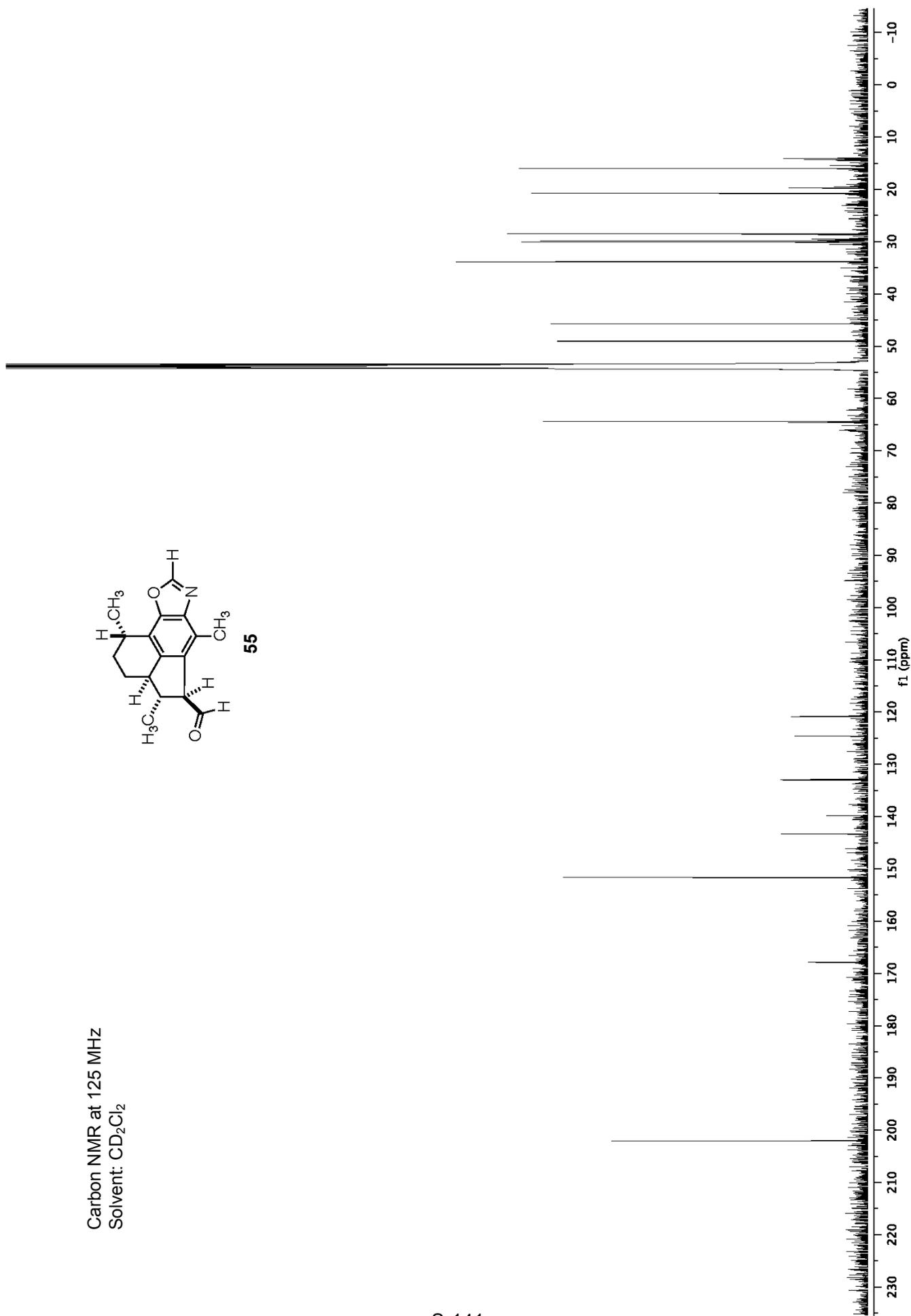
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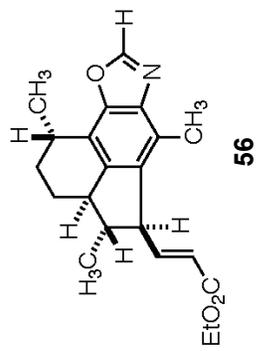
Carbon NMR at 125 MHz
