Nickel-Catalyzed C-Alkylation of Nitroalkanes with Unactivated Alkyl Iodides

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Supporting Information

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1. General Information

All reactions were run in oven- or flame-dried glassware under positive nitrogen or argon pressure if not otherwise noted. Anhydrous methyl *tert*-butyl ether (MTBE), dioxane, tetrahydrofuran (THF), dichloromethane (DCM), *N*,*N*-dimethylformamide (DMF), and diethyl ether were dried and purified by passing the solvent through activated alumina using a Pure Solv solvent purification system and degassed by bubbling nitrogen or argon in for 30 min. All commercially available substrates and reagents were purchased in highest analytical purity from commercial suppliers and used as received.

2. Instrumentation and Chromatography

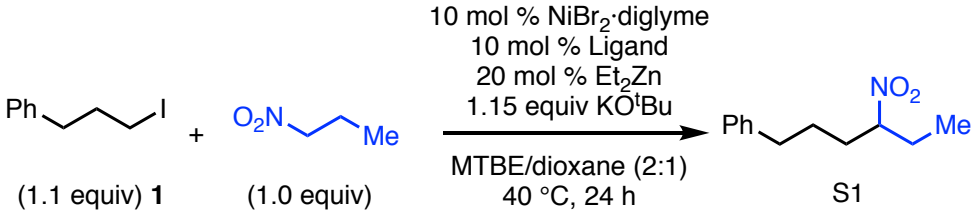
400 MHz ^{1}H, 101 MHz ^{13}C, and 376 MHz ^{19}F NMR spectra were obtained on a 400 MHz FT-NMR spectrometer equipped with a Bruker CryoPlatform. 600 MHz ^{1}H, 151 MHz ^{13}C and 565 MHz ^{19}F spectra were obtained on a 600 MHz FT-NMR spectrometer equipped with a Bruker SMART probe. All samples were analyzed in the indicated deutero-solvent and were recorded at ambient temperatures unless otherwise noted. Chemical shifts are reported in ppm. ^{1}H NMR spectra were calibrated using the residual protio-signal in deutero-solvents as a standard. ^{13}C NMR spectra were calibrated using the deutero-solvent as a standard. All NMR yields are reported using 1,3,5-trimethoxybenzene as an internal standard. IR spectra were recorded on a Nicolet Magma-IR 560 FT-IR spectrometer as thin films on KBr plates. Column chromatography was performed with 40-63 μm silica gel with the eluent reported in parentheses. Analytical thin-layer chromatography (TLC) was performed on precoated glass plates and visualized by UV or by staining with potassium permanganate or iodine. High resolution MS data was obtained on a Thermo Q-Exactive Orbitrap using electrospray ionization (ESI) or a Waters GCT Premier spectrometer using chemical ionization (CI), electron ionization (EI) or liquid injection field desorption ionization (LIFDI).

3.1. Additional Optimization Details

Because of limited space, some details of optimization of the alkylation of nitroalkanes were omitted from the main text and are reported here.

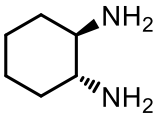
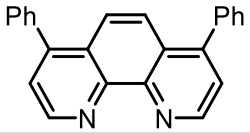
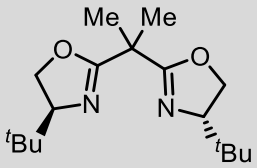
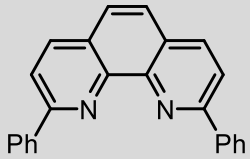
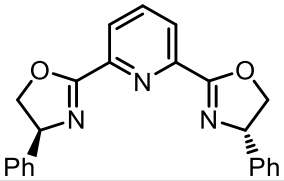
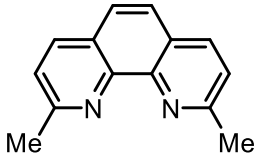
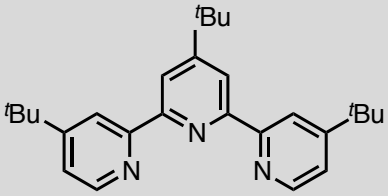
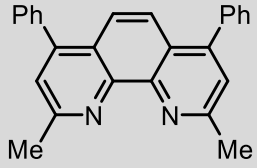
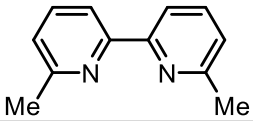
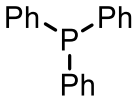
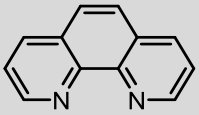
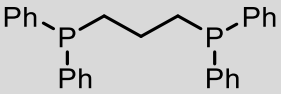
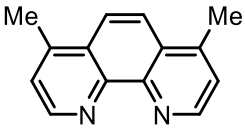
3.2. Experimental Details for Optimization of the Alkylation of Nitroalkanes: In a nitrogen-filled glovebox, a stir bar, $NiBr_2$·diglyme (0.025 mmol) and ligand (0.025 mmol) were added to a 2-dram vial, followed by MTBE (1 mL). The vial was capped and the mixture was stirred for 30 min in the glovebox at ambient temperature. In case of single-component catalyst **8**, no pre-stirring was done. Then, MTBE (1 mL), alkyl iodide (0.275 mmol), nitroalkane (0.25 mmol), and the base (0.29 mmol in 1mL dioxane) were added to the vial and the suspension was stirred vigorously for 1 min. Et_2Zn (0.05 mmol, 1 M in MTBE, 50 µL) was added and stirring continued for another min at ambient temperature. The vial was sealed with a cap, taken outside the glovebox and was stirred in an oil bath at 40 °C for 24 h. The reaction was cooled to rt, diluted with a solution of 1,3,5-trimethoxybenzene (internal standard) in ethyl acetate (1 mL) and quenched with an aqueous solution of saturated NH_4Cl (1 mL). The organic layer was separated and concentration *in vacuo* gave crude material that was dissolved in $CDCl_3$ and quantified by ^1H NMR.

3.3. Effect of Different Ligands



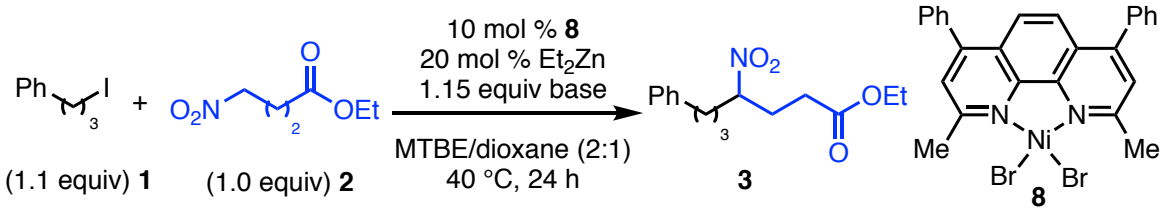
(1.1 equiv) **1** (1.0 equiv) S1

Table S1: Effect of Different Ligands

Entry	Ligand	Yield of S1	Entry	Ligand	Yield of S1
1		0%	**8**		4%
2		4%	**9**		3%
3		4%	**10**		28%
4		2%	**11**		82%
5		1%	**12**[a]		0%
6		0%	**13**		1%
7		3%			

[a] 40 mol % was used

3.4. Effect of Different Bases



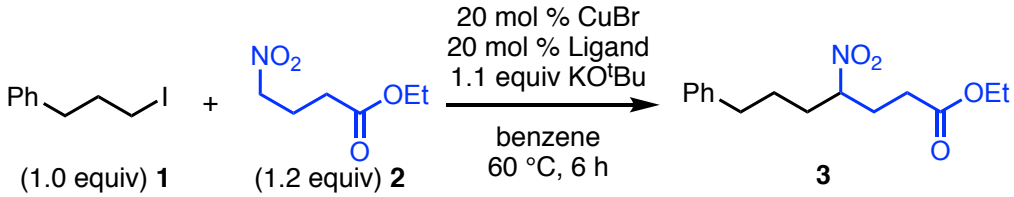
(1.1 equiv) **1** (1.0 equiv) **2** **3** **8**

Table S2: Effect of Different Bases

Entry	Base	Yield of 3
1	DBU	2%
2	LiO^tBu	0%
3	NaO^tBu	24%
4	KO^tBu	76%
5	$NaOSiMe_3$	5%
6	$KOSiMe_3$	11%

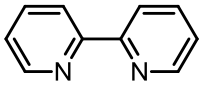
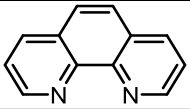
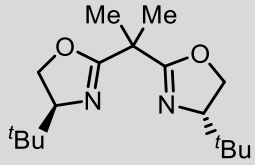
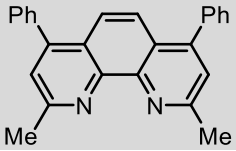
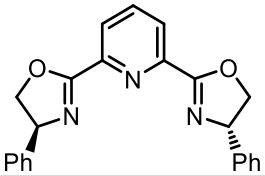
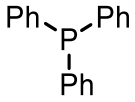
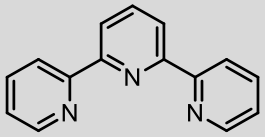
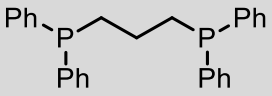
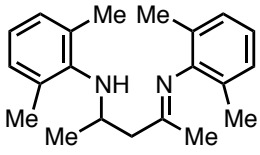
3.4. Screening Copper with Different Ligands

Copper was ineffective in catalyzing the reaction of nitroalkanes with unactivated alkyl iodides, despite being effective with alkyl bromides bearing adjacent radical stabilizing group such as benzyl bromides, α−bromocarbonyls, and α-bromonitriles. Representative experiments using copper catalysts are shown in Table S3.



(1.0 equiv) **1** (1.2 equiv) **2** **3**

Table S3: Screening Copper with Different Ligands

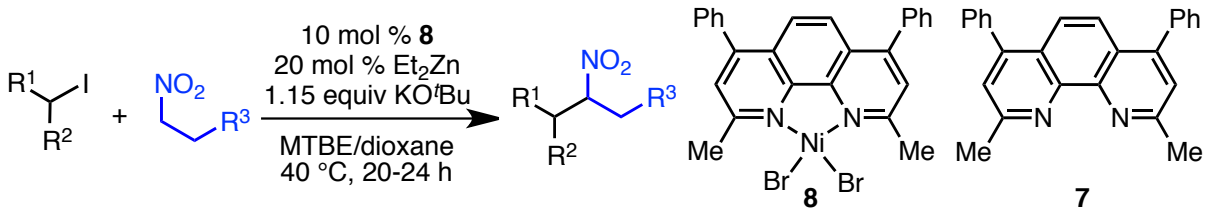
Entry	Ligand	Yield of 3	Entry	Ligand	Yield of 3
1		0%	**6**		0%
2		0%	**7**		1%
3		0%	**8**[a]		0%
4		0%	**9**		0%
5		0%			

[a] 40 mol % was used.

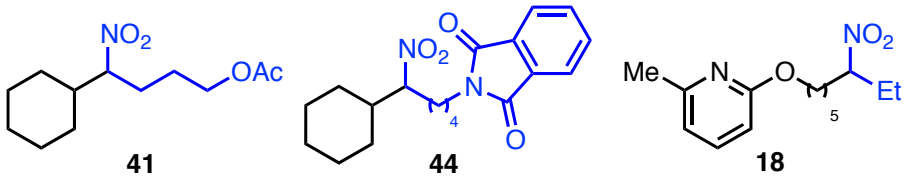
Experimental Details for Table S3: In a nitrogen-filled glovebox, CuBr (0.05 mmol), ligand (0.05 mmol), potassium *tert*-butoxide (0.275 mmol), and a stir bar were added to a 2-dram vial, followed by benzene (2 mL), **2** (0.3 mmol), and **1** (0.25 mmol). The vial was sealed with a cap and the mixture was stirred for 2 min in the glovebox at ambient temperature. The vial was then taken outside the glovebox and stirred in an oil bath at 60 °C for 6 h. The reaction was cooled to rt, diluted with a solution of 1,3,5-trimethoxybenzene (internal standard) in ethyl acetate (1 mL) and quenched with an aqueous solution of saturated NH_4Cl (1 mL). The organic layer was separated and concentration *in vacuo* gave crude material that was dissolved in $CDCl_3$ and quantified by ^{1}H-NMR.

3.5. Effect of Additional Ligand on the Yield in Case of Some Starting Materials Bearing Lewis Basic Functional Groups

Some heteroatom containing substrates showed lower reactivity under standard conditions. By adding 10 mol % additional ligand (bathocuproine, **7**), the reactivity can be restored. Scheme S2 summarizes the differences in reactivity with and without additional ligand.



Scheme S1: Effect of Additional Ligand on the Yield in Case of Some Starting Materials Bearing Lewis Basic Functional Groups



standard condition (NMR yield):	23%	31%	35%
with 10 mol% **7** (isolated yield):	72%	60%	48%

Experimental details for Scheme S2:

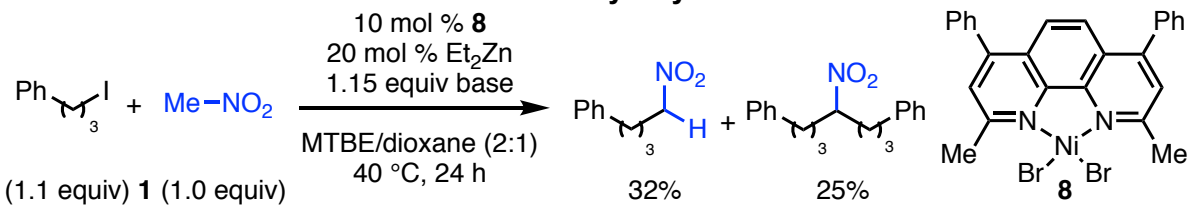
Standard condition: refer to (3.1. Experimental Details for Optimization of the Alkylation of Nitroalkanes)

With 10 mol % 7: In a nitrogen-filled glovebox, **8** (0.1 mmol), and bathocuproine (0.1 mmol) were added to a 20 mL scintillation vial with stir bar, followed by MTBE (4 mL) and the mixture was stirred for 30 min at ambient temperature. Then, MTBE (4 mL), alkyl iodide (1.1 mmol), nitroalkane (1 mmol), and the base (1.15 mmol in 4 mL dioxane) were added to the vial and the suspension was stirred vigorously for 1 min. Et_2Zn (0.2 mmol, 1 M in MTBE, 200 µL) was added and stirring continued for another min at ambient temperature. The vial was sealed, taken outside the glovebox and was stirred in an oil bath at 40 °C for 24 h. The reaction was cooled to rt, Then, EtOAc (20 mL) was added and the mixture was washed with saturated aqueous NH_4Cl (20 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvents were removed under reduced pressure. The crude product was purified by flash column chromatography silica gel.

3.6. Reaction of Nitromethane with Primary Alkyl Iodides

The reaction of nitromethane with primary alkyl iodides results in a mixture of mono- and double-alkylated products.

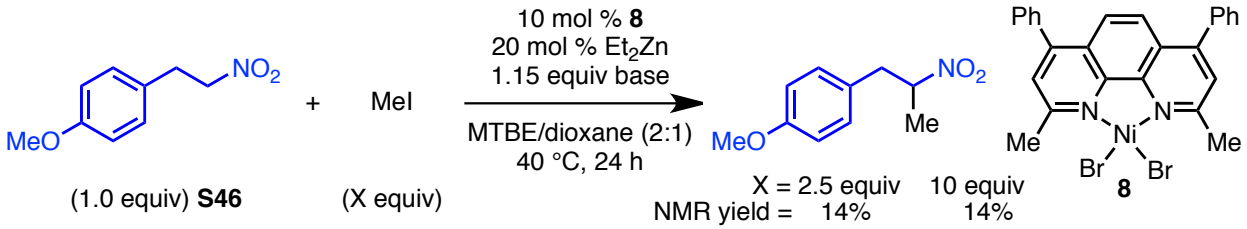
Scheme S2: Reaction of Nitromethane with Primary Alkyl Iodides



3.7. Reaction of Nitroalkanes with Iodomethane

Iodomethane reacts with nitroalkanes under standard conditions, however the yields are poor. An example is shown in Scheme S3. Yields were determined by ^{1}H NMR against an internal standard and with comparison to known spectra.

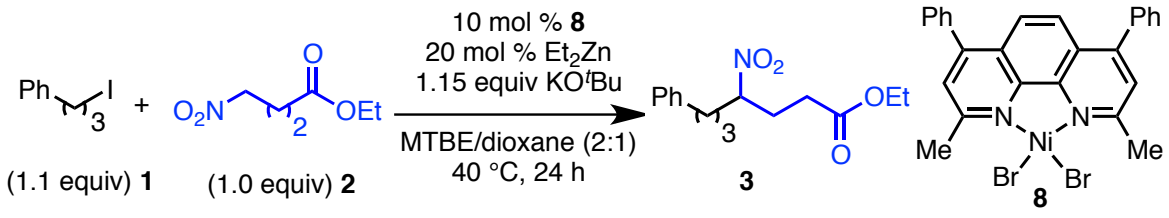
Scheme S3: Reaction of S46 with Iodomethane



3.8. Effect of Ambient Light

Excluding the alkylation reaction from ambient light showed no deterioration of the yield, which rules out the involvement of light in reaction mechanism. Yields were determined by ^{1}H NMR against an internal standard and with comparison to known spectra.

Scheme S4: Effect of Ambient Light on the Reaction



NMR yield of **3**:	with ambient light	in dark[a]
	76%	78%

[a] vial is covered with aluminum foil

3.9. Effect of Different Reductants

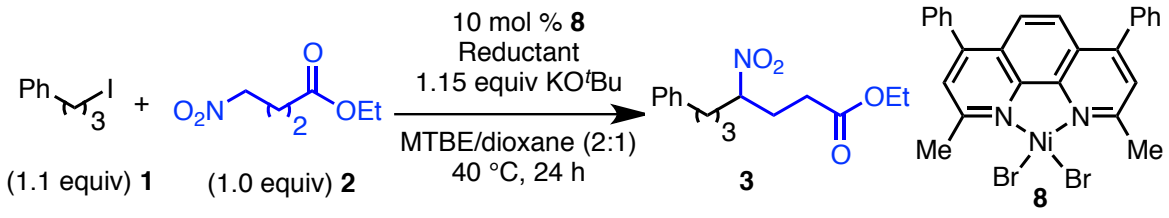


Table S4: Effect of Different Reductants[a]

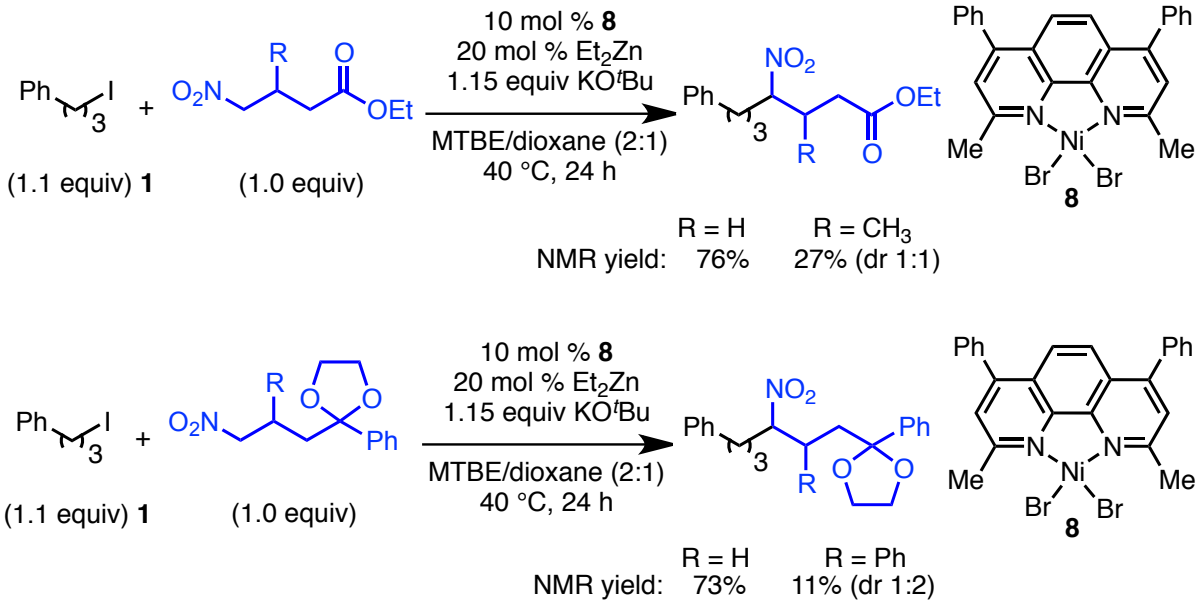
Entry	Reductant	Yield of 3
1	-	<1%
2	2 equiv Mn powder	<1%
3	2 equiv Zn powder	<1%
4	0.2 equiv MeMgCl	<1%
5	0.2 equiv $PhB(OH)_2$	3%
6	0.2 equiv $LiAlH_4$	15%
7	0.2 equiv Et_2Zn	76%

[a] Yields were determined by ^1H NMR against an internal standard and with comparison to known spectra.

3.10. Effect of β - Substitution of Nitroalkanes on the Reactivity

Under standard reaction conditions, β −branched nitroalkanes showed poor reactivity. Illustrative examples are shown in Scheme S5. Yields were determined by ^{1}H NMR against an internal standard and with comparison to known spectra.

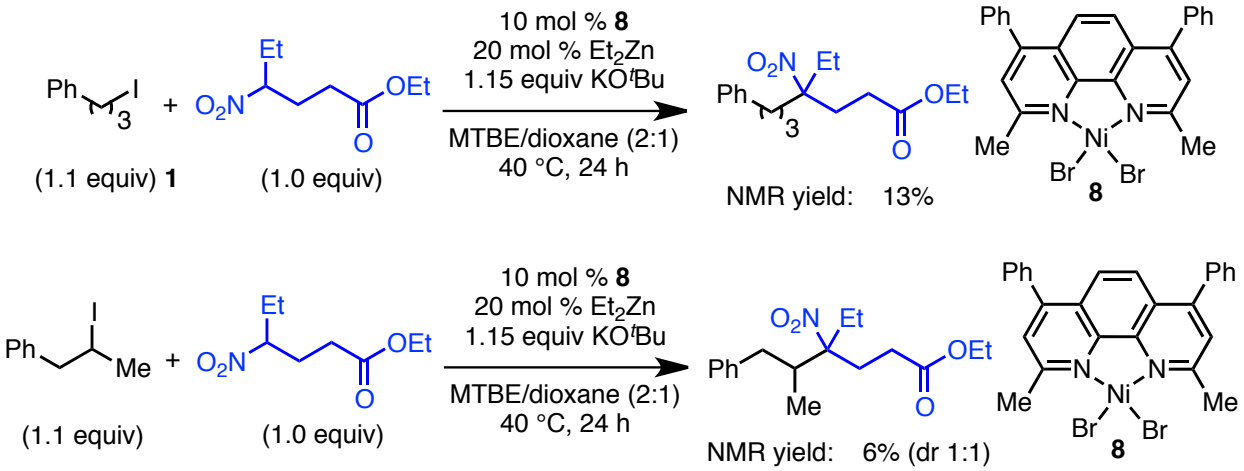
Scheme S6: Effect of β - Substitution of Nitroalkanes on the Reactivity



3.11. Secondary Nitroalkanes

Secondary nitroalkanes showed poor reactivity under standard reaction conditions. Illustrative examples are shown in Scheme S6. Yields were determined by ^{1}H NMR against an internal standard and with comparison to known spectra.

Scheme S6: Secondary Nitroalkanes



4. General procedures

4.1. Nickel-catalyzed Alkylation of Nitroalkanes with Alkyl Iodides

General procedure A: Nickel-Catalyzed C-Alkylation of Nitroalkanes with Alkyl Iodides in Glovebox

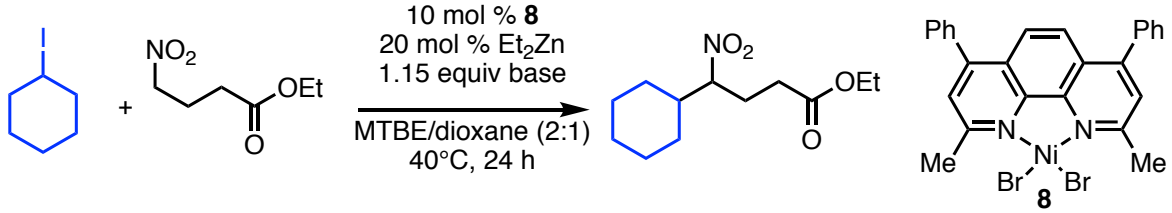
A 50 mL oven-dried round-bottom flask charged with a stir bar was transferred to a nitrogen-filled glovebox. After cooling the vial to ambient temperature, **8** (0.1 equiv) was added, followed by alkyl iodide (1.1 equiv), nitroalkane (1.0 equiv) and MTBE (0.125 M with respect to nitroalkane). The mixture was stirred for 5 min at ambient temperature, then a solution of potassium *tert*-butoxide in dioxane (0.29 M, 1.15 equiv, anhydrous and anaerobic) was added. The reaction was stirred vigorously for 1 min, then Et_2Zn (0.2 equiv) was added and the mixture stirred for another min at ambient temperature. The flask was sealed with rubber septum, taken outside the glovebox, placed in an oil bath at 40°C, and stirred for the indicated time (ca. 20-28 h). After cooling to rt, EtOAc (30 mL) was added and the mixture was washed with saturated aqueous NH_4Cl (50 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered through a glass frit, and the solvents were removed under reduced pressure. The crude product was purified by flash silica gel column chromatography.

General procedure B: Nickel-Catalyzed C-Alkylation of Nitroalkanes with Alkyl Iodides in Glovebox

A 50 mL oven-dried round-bottom flask charged with a stir bar was transferred to a nitrogen-filled glovebox. After cooling the vial to ambient temperature, **8** (0.1 equiv) was added, followed by MTBE (0.125 M with respect to nitroalkane) and Et_2Zn (0.2 equiv). The mixture was stirred for 5 min at ambient temperature, then alkyl iodide (1.1 equiv), nitroalkane (1.0 equiv), and a solution of potassium *tert*-butoxide in dioxane (0.29 M, 1.15 equiv, anhydrous and anaerobic) was added. The mixture was vigorously stirred for 1 min at ambient temperature, then the flask was secured with rubber septum, taken outside the glovebox, placed in an oil bath at 40°C, and stirred for the indicated time (ca. 20-28 h). After cooling to rt, EtOAc (30 mL) was added and the mixture was washed with saturated aqueous NH_4Cl (50 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered through a glass frit, and the solvents were removed under reduced pressure. The crude product was purified by flash silica gel column chromatography.

Note: General procedure A and B differ only based on the order of addition of reagents. It is noteworthy to mention that Et_2Zn can be added before or after the substrates with no effect on the yield. An example is shown in the Scheme S4.

Scheme S4: Comparison of General Procedure A and B



	Procedure A	Procedure B
26 (NMR Yield):	74%	75%

General procedure C: Nickel-Catalyzed C-Alkylation of Nitroalkanes with Alkyl Iodides on Benchtop

Using an argon-filled double manifold equipped with a mercury bubbler, an oven-dried 25 mL Schlenk flask equipped with a stirbar and rubber septum was cooled under vacuum. The flask was filled with argon, and opened to air. Complex **8** (0.1 mmol, 58 mg), non-volatile alkyl iodides (1.1 mmol), and non-volatile nitroalkanes (1.0 mmol) were charged to the flask. The flask was then sealed with a rubber septum and evacuated-backfilled with argon (3X). MTBE (8 mL) was then added. If the alkyl iodide (1.2 mmol) or nitroalkane (1.1 mmol) were volatile, they were added at this point under argon via syringe. A solution of potassium *tert*-butoxide in dioxane (0.29 M in dioxane, 4 mL, anhydrous and anaerobic) was then added via syringe, and the reaction mixture was stirred vigorously for 1 min. The flask was purged with argon for 3 min using a vent needle. Et_2Zn (1.0 M in MTBE, 0.2 mmol, 200 µL) was then added via syringe. The side-arm of the flask was then sealed, the flask was disconnected from the manifold, and reaction was placed in a 40 °C oil bath where it was maintained for the indicated time (ca. 20-28 h) with stirring. The reaction was then cooled to rt, and EtOAc (20 mL) was added. The mixture was washed with saturated aqueous NH_4Cl (20 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered through a glass frit, and the solvents were removed under reduced pressure. The crude product was purified by silica gel column chromatography.

4.2. General Procedures for Synthesis of Starting Materials

General procedure D: Conversion of Primary and Secondary Alcohols to Alkyl Iodides

A 200 mL oven-dried round-bottom flask equipped with a stirbar and rubber septum is cooled under a stream of nitrogen. The flask was opened to air, and triphenylphosphine (1.2 equiv), imidazole (1.3 equiv), and DCM (non-anhydrous) were added under air. The rubber septum was replaced, and the flask was purged with nitrogen for ca. 5 min. The flask was then placed in an ice-bath. After 5 min of stirring, the rubber septum was partly removed and iodine (1.2 equiv) was added under a stream of nitrogen. The rubber septum was replaced and the reaction was stirred for another 15 min. The alcohol was then added. For solid alcohols, the rubber septum was partly removed, the alcohol was added under a stream of nitrogen, and the rubber septum was returned. For liquid alcohols, the alcohol was added via syringe through the rubber septum.

After 30 min, the ice bath was removed and reaction stirred at rt for the indicated time under nitrogen. To quench the reaction, water was added and the layers were separated. The aqueous layer was washed with DCM and the combined organic phases were dried over anhydrous $MgSO_4$ and filtered through glass frit. The solvent was removed under reduced pressure and the crude product was purified by flash silica gel column chromatography.

General procedure E: Synthesis of Amides by Schotten-Baumann Reaction

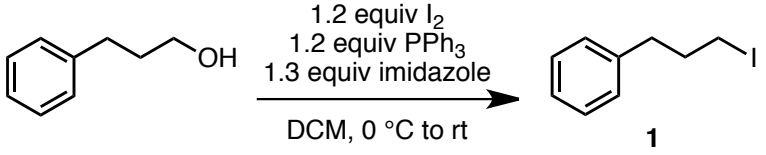
To a solution of K_3PO_4 or NaOH (3.0 equiv) in water in a 500 mL flask with a stirbar was added DCM followed by the amine (1.5 equiv) under air. Then a solution of acyl chloride (1.0 equiv) in DCM was added dropwise while vigorously stirring and keeping the temperature at 0 °C with an ice bath. After complete addition, the reaction was vigorously stirred at rt for the indicated time. The crude mixture was extracted with DCM and sequentially washed with 1.0 M aqueous NaOH, 1.0 M aqueous HCl, and brine. The combined organic phase was dried over anhydrous $MgSO_4$, filtered through a glass frit. The solvent was removed under reduced pressure, and if necessary, the crude product was purified by silica gel column chromatography and/or crystallization.

General procedure F: Conversion of Alkyl Iodides to Nitroalkanes with Silver(I) Nitrite

According to published literature procedure[1], $AgNO_2$ (4.0 equiv) was added to a mixture of alkyl iodide (1.0 equiv) in water in a 100 mL flask under air. The flask was protected from light by wrapping with aluminum foil. After stirring for the indicated time at reported temperature, the mixture was filtered through Celite, and extracted with EtOAc. The combined organic phase was dried over anhydrous $MgSO_4$, filtered through a glass frit, the solvent was removed under reduced pressure and the crude product was purified by flash silica gel chromatography.

5. Synthesis of Alkyl Iodides

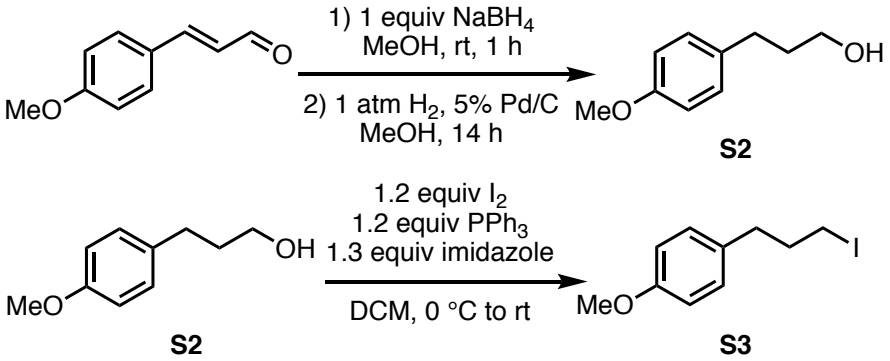
Note: The reactions and the yields to synthesize starting alkyl iodides are not optimized.



1

1: According to general procedure D, 3-phenylpropan-1-ol (30 mmol, 4.09 g), iodine (36 mmol, 9.14 g), triphenylphosphine (36 mmol, 9.47 g), and imidazole (39 mmol, 2.65 g) in DCM (100 mL) for 3 h, afforded, after flash silica gel chromatography (95:5 hexanes : ethyl acetate), alkyl iodide **1** (6.63 g, 90%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.24 – 7.18 (m, 3H), 3.18 (m, 2H), 2.73 (t, *J* = 7.3 Hz, 2H), 2.13 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.5, 128.7, 128.6, 126.3, 36.4, 35.0, 6.9.

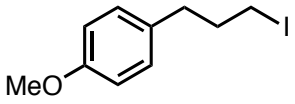
1 is a known compound and its spectra are in accord with published data.[2]



S2

S2: Using a 100 mL round-bottom flask charged with a stir bar, *p*-methoxycinnamaldehyde (40 mmol, 6.48 g) was dissolved in non-anhydrous methanol (50 mL), followed by addition of sodium borohydride (40 mmol, 1.52 g) in 3 portions over 10 min while stirring at rt under air. After 1 h of stirring, excess borohydride was quenched by slow addition of 1M aqueous HCl, until no bubbling occurred. Water (50 mL) was then added and the aqueous phase was extracted with ethyl acetate (3x50 mL). The organic phase was dried over anhydrous $MgSO_4$ and the solvents were evaporated under reduced pressure. The crude mixture was added under air to a 100 mL round-bottom flask charged with a stir bar, followed by non-anhydrous methanol (50 mL) and 5% Pd/C (5 wt %, 324 mg). The flask was secured with a rubber septum and stirred under 1 atmosphere of hydrogen (balloon) for 14 h. The mixture was then filtered through Celite and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (90:10 to 60:40 hexanes : ethyl acetate) to afford **S2** (3.97 g, 60%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 – 7.09 (m, 2H), 6.86 – 6.81 (m, 2H), 3.79 (s, 3H), 3.67 (t, *J* = 6.4 Hz, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 1.91 – 1.80 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.0, 134.0, 129.4, 114.0, 62.4, 55.4, 34.6, 31.3.

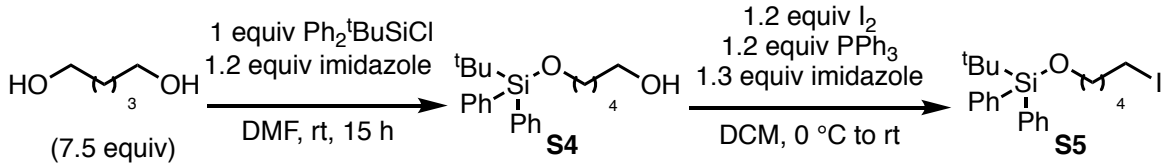
S2 is a known compound and its spectra are in accord with published data.[3]

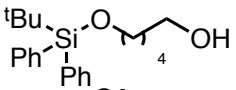


S3

S3: According to general procedure D, **S2** (23.67 mmol, 3.93 g), iodine (28.4 mmol, 7.21 g), triphenylphosphine (28.4 mmol, 7.47 g), and imidazole (30.77 mmol, 2.09 g) in DCM (50 mL) for 15 h, afforded, after flash silica gel chromatography (97:3 hexanes : ethyl acetate), alkyl iodide **S3** (6.15 g, 94%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 – 7.08 (m, 2H), 6.84 (m, 2H), 3.79 (s, 3H), 3.16 (t, *J* = 6.8 Hz, 2H), 2.67 (t, *J* = 7.2 Hz, 2H), 2.09 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.2, 132.6, 129.6, 114.0, 55.4, 35.4, 35.2, 6.6.

S3 is a known compound and its spectra are in accord with published data.[4]

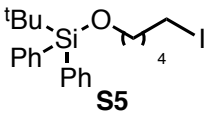




S4

S4: A 100 mL oven-dried round-bottom flask charged with a stir bar was secured with a rubber septum and cooled under a stream of N_2. The rubber septum was partially removed and imidazole (24 mmol, 1.632 g) was added. The rubber septum was replaced, then 1,5-pentanediol (150 mmol, 15.6 g) and DMF (20 mL) were added sequentially under nitrogen via syringe, followed by diphenyl-tert-butylsilyl chloride (20 mmol, 5.5 g). After 15 h of stirring at rt under nitrogen, diethyl ether (100 mL) was added to the mixture and the organic phase was washed with water (3x100 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered through a glass frit, and the solvents were removed under reduced pressure. The crude product was purified by flash silica gel chromatography (100:0 to 80:20 hexanes : ethyl acetate) to afford **S4** (3.41 g, 50%) as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 4H), 7.46 – 7.34 (m, 6H), 3.67 (t, *J* = 6.4 Hz, 2H), 3.62 (t, *J* = 6.5 Hz, 2H), 1.57 (m, 4H), 1.47 – 1.39 (m, 2H), 1.05 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 134.1, 129.6, 127.7, 63.9, 63.1, 32.6, 32.4, 27.0, 22.01, 19.3.

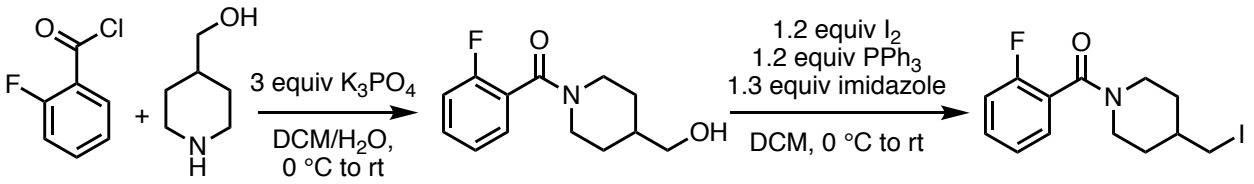
S4 is a known compound and its spectra are in accord with published data.[5]



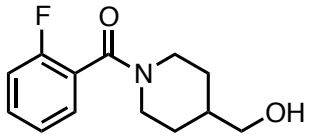
S5

S5: According to general procedure D, **S4** (10 mmol, 3.42 g), iodine (12 mmol, 3.05 g), triphenylphosphine (12 mmol, 3.16 g), and imidazole (13 mmol, 884 mg) in DCM (30 mL) for 15 h, afforded, after flash silica gel chromatography (100:0 to 95:5 hexanes : ethyl acetate), alkyl iodide **S5** (3.82 g, 85%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (m, 4H), 7.45 – 7.41 (m, 2H), 7.39 (m, 4H), 3.67 (t, *J* = 6.3 Hz, 2H), 3.17 (t, *J* = 7.0 Hz, 2H), 1.81 (p, *J* = 7.2 Hz, 2H), 1.61 – 1.54 (m, 2H), 1.52 – 1.44 (m, 2H), 1.06 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.7, 134.2, 129.7, 127.8, 63.7, 33.4, 31.6, 27.0, 19.4, 7.2.

S5 is a known compound and its spectra are in accord with published data.[6]

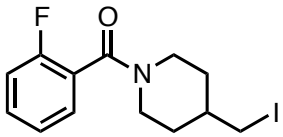


(1.0 eqiuv) (1.5 equiv) **S6** **S7**



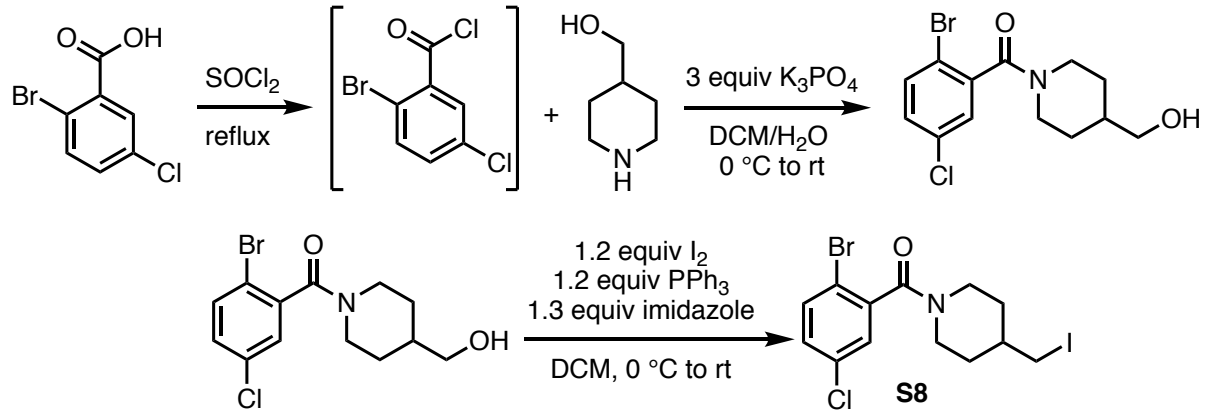
S6

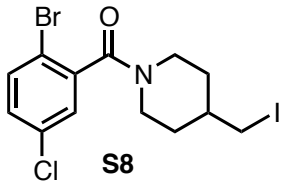
S6: According to general procedure E, 2-fluorobenzoyl chloride (30 mmol, 4.75 g) in 20 mL DCM, piperidine-4-ylmethanol (45 mmol, 5.18 g), and K_3PO_4 (90 mmol, 19.1 g) in DCM (50 mL) and water (50 mL) afforded 6.48 g (91%) **S6** as white crystals. mp = 123-125 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 2H), 7.19 (td, *J* = 7.5, 1.3 Hz, 1H), 7.08 (m, 1H), 4.79 (m, 1H), 3.63 – 3.42 (m, 3H), 3.04 (br s, 1H), 2.79 (t, *J* = 13.0 Hz, 1H), 1.92 – 1.82 (m, 1H), 1.82 – 1.67 (m, 2H), 1.60-1.44 (br s, 1H) 1.36 – 1.01 (m, 2H); ^{13}C NMR (151 MHz, DMSO-d6) δ 163.7, 157.5 (d, *J* = 244.5 Hz), 131.1 (d, *J* = 7.5 Hz), 128.5 (d *J* = 3 Hz), 124.8 (d, *J* = 3 Hz), 124.6 (d, *J* = 18 Hz), 115.7 (d, *J* = 21 Hz), 65.4, 46.5, 41.1, 38.3, 29.0, 28.3; ^{19}F NMR (565 MHz, CDCl3) δ -115.20; FTIR (cm^{-1}) 3367, 2865, 1606, 767. HRMS (EI) m/z, calculated for $[C_{13}H_{16}FNO_2]^+$: 237.1165; found: 237.1147.



S7

S7: According to general procedure D, **S6** (20 mmol, 4.74 g), iodine (24 mmol, 6.1 g), triphenylphosphine (24 mmol, 6.31 g), and imidazole (26 mmol, 1.77 g) in DCM (50 mL) for 4 h, afforded, after flash silica gel chromatography (80:20 to 70:30 hexanes : ethyl acetate), alkyl iodide **S7** (5.06 g, 73%) as a white crystalline solid. mp = 77-79 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 2H), 7.20 (td, *J* = 7.5, 1.1 Hz, 1H), 7.09 (ddd, *J* = 9.4, 8.3, 1.1 Hz, 1H), 4.80 (ddt, *J* = 13.3, 4.6, 2.3 Hz, 1H), 3.58 (m, 1H), 3.19 – 3.09 (m, 2H), 3.04 (br s, 1H), 2.77 (t, *J* = 13.1 Hz, 1H), 1.99 (dt, *J* = 13.3, 2.9 Hz, 1H), 1.85 (d, *J* = 13.1 Hz, 1H), 1.74 (m, 1H), 1.34-1.25 (m, 1H), 1.21 (br s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.1, 158.2 (d, *J* = 248 Hz), 131.2 (d, J = 8 Hz), 129.1 (d, *J* = 4 Hz), 124.8 (d, *J* = 4 Hz), 124.5 (d, *J* = 18 Hz), 115.8 (d, *J* = 23 Hz), 47.0, 41.8, 38.8, 33.2, 32.4, 12.7;^{19}F NMR (565 MHz, CDCl3) δ -115.13; FTIR (cm^{-1}) 2936, 2856, 1637, 1453, 1435, 1221, 965. HRMS (EI) m/z, calculated for $[C_{13}H_{15}FINO]^+$: 347.0182; found: 347.0192.

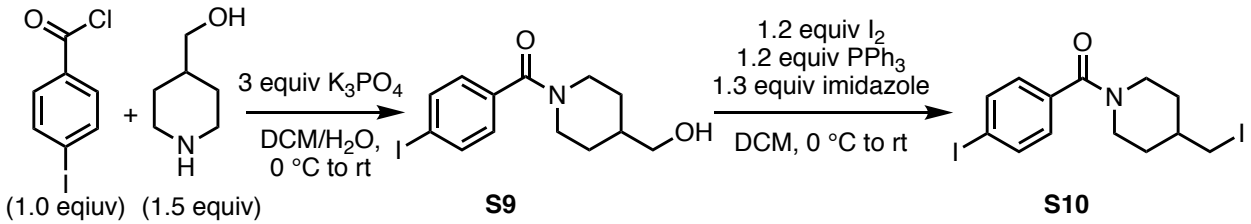




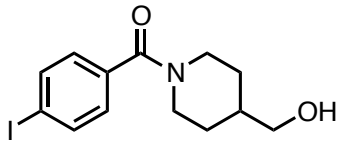
S8: 2-bromo-5-chlorobenzoic acid (50 mmol, 11.77 g) was added to a 100 mL round-bottom flask charged with a stir bar followed by thionyl chloride (25 mL) under air. A reflux condenser was attached to the flask and the condenser was secured with a rubber septum. The mixture was refluxed with stirring (oil bath temperature was set to 85 °C) for 3 h under a balloon of nitrogen. After cooling to rt, the excess thionyl chloride was removed under reduced pressure and the resulting acyl chloride was directly used in next step.

According to general procedure E, 2-bromo-5-chloro-benzoyl chloride in 20 ml DCM, piperidine-4-ylmethanol (75 mmol, 8.62 g), and K_3PO_4 (150 mmol, 31.8 g) in DCM (50 mL) and water (75 mL) were stirred. After 30 min, 400 mL ethyl acetate was added; the organic phase was sequentially washed with 1.0 M aqueous NaOH (150 mL), 1.0 M aqueous HCl (150 mL), and water (150 mL); dried over anhydrous $MgSO_4$, filtered through glass frit, and the solvents were removed under reduced pressure. The white solid that formed was washed with hexanes (100 mL), Et_2O (100 mL), and was used in next step without further purification.

According to general procedure D, the alcohol (15 mmol, 4.99 g), iodine (18 mmol, 4.57 g), triphenylphosphine (18 mmol, 4.73 g), and imidazole (19.5 mmol, 1.33 g) in DCM (40 mL) for 1 h, afforded, after flash silica gel chromatography (80:20 to 60:40 hexanes : ethyl acetate), alkyl iodide **S8** (3.66 g, 46% over two steps) as a white crystalline solid. mp = 98-100 °C; (Two rotamers are observable in ^{1}H-NMR and ^{13}C-NMR spectra at rt; the peaks coalesce at 340 K.) ^{1}H NMR (400 MHz, DMSO-d_6, 299 K) δ 7.69 (d, J = 3.7 Hz, 1H), 7.48 (d, J = 2.5 Hz, 1H), 7.46 – 7.43 (m, 1H), 7.43 – 7.40 (m, 1H), 4.49 (ddq, J = 15.4, 11.1, 2.3 Hz, 2H), 3.24 (m, 6H), 3.13 – 2.94 (m, 2H), 2.77 (tt, J = 12.4, 2.7 Hz, 2H), 1.87 (m, 2H), 1.81 – 1.57 (m, 4H), 1.35 – 1.01 (m, 4H); ^{1}H NMR (400 MHz, DMSO-d_6, 344 K) δ 7.68 (d, J = 8.9 Hz, 1H), 7.40 (m, 2H), 4.47 (br s, 1H), 3.28 (br m, 1H), 3.26 (d, J = 6.5 Hz, 2H), 3.03 (m, 1H), 2.91 – 2.70 (m, 1H), 1.89 (d, J = 13.2 Hz, 1H), 1.74 (d, J = 12.7 Hz, 2H), 1.22 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.22, 166.03, 139.82, 139.70, 134.22, 134.15, 134.05, 134.04, 130.47, 130.37, 127.74, 127.65, 117.17, 117.14, 47.19, 46.31, 41.66, 41.45, 38.65, 38.55, 33.20, 33.02, 32.31, 32.14, 12.72, 12.56; FTIR (cm^{-1}) 2937, 2858, 1639, 1440, 1276, 1095, 964. HRMS (EI) m/z, calculated for $[C_{13}H_{14}BrClINO]^+$: 439.8414; found: 439.8908.

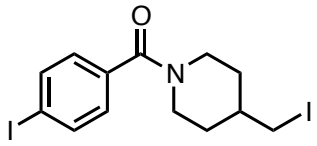


(1.0 eqiuv) (1.5 equiv) **S9** **S10**



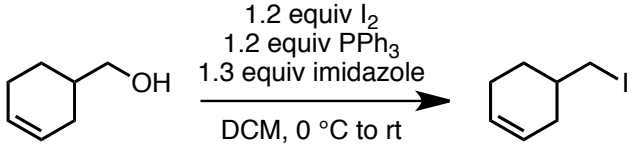
S9

S9: According to general procedure E, 4-iodobenzoyl chloride (30 mmol, 7.99 g), piperidine-4-ylmethanol (45 mmol, 5.18 g), and K_3PO_4 (90 mmol, 19.1 g) in DCM (50 mL) and water (50 mL) for 2 h, afforded 8.01 g (77%) **S9** as white crystals. mp = 138-140 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 2H), 7.16 – 7.11 (m, 2H), 4.71 (br s, 1H), 3.74 (br s, 1H), 3.58 – 3.47 (m, 2H), 3.00 (br s, 1H), 2.77 (br s, 1H), 1.93 – 1.65 (m, 3H), 1.58 – 1.44 (m, 1H), 1.37 – 1.08 (m, 2H); ^{13}C NMR (151 MHz, CDCl3) δ 169.5, 137.7, 135.8, 128.7, 95.8, 67.1, 47.9, 42.3, 38.9, 29.5, 28.5; FTIR (cm^{-1}) 3401, 2915, 2860, 1612, 1444, 1006. HRMS (EI) m/z, calculated for $[C_{13}H_{16}INO_2]^+$: 345.0226; found: 345.0237.

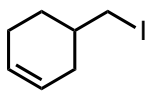


S10

S10: According to general procedure D, **S9** (15 mmol, 5.18 g), iodine (18 mmol, 4.57 g), triphenylphosphine (18 mmol, 4.73 g), and imidazole (19.5 mmol, 1.33 g) in DCM (50 mL) for 4 h, afforded, after flash silica gel chromatography (80:20 to 60:40 hexanes : ethyl acetate), alkyl iodide **S10** as a white crystalline solid (5.66 g, 83%). mp = 137-138 °C; ^{1}H NMR (600 MHz, CDCl3) δ 7.78 – 7.73 (m, 2H), 7.16 – 7.11 (m, 2H), 4.71 (br s, 1H), 3.74 (br s, 1H), 3.13 (br s, 2H), 3.00 (br s, 1H), 2.76 (br s, 1H), 2.05-1.78 (m, 2H), 1.74 (m, 1H), 1.38-1.09 (m, 2H); ^{13}C NMR (151 MHz, CDCl3) δ 169.4, 137.8, 135.6, 128.8, 95.9, 47.7, 42.2, 38.7, 33.4, 32.5, 12.8; FTIR (cm^{-1}) 2940, 2846, 1627, 1432, 1106. HRMS (ESI) m/z, calculated for $[C_{13}H_{16}NOI_2]^+$ ([M+H]$^+$): 455.9316; found: 455.9325.



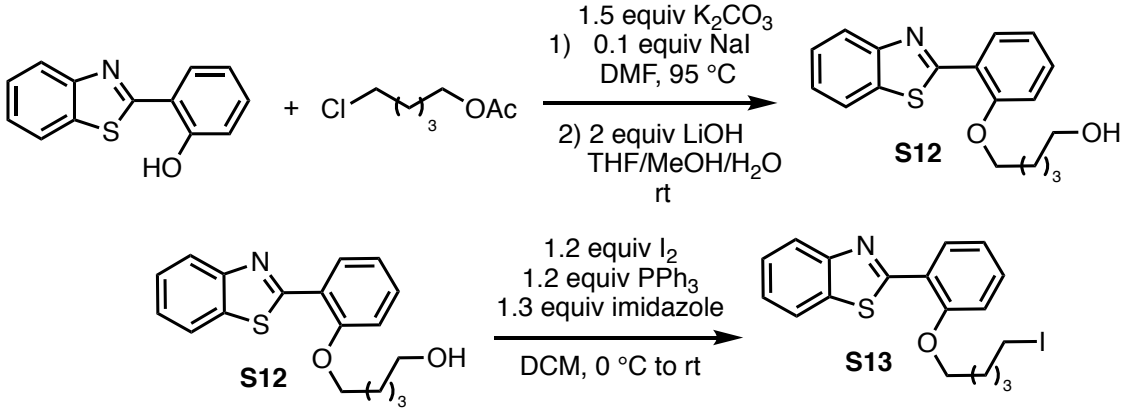
S11

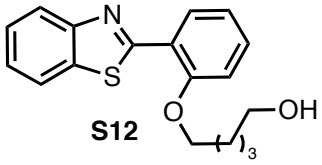


S11

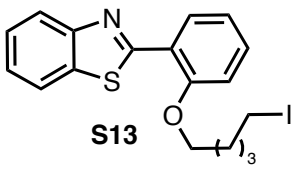
S11: According to general procedure D, cyclohex-3-en-1-ylmethanol (20 mmol, 2.24 g), iodine (24 mmol, 6.1 g), triphenylphosphine (24 mmol, 6.31 g), and imidazole (26 mmol, 1.77 g) in DCM (50 mL) for 16 h, afforded, after flash silica gel chromatography (100% hexanes), alkyl iodide **S11** as a colorless oil (4.09 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68-5.59 (m, 2H), 3.18 (d, *J* = 5.9 Hz, 2H), 2.30 – 2.15 (m, 1H), 2.09 (m, 2H), 1.87 (m, 1H), 1.82 – 1.69 (m, 2H), 1.39 – 1.22 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 127.0, 125.7, 36.2, 32.2, 29.4, 25.0, 15.1.

S11 is a known compound and its spectra are in accord with published data.[7]



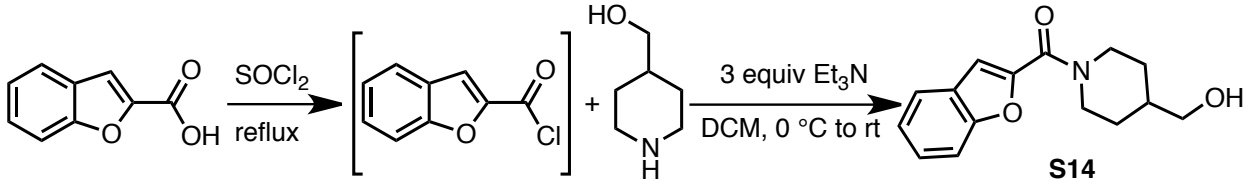


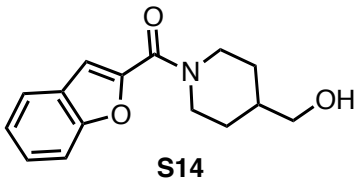
S12: A 100 mL oven-dried round-bottom flask was charged with a stir bar, K_2CO_3 (45 mmol, 6.2 g), and NaI (3 mmol, 450 mg). A rubber septum was placed and the flask was cooled under a stream of nitrogen. The rubber septum was partially removed and 2-(benzothiazol-2-yl)phenol (30 mmol, 6.82 g) was added. The rubber septum was replaced and DMF (30 mL), and 5-chloropentyl acetate (36 mmol, 5.93 g) were added sequentially via syringe under nitrogen and the mixture was stirred at 95 °C in an oil bath for 16 h. After cooling to rt, diethyl ether (200 mL) was added and the organic phase was sequentially washed with water (3x150 mL) and 1.0 M aqueous NaOH (150 mL), dried over anhydrous $MgSO_4$, filtered through a glass frit. The solvents were removed under reduced pressure. The crude material was dissolved in THF (100 mL) in a 250 mL round-bottom flask charged with a stir bar and then a solution of $LiOH \cdot H_2O$ (60 mmol, 2.54 g) in water (25 mL) was added to the mixture while stirring vigorously, followed by MeOH to convert the biphasic mixture into a monophasic mixture (ca. 30 mL). Upon completion of hydrolysis (monitored by TLC), ethyl acetate (100 mL) was added and the organic phase was washed with brine (50 mL), dried over anhydrous $MgSO_4$, and filtered through a glass frit. The solvents were removed under reduced pressure and the crude product was purified by flash silica gel chromatography (80:20 to 0:100 hexanes : ethyl acetate) to afford **S12** (7.33 g, 78%) as a white solid. mp = 77-79 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 7.9, 1.8 Hz, 1H), 8.09 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.94 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.49 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 7.44 (ddd, *J* = 8.3, 7.3, 1.8 Hz, 1H), 7.37 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.12 (ddd, *J* = 8.1, 7.3, 1.1 Hz, 1H), 7.05 (dd, *J* = 8.4, 1.0 Hz, 1H), 4.24 (t, *J* = 6.4 Hz, 2H), 3.72 (m, 2H), 2.08 (p, *J* = 6.9 Hz, 2H), 1.72 (m, 4H), 1.29 (t, *J* = 5.4 Hz, 1H); ^{13}C NMR (151 MHz, CDCl3) δ 163.3, 156. 8, 152.2, 136.2, 131.9, 129.8, 126.0, 124.7, 122.9, 122.4, 121.4, 121.1, 112.4, 69.2, 62.8, 32.5, 29.1, 22.7; FTIR (cm^{-1}) 3357, 2940, 2871, 1598, 1452, 1248, 1116. HRMS (EI) m/z, calculated for $[C_{18}H_{19}NO_2S]^+$: 313.1136; found: 313.1137.



S13: According to general procedure D, **S12** (10 mmol, 3.13 g), iodine (12 mmol, 3.05 g), triphenylphosphine (12 mmol, 3.16 g), and imidazole (13 mmol, 884 mg) in DCM (30 mL) for 17 h afforded, after flash silica gel chromatography (100:0 to 80:20 hexanes : ethyl acetate), alkyl iodide **S13** (4.12 g, 97%) as a white crystalline solid. mp

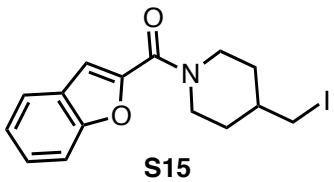
= 96-98 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 7.9, 1.8 Hz, 1H), 8.09 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.95 (ddd, *J* = 7.9, 1.2, 0.7 Hz, 1H), 7.49 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.44 (ddd, *J* = 8.3, 7.3, 1.8 Hz, 1H), 7.38 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.12 (ddd, *J* = 8.2, 7.3, 1.0 Hz, 1H), 7.04 (dd, *J* = 8.4, 1.1 Hz, 1H), 4.24 (t, *J* = 6.3 Hz, 2H), 3.26 (t, *J* = 6.9 Hz, 2H), 2.11 – 2.03 (m, 2H), 1.99 (p, *J* = 7.0 Hz, 2H), 1.82 – 1.73 (m, 2H); ^{13}C NMR (151 MHz, CDCl3) δ 163.2, 156.7, 152.3, 136.3, 131.9, 129.8, 126.0, 124.7, 122.9, 122.5, 121.4, 121.2, 112.3, 69.0, 33.4, 28.5, 27.6, 6.8; FTIR (cm^{-1}) 2939, 1596, 1451, 1291, 1247, 1115, 754. HRMS (EI) m/z, calculated for $[C_{18}H_{18}INOS]^{+}$: 423.0154; found: 423.0175.





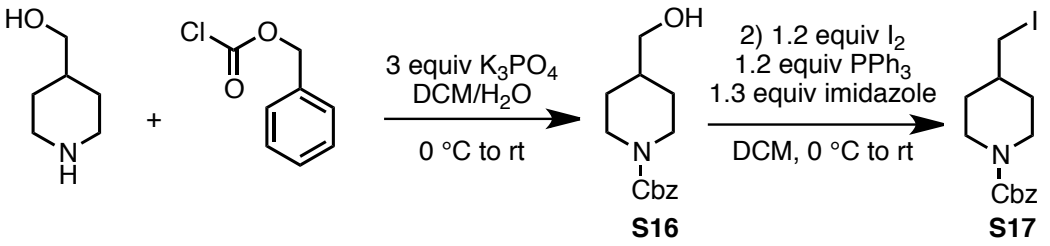
S14: Benzofuran-2-carboxylic acid (20 mmol, 3.24 g) was added to a 25 mL round-bottom flask charged with a stir bar followed by thionyl chloride (10 mL) under air. A reflux condenser was attached to the flask and the condenser was secured with a rubber septum. The mixture was refluxed with stirring (oil bath temperature was set to 85 °C) for 1 h under a balloon of nitrogen. After cooling to rt, the excess thionyl chloride was removed under reduced pressure and the resulting acyl chloride was directly used in next step. A 100 mL oven-dried round-bottom flask charged with a stir bar was sealed with a rubber septum and cooled under a stream of nitrogen. The rubber septum was partly removed and piperidine-4-ylmethanol (30 mmol, 3.45 g) was added. The rubber septum was replaced, then non-anhydrous triethylamine (60 mmol, 6 g), and DCM (50 mL) were added via syringe under nitrogen. The flask was placed in an ice bath and benzofuran-2-carbonyl chloride dissolved in DCM (10 mL) was added drop wise to the solution via syringe while stirring. After addition was complete, the ice bath was removed and reaction stirred at rt for 2 h. The organic phase was then washed with water (50 mL), 1.0 M aqueous HCl (2x50 mL), and 1.0 M aqueous NaOH (50 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered through a glass frit, and the solvent was removed under reduced pressure. The crude material was crystallized from DCM/Pentane to afford **S14** (2.81 g, 54%) as golden-brown crystals. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.66 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.58 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.35 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.25 (m, 2H), 4.45 (t, *J* = 5.3 Hz, 1H), 4.35 (br s, 1H), 4.15 (br s, 1H), 3.21 (t, *J* = 5.7 Hz, 2H), 3.19 – 2.97 (m, 1H), 2.74 (br s, 1H), 2.42 (p, *J* = 1.8 Hz, 1H), 1.69 (br s, 1H), 1.62 (m, 1H), 1.07 (br m, 2H); ^{13}C NMR (151 MHz, DMSO) δ 158.8, 153.8, 148.7, 126.7, 126.3, 123.6, 122.3, 111.7, 110.0, 65.4, 54.9, 46.4, 42.2, 38.4, 29.3, 28.5.

S14 is a known compound and its spectra are in accord with published data.[8]

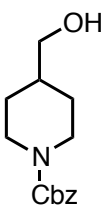


S15

S15: According to general procedure D, **S14** (10 mmol, 2.59 g), iodine (12 mmol, 3.05 g), triphenylphosphine (12 mmol, 3.16 g), and imidazole (13 mmol, 884 mg) in DCM (30 mL) for 4 h, afforded, after flash silica gel chromatography (80:20 to 70:30 hexanes : ethyl acetate), alkyl iodide **S15** (2.36 g, 64%) as a white solid. mp = 113-115 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (dt, J = 7.8, 1.0 Hz, 1H), 7.53 (dq, J = 8.4, 0.9 Hz, 1H), 7.40 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.31 – 7.26 (m, 2H), 4.61 (br s, 2H), 3.15 (d, J = 6.5 Hz, 2H), 2.85 (br s, 2 H), 2.05 – 1.95 (m, 2H), 1.81 (m, 1H), 1.40 – 1.28 (qd, *J* = 12.6, 4.3 Hz, 2H); ^{13}C NMR (101 MHz, CDCl3) δ 159.9, 154.6, 149.2, 127.1, 126.5, 123.7, 122.3, 112.0, 111.8, 46.7, 43.0, 38.8, 33.4, 32.6, 12.8; FTIR (cm^{-1}) 2937, 2852, 1635, 1561, 1435, 1254, 1169, 966, 746. HRMS (EI) m/z, calculated for $[C_{15}H_{16}INO_2]^+$: 369.0226; found: 369.0230.



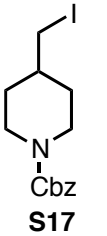
S16 **S17**



S16

S16: According to general procedure E, benzylchloroformate (30 mmol, 8 g), piperidine-4-ylmethanol (45 mmol, 5.18 g), and K_3PO_4 (90 mmol, 19.1 g) in DCM (50 mL) and water (50 mL) for 1 h, afforded, after silica gel chromatography (75:25 to 25:75 hexanes : ethyl acetate) **S16** (4.35 g, 54%) as pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (m, 4H), 7.33 – 7.29 (m, 1H), 5.13 (s, 2H), 4.22 (br s, 2H), 3.51 (t, *J* = 5.9 Hz, 2H), 2.79 (br s, 2H), 1.80 – 1.71 (m, 2H), 1.71-1.63 (m, 1H), 1.35 – 1.30 (m, 1H), 1.19 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 136.8, 128.5, 128.0, 127.8, 67.3, 67.2, 67.0, 43.9, 38.6, 28.6, 28.5.

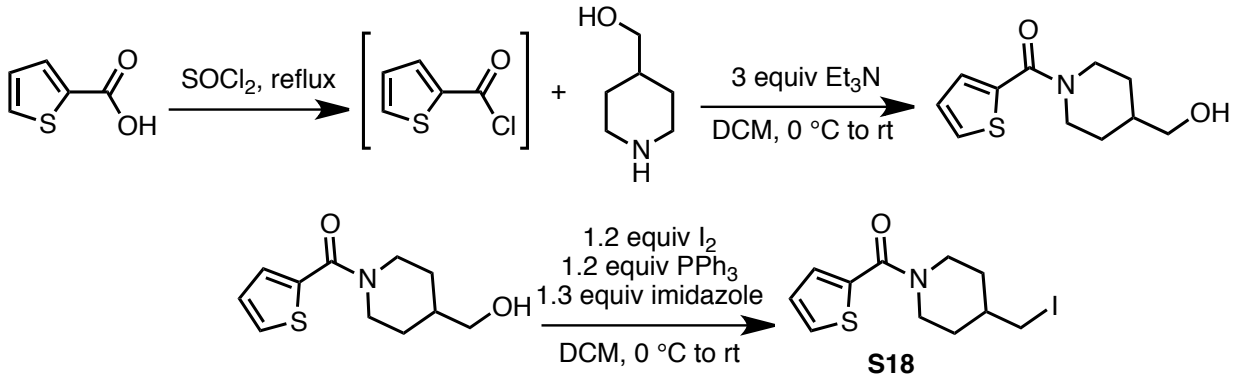
S16 is a known compound and its spectra are in accord with published data.[9]

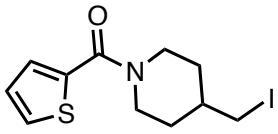


S17

S17: According to general procedure D, **S16** (10 mmol, 2.49 g), iodine (12 mmol, 3.05 g), triphenylphosphine (12 mmol, 3.16 g), and imidazole (13 mmol, 884 mg) in DCM (30 mL) for 1 h, afforded, after flash silica gel chromatography (95:5 to 75:25 hexanes : ethyl acetate), alkyl iodide **S17** (1.49 g, 42%) as a pale yellow oil. ^{1}H NMR (400 MHz, CDCl3) δ 7.40 – 7.28 (m, 5H), 5.12 (s, 2H), 4.21 (br s, 2H), 3.10 (d, J = 6.5 Hz, 2H), 2.77 (br s, 2H), 1.85 (br m, 2H), 1.70 – 1.59 (m, 1H), 1.16 (br m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 136.9, 128.6, 128.1, 128.0, 67.2, 43.9, 38.6, 32.6, 13.4.

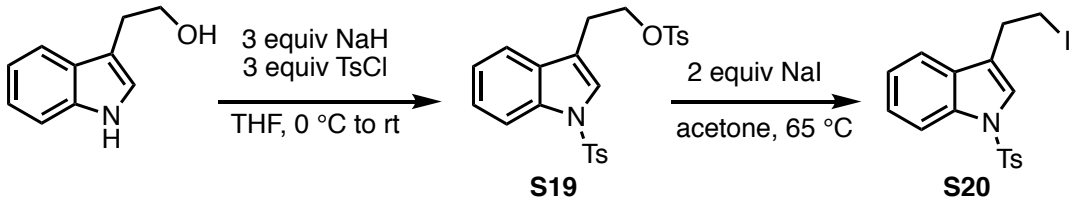
S17 is a known compound and its spectra are in accord with published data.[10]



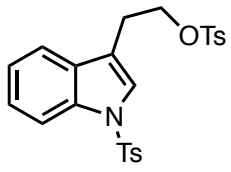


S18

S18: Thiophene-2-carboxylic acid (20 mmol, 2.56 g) was added to a 25 mL round-bottom flask charged with a stir bar followed by thionyl chloride (10 mL) under air. A reflux condenser was attached to the flask and the condenser was secured with a rubber septum. The mixture was refluxed with stirring (oil bath temperature was set to 85 °C) for 1 h under a balloon of nitrogen. After cooling to rt, the excess thionyl chloride was removed under reduced pressure and the resulting acyl chloride was directly used in next step. A 100 mL oven-dried round-bottom flask charged with a stir bar was sealed with a rubber septum and cooled under a stream of nitrogen. The rubber septum was partly removed and piperidine-4-ylmethanol (30 mmol, 3.45 g) was added. The rubber septum was replaced and non-anhydrous triethylamine (60 mmol, 6 g) and DCM (50 mL) were added via syringe under nitrogen. The flask was placed in an ice bath and thiophene-2-carbonyl chloride dissolved in DCM (10 mL) was added drop wise to the solution via syringe while stirring. After addition was complete, the ice bath was removed and the mixture was stirred at rt for 2 h. The organic phase was washed with water (50 mL), 1 M HCl (2x50 mL), and 1 M NaOH (50 mL); then it was dried over anhydrous $MgSO_4$, filtered through a glass frit, and the volatiles were removed under reduced pressure. To hydrolyze the unwanted ester, the crude mixture was dissolved in THF (100 mL) in a 250 mL round-bottom flask charged with a stir bar and then a solution of $LiOH{\cdot}H_2O$ (20 mmol, 840 mg) in water (20 mL) was added to the mixture under air while stirring vigorously, followed by MeOH to convert the biphasic mixture into a monophasic mixture (ca. 20 mL). Upon completion of hydrolysis of the ester (monitored by TLC), ethyl acetate (100 mL) was added and the organic phase was washed with sequentially with 1 M aqueous NaOH (50 mL), brine (50 mL), dried over anhydrous $MgSO_4$, and filtered through a glass frit. The solvents were removed under reduced pressure to afford the alcohol (3.21 g, 71%) as white crystalline solid. The resulting alcohol was used in next step without further purification. According to general procedure D, the alcohol (10 mmol, 2.25 g), iodine (12 mmol, 3.05 g), triphenylphosphine (12 mmol, 3.16 g), and imidazole (13 mmol, 884 mg) in DCM (30 mL) for 42 h, afforded, after flash silica gel chromatography (85:15 to 75:25 hexanes : ethyl acetate), alkyl iodide **S18** (3.245 g, 97%) as a white crystalline solid. mp = 58-60 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 5.0 Hz, 1H), 7.34 (d, *J* = 3.6 Hz, 1H), 7.11 (t, *J* = 4.3 Hz, 1H), 4.55 (br s, 2H), 3.20 (d, *J* = 6.5 Hz, 2H), 3.02 (br s, 2H), 2.02 (br m, 2H), 1.84 (m, 1H), 1.34 (m, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 163.6, 137.3, 128.6, 128.5, 126.7, 45.5, 38.8, 32.9, 12.9; FTIR (cm^{-1}) 2934, 2850, 1613, 1521, 1439, 1271, 964, 735. HRMS (EI) m/z, calculated for $[C_{11}H_{14}INOS]^+$: 334.9841; found: 334.9849.

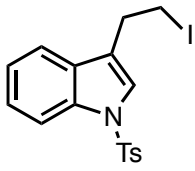


S19 **S20**



S19

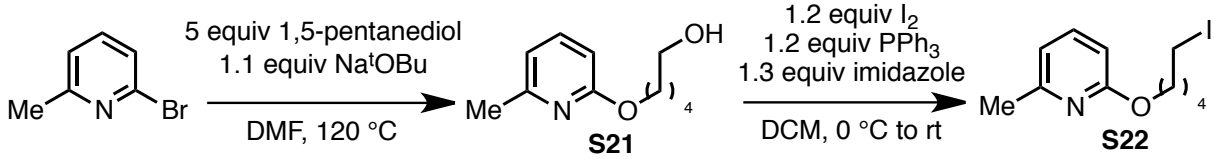
S19: was made according to the literature and its spectra are in accord with published data.[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 8.1 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 7.5 Hz, 3H), 7.22 (d, J = 8.1 Hz, 2H), 7.17 (t, J = 8.3 Hz, 3H), 4.24 (t, J = 6.6 Hz, 2H), 3.01 (t, J = 6.6 Hz, 2H), 2.39 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.1, 144.9, 135.4, 135.2, 132.8, 130.4, 130.1, 129.8, 127.8, 127.0, 124.9, 124.2, 123.3, 119.2, 117.3, 113.9, 68.9, 25.1, 21.8, 21.7.



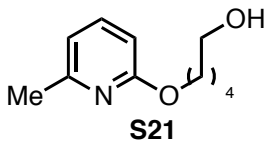
S20

S20: S19 (5 mmol, 2.34 g), sodium iodide (10 mmol, 1.5 g), and non-anhydrous acetone (10 mL) were added to a 20 mL scintillation vial charged with a stir bar under air. The vial was capped, placed in oil bath at 65 °C, and stirred vigorously for 1 h. The mixture cooled to rt and DCM (50 mL) was added to the mixture. The suspension was filtered through Celite and the solids were washed with more DCM (50 mL). The solvents were removed under reduced pressure and the crude product was purified by flash silica gel chromatography (90:10 hexanes : ethyl acetate) to afford alkyl iodide **S20** (2.04 g, 96%) as a light yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.79 – 7.72 (m, 2H), 7.45 (tt, *J* = 4.6, 1.0 Hz, 2H), 7.32 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.24 (ddd, *J* = 8.1, 7.3, 1.0 Hz, 1H), 7.23 – 7.17 (m, 2H), 3.41 (t, *J* = 7.4 Hz, 2H), 3.25 (t, *J* = 7.4 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.0, 135.4, 135.4, 130.3, 130.0, 127.0, 125.0, 123.7, 123.3, 121.6, 119.2, 114.1, 29.8, 21.7, 3.9.

