

Electronic Supplementary Information

Direct Synthesis of Haloaromatics from Nitroarenes via Sequential One-pot Mo-catalyzed Reduction / Sandmeyer Reaction

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General information:

Materials. All reactions involving air-sensitive compounds were carried out under inert atmosphere using a N₂ current and oven-dried glassware. All common reagents and solvents were obtained from commercial suppliers (Aldrich or Alfa-Aesar) and used without any further purification. The catalyst, MoO₂Cl₂(DMF)₂, was prepared as previously reported from Na₂Mo₄·2H₂O.¹

Chromatography. Thin layer chromatography (TLC) was carried out on Merck aluminum-backed plates coated with silica gel (60F-254), using UV light as visualizing agent and Ce/Mo solution and heat as developing agent. Flash column chromatography was carried out on silica gel 60, 230-400 mesh.

Characterization. NMR spectra for the characterization of compounds were recorded at room temperature on Varian or Bruker instruments 300 MHz (¹H) and at 75.4 MHz (¹³C). Chemical shifts (δ) are reported in ppm, using the residual solvent peak in CDCl₃ (δ_H = 7.26 and δ_C = 77.16 ppm) as internal reference, and coupling constants (*J*) are given in Hertz (Hz). Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, p: quintuplet, sex: sextet, dd: doublet of doublets, dt: doublet of triplets, td: triplet of doublets, tt: triplet of triplets, ddd: doublet of doublets of doublets, ddt: doublet of doublets of triplets, m: multiplet, b: broad, a: apparent), coupling constants and integration. Carbon multiplicities were assigned by DEPT experiments.

GC-MS spectra were recorded on an Agilent 6890N/5973 Network GC System, equipped with an HP-5MS column or a Thermo 1300GC instrument equipped with an MS 7000ISQ STDNOVPI MS detector, using Chromeleon software. Low-resolution electron impact mass spectra (EI-LRMS) were obtained at 70 eV on a mass spectrometer, and only the molecular ions and/or base peaks, as well as significant peaks in MS, are given.

High-resolution mass spectra (HRMS) were determined with a LC-MS system equipped with an Agilent 1260 Infinity Liquid Chromatography instrument and an Agilent 6545 Q-TOF Mass Spectrometer using ESI ion sources, as specified.

Melting points (m.p.) were measured on a Gallenkamp apparatus using open capillary tubes and are uncorrected.

Experimental details. Reactions were performed in common pyrex round bottom flasks or 10 mL microwave vials crimped on top with 20 mm Sil/PTFE Septa. When needed, pH values were determined by using pH indicator strips (pH 0-14 Universal indicator paper, Merck MColorpHaspt).

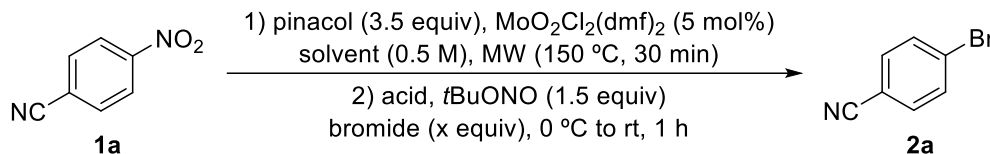
Microwave irradiation was realized with a CEM Discover S-Class Reactor with a single-mode microwave cavity producing continuous irradiation. Temperature measurements were conducted using an IR sensor located below the microwave cavity floor, and reaction times refer to the total hold time at the indicated temperature. The maximum wattage supplied was 220 W.

¹ R. Sanz, J. Escribano, R. Aguado, M. R. Pedrosa and F. J. Arnáiz, *Synthesis*, 2004, 1629–1632.

Synthesis of bromides 2:

Optimization of the reaction:

Table S1: Optimization of the one-pot sequential nitro reduction–diazotization–bromination of **1a**.^a

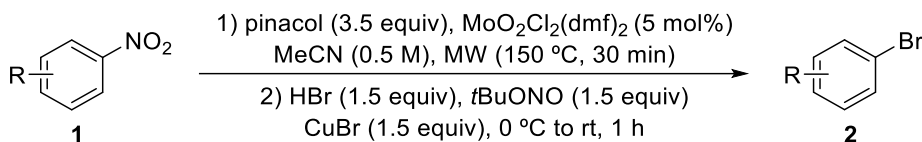


entry	acid (x equiv)	bromide (x equiv)	solvent	2a (%) ^b
1	PTSA (2)	KBr (1.5)	PhMe	– ^c
2	–	CuBr (1.5)	PhMe	– ^d
3	–	CuBr ₂ (1.5)	PhMe	56 ^e
4	–	CuBr ₂ (2)	PhMe	66 ^e
5	–	CuBr ₂ (1.5)	PhCF ₃	55
6	HBr (2)	CuBr (1.5)	MeCN	75
7	HBr (1.5)	CuBr (1.5)	MeCN	87 (82) ^f
8	–	CuBr (1.5)	MeCN	14
9	HBr (1.5)	CuBr (10 mol%)	MeCN	75
10	HBr (1.5)	–	MeCN	35
11 ^g	HBr (1.5)	–	MeCN	68

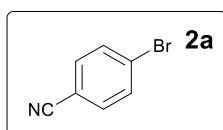
^a Reaction conditions: **1a** (1.0 mmol), under air. ^b Determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. ^c Decomposition was observed. ^d Unconverted 4-aminobenzonitrile was recovered. ^e An unidentified compound was detected. ^f Isolated yield. ^g Reaction time = 4 h.

Optimization of the reaction was carried out using 4-nitrobenzonitrile (**1a**) as model starting material (Table S1). First, toluene was chosen as solvent and a screen of different bromide salts was performed (entries 1–3). The use of potassium bromide led to decomposition (entry 1), while there was no conversion of the intermediate amine with copper(I) bromide (entry 2). The desired brominated product (**2a**) was only observed in the presence of copper(II) bromide along with an unidentified byproduct likely derived from a competitive reaction of the diazonium salt with toluene (entries 3 and 4). The results did not improve when using α,α,α -trifluorotoluene as solvent (entry 5). Gratifyingly, it was observed that the complementary use of copper(I) bromide and hydrobromic acid in acetonitrile led to a more efficient synthesis of **2a** that could be obtained in good yield and without need for further purification (entries 6 and 7). It was demonstrated that the presence of hydrobromic acid is crucial for the reaction (entry 8). We also checked that catalytic amounts of the copper salt could also be used resulting in slightly lower yields (entry 9). In the absence of copper(I) bromide a good yield was obtained only with longer reaction times (entry 11), while a low yield was obtained after 1 h (entry 10).

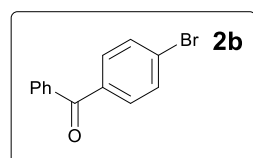
General procedure A:



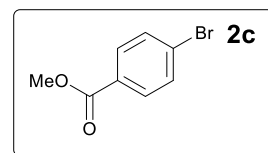
In a 10 mL reaction vessel, the corresponding nitroarene (1 equiv), anhydrous MeCN (0.5 M), pinacol (3.5 equiv) and MoO₂Cl₂(dmf)₂ (5 mol%) were mixed together. The vessel was sealed with a septum and the reaction mixture was stirred at 150 °C for 30 min under microwave irradiation. The mixture was then cooled to 0 °C and hydrobromic acid (48 wt.% in H₂O, 1.5 equiv), a previously prepared solution of *tert*-butylnitrite (1.5 equiv) in MeCN (1.5 M), and copper(I) bromide (1.5 equiv) were added. The reaction was stirred for 1 h from 0 °C to rt, then quenched with brine (5 mL) and extracted with Et₂O (3 × 10 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The product was either obtained pure or, when necessary, the residue was purified by silica gel flash column chromatography (hexane/EtOAc) to afford the bromides **2**.



4-Bromobenzonitrile (2a):² General procedure A was followed using 4-nitrobenzonitrile (**1a**) (148.1 mg, 1 mmol), pinacol (413.6 mg, 3.5 mmol), catalyst (17.3 mg, 0.05 mmol), HBr (170 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and CuBr (215.2 mg, 1.5 mmol). The product was obtained without the need for further purification as a white solid (150 mg, 82%); mp = 111–113 °C; ¹H NMR (300 MHz, (CD₃)₂CO): δ 7.74 (d, *J* = 8.6 Hz, 2H), 7.80 (d, *J* = 8.6 Hz, 2H) ppm; ¹³C{¹H} NMR (75.4 MHz, (CD₃)₂CO): δ 112.2 (C), 118.7 (C), 128.3 (C), 133.6 (2 × CH), 134.7 (2 × CH) ppm.



4-Bromobenzophenone (2b):³ General procedure A was followed using 4-nitrobenzophenone (**1b**) (227 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (170 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The product was obtained without the need for further purification as a white solid (237 mg, 91%); mp = 85–87 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.40–7.50 (m, 2H), 7.53–7.62 (m, 3H), 7.63–7.68 (m, 2H), 7.73–7.79 (m, 2H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 127.5 (C), 128.4 (2 × CH), 129.9 (2 × CH), 131.6 (2 × CH), 131.6 (2 × CH), 132.7 (CH), 136.3 (C), 137.2 (C), 195.5 (C) ppm.



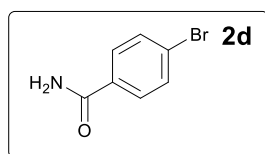
Methyl 4-bromobenzoate (2c):⁴ General procedure A was followed using methyl 4-nitrobenzoate (**1c**) (199 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (170 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The product was obtained without the need for further purification as a brown solid (204 mg, 95%); mp = 79–81 °C; ¹H NMR (300 MHz,

² Y.-T. Li, B.-S. Liao, H.-P. Chen and S.-T. Liu, *Synthesis*, 2011, 2639–2643. Commercially available [CAS: 623-00-7].

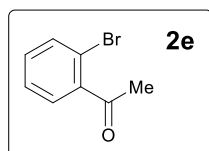
³ C. Jin, L. Zhang and W. Su, *Synlett*, 2011, 1435–1438. Commercially available [CAS: 90-90-4].

⁴ S.-I. Hirashima, T. Nobuta, N. Tad, T. Miura and A. Itoh, *Org. Lett.*, 2010, **12**, 3645–3647. Commercially available [CAS: 619-42-1].

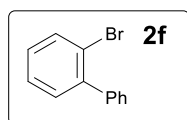
(CD₃)₂CO): δ 3.89 (s, 3H), 7.69 (d, J = 8.3 Hz, 2H), 7.91 (d, J = 8.3 Hz, 2H) ppm; ¹³C{¹H} NMR (75.4 MHz, (CD₃)₂CO): δ 52.6 (CH₃), 128.2 (C), 130.2 (C), 131.9 (2 × CH), 132.6 (2 × CH), 166.4 (C) ppm.



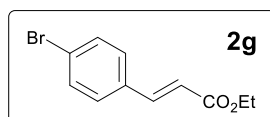
4-Bromobenzamide (2d):⁵ General procedure A was followed using 4-nitrobenzamide (**1d**) (166 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (170 μ L, 1.5 mmol), *t*BuONO (198 μ L, 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The product was obtained without the need for further purification as a white solid (186 mg, 93%); mp = 189–191 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 7.44 (bs, 1H), 7.66 (d, J = 8.6 Hz, 2H), 7.81 (d, J = 8.6 Hz, 2H), 8.03 (bs, 1H) ppm; ¹³C{¹H} NMR (75.4 MHz, DMSO-*d*₆): δ 124.9 (C), 129.5 (2 × CH), 131.2 (2 × CH), 133.4 (C), 166.9 (C) ppm.



2'-Bromoacetophenone (2e):⁶ General procedure A was followed using methyl 2'-nitroacetophenone (**1e**) (165 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (170 μ L, 1.5 mmol), *t*BuONO (198 μ L, 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The product was obtained without the need for further purification as a brownish liquid (189 mg, 95%); ¹H NMR (300 MHz, (CD₃)₂CO): δ 2.57 (s, 3H), 7.36–7.53 (m, 2H), 7.59 (d, J = 7.4 Hz, 1H), 7.68 (d, J = 7.5 Hz, 1H) ppm; ¹³C{¹H} NMR (75.4 MHz, (CD₃)₂CO): δ 30.3 (CH₃), 118.7 (C), 128.5 (CH), 129.7 (CH), 132.7 (CH), 134.4 (CH), 142.5 (C), 200.9 (C) ppm.



2-Bromobiphenyl (2f):⁷ General procedure A was followed using 2-nitrobiphenyl (**1f**) (199 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (170 μ L, 1.5 mmol), *t*BuONO (198 μ L, 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 50/1) affording pure **2f** as a colorless liquid (186 mg, 80%); R_f = 0.60 (hexane/EtOAc, 20/1); ¹H NMR (300 MHz, CDCl₃): δ 7.24–7.33 (m, 1H), 7.40–7.46 (m, 2H), 7.46–7.56 (m, 5H), 7.77 (d, J = 8.6 Hz, 1H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 122.8 (C), 127.5 (CH), 127.7 (CH), 128.1 (2 × CH), 128.8 (CH), 129.5 (2 × CH), 131.4 (CH), 133.2 (CH), 141.2 (C), 142.7 (C) ppm.



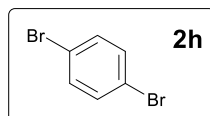
Ethyl 4-bromocinnamate (2g):⁸ General procedure A was followed using ethyl 4-nitrocinnamate (**1g**) (221 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (170 μ L, 1.5 mmol), *t*BuONO (198 μ L, 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 20/1 to 10/1) affording pure **2g** as a colorless liquid (171 mg, 67%); R_f = 0.25 (hexane/EtOAc, 20/1); ¹H NMR (300 MHz, CDCl₃): δ 1.32 (td, J = 7.0, 0.6 Hz, 3H), 4.25 (q, J = 7.2 Hz, 2H), 6.40 (dd, J = 16.0, 0.9 Hz, 1H), 7.32–7.38 (m, 2H), 7.44–7.53 (m, 2H), 7.59 (d, J = 16.0 Hz, 1H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 14.4 (CH₃), 60.7 (CH₂), 119.1 (CH), 124.5 (C), 129.5 (2 × CH), 132.2 (2 × CH), 133.5 (C), 143.2 (CH), 166.7 (C) ppm.

⁵ X.-Q. Li, W.-K. Wang, Y.-X. Han and C. Zhang, *Adv. Synth. Catal.*, 2010, **352**, 2588–2598. Commercially available [CAS: 698-67-9].

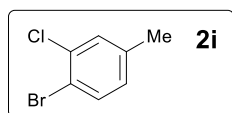
⁶ B. Scheiper, M. Bonnekesel, H. Krause and A. Fürstner, *J. Org. Chem.*, **2004**, **69**, 3943–3949. Commercially available [CAS: 2142-69-0].

⁷ A. S. Demir, H. Findik, N. Saygili and T. Subasi, *Tetrahedron*, 2010, **66**, 1308–1312. Commercially available [CAS: 2052-07-5].

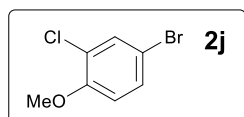
⁸ J. Lu and P. H. Toy, *Synlett*, 2011, 1723–1726. Commercially available [CAS: 24393-53-1].



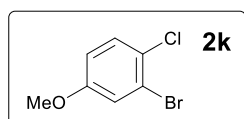
1,4-Dibromobenzene (2h):⁹ General procedure A was followed using ethyl 1-bromo-4-nitrobenzene (**1h**) (202 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (170 μ L, 1.5 mmol), *t*BuONO (198 μ L, 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 50/1) affording pure **2h** as a white solid (191 mg, 81%); R_f = 0.26 (hexane/EtOAc, 50/1); mp = 84–86 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.35 (s, 4H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 121.2 (2 \times C), 133.2 (4 \times CH) ppm.



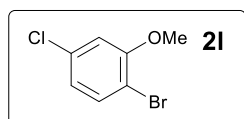
3-Chloro-4-bromotoluene (2i):¹⁰ General procedure A was followed using 3-chloro-4-nitrotoluene (**1i**) (172 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (170 μ L, 1.5 mmol), *t*BuONO (198 μ L, 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The product was obtained without the need for further purification as a brown liquid (144 mg, 70%); ^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$): δ 2.30 (s, 3H), 7.07 (dd, J = 8.1, 1.9 Hz, 1H), 7.37 (d, J = 1.9 Hz, 1H), 7.55 (d, J = 8.1 Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, $(\text{CD}_3)_2\text{CO}$): δ 19.8 (CH₃), 118.3 (C), 129.4 (CH), 130.9 (CH), 133.4 (C), 133.5 (CH), 139.6 (C) ppm.



4-Bromo-2-chloroanisole (2j):¹¹ General procedure A was followed using 2-chloro-4-nitroanisole (**1j**) (188 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (170 μ L, 1.5 mmol), *t*BuONO (198 μ L, 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 40/1 to 30/1) affording pure **2j** as a white solid (146 mg, 66%); R_f = 0.25 (hexane/EtOAc, 40/1); mp = 81–83 °C; ^1H NMR (300 MHz, CDCl_3): δ 3.87 (d, J = 1.1 Hz, 3H), 6.78 (dd, J = 8.7, 1.2 Hz, 1H), 7.32 (ddd, J = 8.7, 2.4, 1.1 Hz, 1H), 7.48 (dd, J = 2.4, 1.2 Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 56.3 (CH₃), 112.6 (C), 113.4 (CH), 123.7 (C), 130.6 (CH), 132.7 (CH), 154.4 (C) ppm.



3-Bromo-4-chloroanisole (2k):¹² General procedure A was followed using 4-chloro-3-nitroanisole (**1k**) (188 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (170 μ L, 1.5 mmol), *t*BuONO (198 μ L, 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 40/1) affording pure **2k** as a colorless liquid (173 mg, 78%); R_f = 0.21 (hexane/EtOAc, 40/1); ^1H NMR (300 MHz, CDCl_3): δ 3.77 (d, J = 5.3 Hz, 3H), 6.73–6.85 (m, 1H), 7.11–7.17 (m, 1H), 7.25–7.33 (m, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 55.9 (CH₃), 114.9 (C), 119.0 (CH), 122.7 (C), 126.0 (C), 130.6 (CH), 158.7 (CH) ppm.



2-Bromo-5-chloroanisole (2l):¹³ General procedure A was followed using 5-chloro-2-nitroanisole (**1l**) (188 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (170 μ L, 1.5 mmol), *t*BuONO (198 μ L, 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The obtained crude product was purified by flash column

⁹ T. Makino, R. Yamasaki and S. Saito, *Synthesis*, 2008, 859–864. Commercially available [CAS: 106-37-6].

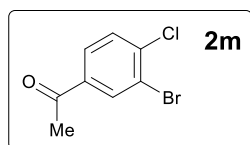
¹⁰ Commercially available [CAS: 6627-51-6].

¹¹ Commercially available [CAS: 50638-47-6].

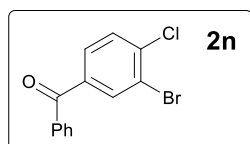
¹² Commercially available [CAS: 2732-80-1].

¹³ Commercially available [CAS: 174913-09-8].

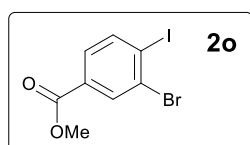
chromatography (hexane/EtOAc, 20/1) affording pure **2l** as a colorless oil (144 mg, 65%); $R_f = 0.28$ (hexane/EtOAc, 20/1); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 3.88 (d, $J = 1.4$ Hz, 3H), 6.79–6.85 (m, 1H), 6.86–6.89 (m, 1H), 7.44 (dd, $J = 8.3, 1.3$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 56.5 (CH_3), 109.9 (C), 112.7 (CH), 121.9 (CH), 133.9 (CH), 134.1 (C), 156.5 (C) ppm.



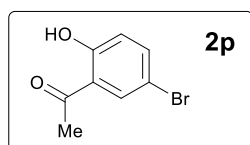
3-Bromo-4-chloroacetophenone (2m):¹⁴ General procedure A was followed using 4-chloro-3-nitroacetophenone (**1m**) (200 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (170 μL , 1.5 mmol), *t*BuONO (198 μL , 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The product was obtained without the need for further purification as a white solid (219 mg, 94%); mp = 80–82 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 2.61 (s, 3H), 7.69 (d, $J = 8.2$ Hz, 1H), 7.96 (dd, $J = 8.2, 1.8$ Hz, 1H), 8.23 (d, $J = 1.8$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 26.7 (CH_3), 123.0 (C), 129.4 (CH), 131.5 (CH), 134.1 (CH), 138.0 (C), 139.3 (C), 195.8 (C) ppm.



3-Bromo-4-chlorobenzophenone (2n): General procedure A was followed using 4-chloro-3-nitrobenzophenone (**1n**) (262 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (170 μL , 1.5 mmol), *t*BuONO (198 μL , 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 40/1 to 20/1) affording pure **2n** as a white solid (236 mg, 80%); $R_f = 0.14$ (hexane/EtOAc, 40/1); mp = 109–111 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.41–7.53 (m, 2H), 7.52 (d, $J = 8.3$ Hz, 1H), 7.53–7.65 (m, 1H), 7.64 (dd, $J = 8.3, 2.0$ Hz, 1H), 7.70–7.79 (m, 2H), 8.03 (d, $J = 2.0$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 122.7 (C), 128.5 (2 \times CH), 129.7 (CH), 129.9 (2 \times CH), 130.2 (CH), 132.9 (CH), 135.0 (CH), 136.6 (C), 137.2 (C), 138.8 (C), 193.8 (C) ppm; HRMS (ESI-TOF) calculated for $\text{C}_{13}\text{H}_9\text{BrClO}$ [$\text{M}+\text{H}$] $^+$ 294.9520, found 294.9508.



Methyl 3-bromo-4-iodobenzoate (2o):¹⁵ General procedure A was followed using methyl 4-iodo-3-nitrobenzoate (**1o**) (307 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (170 μL , 1.5 mmol), *t*BuONO (198 μL , 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 20/1) affording pure **2o** as a white solid (283 mg, 83%); $R_f = 0.32$ (hexane/EtOAc, 20/1); mp = 70–72 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 3.89 (s, 3H), 7.56 (dd, $J = 8.2, 2.0$ Hz, 1H), 7.89 (d, $J = 8.2$ Hz, 1H), 8.18 (d, $J = 2.0$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 52.6 (CH_3), 107.7 (C), 128.9 (CH), 130.0 (C), 131.5 (C), 133.3 (CH), 140.4 (CH), 165.2 (C) ppm.



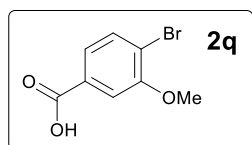
5'-Bromo-2'-hydroxyacetophenone (2p):¹⁶ General procedure A was followed using 2'-hydroxy-5'-nitroacetophenone (**1p**) (181 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (170 μL , 1.5 mmol), *t*BuONO (198 μL , 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 40/1 to 30/1) affording pure **2p** as a white solid

¹⁴ Commercially available [CAS: 54826-14-1].

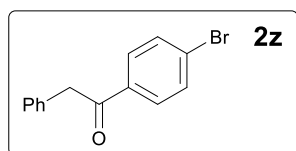
¹⁵ Commercially available [CAS: 249647-24-3].

¹⁶ Commercially available [CAS: 1450-75-5].

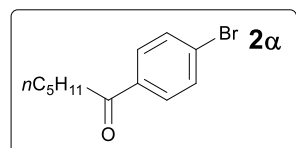
(144 mg, 67%); $R_f = 0.18$ (hexane/EtOAc, 40/1); mp = 60–62 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 2.59 (d, $J = 2.7$ Hz, 3H), 6.85 (dd, $J = 8.9, 3.8$ Hz, 1H), 7.50 (ddd, $J = 8.9, 3.7, 2.3$ Hz, 1H), 7.75–7.83 (m, 1H), 12.13 (d, $J = 2.3$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 26.7 (CH_3), 110.4 (C), 120.5 (CH), 120.9 (C), 132.9 (CH), 139.1 (CH), 161.3 (C), 203.6 (C) ppm.



4-Bromo-3-methoxybenzoic acid (2q):¹⁷ General procedure A was followed using 3-methoxy-4-nitrobenzoic acid (**1q**) (197 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (170 μL , 1.5 mmol), *t*BuONO (198 μL , 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The obtained crude product was purified by filtration with cold Et_2O and cold CH_2Cl_2 affording pure **2q** as an orange solid (203 mg, 88%); mp = 223–225 °C; $^1\text{H NMR}$ (300 MHz, $(\text{CD}_3)_2\text{CO}$): δ 3.92 (s, 3H), 7.46 (dd, $J = 8.2, 1.6$ Hz, 1H), 7.55 (d, $J = 1.6$ Hz, 1H), 7.72 (d, $J = 8.2$ Hz, 1H), 13.21 (bs, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, $(\text{CD}_3)_2\text{CO}$): δ 56.3 (CH_3), 112.7 (C), 116.0 (CH), 122.8 (CH), 131.0 (C), 133.2 (CH), 155.5 (C), 166.5 (C) ppm.



1-(4-Bromophenyl)-2-phenylethan-1-one (2z):¹⁸ General procedure A was followed using 1-(phenylethynyl)-4-nitrobenzene (**1z**) (223 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (81 μL , 1.5 mmol), *t*BuONO (198 μL , 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 20/1) affording pure **2z** as a white solid (203 mg, 74%); $R_f = 0.29$ (hexane/EtOAc, 20/1); mp = 115–117 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 4.27 (s, 2H), 7.25–7.39 (m, 5H), 7.51–7.72 (m, 2H), 7.82–8.05 (m, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 45.7 (CH_2), 127.2 (CH), 128.5 (C), 128.9 (2 \times CH), 129.5 (2 \times CH), 130.3 (2 \times CH), 132.1 (2 \times CH), 134.3 (C), 135.4 (C), 196.7 (C) ppm. Product is slightly contaminated with the corresponding chlorinated analogue **3z** due to trace amounts of chloride in the reaction media from the catalyst.

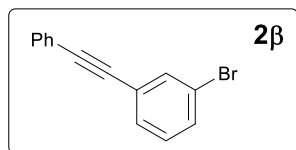


1-(4-Bromophenyl)hexan-1-one (2 α):¹⁹ General procedure A was followed using 1-(hex-1-yn-1-yl)-4-nitrobenzene (**1 α**) (203 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (81 μL , 1.5 mmol), *t*BuONO (198 μL , 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 20/1) affording pure **2 α** as a colourless oil (191 mg, 75%); $R_f = 0.35$ (hexane/EtOAc, 20/1); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 1.23–1.81 (m, 3H), 1.36–1.39 (m, 4H), 1.70–1.80 (m, 2H), 2.94 (t, $J = 7.4$ Hz, 2H), 7.59–7.64 (m, 2H), 7.82–7.86 (m, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 14.1 (CH_3), 22.6 (CH_2), 24.1 (CH_2), 31.6 (CH_2), 38.7 (CH_2), 128.1 (C), 129.7 (2 \times CH), 132.0 (2 \times CH), 135.9 (C), 199.6 (C) ppm. Product is slightly contaminated with the corresponding chlorinated analogue **3 α** due to trace amounts of chloride in the reaction media from the catalyst.

¹⁷ T.-H. Nguyen, T. T. Chau, A.-S. Castanet, K. P. P. Nguyen and J. Mortier, *Org. Lett.*, 2005, **7**, 2445–2448. Commercially available [CAS: 56256-14-5].

¹⁸ Y.-C. Wong, K. Parthasarathy and C.-H. Cheng, *Org. Lett.*, 2010, **12**, 1736–1739. Commercially available [CAS: 2001-29-8].

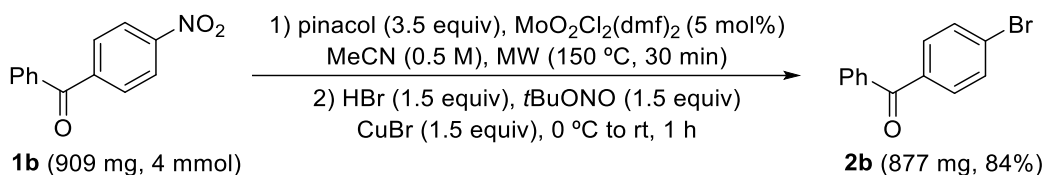
¹⁹ F. Rakotonradany, H. Fenniri, P. Rahimi, K. L. Gawrys, P. K. Kilpatrick and M. R. Gray, *Energy & Fuels*, 2006, **20**, 2439–2447. Commercially available [CAS: 7295-46-7].



1-Bromo-3-(phenylethynyl)benzene (2β):²⁰ General procedure A was followed using 1-(phenylethynyl)-3-nitrobenzene (**1β**) (223 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBr (81 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and CuBr (215 mg, 1.5 mmol). The obtained crude product

was purified by flash column chromatography (hexane/EtOAc, 20/1) affording pure **2β** as a yellowish oil (170 mg, 66%); $R_f = 0.37$ (hexane/EtOAc, 20/1); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.22 (t, $J = 7.9$ Hz, 1H), 7.36–7.39 (m, 3H), 7.46–7.49 (m, 2H), 7.53–7.57 (m, 2H), 7.71 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 87.9 (C), 90.8 (C), 122.3 (C), 122.9 (C), 125.4 (C), 128.5 (2 × CH), 128.8 (CH), 129.9 (CH), 130.3 (CH), 131.5 (CH), 131.8 (2 × CH), 134.4 (CH) ppm.

Gram scale synthesis of **2b**:



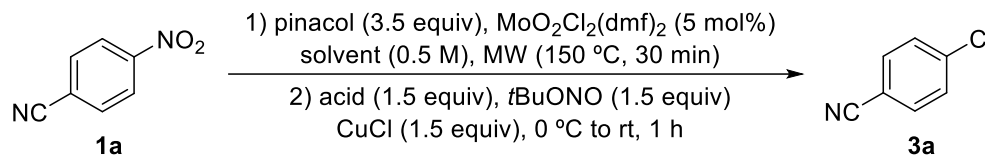
In a 35 mL reaction vessel, 4-nitrobenzophenone (**1b**) (909 mg, 4 mmol), anhydrous MeCN (8 mL), pinacol (1.655 g, 14 mmol) and $\text{MoO}_2\text{Cl}_2(\text{dmf})_2$ (69 mg, 5 mol%) were mixed together. The vessel was sealed with a septum and the reaction mixture was stirred at 150 °C for 30 min under microwave irradiation. The mixture was then cooled to 0 °C and hydrobromic acid (48 wt.% in H_2O , 0.67 mL, 6 mmol), a previously prepared solution of *tert*-butylnitrite (618 mg, 6 mmol) in MeCN (4 mL), and copper(I) bromide (861 mg, 6 mmol) were added. The reaction was stirred for 1 h from 0 °C to rt, then quenched with brine (15 mL) and extracted with Et_2O (3 × 15 mL). The organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 10/1) affording pure **2b** as a white solid (877 mg, 84%).

²⁰ G. Hamasaka, D. Roy, A. Tazawa and Y. Uozumi, *ACS Catal.*, 2019, **9**, 11640–11646.

Synthesis of chlorides 3:

Optimization of the reaction:

Table S2: Optimization of the one-pot sequential nitro reduction–diazotization–chlorination of **1a**.^a

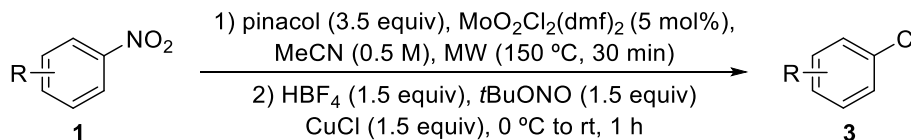


entry	acid	3a (%) ^b
1	HCl	68
2	HBr	11 ^c
3	H ₂ SO ₄	30
4	HOAc	<5 ^d
5	HBF ₄	84 (80) ^e
6 ^f	HCl	10 ^d

^a Reaction conditions: **1a** (1.0 mmol), under air. ^b Determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. ^c A 63% of the bromide **2a** was obtained. ^d Decomposition was observed. ^e Isolated yield. ^f Conducted with CuCl (10 mol%).

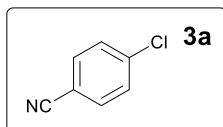
Starting from analogous conditions to the bromination reaction (MeCN as solvent and CuCl as salt), a screen of several acids was performed using model starting material **1a** (Table S2). Hydrochloric acid proved to be efficient to help promote this transformation leading to a good yield of the corresponding chloride **3a** (entry 1). However, hydrobromic acid was unsuitable as the bromination reaction was favored obtaining a 63% yield of the undesired bromide **2a** (entry 2). Both sulfuric acid and acetic acid resulted in lower yield or only traces of the desired product along with decomposition (entries 3 and 4, respectively). Gratifyingly, pure 4-chlorobenzonitrile (**3a**) was obtained in 80% isolated yield when tetrafluoroboric acid was employed without the need for further purification (entry 5). It was also checked that catalytic amounts of the copper(I) chloride led to lower yields of the desired product along with decomposition (entry 6).

General procedure B:

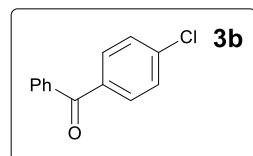


In a 10 mL reaction vessel, the corresponding nitroarene (1 equiv), anhydrous MeCN (0.5 M), pinacol (3.5 equiv) and MoO₂Cl₂(dmf)₂ (5 mol%) were mixed together. The vessel was sealed with a septum and the reaction mixture was stirred at 150 °C for 30 min under microwave irradiation. The mixture was then cooled to 0 °C and tetrafluoroboric acid (48 wt.% in H₂O, 1.5 equiv), a previously prepared solution of *tert*-butylnitrite (1.5 equiv) in MeCN (1.5 M), and copper(I) chloride (1.5 equiv) were added. The reaction was

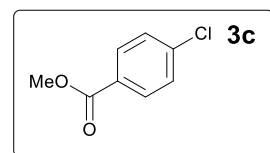
stirred for 1 h from 0 °C to rt, then quenched with brine (5 mL) and extracted with Et₂O (3 × 10 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The product was either obtained pure or, when necessary, the residue was purified by silica gel flash column chromatography (hexane/EtOAc) to afford the chlorides **3**.



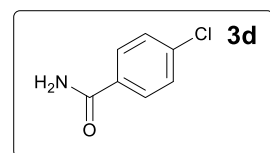
4-Chlorobenzonitrile (3a):²¹ General procedure B was followed using 4-nitrobenzonitrile (**1a**) (148 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and CuCl (148.5 mg, 1.5 mmol). The product was obtained without the need for further purification as a brown solid (110 mg, 80%); mp = 83–85 °C; ¹H NMR (300 MHz, (CD₃)₂CO): δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 2H) ppm; ¹³C{¹H} NMR (75.4 MHz, (CD₃)₂CO): δ 111.8 (C), 118.5 (C), 130.6 (2 × CH), 134.7 (2 × CH), 139.7 (C) ppm.



4-Chlorobenzophenone (3b):²² General procedure B was followed using 4-nitrobenzophenone (**1b**) (227 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and CuCl (148.5 mg, 1.5 mmol). The product was obtained without the need for further purification as a white solid (191 mg, 88%); mp = 75–77 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.41–7.53 (m, 4H), 7.55–7.63 (m, 1H), 7.71–7.82 (m, 4H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 128.5 (2 × CH), 128.7 (2 × CH), 130.0 (2 × CH), 131.5 (2 × CH), 132.7 (CH), 136.0 (C), 137.3 (C), 139.0 (C), 195.5 (C) ppm.



Methyl 4-chlorobenzoate (3c):²³ General procedure B was followed using methyl 4-nitrobenzoate (**1c**) (199 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and CuCl (148.5 mg, 1.5 mmol). The product was obtained without the need for further purification as a white solid (147 mg, 86%); mp = 41–43 °C; ¹H NMR (300 MHz, (CD₃)₂CO): δ 3.91 (s, 3H), 7.36–7.45 (m, 2H), 7.92–8.00 (m, 2H) ppm; ¹³C{¹H} NMR (75.4 MHz, (CD₃)₂CO): δ 52.4 (CH₃), 128.7 (C), 128.9 (2 × CH), 131.1 (2 × CH), 139.5 (C), 166.4 (C) ppm.



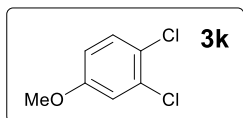
4-Chlorobenzamide (3d):²⁴ General procedure B was followed using 4-nitrobenzamide (**1d**) (166 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and CuCl (148.5 mg, 1.5 mmol). The product was obtained without the need for further purification as a white solid (127.5 mg, 82%); mp = 172–174 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ 7.45–7.56 (m, 3H), 7.89–7.94 (m, 2H), 8.08 (bs, 1H) ppm; ¹³C{¹H} NMR (75.4 MHz, DMSO-*d*₆): δ 128.3 (2 × CH), 129.5 (2 × CH), 133.1 (C), 136.2 (C), 167.0 (C) ppm.

²¹ S. Enthaler, *Chem. Eur. J.*, 2011, **17**, 9316–9319. Commercially available [CAS: 623-03-0].

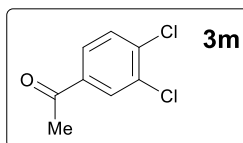
²² C. Jin, L. Zhang and W. Su, *Synlett*, **2011**, 1435–1438. Commercially available [CAS: 134-85-0].

²³ Y. B. Kiran, R. Ikeda, N. Sakai and T. Konakahara, *Synthesis*, 2010, 276–282. Commercially available [CAS: 1126-46-1].

²⁴ S. K. Sharma, S. D. Bishopp, C. L. Allen, R. Lawrence, M. J. Bamford, A. A. Lapkin, P. Plucinski, R. J. Watson and J. M. J. Williams, *Tetrahedron Lett.*, 2011, **52**, 4252–4255. Commercially available [CAS: 619-56-7].

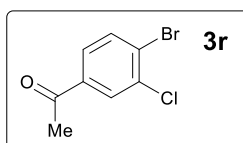


3,4-Dichloroanisole (3k):²⁵ General procedure B was followed using 4-chloro-3-nitroanisole (**1k**) (188 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and CuCl (148.5 mg, 1.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 50/1 to 30/1) affording pure **3k** as a colorless liquid (119 mg, 67%); *R*_f = 0.30 (hexane/EtOAc, 30/1); ¹H NMR (300 MHz, CDCl₃): δ 3.78 (s, 3H), 6.75 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.99 (d, *J* = 2.9 Hz, 1H), 7.31 (d, *J* = 8.9 Hz, 1H) ppm; ¹³C {¹H} NMR (75.4 MHz, CDCl₃): δ 55.9 (CH₃), 114.2 (CH), 115.8 (CH), 124.0 (C), 130.8 (CH), 133.0 (C), 158.8 (C) ppm.



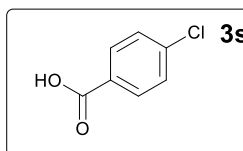
3,4-Dichloroacetophenone (3m):²⁶ General procedure A was followed using 4-chloro-3-nitroacetophenone (**1m**) (200 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and CuCl (148.5 mg, 1.5 mmol). The obtained crude product was purified

by flash column chromatography (hexane/EtOAc, 60/1 to 50/1) affording pure **3m** as a pale brown solid (151 mg, 80%); *R*_f = 0.34 (hexane/EtOAc, 50/1); mp = 73–75 °C; ¹H NMR (300 MHz, CDCl₃): δ 2.55 (s, 3H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.73 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.97 (d, *J* = 2.0 Hz, 1H) ppm; ¹³C {¹H} NMR (75.4 MHz, CDCl₃): δ 26.6 (CH₃), 127.4 (CH), 130.3 (CH), 130.8 (CH), 133.3 (C), 136.6 (C), 137.7 (C), 195.7 (C) ppm.



4'-Bromo-3'-chloroacetophenone (3r):²⁷ General procedure B was followed using 4'-bromo-3'-nitroacetophenone (**1r**) (244 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and CuCl (148.5 mg, 1.5 mmol). The obtained crude product was purified

by flash column chromatography (hexane/EtOAc, 20/1 to 10/1) affording pure **3r** as a white solid (184 mg, 79%); *R*_f = 0.33 (hexane/EtOAc, 7/1); mp = 82–84 °C; ¹H NMR (300 MHz, CDCl₃): δ 2.57 (s, 3H), 7.61–7.67 (m, 1H), 7.67–7.73 (m, 1H) 7.95–7.99 (m, 1H) ppm; ¹³C {¹H} NMR (75.4 MHz, CDCl₃): δ 26.5 (CH₃), 127.4 (CH), 128.1 (C), 130.0 (CH), 134.0 (CH), 135.2 (C), 137.2 (C), 195.8 (C) ppm.



4-Chlorobenzoic acid (3s):²⁸ General procedure B was followed using 4-nitrobenzoic acid (**1s**) (167 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and CuCl (148.5 mg, 1.5 mmol). The product was obtained without the need for further purification as a white solid (122 mg, 78%); mp = 238–240 °C; ¹H NMR (300

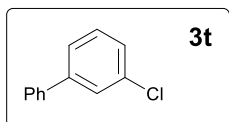
MHz, DMSO-*d*₆): δ 7.56 (d, *J* = 8.5 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 2H), 13.17 (s, 1H) ppm; ¹³C {¹H} NMR (75.4 MHz, DMSO-*d*₆): δ 128.7 (2 × CH), 129.6 (C), 131.1 (2 × CH), 137.8 (C), 166.5 (C) ppm.

²⁵ Commercially available [CAS: 36404-30-5].

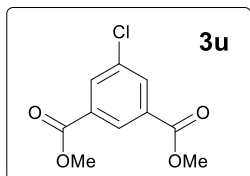
²⁶ Commercially available [CAS: 2642-63-9].

²⁷ Commercially available [CAS: 3114-31-6].

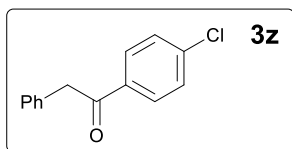
²⁸ K. Alagiri and K. R. Prabhu, *Tetrahedron*, **2011**, *67*, 6544–8551. Commercially available [CAS: 74-11-3].



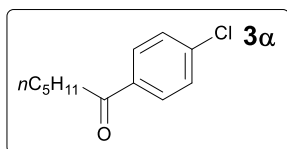
3-Chlorobiphenyl (3t):²⁹ General procedure B was followed using 3-nitrobiphenyl (**1t**) (199 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and CuCl (148.5 mg, 1.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 100/1) affording pure **3t** as a colorless liquid (141 mg, 75%); *R*_f = 0.57 (hexane/EtOAc, 40/1); ¹H NMR (300 MHz, CDCl₃): δ 7.31–7.43 (m, 3H), 7.44–7.52 (m, 3H), 7.57–7.64 (m, 3H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 125.4 (CH), 127.2 (2 × CH), 127.4 (CH), 127.4 (CH), 128.0 (CH), 129.0 (2 × CH), 130.1 (CH), 134.8 (C), 139.9 (C), 143.2 (C) ppm.



Dimethyl 5-chloroisophthalate (3u):³⁰ General procedure B was followed using dimethyl 5-nitroisophthalate (**1u**) (239 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and CuCl (148.5 mg, 1.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 4/1) affording pure **3u** as a white solid (160 mg, 70%); *R*_f = 0.33 (hexane/EtOAc, 5/1); mp = 79–81 °C; ¹H NMR (300 MHz, CDCl₃): δ 3.91 (s, 6H), 8.09 (d, *J* = 1.5 Hz, 2H), 8.45 (t, *J* = 1.5 Hz, 1H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 52.6 (2 × CH₃), 128.7 (CH), 132.1 (2 × C), 133.6 (2 × CH), 134.9 (C), 164.9 (2 × C) ppm.



1-(4-Chlorophenyl)-2-phenylethan-1-one (3z):³¹ General procedure B was followed using 1-(phenylethynyl)-4-nitrobenzene (**1z**) (223 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and CuCl (148.5 mg, 1.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 20/1 to 15/1) affording pure **3z** as a white solid (166 mg, 72%); *R*_f = 0.23 (hexane/EtOAc, 15/1); mp = 104–106 °C; ¹H NMR (300 MHz, CDCl₃): δ 4.28 (s, 2H), 7.25–7.32 (m, 3H), 7.33–7.40 (m, 2H), 7.42–7.48 (m, 2H), 7.94–8.01 (m, 2H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 45.6 (CH₂), 127.1 (CH), 128.9 (2 × CH), 129.0 (2 × CH), 129.5 (2 × CH), 130.1 (2 × CH), 134.3 (C), 134.9 (C), 139.7 (C), 196.5 (C) ppm.



1-(4-Chlorophenyl)hexan-1-one (3α):³² General procedure B was followed using 1-(hex-1-yn-1-yl)-4-nitrobenzene (**1α**) (203 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and CuCl (148.5 mg, 1.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 15/1) affording pure **3α** as a white solid (145 mg, 69%); *R*_f = 0.45 (hexane/EtOAc, 10/1); mp = 91–93 °C; ¹H NMR (300 MHz, CDCl₃): δ 0.78–1.04 (m, 3H), 1.22–1.45 (m, 4H), 1.65–1.77 (m, 2H), 2.77–3.18 (m, 2H), 7.38–7.45 (m, 2H), 7.85–7.92 (m, 2H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 14.1 (CH₃), 22.6 (CH₂), 24.1 (CH₂), 31.6 (CH₂), 38.7 (CH₂), 100.8 (C), 129.0 (2 × CH), 129.6 (2 × CH), 135.5 (C), 139.4 (C), 199.6 (C) ppm.

²⁹ J. L. Bolliger and C. M. Frech, *Adv. Synth. Catal.*, 2010, **352**, 1075–1080.

³⁰ Commercially available [CAS: 20330-90-0].

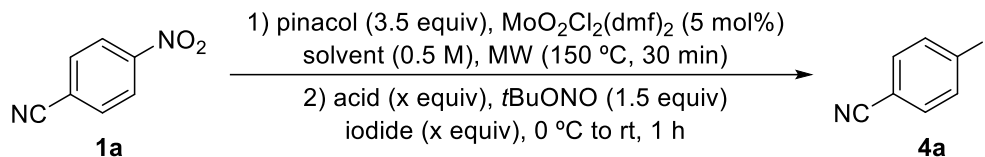
³¹ Z.-L. Shen, X.-P. Xua and S.-J. Ji, *J. Org. Chem.*, 2010, **75**, 1162–1167. Commercially available [CAS: 1889-71-0].

³² J. Ruan, O. Saidi, J. A. Iggo and J. Xiao, *J. Am. Chem. Soc.*, 2008, **130**, 10510–10511. Commercially available [CAS: 7295-50-3].

Synthesis of iodides 4:

Optimization of the reaction:

Table S3: Optimization of the one-pot sequential nitro reduction-diazotization-iodination of **1a**.^a



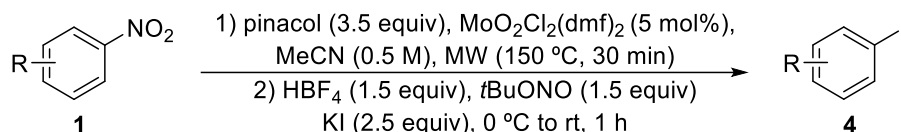
entry	acid (x equiv)	iodide (x equiv)	solvent	2a (%) ^b
1 ^c	PTSA (2)	KI (2.5)	PhMe	72
2 ^c	PTSA (2)	KI (2.5)	PhMe + MeCN	73
3	PTSA (1.5)	KI (2.5)	PhMe	57 ^d
4	PTSA (2)	KI (2.5)	PhMe	76 ^d
5	PTSA (2)	KI (2.5)	PhMe	71 ^{d,e}
6 ^f	PTSA (2)	KI (2.5)	PhMe	56 ^{d,e}
7	ascorbic acid (10 mol%)	KI (2.5)	PhMe	– ^e
8 ^f	–	KI (2.5)	MeCN	28 ^{d,e}
9	HI (1.5)	KI (2.5)	MeCN	40 ^d
10	HBr (1.5)	KI (2.5)	MeCN	63 ^g
11	HBF ₄ (1.5)	KI (2.5)	MeCN	92 (89) ^h
12	HBF ₄ (1.5)	KI (1.5)	MeCN	83
13	PTSA (1.5)	KI (2.5)	MeCN	43 ^e
14	–	CuI (1.5)	MeCN	28 ^e
15	HBF ₄ (1.5)	CuI (1.5)	MeCN	83

^a Reaction conditions: **1a** (1.0 mmol), under air. ^b Determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. ^c Performed using 2.0 equiv of *t*-BuONO. ^d An unidentified product was detected. ^e Unconverted intermediate 4-aminobenzotrile was detected. ^f Performed using 1.1 equiv of *t*-BuONO. ^g ~19% of 4-bromobenzotrile (**2a**) was also generated. ^h Isolated yield.

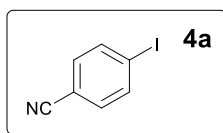
Initially, the employment of PTSA as acid, KI as iodide source and toluene as solvent along with two equivalents of the nitrite, led to the formation of the desired product **4a** in good yield (entry 1). Using MeCN as co-solvent to increase polarity of the reaction media did not have an effect in the outcome of the reaction (entry 2). It was checked that a lower amount of the acid led to lower yield of **4a** and the formation of small amounts of an unidentified compound (entry 3), while only 1.5 equiv of *t*BuONO were necessary (entry 4). On the other hand, further decreasing the amount of KI and nitrite resulted in no complete conversion and lower yields (entries 5 and 6). Catalytic amounts of ascorbic acid were used to try and promote the reaction, but the desired product was not observed as the intermediate amine was not converted (entry 7). A common problem of all the previous essays performed in toluene was the presence of an undesired byproduct, likely as a result of a secondary reaction of the in-situ formed diazonium salt and the

solvent. Therefore, acetonitrile was again selected as solvent and a screen of different acids was performed (entries 8–13). It was demonstrated that the presence of acid is necessary to achieve good results, as intermediate amine (20%) was recovered, and a different unidentified byproduct was formed (21%) (entry 8). The use of HI was unsuitable leading to a low yield of **4a** and an undesired byproduct (entry 9). Hydrobromic acid promote the reaction, but led to the competitive formation of 4-bromobenzonitrile (**2a**) (entry 10). The best yield was obtained when HBF₄ was employed (entry 11). Lowering the amount of KI to 1.5 equiv led to a slightly lower yield (entry 12). The combined use of PTSA as acid and MeCN as solvent resulted in low yields of the final iodide and a ~35% yield of unconverted amine (entry 13). It was also checked that the use of CuI instead of KI did not lead to improved yields neither in the absence (with still 26% of unconverted aniline) nor in the presence of acid (entries 14 and 15).

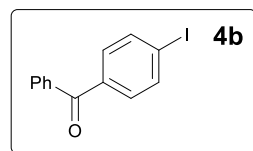
General procedure C:



In a 10 mL reaction vessel, the corresponding nitroarene (1 equiv), anhydrous MeCN (0.5 M), pinacol (3.5 equiv) and MoO₂Cl₂(dmf)₂ (5 mol%) were mixed together. The vessel was sealed with a septum and the reaction mixture was stirred at 150 °C for 30 min under microwave irradiation. The mixture was then cooled to 0 °C and HBF₄ (48 wt.% in H₂O, 1.5 equiv), a previously prepared solution of *t*BuONO (1.5 equiv) in MeCN (1.5 M), and KI (2.5 equiv) were added. The reaction was stirred for 1 h from 0 °C to rt, then quenched with brine (5 mL) and extracted with Et₂O (3 × 10 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The product was either obtained pure or, when necessary, the residue was purified by silica gel flash column chromatography (hexane/EtOAc) to afford the iodides **4**.



4-Iodobenzonitrile (4a):³³ General procedure C was followed using 4-nitrobenzonitrile (**1a**) (148 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and KI (415 mg, 2.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 15/1 to 5/1) affording pure **4a** as a white solid (204 mg, 89%); *R*_f = 0.39 (hexane/EtOAc, 5/1); mp = 122–124 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.32–7.40 (m, 2H), 7.80–7.88 (m, 2H) ppm; ¹³C {¹H} NMR (75.4 MHz, CDCl₃): δ 100.4 (C), 111.9 (C), 118.3 (C), 133.3 (2 × CH), 138.6 (2 × CH) ppm.

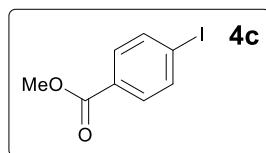


4-Iodobenzophenone (4b):³⁴ General procedure C was followed using 4-nitrobenzophenone (**1b**) (227 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and KI (415 mg, 2.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 20/1 to 5/1) affording pure **4b** as a white solid

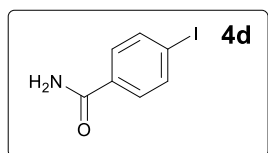
³³ W. Zhou, J. Xu, L. Zhang and N. Jiao, *Org. Lett.*, 2010, **12**, 2888–2891. Commercially available [CAS: 3058-39-7].

³⁴ H. Kim, A. Nagaki and J.-I. Yoshida, *Nat. Comm.*, 2011, **2**:264, doi: 10-1038/ncomms1264.

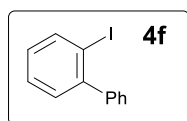
(287 mg, 93%); R_f = 0.28 (hexane/EtOAc, 2071); mp = 100–102 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.45–7.55 (m, 4H), 7.57–7.63 (m, 1H), 7.75–7.80 (m, 2H), 7.82–7.90 (m, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 100.1 (C), 128.4 (2 \times CH), 130.0 (2 \times CH), 131.5 (2 \times CH), 132.7 (CH), 136.9 (C), 137.1 (C), 137.6 (2 \times CH), 195.9 (C) ppm.



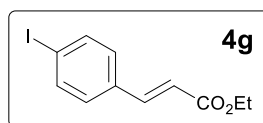
Methyl 4-iodobenzoate (4c):³⁵ General procedure C was followed using methyl 4-nitrobenzoate (**1c**) (199 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF_4 (196 μL , 1.5 mmol), $t\text{BuONO}$ (198 μL , 1.5 mmol) and KI (415 mg, 2.5 mmol). The product was obtained without the need for further purification as a white solid (238 mg, 91%); mp = 110–112 °C; ^1H NMR (300 MHz, CDCl_3): δ 3.89 (s, 3H), 7.68–7.74 (m, 2H), 7.75–7.80 (m, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 52.3 (CH_3), 100.8 (C), 129.6 (C), 131.0 (2 \times CH), 137.7 (2 \times CH), 166.5 (C) ppm.



4-Iodobenzamide (4d):³⁶ General procedure C was followed using 4-nitrobenzamide (**1d**) (166 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF_4 (196 μL , 1.5 mmol), $t\text{BuONO}$ (198 μL , 1.5 mmol) and KI (415 mg, 2.5 mmol). The product was obtained without the need for further purification as a white solid (225 mg, 91%); mp = 214–216 °C; ^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ 7.45 (bs, 1H), 7.66 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 8.04 (bs, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, $\text{DMSO}-d_6$): δ 98.9 (C), 129.5 (2 \times CH), 133.7 (C), 137.1 (2 \times CH), 167.3 (C) ppm.



2-Iodobiphenyl (4f):³⁷ General procedure C was followed using methyl 2-nitrophenyl (**1f**) (199 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF_4 (196 μL , 1.5 mmol), $t\text{BuONO}$ (198 μL , 1.5 mmol) and KI (415 mg, 2.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 25/1 to 10/1) affording pure **4f** as a colorless liquid (252 mg, 90%); R_f = 0.68 (hexane/EtOAc, 7/1); ^1H NMR (300 MHz, CDCl_3): δ 7.03–7.10 (m, 1H), 7.32–7.43 (m, 4H), 7.44–7.52 (m, 3H), 8.00 (ddd, J = 7.9, 1.3, 0.4 Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 98.8 (C), 127.7 (CH), 128.1 (2 \times CH), 128.2 (CH), 128.9 (CH), 129.4 (2 \times CH), 130.2 (CH), 139.6 (CH), 144.3 (C), 146.7 (C) ppm.

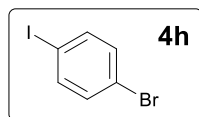


Ethyl 4-iodocinnamate (4g): General procedure C was followed using ethyl 4-nitrocinnamate (**1g**) (221 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF_4 (196 μL , 1.5 mmol), $t\text{BuONO}$ (198 μL , 1.5 mmol) and KI (415 mg, 2.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 2/1 to 1/2) affording pure **4g** as a yellow solid (242 mg, 80%); R_f = 0.37 (hexane/EtOAc, 1/1); mp = 32–34 °C; ^1H NMR (300 MHz, CDCl_3): δ 1.33 (t, J = 7.1 Hz, 3H), 4.26 (q, J = 7.1 Hz, 2H), 6.43 (d, J = 16.0 Hz, 1H), 7.20–7.27 (m, 2H), 7.58 (d, J = 16.0 Hz, 1H), 7.67–7.74 (m, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 14.3 (CH_3), 60.6 (CH_2), 96.4 (C), 119.1 (CH), 129.5 (2 \times CH), 133.9 (C), 138.1 (2 \times CH), 143.3 (CH), 166.7 (C) ppm; HRMS (ESI-TOF) calculated for $\text{C}_{11}\text{H}_{11}\text{IO}_2$ [$\text{M}+\text{H}$] $^+$ 302.9877, found 302.9871.

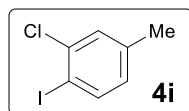
³⁵ H. Yang, Y. Li, M. Jiang, J. Wang and H. Fu, *Chem. Eur. J.*, 2011, **17**, 5652–5660. Commercially available [CAS: 619-44-3].

³⁶ Commercially available [CAS: 3956-07-8].

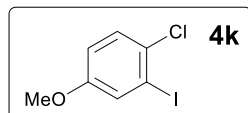
³⁷ I. Bonnaventure and A. B. Charette, *J. Org. Chem.*, 2008, **73**, 6330–6340. Commercially available [CAS: 2113-51-1].



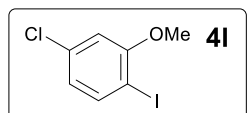
1-Bromo-4-iodobenzene (4h):³⁸ General procedure C was followed using 1-bromo-4-nitrobenzene (**1h**) (202 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and KI (415 mg, 2.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 70/1) affording pure **4h** as a white solid (226 mg, 80%); *R*_f = 0.36 (hexane/EtOAc, 50/1); mp = 90–92 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.21–7.27 (m, 2H), 7.52–7.59 (m, 2H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 92.2 (C), 122.3 (C), 133.2 (2 × CH), 139.1 (2 × CH) ppm.



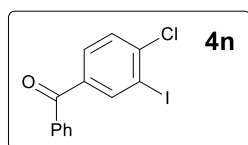
3-Chloro-4-iodotoluene (4i):³⁹ General procedure C was followed using 3-chloro-4-nitrotoluene (**1i**) (172 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and KI (415 mg, 2.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 60/1) affording pure **4i** as a colorless liquid (227 mg, 90%); *R*_f = 0.62 (hexane/EtOAc, 40/1); ¹H NMR (300 MHz, CDCl₃): δ 2.31 (s, 3H), 6.75–6.82 (m, 1H), 7.27–7.32 (m, 1H), 7.72 (d, *J* = 8.1 Hz, 1H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 20.9 (CH₃), 93.9 (C), 129.1 (CH), 130.2 (CH), 138.2 (C), 139.9 (CH), 140.0 (C) ppm.



4-Chloro-3-iodoanisole (4k):⁴⁰ General procedure C was followed using 4-chloro-3-nitroanisole (**1k**) (188 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and KI (415 mg, 2.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 7/1 to 3/1) affording pure **4k** as a yellow liquid (196 mg, 73%); *R*_f = 0.36 (hexane/EtOAc, 3/1); ¹H NMR (300 MHz, CDCl₃): δ 3.77 (s, 3H), 6.83 (dd, *J* = 8.8, 2.9 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.37 (d, *J* = 2.9 Hz, 1H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 55.8 (CH₃), 98.1 (C), 115.9 (CH), 125.2 (CH), 129.4 (CH), 130.1 (C), 158.3 (C) ppm.



2-Iodo-5-chloroanisole (4l):⁴¹ General procedure C was followed using 5-chloro-2-nitroanisole (**1l**) (188 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and KI (415 mg, 2.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/DCM, 2/1) affording pure **4l** as a yellow liquid (204 mg, 76%); *R*_f = 0.69 (hexane/DCM, 1/1); ¹H NMR (300 MHz, CDCl₃): δ 3.86 (s, 3H), 6.71 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.79 (d, *J* = 2.2 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 56.6 (CH₃), 83.4 (C), 111.7 (CH), 122.6 (CH), 135.3 (C), 139.8 (CH), 158.7 (C) ppm.



4-Chloro-3-iodobenzophenone (4n): General procedure C was followed using 4-chloro-3-nitrobenzophenone (**1n**) (262 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μL, 1.5 mmol), *t*BuONO (198 μL, 1.5 mmol) and KI (415 mg, 2.5 mmol). The product was obtained without the need for further purification as an off white solid (322 mg, 94%); mp = 102–104 °C; ¹H NMR (300 MHz, CDCl₃):

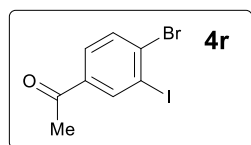
³⁸ R. S. da Ribeiro, P. M. Esteves and M. C. S. de Mattos, *Synthesis*, 2011, 739–744. Commercially available [CAS: 589-87-7].

³⁹ C.-G. Dong and Q.-S. Hu, *Tetrahedron*, 2008, **64**, 2537–2552. Commercially available [CAS: 116632-42-9].

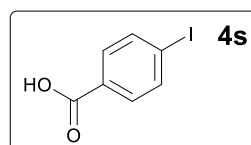
⁴⁰ Commercially available [CAS: 2401-25-4].

⁴¹ C.-Y. Zhou, J. Li, S. Peddibhotla and D. Romo, *Org. Lett.*, 2010, **12**, 2104–2107. Commercially available [CAS: 755027-21-5].

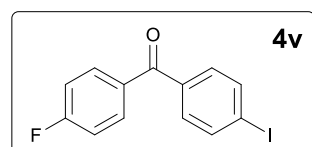
δ 7.43–7.55 (m, 3H), 7.56–7.63 (m, 1H), 7.68 (dd, $J = 8.3, 2.0$ Hz, 1H), 7.71–7.78 (m, 2H), 8.26 (d, $J = 2.0$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 98.2 (C), 128.6 (2 \times CH), 129.1 (CH), 129.9 (2 \times CH), 130.8 (CH), 133.0 (CH), 136.7 (C), 137.1 (C), 141.5 (CH), 142.9 (C), 193.9 (C) ppm; HRMS (ESI-TOF) calculated for $\text{C}_{13}\text{H}_9\text{ClIO}$ $[\text{M}+\text{H}]^+$ 342.9381, found 342.9371.



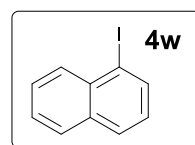
4'-Bromo-3'-iodoacetophenone (4r):⁴² General procedure C was followed using 4'-bromo-3'-nitroacetophenone (**1r**) (244 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF_4 (196 μL , 1.5 mmol), $t\text{BuONO}$ (198 μL , 1.5 mmol) and KI (415 mg, 2.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 10/1 to 5/1) affording pure **4r** as a white solid (247 mg, 76%); $R_f = 0.21$ (hexane:EtOAc, 15:1); mp = 80–82 $^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3): δ 2.56 (s, $J = 0.7$ Hz, 3H), 7.69 (d, $J = 8.3$ Hz, 1H), 7.74 (dd, $J = 8.3, 2.0$ Hz, 1H), 8.37 (d, $J = 2.0$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 26.6 (CH_3), 101.7 (C), 128.9 (CH), 132.9 (CH), 135.5 (C), 136.9 (C), 140.1 (CH), 195.7 (C) ppm.



4-Iodobenzoic acid (4s):⁴³ General procedure C was followed using 4-nitrobenzoic acid (**1s**) (167 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF_4 (196 μL , 1.5 mmol), $t\text{BuONO}$ (198 μL , 1.5 mmol) and KI (415 mg, 2.5 mmol). The product was obtained without the need for further purification as a white solid (199 mg, 80%); mp = 267–269 $^\circ\text{C}$; ^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ 7.65–7.71 (m, 2H), 7.83–7.89 (m, 2H), 13.10 (bs, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, $\text{DMSO}-d_6$): δ 101.2 (C), 130.3 (C), 131.1 (2 \times CH), 137.6 (2 \times CH), 166.9 (C) ppm.



4-Fluoro-4'-iodobenzophenone (4v):⁴⁴ General procedure C was followed using 4-fluoro-4'-nitrobenzophenone (**1v**) (245 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF_4 (196 μL , 1.5 mmol), $t\text{BuONO}$ (198 μL , 1.5 mmol) and KI (415 mg, 2.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 10/1) affording pure **4v** as a white solid (264 mg, 81%); $R_f = 0.23$ (hexane/EtOAc, 10/1); mp = 136–138 $^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3): δ 7.10–7.20 (m, 2H), 7.44–7.52 (m, 2H), 7.76–7.87 (m, 4H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 100.2 (C), 115.7 (d, $^2J_{\text{C-F}} = 21.8$ Hz, 2 \times CH), 131.4 (2 \times CH), 132.7 (d, $^3J_{\text{C-F}} = 9.3$ Hz, 2 \times CH), 133.4 (C), 136.8 (C), 137.8 (2 \times CH), 165.6 (d, $^1J_{\text{C-F}} = 254.8$ Hz, C), 194.4 (C) ppm; HRMS (ESI-TOF) calculated for $\text{C}_{13}\text{H}_9\text{FIO}$ $[\text{M}+\text{H}]^+$ 326.9677, found 326.9671.



1-Iodonaphthalene (4w):⁴⁵ General procedure C was followed using 1-nitronaphthalene (**1w**) (173 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF_4 (196 μL , 1.5 mmol), $t\text{BuONO}$ (198 μL , 1.5 mmol) and KI (415 mg, 2.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 60/1) affording pure **4w** as a brown liquid (196 mg, 77%); $R_f = 0.30$ (hexane/EtOAc, 50/1); ^1H NMR (300

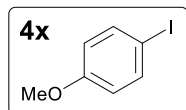
⁴² P. Vital and D. Tanner, *Org. Biomol. Chem.*, 2006, **4**, 4292–4298. Commercially available [CAS: 919124-08-6].

⁴³ K. Kobayashi and Y. Kondo, *Org. Lett.*, 2009, **11**, 2035–2037. Commercially available [CAS: 619-58-9].

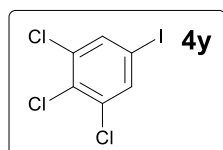
⁴⁴ Commercially available [CAS: 141763-55-5].

⁴⁵ T. Jin and Y. Yamamoto, *Org. Lett.*, 2008, **10**, 3137–3139. Commercially available [CAS: 90-14-2].

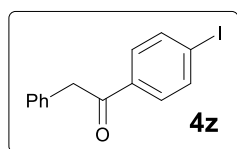
MHz, CDCl₃): δ 7.19 (dd, J = 8.2, 7.3 Hz, 1H), 7.52 (ddd, J = 8.1, 6.9, 1.4 Hz, 1H), 7.58 (ddd, J = 8.5, 6.9, 1.6 Hz, 1H), 7.75–7.80 (m, 1H), 7.84 (d, J = 8.2 Hz, 1H), 8.07–8.13 (m, 2H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 92.2 (C), 126.8 (CH), 126.9 (CH), 127.7 (CH), 128.6 (CH), 129.0 (CH), 132.2 (CH), 134.2 (C), 134.4 (C), 137.5 (CH) ppm.



