

Supporting Information

Convenient *in situ* Generation of Various Dichlorinating Agents from Oxone and Chloride: Diastereoselective Dichlorination of Allylic and Homoallylic Alcohol Derivatives

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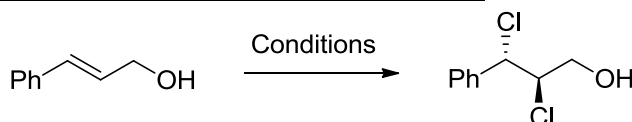
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General Information: Unless otherwise noted, all reactions were performed in round bottom flask under an air atmosphere. Dichloromethane was freshly distilled before use from calcium hydride (CaH₂). Deionized water was used for the reactions. All other anhydrous solvents were dried over 3Å or 4Å molecular sieves. Solvents used in workup, extraction and column chromatography were used as received from commercial suppliers without prior purification. Reagents used for experiments were purchased from commercial sources and used as received without further purification. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC, 0.25 mm) on Merck pre-coated silica gel plates. Flash chromatography was performed with silica gel 60 (particle size 0.040 – 0.062 mm) supplied by Grace. Infrared spectra (IR) were collected on a Bruker model TENSOR27 spectrophotometer. ¹H and ¹³C NMR

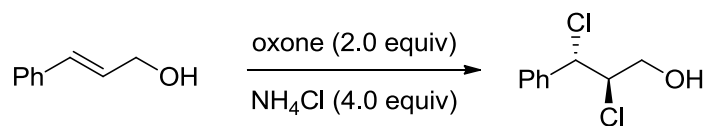
spectra were recorded on a Bruker AV-400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C). Chemical shifts are reported in parts per million (ppm) as values relative to the internal chloroform (7.27 ppm for ^1H and 77.23 ppm for ^{13}C). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High resolution mass spectra (HRMS) were measured at the Hong Kong University of Science and Technology Mass Spectrometry Service Center on either an Agilent GC/MS 5975C system or an API QSTAR XL System.

Other Conditions for Dichlorination of Cinnamyl Alcohol



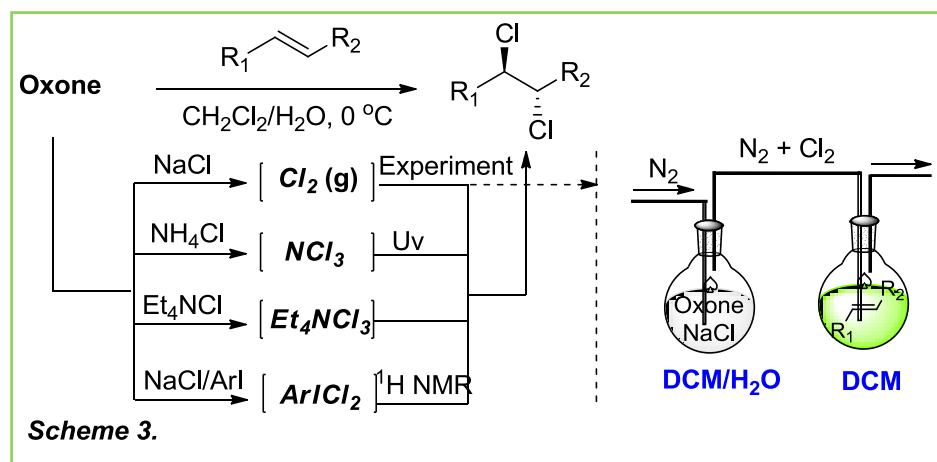
Entry	Oxidant (equiv)	Cl- source (equiv)	Solvent	Additive (equiv)	Temp. (°C)	Yield (%)
1	KMnO ₄ (1)	TMSCl (4)	DCM	Et ₄ NCl (1)	0	61
2	<i>n</i> Bu ₄ NHSO ₅ (2)	TMSCl (4)	DCM	-	rt	15
3	Oxone (2)	TMSCl (4)	DCM	Et ₄ NCl (1)	rt	55
4	Oxone (2)	Et ₄ NCl	DCM/H ₂ O (5:1)	-	rt	29
5	Oxone (2)	NaCl (4)	DCM/H ₂ O (5:1)	-	rt	55
6	Oxone (2)	NH ₄ Cl (4)	DCM/H ₂ O (5:1)	-	rt	63
7	Oxone (2)	NH ₄ Cl (6)	DCM/H ₂ O (5:1)	-	rt	67
8	Oxone (2)	NH ₄ Cl (8)	DCM/H ₂ O (5:1)	-	rt	68
9	Oxone (2)	NH ₄ Cl (4)	DCM/H ₂ O (5:1)	4-MePhI (1)	rt	53
10	<i>n</i> Bu ₄ NHSO ₅ (2)	NH ₄ Cl (4)	DCM	-	rt	46
11	NCS (2)	NH ₄ Cl (4)	DCM	-	rt	<5
12	MnO ₂ (2)	NH ₄ Cl (4)	DCM	-	rt	<5
13	PhI(OAc) ₂ (1)	NH ₄ Cl (4)	DCM	-	rt	<5
14	CAN (2)	NH ₄ Cl (4)	DCM	-	rt	<5
15	Na(ClO ₂) ₂ (2)	NH ₄ Cl (4)	DCM/H ₂ O (5:1)	-	rt	<5
16	NaIO ₄	NH ₄ Cl (4)	HOAc		rt	<5

The Effect of Solvents on Dichlorination of Cinnamyl Alcohol Using Oxone[®]/NH₄Cl System



Entry	Solvents	Yield (%)	Entry	Solvents	Yield (%)
1	CH ₃ CN/H ₂ O (1:0)	15	8	DCM/H ₂ O (100:1)	55
2	CH ₃ CN/H ₂ O (1:1)	<5	9	DCM/H ₂ O (1:0)	52
3	DCM/H ₂ O (1:1)	46	10	CHCl ₃ /H ₂ O (5:1)	51
4	DCM/H ₂ O (5:1)	63	11	CCl ₄ /H ₂ O (5:1)	43
5	DCM/H ₂ O (10:1)	60	12	Hexane/H ₂ O (1:1)	40
6	DCM/H ₂ O (20:1)	61	13	DMSO/H ₂ O (5:1)	<5
7	DCM/H ₂ O (50:1)	60	14	DMF/H ₂ O (5:1)	<5

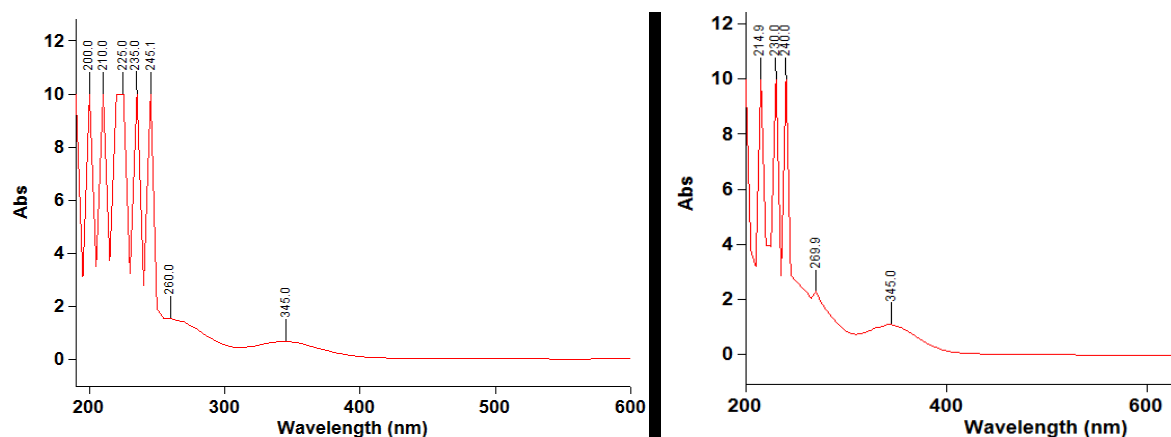
Some Evidences for Hypothetic Active Dichlorinating Species (Scheme 3)



Experimental evidence for generation of molecular chlorine from oxone and sodium chloride: An experiment was designed as in Scheme 3 (right). Two round-bottom flasks were connected by a double-headed needle. One flask with inlet of nitrogen (N_2) was charged with oxone (9.80 g, 32 mmol, 32 equiv.), NaCl (1.87g, 32 mmol, 32 equiv.) and H_2O (10 mL) and the other flask with gas outlet was charged with *trans*-crotyl benzylether (**1e**, 162 mg, 1.0 mmol, 1.0 equiv) in DCM (10 mL) and cooled to 0 °C. The nitrogen stream will carry any chlorine generated *in situ* from oxone and NaCl into the other flask containing the alkene. After 30 min, the *trans*-crotyl benzylether was completely consumed as indicated by TLC. After workup, pure dichloride product **2e** was obtained in 81% yield (189 mg) as a colorless oil. This is a strong evidence for generation of molecular chlorine from oxone and NaCl.

Uv-vis spectra of dichlorinating species generated from oxone and NH_4Cl : A DCM solution of NCl_3 was prepared from oxone and NH_4Cl as follows: A round-bottom flask was charged with oxone (1.23 g, 4.0 mmol) and chloride salt (4.0 mmol). CH_2Cl_2 (10 mL) and H_2O (2 mL) were then added via syringes with stirring and the reaction suspension was stirred at 0 °C with shielding from light by aluminium foil. After 30 min, the mixture was filtered through a pad of celite to remove excess of oxone and related salts. The organic layer from filtrate was collected and the aqueous layer was extracted with CH_2Cl_2 (5 mL). The combined organic fractions were dried with anhydrous Na_2SO_4 and filtered. In addition, we also prepared the NCl_3 from calcium

hypochlorite and NH_4Cl by following the literature procedure¹: A mixture of water (6 mL), DCM (9 mL) and calcium hypochlorite (2.7 g, 13.2 mmol) was cooled to 0 – 10 °C. A solution of NH_4Cl (660 mg, 12.3 mmol) in concentrated hydrochloric acid (1.50 mL) and water (4.5 mL) was added dropwise with stirring over a 30 min period at 0 – 10 °C. After 20 min, the organic layer was collected, washed with cold water (3 x 10 mL), dried over anhydrous Na_2SO_4 and filtered to give the yellow DCM solution of NCl_3 . We then recorded Uv-vis spectra of the DCM solution of NCl_3 prepared by these two methods.



NCl_3 in DCM prepared from $\text{Ca}(\text{OCl})_2$ and NH_4Cl

DCM solution from NH_4Cl and Oxone

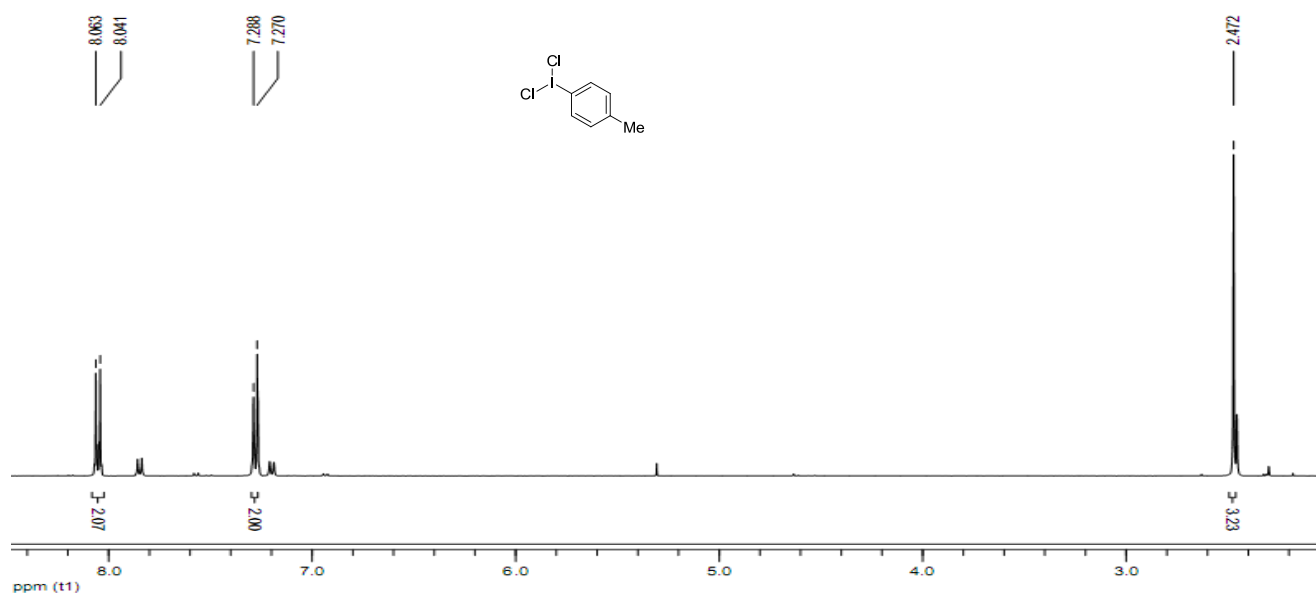
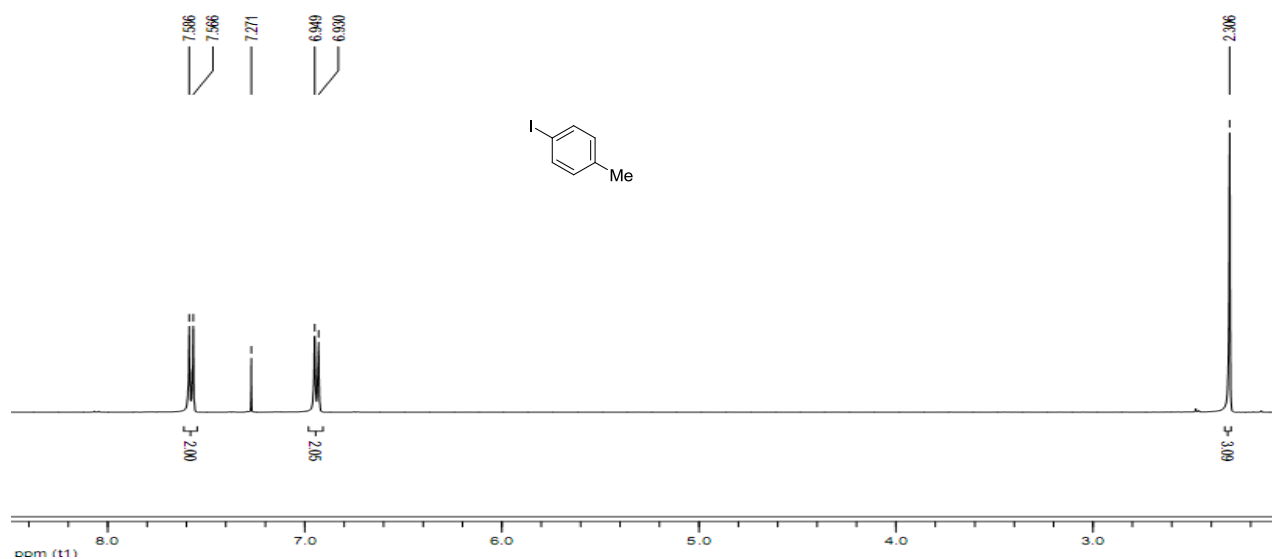
As indicated in these two spectra, we speculated that NCl_3 was generated as an active dichlorinating agent from oxone and NH_4Cl under our conditions. Characteristic absorptions of NCl_3 around 220, 294, and 336 nm have been reported in the literature.² However, we could not rule out the possibility of formation of a mixture of H_2NCl , HNCl_2 and NCl_3 .

¹H NMR spectra of hypervalent iodine dichloride from oxone, NaCl and 4-iodotoluene: A round-bottom flask equipped with a stir bar was charged with oxone (1.23 g, 4.0 mmol, 4.0 equiv), sodium chloride (4.0 mmol, 4.0 equiv) and 4-iodotoluene (436 mg, 2.0 mmol, 1.0 equiv). CH_2Cl_2 (10 mL) and H_2O (2 mL) were then added via syringes with stirring and the reaction suspension was stirred at 0 °C with shielding from light by aluminium foil. After 30 min, the mixture was filtered through a pad of celite to remove excess of oxone and related salts. The organic layer from filtrate was collected and the aqueous layer was extracted with CH_2Cl_2 (5

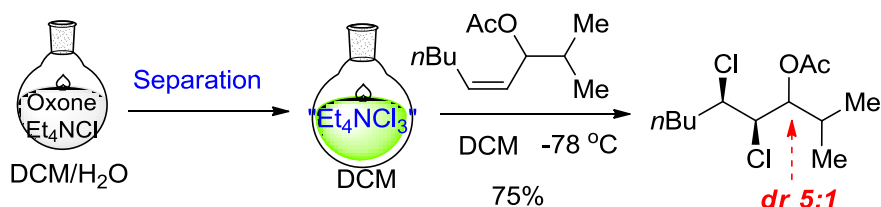
¹ P. Kovacic, S. S. Chaudhary, *Org. Syn.* **1973**, Coll. Vol. 5, 35.

² V. C. Hand, D. W. Margerum, *Inorg. Chem.* **1983**, 22, 1449.

mL). The combined organic fractions were dried with anhydrous Na_2SO_4 , filtered and concentrated. An aliquot of the resulting residue was dissolved in CDCl_3 for recording ^1H NMR. 4-MePhI, ^1H NMR (400 MHz, CDCl_3): δ 7.58 (d, $J = 8.0$ Hz, 2H), 6.94 (d, $J = 7.6$ Hz, 2H), 2.31 (s, 3H). 4-Methyl-periodobenzene dichloride: ^1H NMR (400 MHz, CDCl_3): δ 8.05 (d, $J = 8.8$ Hz, 2H), 7.28 (d, $J = 7.2$ Hz, 2H), 2.47 (s, 3H). The ^1H NMR data of ArICl_2 is identical with the reported values (N. P. Tale, A. V. Shelke and N. N. Karade, *Synth. Commun.* **2012**, 42, 2959-2965).



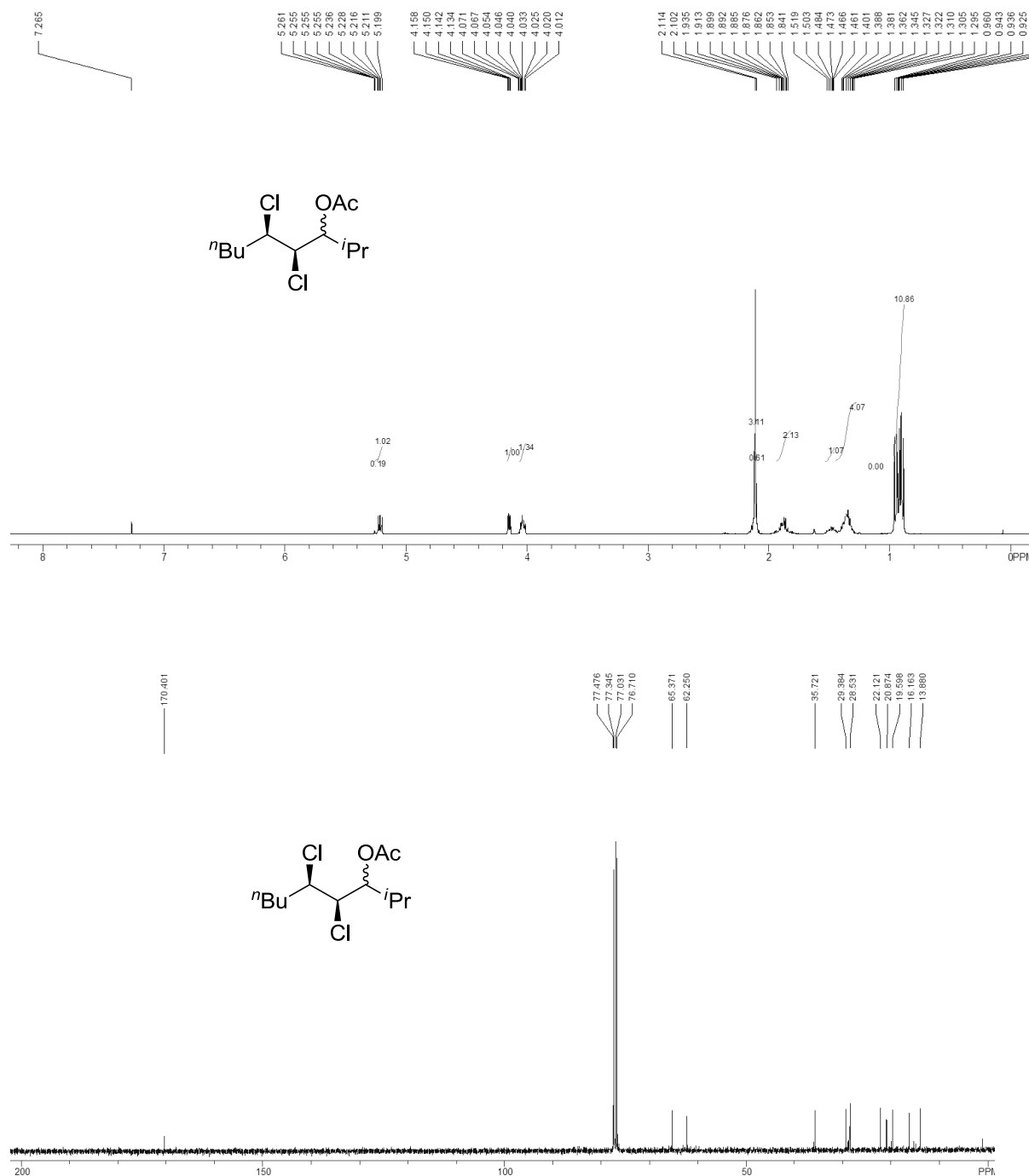
Evidence of Mioskowski's reagent(Et_4NCl_3) generated from Oxone and Et_4NCl



As observed by Vanderwal (Ref. 13: G. M. Shibuya, J. S. Kanady and C. D. Vanderwal, *J. Am. Chem. Soc.*, **2008**, 130, 12514.), diastereoselectivity of dichlorination of cis-allylic ester at low temperature ($-78\text{ }^\circ\text{C}$) could be improved to be 5:1 when Mioskowski's reagent was employed. So we performed the dichlorination of similar cis-allylic ester using the dry DCM solution separated from oxone and Et_4NCl . We found that the diastereoselectivity of dichlorination was 5:1, which is consistent with the results reported by Vanderwal and provided evidence that Mioskowski's reagent was formed from oxone and Et_4NCl . (note: this experiment was suggested by the reviewer as evidence of generation of Mioskowski's reagent).

Procedure: A round bottom flask equipped with a stir bar was charged with Oxone (1.23 g, 4 mmol, 4 equiv.) and Et_4NCl (662.8 mg, 4 mmol, 4 equiv.). CH_2Cl_2 (10 mL) and H_2O (2 mL) were added in turn to round bottom flask via syringes. With stirring, the reaction was run at $0\text{ }^\circ\text{C}$ and protected from light. After 30 minutes, the mixture was filtered through a pad of celite, and extracted with CH_2Cl_2 ($3 \times 5\text{ mL}$). Organic layer was collected, dried by anhydrous Na_2SO_4 . Then the mixture was filtered, and added to a round bottom flask. To the resulting solution self-prepared Ac-Protected (Z)-2-methylnon-4-en-3-ol (184.3 mg, 1 mmol, 1 equiv.) was added. The solution was allowed to stir at $-78\text{ }^\circ\text{C}$ until the starting material had been totally consumed (as monitored by TLC). Saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution (10 mL) was added. The resulting mixture was extracted with CH_2Cl_2 ($3 \times 10\text{ mL}$). Organic layer was collected, then washed with brine ($3 \times 20\text{ mL}$), dried by anhydrous Na_2SO_4 , filtered and concentrated. The reaction mixtures were purified by flash column chromatography on silica gel (hexane) to afford 187.0 mg (75%, 5:1 d.r.) product as colorless oil. Data for major isomer: $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 5.22 (dd, $J = 6.8, 4.8\text{ Hz}$, 1H), 4.15 (dd, $J = 6.8, 3.6\text{ Hz}$, 1H), 4.06–4.01 (m, 1H), 2.12 (s, 3H), 1.92 – 1.85 (m, 2H), 1.53 – 1.45 (m, 1H), 1.42 – 1.31 (m, 4H), 0.97 – 0.89 (m, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): 170.4, 77.5, 65.3, 62.2, 35.7, 29.4, 28.5, 22.1, 20.8, 19.6, 16.1, 13.9.

