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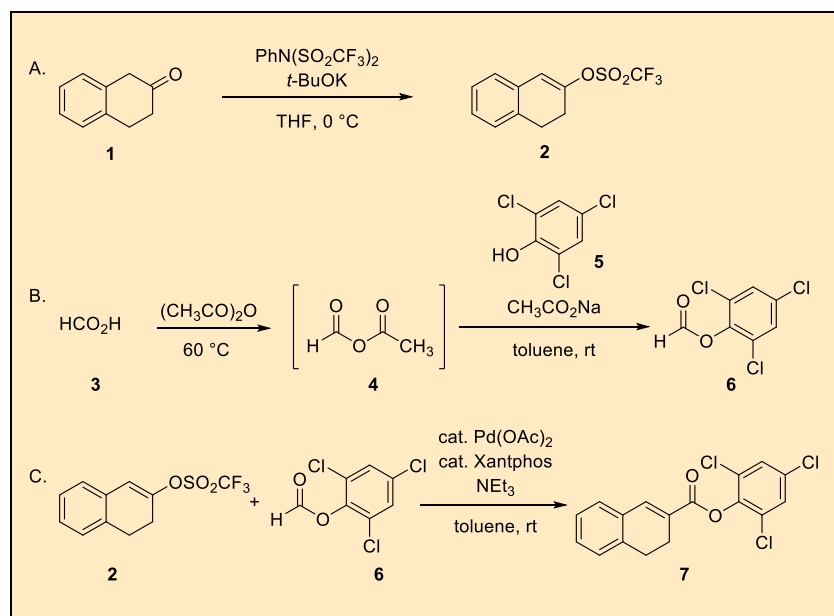
September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Pd-Catalyzed External-CO-Free Carbonylation: Preparation of 2,4,6-Trichlorophenyl 3,4- Dihydronaphthalene-2-Carboxylate

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Procedure

Caution! The carbonylation (part C) should be performed in a well-ventilated hood in case of a leak of carbon monoxide.

A. *3,4-Dihydronaphthalen-2-yl trifluoromethanesulfonate* (2). An oven-dried, 500-mL, three-necked, round-bottomed flask equipped with a Teflon-coated magnetic stir bar (40 × 20 mm), rubber septa (all three necks), and an argon inlet needle (center neck) is charged with β -tetralone (1) (4.16 mL, 4.60 g, 31.5 mmol, 1.05 equiv) (Note 1) and tetrahydrofuran (THF) (120 mL) (Note 2) via syringes through a septum. The flask is cooled to $-20\text{ }^{\circ}\text{C}$ (bath temperature) in a cooling bath (*i*-PrOH/dry-ice). Potassium *tert*-butoxide (3.53 g, 31.5 mmol, 1.05 equiv) is added slowly to the solution of β -tetralone over 10 min (Note 3). After completing the addition, the mixture is warmed to $0\text{ }^{\circ}\text{C}$ in an ice-water bath and stirred for 1 h. Afterward, the dark-blue solution is cooled to $-20\text{ }^{\circ}\text{C}$ (bath temperature) in a cooling bath (*i*-PrOH/dry-ice). After the septum is removed, *N*-phenylbis(trifluoromethanesulfonimide) (10.7 g, 30.0 mmol, 1.00 equiv) (Note 1) is added over 1 min to the solution under a positive pressure of argon. Argon is immediately flushed into the flask and a new rubber septum is inserted. The mixture is warmed to $0\text{ }^{\circ}\text{C}$ in an ice-water bath and stirred for 4 h. At this point, full conversion to the product is confirmed by TLC analysis (Note 4), and the mixture is concentrated under reduced pressure ($40\text{ }^{\circ}\text{C}$, *ca.* 100 mmHg) to approximately one-fourth of the original volume in a rotary evaporator. The resulting mixture is diluted with EtOAc (80 mL) and H_2O (80 mL), and the layers are then partitioned in a 500-mL separatory funnel (Note 5). The aqueous layer is extracted with EtOAc (80 mL × 2). The combined organic layers are washed with brine (80 mL), dried over anhydrous Na_2SO_4 (50 g) (Note 1), filtered through a 75 mL medium-porosity fritted funnel, and concentrated on a rotary evaporator under reduced pressure ($40\text{ }^{\circ}\text{C}$, *ca.* 60 mmHg) to afford a black solid. The obtained residue is purified by column chromatography (SiO_2 , hexane/EtOAc 100/1) (Note 6) to afford 7.75–8.09 g (93–97%, 27.8–29.0 mmol) of product 2 (Notes 7 and 8).

B. *2,4,6-Trichlorophenyl formate* (6). A 1-L, three-necked, round-bottomed flask is equipped with a Teflon-coated magnetic stir bar (40 × 20 mm), rubber septa (both side necks) and a reflux-condenser (center neck). The reflux-condenser is fitted with a rubber septum and an argon inlet needle. The flask is charged with formic acid (18.9 mL, 500 mmol, 5.00 equiv) and acetic anhydride (37.8 mL, 400 mmol, 4.00 equiv) (Note 1). The mixture in the flask is heated to $60\text{ }^{\circ}\text{C}$ (bath temperature) in an oil bath and stirred for 1 h. Subsequently, the mixture is cooled to $0\text{ }^{\circ}\text{C}$ in an ice-water bath. Toluene (300 mL) (Note 2), 2,4,6-trichlorophenol (5) (19.7 g, 100 mmol, 1.00 equiv),

and sodium acetate (8.20 g, 100 mmol, 1.00 equiv) are added to the solution (Notes 1 and 9). After 10 min, the ice-water bath is removed and the reaction is warmed to room temperature. During this time, a white precipitate gradually appears. The mixture is stirred for 30 min at room temperature. At this point, full conversion to the product is confirmed by TLC analysis (Note 4), and H₂O (100 mL) is added to the solution, resulting in the dissolution of the white precipitate. The layers are partitioned in a 1-L separatory funnel. The organic layer is washed with H₂O (100 mL × 3) and brine (100 mL × 2), dried over anhydrous Na₂SO₄ (50 g) (Note 1), filtered through a 75 mL medium-porosity fritted funnel, and concentrated on a rotary evaporator under reduced pressure (40 °C, *ca.* 20 mmHg) to afford a pale yellow oil, which crystallizes upon standing at ambient temperature. The obtained residue is recrystallized from hexane/EtOAc (50/1 v/v, *ca.* 150 mL) (Note 10) to afford 21.0 g (93% yield, 93.1 mmol) of product **6** (Notes 11 and 12).

