Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Diastereoselective Synthesis of 1,1,3,3-Tetrasubstituted Cyclobutanes Enabled by Cycloaddition of Bicyclo[1.1.0]butanes

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Supporting Information

Contents

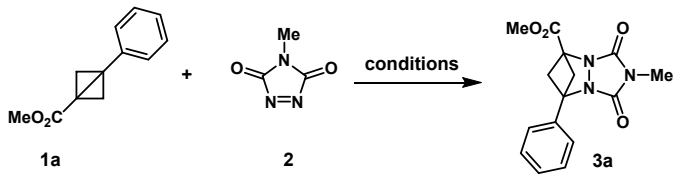
Synthesis

General Information. All reactions were carried out under an inert atmosphere of dry argon in oven or flame-dried glassware, unless the reaction procedure states otherwise. Tetrahydrofuran (THF), 1,4-dioxane, toluene and ether (diethyl ether) were distilled from sodium-benzophenone in a continuous still under an atmosphere of argon. Dichloromethane and triethylamine were distilled from calcium hydride in a continuous still under and atmosphere of argon. Reaction temperatures were controlled by Heidolph MR Hei-Standard. Analytical thin-layer chromatography (TLC) was performed using pre-coated TLC plates and visualized using combinations of UV, anisaldehyde, ceric ammonium molybdate (CAM), potassium permanganate, and iodine staining. Flash column chromatography was preformed using 300-400 mesh silica gel (Huanghai, Shandong) as the stationary phase. Proton nuclear magnetic resonance spectra were recorded at Agilent–400 MHz spectrometer. Carbon nuclear magnetic resonance spectra were recorded at Agilent–100 MHz spectrometer. Optical Rotations were measured on a Rudolph Autopol III S2 polarimeter.

Bicyclo[1.1.0]butanes **1a-1d**,[1-2] **1f**,[2] **1h**,[3] **1n**,[4] **1q-1s**,[5] housanes **4a**,[6] 2-nitrosonaphthalene,[7] and nitrosoarene **9**[8] were prepared according to the literatures.

I. Optimization of the cycloaddition of 1a and 2

Table S1



1a **2** **3a**

entry	conditions	yield of 3a
1	dioxane (0.025 M), rt	47%
2	dioxane (0.025 M), 85 °C	62%
3	dioxane (0.05 M), 85 °C	46%[b]
4	DCM (0.025 M), rt, hν (310 nm)	35%[b]
5	DCM (0.025 M), rt, hν (256 nm)	35%[b]
6	dioxane (0.025 M), 85 °C	79%[c]

[a] **1a** (0.2 mmol) and **2** (1.2 equiv.) in solvent, 85 °C or rt (irradiation); [b] NMR yield;
[c] **2** (1.5 equiv.) was used.

[1] (a) R. M. Bychek, V. Hutskalova, Y. P. Bas, O. A. Zaporozhets, S. Zozulya, V. V. Levterov, P. K. Mykhailiuk, *J. Org. Chem.* **2019**, *84*, 15106−15117.
[2] X. Ma, D. L. Sloman, Y. Han, D. J. Bennett, *Org. Lett.* **2019**, *21*, 7199−7203.
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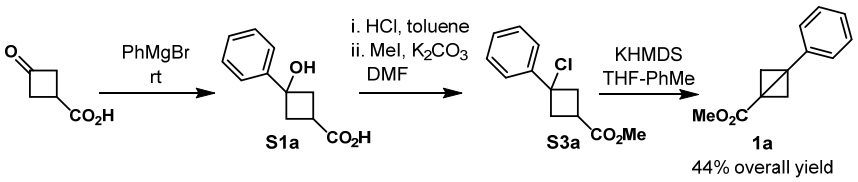
[5] (a) C. Qin, H. M. L. Davies, *Org. Lett.* **2013**, *15*, 310–313. (b) R. Panish, S. R. Chintala, D. T. Boruta, Y. Fang, M. T. Taylor, J. M. Fox, *J. Am. Chem. Soc.* **2013**, *135*, 9283–9286. (c) Y. Gaoni, *J. Org. Chem.* **1982**, *47*, 2564–2571.
[6] V. V. Semeno, V. O. Vasylchenko, B. V. Vashchenko, D. O. Lutsenko, R. T. Iminov, O. B. Volovenko, O. O. Grygorenko, *J. Org. Chem.* **2020**, *85*, 2321–2337.
[7] W.-Y., Ding, P. Yu, Q.-J. An, K. L. Bay, S.-H. Xiang, S. Li, Y. Chen, K. N. Houk; B. Tan, *Chem*, **2020**, *6*, 2046–2059.
[8] Y. Yamamoto, H. Yamamoto, *J. Am. Chem. Soc.* **2004**, *126*, 4128-4129.

II. Preparation of bicyclo[1.1.0]butanes 1 and housanes 4

a. Preparation of bicyclo[1.1.0]butanes **1**



General Procedure A:

Methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (1a)

To a solution of 3-oxocyclobutane-1-carboxylic acid (11.4 g, 0.100 mol) in THF (125 mL) was added PhMgBr (3.0 M in THF, 80 mL, 0.240 mol) dropwise at 0 °C and the resulting mixture was stirred at the same temperature for 24 h. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl and extracted with DCM. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated. The residue contained a mixture of cis- and trans-isomers of 3-hydroxy-3-phenylcyclobutane-1-carboxylic acid S1a (19.2 g), which was directly used in the next step without further purification.

To a solution of above crude acid **S1a** in toluene (180 mL) was added concentrated HCl (120 mL) and the resulting mixture was stirred at rt for 4 h. Then the reaction mixture was separated and extracted with EtOAc. The combined organic phase was sequentially washed with H_2O, $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated. The residue contained a mixture of *cis*- and *trans*-isomers of methyl 3-chloro-3-phenylcyclobutane-1-carboxylate **S2a** (20.9 g), which was used directly in the next step without further purification.

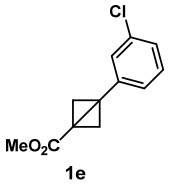
To a solution of above crude chloride **S2a** in DMF (150 mL) was added K_2CO_3 (27.6 g, 0.200 mol) and MeI (9.3 mL, 0.150 mol). Then the reaction mixture was stirred at rt overnight before quenched with H_2O and extracted with EtOAc. The combined organic phase was sequentially washed with H_2O and brine, dried over Na_2SO_4, and concentrated. The residue contained a mixture of *cis*- and *trans*-isomers of methyl 3-chloro-3-phenylcyclobutane-1-carboxylate **S3a** (20.5 g), which was directly used in the next step.

To a solution of above crude ester **S3a** (20.5 g) in toluene (150 mL) was added a solution of KHMDS (1.0 M in THF, 120 mL, 0.120 mol) dropwise at 0 °C. The reaction mixture was stirred for 30 min at 0 °C before warmed to rt. After 2 h, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl at 0 °C. The reaction mixture was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, concentrated, and the residue was purified by column chromatography on silica gel (5% ethyl acetate in petroleum ether) to afford the product **1a** (8.21 g, 43.6 mmol, 44% yield over 4 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.32-7.28 (m, 4H), 7.25 – 7.21 (m, 1H), 3.48 (s, 3H), 2.93 (s, 2H), 1.60 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.03, 133.58, 128.43, 126.95, 125.90, 51.74, 35.73, 32.89, 23.20.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{12}H_{13}O_2$, 189.0910; found, 189.0909.



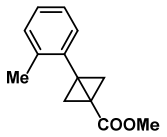
Methyl 3-(3-chlorophenyl)bicyclo[1.1.0]butane-1-carboxylate (1e)

BCB **1e** was prepared according to **General Procedure A**.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.33 – 7.29 (m, 1 H), 7.28 – 7.24 (m, 2 H), 7.22 – 7.18 (m, 1H), 3.56 (s, 3H), 2.94 (s, 2H), 1.66 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 169.60, 136.02, 134.43, 129.68, 127.09, 126.15, 123.95, 51.95, 35.82, 31.87, 23.82.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{12}H_{12}O_2Cl$, 223.0520; found, 223.0519.



1g

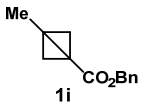
Methyl 3-(*o*-tolyl)bicyclo[1.1.0]butane-1-carboxylate (1g)

BCB **1g** was prepared according to **General Procedure A**.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.22 – 7.00 (m, 4H), 3.68 (s, 3H), 2.60 (s, 2H), 2.45 (s, 3H), 1.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 171.20, 139.10, 132.42, 130.57, 127.25, 125.91, 125.05, 51.88, 38.80, 30.83, 20.62, 20.21.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{13}H_{15}O_2$, 203.1067; found, 203.1065.



1i

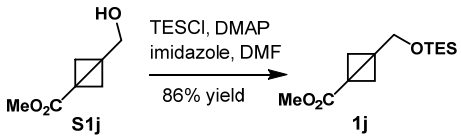
Benzyl 3-methylbicyclo[1.1.0]butane-1-carboxylate (1i)

BCB **1i** was prepared according to **General Procedure A**.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.41 – 7.26 (m, 5H), 5.14 (s, 2H), 2.21 (s, 2H), 1.47 (s, 3H), 1.23 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 171.78, 136.52, 128.33, 127.94, 127.92, 65.96, 38.68, 27.70, 12.92, 12.54.

HRMS-DART (*m*/*z*): $[M+H]^+$ calcd. for $C_{13}H_{15}O_2$, 203.1067; found, 203.1063.



S1j 1j

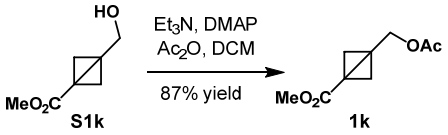
Methyl 3-(((triethylsilyl)oxy)methyl)bicyclo[1.1.0]butane-1-carboxylate (1j)

To a solution of alcohol **S1j**[9] (0.801 g, 5.63 mmol), DMAP (68.7 mg, 0.56 mmol), and imidazole (0.762 g, 11.2 mmol) in DMF (40 mL) was added TESCl (1.7 mL, 1.69 g, 11.2 mmol) at 0 °C. After stirring at rt overnight, the reaction mixture was quenched with H_2O and extracted with DCM. The combined organic phase was washed with brine, dried over Na_2SO_4, concentrated, and the residue was purified by column chromatography on silica gel (PE:EA = 20:1) to afford the pure product **1j** (1.24 g, 4.83 mmol, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.01 (s, 2H), 3.64 (s, 3H), 2.37 (s, 2H), 1.24 (s, 2H), 0.92 (t, *J* = 8.0 Hz, 9H), 0.56 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 171.69, 60.40, 51.67, 36.48, 29.96, 12.77, 6.58, 4.31.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{13}H_{25}O_3Si$, 257.1567; found, 257.1565.



S1k 1k

Methyl 3-(acetoxymethyl)bicyclo[1.1.0]butane-1-carboxylate (1k)

To a solution of methyl 3-(hydroxymethyl)bicyclo[1.1.0]butane-1-carboxylate **S1k** (0.581 g, 4.08 mmol), DMAP (49.9 mg, 0.408 mmol), and Et_3N (1.20 mL, 0.871 g, 8.16 mmol) in DCM (40 mL) was added Ac_2O (0.766 mL, 0.833 g, 8.16 mmol) at 0 °C. After

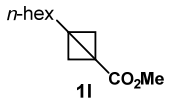
[9] V. V. Razin, N. V. Ulin, *Russ. J. Org. Chem.* **2003**, *39,* 33-39.

stirring at rt for 3h, the reaction mixture was quenched with H_2O (40 mL) and extracted with DCM. The combined organic phase was washed with brine, dried over Na_2SO_4, concentrated, and the residue was purified by column chromatography on silica gel (PE:EA = 5:1) to afford the pure product **1k** (0.655 g, 3.56 mmol, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.49 (s, 2H), 3.69 (s, 3H), 2.37 (s, 2H), 2.05 (s, 3H), 1.32 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.93, 170.51, 62.13, 52.01, 37.05, 25.94, 20.54, 13.64.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_9H_{13}O_4$, 185.0808; found, 185.0807.



1l

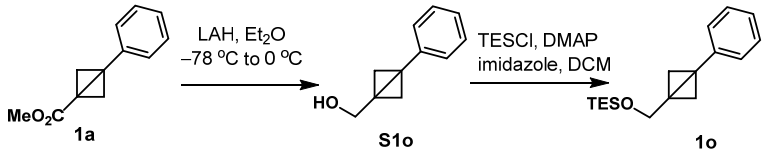
Methyl 3-hexylbicyclo[1.1.0]butane-1-carboxylate (1l)

BCB **1l** was prepared according to **General Procedure A**.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.68 (s, 3H), 2.19 (s, 2H), 1.83 – 1.74 (m, 2H), 1.47 – 1.38 (m, 2H), 1.37 – 1.22 (m, 6H), 1.18 (s, 2H), 0.88 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 172.65, 51.65, 37.27, 31.58, 31.36, 28.97, 27.79, 27.35, 22.54, 14.03, 12.95.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{12}H_{20}O_2$, 196.1458; found, 196.1460.



1a S1o 1o

(3-Phenylbicyclo[1.1.0]butan-1-yl)methanol (S1o)

To a solution of methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **1a** (0.565 g, 3.00 mmol) in Et_2O (30 mL) was added $LiAlH_4$ (0.171 g , 4.50 mmol) at −78°C. The mixture was stirred for 30 min at −78°C, then gradually warmed to 0 °C for further 10 min. The reaction mixture was quenched with 0.3 mL of a saturated solution of Na_2SO_4, then filtered. The filtrate was concentrated to afford the crude product (3-phenylbicyclo[1.1.0]butan-1-yl)methanol **S1o**, which was directly submitted to the next step. Of note, decomposition took place when the residue was purified by column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 – 7.11 (m, 5H), 3.90 (d, *J* = 6.1 Hz, 2H), 2.27 (s, 2H), 1.23 (s, 2H).

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{11}H_{13}O$, 161.0961; found, 161.0959.

Triethyl((3-phenylbicyclo[1.1.0]butan-1-yl)methoxy)silane (1o)

To a solution of above alcohol **S1o** (from **1a** (3.00 mmol)), DMAP (36.7 mg, 0.31 mmol), and imidazole (0.409 g, 6.00 mmol) in DCM (30 mL) was added TESCl (0.760 mL, 4.53 mmol) at 0 °C. After stirring for 5 h, the reaction mixture was quenched with H_2O (20 mL), and extracted with DCM. The combined organic phase was washed with brine, dried over Na_2SO_4, concentrated, and the residue was purified by column chromatography on silica gel (PE:EA = 20:1) to afford the crude product triethyl((3-phenylbicyclo[1.1.0]butan-1-yl)methoxy)silane **1o** (from **1a** (3.00 mmol)), which was directly submitted to the next step. Of note, decomposition took place when the residue was purified by column chromatography.

^{1}H NMR (400 MHz, C_6D_6) δ (ppm): 7.13 (d, *J* = 4.2 Hz, 4H), 7.06 – 6.98 (m, 1H), 3.83 (s, 2H), 2.12 (s, 2H), 1.11 (s, 2H), 0.92 (t, *J* = 8.0 Hz, 9H), 0.50 (q, *J* = 8.0 Hz, 6H).

^{13}C NMR (101 MHz, C_6D_6) δ (ppm): 137.57, 128.43, 126.00, 125.20, 62.05, 33.32, 24.41, 18.12, 7.04, 4.85.

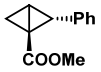
S1o 1p

(3-Phenylbicyclo[1.1.0]butan-1-yl)methyl acetate (1p)

To a solution of crude alcohol **S1o** (from **1a** (0.200 mmol)), DMAP (2.4 mg, 20.0 μmol), and Et_3N (55.6 μL, 0.400 mmol) in DCM (2 mL) was added Ac_2O (37.6 μL, 0.400 mmol) at 0 °C. After stirring at rt for 10 h, the reaction mixture was quenched with 2 mL of H_2O and extracted with DCM. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated to afford the crude product (3-phenylbicyclo[1.1.0]butan-1-yl)methyl acetate **1p**, which was directly submitted to the next step. Of note, decomposition took place when the residue was purified by column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.31 – 6.96 (m, 5H), 4.18 (s, 2H), 2.18 (s, 2H), 1.90 (s, 3H), 1.20 (s, 2H).

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{13}H_{15}O_2$, 203.1067; found, 203.1067.



1t

Methyl (1S,2R)-2-phenylbicyclo[1.1.0]butane-1-carboxylate (1t)

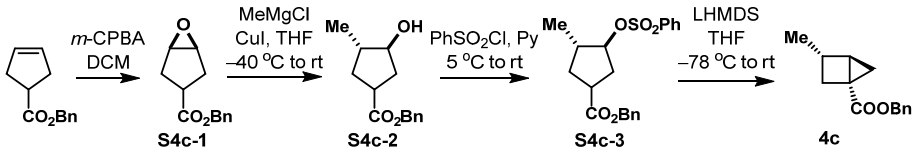
The title compound was prepared according to **reference 5c**.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.33 – 7.11 (m, 5H), 4.30 (t, J = 3.9 Hz, 1H), 3.75 (s, 3H), 2.61 – 2.51 (m, 1H), 2.47 (dd, *J* = 6.5, 3.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 172.96, 134.42, 129.25, 128.07, 127.10, 53.79, 52.00, 35.23, 22.91, 15.69.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{12}H_{13}O_2$, 189.0910; found, 189.0909.

b. Preparation of housanes **4**



S4c-1 S4c-2 S4c-3 4c

Benzyl (3*S,4*R**)-3-methylbicyclo[2.1.0]pentane-1-carboxylate (4c)**

Benzyl 6-oxabicyclo[3.1.0]hexane-3-carboxylate (S4c-1)

To a solution of benzyl cyclopent-3-ene-1-carboxylate (8.89 g, 44.0 mmol) in CH_2Cl_2 (100 mL) was added *m*-CPBA (85%, 13.4 g, 66.0 mmol) in portions at 0 °C, and the resulting mixture was stirred at r.t. overnight. The precipitate was filtered off, and the filtrate was washed sequentially with a aqueous solution of $NaHCO_3$ and brine, dried over Na_2SO_4, concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 3:1) to afford the product benzyl 6-oxabicyclo[3.1.0]hexane-3-carboxylate **S4c-1** (5.39 g, 24.7 mmol, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.44 – 7.29 (m, 5H), 5.12 (s, 2H), 3.51 (s, 2H), 2.77-2.66 (m, 1H), 2.37 (dd, *J* = 14.1, 8.1 Hz, 2H), 1.91 (dd, *J* = 14.0, 9.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 174.70, 135.86, 128.53, 128.19, 127.99, 66.39, 56.22, 37.45, 31.15.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{13}H_{14}O_3$, 218.0937; found, 218.0940.

Benzyl (3*S,4*S**)-3-hydroxy-4-methylcyclopentane-1-carboxylate (S4c-2)**

To a solution of benzyl 6-oxabicyclo[3.1.0]hexane-3-carboxylate **S4c-1** (1.00 g, 4.58 mol) and CuI (87.6 mg, 0.460 mmol) in THF (150 mL) was added MeMgCl (3 M in THF, 3.1 mL, 9.30 mmol) dropwise at −40 °C. After stirring at rt overnight, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl at −20 °C. The reaction mixture was extracted with EtOAc, and the combined organic phase was washed with brine, dried over Na_2SO_4, concentrated and the residue was purified by column

chromatography on silica gel (PE:EA = 3:1) to afford the product **S4c-2** (0.498 g, 2.13 mmol, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.45-7.29 (m, 5H), 5.30 – 5.06 (m, 2H), 3.96 – 3.75 (m, 1H), 3.16 – 2.94 (m, 1H), 2.35 – 2.15 (m, 2H), 1.96 – 1.79 (m, 2H), 1.72 (brs, 1H), 1.54 – 1.38 (m, 1H), 1.13 – 0.96 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 176.01, 136.08, 128.53, 128.14, 128.00, 79.29, 66.26, 42.74, 40.56, 37.38, 35.70, 17.91.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{14}H_{18}O_3$, 234.1250; found, 234.1247.

Benzyl (3*S,4*S**)-3-methyl-4-((phenylsulfonyl)oxy)cyclopentane-1-carboxylate (S4c-3)**

To a solution of alcohol benzyl (3*S**,4*S**)-3-hydroxy-4-methylcyclopentane-1-carboxylate **S4c-2** (0.424 g, 1.81 mmol) in pyridine (1.8 mL) was added $PhSO_2Cl$ (0.413 g, 2.34 mmol) at 0 °C. The mixture was stirred at rt overnight. The residue was dissolved in CH_2Cl_2 (20 mL), and the solution was washed sequentially with the aqueous solution of $NaHSO_4$ (10%) and brine, dried over Na_2SO_4, concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 4:1) to afford the product benzyl (3S,4S)-3-methyl-4-((phenylsulfonyl)oxy)cyclopentane-1-carboxylate **S4c-3** (0.596 g, 1.59 mmol, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.90 (d, *J* = 7.9 Hz, 2H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.28 (m, 5H), 5.09 (s, 2H), 4.56 – 4.43 (m, 1H), 3.08 – 2.94 (m, 1H), 2.31 – 2.11 (m, 3H), 2.07 – 1.93 (m, 1H), 1.44 – 1.31 (m, 1H), 0.90 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 174.77, 136.94, 135.78, 133.67, 129.20, 128.56, 128.25, 128.05, 127.72, 88.89, 66.48, 41.01, 40.48, 35.18, 34.93, 17.50.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{20}H_{23}O_5S$, 375.1261; found, 375.1253.

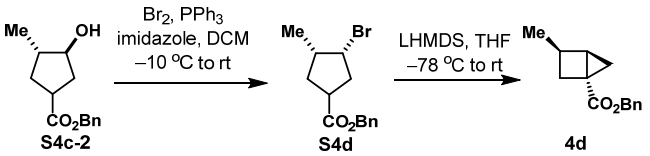
Benzyl (1*R,3*S**,4*R**)-3-methylbicyclo[2.1.0]pentane-1-carboxylate (4c)**

To a solution of benzyl (3*S**,4*S**)-3-methyl-4-((phenylsulfonyl)oxy)cyclopentane-1-carboxylate **S4c-3** (0.549 g, 1.47 mmol) in THF (12 mL) was added LHMDS (1.0 M in THF, 3.7 mL, 3.70 mmol) dropwise at −78 °C, and the mixture was warmed up to rt and stirred for further 30 min before quenched with a saturated aqueous solution of NH_4Cl. The reaction mixture was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 20:1) to afford the product benzyl (1*R**,3*S**,4*R**)-3-methylbicyclo[2.1.0]pentane-1-carboxylate **4c** (0.245 g, 1.13 mmol, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.45 – 7.27 (m, 5H), 5.14 (d, *J* = 12.6 Hz, 1H), 5.09 (d, *J* = 12.6 Hz, 1H), 2.19 – 2.12 (m, 1H), 1.93 – 1.80 (m, 2H), 1.79 – 1.66 (m, 2H), 1.30 – 1.24 (m, 1H), 1.20 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 173.64, 136.41, 128.45, 127.95, 127.77, 65.79, 34.87, 31.25, 29.14, 25.51, 22.54, 21.08.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{14}H_{17}O_2$, 217.1223; found, 217.1220.



Benzyl (3*R,4*S**)-3-bromo-4-methylcyclopentane-1-carboxylate (S4d)**

To a solution benzyl (3*S**,4*S**)-3-hydroxy-4-methylcyclopentane-1-carboxylate **S4c-2** (0.117 g, 0.500 mmol), PPh_3 (0.144 g, 0.550 mmol) and imidazole (40.8 mg, 0.599 mmol) in CH_2Cl_2 (10 mL) was added Br_2 (28.2 μL, 87.9 mg, 0.550 mmol) dropwise at −10 °C. After stirring at rt overnight, the reaction mixture was quenched with a saturated aqueous solution of Na_2SO_3, and extracted with CH_2Cl_2. The combined organic phase was washed sequentially with a saturated aqueous solution of Na_2SO_3 and brine, dried over Na_2SO_4, concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 10:1) to afford the product **S4d** (89.0 mg, 0.300 mmol, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.41 – 7.29 (m, 5H), 5.12 (s, 2H), 3.99 – 3.76 (m, 1H), 3.15 – 2.96 (m, 1H), 2.35 – 2.12 (m, 2H), 1.93 – 1.78 (m, 2H), 1.54 (brs, 1H), 1.50 – 1.38 (m, 1H), 1.04 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm):176.01, 136.09, 128.54, 128.15, 128.01, 79.30, 66.26, 42.76, 40.56, 37.39, 35.70, 17.92.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{14}H_{17}O_2Br$, 296.0406; found, 296.0409.

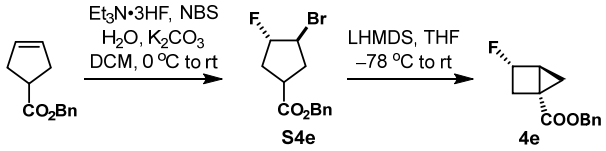
Benzyl (1*R,3*R**,4*R**)-3-methylbicyclo[2.1.0]pentane-1-carboxylate (4d)**

To a solution of benzyl (3R,4S)-3-bromo-4-methylcyclopentane-1-carboxylate **S4d** (1.58 g, 5.32 mmol) in THF (40 mL) was added LHMDS (1.0 M in THF, 13.3 mL, 13.3 mmol) dropwise at −78 °C, and the mixture was stirred for further 30 min before warmed to rt. After 0.5 h, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl at −20 °C. The reaction mixture was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 10:1) to afford the product benzyl (1*R**,3*R**,4*R**)-3-methylbicyclo[2.1.0]pentane-1-carboxylate **4d** (1.12 g, 5.20 mmol, 98% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.41 – 7.28 (m, 5H), 5.12 (d, *J* = 12.6 Hz, 1H), 5.08 (d, *J* = 12.6 Hz, 1H), 2.70 – 2.53 (m, 2H), 2.42 – 2.28 (m, 1H), 1.63 – 1.52 (m, 2H), 1.38 – 1.32 (m, 1H), 1.23 – 1.17 (m, 1H), 0.83 (d, *J* = 6.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 173.42, 136.41, 128.46, 127.97, 127.88, 65.82, 53.40, 31.80, 29.21, 25.98, 20.96, 19.98, 15.67.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{14}H_{17}O_2$, 217.1223; found, 217.1220.



Benzyl (3*S,4*S**)-3-bromo-4-fluorocyclopentane-1-carboxylate (S4e)**

To a solution of benzyl cyclopent-3-ene-1-carboxylate (2.02 g, 10.0 mmol) and $Et_3N{\cdot}3HF$ (4.84 g, 30.0 mmol) in CH_2Cl_2 (20 mL) was added NBS (2.14 g, 12.0 mol) at 0 °C. After stirring at rt overnight, the reaction mixture was quenched with H_2O and extracted with ethyl acetate. The combined organic phase was washed sequentially with an aqueous solution of K_2CO_3 (10%), brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (PE:EA = 10:1) to afford the product benzyl (3*S**,4*S**)-3-bromo-4-fluorocyclopentane-1-carboxylate **S4e** (0.151 g, 0.502 mmol, 50% yield, 2:1 dr). The product was directly submitted to the next step.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.49 – 7.29 (m, 5H), 5.35 – 5.04 (m, 3H), 4.47 – 4.22 (m, 1H), 3.47 – 3.10 (m, 1H), 2.94 – 2.16 (m, 4H).

Benzyl (1*R,3*S**,4*S**)-3-fluorobicyclo[2.1.0]pentane-1-carboxylate (4e)**

To a solution of LHMDS (1.0 M in THF, 2.50 mL, 2.5 mmol) was added a solution of benzyl (3*S**,4*S**)-3-bromo-4-fluorocyclopentane-1-carboxylate **S4e** (0.151 g, 0.501 mmol) in THF (2 mL) at −78 °C. After0.5 h, the reaction mixture was warmed to rt and stirred for further 0.5 h before quenched with a saturated aqueous solution of NH_4Cl. The reaction mixture was extracted with ethyl acetate. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 9:1) to afford the product **4e** (99.4 mg, 0.452 mmol, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.42 – 7.31 (m, 5H), 5.16 (s, 2H), 4.57 (dd, *J* = 58.2, 3.3 Hz, 1H), 2.77 – 2.67 (m, 1H), 2.52 (dd, *J* = 34.5, 12.2 Hz, 1H), 2.16 – 2.02 (m, 1H), 1.90 – 1.83 (m, 1H), 1.27 – 1.18 (m, 1H).

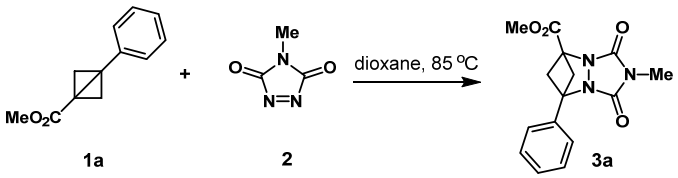
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 171.86, 135.89, 128.54, 128.20, 128.04, 87.85 (d, *J* = 197.6 Hz), 66.34, 33.84 (d, *J* = 8.9 Hz), 33.59 (d, *J* = 1.7 Hz), 25.13, 23.02 (d, *J* = 4.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): −175.39.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{13}H_{13}O_2F$, 220.0894; found, 220.0898.

III. Cycloaddition of bicyclo[1.1.0]butanes 1 and housanes 4 with electrophiles

a. Cycloaddition of BCBs **1** with MTAD **2**



General Procedure B:

Methyl 2-methyl-1,3-dioxo-7-phenyltetrahydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4]triazole-5-carboxylate (3a)

To a solution of **1a** (188 mg, 0.200 mmol) in 1,4-dioxane (4 mL) was added 4-methyl-1,2,4-triazole-3,5-dione (MTAD, 33.9 mg, 0.300 mmol), followed by additional 1,4-dioxane (4 mL). The reaction mixture was heated at 85 °C in the dark. After 0.5 h, the reaction mixture was concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 10:1) to afford the product **3a** (47.7 mg, 0.158 mmol, 79% yield).

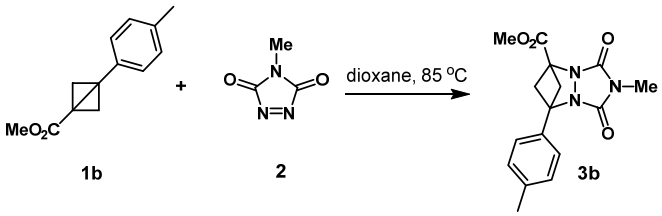
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.60 – 7.32 (m, 5H), 3.89 (s, 3H), 2.98 (s, 3H), 2.72 – 2.63 (m, 2H), 2.51 – 2.42 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 165.20, 159.88, 159.25, 132.05, 129.14, 128.33, 126.88, 74.08, 68.58, 52.79, 45.77, 25.56.

HRMS-DART (*m*/*z*): $[M+H]^+$ calcd. for $C_{15}H_{16}O_4N_3$, 302.1135; found, 302.1132.

5 mmol Scale Reaction

To a solution of **1a** (0.949 g, 5.04 mmol) in 1,4-dioxane (190 mL) was added MTAD (0.850 g, 7.52 mmol) and additional 1,4-dioxane (10 mL) sequentially. The reaction mixture was heated at 85 °C in the dark. After 0.5 h, the reaction mixture was concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 3:1) to afford the product **3a** (0.9111 g, 3.02 mmol, 60 % yield).



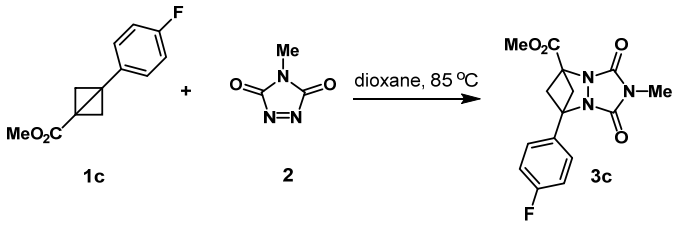
Methyl 2-methyl-1,3-dioxo-7-(*p*-tolyl)tetrahydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4]triazole-5-carboxylate (3b)

The title compound was prepared according to **General Procedure B**, using **1b** (0.202 g, 1.00 mmol), MTAD (0.170 g, 1.50 mmol) in 1,4-dioxane (40 mL) at 85 ºC for 0.5 h; column chromatography on silica gel (PE:EA = 4:1) afforded the product **3b** (0.190 g, 0.603 mmol, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.31 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 3.90 (s, 3H), 3.00 (s, 3H), 2.70 – 2.60 (m, 2H), 2.50 – 2.41 (m, 2H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 165.34, 160.00, 159.33, 139.22, 129.14, 129.08, 126.82, 74.15, 68.64, 52.87, 45.87, 25.63, 21.20.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{16}H_{18}O_4N_3$, 316.1292; found, 316.1289.



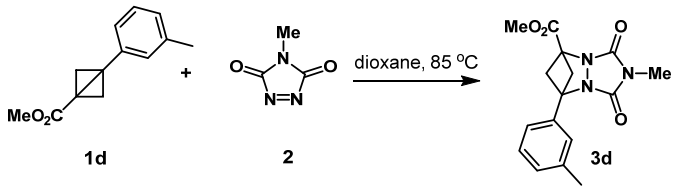
Methyl 7-(4-fluorophenyl)-2-methyl-1,3-dioxotetrahydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4] triazole-5-carboxylate (3c)

The title compound was prepared according to **General Procedure B**, using **1c** (0.206 g, 1.00 mmol), MTAD (0.170 g, 1.50 mmol) in 1,4-dioxane (40 mL) at 85 °C for 0.5 h; column chromatography on silica gel (PE:EA = 4:1) afforded the product **3c** (0.252 g, 0.790 mmol, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 – 7.33 (m, 2H), 7.16 – 7.00 (m, 2H), 3.90 (s, 3H), 3.01 (s, 3H), 2.70-2.61 (m, 2H), 2.49-2.40 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 165.21, 163.09 (d, J = 249.0 Hz), 159.91, 159.44, 128.98 (d, J = 8.5 Hz), 128.10 (d, J = 3.3 Hz), 115.63 (d, J = 21.9 Hz), 73.60, 68.68, 52.99, 46.00, 25.74.

HRMS-ESI (m/z): $[M+H]^+$ calcd. for $C_{15}H_{15}O_4N_3F$, 320.1041; found, 320.1038.



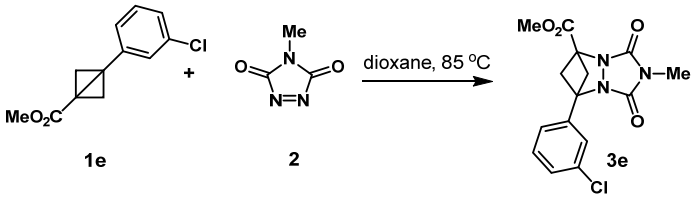
Methyl 2-methyl-1,3-dioxo-7-(*m*-tolyl)tetrahydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4]triazole-5-carboxylate (3d)

The title compound was prepared according to **General Procedure B**, using **1d** (0.203 g, 1.00 mmol), MTAD (0.170 g, 1.50 mmol) in 1,4-dioxane (40 mL) at 85 °C for 0.5 h; column chromatography on silica gel (PE:EA = 4:1) afforded the product **3d** (0.197 g, 0.625 mmol, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.30 (t, J = 7.4 Hz, 1H), 7.25 – 7.18 (m, 3H), 3.89 (s, 3H), 2.99 (s, 3H), 2.70 – 2.62 (m, 2H), 2.50 – 2.41 (m, 2H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 165.27, 159.93, 159.27, 138.07, 131.96, 129.97, 128.25, 127.46, 123.97, 74.13, 68.59, 52.81, 45.82, 25.58, 21.21.

HRMS-ESI (m/z): $[M+H]^+$ calcd. for $C_{16}H_{18}O_4N_3$, 316.1292; found, 316.1293.



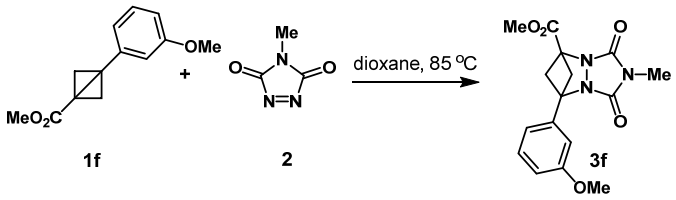
Methyl 7-(3-chlorophenyl)-2-methyl-1,3-dioxotetrahydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4] triazole-5-carboxylate (3e)

The title compound was prepared according to **General Procedure B**, using **1e** (0.223 g, 1.00 mmol), MTAD (0.170 g, 1.50 mmol) in 1,4-dioxane (40 mL) at 85 °C for 3 h; column chromatography on silica gel (PE:EA = 4:1) afforded the product **3e** (0.240 g, 0.716 mmol, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.44 – 7.28 (m, 4H), 3.89 (s, 3H), 3.00 (s, 3H), 2.70 – 2.61 (m, 2H), 2.47 – 2.39 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 165.05, 159.82, 159.35, 134.40, 134.13, 129.80, 129.45, 127.24, 125.25, 73.35, 68.70, 52.97, 45.94, 25.73.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{15}H_{15}O_4N_3Cl$, 336.0746; found, 336.0742.



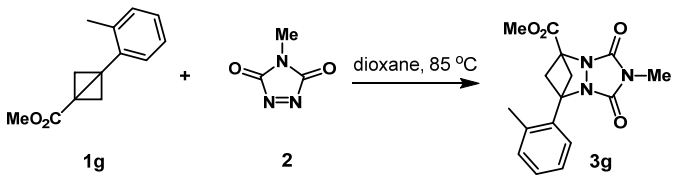
Methyl 7-(3-methoxyphenyl)-2-methyl-1,3-dioxotetrahydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4]triazole-5-carboxylate (3f)

The title compound was prepared according to **General Procedure B**, using **1f** (0.233 g, 1.07 mmol), MTAD (0.182 g, 1.61 mmol) in 1,4-dioxane (42 mL) at 85 °C for ^{20} min; column chromatography on silica gel (PE:EA = 4:1) afforded the product **3f** (0.211 g, 0.64 mmol, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.34 (t, *J* = 7.9 Hz, 1H), 7.02 – 6.92 (m, 3H), 3.92 (s, 3H), 3.82 (s, 3H), 3.03 (s, 3H), 2.71 – 2.62 (m, 2H), 2.51 – 2.41 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 165.40, 160.09, 159.63, 159.42, 133.61, 129.70, 119.26, 114.68, 112.95, 74.21, 68.74, 55.28, 53.06, 46.13, 25.82.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{16}H_{18}O_5N_3$, 332.1241; found, 332.1237.



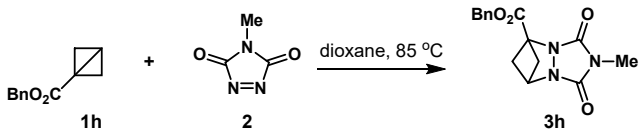
Methyl 2-methyl-1,3-dioxo-7-(o-tolyl)tetrahydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4]triazole-5-carboxylate (3g)

The title compound was prepared according to **General Procedure B**, using **1g** (0.464 g, 2.29 mmol), MTAD (0.389 g, 3.44 mmol) in 1,4-dioxane (92 mL) at 85 °C for 8 h; column chromatography on silica gel (PE:EA = 4:1) afforded the product **3g** (0.291 g, 1.05 mmol, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.31 (t, J = 7.4 Hz, 1H), 7.21 (dd, J = 13.2, 7.1 Hz, 2H), 7.12 (d, J = 7.5 Hz, 1H), 3.91 (s, 3H), 3.00 (s, 3H), 2.69 (d, J = 7.2 Hz, 2H), 2.62 (brs, 2H), 2.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 165.37, 160.07, 158.92, 137.73, 131.19, 130.01, 129.56, 128.20, 125.73, 74.62, 68.24, 52.92, 45.85, 25.68, 19.85.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{16}H_{18}O_4N_3$, 316.1292; found, 316.1290.



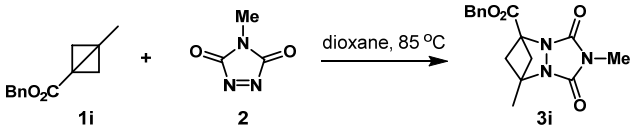
Benzyl 2-methyl-1,3-dioxotetrahydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4]triazole-5-carboxylate (3h)

The title compound was prepared according to **General Procedure B**, using **1h** (0.188 g, 1.00 mmol), MTAD (0.170 g, 1.50 mmol) in 1,4-dioxane (40 mL) at 85 °C for 3 h; column chromatography on silica gel (PE:EA = 3:1) afforded the product **3h** (0.181 g, 0.601mmol, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.47 – 7.28 (m, 5H), 5.29 (s, 2H), 4.63 (t, J = 2.0 Hz, 1H), 3.05 (s, 3H), 2.54 – 2.43 (m, 2H), 2.07 – 1.97 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 164.61, 160.56, 160.29, 134.67, 128.48, 128.42, 128.24, 71.57, 67.74, 59.56, 42.77, 25.80.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{15}H_{16}O_4N_3$, 302.1135; found, 302.1132.



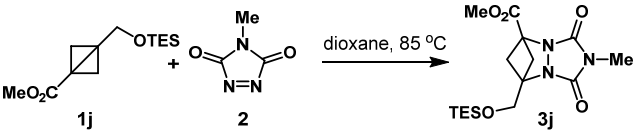
Benzyl 2,7-dimethyl-1,3-dioxotetrahydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4]triazole-5-carboxylate (3i)

The title compound was prepared according to **General Procedure B**, using **1i** (60.7 mg, 0.300 mmol), MTAD (50.9 mg, 0.450 mmol) in 1,4-dioxane (12 mL) at 85 °C for 1.75 h; column chromatography on silica gel (PE:EA = 4:1) to afforded the product **3i** (38.0 mg, 0.121 mmol, 40% yield) and recycled the starting material (34.5 mg, 0.171 mmol, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43 – 7.30 (m, 5H), 5.29 (s, 2H), 3.06 (s, 3H), 2.36 – 2.26 (m, 2H), 2.11 – 2.02 (m, 2H), 1.80 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 165.03, 160.02, 134.83, 128.57, 128.49, 128.33, 70.41, 69.30, 67.76, 46.53, 25.78, 15.55.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{16}H_{18}O_4N_3$, 316.1292; found, 316.1289.



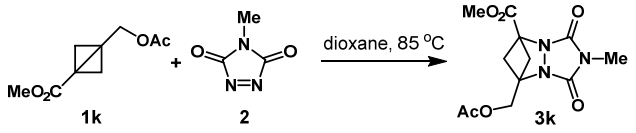
Methyl 2-methyl-1,3-dioxo-7-(((triethylsilyl)oxy)methyl)tetrahydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4]triazole-5-carboxylate (3j)

The title compound was prepared according to **General Procedure B**, using **1j** (0.256 g, 1.00 mmol), MTAD (0.170 g, 1.50 mmol) in 1,4-dioxane (40 mL) at 85 °C for 7 h; column chromatography on silica gel (PE:EA = 6:1) afforded the product **3j** (0.160 g, 0.433 mmol, 43% yield) and recovered **1j** (0.100 g, 0.390mmol, 39% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.17 (s, 2H), 3.83 (s, 3H), 3.01 (s, 3H), 2.55 – 2.46 (m, 2H), 1.95 – 1.86 (m, 2H), 0.91 (t, *J* = 7.9 Hz, 9H), 0.58 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 165.46, 160.04, 159.99, 73.68, 69.08, 58.54, 52.79, 42.88, 25.69, 6.53, 4.13.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{16}H_{28}O_5N_3Si$, 370.1793; found, 370.1790.



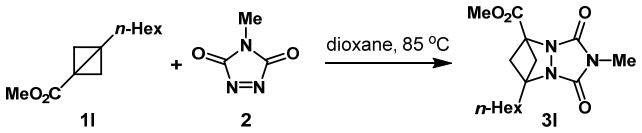
Methyl 7-(acetoxymethyl)-2-methyl-1,3-dioxotetrahydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4] triazole-5-carboxylate (3k)

The title compound was prepared according to General Procedure B, using 1k (36.8 mg, 0.200 mmol), MTAD (33.9 mg, 0.300 mmol) in 1,4-dioxane (8 mL) at 85 °C for 20 h; column chromatography on silica gel (PE:EA = 6:1) afforded the product **3k** (38.0 mg, 0.128 mmol, 64% yield) and recovered **1k** (8.1 mg, 44.0 μmol, 22% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.73 (s, 2H), 3.87 (s, 3H), 3.06 (s, 3H), 2.51 – 2.42 (m, 2H), 2.11 (s, 3H), 2.11 – 2.01 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.21, 165.06, 159.90, 159.77, 70.71, 69.28, 59.63, 53.03, 44.00, 25.90, 20.57.

HRMS-DART (*m*/*z*): $[M+H]^+$ calcd. for $C_{12}H_{16}O_6N_3$, 298.1034; found, 298.1028.



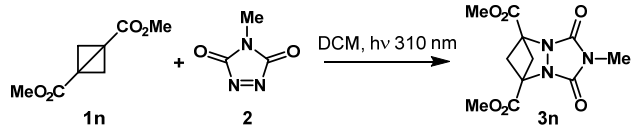
Methyl 7-hexyl-2-methyl-1,3-dioxotetrahydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4]triazole-5-carboxylate (3l)

The title compound was prepared according to **General Procedure B**, using **1l** (0.196 g, 1.00 mmol), MTAD (0.170 g, 1.50 mmol) in 1,4-dioxane (40 mL) at 85 °C for 3 h; column chromatography on silica gel (PE:EA = 6:1) to afford the product **3l** (49.8 mg, 0.161 mmol, 16% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.86 (s, 3H), 3.04 (s, 3H), 2.36 – 2.27 (m, 2H), 2.16 – 2.10 (m, 2H), 2.04 – 1.96 (m, 2H), 1.53 – 1.43 (m, 2H), 1.41 – 1.23 (m, 6H), 0.87 (t, J = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 165.67, 160.07, 159.68, 74.36, 68.94, 52.88, 44.82, 31.51, 29.13, 28.68, 25.71, 24.95, 22.46, 13.98.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{15}H_{24}O_4N_3$, 310.1761; found, 310.1757



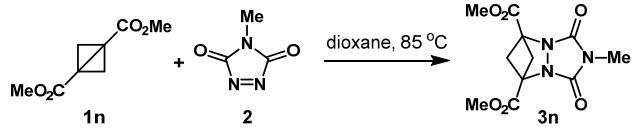
Dimethyl 2-methyl-1,3-dioxodihydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4]triazole-5,7(6H)-dicarboxylate (3n)

A solution of **1n** (17.0 mg, 0.100 mmol) MTAD (17.0 mg, 0.150 mmol) in DCM (2 mL) was irradiated at 310 nm UV light for 17 h. The reaction mixture was concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 3:1) to afford the product **3n** (18.3 mg, 0.0646 mmol, 65% yield) and recovered **1n** (4.9 mg, 0.0288 mmol, 29% yield).

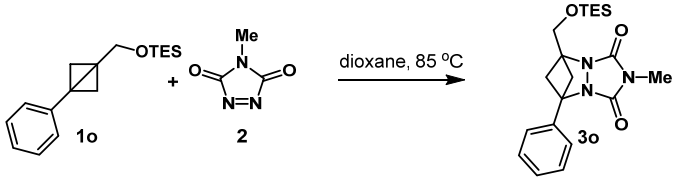
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.90 (s, 6H), 3.07 (s, 3H), 2.78 – 2.68 (m, 2H), 2.36 – 2.26 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 164.48, 159.77, 68.95, 53.23, 45.04, 26.05.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{11}H_{14}O_6N_3$, 284.0877; found, 284.0875.



The title compound was prepared according to **General Procedure B**, using **1n** (34.0 mg, 0.200 mmol), MTAD (33.9 mg, 0.300 mmol) in 1,4-dioxane (8 mL) at 85 °C for 108 h; column chromatography on silica gel (PE:EA = 3:1) to afford the product **3n** (20.4 mg, 0.0720 mmol, 36% yield).



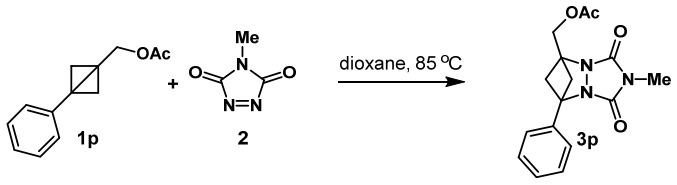
2-Methyl-5-phenyl-7-(((triethylsilyl)oxy)methyl)dihydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4] triazole-1,3(2H)-dione (3o)

The title compound was prepared according to **General Procedure B**, using the crude **1o** (from **1a** (0.200 mmol)), MTAD (33.9 mg, 0.300 mmol) in 1,4-dioxane (8 mL) at rt for 12 h; column chromatography on silica gel (PE:EA = 6:1) afforded the product **3o** (23.3 mg, 60.1 μmol, 30% yield over 3 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.57 – 7.31 (m, 5H), 4.30 (s, 2H), 3.02 (s, 3H), 2.55 – 2.45 (m, 2H), 2.18 – 2.09 (m, 2H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.64 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 160.23, 159.78, 133.41, 128.95, 128.41, 127.11, 74.24, 73.34, 59.03, 43.99, 25.63, 6.70, 4.30.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{20}H_{30}O_3N_3Si$, 388.2051; found, 388.2048.



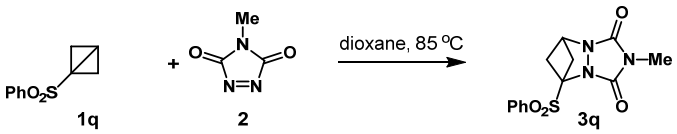
(2-Methyl-1,3-dioxo-7-phenyltetrahydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4]triazol-5-yl)methyl acetate (3p).

The title compound was prepared according to **General Procedure B**, using the crude **1p** (from **1a** (0.200 mmol)), MTAD **2** (33.9 mg, 0.300 mmol) in 1,4-dioxane (8 mL) at rt for 75 min; column chromatography on silica gel (PE:EA = 6:1) afforded the product **3p** (37.5 mg, 0.119 mmol, 59% yield over 3 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.46 – 7.38 (m, 5H), 4.82 (s, 2H), 3.03 (s, 3H), 2.45 – 2.36 (m, 2H), 2.30 – 2.21 (m, 2H), 2.13 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.35, 159.94, 159.52, 132.80, 129.15, 128.47, 127.02, 74.41, 70.22, 60.11, 44.99, 25.69, 20.64.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{16}H_{18}O_4N_3$, 316.1292; found, 316.1290.



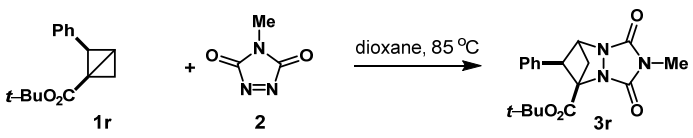
2-Methyl-5-(phenylsulfonyl)dihydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4]triazole-1,3(2H)-dione (3q)

The title compound was prepared according to **General Procedure B**, using **1q** (0.194 g, 1.00 mmol), MTAD (0.170 g, 1.50 mmol) in 1,4-dioxane (40 mL) at 85 °C for 29 h; column chromatography on silica gel (PE:EA = 3:1) to afford the product **3q** (0.121 g, 0.394 mmol, 39% yield) and recovered **1q** (90.8 mg, 0.468 mmol, 47% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.14 (d, *J* = 7.8 Hz, 2H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 2H), 4.75 (t, *J* = 2.0 Hz, 1H), 3.04 (s, 3H), 2.86 – 2.79 (m, 2H), 2.05 – 1.96 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 159.46, 157.59, 134.91, 134.84, 129.97, 129.09, 84.55, 57.58, 42.43, 26.13.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{13}H_{14}O_4N_3S$, 308.0700; found, 308.0698.



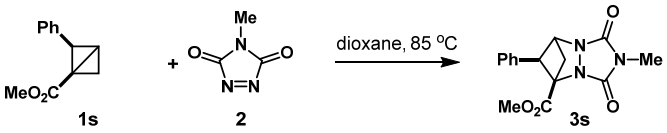
***Tert*-butyl (5*S**,6*S**)-2-methyl-1,3-dioxo-6-phenyltetrahydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4] triazole-5-carboxylate (3r)**

The title compound was prepared according to **General Procedure B**, using **1r** (25.0 mg, 0.109 mmol), MTAD (18. 4 mg, 0.163 mmol) in 1,4-dioxane (4.5 mL) at 85 °C for 1 h; column chromatography on silica gel (PE:EA = 4:1) to afford the product **3r** (7.4 mg, 21.5 μmol, 20% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.40 – 7.28 (m, 3H), 7.21 (d, *J* = 7.2 Hz, 2H), 4.91 (s, 1H), 4.04 (d, *J* = 8.5 Hz, 1H), 3.11 (s, 3H), 2.80 (d, *J* = 10.0 Hz, 1H), 1.78 (t, *J* = 9.3 Hz, 1H), 1.55 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 163.31, 160.81, 160.33, 132.79, 128.89, 127.98, 127.82, 83.91, 75.24, 62.50, 61.31, 37.07, 27.85, 25.91.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{18}H_{22}O_4N_3$, 344.1605; found, 344.1606.



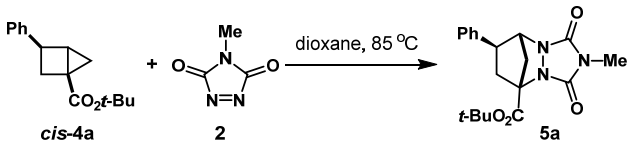
Methyl (5*S,6*S**)-2-methyl-1,3-dioxo-6-phenyltetrahydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4] triazole-5-carboxylate (3s)**

The title compound was prepared according to **General Procedure B**, using **1s** (37.6 mg, 0.200 mmol), MTAD (33.9 mg, 0.300 mmol) in 1,4-dioxane (8 mL) at 85 °C for 3.5 h; column chromatography on silica gel (PE:EA = 4:1) to afford the product **3s** (18.9 mg, 0.0627 mmol, 31% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.46 – 7.28 (m, 3H), 7.15 (d, *J* = 7.3 Hz, 2H), 4.96 (s, 1H), 4.07 (d, *J* = 8.6 Hz, 1H), 3.88 (s, 3H), 3.12 (s, 3H), 2.87 (d, *J* = 10.0 Hz, 1H), 1.84 (t, *J* = 9.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 164.77, 160.71, 160.36, 132.47, 129.08, 128.10, 127.64, 74.30, 62.63, 61.65, 53.00, 37.17, 25.99.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{15}H_{16}O_4N_3$, 302.1135; found, 302.1134.



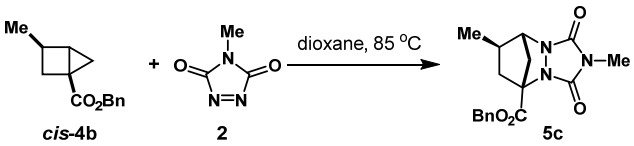
Tert-butyl (5*S,7*R**,8*S**)-2-methyl-1,3-dioxo-7-phenyltetrahydro-1H-5,8-methano[1,2,4]triazolo[1,2-a] pyridazine-5(6H)-carboxylate (5a)**

The title compound was prepared according to **General Procedure B**, using *cis*-**4a** (48.9 mg, 0.200 mmol), MTAD (33.9 mg, 0.300 mmol) in 1,4-dioxane (8 mL) at 85 °C for 32 h; column chromatography on silica gel (PE:EA = 3:1) to afford the product **5a** (58.6 mg, 0.164 mmol, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.28 (t, *J* = 7.5 Hz, 1H), 7.24 – 7.07 (m, 3H), 4.45 (s, 1H), 3.31 – 3.24 (m, 1H), 3.03 (s, 3H), 2.52 (dd, *J* = 14.2, 5.5 Hz, 1H), 2.43 – 2.28 (m, 3H), 1.50 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 165.92, 156.91, 156.33, 139.36, 128.95, 127.32, 127.05, 83.58, 72.34, 64.75, 45.29, 41.64, 36.33, 27.89, 25.74.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{19}H_{24}O_4N_3$, 358.1761; found, 358.1753.



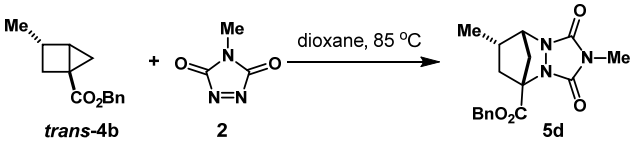
Benzyl (5*S,7*S**,8*S**)-2,7-dimethyl-1,3-dioxotetrahydro-1H-5,8-methano[1,2,4]triazolo[1,2-a]pyridazine-5(6H)-carboxylate (5c)**

The title compound was prepared according to **General Procedure B**, using *cis*-**4b** (43.3 mg, 0.200 mmol), MTAD (33.9 mg, 0.300 mmol) in 1,4-dioxane (8 mL) at 85 °C for 60 h; column chromatography on silica gel (PE:EA = 1:1) afforded the product **5c** (56.0 mg, 0.170 mmol, 85% yield) and recovered *cis*-**4b** (4.9 mg, 22.7 μmol, 11% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43 – 7.30 (m, 5H), 5.30 (d, J = 17.0 Hz, 1H), 5.23 (d, J = 17.1 Hz, 1H), 4.40 (s, 1H), 3.05 (s, 3H), 2.43 – 2.29 (m, 2H), 2.13 – 2.05 (mk, 2H), 1.75 – 1.65 (m, 1H), 1.14 (d, J = 5.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 166.45, 158.84, 157.21, 134.99, 128.56, 128.45, 128.35, 73.54, 67.93, 64.59, 42.65, 39.31, 35.95, 25.67, 16.08.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{17}H_{19}O_4N_3$, 329.1370; found, 329.1371.



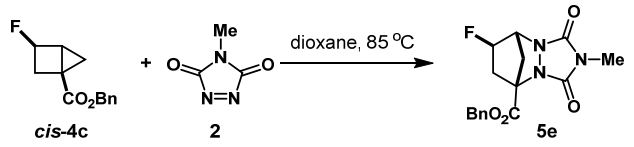
Benzyl (5*S,7*R**,8*S**)-2,7-dimethyl-1,3-dioxotetrahydro-1H-5,8-methano[1,2,4]triazolo[1,2-a]pyridazine-5(6H)-carboxylate (5d)**

The title compound was prepared according to **General Procedure B**, using *trans*-**4b** (43.3 mg, 0.200 mmol), MTAD (33.9 mg, 0.300 mmol) in 1,4-dioxane (8 mL) at 85 °C for 60 h; column chromatography on silica gel (PE:EA =1:1) afforded the product **5d** (18.5 mg, 56.2 μmol, 28% yield) and recovered *trans*-**4b** (28.1 mg, 0.130 mmol, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.44 – 7.30 (m, 5H), 5.35 – 5.26 (m, 2H), 4.23 (s, 1H), 3.05 (s, 3H), 2.45 (d, J = 10.5 Hz, 1H), 2.37 – 2.28 (m, 2H), 2.20 – 2.09 (m, 1H), 1.83 (dd, J = 13.7, 4.9 Hz, 1H), 1.06 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 167.13, 156.96, 156.35, 135.01, 128.61, 128.47, 128.16, 71.54, 67.91, 64.51, 41.46, 38.79, 34.87, 25.70, 19.59.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{17}H_{19}O_4N_3$, 329.1370; found, 329.1370.



Benzyl (5*R,7*S**,8*S**)-7-fluoro-2-methyl-1,3-dioxotetrahydro-1H-5,8-methano[1,2,4]triazolo[1,2-a] pyridazine-5(6H)-carboxylate (5e)**

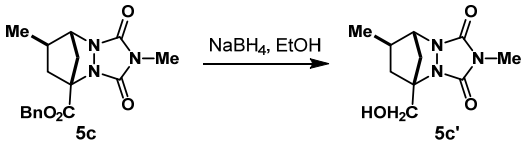
The title compound was prepared according to **General Procedure B**, using *cis*-**4c** (44.0 mg, 0.200 mmol), MTAD (33.9 mg, 0.300 mmol) in 1,4-dioxane (8.00 mL) at 85 °C for 70 h; column chromatography on silica gel (PE:EA = 1:1) afforded the product **5e** (17.7 mg, 53.1 μmol, 27% yield) and recovered *cis*-**4c** (19.9 mg, 9.04 μmol, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43 – 7.33 (m, 5H), 5.34 (d, J = 12.2 Hz, 1H), 5.31 (d, J = 12.2 Hz, 1H), 4.93 (dd, J = 51.4, 5.9 Hz, 1H), 4.65 (s, 1H), 3.05 (s, 3H), 2.52 – 2.30 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 165.68, 156.63, 156.59, 134.68, 128.66, 128.64, 128.33, 88.34 (d, J = 195.5 Hz), 70.41, 68.31, 61.19 (d, J = 28.8 Hz), 40.27, 39.97 (d, J = 22.3 Hz), 25.87.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): −170.21.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{16}H_{16}FO_4N_3$, 333.1119; found, 333.1121.



(5*S,7*S**,8*S**)-5-(hydroxymethyl)-2,7-dimethyltetrahydro-1H-5,8-methano[1,2,4]triazolo[1,2-a]pyridazine-1,3(2H)-dione (5c').**

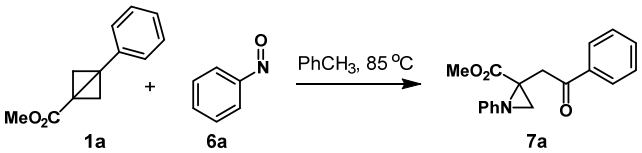
To a solution of **5c** (54.2 mg, 0.165 mmol) in EtOH (1 mL) was added $NaBH_4$ (31.1 mg, 0.822 mmol) at room temperature. After 4 h, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl, and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated, and the residue was purified by flash chromatography on silica gel (PE:EA = 1:1) to afford the pure product **5c'** (34.1 mg, 0.151 mmol, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.15 (d, *J* = 21.5 Hz, 1H), 4.06 (dd, *J* = 18.5, 11.4 Hz, 2H), 4.01 – 3.84 (m, 1H), 3.03 (s, 3H), 2.23 – 2.02 (m, 3H), 1.95 (d, *J* = 10.6 Hz, 1H), 1.30 (dd, *J* = 12.6, 3.5 Hz, 1H), 1.00 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 157.24, 156.06, 74.74, 63.81, 62.25, 38.86, 38.50, 35.15, 25.67, 19.58.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{10}H_{15}O_3N_3$, 225.1108; found, 225.1107.

b. Cycloaddition of BCBs 1 with nitrosoarenes



General Procedure C:

Methyl 2-(2-oxo-2-phenylethyl)-1-phenylaziridine-2-carboxylate (7a)

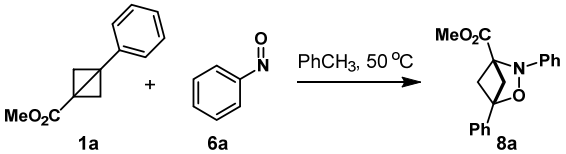
A solution of **1** (18.8 mg, 0.100 mmol) and nitrosobenzene **6a** (16.1 mg, 0.150 mmol) in toluene (2 mL) was heated at 85 °C for 24 h. The reaction mixture was concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 8:1) to afford the product **7a** (21.7 mg, 73.5 μmol, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.95 – 7.88 (m, 2H), 7.61 – 7.52 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.19 (m, 2H), 7.04 – 6.95 (m, 3H), 3.86 (d, *J* = 17.9 Hz, 1H), 3.59 (s, 3H), 3.06 (s, 1H), 2.99 (d, *J* = 17.9 Hz, 1H), 2.39 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 196.65, 169.87, 148.71, 136.30, 133.30, 128.87, 128.54, 127.90, 122.90, 120.30, 52.32, 42.58, 41.22, 37.45.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{18}H_{17}NO_3$, 295.1203; found, 295.1205.

Methyl (1*S,4*S**)-1,3-diphenyl-2-oxa-3-azabicyclo[2.1.1]hexane-4-carboxylate (8a)**

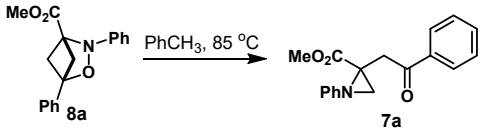


A solution of **1a** (18.8 mg, 0.100 mmol) and nitrosobenzene **6a** (16.1 mg, 0.150 mmol) in toluene (2 mL) was heated at 50 °C for 13 h. The reaction mixture was concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 8:1) to afford the product **8a** (16.4 mg, 55.6 μmol, 56% yield).

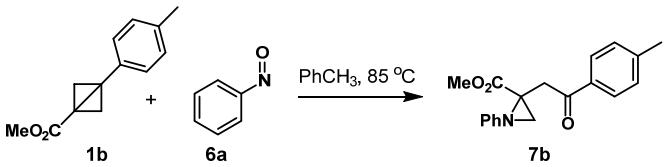
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.50 – 7.43 (m, 2H), 7.46 – 7.36 (m, 3H), 7.35 – 7.27 (m, 2H), 7.23 – 7.16 (m, 2H), 7.15 – 7.06 (m, 1H), 3.86 (s, 3H), 2.72 – 2.62 (m, 2H), 2.62 – 2.53 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 167.97, 149.50, 133.89, 129.00, 128.67, 128.54, 126.49, 124.48, 119.51, 87.56, 72.11, 52.52, 45.59.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{18}H_{17}NO_3$, 295.1203; found, 295.1207.



A solution of **8a** (10.3 mg, 34.9 μmol) in toluene (1 mL) was heated at 85 °C for 14 h. The reaction mixture was concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 8:1) to afford the product **8a** (8.2 mg, 27.8 μmol, 80% yield).



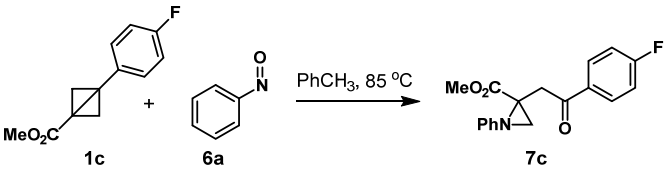
Methyl 2-(2-oxo-2-(p-tolyl)ethyl)-1-phenylaziridine-2-carboxylate (7b)

The title compound was prepared according to **General Procedure C**, using **1b** (40.4 mg, 0.200 mmol), nitrosobenzene **6a** (32.1 mg, 0.300 mmol) in toluene (4 mL) at 85 °C for 24 h; column chromatography on silica gel (PE:EA = 8:1) afforded the product **7b** (39.2 mg, 0.126 mmol, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.81 (d, *J* = 7.8 Hz, 2H), 7.28 – 7.20 (m, 4H), 7.04 – 6.95 (m, 3H), 3.84 (d, *J* = 17.8 Hz, 1H), 3.58 (s, 3H), 3.06 (s, 1H), 2.96 (d, *J* = 17.8 Hz, 1H), 2.40 (s, 3H), 2.38 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 196.21, 169.84, 148.77, 144.08, 133.90, 129.16, 128.82, 127.99, 122.82, 120.27, 52.23, 42.65, 41.09, 37.41, 21.52.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{19}H_{19}NO_3$, 309.1359; found, 309.1362.



Methyl 2-(2-(4-fluorophenyl)-2-oxoethyl)-1-phenylaziridine-2-carboxylate (7c)

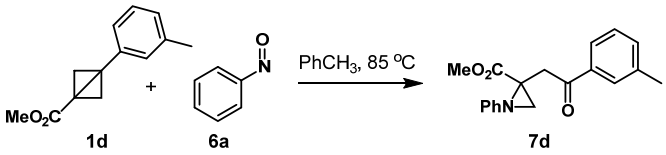
The title compound was prepared according to **General Procedure C**, using **1c** (41.2 mg, 0.200 mmol), nitrosobenzene **6a** (32.1 mg, 0.300 mmol) in toluene (4 mL) at 85 °C for 22 h; column chromatography on silica gel (PE:EA = 8:1) afforded the product **7c** (28.6 mg, 0.914 mmol, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.98 – 7.90 (m, 2H), 7.29 – 7.20 (m, 2H), 7.16 – 7.08 (m, 2H), 7.04 – 6.94 (m, 3H), 3.82 (d, *J* = 17.6 Hz, 1H), 3.58 (s, 3H), 3.06 (s, 1H), 2.96 (d, *J* = 17.8 Hz, 1H), 2.40 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 195.00, 169.76, 165.71 (d, *J* = 255.4 Hz), 148.57, 132.68 (d, *J* = 3.1 Hz), 130.50 (d, *J* = 9.4 Hz), 128.82, 122.87, 120.19, 115.60 (d, *J* = 21.9 Hz), 52.27, 42.48, 41.05, 37.37.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): −104.52.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{18}H_{16}FNO_3$, 313.1109; found, 313.1109.



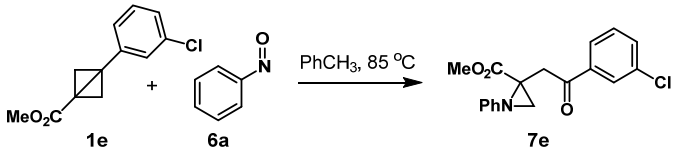
Methyl 2-(2-oxo-2-(m-tolyl)ethyl)-1-phenylaziridine-2-carboxylate (7d)

The title compound was prepared according to **General Procedure C**, using **1d** (40.4 mg, 0.200 mmol), nitrosobenzene **6a** (32.1 mg, 0.300 mmol) in toluene (4 mL) at 85 °C for 24 h; column chromatography on silica gel (PE:EA = 8:1) afforded the product **7d** (39.2 mg, 0.126 mmol, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.73 (s, 1H), 7.70 (d, *J* = 7.4 Hz, 1H), 7.34 (dt, *J* = 14.9, 7.5 Hz, 2H), 7.24 (t, *J* = 7.7 Hz, 2H), 7.04 – 6.95 (m, 3H), 3.83 (d, *J* = 17.9 Hz, 1H), 3.58 (s, 3H), 3.05 (s, 1H), 3.00 (d, *J* = 17.8 Hz, 1H), 2.39 (s, 3H), 2.38 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 196.46, 169.48, 148.36, 137.95, 135.95, 133.69, 128.50, 128.05, 128.02, 124.76, 122.50, 119.93, 51.97, 42.23, 40.92, 37.11, 20.90.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{19}H_{19}NO_3$, 309.1359; found, 309.1360.



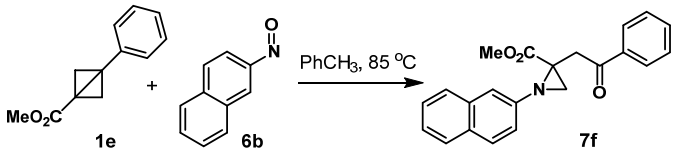
Methyl 2-(2-(3-chlorophenyl)-2-oxoethyl)-1-phenylaziridine-2-carboxylate (7e)

The title compound was prepared according to **General Procedure C**, using **1e** (44.4 mg, 0.200 mmol), nitrosobenzene **6a** (32.1 mg, 0.300 mmol) in toluene (4 mL) at 85 °C for 24 h; column chromatography on silica gel (PE:EA = 8:1) afforded the product **7e** (39.9 mg, 0.121 mmol, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.89 (t, *J* = 1.8 Hz, 1H), 7.78 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.03 – 6.94 (m, 3H), 3.78 (d, *J* = 18.0 Hz, 1H), 3.58 (s, 3H), 3.05 (s, 1H), 2.99 (d, *J* = 17.9 Hz, 1H), 2.40 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 195.41, 169.69, 148.53, 137.78, 134.85, 133.17, 129.85, 128.86, 127.98, 125.96, 122.94, 120.20, 52.32, 42.41, 41.26, 37.41.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{18}H_{16}ClNO_3$, 329.0813; found, 329.0815.



