Supporting Information

Visible-Light-Mediated Synthesis of 2-Oxetanes via Giese Addition to α-Oxy Radicals

Matthew Liu[1], Elvis C. McFee[1], Corinna S. Schindler*[1,2,3]

[1]Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC V6T 1Z1, Canada.
[2]Department of Biochemistry and Molecular Biology, University of British Columbia, 2350 Health Sciences Mall, Vancouver, BC V6T 1Z3, Canada.
[3]BC Cancer Research Institute, 675 West 10th Ave, Vancouver, BC V5Z 1L3, Canada.

Corresponding author: schindler@chem.ubc.ca

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General Information

General Laboratory Procedures: All air- or moisture-sensitive reactions were carried out in flame-dried glassware under an atmosphere of N_2. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F254 plates using UV light (254 or 366 nm), $KMnO_4$ stain, or CAM stain for visualization. Flash chromatography was performed using silica gel Silia Flash® 40-63 micron (230-400 mesh) from Silicycle or pre-packed columns purchased from Biotage®. Most flash chromatography was performed on Biotage Isolera or Selekt systems with self-packed or pre-packed columns, unless otherwise noted.

Instrumentation: Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on Bruker Avance Neo 500, Brucker Avance III, Bruker AV III HD, and Bruker 600txi spectrometers and are referenced to residual protic NMR solvent ($CDCl_3$: δ 7.26 ppm). Data for 1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, ddt = doublet of doublet of triplets, dq = doublet of quartets, p = pentet, t = triplet, td = triplet of doublets, q = quartet, m = multiplet, b = broad), coupling constant (Hz), integration. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker Avance Neo 500, Brucker Avance III, Bruker AV III HD, and Bruker 600txi spectrometers and are referenced to the carbon resonances of the NMR solvent ($CDCl_3$: δ 77.16 ppm). High resolution mass spectrometry (MS) data was recorded at the Mass Spectrometry/Microanalysis Facility at the University of British Columbia in Vancouver, CA on an Agilent 6545 QTOF (ESI) or (APCI). Infrared (IR) spectra were obtained using a PerkinElmer Frontier FT-IR. IR data are represented as frequency of absorption (cm^{-1}).

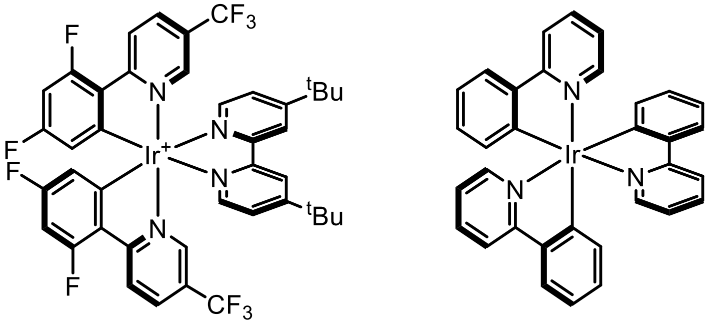
Materials: All chemicals were purchased from Sigma-Aldrich, Alfa Aeser, Acros Organics, Oakwood, TCI America, Frontier Scientific, Matric Scientific, Ark Pharm, Chem Impex International, and Strem Chemicals, and were used as received unless otherwise noted. THF, DCM, Et_2O, MeCN, toluene, EtOAc, and DMF were dried by being passed through a column of activated alumina under argon using JC-Meyer Solvent Systems. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a temperature-controlled water bath. $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ was purchased from Millipore-Sigma, Ambeed, and Strem Chemicals. fac-Ir(4'-CF_3-ppy)$_3$ was purchased from Strem Chemicals. 4CzIPN was purchased from Ambeed. MesAcr1 was purchased from Millipore-Sigma. The following oxetane starting materials were purchased from Ambeed with their respective CAS numbers listed: Oxetane-2-carboxylic acid (CAS No.: 864373-47-7), 2-Methyloxetane-2-carboxylic acid (CAS No.: 1305207-92-4), 6-Tosyl-2-oxa-6-azaspiro[3.3]heptane-1-carboxylic acid (CAS No.: 1349199-54-7). Details for the upstream synthesis of Oxetane-2-carboxylic acid can be found on https://www.ambeed.com/products/864373-47-7.html.

Photochemical Set-Up: Visible-light-mediated reactions were carried out using two 40W PR160 Kessil lights (100% intensity) that were placed on either side of a stir plate at a distance of approx. 5 cm (Supplementary Figure 1). For multiple reactions being carried out at the same time, vials were evenly distributed on the plate with a maximum of six 1-dram vials and no more than two vials side-by-side between the lights. A temperature of approx. 35 °C was maintained with the use of a fan placed in front of the stir plate. An orange- (for visible light) shield box was placed in front of the reactor for eye protection.

Figure S1: Photochemical setup for visible-light-mediated synthesis of 2-oxetanes.

Abbreviations Used: approx. = approximately, aq. = aqueous, CAM = cerium ammonium molybdate, conv. = conversion, DCM = dichloromethane, decomp. = decomposition, DMF = dimethylformamide, d.r. = diastereomeric ratio, equiv. = equivalents, ESI = electrospray ionization, ET = triplet energy, EtOAc = ethyl acetate, EtOH = ethanol, FT-IR = Fourier transform infrared, hr = hour, HRMS = high-resolution mass spectrometry, IR = infrared, MeCN = acetonitrile, min. = minute, MS = mass spectrometry, NMR = nuclear magnetic resonance, rt = room temperature, sat. = saturated, SCE = saturated calomel electrode, SM = starting material, std. = standard, temp. = temperature, THF = tetrahydrofuran, TLC = thin-layer chromatography, TOF = time-offlight, UV = ultraviolet, UV-vis = ultraviolet visible.

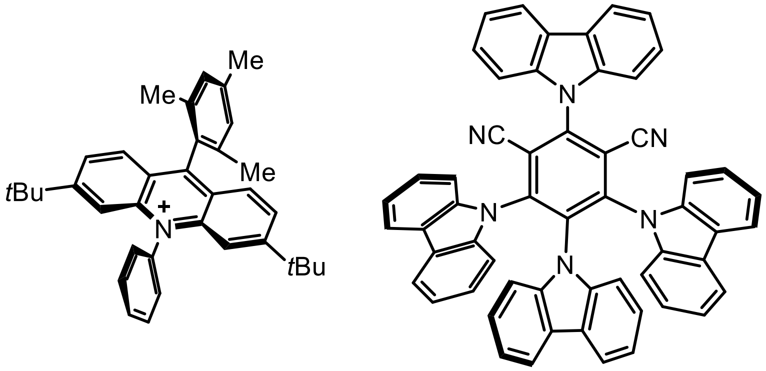
Overview of Photocatalysts Used in This Work



Ir1
$[Ir(dF(CF_3)ppy)_2(dtbbpy)]^+$
E_T = 60.1 kcal • mol-1
$E_1/_2{}^{(M+/M*)}$ = -0.89. V
$E_1/_2{}^{(M*/M-)}$ = +1.21 V

Ir2
fac-$[Ir(ppy)_3]$
E_T = 55.2 kcal • mol-1
$E_{1/2}{}^{(M+/M*)}$ = -1.73 V
$E_1/_2{}^{(M*/M-)}$ = +0.31 V

Figure S2: Overview of iridium-based photocatalysts used in this study. All potentials (given versus the saturated calomel electrode (SCE)) and triplet state energy (ET) values were obtained from the literature.[1,2]



MesAcr1

$E_{1/2}^{(M^*/M^-)} = +2.08$ V

4CzIPN

$E_T = 58.3$ kcal • mol-1

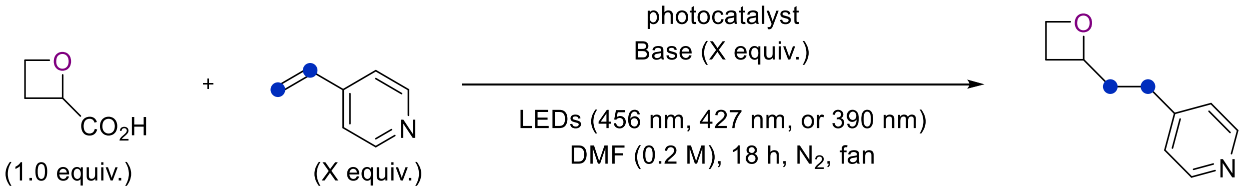
$E_{1/2}^{(M^+/M^*)} = -1.21$ V

$E_{1/2}^{(M^*/M^-)} = +1.35$ V

Figure S3: Overview of organic photocatalysts used in this study. All potentials (given versus the saturated calomel electrode (SCE)) and triplet state energy (ET) values were obtained from the literature.[3–5]

Reaction Optimization for Giese Addition to α-Oxy Radicals

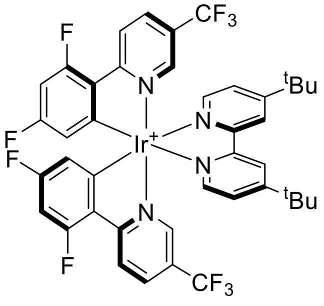
Model Reaction



General Procedure: A 1-dram vial was charged with oxetane-2-carboxylic acid (25.5 mg, 0.25 mmol, 1.0 equiv.), photocatalyst (2.5 mol %) and solvent (2.5 mL, 0.1 M). The vial was subsequently sealed with a septum-equipped cap and the reaction mixture degassed by sparging with nitrogen gas for 2 min. Then, 4-vinylpyridine (67 µL, 0.625 mmol, 2.5 equiv.) was added via syringe and the reaction stirred under irradiation with a blue or violet LED light (456 nm, 427 nm, or 390 nm) at ambient temperature (fan cooling) for 18 h. The crude reaction mixture was analyzed by ^{1}H NMR

entry	photocatalyst (mol %)	Alkene (equiv.)	Base (equiv.)	Solvent (M)	Yield (%)[a]
12	**Ir1** • PF_6 (2.5)	2.0	LiOH • H_2O (1.1)	EtOAc (0.2)	59
13	**Ir1** • PF_6 (2.5)	2.0	LiOH • H_2O (1.1)	THF (0.2)	62
14	**Ir1** • PF_6 (2.5)	2.0	LiOH • H_2O (1.1)	MeCN (0.2)	2
15	**Ir1** • PF_6 (2.5)	2.0	LiOH • H_2O (1.1)	DMF (0.4)	59
16	**Ir1** • PF_6 (2.5)	2.0	K_3PO_4 (1.1)	DMF (0.2)	70
17	**Ir1** • PF_6 (2.5)	2.0	BTMG (1.1)	DMF (0.2)	61
18	**Ir1** • PF_6 (2.5)	2.0	LiOH • H_2O (1.1)	DMF (0.2)	59
19	**Ir1** • PF_6 (2.5)	2.0	2,4,6-Collidine (1.1)	DMF (0.2)	8
20	**Ir1** • PF_6 (2.5)	2.0	Cs_2CO_3 (1.1)	THF (0.4)	n.r
21	**Ir1** • PF_6 (2.5)	2.5	Cs2CO3 (1.1)	DMF (0.05)	59
22	**Ir1** • PF_6 (2.5)	1.5	LiOH • H_2O (1.1)	DMF (0.2)	60
23	**Ir1** • PF_6 (2.5)	2.0	LiOH • H_2O (1.1)	DMF (0.1)	65
24	**Ir1** • PF_6 (2.5)	2.0	Cs_2CO_3 (1.5)	DMF (0.1)	34
25	**Ir1** • PF_6 (2.5)	2.5	Cs_2CO_3 (1.5)	DMF (0.1)	51
26	**Ir1** • PF_6 (2.5)	2.5	Cs_2CO_3 (1.5)	DMF (0.05)	57
27	**Ir1** • PF_6 (2.5)	2.5	BTMG (1.1)	DMF (0.1)	68

Conditions: [a]Yield determined by quantitative ^1H NMR analysis. 1,3,5-trimethoxybenzene used as an internal standard.



Ir1

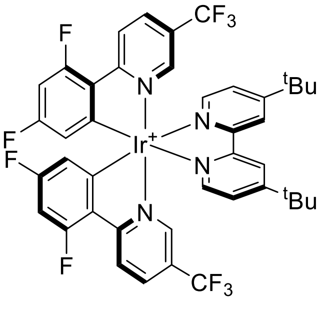
$[Ir(dF(CF_3)ppy)_2(dtbbpy)]^+$

Figure S4. Supplementary optimization figure.

Mechanistic Experiments

Control reactions:

entry	*Deviation from above conditions*	
9	No light	n.r
10	No base (LiOH • H_2O)	n.r
11	No light, 40 °C	n.r



Ir1
$[Ir(dF(CF_3)ppy)_2(dtbbpy)]^+$

Figure S5. Control reactions. Conditions: [a]Yield determined by quantitative 1H NMR analysis. 1,3,5-trimethoxybenzene used as an internal standard. [b]Average yields over 3 runs. n.r = No Reactivity.

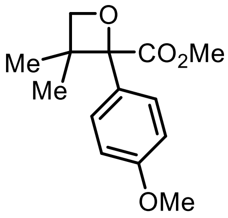
Using optimal conditions: A 1-dram vial was charged with oxetane-2-carboxylic acid (25.5 mg, 0.25 mmol, 1.0 equiv.), **Ir1** (2.5 mol %) and DMF (2.5 mL, 0.1 M). Then, 4-vinylpyridine (67 µL, 0.625 mmol, 2.5 equiv.) was added via syringe and the vial was subsequently sealed with a septum-equipped cap and the reaction mixture degassed by sparging with nitrogen gas for 2 min. The reaction stirred under irradiation with a blue LED light (456 nm) at ambient temperature (fan cooling) for 18 h. The crude reaction mixture was analyzed by ^1H NMR using 1,3,5-trimethoxybenzene as internal standard.

General Procedure for Radical Polarity Studies:

Using optimal conditions: A 1-dram vial was charged with oxetane-2-carboxylic acid (25.5 mg, 0.25 mmol, 1.0 equiv.), **Ir1** (2.5 mol %) and DMF (2.5 mL, 0.1 M). Then, alkene (0.625 mmol, 2.5 equiv.) was added via syringe and the vial was subsequently sealed with a septum-equipped cap and the reaction mixture degassed by sparging with nitrogen gas for 2 min. The reaction stirred under irradiation with a blue LED light (456 nm) at ambient temperature (fan cooling) for 18 h. The crude reaction mixture was analyzed by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard.

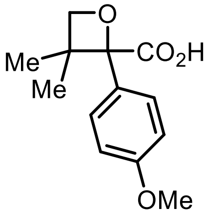
Experimental Procedures

Synthesis of aryl oxetane carboxylic acids



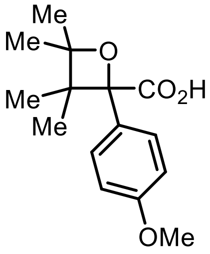
S6

methyl 2-(4-methoxyphenyl)-3,3-dimethyloxetane-2-carboxylate (S6): Prepared according to previously reported procedures. Results agree with previously reported data.[6]



S7

methyl 2-(4-methoxyphenyl)-3,3-dimethyloxetane-2-carboxylic acid (S7): Prepared according to previously reported procedures. Results agree with previously reported data.[7]



S8

2-(4-methoxyphenyl)-3,3,4,4-tetramethyloxetane-2-carboxylic acid (S8): Prepared according to previously reported procedures. Results agree with previously reported data.[7]

General procedure for the synthesis of 2-alkyl oxetanes (GP-1)

To a vial were added (Ir[dF(CF$_3$)ppy]$_2$(dtbbpy))PF$_6$ (14.0 mg, 12.5 µmol, 2.5 mol), oxetane carboxylic acid (500.0 µmol, 1.00 equiv), lithium hydroxide monohydrate (31.5 mg, 750.0 µmol, 1.5 equiv). Alkene (1.25 mmol, 2.50 equiv) and DMF (5.0 mL; anhydrous) was added. The reaction was degassed with nitrogen for two minutes then the vial was sealed and irradiated (at 456 nm, 100% LED) for 18 h with a fan. The reaction was poured into water (15 mL) and extracted with EtOAc (3 × 30 mL). The organic layers were pooled, washed with 10% LiCl solution, brine (3 × 10 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified using a Biotage® Sfar™ 10 g silica cartridge, eluting with a gradient of **0% to 100% EtOAc in CH_2Cl_2** to afford the desired oxetane as a yellow oil.

Modified general procedure A for the synthesis of 2-alkyl oxetanes (GP-1A)

To a vial were added (Ir[dF(CF_3)ppy]$_2$(dtbbpy))PF_6 (14.0 mg, 12.5 µmol, 2.5 mol), oxetane-2-carboxylic acid (51.0 mg, 500.0 µmol, 1.00 equiv), lithium hydroxide monohydrate (31.5 mg, 750.0 µmol, 1.5 equiv). Alkene (2.50 mmol, 5.00 equiv) and DMF (5.0 mL; anhydrous) was added. The reaction was degassed with nitrogen for two minutes then the vial was sealed and irradiated (at 456 nm, 100% LED) for 18 h with a fan. The reaction was poured into water (15 mL) and extracted with EtOAc (3 × 30 mL). The organic layers were pooled, washed with 10% LiCl solution, brine (3 × 10 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified using a Biotage® Sfar™ 10 g silica cartridge, eluting with a gradient of **0% to 100% EtOAc in CH_2Cl_2** to afford the desired oxetane as a yellow oil.

Modified general procedure B for the synthesis of 2-alkyl oxetanes (GP-1B)

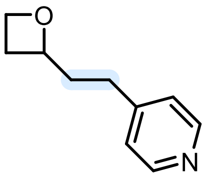
To a vial were added 4CzIPN (9.86 mg, 12.5 µmol, 2.5 mol), oxetane-2-carboxylic acid (51.0 mg, 500.0 µmol, 1.00 equiv), lithium hydroxide monohydrate (31.5 mg, 750.0 µmol, 1.5 equiv). Alkene (2.50 mmol, 5.00 equiv) and DMF (5.0 mL; anhydrous) was added. The reaction was degassed with nitrogen for two minutes then the vial was sealed and irradiated (at 390 nm, 100% LED) for 18 h with a fan. The reaction was poured into water (15 mL) and extracted with EtOAc (3 × 30 mL). The organic layers were pooled, washed with 10% LiCl solution, brine (3 × 10 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified using a Biotage® Sfar™ 10 g silica cartridge, eluting with a gradient of **0% to 100% EtOAc in CH_2Cl_2** to afford the desired oxetane as a yellow oil.

Modified general procedure C for the synthesis of 2-alkyl oxetanes (GP-1C)

To a vial were added 4CzIPN (9.86 mg, 12.5 µmol, 2.5 mol), oxetane-2-carboxylic acid (51.0 mg, 500.0 µmol, 1.00 equiv), Cesium carbonate (244.4 mg, 750.0 µmol, 1.5 equiv). Alkene (1.25 mmol, 2.50 equiv) and DMF (5.0 mL; anhydrous) was added. The reaction was degassed with nitrogen for two minutes then the vial was sealed and irradiated (at 390 nm, 100% LED) for 18 h with a fan. The reaction was poured into water (15 mL) and extracted with EtOAc (3 × 30 mL). The organic layers were pooled, washed with 10% LiCl solution, brine (3 × 10 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified using a Biotage® Sfar™ 10 g silica cartridge, eluting with a gradient of **0% to 100% EtOAc in CH_2Cl_2** to afford the desired oxetane as a yellow oil.

General procedure for 1.0 mmol scale-up reaction

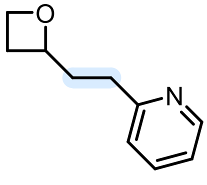
To a vial were added (Ir[dF(CF_3)ppy]$_2$(dtbbpy))PF_6 (28.0 mg, 25.0 µmol, 2.5 mol %), oxetane-2-carboxylic acid (102.1 mg, 1.0 mmol, 1.00 equiv), lithium hydroxide monohydrate (62.9 mg, 1.50 mmol, 1.5 equiv). phenyl acrylate (370.0 mg, 2.50 mmol, 2.50 equiv) and DMF (10.0 mL; anhydrous) was added. The reaction was degassed with nitrogen for two minutes then the vial was sealed and irradiated (at 456 nm, 100% LED) for 18 h with a fan. The reaction was poured into water (30 mL) and extracted with EtOAc (3 × 60 mL). The organic layers were pooled, washed with 10% LiCl solution, brine (3 × 20 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified using a Biotage® Sfar™ 25 g silica cartridge, eluting with a gradient of **0% to 100% EtOAc in CH_2Cl_2** to afford the desired oxetane as a yellow oil.



12

4-(2-(oxetan-2-yl)ethyl)pyridine (12): Prepared according to GP-1 using 4-vinylpyridine (131.0 mg, 1.25 mmol, 2.5 equiv.). Silica gel column chromatography, eluting with 0 – 100% **EtOAc in CH_2Cl_2**, afforded product 12 as a yellow oil (60.6 mg, 74%).

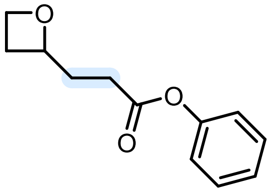
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), 5.12–5.04 (m, 1H), 4.96–4.85 (m, 2H), 3.78 (d, J = 6.4 Hz, 2H), 2.98–2.88 (m, 2H), 2.75–2.65 (m, 2H), 2.42–2.32 (m, 2H), 2.16–2.06 (m, 2H), 1.99–1.90 (m, 1H). **^{13}C NMR** (300 MHz, $CDCl_3$) δ: 150.1, 135.3, 129.1, 103.1, 79.1, 77.9, 76.4, 69.1, 38.5, 29.9, 27.4. **IR** (cm^{-1}): 2932, 2881, 1603, 1559, 1452, 1417, 1222, 1112, 1070, 992, 972, 952, 866, 843, 807; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{10}H_{13}NONa^+$ 163.0997; Found 163.1001.



13

2-(2-(oxetan-2-yl)ethyl)pyridine (13): Prepared according to GP-1 using 2-vinylpyridine (131.0 mg, 1.25 mmol, 2.5 equiv.). Silica gel column chromatography, eluting with 0 – 100% **EtOAc in CH_2Cl_2**, afforded product 13 as a yellow oil (61.3 mg, 75%).

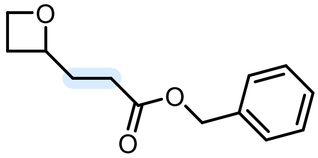
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.52 (d, J = 4.6 Hz, 1H), 7.58 (td, J = 7.7, 1.9 Hz, 1H), 7.16 (d, J = 7.8 Hz, 1H), 7.10 (ddd, J = 7.6, 4.9, 1.2 Hz, 1H), 4.86 (qd, J = 7.2, 5.8 Hz, 1H), 4.67 (ddd, J = 8.4, 7.6, 5.9 Hz, 1H), 4.53 (dt, J = 9.1, 5.9 Hz, 1H), 2.88 (ddd, J = 13.9, 9.8, 5.7 Hz, 1H), 2.66 (dddd, J = 11.0, 8.4, 7.4, 5.8 Hz, 1H), 2.35 (dddd, J = 11.0, 9.1, 7.6, 6.9 Hz, 1H), 2.22 (dddd, J = 13.1, 9.6, 7.3, 5.7 Hz, 1H), 2.18 – 2.04 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.37, 149.29, 136.35, 122.83, 121.07, 82.04, 77.22, 77.00, 76.79, 68.16, 37.71, 32.88, 27.44. **IR** (cm^{-1}): 3000, 2972, 2940, 2881, 2361, 2344, 1751, 1733, 1593, 1475, 1436, 1372, 1218, 1229, 1149, 1052, 974, 953, 868, 752; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{10}H_{13}NONa^+$ 163.0997; Found 163.1005.



14

Phenyl 3-(oxetan-2-yl)propanoate (14): Prepared according to GP-1 using phenyl acrylate (185.0 mg, 1.25 mmol, 2.5 equiv.). Silica gel column chromatography, eluting with 0 – 20% **EtOAc in CH_2Cl_2**, afforded product 13 as a yellow oil (91.8 mg, 89%).

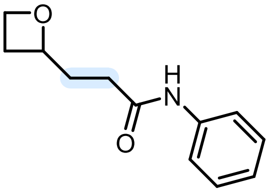
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.25 – 7.17 (m, 1H), 7.08 (dt, J = 7.8, 1.1 Hz, 2H), 4.93 (qd, J = 7.3, 5.0 Hz, 1H), 4.69 (ddd, J = 8.4, 7.5, 5.9 Hz, 1H), 4.55 (dt, J = 9.1, 5.9 Hz, 1H), 2.79 – 2.56 (m, 3H), 2.41 (ddt, J = 11.1, 9.1, 7.2 Hz, 1H), 2.27 – 2.08 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.75, 150.73, 129.42, 129.40, 125.77, 121.52, 81.30, 77.44, 77.01, 76.59, 68.16, 32.75, 29.28, 27.10. **IR** (cm^{-1}): 2972, 2885, 1753, 1594, 1494, 1457, 1366, 1331, 1296, 1229, 1218, 1194, 1163, 1023, 953, 844; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{12}H_{14}O_3Na^+$ 206.0943; Found 206.0943.



15

Benzyl 3-(oxetan-2-yl)propanoate (15): Prepared according to GP-1 using benzyl acrylate (203 mg, 1.25 mmol, 2.5 equiv.). Silica gel column chromatography, eluting with 0 – 20% **EtOAc in CH_2Cl_2**, afforded product 15 as a orange oil (81.3 mg, 74%).

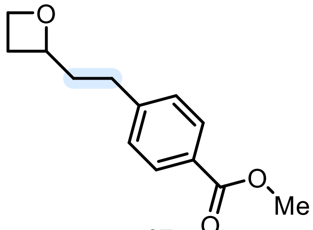
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 5.37 – 4.98 (m, 2H), 4.84 (qd, J = 7.2, 5.4 Hz, 1H), 4.73 – 4.56 (m, 1H), 4.49 (dt, J = 9.2, 5.9 Hz, 1H), 2.67 (dddd, J = 10.9, 8.3, 7.5, 5.8 Hz, 1H), 2.55 – 2.24 (m, 3H), 2.23 – 1.73 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.01, 136.00, 128.55, 128.21, 128.20, 81.37, 77.22, 77.00, 76.79, 68.08, 66.30, 32.79, 29.09, 27.10. **IR** (cm-^{1}): 2949, 2884, 1733, 1498, 1456, 1379, 1355, 1260, 1159, 1115, 1010, 973, 954, 914, 879, 738; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{13}H_{16}O_3Na^+$ 220.1099; Found 220.1095.



16

3-(oxetan-2-yl)-N-phenylpropanamide (16): Prepared according to GP-1 using *N*-phenylacrylamide (184 mg, 1.25 mmol, 2.5 equiv.). Silica gel column chromatography, eluting with 0 – 20% **EtOAc in CH_2Cl_2**, afforded product 16 as a light-yellow oil (52.7 mg, 51%).

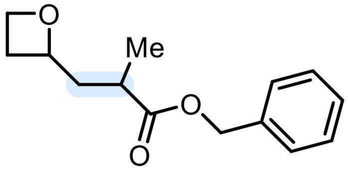
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.23 (m, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 4.93 (qd, *J* = 7.4, 4.6 Hz, 1H), 4.70 (td, *J* = 8.1, 6.1 Hz, 1H), 4.55 (dt, *J* = 9.1, 5.9 Hz, 1H), 2.81 – 2.64 (m, 1H), 2.58 – 2.30 (m, 3H), 2.26 – 2.01 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 170.83, 138.19, 128.93, 124.07, 119.75, 82.11, 77.46, 77.04, 76.61, 68.28, 33.24, 32.92, 27.18. . **IR** (cm^{-1}): 3305, 2889, 2361, 2342, 2243, 2043, 1664, 1599, 1543, 1499, 1443, 1365, 1312, 1253, 1177, 1080, 1036, 1003, 974, 951, 908, 868, 755; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{12}H_{15}NO_2Na^+$ 205.1103; Found 205.1102.



17

Methyl 4-(2-(oxetan-2-yl)ethyl)benzoate (17): Prepared according to GP-1A using methyl 4-vinylbenzoate (184 mg, 1.25 mmol, 2.5 equiv.). Silica gel column chromatography, eluting with 0 – 20% **EtOAc in CH_2Cl_2**, afforded product 17 as a light-yellow oil (83.4 mg, 76%).

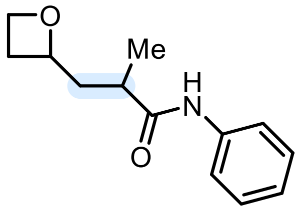
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 4.83 (qd, J = 7.3, 5.5 Hz, 1H), 4.68 (td, J = 8.0, 5.9 Hz, 1H), 4.53 (dt, J = 9.1, 5.8 Hz, 1H), 3.90 (s, 3H), 2.85 – 2.57 (m, 3H), 2.33 (ddt, J = 10.9, 9.1, 7.2 Hz, 1H), 2.15 (dddd, J = 13.2, 9.4, 7.5, 5.7 Hz, 1H), 1.96 (dddd, J = 13.4, 9.8, 6.6, 5.5 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.08, 147.18, 129.77, 128.43, 127.98, 81.72, 77.22, 77.01, 76.80, 68.16, 51.95, 39.18, 30.55, 27.46. **IR** (cm^{-1}): 2951, 2882, 1718, 1611, 1575, 1511, 1436, 1417, 1377, 1311, 1276, 1228, 1179, 1108, 1021, 973, 953, 870, 765; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{12}H_{15}NO_2Na^+$ 220.1099; Found 220.1092.



18

Benzyl 2-methyl-3-(oxetan-2-yl)propanoate (18): Prepared according to GP-1 using benzyl methacrylate (220 mg, 1.25 mmol, 2.5 equiv.). Silica gel column chromatography, eluting with 0 – 20% **EtOAc in CH_2Cl_2**, afforded product 16 as a yellow oil (86.0 mg, 73%) d.r. = 1.25:1.

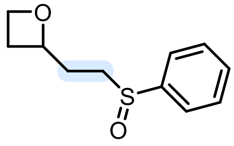
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 5.76 – 4.95 (m, 3H), 4.94 – 4.79 (m, 1H), 4.68 – 4.32 (m, 2H), 2.73 – 2.47 (m, 1H), 2.38 – 2.18 (m, 1H), 2.15 – 1.72 (m, 2H), 1.21 – 1.09 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.07, 136.14, 128.53, 128.14, 80.19, 68.13, 66.20, 41.36, 35.74, 27.81, 17.78, 16.77. **IR** (cm^{-1}): 2982, 2940, 2880, 1730, 1499, 1456, 1384, 1214, 1137, 1151, 1029, 974, 909, 843, 751, 737, 697; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{14}H_{18}O_3Na^+$ 234.1256; Found 234.1256.



19

2-methyl-3-(oxetan-2-yl)-N-phenylpropanamide (19): Prepared according to GP-1 using *N*-phenylmethacrylamide (201 mg, 1.25 mmol, 2.5 equiv.). Silica gel column chromatography, eluting with 0 – 20% **EtOAc in CH_2Cl_2**, afforded product 16 as a yellow oil (54.9 mg, 50%). Product was isolated as a single diastereomer.

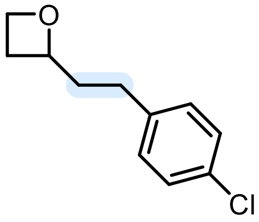
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.33 – 7.26 (m, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 5.00 – 4.85 (m, 1H), 4.69 (q, *J* = 7.4 Hz, 1H), 4.55 (q, *J* = 6.6 Hz, 1H), 2.65 (dh, *J* = 12.2, 7.2 Hz, 2H), 2.37 (t, *J* = 9.1 Hz, 1H), 2.01 (tt, *J* = 14.2, 10.1 Hz, 2H), 1.27 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 174.10, 138.14, 128.92, 124.05, 119.68, 80.75, 68.37, 42.39, 37.94, 27.67, 18.23. **IR** (cm^{-1}): 3298, 2968, 2935, 2882, 1664, 1541, 1442, 1377, 1307, 1249, 1178, 1077, 1032, 962, 945, 904, 849, 804, 754, 693; **HRMS (ESI)** m/z: [M+Na]$^+$ Calcd for $C_{13}H_{17}NO_2Na^+$ 219.1259; Found 219.1258.



20

2-(2-(phenylsulfinyl)ethyl)oxetane (20): Prepared according to GP-1C using (vinylsulfinyl)benzene (190.3 mg, 1.25 mmol, 2.5 equiv.). Silica gel column chromatography, eluting with 0 – 20% **EtOAc in CH_2Cl_2**, afforded product 16 as a yellow oil (69.3 mg, 66%).

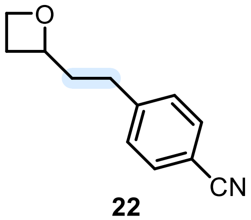
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.06 (m, 5H), 4.98 (qd, *J* = 7.4, 5.0 Hz, 1H), 4.71 (td, *J* = 8.0, 5.9 Hz, 1H), 4.55 (dt, *J* = 9.1, 5.9 Hz, 1H), 3.06 (ddd, *J* = 12.9, 9.0, 5.5 Hz, 1H), 2.93 (ddd, *J* = 13.0, 8.9, 6.6 Hz, 1H), 2.73 (dtd, *J* = 11.1, 8.1, 5.9 Hz, 1H), 2.43 – 2.34 (m, 1H), 2.20 (dtd, *J* = 13.8, 8.2, 5.4 Hz, 1H), 2.03 – 1.95 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 136.34, 129.08, 126.01, 81.27, 77.35, 77.13, 76.92, 68.40, 37.34, 29.81, 28.44, 27.40. **IR** (cm^{-1}): 2965, 2929, 2885, 2859, 1685, 1584, 1479, 1439, 1260, 1091, 1026, 800, 739, 691; **HRMS (ESI)** m/z: [M+Na]$^+$ Calcd for $C_{11}H_{14}O_2SNa^+$ 210.0715; Found 210.0713.



21

2-(4-chlorophenethyl)oxetane (21): Prepared according to GP-1B using 1-chloro-4-vinylbenzene (173 mg, 1.25 mmol, 2.5 equiv.). Silica gel column chromatography, eluting with 0 – 10% **EtOAc in Hexanes**, afforded product 16 as a yellow oil (44.2 mg, 45%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.6 Hz, 2H), 7.11 (d, 2H), 4.82 (qd, *J* = 7.3, 5.5 Hz, 1H), 4.68 (td, *J* = 8.0, 5.9 Hz, 1H), 4.52 (dt, *J* = 9.1, 5.8 Hz, 1H), 2.76 – 2.49 (m, 3H), 2.45 – 2.24 (m, 1H), 2.12 (dddd, *J* = 13.3, 9.4, 7.5, 5.7 Hz, 1H), 1.91 (dddd, *J* = 13.5, 9.8, 6.7, 5.5 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 140.05, 131.60, 129.75, 128.48, 81.73, 68.18, 39.47, 29.83, 27.46. **IR** (cm^{-1}): 3001, 2933, 2879, 1492, 1451, 1408, 1377, 1228, 1178, 1092, 1015, 975, 953, 868, 817; **HRMS (ESI)** m/z: [M+Na]$^+$ Calcd for $C_{11}H_{13}ClONa^+$ 194.0498; Found 194.0496.

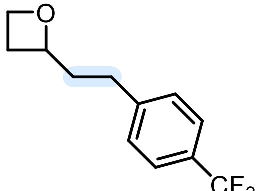


22

4-(2-(oxetan-2-yl)ethyl)benzonitrile (22): Prepared according to GP-1 using 4-Cyanostyrene (161.5 mg, 1.25 mmol, 2.5 equiv.). Silica gel column chromatography, eluting with 0 – 10% **EtOAc in Hexanes**, afforded product 22 as a yellow oil (30.9 mg, 33%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 2H), 7.33 – 7.23 (m, 2H), 4.81 (qd, *J* = 7.3, 5.2 Hz, 1H), 4.72 – 4.60 (m, 1H), 4.52 (dt, *J* = 9.1, 5.8 Hz, 1H), 2.86 – 2.59 (m, 3H), 2.42 – 2.25 (m, 1H), 2.13 (dddd, *J* = 13.4, 9.5, 7.7, 5.6 Hz, 1H), 1.93

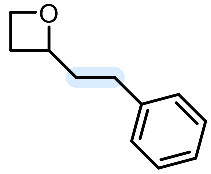
(dddd, J = 13.5, 9.8, 6.7, 5.2 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 147.36, 132.24, 129.22, 119.04, 109.85, 81.45, 77.47, 77.25, 77.04, 76.62, 68.18, 38.99, 30.71, 27.39. **IR** (cm^{-1}): 3006, 2934, 2881, 2228, 1607, 1506, 1451, 1416, 1379, 1229, 1178, 1115, 1030, 974, 953, 868, 844, 823, 733, 668; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{12}H_{13}NONa^+$ 188.1075; Found 188.1076.