C. *2,4,6-Trichlorophenyl 3,4-dihydronaphthalene-2-carboxylate (7)*. An oven-dried, 300-mL, three-necked, round-bottomed flask equipped with a Teflon-coated magnetic stir bar (40 × 20 mm), rubber septa (all three necks), an argon inlet (center neck), and a bubbler (side neck) is charged with palladium acetate (135 mg, 0.600 mmol, 0.03 equiv) (Note 1), Xantphos (694 mg, 1.20 mmol, 0.06 equiv) (Note 1), and 2,4,6-trichlorophenyl formate (**6**) (5.41 g, 24.0 mmol, 1.20 equiv). The flask is evacuated and backfilled with argon three times. An oven-dried, 50-mL, single-necked, round-bottomed flask is charged with 3,4-dihydronaphthalen-2-yl trifluoromethanesulfonate (**2**) (5.57 g, 20.0 mmol, 1.00 equiv) and equipped with a rubber septa and an argon inlet. The flask is evacuated and backfilled with argon three times. Then, toluene (20 mL) (Note 2) is added to the flask via a syringe. The triflate solution is added to the 300-mL flask via a gastight syringe. Toluene (10 mL × 2) (Note 2) is added to the 50-mL flask to wash its interior, and the washing is transferred to the 300-mL flask via the same syringe. After the mixture is stirred for 5 min at ambient temperature, triethylamine (3.33 mL, 24.0 mmol, 1.20 equiv) (Note 1) is added over 15 min via a syringe (Note 13). During the addition of triethylamine, a slightly exothermic reaction ensues with gas evolution, and the brown color changes to black. After completing the addition, the mixture is stirred for another 2 h. At this point, full conversion to the product is confirmed by TLC analysis (Note 4), and the mixture is diluted with Et₂O (100 mL) and H₂O (100 mL). The layers are partitioned in a 500-mL separatory funnel. The aqueous layer is extracted with Et₂O (50 mL × 2). The combined organic layers are washed

with aqueous NaOH solution (0.5 M, 60 mL) and brine (100 mL), dried over anhydrous Na₂SO₄ (40 g) (Note 1), filtered through a 75 mL medium-porosity fritted funnel, and concentrated under reduced pressure (40 °C, ca. 60 mmHg) in a rotary evaporator to afford a brown oil. The obtained residue is purified by column chromatography (SiO₂, hexane/EtOAc 100/1) (Note 14) to afford 6.73 g (96%, 19.1 mmol) of product 7 as a white solid (Notes 15 and 16).

Notes

1. The checkers purchased β-tetralone (98%) and Pd(OAc)₂ (≥99.9% trace metal basis) from Sigma-Aldrich and used as received. Formic acid (98+%) and acetic anhydride (97+%) were purchased from Merck and used as received. Xantphos (98%), sodium acetate (98.5+%), anhydrous sodium sulfate (99+%), and potassium *tert*-butoxide (98+%) were purchased from Acros Organics and used as received. *N*-Phenylbis(trifluoromethanesulfonimide) (>98.0%) and 2,4,6-trichlorophenol (>96.0%) were purchased from Tokyo Chemical Industry Co., Ltd. and used as received. Triethylamine (99+%) was purchased from Sigma-Aldrich and distilled from CaH₂ prior to use. The submitters purchased β-tetralone (97+%), anhydrous sodium sulfate (99+%), formic acid (98+%), acetic anhydride (97+%), sodium acetate (98.5+%), and Xantphos (98+) from Wako Pure Chemical Industries, Ltd. and used as received. Potassium *tert*-butoxide solution in THF (12%, ca. 1 M), *N*-phenylbis(trifluoromethanesulfonimide) (>98.0%), and 2,4,6-trichlorophenol (>96.0%) were purchased from Tokyo Chemical Industry Co., Ltd. and used as received. Pd(OAc)₂ (≥99.9% trace metal basis) was purchased from Sigma-Aldrich and used as received. Triethylamine (99+%) was purchased from Wako and distilled from CaH₂ prior to use.
2. The checkers purchased THF (>99.5%) and toluene (>99.5%) from Sigma-Aldrich and passed it through a column of alumina before use. The submitters purchased dehydrated, stabilizer-free THF (>99.5% "Super Plus") and dehydrated toluene (>99.5% "Super Plus") from Kanto, which was purified by using a Glass Contour Solvent Purification Systems prior to use.

- The submitters equipped the 500-mL, three-necked round-bottomed flask with rubber septa (both side necks) and a 100 mL pressure-equalizing addition funnel (center neck). After the 500-mL flask was charged with β -tetralone (**1**) (4.16 mL, 4.60 g, 31.5 mmol, 1.05 equiv) and THF (120 mL), the addition funnel was charged with a solution of potassium *tert*-butoxide in THF (*ca.* 1.0 M, 31.5 mL, 31.5 mmol, 1.05 equiv) via a syringe that was then added dropwise to the solution of β -tetralone over 10 min.
- TLC analysis was performed on Merck glass plates coated with 0.25-mm 230–400 mesh silica gel containing a fluorescent indicator. The plate was eluted with hexane/EtOAc (9/1) and visualized by ultraviolet lamp at 254 nm. The following R_f values were obtained: 3,4-dihydronaphthalen-2-yl trifluoromethanesulfonate (0.63), 2,4,6-trichlorophenyl formate (0.57), and 2,4,6-trichlorophenyl 3,4-dihydronaphthalene-2-carboxylate (0.57). As for 2,4,6-trichlorophenyl formate, partial decomposition resulting in the appearance of a spot of 2,4,6-trichlorophenol was observed.
- The interface of the two phases is difficult to recognize because of the deep color (organic phase: dark blue-black, aqueous phase: dark yellow-black). Care should be taken in the separation of the two phases. Additional amounts of EtOAc and H₂O may lead to easier separation.
- Column chromatography is performed using a 7.5-cm wide, 22-cm high column of 270 g of Fluka Silica gel (high purity grade, 60 Å pore size, 230–400 mesh) (The submitters used Kanto Silica Gel 60 N (spherical, neutral, 63–210 μ m)) packed by slurring the silica gel with hexane. The residue is dissolved with a minimum amount of CH₂Cl₂ (30 mL), and loaded onto the column. Elution with 400 mL of hexane and then hexane/EtOAc (100/1) (50 mL initial collection followed by 200 mL fractions) afforded the production in fractions 2–24. The combined fractions containing the desired product are concentrated on a rotary evaporator under reduced pressure (40 °C, *ca.* 120 mmHg).
- The submitters reported two runs. Starting with compound **1**, triflate **2** was obtained in 97–98% yield (8.06–8.16 g, 29.0–29.3 mmol).
- 3,4-Dihydronaphthalen-2-yl trifluoromethanesulfonate (**2**) showed the following characterization data: $R_f = 0.63$ (hexane/EtOAc 9/1); ¹H NMR (400 MHz, CDCl₃) δ : 2.70 (t, $J = 8.4$ Hz, 2 H), 3.06 (t, $J = 8.2$ Hz, 2 H), 6.48 (s, 1 H), 7.05 – 7.10 (m, 1 H), 7.12 – 7.16 (m, 1 H), 7.17 – 7.23 (m, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ : 26.5, 28.5, 118.5, 118.5 (q, $^1J_{CF} = 320.7$ Hz), 127.3, 127.5, 128.4, 131.1, 132.9, 149.9. ¹⁹F NMR (376 MHz, CDCl₃) δ :