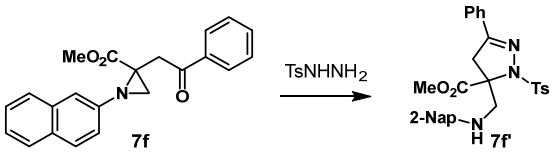
Methyl 1-(naphthalen-2-yl)-2-(2-oxo-2-phenylethyl)aziridine-2-carboxylate (7f)

The title compound was prepared according to **General Procedure C**, using **1a** (37.6 mg, 0.200 mmol), nitrosobenzene **6b** (37.7 mg, 0.240 mmol) in toluene (4 mL) at 85 °C for 24 h; column chromatography on silica gel (PE:EA = 8:1) afforded the product **7f** (58.0 mg, 0.168 mmol, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.92 – 7.85 (m, 2H), 7.78 – 7.68 (m, 3H), 7.58 – 7.49 (m, 1H), 7.46 – 7.38 (m, 3H), 7.38 – 7.30 (m, 1H), 7.31 – 7.22 (m, 2H), 3.87 (d, *J* = 17.9 Hz, 1H), 3.59 (s, 3H), 3.17 (s, 1H), 3.02 (d, *J* = 17.9 Hz, 1H), 2.50 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 196.70, 170.07, 146.59, 136.32, 134.04, 133.37, 130.30, 128.87, 128.59, 127.95, 127.68, 126.87, 126.34, 124.33, 121.59, 115.93, 52.48, 42.73, 41.09, 37.71.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{12}H_{19}NO_3$, 345.1359; found, 345.1365.



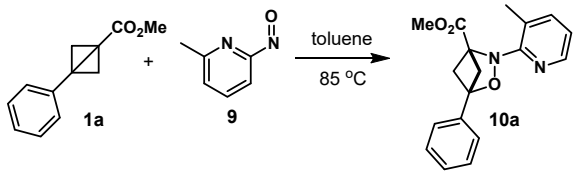
Methyl 5-((naphthalen-2-ylamino)methyl)-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole-5-carboxylate (7f')

A solution of **7f** (24.7 mg, 71.6 μmol) and $TsNHNH_2$ (16.0 mg, 85.9 μmol) in MeOH (1 mL) was heated at 60 °C for 72 h. The reaction mixture was concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 5:1) to afford the product **7f'** (13.3 mg, 25.9 μmol, 36% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.92 (d, *J* = 8.2 Hz, 2H), 7.68 – 7.53 (m, 4H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.27 (m, 6H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.78 (s, 1H), 6.74 (dd, *J* = 8.7, 2.3 Hz, 1H), 4.07 (d, *J* = 13.6 Hz, 1H), 3.87 (d, *J* = 13.6 Hz, 1H), 3.79 (s, 3H), 3.68 (d, *J* = 17.1 Hz, 1H), 3.48 (d, *J* = 17.1 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.94, 153.17, 145.42, 144.18, 136.40, 134.86, 130.47, 130.21, 129.53, 129.01, 128.60, 127.85, 127.51, 126.72, 126.40, 125.97, 122.40, 118.20, 105.03, 73.68, 53.08, 46.81, 43.64, 21.60.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{29}H_{27}N_3O_4S$, 513.1717; found, 513.1714.



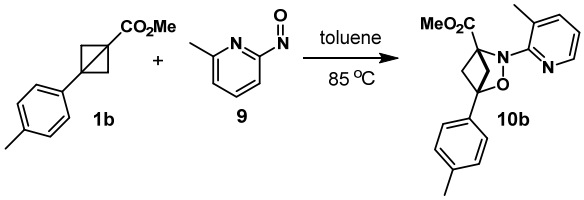
Methyl (1*S,4*S**)-3-(3-methylpyridin-2-yl)-1-phenyl-2-oxa-3-azabicyclo[2.1.1]hexane-4-carboxylate (10a)**

The title compound was prepared according to **General Procedure C**, using **1a** (37.6 mg, 0.200 mmol), nitrosoarene **9** (29.3 mg, 0.240 mmol) in toluene (4 mL) at 85 °C for 2.5h; column chromatography on silica gel (PE:EA = 10:1) afforded the product **10a** (56.4 mg, 0.182 mmol, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.51 (t, *J* = 7.8 Hz, 1H), 7.45 – 7.34 (m, 5H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 3.89 (s, 3H), 2.64 – 2.56 (m, 2H), 2.46 – 2.40 (m, 2H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 168.36, 161.71, 155.88, 137.82, 133.94, 128.99, 128.49, 126.47, 117.94, 111.03, 88.91, 70.17, 52.22, 45.83, 23.91.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{18}H_{18}N_2O_3$, 310.1312; found, 310.1312.



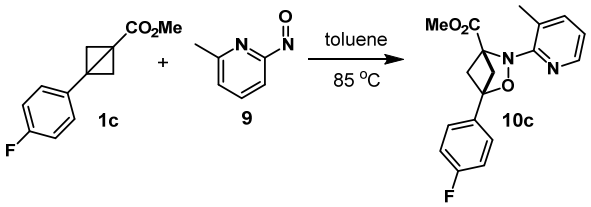
Methyl (1*S,4*S**)-3-(3-methylpyridin-2-yl)-1-(*p*-tolyl)-2-oxa-3-azabicyclo[2.1.1]hexane-4-carboxylate (10b)**

The title compound was prepared according to **General Procedure C**, using **1b** (20.2 mg, 0.100 mmol), nitrosoarene **9** (14.6 mg, 0.120 mmol) in toluene (2 mL) at 85 °C for 3 h; column chromatography on silica gel (PE:EA = 10:1) afforded the product **10b** (28.3 mg, 87.3 μmol, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 – 7.47 (m, 1H), 7.35 – 7.29 (m, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.77 (d, *J* = 7.4 Hz, 1H), 3.89 (s, 3H), 2.61 – 2.53 (m, 2H), 2.46 – 2.37 (m, 2H), 2.38 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 168.47, 161.79, 155.88, 138.99, 137.82, 130.98, 129.18, 126.44, 117.90, 111.05, 88.90, 70.19, 52.24, 45.79, 23.94, 21.27.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{19}H_{20}N_2O_3$, 324.1468; found, 324.1473.



Methyl (1*S,4*S**)-1-(4-fluorophenyl)-3-(3-methylpyridin-2-yl)-2-oxa-3-azabicyclo[2.1.1]hexane-4-carboxylate (10c)**

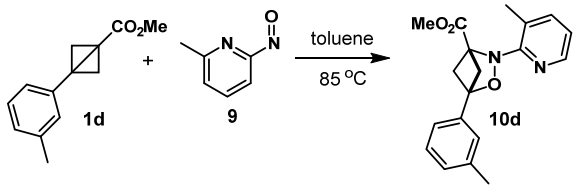
The title compound was prepared according to **General Procedure C**, using **1c** (41.2 mg, 0.200 mmol), nitrosoarene **9** (29.3 mg, 0.240 mmol) in toluene (4 mL) at 85 °C for 3 h; column chromatography on silica gel (PE:EA = 10:1) afforded the product **10c** (50.1 mg, 0.153 mmol, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.51 (t, *J* = 7.8 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.11 – 7.04 (m, 2H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.78 (d, *J* = 7.4 Hz, 1H), 3.88 (s, 3H), 2.62 – 2.54 (m, 2H), 2.46 – 2.37 (m, 2H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 168.22, 163.03 (d, *J* = 248.0 Hz), 161.57, 155.92, 137.86, 129.87 (d, *J* = 3.2 Hz), 128.43 (d, *J* = 8.5 Hz), 118.03, 115.51 (d, *J* = 21.8 Hz), 111.03, 88.34, 70.11, 52.25, 45.83, 23.90.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): −112.05.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{18}H_{17}FN_2O_3$, 328.1218; found, 328.1218.



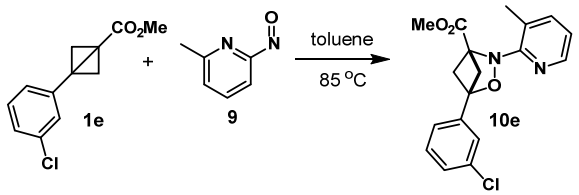
Methyl (1*S,4*S**)-3-(3-methylpyridin-2-yl)-1-(m-tolyl)-2-oxa-3-azabicyclo[2.1.1]hexane-4-carboxylate (10d)**

The title compound was prepared according to **General Procedure C**, using **1d** (40.4 mg, 0.200 mmol), nitrosoarene **9** (29.3 mg, 0.240 mmol) in toluene (4 mL) at 85 °C for 3h; column chromatography on silica gel (PE:EA = 10:1) afforded the product **10d** (56.9 mg, 0.176 mmol, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.51 (t, *J* = 7.8 Hz, 1H), 7.33 – 7.15 (m, 4H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.78 (d, *J* = 7.4 Hz, 1H), 3.89 (s, 3H), 2.62 – 2.53 (m, 2H), 2.46 – 2.38 (m, 2H), 2.38 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 168.44, 161.75, 155.89, 138.28, 137.83, 133.83, 129.78, 128.43, 127.10, 123.55, 117.93, 111.06, 88.97, 70.18, 52.24, 45.82, 23.93, 21.34.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{19}H_{20}N_2O_3$, 324.1468; found, 324.1471.



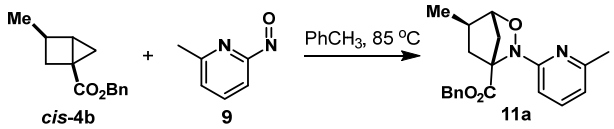
Methyl (1*S,4*S**)-1-(3-chlorophenyl)-3-(3-methylpyridin-2-yl)-2-oxa-3-azabicyclo[2.1.1]hexane-4-carboxylate (10e)**

The title compound was prepared according to **General Procedure C**, using **1e** (44.4 mg, 0.200 mmol), nitrosoarene **9** (29.3 mg, 0.240 mmol) in toluene (4 mL) at 85 °C for 3 h; column chromatography on silica gel (PE:EA = 10:1) afforded the product **10e** (53.7 mg, 0.156 mmol, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.52 (t, *J* = 7.8 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.37 – 7.28 (m, 3H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.79 (d, *J* = 7.4 Hz, 1H), 3.88 (s, 3H), 2.65 – 2.54 (m, 2H), 2.45 – 2.35 (m, 2H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 168.08, 161.46, 155.94, 137.90, 135.92, 134.49, 129.84, 129.11, 126.73, 124.63, 118.11, 111.06, 88.16, 70.13, 52.27, 45.97, 23.89.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{18}H_{17}ClN_2O_3$, 344.0922; found, 344.0923.



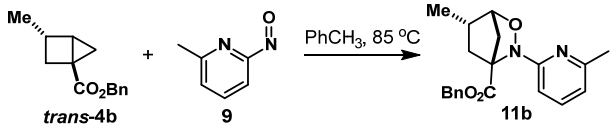
Benzyl (1*R,4*R**,6*R**)-6-methyl-3-(6-methylpyridin-2-yl)-2-oxa-3-azabicyclo[2.2.1]heptane-4-carboxylate (11a)**

The title compound was prepared according to **General Procedure C**, using *cis*-**4b** (21.6 mg, 0.100 mmol), nitrosoarene **9** (14.6 mg, 0.120 mmol) in toluene (2 mL) at 85 °C for 31 h; column chromatography on silica gel (PE:EA = 8:1) afforded the product **11a** (21.4 mg, 63.3 μmol, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.49 – 7.41 (m, 1H), 7.41 – 7.31 (m, 5H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.71 (d, *J* = 7.5 Hz, 1H), 5.26 (s, 2H), 4.71 (s, 1H), 2.56 – 2.35 (m, 2H), 2.44 (s, 3H), 2.07 (dd, *J* = 10.5, 1.2 Hz, 1H), 1.90 (ddt, *J* = 10.5, 3.1, 1.7 Hz, 1H), 1.62 (dd, *J* = 12.5, 4.6 Hz, 1H), 1.12 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 169.37, 162.99, 156.62, 137.95, 135.44, 128.58, 128.32, 127.89, 117.09, 108.39, 87.02, 68.75, 66.90, 42.56, 37.33, 35.17, 24.26, 19.77.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{20}H_{22}N_2O_3$, 338.1625; found, 338.1625.



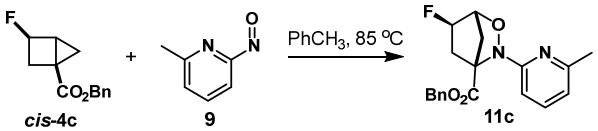
Benzyl (1*R,4*R**,6*S**)-6-methyl-3-(6-methylpyridin-2-yl)-2-oxa-3-azabicyclo[2.2.1]heptane-4-carboxylate (11b)**

The title compound was prepared according to **General Procedure C**, using *trans*-**4b** (21.6 mg, 0.100 mmol), nitrosoarene **9** (24.4 mg, 0.200 mmol) in toluene (2 mL) at 85 °C for 41h; column chromatography on silica gel (PE:EA = 8:1) afforded the product **11a** (5.0 mg, 14.8 μmol, 15% yield) and recovered *trans*-**4b** (14.5 mg, 67.0 μmol, 67% yield),.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.44 (t, *J* = 7.8 Hz, 1H), 7.41 – 7.29 (m, 5H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.69 (d, *J* = 7.4 Hz, 1H), 5.25 (s, 2H), 4.93 (s, 1H), 2.49-2.38 (m, 1H), 2.43 (s, 3H), 2.35 (t, *J* = 11.6 Hz, 1H), 1.99 (d, *J* = 10.1 Hz, 1H), 1.94 (ddd, *J* = 10.2, 2.8, 1.8 Hz, 1H), 1.71 – 1.64 (m, 1H), 1.31 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 169.42, 164.02, 156.52, 137.76, 135.47, 128.58, 128.31, 127.88, 116.80, 108.40, 88.10, 67.82, 66.86, 41.53, 41.49, 34.36, 24.34, 16.26.

HRMS-EI (m/z): [M]+ calcd. for $C_{20}H_{22}N_2O_3$, 338.1625; found, 338.1624.



Benzyl (1*R,4*S**,6*R**)-6-fluoro-3-(6-methylpyridin-2-yl)-2-oxa-3-azabicyclo[2.2.1]heptane-4-carboxylate (11c)**

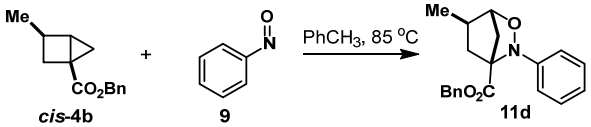
The title compound was prepared according to **General Procedure C**, using *cis*-**4c** (22.0 mg, 0.100 mmol), nitrosoarene **9** (14.6 mg, 0.120 mmol) in toluene (2 mL) at 85 °C for 31h; column chromatography on silica gel (PE:EA = 8:1) afforded the product **11a** (7.9 mg, 23.1 μmol, 23% yield) and recovered *cis*-**4c** (9.7 mg, 44.1 μmol, 44% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.48 (t, *J* = 7.8 Hz, 1H), 7.41 – 7.32 (m, 5H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.76 (d, *J* = 7.5 Hz, 1H), 5.33 – 5.11 (m, 4H), 2.67 – 2.52 (m, 1H), 2.45 (s, 3H), 2.35 – 2.18 (m, 2H), 2.09 – 2.03 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 167.98, 161.39, 161.36, 156.81, 138.16, 135.12, 128.66, 128.50, 128.02, 117.59, 108.30, 91.15 (d, *J* = 188.3 Hz), 85.33 (d, *J* = 2.7 Hz), 67.29, 65.81 (d, *J* = 29.5 Hz), 43.44 (d, *J* = 21.5 Hz), 37.40, 24.24.

^{19}F NMR (376 MHz, $CDCl_3$) δ(ppm): −173.68.

HRMS-EI (m/z): $[M]^+$ calcd. for $C_{19}H_{19}FN_2O_3$, 342.1374; found, 342.1377.



Benzyl (1*R,4*R**,6*R**)-6-methyl-3-phenyl-2-oxa-3-azabicyclo[2.2.1]heptane-4-carboxylate (11d)**

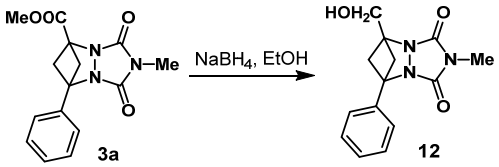
The title compound was prepared according to **General Procedure C**, using *cis*-**4b** (43.3 mg, 0.200 mmol), nitrosoarene **9** (32.1 mg, 0.300 mmol) in toluene (4 mL) at 85 °C for 41 h; column chromatography on silica gel (PE:EA = 8:1) afforded the product **11d** (26.8 mg, 83.0 μmol, 42% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.47 – 7.32 (m, 5H), 7.28 – 7.22 (m, 2H), 7.13 – 7.07 (m, 2H), 6.99 – 6.94 (m, 1H), 5.31 (d, *J* = 12.5 Hz, 1H), 5.26 (d, *J* = 12.5 Hz, 1H), 3.85 (s, 1H), 2.53 – 2.42 (m, 1H), 2.42 – 2.31 (m, 1H), 2.18 – 2.09 (m, 1H), 2.04 (d, *J* = 10.4 Hz, 1H), 1.69 – 1.57 (m, 2H), 1.09 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm):169.47, 151.33, 135.44, 128.61, 128.59, 128.33, 127.95, 122.49, 116.72, 86.18, 72.05, 66.96, 42.36, 36.57, 35.10, 19.80.

HRMS-EI (m/z): [M]+ calcd. for $C_{20}H_{21}NO_3$, 323.1516; found, 323.1518.

IV. Elaborations of cycloadducts



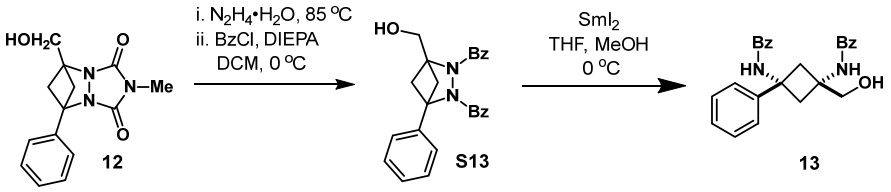
5-(Hydroxymethyl)-2-methyl-7-phenyldihydro-1*H*,5*H*-5,7-methanopyrazolo[1,2-a][1,2,4]triazole-1,3(2H)-dione (12).

To a solution of **3a** (0.515 g, 1.71 mmol) in EtOH (30 mL) was added $NaBH_4$ (0.325 g, 8.55 mmol) at rt. After 12 h, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl, and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated, and the residue was purified by flash chromatography on silica gel (PE:EA = 1:1) to afford the pure product **12** (0.397 g, 1.45 mmol, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.54 – 7.35 (m, 5H), 4.18 (d, *J* = 2.4 Hz, 2H), 3.67 (t, *J* = 2.4 Hz, 1H), 3.04 (s, 3H), 2.36 – 2.29 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 161.31, 159.08, 132.75, 129.13, 128.45, 126.98, 74.46, 72.70, 60.39, 44.97, 25.80.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{14}H_{16}O_3N_3$, 274.1186; found, 274.1184.



***N*,*N*'-((1*S**,3*S**)-1-(hydroxymethyl)-3-phenylcyclobutane-1,3-diyl)dibenzamide (13).**

A solution of **12** (54.6 mg, 0.200 mmol) in $N_2H_4 \cdot H_2O$ (85% in H_2O, 0.4 mL, 6.80 mmol, 34 equiv.) was heated at 85 °C for 5 h. The reaction mixture was concentrated, and the residue was directly submitted to the next step.

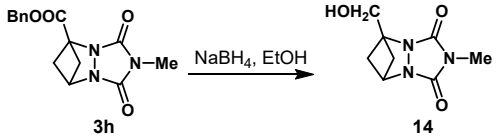
To a solution of above residue in CH_2Cl_2 (16 mL) was added BzCl (0.12 mL, 141 mg, 1.00 mmol), DIEPA (0.33 mL, 258 mg, 2.00 mmol) at 0 °C. After 4 h, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated, and the residue was purified by flash chromatography on silica gel to afford the product **S13** (50.8 mg, 0.127 mmol).

To a stirred solution of **S13** (50.8 mg, 0.127 mmol) in MeOH/THF (10 mL: 3.6 mL) at 0 °C was added a solution of SmI_2 (0.1 M in THF, 6.4 mL, 0.637 mmol) over 5 min. The solution was stirred at rt for 10 min before quenched with a saturated aqueous solution of NH_4Cl and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on silica gel to afford the pure product **13** (36.2 mg, 90.4 μmol, 45% yield over 3 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69 (d, *J* = 7.1 Hz, 2H), 7.32 – 7.17 (m, 3H), 7.15 – 6.89 (m, 8H), 6.81 (t, *J* = 7.6 Hz, 2H), 4.86 (t, *J* = 7.0 Hz, 1H), 4.31 (d, *J* = 5.5 Hz, 2H), 2.77 (d, *J* = 5.4 Hz, 2H), 2.23 (d, *J* = 3.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 177.14, 170.46, 136.02, 134.59, 134.13, 131.55, 130.10, 129.00, 128.57, 128.02, 127.76, 127.69, 127.26, 127.16, 77.20, 75.32, 72.96, 60.92.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{25}H_{25}O_3N_2$, 401.1860; found, 401.1859.



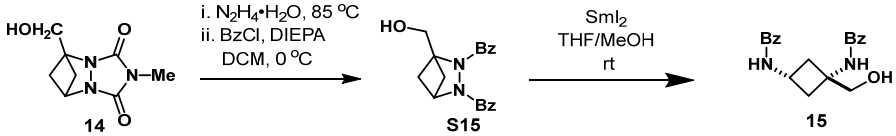
5-(Hydroxymethyl)-2-methyldihydro-1H,5H-5,7-methanopyrazolo[1,2-a][1,2,4]triazole-1,3(2H)-dione (14).

To a solution of **3h** (1.00 g, 3.32 mmol) in EtOH (30 mL) was added $NaBH_4$ (0.630 g, 16.6 mmol) at room temperature. After 12 h, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl, and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated, and the residue was purified by flash chromatography on silica gel (PE:EA = 1:2) to afford the pure product **15** (0.626 g, 3.17 mmol, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.69 (t, *J* = 1.9 Hz, 1H), 4.10 (s, 2H), 3.55 (brs, 1H), 3.07 (s, 3H), 2.21 – 2.10 (m, 2H), 1.86 – 1.77 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) 161.76, 160.25, 76.00, 60.21, 59.77, 41.63, 25.89.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_8H_{12}O_3N_3$, 198.0873; found, 198.0872.



***N*,*N*'-((1*S**,3*S**)-1-(hydroxymethyl)cyclobutane-1,3-diyl)dibenzamide (15).**

A solution of **14** (39.4 mg, 0.200 mmol) in $N_2H_4{\cdot}H_2O$ (85% in H_2O, 0.4 mL, 6.80 mmol, 34 equiv.) was heated at 85 ºC for 5 h. The reaction mixture was concentrated, and the residue was directly submitted to the next step.

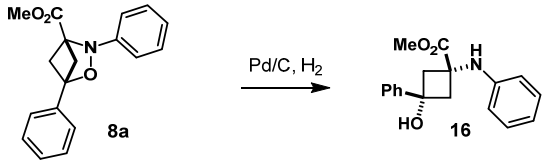
To a solution of above residue in CH_2Cl_2 (16 mL) was added BzCl (0.12 mL, 0.141 g, 1.00 mmol), DIEPA (0.33 mL, 0.258 g, 2.00 mmol) at 0 °C. After 4 h, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated, and the residue was purified by flash chromatography on silica gel to afford the product **S15** (58.0 mg, 0.160 mmol).

To a stirred solution of **S15** (58.0 mg, 0.160 mmol) in MeOH/THF (10 mL: 3.6 mL) at 0 °C was added a solution of SmI_2 (6.4 mL, 0.1 M in THF, 0.637 mmol) over 5 min. The solution was stirred at rt for 10 min before quenched with a saturated aqueous solution of NH_4Cl and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on silica gel to afford the pure product **15** (48.7 mg, 0.150 mmol, 75% yield over 3 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.09 (d, *J* = 7.8 Hz, 2H), 7.89 (d, *J* = 7.5 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.55 – 7.40 (m, 9H), 4.79 – 4.65 (m, 1H), 4.60 (s, 2H), 3.05 – 2.95 (m, 2H), 2.88 – 2.76 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 168.04, 167.45, 166.52, 134.37, 134.31, 133.68, 131.70, 131.35, 129.84, 129.15, 128.63, 128.57, 128.47, 127.08, 126.81, 69.83, 52.24, 37.73, 37.17.

HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd. for $C_{19}H_{21}O_3N_2$, 325.1547; found, 325.1545.



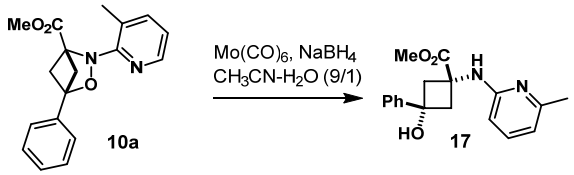
Methyl (1S*,3S*)-3-hydroxy-3-phenyl-1-(phenylamino)cyclobutane-1-carboxylate (16)

A solution of **8a** (23.4 mg, 79.7 μmol), 10% Pd/C (8.5 mg, 8.02 μmol) in MeOH (1 mL) was stirred at rt for 13 h under 1atm H_2 atmosphere. The reaction mixture was filtered, and filtrate was concentrated. The residue was purified by column chromatography on silica gel (PE:EA = 5:1) to afford the product **16** (15.3 mg, 51.5 μmol, 65% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.46 (m, 2H), 7.43 – 7.35 (m, 2H), 7.33 – 7.25 (m, 1H), 7.25 – 7.17 (m, 2H), 6.88 – 6.80 (m, 1H), 6.61 – 6.54 (m, 2H), 4.67 (brs, 1H), 3.66 (s, 3H), 3.36 – 3.28 (m, 2H), 3.24 (brs, 1H), 2.59 – 2.53 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.71, 145.00, 144.65, 129.30, 128.44, 127.51, 124.88, 119.59, 114.79, 73.70, 55.42, 52.61, 46.07.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{18}H_{19}NO_3$, 297.1359; found, 297.1360.

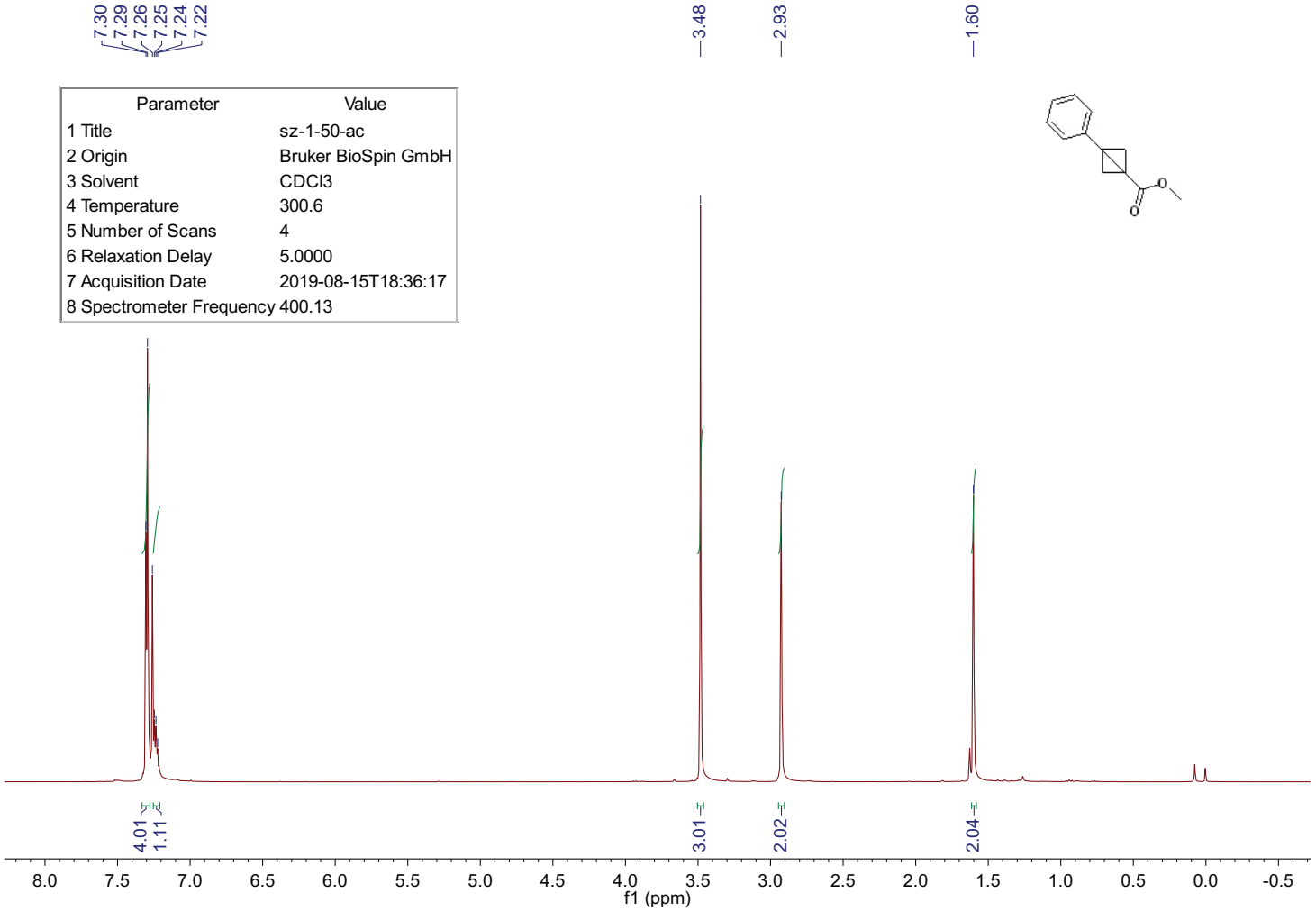


To a solution of **10a** (32.6 mg, 0.105 mmol) in CH_3CN-H_2O (9/1) was added sequentially $Mo(CO)_6$ (27.8 mg, 0.105 mmol) and $NaBH_4$ (8.8 mg, 0.231 mmol). The reaction mixture was heated at 65 ºC for 12 h, then concentrated. The residue was purified by column chromatography on silica gel (PE:EA = 5:1) to afford the product **17** (19.7 mg, 63.1 μmol, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.67 – 7.60 (m, 2H), 7.43 – 7.31 (m, 3H), 7.32 – 7.25 (m, 1H), 6.51 (d, *J* = 7.2 Hz, 1H), 6.33 (d, *J* = 8.3 Hz, 1H), 5.76 (brs, 1H), 3.76 (s, 3H), 3.43 – 3.33 (m, 2H), 3.16 – 3.08 (m, 2H), 2.44 (s, 3H), 1.68 (brs, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 175.84, 155.81, 155.57, 145.41, 138.01, 128.17, 126.98, 125.25, 112.78, 107.89, 71.14, 53.23, 52.90, 47.46, 23.49.

HRMS-EI (*m*/*z*): $[M]^+$ calcd. for $C_{18}H_{20}N_2O_3$, 312.1468; found, 312.1471.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7.24
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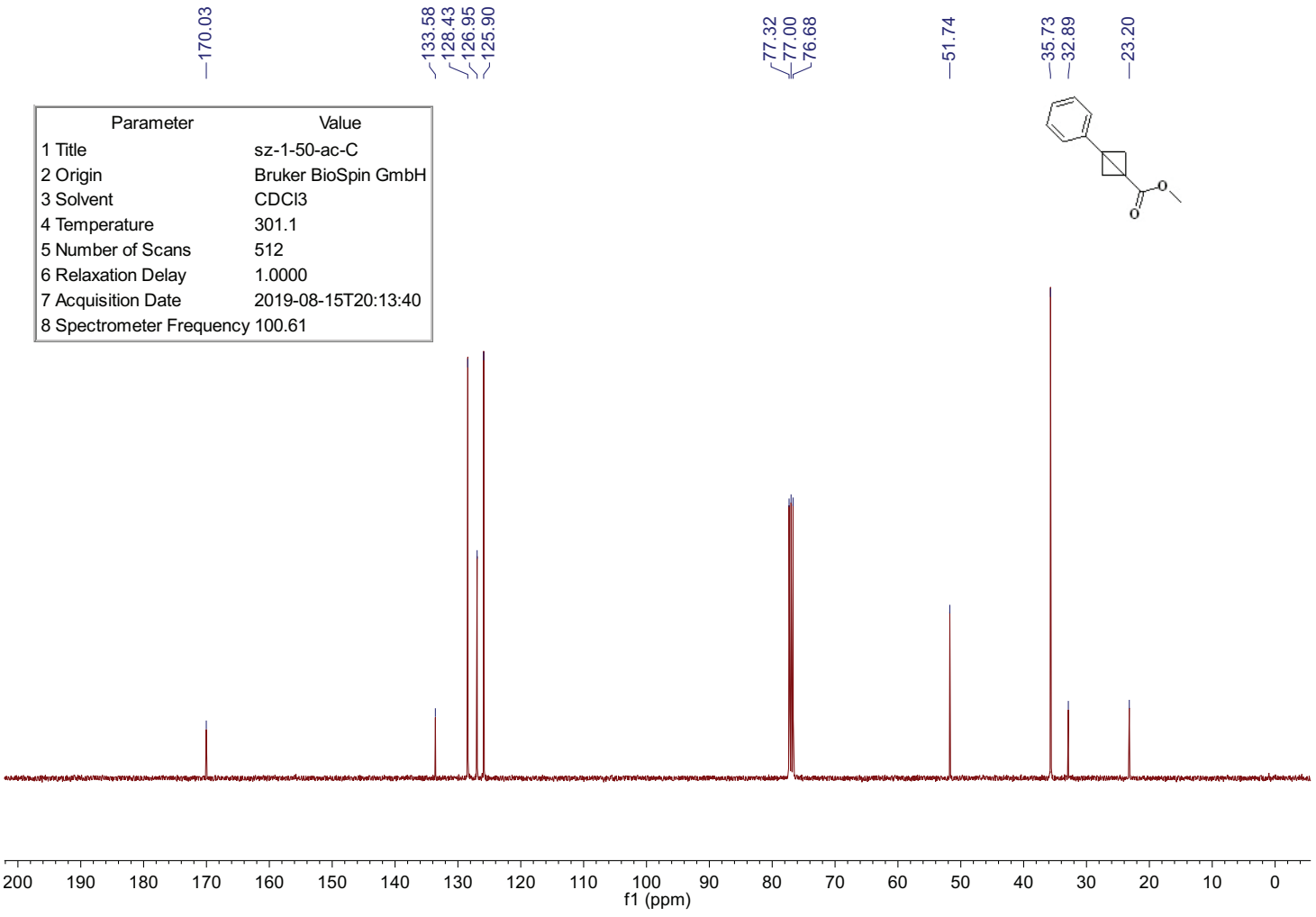
2.04
f1 (ppm)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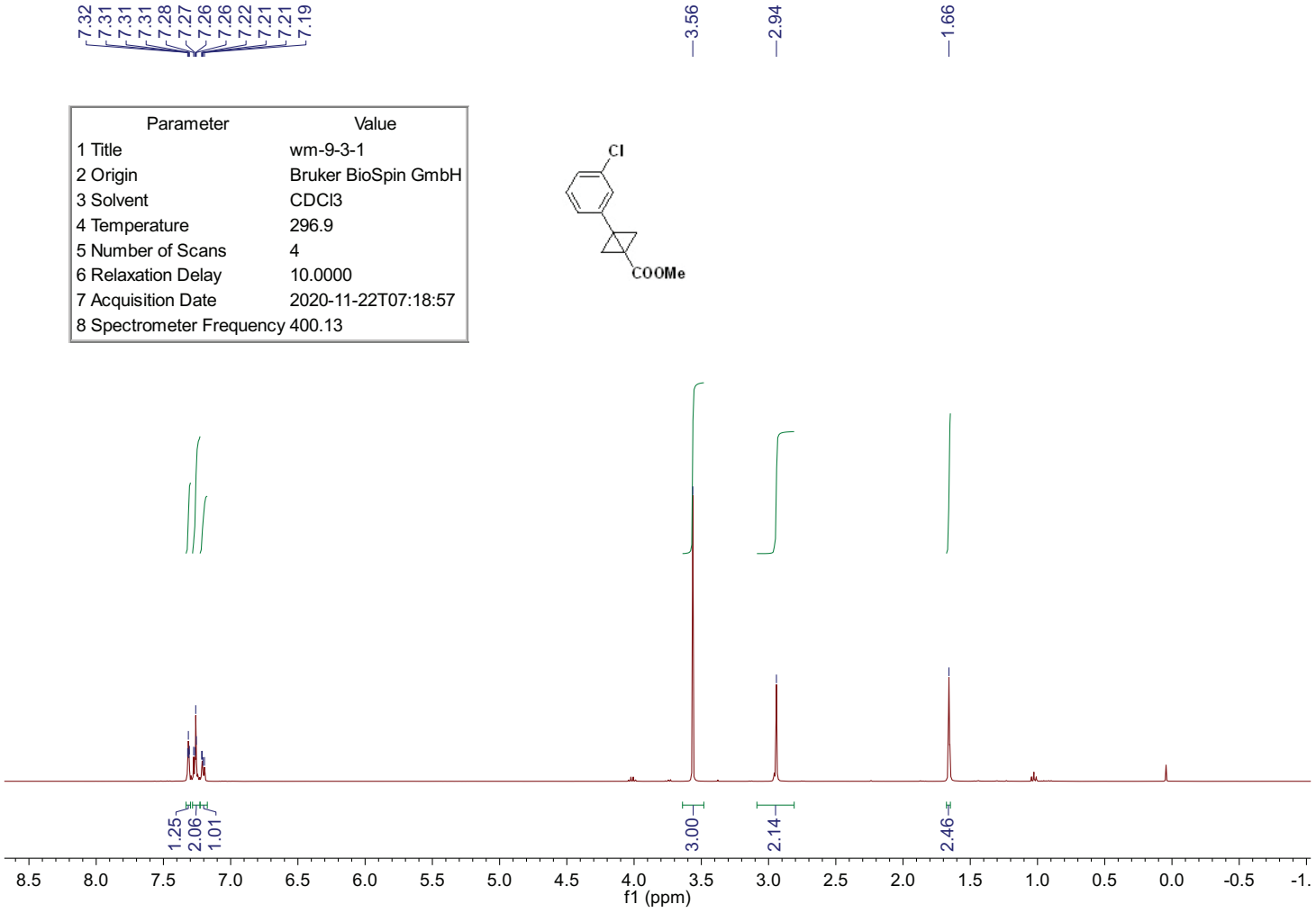
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2.14
2.46
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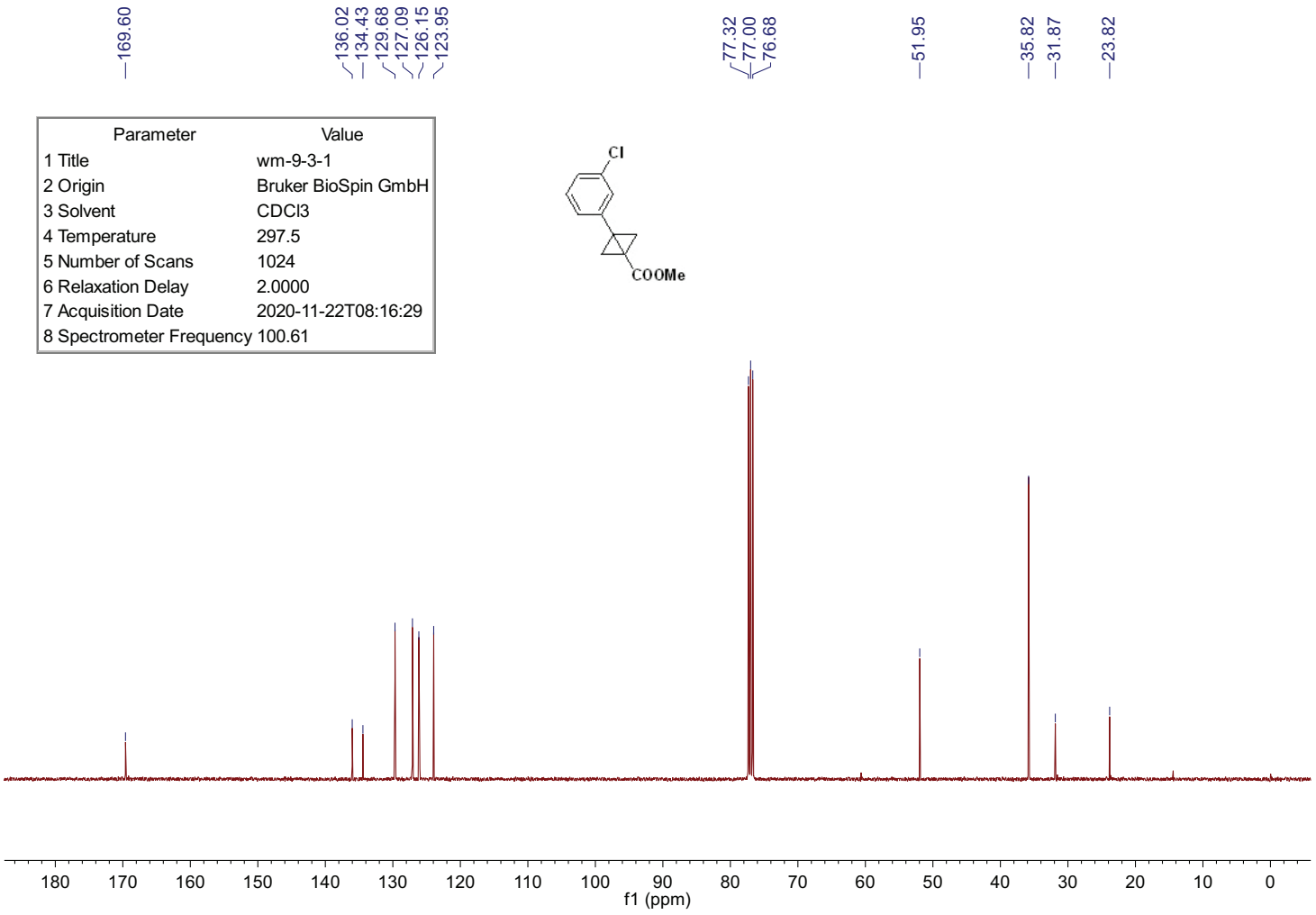
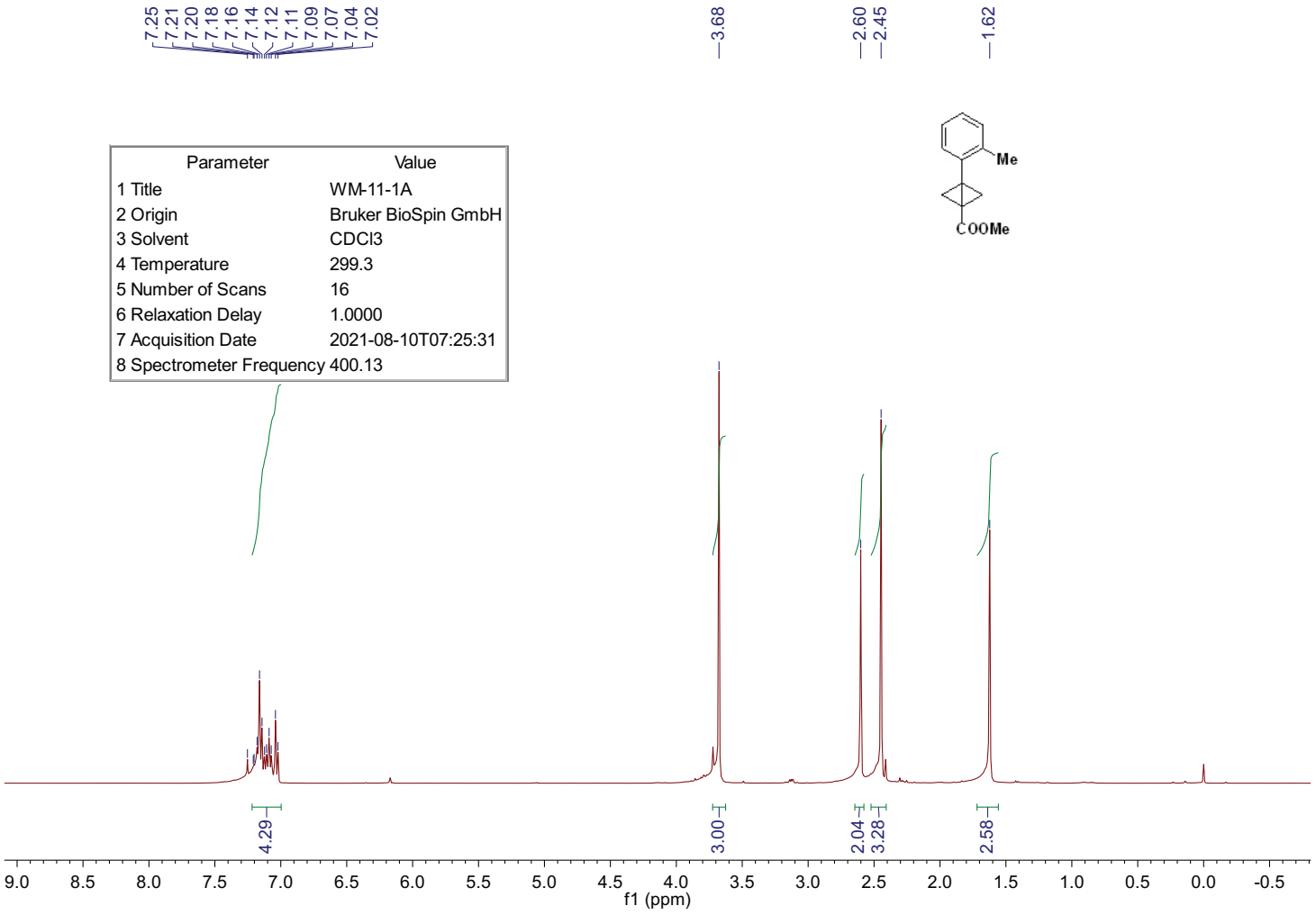
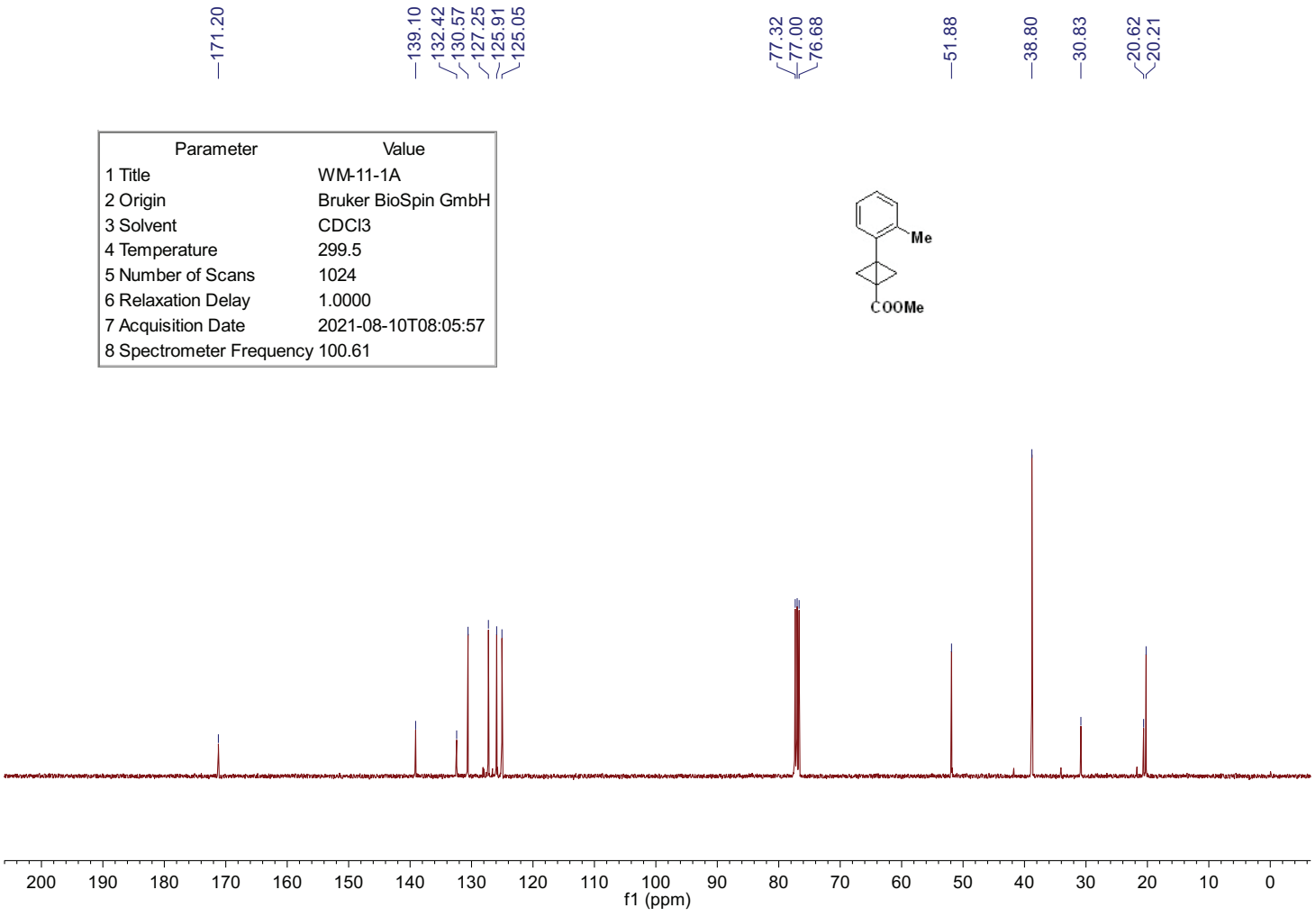
f1 (ppm)

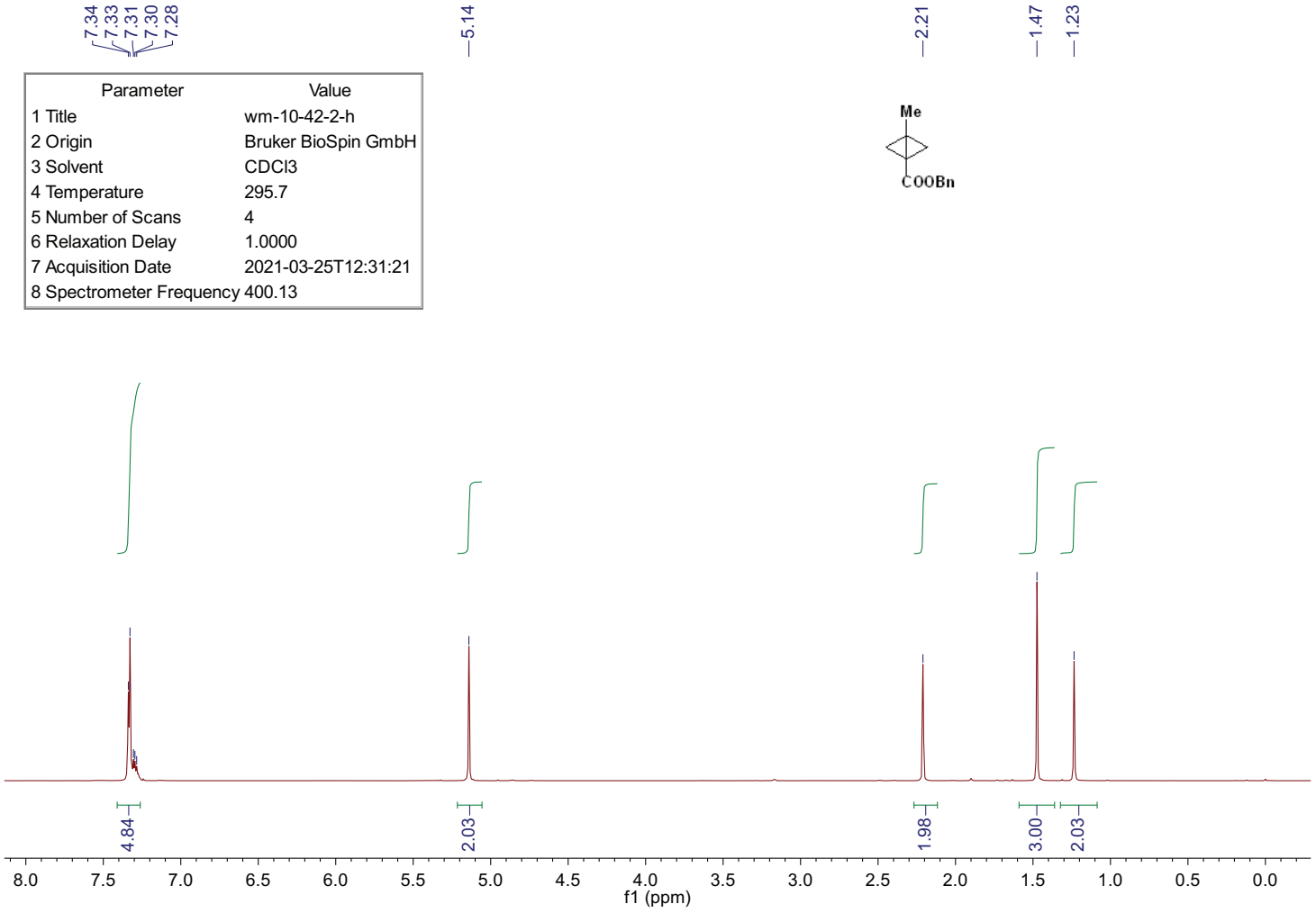

169.60
136.02
134.43
129.68
127.09
126.15
123.95
77.32
77.00
76.68
51.95
35.82
31.87
23.82
Parameter Value
1 Title wm-9-3-1
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 297.5
5 Number of Scans 1024
6 Relaxation Delay 2.0000
7 Acquisition Date 2020-11-22T08:16:29
8 Spectrometer Frequency 100.61
Cl
COOMe
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



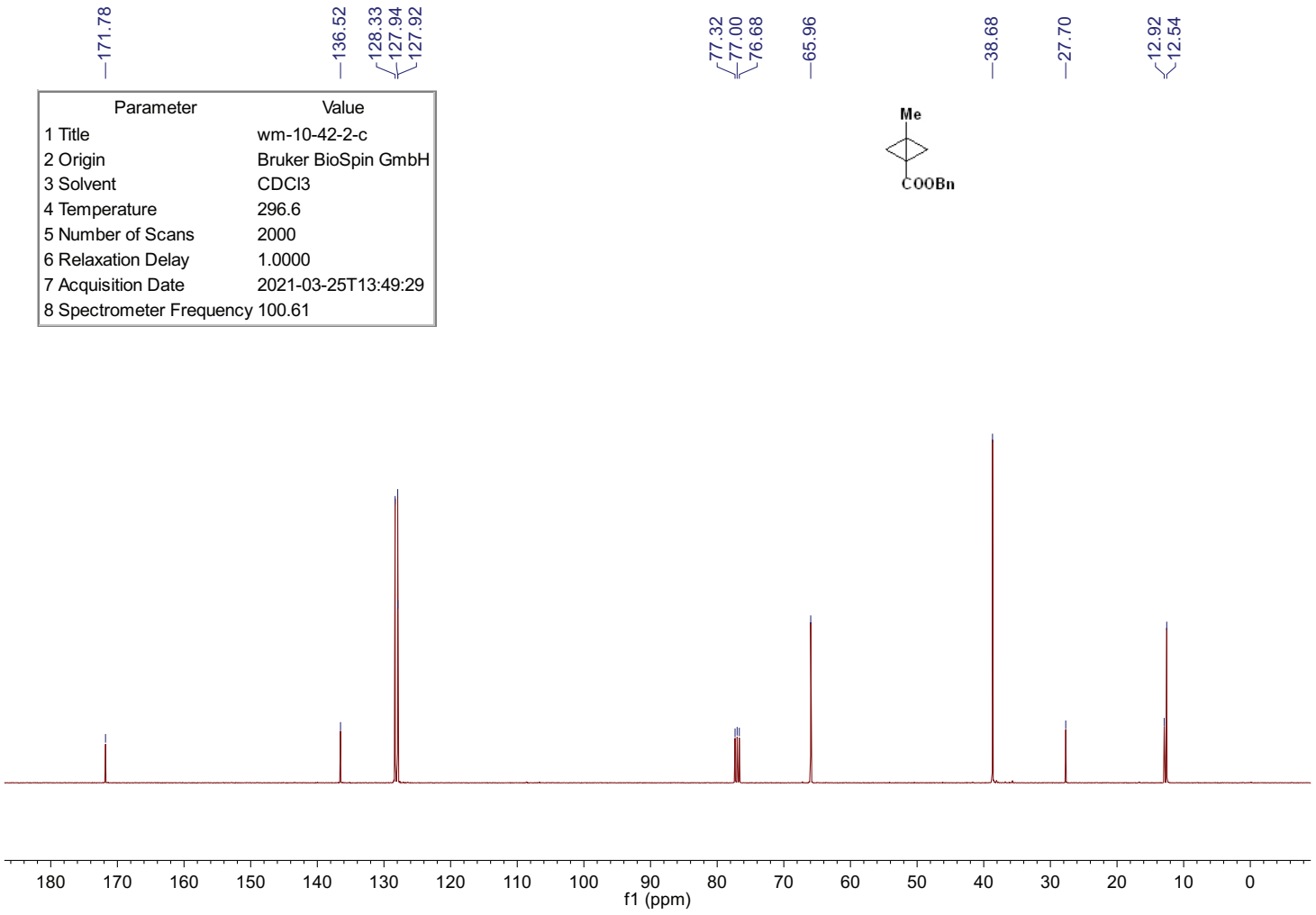
Parameter	Value
1 Title	WM-11-1A
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.3
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-08-10T07:25:31
8 Spectrometer Frequency	400.13



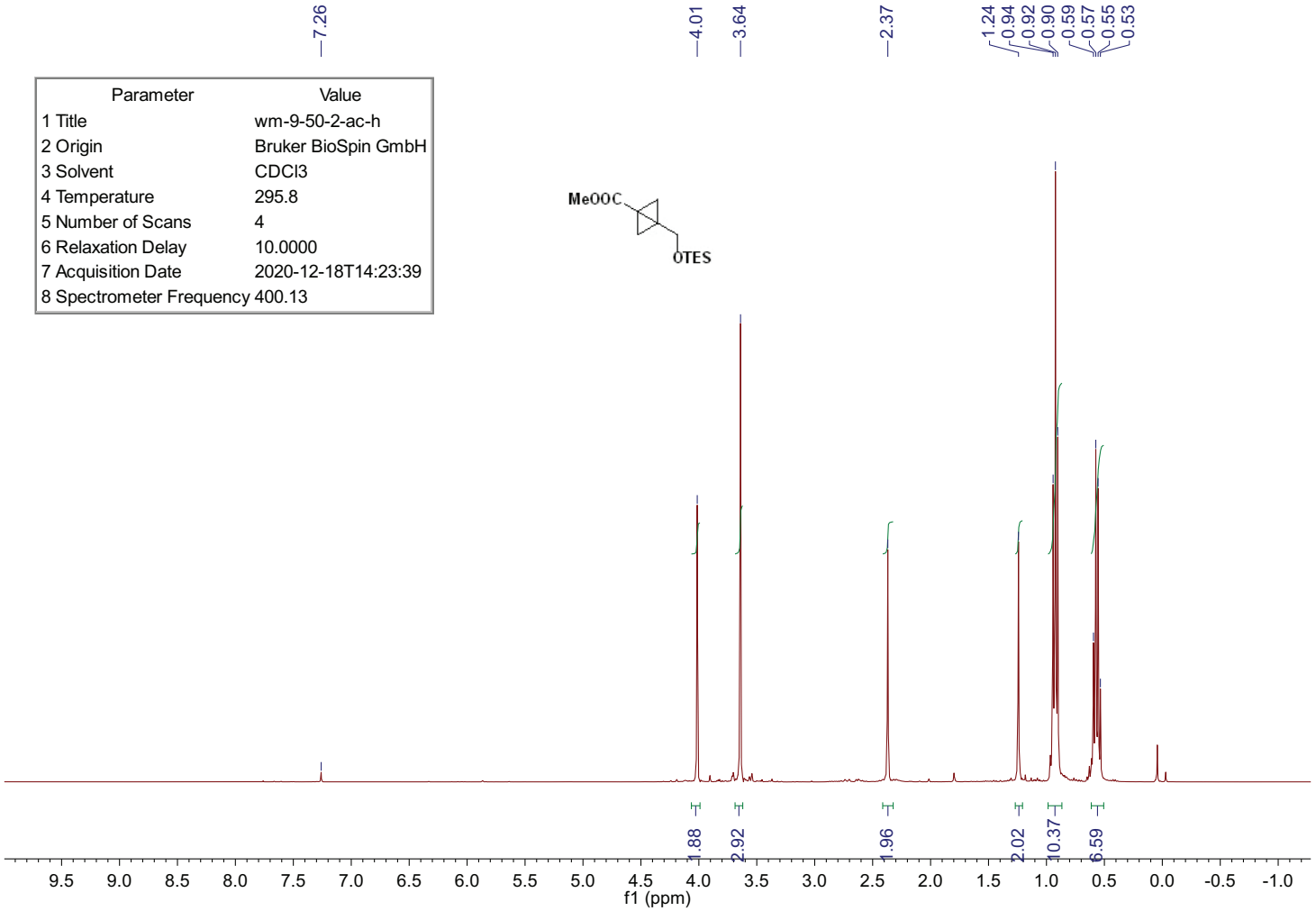
Parameter	Value
1 Title	WM-11-1A
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.5
5 Number of Scans	1024
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-08-10T08:05:57
8 Spectrometer Frequency	100.61

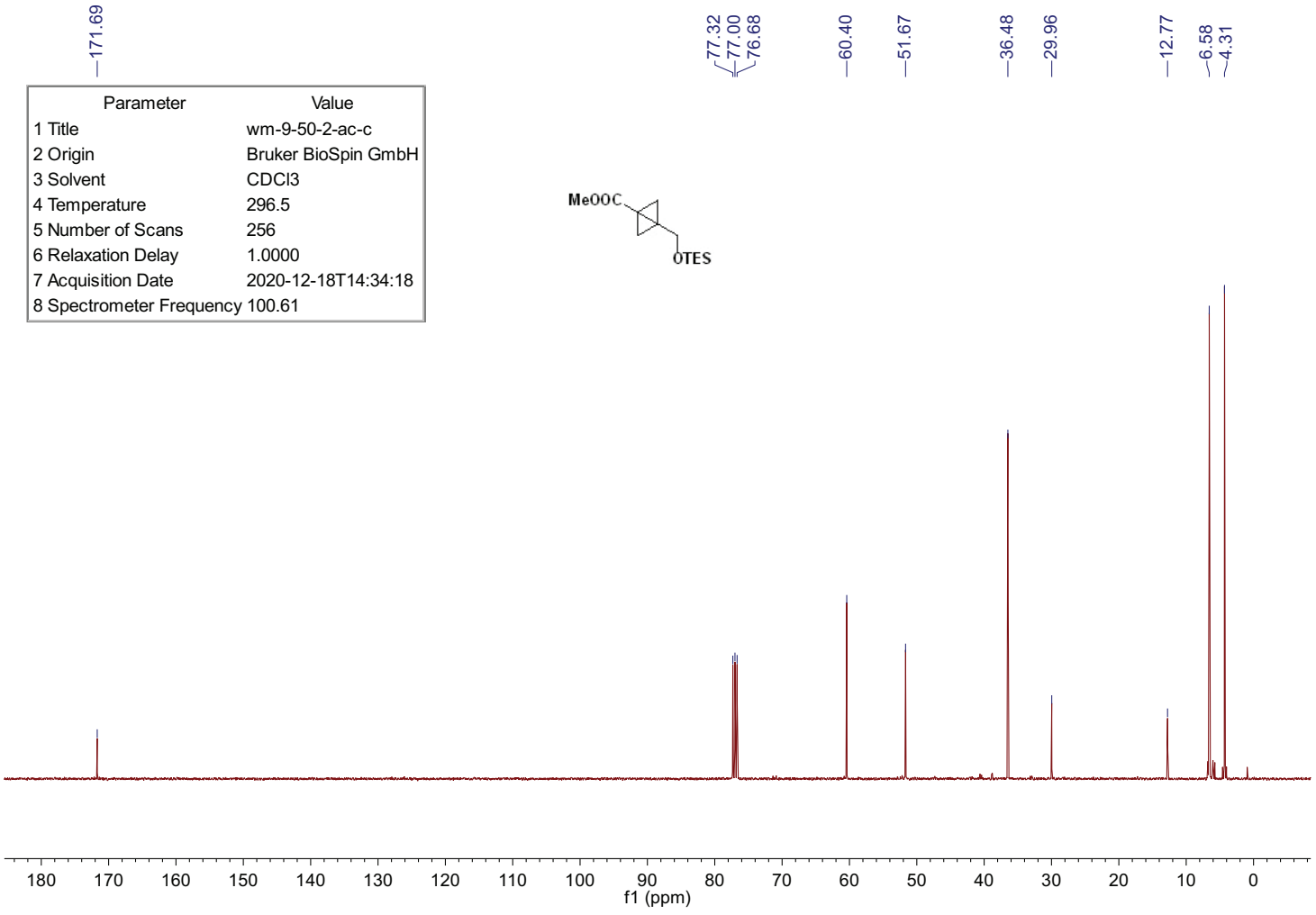


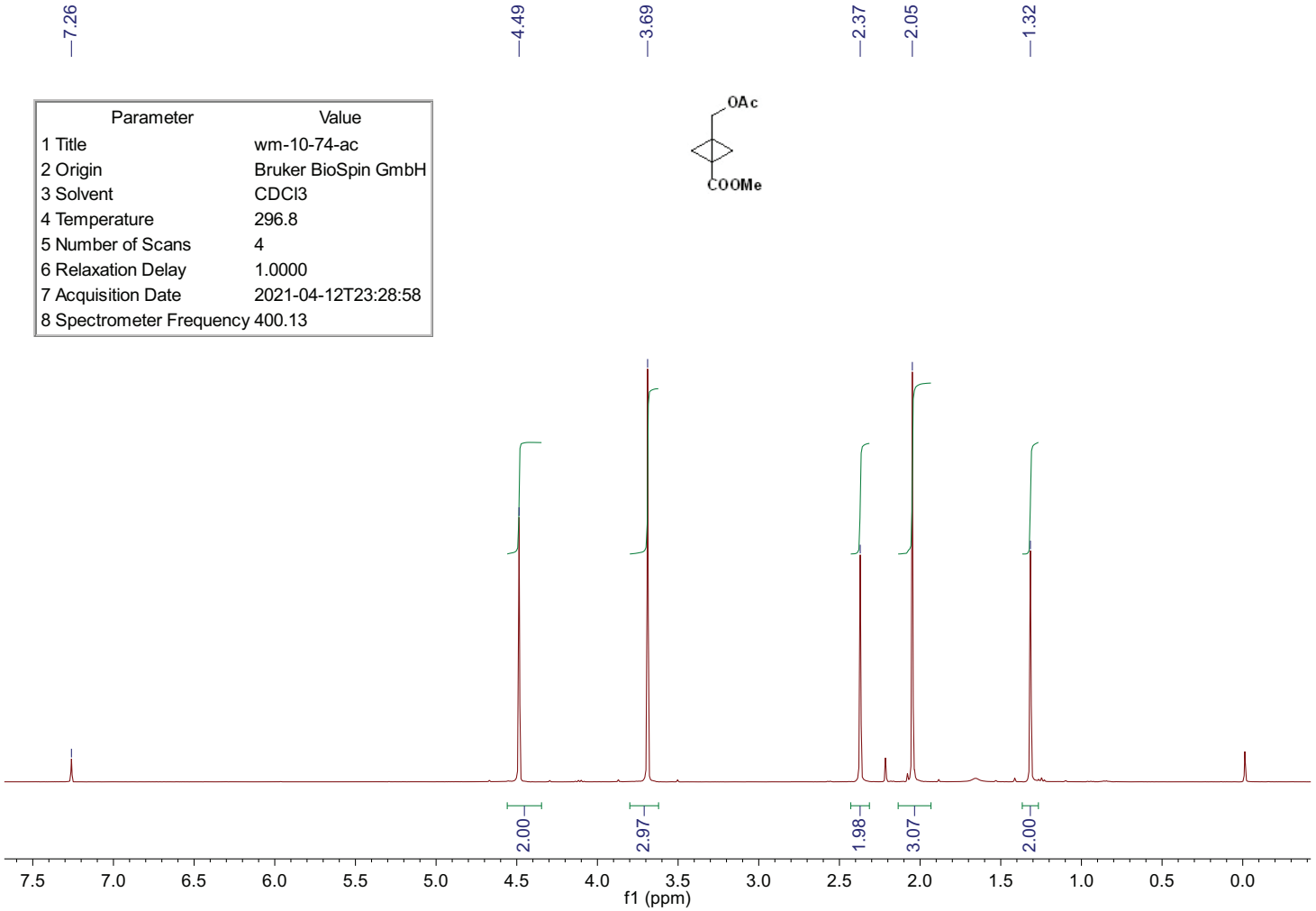
Parameter	Value
1 Title	wm-10-42-2-h
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.7
5 Number of Scans	4
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-03-25T12:31:21
8 Spectrometer Frequency	400.13



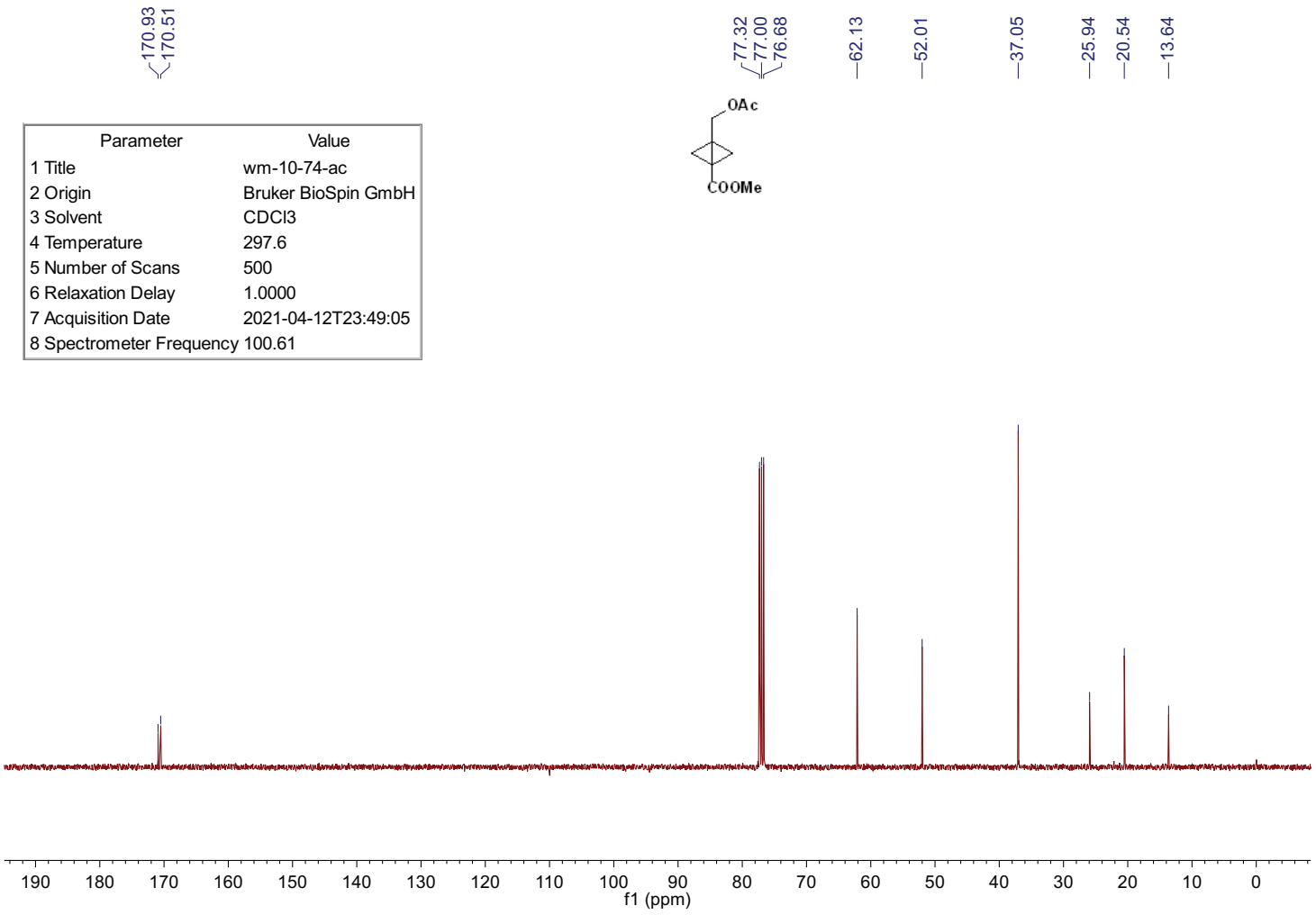
Parameter	Value
1 Title	wm-10-42-2-c
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.6
5 Number of Scans	2000
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-03-25T13:49:29
8 Spectrometer Frequency	100.61