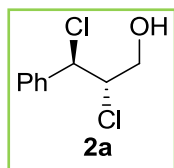
Data for minor isomer: ^1H NMR (400 MHz, CDCl_3): δ 5.25 (dd, $J = 7.6, 2.4$ Hz, 1H), 4.08 – 4.02 (m, 2H), 2.11 (s, 3H), 1.92 – 1.85 (m, 2H), 1.53 – 1.45 (m, 1H), 1.42 – 1.31 (m, 4H), 0.97 – 0.89 (m, 9H).



Experimental procedure for dichlorination of various alkenes

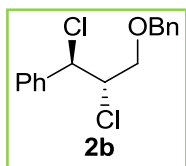
General Procedure A (One-Pot): A round-bottom flask equipped with a stir bar was charged with oxone (1.23 g, 4.0 mmol) and chloride salt (4.0 mmol). CH_2Cl_2 (10 mL) and H_2O (2 mL) were then added via syringes with stirring and the reaction suspension was stirred at 0 °C with shielding from light by aluminium foil. After 30 min, alkene (1.0 mmol) was added to the solution and the mixture was allowed to stir at 0 °C until the alkene was completely consumed (as monitored by TLC, about 30 min). The reaction mixture was diluted with CH_2Cl_2 (10 mL) and quenched by addition of aqueous sat. $\text{Na}_2\text{S}_2\text{O}_3$ solution (10 mL). The resulting mixture was filtered through a pad of celite. The organic layer of filtrate was collected and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic fractions were washed with brine (20 mL × 3), dried by anhydrous Na_2SO_4 , filtered and concentrated. The resulting residue was purified by flash column chromatography over silica gel with hexane/ ethyl acetate as eluent to give the desired dichloride product with yields indicated in Table 2.

General Procedure B: A round-bottom flask was charged with oxone (1.23 g, 4.0 mmol) and chloride salt (4.0 mmol). CH_2Cl_2 (10 mL) and H_2O (2 mL) were then added via syringes with stirring and the reaction suspension was stirred at 0 °C with shielding from light by aluminium foil. After 30 min, the mixture was filtered through a pad of celite to remove excess of oxone and related salts. The organic layer from filtrate was collected and the aqueous layer was extracted with CH_2Cl_2 (5 mL). The combined organic fractions were dried with anhydrous Na_2SO_4 and filtered. The resulting dry CH_2Cl_2 solution was added to a solution of alkene (1 mmol) in CH_2Cl_2 (2 mL) at 0 °C. The solution was allowed to stir at 0 °C until the alkene was completely consumed (as monitored by TLC). Aqueous sat. $\text{Na}_2\text{S}_2\text{O}_3$ solution (10 mL) was added to quench the reaction. The organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic fractions were washed with brine (20 mL), dried by anhydrous Na_2SO_4 , filtered and concentrated. The resulting residue was purified by flash column chromatography over silica gel with hexane/ ethyl acetate as eluent to give the dichloride product with yields indicated in Table 2.



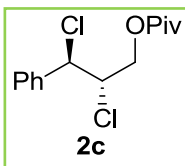
(2a, Table 1) Method 1: Following the *General Procedure A*, reaction of cinnamyl alcohol (**1a**, 134 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and chloride salt (4.0 mmol) afforded dichloride product **2a**³ as a 3.6:1 diastereomeric mixture with indicated yield in Table 1: NaCl: 147 mg, 72% yield; NH₄Cl: 151

mg, 74% yield; Et₄NCl: 141 mg, 69% yield; NaCl/4-MePhI: 153 mg, 75% yield. **Method 2:** Following the *General Procedure B*, reaction of cinnamyl alcohol (**1a**, 134 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and chloride salt (4.0 mmol) afforded dichloride product **2a** with indicated yield in Scheme 2: NaCl: <15% yield; NH₄Cl: 155 mg, 76% yield; Et₄NCl: 90 mg, 44% yield; NaCl/4-MePhI: 139 mg, 68% yield. Major Diastereomer: ¹H NMR (400 MHz, CDCl₃): δ 7.45 – 7.36 (m, 5H), 5.12 (d, *J* = 9.6 Hz, 1H), 4.45 (ddd, *J* = 9.6, 4.8, 3.2 Hz, 1H), 4.20 (dd, *J* = 7.6, 4.8 Hz, 1H), 4.10 (dd, *J* = 7.6, 3.2 Hz, 1H), 2.29 (br, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 137.6, 128.4, 128.0 (2 x C), 127.3 (2 x C), 65.4, 63.6, 60.9.



(2b, Table 2): Following the *General Procedure A*, reaction of cinnamyl benzyl ether⁴ (**1b**, 224 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2b** (244 mg, 83% yield) as a 2:1 diastereomeric mixture. Major diastereomer (colorless oil, *R*_f = 0.51, 5% acetate in hexane): ¹H

NMR (400 MHz, CDCl₃): δ 7.45 – 7.34 (m, 10H), 5.26 (d, *J* = 8.0 Hz, 1H), 4.65 (s, 2H), 4.47 (ddd, *J* = 10.8, 6.8, 4.4 Hz, 1H), 3.99 (dd, *J* = 10.8, 6.8 Hz, 1H), 3.77 (dd, *J* = 10.8, 4.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 137.8, 137.7, 129.1, 128.7 (2 x C), 128.6, 128.4 (2 x C), 128.2 (2 x C), 128.0 (2 x C), 73.8, 71.2, 63.3, 61.8. IR (neat, cm⁻¹): 2865, 1494, 1362, 1116. HRMS (CI⁺) *m/z* calculated for C₁₆H₁₆Cl₂O [M]⁺ 294.0578, found: 294.0574.



(2c, Table 2): Following the *General Procedure A*, reaction of cinnamyl pivalate⁵ (**1c**, 218 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2c** (153 mg, 53% yield) as a 2:1 diastereomeric mixture. Major diastereomer (colorless oil, *R*_f = 0.51, 5% acetate in hexane):

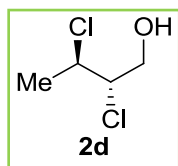
¹H NMR (400 MHz, CDCl₃): δ 7.45 – 7.38 (m, 5H), 5.06 (d, *J* = 8.0 Hz, 1H), 4.57 – 4.53 (m,

³ K. C. Nicolaou, N. L. Simmons, Y. Ying, P. M. Heretsch, J. S. Chen, *J. Am. Chem. Soc.* **2011**, *133*, 8134.

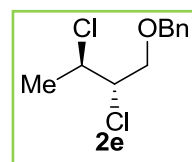
⁴ A. B. Charette, C. Molinaro, C. Brochu, *J. Am. Chem. Soc.*, **2001**, *123*, 12160.

⁵ C.-C. Chen, J.-H. Kuo, V. D. Pawar, Y. S. Munot, S.-S. Weng, C.-H. Ku, C.-Y. Liu, *J. Org. Chem.*, **2005**, *70*, 1188.

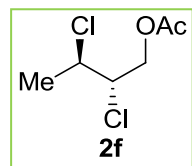
2H), 4.52 – 4.44 (m, 1H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 177.2, 137.0, 128.5, 128.1, 128.0, 127.3, 127.0, 64.3, 61.3, 61.1, 38.3, 26.5 (3 x C). **IR** (neat, cm^{-1}): 2963, 2928, 1736, 1457, 1282, 1150. **HRMS** (Cl^+) m/z calculated for $\text{C}_{14}\text{H}_{19}\text{Cl}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 289.0762, found: 289.0760.



(2d, Table 2): Following the *General Procedure A*, reaction of *trans*-crotyl alcohol (**1d**, 72 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2d**⁶ (122 mg, 85% yield, colorless oil) as a 6:1 diastereomeric mixture. ^1H NMR (400 MHz, CDCl_3): δ 4.24 (dq, J = 13.2, 6.6 Hz, 1H), 4.07 – 4.02 (m, 1H), 4.01 (d, J = 4.7 Hz, 2H), 1.95 (br, 1H), 1.69 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 67.2, 63.8, 55.5, 21.9.



(2e, Table 2): Method 1: Following the *General Procedure A*, reaction of *trans*-crotyl benzyl ether⁷ (**1e**, 162 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2e** (188 mg, 81% yield, colorless oil) as a single diastereomer. **Method 2:** Following the *General Procedure B*, reaction of *trans*-crotyl benzyl ether (**1a**, 134 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and chloride salt (4.0 mmol) afforded dichloride product **2e** as a single diastereomer with indicated yield in Scheme 2: NaCl: <15% yield; NH_4Cl : 174 mg, 75% yield; Et_4NCl : 179 mg, 77% yield; NaCl/4-MePhI: 195 mg, 84 % yield. ^1H NMR (400 MHz, CDCl_3): δ 7.40 – 7.27 (m, 5H), 4.59 (s, 2H), 4.38 (qd, J = 6.8, 6.4 Hz, 1H), 4.15 (ddd, J = 6.4, 6.0, 3.9 Hz, 1H), 3.85 (dd, J = 5.6, 3.9 Hz, 1H), 3.77 (dd, J = 6.0, 5.6 Hz, 1H), 1.62 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 136.9, 127.9 (2 x C), 127.3 (2 x C), 127.1, 72.8, 70.6, 63.8, 56.0, 20.6. **IR** (neat, cm^{-1}): 2867, 1496, 1362, 1113. **HRMS** (Cl^+) m/z calculated for $\text{C}_{11}\text{H}_{14}\text{Cl}_2\text{O}$ $[\text{M}]^+$ 232.0422, found: 232.0423.



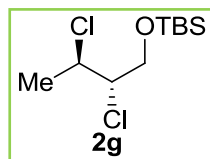
(2f, Table 2): Following the *General Procedure A*, reaction of *trans*-crotyl acetate⁸ (**1f**, 114 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2f** (119 mg, 64 % yield, colorless oil) as a single diastereomer. ^1H NMR (400 MHz, CDCl_3): δ 4.49 (dd, J = 12.1, 4.2 Hz, 1H), 4.40 (dd, J = 12.1,

⁶ A. Kohda, K. Ueda, S. Tadashi, *J. Org. Chem.* **1981**, *46*, 509.

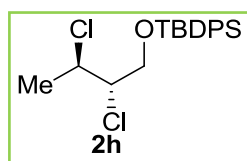
⁷ B. Lygo, N. O'connor, P. R. Wilson, *Tetrahedron*, **1988**, *44*, 6881.

⁸ R. Dalpozzo, A. De Nino, L. Maiuolo, M. Oliverio, A. Procopio, B. Russo, A. Tocci, *Austra. J. Chem.* **2007**, *60*, 75.

5.8 Hz, 1H), 4.25 – 4.18 (m, 1H), 4.13 (ddd, $J = 7.3, 5.8, 4.2$ Hz, 1H), 2.12(s, 3H), 1.66 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 169.7, 64.5, 62.2, 55.8, 21.4, 20.0. IR (neat, cm^{-1}): 2987, 2961, 2938, 1749, 1450, 1383, 1226, 1072, 1040, 661. HRMS (Cl^-) m/z calculated for $\text{C}_6\text{H}_{10}\text{Cl}_3\text{O}_2$ $[\text{M}+\text{Cl}]^-$ 218.9746, found: 218.9752.



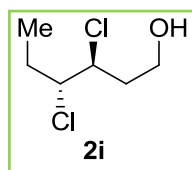
(2g, Table 2): Following the *General Procedure A*, reaction of *trans*-crotyl *tert*-butyldimethylsilylether⁹ (**1g**, 186 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2g** (209 mg, 81% yield, colorless oil) as a single diastereomer. Gram-scale dichlorination of **1g** (1.86 g, 10.0 mmol) was performed to give the desired dichloride **2g** (1.87g, 73% yield): ^1H NMR (400 MHz, CDCl_3): δ 4.35 (m, 1H), 4.03 (dd, $J = 8.0, 4.8$ Hz, 1H), 3.98 (dd, $J = 8.0, 4.8$ Hz, 1H), 3.81 (ddd, $J = 8.0, 6.5, 4.8$ Hz, 1H), 1.58 (d, $J = 6.6$ Hz, 3H), 0.89 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 66.7, 64.8, 56.5, 26.0 (3 x C), 21.2, 18.5, -5.2, -5.3. IR (neat, cm^{-1}): 2956, 2933, 2859, 1296, 1195, 1130, 838, 779, 657. HRMS (Cl^-) m/z calculated for $\text{C}_{10}\text{H}_{22}\text{Cl}_3\text{OSi}$ $[\text{M}+\text{Cl}]^-$ 291.0505, found: 291.0497.



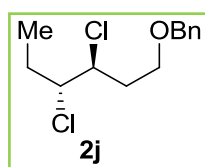
(2h, Table 2): Following the *General Procedure A*, reaction of *trans*-crotyl *tert*-butyldiphenylsilylether¹⁰ (**1h**, 311 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2h** (340 mg, 89% yield, colorless oil) as a single diastereomer. ^1H NMR (400 MHz, CDCl_3): δ 7.78 – 7.62 (m, 4H), 7.53 – 7.36 (m, 6H), 4.56 – 4.40 (m, 1H), 4.09 – 4.03 (m, 2H), 3.86 (dq, $J = 11.6, 2.4$ Hz, 1H), 1.61 (d, $J = 6.6$ Hz, 3H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 135.0 (4 x C), 134.9 (2 x C), 129.3 (2 x C), 127.2 (4 x C), 65.7, 64.5, 55.6, 26.1 (3 x C), 20.6, 18.7. IR (neat, cm^{-1}): 3071, 2958, 2933, 2885, 2859, 1110, 822, 704, 615. HRMS (Cl^-) m/z calculated for $\text{C}_{20}\text{H}_{26}\text{Cl}_3\text{OSi}$ $[\text{M}+\text{Cl}]^-$ 415.0819, found: 415.0813.

⁹ M. Völkert, K. Uwai, A. Tebbe, B. Popkova, M. Wagner, J. Kuhlmann, H. Waldmann, *J. Am. Chem. Soc.*, **2003**, *125*, 12749.

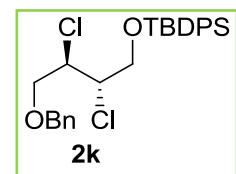
¹⁰ R. L. Nyland, II; Y. Xiao, P. Liu, C. L. F. Meyers, *J. Am. Chem. Soc.*, **2009**, *131*, 17734.



(2i, Table 2): Following the *General Procedure A*, reaction of 3-hexene-1-ol (**1i**, 100 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2i**¹¹ (140 mg, 82% yield, colorless oil) as a 6:1 diastereomeric mixture. ¹H NMR (400 MHz, CDCl₃): δ 4.38 – 4.34 (m, 1H), 4.01 – 3.97 (m, 1H), 3.84 (dd, *J* = 7.2, 4.4 Hz, 2H), 2.18 – 2.10 (m, 2H), 2.07 – 1.93 (m, 2H), 1.90 – 1.80 (m, 1H), 1.07 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 66.9, 61.0, 58.6, 36.8, 27.6, 10.8. IR (neat, cm⁻¹): 3339, 2970, 2881, 1459, 1052. Multiple attempts to find parent peak in MS failed due to fragmentation.



(2j, Table 2): Following the *General Procedure A*, reaction of (E)-((hex-3-en-1-yloxy)methyl)benzene¹² (**1j**, 190 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2j** (226 mg, 87% yield, colorless oil) as a single diastereomer. ¹H NMR (400 MHz, CDCl₃): δ 7.38 – 7.26 (m, 5H), 4.54 (s, 2H), 4.43 – 4.35 (dt, *J* = 8.0, 4.0 Hz, 1H), 3.97 (ddd, *J* = 9.2, 4.4, 2.5 Hz, 1H), 3.76 – 3.59 (m, 2H), 2.23 – 2.22 (m, 1H), 2.12 – 2.04 (m, 1H), 2.01 – 1.93 (m, 1H), 1.91 – 1.85 (m, 1H), 1.07 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 138.1, 128.5, 128.4, 127.9, 127.7, 127.6, 73.1, 67.4, 66.4, 61.8, 35.4, 28.4, 11.4. IR (neat, cm⁻¹): 3031, 2970, 2872, 1456, 1362, 1107, 734, 698. HRMS (CI⁻) *m/z* calculated for C₁₃H₁₈Cl₂O [M+Cl]⁻ 295.0423, found: 295.0417.



(2k, Table 2): Following the *General Procedure A*, reaction of (E)-4-(benzyloxy)but-2-enyloxy(tert-butyl)diphenylsilane¹³ (**1k**, 416 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2k**¹⁴ (390 mg, 80% yield, colorless oil) as a single diastereomer. ¹H NMR (400 MHz, CDCl₃): δ 7.75 – 7.69 (m, 4H), 7.46 – 7.32 (m, 11H), 4.63 (d, *J* = 2.0 Hz, 2H), 4.54 – 4.48 (m, 1H), 4.30 (ddd, *J* = 7.6, 4.0, 3.6 Hz, 1H), 4.15 (dd, *J* = 7.2, 4.0 Hz, 1H), 3.97 (dd, *J* = 6.0, 4.0 Hz, 1H), 3.95 – 3.92 (m, 2H), 1.09 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 137.8, 135.9

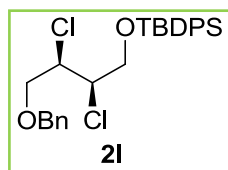
¹¹ N. I. Shuikin, I. F. Bel'skii, I. E. Grushko, R. A. Karakhanov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1963**, 6, 988.

¹² L. A. Flippin, P. A. Brown, K. Jalali-Araghi, *J. Org. Chem.* **1989**, 54, 3588.

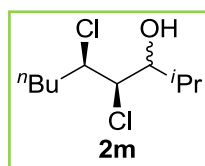
¹³ M. Isobe, M. Kurono, K. Tsuboi, A. Takai, *Chem. Asian. J.* **2007**, 2, 377.

¹⁴ T. Yoshimitsu, N. Fukumoto, T. Tanaka, *J. Org. Chem.* **2009**, 74, 696.

(2 x C), 135.8, 133.1, 133.0, 130.0 (2 x C), 128.6 (2 x C), 127.9 (4 x C), 127.8 (4 x C), 73.6, 71.4, 65.2, 62.0, 59.8, 26.9 (3 x C), 19.5.

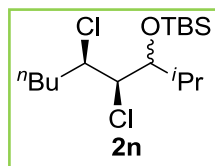


(2l, Table 2): Following the *General Procedure A*, reaction of (Z)-4-(benzyloxy)but-2-enedioxy(tert-butyl)diphenylsilane¹¹ (**1k**, 416 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2l**¹² (424 mg, 87% yield, colorless oil) as a single diastereomer. ¹H NMR (400 MHz, CDCl₃): δ 7.73 – 7.65 (m, 4H), 7.49 – 7.33 (m, 11H), 4.69 (ddd, *J* = 8.0, 4.0, 2.0 Hz, 1H), 4.62 (d, *J* = 2.0 Hz, 2H), 4.44 (ddd, *J* = 7.6, 3.2, 2.0 Hz, 1H), 3.96 (dd, *J* = 10.0, 8.8 Hz, 1H), 3.90 – 3.82 (m, 2H), 3.78 (dd, *J* = 10.0, 6.0 Hz, 1H), 1.09 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 137.7, 135.8 (2 x C), 135.7, 133.0, 132.8, 130.2, 130.1, 128.7 (2 x C), 128.1 (2 x C), 128.0 (2 x C), 127.9 (4 x C), 73.6, 71.0, 64.5, 60.1, 58.1, 26.9 (3 x C), 19.4.

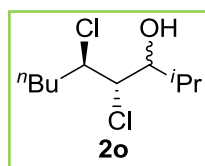


(2m, Table 2): Following the *General Procedure A*, reaction of (Z)-2-methylnon-4-en-3-ol¹⁵ (**1m**, 156 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2m** (173 mg, 76% yield, colorless oil) as a 1.4:1 diastereomeric mixture. Major diastereomer (*R_f* = 0.61, 20% ethyl acetate in hexane): ¹H NMR (400 MHz, CDCl₃): δ 4.21 – 4.09 (m, 2H), 3.69 – 3.64 (m, 1H), 2.04 – 1.98 (m, 1H), 1.97 – 1.88 (m, 2H), 1.56 – 1.48 (m, 1H), 1.46 – 1.33 (m, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H), OH (not found). ¹³C NMR (100 MHz, CDCl₃): δ 76.6, 69.6, 63.9, 35.3, 31.1, 28.7, 22.4, 19.9, 16.7, 14.1. IR (neat, cm⁻¹): 3464, 2873, 1076, 931, 766. HRMS (CI⁻) *m/z* calculated for C₁₀H₂₀Cl₃O [M+Cl]⁻ 261.0580, found: 261.0577. Minor diastereomer (*R_f* = 0.60, 20% ethyl acetate in hexane): ¹H NMR (400 MHz, CDCl₃): δ 4.54 (ddd, *J* = 9.2, 3.6, 1.6 Hz, 1H), 3.88 (dd, *J* = 7.6, 1.6 Hz, 1H), 3.83 – 3.79 (m, 1H), 2.33 – 2.24 (m, 1H), 2.06 – 1.96 (m, 1H), 1.86 – 1.77 (m, 1H), 1.58 – 1.50 (m, 1H), 1.43 – 1.33 (m, 3H), 1.04 (d, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H), OH (not found). ¹³C NMR (100 MHz, CDCl₃): δ 76.2, 65.0, 62.9, 36.4, 28.9, 28.7, 22.4, 20.3, 14.1, 13.8. IR (neat, cm⁻¹): 3457, 2872, 1125, 799.

¹⁵ G. M. Shibuya, J. S. Kanady, C. D. Vanderwal, *J. Am. Chem. Soc.* **2008**, *130*, 12514.

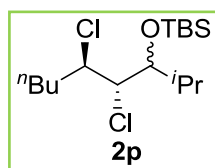


(2n, Table 2): Following the *General Procedure A*, reaction of (Z)-2-methylnon-4-en-3-ol *tert*-butyldimethylsilylether (**1n**, 271 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2n** (286 mg, 84% yield, colorless oil) as a 1.7:1 diastereomeric mixture. Major diastereomer ($R_f = 0.61$, 5% ethyl acetate in hexane): $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 4.39 (ddd, $J = 9.0, 3.6, 2.0$ Hz, 1H), 3.85 (dd, $J = 8.0, 1.2$ Hz, 1H), 3.81 (dd, $J = 9.2, 1.2$ Hz, 1H), 2.32 – 2.25 (m, 1H), 2.06 – 1.96 (m, 1H), 1.84 – 1.74 (m, 1H), 1.56 – 1.49 (m, 1H), 1.42 – 1.32 (m, 3H), 1.01 (d, $J = 7.1$ Hz, 3H), 0.95 – 0.89 (m, 15H), 0.19 (s, 3H), 0.14 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 77.2, 66.1, 62.8, 36.5, 30.3, 28.9, 26.5 (3 x C), 22.3, 20.2, 18.9, 15.0, 14.1, -3.6, -3.8. **IR** (neat, cm^{-1}): 2859, 1114, 853, 776. HRMS (Cl^-) m/z calculated for $\text{C}_{16}\text{H}_{34}\text{Cl}_2\text{OSi}$ $[\text{M}+\text{Cl}]^-$ 375.1445, found: 375.1442. Minor diastereomer ($R_f = 0.60$, 5% ethyl acetate in hexane): $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 4.08 (ddd, $J = 8.0, 6.0, 2.4$ Hz, 1H), 3.96 (dd, $J = 5.2, 2.4$ Hz, 1H), 3.81 (dd, $J = 5.6, 2.0$ Hz, 1H), 2.03 – 1.97 (m, 1H), 1.95 – 1.83 (m, 2H), 1.39 – 1.26 (m, 4H), 1.01 (d, $J = 7.2$ Hz, 3H), 0.94 – 0.89 (m, 12H), 0.86 (d, $J = 6.8$ Hz, 3H), 0.18 (s, 3H), 0.11 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 79.5, 69.3, 62.8, 36.8, 30.3, 28.7, 26.5, 22.5, 22.4, 21.3, 18.9, 15.1, 14.2, 14.1, -3.0, -3.3. **IR** (neat, cm^{-1}): 2859, 1131, 1058, 838, 778.