23

2-(4-(trifluoromethyl)phenethyl)oxetane (23): Prepared according to GP-1 using 1-ethenyl-4-(trifluoromethyl)benzene (215 mg, 1.25 mmol, 2.5 equiv.). Silica gel column chromatography, eluting with 0 – 10% **EtOAc in Hexanes**, afforded product 23 as a yellow oil (71.8 mg, 62%).

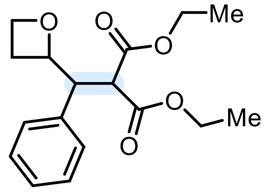
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 4.82 (td, J = 7.2, 5.3 Hz, 1H), 4.69 (td, J = 8.1, 5.9 Hz, 1H), 4.53 (dt, J = 9.0, 5.7 Hz, 1H), 2.85 – 2.57 (m, 3H), 2.34 (ddt, J = 11.1, 9.3, 7.2 Hz, 1H), 2.15 (dddd, J = 13.4, 9.6, 7.5, 5.6 Hz, 1H), 1.95 (dddd, J = 13.7, 9.9, 6.7, 5.4 Hz, 1H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ 145.91, 128.86, 125.54, 125.49, 125.44, 81.76, 77.58, 77.16, 76.74, 68.33, 39.40, 30.50, 27.56. **IR** (cm^{-1}): 2967, 2939, 2882, 1619, 1453, 1419, 1323, 1263, 1230, 1161, 1115, 1067, 1019, 976, 954, 841, 823, 734; **HRMS (APCI)** m/z: $[M+Na]^+$ Calcd for $C_{12}H_{13}F_3ONa^+$ 230.0918; Found 230.0919.



24

2-phenethyloxetane (24): Prepared according to GP-1B using styrene (260 mg, 2.50 mmol, 5.0 equiv.). Silica gel column chromatography, eluting with 0 – 10% **EtOAc in Hexanes**, afforded product 24 as a clear oil (18.2 mg, 22%).

^{1}H NMR δ 7.35 – 7.20 (m, 5H), 4.90 (p, J = 6.8 Hz, 1H), 4.81 – 4.66 (m, 1H), 4.65 – 4.51 (m, 1H), 2.71 (ddd, J = 19.5, 8.9, 5.7 Hz, 3H), 2.48 – 2.31 (m, 1H), 2.26 – 2.14 (m, 1H), 2.07 – 1.94 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.76, 128.63, 128.52, 126.00, 82.12, 77.58, 77.16, 76.74, 68.31, 39.74, 30.58, 27.65. **IR** (cm^{-1}): 3028, 2928, 2879, 1603, 1494, 1453, 1378, 1227, 1030, 976, 751, 699; **HRMS (APCI)** m/z: $[M+Na]^+$ Calca for $C_{11}H_{14}ONa^+$ 162.1045; Found 162.1045.

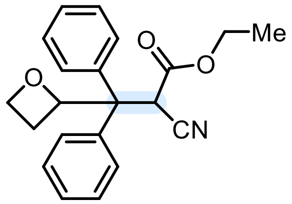


25

Diethyl 2-(oxetan-2-yl(phenyl)methyl)malonate (25): Prepared according to GP-1 using diethyl 2-benzylidenemalonate (310 mg, 1.25 mmol, 2.5 equiv.). Silica gel column chromatography, eluting with 0 – 6% **EtOAc in Pentanes**, afforded product 24 as a light yellow oil (25.6 mg, 17%, d.r.: 1.75:1).

Note: the following NMR characterization corresponds to a d.r.: of 1.75:1 **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 – 7.20 (m, 9H), 5.16 (td, J = 7.4, 4.3 Hz, 1H), 5.00 (ddd, J = 9.6, 7.6, 6.2 Hz, 1H), 4.56 – 4.44 (m, 2H), 4.26 – 4.15 (m, 3H), 4.08 (dt, J = 9.4, 5.9 Hz, 1H), 4.01

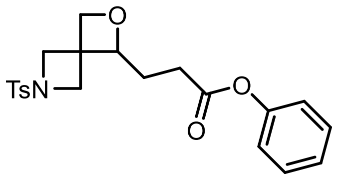
– 3.82 (m, 5H), 3.76 (d, J = 9.6 Hz, 1H), 3.58 (dd, J = 11.4, 4.3 Hz, 1H), 2.57 – 2.45 (m, 2H), 2.24 (ddtd, J = 11.0, 8.9, 6.9, 4.5 Hz, 2H), 1.28 (dt, J = 16.3, 7.1 Hz, 6H), 0.97 (t, J = 7.1 Hz, 2H), 0.92 (t, J = 7.1 Hz, 3H). **13C NMR** (151 MHz, $CDCl_3$) δ 168.36, 167.81, 137.11, 136.88, 129.84, 129.06, 128.58, 128.36, 127.60, 127.54, 83.57, 82.24, 77.37, 77.16, 76.95, 68.33, 67.95, 61.84, 61.70, 61.38, 61.33, 55.09, 53.48, 52.57, 50.48, 26.40, 24.73, 14.19, 14.09, 13.85, 13.78. **IR** (cm^{-1}): 2984, 2935, 2967. 2885, 1756, 1731, 1454, 1302, 1259, 1223, 1175, 1155, 1096, 1032, 970, 915, 802, 732; **HRMS (ESI)** m/z: $[M+Na]^+$ Calca for $C_{17}H_{22}O_5Na^+$ 306.1467; Found 306.1468.



26

ethyl 2-cyano-3-(oxetan-2-yl)-3,3-diphenylpropanoate (26): Prepared according to GP-1 using ethyl 2-cyano-3,3-diphenylacrylate (347 mg, 1.25 mmol, 2.5 equiv.). Silica gel column chromatography, eluting with 0 – 7% **EtOAc in Pentanes**, afforded product 24 as a yellow oil (23.1 mg, 14%, 1.05:1).

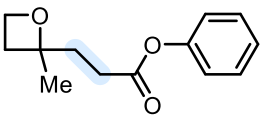
Note: the following NMR characterization corresponds to a d.r.: of 1.05:1 **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26 (s, 20H), 5.15 (t, J = 7.1 Hz, 1H), 4.95 (t, J = 7.3 Hz, 1H), 4.48 (td, J = 16.0, 8.5 Hz, 6H), 4.09 (dqd, J = 15.5, 7.5, 3.0 Hz, 4H), 3.21 – 2.94 (m, 1H), 2.61 (dq, J = 14.6, 7.7 Hz, 1H), 2.14 (tt, J = 20.4, 9.5 Hz, 2H), 1.08 (t, J = 7.1 Hz, 3H), 0.99 (t, J = 7.1 Hz, 3H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.54, 166.48, 138.81, 138.78, 137.87, 137.51, 129.48, 128.97, 128.80, 128.54, 128.09, 127.78, 117.80, 117.65, 84.92, 83.83, 77.37, 77.16, 76.95, 69.87, 68.80, 63.17, 63.10, 60.80, 59.14, 54.19, 54.15, 25.52, 23.93, 13.92, 13.80. **IR** (cm^{-1}): 2976, 2254, 1740, 1499, 1453, 1370, 1234, 1097, 1008, 980, 908, 856, 727, 702; **HRMS (APCI)** m/z: $[M+Na]^+$ Calca for $C_{21}H_{21}NO_3Na^+$ 335.1521; Found 335.1524.



27

phenyl 3-(6-tosyl-2-oxa-6-azaspiro[3.3]heptan-1-yl)propanoate (27): Prepared according to GP-1 using phenyl acrylate (185 mg, 1.25 mmol, 2.5 equiv.). Silica gel column chromatography, eluting with 0 – 40% **EtOAc in Pentanes**, afforded product 24 as a green-yellow oil (101.0 mg, 50.3%).

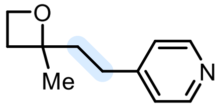
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 2H), 7.38 – 7.06 (m, 7H), 4.61 – 4.40 (m, 3H), 4.00 – 3.73 (m, 4H), 2.60 – 2.37 (m, 5H), 2.02 – 1.79 (m, 2H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.16, 150.68, 144.61, 131.31, 129.96, 129.50, 128.43, 125.95, 121.50, 86.26, 77.66, 77.37, 77.16, 76.95, 59.28, 55.80, 39.90, 28.97, 28.18, 21.64. **IR** (cm^{-1}): 3027, 2989, 2945, 2875, 1759, 1748, 1595, 1494, 1345, 1194, 1163, 1140, 1093, 970, 908, 817, 726, 690, 679; **HRMS (APCI)** m/z: $[M+Na]^+$ Calca for $C_{21}H_{23}NO_5SNa^+$ 401.1297; Found 401.1302.



28

Phenyl 3-(2-methyloxetan-2-yl)propanoate (28): Prepared according to GP-1 using phenyl acrylate (185 mg, 1.25 mmol, 2.5 equiv.). Silica gel column chromatography, eluting with 0 – 10% **EtOAc in CH_2Cl_2**, afforded product 25 as a yellow oil (105.1 mg, 95%).

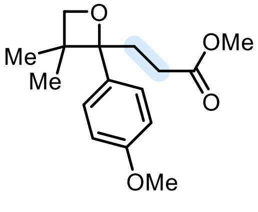
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 2H), 7.26 – 7.15 (m, 1H), 7.12 – 7.03 (m, 2H), 4.50 (ddt, *J* = 21.2, 8.9, 6.4 Hz, 2H), 2.72 (t, *J* = 7.8 Hz, 2H), 2.48 (dddd, *J* = 39.3, 11.1, 8.8, 6.8 Hz, 2H), 2.25 – 2.01 (m, 2H), 1.49 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.17, 150.80, 129.40, 125.75, 121.53, 85.48, 64.20, 36.64, 32.05, 29.12, 27.41. **IR** (cm^{-1}): 2967, 2931, 2882, 1754, 1594, 1493, 1449, 1376, 1331, 1296, 1191, 1163, 1129, 1099, 1071, 1025, 992, 960, 934, 842, 815, 748, 721, 690, 662; **HRMS (ESI)** m/z: $[M+Na]^+$ Calca for $C_{13}H_{16}O_3Na^+$ 220.1099; Found 220.1098.



29

4-(2-(2-methyloxetan-2-yl)ethyl)pyridine (29): Prepared according to GP-1 using 4-vinylpyridine (131 mg, 1.25 mmol, 2.5 equiv.). Silica gel column chromatography, eluting with 0 – 13% **EtOAc in CH_2Cl_2**, afforded product 26 as a yellow oil (66.3 mg, 75%).

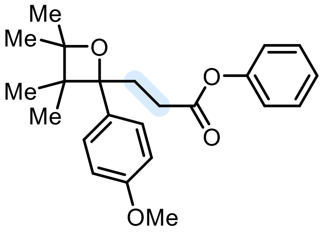
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 – 8.46 (m, 2H), 7.20 – 7.12 (m, 2H), 4.60 – 4.39 (m, 2H), 2.74 (dd, *J* = 9.6, 7.4 Hz, 2H), 2.45 (dddd, *J* = 34.1, 10.9, 8.9, 6.8 Hz, 2H), 2.11 – 1.85 (m, 2H), 1.48 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 151.44, 149.60, 123.86, 85.87, 64.25, 42.63, 32.30, 29.33, 27.27. **IR** (cm^{-1}): 2968, 2933, 2879, 2340, 2358, 1602, 1560, 1500, 1449, 1418, 1376, 1261, 1221, 1102, 992, 958, 843, 806, 729, 690; **HRMS (ESI)** m/z: $[M+Na]^+$ Calca for $C_{11}H_{15}NONa^+$ 177.1154; Found 177.1152.



30

Methyl 3-(2-(4-methoxyphenyl)-3,3-dimethyloxetan-2-yl)propanoate (30): A 1 dram vial with a stir bar was flame dried and cooled under a stream of nitrogen gas. 2-(4-methoxyphenyl)-3,3-dimethyloxetane-2-carboxylic acid (11.3 mg, 47.8 µmol, 1 equiv), cesium carbonate (21.6 mg, 66.3 µmol, 1.39 equiv,), and (Ir[dF(CF_3)ppy]$_2$(dtbbpy))PF_6 (0.6 mg, 0.5 µmol, 0.01 Eq,) were added sequentially. Vial capped with PTFE screw cap. Sides of cap/glass junction wrapped with electrical tape. DMF (0.25 mL) was added. Solution sparged for 7 min. Sparge needle pulled above solvent level. Vent needle removed. methyl acrylate (7 mg, 7 µL, 2 Eq, 0.08 mmol) added using microsyringe. The reaction was then irradiated at 456 nm, and temperature maintained around 35 C with fan cooling. The reaction mixture was transferred to a separatory funnel containing 5 mL water. Vial rinsed with water (2 x 2.5 mL), and ether (2.5 mL). Shaken, org collected. Aqueous extracted further with ether (3 x 10 mL). Combined organics washed with water (2 x 10 mL), brine (10 mL), and dried over MgSO4. Filtered and concentrated. Product isolated on a Biotage® Sfar™ 10 g silica cartridge eluting in 6 - 60% Et_2O in hexane. Product 27 was isolated as a yellow oil (5.8 mg, 44%).

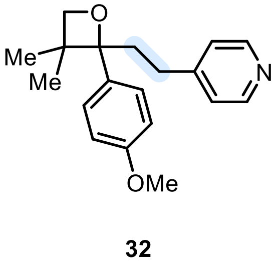
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 6.97 (m, 2H), 6.91 (d, *J* = 1.9 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 2H), 4.41 (d, *J* = 5.4 Hz, 1H), 4.08 (d, *J* = 5.4 Hz, 1H), 3.83 (s, 1H), 3.83 (s, 2H), 3.61 (s, 2H), 3.60 (s, 1H), 2.73 (d, *J* = 7.3 Hz, 0H), 2.79 – 2.66 (m, 1H), 2.33 – 2.24 (m, 1H), 2.13 (ddd, *J* = 14.2, 11.3, 4.8 Hz, 1H), 1.78 (ddd, *J* = 16.1, 11.0, 4.9 Hz, 1H), 1.31 (s, 3H), 0.83 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.64, 158.42, 134.72, 113.53, 92.49, 79.03, 55.35, 51.64, 41.96, 32.04, 30.46, 29.85, 28.55, 26.03, 21.76. **IR** (cm^{-1}): 2956, 2926, 2865, 1737, 1613, 1583, 1511, 1464, 1439, 1369, 1298, 1246, 1174, 1099, 1063, 1034, 973, 912, 887, 832, 7378, 662; **HRMS (ESI)** m/z: [$C_{16}H_{22}O_4$ - CH_2O + H] = 249.1485 (retro [2+2] fragmentation under MS ionization); Found: 249.1486.



31

phenyl 3-(2-(4-methoxyphenyl)-3,3,4,4-tetramethyloxetan-2-yl)propanoate (31): Prepared according to GP-1 with the following modifications: (4-carboxy-4-(4-methoxyphenyl)-2,3,3-trimethyloxetan-2-yl)methylium (15.8 mg, 60.0 µmol, 1.0 equiv) was used along with phenyl acrylate (22.2 mg, 150.0 µmol, 2.5 equiv.), (Ir[dF(CF_3)ppy]$_2$(dtbbpy))PF_6 (1.68 mg, 1.5 µmol, 0.025 equiv), and Lithium hydroxide monohydrate (3.78 mg, 90.0 µmol, 1.5 equiv). DMF (0.6 mL) was added. Silica gel column chromatography, eluting with 0 – 16% **Et_2O in Hexanes**, afforded product 28 as a colourless oil (10.5 mg, 48%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 – 7.41 (m, 1H), 7.46 – 7.28 (m, 2H), 7.23 – 7.15 (m, 1H), 7.03 – 6.97 (m, 2H), 6.90 (d, *J* = 8.1 Hz, 2H), 3.82 (s, 3H), 2.72 (ddd, *J* = 13.6, 10.8, 4.9 Hz, 1H), 2.52 – 2.44 (m, 1H), 2.23 (ddd, *J* = 13.6, 11.1, 5.2 Hz, 1H), 1.98 – 1.89 (m, 1H), 1.47 (s, 3H), 1.31 (s, 3H), 1.26 (s, 3H), 0.72 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.58, 158.26, 150.82, 135.93, 129.24, 125.54, 121.56, 87.86, 83.77, 55.21, 44.21, 34.11, 28.79, 27.06, 26.34, 23.86, 20.01. **IR** (cm^{-1}): 2999, 2962, 2924, 1758, 1611, 1595, 1509, 1494, 1457, 1393, 1366, 1302, 1246, 1195, 1163, 1130, 1112, 1086, 1053, 1033, 988, 852, 832, 813, 754, 717; **HRMS (ESI)** m/z: $C_{23}H_{28}O_4Na^+$ = 368.1988; Found: 368.1988.



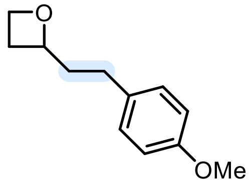
32

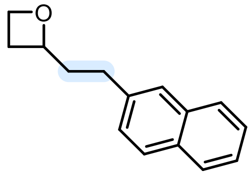
4-(2-(2-(4-methoxyphenyl)-3,3-dimethyloxetan-2-yl)ethyl)pyridine (32): Prepared according to GP-1 with the following modifications: 2-(4-methoxyphenyl)-3,3-dimethyloxetane-2-carboxylic acid (34.7 mg, 0.147 mmol , 1.0 equiv) was used along with 4-vinylpyridine (38.6 mg, 0.367 mmol, 2.5 equiv.), (Ir[dF(CF_3)ppy]$_2$(dtbbpy))PF_6 (4.12 mg, 3.675 µmol, 0.025 equiv), and Lithium hydroxide monohydrate (9.25 mg, 0.220 mmol, 1.5 equiv). DMF (1.47 mL) was added. Silica gel column chromatography, eluting with 0 – 17% **EtOAc in Hexanes**, afforded product 29 as a yellow oil (15.7 mg, 36%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 – 8.40 (m, 2H), 7.18 (s, 2H), 7.08 – 7.02 (m, 2H), 6.95 – 6.88 (m, 2H), 4.40 (d, J = 5.5 Hz, 1H), 4.11 (d, J = 5.5 Hz, 1H), 3.83 (s, 3H), 2.65 – 2.49 (m, 2H), 2.15 – 1.92 (m, 2H), 1.26 (s, 3H), 0.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.35, 152.52, 149.12, 134.90, 125.82, 124.06, 113.53, 92.87, 79.03, 55.27, 41.96, 38.02, 29.26, 25.92, 21.74. **IR** (cm^{-1}): 2957, 2866, 174, 1602, 1582, 1559, 1510, 1464, 1388, 1373, 1300, 1245, 1174, 1093, 1031, 973, 909, 831, 807, 794, 734 676; **HRMS (ESI)** m/z: $C_{19}H_{23}NO_2Na^+$ = 297.1729; Found: 297.1727.

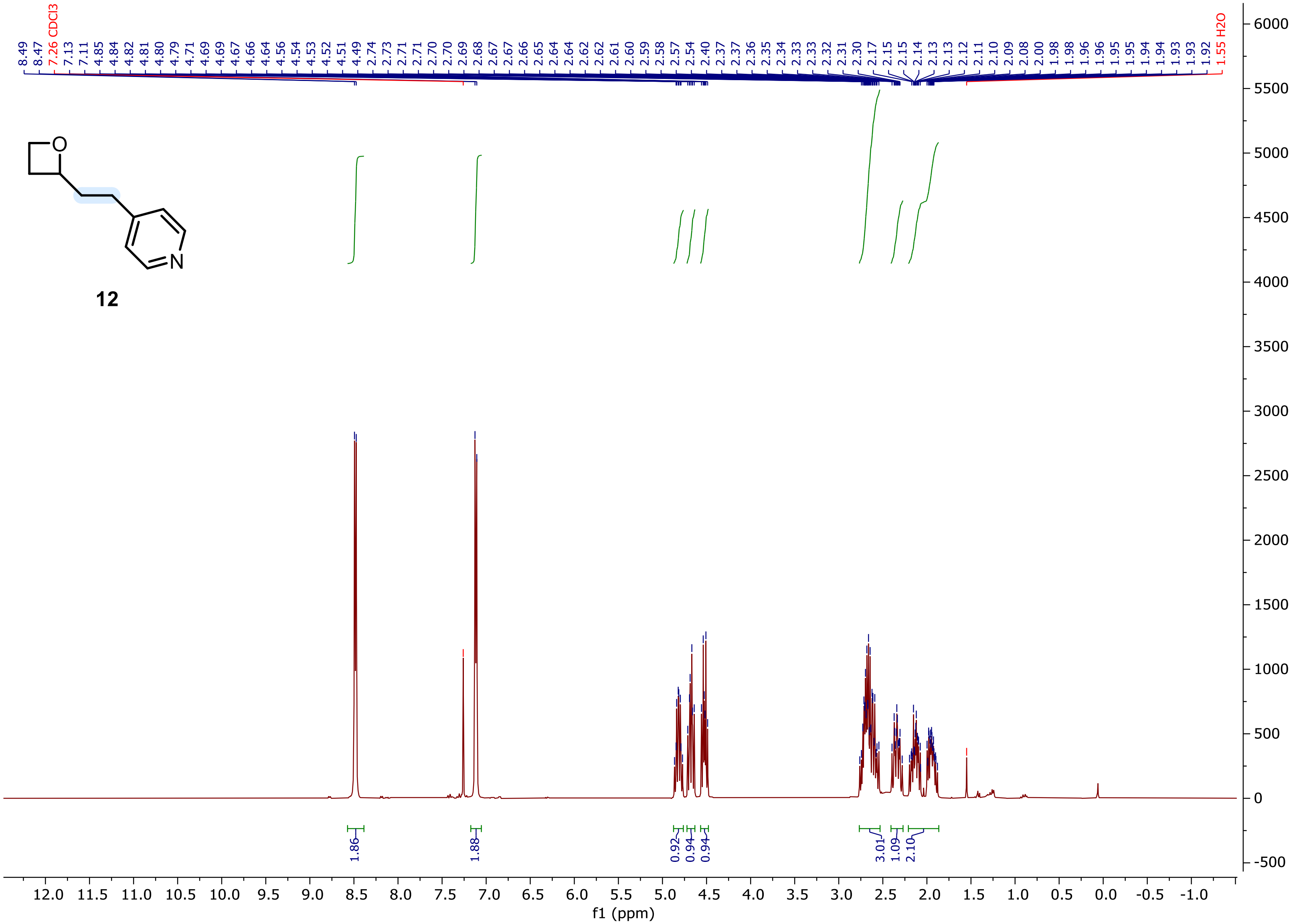
Unsuccessful Examples

The following examples were found to be unsuccessful with the current optimized reaction conditions.





NMR Spectra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4.69
4.69
4.67
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4.64
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4.54
4.54
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4.51
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1.93
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0.94
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11.0
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10.0
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3000
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1000
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0
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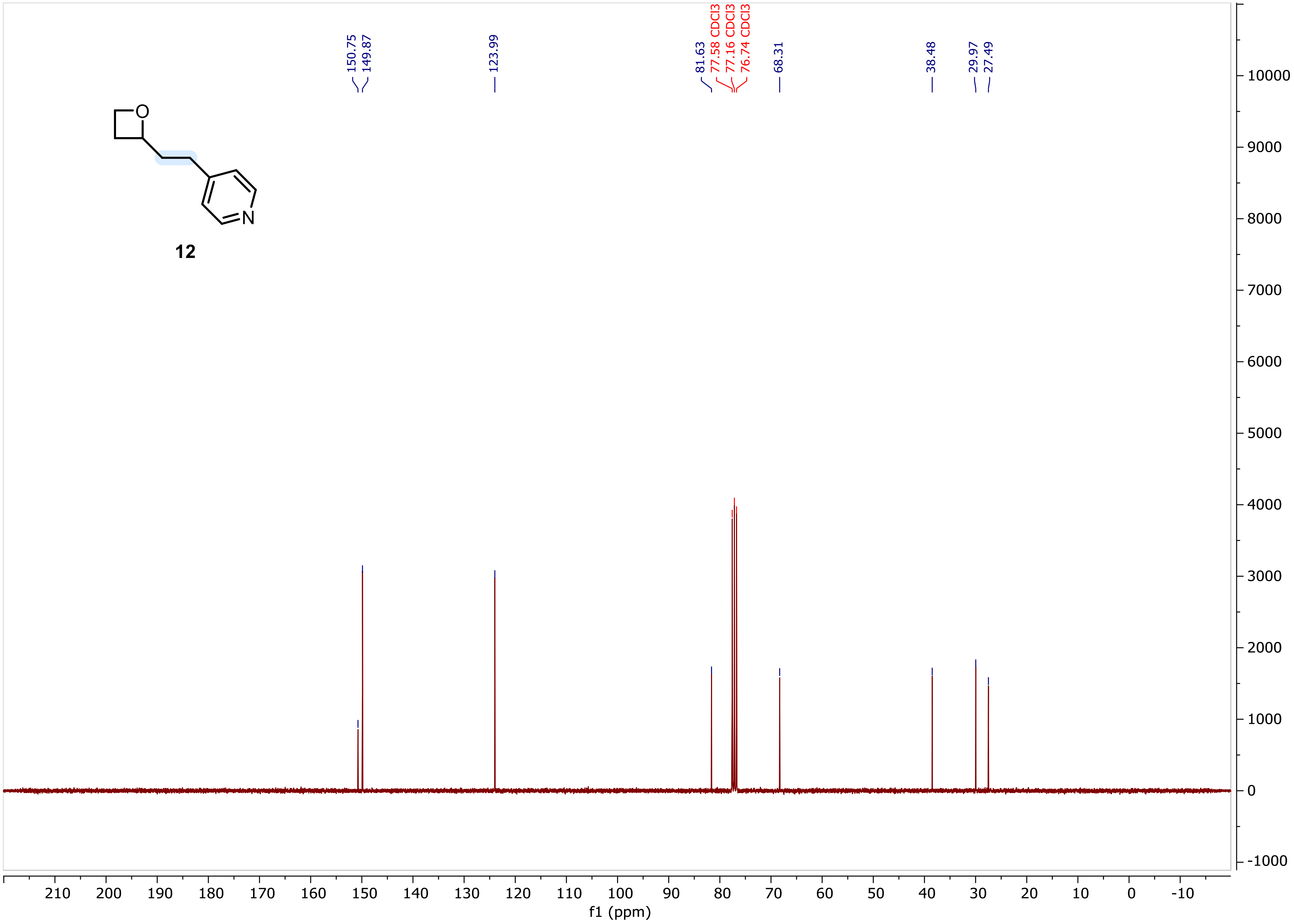
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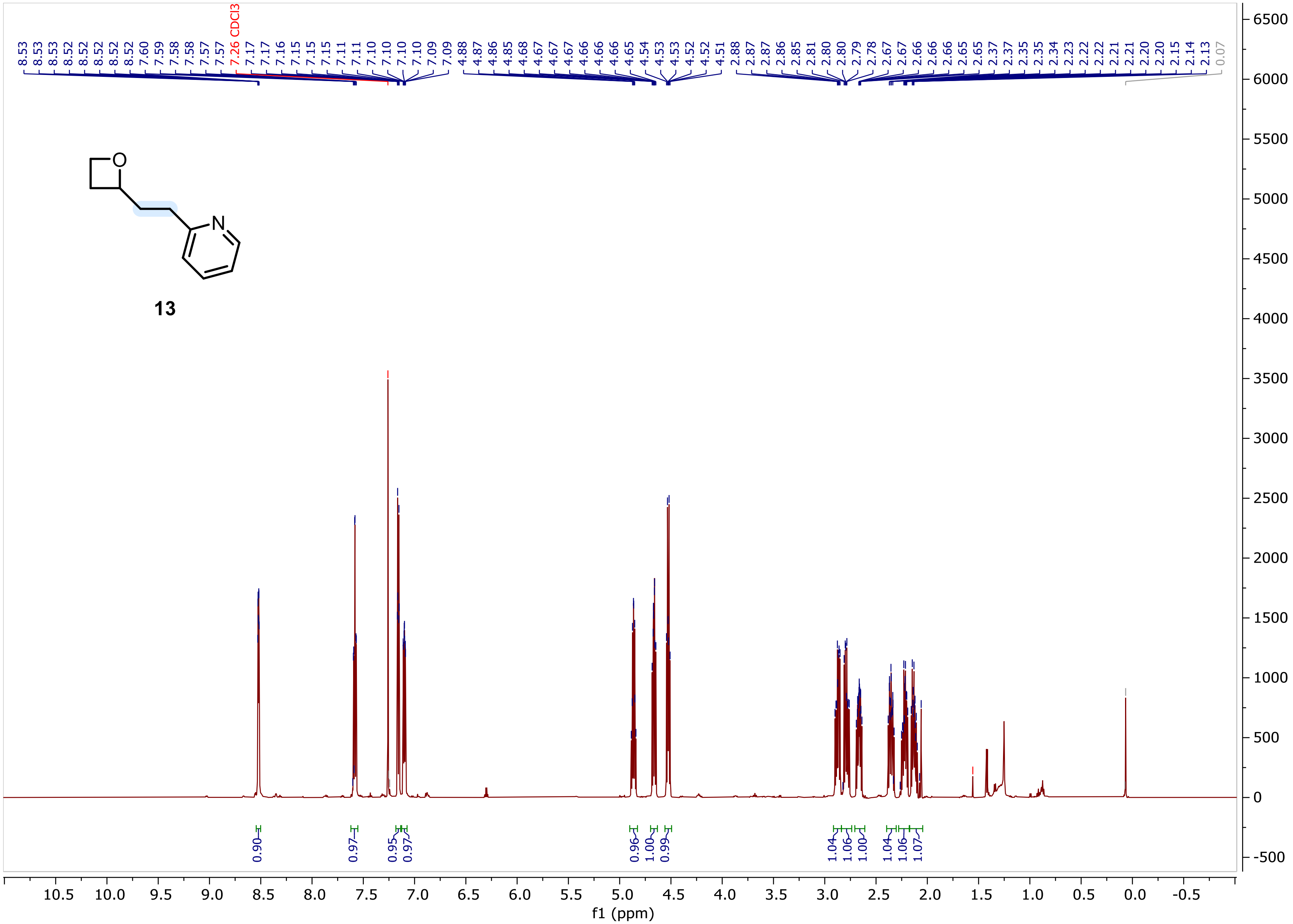
f1 (ppm)

12

8.53
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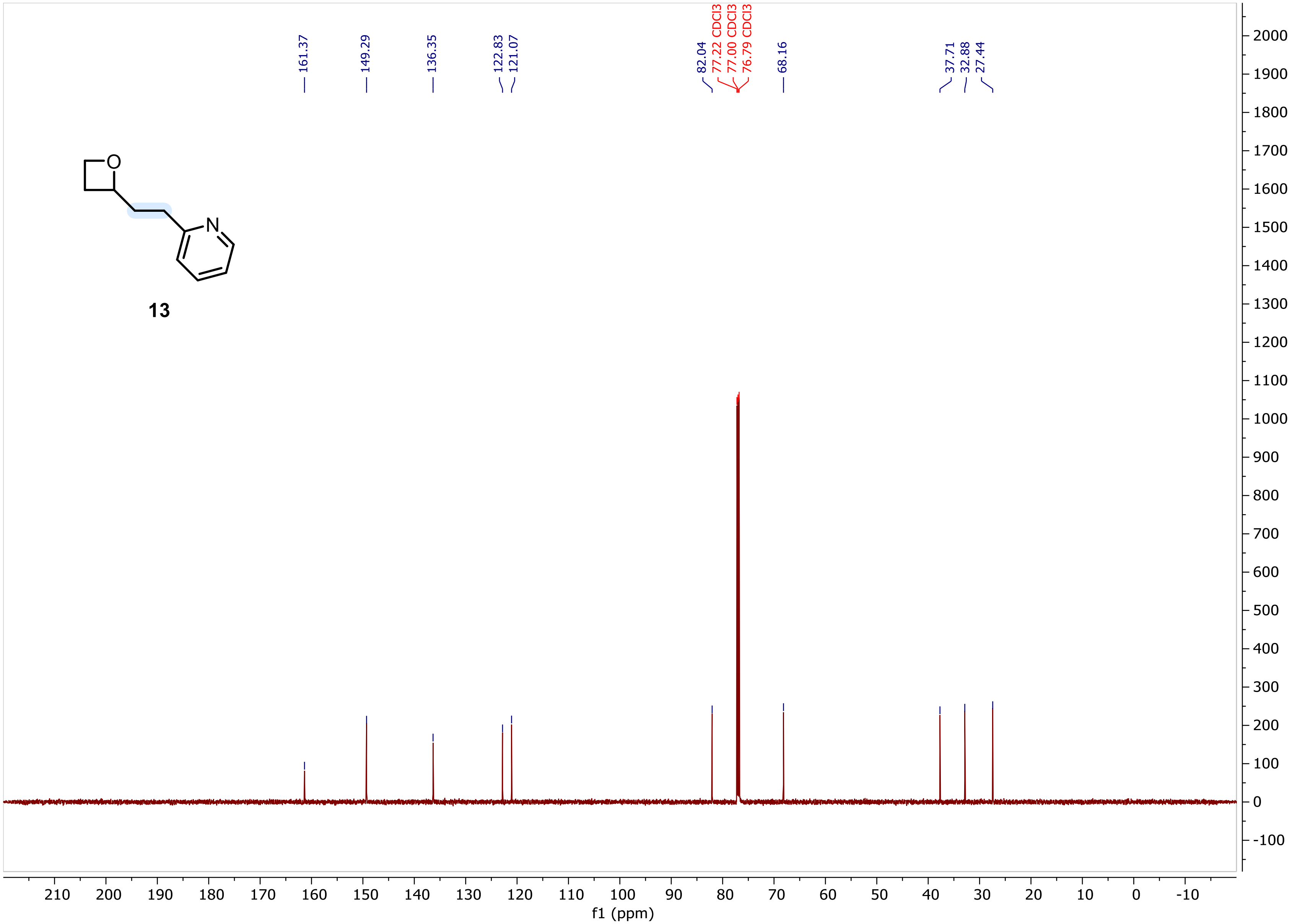