7.26
4.01
3.64
2.37
1.24
0.94
0.92
0.90
0.59
0.57
0.55
0.53
Parameter Value
1 Title wm-9-50-2-ac-h
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 295.8
5 Number of Scans 4
6 Relaxation Delay 10.0000
7 Acquisition Date 2020-12-18T14:23:39
8 Spectrometer Frequency 400.13
MeOOC
OTES
1.88
2.92
1.96
2.02
10.37
6.59
f1 (ppm)

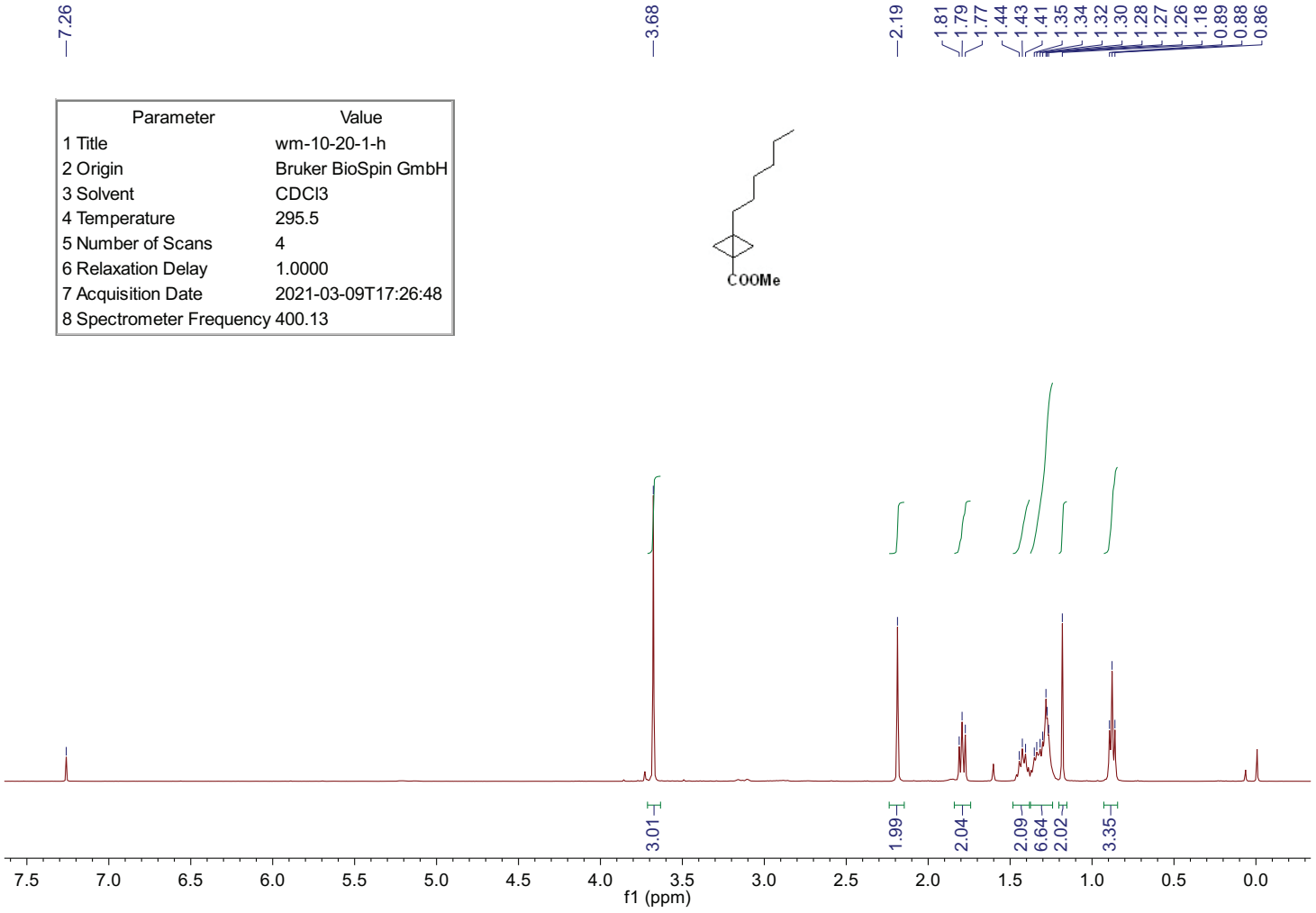

171.69
77.32
77.00
76.68
60.40
51.67
36.48
29.96
12.77
6.58
4.31
Parameter Value
1 Title wm-9-50-2-ac-c
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 296.5
5 Number of Scans 256
6 Relaxation Delay 1.0000
7 Acquisition Date 2020-12-18T14:34:18
8 Spectrometer Frequency 100.61
MeOOC
OTES
f1 (ppm)



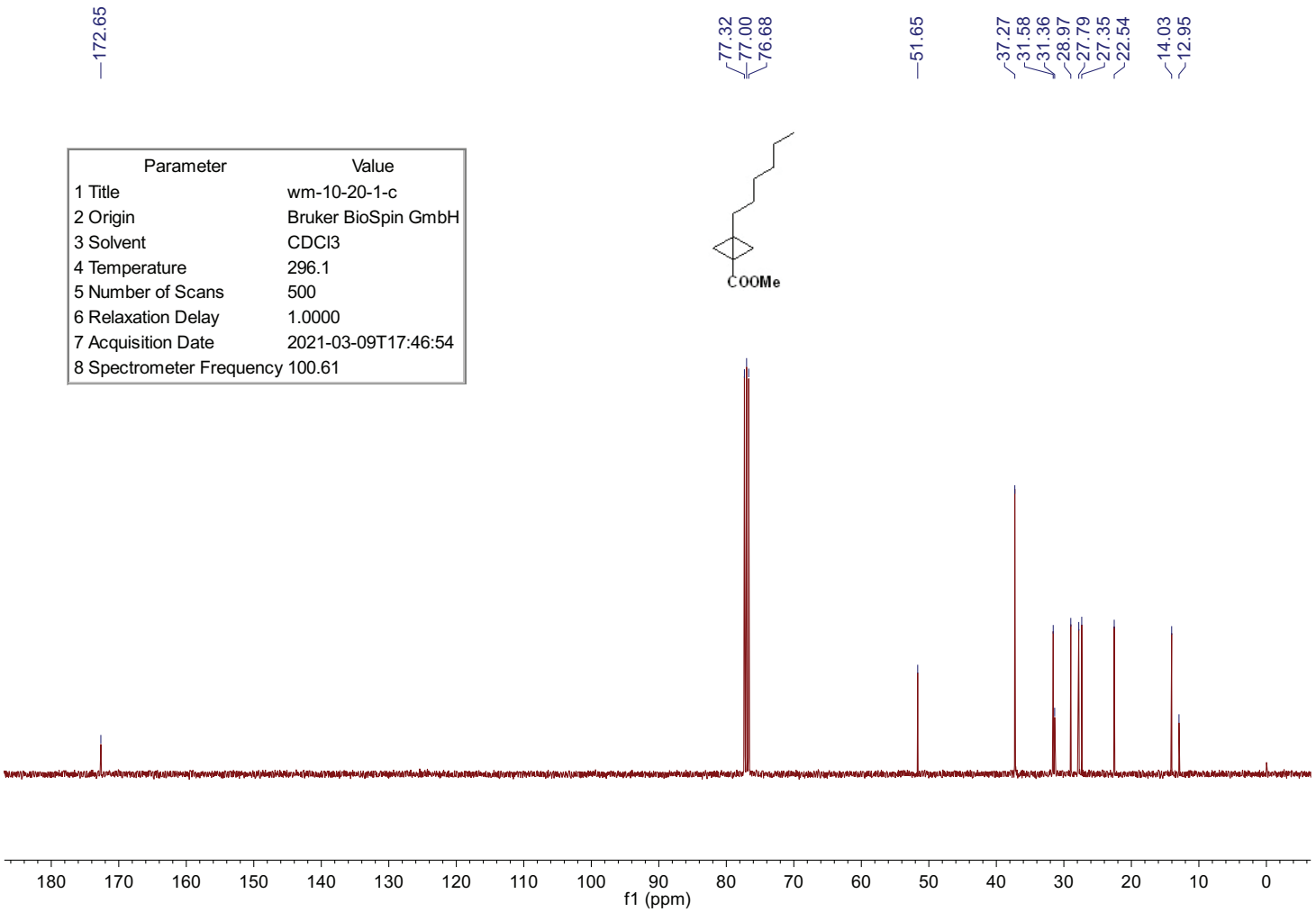
Parameter	Value
1 Title	wm-10-74-ac
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.8
5 Number of Scans	4
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-04-12T23:28:58
8 Spectrometer Frequency	400.13



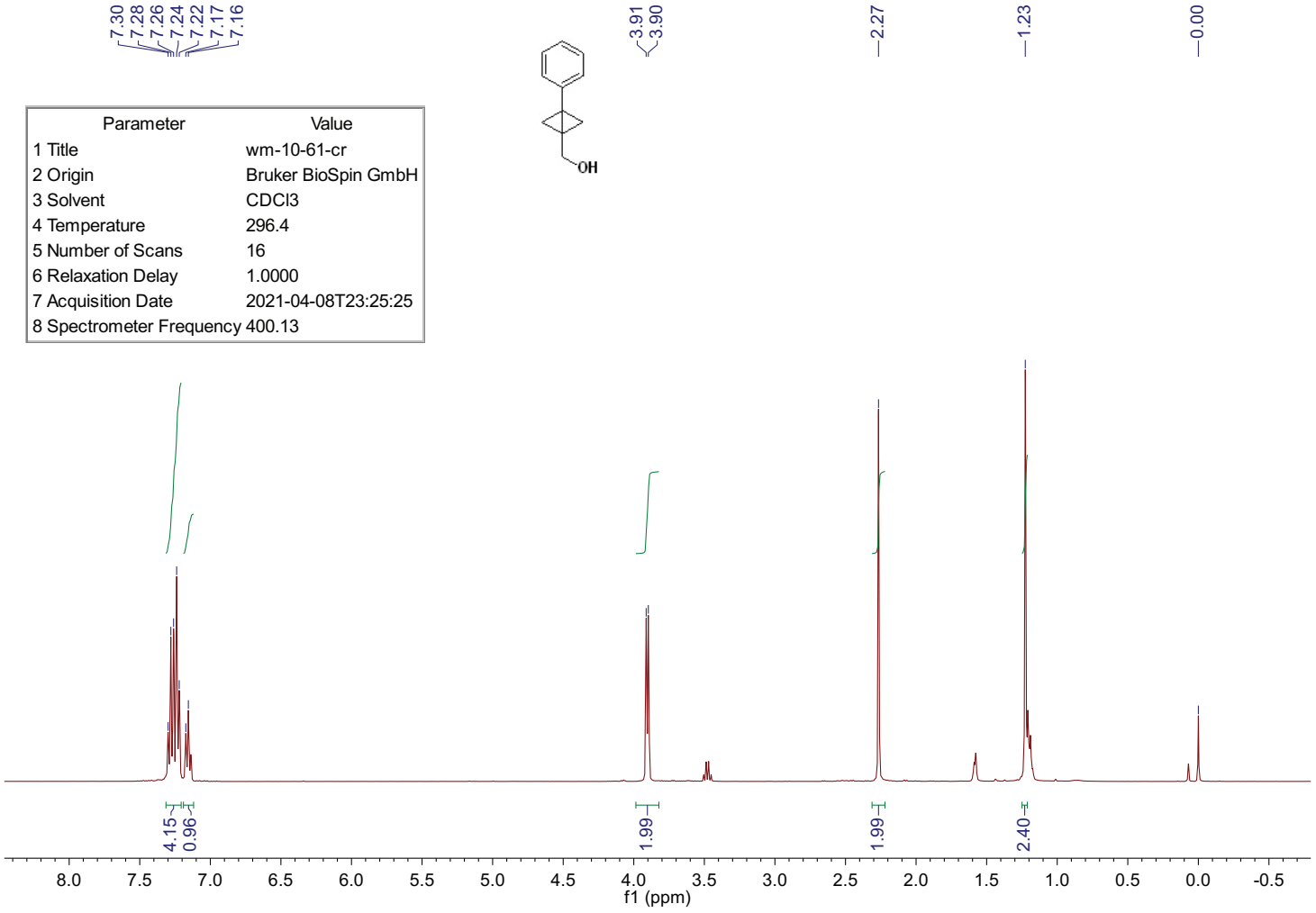
Parameter	Value
1 Title	wm-10-74-ac
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.6
5 Number of Scans	500
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-04-12T23:49:05
8 Spectrometer Frequency	100.61

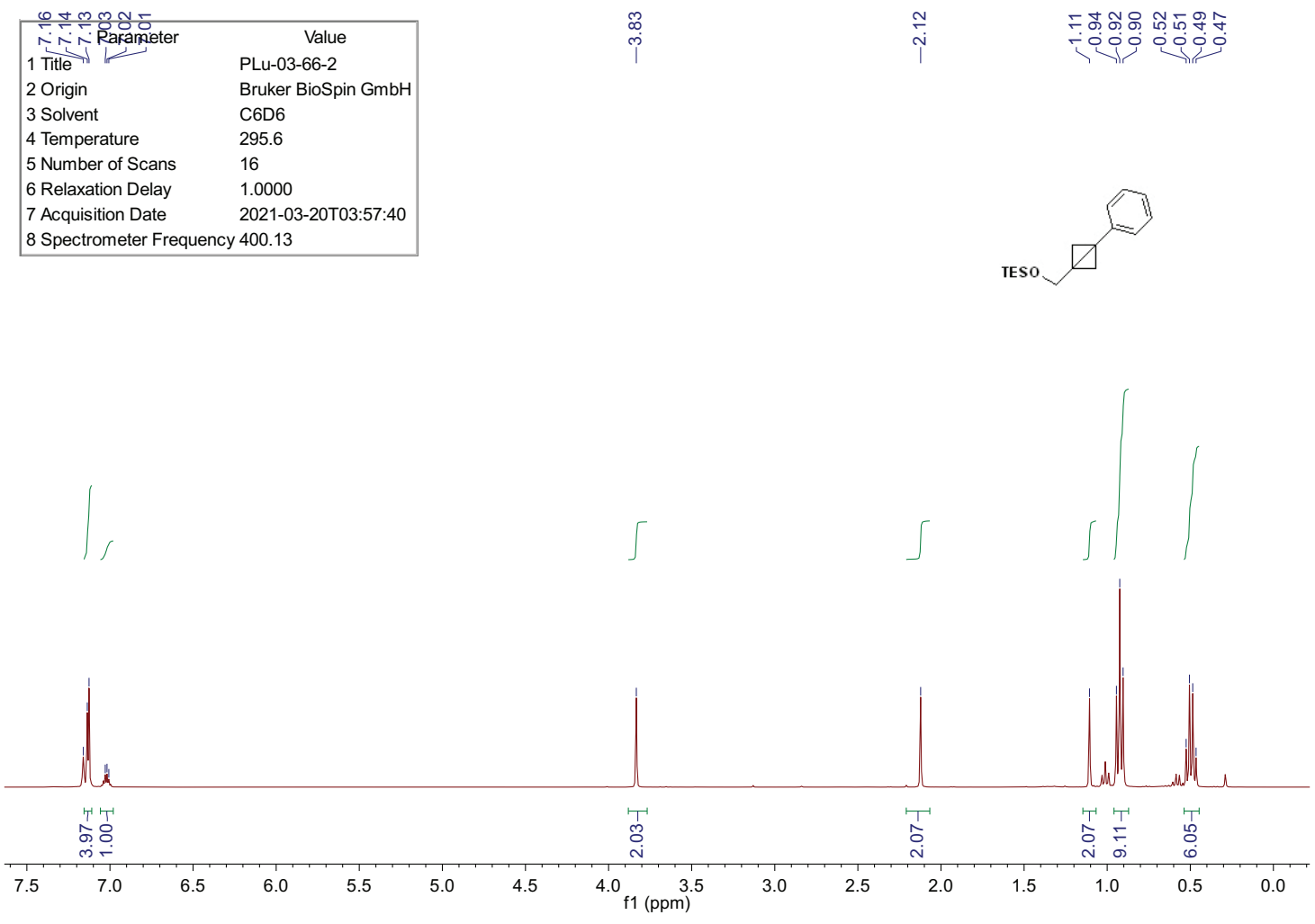


Parameter	Value
1 Title	wm-10-20-1-h
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.5
5 Number of Scans	4
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-03-09T17:26:48
8 Spectrometer Frequency	400.13



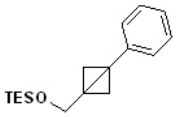
Parameter	Value
1 Title	wm-10-20-1-c
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.1
5 Number of Scans	500
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-03-09T17:46:54
8 Spectrometer Frequency	100.61


7.30
7.28
7.26
7.24
7.22
7.17
7.16
3.91
3.90
2.27
1.23
0.00
OH
Parameter Value
1 Title wm-10-61-cr
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 296.4
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-04-08T23:25:25
8 Spectrometer Frequency 400.13
4.15
0.96
1.99
1.99
2.40
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


7.16
7.14
7.13
7.03
7.02
7.01
3.83
2.12
1.11
0.94
0.92
0.90
0.52
0.51
0.49
0.47
TESO
Parameter Value
1 Title PLu-03-66-2
2 Origin Bruker BioSpin GmbH
3 Solvent C6D6
4 Temperature 295.6
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-03-20T03:57:40
8 Spectrometer Frequency 400.13
3.97
1.00
2.03
2.07
2.07
9.11
6.05
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

Parameter	Value
1 Title	PLu-03-66-2
2 Origin	Bruker BioSpin GmbH
3 Solvent	C6D6
4 Temperature	297.0
5 Number of Scans	1024
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-04-03T11:21:45
8 Spectrometer Frequency	100.61

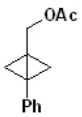
137.57
128.43
128.30
128.06
127.82
126.00
125.20
62.05
33.32
24.41
18.12
7.04
4.85



190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

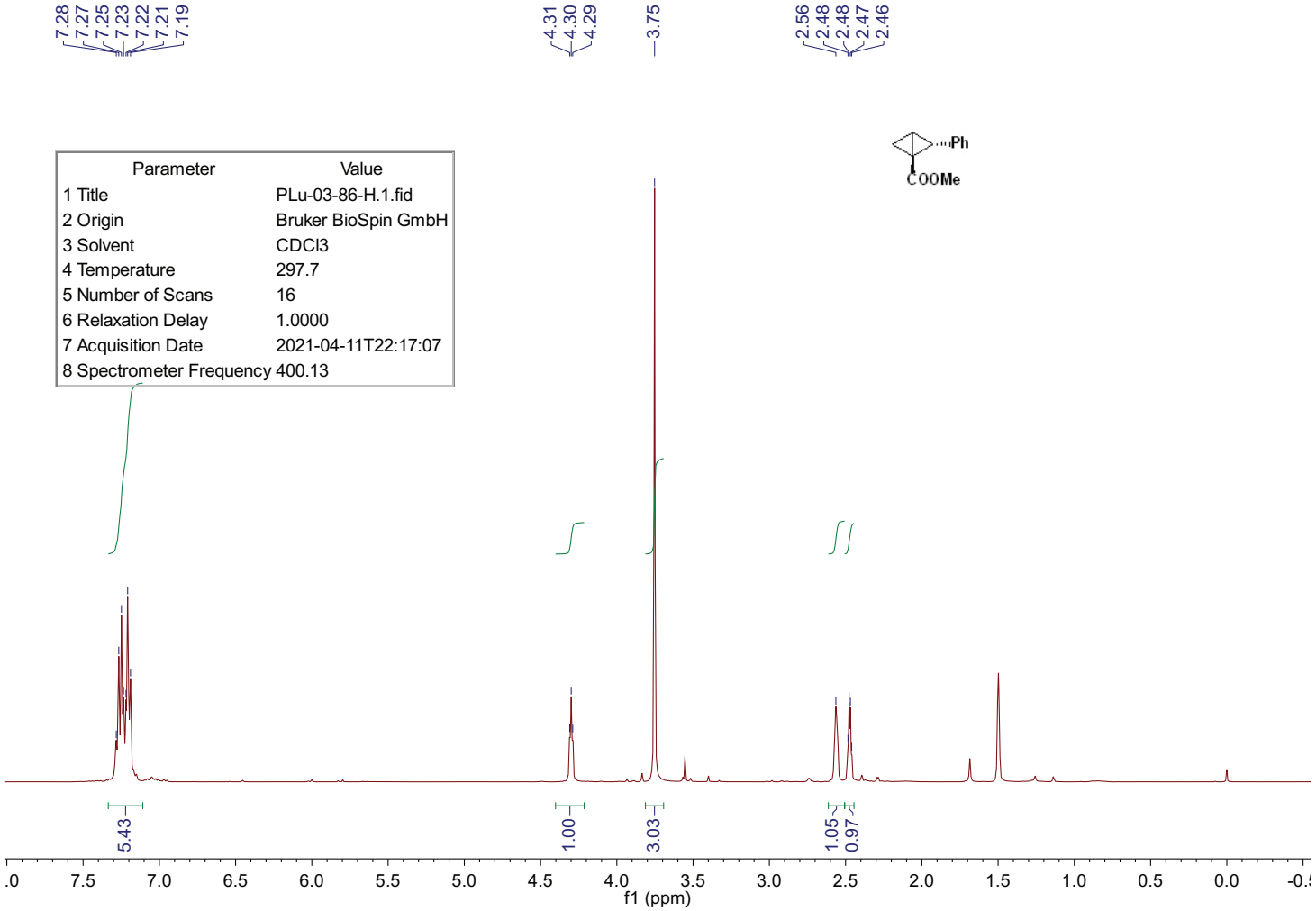
7.22
7.20
7.18
7.15
7.13
7.11
7.09
7.07
4.18
2.18
1.90
1.20
0.00

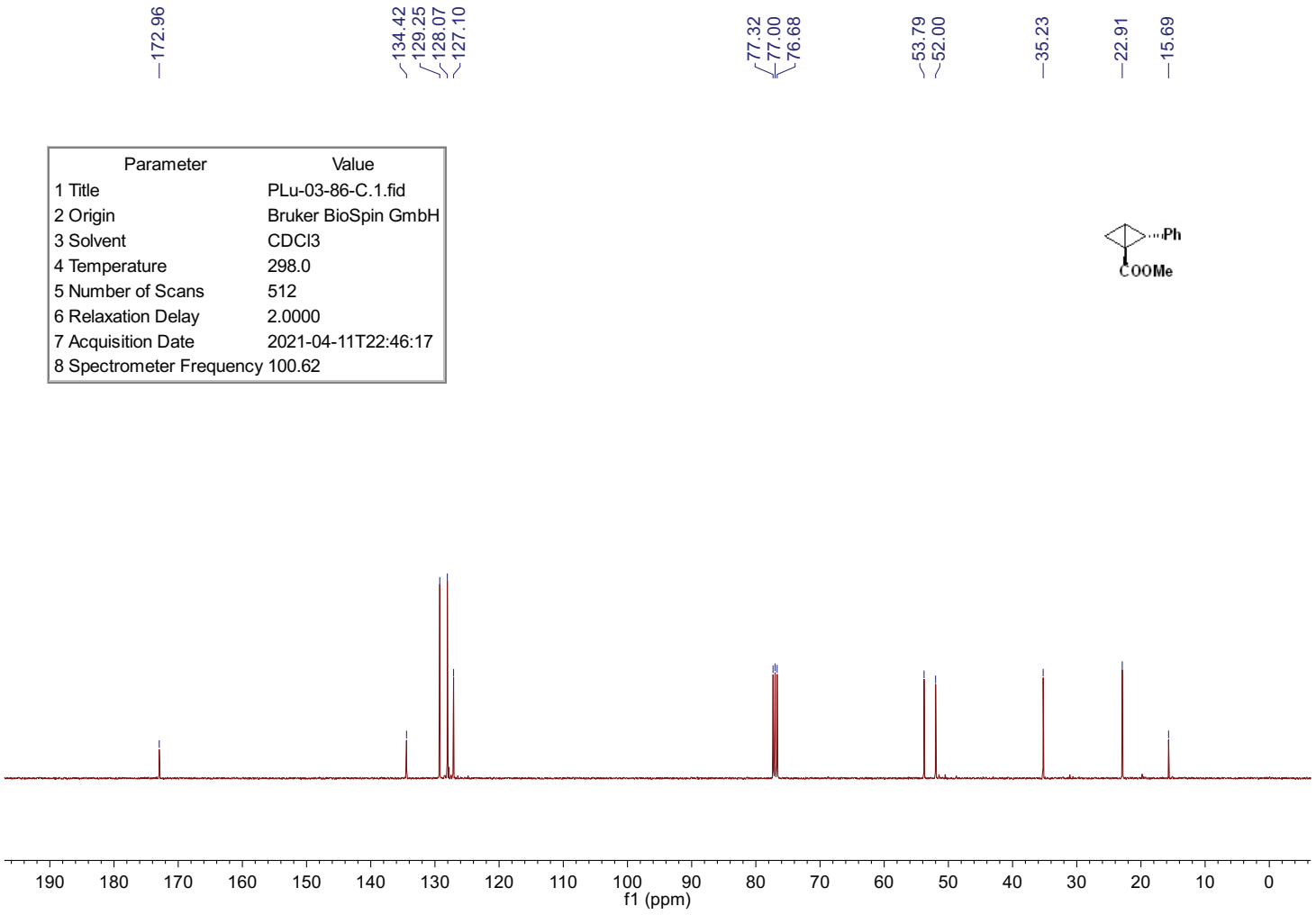
Parameter	Value
1 Title	wm-10-63-b-cr
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.4
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-04-09T17:08:34
8 Spectrometer Frequency	400.13



3.78
1.02
2.00
2.10
2.74
2.07

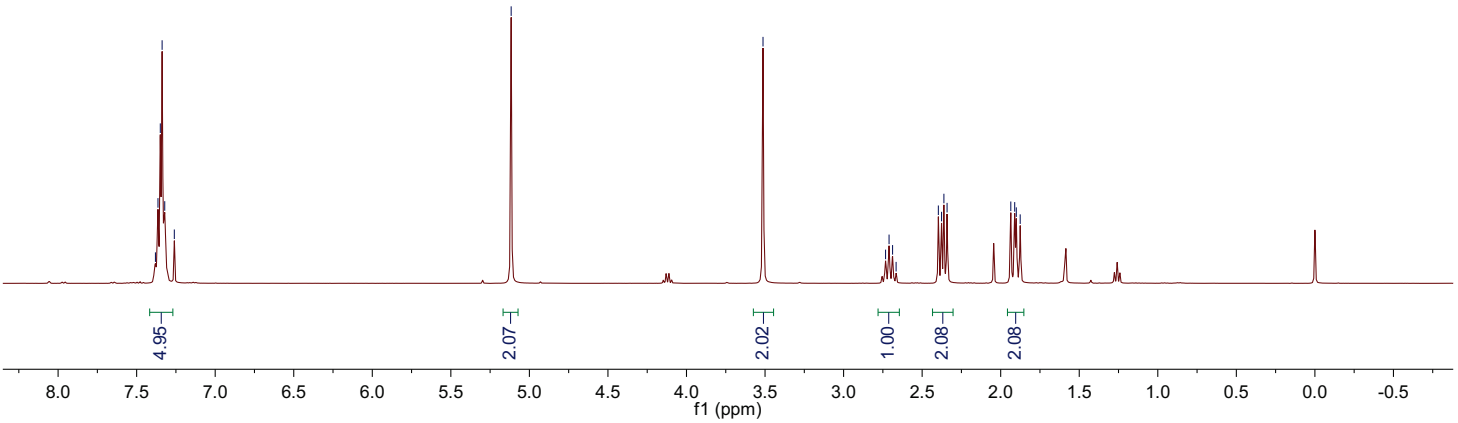
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


7.28
7.27
7.25
7.23
7.22
7.21
7.19
4.31
4.30
4.29
3.75
2.56
2.48
2.48
2.47
2.46
Ph
COOMe
Parameter Value
1 Title PLu-03-86-H.1.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 297.7
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-04-11T22:17:07
8 Spectrometer Frequency 400.13
5.43
1.00
3.03
1.05
0.97
f1 (ppm)


172.96
134.42
129.25
128.07
127.10
77.32
77.00
76.68
53.79
52.00
35.23
22.91
15.69
Parameter Value
1 Title PLu-03-86-C.1.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 512
6 Relaxation Delay 2.0000
7 Acquisition Date 2021-04-11T22:46:17
8 Spectrometer Frequency 100.62
Ph
COOMe
f1 (ppm)

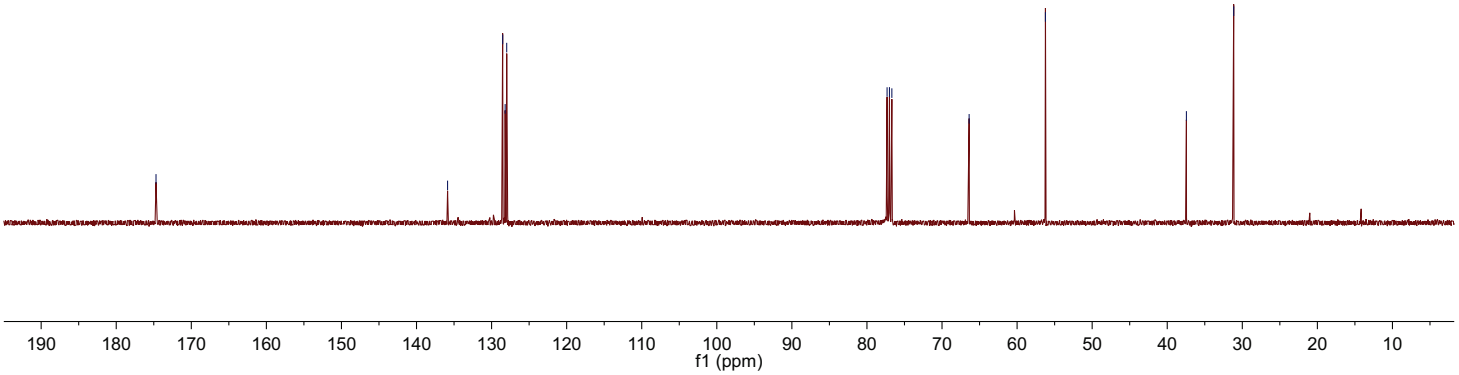
7.38
7.36
7.35
7.34
7.32
7.26
5.12
3.51
2.73
2.71
2.69
2.67
2.40
2.38
2.36
2.34
1.94
1.91
1.90
1.88

Parameter	Value
1 Title	hyc-5-187-2ac
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.2
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-04-01T20:07:55
8 Spectrometer Frequency	400.13

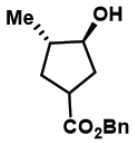


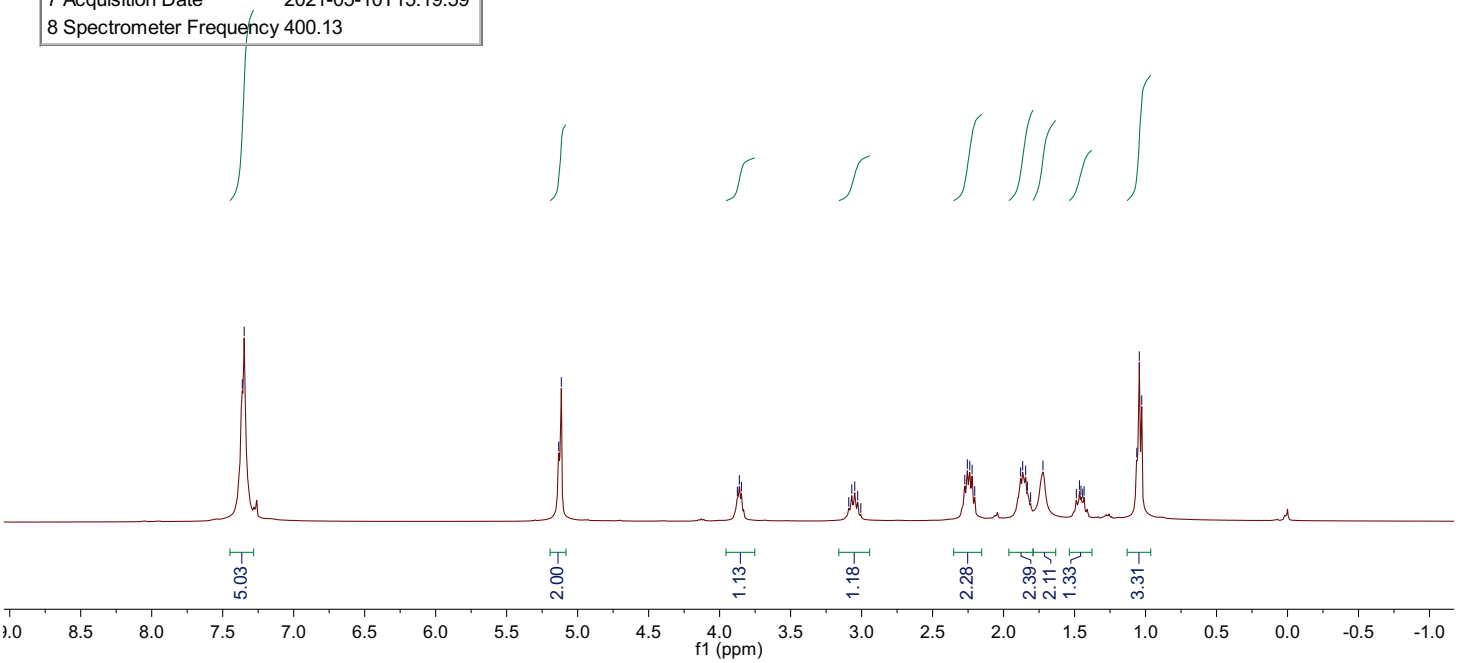
174.70
135.86
128.53
128.19
127.99
77.32
77.00
76.68
66.39
56.22
37.45
31.15

Parameter	Value
1 Title	hyc-5-193ac C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.7
5 Number of Scans	500
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-04-12T12:11:45
8 Spectrometer Frequency	100.62

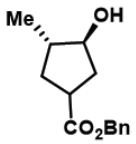


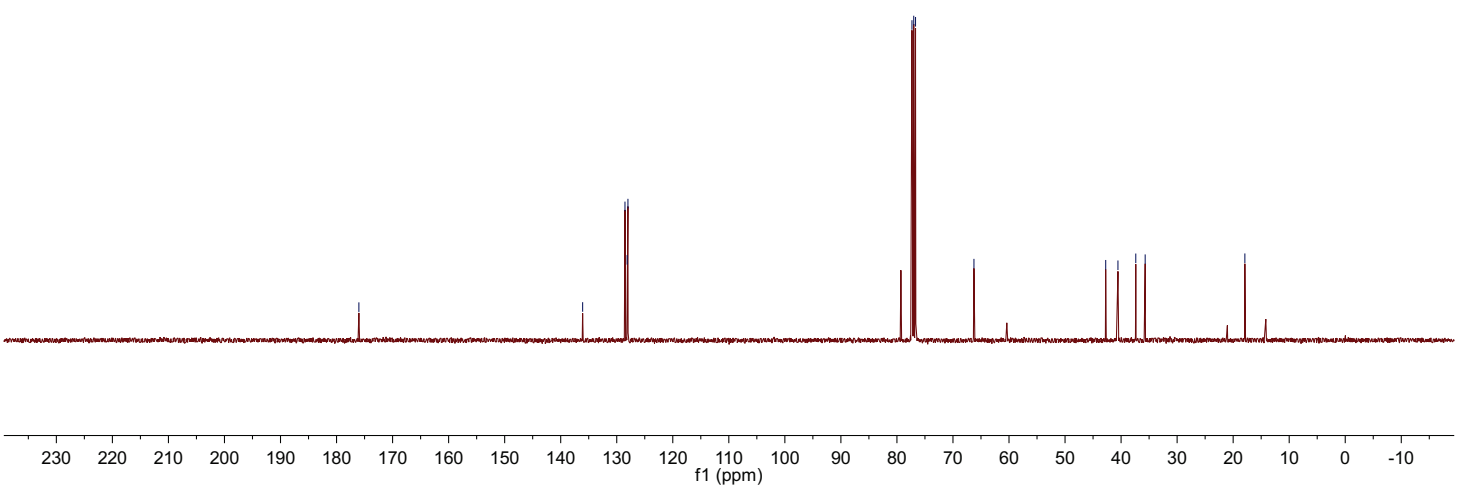
Parameter	Value
1 Title	hyc-5-191ac H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.3
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-05-10T15:19:59
8 Spectrometer Frequency	400.13





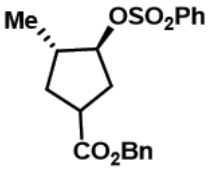
Parameter	Value
1 Title	hyc-5-191ac C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.7
5 Number of Scans	500
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-04-12T11:03:49
8 Spectrometer Frequency	100.61

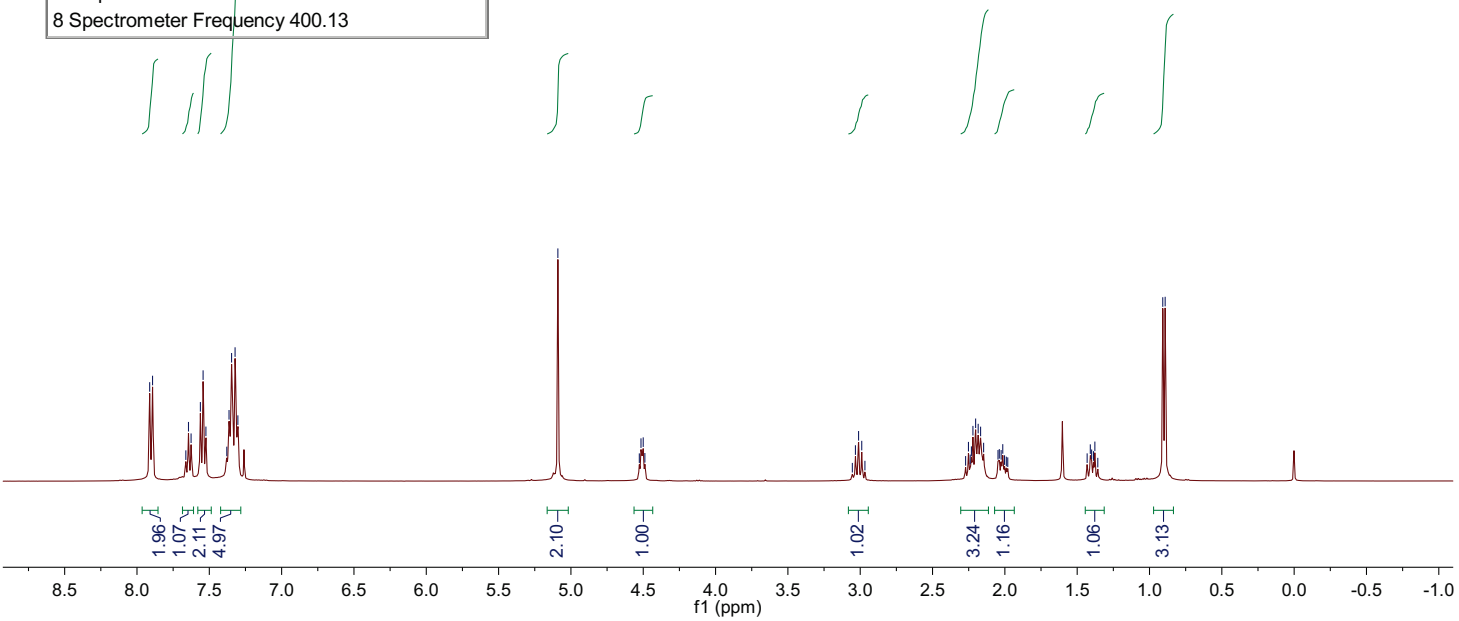




7.91 7.89 7.66 7.64 7.63 7.56 7.54 7.52 7.38 7.36 7.35 7.32 7.30 5.09 4.53 4.52 4.50 4.49 3.05 3.03 3.01 2.99 2.97 2.27 2.25 2.24 2.23 2.22 2.20 2.18 2.17 2.15 2.05 2.04 2.03 2.01 2.00 1.99 1.98 1.43 1.41 1.40 1.39 1.38 1.36 0.91 0.89

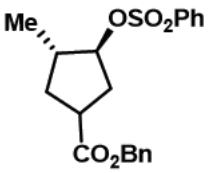
Parameter	Value
1 Title	hyc-5-194ac H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.3
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-04-12T12:45:05
8 Spectrometer Frequency	400.13

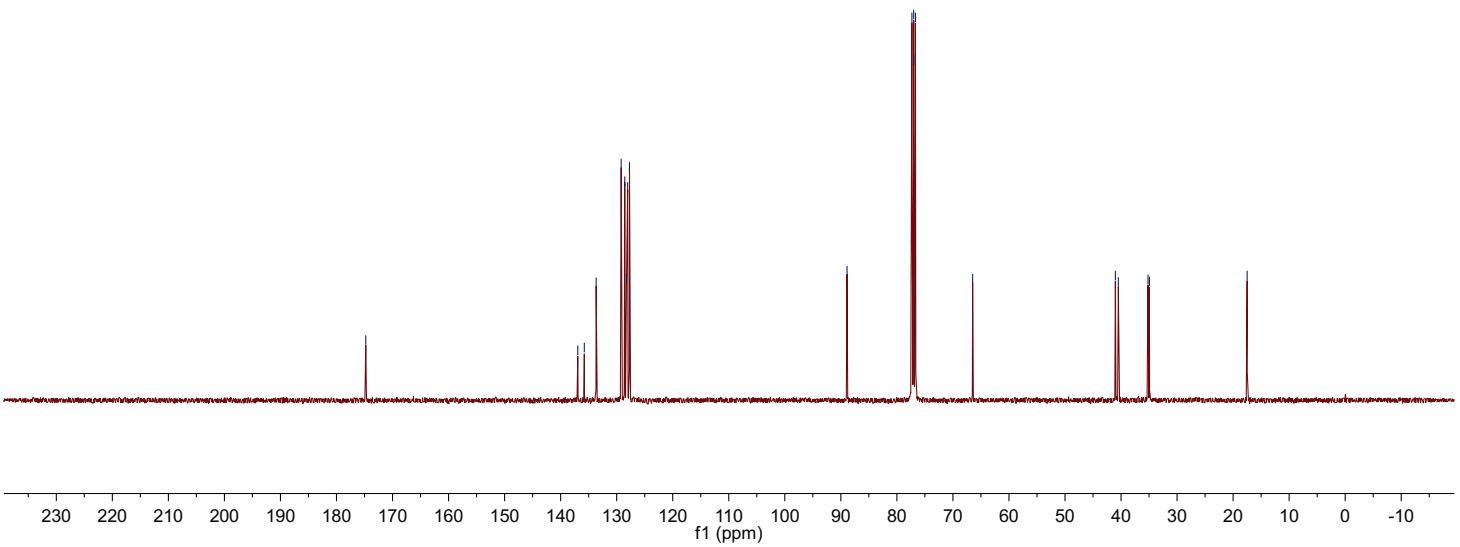


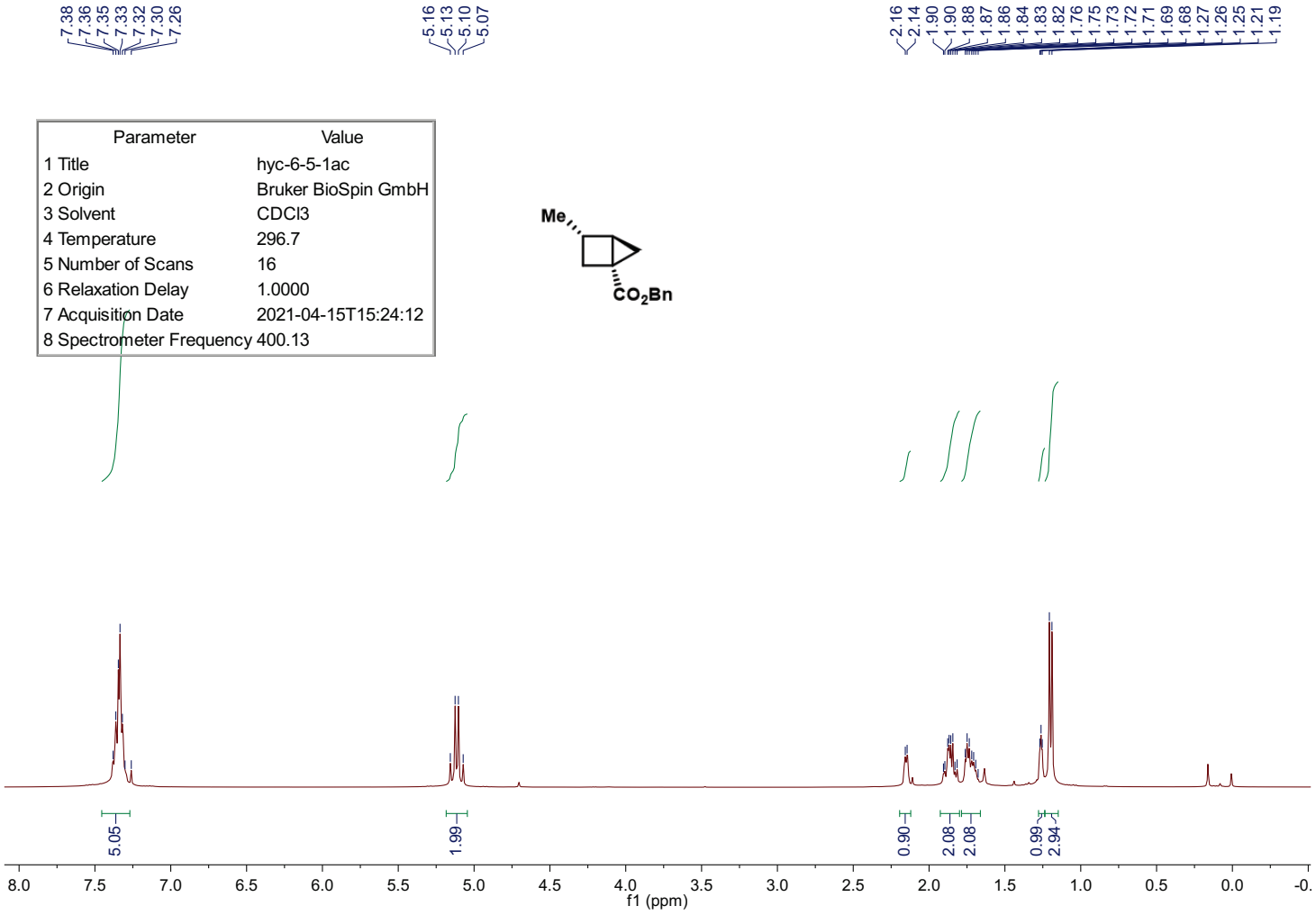


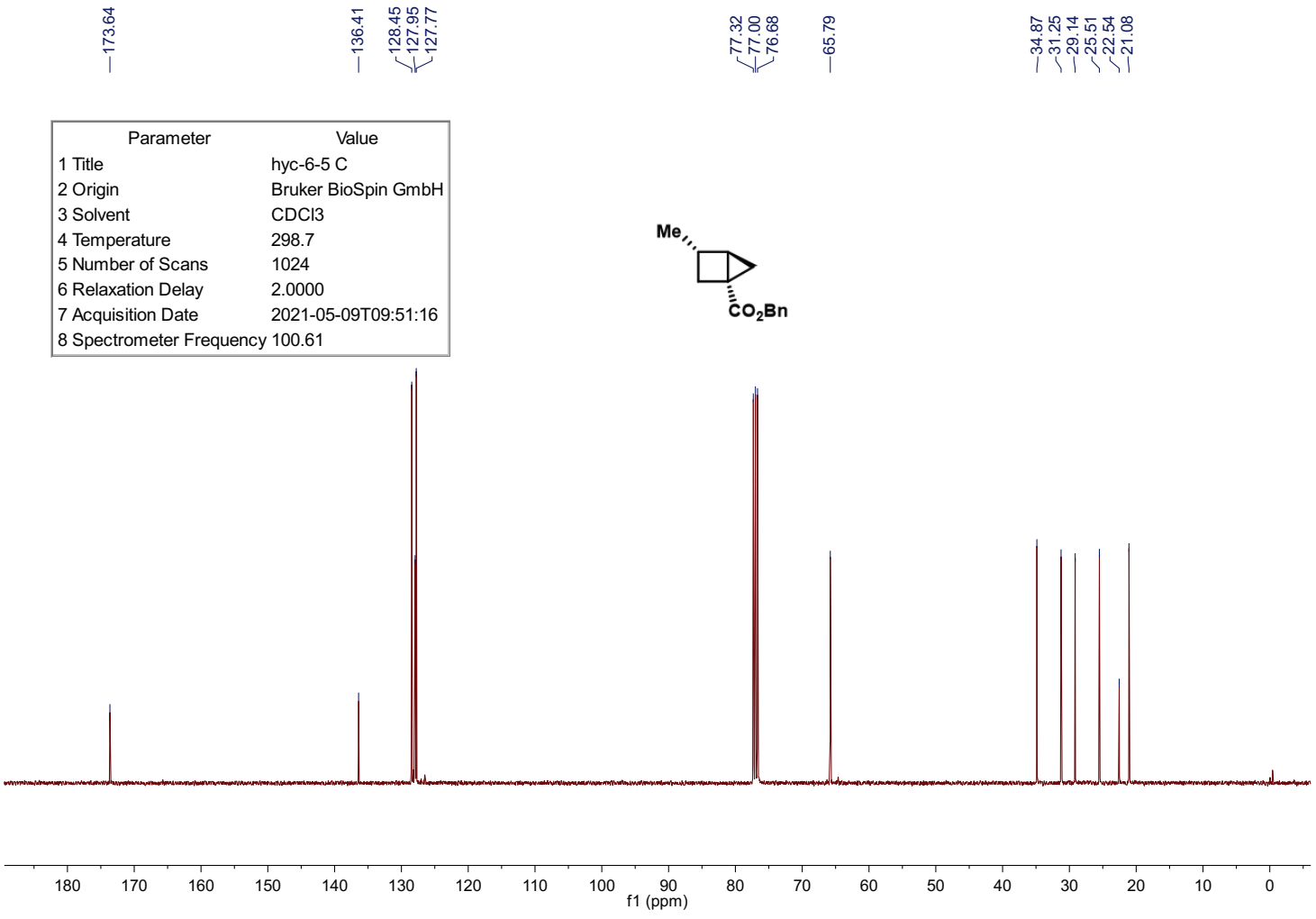
174.77 136.94 135.78 133.67 129.20 128.56 128.25 128.05 127.72 88.89 77.32 77.00 76.99 76.68 66.48 41.01 40.48 35.18 34.93 17.50

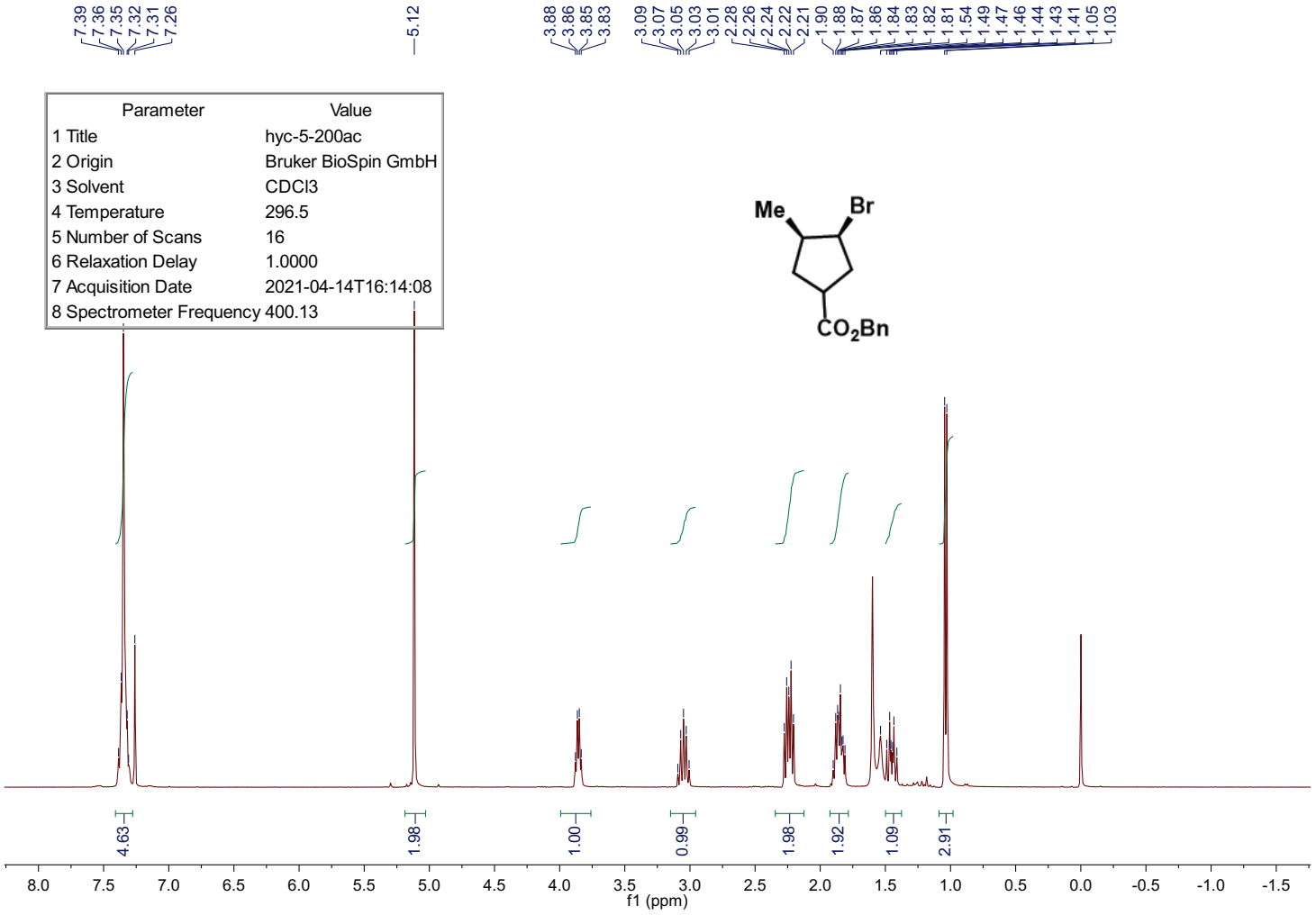
Parameter	Value
1 Title	hyc-5-199-2 C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.7
5 Number of Scans	1024
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-05-09T08:51:17
8 Spectrometer Frequency	100.61

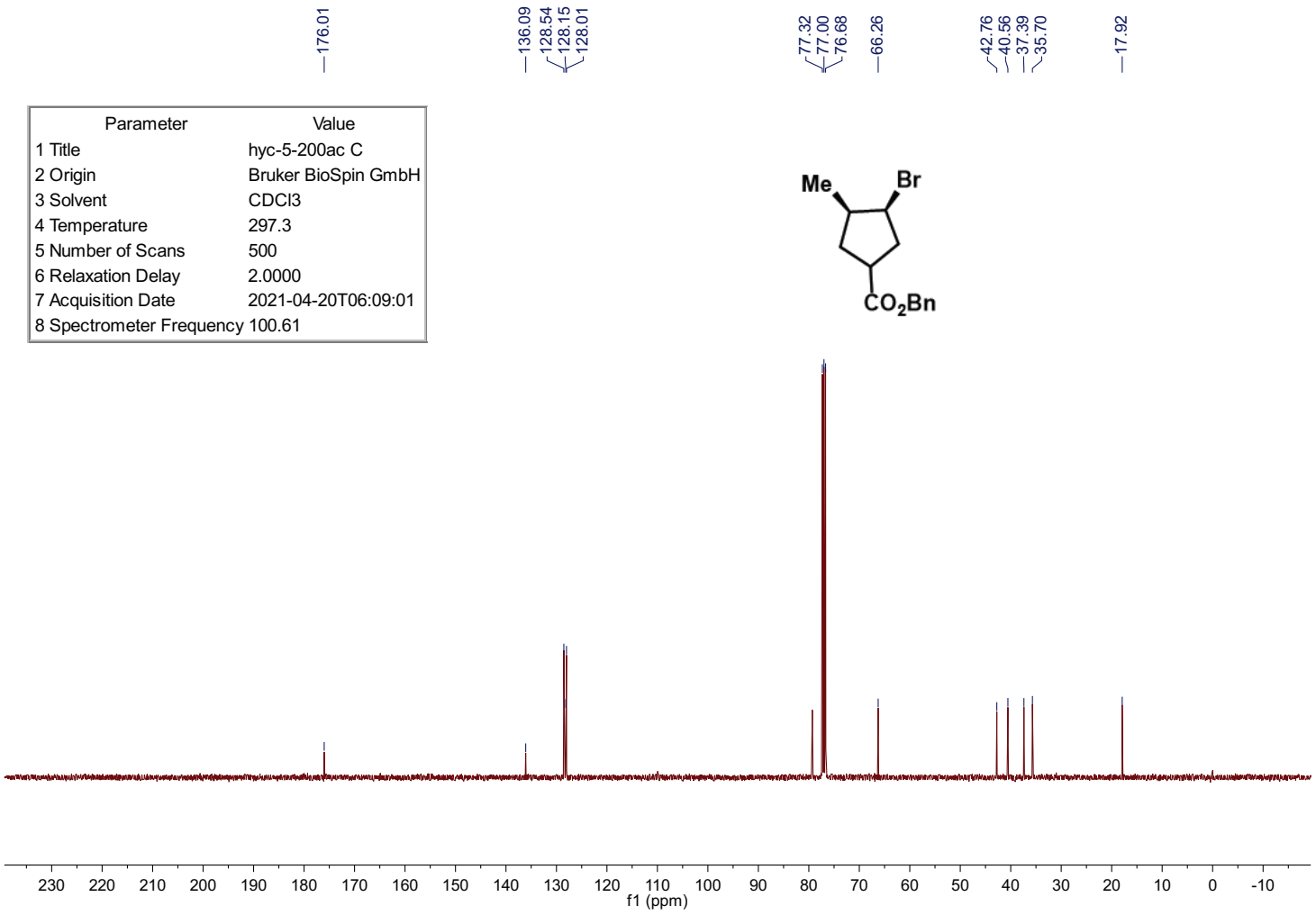


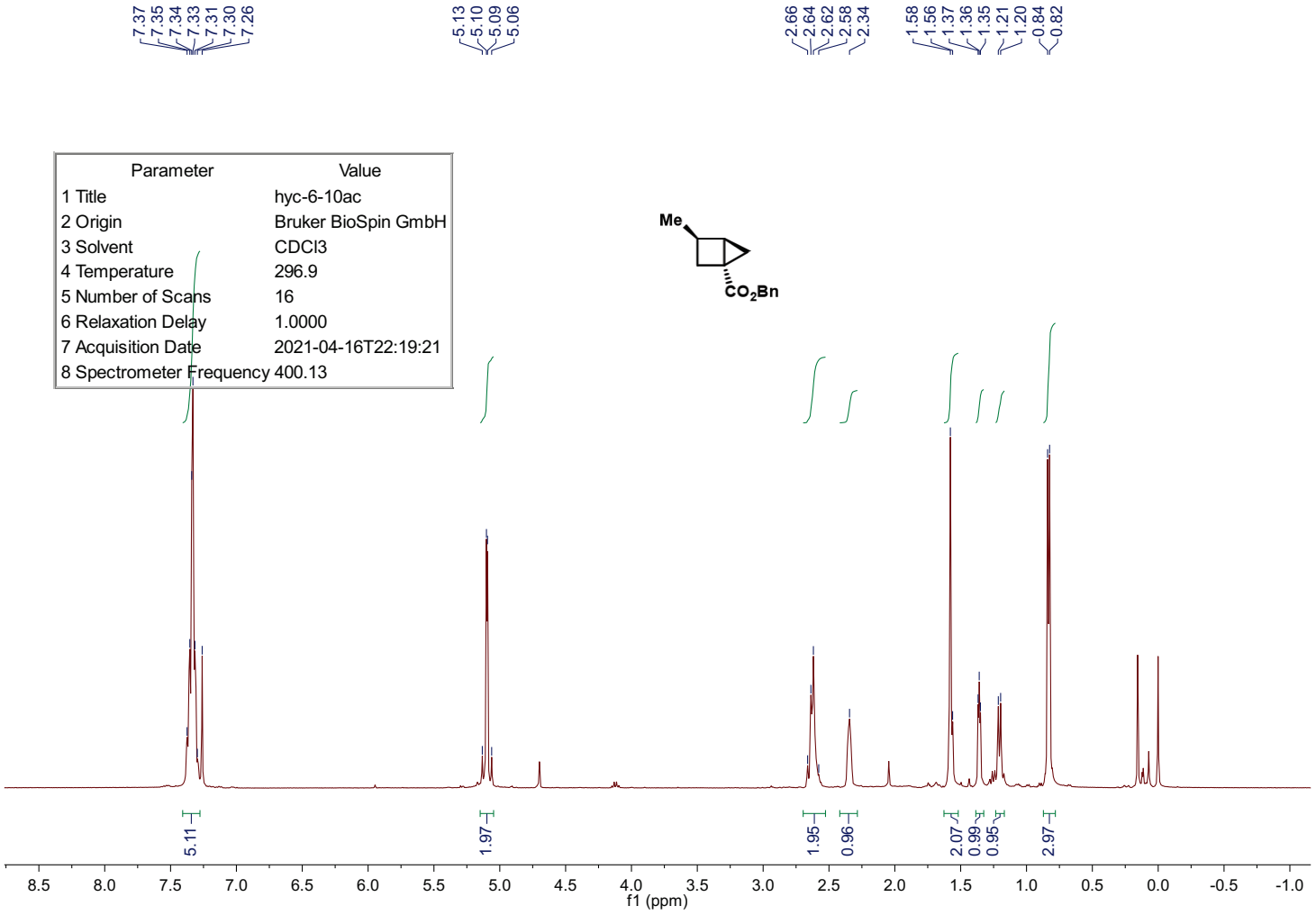


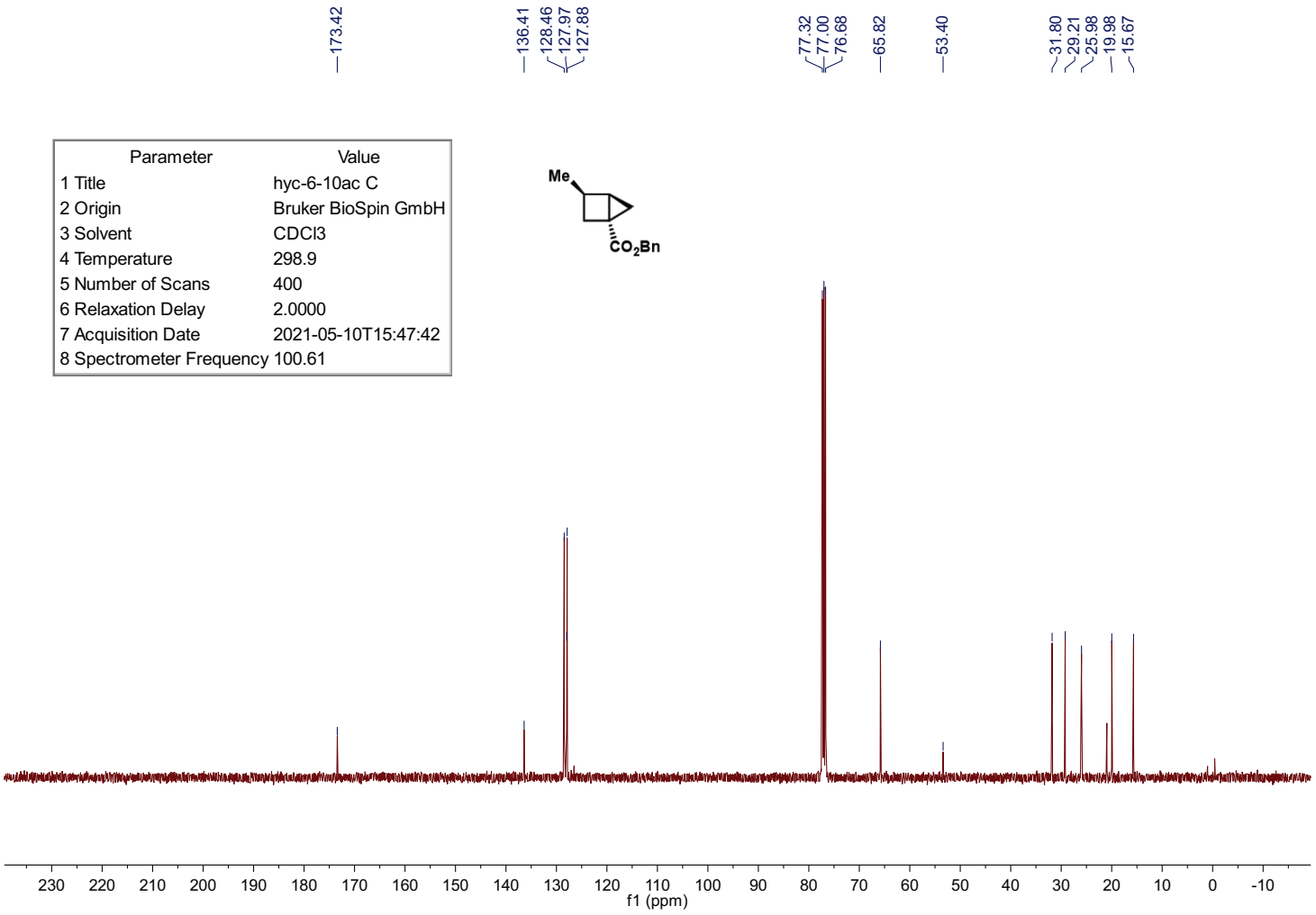

7.38
7.36
7.35
7.33
7.32
7.30
7.26
5.16
5.13
5.10
5.07
2.16
2.14
1.90
1.90
1.88
1.87
1.86
1.84
1.83
1.82
1.76
1.75
1.73
1.72
1.71
1.69
1.68
1.27
1.26
1.25
1.21
1.19
Parameter Value
1 Title hyc-6-5-1ac
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 296.7
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-04-15T15:24:12
8 Spectrometer Frequency 400.13
Me
CO2Bn
5.05
1.99
0.90
2.08
2.08
0.99
2.94
f1 (ppm)


173.64
136.41
128.45
127.95
127.77
77.32
77.00
76.68
65.79
34.87
31.25
29.14
25.51
22.54
21.08
Parameter Value
1 Title hyc-6-5 C
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.7
5 Number of Scans 1024
6 Relaxation Delay 2.0000
7 Acquisition Date 2021-05-09T09:51:16
8 Spectrometer Frequency 100.61
Me
CO2Bn
f1 (ppm)

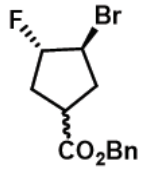

7.39
7.36
7.35
7.32
7.31
7.26
5.12
3.88
3.86
3.85
3.83
3.09
3.07
3.05
3.03
3.01
2.28
2.26
2.24
2.22
2.21
1.90
1.88
1.87
1.86
1.84
1.83
1.82
1.81
1.54
1.49
1.47
1.46
1.44
1.43
1.41
1.05
1.03
Parameter Value
1 Title hyc-5-200ac
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 296.5
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-04-14T16:14:08
8 Spectrometer Frequency 400.13
Me
Br
CO2Bn
4.63
1.98
1.00
0.99
1.98
1.92
1.09
2.91
f1 (ppm)


176.01
136.09
128.54
128.15
128.01
77.32
77.00
76.68
66.26
42.76
40.56
37.39
35.70
17.92
Parameter Value
1 Title hyc-5-200ac C
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 297.3
5 Number of Scans 500
6 Relaxation Delay 2.0000
7 Acquisition Date 2021-04-20T06:09:01
8 Spectrometer Frequency 100.61
Me
Br
CO2Bn
f1 (ppm)

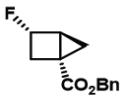

7.37
7.35
7.34
7.33
7.31
7.30
7.26
5.13
5.10
5.09
5.06
2.66
2.64
2.62
2.58
2.34
1.58
1.56
1.37
1.36
1.35
1.21
1.20
0.84
0.82
Parameter Value
1 Title hyc-6-10ac
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 296.9
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-04-16T22:19:21
8 Spectrometer Frequency 400.13
Me
CO2Bn
5.11
1.97
1.95
0.96
2.07
0.99
0.95
2.97
f1 (ppm)


173.42
136.41
128.46
127.97
127.88
77.32
77.00
76.68
65.82
53.40
31.80
29.21
25.98
19.98
15.67
Parameter Value
1 Title hyc-6-10ac C
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.9
5 Number of Scans 400
6 Relaxation Delay 2.0000
7 Acquisition Date 2021-05-10T15:47:42
8 Spectrometer Frequency 100.61
Me
CO2Bn
f1 (ppm)

Parameter	Value
1 Title	hyc-5-192ac
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.6
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-04-09T21:41:10
8 Spectrometer Frequency	400.13

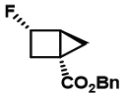


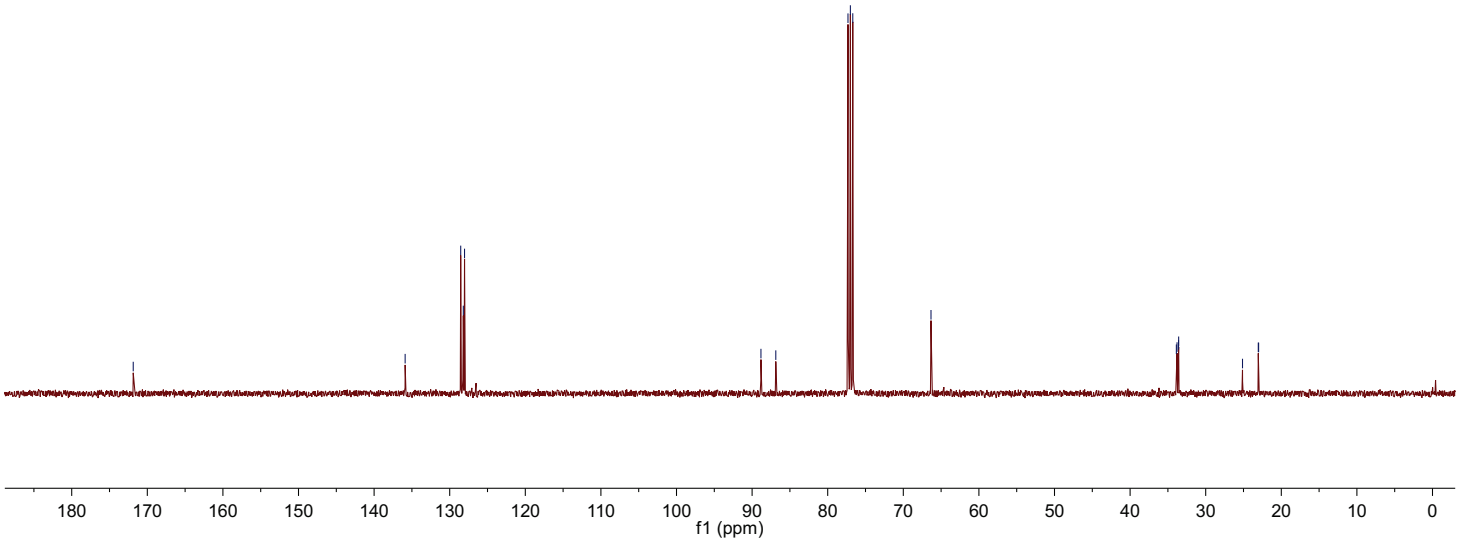
Parameter	Value
1 Title	hyc-5-196ac H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.0
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-04-21T18:13:55
8 Spectrometer Frequency	400.13