S20 is a known compound and its spectra are in accord with published data.[11]



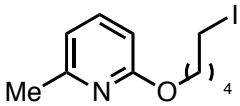
S21 **S22**



S21

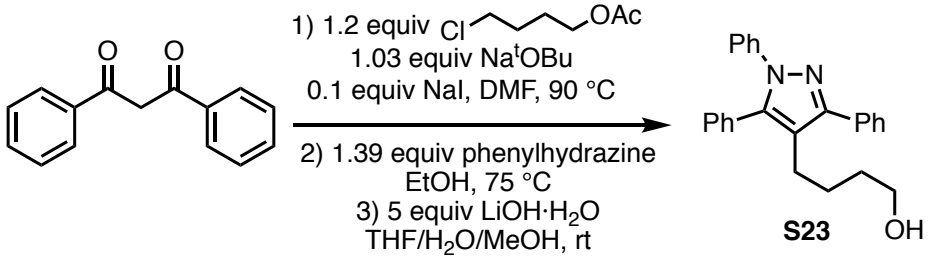
S21: A 50 mL flame-dried round-bottom flask charged with a stir bar was sealed with a rubber septum and cooled under a stream of nitrogen. The rubber septum was partly removed, then sodium *tert*-butoxide (11 mmol, 1.06 g) was added. The rubber septum was replaced and DMF (20 mL), and 1,5-pentanediol (50 mmol, 5.2 g) were added sequentially via syringe under nitrogen. The mixture stirred for 10 min at rt and 2-bromo-6-methylpyridine (10 mmol, 1.72 g) was then added via syringe. The flask was placed in an oil bath at 120 °C and stirred for 7 h under nitrogen. After cooling to rt, diethyl ether (100 mL) was added and the organic phase was washed with water (5x100 mL), dried over anhydrous $MgSO_4$, filtered through a glass frit, and the solvents were removed under reduced pressure. The crude product

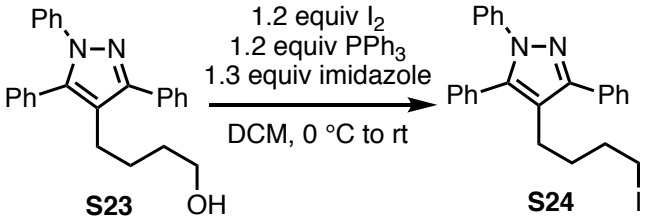
was purified by flash silica gel chromatography (80:20 to 40:60 hexanes : ethyl acetate) to afford **S21** (1.29 g, 66%) as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.3, 7.2 Hz, 1H), 6.69 (d, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 8.2 Hz, 1H), 4.26 (t, *J* = 6.6 Hz, 2H), 3.67 (t, *J* = 6.5 Hz, 2H), 1.80 (p, *J* = 6.7 Hz, 2H), 1.64 (p, *J* = 6.8 Hz, 2H), 1.53 (p, *J* = 7.4, 7.0 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.6, 156.4, 138.9, 115.7, 107.1, 65.8, 63.0, 32.6, 29.0, 24.3, 22.5; FTIR (cm^{-1}) 3340, 2940, 2865, 1597, 1577, 1450, 1306, 1233; HRMS (EI) m/z, calculated for $[C_{11}H_{17}NO_2]^+$: 195.1259; found: 195.1251.

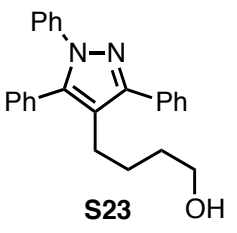


S22

S22: According to general procedure D, **S21** (10 mmol, 1.95 g), iodine (12 mmol, 3.05 g), triphenylphosphine (12 mmol, 3.16 g), and imidazole (13 mmol, 884 mg) in DCM (30 mL) for 4 h (note: the organic phase was washed with saturated aqueous Na_2CO_3 (30 mL) instead of water), afforded, after flash silica gel chromatography (100:0 to 95: 5 hexanes : ethyl acetate), alkyl iodide **S22** (2.90 g, 95%) as a clear oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 1H), 6.70 (d, *J* = 7.2 Hz, 1H), 6.51 (d, *J* = 8.2 Hz, 1H), 4.27 (t, *J* = 6.5 Hz, 2H), 3.22 (t, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 1.91 (p, *J* = 7.1 Hz, 2H), 1.82 – 1.75 (m, 2H), 1.64 – 1.52 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.6, 156.4, 138.9, 115.8, 107.2, 65.4, 33.4, 28.2, 27.4, 24.3, 6.8; FTIR (cm^{-1}) 2943 2861, 1596, 1578, 1449, 1304, 1232, 1030, 789; HRMS (CI) m/z, calculated for $[C_{11}H_{17}INO]^+$: 306.0355; found: 306.0354.

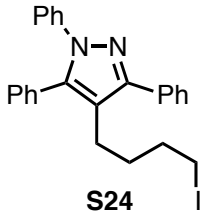






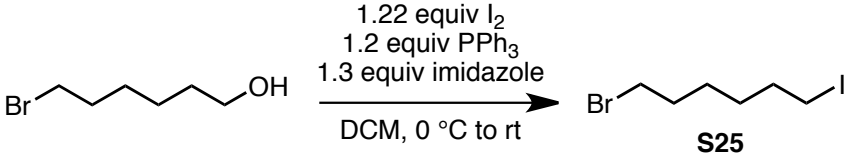
S23: A 100 mL oven-dried round-bottom flask charged with a stir bar was sealed with a rubber septum and cooled under a stream of nitrogen. The rubber septum was partly removed and sodium iodide (3 mmol, 450 mg) and sodium *tert*-butoxide (31 mmol, 2.98 g) were added. The rubber septum was replaced and DMF (30 mL) was added via syringe under nitrogen. The rubber septum was partly removed and 1,3-diphenylpropane-1,3-dione (30 mmol, 6.72 g) was added to the flask. The rubber septum was put back. The mixture was stirred for 10 min at rt under nitrogen, followed by addition of 4-chlorobutyl acetate (36 mmol, 4.95 g) via syringe while stirring. The flask was placed in an oil bath at 90 °C and stirred for 20 h under nitrogen. After cooling to rt, diethyl ether (200 mL) was added and the

organic phase was sequentially washed with water (3x200 mL) and brine (100 mL), dried over anhydrous $MgSO_4$, filtered through a glass frit, and the solvents were removed under reduced pressure. The crude mixture was partially purified by flash silica gel column chromatography (90:10 to 60:40 hexanes: ethyl acetate). The crude material was then dissolved in a mixture of ethanol (40 mL) and phenylhydrazine (43 mmol, 4.65 g) in a 100 mL round-bottom flask equipped with a stir bar under air and the mixture was stirred at 75 °C in an oil bath under a balloon of nitrogen for 24 h. The volatiles were then removed under reduced pressure. The crude material was dissolved in THF (100 mL) in a 250 mL round-bottom flask equipped with a stir bar under air and then a solution of $LiOH \cdot H_2O$ (150 mmol, 6.3 g) in water (25 mL) was added to the mixture while stirring vigorously, followed by MeOH to change biphasic mixture into a single-phase mixture (ca. 25 mL). After 2 h, ethyl acetate (200 mL) was added and the organic phase was washed with water (2x200 mL) and brine (100 mL), dried over anhydrous $MgSO_4$, filtered through a glass frit, and the solvents were removed under reduced pressure. The crude product was purified by flash silica gel chromatography (90:10 to 60:40 hexanes: ethyl acetate). The resulting solid was then crystallized from ethyl acetate/hexanes and the crystals were washed with diethyl ether (50 mL) to afford **S23** (3.56 g, 32% over 3 steps) white crystals. mp = 127-129 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 2H), 7.45 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.37 (m, 4H), 7.26 (tdt, *J* = 8.2, 6.2, 1.6 Hz, 7H), 7.23 – 7.17 (m, 1H), 3.44 (q, *J* = 6.0 Hz, 2H), 2.68 (t, *J* = 7.4 Hz, 2H), 1.47-1.38 (m, 4H), 1.07 – 0.98 (br m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.2, 141.6, 140.2, 134.3, 131.1, 130.2, 128.8, 128.7, 128.6, 128.5, 128.1, 127.8, 126.8, 124.8, 119.2, 62.6, 32.4, 26.7, 23.5; FTIR (cm^{-1}) 3394, 2937, 2863, 1596, 1499, 1453, 1361. HRMS (EI) m/z, calculated for $[C_{25}H_{24}N_2O]^+$: 368.1889; found: 368.1896.

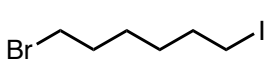


S24

S24: According to general procedure D, **S23** (9 mmol, 3.31 g), iodine (10.8 mmol, 2.74 g), triphenylphosphine (10.8 mmol, 2.84 g), and imidazole (11.7 mmol, 796 mg) in DCM (30 mL) for 1 h, afforded, after flash silica gel chromatography (90:10 hexanes : ethyl acetate), alkyl iodide **S24** (3.98 g, 93%) as a white solid. mp = 95-97 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.41 – 7.33 (m, 4H), 7.32 – 7.23 (m, 6H), 7.23 – 7.16 (m, 1H), 2.97 (t, J = 7.0 Hz, 2H), 2.76 – 2.56 (t, *J* = 7 Hz, 2H), 1.67 (p, *J* = 7.1 Hz, 2H), 1.50 (p, *J* = 7.1, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.2, 141.7, 140.2, 134.2, 131.0, 130.2, 128.81, 128.78, 128.68, 128.56, 128.2, 127.9, 126.9, 124.8, 118.7, 33.3, 31.4, 22.8, 6.5; FTIR (cm^{-1}) 3058, 2936, 1596, 1498, 1452, 1361, 761, 697. HRMS (EI) m/z, calculated for $[C_{25}H_{23}IN_2]^+$: 478.0906; found: 478.0902.



S25

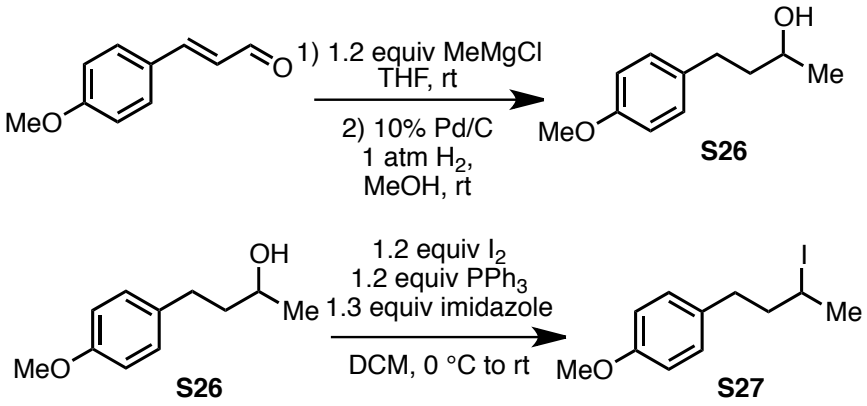


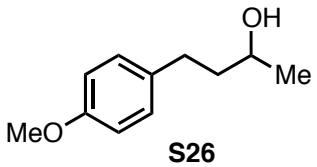
S25

S25: According to general procedure D, 6-bromohexan-1-ol (10 mmol, 1.81 g), iodine (12.2 mmol, 3.1 g), triphenylphosphine (12 mmol, 3.16 g), and imidazole (13 mmol, 884 mg) in DCM (30 mL) for 4 h, afforded, after flash silica gel chromatography (100:0 hexanes : ethyl acetate), alkyl iodide **S25** (2.51 g, 86%)

as a clear oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.41 (t, *J* = 6.8, 2H), 3.19 (t, *J* = 6.9, 2H), 1.92 – 1.79 (m, 4H), 1.52 – 1.38 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 33.7, 33.4, 32.7, 29.8, 27.2, 6.8.

S25 is a known compound and its spectra are in accord with published data.[12]

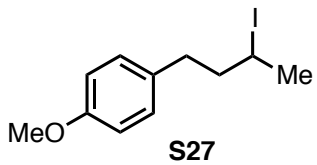




S26

S26: A 100 mL flame-dried round-bottom flask charged with a stir bar was sealed with a rubber septum and cooled under a stream of nitrogen. The rubber septum was partly removed and *p*-methoxycinnamaldehyde (20 mmol, 3.24 g) was added. The rubber septum was replaced and THF (40 mL) was added under nitrogen and the flask was placed in a water bath. MeMgCl (3M in THF, 24 mmol, 8 mL) was added drop wise via syringe under nitrogen to the flask and the mixture stirred at rt for 4 h under nitrogen. Then, saturated aqueous NH_4Cl (20 mL) was added to quench excess Grignard reagent, followed by water (50 mL) and diethyl ether (150 mL). The organic layer was separated, dried over anhydrous $MgSO_4$, filtered through a glass frit, and the solvents were removed under reduced pressure. The crude mixture was dissolved in non-anhydrous methanol (50 mL) in a 100 mL round-bottom flask equipped with a stir bar under air and 5% Pd/C (10 wt %, 324 mg) was added. The flask was sealed with a rubber septum and the mixture was stirred under an atmosphere of hydrogen (balloon) at rt for 14 h. The mixture was then filtered through Celite and the solvent was removed under reduced pressure. The crude product was purified by flash silica gel chromatography (90:10 to 75:25 hexanes : ethyl acetate) to afford **S26 (**2.70 g, 81% over 2 steps) as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 – 7.09 (m, 2H), 6.86 – 6.81 (m, 2H), 3.85 – 3.79 (m, 1H), 3.79 (s, 3H), 2.70 (ddd, *J* = 13.9, 9.5, 6.1 Hz, 1H), 2.62 (ddd, *J* = 13.9, 9.3, 6.8 Hz, 1H), 1.80 – 1.68 (m, 2H), 1.22 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.9, 134.2, 129.4, 114.0, 67.6, 55.4, 41.2, 31.3, 23.8.

S26 is a known compound and its spectra are in accord with published data.[13]

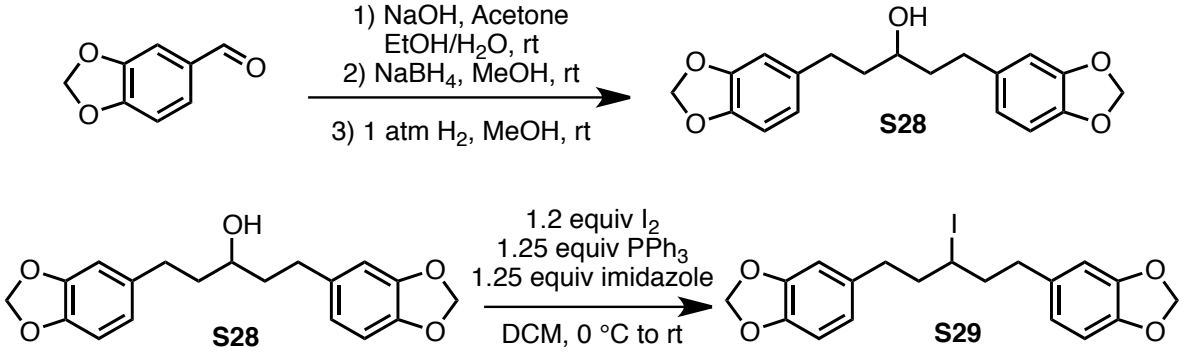


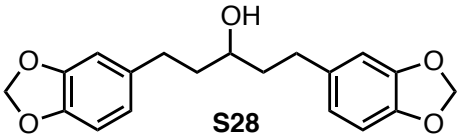
S27

S27: According to general procedure D, **S26** (10 mmol, 1.8 g), iodine (12 mmol, 3.05 g), triphenylphosphine (12 mmol, 3.16 g), and imidazole (13 mmol, 884 mg) in DCM (30 mL) for 4 h, afforded, after flash silica gel chromatography (100:0 to 95:5 hexanes : ethyl acetate), alkyl iodide **S27** (2.81 g, 97%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 – 7.10 (m, 2H), 6.88 – 6.80 (m, 2H), 4.10 (dqd, *J* = 9.1, 6.9, 4.5 Hz, 1H), 3.79 (s, 3H), 2.79 (ddd, *J* = 13.9, 8.8, 5.1 Hz, 1H), 2.64 (ddd, *J* =

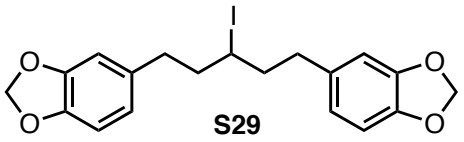
13.9, 8.8, 7.1 Hz, 1H), 2.13 (dtd, *J* = 14.2, 8.9, 5.1 Hz, 1H), 1.94 (d, *J* = 6.8 Hz, 3H), 1.84 (dddd, *J* = 14.7, 8.9, 7.1, 4.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.2, 132.9, 129.6, 114.0, 55.4, 44.8, 35.1, 29.9, 29.1.

S27 is a known compound and its spectra are in accord with published data.[14]



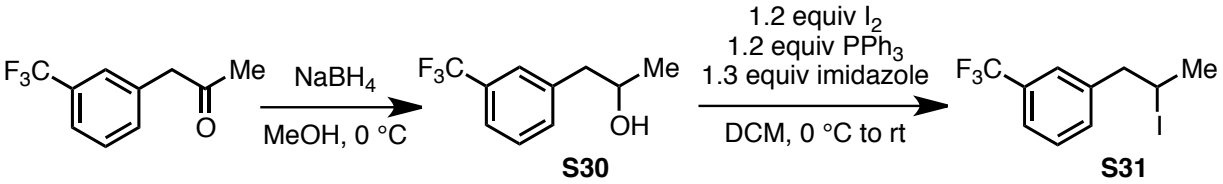


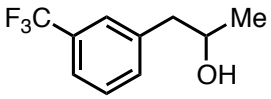
S28: A 200 mL round-bottom flask equipped with a stir bar was sequentially charged with non-anhydrous EtOH (40 mL), non-anhydrous acetone (25 mmol, 1.82 mL), and Piperonal (50 mmol, 7.5 g), followed by 10% aqueous NaOH (50 mL) under air and the mixture stirred at rt for 1 h under air. The flask was then placed in an ice bath and the mixture was stirred for another 10 min under air. The yellow precipitate was filtered, washed with water (200 mL) and crystallized from (EtOH/EtOAc/Acetone, 1:1:3) to afford yellow crystals (4.07 g, 50%). The crystals (10 mmol, 3.22 g) were dissolved in non-anhydrous MeOH (100 mL) in a 200 mL round-bottom flask equipped with a stir bar under air and $NaBH_4$ (60 mmol, 2.28 g) was added while stirring in 4 portions over 1 h under air. The mixture stirred at rt overnight under air. The solvent was removed under reduced pressure. To the crude mixture was added DCM (200 mL), followed by slow addition of 1.0 M aqueous HCl to quench the excess $NaBH_4$ until no bubbling occurred. The organic phase was washed with water (200 mL). The combined aqueous phase was extracted with DCM (2x50 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered through a glass frit, and the solvents were removed under reduced pressure. The crude mixture was added to a 200 mL round-bottom flask charged with a stir bar, followed by 5% Pd/C (10 wt %, 322 mg) and non-anhydrous MeOH (100 mL) under air. The flask was sealed with a rubber septum and the mixture stirred under an atmosphere of H_2 (balloon) at rt for 4 h. After which the mixture was filtered through Celite, the solvent was removed under reduced pressure and the crude product was crystallized from EtOAc/hexanes to afford **S28** (1.87 g, 57% over 2 steps) as white crystals. mp = 98-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (d, *J* = 7.9 Hz, 2H), 6.68 (d, *J* = 1.6 Hz, 2H), 6.63 (dd, *J* = 7.9, 1.7 Hz, 2H), 5.92 (s, 4H), 3.62 (td, *J* = 7.7, 4.0 Hz, 1H), 2.70 (ddd, *J* = 14.9, 9.0, 6.3 Hz, 2H), 2.59 (ddd, *J* = 13.8, 9.0, 7.0 Hz, 2H), 1.82 – 1.65 (m, 4H), 1.38 (br s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.6, 145.7, 135.8, 121.1, 108.9, 108.2, 100.8, 70.6, 39.4, 31.8; FTIR (cm^{-1}) 3350, 2918, 1501, 1486, 1246, 1010. HRMS (EI) m/z, calculated for $[C_{19}H_{20}O_5]^+$: 328.1311; found: 328.1318.



S29

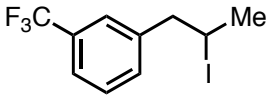
S29: According to general procedure D, **S28** (10.36 mmol, 3.45 g), iodine (12.43 mmol, 3.16 g), triphenylphosphine (12.95 mmol, 3.4 g), and imidazole (12.95 mmol, 881 mg) in DCM (30 mL) for 16 h, afforded, after flash silica gel chromatography (100:0 to 85:15 hexanes : ethyl acetate), alkyl iodide **S29** (3.72 g, 80%) as a white solid. mp = 77-79 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.72 (d, *J* = 7.9 Hz, 2H), 6.66 (d, *J* = 1.7 Hz, 2H), 6.62 (dd, *J* = 7.9, 1.7 Hz, 2H), 5.93 (s, 4H), 3.95 (tt, *J* = 8.9, 4.2 Hz, 1H), 2.79 (ddd, *J* = 13.9, 8.9, 5.1 Hz, 2H), 2.62 (ddd, *J* = 13.8, 8.9, 6.8 Hz, 2H), 2.15 (dtd, *J* = 14.3, 9.0, 5.1 Hz, 2H), 1.93 (dddd, *J* = 14.7, 9.0, 6.9, 4.2 Hz, 2H);^{13}C NMR (151 MHz, $CDCl_3$) δ 147.8, 146.0, 134.6, 121.4, 109.0, 108.3, 101.0, 42.6, 37.9, 35.4; FTIR (cm^{-1}) 2891, 1502, 1488, 1442, 1246, 1039, 935, 810. HRMS (EI) m/z, calculated for $[C_{19}H_{19}IO_4]^+$: 438.0328; found: 438.0327.





S30

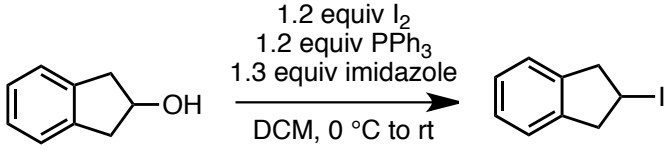
S30: 1-(3-(trifluoromethyl)phenyl)propan-2-one (15 mmol, 3.03 g) was added to a 100 mL round-bottom flask equipped with a stir bar under air. Non-anhydrous MeOH (30 mL) was then added to the flask under air and the flask was placed in an ice bath. To the mixture was added $NaBH_4$ (75 mmol, 2.85 g) slowly over 5 min while stirring under air. The mixture was stirred for 1 h at 0 °C under air, and then quenched with saturated aqueous NH_4Cl, until no bubbling occurred. Water (150 mL) was then added and the aqueous layer was extracted with DCM (2x150 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered through a glass frit, and volatiles were removed under reduced pressure. The product **S30** (2.99 g, 98% light yellow oil) was used in next step without further purification.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.46 – 7.37 (m, 2H), 4.05 (dqd, *J* = 10.6, 5.9, 3.0 Hz, 1H), 2.84 (dd, *J* = 13.7, 4.9 Hz, 1H), 2.77 (dd, *J* = 13.6, 7.8 Hz, 1H), 1.50 (br m, 1H), 1.26 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.7, 130.94 (q, *J* = 32.0 Hz), 129.0, 126.2 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 272.2 Hz), 123.5 (q, *J* = 3.9 Hz), 68.8, 45.5, 23.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.56; FTIR (cm^{-1}) 3360, 2973, 2932, 1597, 1450, 1332, 1125; HRMS (EI) m/z, calculated for $[C_{10}H_{11}F_3O]^+$: 204.0762; found: 204.0771.



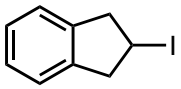
S31

S31: According to general procedure D, **S30** (10 mmol, 2.03 g), iodine (12 mmol, 3.05 g), triphenylphosphine (12 mmol, 3.16 g), and imidazole (13 mmol, 884 mg) in DCM (30 mL) for 20 h, afforded, after flash silica gel chromatography (100:0 to 95:5 hexanes : ethyl acetate), alkyl iodide **S31** (2.55 g, 82%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 1H), 7.48 – 7.41 (m, 2H), 7.41 – 7.36 (m, 1H), 4.38 – 4.24 (m, 1H), 3.30 (dd, *J* = 14.3, 7.7 Hz, 1H), 3.14 (dd, *J* = 14.3, 6.9 Hz, 1H), 1.93 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.6, 132.5, 131 (q, *J* = 32.2 Hz), 129.0, 125.8 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.5 Hz), 123.9 (q, *J* = 3.8 Hz), 49.1, 28.3, 27.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.61; FTIR (cm^{-1}) 2966, 2919, 1491, 1450,

1330, 1165, 1126. HRMS (CI) m/z, calculated for $[C_{10}H_{10}F_2I]^+$ ($[M-F]^+$): 294.9795; found: 294.9780.



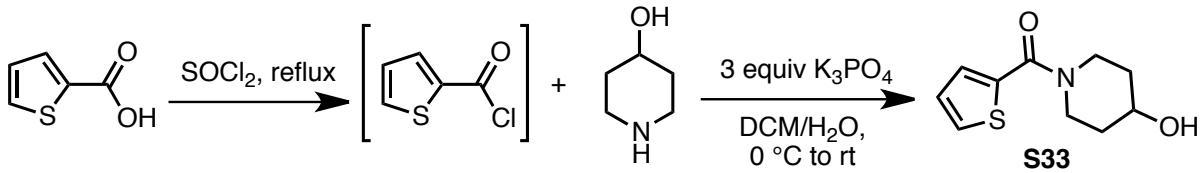
S32



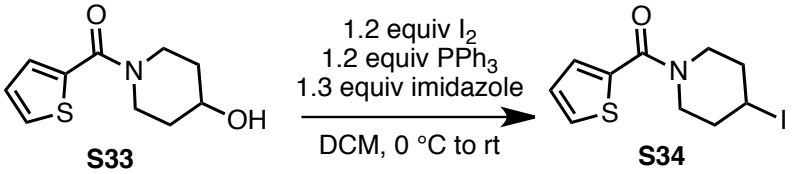
S32

S32: According to general procedure D, 2,3-dihydro-1H-inden-2-ol (15 mmol, 2.01 g), iodine (18 mmol, 4.57 g), triphenylphosphine (18 mmol, 4.74 g), and imidazole (19.5 mmol, 1.33 g) in DCM (30 mL) for 2 h, afforded, after flash silica gel chromatography (100:0 to 95:5 hexanes : ethyl acetate), alkyl iodide **S32** (3.96 g, 81%) as a white crystalline solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 5.5, 3.2 Hz, 2H), 7.24 (dd, *J* = 5.5, 3.2 Hz, 2H), 4.78 – 4.69 (m, 1H), 3.51 (dd, *J* = 16.8, 6.5 Hz, 2H), 3.42 (dd, *J* = 16.8, 5.0 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.6, 127.1, 124.4, 46.7, 24.0.

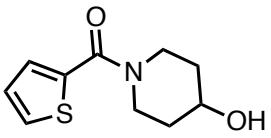
S32 is a known compound and its spectra are in accord with published data.[15]



S33



S33 **S34**

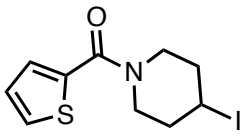


S33

S33: Thiophene-2-carboxylic acid (50 mmol, 6.4 g) was added to a 25 mL round-bottom flask charged with a stir bar followed by thionyl chloride (15 mL) under air. A reflux condenser was attached to the flask and the condenser was secured with a rubber septum. The mixture was refluxed with stirring (oil bath temperature was set to 85 °C) for 3 h under a balloon of nitrogen. After cooling to rt, the excess thionyl chloride was removed under reduced pressure and the resulting acyl chloride was directly used in next step. According to general procedure E, thiophene-2-carbonyl chloride in DCM (20 ml), piperidin-4-ol (75 mmol, 8.62 g), and K_3PO_4 (150 mmol, 31.8 g) in DCM (50 mL) and water (75 mL) were stirred. After 30 min, ethyl acetate (400 mL) was added. The organic phase was sequentially washed with 1.0 M aqueous NaOH (150 mL), 1.0 M aqueous HCl (150 mL), and water (150 mL). The organic phase was dried over anhydrous $MgSO_4$, and filtered through a glass frit. The solvents were removed under reduced pressure. The white solid that formed was washed with hexanes (100 mL) and Et_2O (100 mL) to give **S33** (7.14 g, 63%) which was used in next step

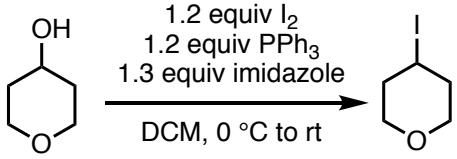
without further purification. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.28 (dd, *J* = 3.6, 1.1 Hz, 1H), 7.04 (dd, *J* = 5.0, 3.6 Hz, 1H), 4.17 – 4.04 (br m, 2H), 4.00 (tq, *J* = 8.0, 3.9 Hz, 1H), 3.42 (m, 2H), 2.00 – 1.88 (m, 2H), 1.59 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.7, 137.2, 128.6, 128.5, 126.7, 66.8, 42.9, 34.3.

S33 is a known compound and its spectra are in accord with published data.[16]

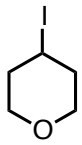


S34

S34: According to general procedure D, **S33** (15 mmol, 3.40 g), iodine (18 mmol, 4.57 g), triphenylphosphine (18 mmol, 4.74 g), and imidazole (19.5 mmol, 1.33 g) in DCM (50 mL) for 8 h, afforded, after flash silica gel chromatography (80:20 to 70:30 hexanes : ethyl acetate) and crystallization from DCM/hexanes, alkyl iodide **S34** (3.16 g, 63%) as a white crystalline solid. mp = 81-83 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.28 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.05 (dd, *J* = 5.0, 3.6 Hz, 1H), 4.55 (p, *J* = 5.8 Hz, 1H), 3.89 (dt, *J* = 13.7, 5.4 Hz, 2H), 3.64 (dt, *J* = 13.7, 5.6 Hz, 2H), 2.12 (q, *J* = 5.6 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.9, 136.9, 128.8, 128.7, 126.8, 45.4, 37.6, 26.8; FTIR (cm^{-1}) 3081, 2949, 2920, 2860, 1620, 1436, 1272, 989, 735. HRMS (EI) m/z, calculated for $[C_{10}H_{12}IONS]^{+}$: 320.9684; found: 320.9696.



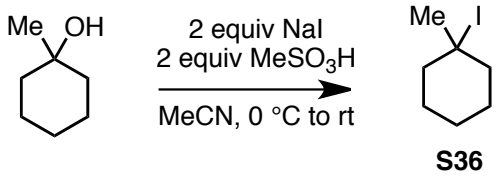
S35



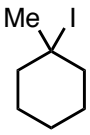
S35

S35: According to procedure E, tetrahydro-2H-pyran-4-ol (30 mmol, 3.06 g), iodine (36 mmol, 9.14 g), triphenylphosphine (36 mmol, 9.47 g), and imidazole (39 mmol, 2.65 g) in DCM (80 mL) for 16 h, afforded, after flash silica gel chromatography (100:0 to 95:5 hexanes : ethyl acetate), alkyl iodide **S35** (4.13 g, 65%) as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.45 (td, *J* = 8.2, 4.2 Hz, 1H), 3.82 (dt, *J* = 11.3, 4.3 Hz, 2H), 3.53 (ddd, *J* = 11.6, 7.3, 4.0 Hz, 2H), 2.21 – 2.09 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 68.0, 38.9, 25.4.

S35 is a known compound and its spectra are in accord with published data.[17]

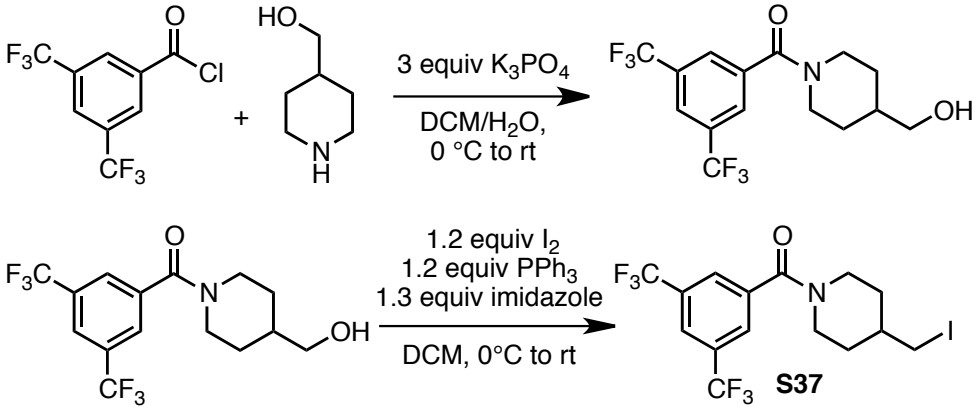


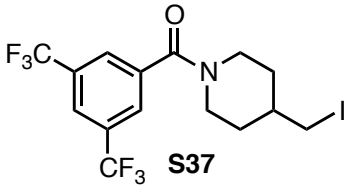
S36



S36

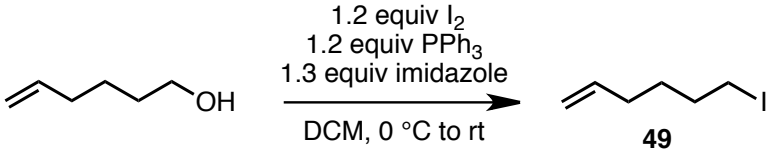
S36: according to literature procedure[18], sodium iodide (60 mmol, 9 g) and 1-methylcyclohexanol (30 mmol, 3.42 g) were added to a 200 mL round-bottom flask equipped with a stir bar under air, followed by non-anhydrous acetonitrile (100 mL). The flask was placed in an ice bath and methanesulfonic acid was added drop wise via syringe to the mixture while vigorously stirring. After the addition was over, the ice bath was removed and the mixture stirred at rt for additional 30 min. Then diethyl ether (200 mL) was added and the organic phase was sequentially washed with water (100 mL), saturated aqueous $NaHCO_3$ (100 mL), aqueous $Na_2S_2O_3$ (1 M, 100 mL), and brine (100 mL). The organic phase was dried over anhydrous $MgSO_4$, and filtered through a glass frit. The volatiles were removed under reduced pressure. The crude product was purified by flash silica gel chromatography (100% hexanes) to afford **S36** (2.37 g, 35%) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.15 (dt, *J* = 14.4, 2.7 Hz, 2H), 2.11 (s, 3H), 1.74 – 1.60 (m, 5H), 1.24 (ddt, *J* = 13.4, 5.9, 3.5 Hz, 1H), 1.01 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 59.5, 46.1, 39.2, 25.4, 25.2; FTIR (cm^{-1}) 2931, 2857, 1443, 1245, 1131; HRMS (CI) m/z, calculated for $[C_7H_{13}I]^+$: 224.0062; found: 224.0060.

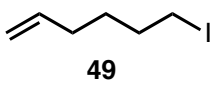




S37: According to general procedure E, 3,5-bis(trifluoromethyl)benzoyl chloride (100 mmol, 27.66 g) in 40 mL DCM, piperidine-4-ylmethanol (150 mmol, 17.25 g), and K_3PO_4 (300 mmol, 63.6 g) in DCM (150 mL) and water (150 mL) afforded white crystals (34.45 g, 97%) which were used in next step without further purification. According to general procedure D, the alcohol (20 mmol, 7.1 g), iodine (24 mmol, 6.1 g), triphenylphosphine (24 mmol, 6.31 g), and imidazole

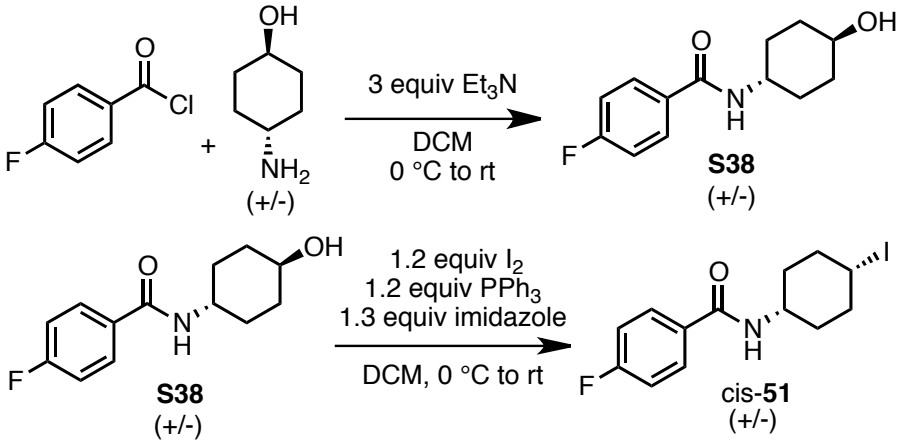
(26 mmol, 1.77 g) in DCM (60 mL) for 1.5 h, afforded, after flash silica gel chromatography (90:10 to 70:30 hexanes : ethyl acetate), alkyl iodide **S37** (5.31 g, 57%) as a white crystalline solid. mp = 117-119 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (m, 1H), 7.89 – 7.83 (m, 2H), 4.74 (br s, 1H), 3.63 (br s, 1H), 3.14 (br s, 3H), 2.83 (br s, 1H), 1.97 (m Hz, 2H), 1.78 (tdd, *J* = 11.5, 6.6, 3.1 Hz, 1H), 1.41 – 1.09 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 138.2, 132.3 (q, *J* = 33.8 Hz), 127.40 (q, *J* = 2.7 Hz), 123.61 (p, *J* = 3.8 Hz), 123.02 (q, *J* = 273.0 Hz), 47.8, 42.5, 38.7, 33.3, 32.3, 12.2;^{19}F NMR (565 MHz, $CDCl_3$) δ -62.97; FTIR (cm^{-1}) 2939, 2861, 1644, 1445, 1280, 1175, 1138. HRMS (ESI) m/z, calculated for $[C_{15}H_{15}F_6INO]^+$ ($[M+H]^+$): 466.0097; found: 466.0105.

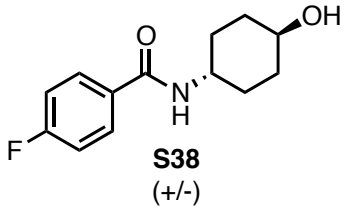




49: According to general procedure D, 5-hexen-1-ol (20 mmol, 2 g), iodine (24 mmol, 6.1 g), triphenylphosphine (24 mmol, 6.31 g), and imidazole (26 mmol, 1.77 g) in DCM (70 mL) for 3 h, afforded, after flash silica gel chromatography (100% pentane), alkyl iodide **49** (2.29 g, 56%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.79 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.02 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.97 (ddt, *J* = 10.2, 2.2, 1.3 Hz, 1H), 3.19 (t, *J* = 7.0 Hz, 2H), 2.12 – 2.03 (m, 2H), 1.84 (dt, *J* = 14.6, 7.1 Hz, 2H), 1.53 – 1.47 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.2, 115.1, 33.1, 32.8, 29.8, 6.9.

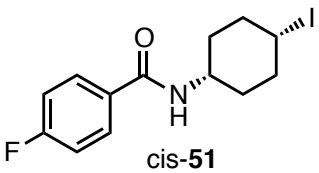
49 is a known compound and its spectra are in accord with published data.[19]





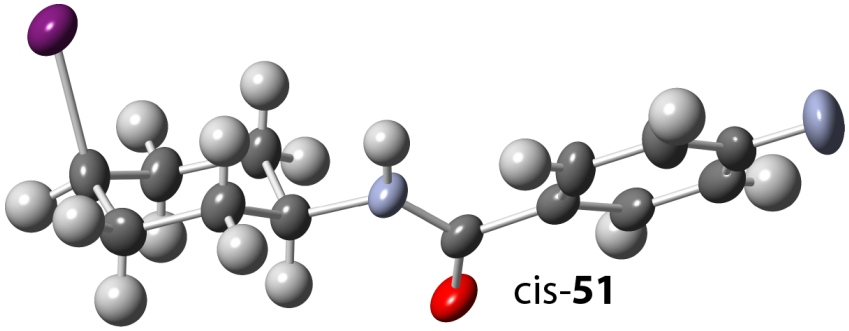
S38: According to general procedure E, 4-Fluorobenzoyl chloride (100 mmol, 15.85 g) in DCM (40 mL), *trans*-4-aminocylohexanol (100 mmol, 11.5 g), and NaOH (200 mmol, 8 g) in DCM (100 mL) and water (100 mL) afforded a white solid that was crystallized from ethanol to give **S38** (13.24 g, 54%) as white crystals. mp = 231-233 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.19 (d, *J* = 7.8 Hz, 1H), 7.93 – 7.86 (m, 2H), 7.31 – 7.22 (m, 2H), 4.56 (d, *J* = 4.4 Hz, 1H), 3.70 (tdt, *J* = 11.6, 7.9, 4.0 Hz, 1H), 3.39 (ddt, *J* = 14.7, 10.7, 4.2 Hz, 1H), 1.89 – 1.76 (m, 4H), 1.42 – 1.31 (m, 2H), 1.23 (tdd, *J* = 13.0, 10.4, 3.2 Hz, 2H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 164.4, 163.6 (d, *J* = 247.9 Hz), 131.2 (d, *J* = 3.0 Hz), 129.8 (d, *J* = 8.9 Hz), 114.9 (d, *J* = 21.6

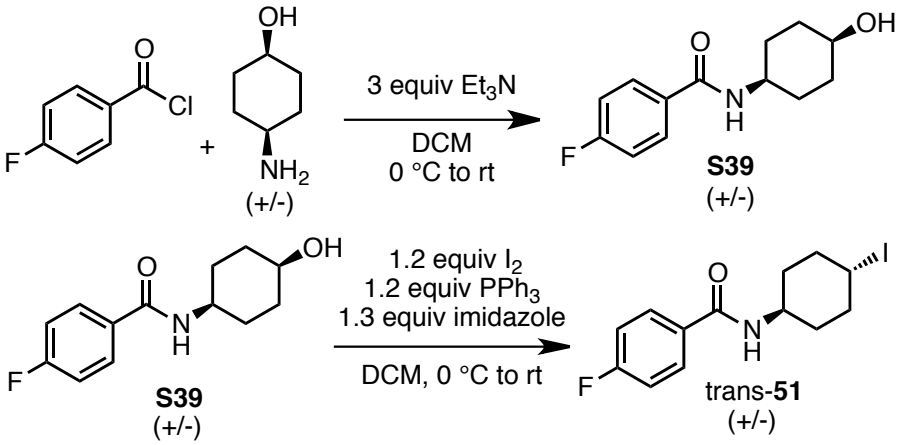
Hz), 68.3, 47.9, 34.2, 30.2; ^{19}F NMR (565 MHz, DMSO-d_6) δ -109.98; FTIR (cm^{-1}) 3300, 2919, 1631, 1540, 1505, 1384. HRMS (ESI) m/z, calculated for $[C_{13}H_{17}FNO_2]^+$ ([M+H]$^+$): 238.1238; found: 238.1235.

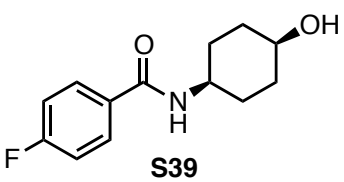


cis-**51**
(+/-)

cis-51: According to general procedure D, **S38** (10 mmol, 2.37 g), iodine (10 mmol, 2.54 g), triphenylphosphine (10 mmol, 2.63 g), and imidazole (10 mmol, 680 mg) in DCM (70 mL) for 20 h, afforded, after flash silica gel chromatography (90:10 to 80:20 hexanes : ethyl acetate), and crystallizing from DCM/pentane, alkyl iodide **cis-51** (668 g, 19%) as a white solid. mp = 154-156 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 2H), 7.12 (t, *J* = 8.4 Hz, 2H), 6.00 (s, 1H), 4.77 (s, 1H), 4.08 (m, 1H), 2.21 – 2.04 (m, 2H), 1.95 (m, 2H), 1.80 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 164.9 (d, *J* = 252.0 Hz), 131 (d, *J* = 3.2 Hz), 129.3 (d, *J* = 8.9 Hz), 115.8 (d, *J* = 22.0 Hz), 47.8, 35.6, 33.4, 29.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -108.27; FTIR (cm^{-1}) 3296, 2940, 1634, 1603, 1545, 1502, 1331, 1229, 1160. HRMS (ESI) m/z, calculated for $[C_{13}H_{16}FINO]^+$ ([M+H]$^+$): 348.0255; found: 348.0250.



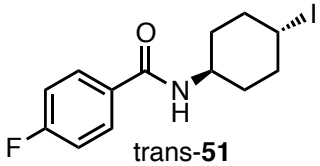




S39
(+/-)

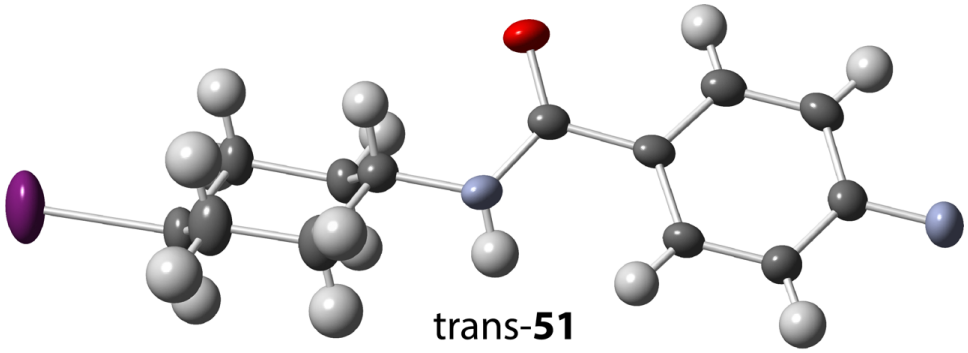
S39: A 200 mL oven dried-round bottom flask charged with a stir bar was sealed with a rubber septum and cooled under a stream of nitrogen. The rubber septum was partly removed and *cis*-4-

aminocyclohexanol (10 mmol, 1.15 g) was added. The rubber septum was replaced and non-anhydrous triethylamine (30 mmol, 3.03 g) and DCM (100 mL) were added via syringe under nitrogen. The flask was placed in an ice bath and 4-fluorobenzoyl chloride dissolved in 10 mL DCM was added drop wise via syringe to the solution. After the addition was complete, the ice bath was removed and reaction stirred at rt for 2 h. The organic phase was sequentially washed with water (50 mL), 1.0 M aqueous HCl (2x50 mL), and 1.0 M aqueous NaOH (50 mL). The organic phase was dried over anhydrous $MgSO_4$ and filtered through a glass frit. The volatiles were removed under reduced pressure and the crude product was purified with flash silica gel chromatography (50:50 to 20:80 hexanes : ethyl acetate) to afford **S39** (1.59 g, 67%) as an off-white crystalline solid. mp = 144-146 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.69 (m, 2H), 7.14 – 6.98 (m, 2H), 6.07 (d, *J* = 7.8 Hz, 1H), 4.03 (m, 1H), 3.97 (m, 1H), 1.84 – 1.70 (m, 8H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 164.8 (d, *J* = 251.7 Hz), 131.2 (d, *J* = 3.2 Hz), 129.3 (d, *J* = 8.6 Hz), 115.7 (d, *J* = 22.0 Hz), 66.2, 47.5, 31.5, 27.4; ^{19}F NMR (565 MHz, $CDCl_3$) δ -108.46; FTIR (cm^{-1}) 3309, 2932, 1637, 1604, 1545, 1502, 1383, 1231. HRMS (ESI) m/z, calculated for $[C_{13}H_{17}FNO_2]^+$ ($[M+H]^+$): 238.1238; found: 238.1235.



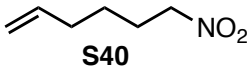
trans-**51**
(+/-)

trans-51: According to general procedure D, **S39** (5.5 mmol, 1.3 g), Iodine (5.5 mmol, 1.4 g), triphenylphosphine (5.5 mmol, 1.45 g), and imidazole (5.5 mmol, 374 mg) in DCM (20 mL) for 20 h, afforded, after flash silica gel chromatography (90:10 to 88:12 hexanes : ethyl acetate), and crystallizing from DCM/pentane, alkyl iodide **trans-51** (350 g, 18%) as a white solid. mp = 180-182 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.69 (m, 2H), 7.10 (t, *J* = 8.6 Hz, 2H), 5.79 (s, 1H), 4.09 (m, 1H), 4.03 (m, 1H), 2.48 – 2.37 (m, 2H), 2.13 (qd, *J* = 12.5, 3.5 Hz, 2H), 2.07 – 1.96 (m, 2H), 1.35 (qd, *J* = 12.7, 3.5 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 164.9 (d, *J* = 251.9 Hz), 131 (d, *J* = 3 Hz), 129.3 (d, *J* = 8.7 Hz), 115.8 (d, *J* = 21.9 Hz), 47.6, 38.8, 35.1, 26.7; ^{19}F NMR (565 MHz, $CDCl_3$) δ -108.16; FTIR (cm^{-1}) 3333, 2918, 1632, 1543, 1501, 1383, 1229. HRMS (ESI) m/z, calculated for $[C_{13}H_{16}FINO]^+$ ($[M+H]^+$): 348.0255; found: 348.0252.



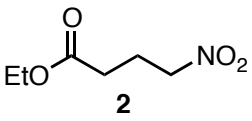
6. Synthesis of Starting Nitroalkanes

Note: The reactions and the yields to synthesize starting nitroalkanes are not optimized.



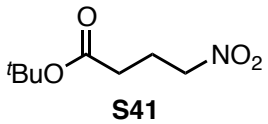
S40

S40: 6-nitrohex-1-ene is made according to the literature procedure and its spectra are in accord with published data.[20] ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.77 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.04 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.01 (ddt, *J* = 10.2, 2.0, 1.2 Hz, 1H), 4.39 (t, *J* = 7.0 Hz, 2H), 2.19 – 2.09 (m, 2H), 2.03 (p, *J* = 7.1 Hz, 2H), 1.57 – 1.46 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 115.5, 75.5, 32.8, 26.7, 25.4.



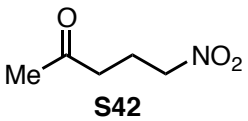
2

2: ethyl 4-nitrobutanoate is made according to the literature procedure and its spectra are in accord with published data.[21] ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.48 (t, *J* = 6.7 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.46 (t, *J* = 7.0 Hz, 2H), 2.31 (p, *J* = 6.9 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 74.5, 61.0, 30.6, 22.5, 14.3.



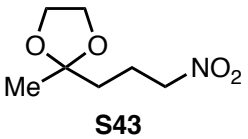
S41

S41: *tert*-butyl 4-nitrobutanoate is made according to the literature procedure and its spectra are in accord with published data.[22] ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.46 (t, *J* = 6.7 Hz, 2H), 2.37 (t, *J* = 6.9 Hz, 1H), 2.26 (p, *J* = 6.8 Hz, 1H), 1.45 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 81.3, 74.6, 31.8, 28.2, 22.7.



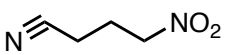
S42

S42: 5-nitropentan-2-one is made according to the literature procedure and its spectra are in accord with published data.[23] ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.42 (t, *J* = 6.6 Hz, 2H), 2.59 (t, *J* = 6.8 Hz, 2H), 2.23 (p, *J* = 6.7 Hz, 2H), 2.15 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.5, 74.6, 39.4, 30.1, 21.2.



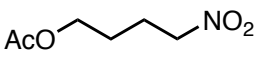
S43

S43: 2-methyl-2-(3-nitropropyl)-1,3-dioxolane is made according to the literature procedure and its spectra are in accord with published data.[24] ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.42 (t, *J* = 7.1 Hz, 1H), 3.99 – 3.95 (m, 1H), 3.95 – 3.90 (m, 1H), 2.17 – 2.07 (m, 1H), 1.79 – 1.71 (m, 1H), 1.32 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 109.3, 75.7, 64.9, 35.5, 24.0, 22.2.



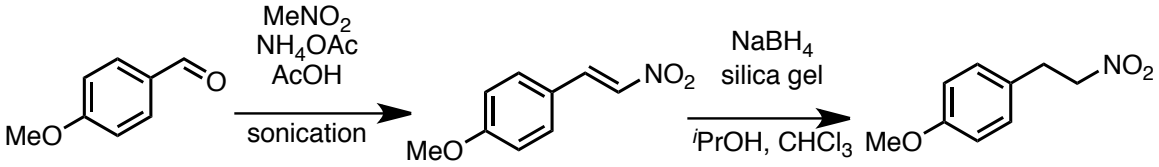
S44

S44: 4-nitrobutanenitrile is made according to the literature procedure and its spectra are in accord with published data.[25] ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.63 – 4.46 (t, *J* = 6.4 Hz, 2H), 2.57 (t, *J* = 7.0 Hz, 2H), 2.36 (p, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 117.9, 73.0, 23.2, 23.0, 14.8.

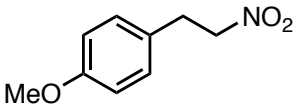


S45

S45: 4-nitrobutyl acetate is made according to the literature procedure and its spectra are in accord with published data.[1, 26] ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.43 (t, *J* = 6.9 Hz, 2H), 4.12 (t, *J* = 6.2 Hz, 2H), 2.15 – 2.07 (m, 2H), 2.06 (s, 3H), 1.79 – 1.70 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 75.2, 63.3, 25.7, 24.3, 21.0.

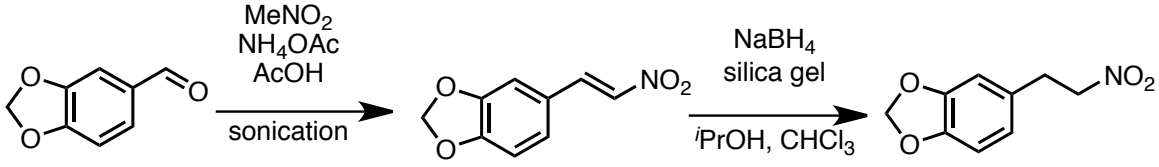


S46

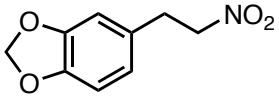


S46

S46: 1-methoxy-4-(2-nitroethyl)benzene is made according to the literature procedure[27] and its spectra are in accord with published data.[28] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 – 7.09 (m, 2H), 6.88 – 6.83 (m, 2H), 4.57 (t, *J* = 7.4 Hz, 2H), 3.79 (s, 3H), 3.26 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 129.6, 127.6, 114.2, 76.5, 55.2, 32.5.

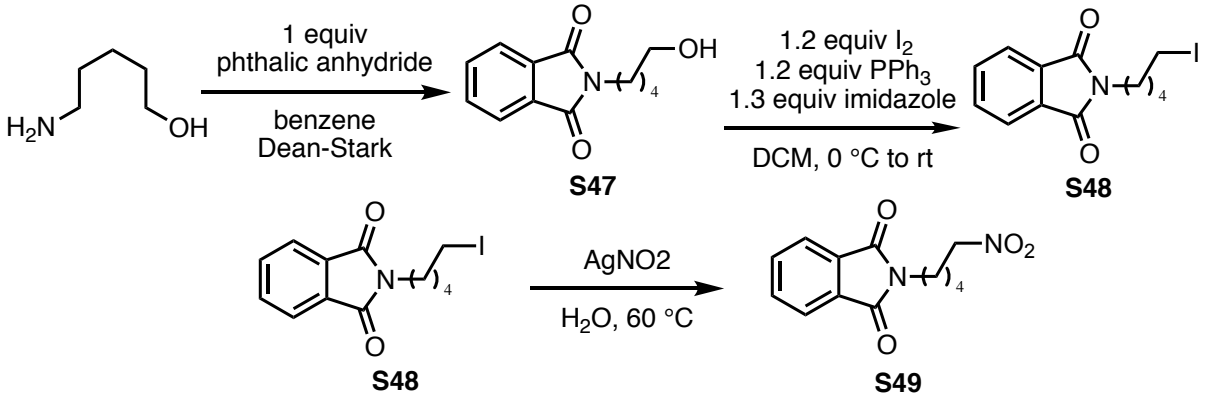


47

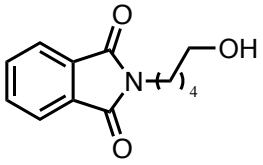


47

47: 5-(2-nitroethyl)benzo[d][1,3]dioxole is made according to the literature procedure[27] and its spectra are in accord with published data.[29] ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.75 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 1.7 Hz, 1H), 6.65 (dd, *J* = 7.9, 1.8 Hz, 1H), 5.95 (s, 2H), 4.56 (t, *J* = 7.3 Hz, 2H), 3.23 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.2, 147.1, 129.3, 121.9, 109.0, 108.8, 101.3, 76.7, 33.4.

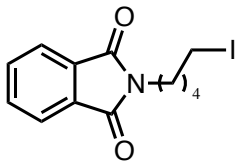


S48 **S47** **S48** **S49**



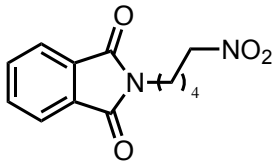
S47

S47: is made according to the literature procedure and its spectra are in accord with published data.[30] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 3.70 (t, *J* = 7.2 Hz, 2H), 3.64 (t, *J* = 6.5 Hz, 2H), 1.71 (p, *J* = 7.4 Hz, 2H), 1.62 (m, 2H), 1.46 – 1.40 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.6, 134.0, 132.3, 123.3, 62.8, 38.0, 32.4, 28.5, 23.2.



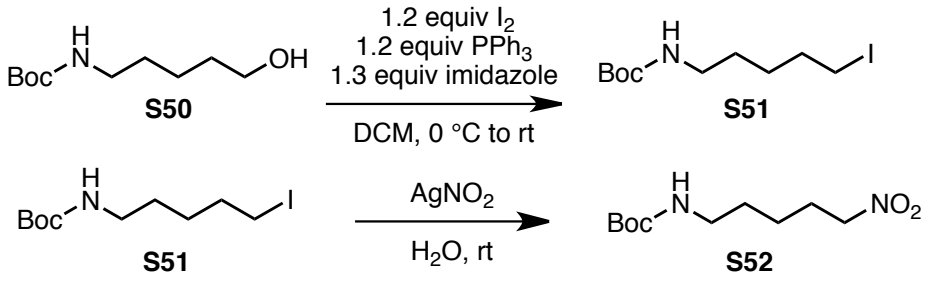
S48

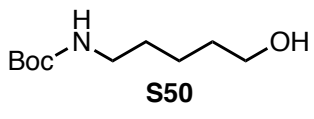
S48: According to general procedure D, **S47** (20 mmol, 4.66 g), iodine (24 mmol, 6.1 g), triphenylphosphine (24 mmol, 6.31 g), and imidazole (26 mmol, 1.77 mg) in DCM (60 mL) for 4 h, afforded, after flash silica gel chromatography (90:10 to 75:25 hexanes : ethyl acetate), alkyl iodide **S48** (6.49 g, 95%) as a white crystalline solid. mp = 50-52 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.71 (dd, *J* = 5.5, 3.0 Hz, 2H), 3.69 (t, *J* = 7.3 Hz, 2H), 3.18 (t, *J* = 7.0 Hz, 2H), 1.88 (p, *J* = 7.1 Hz, 2H), 1.76 – 1.65 (m, 2H), 1.50 – 1.41 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 134.1, 132.3, 123.4, 37.8, 33.1, 27.9, 27.7, 6.4; FTIR (cm^{-1}) 2937, 2860, 1771, 1709, 1396, 1188. HRMS (ESI) m/z, calculated for $[C_{13}H_{15}NO_4I]^+$ ($[M+H]^+$): 344.0142; found: 344.0143.



S49

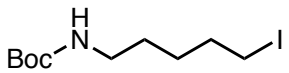
S49: According to general procedure F, **S48** (10 mmol, 3.43 g), Silver nitrite (40 mmol, 6.16 g) in water (20 mL) for 1 h at 60 °C, afforded, after flash silica gel column chromatography (85:15 to 60:40 hexanes : ethyl acetate), nitroalkane **S49** (1.81 g, 69%) as a white crystalline solid. mp = 40-42 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.38 (t, *J* = 7.0 Hz, 2H), 3.70 (t, *J* = 7.1 Hz, 2H), 2.07 (p, *J* = 7.1 Hz, 2H), 1.75 (p, *J* = 7.3 Hz, 2H), 1.49 – 1.41 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 134.1, 132.2, 123.4, 75.5, 37.5, 28.0, 27.0, 23.7; FTIR (cm^{-1}) 2942, 2866, 1772, 1708, 1549, 1436, 1397, 1188. HRMS (ESI) m/z, calculated for $[C_{13}H_{15}N_2O_4]^+$ ($[M+H]^+$): 263.1026; found: 263.1029.





S50

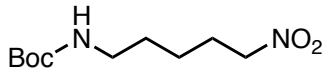
S50: *tert*-butyl N-(5-hydroxypentyl)carbamate is made according to the literature procedure and its spectra are in accord with published data.[31] ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.54 (br s, 1H), 3.64 (t, *J* = 6.5 Hz, 2H), 3.12 (t, *J* = 6.8 Hz, 2H), 1.62 – 1.55 (m, 2H), 1.50 (q, *J* = 7.3 Hz, 3H), 1.44 (s, 9H), 1.43 – 1.36 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.2, 62.9, 40.6, 32.4, 30.0, 28.6, 23.1.



S51

S51: According to general procedure D, **S50** (15 mmol, 3.045 g), iodine (18 mmol, 4.57 g), triphenylphosphine (18 mmol, 4.73 g), and imidazole (19.5 mmol, 1.33 mg) in DCM (50 mL) for 4 h, afforded, after flash silica gel chromatography (90:10 to 75:25 hexanes : ethyl acetate), alkyl iodide **S51** (4.31 g, 92%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 (br s, 1H), 3.18 (t, *J* = 6.9 Hz, 2H), 3.12 (q, *J* = 6.6 Hz, 2H), 1.83 (p, *J* = 7.0 Hz, 2H), 1.55 – 1.36 (m, 13H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 79.2, 40.4, 33.1, 29.1, 28.5, 27.7, 7.0.

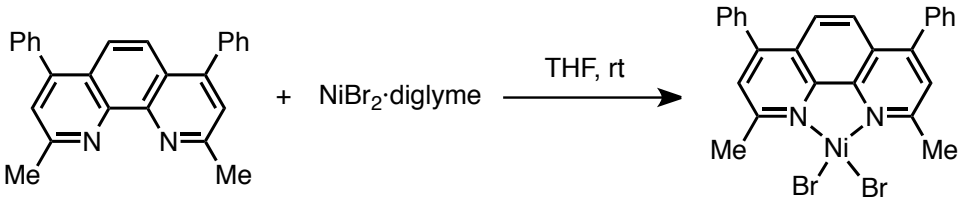
S51 is a known compound and its spectra are in accord with published data.[32]



S52

S52: According to general procedure F, **S51** (10 mmol, 3.13 g), Silver nitrite (40 mmol, 6.16 g) in water (20 mL) for 1 h at rt, afforded, after flash silica gel column chromatography (90:10 to 80:20 hexanes : ethyl acetate), nitroalkane **S52** (1.56 g, 67%) as an off-white crystalline solid. mp = 44-46 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.52 (br s, 1H), 4.38 (t, *J* = 6.9 Hz, 2H), 3.13 (q, *J* = 6.7 Hz, 2H), 2.07 – 1.97 (m, 2H), 1.56 – 1.50 (m, 2H), 1.48 – 1.38 (m, 11H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 79.4, 75.6, 40.2, 29.6, 28.6, 27.1, 23.6; FTIR (cm^{-1}) 3371, 2984, 2950, 1687, 1564, 1524, 1387, 1364, 1173. HRMS (ESI) m/z, calculated for $[C_{10}H_{21}N_2O_4]^+$ ($[M+H]^+$): 233.1496; found: 233.1498.

7. Preparation of the Single-component Pre-catalyst 8

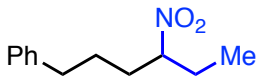


7 **8**

A 100 mL oven-dried round-bottom flask was sealed with a rubber septum and cooled under a stream of nitrogen. The rubber septum was removed partly and bathocuproine (12.5 mmol, 4.5 g) and Nickel(II) bromide·diglyme (12.5 mmol, 4.4 g) were added. The rubber septum was replaced and THF (70 ml) was added under nitrogen. The mixture stirred at rt for 46 h. The resulting pink suspension was filtered and the solid was washed with diethyl ether (100 mL) to afford 6.51 g (90%) complex **8** as a pink powder. The powder was crystallized from DMF/diethyl ether for analytical purposes. The X-ray quality crystals were grown from slow evaporation of DCM solution. The powder shows the same reactivity as crystals in alkylation of nitroalkanes and can be used without further purification.

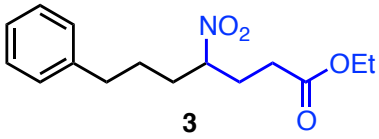
The complex **8** is a known compound and its spectra and X-ray crystallographic data are in accord with published data.[33] Anal. Calculated: C, 53.94%; H, 3.48%; N, 4.84%; Found: C, 53.96%; H, 3.52%; N, 4.94%. HRMS (LIFDI) m/z, calculated for $[C_{26}H_{20}Br_2N_2Ni]^+$ ($[M]^+$): 577.9324; found: 577.9309.

8. Nickel-catalyzed Alkylation of Nitroalkanes with Alkyl Iodides



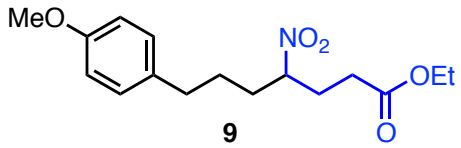
S1

S1: According to general procedure A, **1** (1.1 mmol, 270.6 mg), 1-nitropropane (1.0 mmol, 89 mg), potassium *tert*-butoxide (1.15 mmol, 128.8 mg), **8** (0.1 mmol, 57.8 mg), Et_2Zn (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) and dioxane (4 mL) for 24 h afforded, after flash silica gel chromatography (100:0 to 97:3 hexanes : ethyl acetate), **S1** (169 mg, 82%) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.24 – 7.15 (m, 1H), 7.15 (m, 2H), 4.40 (tt, J = 9.3, 4.4 Hz, 1H), 2.64 (t, J = 7.4 Hz, 2H), 2.20 – 1.89 (m, 2H), 1.84 – 1.69 (m, 2H), 1.68 – 1.59 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 128.6, 128.5, 126.2, 90.4, 35.2, 33.1, 27.6, 27.3, 10.4; FTIR (cm^{-1}) 3027, 2929, 1547, 1383, 750, 699. HRMS (CI) m/z, calculated for $[C_{12}H_{17}]^+$ ($[M-NO_2]^+$): 161.1330; found: 161.1330.



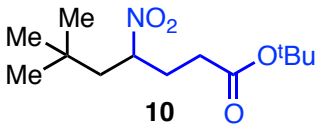
3

3: According to general procedure B, **1** (3.3 mmol, 812 mg), **2** (3.0 mmol, 483 mg), potassium *tert*-butoxide (3.45 mmol, 386 mg), **8** (0.3 mmol, 173 mg), diethylzinc (0.6 mmol, 74 mg) in MTBE (24 mL) and dioxane (12 mL) for 22 h afforded, after flash silica gel chromatography (100:0 to 96:4 hexanes : ethyl acetate), **3** (608 mg, 73%) as pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.23 – 7.17 (m, 1H), 7.17 – 7.11 (m, 2H), 4.61 – 4.53 (m, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.42 – 2.26 (m, 2H), 2.21 (dddd, *J* = 14.8, 10.0, 7.4, 5.7 Hz, 1H), 2.12 – 2.04 (m, 1H), 2.04 – 1.96 (m, 1H), 1.81 – 1.71 (m, 1H), 1.71 – 1.63 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 141.1, 128.6, 128.5, 126.3, 87.8, 61.0, 35.2, 33.4, 30.3, 28.8, 27.5, 14.3; FTIR (cm^{-1}) 3027, 2936, 1730, 1548, 1452, 1377, 1182. HRMS (CI) m/z, calculated for $[C_{15}H_{22}NO_4]^+$ ($[M+H]^+$): 280.1549; found: 280.1547.



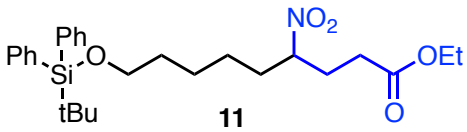
9

9: According to general procedure A, **S3** (3.3 mmol, 911 mg), **2** (3.0 mmol, 483 mg), potassium *tert*-butoxide (3.45 mmol, 386 mg), **8** (0.3 mmol, 173 mg), diethylzinc (0.6 mmol, 74mg) in MTBE (24 mL) and dioxane (12 mL) for 23 h afforded, after flash silica gel chromatography (100:0 to 95:5 hexanes : ethyl acetate), **9** (635 mg, 69%) as pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.6 Hz, 2H), 6.87 – 6.79 (m, 2H), 4.61 – 4.51 (m, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 2.58 (t, *J* = 7.5 Hz, 2H), 2.40 – 2.26 (m, 2H), 2.20 (dddd, *J* = 14.7, 9.9, 7.4, 5.7 Hz, 1H), 2.07 (dtd, *J* = 14.7, 7.9, 3.8 Hz, 1H), 1.99 (dtd, *J* = 14.1, 9.1, 7.1 Hz, 1H), 1.74 (dddd, *J* = 14.2, 9.9, 6.8, 4.7 Hz, 1H), 1.68 – 1.59 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 158.1, 133.2, 129.4, 114.1, 87.8, 61.0, 55.4, 34.2, 33.3, 30.3, 28.8, 27.7, 14.3; FTIR (cm^{-1}) 2936, 2837, 1729, 1612, 1549, 1512, 1377, 1246, 1034. HRMS (CI) m/z, calculated for $[C_{16}H_{24}NO_5]^+$ ($[M+H]^+$): 310.1654; found: 310.1651.



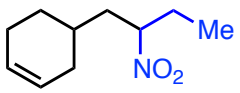
10

10: According to general procedure A, *neo*-pentyliodide (1.1 mmol, 218 mg), **S41** (1.0 mmol, 189 mg), potassium *tert*-butoxide (1.15 mmol, 129 mg), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) and dioxane (4 mL) for 23 h afforded, after flash silica gel chromatography (100:0 to 97:3 hexanes : ethyl acetate), **10** (129 mg, 46%) as a pale yellow semi-solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.67 (tdd, *J* = 9.4, 4.5, 2.5 Hz, 1H), 2.31 – 2.08 (m, 4H), 2.00 (dtd, *J* = 14.5, 7.8, 4.5 Hz, 1H), 1.50 (dd, *J* = 15.3, 2.5 Hz, 1H), 1.45 (s, 9H), 0.92 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 85.1, 81.2, 47.1, 31.5, 31.4, 30.7, 29.1, 28.2; FTIR (cm^{-1}) 2962, 1729, 1552, 1367, 1153, 850. HRMS (CI) m/z, calculated for $[C_{13}H_{26}NO_4]^+$ ($[M+H]^+$): 260.1862; found: 260.1872.



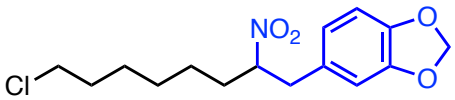
11

11: According to general procedure B, **S5** (3.3 mmol, 1.492 g), **2** (3.0 mmol, 483 mg), potassium *tert*-butoxide (3.45 mmol, 386 mg), **8** (0.3 mmol, 173 mg), diethylzinc (0.6 mmol, 74 mg) in MTBE (24 mL) and dioxane (12 mL) for 22 h afforded, after flash silica gel chromatography (100:0 to 96:4 hexanes : ethyl acetate), **11** (797 mg, 55%) as pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (dqd, *J* = 6.7, 1.6, 1.1 Hz, 4H), 7.45 – 7.40 (m, 2H), 7.40 – 7.35 (m, 4H), 4.52 (tt, *J* = 9.2, 4.8 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.64 (t, *J* = 6.3 Hz, 2H), 2.42 – 2.27 (m, 2H), 2.21 (dddd, *J* = 14.7, 9.9, 7.5, 5.7 Hz, 1H), 2.08 (dtd, *J* = 14.7, 7.9, 3.9 Hz, 1H), 2.02 – 1.92 (m, 1H), 1.75 – 1.65 (m, 1H), 1.53 (m, 2H), 1.46 – 1.28 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.05 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 135.7, 134.2, 129.7, 127.8, 87.9, 63.7, 61.0, 34.0, 32.3, 30.4, 28.8, 27.0, 25.6, 25.4, 19.4, 14.3; FTIR (cm^{-1}) 2933, 2859, 1737, 1550, 1427, 1377, 1112. HRMS (ESI) m/z, calculated for $[C_{27}H_{40}NO_5Si]^+$ ($[M+H]^+$): 486.26703; found: 486.26842.



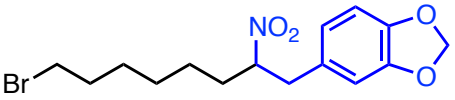
12

12: According to general procedure A, **S11** (1.1 mmol, 244 mg), 1-nitropropane (1.0 mmol, 89 mg), potassium *tert*-butoxide (1.15 mmol, 129 mg), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) and dioxane (4 mL) for 24 h afforded, after flash silica gel chromatography (100:0 to 95:5 hexanes : diethyl ether), **12** (122 mg, 67%) as a pale yellow oil. NMR analysis of crude product revealed a ratio of 50:50 diastereomers, the product was isolated as a mixture of diastereomers (dr: 50:50). A duplicate run afforded **12** (118 mg, 64%). The reported spectra are for a mixture of two diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.73 – 5.55 (m, 4H), 4.55 (m, 2H), 2.27 – 2.20 (m, 1H), 2.11 – 1.91 (m, 9H), 1.86 – 1.80 (m, 1H), 1.77 (m Hz, 2H), 1.72 – 1.50 (m, 7H), 1.30 – 1.23 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 127.27, 127.11, 125.80, 125.48, 88.37, 88.35, 40.63, 40.08, 31.86, 31.03, 30.64, 30.52, 29.11, 27.96, 27.81, 24.85, 24.78, 10.44; FTIR (cm^{-1}) 3024, 2973, 2915, 1549, 1438, 1374, 1336, 849, 656; HRMS (CI) m/z, calculated for $[C_{10}H_{18}NO_2]^+$ ($[M+H]^+$): 184.1338; found: 184.1343.