13

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121.07
82.04
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76.79 CDCl3
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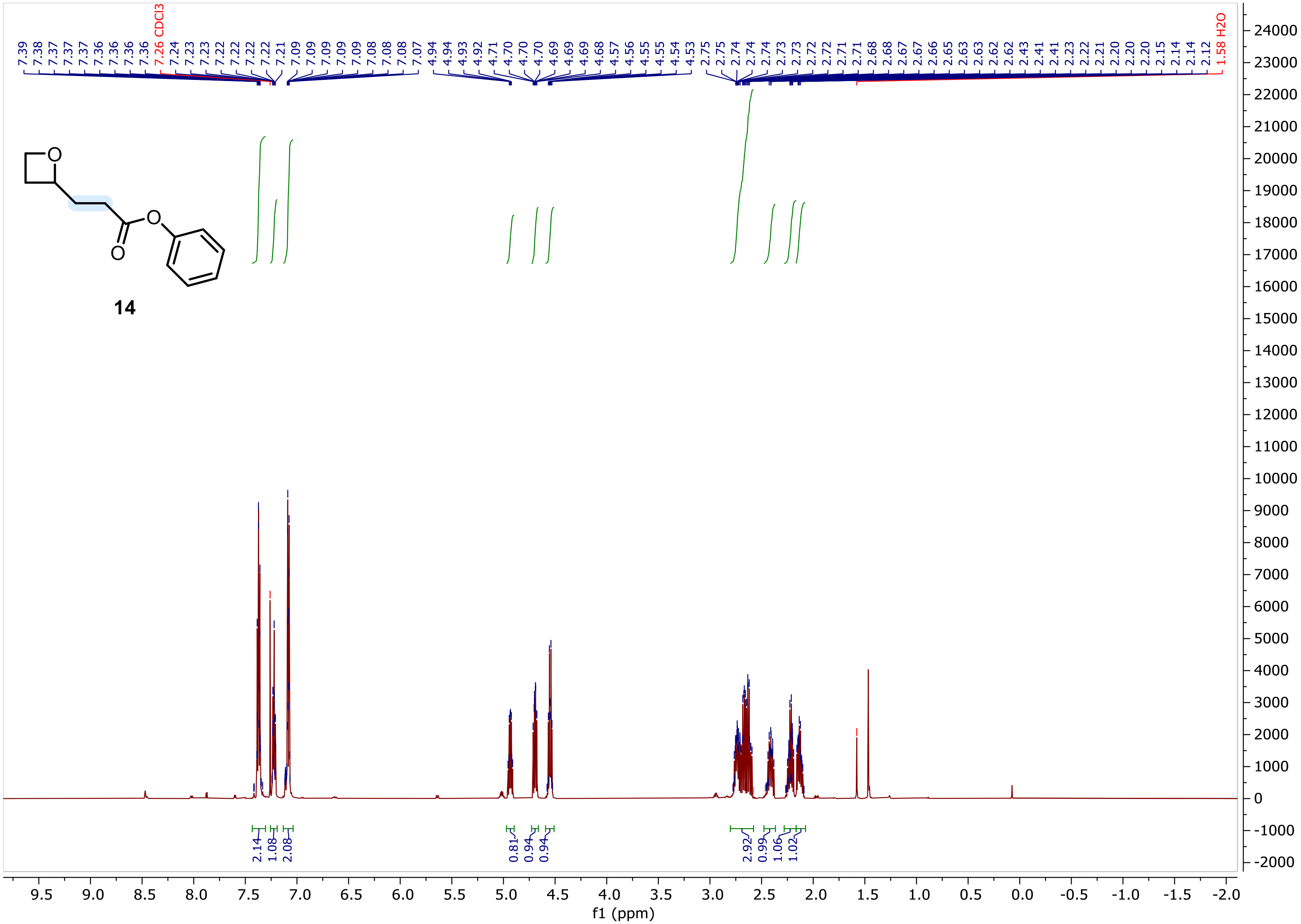
f1 (ppm)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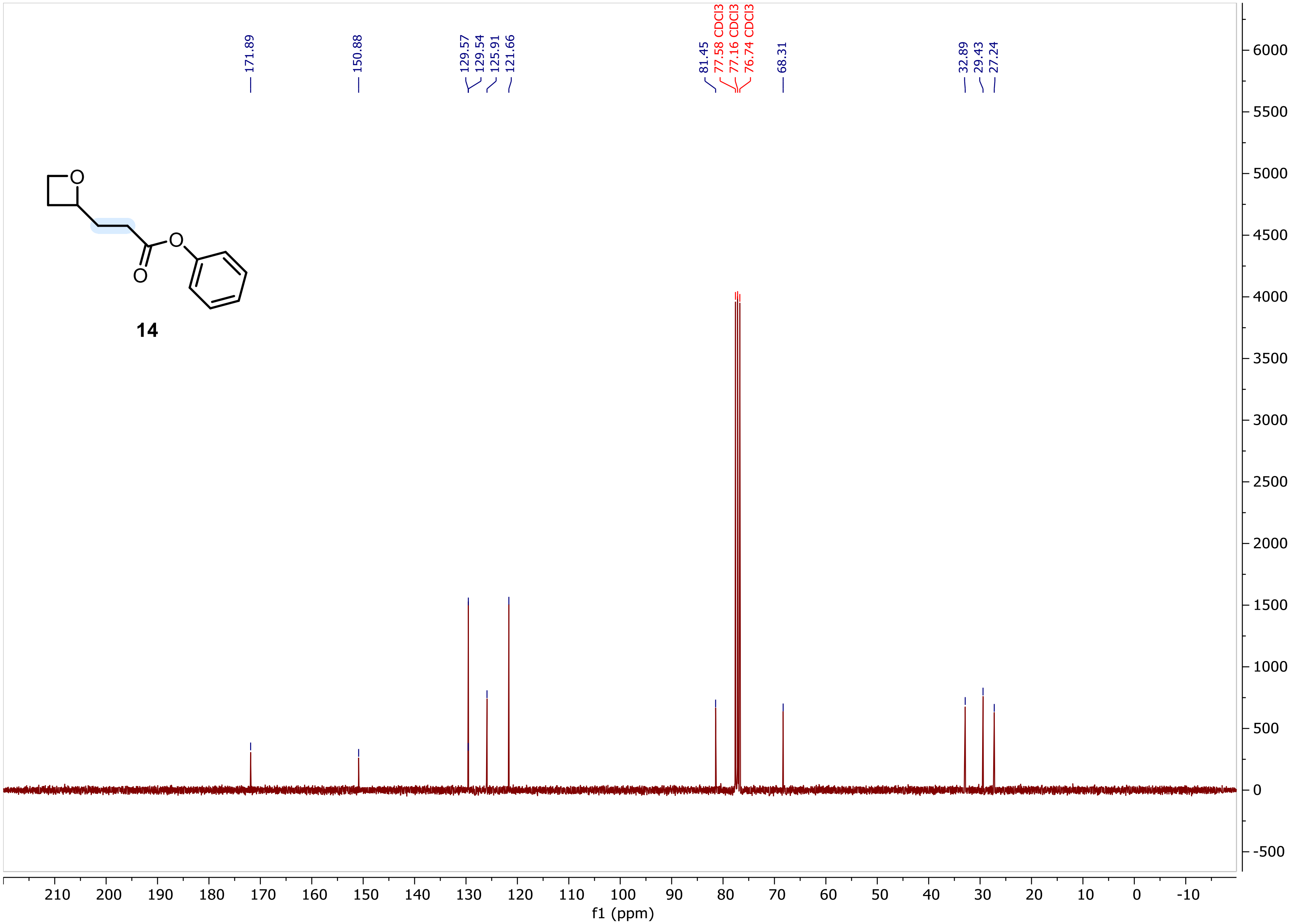
14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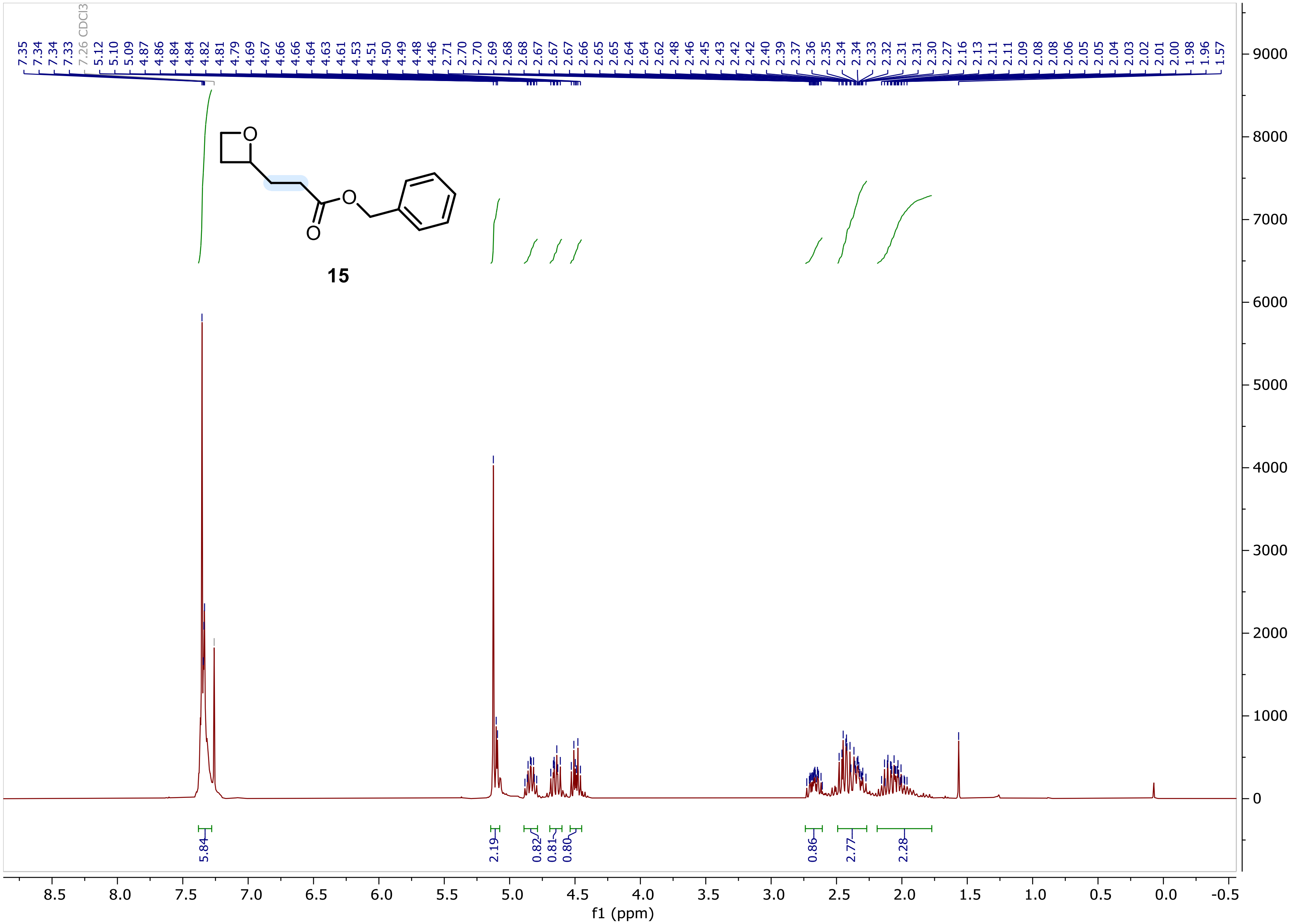
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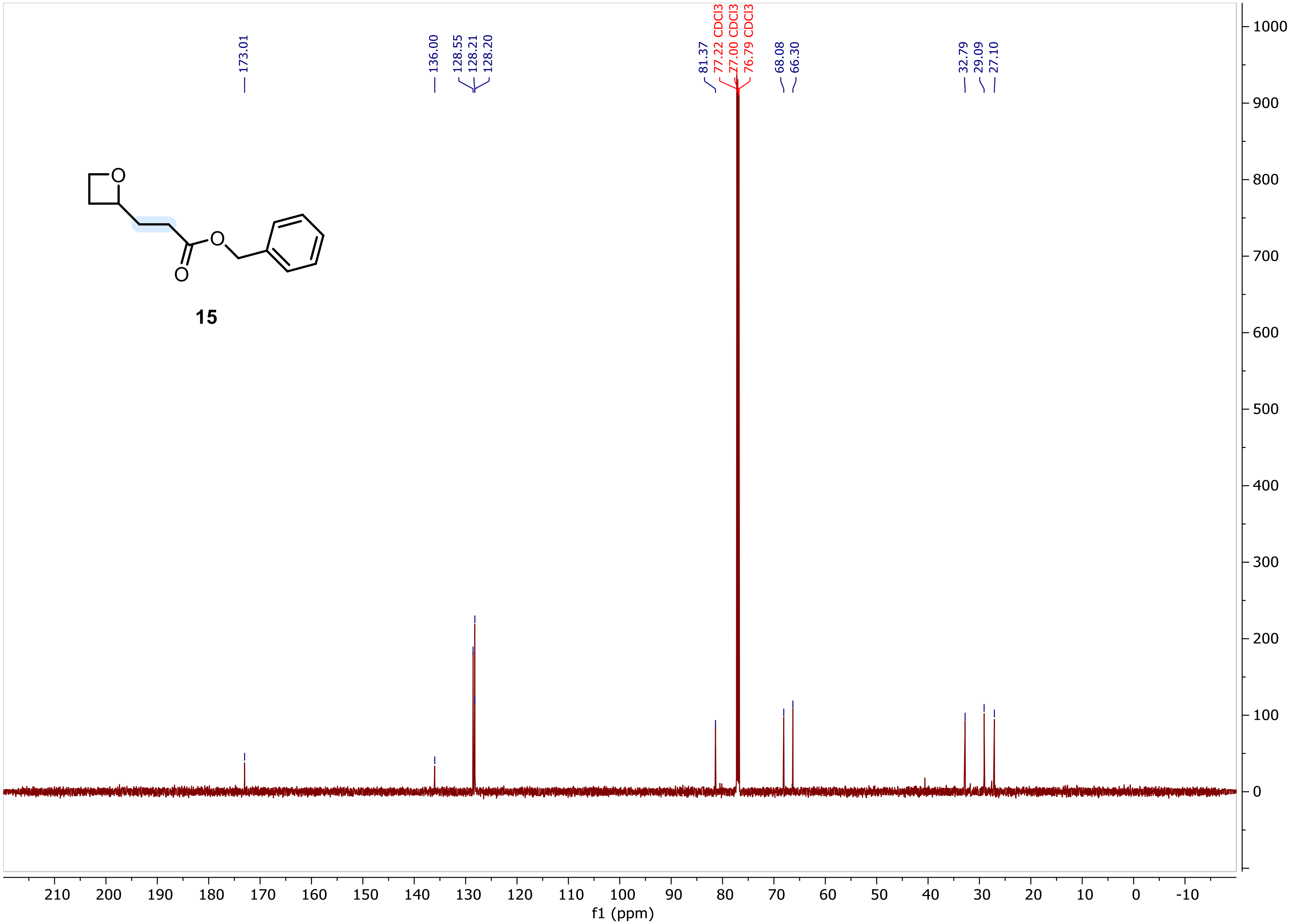

15

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76.79 CDCl3
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27.10
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f1 (ppm)
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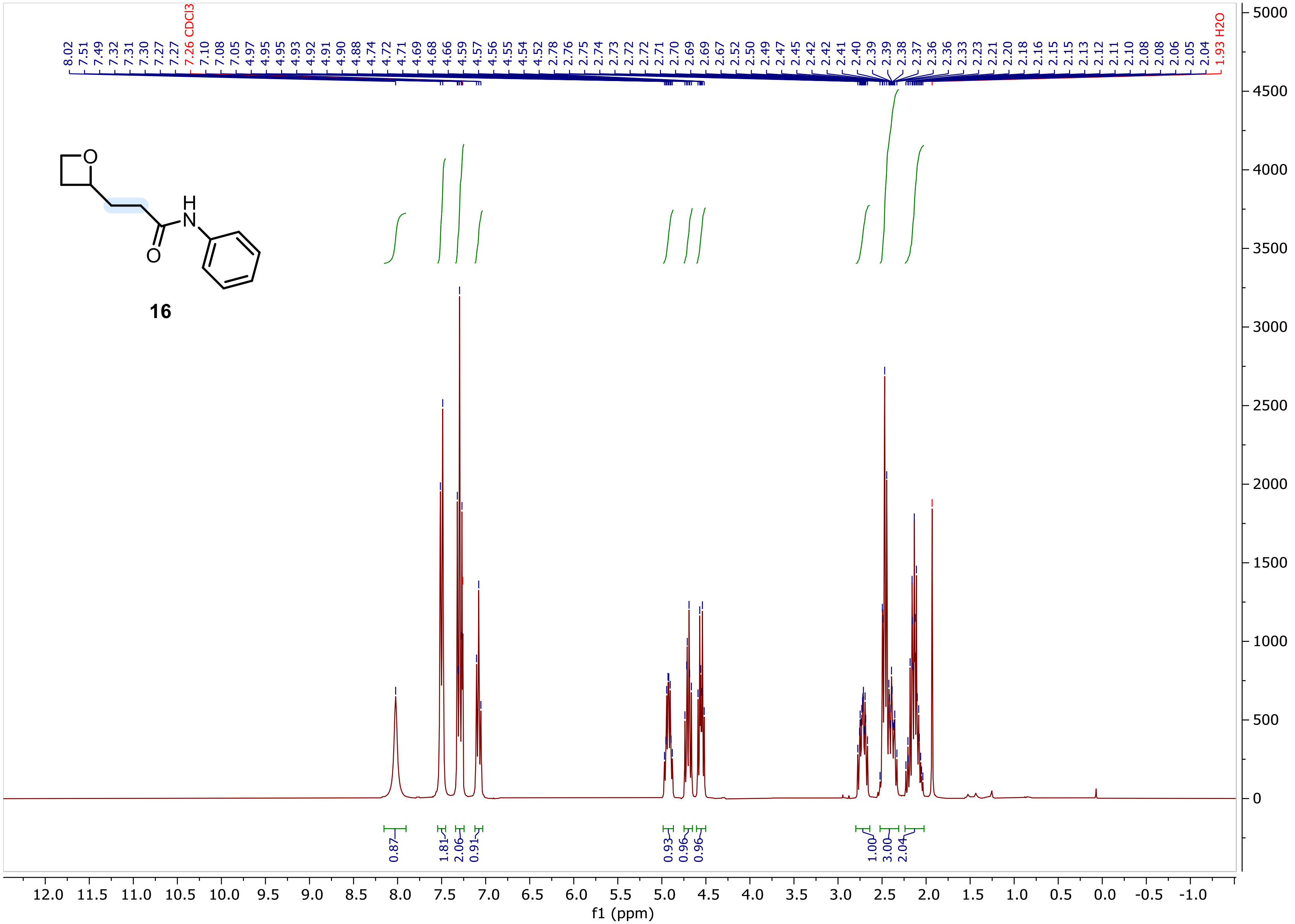
O
O



16

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3.00
2.04
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H
N
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3500
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1000
500
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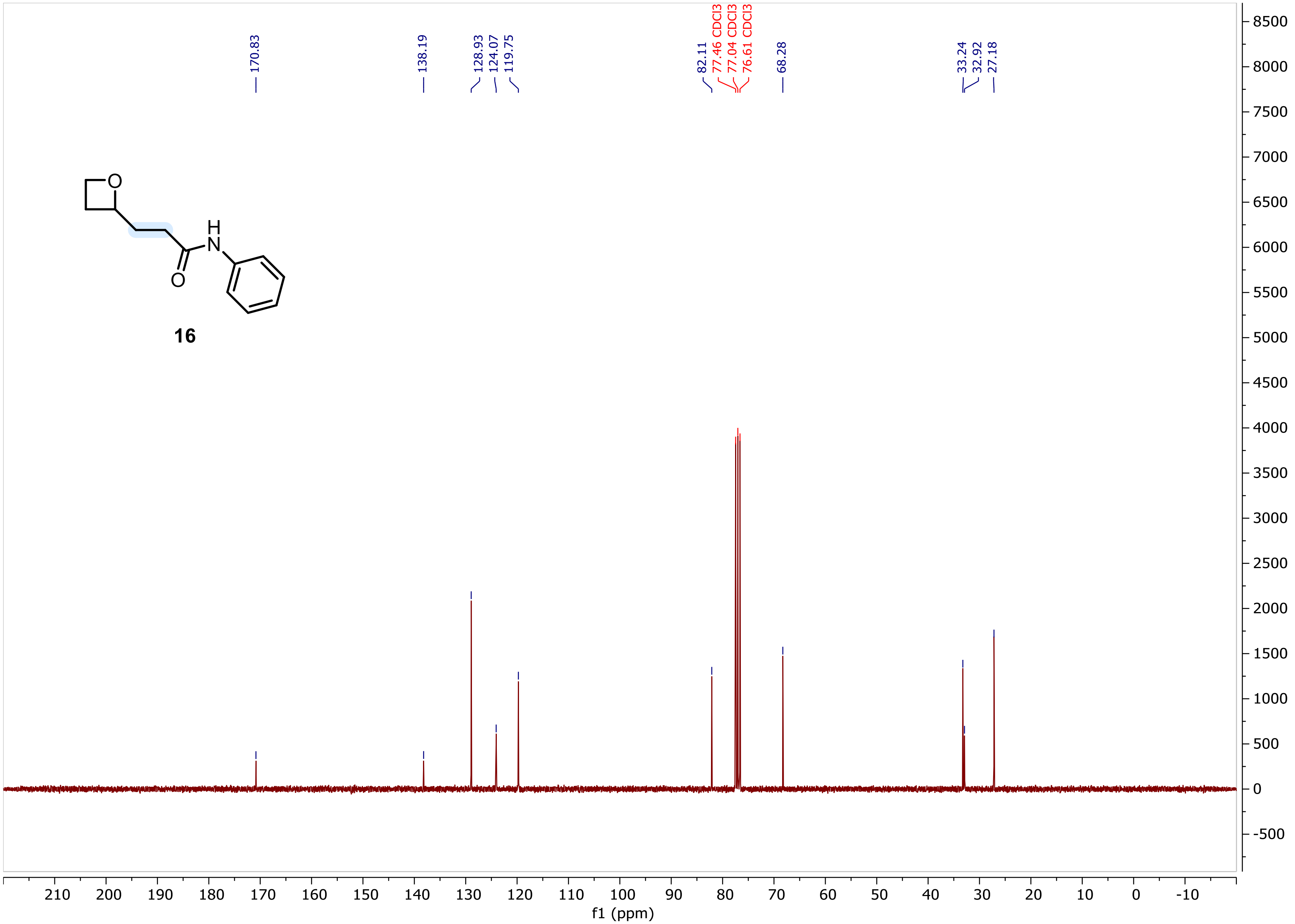
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82.11
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76.61 CDCl3
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O
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8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
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200
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180
170
160
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100
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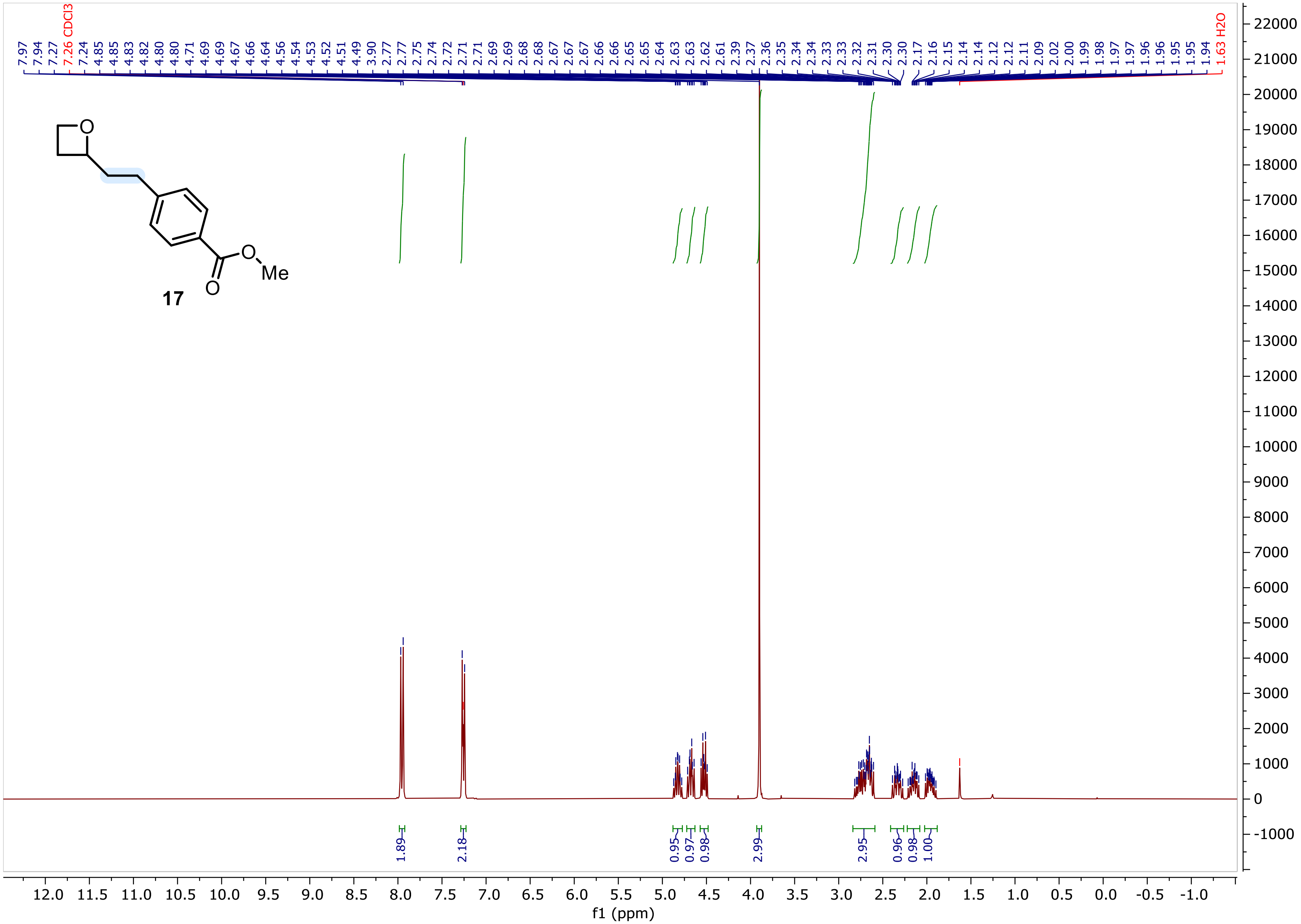
20
10
0
-10
f1 (ppm)

16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4.52
4.51
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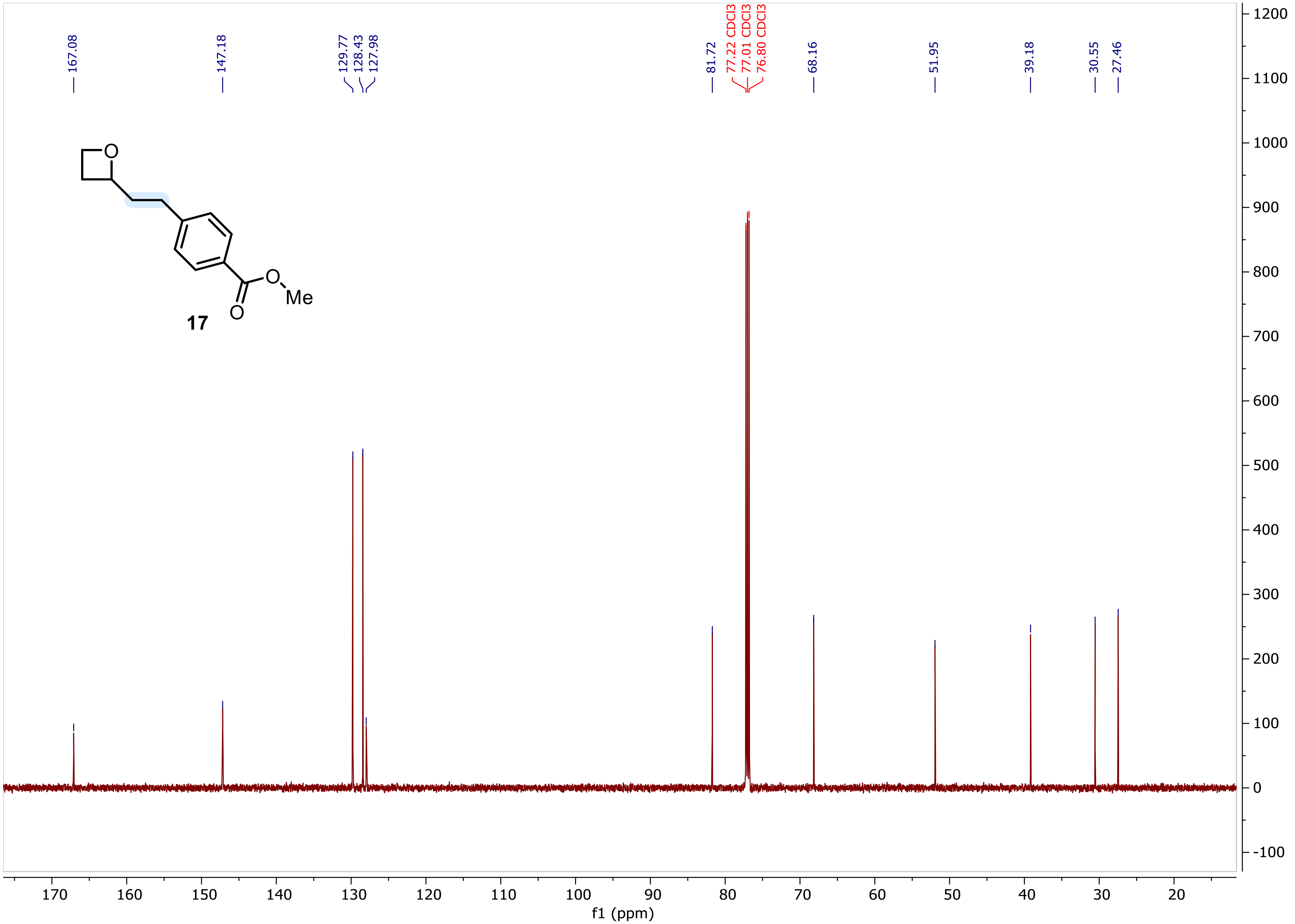
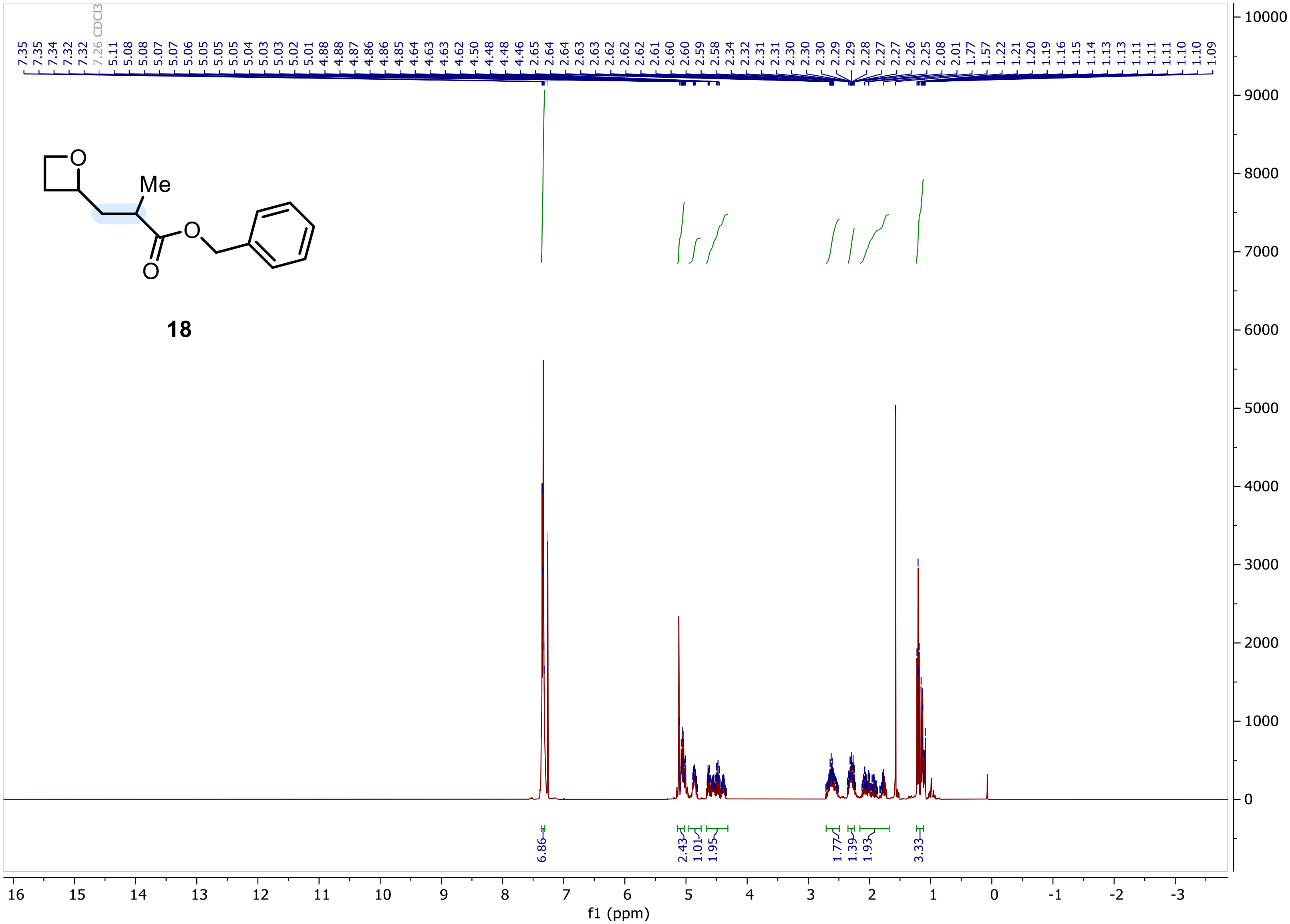
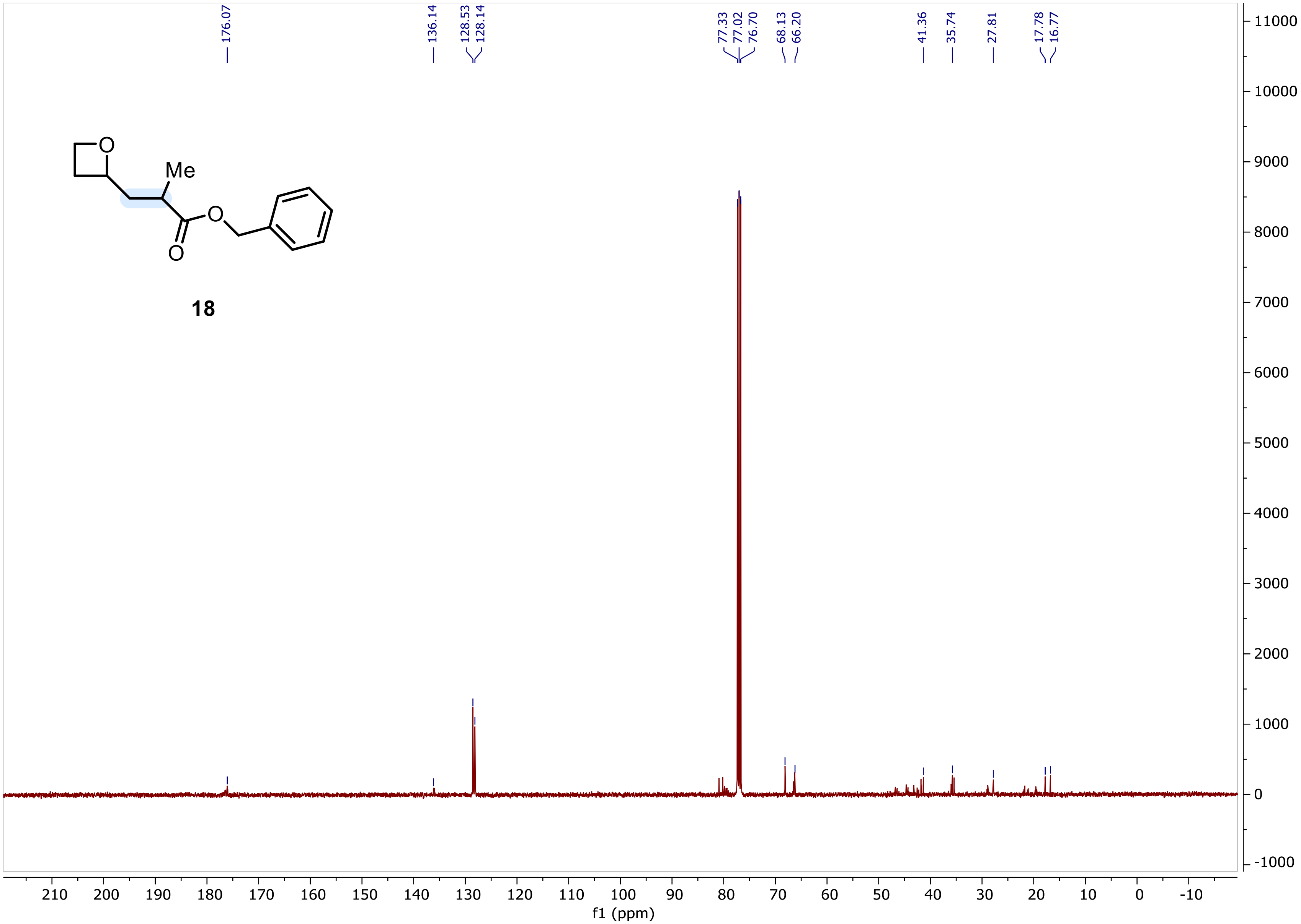
2.77
2.77
2.75
2.74
2.72
2.71
2.71
2.69
2.69
2.68
2.68
2.67
2.67
2.67
2.66
2.66
2.65
2.65
2.64
2.63
2.63
2.62
2.61
2.39
2.37
2.36
2.35
2.34
2.34
2.33
2.32
2.31
2.30
2.30
2.17
2.16
2.15
2.14
2.14
2.12
2.12
2.11
2.09
2.02
2.00
1.99
1.98
1.97
1.97
1.96
1.96
1.95
1.95
1.94
1.63 H2O
O
O
O
Me
17
1.89
2.18
0.95
0.97
0.98
2.99
2.95
0.96
0.98
1.00
12.0 11.5 11.0 10.5 10.0 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 -0.5 -1.0
f1 (ppm)
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


167.08
147.18
129.77
128.43
127.98
81.72
77.22 CDCl3
77.01 CDCl3
76.80 CDCl3
68.16
51.95
39.18
30.55
27.46
O
O
O
Me
17
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