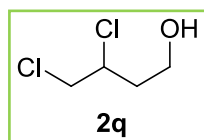


(2o, Table 2): Following the *General Procedure A*, reaction of (E)-2-methylnon-4-en-3-ol (**1o**, 156 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2o** (168 mg, 74% yield, colorless oil) as a 2:1 diastereomeric mixture. Major diastereomer ($R_f = 0.61$, 20% ethyl acetate in hexane): $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 4.48 (ddd, $J = 6.4, 5.6, 3.2$ Hz, 1H), 4.17 (dd, $J = 8.4, 3.2$ Hz, 1H), 3.71 – 3.65 (m, 1H), 2.26 – 2.18 (m, 1H), 1.96 – 1.80 (m, 2H), 1.67 – 1.58 (m, 1H), 1.45 – 1.30 (m, 3H), 1.02 (d, $J = 7.2$ Hz, 3H), 0.94 (m, 6H), OH (not found). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 77.2, 68.2, 63.4, 32.7, 29.8, 28.9, 22.4, 20.1, 14.9, 14.2. **IR** (neat, cm^{-1}): 3458, 2872, 1120, 798, 733. HRMS (Cl^-) m/z calculated for $\text{C}_{10}\text{H}_{20}\text{Cl}_2\text{O}$ $[\text{M}+\text{Cl}]^-$ 261.0580, found 261.0562. Minor diastereomer ($R_f = 0.60$, 20% ethyl acetate in hexane): $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 4.29 – 4.20 (m, 1H), 4.08 (dd, $J = 8.4, 1.2$ Hz, 1H), 3.83 – 3.78 (m, 1H), 2.24 – 2.15 (m, 1H), 1.88 – 1.76 (m, 2H), 1.50 – 1.34 (m, 4H), 1.09 (d, $J = 6.8$ Hz, 3H), 0.97 – 0.91 (m, 6H), OH

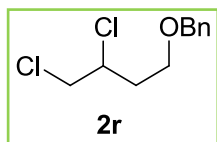
(not found). ^{13}C NMR (100 MHz, CDCl_3): δ 75.9, 67.5, 62.3, 34.7, 32.3, 27.5, 22.1, 19.4, 18.5, 13.9. IR (neat, cm^{-1}): 3469, 2869, 1101, 795, 729.



(2p, Table 2): Following the *General Procedure A*, reaction of (E)-2-methylnon-4-en-3-ol *tert*-butyldimethylsilylether (**1p**, 271 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2p** (212 mg, 62% yield, colorless oil) as a 4:1 diastereomeric mixture. Major diastereomer ($R_f = 0.61$, 5% ethyl acetate in hexane): ^1H NMR (400 MHz, CDCl_3): δ 4.28 (ddd, $J = 7.6, 5.2, 2.8$ Hz, 1H), 4.16 – 4.12 (m, 1H), 3.84 (dd, $J = 5.6, 3.6$ Hz, 1H), 2.14 – 2.06 (m, 1H), 2.02 – 1.92 (m, 1H), 1.88 – 1.78 (m, 1H), 1.69 – 1.60 (m, 1H), 1.40 – 1.32 (m, 3H), 0.98 (d, $J = 5.6$ Hz, 3H), 0.69 (d, $J = 5.2$ Hz, 6H), 0.93 (s, 9H), 0.11 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 78.1, 69.4, 63.1, 33.5, 31.7, 28.6, 26.2, 22.6 (3 x C), 20.2, 18.5, 17.7, 14.1, -3.8, -3.7. IR (neat, cm^{-1}): 2859, 1121, 836, 776. HRMS (Cl^-) m/z calculated for $\text{C}_{16}\text{H}_{34}\text{Cl}_2\text{OSi}$ $[\text{M}+\text{Cl}]^-$ 375.1445, found: 375.1448.



(2q, Table 2): Following the *General Procedure A*, reaction of 3-butene-1-ol (**1q**, 72 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2q**¹⁶ (143 mg, 99% yield, colorless oil). ^1H NMR (400 MHz, CDCl_3): δ 4.33 – 4.27 (m, 1H), 3.88 – 3.80 (m, 3H), 3.76-3.71 (m, 1H), 2.31 – 2.23 (m, 1H), 2.05 (br, 1H), 1.95 – 1.86 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 58.5, 57.3, 48.0, 37.0. IR (neat, cm^{-1}): 3356, 2957, 1431, 1047.

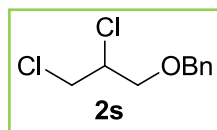


(2r, Table 2): Following the *General Procedure A*, reaction of 3-buten-benzylether¹⁷ (**1r**, 162 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2r**¹⁸ (219 mg, 94% yield, colorless oil). ^1H NMR (400 MHz, CDCl_3): δ 7.42 – 7.32 (m, 5 H), 4.56 (s, 2 H), 4.38 – 4.34 (m, 1 H), 3.84 – 3.80 (dd, $J = 11.6, 5.6$ Hz, 1 H), 3.78 – 3.74 (dd, $J = 11.6, 6.4$ Hz, 1 H), 3.73 – 3.69 (m, 2 H), 2.38 – 2.31 (m, 1 H), 2.02 – 1.95 (m, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ 137.5, 127.8, 127.1 (2 x C), 127.0 (2 x C), 72.5, 65.7, 57.6, 48.2, 34.9.

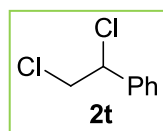
¹⁶ P. E. Peterson, B. R. Bonazza, *J. Am. Chem. Soc.* **1972**, *94*, 5017.

¹⁷ S. K. Murphy, D. A. Petrone, M. M. Coulter, V. M. Dong, *Org. Lett.* **2011**, *13*, 6216.

¹⁸ C. Liu, J. K. Coward, *J. Org. Chem.* **1991**, *56*, 2262.



(2s, Table 2): Following the *General Procedure A*, reaction of allyl benzylether¹⁹ (**1s**, 148 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2s**²⁰ (182 mg, 83% yield, colorless oil). ¹H NMR (400 MHz, CDCl₃): δ 7.42 – 7.33 (m, 5H), 4.62 (s, 2H), 4.24 – 4.19 (m, 1H), 3.93 – 3.89 (m, 1H), 3.85 – 3.83 (m, 1H), 3.81 – 3.76 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 136.9, 127.9, 127.3 (2 x C), 127.1 (2 x C), 72.9, 69.7, 75.7, 44.7.

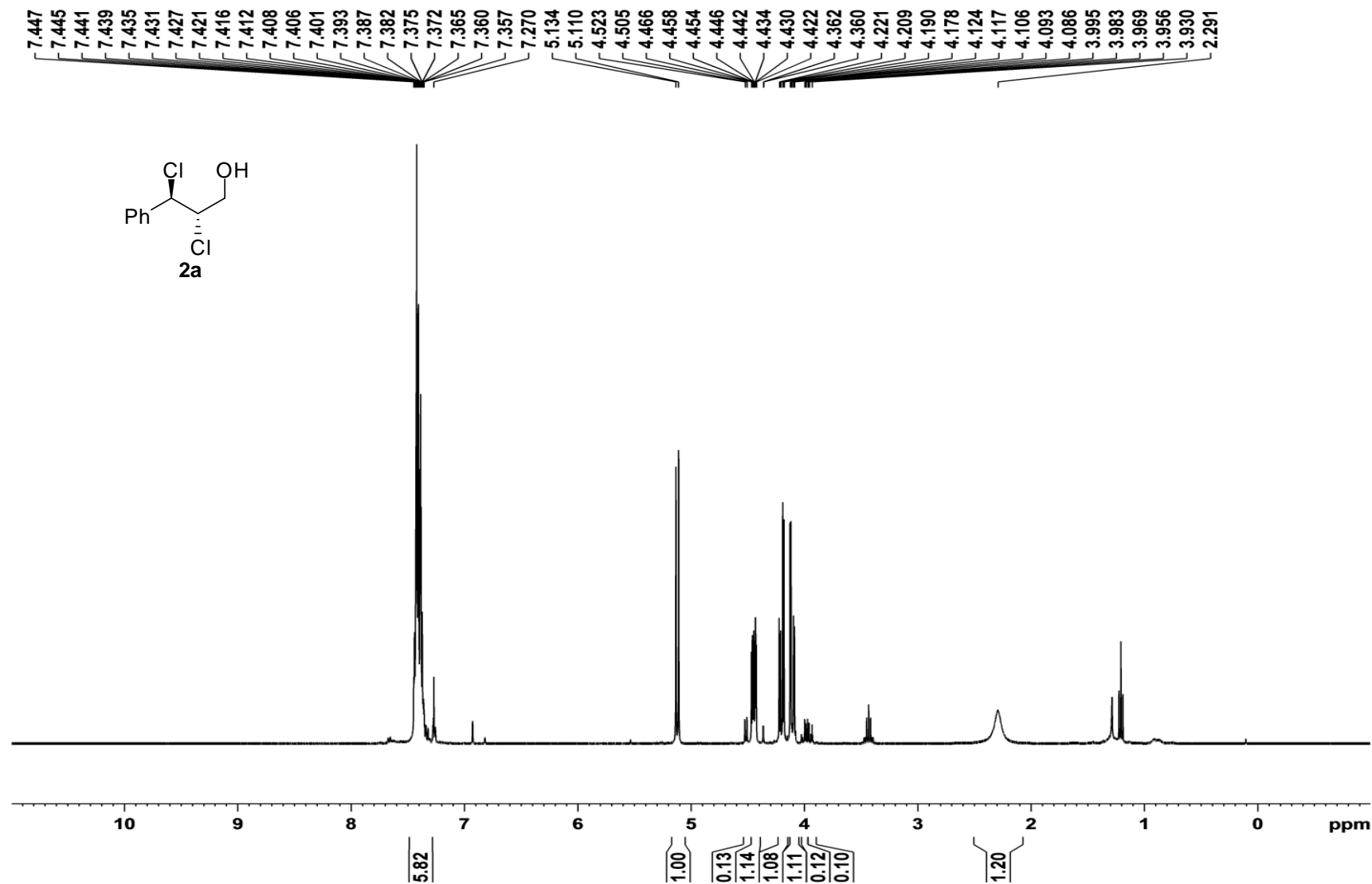


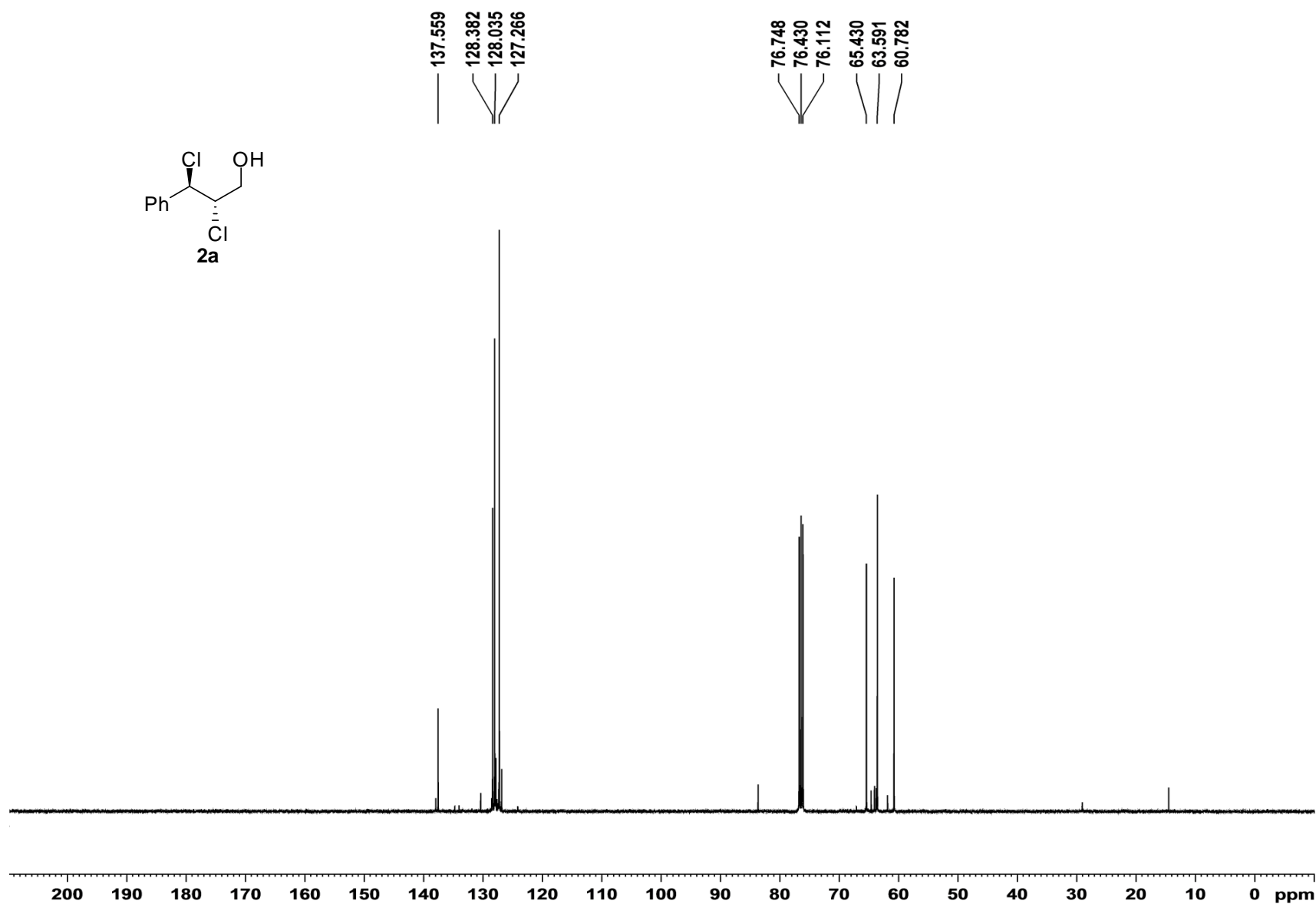
(2t, Table 2): Following the *General Procedure A*, reaction of styrene (**1t**, 104 mg, 1.0 mmol), oxone (1.23 g, 4.0 mmol) and NaCl (234 mg, 4.0 mmol) afforded dichloride **2t**²¹ (139.8 mg, 80% yield, colorless oil). ¹H NMR (400 MHz, CDCl₃): δ 7.45 – 7.37 (m, 5H), 5.02 (dd, *J* = 7.6, 6.4 Hz, 1H), 4.02 (dd, *J* = 6.8, 6.4 Hz, 1H), 3.95 (dd, *J* = 7.6, 6.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 137.4, 128.5, 128.2 (2 x C), 126.8 (2 x C), 61.1, 47.7.

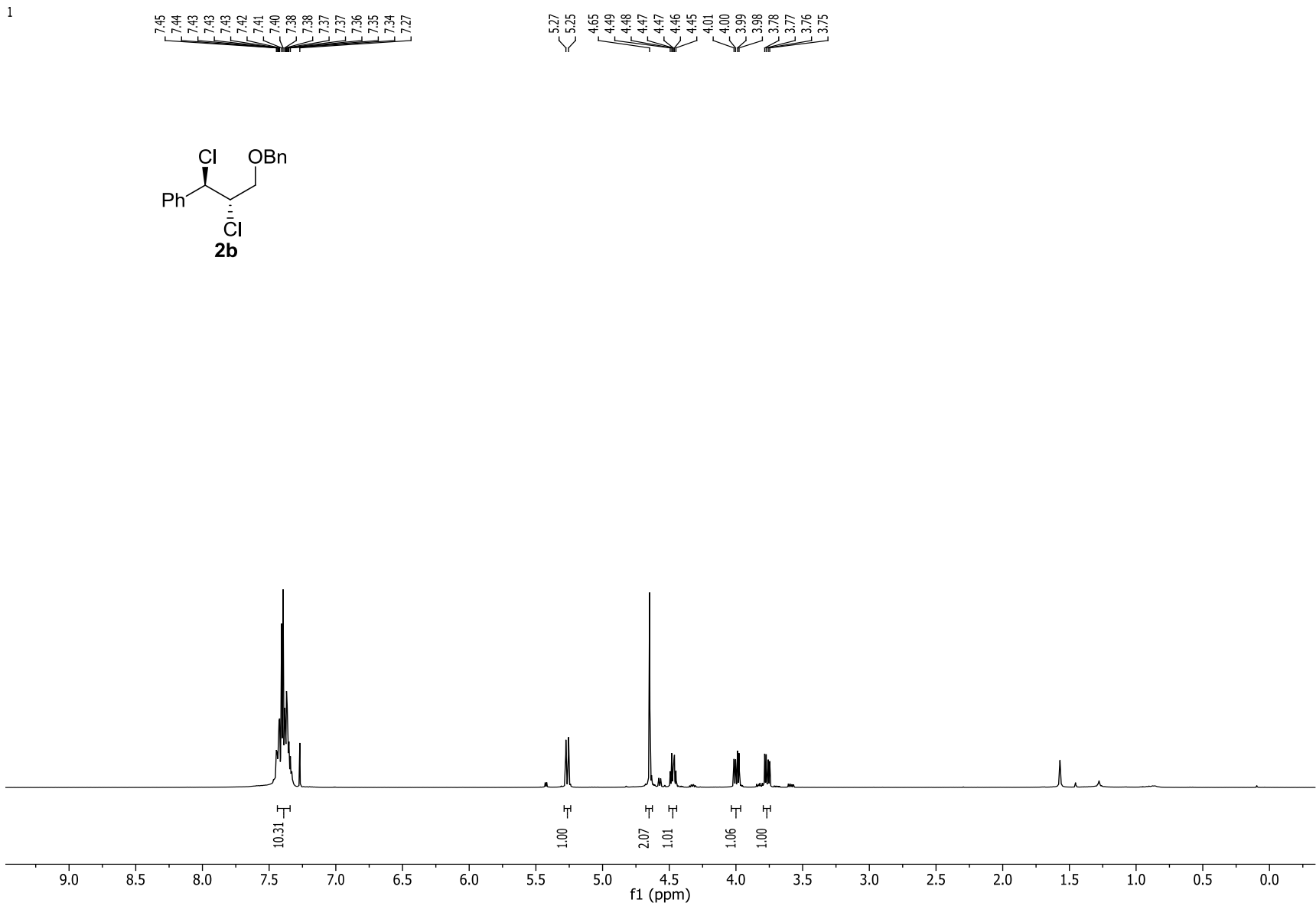
¹⁹ D. M. Heinrich, J.-J. Youte, W. A. Denny, M. Tercel, *Tetrahedron Lett.* **2011**, 52, 7000.

²⁰ M. Nakano, J.-i. Matsuo, T. Mukaiyama, *Chem. Lett.* **2000**, 12, 1352.

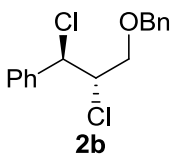
²¹ T. Kitamura, Y. Tazawa, M. H. Morshed, S. Kobayashi, *Synthesis* **2012**, 44, 1159.





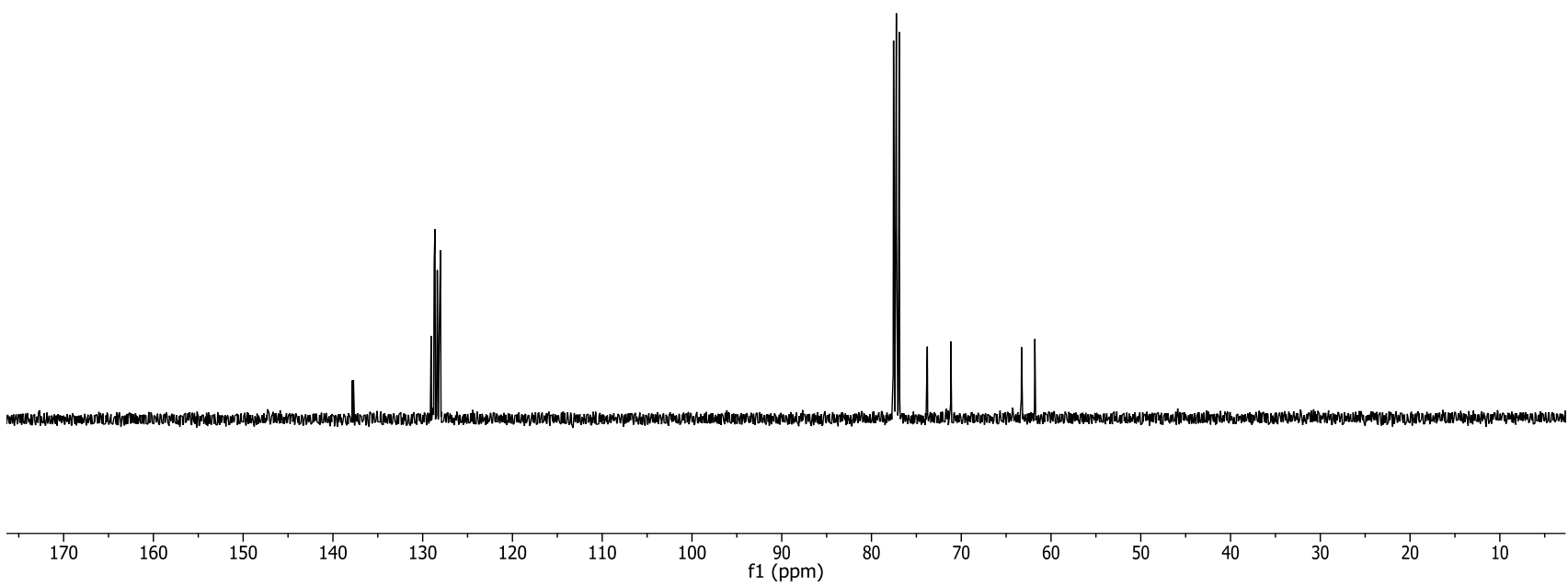


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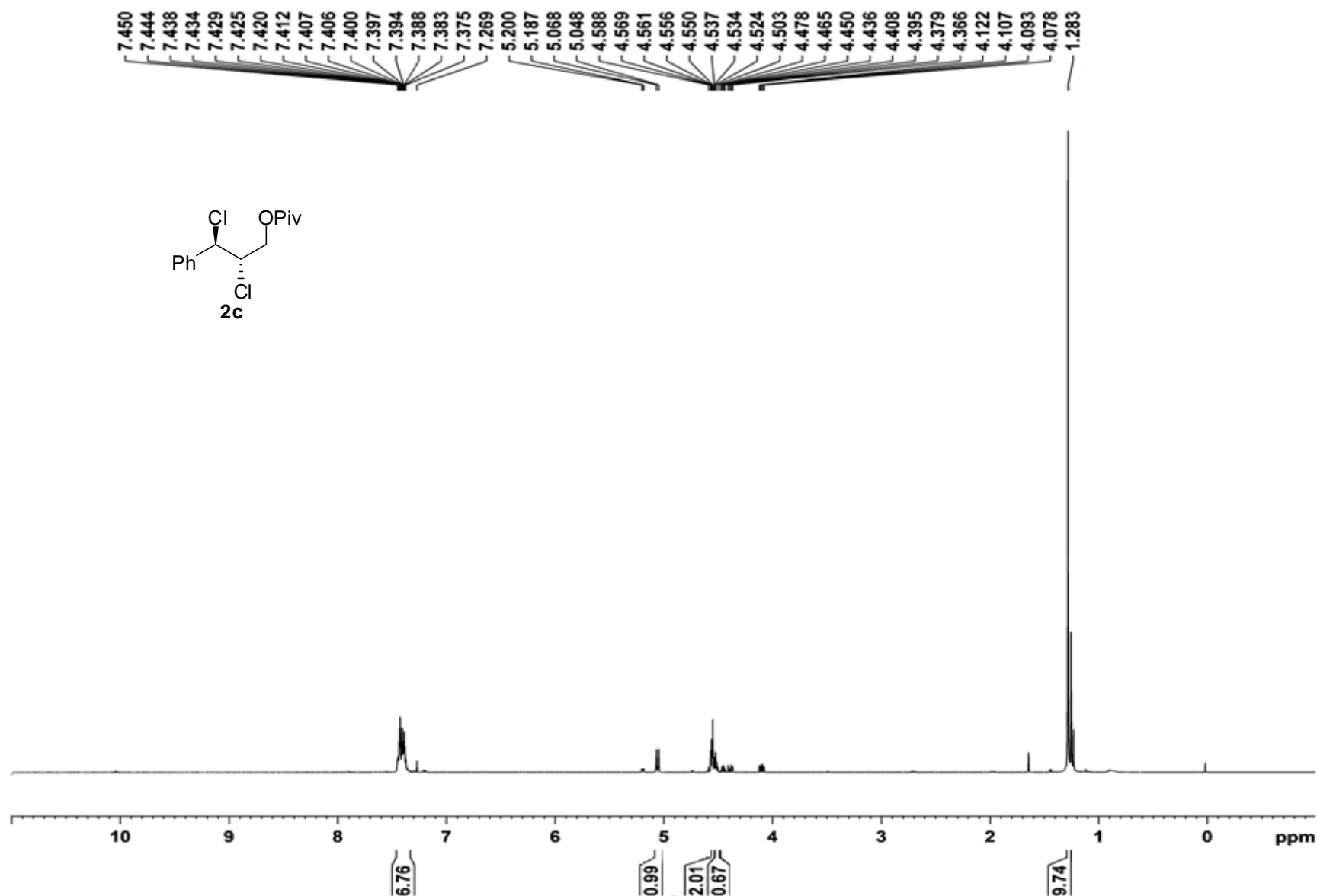