4-Iodoanisole (4x):⁴⁶ General procedure C was followed using 4-nitroanisole (**1x**) (153 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μ L, 1.5 mmol), *t*BuONO (198 μ L, 1.5 mmol) and KI (415 mg, 2.5 mmol). The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 10/1) affording pure **4x** as an orange solid (133 mg, 57%); R_f = 0.45 (hexane/EtOAc, 10/1); mp = 53–55 °C; ¹H NMR (300 MHz, CDCl₃): δ 3.78 (s, 3H), 6.67–6.70 (m, 2H), 7.54–7.57 (m, 2H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 55.5 (CH₃), 82.8 (C), 116.5 (2 \times CH), 138.3 (2 \times CH), 159.6 (C) ppm.

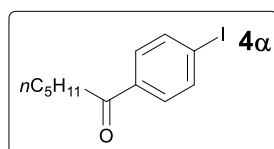


1,2,3-Trichloro-5-iodobenzene (4y):⁴⁷ General procedure C was followed using 1,2,3-trichloro-5-nitrobenzene (**1y**) (226 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μ L, 1.5 mmol), *t*BuONO (198 μ L, 1.5 mmol) and KI (415 mg, 2.5 mmol). The product was obtained without the need for further purification as a brown solid (295 mg, 96%); mp = 50–52 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.69 (s, 2H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 90.0 (C), 131.9 (C), 135.1 (2 \times C), 137.2 (2 \times CH) ppm; HRMS (ESI-TOF) calculated for C₆H₃Cl₃I [M+H⁺] 306.8340, found 306.8342.



1-(4-Iodophenyl)-2-phenylethanone (4z):⁴⁸ General procedure C was followed using 1-(phenylethynyl)-4-nitrobenzene (**1z**) (223 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μ L, 1.5 mmol), *t*BuONO (198 μ L, 1.5 mmol) and KI (415 mg, 2.5 mmol). The obtained crude product was purified by

flash column chromatography (hexane/EtOAc, 7/1) affording pure **4z** as a yellowish solid (283 mg, 88%); R_f = 0.45 (hexane/EtOAc, 7/1); mp = 105–107 °C; ¹H NMR (300 MHz, CDCl₃): δ 4.26 (s, 2H), 7.47–7.17 (m, 5H), 7.71–7.76 (m, 2H), 7.80–7.86 (m, 2H); ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 45.5 (CH₂), 101.3 (C), 127.1 (CH), 128.8 (2 \times CH), 129.5 (2 \times CH), 130.1 (2 \times CH), 134.2 (C), 135.8 (C), 138.0 (2 \times CH), 196.9 (C) ppm.



1-(4-Iodophenyl)hexan-1-one (4 α):⁴⁹ General procedure C was followed using 1-(hex-1-yn-1-yl)-4-nitrobenzene (**1 α**) (203 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (196 μ L, 1.5 mmol), *t*BuONO (198 μ L, 1.5 mmol) and KI (415 mg, 2.5 mmol). The obtained crude product was

purified by flash column chromatography (hexane/EtOAc, 10/1) affording pure **4 α** as a white solid (251 mg, 83%); R_f = 0.35 (hexane/EtOAc, 10/1); mp = 74–76 °C; ¹H NMR (300 MHz, CDCl₃): δ 0.80–0.92 (m, 3H), 1.25–1.37 (m, 4H), 1.62–1.75 (m, 2H), 2.83–2.90 (m, 2H), 7.58–7.65 (m, 2H), 7.72–7.80 (m, 2H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 14.0 (CH₃), 22.5 (CH₂), 23.9 (CH₂), 31.5 (CH₂), 38.5 (CH₂), 100.8 (C), 129.5 (2 \times CH), 136.3 (C), 137.8 (2 \times CH), 199.6 (C) ppm.

⁴⁶ Commercially available [CAS: 696-62-8].

⁴⁷ Commercially available [CAS: 64634-61-3].

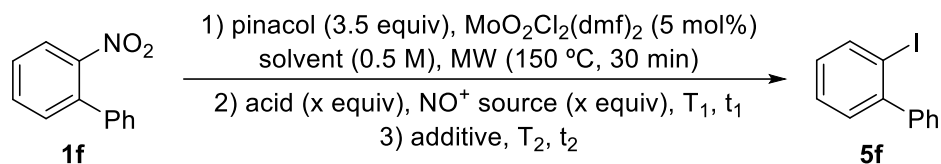
⁴⁸ M. Bouquin, F. Jaroschik and M. Taillefer, *Tetrahedron Lett.*, 2021, **75**, 153208. Commercially available [CAS: 55794-28-0].

⁴⁹ R. Y.Y. Ko, J. C.K. Chu and P. Chiu, *Tetrahedron*, 2011, **67**, 2542–2547. Commercially available [CAS: 160565-78-6].

Synthesis of fluorides 5:

Optimization of the reaction:

Table S4: Optimization of the one-pot sequential nitro reduction-diazotization-fluorination of **1a**.^a



ent.	NO ⁺ source (x equiv)	acid (x equiv)	T ₁ (°C)	t ₁ (min)	additive (x equiv)	solvent	T ₂ (°C)	t ₂ (h)	5f (%) ^b
1	NOBF ₄ (1.2)	–	0	30	–	PhMe	100	3	35
2	NOBF ₄ (1.2)	–	0	30	–	MeCN	100	3	28
3	<i>t</i> BuONO (2)	HBF ₄ (3)	0	30	–	PhMe	100	3	57 (45)
4	<i>t</i> BuONO (2)	HBF ₄ (2.5)	0	30	–	PhCF ₃	100	3	53
5	<i>t</i> BuONO (2)	HBF ₄ (2.5)	0 to rt	120	–	PhMe	100	3	58 ^c
6	<i>t</i> BuONO (2)	HBF ₄ ·OEt ₂ (3)	0	240	–	PhMe	100	3	37 ^d
7	<i>t</i> BuONO (2)	HBF ₄ (3)	0	30	MgSO ₄ (1.5)	PhMe	100	3	53 ^d
8	<i>t</i> BuONO (2)	HBF ₄ (3)	0 to rt	120	MgSO ₄ (1.5)	PhMe	100	3	40 ^d
9	<i>t</i> BuONO (2)	HBF ₄ (3)	0	30	TBAF (1.5)	PhMe	100	3	41
10	<i>t</i> BuONO (2)	PTSA (2)	0	30	CsF (2.5)	PhMe	100	3	9
11	<i>t</i> BuONO (2)	HBF ₄ (3)	0	30	CsF (1.5)	PhMe	100	3	52
12	<i>t</i> BuONO (2)	HBF ₄ (3)	0	30	CsF (2.5)/ Py (4)	MeCN	80	3	10
13	<i>t</i> BuONO (2)	HBF ₄ (3)	0	30	Py (4)	PhMe	80	3	38
14	<i>t</i> BuONO (2)	HBF ₄ (3)	0	30	Py (4)	PhMe	80	16	30
15	<i>t</i> BuONO (2)	HBF ₄ (3)	0	30	–	PhMe	80	1	49

16 ^e	<i>t</i> BuONO (2)	BF ₃ ·OEt ₂ (2.5)	0	15	I(III) (20 mol%)	PhCF ₃	40	36	(35) ^d
17 ^e	<i>t</i> BuONO (1.8)	BF ₃ ·OEt ₂ (2.5)	0	15	I(III) (20 mol%)	PhCF ₃	100	19	(30) ^d
18 ^e	<i>t</i> BuONO (1.8)	BF ₃ ·OEt ₂ (2.5)	0	120	I(III) (20 mol%)	PhCF ₃	100	19	18 ^d
19 ^e	<i>t</i> BuONO (1.8)	HF ₄ (2.5)	0	15	I(III) (20 mol%)	PhCF ₃	100	19	(39)
20 ^e	<i>t</i> BuONO (1.8)	HF ₄ (2.5)	0	15	I(III) (20 mol%)	PhCF ₃	80	19	(49)
21 ^e	<i>t</i> BuONO (1.8)	HF ₄ (2.5)	0	15	I(III) (20 mol%)	PhCF ₃	80	1	(57)
22 ^e	<i>t</i> BuONO (1.8)	HF ₄ (2.5)	0	15	I(III) (20 mol%)	PhCF ₃	80	3	(58)
23 ^e	<i>t</i> BuONO (1.8)	HF ₄ (2.5)	0	15	I(III) (20 mol%)	PhCF ₃	60	3	(64)
24 ^e	<i>t</i> BuONO (1.8))	HF ₄ (2.5)	0	15	I(III) (20 mol%)	PhCF ₃	40	3	(56)
25 ^e	<i>t</i> BuONO (1.8)	HF ₄ (2.5)	0	15	I(III) (20 mol%)	PhCF ₃	60	1	(53)

^a Reaction conditions: **1f** (1.0 mmol), under air. ^b Determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. In brackets isolated yield. ^c ~17% of 2-hydroxybiphenyl was generated. ^d Variable amounts of 2-aminobiphenyl was detected. ^e I(III) = 1-fluoro-3,3-dimethylbenziodoxole.

Initially, the reaction was performed using nitrosonium tetrafluoroborate as both the diazotization agent and fluoride source in the absence of acid and additives (entries 1 and 2).⁵⁰ The reaction was allowed to stir 30 min at 0 °C to allow formation of the diazonium salt prior to heating at 100 °C for 3 h. However, low yields of the desired fluoride **5f** were obtained and reactions looked unclean in both toluene and acetonitrile. We then decided to switch to the combined use of *tert*-butyl nitrite and tetrafluoroboric acid allowing the fluorination of the starting material in moderate yield (entry 3). Similar results were obtained when α,α,α -trifluorotoluene was used as solvent (entry 4). With longer diazotization times the yield of the desired product **5f** was equally good but 17% of undesired byproduct 2-hydroxybiphenyl was observed derived from the reaction of the diazonium salt with the water present in the media (entry 5). To avoid the presence of large amounts of water and, therefore, the formation of this byproduct, HF₄·OEt₂ was used as acid instead (entry 6), but with unsatisfactory results, as there was still a 35% of intermediate 2-aminobiphenyl. As an alternative, the reaction was carried out in the presence of highly hygroscopic MgSO₄, and although formation of the undesired byproduct 2-hydroxybiphenyl was avoided, there was no complete conversion, neither a better yield of **5f** (entries 7 and 8). Our next approach to solve this issue was to use an additive to further promote the fluorination over the hydrolysis of the diazonium salt. *n*Bu₄NF·3H₂O was added but reaction yield was lower (entry 9). The addition of CsF was also tried leading to dramatically worse results

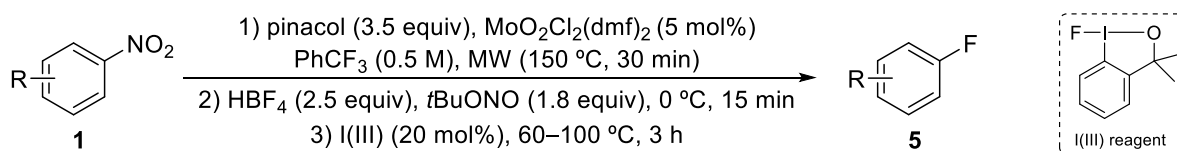
⁵⁰ a) D. J. Milner, *Synth. Commun.*, 1992, **22**, 73–82; b) K. K. Laali and V. J. Gettwert, *J. Fluor. Chem.*, 2001, **107**, 31–34.

in the presence of PTSA as acid (entry 10) and moderate, but slightly lower yields, with HBF₄ (entry 11). Three different experiments were also performed in the presence of pyridine combined with CsF (entry 12) and on its own (entries 13 and 14). However, the reaction yield obtained was lower in all cases. We also checked that a decrease in temperature did not give better results (entry 15).

Inspired by a previous report,⁵¹ we then tried to use 1-fluoro-3,3-dimethylbenziodoxole (I(III)) in substoichiometric amounts as additive to promote the fluorination (entries 16–25). Following the reported method, initially BF₃·OEt₂ was used as acid, α,α,α -trifluorotoluene as solvent and the reaction was performed at 40 °C for 36 h leading to a quite low isolated yield of the fluoride and a 20% of unconverted amine (entry 16). A slight improvement in yield was observed when temperature was increased to 100 °C in lower reaction times but still 24% of 2-aminobiphenyl was observed (entry 17). The yield dropped significantly when a longer diazotization time was allowed and surprisingly, still 25% of aniline was detected (entry 18). We then decided to change the acid to HBF₄ in order to achieve complete conversion of the starting materials. A moderate isolated yield was obtained at 100 °C (entry 19). However, lowering the reaction temperature led to improved results (entry 20). We also checked that much shorter reaction times allowed the obtention of higher yields (entries 21 and 22). The best results were achieved at 60 °C for 3 h (entry 23). It was finally checked that further decreasing the temperature and reaction time negatively affected the obtained yield (entries 24 and 25).

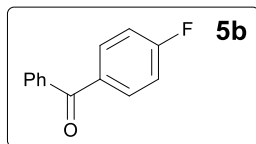
It is worthy to note that subsequent essays with other starting nitrocompounds showed best results at different temperatures between 60–100 °C. Therefore, a temperature optimization was carried out for each depicted substrate.

General procedure D:

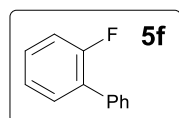


In a 10 mL reaction vessel, the corresponding nitroarene (1 equiv), anhydrous α,α,α -trifluorotoluene (0.5 M), pinacol (3.5 equiv) and MoO₂Cl₂(dmf)₂ (5 mol%) were mixed together. The vessel was sealed with a septum and the reaction mixture was stirred at 150 °C for 30 min under microwave irradiation. The mixture was then cooled to 0 °C and HBF₄ (48 wt.% in H₂O, 2.5 equiv) and a previously prepared solution of *t*BuONO (1.8 equiv) in α,α,α -trifluorotoluene (1.5 M) were added allowing stirring for 15 min. Finally, 1-fluoro-3,3-dimethylbenziodoxole (20 mol%) was added and the reaction was stirred for 3 h at 60–100 °C. The mixture was directly purified by silica gel flash column chromatography (hexane/EtOAc) to afford the fluorides **5**.

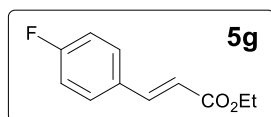
⁵¹ B. Xing, C. Ni and J. Hu, *Angew. Chem. Int. Ed.*, 2018, **57**, 9896–9900.



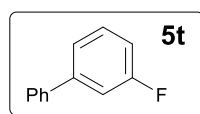
4-Fluorobenzophenone (5b):⁵² General procedure D was followed using 4-nitrobenzophenone (**1b**) (227 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (327 μ L, 2.5 mmol), *t*BuONO (238 μ L, 1.8 mmol) and 1-fluoro-3,3-dimethylbenziodoxole (56 mg, 20 mol%) at 100 °C. The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 20/1 to 15/1) affording pure **5b** as a yellow solid (104 mg, 52%); *R*_f = 0.34 (hexane/EtOAc, 10/1); mp = 47–49 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.08–7.19 (m, 2H), 7.43–7.53 (m, 2H), 7.54–7.62 (m, 1H), 7.75 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.80–7.87 (m, 2H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 115.5 (d, ²*J*_{C-F} = 21.8 Hz, 2 \times CH), 128.4 (2 \times CH), 129.9 (2 \times CH), 132.7 (d, ³*J*_{C-F} = 19.2 Hz, 2 \times CH), 132.7 (CH), 133.9 (d, ⁴*J*_{C-F} = 3.0 Hz, C), 137.6 (C), 165.4 (d, ¹*J*_{C-F} = 254.2 Hz, C), 196.3 (C) ppm; ¹⁹F NMR (282 MHz, CDCl₃): δ -105.93 ppm.



2-Fluorobiphenyl (5f):⁵³ General procedure D was followed using 2-nitrobiphenyl (**1f**) (199 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (327 μ L, 2.5 mmol), *t*BuONO (238 μ L, 1.8 mmol) and 1-fluoro-3,3-dimethylbenziodoxole (56 mg, 20 mol%) at 60 °C. The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 60/1 to 30/1) affording pure **5f** as a white solid (110 mg, 64%); *R*_f = 0.33 (hexane/EtOAc, 40/1); mp = 77–79 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.16–7.25 (m, 2H), 7.27 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.32–7.38 (m, 1H), 7.39–7.46 (m, 1H), 7.47–7.54 (m, 3H), 7.58–7.65 (m, 2H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 116.1 (d, ²*J*_{C-F} = 22.7 Hz, CH), 124.4 (d, ⁴*J*_{C-F} = 3.8 Hz, CH), 127.7 (2 \times CH), 128.5 (2 \times CH), 128.9 (CH), 129.0 (d, ³*J*_{C-F} = 3.0 Hz, CH), 129.3 (C – not able to measure coupling constant), 130.9 (d, ³*J*_{C-F} = 3.4 Hz, CH), 135.9 (C), 159.8 (d, ¹*J*_{C-F} = 247.7 Hz, C) ppm; ¹⁹F NMR (282 MHz, CDCl₃): δ -117.84 ppm.



Ethyl 4-fluorocinnamate (5g):⁵⁴ General procedure D was followed using ethyl 4-nitrocinnamate (**1g**) (221 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (327 μ L, 2.5 mmol), *t*BuONO (238 μ L, 1.8 mmol) and 1-fluoro-3,3-dimethylbenziodoxole (56 mg, 20 mol%) at 100 °C. The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 10/1) affording pure **5g** as a yellow liquid (82 mg, 42%); *R*_f = 0.24 (hexane/EtOAc, 10/1); ¹H NMR (300 MHz, CDCl₃): δ 1.34 (t, *J* = 7.1 Hz, 3H), 4.27 (q, *J* = 7.1 Hz, 2H), 6.36 (dd, *J* = 16.0, 0.6 Hz, 1H), 7.03–7.12 (m, 2H), 7.42–7.55 (m, 2H), 7.65 (d, *J* = 16.0 Hz, 1H) ppm; ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 14.3 (CH₃), 60.5 (CH₂), 116.0 (d, ²*J*_{C-F} = 21.9 Hz, 2 \times CH), 118.04 (d, *J* = 2.3 Hz, C), 129.9 (d, ³*J*_{C-F} = 8.5 Hz, 2 \times CH), 130.7 (d, ⁴*J*_{C-F} = 3.4 Hz, CH), 143.2 (CH), 163.9 (d, ¹*J*_{C-F} = 251.2 Hz, C), 166.8 (C) ppm; ¹⁹F NMR (282 MHz, CDCl₃): δ -109.76 ppm.



3-Fluorobiphenyl (5t):⁵⁵ General procedure D was followed using 3-nitrobiphenyl (**1t**) (199 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (327 μ L, 2.5 mmol), *t*BuONO (238 μ L, 1.8 mmol) and 1-fluoro-3,3-

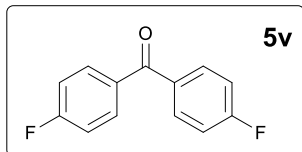
⁵² J. Zhang, Z. Wang, Y. Wang, C. Wan, X. Zheng and Z. Wang, *Green Chem.*, 2009, **11**, 1973–1978. Commercially available [CAS: 345-83-5].

⁵³ M. Döbele, S. Vanderheiden, N. Jung and S. Bräse, *Angew. Chem. Int. Ed.*, 2010, **49**, 5986–5988. Commercially available [CAS: 321-60-8].

⁵⁴ P. S.-W. Leung, Y. Teng and P. H. Toy, *Org. Lett.*, 2010, **12**, 4996–4999. Commercially available [CAS: 352-03-4].

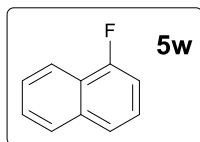
⁵⁵ M. R. Kumar, K. Park and S. Lee, *Adv. Synth. Catal.*, 2010, **352**, 3255–3266.

dimethylbenziodoxole (56 mg, 20 mol%) at 60 °C. The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 80/1) affording pure **5t** as a colorless liquid (83 mg, 48%); $R_f = 0.48$ (hexane/EtOAc, 40/1); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.05–7.16 (m, 1H), 7.32–7.39 (m, 1H), 7.40–7.47 (m, 3H), 7.48–7.55 (m, 2H), 7.60–7.68 (m, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 113.9 (CH), 114.1 (d, $^2J_{\text{C-F}} = 20.9$ Hz, CH), 122.8 (d, $^4J_{\text{C-F}} = 2.8$ Hz, CH), 127.2 (2 \times CH), 127.9 (CH), 129.0 (2 \times CH), 130.3 (d, $^3J_{\text{C-F}} = 8.4$ Hz, CH), 140.0 (d, $^4J_{\text{C-F}} = 2.2$ Hz, C), 143.6 (d, $^3J_{\text{C-F}} = 7.7$ Hz, C), 163.3 (d, $^1J_{\text{C-F}} = 245.5$ Hz, C) ppm; $^{19}\text{F NMR}$ (282 MHz, CDCl_3): δ -113.00 ppm.



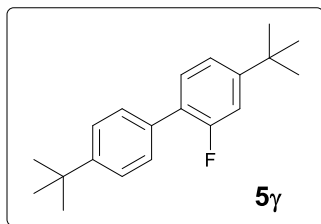
4,4'-Difluorobenzophenone (5v):⁵⁶ General procedure D was followed using (4-fluorophenyl)(4'-nitrophenyl)methanone (**1v**) (245 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF_4 (327 μL , 2.5 mmol), $t\text{BuONO}$ (238 μL , 1.8 mmol) and 1-fluoro-3,3-dimethylbenziodoxole (56 mg, 20 mol%) at 100 °C. The obtained crude product was purified by flash column

chromatography (hexane/EtOAc, 10/1) affording pure **5v** as a white solid (120 mg, 55%); $R_f = 0.42$ (hexane/EtOAc, 10/1); mp = 107–109 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.10–7.20 (m, 4H), 7.75–7.83 (m, 4H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 115.5 (d, $^2J_{\text{C-F}} = 21.8$ Hz, 4 \times CH), 132.5 (d, $^3J_{\text{C-F}} = 9.2$ Hz, 4 \times CH), 133.7 (d, $^4J_{\text{C-F}} = 3.0$ Hz, 2 \times C), 165.4 (d, $^1J_{\text{C-F}} = 254.3$ Hz, 2 \times C), 193.7 (C) ppm; $^{19}\text{F NMR}$ (282 MHz, CDCl_3): δ -105.77 ppm.



1-Fluoronaphthalene (5w):⁵⁷ General procedure D was followed using 1-nitronaphthalene (**1w**) (173 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF_4 (327 μL , 2.5 mmol), $t\text{BuONO}$ (238 μL , 1.8 mmol) and 1-fluoro-3,3-dimethylbenziodoxole (56 mg, 20 mol%) at 100 °C. The obtained crude product was

purified by flash column chromatography (hexane/EtOAc, 60/1 to 50/1) affording pure **5w** as a yellow liquid (88 mg, 60%); $R_f = 0.39$ (hexane/EtOAc, 40/1); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.13–7.23 (m, 1H), 7.43 (td, $J = 7.9, 5.5$ Hz, 1H), 7.52–7.62 (m, 2H), 7.63–7.69 (m, 1H), 7.85–7.94 (m, 1H), 8.12–8.21 (m, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 109.5 (d, $^2J_{\text{C-F}} = 19.9$ Hz, CH), 120.6 (d, $^3J_{\text{C-F}} = 5.2$ Hz, CH), 123.7 (d, $^4J_{\text{C-F}} = 4.0$ Hz, CH), 123.9 (C – not able to measure coupling constant), 125.7 (d, $^3J_{\text{C-F}} = 8.4$ Hz, CH), 126.2 (CH), 126.9 (d, $^4J_{\text{C-F}} = 1.1$ Hz, CH), 127.6 (d, $^4J_{\text{C-F}} = 3.2$ Hz, CH), 134.9 (d, $^3J_{\text{C-F}} = 4.8$ Hz, C), 158.9 (d, $^1J_{\text{C-F}} = 251.5$ Hz, C) ppm; $^{19}\text{F NMR}$ (282 MHz, CDCl_3): δ -123.31 ppm.



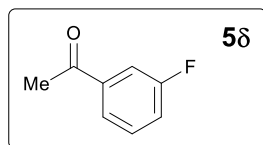
4,4'-Di-tert-butyl-2-fluorobiphenyl (5y): General procedure D was followed using 4,4'-di-tert-butyl-2-nitrobiphenyl (**1y**) (311 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF_4 (327 μL , 2.5 mmol), $t\text{BuONO}$ (238 μL , 1.8 mmol) and 1-fluoro-3,3-dimethylbenziodoxole (56 mg, 20 mol%) at 60 °C. The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 100/1 to 80/1) affording pure **5y** as

a white solid (199 mg, 70%); $R_f = 0.68$ (hexane/EtOAc, 40/1); mp = 92–94 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 1.35–1.49 (m, 18H), 7.20–7.33 (m, 2H), 7.45 (t, $J = 8.3$ Hz, 1H), 7.49–7.61 (m, 4H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR

⁵⁶ Y. Su, L. Zhang and N. Jiao, *Org. Lett.*, 2011, **13**, 2168–2171. Commercially available [CAS: 345-92-6].

⁵⁷ T. Noël, T. J. Maimone and S. L. Buchwald, *Angew. Chem. Int. Ed.*, 2011, **50**, 8900–8903. Commercially available [CAS: 321-38-0].

(75.4 MHz, CDCl₃): δ 31.4 (3 \times CH₃), 31.5 (3 \times CH₃), 34.7 (C), 34.8 (d, $^4J_{C-F}$ = 1.2 Hz, C), 113.3 (d, $^2J_{C-F}$ = 23.3 Hz, CH), 121.4 (d, $^4J_{C-F}$ = 3.0 Hz, CH), 125.2 (d, $^2J_{C-F}$ = 22.6 Hz, C), 125.5 (2 \times CH), 128.7 (2 \times CH), 130.2 (d, $^3J_{C-F}$ = 4.0 Hz, CH), 133.1 (C), 150.4 (C), 152.9 (d, $^3J_{C-F}$ = 6.7 Hz, C), 159.8 (d, $^1J_{C-F}$ = 246.5 Hz, C) ppm; ^{19}F NMR (282 MHz, CDCl₃): δ -118.27 ppm; HRMS could not be recorded.

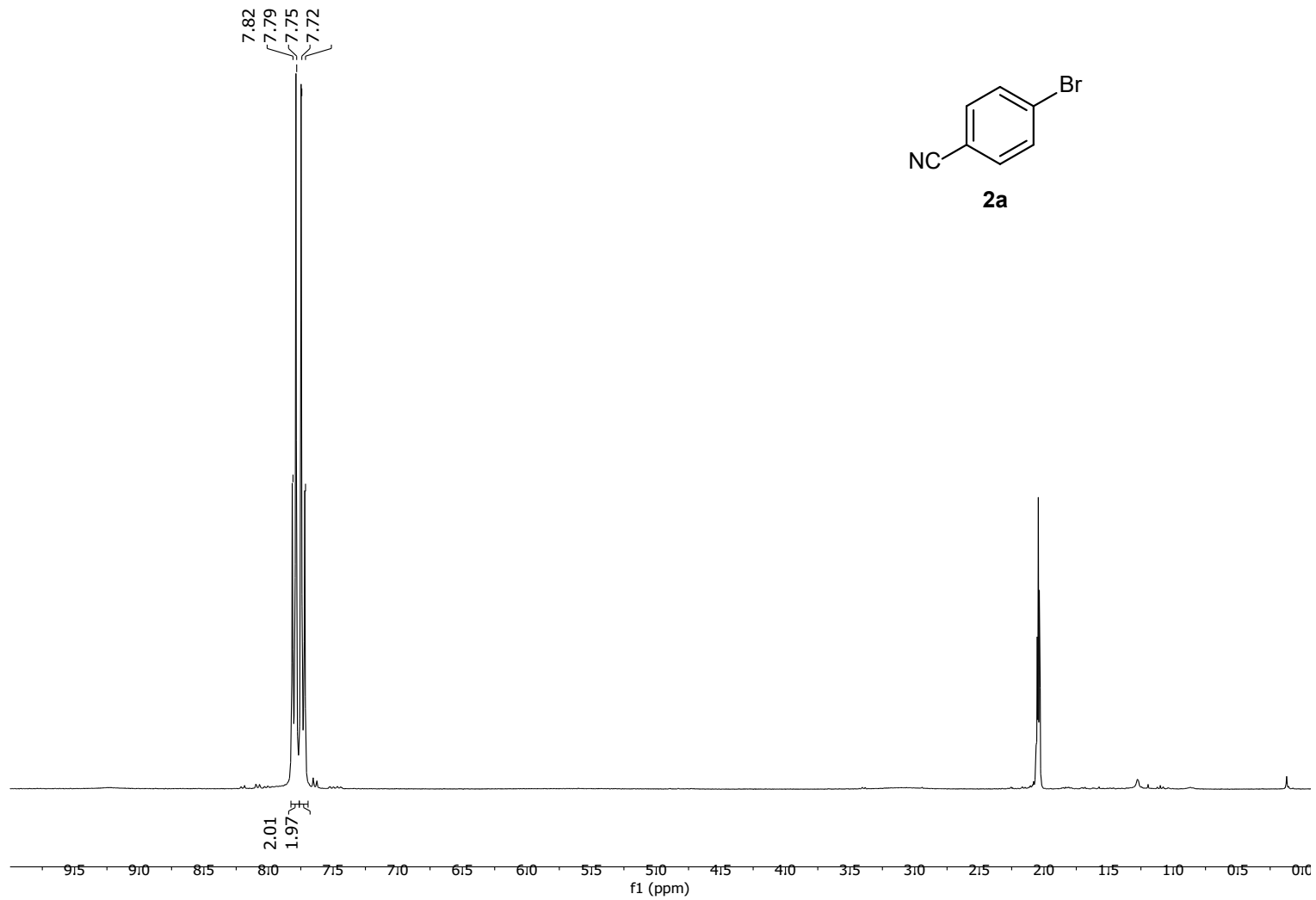


3-Fluoroacetophenone (5 δ):⁵⁸ General procedure D was followed using 3-nitroacetophenone (**1 δ**) (165 mg, 1 mmol), pinacol (414 mg, 3.5 mmol), catalyst (17 mg, 0.05 mmol), HBF₄ (327 μ L, 2.5 mmol), *t*BuONO (238 μ L, 1.8 mmol) and 1-fluoro-3,3-dimethylbenziodoxole (56 mg, 20 mol%) at 100 °C. The obtained crude product was purified by flash column chromatography (hexane/EtOAc, 3/1 to 2/1) affording pure **5 δ** as an orange liquid (61 mg, 44%); R_f = 0.59 (hexane/EtOAc, 2/1); ^1H NMR (300 MHz, CDCl₃): δ 2.61 (d, J = 0.6 Hz, 3H), 7.23–7.32 (m, 1H), 7.41–7.50 (m, 1H), 7.61–7.67 (m, 1H), 7.72–7.77 (m, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl₃): δ 26.7 (CH₃), 114.9 (d, $^2J_{C-F}$ = 22.2 Hz, CH), 120.1 (d, $^2J_{C-F}$ = 21.5 Hz, CH), 124.1 (d, $^4J_{C-F}$ = 3.1 Hz, CH), 130.3 (d, $^3J_{C-F}$ = 7.6 Hz, CH), 139.2 (d, $^3J_{C-F}$ = 6.1 Hz, C), 162.8 (d, $^1J_{C-F}$ = 247.8 Hz, C), 196.7 (C) ppm; ^{19}F NMR (282 MHz, CDCl₃): δ -111.98 ppm.

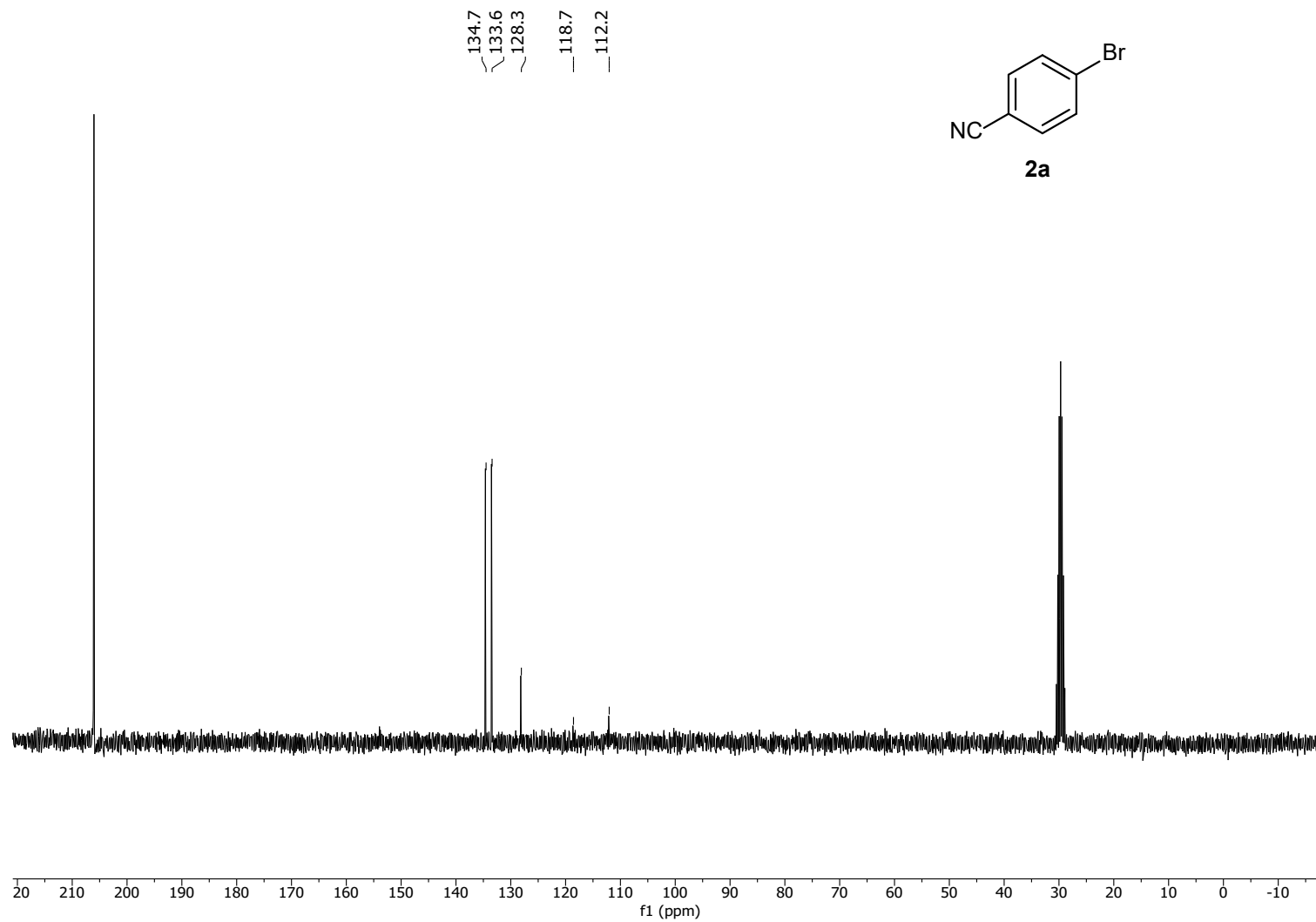
⁵⁸ Z. Hyder, J. Ruan and J. Xiao, *Chem. Eur. J.*, 2008, **14**, 5555–5566. Commercially available [CAS: 455-36-7].

^1H and ^{13}C NMR Spectra

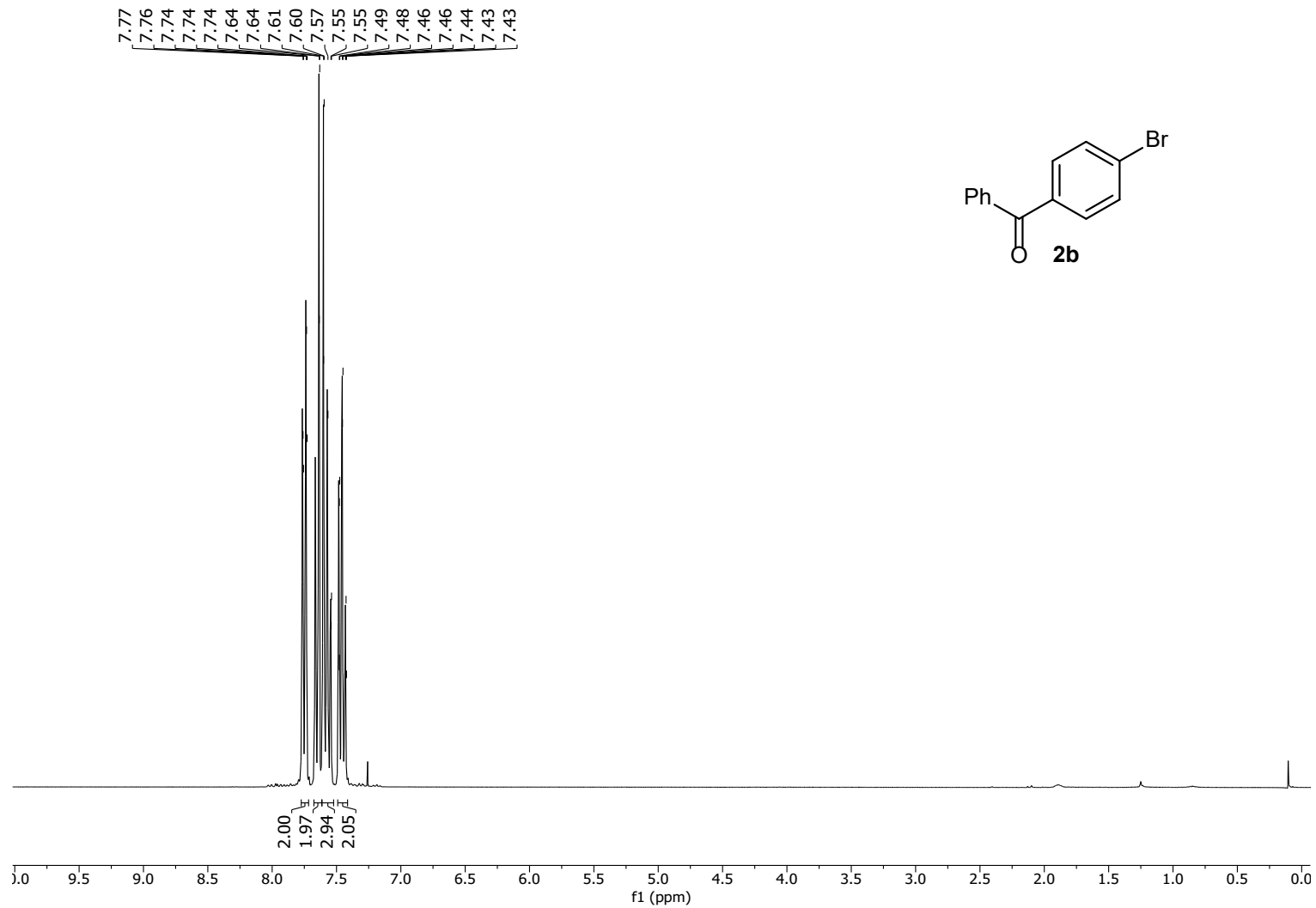
^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$)



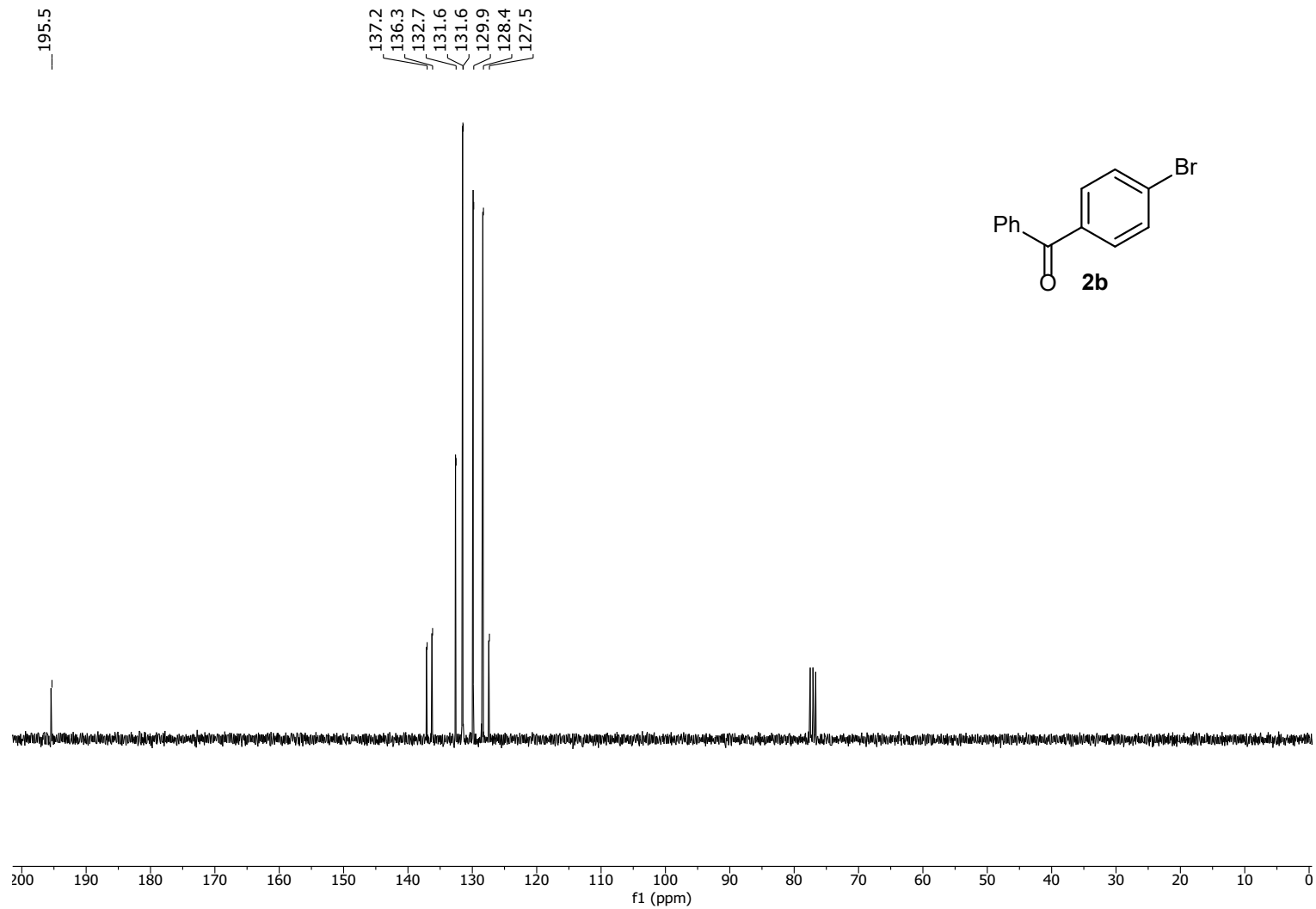
^{13}C NMR (75.4 MHz, $(\text{CD}_3)_2\text{CO}$)



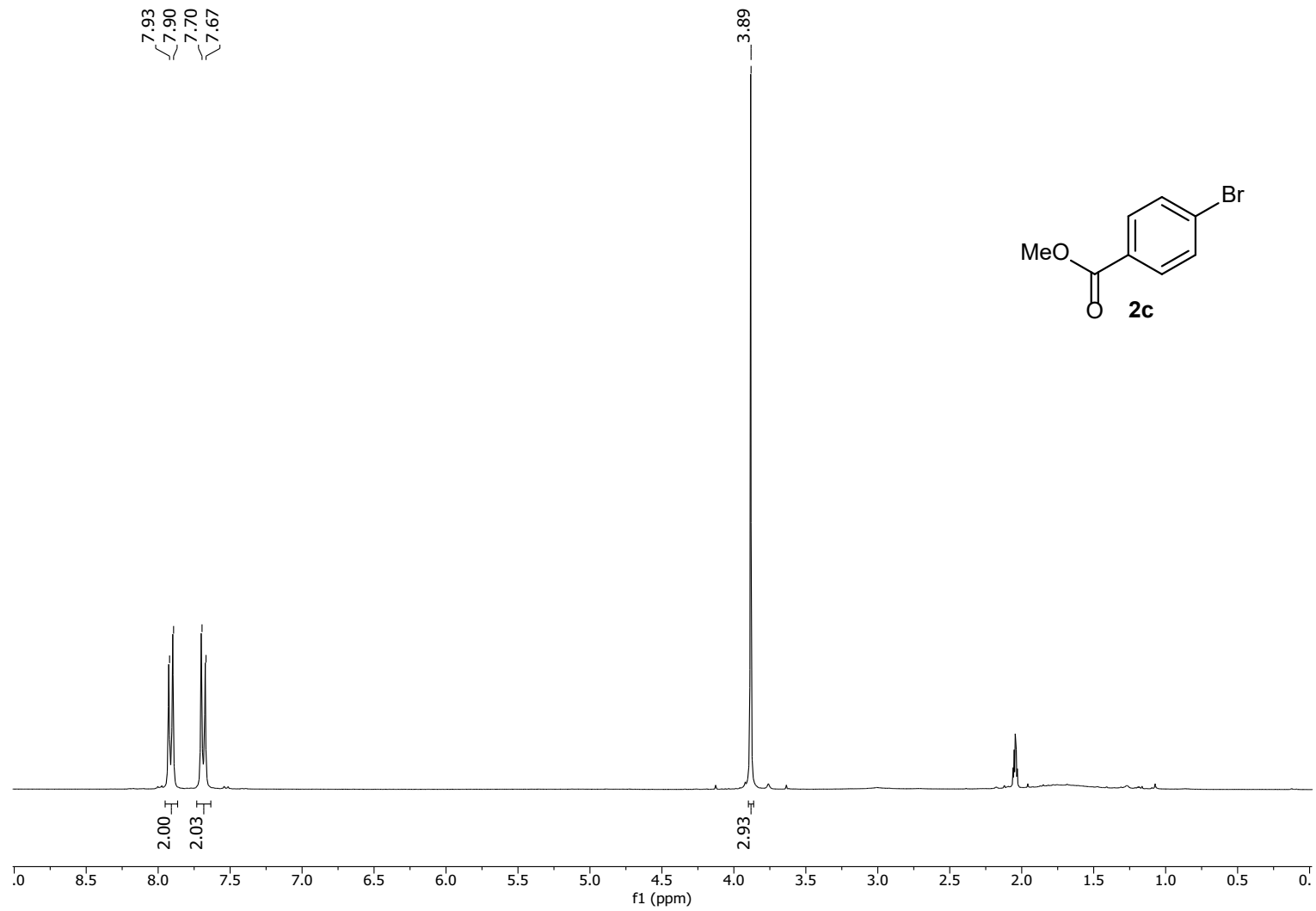
^1H NMR (300 MHz, CDCl_3)



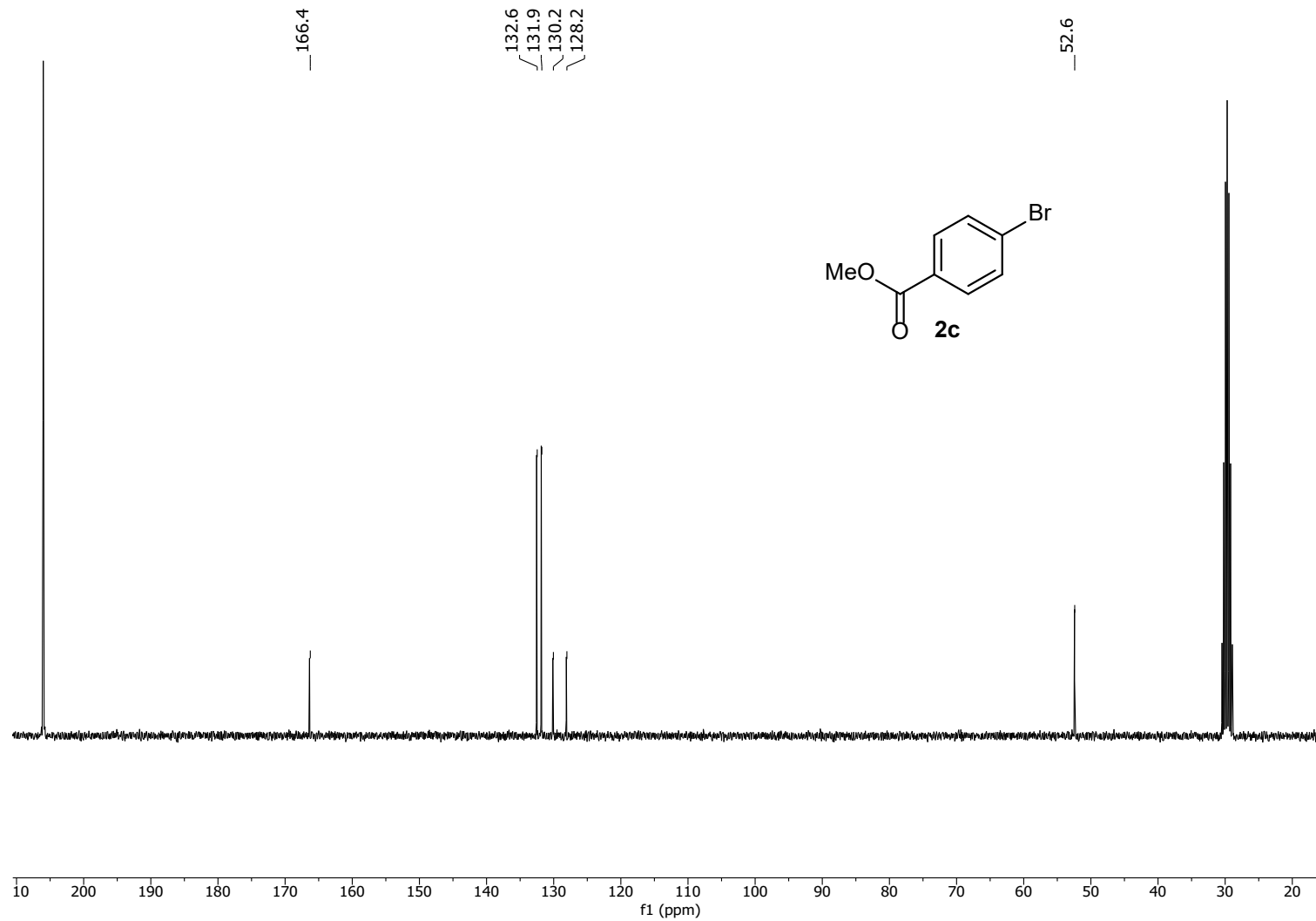
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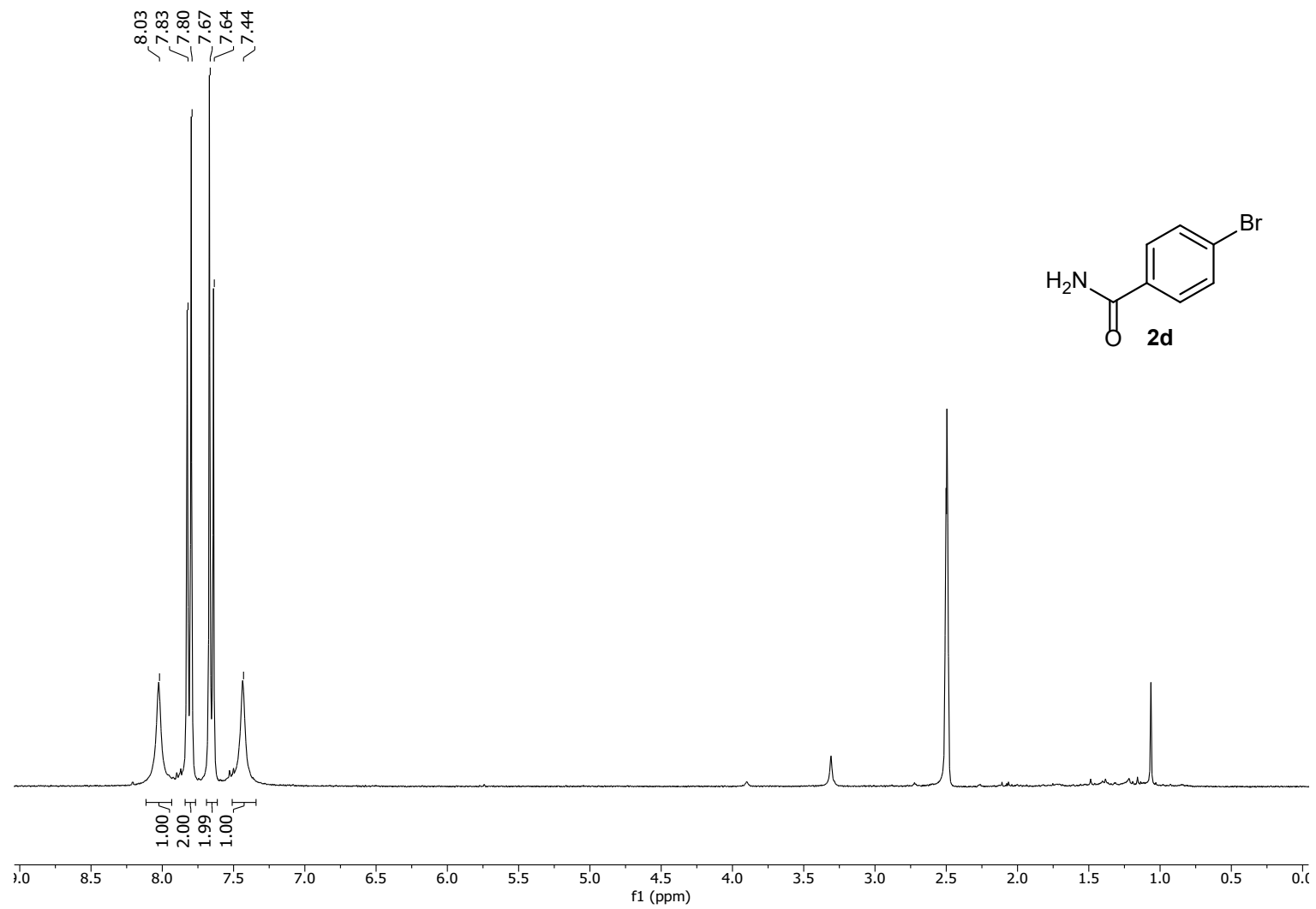
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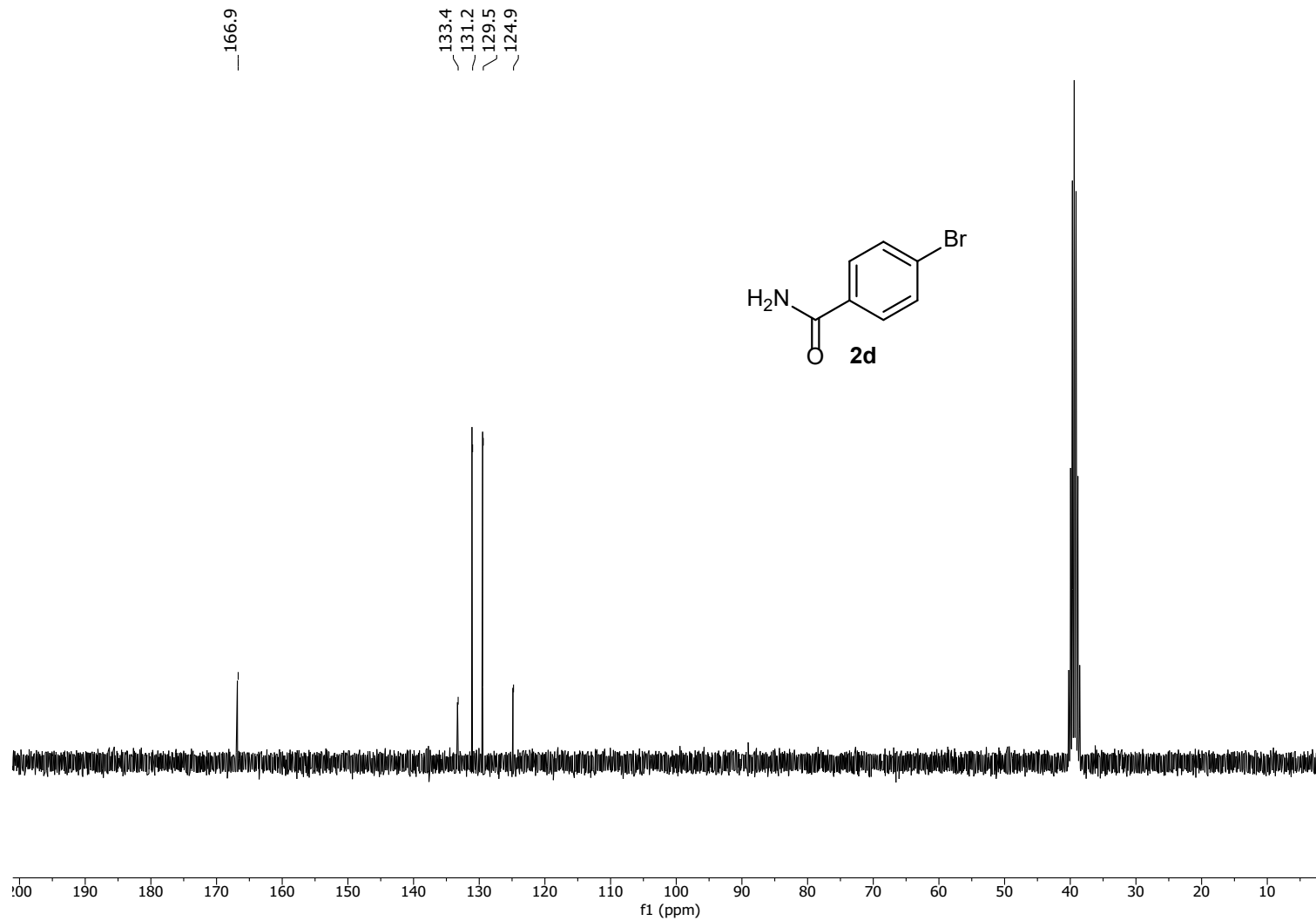
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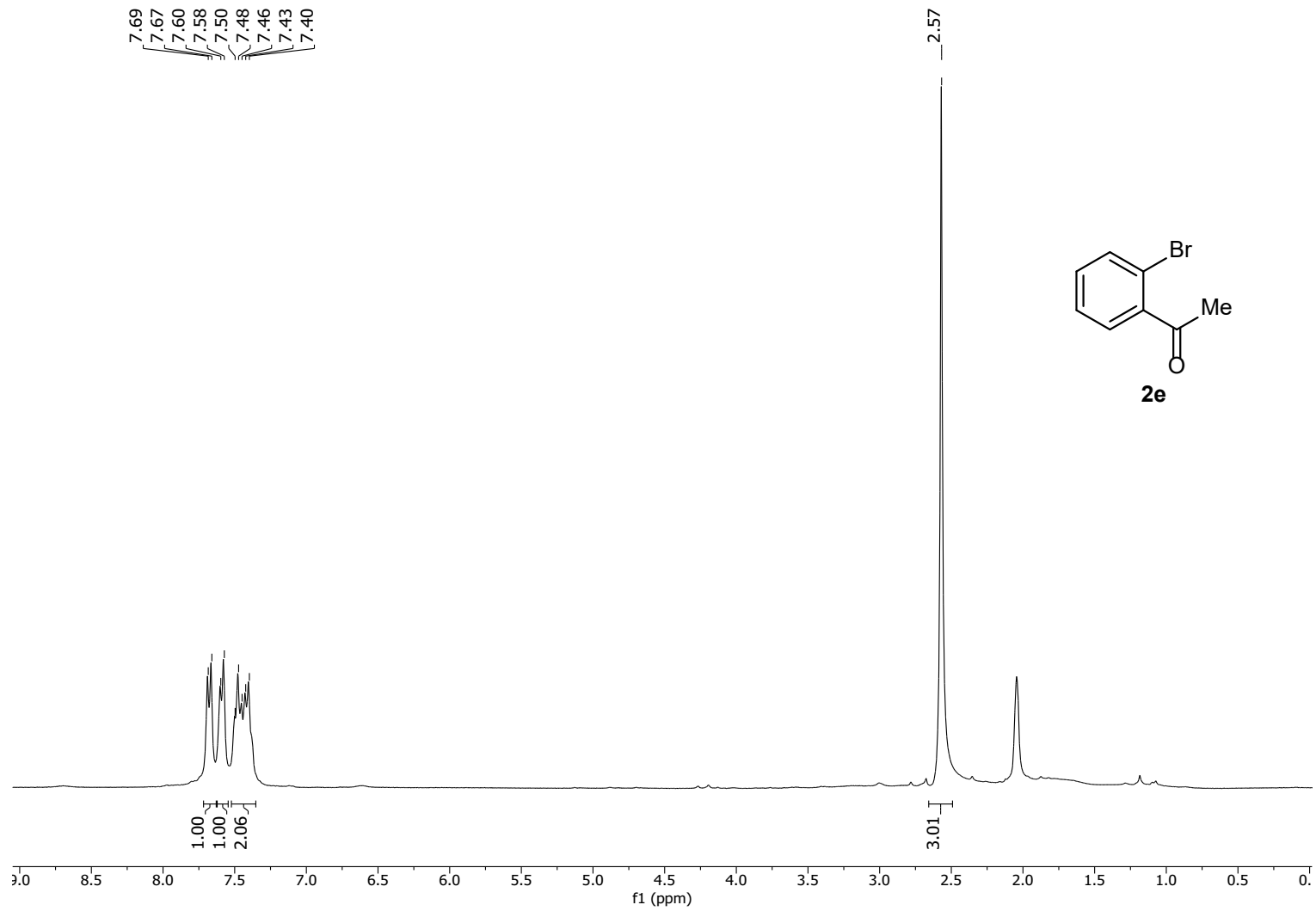
^1H NMR (300 MHz, $\text{DMSO-}d_6$)



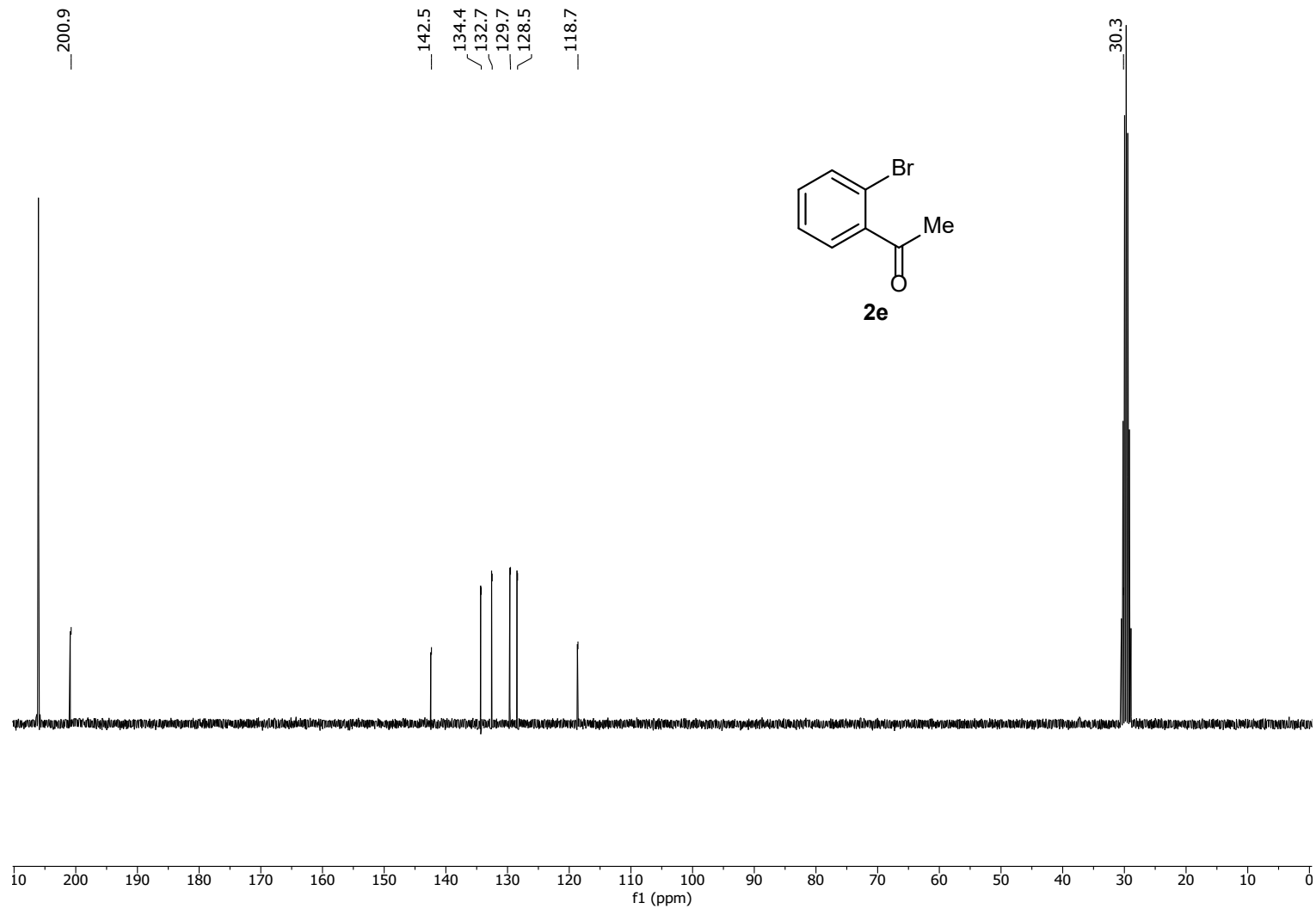
^{13}C NMR (75.4 MHz, $\text{DMSO-}d_6$)



