Supporting Information

Incorporation of Azaheterocycle Functionality in Aerobic, Copper-Catalyzed Alkene Aminooxygenation

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General Information

Methods

All reactions were carried out under a nitrogen atmosphere in flame–dried glassware with magnetic stir bar unless otherwise specified. Stainless steel gas-tight syringes were used to transfer air and moisture-sensitive liquids. Reactions were monitored by thin–layer chromatography (TLC) on pre–coated silica gel 60 F254 glass–supported plates from EMD, and visualized under UV light (254 nm) and/or with p–anisaldehyde followed by heating. Flash chromatography was performed using SiliaFlash P60 (230–400 mesh, SiliCycle) using a Combiflash® NextGen 300+ (Teledyne ISCO) or conventional flash columns. Reported product yields were determined based on material isolated after column purification. Room temperature (rt) for the laboratory is 20 °C.

Materials and Reagents

Reagents were used as obtained from commercial suppliers without further purification unless otherwise noted. Copper salts were purchased from Strem, Aldrich, or Oakwood and stored in a glovebox; 1,10-phenanthroline and 2,2-bipyrdiyl based ligands were used without purification and stored in a glovebox. Reaction solvents – Tetrahydrofuran (THF), acetonitrile (MeCN), dichloromethane (DCM), toluene (PhMe), and methanol (MeOH) – were purchased from Fisher and dried by passing through columns of activated alumina (Pure Process Technology SPS). *N,N*-Dimethylformamide (DMF) (Fisher) and nitromethane ($MeNO_2$) (Fisher) were stored over 3Å molecular sieves. Dimethylsulfoxide (DMSO) (Fisher) was used as obtained. Deuterated solvents $CDCl_3$, CD_3OD and DMSO-*d*6 (Cambridge Isotope Laboratories) were used without further purification. Heteroaryl aldehydes were purchased from Ambeed and stored in a glovebox at –20 °C, unless listed as stable under ambient conditions.

Instrumentation

Proton nuclear magnetic resonance (^{1}H NMR) and proton-decoupled carbon nuclear magnetic resonance (^{13}C, ^{1}H NMR) spectra were recorded on a Bruker DPX–400 or a JEOL JNM–ECZL S instrument (operating at 400 MHz for ^{1}H, 100 MHz for ^{13}C) or a Bruker DPX–500 or JEOL JNM–ECZL R instrument (operating at 500 MHz for ^{1}H, 125 MHz for ^{13}C) at ambient temperature. Proton resonances are referenced to residual protium in the NMR solvent. Carbon resonances are referenced to the carbon resonances of the NMR solvent. Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, app = apparent), coupling constants (*J*) in Hertz (Hz), and integration. Mass spectrometry (MS) data were obtained on a Thermo Fisher Q Exactive Plus spectrometer (University of Rochester Medical Center Mass Spectrometry Resource Laboratory).

Abbreviations Used

aq. = aqueous, bpy = 2,2-bipyridyl, CDI = carbonyldiimidazole, equiv. = equivalents, $Cu(EAA)_2$ = copper (II) ethylacetoacetate, $Cu(EH)_2$ = copper (II) 2-ethylhexanoate, CuTC = copper (I) thiophene-2-carboxylate, DCM = dichloromethane, DIBAL-H = diisobutylaluminum hydride, DIPEA = *N,N*-diisopropylethylamine, DMF = *N,N*-dimethylformamide, d.r. = diastereomeric ratio, equiv. = equivalents, Et_2O = diethyl ether, EtOAc = ethyl acetate, gen = general, h = hours, min = minutes, neocuproine = 2,9-dimethyl-1,10-phenanthroline, rbf = round bottom flask, rpm = revolutions per minute, RSM = recovered starting material, rt = room temperature, sat = saturated, TBS = tertbutyldimethylsilyl, THF = tetrahydrofuran, TMB = 1,3,5-trimethoxybenzene, wt = by weight

Summary of *N*-methoxy-γ-heteroaryl-β,γ-unsaturated carbamates used

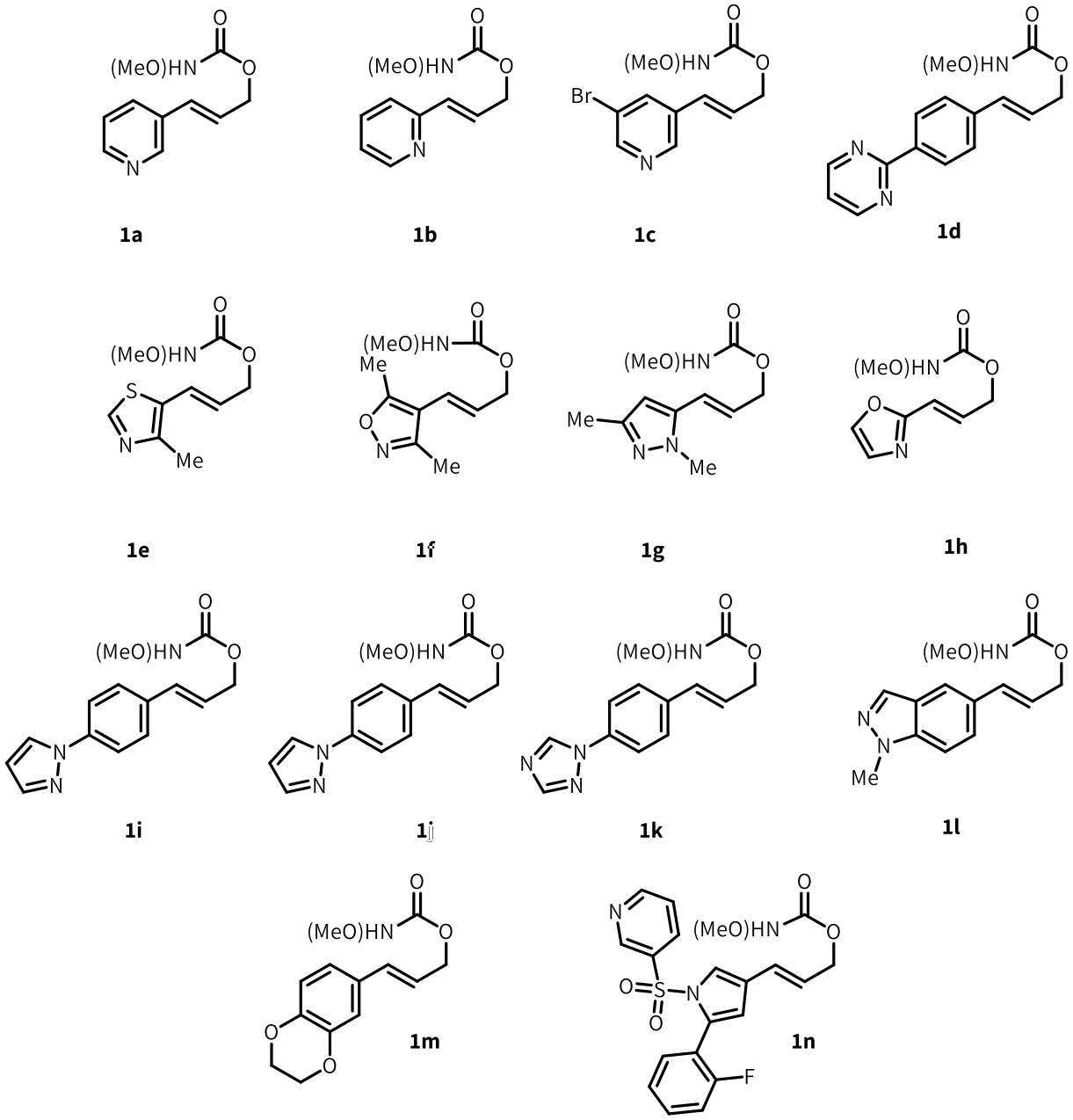
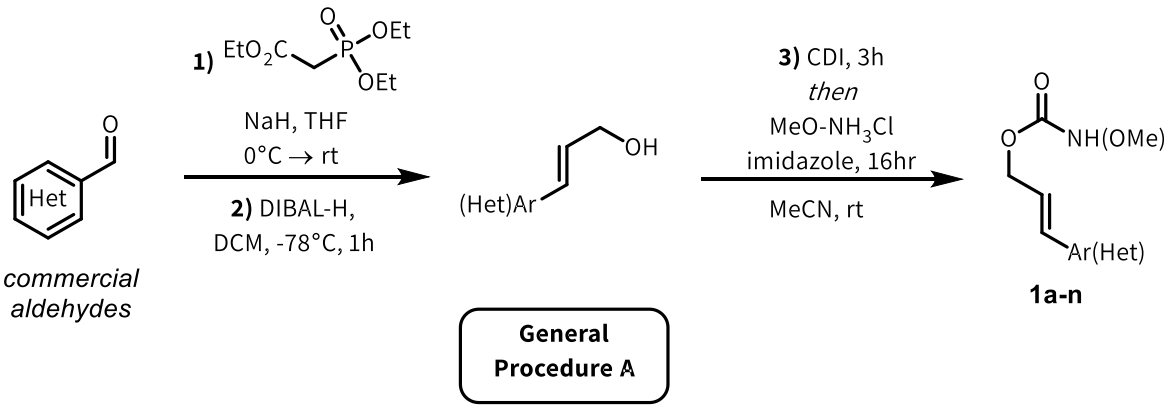


Figure S1. Summary of N-methoxy-γ-heteroaryl-β,γ-unsaturated carbamates used.

Preparation of *N*-methoxy-γ-heteroaryl-β,γ-unsaturated carbamates



General Procedure A:

1) Modified from a literature procedure.[3] NaH (1-2 equiv) was weighed into a flame dried rbf, purged and backfilled with N_2 three times, then suspended in THF (0.3M) and cooled to 0 °C. Triethyl phosphonoacetate (1.1-2.1 equiv.) was added dropwise via syringe. After addition, the mixture was allowed to warm to rt, then stirred an additional 15 min at rt. The mixture was re-cooled to 0 °C and a solution of heteroaryl aldehyde (1.0 equiv.) in THF (0.2 M) was added slowly. After addition, the mixture was warmed to rt and stirred overnight (16 h). Upon completion, the mixture was quenched with sat NH_4Cl (equal to total THF volume). The solution was extracted 3 times with EtOAc (5 mL/mmol aldehyde), washed with brine, dried over $MgSO_4$, then concentrated in vacuo. The crude ester was used in the subsequent step without further purification.

2) Modified from a literature procedure.[3] Substituted ester was transferred to an appropriate rbf then purged and backfilled with N_2 three times. The residue was taken up in dry DCM (0.2M) and cooled to –78 °C, followed by dropwise addition of DIBAL-H (2.2 equiv., 1M in PhMe) over 10 min. The reaction was stirred at –78 °C for 1h. Upon completion the reaction was quenched with 10% aq. NaOH (5 mL/mmol ester). The biphasic mixture was stirred while warming to rt over 1h, then further at rt over another 1h as the emulsion subsided. The layers were separated, and the aq layer was extracted with DCM twice (5mL/mmol ester), unless otherwise noted. The organic layer was washed with brine, dried over $MgSO_4$, then concentrated in vacuo, affording the crude allylic alcohol that was used without further purification.

3) Modified from a literature procedure.[4] Substituted allylic alcohol was taken up in MeCN (0.2M) in a rbf. CDI (1.5 equiv.) was added in one portion at rt. Upon consumption of the alcohol as monitored by TLC (1-3 h), methoxyamine•HCl (4 equiv.) and imidazole (4 equiv.) were added, and the mixture was allowed to stir overnight (16 h). See individual entries for final workup and purification procedures.

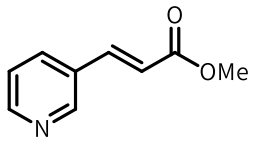
Step 3, General workup A: Diluted with 1M HCl (10 mL/mmol substrate) and extracted 3 times with EtOAc (5 mL/mmol substrate). The organic layer was

discarded. The aqueous layer was adjusted to pH = 7 with 15% NaOH, and extracted three times with DCM (5 mL/mmol substrate). The DCM extract was dried over $MgSO_4$ and concentrated in vacuo. See individual entries for purification conditions.

Step 3, General workup B: Diluted with H_2O (5 mL/mmol substrate) and extracted 3 times with DCM (5 mL/ mmol substrate). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. See individual entries for purification conditions.

Preparation of methyl (*E*)-3-(pyridin-3-yl)acrylate

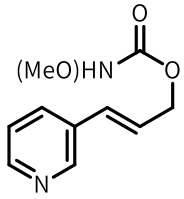
(E)-3-(pyridin-3-yl)acrylate (S1)



Modified from a literature procedure.[1] *(E)*-3-(pyridin-3-yl)acrylic acid (5.00 g, 33.5 mmol, 1.0 equiv.) was weighed into a rbf which was sealed with a septum and purged then backfilled with N_2 three times. The solids were dissolved in dry MeOH (0.5M) and stirred at rt. Thionyl chloride (1.5 equiv.) was added dropwise under a flow of N_2. After addition the flask was equipped with a reflux condenser and heated to 60 °C for 2h, then cooled to rt. The solution was concentrated in vacuo to afford the substituted methyl ester (5.46 g, 33.5 mmol, >99%) which was carried forward through general procedure A (steps 2-3) without further purification.

^{1}H NMR (400 MHz, DMSO-*d*6) δ 9.24 (d, *J* = 2.0 Hz, 1H), 8.90 – 8.80 (m, overlap, 2H), 8.00 (dd, *J* = 8.1, 5.5 Hz, 1H), 7.81 (d, *J* = 16.2 Hz, 1H), 7.03 (d, *J* = 16.1 Hz, 1H), 3.76 (s, 3H). Spectral data in agreement with that reported in the literature.[2]

(*E*)-3-(pyridin-2-yl)allyl methoxycarbamate (1a)



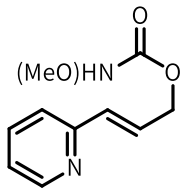
Prepared according to general procedure A: **2)** methyl (*E*)-3-(3-pyridyl)acrylate (**S1)** (5.46 g, 33.5 mmol, 1.0 equiv.), DIBAL-H (1M in PhMe) (74.0 mL, 74.0 mmol, 2.2 equiv.), DCM (167 mL, 0.2M) were used. **3)** CDI (8.15 g, 50.3 mmol, 1.5 equiv0.), MeCN (167 mL, 0.2M), imidazole (9.13 g, 134 mmol, 4.0 equiv.), methoxyamine HCl (11.2 g, 134 mmol, 4.0 equiv.). General workup A used. The residue was purified by flash chromatography on SiO_2 eluting with 50% EtOAc/50% hexanes → 100% EtOAc, then further by pulverizing the resulting solids and trituration in 25%EtOAc/75% hexanes (10 mL). The liquor was decanted, and trituration was repeated for a total of three washes to afford **1a** as a white solid. (2.68 g, 12.9 mmol, 39% over two steps). Additional product can be obtained by repurification of the decanted liquor from trituration.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.49 (d, *J* = 4.9 Hz, 2H), 7.85 (br s, 1H), 7.70 (d, *J* = 7.1 Hz, 1H), 7.25 (m, overlap, 2H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.36 (dt, *J* = 16.1, 6.2 Hz, 1H), 4.82 (d, *J* = 6.1 Hz, 3H), 3.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 149.2, 148.5, 133.3, 131.9, 130.7, 130.7, 125.6, 65.9, 64.9.

HRMS (ESI) *m/z* calculated for $C_{10}H_{13}N_2O_3$ $[M+H]^+$: 209.0921. Found: 209.0923.

(*E*)-3-(pyridin-2-yl)allyl methoxycarbamate (1b)



Prepared according to general procedure A: **1)** NaH (747 mg, 18.7 mmol, 2.0 equiv.) in THF (62 mL, 0.3M), triethyl phosphonoacetate (3.9 mL, 19.6 mmol, 2.1 equiv.) and 2-pyridylcarboxaldehyde (1.00 g, 9.34 mmol, 1.0 equiv.) in THF (47 mL, 0.2M) were used. **2)** DIBAL-H (1M in PhMe) (20.5 mL, 20.5 mmol, 2.2 equiv.), DCM (47 mL, 0.2M) were used. **3)** CDI (2.27 g, 14.0 mmol, 1.5 equiv.), MeCN (47 mL, 0.2M), imidazole (2.54 g, 37.3 mmol, 4.0 equiv.), methoxyamine HCl (3.12 g, 37.3 mmol, 4.0 equiv.). General workup A used. The residue was purified by flash chromatography on SiO_2 eluting with 25% EtOAc/75% hexanes → 100% EtOAc, and subsequent flash chromatography eluting with 50% EtOAc/50% hexanes → 100% EtOAc. Product isolated as a colorless oil (455 mg, 2.19 mmol, 23% over three steps).

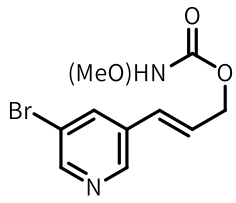
Note: The product was used immediately in the aminooxygenation protocol, or repurified as above prior to use. Product undergoes minor decomposition when heated during rotary evaporation, and at room temperature within several hours. Significant decomposition was observed when stored at –20 °C after 6 months.

^{1}H NMR (400 MHz, CD_3OD) δ 8.47 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.79 (td, *J* = 7.7, 1.8 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.28 (ddd, *J* = 7.6, 4.9, 1.1 Hz, 1H), 6.77 – 6.72 (m, 2H), 4.86 – 4.80 (m, 2H), 3.68 (s, 3H).

^{13}C NMR (101 MHz, CD_3OD) δ 159.22, 156.02, 150.05, 138.77, 132.61, 130.23, 124.12, 123.12, 65.93, 64.57.

HRMS (ESI) *m/z* calculated for $C_{10}H_{13}N_2O_3$ $[M+H]^+$: 209.0921. Found: 209.0923.

(*E*)-3-(5-bromopyridin-3-yl)allyl methoxycarbamate (1c)



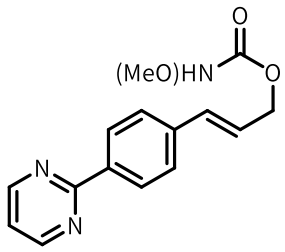
Prepared according to general procedure A: **1)** NaH (1.86 g, 46.7 mmol, 2.0 equiv.) in THF (155 mL, 0.3M), triethyl phosphonoacetate (9.7 mL, 49.0 mmol, 2.1 equiv.) and 5-bromonicotinaldehyde (2.50 g, 23.3 mmol, 1.0 equiv.) in THF (117 mL, 0.2M) were used. **2)** DIBAL-H (1M in PhMe) (51.3 mL, 51.3 mmol, 2.2 equiv.), and DCM (117 mL, 0.2M) were used. **3)** CDI (5.68 g, 35.0 mmol, 1.5 equiv.), MeCN (117 mL, 0.2M), imidazole (6.36 g, 93.4 mmol, 4.0 equiv.), and methoxyamine HCl (7.80 g, 93.4 mmol, 4.0 equiv.) were used. General workup B used. Purified via flash chromatography on SiO_2 eluting with 50% EtOAc/50% hexanes → 100% EtOAc. Product isolated as a white solid (2.19 g, 10.5 mmol, 47% over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (app d, *J* = 17.8 Hz, 1H), 7.95, (br s, 1H), 7.83 (app s, 1H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.41 – 6.31 (m, 1H), 4.81 (app d, *J* = 4.7 Hz, 2H) 3.74 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 150.0, 146.5, 135.7, 133.6, 128.8, 127.3, 121.0, 65.5, 64.8.

HRMS (ESI) *m/z* calculated for $C_{10}H_{12}BrN_2O_3$ $[M+H]^+$: 287.0026. Found: 287.0027.

(*E*)-3-(4-(pyrimidin-2-yl)phenyl)allyl methoxycarbamate (1d)



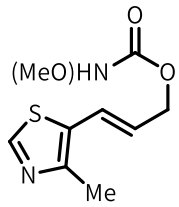
Prepared according to general procedure A: **1)** NaH (434 mg, 10.6 mmol, 2.0 equiv.) in THF (36 mL, 0.3M), triethyl phosphonoacetate (2.3 mL, 11.4 mmol, 2.1 equiv.) and 4-(pyrimidin-2-yl)-benzaldehyde (1.00 g, 5.43 mmol, 1.0 equiv.) in THF (27 mL, 0.2M) were used. **2)** DIBAL-H (1M in PhMe) (11.9 mL, 11.9 mmol, 2.2 equiv.), and DCM (27 mL, 0.2M) were used. **3)** CDI (1.32 g, 8.14 mmol, 1.5 equiv.), MeCN (27 mL, 0.2M), imidazole (1.48 g, 21.7 mmol, 4.0 equiv.), and methoxyamine HCl (1.81 g, 21.7 mmol, 4.0 equiv.) were used. Changes to purification: Purified by flash chromatography on SiO_2 eluting with 50% EtOAc/50% hexanes → 100% EtOAc, then the resulting solids were recrystallized over MeOH. Product isolated as a white solid (906 mg, 3.18 mmol, 58% over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.8 Hz, 2H), 8.41 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.45 (br s, 1H), 7.19 (t, *J* = 4.8 Hz, 1H), 6.74 (d, *J* = 15.9 Hz, 1H), 6.41 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.85 (dd, *J* = 6.4, 1.4 Hz, 2H), 3.77 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 157.5, 157.4, 138.5, 137.4, 134.1, 128.6, 127.1, 124.3, 119.2, 66.4, 64.9.

HRMS (ESI) *m/z* calculated for $C_{15}H_{15}N_3O_3$ $[M+H]^+$: 286.1186. Found: 286.1184.

(*E/Z*)-3-(4-methylthiazol-5-yl)allyl methoxycarbamate (1e)



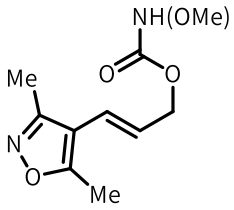
Prepared according to general procedure A: **1)** NaH (1.57 g, 39.3 mmol, 2.0 equiv.) in THF (130 mL, 0.3M), triethyl phosphonoacetate (8.2 mL, 41.3 mmol, 2.1 equiv.) and 4-methylthiazole-5-carbaldehyde (2.5 g, 19.7 mmol, 1.0 equiv.) in THF (100 mL, 0.2M) were used. **2)** DIBAL-H (1M in PhMe) (43.3 mL, 43.3 mmol, 2.2 equiv.), and DCM (100 mL, 0.2M) were used. **3)** CDI (4.78 g, 29.5 mmol, 1.5 equiv.), MeCN (100 mL, 0.2M), imidazole (5.35 g, 78.6 mmol, 4.0 equiv.), and methoxyamine HCl (6.57 g, 78.6 mmol, 4.0 equiv.) were used. General workup B used. Purified via flash chromatography on SiO_2 eluting with 50% EtOAc/50% hexanes → 100% EtOAc. Product isolated as a white solid (2.39 g, 10.4 mmol, 53% over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.56 (s, 1H), 6.78 (d, *J* = 14.6 Hz, 1H), 6.03 (dt, *J* = 15.6, 6.5 Hz, 1H), 4.78 (d, *J* = 6.5 Hz, 2H), 3.75 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 151.2, 150.4, 129.2, 125.4, 124.4, 65.9, 64.8, 15.3.

HRMS (ESI) *m/z* calculated for $C_9H_{13}N_2O_3S$ $[M+H]^+$: 229.0642. Found: 229.0641.

(*E*)-3-(3,5-dimethylisoxazol-4-yl)allyl methoxycarbamate (1f)



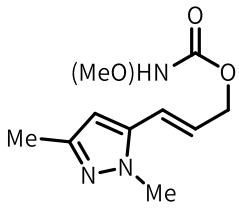
Prepared according to general procedure A: **1)** NaH (639 mg, 16.0 mmol, 2.0 equiv.) in THF (53 mL, 0.3M), triethyl phosphonoacetate (3.33 mL, 16.8 mmol, 2.1 equiv.) and 3,5-dimethylisoxazole-4-carbaldehyde (1.00 g, 8.00 mmol, 1.0 equiv.) in THF (40 mL) were used. **2)** DIBAL-H (1M in PhMe) (17.6 mL, 17.6 mmol, 2.2 equiv.), and DCM (40 mL) were used. **3)** CDI (1.94 g, 12.0 mmol, 1.5 equiv.), MeCN (40 mL, 0.2M), imidazole (2.18 g, 32.0 mmol, 4.0 equiv.), and methoxyamine HCl (2.67 g, 32.0 mmol, 4.0 equiv.) were used. General workup B used. Purified via flash chromatography on SiO_2 eluting with 50% EtOAc/50% hexanes → 100% EtOAc. Product isolated as a white solid (1.09 g, 4.8 mmol, 60% over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 6.36 (d, *J* = 16.2 Hz, 1H), 5.97 (dt, *J* = 16.2, 6.4 Hz, 1H), 4.76 (d, *J* = 6.5 Hz, 1H), 3.75 (s, 2H), 2.41 (s, 2H), 2.31 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 158.3, 157.4, 124.1, 122.9, 111.9, 66.6, 64.8, 11.8, 11.5.

HRMS (ESI) *m/z* calculated for $C_{10}H_{14}N_2O_4$ $[M+H]^+$: 227.1027. Found: 227.1024.

(*E*)-3-(1,3-dimethyl-1H-pyrazol-5-yl)allyl methoxycarbamate (1g)



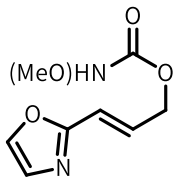
Prepared according to general procedure A: **1)** NaH (387 mg, 16.1 mmol, 2.0 equiv.) in THF (50 mL, 0.3M), triethyl phosphonoacetate (3.79 mL, 16.9 mmol, 2.1 equiv.) and 1,3-dimethylpyrazole-5-carbaldehyde (1.00 g, 8.06 mmol, 1.0 equiv.) in THF (40 mL, 0.2M) were used. **2)** DIBAL-H (1M in PhMe) (17.7 mL, 17.7 mmol, 2.2 equiv.), and DCM (40 mL, 0.2M) were used. **3)** CDI (1.96 g, 12.1 mmol, 1.5 equiv.), MeCN (40 mL, 0.2M), imidazole (2.19 g, 32.2 mmol, 4.0 equiv.), and methoxyamine HCl (2.69 g, 32.2 mmol, 4.0 equiv.) were used. General workup A used. Purified via flash chromatography on SiO_2 eluting with 50% EtOAc/50% hexanes → 100% EtOAc. Product isolated as a white solid (692 mg, 3.07 mmol, 38%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (br s, 1H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.22 – 6.09 (m, overlap, 2H), 4.77 (d, *J* = 4.9 Hz, 2H), 3.77 (s, 3H), 3.73 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 147.7, 140.2, 126.1, 120.8, 103.1, 65.7, 64.8, 36.2, 13.4.

HRMS (ESI) *m/z* calculated for $C_{10}H_{16}N_3O_3$ $[M+H]^+$: 226.1186. Found: 226.1184.

(*E*)-3-(oxazol-4-yl)allyl methoxycarbamate (1h)



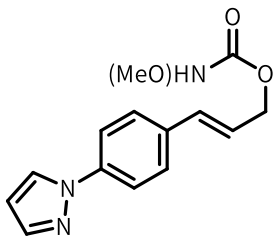
Prepared according to general procedure A: **1)** NaH (824 mg, 20.6 mmol, 2.0 equiv.) in THF (70 mL, 0.3M), triethyl phosphonoacetate (4.3 mL, 21.6 mmol, 2.1 equiv.) and oxazole-4-carbaldehyde (1.00 g, 10.3 mmol, 1.0 equiv.) in THF (50 mL, 0.2M) were used. **2)** DIBAL-H (1M in PhMe) (23 mL, 23.0 mmol, 2.2 equiv.), and DCM (50 mL, 0.2M) were used. **3)** CDI (2.51 g, 15.5 mmol, 1.5 equiv.), MeCN (50 mL, 0.2M), imidazole (2.81 g, 41.2 mmol, 4.0 equiv.), and methoxyamine HCl (3.44 g, 41.2 mmol, 4.0 equiv.) were used. General workup B used. Purified via flash chromatography on SiO_2 eluting with 50% EtOAc/50% hexanes → 100% EtOAc. Product isolated as a white solid (704 mg, 3.55 mmol, 35% over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (br s, 1H), 7.82 (s, 1H), 7.58 (s, 1H), 6.49 (app s, 2H), 4.77 (d, *J* = 3.1 Hz, 2H), 3.72 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 151.4, 137.6, 135.8, 125.6, 121.7, 65.6, 64.7.

HRMS (ESI) *m/z* calculated for $C_8H_{11}N_2O_4$ $[M+H]^+$: 199.0714. Found: 199.0710.

(*E*)-3-(4-(1H-pyrazol-1-yl)phenyl)allyl methoxycarbamate (1i)



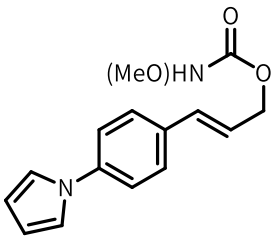
Prepared according to general procedure A: **1)** NaH (465 mg, 11.6 mmol, 2.0 equiv.) in THF (39 mL, 0.2M), triethyl phosphonoacetate (2.4 mL, 12.2 mmol, 2.1 equiv.) and 4-(1*H*-pyrazol-1-yl)benzaldehyde (1.00 g, 5.81 mmol, 1.0 equiv.) in THF (30 mL, 0.2M) were used. **2)** DIBAL-H (1M in PhMe) (13.1 mL, 13.1 mmol, 2.2 equiv.), and DCM (30 mL, 0.2M) were used. **3)** CDI (1.43 g, 8.80 mmol, 1.5 equiv.), MeCN (30 mL, 0.2M), imidazole (1.60 g, 23.5 mmol, 4.0 equiv.), and methoxyamine HCl (1.96 g, 23.5 mmol, 4.0 equiv.) were used. General workup B was used. Purified via flash chromatography on SiO_2 eluting with 50% EtOAc/50% hexanes → 100% EtOAc. Product isolated as a white solid (2.98 g, 10.9 mmol, 75% over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 2.5 Hz, 1H), 7.73 (d, *J* = 1.8 Hz, 1H), 7.66 (d, *J* = 8.9 Hz, 2H), 7.52 (s, 1H), 7.47 (d, *J* = 8.9 Hz, 2H), 6.68 (d, *J* = 15.9 Hz, 1H), 6.47 (t, *J* = 2.2 Hz, 1H), 6.30 (dt, *J* = 15.8, 6.4 Hz, 1H), 4.83 (d, *J* = 6.5 Hz, 2H), 3.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 141.4, 139.9, 134.4, 133.7, 127.9, 126.8, 123.2, 119.3, 107.9, 66.4, 64.9.

HRMS (ESI) *m/z* calculated for $C_{14}H_{16}N_3O_3$ $[M+H]^+$: 274.1186. Found: 226.1183.

(*E*)-3-(4-(1*H*-pyrrol-1-yl)phenyl)allyl methoxycarbamate (1j)



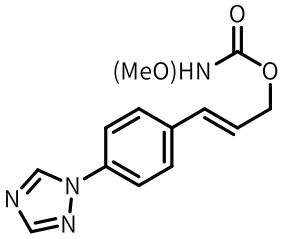
Prepared according to general procedure A: **1)** NaH (467 mg, 11.7 mmol, 2.0 equiv.) in THF (40 mL, 0.2M), triethyl phosphonoacetate (2.4 mL, 12.2 mmol, 2.1 equiv.) and 4-(1*H*-pyrrol-1-yl)benzaldehyde (1.00 g, 5.84 mmol, 1.0 equiv.) in THF (30 mL, 0.2M) were used. **2)** DIBAL-H (1M in PhMe) (12.9 mL, 12.9 mmol, 2.2 equiv.), and DCM (30 mL, 0.2M) were used. **3)** CDI (1.42 g, 8.76 mmol, 1.5 equiv.), MeCN (30 mL, 0.2M), imidazole (1.59 g, 23.4 mmol, 4.0 equiv.), and methoxyamine HCl (1.95 g, 23.4 mmol, 4.0 equiv.) were used. General workup B used. Purified by recrystallization over EtOH/hexanes. Product isolated as a white solid (1.03 g, 3.78 mmol, 65% over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (app d, *J* = 8.6 Hz, overlap, 3H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.10 (t, *J* = 2.2 Hz, 2H), 6.68 (d, *J* = 15.9 Hz, 1H), 6.35 (t, *J* = 2.2 Hz, 2H), 6.29 (dt, *J* = 15.8, 6.5 Hz, 1H), 4.83 (d, *J* = 6.5 Hz, 2H), 3.77 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 140.5, 133.8, 133.6, 128.0, 122.8, 120.5, 119.2, 110.8, 66.5, 64.9.

HRMS (ESI) *m/z* calculated for $C_{15}H_{17}N_2O_3$ $[M+H]^+$: 273.1234. Found: 273.1229.

(*E*)-3-(4-(1H-1,2,4-triazol-1-yl)phenyl)allyl methoxycarbamate (1k)



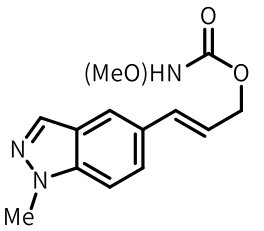
Prepared according to general procedure A: **1)** NaH (1.15, 28.8 mmol, 2.0 equiv.) in THF (72 mL, 0.3M), triethyl phosphonoacetate (6.0 mL, 30.3 mmol, 2.1 equiv.) and 4-(1*H*-1,2,4-triazol-1-yl)benzaldehyde (2.50 g, 14.4 mmol, 1.0 equiv.) in THF (96 mL, 0.2M) were used. **2)** DIBAL-H (1M in PhMe) (32 mL, 32 mmol, 2.2 equiv.), and DCM (96 mL, 0.2M) were used. Note: $CHCl_3$ used for extraction in place of DCM. **3)** CDI (3.51 g, 21.7 mmol, 1.5 equiv.), MeCN (72 mL, 0.2M), imidazole (3.93 g, 57.7 mmol, 4.0 equiv.), and methoxyamine HCl (4.82 g, 57.7 mmol, 4.0 equiv.) were used. General workup B used. Note: $CHCl_3$ used for extraction in place of DCM. Purified via flash chromatography on SiO_2 eluting with 50% EtOAc/50% hexanes → 100% EtOAc. Product isolated as a white solid (1.50 g, 5.49 mmol, 38% over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.09 (s, 1H), 7.83 (br s, 1H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 15.2 Hz, 2H), 6.33 (dt, *J* = 15.9, 6.3 Hz, 1H), 4.82 (d, *J* = 6.3 Hz, 1H), 3.75 (s, 3H).f

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 152.7, 140.9, 136.5, 136.2, 132.9, 128.0, 124.5, 120.2, 66.1, 64.8.

HRMS (ESI) *m/z* calculated for $C_{13}H_{15}N_4O_3$ $[M+H]^+$: 274.1139. Found: 273.1136.

(*E*)-3-(1-methyl-1H-indazol-5-yl)allyl methoxycarbamate (1l)



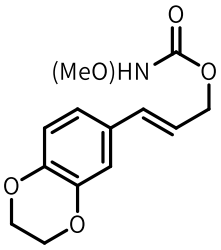
Prepared according to general procedure A: **1)** NaH (500 mg, 12.5 mmol, 2.0 equiv.) in THF (40 mL, 0.3M), triethyl phosphonoacetate (2.6 mL, 13.1 mmol, 2.1 equiv.) and 1-methyl-1*H*-indazole-5-carbaldehyde (1.00 g, 6.24 mmol, 1.0 equiv.) in THF (30 mL, 0.2M) were used. **2)** DIBAL-H (1M in PhMe) (14 mL, 14.0 mmol, 2.2 equiv.), and DCM (30 mL, 0.2M) were used. **3)** CDI (1.52 g, 9.37 mmol, 1.5 equiv.), MeCN (30 mL, 0.2M), imidazole (1.70 g, 25.0 mmol, 4.0 equiv.), and methoxyamine HCl (2.09 g, 25.0 mmol, 4.0 equiv.) were used. General workup B used. Purified via flash chromatography on SiO_2 eluting with 50% EtOAc/50% hexanes → 100% EtOAc. Product isolated as a white solid (1.19 g, 4.55 mmol, 73% over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.70 (br s, 1H), 7.64 (s, 1H), 7.49 (d, *J* = 8.8 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 1H), 6.76 (d, *J* = 15.8 Hz, 1H), 6.33 – 6.20 (m, 1H), 4.82 (d, *J* = 6.6 Hz, 2H), 4.05 (s, 3H), 3.75 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 139.8, 135.3, 133.2, 129.1, 124.8, 124.3, 121.4, 120.1, 109.3, 66.7, 64.8, 35.7.

HRMS (ESI) *m/z* calculated for $C_{13}H_{15}N_3O_3$ $[M+H]^+$: 262.1186. Found: 262.1184.

(*E*)-3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)allyl methoxycarbamate (1m)



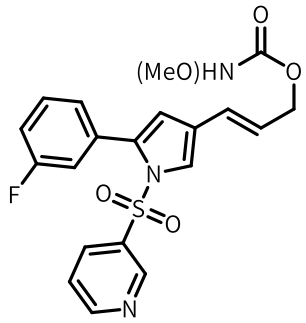
Prepared according to general procedure A: **1)** NaH (1.22 g, 30.5 mmol, 2.0 equiv.) in THF (100 mL, 0.3M), triethyl phosphonoacetate (6.3 mL, 32.0 mmol, 2.1 equiv.) and 2,3-dihydrobenzo[*b*][1,4]dioxine-6-carbaldehyde (2.50 g, 15.2 mmol, 1.0 equiv.) in THF (75 mL, 0.2M) were used. **2)** DIBAL-H (1M in PhMe) (33 mL, 33.0 mmol, 2.2 equiv.), and DCM (75 mL, 0.2M) were used. **3)** CDI (3.64 g, 22.5 mmol, 4.0 equiv.), MeCN (75 mL), imidazole (4.08 g, 59.9 mmol, 4.0 equiv.), and methoxyamine HCl (5.00 g, 59.9 mmol, 4.0 equiv.) were used. Workup: Diluted with 1M HCl (150 mL) and extracted three times with EtOAc (75 mL). The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash chromatography on SiO_2 eluting with 25% EtOAc/75% hexanes → 100% EtOAc. Product isolated as a white solid (2.00 g, 7.54 mmol, 50% over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (br s, 1H), 6.93 – 6.84 (m, 2H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.12 (dt, *J* = 17.1, 6.6 Hz, 1H), 4.76 (d, *J* = 6.6 Hz, 2H), 4.24 (app s, 4H), 3.73 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 143.9, 143.6, 134.4, 129.9, 121.2, 120.3, 117.5, 115.4, 66.6, 64.8, 64.5, 64.4.

HRMS (ESI) *m/z* calculated for $C_{13}H_{15}NO_5Na$ $[M+Na]^+$: 288.0839. Found: 288.0848

(*E*)-3-(5-(3-fluorophenyl)-1-(pyridin-3-ylsulfonyl)-1H-pyrrol-3-yl)allyl methoxycarbamate (1n)



Prepared according to general procedure A: **1)** NaH (242 mg, 6.05 mmol, 2.0 equiv.) in THF (20 mL, 0.3M), triethyl phosphonoacetate (1.26 mL, 6.36 mmol, 2.1 equiv.) and 5-(3-fluorophenyl)-1-(pyridin-3-ylsulfonyl)-1*H*-pyrrole-3-carbaldehyde (1.00 g, 3.03 mmol, 1.0 equiv.) in THF (15 mL, 0.2M) were used. **2)** DIBAL-H (1M in PhMe) (6.7 mL, 6.70 mmol, 2.2 equiv.), and DCM (15 mL, 0.2M) were used. **3)** CDI (736 mg, 4.54 mmol, 1.5 equiv.), MeCN (15 mL, 0.2M), imidazole (824 mg, 12.1 mmol, 4.0 equiv.), and methoxyamine HCl (1.01 g, 12.1 mmol, 4.0 equiv.) were used. General workup B used. Purified via flash chromatography on SiO_2 eluting with 50% EtOAc/50% hexanes → 100% EtOAc. Product isolated as a white solid (794 mg, 1.84 mmol, 61% over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.58 (d, *J* = 2.4 Hz, 1H), 7.69 (ddd, *J* = 8.1, 2.4, 1.6 Hz, 1H), 7.48 (br s, 1H), 7.47 – 7.38 (m, 2H), 7.37 – 7.30 (m, 1H), 7.21 – 7.10 (m, 2H), 7.04 (app t, *J* = 9.1 Hz, 1H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.41 (d, *J* = 1.9 Hz, 1H), 6.04 (dt, *J* = 15.8, 6.5 Hz, 1H), 4.75 (d, *J* = 6.5, 2H), 3.74 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8 (d, $J_{1C—F}$ = 249.1 Hz), 157.4, 154.4, 148.0, 135.0, 134.8, 133.3 (d, $J_{6C—F}$ = 1.9 Hz), 131.5 (d, $J_{4C—F}$ = 8.2 Hz), 129.6, 125.9, 125.5, 123.7, 123.6 (d, $J_{5C—F}$ = 3.4 Hz), 123.5, 122.1, 118.7 (d, $J_{3C—F}$ = 14.9 Hz), 115.7 (d, $J_{2C—F}$ = 22.2 Hz), 115.2, 66.2, 64.9.

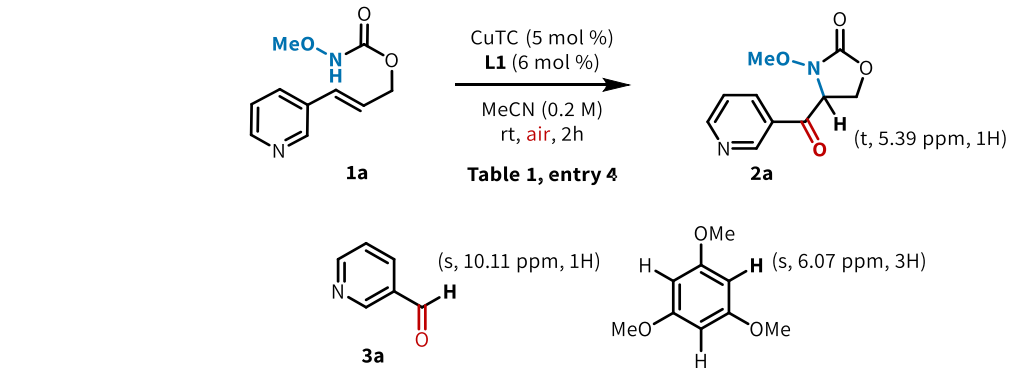
HRMS (ESI) *m/z* calculated for $C_{20}H_{19}FN_3O_5S$ $[M+H]^+$: 432.1024. Found: 432.1016

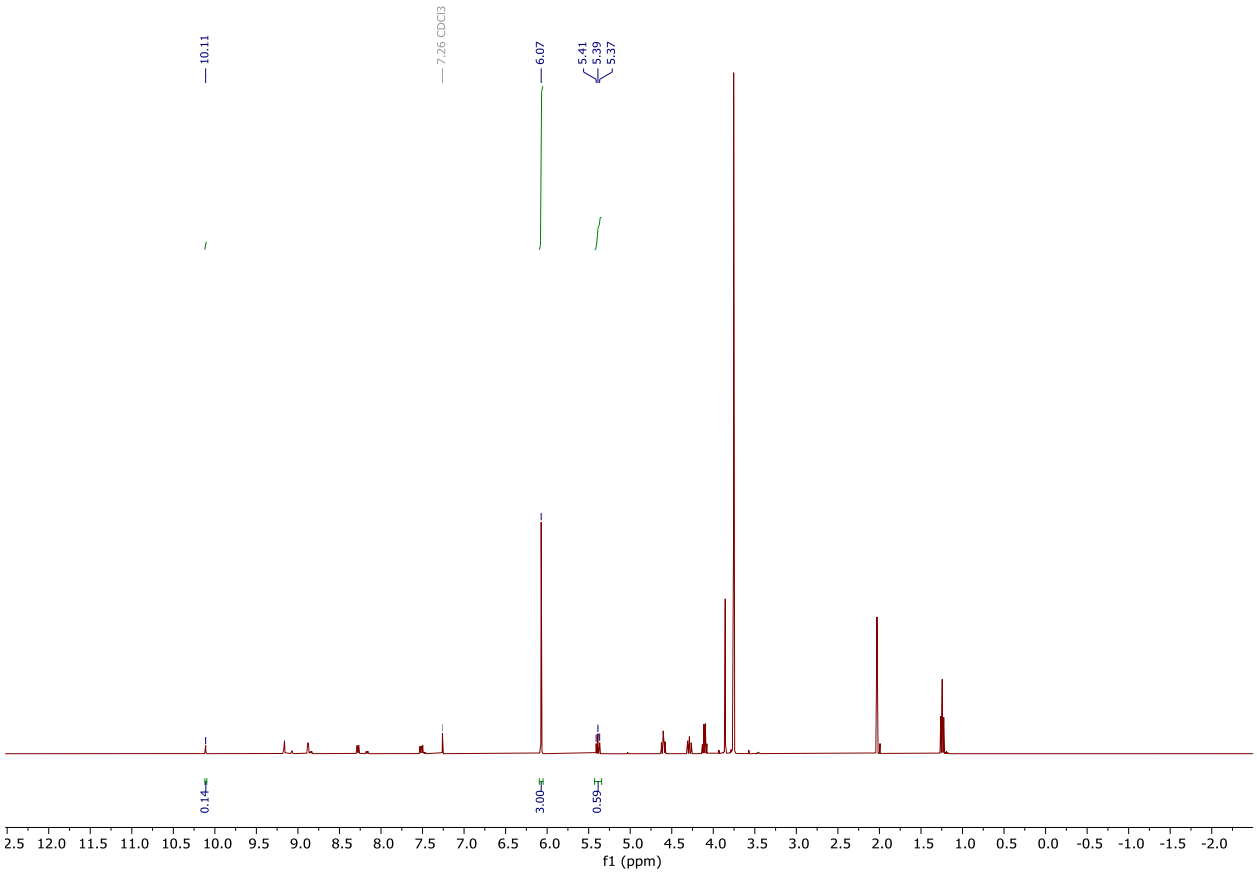
Reaction Investigations

Example of quantitative NMR analysis

For yields determined by quantitative NMR, 1,3,5-trimethoxybenzene (1.0 equiv.) was added to the filtrate and concentrated in vacuo. The residue was taken up in $CDCl_3$ for analysis.

Representative example: Table 1, entry 4.





Copper Source Screening

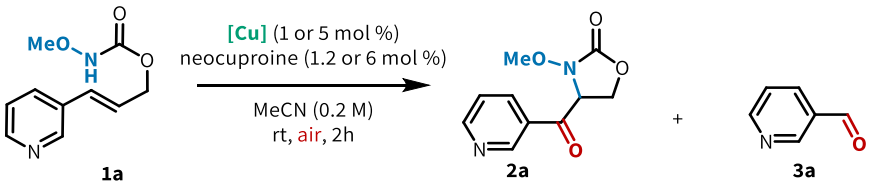


Table S1. Copper source screening for aminooxygenation with heterocyclic substrates. Yields in triplicate (entries 1-2, 5-6, 18) or duplicate by QNMR using 1,3,5-trimethoxybenzene as internal standard.