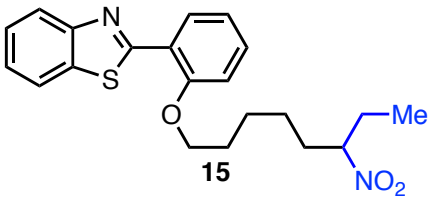
13

13: According to general procedure A, 1-iodo-6-chlorohexane (1.1 mmol, 271 mg), **47** (1.0 mmol, 195 mg), potassium *tert*-butoxide (1.15 mmol, 129 mg), **8** (0.15 mmol, 87 mg), diethylzinc (1 M in MTBE, 0.3 mmol, 0.3 mL) in MTBE (8 mL) and dioxane (4 mL) for 24 h afforded, after flash silica gel chromatography (98:2 to 96:4 hexanes : ethyl acetate), **13** (201 mg, 64%) as a clear oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.73 (d, *J* = 7.9 Hz, 1H), 6.63 (d, *J* = 1.7 Hz, 1H), 6.60 (dd, *J* = 7.9, 1.8 Hz, 1H), 5.94 (s, 2H), 4.62 (dddd, *J* = 9.8, 8.7, 5.7, 4.1 Hz, 1H), 3.52 (t, *J* = 6.6 Hz, 2H), 3.16 (dd, *J* = 14.3, 8.7 Hz, 1H), 2.93 (dd, *J* = 14.3, 5.7 Hz, 1H), 2.04 – 1.93 (m, 1H), 1.79 – 1.68 (m, 3H), 1.46 – 1.39 (m, 2H), 1.39 – 1.28 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.1, 147.1, 129.3, 122.1, 109.3, 108.7, 101.3, 90.3, 45.0, 40.0, 33.4, 32.5, 28.3, 26.6, 25.8; FTIR (cm^{-1}) 2933, 1609, 1549, 1491, 1445, 1366, 1248, 1039. HRMS (CI) m/z, calculated for $[C_{15}H_{20}ClNO_4]^+$: 313.1081; found: 313.1086.



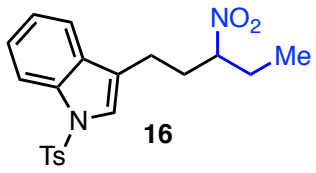
14

14: According to general procedure A, **S25** (1.2 mmol, 349 mg), **47** (1.0 mmol, 195 mg), potassium *tert*-butoxide (1.15 mmol, 129 mg), **8** (0.15 mmol, 87 mg), diethylzinc (1 M in MTBE, 0.3 mmol, 0.3 mL) in MTBE (8 mL) and dioxane (4 mL) for 24 h afforded, after flash silica gel chromatography (100: 0 to 96:4 hexanes : ethyl acetate), **14** (184 mg, 51%) as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.73 (d, *J* = 7.9 Hz, 1H), 6.63 (d, *J* = 1.7 Hz, 1H), 6.60 (dd, *J* = 7.9, 1.8 Hz, 1H), 5.94 (s, 2H), 4.62 (dddd, *J* = 9.8, 8.7, 5.7, 4.1 Hz, 1H), 3.39 (t, *J* = 6.7 Hz, 2H), 3.16 (dd, *J* = 14.3, 8.6 Hz, 1H), 2.93 (dd, *J* = 14.3, 5.7 Hz, 1H), 2.06 – 1.93 (m, 1H), 1.88 – 1.80 (m, 2H), 1.80 – 1.70 (m, 1H), 1.46 – 1.38 (m, 2H), 1.38 – 1.29 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.1, 147.1, 129.3, 122.2, 109.3, 108.7, 101.3, 90.3, 40.0, 33.8, 33.4, 32.6, 28.2, 27.9, 25.8; FTIR (cm^{-1}) 2932, 2860, 1549, 1490, 1445, 1365, 1249, 1039. HRMS (CI) m/z, calculated for $[C_{15}H_{20}BrNO_4]^+$: 357.0576; found: 357.0585.



15

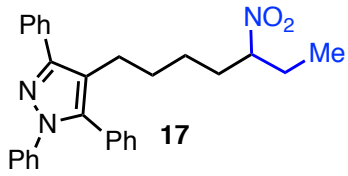
15: According to general procedure B, **S13** (3.3 mmol, 1.40 g), 1-nitropropane (3.0 mmol, 267 mg), potassium *tert*-butoxide (3.45 mmol, 386 mg), **8** (0.3 mmol, 173 mg), diethylzinc (0.6 mmol, 74 mg) in MTBE (24 mL) and dioxane (12 mL) for 28 h afforded, after flash silica gel chromatography (95:5 to 90:10 hexanes : ethyl acetate), **15** (598 mg, 52%) as a white solid. mp = 82-84 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 7.9, 1.8 Hz, 1H), 8.09 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.49 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 7.44 (ddd, *J* = 8.5, 7.3, 1.8 Hz, 1H), 7.42 – 7.35 (m, 1H), 7.16 – 7.10 (m, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 4.43 (m, 1H), 4.21 (t, *J* = 6.3 Hz, 2H), 2.09 – 1.93 (m, 4H), 1.82 – 1.58 (m, 4H), 1.51 – 1.42 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.2, 156.7, 152.3, 136.2, 131.9, 129.9, 126.1, 124.8, 122.9, 122.5, 121.4, 121.2, 112.4, 90.5, 69.0, 33.6, 29.1, 27.4, 26.0, 25.8, 10.4; FTIR (cm^{-1}) 2940, 2876, 1598, 1547, 1452, 1377, 1292, 1116. HRMS (CI) m/z, calculated for $[C_{21}H_{25}N_2O_3S]^+$ ($[M+H]^+$): 385.1586; found: 385.1596.



16

16 (in the glovebox)**:** According to general procedure A, **S20** (3.3 mmol, 1.40 g), 1-nitropropane (3.0 mmol, 267 mg), potassium *tert*-butoxide (3.45 mmol, 386 mg), **8** (0.3 mmol, 173 mg), diethylzinc (0.6 mmol, 74 mg) in MTBE (24 mL) and dioxane (12 mL) for 25 h afforded, after flash silica gel chromatography (95:5 to 92:8 hexanes : ethyl acetate), **16** (536 mg, 46%) as white crystals.

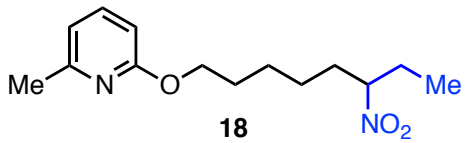
16 (on the bench): According to general procedure C, **S20** (1.0 mmol, 425 mg), 1-nitropropane (1.1 mmol, 98 mg), potassium *tert*-butoxide (1.15 mmol, 0.29 M in dioxane, 4 mL), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) for 24 h afforded, after flash silica gel chromatography (95:5 to 92:8 hexanes : ethyl acetate), **16** (185 mg, 48%) as white crystals. mp = 103-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.81 – 7.71 (m, 2H), 7.43 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.38 – 7.28 (m, 2H), 7.26 – 7.19 (m, 3H), 4.38 (m, 1H), 2.85 – 2.55 (m, 2H), 2.42 – 2.31 (m, 1H), 2.33 (s, 3H), 2.11 – 1.89 (m, 2H), 1.76 (dqd, *J* = 14.8, 7.5, 4.6 Hz, 1H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.0, 135.6, 135.4, 130.5, 130.0, 127.0, 125.1, 123.4, 123.4, 120.8, 119.3, 114.1, 89.6, 32.8, 27.4, 21.7, 21.5, 10.3; FTIR (cm^{-1}) 2973, 1547, 1369, 1173, 1122. HRMS (CI) m/z, calculated for $[C_{20}H_{23}N_2O_4S]^+$ ([M+H]$^+$): 387.1379; found: 387.1395.



17

17 (in the glovebox)**:** According to general procedure A, **S24** (1.1 mmol, 526 mg), 1-nitropropane (1.0 mmol, 89 mg), potassium *tert*-butoxide (1.15 mmol, 129 mg), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) and dioxane (4 mL) for 24 h afforded, after flash silica gel chromatography (95: 5 to 93:7 hexanes : ethyl acetate), **17** (319 mg, 73%) as a pale yellow viscous oil.

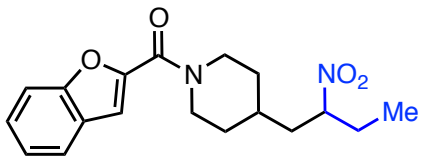
17 (on the bench)**:** according to general procedure C, **S24** (1.0 mmol, 478 mg), 1-nitropropane (1.1 mmol, 98 mg), potassium *tert*-butoxide (0.29 M in dioxane, 1.15 mmol, 4 mL), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) for 24 h afforded, after flash silica gel chromatography (95:5 to 93:7 hexanes : ethyl acetate), **17** (309 mg, 70%) as a pale yellow viscous oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.41 – 7.35 (m, 4H), 7.30 – 7.26 (m, 4H), 7.24 – 7.22 (m, 2H), 7.22 – 7.18 (m, 1H), 4.16 (tt, *J* = 9.3, 4.5 Hz, 1H), 2.68 – 2.58 (m, 2H), 1.90 – 1.68 (m, 2H), 1.61 (dtd, *J* = 14.5, 7.4, 4.5 Hz, 1H), 1.50 – 1.31 (m, 3H), 1.14 (p, *J* = 7.6 Hz, 2H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.2, 141.6, 140.2, 134.2, 131.1, 130.2, 128.8, 128.8, 128.7, 128.6, 128.1, 127.9, 126.9, 124.8, 118.8, 90.3, 33.1, 29.8, 27.2, 25.4, 23.4, 10.4; FTIR (cm^{-1}) 3060, 2938, 2863, 1596, 1547, 1499, 1453, 1363. HRMS (CI) m/z, calculated for $[C_{28}H_{30}N_3O_2]^+$ ([M+H]$^+$): 440.2338; found: 440.2351.



18

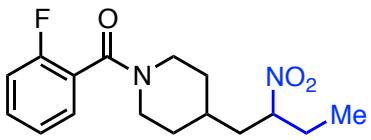
18: In a nitrogen-filled glovebox, **8** (0.1 mmol, 58 mg), bathocuproine (0.1 mmol, 36 mg), and MTBE (8 mL), were added to a 20 mL scintillation vial charged with a stir bar. The mixture stirred for 30 min at ambient temperature, then diethylzinc (0.2 mmol, 1 M in MTBE, 0.2 mL) was added and stirring continued for another 10 min at ambient temperature, after which **S22** (1.1 mmol, 305 mg), 1-nitropropane (1.0 mmol, 89 mg), and potassium *tert*-butoxide

(0.29 M in dioxane, 1.15 mmol, 4 mL) were added sequentially. The mixture stirred vigorously for 1 min at ambient temperature, then the vial was capped and sealed, taken outside the glovebox and stirred in an oil bath at 40 °C for 24 h. After cooling to rt, EtOAc (20 mL) was added and the mixture was washed with saturated aqueous NH_4Cl (20 ml). The organic layer was separated, dried over anhydrous $MgSO_4$, and filtered through a glass frit. The solvents were removed under reduced pressure. The crude product was purified by flash silica gel column chromatography (100:0 to 98:2 hexanes : ethyl acetate) to afford **18** (127 mg, 48%) as a clear oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 1H), 6.69 (d, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 8.2 Hz, 1H), 4.40 (tt, *J* = 9.2, 4.5 Hz, 1H), 4.24 (t, *J* = 6.5 Hz, 2H), 2.43 (s, 3H), 2.05 – 1.91 (m, 2H), 1.83 – 1.67 (m, 4H), 1.54 – 1.32 (m, 4H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 164.0, 156.4, 138.9, 115.6, 108.0, 90.2, 65.5, 33.6, 29.1, 27.1, 25.87, 25.76, 24.3, 10.2.; FTIR (cm^{-1}) 2942, 1597, 1549, 1451, 1375, 1305, 1233. HRMS (ESI) m/z, calculated for $[C_{14}H_{23}N_2O_3]^+$ ($[M+H]^+$): 267.1703; found: 267.1708.



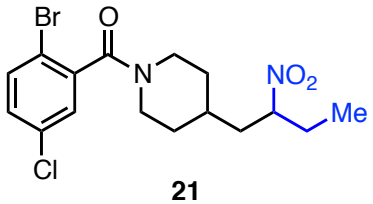
19

19: According to general procedure A, **S15** (1.1 mmol, 406 mg), 1-nitropropane (1.0 mmol, 89 mg), potassium *tert*-butoxide (1.15 mmol, 129 mg), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) and dioxane (4 mL) for 23 h afforded, after flash silica gel chromatography (80:20 hexanes : ethyl acetate), **19** (267 mg, 81%) as an off-white solid. mp = 78-80 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.52 (dq, *J* = 8.4, 0.9 Hz, 1H), 7.39 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.29 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1H), 7.26 (s, 1H), 4.86 – 4.35 (m, 3H), 3.12 (br s, 1H), 2.80 (br s, 1H), 2.08 (td, *J* = 10.5, 5.4 Hz, 1H), 2.03 – 1.92 (m, 2H), 1.76 (dddd, *J* = 19.0, 14.4, 9.5, 5.8 Hz, 2H), 1.58 – 1.52 (m, 2H), 1.30 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.9, 154.7, 149.3, 127.1, 126.5, 123.7, 122.3, 112.0, 111.68, 111.67, 87.8, 46.9, 43.3, 40.2, 33.3, 32.2, 31.5, 27.9, 10.4; FTIR (cm^{-1}) 2935, 1638, 1547, 1439, 1375, 1256, 1175. HRMS (CI) m/z, calculated for $[C_{18}H_{23}N_2O_4]^+$ ($[M+H]^+$): 331.1658; found: 331.1654.



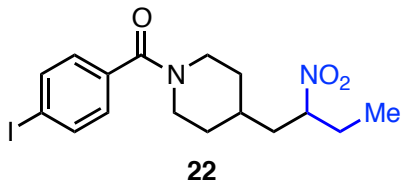
20

20: According to general procedure A, **S7** (3.3 mmol, 1.14 g), 1-nitropropane (3.0 mmol, 267 mg), potassium *tert*-butoxide (3.45 mmol, 386 mg), **8** (0.3 mmol, 173 mg), diethylzinc (0.6 mmol, 74 mg) in MTBE (24 mL) and dioxane (12 mL) for 24 h afforded, after flash silica gel chromatography (80:20 to 75:25 hexanes : ethyl acetate), **20** (712 mg, 77%) as a colorless oil that crystallizes slowly. mp = 52-54 °C ; (Two rotamers are observable in ^{13}C-NMR at rt; the peaks coalesce at 360 K.) ^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.55 – 7.42 (m, 1H), 7.35 (d, J = 7.2 Hz, 1H), 7.31 – 7.21 (m, 2H), 4.67 (m, 1H), 4.46 (t, J = 13.9 Hz, 1H), 3.29 (m, 1H), 3.09 – 2.92 (m, 1H), 2.86 – 2.65 (m, 1H), 1.98 – 1.37 (m, 7H), 1.08 m, 2H), 0.85 (dt, J = 7.3, 3.7 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6, 360 K) δ 163.4, 157.2 (d, *J* = 245.4 Hz), 130.5 (d, *J* = 8.0 Hz), 128.0 (d, *J* = 4.1 Hz), 124.4, 124.2 (d, *J* = 3.3 Hz), 115.1 (d, *J* = 21.4 Hz), 87.1, 45.8, 40.8, 38.4, 32.0, 31.2, 30.6, 26.4, 9.1; ^{19}F NMR (565 MHz, CDCl3) δ -115.08; FTIR (cm^{-1}) 2936, 1639, 1547, 1453, 1374, 1286, 1223, 1095. HRMS (CI) m/z, calculated for $[C_{16}H_{22}FN_2O_3]^+$ ($[M+H]^+$): 309.1614; found: 309.1612.



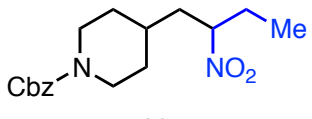
21

21: According to general procedure A, **S8** (3.3 mmol, 1.47 g), 1-nitropropane (3 mmol, 267 mg), potassium *tert*-butoxide (3.45 mmol, 386.4 mg), **8** (0.3 mmol, 173 mg), diethylzinc (0.6 mmol, 74 mg) in MTBE (24 mL) and dioxane (12 mL) for 24 h afforded, after flash silica gel chromatography (85:15 to 70:30 hexanes : ethyl acetate), **21** (862 mg, 71%) as white crystals. mp = 103-105 °C; (Two rotamers can be seen in ^{1}H and ^{13}C-NMR spectra at rt; the peaks coalesce at 343 K for ^{1}H and 360 K for ^{13}C-NMR.) ^{1}H NMR (400 MHz, DMSO-d_6, 343 K) δ 7.66 (d, *J* = 8.6 Hz, 1H), 7.47 – 7.32 (m, 2H), 4.63 (d, *J* = 9.6 Hz, 1H), 4.43 (m, 1H), 3.20 (d, *J* = 13.2 Hz, 1H), 3.02 (d, *J* = 16.5 Hz, 1H), 2.78 (d, *J* = 11.2 Hz, 1H), 1.98 – 1.45 (m, 7H), 1.32 – 1.10 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H; ^{13}C NMR (101 MHz, DMSO-d_6, 360 K) δ 164.3, 139.7, 133.8, 132.5, 129.7, 127.0, 116.4, 87.1, 45.6, 40.4, 38.4, 32.0, 30.6, 30.0, 26.5, 9.2; FTIR (cm^{-1}) 2935, 2836, 1642, 1547, 1375, 1282, 1096. HRMS (CI) m/z, calculated for $[C_{16}H_{20}BrClN_2O_3]^+$ ([M+H]$^+$): 403.0424; found: 403.0429.



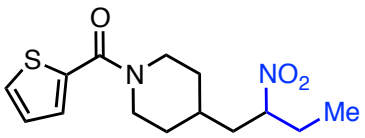
22

22: According to general procedure A, **S10** (1.1 mmol, 500 mg), 1-nitropropane (1.0 mmol, 89 mg), potassium *tert*-butoxide (1.15 mmol, 129 mg), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) and dioxane (4 mL) for 24 h afforded, after flash silica gel chromatography (85:15 to 75:25 hexanes : ethyl acetate), **22** (322 mg, 77%) as a white solid. A duplicate run afforded **22** (309 mg, 74%). mp = 97-99 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 2H), 7.15 – 7.09 (m, 2H), 4.69 (br s, 1H), 4.53 (br s, 1H), 3.70 (br s, 1H), 2.97 (br s, 1H), 2.71 (br s, 1H), 2.06 (t, *J* = 10.6 Hz, 1H), 2.03 – 1.73 (m, 3H), 1.55 – 1.48 (m, 2H), 1.37 – 1.01 (m, 3H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 137.7, 135.6, 128.7, 95.8, 87.7, 47.7, 42.4, 40.1, 33.2, 32.2, 31.1, 27.9, 10.4; FTIR (cm^{-1}) 2933, 1631, 1546, 1439, 1374, 1281, 1006. HRMS (CI) m/z, calculated for $[C_{16}H_{22}IN_2O_3]^+$ ([M+H]$^+$): 417.0675; found: 417.0678.



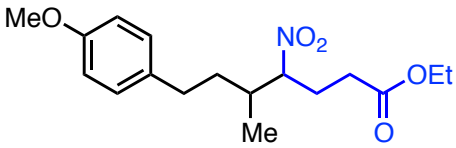
23

23: According to general procedure A, **S17** (1.1 mmol, 395 mg), 1-nitropropane (1.0 mmol, 89 mg), potassium *tert*-butoxide (1.15 mmol, 129 mg), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) and dioxane (4 mL) for 24 h afforded, after flash silica gel chromatography (90:10 to 85:15 hexanes : ethyl acetate), **23** (254 mg, 79%) as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 4H), 7.33 – 7.29 (m, 1H), 5.12 (s, 2H), 4.52 (ddd, *J* = 14.0, 7.4, 4.3 Hz, 1H), 4.27 – 4.06 (m, 2H), 2.74 (br s, 2H), 2.08 – 1.92 (m, 2H), 1.88 – 1.68 (m, 2H), 1.58 (br s, 1H), 1.50 (ddd, *J* = 14.5, 9.4, 3.7 Hz, 1H), 1.46 – 1.34 (m, 1H), 1.12 (br m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.3, 137.0, 128.6, 128.1, 128.0, 87.8, 67.2, 44.1, 44.0, 40.3, 33.0, 32.4, 31.3, 27.9, 10.4; FTIR (cm^{-1}) 2936, 1693, 1547, 1432, 1365, 1241, 1136, 1025. HRMS (CI) m/z, calculated for $[C_{17}H_{25}N_2O_4]^+$ ([M+H]$^+$): 321.1814; found: 321.1802.



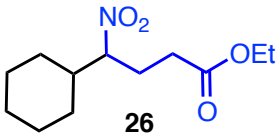
24

24: According to general procedure A, **S18** (1.1 mmol, 369 mg), 1-nitropropane (1.0 mmol, 89 mg), potassium *tert*-butoxide (1.15 mmol, 129 mg), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) and dioxane (4 mL) for 24 h afforded, after flash silica gel chromatography (85:15 to 75:25 hexanes : ethyl acetate), **24** (221 mg, 75%) as white crystals. A duplicate run afforded 234 mg (79%) product. mp = 71-73 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.03 (dd, *J* = 5.0, 3.6 Hz, 1H), 4.58 – 4.52 (m, 1H), 4.58-4.30 (br s, 2H), 2.91 (br s, 2H), 2.07 (m, 1H), 1.99 (ddq, *J* = 14.6, 9.3, 7.3 Hz, 1H), 1.92 (d, *J* = 13.2 Hz, 1H), 1.76 (dqd, *J* = 14.8, 7.5, 4.6 Hz, 1H), 1.69 (d, *J* = 13.4 Hz, 1H), 1.55 – 1.49 (m, 2H), 1.25 – 1.16 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.6, 137.4, 128.7, 128.5, 126.7, 87.8, 46.5, 40.2, 33.3, 32.8, 31.6, 29.8, 27.9, 10.4; FTIR (cm^{-1}) 2924, 2852, 1614, 1546, 1441, 1374, 1275, 1097. HRMS (CI) m/z, calculated for $[C_{14}H_{21}N_2O_3S]^+$ ($[M+H]^+$): 297.1273; found: 297.1282.



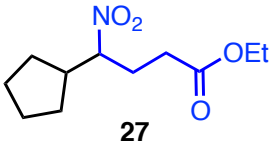
25

25: According to general procedure B, **S27** (3.3 mmol, 870 mg), **2** (3.0 mmol, 483 mg), potassium *tert*-butoxide (3.45 mmol, 386 mg), **8** (0.3 mmol, 173 mg), diethylzinc (0.6 mmol, 74 mg) in MTBE (24 mL) and dioxane (12 mL) for 22 h afforded, after flash silica gel chromatography (100:0 to 95:15 hexanes : ethyl acetate), **25** (744 mg, 77%) as a pale yellow oil. NMR analysis of crude product revealed a ratio of 52:48 diastereomers, the product was isolated as a mixture of diastereomers (dr: 50:50). The reported spectra are for a mixture of two diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 – 7.04 (m, 4H), 6.85 – 6.79 (m, 4H), 4.47 (m, 2H), 4.14 (q, *J* = 7.1 Hz, 4H), 3.79 (s, 3H), 3.78 (s, 3H), 2.68 (m, 2H), 2.61 – 2.48 (m, 2H), 2.44 – 2.32 (m, 2H), 2.31 – 2.17 (m, 4H), 2.16 – 1.96 (m, 4H), 1.78 (m, 1H), 1.69 (m, 1H), 1.54 – 1.45 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 6H), 1.04 (d, *J* = 6.5 Hz, 1H), 1.03 (d, *J* = 6.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.20, 172.15, 158.12, 158.10, 133.45, 133.40, 129.34, 114.10, 114.07, 92.34, 92.16, 60.95, 55.42, 36.72, 36.58, 35.16, 34.80, 32.07, 32.02, 30.59, 30.55, 26.01, 24.93, 15.49, 15.22, 14.31; FTIR (cm^{-1}) 2938, 1733, 1548, 1513, 1374, 1247, 1179, 1036. HRMS (EI) m/z, calculated for $[C_{17}H_{25}NO_5]^+$: 323.1733; found: 323.1742.



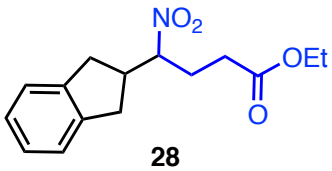
26

26: According to general procedure B, iodocyclohexane (3.3 mmol, 945 mg), **2** (3.0 mmol, 483 mg), potassium *tert*-butoxide (3.45 mmol, 386 mg), **8** (0.3 mmol, 173 mg), diethylzinc (0.6 mmol, 74 mg) in MTBE (24 mL) and dioxane (12 mL) for 20 h afforded, after flash silica gel chromatography (100:0 to 97:3 hexanes : ethyl acetate), **26** (512 mg, 70%) as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.33 (td, *J* = 8.1, 5.7 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.42 – 2.33 (m, 1H), 2.27 (ddd, *J* = 16.7, 8.3, 7.2 Hz, 1H), 2.18 (tdd, *J* = 8.3, 6.4, 1.5 Hz, 2H), 1.89 – 1.73 (m, 4H), 1.71 – 1.59 (m, 2H), 1.32 – 1.00 (m, 8H); ^{13}C NMR (101 MHz, C_6D_6) δ 171.7, 93.2, 60.5, 41.4, 30.3, 29.4, 28.8, 25.99, 25.94, 25.84, 25.68, 14.2.; FTIR (cm^{-1}) 2933, 2856, 1736, 1549, 1449, 1376, 1188, 1034. HRMS (CI) m/z, calculated for $[C_{12}H_{22}NO_4]^+$ ($[M+H]^+$): 244.1549; found: 244.1547.



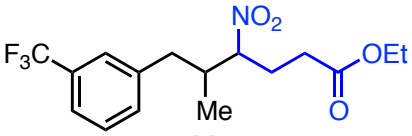
27

27: According to general procedure B, iodocyclopentane (3.3 mmol, 882 mg), **2** (3.0 mmol, 483 mg), potassium *tert*-butoxide (3.45 mmol, 386 mg), **8** (0.3 mmol, 173 mg), diethylzinc (0.6 mmol, 74 mg) in MTBE (24 mL) and dioxane (12 mL) for 25 h afforded, after flash silica gel chromatography (100:0 to 96:4 hexanes : ethyl acetate), **27** (506 mg, 74%) as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.34 (td, *J* = 9.7, 4.1 Hz, 1H), 4.18 – 4.09 (m, 2H), 2.42 – 2.24 (m, 3H), 2.25 – 2.11 (m, 2H), 1.86 (dtd, *J* = 11.8, 7.4, 3.7 Hz, 1H), 1.76 – 1.53 (m, 5H), 1.38 – 1.21 (m, 5H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 92.9, 60.9, 43.9, 30.4, 30.0, 29.4, 28.0, 25.4, 25.0, 14.3; FTIR (cm^{-1}) 2960, 2873, 1736, 1548, 1376, 1184, 1033, 803. HRMS (LIFDI) m/z, calculated for $[C_{11}H_{19}O_2]^+$ ($[M\text{-}NO_2]^+$): 183.1385; found: 183.1382.



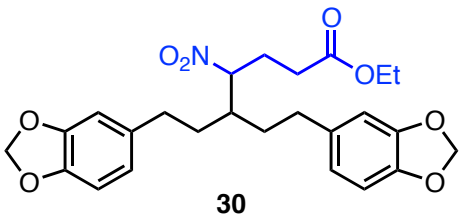
28

28: According to general procedure B, **S32** (3.3 mmol, 805 mg), **2** (3.0 mmol, 483 mg), potassium *tert*-butoxide (3.45 mmol, 386 mg), **8** (0.3 mmol, 173 mg), diethylzinc (0.6 mmol, 74 mg) in MTBE (24 mL) and dioxane (12 mL) for 24 h afforded, after flash silica gel chromatography (100:0 to 94:6 hexanes : ethyl acetate), **28** (603 mg, 73%) as a pale yellow oil which crystallizes very slowly. mp = 42-44 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 – 7.13 (m, 4H), 4.62 (td, *J* = 9.5, 3.7 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.19 – 3.10 (m, 1H), 3.06 – 2.94 (m, 2H), 2.90 – 2.75 (m, 2H), 2.44 (ddd, *J* = 16.7, 7.7, 5.3 Hz, 1H), 2.40 – 2.33 (m, 1H), 2.33 – 2.21 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 141.4, 141.2, 127.0, 126.9, 124.7, 124.5, 92.0, 61.0, 43.4, 36.5, 35.8, 30.3, 27.6, 14.3; FTIR (cm^{-1}) 2982, 2941, 1734, 1548, 1376, 1187, 1027, 748. HRMS (CI) m/z, calculated for $[C_{15}H_{20}NO_4]^+$ ($[M+H]^+$): 278.1392; found: 278.1396.



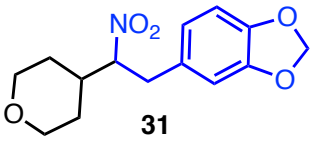
29

29: According to general procedure B, **S31** (3.3 mmol, 1.03 g), **2** (3.0 mmol, 483 mg), potassium *tert*-butoxide (3.45 mmol, 386 mg), **8** (0.3 mmol, 173 mg), diethylzinc (0.6 mmol, 74 mg) in MTBE (24 mL) and dioxane (12 mL) for 23 h afforded, after flash silica gel chromatography (100:0 to 94:6 hexanes : ethyl acetate), **29** (649 mg, 62%) as pale yellow oil. NMR analysis of crude product revealed a ratio of 50:50 diastereomers, the product was isolated as a mixture of diastereomers (dr: 57:43). A duplicate run afforded **29** (608 mg, 59%). The reported spectra are for a mixture of two diastereoisomers ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (m, 2H), 7.46 – 7.39 (m, 4H), 7.36 (m, 2H), 4.52 – 4.43 (m, 2H), 4.18 – 4.09 (m, 4H), 2.93 (dd, *J* = 13.7, 5.6 Hz, 1H), 2.83 (dd, *J* = 13.2, 4.0 Hz, 1H), 2.54 – 2.34 (m, 6H), 2.34 – 2.10 (m, 6H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.07, 172.03, 139.92, 139.75, 132.74, 132.67, 131.14 (q, *J* = 32.2 Hz), 131.09 (q, *J* = 32.2 Hz), 129.19, 129.17, 125.93 (m), 124.21 (q, *J* = 272.2 Hz), 123.68 (m), 92.12, 91.12, 61.04, 39.32, 39.21, 39.08, 39.05, 30.61, 30.47, 26.09, 25.35, 15.18, 14.98, 14.30, 14.28; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.64; FTIR (cm^{-1}) 2982, 2940, 1733, 1549, 1449, 1375, 1330, 1165, 1125. HRMS (CI) m/z, calculated for $[C_{16}H_{21}F_3NO_4]^+$ ($[M+H]^+$): 348.1423; found: 348.1433.



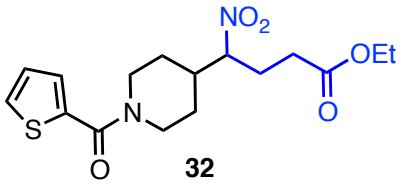
30

30: According to general procedure B, **S29** (3.3 mmol, 1.44 g), **2** (3.0 mmol, 483 mg), potassium *tert*-butoxide (3.45 mmol, 386 mg), **8** (0.3 mmol, 173 mg), diethylzinc (0.6 mmol, 74 mg) in MTBE (24 mL) and dioxane (12 mL) for 26 h afforded, after flash silica gel chromatography (98.5:2.5 to 87.5:12.5 hexanes : ethyl acetate), **30** (1.062 g, 75%) as a pale yellow viscous oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.72 (dd, *J* = 7.9, 5.6 Hz, 2H), 6.62 (dd, *J* = 8.2, 1.7 Hz, 2H), 6.57 (td, *J* = 8.0, 1.7 Hz, 2H), 5.93 (s, 2H), 5.92 (s, 2H), 4.67 (ddd, *J* = 10.5, 5.7, 3.0 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.61 (ddd, *J* = 13.7, 9.6, 5.8 Hz, 1H), 2.56 (ddd, *J* = 8.9, 6.8, 2.1 Hz, 2H), 2.50 (ddd, *J* = 13.7, 9.5, 6.6 Hz, 1H), 2.42 – 2.32 (m, 1H), 2.30 – 2.19 (m, 2H), 2.03 (dddd, *J* = 16.9, 8.9, 5.0, 2.0 Hz, 1H), 1.99 – 1.91 (m, 1H), 1.77 – 1.52 (m, 5H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.21, 147.88, 147.85, 146.03, 146.01, 135.13, 135.09, 121.28, 121.22, 108.92, 108.87, 108.42, 108.39, 101.01, 100.99, 89.60, 61.00, 40.57, 32.69, 32.44, 31.97, 31.57, 30.46, 25.16, 14.33; FTIR (cm^{-1}) 2937, 1732, 1547, 1489, 1443, 1371, 1246, 1189, 1039. HRMS (LIFDI) m/z, calculated for $[C_{25}H_{29}NO_8]^+$: 471.1893; found: 471.1874.



31

31: According to general procedure A, **S35** (3.3 mmol, 700 mg), **47** (3.0 mmol, 585 mg), potassium *tert*-butoxide (3.45 mmol, 386 mg), **8** (0.45 mmol, 260 mg), diethylzinc (0.9 mmol, 111 mg) in MTBE (24 mL) and dioxane (12 mL) for 24 h afforded, after flash silica gel chromatography (90:10 to 75:25 hexanes : ethyl acetate), **31** (557 mg, 67%) as a light yellow solid. mp = 98-100 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.72 (d, *J* = 7.9 Hz, 1H), 6.63 – 6.56 (m, 2H), 5.93 (s, 2H), 4.46 (ddd, *J* = 10.4, 8.2, 4.1 Hz, 1H), 4.08 – 3.98 (m, 2H), 3.46 – 3.34 (m, 2H), 3.13 – 3.00 (m, 2H), 2.19 – 2.10 (m, 1H), 1.74 (ddd, *J* = 13.0, 4.0, 1.9 Hz, 1H), 1.57 – 1.45 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.1, 147.1, 129.2, 122.0, 109.1, 108.7, 101.3, 95.4, 67.4, 67.3, 39.0, 36.6, 29.4, 29.3; FTIR (cm^{-1}) 2954, 2849, 1549, 1490, 1445, 1366, 1248, 1093, 1039. HRMS (CI) m/z, calculated for $[C_{14}H_{18}NO_5]^+$ ($[M+H]^+$): 279.1107; found: 279.1104.

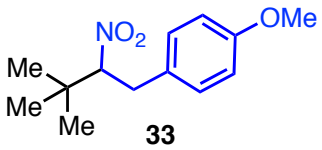


32

32 (in the glovebox)**:** According to general procedure B, **S34** (3.3 mmol, 1.11 g), **2** (3.0 mmol, 483 mg), potassium *tert*-butoxide (3.45 mmol, 386 mg), **8** (0.3 mmol, 173 mg), diethylzinc (0.6 mmol, 74 mg) in MTBE (24 mL) and dioxane (12 mL) for 22 h afforded, after flash silica gel chromatography (80:20 to 60:40 hexanes : ethyl acetate), **32** (841 mg, 77%) as a pale yellow oil that crystallizes slowly.

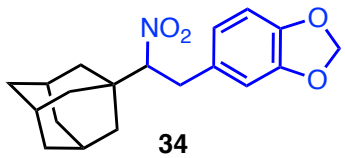
32 (on the bench)**:** According to general procedure C, **S34** (1.1 mmol, 371 mg), **2** (1 mmol, 161 mg), potassium *tert*-butoxide (0.29 M in dioxane, 1.15 mmol, 4 mL), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) for 24 h afforded, after flash silica gel chromatography (80:20 to 60:40 hexanes : ethyl acetate), **32** (282 mg, 76%) as a pale yellow oil that crystallizes slowly. mp = 97-99 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.27 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.04 (dd, *J* = 5.0, 3.6 Hz, 1H), 4.52 (br m, 2H), 4.42 (td, *J* = 8.4, 5.0 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.93 (br m, 2H), 2.46 – 2.37 (m, 1H), 2.30

(ddd, *J* = 16.9, 8.4, 7.1 Hz, 1H), 2.24 – 2.11 (m, 3H), 1.87 (dt, *J* = 13.1, 3.0 Hz, 1H), 1.68 (dt, *J* = 13.3, 3.0 Hz, 1H), 1.41 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 163.7, 137.0, 128.9, 128.8, 126.8, 92.1, 61.1, 40.0, 30.2, 29.0, 28.4, 25.7, 14.3; FTIR (cm^{-1}) 2942, 1732, 1618, 1548, 1441, 1374, 1277, 1188, 1096, 736. HRMS (CI) m/z, calculated for $[C_{16}H_{22}N_2O_5S]^+$ ($[M+H]^+$): 355.1328; found: 355.1313.



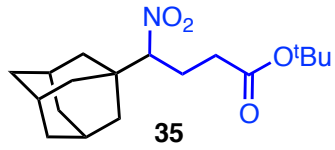
33

33: According to general procedure A, *tert*-butyl iodide (3.75 mmol, 690 mg), **S46** (3.0 mmol, 543 mg), potassium *tert*-butoxide (3.45 mmol, 386 mg), **8** (0.45 mmol, 260 mg), diethylzinc (0.9 mmol, 111 mg) in MTBE (24 mL) and dioxane (12 mL) for 24 h afforded, after flash silica gel chromatography (100:0 to 97.5:2.5 hexanes : ethyl acetate), **33** (498 mg, 70%) as a white crystalline solid. mp = 86-88 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 – 7.02 (m, 2H), 6.85 – 6.78 (m, 2H), 4.47 (dd, *J* = 11.9, 2.5 Hz, 1H), 3.77 (s, 3H), 3.21 (dd, *J* = 14.7, 11.9 Hz, 1H), 2.98 (dd, *J* = 14.7, 2.5 Hz, 1H), 1.12 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 129.8, 128.6, 114.4, 100.0, 55.4, 34.6, 34.2, 26.7; FTIR (cm^{-1}) 2966, 1613, 1549, 1514, 1368, 1250, 1179, 1035, 860. HRMS (LIFDI) m/z, calculated for $[C_{13}H_{19}NO_3]^+$: 237.1365; found: 237.1360.



34

34: According to general procedure A, 1-iodoadamantane (3.3 mmol, 865 mg), **47** (3.0 mmol, 585 mg), potassium *tert*-butoxide (3.45 mmol, 386 mg), **8** (0.45 mmol, 260 mg), diethylzinc (0.9 mmol, 111 mg) in MTBE (24 mL) and dioxane (12 mL) for 24 h afforded, after flash silica gel chromatography (100:0 to 97:3 hexanes : ethyl acetate), **34** (422 mg, 43%) as a white solid. mp = 178-180 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.71 (d, *J* = 7.9 Hz, 1H), 6.62 – 6.55 (m, 2H), 5.92 (s, 2H), 4.29 (dd, *J* = 11.9, 2.4 Hz, 1H), 3.15 (dd, *J* = 14.6, 11.9 Hz, 1H), 2.97 (dd, *J* = 14.6, 2.4 Hz, 1H), 2.08 (m, 3H), 1.78 (m, 6H), 1.71 – 1.61 (m, 3H), 1.61 – 1.54 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.0, 146.9, 130.4, 122.0, 109.2, 108.7, 101.2, 101.0, 38.7, 36.7, 36.3, 33.2, 28.4; FTIR (cm^{-1}) 2904, 1534, 1371, 1249, 1041. HRMS (LIFDI) m/z, calculated for $[C_{19}H_{23}NO_4]^+$: 329.1627; found: 329.1632.

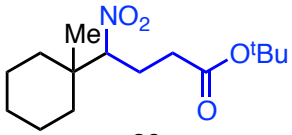


35

35 (in the glovebox)**:** According to general procedure A, 1-iodoadamantane (3.3 mmol, 865 mg), **S41** (3.0 mmol, 567 mg), potassium *tert*-butoxide (3.45 mmol, 386 mg), **8** (0.3 mmol, 173 mg), diethylzinc (0.6 mmol, 74 mg) in MTBE (24 mL) and dioxane (12 mL) for 24 h afforded, after flash silica gel chromatography (100:0 to 98:2 hexanes : ethyl acetate), **35** (536 mg, 55%) as a light yellow oil.

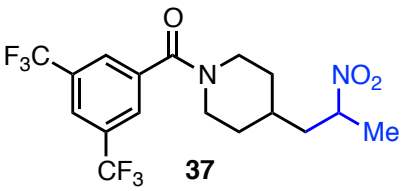
35 (on the bench)**:** According to general procedure C, 1-iodoadamantane (1.1 mmol, 288 mg), **S41** (1 mmol, 189 mg), potassium *tert*-butoxide (0.29 M in dioxane, 1.15 mmol, 4 mL), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) for 24 h afforded, after flash silica gel chromatography (100:0 to 98:2 hexanes : ethyl acetate), **35** (192 mg, 59%) as a light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.16 (dd, *J* = 11.8, 2.1 Hz, 1H), 2.31 – 2.18 (m, 2H), 2.16 – 2.06 (m, 2H), 2.04 (m, 3H), 1.76 – 1.68 (m, 6H), 1.67 – 1.59 (m, 3H), 1.54 – 1.48 (m, 3H), 1.44 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 98.3, 81.2, 38.6, 36.7, 36.6, 36.2,

32.0, 28.5, 28.4, 28.2, 22.6; FTIR (cm^{-1}) 2908, 2852, 1729, 1547, 1449, 1367, 1155, 848. HRMS (ESI) m/z, calculated for $[C_{18}H_{30}NO_4]^+$ ($[M+H]^+$): 324.2169; found: 324.2172.



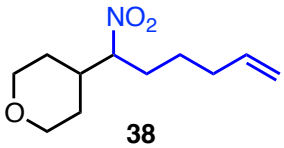
36

36: According to general procedure A, **S36** (1.1 mmol, 246 mg), **S41** (1.0 mmol, 189 mg), potassium *tert*-butoxide (1.15 mmol, 129 mg), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) and dioxane (4 mL) for 24 h afforded, after flash silica gel chromatography (100:0 to 97:3 hexanes : ethyl acetate), **36** (241 mg, 85%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.45 (dd, *J* = 11.8, 2.2 Hz, 1H), 2.34 – 2.19 (m, 2H), 2.14 (ddd, *J* = 16.0, 8.0, 6.8 Hz, 1H), 2.06 (dtd, *J* = 14.0, 7.7, 2.0 Hz, 1H), 1.64 – 1.41 (m, 16H), 1.36 – 1.25 (m, 3H), 1.03 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 171.3, 96.6, 80.4, 36.9, 35.0, 34.8, 31.7, 28.0, 25.9, 23.3, 21.63, 21.58, 19.2.; FTIR (cm^{-1}) 2932, 2864, 1729, 1548, 1462, 1367, 1155, 848. HRMS (LIFDI) m/z, calculated for $[C_{11}H_{18}NO_4]^+$ ($[M-^tBu]^+$): 228.1236; found: 228.1230.



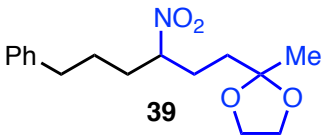
37

37: According to general procedure A, **S37** (1.1 mmol, 512 mg), nitroethane (1.0 mmol, 75 mg), potassium *tert*-butoxide (1.15 mmol, 129 mg), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) and dioxane (4 mL) for 24 h afforded, after flash silica gel chromatography (90:10 to 80:20 hexanes : ethyl acetate), **37** (320 mg, 78%) as a colorless viscous oil. A duplicate run afforded **37** (319 mg, 78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (br s, 1H), 7.84 (br m, 2H), 4.71 (br s, 2H), 3.60 (br s, 1H), 3.08 (br s, 1H), 2.79 (br s, 1H), 2.11 (t, *J* = 10.7 Hz, 1H), 2.05-1.63 (br m, 2H), 1.69– 1.55 (m, 5H), 1.37 – 1.25 (m, 1H), 1.16 (br s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 138.3, 132.31 (q, *J* = 33.7 Hz), 127.41 (d, *J* = 3.8 Hz), 123.61 (p, *J* = 3.9 Hz), 123.04 (q, *J* = 273.0 Hz), 81.0, 47.9, 42.6, 41.7, 33.2, 32.0, 31.1, 20.1; ^{19}F NMR (376 MHz, CDCl3) δ -62.94; FTIR (cm^{-1}) 2995, 2939, 2868, 1643, 1551, 1447, 1369, 1279, 1133. HRMS (CI) m/z, calculated for $[C_{17}H_{19}F_6N_2O_3]^+$ ($[M+H]^+$): 413.1300; found: 413.1299.



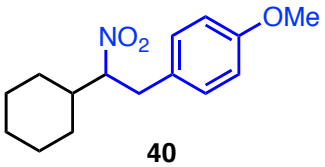
38

38: According to general procedure A, **S35** (1.0 mmol, 212 mg), **S40** (1.1 mmol, 141.9 mg), potassium *tert*-butoxide (1.25 mmol, 140 mg), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) and dioxane (4 mL) for 24 h afforded, after flash silica gel chromatography (100:0 to 92:8 hexanes : ethyl acetate), **38** (145 mg, 68%) as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.74 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.06 – 4.95 (m, 2H), 4.27 (ddd, *J* = 11.4, 8.6, 3.1 Hz, 1H), 4.05 – 3.94 (m, 2H), 3.42 – 3.33 (m, 2H), 2.15 – 1.99 (m, 3H), 1.94 (dddd, *J* = 14.7, 11.1, 9.0, 5.9 Hz, 1H), 1.83 – 1.73 (m, 1H), 1.64 (m, 1H), 1.47 (tt, *J* = 7.1, 3.9 Hz, 2H), 1.44 – 1.33 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.5, 115.8, 93.8, 67.374, 67.369, 39.0, 33.0, 29.8, 29.6, 29.2, 25.0; FTIR (cm^{-1}) 2933, 2847, 1641, 1548, 1364, 1246, 1143, 1094. HRMS (CI) m/z, calculated for $[C_{11}H_{20}NO_3]^+$ ($[M+H]^+$): 214.1443; found: 214.1448.



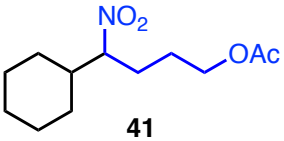
39

39: According to general procedure A, **1** (1.1 mmol, 271 mg), **S43** (1.0 mmol, 175mg), potassium *tert*-butoxide (1.15 mmol, 129 mg), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) and dioxane (4 mL) for 24 h afforded, after flash silica gel chromatography (95:5 to 90:10 hexanes : ethyl acetate), **39** (185 mg, 63%) as a clear oil. A duplicate run afforded 198 mg (68%) product. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.22 – 7.18 (m, 1H), 7.17 – 7.12 (m, 2H), 4.51 (tt, *J* = 9.2, 4.4 Hz, 1H), 4.00 – 3.83 (m, 4H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.10 – 1.95 (m, 2H), 1.81 (dddd, *J* = 14.5, 10.2, 5.6, 4.5 Hz, 1H), 1.74 (dtd, *J* = 16.2, 7.5, 6.7, 4.5 Hz, 1H), 1.70 – 1.60 (m, 4H), 1.29 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.2, 128.6, 128.5, 126.2, 109.2, 88.8, 64.87, 64.85, 35.2, 35.1, 33.5, 28.4, 27.5, 24.0; FTIR (cm^{-1}) 2933, 1547, 1495, 1452, 1378, 1219, 1039. HRMS (CI) m/z, calculated for $[C_{16}H_{24}NO_4]^+$ ($[M+H]^+$): 294.1705; found: 294.1711.



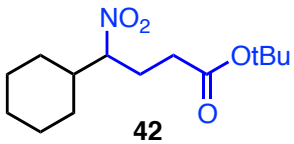
40

40: According to general procedure A, iodocyclohexane (1.1 mmol, 231 mg), **S46** (1.0 mmol, 181 mg), potassium *tert*-butoxide (1.15 mmol, 129 mg), **8** (0.15 mmol, 86.7 mg), diethylzinc (1 M in MTBE, 0.3 mmol, 0.3 mL) in MTBE (8 mL) and dioxane (4 mL) for 24 h afforded, after flash silica gel chromatography (100:0 to 98:2 hexanes : ethyl acetate), **40** (183 mg, 70%) as an off-white solid. mp = 71-73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.03 (m, 2H), 6.89 – 6.79 (m, 2H), 4.48 (ddd, *J* = 10.0, 7.5, 4.5 Hz, 1H), 3.80 (s, 3H), 3.22 – 2.98 (m, 2H), 1.97 – 1.65 (m, 6H), 1.38 – 1.07 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 129.9, 128.2, 114.3, 96.1, 55.4, 41.5, 36.2, 29.4, 29.3, 26.0, 25.9, 25.7; FTIR (cm^{-1}) 2931, 2854, 1613, 1549, 1513, 1369, 1249, 1179, 1035. HRMS (CI) m/z, calculated for $[C_{15}H_{22}NO_3]^+$ ($[M+H]^+$): 264.1600; found: 264.1613.



41

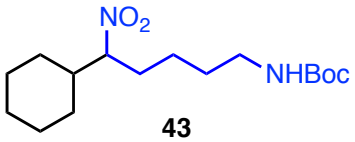
41: In a nitrogen-filled glovebox, **8** (0.1 mmol, 58 mg), bathocuproine (0.1 mmol, 36 mg), and MTBE (8 mL), were added to a 20 mL scintillation vial charged with a stir bar. The mixture stirred for 30 min at ambient temperature, then diethylzinc (0.2 mmol, 1 M in MTBE, 0.2 mL) was added and stirring continued for another 10 min at ambient temperature, after which iodocyclohexane (1.1 mmol, 231 mg), **S45** (1.0 mmol, 161 mg), and potassium *tert*-butoxide (1.15 mmol, 0.29 M in dioxane, 4 mL) were added sequentially. The vial was stirred vigorously for 1 min at ambient temperature, capped and sealed, taken outside the glovebox, and stirred at in an oil bath at 40 °C for 23 h. After cooling to rt, EtOAc (20 mL) was added and the organic layer was washed with saturated aqueous NH_4Cl (20 ml). The organic layer was dried over anhydrous $MgSO_4$ and filtered through a glass frit. The solvents were removed under reduced pressure. The crude product was purified by flash silica gel column chromatography (100:0 to 95:5 hexanes : ethyl acetate) to afford **41** (176 mg, 72%) as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.28 (ddd, *J* = 11.1, 8.0, 3.2 Hz, 1H), 4.14 – 4.00 (m, 2H), 2.05 (s, 3H), 2.04 – 1.97 (m, 1H), 1.89 – 1.73 (m, 5H), 1.68 (dtd, *J* = 12.9, 5.0, 4.1, 2.4 Hz, 1H), 1.66 – 1.59 (m, 3H), 1.25 (m, 2H), 1.16 (tt, *J* = 12.8, 3.3 Hz, 1H), 1.11 – 1.04 (m, 1H), 1.01 (qd, *J* = 12.0, 11.3, 2.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 94.0, 63.4, 41.6, 29.5, 29.2, 27.5, 26.0, 25.9, 25.7, 25.4, 21.0; FTIR (cm^{-1}) 2932, 2856, 1741, 1548, 1449, 1366, 1238, 1043. HRMS (CI) m/z, calculated for $[C_{12}H_{22}NO_4]^+$ ($[M+H]^+$): 244.1549; found: 244.1538.



42

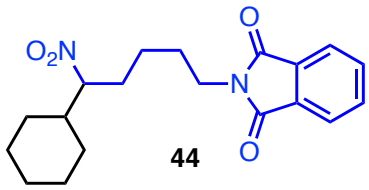
42 (in the glovebox)**:** According to general procedure A, iodocyclohexane (1.1 mmol, 231 mg), **S41** (1.0 mmol, 189 mg), potassium *tert*-butoxide (1.15 mmol, 129 mg), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) and dioxane (4 mL) for 24 h afforded, after flash silica gel chromatography (100:0 to 98:2 hexanes : ethyl acetate), **42** (208 mg, 77%) as a pale yellow oil.

42 (on the bench)**:** according to general procedure C, iodocyclohexane (1.1 mmol, 231 mg), **S41** (1 mmol, 189 mg), potassium *tert*-butoxide (0.29 M in dioxane, 1.15 mmol, 4 mL), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) for 24 h afforded, after flash silica gel chromatography (100:0 to 98:2 hexanes : ethyl acetate), **42** (202 mg, 74%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.39 – 4.24 (m, 1H), 2.35 – 2.24 (m, 1H), 2.24 – 2.17 (m, 1H), 2.17 – 2.06 (m, 2H), 1.90 – 1.71 (m, 4H), 1.66 (dddd, *J* = 15.6, 9.2, 3.4, 1.7 Hz, 2H), 1.44 (s, 9H), 1.33 – 0.98 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 93.5, 81.2, 41.5, 31.6, 29.5, 29.0, 28.2, 26.0, 25.9, 25.8, 25.7; FTIR (cm^{-1}) 2979, 2933, 2856, 1730, 1549, 1450, 1368, 1156. HRMS (ESI) m/z, calculated for $[C_{14}H_{26}NO_4]^+$ ($[M+H]^+$): 272.1856; found: 272.1858.



43

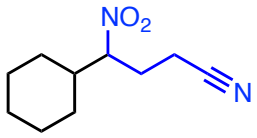
43: according to general procedure A, iodocyclohexane (1.1 mmol, 231 mg), **S52** (1.0 mmol, 232 mg), potassium *tert*-butoxide (1.15 mmol, 128.8 mg), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) and dioxane (4 mL) for 23 h afforded, after flash silica gel chromatography (95:5 to 90:10 hexanes : ethyl acetate), **43** (261 mg, 83%) as a colorless viscous oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.50 (br s, 1H), 4.23 (ddd, *J* = 11.1, 8.0, 3.1 Hz, 1H), 3.09 (m, 2H), 1.96 (tdd, *J* = 14.7, 11.2, 7.2 Hz, 1H), 1.87 – 1.70 (m, 5H), 1.70 – 1.64 (m, 1H), 1.63 – 1.58 (m, 1H), 1.55 – 1.45 (m, 2H), 1.44 (s, 9H), 1.35 – 1.18 (m, 4H), 1.15 (tt, *J* = 12.7, 3.2 Hz, 1H), 1.12 – 0.95 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 94.5, 79.4, 41.5, 40.2, 30.4, 29.6, 29.5, 29.2, 28.6, 26.1, 25.9, 25.7, 23.4; FTIR (cm^{-1}) 3352, 2932, 2857, 1704, 1548, 1366, 1251, 1173; HRMS (CI) m/z, calculated for $[C_{16}H_{31}N_2O_4]^+$: 315.2278; found: 315.2280.



44

44 (in the glovebox)**:** In a nitrogen-filled glovebox, **8** (0.1 mmol, 58 mg), bathocuproine (0.1 mmol, 36 mg), and MTBE (8 mL), were added to a 20 mL scintillation vial charged with a stir bar. The mixture stirred for 30 min at ambient temperature, then diethylzinc (0.2 mmol, 1 M in MTBE, 0.2 mL) was added and stirring continued for another 10 min at ambient temperature, after which iodocyclohexane (1.1 mmol, 231 mg), **S49** (1.0 mmol, 262 mg), and potassium *tert*-butoxide (1.15 mmol, 0.29 M in dioxane, 4 mL) were added sequentially. The vial was stirred vigorously for 1 min at ambient temperature, capped and sealed, taken outside the glovebox, and stirred at in an oil bath at 40 °C for 23 h. After cooling to rt, EtOAc (20 mL) was added and the mixture was washed with saturated aqueous NH_4Cl (20 ml). The organic layer was dried over anhydrous $MgSO_4$, and filtered through a glass frit. The solvents were removed under reduced pressure. The crude product was purified by flash silica gel column chromatography (95:5 to 90:10 hexanes : ethyl acetate) to afford **44** (205 mg, 60%) as a colorless viscous oil.

44 (on the bench) was made with a slight modification of general procedure C: Using an argon-filled double manifold equipped with a mercury bubbler, an oven-dried 25 mL Schlenk flask charged with a stir bar was sealed with a rubber septum and cooled under vacuum. The rubber septum was removed partly and **8** (0.1 mmol, 58mg), bathocuproine (0.1 mmol, 36 mg), and **S49** (1.0 mmol, 262 mg) were added to the flask. The rubber septum was replaced and the flask is evacuated-backfilled with argon (3X); then MTBE (8 mL) was added under argon and the mixture was stirred at rt for 30 min. Anaerobic and anhydrous iodocyclohexane (1.2 mmol, 252 mg, 155 µL) and potassium *tert*-butoxide (1.15 mmol, 0.29 M in dioxane, 4 mL) were added via syringe, followed by 1 min of vigorous stirring. The flask was purged with argon for 3 min using a vent needle. Et_2Zn (1 M in MTBE, 0.2 mmol, 200 µL) was then added. The side-arm of the flask was then sealed, the flask was disconnected from the manifold, and reaction was placed in a 40 °C oil bath where it was maintained for 24 h with stirring. After cooling to rt , EtOAc (20 mL) was added and the mixture was washed with saturated aqueous NH_4Cl (20 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered through a glass frit. The solvents were removed under reduced pressure. The crude product was purified by silica gel column chromatography (95:5 to 90:10 hexanes : ethyl acetate) to afford **44** (204 mg, 59%) as a colorless viscous oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.26 (ddd, *J* = 11.0, 7.9, 3.1 Hz, 1H), 3.77 – 3.62 (m, 2H), 2.01 (dddd, *J* = 14.8, 11.0, 9.5, 5.5 Hz, 1H), 1.92 – 1.67 (m, 8H), 1.67 – 1.59 (m, 1H), 1.36 (dddd, *J* = 17.2, 14.9, 8.3, 4.4 Hz, 2H), 1.31 – 1.23 (m, 2H), 1.21 – 1.00 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 134.1, 132.2, 123.4, 94.3, 41.5, 37.4, 30.1, 29.5, 29.2, 28.0, 26.0, 25.9, 25.7, 23.3; FTIR (cm^{-1}) 2932, 2855, 1772, 1710, 1546, 1466, 1396, 1371, 1188, 1036, 721. HRMS (ESI) m/z, calculated for $[C_{19}H_{25}N_2O_4]^+$ ($[M+H]^+$): 345.1809; found: 345.1812.



45

45: according to general procedure A, iodocyclohexane (3.75 mmol, 788 mg), **S44** (3.0 mmol, 342 mg), potassium *tert*-butoxide (3.45 mmol, 386 mg), **8** (0.3 mmol, 173 mg), diethylzinc (0.6 mmol, 74 mg) in MTBE (24 mL) and dioxane (12 mL) for 23 h afforded, after flash silica gel chromatography (90:10 to 85:15 hexanes : ethyl acetate), **45** (196 mg, 34%) as a pale brown oil that crystallizes slowly. mp = 30-32 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.40 (ddd, *J* = 10.7, 7.6, 2.7 Hz, 1H), 2.54 – 2.40 (m, 1H), 2.40 – 2.26 (m, 2H), 2.19 – 2.08 (m, 1H), 1.89 (tdt, *J* = 11.3, 7.2, 3.4 Hz, 1H), 1.85 – 1.61 (m, 5H), 1.33 – 1.21 (m, 2H), 1.21 – 1.01 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 117.9, 92.2, 41.4, 29.4, 28.9, 26.6, 25.9, 25.8, 25.6, 14.6; FTIR (cm^{-1}) 2927, 2854, 2249, 1547, 1450, 1370. HRMS (CI) m/z, calculated for $[C_{10}H_{17}N_2O_2]^+$ ($[M+H]^+$): 197.1290; found: 197.1289.

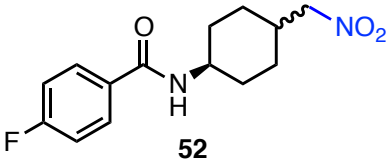
48

48: according to general procedure A, **46** (1.2 mmol, 218.4 mg), **47** (1.0 mmol, 195 mg), potassium *tert*-butoxide (1.15 mmol, 129 mg), **8** (0.15 mmol, 87 mg), diethylzinc (1 M in MTBE, 0.3 mmol, 0.3 mL) in MTBE (8 mL) and dioxane (4 mL) for 24 h afforded, after flash silica gel chromatography (100:0 to 98:2 hexanes : ethyl acetate), **48** (159 mg, 64%) as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.73 (d, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 1.7 Hz, 1H), 6.60 (dd, *J* = 7.9, 1.8 Hz, 1H), 5.94 (s, 2H), 5.78 – 5.68 (m, 1H), 5.10 – 4.99 (m, 2H), 4.71 – 4.60 (m, 1H), 3.17 (dd, *J* = 14.3, 8.7 Hz, 1H), 2.95 (dd, *J* = 14.3, 5.7 Hz, 1H), 2.19 – 1.99 (m, 3H), 1.83 (ddt, *J* = 10.6, 9.0, 3.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ

148.12, 147.11, 135.9, 129.2, 122.2, 116.8, 109.3, 108.7, 101.3, 89.5, 40.0, 32.5, 30.0; FTIR (cm^{-1}) 3078, 2925, 1641, 1549, 1491, 1445, 1376, 1249, 1040, 927; HRMS (CI) m/z, calculated for $[C_{13}H_{15}NO_4]^+$: 249.1001; found: 249.0997.

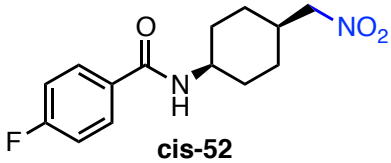
50

50: according to general procedure A, **49** (1.2 mmol, 252 mg), **47** (1.0 mmol, 195 mg), potassium *tert*-butoxide (1.15 mmol, 129 mg), **8** (0.15 mmol, 87 mg), diethylzinc (1 M in MTBE, 0.3 mmol, 0.3 mL) in MTBE (8 mL) and dioxane (4 mL) for 23 h afforded , after flash silica gel chromatography (100:0 to 98:2 hexanes : ethyl acetate) then preparative TLC (98:2 hexanes : ethyl acetate) , **50** (167 mg, 60%) as a pale yellow oil that crystallizes slowly. mp = 42-44 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.73 (d, *J* = 7.9 Hz, 1H), 6.63 (d, *J* = 1.8 Hz, 1H), 6.60 (dd, *J* = 7.9, 1.8 Hz, 1H), 5.94 (s, 2H), 4.72 – 4.64 (m, 1H), 3.14 (dd, *J* = 14.3, 8.9 Hz, 1H), 2.93 (dd, *J* = 14.3, 5.4 Hz, 1H), 2.14 (ddd, *J* = 14.0, 10.0, 5.1 Hz, 1H), 1.86 (ddd, *J* = 11.8, 7.8, 5.0 Hz, 1H), 1.81 – 1.69 (m, 2H), 1.69 – 1.57 (m, 3H), 1.54 – 1.48 (m, 2H), 1.07 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.1, 147.1, 129.5, 122.2, 109.3, 108.7, 101.2, 90.0, 40.4, 40.0, 37.0, 32.8, 32.2, 25.09, 25.09; FTIR (cm^{-1}) 2951, 2870, 1550, 1490, 1445, 1365, 1249, 1040. HRMS (CI) m/z, calculated for $[C_{15}H_{19}NO_4]^+$: 277.1314; found: 277.1303.



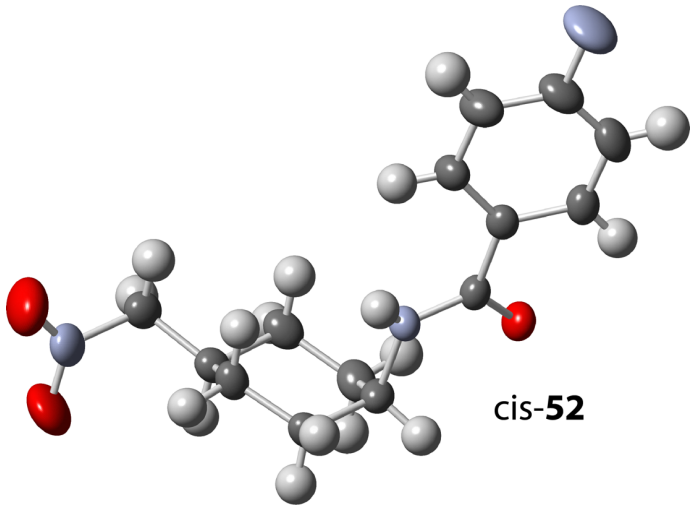
52
(+/-)

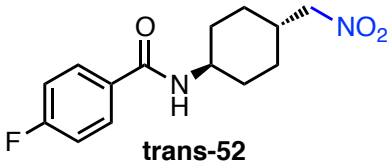
52: according to general procedure A, **cis-51** (0.25 mmol, 87 mg), nitromethane (0.275 mmol, 16.8 mg), potassium *tert*-butoxide (0.3125 mmol, 35 mg), **8** (0.025 mmol, 14.5 mg), diethylzinc (1 M in MTBE, 0.05 mmol, 0.05 mL) in MTBE (2 mL) and dioxane (1 mL) for 23 h afforded, after preparative TLC (75:25 to 70:30 hexanes : ethyl acetate) for identification purposes, **cis-52** and **trans-52** as white solids. The X-ray quality crystals can be obtained from DCM/pentane.



cis-52
(+/-)

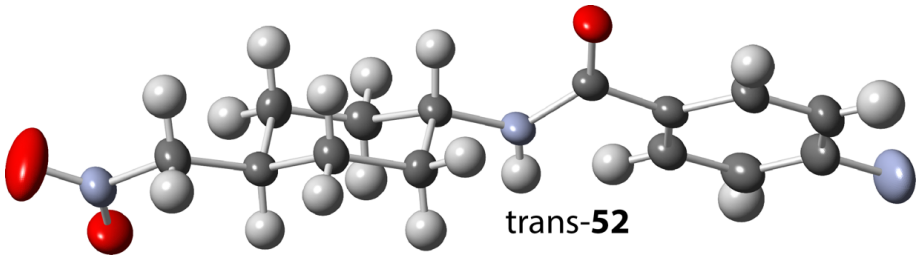
cis-52 mp = 149-150 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 2H), 7.18 – 7.06 (m, 2H), 6.02 (s, 1H), 4.37 (d, *J* = 7.4 Hz, 2H), 4.30 – 4.15 (m, 1H), 2.40 (m, 1H), 1.80 (dd, *J* = 12.7, 7.3 Hz, 4H), 1.76 (q, *J* = 4.9 Hz, 2H), 1.44 (dq, *J* = 14.2, 7.4 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.1, 164.8 (d, *J* = 252.1 Hz), 131.0 (d, *J* = 3.3 Hz), 129.3 (d, *J* = 9.0 Hz), 115.8 (d, *J* = 21.9 Hz), 80.1, 45.9, 34.8, 28.8, 25.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.05; FTIR (cm^{-1}) 3305, 2935, 1637, 1548, 1501, 1383, 1360, 1233, 853. HRMS (ESI) m/z, calculated for $[C_{14}H_{18}FN_2O_3]^+$ ($[M+H]^+$): 281.1296; found: 281.1300.

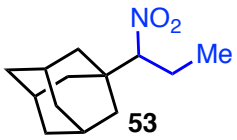




trans-52
(+/-)

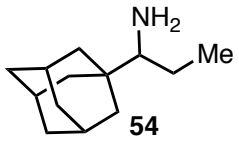
trans-52: mp = 173-175 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 – 7.51 (m, 2H), 7.10 (t, J = 8.6 Hz, 2H), 5.85 (d, J = 8.0 Hz, 1H), 4.27 (d, J = 7.2 Hz, 2H), 3.95 (dq, J = 11.0, 3.3 Hz, 1H), 2.19 (m, 3H), 1.94 – 1.79 (m, 3H), 1.39 – 1.17 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 164.8 (d, *J* = 251.8 Hz), 130.88 (d, *J* = 3.2 Hz), 129.28 (d, *J* = 8.9 Hz), 115.76 (d, *J* = 21.9 Hz), 81.3, 48.6, 36.2, 32.2, 28.9; ^{19}F NMR (565 MHz, $CDCl_3$) δ -108.23; FTIR (cm^{-1}) 3315, 2918, 1635, 1546, 1502, 1384, 1333, 1162. HRMS (ESI) m/z, calculated for $[C_{14}H_{18}FN_2O_3]^+$ ($[M+H]^+$): 281.1296; found: 281.1293.





53

53: according to general procedure A, 1-iodoadamantane (1.0 mmol, 262 mg), 1-nitropropane (1.1 mmol, 98 mg), potassium *tert*-butoxide (0.29 M in dioxane, 1.25 mmol, 4.35 mL), **8** (0.1 mmol, 58 mg), diethylzinc (1 M in MTBE, 0.2 mmol, 0.2 mL) in MTBE (8 mL) for 24 h afforded, after flash silica gel chromatography (100:0 to 98:2 hexanes : ethyl acetate), **53** (121 mg, 54%) as a pale yellow solid. mp = 47-48 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.02 (dd, *J* = 12.1, 2.4 Hz, 1H), 2.07 – 1.95 (m, 4H), 1.71 (m, 7H), 1.62 (m, 3H), 1.48 (m, 3H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 101.2, 38.7, 36.7, 36.1, 28.4, 20.4, 11.2; FTIR (cm^{-1}) 2908, 2852, 1544, 1456, 1445, 1365, 1316, 1081. HRMS (ESI) m/z, calculated for $[C_{13}H_{21}NO_2]^+$ ($[M+H]^+$): 224.1645; found: 224.1651



54

54: **53** (0.2 mmol, 45 mg) and wet Raney nickel (20 w%, 9 mg) were added to a 20 mL scintillation vial under air, followed by THF (4 mL) and ethanol (4 mL). The vial was placed in a high-pressure reactor and evacuated-backfilled with hydrogen (3X). The mixture was stirred under 750 psi hydrogen gas at rt for 24 h. The mixture was then filtered through a pad of Celite and the solid on Celite was washed with DCM (100 ml). The solvents were removed under reduced pressure to afford 37 mg (95%) **54** as a pale yellow oil. ^{1}H NMR (600 MHz, C_6D_6) δ 1.94 (m, 3H), 1.87 (dd, *J* = 10.5, 2.3 Hz, 1H), 1.69 (m, 3H), 1.63 – 1.59 (m, 3H), 1.52 (dqd, *J* = 13.1, 7.3, 2.2 Hz, 1H), 1.43 (m, 6H), 0.95 (t, *J* = 7.3 Hz, 3H), 0.89 – 0.82 (m, 1H); ^{13}C NMR (151 MHz, CD_2Cl_2) δ 63.3, 39.0, 38.0, 36.8, 29.4, 23.8, 12.8; FTIR (cm^{-1}) 3396, 3319, 2904, 2847, 1632, 1450, 1361, 1101. HRMS (ESI) m/z, calculated for $[C_{13}H_{23}N]^+$ ($[M+H]^+$): 194.1903; found: 194.1900.

9. Crystallographic Details

X-ray structural analysis for cis-51, trans-51, cis-52, and trans-52: Crystals were mounted using viscous oil onto a plastic mesh and cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX II DUO CCD diffractometer with Cu-Kα radiation (λ = 1.54178 Å) monochromated with graphite. Unit cell parameters were obtained from 36 data frames, 0.5º ω, from three different sections of the Ewald sphere. The unit-cell parameters and systematic absences were uniquely consistent to the reported space groups. The data were treated with multi-scan absorption corrections.[34] The structures were solved using intrinsic phasing and refined with full-matrix, least-squares procedures on F^2.

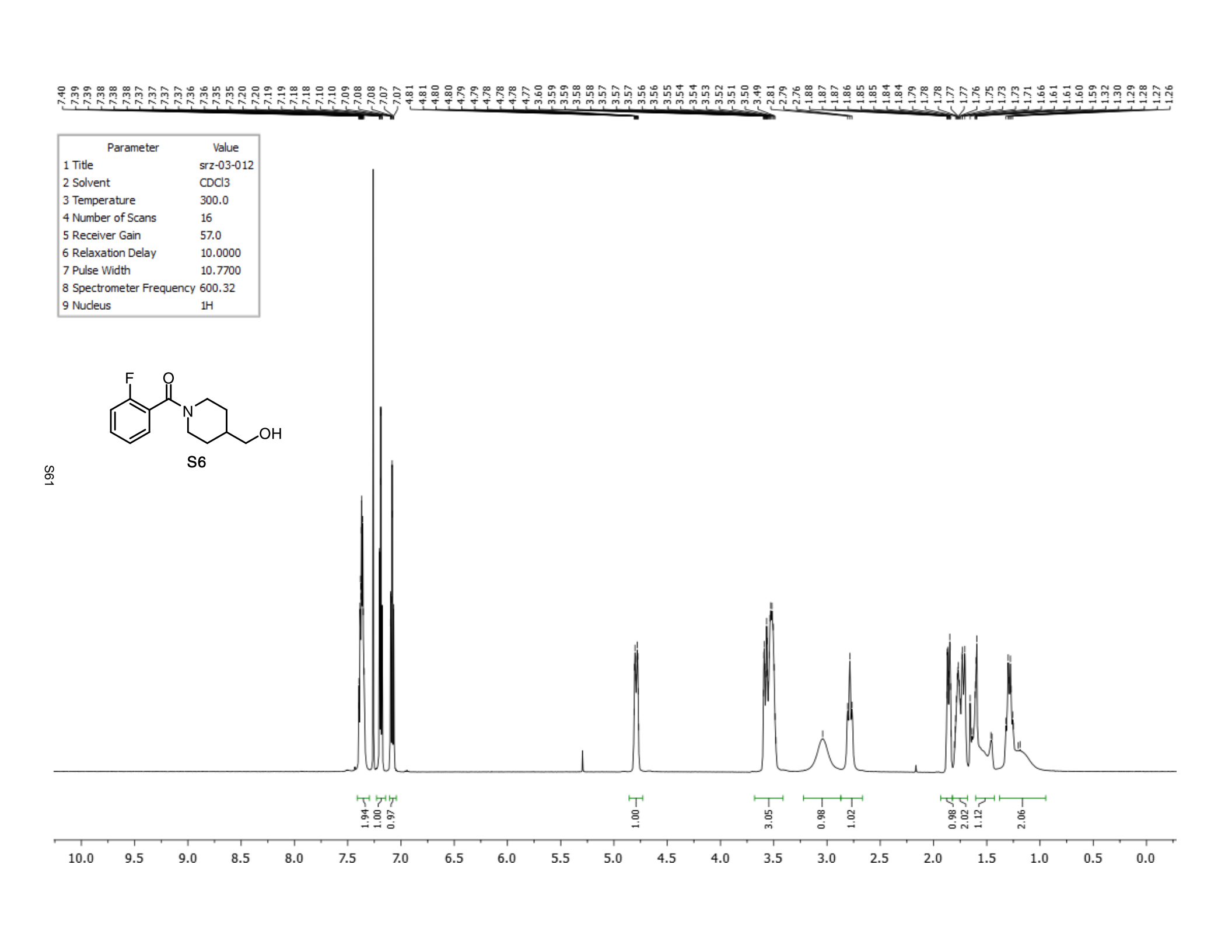
Two compound molecules (Z' = 2) were located in the asymmetric units of **cis-51** and **trans-52**. All non-hydrogen atoms were refined with anisotropic displacement parameters. H-atoms on nitrogen atoms were treated differently as allowed by the data quality: assigned calculated positions (**cis-52**); or located from the difference map, treated with constrained N-H distance (**trans-51, cis-51**), or N-H restrained to be similar in both symmetry independent molecules (**trans-52**); and treated with U_{iso} = 1.2(N-U_{eq}). All other hydrogen atoms were treated as idealized contributions with geometrically calculated positions and with U_{iso} equal to 1.2, or 1.5 for methyl, U_{eq} of the attached atom. Atomic scattering factors are contained in the SHELXTL program library.[35]

The CIF for these structures have been deposited under CCDC 1542942 = **cis-52**, 1542943 = **trans-52**, 1542944 = **cis-51**, 1542945 = **trans-51**.