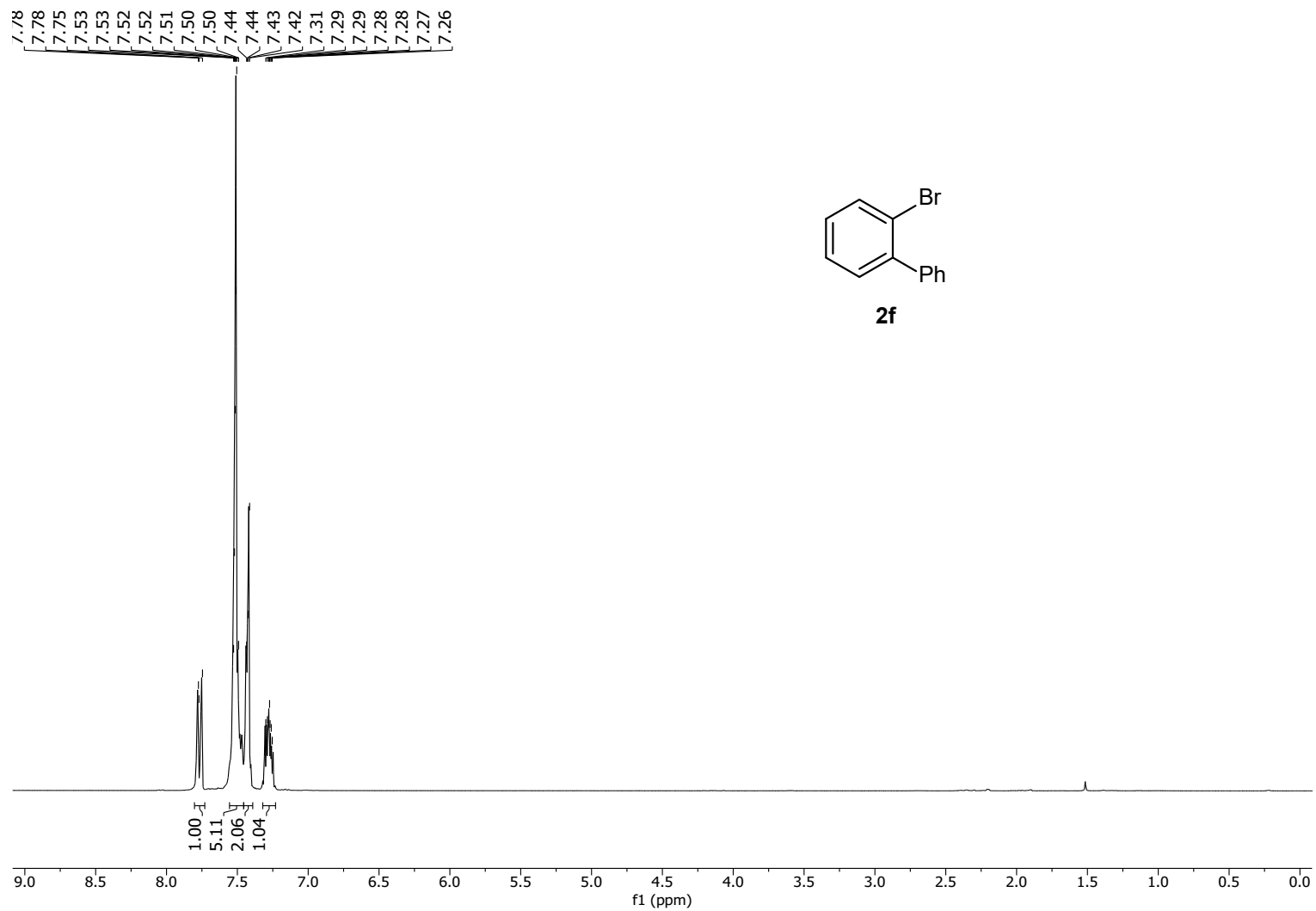
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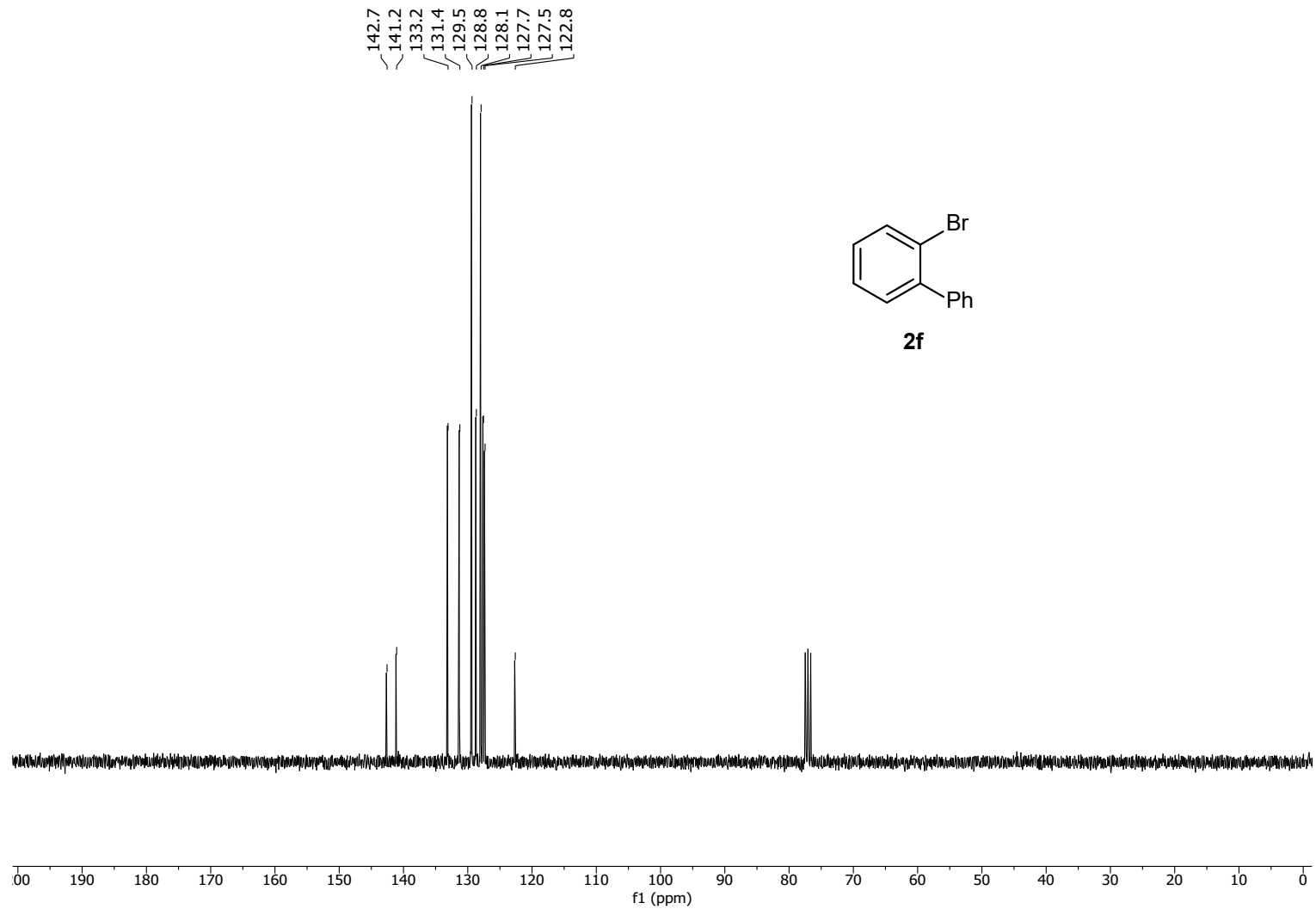
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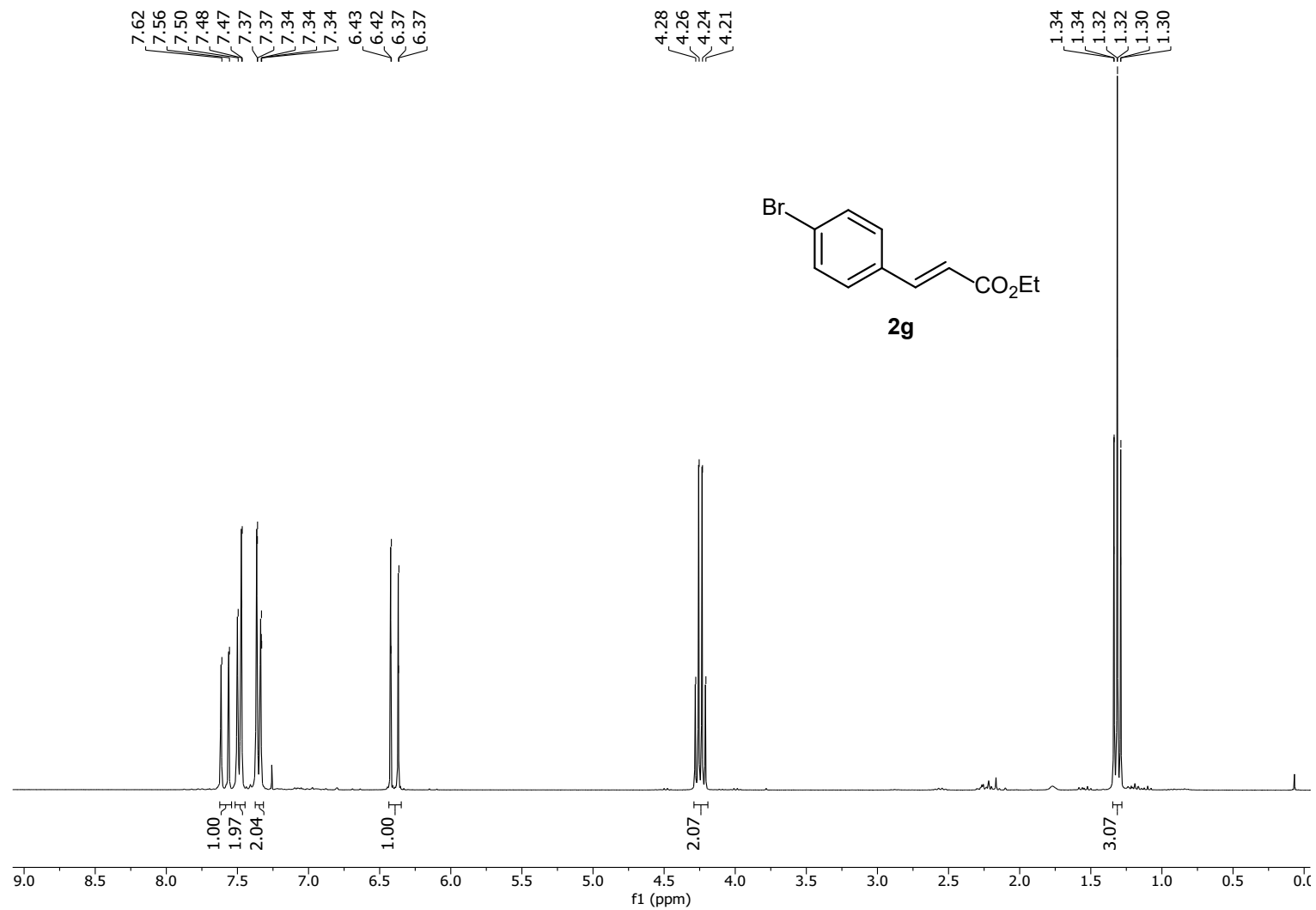
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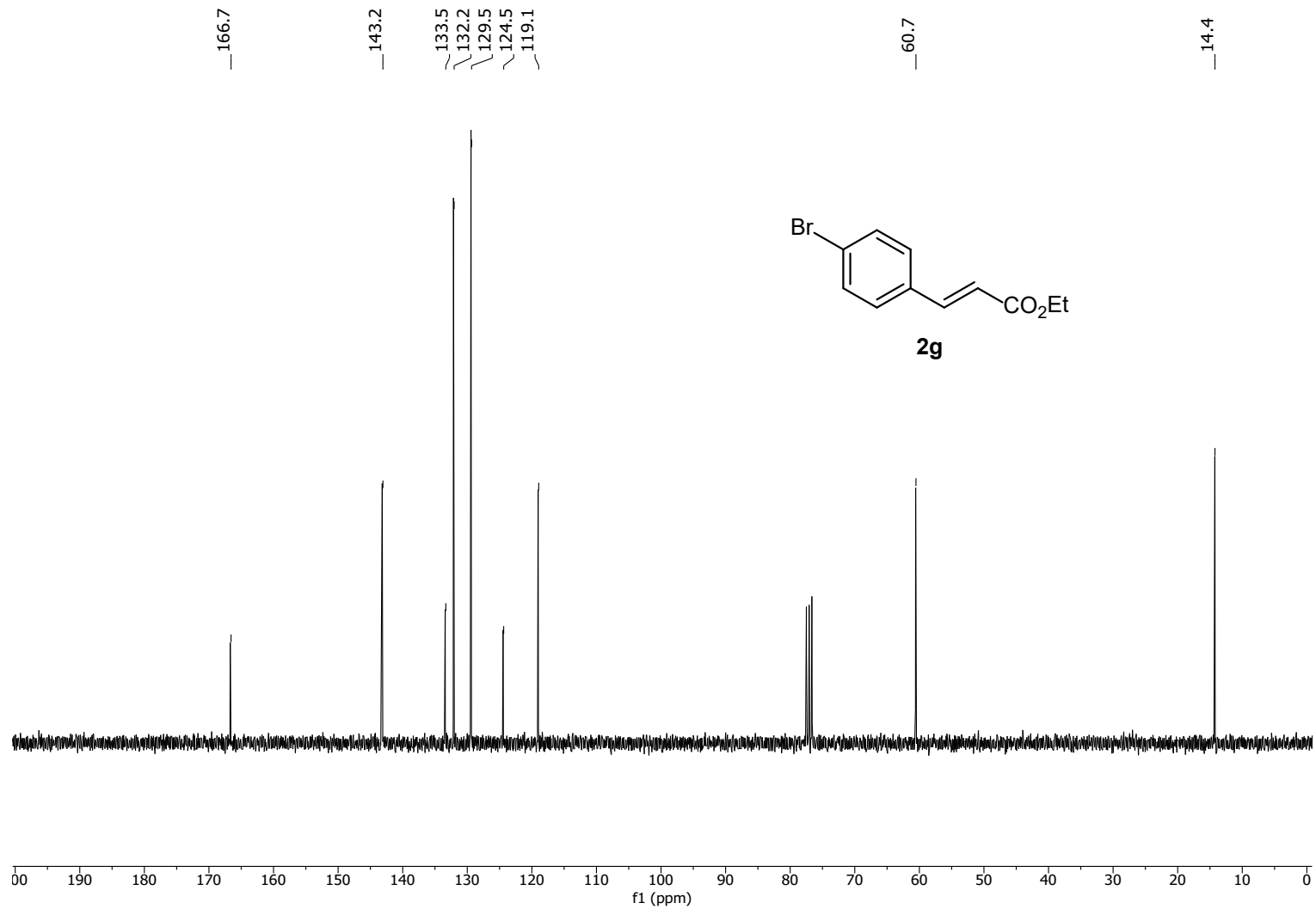
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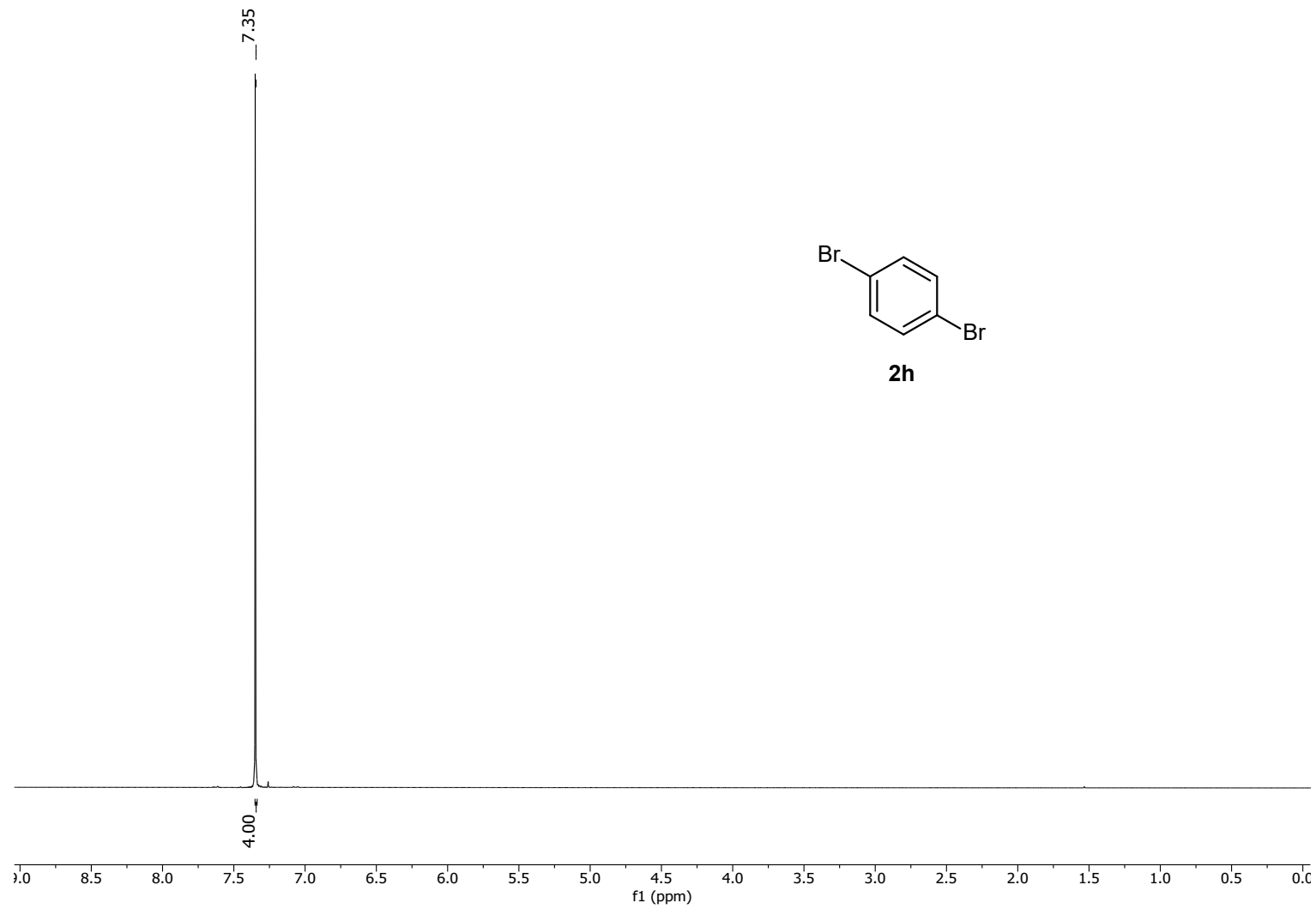
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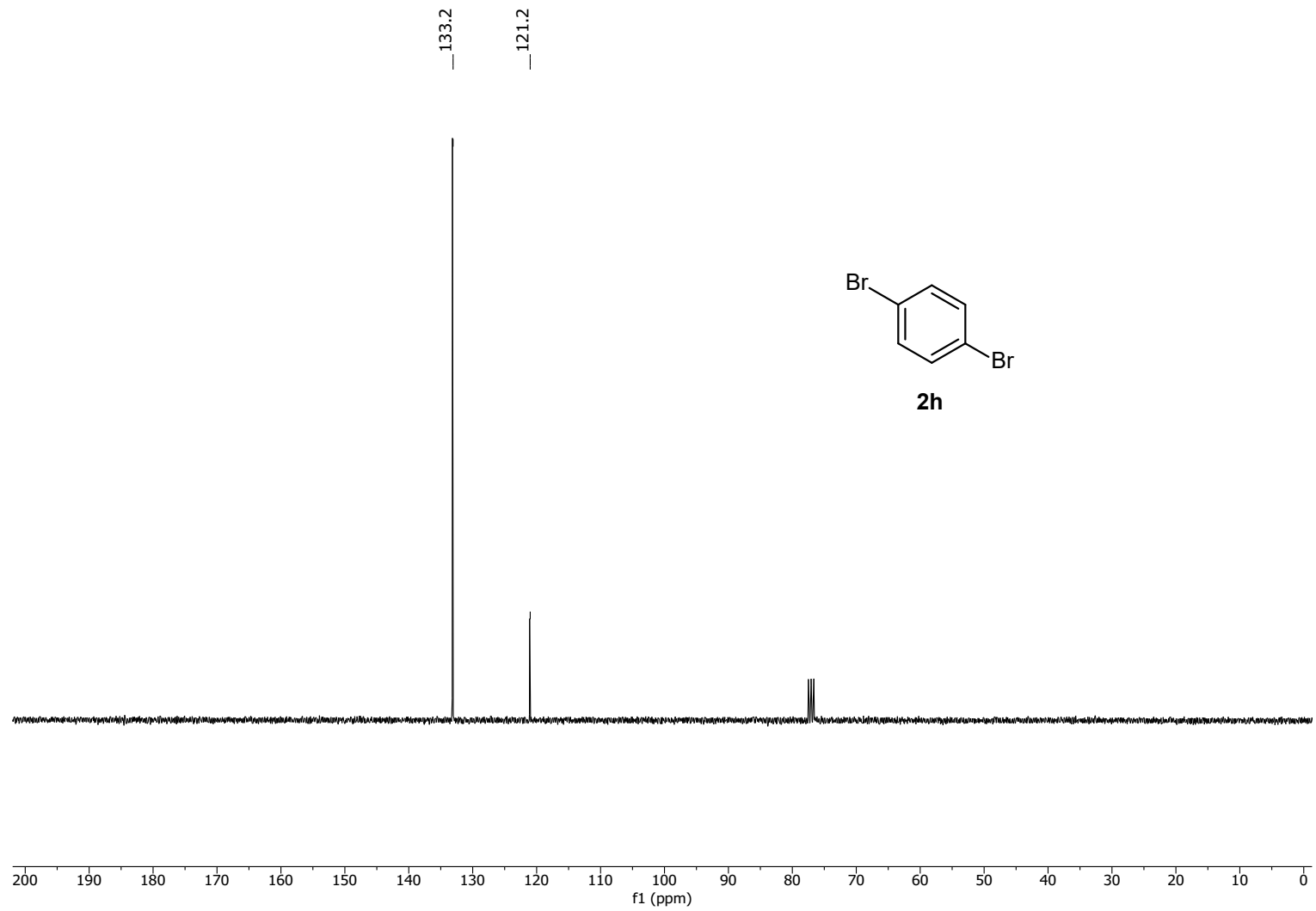
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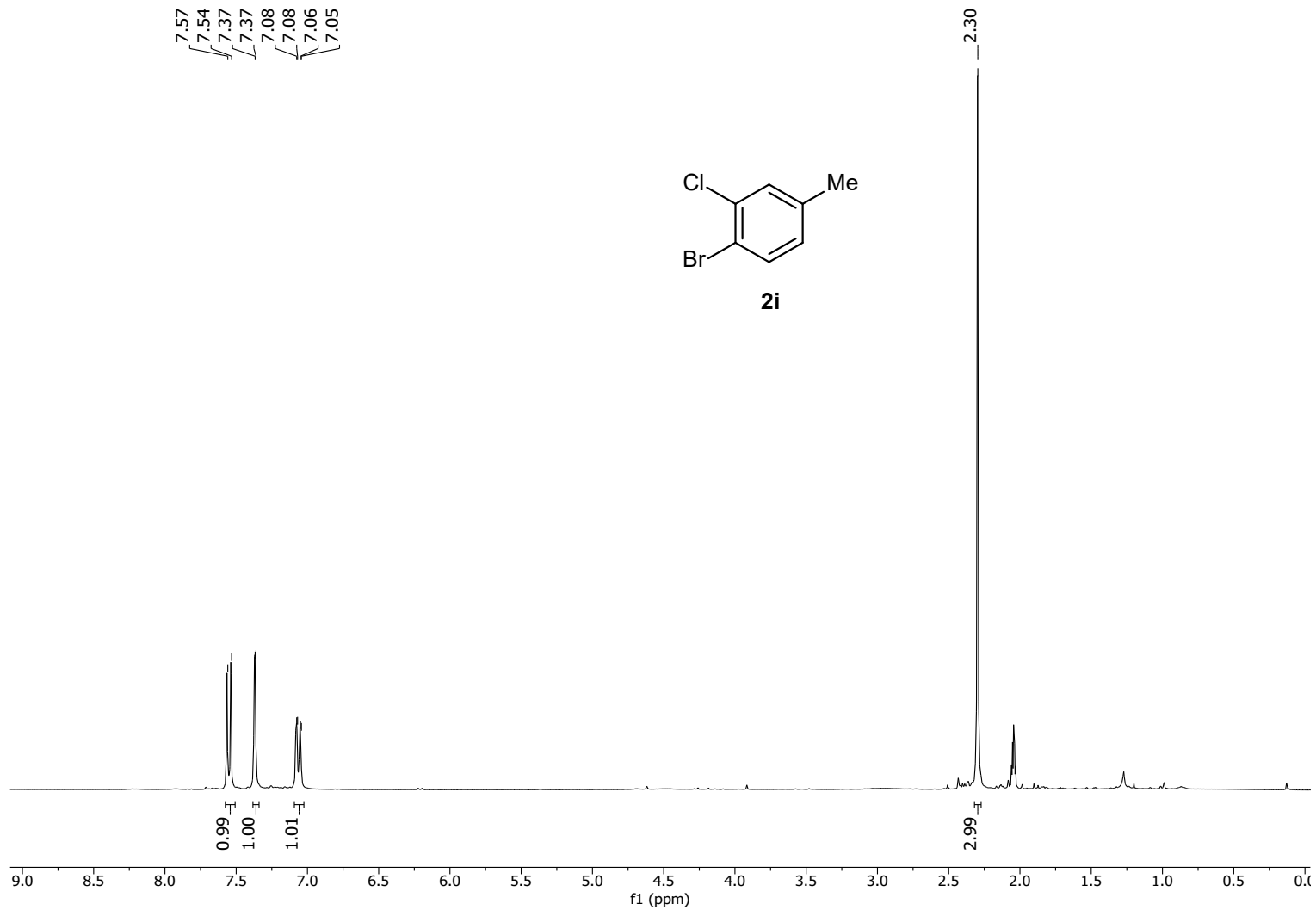
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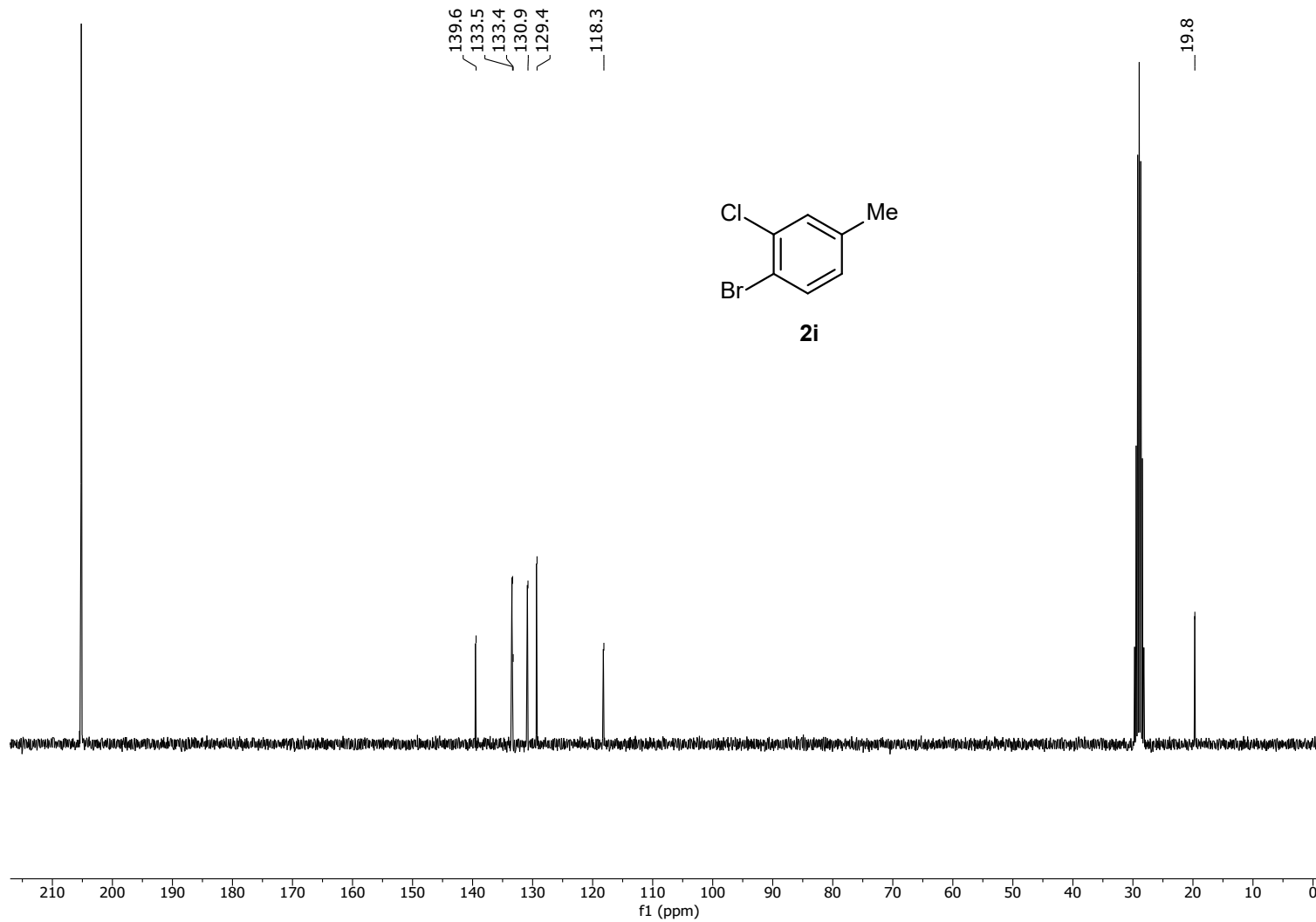
^{13}C NMR (75.4 MHz, CDCl_3)



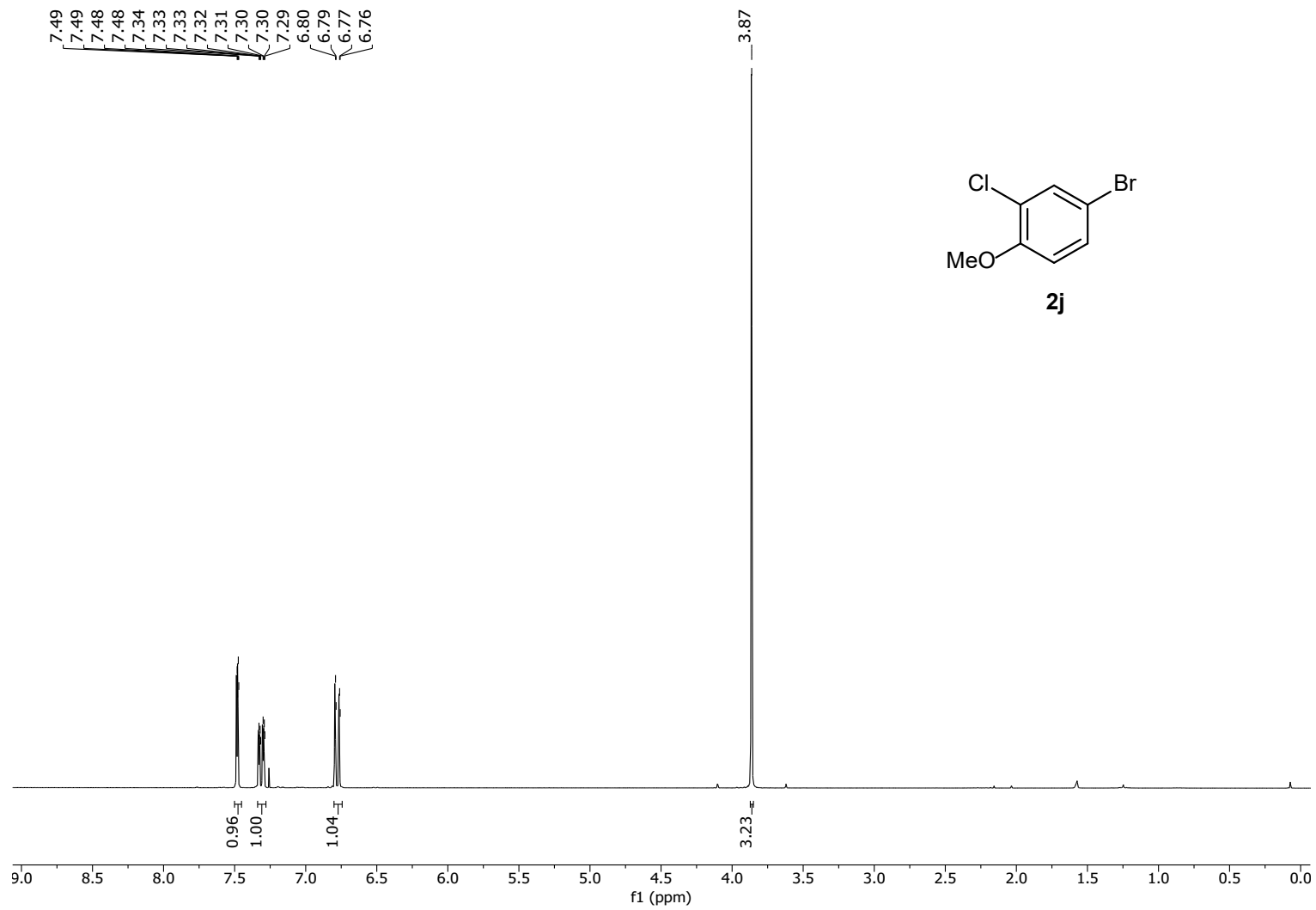
^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$)



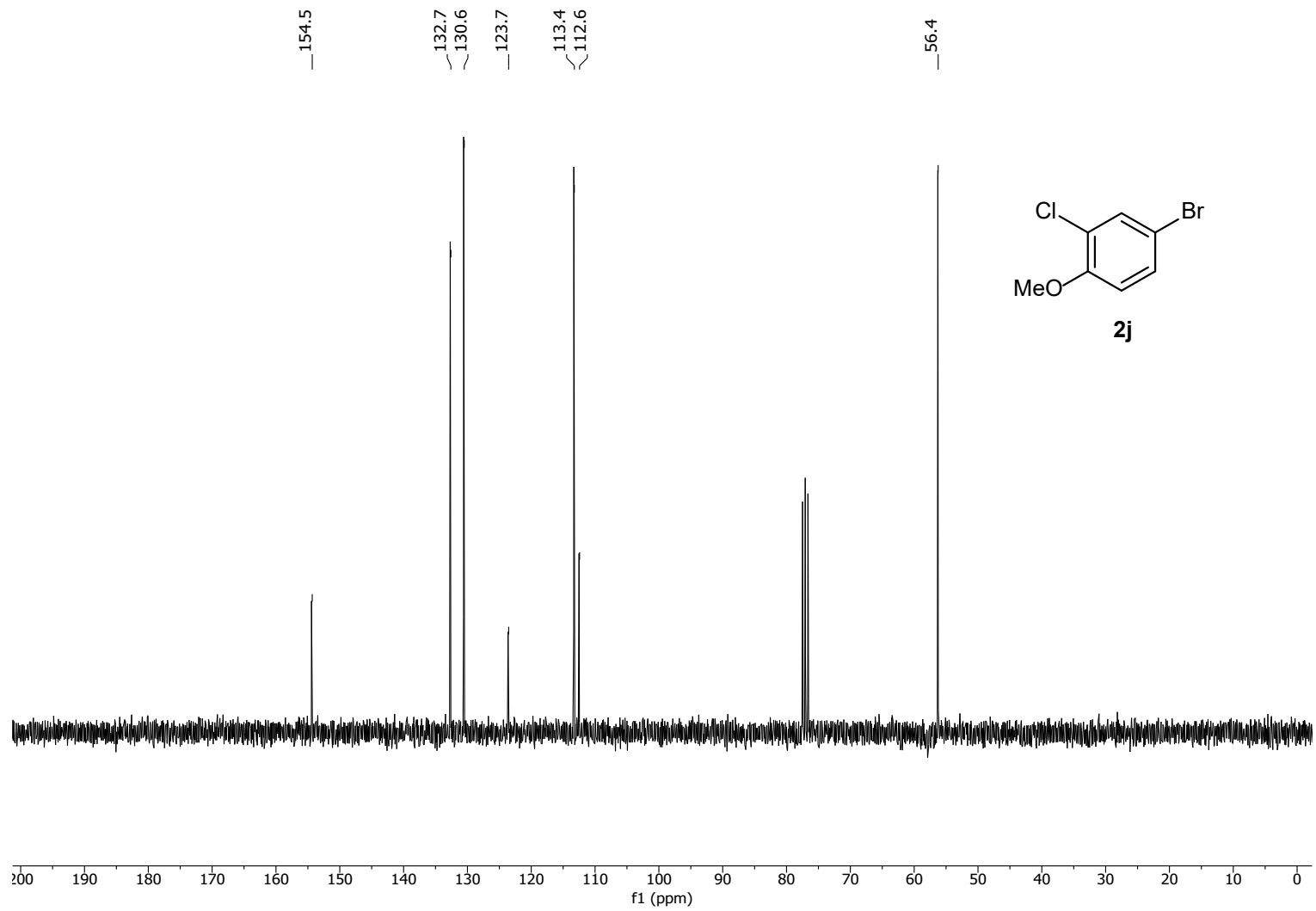
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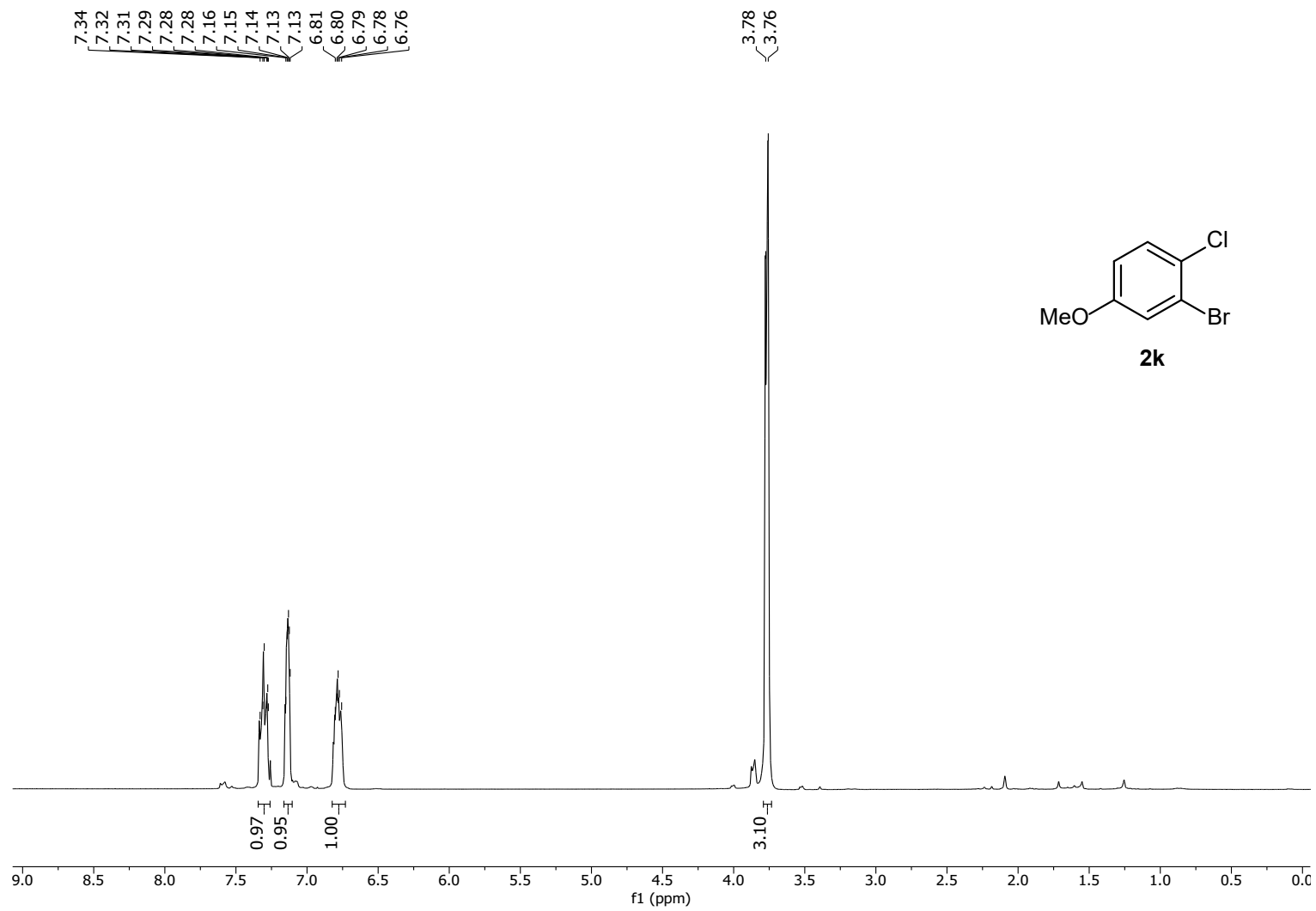
¹H NMR (300 MHz, CDCl₃)



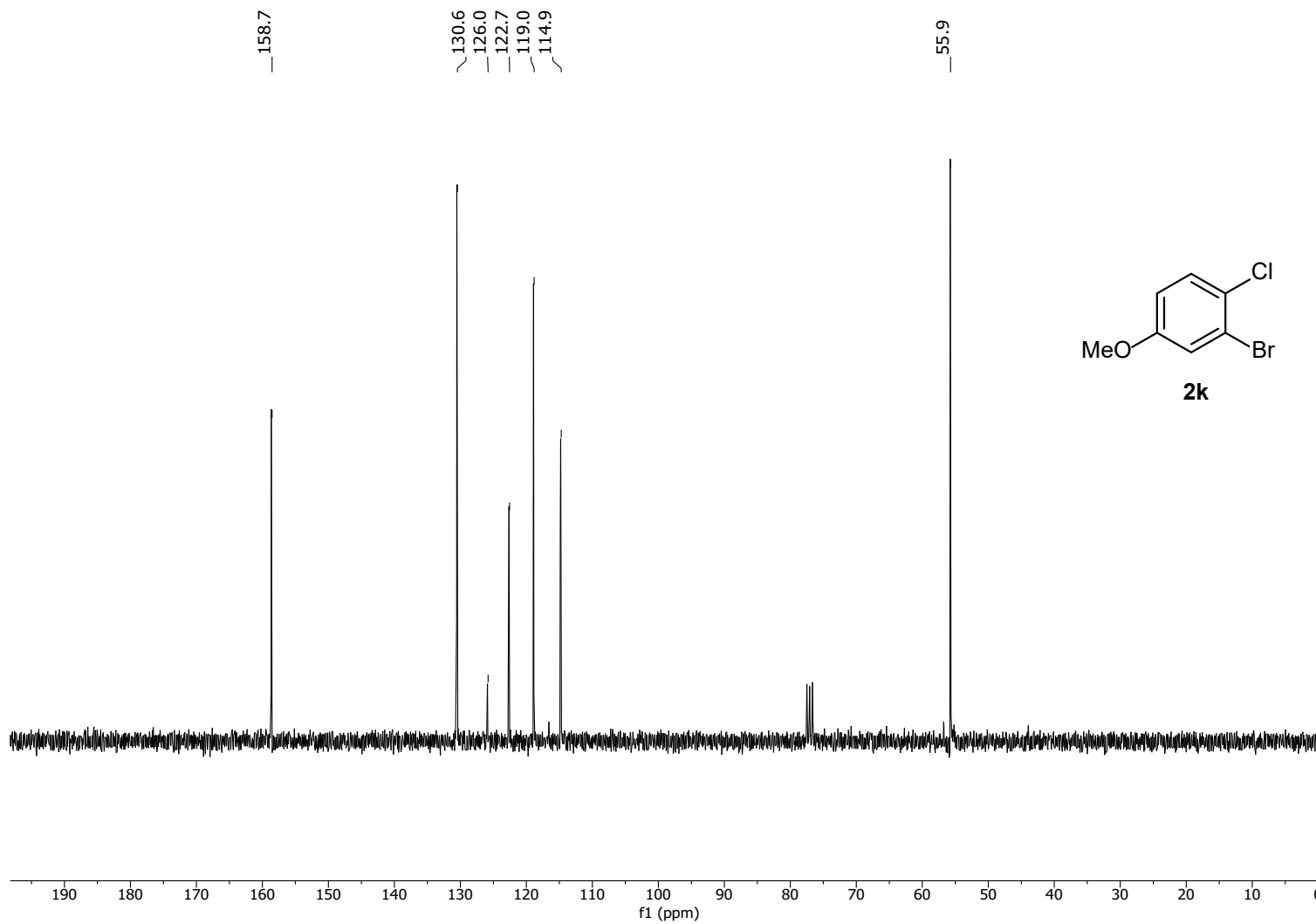
^{13}C NMR (75.4 MHz, CDCl_3)



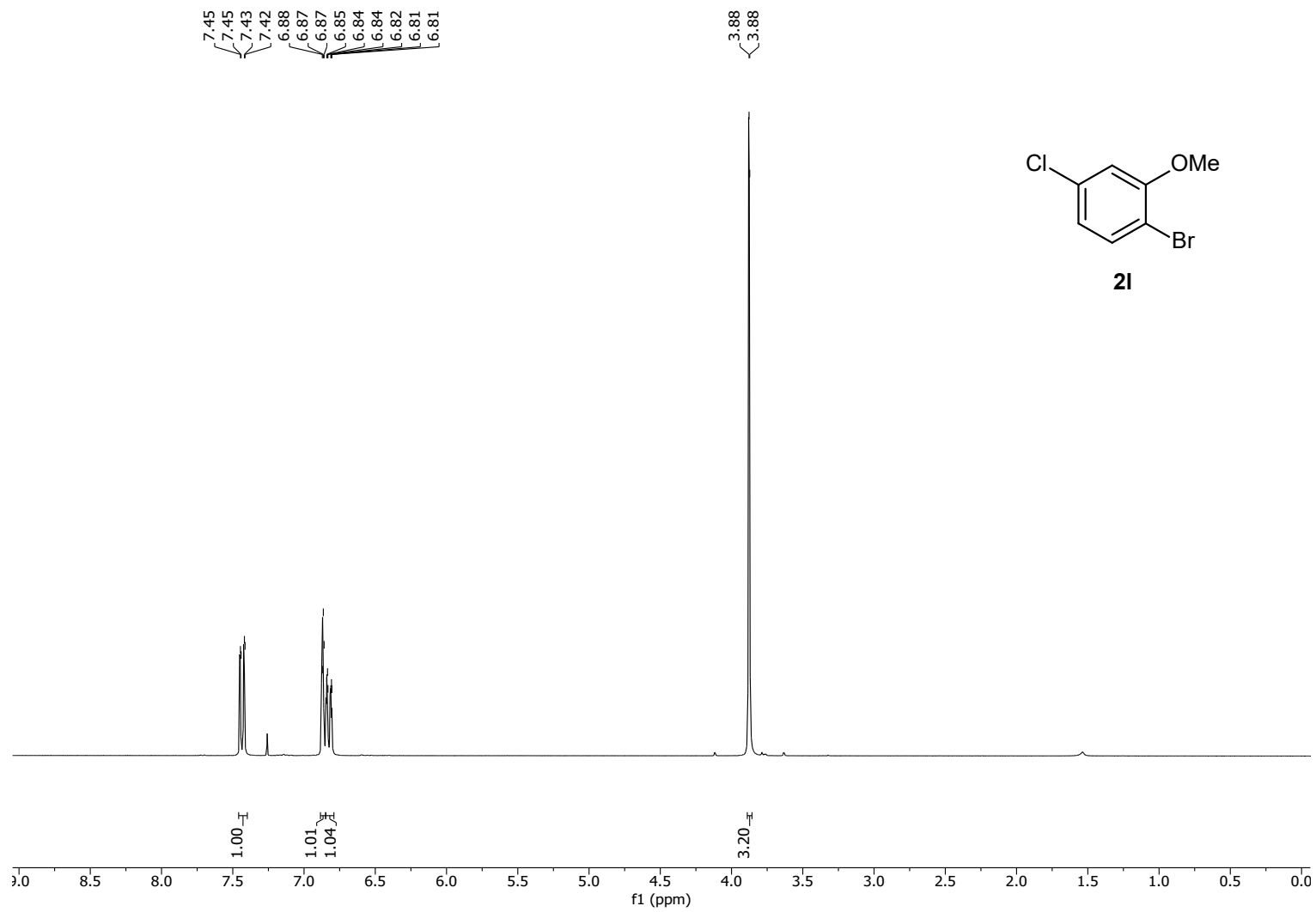
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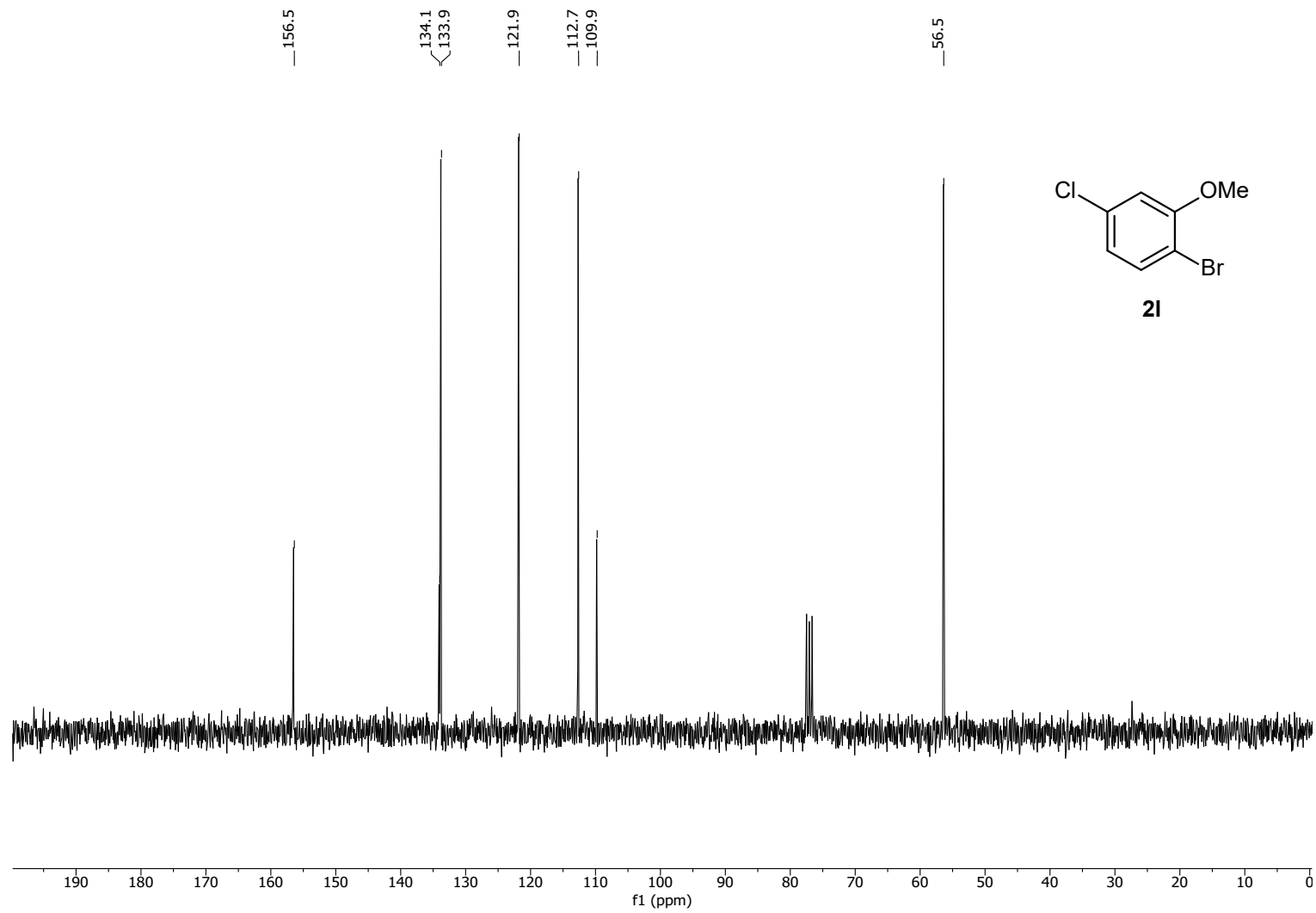
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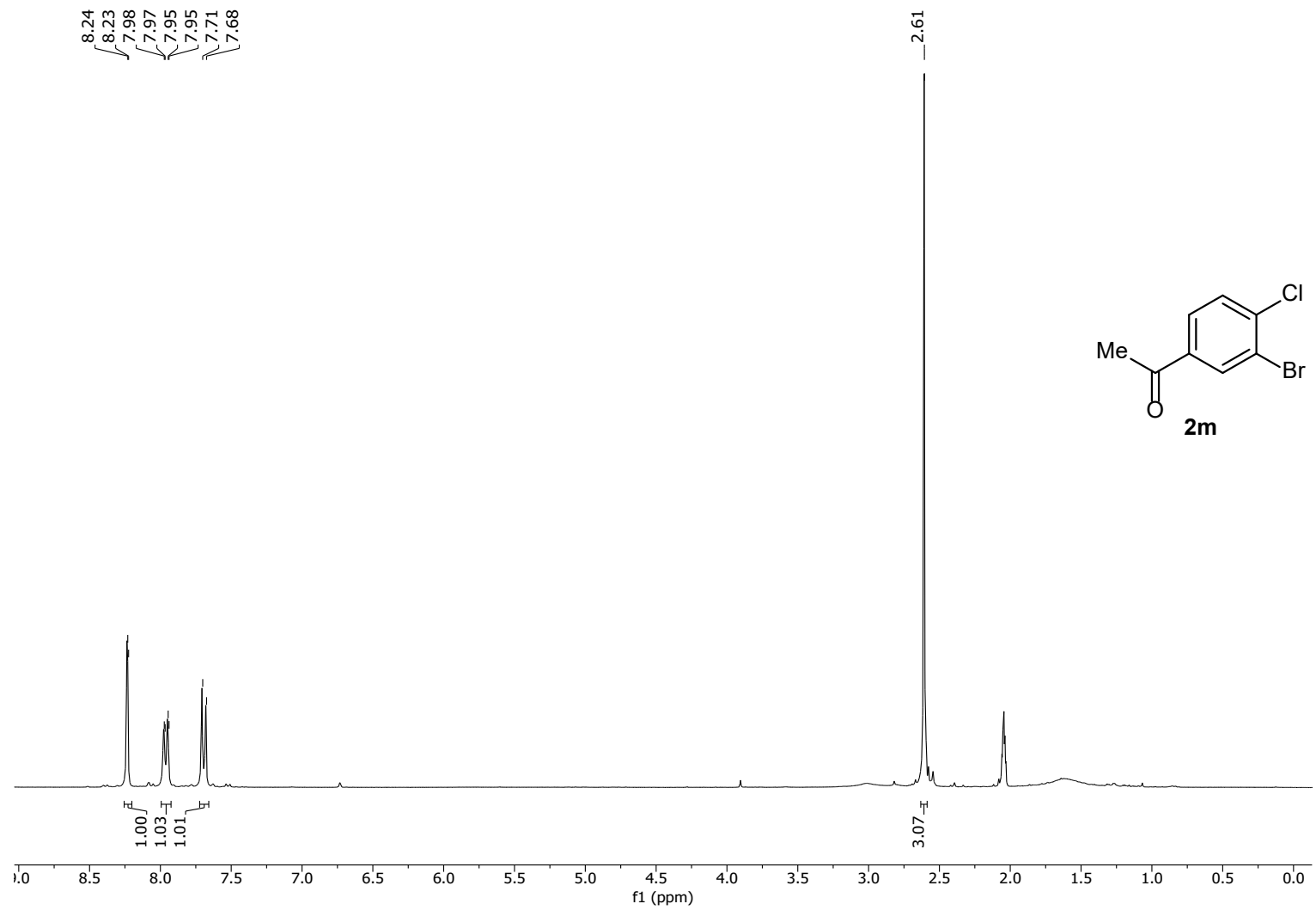
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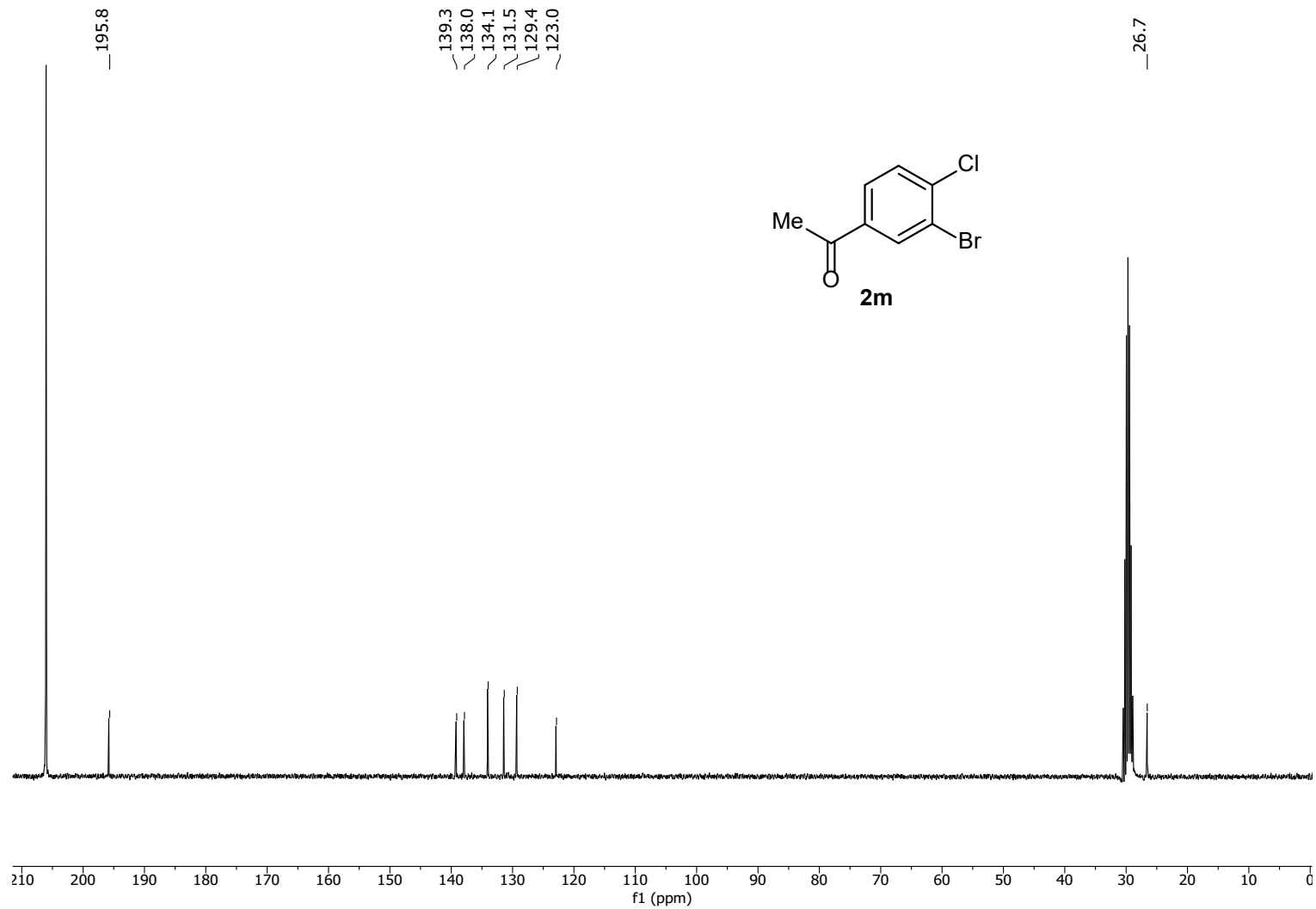
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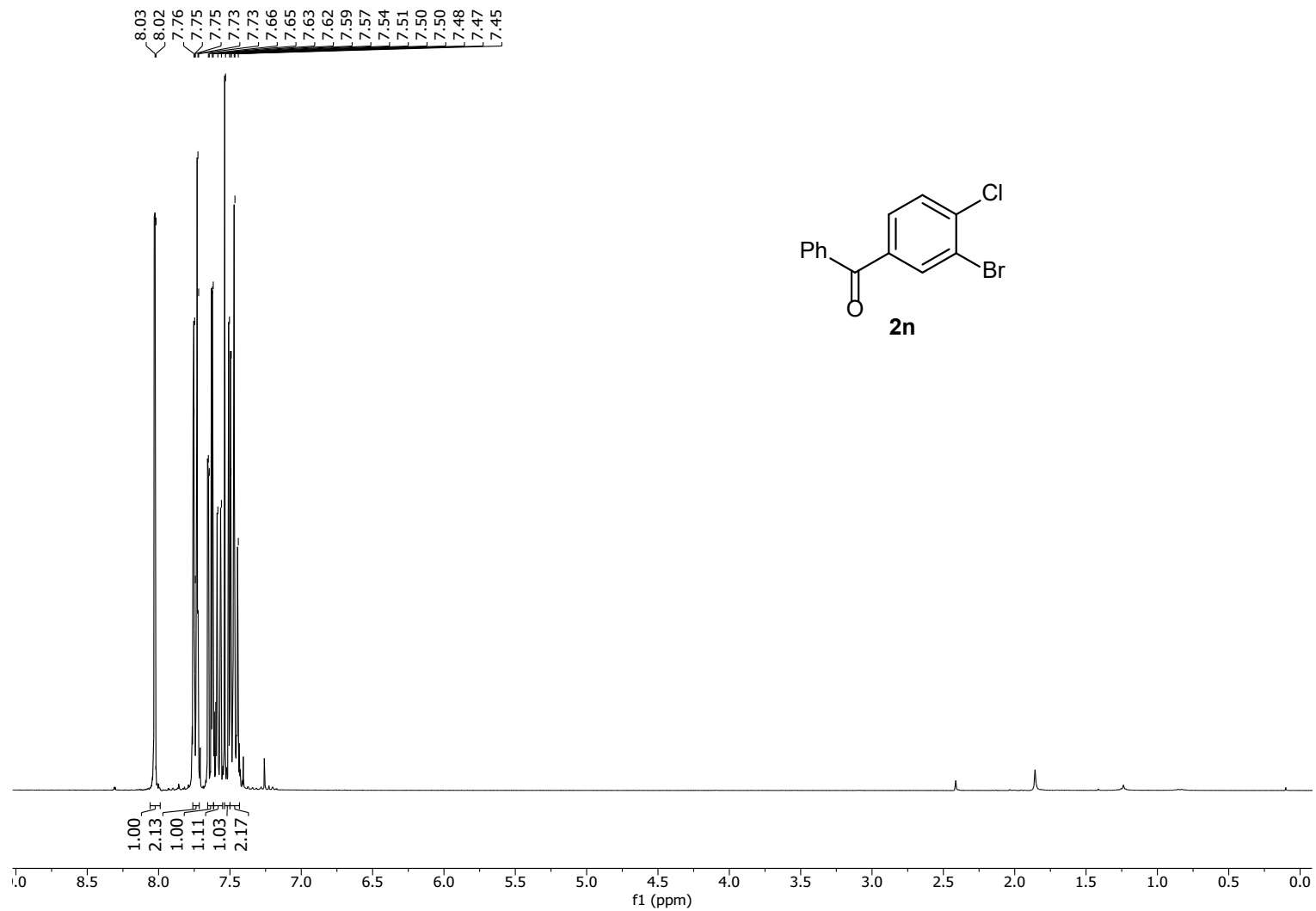
^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$)



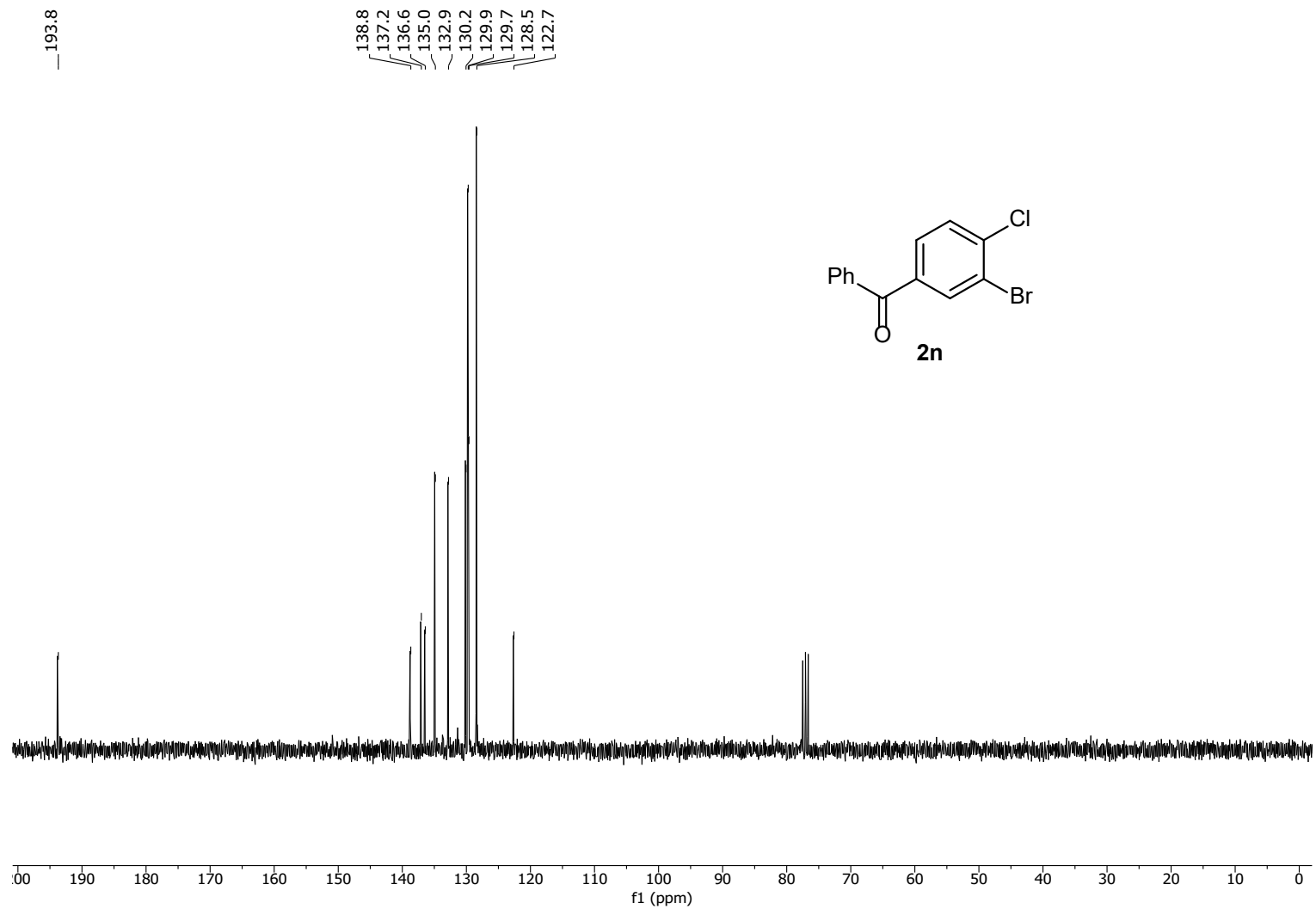
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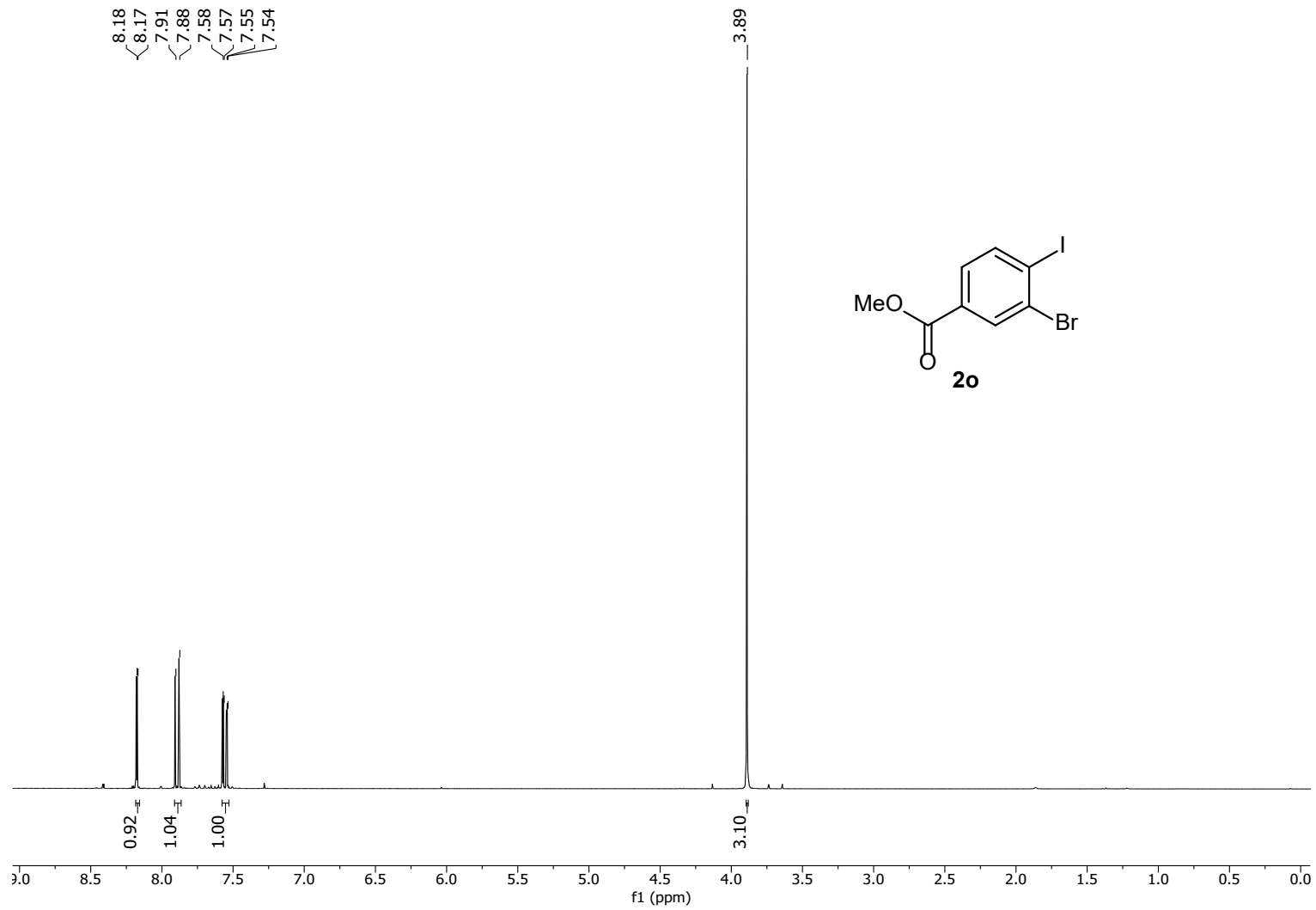
^1H NMR (300 MHz, CDCl_3)