171.86
135.89
128.54
128.20
128.04
88.83
86.87
77.32
77.00
76.68
66.34
33.88
33.79
33.59
33.58
25.13
23.04
23.00

Parameter	Value
1 Title	hyc-5-196ac C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.7
5 Number of Scans	400
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-04-21T18:37:10
8 Spectrometer Frequency	100.61

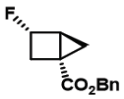


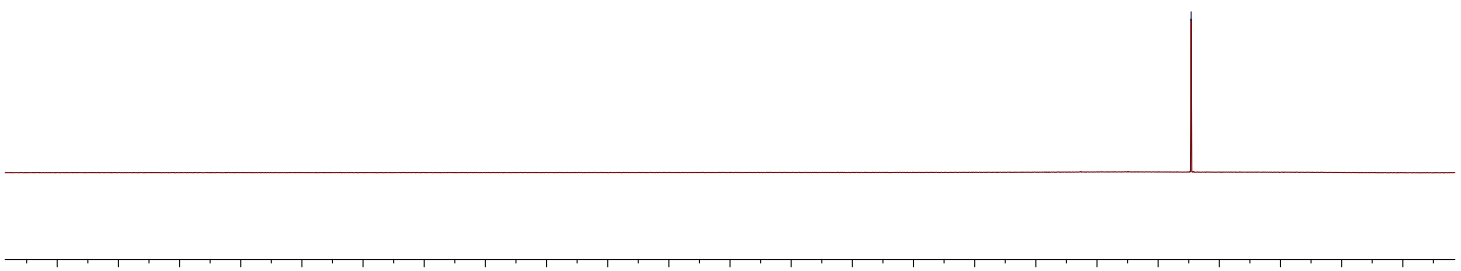


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

175.39

Parameter	Value
1 Title	hyc-5-196ac F
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.1
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-04-21T18:12:03
8 Spectrometer Frequency	376.50





10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

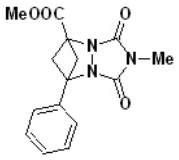
7.43
7.42
7.41
7.40
7.39
7.26

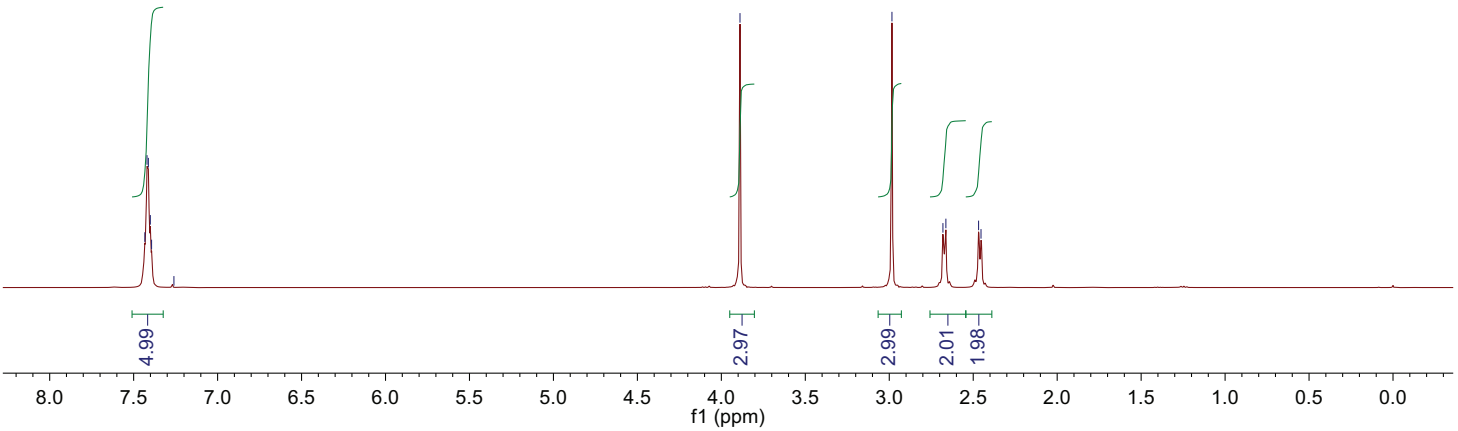
3.89

2.98

2.68
2.66
2.47
2.45

Parameter	Value
1 Title	wm-9-115-ac
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.2
5 Number of Scans	4
6 Relaxation Delay	10.0000
7 Acquisition Date	2021-01-13T23:19:54
8 Spectrometer Frequency	400.13





165.20
159.88
159.25

132.05
129.14
128.33
126.88

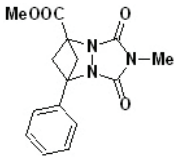
77.32
77.00
76.68
74.08
68.58

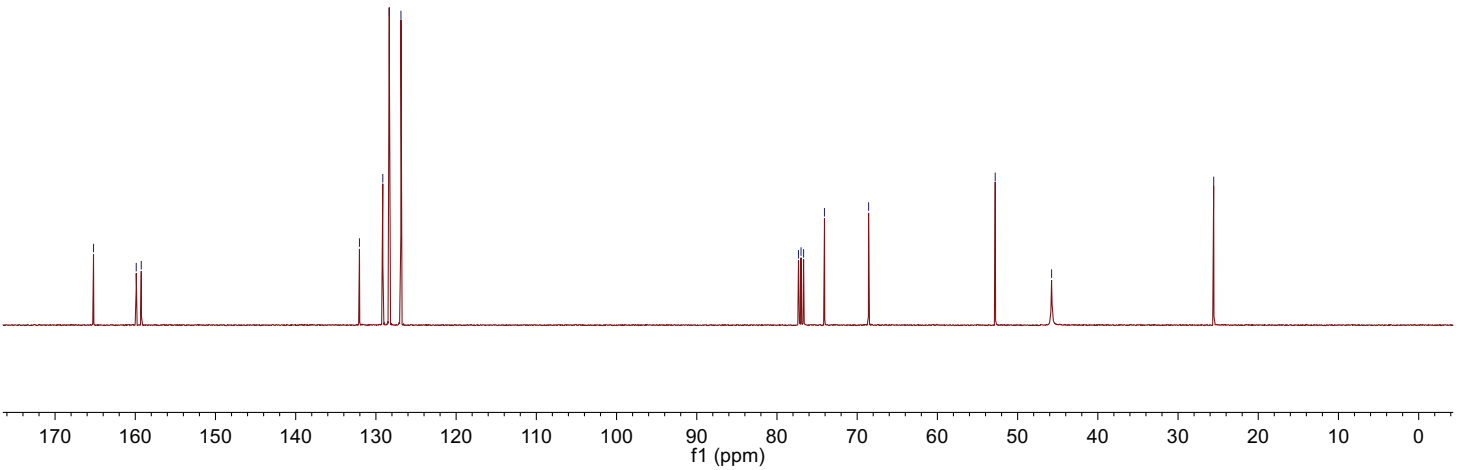
52.79

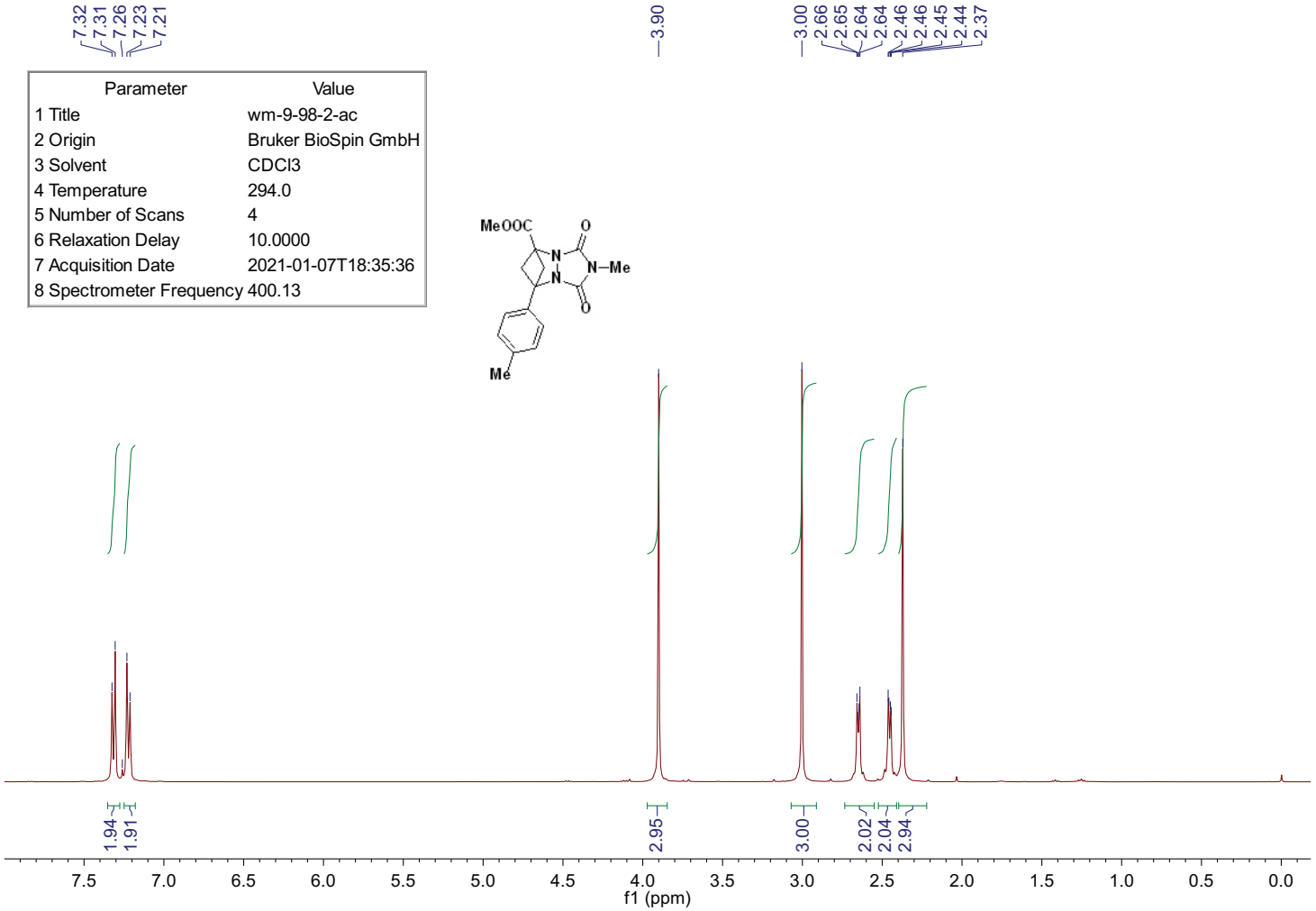
45.77

25.56

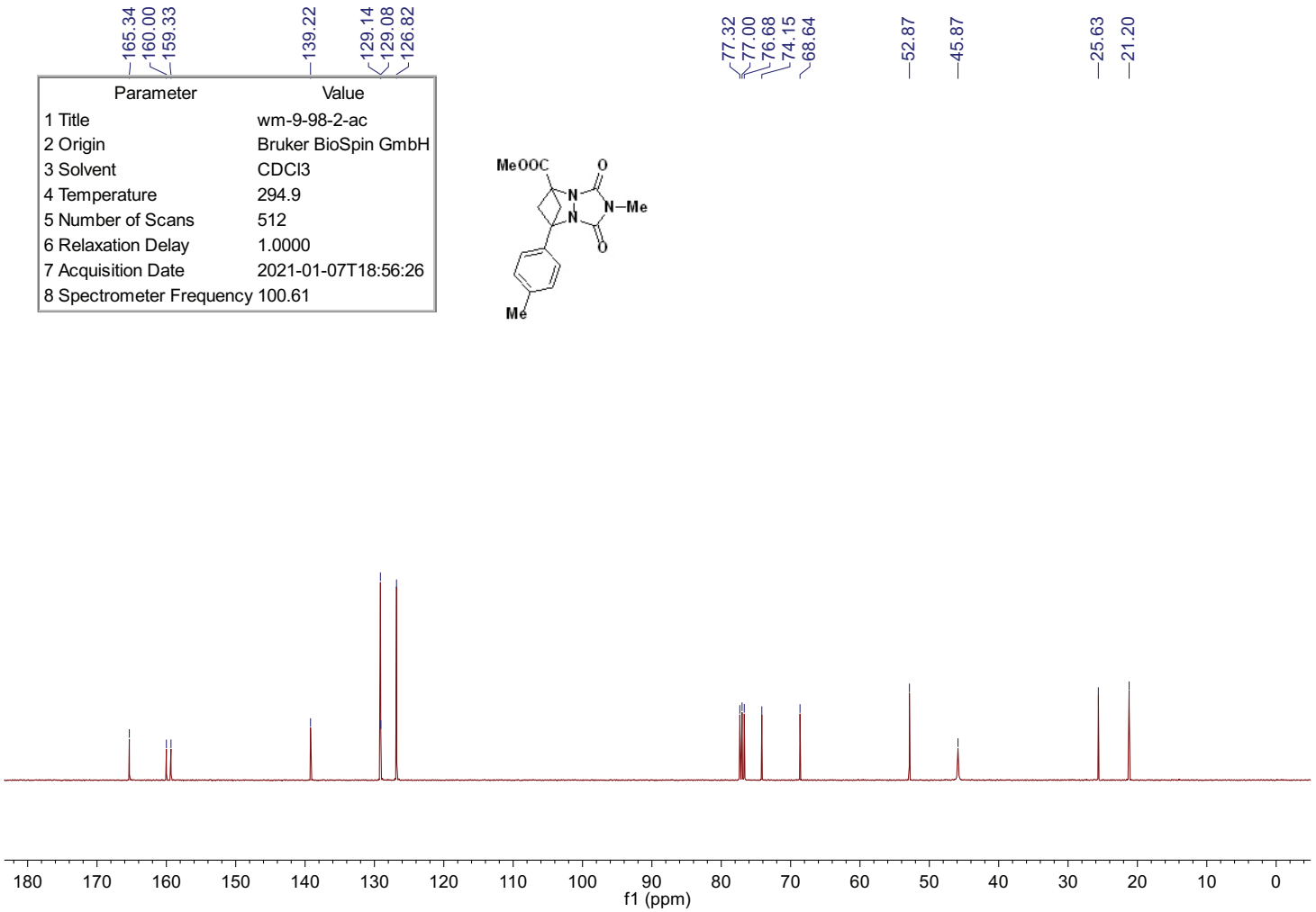
Parameter	Value
1 Title	wm-9-115-ac
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.0
5 Number of Scans	512
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-01-13T23:40:34
8 Spectrometer Frequency	100.61







Parameter	Value
1 Title	wm-9-98-2-ac
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	294.0
5 Number of Scans	4
6 Relaxation Delay	10.0000
7 Acquisition Date	2021-01-07T18:35:36
8 Spectrometer Frequency	400.13

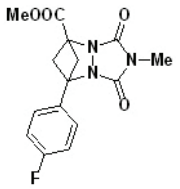


Parameter	Value
1 Title	wm-9-98-2-ac
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	294.9
5 Number of Scans	512
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-01-07T18:56:26
8 Spectrometer Frequency	100.61

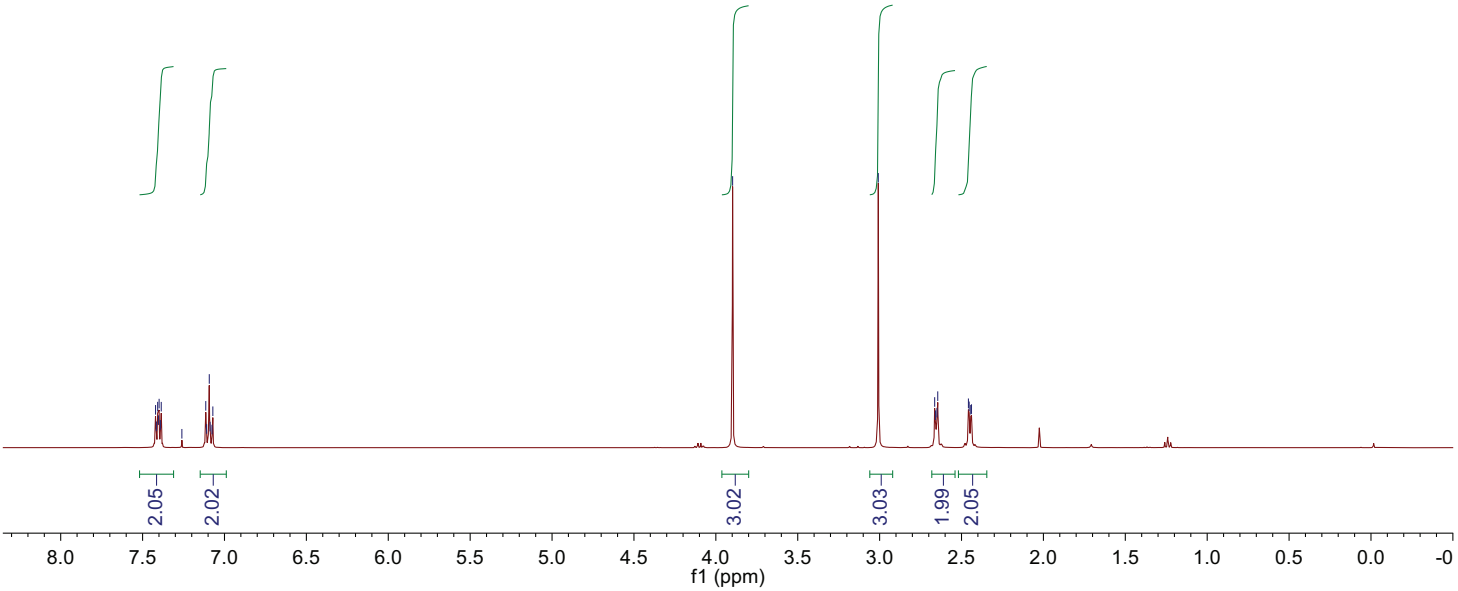
7.42 7.42 7.41 7.40 7.40 7.39 7.39 7.26 7.11 7.11 7.09 7.09 7.08 7.07

3.90

3.01 2.66 2.66 2.65 2.65 2.46 2.45 2.44 2.44



Parameter	Value
1 Title	wm-9-47-2-ac-h
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.9
5 Number of Scans	4
6 Relaxation Delay	10.0000
7 Acquisition Date	2020-12-18T13:28:30
8 Spectrometer Frequency	400.13



165.21 164.32 161.85 159.91 159.44

129.02 128.94 128.11 128.08

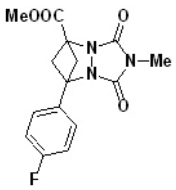
115.74 115.52

77.32 77.00 76.68 73.60 68.68

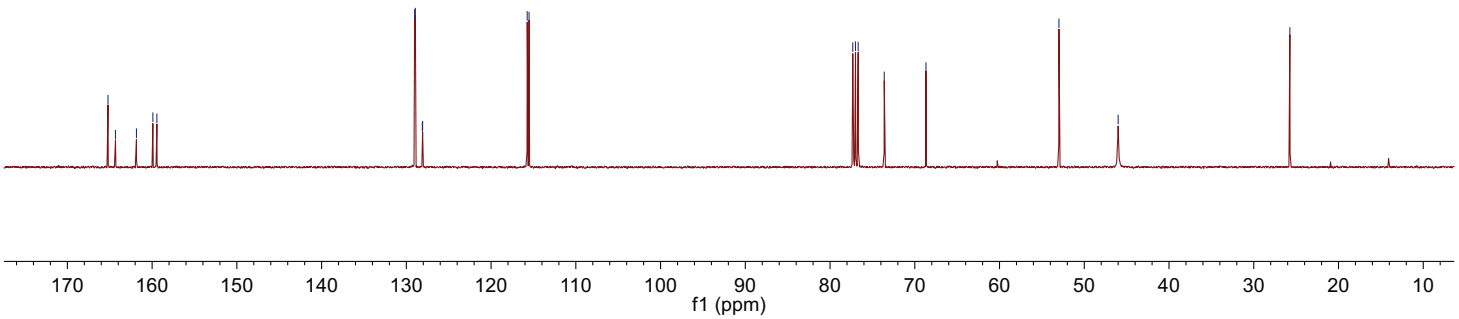
52.99

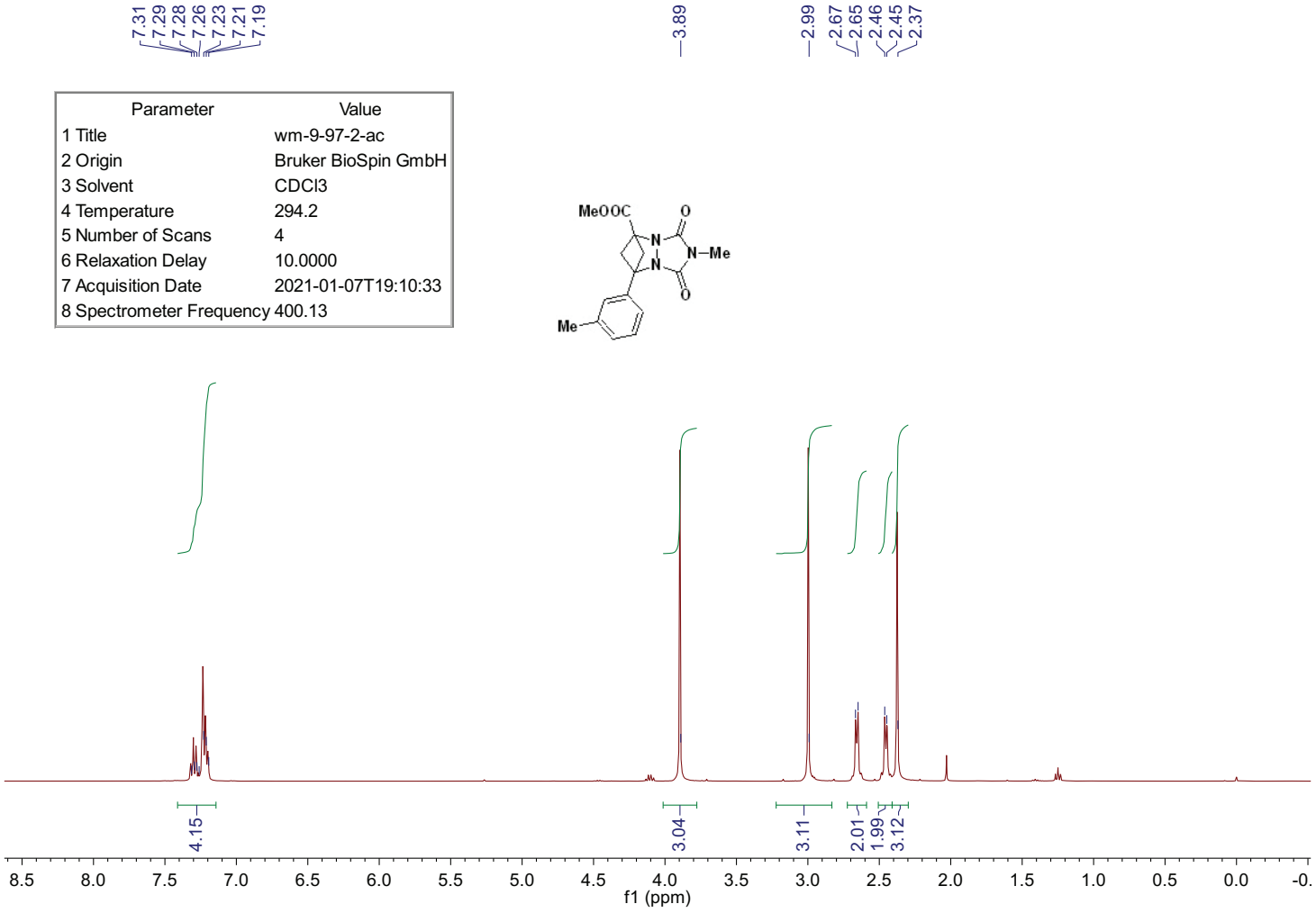
46.00

25.74

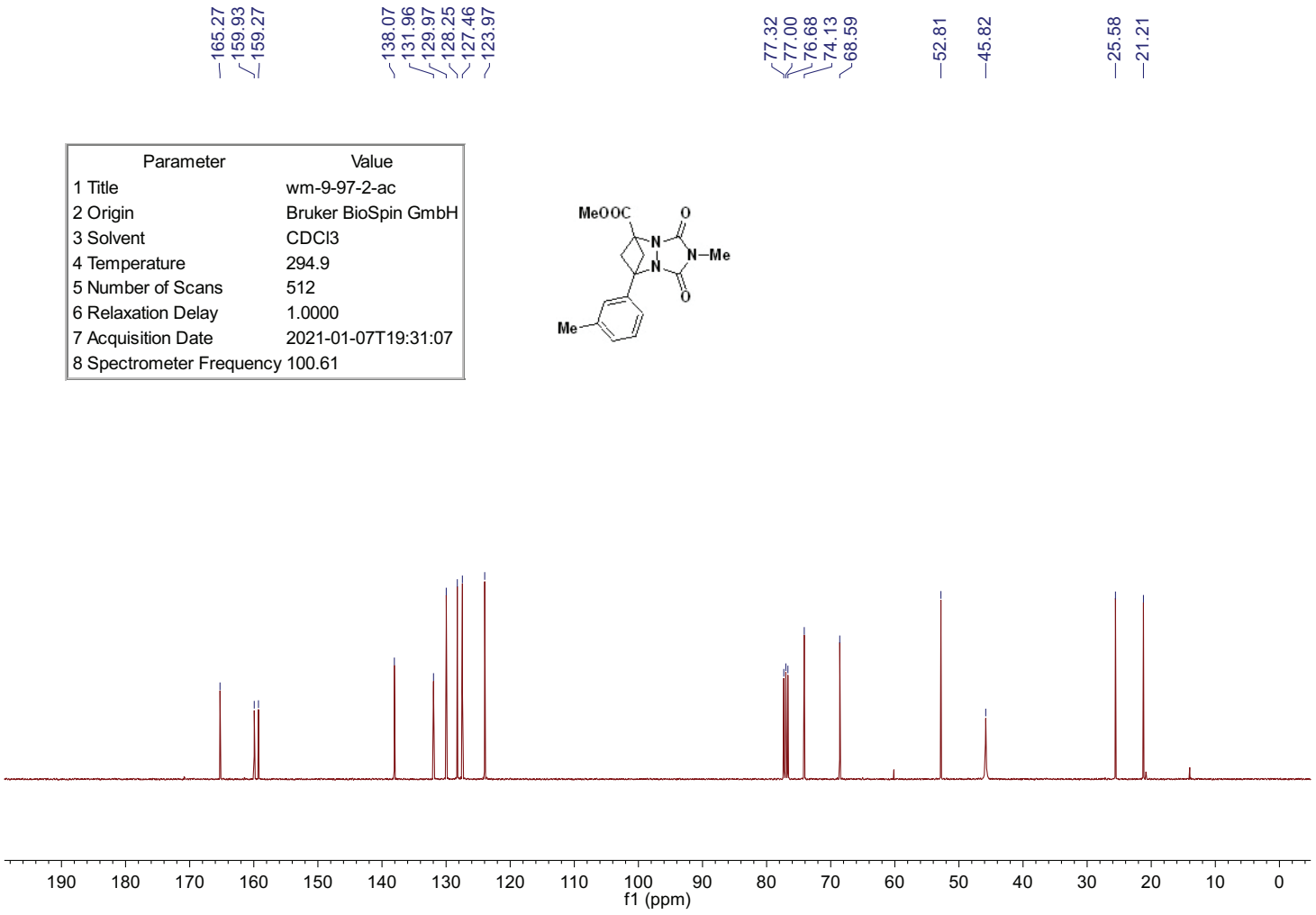


Parameter	Value
1 Title	wm-9-47-2-ac-c
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.6
5 Number of Scans	512
6 Relaxation Delay	1.0000
7 Acquisition Date	2020-12-18T13:49:04
8 Spectrometer Frequency	100.61





Parameter	Value
1 Title	wm-9-97-2-ac
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	294.2
5 Number of Scans	4
6 Relaxation Delay	10.0000
7 Acquisition Date	2021-01-07T19:10:33
8 Spectrometer Frequency	400.13



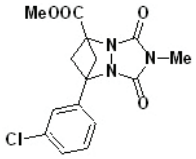
Parameter	Value
1 Title	wm-9-97-2-ac
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	294.9
5 Number of Scans	512
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-01-07T19:31:07
8 Spectrometer Frequency	100.61

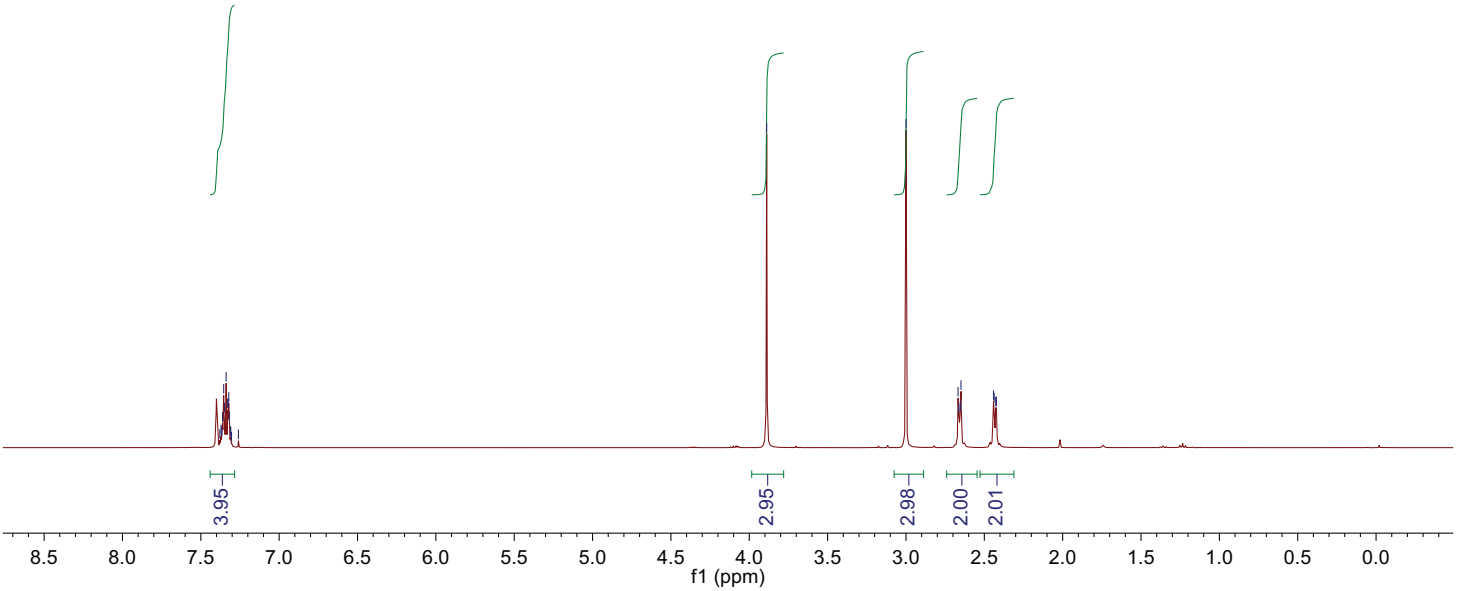
7.38 7.37 7.37 7.36 7.35 7.35 7.34 7.33 7.32 7.32 7.32 7.31 7.31 7.30 7.26

3.89

3.00 2.67 2.66 2.65 2.65 2.44 2.44 2.43 2.42

Parameter	Value
1 Title	wm-9-46-2-ac-h
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.0
5 Number of Scans	4
6 Relaxation Delay	10.0000
7 Acquisition Date	2020-12-18T13:03:34
8 Spectrometer Frequency	400.13





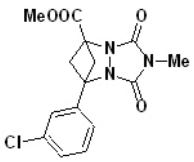
165.05 159.82 159.35

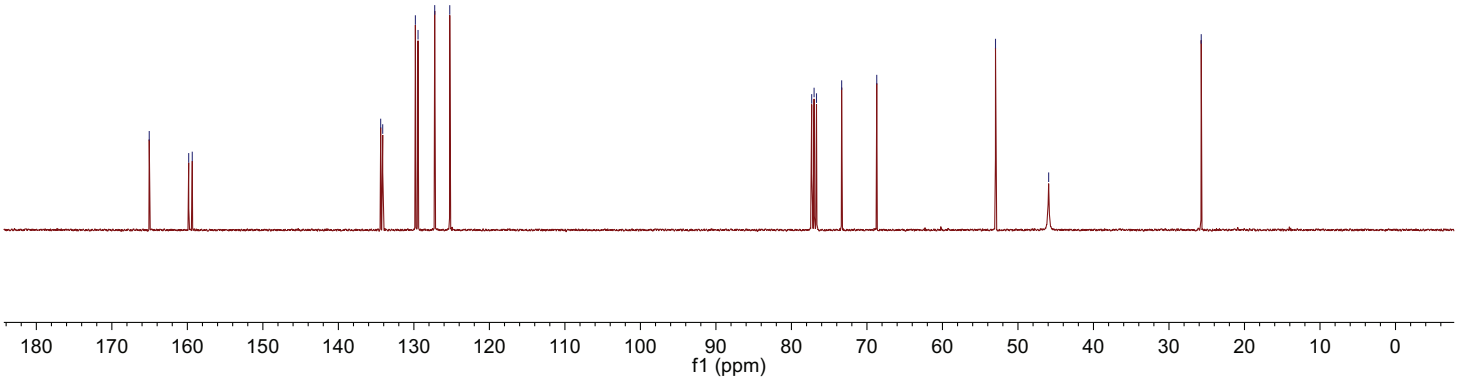
134.40 134.13 129.80 129.45 127.24 125.25

77.32 77.00 76.68 73.35 68.70

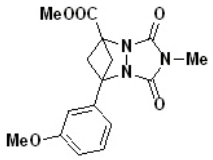
52.97 45.94 25.73

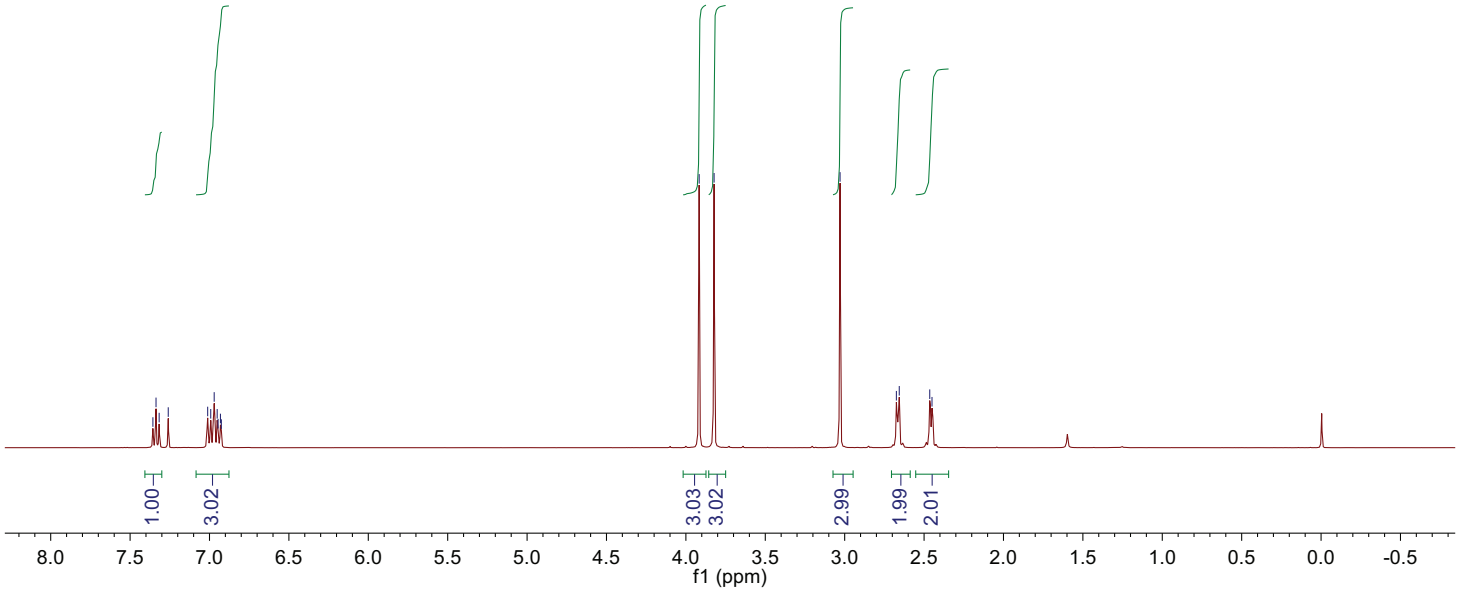
Parameter	Value
1 Title	wm-9-46-2-ac-c
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.7
5 Number of Scans	512
6 Relaxation Delay	1.0000
7 Acquisition Date	2020-12-18T13:24:09
8 Spectrometer Frequency	100.61



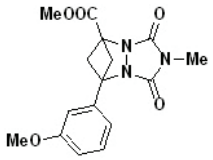


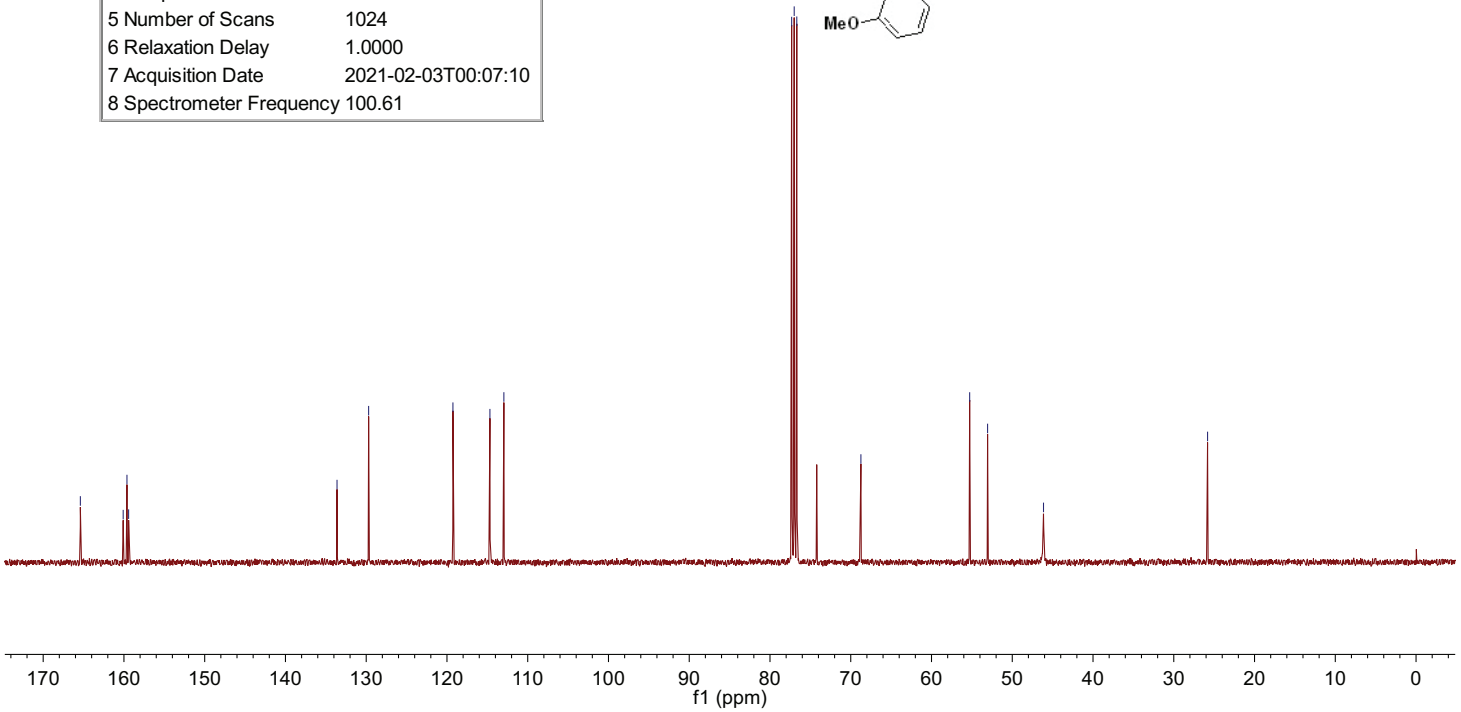
Parameter	Value
1 Title	wm-9-135
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.4
5 Number of Scans	4
6 Relaxation Delay	10.0000
7 Acquisition Date	2021-02-02T23:26:47
8 Spectrometer Frequency	400.13

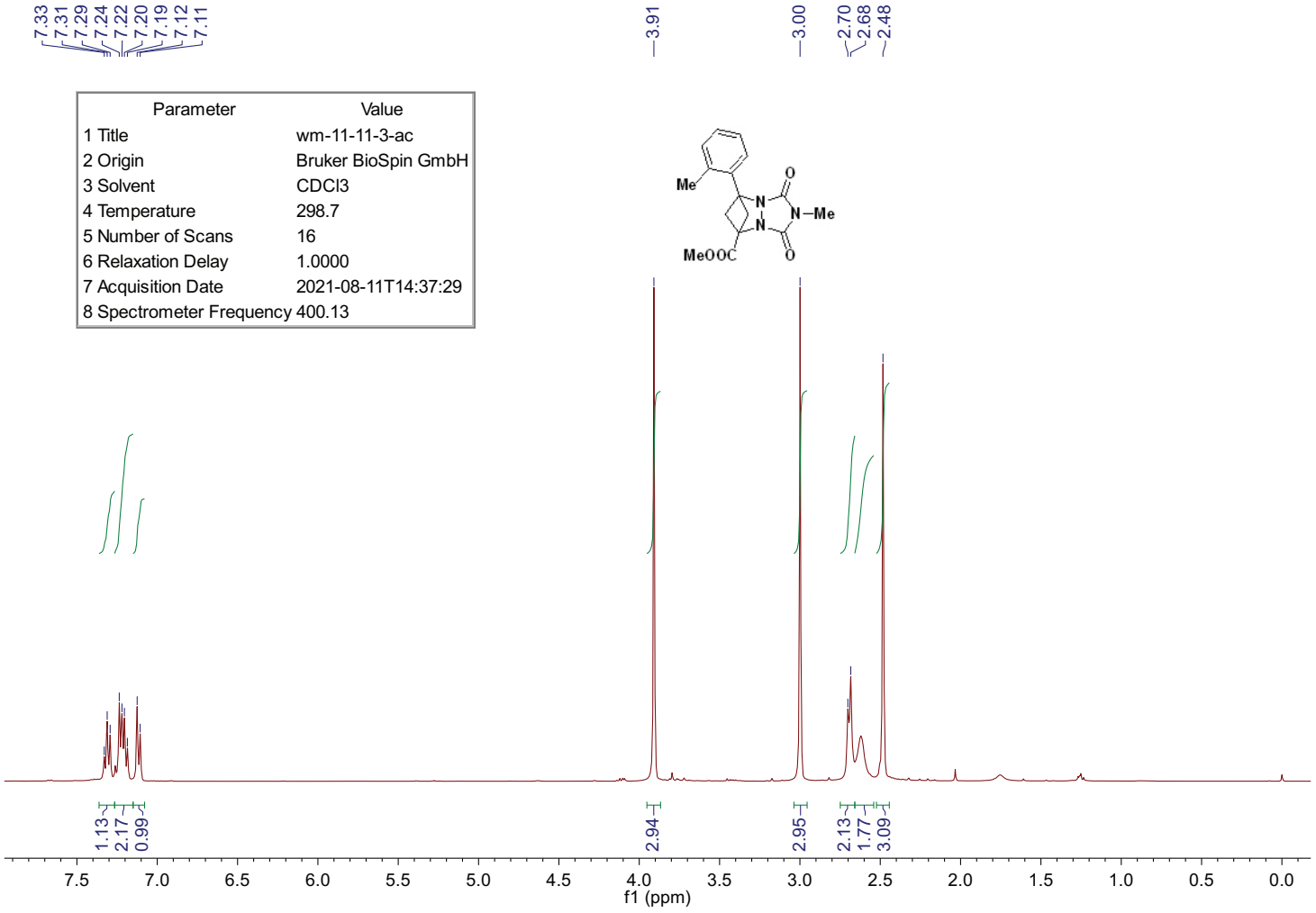


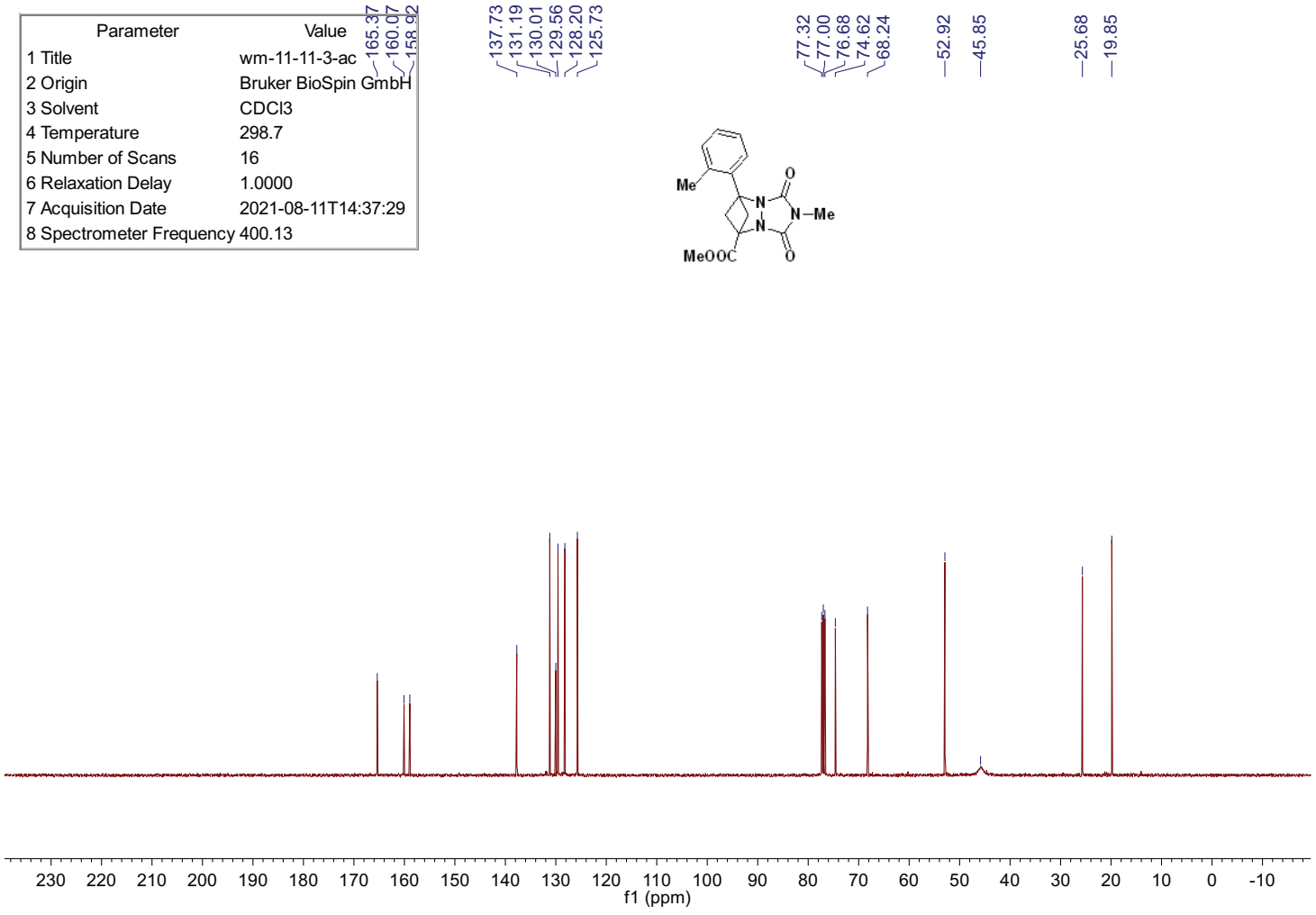


Parameter	Value
1 Title	wm-9-135
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.3
5 Number of Scans	1024
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-02-03T00:07:10
8 Spectrometer Frequency	100.61

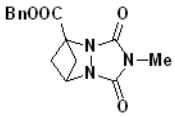


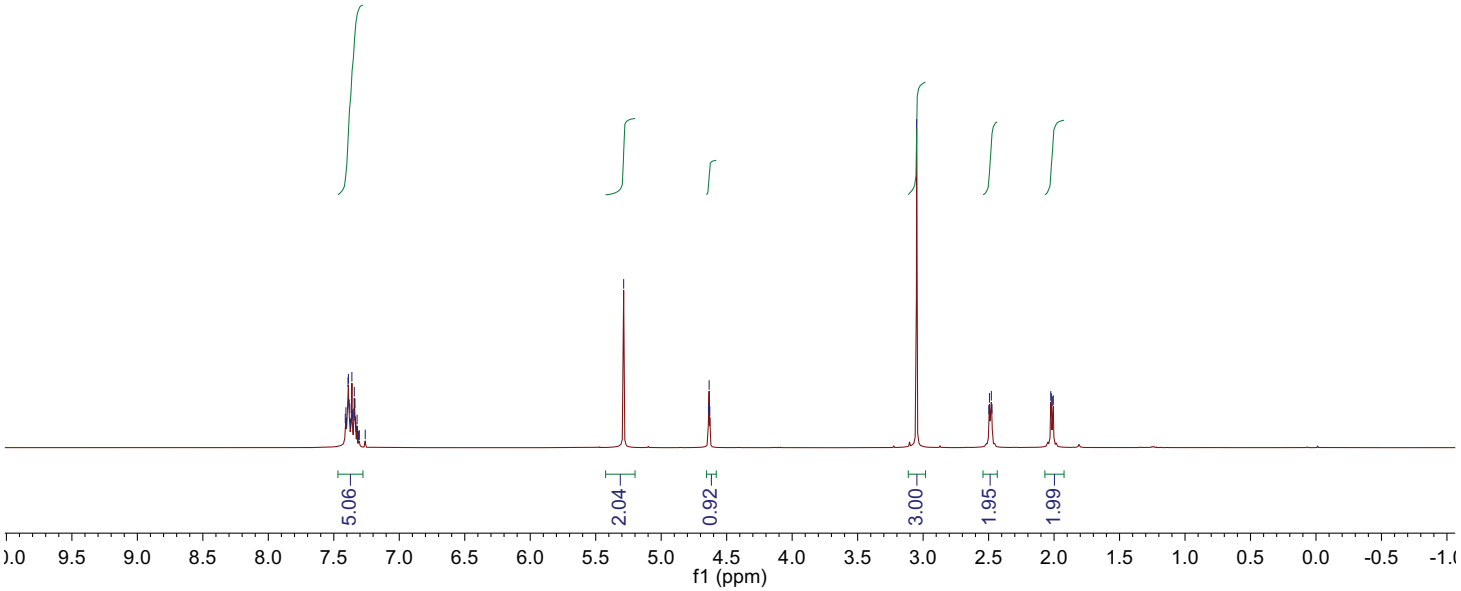



7.33
7.31
7.29
7.24
7.22
7.20
7.19
7.12
7.11
3.91
3.00
2.70
2.68
2.48
Parameter Value
1 Title wm-11-11-3-ac
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.7
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-08-11T14:37:29
8 Spectrometer Frequency 400.13
Me
N
N
N–Me
MeOOC
O
O
O
1.13
2.17
0.99
2.94
2.95
2.13
1.77
3.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

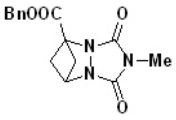

165.37
160.07
158.92
137.73
131.19
130.01
129.56
128.20
125.73
77.32
77.00
76.68
74.62
68.24
52.92
45.85
25.68
19.85
Parameter Value
1 Title wm-11-11-3-ac
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.7
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-08-11T14:37:29
8 Spectrometer Frequency 400.13
Me
N
N
N–Me
MeOOC
O
O
O
230
220
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)

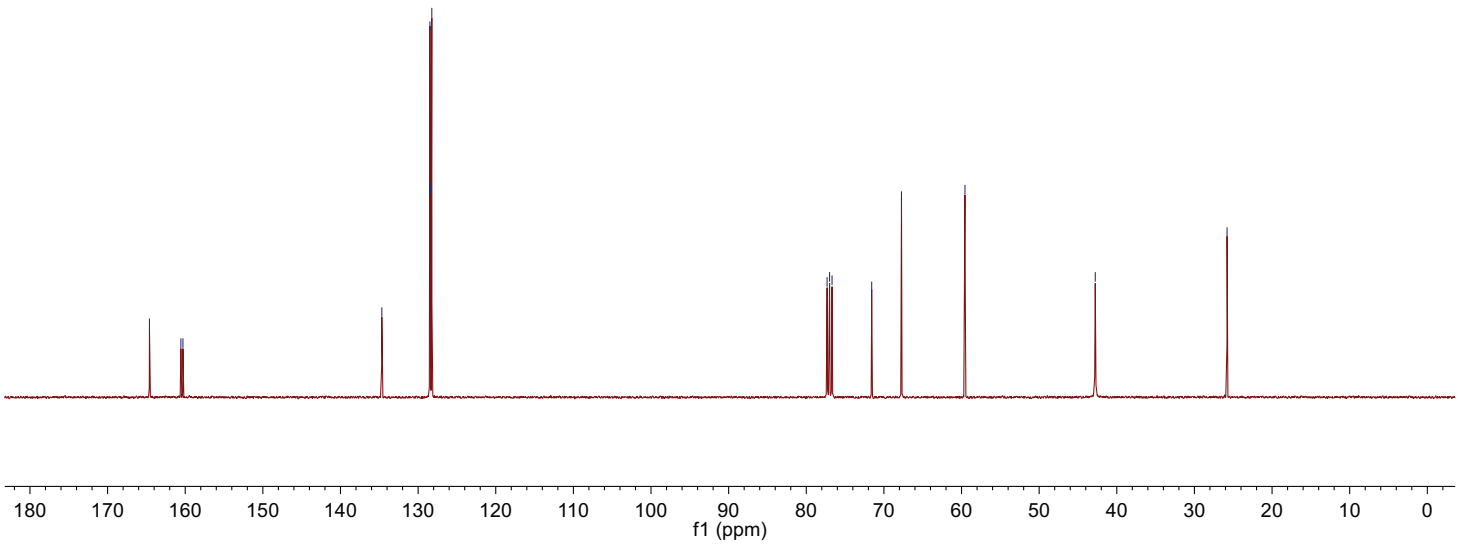
Parameter	Value
1 Title	wm-9-48-1-ac-h
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.9
5 Number of Scans	4
6 Relaxation Delay	10.0000
7 Acquisition Date	2020-12-18T13:53:29
8 Spectrometer Frequency	400.13

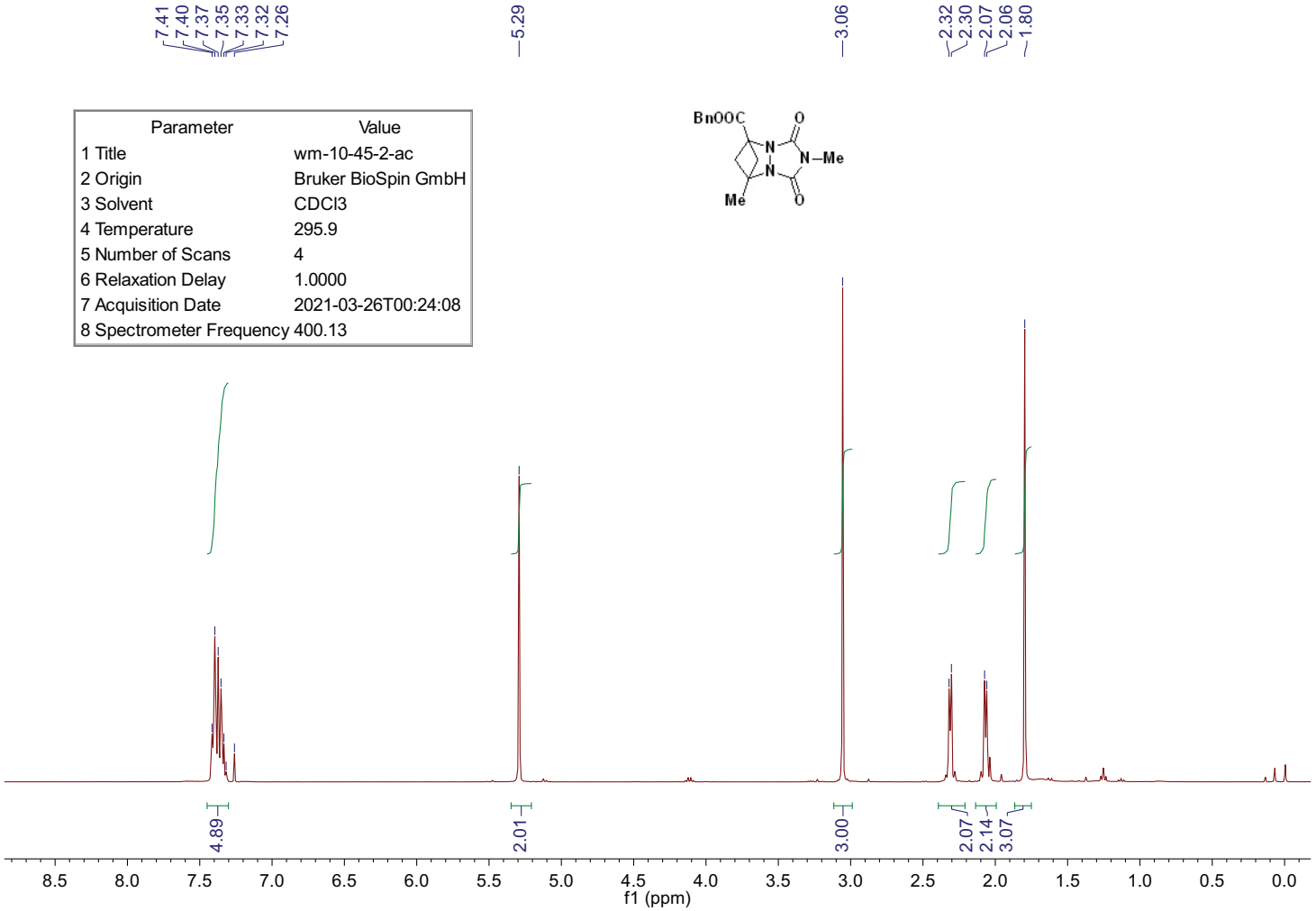




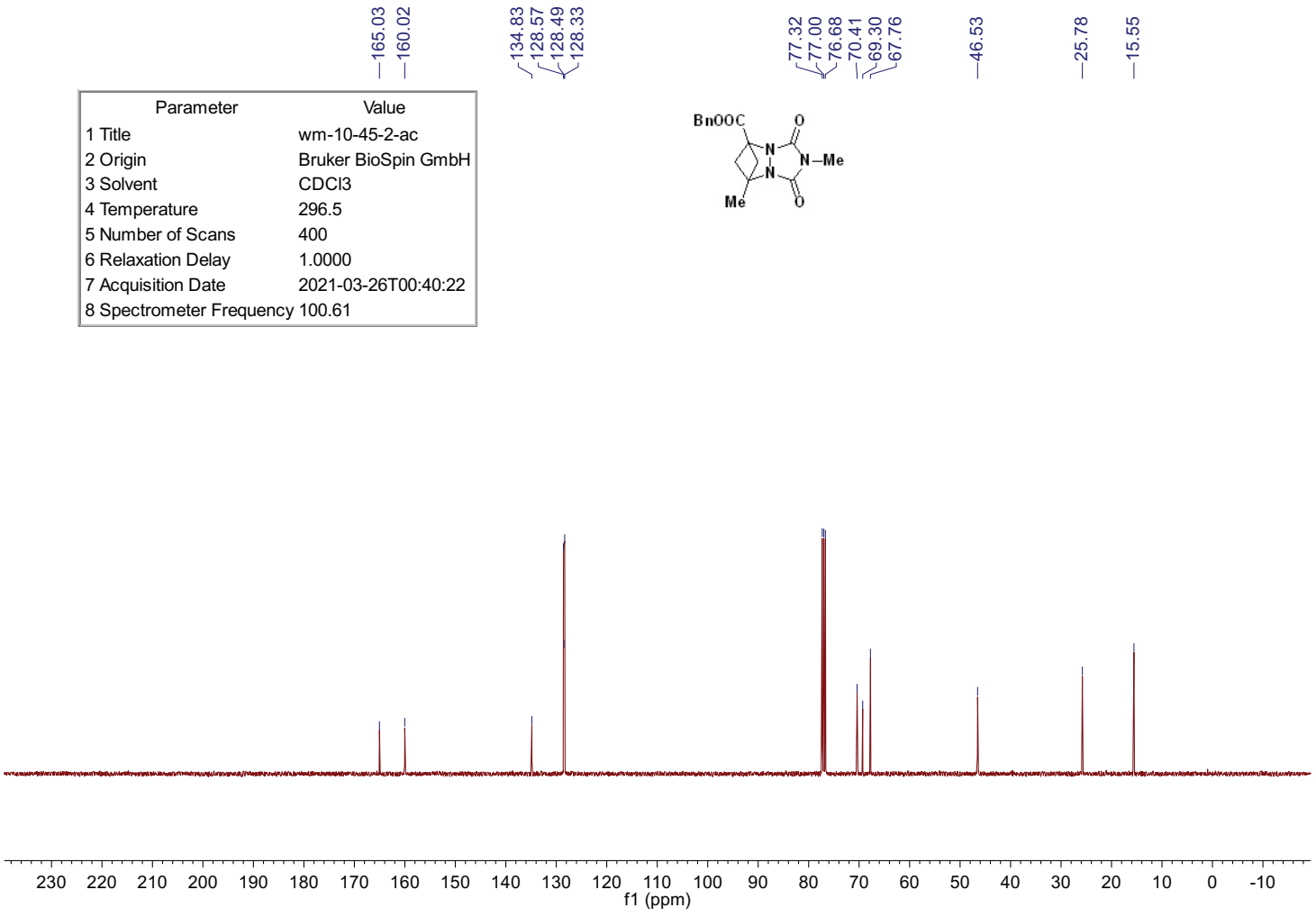
Parameter	Value
1 Title	wm-9-48-1-ac-c
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.7
5 Number of Scans	512
6 Relaxation Delay	1.0000
7 Acquisition Date	2020-12-18T14:14:03
8 Spectrometer Frequency	100.61



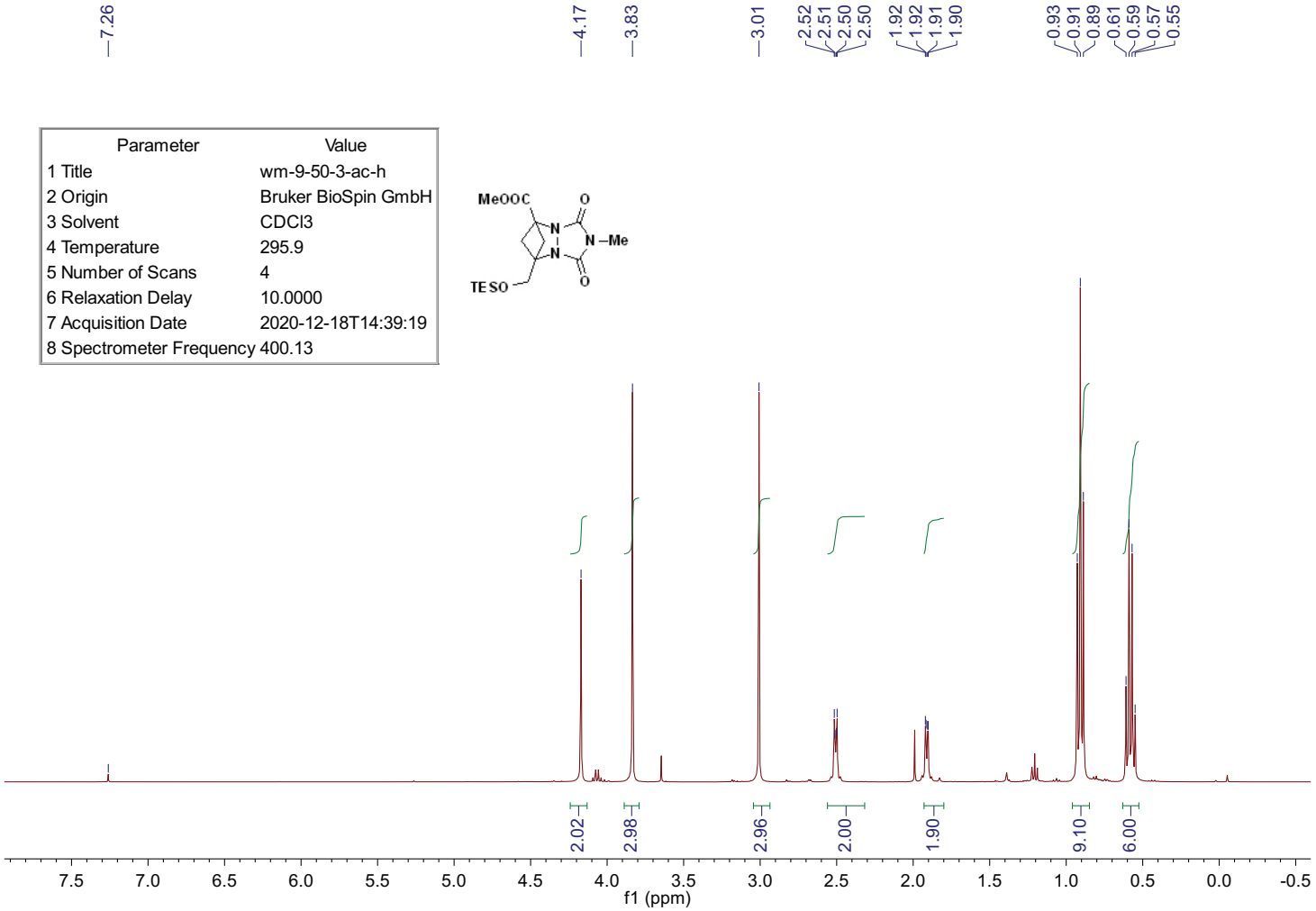




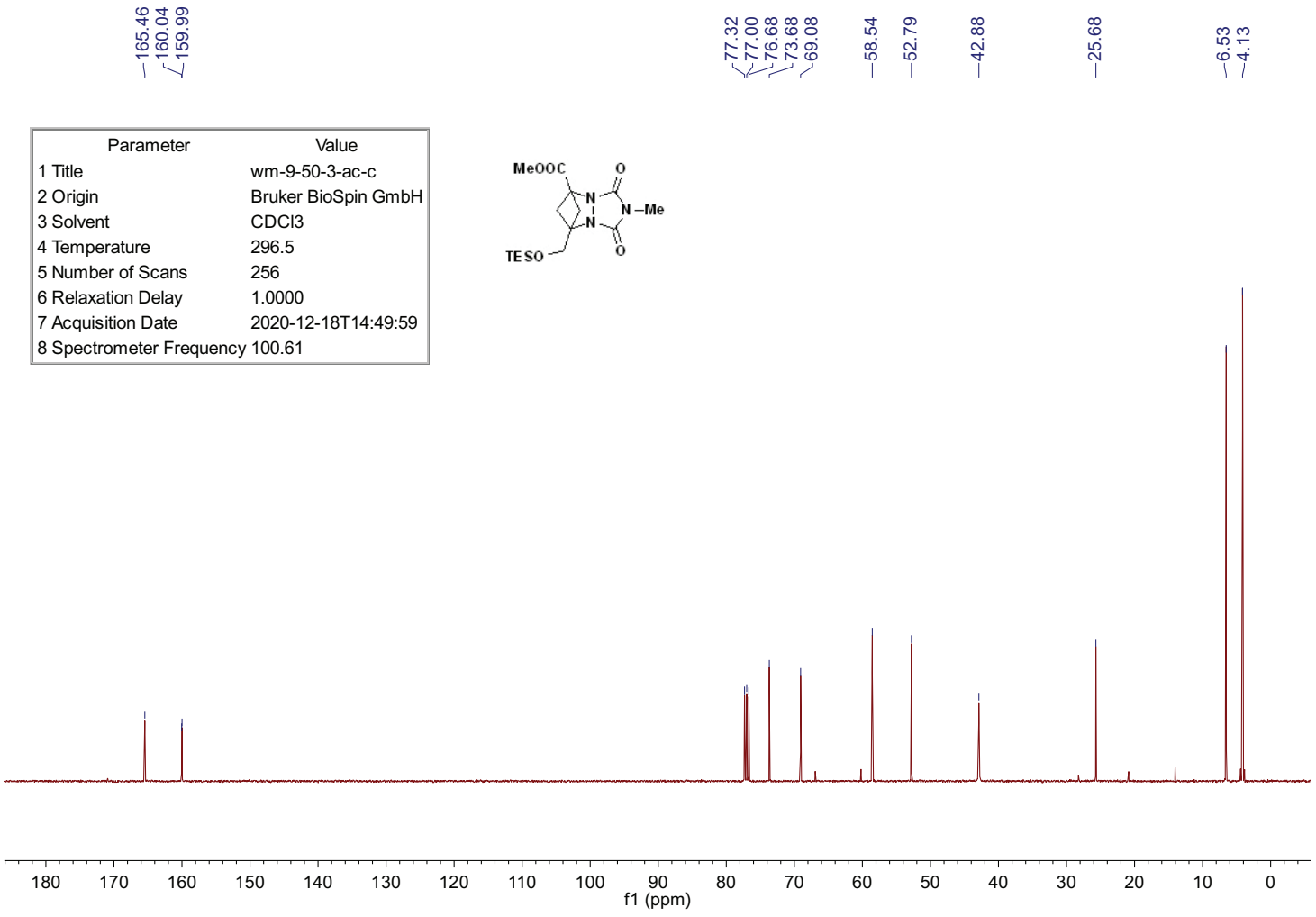
Parameter	Value
1 Title	wm-10-45-2-ac
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.9
5 Number of Scans	4
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-03-26T00:24:08
8 Spectrometer Frequency	400.13