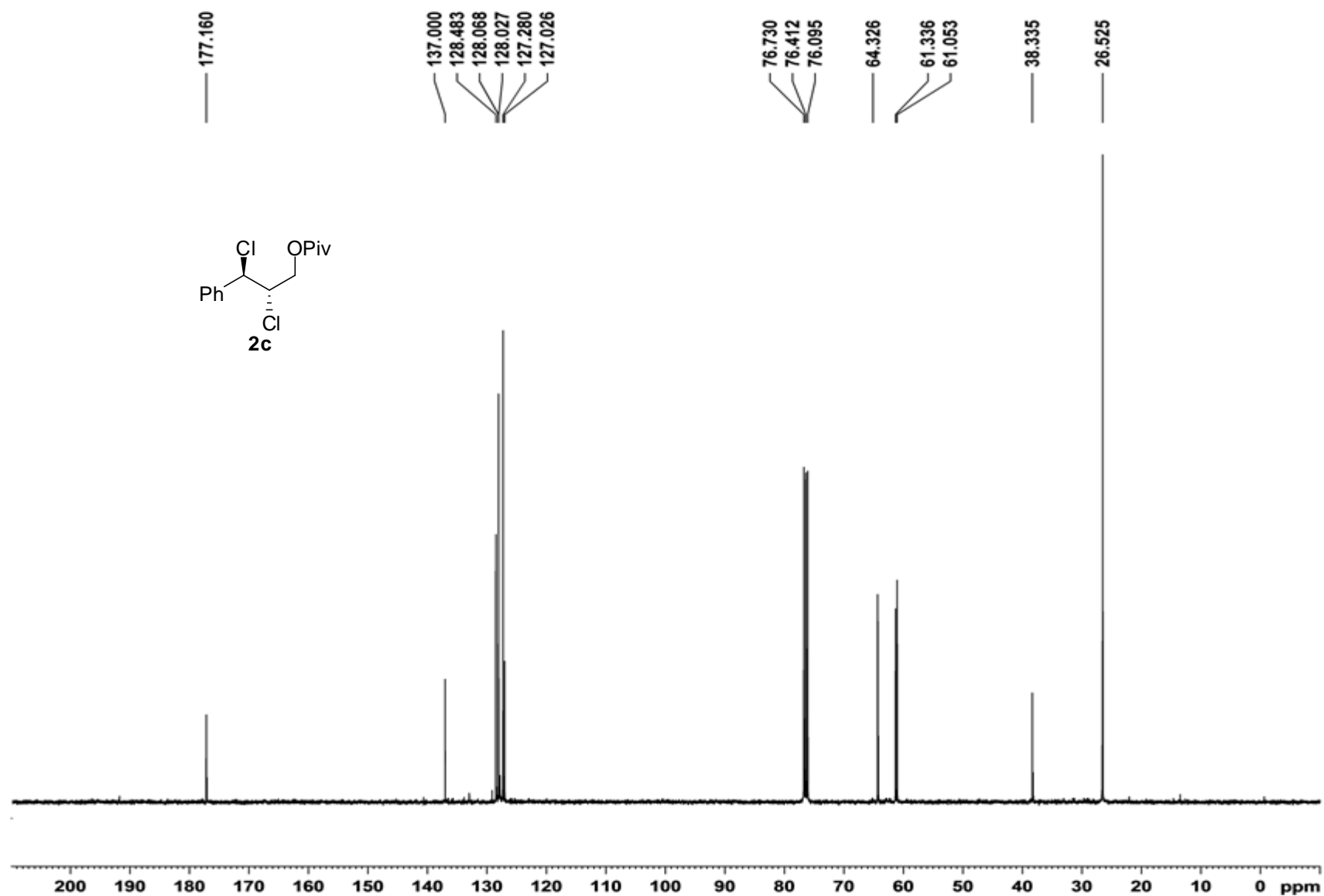
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137.71
129.06
128.71
128.63
128.37
128.15
128.02

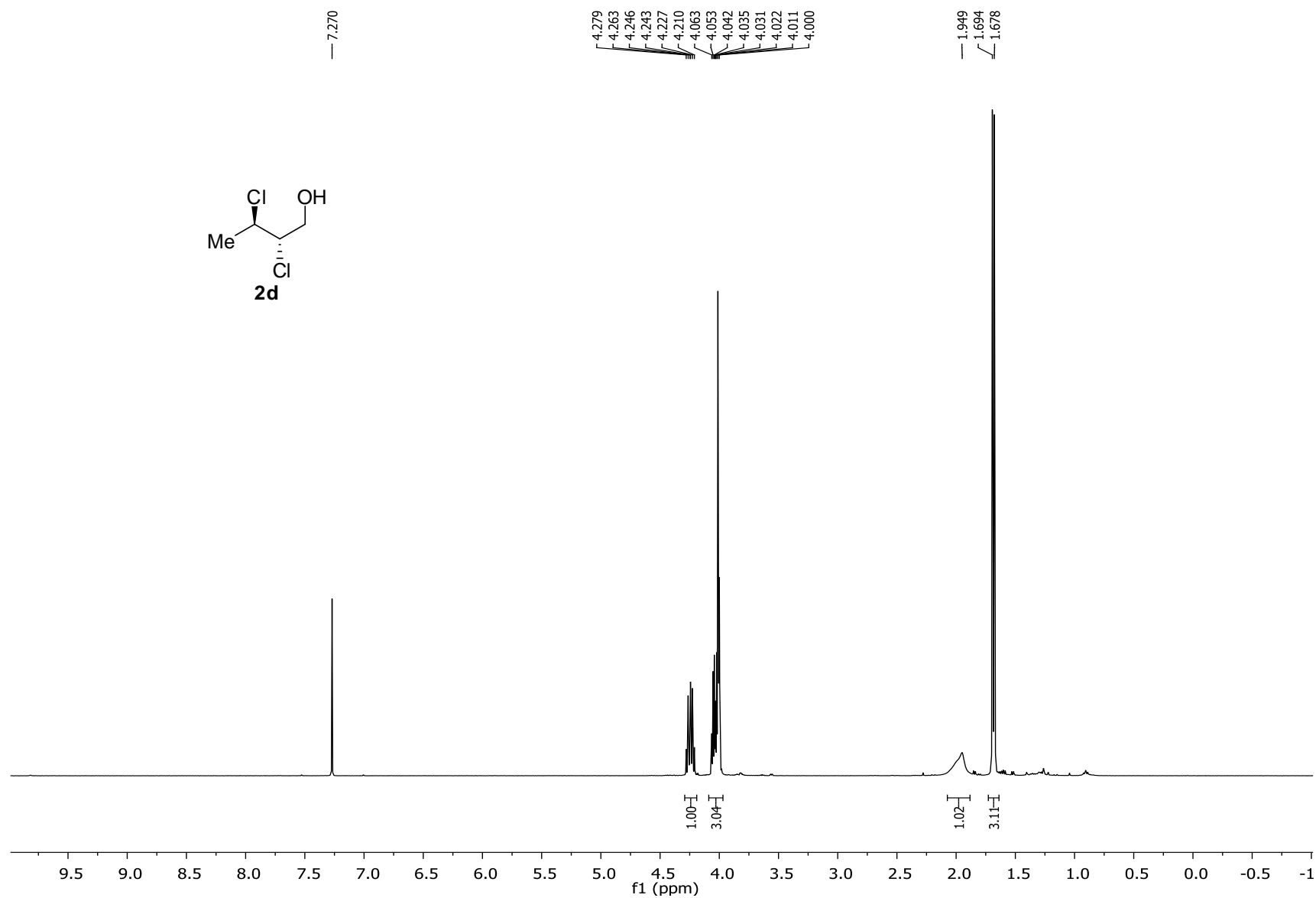
77.55
77.23
76.91
73.78
71.17
63.29
61.79

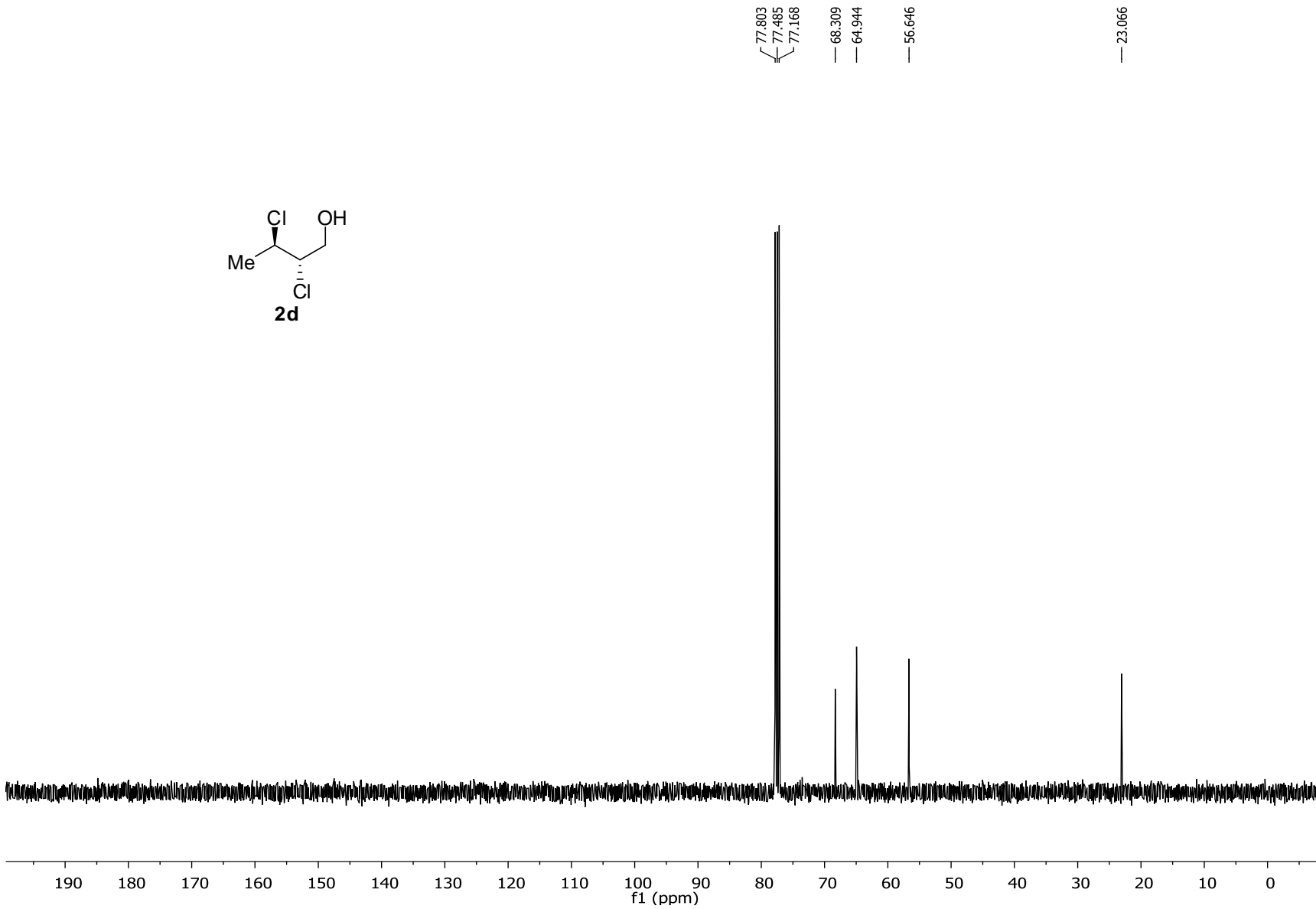
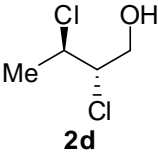