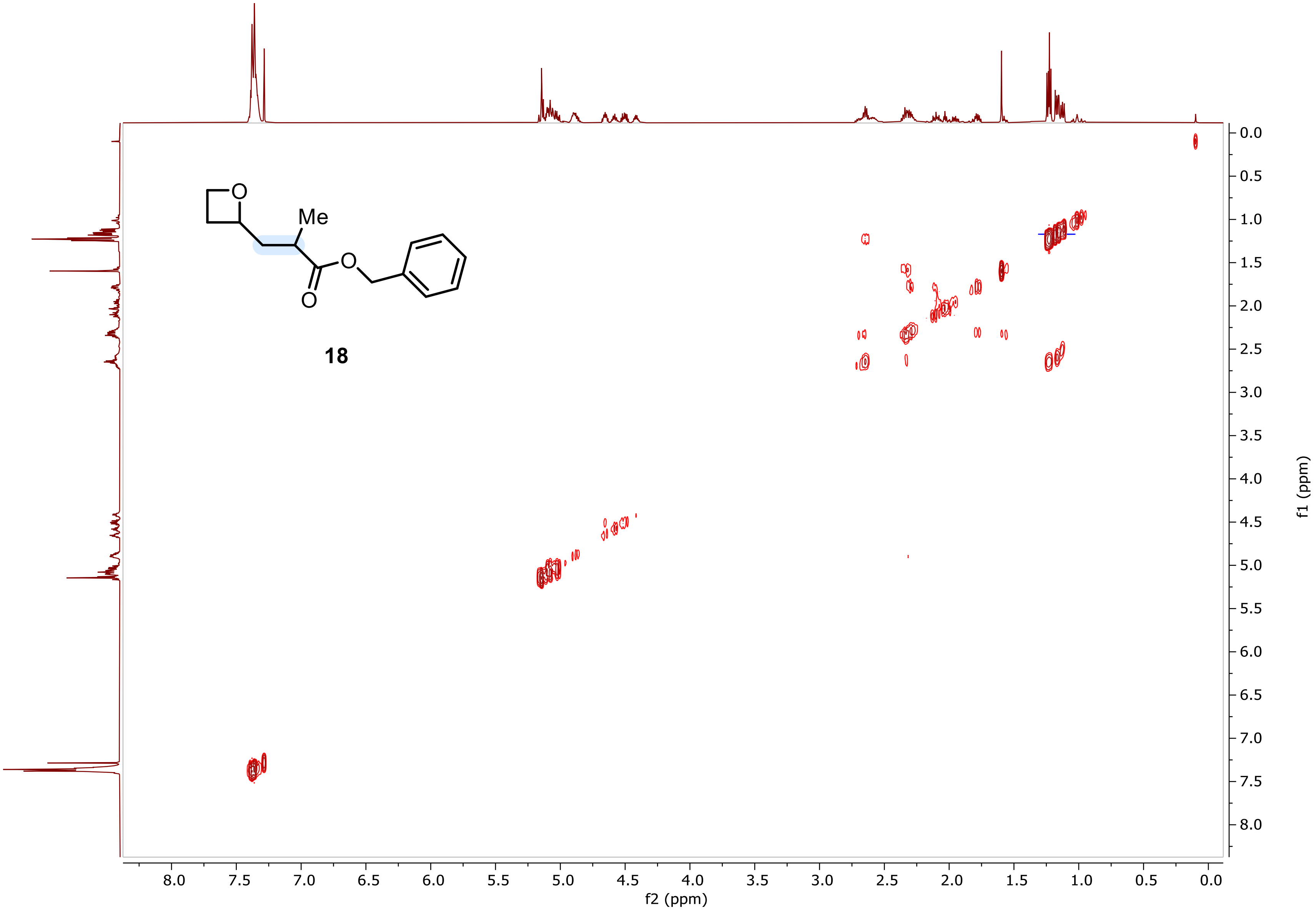

7.35
7.35
7.34
7.32
7.32
7.26 CDCl3
5.11
5.08
5.08
5.07
5.07
5.06
5.05
5.05
5.04
5.03
5.03
5.02
5.01
4.88
4.88
4.87
4.86
4.86
4.85
4.64
4.63
4.63
4.62
4.50
4.48
4.48
4.46
2.65
2.64
2.64
2.63
2.63
2.62
2.62
2.62
2.61
2.60
2.60
2.59
2.58
2.34
2.32
2.31
2.31
2.30
2.30
2.30
2.29
2.29
2.28
2.27
2.27
2.26
2.25
2.08
2.01
1.77
1.57
1.22
1.21
1.20
1.19
1.16
1.15
1.14
1.13
1.13
1.11
1.11
1.10
1.10
1.09
O
Me
O
O
6.86
2.43
1.01
1.95
1.77
1.39
1.93
3.33
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

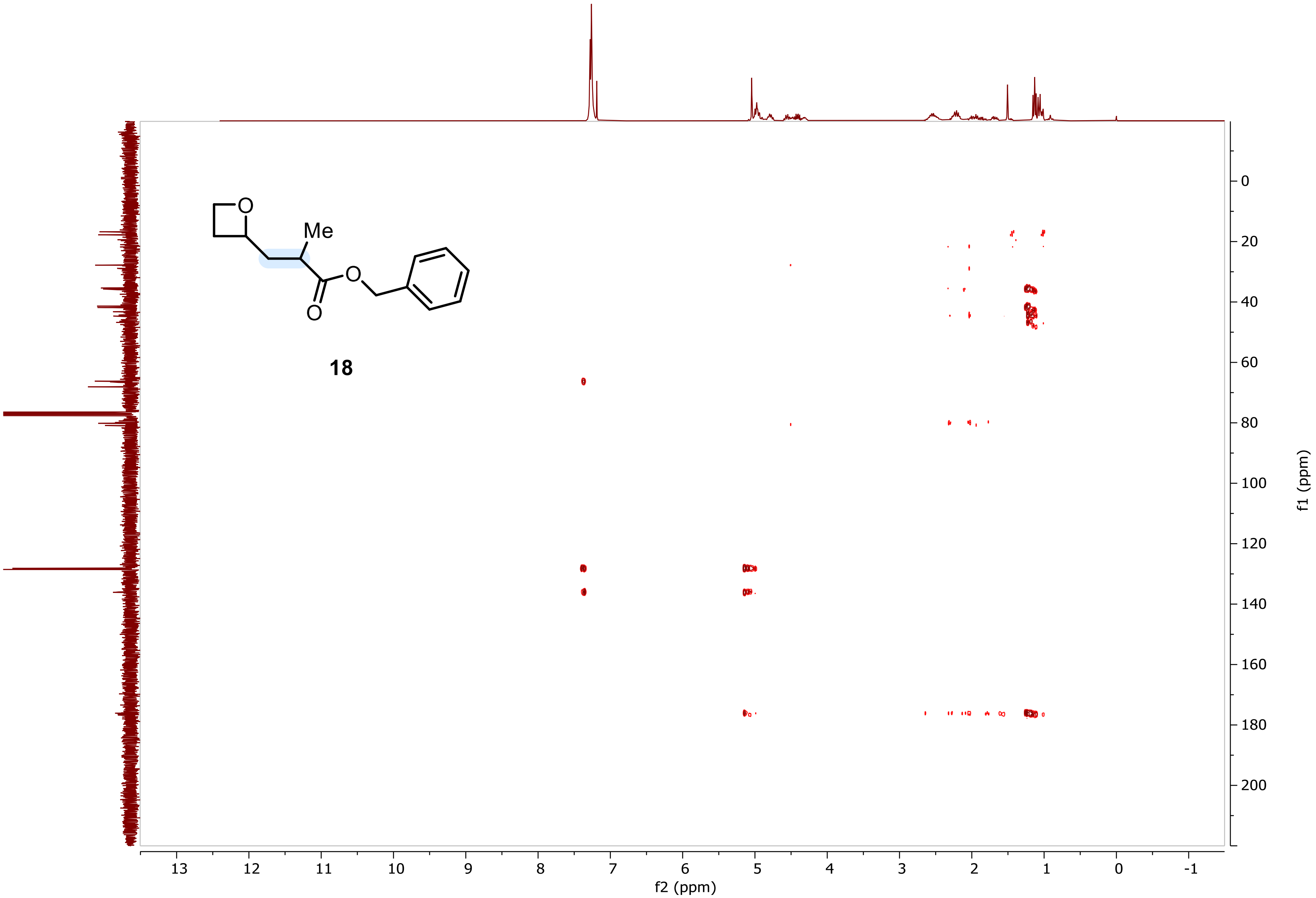
18



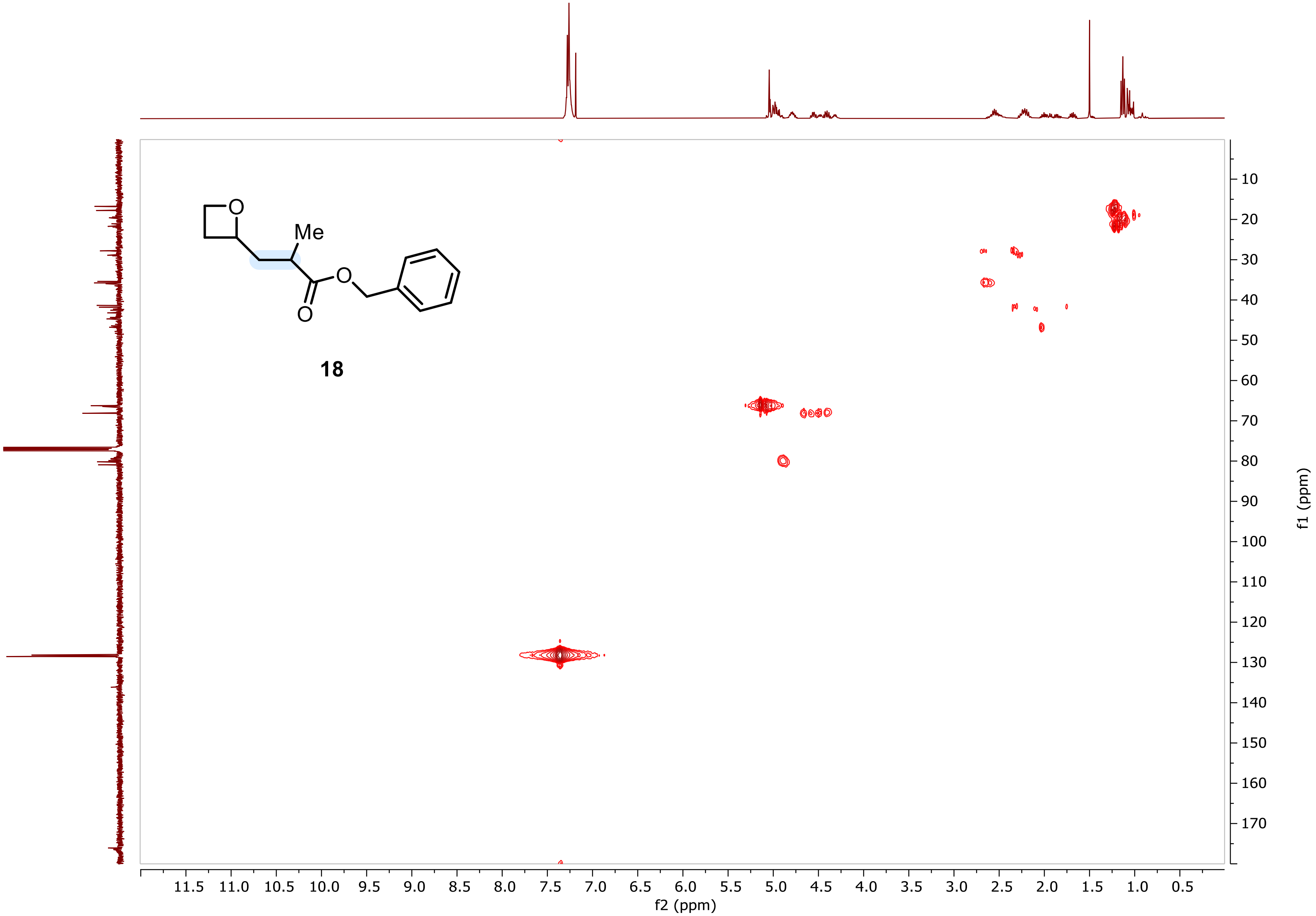
18

176.07
136.14
128.53
128.14
77.33
77.02
76.70
68.13
66.20
41.36
35.74
27.81
17.78
16.77
Me
O
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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)


Me
O
O
O
18
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
f2 (ppm)
f1 (ppm)

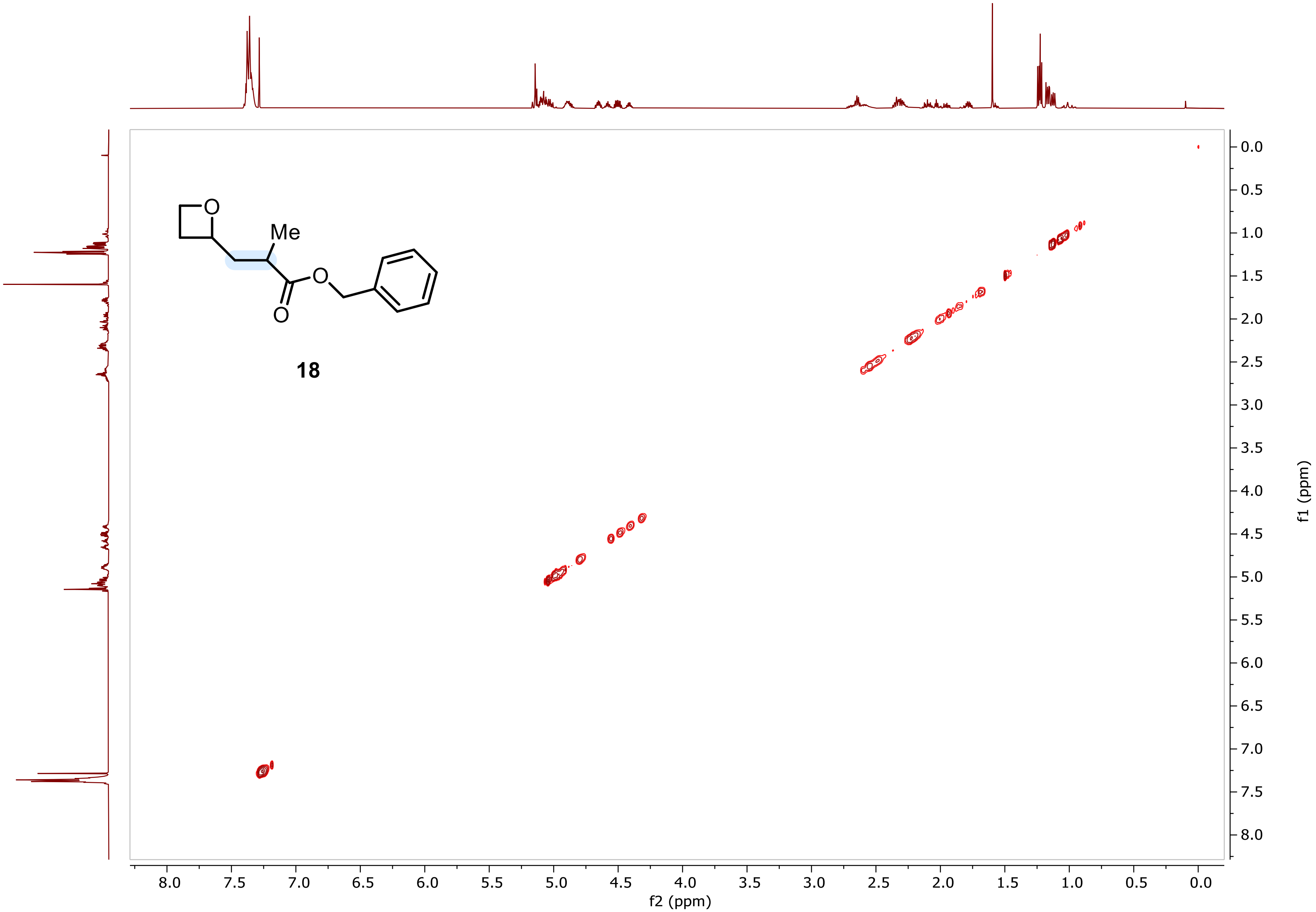

O
Me
O
O
f2 (ppm)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)
0
20
40
60
80
100
120
140
160
180
200

18

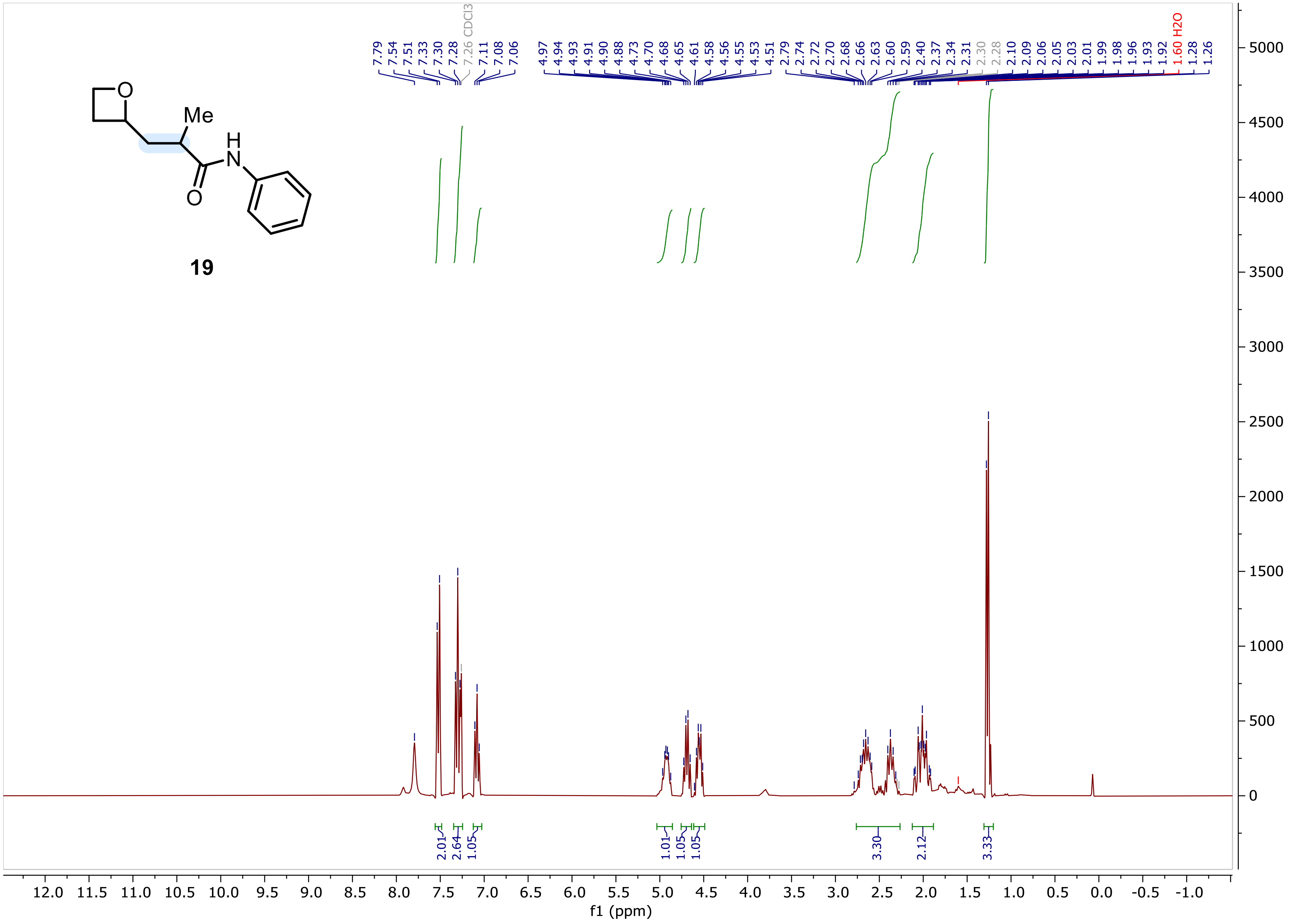


O
Me
O
O
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
f1 (ppm)

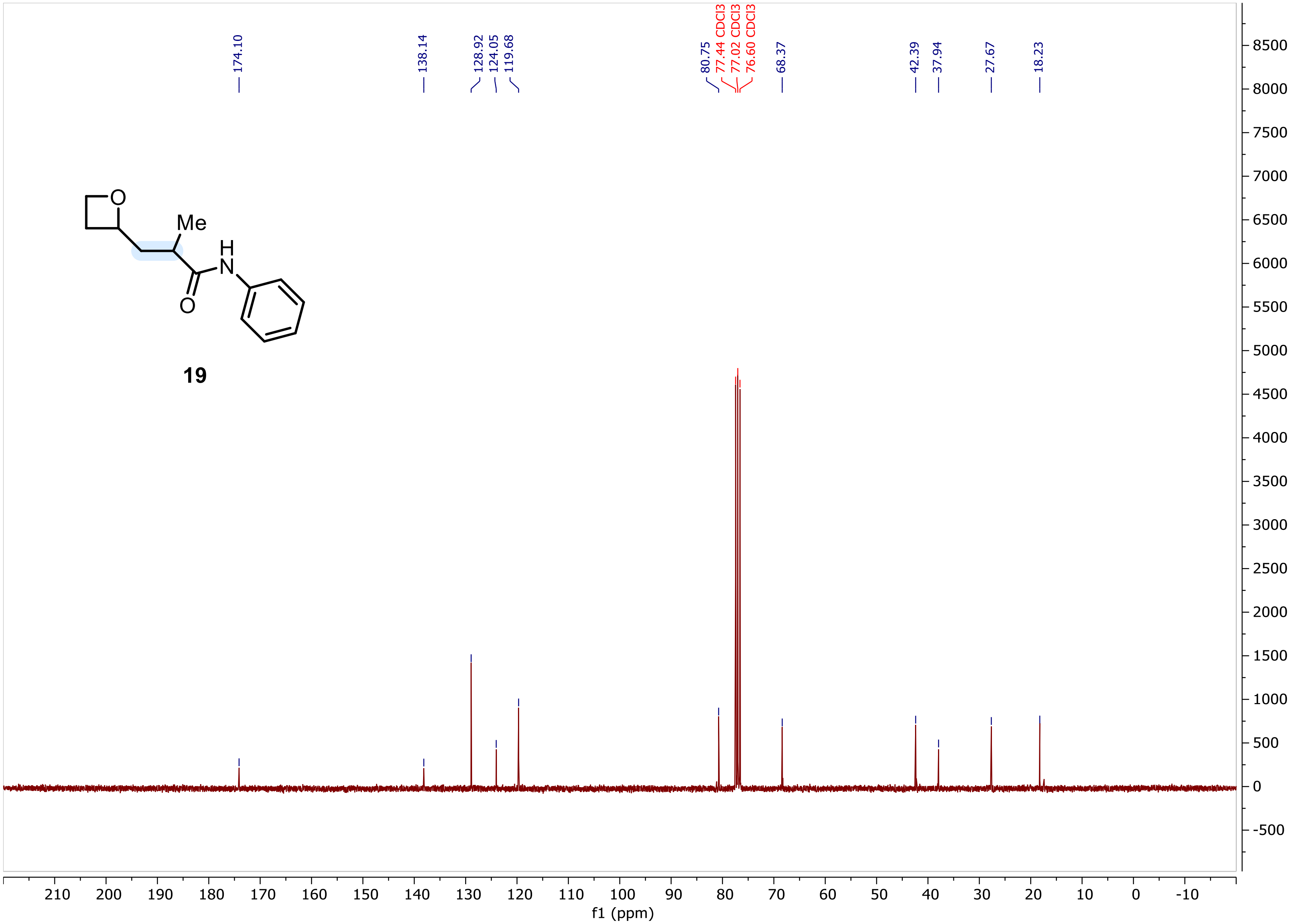
18

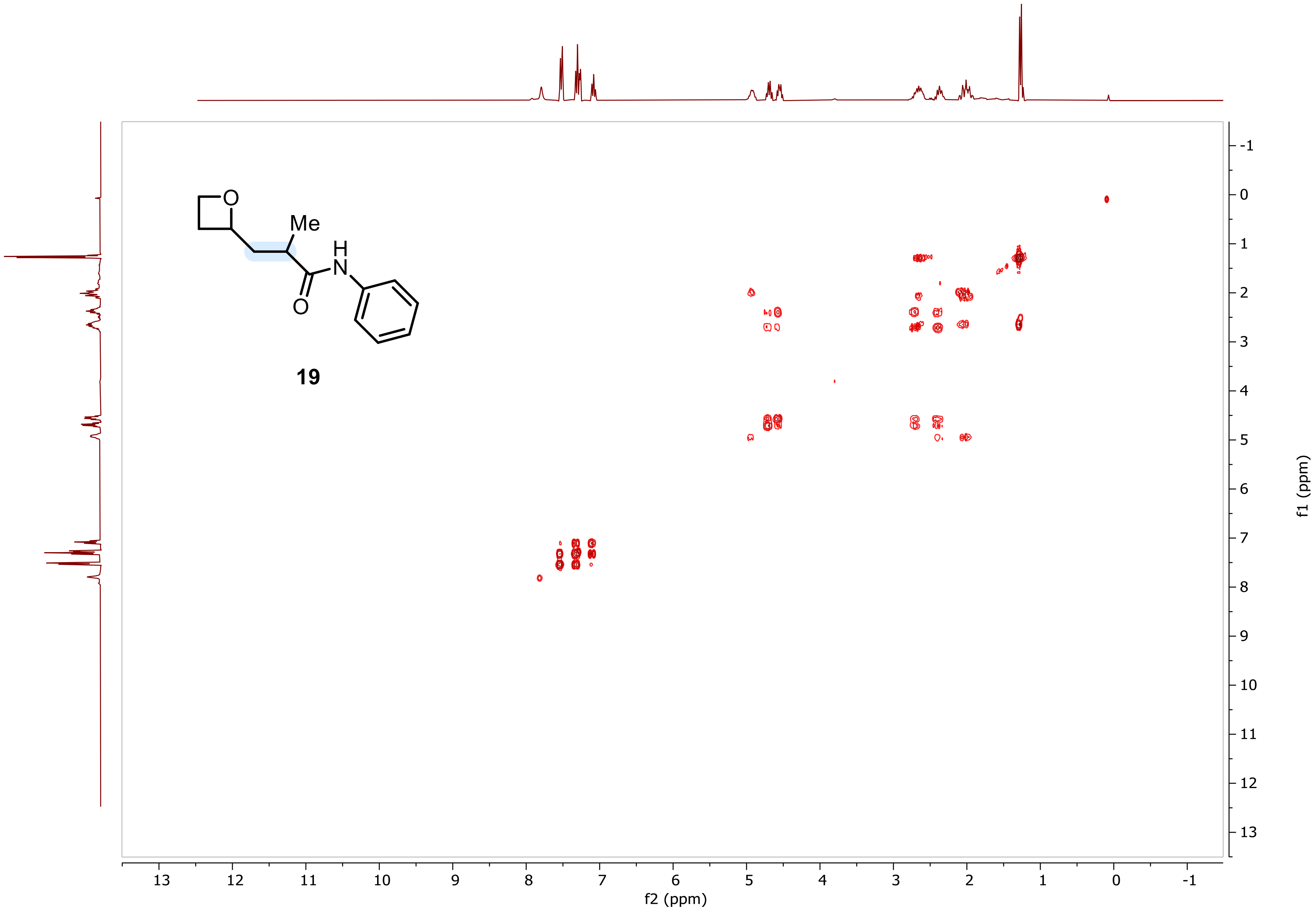

O
Me
O
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)

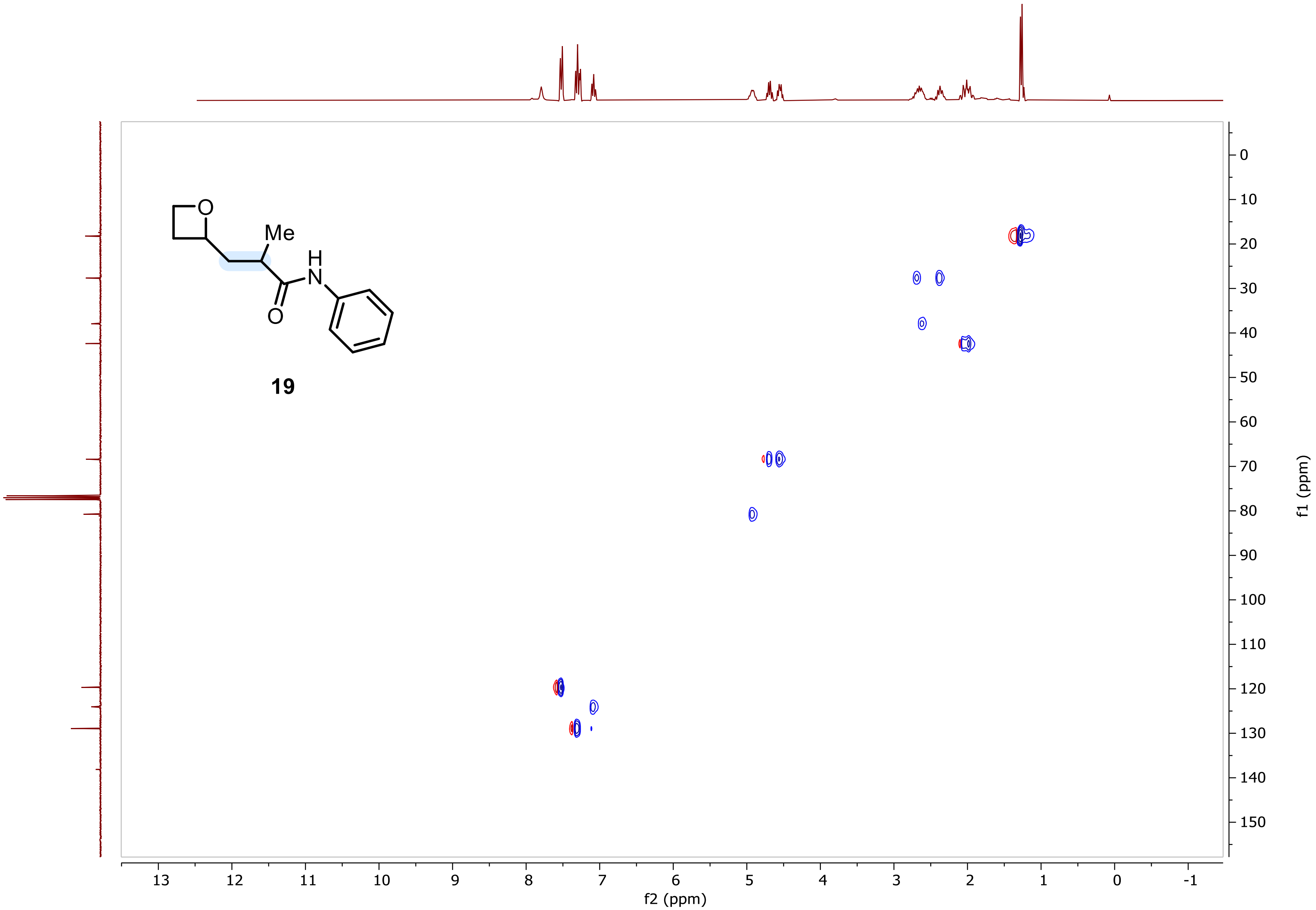
18

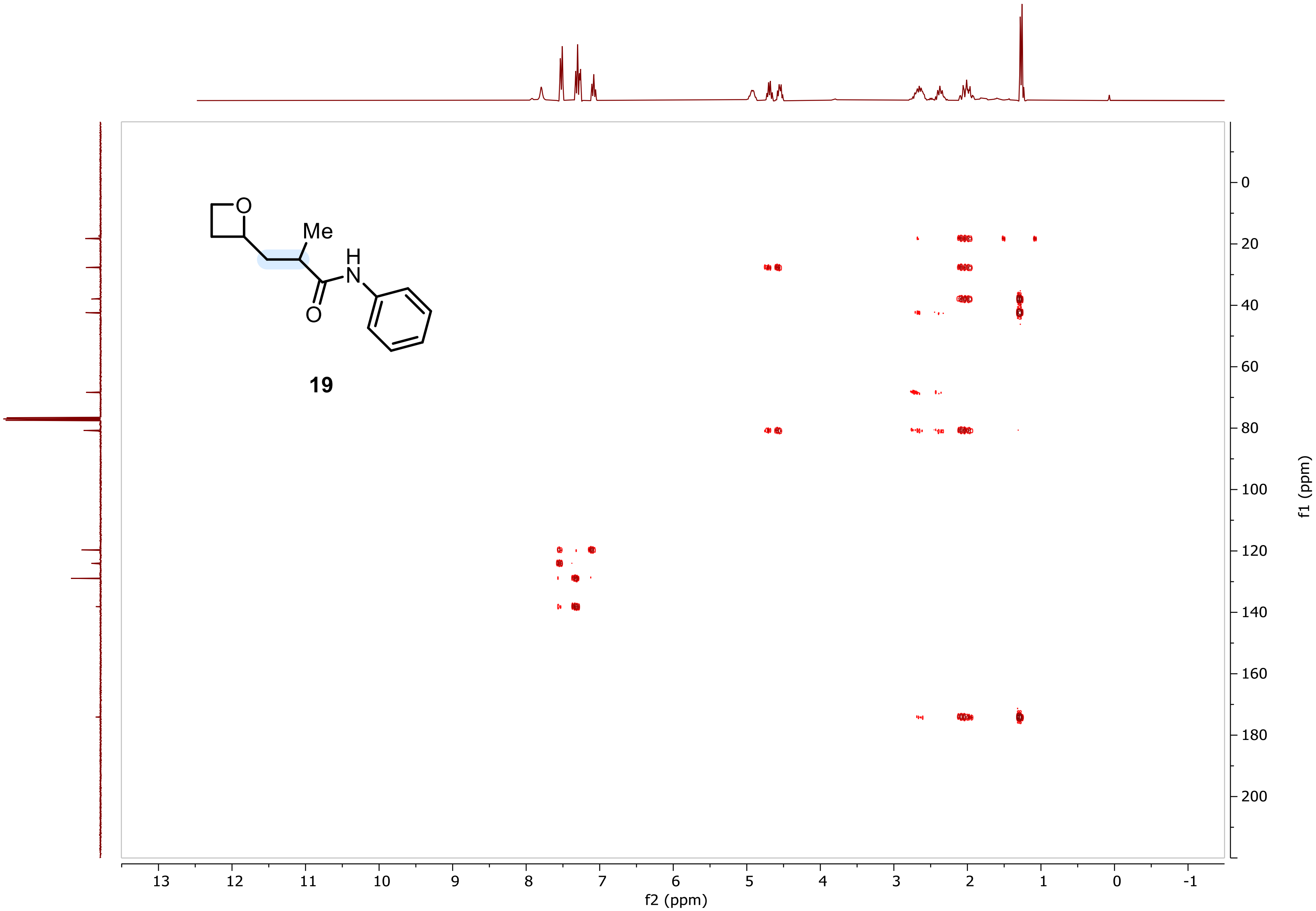

O
Me
H
N
O
7.79
7.54
7.51
7.33
7.30
7.28
7.26 CDCl3
7.11
7.08
7.06
4.97
4.94
4.93
4.91
4.90
4.88
4.73
4.70
4.68
4.65
4.61
4.58
4.56
4.55
4.53
4.51
2.79
2.74
2.72
2.70
2.68
2.66
2.63
2.60
2.59
2.40
2.37
2.34
2.31
2.30
2.28
2.10
2.09
2.06
2.05
2.03
2.01
1.99
1.98
1.96
1.93
1.92
1.60 H2O
1.28
1.26
2.01
2.64
1.05
1.01
1.05
1.05
3.30
2.12
3.33
12.0
11.5
11.0
10.5
10.0
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
-0.5
-1.0
f1 (ppm)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0