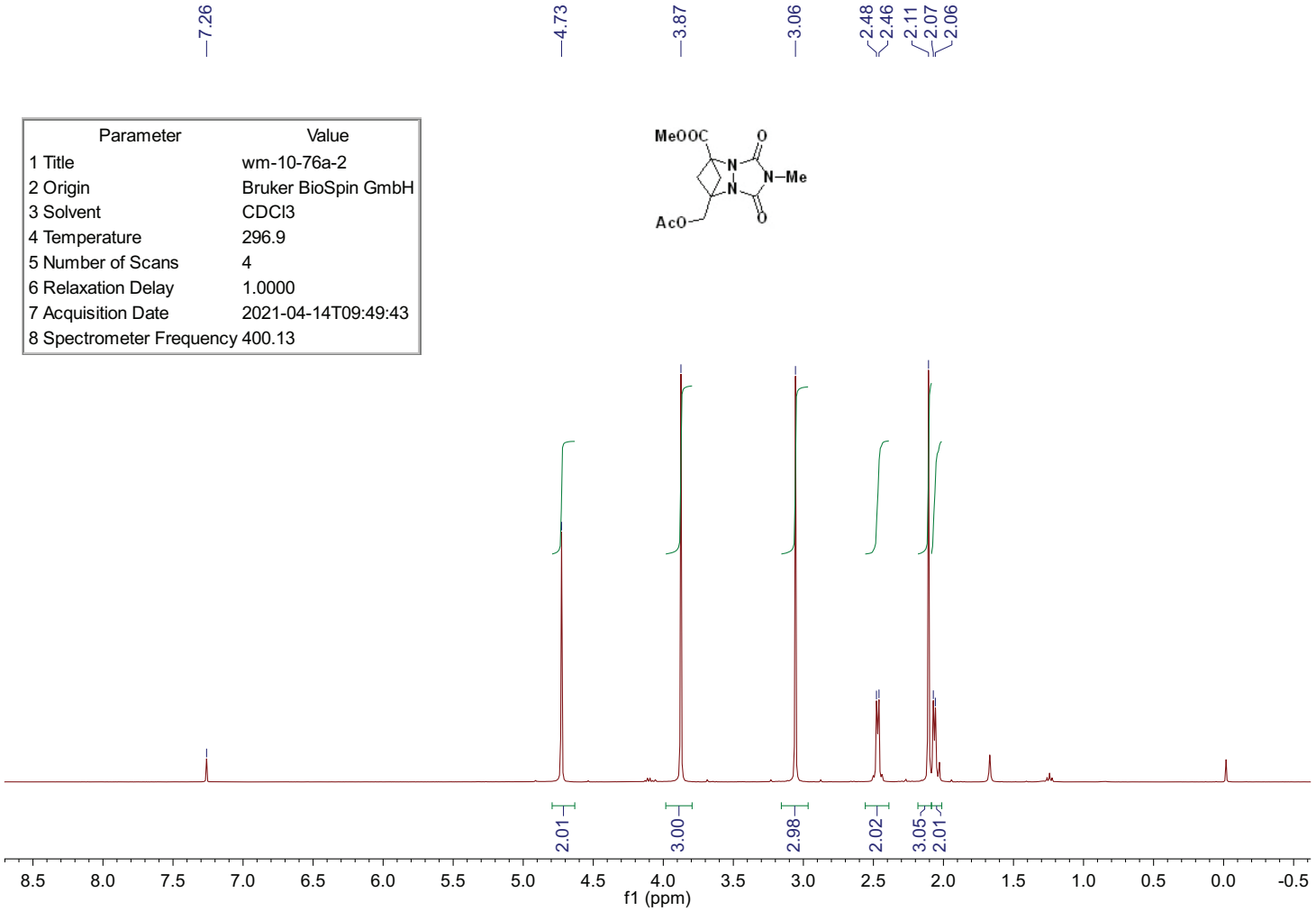
Parameter	Value
1 Title	wm-10-45-2-ac
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.5
5 Number of Scans	400
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-03-26T00:40:22
8 Spectrometer Frequency	100.61

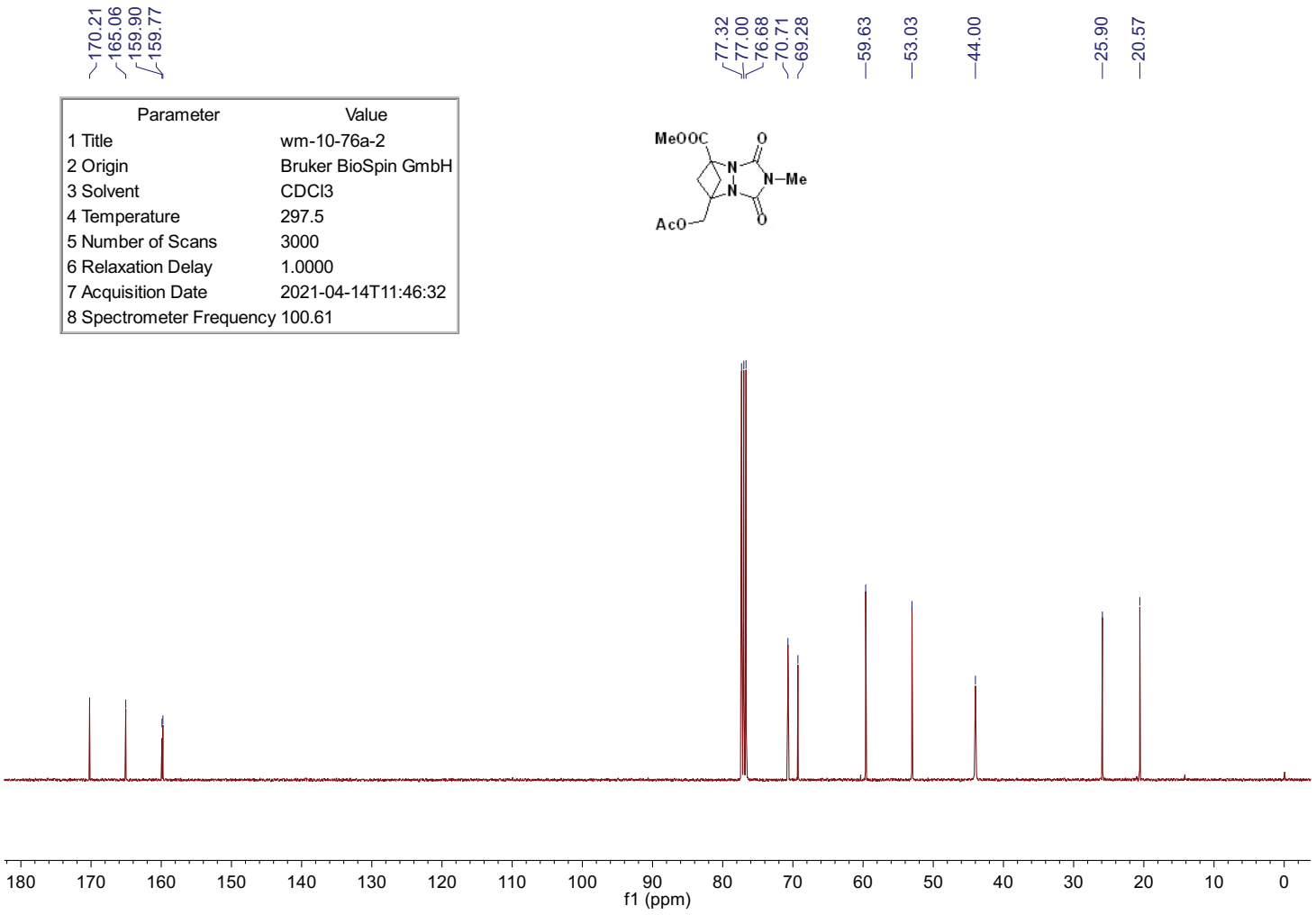


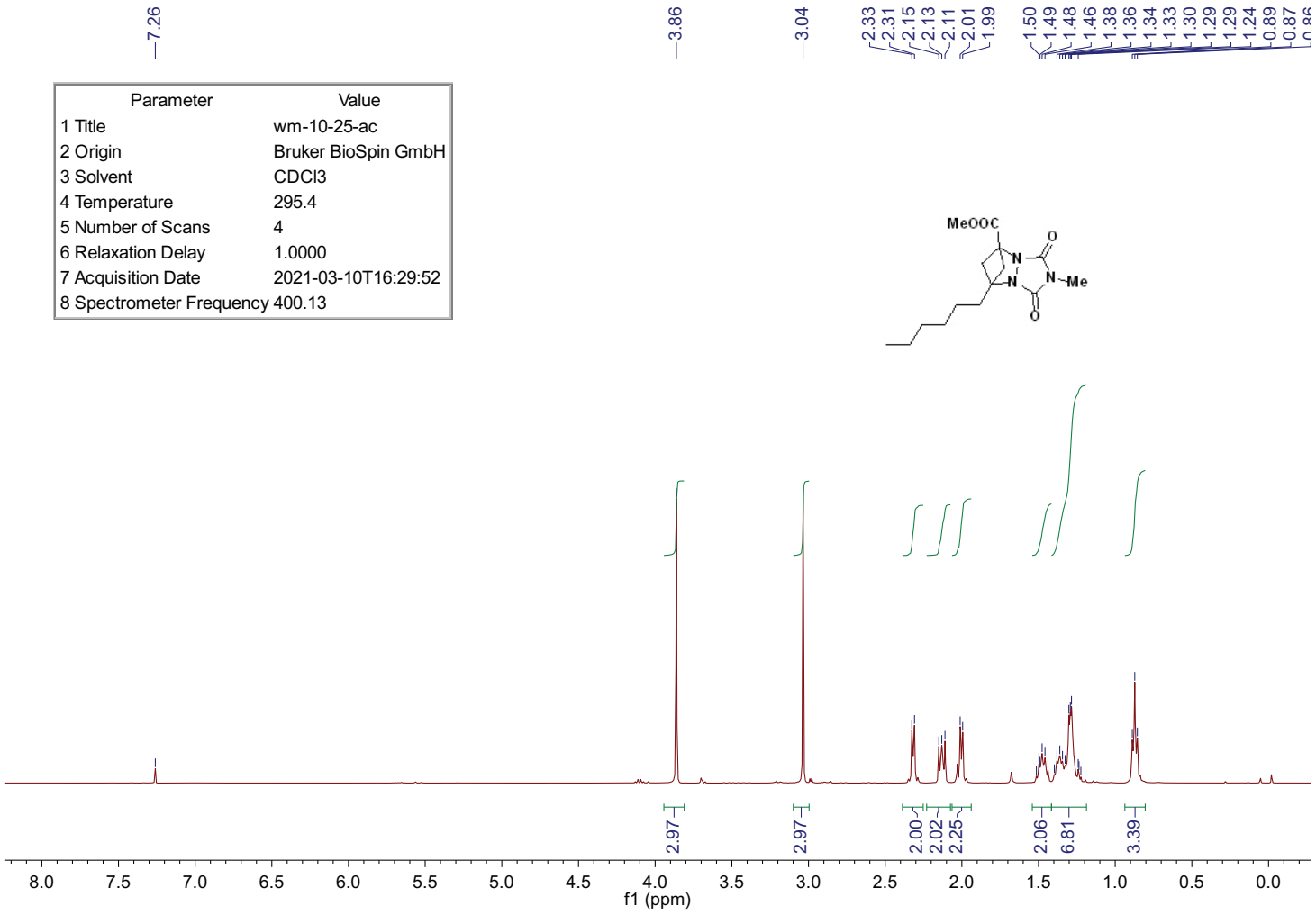
Parameter	Value
1 Title	wm-9-50-3-ac-h
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.9
5 Number of Scans	4
6 Relaxation Delay	10.0000
7 Acquisition Date	2020-12-18T14:39:19
8 Spectrometer Frequency	400.13

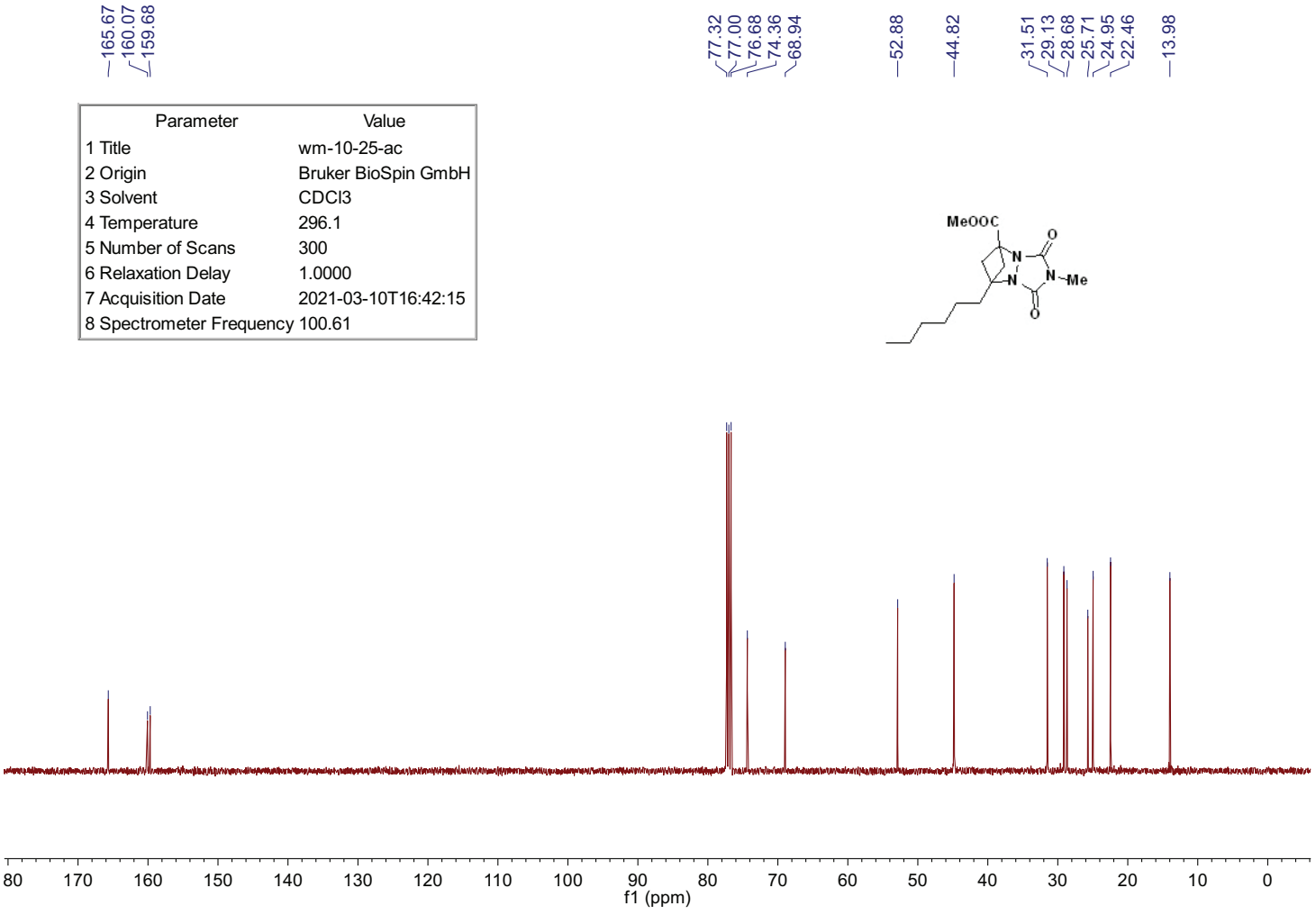


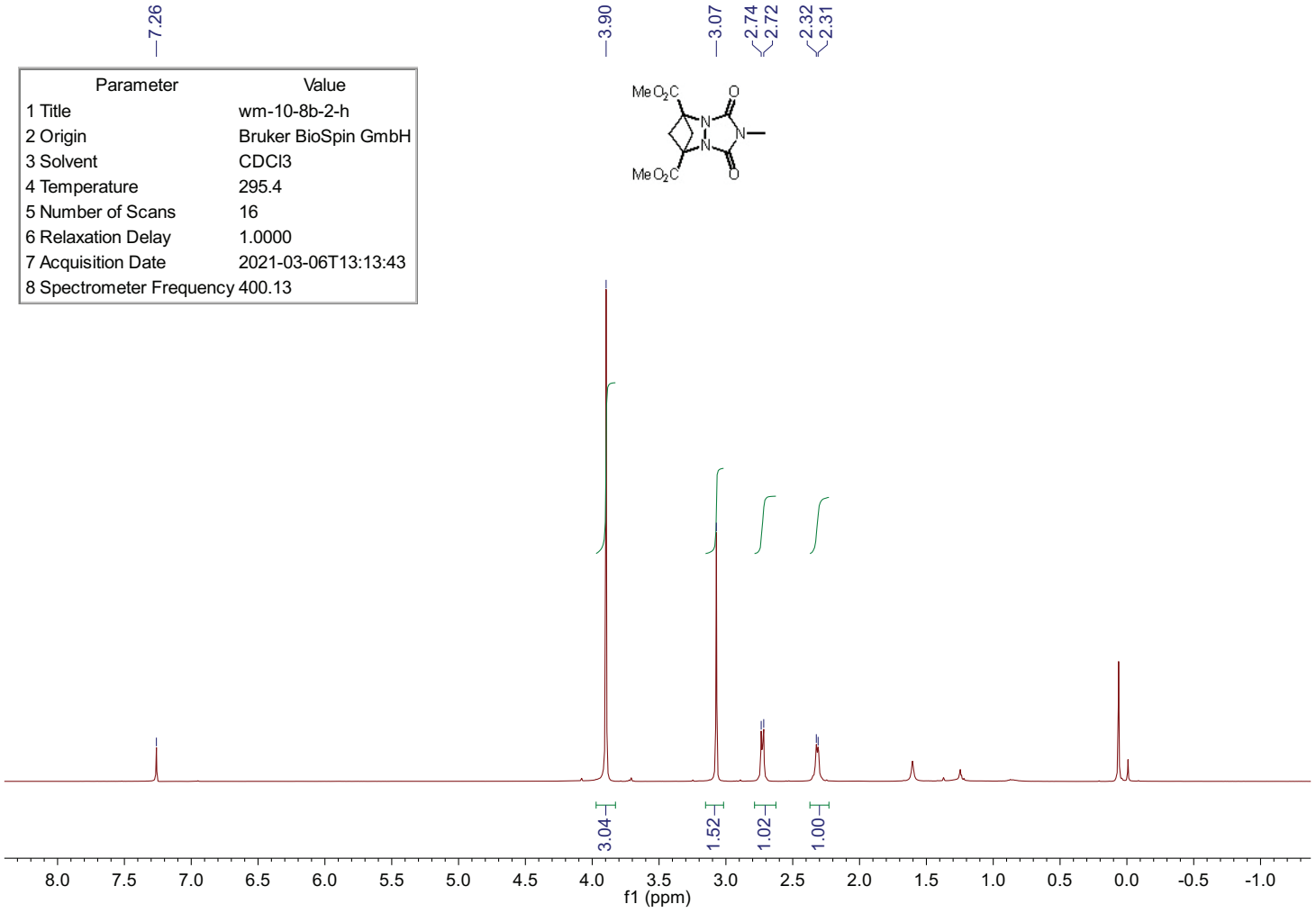
Parameter	Value
1 Title	wm-9-50-3-ac-c
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.5
5 Number of Scans	256
6 Relaxation Delay	1.0000
7 Acquisition Date	2020-12-18T14:49:59
8 Spectrometer Frequency	100.61


7.26
4.73
3.87
3.06
2.48
2.46
2.11
2.07
2.06
Parameter Value
1 Title wm-10-76a-2
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 296.9
5 Number of Scans 4
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-04-14T09:49:43
8 Spectrometer Frequency 400.13
MeOOC
AcO
N–Me
2.01
3.00
2.98
2.02
3.05
2.01
f1 (ppm)

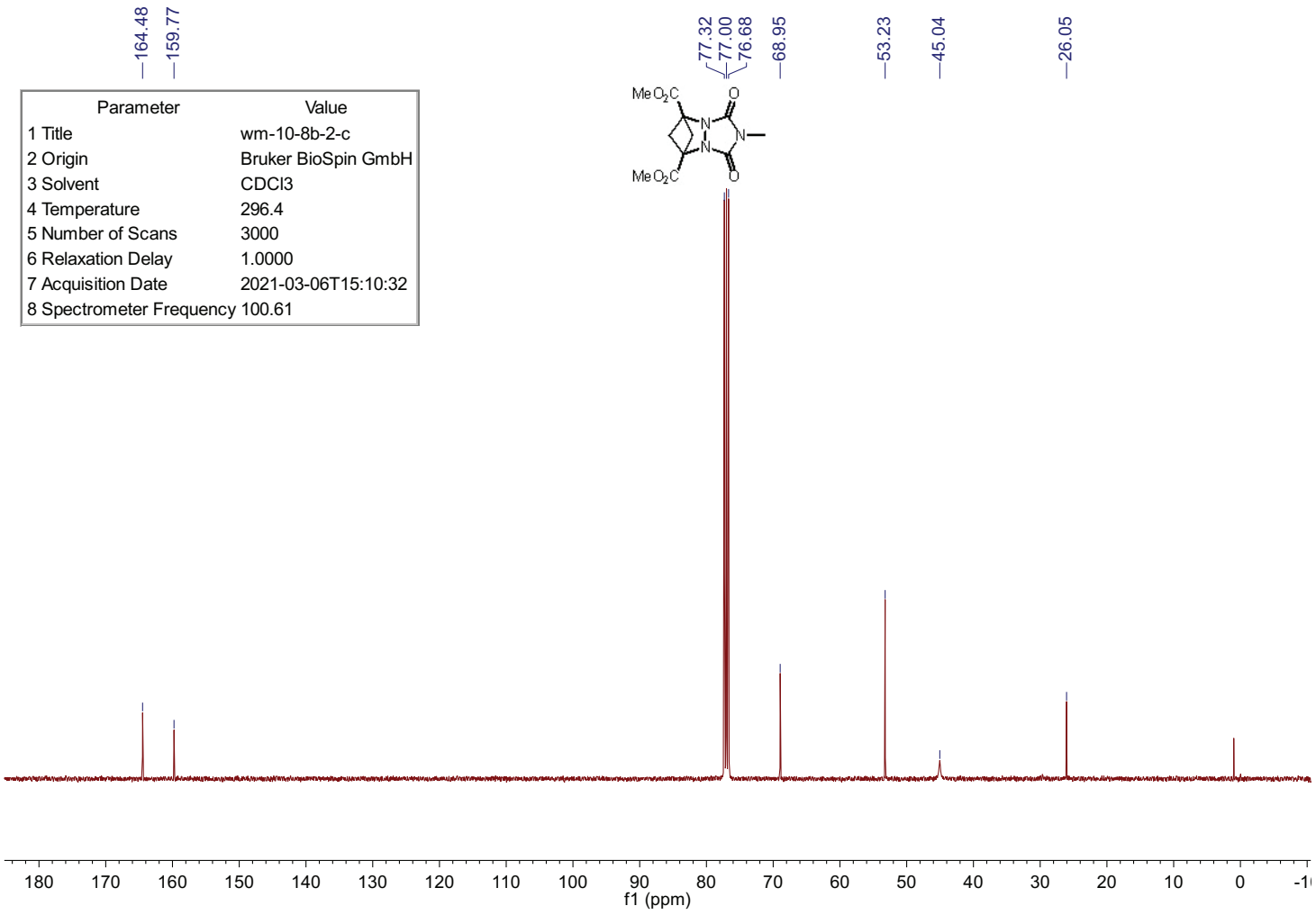

170.21
165.06
159.90
159.77
77.32
77.00
76.68
70.71
69.28
59.63
53.03
44.00
25.90
20.57
Parameter Value
1 Title wm-10-76a-2
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 297.5
5 Number of Scans 3000
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-04-14T11:46:32
8 Spectrometer Frequency 100.61
MeOOC
AcO
N–Me
f1 (ppm)


7.26
3.86
3.04
2.33
2.31
2.15
2.13
2.11
2.01
1.99
1.50
1.49
1.48
1.46
1.38
1.36
1.34
1.33
1.30
1.29
1.29
1.24
0.89
0.87
Parameter Value
1 Title wm-10-25-ac
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 295.4
5 Number of Scans 4
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-03-10T16:29:52
8 Spectrometer Frequency 400.13
MeOOC
N
N
O
N
Me
O
O
2.97
2.97
2.00
2.02
2.25
2.06
6.81
3.39
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

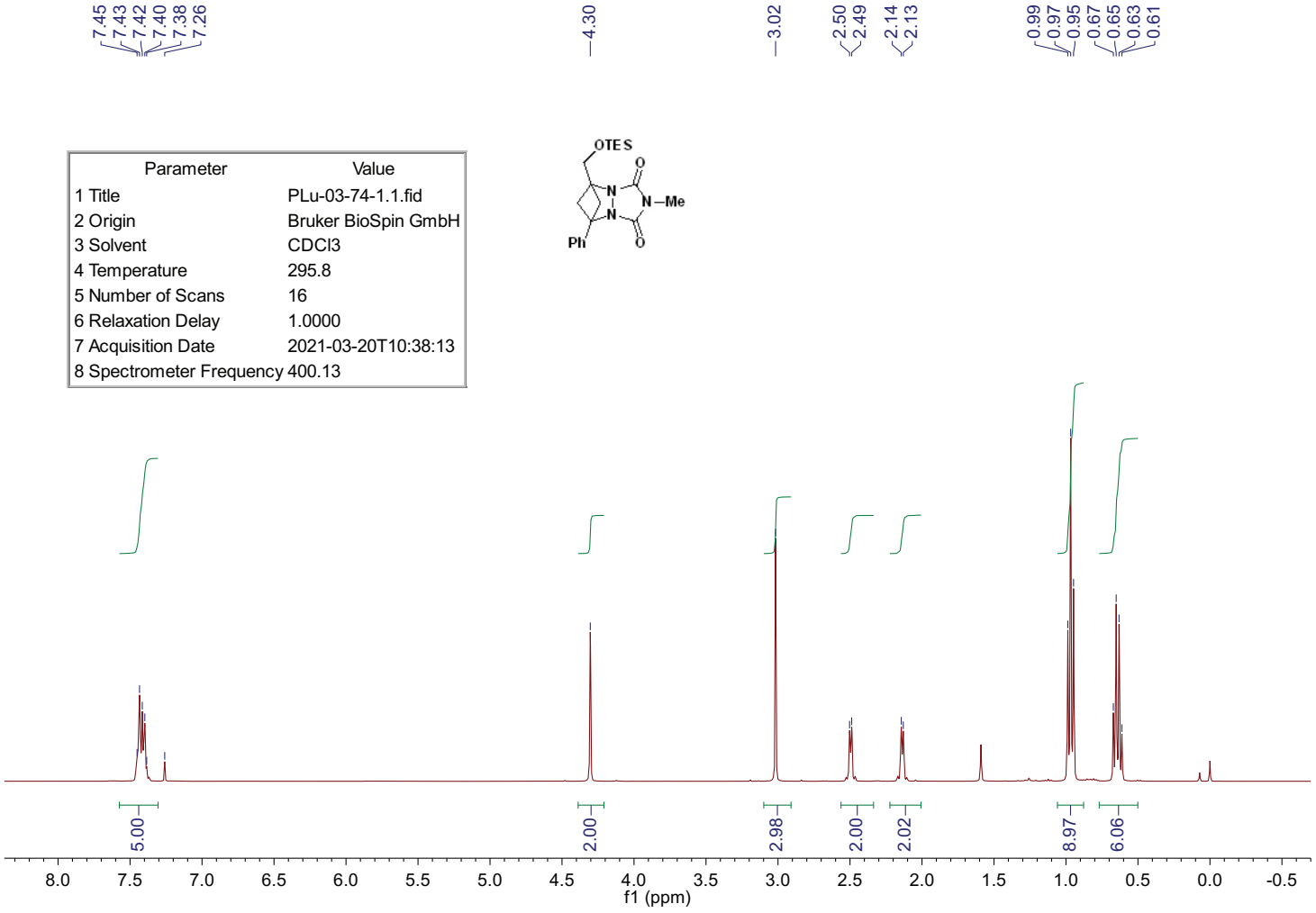

165.67
160.07
159.68
77.32
77.00
76.68
74.36
68.94
52.88
44.82
31.51
29.13
28.68
25.71
24.95
22.46
13.98
Parameter Value
1 Title wm-10-25-ac
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 296.1
5 Number of Scans 300
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-03-10T16:42:15
8 Spectrometer Frequency 100.61
MeOOC
N
N
O
N
Me
O
O
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



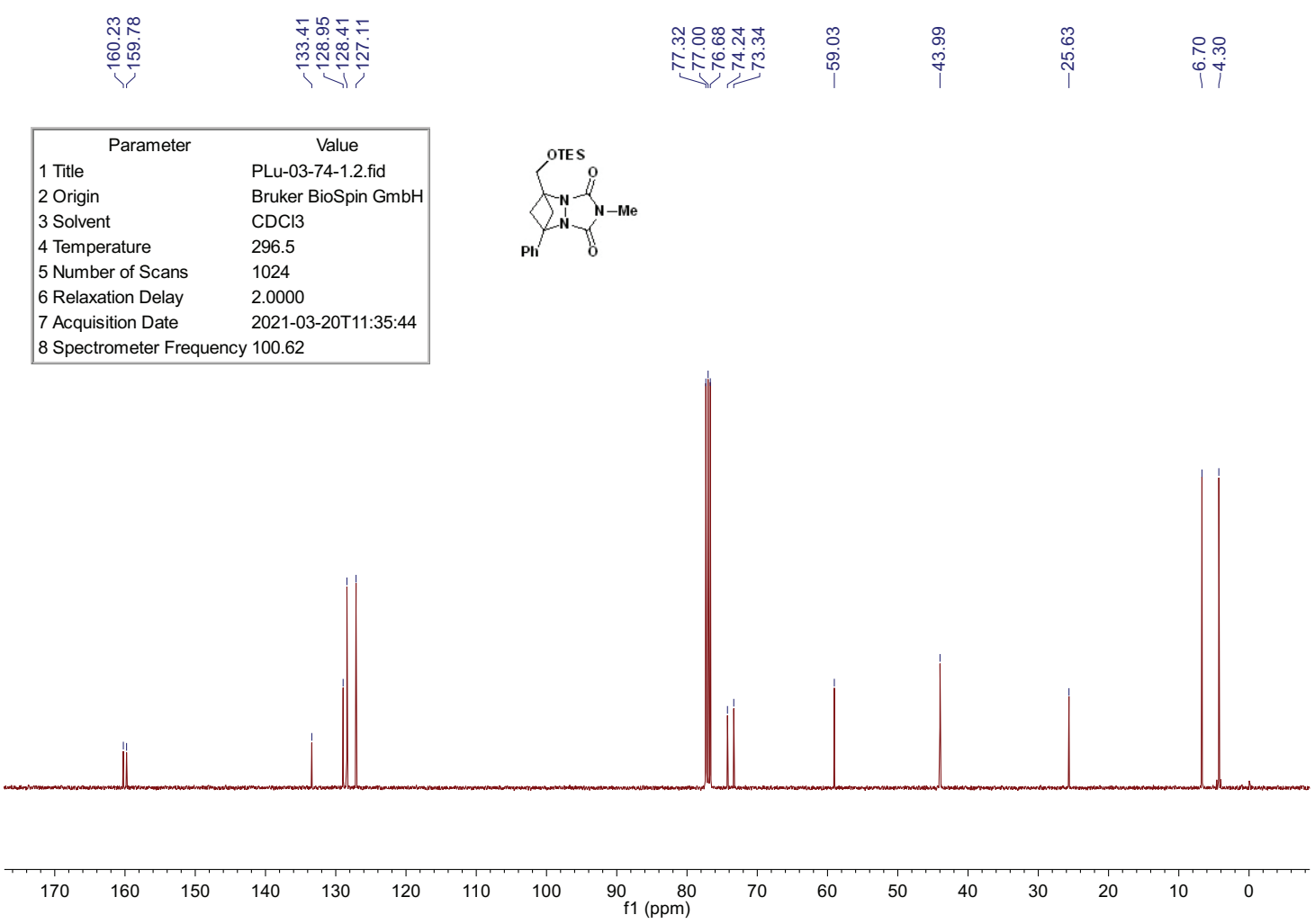
Parameter	Value
1 Title	wm-10-8b-2-h
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.4
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-03-06T13:13:43
8 Spectrometer Frequency	400.13



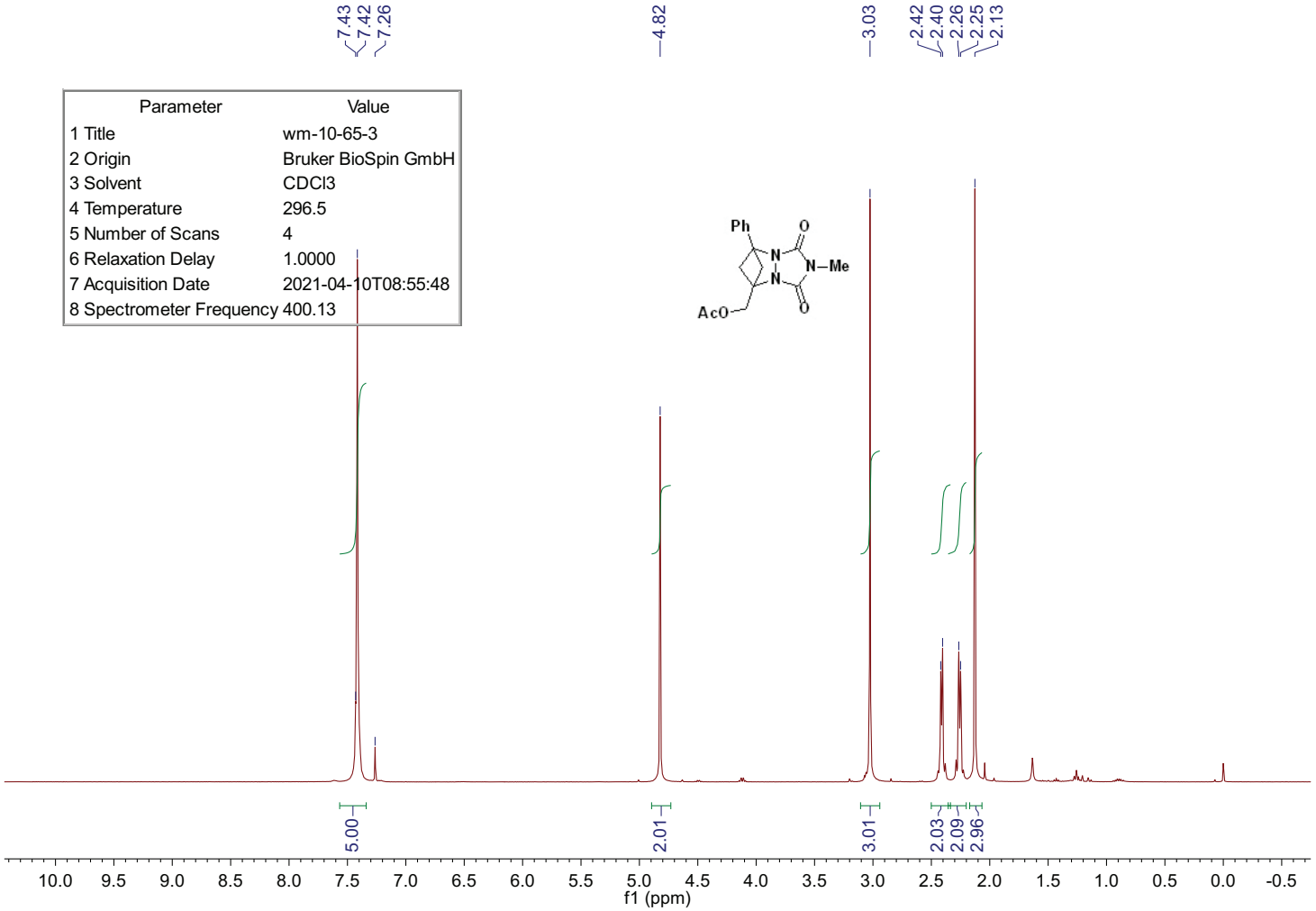
Parameter	Value
1 Title	wm-10-8b-2-c
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.4
5 Number of Scans	3000
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-03-06T15:10:32
8 Spectrometer Frequency	100.61



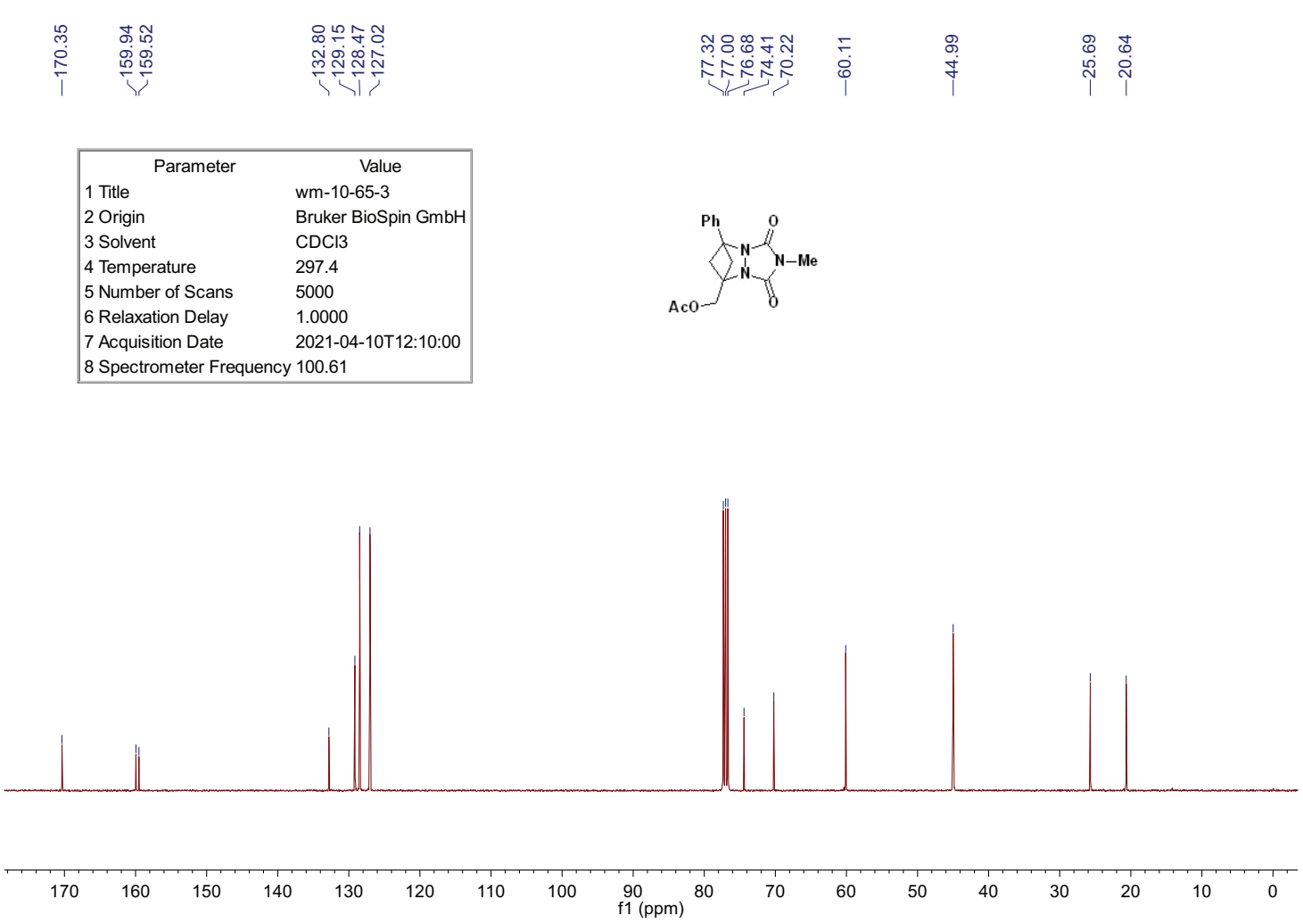
Parameter	Value
1 Title	PLu-03-74-1.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.8
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-03-20T10:38:13
8 Spectrometer Frequency	400.13



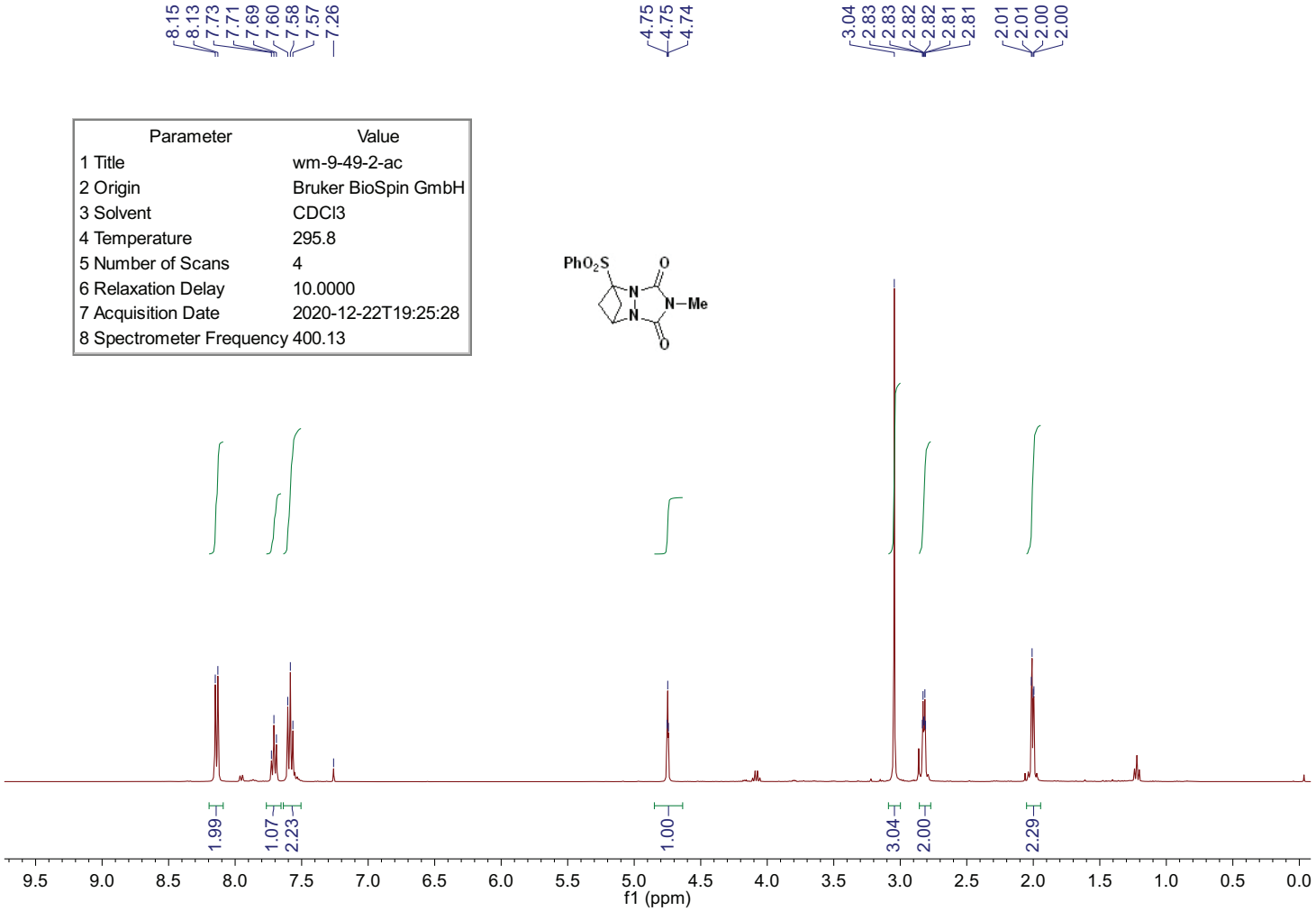
Parameter	Value
1 Title	PLu-03-74-1.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.5
5 Number of Scans	1024
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-03-20T11:35:44
8 Spectrometer Frequency	100.62

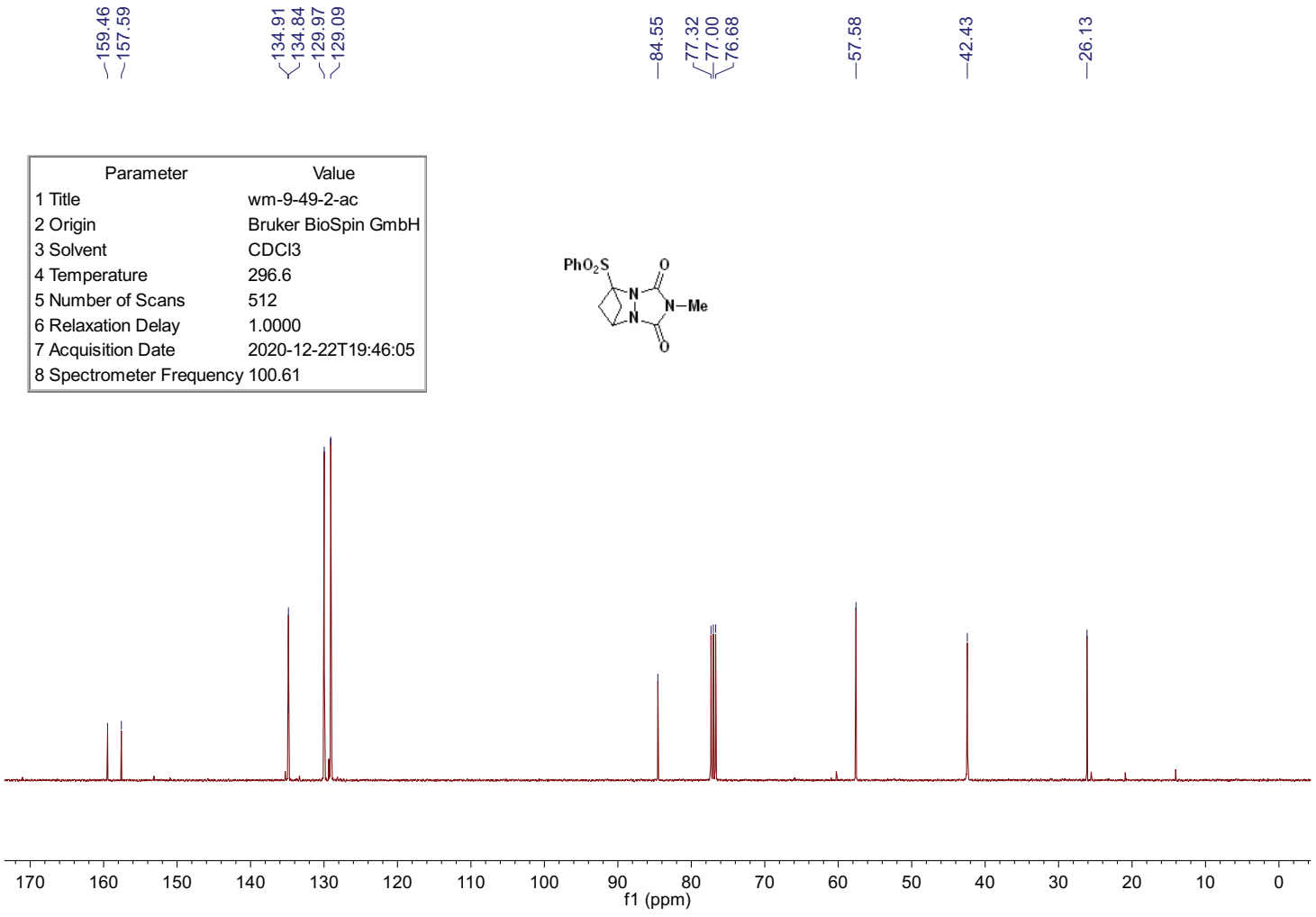


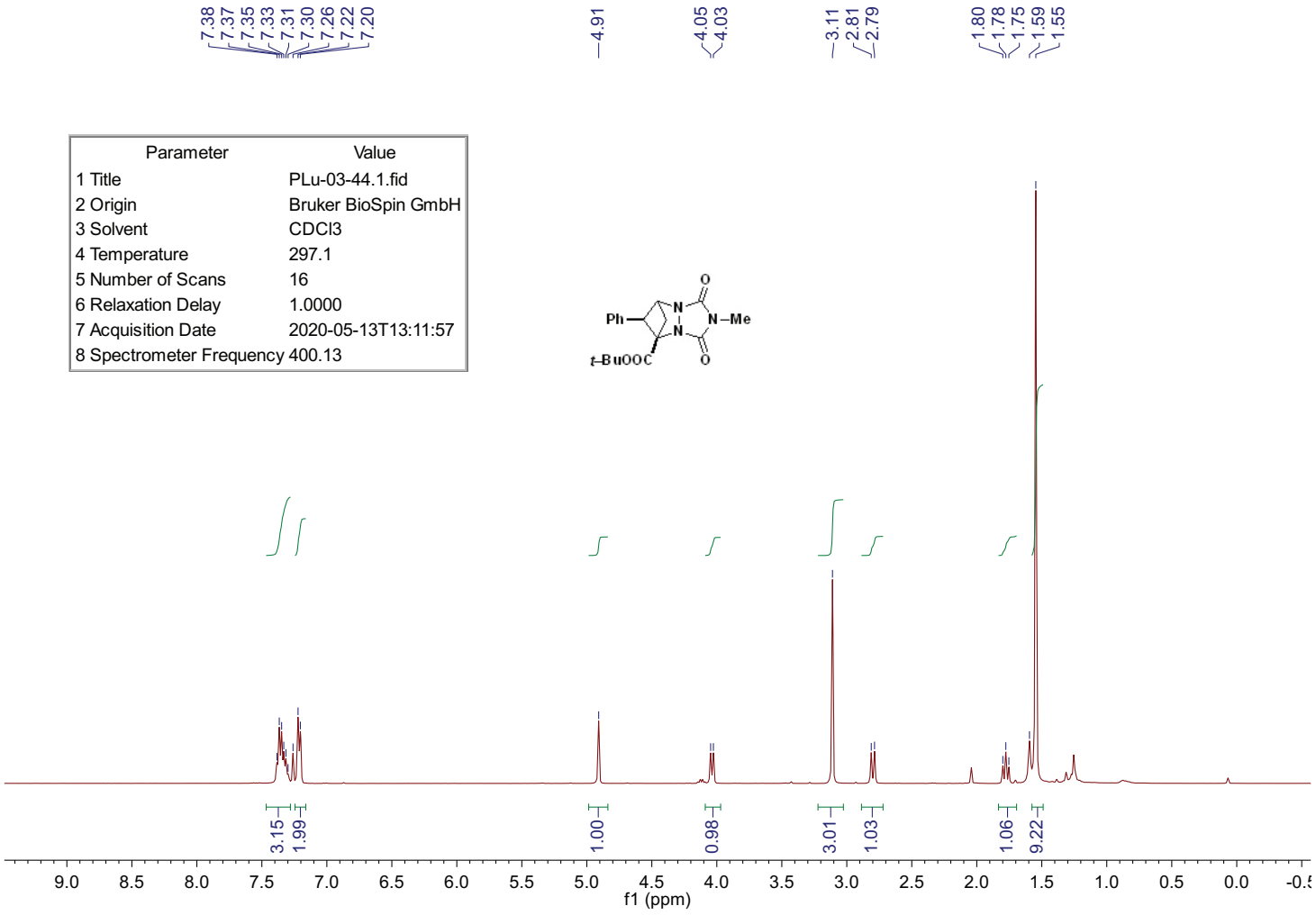
Parameter	Value
1 Title	wm-10-65-3
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.5
5 Number of Scans	4
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-04-10T08:55:48
8 Spectrometer Frequency	400.13

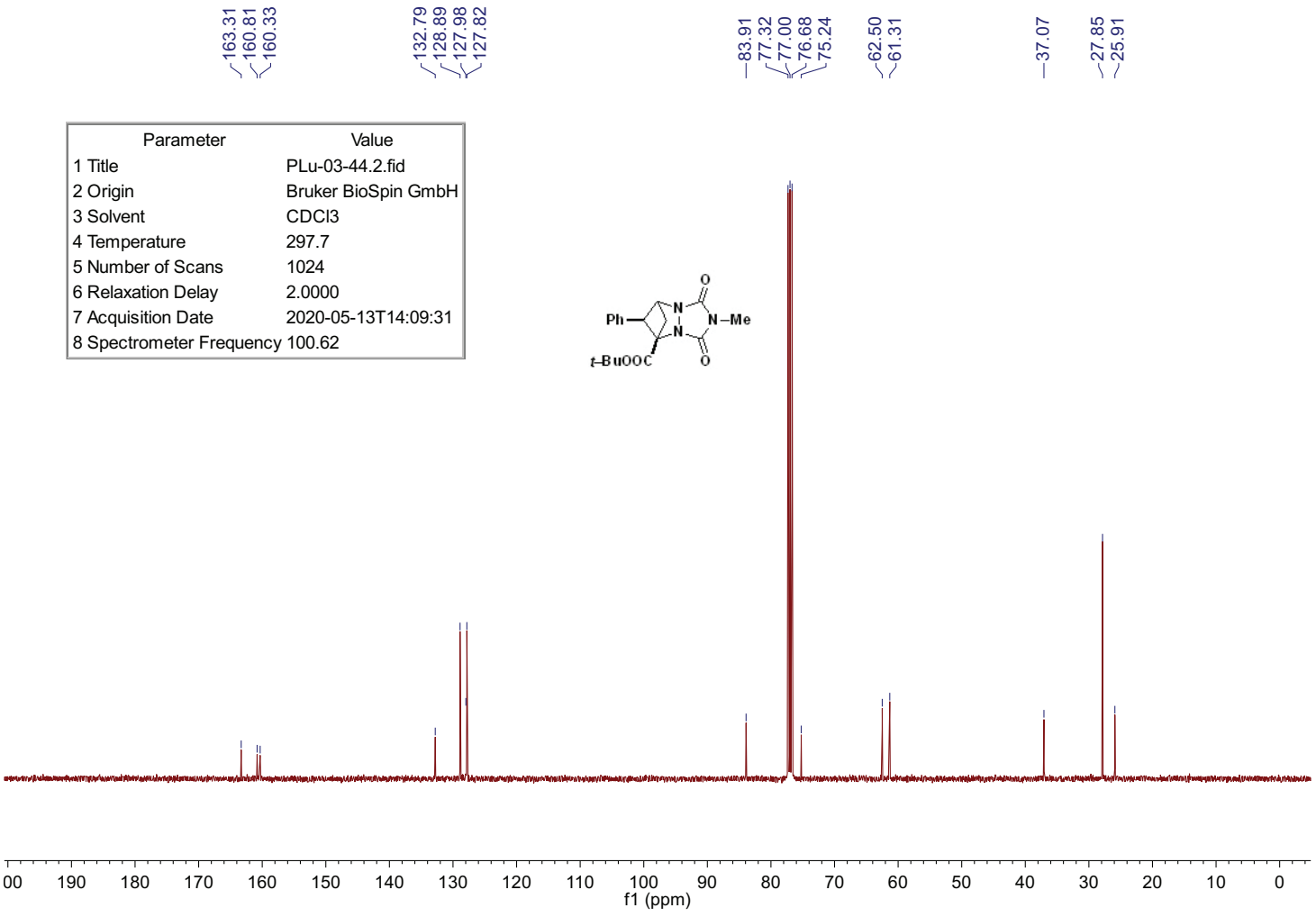


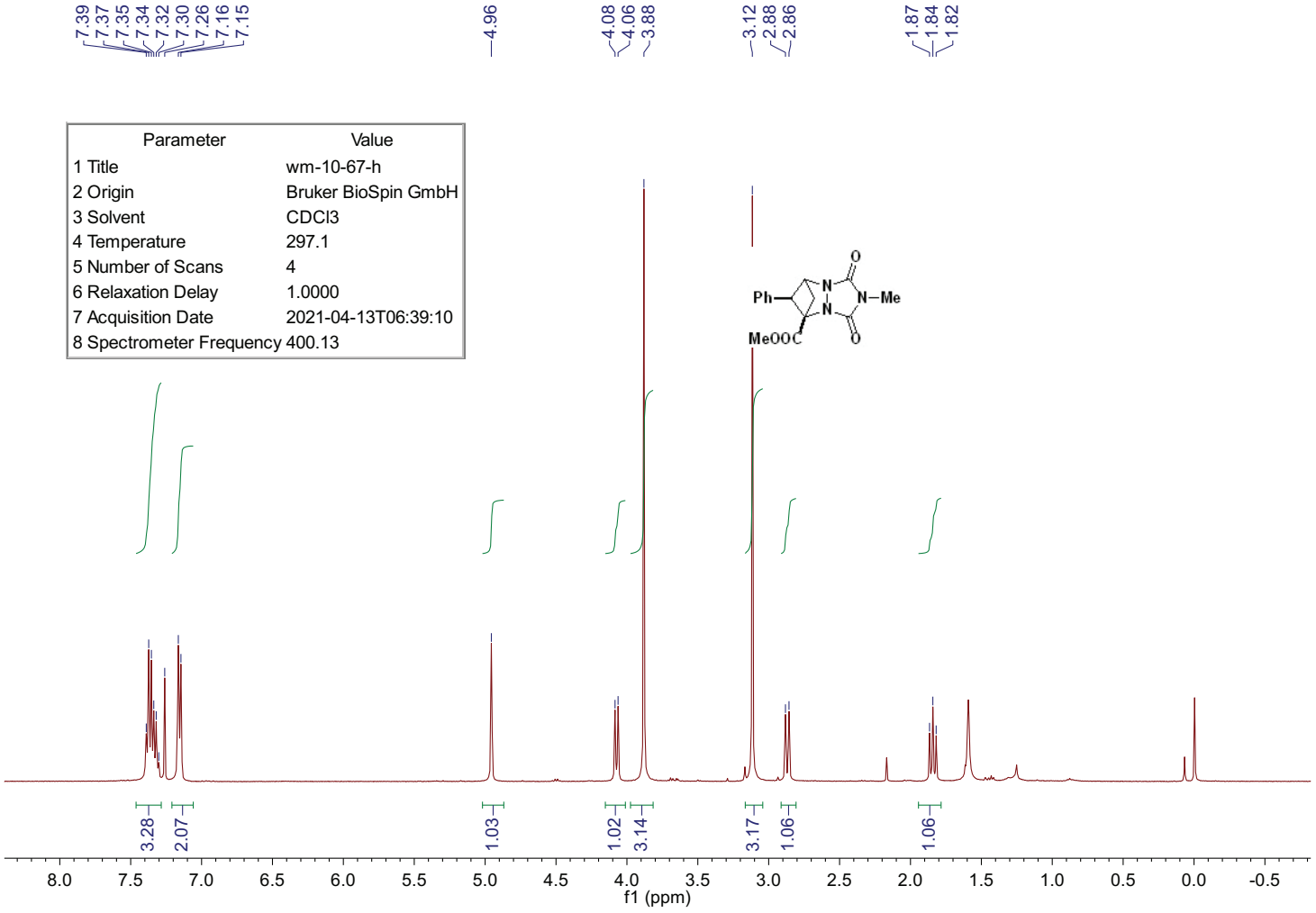
Parameter	Value
1 Title	wm-10-65-3
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.4
5 Number of Scans	5000
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-04-10T12:10:00
8 Spectrometer Frequency	100.61

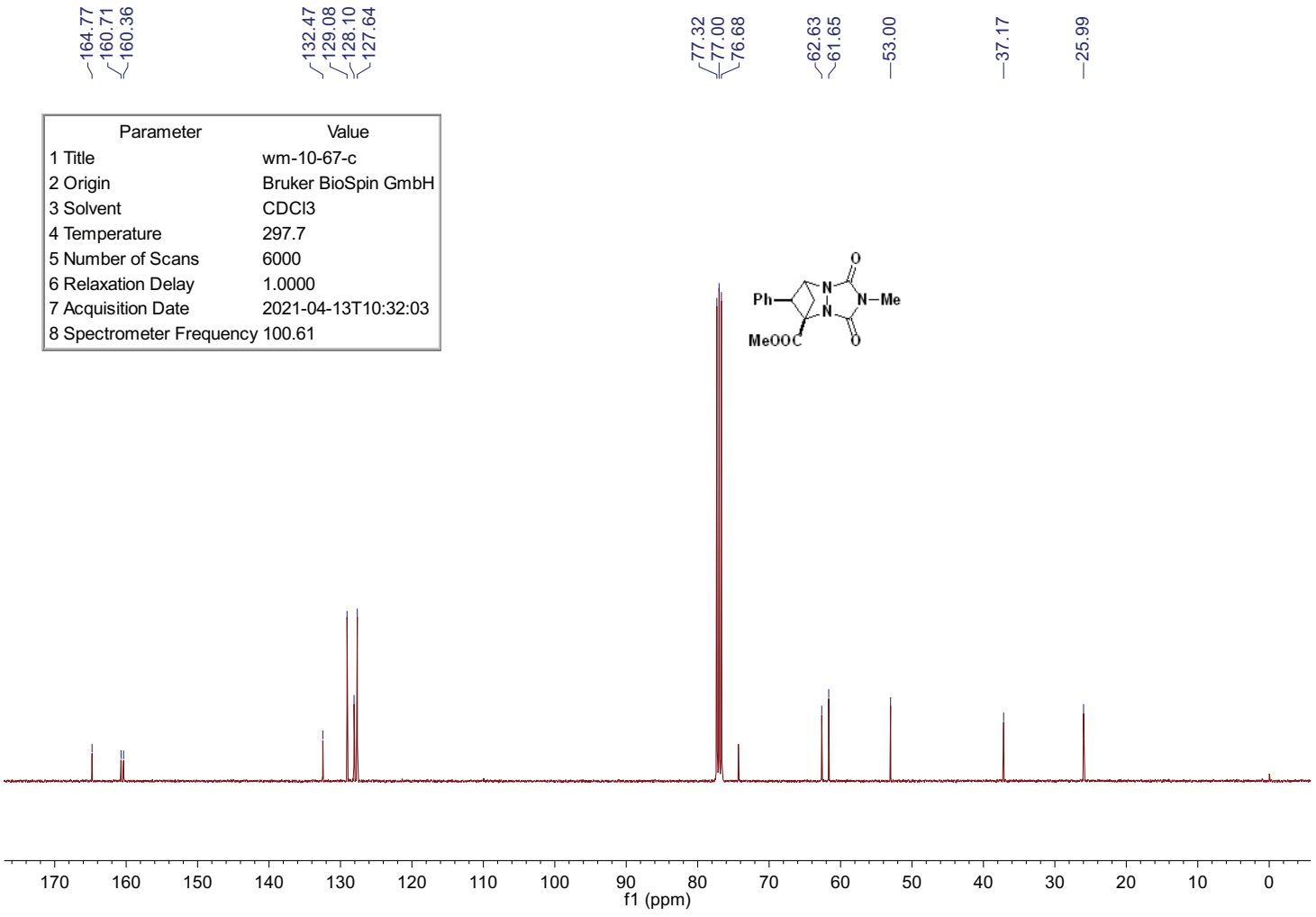

8.15
8.13
7.73
7.71
7.69
7.60
7.58
7.57
7.26
4.75
4.75
4.74
3.04
2.83
2.83
2.82
2.82
2.81
2.81
2.01
2.01
2.00
2.00
Parameter Value
1 Title wm-9-49-2-ac
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 295.8
5 Number of Scans 4
6 Relaxation Delay 10.0000
7 Acquisition Date 2020-12-22T19:25:28
8 Spectrometer Frequency 400.13
PhO2S
N
N
O
N–Me
O
1.99
1.07
2.23
1.00
3.04
2.00
2.29
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

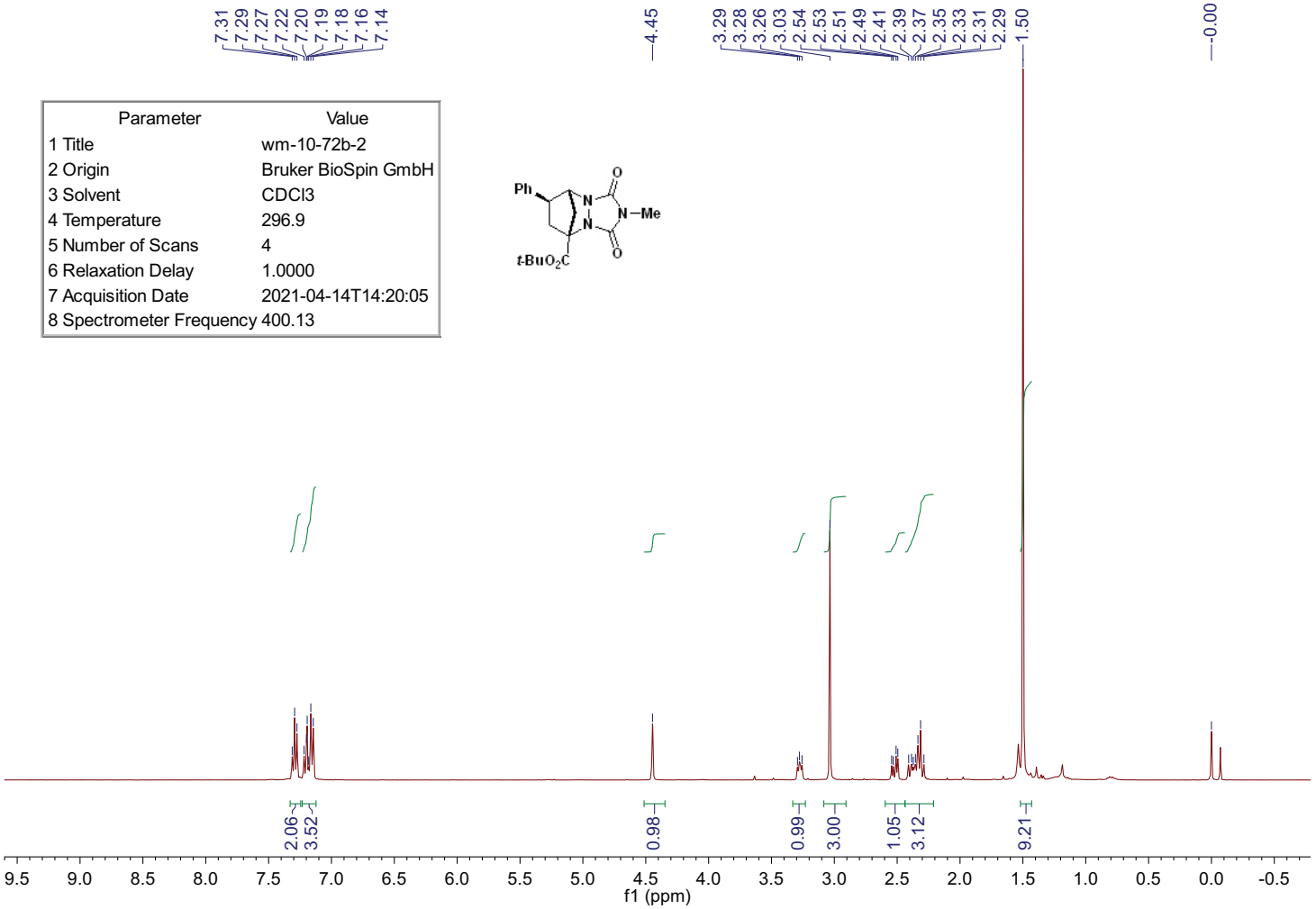

159.46
157.59
134.91
134.84
129.97
129.09
84.55
77.32
77.00
76.68
57.58
42.43
26.13
Parameter Value
1 Title wm-9-49-2-ac
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 296.6
5 Number of Scans 512
6 Relaxation Delay 1.0000
7 Acquisition Date 2020-12-22T19:46:05
8 Spectrometer Frequency 100.61
PhO2S
N
N
O
N–Me
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.38
7.37
7.35
7.33
7.31
7.30
7.26
7.22
7.20
4.91
4.05
4.03
3.11
2.81
2.79
1.80
1.78
1.75
1.59
1.55
Parameter Value
1 Title PLu-03-44.1.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 297.1
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2020-05-13T13:11:57
8 Spectrometer Frequency 400.13
Ph
N
N–Me
t-BuOOC
O
3.15
1.99
1.00
0.98
3.01
1.03
1.06
9.22
f1 (ppm)

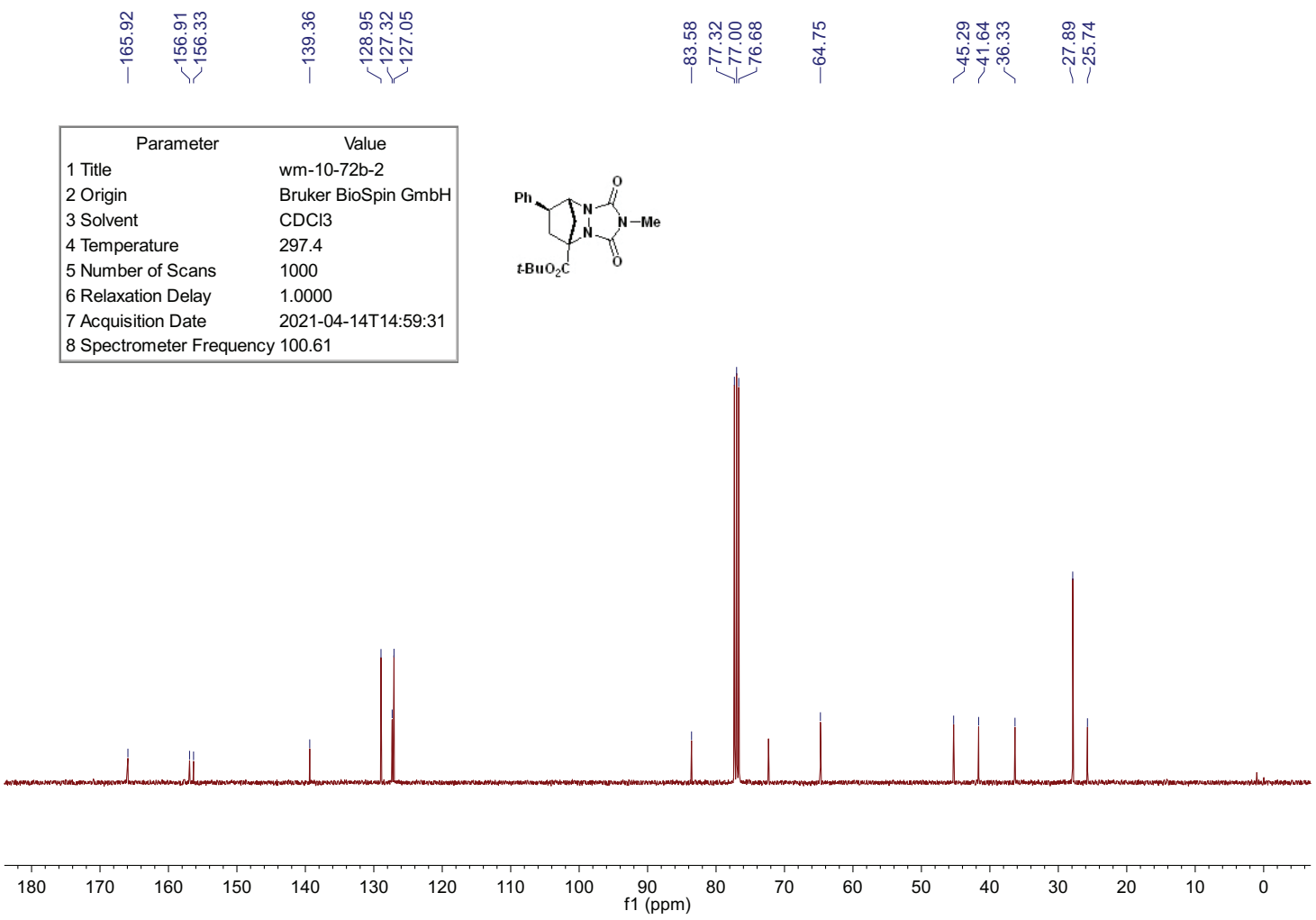

163.31
160.81
160.33
132.79
128.89
127.98
127.82
83.91
77.32
77.00
76.68
75.24
62.50
61.31
37.07
27.85
25.91
Parameter Value
1 Title PLu-03-44.2.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 297.7
5 Number of Scans 1024
6 Relaxation Delay 2.0000
7 Acquisition Date 2020-05-13T14:09:31
8 Spectrometer Frequency 100.62
Ph
N
N–Me
t-BuOOC
O
f1 (ppm)


7.39
7.37
7.35
7.34
7.32
7.30
7.26
7.16
7.15
4.96
4.08
4.06
3.88
3.12
2.88
2.86
1.87
1.84
1.82
Parameter Value
1 Title wm-10-67-h
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 297.1
5 Number of Scans 4
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-04-13T06:39:10
8 Spectrometer Frequency 400.13
Ph
N
N
N–Me
O
O
O
MeOOC
3.28
2.07
1.03
1.02
3.14
3.17
1.06
1.06
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