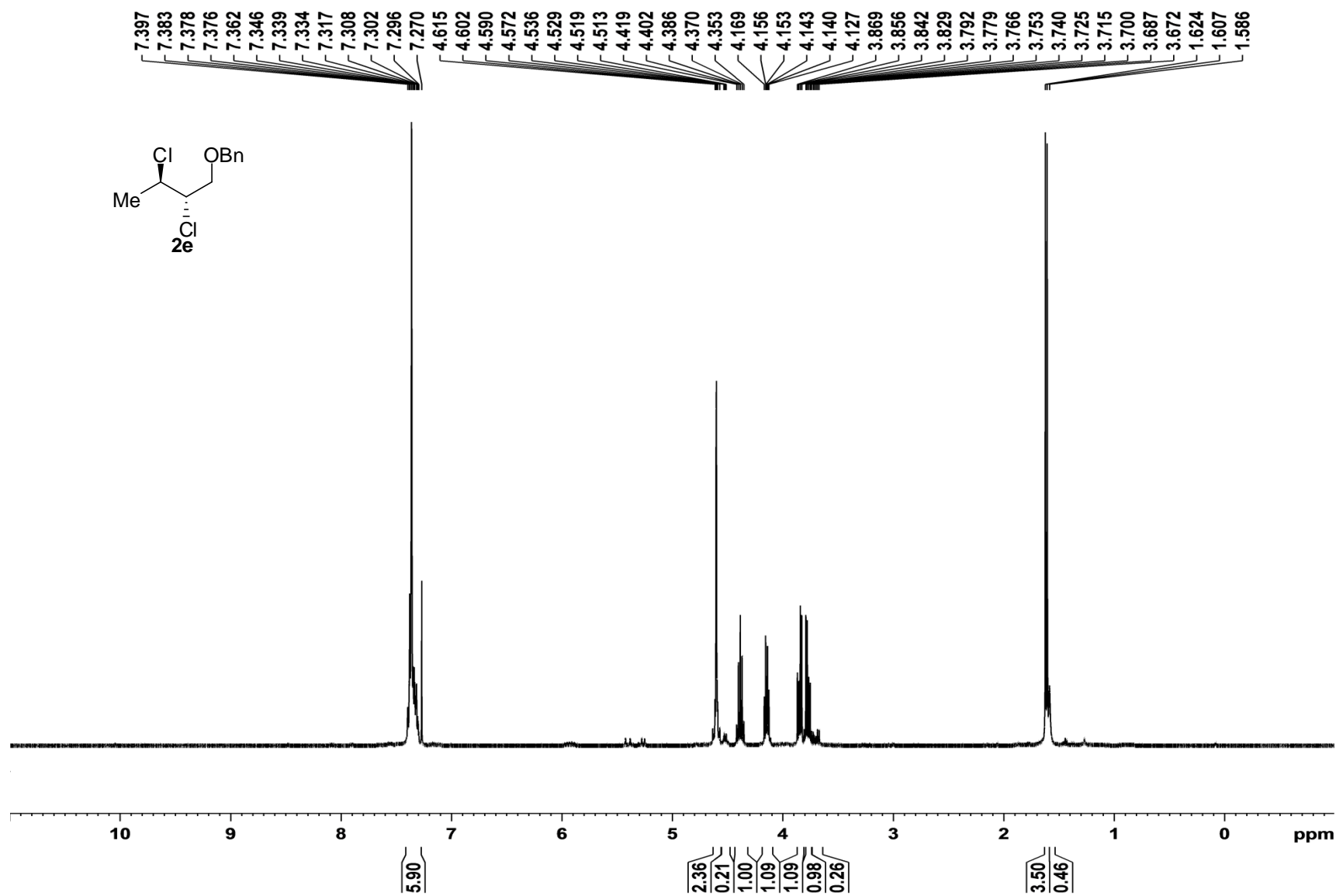
S21

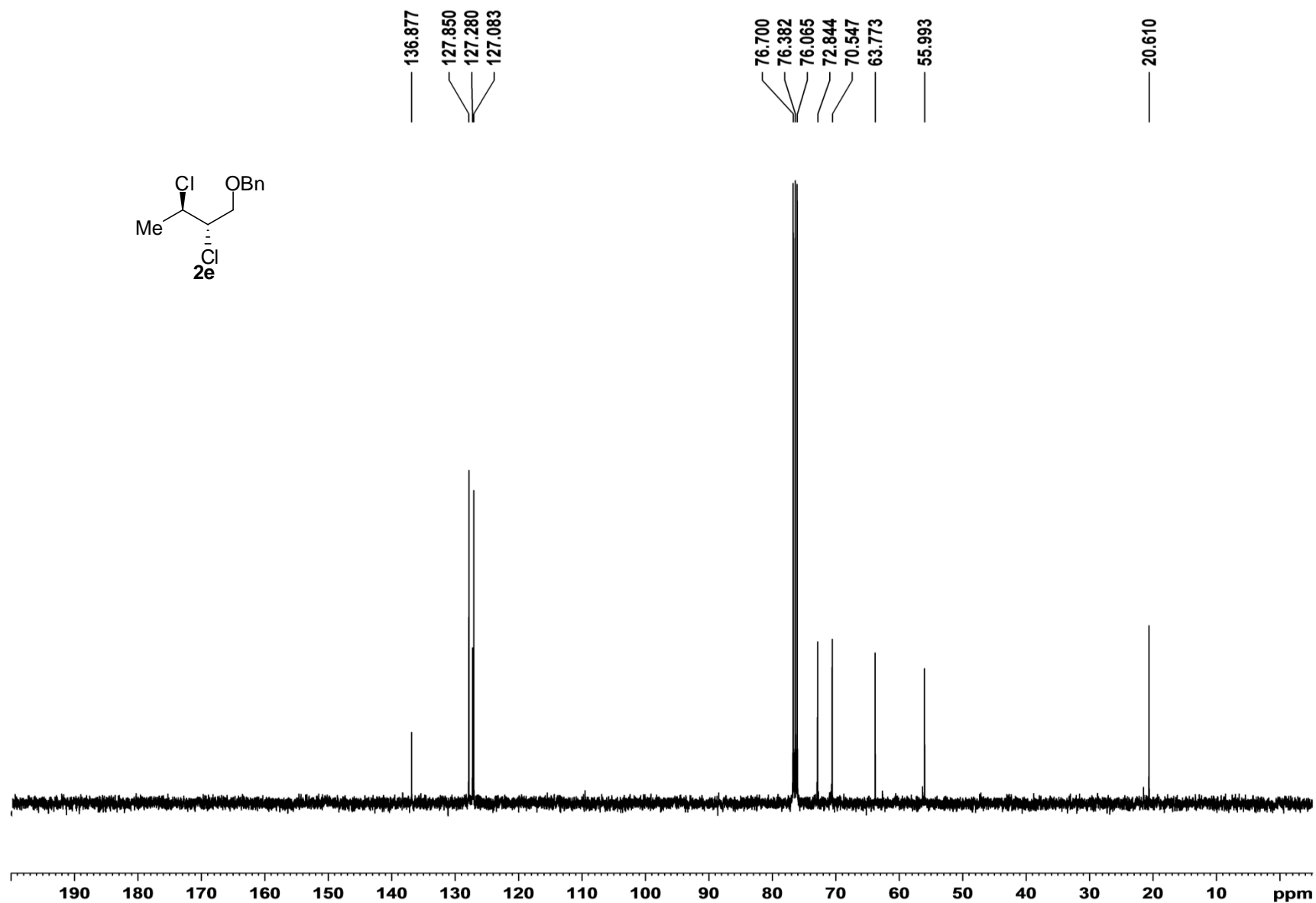


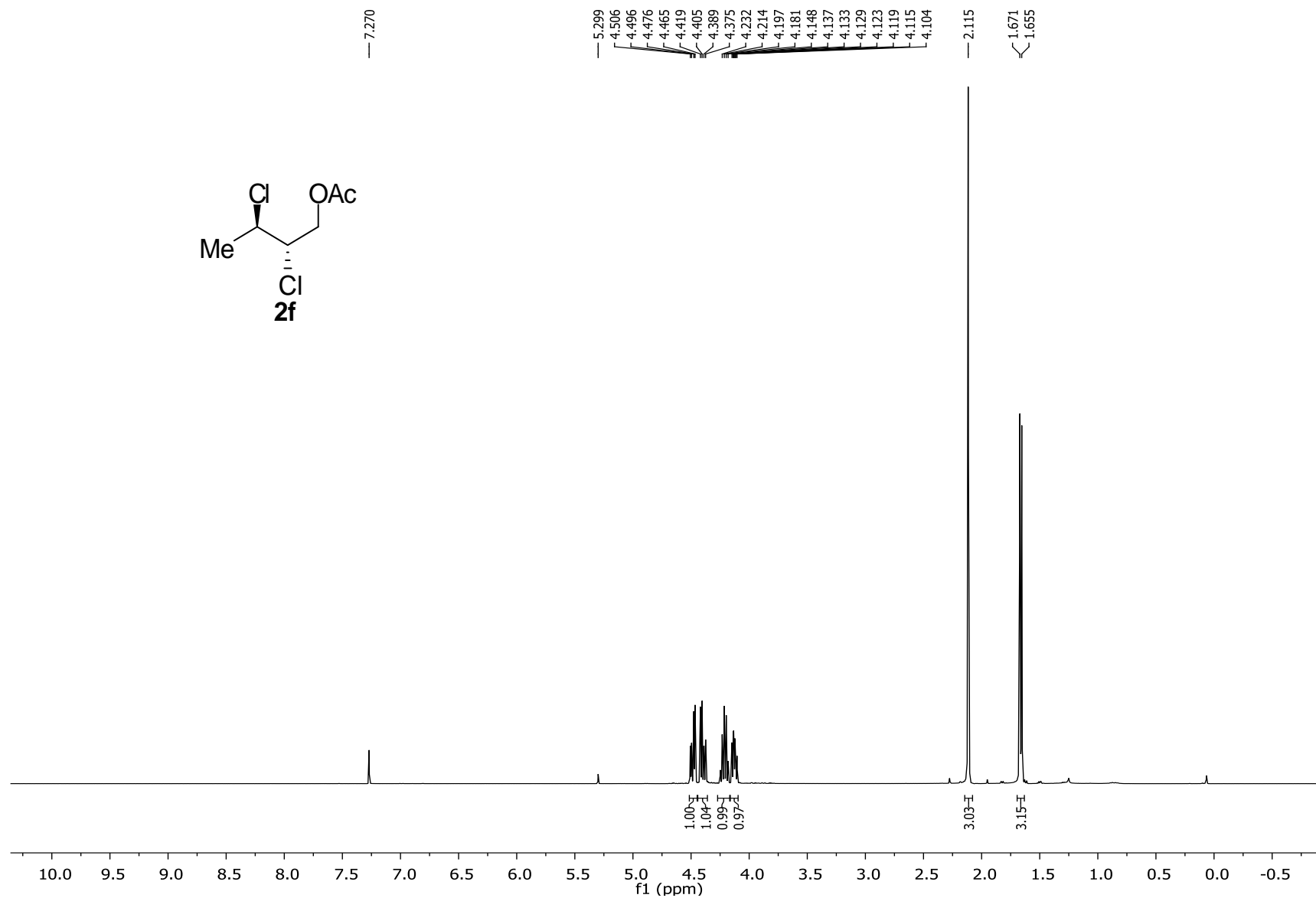


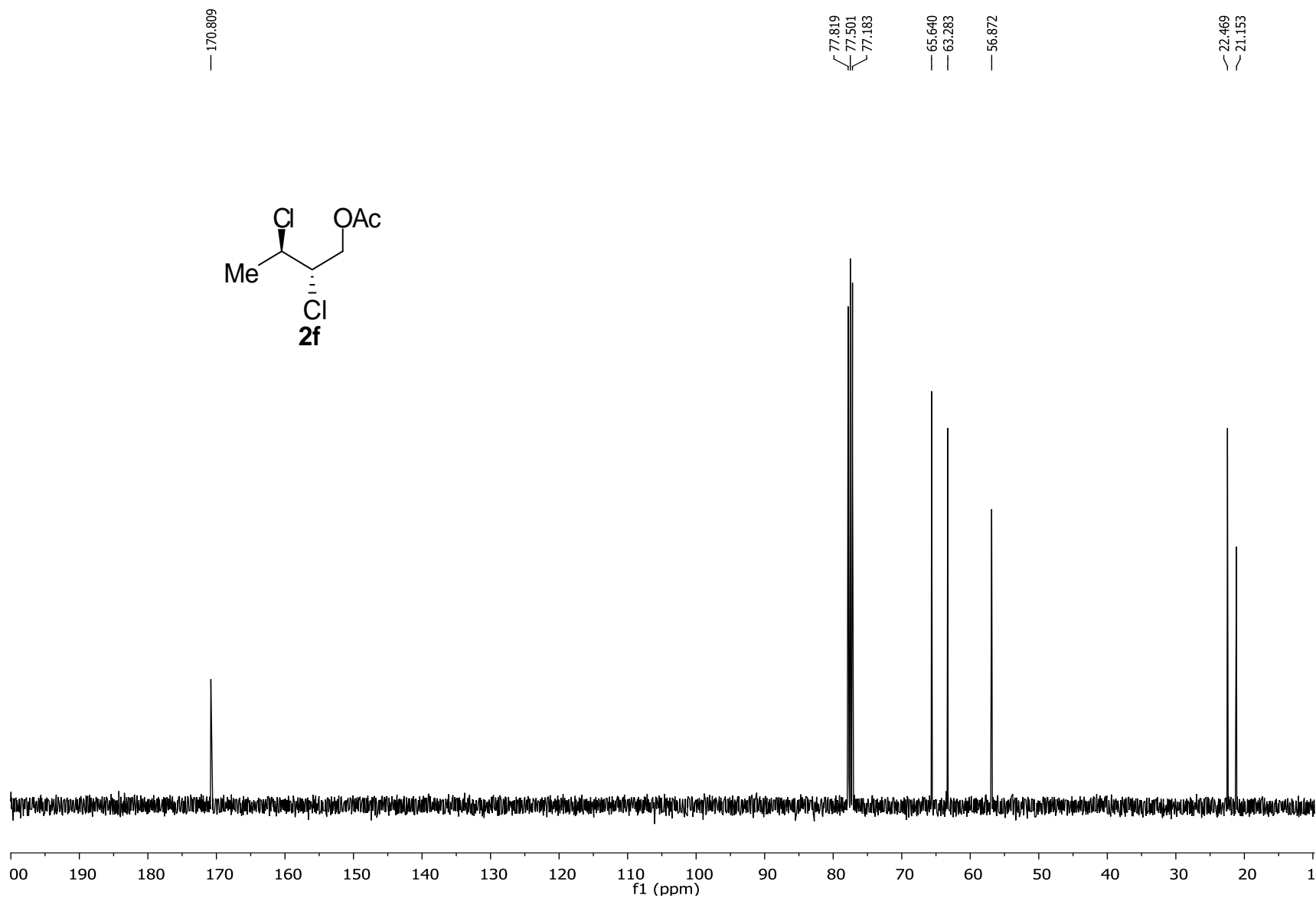


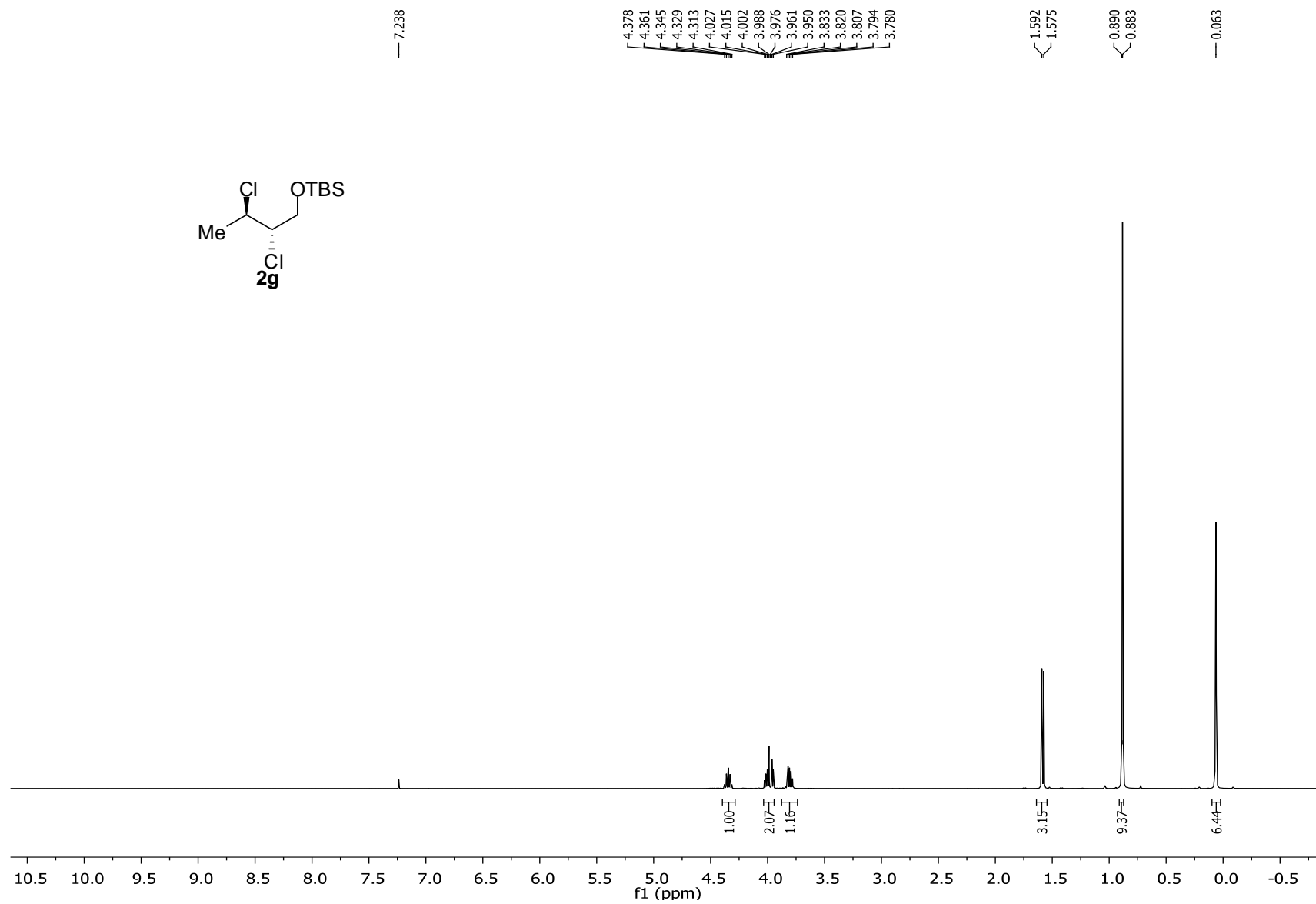




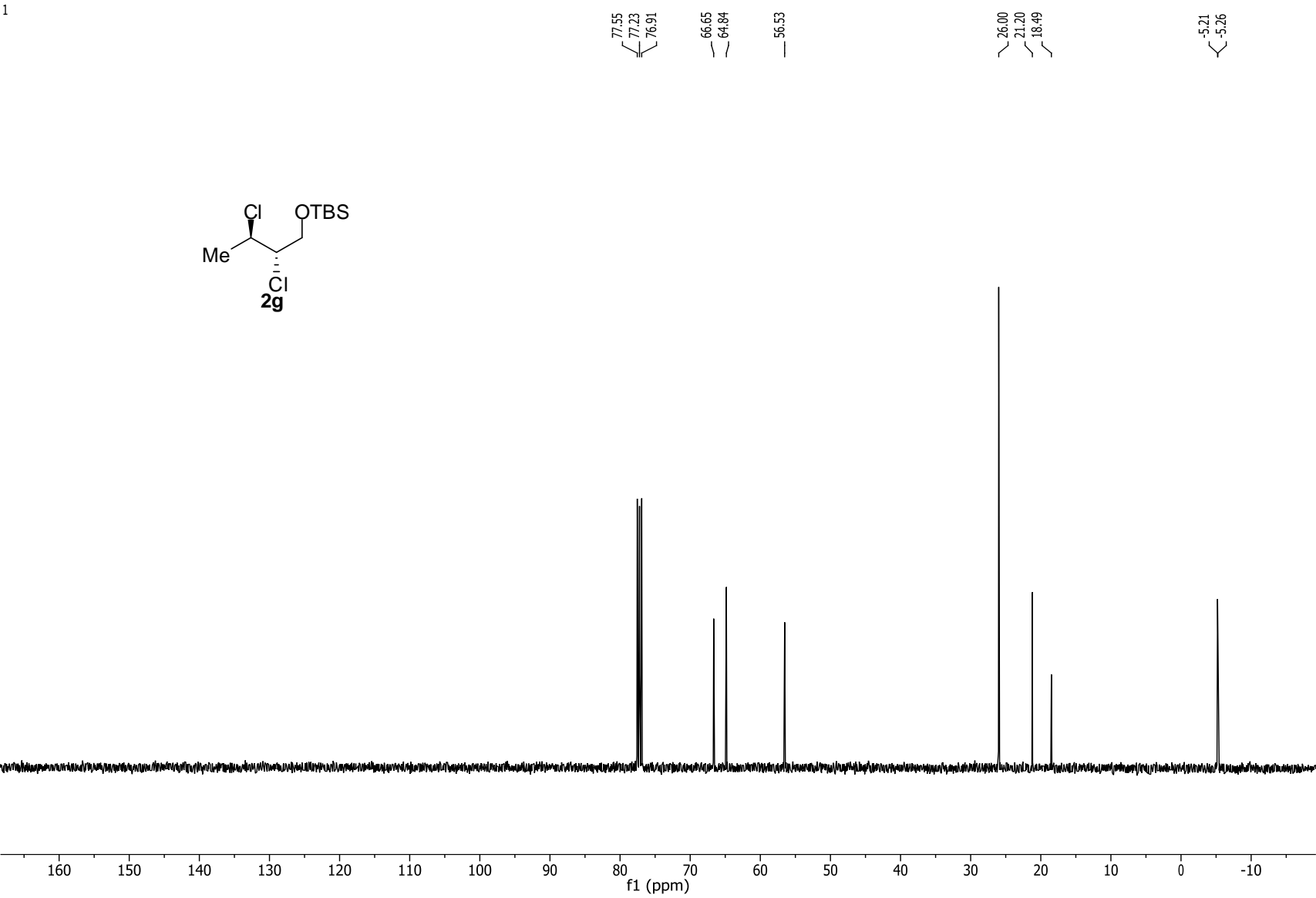




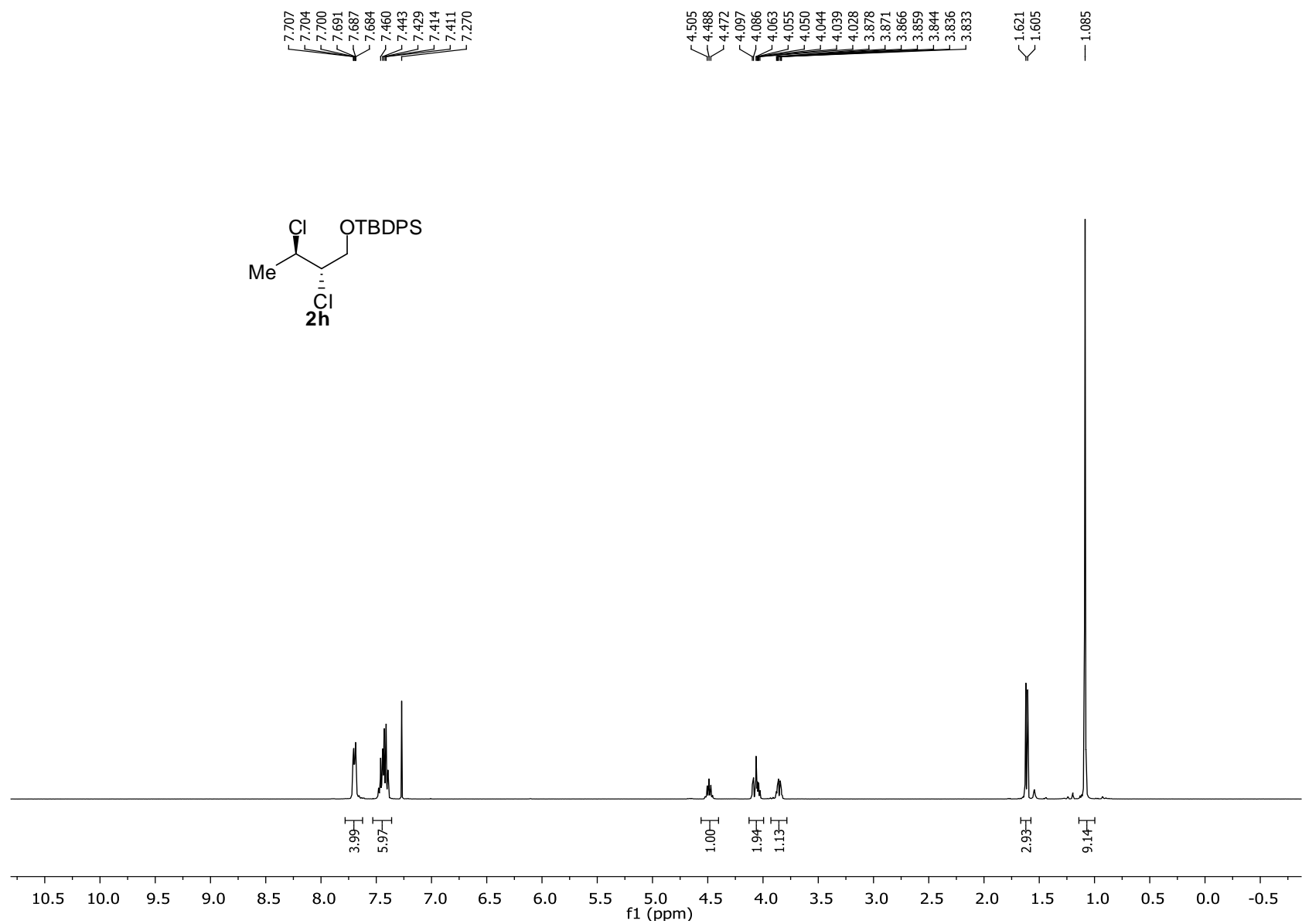


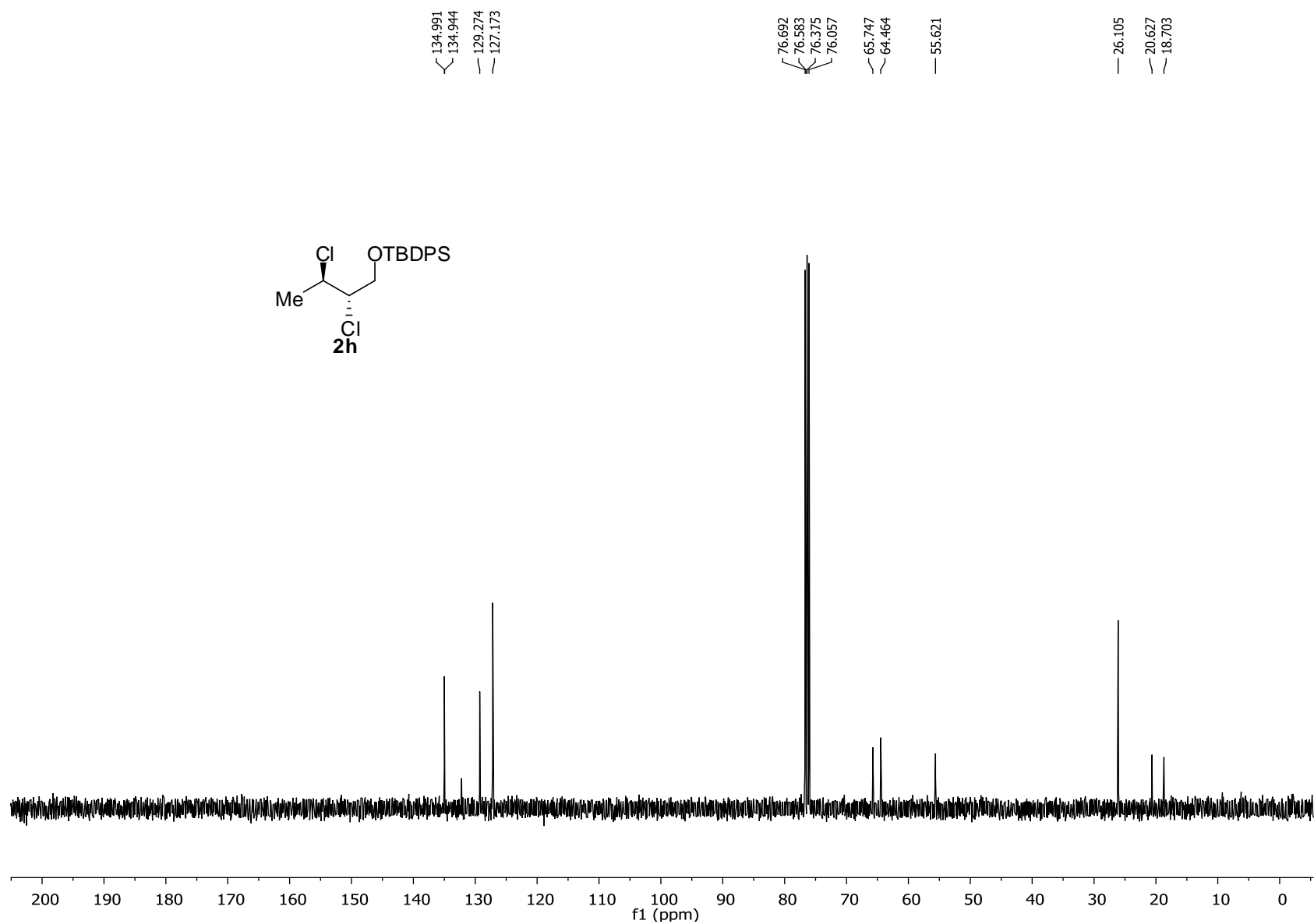


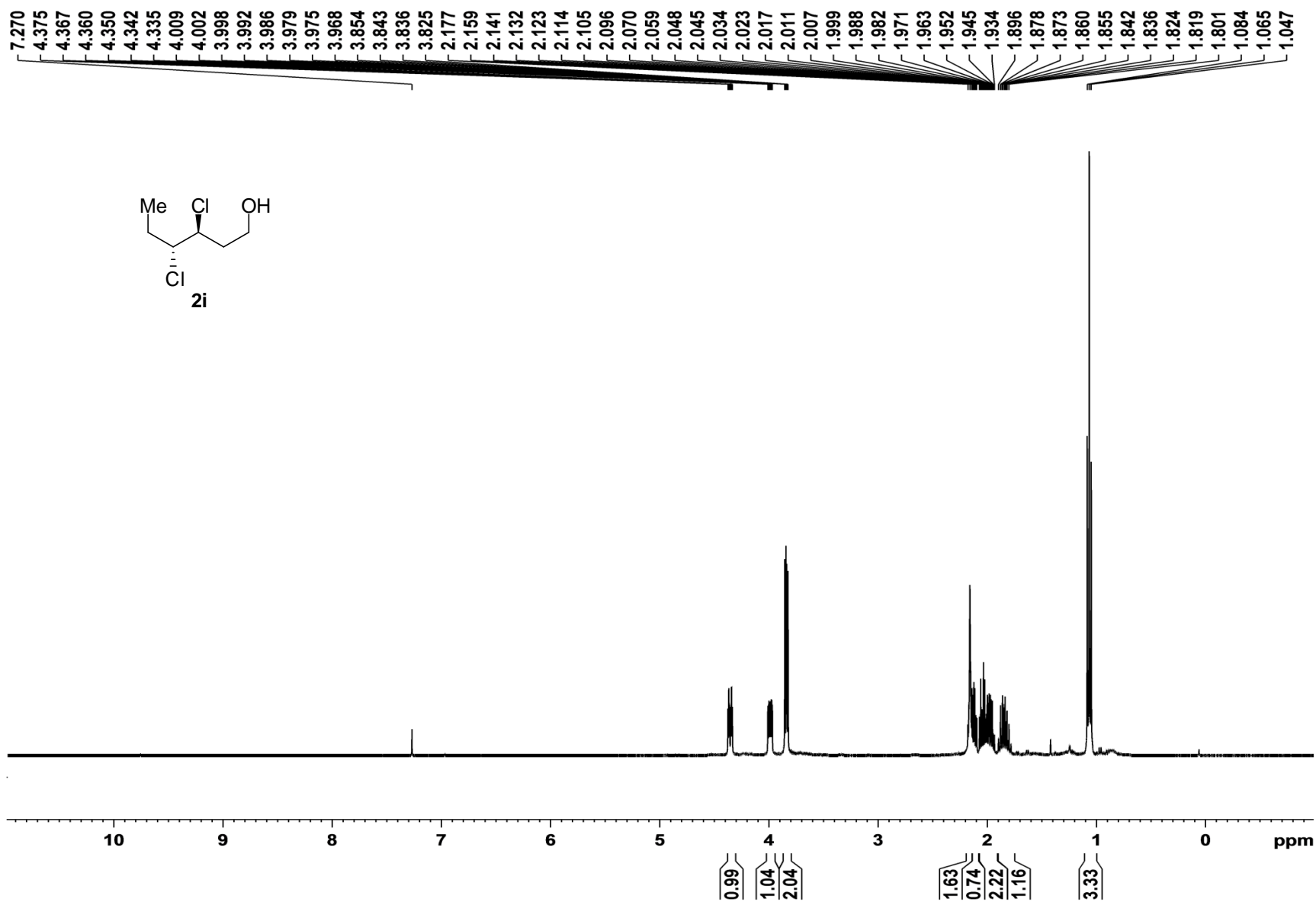
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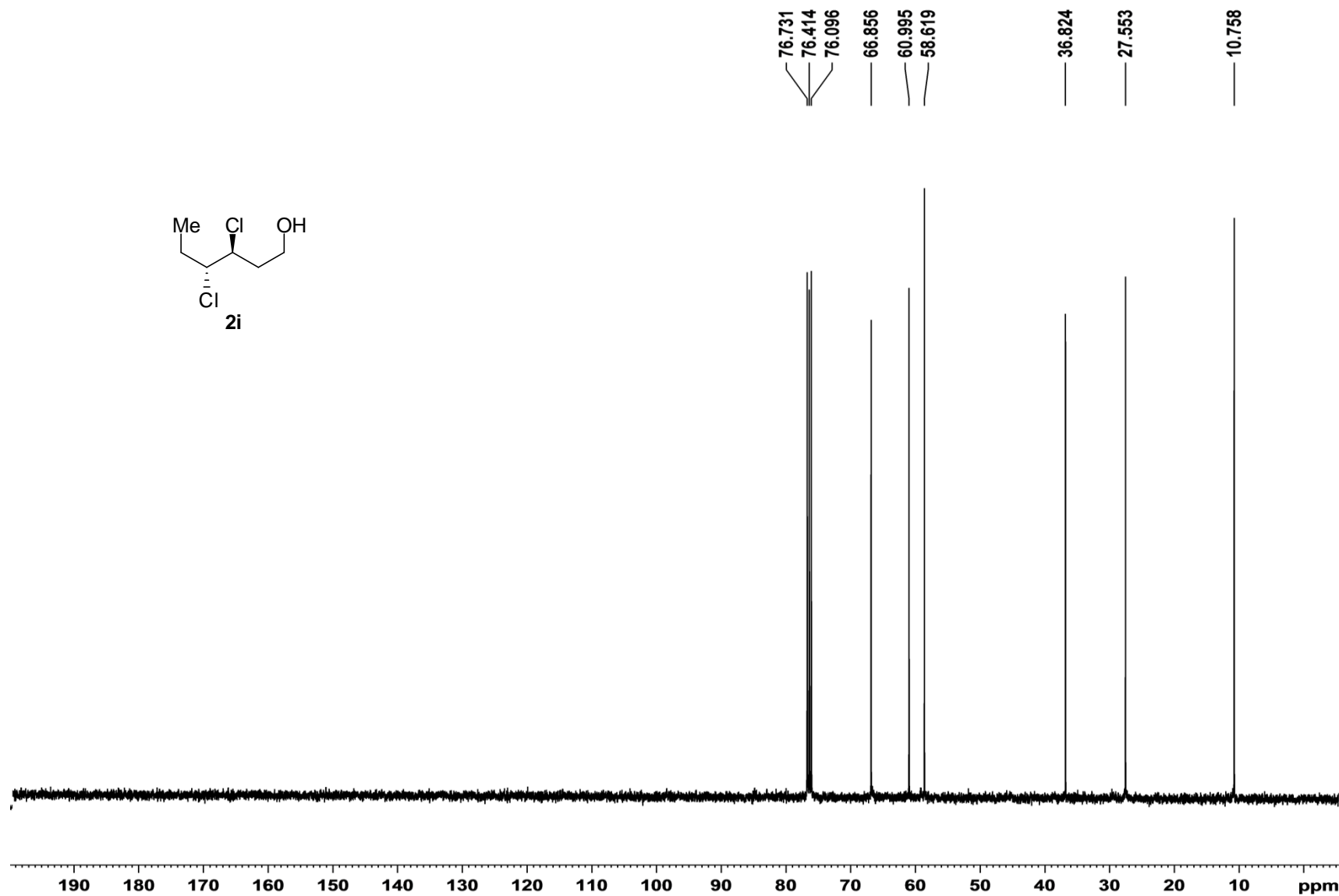