1 mol %				**5 mol %**			
Entry	[Cu] (1 mol %)	Yield **2a**	Yield **3a**	Entry	[Cu] (5 mol %)	Yield **2a**	Yield **3a**
1	CuTC	59%	13%	2	CuTC	59%	13%
3	CuOAc	49%	11%	4	CuOAc	52%	13%
5	$Cu(OAc)_2$	54%	12%	6	$Cu(OAc)_2$	50%	12%
7	CuCl	49%	14%	8	CuCl	42%	9%
9	CuBr	46%	13%	10	CuBr	51%	13%
11	CuI	52%	13%	12	CuI	41%	11%
13	$CuCl_2$	50%	14%	14	$CuCl_2$	41%	13%
15	$CuBr_2$	48%	11%	16	$CuBr_2$	20%	1%
17	$Cu(EH)_2$	54%	13%	18	$Cu(EH)_2$	51%	11%
19	$Cu(OTf)_2$	39%	9%	20	$Cu(OTf)_2$	42%	17%
21	$Cu(NTf_2)_2$	41%	15%	22	$Cu(NTf_2)_2$	34%	18%
23	$Cu(acac)_2$	37%	7%	24	$Cu(acac)_2$	34%	3%
25	$Cu(hfacac)_2$	48%	11%	26	$Cu(hfacac)_2$	44%	13%
27	$[(MeCN)_4Cu]PF_6$	46%	14%	28	$[(MeCN)_4Cu]PF_6$	6%	0%
29	$Cu(propionate)_2$	53%	13%	30	$Cu(propionate)_2$	50%	14%
31	$Cu(EAA)_2$	43%	7%	32	$Cu(EAA)_2$	33%	4%

33	$Cu(isobutyrate)_2$	53%	11%	34	$Cu(isobutyrate)_2$	49%	12%

CuTC = copper (I) thiophene-2-carboxylate, $Cu(EH)_2$ = copper (II) 2-ethylhexanoate, $Cu(EAA)_2$ = copper (II) ethylacetoacetate

General Procedure for copper source optimization:

Catalyst stock solution: Copper salt (100 µmol, 1.0 equiv.) and neocuproine (**L1**) (120 µmol, 1.2 equiv.) were weighed into a 20 mL scintillation vial in a glovebox. The vial was sealed, removed from the glovebox and the solids were taken up in MeCN (10 mL, 10.0 mM) and stirred open to air for 15 min.

Reaction, 5 mol %: 1.0 mL of the catalyst stock solution (containing copper salt (10.0 µmol, 0.050 equiv.) and ligand (12.0 µmol, 0.060 equiv.)) was transferred to an uncapped, flame-dried 20 mL scintillation vial equipped with a stir bar. (*E*)-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) was added in one portion and the reaction mixture was stirred at 500 rpm for 2h in the uncapped vial. The reaction was quenched by filtering through a ~2 cm pad of SiO_2 in a Pasteur pipette and eluting with ~10 mL EtOAc. Yield was determined by quantitative NMR using 1,3,5-trimethoxybenzene as internal standard.

Reaction, 1 mol %: 0.2 mL of the catalyst stock solution (containing copper salt (2.00 µmol, 0.010 equiv.) and neocuproine (1.3 mg, 2.40 µmol, 0.012 equiv.)) was transferred to an uncapped, flame-dried 2 dram vial equipped with a stir bar. (*E*)-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) was added in one portion and the reaction mixture was stirred at 500 rpm for 2h in the uncapped vial. The reaction was quenched by filtering through a ~2 cm pad of SiO_2 in a Pasteur pipette and eluting with ~10 mL EtOAc. Yield was determined by quantitative NMR using 1,3,5-trimethoxybenzene as internal standard.

Entry 1: 1 mol % CuTC General procedure for copper source optimization was followed. 0.2 mL catalyst stock solution (containing CuTC (0.38 mg, 2.00 µmol, 0.010 equiv.) and neocuproine (**L1**) (0.50 mg, 2.40 µmol, 0.012 equiv.)), 0.8 mL MeCN and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.118 mmol, 59%) (0.026 mmol, 13%) (0% RSM)
Run 2: (0.116 mmol, 58%) (0.024 mmol, 12%) (0% RSM)
Run 3: (0.118 mmol, 59%) (0.026 mmol, 13%) (0% RSM)
Average: 59% yield

Entry 2: 5 mol % CuTC General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.122 mmol, 61%) (0.026 mmol, 13%) (0% RSM)
Run 2: (0.114 mmol, 57%) (0.026 mmol, 13%) (0% RSM)
Run 3: (0.118 mmol, 59%) (0.026 mmol, 13%) (0% RSM)
Average: 59% yield

Entry 3: 1 mol % CuOAc General procedure for copper source optimization was followed. 0.2 mL catalyst stock solution (containing CuOAc (0.25 mg, 2.00 µmol, 0.010 equiv.) and neocuproine (**L1**) (0.50 mg, 2.40 µmol, 0.012 equiv.)), 0.8 mL MeCN and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.100 mmol, 50%) (0.022 mmol, 11%) (0% RSM)
Run 2: (0.096 mmol, 48%) (0.022 mmol, 11%) (0% RSM)
Average: 49% yield

Entry 4: 5 mol % CuOAc General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing CuOAc (1.2 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.106 mmol, 53%) (0.026 mmol, 13%) (0% RSM)
Run 2: (0.100 mmol, 50%) (0.024 mmol, 12%) (0% RSM)
Average: 52% yield

Entry 5: 1 mol % $Cu(OAc)_2$ General procedure for copper source optimization was followed. 0.2 mL catalyst stock solution (containing $Cu(OAc)_2$ (0.36 mg, 2.00 µmol, 0.010 equiv.) and neocuproine (**L1**) (0.50 mg, 2.40 µmol, 0.012 equiv.)), 0.8 mL MeCN and *(E)*-

3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.108 mmol, 54%) (0.024 mmol, 12%) (0% RSM)
Run 2: (0.108 mmol, 54%) (0.022 mmol, 11%) (0% RSM)
Run 3: (0.108 mmol, 54%) (0.026 mmol, 13%) (0% RSM)
Average: 54% yield

Entry 6: 5 mol % $Cu(OAc)_2$ General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing CuOAc (1.8 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.096 mmol, 48%) (0.022 mmol, 12%) (0% RSM)
Run 2: (0.102 mmol, 51%) (0.024 mmol, 11%) (0% RSM)
Run 3: (0.104 mmol, 52%) (0.028 mmol, 14%) (0% RSM)
Average: 50% yield

Entry 7: 1 mol % CuCl General procedure for copper source optimization was followed. 0.2 mL catalyst stock solution (containing CuCl (0.20 mg, 2.00 µmol, 0.010 equiv.) and neocuproine (**L1**) (0.50 mg, 2.40 µmol, 0.012 equiv.)), 0.8 mL MeCN and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.100 mmol, 50%) (0.026 mmol, 13%) (0% RSM)
Run 2: (0.096 mmol, 48%) (0.028 mmol, 14%) (0% RSM)
Average: 49% yield

Entry 8: 5 mol % CuCl General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing CuCl (1.0 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.) were used. Product

yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.084 mmol, 42%) (0.014 mmol, 7%) (0% RSM)
Run 2: (0.084 mmol, 42%) (0.022 mmol, 11%) (0% RSM)
Average: 42% yield

Entry 9: 1 mol % CuBr General procedure for copper source optimization was followed. 0.2 mL catalyst stock solution (containing CuCl (0.29 mg, 2.00 µmol, 0.010 equiv.) and neocuproine (**L1**) (0.50 mg, 2.40 µmol, 0.012 equiv.)), 0.8 mL MeCN and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.086 mmol, 43%) (0.024 mmol, 12%) (0% RSM)
Run 2: (0.096 mmol, 48%) (0.026 mmol, 13%) (0% RSM)
Average: 46% yield

Entry 10: 5 mol % CuBr General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing CuBr (1.4 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.102 mmol, 51%) (0.028 mmol, 14%) (0% RSM)
Run 2: (0.100 mmol, 50%) (0.028 mmol, 11%) (0% RSM)
Average: 51% yield

Entry 11: 1 mol % CuI General procedure for copper source optimization was followed. 0.2 mL catalyst stock solution (containing CuI (0.38 mg, 2.00 µmol, 0.010 equiv.) and neocuproine (**L1**) (0.50 mg, 2.40 µmol, 0.012 equiv.)), 0.8 mL MeCN and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.106 mmol, 53%) (0.026 mmol, 13%) (0% RSM)
Run 2: (0.102 mmol, 51%) (0.026 mmol, 13%) (0% RSM)
Average: 52% yield

Entry 12: 5 mol % CuI General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing CuI (1.9 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.080 mmol, 40%) (0.022 mmol, 11%) (0% RSM)
Run 2: (0.082 mmol, 41%) (0.020 mmol, 10%) (0% RSM)
Average: 41% yield

Entry 13: 1 mol % $CuCl_2$ General procedure for copper source optimization was followed. 0.2 mL catalyst stock solution (containing $CuCl_2$ (0.27 mg, 2.00 µmol, 0.010 equiv.) and neocuproine (**L1**) (0.50 mg, 2.40 µmol, 0.012 equiv.)), 0.8 mL MeCN and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.102 mmol, 51%) (0.026 mmol, 13%) (0% RSM)
Run 2: (0.098 mmol, 49%) (0.028 mmol, 14%) (0% RSM)
Average: 50% yield

Entry 14: 5 mol % $CuCl_2$ General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing $CuCl_2$ (1.3 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.080 mmol, 40%) (0.020 mmol, 10%) (0% RSM)
Run 2: (0.084 mmol, 42%) (0.032 mmol, 16%) (0% RSM)
Average: 41% yield

Entry 15: 1 mol % $CuBr_2$ General procedure for copper source optimization was followed. 0.2 mL catalyst stock solution (containing $CuBr_2$ (0.45 mg, 2.00 µmol, 0.010 equiv.) and neocuproine (**L1**) (0.50 mg, 2.40 µmol, 0.012 equiv.)), 0.8 mL MeCN and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.096 mmol, 48%) (0.026 mmol, 13%) (0% RSM)
Run 2: (0.096 mmol, 48%) (0.018 mmol, 9%) (0% RSM)
Average: 48% yield

Entry 16: 5 mol % $CuBr_2$ General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing $CuBr_2$ (2.2 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.042 mmol, 21%) (0.002 mmol, 1%) (0.092 mmol, 46% RSM)
Run 2: (0.036 mmol, 18%) (0.002 mmol, 1%) (0.098 mmol, 49% RSM)
Average: 20% yield

Entry 17: 1 mol % $Cu(EH)_2$ General procedure for copper source optimization was followed. 0.2 mL catalyst stock solution (containing $Cu(EH)_2$ (0.70 mg, 2.00 µmol, 0.010 equiv.) and neocuproine (**L1**) (0.50 mg, 2.40 µmol, 0.012 equiv.)), 0.8 mL MeCN and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.102 mmol, 51%) (0.024 mmol, 12%) (0% RSM)
Run 2: (0.112 mmol, 56%) (0.026 mmol, 13%) (0% RSM)
Average: 54% yield

Entry 18: 5 mol % $Cu(EH)_2$ General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing $Cu(EH)_2$ (3.5 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.106 mmol, 53%) (0.024 mmol, 12%) (0% RSM)
Run 2: (0.098 mmol, 49%) (0.026 mmol, 13%) (0% RSM)
Run 3: (0.102 mmol, 51%) (0.014 mmol, 7%) (0% RSM)
Average: 51% yield

Entry 19: 1 mol % $Cu(OTf)_2$ General procedure for copper source optimization was followed. 0.2 mL catalyst stock solution (containing $Cu(OTf)_2$ (0.72 mg, 2.00 µmol, 0.010 equiv.) and neocuproine (**L1**) (0.50 mg, 2.40 µmol, 0.012 equiv.)), 0.8 mL MeCN and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.078 mmol, 39%) (0.022 mmol, 11%) (0% RSM)
Run 2: (0.076 mmol, 38%) (0.012 mmol, 6%) (0% RSM)
Average: 39% yield

Entry 20: 5 mol % $Cu(OTf)_2$ General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing $Cu(OTf)_2$ (3.6 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.086 mmol, 43%) (0.032 mmol, 16%) (0% RSM)
Run 2: (0.080 mmol, 40%) (0.034 mmol, 17%) (0% RSM)
Average: 42% yield

Entry 21: 1 mol % $Cu(NTf_2)_2$ General procedure for copper source optimization was followed. 0.2 mL catalyst stock solution (containing $Cu(NTf_2)_2$ (1.3 mg, 2.00 µmol, 0.010 equiv.) and neocuproine (**L1**) (0.50 mg, 2.40 µmol, 0.012 equiv.)), 0.8 mL MeCN and *(E)*-

3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.084 mmol, 42%) (0.026 mmol, 13%) (0% RSM)
Run 2: (0.080 mmol, 40%) (0.034 mmol, 17%) (0% RSM)
Average: 41% yield

Entry 22: 5 mol % $Cu(NTf_2)_2$ General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing $Cu(NTf_2)_2$ (6.2 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.064 mmol, 32%) (0.038 mmol, 19%) (0% RSM)
Run 2: (0.072 mmol, 36%) (0.034 mmol, 17%) (0% RSM)
Average: 34% yield

Entry 23: 1 mol % $Cu(acac)_2$ General procedure for copper source optimization was followed. 0.2 mL catalyst stock solution (containing $Cu(acac)_2$ (0.52 mg, 2.00 µmol, 0.010 equiv.) and neocuproine (**L1**) (0.50 mg, 2.40 µmol, 0.012 equiv.)), 0.8 mL MeCN and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.070 mmol, 35%) (0.008 mmol, 4%) (0.062 mmol, 31% RSM)
Run 2: (0.076 mmol, 38%) (0.018 mmol, 9%) (0.060 mmol, 30% RSM)
Average: 37% yield

Entry 24: 5 mol % $Cu(acac)_2$ General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing $Cu(acac)_2$ (2.6 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.062 mmol, 31%) (0.006 mmol, 3%) (0.020 mmol, 10% RSM)
Run 2: (0.072 mmol, 36%) (0.006 mmol, 3%) (0.022 mmol, 11% RSM)
Average: 34% yield

Entry 25: 1 mol % $Cu(hfacac)_2$ General procedure for copper source optimization was followed. 0.2 mL catalyst stock solution (containing $Cu(hfacac)_2$ (0.96 mg, 2.00 µmol, 0.010 equiv.) and neocuproine (**L1**) (0.50 mg, 2.40 µmol, 0.012 equiv.)), 0.8 mL MeCN and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.098 mmol, 49%) (0.022 mmol, 11%) (0.016 mmol, 8% RSM)
Run 2: (0.092 mmol, 46%) (0.020 mmol, 10%) (0.060 mmol, 7% RSM)
Average: 48% yield

Entry 26: 5 mol % $Cu(hfacac)_2$ General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing $Cu(hfacac)_2$ (4.8 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.084 mmol, 42%) (0.026 mmol, 13%) (0.022 mmol, 11% RSM)
Run 2: (0.092 mmol, 46%) (0.024 mmol, 12%) (0.022 mmol, 11% RSM)
Average: 44% yield

Entry 27: 1 mol % $(MeCN)_4CuPF_6$ General procedure for copper source optimization was followed. 0.2 mL catalyst stock solution (containing $(MeCN)_4CuPF_6$ (0.75 mg, 2.00 µmol, 0.010 equiv.) and neocuproine (**L1**) (0.50 mg, 2.40 µmol, 0.012 equiv.)), 0.8 mL MeCN and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.090 mmol, 45%) (0.032 mmol, 16%) (0% RSM)

Run 2: (0.092 mmol, 46%) (0.024 mmol, 12%) (0% RSM)
Average: 46% yield

Entry 28: 5 mol % $(MeCN)_4CuPF_6$ General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing $(MeCN)_4CuPF_6$ (3.7 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.012 mmol, 6%) (0.000 mmol, 0%) (0.170 mmol, 85% RSM)
Run 2: (0.012 mmol, 6%) (0.000 mmol, 0%) (0.152 mmol, 76% RSM)
Average: 6% yield

Entry 29: 1 mol % $Cu(propionate)_2$ General procedure for copper source optimization was followed. 0.2 mL catalyst stock solution (containing $Cu(propionate)_2$ (0.42 mg, 2.00 µmol, 0.010 equiv.) and neocuproine (**L1**) (0.50 mg, 2.40 µmol, 0.012 equiv.)), 0.8 mL MeCN and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.106 mmol, 53%) (0.026 mmol, 13%) (0% RSM)
Run 2: (0.106 mmol, 53%) (0.026 mmol, 13%) (0% RSM)
Average: 53% yield

Entry 30: 5 mol % $Cu(propionate)_2$ General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing $Cu(propionate)_2$ (2.1 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.100 mmol, 50%) (0.026 mmol, 13%) (0% RSM)
Run 2: (0.098 mmol, 49%) (0.028 mmol, 14%) (0% RSM)
Average: 50% yield

Entry 31: 1 mol % Cu(EAA)$_2$ General procedure for copper source optimization was followed. 0.2 mL catalyst stock solution (containing Cu(EAA)$_2$ (0.64 mg, 2.00 µmol, 0.010 equiv.) and neocuproine (**L1**) (0.50 mg, 2.40 µmol, 0.012 equiv.)), 0.8 mL MeCN and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.084 mmol, 42%) (0.014 mmol, 7%) (0.038 mmol, 19% RSM)
Run 2: (0.086 mmol, 43%) (0.012 mmol, 6%) (0.046 mmol, 23% RSM)
Average: 43% yield

Entry 32: 5 mol % Cu(EAA)$_2$ General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing Cu(EAA)$_2$ (3.2 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.062 mmol, 31%) (0.010 mmol, 5%) (0.058 mmol, 29% RSM)
Run 2: (0.068 mmol, 34%) (0.004 mmol, 2%) (0.058 mmol, 29% RSM)
Average: 33% yield

Entry 33: 1 mol % Cu(isobutyrate)$_2$ General procedure for copper source optimization was followed. 0.2 mL catalyst stock solution (containing Cu(isobutyrate)$_2$ (0.48 mg, 2.00 µmol, 0.010 equiv.) and neocuproine (**L1**) (0.50 mg, 2.40 µmol, 0.012 equiv.)), 0.8 mL MeCN and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.104 mmol, 52%) (0.022 mmol, 11%) (0% RSM)
Run 2: (0.108 mmol, 54%) (0.022 mmol, 11%) (0% RSM)
Average: 53% yield

Entry 34: 5 mol % Cu(isobutyrate)$_2$ General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing Cu(isobutyrate)$_2$ (2.4 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.)

were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.098 mmol, 49%) (0.024 mmol, 12%) (0% RSM)
Run 2: (0.096 mmol, 48%) (0.022 mmol, 11%) (0% RSM)
Average: 49% yield

Ligand Structure/Reactivity Study

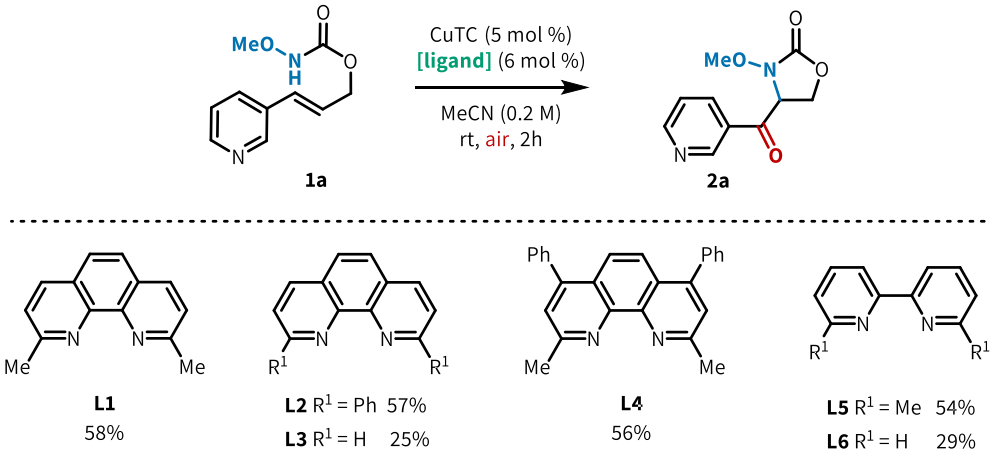


Table S2. Evaluation of ligands using CuTC at 5 mol % loading. Yields in duplicate by QNMR using 1,3,5-trimethoxybenzene as internal standard.

Entry	Ligand	Yield 2a	Recovered 1a
1	**L1**	58%	0%
2	**L2**	57%	0%
3	**L3**	25%	33%
4	**L4**	56%	0%
5	**L5**	54%	0%
6	**L6**	29%	19%

General Procedure for ligand evaluation:

Catalyst stock solution: CuTC (19.1 mg, 0.010 mmol, 1.0 equiv.) and ligand (0.012 mmol, 1.2 equiv.) were weighed into a 20 mL scintillation vial in a glovebox. The vial was sealed was removed from the glovebox and the solids were taken up in MeCN (10 mL, 10 mM) and stirred at rt for 15 min as the vial is exposed to air.

Reaction: 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and ligand (12.0 µmol, 0.060 equiv.)) was transferred to an uncapped, flame-dried 20 mL scintillation vial equipped with a stir bar. (*E*)-3-(pyridin-2-yl)allyl methoxycarbamate (1**a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) was added in one portion and the reaction mixture was stirred at 500 rpm for 2h in the uncapped vial. The reaction was quenched by filtering through a ~2 cm pad of SiO_2 in a Pasteur pipette and eluting with ~10 mL EtOAc. Internal standard 1,3,5-trimethoxybenzene (33.6 mg, 0.200 mmol, 1.0 equiv.) was added to the filtrate and concentrated in vacuo. Yield was determined by quantitative NMR.

Ligand L1: **2,9-dimethyl-1,10-phenanthroline** (neocuproine)
General procedure for the ligand evaluation was followed: 1.0 mL catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.05 equiv.) and (neocuproine (**L1**) (2.5 mg, 6.0 µmol, 0.012 equiv.)), and *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.). Yield was determined by quantitative NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.112 mmol, 56%) (0.026 mmol, 13%) (0% RSM)
Run 2: (0.118 mmol, 59%) (0.024 mmol, 12%) (0% RSM)
Average: 58% yield

Ligand L2: **2,9-diphenyl-1,10-phenanthroline**
General procedure for the ligand evaluation was followed: 1.0 mL catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and 2,9-diphenyl-1,10-phenanthroline (**L2**) (4.0 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.). Yield was determined by quantitative NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** percent)

Run 1: (0.114 mmol, 57%) (0.024 mmol, 12%) (0% RSM)
Run 2: (0.112 mmol, 56%) (0.026 mmol, 13%) (0% RSM)
Average: 57% yield

Ligand L3: **1,10 phenanthroline**
General procedure for the ligand evaluation was followed: 1.0 mL catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and 1,10-phenanthroline (**L3**) (2.2 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.). Yield was determined by quantitative NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.050 mmol, 25%) (0.030 mmol, 15%) (0.062 mmol, 31% RSM)
Run 2: (0.050 mmol, 25%) (0.030 mmol, 15%) (0.068 mmol, 34% RSM)
Average: 57% yield

Ligand L4: **4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline (bathocuproine)**
General procedure for the ligand evaluation was followed: 1.0 mL catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline (**L4**) (4.3 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.). Yield was determined by quantitative NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.110 mmol, 55%) (0.030 mmol, 15%) (0% RSM)
Run 2: (0.114 mmol, 57%) (0.024 mmol, 12%) (0% RSM)
Average: 56% yield

Ligand L5: **6,6'-dimethyl-2,2-bipyridyl**
General procedure for the ligand evaluation was followed: 1.0 mL catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and 6,6'-dimethyl-2,2-bipyridyl (**L5**) (2.2 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.). Yield was determined by quantitative NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.110 mmol, 55%) (0.026 mmol, 13%) (0% RSM)
Run 2: (0.106 mmol, 53%) (0.026 mmol, 13%) (0% RSM)
Average: 54% yield

Ligand L6: **2,2-bipyridyl**
General procedure for the ligand evaluation was followed: 1.0 mL catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and 2,2-bipyridyl (**L6**) (1.9 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.). Yield was determined by quantitative NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Run Number: (product yield in mmol, product yield in percent) (yield **3a** in mmol, yield **3a** percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.058 mmol, 29%) (0.028 mmol, 14%) (0.036 mmol, 18% RSM)
Run 2: (0.058 mmol, 29%) (0.030 mmol, 15%) (0.038 mmol, 19% RSM)
Average: 29% yield

Base, additive, and solvent screening

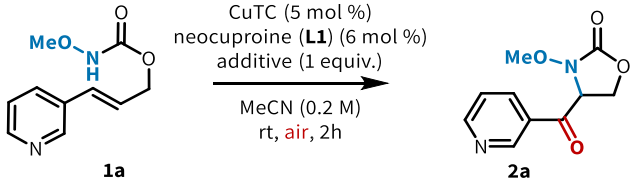


Table S3. Base, additive, and solvent effects for heteroaryl alkene aminooxygenation. RSM = recovered starting material. Yields in duplicate by QNMR with 1,3,5-trimethoxybenzene used as internal standard.

Entry	Additive	Solvent	Yield 2a	Recovered 1a
Base Screening				
1	Li_2CO_3	MeCN	47%	0%
2	Na_2CO_3	MeCN	34%	0%
3	K_2CO_3	MeCN	0%	62%
4	Cs_2CO_3	MeCN	0%	73%
5	KOAc	MeCN	6%	17%
6	Na_2HPO_4	MeCN	48%	0%
7	$NaHCO_3$	MeCN	59%	0%
Solvent				
8	-	MeCN	59%	0%

9	-	$MeNO_2$	57%	0%
10		DMF	18%	0%
11	-	THF	49%	22%
12	-	PhMe	22%	48%
13	-	DMSO	31%	13%
Acid Additives				
14	PivOH	MeCN	0%	>95%
15	TFA	MeCN	0%	33%
16	HCl (4M in dioxane)	MeCN	0%	0%
17	AcOH	MeCN	0%	>95%
Salt Additives				
18	TBACl	MeCN	39%	0%
19	TBABr	MeCN	41%	0%
20	TBAI	MeCN	16%	54%

General Procedure for additive and solvent screening:

Catalyst stock solution: CuTC (19.1 mg, 100 µmol, 1.0 equiv.) and neocuproine (**3a**) (25.0 mg, 120 µmol, 1.2 equiv.) were weighed into a 20 mL scintillation vial in a glovebox. The vial was sealed, removed from the glovebox and the solids were taken up in MeCN (10 mL, 10.0mM) and stirred open to air for 15 min.

Catalyst stock solution (entries 8-13): CuTC (19.1 mg, 100 µmol, 1.0 equiv.) and neocuproine (**L1**) (25.0 mg, 120 µmol, 1.2 equiv.) were weighed into a 20 mL scintillation vial in a glovebox. The vial was sealed, removed from the glovebox and the solids were taken up in solvent (10 mL, 10.0mM) and stirred open to air for 15 min.

Reaction: 1.0 mL of the catalyst stock solution (CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12 µmol, 0.060 equiv.)) was transferred to an uncapped, flame-dried 2-dram vial equipped with a stir bar. Additive (1.0 equiv) was added, followed by (*E*)-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) in one portion and the reaction mixture was stirred at 500 rpm for 2h in the uncapped vial. The reaction was quenched by filtering through a ~2 cm pad of SiO_2 in a Pasteur pipette

and eluting with ~10 mL EtOAc. Internal standard 1,3,5-trimethoxybenzene (33.6 mg, 0.200 mmol, 1.0 equiv.) was added to the filtrate and concentrated in vacuo. Yield determined by quantitative NMR.

Entry 1: Li_2CO_3 General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.) in MeCN,, *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.), and Li_2CO_3 (14.8 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run Number: (yield in mmol, yield in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.094 mmol, 47%) (0% RSM)
Run 2: (0.092 mmol, 46%) (0% RSM)
Average: 47% yield

Entry 2: Na_2CO_3 General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.) in MeCN,, (*E*)-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.), and Na_2CO_3 (21.2 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run Number: (yield in mmol, yield in percent) (recovered S.M. in mmol, recovered S.M. in %)05

Run 1: (0.068 mmol, 34%) (0% RSM)
Run 2: (0.066 mmol, 33%) (0% RSM)
Average: 34% yield

Entry 3: K_2CO_3 General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.) in MeCN, (*E*)-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.), and K_2CO_3 (27.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run Number: (yield in mmol, yield in percent) (recovered S.M. in mmol, recovered S.M. in %)05

Run 1: (0.000 mmol, 0%) (0.122 mmol, 61% RSM)
Run 2: (0.000 mmol, 0%) (0.124 mmol, 62% RSM)
Average: 0% yield

Entry 4: Cs_2CO_3 General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and

neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.) in MeCN, (*E*)-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.), and K_2CO_3 (65.2 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run Number: (yield in mmol, yield in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.000 mmol, 0%) (0.136 mmol, 68% RSM)
Run 2: (0.000 mmol, 0%) (0.144 mmol, 77% RSM)
Average: 0% yield

Entry 5: KOAc General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.) in MeCN, (*E*)-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.), and KOAc (19.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run Number: (yield in mmol, yield in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.014 mmol, 7%) (0.042 mmol, 21% RSM)
Run 2: (0.008 mmol, 4%) (0.026 mmol, 13% RSM)
Average: 6% yield

Entry 6: Na_2HPO_4 General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.) in MeCN, (*E*)-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.), and KOAc (19.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run Number: (yield in mmol, yield in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.102 mmol, 51%) (0% RSM)
Run 2: (0.090 mmol, 45%) (0% RSM)
Average: 48% yield

Entry 7: $NaHCO_3$ General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.) in MeCN, (*E*)-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.), and KOAc (19.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run Number: (yield in mmol, yield in percent) (recovered S.M. in mmol, recovered S.M. in %)

Run 1: (0.116 mmol, 58%) (0% RSM)
Run 2: (0.120 mmol, 60%) (0% RSM)
Average: 59% yield

Entry 9: $MeNO_2$ General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.) in $MeNO_2$, and *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run 1: (0.112 mmol, 56%) (0% RSM)
Run 2: (0.116 mmol, 58%) (0% RSM)
Average: 57% yield

Entry 10: DMF General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.) in DMF, and *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run 1: (0.038 mmol, 19%) (0% RSM)
Run 2: (0.034 mmol, 17%) (0% RSM)
Average: 18% yield

Entry 11: THF General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.) in THF, and *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run 1: (0.098 mmol, 49%) (0.036 mmol, 18% RSM)
Run 2: (0.098 mmol, 49%) (0.050 mmol, 25% RSM)
Average: 49% yield

Entry 12: PhMe General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.) in PhMe, and *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run 1: (0.044 mmol, 22%) (0.090 mmol, 45% RSM)

Run 2: (0.042 mmol, 21%) (0.100 mmol, 50% RSM)
Average: 22% yield

Entry 13: DMSO General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.) in DMSO, and *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run 1: (0.068 mmol, 34%) (0.022 mmol, 11% RSM)
Run 2: (0.056 mmol, 28%) (0.028 mmol, 14% RSM)
Average: 31% yield

Entry 14: PivOH General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.05 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.06 equiv.) in MeCN, *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) and PivOH (23.0 µL, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run 1: (0.000 mmol, 0%) (0.190 mmol, 95% RSM)
Run 2: (0.000 mmol, 0%) (0.192 mmol, 96% RSM)
Average: 0% yield

Entry 15: TFA General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.05 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.06 equiv.) in MeCN, *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) and TFA (15.3 µL, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run 1: (0.000 mmol, 0%) (0.072 mmol, 36% RSM)
Run 2: (0.000 mmol, 0%) (0.060 mmol, 30% RSM)
Average: 0% yield

Entry 16: HCl General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.05 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.06 equiv.) in MeCN, *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) and HCl (4M in dioxane) (50.0 µL, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run 1: (0.000 mmol, 0%) (0% RSM)
Run 2: (0.000 mmol, 0%) (0% RSM)
Average: 0% yield

Entry 17: AcOH General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.05 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.06 equiv.) in MeCN, *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) and AcOH (4M in dioxane) (5.0 µL, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run 1: (0.000 mmol, 0%) (0.192 mmol, 96% RSM)
Run 2: (0.000 mmol, 0%) (0.190 mmol, 95% RSM)
Average: 0% yield

Entry 18: TBACl General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.05 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.06 equiv.) in MeCN, *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) and TBACl (55.6 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run 1: (0.074 mmol, 37%) (0% RSM)
Run 2: (0.082 mmol, 41%) (0% RSM)
Average: 39% yield

Entry 19: TBABr General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.05 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.06 equiv.) in MeCN, *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) and TBACl (64.5 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run 1: (0.080 mmol, 40%) (0% RSM)
Run 2: (0.082 mmol, 41%) (0% RSM)
Average: 41% yield

Entry 20: TBAI General procedure for additive optimization screening was followed. 1.0 mL of the catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.05 equiv.) and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.06 equiv.) in MeCN, *(E)*-3-(4-(trifluoromethyl)phenyl)allyl methoxycarbamate (**1a**) (41.6 mg, 0.200 mmol, 1.0 equiv.) and TBACl (73.9 mg, 0.200 mmol, 1.0 equiv.) were used. Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as internal standard.

Run 1: (0.028 mmol, 14%) (0.120 mmol, 60% RSM)
Run 2: (0.034 mmol, 17%) (0.096 mmol, 48% RSM)
Average: 16% yield

Reaction Optimization (Table 1)

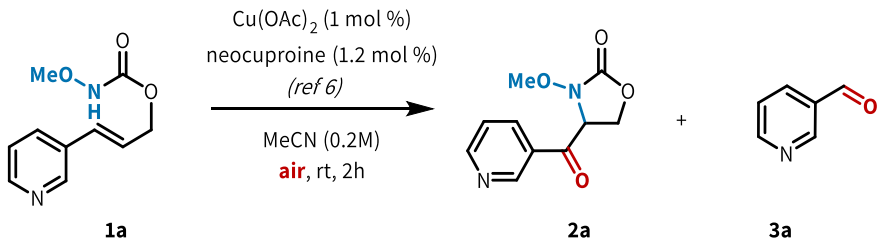


Table 4. Optimization for alkene aminooxygenation with azaheterocycles.

Entry	Changes to conditions	Yield 2a	Yield 3a	Recovered 1a
1	none	54%	12%	trace
2	5 mol % $Cu(OAc)_2$	50%	11%	0%
3	5 mol % $Cu(EH)_2$	51%	10%	0%
4	5 mol % CuTC	59%	12%	0%
5	1 mol % CuTC	59%	12%	0%
6	**As in entry 4**, 1 eq K_2CO_3	12%	3%	61%
7	**As in entry 4**, 1 eq PivOH added	0%	0%	>95%
8	20 mol % CuTC	42%	10%	16%
9	5 mol % CuTC, 70°C	3%	8%	42%
10	20 mol % CuTC, 70°C	4%	8%	41%

Entries 1-5: General procedure for copper source screening was followed. See results in section.

Entries 6-7: General procedure for additive screening was followed**.** See results in section.

Entries 8, 10: General procedure for copper source screening was followed except the following catalyst stock solution was used. See results below:

Catalyst stock solution: CuTC (76.4mg, 400 µmol, 1.0 equiv.) and neocuproine (**L1**) (100.0 mg, 480 µmol, 1.2 equiv.) were weighed into a 20 mL scintillation vial in a glovebox. The vial was sealed, removed from the glovebox and the solids were taken up in MeCN (10 mL, 40.0mM) and stirred open to air for 15 min.

Entries 9, 10: General procedure for copper salt screening was followed except the reaction was heated to 70 °C. See results below:

Entry 8: 20 mol % CuTC General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing CuTC (7.6 mg, 40.0 µmol, 0.200 equiv.), and neocuproine (**L1**) (10.0mg, 48.0 µmol, 0.240 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.). Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (yield in mmol, yield in percent), (yield **3a** in mmol, yield **3a** in percent) (recovered starting material mmol, percent recovered)

Run 1: (0.088 mmol, 44%) (0.026 mmol, 13%) (0.026 mmol, 13%)
Run 2: (0.078 mmol, 39%) (0.016mmol, 8%) (0.034 mmol, 17%)
Run 3: (0.084 mmol, 42%) (0.018 mmol, 9%) (0.028 mmol, 14%)
Average: 42% yield

Entry 9: 5 mol % CuTC, 70 °C General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing CuTC (1.9 mg, 10.0 µmol, 0.050 equiv.), and neocuproine (**L1**) (2.5 mg, 12.0 µmol, 0.060 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.). Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (yield in mmol, yield in percent), (yield **3a** in mmol, yield **3a** in percent) (recovered starting material mmol, percent recovered)

Run 1: (0.002 mmol, 1%) (0.018 mmol, 9%) (0.084 mmol, 42%)
Run 2: (0.006 mmol, 3%) (0.016 mmol, 8%) (0.080 mmol, 40%)
Run 3: (0.002 mmol, 1%) (0.016 mmol, 8%) (0.088 mmol, 44%)
Average: 3% yield

Entry 10: 20 mol % CuTC, 70 °C General procedure for catalyst optimization screening was followed. 1.0 mL catalyst stock solution (containing CuTC (7.6 mg, 40.0 µmol, 0.200 equiv.), and neocuproine (**L1**) (10.0 mg, 48.0 µmol, 0.240 equiv.)), and *(E)*-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (46.1 mg, 0.200 mmol, 1.0 equiv.). Product yield was analyzed by quantitative NMR using 1,3,5-trimethoxy benzene as an internal standard.

Run Number: (yield in mmol, yield in percent), (yield **3a** in mmol, yield **3a** in percent) (recovered starting material mmol, percent recovered)

Run 1: (0.000 mmol, 0%) (0.012 mmol, 6%) (0.106 mmol, 53%)
Run 2: (0.010 mmol, 5%) (0.020 mmol, 10%) (0.060 mmol, 30%)
Run 3: (0.004 mmol, 2%) (0.016 mmol, 8%) (0.072 mmol, 39%)
Average: 4% yield

Methodology Limitations

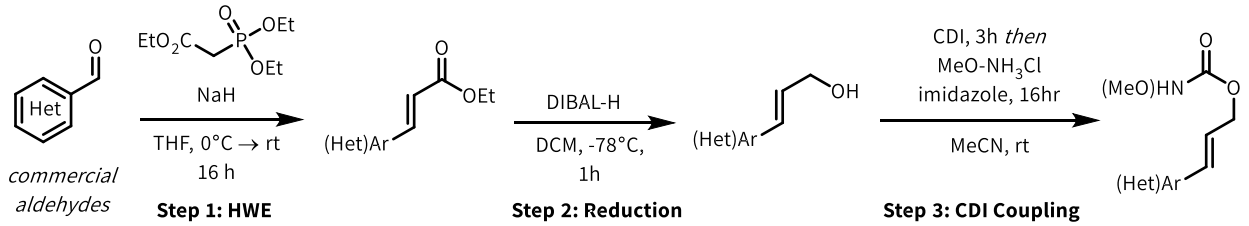
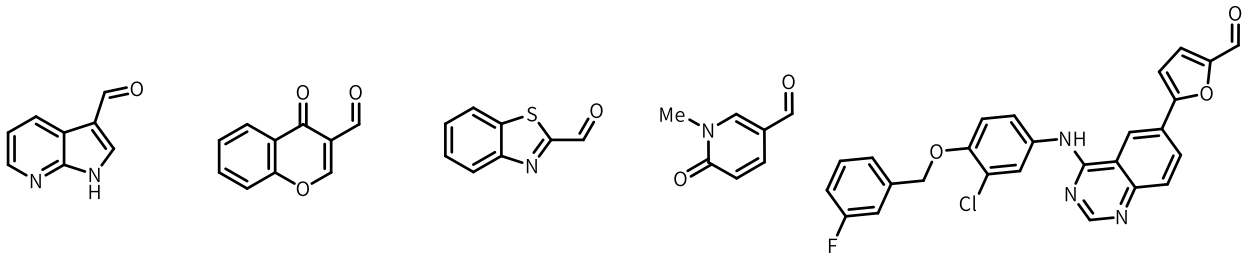
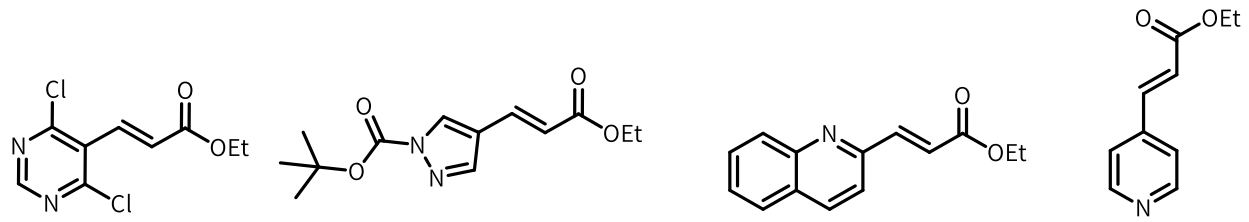


Figure S2. Method limitations in substrate synthesis.

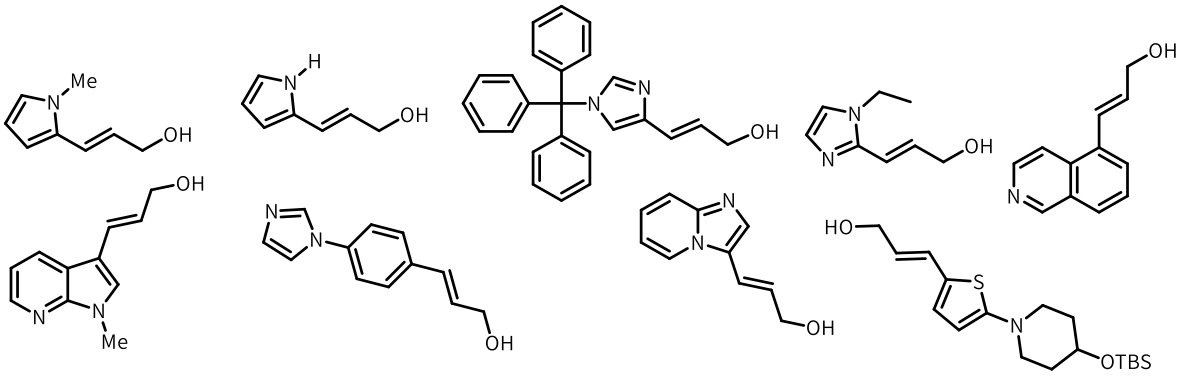
The following heteroaryl aldehydes produced an intractable mixture after the HWE reaction in step 1:



The following α,β-unsaturated esters produced an intractable mixture, or underwent undesired overreduction after the DIBAL reduction in step 2:



The following allylic alcohols produced an intractable mixture after the CDI coupling in step 3:



The following substrates were incompatible in the aminooxygenation protocol, producing low product yield accompanied by decomposition of the reaction components:

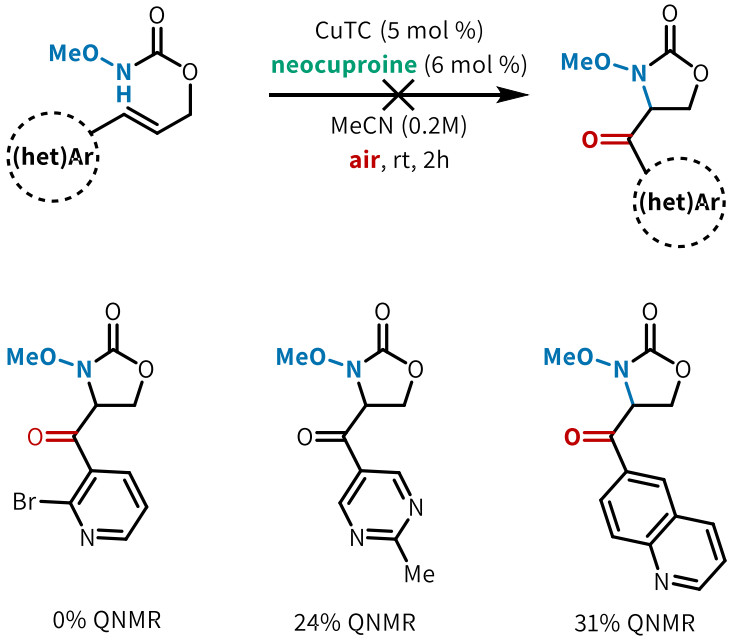


Figure S3. Incompatible substrates in the aminooxygenation protocol.

Scope of 4-(heteroarylcarbonyl)oxazolidin-2-ones

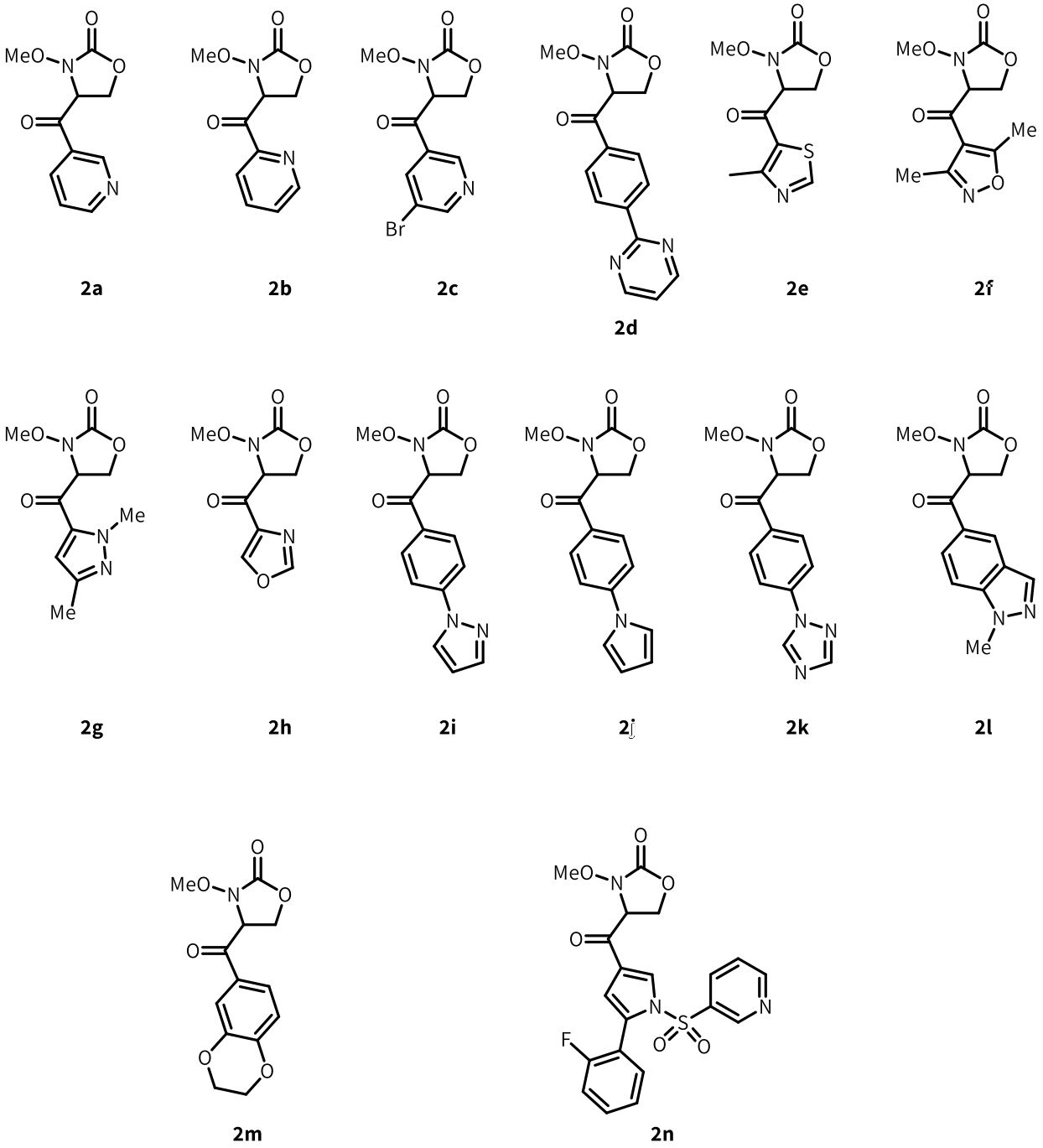
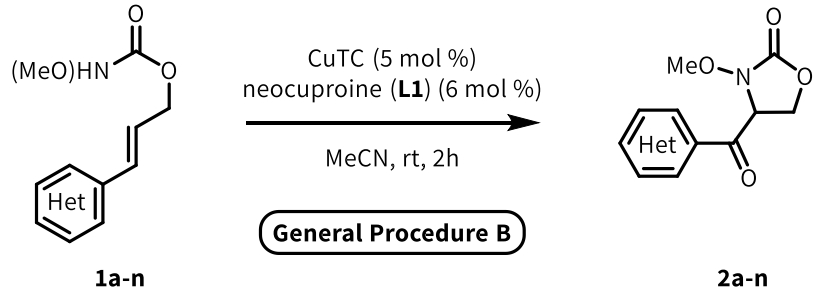


Figure S4. Summary of *N*-methoxy-γ-heteroaryl-β,γ-unsaturated carbamates synthesized.