10. References

(1) Ballini, R.; Barboni, L.; Giarlo, G., *J. Org. Chem.* **2004,** *69* (20), 6907-6908.
(2) Smith, S. M.; Takacs, J. M., *J. Am. Chem. Soc.* **2010,** *132* (6), 1740-1741.
(3) Szostak, M.; Spain, M.; Procter, D. J., *Chem. Commun.* **2011,** *47* (37), 10254-10256.
(4) Dai, C.; Narayanam, J. M. R.; Stephenson, C. R. J., *Nat. Chem.* **2011,** *3* (2), 140-145.
(5) Zhu, G.; Negishi, E.-i., *Org. Lett.* **2007,** *9* (15), 2771-2774.
(6) Boerjesson, L.; Csoeregh, I.; Welch, C. J., *J. Org. Chem.* **1995,** *60* (10), 2989-2999.
(7) Mash, E. A.; Gregg, T. M., *J. Org. Chem.* **1995,** *60* (19), 6180-6182.
(8) Campiani, G.; Butini, S.; Trotta, F.; Fattorusso, C.; Catalanotti, B.; Aiello, F.; Gemma, S.; Nacci, V.; Novellino, E.; Stark, J. A.; Cagnotto, A.; Fumagalli, E.; Carnovali, F.; Cervo, L.; Mennini, T., *J. Med. Chem.* **2003,** *46* (18), 3822-3839.
(9) Boyer, N.; Gloanec, P.; De Nanteuil, G.; Jubault, P.; Quirion, J.-C., *Eur. J. Org. Chem.* **2008,** *2008* (25), 4277-4295.
(10) Aquila, B.; Lyne, P.; Pontz, T. Quinazolinone derivatives and their use as b-raf inhibitors. WO2006/24834 A1, 2006.
(11) Adachi, H.; Palaniappan, K. K.; Ivanov, A. A.; Bergman, N.; Gao, Z.-G.; Jacobson, K. A., *J. Med. Chem.* **2007,** *50* (8), 1810-1827.
(12) Ghiaci, M.; Sedaghat, M. E.; Kalbasi, R. J.; Abbaspur, A., *Tetrahedron* **2005,** *61* (23), 5529-5534.
(13) Zhao, Q.; Curran, D. P.; Malacria, M.; Fensterbank, L.; Goddard, J.-P.; Lacôte, E., *Chem. Eur. J.* **2011,** *17* (36), 9911-4.
(14) Atack, T. C.; Lecker, R. M.; Cook, S. P., *J. Am. Chem. Soc.* **2014,** *136* (27), 9521-9523.
(15) Dai, Y.; Wu, F.; Zang, Z.; You, H.; Gong, H., *Chem. Eur. J.* **2012,** *18* (3), 808-12.
(16) Mori-Quiroz, L. M.; Shimkin, K. W.; Rezazadeh, S.; Kozlowski, R. A.; Watson, D. A., *Chem. Eur. J.* **2016,** *22* (44), 15654-15658.
(17) Fernández-Salas, J. A.; Maestro, M. C.; Rodríguez-Fernández, M. M.; García-Ruano, J. L.; Alonso, I., *Org. Lett.* **2013,** *15* (7), 1658-1661.
(18) Dudnik, A. S.; Fu, G. C., *J. Am. Chem. Soc.* **2012,** *134* (25), 10693-10697.
(19) Ashby, E. C.; DePriest, R. N.; Goel, A. B.; Wenderoth, B.; Pham, T. N., *J. Org. Chem.* **1984,** *49* (19), 3545-3556.
(20) Marsh, G. P.; Parsons, P. J.; McCarthy, C.; Corniquet, X. G., *Org. Lett.* **2007,** *9* (14), 2613-2616.
(21) Choudary, B. M.; Lakshmi Kantam, M.; Kavita, B.; Venkat Reddy, C.; Figueras, F., *Tetrahedron* **2000,** *56* (47), 9357-9364.
(22) Kher, S. S.; Penzo, M.; Fulle, S.; Finn, P. W.; Blackman, M. J.; Jirgensons, A., *Bioorg. Med. Chem. Lett.* **2014,** *24* (18), 4486-4489.
(23) Wahlström, N.; Stensland, B.; Bergman, J., *Tetrahedron* **2004,** *60* (9), 2147-2153.
(24) Motokura, K.; Fujita, N.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K., *J. Am. Chem. Soc.* **2005,** *127* (27), 9674-9675.
(25) Danilenko, V. M.; Tishkov, A. A.; Ioffe, S. L.; Lyapkalo, I. M.; Strelenko, Y. A.; Tartakovsky, V. A., *Synthesis* **2002,** *2002* (05), 635-647.
(26) Cho, S.-D.; Chung, J.-W.; Choi, W.-Y.; Kim, S.-K.; Yoon, Y.-J., *J. Heterocycl. Chem* **1994,** *31* (5), 1199-1208.
(27) (a) Sinhababu, A. K.; Borchardt, R. T., *Tetrahedron Lett.* **1983,** *24* (3), 227-230; (b) McNulty, J.; Steere, J. A.; Wolf, S., *Tetrahedron Lett.* **1998,** *39* (44), 8013-8016.
(28) Cai, S.; Zhang, S.; Zhao, Y.; Wang, D. Z., *Org. Lett.* **2013,** *15* (11), 2660-2663.
(29) Bhattacharjya, A.; Mukhopadhyay, R.; Pakrashi, S. C., *Synthesis* **1985,** *1985* (09), 886-887.

(30) Xiao, X.; Antony, S.; Kohlhagen, G.; Pommier, Y.; Cushman, M., *Bioorg. Med. Chem.* **2004,** *12* (19), 5147-5160.
(31) Otsuki, S.; Nishimura, S.; Takabatake, H.; Nakajima, K.; Takasu, Y.; Yagura, T.; Sakai, Y.; Hattori, A.; Kakeya, H., *Bioorg. Med. Chem. Lett.* **2013,** *23* (6), 1608-1611.
(32) Maharvi, G. M.; Bharucha, A. E.; Fauq, A. H., *Bioorg. Med. Chem. Lett.* **2013,** *23* (9), 2808-2811.
(33) Kinnunen, T.-J. J.; Haukka, M.; Pakkanen, T. T.; Pakkanen, T. A., *J. Organomet. Chem.* **2000,** *613* (2), 257-262.
(34) *Apex3 software suite; Bruker AXS, Inc., Madison, WI, 2015.*
(35) Sheldrick, G. M., *Acta Crystallogr. Sect. C* **2015,** *71* (1), 3-8.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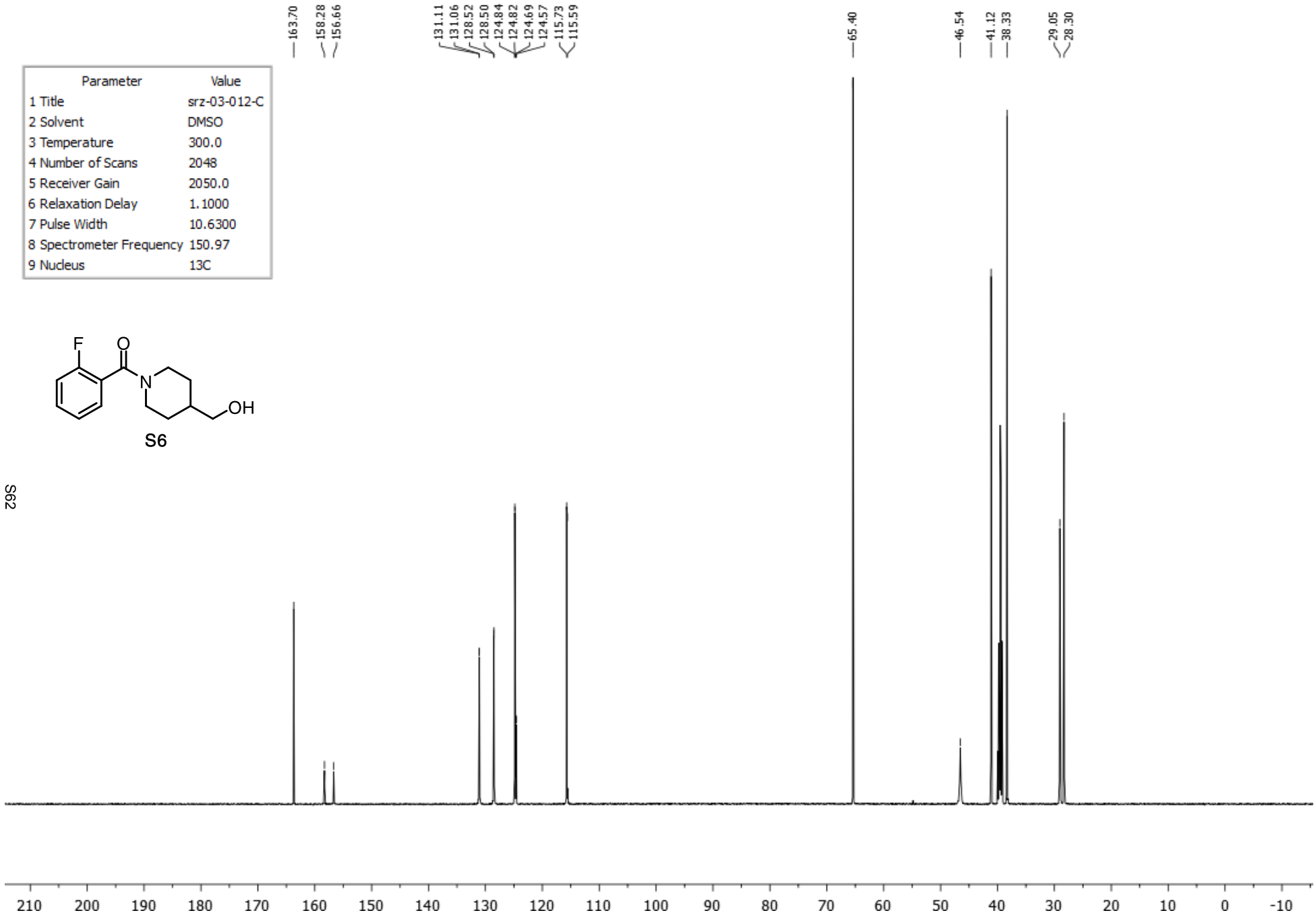
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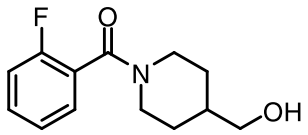
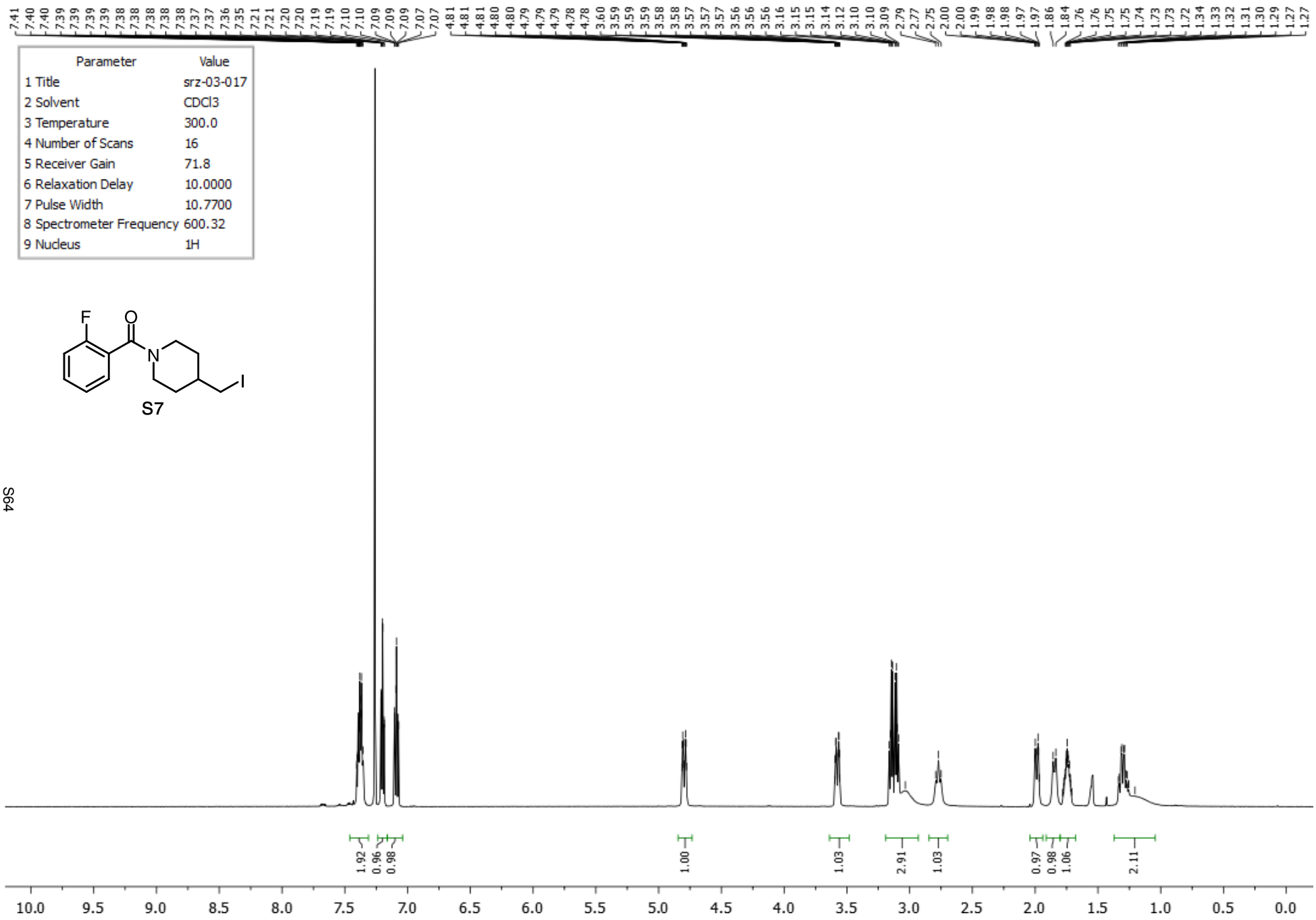


S6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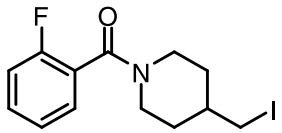

S7

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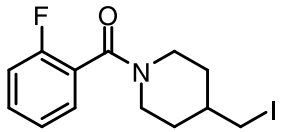
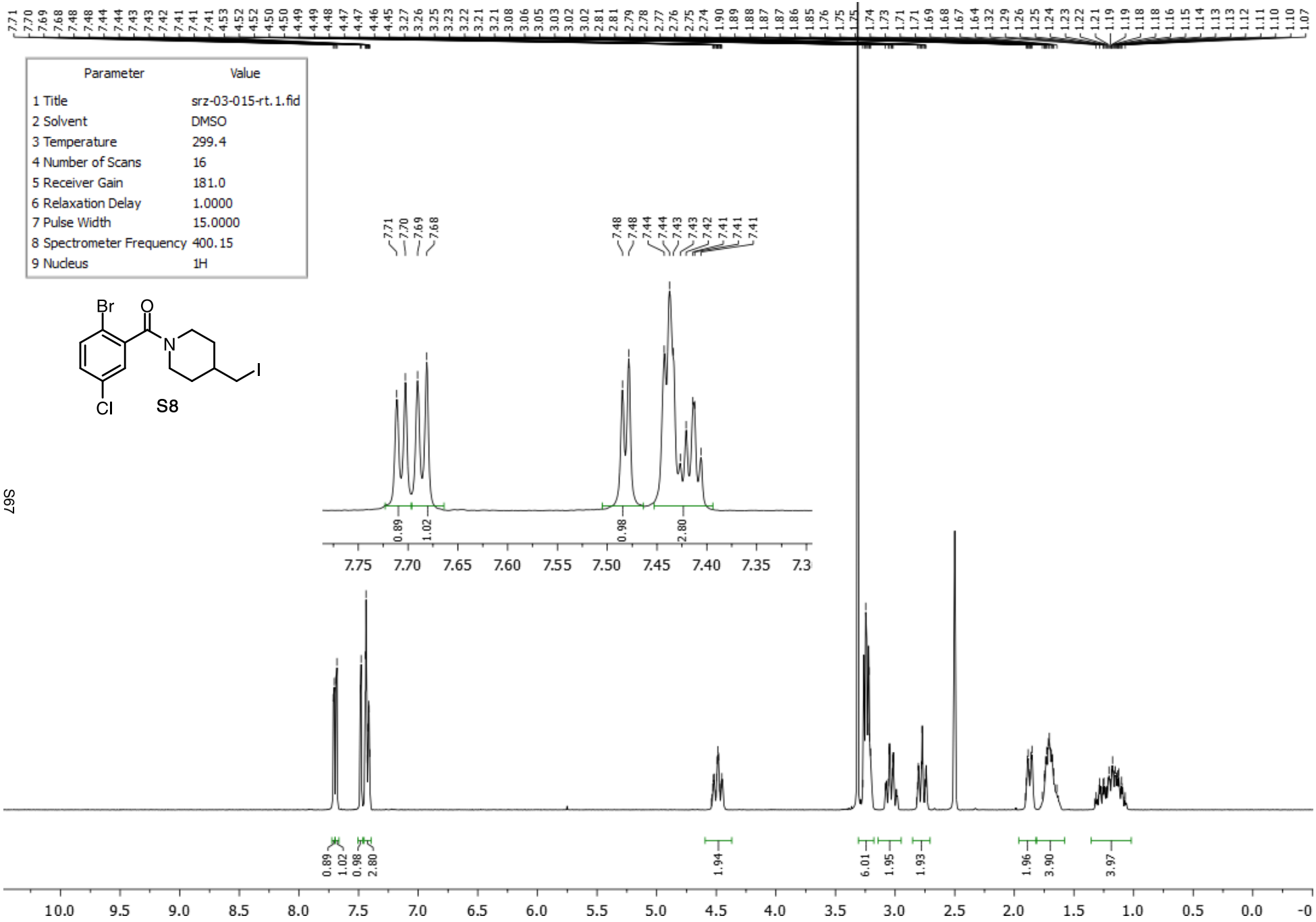
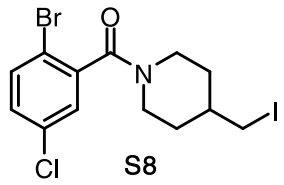
8 Spectrometer Frequency	564.81
9 Nucleus	19F



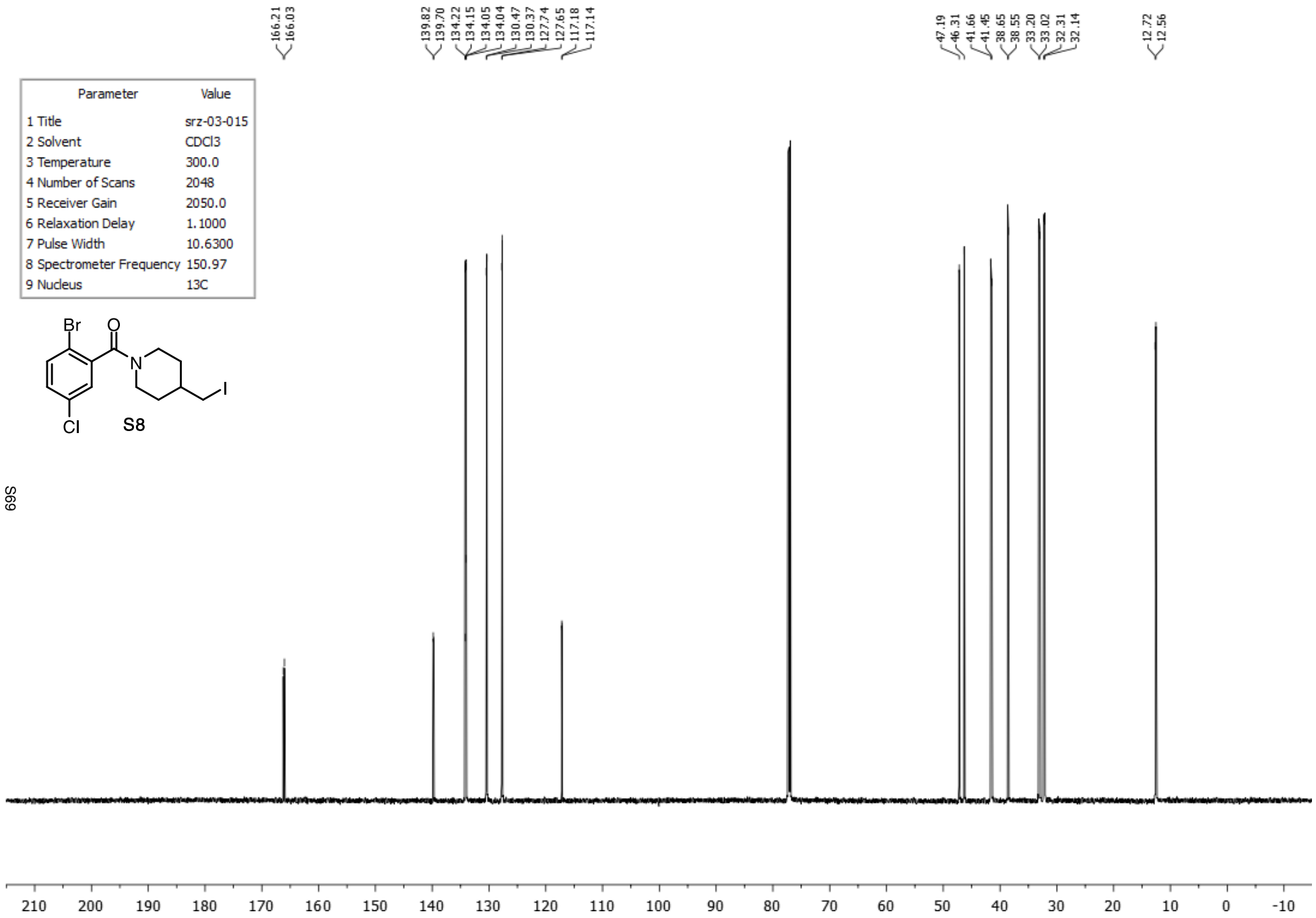
S7

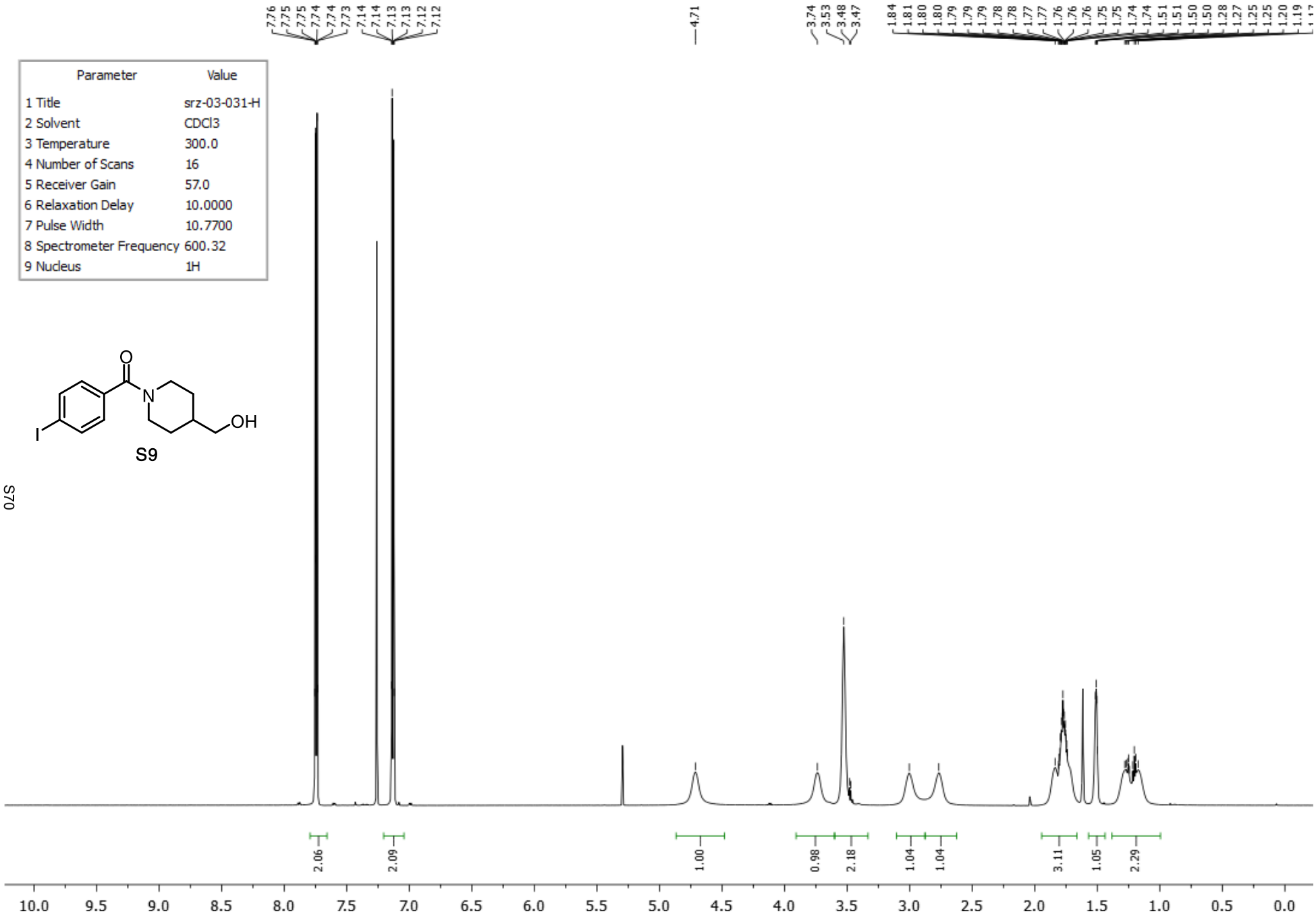

Parameter Value
1 Title srz-03-015-rt.1.fid
2 Solvent DMSO
3 Temperature 299.4
4 Number of Scans 16
5 Receiver Gain 181.0
6 Relaxation Delay 1.0000
7 Pulse Width 15.0000
8 Spectrometer Frequency 400.15
9 Nucleus 1H
Br
O
N
I
Cl
S8
0.89
1.02
0.98
2.80
1.94
6.01
1.95
1.93
1.96
3.90
3.97

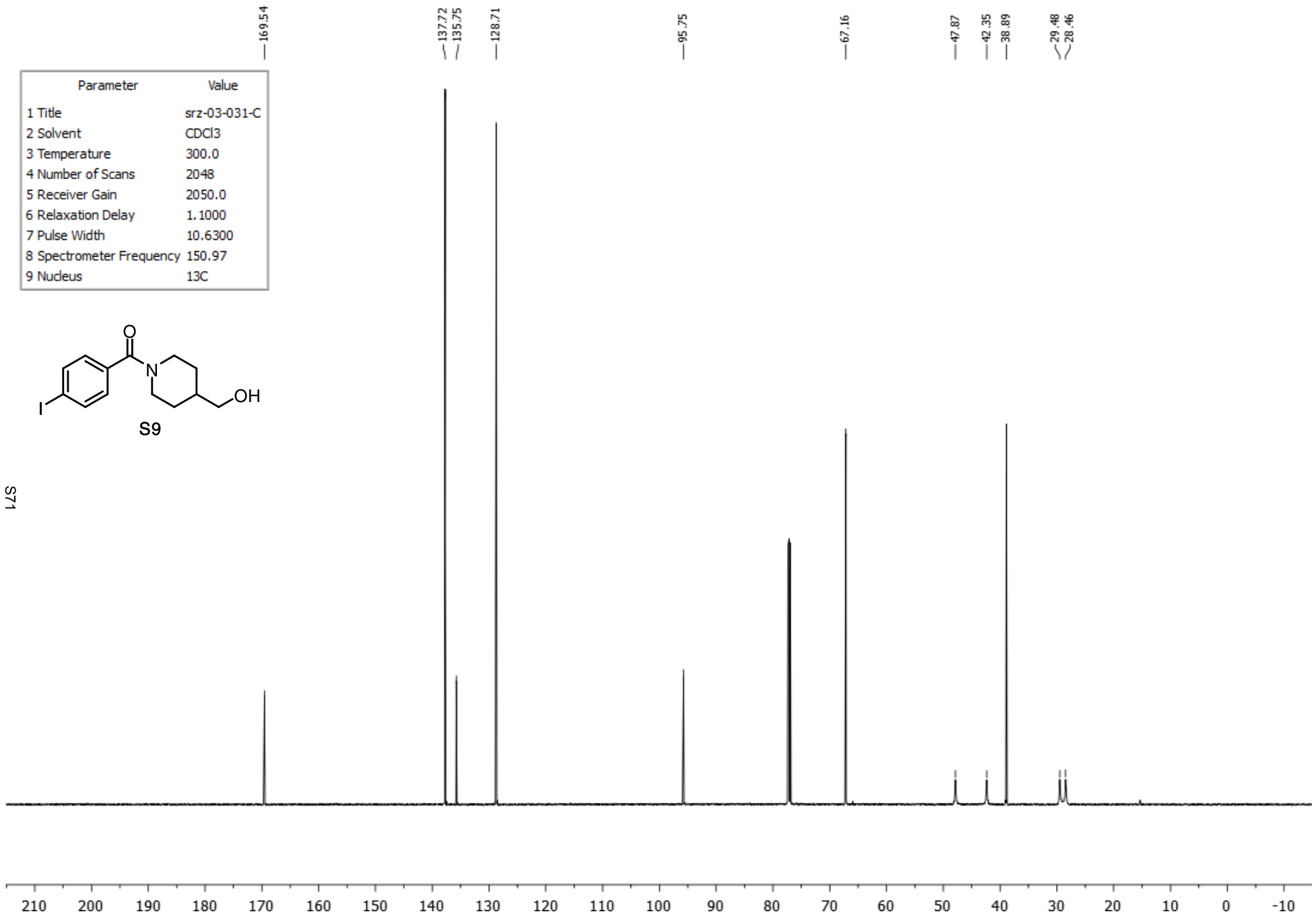
Parameter	Value
1 Title	srz-03-015-340K.1.fid
2 Solvent	DMSO
3 Temperature	344.2
4 Number of Scans	16
5 Receiver Gain	203.0
6 Relaxation Delay	1.0000
7 Pulse Width	15.0000
8 Spectrometer Frequency	400.15
9 Nucleus	1H



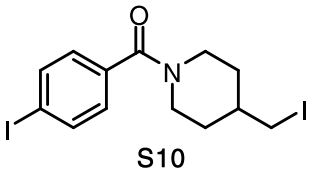
S8


166.21
166.03
139.82
139.70
134.22
134.15
134.05
134.04
130.47
130.37
127.74
127.65
117.18
117.14
47.19
46.31
41.66
41.45
38.65
38.55
33.20
33.02
32.31
32.14
12.72
12.56
Parameter Value
1 Title srz-03-015
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
Br
O
N
I
Cl
S8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

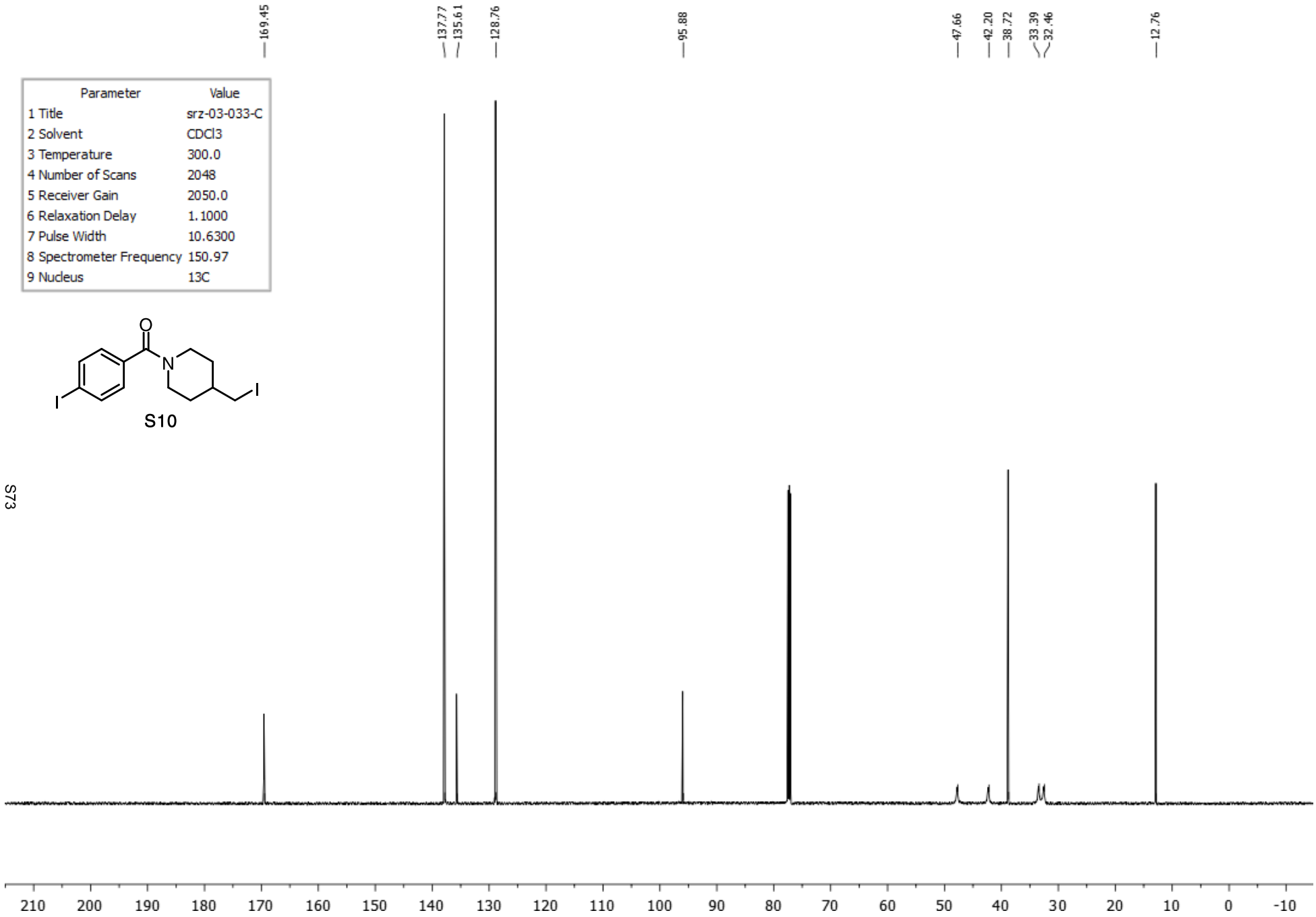

Parameter Value
1 Title srz-03-031-H
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 57.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
O
N
OH
I
S9
S70
7.76 7.75 7.75 7.74 7.74 7.73 7.14 7.14 7.13 7.13 7.12 7.12
4.71
3.74 3.53 3.48 3.47
1.84 1.81 1.80 1.80 1.79 1.79 1.79 1.78 1.78 1.77 1.77 1.76 1.76 1.76 1.75 1.75 1.74 1.74 1.51 1.51 1.50 1.50 1.28 1.27 1.25 1.25 1.20 1.19
2.06 2.09 1.00 0.98 2.18 1.04 1.04 3.11 1.05 2.29
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

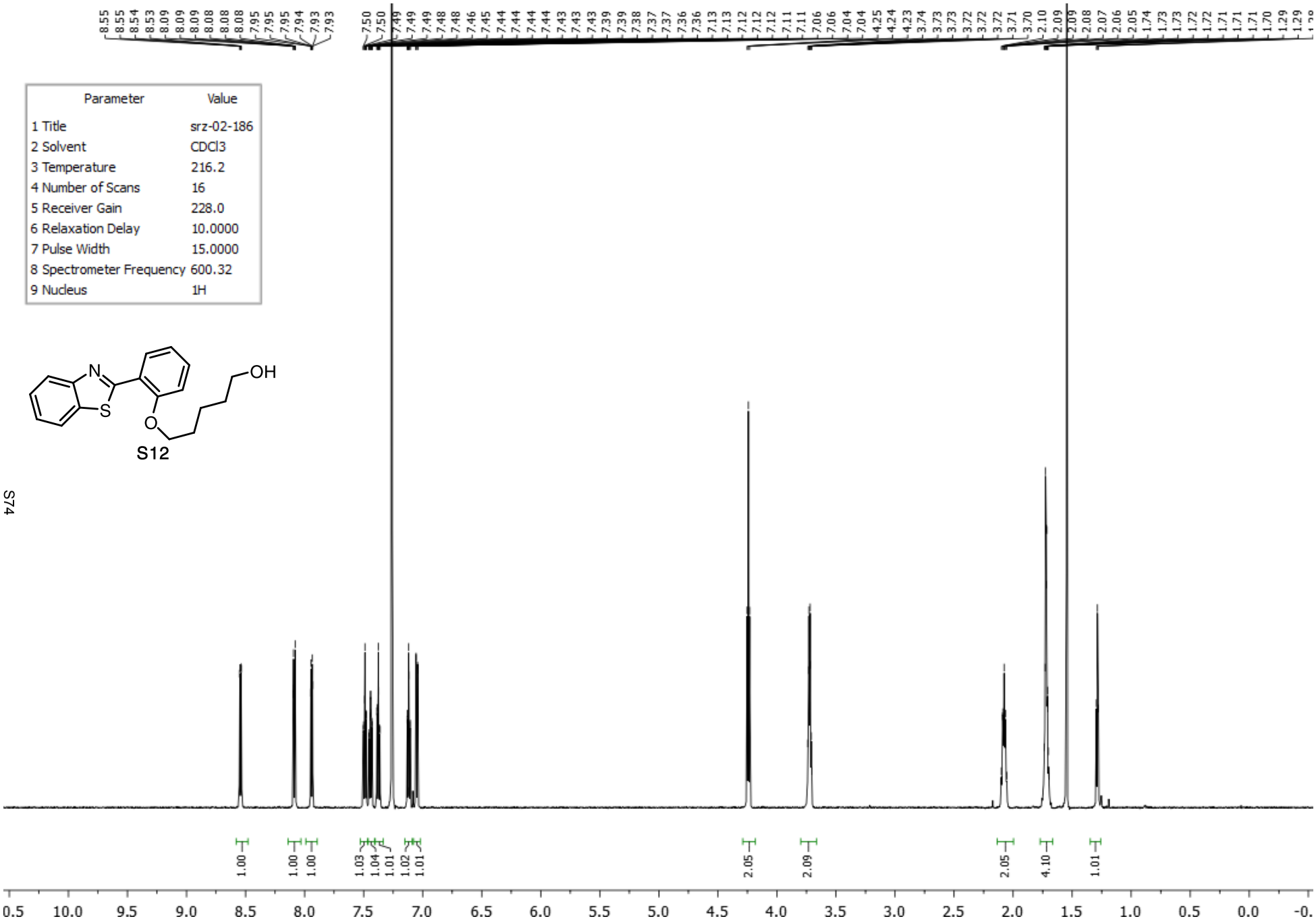

169.54
137.72
135.75
128.71
95.75
67.16
47.87
42.35
38.89
29.48
28.46
Parameter Value
1 Title srz-03-031-C
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
O
N
OH
I
S9
S71
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

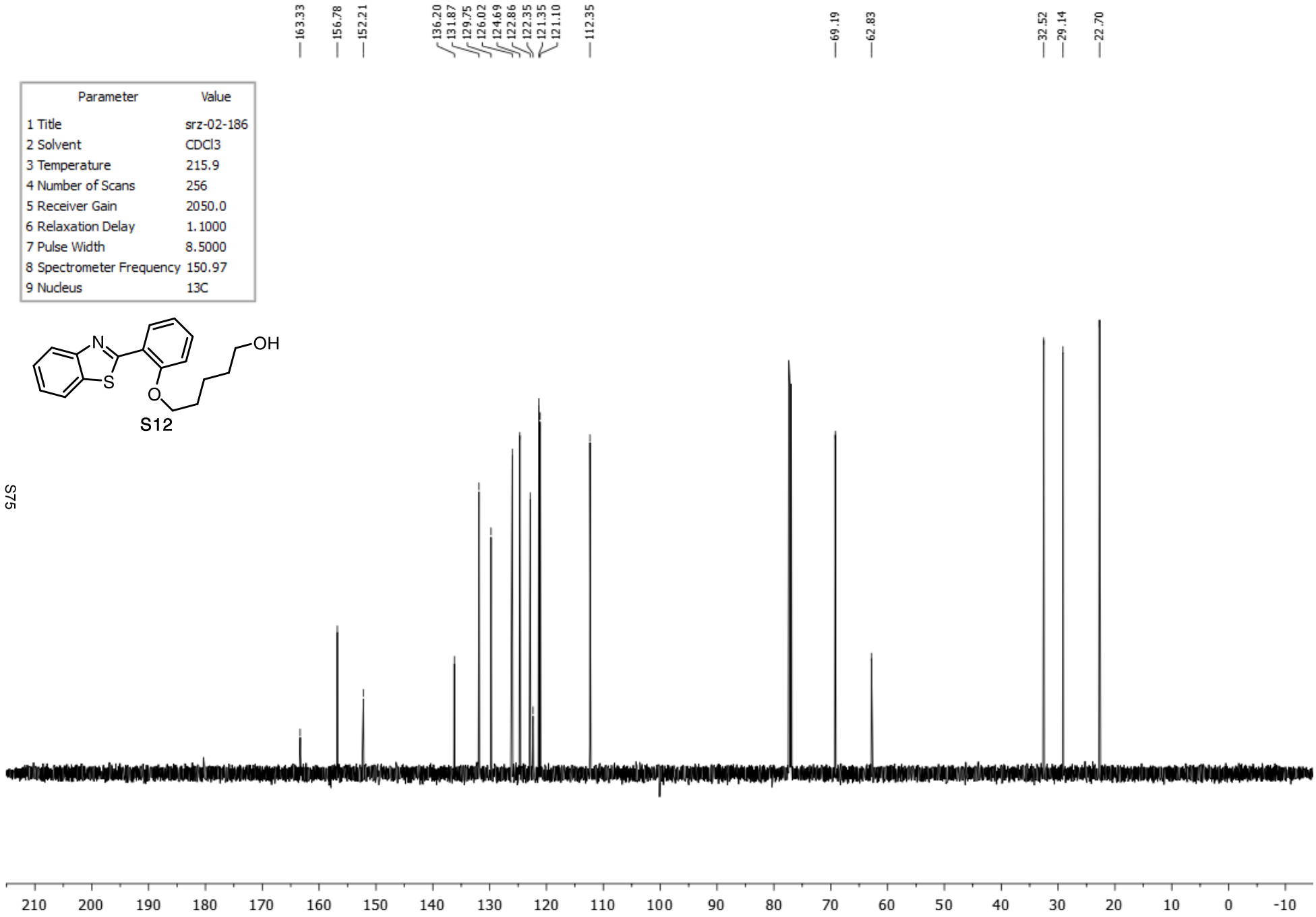
	Parameter	Value
1	Title	srz-03-033-H
2	Solvent	CDCl3
3	Temperature	300.0
4	Number of Scans	16
5	Receiver Gain	71.8
6	Relaxation Delay	10.0000
7	Pulse Width	10.7700
8	Spectrometer Frequency	600.32
9	Spectral Width	12335.5
10	Nucleus	1H

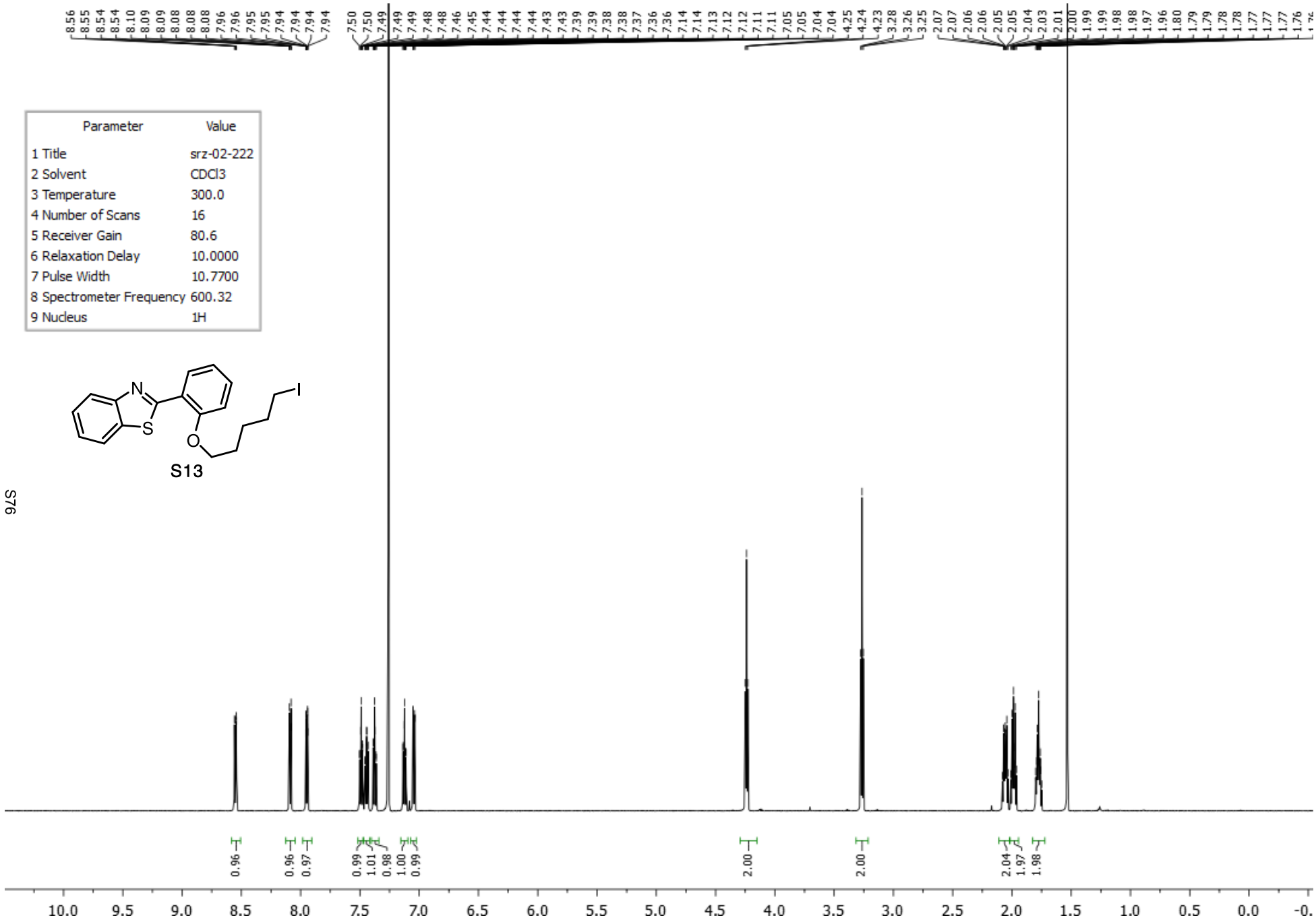


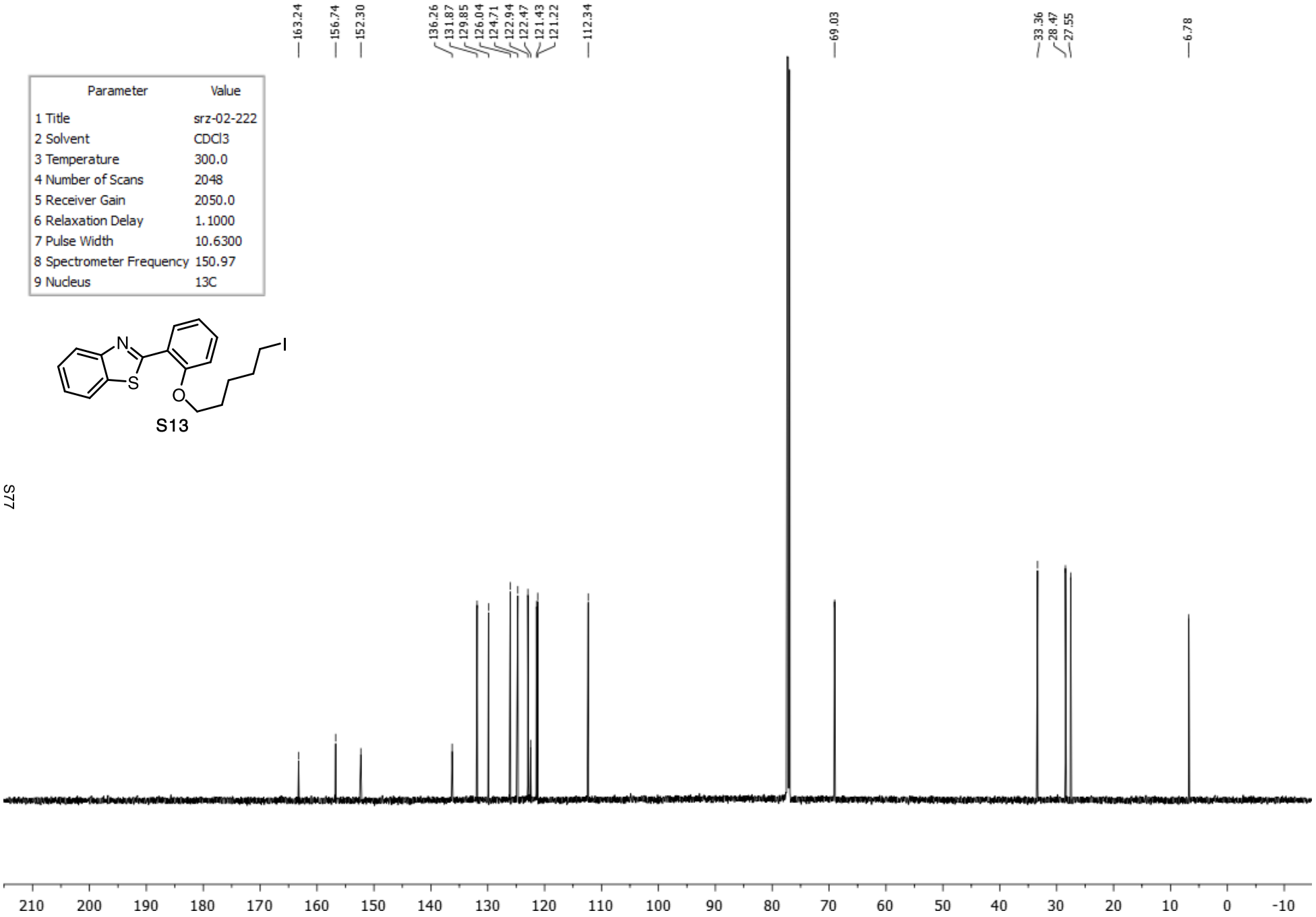
S10

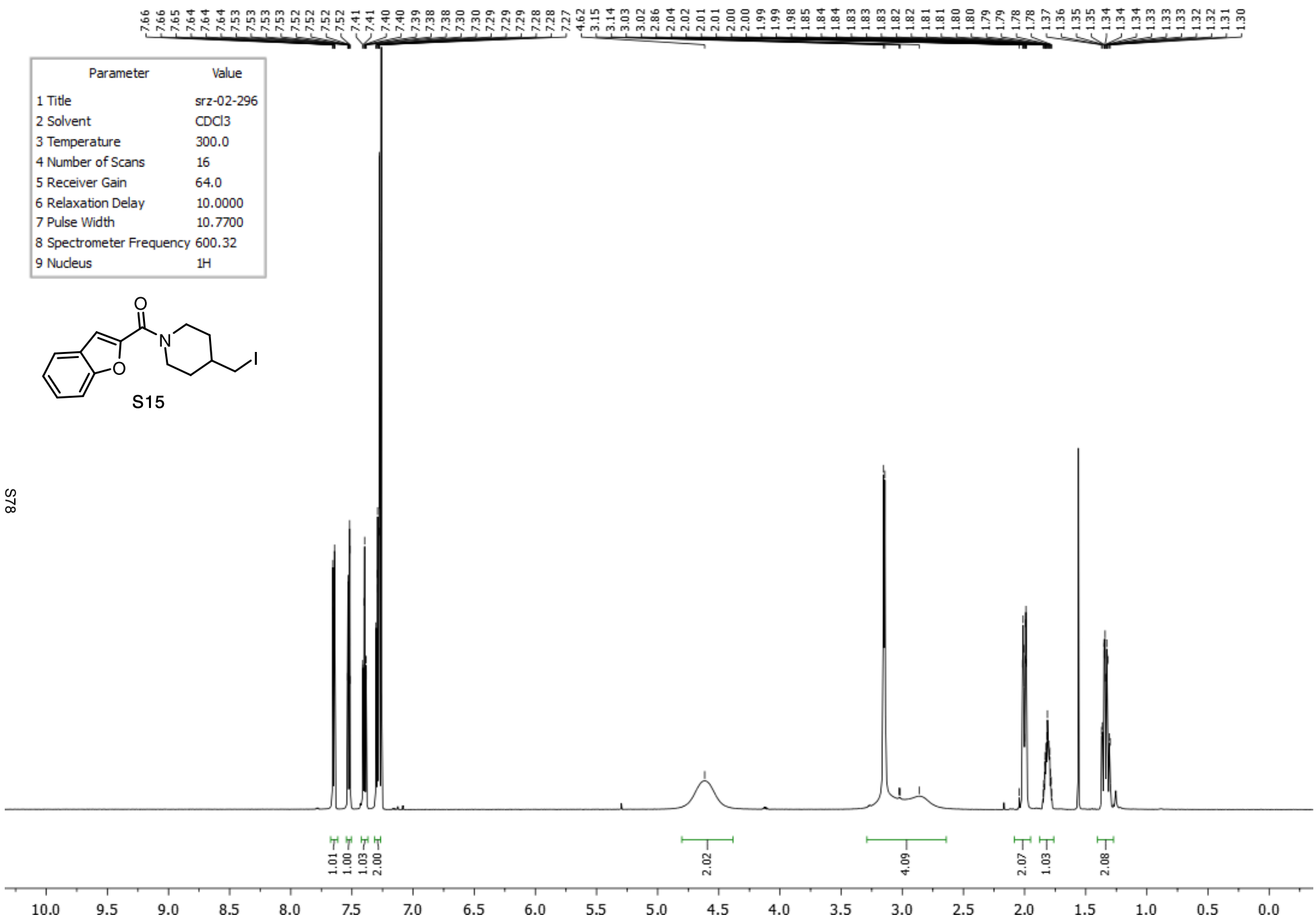

169.45
137.77
135.61
128.76
95.88
47.66
42.20
38.72
33.39
32.46
12.76
Parameter Value
1 Title srz-03-033-C
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
O
N
I
I
S10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


Parameter Value
1 Title srz-02-186
2 Solvent CDCl3
3 Temperature 216.2
4 Number of Scans 16
5 Receiver Gain 228.0
6 Relaxation Delay 10.0000
7 Pulse Width 15.0000
8 Spectrometer Frequency 600.32
9 Nucleus 1H
N
S
O
OH
S12
1.00
1.00
1.00
1.03
1.04
1.01
1.02
1.01
2.05
2.09
2.05
4.10
1.01

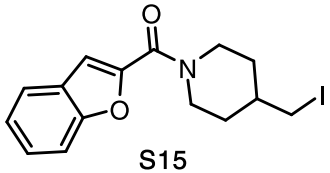

163.33
156.78
152.21
136.20
131.87
129.75
126.02
124.69
122.86
122.35
121.35
121.10
112.35
69.19
62.83
32.52
29.14
22.70
Parameter Value
1 Title srz-02-186
2 Solvent CDCl3
3 Temperature 215.9
4 Number of Scans 256
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 8.5000
8 Spectrometer Frequency 150.97
9 Nucleus 13C
N
S
O
OH
S12
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


Parameter Value
1 Title srz-02-222
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 80.6
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
N
S
O
I
S13
0.96
0.96
0.97
0.99
1.01
0.98
1.00
0.99
2.00
2.00
2.04
1.97
1.98
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


163.24
156.74
152.30
136.26
131.87
129.85
126.04
124.71
122.94
122.47
121.43
121.22
112.34
69.03
33.36
28.47
27.55
6.78
Parameter Value
1 Title srz-02-222
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
N
S
O
I
S13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

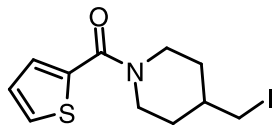

Parameter Value
1 Title srz-02-296
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 64.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
O
N
O
I
S15
1.01
1.00
1.03
2.00
2.02
4.09
2.07
1.03
2.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

	Parameter	Value
1	Title	srz-02-296.1.fid
2	Solvent	CDCl3
3	Temperature	298.2
4	Number of Scans	1024
5	Receiver Gain	512.0
6	Relaxation Delay	2.0000
7	Pulse Width	9.2500
8	Spectrometer Frequency	100.62
9	Spectral Width	23980.8
10	Nucleus	13C



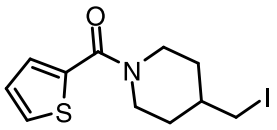
S15

Parameter	Value
1 Title	srz-02-203
2 Solvent	CDCl3
3 Temperature	297.2
4 Number of Scans	16
5 Receiver Gain	71.8
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H

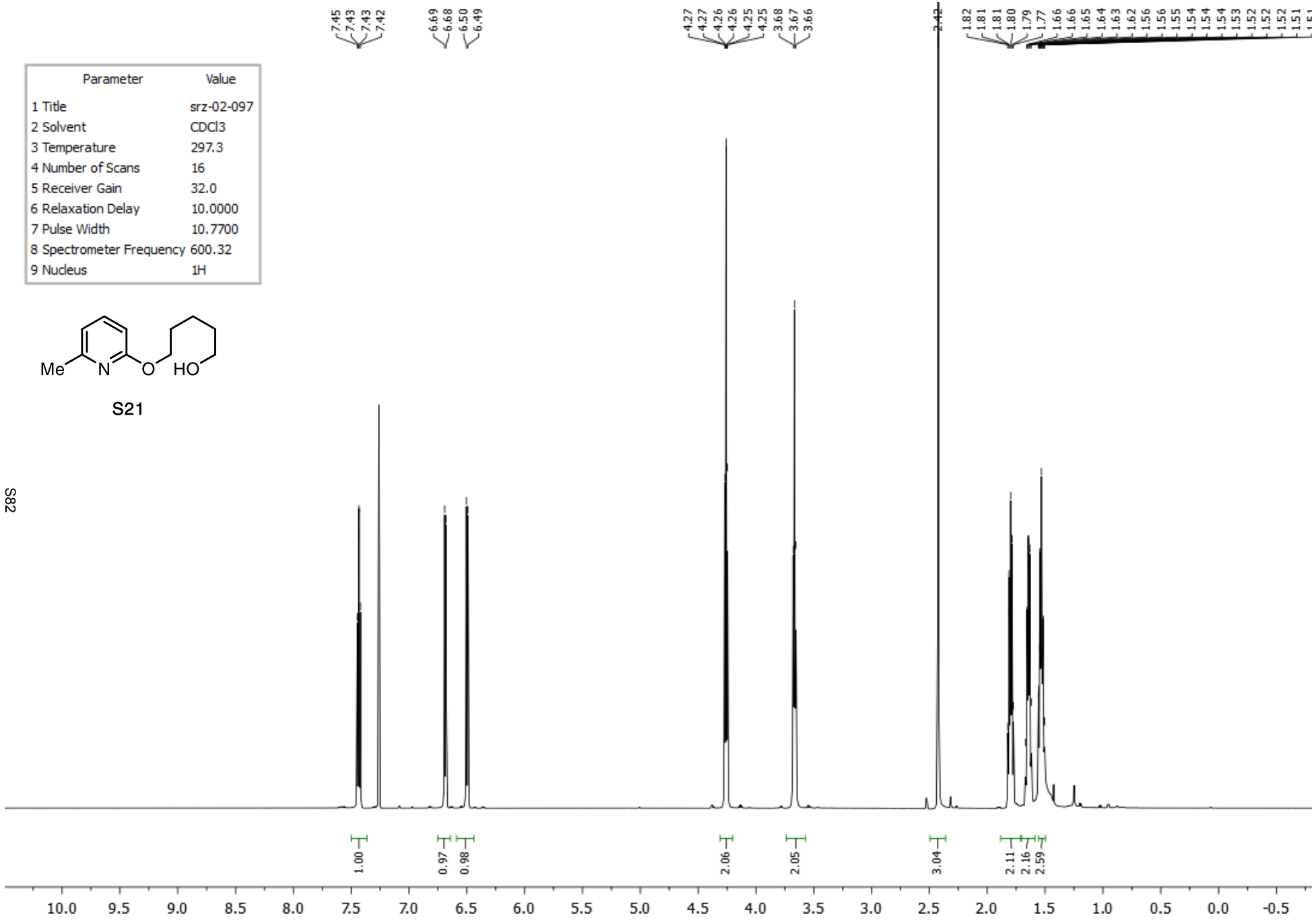


S18

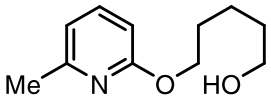
Parameter	Value
1 Title	srz-02-203.1.fid
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	1024
5 Receiver Gain	512.0
6 Relaxation Delay	2.0000
7 Pulse Width	9.2500
8 Spectrometer Frequency	100.62
9 Nucleus	13C



S18

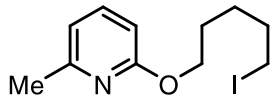

Parameter Value
1 Title srz-02-097
2 Solvent CDCl3
3 Temperature 297.3
4 Number of Scans 16
5 Receiver Gain 32.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
Me
N
O
HO
S21
7.45 7.43 7.43 7.42
6.69 6.68 6.50 6.49
4.27 4.27 4.26 4.26 4.25 4.25
3.68 3.67 3.66
2.42
1.82 1.81 1.81 1.80 1.79 1.77 1.66 1.66 1.65 1.64 1.63 1.62 1.56 1.56 1.55 1.54 1.54 1.54 1.53 1.52 1.52 1.52 1.51
1.00 0.97 0.98 2.06 2.05 3.04 2.11 2.16 2.59
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

Parameter	Value
1 Title	srz-02-097
2 Solvent	CDCl3
3 Temperature	298.9
4 Number of Scans	256
5 Receiver Gain	2050.0
6 Relaxation Delay	5.0000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C

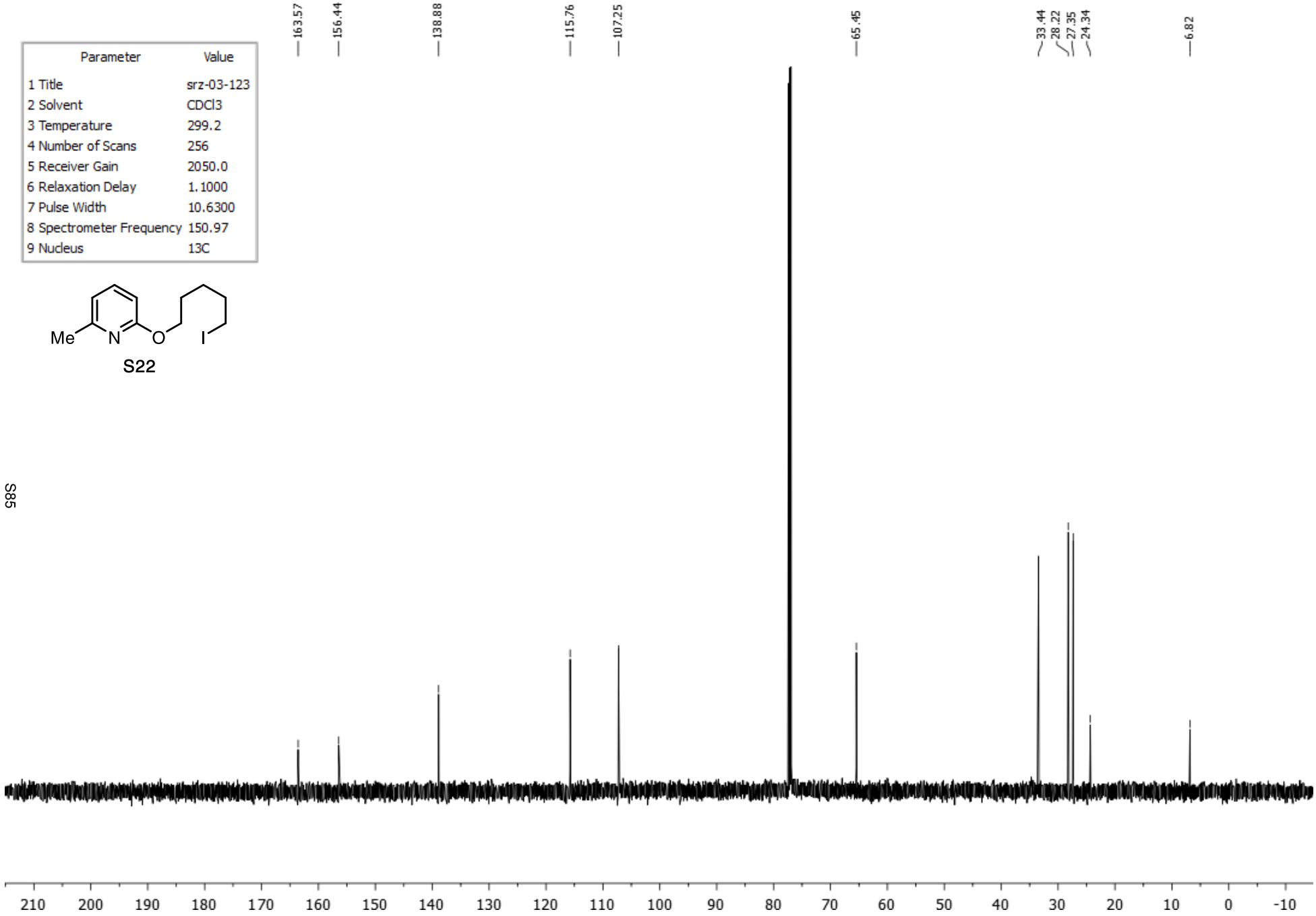


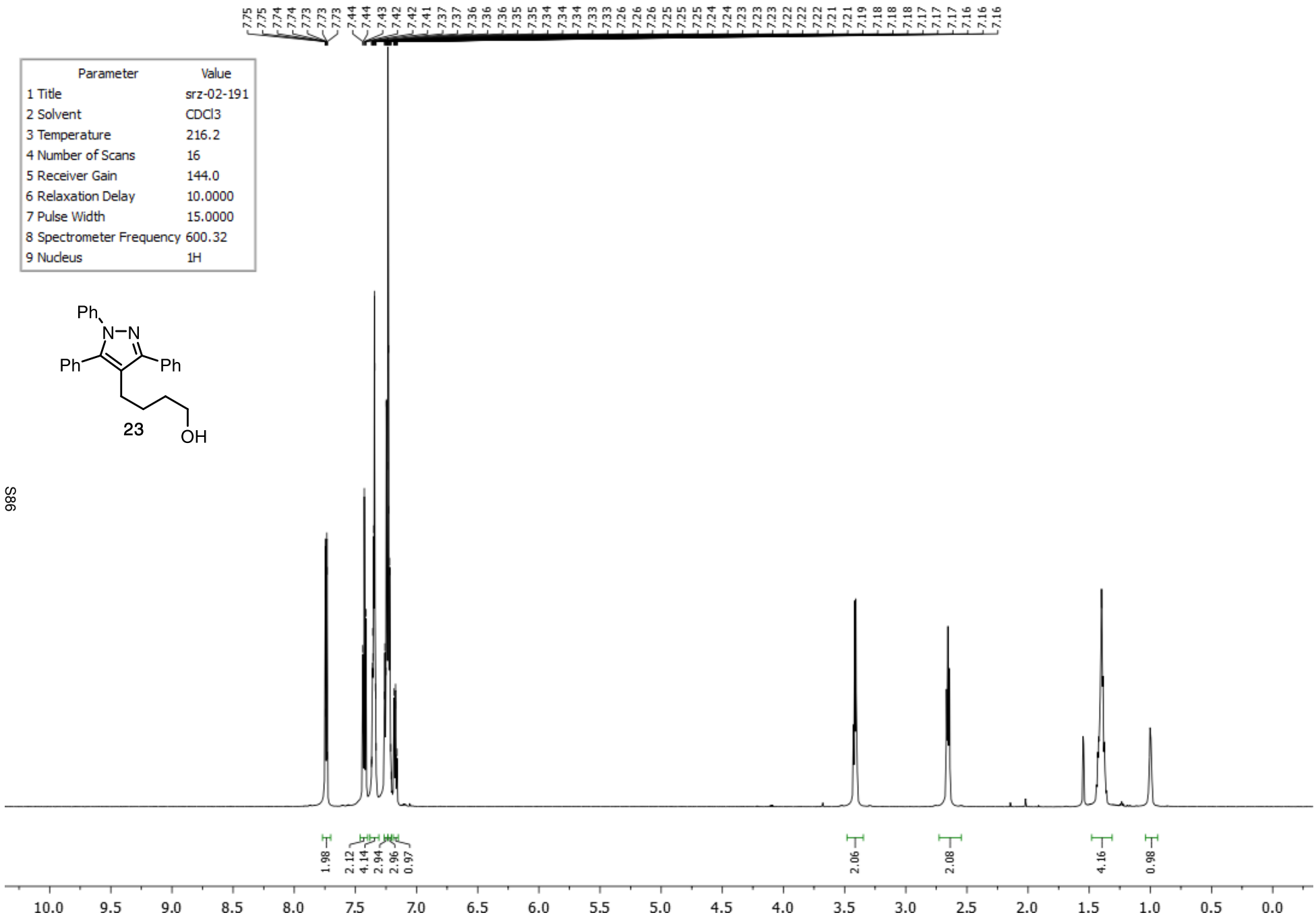
S21

Parameter	Value
1 Title	srz-03-123
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	16
5 Receiver Gain	57.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H

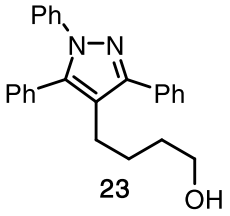


S22

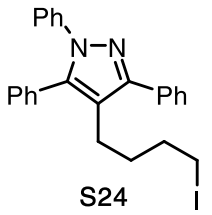

163.57
156.44
138.88
115.76
107.25
65.45
33.44
28.22
27.35
24.34
6.82
Parameter Value
1 Title srz-03-123
2 Solvent CDCl3
3 Temperature 299.2
4 Number of Scans 256
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
Me
N
O
I
S22
S85
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.75 7.75 7.74 7.74 7.73 7.73 7.73 7.44 7.44 7.43 7.42 7.42 7.41 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.26 7.26 7.25 7.25 7.25 7.24 7.23 7.23 7.23 7.22 7.22 7.21 7.21 7.19 7.18 7.18 7.18 7.17 7.17 7.17 7.16 7.16 7.16
Parameter Value
1 Title srz-02-191
2 Solvent CDCl3
3 Temperature 216.2
4 Number of Scans 16
5 Receiver Gain 144.0
6 Relaxation Delay 10.0000
7 Pulse Width 15.0000
8 Spectrometer Frequency 600.32
9 Nucleus 1H
Ph
N–N
Ph
Ph
23
OH
S86
1.98 2.12 4.14 2.94 2.96 0.97 2.06 2.08 4.16 0.98
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

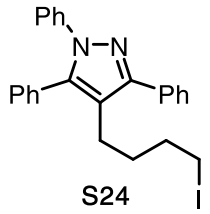
Parameter	Value
1 Title	srz-02-191
2 Solvent	CDCl3
3 Temperature	216.3
4 Number of Scans	256
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	8.5000
8 Spectrometer Frequency	150.97
9 Nucleus	13C



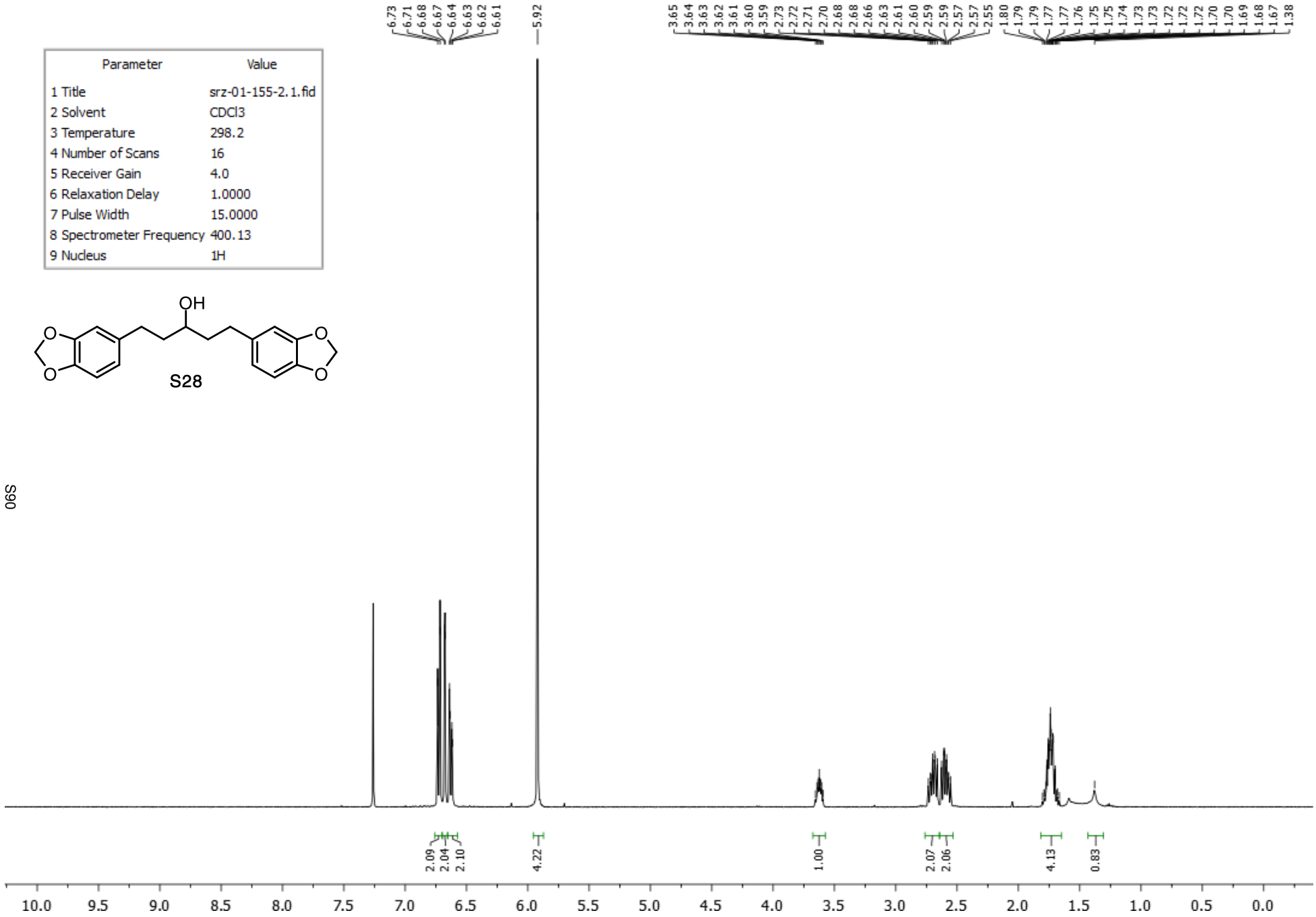
Parameter	Value
1 Title	srz-03-007
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	32.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