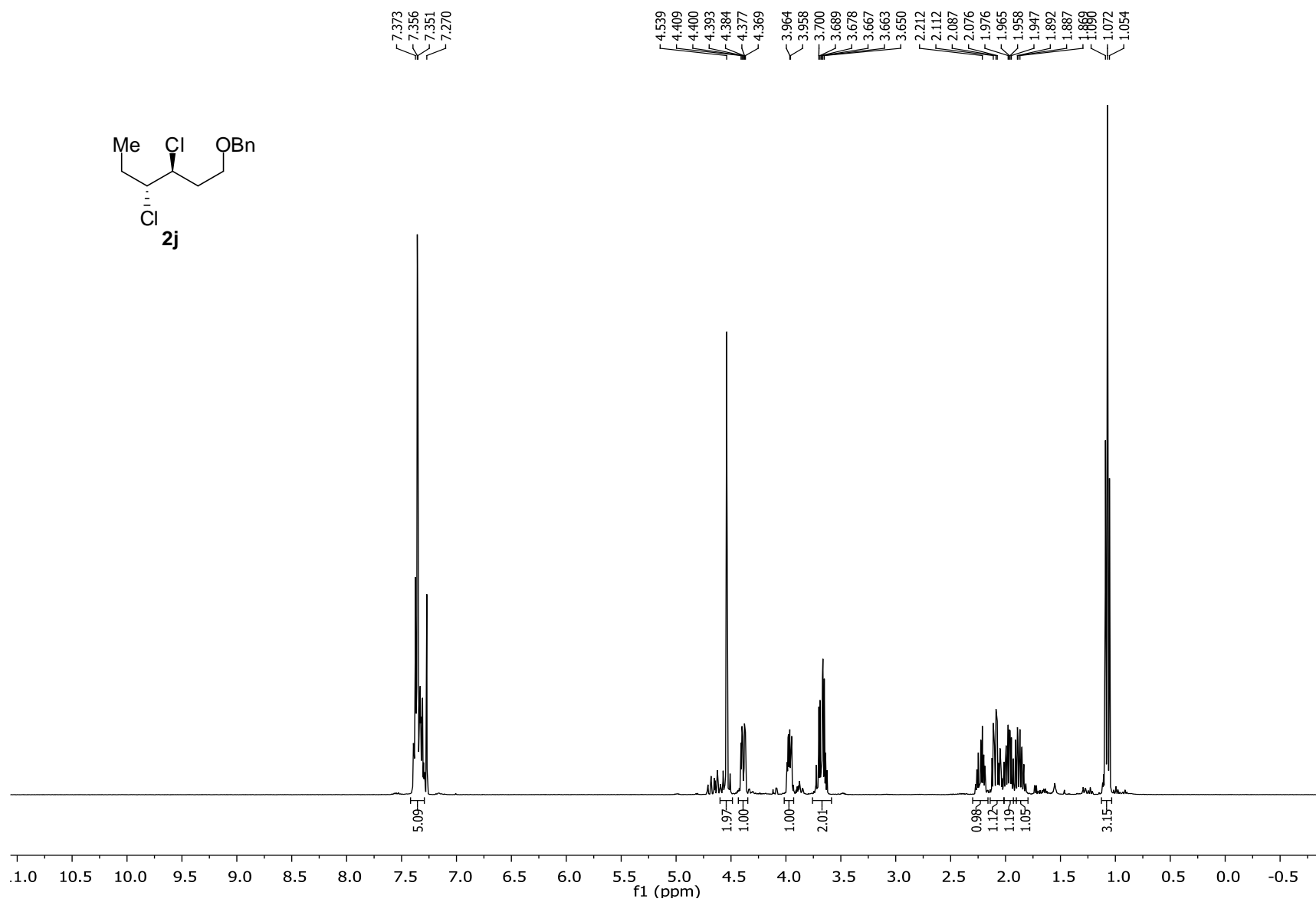
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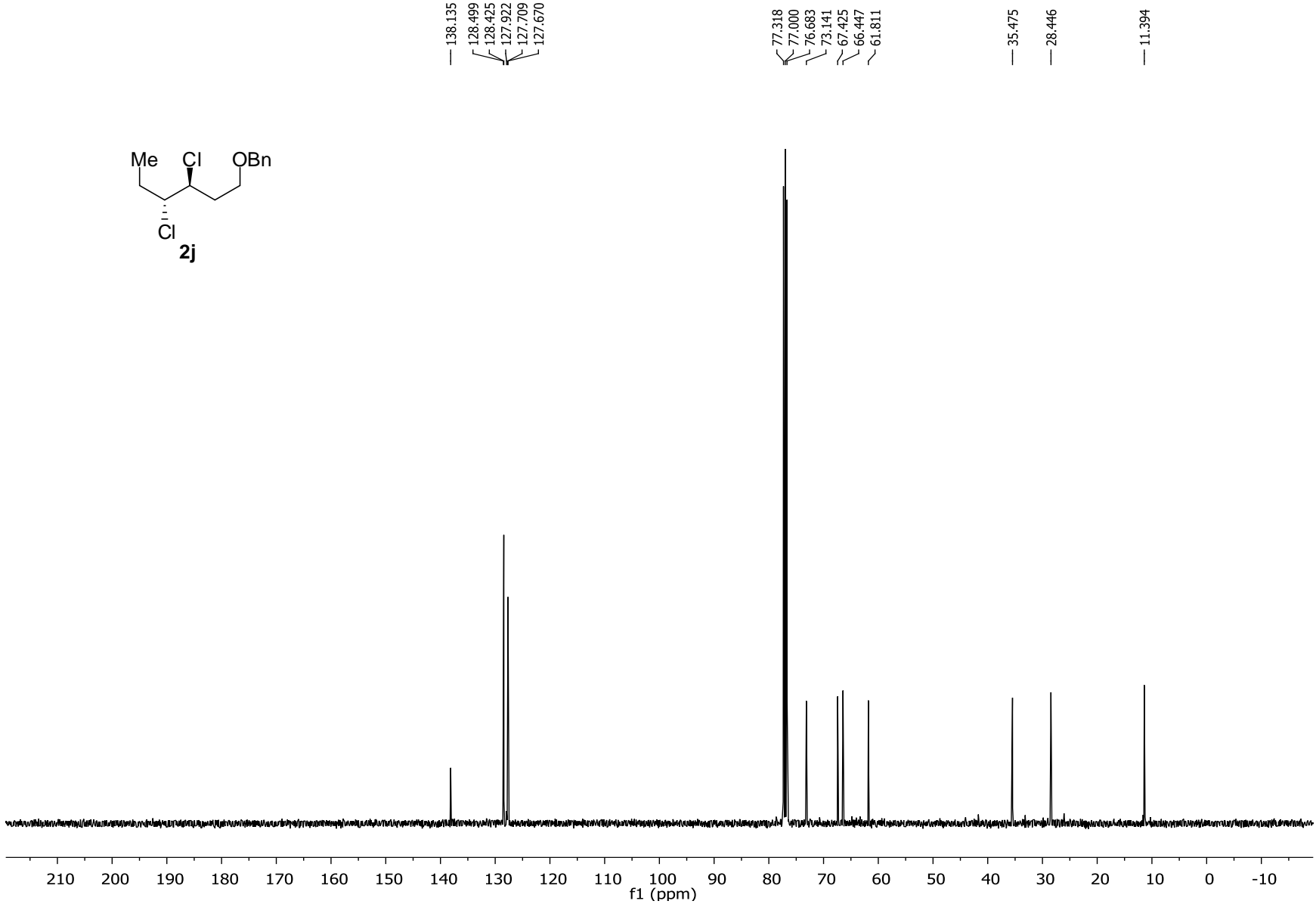




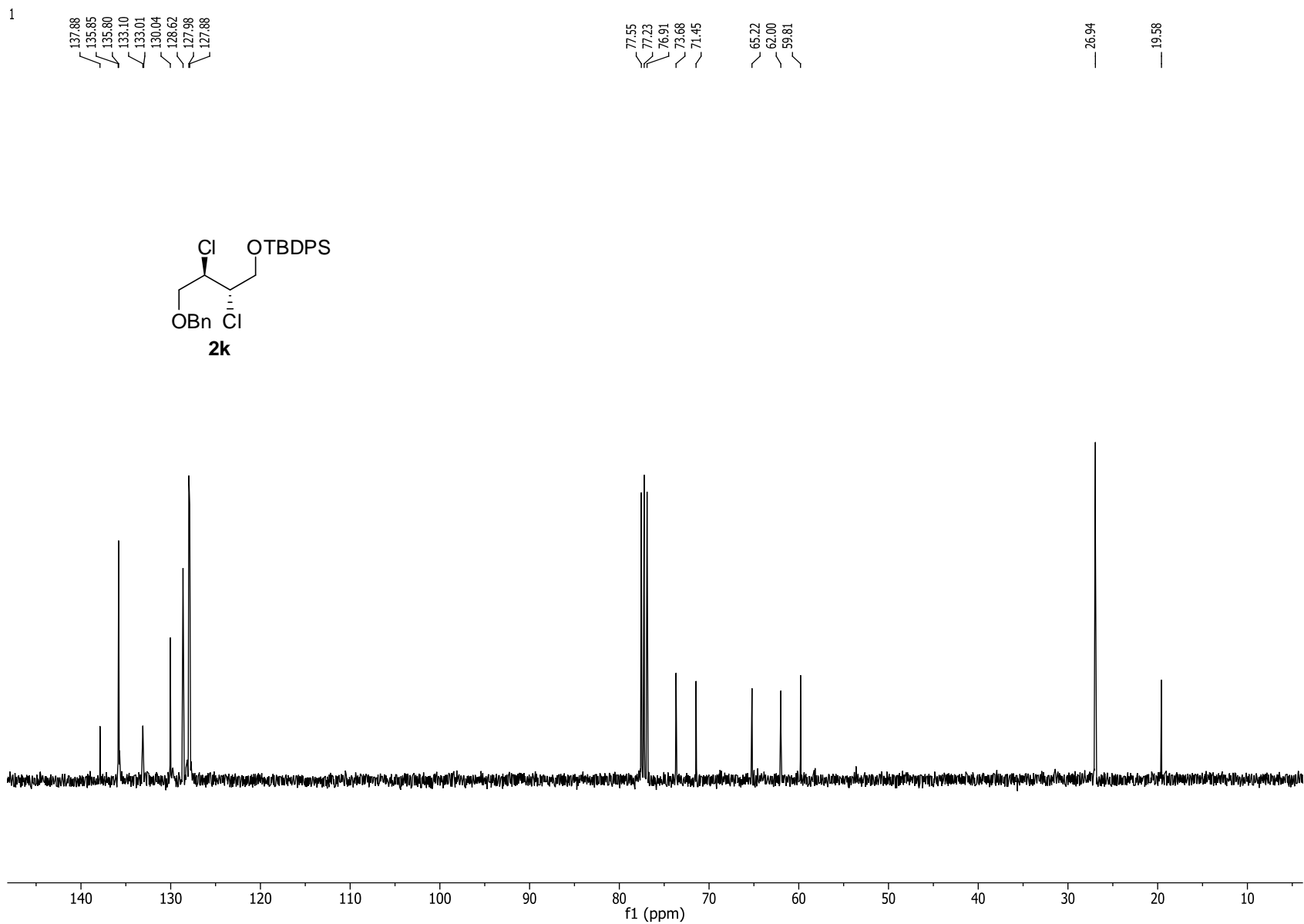


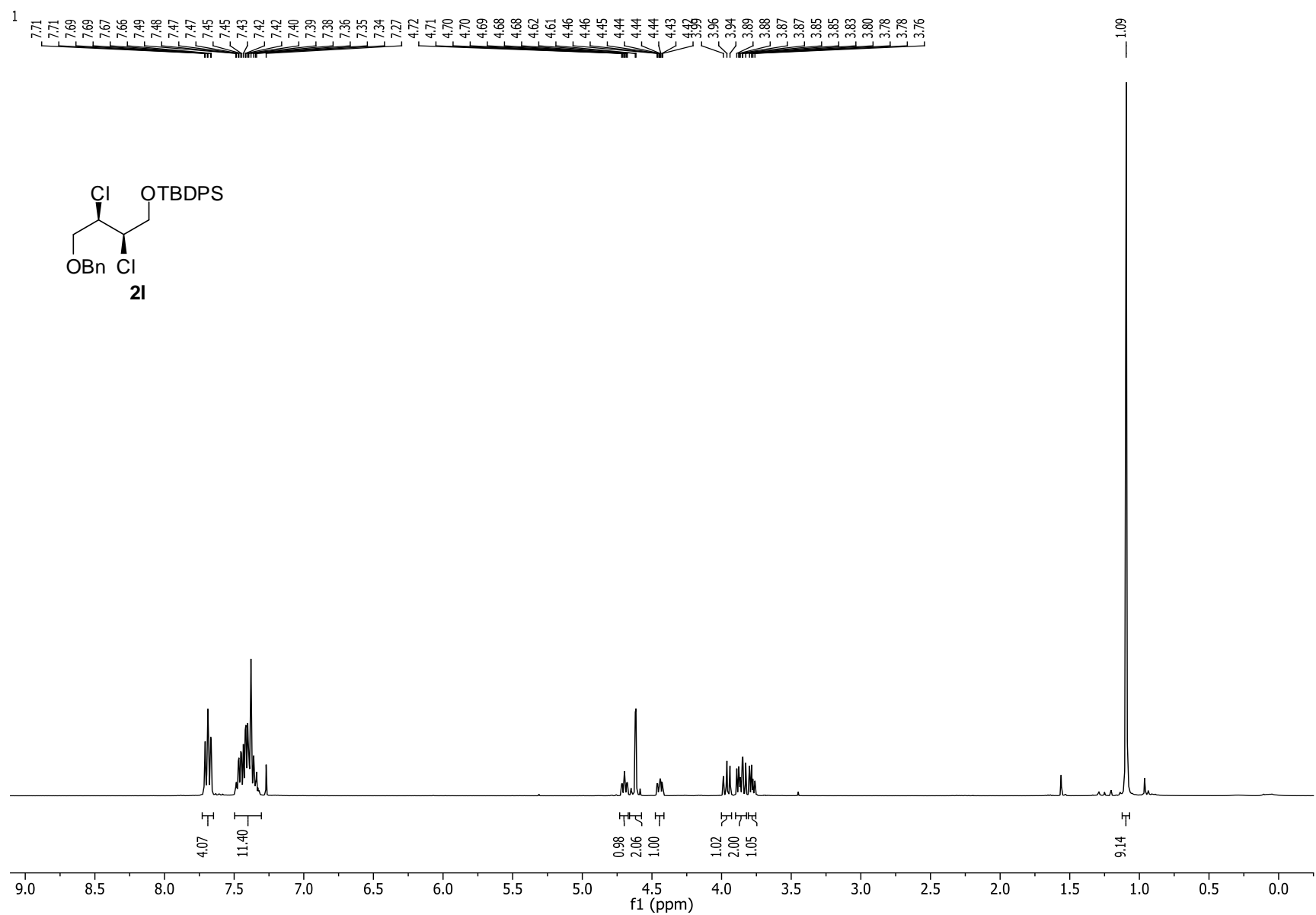




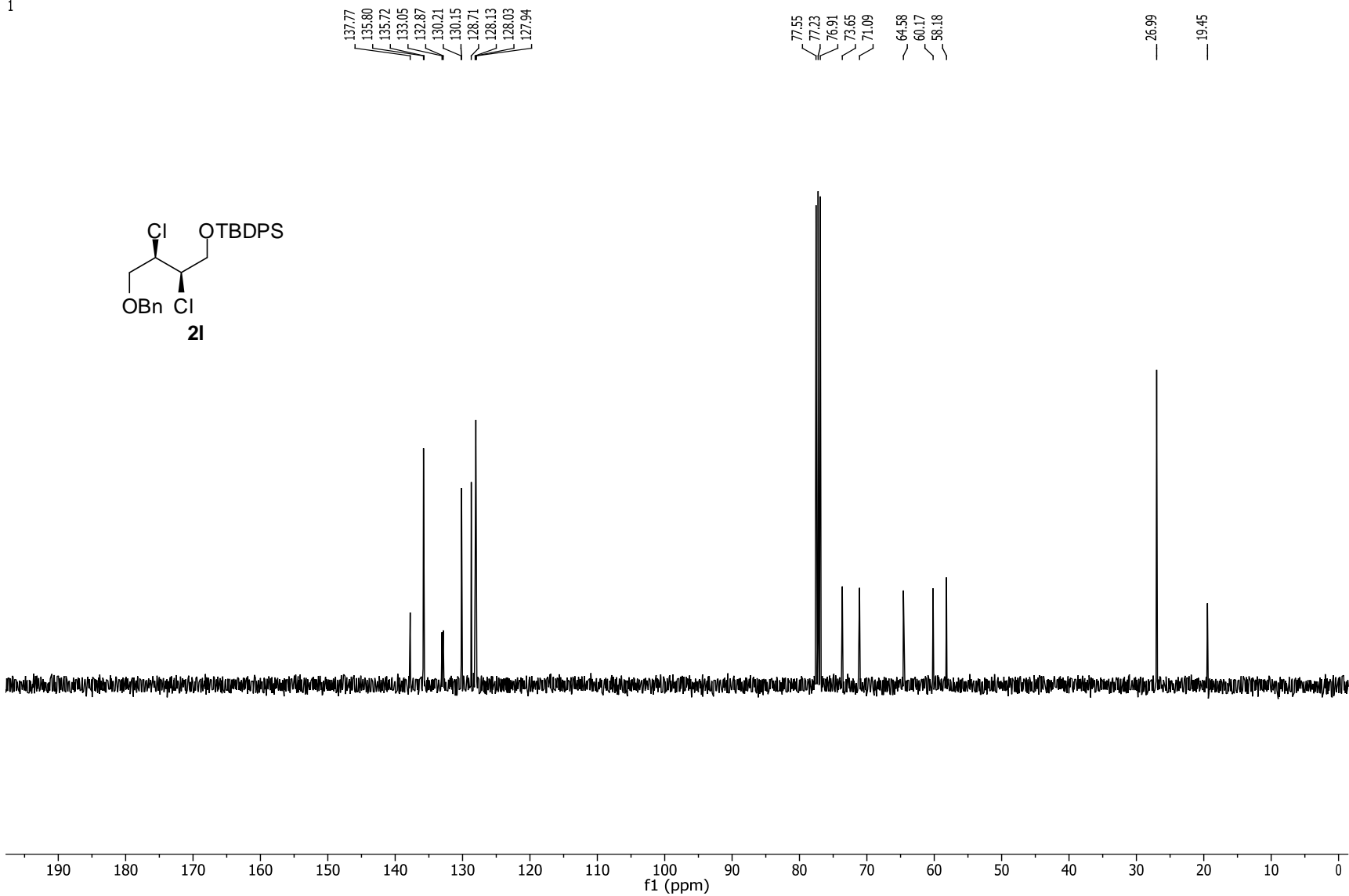




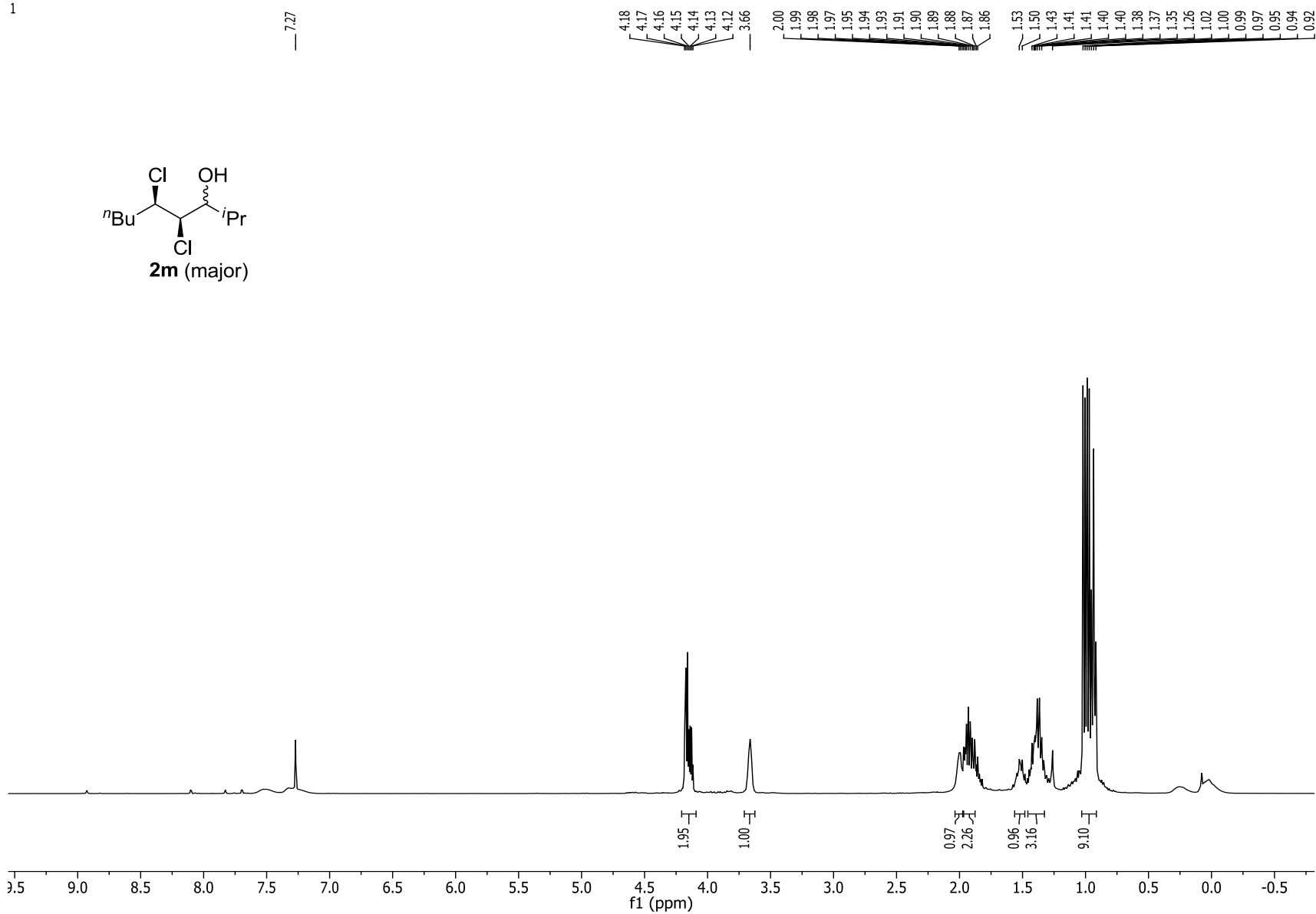




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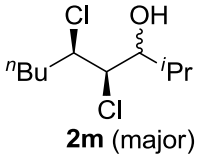