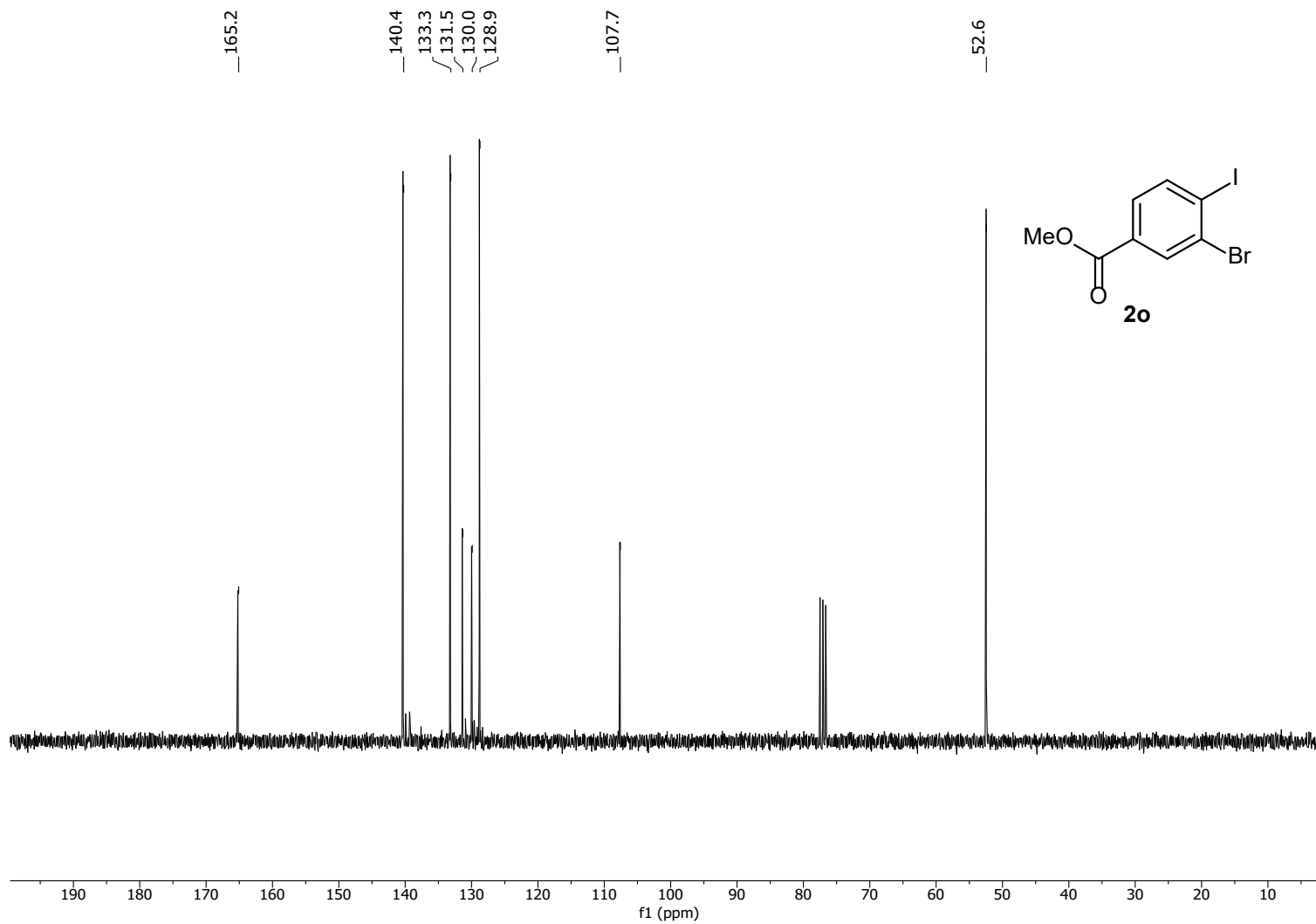
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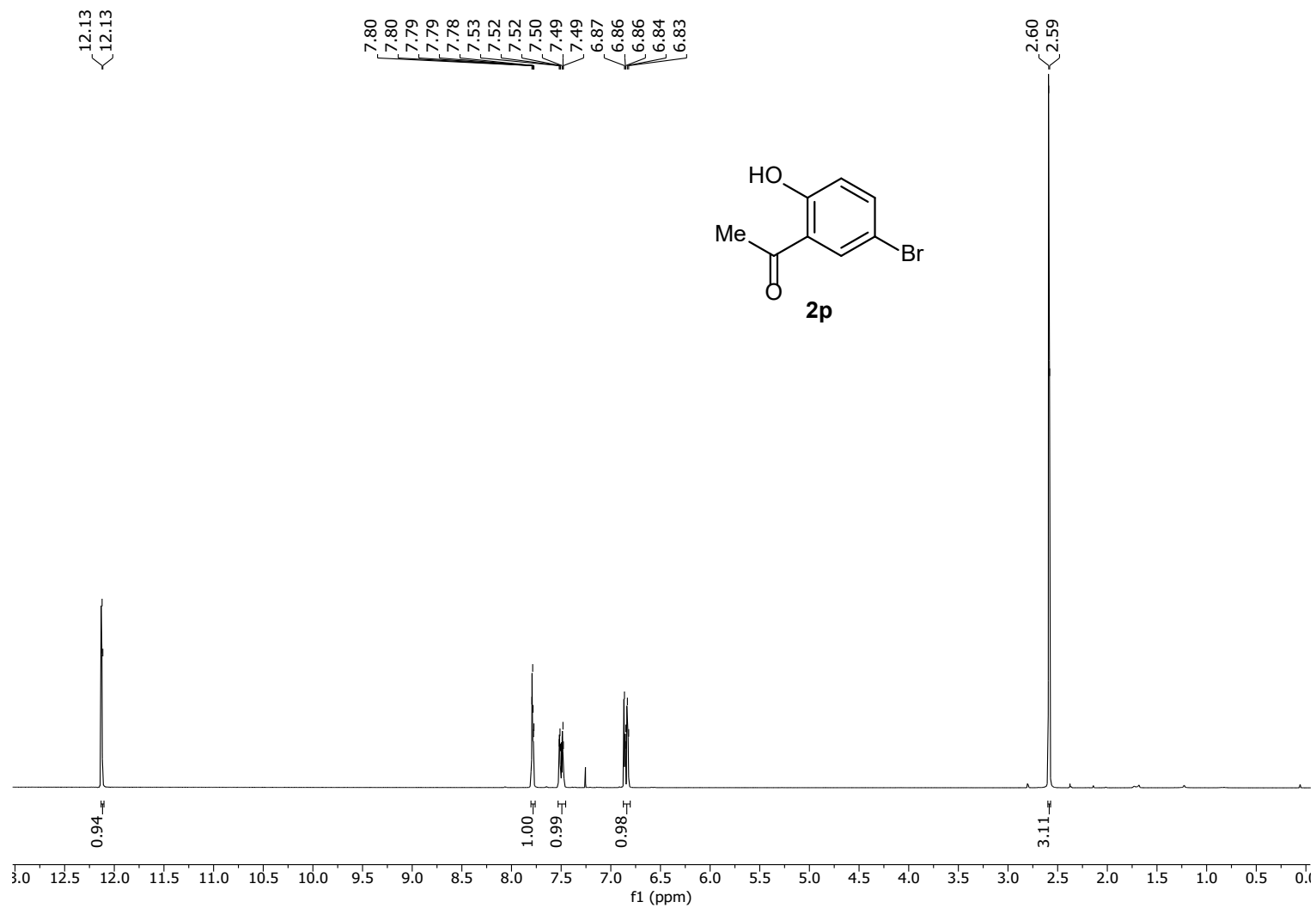
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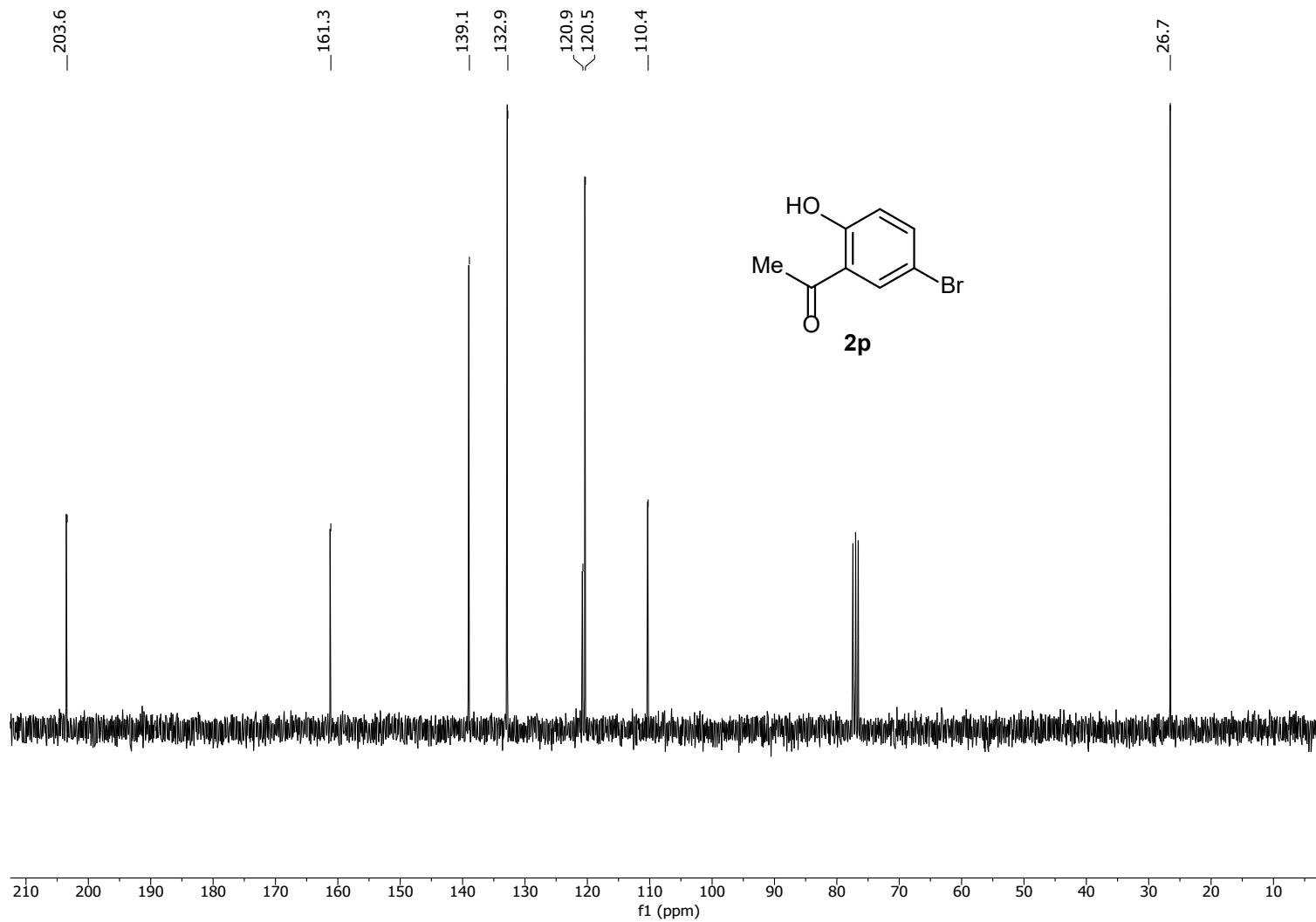
^{13}C NMR (75.4 MHz, CDCl_3)



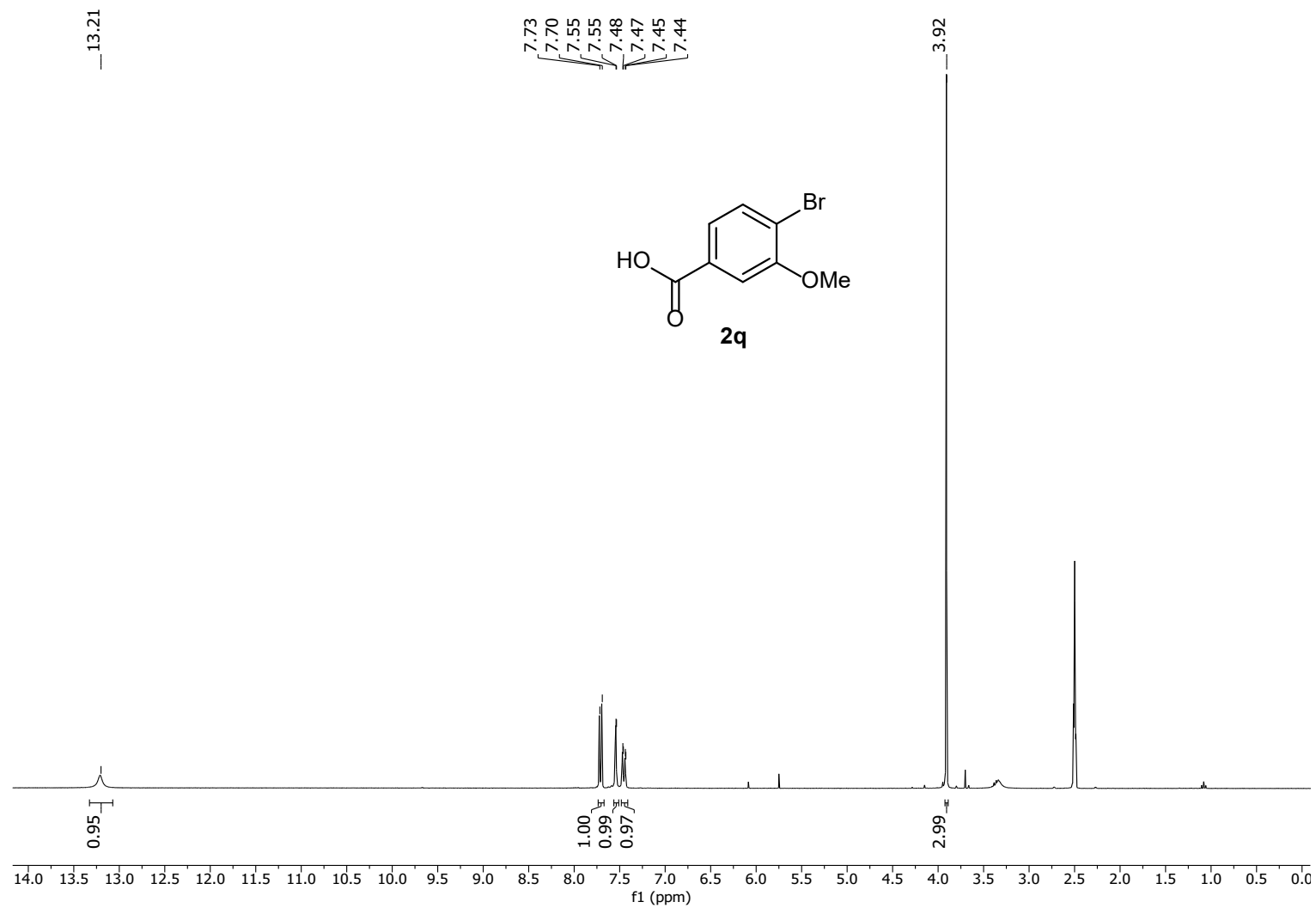
^1H NMR (300 MHz, CDCl_3)



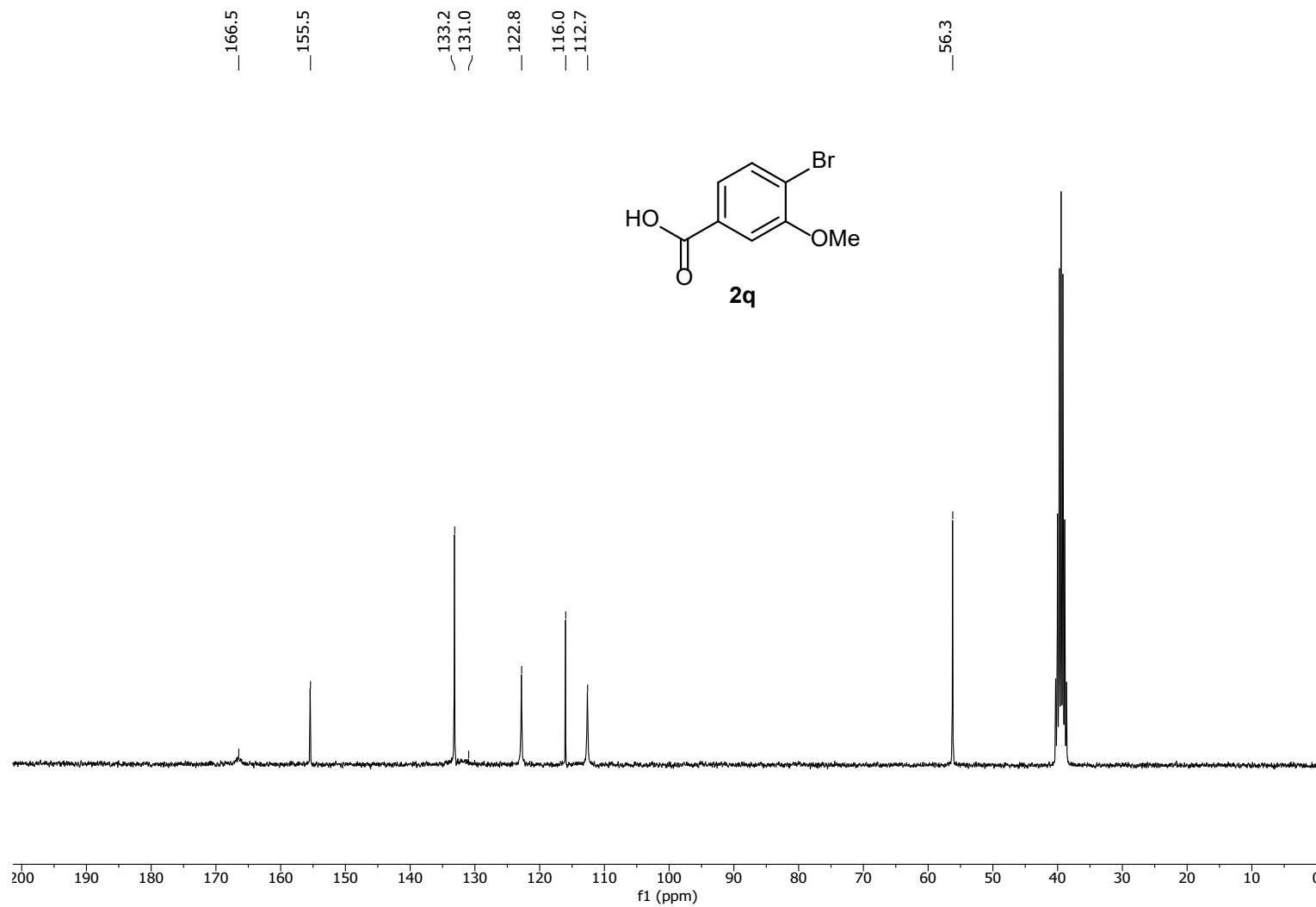
^{13}C NMR (75.4 MHz, CDCl_3)



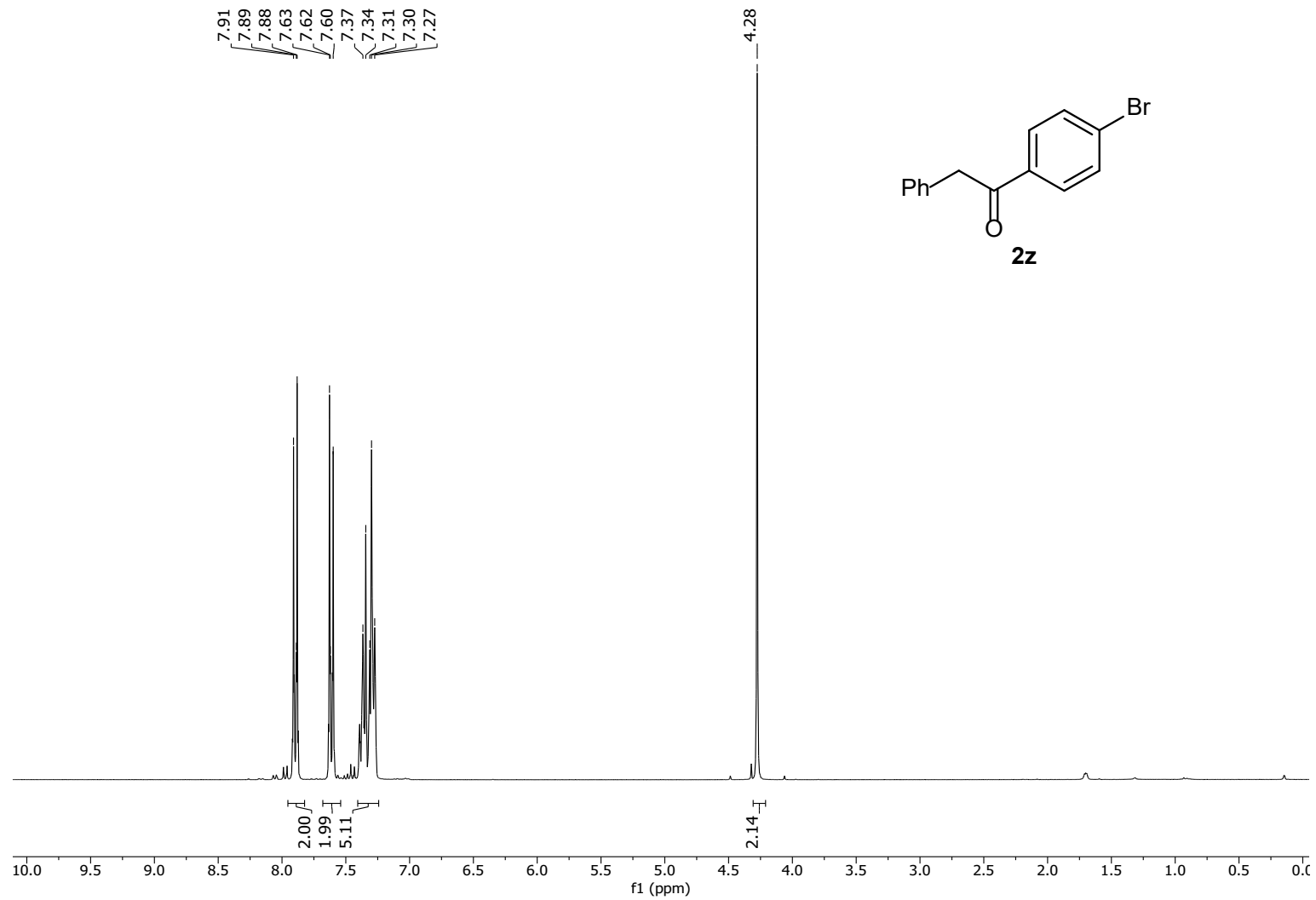
^1H NMR (300 MHz, $\text{DMSO}-d_6$)



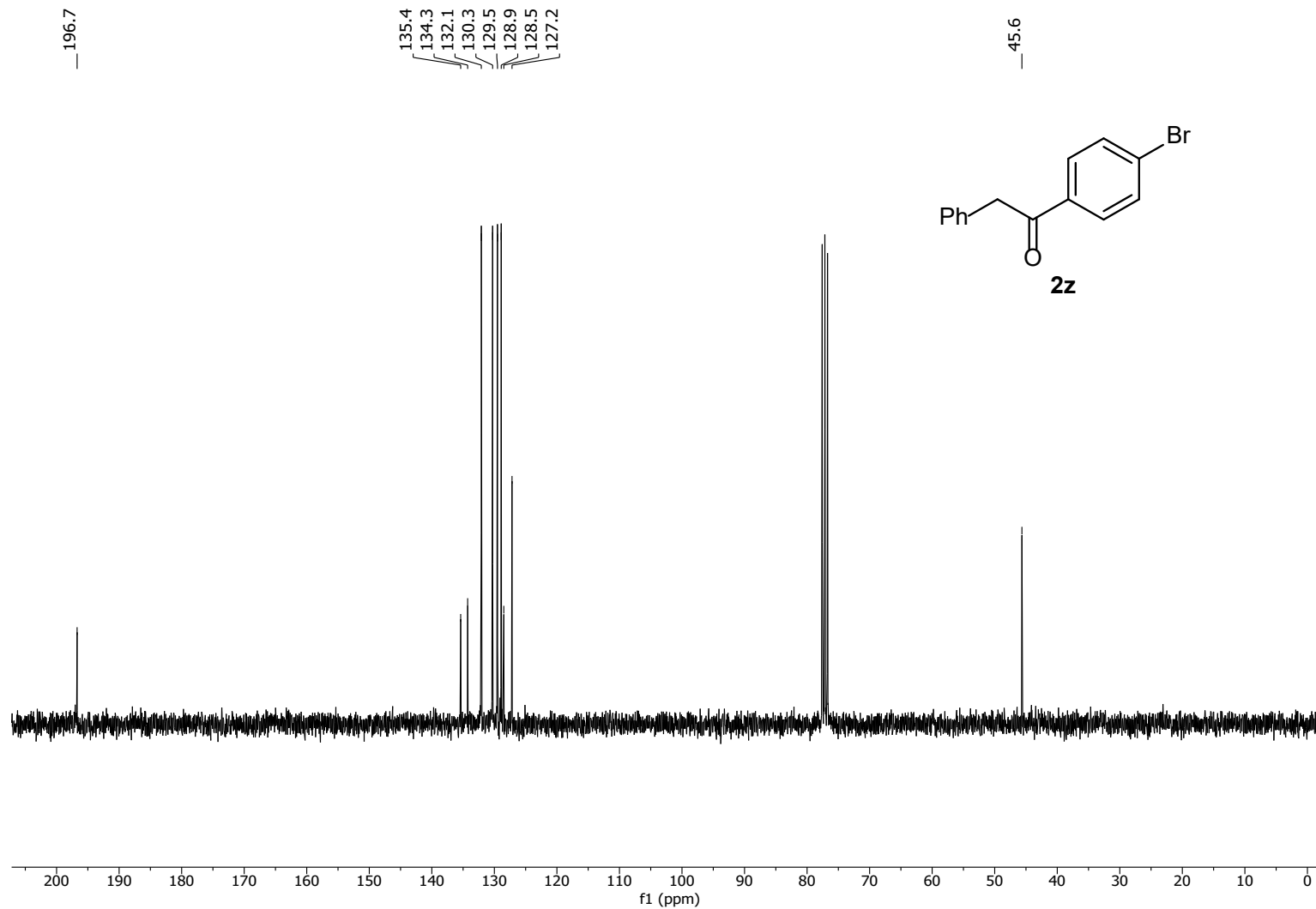
^{13}C NMR (75.4 MHz, $\text{DMSO-}d_6$)



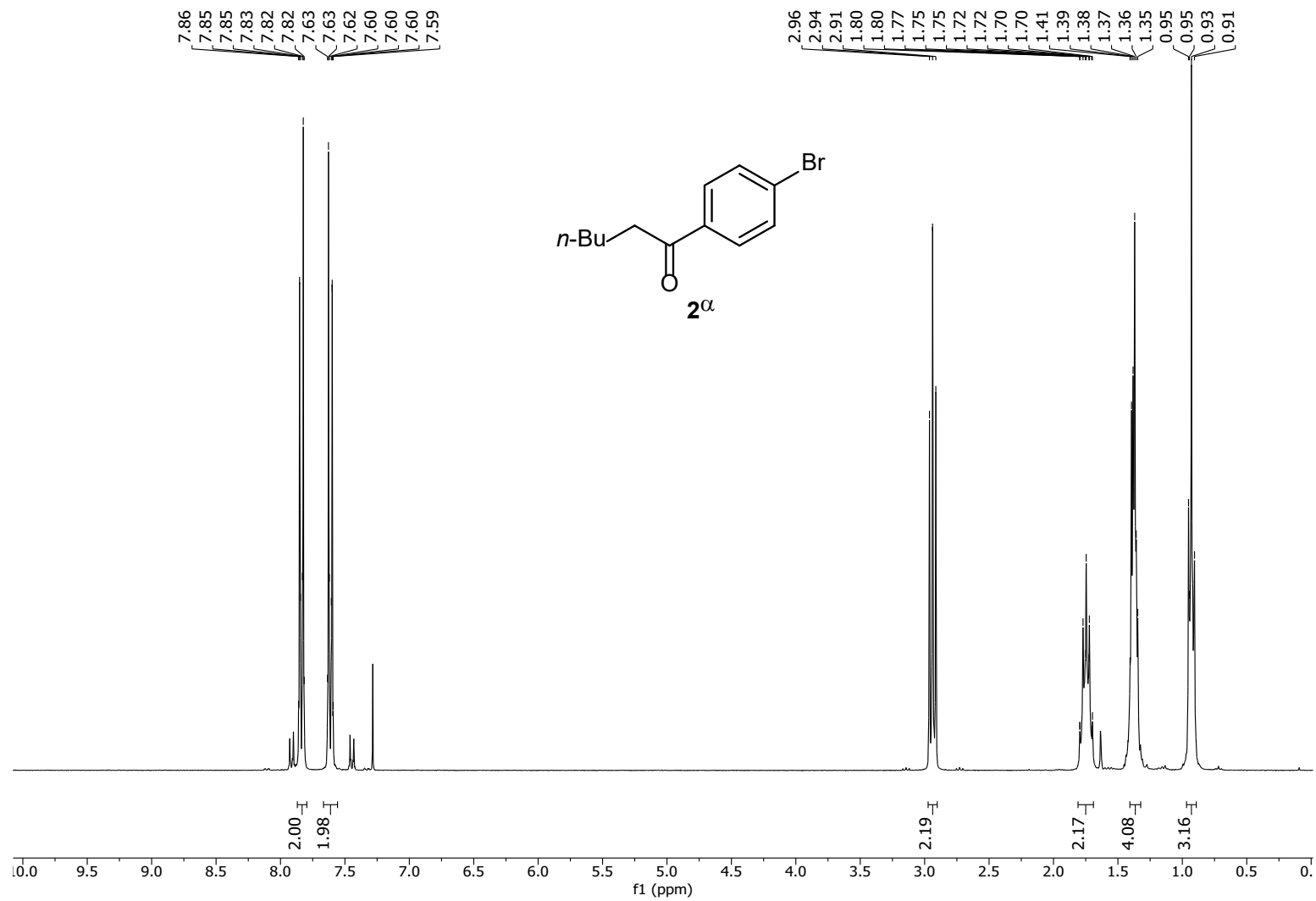
^1H NMR (300 MHz, CDCl_3)



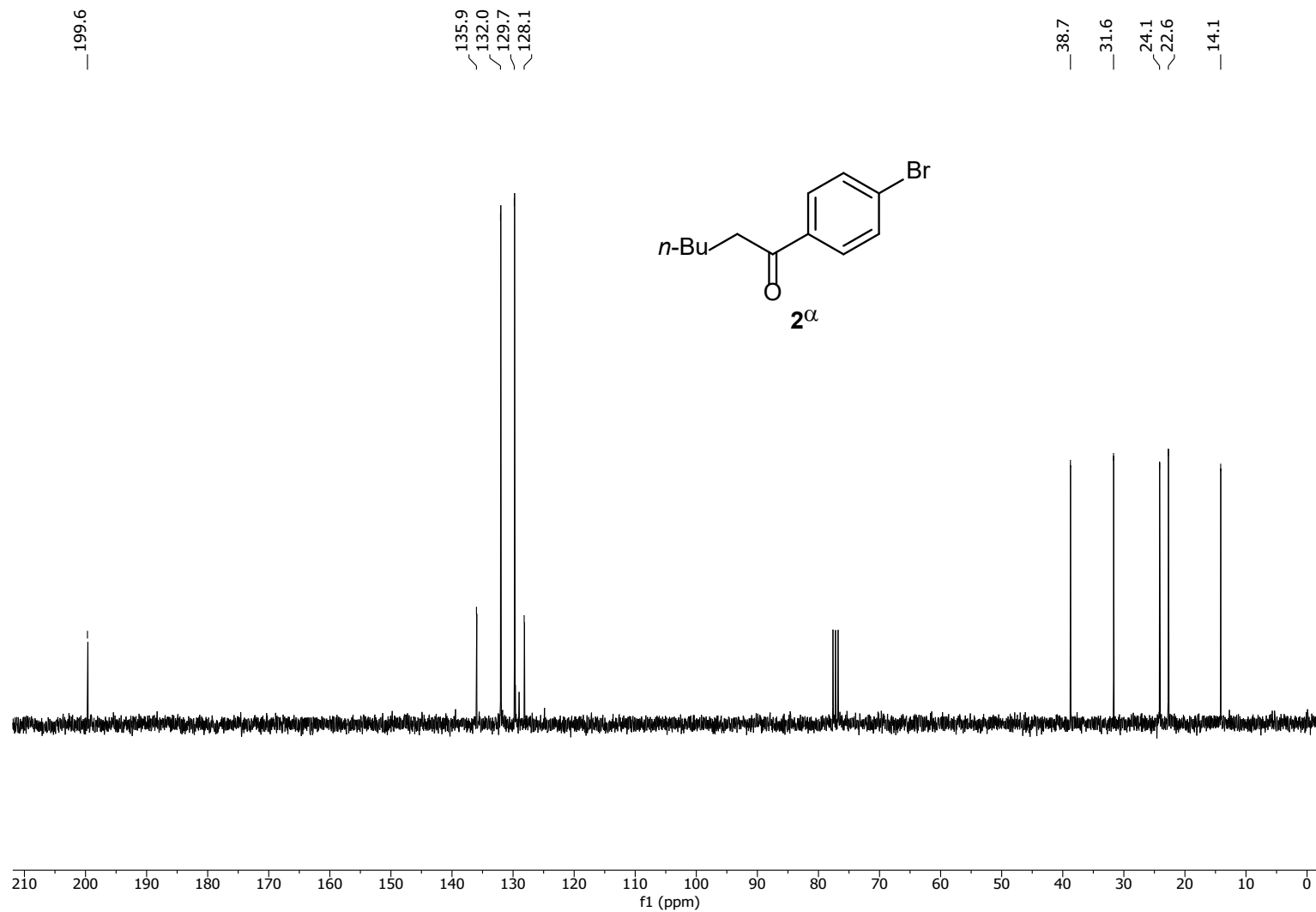
^{13}C NMR (75.4 MHz, CDCl_3)



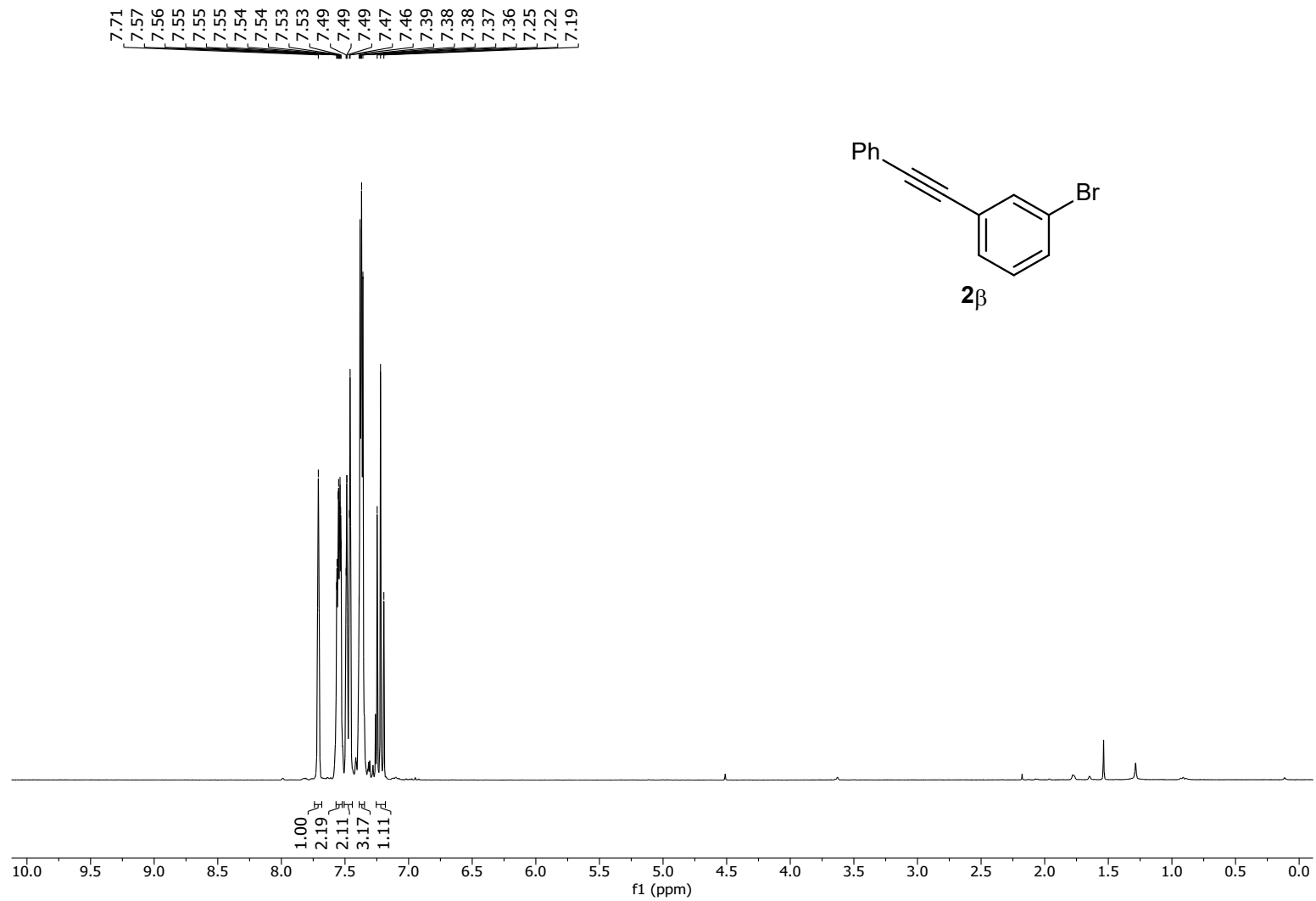
^1H NMR (300 MHz, CDCl_3)



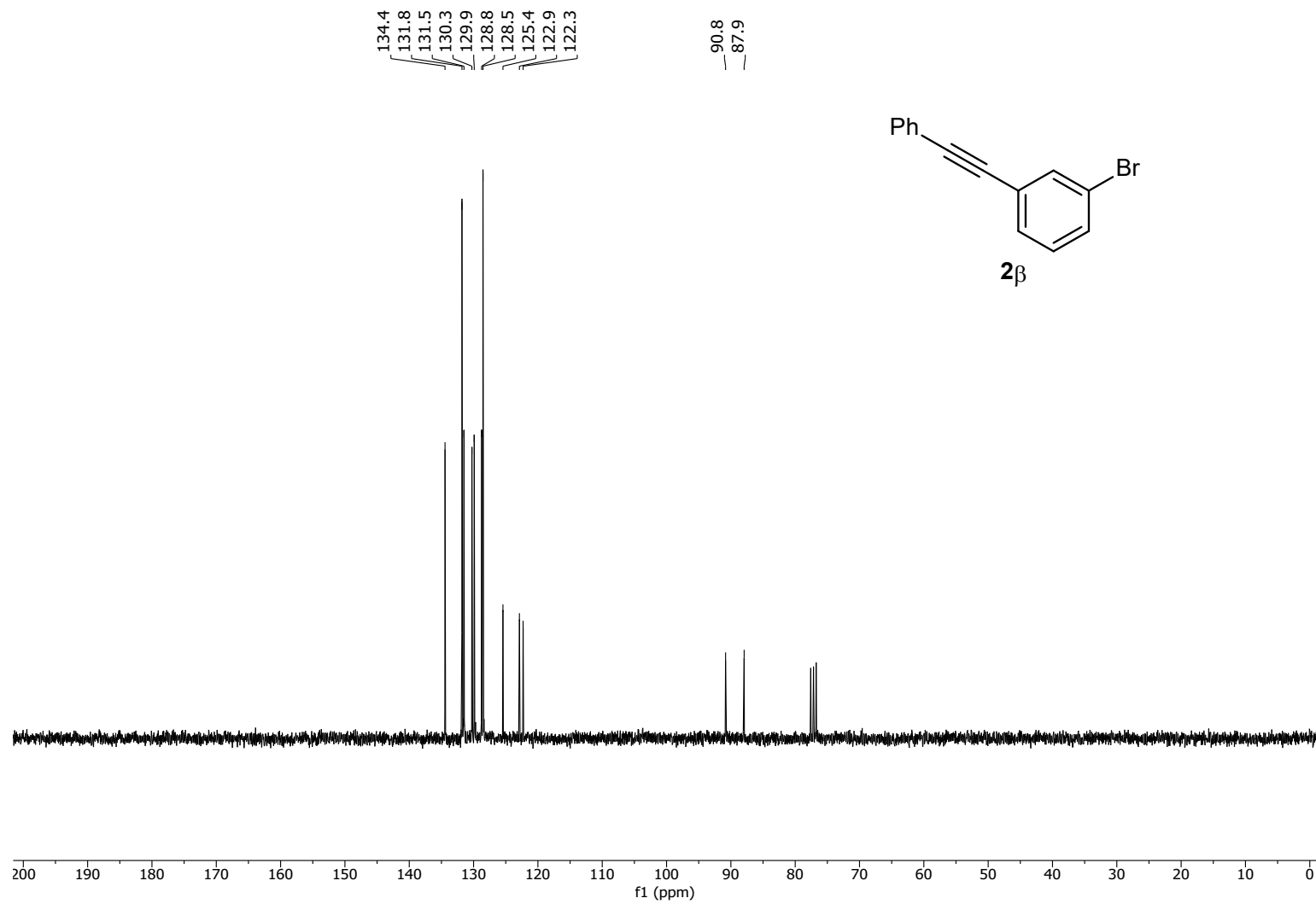
^{13}C NMR (75.4 MHz, CDCl_3)



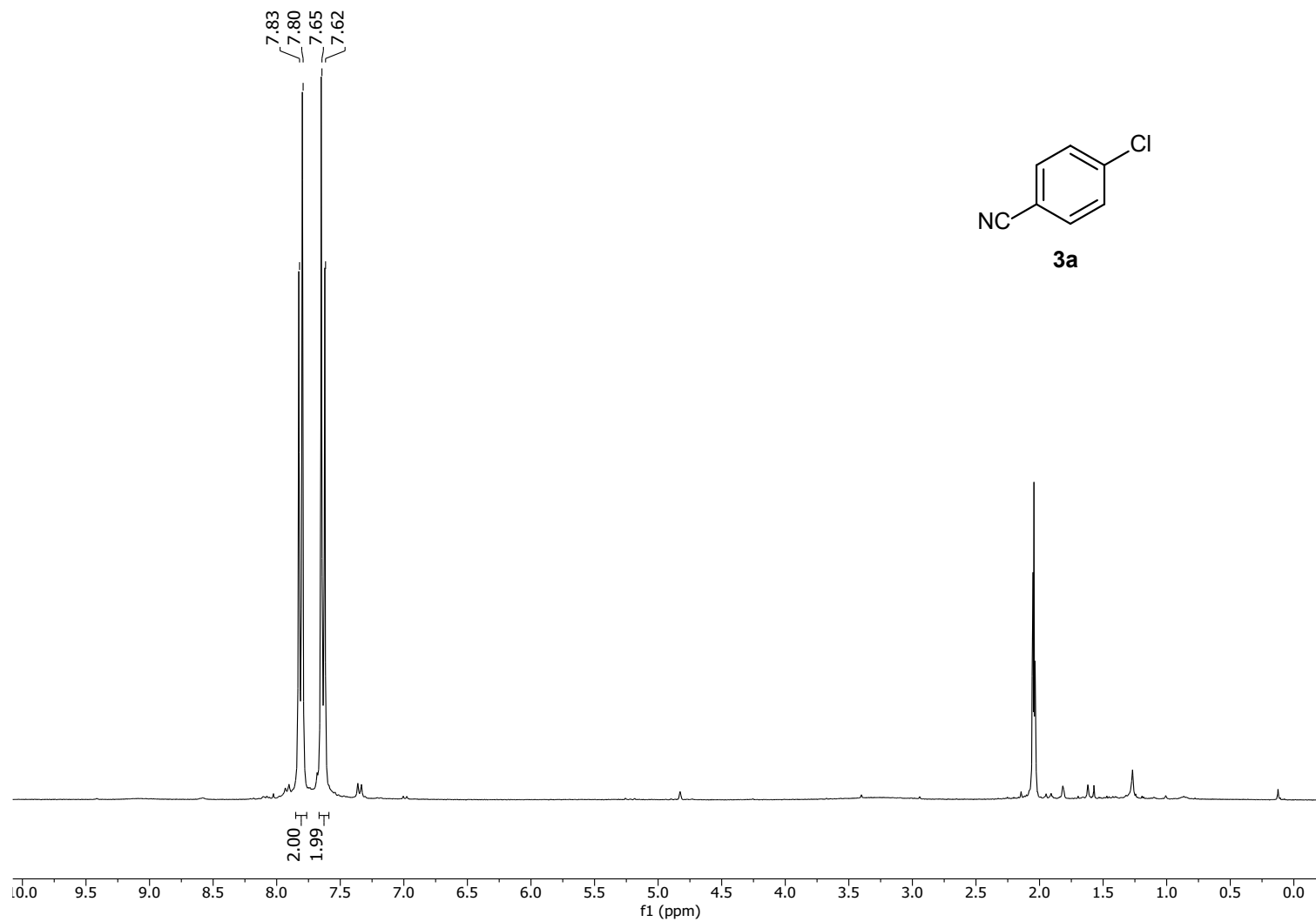
^1H NMR (300 MHz, CDCl_3)



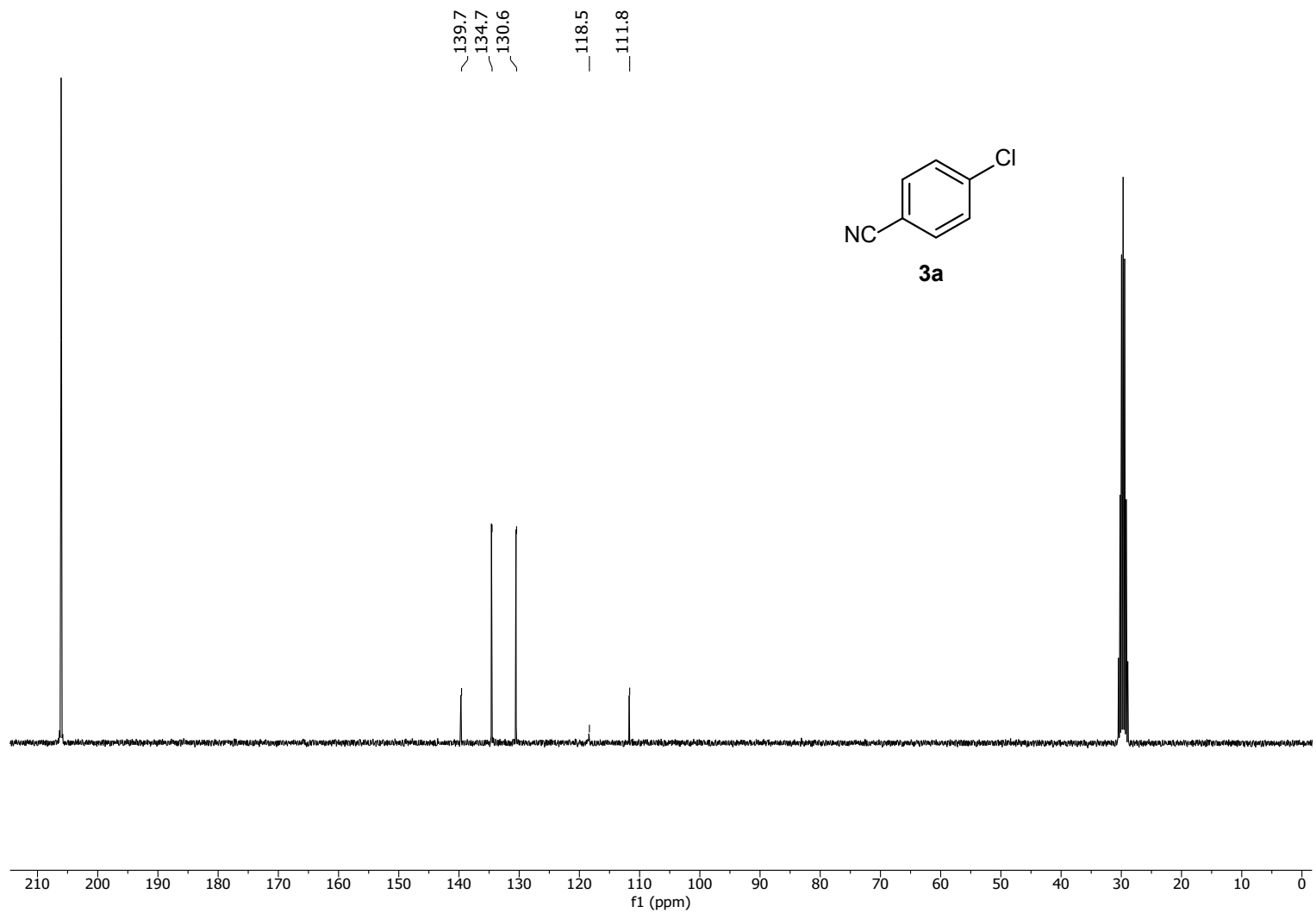
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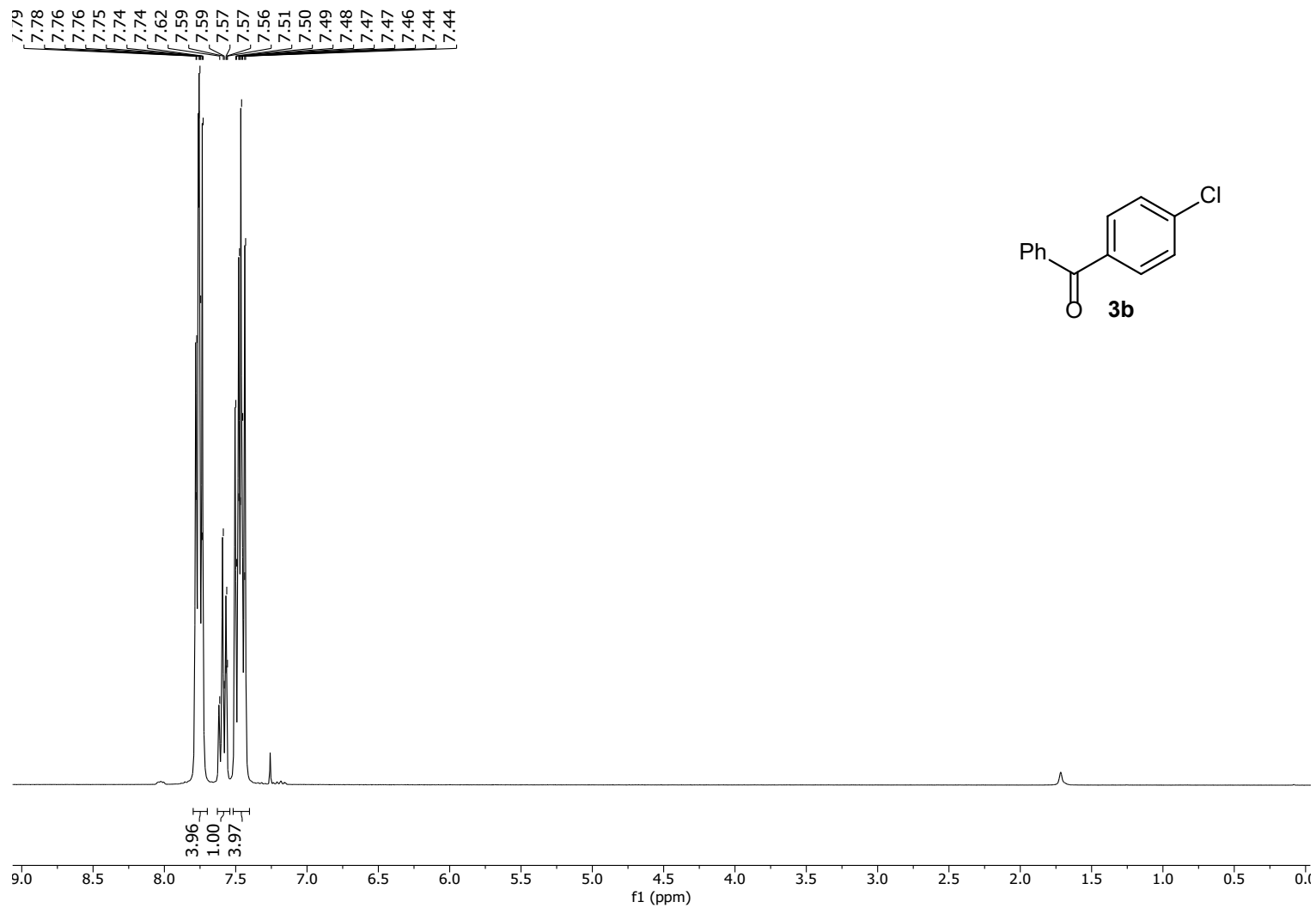
^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$)



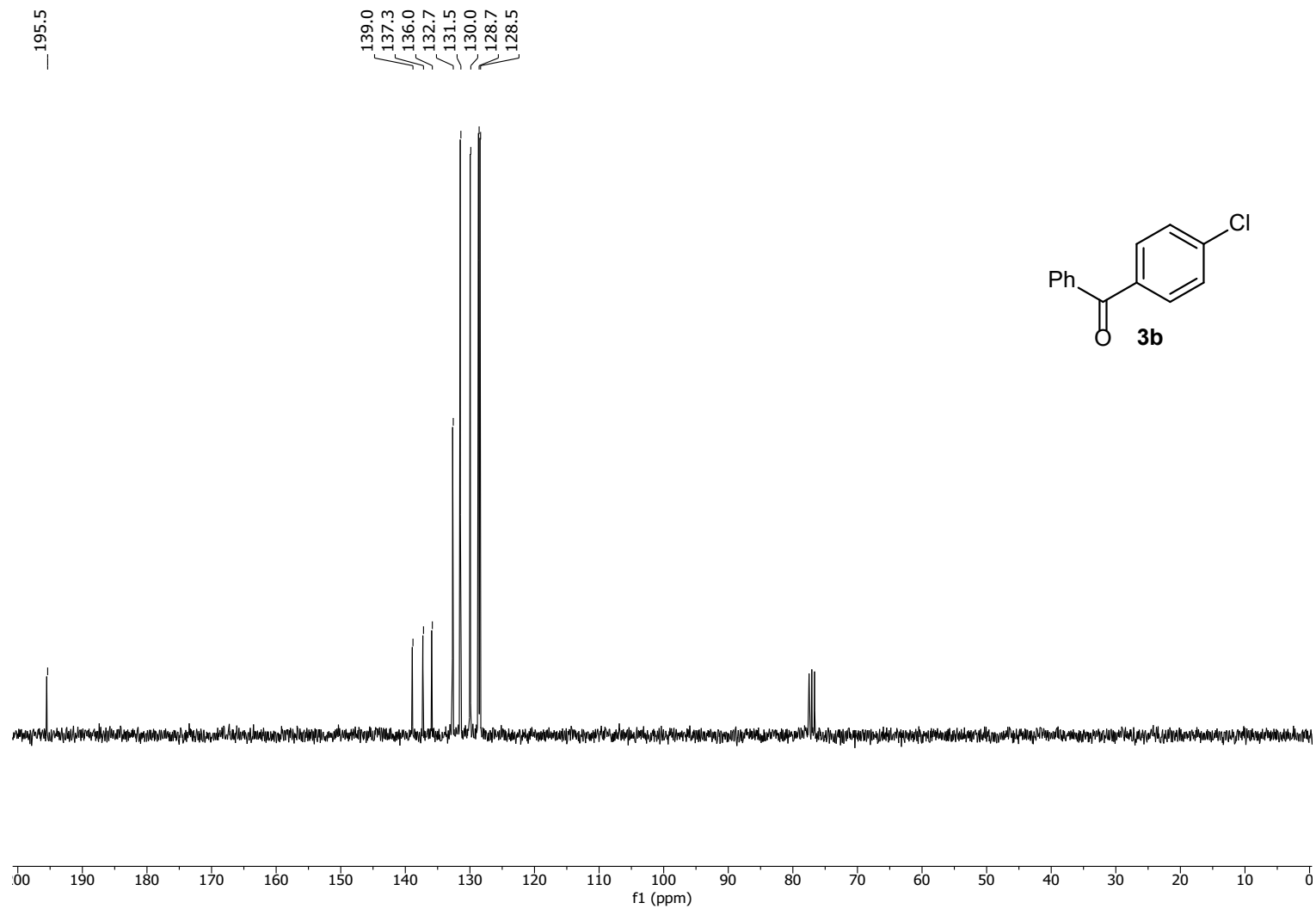
^{13}C NMR (75.4 MHz, $(\text{CD}_3)_2\text{CO}$)



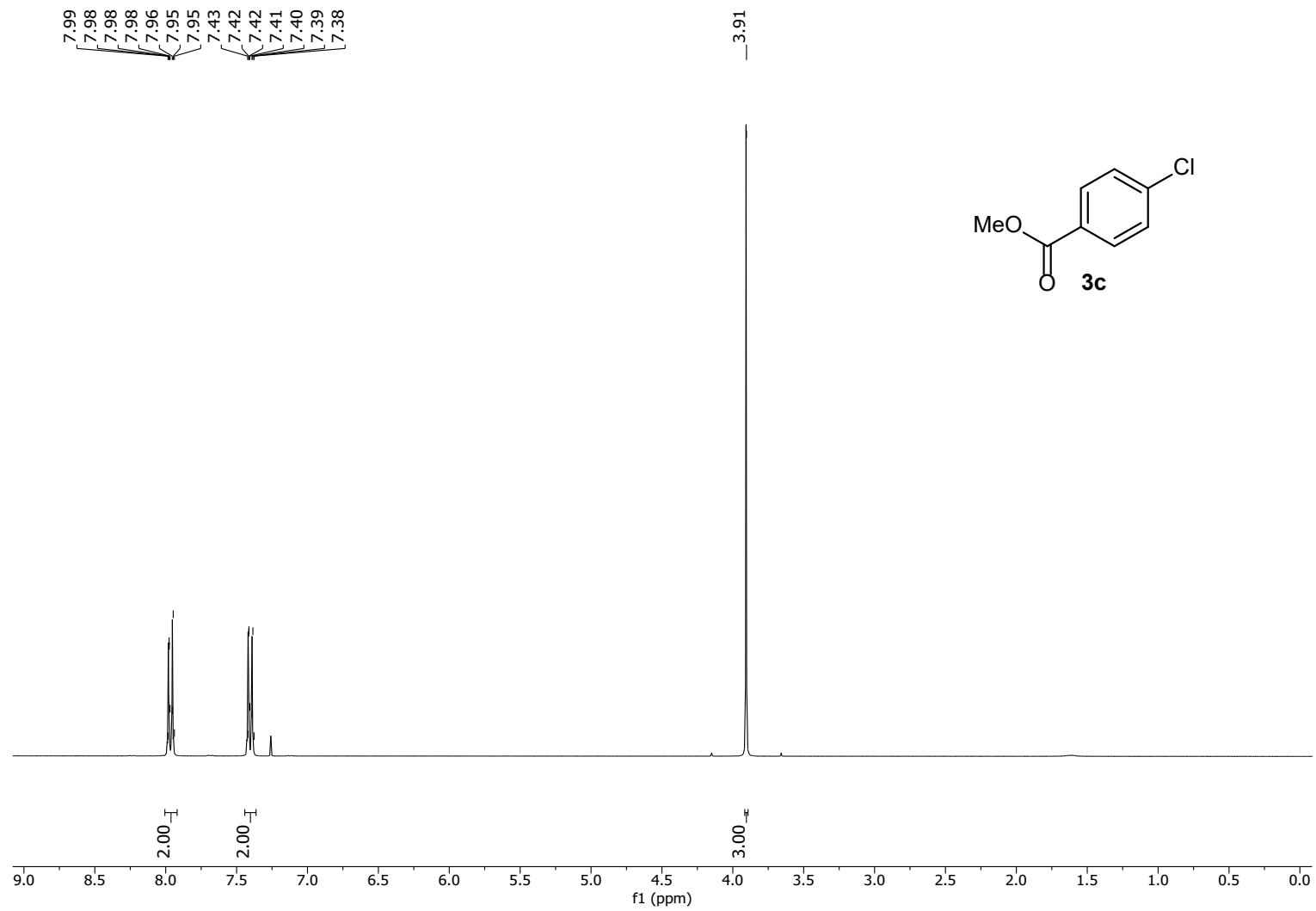
^1H NMR (300 MHz, CDCl_3)



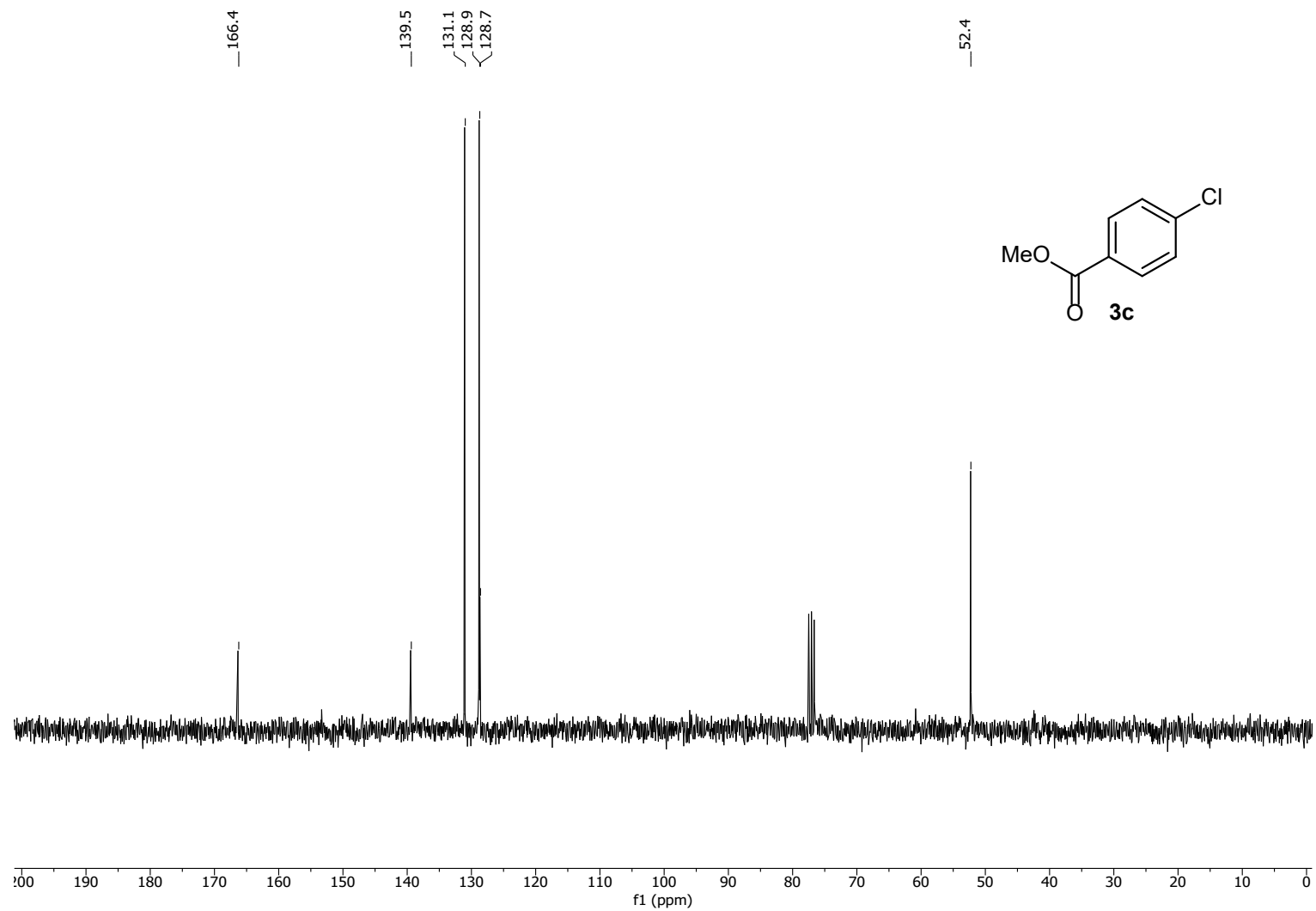
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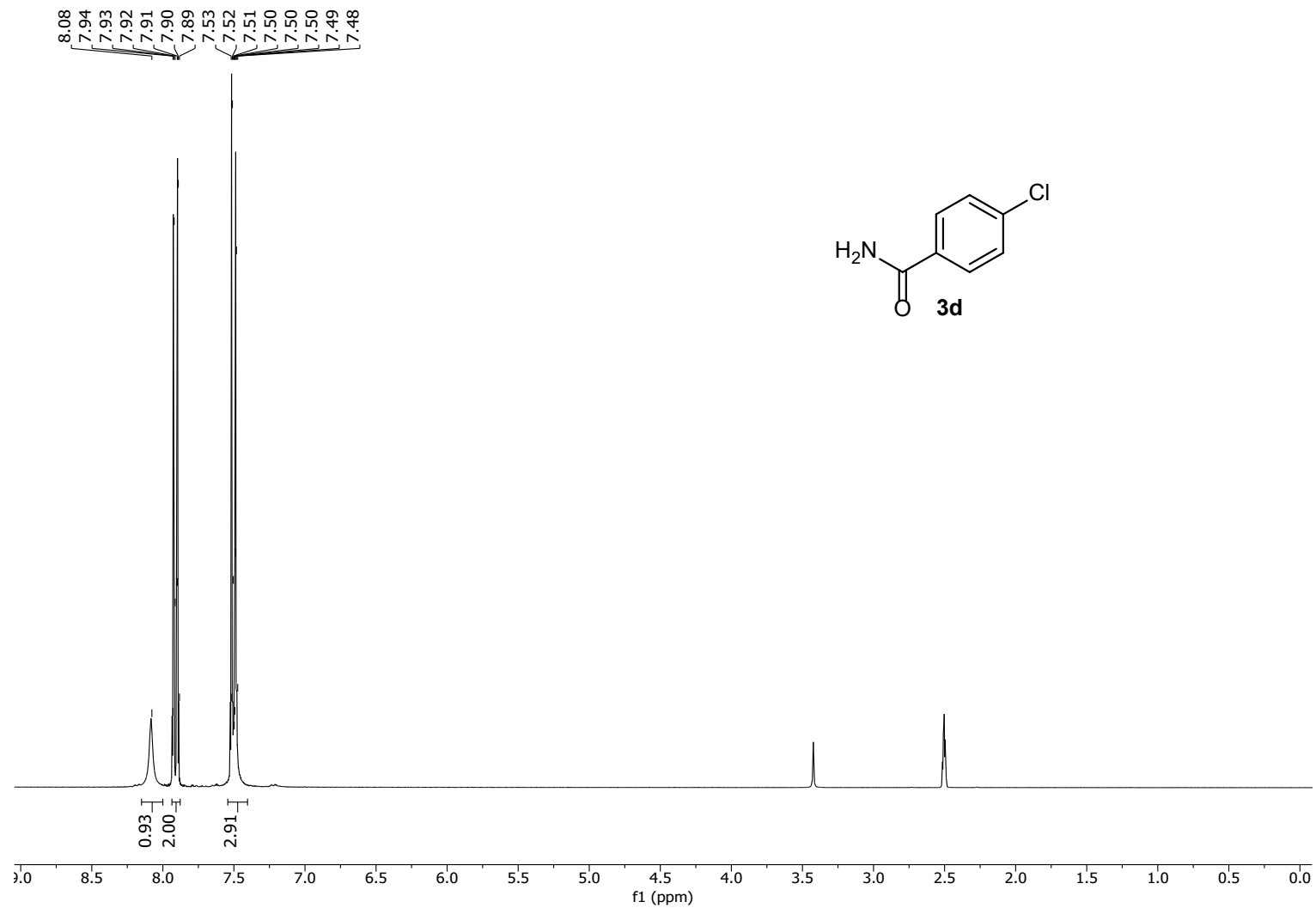
^1H NMR (300 MHz, CDCl_3)