- 73.6. IR (ATR, neat) cm^{-1} : 1664, 1416, 1248, 1202, 1137, 1062, 985, 895, 824, 753, 610. HMRS (EI): m/z calcd for $\text{C}_{11}\text{H}_9\text{F}_3\text{O}_3\text{S}$ [M^+] 278.0219, found 278.0222. Elemental Analysis: Anal. Calcd. for $\text{C}_{11}\text{H}_9\text{F}_3\text{O}_3\text{S}$: C, 47.48; H, 3.26. Found: C, 47.27; H, 3.19. This compound tends to develop a brown color; storage by refrigeration is recommended.
9. The submitters reported that an exothermic reaction occurred after addition of sodium acetate. The checkers avoided this exotherm by cooling the reaction to 0 °C prior to addition of sodium acetate.
10. Recrystallization is performed as follows. The residue is transferred to a 500-mL, round-bottomed flask equipped with a Teflon-coated magnetic stir bar (30 x 6 mm). Hexane/EtOAc (50/1 v/v, ca. 150 mL) is added to the flask and the flask is heated to 60 °C by an oil bath with stirring. After dissolution of the solid, magnetic stirring is turned off and the solution was allowed to cool to ambient temperature and crystallize for 5 h. The resulting crystals were collected by suction filtration on a 75 mL medium-porosity fritted funnel with a 250 mL round-bottomed receiving flask, and washed with ice-cold hexane (5 mL x 2). The mother liquor is concentrated on a rotary evaporator under reduced pressure (40 °C, ca. 20 mmHg) to give a yellow solid. A Teflon-coated magnetic stir bar (30 x 6 mm) and hexane/EtOAc (50/1 v/v, ca. 50 mL) were added to the flask and the flask was heated to 60 °C by an oil bath with stirring. Crystallization was carried out as described for the first crop. After filtration, the mother liquor, which was collected in a 100 mL round-bottomed flask, was concentrated on a rotary evaporator under reduced pressure (40 °C, ca. 20 mmHg) to give a yellow solid. A Teflon-coated magnetic stir bar (30 x 6 mm) and hexane/EtOAc (50/1 v/v, ca. 10 mL) were added to the flask and the flask was heated to 60 °C by an oil bath with stirring. Crystallization was carried out as described for the first crop. The three crops are dried overnight in a desiccator at ambient temperature under vacuum (3 mmHg).
11. The checkers completed two runs. The first run was completed on half the scale. Compound **6** was obtained in 95% yield (10.7 g, 47.4 mmol). The quantities and yields obtained from the three crops after recrystallization were as follows: first crop (6.90 g, 30.6 mmol, 61%), second crop (3.38 g, 15.0 mmol, 30%), and third crop (0.440 g, 1.95 mmol, 4%). For the second (full-scale) run, the quantities and yields obtained from the three crops after recrystallization were as follows: first crop (13.8 g, 61.2 mmol, 61%), second crop (6.40 g, 28.3 mmol, 28%), and third crop (0.88 g, 3.90 mmol, 4%).

12. 2,4,6-Trichlorophenyl formate (**6**) showed the following characterization data: mp 72–73 °C; R_f = 0.57 (hexane/EtOAc 9/1); ^1H NMR (400 MHz, CDCl_3) δ : 7.41 (s, 2 H), 8.28 (s, 1 H). ^{13}C NMR (100 MHz, CDCl_3) δ : 128.7, 129.2, 132.6, 141.9, 156.2. IR (ATR, neat) cm^{-1} : 3078, 1732, 1563, 1447, 1385, 1227, 1085, 1057, 850, 820, 805, 678, 562. HRMS (ESI-TOF): m/z calcd for $\text{C}_7\text{H}_3\text{Cl}_3\text{O}_2$ [M^+] 223.9194, found 223.9190. Elemental Analysis: Anal. Calcd. for $\text{C}_7\text{H}_3\text{Cl}_3\text{O}_2$: C, 37.29; H, 1.34. Found: C, 37.10; H, 1.40.
13. Triethylamine should be added slowly. Fast addition of triethylamine causes sudden decomposition of the formate.
14. Column chromatography is performed using a 7.5-cm wide, 22-cm high column of 270 g of Fluka Silica gel (high purity grade, 60 Å pore size, 230–400 mesh) (The submitters used Kanto Silica Gel 60 N (spherical, neutral, 63–210 μm)) packed by slurring the silica gel with hexane. The residue is dissolved with a minimum amount of CH_2Cl_2 (30 mL), and loaded onto the column. Elution with 400 mL of hexane and then hexane/ EtOAc (100/1) (2 L initial collection followed by 200 mL fractions) afforded the production in fractions 10–16. The combined fractions containing the desired product were concentrated on a rotary evaporator under reduced pressure (40 °C, *ca.* 120 mmHg).
15. The checkers completed two runs. The first run was completed on half the scale. Compound **7** was obtained in 92% yield (3.22 g, 9.14 mmol). The submitters reported two runs. Compound **7** was obtained as white needles in 94–96% yield (6.67–6.76 g, 18.9–19.1 mmol).
16. 2,4,6-Trichlorophenyl 3,4-dihydronaphthalene-2-carboxylate (**7**) showed the following characterization data: mp 80–82 °C; R_f = 0.57 (hexane/EtOAc 9/1); ^1H NMR (400 MHz, CDCl_3) δ : 2.76 (t, J = 7.9 Hz, 2 H), 2.97 (t, J = 8.3 Hz, 2H), 7.20 – 7.35 (m, 4 H), 7.40 (s, 2 H), 7.86 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 22.2, 27.4, 126.7, 126.9, 127.8, 128.5, 129.0, 129.8, 130.3, 131.8, 132.0, 137.2, 139.9, 143.3, 163.5. IR (ATR, neat) cm^{-1} : 1733, 1624, 1564, 1448, 1380, 1275, 1238, 1201, 1184, 1171, 1022, 958, 855, 757, 737, 714. HRMS (EI): m/z calcd for $\text{C}_{17}\text{H}_{12}\text{Cl}_3\text{O}_2$ [$\text{M}+\text{H}^+$] 352.9897, found 352.9896. Elemental Analysis: Anal. Calcd. for $\text{C}_{17}\text{H}_{11}\text{Cl}_3\text{O}_2$: C, 57.74; H, 3.14. Found: C, 57.72; H, 3.08.

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Discussion

Palladium-catalyzed carbonylation of organic (pseudo)halides employing carbon monoxide (CO) has received much attention because of its versatility for the synthesis of carbonyl-containing compounds.² One of the major drawbacks to this methodology is the use of CO in gaseous form, which is highly toxic, and, can, therefore, be problematic for production on both laboratory and multikilogram scales. A simple solution to this problem involves replacing gaseous CO with another, less toxic, carbonyl source. Given the increasing demand for CO surrogates, several carbonyl sources have been developed.³ Aldehydes can be decomposed through transition metal catalysis to generate CO.⁴ Formic anhydrides⁵ and formic esters⁶ are also known to produce CO in the presence of a transition metal or a strong base. However, these CO surrogates require high temperatures or harsh reaction conditions to promote the generation of CO, making them less attractive. Although metal carbonyl complexes have been reported to generate CO by thermal decomposition using a microwave,⁷ the need for a large excess of the complex is unfavorable for handling and poses environmental issues. Recently, 9-methylfluorene-9-carbonyl chloride⁸ and silacarboxylic acid⁹ have been reported as CO precursors. However, tedious procedures are required for their synthesis, and a special two-chamber

system must be used for the carbonylation reaction. It is noted that acylpalladium precatalyst works well in hydroxycarbonylation of aryl halides using potassium formate as a CO source.¹⁰

We have recently developed a Pd-catalyzed external-CO-free carbonylation of aryl, alkenyl, allyl halides, and sulfonates by using phenyl formate as a phenoxycarbonylating source.¹¹⁻¹³ This method is based on the finding that phenyl formate can undergo facile decarbonylation in the presence of weak base such as triethylamine to afford CO and phenol, which subsequently react with an electrophile.