19

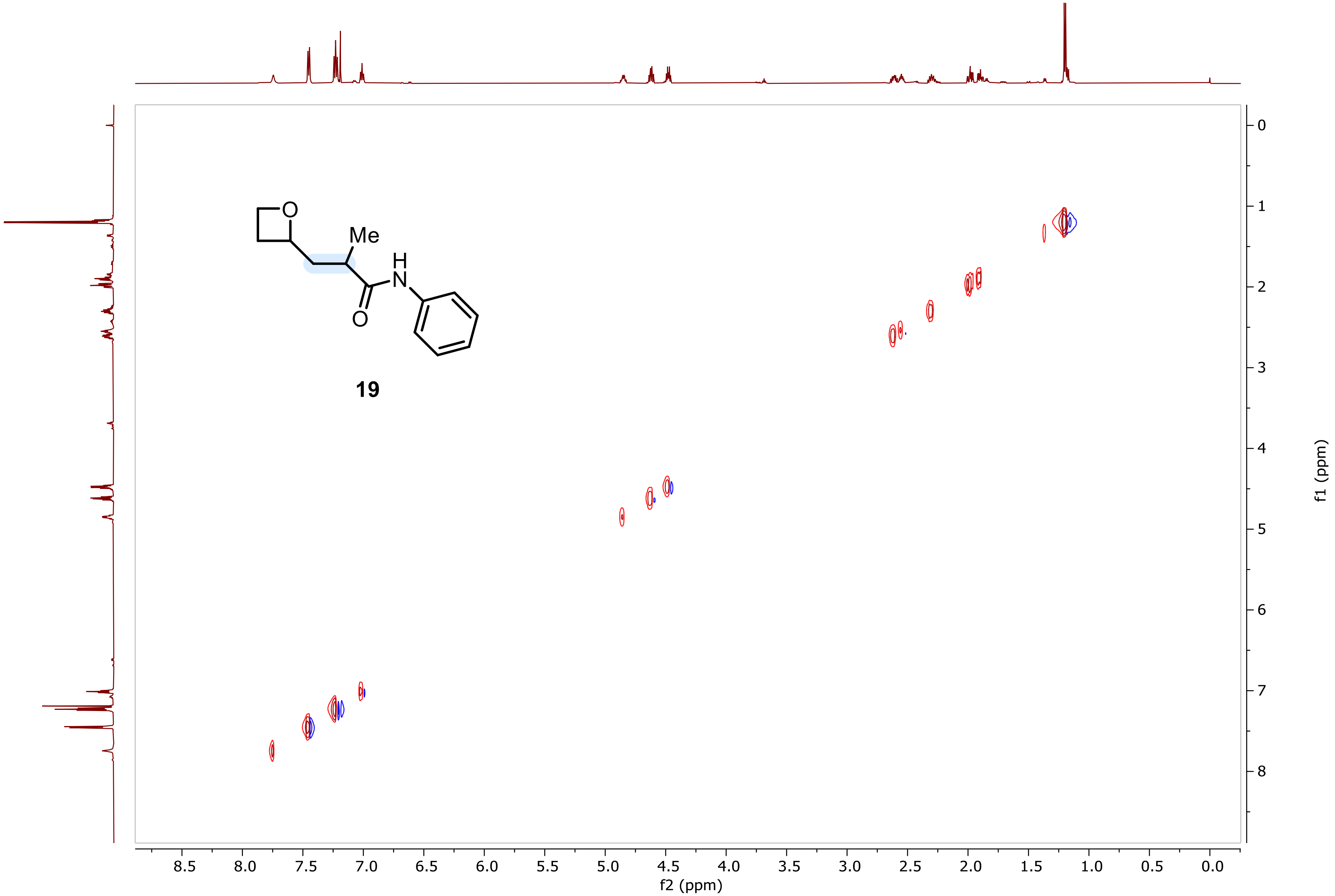

174.10
138.14
128.92
124.05
119.68
80.75
77.44 CDCl3
77.02 CDCl3
76.60 CDCl3
68.37
42.39
37.94
27.67
18.23
O
Me
H
N
O
19
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
Me
H
N
O
19
f2 (ppm)
f1 (ppm)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1

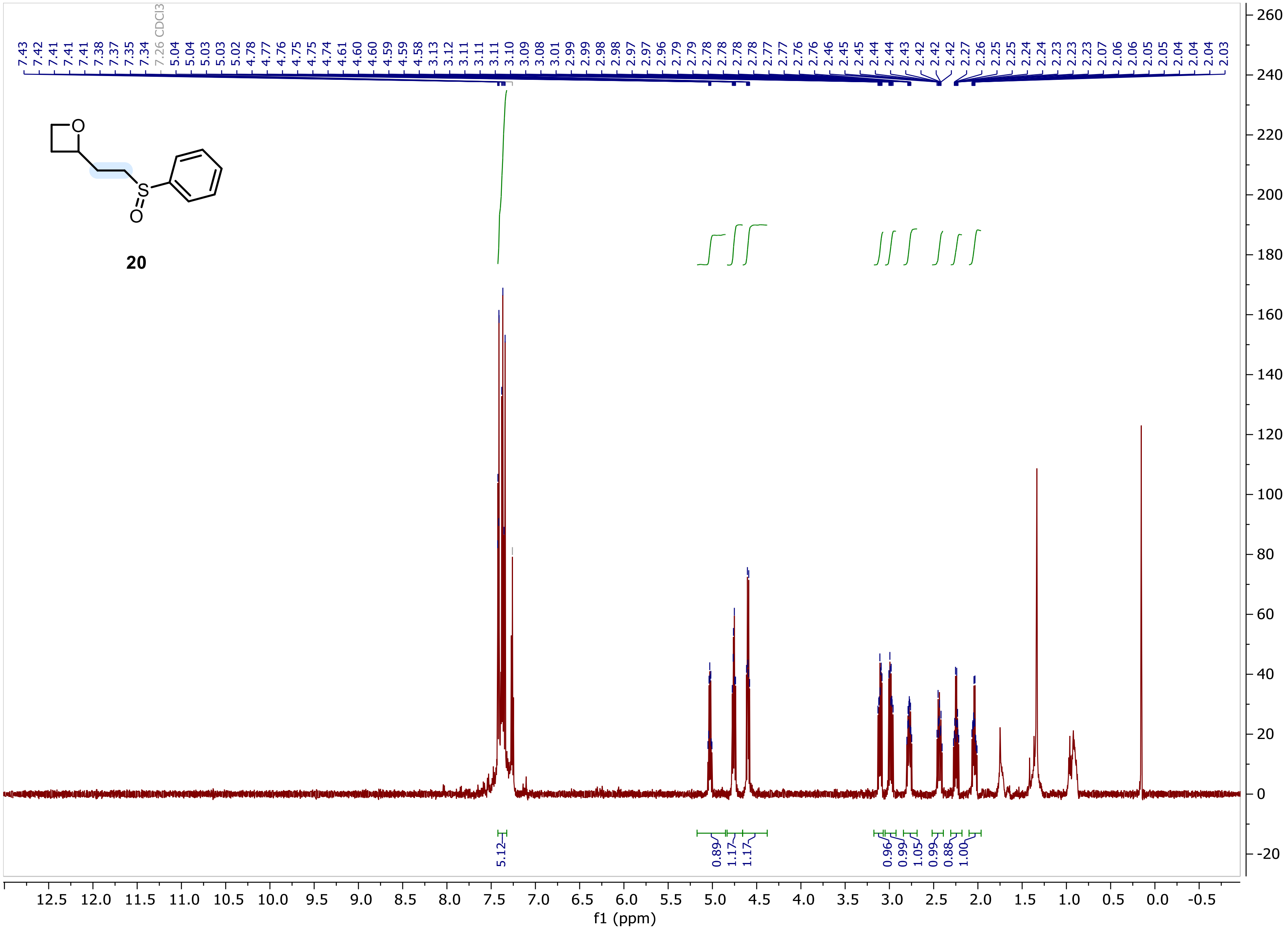

O
Me
H
N
O
19
f2 (ppm)
f1 (ppm)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150


O
Me
H
N
O
0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f2 (ppm)

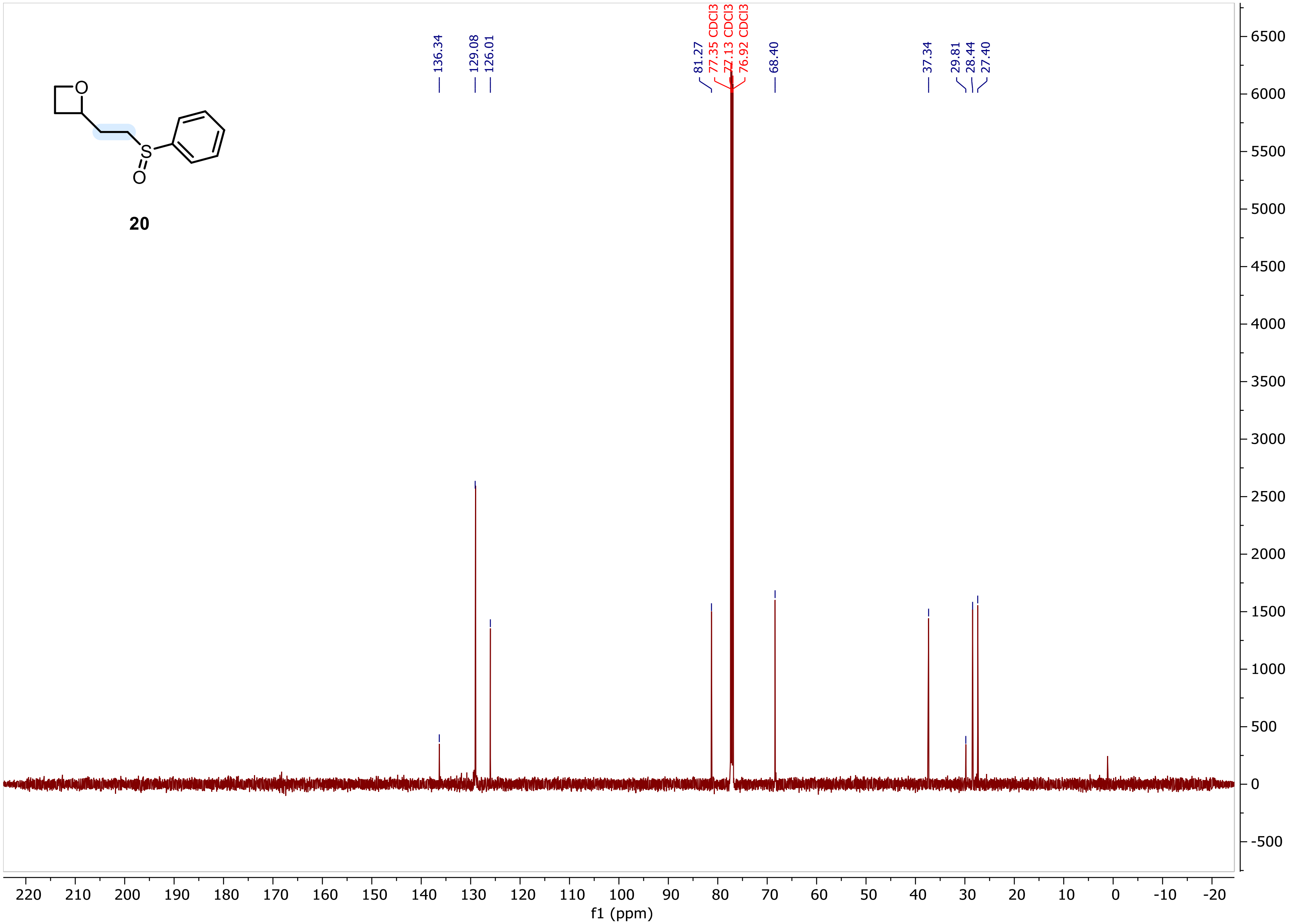
19


O
Me
H
N
O
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
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

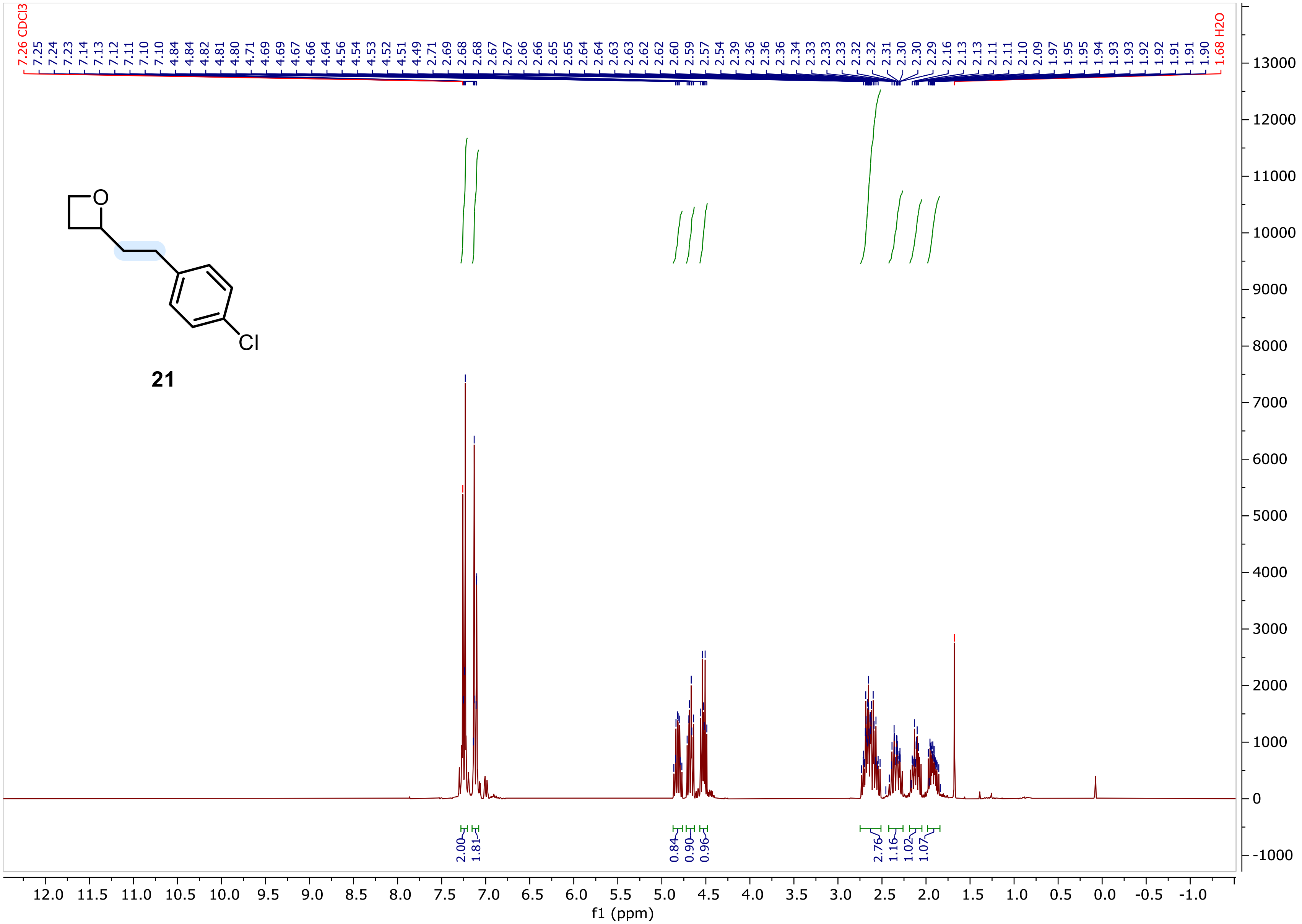
19


7.43
7.42
7.41
7.41
7.41
7.38
7.37
7.35
7.34
7.26 CDCl3
5.04
5.04
5.03
5.03
5.02
4.78
4.77
4.76
4.75
4.75
4.74
4.61
4.60
4.59
4.59
4.58
3.13
3.12
3.11
3.11
3.11
3.10
3.09
3.08
3.01
2.99
2.99
2.98
2.97
2.97
2.96
2.79
2.79
2.78
2.78
2.78
2.78
2.77
2.77
2.76
2.76
2.46
2.45
2.45
2.44
2.44
2.43
2.42
2.42
2.42
2.27
2.26
2.25
2.25
2.24
2.24
2.23
2.23
2.23
2.07
2.06
2.06
2.05
2.05
2.04
2.04
2.04
2.03
O
S
O
5.12
0.89
1.17
1.17
0.96
0.99
1.05
0.99
0.88
1.00
12.5 12.0 11.5 11.0 10.5 10.0 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 -0.5
f1 (ppm)
260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20

20

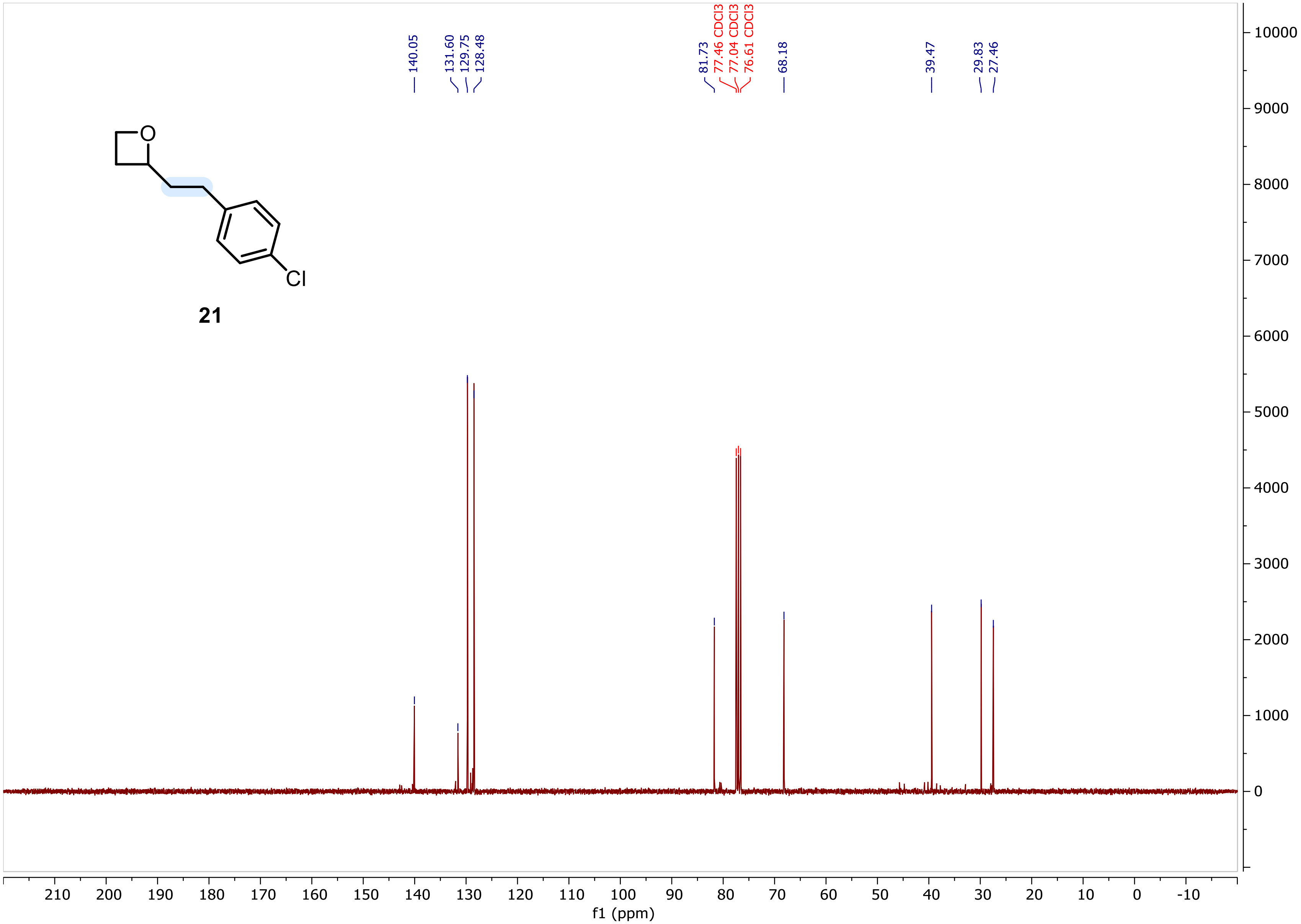

20

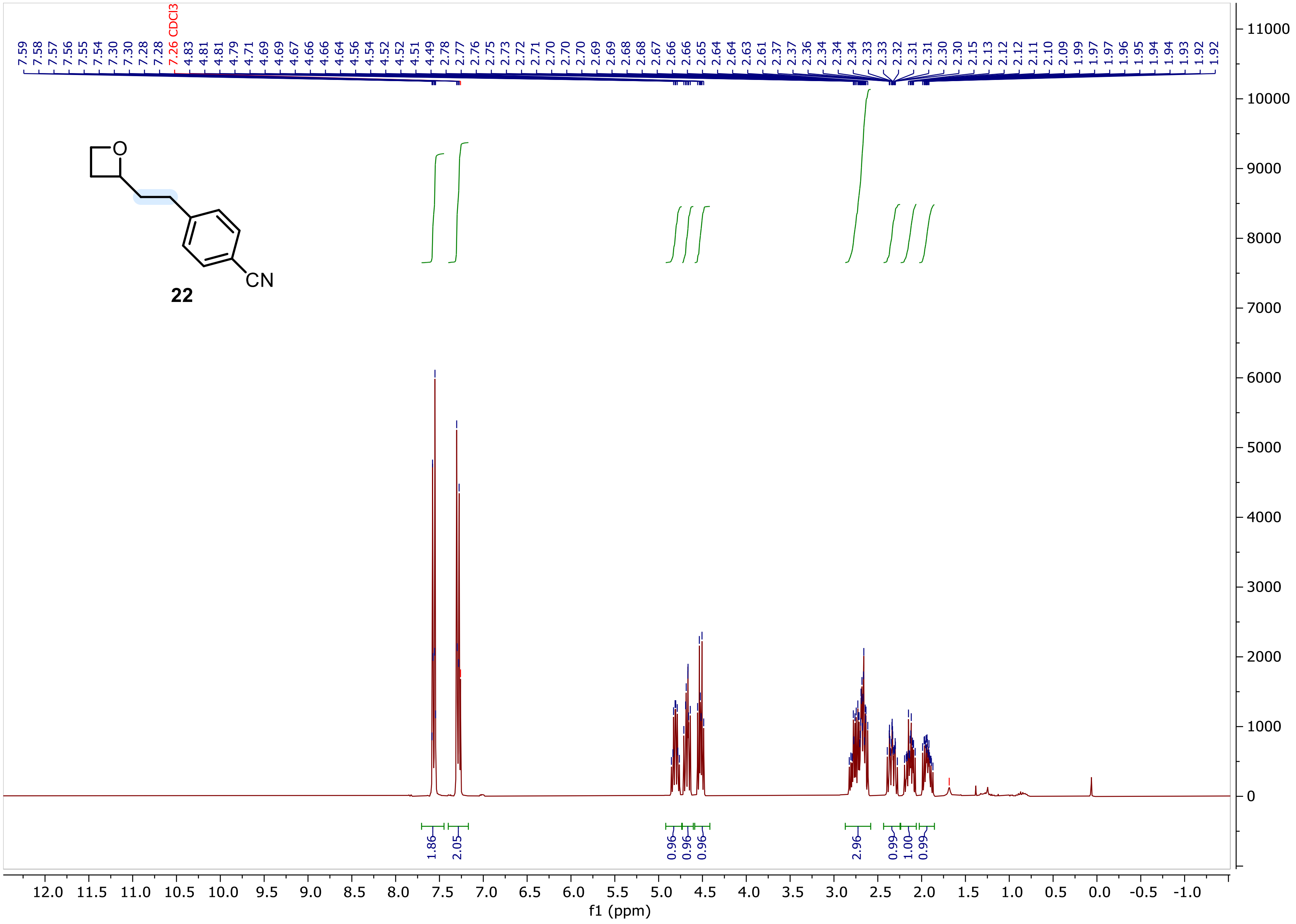
136.34
129.08
126.01
81.27
77.35 CDCl3
77.13 CDCl3
76.92 CDCl3
68.40
37.34
29.81
28.44
27.40
O
S
O
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



21

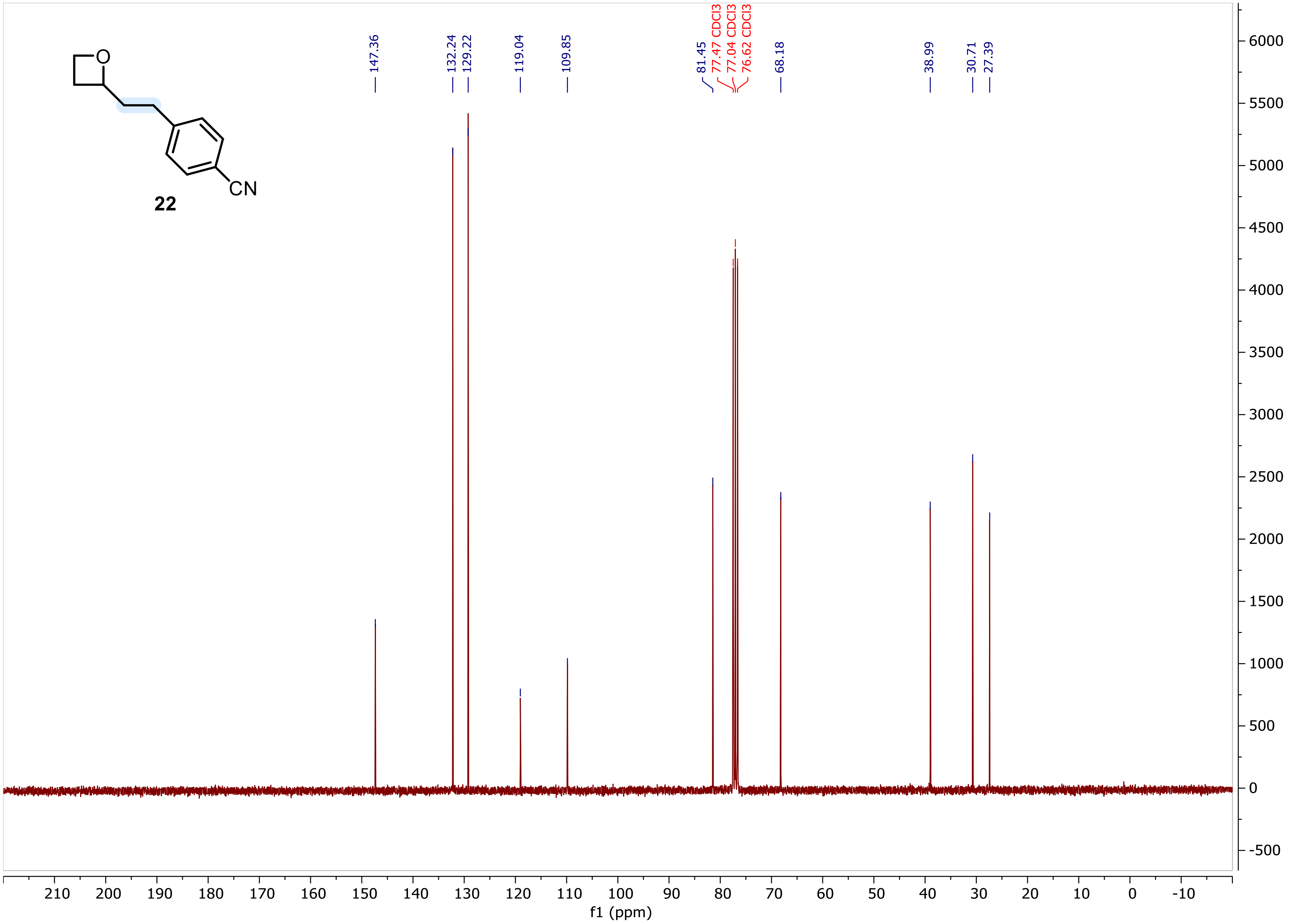
7.26 CDCl3
7.25
7.24
7.23
7.14
7.13
7.12
7.11
7.10
4.84
4.84
4.82
4.81
4.80
4.71
4.69
4.69
4.67
4.66
4.64
4.56
4.54
4.53
4.52
4.51
4.49
2.71
2.69
2.68
2.68
2.67
2.67
2.66
2.66
2.65
2.65
2.64
2.64
2.63
2.63
2.62
2.60
2.59
2.57
2.54
2.39
2.36
2.36
2.36
2.34
2.33
2.33
2.33
2.32
2.32
2.31
2.30
2.30
2.29
2.16
2.13
2.13
2.11
2.11
2.10
2.09
1.97
1.95
1.95
1.94
1.93
1.93
1.92
1.92
1.91
1.91
1.90
1.68 H2O
O
Cl
2.00
1.81
0.84
0.90
0.96
2.76
1.16
1.02
1.07
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
12.0
11.5
11.0
10.5
10.0
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
-0.5
-1.0
f1 (ppm)


140.05
131.60
129.75
128.48
81.73
77.46 CDCl3
77.04 CDCl3
76.61 CDCl3
68.18
39.47
29.83
27.46
O
Cl
21
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
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)



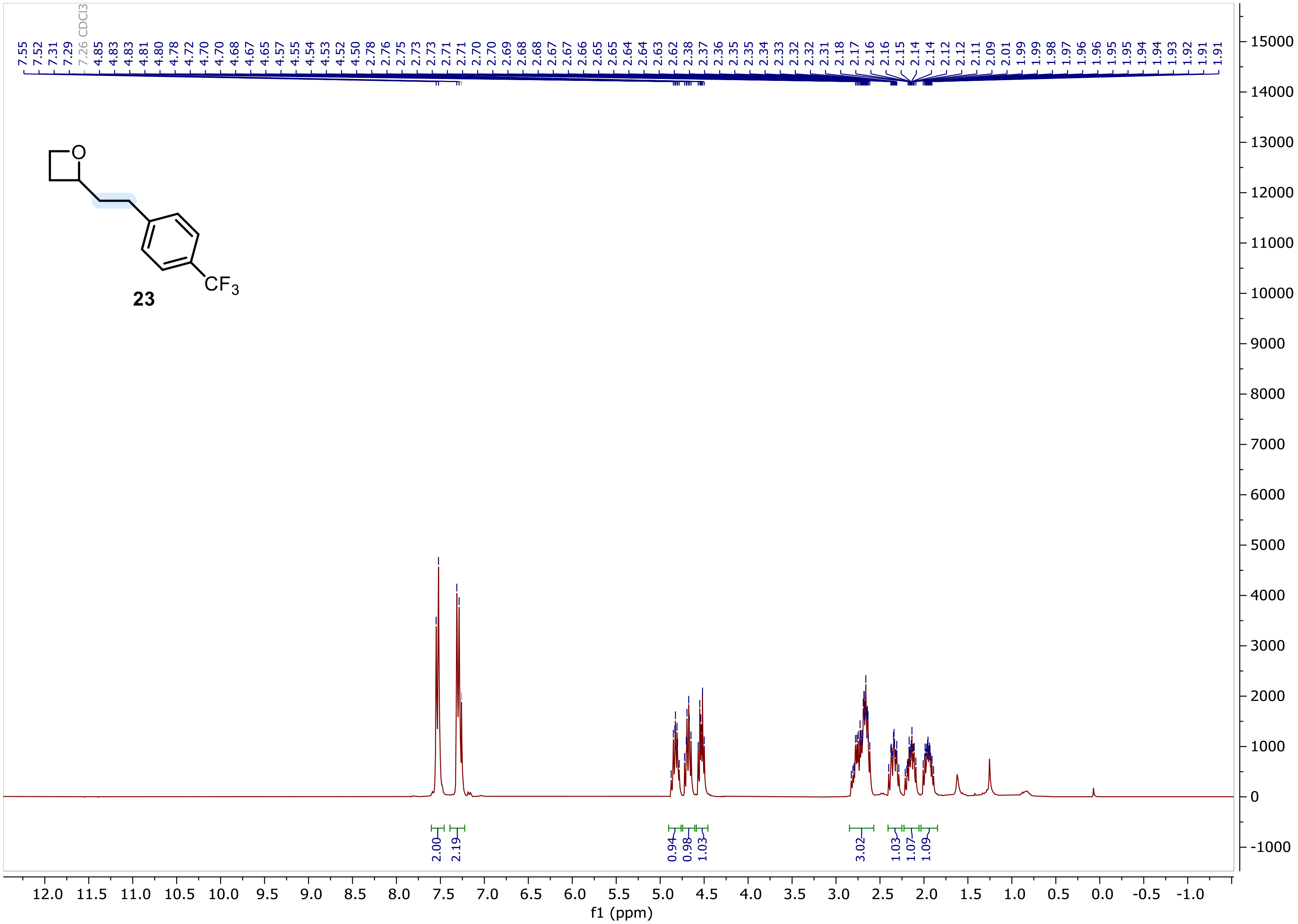
22

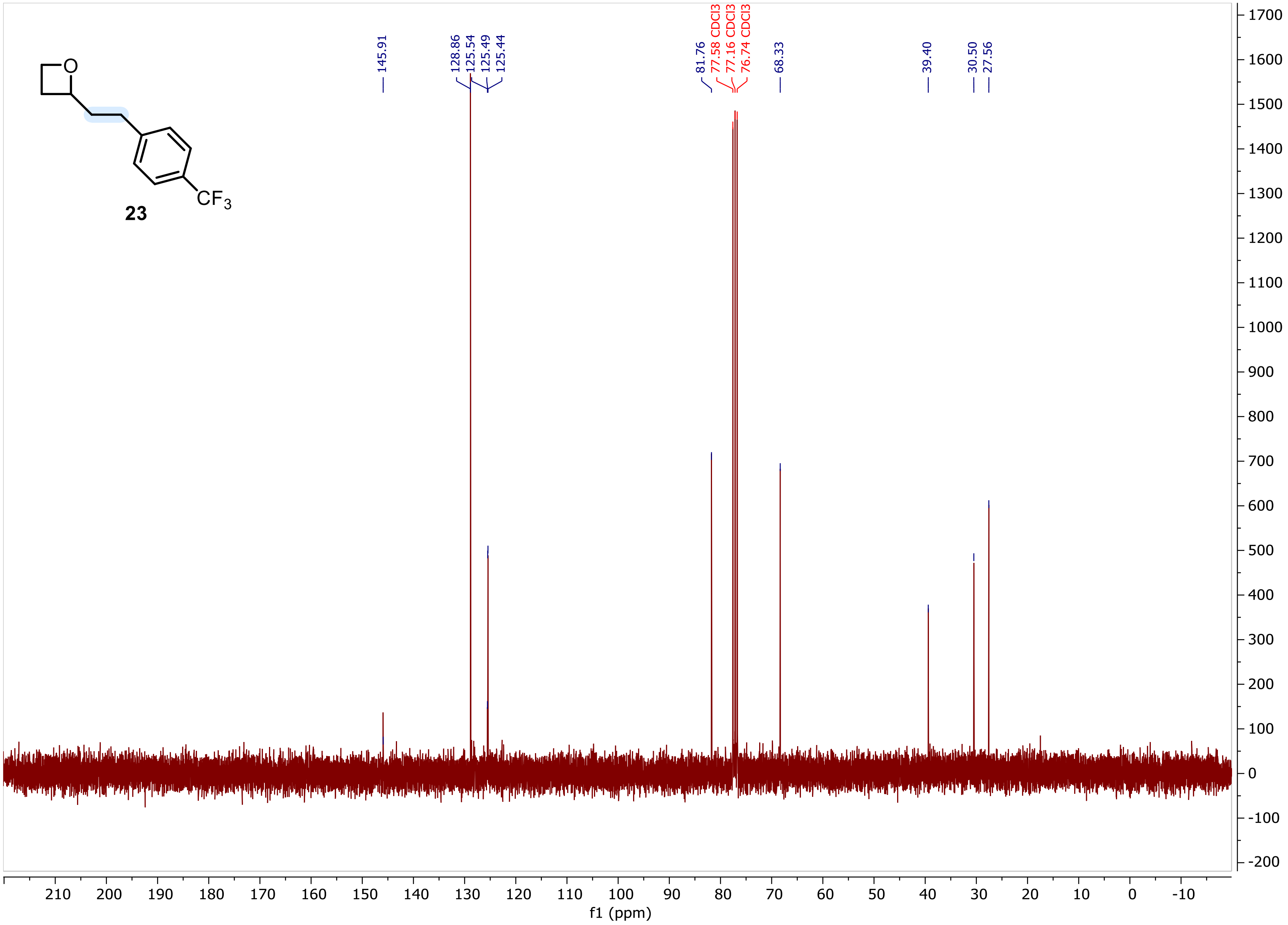
7.59 7.58 7.57 7.56 7.55 7.54 7.30 7.30 7.28 7.28 7.26 CDCl3 4.83 4.81 4.81 4.79 4.71 4.69 4.69 4.67 4.66 4.66 4.64 4.56 4.54 4.52 4.52 4.51 4.49 2.78 2.77 2.76 2.75 2.73 2.72 2.71 2.70 2.70 2.70 2.69 2.69 2.68 2.68 2.67 2.66 2.66 2.65 2.64 2.64 2.63 2.61 2.37 2.37 2.36 2.34 2.34 2.34 2.33 2.32 2.31 2.31 2.30 2.30 2.15 2.13 2.12 2.12 2.11 2.10 2.09 1.99 1.97 1.97 1.96 1.95 1.94 1.94 1.93 1.92 1.92
O
CN
1.86
2.05
0.96
0.96
0.96
2.96
0.99
1.00
0.99
12.0 11.5 11.0 10.5 10.0 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 -0.5 -1.0
f1 (ppm)
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0