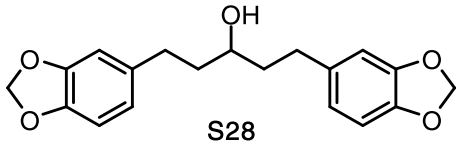
Parameter	Value
1 Title	srz-03-007
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	256
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C



S24

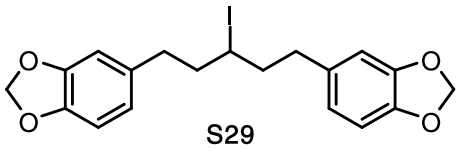

Parameter Value
1 Title srz-01-155-2.1.fid
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 16
5 Receiver Gain 4.0
6 Relaxation Delay 1.0000
7 Pulse Width 15.0000
8 Spectrometer Frequency 400.13
9 Nucleus 1H
OH
S28
S90
6.73 6.71 6.68 6.67 6.64 6.63 6.62 6.61
5.92
3.65 3.64 3.63 3.62 3.61 3.60 3.59 2.73 2.72 2.71 2.70 2.68 2.68 2.66 2.63 2.61 2.60 2.59 2.59 2.57 2.57 2.55
1.80 1.79 1.79 1.77 1.77 1.76 1.75 1.75 1.74 1.73 1.73 1.72 1.72 1.72 1.70 1.70 1.69 1.68 1.67 1.38
2.09 2.04 2.10 4.22 1.00 2.07 2.06 4.13 0.83
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

Parameter	Value
1 Title	srz-01-155-2
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	256
5 Receiver Gain	2050.0
6 Relaxation Delay	5.0000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C

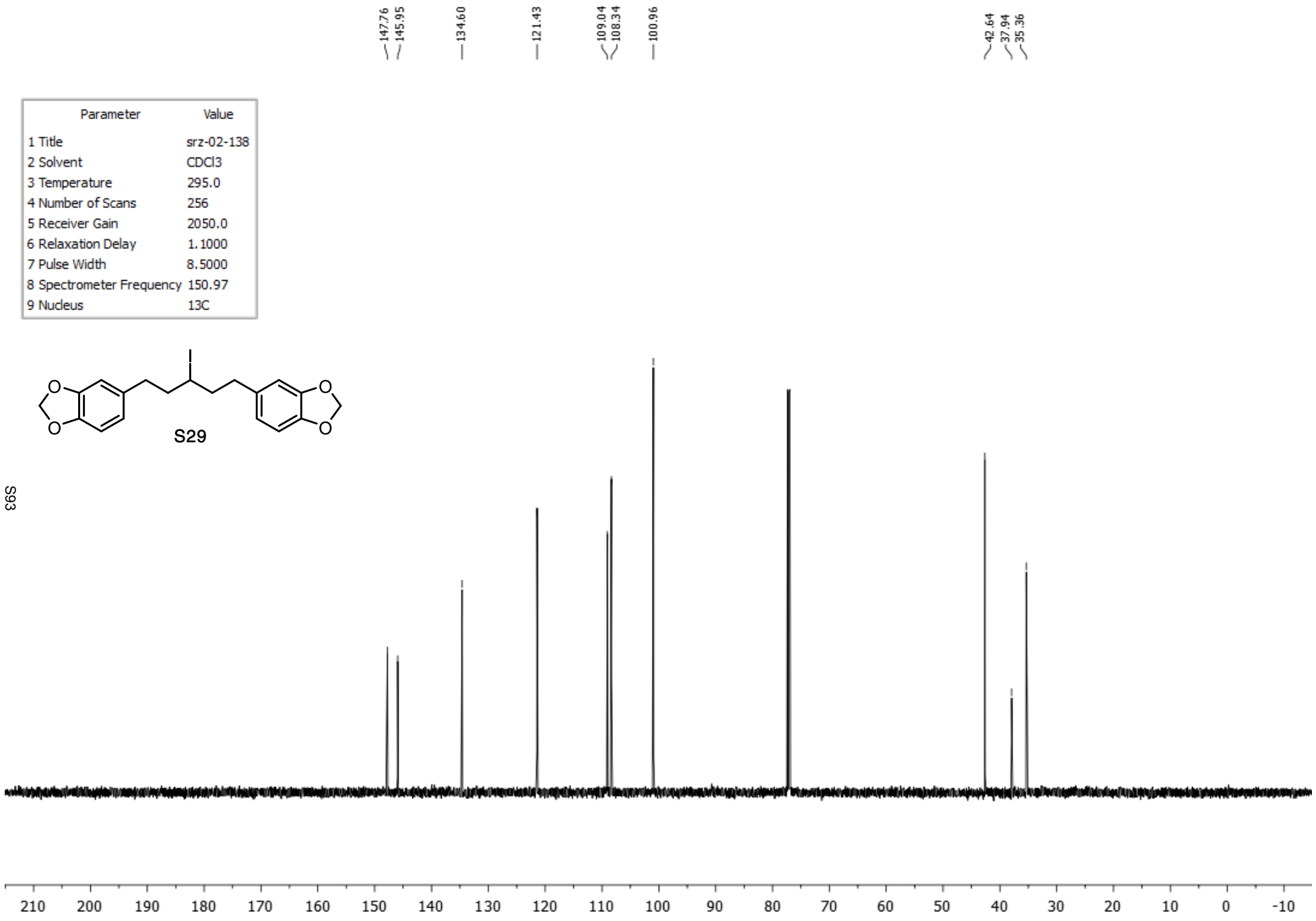


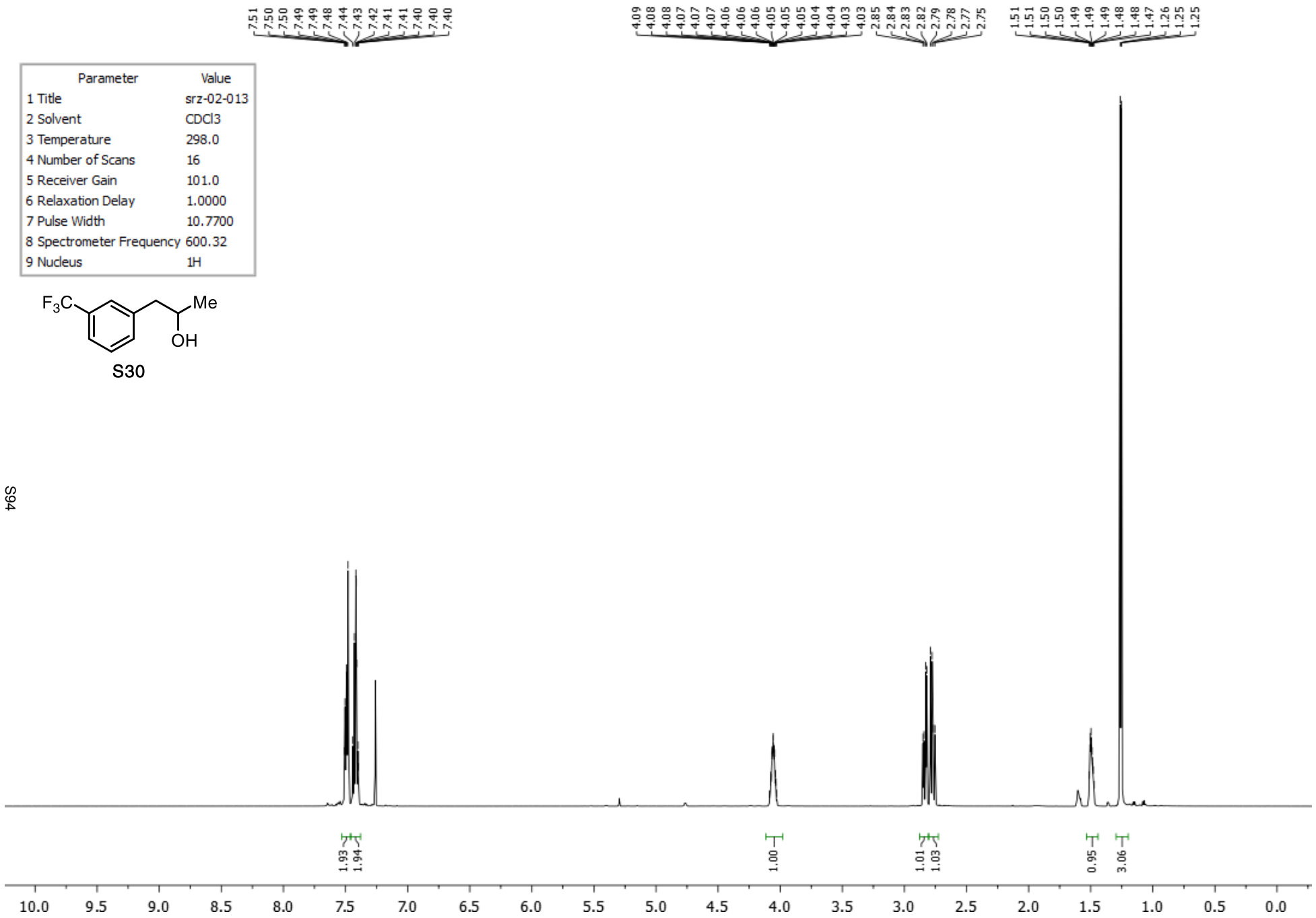
S28

Parameter	Value
1 Title	srz-02-138
2 Solvent	CDCl3
3 Temperature	295.0
4 Number of Scans	16
5 Receiver Gain	322.0
6 Relaxation Delay	1.0000
7 Pulse Width	15.0000
8 Spectrometer Frequency	600.32
9 Nucleus	1H

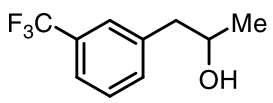


S29


147.76
145.95
134.60
121.43
109.04
108.34
100.96
42.64
37.94
35.36
Parameter Value
1 Title srz-02-138
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 256
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 8.5000
8 Spectrometer Frequency 150.97
9 Nucleus 13C
S29
S93
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

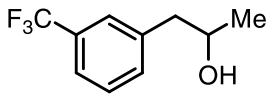

7.51 7.50 7.50 7.49 7.49 7.48 7.44 7.43 7.42 7.41 7.41 7.40 7.40 7.40
4.09 4.08 4.08 4.07 4.07 4.07 4.06 4.06 4.06 4.05 4.05 4.05 4.04 4.04 4.03 4.03
2.85 2.84 2.83 2.82 2.79 2.78 2.77 2.75
1.51 1.51 1.50 1.50 1.49 1.49 1.48 1.48 1.47 1.26 1.25 1.25
Parameter Value
1 Title srz-02-013
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 101.0
6 Relaxation Delay 1.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
F3C
Me
OH
S30
1.93
1.94
1.00
1.01
1.03
0.95
3.06
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

Parameter	Value
1 Title	srz-02-013
2 Solvent	CDCl3
3 Temperature	298.0
4 Number of Scans	256
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C



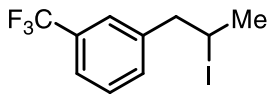
S30

Parameter	Value
1 Title	srz-02-013.1.fid
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	16
5 Receiver Gain	181.0
6 Relaxation Delay	1.0000
7 Pulse Width	15.0300
8 Spectrometer Frequency	376.46
9 Nucleus	19F



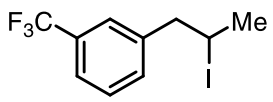
S30

Parameter	Value
1 Title	srz-02-245
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	32.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



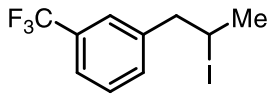
S31

Parameter	Value
1 Title	srz-02-245
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	1024
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C

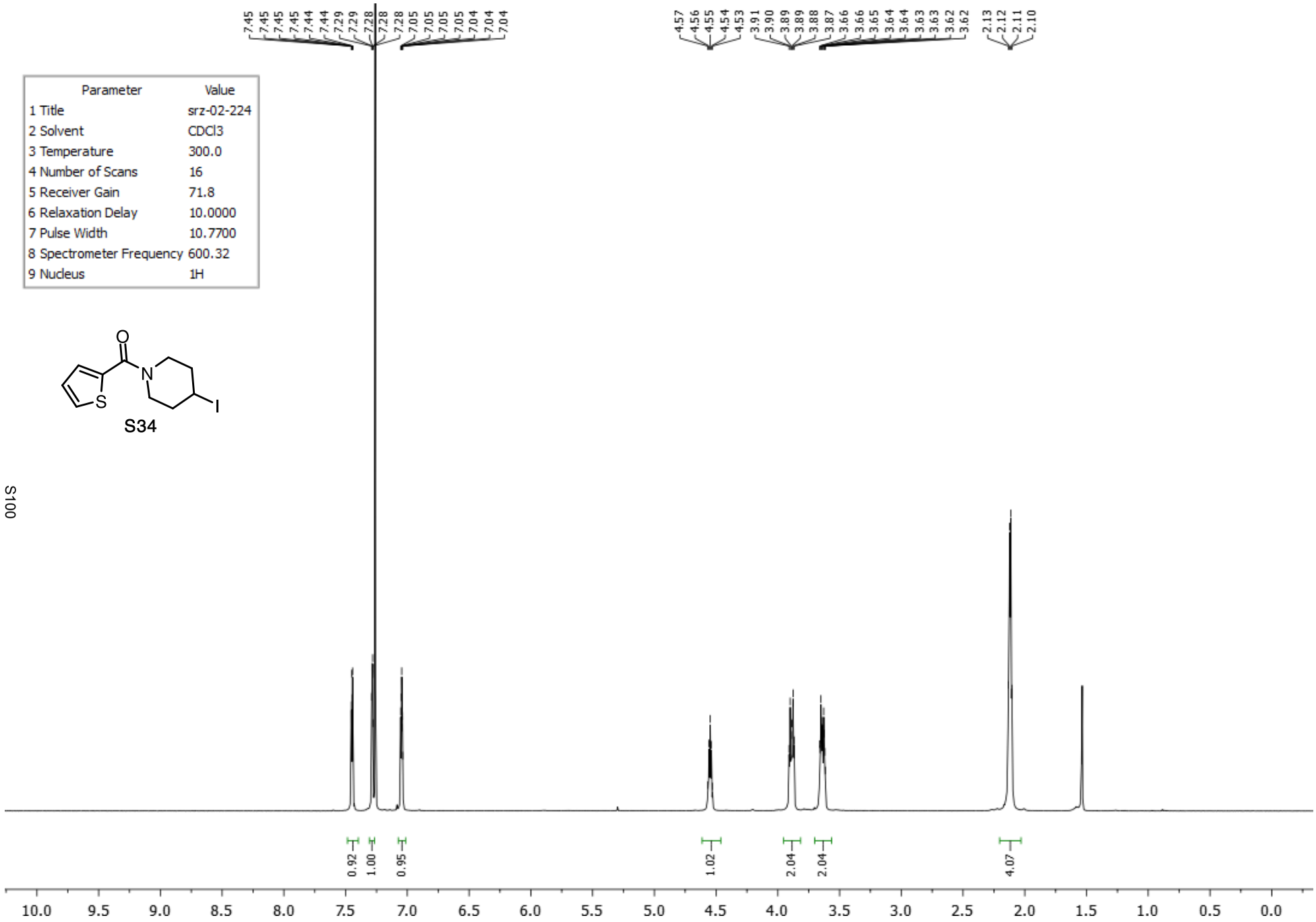


S31

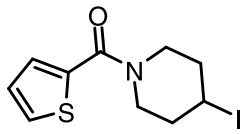
Parameter	Value
1 Title	srz-02-245
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	32
5 Receiver Gain	161.0
6 Relaxation Delay	3.0000
7 Pulse Width	11.6200
8 Spectrometer Frequency	564.81
9 Nucleus	19F



S31

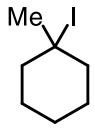

7.45 7.45 7.45 7.44 7.44 7.29 7.29 7.28 7.28 7.28 7.05 7.05 7.05 7.05 7.04 7.04 7.04
4.57 4.56 4.55 4.54 4.53 3.91 3.90 3.89 3.89 3.88 3.87 3.66 3.66 3.65 3.64 3.64 3.63 3.63 3.62 3.62
2.13 2.12 2.11 2.10
Parameter Value
1 Title srz-02-224
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 71.8
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
O
N
S
I
S34
S100
0.92 1.00 0.95 1.02 2.04 2.04 4.07
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

Parameter	Value
1 Title	srz-02-224
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	2048
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C



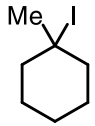
S34

Parameter	Value
1 Title	srz-03-104
2 Solvent	CDCl3
3 Temperature	297.8
4 Number of Scans	16
5 Receiver Gain	161.0
6 Relaxation Delay	1.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H

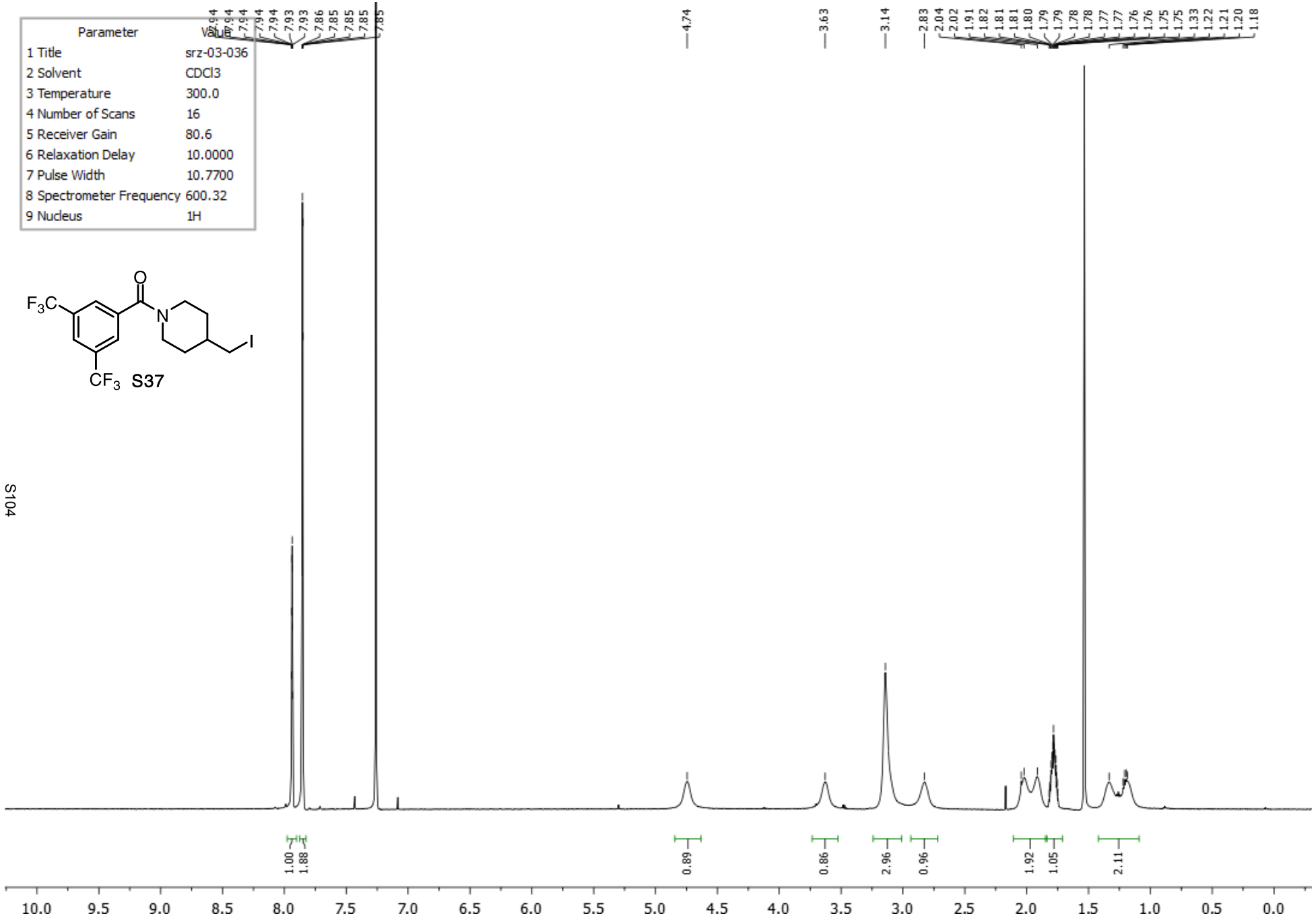


S36

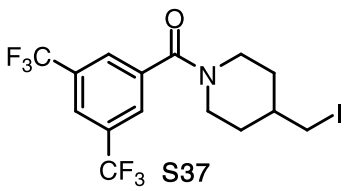
Parameter	Value
1 Title	srz-03-104
2 Solvent	CDCl3
3 Temperature	299.9
4 Number of Scans	2048
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C



S36

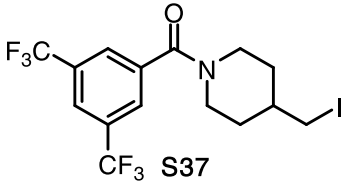

Parameter Value
1 Title srz-03-036
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 80.6
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
F3C
O
N
I
CF3
S37
7.94 7.94 7.94 7.94 7.94 7.93 7.93 7.86 7.85 7.85 7.85
4.74
3.63
3.14
2.83 2.04 2.02 1.91 1.82 1.81 1.81 1.80 1.79 1.79 1.78 1.78 1.77 1.77 1.76 1.76 1.75 1.75 1.33 1.22 1.21 1.20 1.18
1.00 1.88 0.89 0.86 2.96 0.96 1.92 1.05 2.11
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

Parameter	Value
1 Title	srz-03-036-C
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	2048
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C

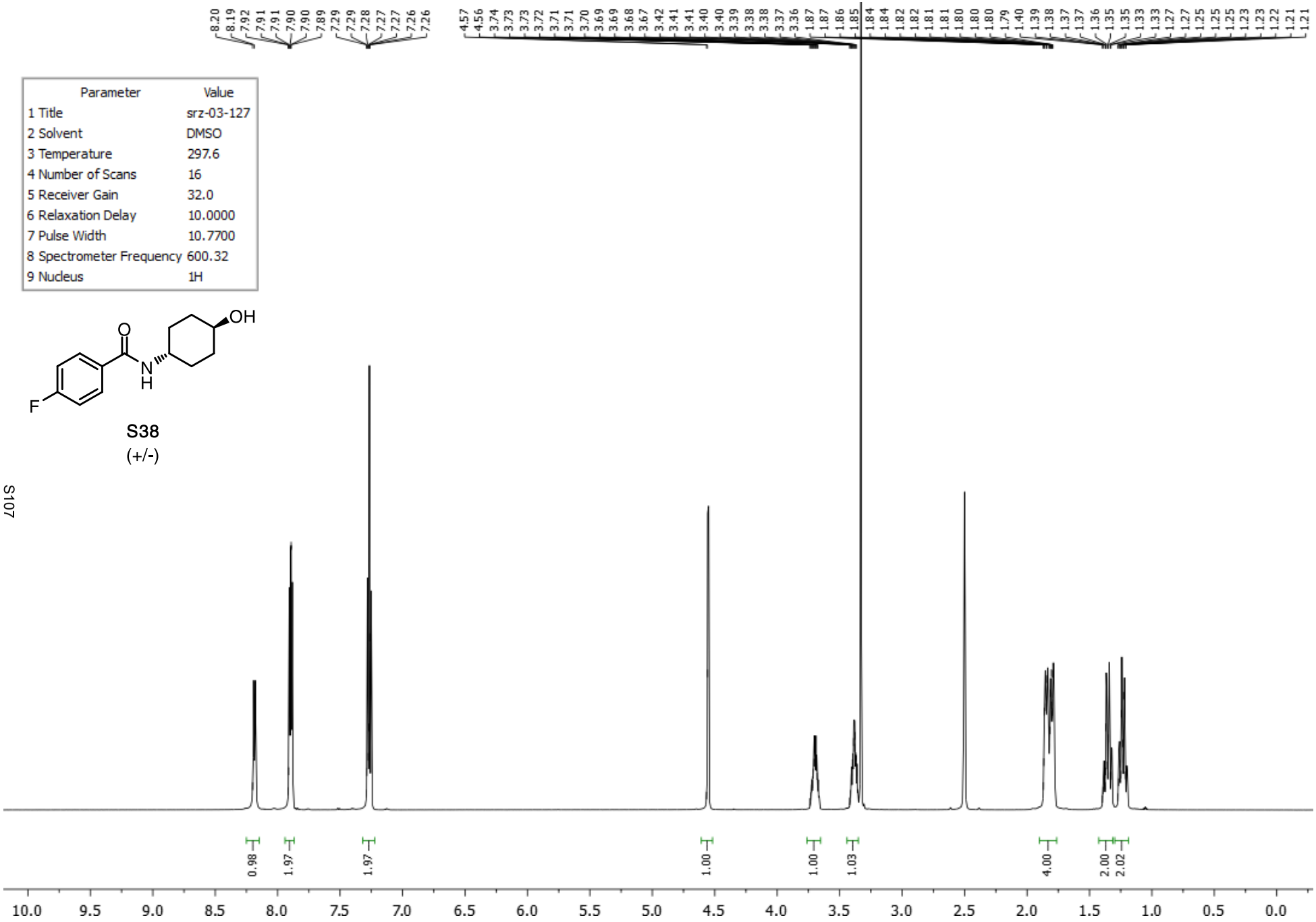


S37

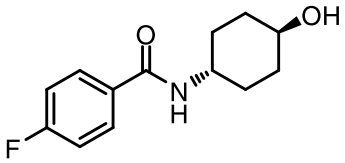
Parameter	Value
1 Title	srz-03-036
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	406.0
6 Relaxation Delay	3.0000
7 Pulse Width	11.6200
8 Spectrometer Frequency	564.81
9 Nucleus	19F



S37


Parameter Value
1 Title srz-03-127
2 Solvent DMSO
3 Temperature 297.6
4 Number of Scans 16
5 Receiver Gain 32.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
OH
O
N
H
F
S38
(+/-)
S107
0.98
1.97
1.97
1.00
1.00
1.03
4.00
2.00
2.02
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

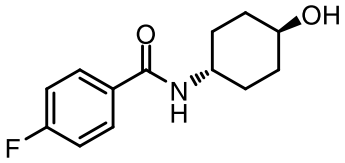
Parameter	Value
1 Title	srz-03-127
2 Solvent	DMSO
3 Temperature	299.3
4 Number of Scans	1024
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C



S38

(+/-)

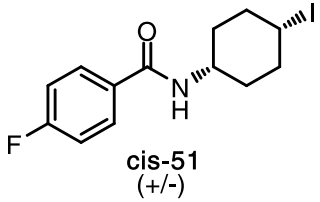
Parameter	Value
1 Title	srz-03-127
2 Solvent	DMSO
3 Temperature	298.6
4 Number of Scans	32
5 Receiver Gain	161.0
6 Relaxation Delay	3.0000
7 Pulse Width	11.6200
8 Spectrometer Frequency	564.81
9 Nucleus	19F



S38

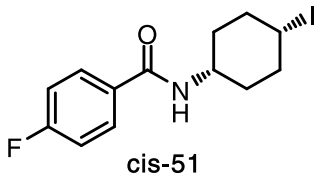
(+/-)

Parameter	Value
1 Title	srz-0-131
2 Solvent	CDCl3
3 Temperature	300.2
4 Number of Scans	16
5 Receiver Gain	71.8
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



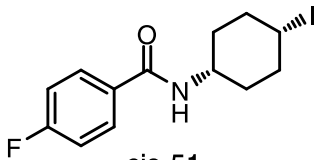
cis-51
(+/-)

Parameter	Value
1 Title	srz-03-131
2 Solvent	CDCl3
3 Temperature	298.7
4 Number of Scans	2048
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C

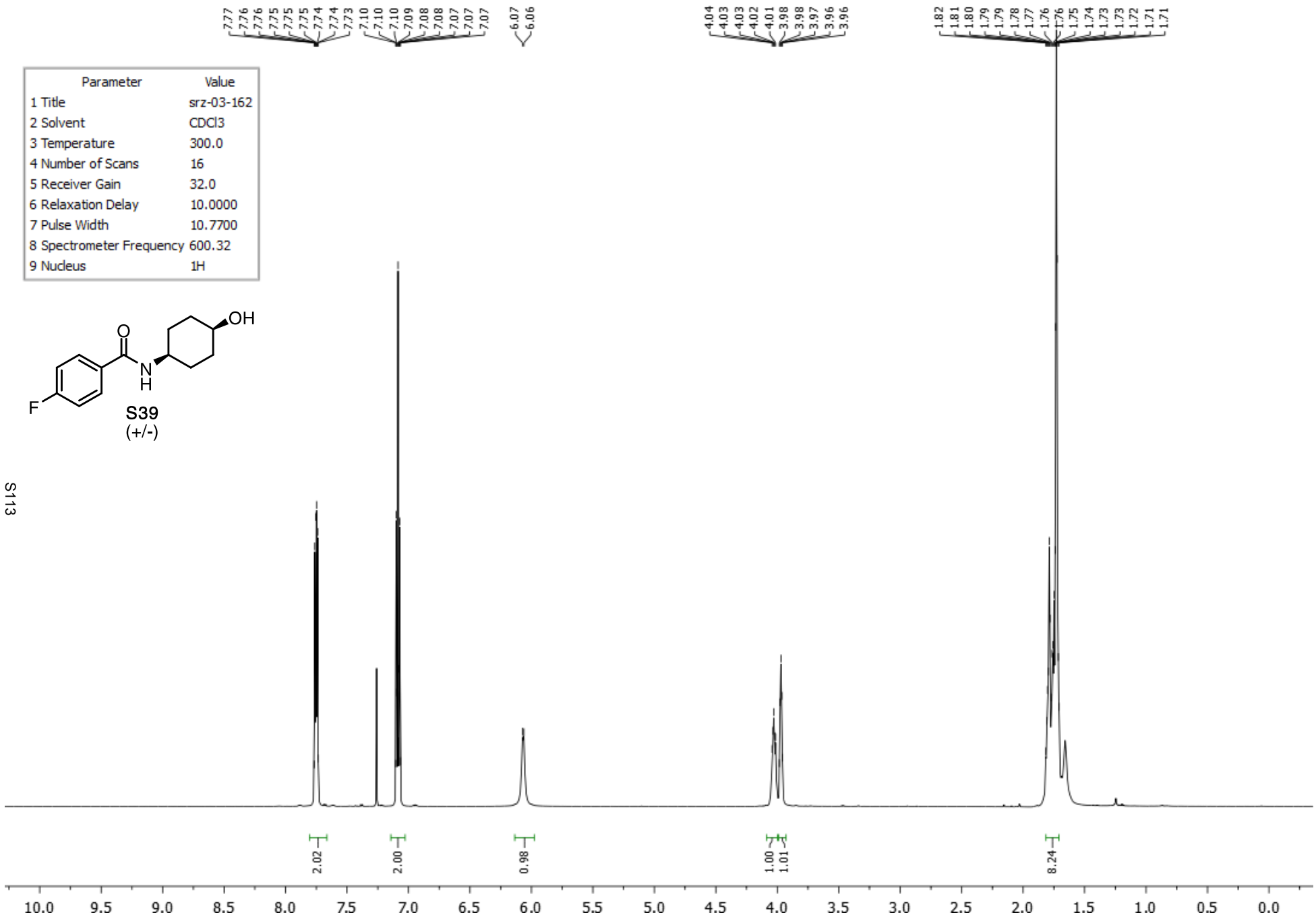


cis-51
(+/-)

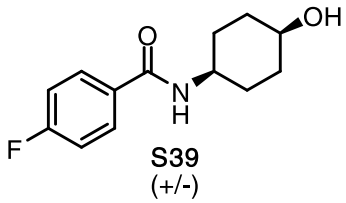
Parameter	Value
1 Title	srz-0-131
2 Solvent	CDCl3
3 Temperature	300.2
4 Number of Scans	32
5 Receiver Gain	181.0
6 Relaxation Delay	3.0000
7 Pulse Width	11.6200
8 Spectrometer Frequency	564.81
9 Nucleus	19F



cis-51
(+/-)

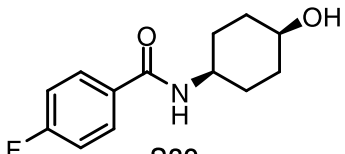

7.77 7.76 7.76 7.75 7.75 7.75 7.74 7.74 7.73
7.10 7.10 7.09 7.08 7.08 7.07 7.07 7.07
6.07 6.06
4.04 4.03 4.03 4.02 4.01 3.98 3.98 3.97 3.96 3.96
1.82 1.81 1.80 1.79 1.79 1.78 1.77 1.76 1.76 1.75 1.74 1.73 1.73 1.72 1.71 1.71
Parameter Value
1 Title srz-03-162
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 32.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
OH
O
N
H
F
S39
(+/-)
2.02
2.00
0.98
1.00
1.01
8.24
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

Parameter	Value
1 Title	srz-03-162
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	2048
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C

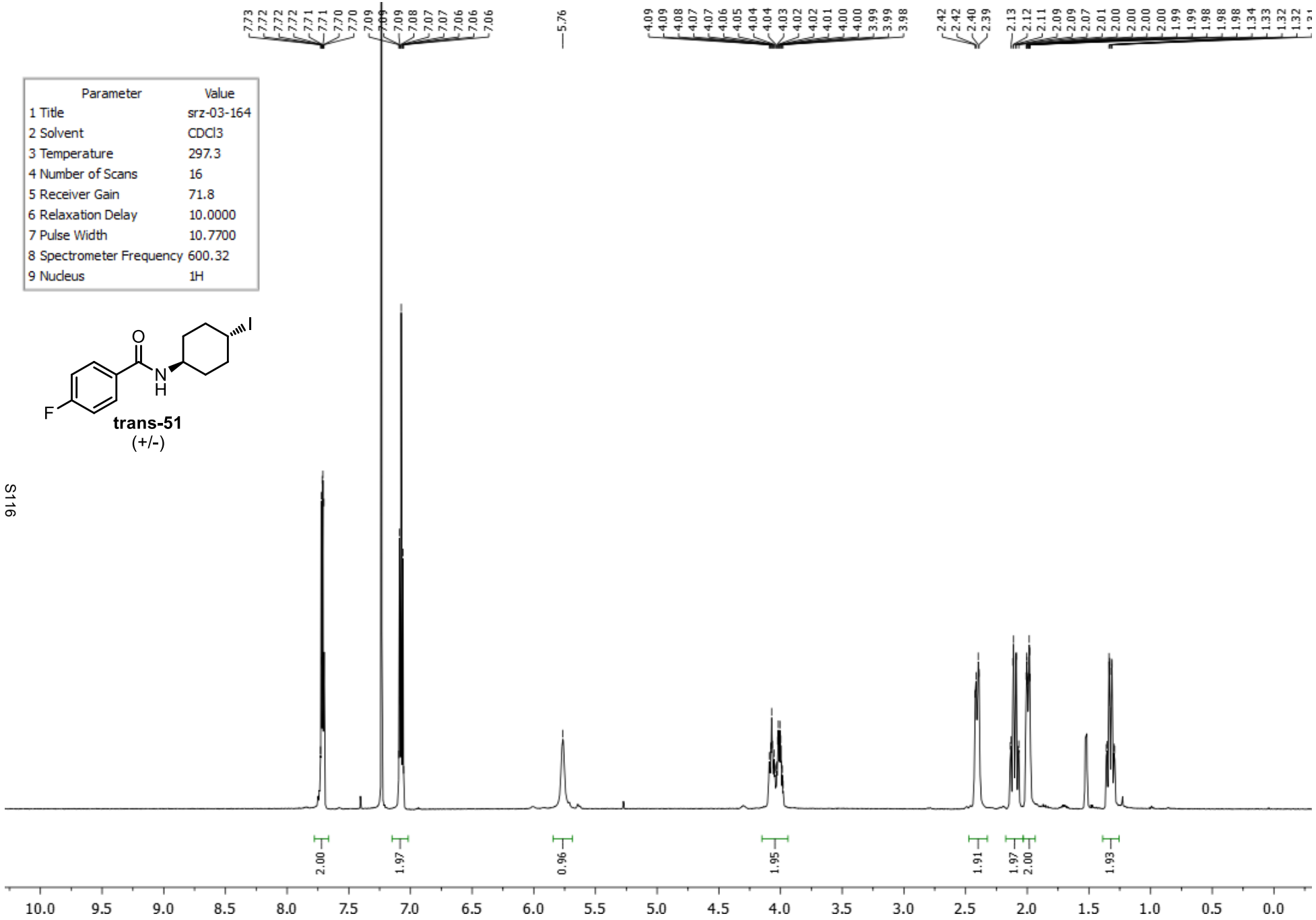


S39
(+/-)

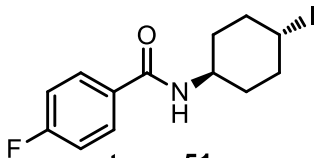
Parameter	Value
1 Title	srz-03-162
2 Solvent	CDCl3
3 Temperature	297.3
4 Number of Scans	16
5 Receiver Gain	406.0
6 Relaxation Delay	3.0000
7 Pulse Width	11.6200
8 Spectrometer Frequency	564.81
9 Nucleus	19F



S39
(+/-)

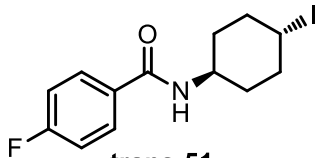

Parameter Value
1 Title srz-03-164
2 Solvent CDCl3
3 Temperature 297.3
4 Number of Scans 16
5 Receiver Gain 71.8
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
trans-51
(+/-)
S116
2.00
1.97
0.96
1.95
1.91
1.97
2.00
1.93

Parameter	Value
1 Title	srz-03-164
2 Solvent	CDCl3
3 Temperature	298.5
4 Number of Scans	1024
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C



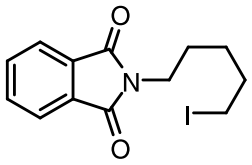
trans-51
(+/-)

Parameter	Value
1 Title	srz-03-164
2 Solvent	CDCl3
3 Temperature	297.3
4 Number of Scans	16
5 Receiver Gain	406.0
6 Relaxation Delay	3.0000
7 Pulse Width	11.6200
8 Spectrometer Frequency	564.81
9 Nucleus	19F

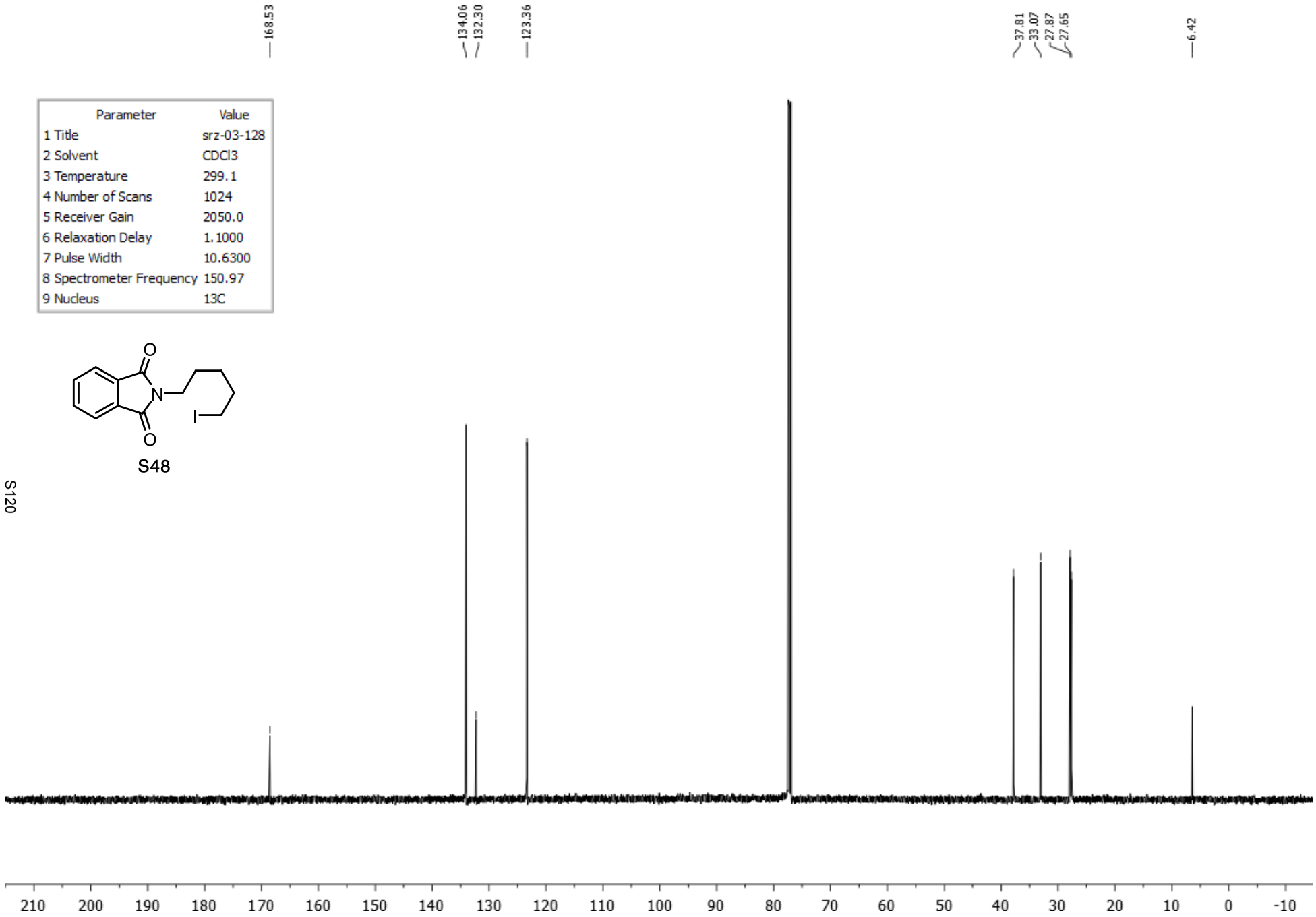


trans-51
(+/-)

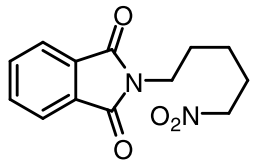
Parameter	Value
1 Title	srz-03-128
2 Solvent	CDCl3
3 Temperature	298.0
4 Number of Scans	16
5 Receiver Gain	71.8
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



S48


168.53
134.06
132.30
123.36
37.81
33.07
27.87
27.65
6.42
Parameter Value
1 Title srz-03-128
2 Solvent CDCl3
3 Temperature 299.1
4 Number of Scans 1024
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
O
N
I
O
S48
S120
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

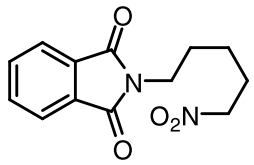
Parameter	Value
1 Title	srz-03-132
2 Solvent	CDCl3
3 Temperature	297.6
4 Number of Scans	16
5 Receiver Gain	64.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



S49

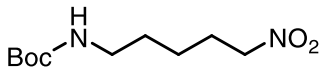
S121

Parameter	Value
1 Title	srz-03-132
2 Solvent	CDCl3
3 Temperature	299.4
4 Number of Scans	2048
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C



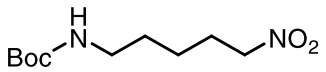
S49

Parameter	Value
1 Title	srz-03-139
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	64.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H

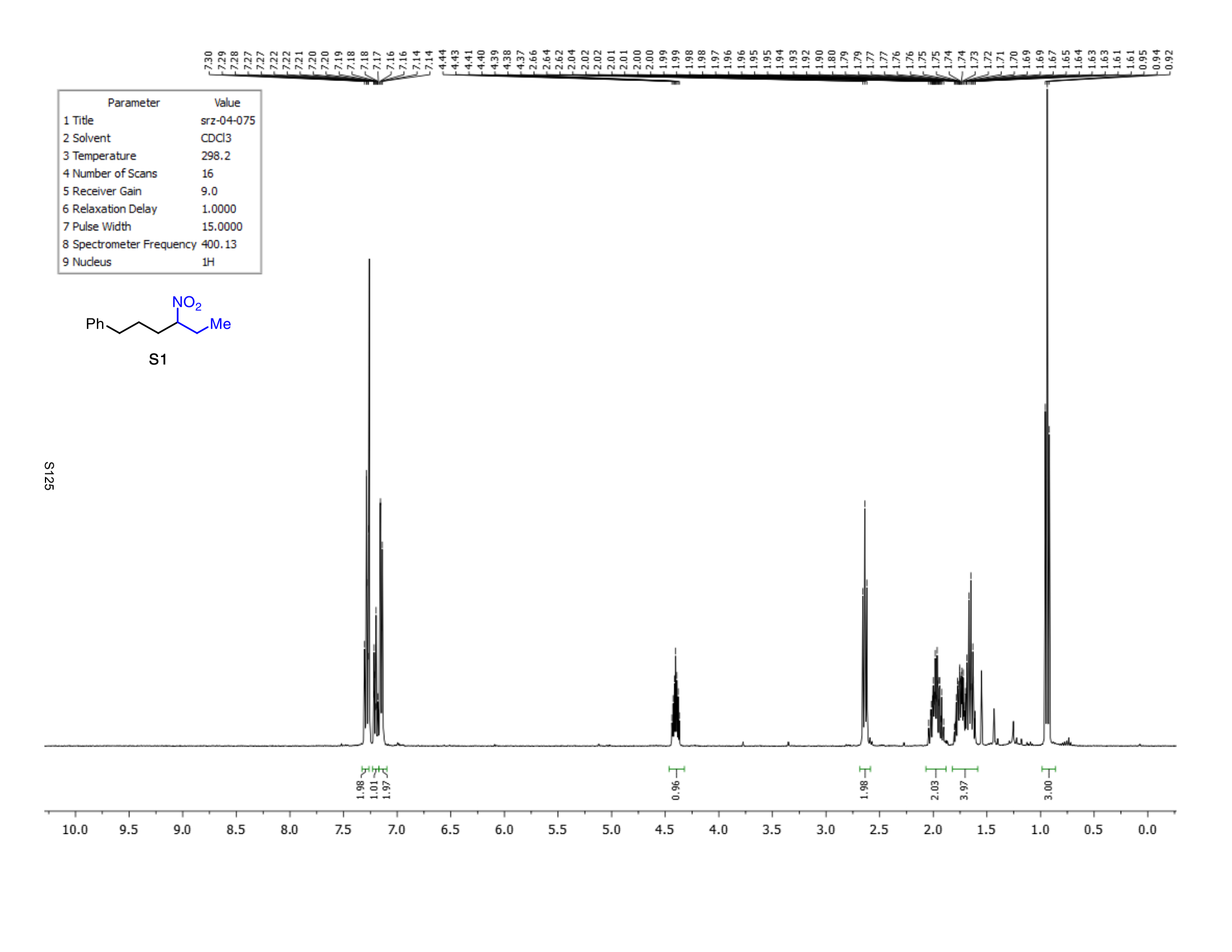


S52

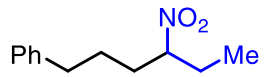
Parameter	Value
1 Title	srz-03-139
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	1024
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C



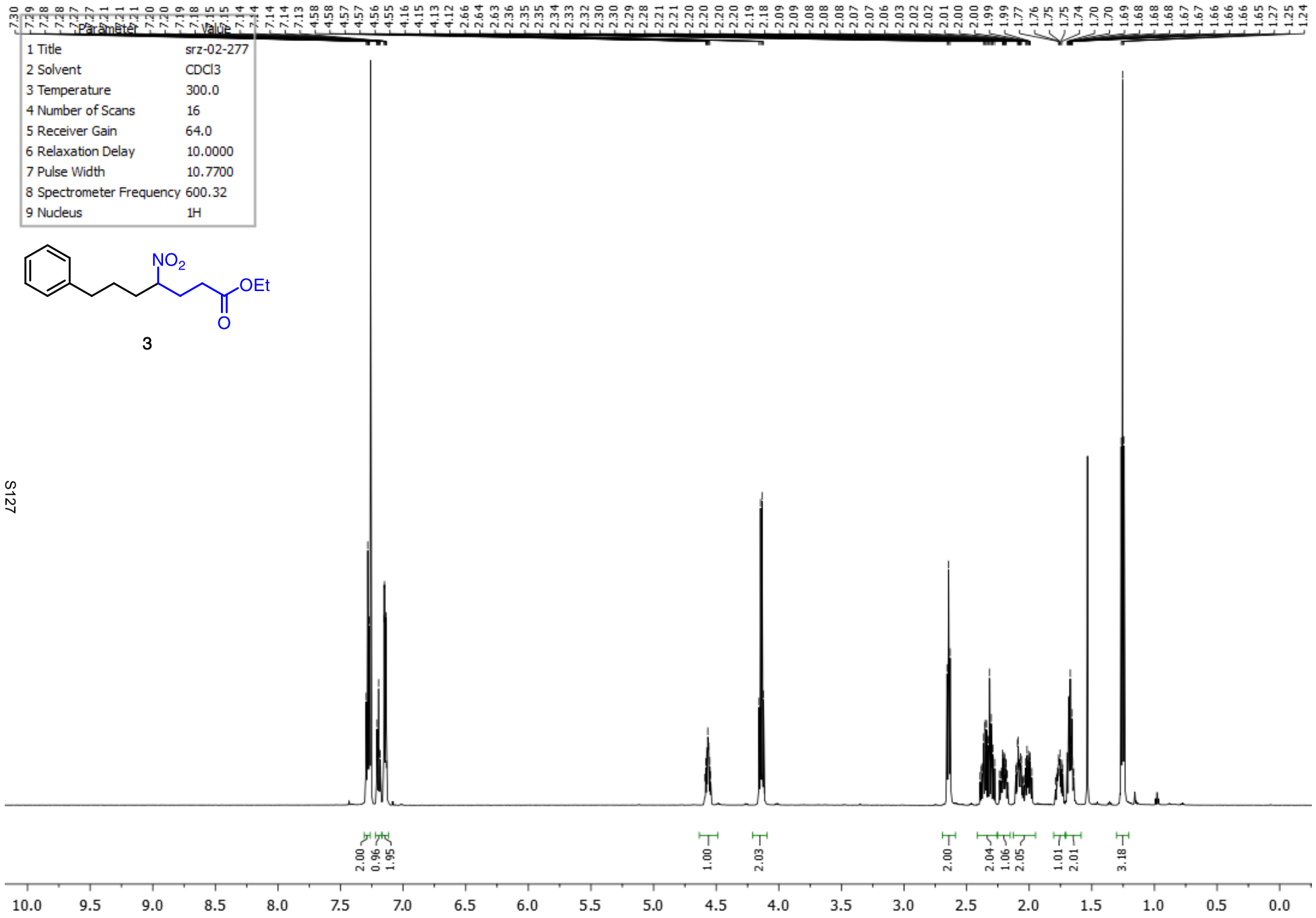
S52

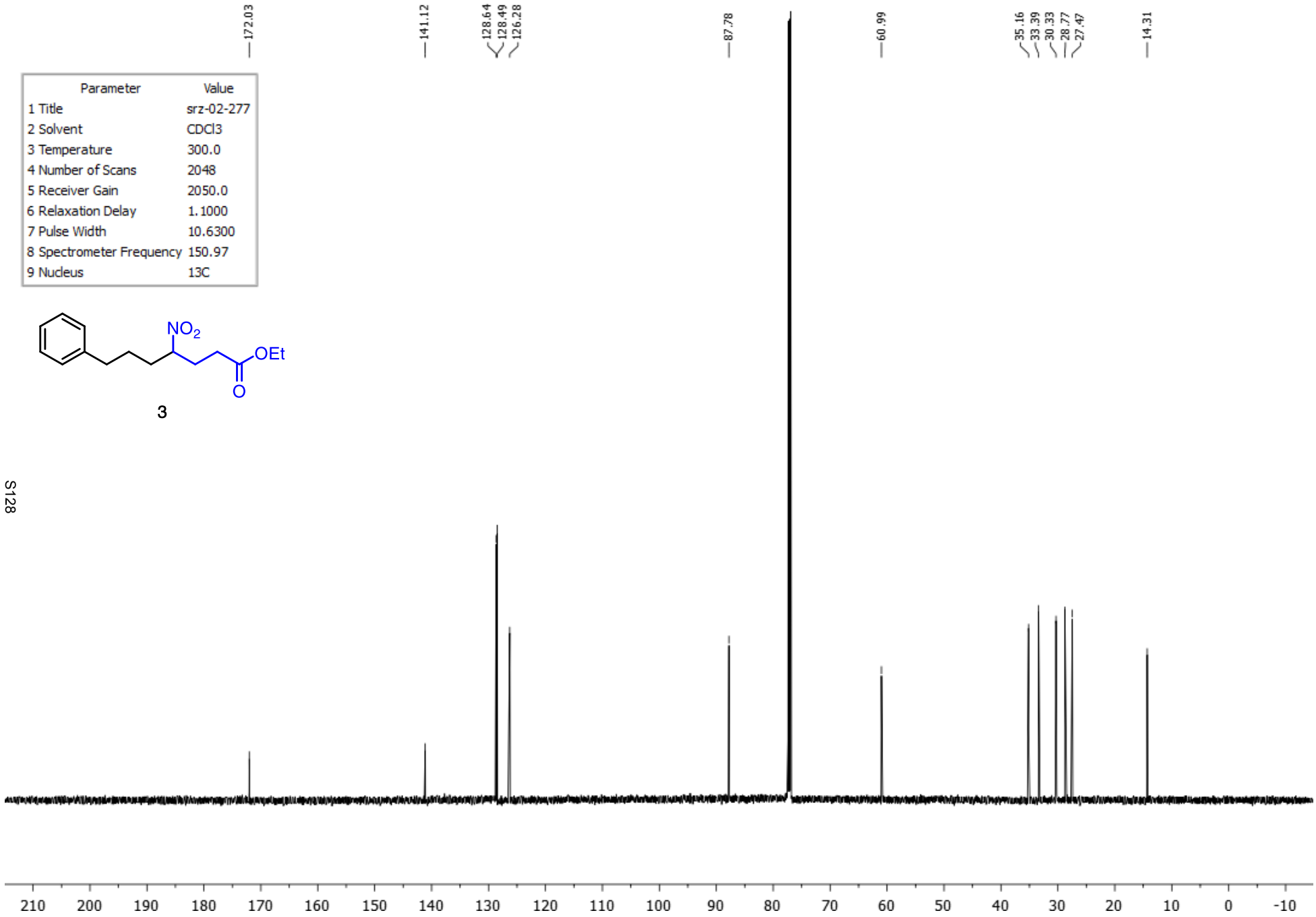

Parameter Value
1 Title srz-04-075
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 16
5 Receiver Gain 9.0
6 Relaxation Delay 1.0000
7 Pulse Width 15.0000
8 Spectrometer Frequency 400.13
9 Nucleus 1H
NO2
Ph
Me
S1
S125
1.98
1.01
1.97
0.96
1.98
2.03
3.97
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

Parameter	Value
1 Title	srz-04-075
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	1024
5 Receiver Gain	512.0
6 Relaxation Delay	2.0000
7 Pulse Width	9.2500
8 Spectrometer Frequency	100.62
9 Nucleus	13C

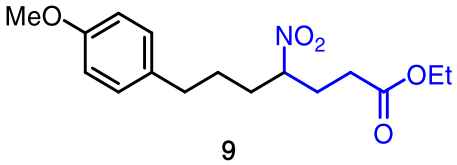


S1

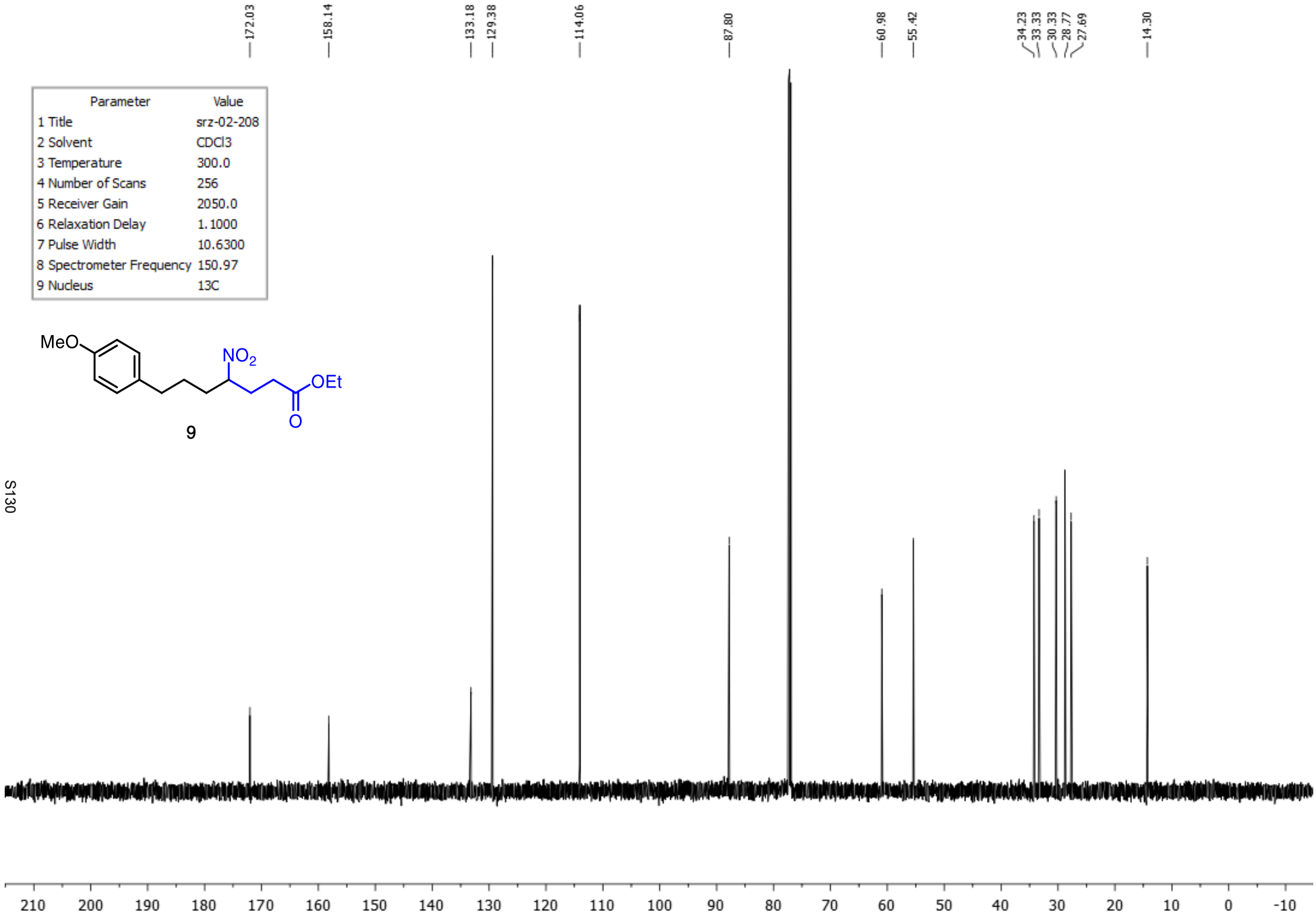

Parameter Value
1 Title srz-02-277
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 64.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
NO2
OEt
O
3
2.00
0.96
1.95
1.00
2.03
2.00
2.04
1.06
2.05
1.01
2.01
3.18
10.0
9.5
9.0
8.5
8.0
7.5
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

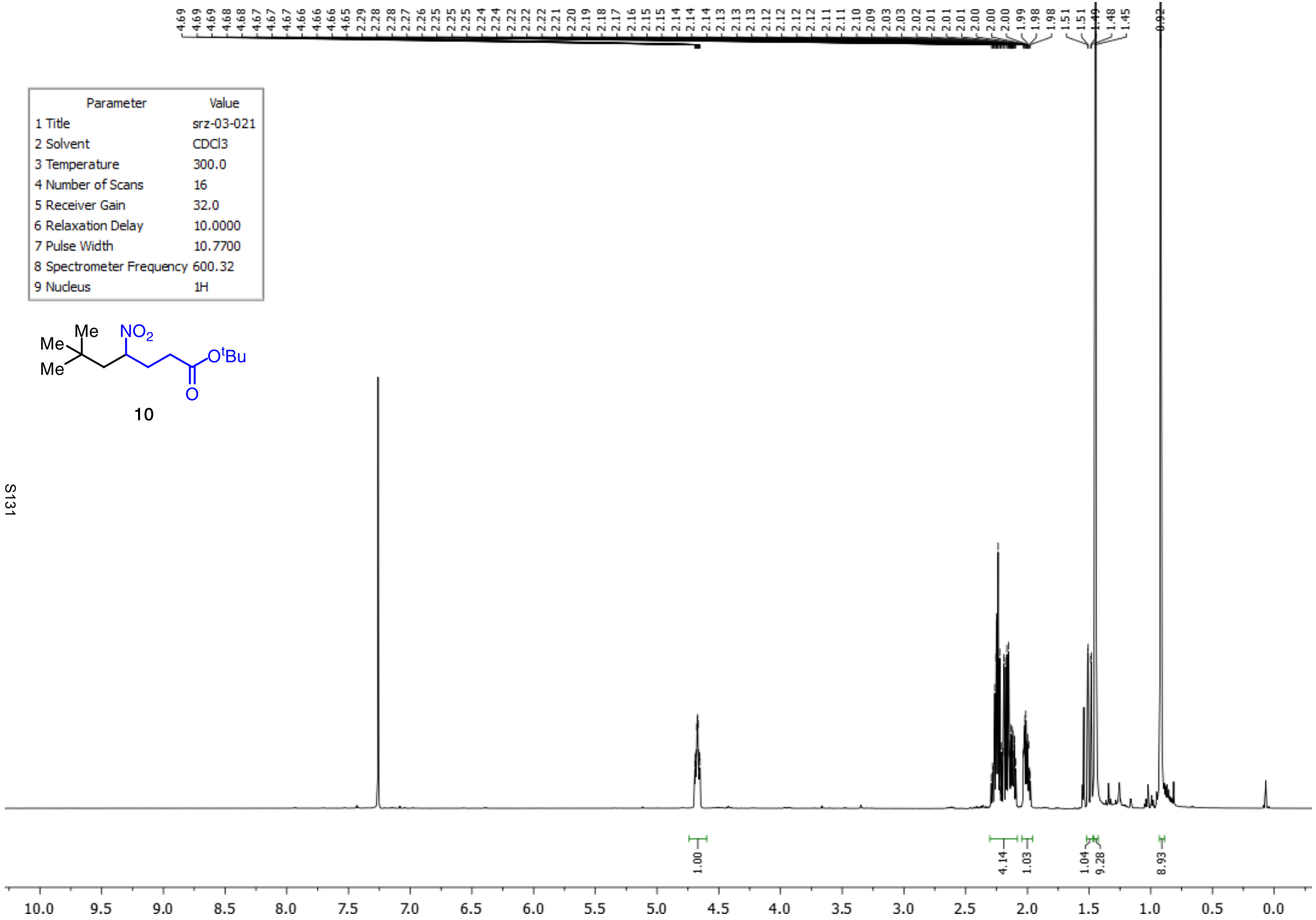

172.03
141.12
128.64
128.49
126.28
87.78
60.99
35.16
33.39
30.33
28.77
27.47
14.31
Parameter Value
1 Title srz-02-277
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
NO2
OEt
O
3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

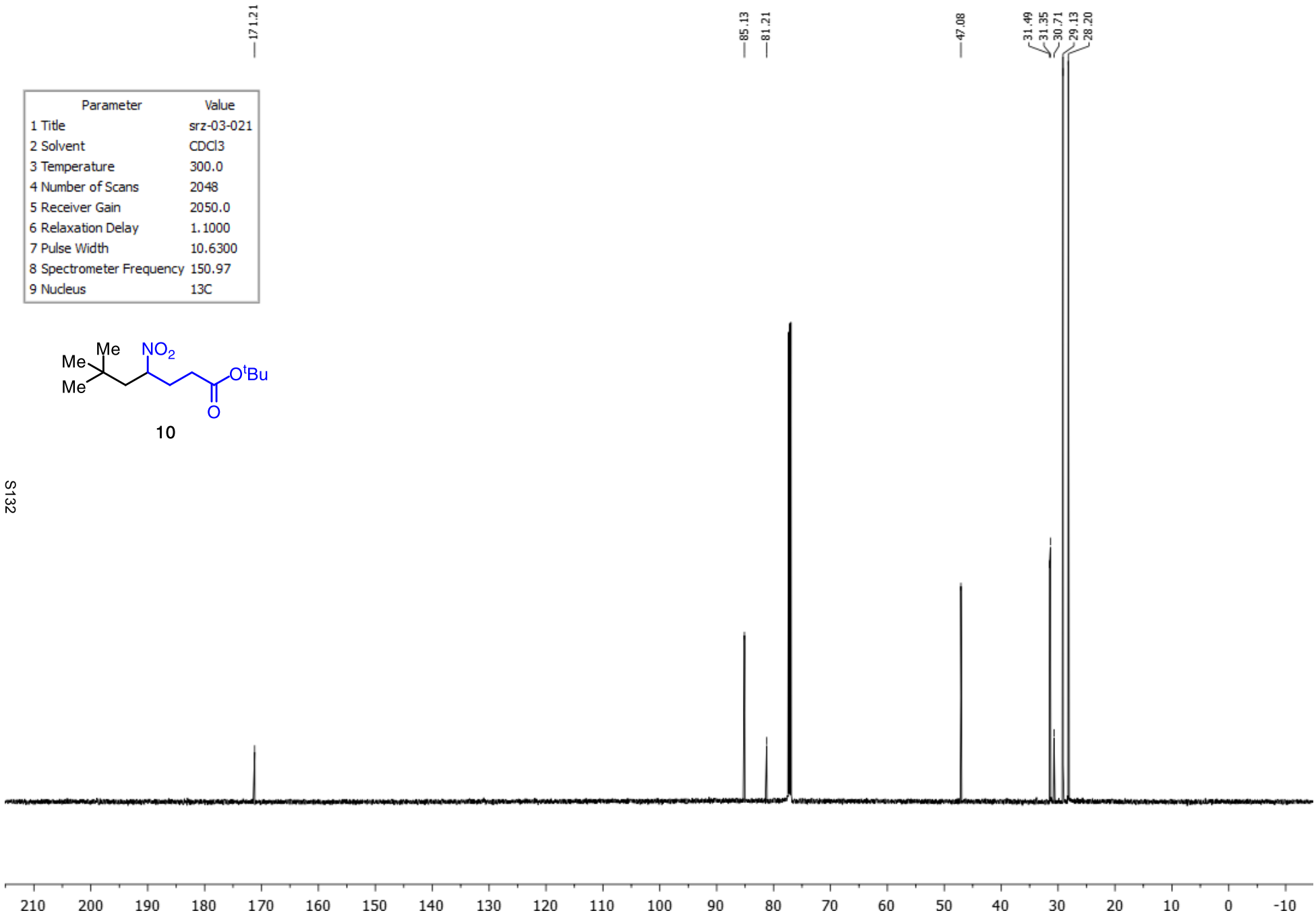
Parameter	Value
1 Title	srz-02-208
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	128.0
6 Relaxation Delay	1.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



9

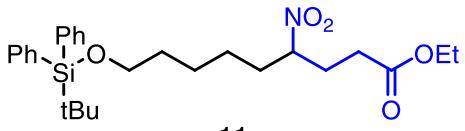

172.03
158.14
133.18
129.38
114.06
87.80
60.98
55.42
34.23
33.33
30.33
28.77
27.69
14.30
Parameter Value
1 Title srz-02-208
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 256
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
MeO
NO2
OEt
O
9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


Parameter Value
1 Title srz-03-021
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 32.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
Me
Me
Me
NO2
OtBu
O
10
1.00
4.14
1.03
1.04
9.28
8.93
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

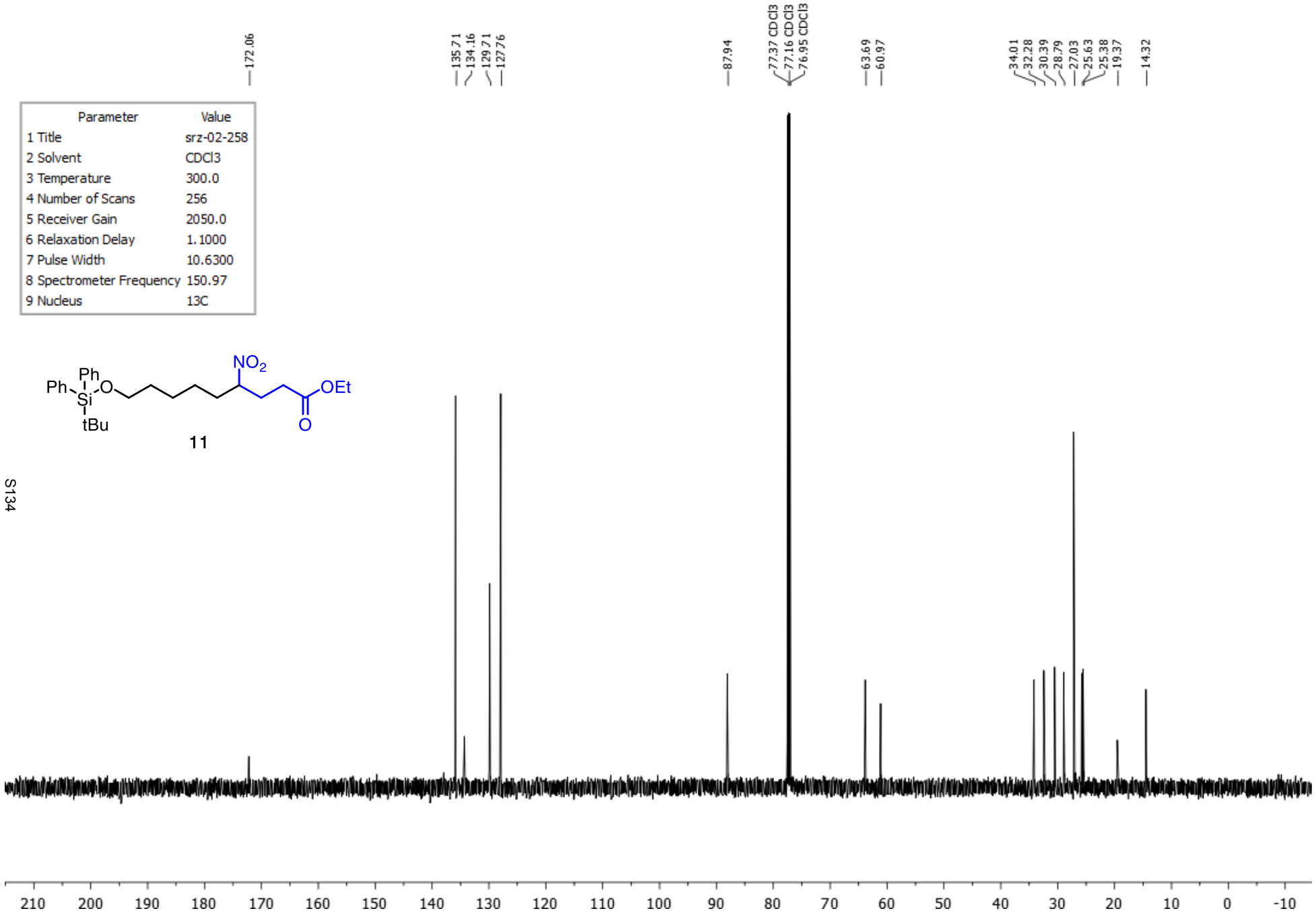

171.21
85.13
81.21
47.08
31.49
31.35
30.71
29.13
28.20
Parameter Value
1 Title srz-03-021
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
Me
Me
Me
NO2
O
tBu
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

10

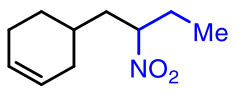
Parameter	Value
1 Title	srz-02-258
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	57.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



11

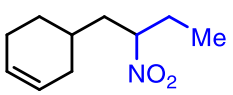

172.06
135.71
134.16
129.71
127.76
87.94
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
63.69
60.97
34.01
32.28
30.39
28.79
27.03
25.63
25.38
19.37
14.32
Parameter Value
1 Title srz-02-258
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 256
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
Ph
Ph
Si
O
tBu
NO2
OEt
O
11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Parameter	Value
1 Title	srz-03-076
2 Solvent	CDCl3
3 Temperature	297.6
4 Number of Scans	16
5 Receiver Gain	64.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



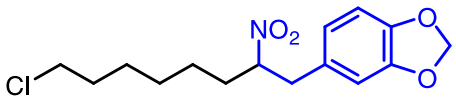
12

Parameter	Value
1 Title	srz-03-076
2 Solvent	CDCl3
3 Temperature	299.5
4 Number of Scans	2048
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C