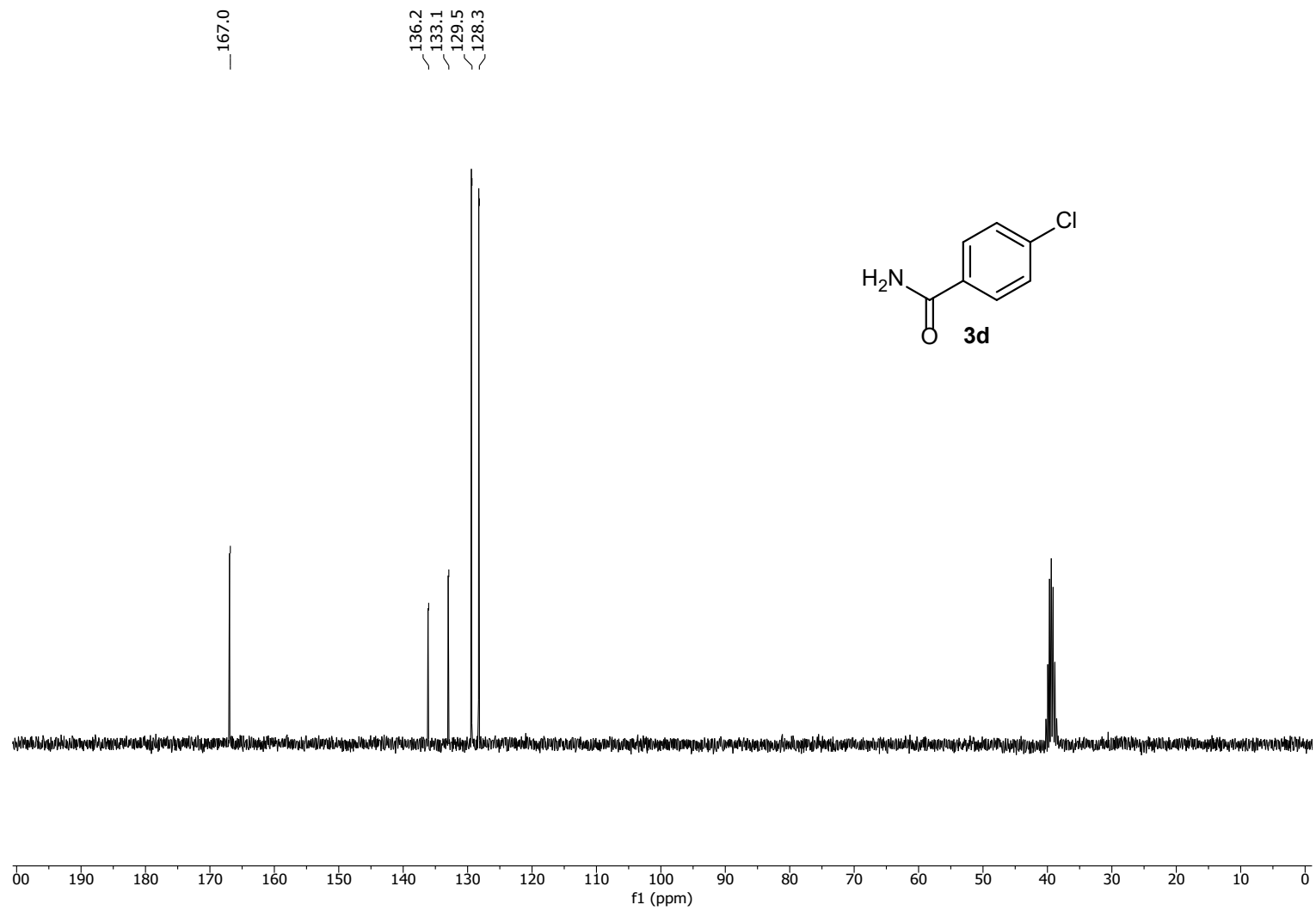
^{13}C NMR (75.4 MHz, CDCl_3)



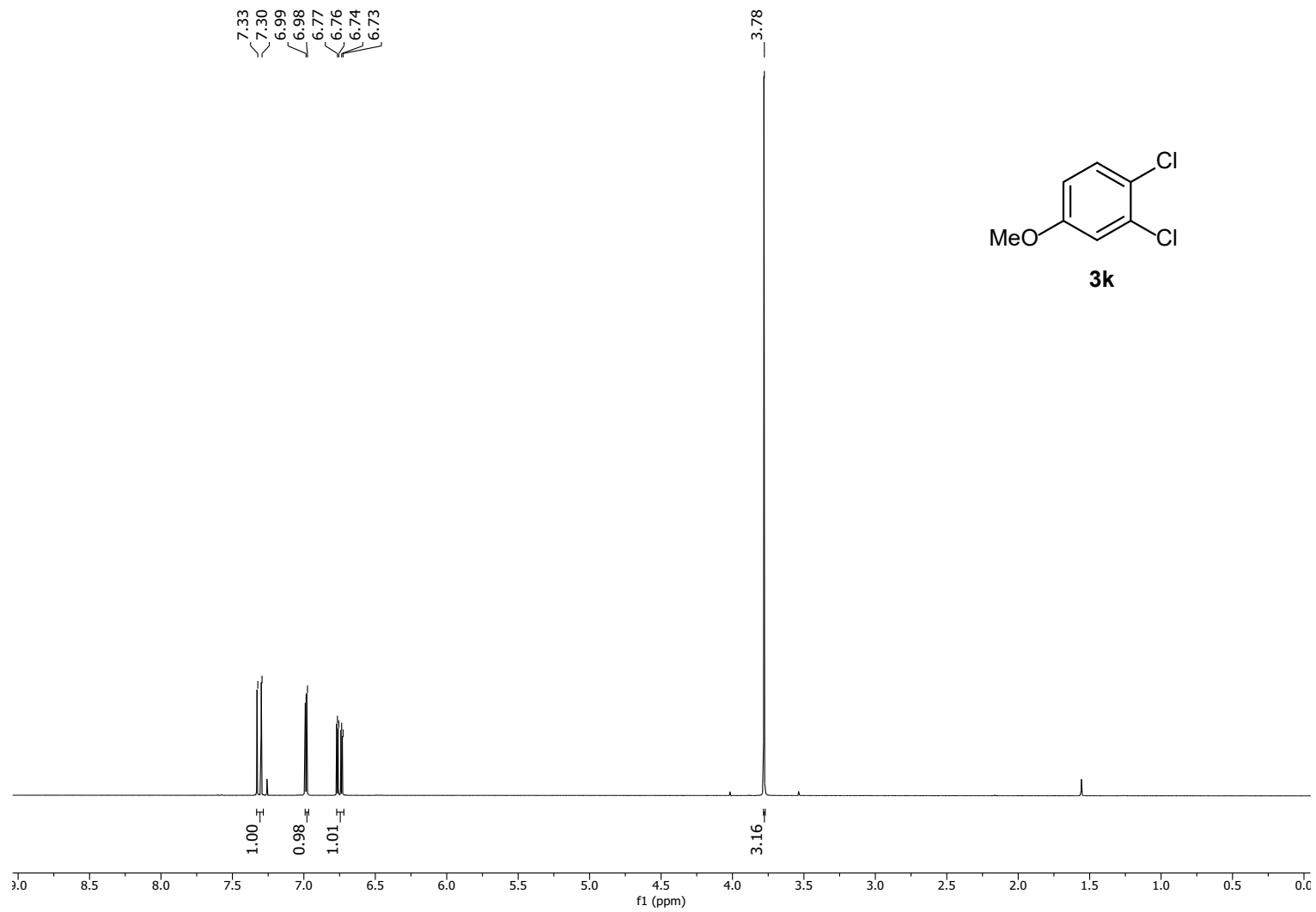
^1H NMR (300 MHz, $\text{DMSO-}d_6$)



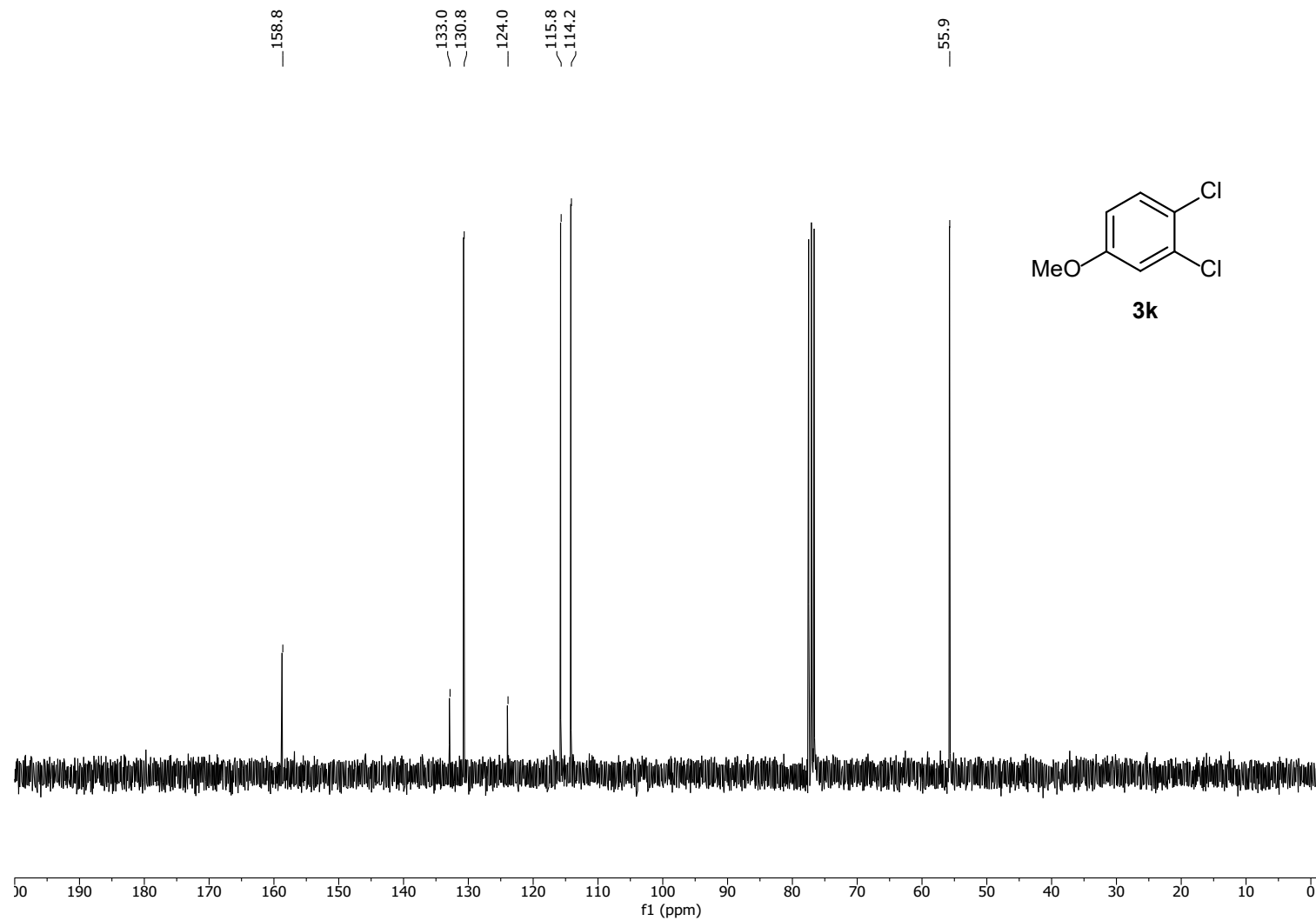
^{13}C NMR (75.4 MHz, $\text{DMSO-}d_6$)



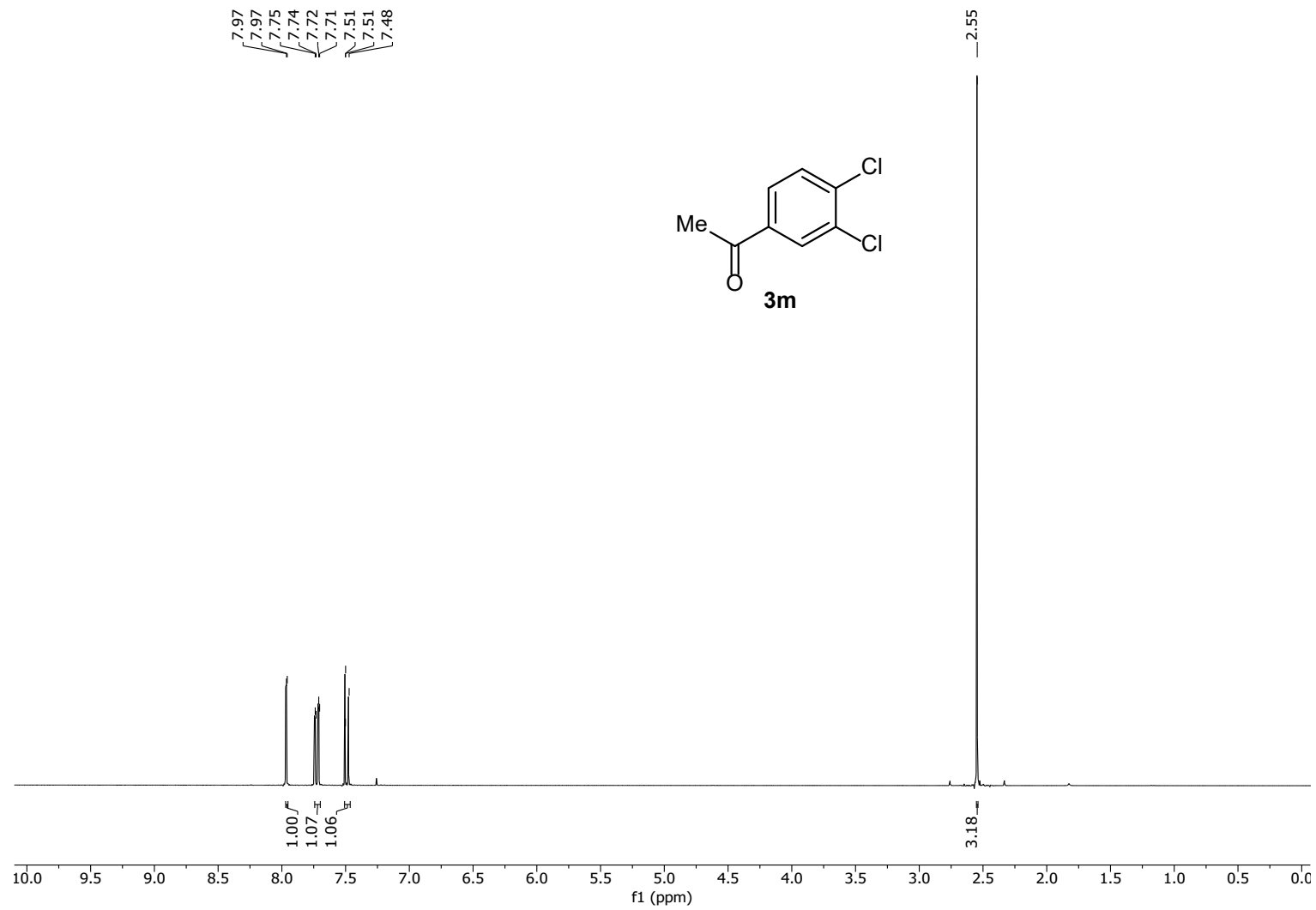
^1H NMR (300 MHz, CDCl_3)



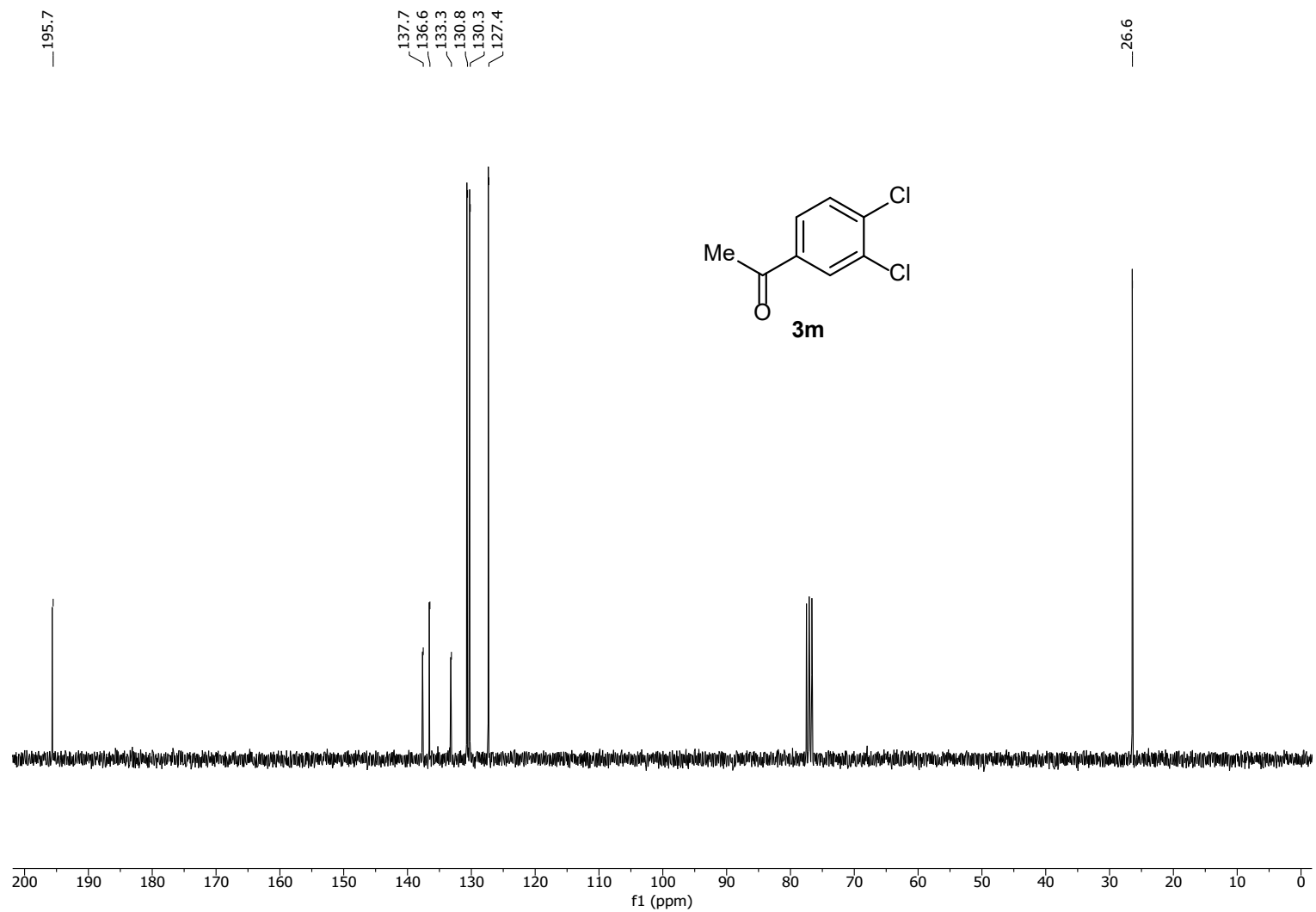
^{13}C NMR (75.4 MHz, CDCl_3)



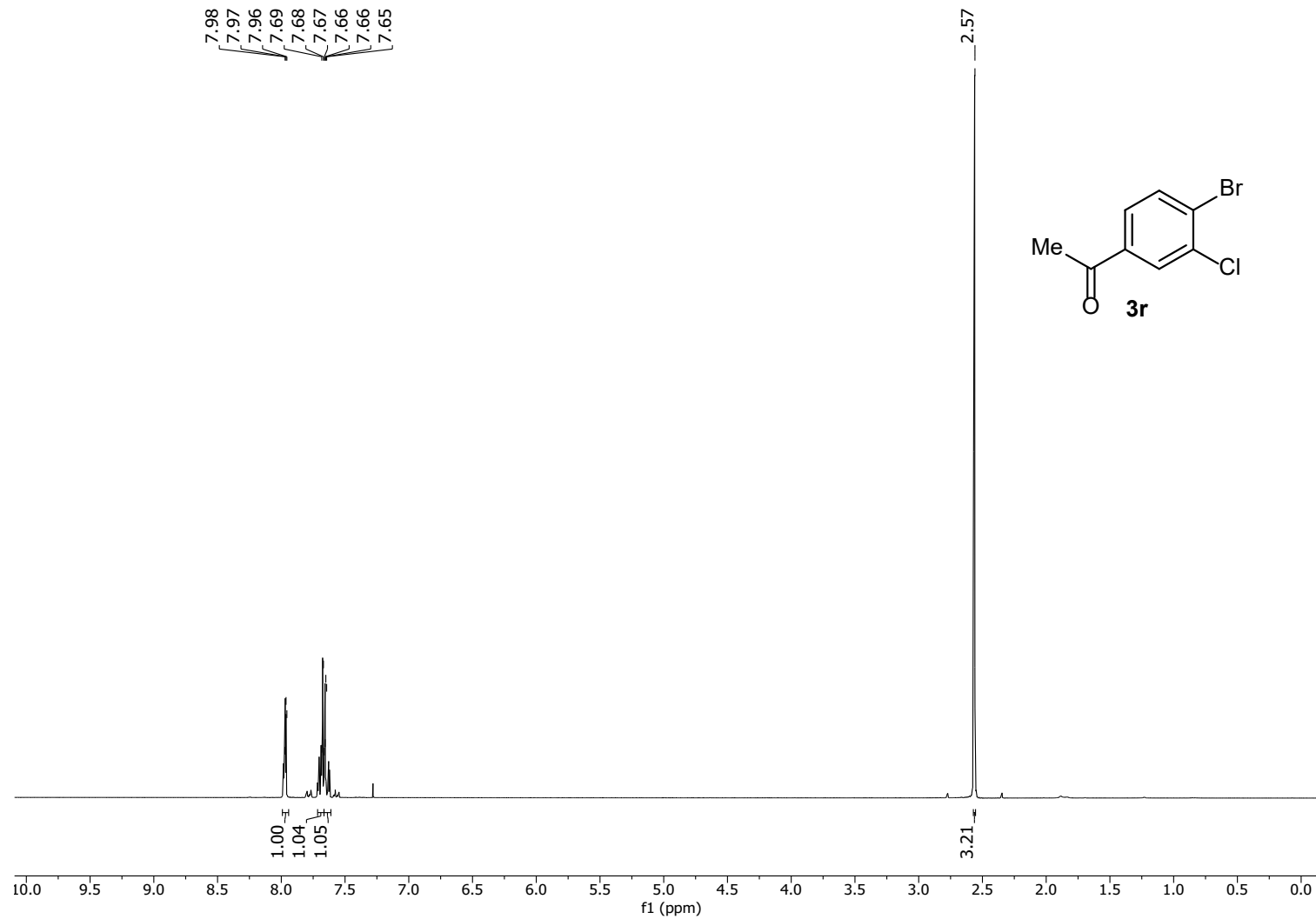
^1H NMR (300 MHz, CDCl_3)



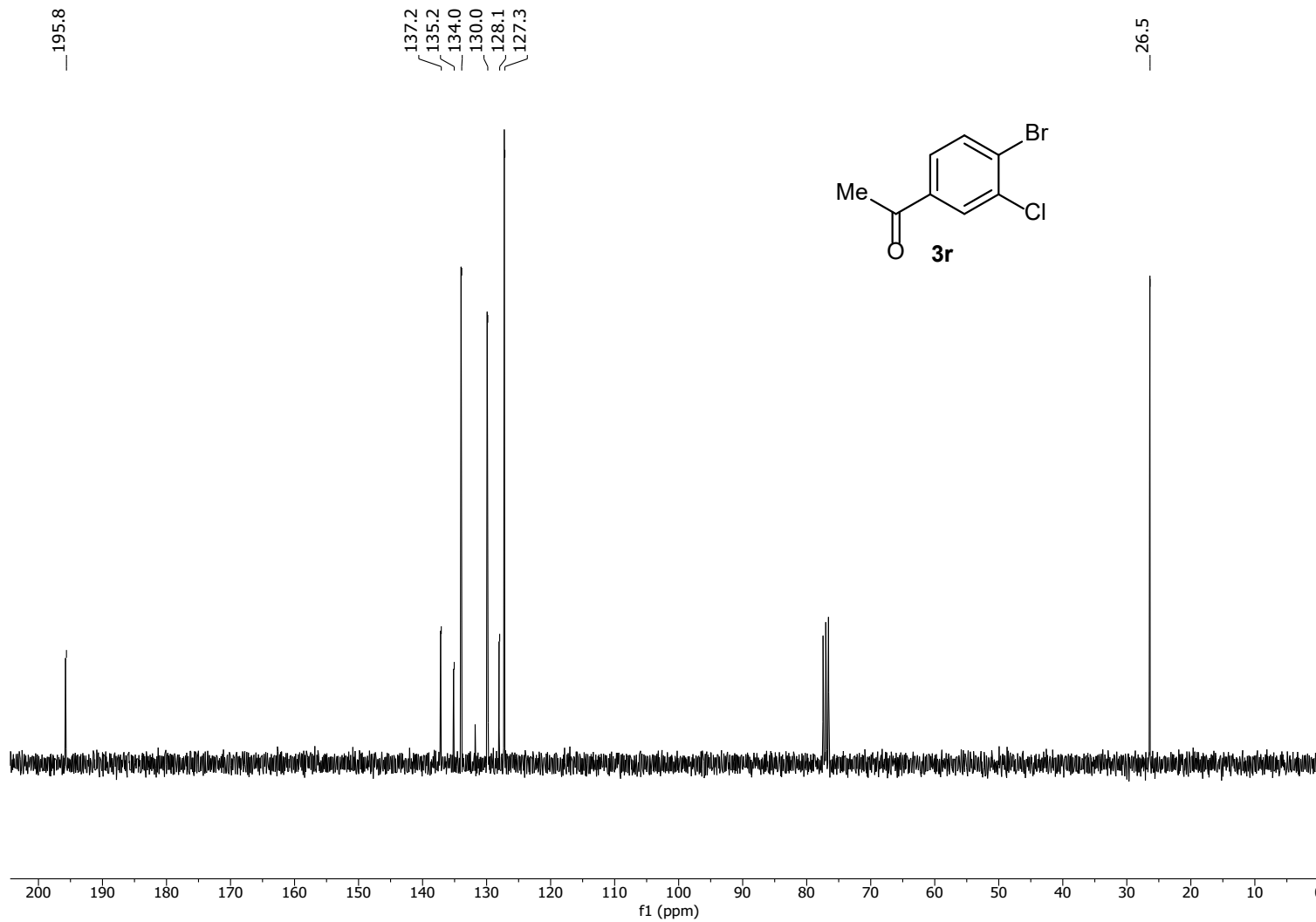
^{13}C NMR (75.4 MHz, CDCl_3)



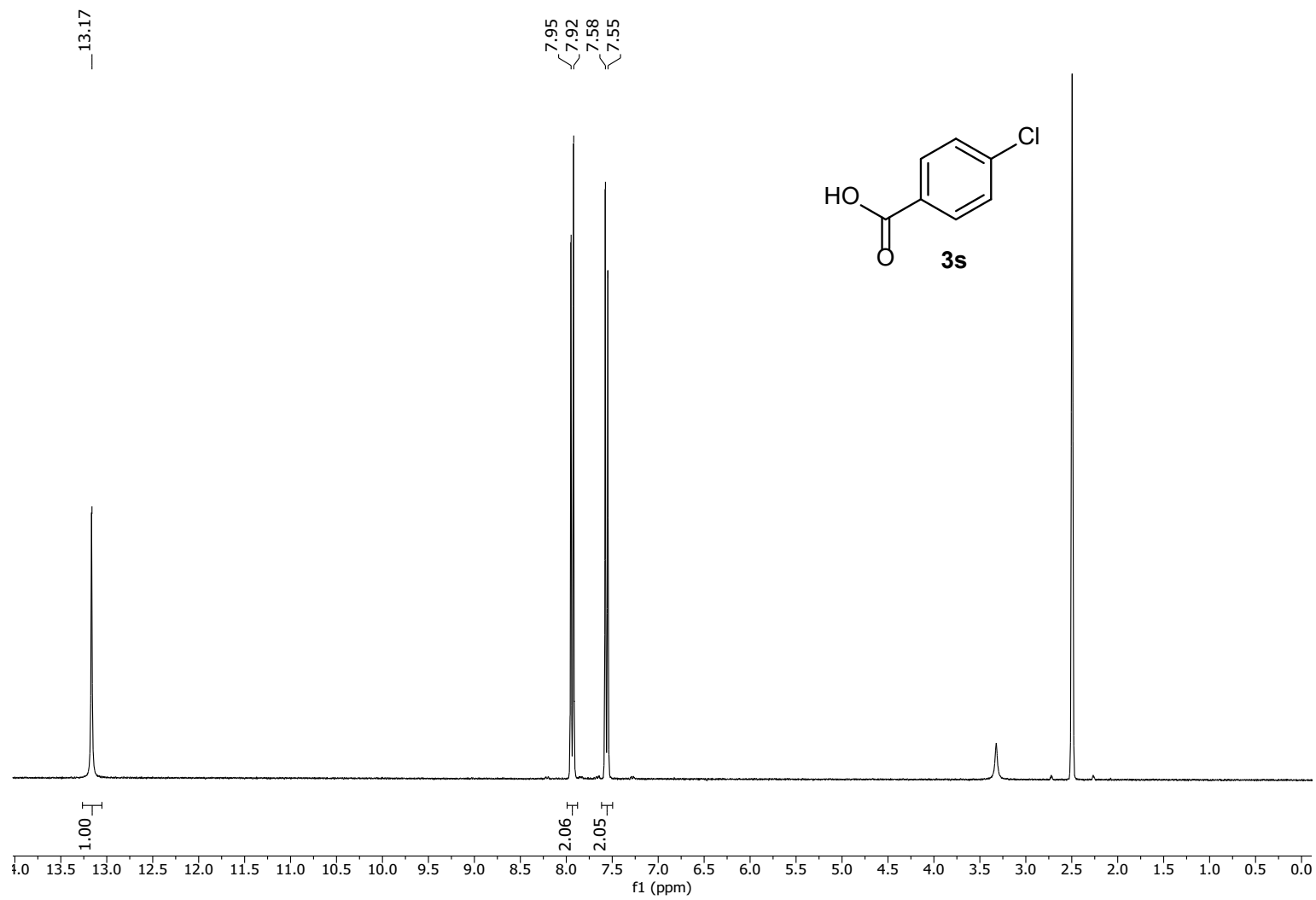
^1H NMR (300 MHz, CDCl_3)



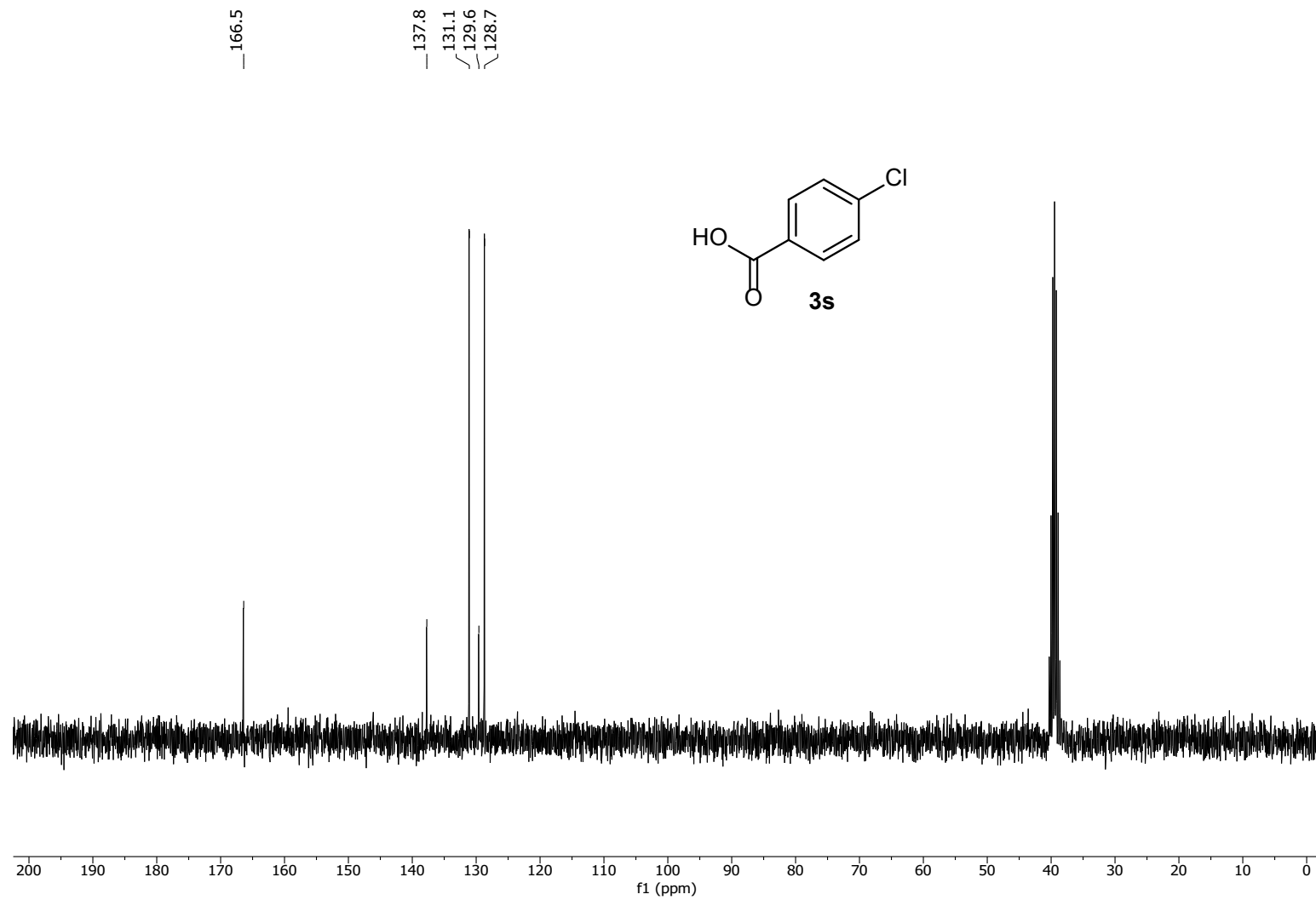
^{13}C NMR (75.4 MHz, CDCl_3)



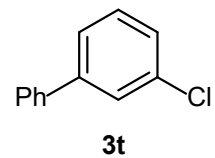
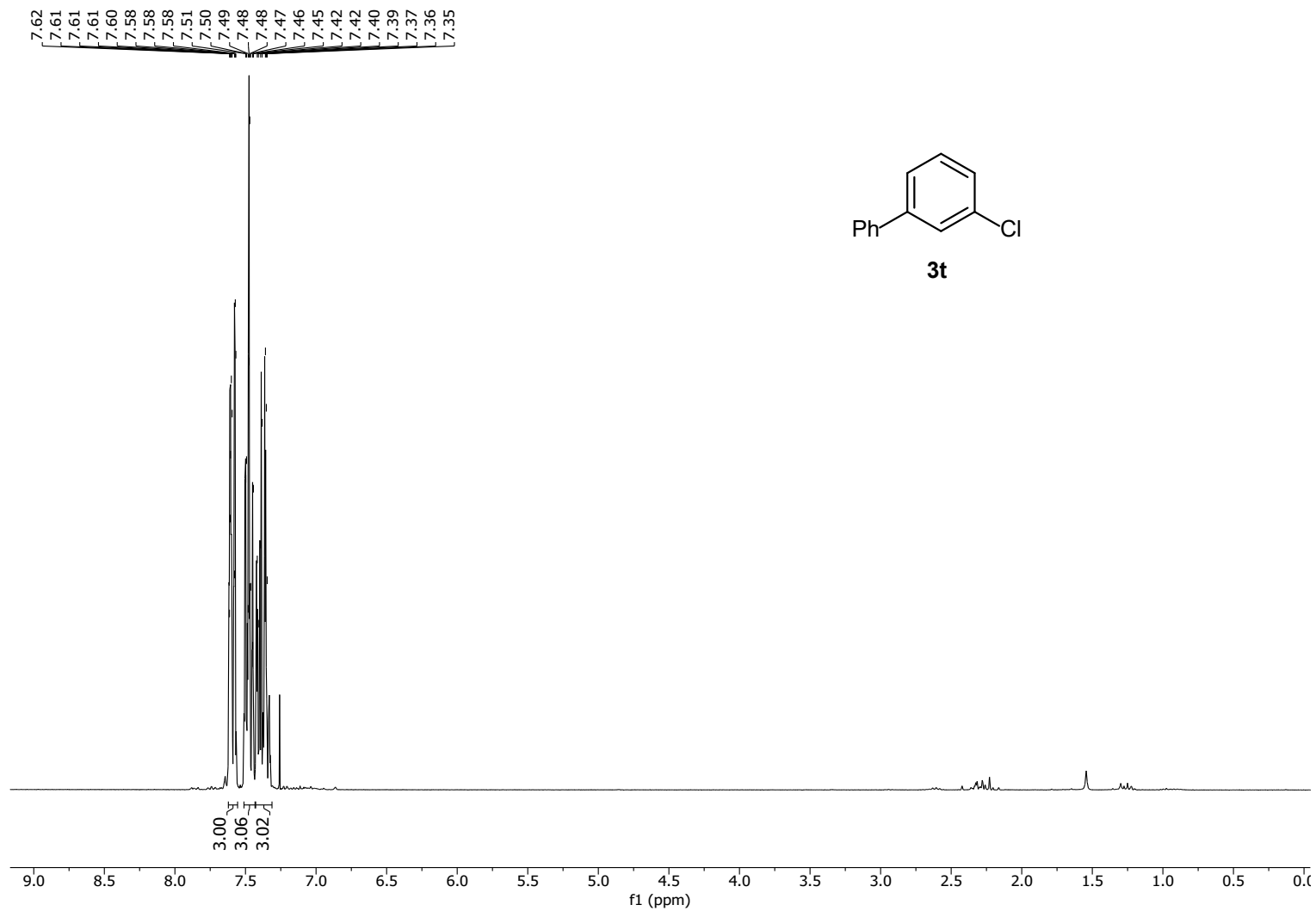
^1H NMR (300 MHz, $\text{DMSO-}d_6$)



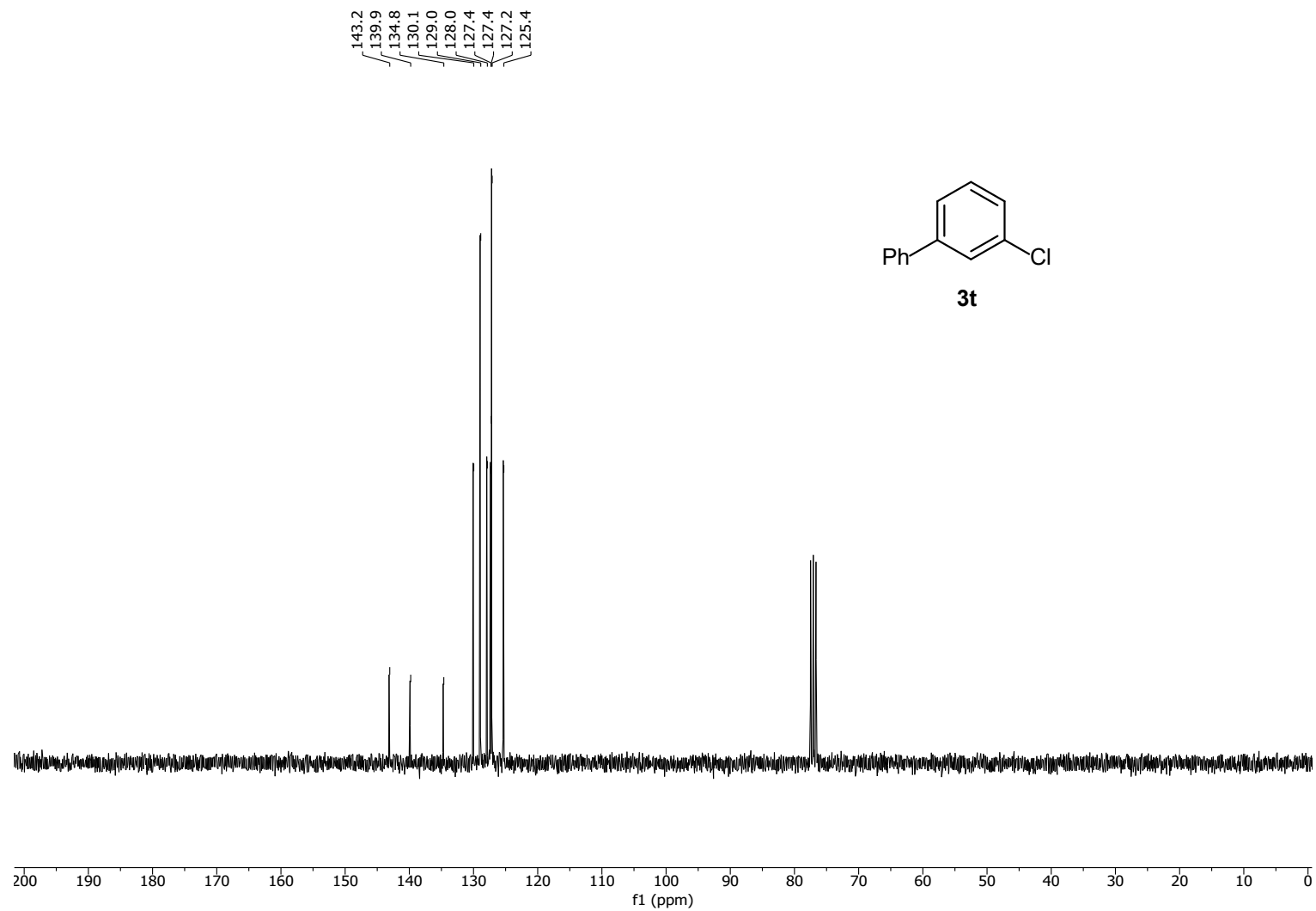
^{13}C NMR (75.4 MHz, $\text{DMSO-}d_6$)



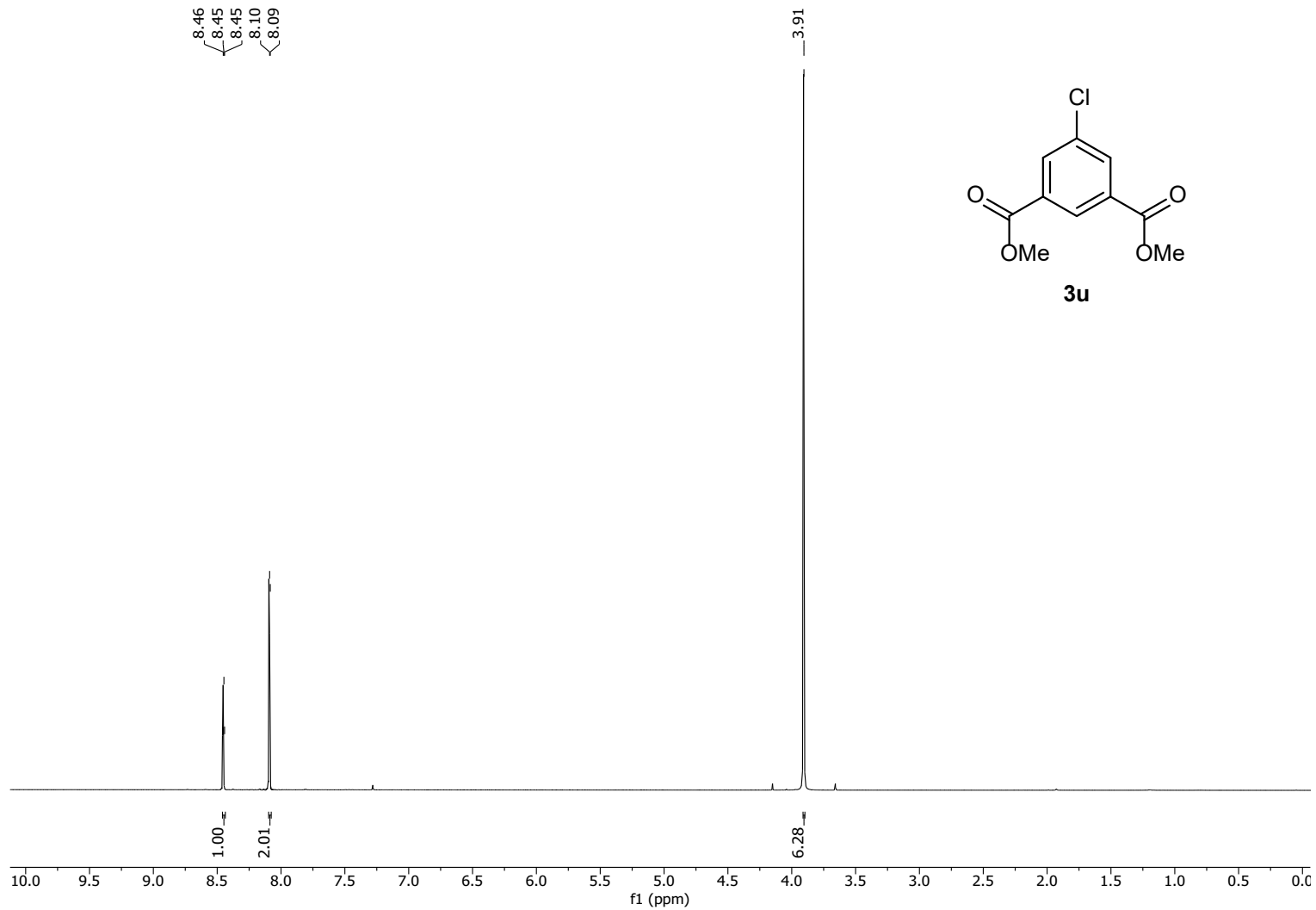
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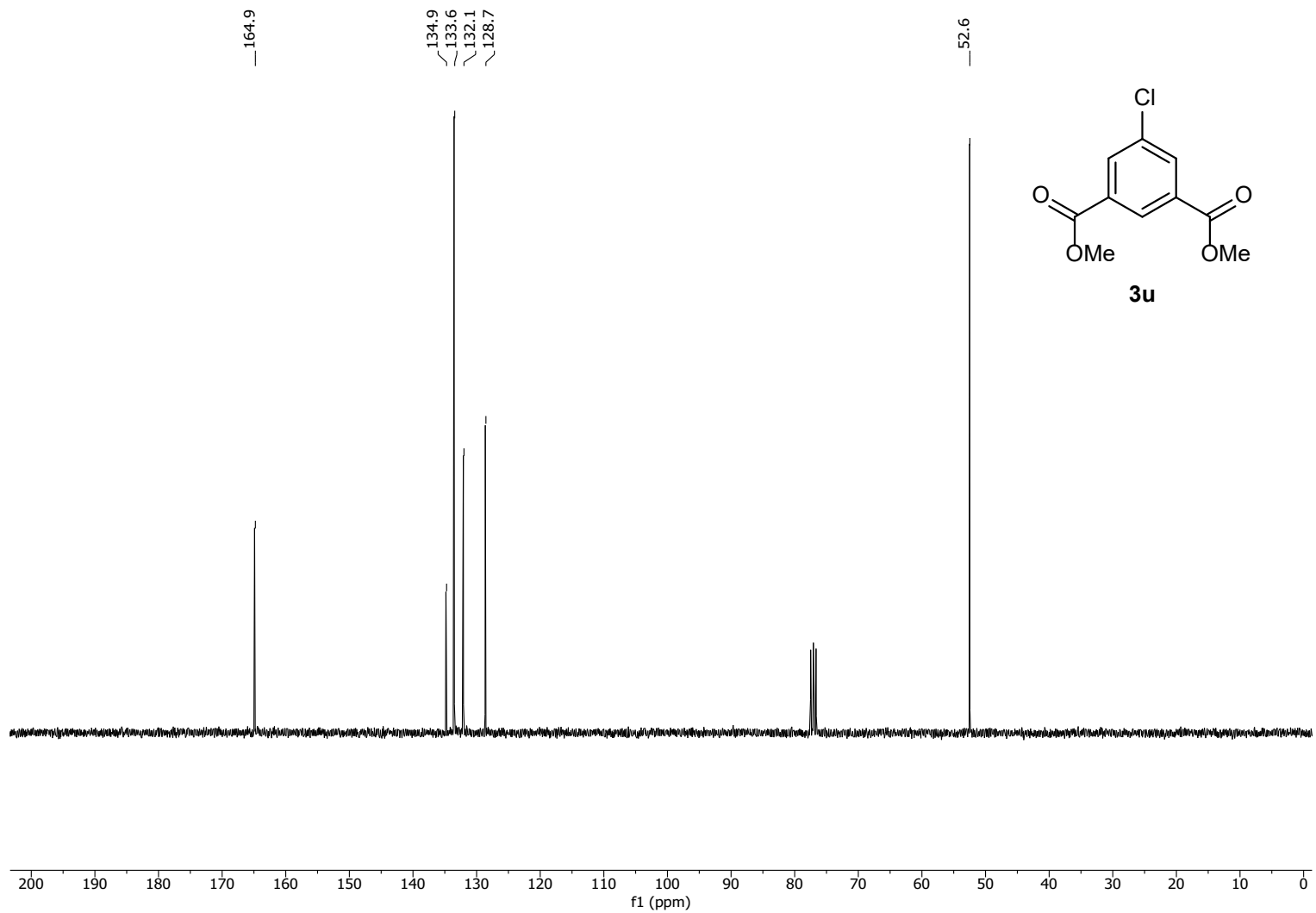
^{13}C NMR (75.4 MHz, CDCl_3)



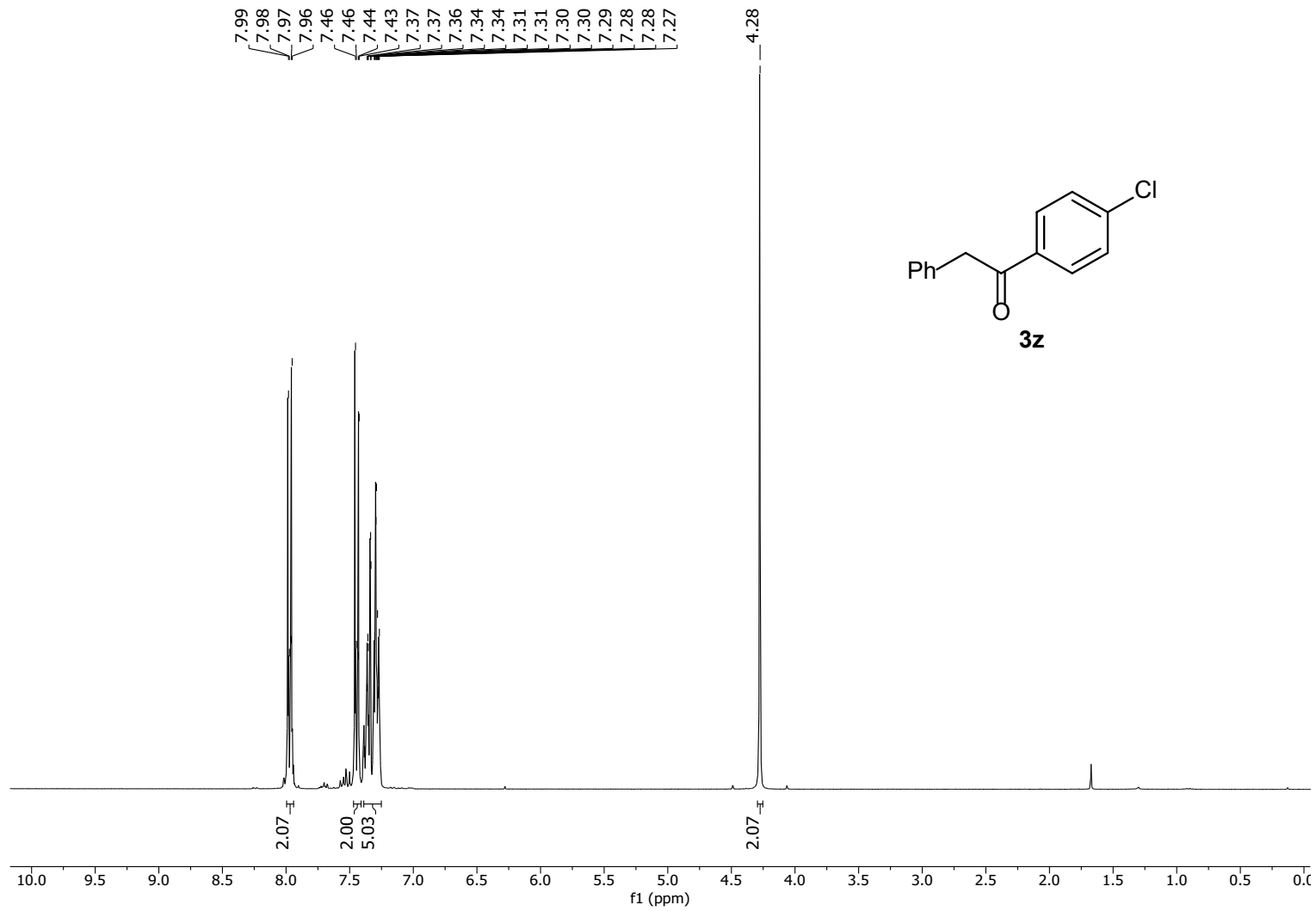
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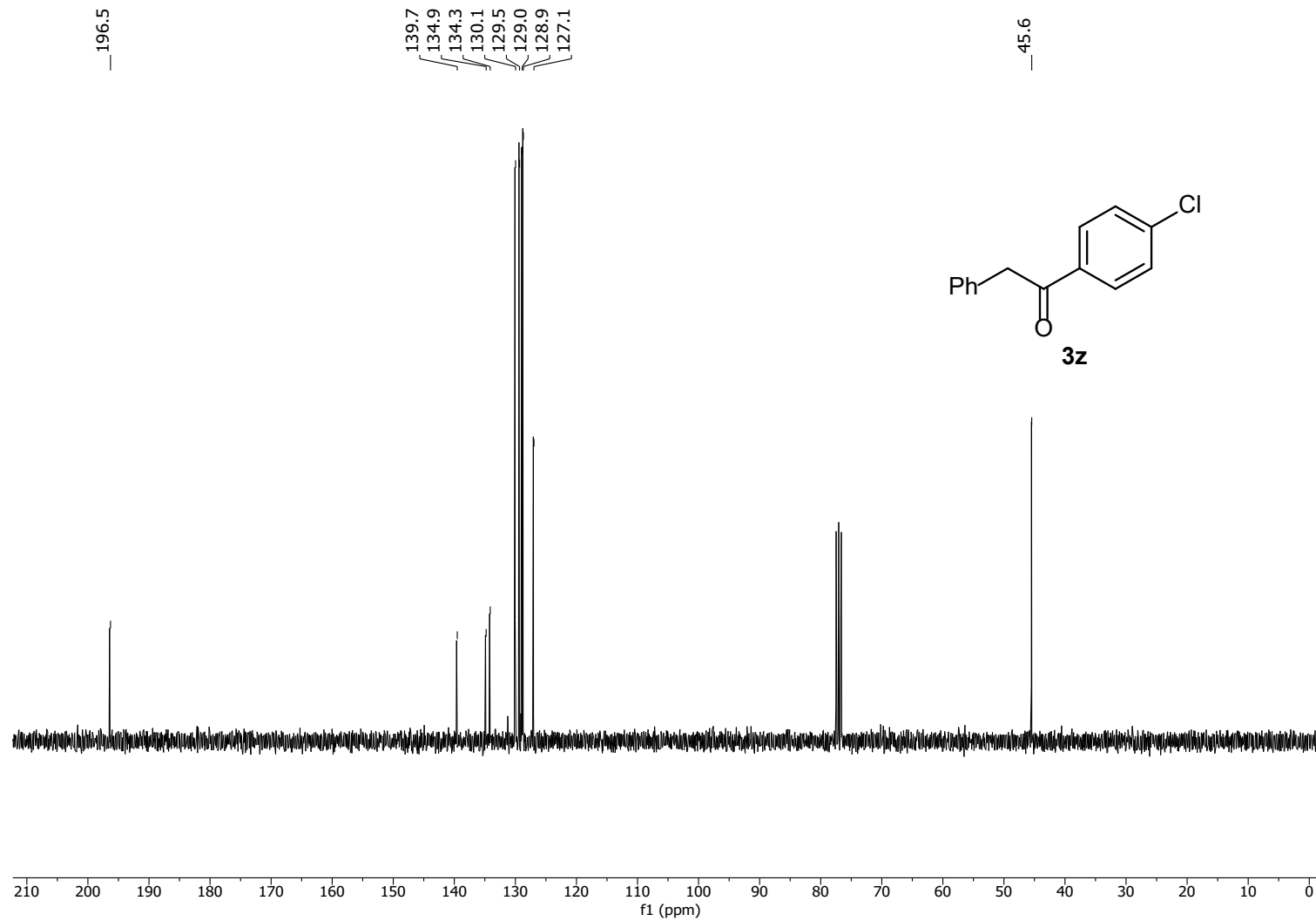
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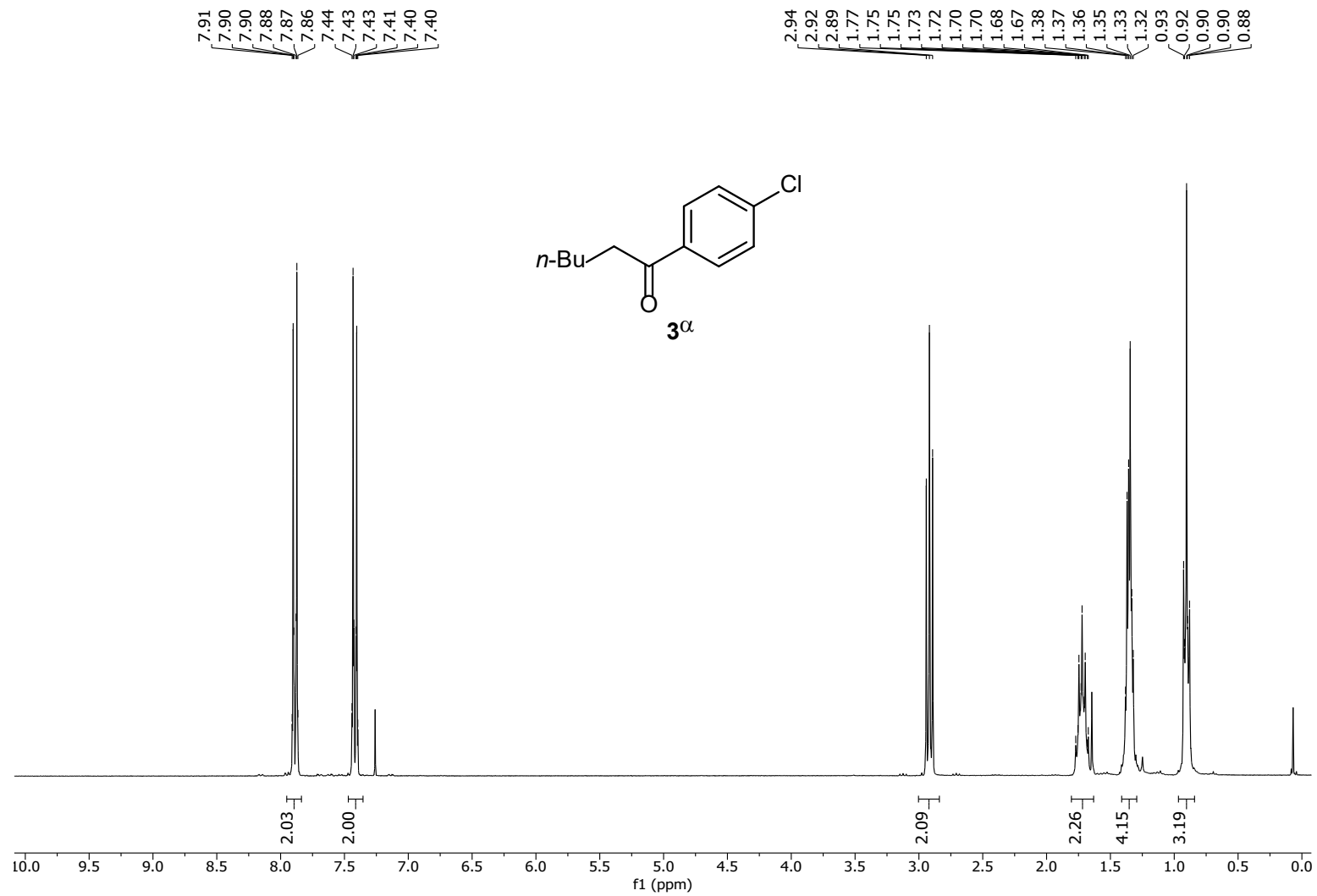
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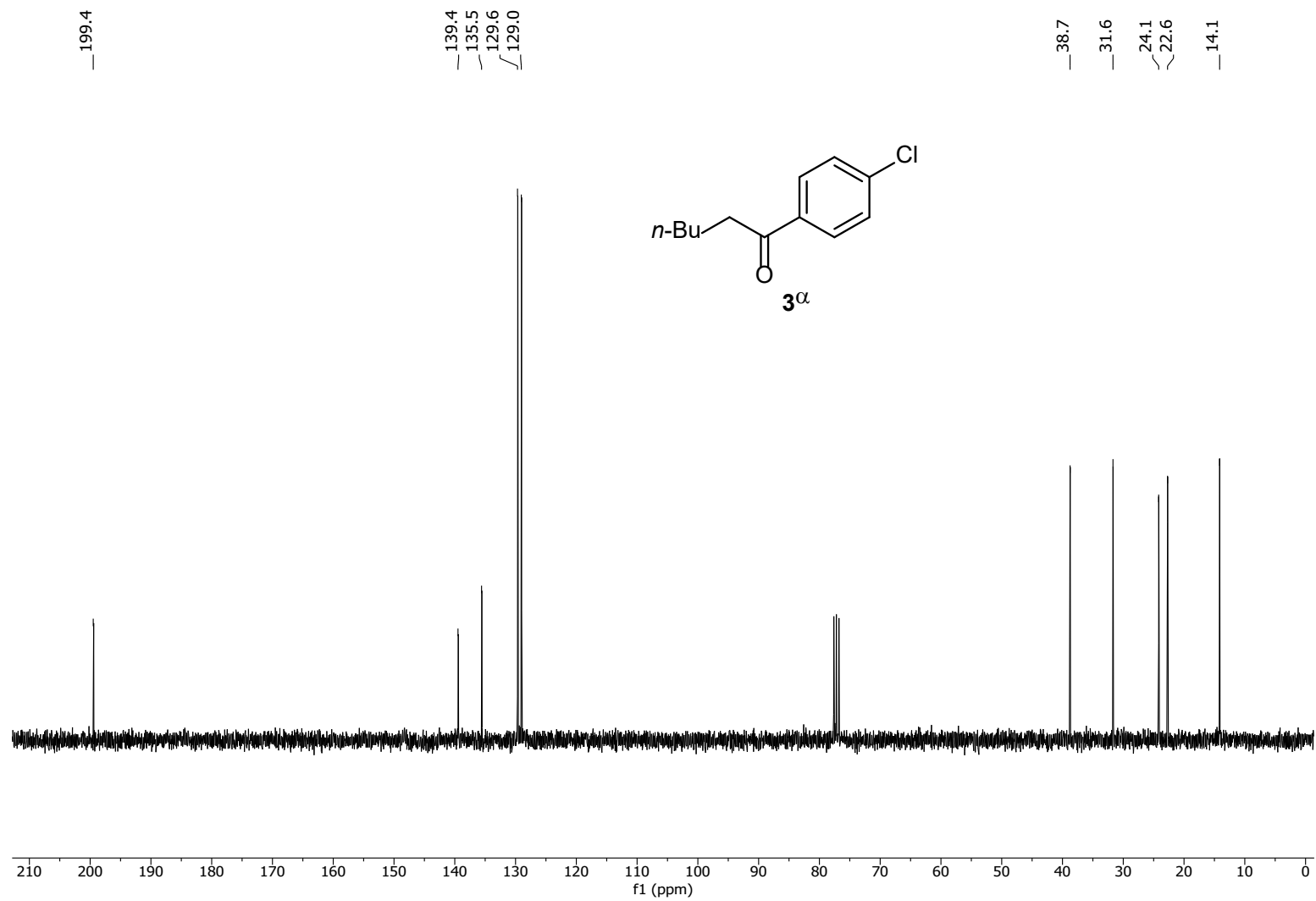
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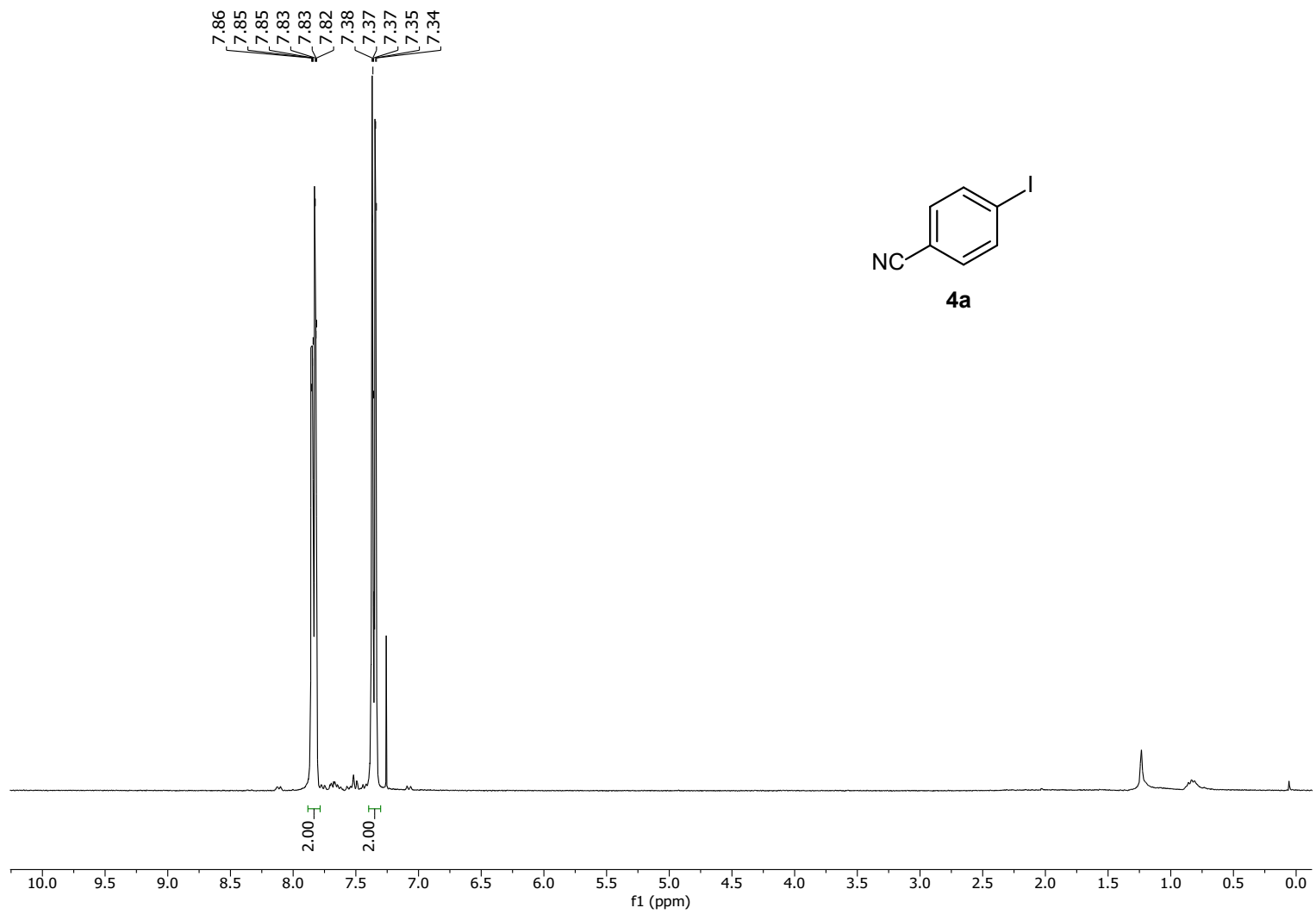
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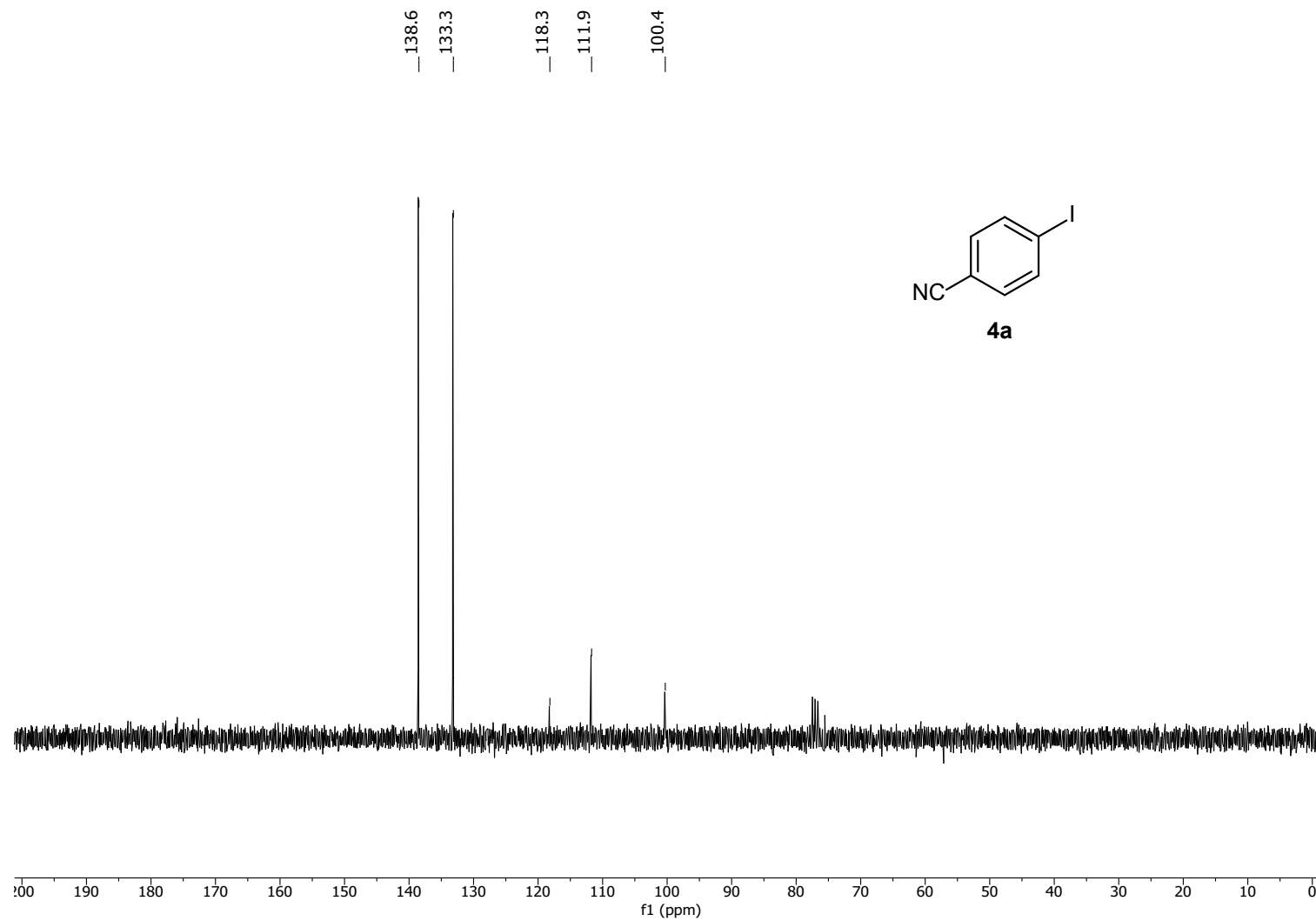
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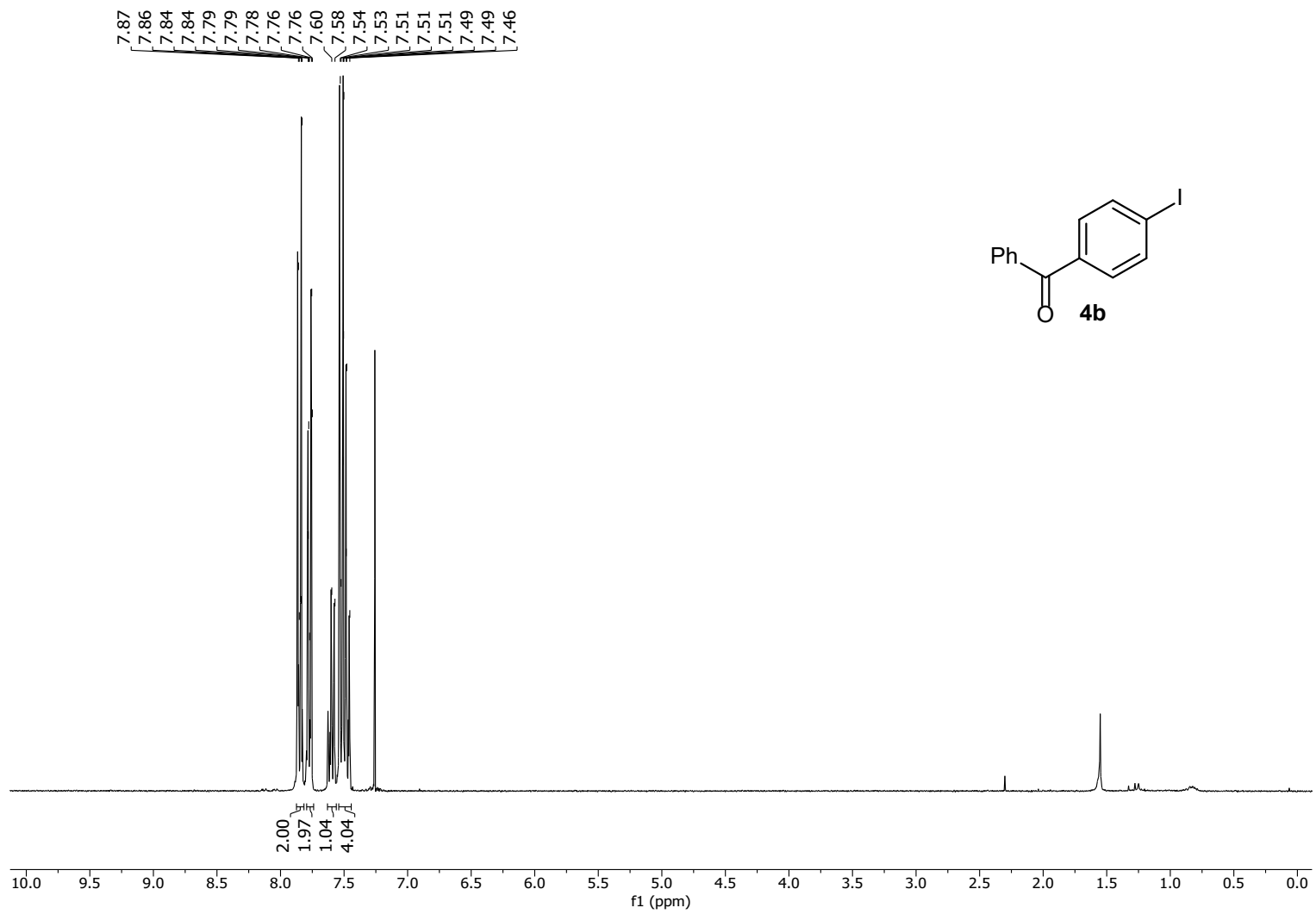
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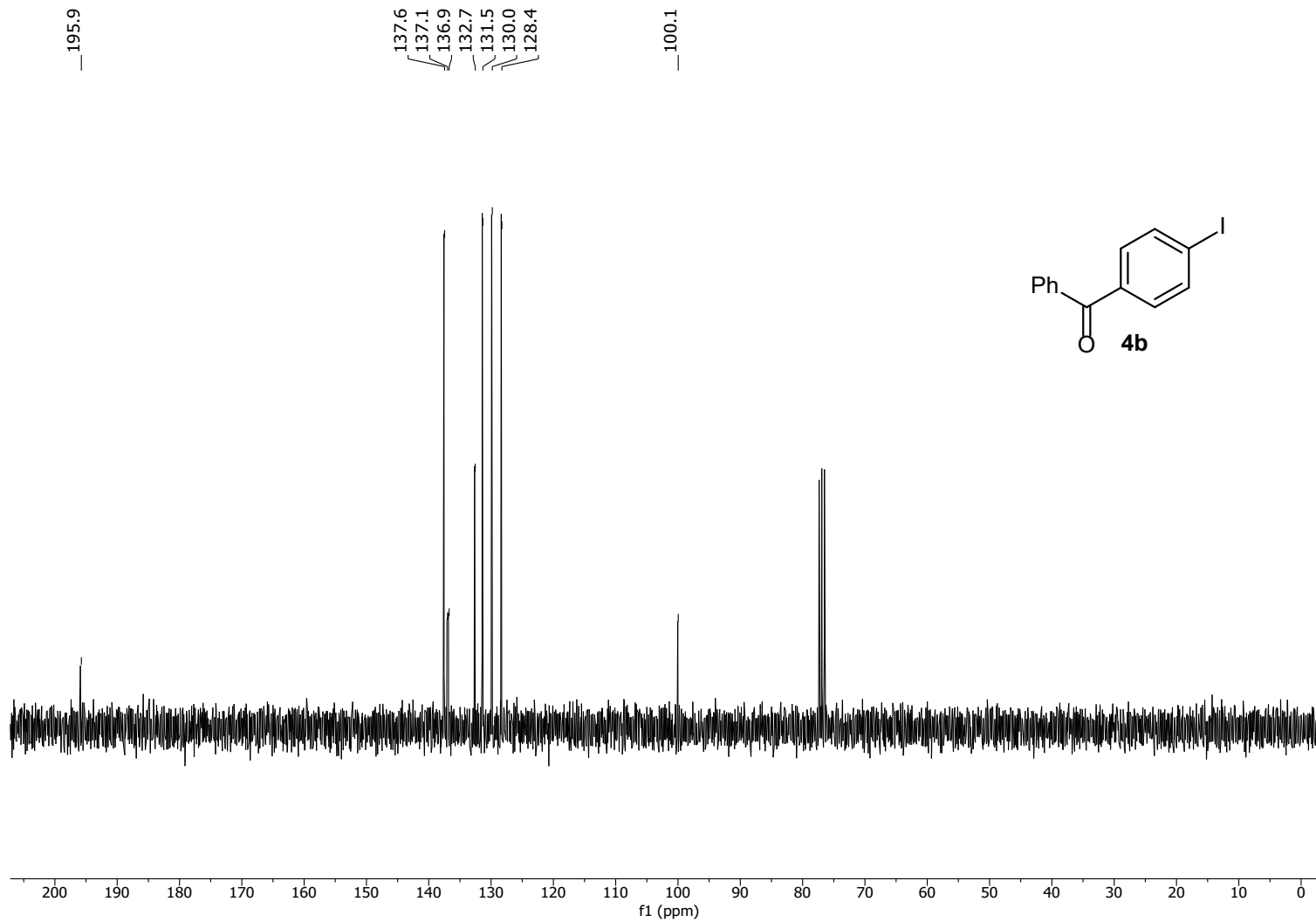
^{13}C NMR (75.4 MHz, CDCl_3)