Though aryl formates easily decompose to generate CO in the presence of tertiary amines, alkyl formates do not.¹¹ The rate of decomposition increases as electron-withdrawing groups are introduced into the aromatic rings of aryl formates.¹⁴

Among the aryl formates with electron-withdrawing groups, 2,4,6-trichlorophenyl formate was found to have the potential to promote the external-CO-free carbonylation reaction under much milder conditions, i.e., at ambient temperature.¹⁴ 2,4,6-Trichlorophenyl formate is a stable crystalline compound and is easily accessible from 2,4,6-trichlorophenol, an inexpensive chemical feedstock.¹⁵ It allows mild and fast aryloxycarbonylation of aryl iodides and alkenyl trifluoromethanesulfonates (triflates) to afford the corresponding 2,4,6-trichlorophenyl esters in excellent yields. In the case of large-scale synthesis, the reaction proceeds without any difficulties, although adjustment of the rate of addition of triethylamine is recommended to prevent sudden decomposition of the formate. Because the reaction does not require toxic gaseous CO or pressure-resistant apparatus, the experimental procedure disclosed herein is safer and more practical than those that use CO gas or other CO surrogates, as mentioned above.

Furthermore, 2,4,6-trichlorophenyl formate can be regarded as "weighable CO." This additional merit is ascribed to the ease of adjusting the amount of CO. Its chemical nature to produce CO under very mild conditions has potential to be applied to various organic reactions using CO as a reactant or a ligand.

Because products obtained via this method are esters with highly electrophilic nature, further derivatization can easily be achieved. As described in our previous paper,¹⁴ trichlorophenyl esters can react with a slight excess quantity of nucleophiles, resulting in successful conversion into various compounds, including alkyl esters, thioesters, carboxylic acids, and amides. One-pot syntheses from (pseudo)halides to amides have also

been demonstrated.¹³ Analogous one-pot reactions have been shown to be feasible with other nucleophiles. When a nucleophile is used to release 2,4,6-trichlorophenol as a by-product, simple washing with diluted aqueous NaOH solution is sufficient for removal of 2,4,6-trichlorophenol. This characteristic further increases the practicality of the reaction protocol.

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Appendix

Chemical Abstracts Nomenclature (Registry Number)

- β -Tetralone: 2(1*H*)-Naphthalenone, 3,4-dihydro-; (530-93-8)
 Potassium *tert*-butoxide: 2-Propanol, 2-methyl-, potassium salt (1:1); (865-47-4)
N-Phenylbis(trifluoromethanesulfonimide): Methanesulfonamide, 1,1,1-trifluoro-*N*-phenyl-*N*-[(trifluoromethyl)sulfonyl]-; (37595-74-7)
 3,4-Dihydronaphthalen-2-yl trifluoromethanesulfonate: Methanesulfonic acid, 1,1,1-trifluoro-, 3,4-dihydro-2-naphthalenyl ester; (143139-14-4)
 Formic acid; (64-18-6)
 Acetic anhydride: Acetic acid, 1,1'-anhydride; (108-24-7)
 2,4,6-Trichlorophenol: Phenol, 2,4,6-trichloro-; (88-06-2)
 Sodium acetate: Acetic acid, sodium salt (1:1); (127-09-3)
 2,4,6-Trichlorophenyl formate: Phenol, 2,4,6-trichloro-, 1-formate; (4525-65-9)
 Palladium acetate: Acetic acid, palladium(2+) salt (2:1); (3375-31-3)
 Xantphos: Phosphine, 1,1'-(9,9-dimethyl-9*H*-xanthene-4,5-diyl)bis[1,1-diphenyl-]; (161265-03-8)
 2,4,6-Trichlorophenyl 3,4-dihydronaphthalene-2-carboxylate: 2-Naphthalenecarboxylic acid, 3,4-dihydro-, 2,4,6-trichlorophenyl ester; (1402012-58-1)



Kei Manabe was born in Kanagawa, Japan. He completed his doctoral work in 1993 at the University of Tokyo. After working as a postdoctoral fellow at Columbia University, USA, he went back to the University of Tokyo and worked as an Assistant Professor, Lecturer, and Associate Professor. In 2005, he moved to RIKEN as an Initiative Research Scientist. He joined the faculty at the University of Shizuoka as a Professor in 2009. His research interests include development of new catalytic reactions for organic synthesis.



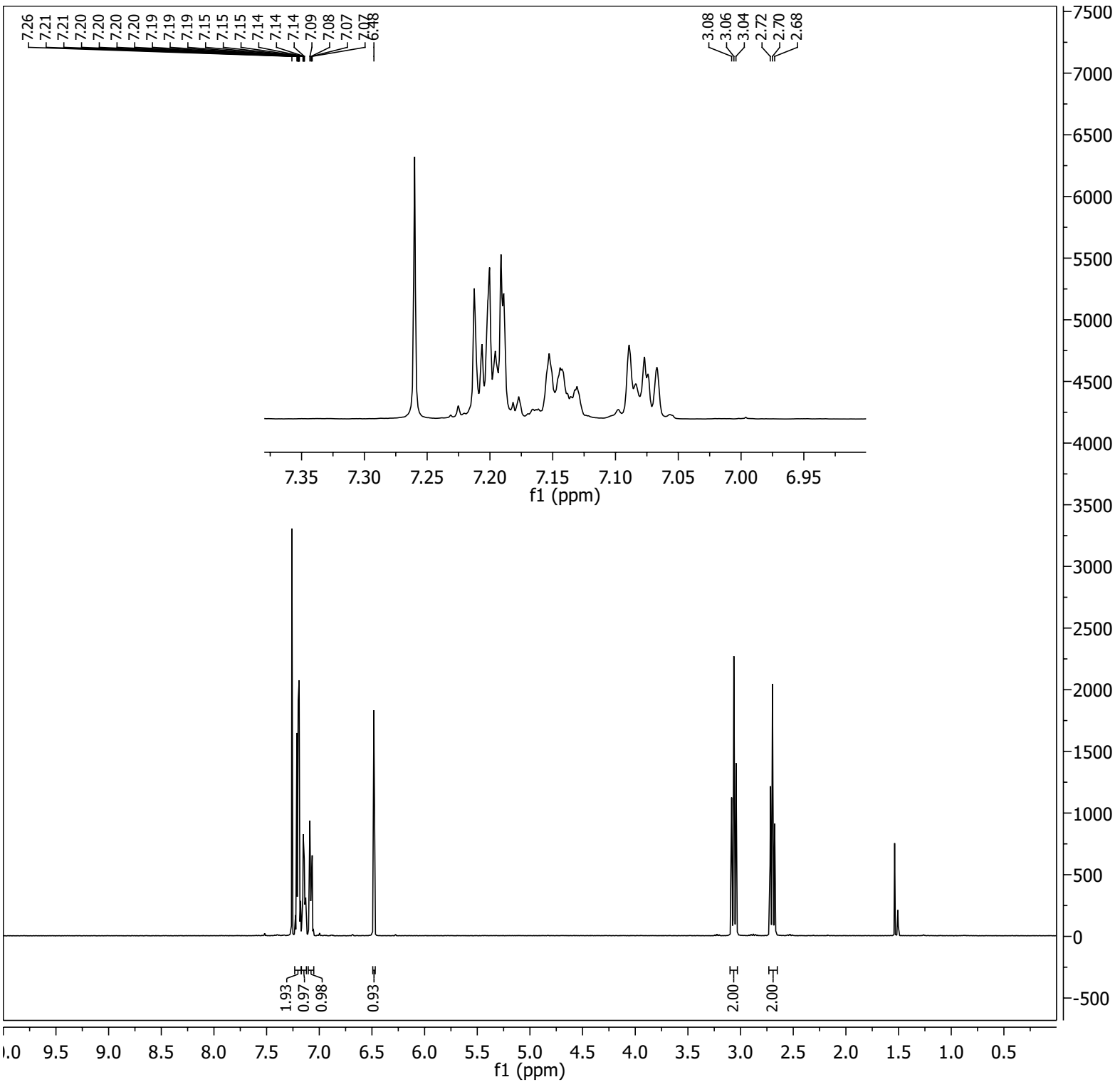
Hideyuki Konishi was born in Takamatsu, Japan in 1979. He obtained his Ph.D. degree in pharmaceutical sciences at the University of Tokyo in 2008 under the direction of Professor Shu Kobayashi. He carried out his postdoctoral research in Professor Viresh H. Rawal's laboratory at the University of Chicago. In 2009, he became a Research Assistant Professor in the group of Professor Kei Manabe at the University of Shizuoka. His research interests include development of practical and efficient catalytic reactions for construction of pharmaceutically and synthetically important compounds.