General procedure for the aminooxygenation protocol

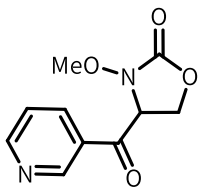


1a-n **2a-n**

General Procedure B: Catalyst stock solution: CuTC (19.1 mg, 0.100 mmol, 1.0 equiv.) and neocuproine (**L1**) (25.0 mg, 0.120 mmol, 1.2 equiv.) were weighed into a 20 mL scintillation vial in a glovebox. The vial was sealed was removed from the glovebox and the solids were taken up in MeCN (10 mL, 10mM) and stirred at rt for 15 min as the vial was exposed to air.

Reaction: 2.5 mL of the catalyst stock solution (containing CuTC (4.8 mg, 25.0 µmol, 0.050 equiv.) and neocuproine (**L1**) (6.2 mg, 30 µmol, 0.060 equiv.)) was transferred to an uncapped, flame-dried 20 mL scintillation vial equipped with a stir bar. β,γ-unsaturated carbamate (0.5 mmol, 1.0 equiv.) was added in one portion and the reaction mixture was stirred at 500 rpm for 2h in the uncapped vial. The reaction was quenched by filtering through a ~2 cm pad of SiO_2 in a Pasteur pipette and eluting with ~10 mL EtOAc. The filtrate was concentrated in vacuo and the crude residue was purified by flash chromatography on SiO_2.

3-methoxy-4-nicotinoyloxazolidin-2-one (2a)



Prepared according to general procedure B: 2.5 mL stock catalyst solution (containing CuTC (4.8 mg, 25.0 µmol, 0.050 equiv.), and neocuproine (6.2 mg, 30 µmol, 0.060 equiv.)) and (*E*)-3-(pyridin-2-yl)allyl methoxycarbamate (**1a**) (104 mg, 0.500 mmol, 1.0 equiv.) were used. Crude material was purified via flash chromatography on SiO_2 using a Combiflash® NextGen 300+ auto column with a 50 g stationary phase cartridge eluting with 25% EtOAc/75% hexanes → 100% EtOAc over 15 min (80 mL/min). Yield for all three runs was also determined by quantitative NMR using 1,3,5-trimethoxybenzene (84.1 mg, 0.500 mmol, 1.0 equiv.) as internal standard.

Note: After purification, some inseparable impurities remained in the sample. Yields were adjusted by QNMR using 1,3,5-trimethoxybenzene as an internal standard. The isolated sample was dissolved in its entirety in $CDCl_3$ with 1,3,5-trimethoxybenzene and mixed thoroughly.

Run 1: (65.3 mg, 0.293 mmol, 59%) Purity (wt): 91% → (59.4 mg, 0.267 mmol, 53%)

Run 2: (67.2 mg, 0.302 mmol, 60%) Purity (wt): 92% → (61.6 mg, 0.277 mmol, 55%)
Run 3: (69.6 mg, 0.313 mmol, 63%) Purity (wt): 90% → (62.4 mg, 0.281 mmol, 56%)
Average: 55% yield

Run 1: 1,3,5-TMB (22.8 mg, 0.136 mmol) used. Molar ratio (**2a** : TMB) = 1.97
Run 2: 1,3,5-TMB (21.5 mg, 0.127 mmol) used. Molar ratio (**2a** : TMB) = 2.17
Run 3: 1,3,5-TMB (38.7 mg, 0.230 mmol) used. Molar ratio (**2a** : TMB) = 1.22

Run 1: (0.275 mmol, 55%) QNMR yield
Run 2: (0.285 mmol, 57%) QNMR yield
Run 3: (0.300 mmol, 60%) QNMR yield

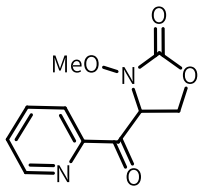
An analytical sample was prepared by combining the purified reaction products from runs 1-3, which were further purified via flash chromatography on SiO_2 eluting with 25% EtOAc/75% hexanes → 100% EtOAc, followed by a second purification via flash chromatography on SiO_2 eluting with 50% EtOAc/50% hexanes → 100% EtOAc using ~50 g silica for each purification. Product was isolated as a white solid (9.1 mg).

^{1}H NMR (400 MHz, CDCl3) δ 9.17 (s, 1H), 8.88 (d, *J* = 4.8 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 7.52 (dd, *J* = 8.0, 4.8 Hz, 1H), 5.40 (t, *J* = 8.5 Hz, 1H), 4.62 (t, *J* = 8.7 Hz, 1H), 4.30 (t, *J* = 8.5 Hz, 1H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 158.2, 155.1, 149.7, 136.1, 130.2, 124.4, 64.6, 62.9, 62.3.

HRMS (ESI) *m/z* calculated for $C_{10}H_{11}N_2O_4$ $[M+H]^+$: 223.0714. Found 223.0714.

3-methoxy-4-nicotinoyloxazolidin-2-one (2b)



Prepared according to general procedure B: 2.5 mL stock catalyst solution (containing CuTC (4.8 mg, 25.0 µmol, 0.050 equiv.), and neocuproine (**L1**) (6.2 mg, 30 µmol, 0.060 equiv.)), and (*E*)-3-(pyridin-2-yl)allyl methoxycarbamate (**1b**) (111 mg, 0.500 mmol, 1.0 equiv.) were used. Crude material was purified via flash chromatography on SiO_2 using 50 g of silica eluting with 50% EtOAc/50% hexanes → 100% EtOAc, followed by a subsequent purification via flash chromatography on SiO_2 using 50 g of silica eluting with 50% EtOAc/50% hexanes → 100% EtOAc. Yield for run 3 was determined by quantitative NMR using 1,3,5-trimethoxybenzene as internal standard (84.1 mg, 0.500 mmol, 1.0 equiv.).

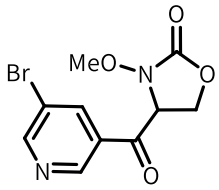
Run 1: (42.0 mg, 0.189 mmol, 38%)
Run 2: (44.2 mg, 0.199 mmol, 40%)
Run 3: (0.215 mmol, 43%) QNMR yield
Average: 39% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (dd, *J* = 4.7, 0.8 Hz, 1H), 8.12 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.92 (td, *J* = 7.7, 1.7 Hz, 1H), 7.57 (ddd, *J* = 7.6, 4.8, 1.3 Hz, 1H), 5.64 (t, *J* = 9.2 Hz, 1H), 4.98 (t, *J* = 9.2 Hz, 1H), 4.11 (t, J = 9.0 Hz, 1H), 4.02 (s, 3H).k

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 159.0, 151.1, 149.5, 137.6, 128.6, 122.9, 64.5, 64.4, 63.8.

HRMS (ESI) *m/z* calculated for $C_{10}H_{11}N_2O_4$ $[M+H]^+$: 223.0714. Found: 223.0712.

4-(5-bromonicotinoyl)-3-methoxyoxazolidin-2-one (2c)



Prepared according to general procedure B: 2.5 mL stock catalyst solution (containing CuTC (4.8 mg, 25.0 µmol, 0.050 equiv.), and neocuproine (**L1**) (6.2 mg, 30 µmol, 0.060 equiv.)), and (*E*)-3-(5-bromopyridin-3-yl)allyl methoxycarbamate (**1c**) (144 mg, 0.500 mmol, 1.0 equiv.) were used. Yield was determined by quantitative NMR using 1,3,5-trimethoxybenzene (84.1 mg, 0.500 mmol, 1.0 equiv.) as internal standard. An analytical sample was prepared by combining crude reaction mixtures from runs 1-3 and purified via flash chromatography on SiO_2 using ~50 g of silica eluting with 25% EtOAc/75% hexanes → 100% EtOAc, followed by recrystallization over DCM/heptane. Product was isolated as a white solid (109 mg).

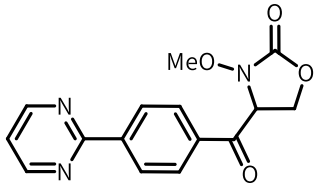
Run 1: (0.255 mmol, 54%) QNMR yield
Run 2: (0.270 mmol, 51%) QNMR yield
Run 3: (0.270 mmol, 51%) QNMR yield
Average: 52% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.95 (s, 1H), 8.42 (t, *J* = 2.1 Hz, 1H), 5.35 (t, *J* = 8.4 Hz, 1H), 4.61 (t, *J* = 8.7 Hz, 1H), 4.31 (t, *J* = 8.9, Hz, 1H), 3.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 158.0, 156.2, 147.5, 138.5, 131.3, 122.0, 64.6, 62.7, 62.3.

HRMS (ESI) *m/z* calculated for $C_{10}H_{10}BrN_2O_4$ $[M+H]^+$: 300.9819. Found 300.9817.

3-methoxy-4-(4-(pyrimidin-2-yl)benzoyl)oxazolidin-2-one (2d)



Prepared according to general procedure B: 2.5 mL stock catalyst solution (containing CuTC (4.8 mg, 25.0 µmol, 0.050 equiv.), and neocuproine (**L1**) (6.2 mg, 30 µmol, 0.060 equiv.)), and (*E*)-3-(4-(pyrimidin-2-yl)phenyl)allyl methoxycarbamate (**1d**) (143 mg, 0.500 mmol, 1.0 equiv.) were used. Crude material was purified via flash chromatography on SiO_2 using 50 g of silica eluting with 50% EtOAc/50% hexanes → 100% EtOAc. Yield for run 3 was also determined by quantitative NMR using 1,3,5-trimethoxybenzene (84.1 mg, 0.500 mmol, 1.0 equiv.) as internal standard.

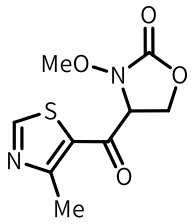
Run 1: (74.5 mg, 0.249 mmol, 50%)
Run 2: (74.3 mg, 0.248 mmol, 50%)
Run 3: (73.9 mg, 0.247 mmol, 49%)
Run 3: (0.305 mmol, 61%) QNMR
Average: 50% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 4.8 Hz, 2H), 8.63 (d, *J* = 8.8 Hz, 2H), 8.07 (d, *J* = 8.8 Hz, 2H), 7.30 (t, *J* = 4.8 Hz, 1H), 5.46 (t, *J* = 8.8 Hz, 1H), 4.63 (t, *J* = 8.8 Hz, 1H), 4.27 (t, *J* = 8.8 Hz, 1H), 3.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 163.2, 158.5, 157.6, 143.3, 135.8, 129.0, 128.9, 120.2, 64.6, 63.3, 62.6.

HRMS (ESI) *m/z* calculated for $C_{15}H_{14}N_3O_4$ $[M+H]^+$: 300.0979. Found: 300.0977.

3-methoxy-4-(4-methylthiazole-5-carbonyl)oxazolidin-2-one (2e)



Prepared according to general procedure B: 2.5 mL stock catalyst solution (containing CuTC (4.8 mg, 25.0 µmol, 0.050 equiv.), and neocuproine (**L1**) (6.2 mg, 30 µmol, 0.060 equiv.)), and (*E*)-3-(4-methylthiazol-5-yl)allyl methoxycarbamate (**1e**) (114 mg, 0.500 mmol, 1.0 equiv.) were used. Crude material was purified via flash chromatography on SiO_2 using 50 g of silica and eluting with 50% EtOAc/50% hexanes → 100% EtOAc over 15 min (40 mL/min). Yield for run 3 was determined by quantitative NMR using 1,3,5-trimethoxybenzene (84.1 mg, 0.500 mmol, 1.0 equiv.) as internal standard.

Run 1: (46.6 mg, 0.192 mmol, 38%) Purity (wt): 92% → (42.6 mg, 0.176 mmol, 35%)
Run 2: (42.7 mg, 0.176 mmol, 35%) Purity (wt): >99%
Run 3: (40.0 mg, 0.194 mmol, 33%) Purity (wt): 98% → (39.1 mg, 0.161 mmol, 32%)
Run 3: (0.245 mmol, 49%) QNMR yield
Average: 34% yield

Note: During purification, some inseparable impurities remained in the purified sample. Yields were adjusted according to quantification by NMR using 1,3,5-trimethoxybenzene as an internal standard. The isolated sample was dissolved in its entirety in $CDCl_3$ with 1,3,5-trimethoxybenzene and mixed thoroughly.

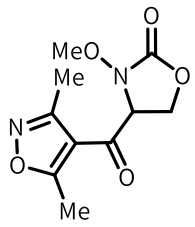
Run 1: 1,3,5-TMB (28.2 mg, 0.168 mmol) used. Molar ratio (**2e** : TMB) = 1.05
Run 2: 1,3,5-TMB (25.5 mg, 0.152 mmol) used. Molar ratio (**2e** : TMB) = 1.16
Run 3: 1,3,5-TMB (12.5 mg, 0.165 mmol) used. Molar ratio (**2e** : TMB) = 2.17

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 4.99 (t, *J* = 8.3 Hz, 1H), 4.55 (t, *J* = 8.7 Hz, 1H), 4.25 (t, *J* = 8.5 Hz, 1H), 3.87 (s, 3H), 2.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.1, 163.6, 157.9, 156.0, 126.4, 65.7, 64.5, 63.2, 18.8.

HRMS (ESI) *m/z* calculated for $C_9H_{11}N_2O_4S$ $[M+H]^+$: 243.0434. Found: 243.0434.

3-methoxy-4-(4-(pyrimidin-2-yl)benzoyl)oxazolidin-2-one (2f)



Prepared according to general procedure B: 2.5 mL stock catalyst solution (containing CuTC (4.8 mg, 25.0 µmol, 0.050 equiv.), and neocuproine (**L1**) (6.2 mg, 30 µmol, 0.060 equiv.)), and (*E*)-3-(3,5-dimethylisoxazol-4-yl)allyl methoxycarbamate (**1f**) (113 mg, 0.500 mmol, 1.0 equiv.) were used. Crude material was purified via flash chromatography on SiO_2 using a Combiflash® NextGen 300+ auto column with a 25 g stationary phase cartridge eluting with 25% EtOAc/75% hexanes → 100% EtOAc over 15 min (40 mL/min). Yield for run 3 was determined by quantitative NMR using 1,3,5-trimethoxybenzene (84.1 mg, 0.500 mmol, 1.0 equiv.) as internal standard.

Run 1: (62.1 mg, 0.258 mmol, 52%) Purity (wt): 91% → (56.8 mg, 0.237 mmol, 47%)
Run 2: (64.9 mg, 0.270 mmol, 54%) Purity (wt): 83% → (54.1 mg, 0.225 mmol, 45%)
Run 3: (0.240 mmol, 48%) QNMR yield
Average: 46% yield

Note: After purification, some inseparable impurities remained in the sample. Yields were adjusted by QNMR using 1,3,5-trimethoxybenzene as an internal standard. The isolated sample was dissolved in its entirety in $CDCl_3$ with 1,3,5-trimethoxybenzene and mixed thoroughly.

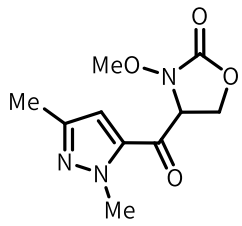
Run 1: 1,3,5-TMB (39.0 mg, 0.232 mmol) used. Molar ratio (**2f** : TMB) = 1.02
Run 2: 1,3,5-TMB (35.5 mg, 0.210 mmol) used. Molar ratio (**2f** : TMB) = 1.07

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.04 (dd, *J* = 8.2, 7.4 Hz, 1H), 4.47 (dd, *J* = 8.7, 8.2 Hz, 1H), 4.26 (dd, *J* = 8.7, 7.5 Hz, 1H), 3.84 (s, 3H), 2.74 (s, 3H), 2.49 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.9, 175.6, 158.9, 157.9, 115.7, 93.0, 64.6, 63.2, 62.9, 55.4, 14.6, 12.6.

HRMS (ESI) *m/z* calculated for $C_{10}H_{13}N_2O_5$ $[M+H]^+$: 241.0819. Found: 241.0816.

3-methoxy-4-(4-(pyrimidin-2-yl)benzoyl)oxazolidin-2-one (2g)



Prepared according to general procedure B: 2.5 mL stock catalyst solution (containing CuTC (4.8 mg, 25.0 µmol, 0.050 equiv.), and neocuproine (**L1**) (6.2 mg, 30 µmol, 0.060 equiv.)), and (*E*)-3-(1,3-dimethyl-1*H*-pyrazol-5-yl)allyl methoxycarbamate (**1g**) (113 mg, 0.500 mmol, 1.0 equiv.) were used. Crude material was purified via flash chromatography on SiO_2 using 50 g of silica eluting with 50% EtOAc/50% hexanes → 100% EtOAc. Yield for run 4 was determined by quantitative NMR using 1,3,5-trimethoxybenzene (84.1 mg, 0.500 mmol, 1.0 equiv.) as internal standard.

Run 1: (62.4 mg, 0.261 mmol, 52%)
Run 2: (64.0 mg, 0.268 mmol, 54%)

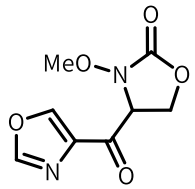
Run 2: (0.270 mmol, 54%) QNMR yield
Run 3: (65.2 mg, 0.273 mmol, 55%)
Average: 54% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 (s, 1H), 5.06 (t, *J* = 8.6 Hz, 1H), 4.53 (t, *J* = 8.7 Hz, 1H), 4.22 (t, *J* = 8.7 Hz, 1H), 4.15 (s, 3H), 3.87 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 183.6, 158.2, 147.9, 136.7, 111.3, 64.6, 63.6, 63.4, 40.3, 13.3.

HRMS (ESI) *m/z* calculated for $C_{10}H_{14}N_3O_4$ $[M+H]^+$: 240.0979. Found: 240.0975.

3-methoxy-4-(oxazole-4-carbonyl)oxazolidin-2-one (2h)



Prepared according to general procedure B: 2.5 mL stock catalyst solution (containing CuTC (4.8 mg, 25.0 µmol, 0.050 equiv.), and neocuproine (**L1**) (6.2 mg, 30 µmol, 0.060 equiv.)), and (*E*)-3-(oxazol-4-yl)allyl methoxycarbamate (**1h**) (99.1 mg, 0.500 mmol, 1.0 equiv.) were used. Crude material was purified via flash chromatography on SiO_2 using 50 g of silica eluting with 50% EtOAc/50% hexanes. Yield for run 3 was determined by quantitative NMR using 1,3,5-trimethoxybenzene (84.1 mg, 0.500 mmol, 1.0 equiv.) as internal standard.

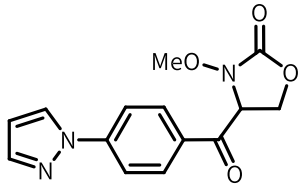
Run 1: (52.8 mg, 0.249 mmol, 50%)
Run 2: (50.0 mg, 0.236 mmol, 47%)
Run 3: (0.250 mmol, 50%) QNMR yield
Average: 49% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.96 (s, 1H), 5.30 (t, *J* = 8.9 Hz, 1H), 4.80 (t, *J* = 9.0 Hz, 1H), 4.14 (t, *J* = 8.7 Hz, 1H), 3.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.5, 158.5, 151.5, 143.8, 138.0, 64.4, 64.3, 63.0.

HRMS (ESI) *m/z* calculated for $C_8H_9N_2O_5$ $[M+H]^+$: 213.0506. Found: 213.0504.

4-(4-(1H-pyrazol-1-yl)benzoyl)-3-methoxyoxazolidin-2-one (2i)



Prepared according to general procedure B: 2.5 mL stock catalyst solution (containing CuTC (4.8 mg, 25.0 µmol, 0.050 equiv.), and neocuproine (**L1**) (6.2 mg, 30 µmol, 0.060 equiv.)), and (*E*)-3-(4-(1H-pyrazol-1-yl)phenyl)allyl methoxycarbamate (**1i**) (137 mg, 0.500 mmol, 1.0 equiv.) were used. Crude material was purified via flash chromatography on SiO_2 using 50 g of silica eluting with 25% EtOAc/75% hexanes → 100% EtOAc. Yield for run 3 was determined by quantitative NMR using 1,3,5-trimethoxybenzene as internal standard (84.1 mg, 0.500 mmol, 1.0 equiv.).

Run 1: (82.9 mg, 0.289 mmol, 58%)

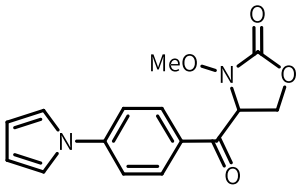
Run 2: (78.9 mg, 0.275 mmol, 55%)
Run 3: (0.295 mmol, 59%) QNMR yield
Average: 57% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.02 (m, overlap, 3H), 7.94 – 7.85 (m, 2H), 7.79 (d, *J* = 1.8 Hz, 1H), 6.55 (dd, *J* = 2.6, 1.7 Hz, 1H), 5.43 (t, *J* = 8.7 Hz, 1H), 4.61 (t, *J* = 8.7 Hz, 1H), 4.28 (t, *J* = 8.7 Hz, 1H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 158.4, 144.6, 142.7, 131.9, 130.5, 127.2, 118.8, 109.2, 64.6, 63.3, 62.2.

HRMS (ESI) *m/z* calculated for $C_{14}H_{14}N_3O_4$ $[M+H]^+$: 288.0979. Found: 288.0973.

3-methoxy-4-(4-(pyrimidin-2-yl)benzoyl)oxazolidin-2-one (2j)



Prepared according to general procedure B: 2.5 mL stock catalyst solution (containing CuTC (4.8 mg, 25.0 µmol, 0.050 equiv.), and neocuproine (**L1**) (6.2 mg, 30 µmol, 0.060 equiv.)), and (*E*)-3-(4-(1H-pyrrol-1-yl)phenyl)allyl methoxycarbamate (**1j**) (136 mg, 0.500 mmol, 1.0 equiv.) were used. Crude material was purified via flash chromatography on SiO_2 using 50 g of silica eluting with 50% EtOAc/50% hexanes → 100% EtOAc. Yield for run 3 was determined by quantitative NMR using 1,3,5-trimethoxybenzene (84.1 mg, 0.500 mmol, 1.0 equiv.) as internal standard.

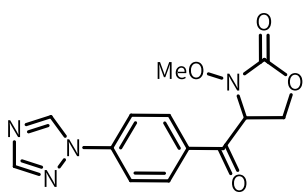
Run 1: (81.3 mg, 0.283 mmol, 57%)
Run 2: (82.2 mg, 0.286 mmol, 57%)
Run 3: (0.295 mmol, 59%) QNMR yield
Average: 57% yield

^{1}H NMR (400 MHz, DMSO-*d*6) δ 8.11 (d, *J* = 8.9 Hz, 2H), 7.83 (d, *J* = 8.9 Hz, 2H), 7.59 (t, *J* = 2.2 Hz, 2H), 6.35 (t, *J* = 2.2 Hz, 2H), 5.89 (dd, *J* = 8.5, 5.7 Hz, 1H), 4.64 (t, *J* = 8.7 Hz, 1H), 4.27 (dd, *J* = 8.9, 5.8 Hz, 1H), 3.75 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d*6) δ 192.8, 157.7, 144.1, 130.7, 130.6, 119.2, 118.6, 111.9, 63.7, 63.3, 60.1.

HRMS (ESI) *m/z* calculated for $C_{15}H_{15}N_2O_4$ $[M+H]^+$: 287.1027. Found: 287.1021.

3-methoxy-4-(4-(pyrimidin-2-yl)benzoyl)oxazolidin-2-one (2k)



Prepared according to general procedure B: 2.5 mL stock catalyst solution (containing CuTC (4.8 mg, 25.0 µmol, 0.050 equiv.), and neocuproine (**L1**) (6.2 mg, 30 µmol, 0.060 equiv.)), and (*E*)-3-(4-(1H-1,2,4-triazol-1-yl)phenyl)allyl methoxycarbamate (**1k**) (137 mg, 0.500 mmol, 1.0 equiv.) were used. Crude material was purified via flash chromatography on SiO_2 using 50 g of silica

eluting with 50% EtOAc/50% hexanes → 100% EtOAc. Yield for run 3 was determined by quantitative NMR using 1,3,5-trimethoxybenzene (84.1 mg, 0.500 mmol, 1.0 equiv.) as internal standard.

Run 1: (75.4 mg, 0.262 mmol, 52%) Purity (wt): >99%
Run 2: (74.2 mg, 0.257 mmol, 52%) Purity (wt): >99%
Run 3: (0.280 mmol, 56%) QNMR yield
Average: 52% yield

Note: After purification, some inseparable impurities were visible by NMR but accounted for <1% wt of the sample.

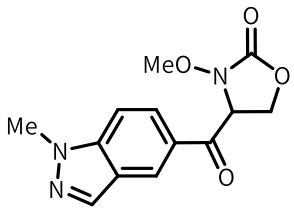
Run 1: 1,3,5-TMB (37.9 mg, 0.225 mmol) used. Molar ratio (**2k** : TMB) = 1.18
Run 2: 1,3,5-TMB (36.6 mg, 0.218 mmol) used. Molar ratio (**2k** : TMB) = 1.22

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.19 – 8.08 (m, overlap, 3H), 7.92 (d, *J* = 8.7 Hz, 2H), 5.43 (t, *J* = 8.6 Hz, 1H), 4.61 (t, *J* = 8.8 Hz, 1H), 4.30 (t, *J* = 8.6 Hz, 1H), 3.88 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 158.3, 153.5, 141.4 141.3, 133.6, 130.7, 120.0, 64.6, 63.2, 62.2.

HRMS (ESI) *m/z* calculated for $C_{13}H_{13}N_4O_4$ $[M+H]^+$: 289.0932. Found: 289.0929.

3-methoxy-4-(1-methyl-1H-indazole-5-carbonyl)oxazolidin-2-one (2l)



Prepared according to general procedure B: 2.5 mL stock catalyst solution (containing CuTC (4.8 mg, 25.0 µmol, 0.050 equiv.), and neocuproine (**L1**) (6.2 mg, 30 µmol, 0.060 equiv.)), and (*E*)-3-(1-methyl-1H-indazol-5-yl)allyl methoxycarbamate (**1l**) (131 mg, 0.500 mmol, 1.0 equiv.) were used. The crude residue was purified on a CombiFlash NextGen 300+ using a 50 g stationary phase cartridge, eluting with 25% EtOAc/75% hexanes → 100% EtOAc over 15 min (80 mL/min). Yield for run 3 was determined by quantitative NMR using 1,3,5-trimethoxybenzene (84.1 mg, 0.500 mmol, 1.0 equiv.) as internal standard.

Note: For run 2, after purification, some inseparable impurities remained in the sample. Yields were adjusted by QNMR using 1,3,5-trimethoxybenzene as an internal standard. The isolated sample was dissolved in its entirety in $CDCl_3$ with 1,3,5-trimethoxybenzene and mixed thoroughly.

Run 1: (66.4 mg, 0.241 mmol, 48%)
Run 2: (78.7 mg, 0.286 mmol, 57%) Purity (wt): 83% → (70.0 mg, 0.254 mmol, 51%)
Run 3: (0.260 mmol, 52%) QNMR yield
Average: 50% yield

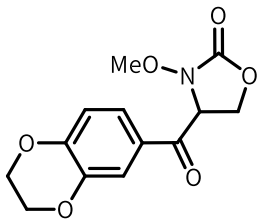
Run 2: 1,3,5-TMB (39.6 mg, 0.235 mmol) used. Molar ratio (**2l** : TMB) = 1.08

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 1.7, 0.8 Hz, 1H), 8.16 (d, *J* = 1.0 Hz, 1H), 8.05 (dd, *J* = 8.9, 1.6 Hz, 1H), 7.50 (dt, *J* = 8.9, 0.9 Hz, 1H),,5.50 (t, *J* = 8.7 Hz, 1H), 4.62 (t, *J* = 8.7 Hz, 1H), 4.28 (t, *J* = 8.7 Hz, 1H), 4.13 (s, 3H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 158.6, 142.1, 135.4, 127.9, 126.0, 124.3, 123.8, 110.1, 64.5, 63.6, 62.2, 36.0.

HRMS (ESI) *m/z* calculated for $C_{13}H_{14}N_3O_4$ $[M+H]^+$: 276.0979. Found: 276.0977.

4-(2,3-dihydrobenzo[*b*][1,4]dioxine-6-carbonyl)-3-methoxyoxazolidin-2-one (2m)



Prepared according to general procedure B: 2.5 mL stock catalyst solution (containing CuTC (4.8 mg, 25.0 µmol, 0.050 equiv.), and neocuproine (**L1**) (6.2 mg, 30 µmol, 0.060 equiv.)), and (*E*)-3-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)allyl methoxycarbamate (**1m**) (133 mg, 0.500 mmol, 1.0 equiv.) were used. After addition of substrate, the reaction was placed in a pre-heated aluminum block at 70 °C and stirred for two hours. Crude material was purified via flash chromatography on SiO_2 using 50 g of silica eluting with 50% EtOAc/50% hexanes → 100% EtOAc . Yield for run 3 was determined by quantitative NMR using 1,3,5-trimethoxybenzene (84.1 mg, 0.500 mmol, 1.0 equiv.) as internal standard.

Run 1: (62.0 mg, 0.222 mmol, 44%) Purity (wt): 87% → (53.9 mg, 0.157 mmol, 39%)
Run 2: (66.1 mg, 0.237 mmol, 47%) Purity (wt): 91% → (59.9 mg, 0.243 mmol, 43%)
Run 3: (0.240 mmol, 48%) QNMR yield
Average: 41% yield

Note: After purification, some inseparable impurities remained in the sample. Yields were adjusted by QNMR using 1,3,5-trimethoxybenzene as an internal standard. The isolated sample was dissolved in its entirety in $CDCl_3$ with 1,3,5-trimethoxybenzene and mixed thoroughly.

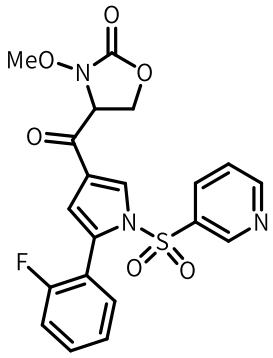
Run 1: 1,3,5-TMB (26.4 mg, 0.157 mmol) used. Molar ratio (**2m** : TMB) = 1.23
Run 2: 1,3,5-TMB (41.0 mg, 0.244 mmol) used. Molar ratio (**2m** : TMB) = 0.88

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, overlap, 2H), 6.97 (d, *J* = 8.5 Hz, 1H), 5.35 – 5.29 (t, *J* = 8.9 Hz, 1H), 4.55 (t, *J* = 8.8 Hz, 1H), 4.37 – 4.27 (m, 4H), 4.19 (t, *J* = 8.8 Hz, 1H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 158.6, 149.7, 144.0, 128.3, 122.8, 118.1, 118.0, 64.9, 64.5, 64.2, 63.5, 62.3.

HRMS (ESI) *m/z* calculated for $C_{13}H_{14}NO_6$ $[M+H]^+$: 280.0816. Found: 280.0815.

4-(5-(2-fluorophenyl)-1-(pyridin-3-ylsulfonyl)-1*H*-pyrrole-3-carbonyl)-3-methoxyoxazolidin-2-one (2n)



Prepared according to general procedure B:

Run 1: 1.7 mL stock catalyst solution (containing CuTC (3.2 mg, 16.9 µmol, 0.050 equiv.), and neocuproine (**L1**) (4.2 mg, 20.3 µmol, 0.060 equiv.)) and (*E*)-3-(5-(3-fluorophenyl)-1-(pyridin-3-ylsulfonyl)-1H-pyrrol-3-yl)allyl methoxycarbamate **(1n)** (146 mg, 0.338 mmol, 1.0 equiv.) were used.

Run 2: 2.5 mL stock catalyst solution (containing CuTC (4.8 mg, 25.0 µmol, 0.050 equiv.), and neocuproine (**L1**) (6.2 mg, 30 µmol, 0.060 equiv.)) and (*E*)-3-(5-(3-fluorophenyl)-1-(pyridin-3-ylsulfonyl)-1H-pyrrol-3-yl)allyl methoxycarbamate **(1n)** (223 mg, 0.500 mmol, 1.0 equiv.) were used.

Run 3: 2.3 mL stock catalyst solution (containing CuTC (4.4 mg, 23.0 µmol, 0.050 equiv.), and neocuproine (**L1**) (5.7 mg, 27.6 µmol, 0.060 equiv.)) and (*E*)-3-(5-(3-fluorophenyl)-1-(pyridin-3-ylsulfonyl)-1H-pyrrol-3-yl)allyl methoxycarbamate **(1n)** (198 mg, 0.460 mmol, 1.0 equiv.) were used.

Crude material was purified via flash chromatography on SiO_2 using 50 g of silica eluting with 50% EtOAc/50% hexanes → 100% EtOAc. Yield for run 3 was also determined by isolation and quantitative NMR using 1,3,5-trimethoxybenzene (77.3 mg, 0.460 mmol, 1.0 equiv.) as internal standard. Note: varying S.M. quantities used.

Run 1: (66.1 mg, 0.148 mmol, 44%)
Run 2: (98.5 mg, 0.221 mmol, 44%)
Run 3: (92.2 mg, 0.207 mmol, 45%)
Run 3: (0.280 mmol, 56%) QNMR yield
Average: 44% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.58 (d, *J* = 2.4 Hz, 1H), 8.23 (d, *J* = 1.9 Hz, 1H), 7.71 (ddd, *J* = 8.2, 2.5, 1.6 Hz, 1H), 7.55 – 7.42 (m, 1H), 7.42 – 7.32 (m, 1H), 7.21 – 7.13 (m, 2H), 7.02 (t, *J* = 9.0 Hz, 1H), 6.73 (d, *J* = 1.9 Hz, 1H), 5.08 (t, *J* = 8.6 Hz, 1H), 4.56 (t, *J* = 8.6 Hz, 1H), 4.33 (t, *J* = 8.7 Hz, 1H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.5, 160.9 (d, $J_{1C—F}$ = 250.0 Hz), 158.3, 155.3, 148.7, 135.5, 134.0, 133.64 (d, $J_{6C—F}$ = 1.4 Hz), 132.5 (d, $J_{4C—F}$ = 8.2 Hz), 129.9, 127.9, 124.8, 123.9 (d, $J_{5C—F}$ = 3.9 Hz), 117.14 (d, $J_{3C—F}$ = 15.9 Hz), 115.7 (d, $J_{2C—F}$ = 21.7 Hz). 115.3, 64.6, 63.3, 63.2.

HRMS (ESI) *m/z* calculated for $C_{20}H_{17}FN_3O_6S$ $[M+H]^+$: 446.0817. Found: 446.0806.

Synthesis of Pyrazolyl Amphenicol Analogue

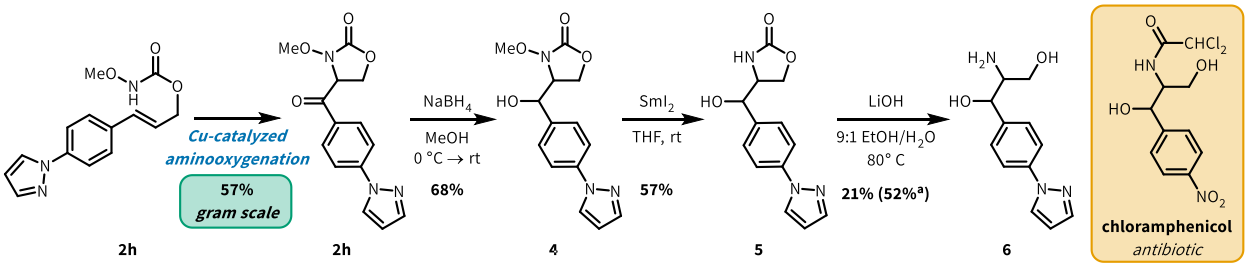
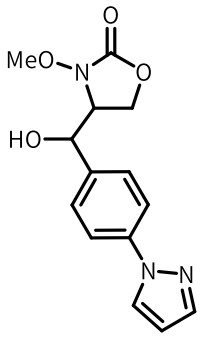


Figure 3. Gram scale preparation of **2h** and derivatization to amphenicol antibiotic analogue **6**.

Gram scale preparation of 4-(4-(1H-pyrazol-1-yl)benzoyl)-3-methoxyoxazolidin-2-one (2h): CuTC (47.7 mg, 0.250 mmol, 0.05 equiv.) and neocuproine (62.5 mg, 0.300 mmol, 0.06 equiv.), were weighed into a 20 mL scintillation vial in a glovebox. The vial was removed and the solids were transferred with MeCN to a 150 mL beaker, and diluted with MeCN for a final volume of 25 mL (0.2M). The solution was stirred open to air for 15 min. (*E*)-3-(4-(1H-pyrazol-1-yl)phenyl)allyl methoxycarbamate **1h** (1.37 g, 5.0 mmol, 1.0 eq) was added in one portion and the reaction was stirred for 2h open to air. The solution was filtered through a short pad of silica in a fritted funnel and eluted with EtOAc (100 mL). The solution was concentrated in vacuo. Crude material was purified via flash chromatography on SiO_2 using 300 g of silica eluting with 25% EtOAc/75% hexanes → 100% EtOAc. Product was isolated as a white solid (826 mg, 2.88 mmol, 58%). Spectral data matched that obtained from the 0.500 mmol scale reaction (page S48).

4-((4-(1H-pyrazol-1-yl)phenyl)(hydroxy)methyl)-3-methoxyoxazolidin-2-one (4)



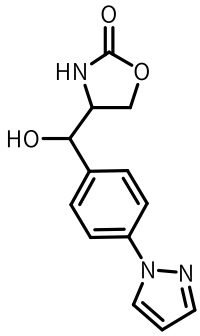
4-(4-(1H-pyrazol-1-yl)benzoyl)-3-methoxyoxazolidin-2-one (**2h**) (318 mg, 1.11 mmol, 1.0 equiv.) was dissolved in MeOH (6 mL, 0.2M) in a rbf and cooled to 0 °C. $NaBH_4$ (46.0 mg, 1.26 mmol, 1.1 equiv.) was added in 5 portions. The reaction was stirred at 0 °C for 1h. Upon completion, the reaction was quenched at 0 °C with sat. NH_4Cl (10 mL), diluted with H_2O (5 mL) and extracted three times with EtOAc (3 x 20 mL). The organic layer was washed with brine (30 mL), dried over $MgSO_4$ and concentrated in vacuo. The crude residue was purified on a CombiFlash NextGen 300+ using a 25 g silica cartridge, eluting with 25% EtOAc/75% hexanes → 100% EtOAc over 15 min (40 mL/min). Product (216 mg, 0.747 mmol, 68%) was carried forward without further purification as a mixture of diastereomers.

^{1}H NMR (500 MHz, DMSO-D_6) δ 8.50 (d, *J* = 2.5 Hz, 1H), 7.82 (d, *J* = 6.7 Hz, 2H), 7.74 (d, *J* = 1.7 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 2H), 6.54 (dd, *J* = 2.5, 1.7 Hz, 1H), 5.95 (app d, *J* = 4.9 Hz, 1H, *O–H/D*), 4.87 (app t, *J* = 5.0 Hz, 1H), 4.30 (app ddd, *J* = 8.1, 6.6, 4.8 Hz, 1H), 4.14 (app t, *J* = 8.5 Hz, 1H), 4.08 (app dd, *J* = 8.8, 6.6 Hz, 1H), 3.66 (s, 3H). Note: diastereomers are unresolved.

^{13}C NMR (126 MHz, DMSO-D_6) δ 157.7, 140.9, 139.0, 138.5, 138.5, 127.6, 127.6, 117.9, 107.9, 70.6 (diastereomer A), 70.5 (diastereomer B), 62.8 (diastereomer B), 62.7 (diastereomer A), 61.0 (diastereomer A), 60.9 (diastereomer B). Note: arene, C=O, and OCH_3 signals are unresolved.

HRMS (ESI) *m/z* calculated for $C_{14}H_{16}N_3O_4$ $[M+H]^+$: 290.1136. Found: 290.1128

4-((4-(1H-pyrazol-1-yl)phenyl)(hydroxy)methyl)oxazolidin-2-one (5)



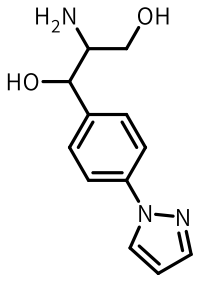
4-((4-(1H-pyrazol-1-yl)phenyl)(hydroxy)methyl)-3-methoxyoxazolidin-2-one (**4**) (180 mg, 0.622 mmol, 1.0 equiv.) was taken up in THF (16 mL, 0.04M) in a rbf under N_2 and SmI_2 (0.1M in THF) (50 mL, 5.00 mmol, 8.0 equiv.) was added via syringe. The reaction was stirred at rt for 2h. The reaction was quenched by addition of sat. $Na_2S_2O_3$ (16 mL) then diluted with EtOAc (150 mL). The mixture was washed with brine (50 mL), dried over $MgSO_4$ and concentrated in vacuo. The crude residue was purified on a CombiFlash NextGen 300+ using a 25 g silica cartridge, eluting with 25% EtOAc/75% hexanes → 100% EtOAc over 15 min (40 mL/min). Product was isolated as a white solid (91.7 mg, 0.354 mmol, 57%).

^{1}H NMR (400 MHz, DMSO-D_6) δ 8.50 (d, *J* = 2.6 Hz, 1H), 7.91 – 7.78 (m, 3H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 6.60 – 6.49 (m, 1H), 5.81 (d, *J* = 4.4 Hz, 1H, *O–H/D*), 4.65 – 4.50 (m, 1H), 4.26 – 4.09 (m, 1H), 4.13 – 4.01 (m, 1H), 4.04 – 3.93 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, DMSO-D_6) δ 158.8, 141.0, 139.1, 138.8, 127.9, 127.7, 118.0, 107.9, 73.1, 65.1, 57.1.

HRMS (ESI) *m/z* calculated for $C_{13}H_{14}N_3O_3$ $[M+H]^+$: 260.1030. Found: 260.1023

1-(4-(1H-pyrazol-1-yl)phenyl)-2-aminopropane-1,3-diol (6)



4-((4-(1H-pyrazol-1-yl)phenyl)(hydroxy)methyl)oxazolidin-2-one **(5**) (40.0 mg, 0.154 mmol, 1.0 equiv.) was taken up in EtOH (1 mL, 0.15M) in a 2 dram vial. LiOH•H_2O (19.0 mg, 0.462 mmol, 3.0 equiv.) was added, followed by 1 mL of 30% aq EtOH. The vial was sealed with a septum, heated to 80 °C and stirred for 16 h. Upon completion, the reaction was cooled to rt and concentrated in vacuo. The crude residue was purified on a CombiFlash NextGen 300+ using a 25 g silica cartridge eluting with DCM → 50 % (3% NEt_3 in MeOH) / 50% DCM over 15 min (40 mL/min). Product was isolated as a colorless oil (9.1 mg). Adjusted yield based on H_2O in sample: (7.4 mg, 0.032 mmol, 21%). Quantitative NMR analysis of the crude reaction was

performed on a second run as above by filtering the crude residue through a silica plug eluting with ~10 mL 50% (3% NEt_3 in MeOH) / 50% DCM and 1,3,5-trimethoxybenzene was added to the filtrate as an internal standard, then concentrated in vacuo and taken up in CD_3OD. (0.083 mmol, 54% QNMR yield).

^1H NMR (500 MHz, CD_3OD) δ 8.22 (d, *J* = 2.6 Hz, 1H), 7.80 – 7.68 (m, 3H), 7.53 (d, *J* = 8.7 Hz, 2H), 6.53 (dd, *J* = 2.6, 1.9 Hz, 1H), 4.71 (d, *J* = 7.4 Hz, 1H), 3.54 (dd, *J* = 11.2, 4.3 Hz, 1H), 3.40 (dd, *J* = 11.2, 6.0 Hz, 1H), 3.08 (s, 1H), 1.89 (s, 1H).

^{13}C NMR (101 MHz, CD_3OD) δ 142.2, 142.0, 141.0, 129.1, 129.0, 120.4, 108.8, 73.6, 62.4, 60.0.

HRMS (ESI) *m/z* calculated for $C_{12}H_{15}N_3O_2$ $[M+H]^+$: 234.1237. Found: 234.1232

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(1) Dörfler, J.; Preuß, T.; Schischko, A.; Schmidtmann, M.; Doye, S. A 2,6-Bis(phenylamino)pyridinato Titanium Catalyst for the Highly Regioselective Hydroaminoalkylation of Styrenes and 1,3-Butadienes. *Angew. Chem. Int. Ed.* **2014**, *53*, 7918-7922.