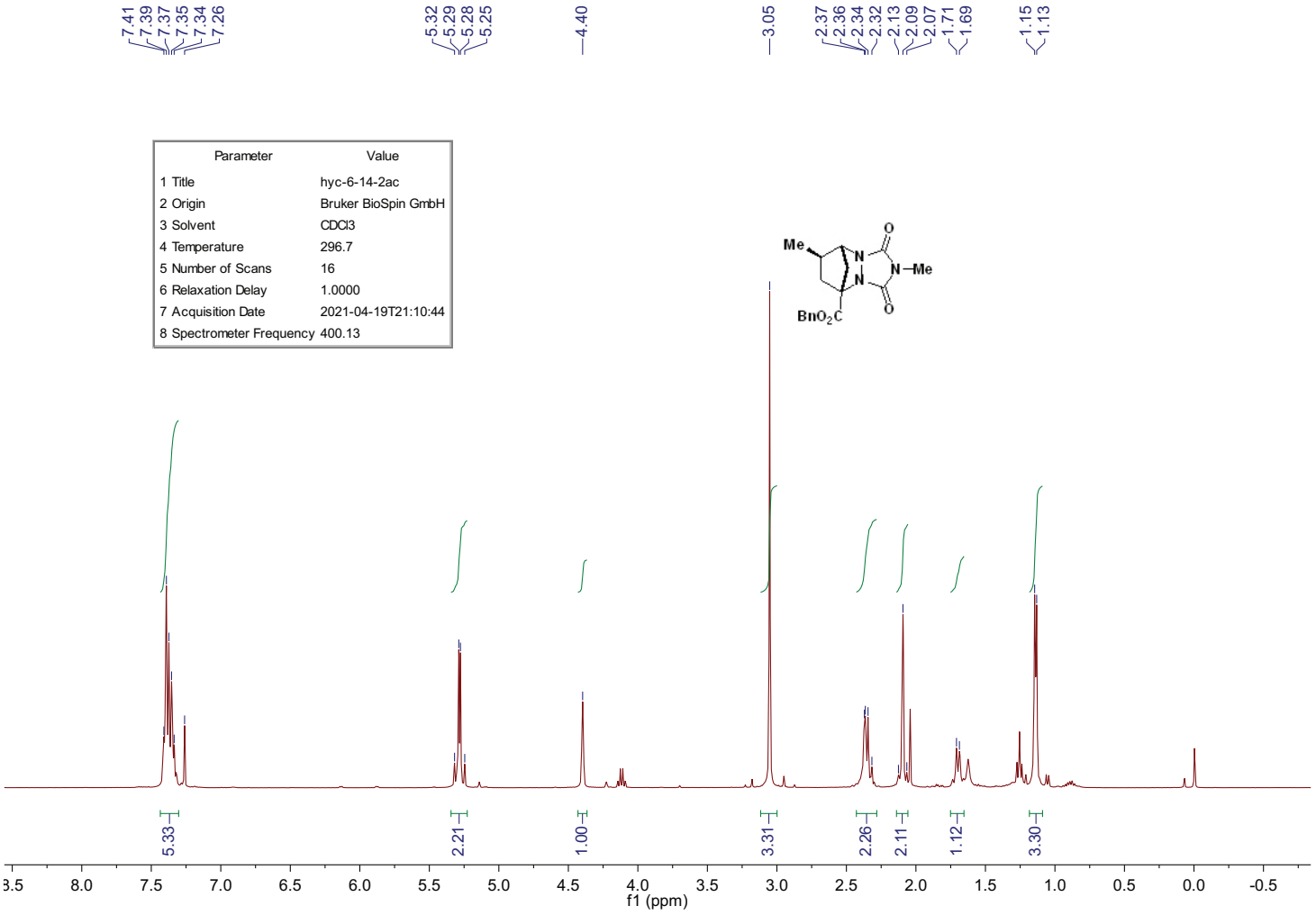

164.77
160.71
160.36
132.47
129.08
128.10
127.64
77.32
77.00
76.68
62.63
61.65
53.00
37.17
25.99
Parameter Value
1 Title wm-10-67-c
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 297.7
5 Number of Scans 6000
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-04-13T10:32:03
8 Spectrometer Frequency 100.61
Ph
N
N
N–Me
O
O
O
MeOOC
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

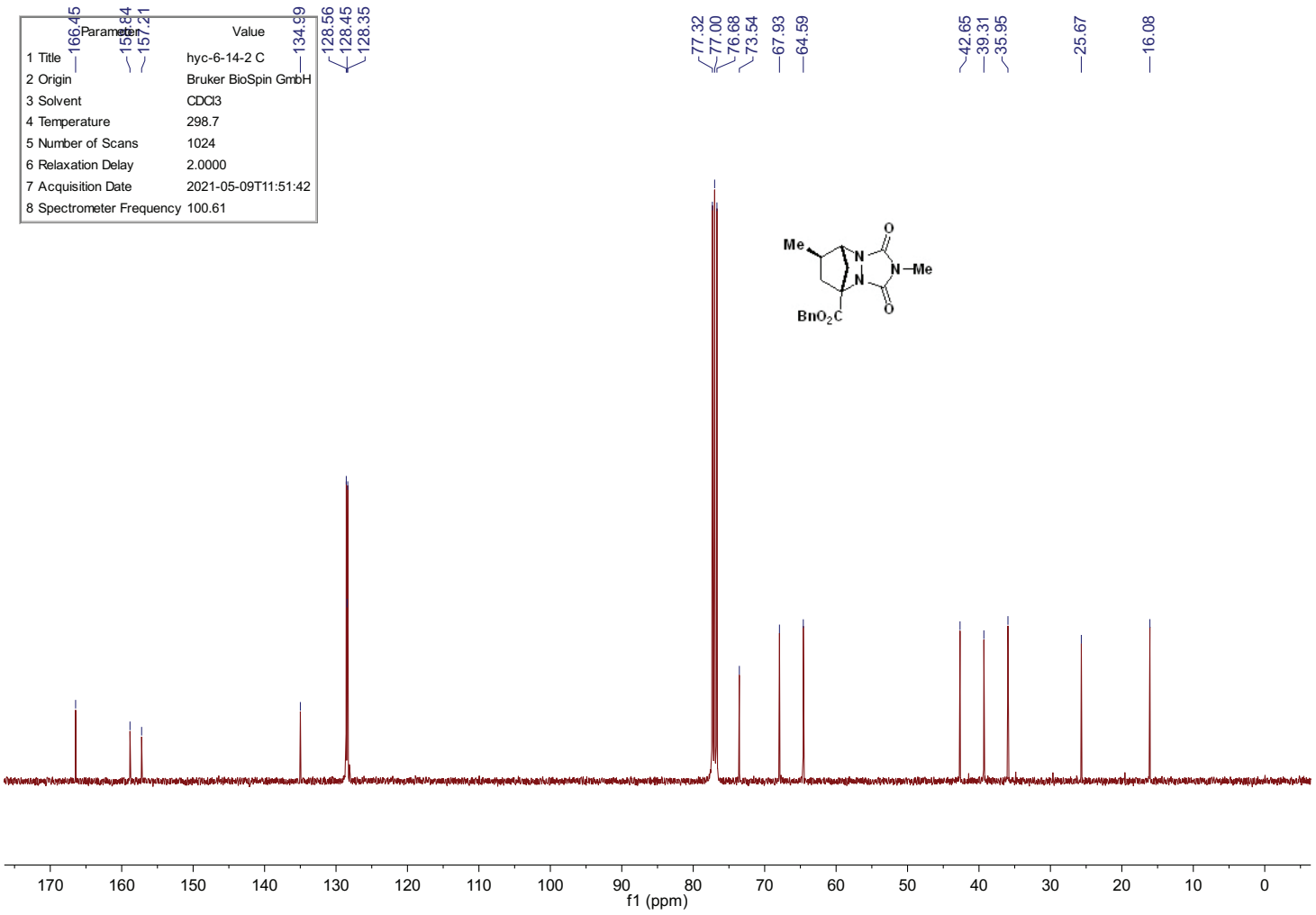


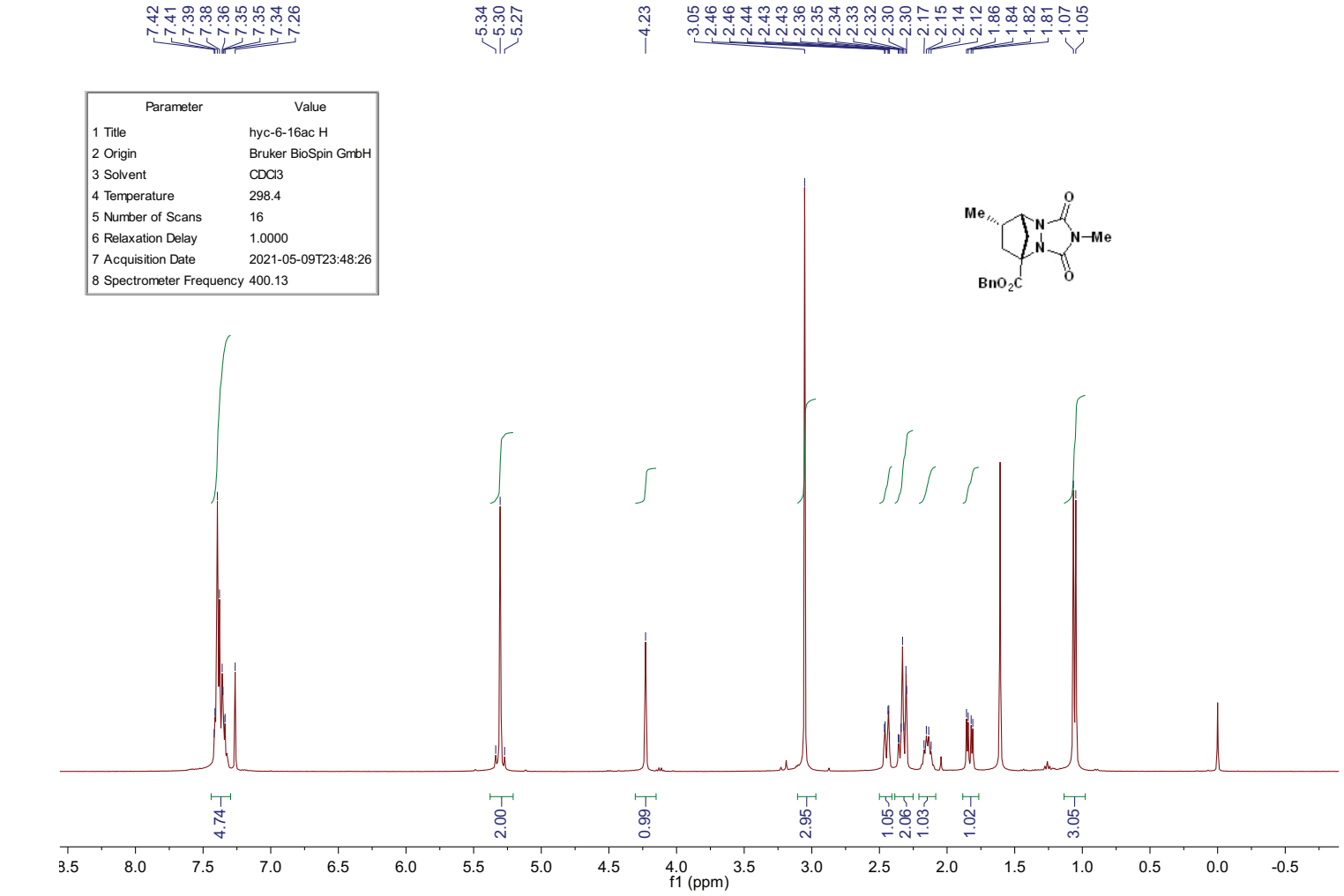
Parameter	Value
1 Title	wm-10-72b-2
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.9
5 Number of Scans	4
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-04-14T14:20:05
8 Spectrometer Frequency	400.13

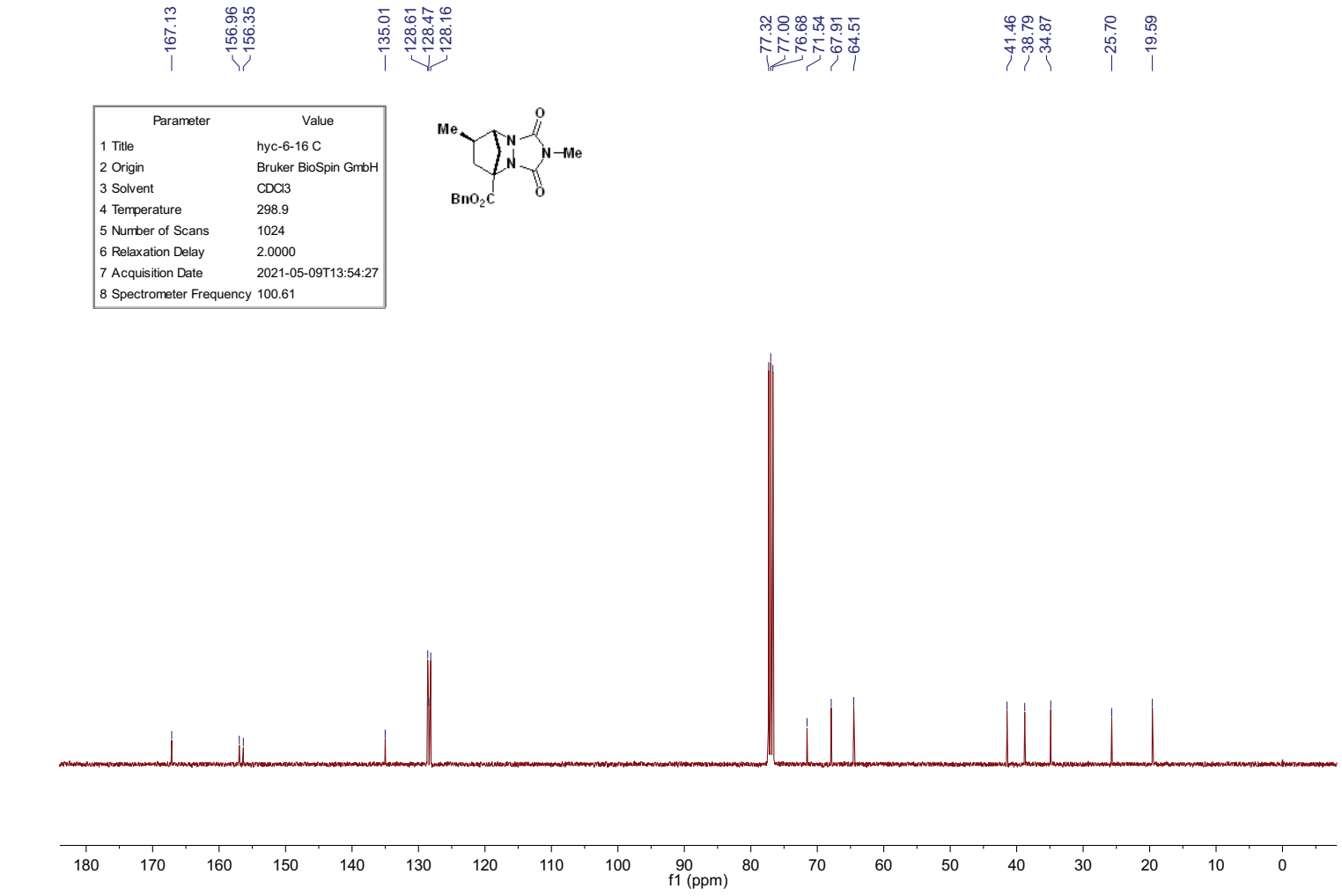


Parameter	Value
1 Title	wm-10-72b-2
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.4
5 Number of Scans	1000
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-04-14T14:59:31
8 Spectrometer Frequency	100.61

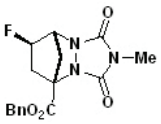

7.41
7.39
7.37
7.35
7.34
7.26
5.32
5.29
5.28
5.25
4.40
3.05
2.37
2.36
2.34
2.32
2.13
2.09
2.07
1.71
1.69
1.15
1.13
Parameter Value
1 Title hyc-6-14-2ac
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 296.7
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-04-19T21:10:44
8 Spectrometer Frequency 400.13
Me
N
N
O
N–Me
O
BnO2C
5.33
2.21
1.00
3.31
2.26
2.11
1.12
3.30
f1 (ppm)

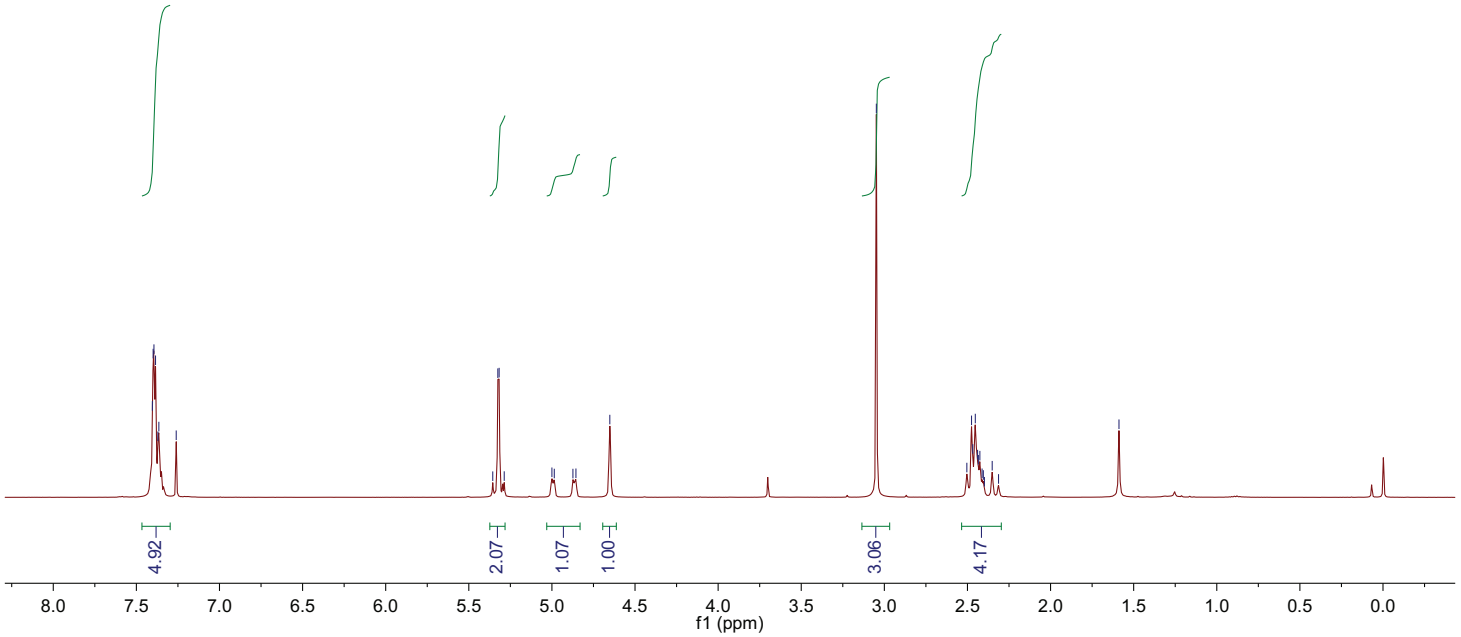

166.45
158.84
157.21
134.99
128.56
128.45
128.35
77.32
77.00
76.68
73.54
67.93
64.59
42.65
39.31
35.95
25.67
16.08
Parameter Value
1 Title hyc-6-14-2 C
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.7
5 Number of Scans 1024
6 Relaxation Delay 2.0000
7 Acquisition Date 2021-05-09T11:51:42
8 Spectrometer Frequency 100.61
Me
N
N
O
N–Me
O
BnO2C
f1 (ppm)


7.42
7.41
7.39
7.38
7.36
7.35
7.35
7.34
7.26
5.34
5.30
5.27
4.23
3.05
2.46
2.46
2.44
2.43
2.43
2.36
2.35
2.34
2.33
2.32
2.30
2.30
2.17
2.15
2.14
2.12
1.86
1.84
1.82
1.81
1.07
1.05
Parameter Value
1 Title hyc-6-16ac H
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.4
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-05-09T23:48:26
8 Spectrometer Frequency 400.13
Me
N
N
O
N–Me
O
BnO2C
4.74
2.00
0.99
2.95
1.05
2.06
1.03
1.02
3.05
f1 (ppm)

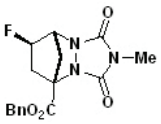

167.13
156.96
156.35
135.01
128.61
128.47
128.16
77.32
77.00
76.68
71.54
67.91
64.51
41.46
38.79
34.87
25.70
19.59
Parameter Value
1 Title hyc-6-16 C
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.9
5 Number of Scans 1024
6 Relaxation Delay 2.0000
7 Acquisition Date 2021-05-09T13:54:27
8 Spectrometer Frequency 100.61
Me
N
N
O
N–Me
O
BnO2C
f1 (ppm)

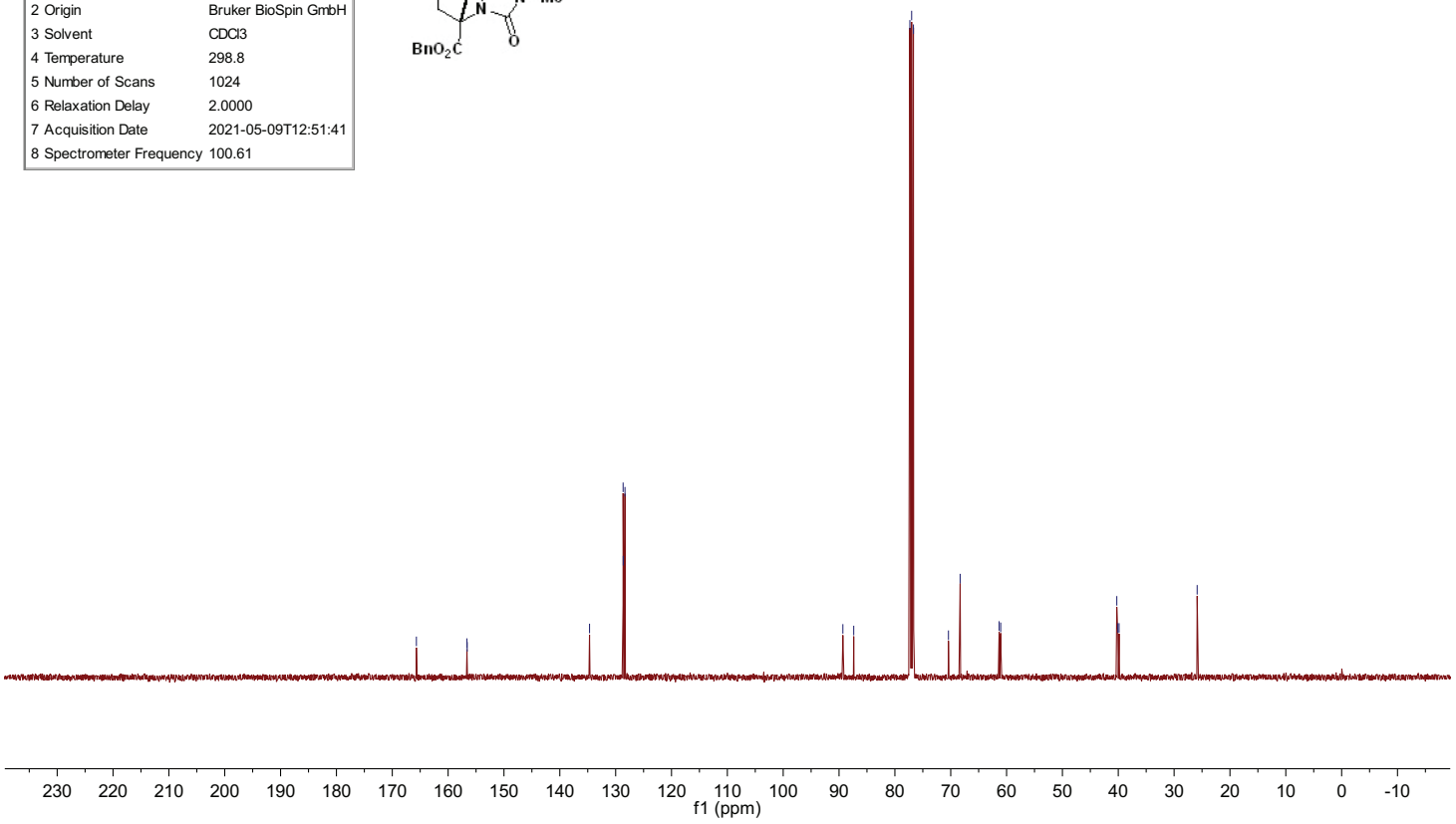
Parameter	Value
1 Title	hyc-6-9-2ac
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.9
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-04-19T20:53:14
8 Spectrometer Frequency	400.13



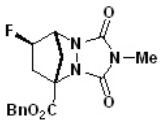


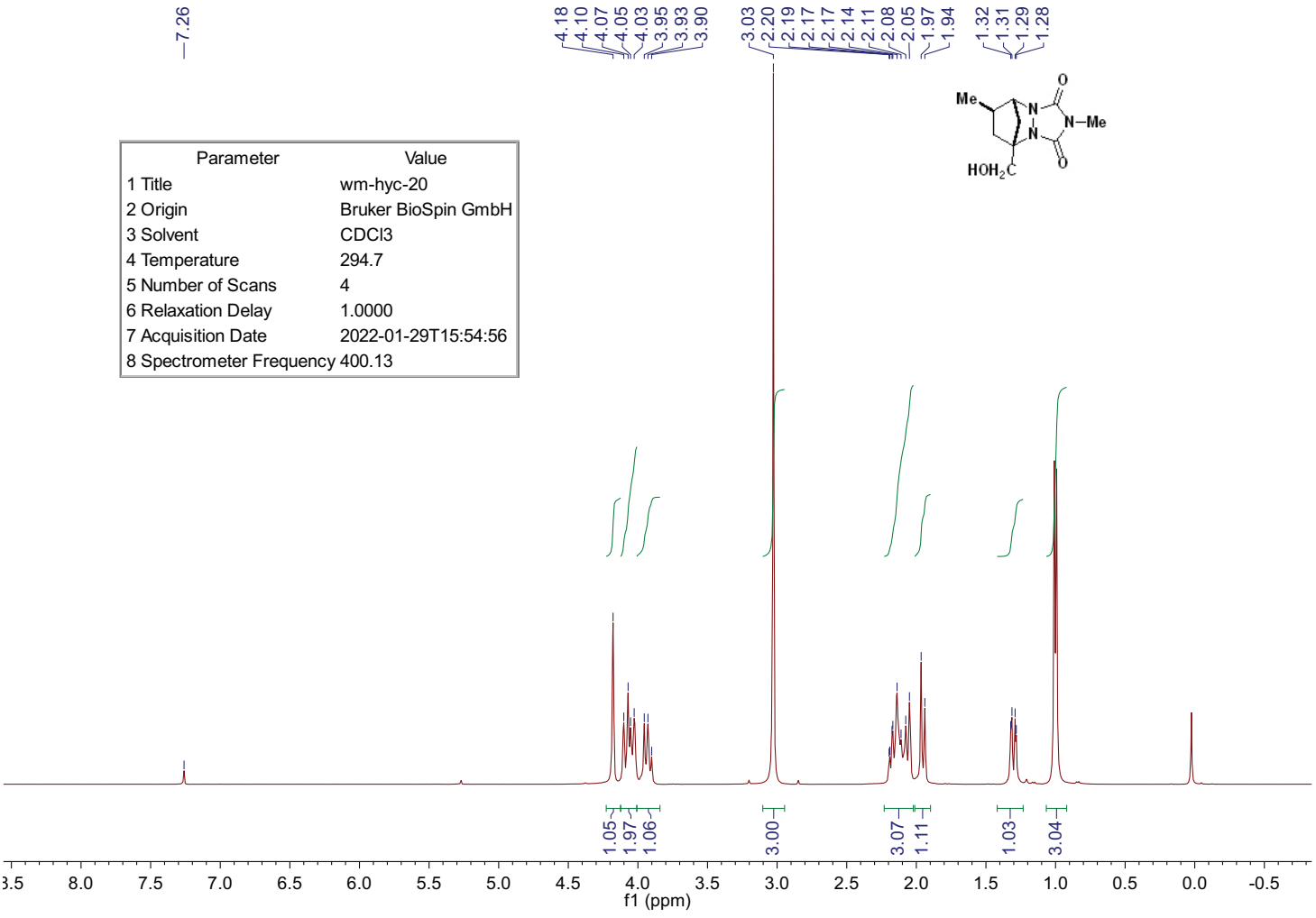
Parameter	Value
1 Title	hyc-6-9-2 C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.8
5 Number of Scans	1024
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-05-09T12:51:41
8 Spectrometer Frequency	100.61



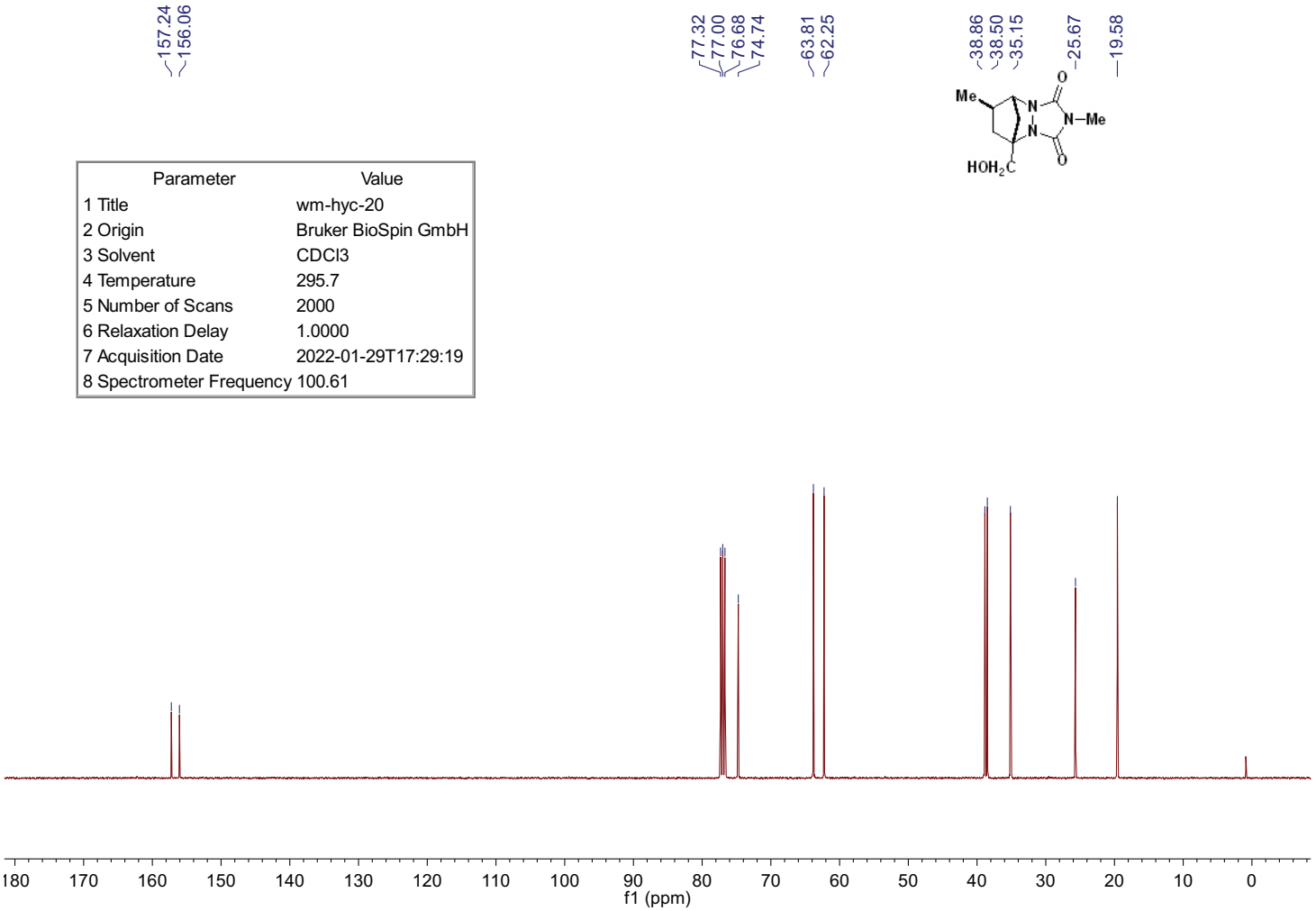


Parameter	Value
1 Title	hyc-6-9-2 F
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.4
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-05-09T12:54:06
8 Spectrometer Frequency	376.50

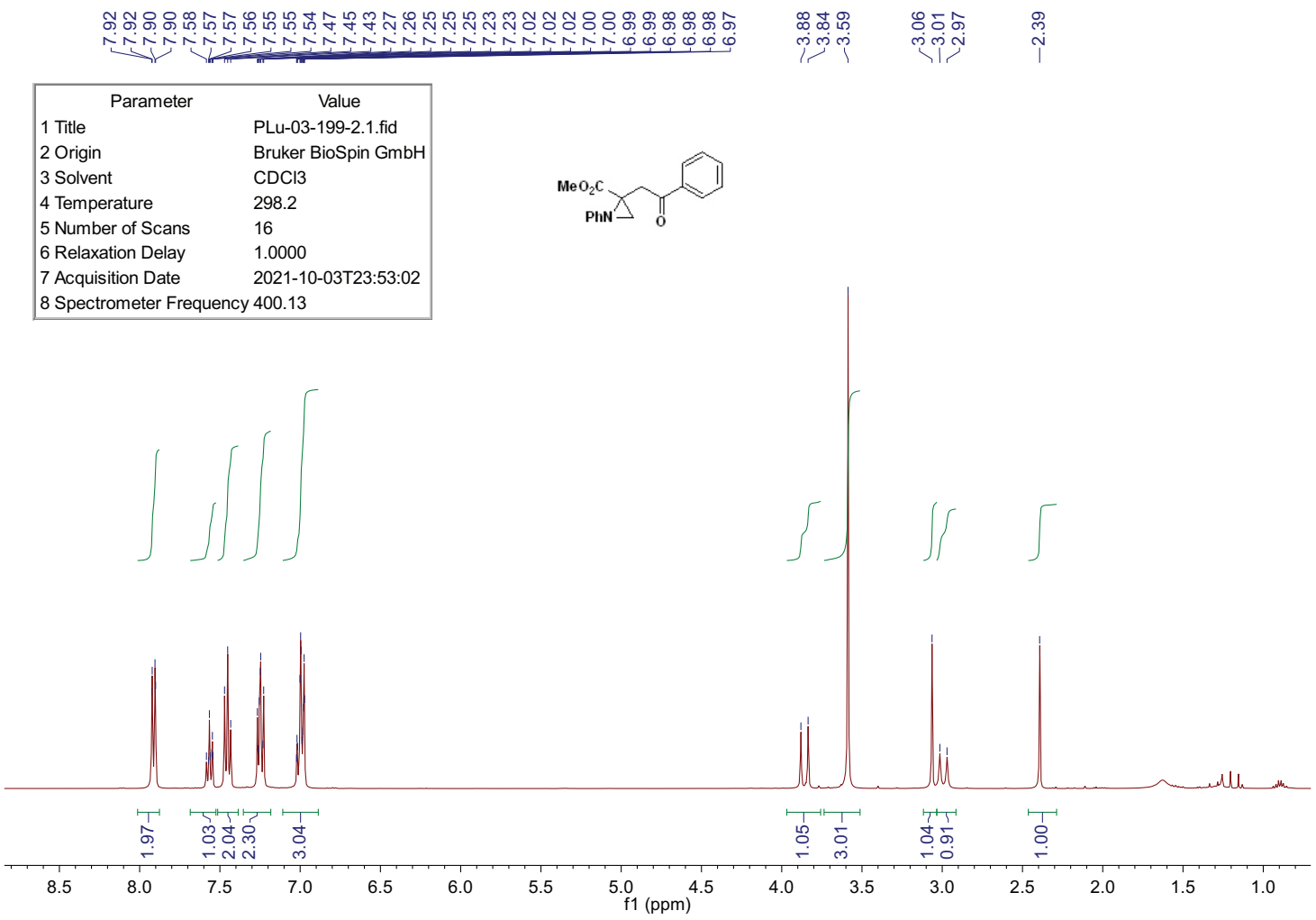




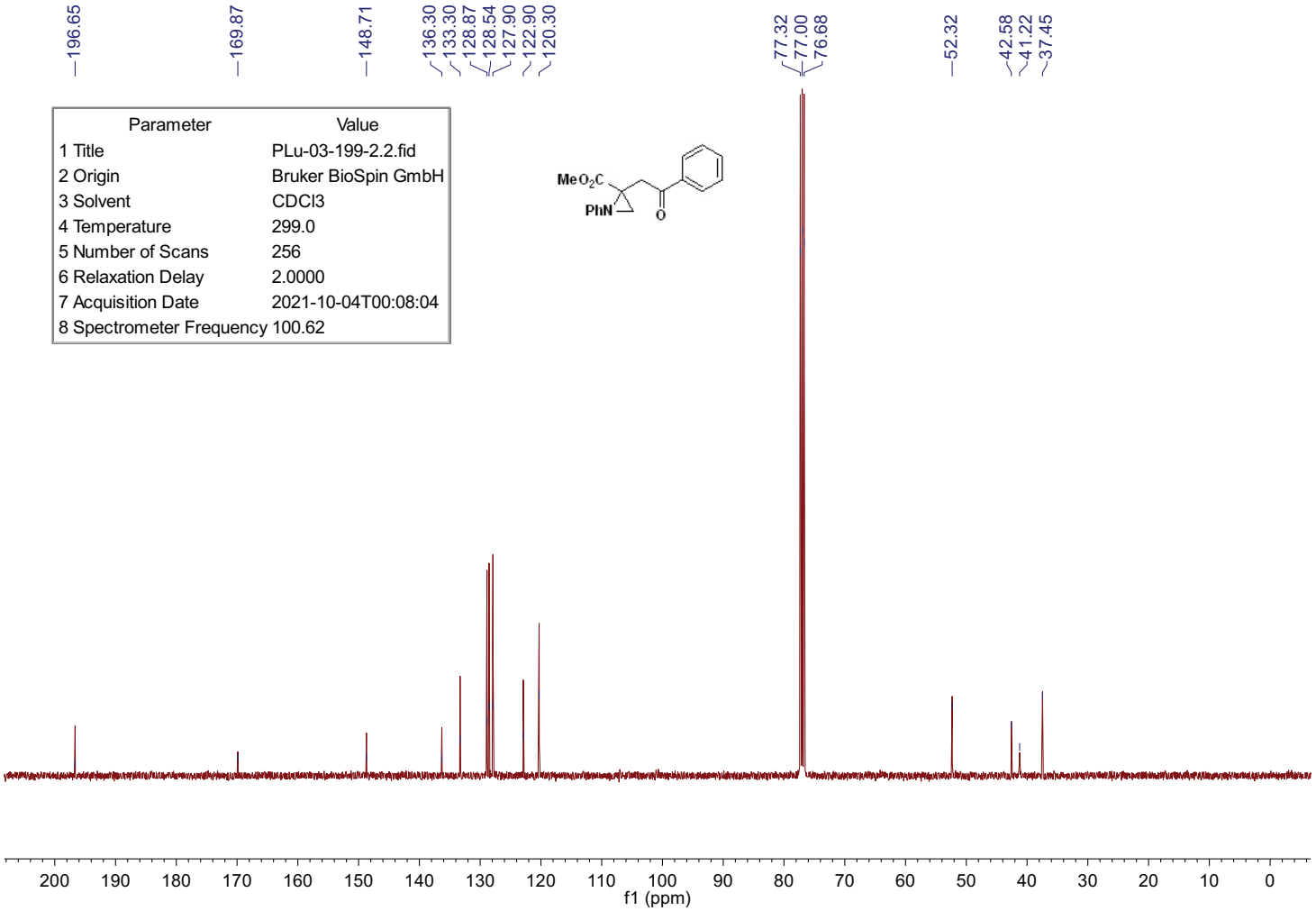
Parameter	Value
1 Title	wm-hyc-20
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	294.7
5 Number of Scans	4
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-01-29T15:54:56
8 Spectrometer Frequency	400.13

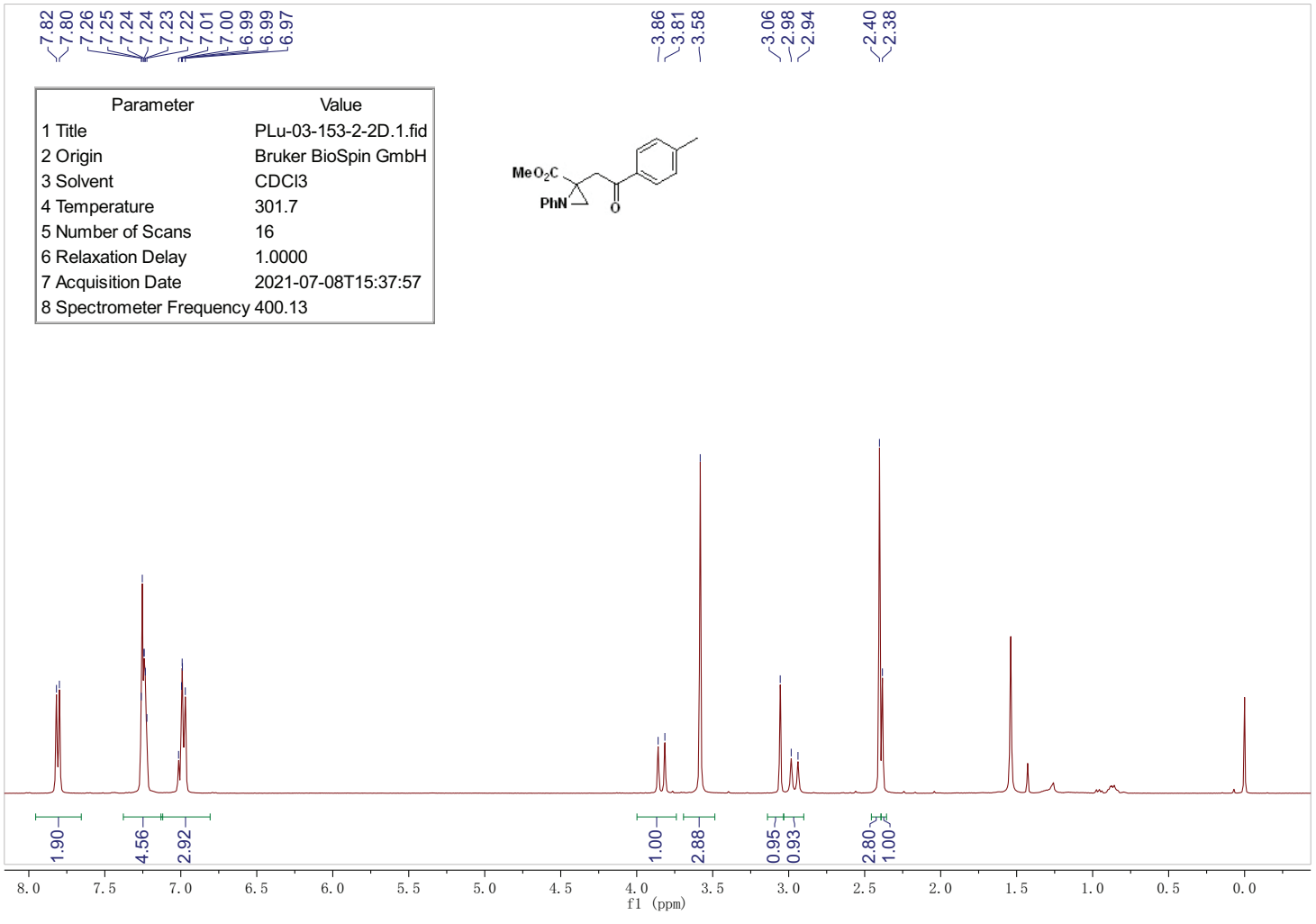


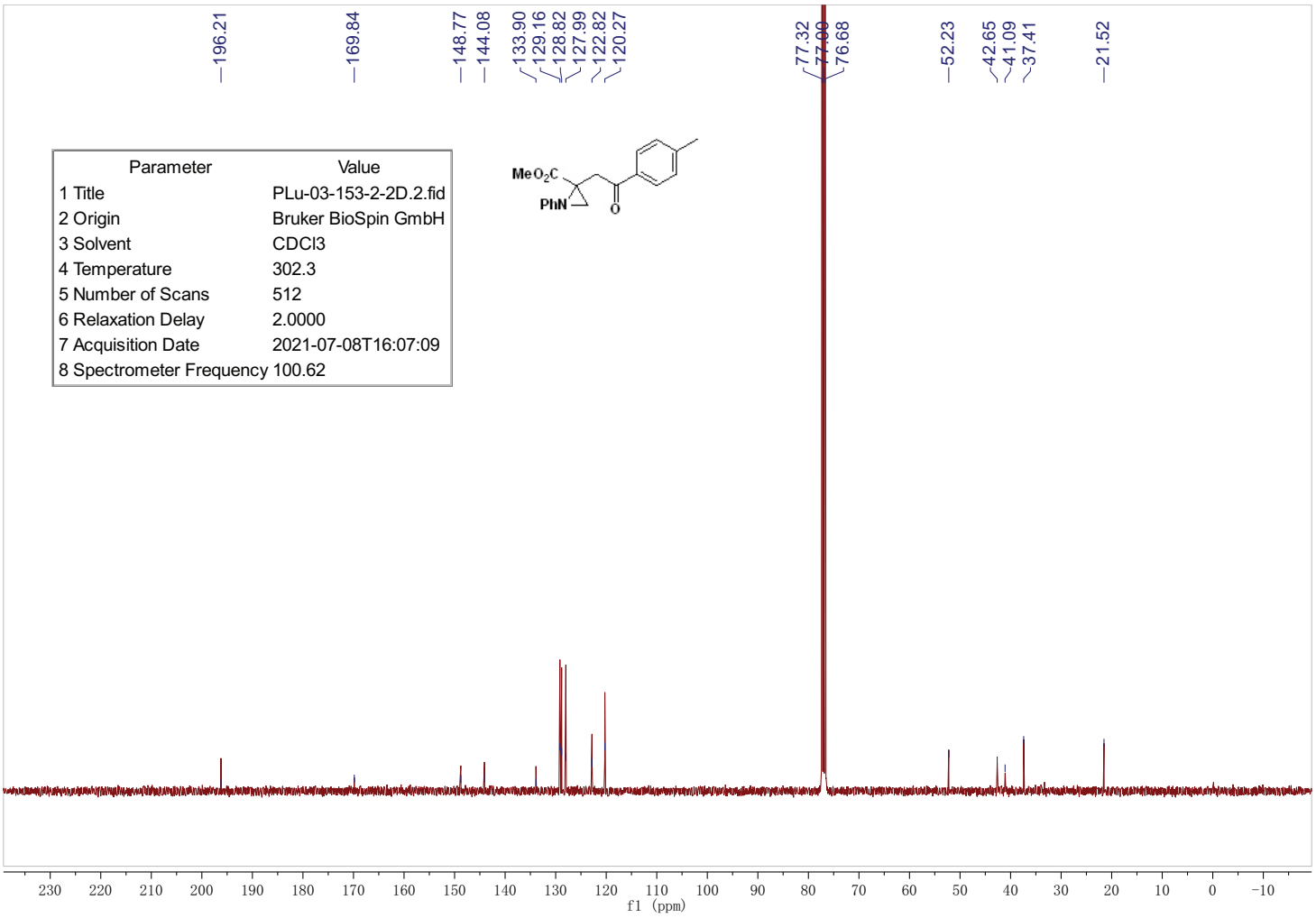
Parameter	Value
1 Title	wm-hyc-20
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.7
5 Number of Scans	2000
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-01-29T17:29:19
8 Spectrometer Frequency	100.61



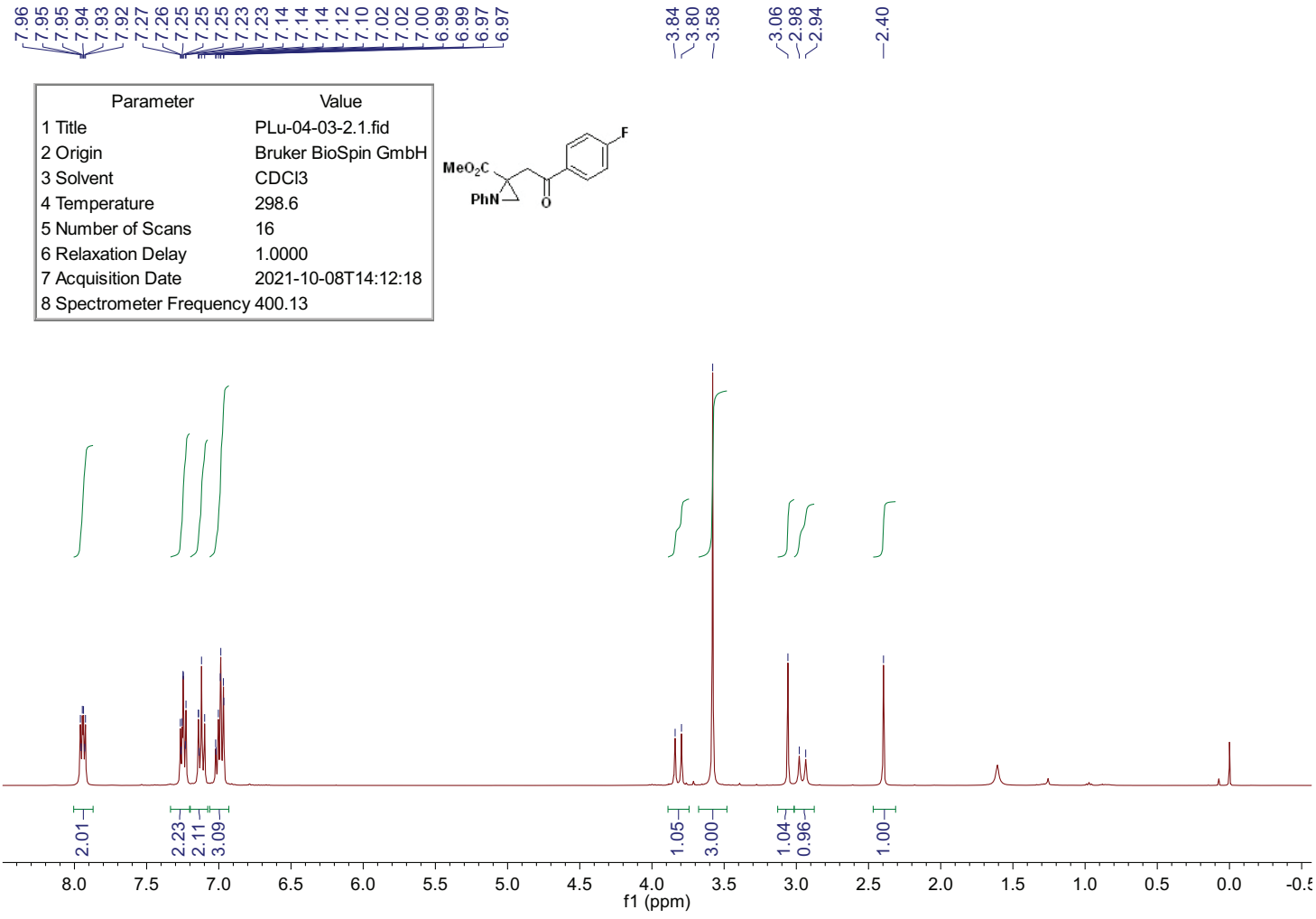
Parameter	Value
1 Title	PLu-03-199-2.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.2
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-10-03T23:53:02
8 Spectrometer Frequency	400.13


196.65
169.87
148.71
136.30
133.30
128.87
128.54
127.90
122.90
120.30
77.32
77.00
76.68
52.32
42.58
41.22
37.45
Parameter Value
1 Title PLu-03-199-2.2.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 299.0
5 Number of Scans 256
6 Relaxation Delay 2.0000
7 Acquisition Date 2021-10-04T00:08:04
8 Spectrometer Frequency 100.62
MeO2C
PhN
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

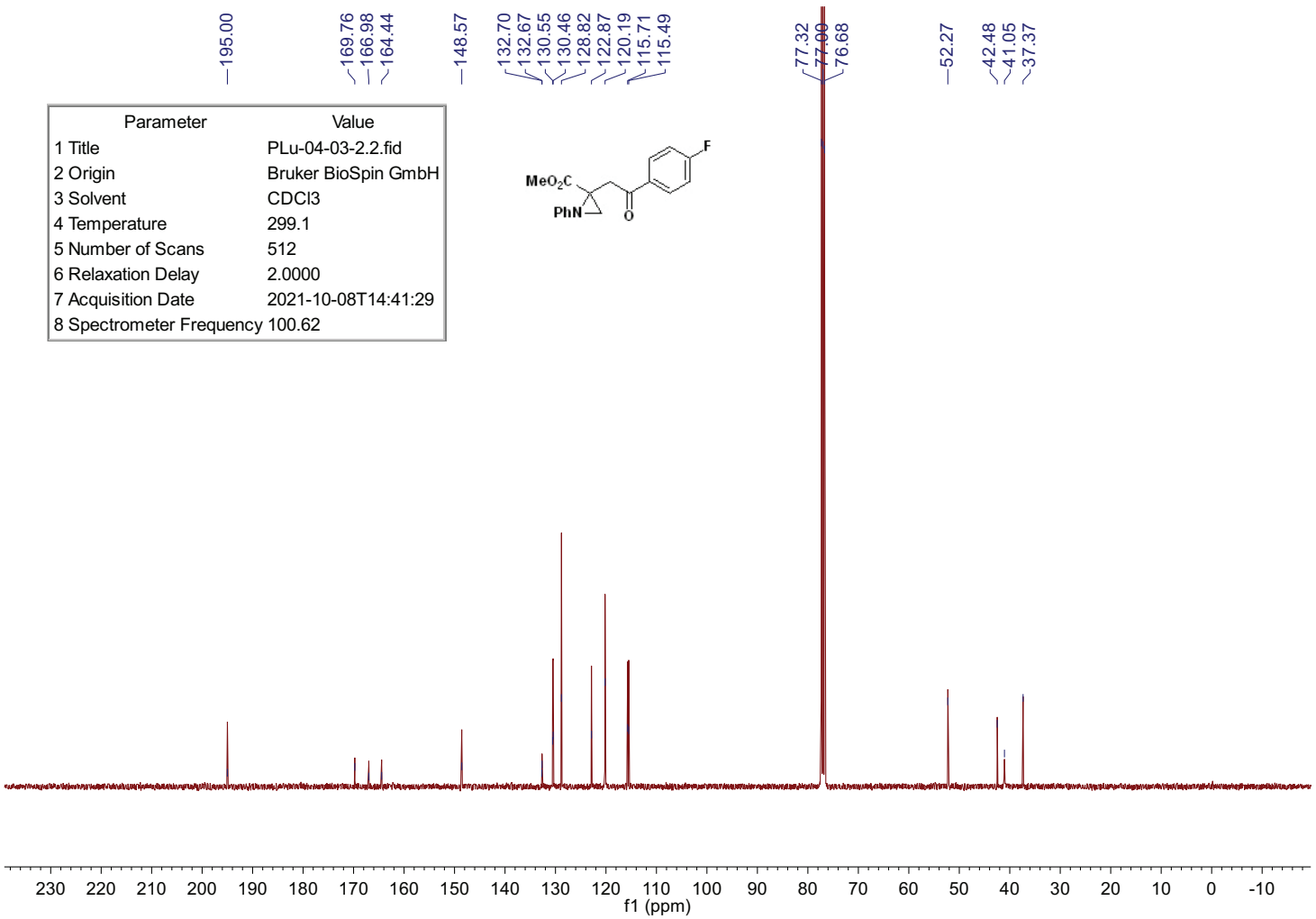

7.82
7.80
7.26
7.25
7.24
7.24
7.23
7.22
7.01
7.00
6.99
6.99
6.97
3.86
3.81
3.58
3.06
2.98
2.94
2.40
2.38
Parameter Value
1 Title PLu-03-153-2-2D.1.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 301.7
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-07-08T15:37:57
8 Spectrometer Frequency 400.13
MeO2C
PhN
O
1.90
4.56
2.92
1.00
2.88
0.95
0.93
2.80
1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



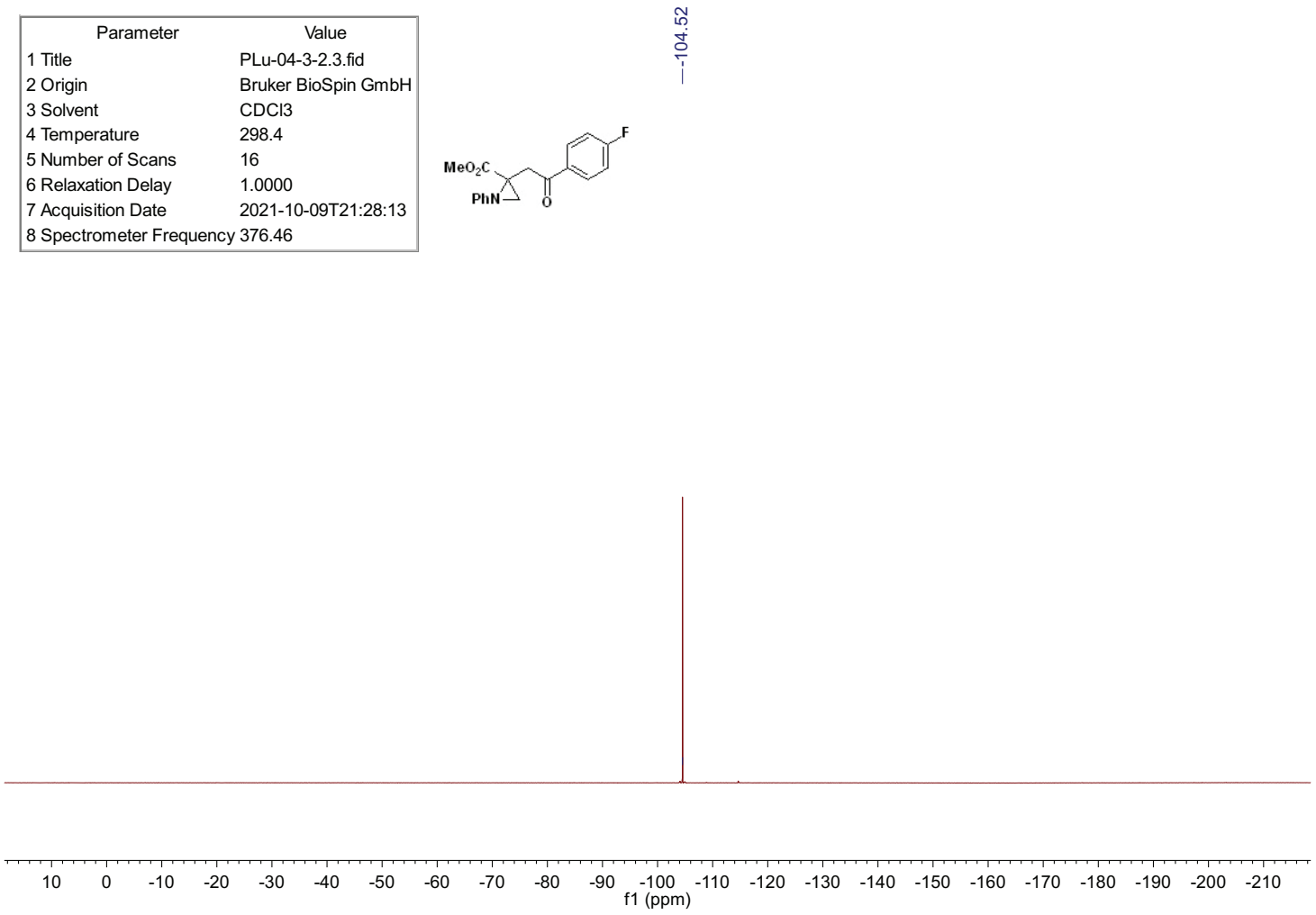
Parameter	Value
1 Title	PLu-03-153-2-2D.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	302.3
5 Number of Scans	512
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-07-08T16:07:09
8 Spectrometer Frequency	100.62



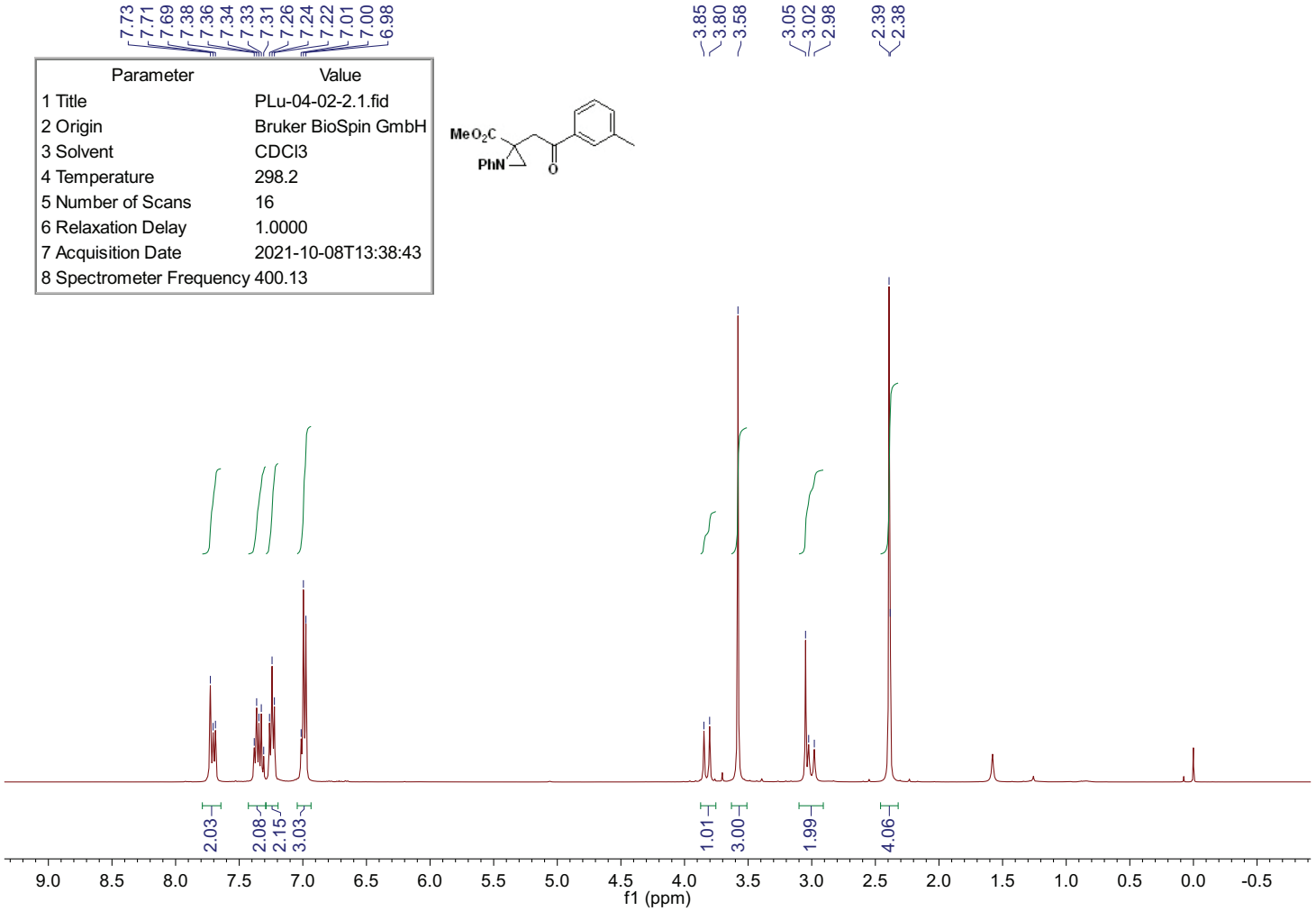
Parameter	Value
1 Title	PLu-04-03-2.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.6
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-10-08T14:12:18
8 Spectrometer Frequency	400.13

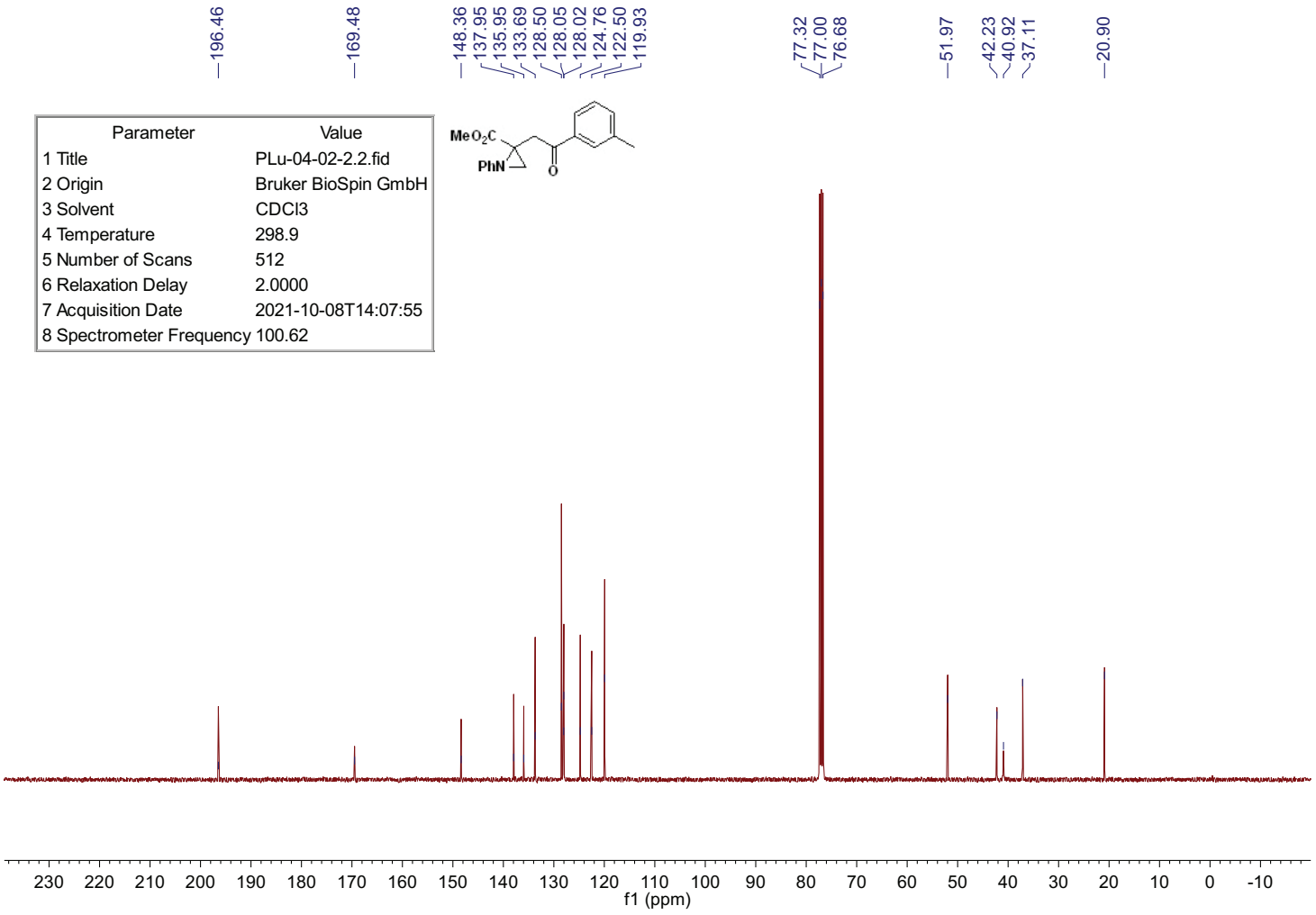


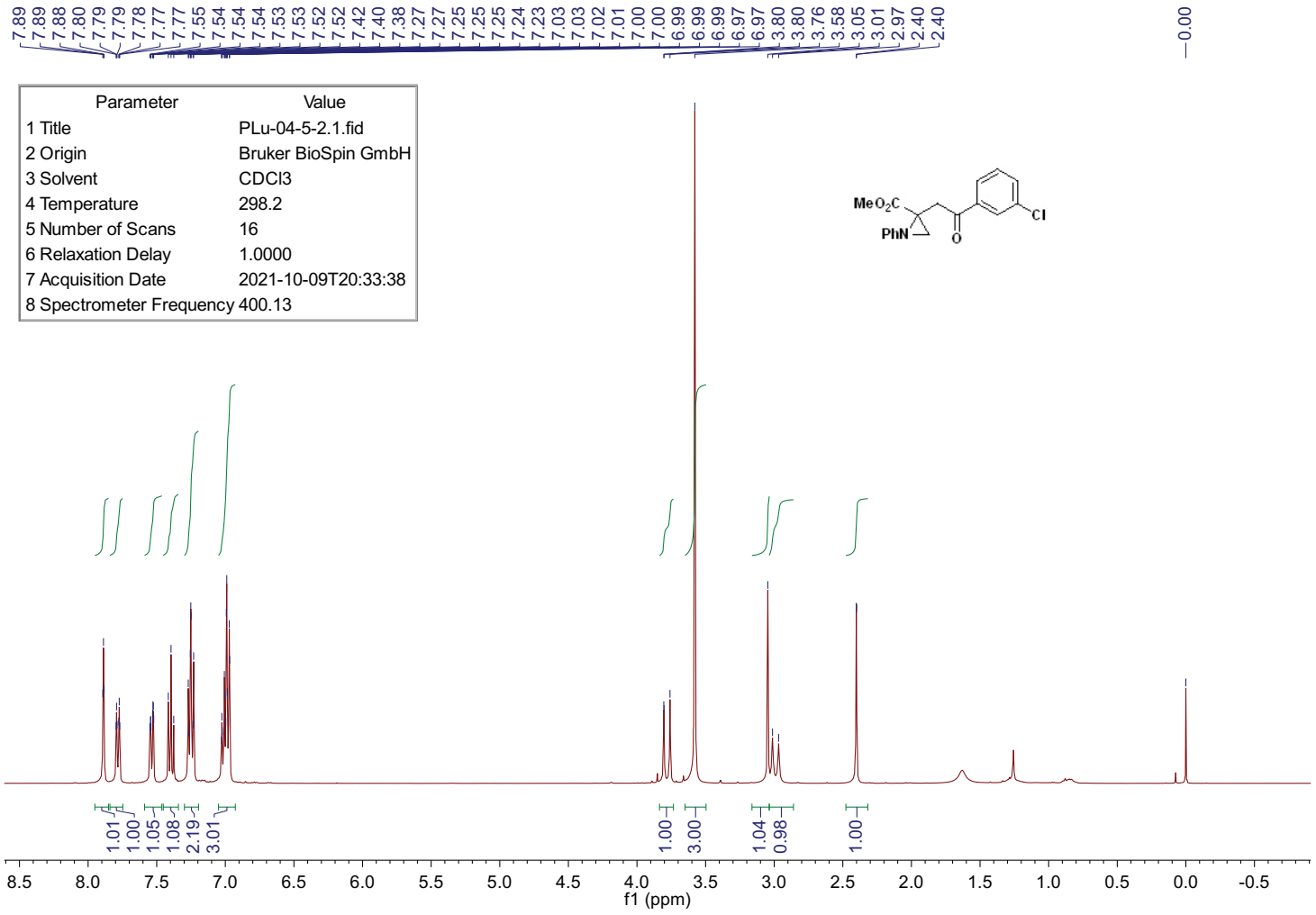
Parameter	Value
1 Title	PLu-04-03-2.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.1
5 Number of Scans	512
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-10-08T14:41:29
8 Spectrometer Frequency	100.62