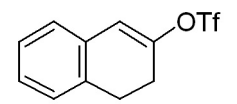
Tsuyoshi Ueda was born in Ishikawa prefecture, Japan, in 1978. He received his M.S. degree in 2003 in Industrial Chemistry from Meiji University and subsequently joined the Department of Process Development at Sankyo Co., Ltd. He completed his Ph.D. under the guidance of Professor Kei Manabe at University of Shizuoka in 2013. He is currently an Associate Senior Researcher in Daiichi Sankyo Co., Ltd., working on the development of practical synthetic methods and large-scale synthesis of active pharmaceutical ingredients.

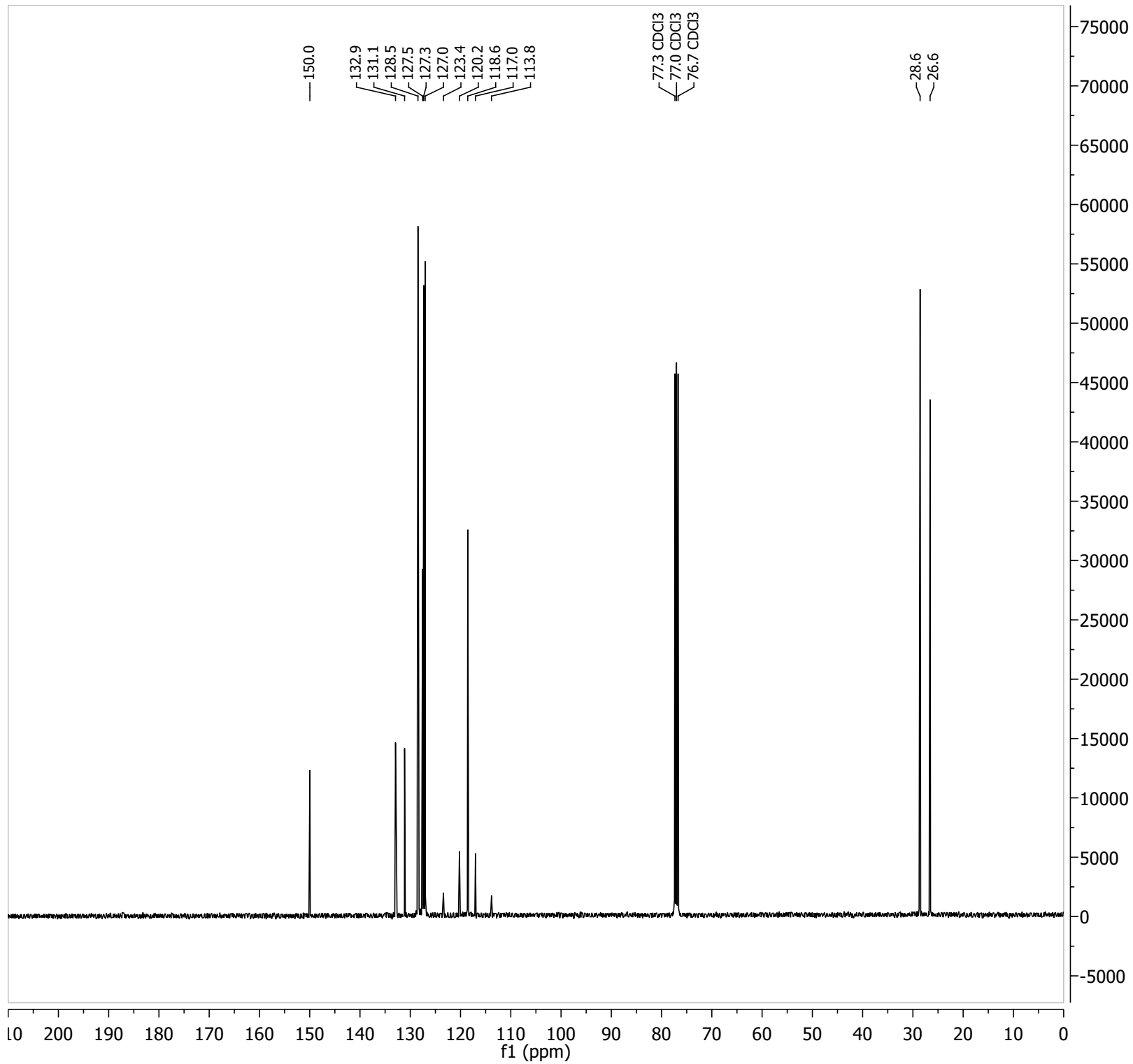


Jennifer Ciesielski received her B.A. degree in Chemistry from Lake Forest College in 2007. She then moved to University of Rochester where she obtained her Ph.D. in 2012. She is currently a National Science Foundation postdoctoral fellow with Professor Erick M. Carreira at the ETH Zürich.