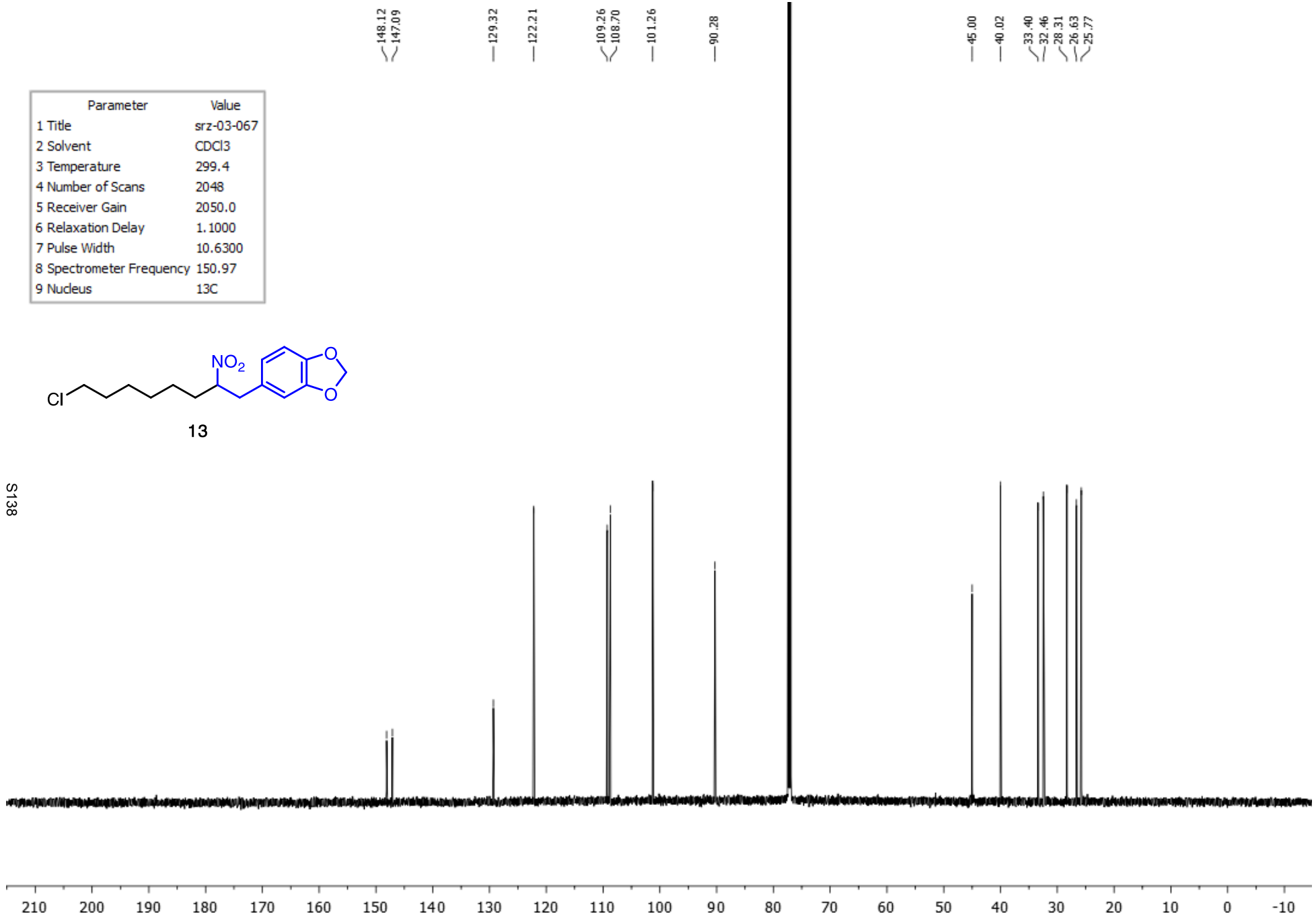


12

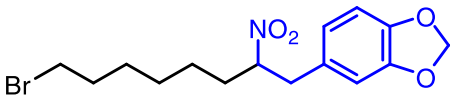
Parameter	Value
1 Title	srz-03-067
2 Solvent	CDCl3
3 Temperature	297.6
4 Number of Scans	16
5 Receiver Gain	64.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



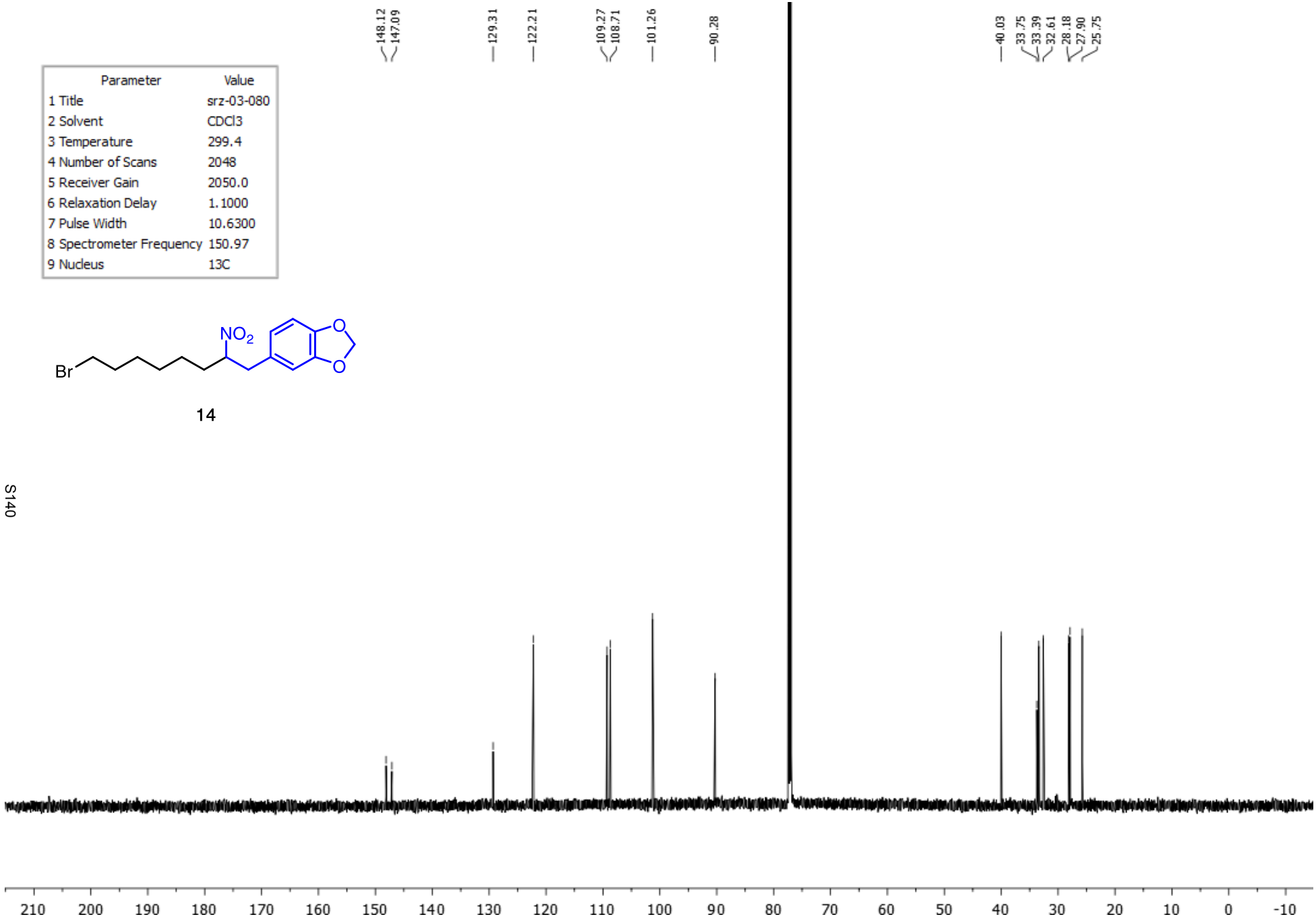
13

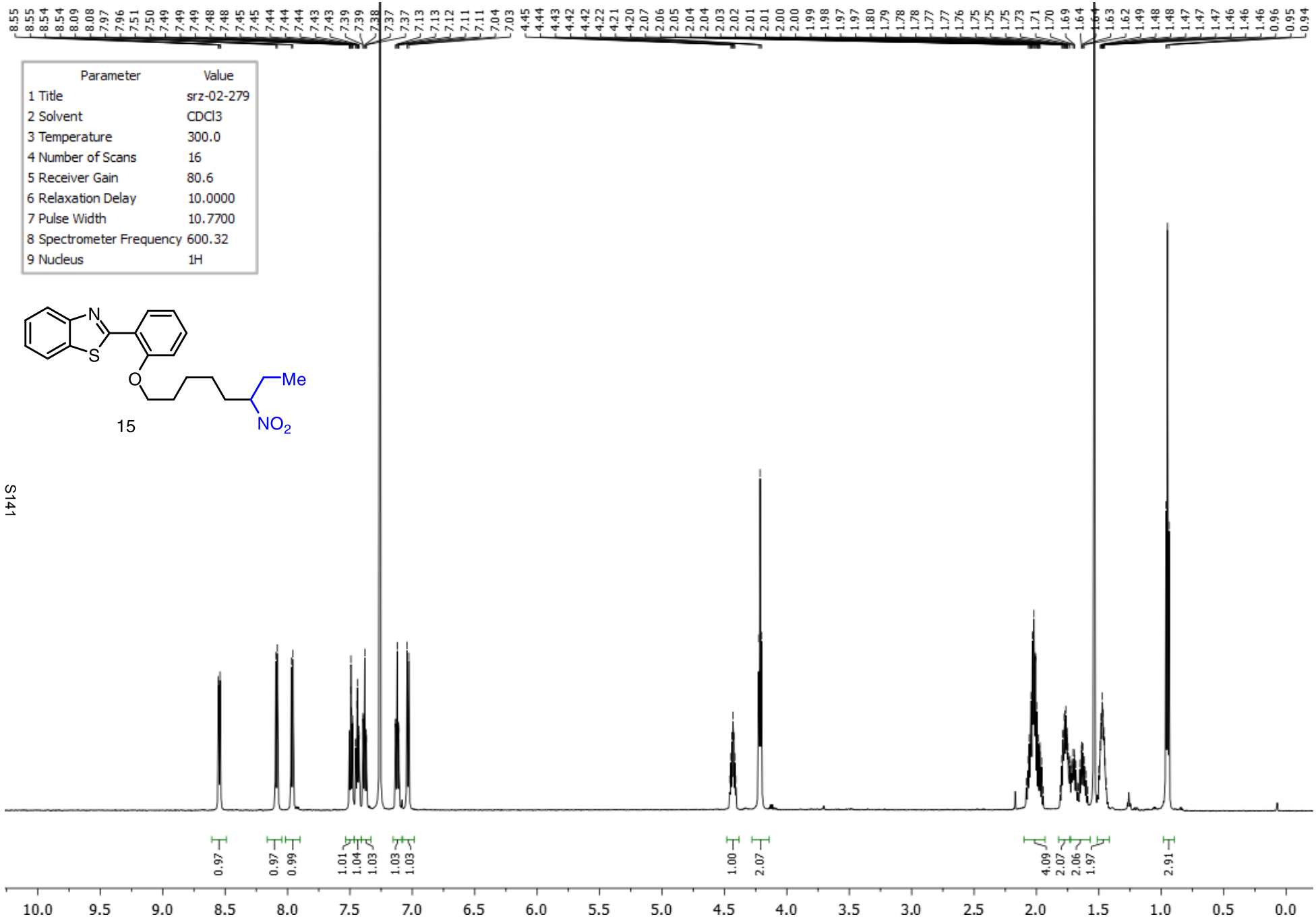

148.12
147.09
129.32
122.21
109.26
108.70
101.26
90.28
45.00
40.02
33.40
32.46
28.31
26.63
25.77
Parameter Value
1 Title srz-03-067
2 Solvent CDCl3
3 Temperature 299.4
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
NO2
Cl
O
O
13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

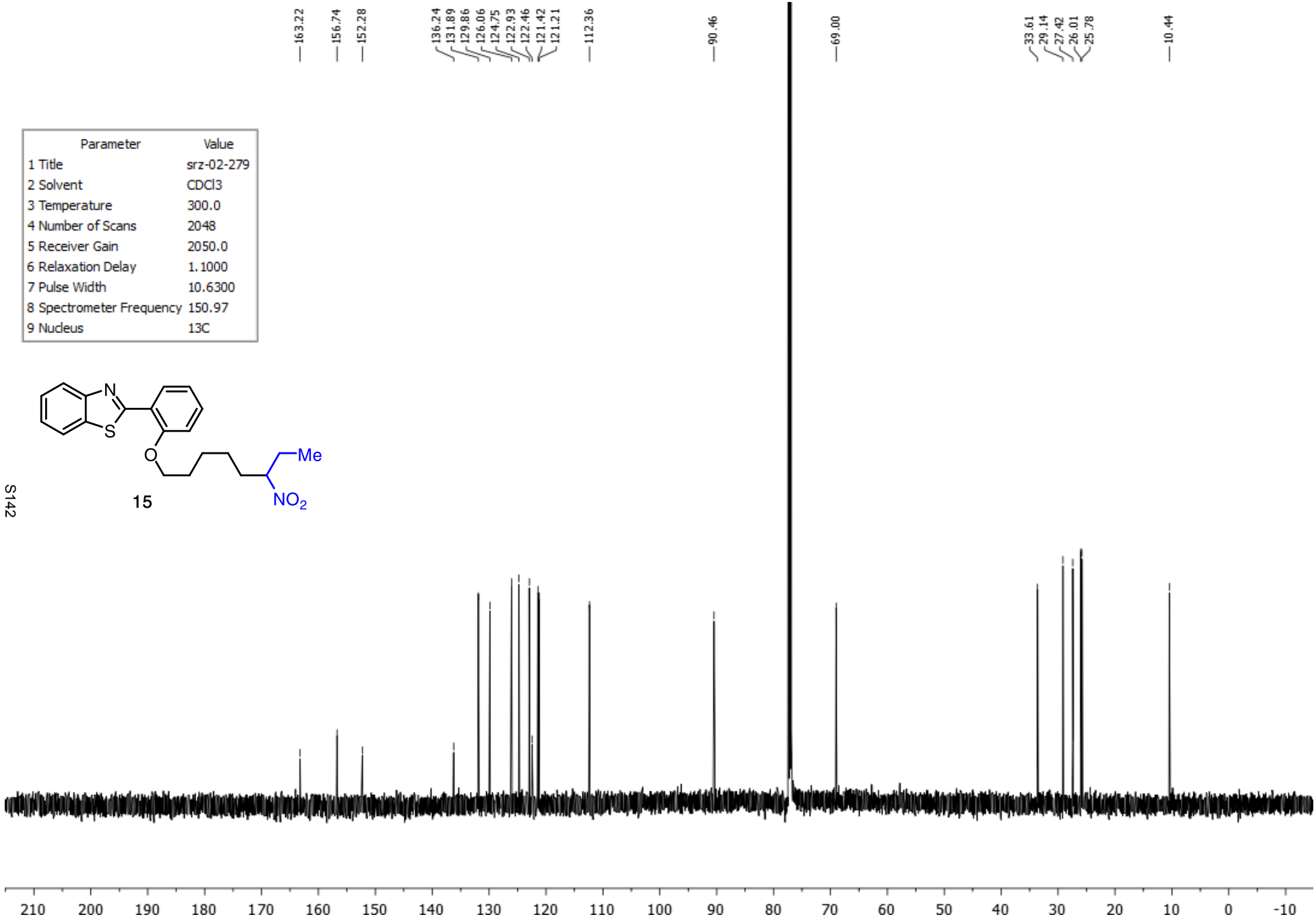
Parameter	Value
1 Title	srz-03-080
2 Solvent	CDCl3
3 Temperature	297.6
4 Number of Scans	16
5 Receiver Gain	71.8
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H

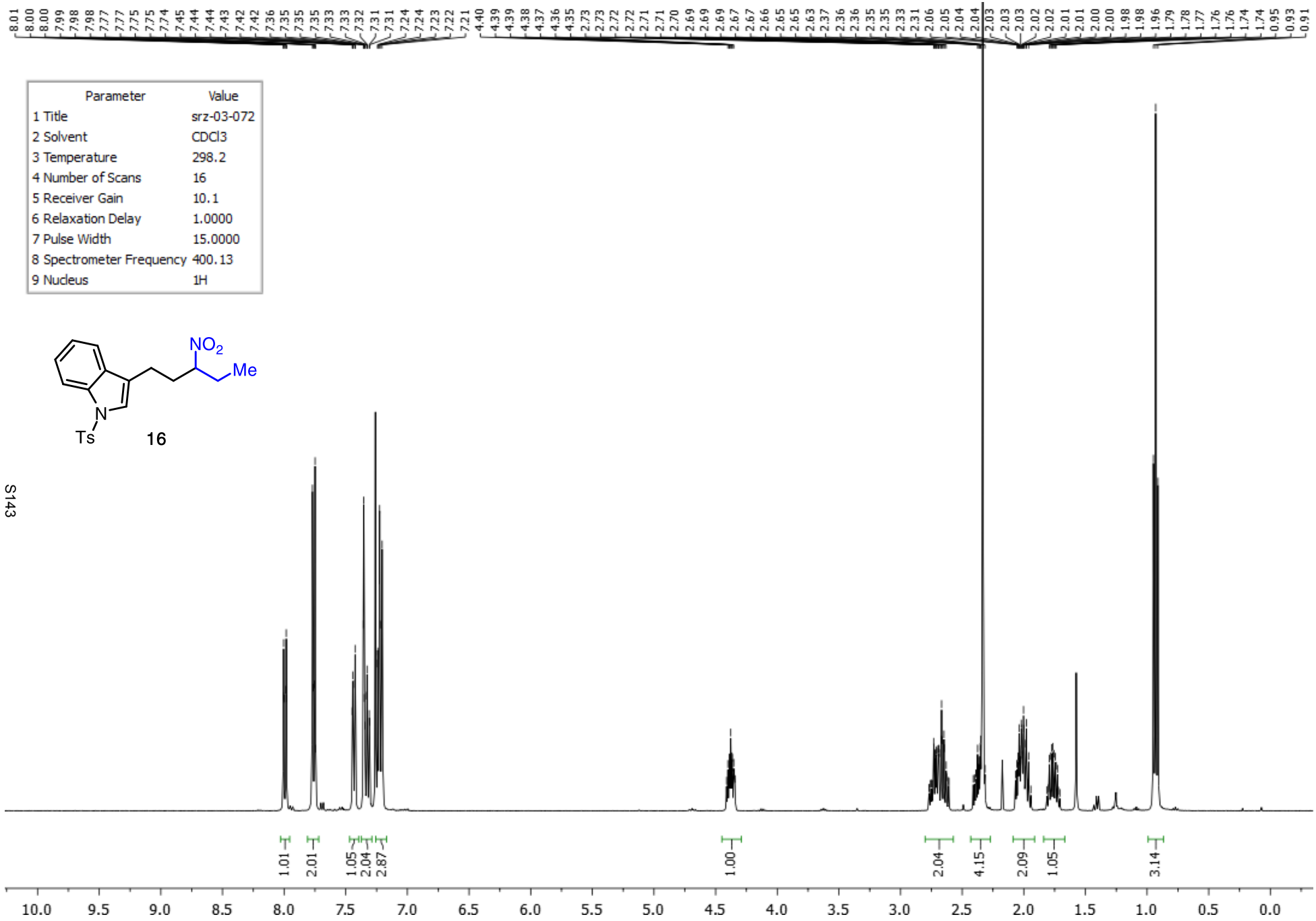


14

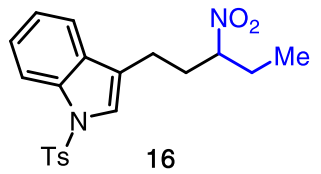

148.12
147.09
129.31
122.21
109.27
108.71
101.26
90.28
40.03
33.75
33.39
32.61
28.18
27.90
25.75
Parameter Value
1 Title srz-03-080
2 Solvent CDCl3
3 Temperature 299.4
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
NO2
Br
O
O
14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


Parameter Value
1 Title srz-02-279
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 80.6
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
N
S
O
Me
NO2
15
0.97
0.97
0.99
1.01
1.04
1.03
1.03
1.03
1.00
2.07
4.09
2.07
2.06
1.97
2.91
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


163.22
156.74
152.28
136.24
131.89
129.86
126.06
124.75
122.93
122.46
121.42
121.21
112.36
90.46
69.00
33.61
29.14
27.42
26.01
25.78
10.44
Parameter Value
1 Title srz-02-279
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
N
S
O
Me
NO2
15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

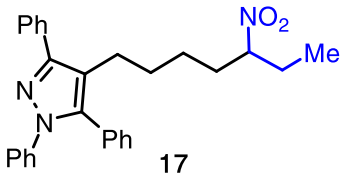

8.01 8.00 8.00 7.99 7.98 7.98 7.77 7.77 7.75 7.75 7.74 7.45 7.44 7.44 7.43 7.42 7.42 7.36 7.35 7.35 7.35 7.33 7.33 7.32 7.31 7.31 7.24 7.24 7.23 7.22 7.21
4.40 4.39 4.39 4.38 4.37 4.36 4.35 2.73 2.73 2.72 2.72 2.71 2.71 2.70 2.69 2.69 2.69 2.67 2.67 2.66 2.65 2.65 2.63 2.37 2.36 2.36 2.35 2.35 2.33 2.31 2.06 2.05 2.04 2.04 2.03 2.03 2.03 2.02 2.02 2.01 2.01 2.00 2.00 1.98 1.98 1.96 1.79 1.78 1.77 1.76 1.76 1.74 1.74 0.95 0.93 0.91
Parameter Value
1 Title srz-03-072
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 16
5 Receiver Gain 10.1
6 Relaxation Delay 1.0000
7 Pulse Width 15.0000
8 Spectrometer Frequency 400.13
9 Nucleus 1H
NO2
Me
N
Ts
16
1.01 2.01 1.05 2.04 2.87 1.00 2.04 4.15 2.09 1.05 3.14
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

Parameter	Value
1 Title	srz-03-072
2 Solvent	CDCl3
3 Temperature	299.4
4 Number of Scans	2048
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C

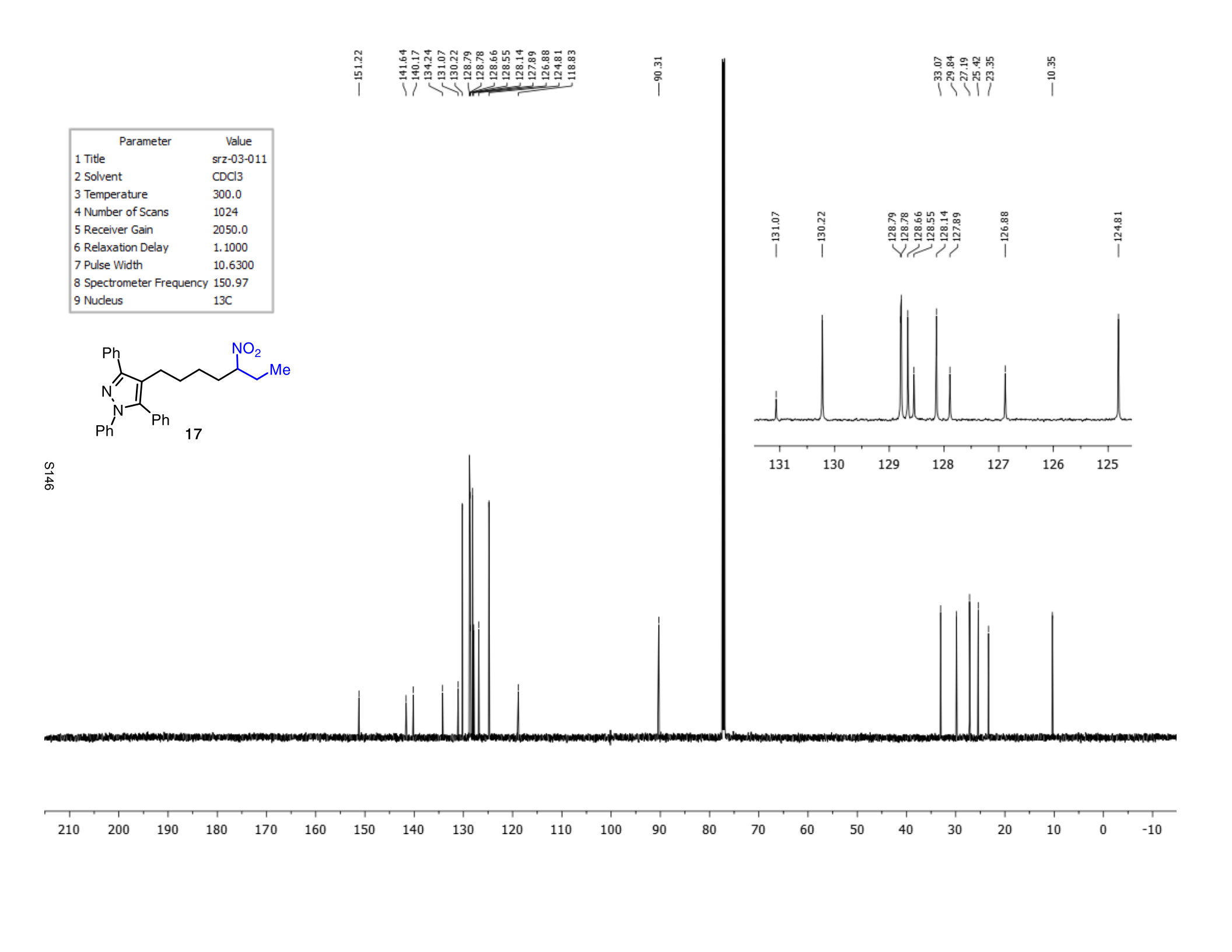


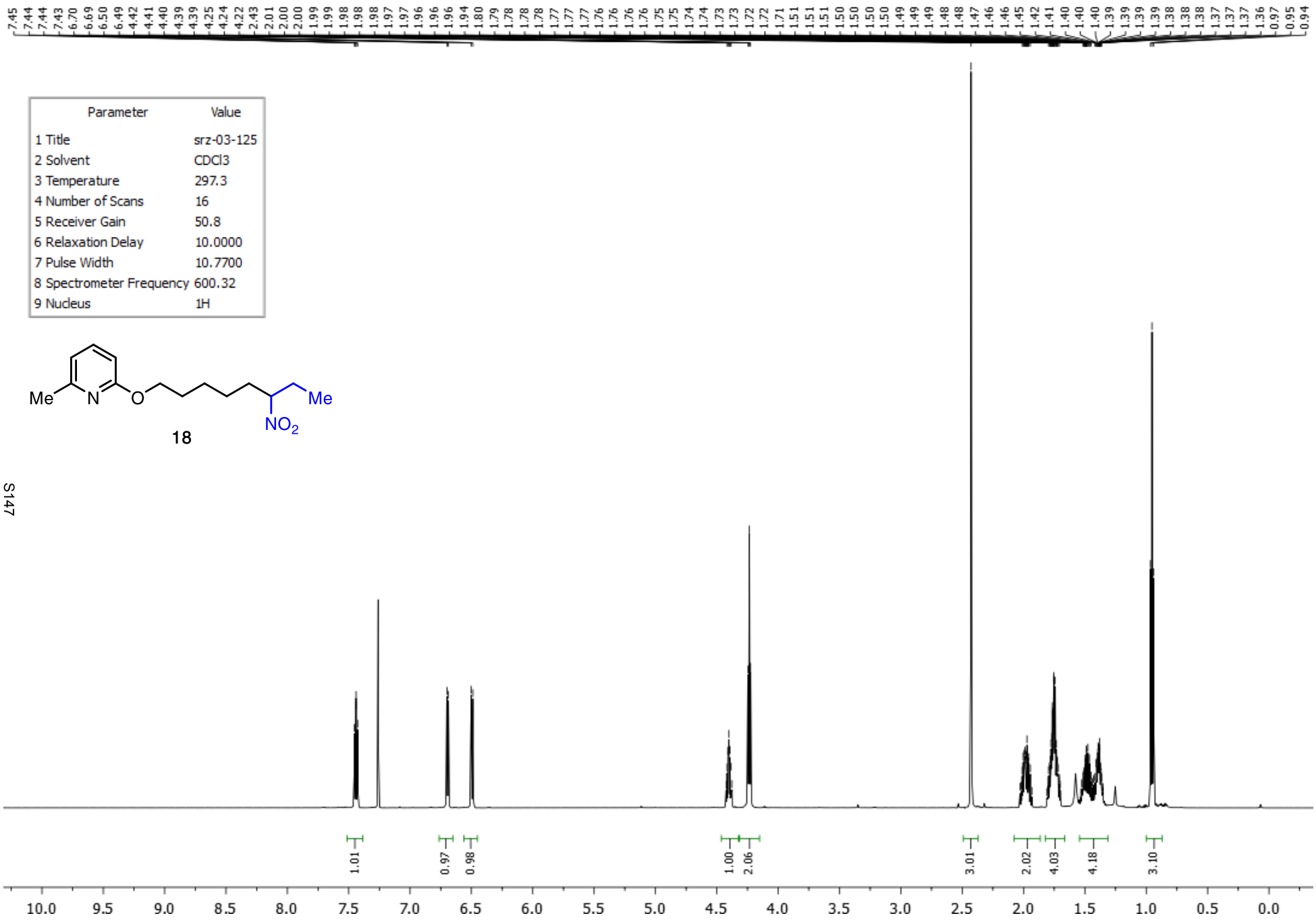
16

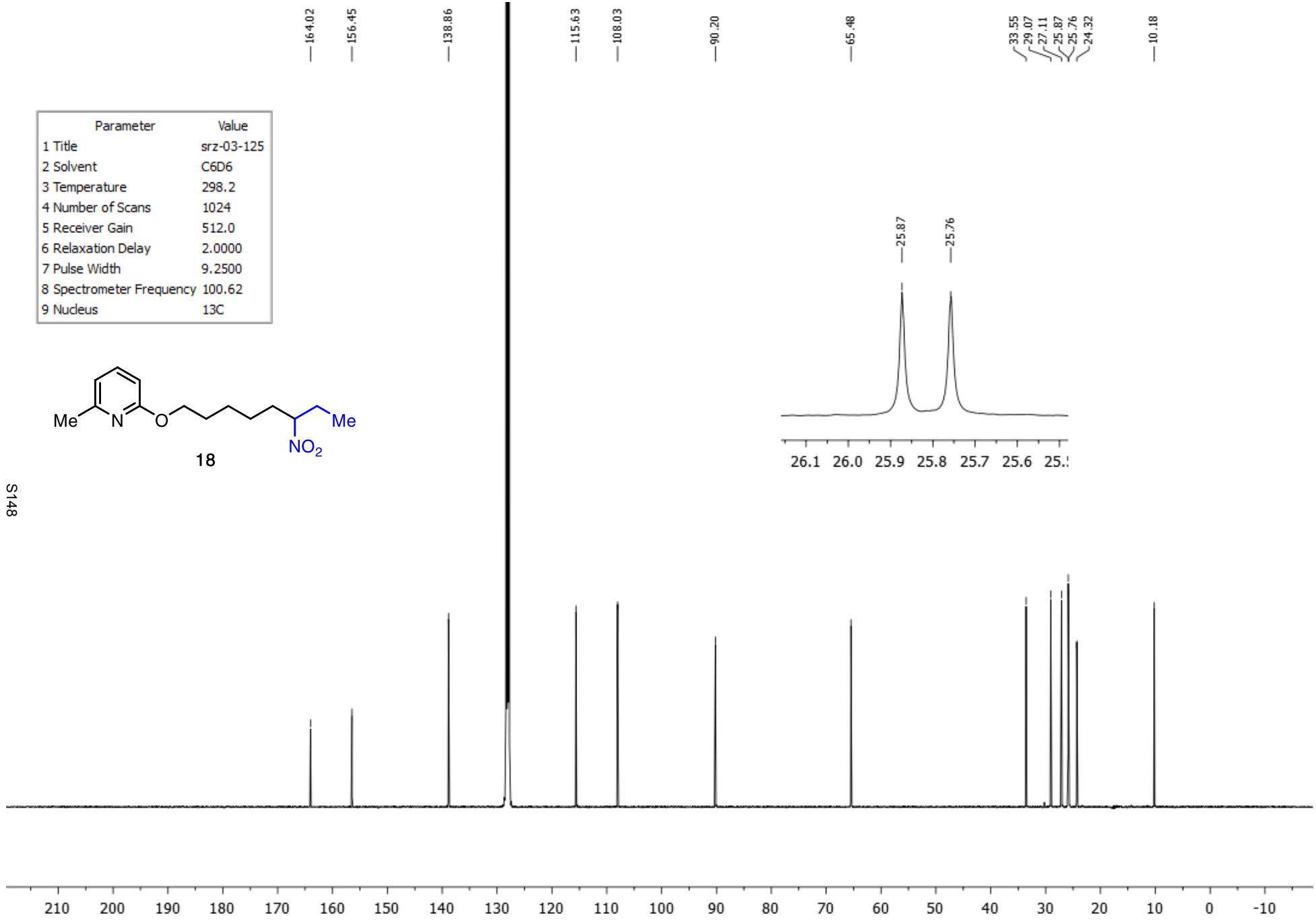
Parameter	Value
1 Title	srz-03-011
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	57.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



17

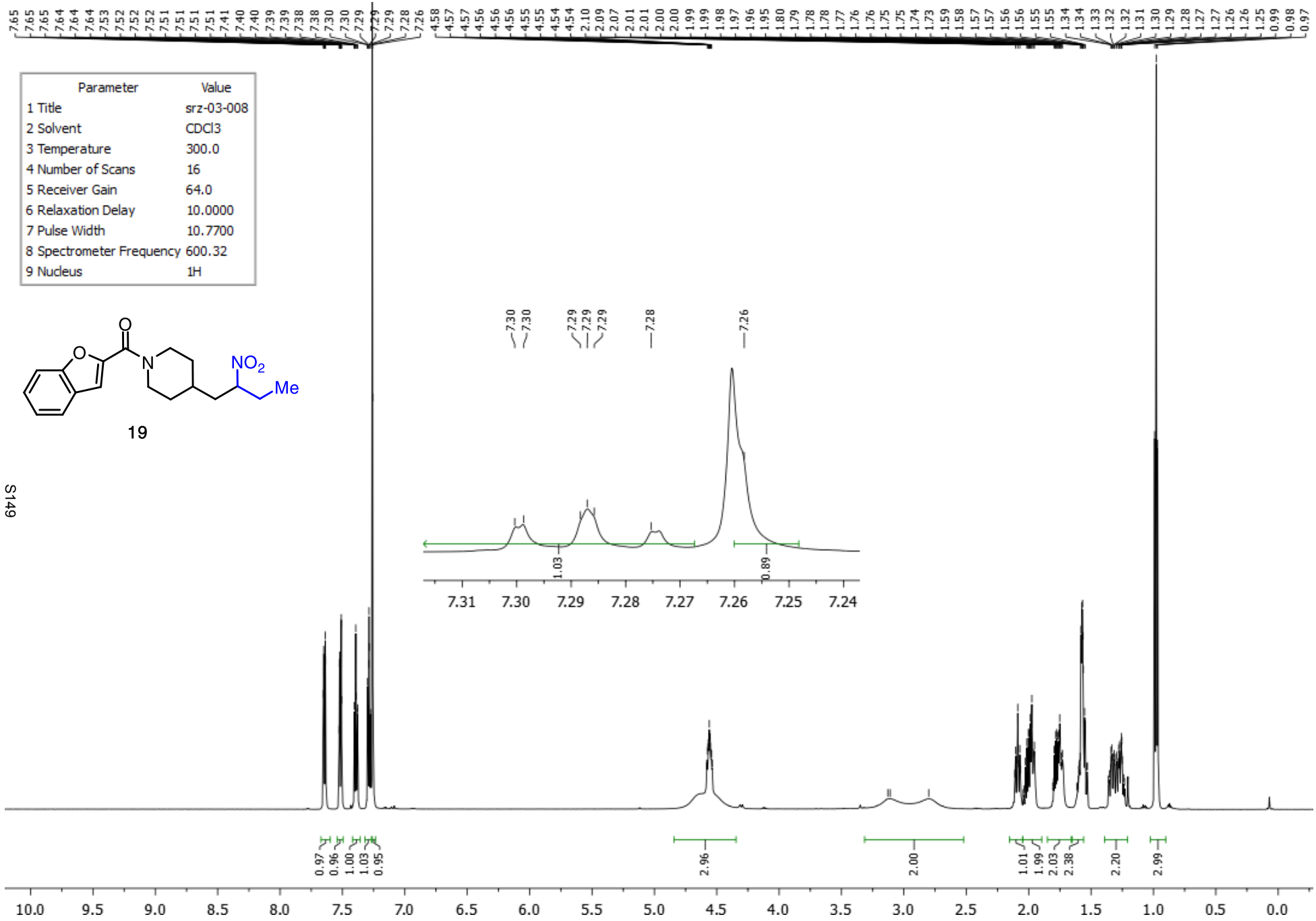

151.22
141.64
140.17
134.24
131.07
130.22
128.79
128.78
128.66
128.55
128.14
127.89
126.88
124.81
118.83
90.31
33.07
29.84
27.19
25.42
23.35
10.35
Parameter Value
1 Title srz-03-011
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 1024
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
Ph
N
N
Ph
Ph
NO2
Me
17
131.07
130.22
128.79
128.78
128.66
128.55
128.14
127.89
126.88
124.81
131
130
129
128
127
126
125
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


Parameter Value
1 Title srz-03-125
2 Solvent CDCl3
3 Temperature 297.3
4 Number of Scans 16
5 Receiver Gain 50.8
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
Me
N
O
Me
NO2
18
1.01
0.97
0.98
1.00
2.06
3.01
2.02
4.03
4.18
3.10
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

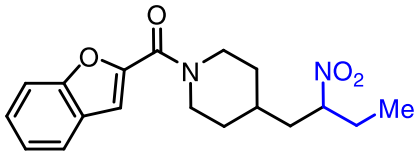


Parameter	Value
1 Title	srz-03-125
2 Solvent	C6D6
3 Temperature	298.2
4 Number of Scans	1024
5 Receiver Gain	512.0
6 Relaxation Delay	2.0000
7 Pulse Width	9.2500
8 Spectrometer Frequency	100.62
9 Nucleus	13C

18

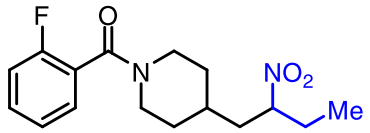

Parameter Value
1 Title srz-03-008
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 64.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
NO2
Me
19
7.31 7.30 7.29 7.28 7.27 7.26 7.25 7.24
1.03
0.89
0.97 0.96 1.00 1.03 0.95
2.96
2.00
1.01 1.99 2.03 2.38
2.20
2.99
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

Parameter	Value
1 Title	srz-03-008
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	2048
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C



19

Parameter	Value
1 Title	srz-03-018-rt
2 Solvent	DMSO
3 Temperature	298.1
4 Number of Scans	16
5 Receiver Gain	181.0
6 Relaxation Delay	1.0000
7 Pulse Width	15.0000
8 Spectrometer Frequency	400.15
9 Nucleus	1H



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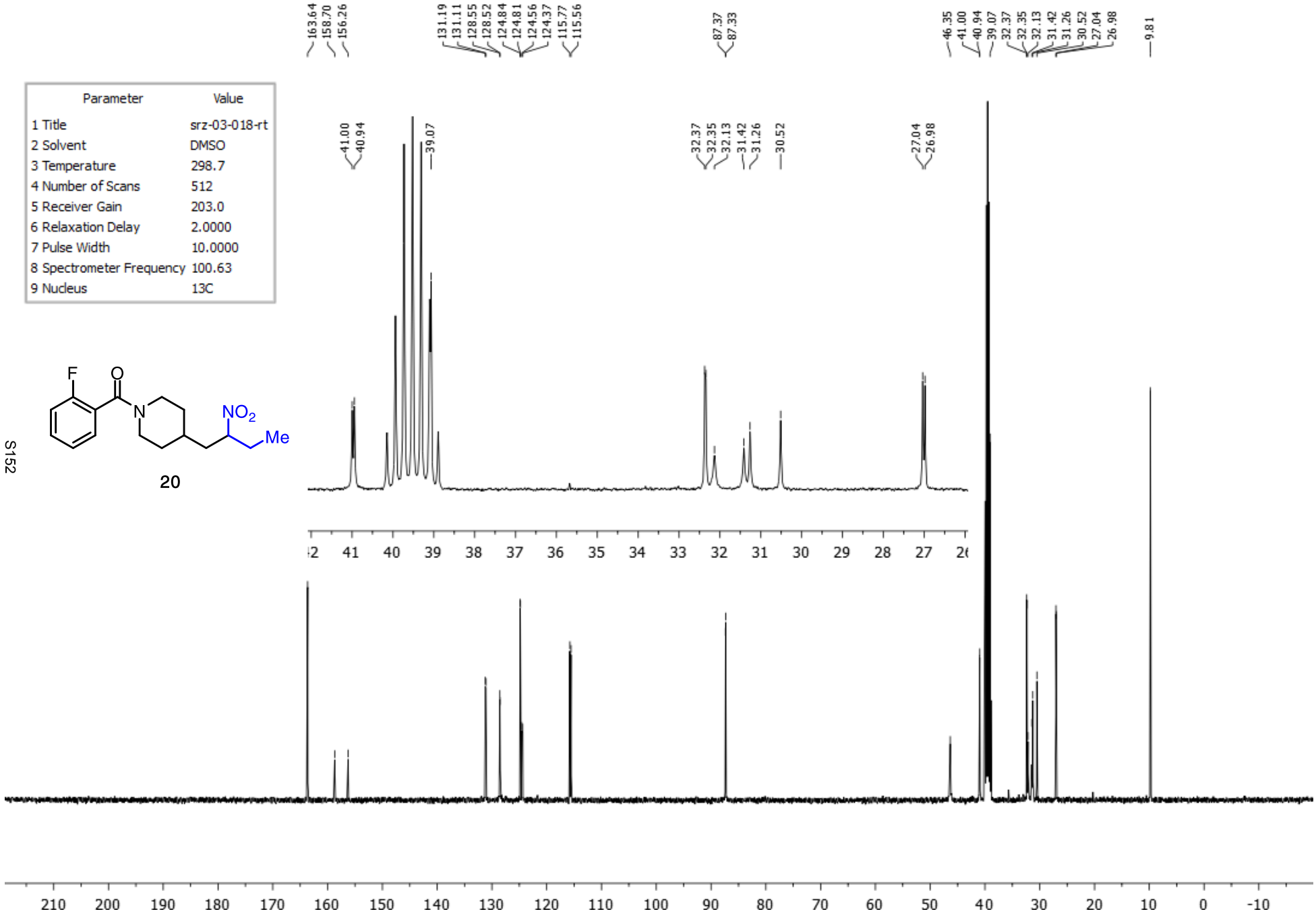
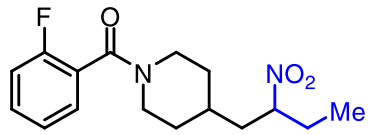
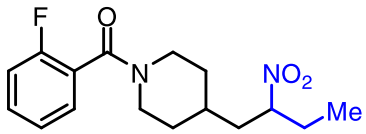

163.64
158.70
156.26
131.19
131.11
128.55
128.52
124.84
124.81
124.56
124.37
115.77
115.56
87.37
87.33
46.35
41.00
40.94
39.07
32.37
32.35
32.13
31.42
31.26
30.52
27.04
26.98
9.81
Parameter Value
1 Title srz-03-018-rt
2 Solvent DMSO
3 Temperature 298.7
4 Number of Scans 512
5 Receiver Gain 203.0
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Spectrometer Frequency 100.63
9 Nucleus 13C
F
O
N
NO2
Me
20

Parameter	Value
1 Title	srz-03-018-360K
2 Solvent	DMSO
3 Temperature	366.2
4 Number of Scans	512
5 Receiver Gain	203.0
6 Relaxation Delay	2.0000
7 Pulse Width	10.0000
8 Spectrometer Frequency	100.63
9 Nucleus	13C



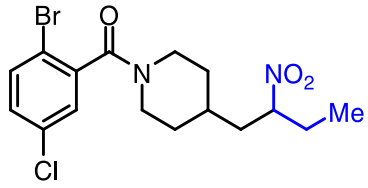
20

Parameter	Value
1 Title	srz-03-018
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	406.0
6 Relaxation Delay	3.0000
7 Pulse Width	11.6200
8 Spectrometer Frequency	564.81
9 Nucleus	19F



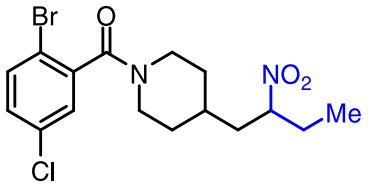
20

Parameter	Value
1 Title	srz-03-016-rt
2 Solvent	DMSO
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	64.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H

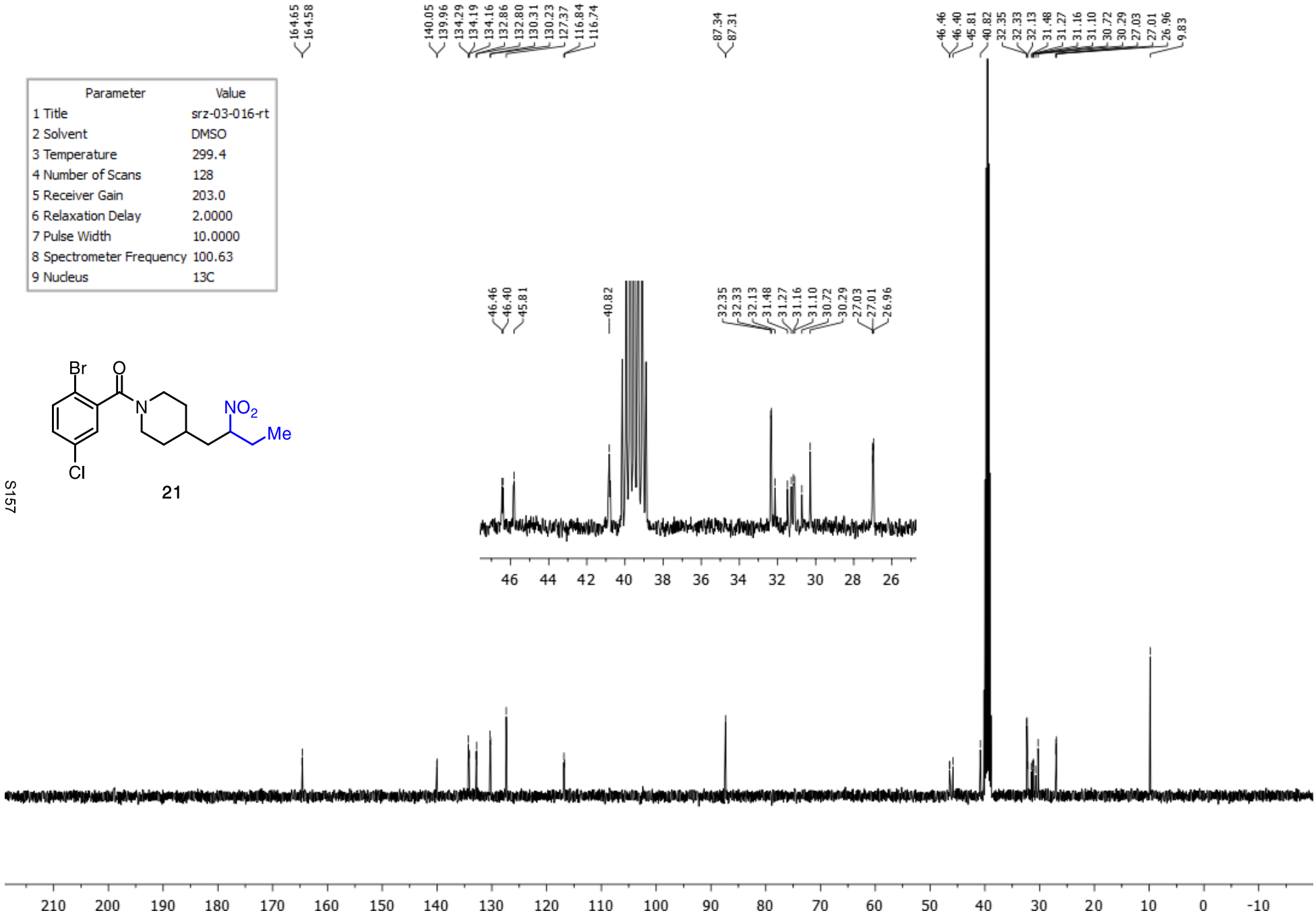


21

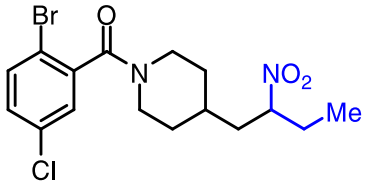
Parameter	Value
1 Title	srz-03-016-340K
2 Solvent	DMSO
3 Temperature	343.9
4 Number of Scans	16
5 Receiver Gain	32.0
6 Relaxation Delay	1.0000
7 Pulse Width	15.0000
8 Spectrometer Frequency	400.15
9 Nucleus	1H



21

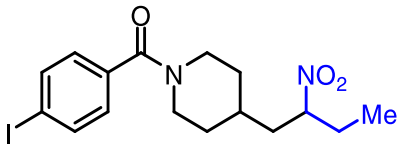

164.65
164.58
140.05
139.96
134.29
134.19
134.16
132.86
132.80
130.31
130.23
127.37
116.84
116.74
87.34
87.31
46.46
46.40
45.81
40.82
32.35
32.33
32.13
31.48
31.27
31.16
31.10
30.72
30.29
27.03
27.01
26.96
9.83
Parameter Value
1 Title srz-03-016-rt
2 Solvent DMSO
3 Temperature 299.4
4 Number of Scans 128
5 Receiver Gain 203.0
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Spectrometer Frequency 100.63
9 Nucleus 13C
Br
O
N
NO2
Me
Cl
21
46 44 42 40 38 36 34 32 30 28 26
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Parameter	Value
1 Title	srz-03-016-C-360K-2.2.fid
2 Solvent	DMSO
3 Temperature	360.0
4 Number of Scans	512
5 Receiver Gain	203.0
6 Relaxation Delay	2.0000
7 Pulse Width	10.0000
8 Spectrometer Frequency	100.63
9 Nucleus	13C

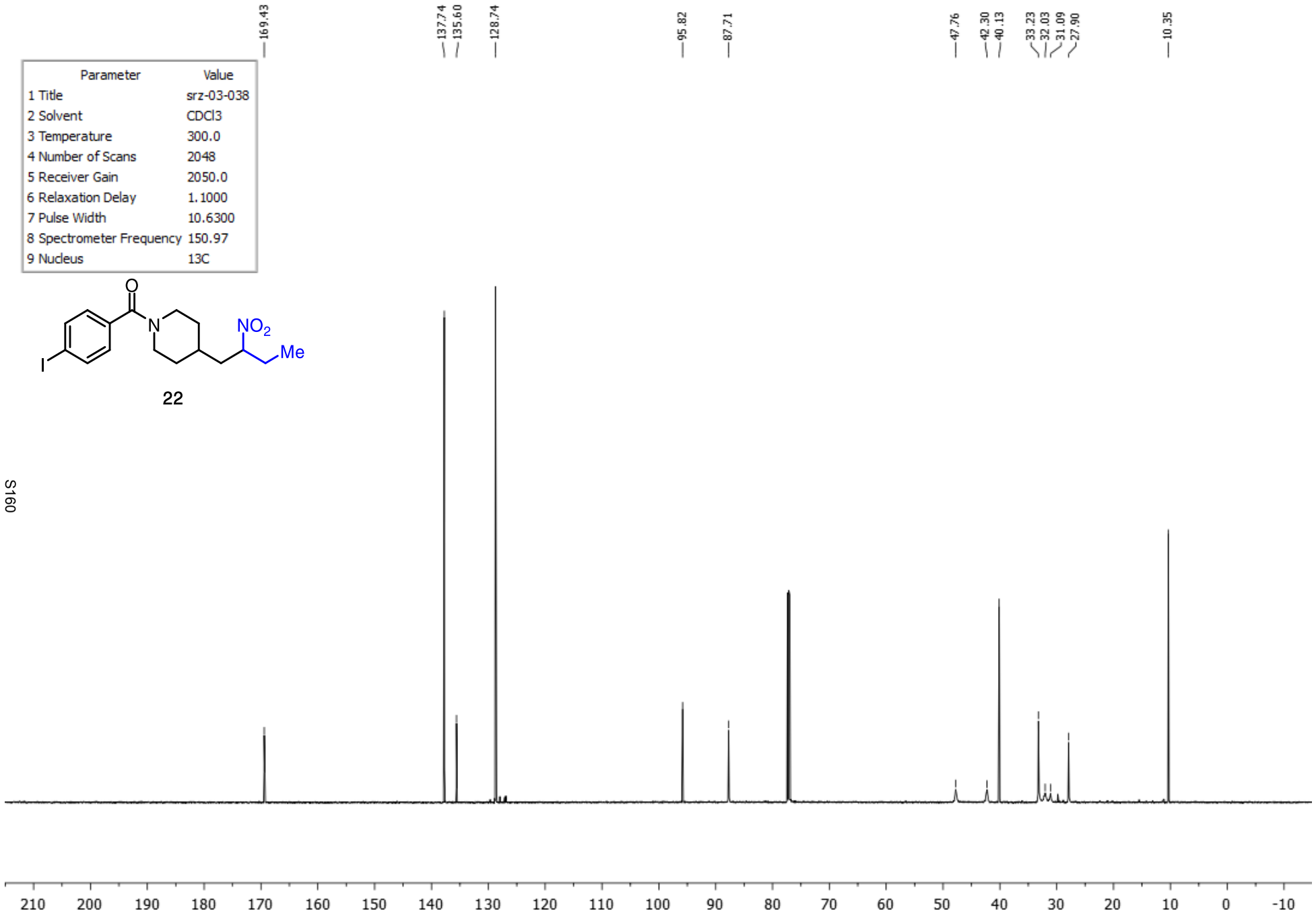


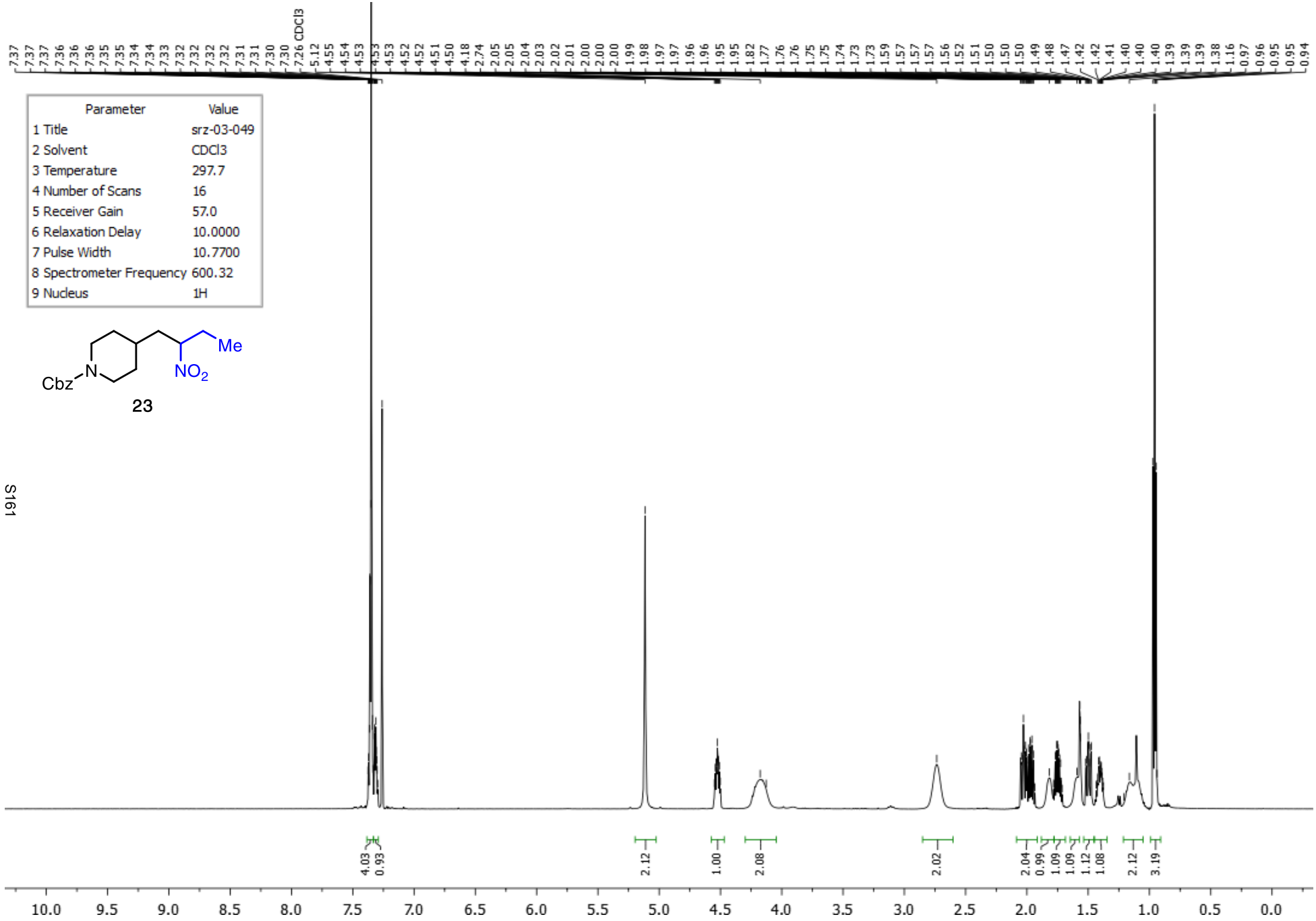
21

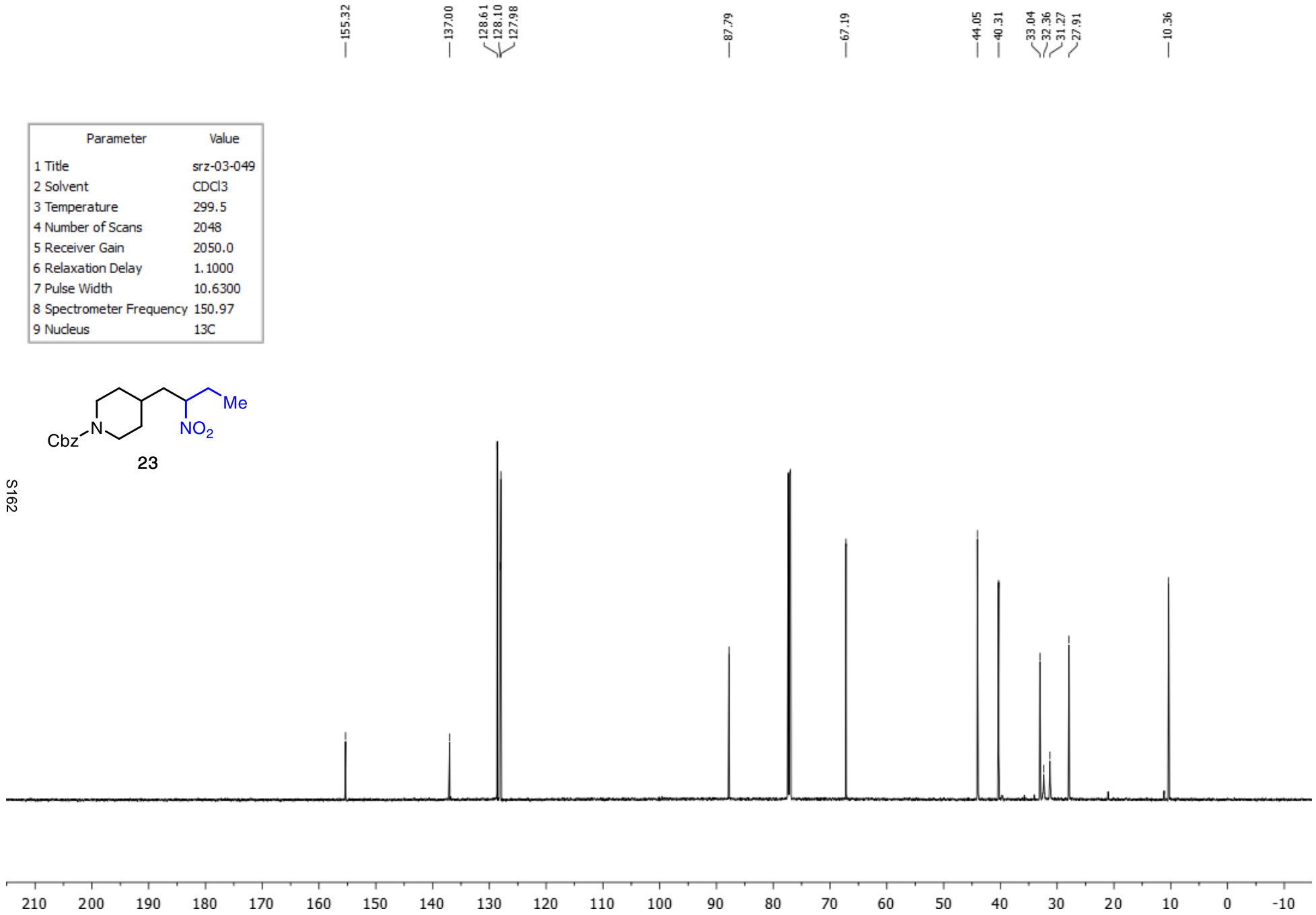
Parameter	Value
1 Title	srz-03-038
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	64.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



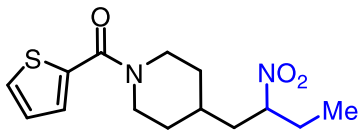
22


169.43
137.74
135.60
128.74
95.82
87.71
47.76
42.30
40.13
33.23
32.03
31.09
27.90
10.35
Parameter Value
1 Title srz-03-038
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
O
N
NO2
Me
I
22
S160
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

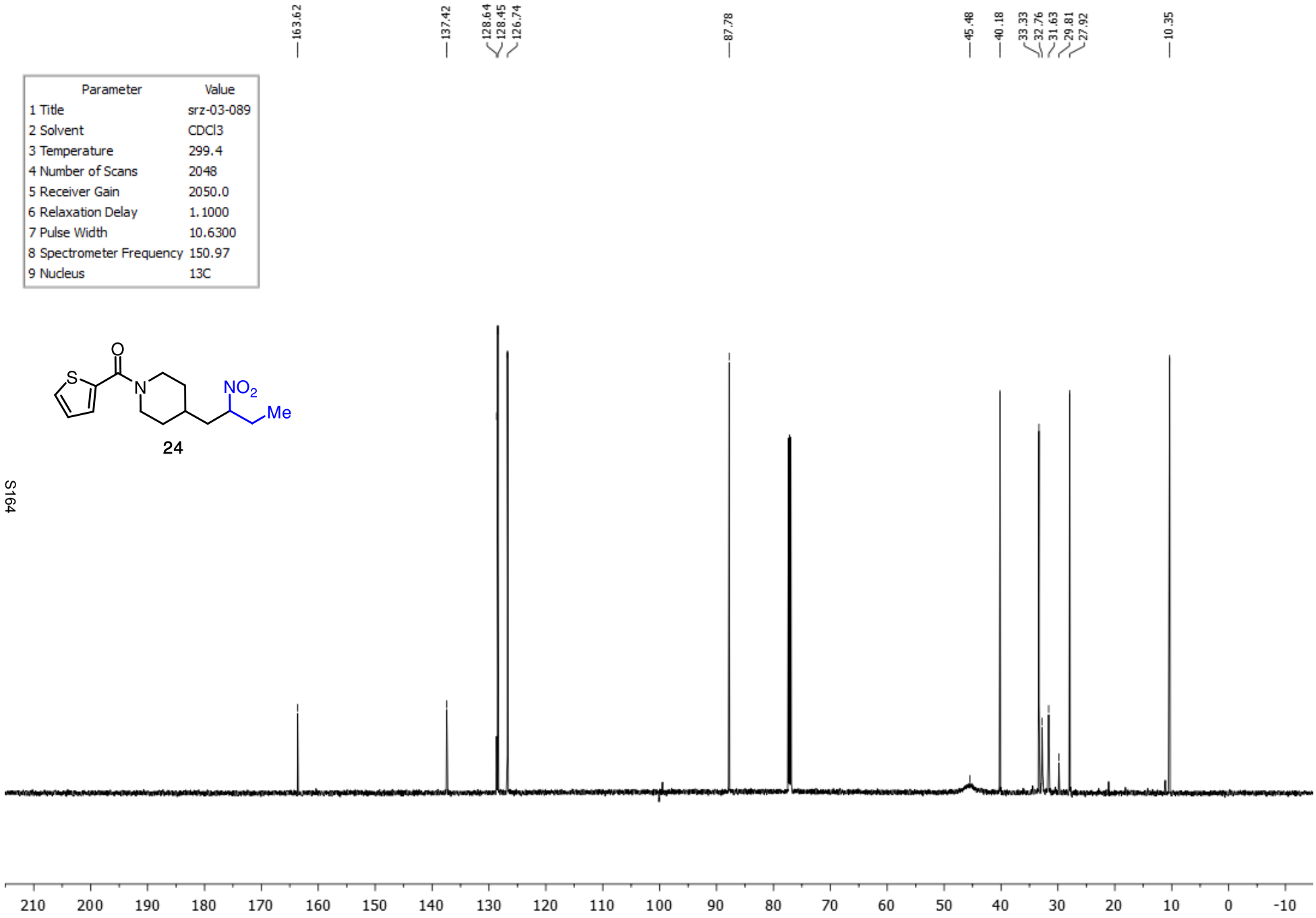

Parameter Value
1 Title srz-03-049
2 Solvent CDCl3
3 Temperature 297.7
4 Number of Scans 16
5 Receiver Gain 57.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
Cbz
N
Me
NO2
23
CDCl3
4.03
0.93
2.12
1.00
2.08
2.02
2.04
0.99
1.09
1.09
1.12
1.08
2.12
3.19
10.0
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


155.32
137.00
128.61
128.10
127.98
87.79
67.19
44.05
40.31
33.04
32.36
31.27
27.91
10.36
Parameter Value
1 Title srz-03-049
2 Solvent CDCl3
3 Temperature 299.5
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
Cbz
N
NO2
Me
23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

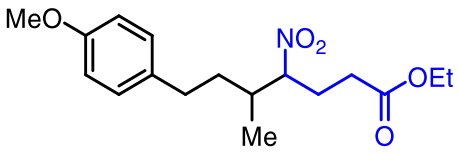
Parameter	Value
1 Title	srz-03-089
2 Solvent	CDCl3
3 Temperature	297.6
4 Number of Scans	16
5 Receiver Gain	71.8
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



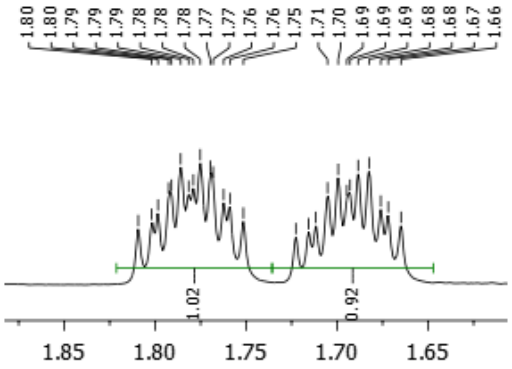
24

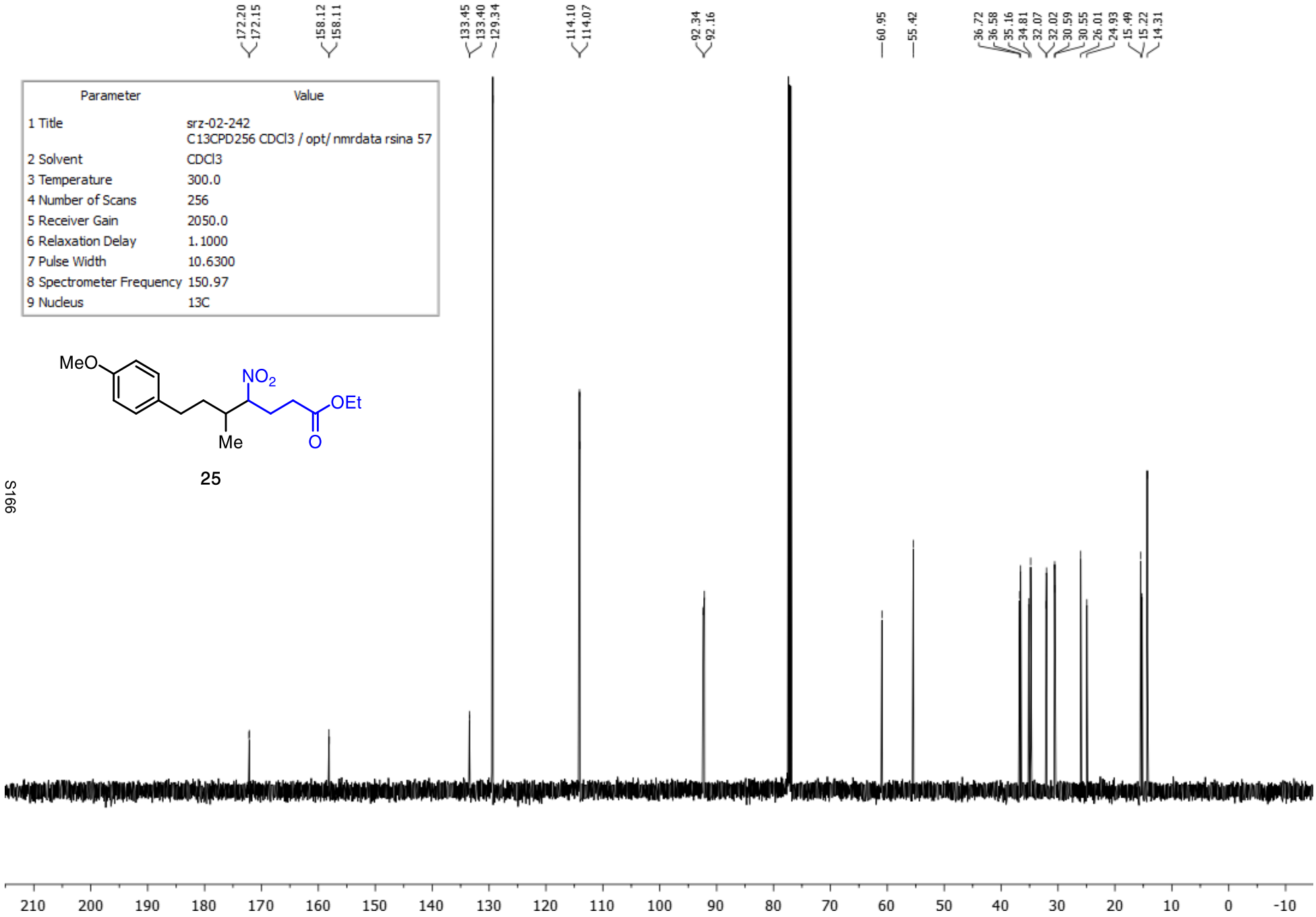

163.62
137.42
128.64
128.45
126.74
87.78
45.48
40.18
33.33
32.76
31.63
29.81
27.92
10.35
Parameter Value
1 Title srz-03-089
2 Solvent CDCl3
3 Temperature 299.4
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
O
S
N
NO2
Me
24
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

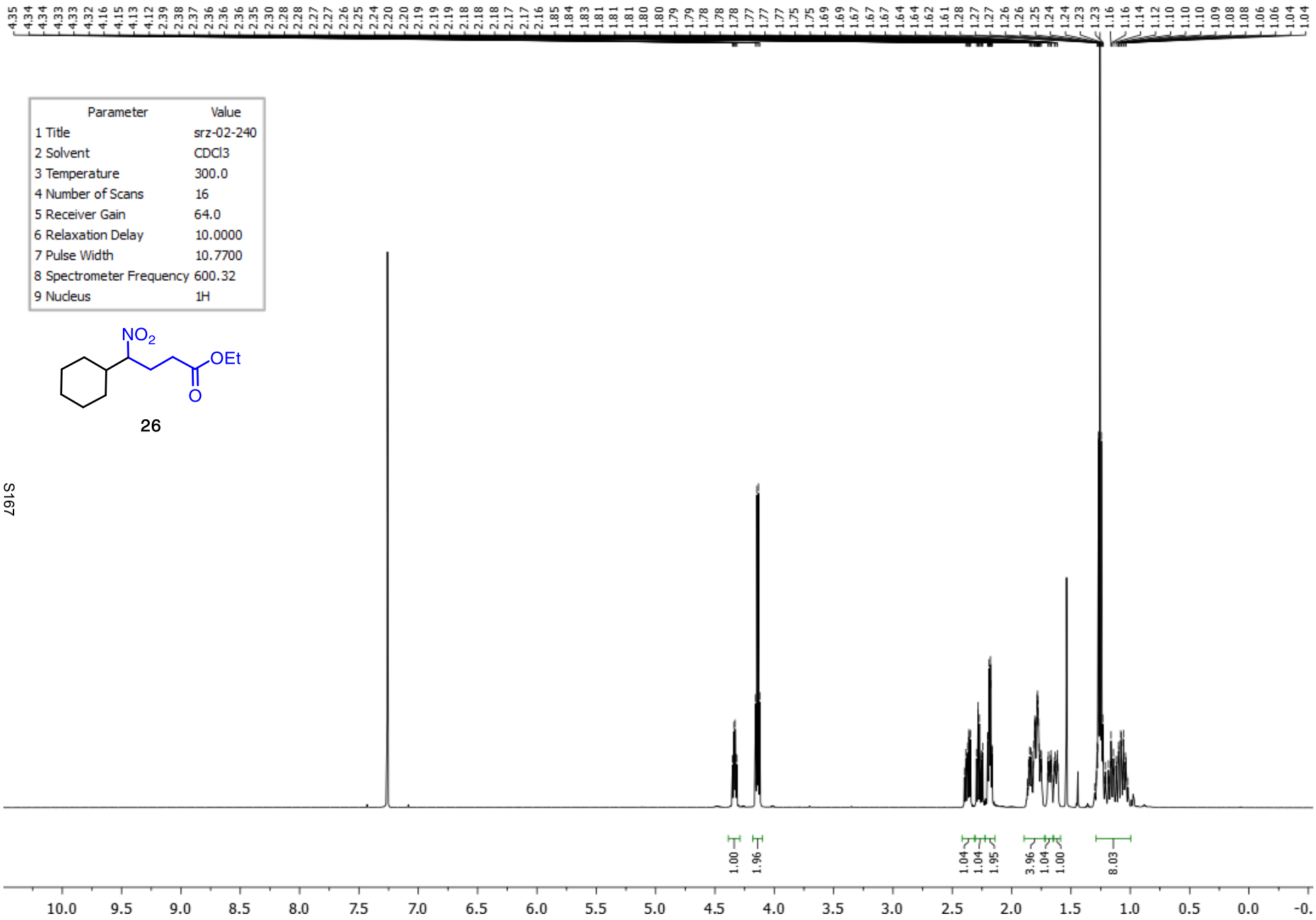
Parameter	Value
1 Title	srz-02-242
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	32.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H