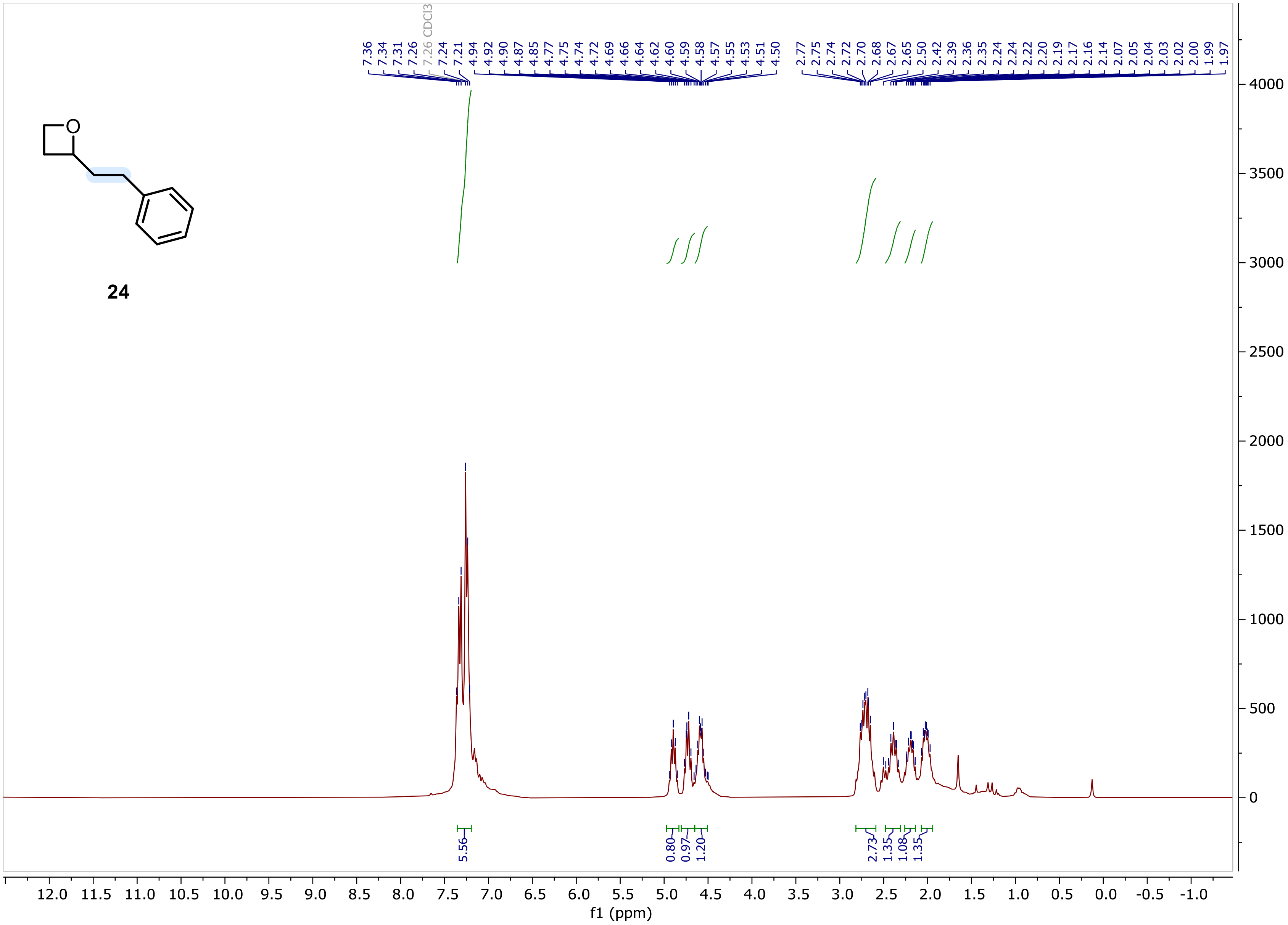
22

O
CN
147.36
132.24
129.22
119.04
109.85
81.45
77.47 CDCl3
77.04 CDCl3
76.62 CDCl3
68.18
38.99
30.71
27.39
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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)

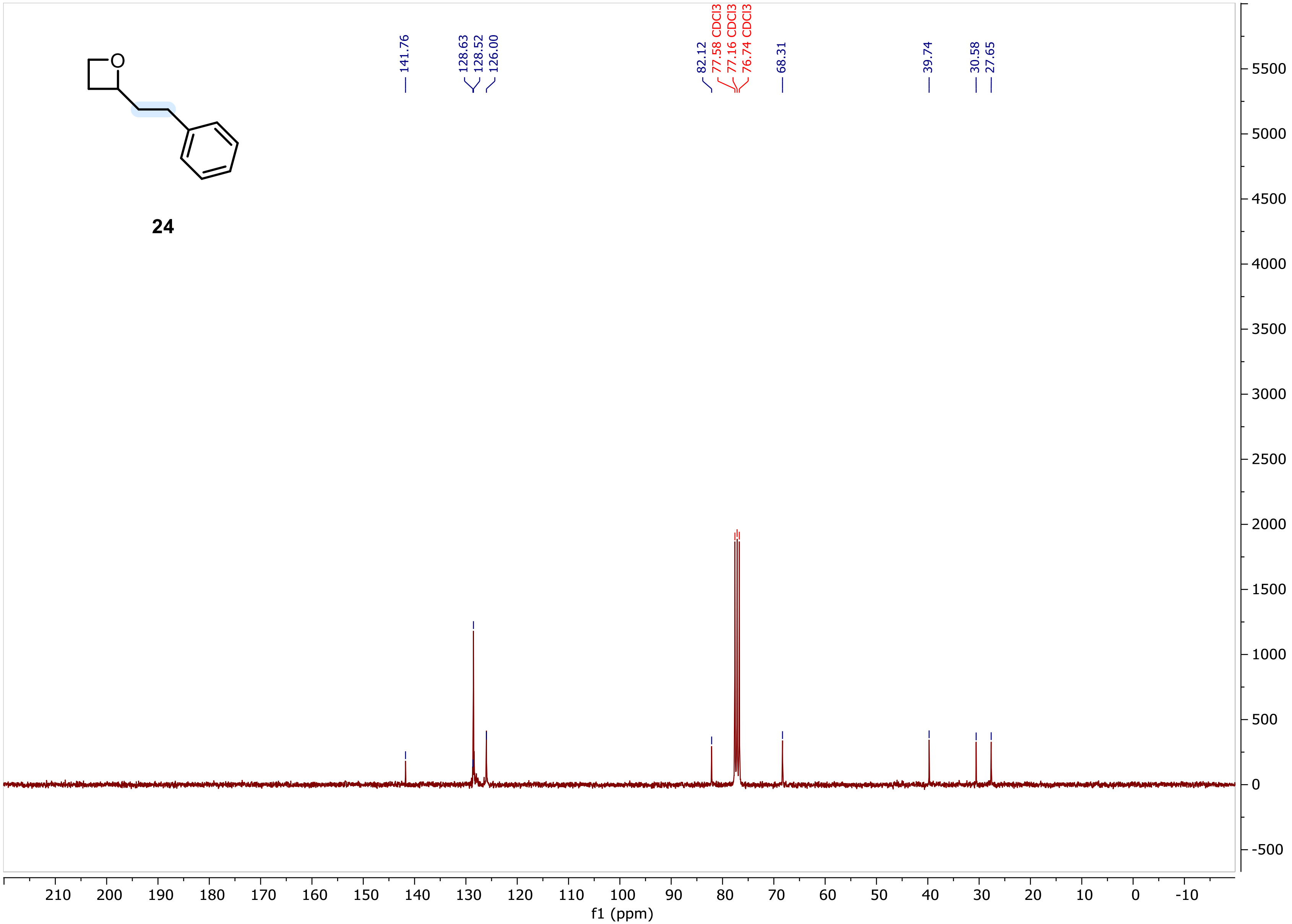

7.55 7.52 7.31 7.29 7.26 CDCl3 4.85 4.83 4.83 4.81 4.80 4.78 4.72 4.70 4.70 4.68 4.67 4.65 4.57 4.55 4.54 4.53 4.52 4.50 2.78 2.76 2.75 2.73 2.73 2.71 2.71 2.70 2.70 2.69 2.68 2.68 2.67 2.67 2.66 2.65 2.65 2.64 2.64 2.63 2.62 2.38 2.37 2.36 2.35 2.35 2.34 2.33 2.32 2.32 2.31 2.18 2.17 2.16 2.16 2.15 2.14 2.14 2.12 2.12 2.11 2.09 2.01 1.99 1.99 1.98 1.97 1.96 1.96 1.95 1.95 1.94 1.94 1.93 1.92 1.91 1.91
O
CF3
23
2.00
2.19
0.94
0.98
1.03
3.02
1.03
1.07
1.09
12.0 11.5 11.0 10.5 10.0 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 -0.5 -1.0
f1 (ppm)
15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000



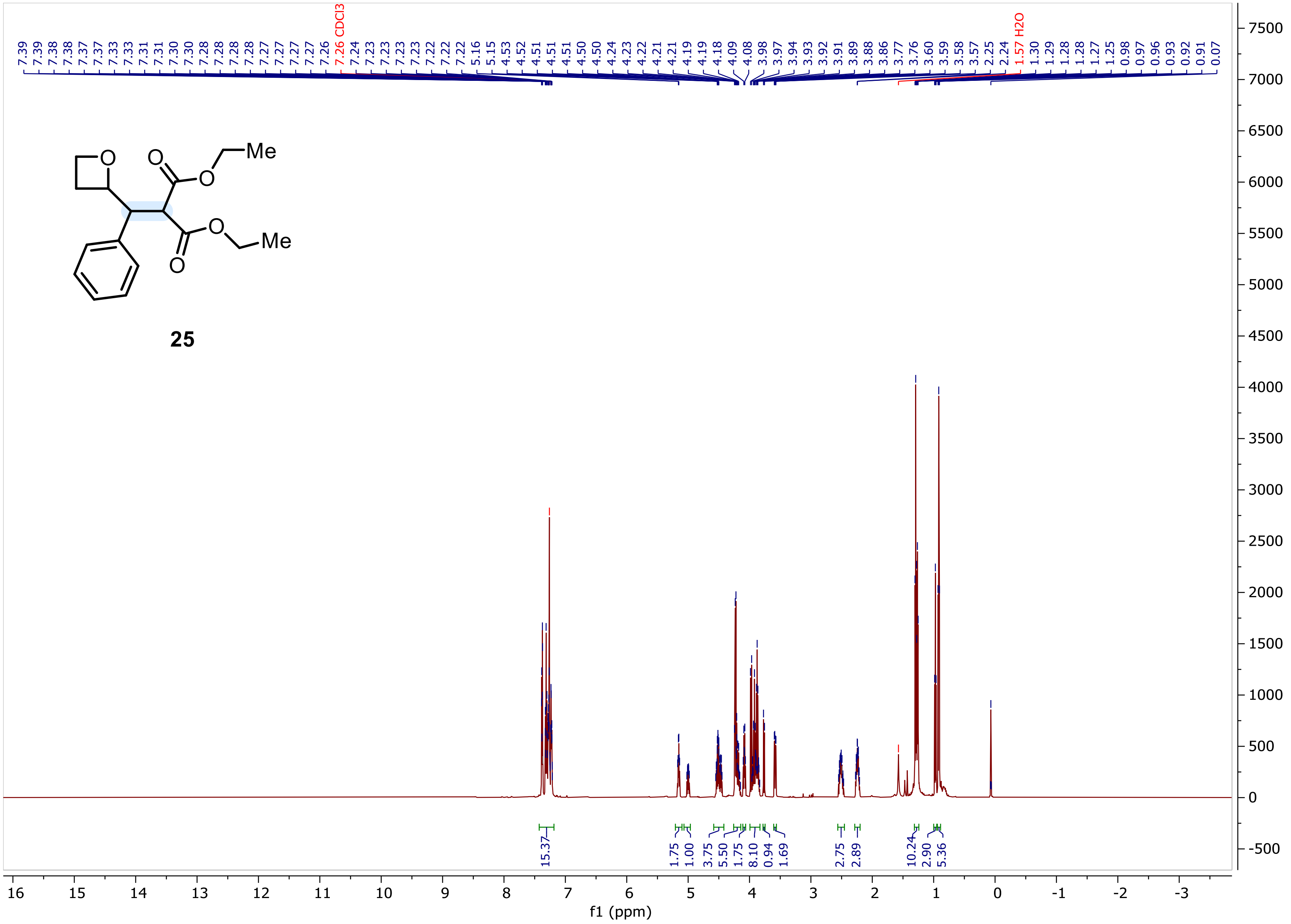
23
CF3
O
145.91
128.86
125.54
125.49
125.44
81.76
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
68.33
39.40
30.50
27.56
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

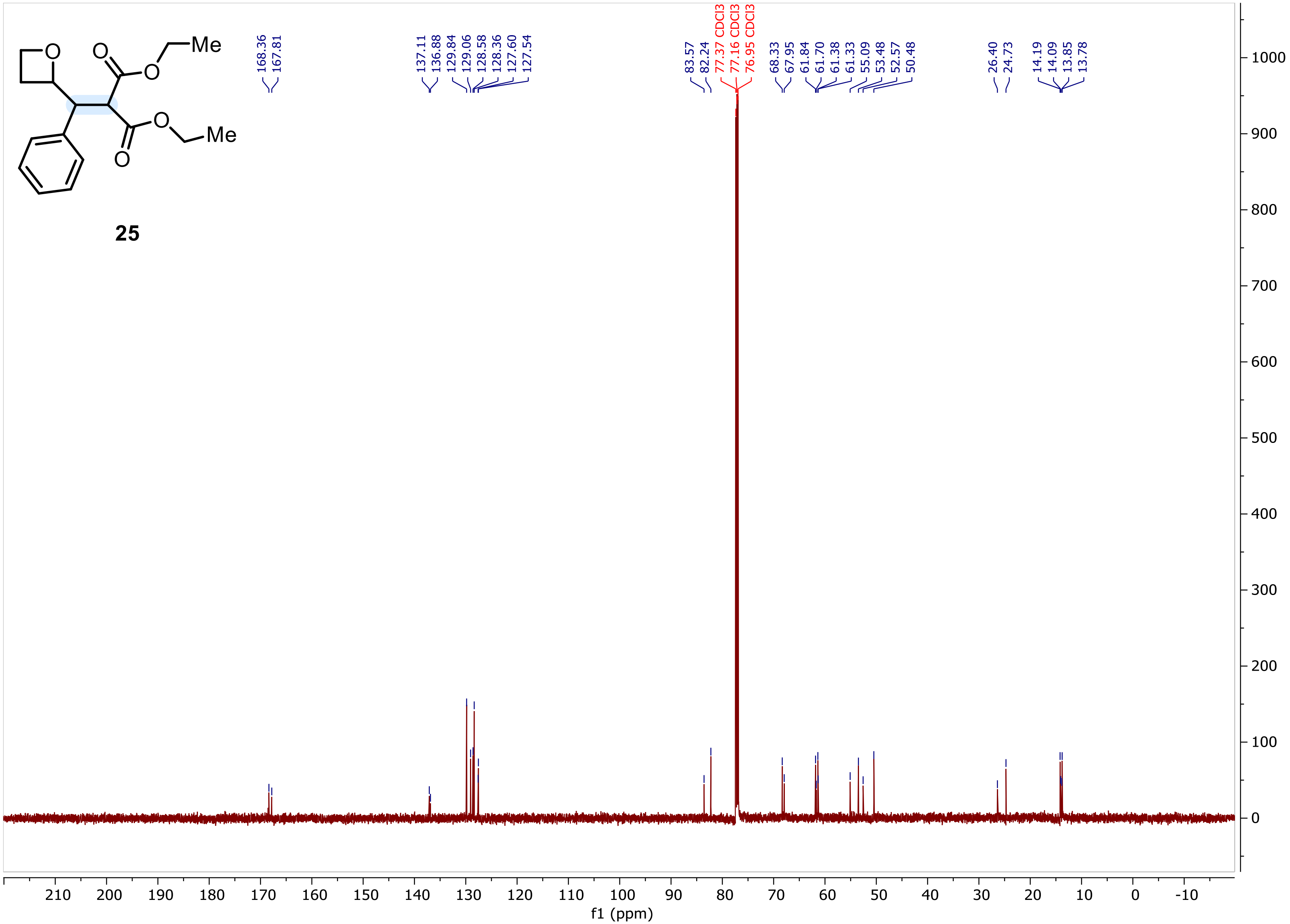

24

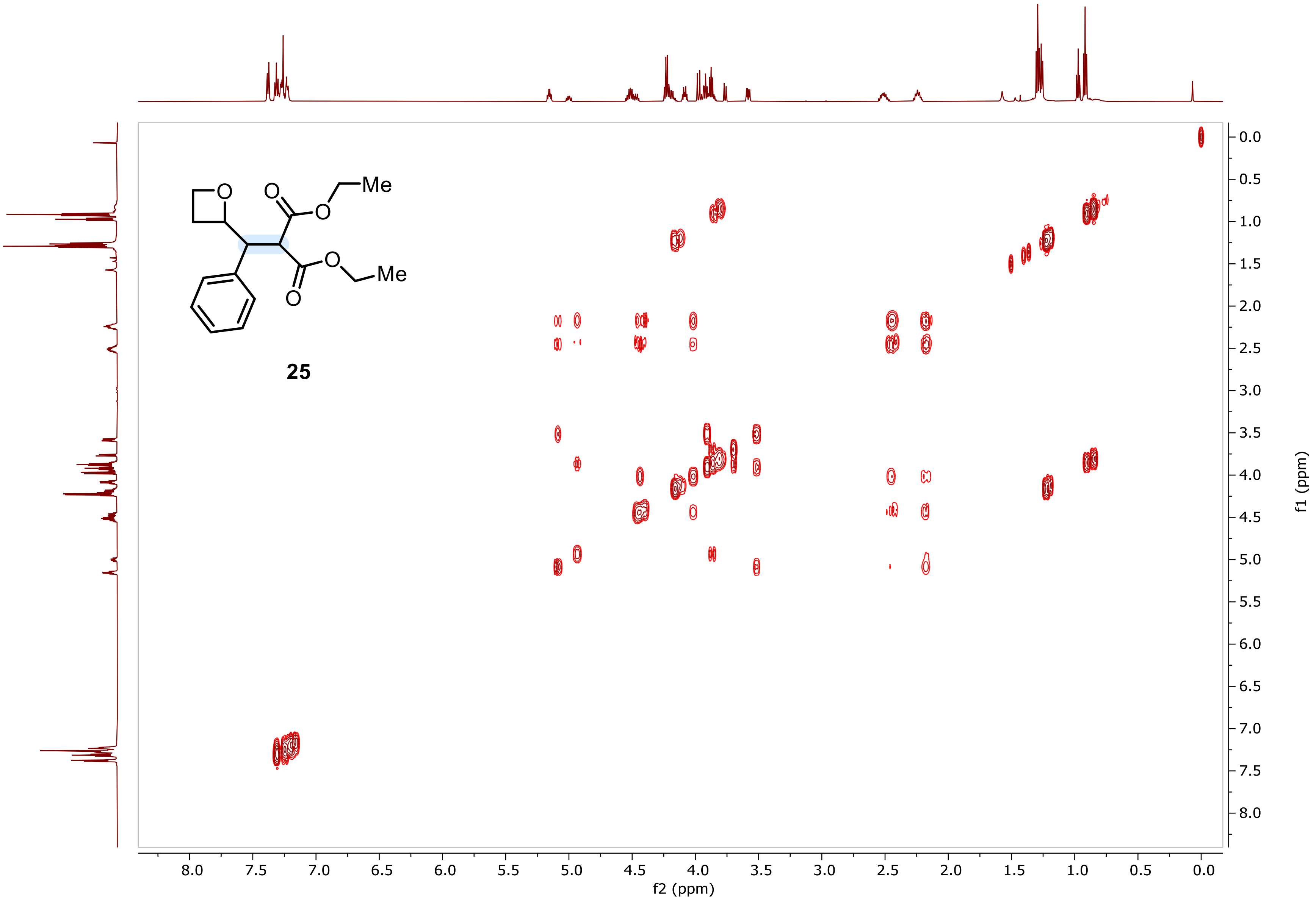
7.36
7.34
7.31
7.26
7.26 CDCl3
7.24
7.21
4.94
4.92
4.90
4.87
4.85
4.77
4.75
4.74
4.72
4.69
4.66
4.64
4.62
4.60
4.59
4.58
4.57
4.55
4.53
4.51
4.50
2.77
2.75
2.74
2.72
2.70
2.68
2.67
2.65
2.50
2.42
2.39
2.36
2.35
2.24
2.24
2.22
2.20
2.19
2.17
2.16
2.14
2.07
2.05
2.04
2.03
2.02
2.00
1.99
1.97
O
5.56
0.80
0.97
1.20
2.73
1.35
1.08
1.35
4000
3500
3000
2500
2000
1500
1000
500
0
12.0
11.5
11.0
10.5
10.0
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
-0.5
-1.0
f1 (ppm)


24

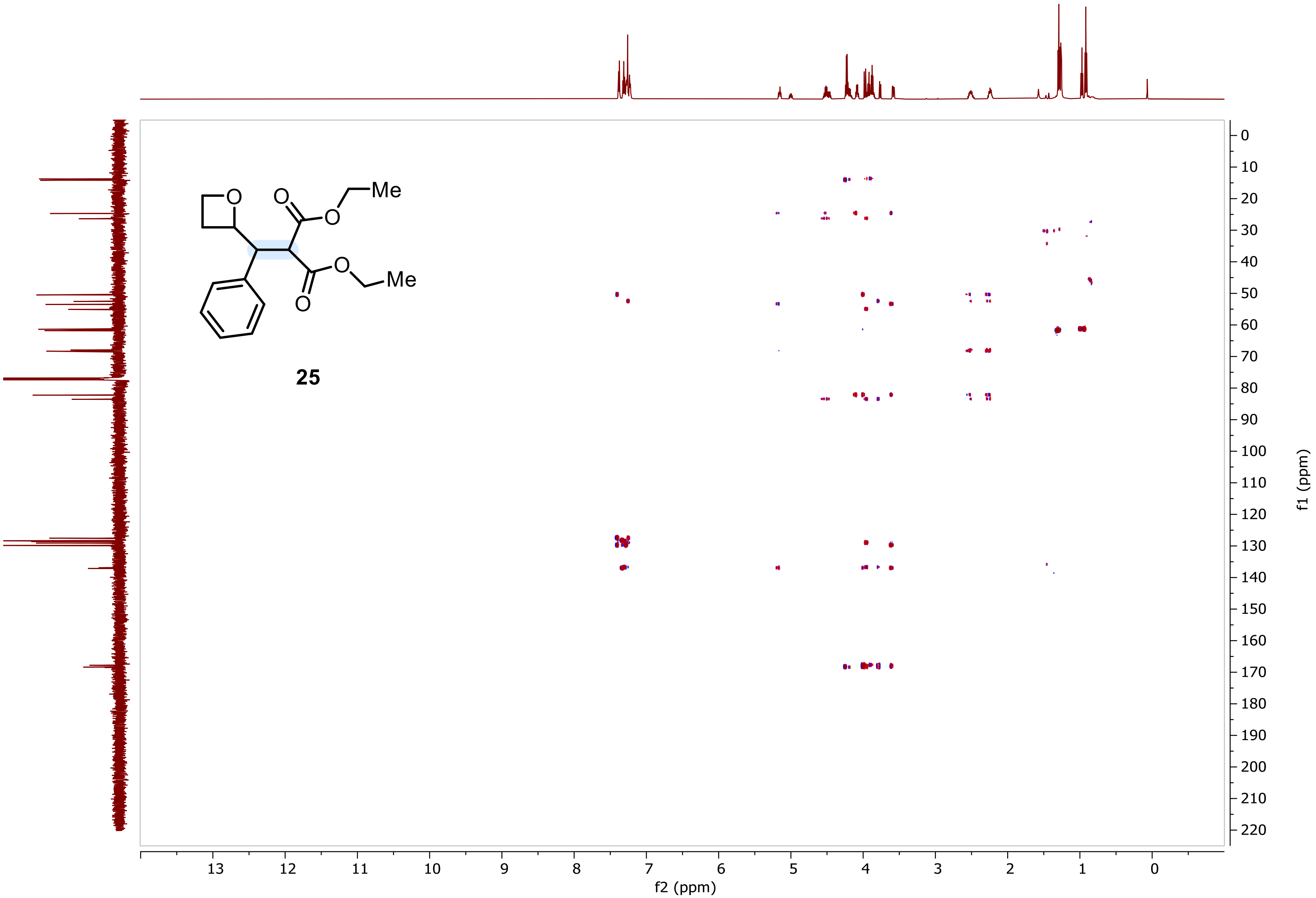
141.76
128.63
128.52
126.00
82.12
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
68.31
39.74
30.58
27.65
O
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.39 7.39 7.38 7.38 7.37 7.37 7.33 7.33 7.31 7.31 7.30 7.30 7.28 7.28 7.28 7.28 7.27 7.27 7.27 7.27 7.26 7.26 CDCl3 7.24 7.23 7.23 7.23 7.23 7.22 7.22 7.22 7.22 5.16 5.15 4.53 4.52 4.51 4.51 4.51 4.50 4.50 4.24 4.23 4.22 4.21 4.21 4.19 4.19 4.18 4.09 4.08 3.98 3.97 3.94 3.93 3.92 3.91 3.89 3.88 3.86 3.77 3.76 3.60 3.59 3.58 3.57 2.25 2.24 1.57 H2O 1.30 1.29 1.28 1.28 1.27 1.25 0.98 0.97 0.96 0.93 0.92 0.91 0.07
O
O
O
Me
O
O
Me
25
15.37
1.75
1.00
3.75
5.50
1.75
8.10
0.94
1.69
2.75
2.89
10.24
2.90
5.36
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

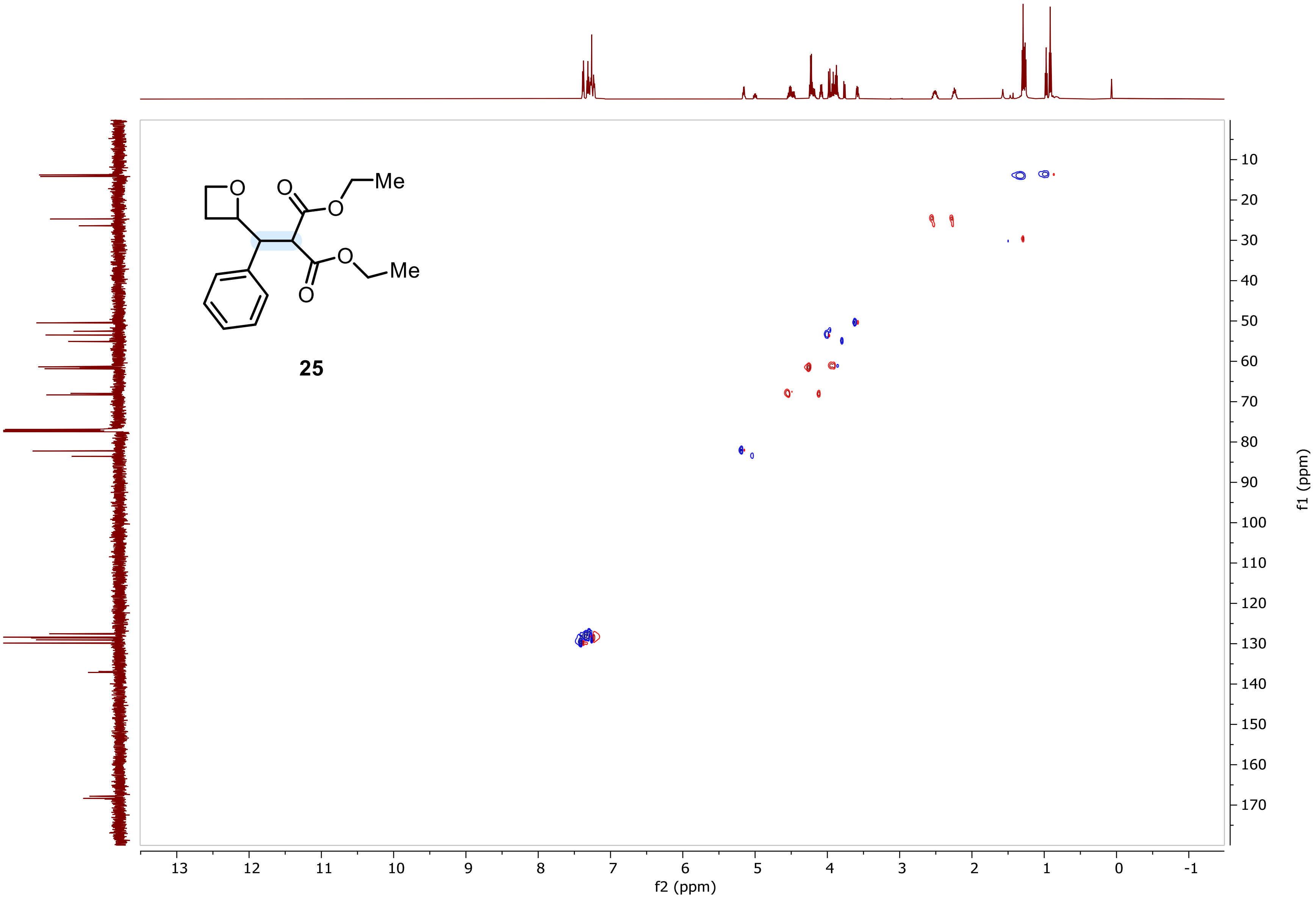

O
O
O
Me
O
O
Me
25
168.36
167.81
137.11
136.88
129.84
129.06
128.58
128.36
127.60
127.54
83.57
82.24
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
68.33
67.95
61.84
61.70
61.38
61.33
55.09
53.48
52.57
50.48
26.40
24.73
14.19
14.09
13.85
13.78
1000
900
800
700
600
500
400
300
200
100
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
Me
O
O
Me
O
O
f2 (ppm)
f1 (ppm)
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

25



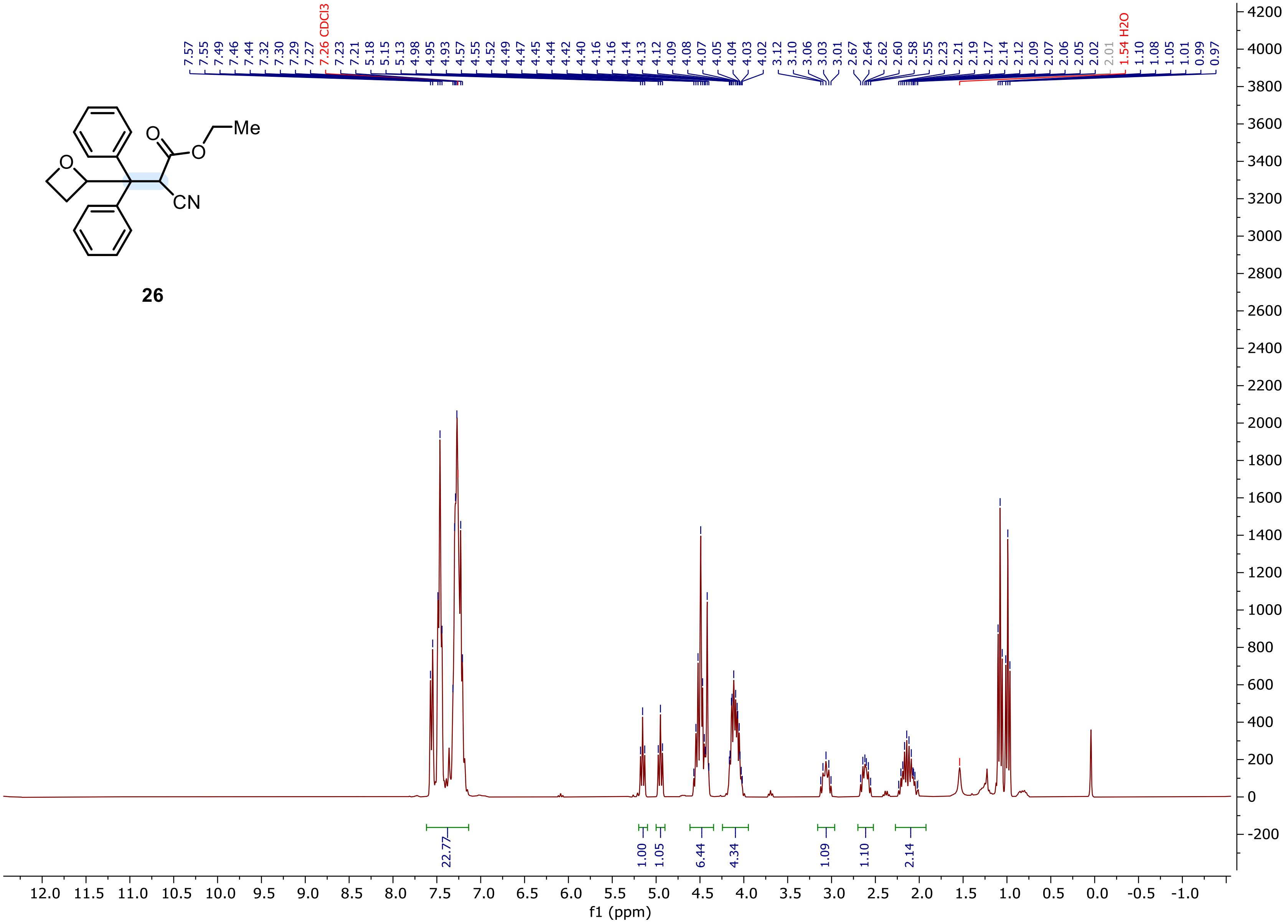
O
O
O
Me
O
O
Me
25
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
f1 (ppm)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f2 (ppm)

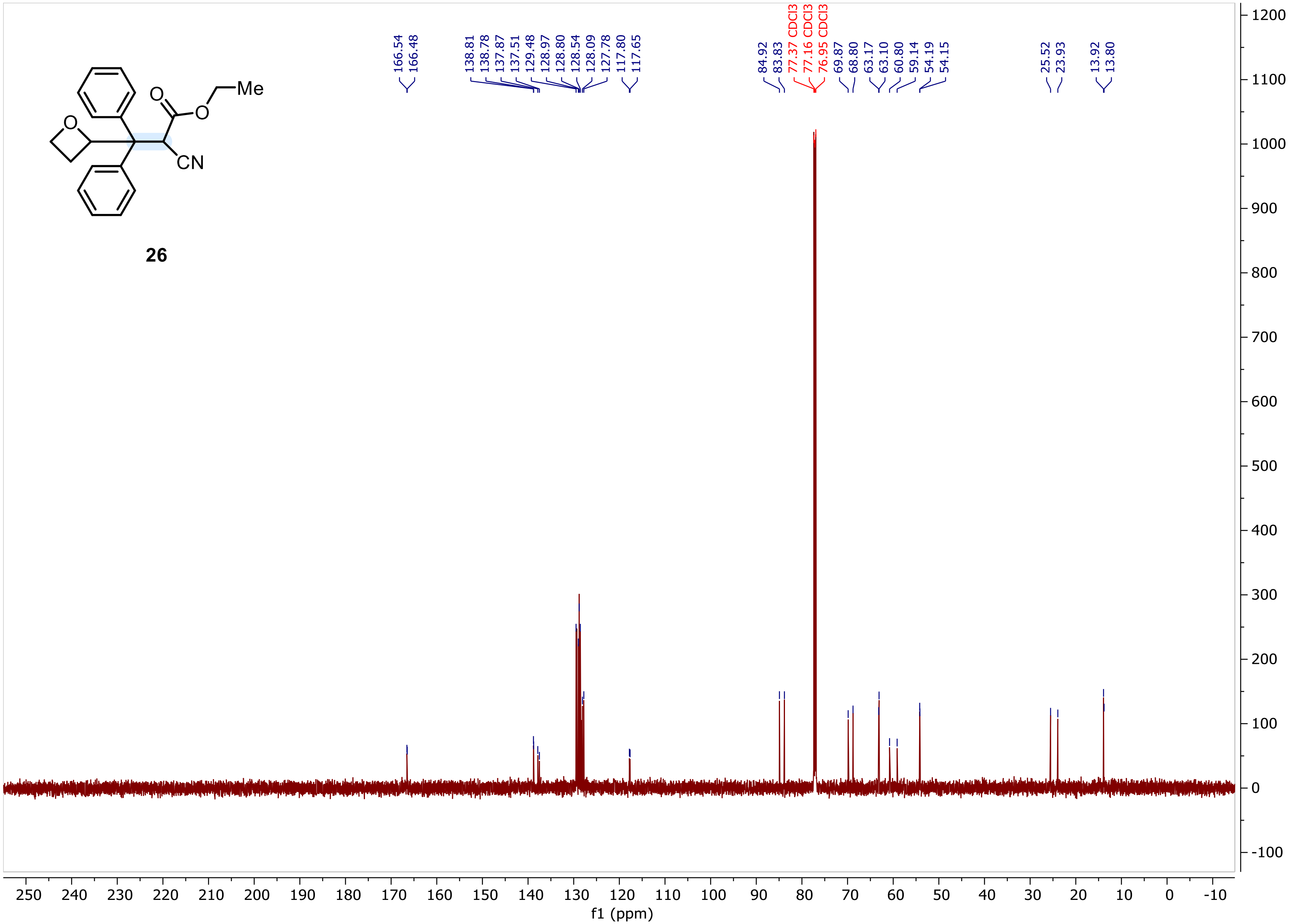


O
O
O
O
O
Me
Me
25
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
f1 (ppm)