Solvent: CD₂Cl₂



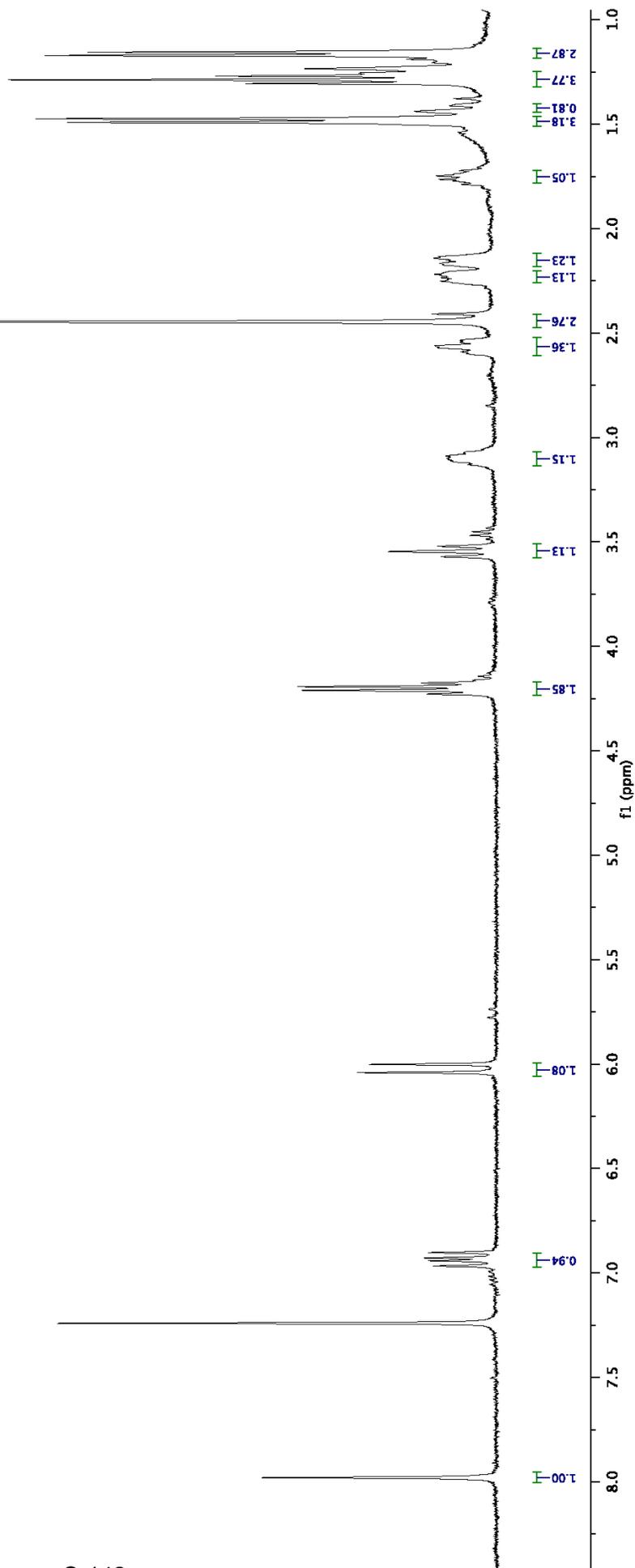
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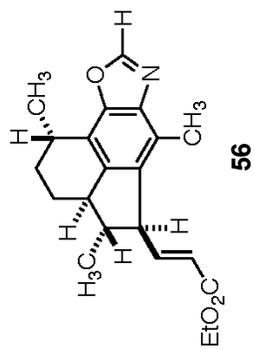
Proton NMR at 500 MHz