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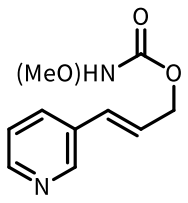
^{1}H NMR and ^{13}C NMR Spectra for New Compounds



1a

— 7.26 CDCl3

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4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.6
7	Pulse Sequence	proton.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	64
11	Receiver Gain	52.0
12	Relaxation Delay	4.0000
13	Pulse Width	2.9960
14	Spectrometer Frequency	399.78
15	Spectral Width	6006.0
16	Lowest Frequency	-999.1
17	Nucleus	1H
18	Acquired Size	14993
19	Spectral Size	52430
20	Digital Resolution	0.11

	Parameter	Value
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2	Comment	
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4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.5
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	4096
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	3.5713
14	Spectrometer Frequency	100.53
15	Spectral Width	25252.5
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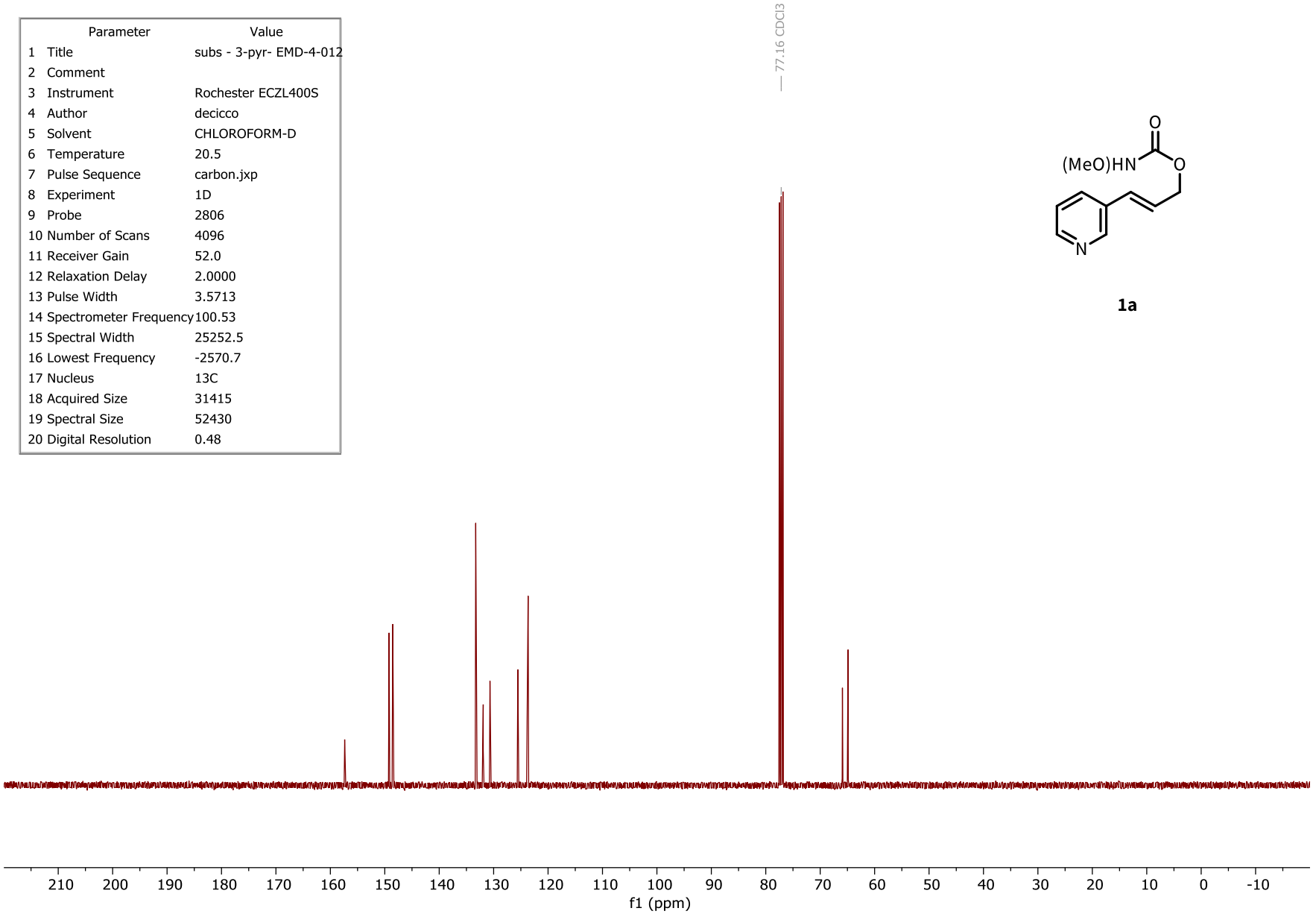
17	Nucleus	13C
18	Acquired Size	31415
19	Spectral Size	52430
20	Digital Resolution	0.48



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4	Author	decicco
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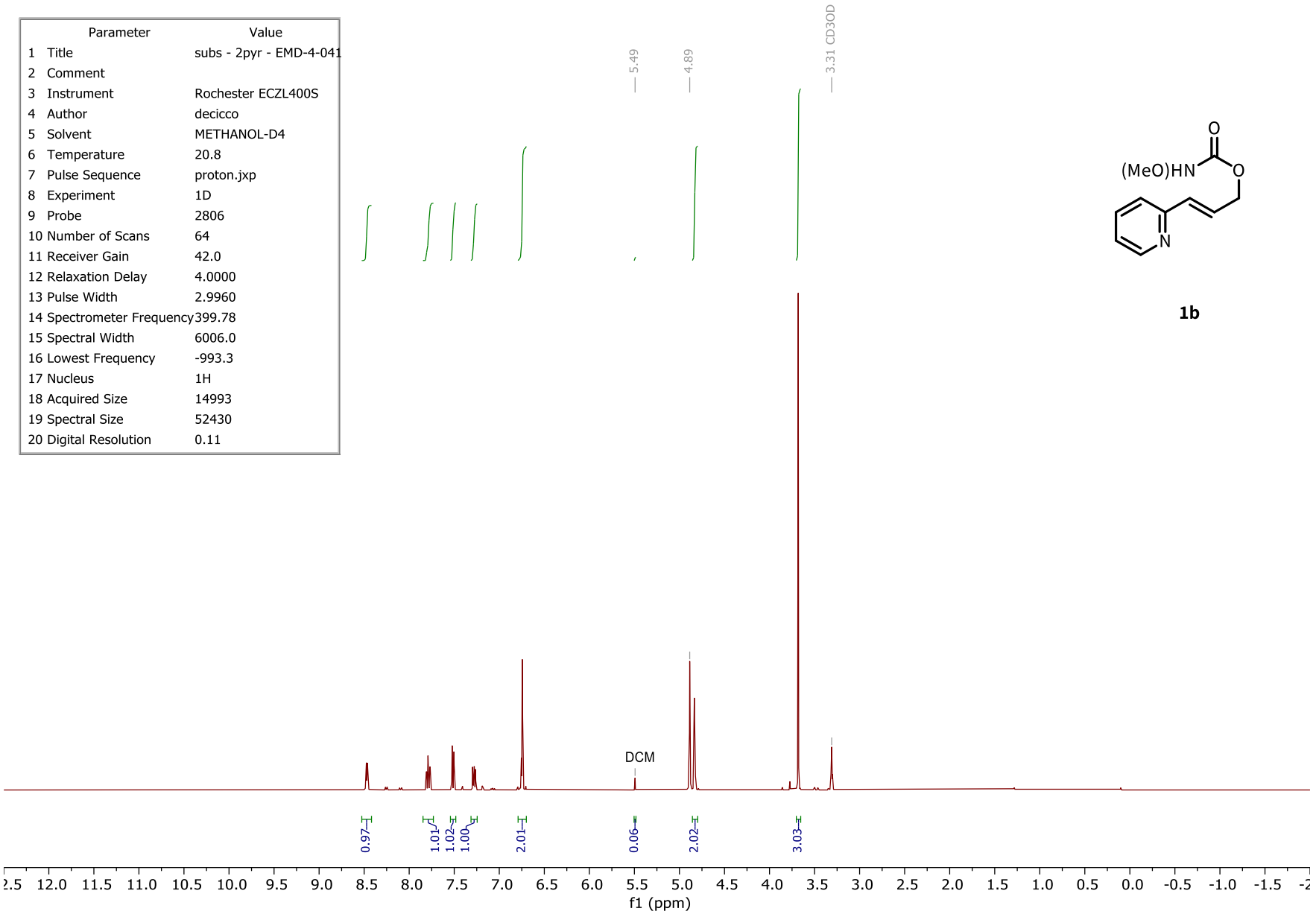

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2 Comment	
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4 Author	decicco
5 Solvent	METHANOL-D4
6 Temperature	20.4
7 Pulse Sequence	carbon.jxp
8 Experiment	1D
9 Probe	2806
10 Number of Scans	4096
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19 Spectral Size	52430
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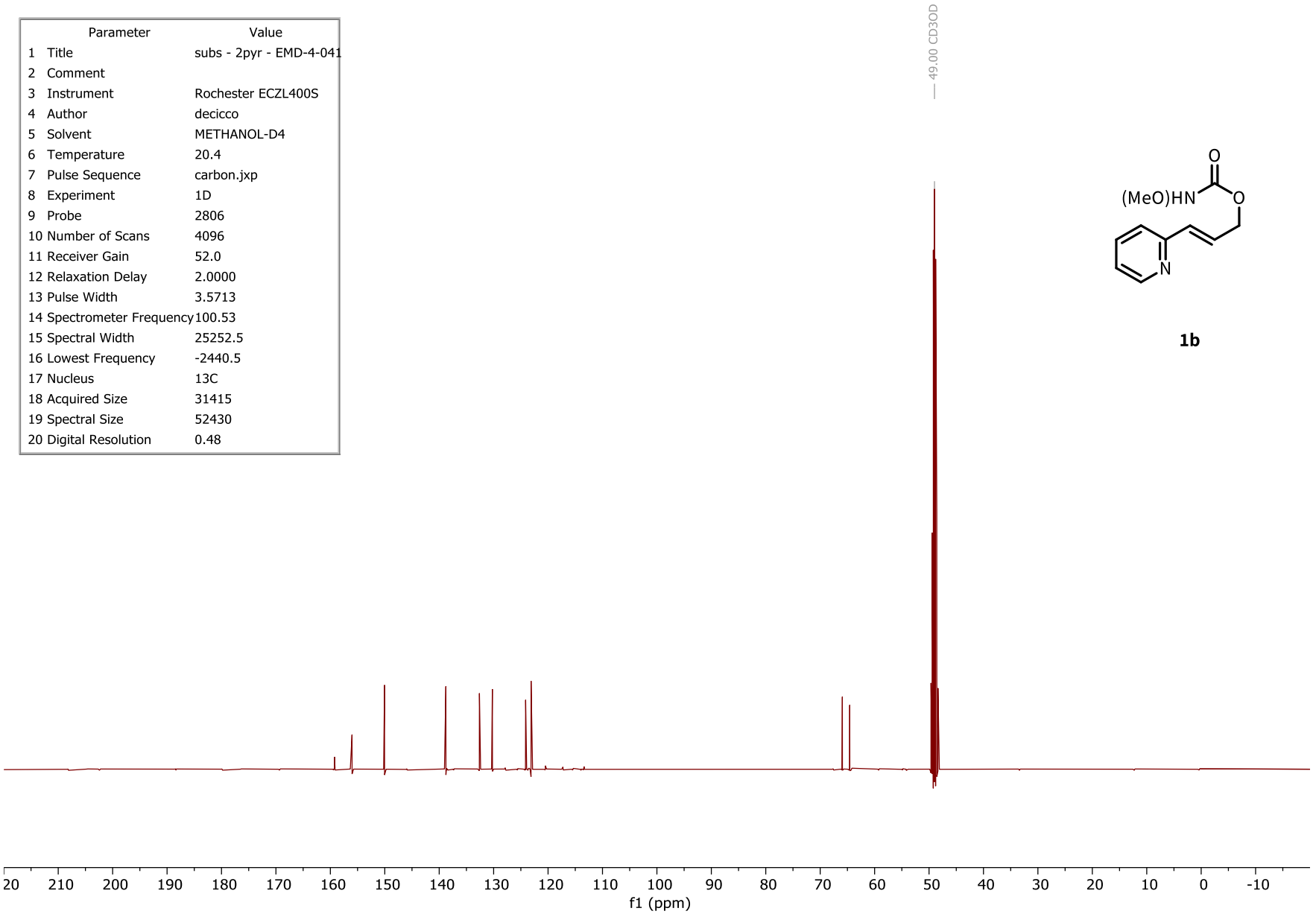

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4	Author	decicco
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6	Temperature	20.8
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9	Probe	2806
10	Number of Scans	64
11	Receiver Gain	52.0
12	Relaxation Delay	4.0000
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15	Spectral Width	6006.0
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17	Nucleus	1H
18	Acquired Size	14993
19	Spectral Size	52430
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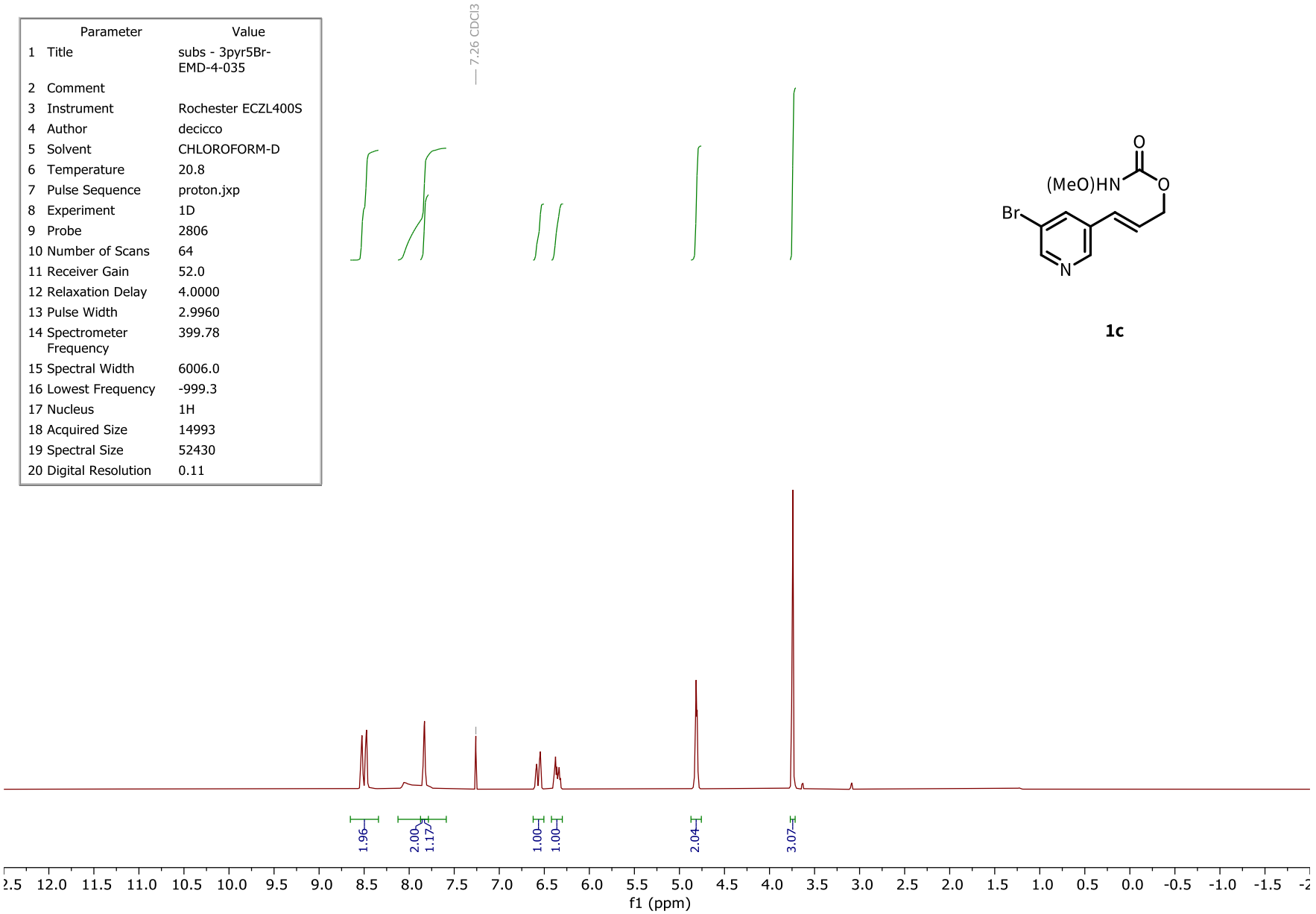

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6	Temperature	20.7
7	Pulse Sequence	carbon.jxp
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10	Number of Scans	4096
11	Receiver Gain	52.0
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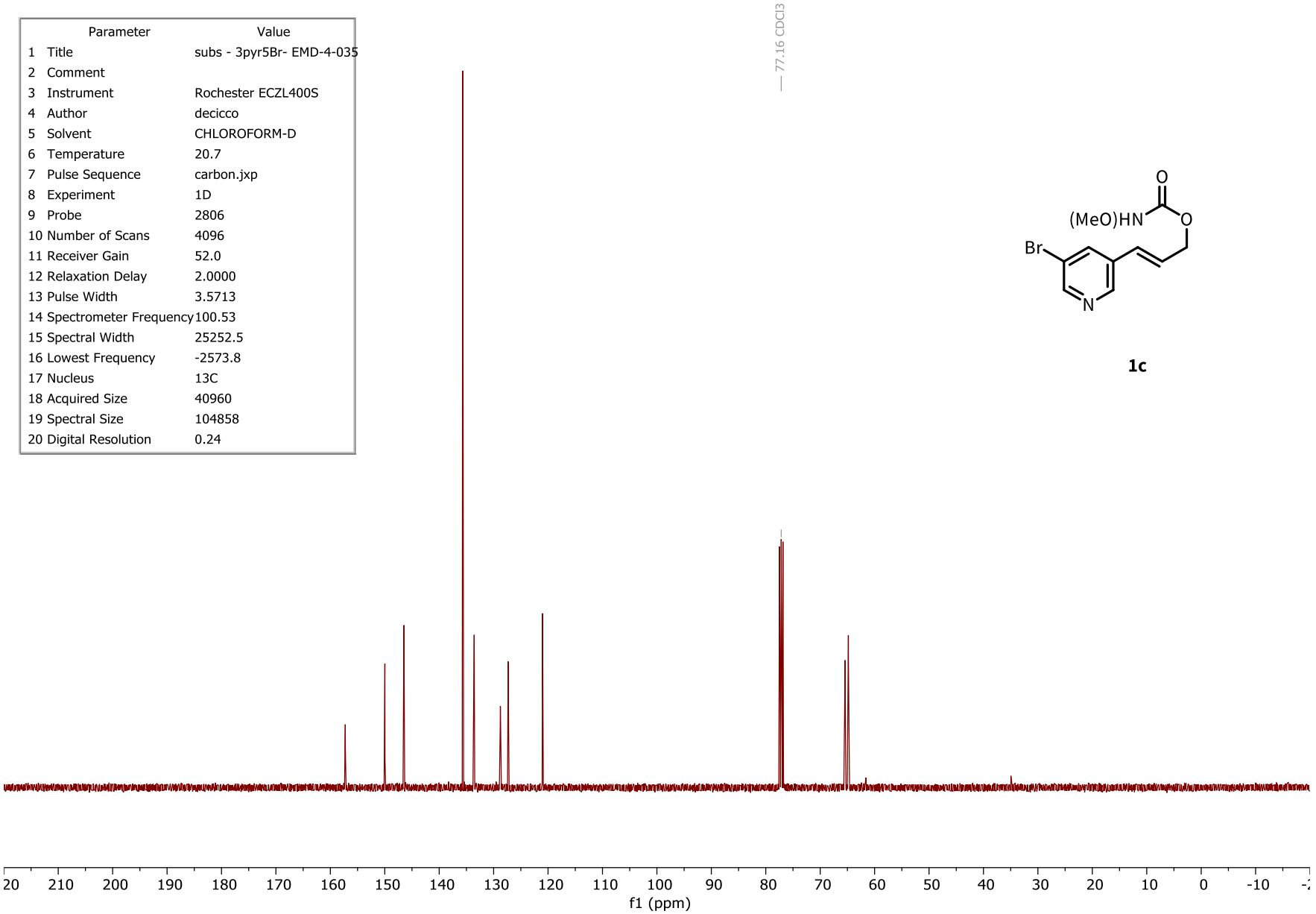

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4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.6
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10	Number of Scans	64
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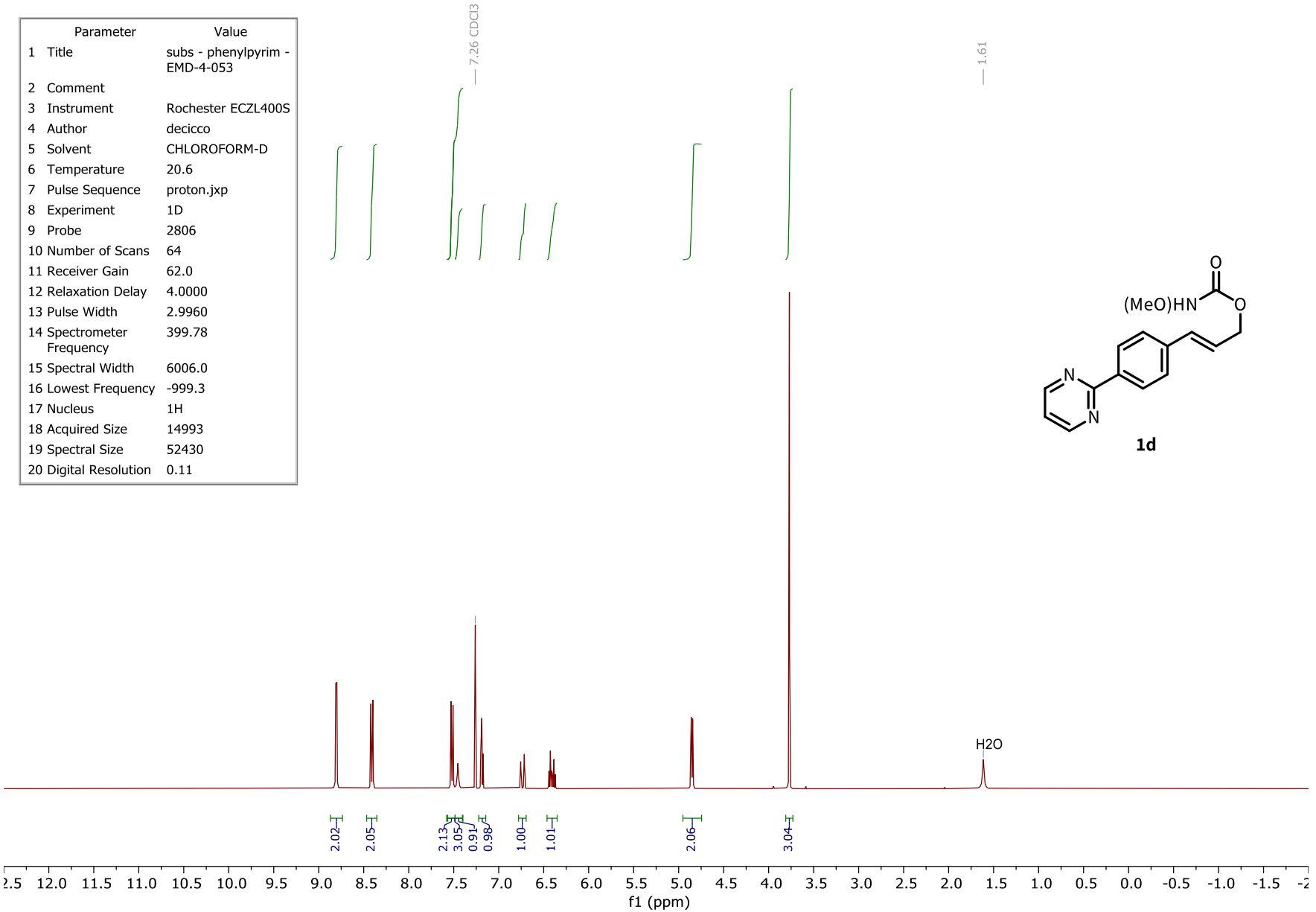
19	Spectral Size	52430
20	Digital Resolution	0.11



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4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.6
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8	Experiment	1D
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10	Number of Scans	4096
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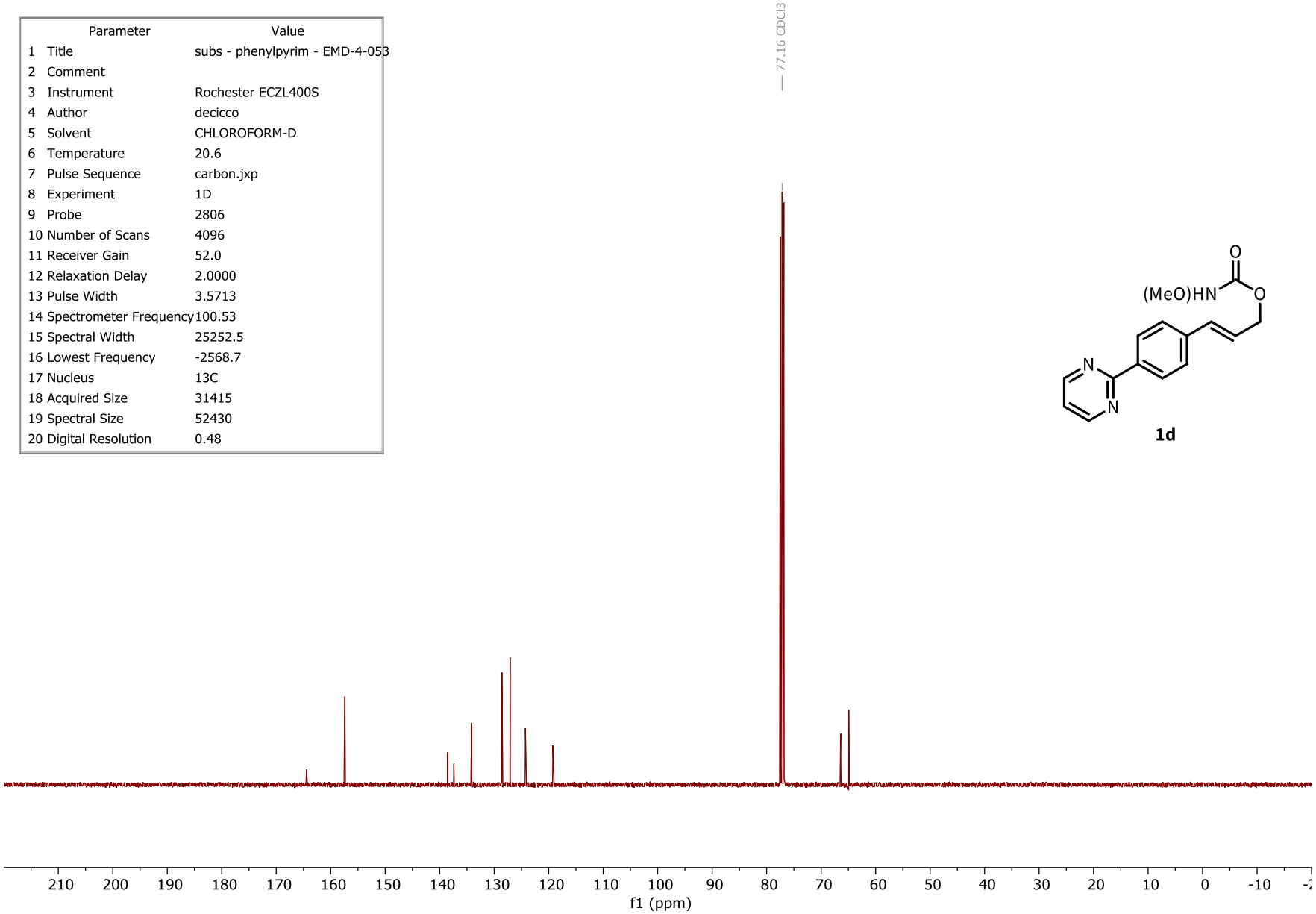

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4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	21.0
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8	Experiment	1D
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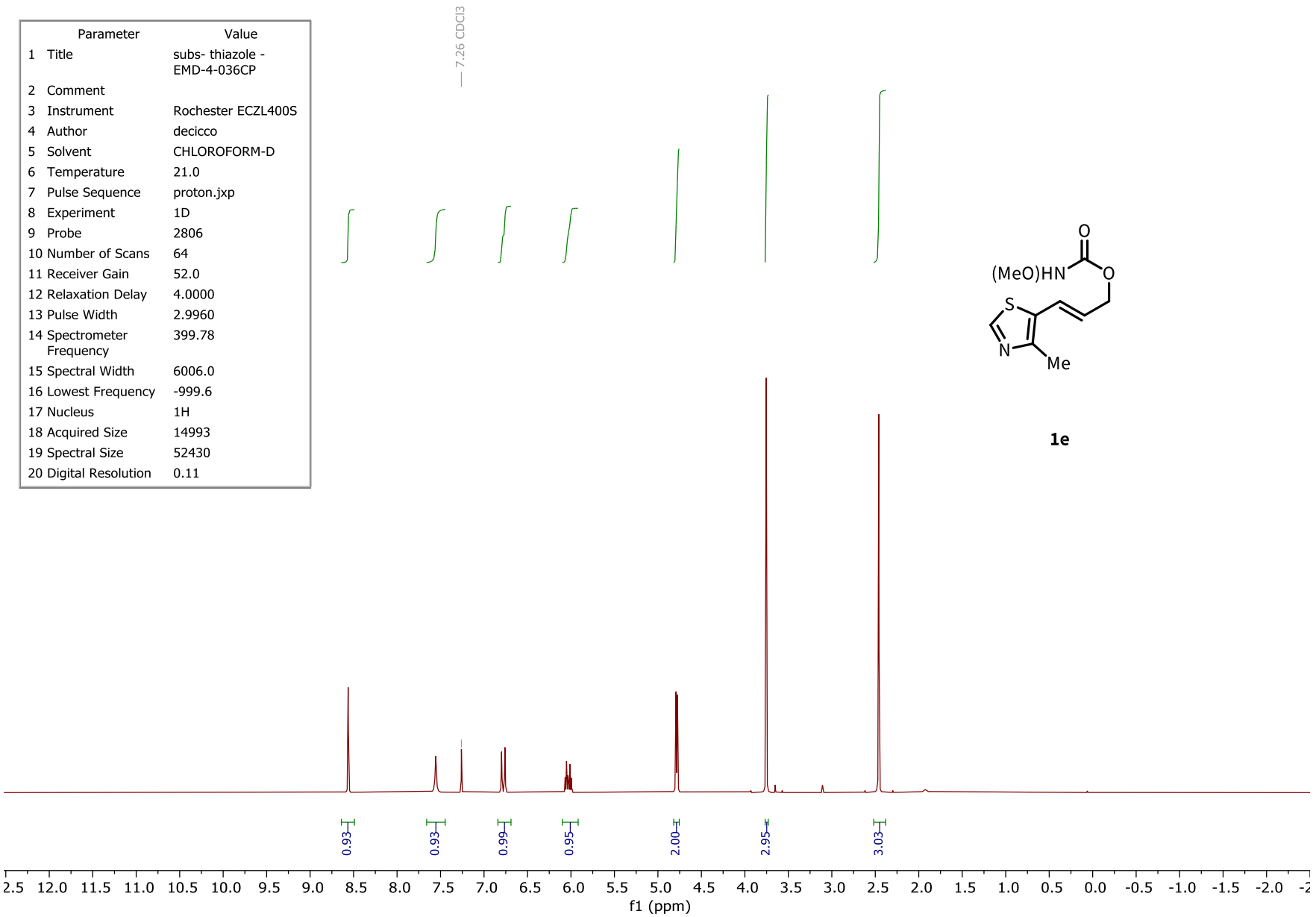

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	Parameter	Value
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3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.8
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8	Experiment	1D
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10	Number of Scans	4096
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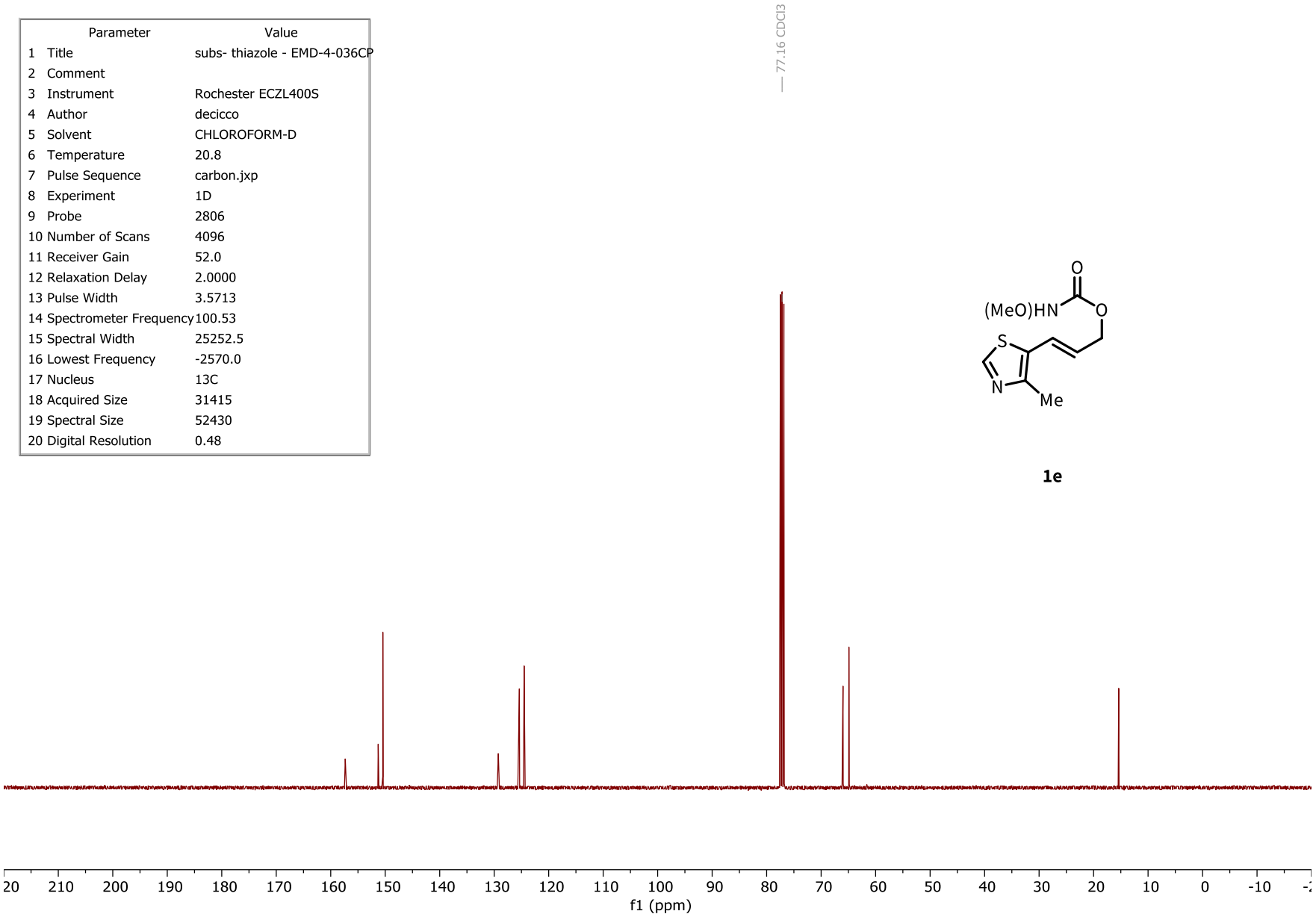

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6	Temperature	20.7
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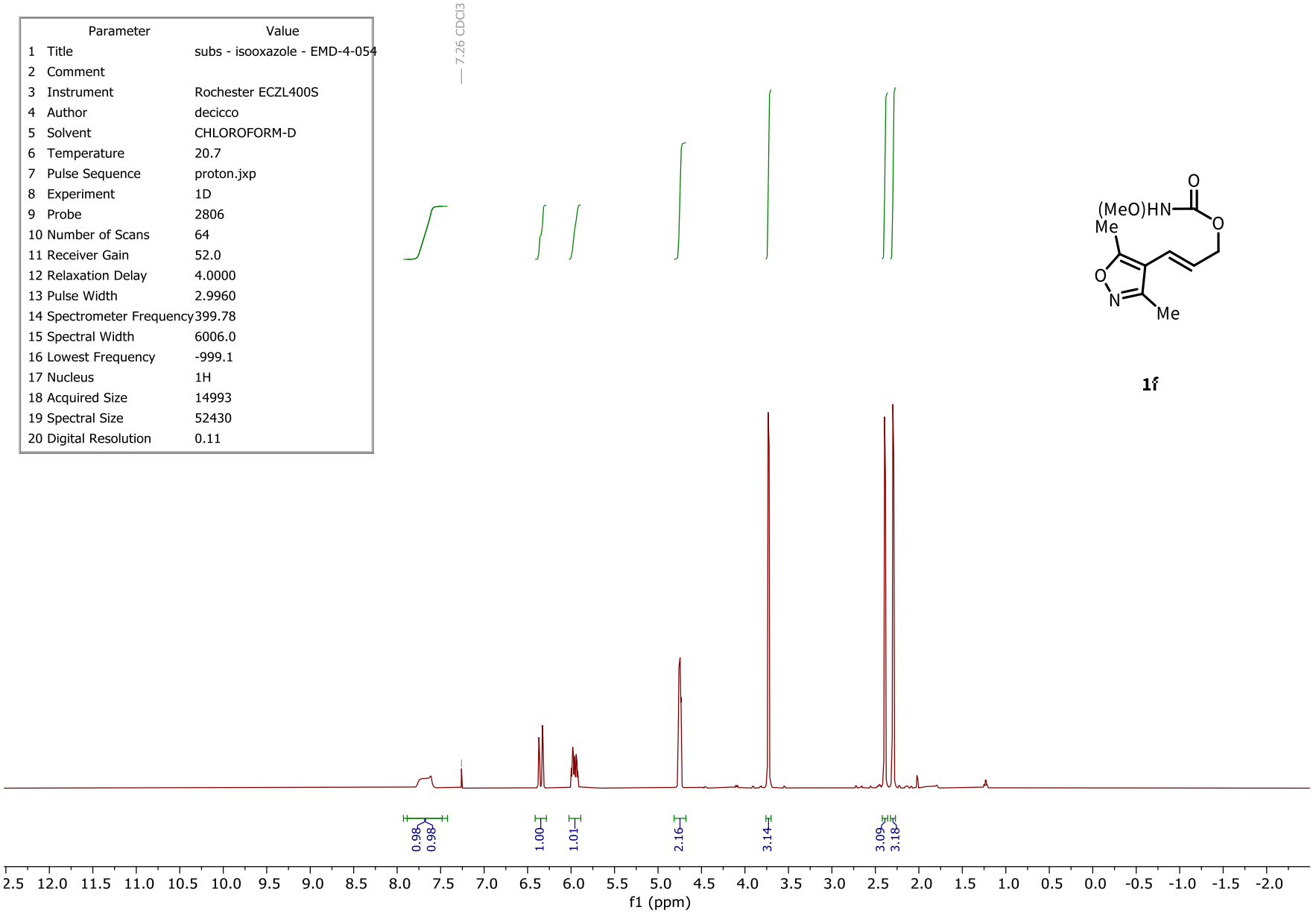

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	Parameter	Value
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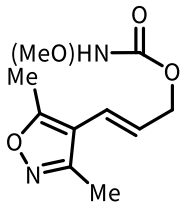
77.16 CDCl3



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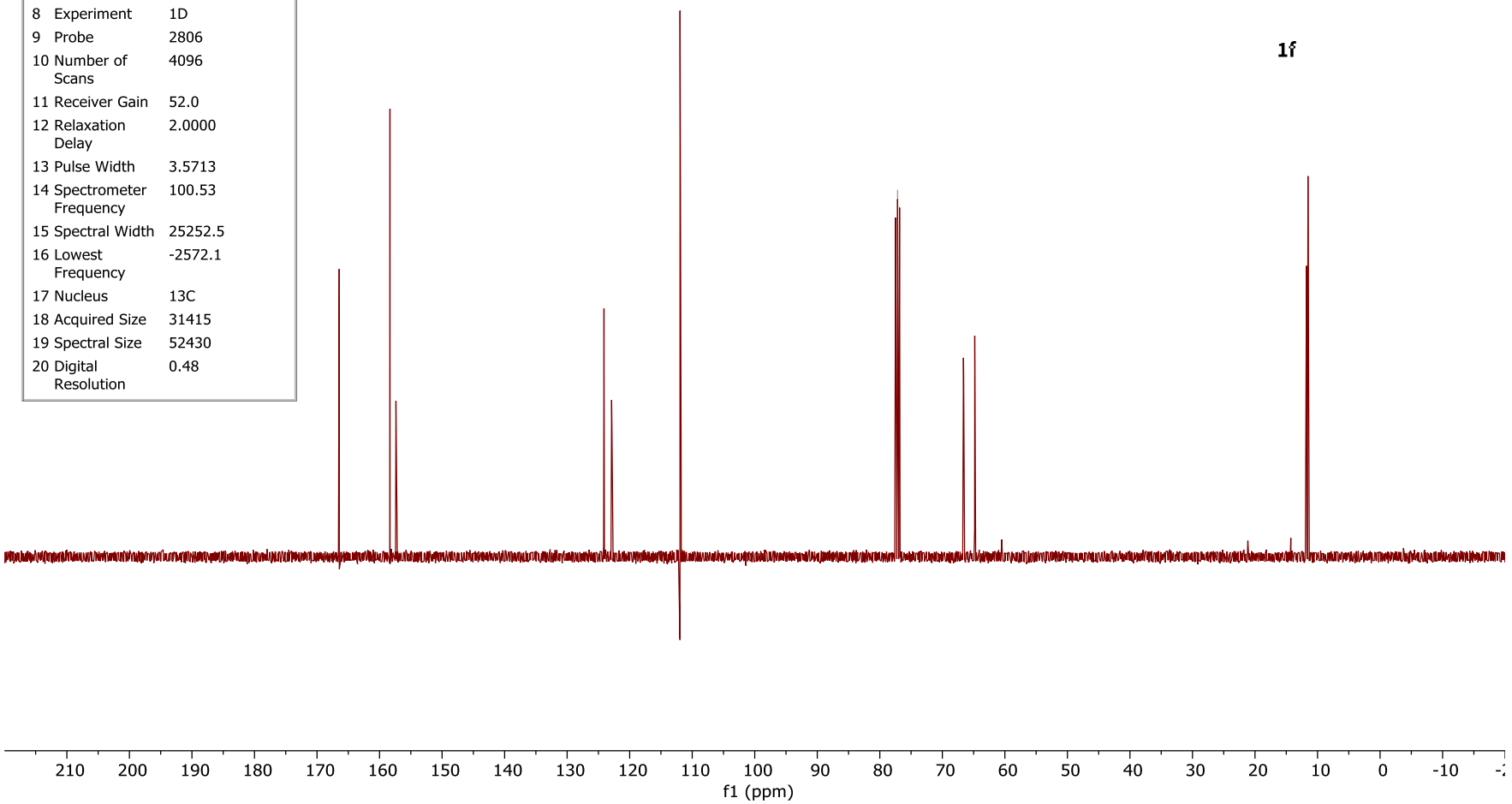

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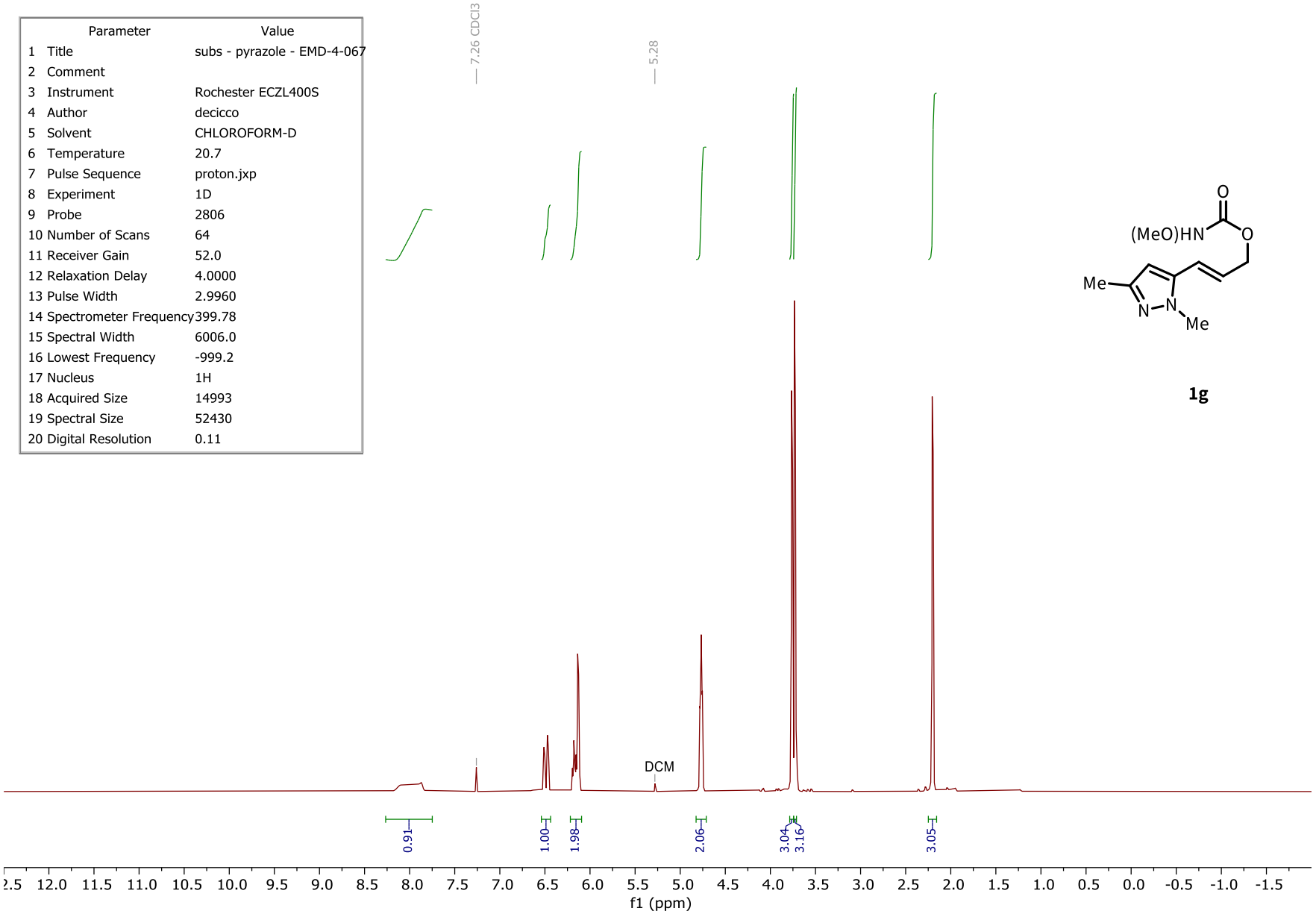

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11	Receiver Gain	52.0
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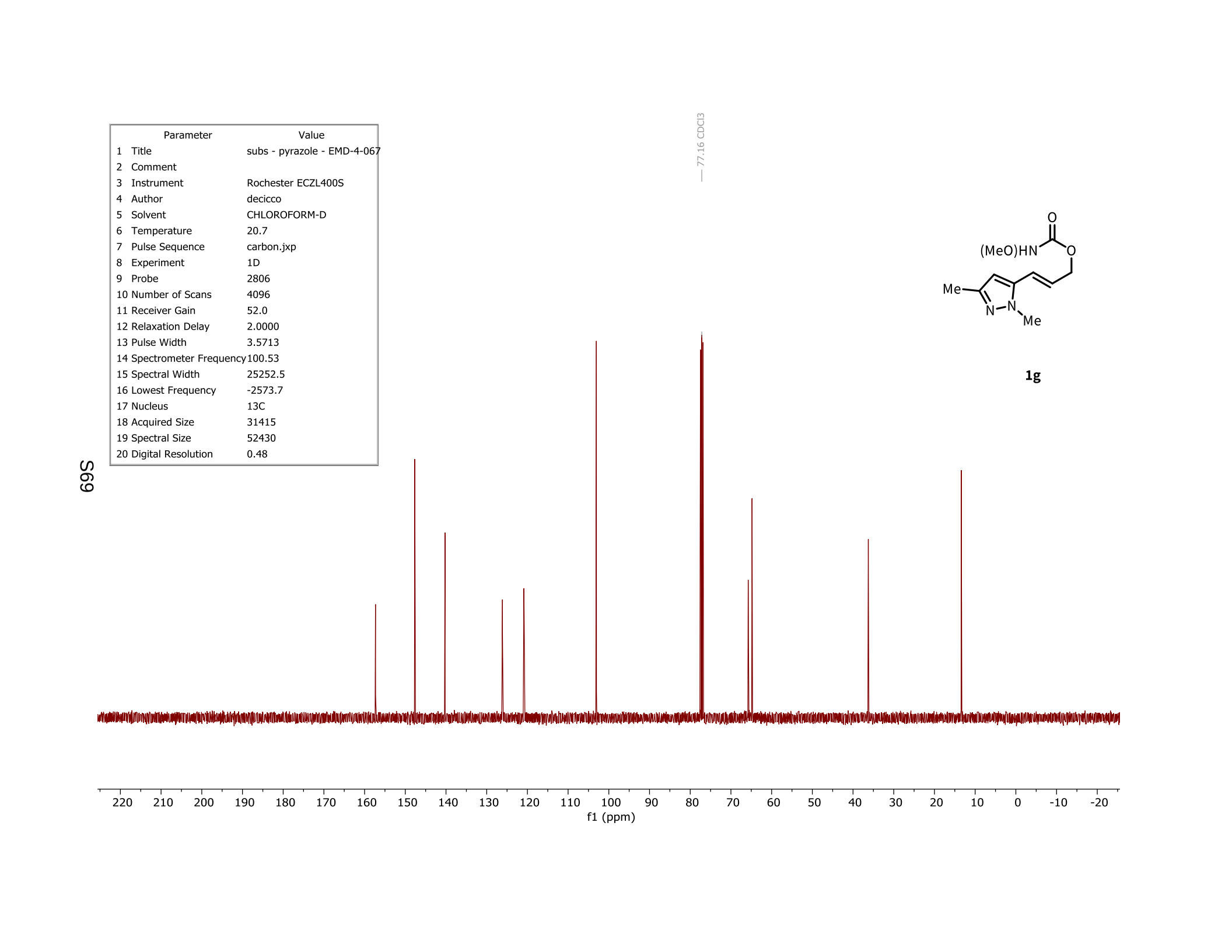