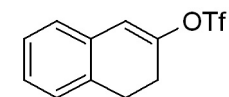


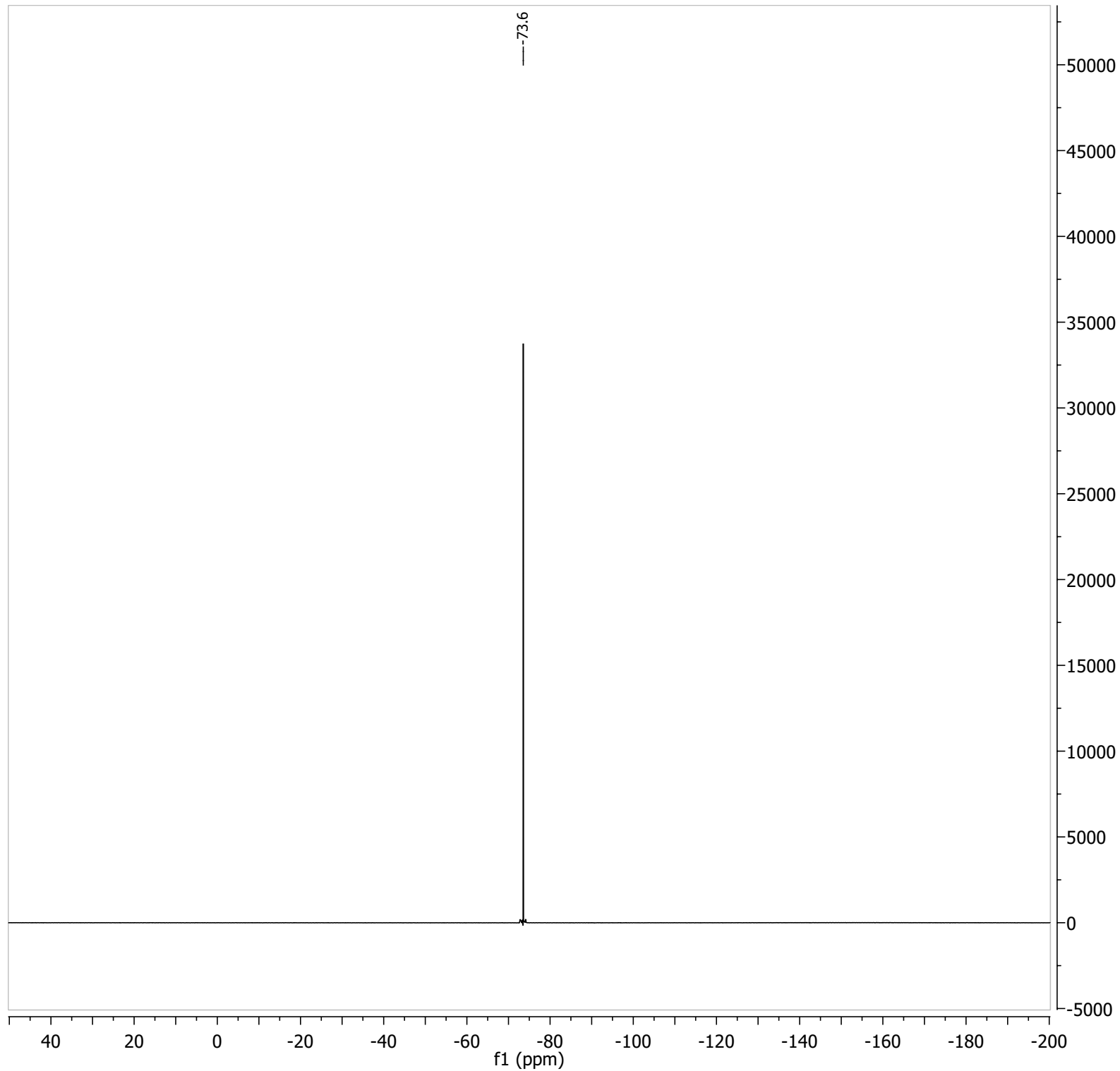
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Spectrometer	spect
3 Solvent	CDC13
4 Temperature	298.0
5 Pulse Sequence	zg30
6 Experiment	1D
7 Number of Scans	16
8 Receiver Gain	146
9 Relaxation Delay	1.0000
10 Pulse Width	9.8000
11 Acquisition Time	3.9846
12 Acquisition Date	2013-08-14T15:49:00
13 Modification Date	2013-08-14T17:23:48
14 Spectrometer Frequency	400.26
15 Spectral Width	8223.7
16 Lowest Frequency	-1651.3
17 Nucleus	1H
18 Acquired Size	32768
19 Spectral Size	131072



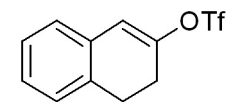


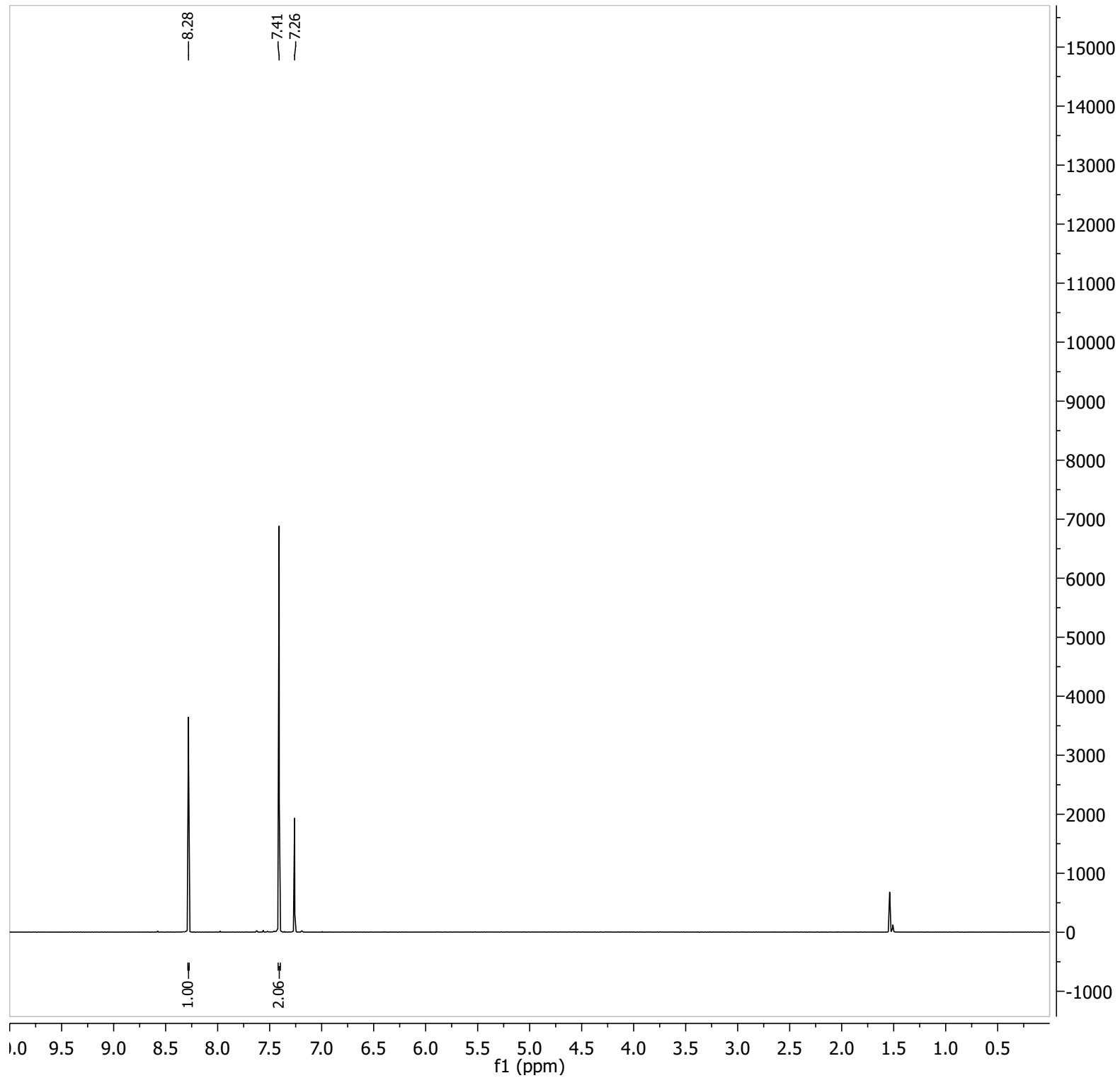
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1 Origin	Bruker BioSpin GmbH
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	298.1
5 Pulse Sequence	zgpg45
6 Experiment	1D
7 Number of Scans	5000
8 Receiver Gain	8192
9 Relaxation Delay	0.3000
10 Pulse Width	7.8000
11 Acquisition Time	2.1000
12 Acquisition Date	2013-09-12T17:23:00
13 Modification Date	2013-09-12T17:29:09
14 Spectrometer Frequency	100.64
15 Spectral Width	24038.5
16 Lowest Frequency	-1957.6
17 Nucleus	13C
18 Acquired Size	50479
19 Spectral Size	65536