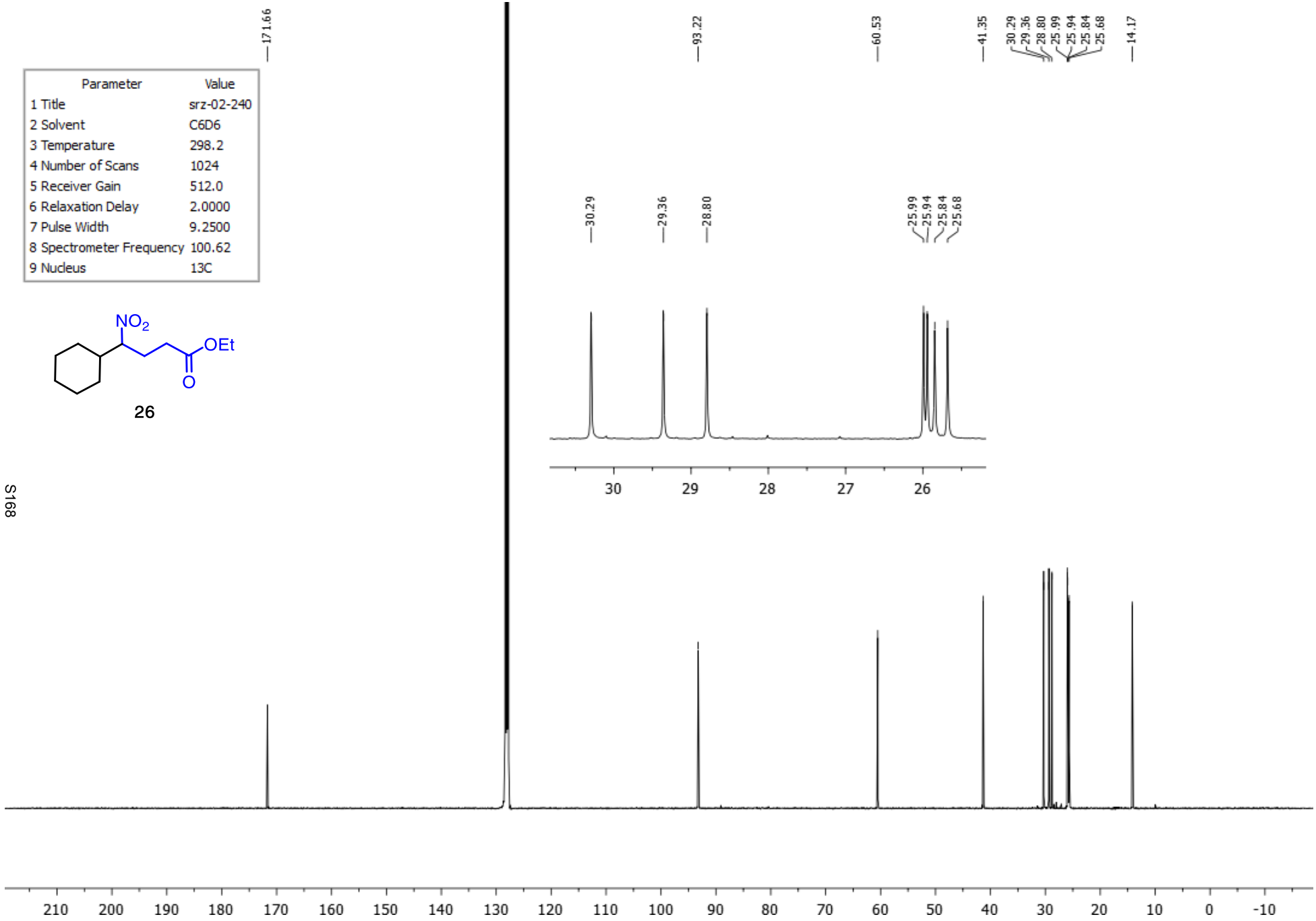


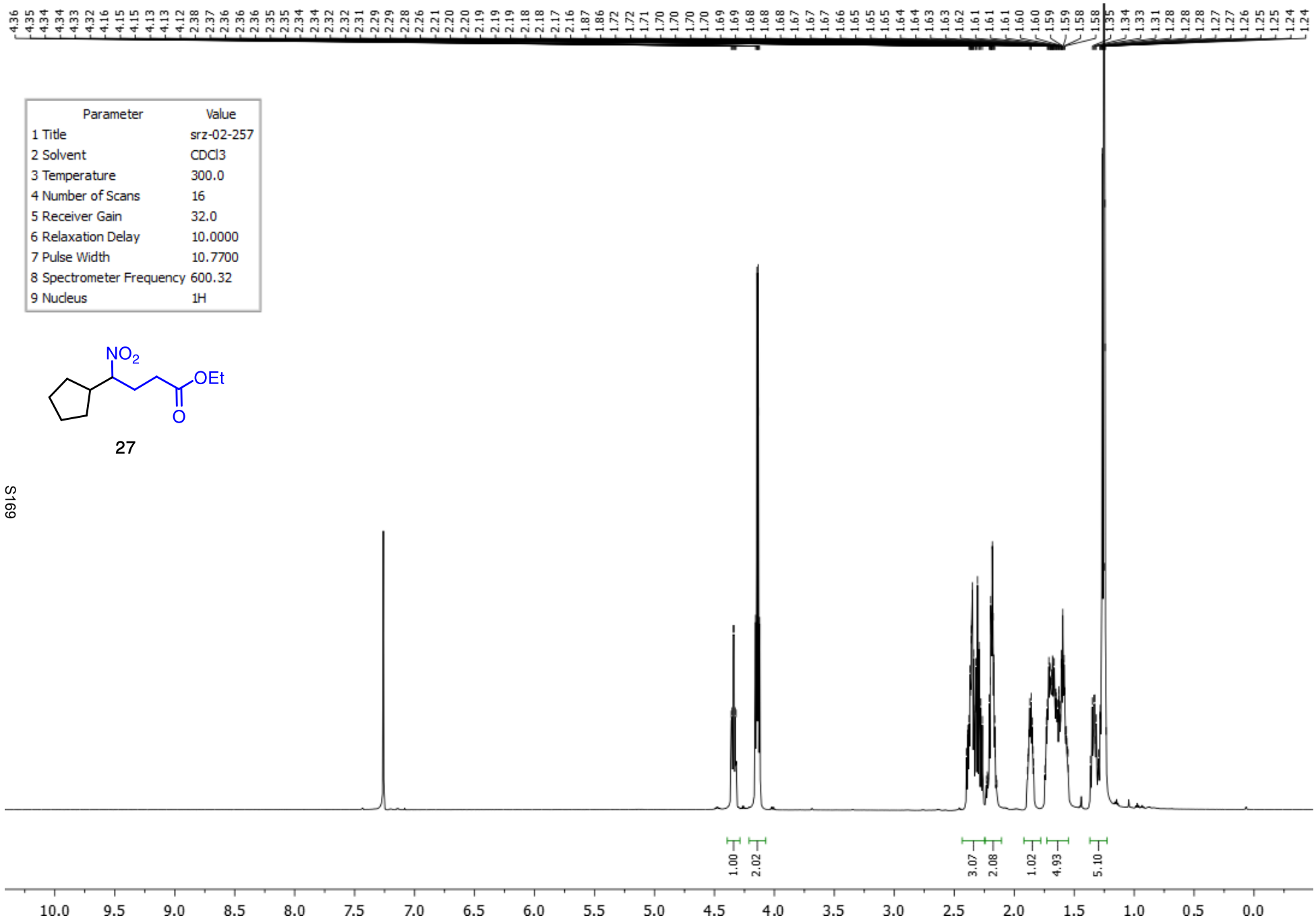
25

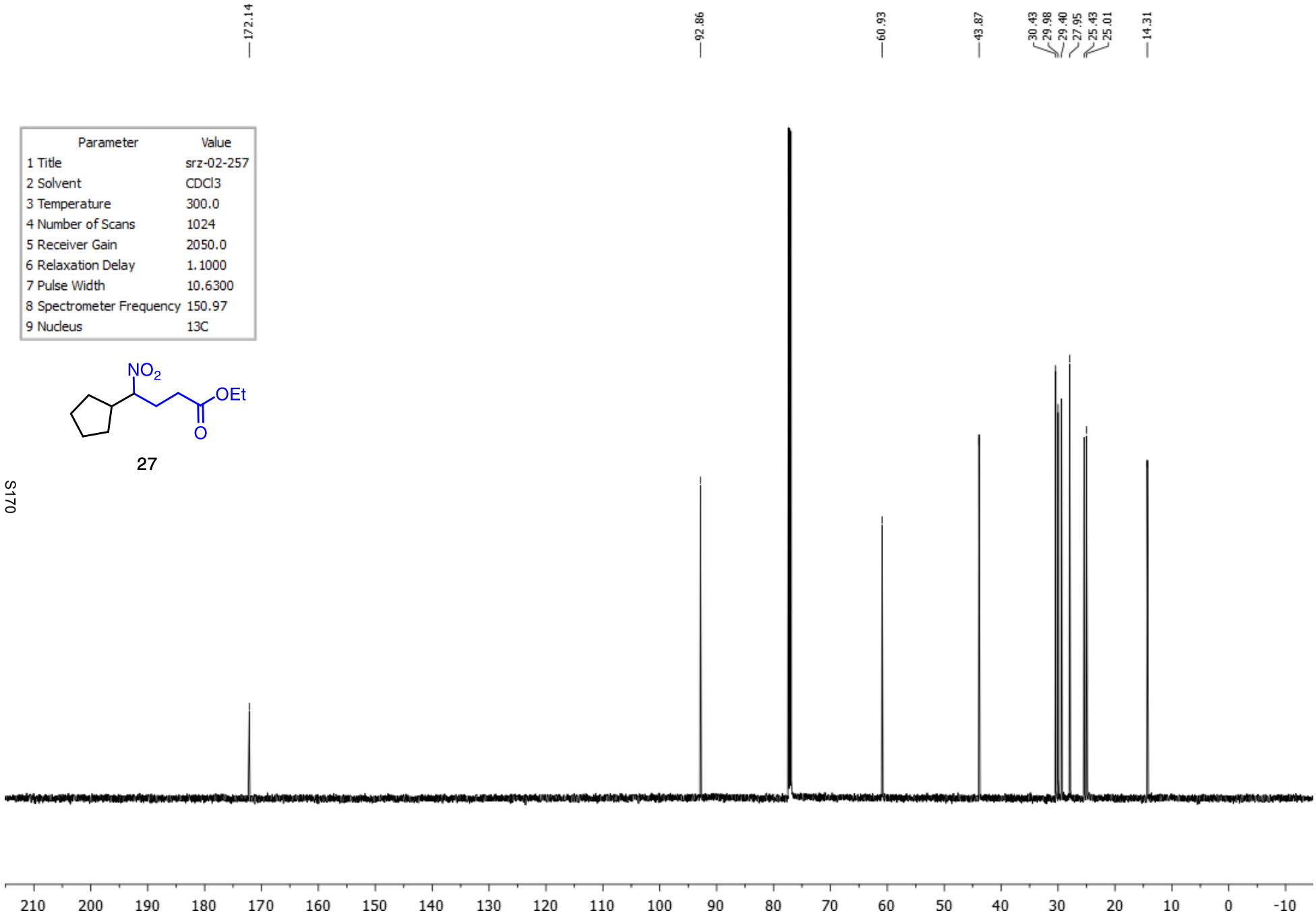


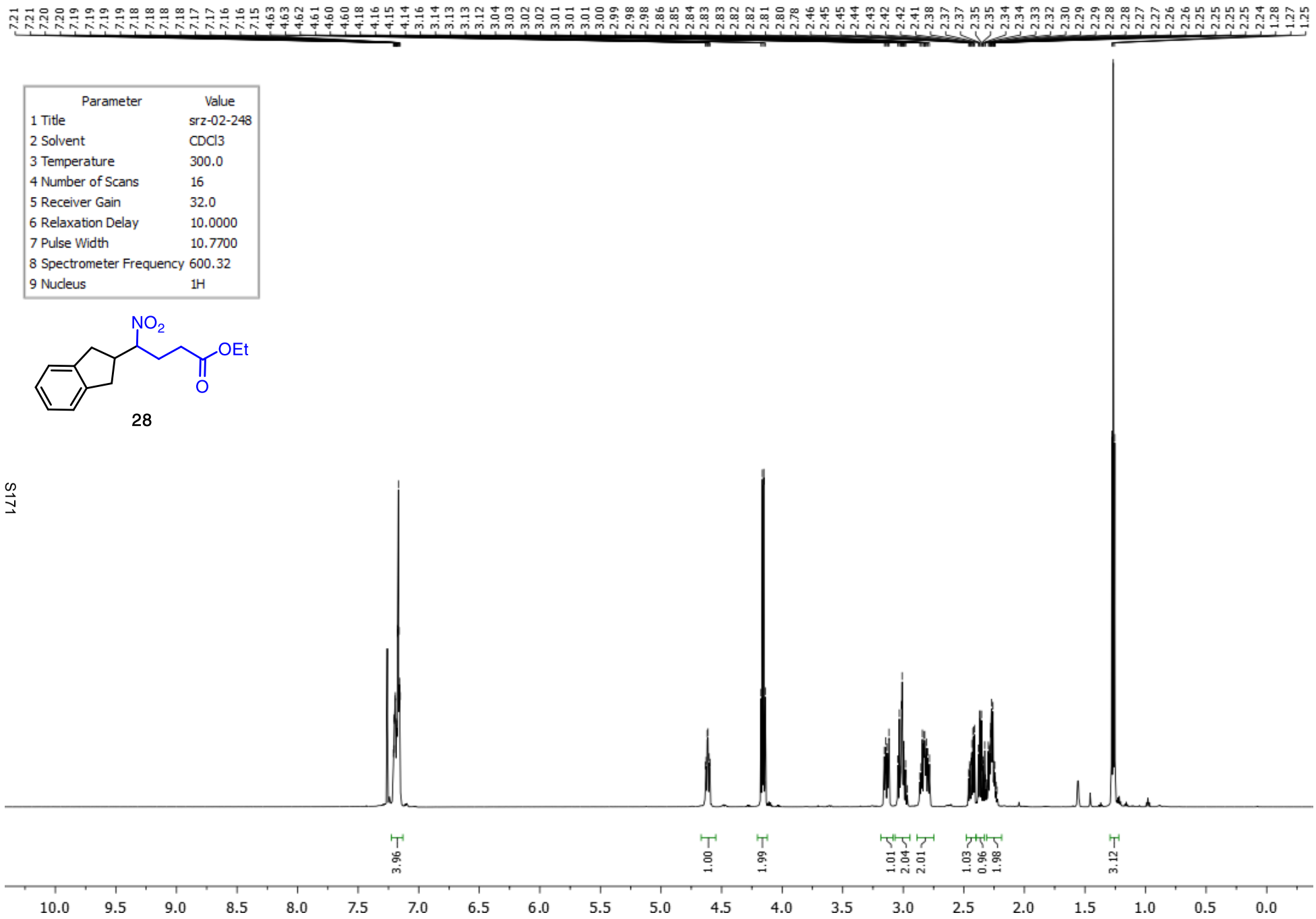

172.20
172.15
158.12
158.11
133.45
133.40
129.34
114.10
114.07
92.34
92.16
60.95
55.42
36.72
36.58
35.16
34.81
32.07
32.02
30.59
30.55
26.01
24.93
15.49
15.22
14.31
Parameter
Value
1 Title
srz-02-242
C13CPD256 CDCl3 / opt/ nmrdata rsina 57
2 Solvent
CDCl3
3 Temperature
300.0
4 Number of Scans
256
5 Receiver Gain
2050.0
6 Relaxation Delay
1.1000
7 Pulse Width
10.6300
8 Spectrometer Frequency
150.97
9 Nucleus
13C
MeO
NO2
OEt
Me
O
25
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

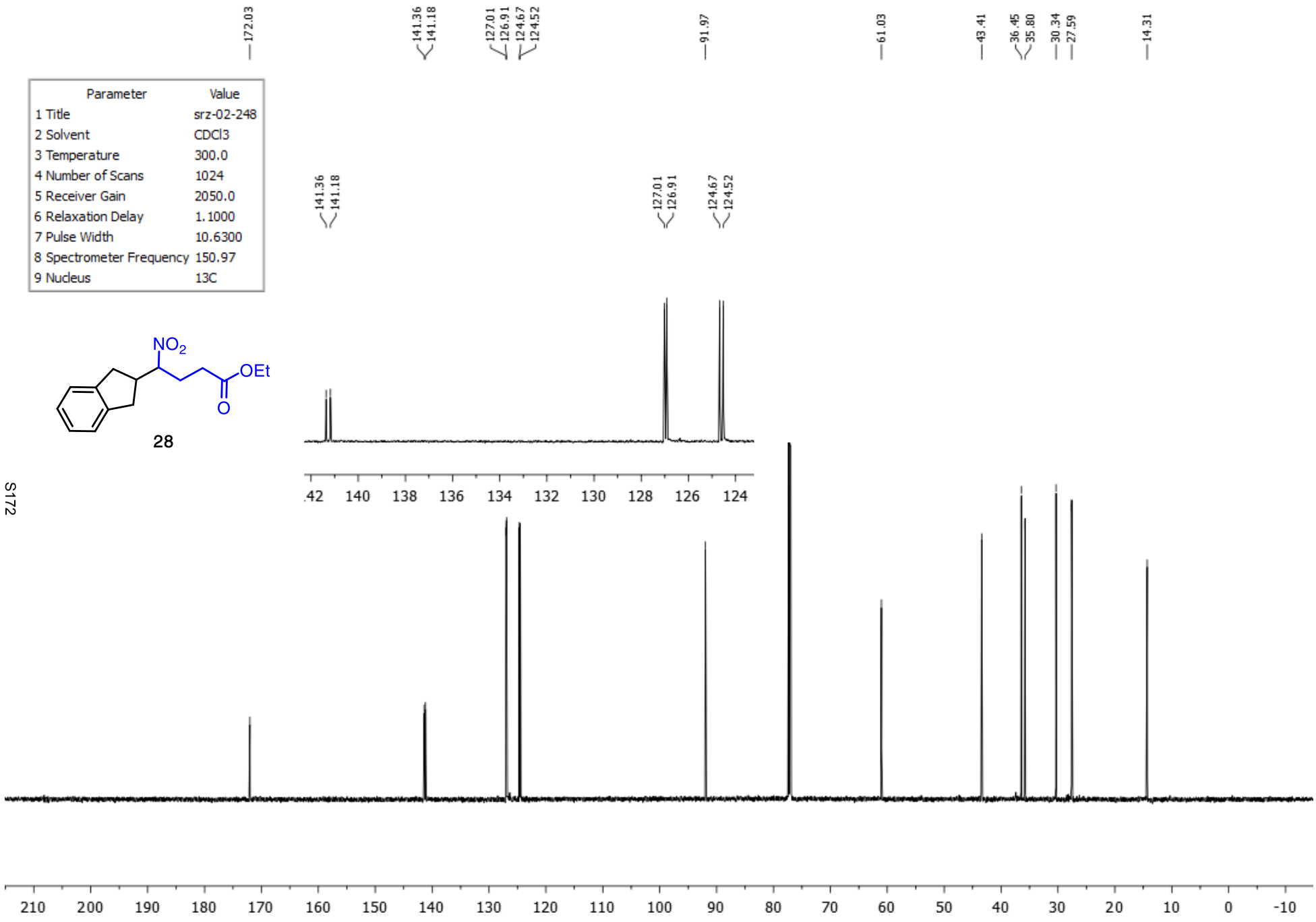

Parameter Value
1 Title srz-02-240
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 64.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
NO2
OEt
O
26
1.00
1.96
1.04
1.04
1.95
3.96
1.04
1.00
8.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


171.66
93.22
60.53
41.35
30.29
29.36
28.80
25.99
25.94
25.84
25.68
14.17
Parameter Value
1 Title srz-02-240
2 Solvent C6D6
3 Temperature 298.2
4 Number of Scans 1024
5 Receiver Gain 512.0
6 Relaxation Delay 2.0000
7 Pulse Width 9.2500
8 Spectrometer Frequency 100.62
9 Nucleus 13C
NO2
OEt
O
26
30.29
29.36
28.80
25.99
25.94
25.84
25.68
30
29
28
27
26
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

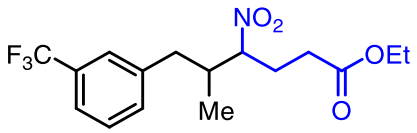

Parameter Value
1 Title srz-02-257
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 32.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
NO2
OEt
O
27
1.00
2.02
3.07
2.08
1.02
4.93
5.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


172.14
92.86
60.93
43.87
30.43
29.98
29.40
27.95
25.43
25.01
14.31
Parameter Value
1 Title srz-02-257
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 1024
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
NO2
OEt
O
27
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


Parameter Value
1 Title srz-02-248
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 32.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
NO2
OEt
O
28
3.96
1.00
1.99
1.01
2.04
2.01
1.03
0.96
1.98
3.12
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


172.03
141.36
141.18
127.01
126.91
124.67
124.52
91.97
61.03
43.41
36.45
35.80
30.34
27.59
14.31
Parameter Value
1 Title srz-02-248
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 1024
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
NO2
OEt
O
28
S172
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
.42 140 138 136 134 132 130 128 126 124

Parameter	Value
1 Title	srz-02-253
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	32.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



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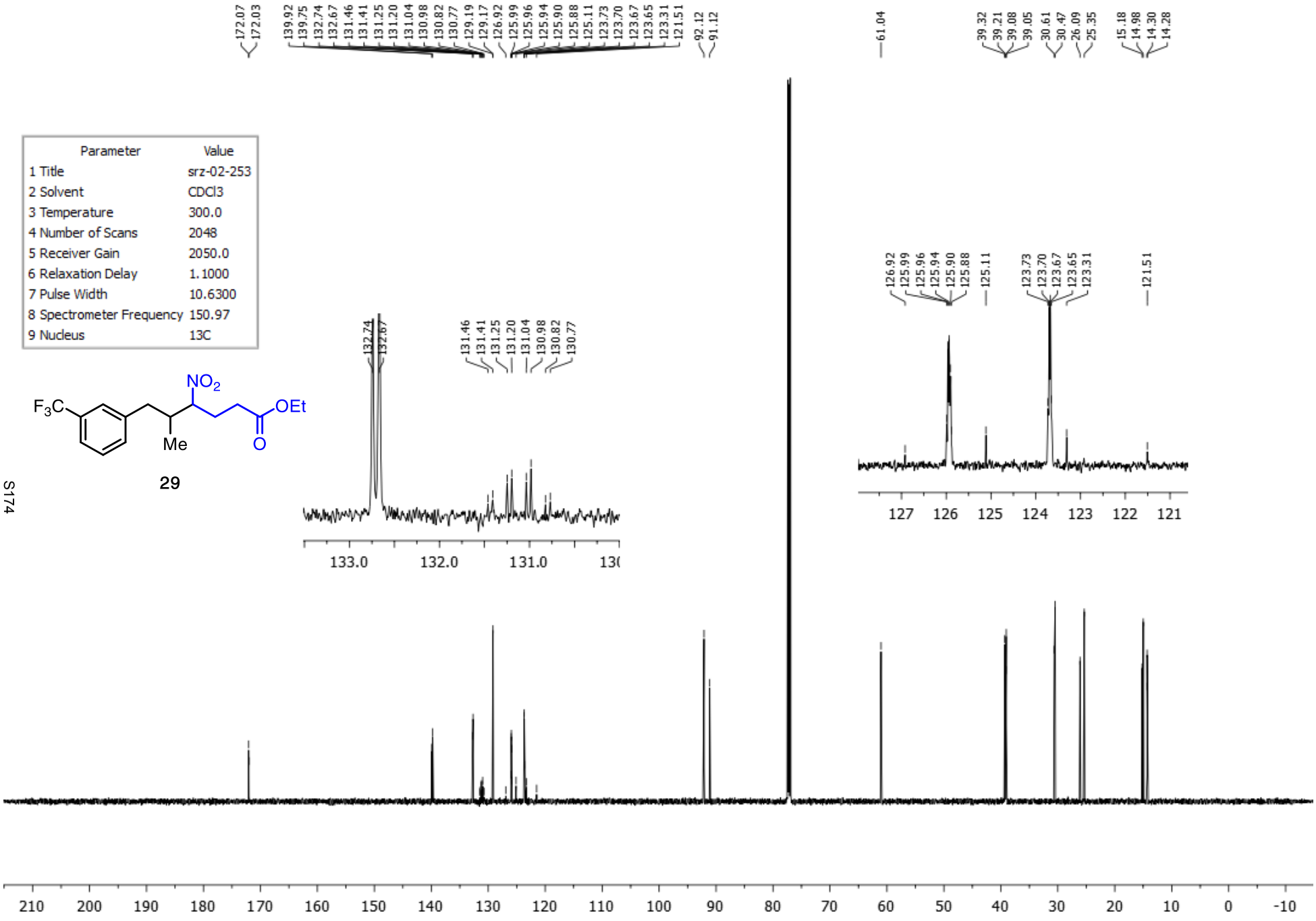
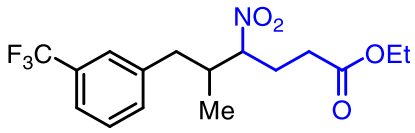

172.07
172.03
139.92
139.75
132.74
132.67
131.46
131.41
131.25
131.20
131.04
130.98
130.82
130.77
129.19
129.17
126.92
125.99
125.96
125.94
125.90
125.88
125.11
123.73
123.70
123.67
123.65
123.31
121.51
92.12
91.12
61.04
39.32
39.21
39.08
39.05
30.61
30.47
26.09
25.35
15.18
14.98
14.30
14.28
Parameter Value
1 Title srz-02-253
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
NO2
F3C
OEt
Me
O
29
S174
133.0
132.0
131.0
127
126
125
124
123
122
121
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

Parameter	Value
1 Title	srz-02-253
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	32
5 Receiver Gain	161.0
6 Relaxation Delay	3.0000
7 Pulse Width	11.6200
8 Spectrometer Frequency	564.81
9 Nucleus	19F



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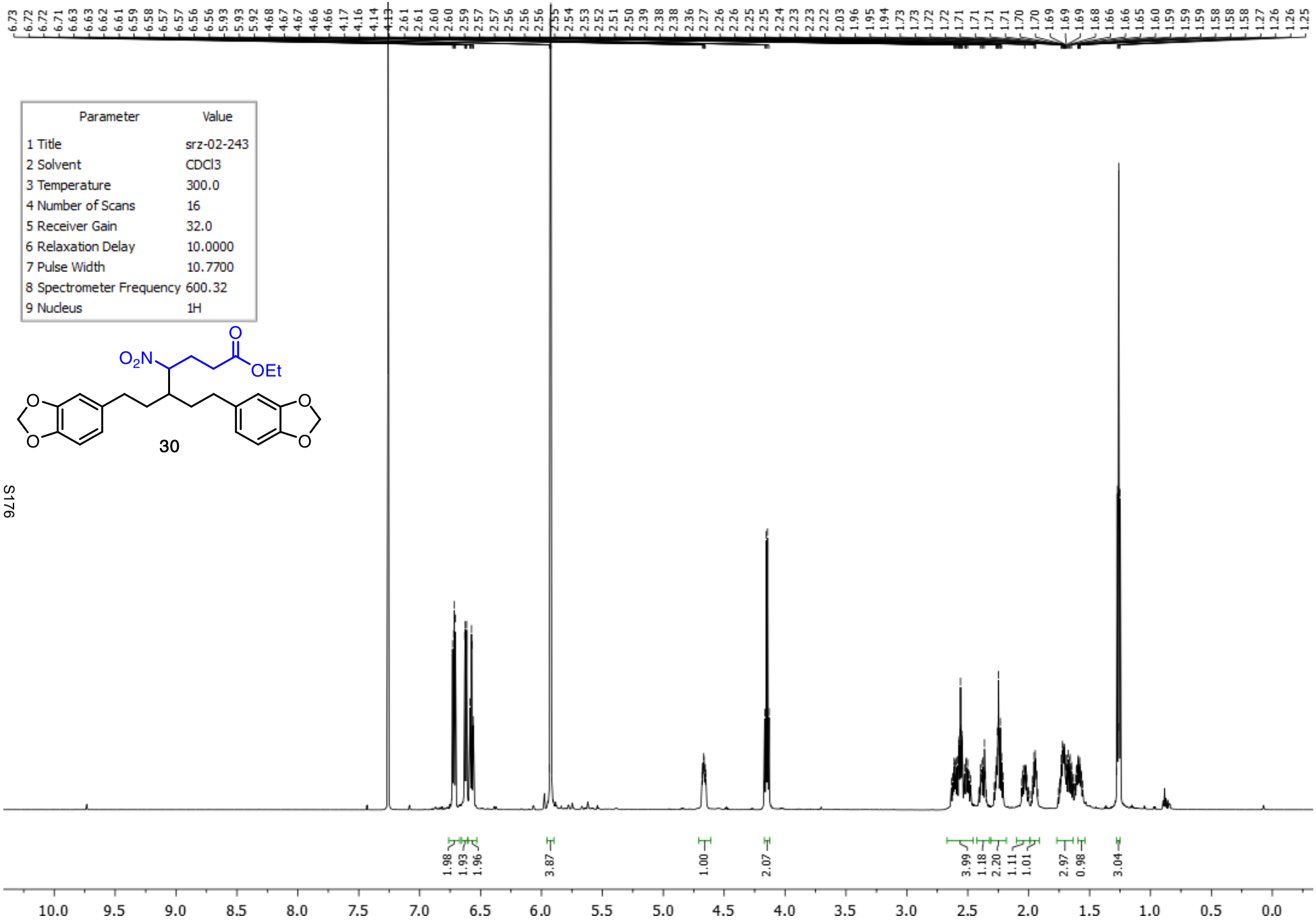
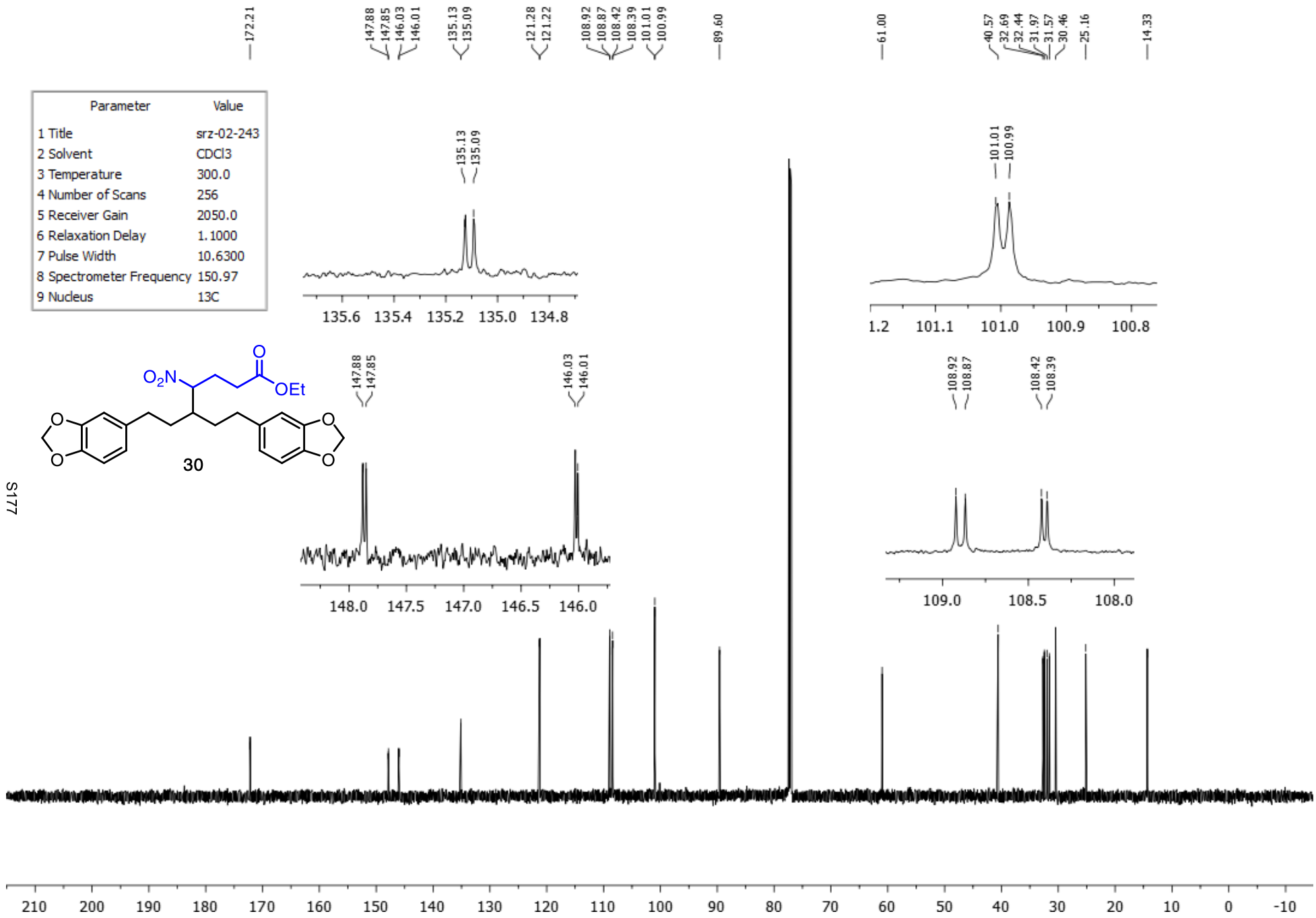
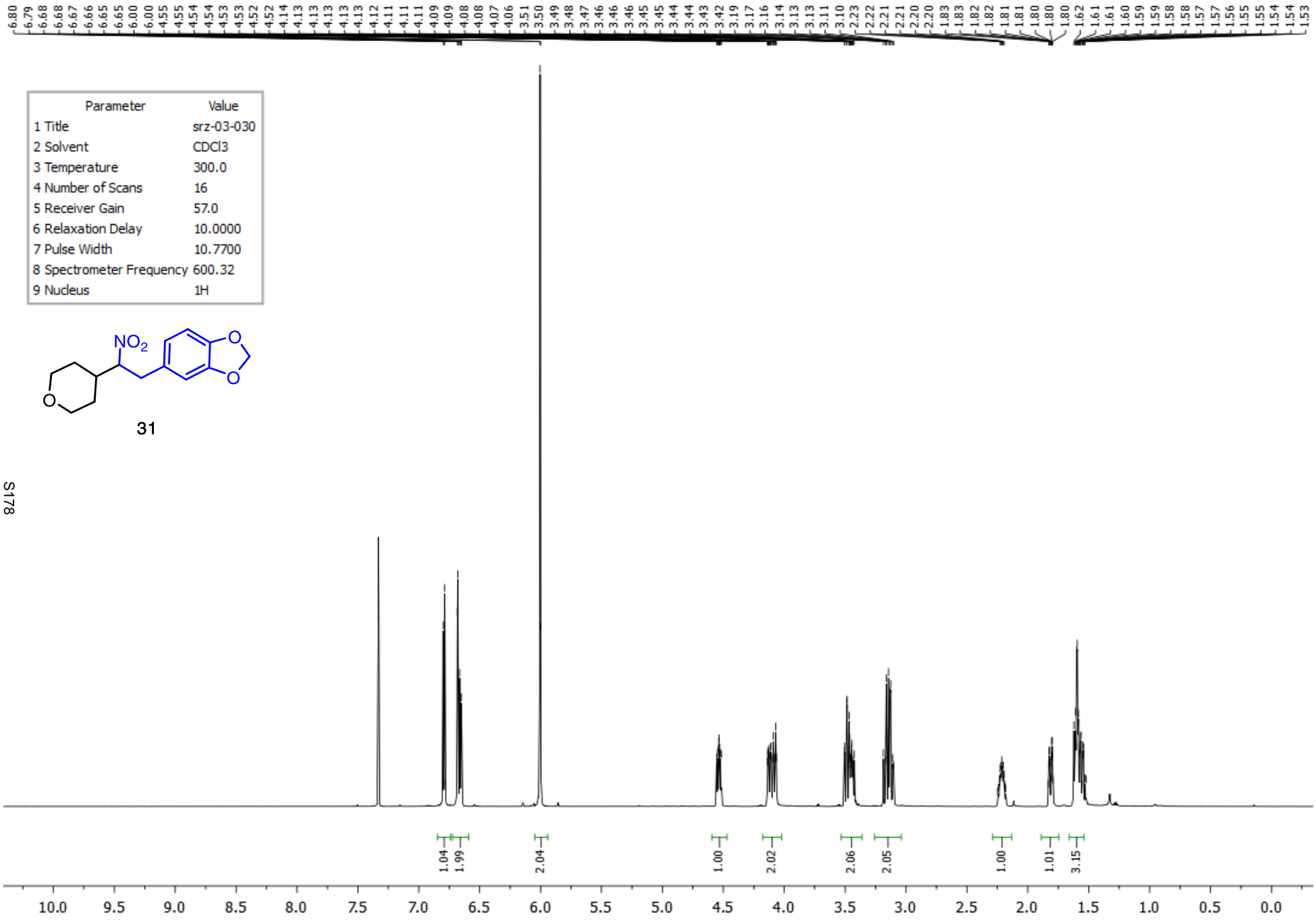
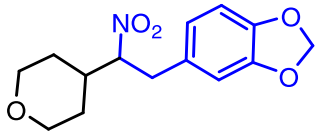

Parameter Value
1 Title srz-02-243
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 32.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
O2N
OEt
O
30
1.98
1.93
1.96
3.87
1.00
2.07
3.99
1.18
2.20
1.11
1.01
2.97
0.98
3.04
10.0
9.5
9.0
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

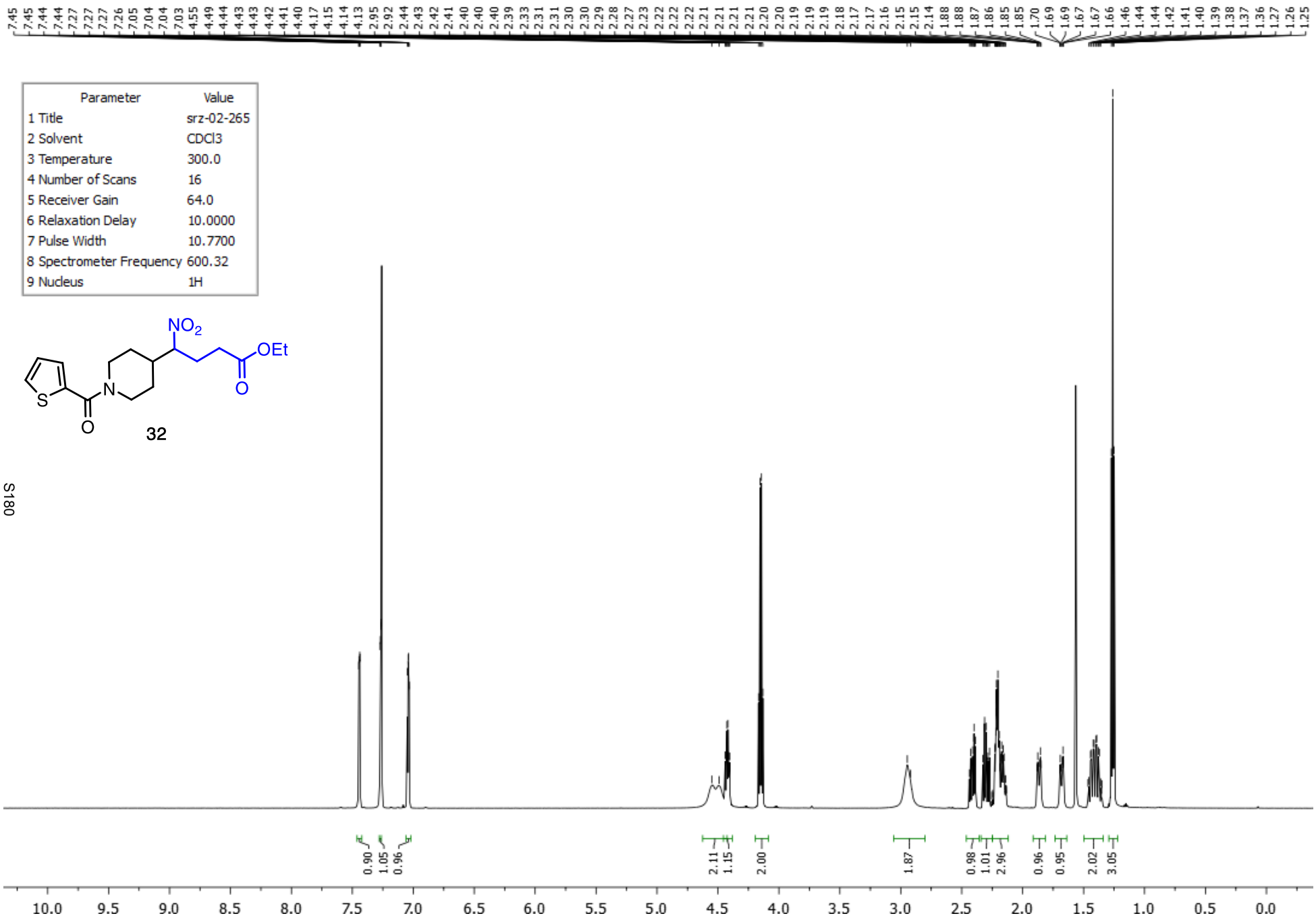

172.21
147.88
147.85
146.03
146.01
135.13
135.09
121.28
121.22
108.92
108.87
108.42
108.39
101.01
100.99
89.60
61.00
40.57
32.69
32.44
31.97
31.57
30.46
25.16
14.33
Parameter Value
1 Title srz-02-243
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 256
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
135.6 135.4 135.2 135.0 134.8
1.2 101.1 101.0 100.9 100.8
148.0 147.5 147.0 146.5 146.0
109.0 108.5 108.0
O2N
OEt
O
30
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


6.80 6.79 6.68 6.68 6.67 6.66 6.65 6.65 6.00 6.00 4.55 4.55 4.54 4.54 4.53 4.53 4.52 4.52 4.14 4.13 4.13 4.13 4.13 4.12 4.11 4.11 4.11 4.09 4.09 4.08 4.08 4.07 4.06 3.51 3.50 3.49 3.48 3.47 3.46 3.46 3.46 3.45 3.45 3.44 3.44 3.43 3.42 3.19 3.17 3.16 3.14 3.13 3.13 3.11 3.10 2.23 2.22 2.21 2.21 2.20 2.20 1.83 1.83 1.82 1.82 1.81 1.81 1.80 1.80 1.80 1.62 1.61 1.61 1.60 1.59 1.59 1.58 1.58 1.57 1.57 1.56 1.55 1.55 1.54 1.54 1.53
Parameter Value
1 Title srz-03-030
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 57.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
NO2
O
O
O
31
1.04
1.99
2.04
1.00
2.02
2.06
2.05
1.00
1.01
3.15
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

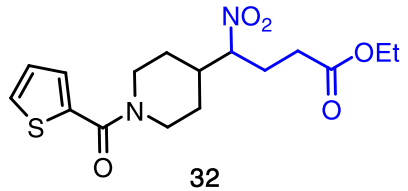
Parameter	Value
1 Title	srz-03-030
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	2048
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C



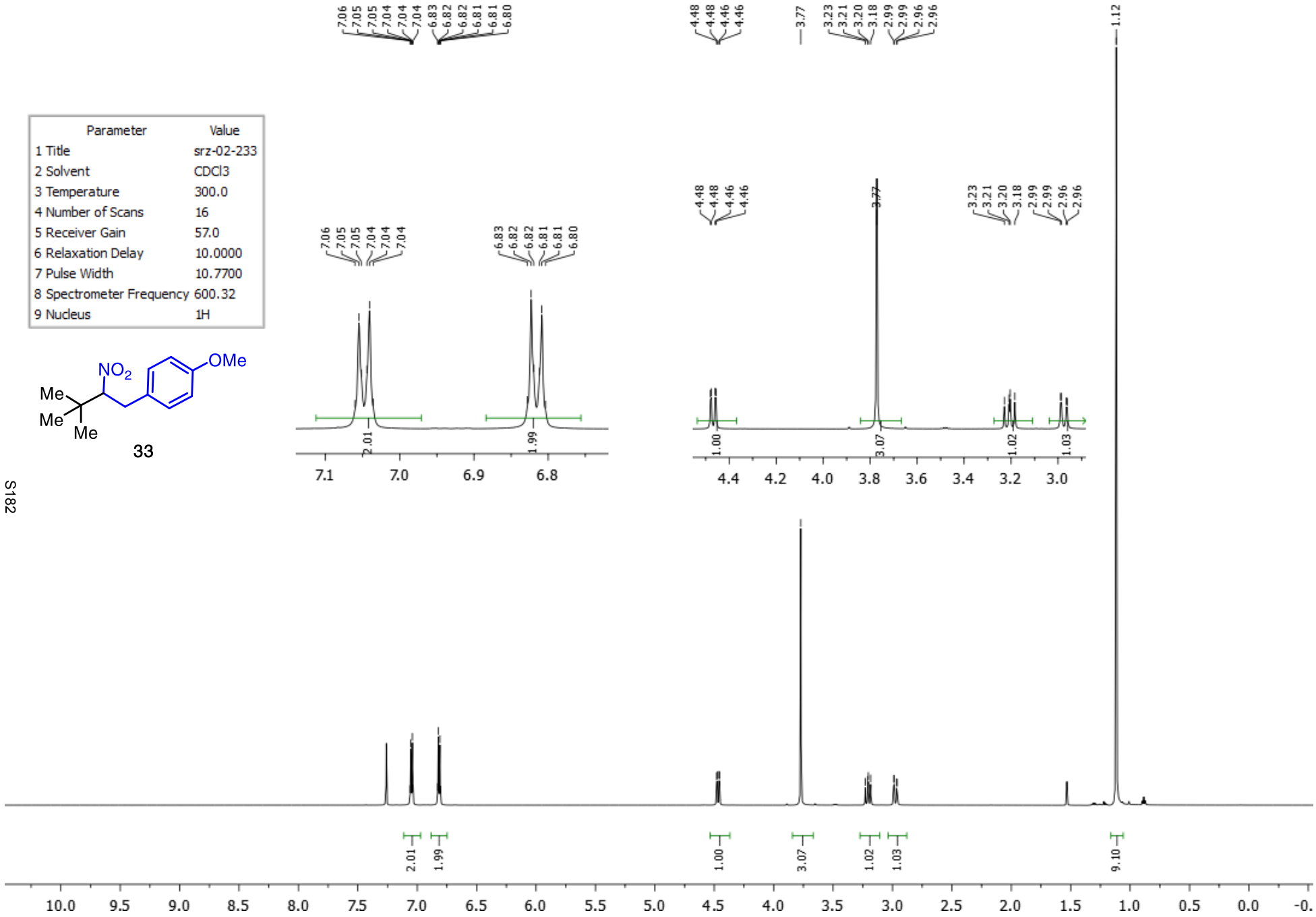
31

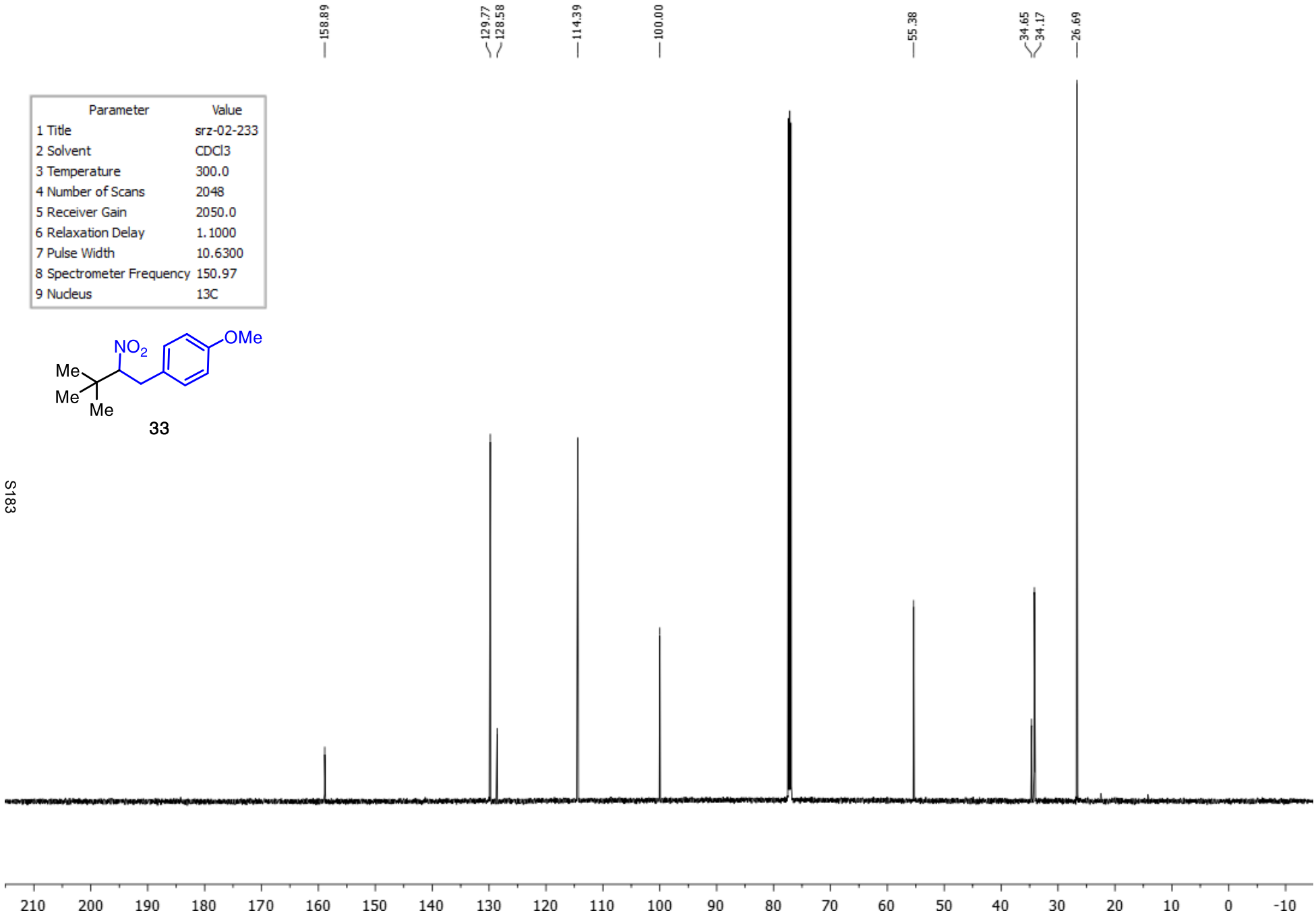

Parameter Value
1 Title srz-02-265
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 64.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
NO2
OEt
O
S
N
O
32
S180
0.90
1.05
0.96
2.11
1.15
2.00
1.87
0.98
1.01
2.96
0.96
0.95
2.02
3.05
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

Parameter	Value
1 Title	srz-02-0265-C.1.fid
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	1024
5 Receiver Gain	512.0
6 Relaxation Delay	2.0000
7 Pulse Width	9.2500
8 Spectrometer Frequency	100.62
9 Nucleus	13C

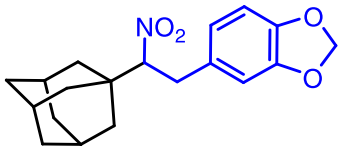


32

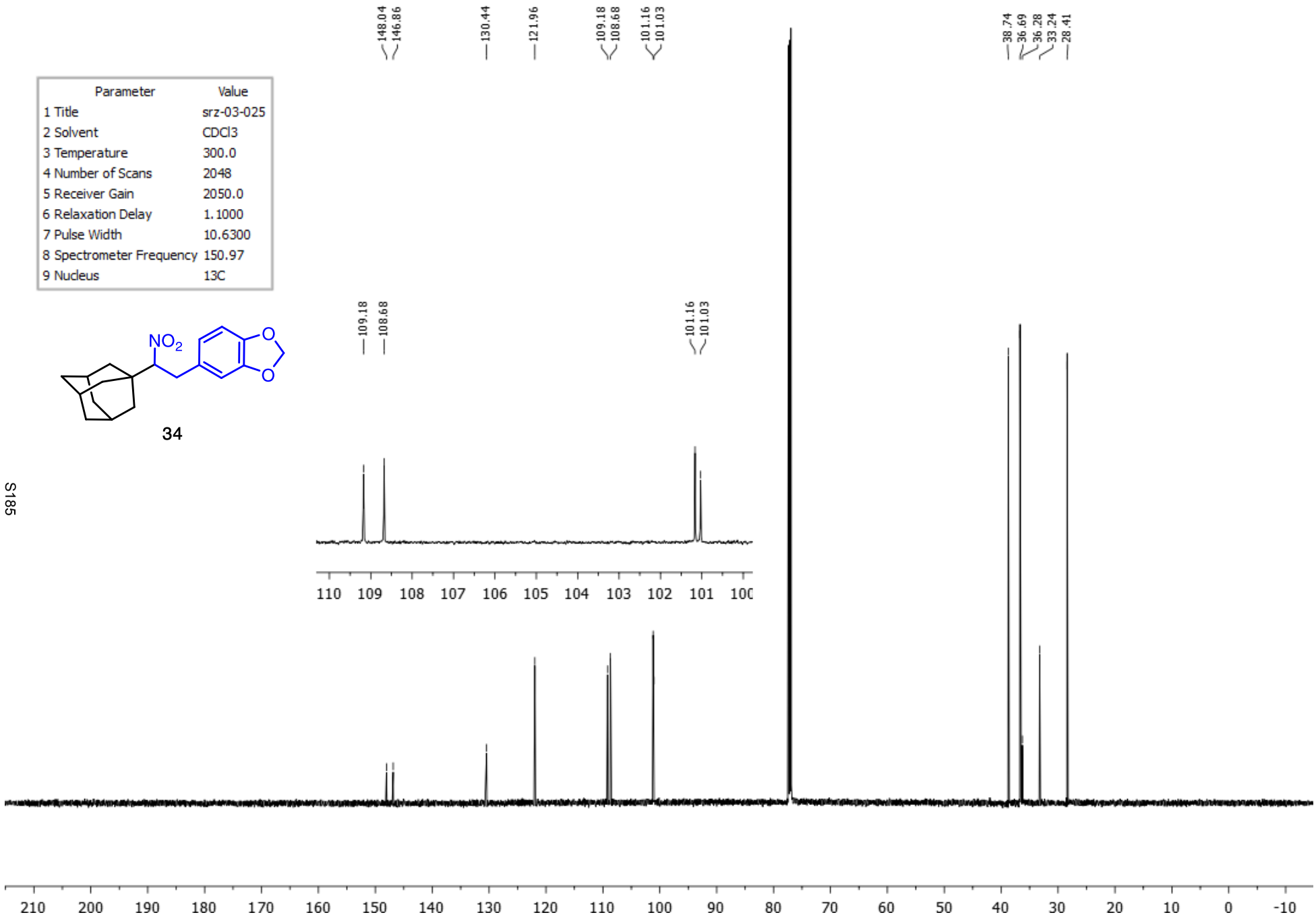

Parameter Value
1 Title srz-02-233
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 57.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
NO2
OMe
Me
Me
Me
33
7.06 7.05 7.05 7.04 7.04 7.04 6.83 6.82 6.82 6.81 6.81 6.80
4.48 4.48 4.46 4.46 3.77 3.23 3.21 3.20 3.18 2.99 2.99 2.96 2.96 1.12
2.01 1.99 1.00 3.07 1.02 1.03 9.10
7.1 7.0 6.9 6.8
4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0
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.


158.89
129.77
128.58
114.39
100.00
55.38
34.65
34.17
26.69
Parameter Value
1 Title srz-02-233
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
NO2
OMe
Me
Me
Me
33
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

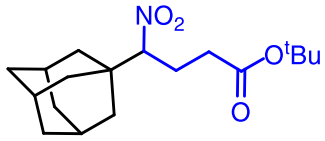
Parameter	Value
1 Title	srz-03-025
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	64.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



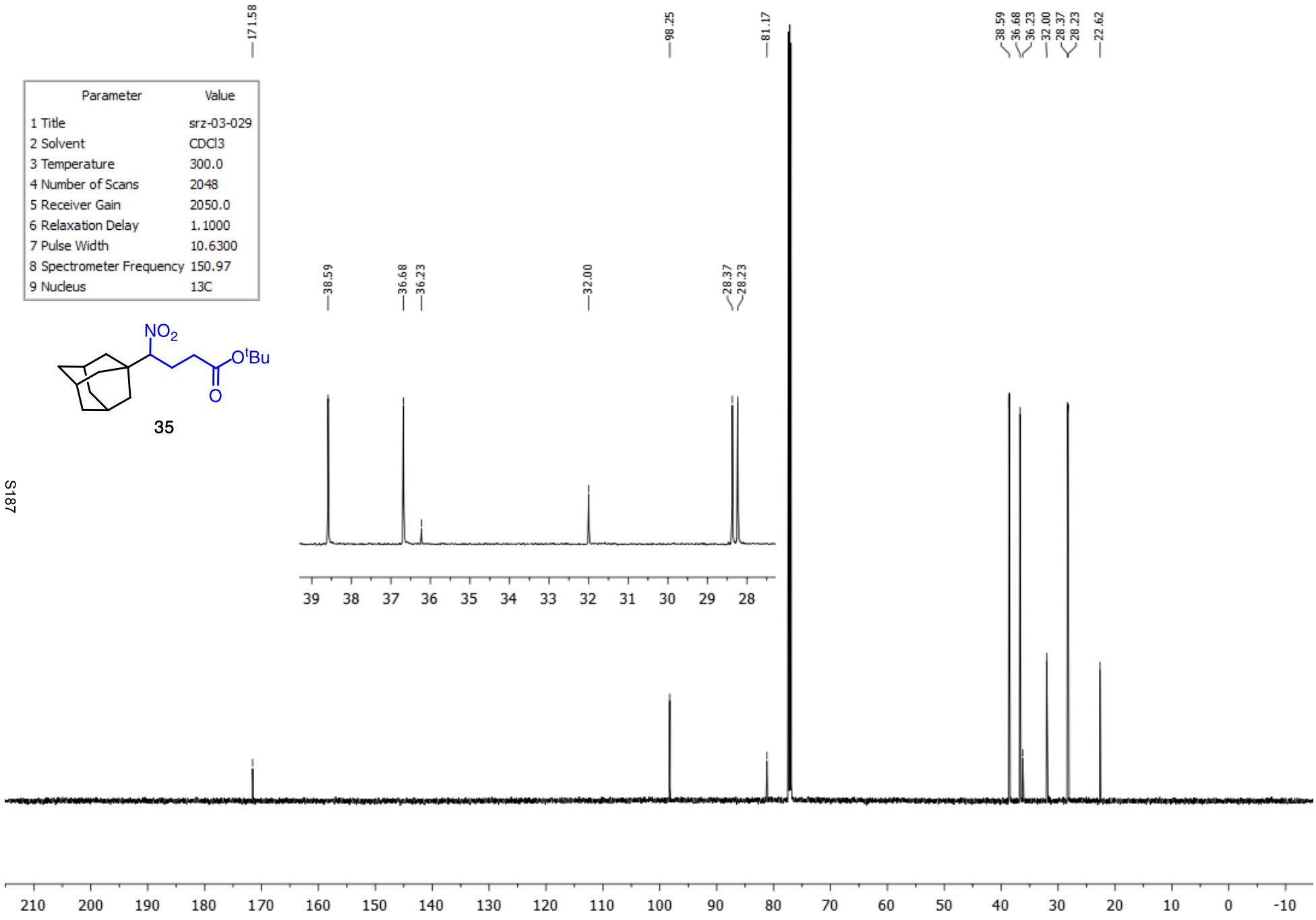
34


148.04
146.86
130.44
121.96
109.18
108.68
101.16
101.03
38.74
36.69
36.28
33.24
28.41
Parameter Value
1 Title srz-03-025
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
NO2
O
O
34
110 109 108 107 106 105 104 103 102 101 100
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

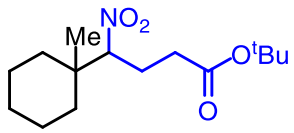
Parameter	Value
1 Title	srz-03-029
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	57.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



35


171.58
98.25
81.17
38.59
36.68
36.23
32.00
28.37
28.23
22.62
Parameter Value
1 Title srz-03-029
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
NO2
O^tBu
O
35
39 38 37 36 35 34 33 32 31 30 29 28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Parameter	Value
1 Title	srz-03-105
2 Solvent	CDCl3
3 Temperature	297.5
4 Number of Scans	16
5 Receiver Gain	64.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



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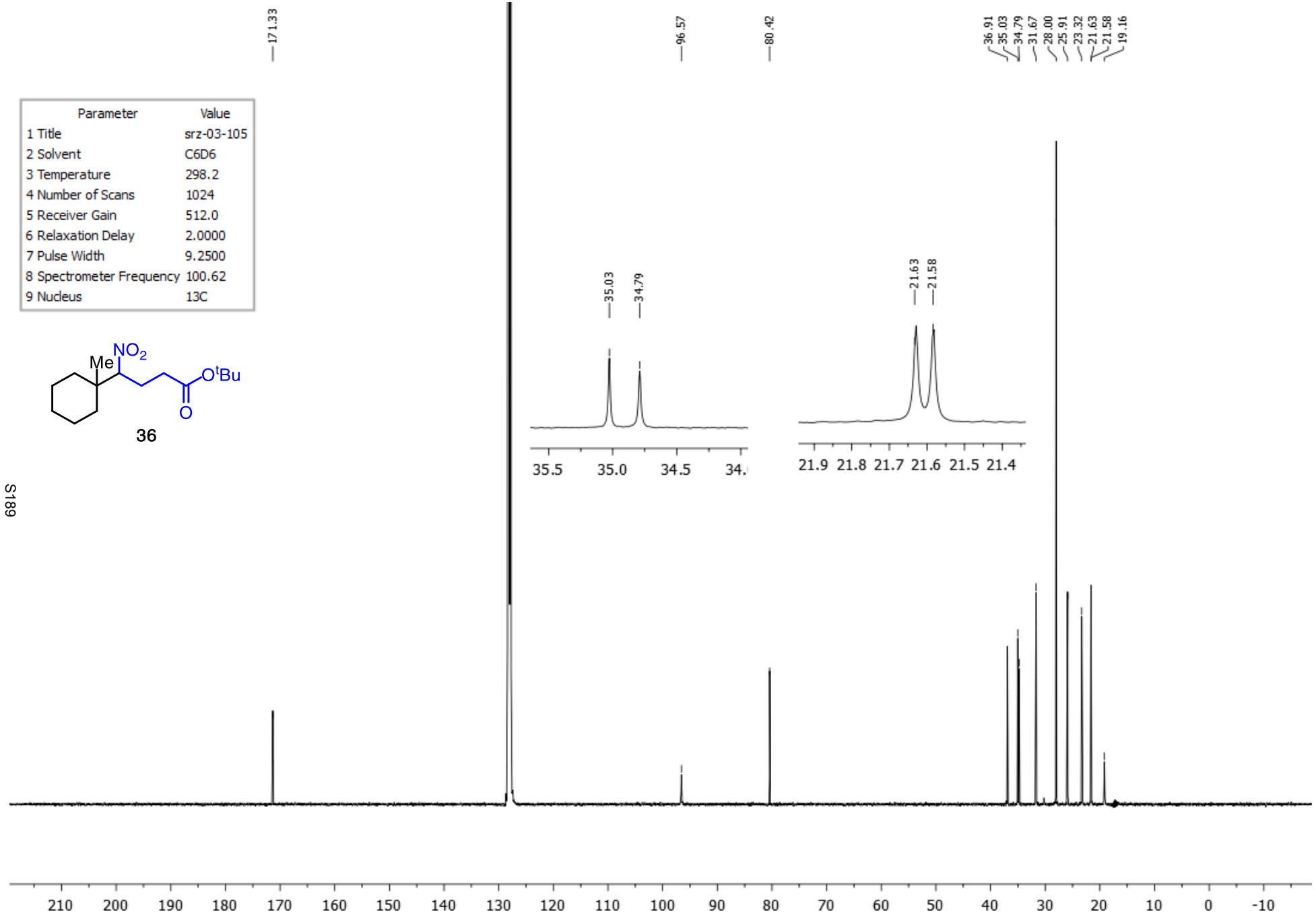
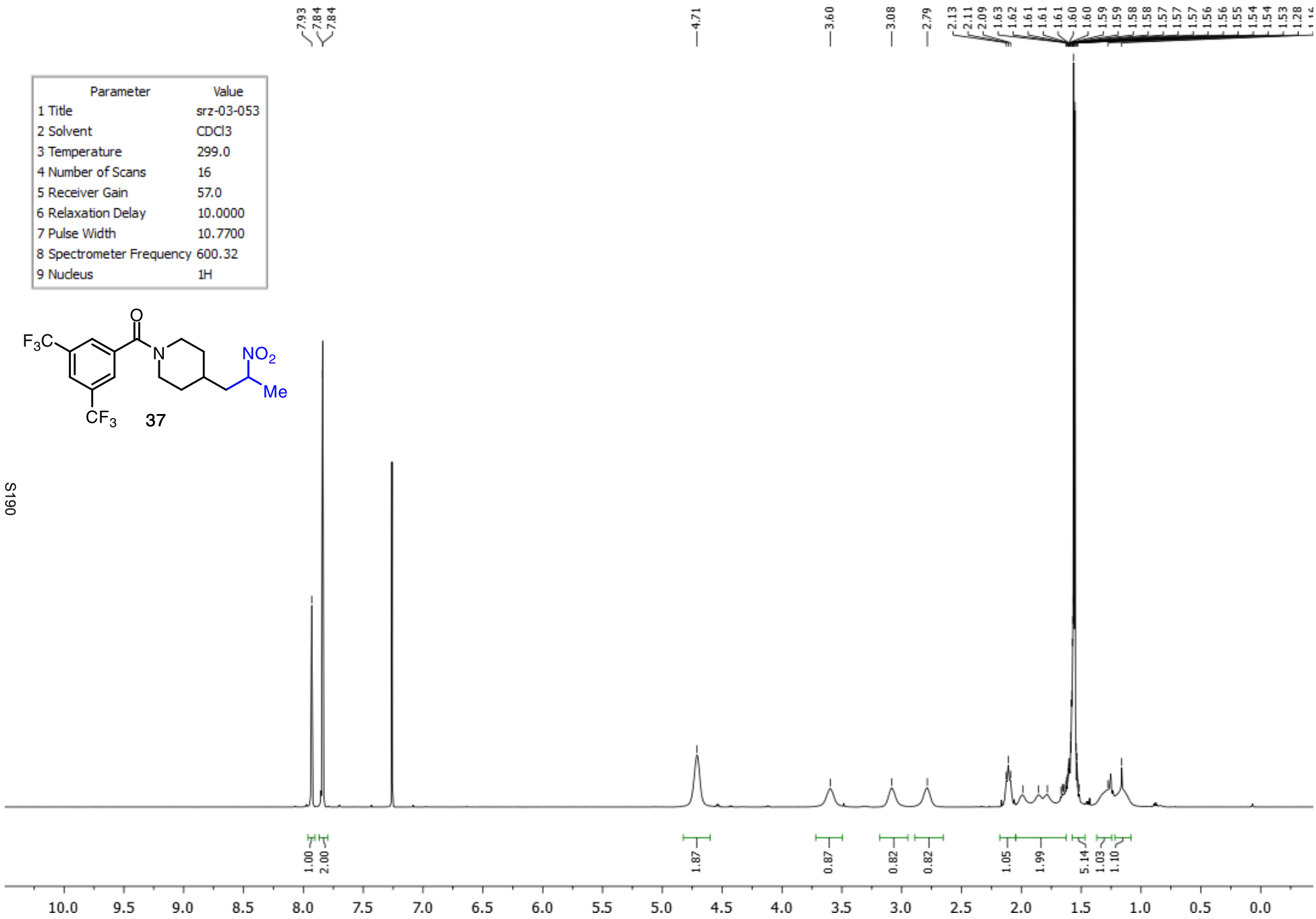
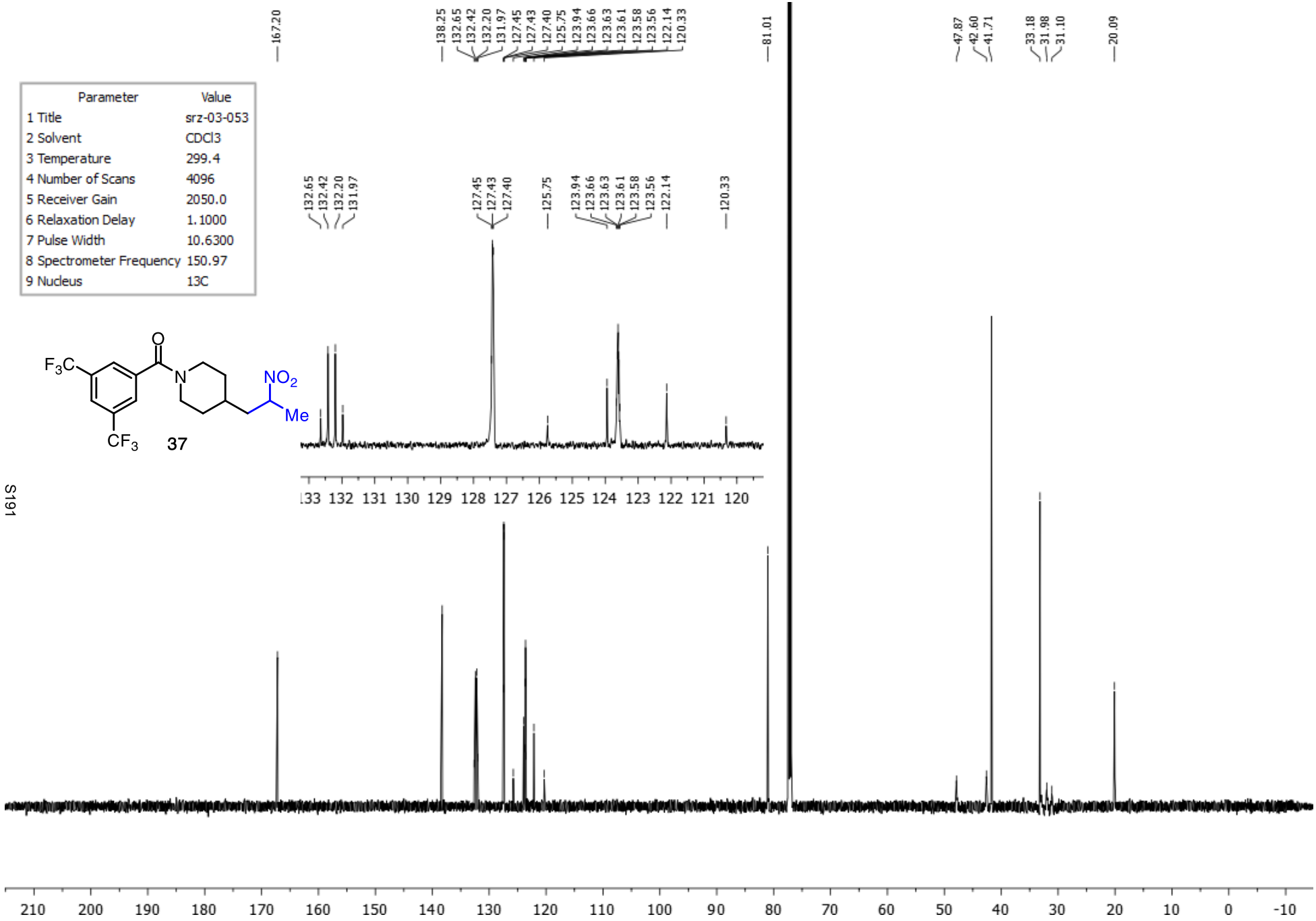
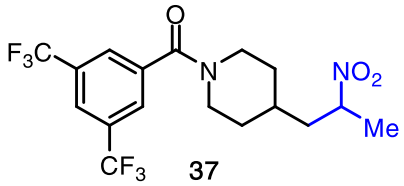

171.33
96.57
80.42
36.91
35.03
34.79
31.67
28.00
25.91
23.32
21.63
21.58
19.16
Parameter Value
1 Title srz-03-105
2 Solvent C6D6
3 Temperature 298.2
4 Number of Scans 1024
5 Receiver Gain 512.0
6 Relaxation Delay 2.0000
7 Pulse Width 9.2500
8 Spectrometer Frequency 100.62
9 Nucleus 13C
Me
NO2
OtBu
O
36
35.03
34.79
21.63
21.58
35.5 35.0 34.5
21.9 21.8 21.7 21.6 21.5 21.4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.93
7.84
7.84
4.71
3.60
3.08
2.79
2.13
2.11
2.09
1.63
1.62
1.61
1.61
1.61
1.60
1.60
1.59
1.59
1.58
1.58
1.57
1.57
1.57
1.56
1.56
1.55
1.54
1.54
1.53
1.28
Parameter Value
1 Title srz-03-053
2 Solvent CDCl3
3 Temperature 299.0
4 Number of Scans 16
5 Receiver Gain 57.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
F3C
CF3
O
N
NO2
Me
37
S190
1.00
2.00
1.87
0.87
0.82
0.82
1.05
1.99
5.14
1.03
1.10
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

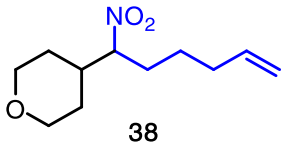

167.20
138.25
132.65
132.42
132.20
131.97
127.45
127.43
127.40
125.75
123.94
123.66
123.63
123.61
123.58
123.56
122.14
120.33
81.01
47.87
42.60
41.71
33.18
31.98
31.10
20.09
Parameter Value
1 Title srz-03-053
2 Solvent CDCl3
3 Temperature 299.4
4 Number of Scans 4096
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
F3C
CF3
O
N
NO2
Me
37
133 132 131 130 129 128 127 126 125 124 123 122 121 120
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Parameter	Value
1 Title	srz-03-053
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	16
5 Receiver Gain	2298.8
6 Relaxation Delay	1.0000
7 Pulse Width	15.0300
8 Spectrometer Frequency	376.46
9 Nucleus	19F

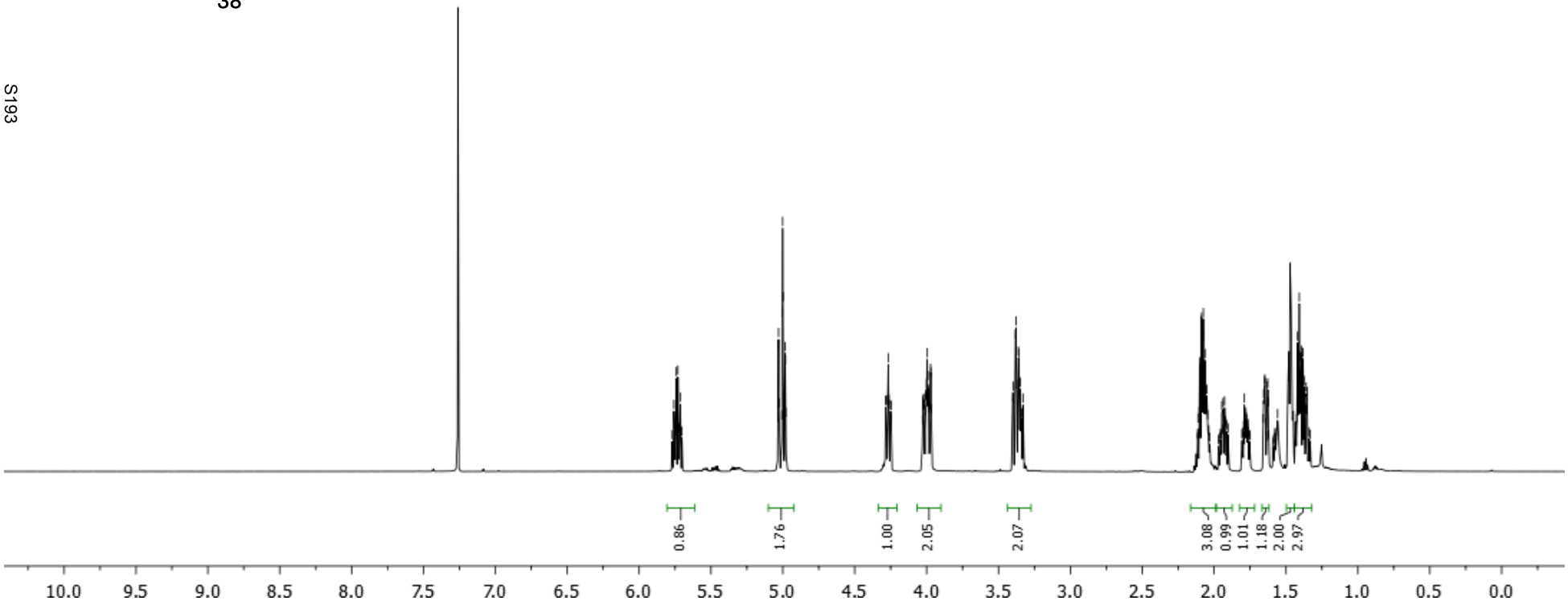


37

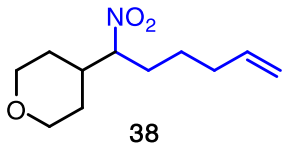
Parameter	Value
1 Title	srz-03-120
2 Solvent	CDCl3
3 Temperature	297.8
4 Number of Scans	16
5 Receiver Gain	57.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