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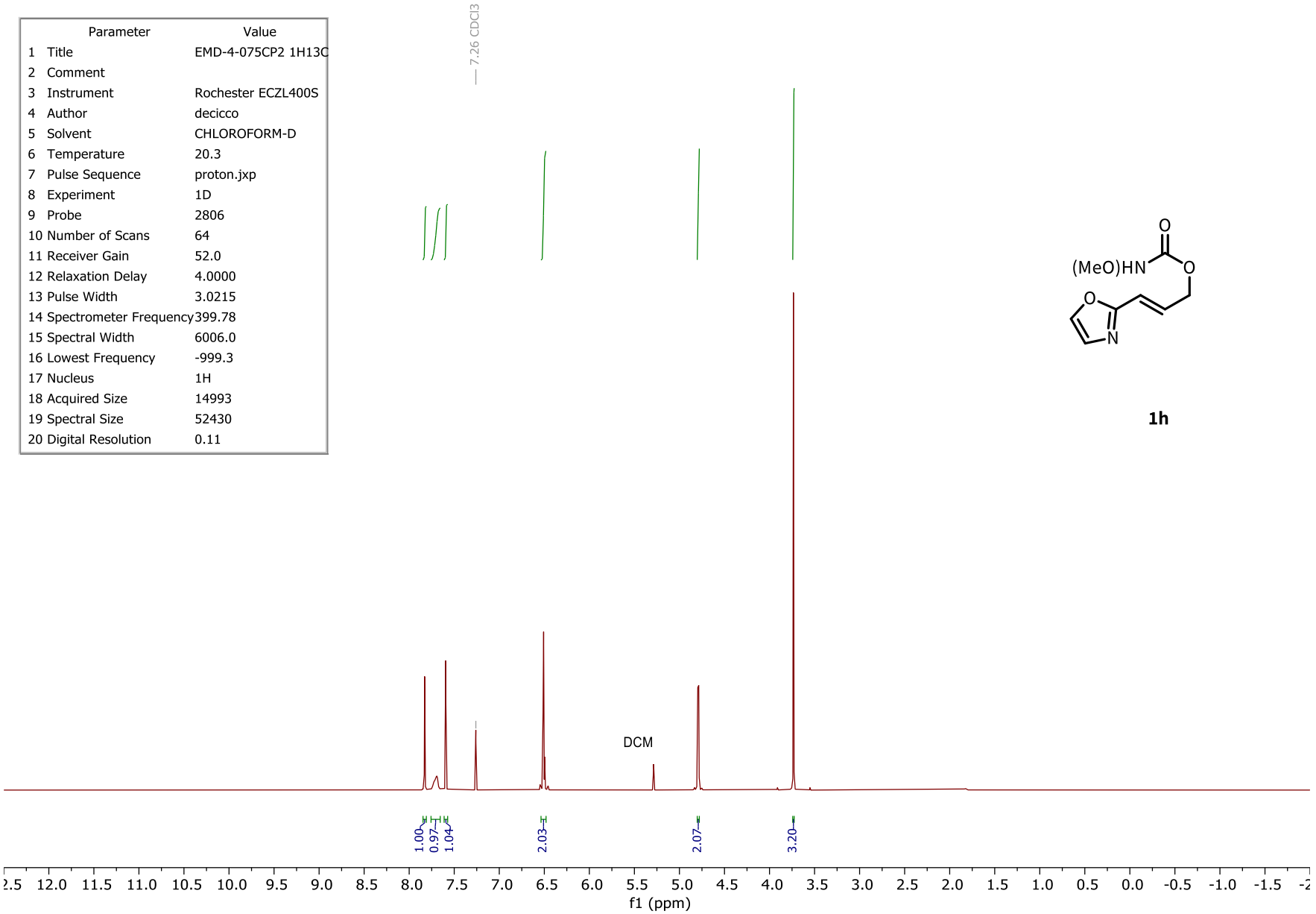

1h

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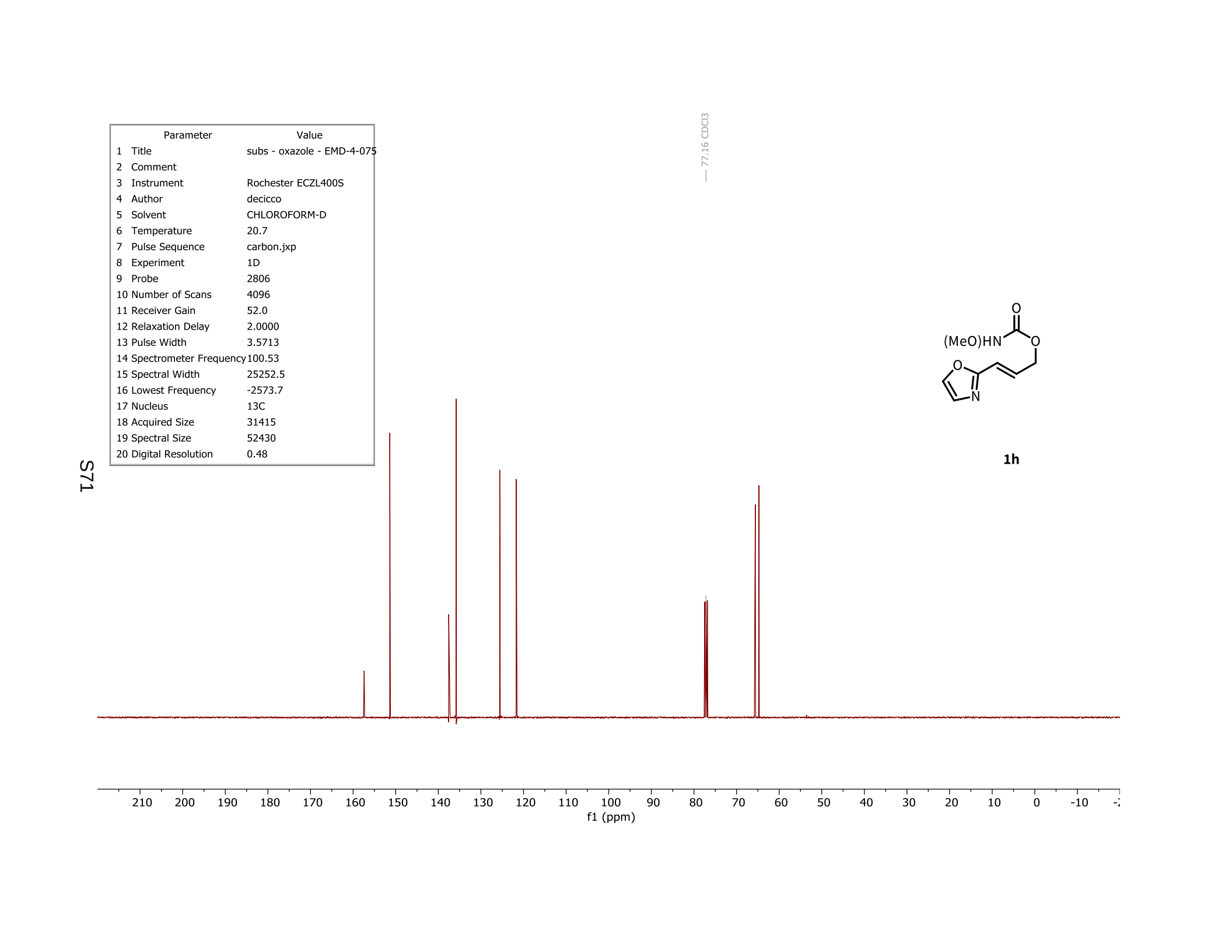

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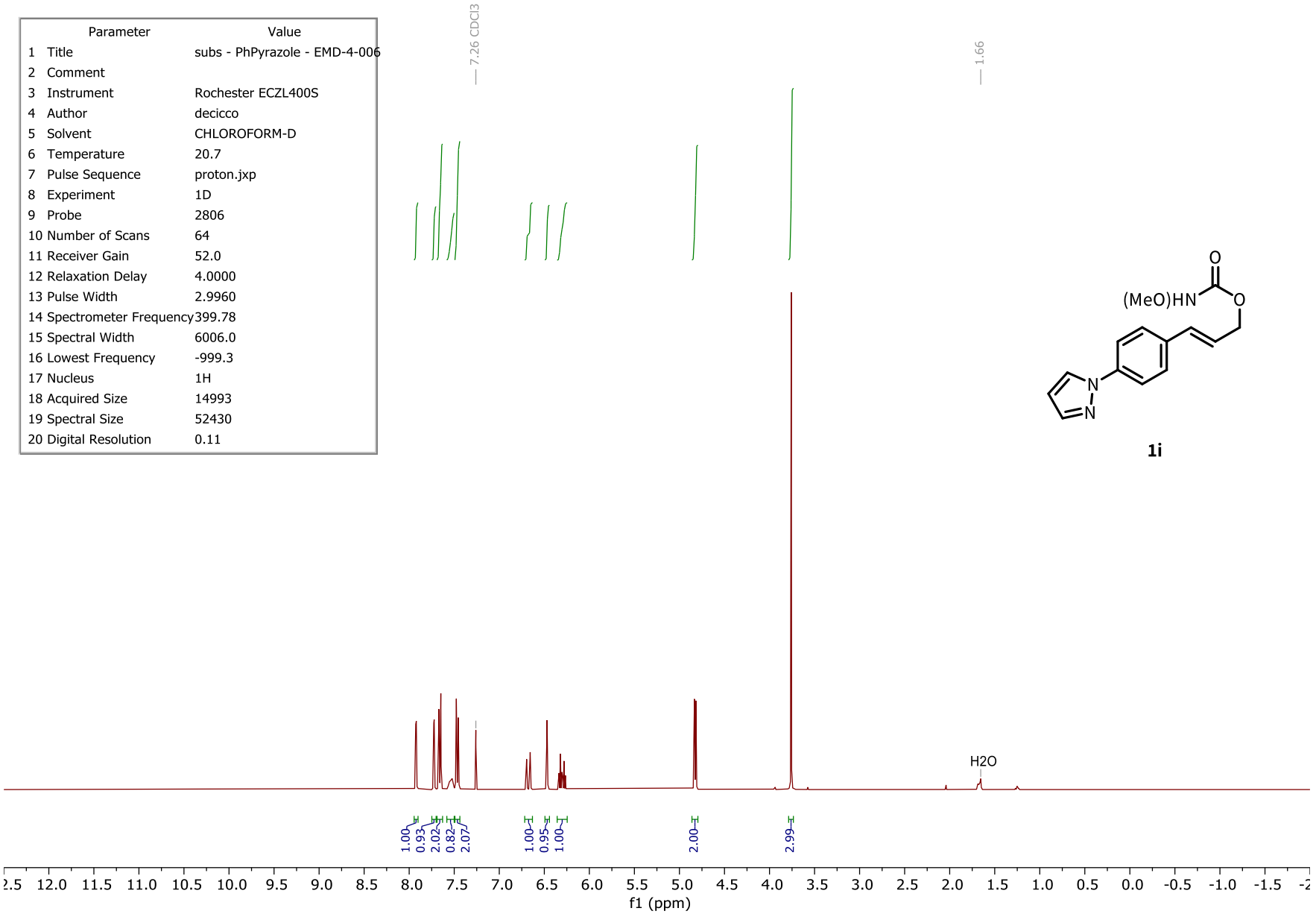

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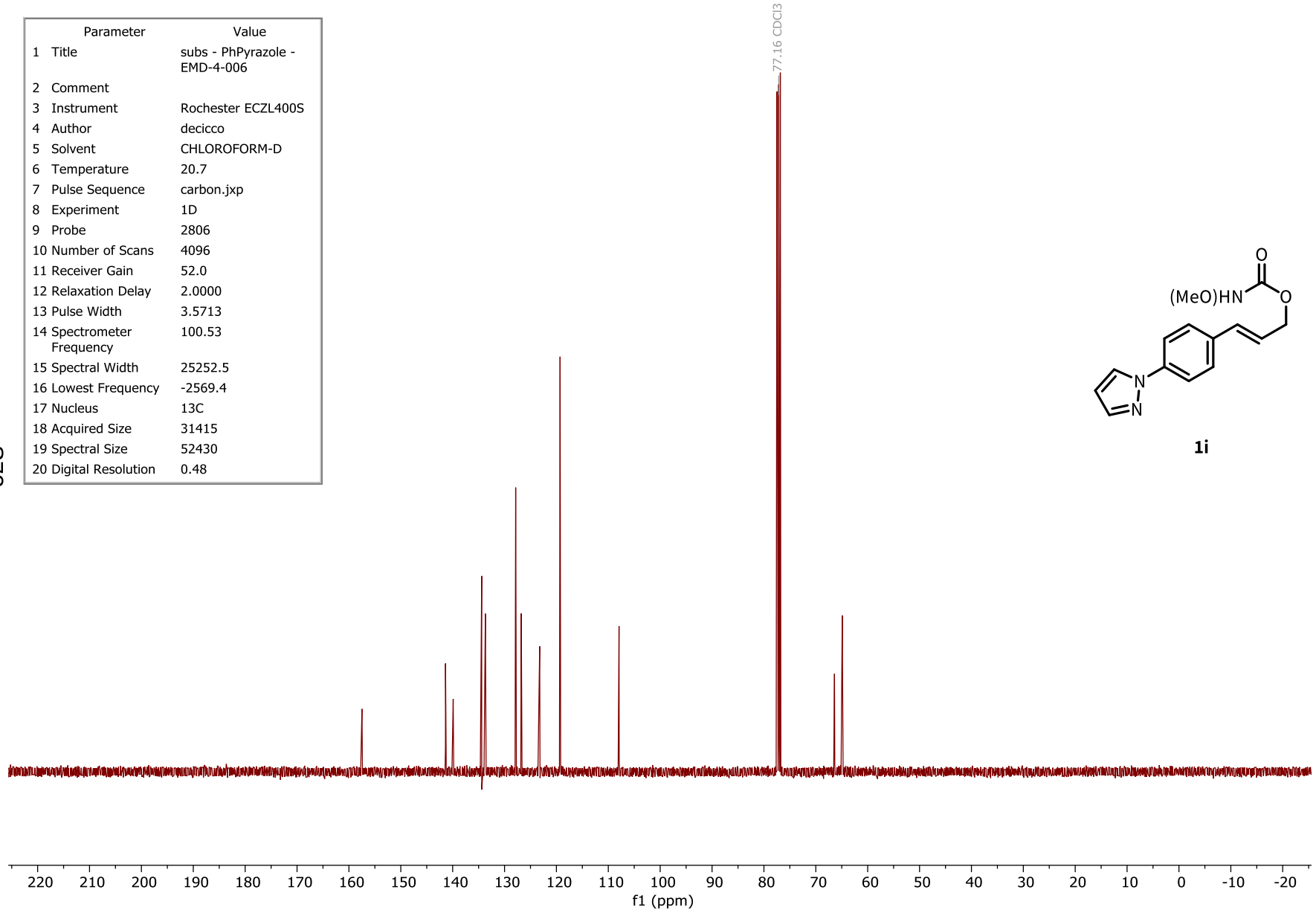

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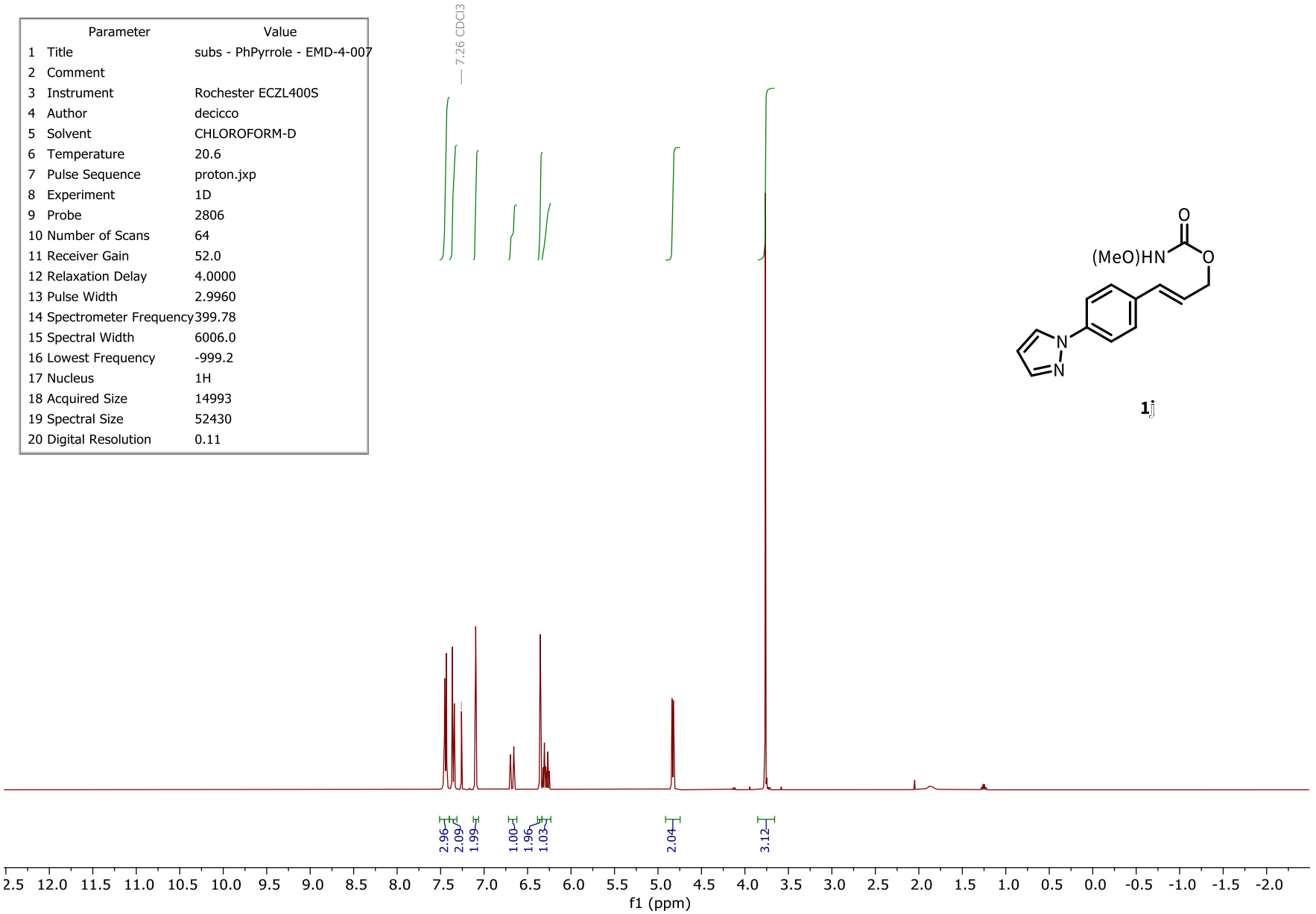

1j

	Parameter	Value
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5	Solvent	CHLOROFORM-D
6	Temperature	20.6
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8	Experiment	1D
9	Probe	2806
10	Number of Scans	4096
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	3.5713
14	Spectrometer Frequency	100.53
15	Spectral Width	25252.5
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17	Nucleus	13C
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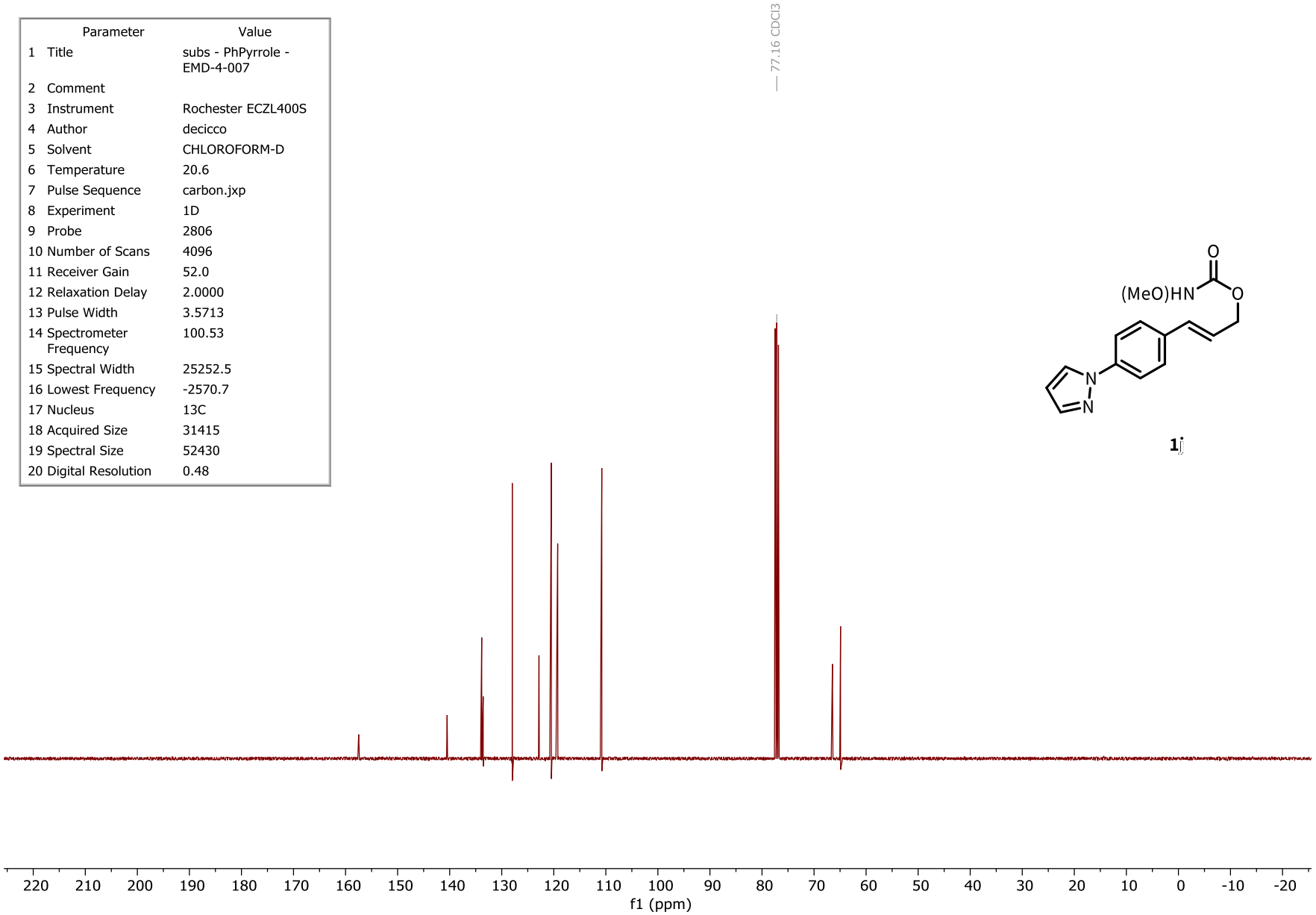
20	Digital Resolution	0.48



1j

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8	Experiment	1D
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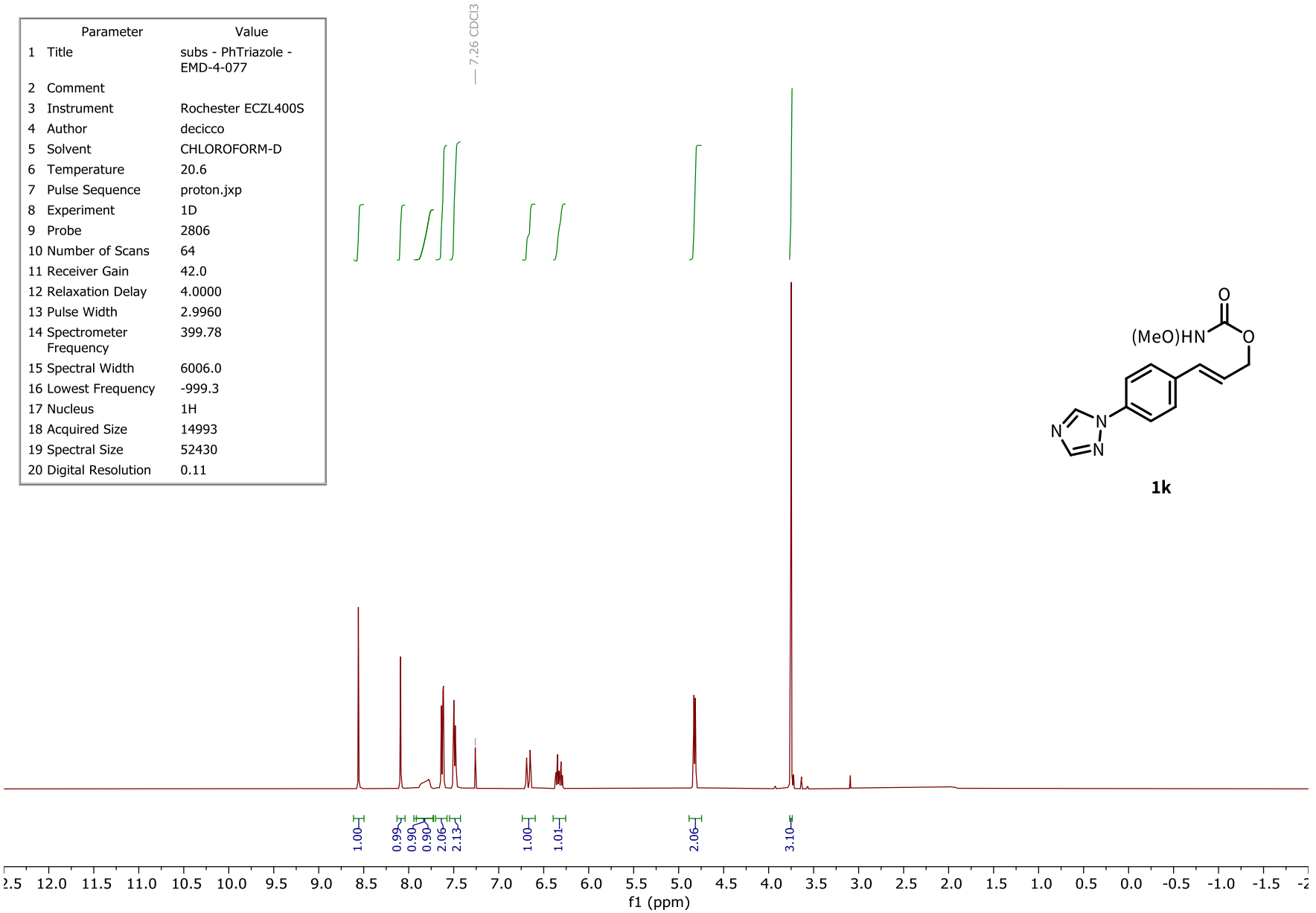
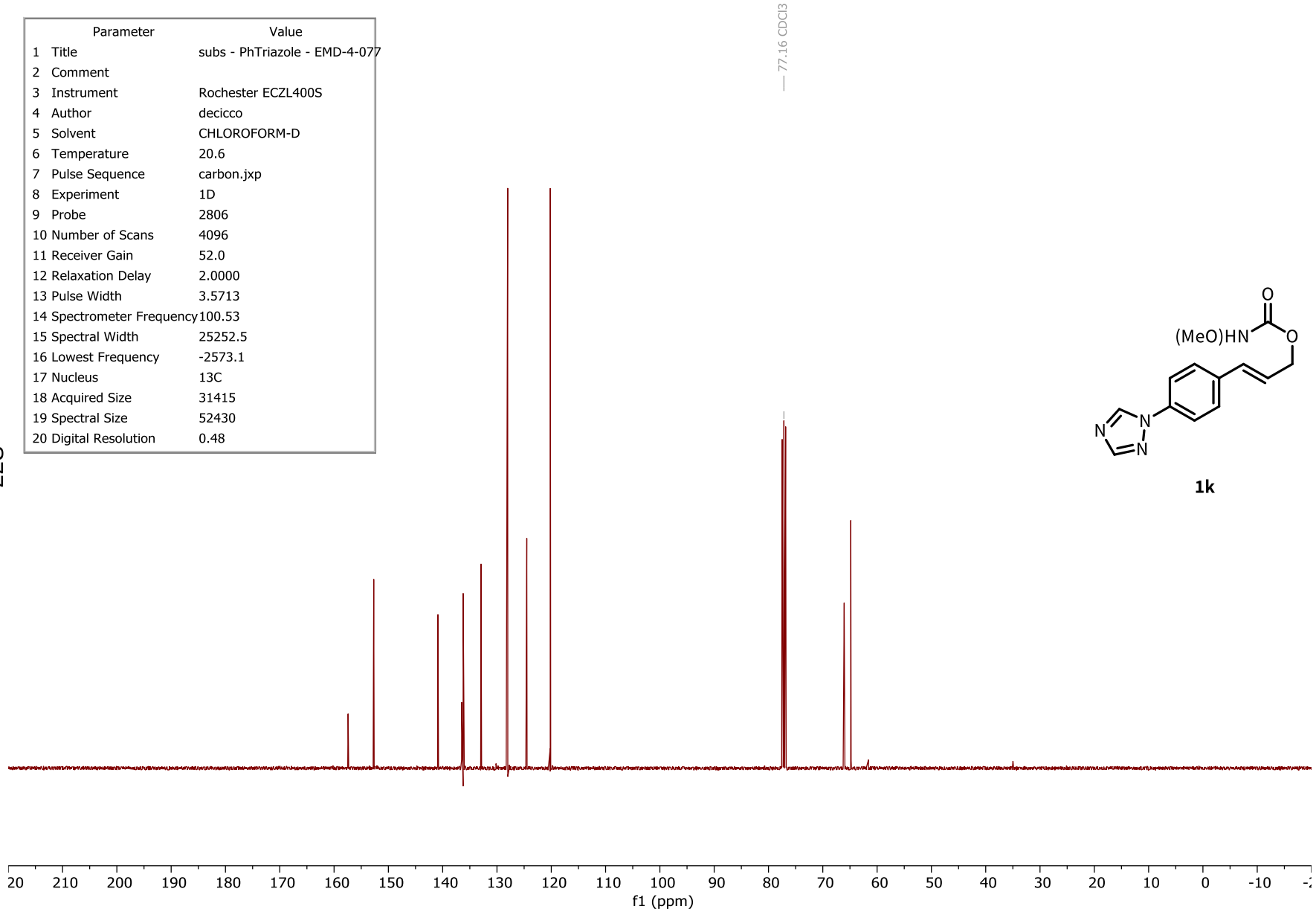
17	Nucleus	1H
18	Acquired Size	14993
19	Spectral Size	52430
20	Digital Resolution	0.11

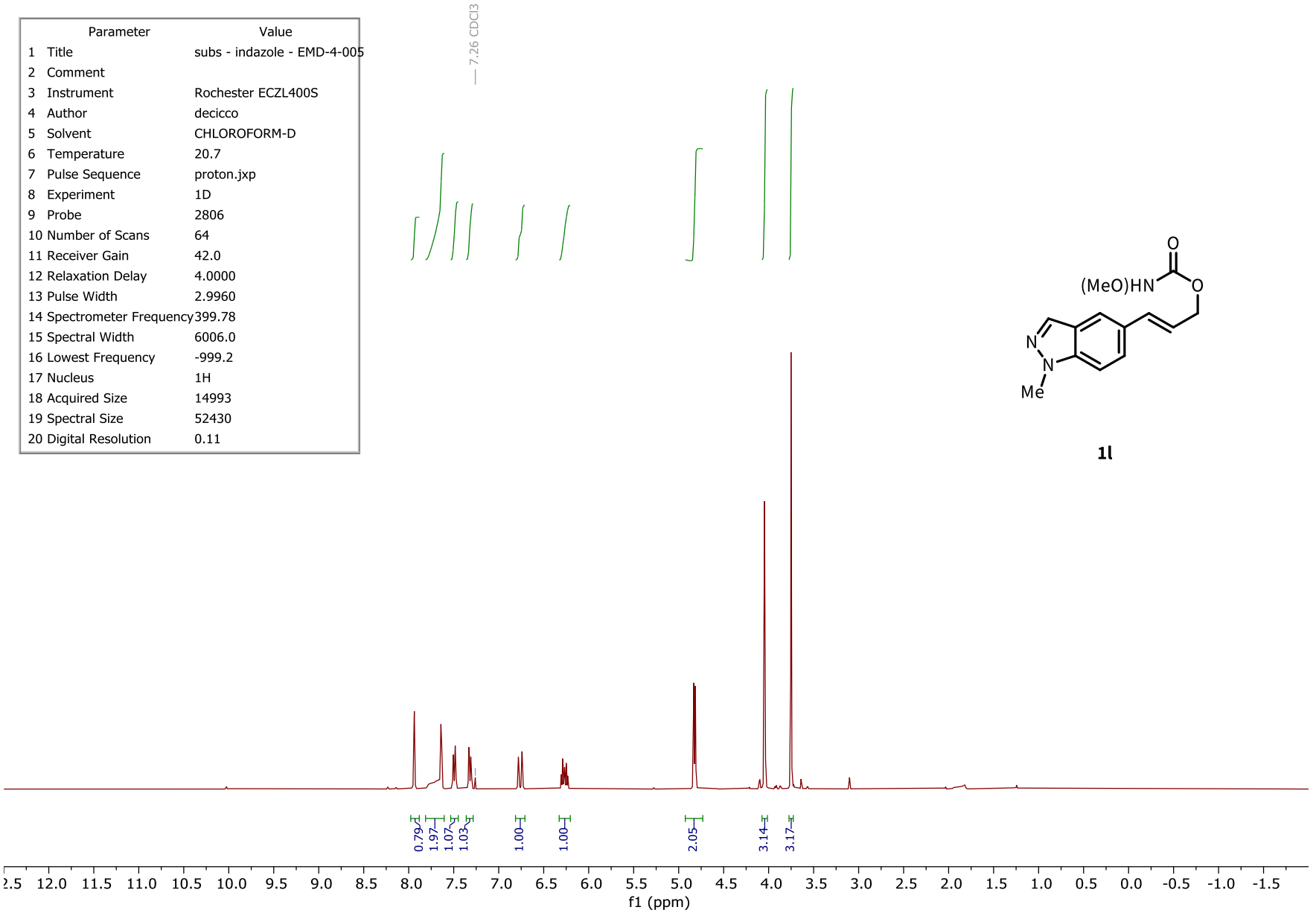


1k

	Parameter	Value
1	Title	subs - PhTriazole - EMD-4-077
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.6
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	4096
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	3.5713
14	Spectrometer Frequency	100.53
15	Spectral Width	25252.5
16	Lowest Frequency	-2573.1
17	Nucleus	13C
18	Acquired Size	31415
19	Spectral Size	52430
20	Digital Resolution	0.48

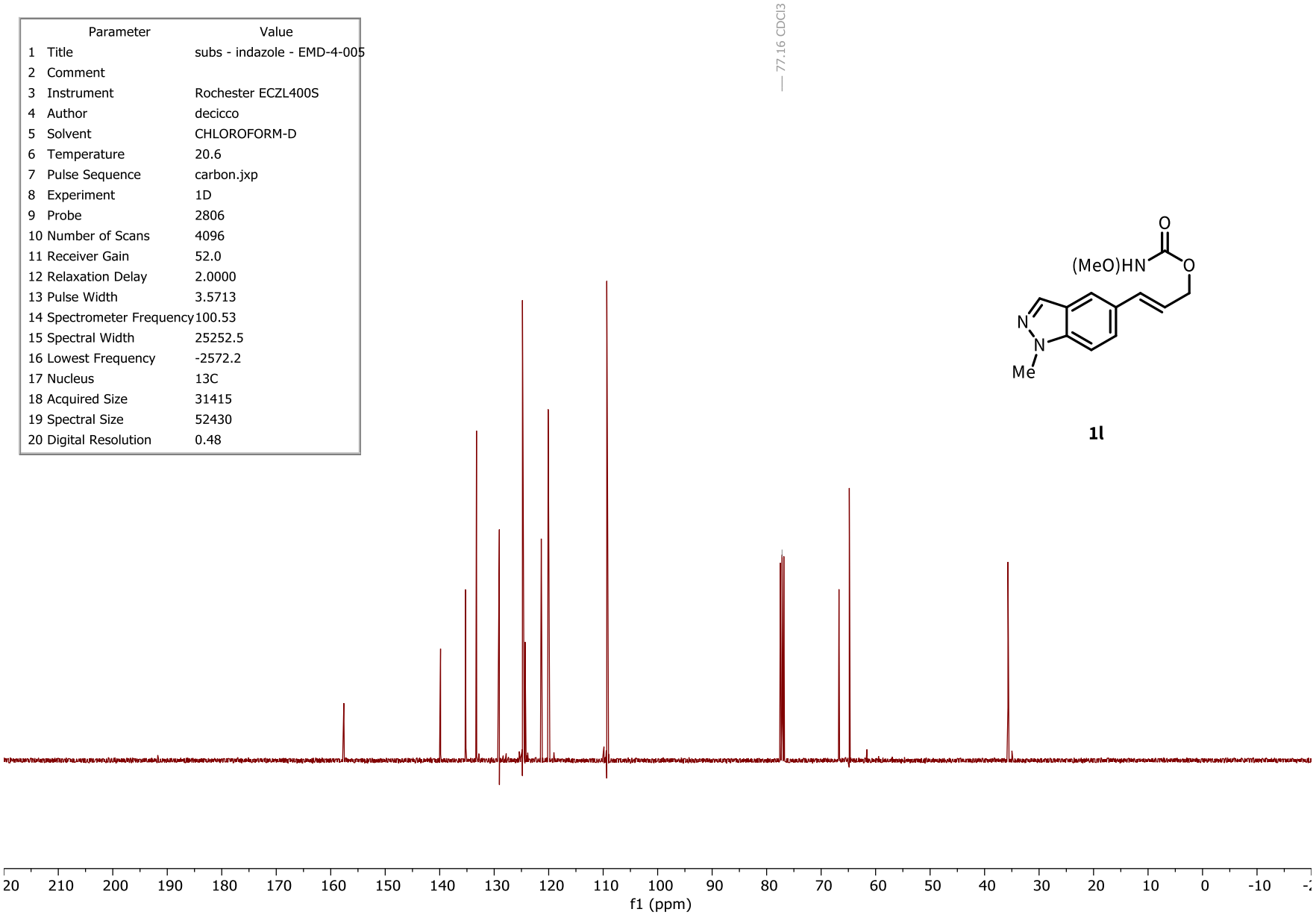


	Parameter	Value
1	Title	subs - indazole - EMD-4-005
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.7
7	Pulse Sequence	proton.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	64
11	Receiver Gain	42.0
12	Relaxation Delay	4.0000
13	Pulse Width	2.9960
14	Spectrometer Frequency	399.78
15	Spectral Width	6006.0
16	Lowest Frequency	-999.2
17	Nucleus	1H
18	Acquired Size	14993
19	Spectral Size	52430
20	Digital Resolution	0.11

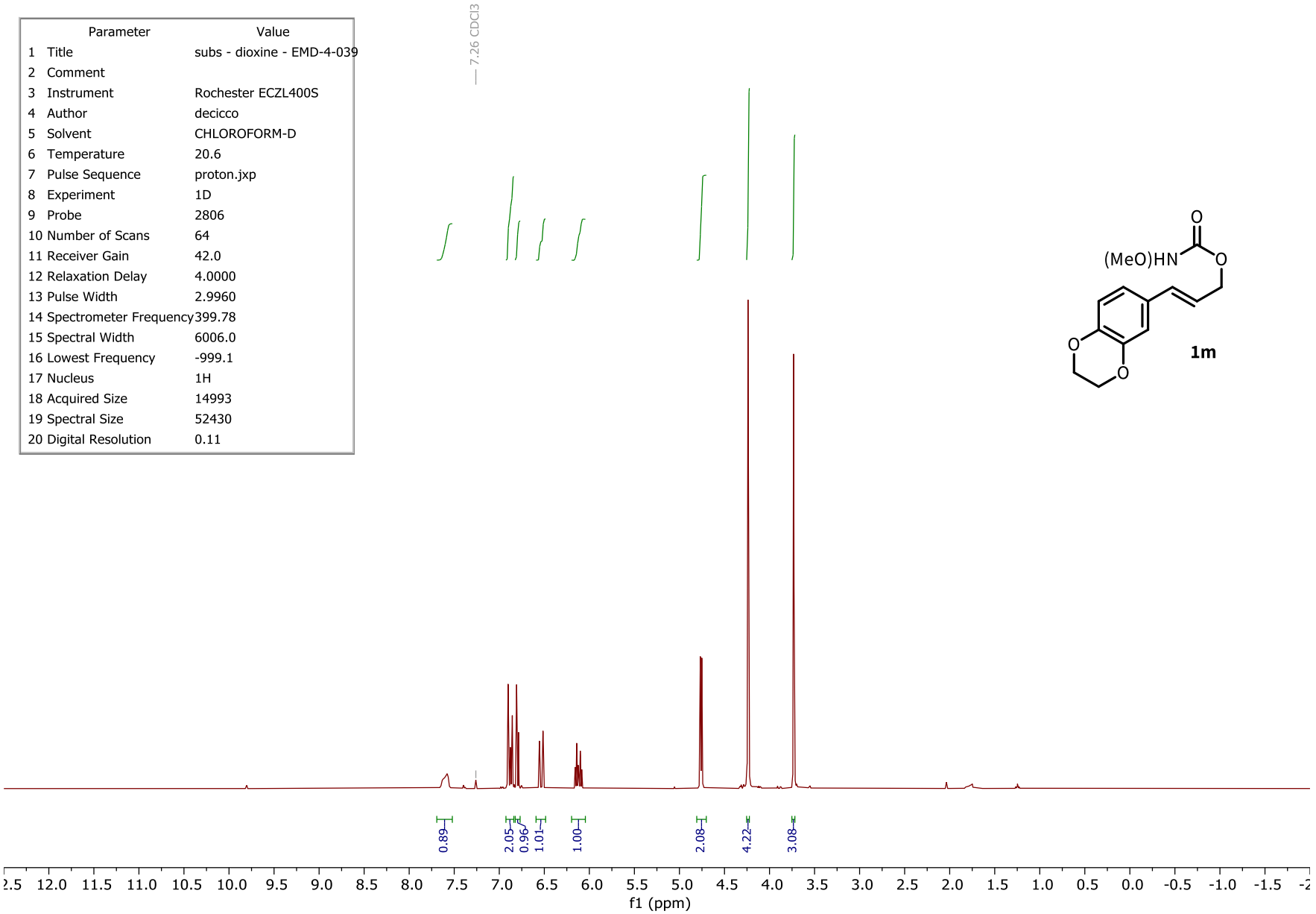


1l

	Parameter	Value
1	Title	subs - indazole - EMD-4-005
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.6
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	4096
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	3.5713
14	Spectrometer Frequency	100.53
15	Spectral Width	25252.5
16	Lowest Frequency	-2572.2
17	Nucleus	13C
18	Acquired Size	31415
19	Spectral Size	52430
20	Digital Resolution	0.48

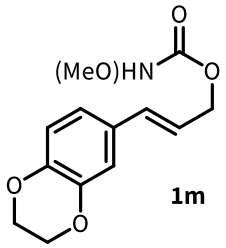


	Parameter	Value
1	Title	subs - dioxine - EMD-4-039
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.6
7	Pulse Sequence	proton.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	64
11	Receiver Gain	42.0
12	Relaxation Delay	4.0000
13	Pulse Width	2.9960
14	Spectrometer Frequency	399.78
15	Spectral Width	6006.0
16	Lowest Frequency	-999.1
17	Nucleus	1H
18	Acquired Size	14993
19	Spectral Size	52430
20	Digital Resolution	0.11

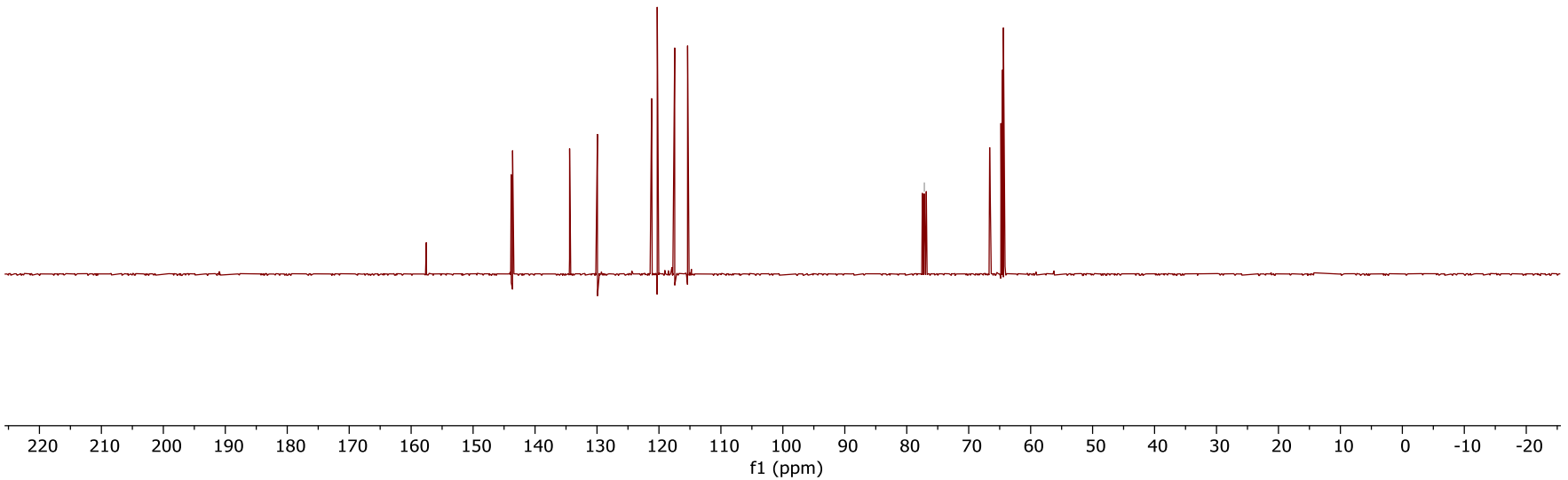


	Parameter	Value
1	Title	subs - dioxine - EMD-4-039
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.6
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	4096
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	3.5713
14	Spectrometer Frequency	100.53
15	Spectral Width	25252.5
16	Lowest Frequency	-2572.6
17	Nucleus	13C
18	Acquired Size	31415
19	Spectral Size	52430
20	Digital Resolution	0.48