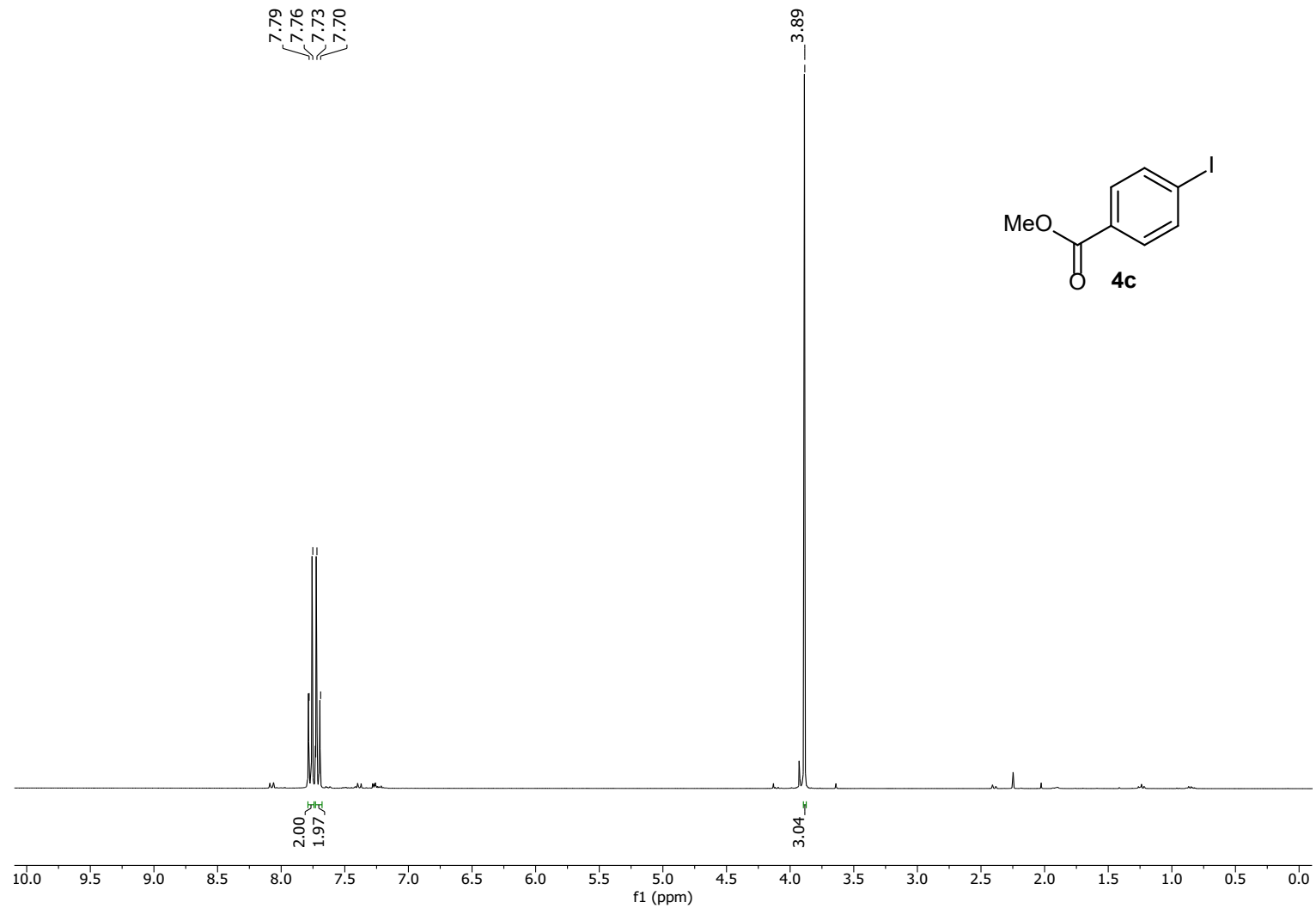
^1H NMR (300 MHz, CDCl_3)



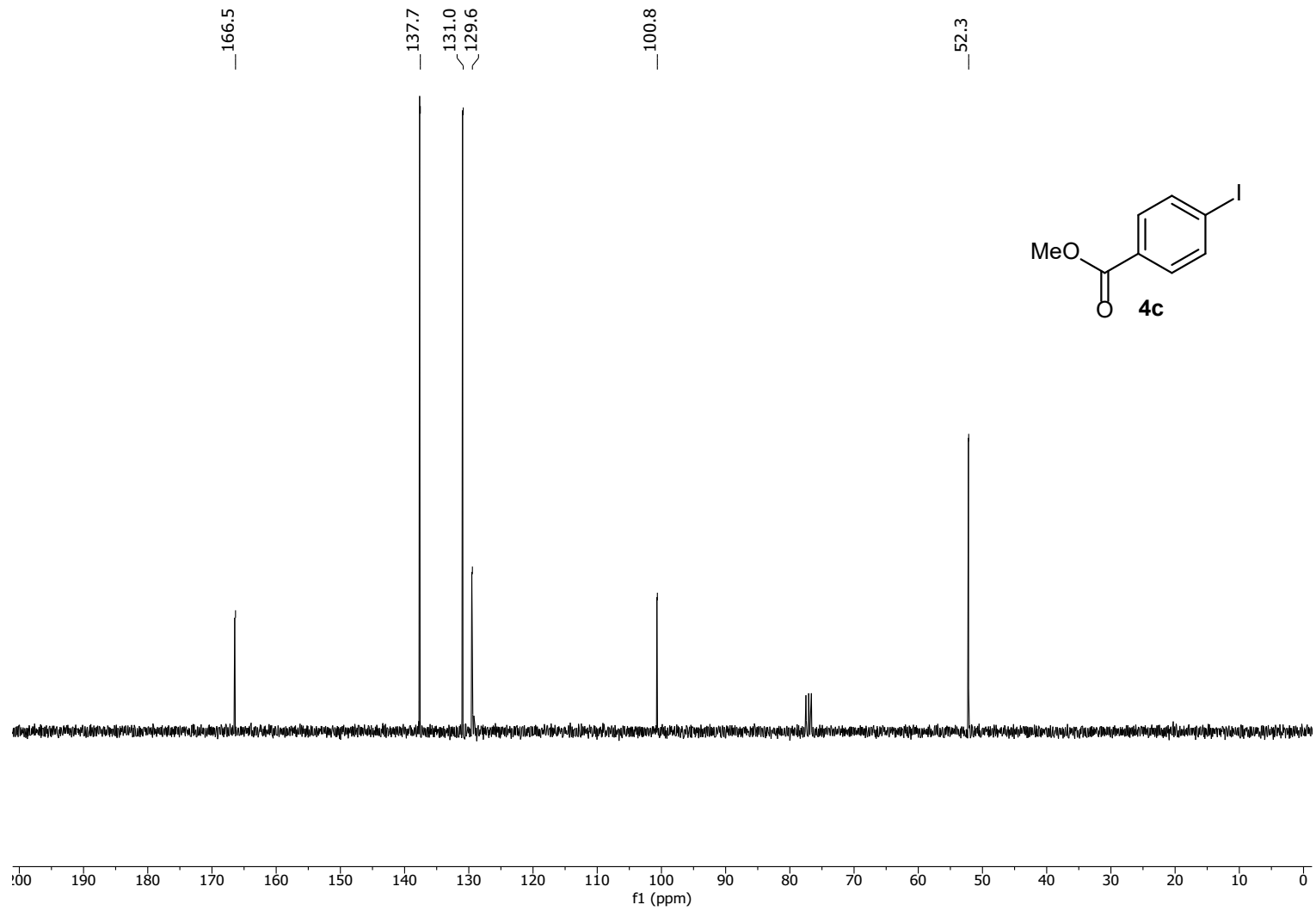
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^1H NMR (300 MHz, CDCl_3)



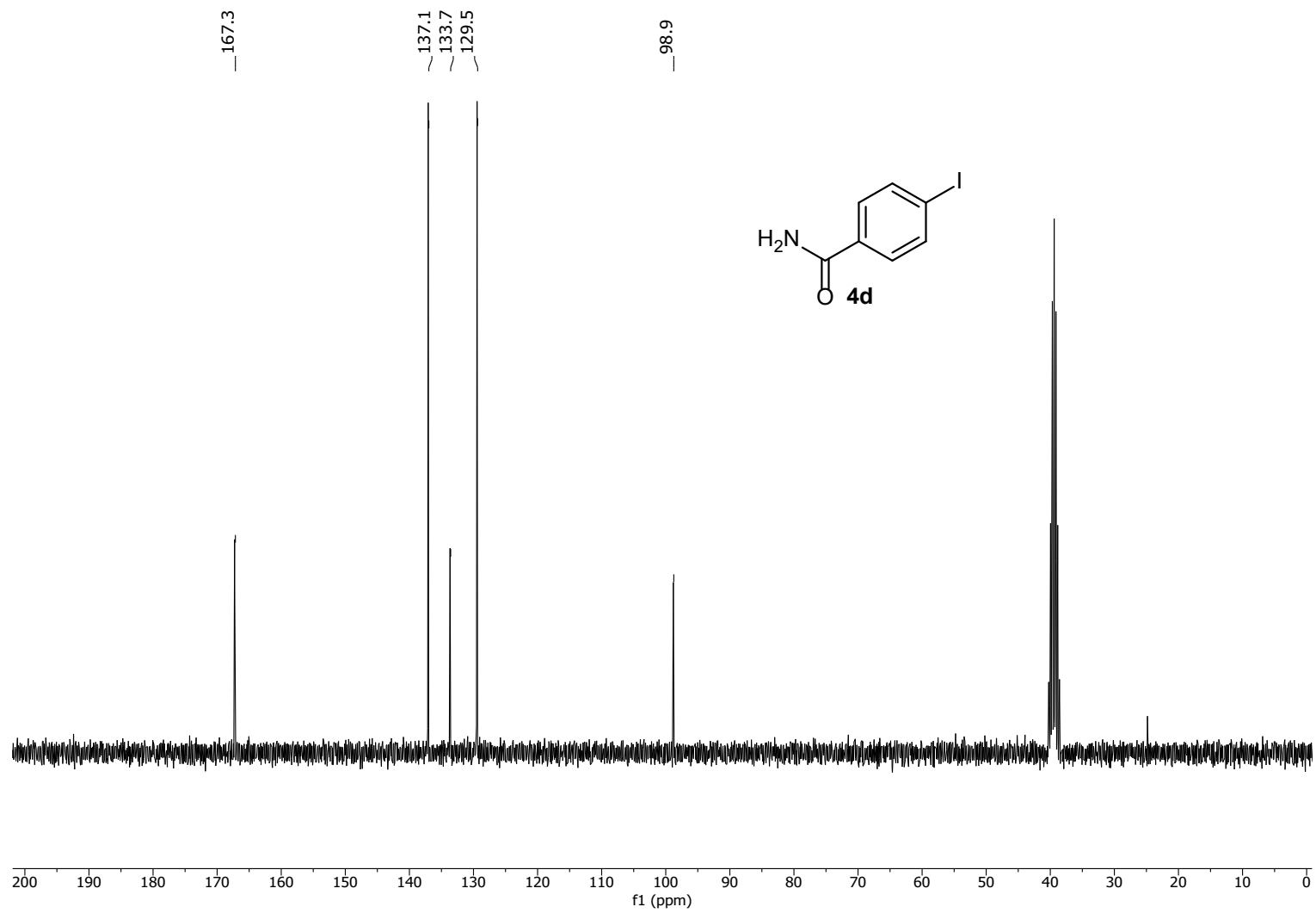
^{13}C NMR (75.4 MHz, CDCl_3)



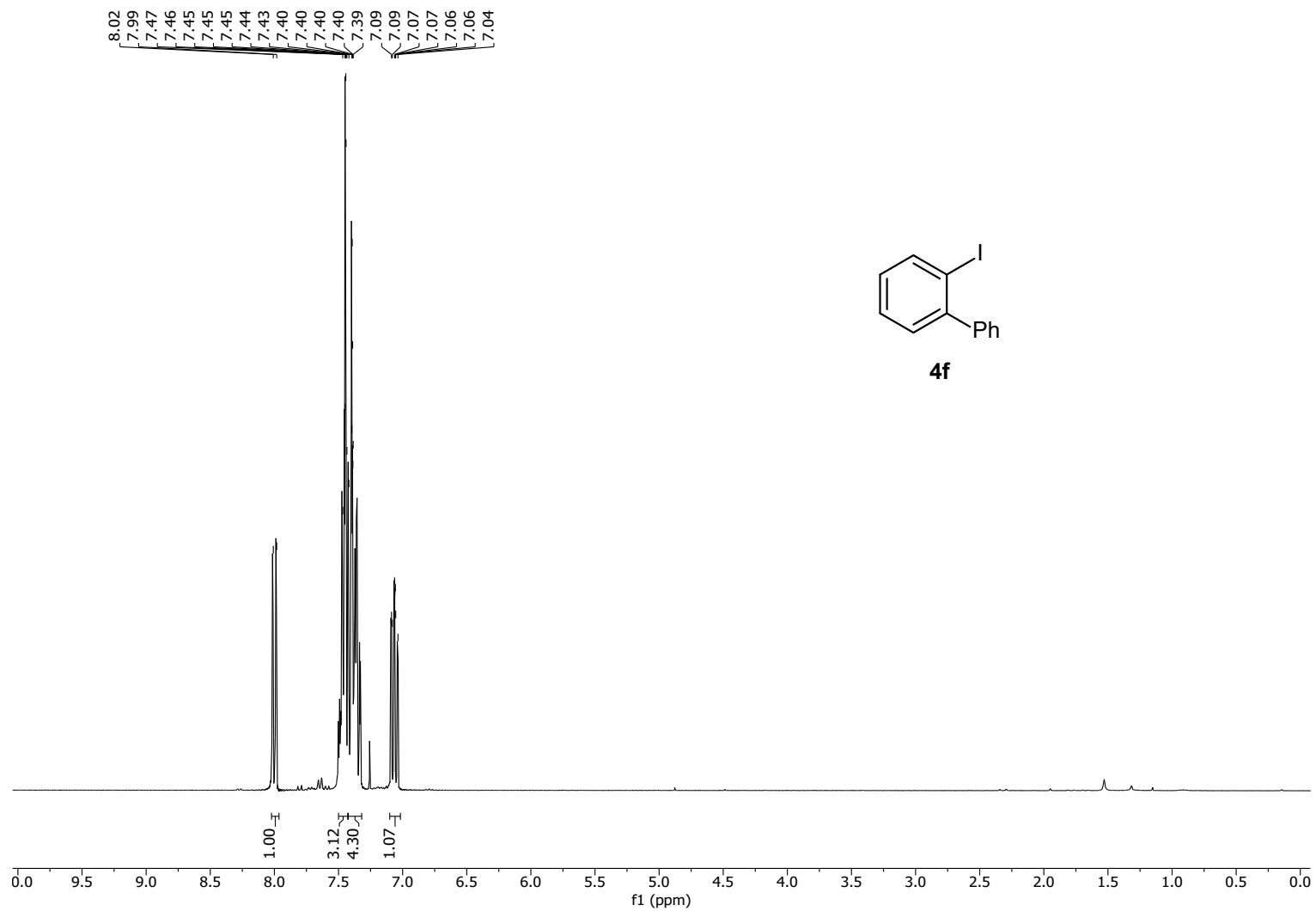
^1H NMR (300 MHz, $\text{DMSO-}d_6$)



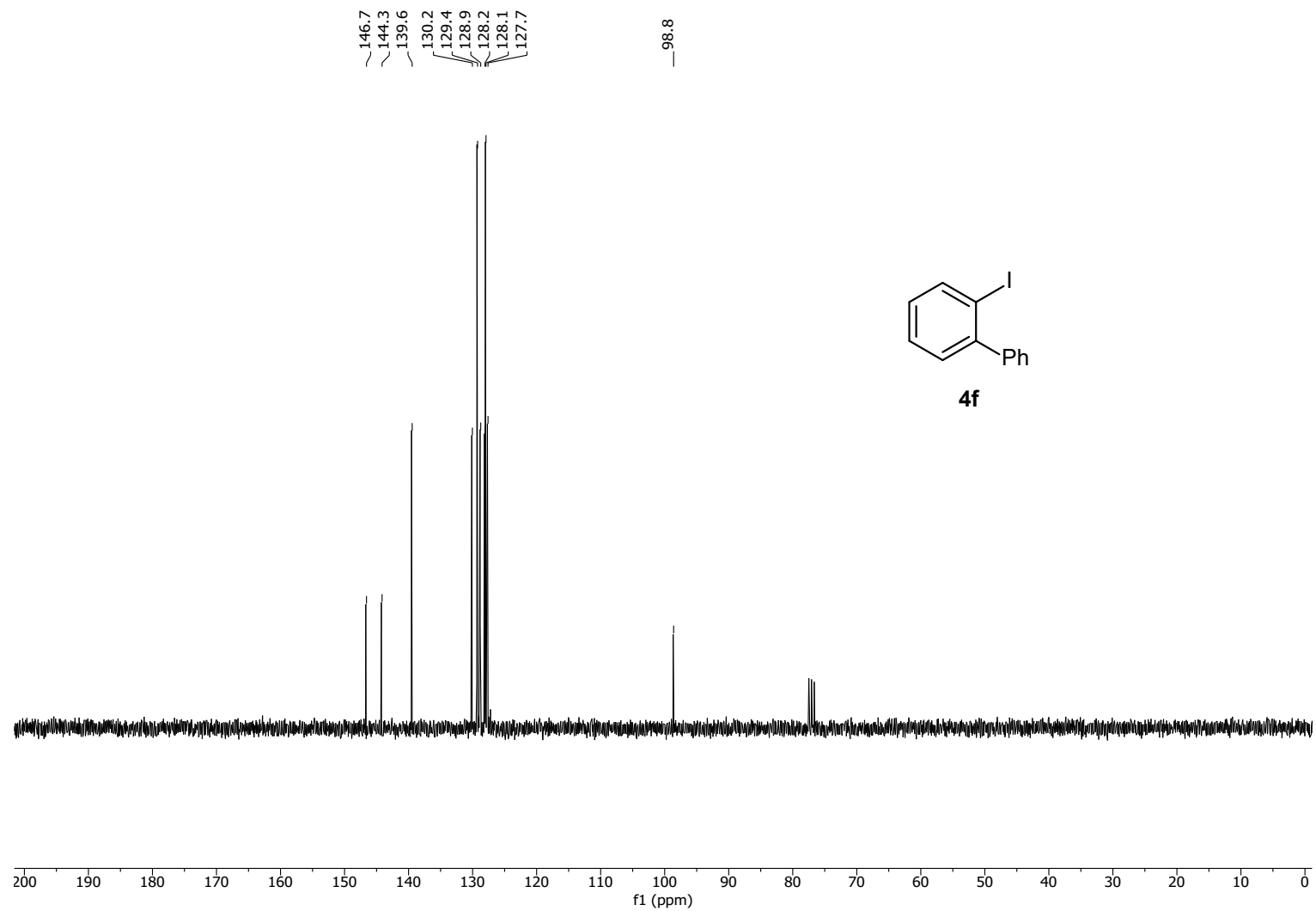
^{13}C NMR (75.4 MHz, $\text{DMSO-}d_6$)



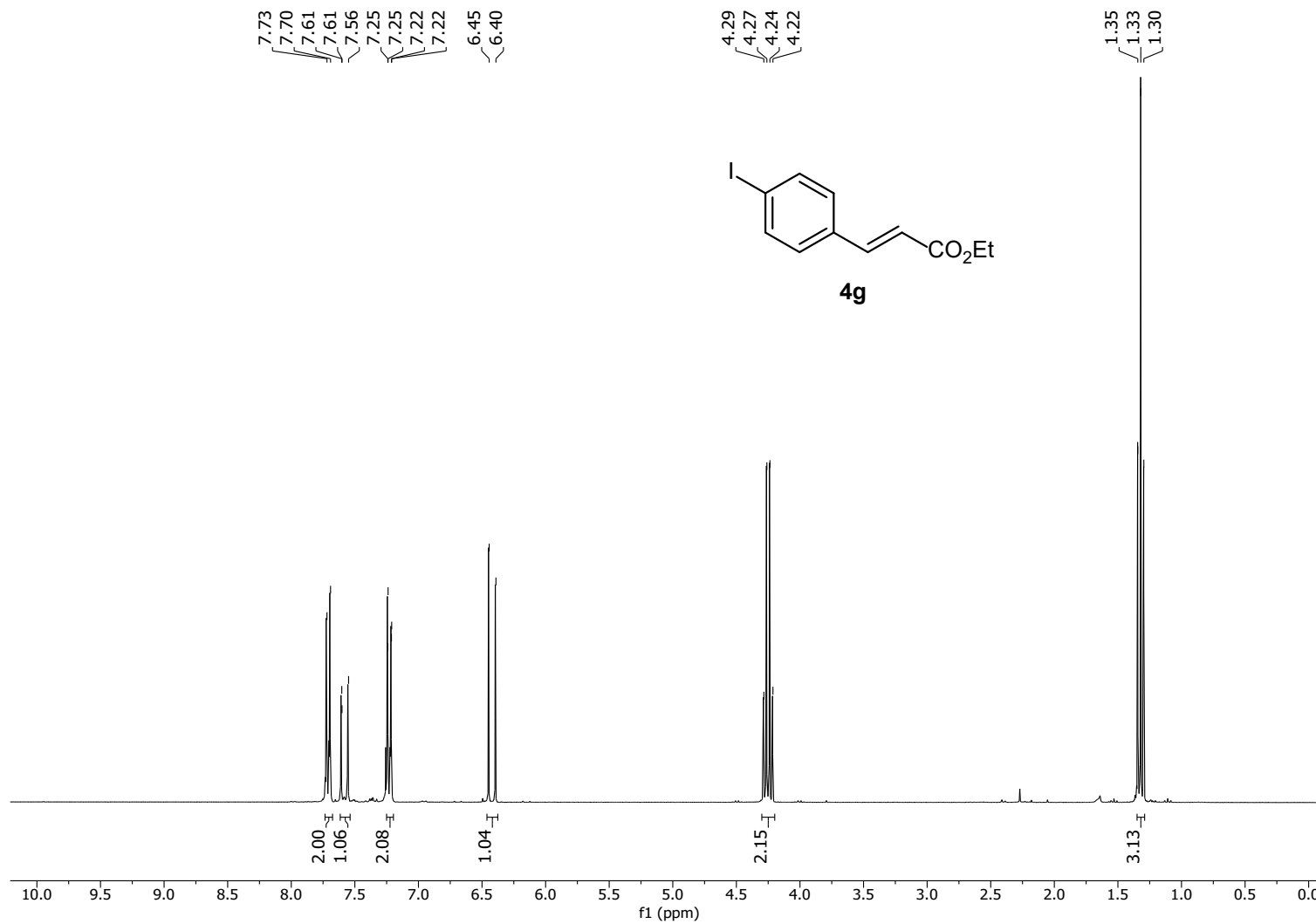
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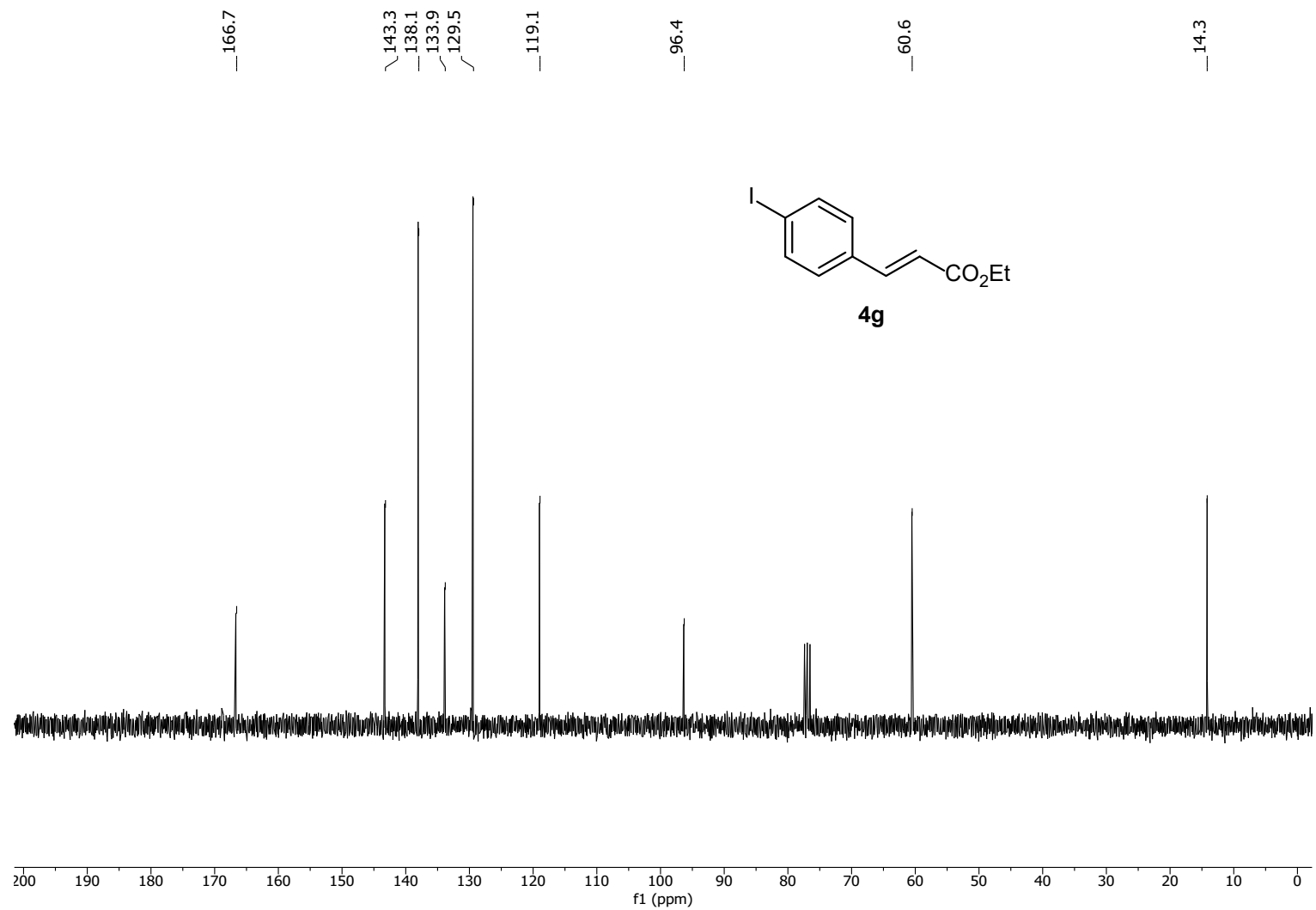
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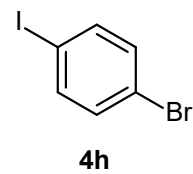
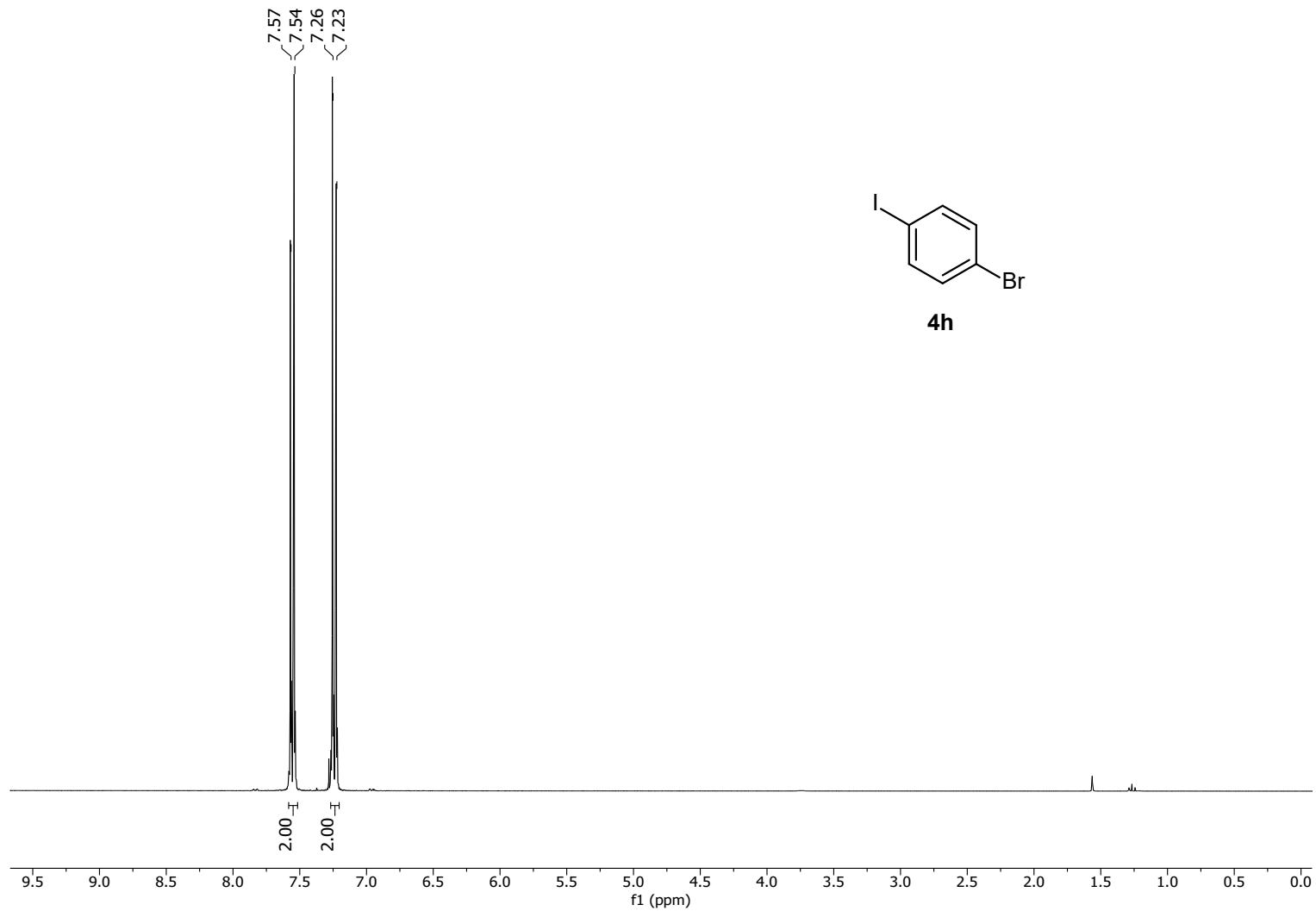
^1H NMR (300 MHz, CDCl_3)



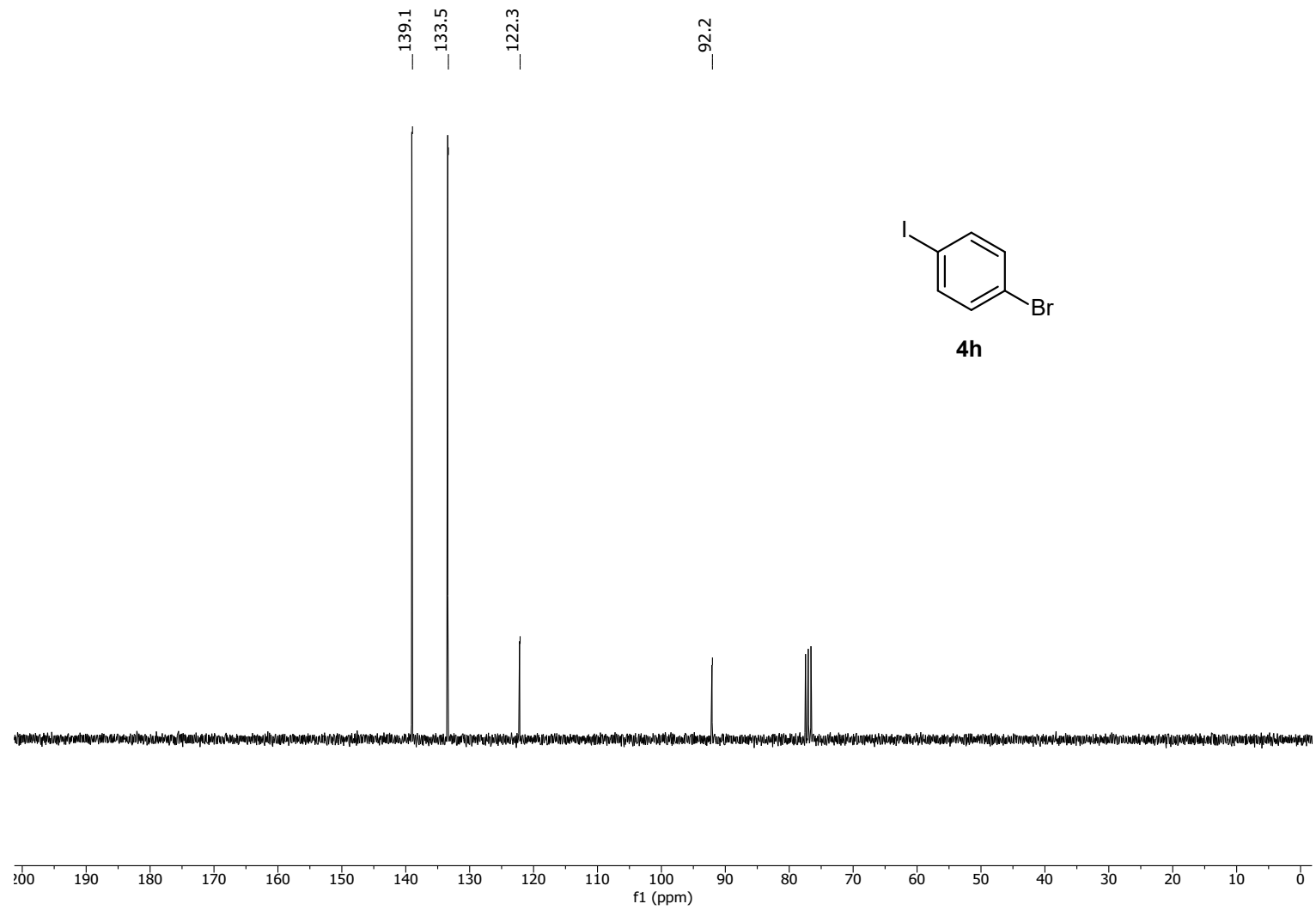
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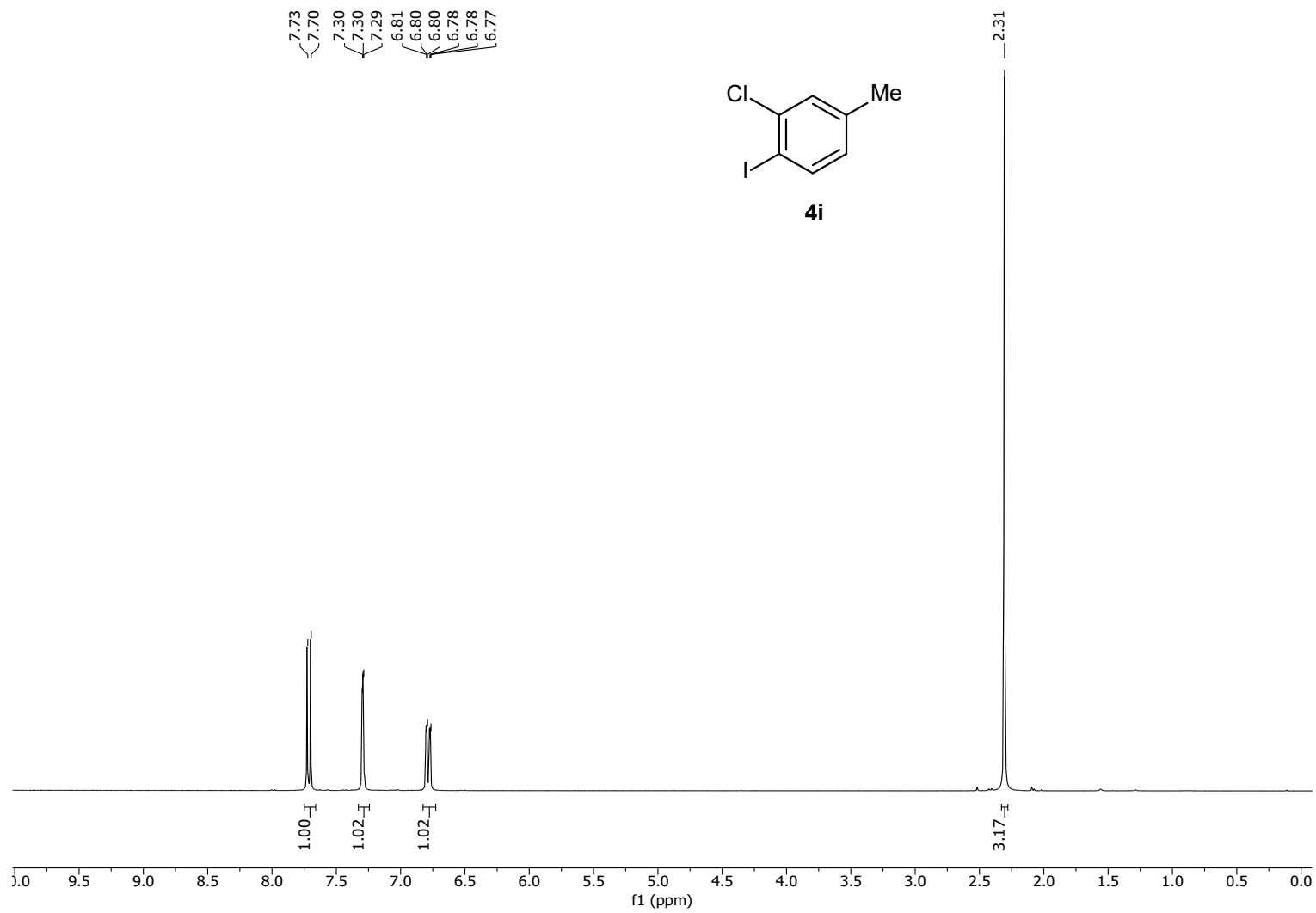
^1H NMR (300 MHz, CDCl_3)



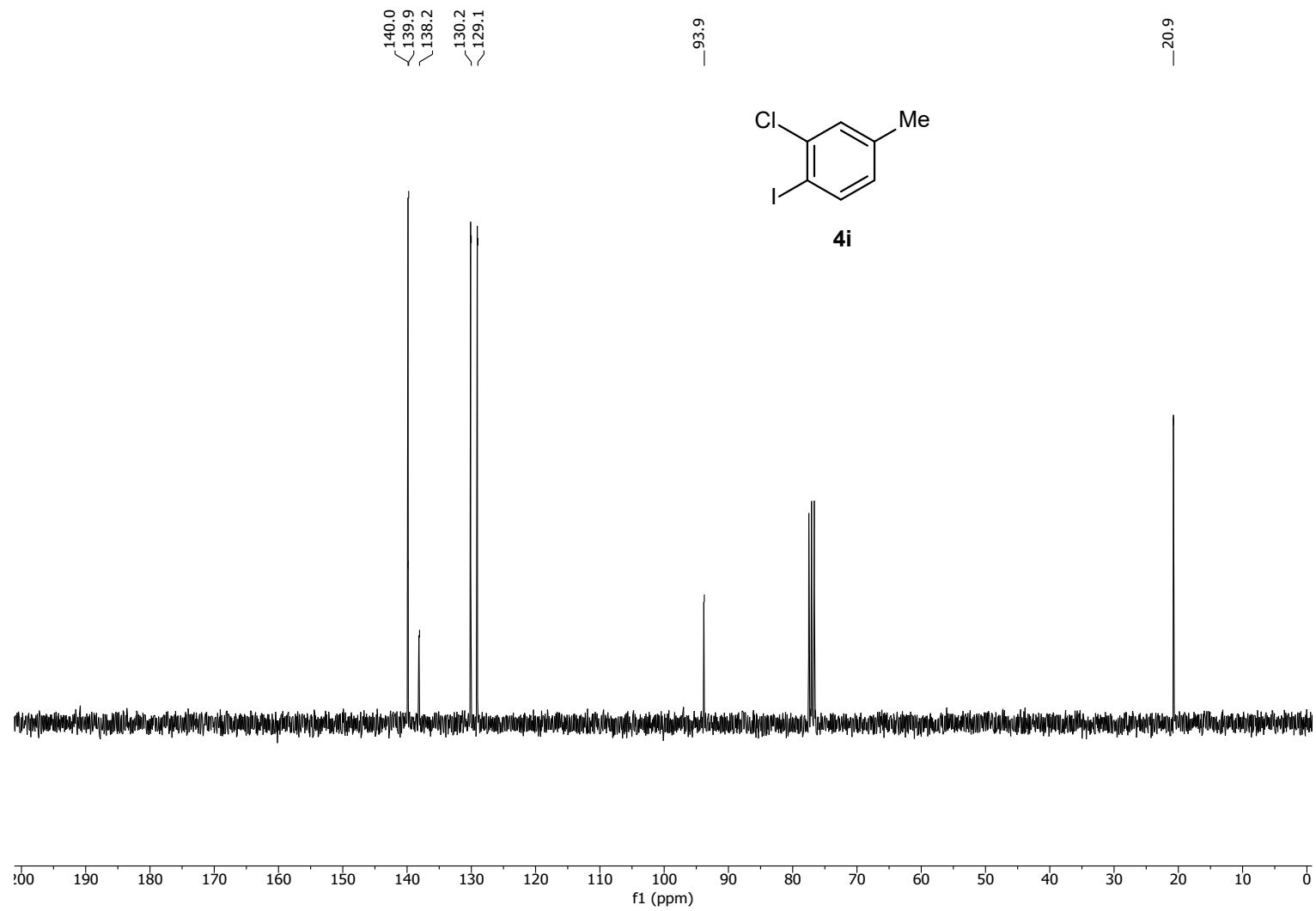
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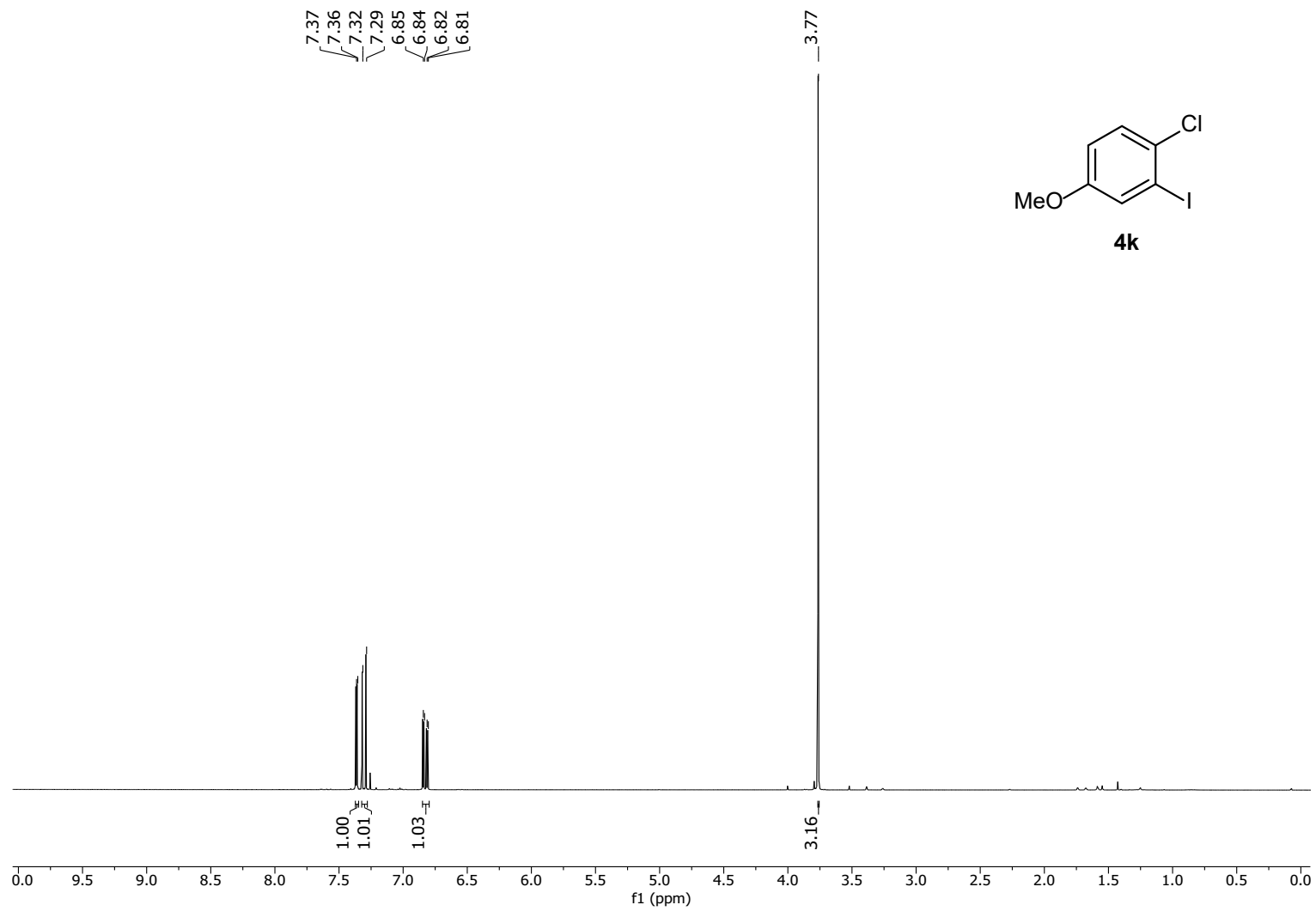
¹H NMR (300 MHz, CDCl₃)