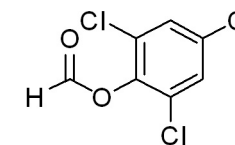


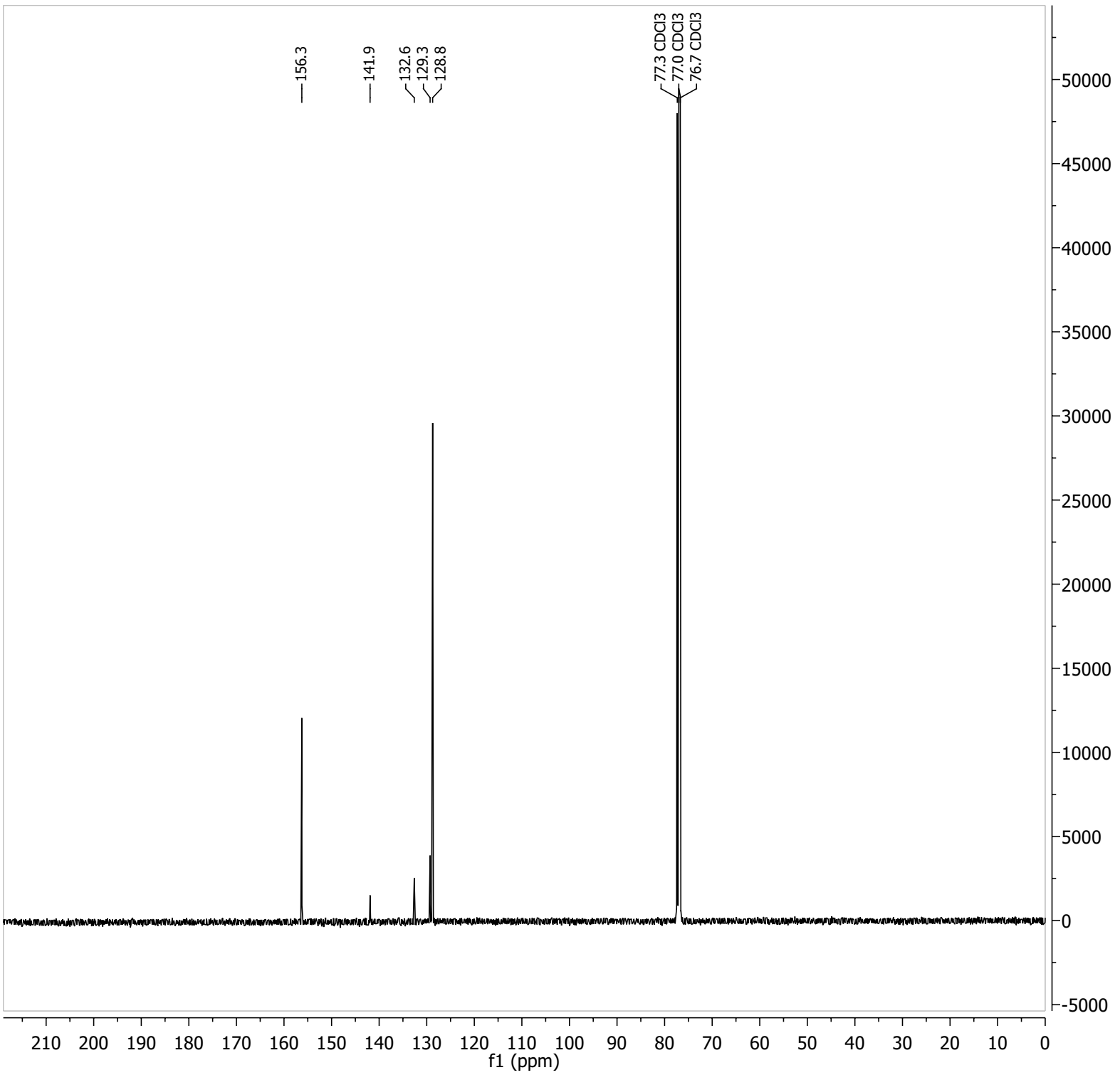
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1 Origin	Bruker BioSpin GmbH
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	298.0
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6 Experiment	1D
7 Number of Scans	32
8 Receiver Gain	912
9 Relaxation Delay	1.0000
10 Pulse Width	14.0000
11 Acquisition Time	0.6947
12 Acquisition Date	2013-09-12T17:26:00
13 Modification Date	2013-09-12T17:29:11
14 Spectrometer Frequency	376.54
15 Spectral Width	94339.6
16 Lowest Frequency	-75411.9
17 Nucleus	19F
18 Acquired Size	65536
19 Spectral Size	65536



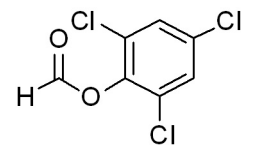


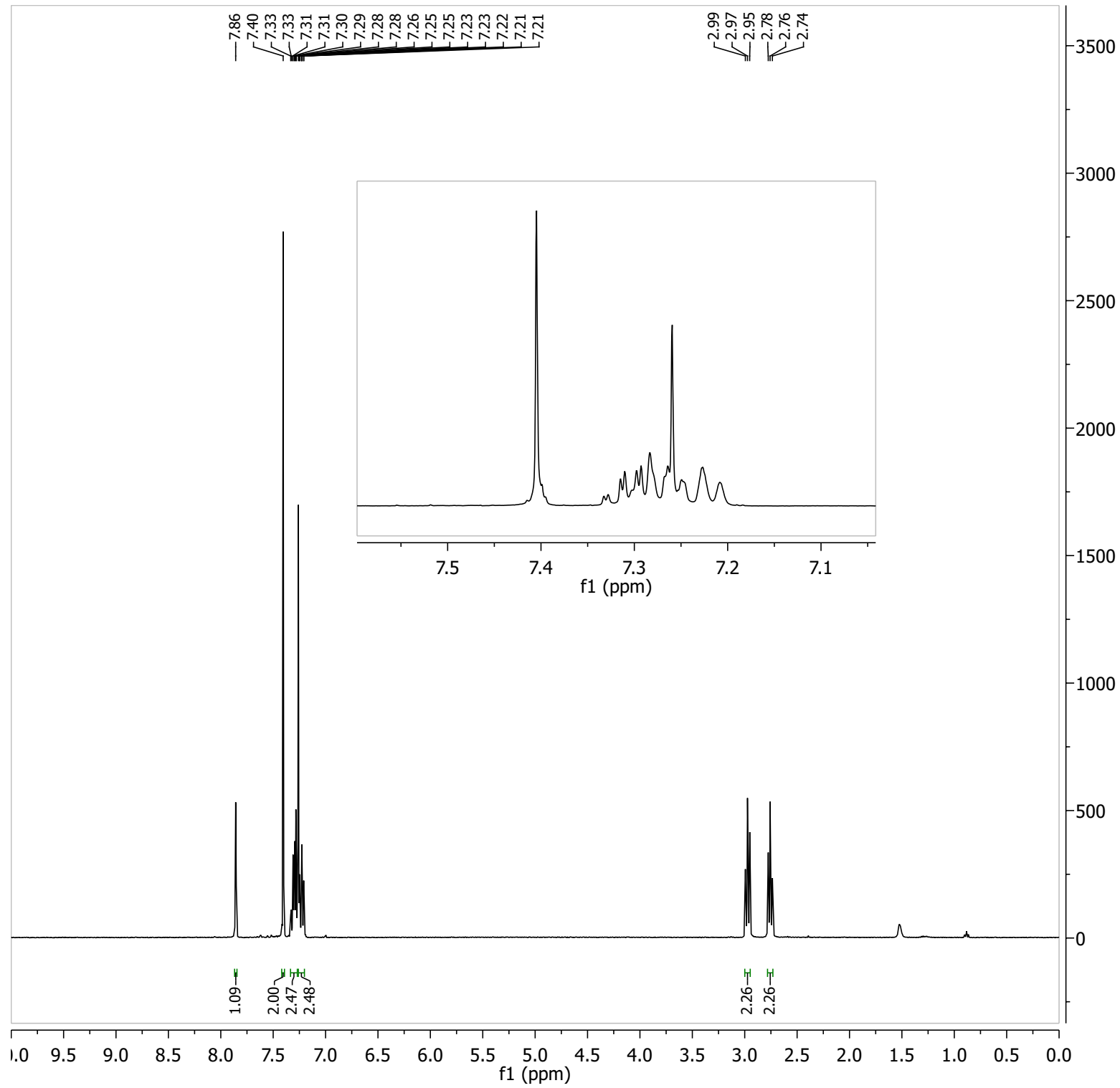
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	298.1
5 Pulse Sequence	zg30
6 Experiment	1D
7 Number of Scans	16
8 Receiver Gain	362
9 Relaxation Delay	1.0000
10 Pulse Width	10.9000
11 Acquisition Time	3.9716
12 Acquisition Date	2013-09-02T22:49:00
13 Modification Date	2013-09-03T09:47:23
14 Spectrometer Frequency	400.20
15 Spectral Width	8250.8
16 Lowest Frequency	-1667.2
17 Nucleus	1H
18 Acquired Size	32768
19 Spectral Size	32768