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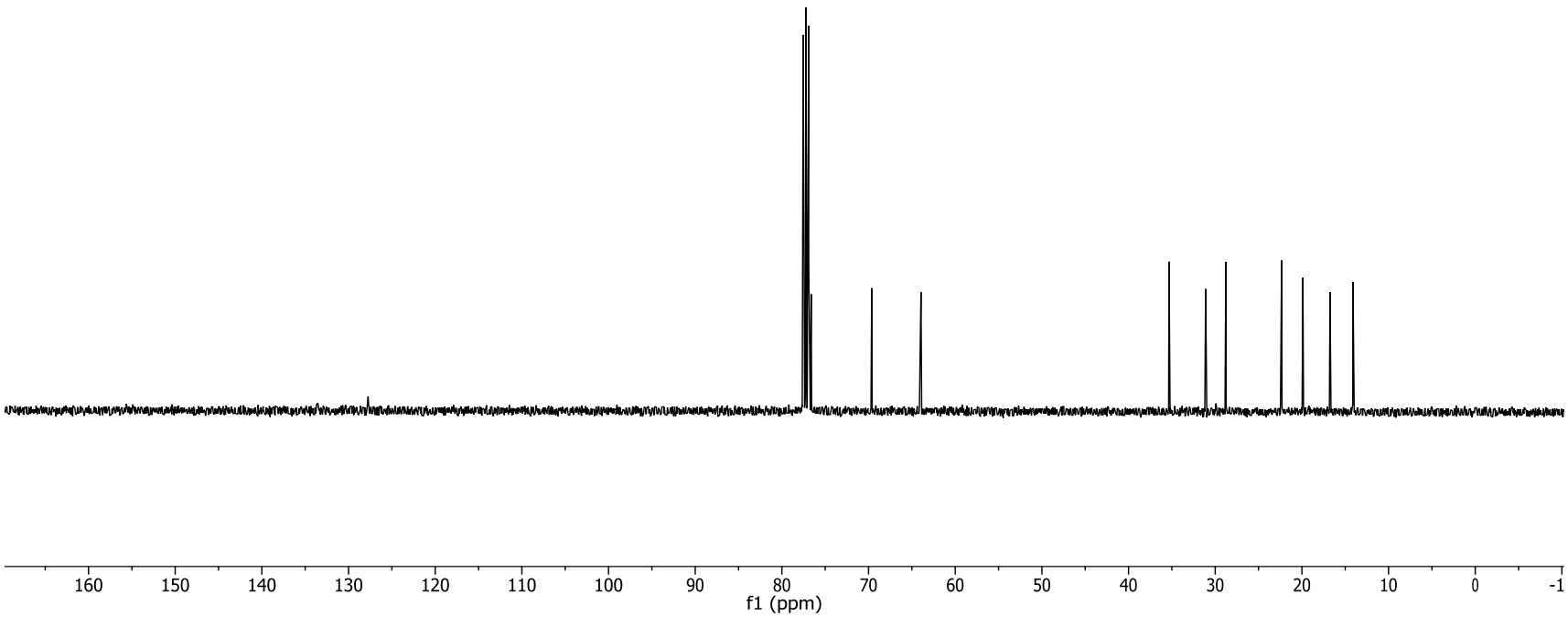


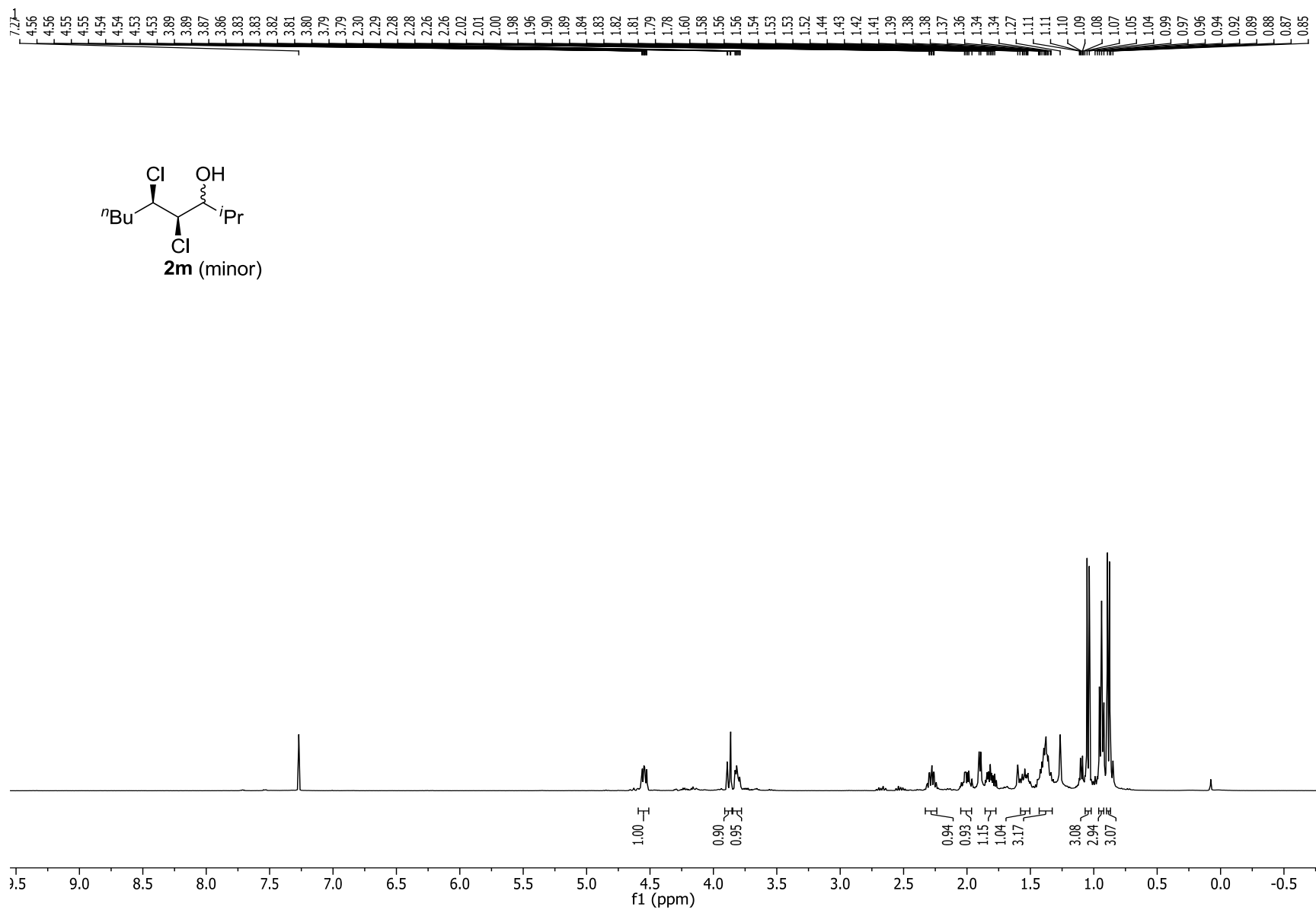
S42

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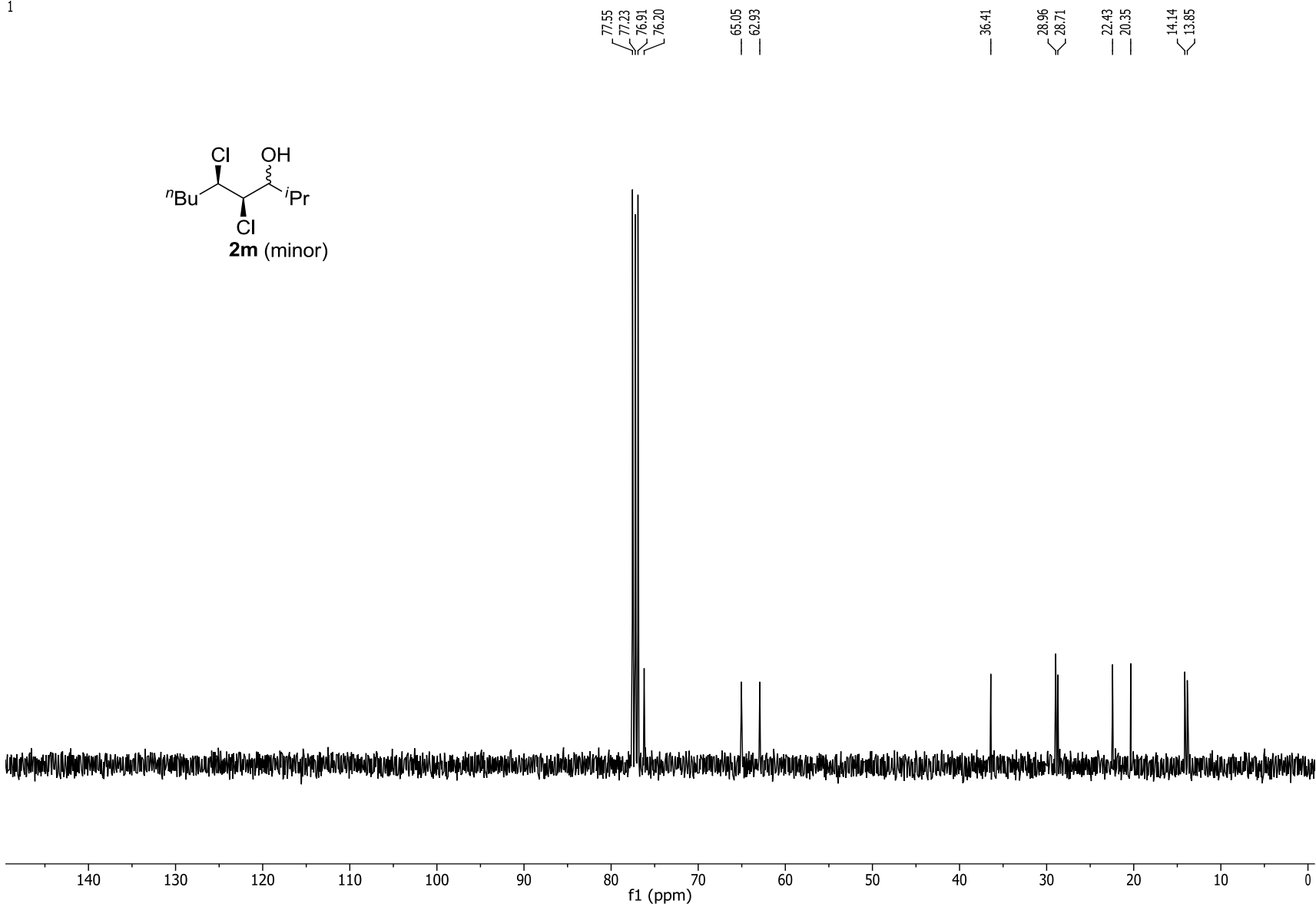
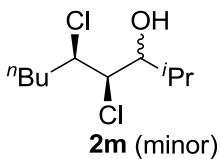


77.55
77.23
76.91
76.62
69.63
63.95
35.33
31.11
28.77
22.34
19.89
16.75
14.10

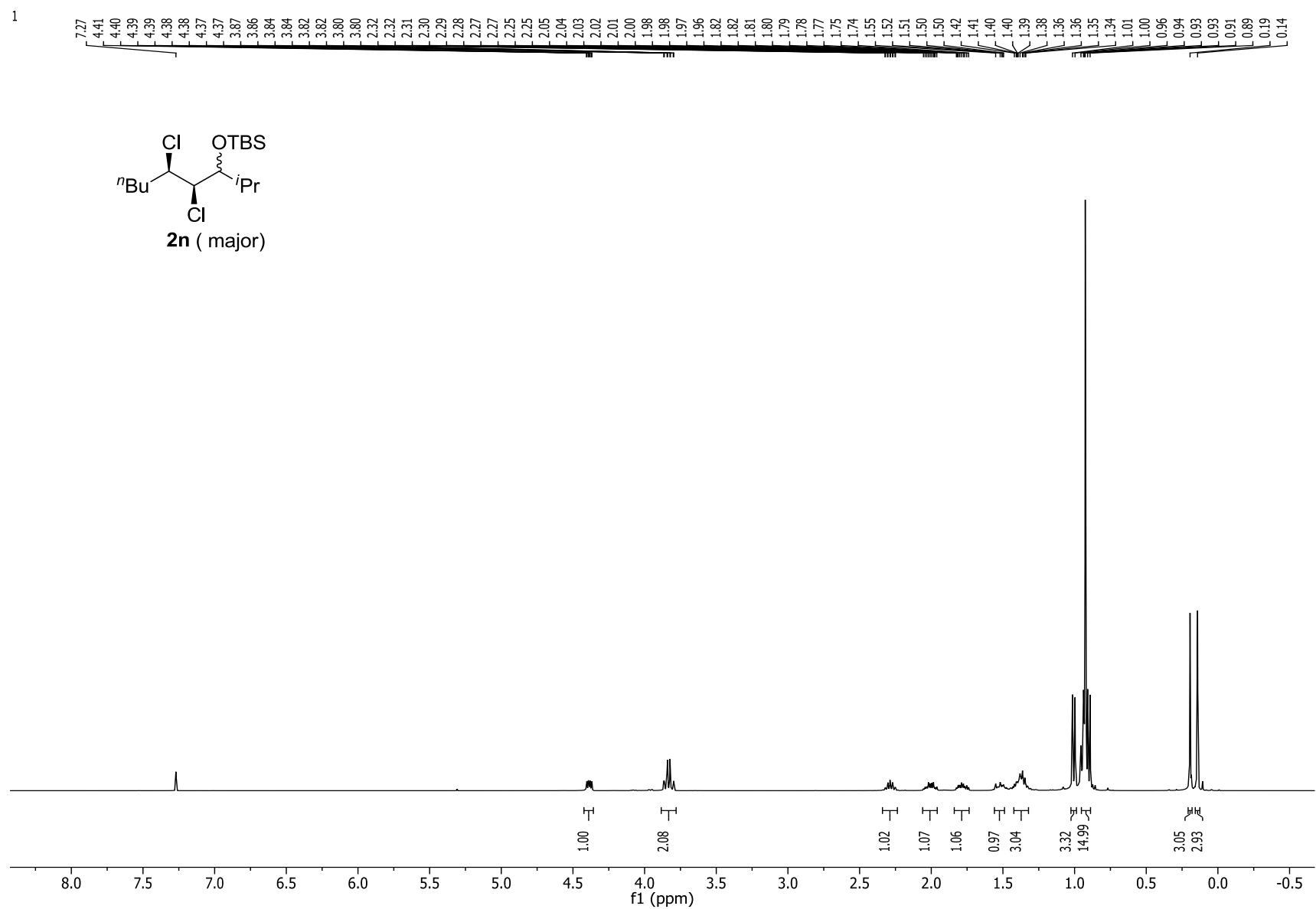




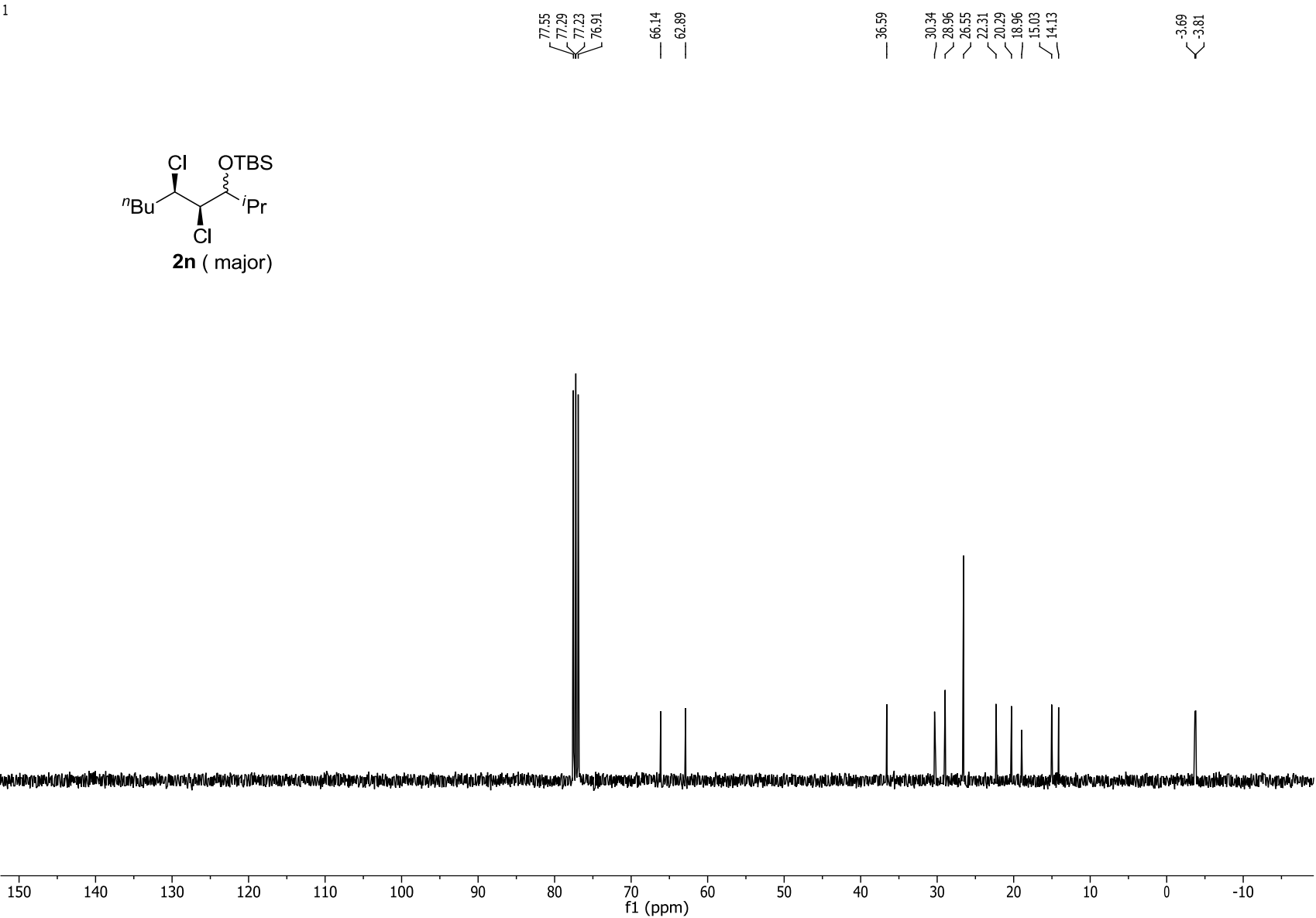
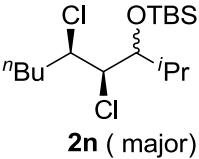
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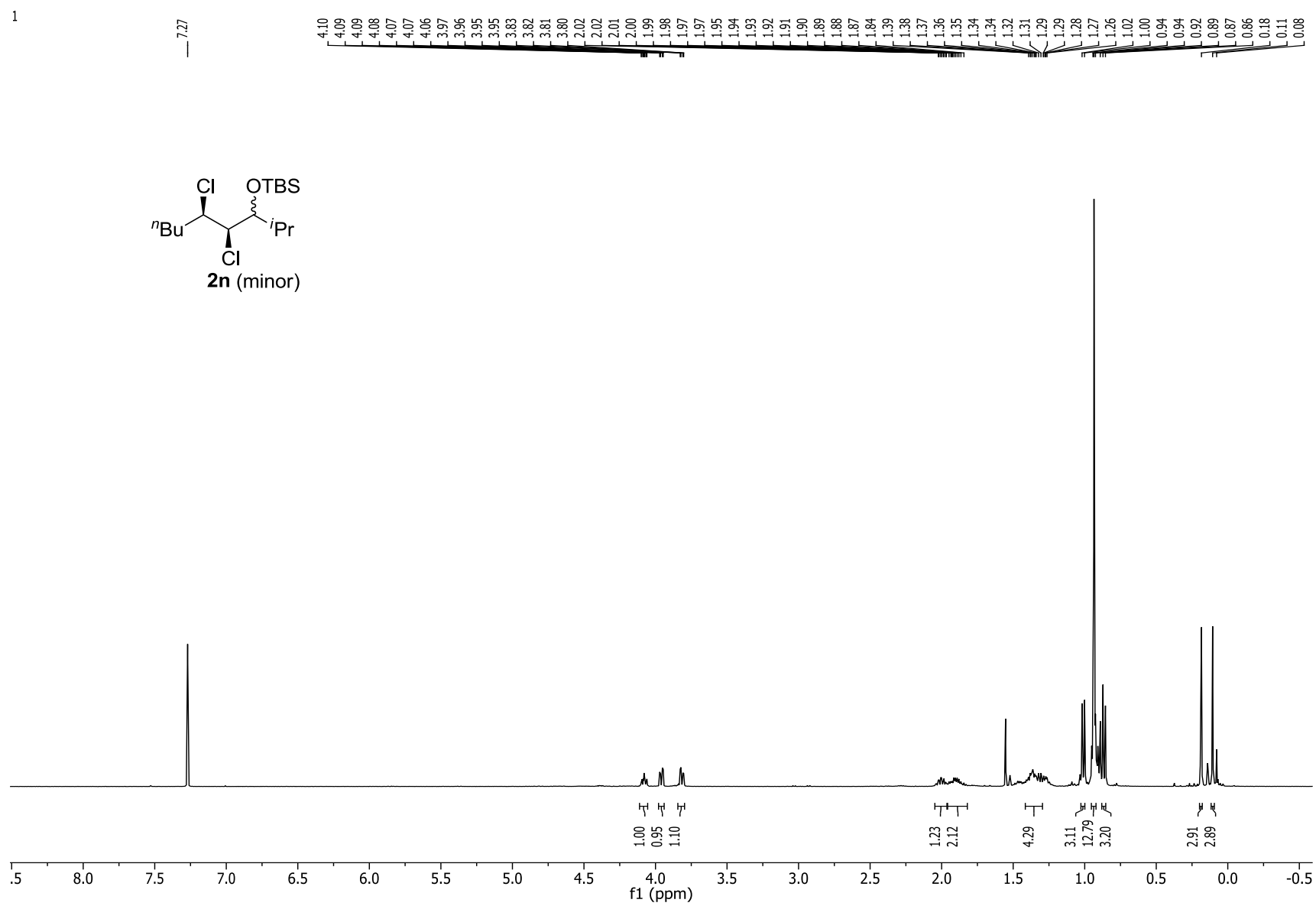