O
O
O
Me
CN

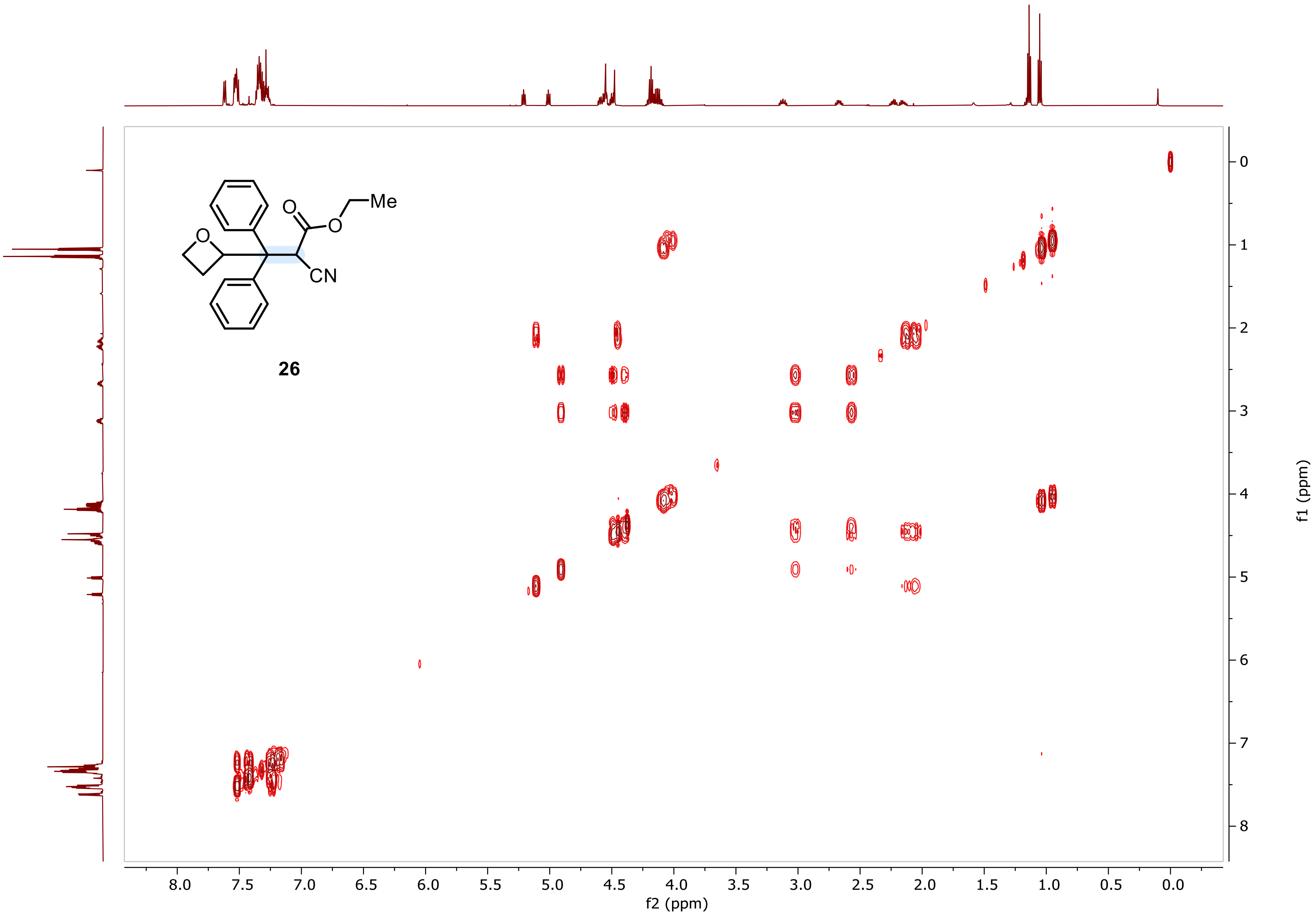
26


7.57
7.55
7.49
7.46
7.44
7.32
7.30
7.29
7.27
7.26 CDCl3
7.23
7.21
5.18
5.15
5.13
4.98
4.95
4.93
4.57
4.55
4.52
4.49
4.47
4.45
4.44
4.42
4.40
4.16
4.16
4.14
4.13
4.12
4.09
4.08
4.07
4.05
4.04
4.03
4.02
3.12
3.10
3.06
3.03
3.01
2.67
2.64
2.62
2.60
2.58
2.55
2.23
2.21
2.19
2.17
2.14
2.12
2.09
2.07
2.06
2.05
2.02
2.01
1.54 H2O
1.10
1.08
1.05
1.01
0.99
0.97
22.77
1.00
1.05
6.44
4.34
1.09
1.10
2.14
12.0
11.5
11.0
10.5
10.0
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
-0.5
-1.0
f1 (ppm)
4200
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200



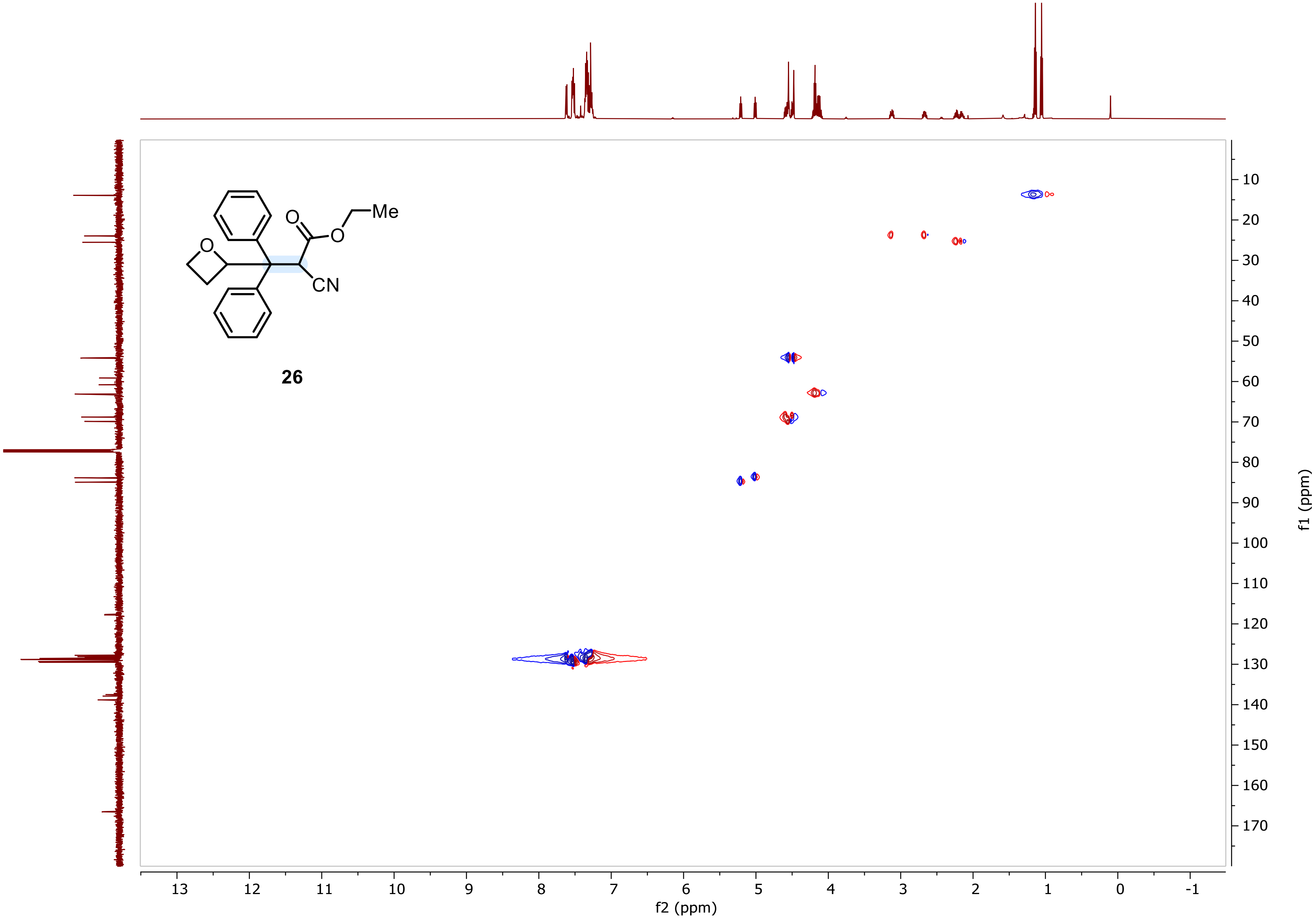
26

Me
O
O
O
CN
166.54
166.48
138.81
138.78
137.87
137.51
129.48
128.97
128.80
128.54
128.09
127.78
117.80
117.65
84.92
83.83
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
69.87
68.80
63.17
63.10
60.80
59.14
54.19
54.15
25.52
23.93
13.92
13.80
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



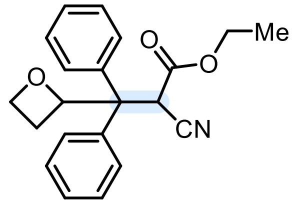
26

O
O
O
Me
CN
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
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

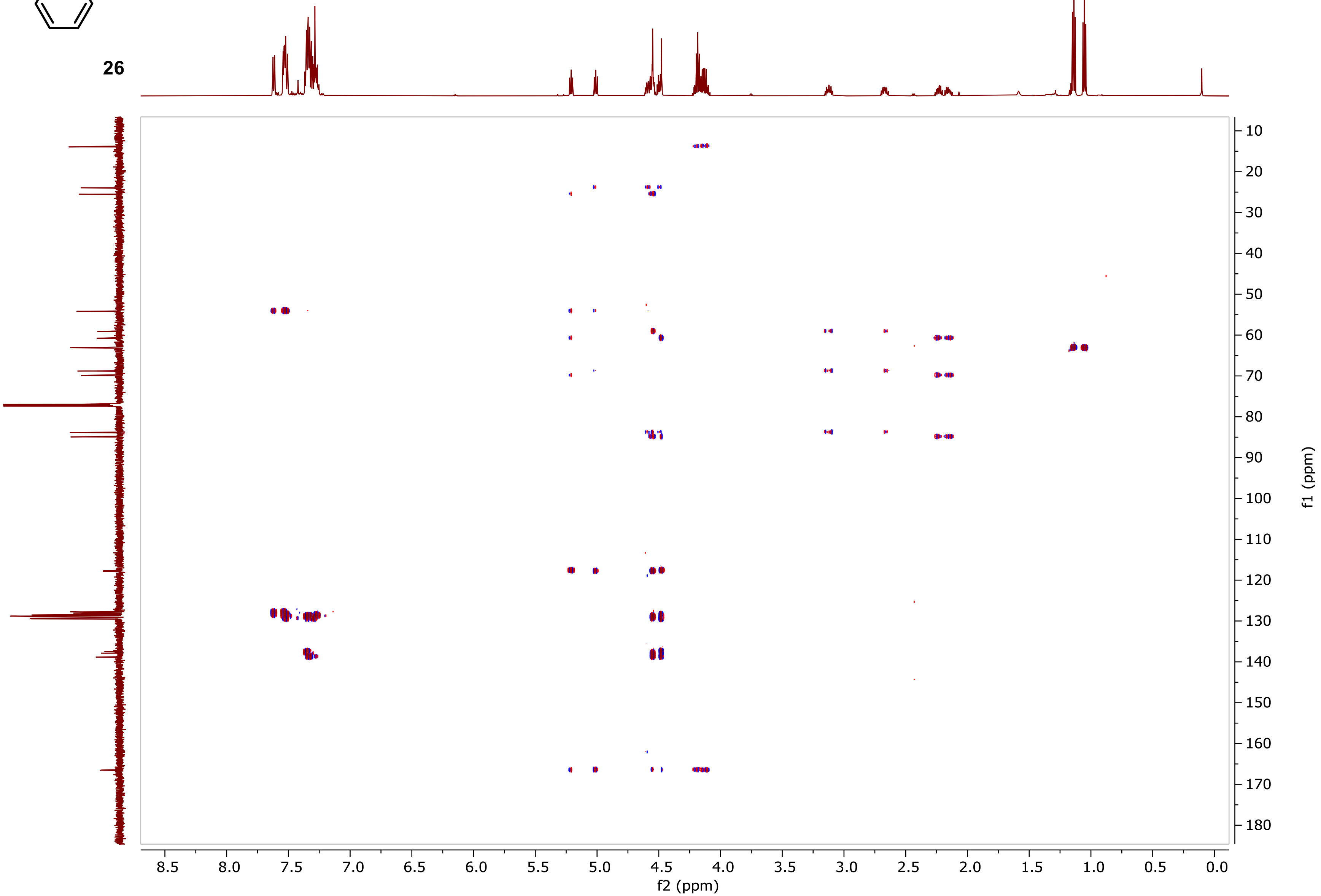


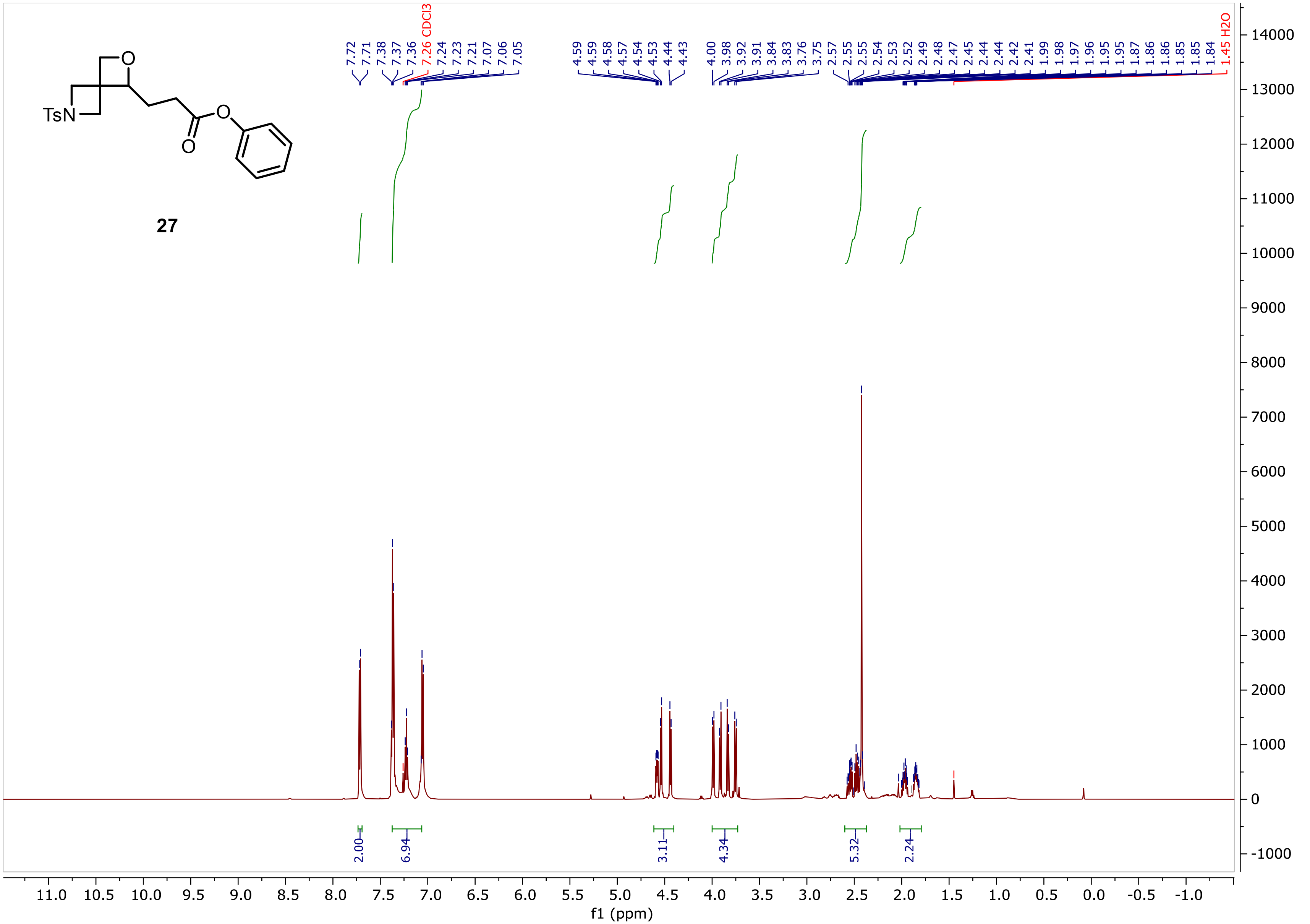
26

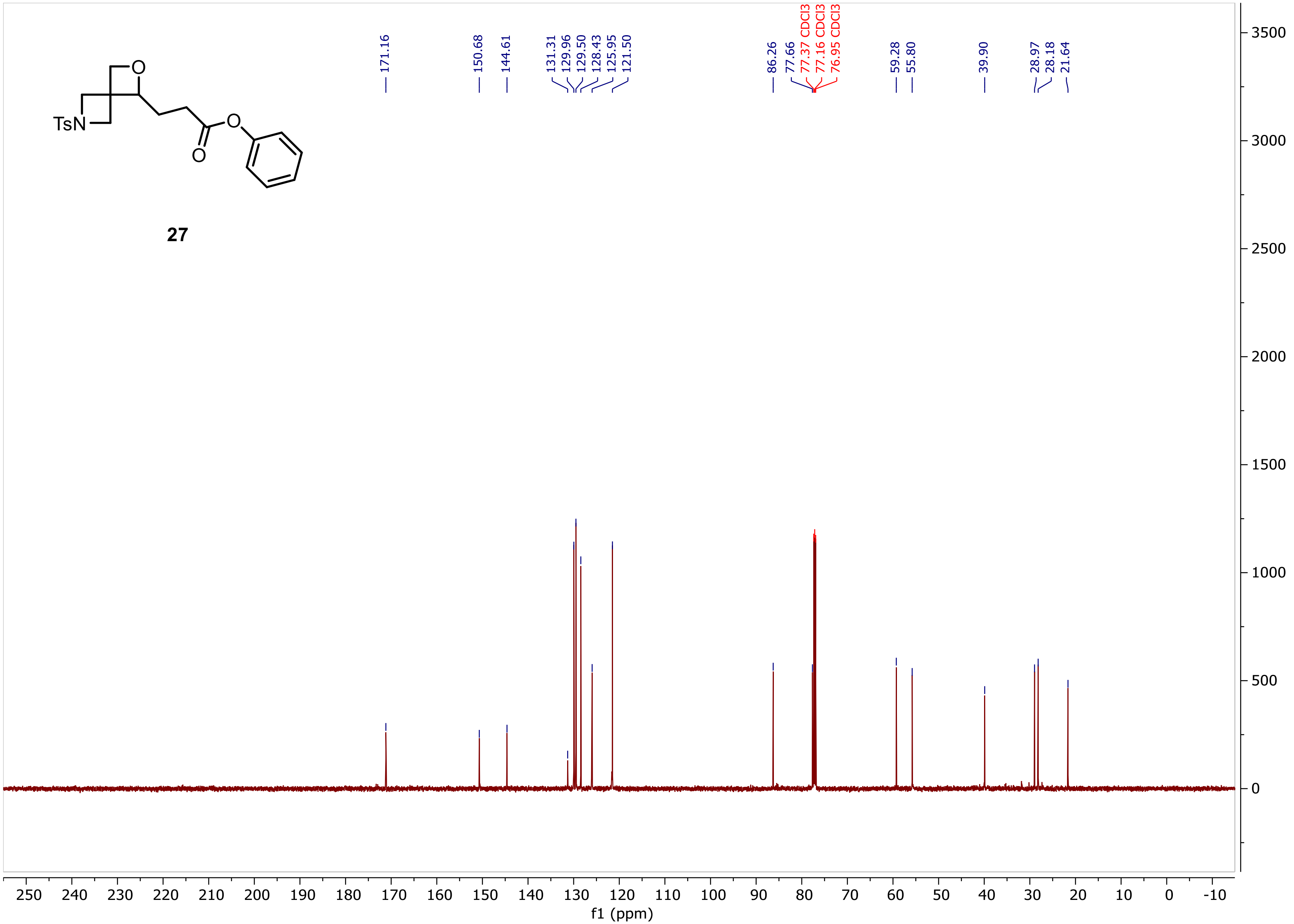
O
O
O
Me
CN
f2 (ppm)
f1 (ppm)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170

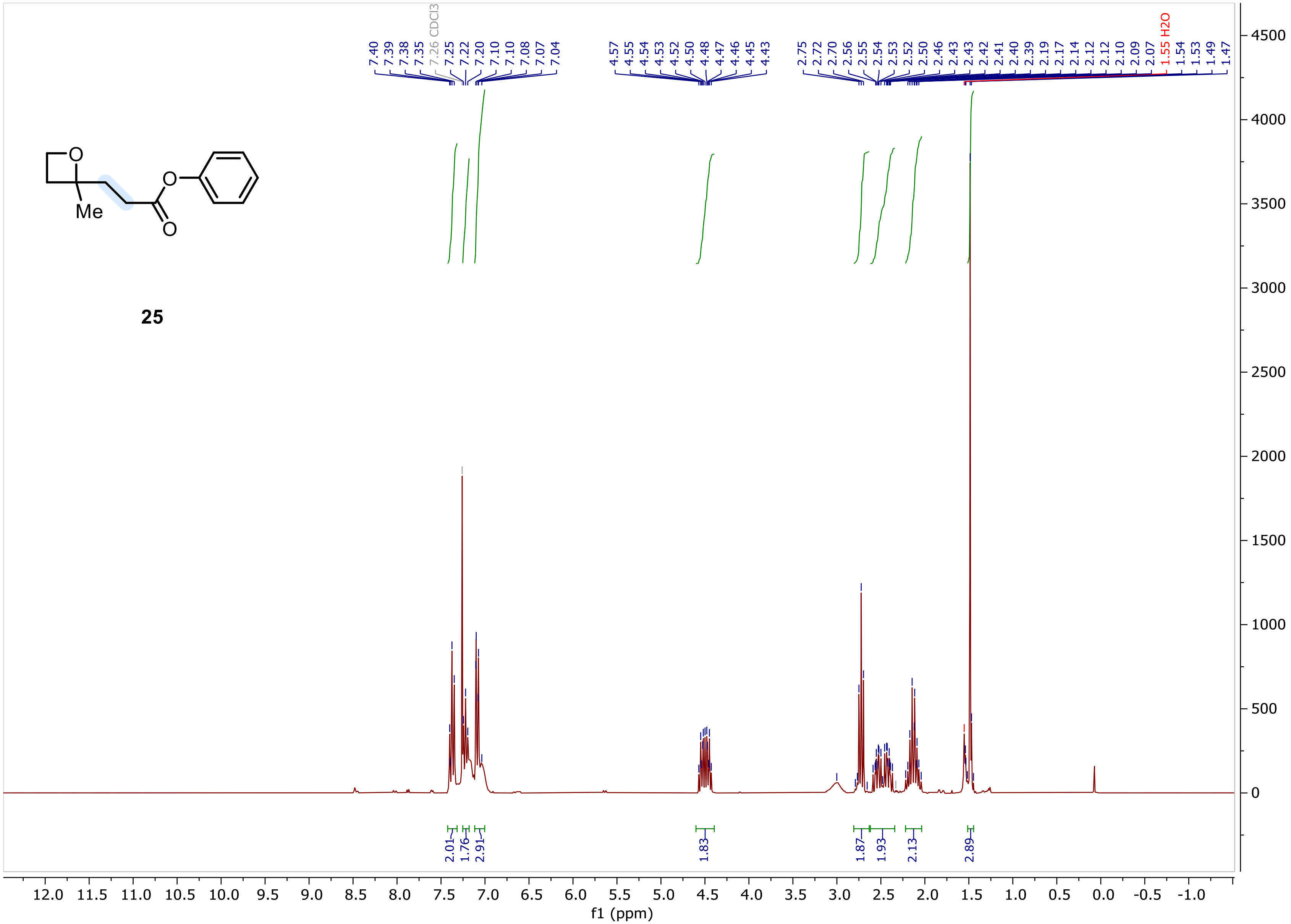

O
O
Me
O
CN

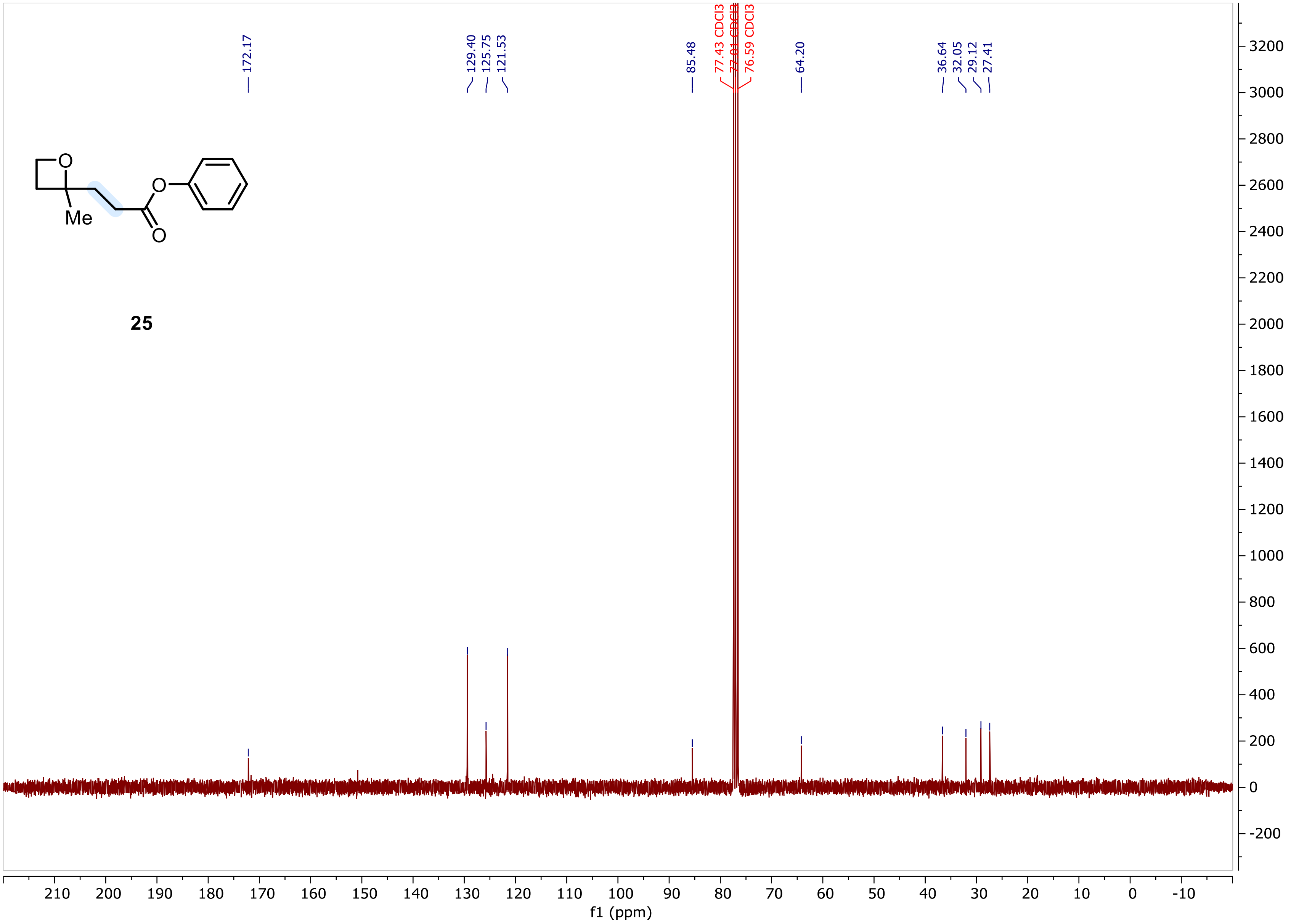
26


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
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)

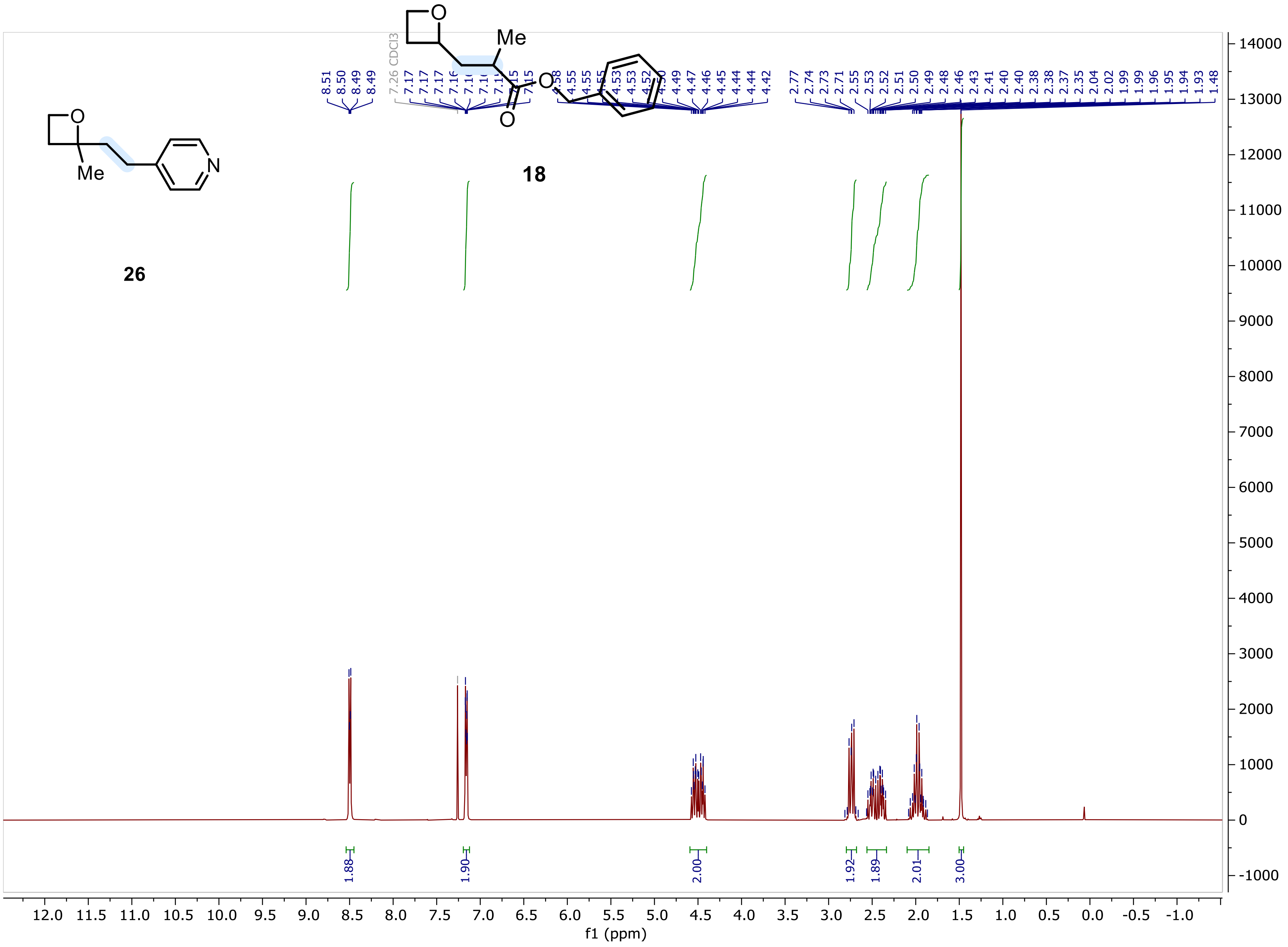

TsN
O
O
O
27
7.72
7.71
7.38
7.37
7.36
7.26 CDCl3
7.24
7.23
7.21
7.07
7.06
7.05
4.59
4.59
4.58
4.57
4.54
4.53
4.44
4.43
4.00
3.98
3.92
3.91
3.84
3.83
3.76
3.75
2.57
2.55
2.55
2.54
2.53
2.52
2.49
2.48
2.47
2.45
2.44
2.44
2.42
2.41
1.99
1.98
1.97
1.96
1.95
1.95
1.87
1.86
1.86
1.85
1.85
1.84
1.45 H2O
2.00
6.94
3.11
4.34
5.32
2.24
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
11.0
10.5
10.0
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
-0.5
-1.0
f1 (ppm)


27
TsN
O
O
O
171.16
150.68
144.61
131.31
129.96
129.50
128.43
125.95
121.50
86.26
77.66
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
59.28
55.80
39.90
28.97
28.18
21.64
3500
3000
2500
2000
1500
1000
500
0
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


25
Me
O
7.40
7.39
7.38
7.35
7.26 CDCl3
7.25
7.22
7.20
7.10
7.10
7.08
7.07
7.04
4.57
4.55
4.54
4.53
4.52
4.50
4.48
4.47
4.46
4.45
4.43
2.75
2.72
2.70
2.56
2.55
2.54
2.53
2.52
2.50
2.46
2.43
2.43
2.42
2.41
2.40
2.39
2.19
2.17
2.14
2.12
2.12
2.10
2.09
2.07
1.55 H2O
1.54
1.53
1.49
1.47
2.01
1.76
2.91
1.83
1.87
1.93
2.13
2.89
f1 (ppm)
12.0
11.5
11.0
10.5
10.0
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
-0.5
-1.0
4500
4000
3500
3000
2500
2000
1500
1000
500
0