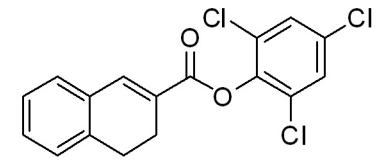


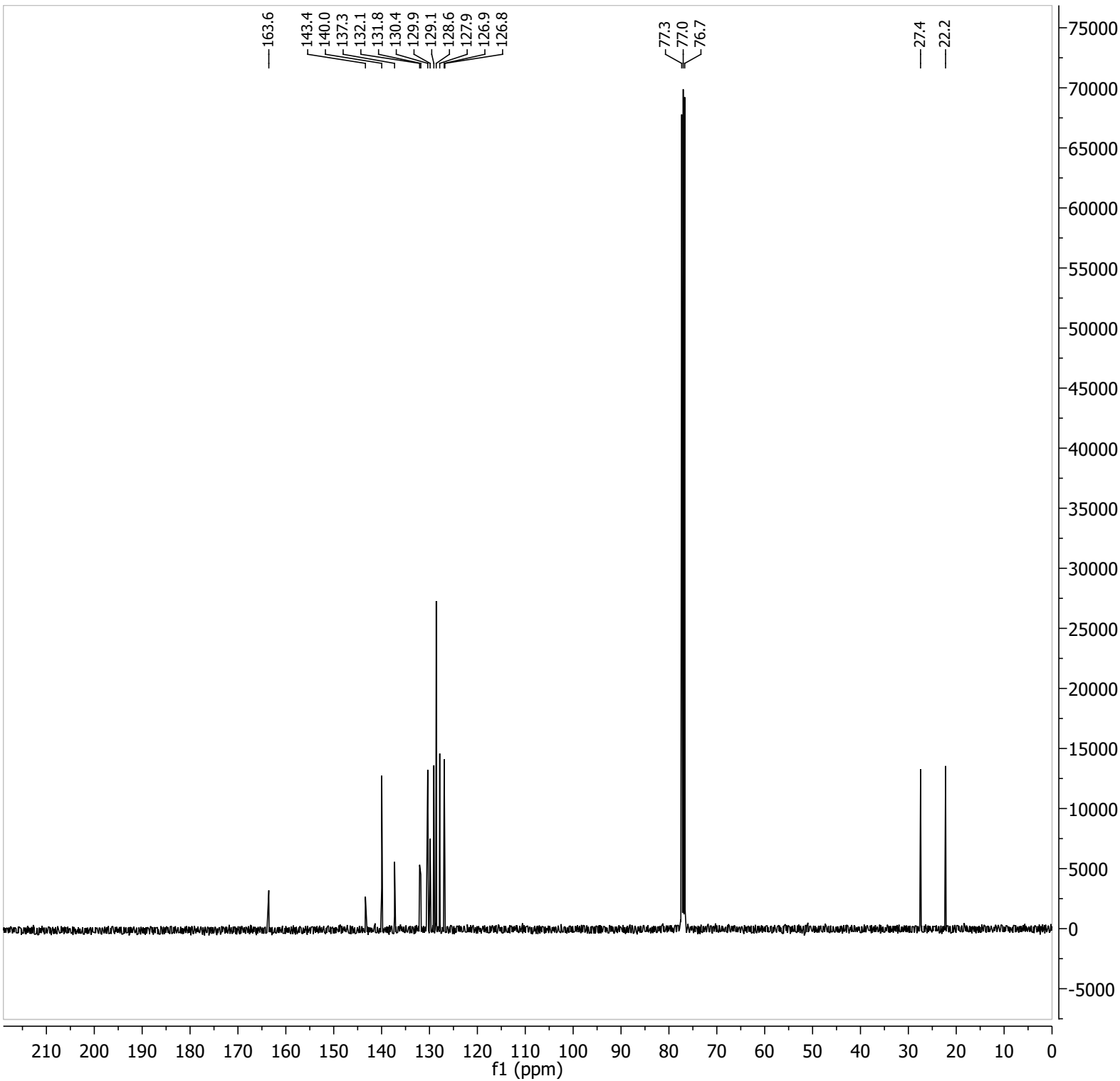
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	298.1
5 Pulse Sequence	zgpg45
6 Experiment	1D
7 Number of Scans	5555
8 Receiver Gain	7298
9 Relaxation Delay	0.3000
10 Pulse Width	7.8000
11 Acquisition Time	2.1000
12 Acquisition Date	2013-09-03T02:38:00
13 Modification Date	2013-09-03T09:47:24
14 Spectrometer Frequency	100.64
15 Spectral Width	24038.5
16 Lowest Frequency	-1957.6
17 Nucleus	13C
18 Acquired Size	50479
19 Spectral Size	65536





Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	298.2
5 Pulse Sequence	zg30
6 Experiment	1D
7 Number of Scans	16
8 Receiver Gain	322
9 Relaxation Delay	1.0000
10 Pulse Width	10.9000
11 Acquisition Time	3.9716
12 Acquisition Date	2013-09-20T16:00:00
13 Modification Date	2013-09-20T20:00:18
14 Spectrometer Frequency	400.20
15 Spectral Width	8250.8
16 Lowest Frequency	-1667.6
17 Nucleus	1H
18 Acquired Size	32768
19 Spectral Size	32768





Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Spectrometer	spect
3 Solvent	CDCl3
4 Temperature	298.1
5 Pulse Sequence	zgpg45
6 Experiment	1D
7 Number of Scans	5700
8 Receiver Gain	11585
9 Relaxation Delay	0.3000
10 Pulse Width	7.8000
11 Acquisition Time	2.1000
12 Acquisition Date	2013-09-20T19:55:00
13 Modification Date	2013-09-20T20:00:19
14 Spectrometer Frequency	100.64
15 Spectral Width	24038.5
16 Lowest Frequency	-1957.6
17 Nucleus	13C
18 Acquired Size	50479
19 Spectral Size	65536