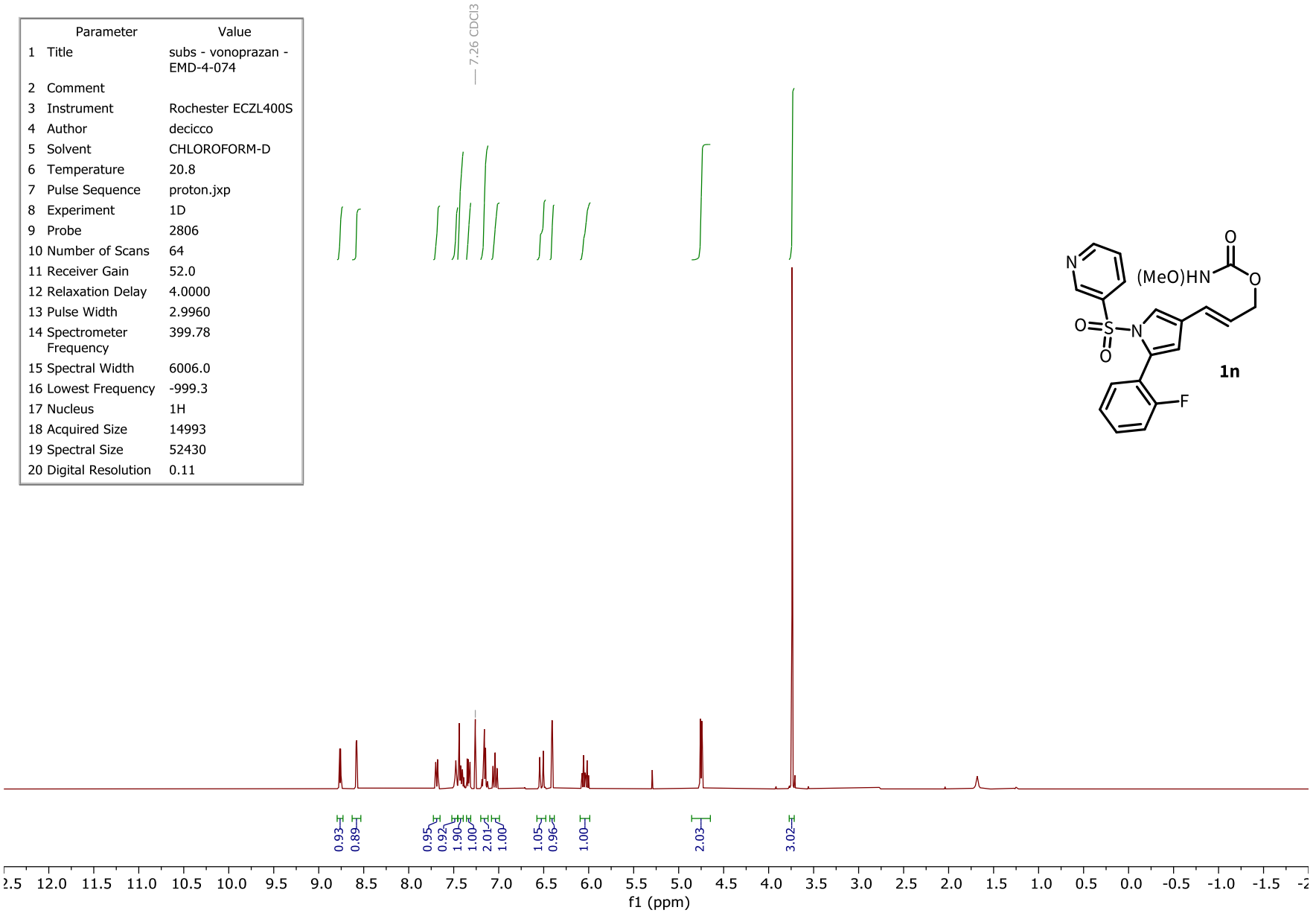
77.16 CDCl3



1m

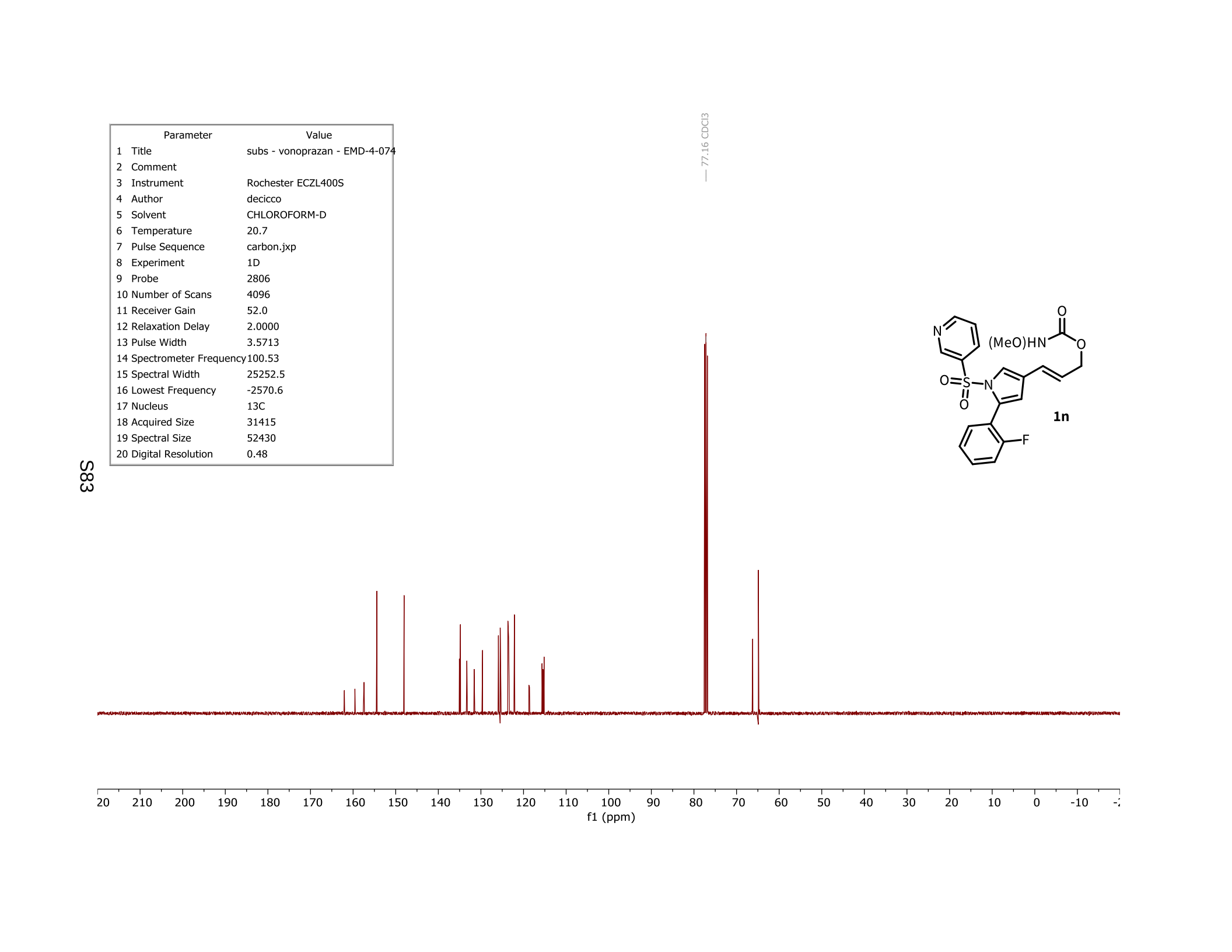


	Parameter	Value
1	Title	subs - vonoprazan - EMD-4-074
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.8
7	Pulse Sequence	proton.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	64
11	Receiver Gain	52.0
12	Relaxation Delay	4.0000
13	Pulse Width	2.9960
14	Spectrometer Frequency	399.78
15	Spectral Width	6006.0
16	Lowest Frequency	-999.3
17	Nucleus	1H
18	Acquired Size	14993
19	Spectral Size	52430
20	Digital Resolution	0.11

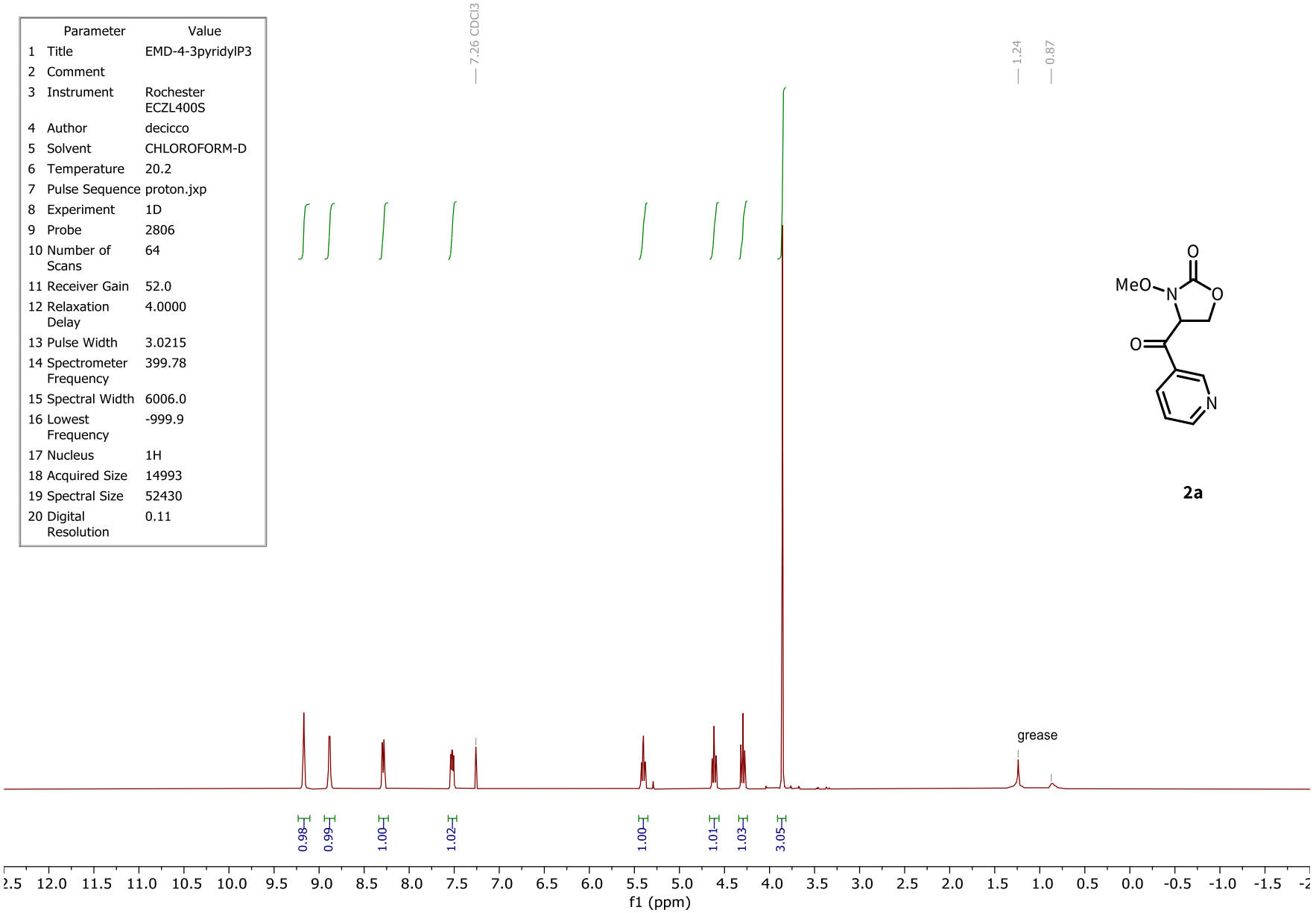


1n

	Parameter	Value
1	Title	subs - vonoprazan - EMD-4-074
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.7
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	4096
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	3.5713
14	Spectrometer Frequency	100.53
15	Spectral Width	25252.5
16	Lowest Frequency	-2570.6
17	Nucleus	13C
18	Acquired Size	31415
19	Spectral Size	52430
20	Digital Resolution	0.48

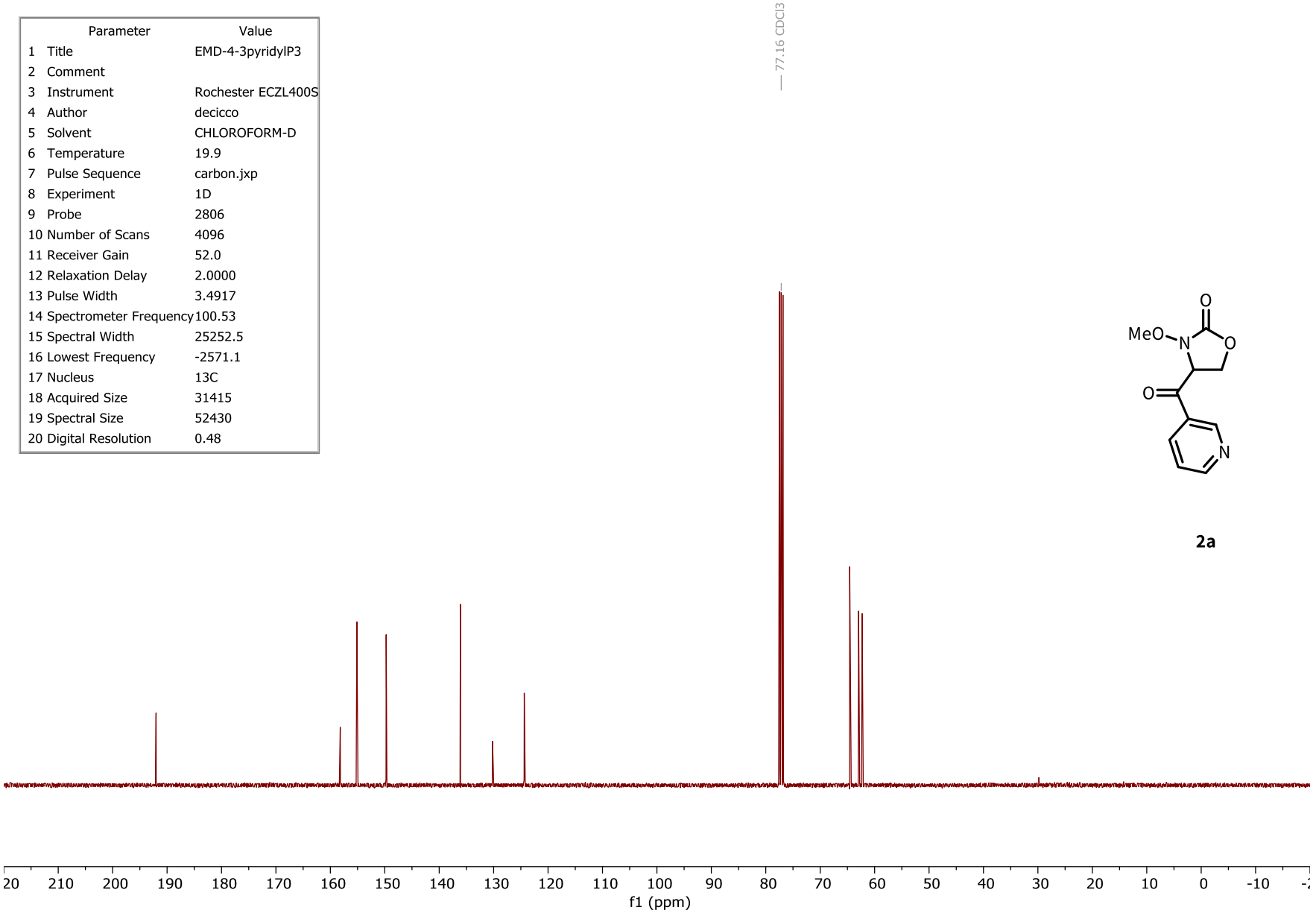


	Parameter	Value
1	Title	EMD-4-3pyridylP3
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.2
7	Pulse Sequence	proton.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	64
11	Receiver Gain	52.0
12	Relaxation Delay	4.0000
13	Pulse Width	3.0215
14	Spectrometer Frequency	399.78
15	Spectral Width	6006.0
16	Lowest Frequency	-999.9
17	Nucleus	1H
18	Acquired Size	14993
19	Spectral Size	52430
20	Digital Resolution	0.11



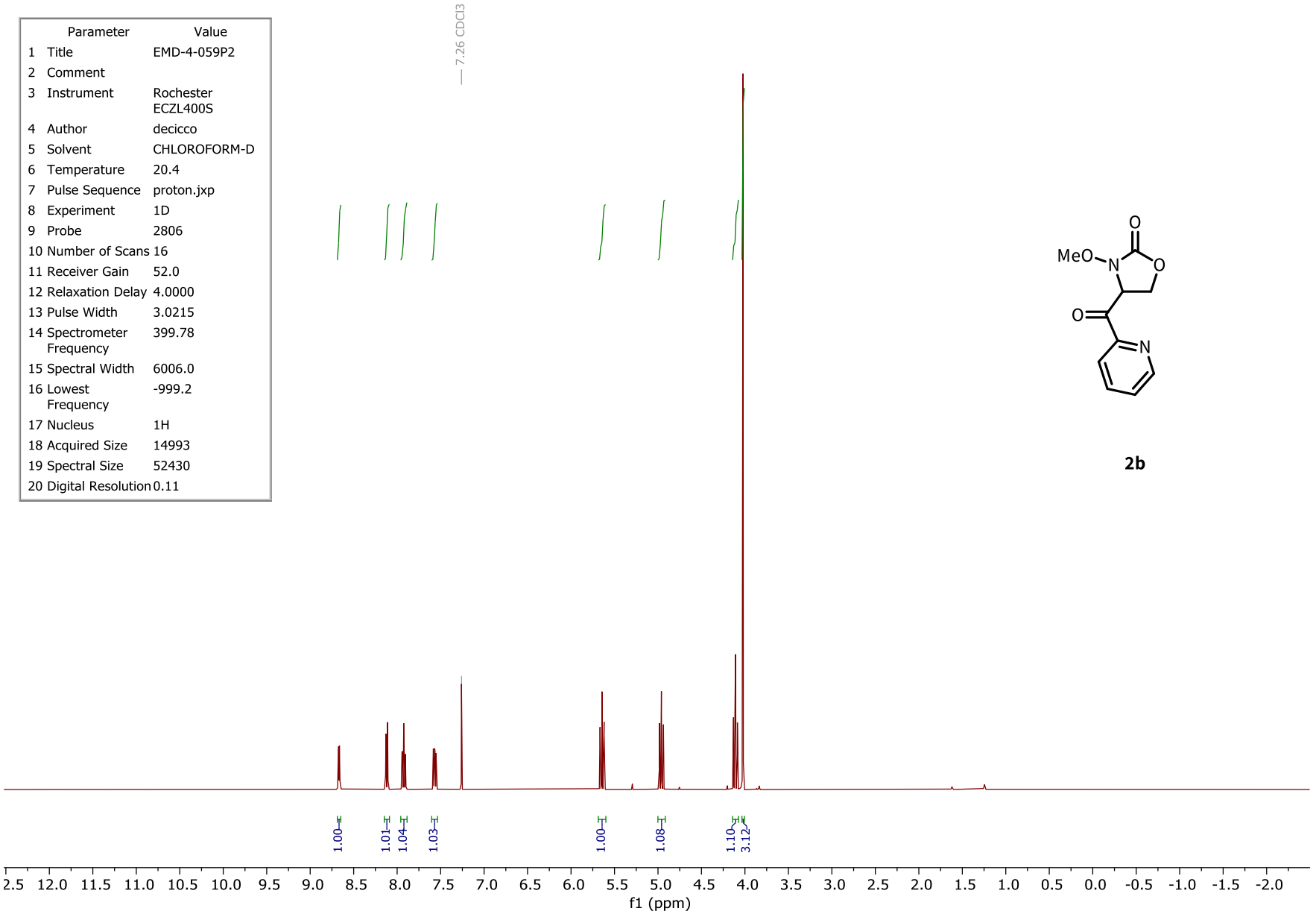
2a

	Parameter	Value
1	Title	EMD-4-3pyridylP3
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	19.9
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	4096
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	3.4917
14	Spectrometer Frequency	100.53
15	Spectral Width	25252.5
16	Lowest Frequency	-2571.1
17	Nucleus	13C
18	Acquired Size	31415
19	Spectral Size	52430
20	Digital Resolution	0.48



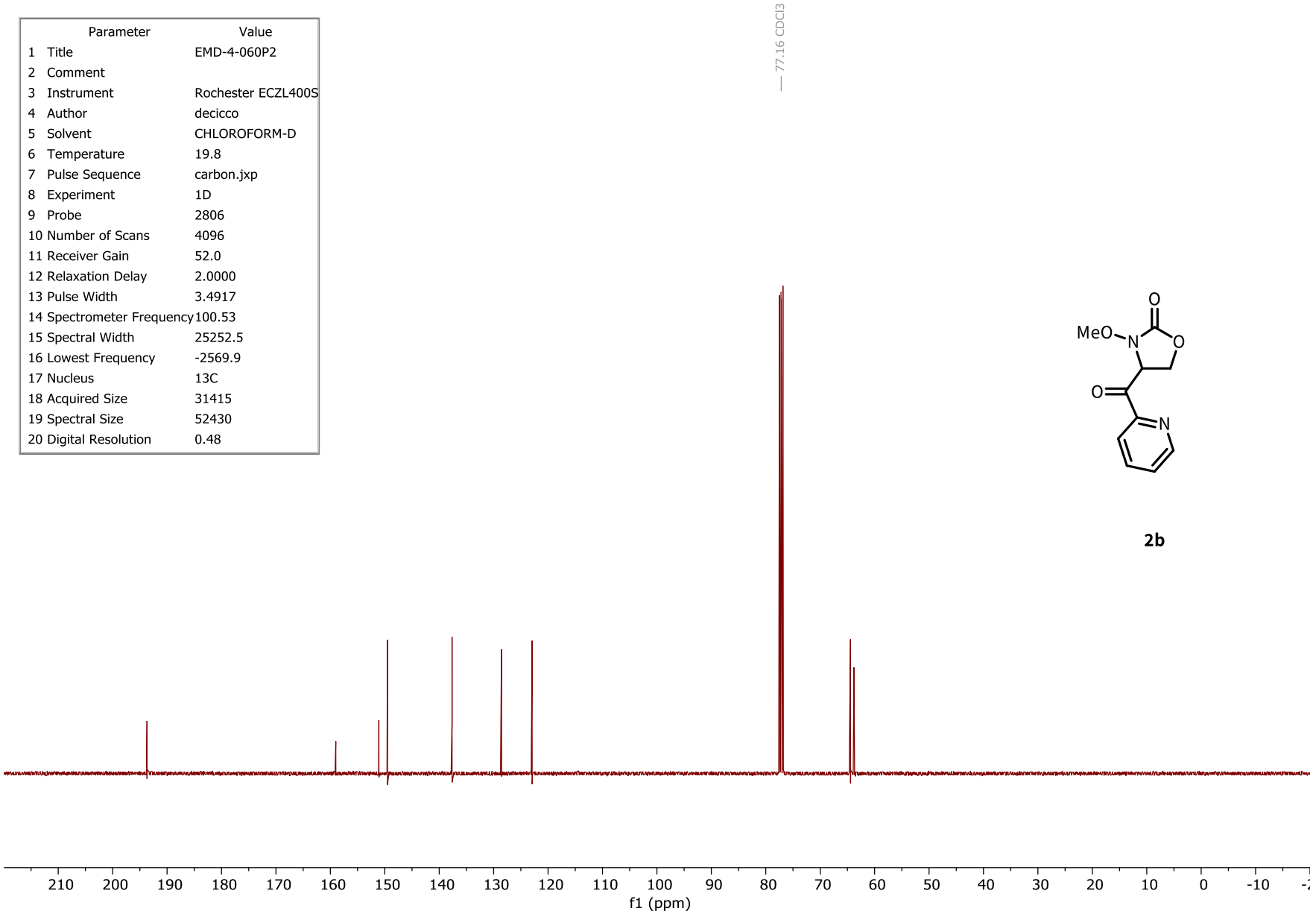
2a

	Parameter	Value
1	Title	EMD-4-059P2
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.4
7	Pulse Sequence	proton.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	16
11	Receiver Gain	52.0
12	Relaxation Delay	4.0000
13	Pulse Width	3.0215
14	Spectrometer Frequency	399.78
15	Spectral Width	6006.0
16	Lowest Frequency	-999.2
17	Nucleus	1H
18	Acquired Size	14993
19	Spectral Size	52430
20	Digital Resolution	0.11



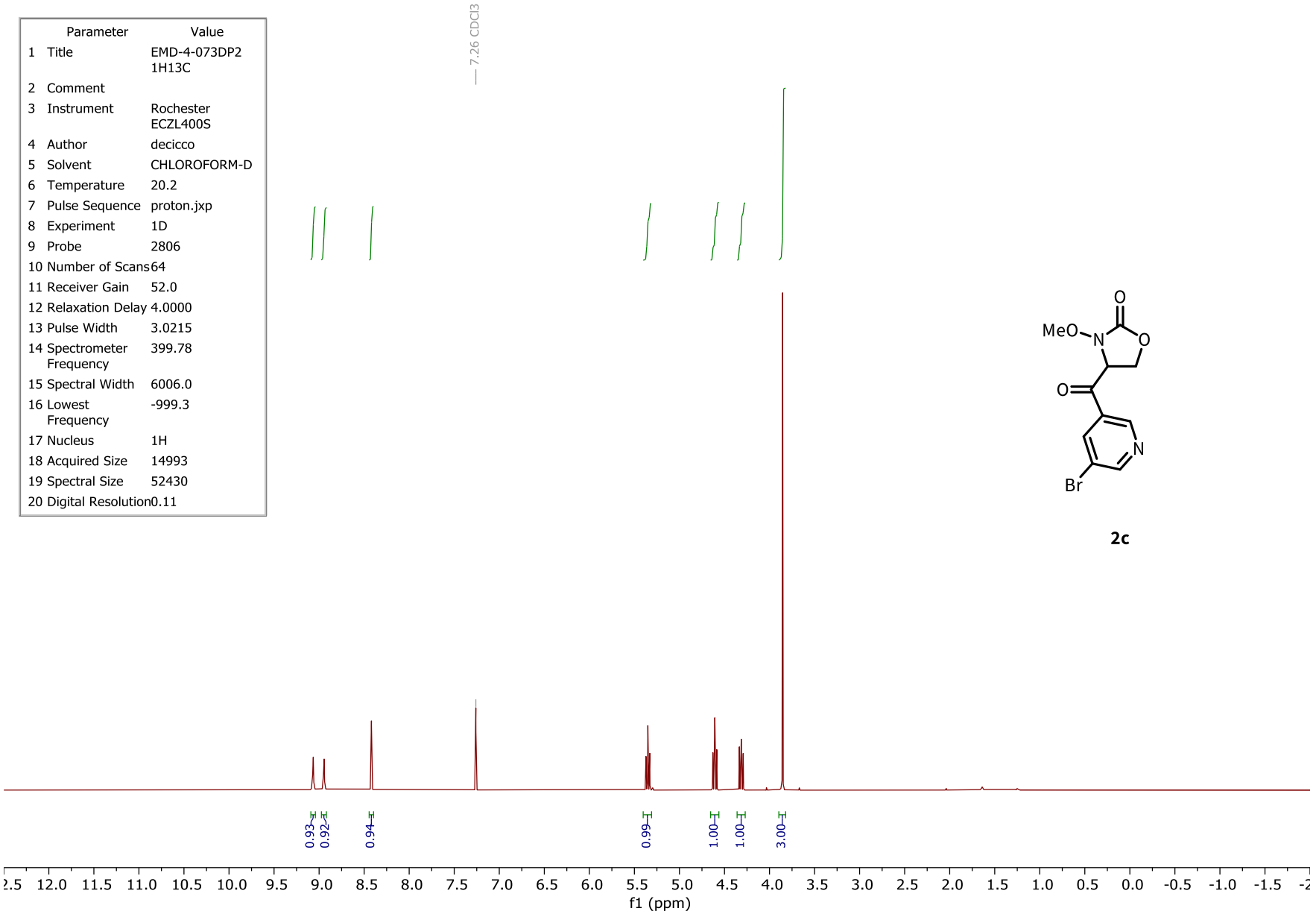
2b

	Parameter	Value
1	Title	EMD-4-060P2
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	19.8
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	4096
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	3.4917
14	Spectrometer Frequency	100.53
15	Spectral Width	25252.5
16	Lowest Frequency	-2569.9
17	Nucleus	13C
18	Acquired Size	31415
19	Spectral Size	52430
20	Digital Resolution	0.48



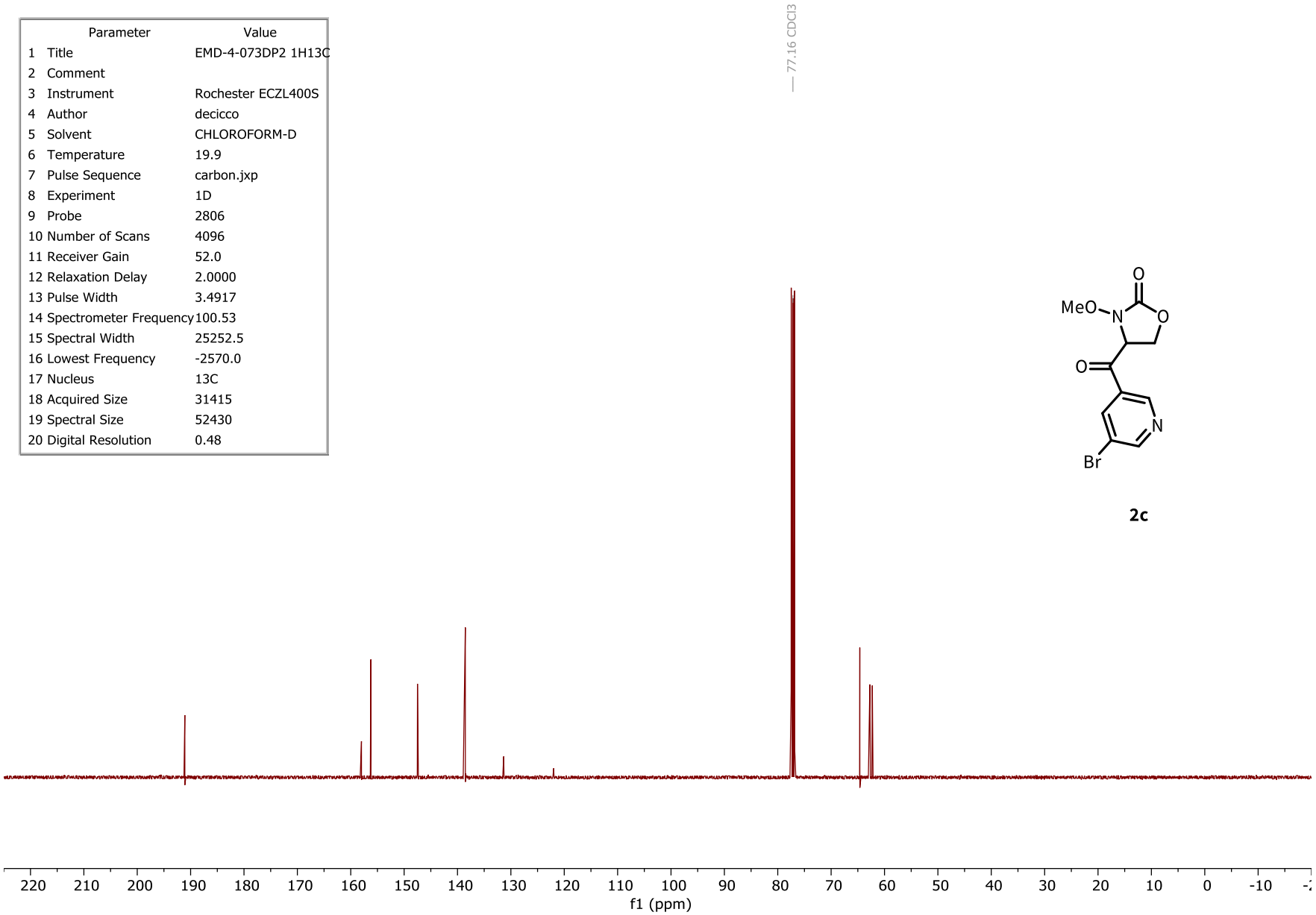
2b

	Parameter	Value
1	Title	EMD-4-073DP2 1H13C
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.2
7	Pulse Sequence	proton.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	64
11	Receiver Gain	52.0
12	Relaxation Delay	4.0000
13	Pulse Width	3.0215
14	Spectrometer Frequency	399.78
15	Spectral Width	6006.0
16	Lowest Frequency	-999.3
17	Nucleus	1H
18	Acquired Size	14993
19	Spectral Size	52430
20	Digital Resolution	0.11



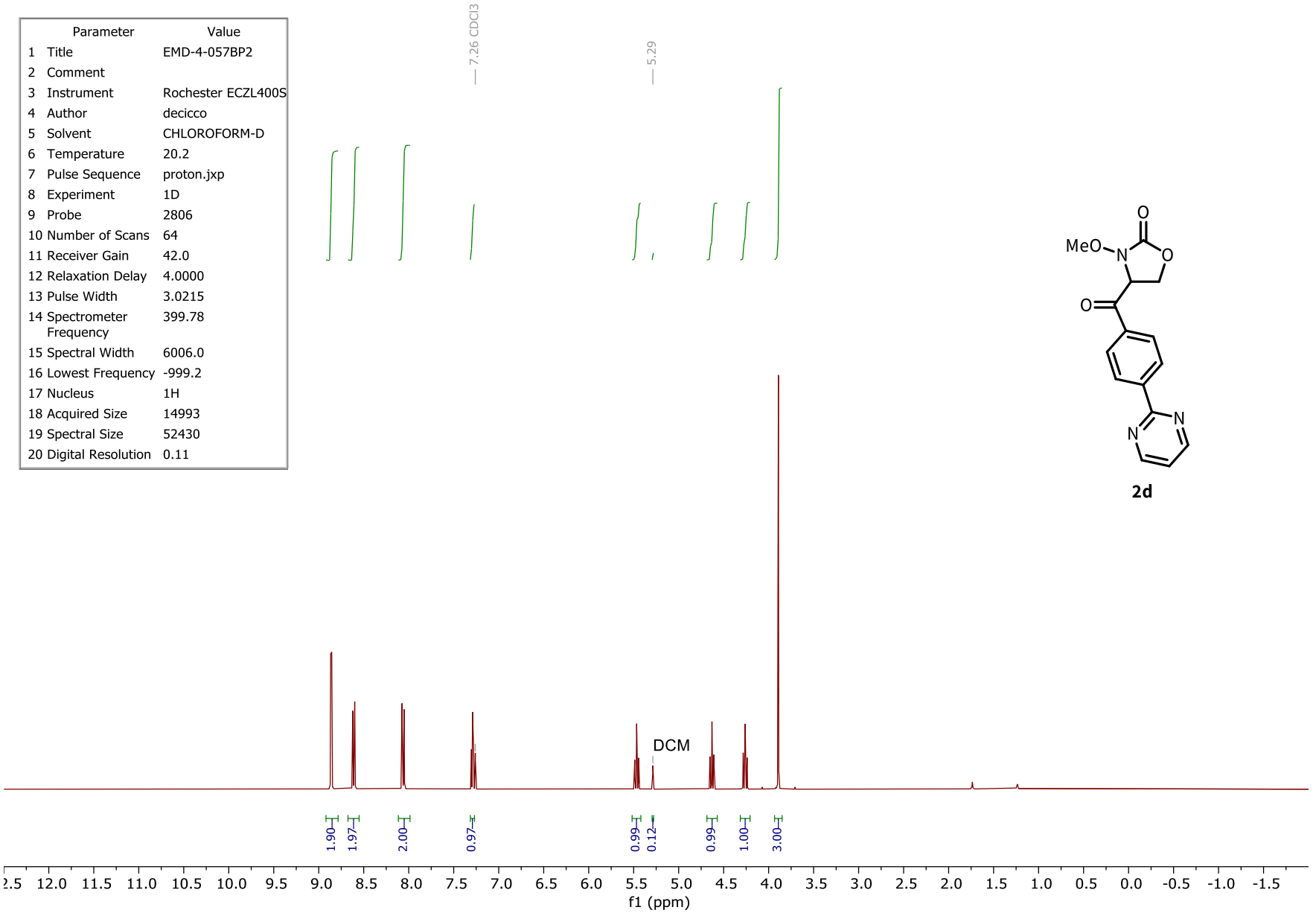
2c

	Parameter	Value
1	Title	EMD-4-073DP2 1H13C
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	19.9
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	4096
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	3.4917
14	Spectrometer Frequency	100.53
15	Spectral Width	25252.5
16	Lowest Frequency	-2570.0
17	Nucleus	13C
18	Acquired Size	31415
19	Spectral Size	52430
20	Digital Resolution	0.48



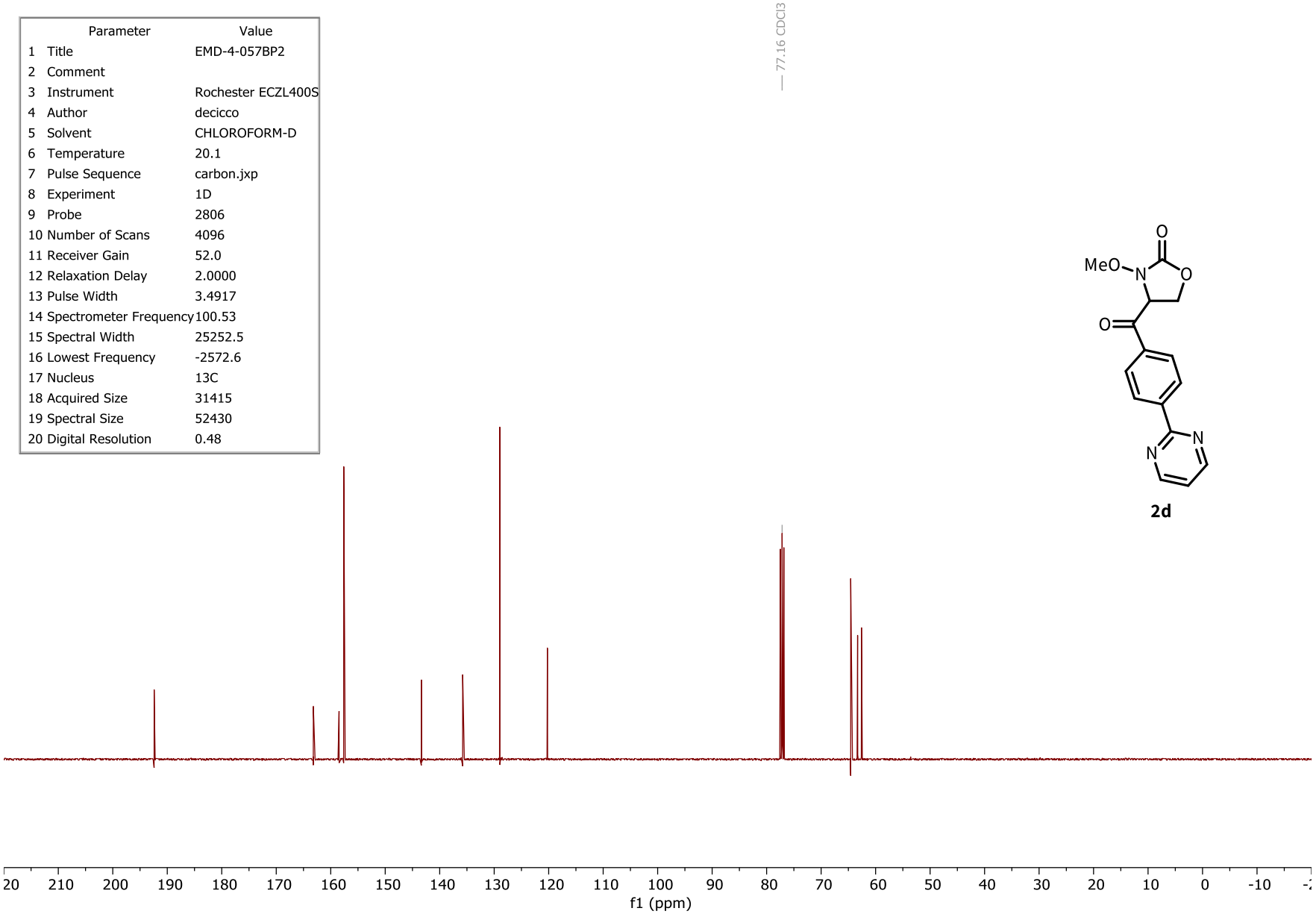
2c

	Parameter	Value
1	Title	EMD-4-057BP2
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.2
7	Pulse Sequence	proton.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	64
11	Receiver Gain	42.0
12	Relaxation Delay	4.0000
13	Pulse Width	3.0215
14	Spectrometer Frequency	399.78
15	Spectral Width	6006.0
16	Lowest Frequency	-999.2
17	Nucleus	1H
18	Acquired Size	14993
19	Spectral Size	52430
20	Digital Resolution	0.11

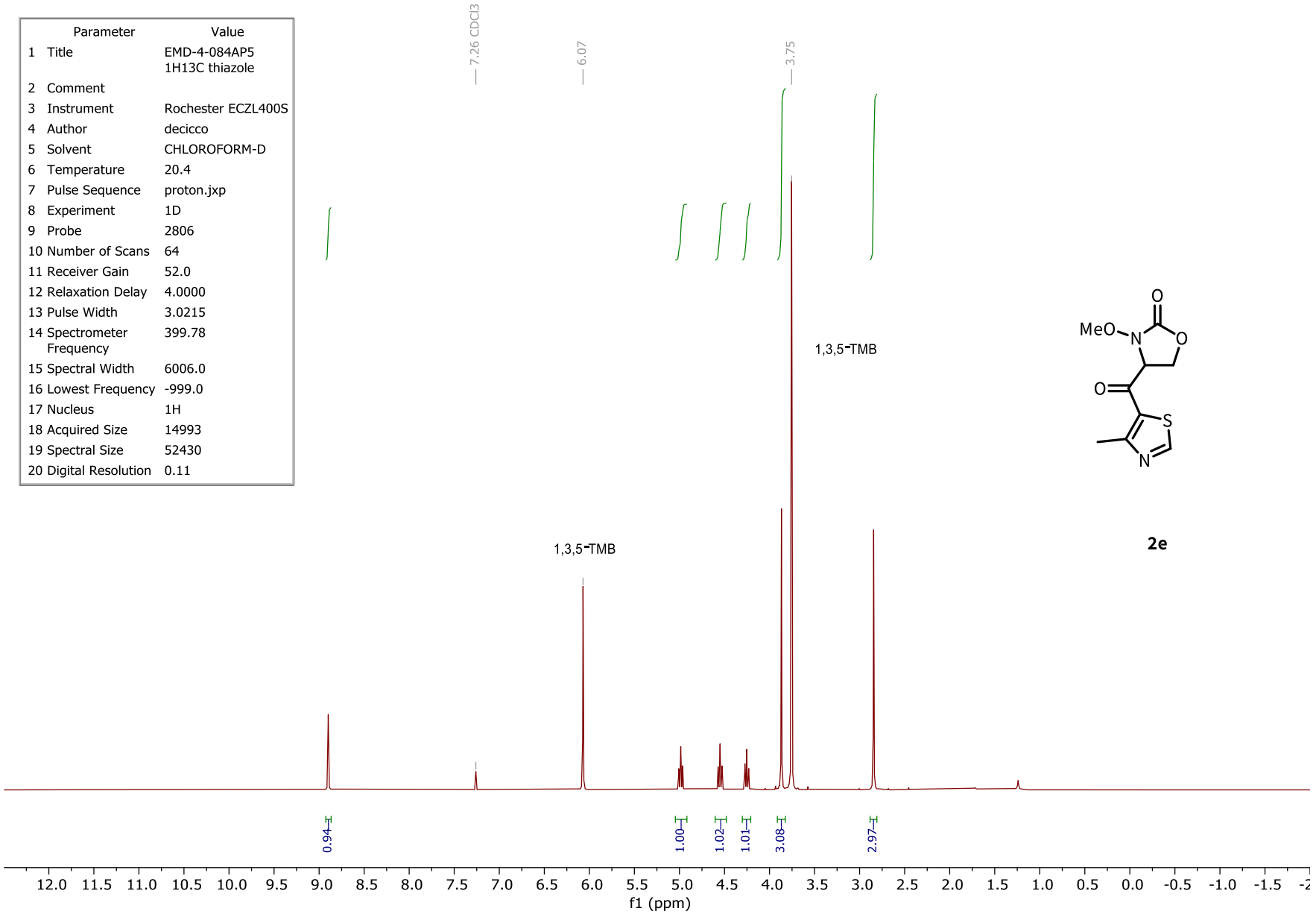


2d

	Parameter	Value
1	Title	EMD-4-057BP2
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.1
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	4096
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	3.4917
14	Spectrometer Frequency	100.53
15	Spectral Width	25252.5
16	Lowest Frequency	-2572.6
17	Nucleus	13C
18	Acquired Size	31415
19	Spectral Size	52430
20	Digital Resolution	0.48

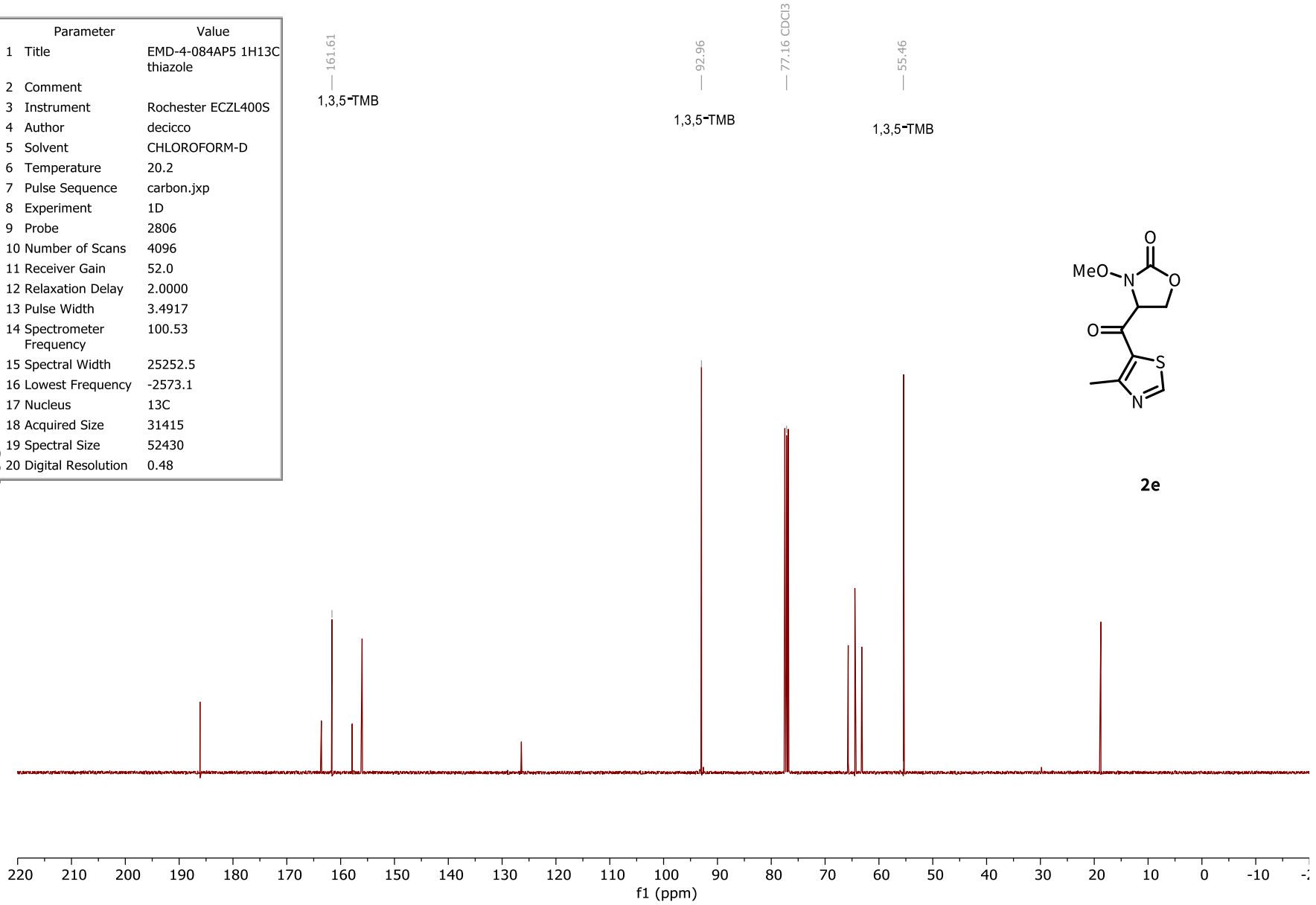


	Parameter	Value
1	Title	EMD-4-084AP5 1H13C thiazole
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.4
7	Pulse Sequence	proton.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	64
11	Receiver Gain	52.0
12	Relaxation Delay	4.0000
13	Pulse Width	3.0215
14	Spectrometer Frequency	399.78
15	Spectral Width	6006.0
16	Lowest Frequency	-999.0
17	Nucleus	1H
18	Acquired Size	14993
19	Spectral Size	52430
20	Digital Resolution	0.11