Solvent: CDCl₃



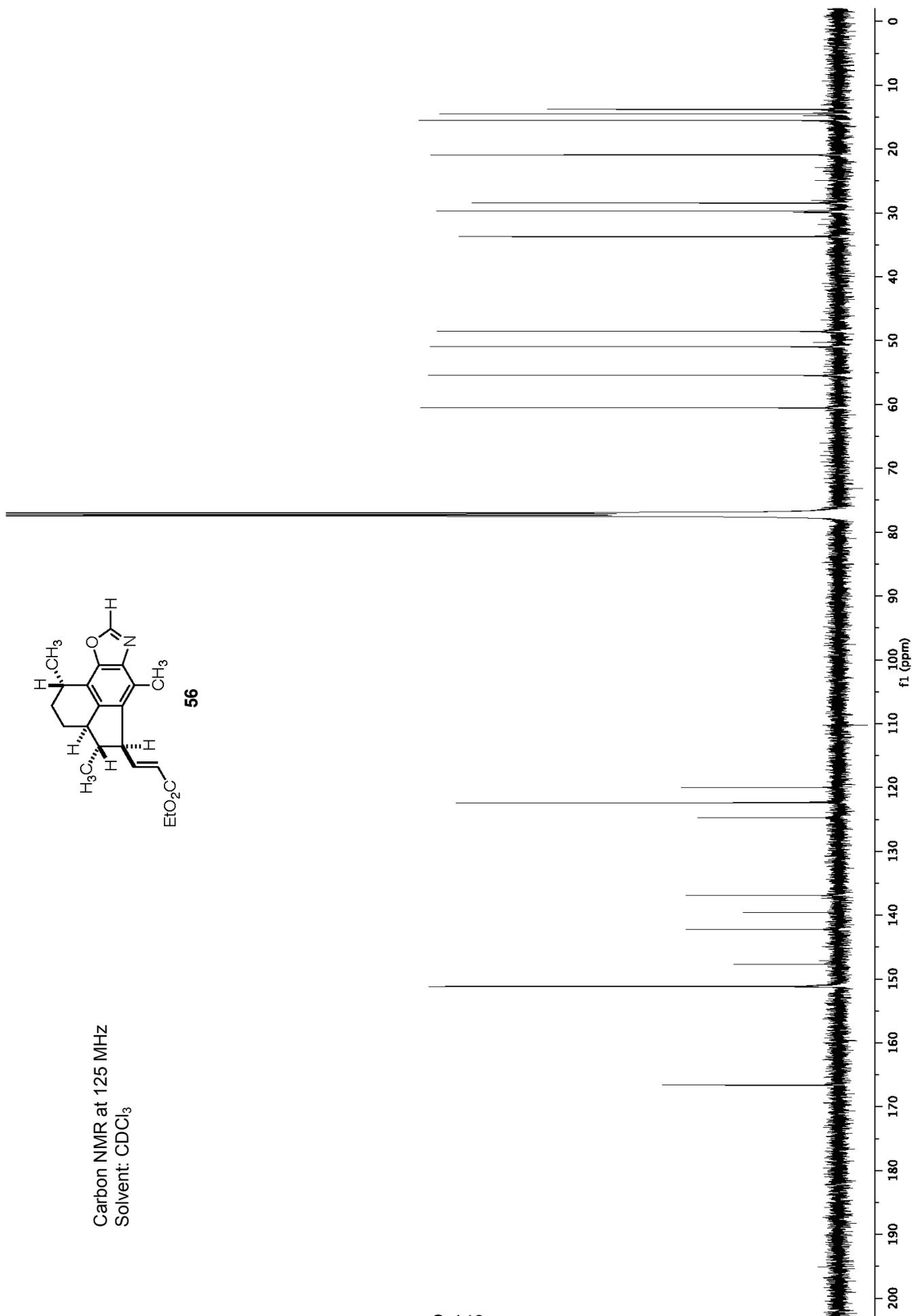
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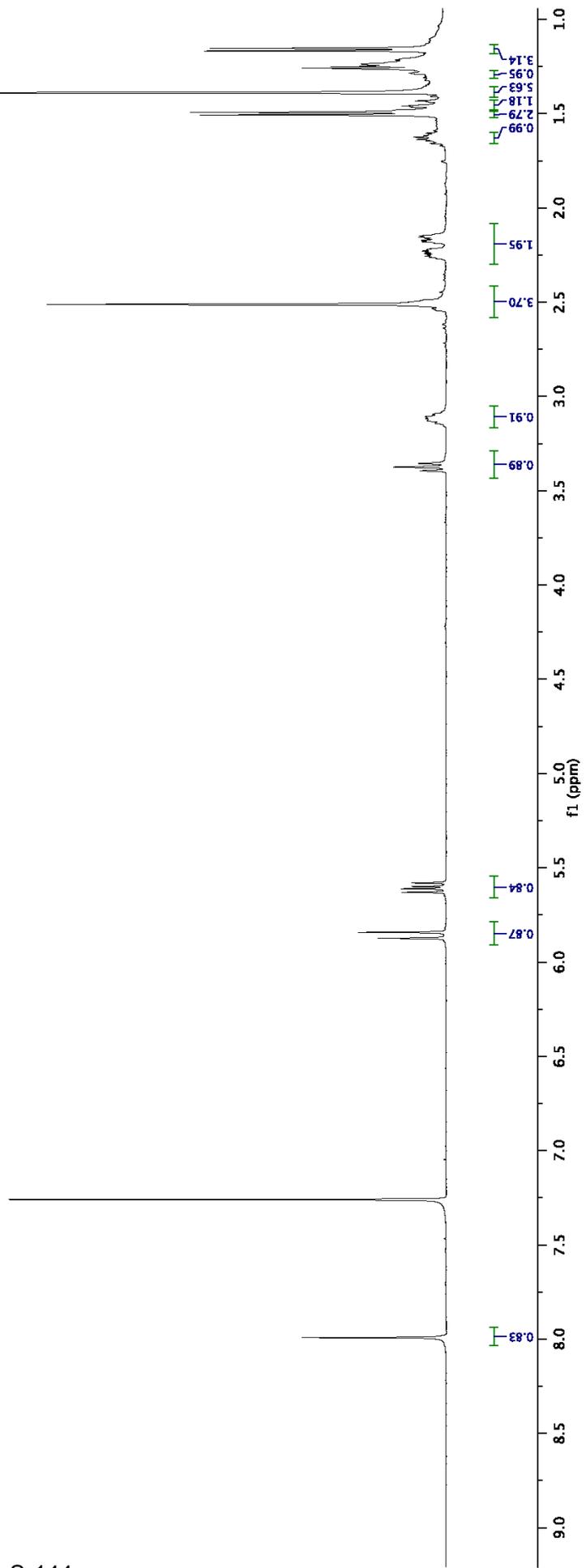