38



Parameter	Value
1 Title	srz-03-120
2 Solvent	CDCl3
3 Temperature	298.8
4 Number of Scans	256
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C



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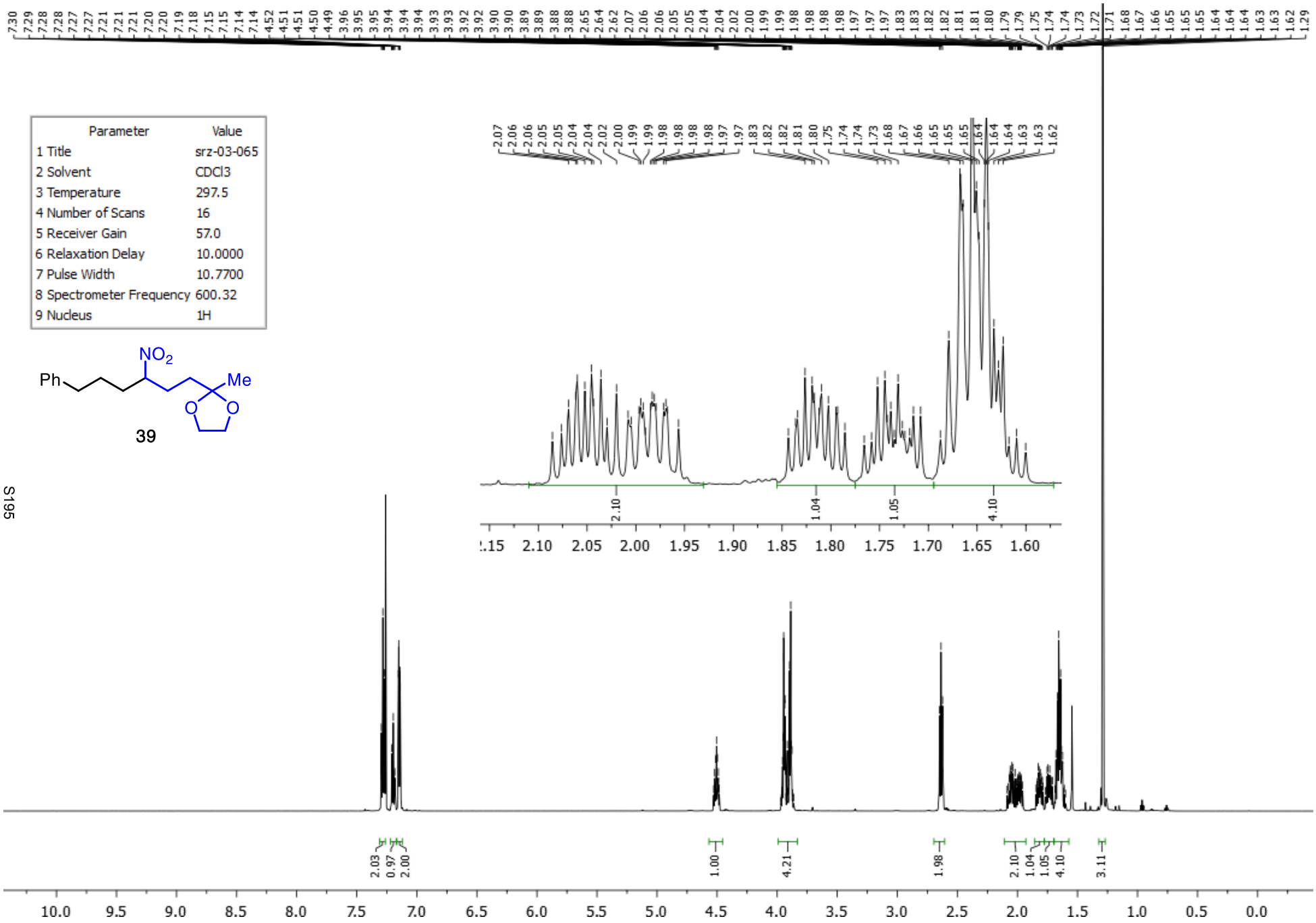
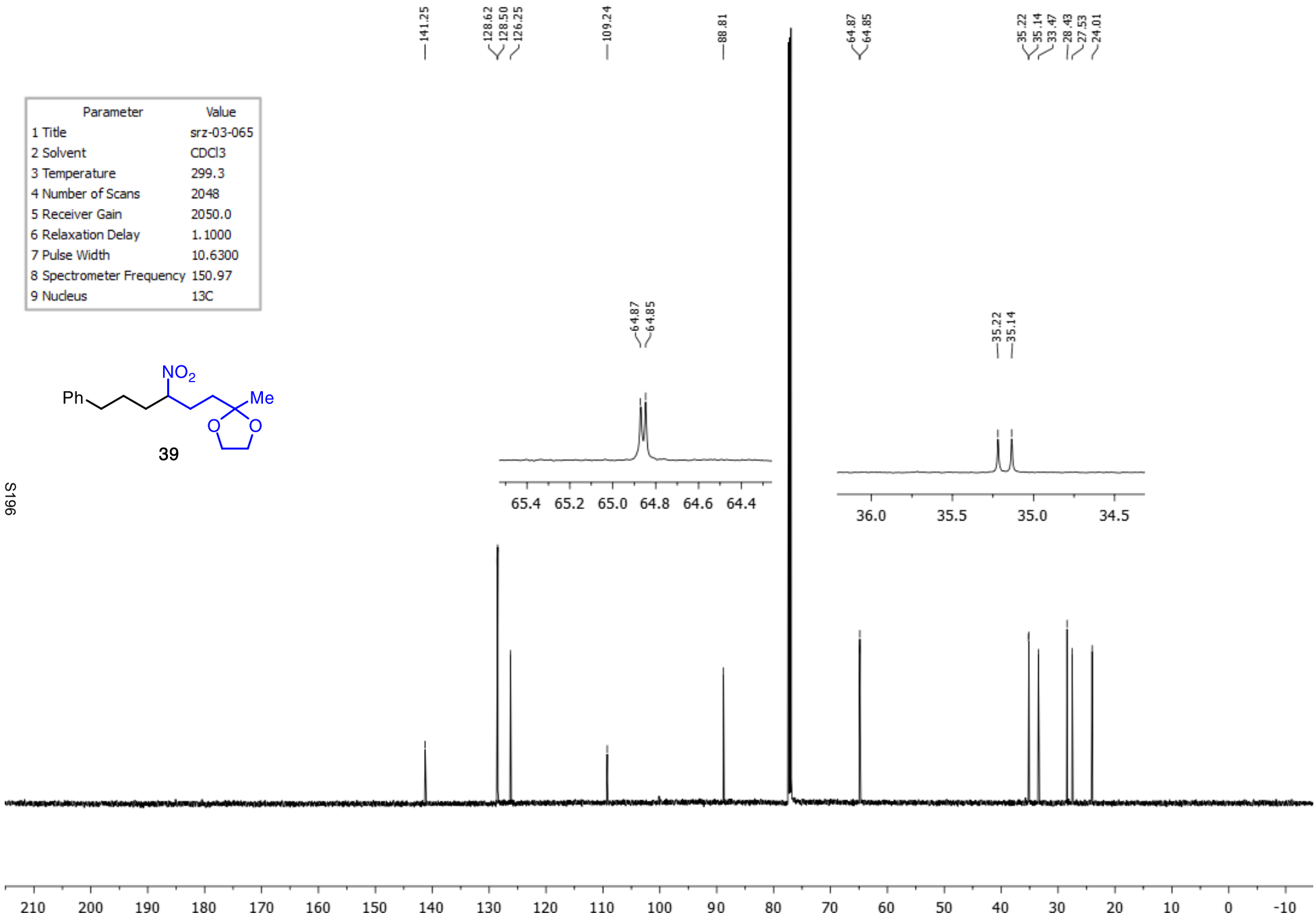
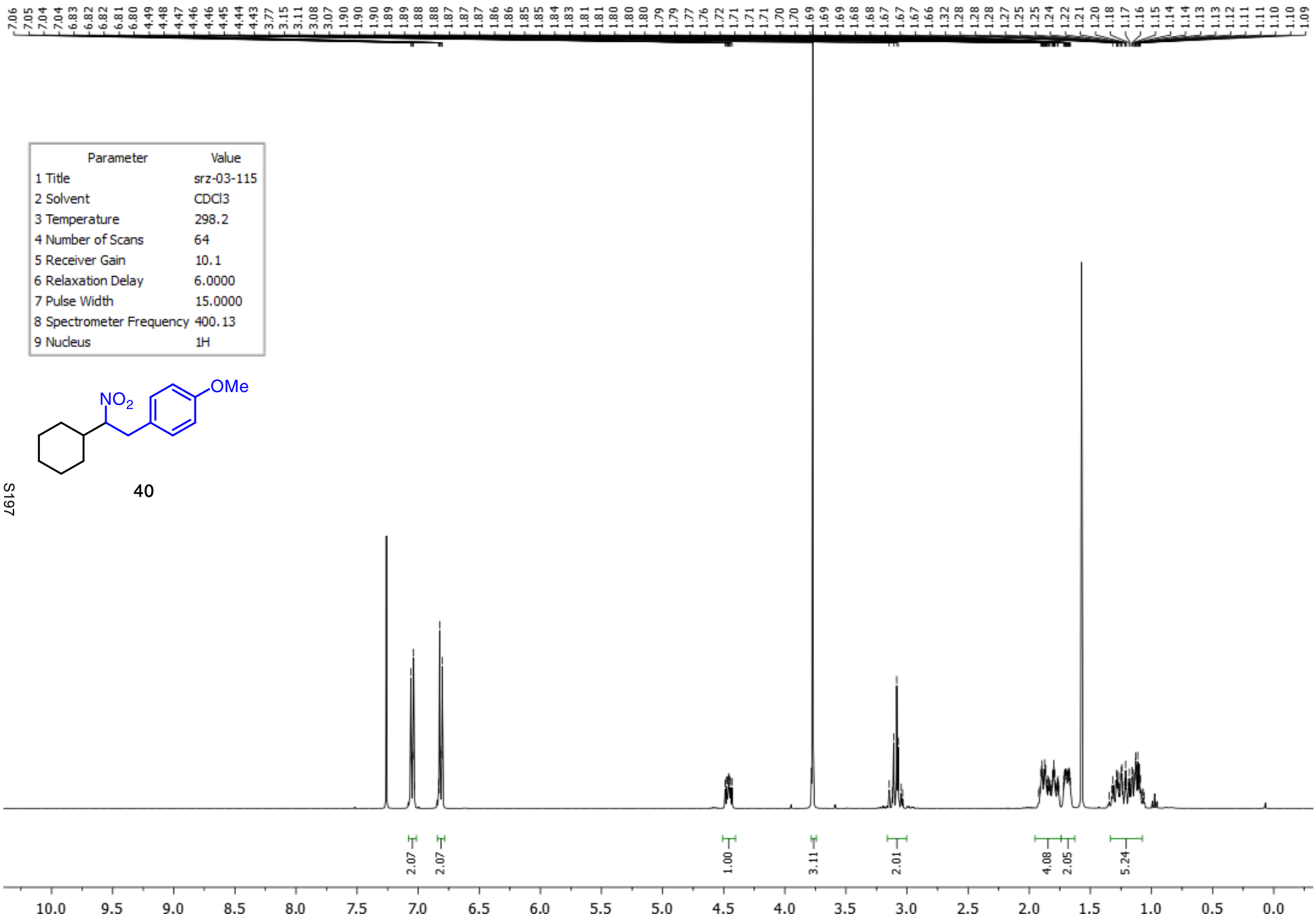
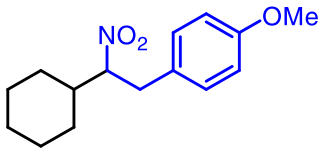

Parameter Value
1 Title srz-03-065
2 Solvent CDCl3
3 Temperature 297.5
4 Number of Scans 16
5 Receiver Gain 57.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
NO2
Ph
Me
O
O
39
S195
2.03
0.97
2.00
1.00
4.21
1.98
2.10
1.04
1.05
4.10
3.11
10.0 9.5 9.0 8.5 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

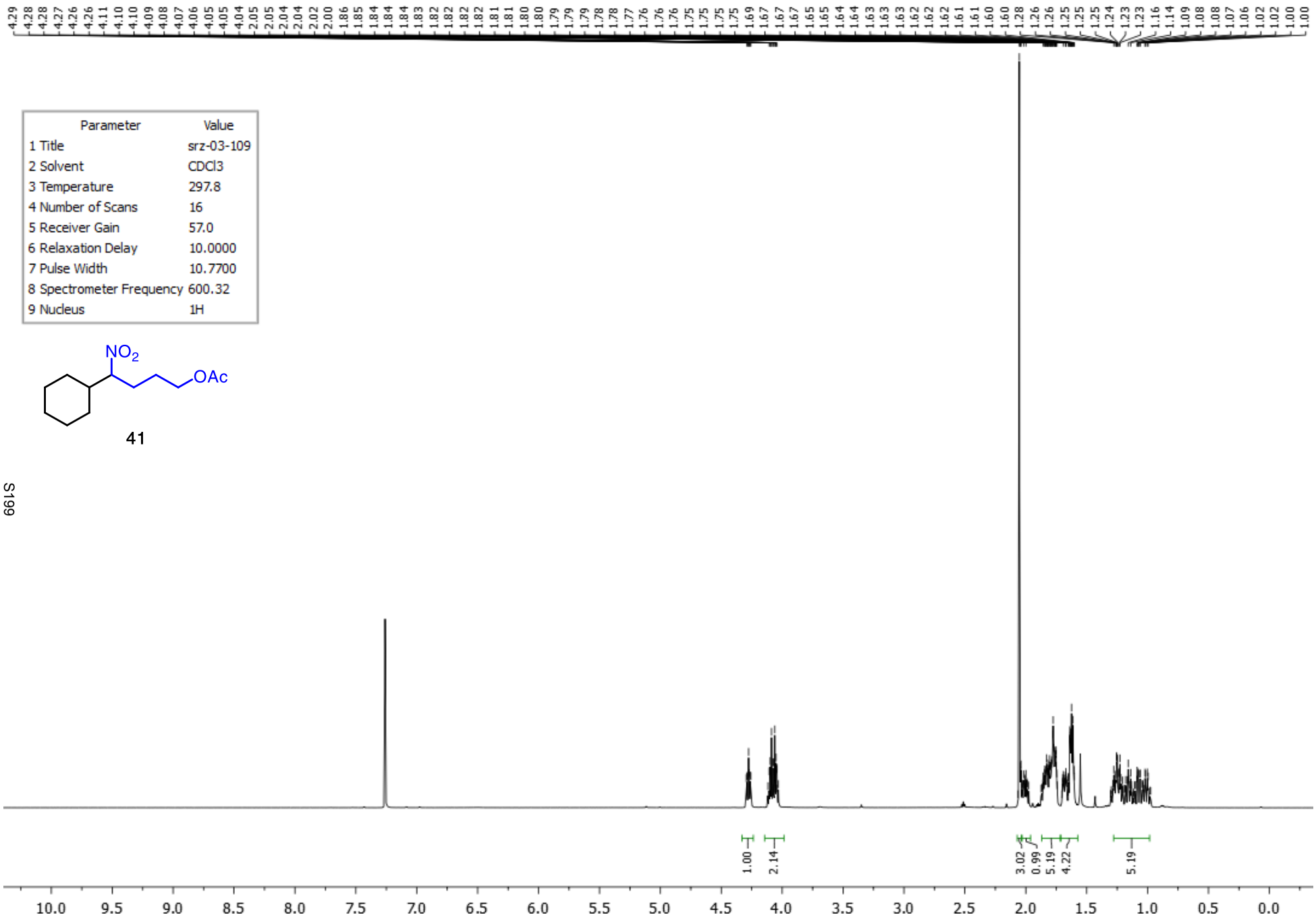

141.25
128.62
128.50
126.25
109.24
88.81
64.87
64.85
35.22
35.14
33.47
28.43
27.53
24.01
Parameter Value
1 Title srz-03-065
2 Solvent CDCl3
3 Temperature 299.3
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
NO2
Ph
Me
O
O
39
65.4 65.2 65.0 64.8 64.6 64.4
36.0 35.5 35.0 34.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

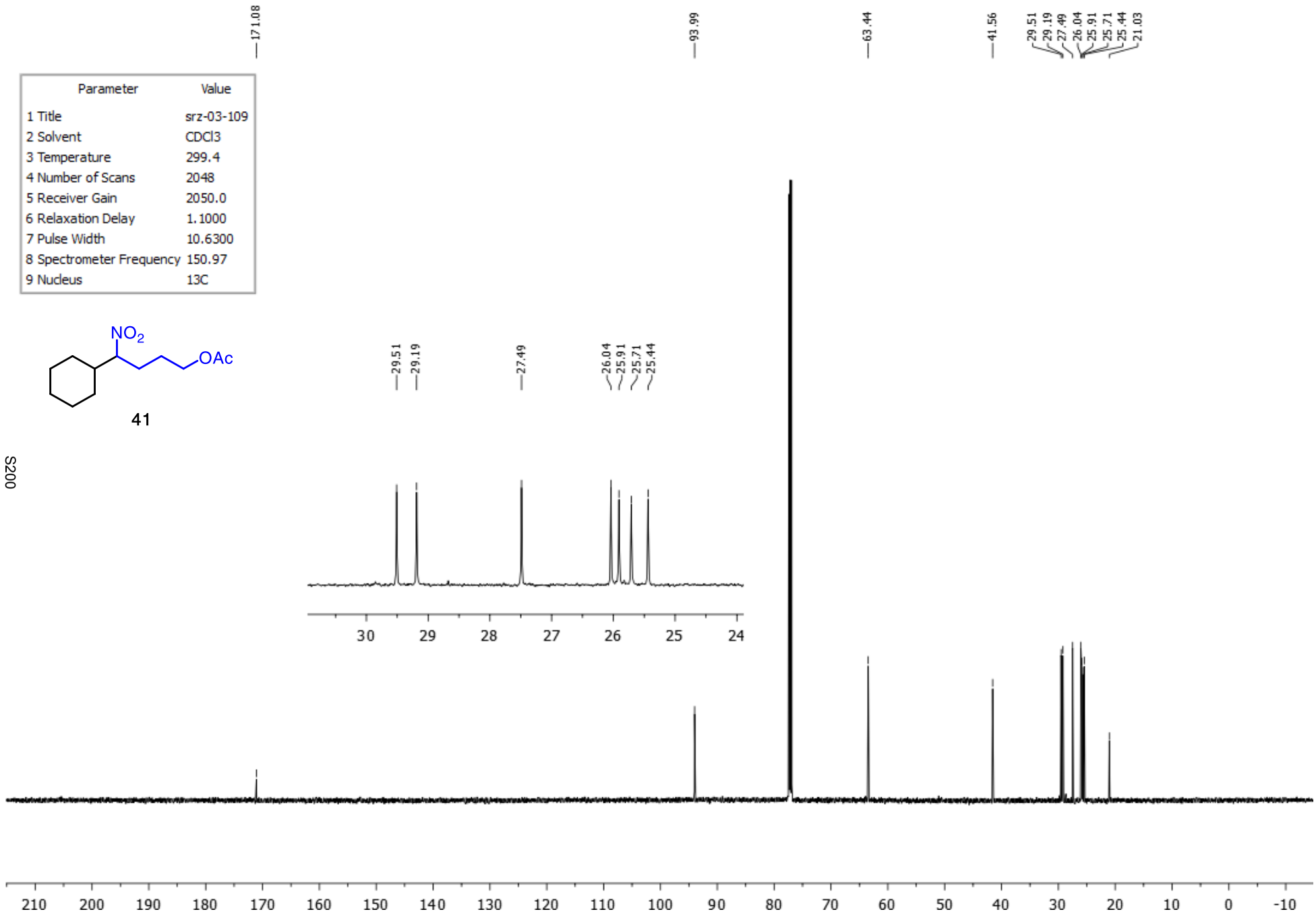

7.06 7.05 7.04 7.04 6.83 6.82 6.82 6.81 6.80 4.49 4.48 4.47 4.46 4.46 4.45 4.44 4.43 3.77 3.15 3.11 3.08 3.07 1.90 1.90 1.89 1.89 1.88 1.88 1.87 1.87 1.87 1.86 1.86 1.85 1.85 1.84 1.83 1.81 1.81 1.80 1.80 1.80 1.79 1.79 1.77 1.76 1.72 1.71 1.71 1.71 1.70 1.70 1.69 1.69 1.69 1.68 1.68 1.67 1.67 1.67 1.66 1.32 1.28 1.28 1.28 1.27 1.25 1.25 1.24 1.22 1.21 1.20 1.18 1.17 1.16 1.15 1.14 1.14 1.13 1.13 1.12 1.11 1.11 1.10 1.10 1.09
Parameter Value
1 Title srz-03-115
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 64
5 Receiver Gain 10.1
6 Relaxation Delay 6.0000
7 Pulse Width 15.0000
8 Spectrometer Frequency 400.13
9 Nucleus 1H
NO2
OMe
40
2.07
2.07
1.00
3.11
2.01
4.08
2.05
5.24
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

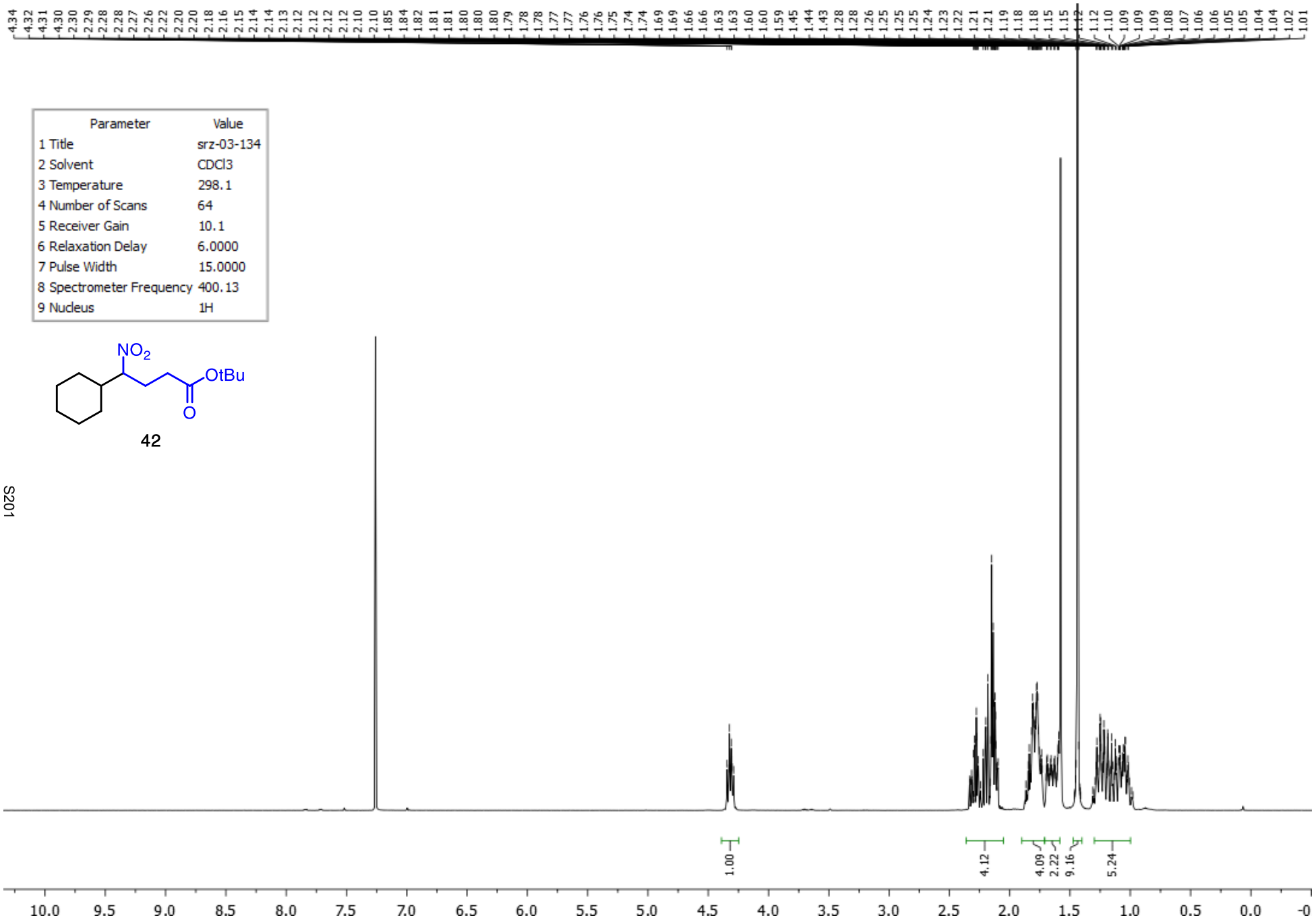
Parameter	Value
1 Title	srz-03-115
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	1024
5 Receiver Gain	512.0
6 Relaxation Delay	2.0000
7 Pulse Width	9.2500
8 Spectrometer Frequency	100.62
9 Nucleus	13C

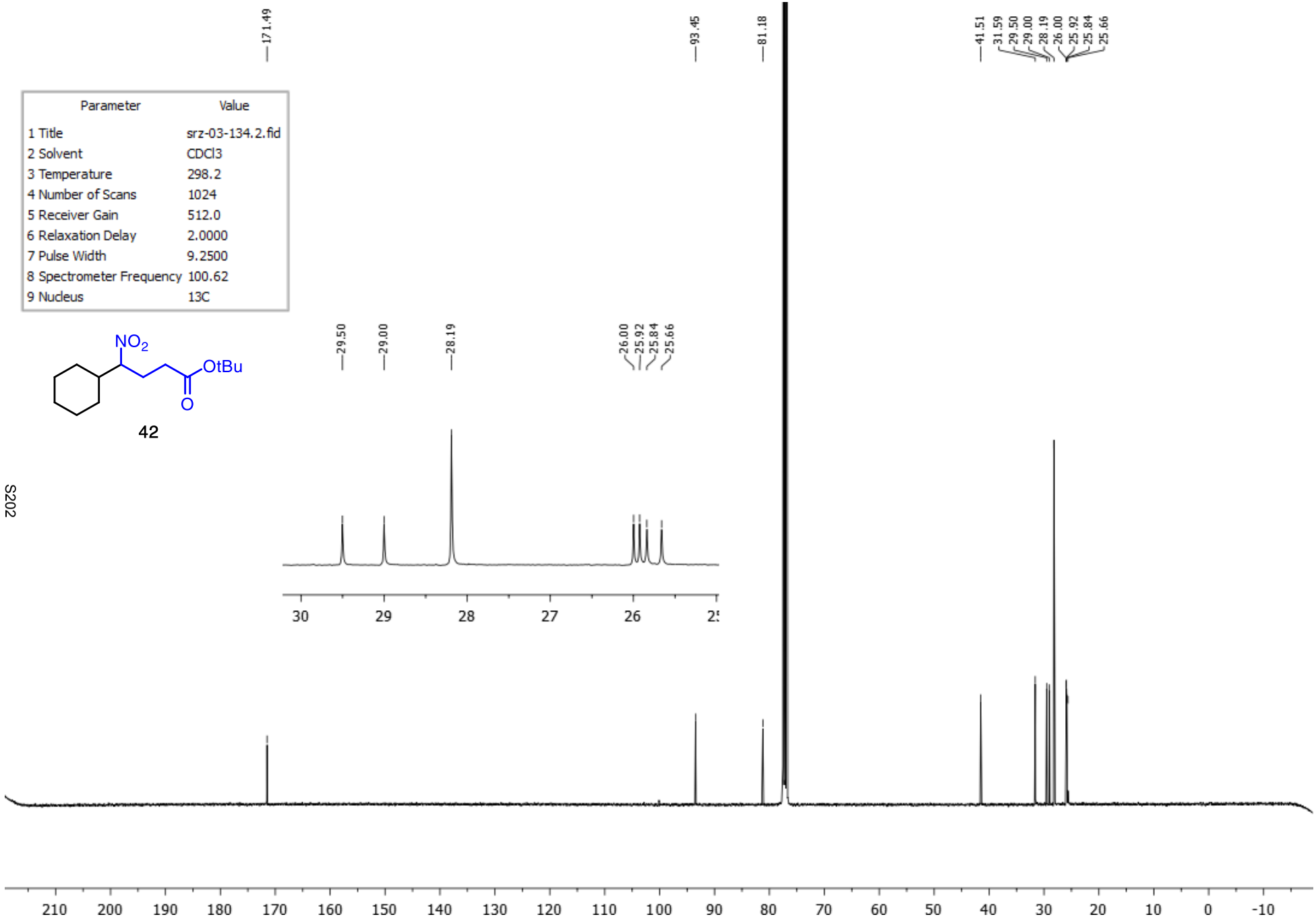


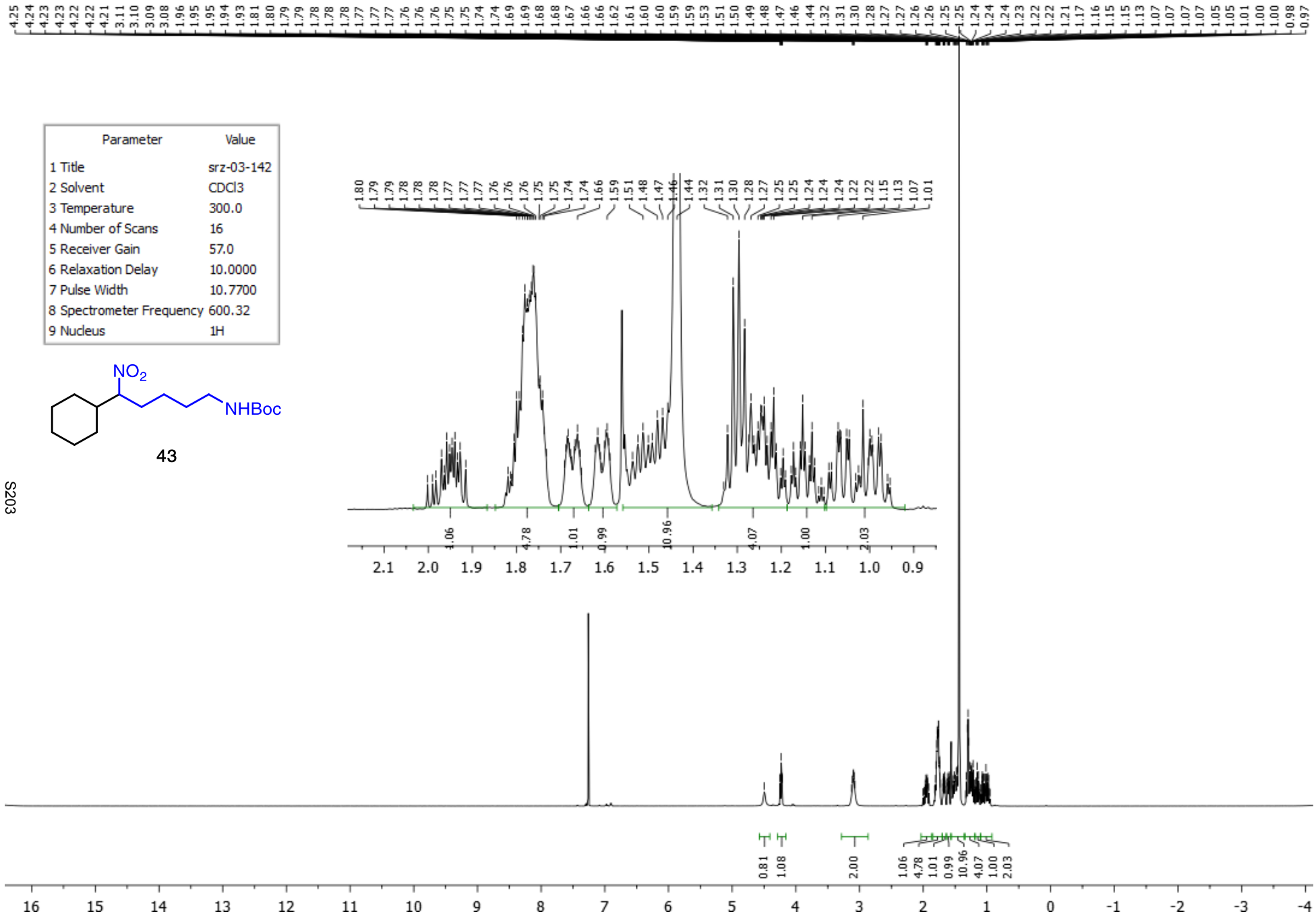
40

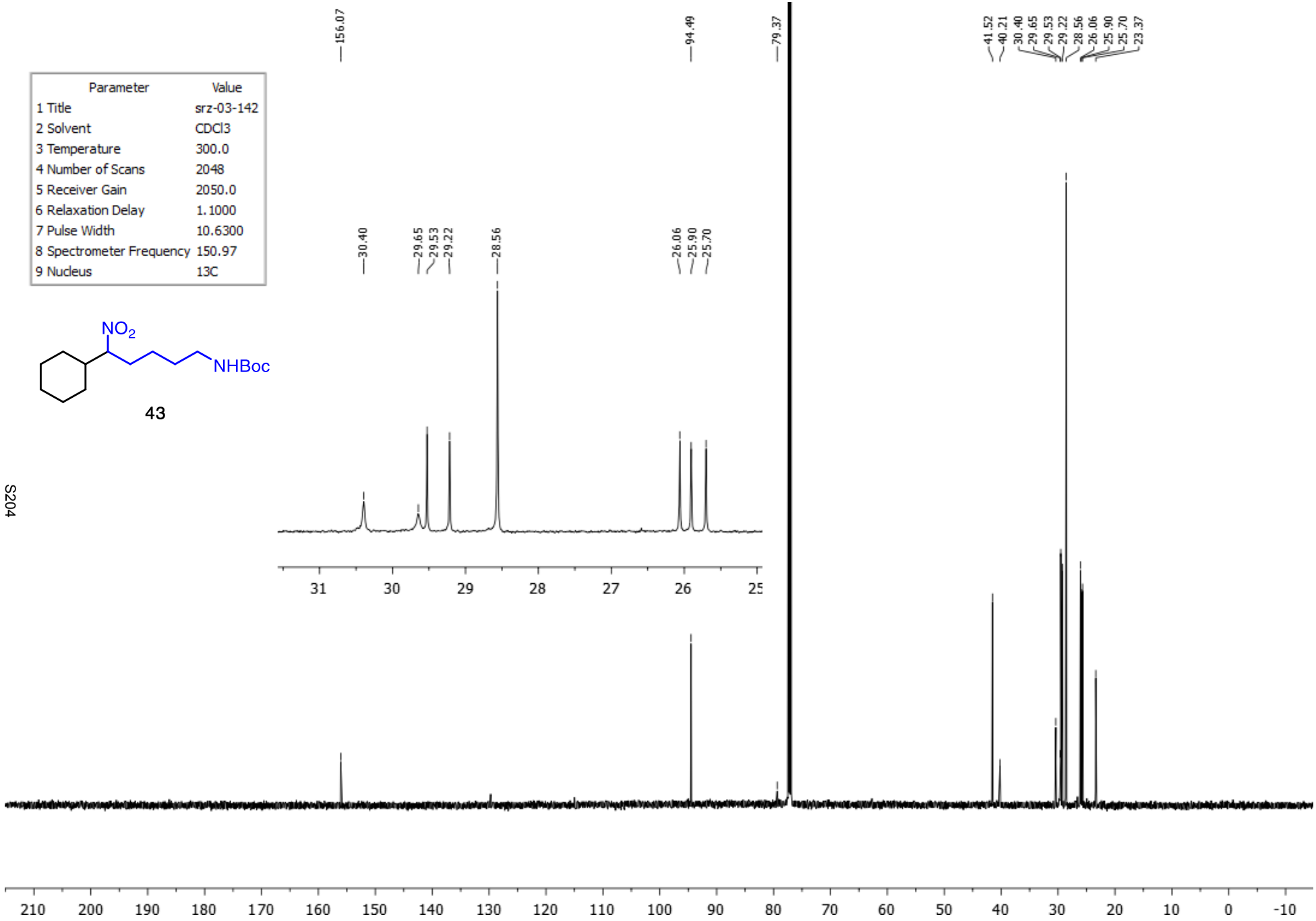

Parameter Value
1 Title srz-03-109
2 Solvent CDCl3
3 Temperature 297.8
4 Number of Scans 16
5 Receiver Gain 57.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
NO2
OAc
41
1.00
2.14
3.02
0.99
5.19
4.22
5.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

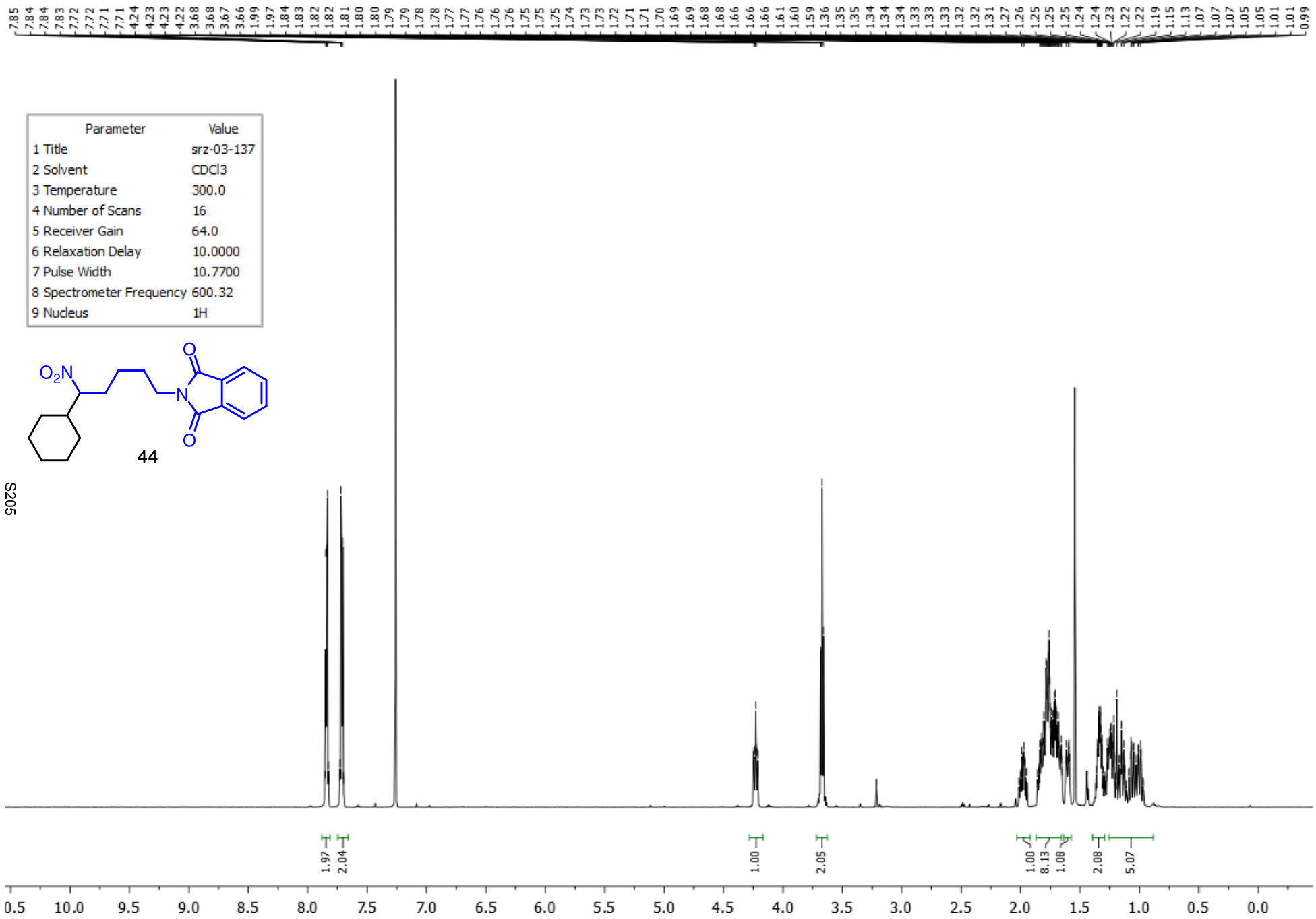

171.08
93.99
63.44
41.56
29.51
29.19
27.49
26.04
25.91
25.71
25.44
21.03
Parameter Value
1 Title srz-03-109
2 Solvent CDCl3
3 Temperature 299.4
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
NO2
OAc
41
S200
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
30 29 28 27 26 25 24


Parameter Value
1 Title srz-03-134
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 64
5 Receiver Gain 10.1
6 Relaxation Delay 6.0000
7 Pulse Width 15.0000
8 Spectrometer Frequency 400.13
9 Nucleus 1H
NO2
OtBu
O
42
1.00
4.12
4.09
2.22
9.16
5.24
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

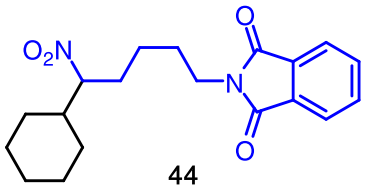

171.49
93.45
81.18
41.51
31.59
29.50
29.00
28.19
26.00
25.92
25.84
25.66
Parameter Value
1 Title srz-03-134.2.fid
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 1024
5 Receiver Gain 512.0
6 Relaxation Delay 2.0000
7 Pulse Width 9.2500
8 Spectrometer Frequency 100.62
9 Nucleus 13C
NO2
OtBu
O
42
S202
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
30 29 28 27 26


Parameter Value
1 Title srz-03-142
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 57.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
NO2
NHBoc
43
0.81
1.08
2.00
1.06
4.78
1.01
0.99
10.96
4.07
1.00
2.03


156.07
94.49
79.37
41.52
40.21
30.40
29.65
29.53
29.22
28.56
26.06
25.90
25.70
23.37
Parameter Value
1 Title srz-03-142
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
NO2
NHBoc
43
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
31 30 29 28 27 26 25

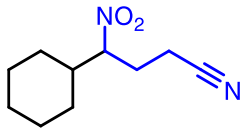

Parameter Value
1 Title srz-03-137
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 64.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
44
S205
1.97
2.04
1.00
2.05
1.00
8.13
1.08
2.08
5.07

Parameter	Value
1 Title	srz-03-137
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	256
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C



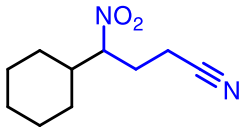
44

Parameter	Value
1 Title	srz-03-040
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	57.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



45

Parameter	Value
1 Title	srz-03-040
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	2048
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C



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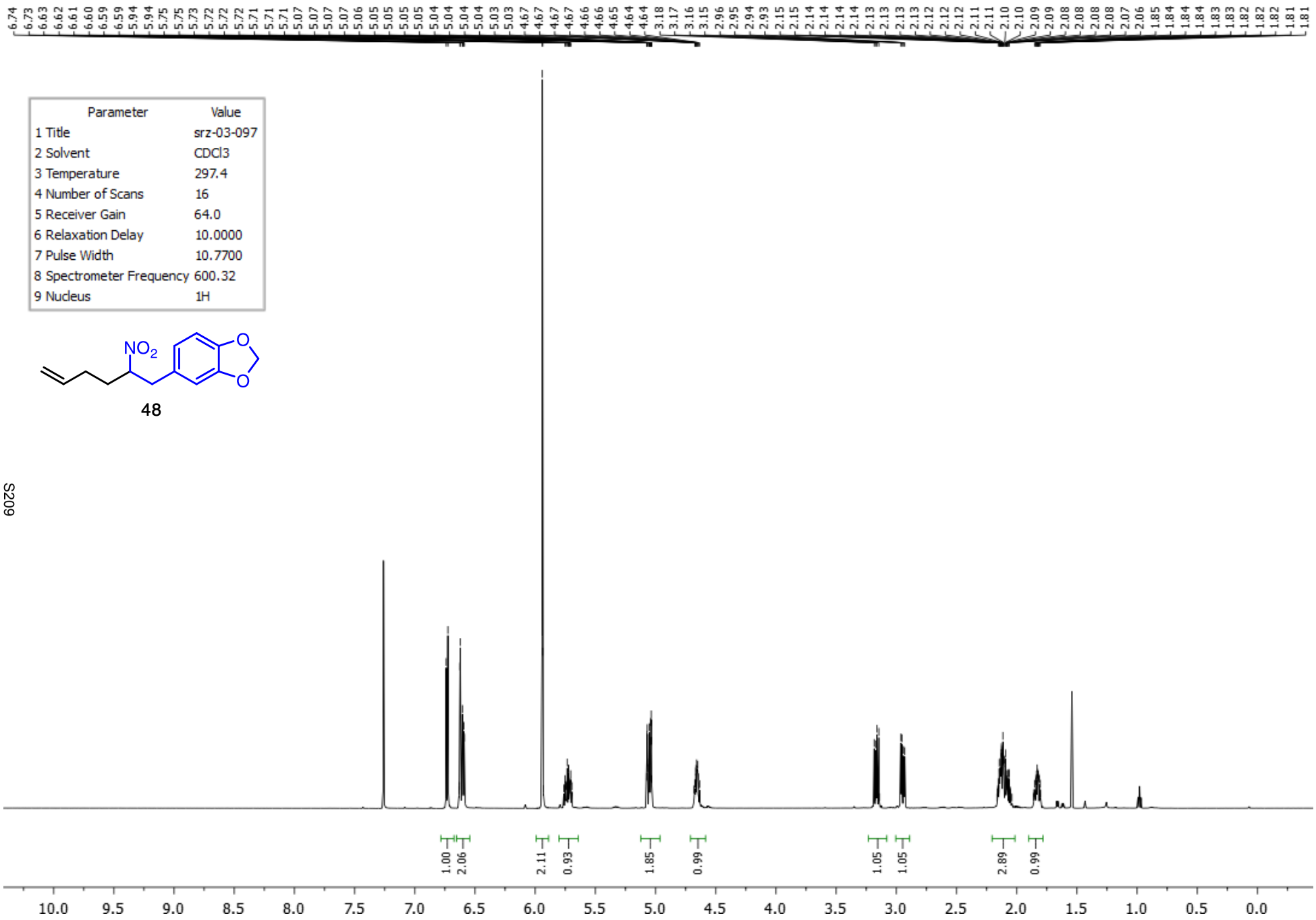
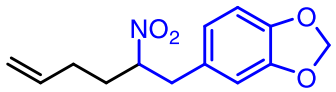
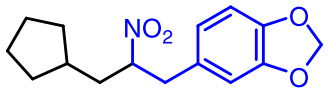

Parameter Value
1 Title srz-03-097
2 Solvent CDCl3
3 Temperature 297.4
4 Number of Scans 16
5 Receiver Gain 64.0
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
NO2
O
O
48
S209
1.00
2.06
2.11
0.93
1.85
0.99
1.05
1.05
2.89
0.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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

Parameter	Value
1 Title	srz-03-097
2 Solvent	CDCl3
3 Temperature	299.4
4 Number of Scans	1024
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C

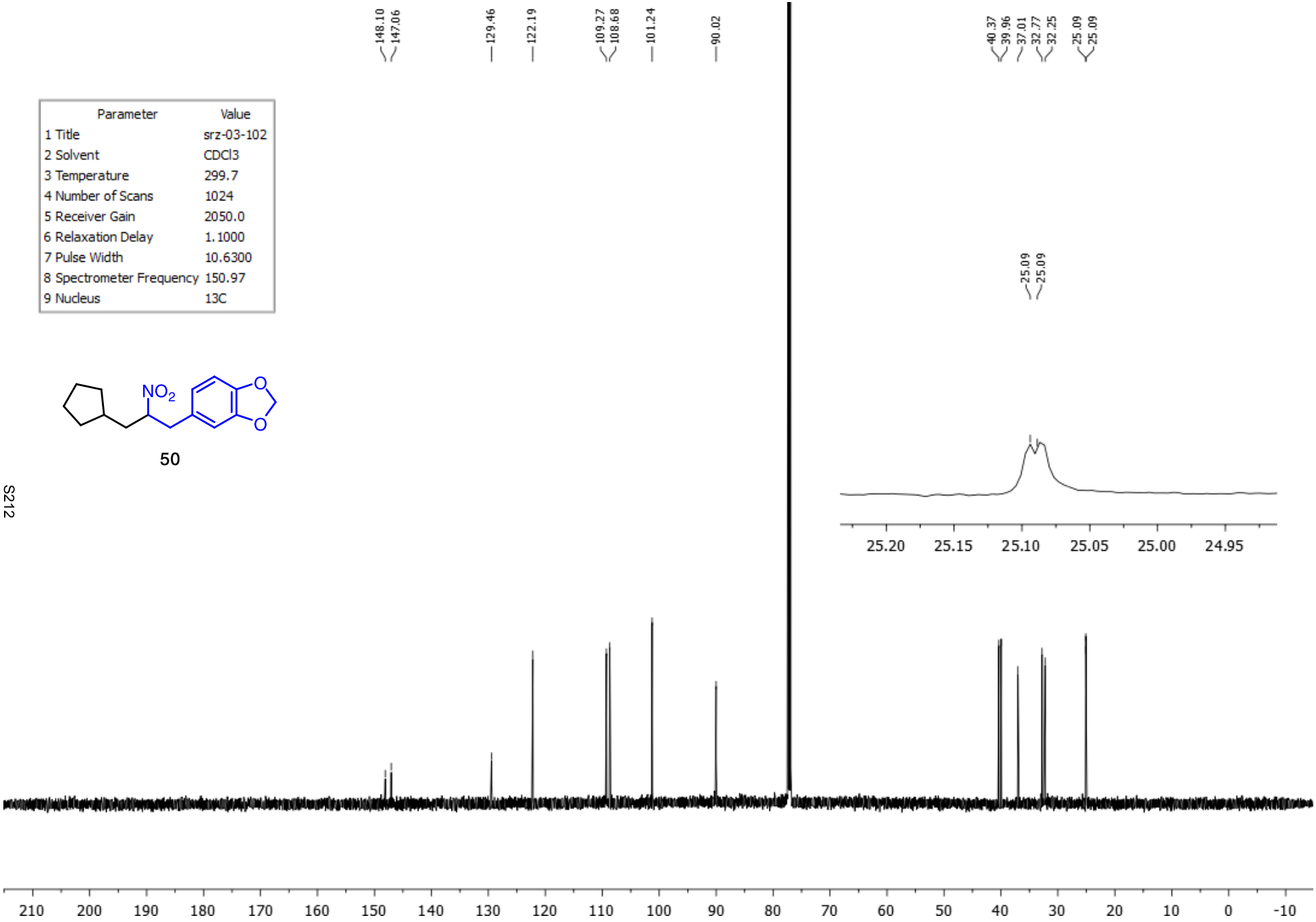


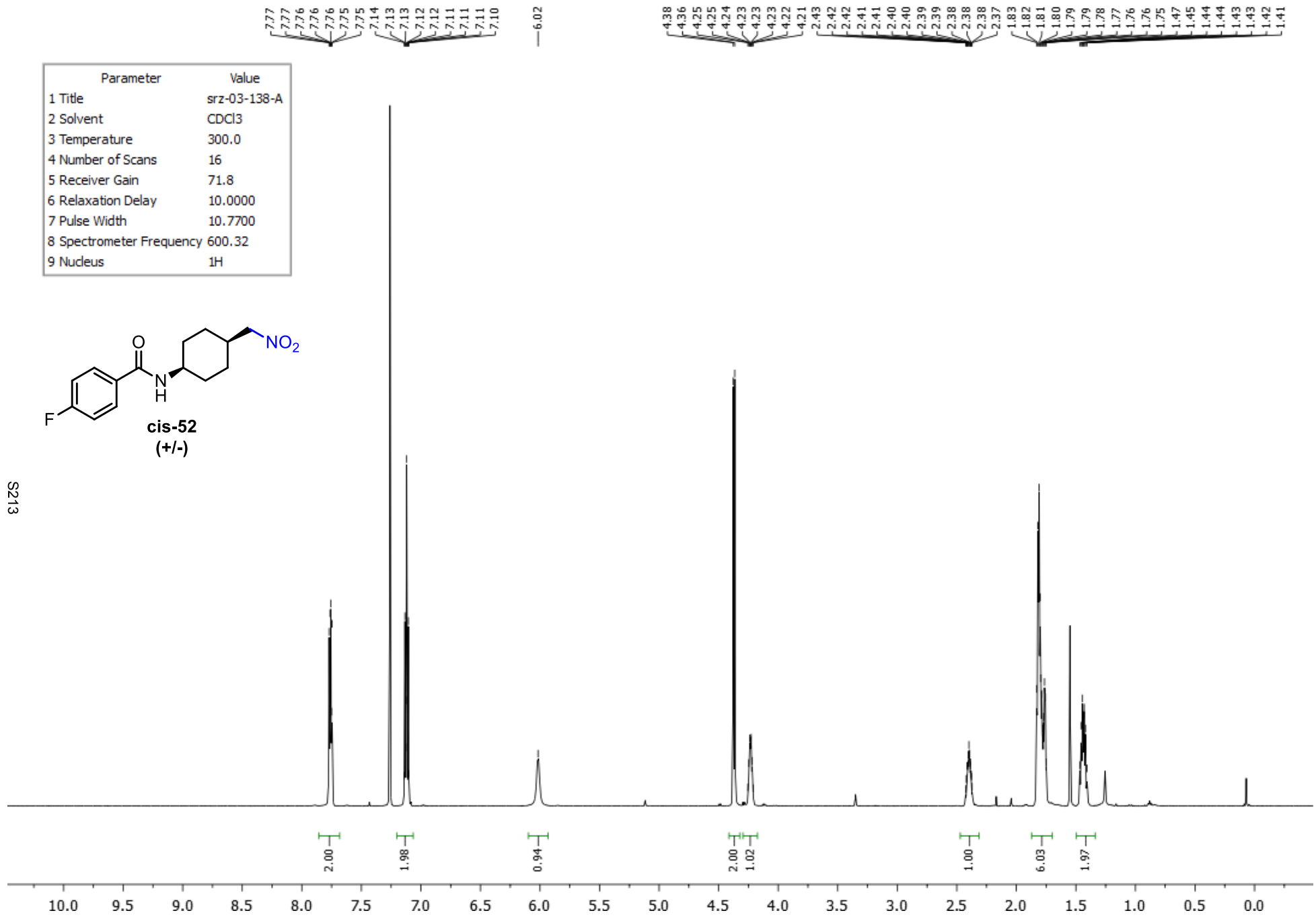
48

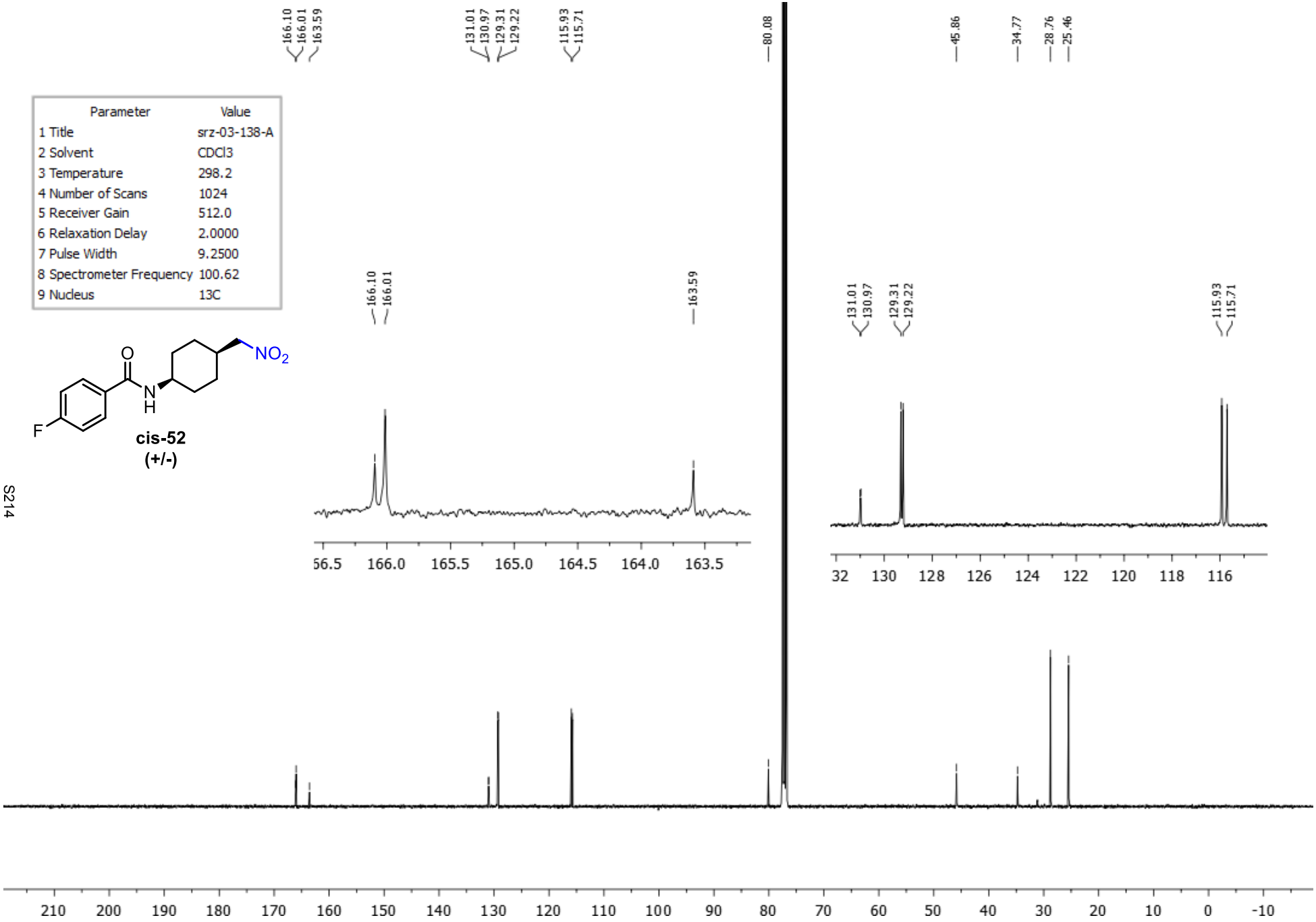
Parameter	Value
1 Title	srz-03-102
2 Solvent	CDCl3
3 Temperature	297.6
4 Number of Scans	16
5 Receiver Gain	64.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



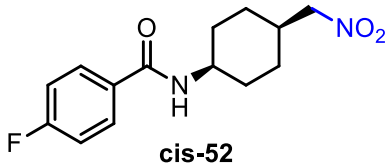
50


148.10
147.06
129.46
122.19
109.27
108.68
101.24
90.02
40.37
39.96
37.01
32.77
32.25
25.09
25.09
25.09
25.09
Parameter Value
1 Title srz-03-102
2 Solvent CDCl3
3 Temperature 299.7
4 Number of Scans 1024
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
NO2
O
O
50
25.20
25.15
25.10
25.05
25.00
24.95
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


Parameter Value
1 Title srz-03-138-A
2 Solvent CDCl3
3 Temperature 300.0
4 Number of Scans 16
5 Receiver Gain 71.8
6 Relaxation Delay 10.0000
7 Pulse Width 10.7700
8 Spectrometer Frequency 600.32
9 Nucleus 1H
O
N
H
F
NO2
cis-52
(+/-)
S213
2.00
1.98
0.94
2.00
1.02
1.00
6.03
1.97
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

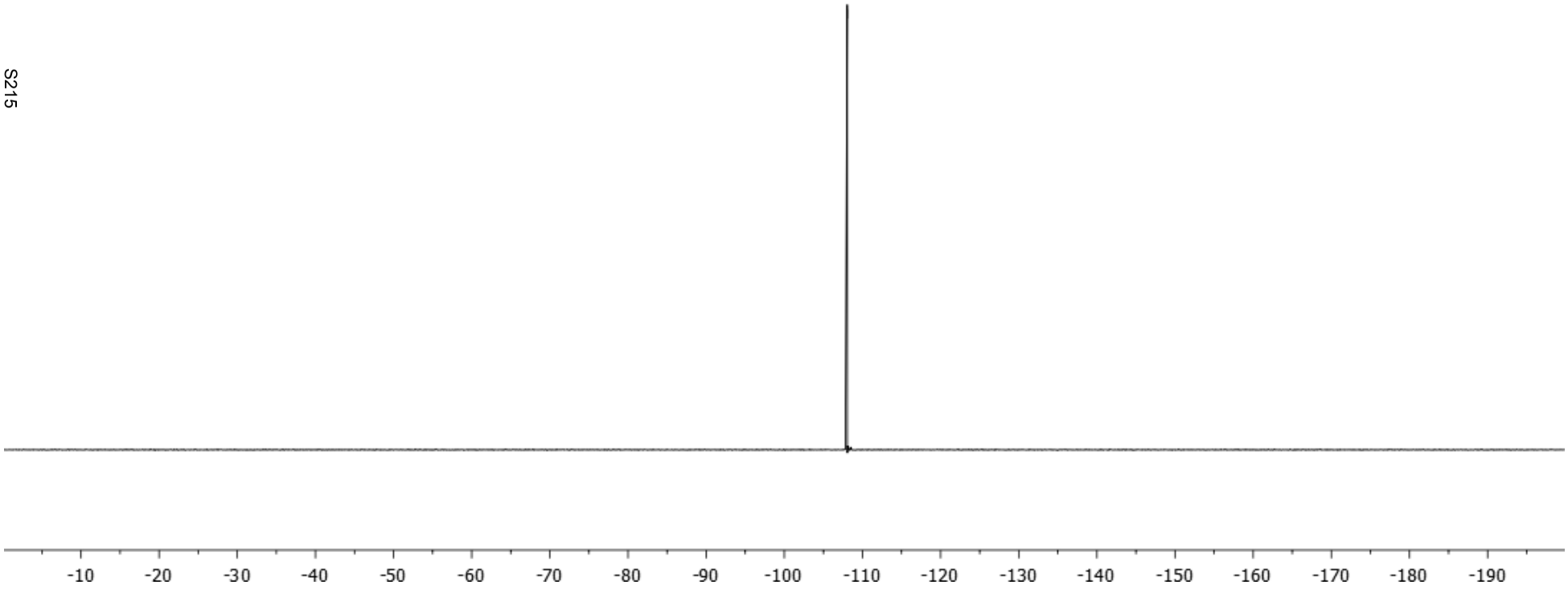

166.10
166.01
163.59
131.01
130.97
129.31
129.22
115.93
115.71
80.08
45.86
34.77
28.76
25.46
Parameter Value
1 Title srz-03-138-A
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 1024
5 Receiver Gain 512.0
6 Relaxation Delay 2.0000
7 Pulse Width 9.2500
8 Spectrometer Frequency 100.62
9 Nucleus 13C
O
N
H
F
NO2
cis-52
(+/-)
166.0
165.5
165.0
164.5
164.0
163.5
130
128
126
124
122
120
118
116
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

Parameter	Value
1 Title	srz-03-138-A
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	16
5 Receiver Gain	4096.0
6 Relaxation Delay	1.0000
7 Pulse Width	15.0300
8 Spectrometer Frequency	376.46
9 Nucleus	19F

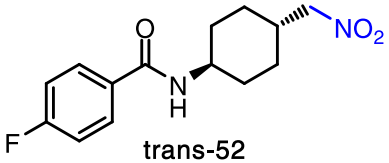


cis-52
(+/-)

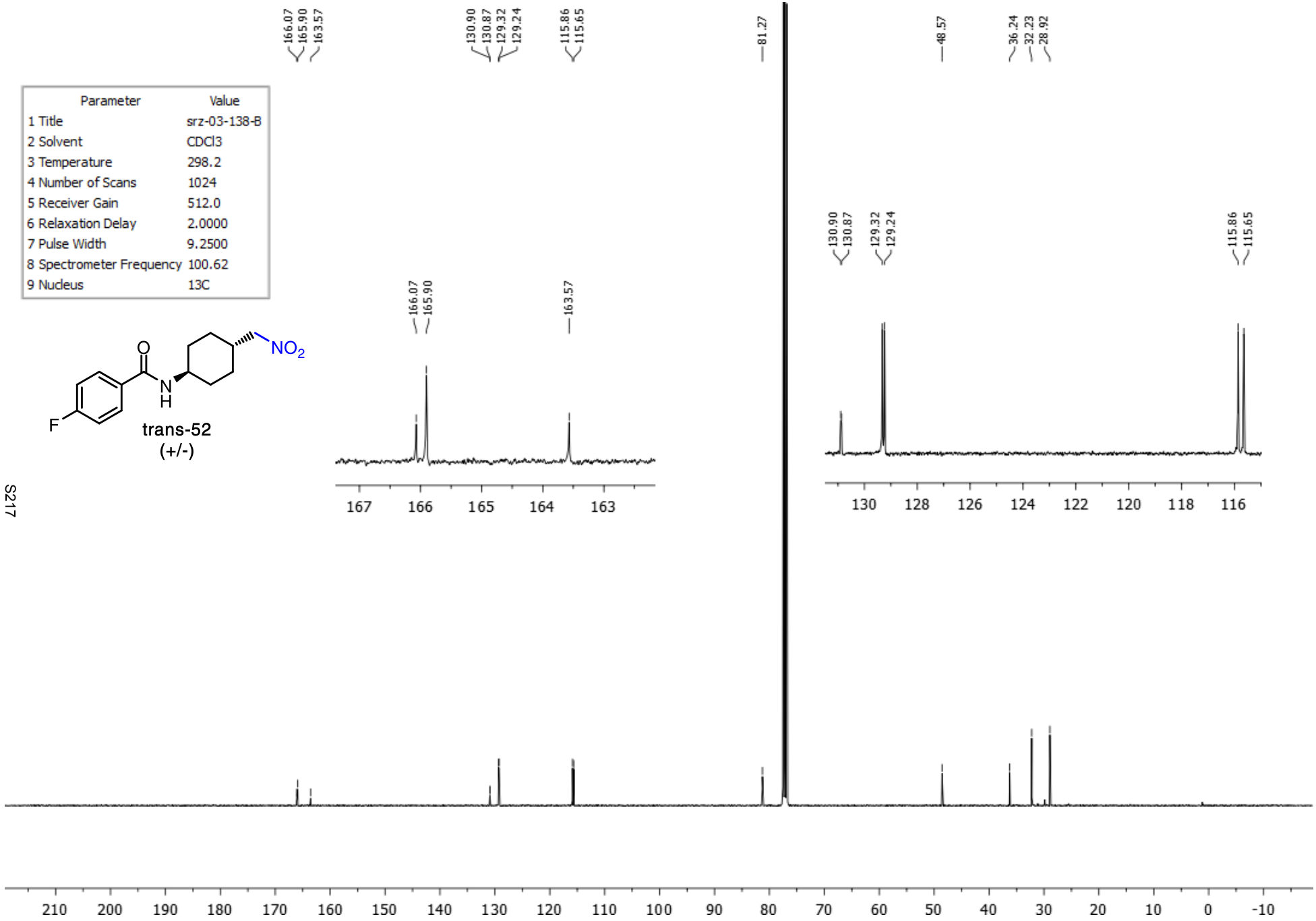
-108.05



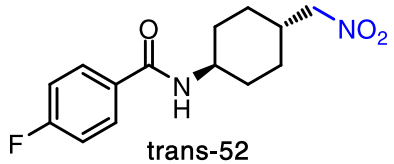
Parameter	Value
1 Title	srz-03-138-B
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	64.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



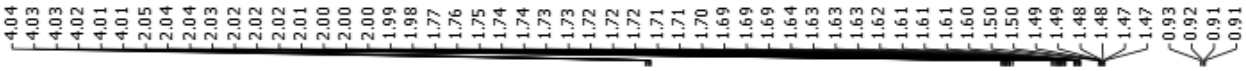
trans-52
(+/-)


166.07
165.90
163.57
130.90
130.87
129.32
129.24
115.86
115.65
81.27
48.57
36.24
32.23
28.92
Parameter Value
1 Title srz-03-138-B
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 1024
5 Receiver Gain 512.0
6 Relaxation Delay 2.0000
7 Pulse Width 9.2500
8 Spectrometer Frequency 100.62
9 Nucleus 13C
O
N
H
F
NO2
trans-52
(+/-)
167
166
165
164
163
130
128
126
124
122
120
118
116
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

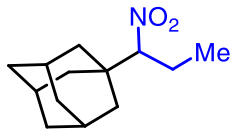
Parameter	Value
1 Title	srz-03-138-B
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	406.0
6 Relaxation Delay	3.0000
7 Pulse Width	11.6200
8 Spectrometer Frequency	564.81
9 Nucleus	19F



trans-52
(+/-)



Parameter	Value
1 Title	srz-03-187
2 Solvent	CDCl3
3 Temperature	297.2
4 Number of Scans	16
5 Receiver Gain	32.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



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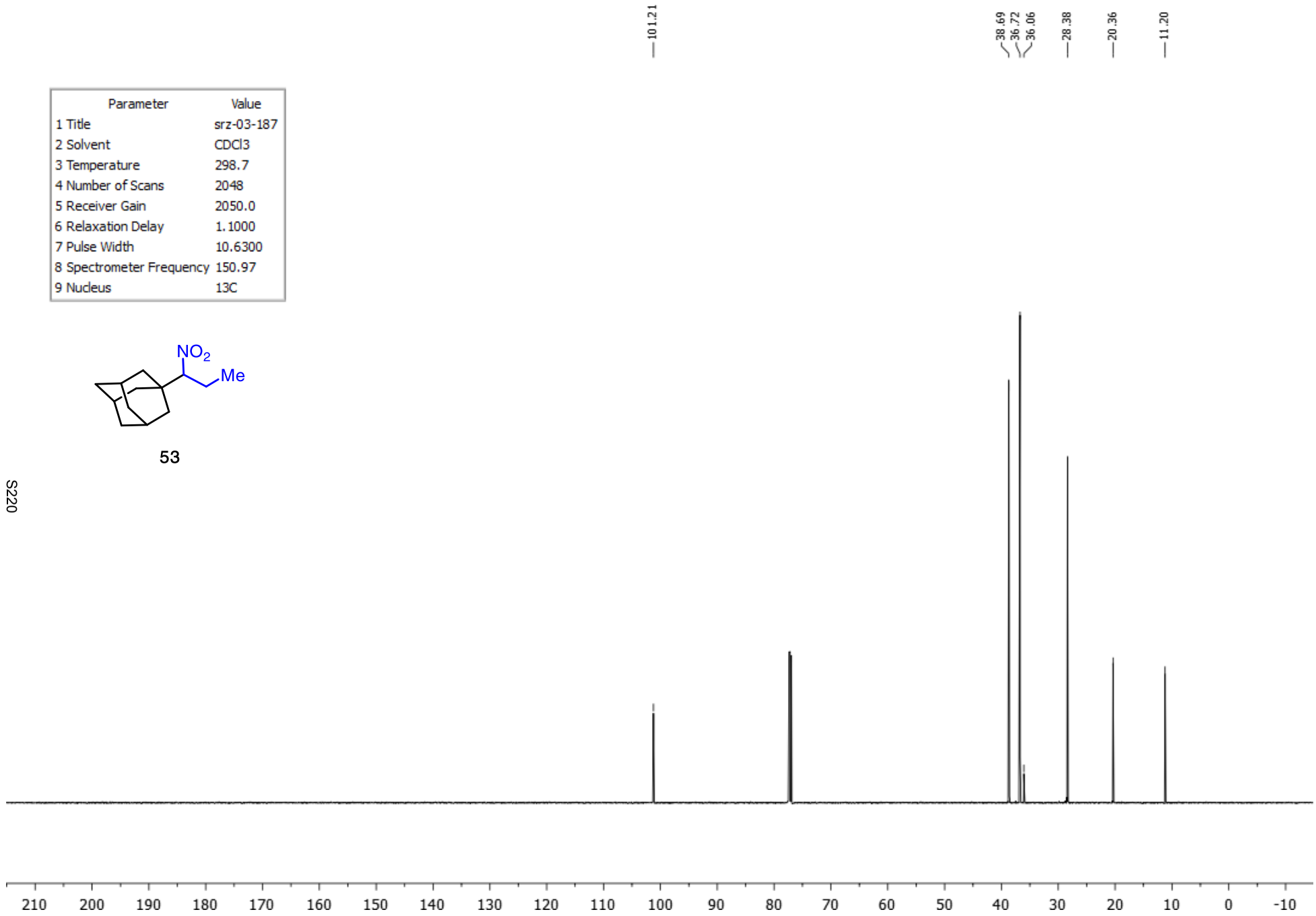
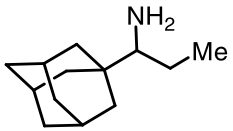

101.21
38.69
36.72
36.06
28.38
20.36
11.20
Parameter Value
1 Title srz-03-187
2 Solvent CDCl3
3 Temperature 298.7
4 Number of Scans 2048
5 Receiver Gain 2050.0
6 Relaxation Delay 1.1000
7 Pulse Width 10.6300
8 Spectrometer Frequency 150.97
9 Nucleus 13C
NO2
Me
53
S220
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Parameter	Value
1 Title	srz-03-184
2 Solvent	C6D6
3 Temperature	297.2
4 Number of Scans	16
5 Receiver Gain	57.0
6 Relaxation Delay	10.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H



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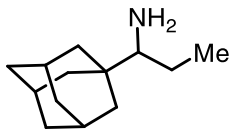
Parameter	Value
1 Title	srz-03-184
2 Solvent	CD2Cl2
3 Temperature	298.1
4 Number of Scans	256
5 Receiver Gain	2050.0
6 Relaxation Delay	1.1000
7 Pulse Width	10.6300
8 Spectrometer Frequency	150.97
9 Nucleus	13C



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