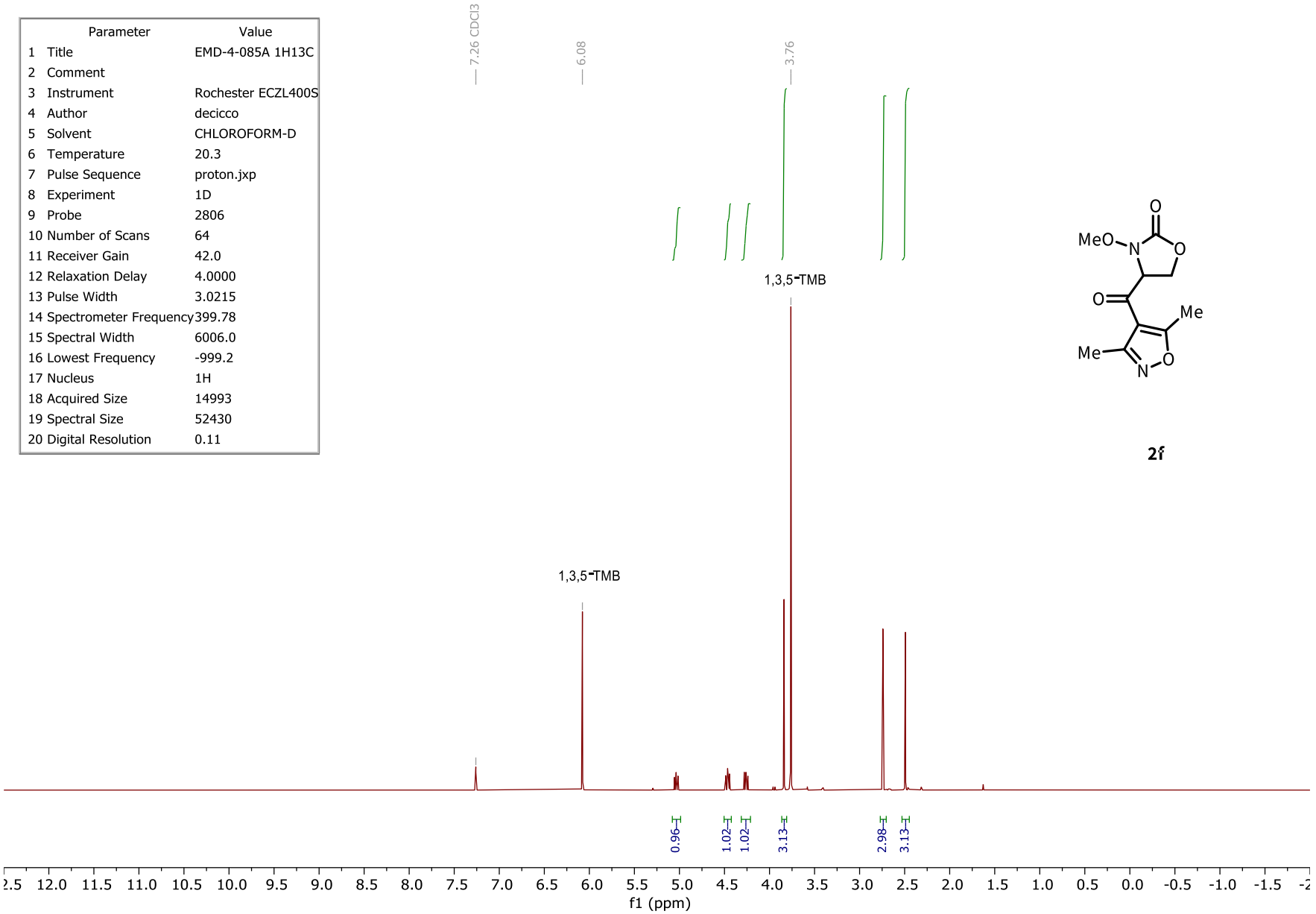


2e

	Parameter	Value
1	Title	EMD-4-084AP5 1H13C thiazole
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.2
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	4096
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	3.4917
14	Spectrometer Frequency	100.53
15	Spectral Width	25252.5
16	Lowest Frequency	-2573.1
17	Nucleus	13C
18	Acquired Size	31415
19	Spectral Size	52430
20	Digital Resolution	0.48

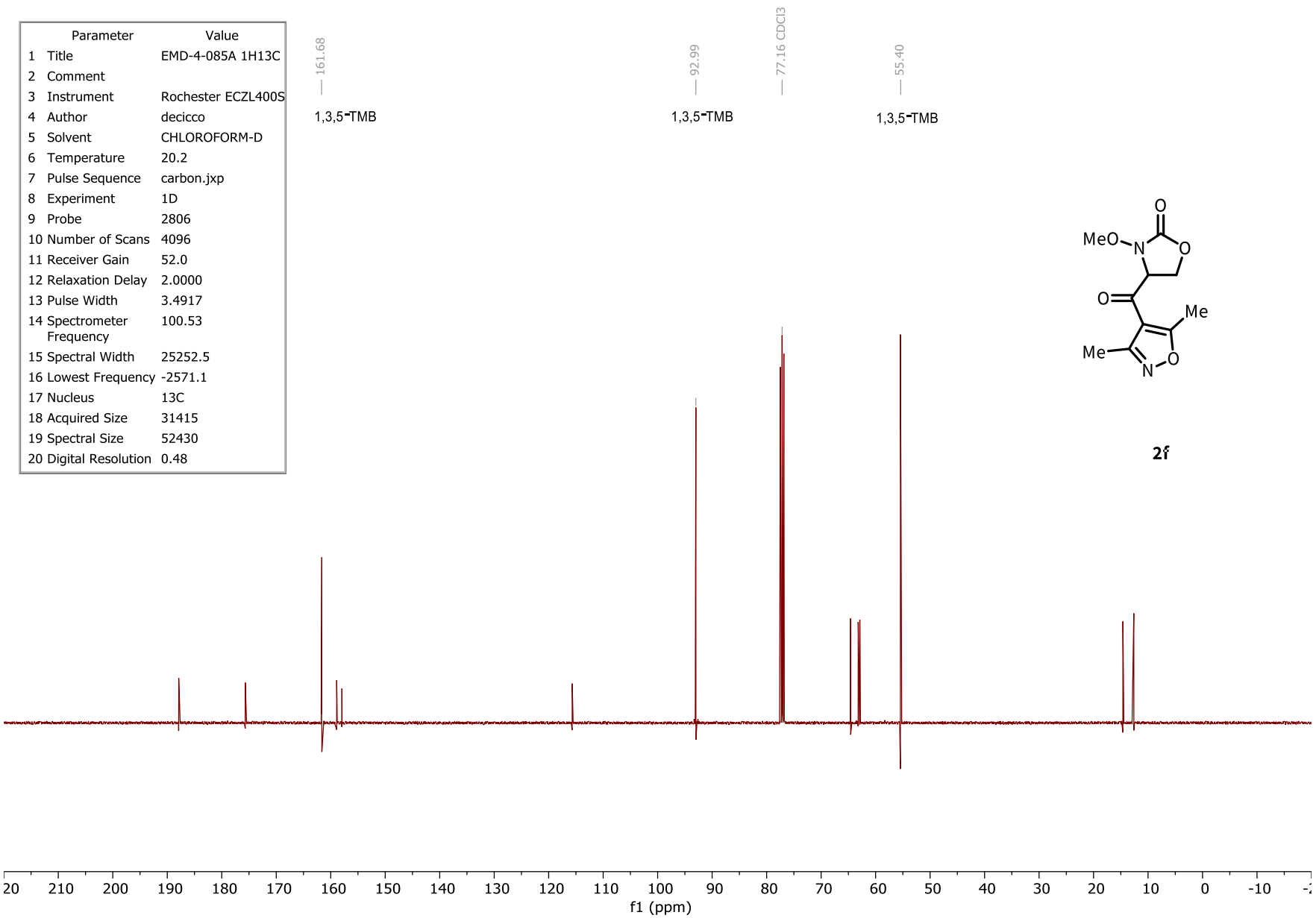


	Parameter	Value
1	Title	EMD-4-085A 1H13C
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.3
7	Pulse Sequence	proton.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	64
11	Receiver Gain	42.0
12	Relaxation Delay	4.0000
13	Pulse Width	3.0215
14	Spectrometer Frequency	399.78
15	Spectral Width	6006.0
16	Lowest Frequency	-999.2
17	Nucleus	1H
18	Acquired Size	14993
19	Spectral Size	52430
20	Digital Resolution	0.11

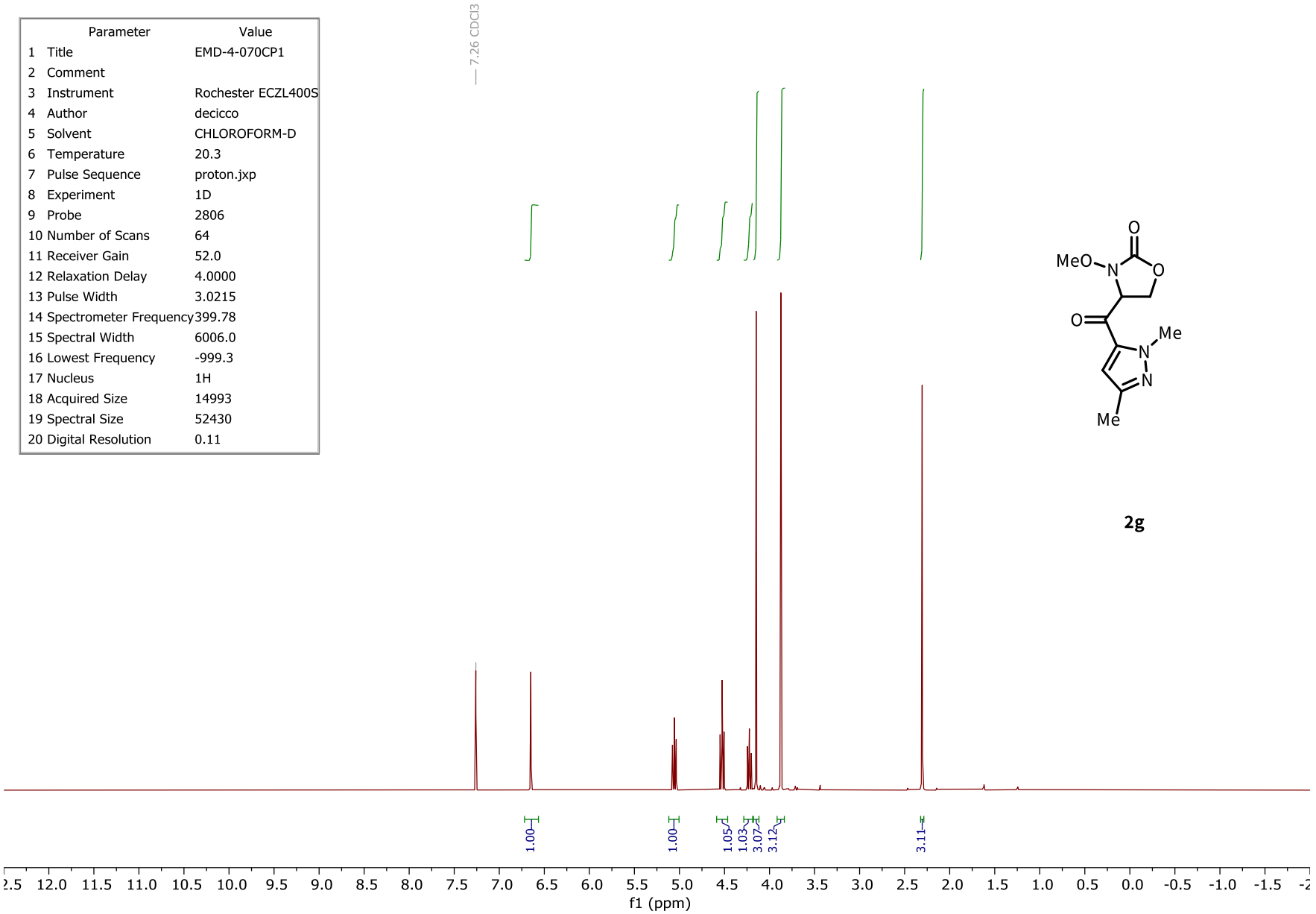


2f

	Parameter	Value
1	Title	EMD-4-085A 1H13C
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.2
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	4096
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	3.4917
14	Spectrometer Frequency	100.53
15	Spectral Width	25252.5
16	Lowest Frequency	-2571.1
17	Nucleus	13C
18	Acquired Size	31415
19	Spectral Size	52430
20	Digital Resolution	0.48

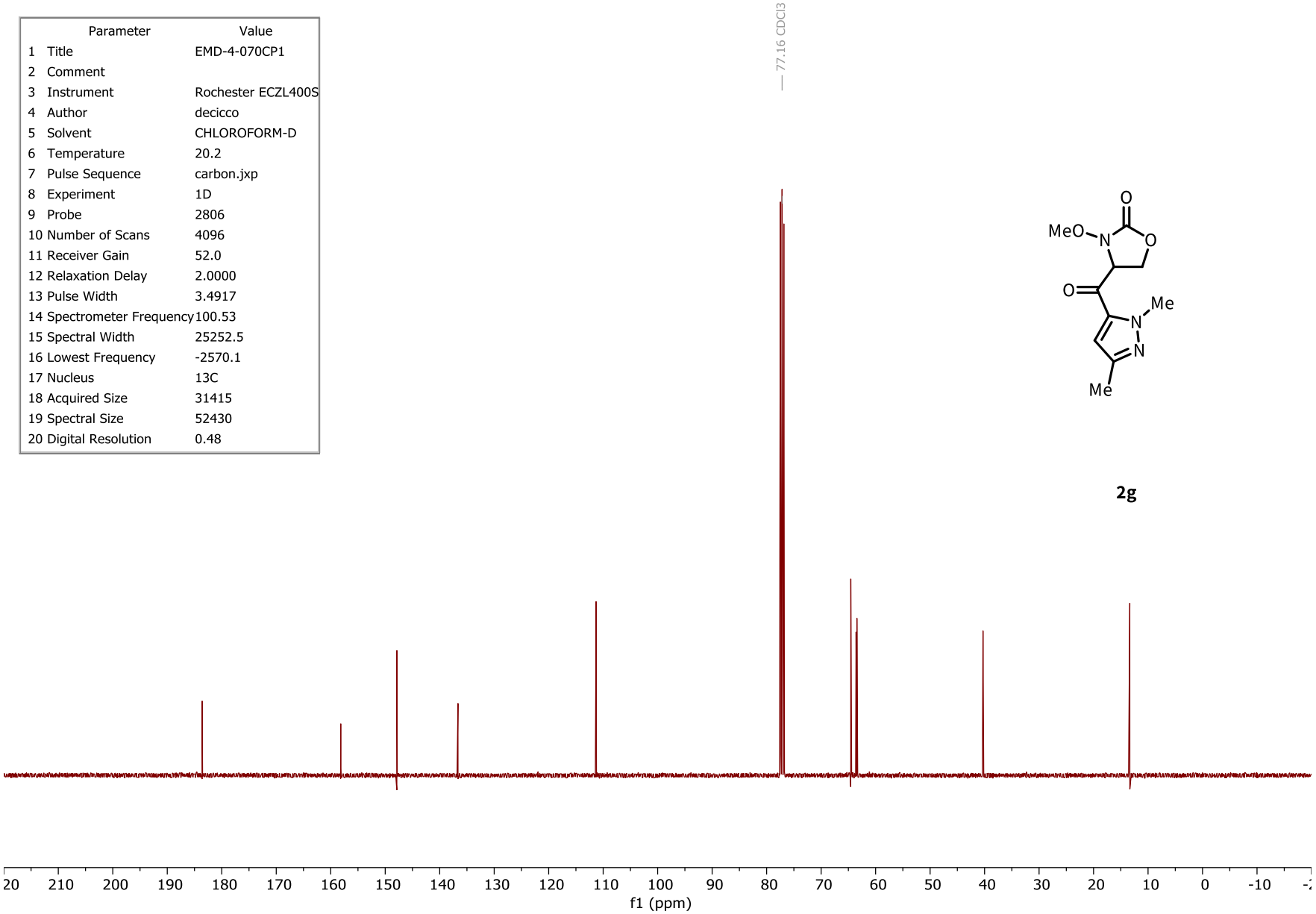


	Parameter	Value
1	Title	EMD-4-070CP1
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.3
7	Pulse Sequence	proton.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	64
11	Receiver Gain	52.0
12	Relaxation Delay	4.0000
13	Pulse Width	3.0215
14	Spectrometer Frequency	399.78
15	Spectral Width	6006.0
16	Lowest Frequency	-999.3
17	Nucleus	1H
18	Acquired Size	14993
19	Spectral Size	52430
20	Digital Resolution	0.11

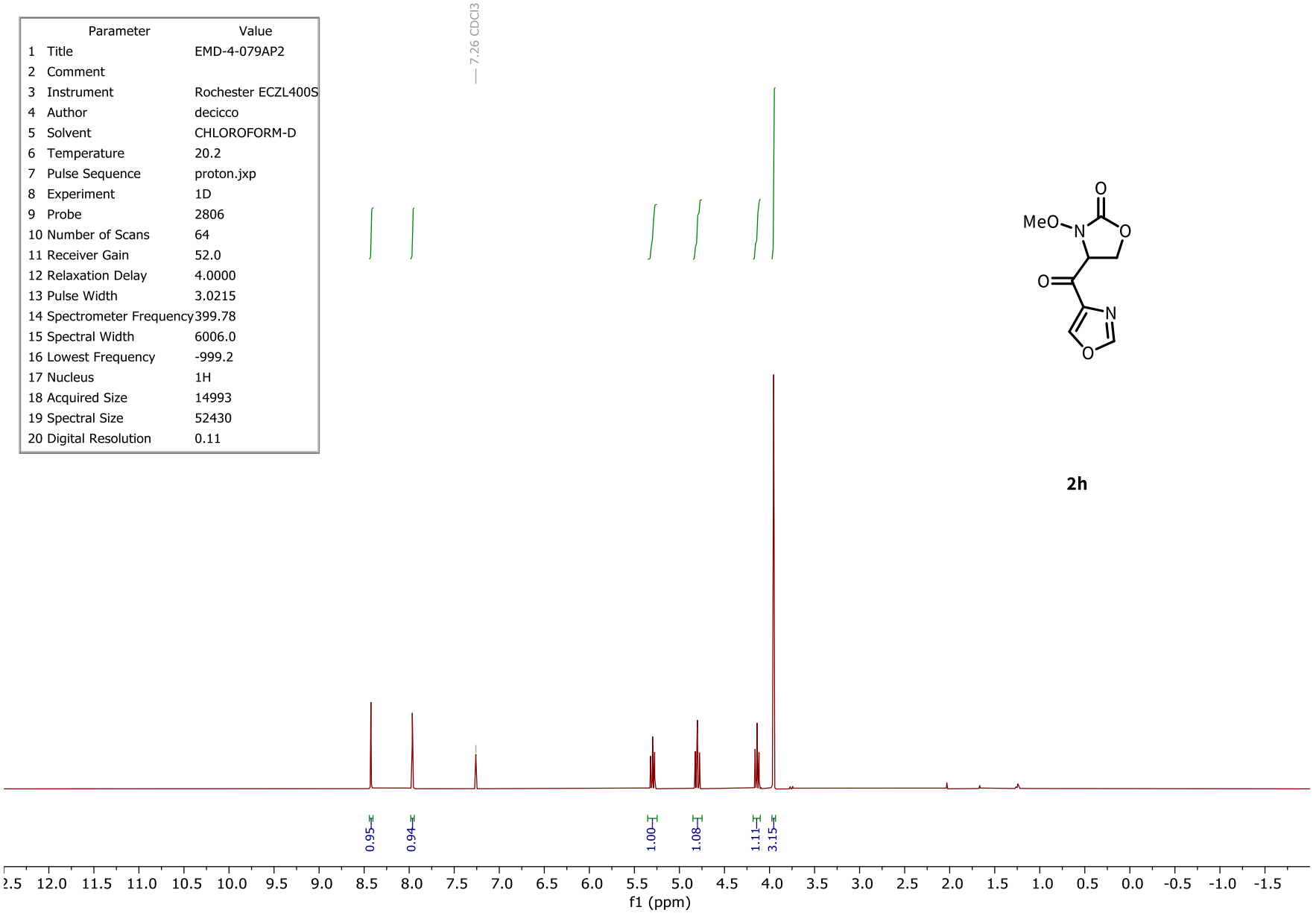


2g

	Parameter	Value
1	Title	EMD-4-070CP1
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.2
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	4096
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	3.4917
14	Spectrometer Frequency	100.53
15	Spectral Width	25252.5
16	Lowest Frequency	-2570.1
17	Nucleus	13C
18	Acquired Size	31415
19	Spectral Size	52430
20	Digital Resolution	0.48

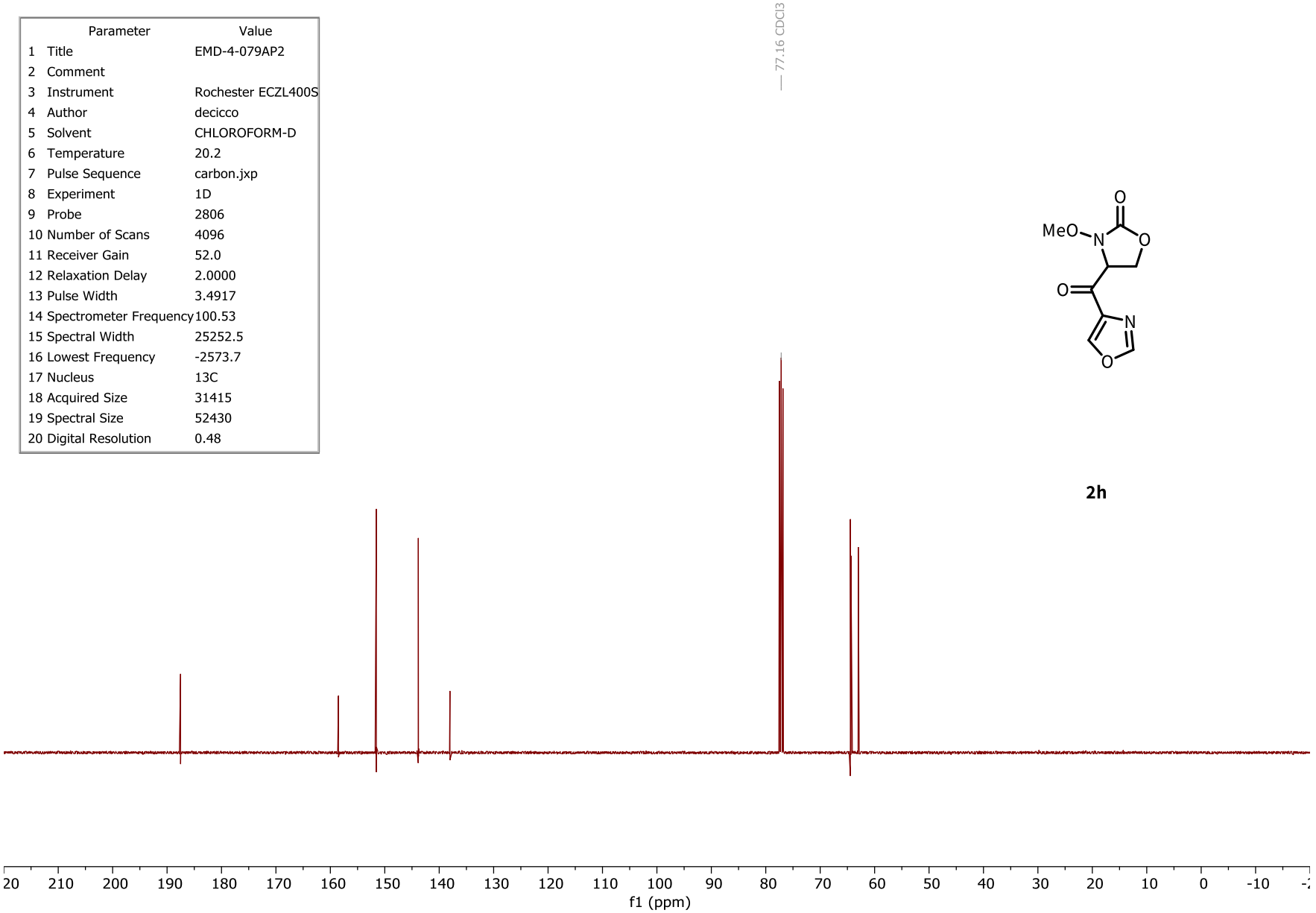


	Parameter	Value
1	Title	EMD-4-079AP2
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.2
7	Pulse Sequence	proton.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	64
11	Receiver Gain	52.0
12	Relaxation Delay	4.0000
13	Pulse Width	3.0215
14	Spectrometer Frequency	399.78
15	Spectral Width	6006.0
16	Lowest Frequency	-999.2
17	Nucleus	1H
18	Acquired Size	14993
19	Spectral Size	52430
20	Digital Resolution	0.11

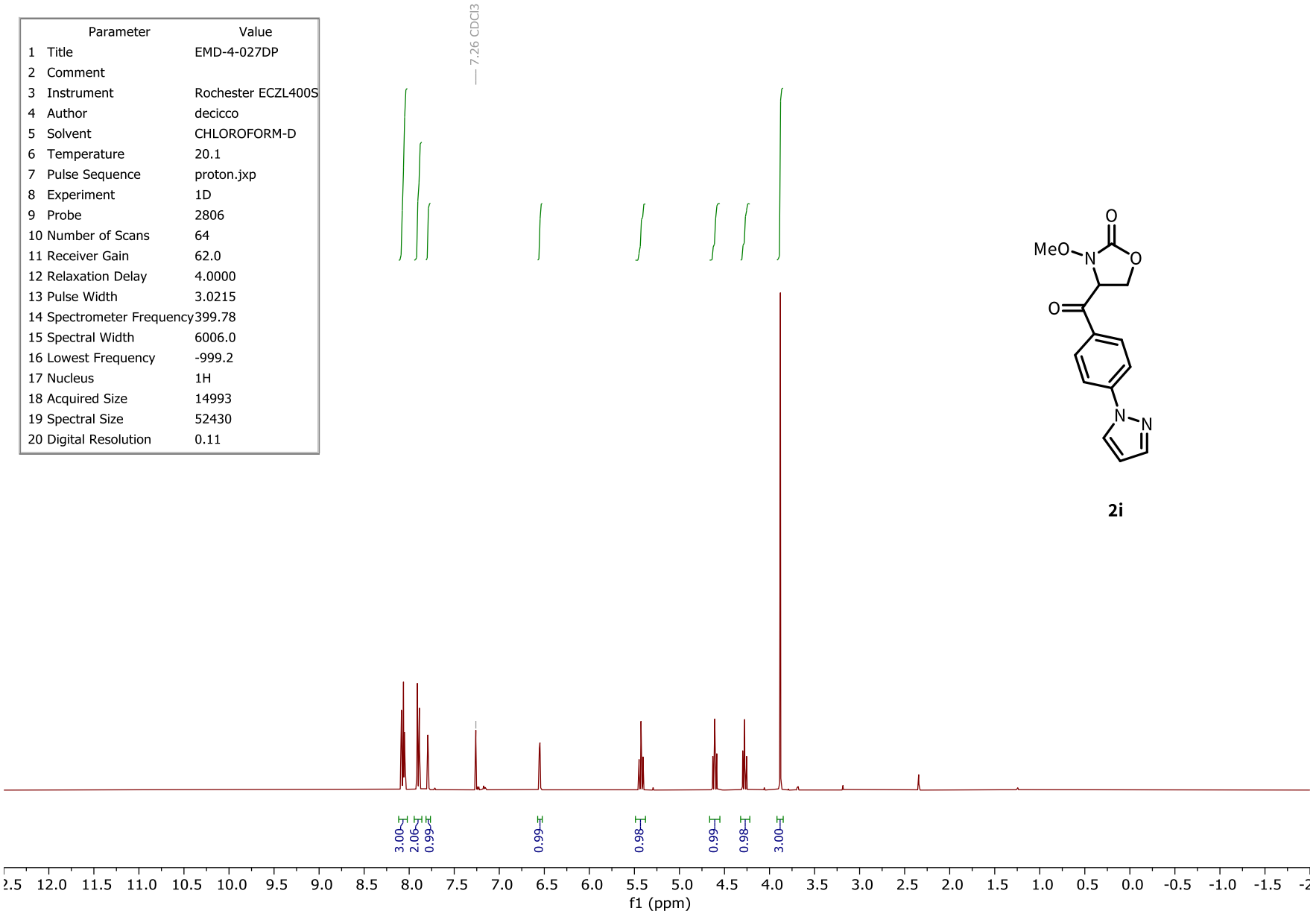


2h

	Parameter	Value
1	Title	EMD-4-079AP2
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.2
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	4096
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	3.4917
14	Spectrometer Frequency	100.53
15	Spectral Width	25252.5
16	Lowest Frequency	-2573.7
17	Nucleus	13C
18	Acquired Size	31415
19	Spectral Size	52430
20	Digital Resolution	0.48

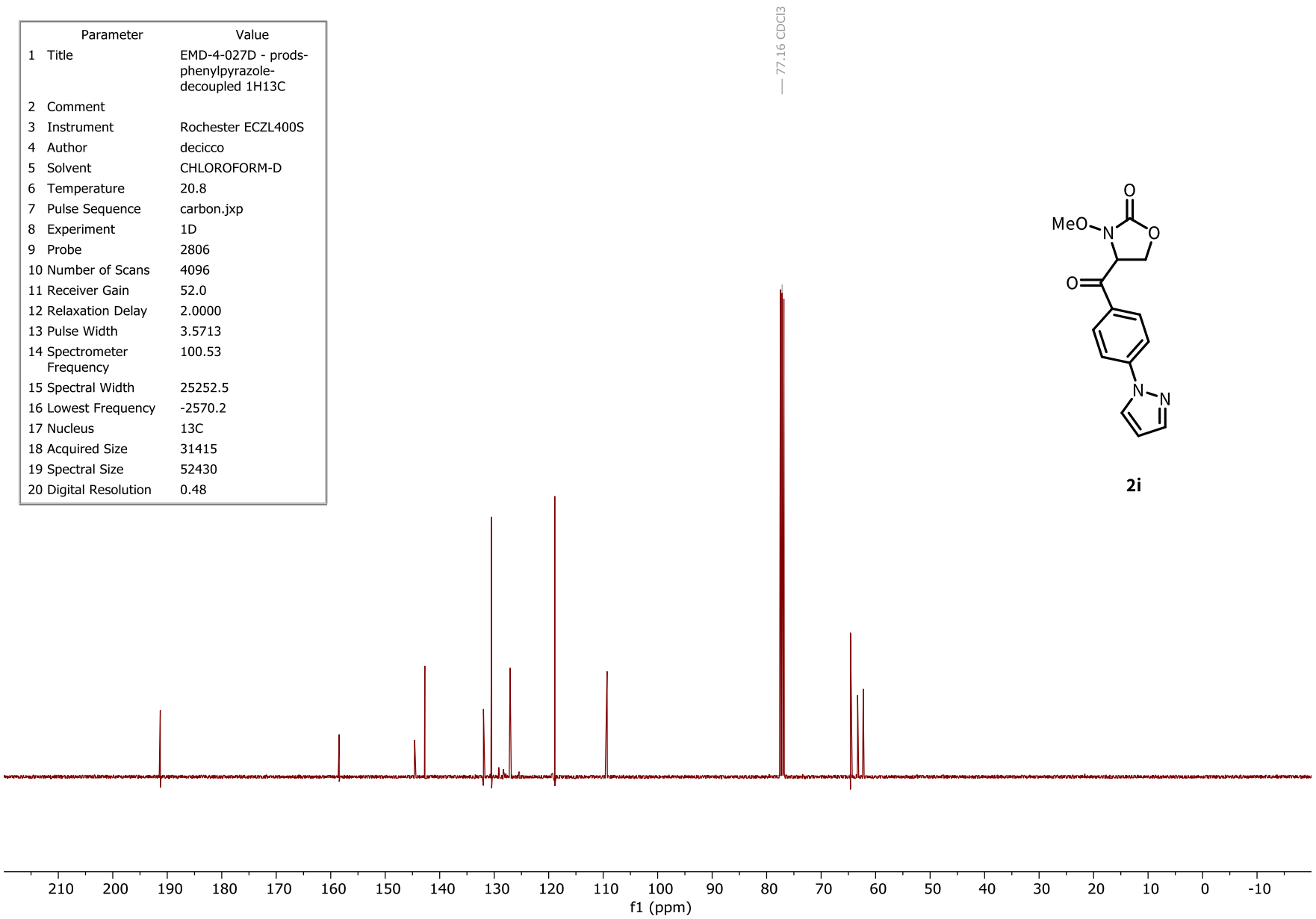


	Parameter	Value
1	Title	EMD-4-027DP
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.1
7	Pulse Sequence	proton.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	64
11	Receiver Gain	62.0
12	Relaxation Delay	4.0000
13	Pulse Width	3.0215
14	Spectrometer Frequency	399.78
15	Spectral Width	6006.0
16	Lowest Frequency	-999.2
17	Nucleus	1H
18	Acquired Size	14993
19	Spectral Size	52430
20	Digital Resolution	0.11

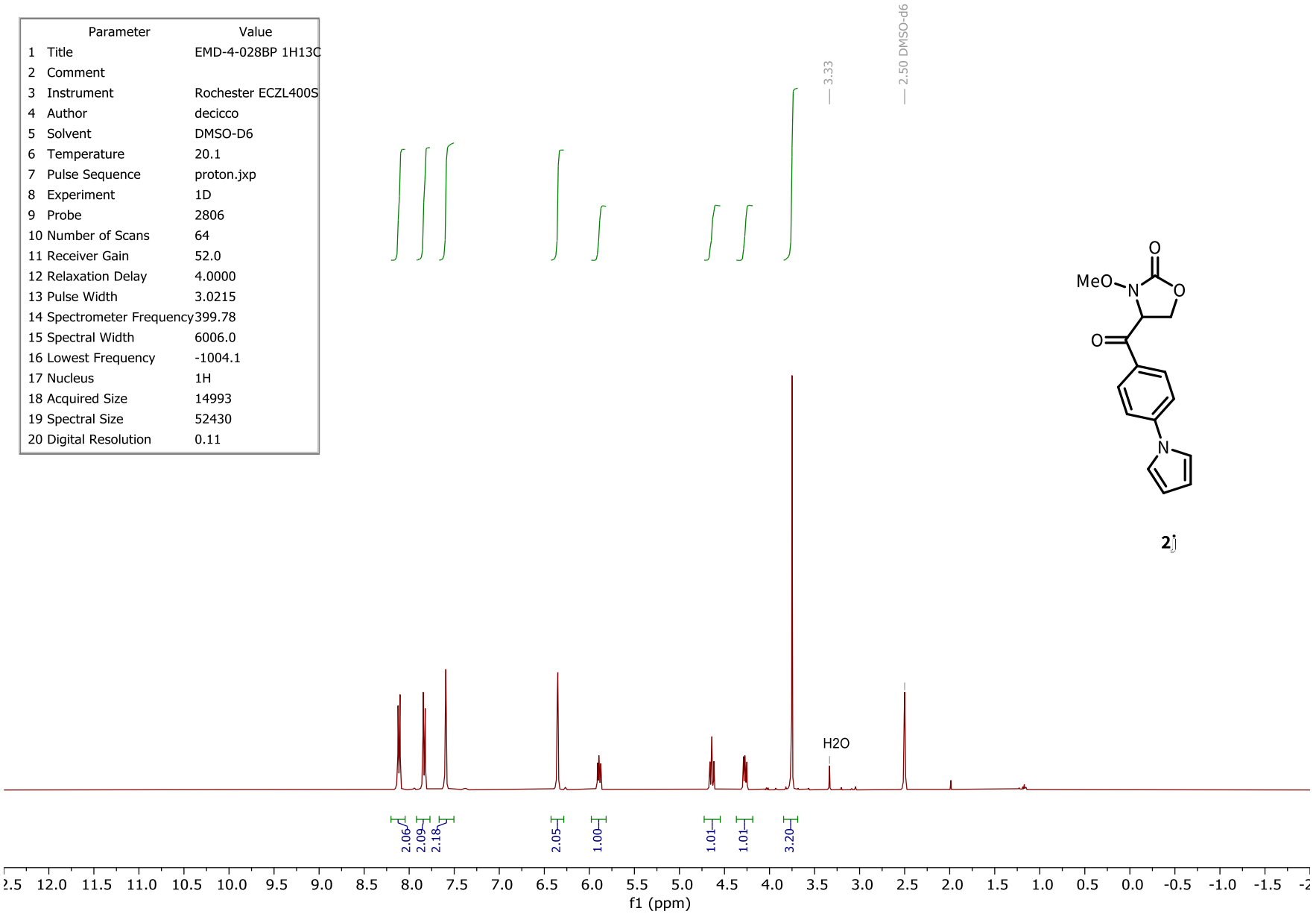


2i

	Parameter	Value
1	Title	EMD-4-027D - prods-phenylpyrazole-decoupled 1H13C
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.8
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	4096
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	3.5713
14	Spectrometer Frequency	100.53
15	Spectral Width	25252.5
16	Lowest Frequency	-2570.2
17	Nucleus	13C
18	Acquired Size	31415
19	Spectral Size	52430
20	Digital Resolution	0.48

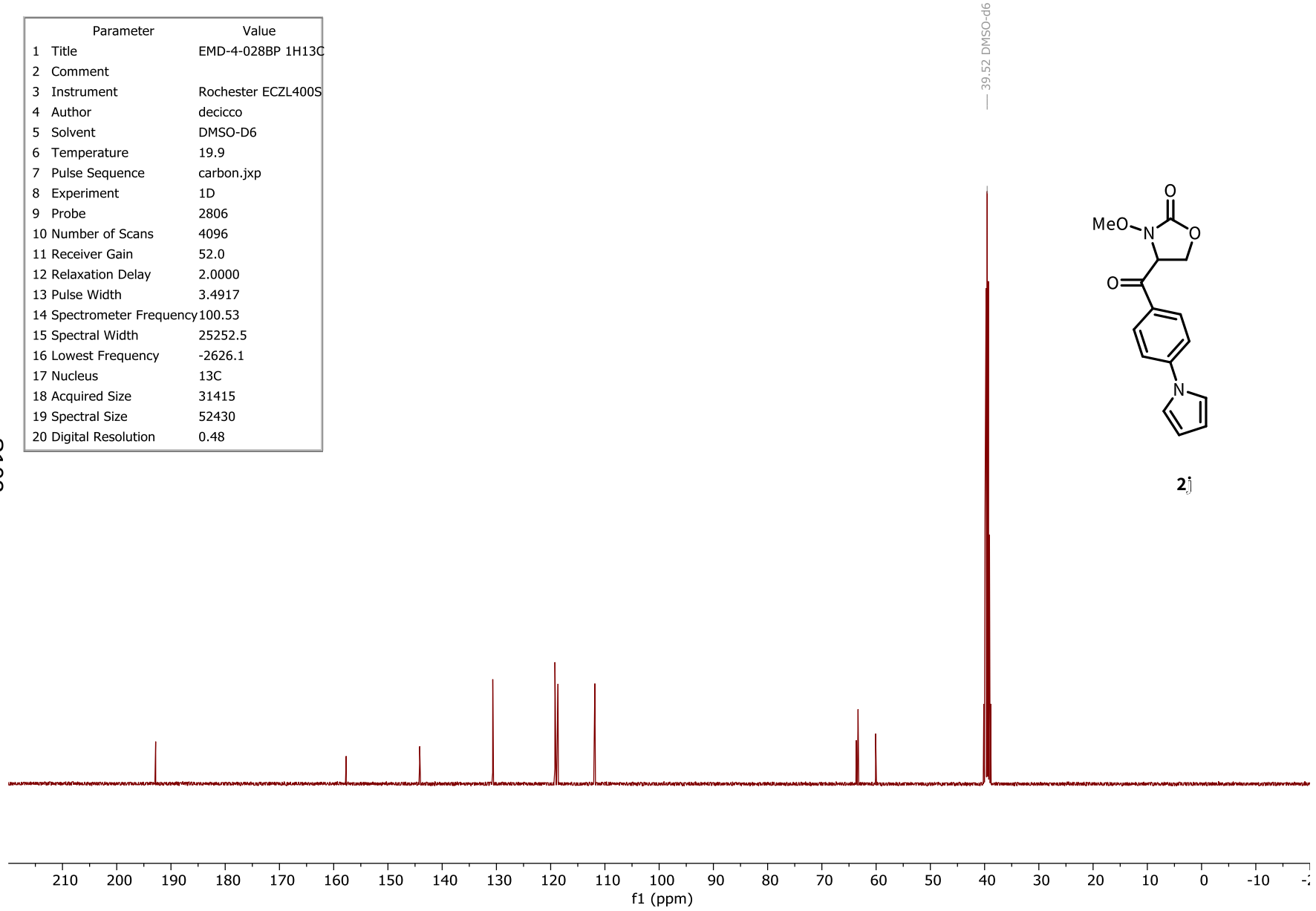


	Parameter	Value
1	Title	EMD-4-028BP 1H13C
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	DMSO-D6
6	Temperature	20.1
7	Pulse Sequence	proton.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	64
11	Receiver Gain	52.0
12	Relaxation Delay	4.0000
13	Pulse Width	3.0215
14	Spectrometer Frequency	399.78
15	Spectral Width	6006.0
16	Lowest Frequency	-1004.1
17	Nucleus	1H
18	Acquired Size	14993
19	Spectral Size	52430
20	Digital Resolution	0.11



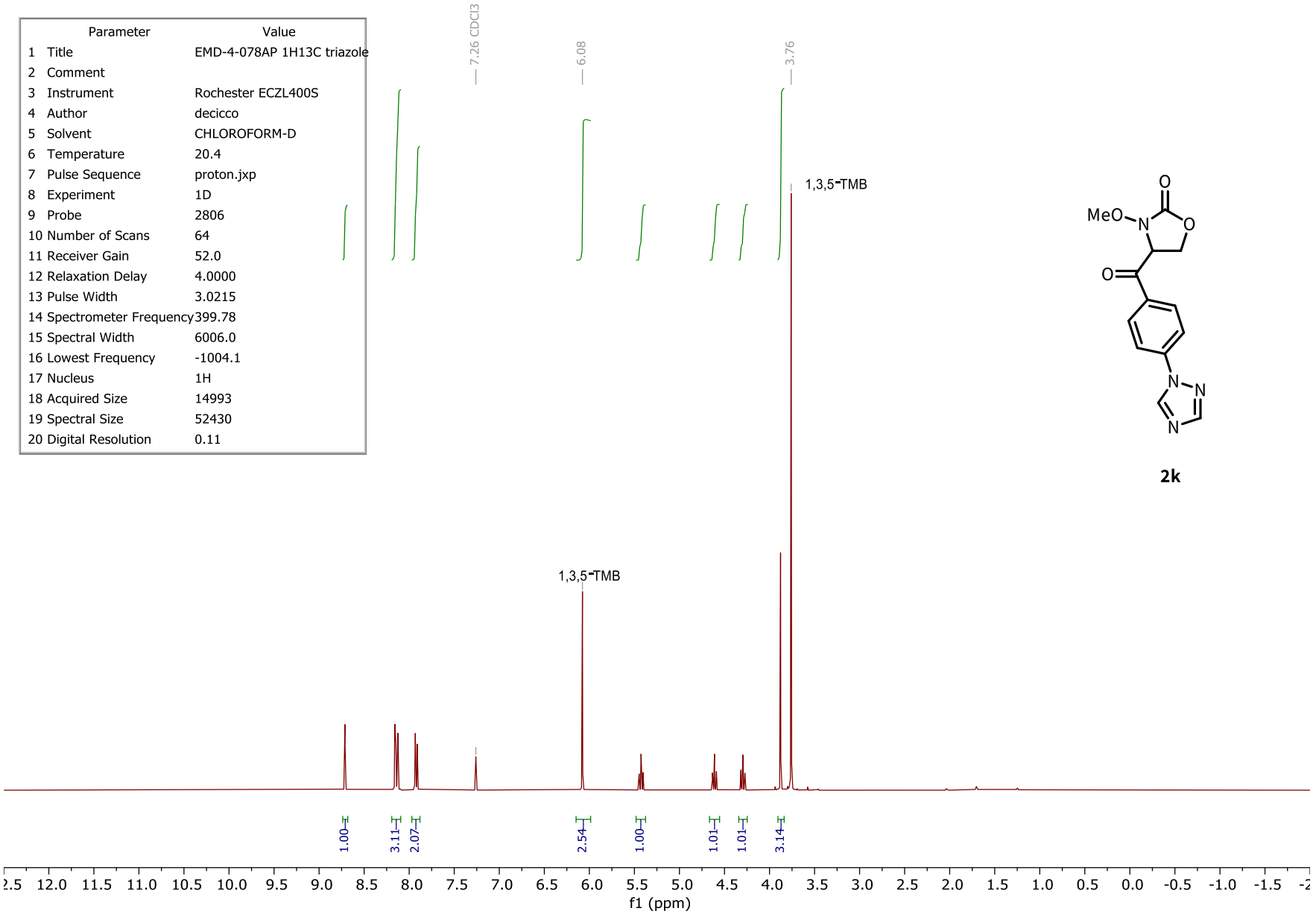
2j

	Parameter	Value
1	Title	EMD-4-028BP 1H13C
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	DMSO-D6
6	Temperature	19.9
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	4096
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	3.4917
14	Spectrometer Frequency	100.53
15	Spectral Width	25252.5
16	Lowest Frequency	-2626.1
17	Nucleus	13C
18	Acquired Size	31415
19	Spectral Size	52430
20	Digital Resolution	0.48