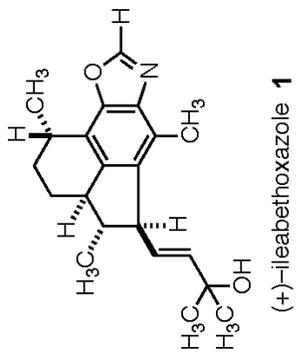
Carbon NMR at 125 MHz
Solvent: CDCl₃



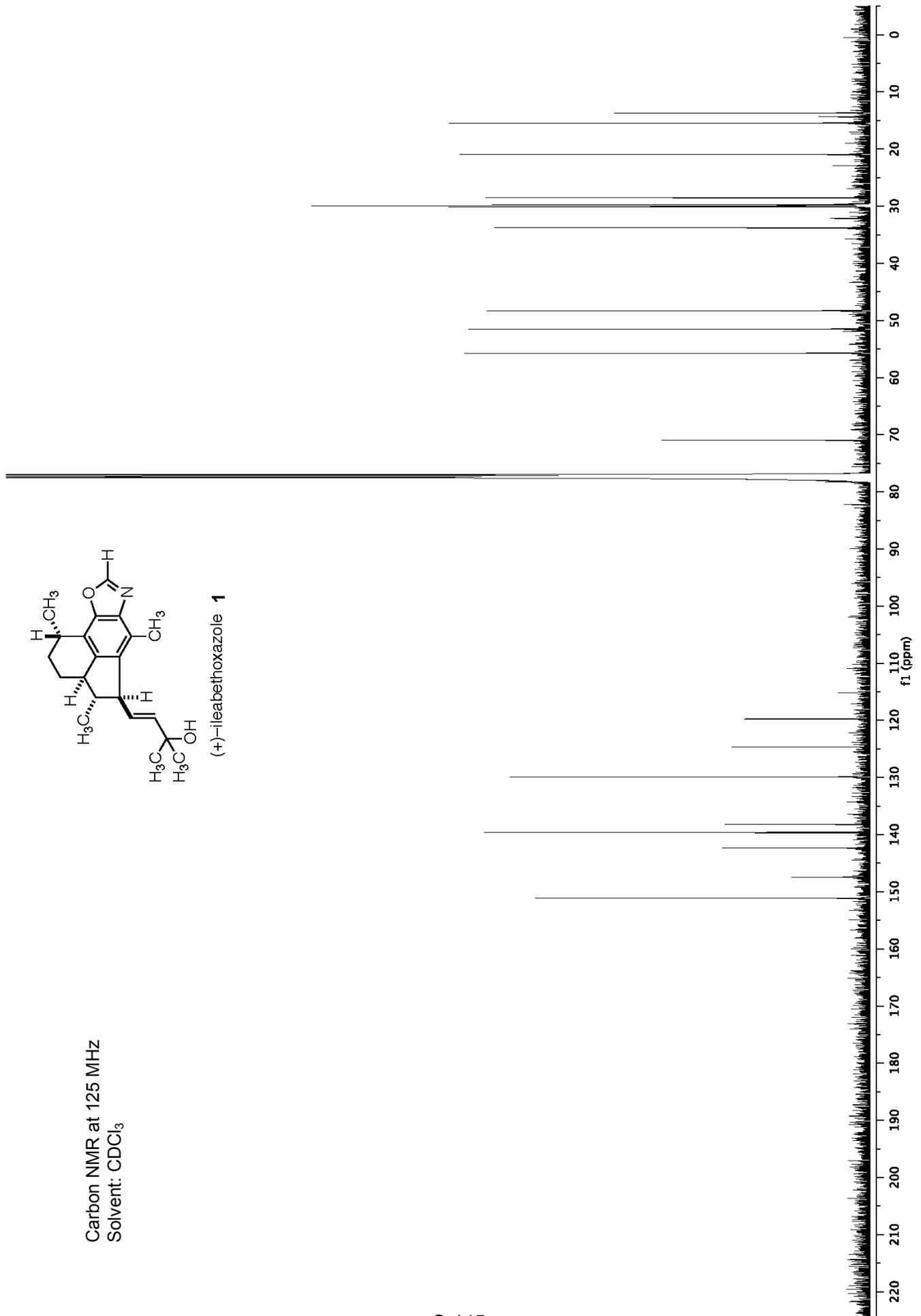
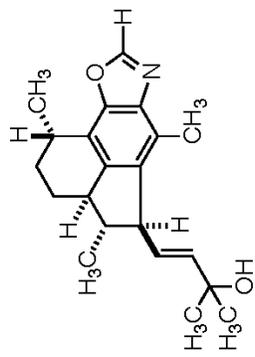
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Proton NMR at 500 MHz
Solvent: CDCl₃



Carbon NMR at 125 MHz
Solvent: CDCl₃



NOESY NMR
Solvent: CD₂Cl₂