S45

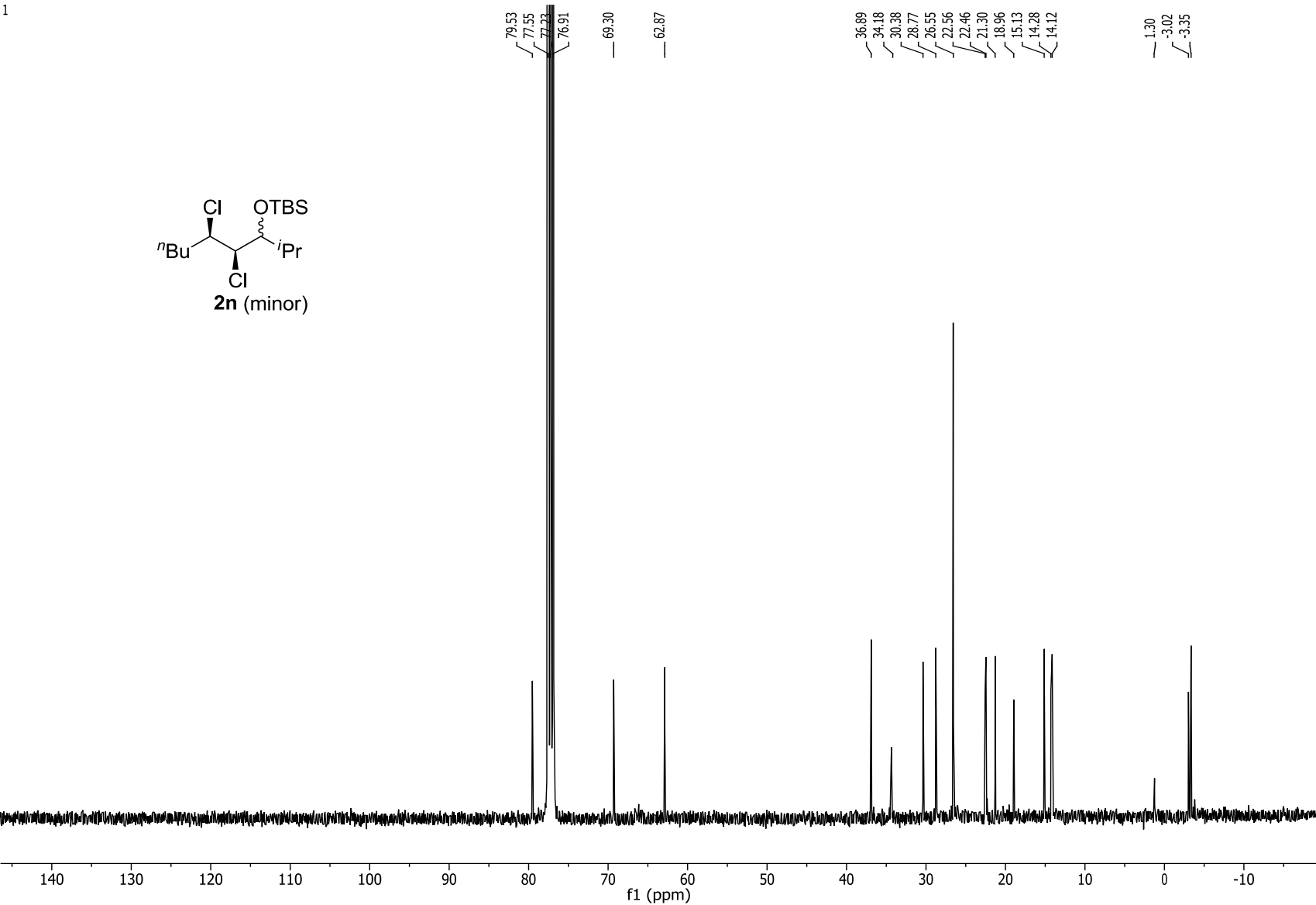


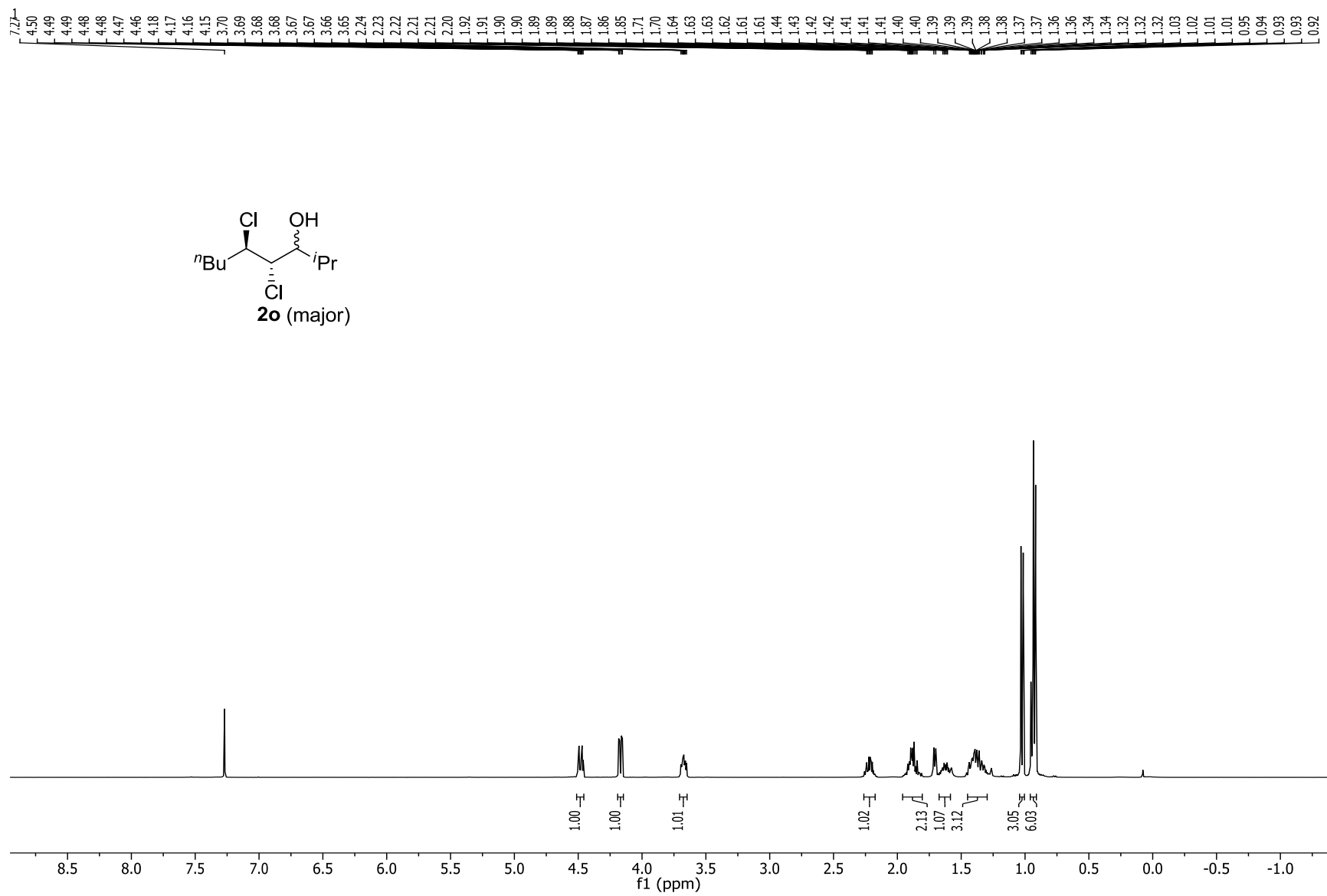
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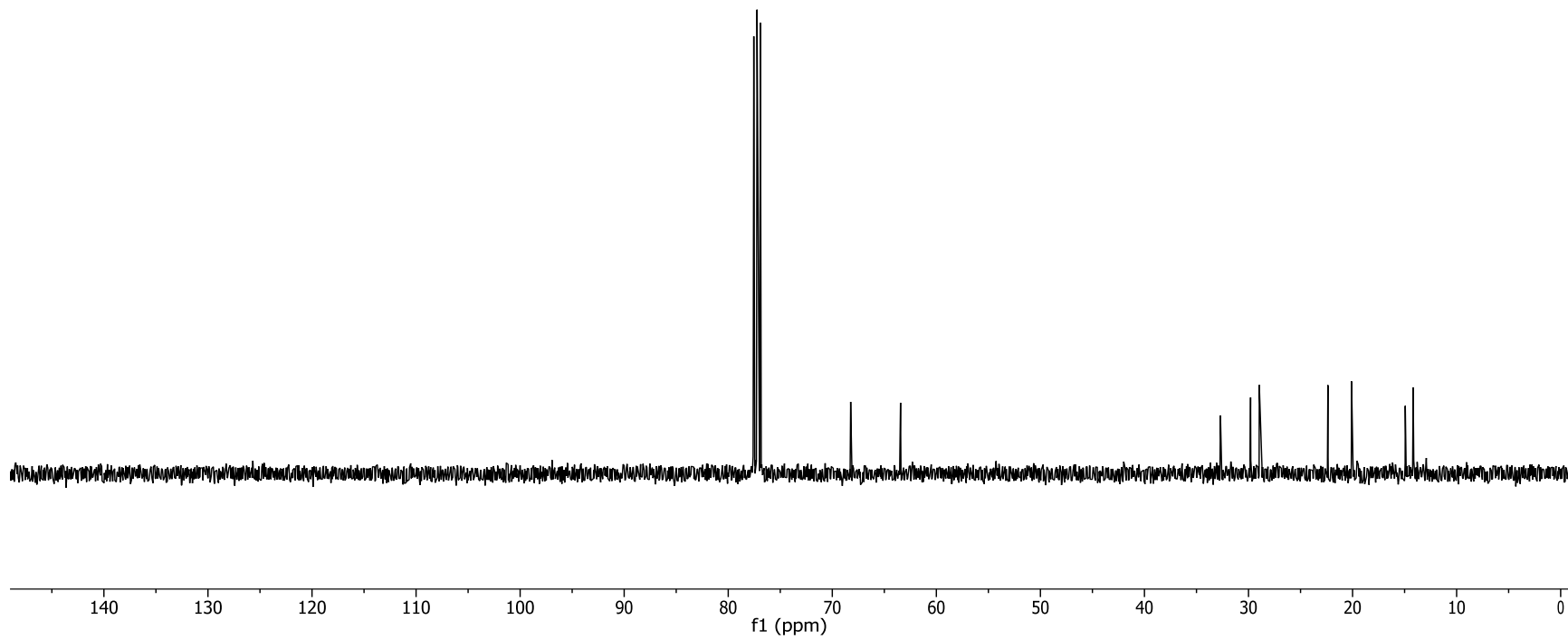
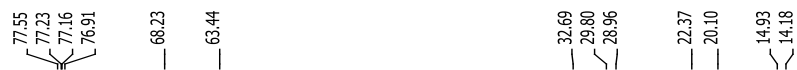
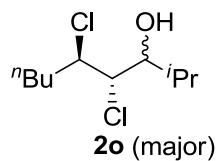


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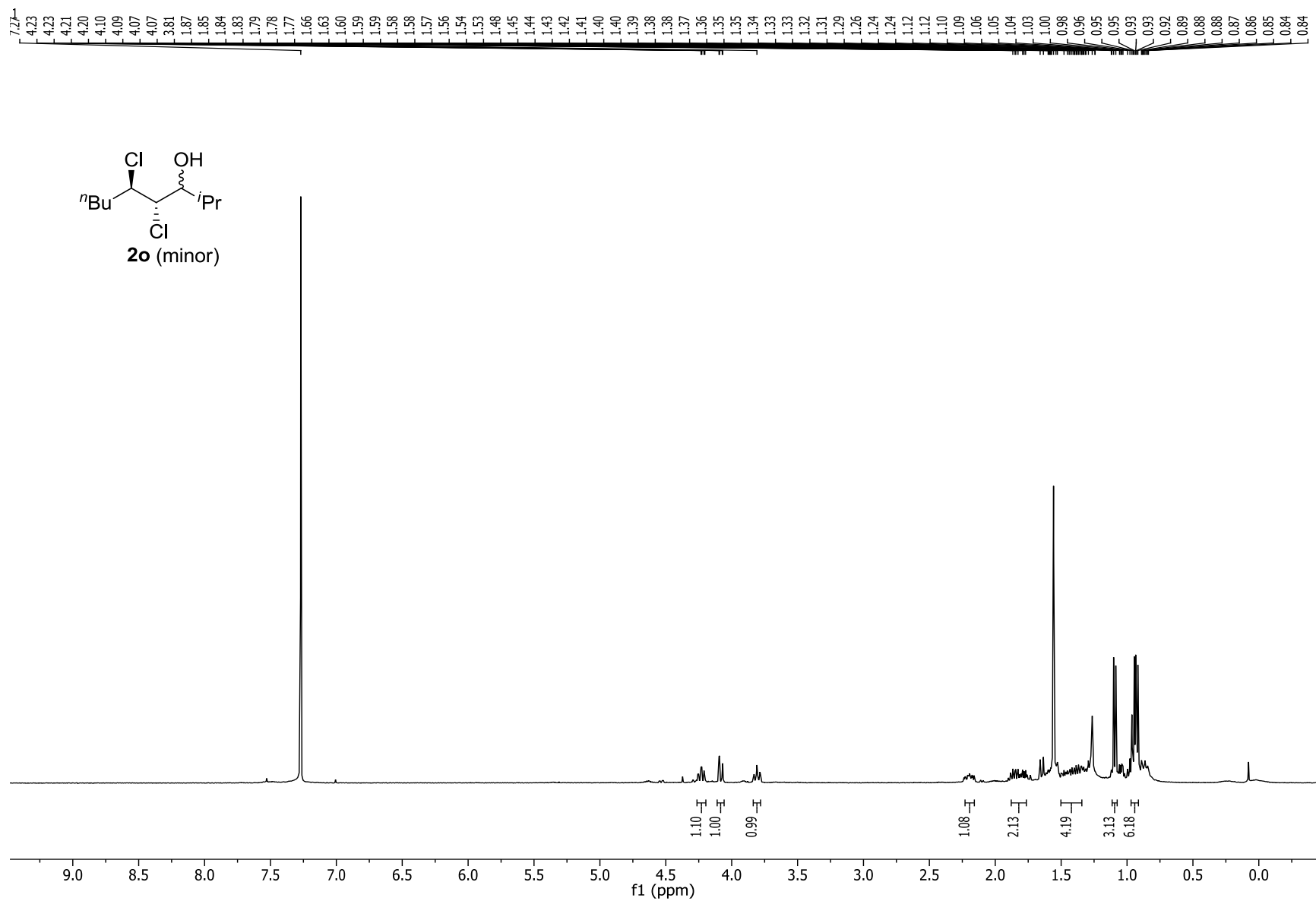




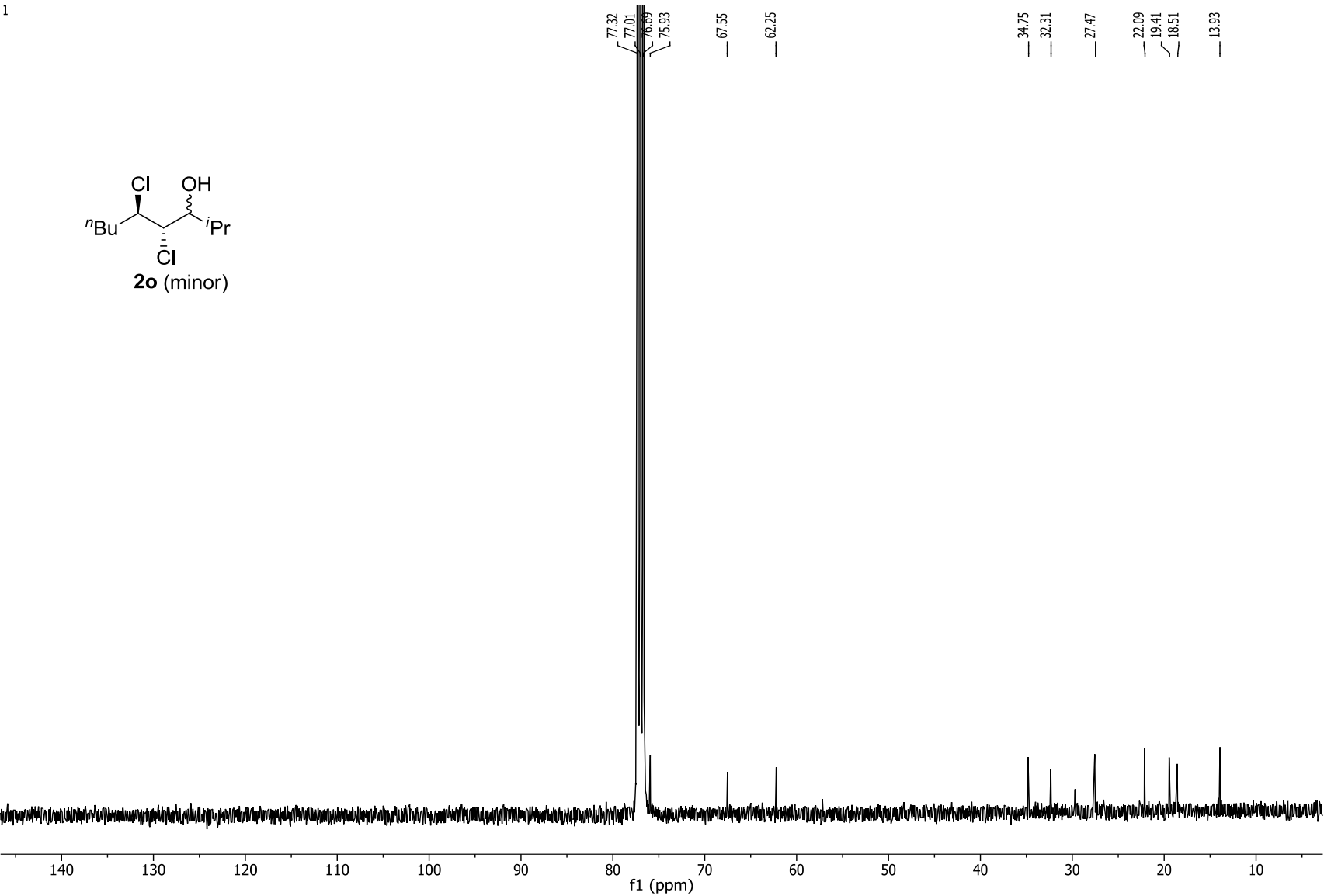
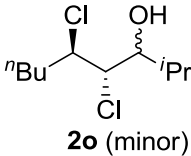
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S51

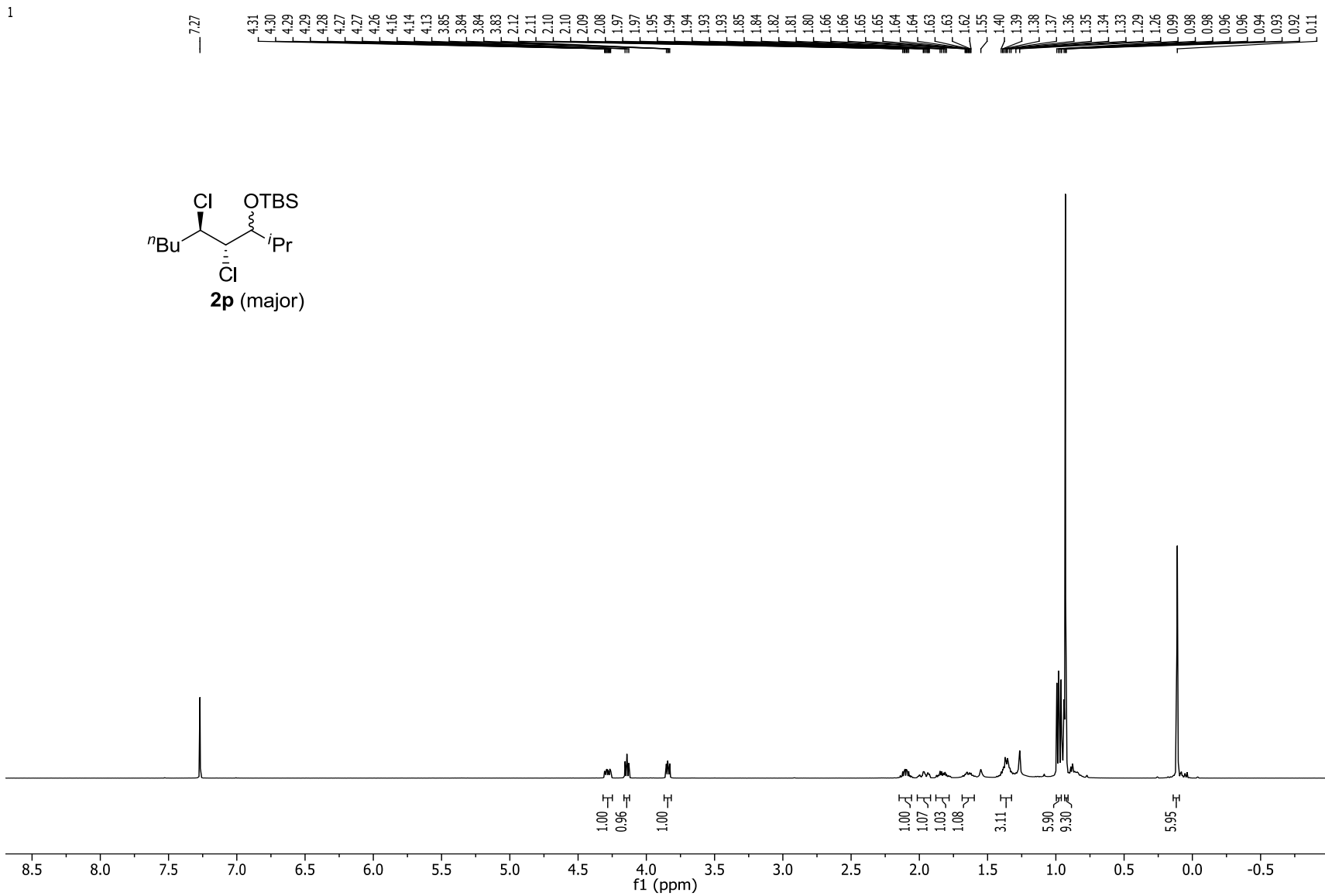


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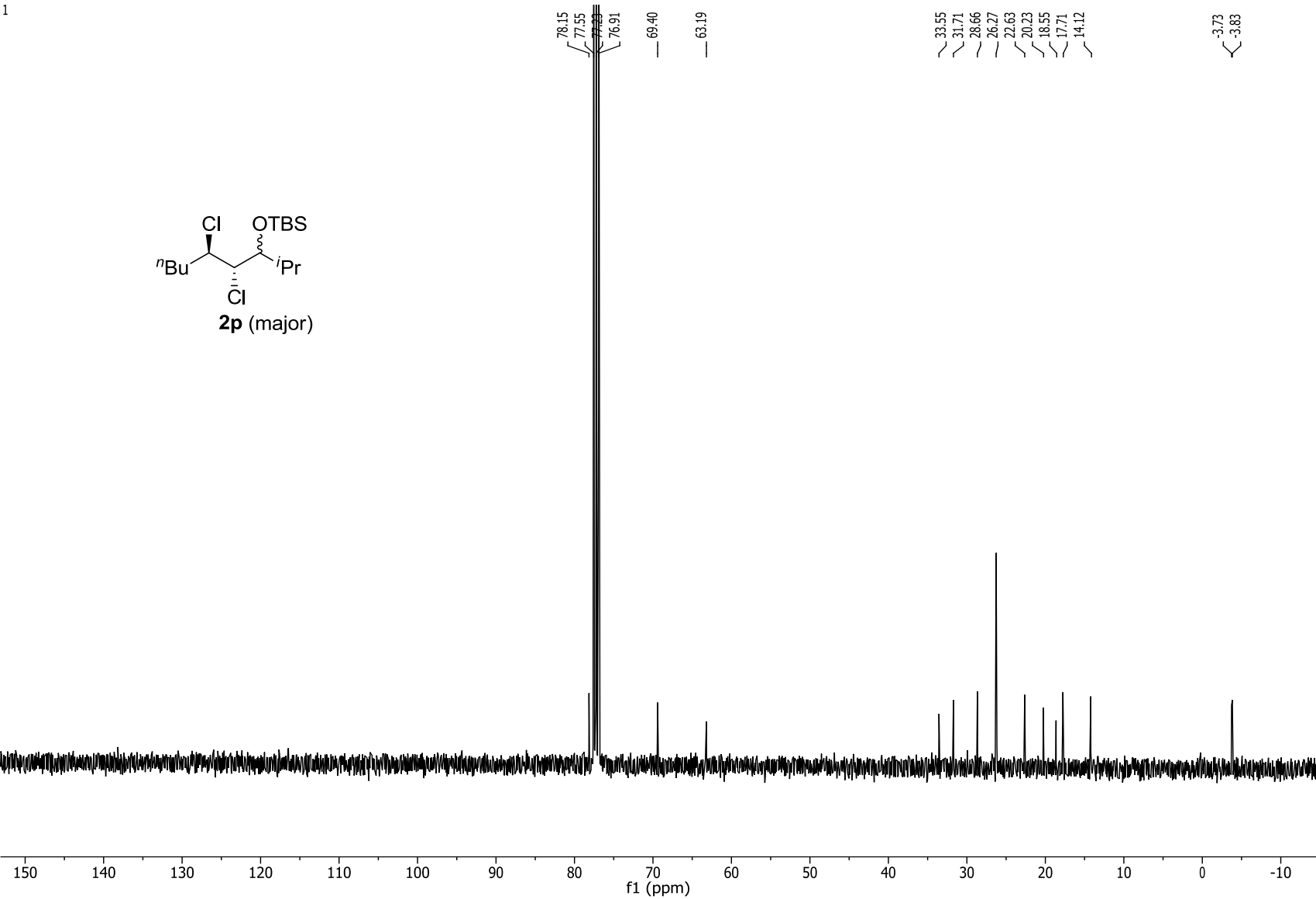


S53

1



1



S55