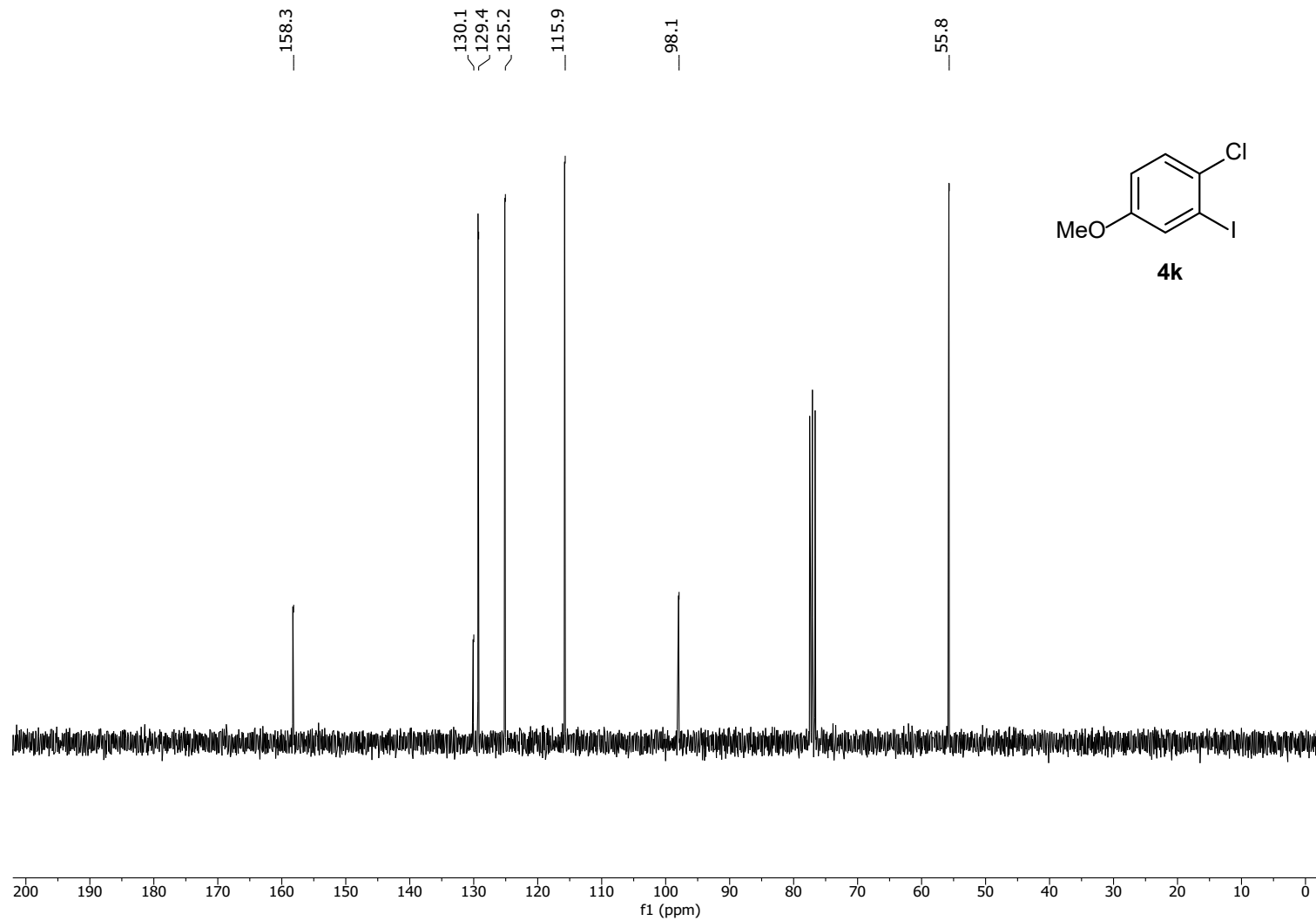
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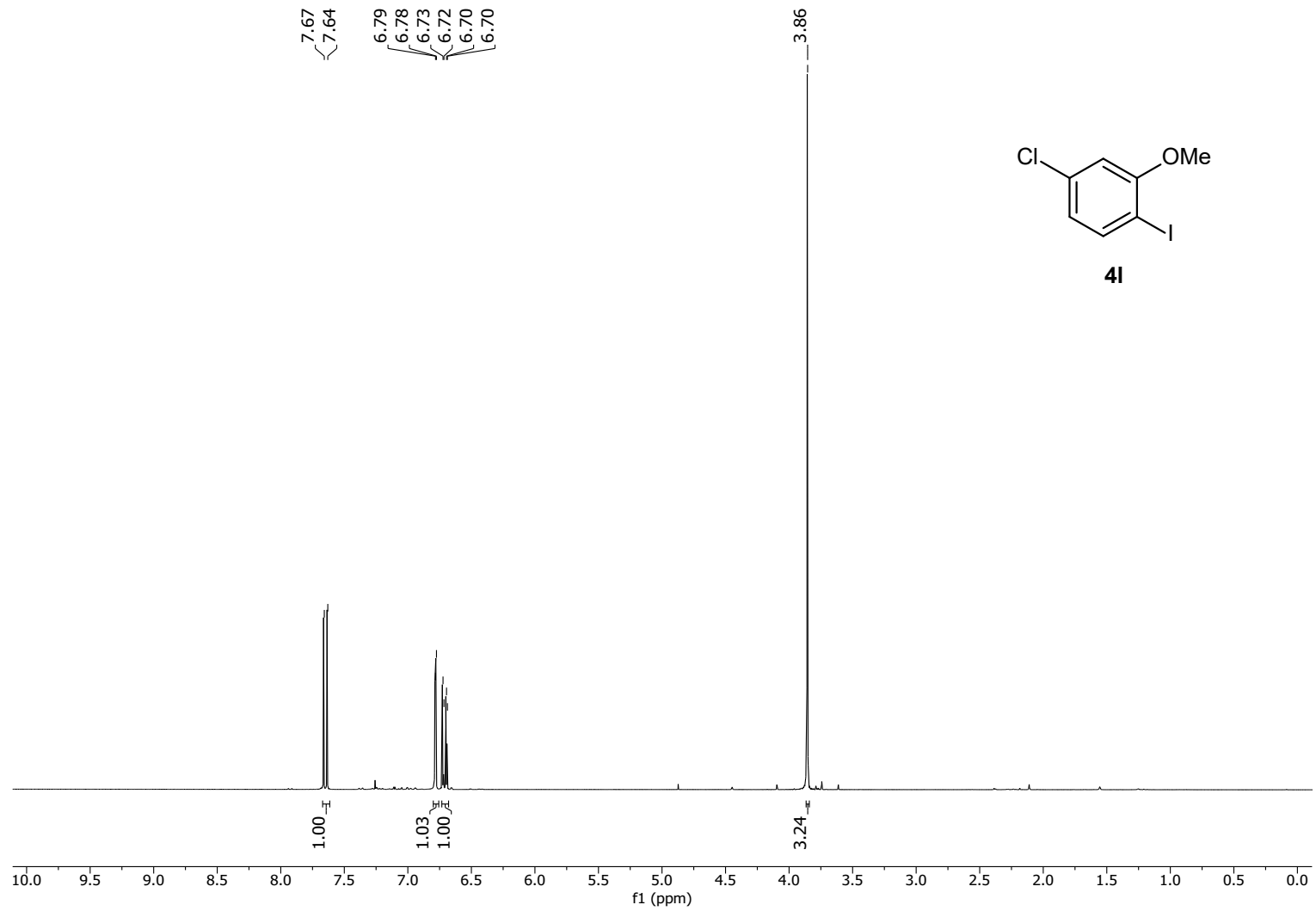
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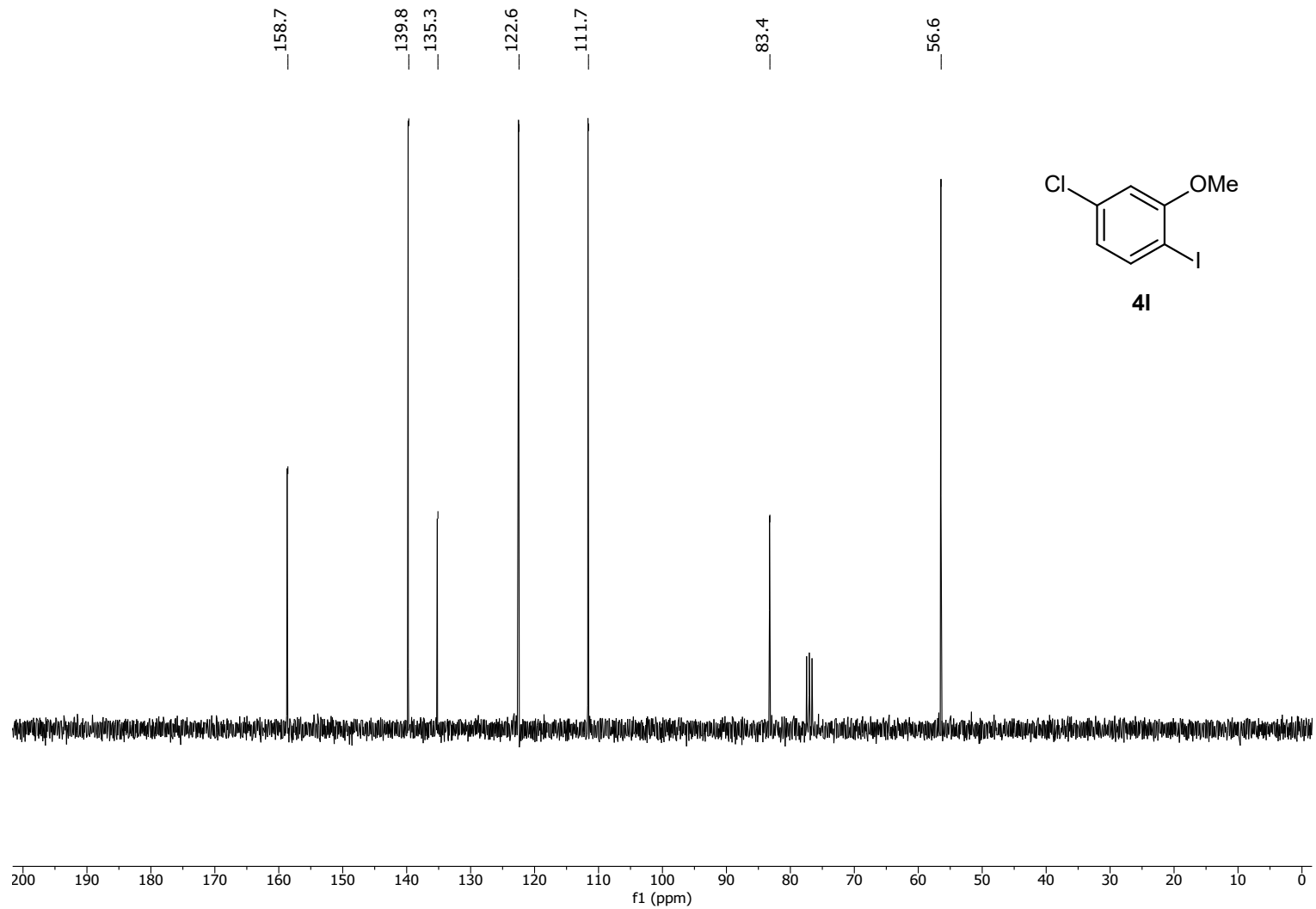
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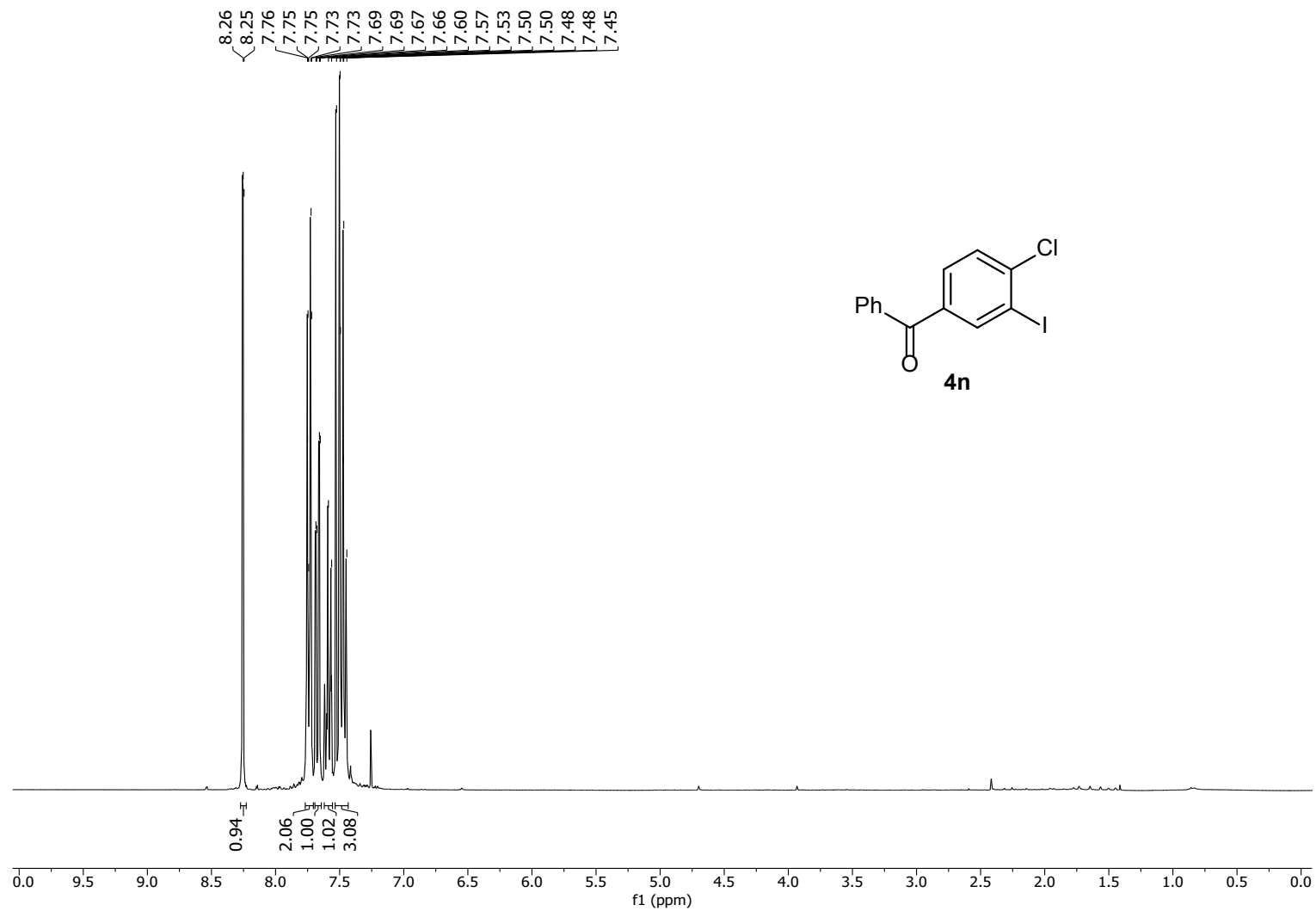
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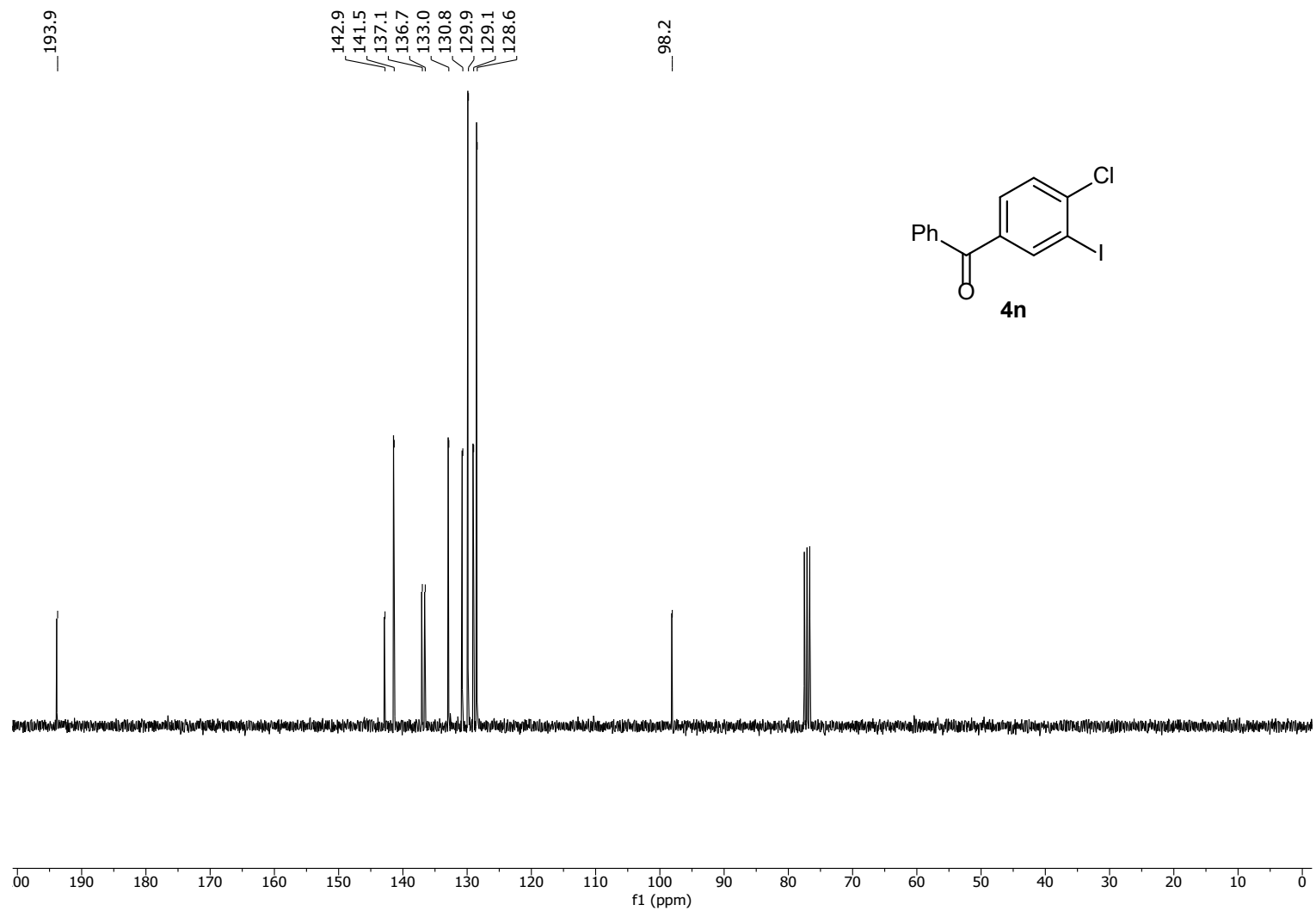
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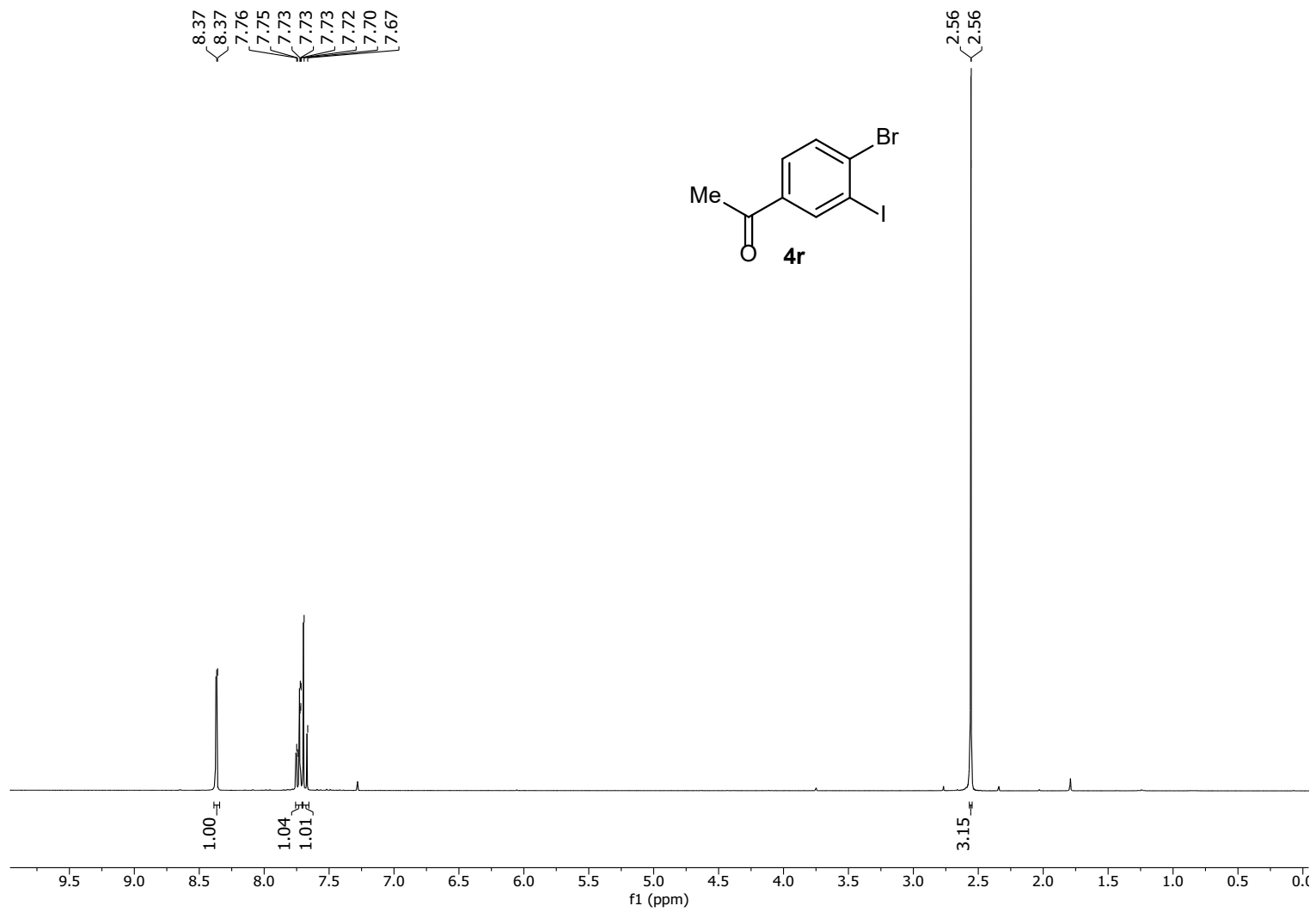
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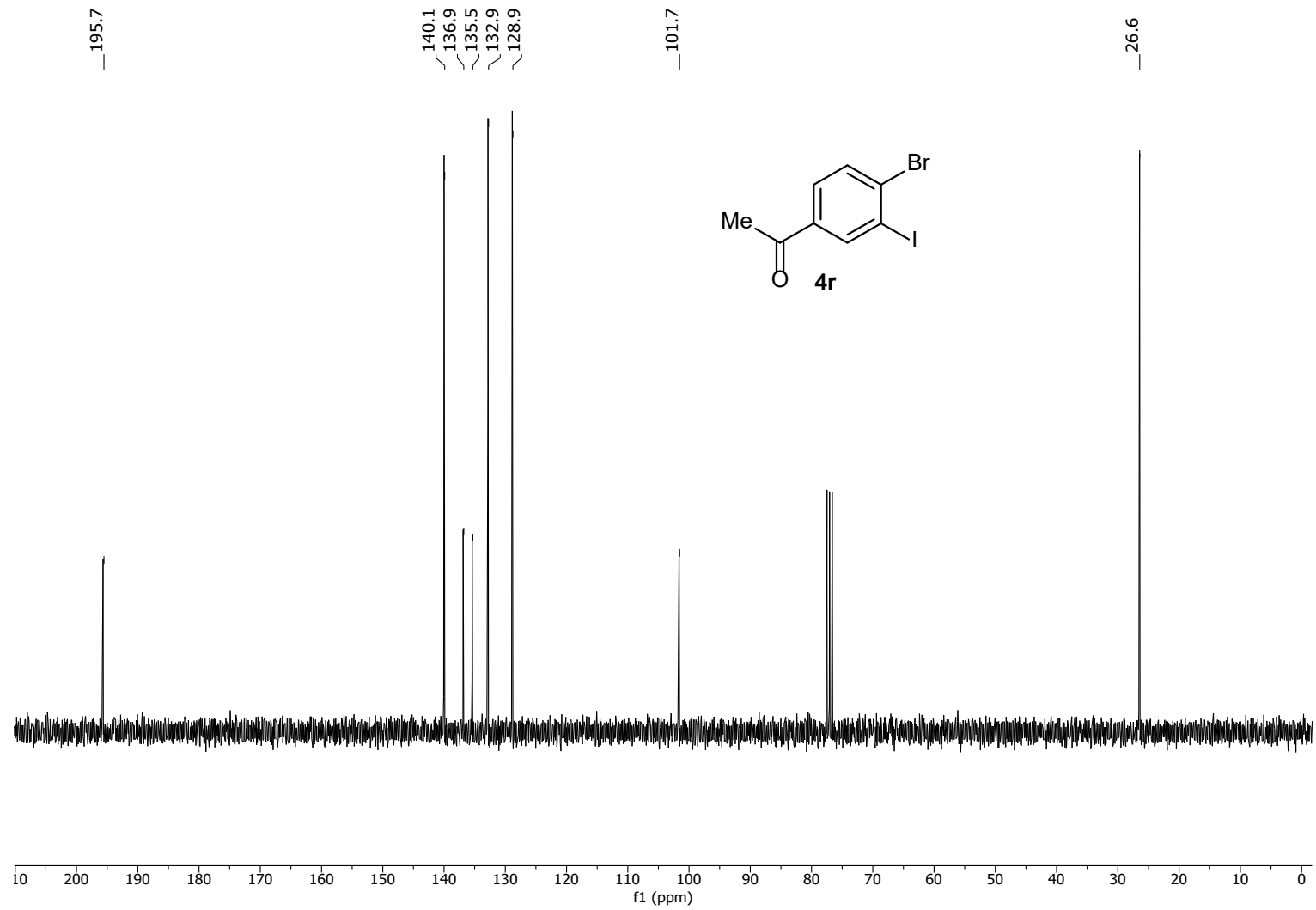
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^1H NMR (300 MHz, CDCl_3)



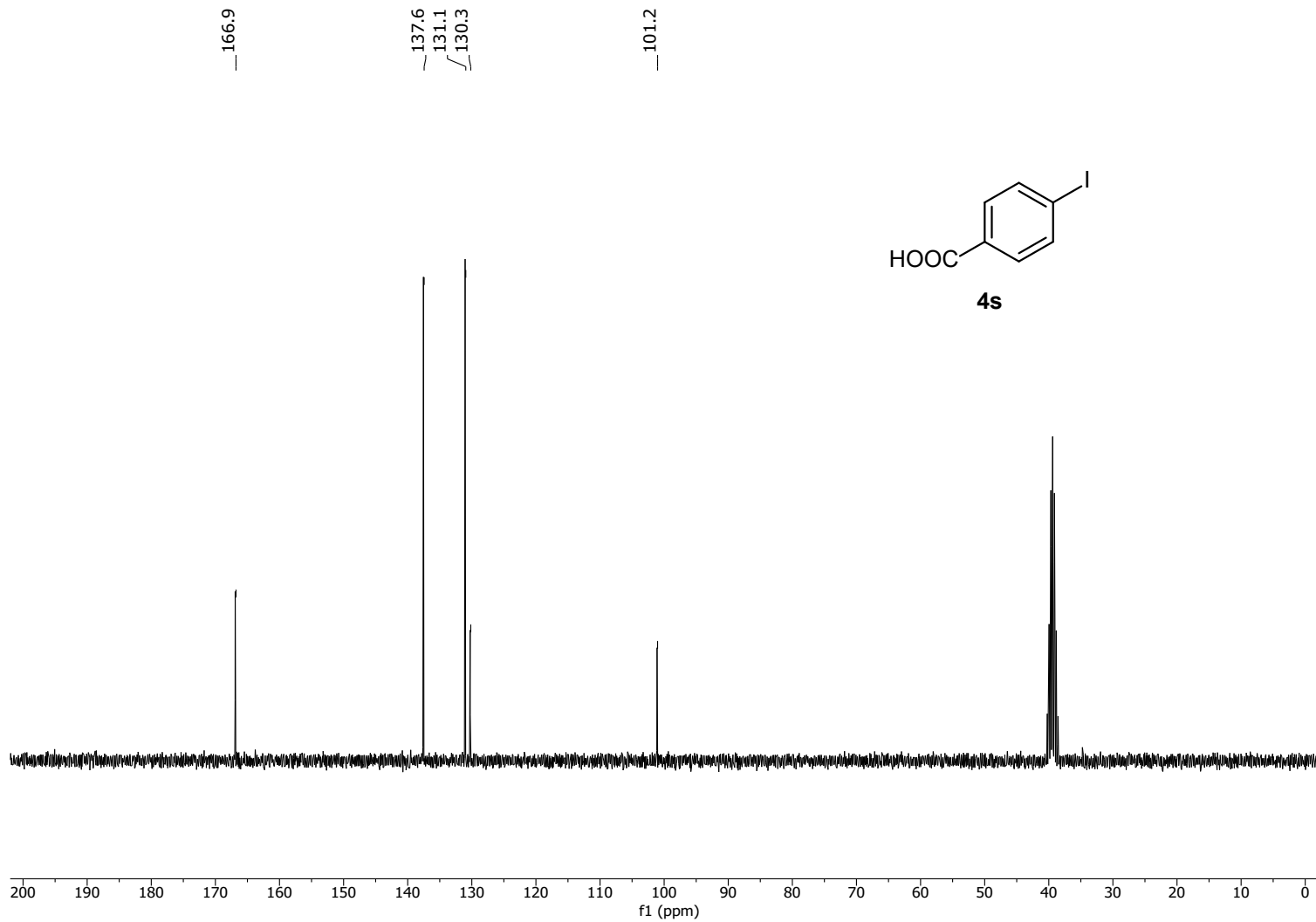
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^1H NMR (300 MHz, $\text{DMSO-}d_6$)



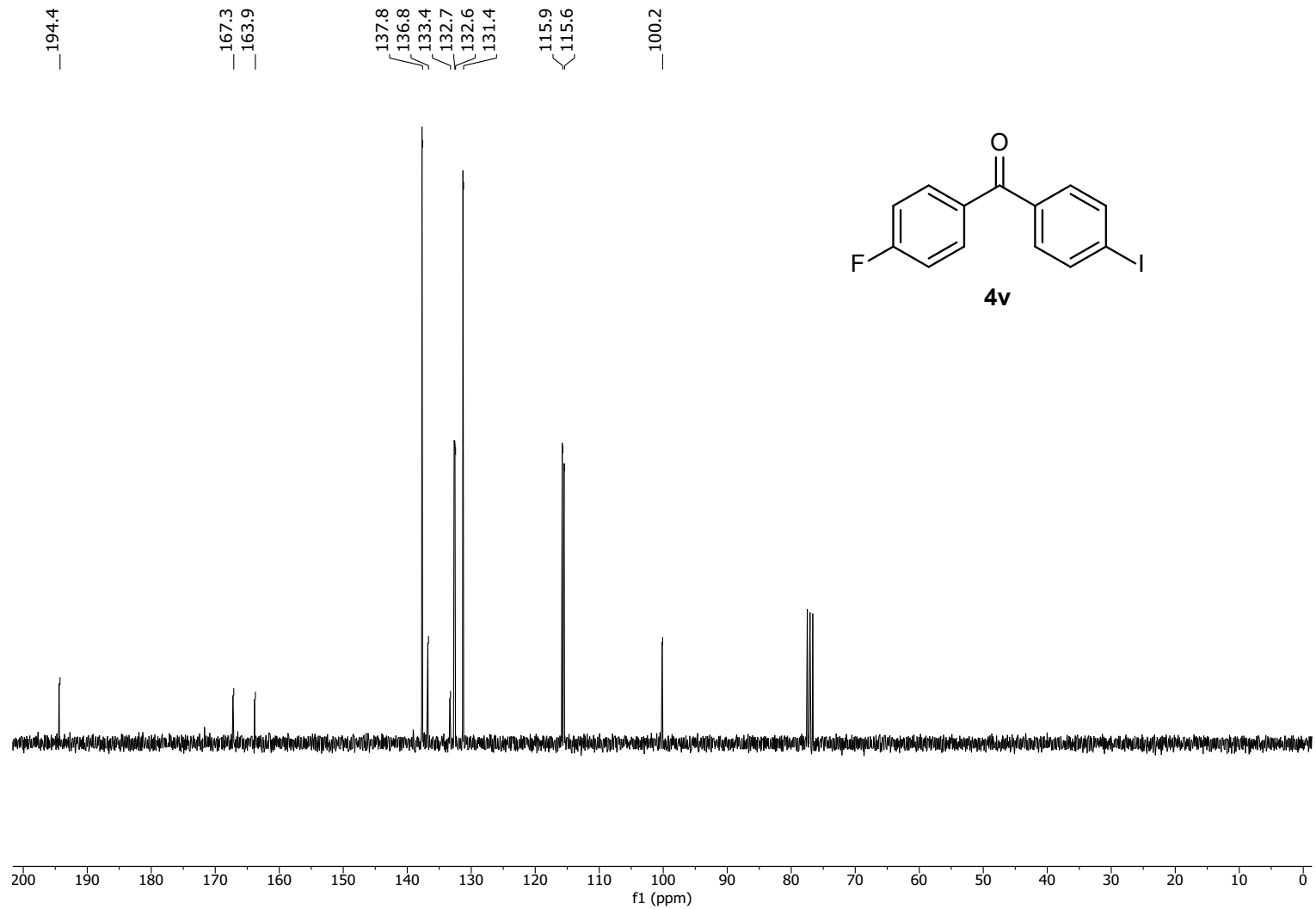
^{13}C NMR (75.4 MHz, $\text{DMSO-}d_6$)



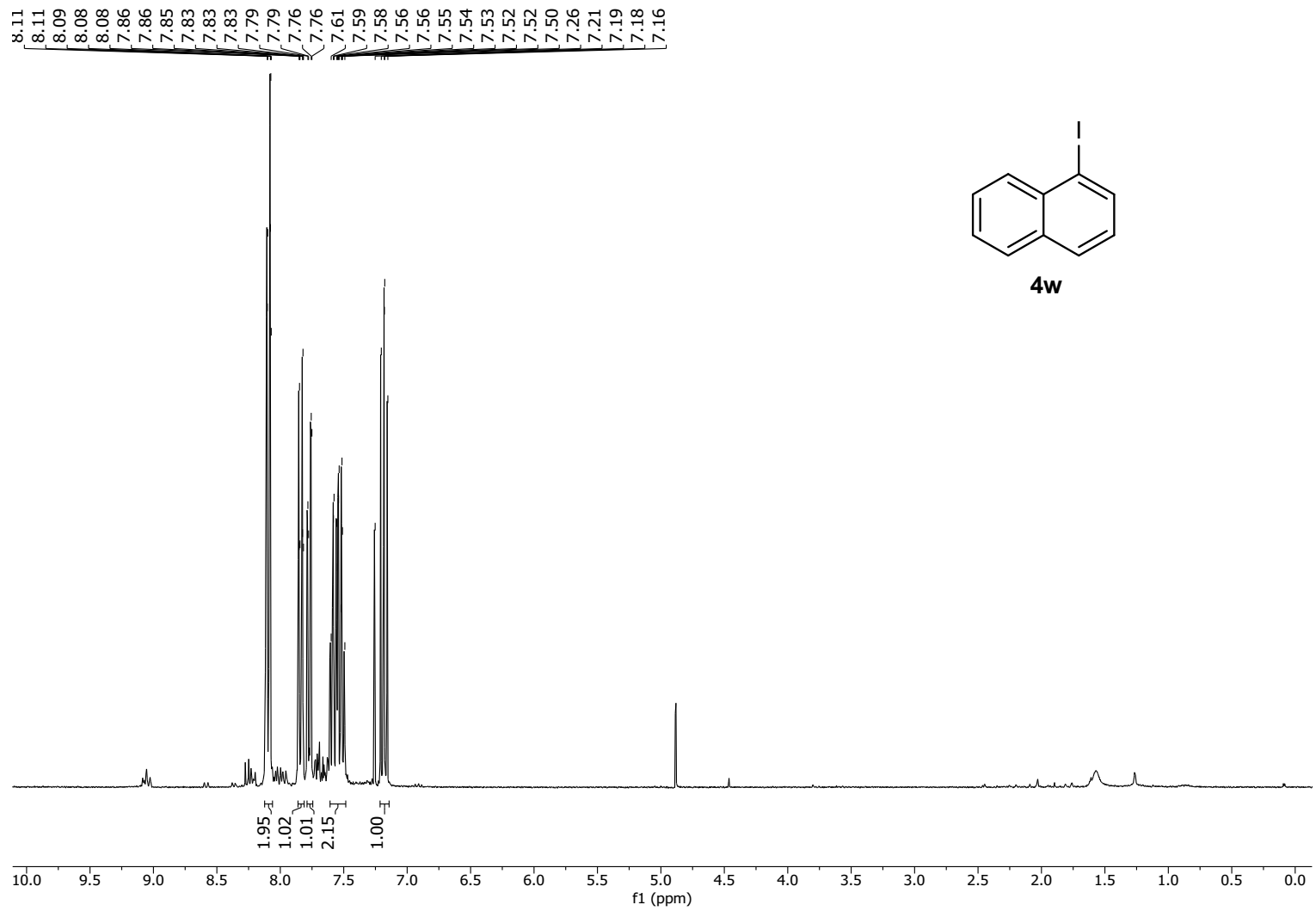
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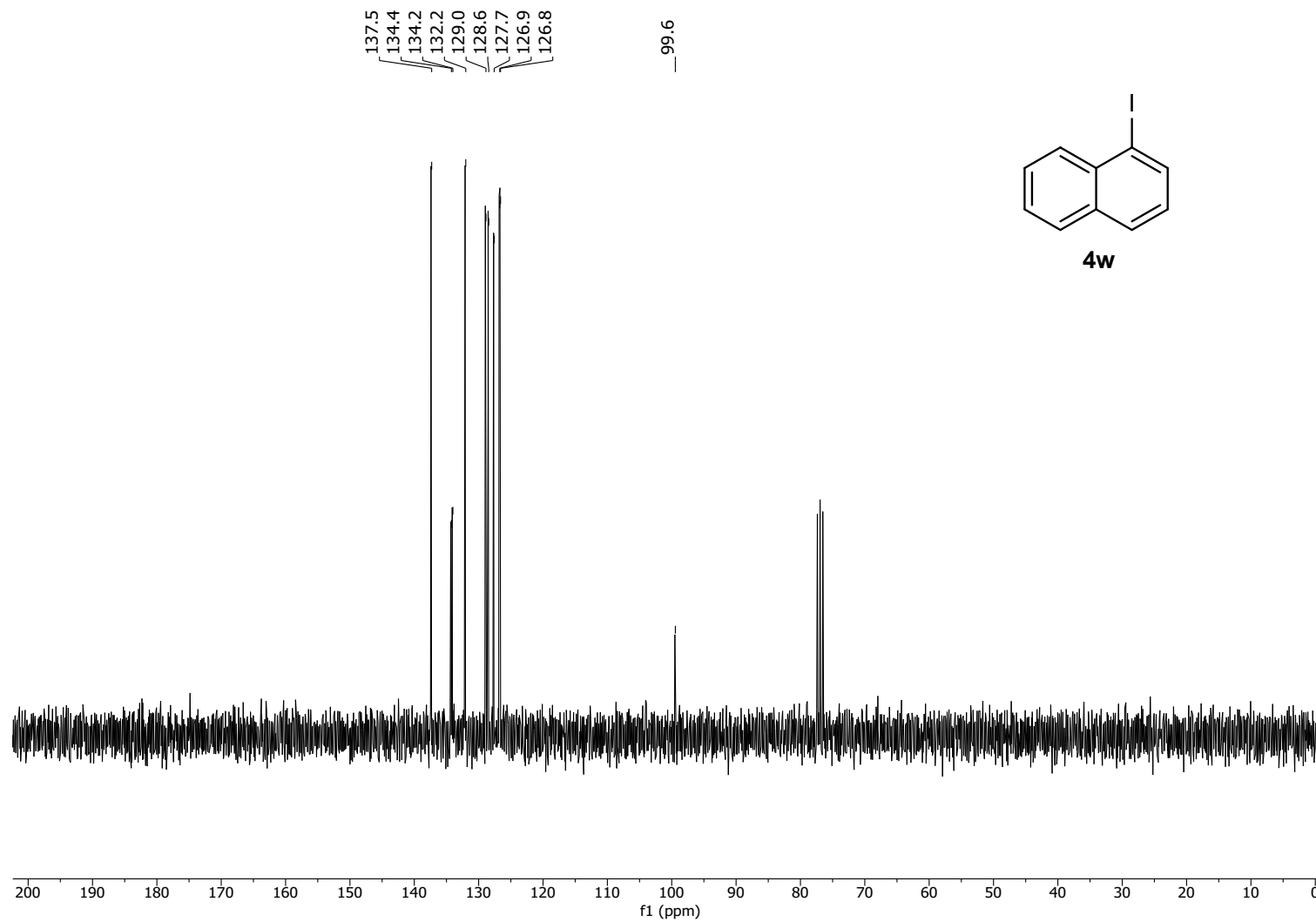
^{13}C NMR (75.4 MHz, CDCl_3)



^1H NMR (300 MHz, CDCl_3)



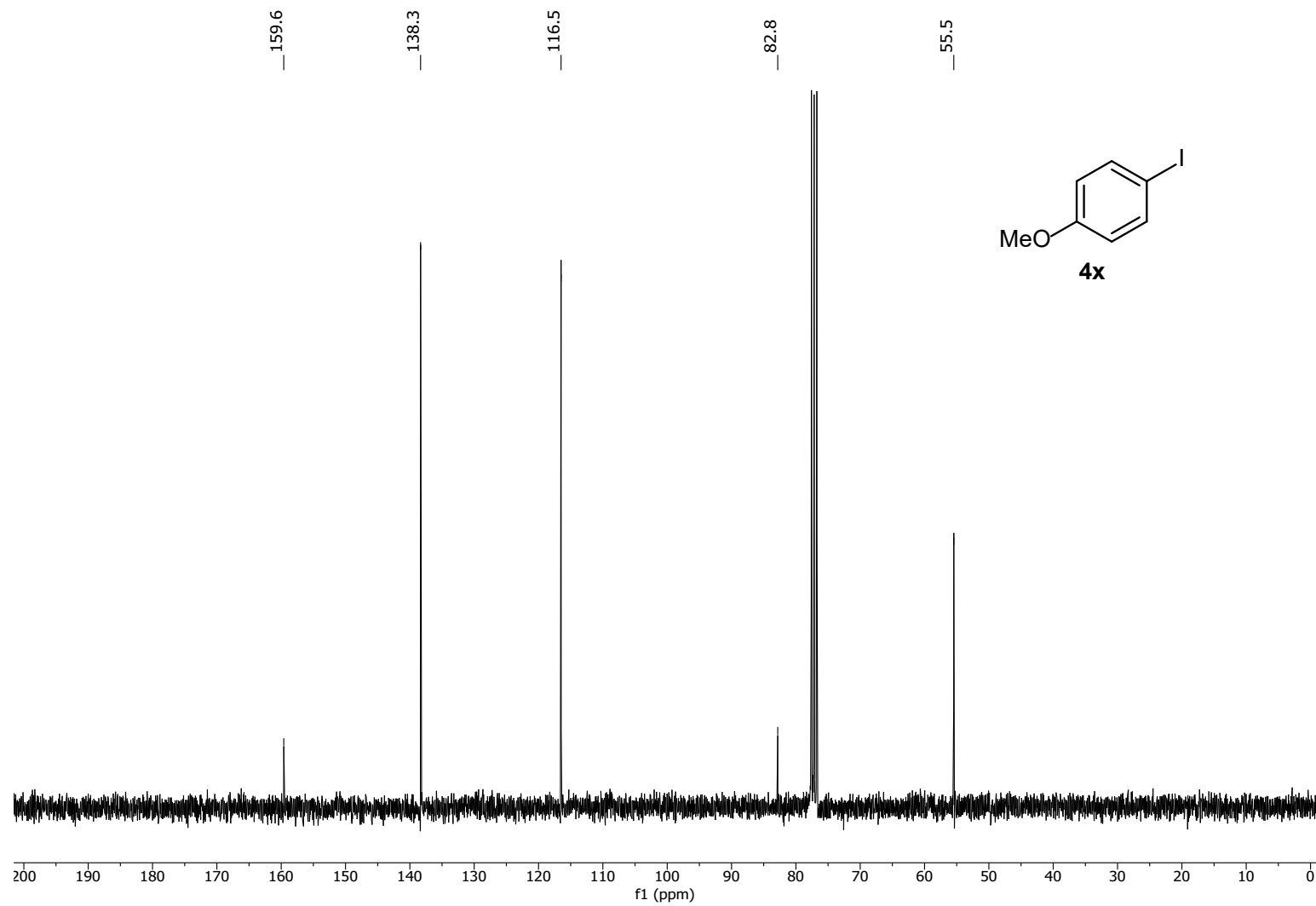
^{13}C NMR (75.4 MHz, CDCl_3)



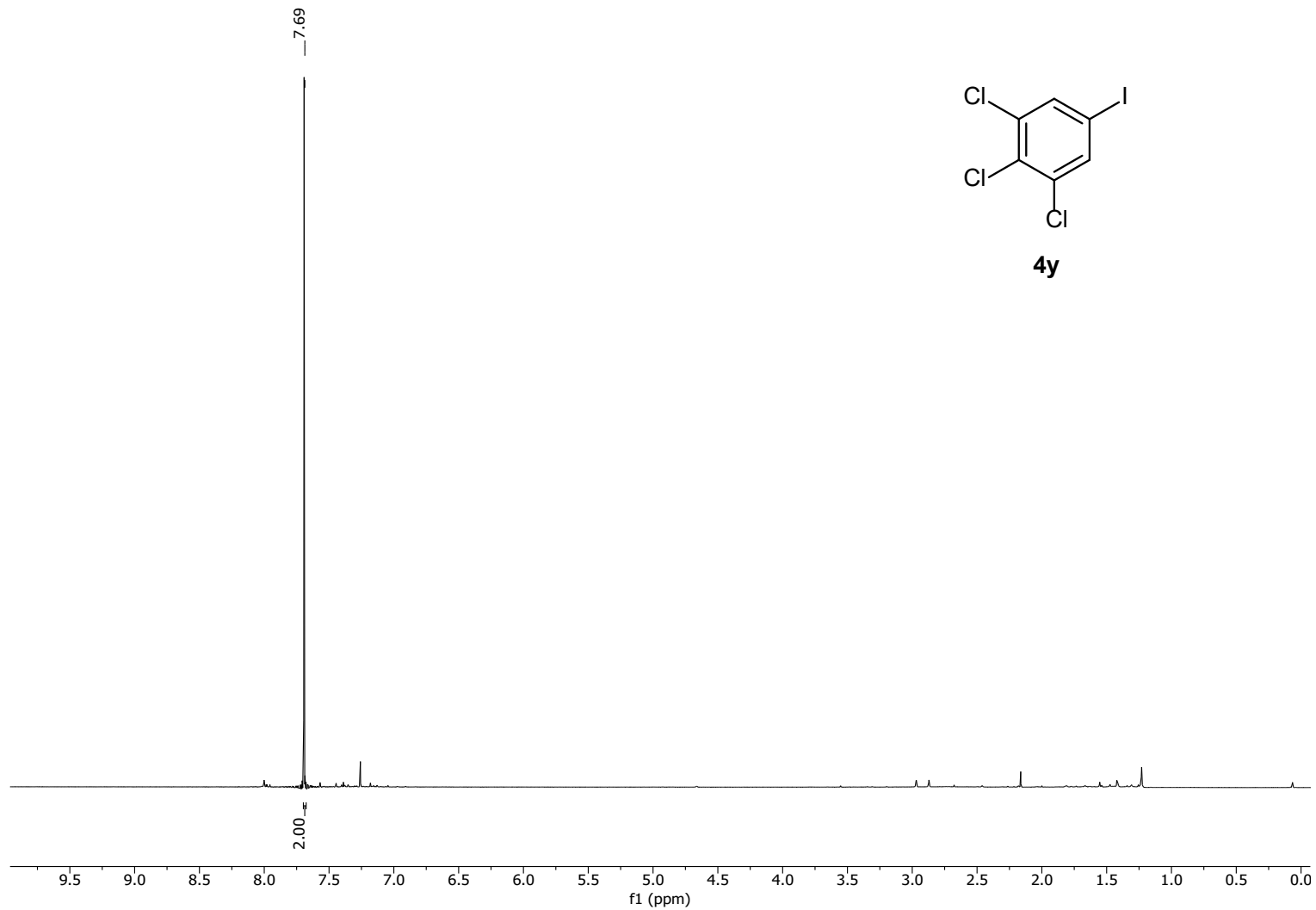
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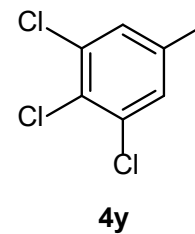
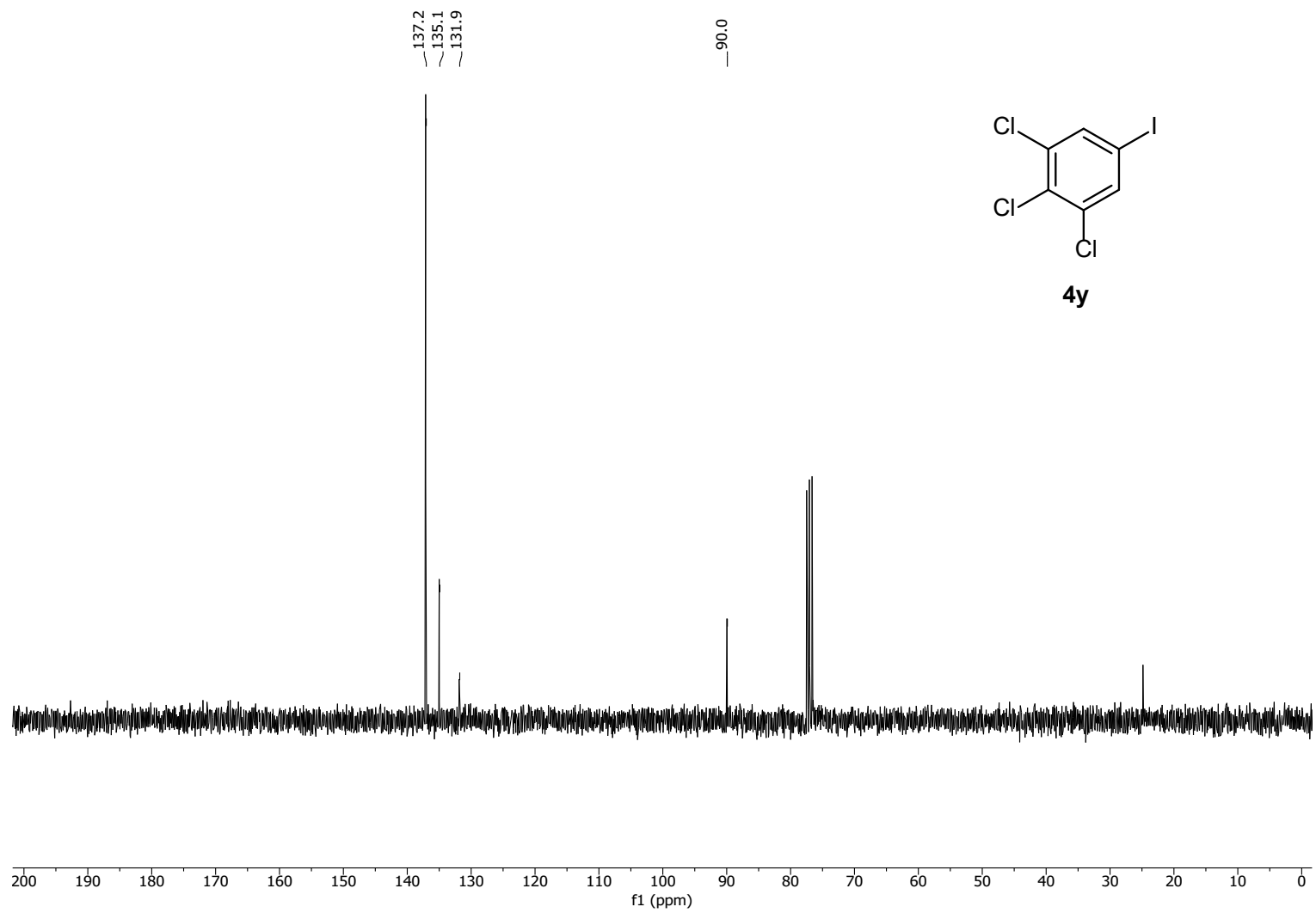
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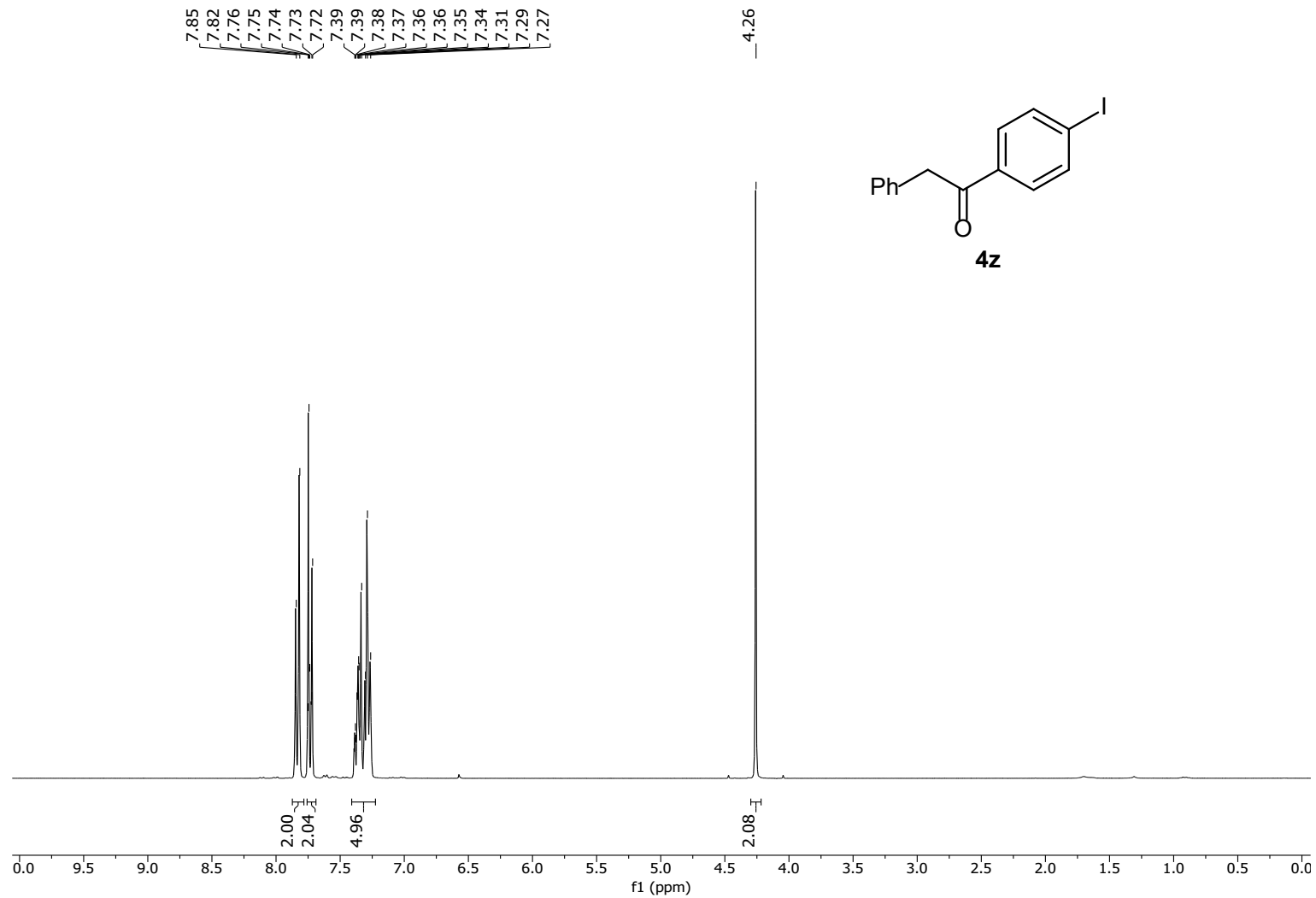
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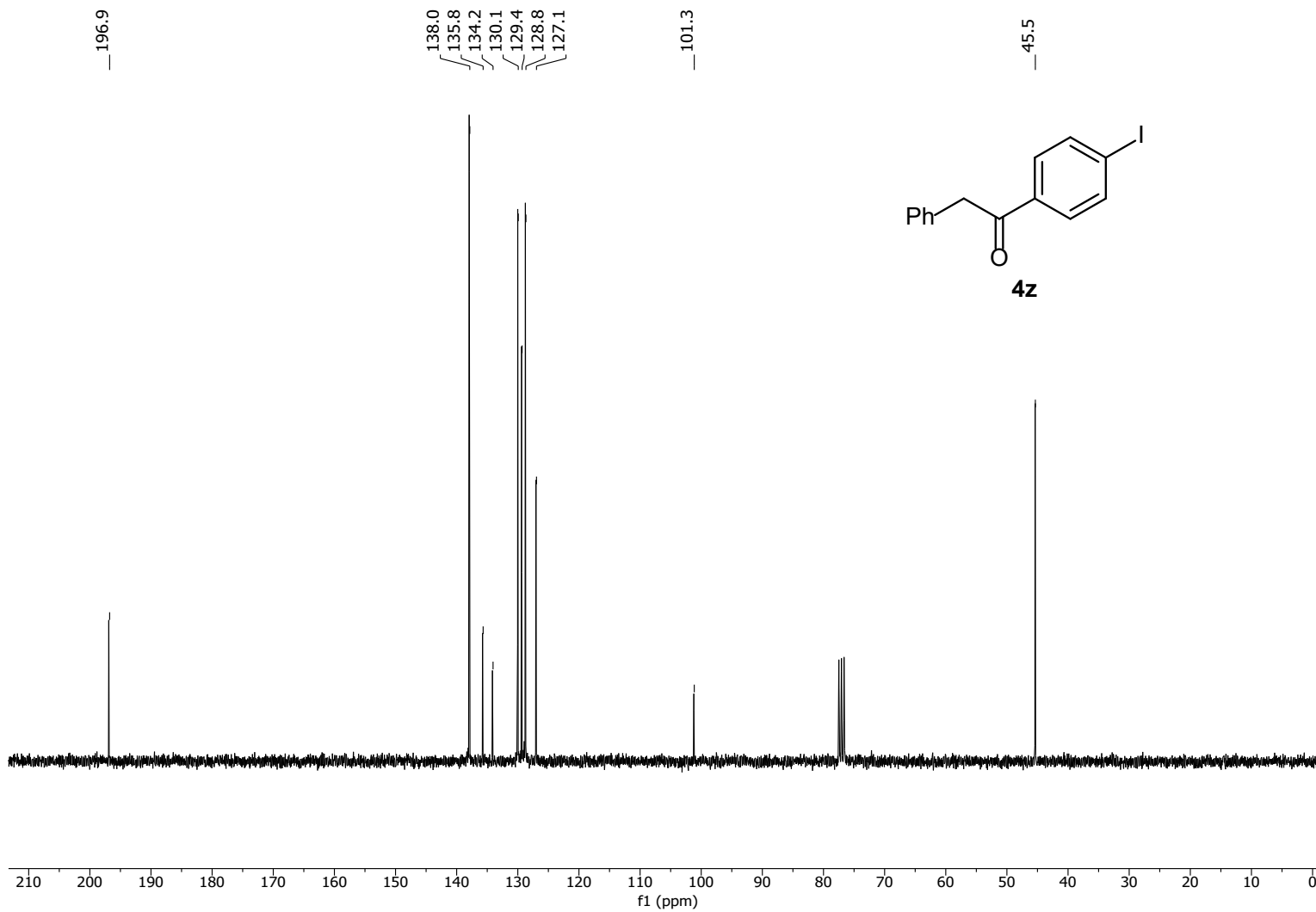
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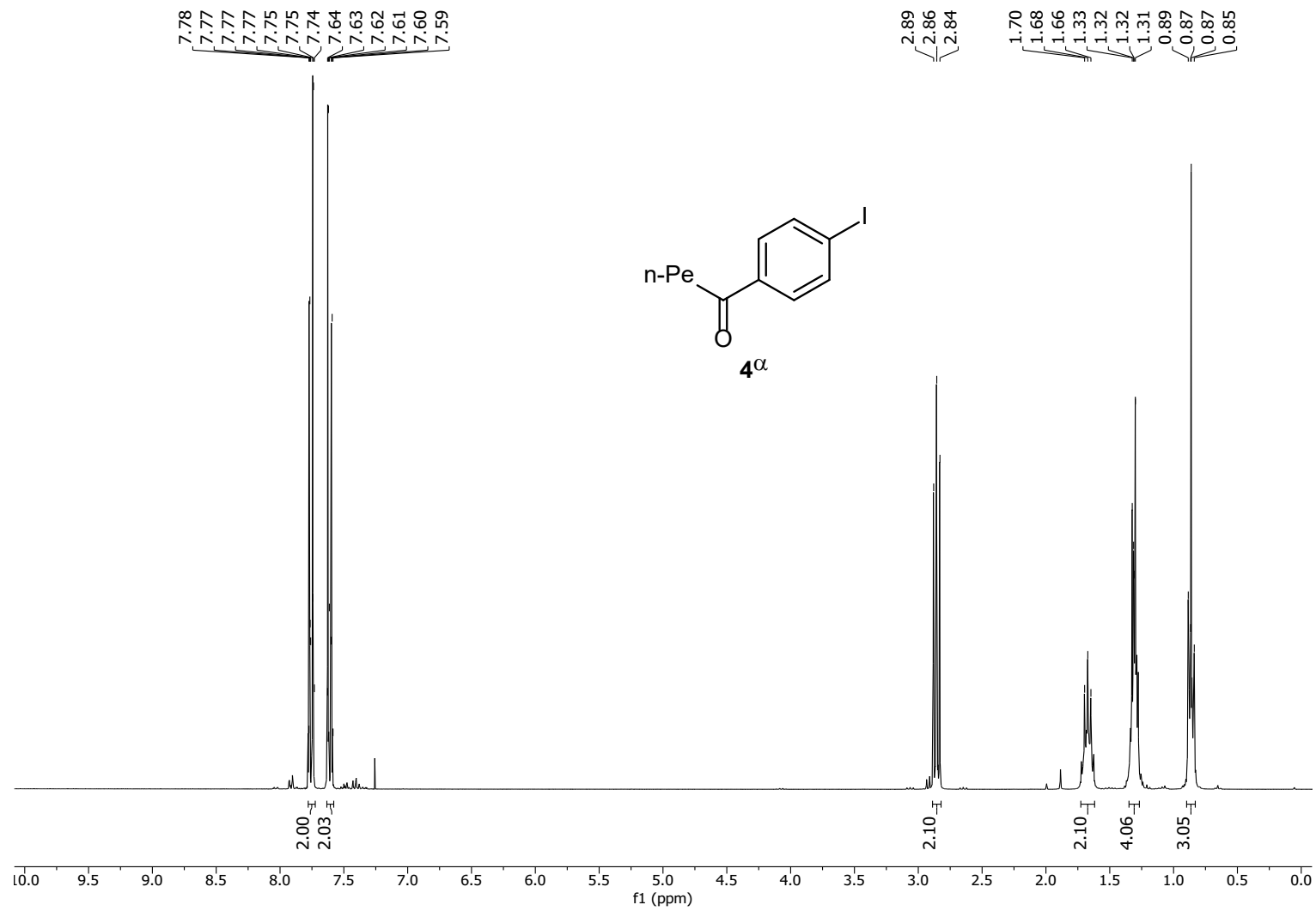
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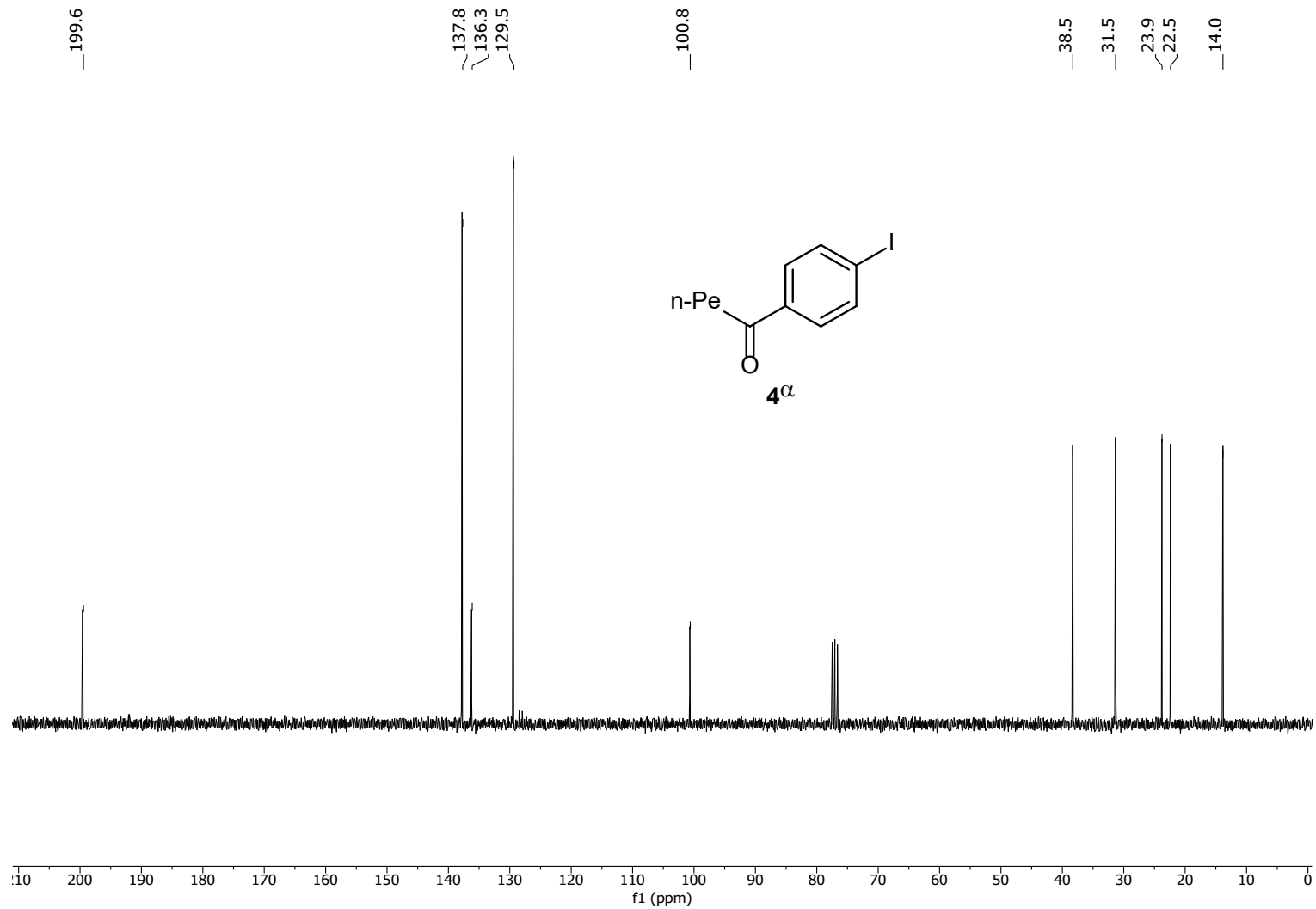
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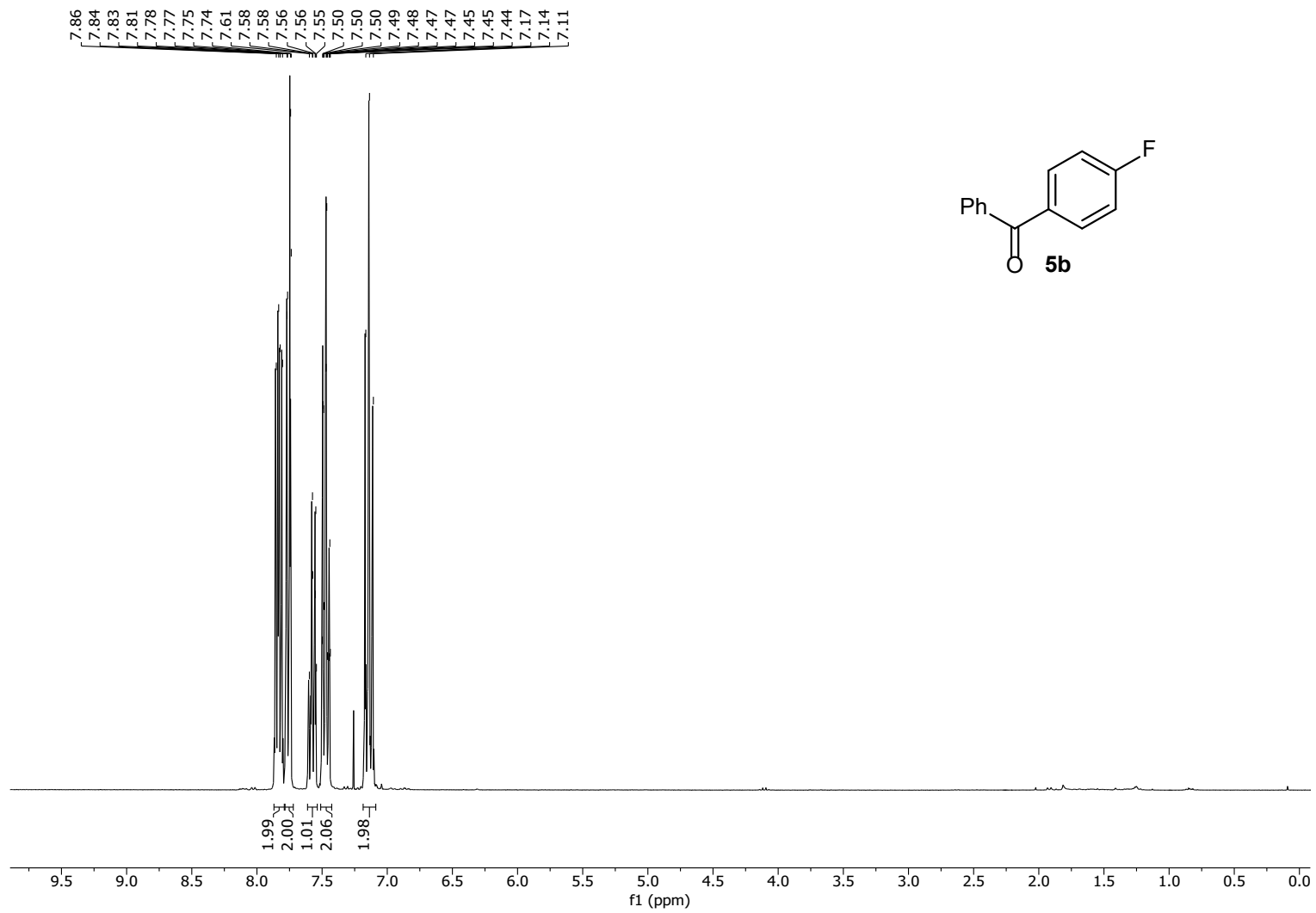
^1H NMR (300 MHz, CDCl_3)



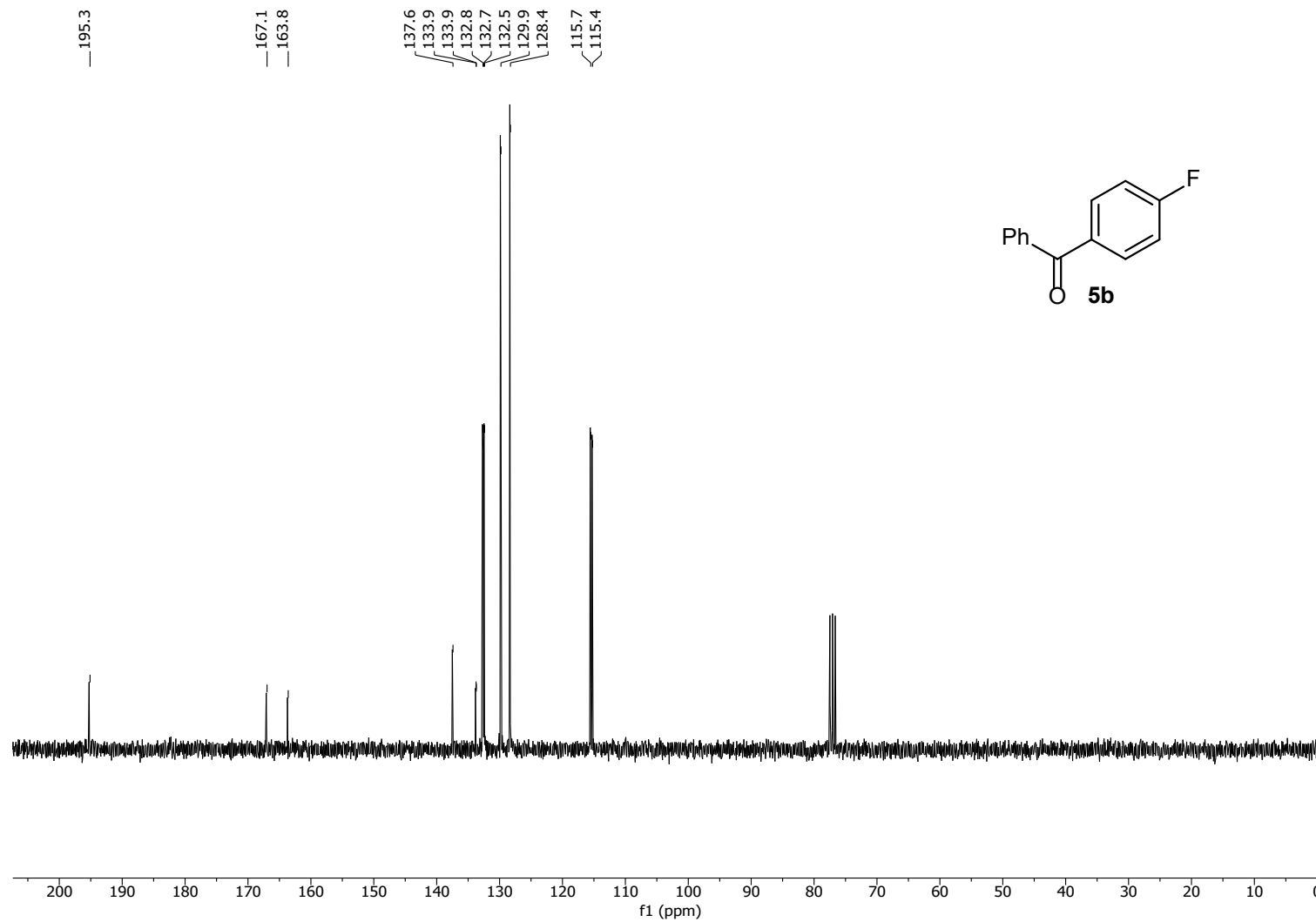
^{13}C NMR (75.4 MHz, CDCl_3)



^1H NMR (300 MHz, CDCl_3)