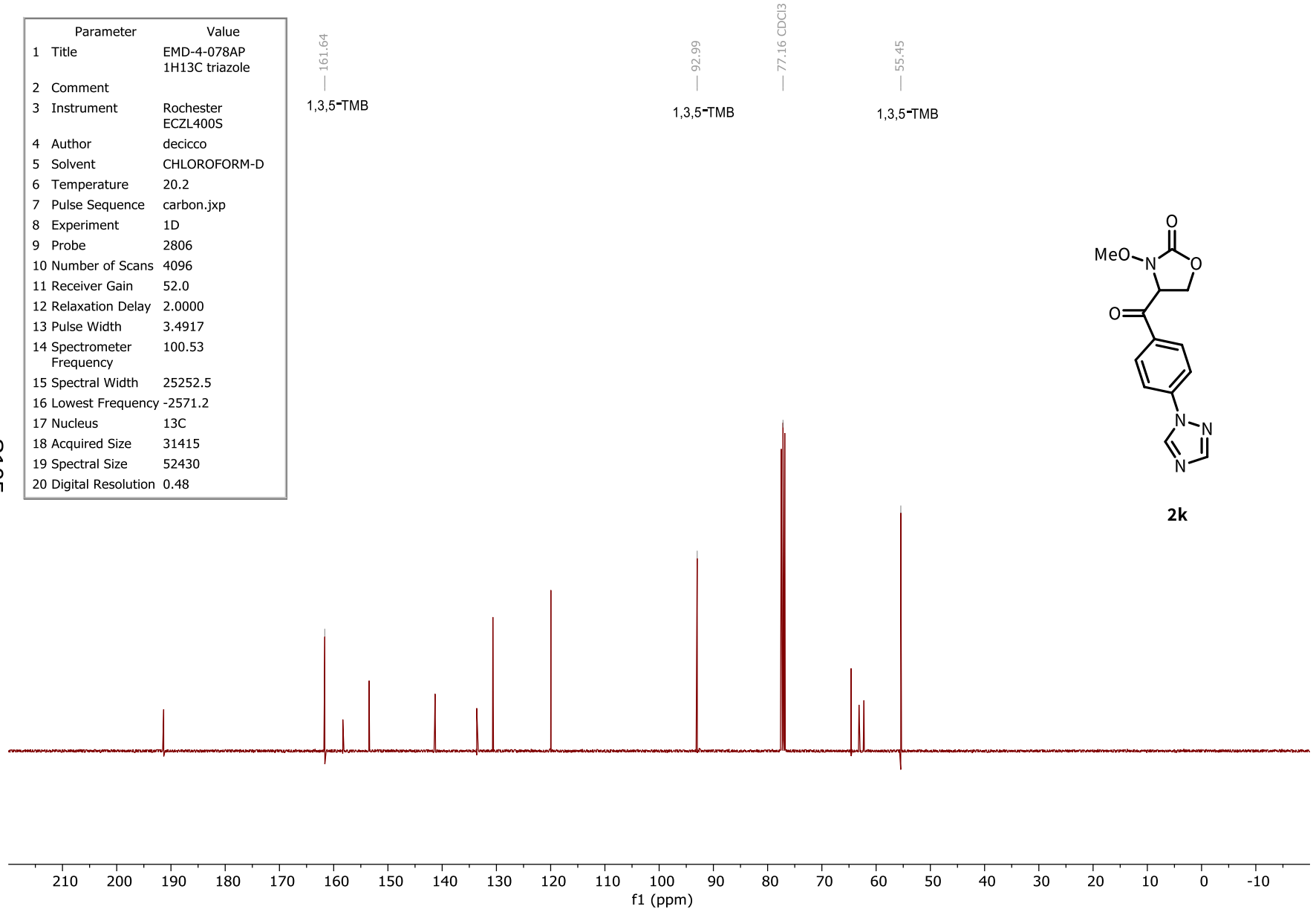
2j

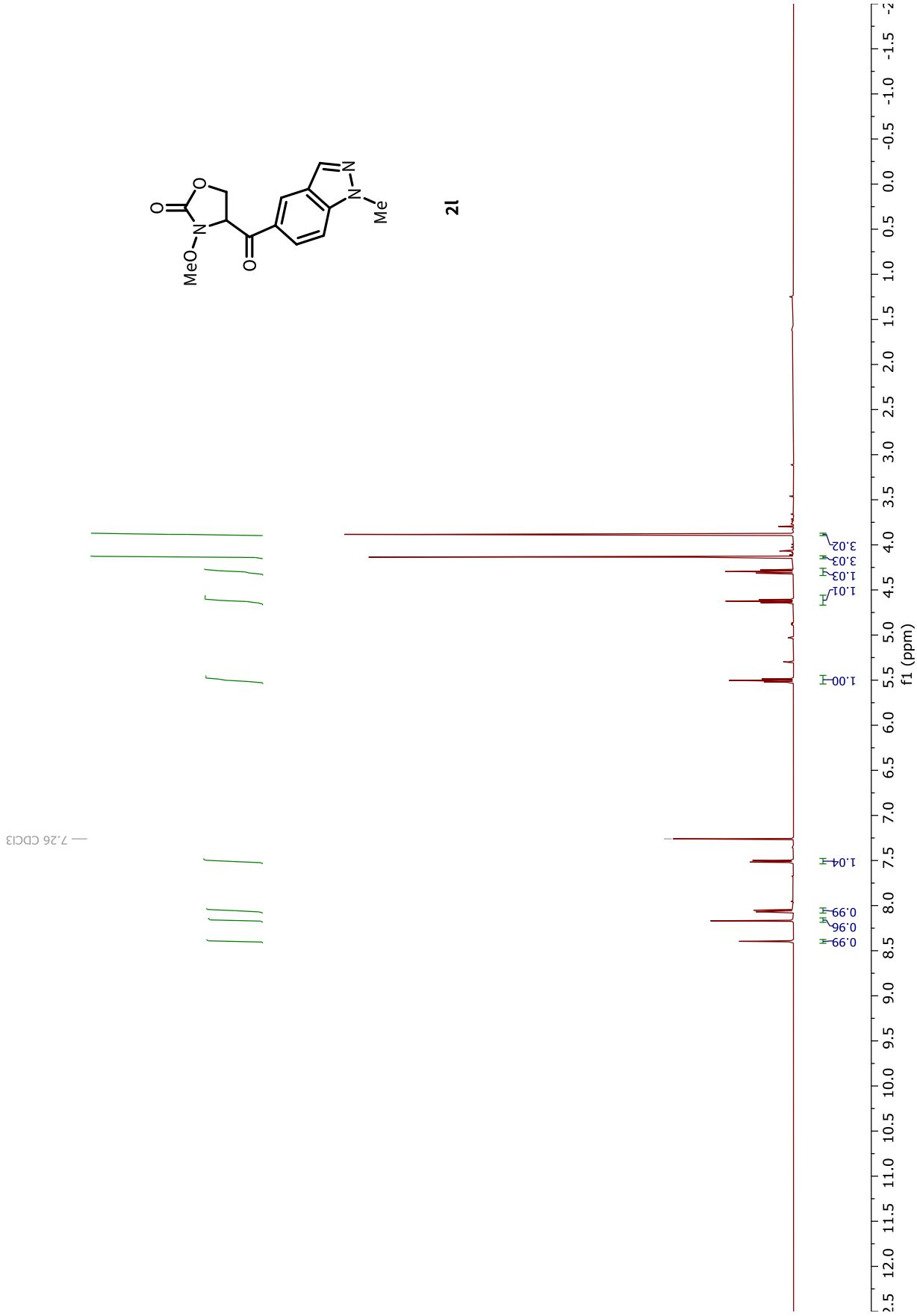
Parameter	Value
1 Title	EMD-4-078AP 1H13C triazole
2 Comment	
3 Instrument	Rochester ECZL400S
4 Author	decicco
5 Solvent	CHLOROFORM-D
6 Temperature	20.4
7 Pulse Sequence	proton.jxp
8 Experiment	1D
9 Probe	2806
10 Number of Scans	64
11 Receiver Gain	52.0
12 Relaxation Delay	4.0000
13 Pulse Width	3.0215
14 Spectrometer Frequency	399.78
15 Spectral Width	6006.0
16 Lowest Frequency	-1004.1
17 Nucleus	1H
18 Acquired Size	14993
19 Spectral Size	52430
20 Digital Resolution	0.11

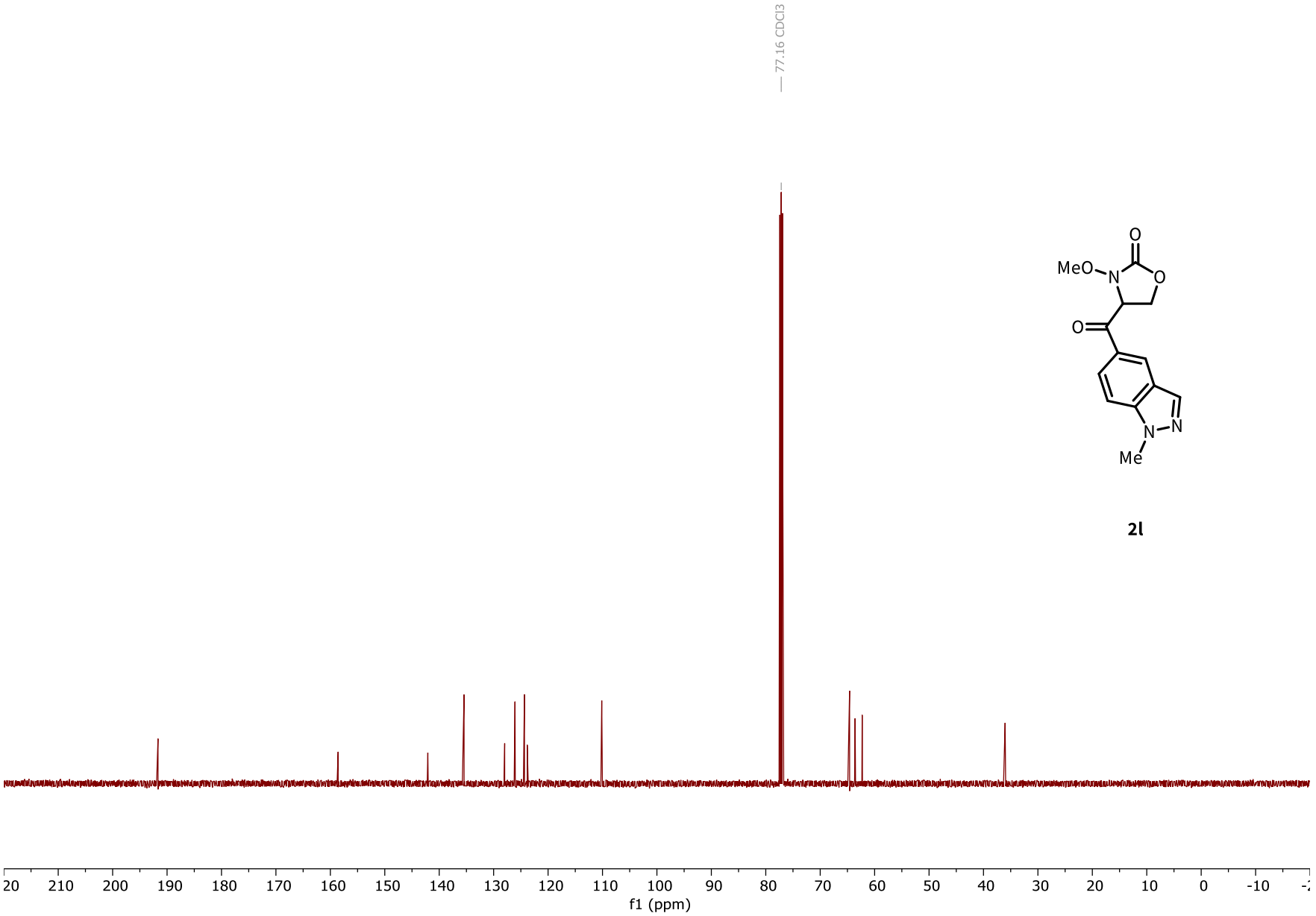


2k

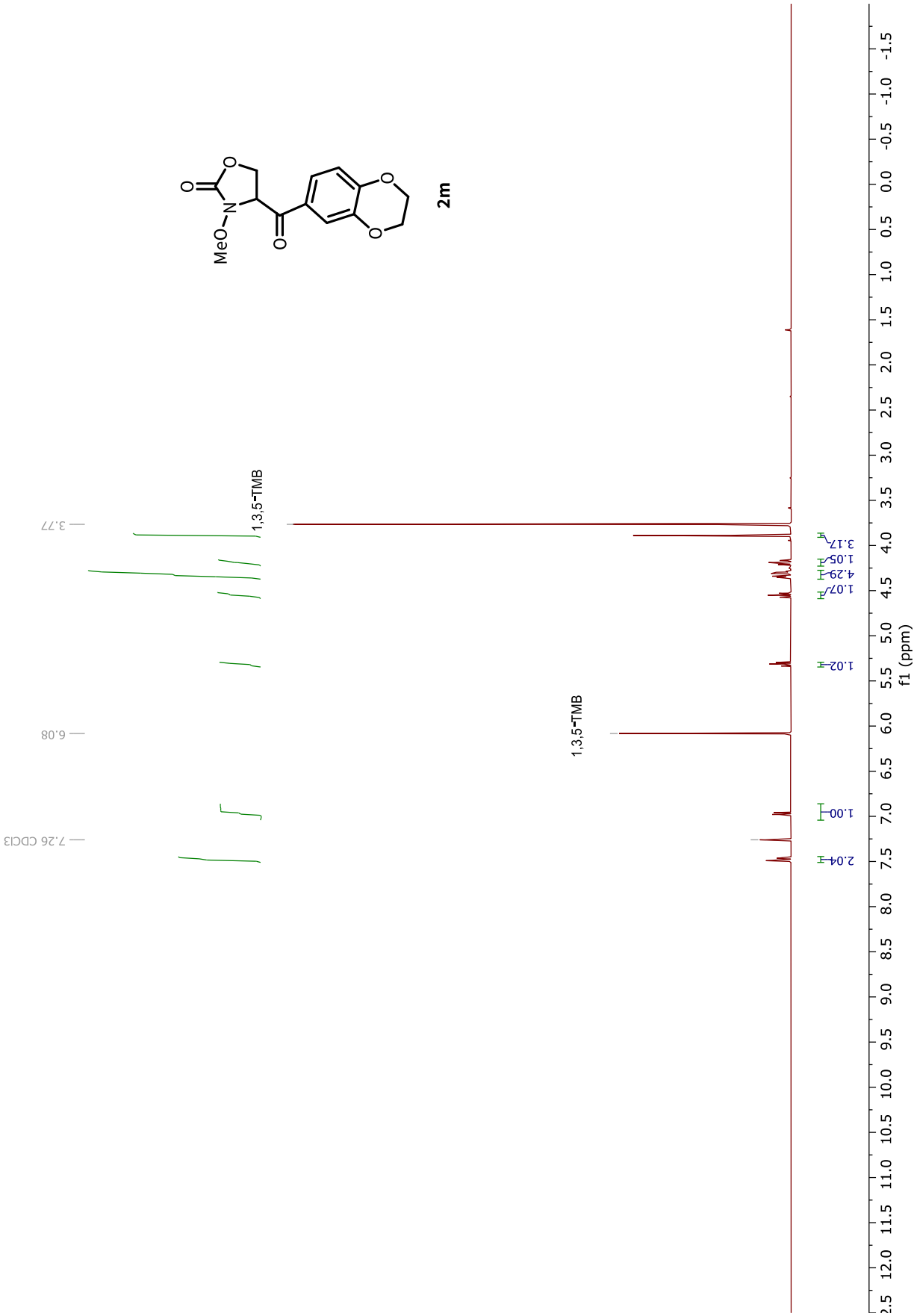
	Parameter	Value
1	Title	EMD-4-078AP 1H13C triazole
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.2
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	4096
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	3.4917
14	Spectrometer Frequency	100.53
15	Spectral Width	25252.5
16	Lowest Frequency	-2571.2
17	Nucleus	13C
18	Acquired Size	31415
19	Spectral Size	52430
20	Digital Resolution	0.48

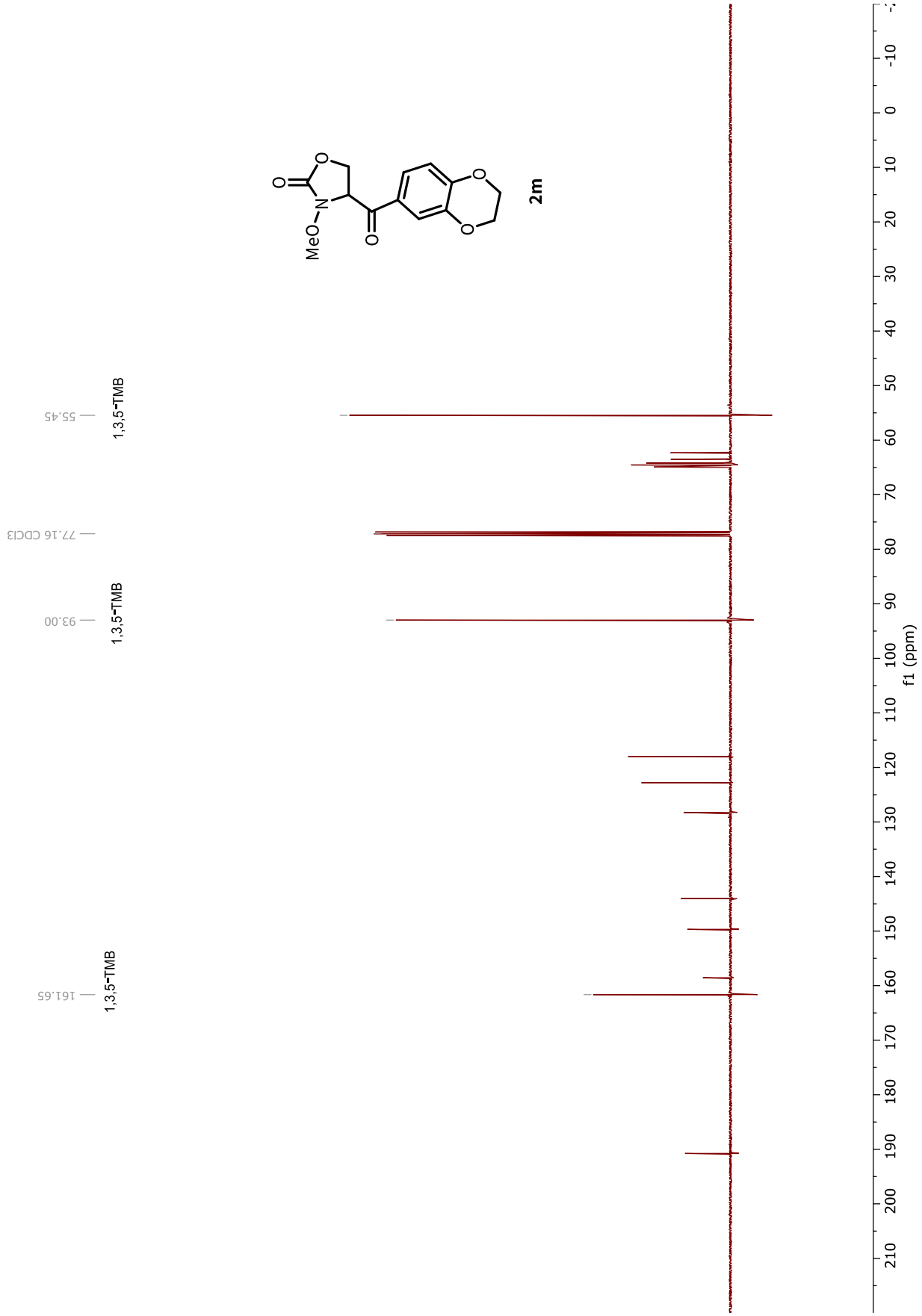



2l
MeO
N
O
O
O
N
N
Me
7.26 CDCl3
3.02
3.03
1.03
1.01
1.00
1.04
0.99
0.96
0.99
f1 (ppm)

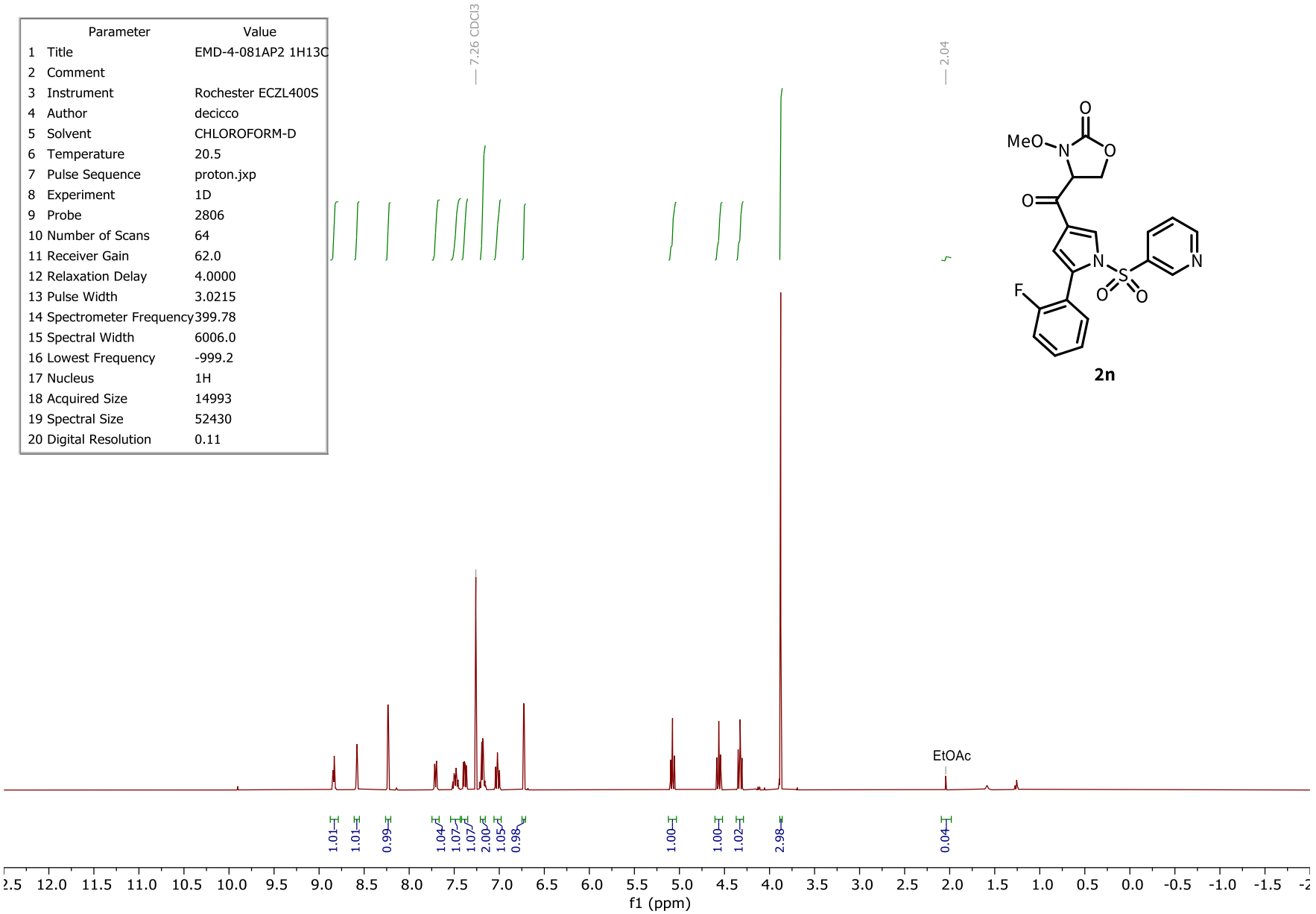


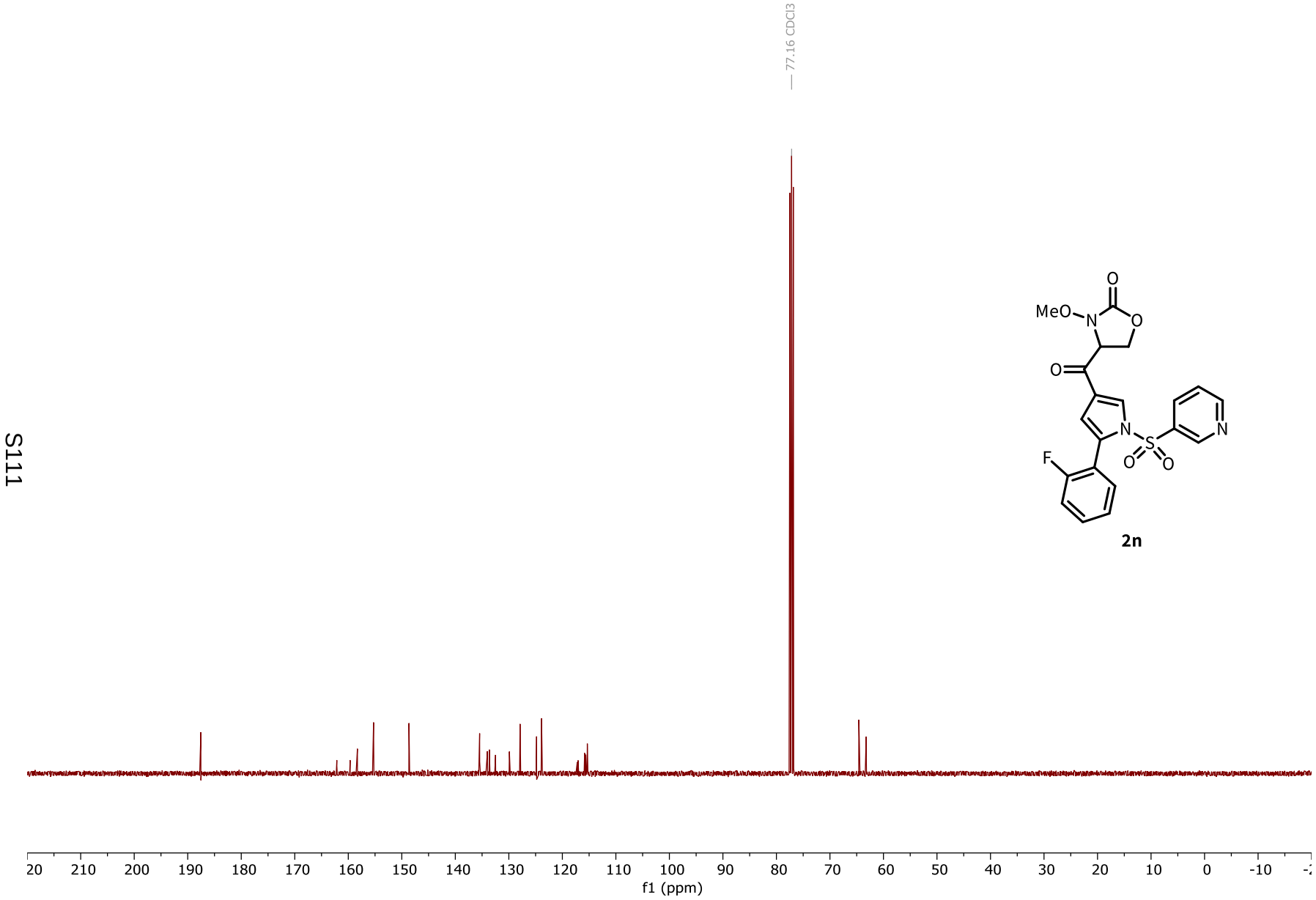
2l


2m
MeO
N
O
O
O
O
O
1,3,5-TMB
1,3,5-TMB
3.77
6.08
7.26 CDCl3
3.17
1.05
4.29
1.07
1.02
1.00
2.04
f1 (ppm)

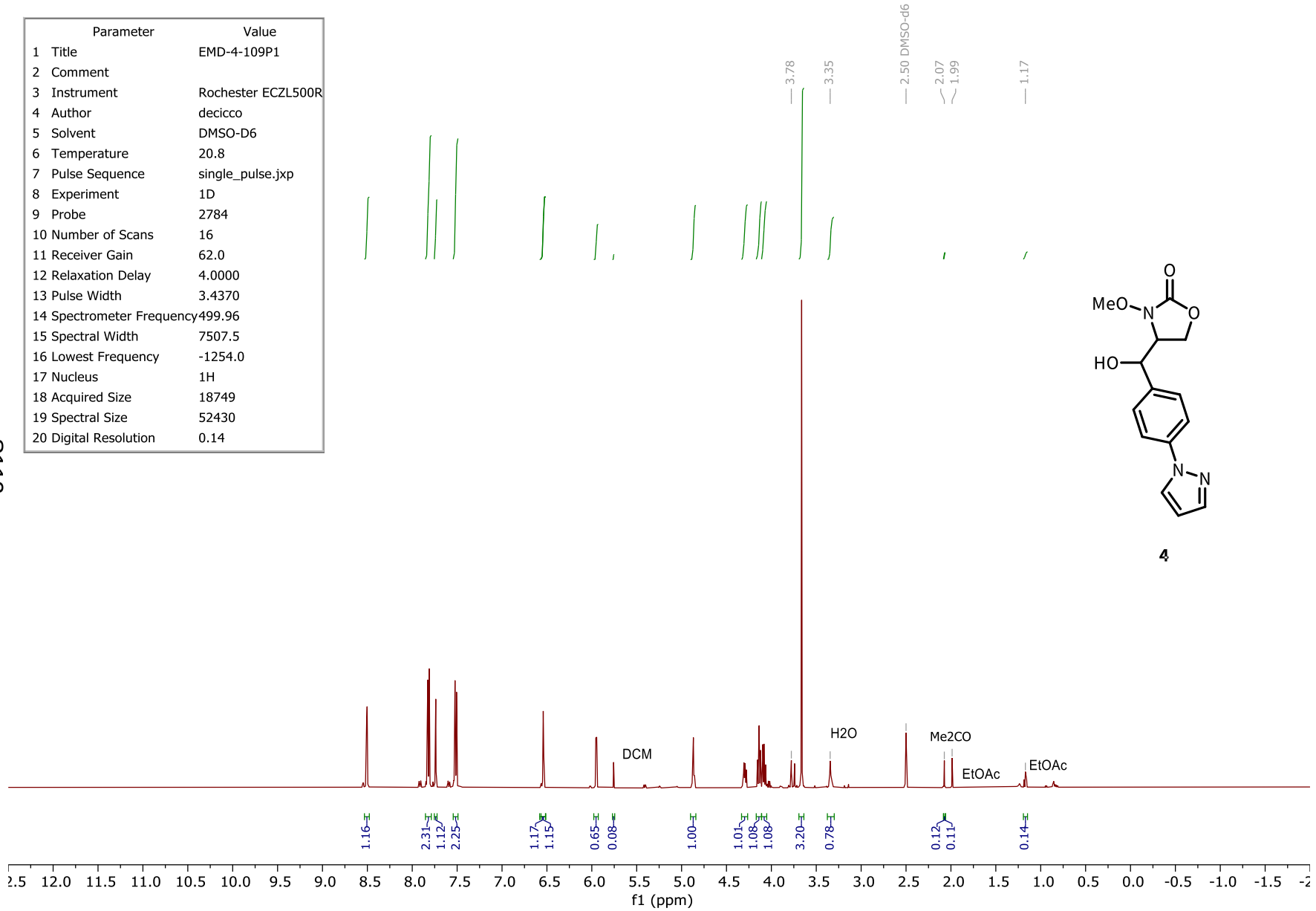

2m
MeO
N
O
O
O
O
O
55.45
1,3,5-TMB
77.16 CDCl3
93.00
1,3,5-TMB
161.65
1,3,5-TMB
f1 (ppm)

	Parameter	Value
1	Title	EMD-4-081AP2 1H13C
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	CHLOROFORM-D
6	Temperature	20.5
7	Pulse Sequence	proton.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	64
11	Receiver Gain	62.0
12	Relaxation Delay	4.0000
13	Pulse Width	3.0215
14	Spectrometer Frequency	399.78
15	Spectral Width	6006.0
16	Lowest Frequency	-999.2
17	Nucleus	1H
18	Acquired Size	14993
19	Spectral Size	52430
20	Digital Resolution	0.11

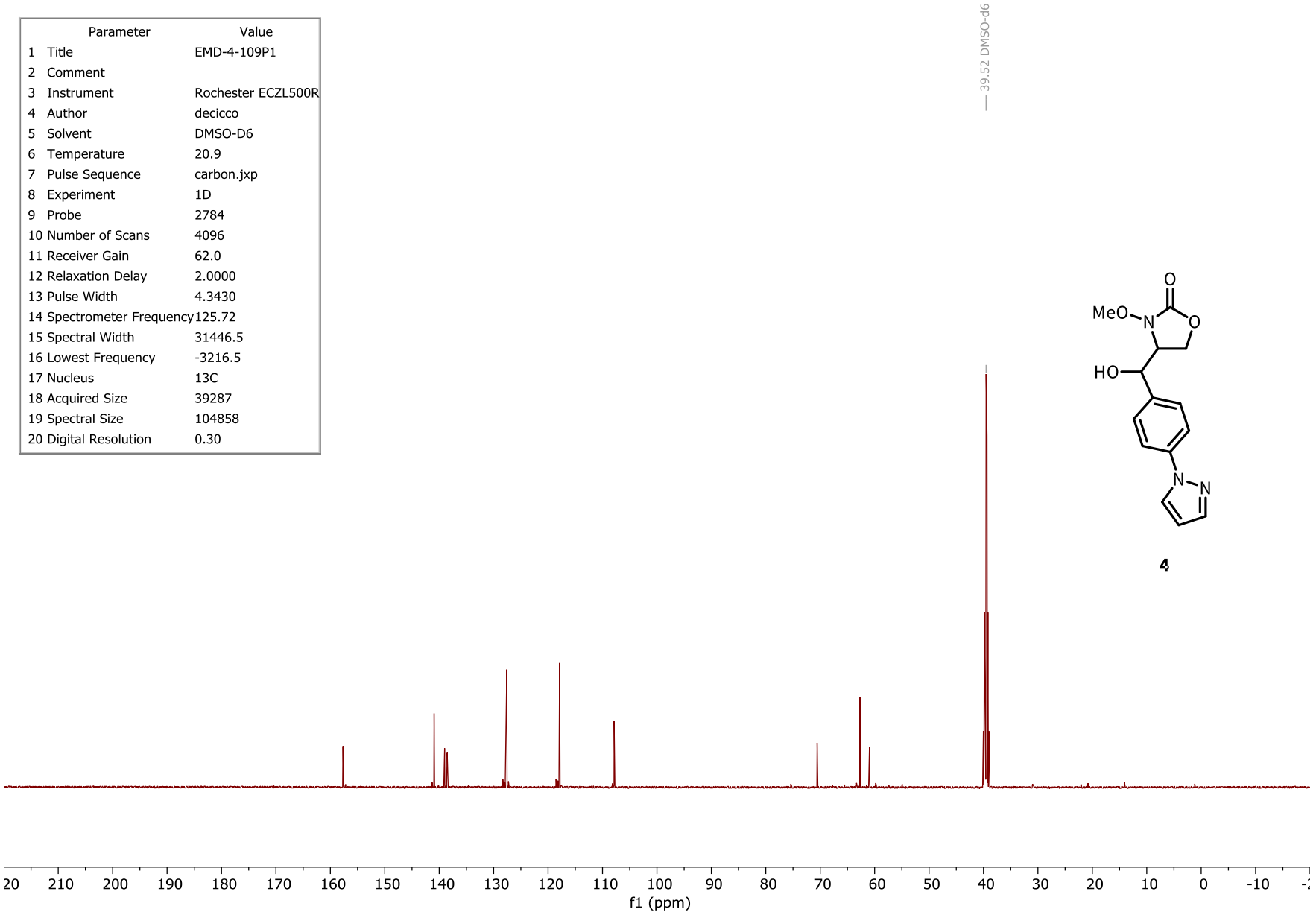



77.16 CDCl3
MeO
N
O
O
O
N
S
O
O
F
N
2n
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

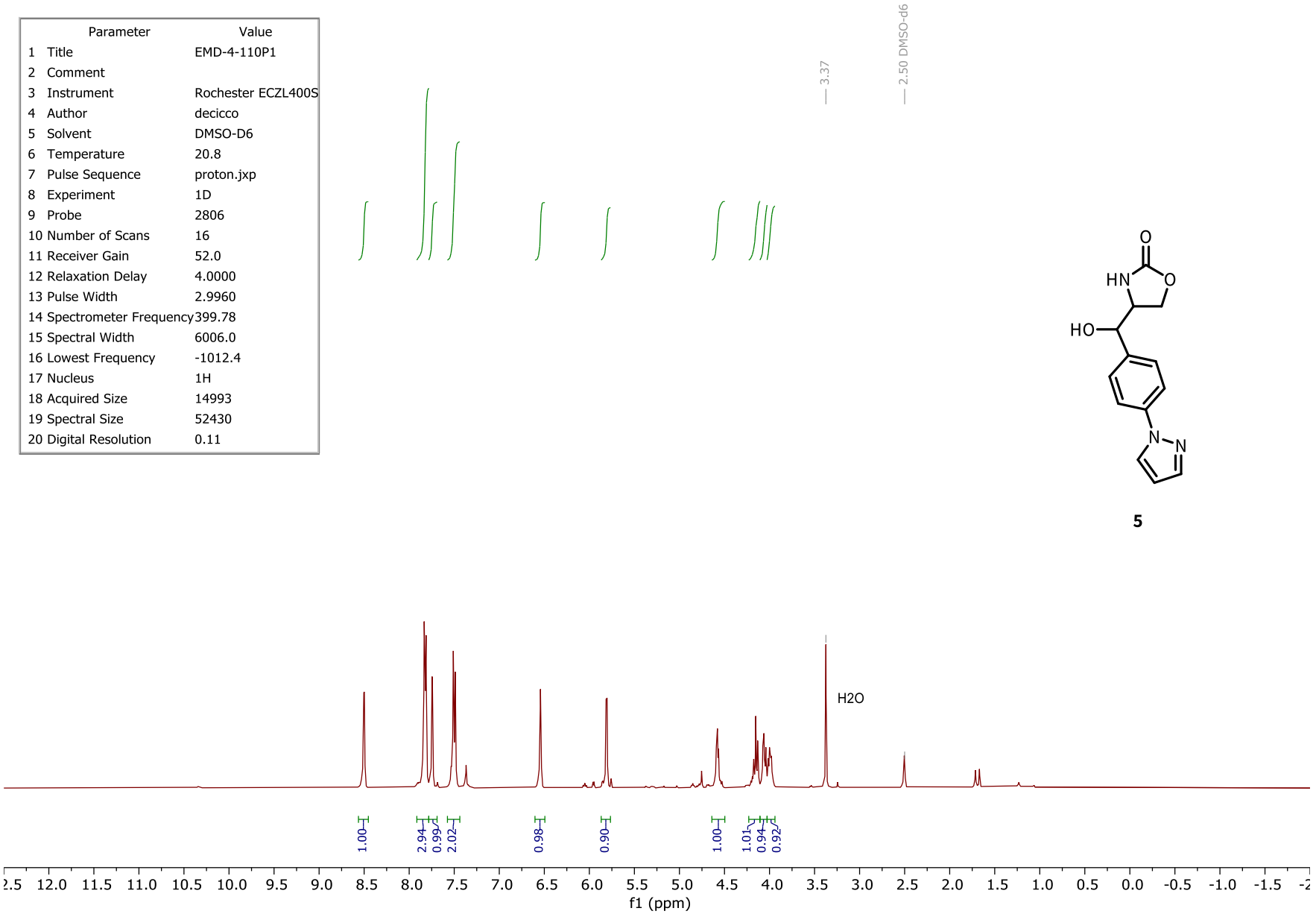
	Parameter	Value
1	Title	EMD-4-109P1
2	Comment	
3	Instrument	Rochester ECZL500R
4	Author	decicco
5	Solvent	DMSO-D6
6	Temperature	20.8
7	Pulse Sequence	single_pulse.jxp
8	Experiment	1D
9	Probe	2784
10	Number of Scans	16
11	Receiver Gain	62.0
12	Relaxation Delay	4.0000
13	Pulse Width	3.4370
14	Spectrometer Frequency	499.96
15	Spectral Width	7507.5
16	Lowest Frequency	-1254.0
17	Nucleus	1H
18	Acquired Size	18749
19	Spectral Size	52430
20	Digital Resolution	0.14



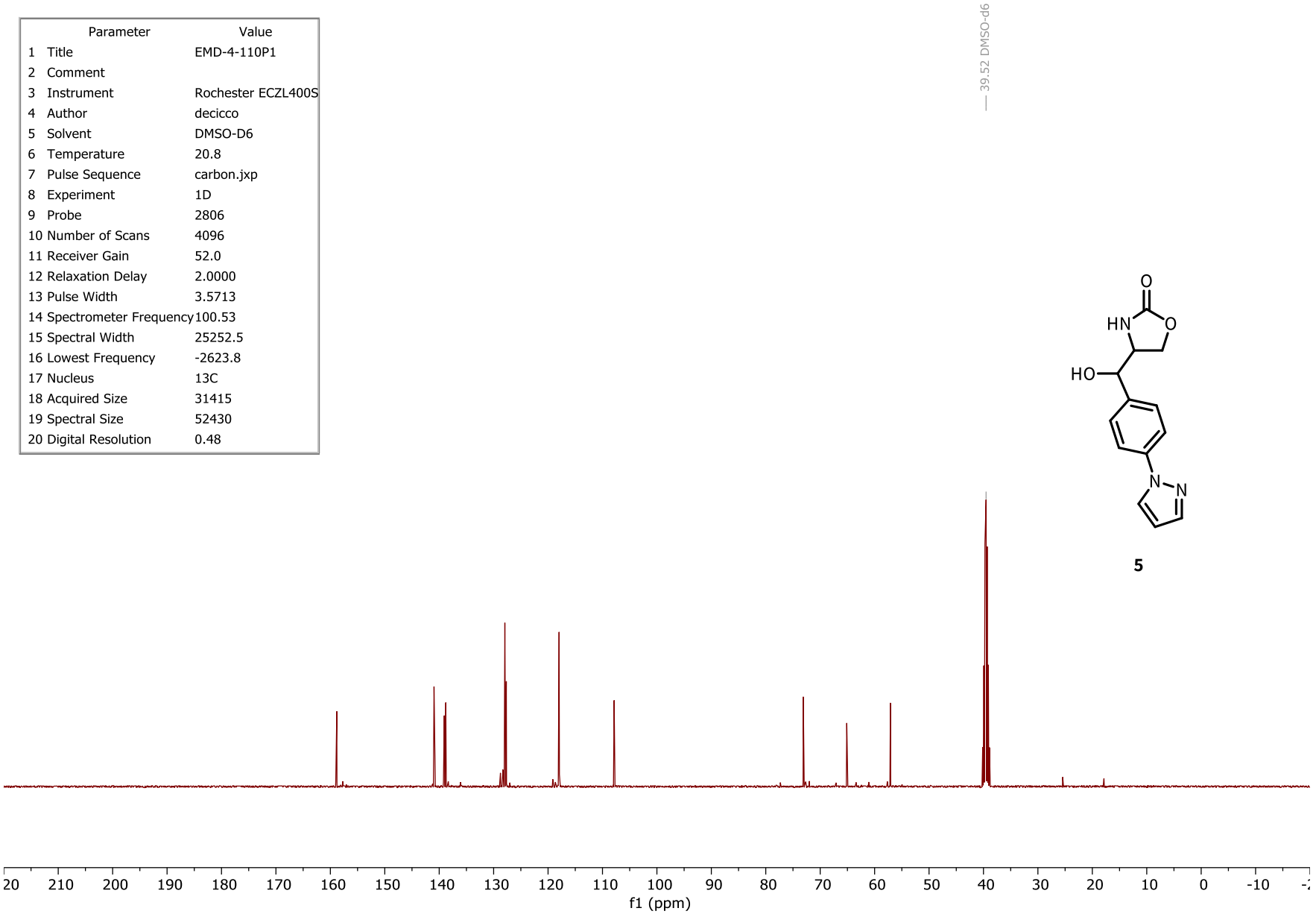
	Parameter	Value
1	Title	EMD-4-109P1
2	Comment	
3	Instrument	Rochester ECZL500R
4	Author	decicco
5	Solvent	DMSO-D6
6	Temperature	20.9
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2784
10	Number of Scans	4096
11	Receiver Gain	62.0
12	Relaxation Delay	2.0000
13	Pulse Width	4.3430
14	Spectrometer Frequency	125.72
15	Spectral Width	31446.5
16	Lowest Frequency	-3216.5
17	Nucleus	13C
18	Acquired Size	39287
19	Spectral Size	104858
20	Digital Resolution	0.30



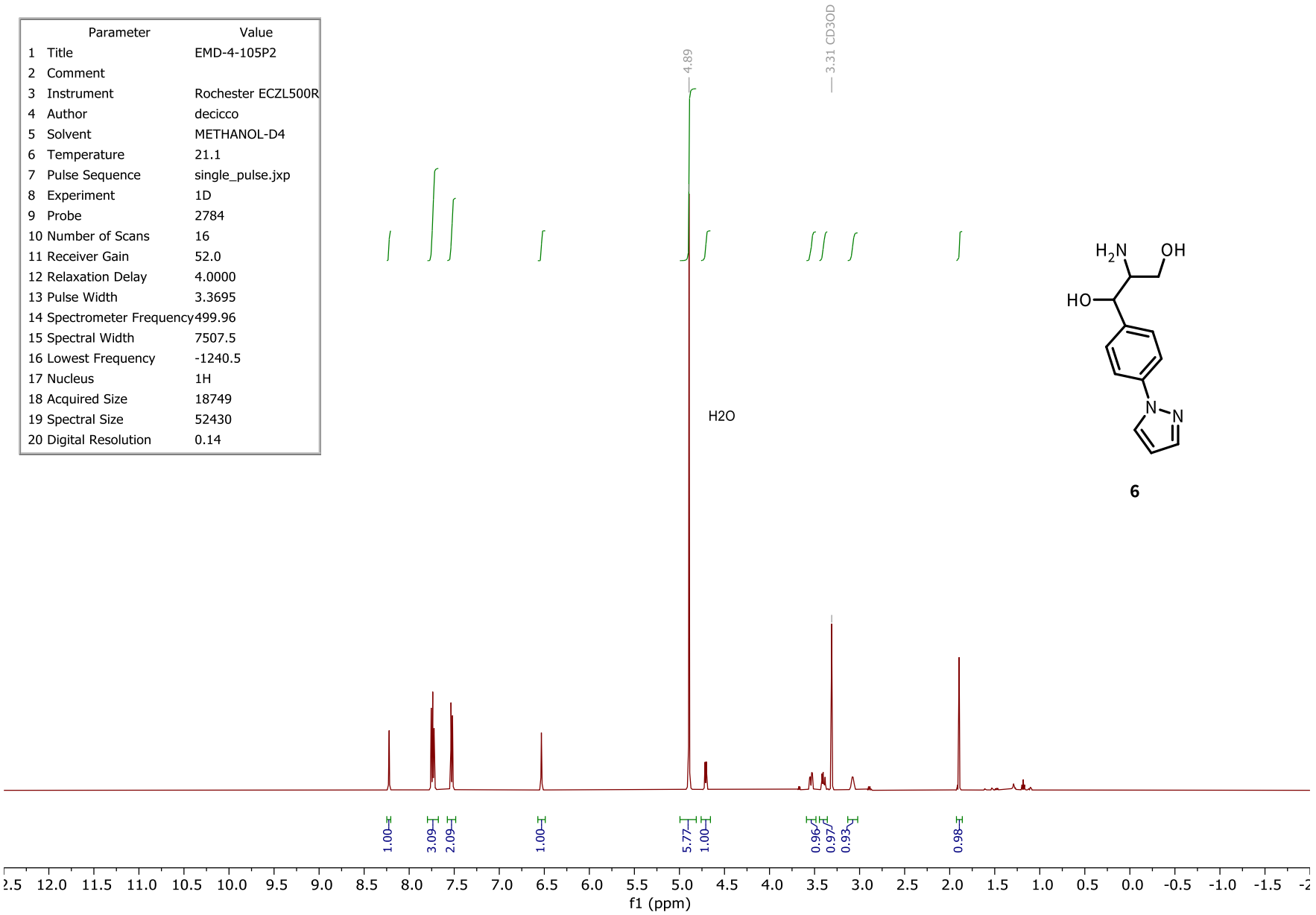
	Parameter	Value
1	Title	EMD-4-110P1
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	DMSO-D6
6	Temperature	20.8
7	Pulse Sequence	proton.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	16
11	Receiver Gain	52.0
12	Relaxation Delay	4.0000
13	Pulse Width	2.9960
14	Spectrometer Frequency	399.78
15	Spectral Width	6006.0
16	Lowest Frequency	-1012.4
17	Nucleus	1H
18	Acquired Size	14993
19	Spectral Size	52430
20	Digital Resolution	0.11



	Parameter	Value
1	Title	EMD-4-110P1
2	Comment	
3	Instrument	Rochester ECZL400S
4	Author	decicco
5	Solvent	DMSO-D6
6	Temperature	20.8
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2806
10	Number of Scans	4096
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	3.5713
14	Spectrometer Frequency	100.53
15	Spectral Width	25252.5
16	Lowest Frequency	-2623.8
17	Nucleus	13C
18	Acquired Size	31415
19	Spectral Size	52430
20	Digital Resolution	0.48



	Parameter	Value
1	Title	EMD-4-105P2
2	Comment	
3	Instrument	Rochester ECZL500R
4	Author	decicco
5	Solvent	METHANOL-D4
6	Temperature	21.1
7	Pulse Sequence	single_pulse.jxp
8	Experiment	1D
9	Probe	2784
10	Number of Scans	16
11	Receiver Gain	52.0
12	Relaxation Delay	4.0000
13	Pulse Width	3.3695
14	Spectrometer Frequency	499.96
15	Spectral Width	7507.5
16	Lowest Frequency	-1240.5
17	Nucleus	1H
18	Acquired Size	18749
19	Spectral Size	52430
20	Digital Resolution	0.14



6

	Parameter	Value
1	Title	EMD-4-105P2
2	Comment	
3	Instrument	Rochester ECZL500R
4	Author	decicco
5	Solvent	METHANOL-D4
6	Temperature	21.3
7	Pulse Sequence	carbon.jxp
8	Experiment	1D
9	Probe	2784
10	Number of Scans	8192
11	Receiver Gain	52.0
12	Relaxation Delay	2.0000
13	Pulse Width	4.2833
14	Spectrometer Frequency	125.72
15	Spectral Width	31446.5
16	Lowest Frequency	-2983.6
17	Nucleus	13C
18	Acquired Size	39287
19	Spectral Size	104858
20	Digital Resolution	0.30