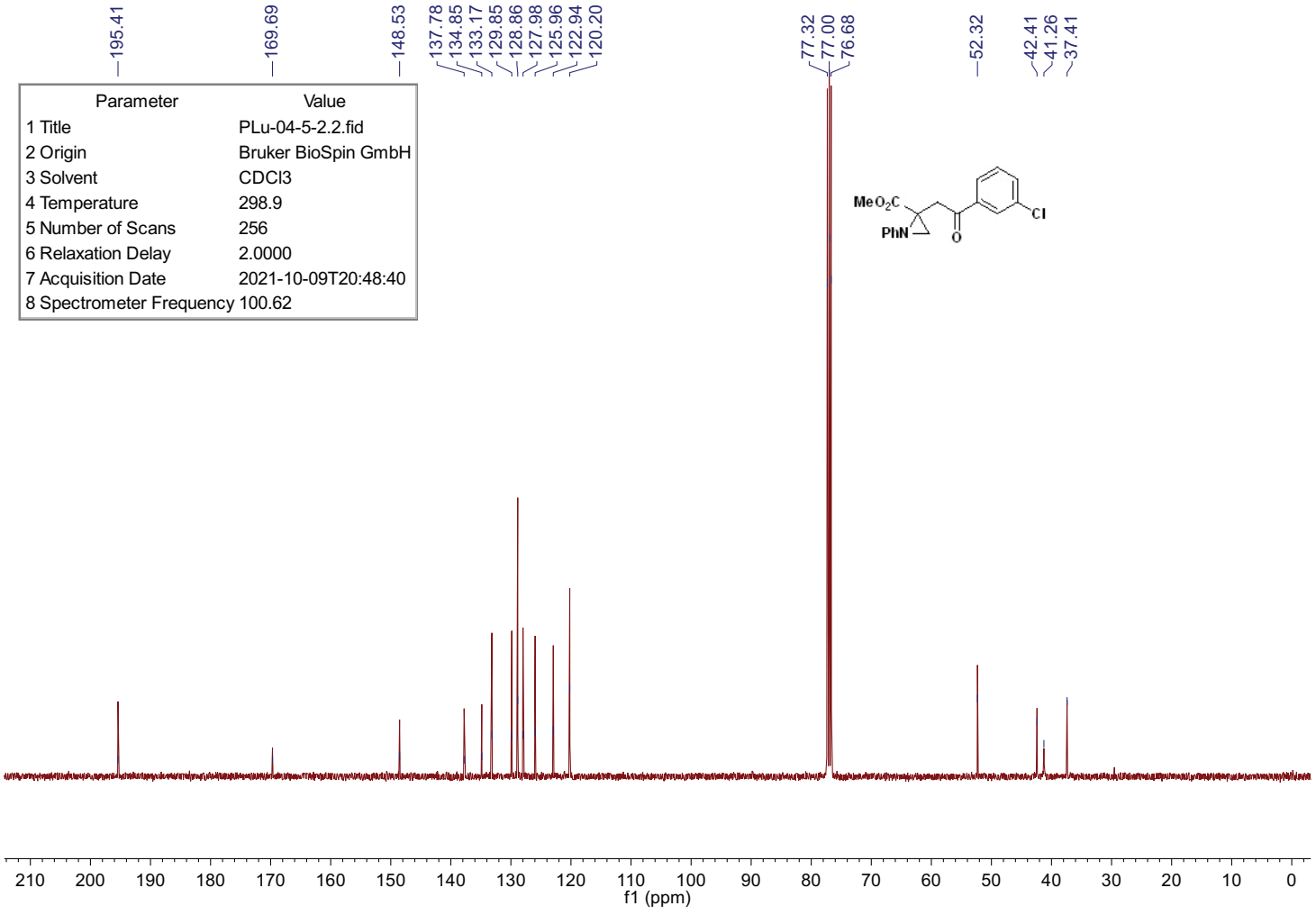


Parameter	Value
1 Title	PLu-04-3-2.3.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.4
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-10-09T21:28:13
8 Spectrometer Frequency	376.46

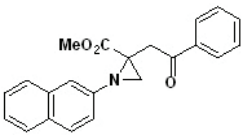

7.73
7.71
7.69
7.38
7.36
7.34
7.33
7.31
7.26
7.24
7.22
7.01
7.00
6.98
3.85
3.80
3.58
3.05
3.02
2.98
2.39
2.38
Parameter Value
1 Title PLu-04-02-2.1.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.2
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-10-08T13:38:43
8 Spectrometer Frequency 400.13
MeO2C
PhN
O
2.03
2.08
2.15
3.03
1.01
3.00
1.99
4.06
f1 (ppm)


196.46
169.48
148.36
137.95
135.95
133.69
128.50
128.05
128.02
124.76
122.50
119.93
77.32
77.00
76.68
51.97
42.23
40.92
37.11
20.90
Parameter Value
1 Title PLu-04-02-2.2.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.9
5 Number of Scans 512
6 Relaxation Delay 2.0000
7 Acquisition Date 2021-10-08T14:07:55
8 Spectrometer Frequency 100.62
MeO2C
PhN
O
f1 (ppm)

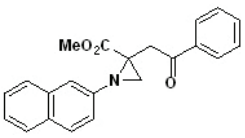

7.89 7.89 7.88 7.80 7.79 7.79 7.78 7.77 7.77 7.55 7.54 7.54 7.54 7.53 7.53 7.52 7.52 7.42 7.40 7.38 7.27 7.27 7.25 7.25 7.25 7.24 7.23 7.03 7.03 7.02 7.01 7.00 7.00 6.99 6.99 6.97 6.97 3.80 3.80 3.76 3.58 3.05 3.01 2.97 2.40 2.40
0.00
Parameter Value
1 Title PLu-04-5-2.1.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.2
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-10-09T20:33:38
8 Spectrometer Frequency 400.13
MeO2C
PhN
O
Cl
1.01 1.00 1.05 1.08 2.19 3.01 1.00 3.00 1.04 0.98 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

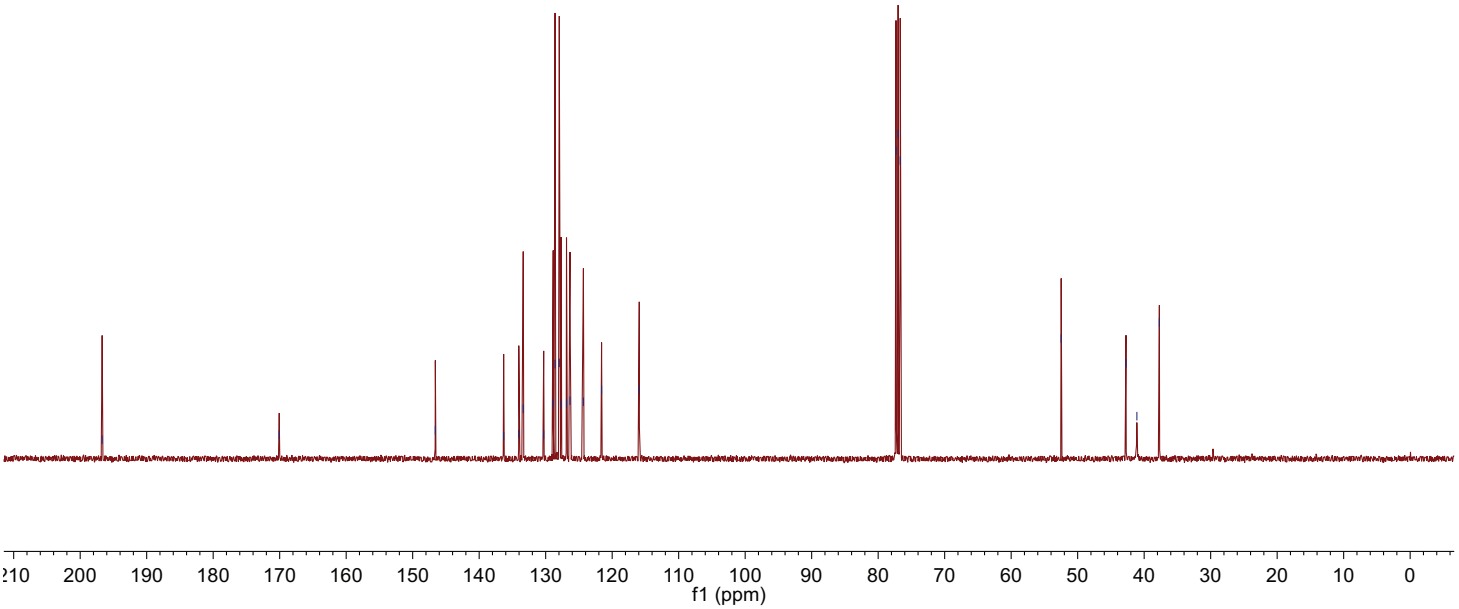

195.41 169.69 148.53 137.78 134.85 133.17 129.85 128.86 127.98 125.96 122.94 120.20 77.32 77.00 76.68 52.32 42.41 41.26 37.41
Parameter Value
1 Title PLu-04-5-2.2.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.9
5 Number of Scans 256
6 Relaxation Delay 2.0000
7 Acquisition Date 2021-10-09T20:48:40
8 Spectrometer Frequency 100.62
MeO2C
PhN
O
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

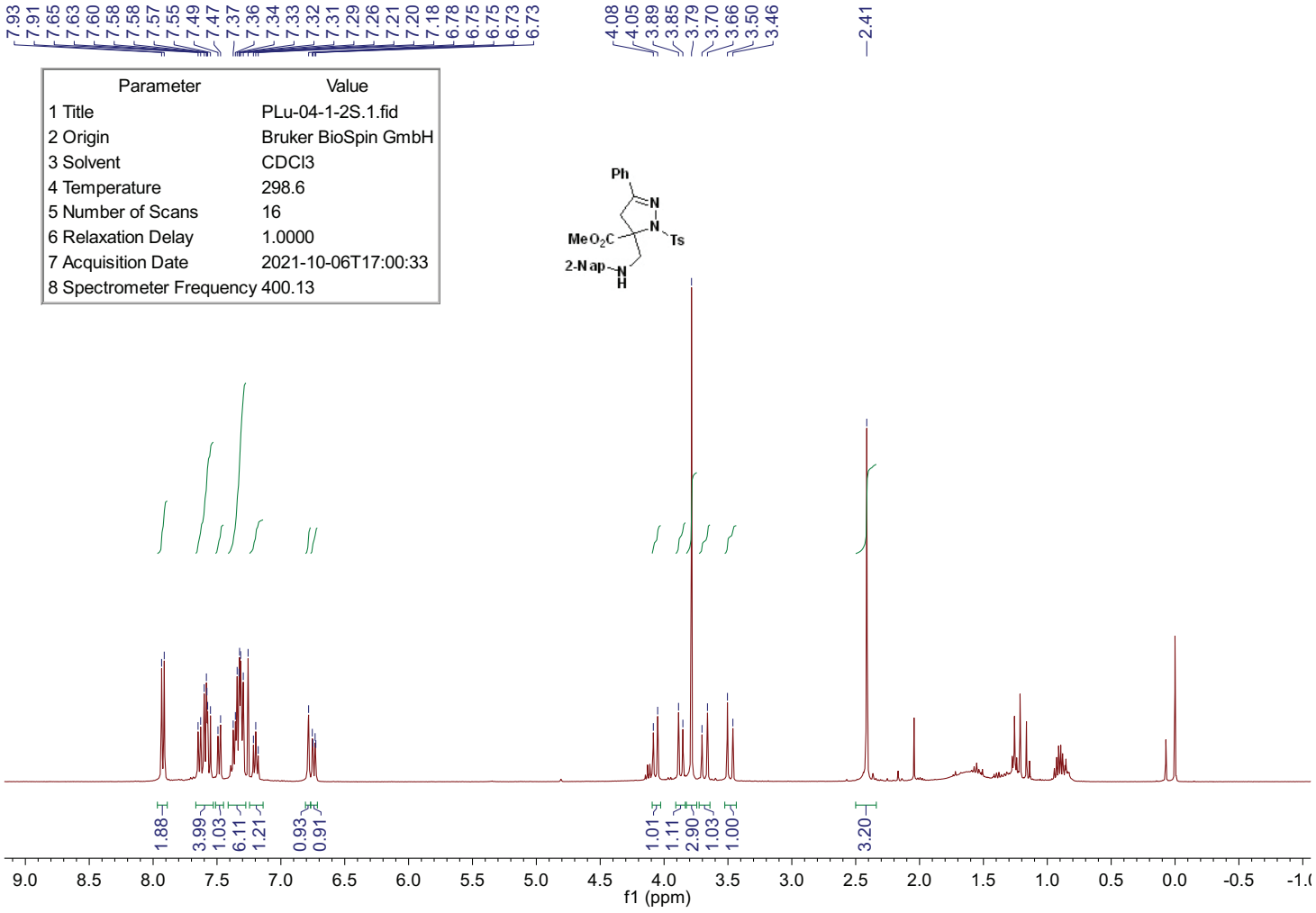
Parameter	Value
1 Title	PLu-03-170-2.3.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.9
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-09-10T08:02:16
8 Spectrometer Frequency	400.13

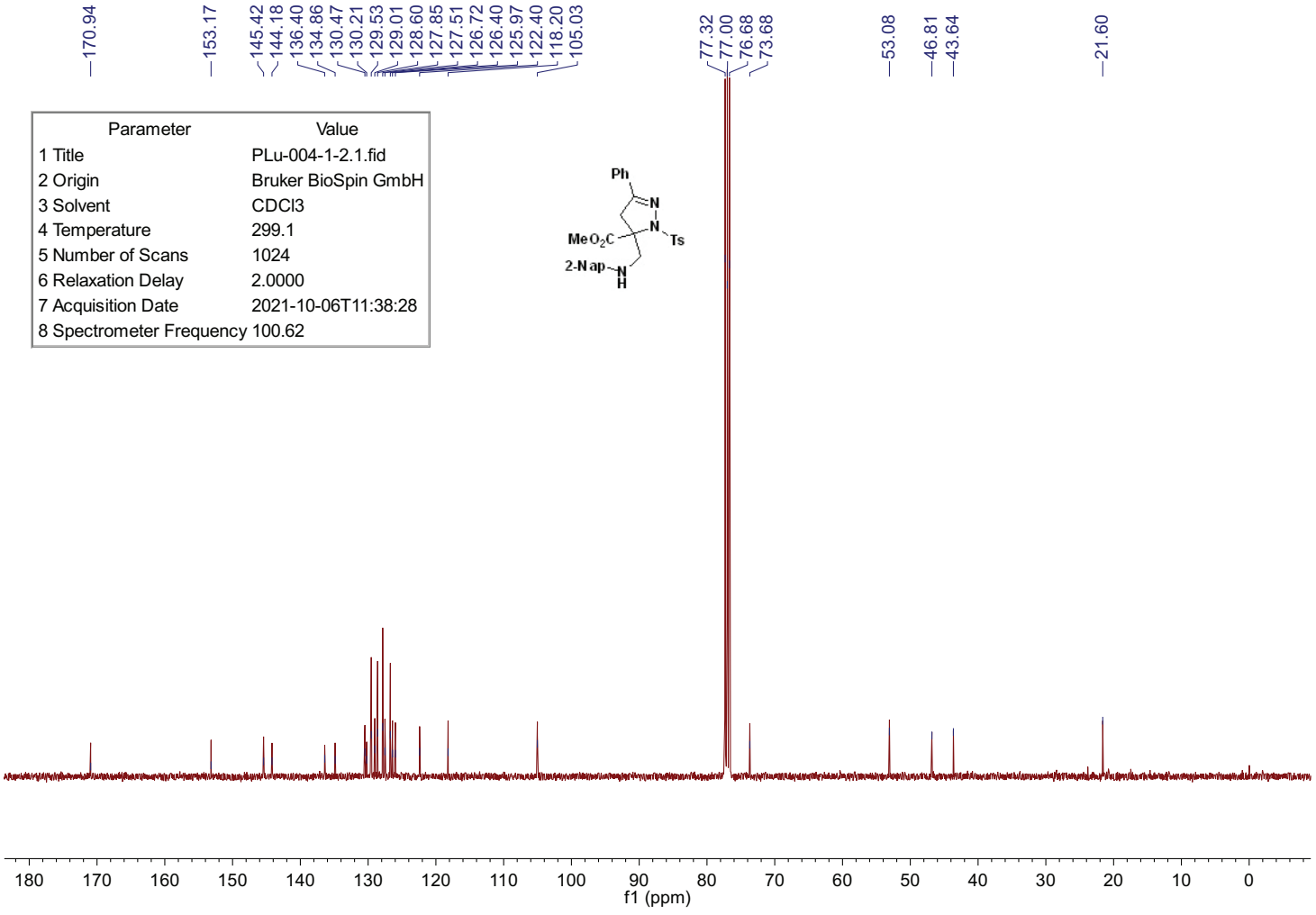


Parameter	Value
1 Title	PLu-03-170-2.4.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.5
5 Number of Scans	512
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-09-10T08:31:27
8 Spectrometer Frequency	100.62



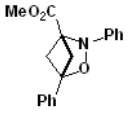


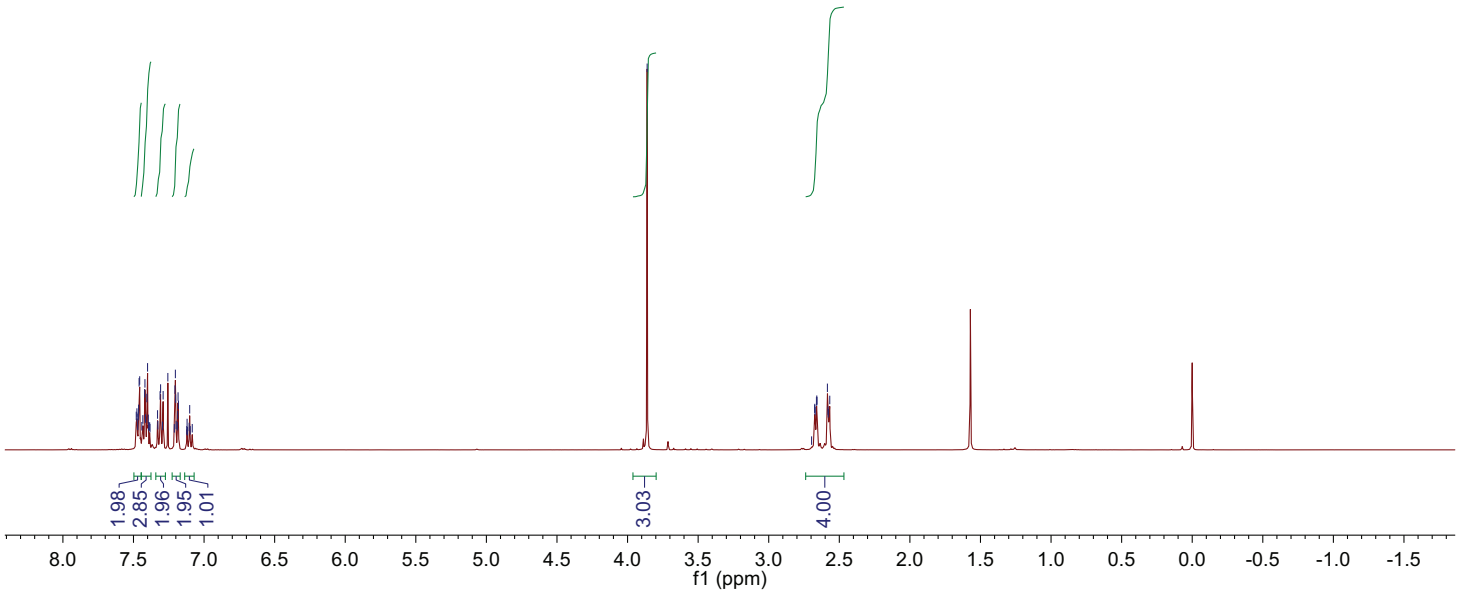

7.93 7.91 7.65 7.63 7.60 7.58 7.58 7.57 7.55 7.49 7.47 7.37 7.36 7.34 7.33 7.32 7.31 7.29 7.26 7.21 7.20 7.18 6.78 6.75 6.75 6.73 6.73
4.08 4.05 3.89 3.85 3.79 3.70 3.66 3.50 3.46
2.41
Parameter Value
1 Title PLu-04-1-2S.1.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.6
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-10-06T17:00:33
8 Spectrometer Frequency 400.13
Ph
N
N
Ts
MeO2C
2-Nap
N
H
1.88 3.99 1.03 6.11 1.21 0.93 0.91 1.01 1.11 2.90 1.03 1.00 3.20
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


170.94 153.17 145.42 144.18 136.40 134.86 130.47 130.21 129.53 129.01 128.60 127.85 127.51 126.72 126.40 125.97 122.40 118.20 105.03
77.32 77.00 76.68 73.68
53.08 46.81 43.64
21.60
Parameter Value
1 Title PLu-004-1-2.1.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 299.1
5 Number of Scans 1024
6 Relaxation Delay 2.0000
7 Acquisition Date 2021-10-06T11:38:28
8 Spectrometer Frequency 100.62
Ph
N
N
Ts
MeO2C
2-Nap
N
H
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

7.48 7.48 7.47 7.47 7.47 7.46 7.46 7.46 7.44 7.43 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.33 7.33 7.31 7.31 7.29 7.29 7.26 7.21 7.21 7.20 7.20 7.20 7.19 7.19 7.18 7.18 7.12 7.12 7.12 7.11 7.10 7.10 7.08 3.86 2.70 2.67 2.67 2.67 2.66 2.66 2.66 2.58 2.58 2.58 2.57

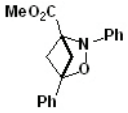
Parameter	Value
1 Title	PLu-03-200-1.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.3
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-10-04T01:25:16
8 Spectrometer Frequency	400.13

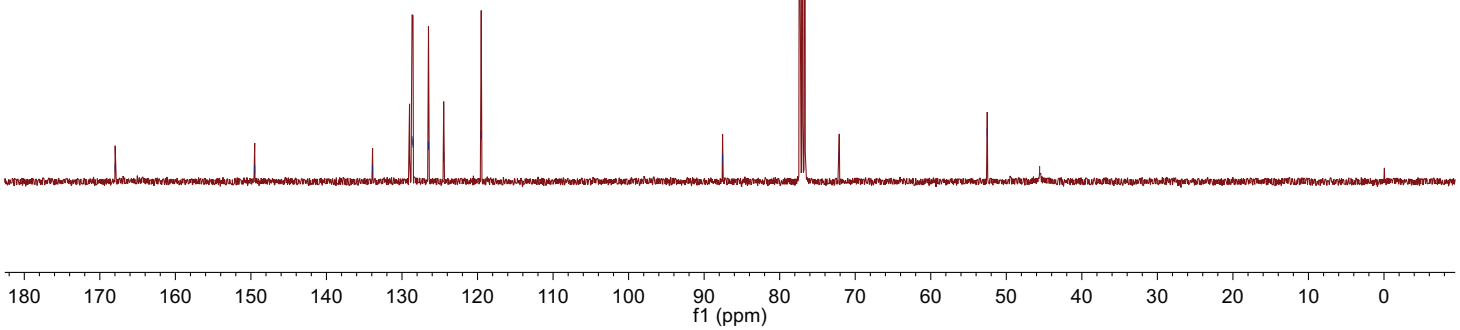


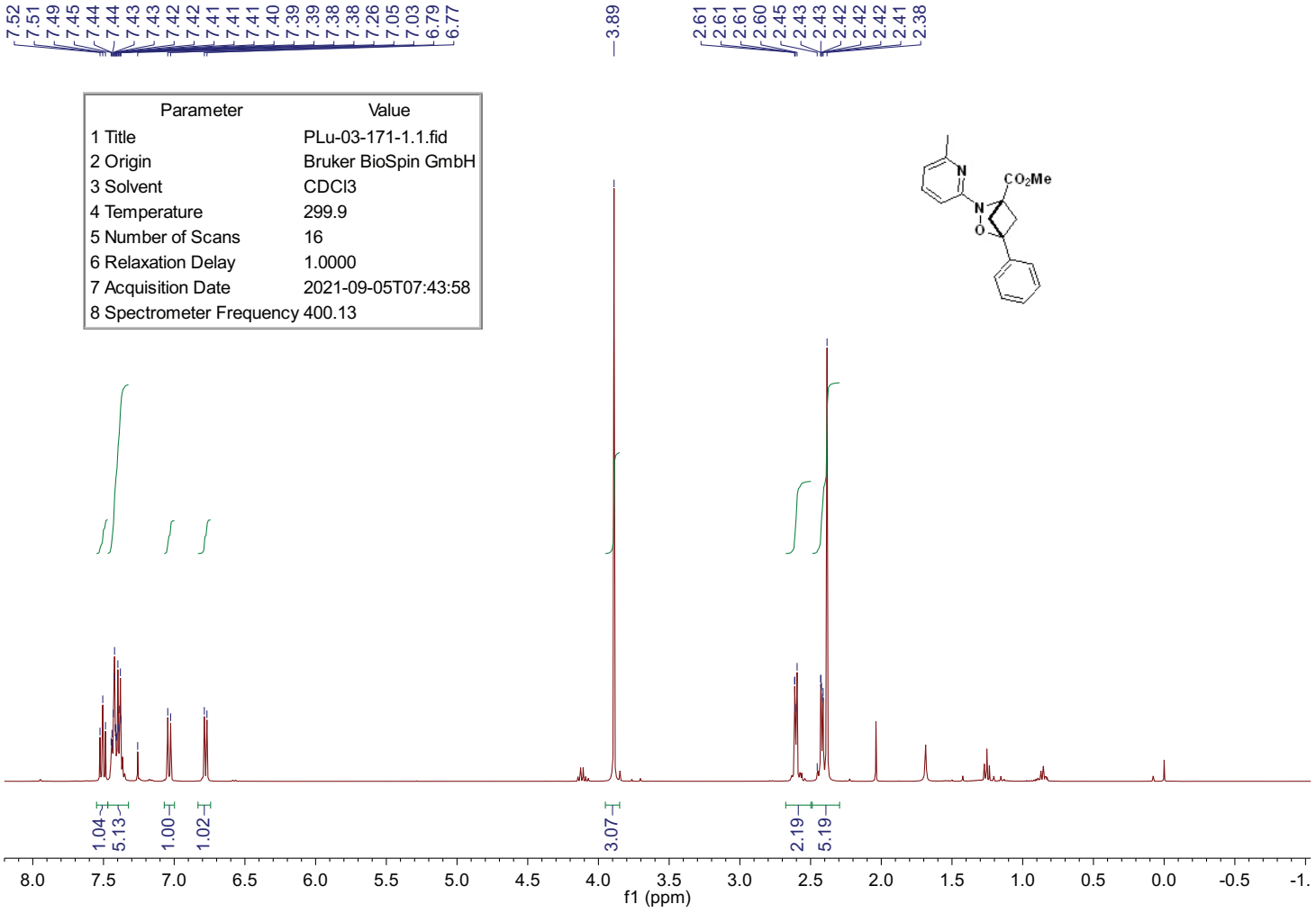


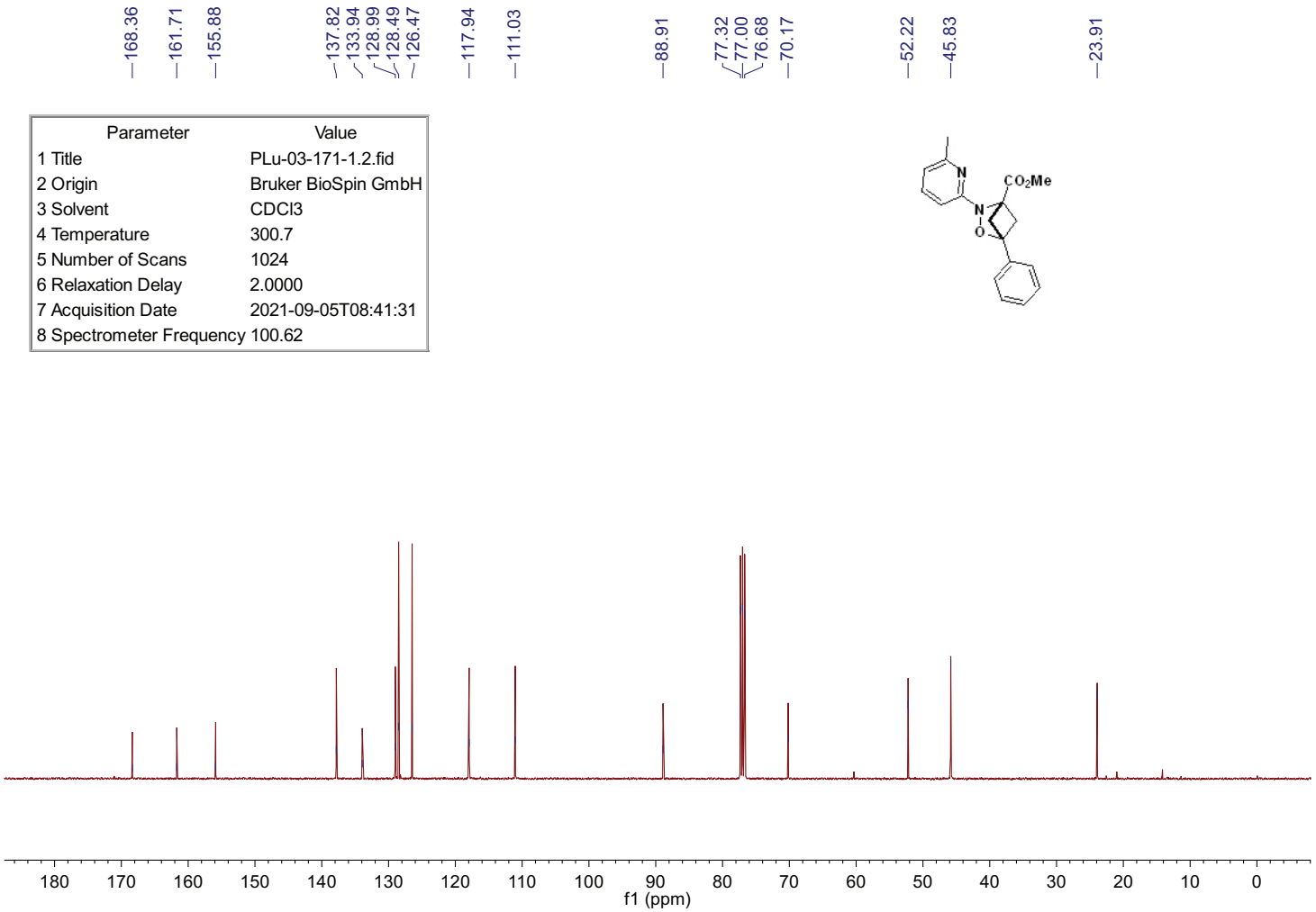
167.97 149.50 133.89 129.00 128.67 128.54 126.49 124.48 119.51 87.56 77.32 77.00 76.68 72.11 52.52 45.59

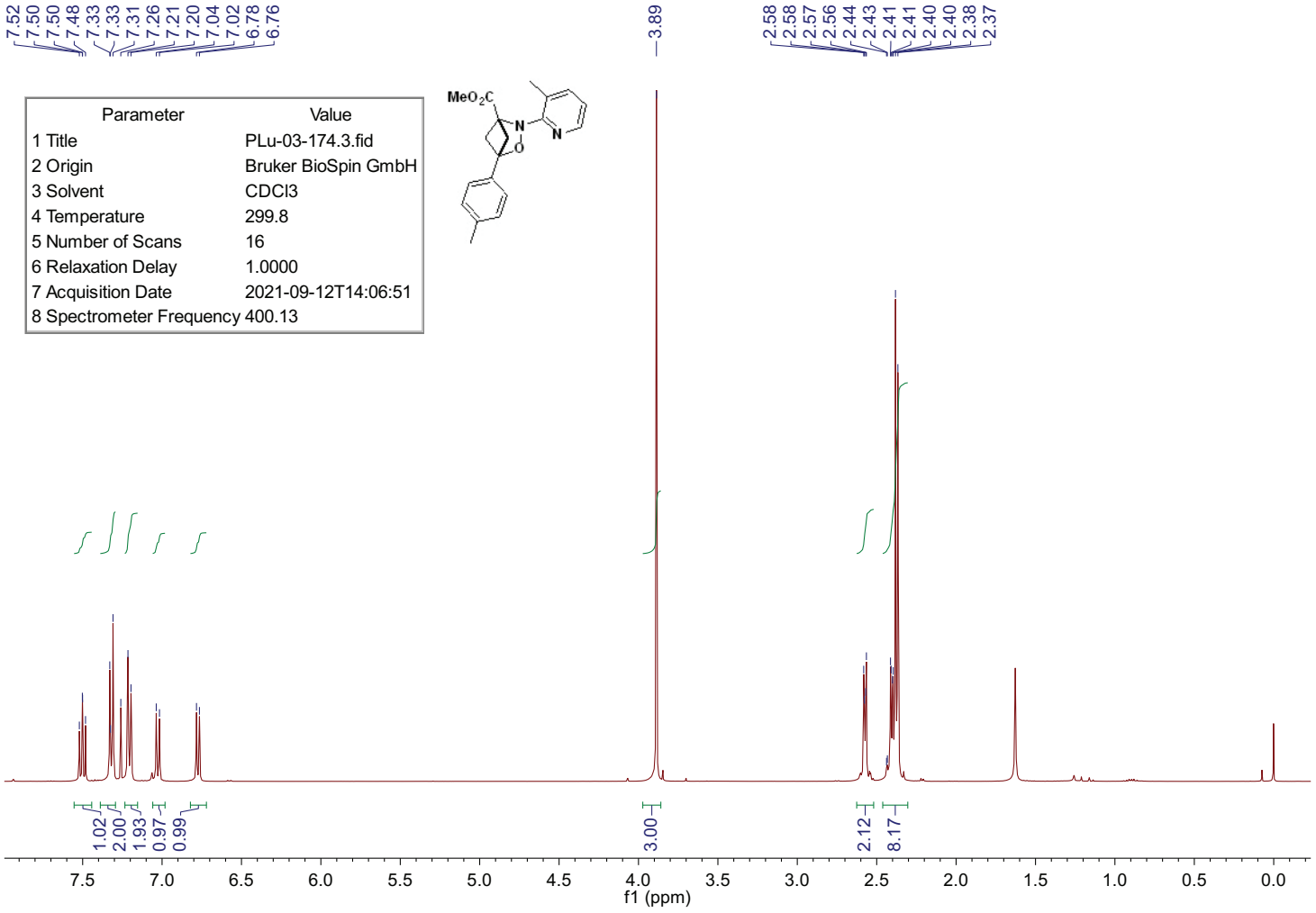
Parameter	Value
1 Title	PLu-03-200-1.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.7
5 Number of Scans	512
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-10-04T01:54:27
8 Spectrometer Frequency	100.62

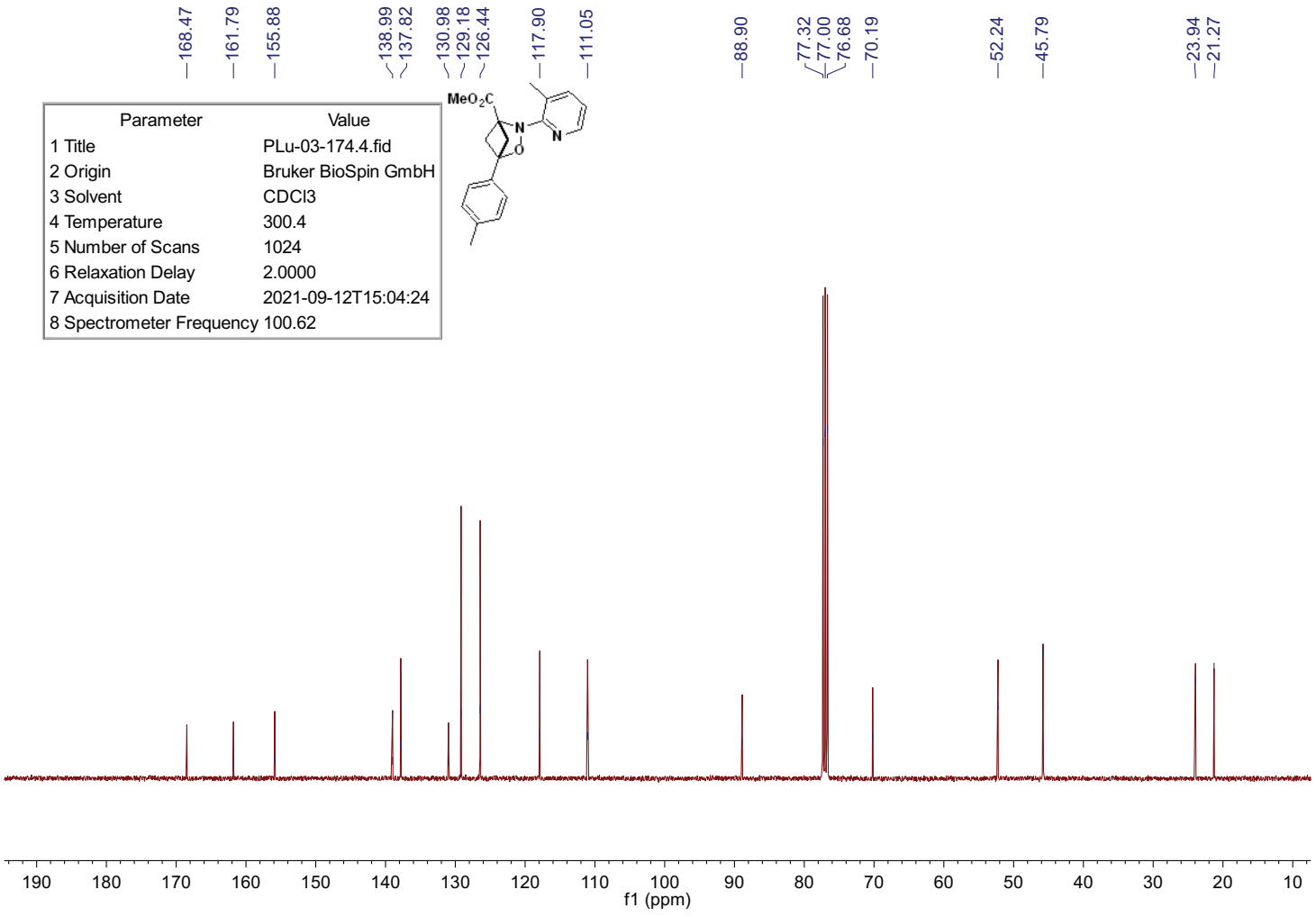




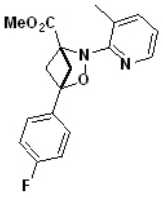

7.52 7.51 7.49 7.45 7.44 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.41 7.40 7.39 7.39 7.38 7.38 7.26 7.05 7.03 6.79 6.77
3.89
2.61 2.61 2.61 2.60 2.45 2.43 2.43 2.42 2.42 2.42 2.41 2.38
Parameter Value
1 Title PLu-03-171-1.1.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 299.9
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-09-05T07:43:58
8 Spectrometer Frequency 400.13
CO2Me
1.04 5.13 1.00 1.02 3.07 2.19 5.19
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

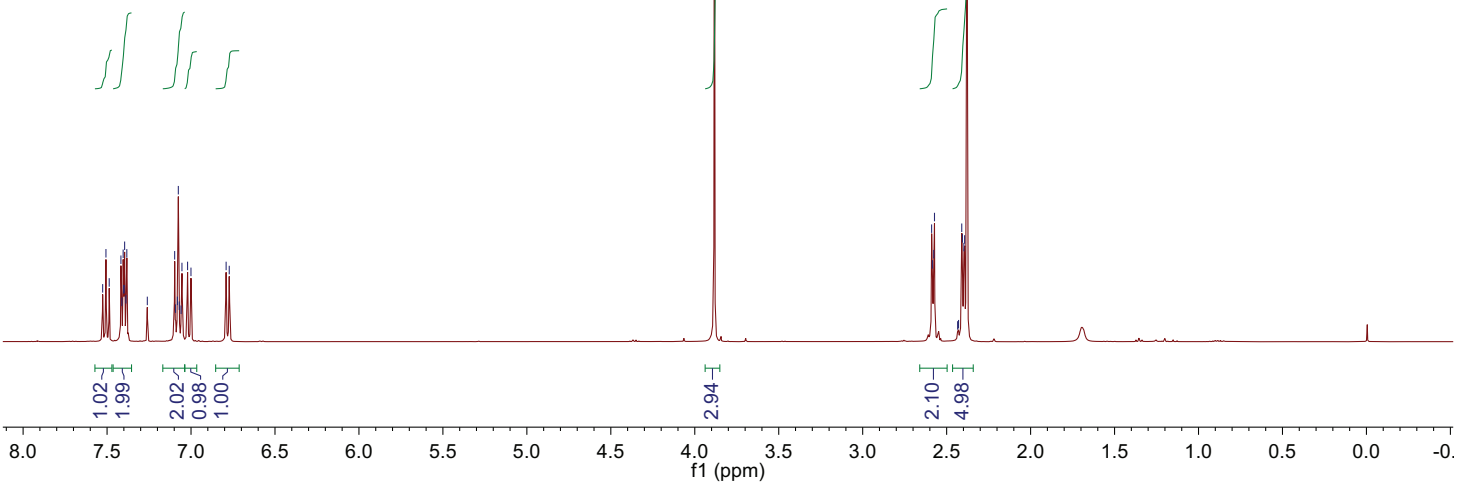

168.36 161.71 155.88 137.82 133.94 128.99 128.49 126.47 117.94 111.03 88.91 77.32 77.00 76.68 70.17 52.22 45.83 23.91
Parameter Value
1 Title PLu-03-171-1.2.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.7
5 Number of Scans 1024
6 Relaxation Delay 2.0000
7 Acquisition Date 2021-09-05T08:41:31
8 Spectrometer Frequency 100.62
CO2Me
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.52
7.50
7.50
7.48
7.33
7.33
7.31
7.26
7.21
7.20
7.04
7.02
6.78
6.76
3.89
2.58
2.58
2.57
2.56
2.44
2.43
2.41
2.41
2.40
2.40
2.38
2.37
MeO2C
N
O
N
Parameter Value
1 Title PLu-03-174.3.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 299.8
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-09-12T14:06:51
8 Spectrometer Frequency 400.13
1.02
2.00
1.93
0.97
0.99
3.00
2.12
8.17
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

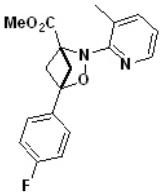

168.47
161.79
155.88
138.99
137.82
130.98
129.18
126.44
117.90
111.05
88.90
77.32
77.00
76.68
70.19
52.24
45.79
23.94
21.27
MeO2C
N
O
N
Parameter Value
1 Title PLu-03-174.4.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.4
5 Number of Scans 1024
6 Relaxation Delay 2.0000
7 Acquisition Date 2021-09-12T15:04:24
8 Spectrometer Frequency 100.62
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

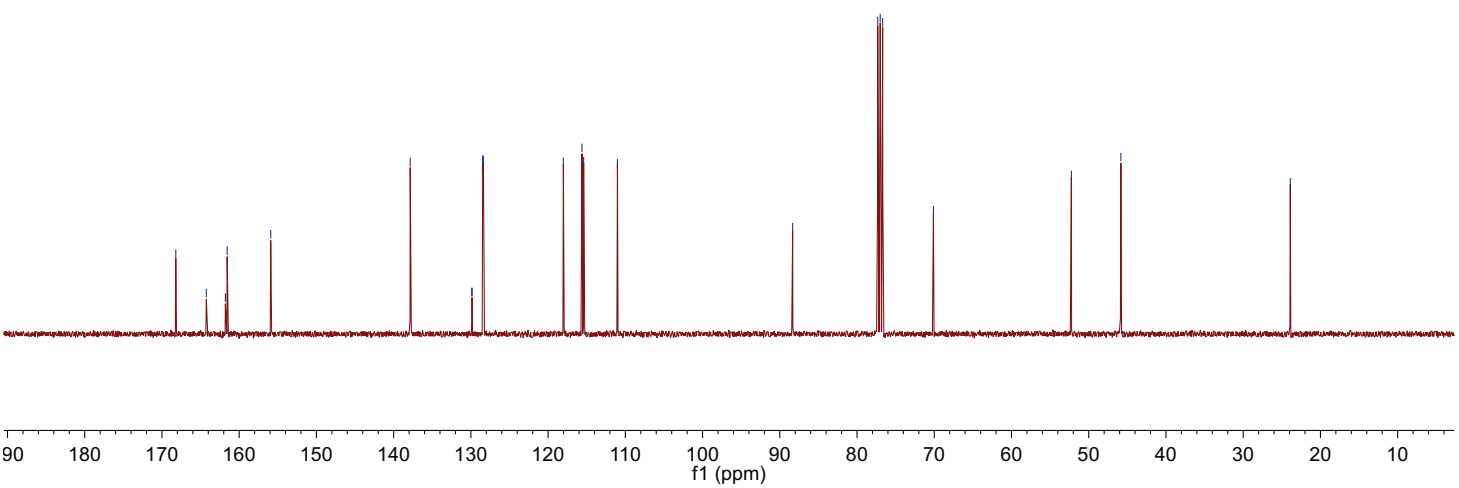
Parameter	Value
1 Title	PLu-03-178-S1.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.8
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-09-15T02:28:58
8 Spectrometer Frequency	400.13



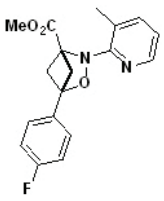


Parameter	Value
1 Title	PLu-03-178-S1.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.3
5 Number of Scans	256
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-09-15T02:44:04
8 Spectrometer Frequency	100.62

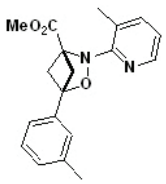


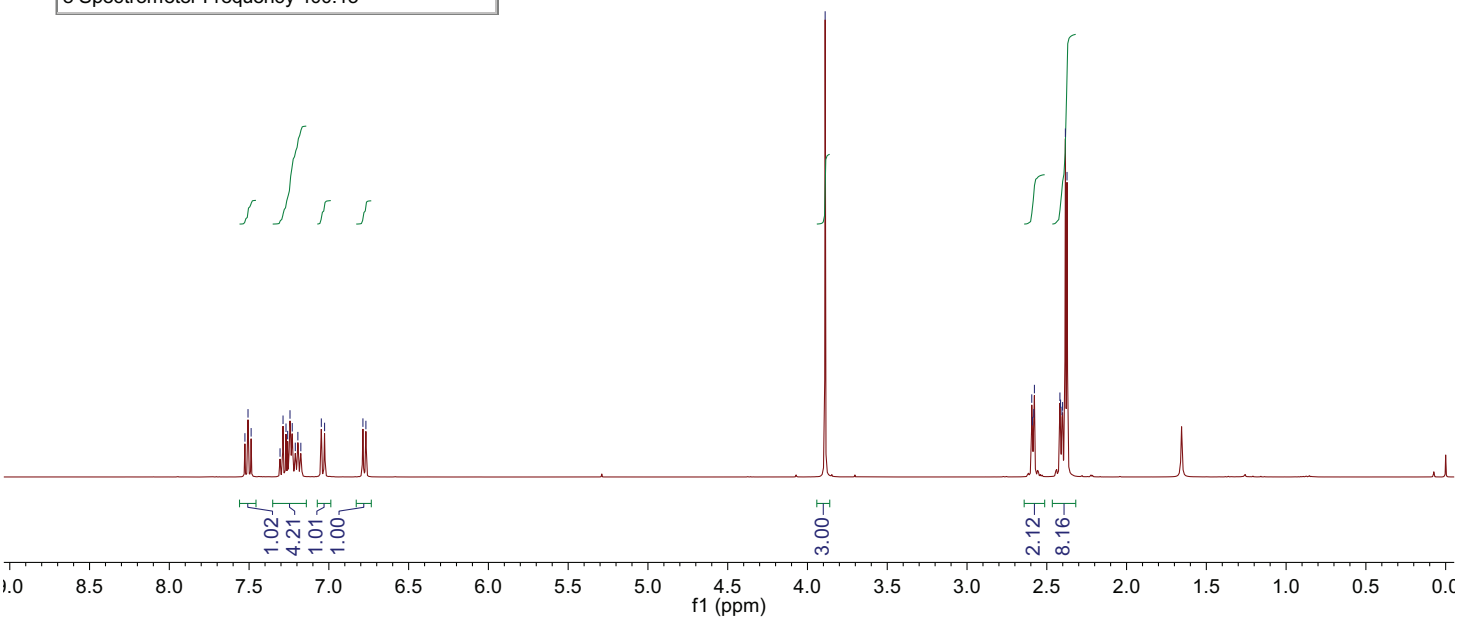


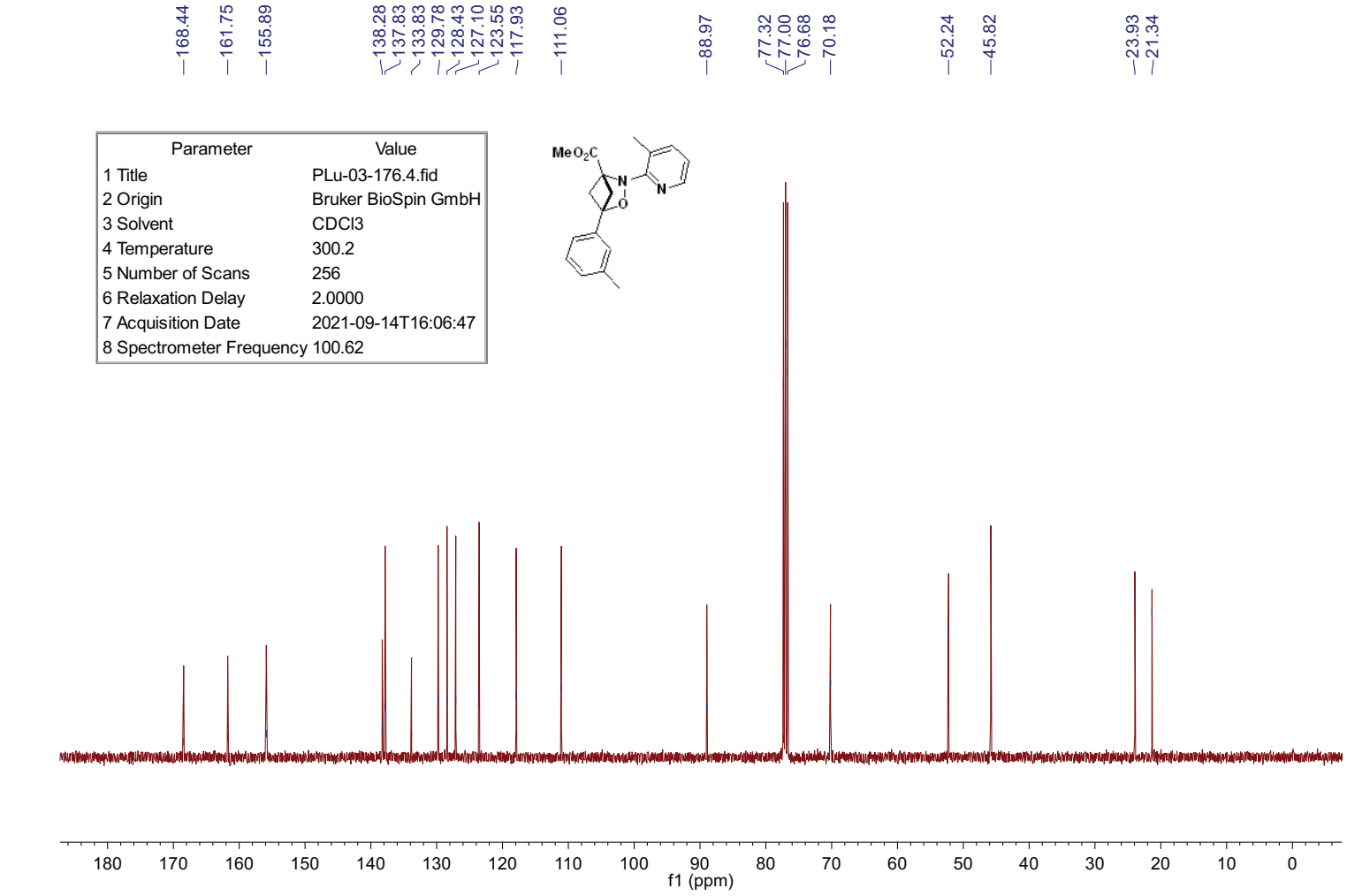
Parameter	Value
1 Title	PLu-03-178-1.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.9
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-09-15T14:50:13
8 Spectrometer Frequency	376.46



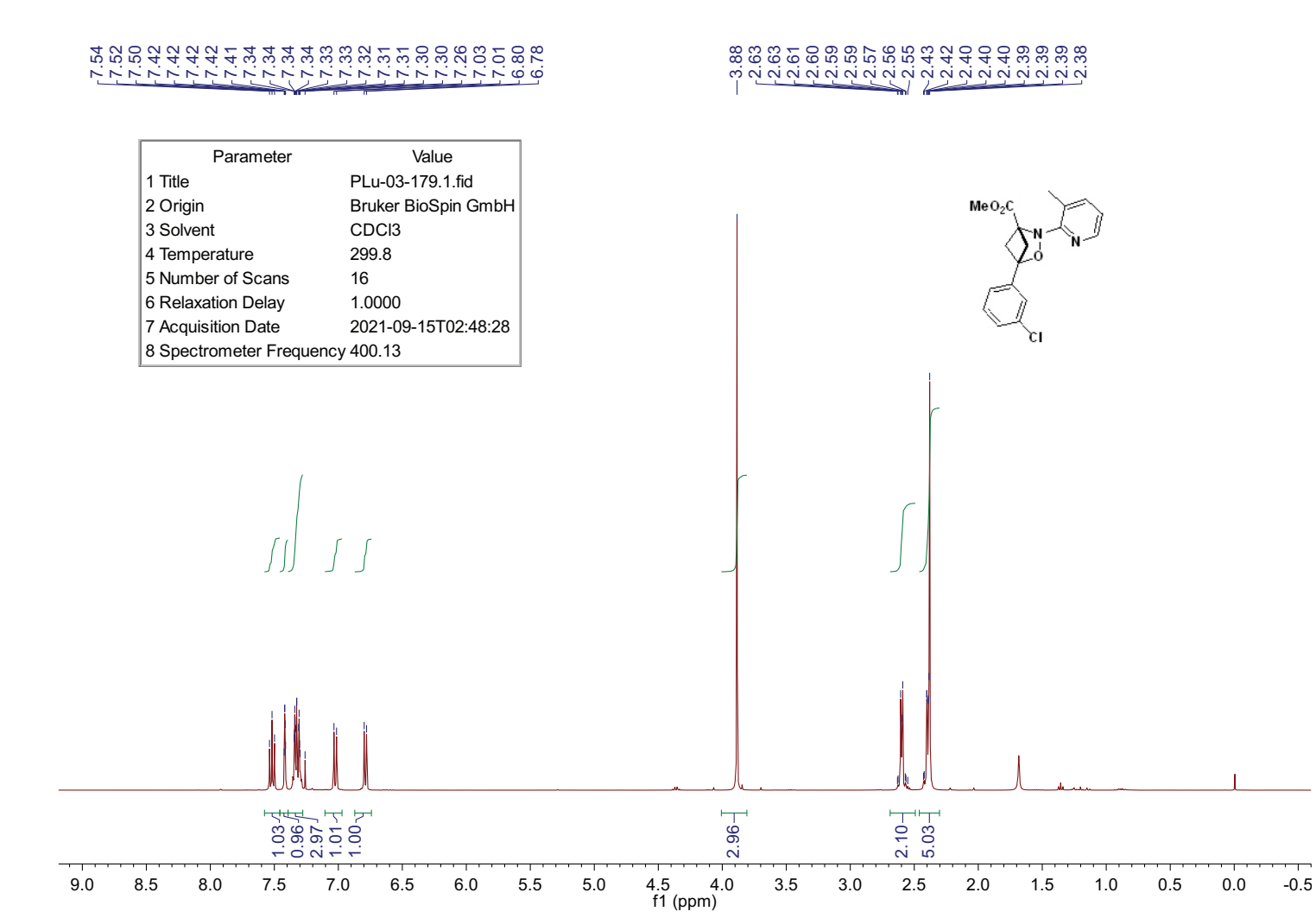
Parameter	Value
1 Title	PLu-03-176.3.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.7
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-09-14T15:51:28
8 Spectrometer Frequency	400.13



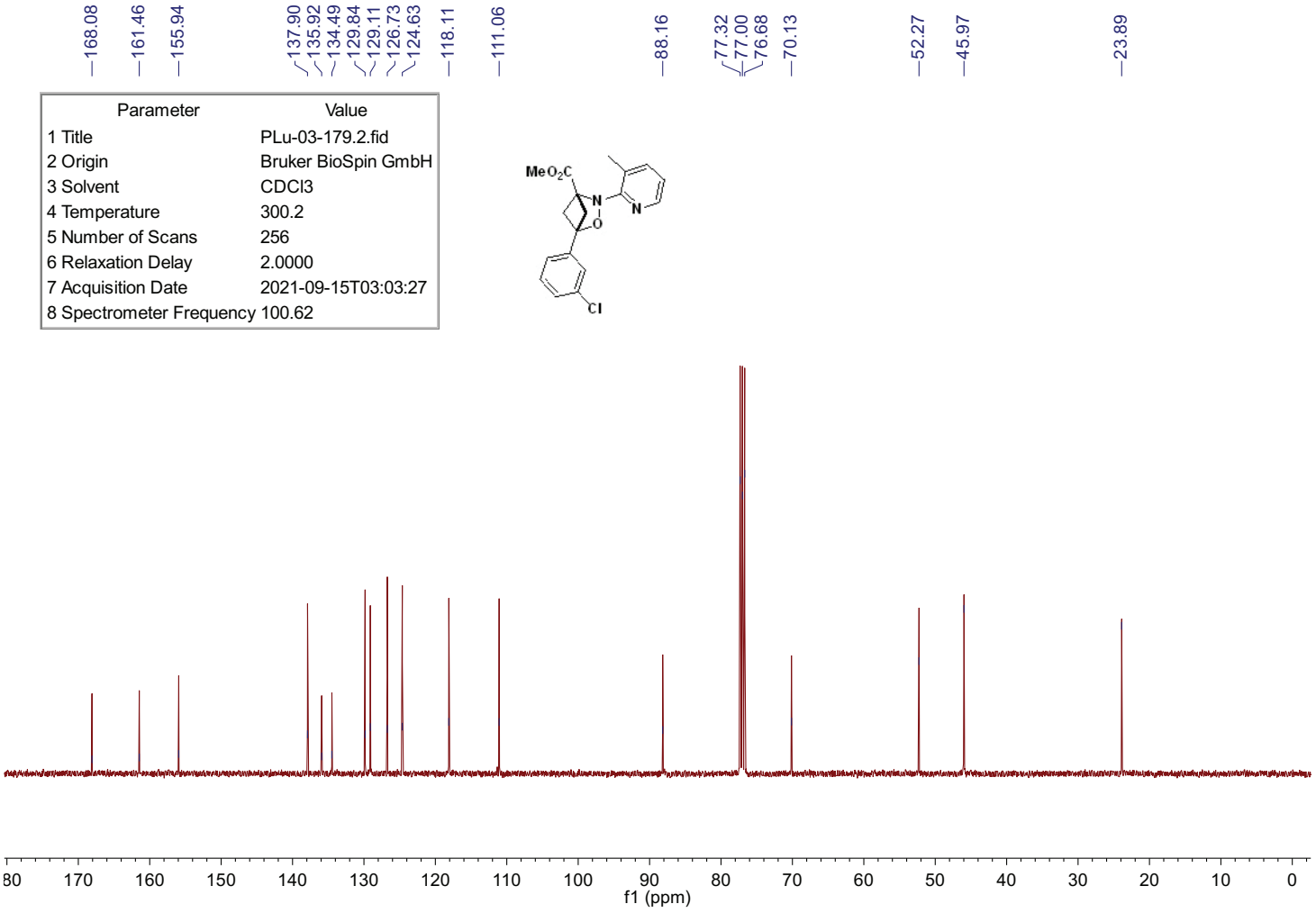


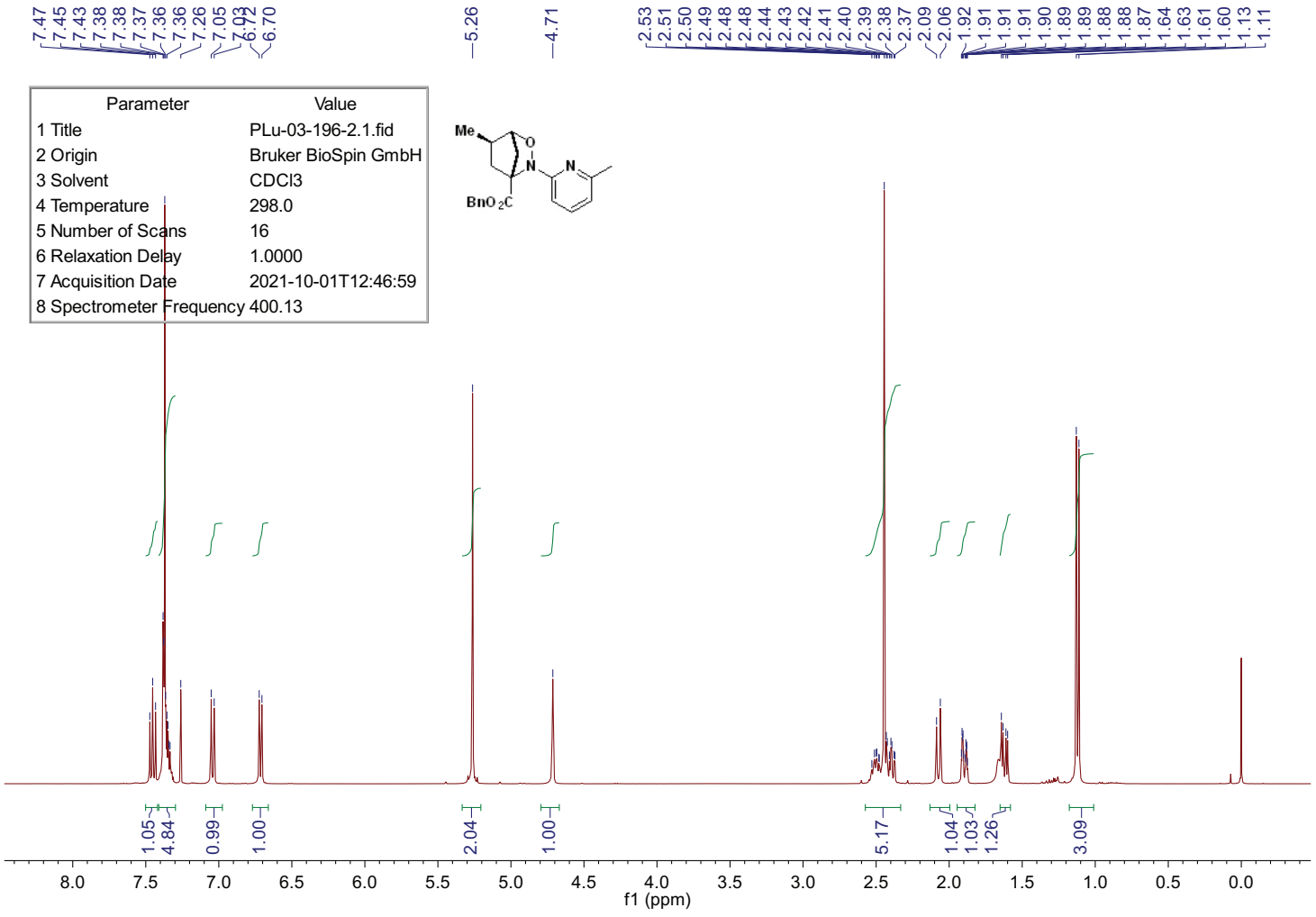


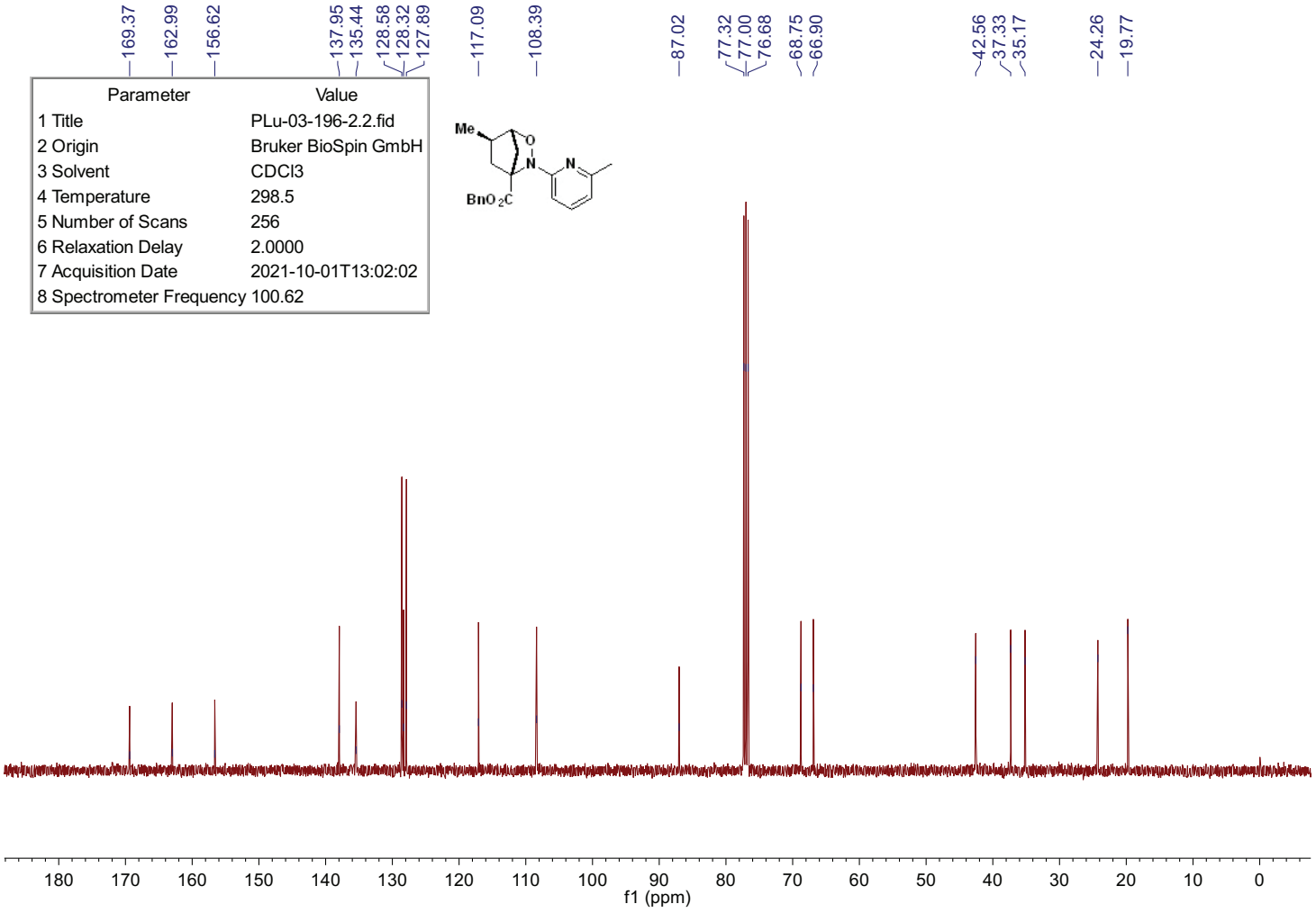
Parameter	Value
1 Title	PLu-03-176.4.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.2
5 Number of Scans	256
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-09-14T16:06:47
8 Spectrometer Frequency	100.62



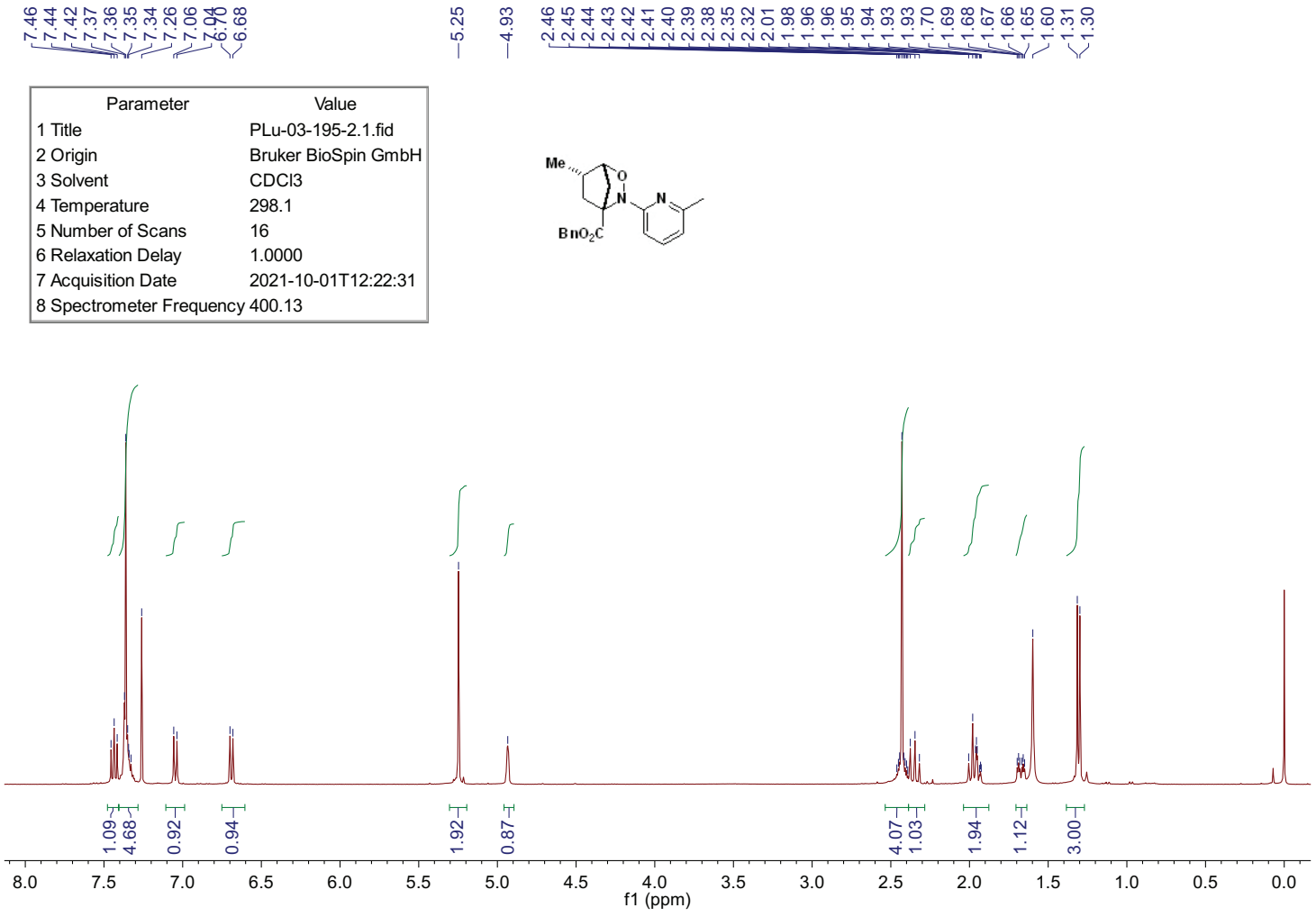
Parameter	Value
1 Title	PLu-03-179.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.8
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-09-15T02:48:28
8 Spectrometer Frequency	400.13


168.08
161.46
155.94
137.90
135.92
134.49
129.84
129.11
126.73
124.63
118.11
111.06
88.16
77.32
77.00
76.68
70.13
52.27
45.97
23.89
Parameter Value
1 Title PLu-03-179.2.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.2
5 Number of Scans 256
6 Relaxation Delay 2.0000
7 Acquisition Date 2021-09-15T03:03:27
8 Spectrometer Frequency 100.62
MeO2C
N
O
N
Cl
f1 (ppm)