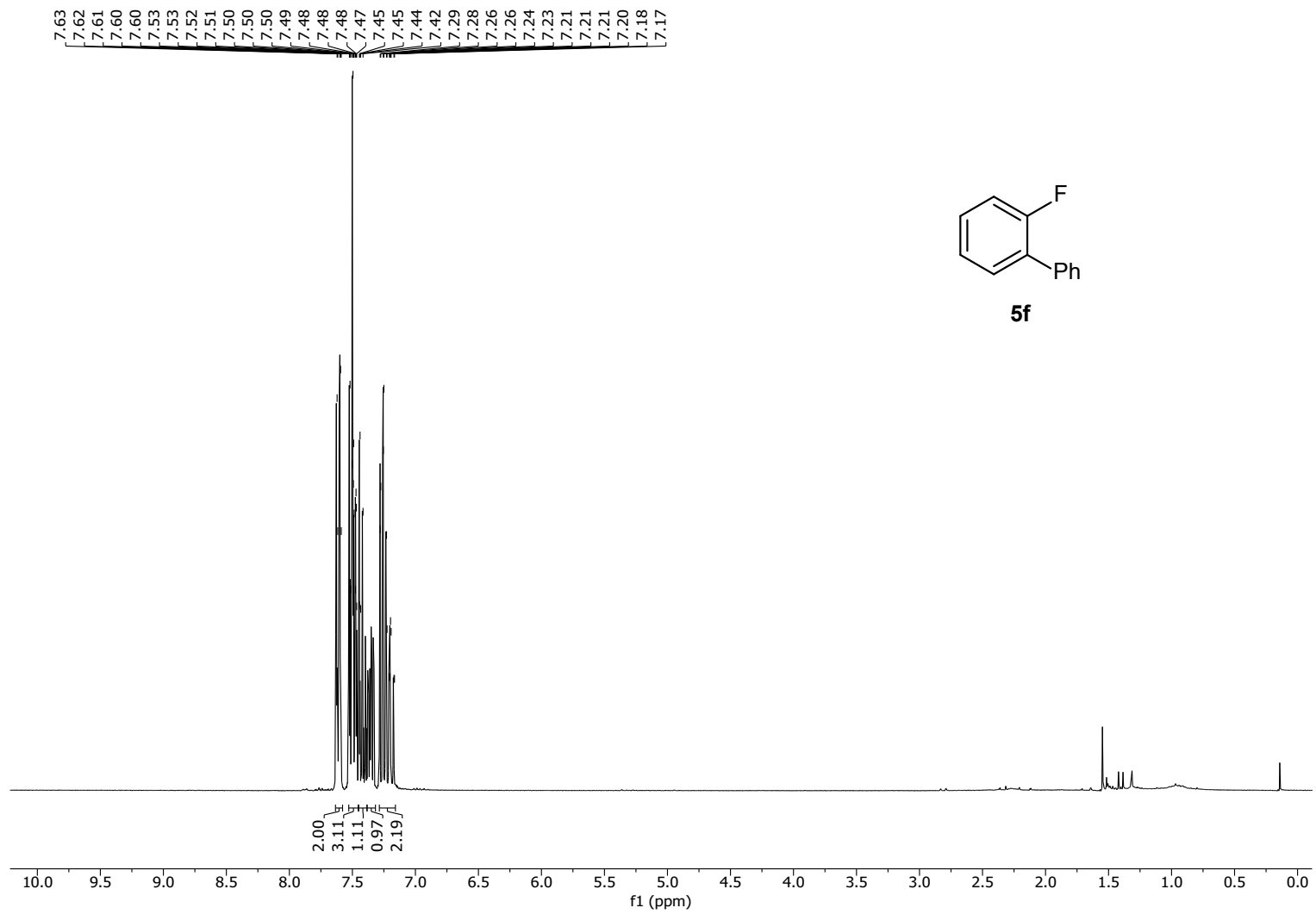
^{13}C NMR (75.4 MHz, CDCl_3)



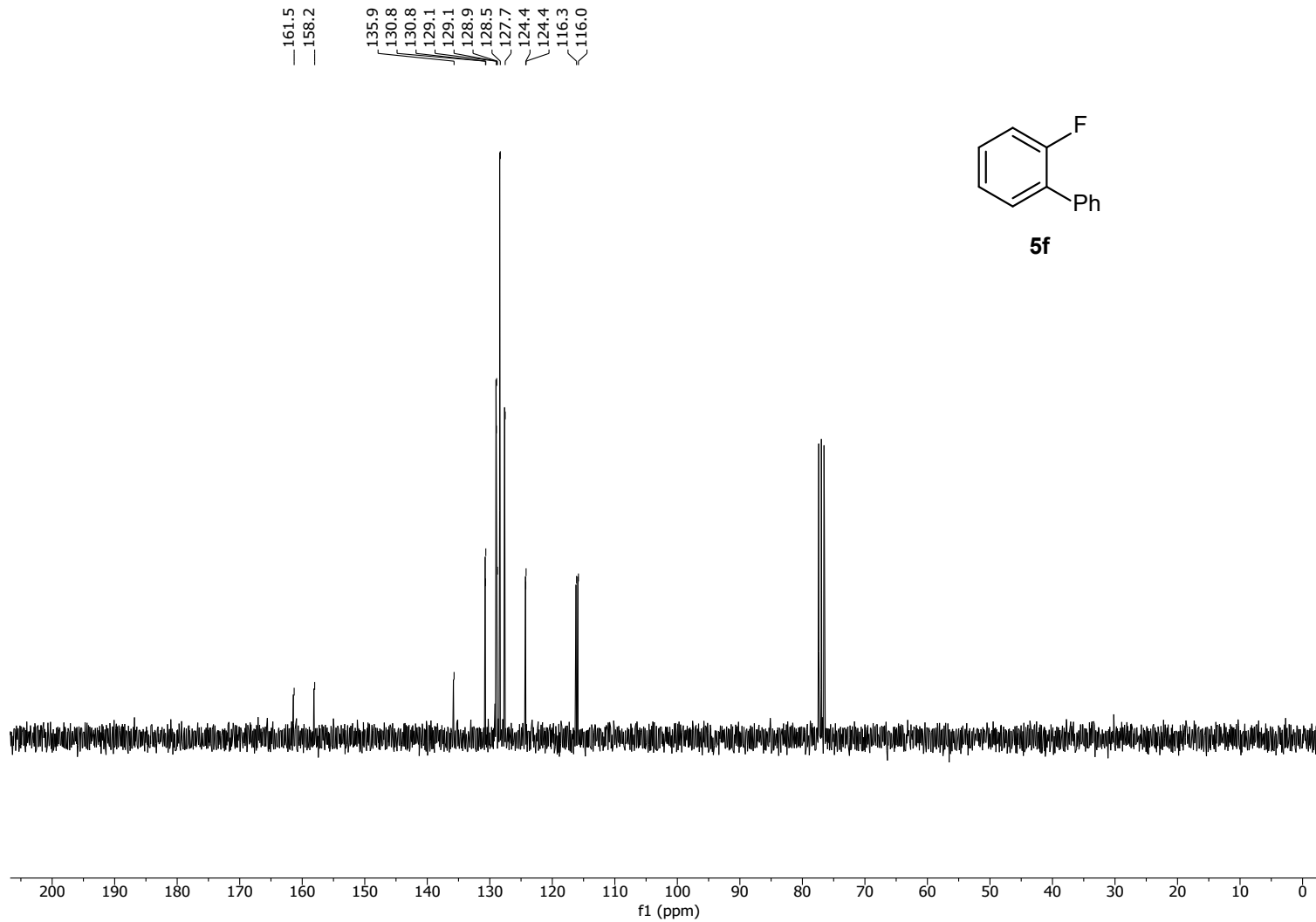
^{19}F NMR (282 MHz, CDCl_3)



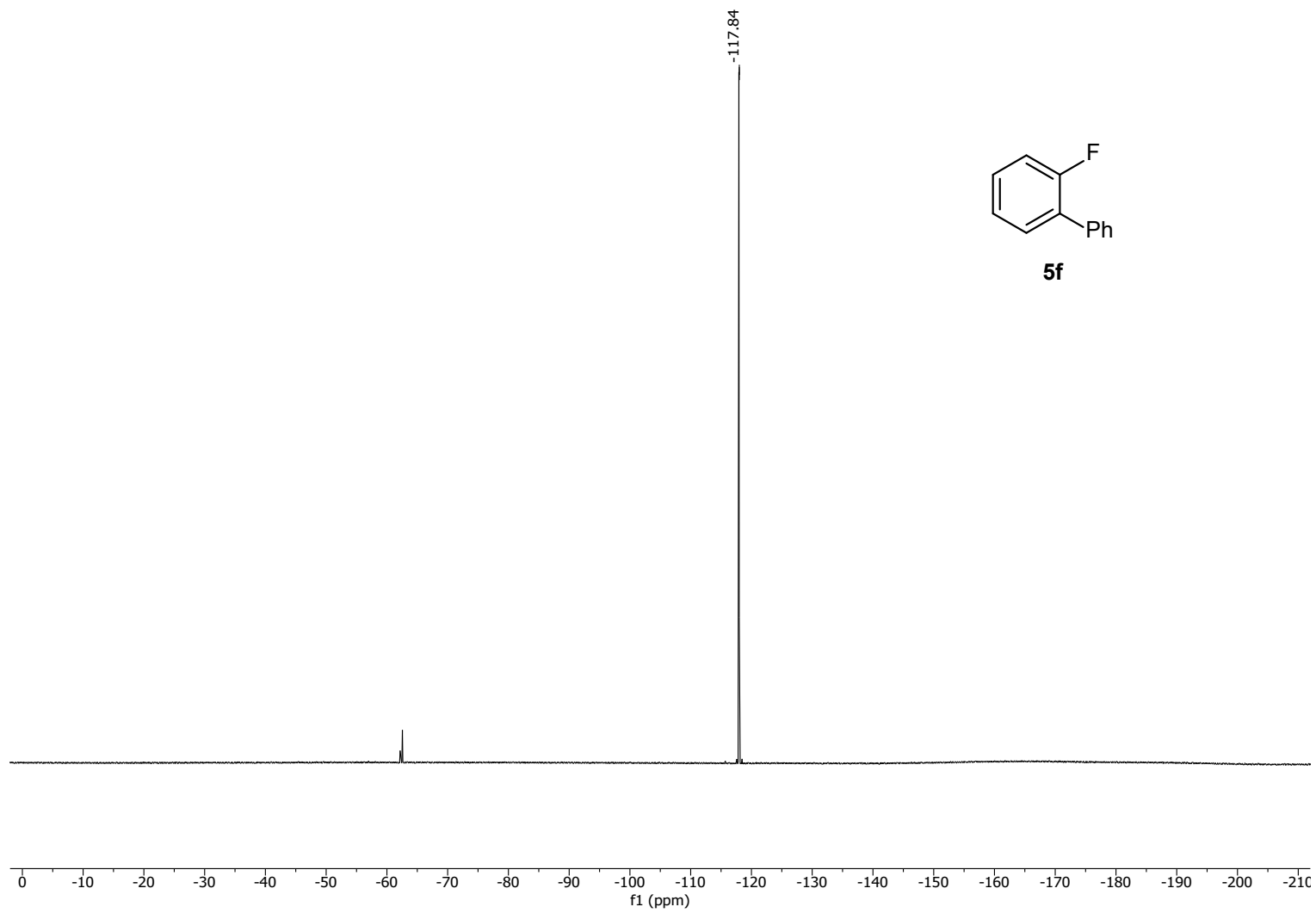
^1H NMR (300 MHz, CDCl_3)



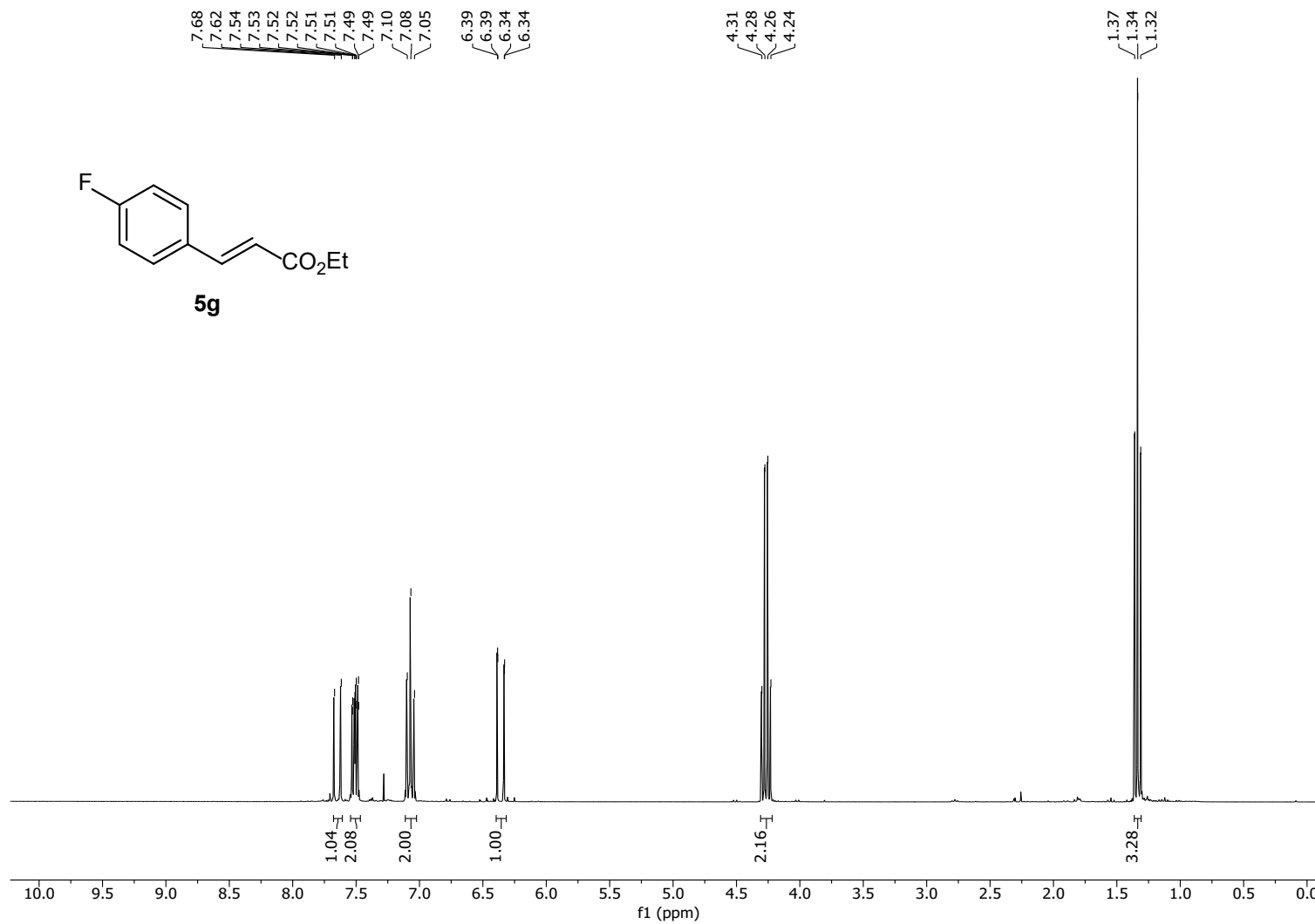
^{13}C NMR (75.4 MHz, CDCl_3)



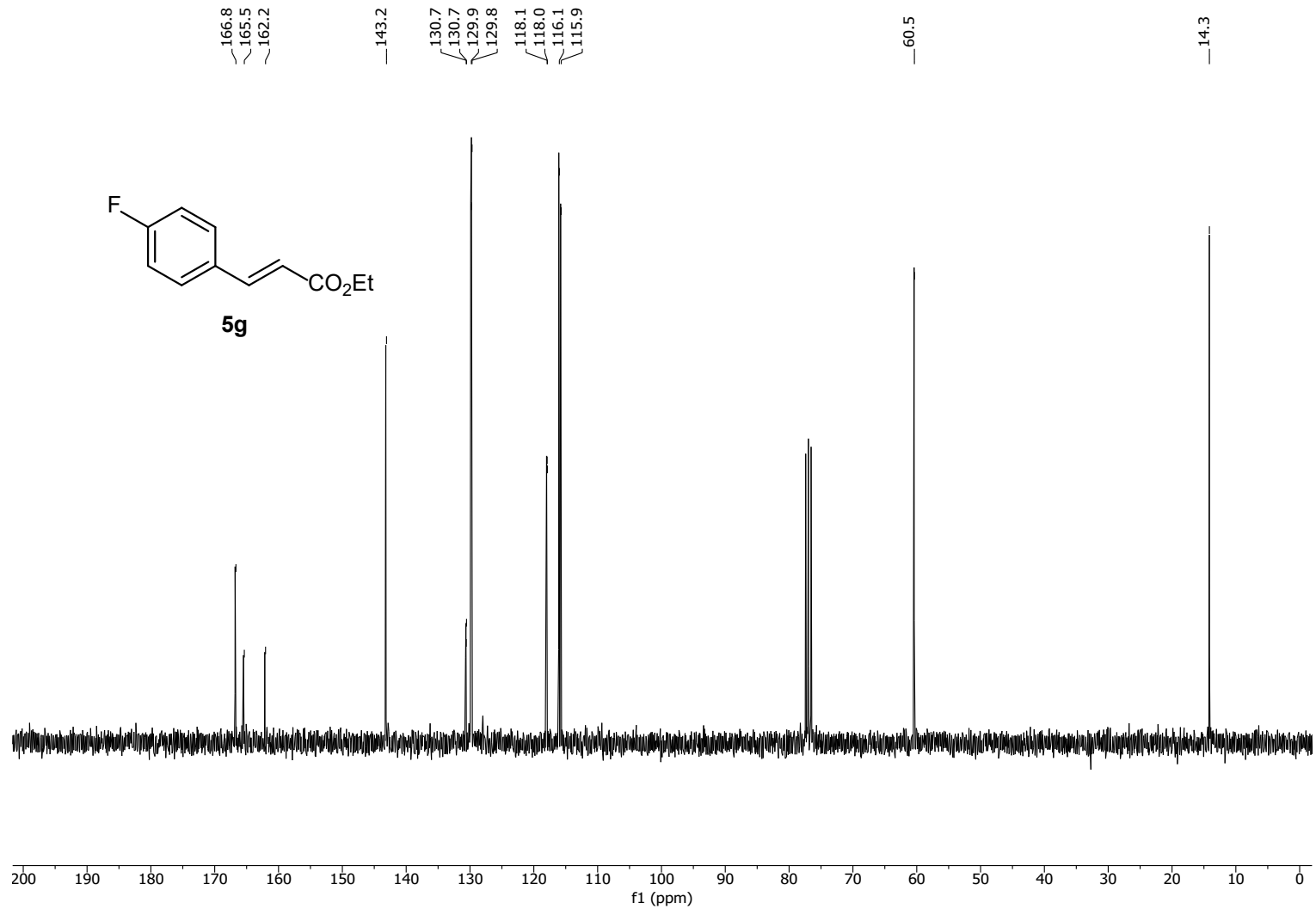
^{19}F NMR (282 MHz, CDCl_3)



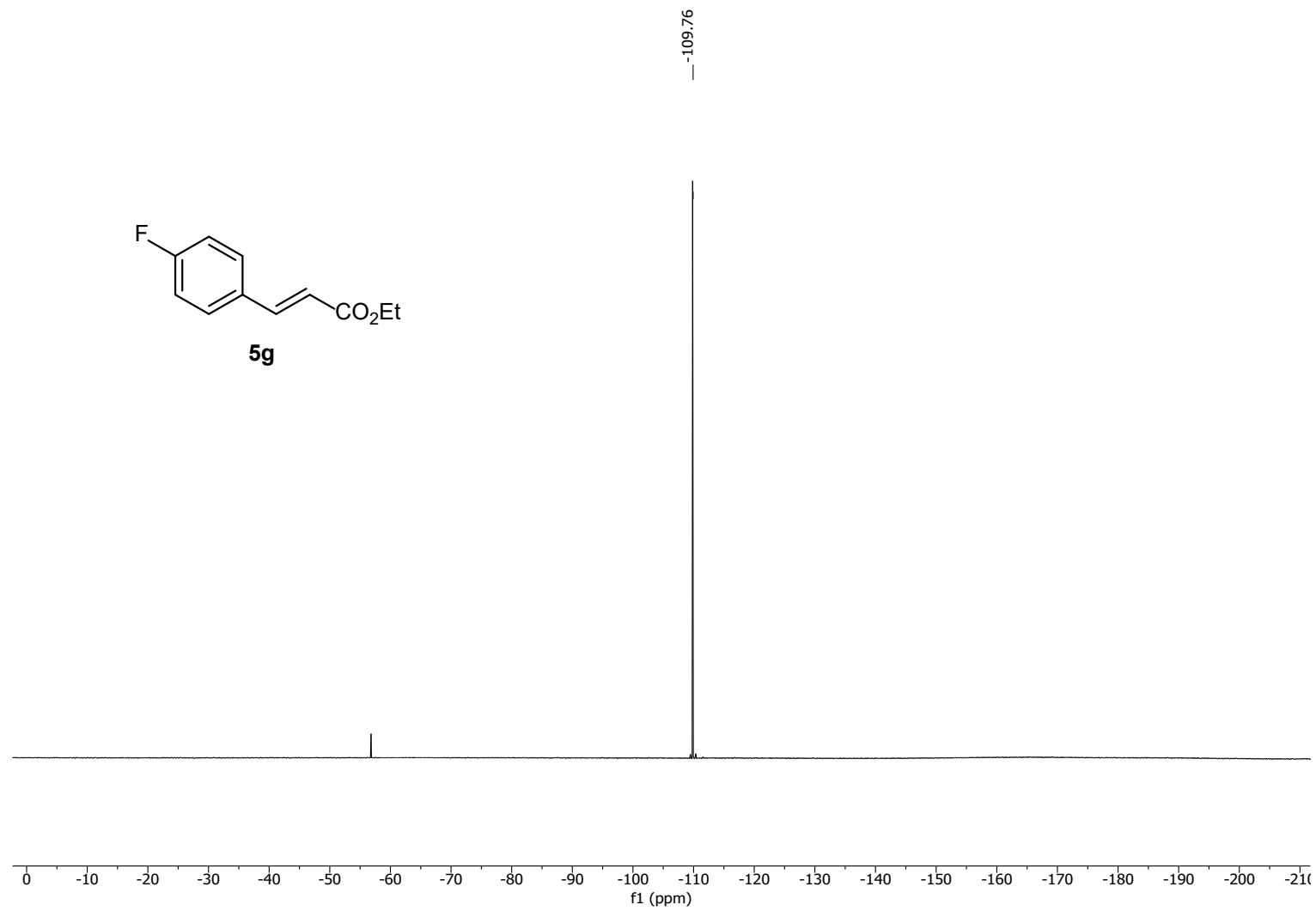
¹H NMR (300 MHz, CDCl₃)



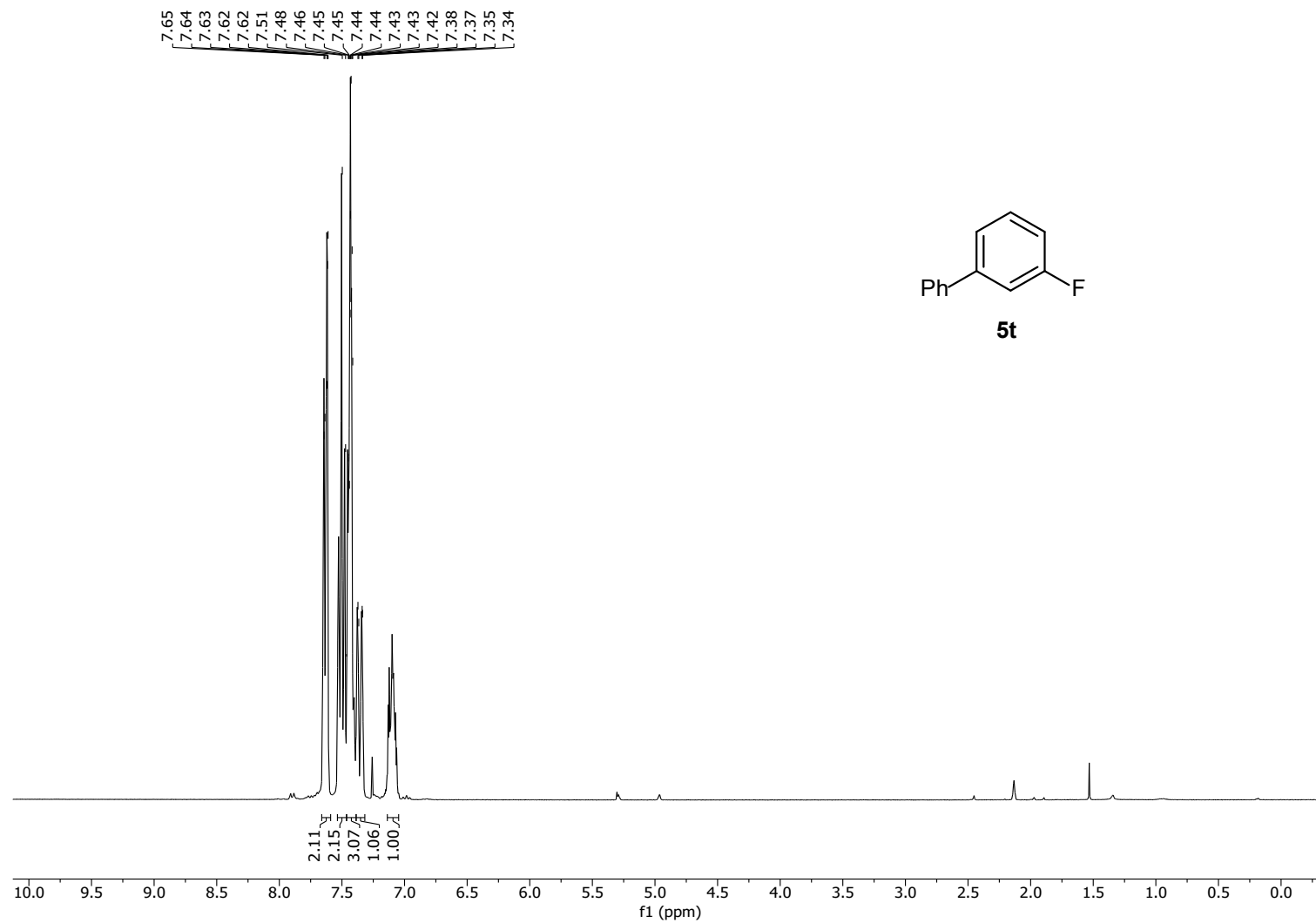
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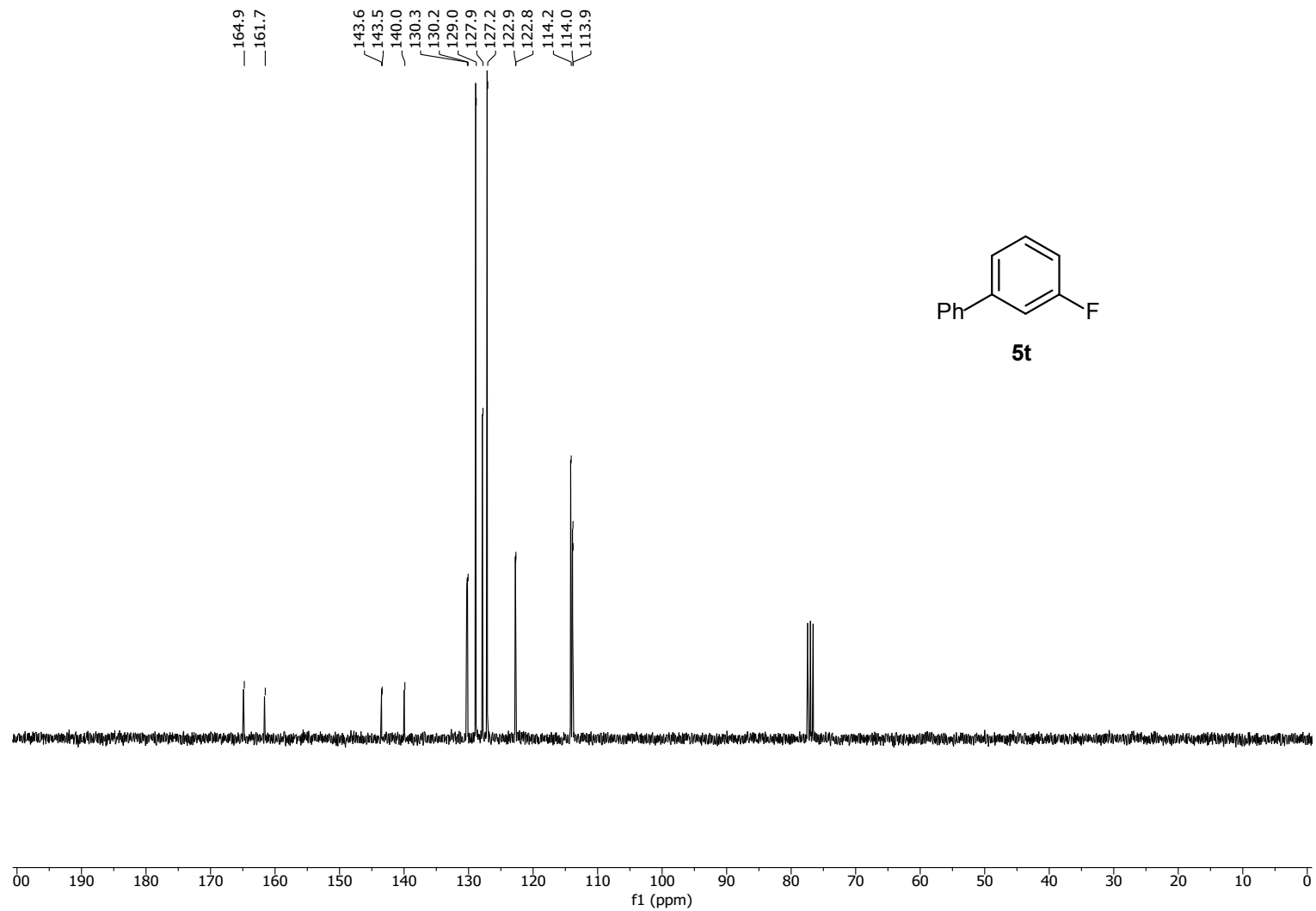
^{19}F NMR (282 MHz, CDCl_3)



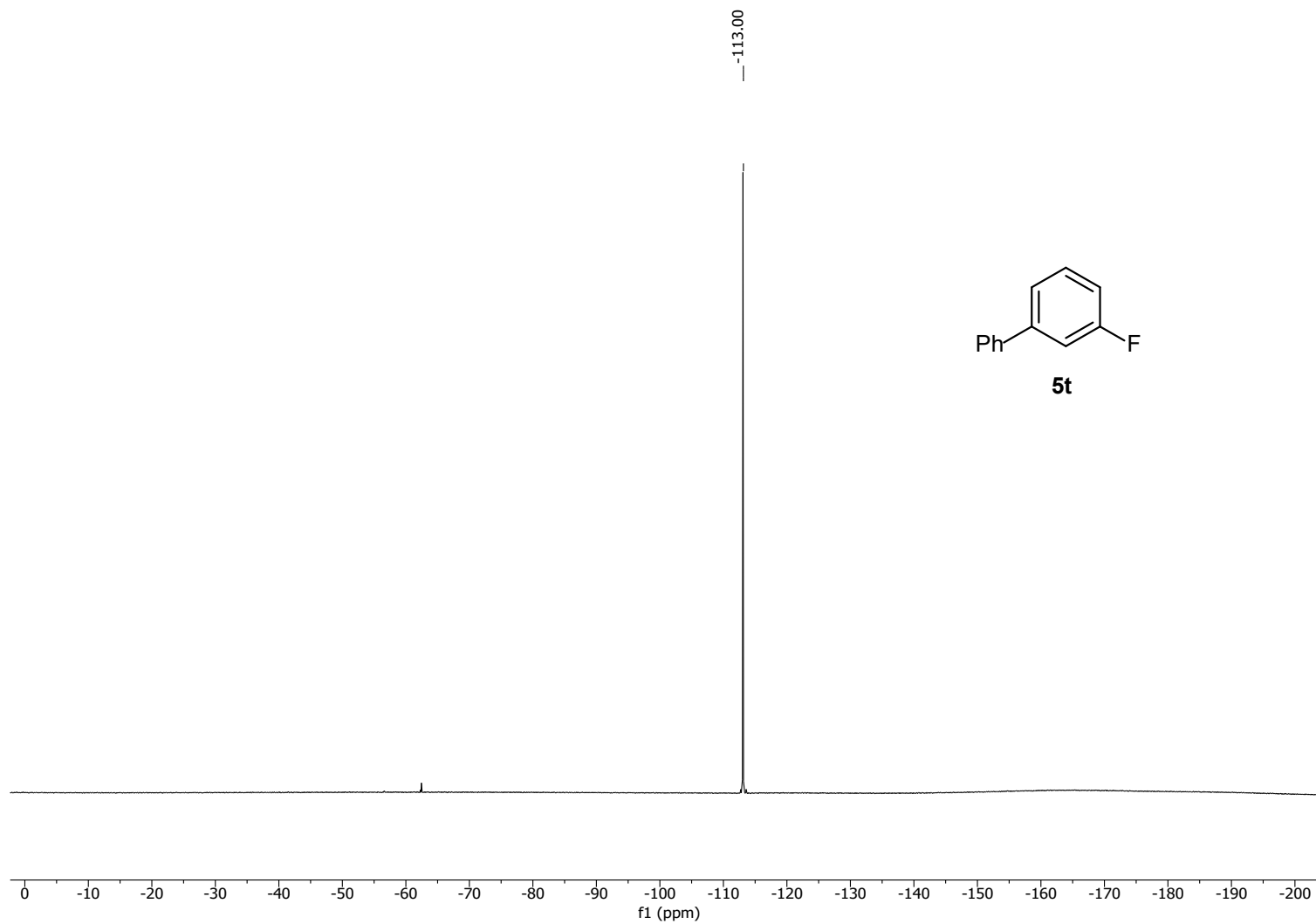
^1H NMR (300 MHz, CDCl_3)



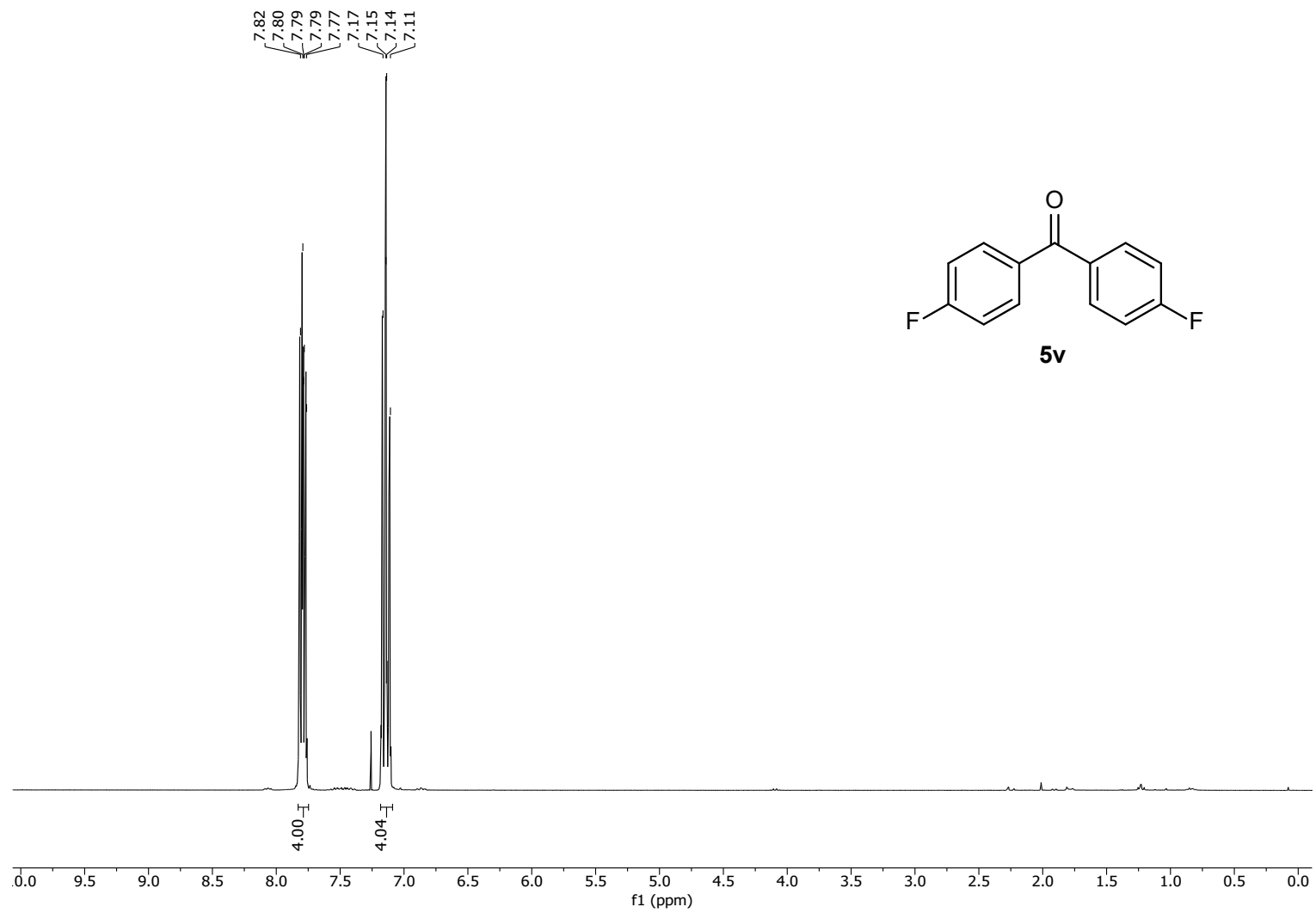
^{13}C NMR (75.4 MHz, CDCl_3)



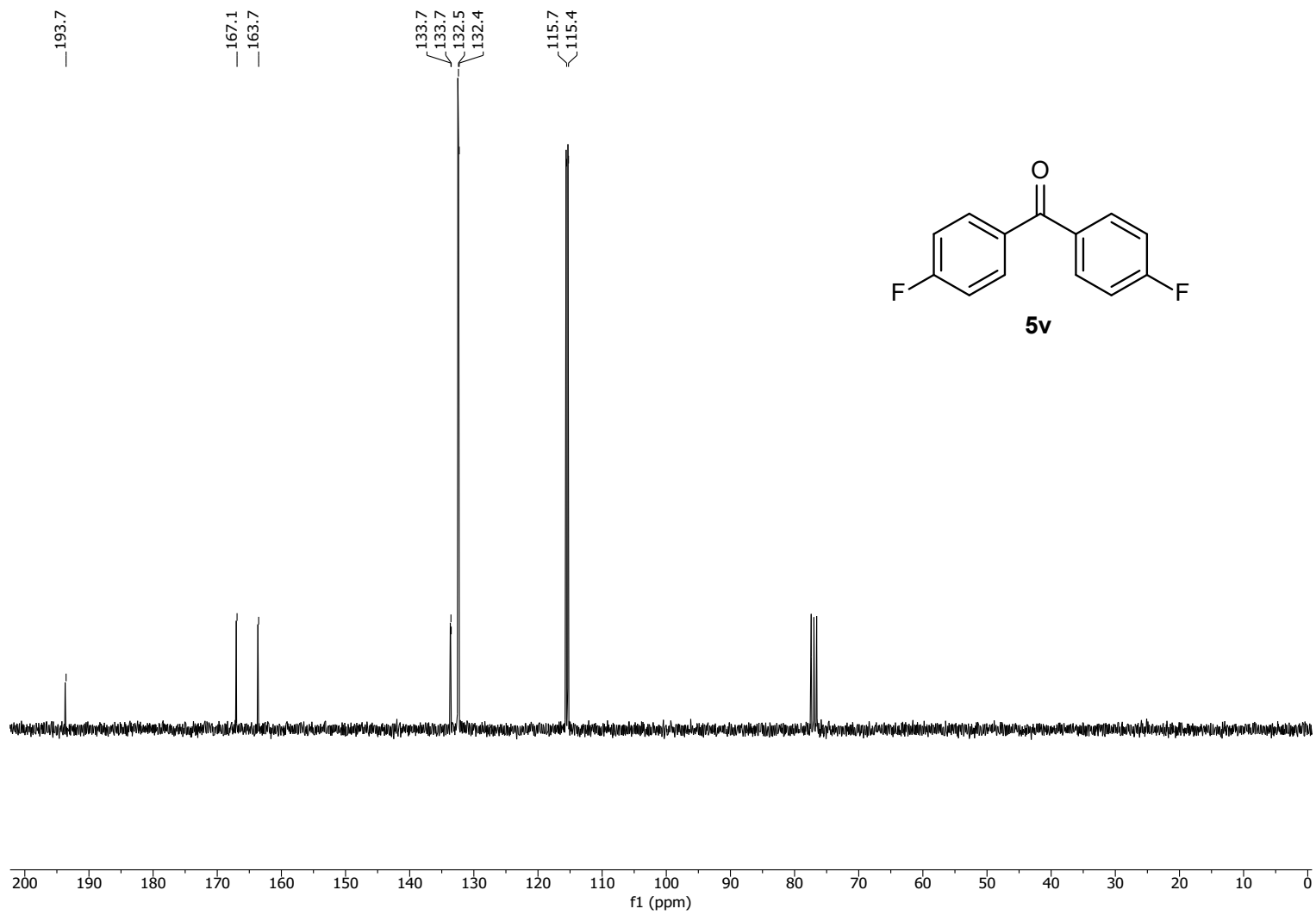
^{19}F NMR (282 MHz, CDCl_3)



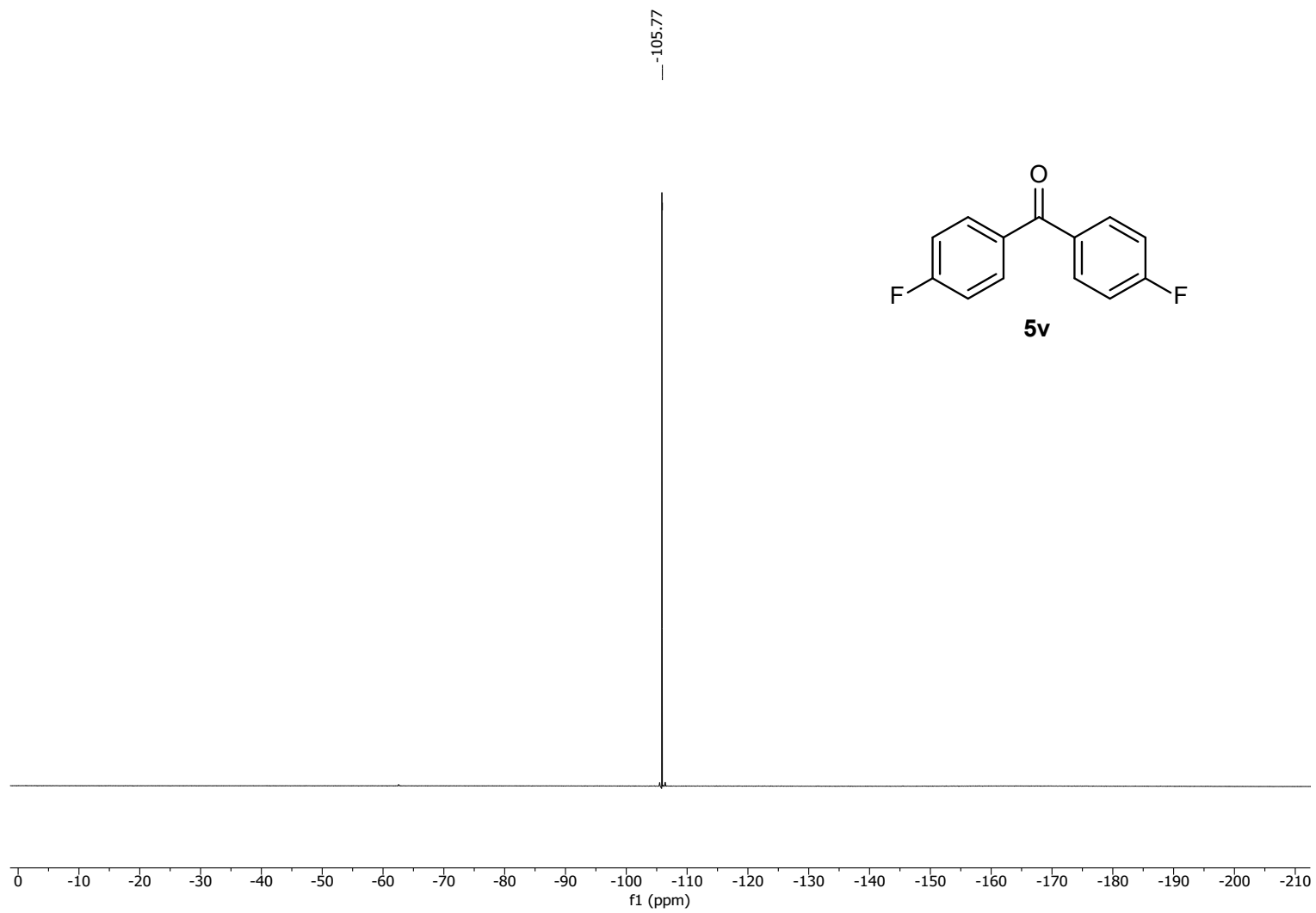
^1H NMR (300 MHz, CDCl_3)



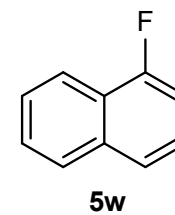
^{13}C NMR (75.4 MHz, CDCl_3)



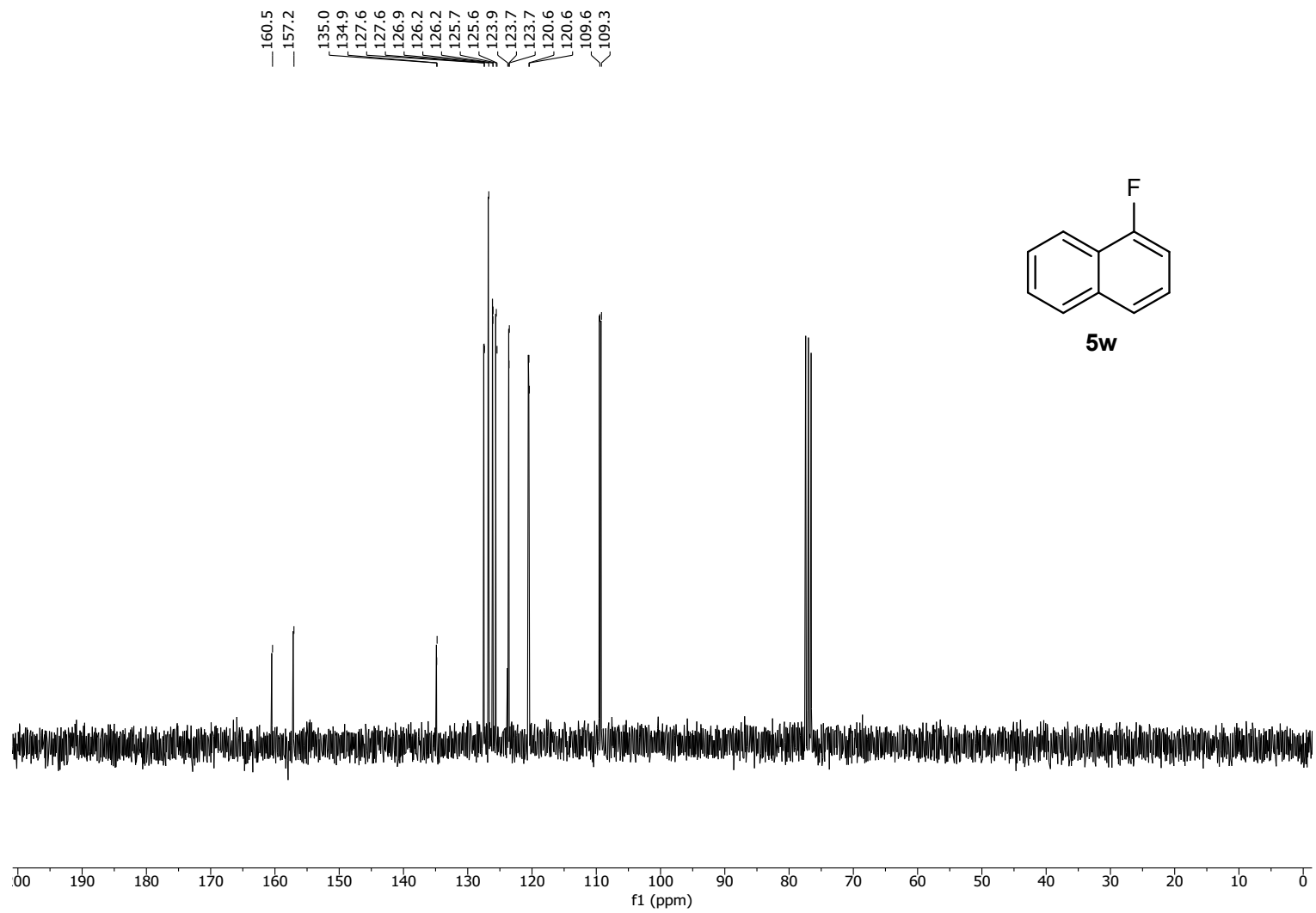
^{19}F NMR (282 MHz, CDCl_3)



^1H NMR (300 MHz, CDCl_3)



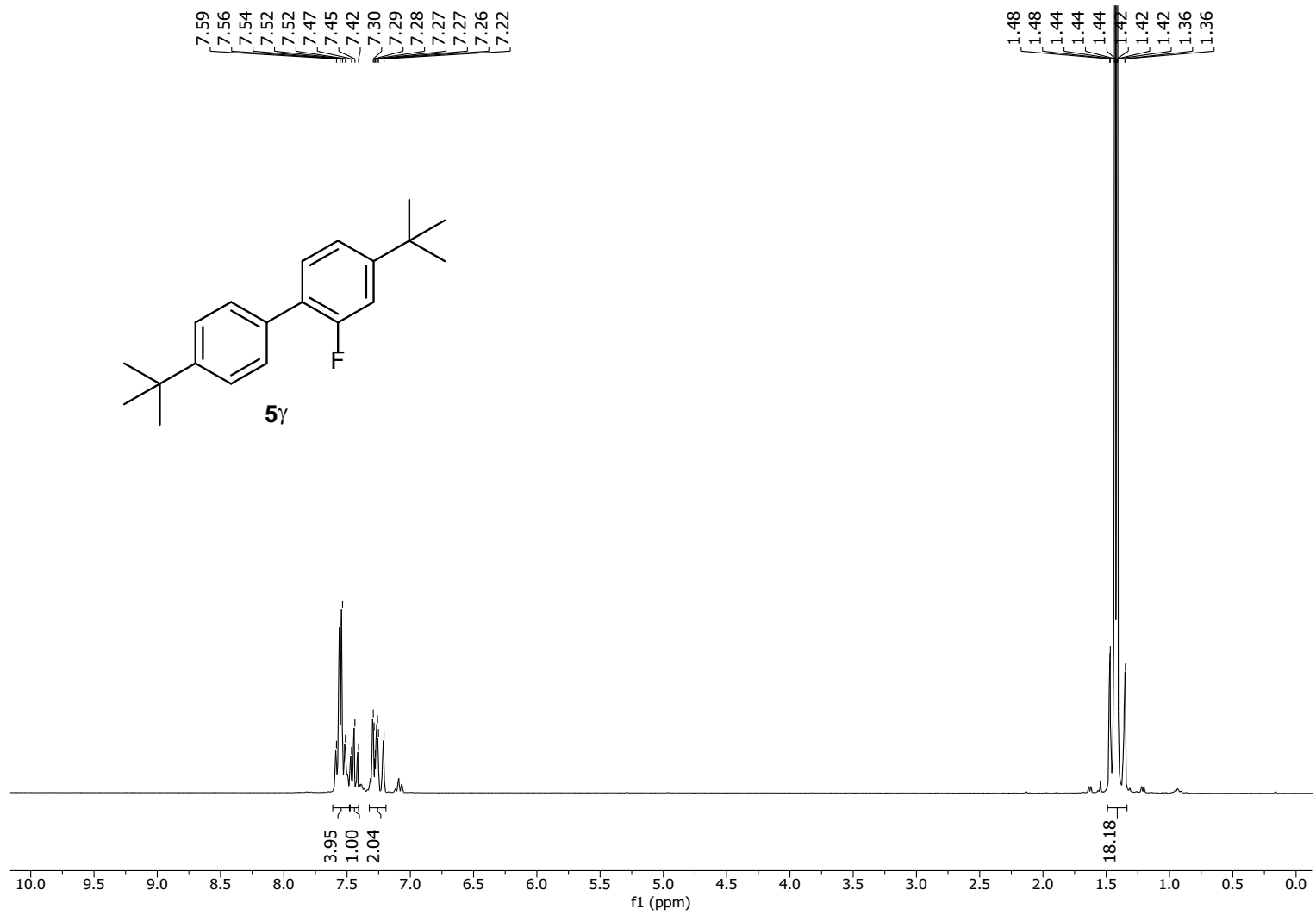
^{13}C NMR (75.4 MHz, CDCl_3)



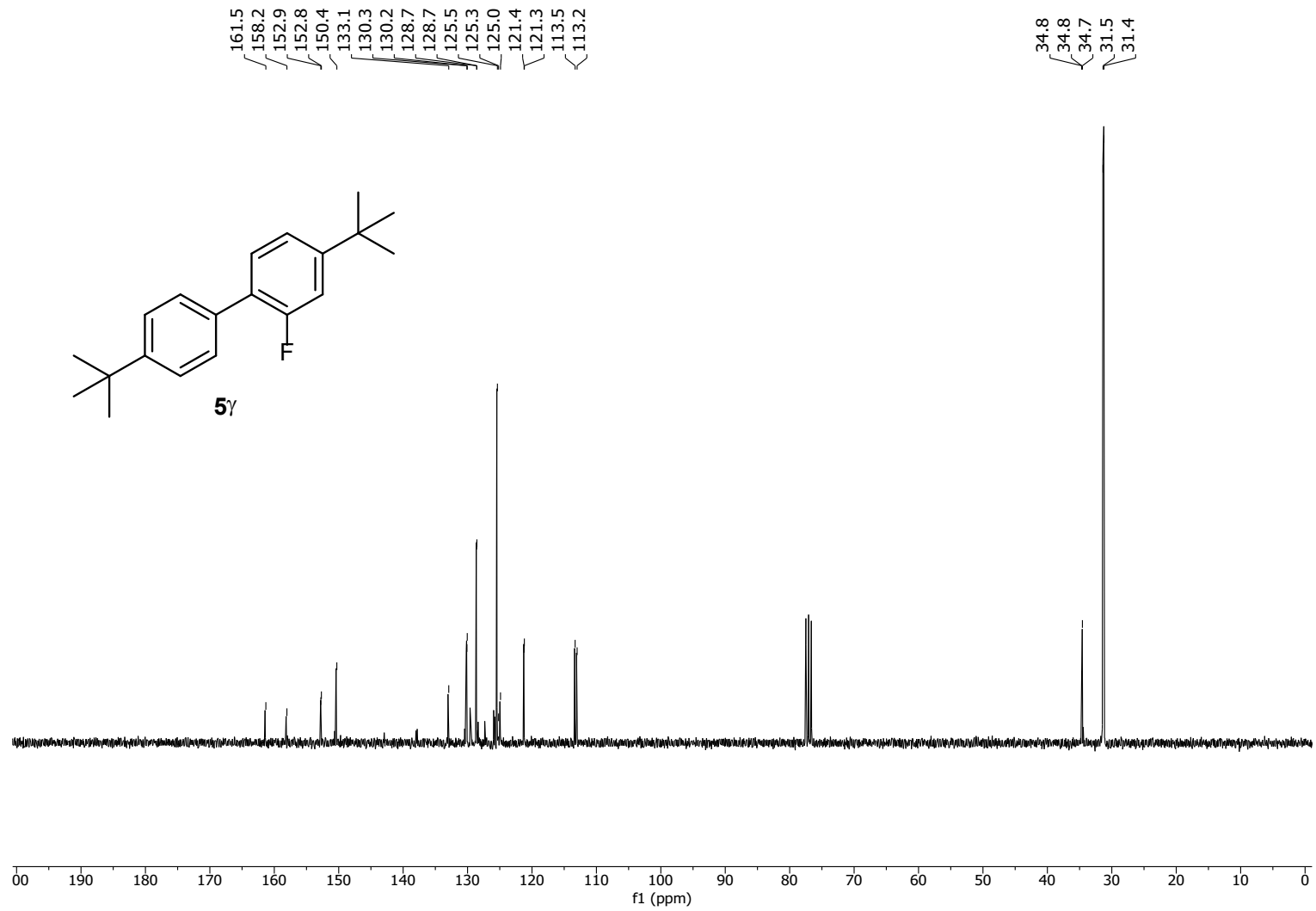
^{19}F NMR (282 MHz, CDCl_3)



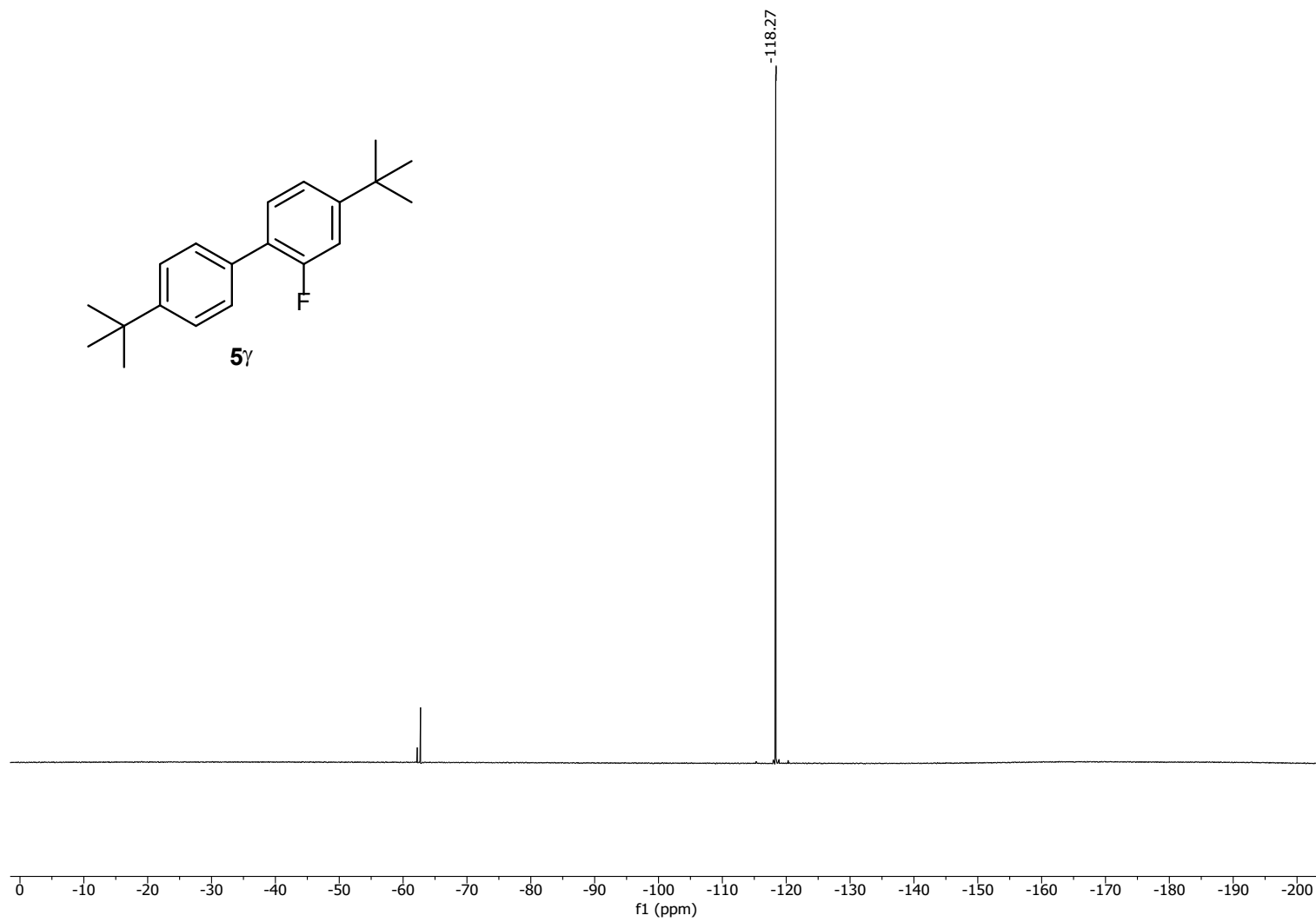
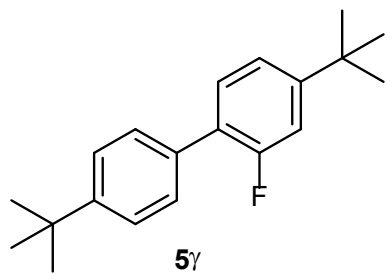
^1H NMR (300 MHz, CDCl_3)



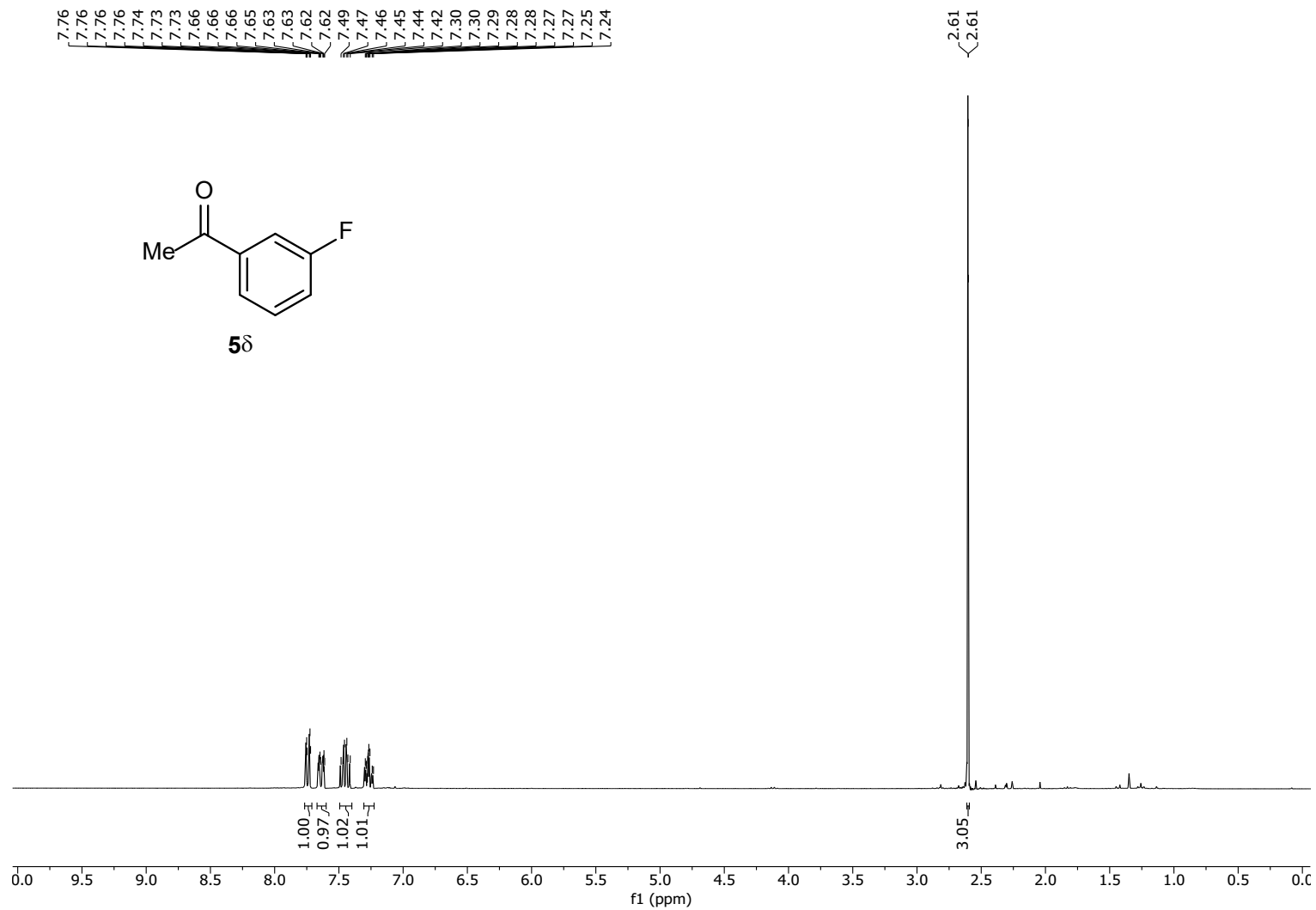
^{13}C NMR (75.4 MHz, CDCl_3)



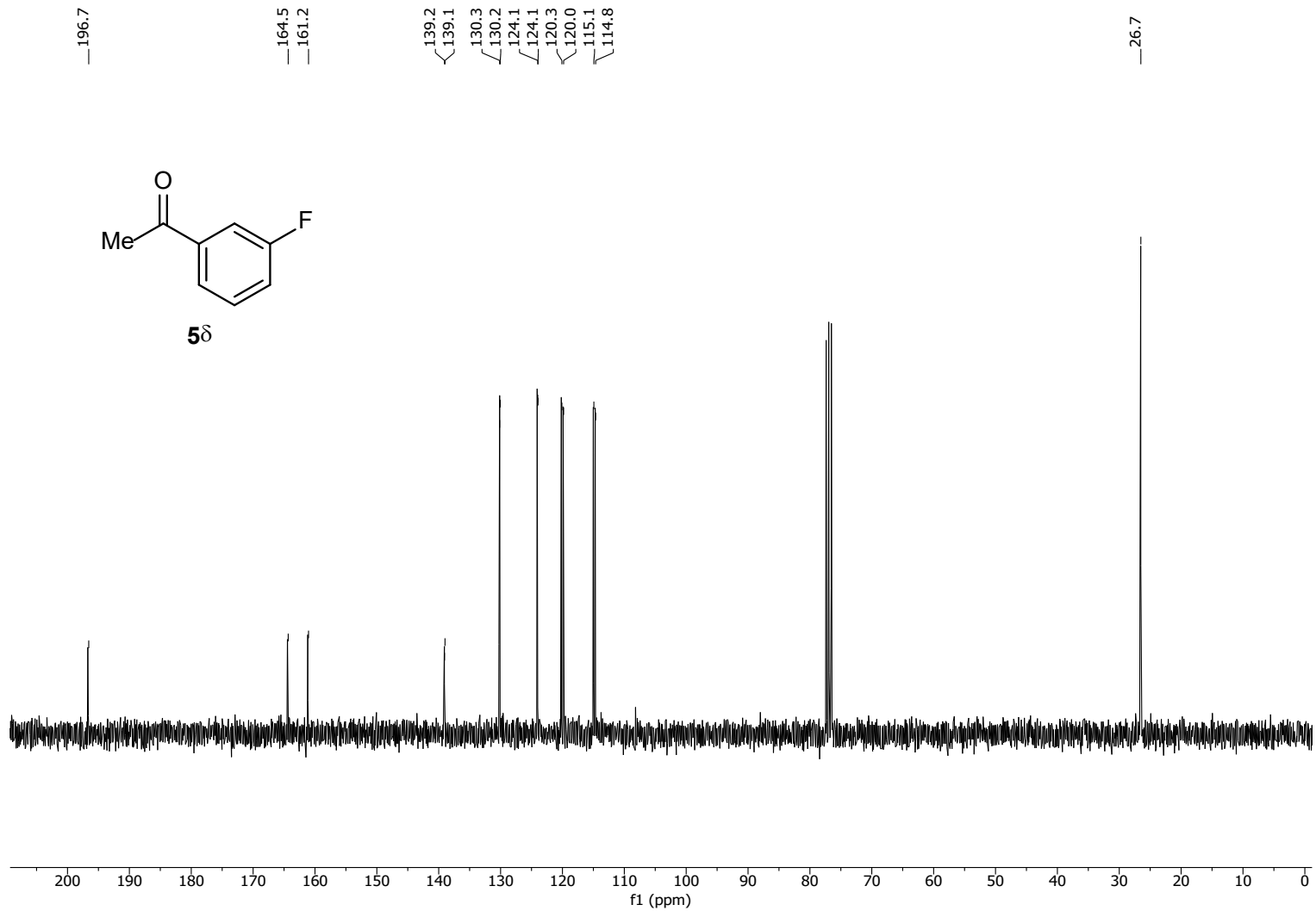
^{19}F NMR (282 MHz, CDCl_3)



^1H NMR (300 MHz, CDCl_3)



^{13}C NMR (75.4 MHz, CDCl_3)



^{19}F NMR (282 MHz, CDCl_3)