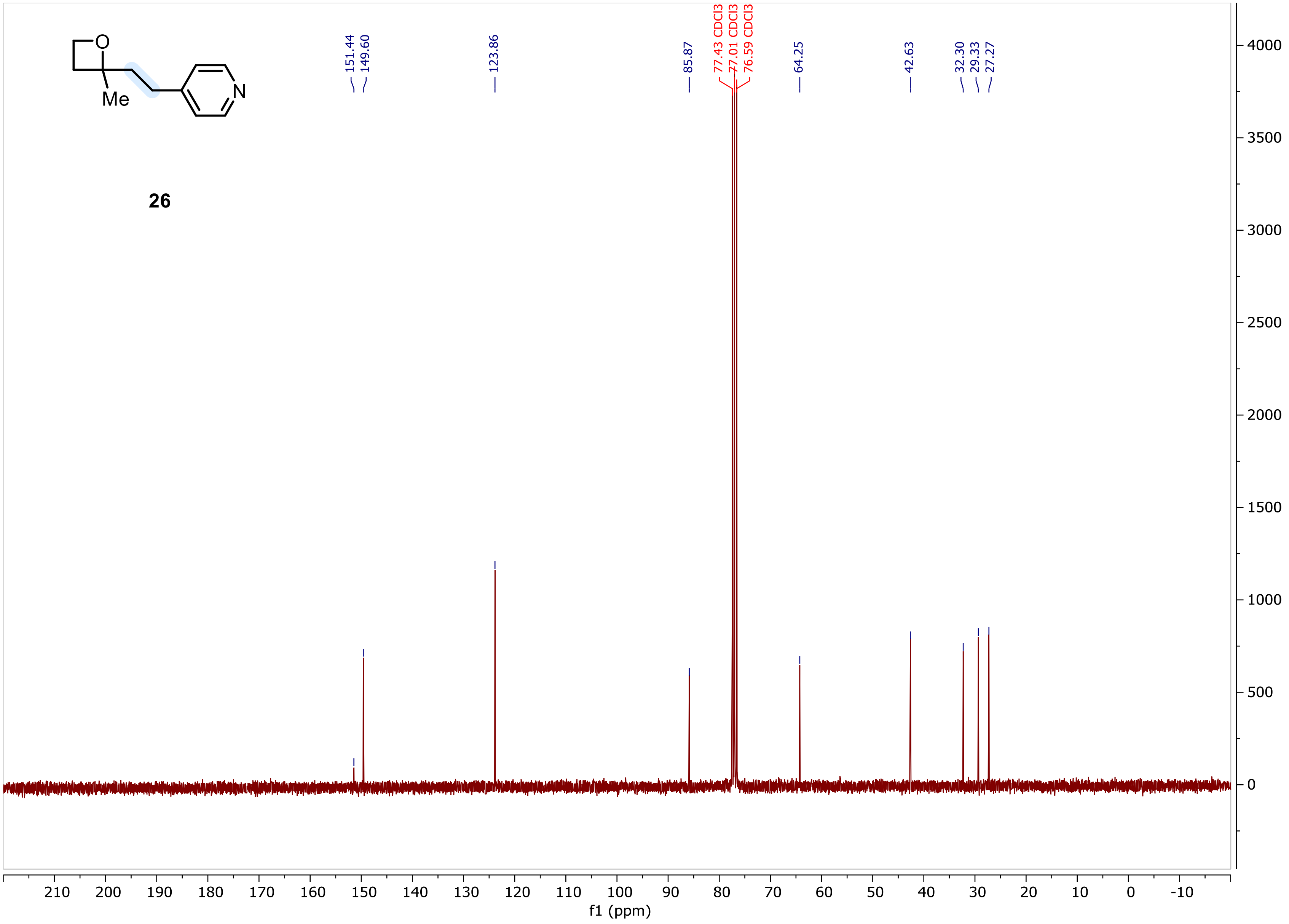

25

172.17
129.40
125.75
121.53
85.48
77.43 CDCl3
77.01 CDCl3
76.59 CDCl3
64.20
36.64
32.05
29.12
27.41
O
O
O
Me
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
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)


Me
O
N
Me
O
O
O
8.51
8.50
8.49
8.49
7.26 CDCl3
7.17
7.17
7.17
7.16
7.15
7.15
4.58
4.55
4.55
4.53
4.53
4.52
4.49
4.47
4.46
4.45
4.44
4.44
4.42
2.77
2.74
2.73
2.71
2.55
2.53
2.52
2.51
2.50
2.49
2.48
2.46
2.43
2.41
2.40
2.38
2.38
2.37
2.35
2.04
2.02
1.99
1.96
1.95
1.94
1.93
1.48
1.88
1.90
2.00
1.92
1.89
2.01
3.00
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
12.0
11.5
11.0
10.5
10.0
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
-0.5
-1.0
f1 (ppm)

26

18

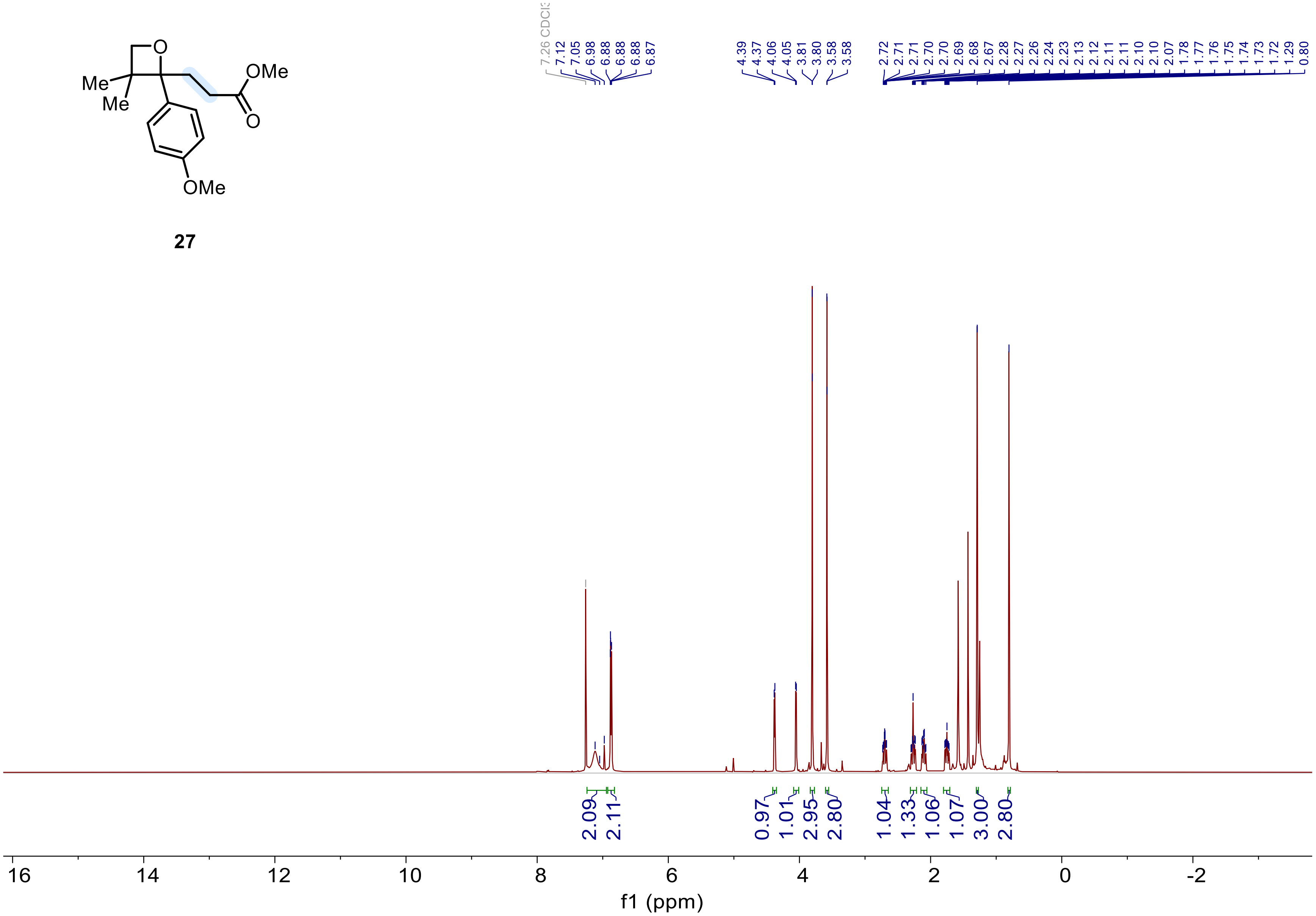


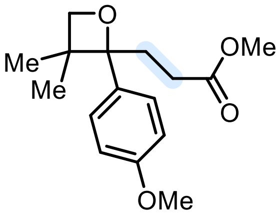
26

O
Me
N
151.44
149.60
123.86
85.87
77.43 CDCl3
77.01 CDCl3
76.59 CDCl3
64.25
42.63
32.30
29.33
27.27
4000
3500
3000
2500
2000
1500
1000
500
0
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)

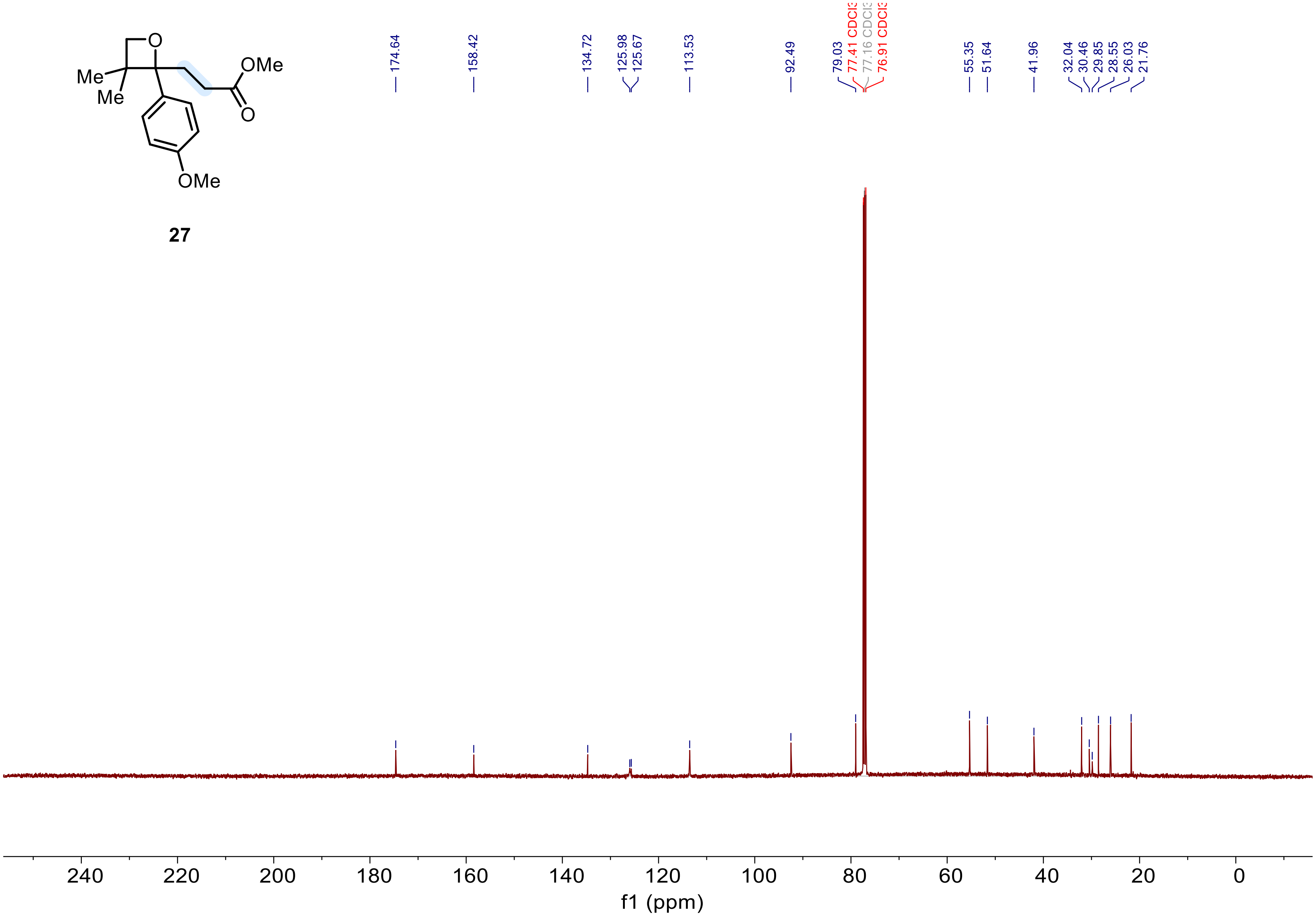
O
OMe
Me
Me
O
OMe

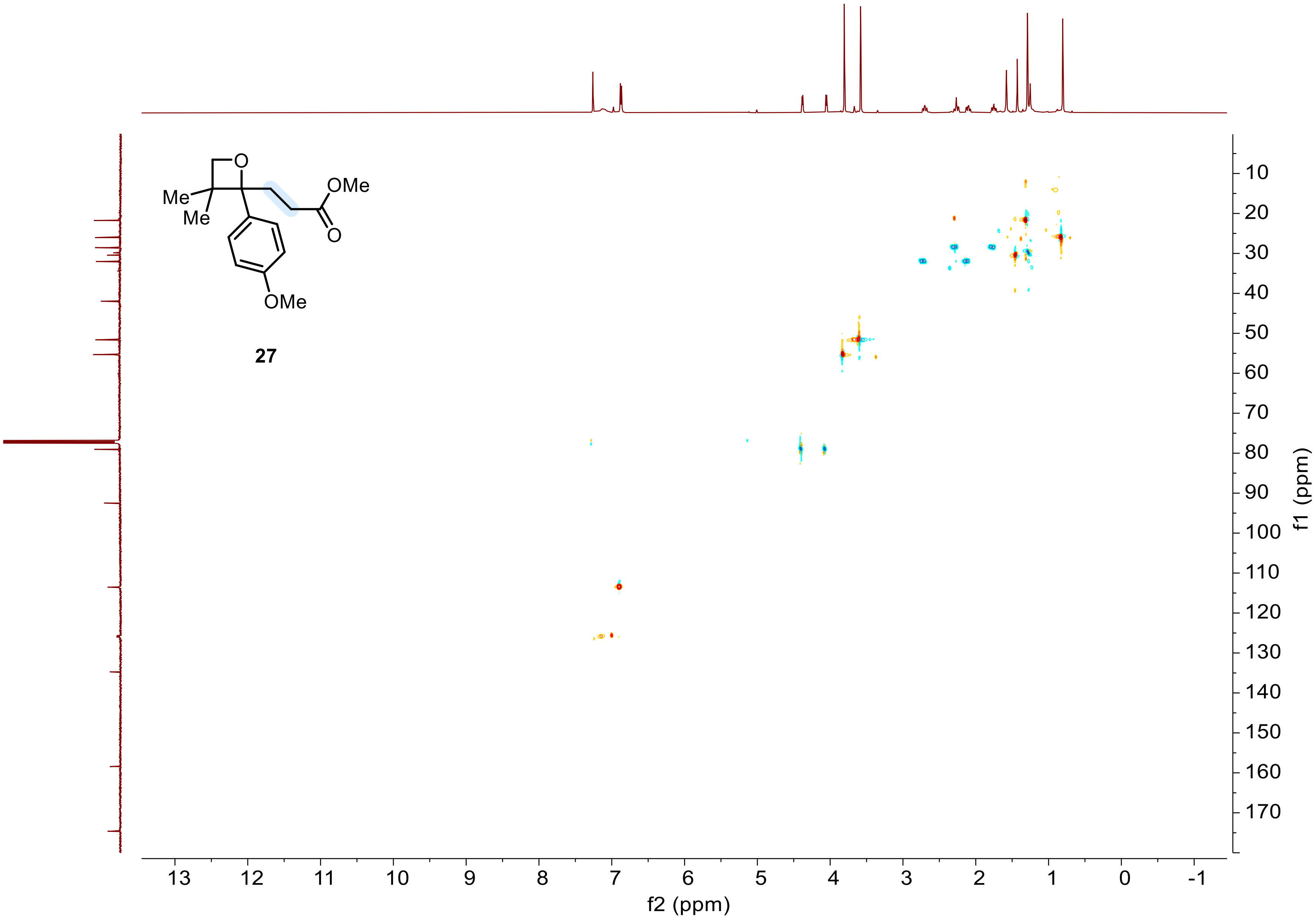
27


7.26 CDCl3
7.12
7.05
6.98
6.88
6.88
6.88
6.87
4.39
4.37
4.06
4.05
3.81
3.80
3.58
3.58
2.72
2.71
2.71
2.70
2.70
2.69
2.68
2.67
2.28
2.27
2.26
2.24
2.23
2.13
2.12
2.11
2.11
2.10
2.10
2.07
1.78
1.77
1.76
1.75
1.74
1.73
1.72
1.29
0.80
2.09
2.11
0.97
1.01
2.95
2.80
1.04
1.33
1.06
1.07
3.00
2.80
16
14
12
10
8
6
4
2
0
-2
f1 (ppm)


O
OMe
Me
Me
O
OMe

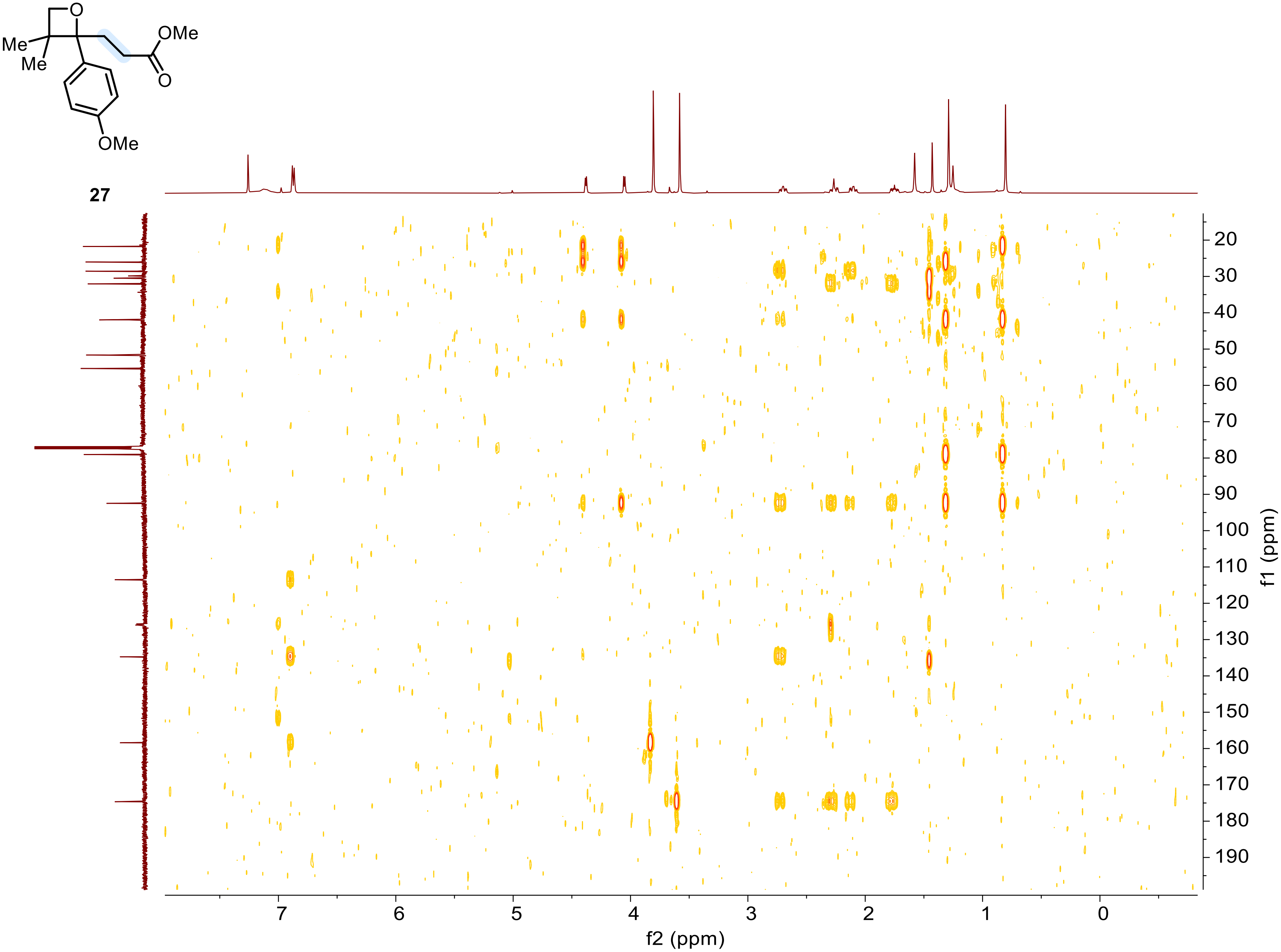
27


174.64
158.42
134.72
125.98
125.67
113.53
92.49
79.03
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
55.35
51.64
41.96
32.04
30.46
29.85
28.55
26.03
21.76
240
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

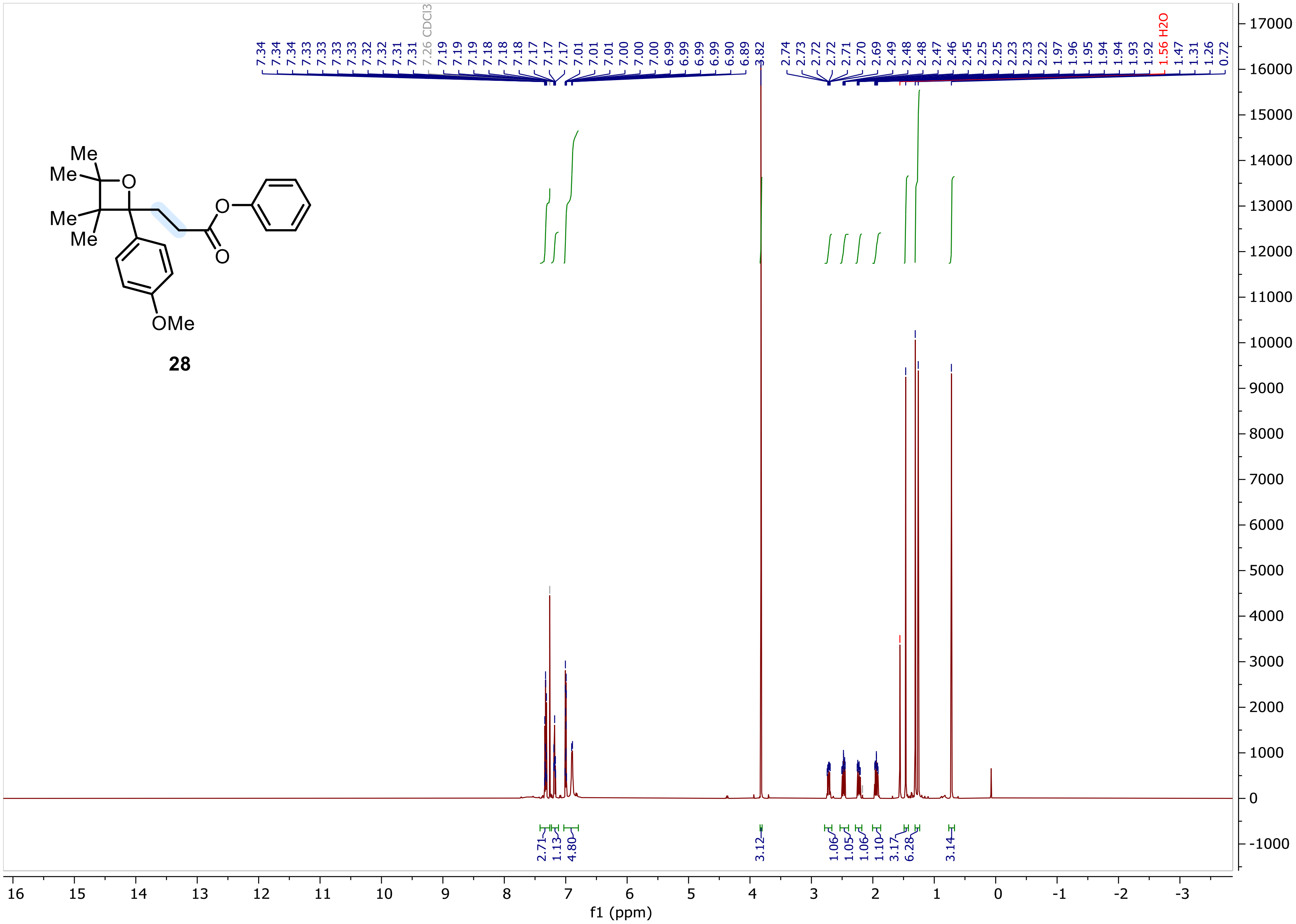


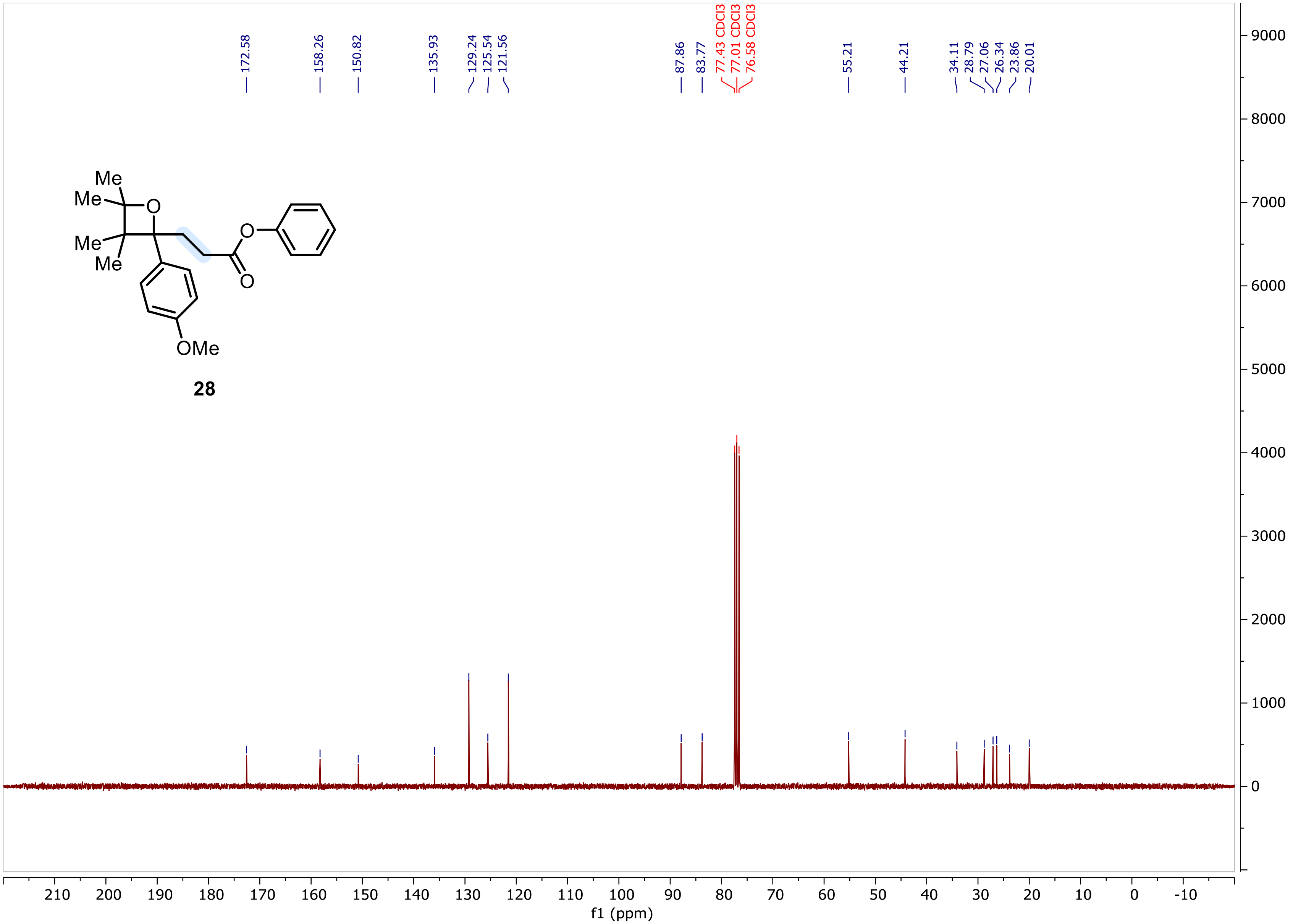
27

OMe
O
Me
Me
O
OMe
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
f1 (ppm)


O
OMe
Me
Me
O
OMe
f1 (ppm)
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
7
6
5
4
3
2
1
0
f2 (ppm)

27


7.34
7.34
7.34
7.33
7.33
7.33
7.33
7.32
7.32
7.31
7.31
7.26 CDCl3
7.19
7.19
7.19
7.18
7.18
7.18
7.17
7.17
7.17
7.17
7.01
7.01
7.01
7.00
7.00
7.00
6.99
6.99
6.99
6.99
6.90
6.89
3.82
2.74
2.73
2.72
2.72
2.71
2.70
2.69
2.49
2.48
2.48
2.47
2.46
2.45
2.25
2.25
2.23
2.23
2.22
1.97
1.96
1.95
1.94
1.94
1.93
1.92
1.56 H2O
1.47
1.31
1.26
0.72
Me
Me
O
O
Me
Me
O
OMe
28
2.71
1.13
4.80
3.12
1.06
1.05
1.06
1.10
3.17
6.28
3.14
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

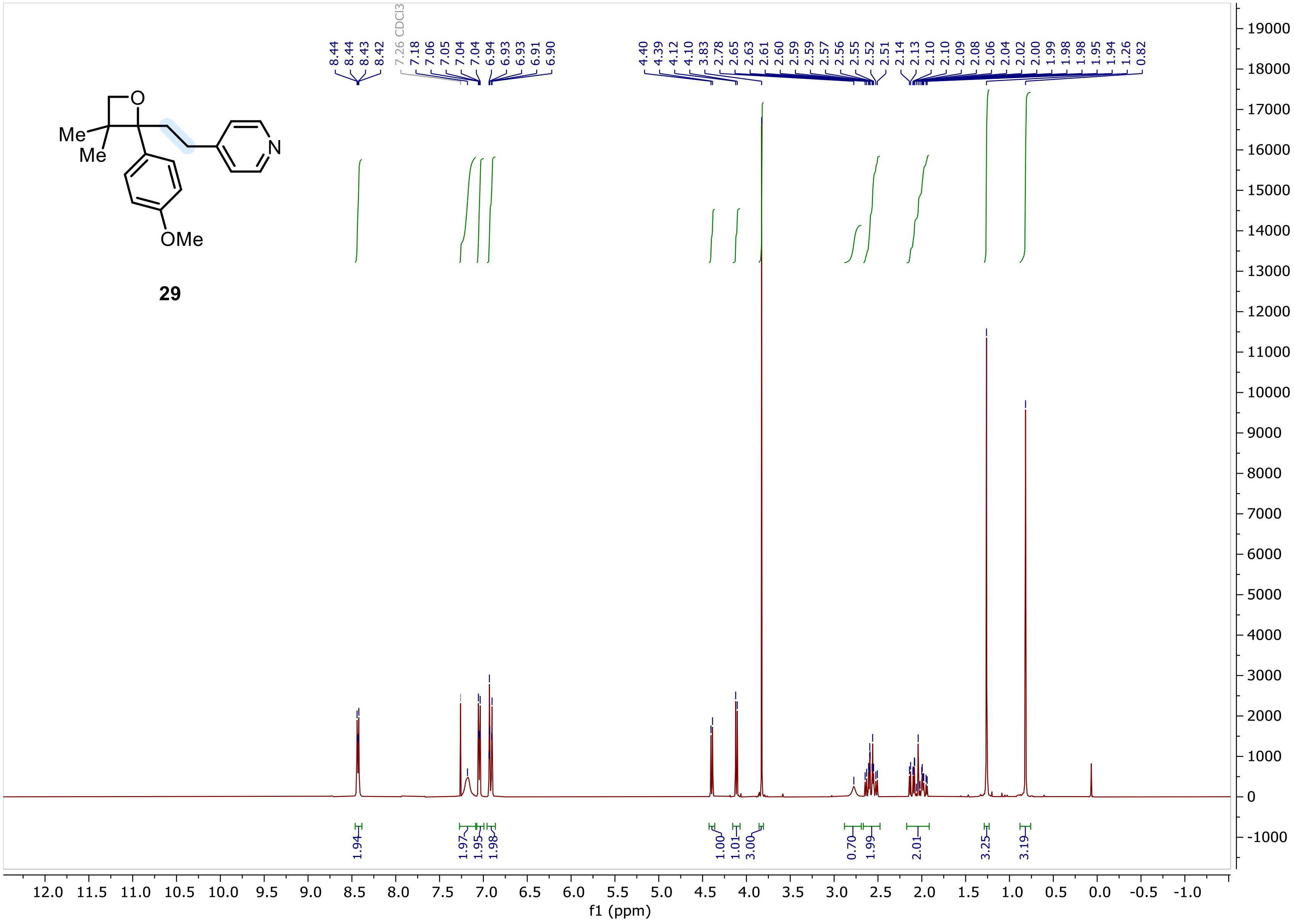


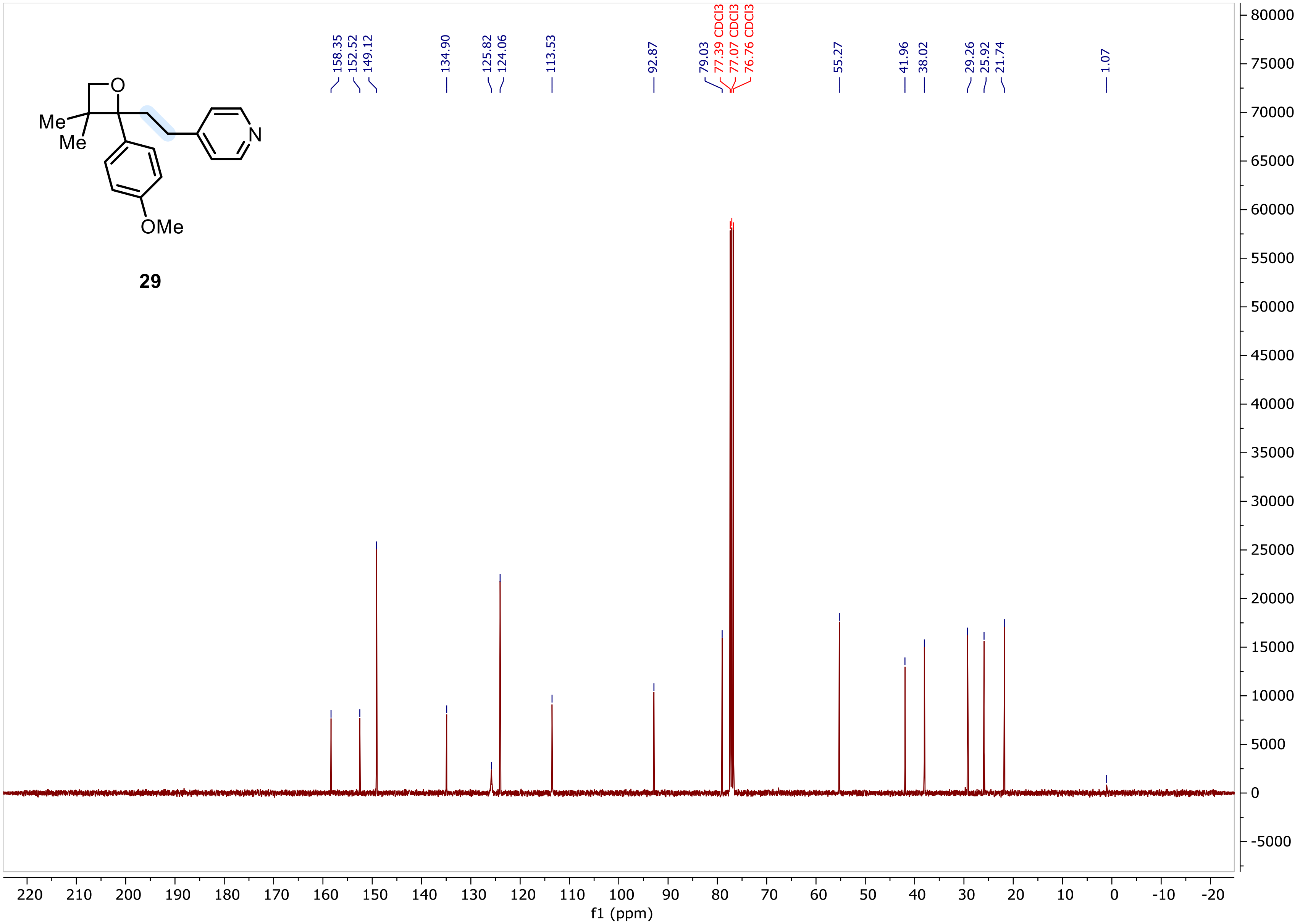
28

172.58
158.26
150.82
135.93
129.24
125.54
121.56
87.86
83.77
77.43 CDCl3
77.01 CDCl3
76.58 CDCl3
55.21
44.21
34.11
28.79
27.06
26.34
23.86
20.01
Me
Me
Me
Me
O
O
O
OMe
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
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)

O
Me
Me
N
OMe

29


8.44
8.44
8.43
8.42
7.26 CDCl3
7.18
7.06
7.05
7.04
7.04
6.94
6.93
6.93
6.91
6.90
4.40
4.39
4.12
4.10
3.83
2.78
2.65
2.63
2.61
2.60
2.59
2.59
2.57
2.56
2.55
2.52
2.51
2.14
2.13
2.10
2.10
2.09
2.08
2.06
2.04
2.02
2.00
1.99
1.98
1.98
1.95
1.94
1.26
0.82
1.94
1.97
1.95
1.98
1.00
1.01
3.00
0.70
1.99
2.01
3.25
3.19
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
12.0
11.5
11.0
10.5
10.0
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
-0.5
-1.0
f1 (ppm)


158.35
152.52
149.12
134.90
125.82
124.06
113.53
92.87
79.03
77.39 CDCl3
77.07 CDCl3
76.76 CDCl3
55.27
41.96
38.02
29.26
25.92
21.74
1.07
Me
Me
O
N
OMe
29
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

References

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