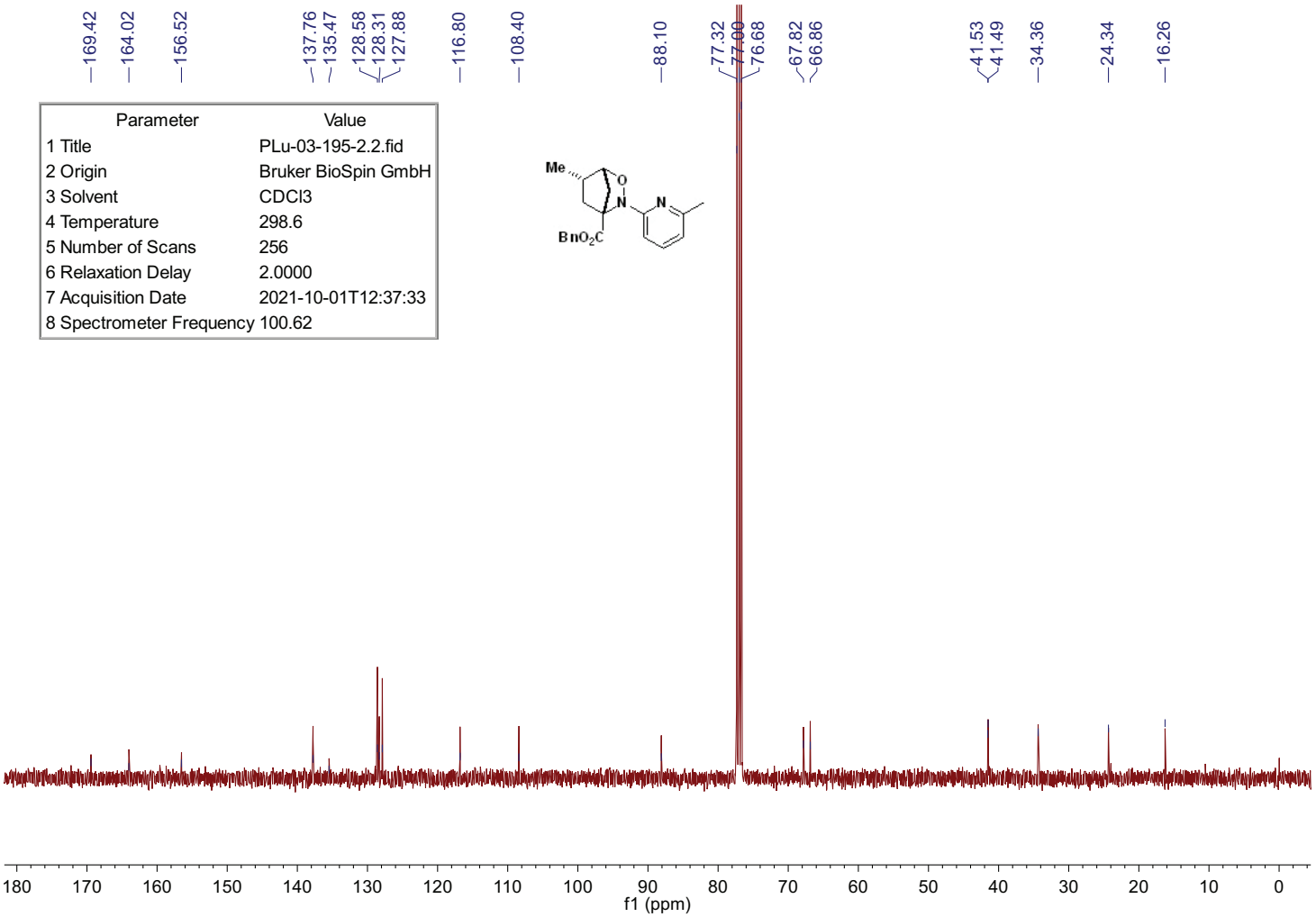

7.47
7.45
7.43
7.38
7.38
7.37
7.36
7.36
7.26
7.05
6.72
6.70
5.26
4.71
2.53
2.51
2.50
2.49
2.48
2.48
2.44
2.43
2.42
2.41
2.40
2.39
2.38
2.37
2.09
2.06
1.92
1.91
1.91
1.91
1.90
1.89
1.89
1.88
1.88
1.87
1.64
1.63
1.61
1.60
1.13
1.11
Parameter Value
1 Title PLu-03-196-2.1.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-10-01T12:46:59
8 Spectrometer Frequency 400.13
Me
O
N
N
BnO2C
1.05
4.84
0.99
1.00
2.04
1.00
5.17
1.04
1.03
1.26
3.09
f1 (ppm)



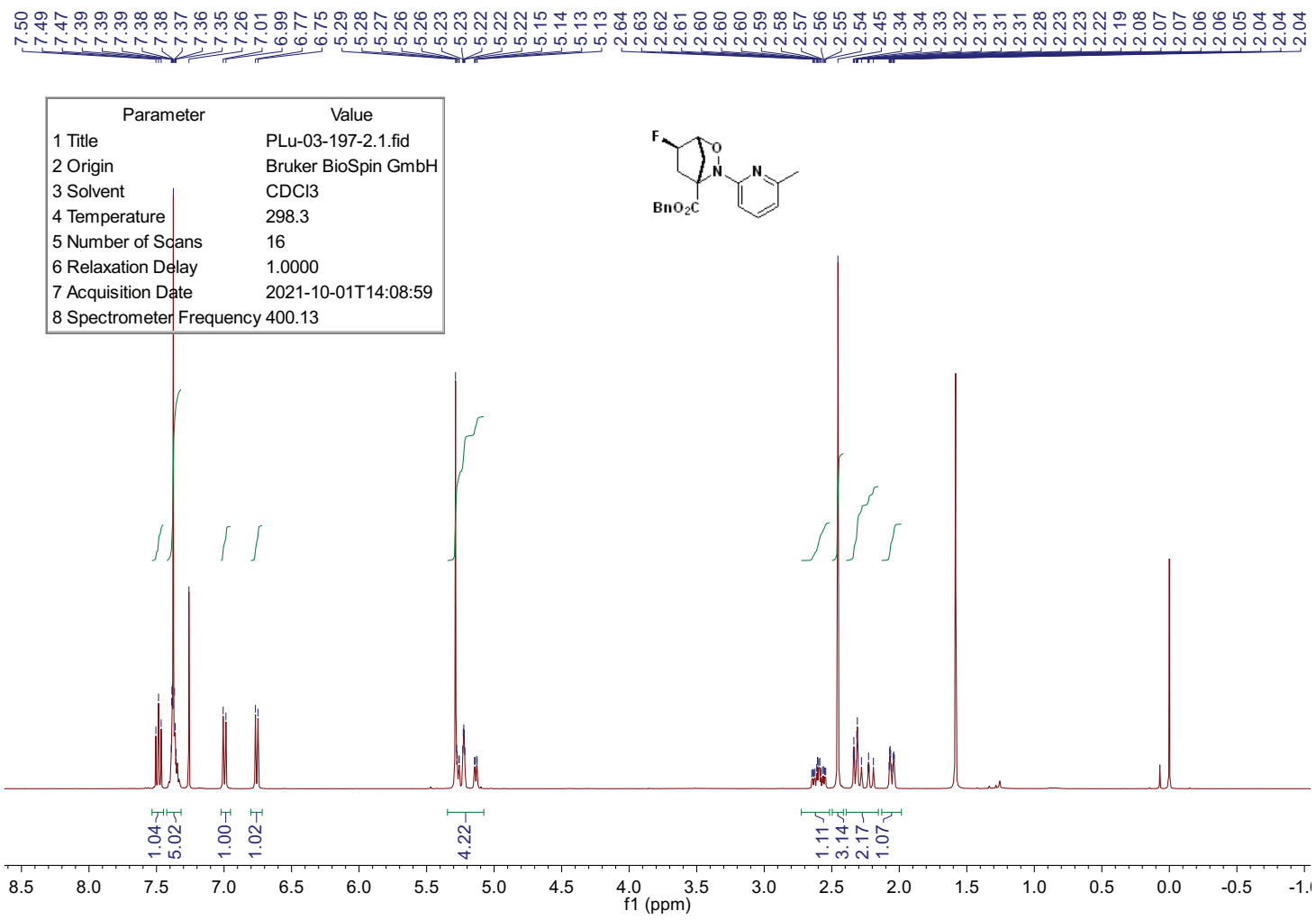
Parameter	Value
1 Title	PLu-03-196-2.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.5
5 Number of Scans	256
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-10-01T13:02:02
8 Spectrometer Frequency	100.62



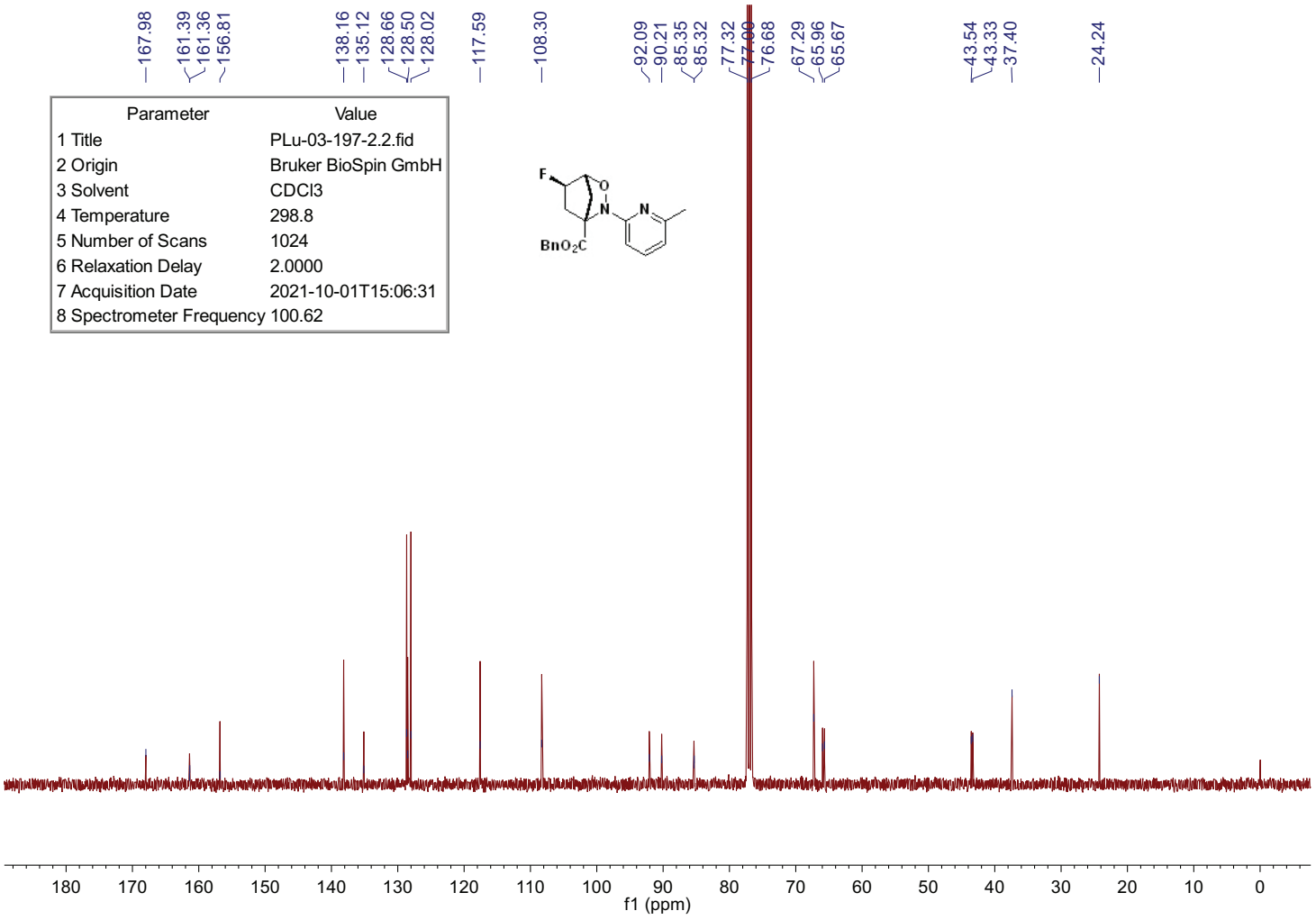
Parameter	Value
1 Title	PLu-03-195-2.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.1
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-10-01T12:22:31
8 Spectrometer Frequency	400.13



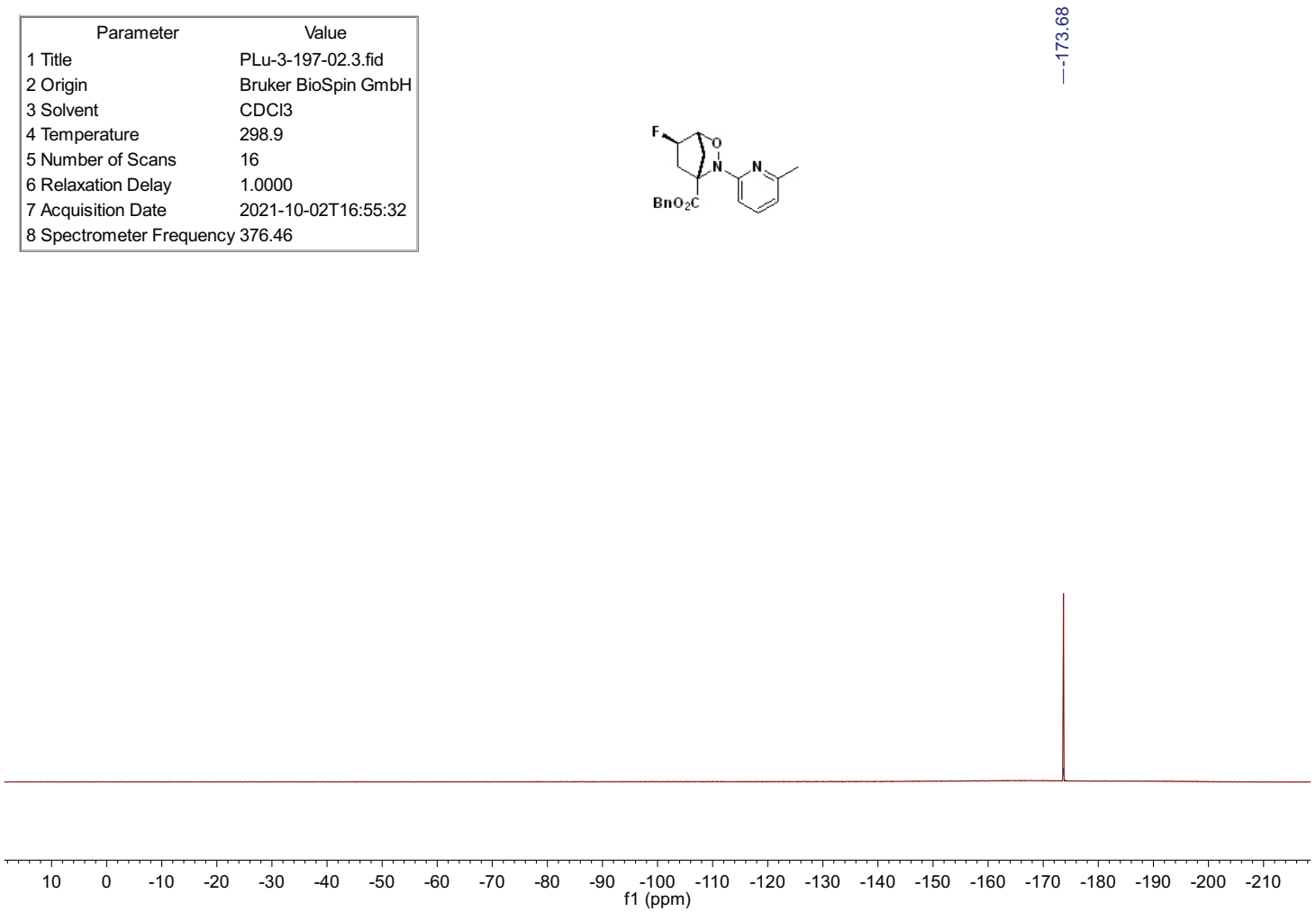
Parameter	Value
1 Title	PLu-03-195-2.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.6
5 Number of Scans	256
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-10-01T12:37:33
8 Spectrometer Frequency	100.62



Parameter	Value
1 Title	PLu-03-197-2.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.3
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-10-01T14:08:59
8 Spectrometer Frequency	400.13

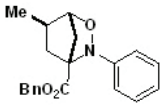


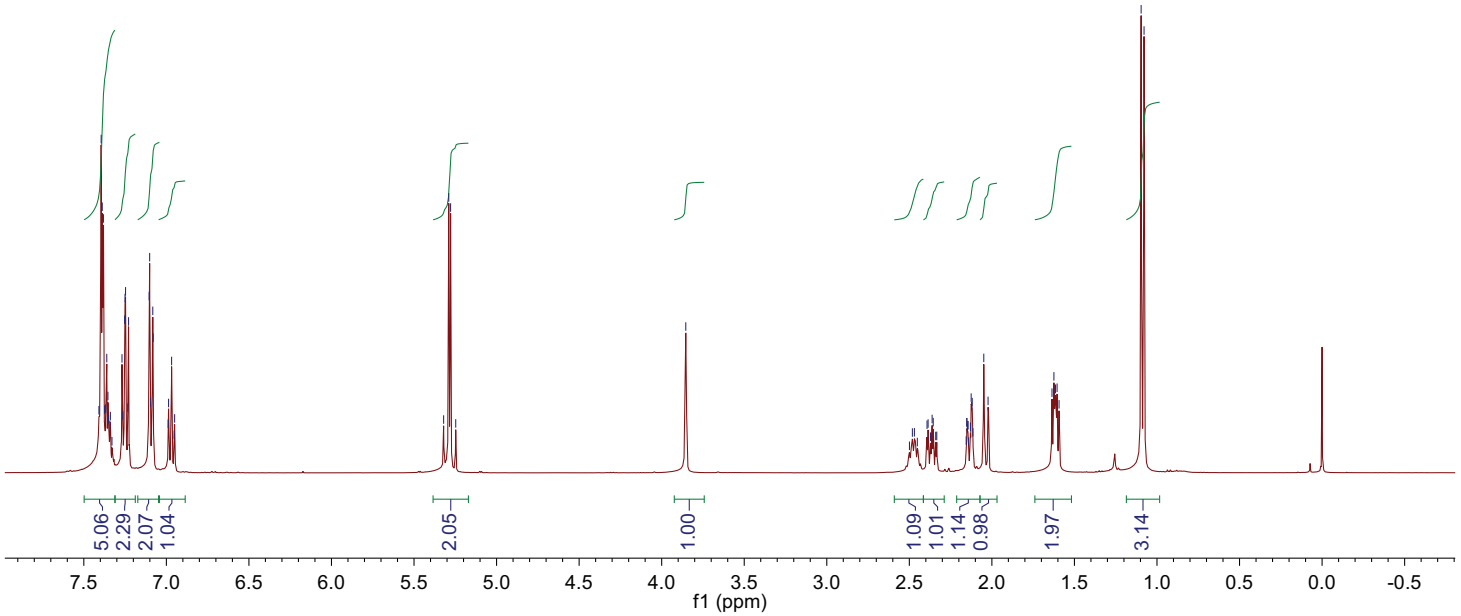
Parameter	Value
1 Title	PLu-03-197-2.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.8
5 Number of Scans	1024
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-10-01T15:06:31
8 Spectrometer Frequency	100.62



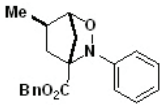
Parameter	Value
1 Title	PLu-3-197-02.3.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.9
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-10-02T16:55:32
8 Spectrometer Frequency	376.46

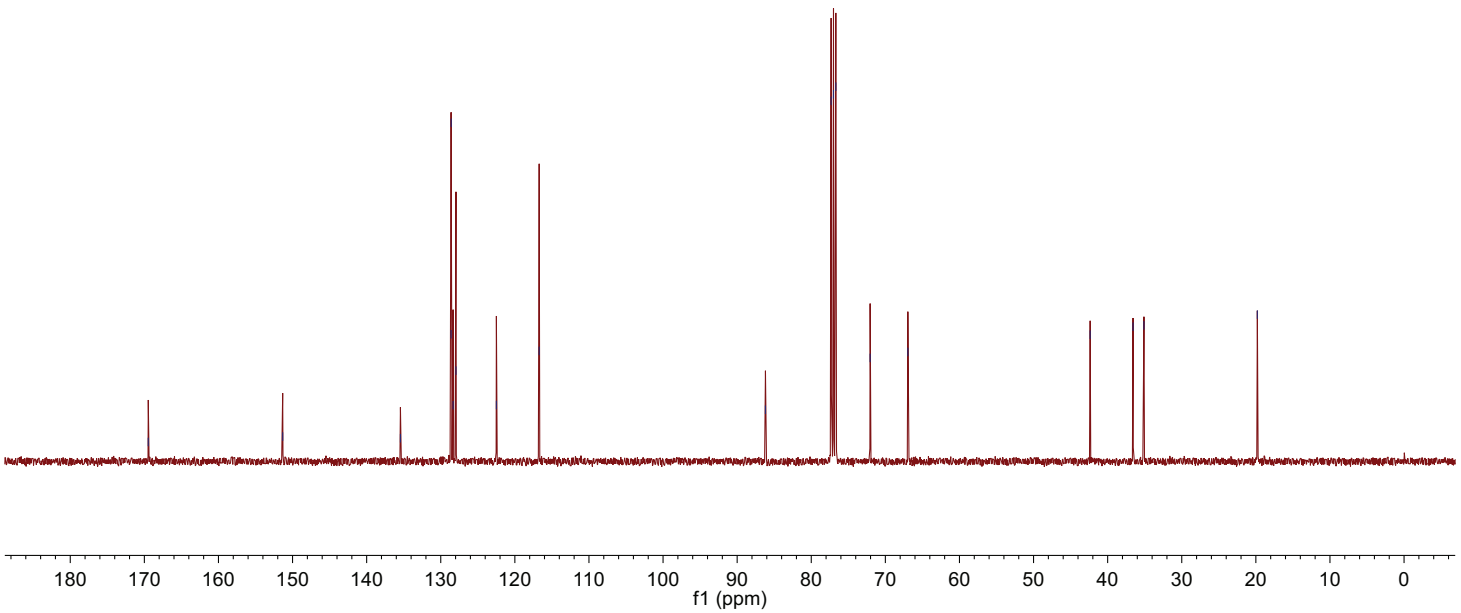
Parameter	Value
1 Title	PLu-04-6-3.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.2
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-10-10T16:05:07
8 Spectrometer Frequency	400.13

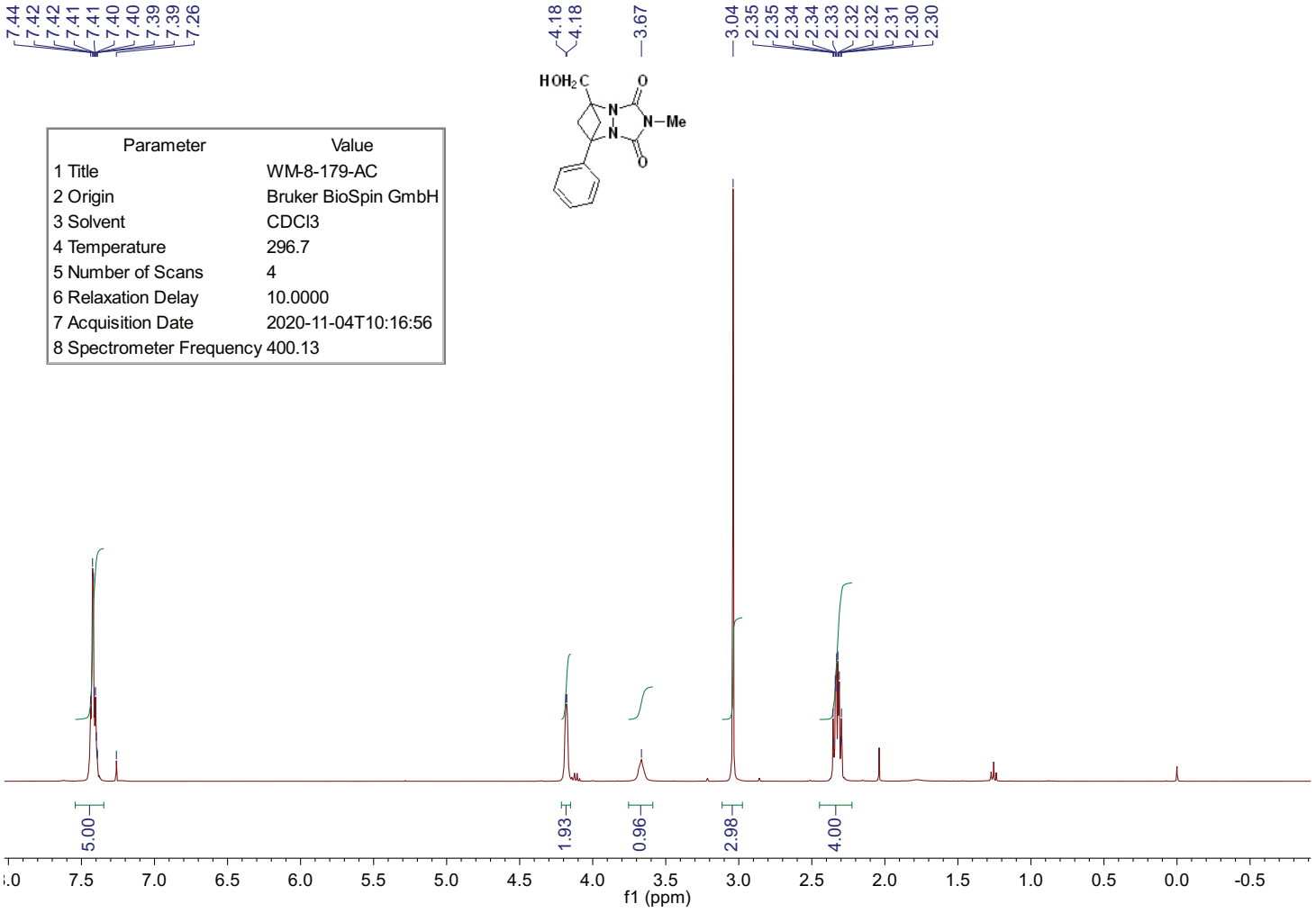


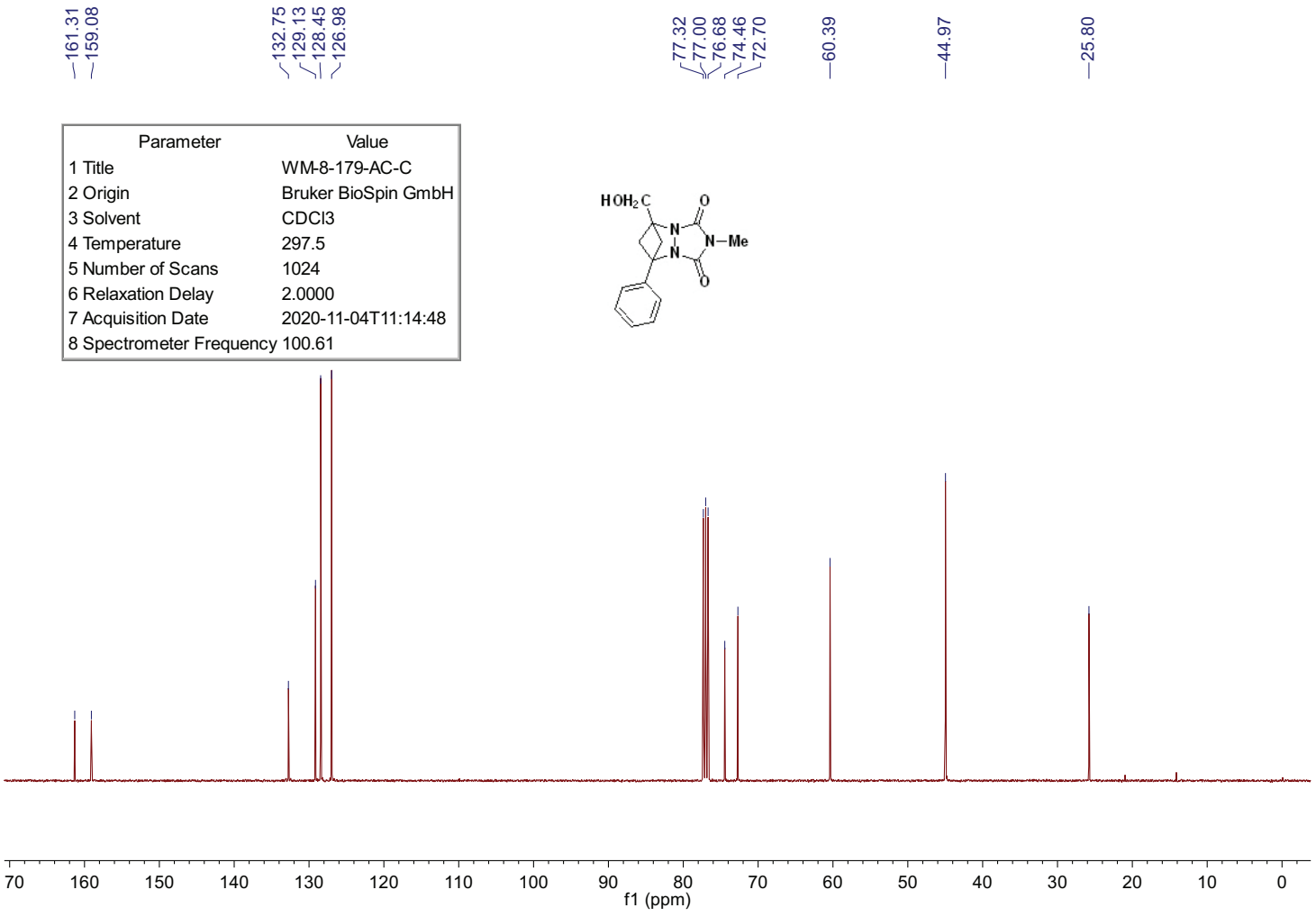


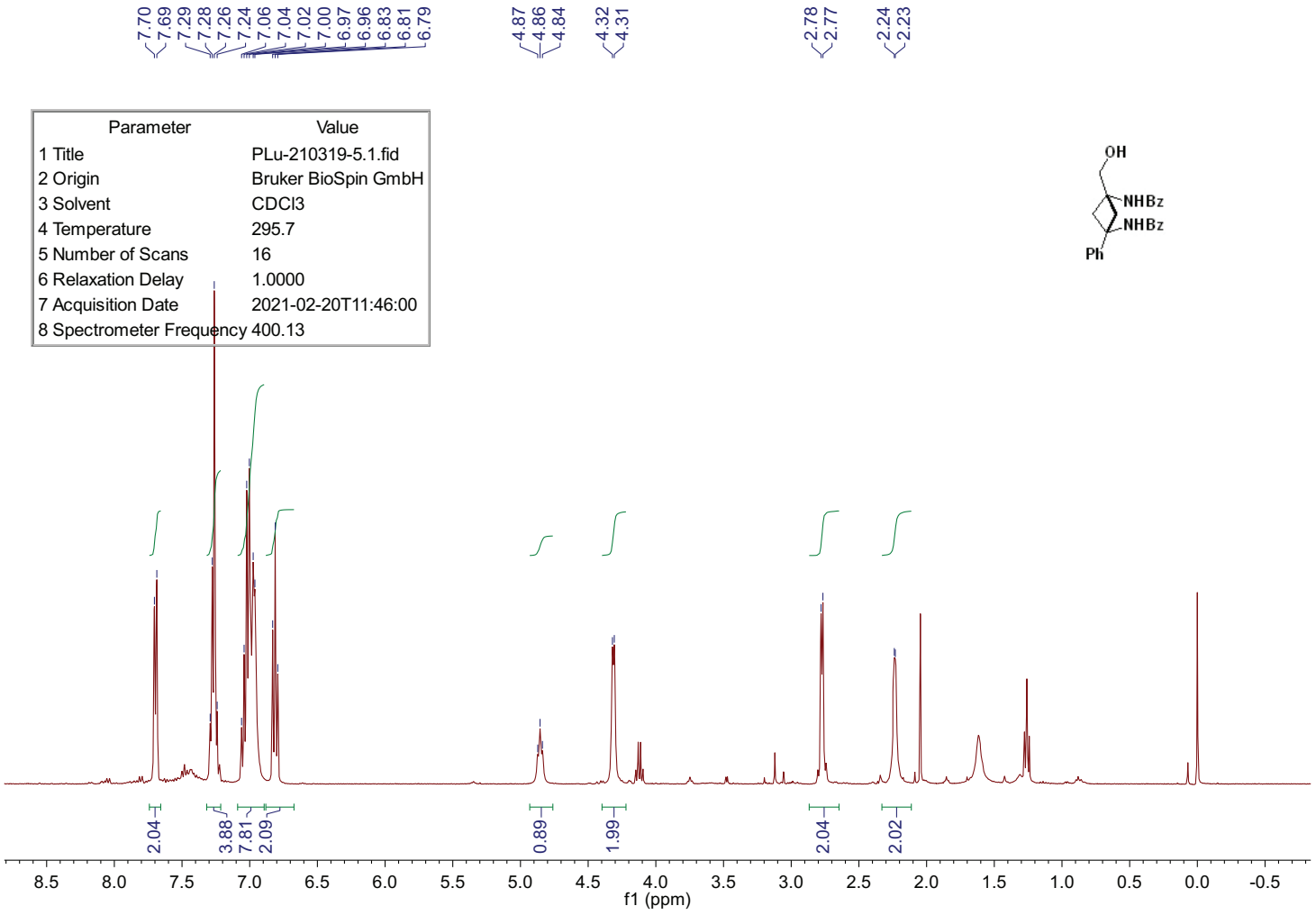
Parameter	Value
1 Title	PLu-04-6-3.3.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.0
5 Number of Scans	512
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-10-11T02:06:01
8 Spectrometer Frequency	100.62

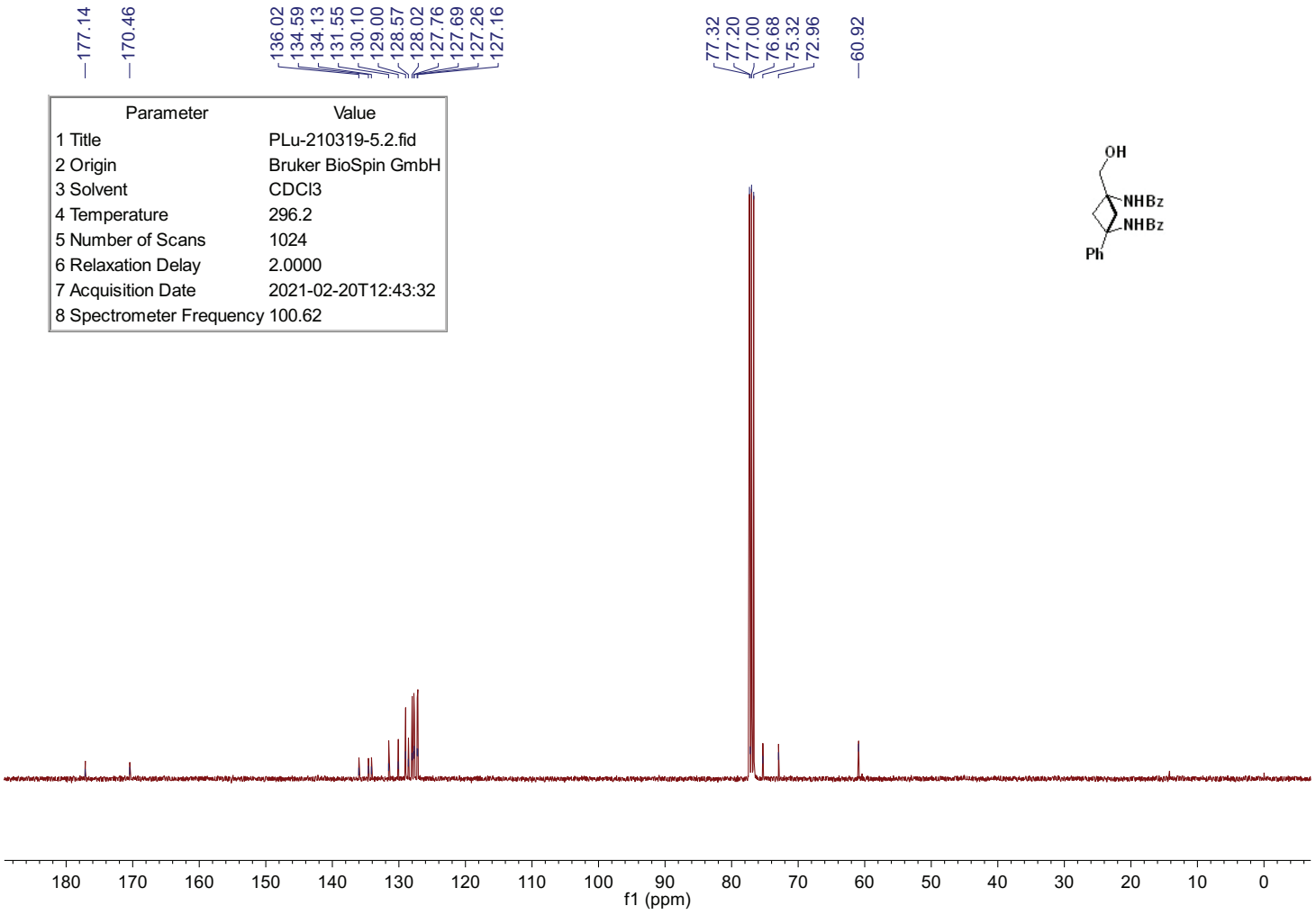


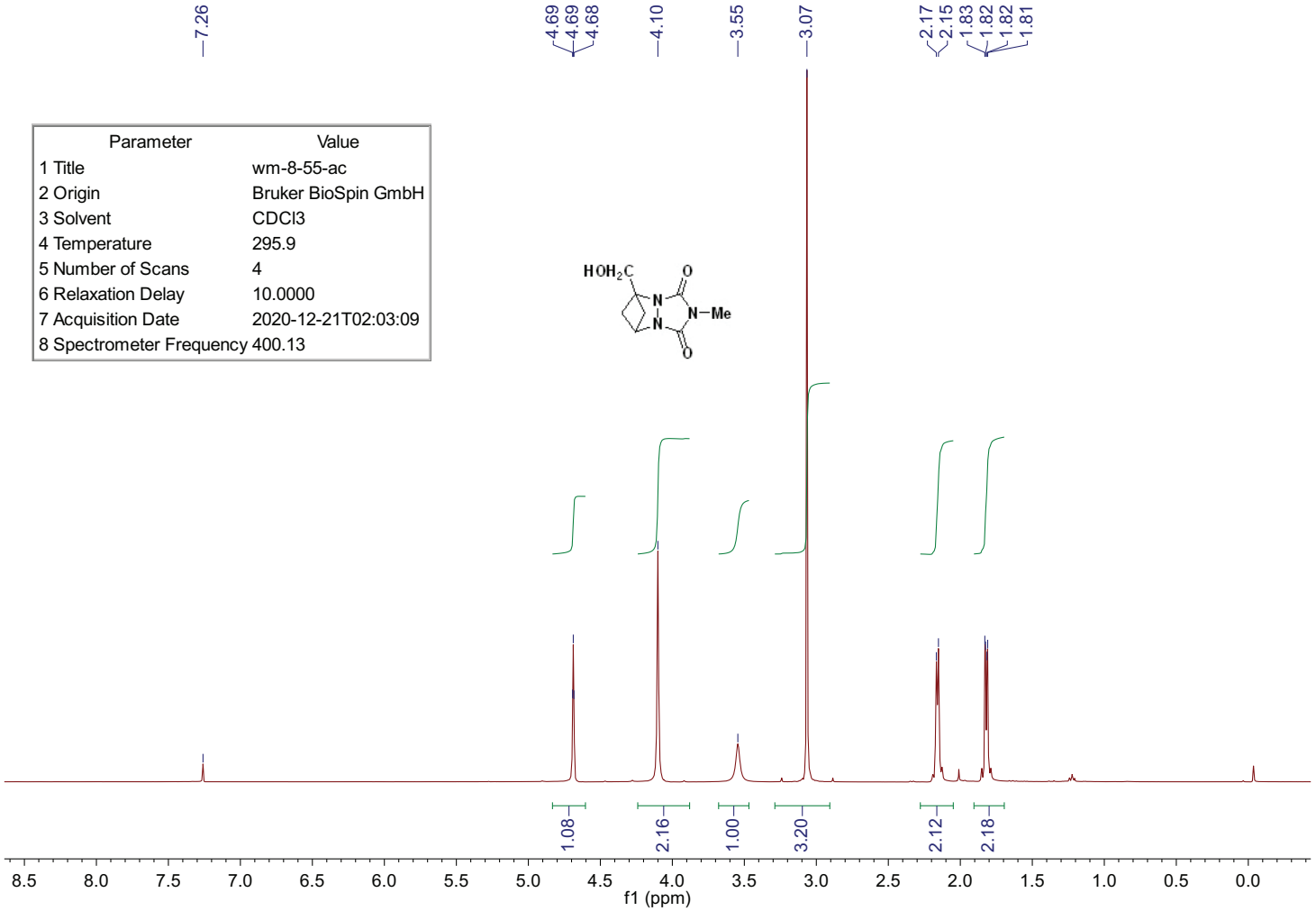


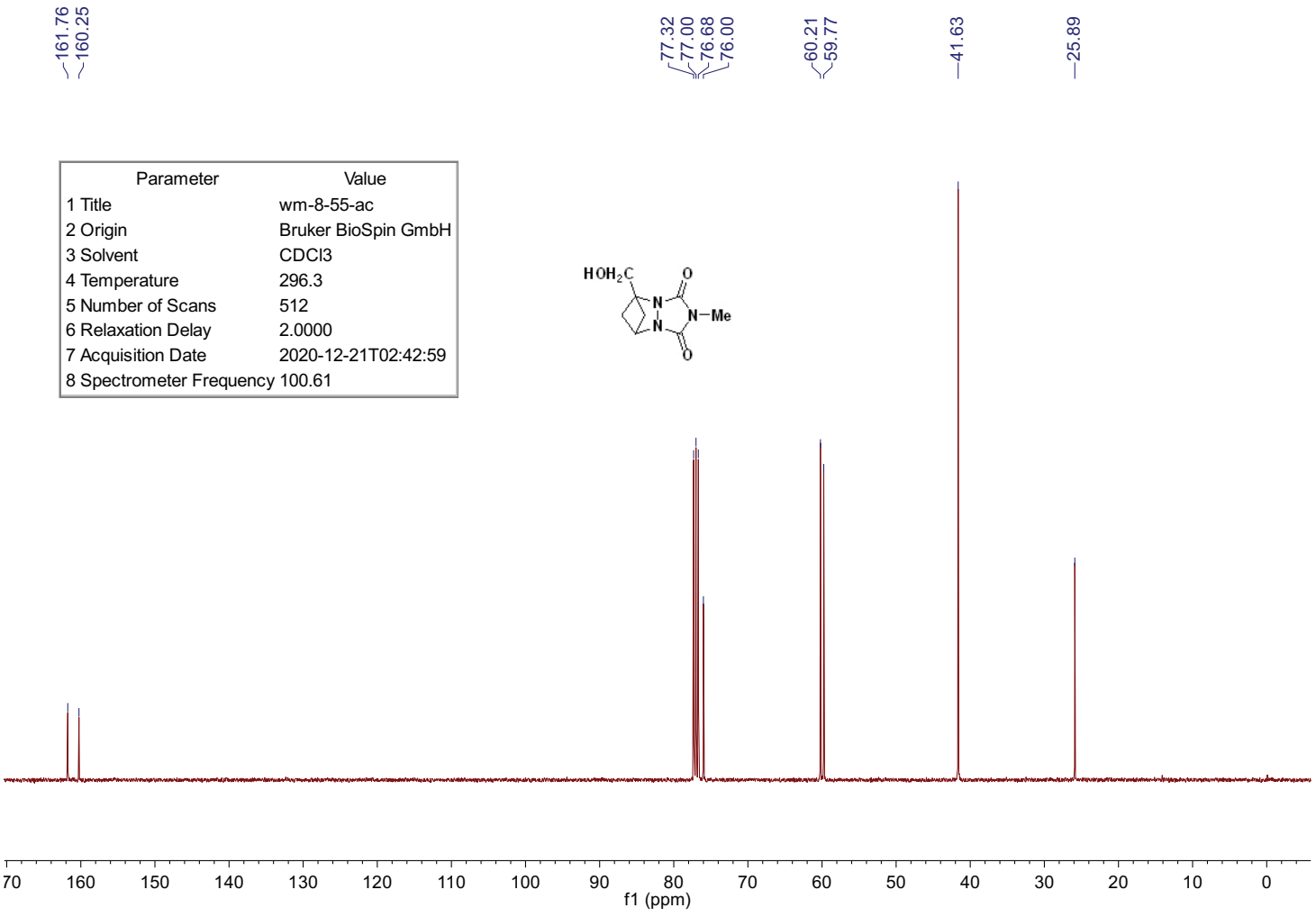

7.44
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.26
4.18
4.18
3.67
3.04
2.35
2.35
2.34
2.34
2.33
2.32
2.32
2.31
2.30
2.30
HOH2C
O
N
N
N–Me
O
Parameter Value
1 Title WM-8-179-AC
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 296.7
5 Number of Scans 4
6 Relaxation Delay 10.0000
7 Acquisition Date 2020-11-04T10:16:56
8 Spectrometer Frequency 400.13
5.00
1.93
0.96
2.98
4.00
f1 (ppm)

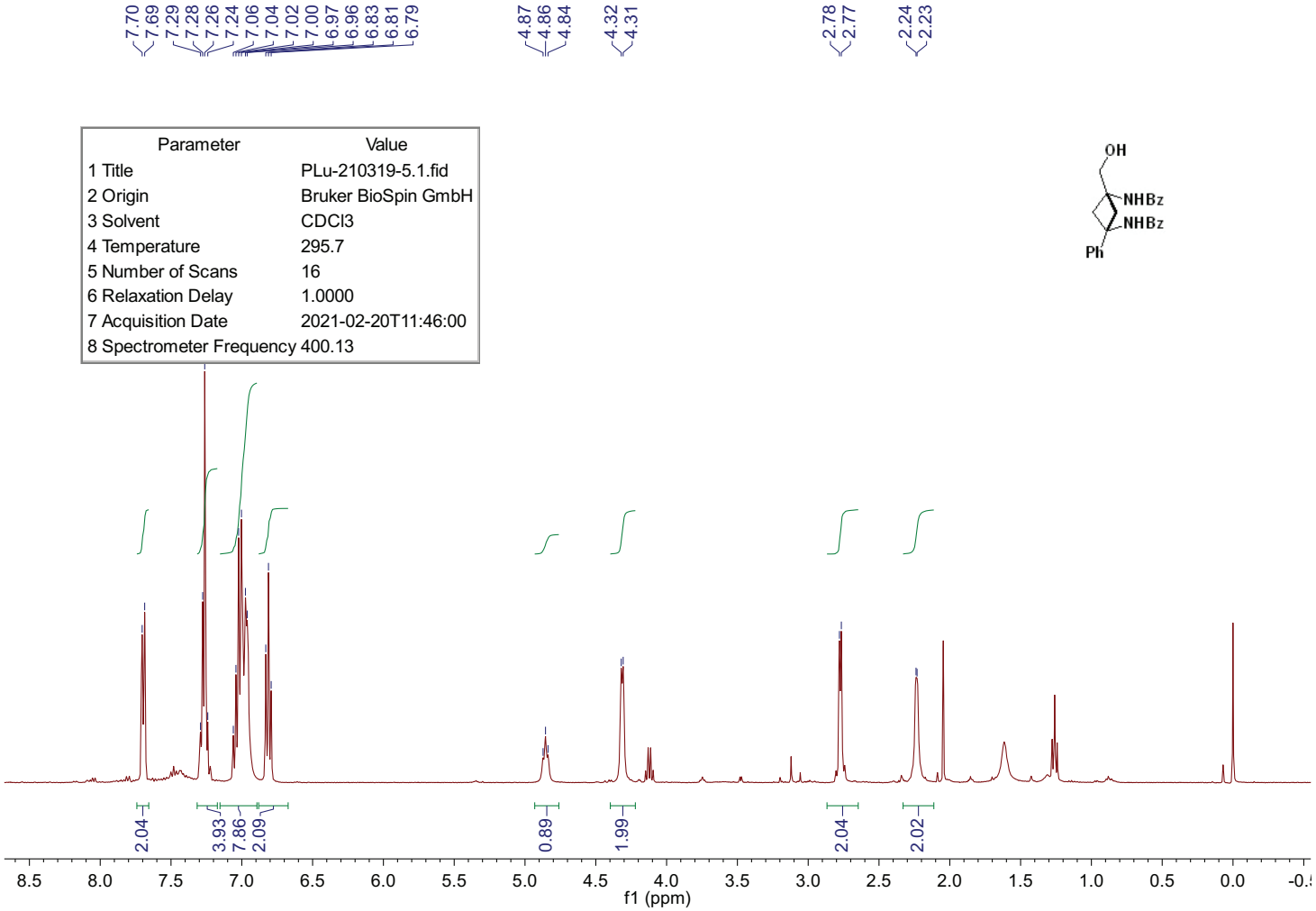

161.31
159.08
132.75
129.13
128.45
126.98
77.32
77.00
76.68
74.46
72.70
60.39
44.97
25.80
HOH2C
O
N
N
N–Me
O
Parameter Value
1 Title WM-8-179-AC-C
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 297.5
5 Number of Scans 1024
6 Relaxation Delay 2.0000
7 Acquisition Date 2020-11-04T11:14:48
8 Spectrometer Frequency 100.61
f1 (ppm)

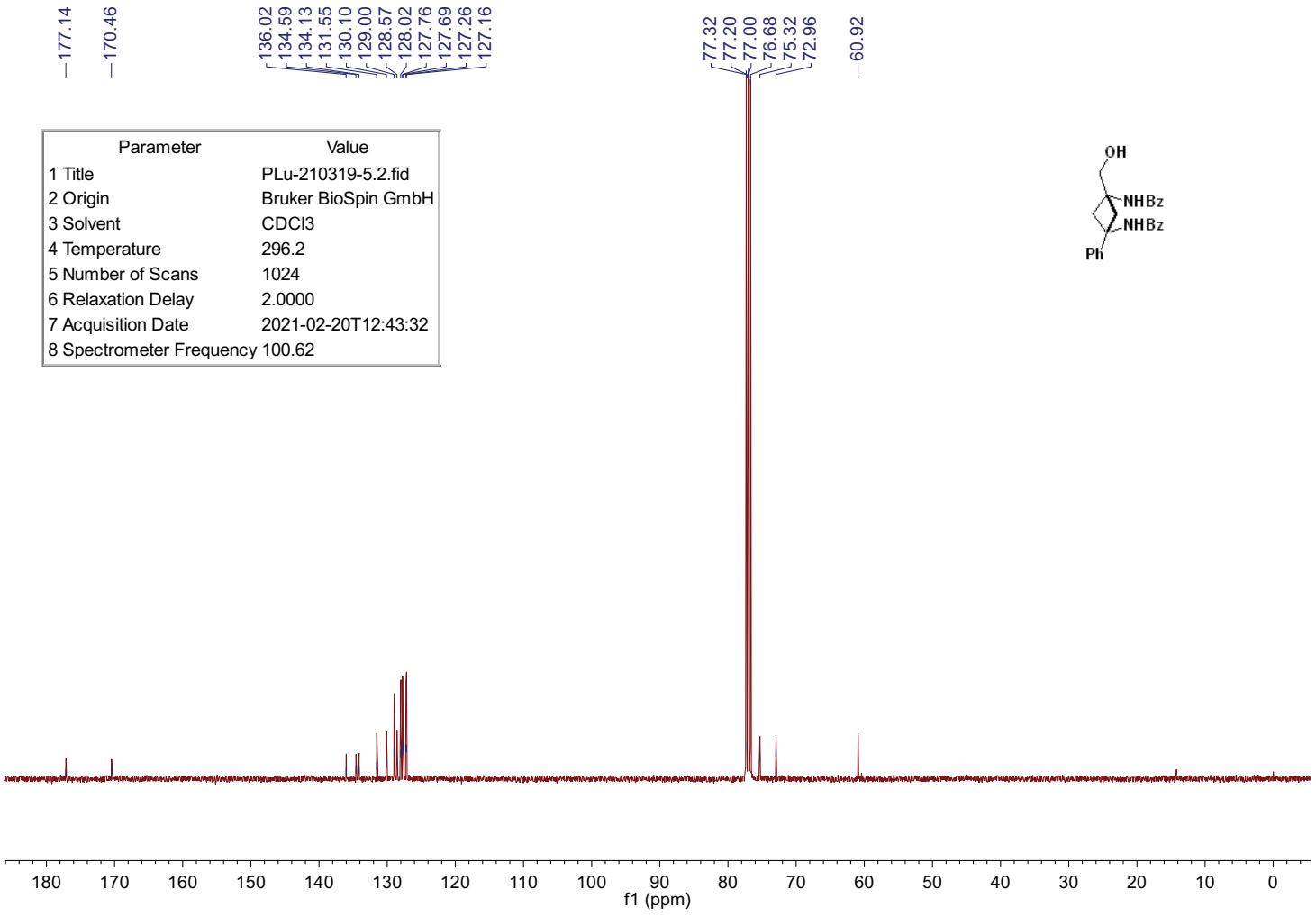

7.70
7.69
7.29
7.28
7.26
7.24
7.06
7.04
7.02
7.00
6.97
6.96
6.83
6.81
6.79
4.87
4.86
4.84
4.32
4.31
2.78
2.77
2.24
2.23
Parameter Value
1 Title PLu-210319-5.1.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 295.7
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-02-20T11:46:00
8 Spectrometer Frequency 400.13
OH
NHBz
NHBz
Ph
2.04
3.88
7.81
2.09
0.89
1.99
2.04
2.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

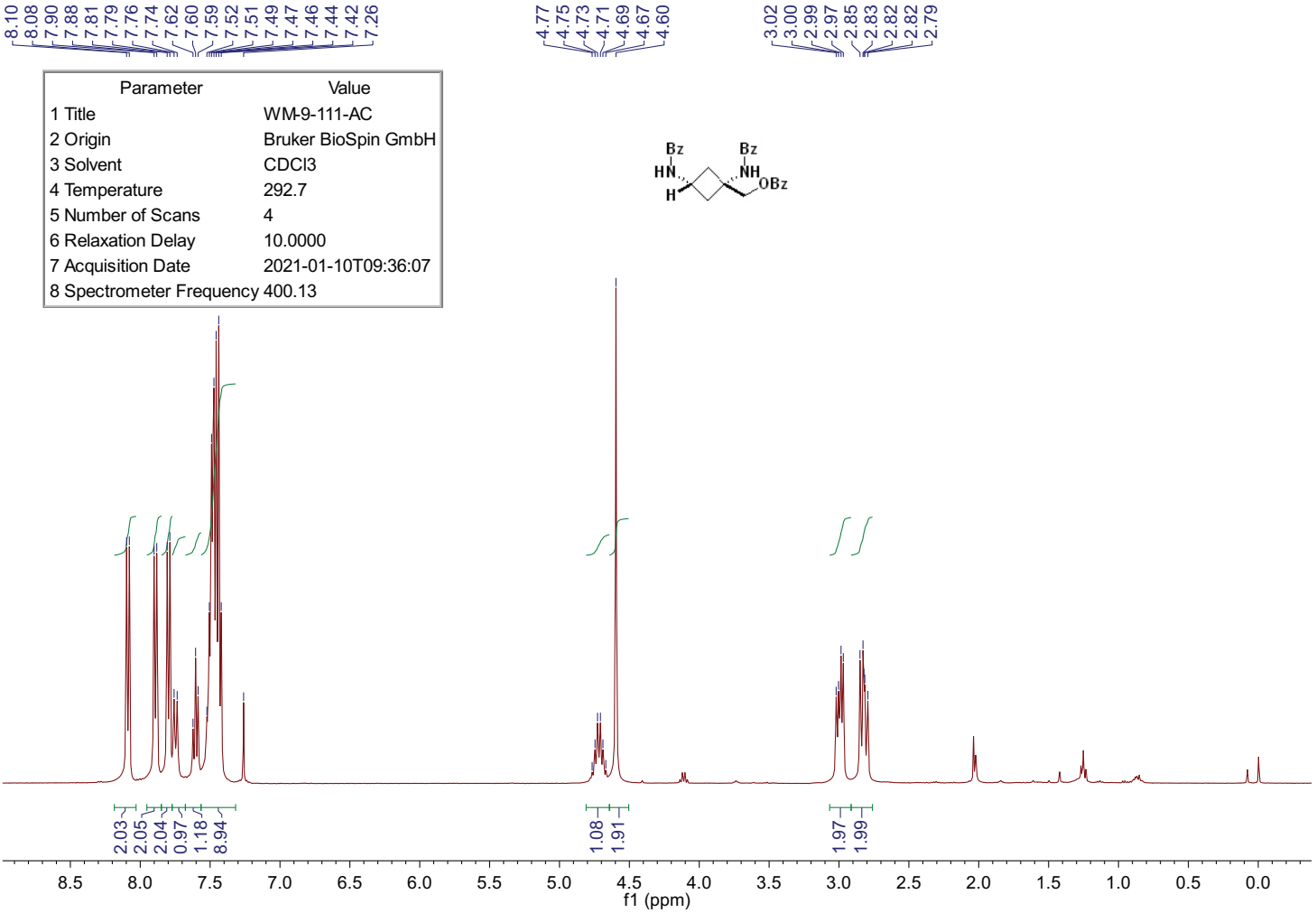

177.14
170.46
136.02
134.59
134.13
131.55
130.10
129.00
128.57
128.02
127.76
127.69
127.26
127.16
77.32
77.20
77.00
76.68
75.32
72.96
60.92
Parameter Value
1 Title PLu-210319-5.2.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 296.2
5 Number of Scans 1024
6 Relaxation Delay 2.0000
7 Acquisition Date 2021-02-20T12:43:32
8 Spectrometer Frequency 100.62
OH
NHBz
NHBz
Ph
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

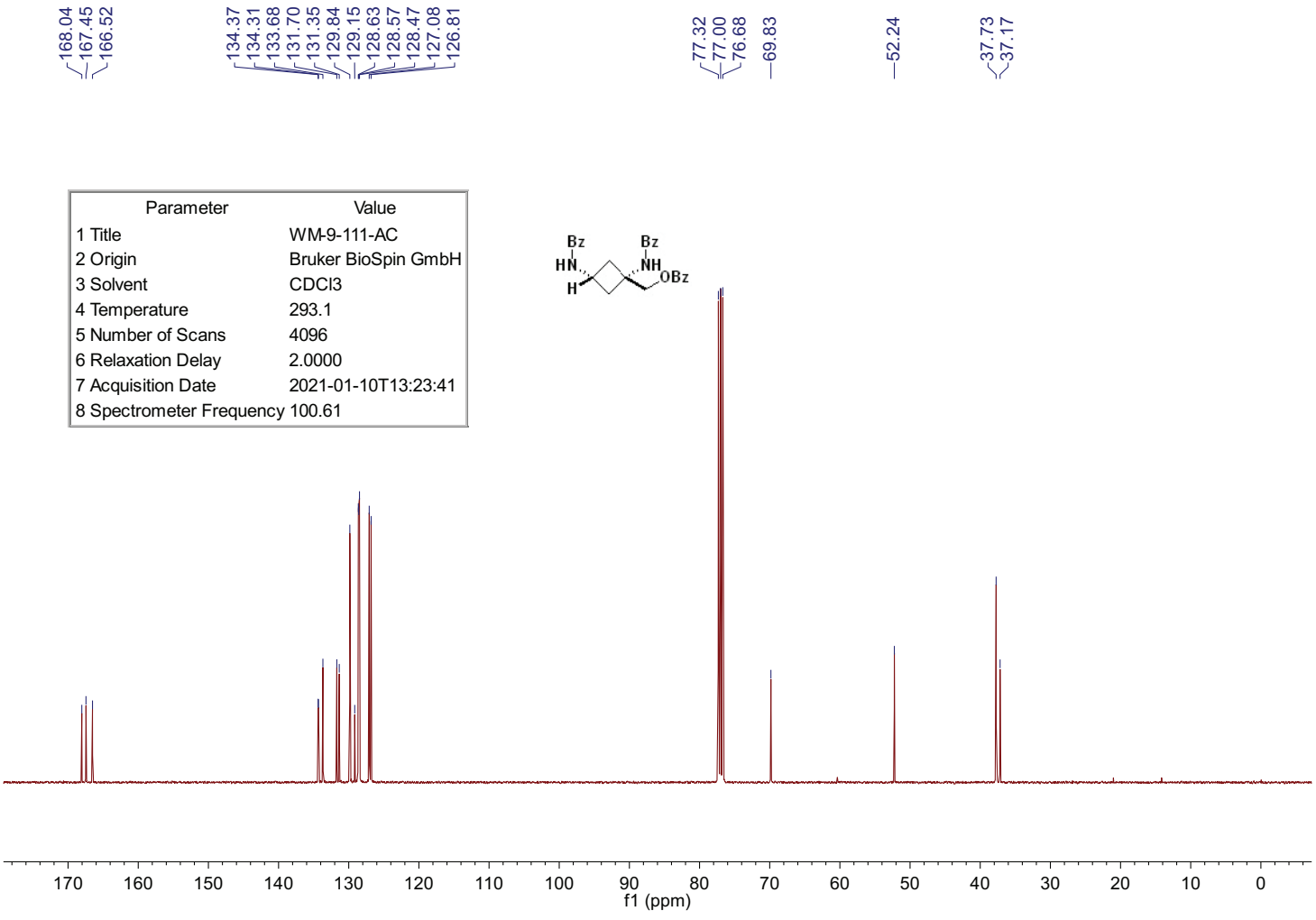

7.26
4.69
4.69
4.68
4.10
3.55
3.07
2.17
2.15
1.83
1.82
1.82
1.81
Parameter Value
1 Title wm-8-55-ac
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 295.9
5 Number of Scans 4
6 Relaxation Delay 10.0000
7 Acquisition Date 2020-12-21T02:03:09
8 Spectrometer Frequency 400.13
HOH2C
N
N
O
O
N–Me
1.08
2.16
1.00
3.20
2.12
2.18
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


161.76
160.25
77.32
77.00
76.68
76.00
60.21
59.77
41.63
25.89
Parameter Value
1 Title wm-8-55-ac
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 296.3
5 Number of Scans 512
6 Relaxation Delay 2.0000
7 Acquisition Date 2020-12-21T02:42:59
8 Spectrometer Frequency 100.61
HOH2C
N
N
O
O
N–Me
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.70
7.69
7.29
7.28
7.26
7.24
7.06
7.04
7.02
7.00
6.97
6.96
6.83
6.81
6.79
4.87
4.86
4.84
4.32
4.31
2.78
2.77
2.24
2.23
Parameter Value
1 Title PLu-210319-5.1.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 295.7
5 Number of Scans 16
6 Relaxation Delay 1.0000
7 Acquisition Date 2021-02-20T11:46:00
8 Spectrometer Frequency 400.13
OH
NHBz
NHBz
Ph
2.04
3.93
7.86
2.09
0.89
1.99
2.04
2.02
f1 (ppm)

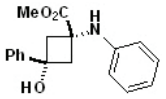

177.14
170.46
136.02
134.59
134.13
131.55
130.10
129.00
128.57
128.02
127.76
127.69
127.26
127.16
77.32
77.20
77.00
76.68
75.32
72.96
60.92
Parameter Value
1 Title PLu-210319-5.2.fid
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 296.2
5 Number of Scans 1024
6 Relaxation Delay 2.0000
7 Acquisition Date 2021-02-20T12:43:32
8 Spectrometer Frequency 100.62
OH
NHBz
NHBz
Ph
f1 (ppm)

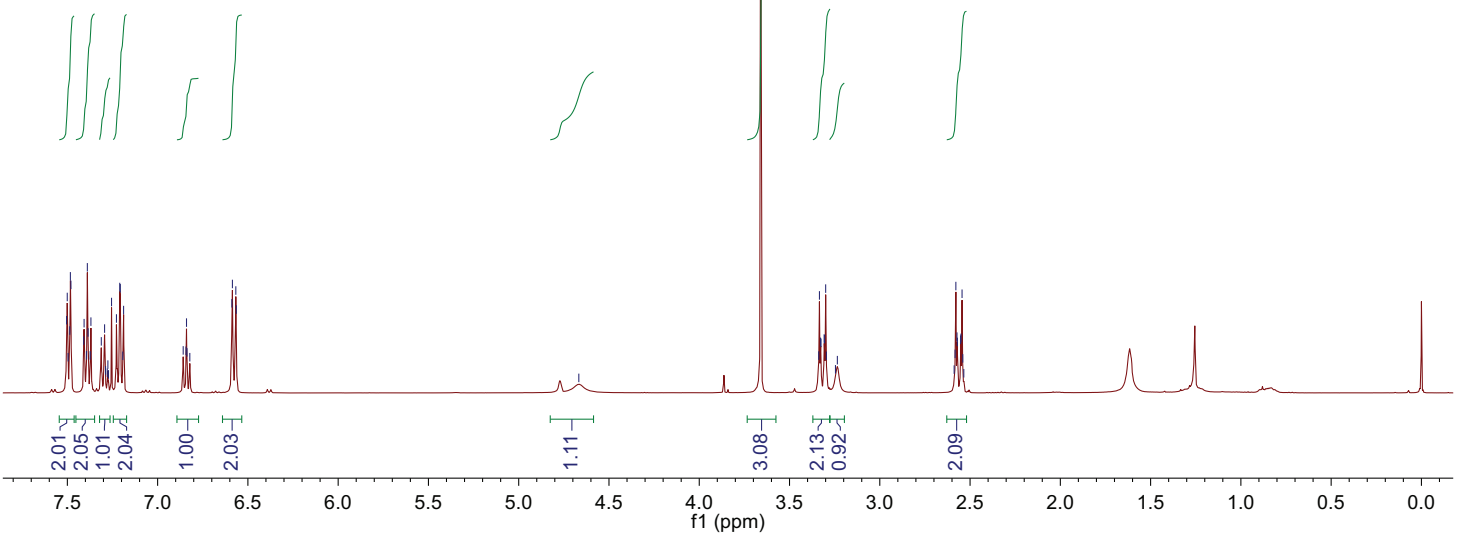

8.10 8.08 7.90 7.88 7.81 7.79 7.76 7.74 7.62 7.60 7.59 7.52 7.51 7.49 7.47 7.46 7.44 7.42 7.26
4.77 4.75 4.73 4.71 4.69 4.67 4.60
3.02 3.00 2.99 2.97 2.85 2.83 2.82 2.82 2.79
Parameter Value
1 Title WM-9-111-AC
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 292.7
5 Number of Scans 4
6 Relaxation Delay 10.0000
7 Acquisition Date 2021-01-10T09:36:07
8 Spectrometer Frequency 400.13
Bz HN H Bz NH OBz
2.03 2.05 2.04 0.97 1.18 8.94 1.08 1.91 1.97 1.99
f1 (ppm)


168.04 167.45 166.52 134.37 134.31 133.68 131.70 131.35 129.84 129.15 128.63 128.57 128.47 127.08 126.81 77.32 77.00 76.68 69.83 52.24 37.73 37.17
Parameter Value
1 Title WM-9-111-AC
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 293.1
5 Number of Scans 4096
6 Relaxation Delay 2.0000
7 Acquisition Date 2021-01-10T13:23:41
8 Spectrometer Frequency 100.61
Bz HN H Bz NH OBz
f1 (ppm)

7.50 7.50 7.50 7.49 7.48 7.48 7.41 7.41 7.39 7.39 7.39 7.37 7.37 7.31 7.29 7.29 7.28 7.28 7.27 7.26 7.23 7.21 7.21 7.19 7.19 6.86 6.84 6.84 6.84 6.82 6.59 6.59 6.57 6.56 4.67 3.66 3.34 3.33 3.33 3.33 3.31 3.31 3.30 3.30 3.25 3.24 2.59 2.58 2.58 2.57 2.57 2.55 2.54 2.54 2.53

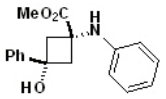
Parameter	Value
1 Title	PLu-04-7.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.1
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-10-14T02:24:10
8 Spectrometer Frequency	400.13



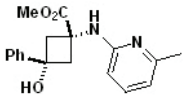


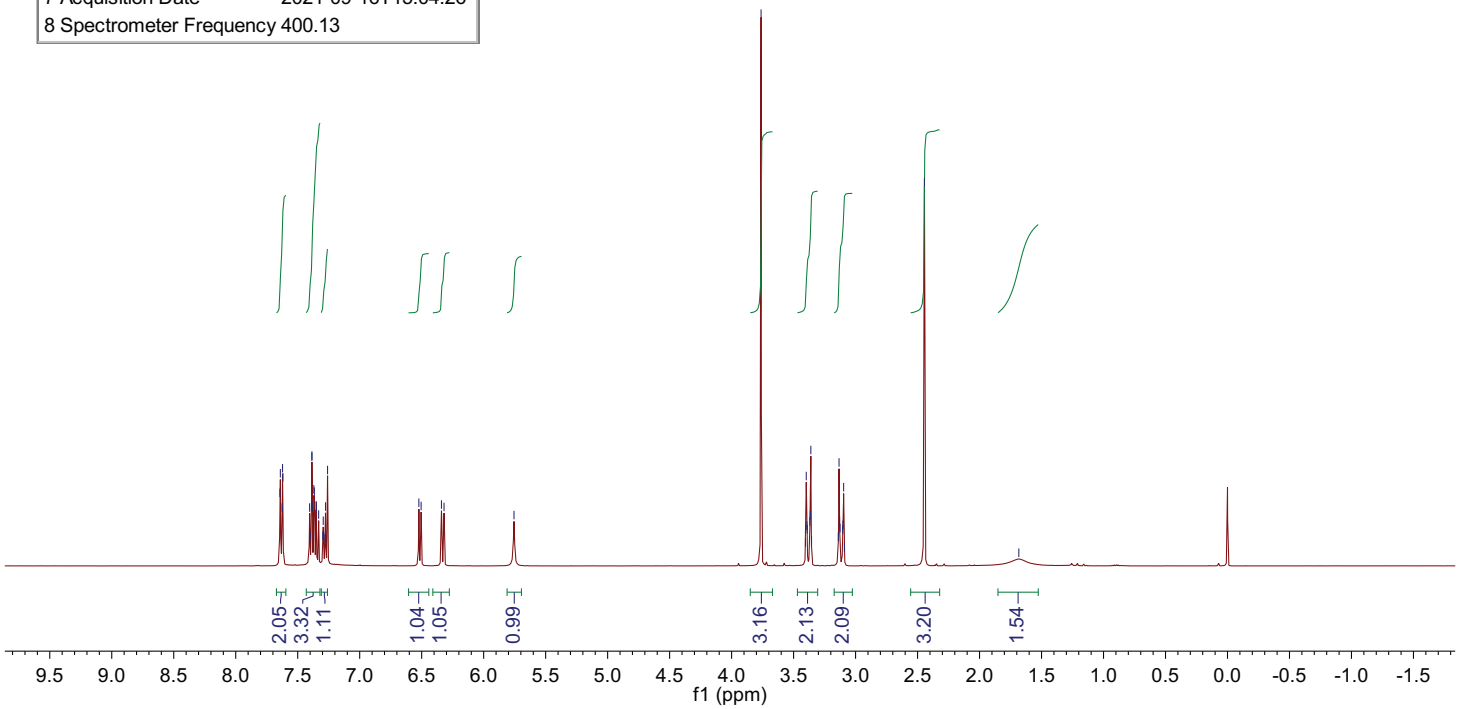
174.71 145.00 144.65 129.30 128.44 127.51 124.88 119.59 114.79 77.32 77.00 76.68 73.70 55.42 52.61 46.07

Parameter	Value
1 Title	PLu-04-7.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.6
5 Number of Scans	256
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-10-14T02:39:10
8 Spectrometer Frequency	100.62



Parameter	Value
1 Title	PLu-03-180.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.6
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-09-16T15:04:26
8 Spectrometer Frequency	400.13





Parameter	Value
1 Title	PLu-03-180.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.1
5 Number of Scans	370
6 Relaxation Delay	2.0000
7 Acquisition Date	2021-09-16T15:25:47
8 Spectrometer Frequency	100.62