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Electronic Supplementary Information

Gas-free alkoxycarbonylation of aryl iodides in a phosphonium-based deep eutectic solvent with $Mo(CO)_6$ as a solid CO source

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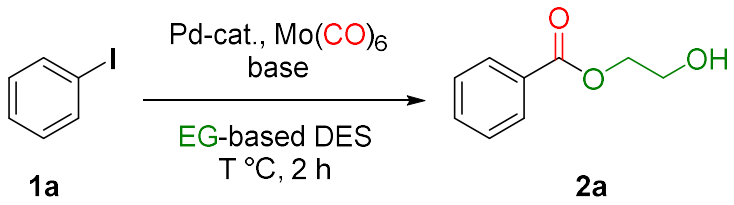
1 General Methods

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer and chemical shifts are reported in parts per million (δ). Dimethyl sulfone has been used as the internal standard for yield determination by ^{1}H NMR analysis of the crude reaction mixtures. The following abbreviations have been used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quin = quintuplet, sext = sextet, sep = septet, br = broad. FT-IR spectra were recorded on a Perkin-Elmer 681 spectrometer. Analytical thin-layer chromatography (TLC) was carried out on pre-coated 0.25 mm thick plates of Kieselgel 60 F254; visualisation was accomplished by UV light (254 nm) or by spraying a solution of 5% (w/v) ammonium molybdate and 0.2% (w/v) cerium(III) sulfate in 100 mL 17.6% (w/v) aq. sulphuric acid and heating to 473 K until blue spots appeared. Chromatography was conducted by using silica gel 60 with a particle size distribution 40–63 µm and 230–400 ASTM. GC-MS analyses were performed on HP 5995C model. High-resolution mass spectrometry (HRMS) analyses were performed using a Bruker microTOF QII mass spectrometer equipped with an electrospray ion source (ESI). Melting points were determined with an Electrothermal melting point apparatus. Reagents and solvents, unless otherwise specified, were purchased from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO, USA) and TCI (Tokyo Chemical Industry, Europe, N. V.) and used without any further purification. Petroleum ether refers to the 40–60 °C boiling fraction. Deep Eutectic Solvents (DES) [$MePh_3PBr$ (MTPBr)/ethylene glycol (EG) (1:5 mol/mol); MTPBr/glycerol (gly) (1:4 mol/mol); cholinium chloride (ChCl)/EG (1:2 mol/mol); tetrabutylammonium bromide (TBAB)/EG (1:4 mol/mol)] were prepared by heating under stirring at 60–80 °C for 10–30 min the corresponding individual components until a clear eutectic mixture was obtained. Full characterization data, including copies of ^{1}H NMR and ^{13}C NMR spectra, have been reported for all the synthesized compounds.

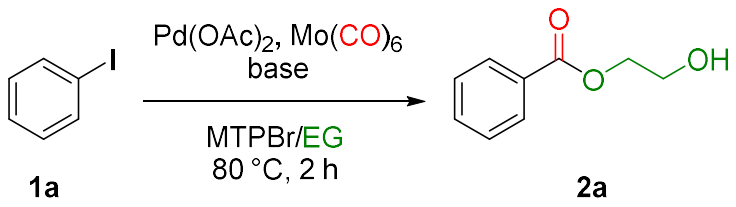
2 Table S1: Supplementary Information about the Screening of the Reaction Conditions for the Alkoxycarbonylation of Iodobenzene 1a with $Mo(CO)_6$ in EG-based Deep Eutectic Solvents[a]



Entry	DES (mL)	T (°C)	Pd-cat. (mol%)	Base (mmol)	1a Conv.[b]	2a Yield[b]
1	MTPBr/EG (2.0 mL)	150	$Pd(OAc)_2$ (5.0)	PPR (3.0)	100%	>98%
2	MTPBr/EG (2.0 mL)	150	$PdCl_2$ (5.0)	PPR (3.0)	100%	78%
3	MTPBr/EG (2.0 mL)	120	$Pd(OAc)_2$ (5.0)	PPR (3.0)	100%	70%
4	MTPBr/EG (2.0 mL)	80	$Pd(OAc)_2$ (5.0)	PPR (3.0)	100%	71%
5	MTPBr/EG (2.0 mL)	80	$Pd(OAc)_2$ (5.0)	PPR (1.5)	100%	70%
6	MTPBr/EG (2.0 mL)	150	$Pd(OAc)_2$ (5.0)	-	100%	41%
7[c]	MTPBr/EG (1.0 mL)	80	$Pd(OAc)_2$ (5.0)	PPR (1.5)	100%	>98%
8[c]	MTPBr/EG (1.0 mL)	80	$Pd(OAc)_2$ (1.0)	PPR (1.5)	100%	>98%
9[d]	MTPBr/EG (1.0 mL)	80	$Pd(OAc)_2$ (0.5)	PPR (1.5)	100%	88%
10[d]	MTPBr/EG (1.0 mL)	80	$Pd(OAc)_2$ (0.5)	K_3PO_4 (1.5)	100%	35%
11[d]	MTPBr/EG (1.0 mL)	80	$Pd(OAc)_2$ (0.5)	K_2CO_3 (1.5)	100%	25%
12[d]	**MTPBr/EG (1.0 mL)**	**80**	**$Pd(OAc)_2$ (0.5)**	**NaOAc (1.5)**	**100%**	**92%**
13[d]	ChCl/EG (1.0 mL)	80	$Pd(OAc)_2$ (0.5)	NaOAc (1.5)	100%	41%
14[d]	TBAB/EG (1.0 mL)	80	$Pd(OAc)_2$ (0.5)	NaOAc (1.5)	100%	51%
15[d]	EG (1.0 mL)	80	$Pd(OAc)_2$ (0.5)	NaOAc (1.5)	100%	60%

PPR = piperidine. [a] Reaction conditions: iodobenzene **1a** (0.5 mmol), $Mo(CO)_6$ (1.0 mmol), $Pd(OAc)_2$ (0.5-5 mol%), base (1.5-3 mmol), DES (1.0-2.0 mL) at 80-150 °C for 2 h.. [b] Calculated via ^1H NMR analysis of the crude reaction mixture using the internal standard technique (NMR internal standard: dimethyl sulfone). [c] Reaction performed with 0.5 mmol of $Mo(CO)_6$. [d] Reaction performed with 0.25 mmol of $Mo(CO)_6$.

3 Table S2: Screening of Different Bases for the Alkoxycarbonylation of Iodobenzene 1a with $Mo(CO)_6$ in MTPBr/EG DES[a]

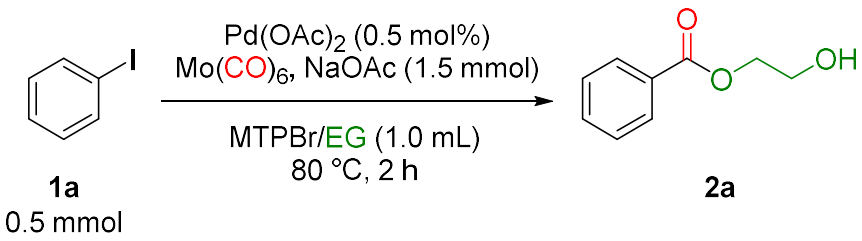


1a **2a**

Entry	Base (mmol)	1a Conv.[b]	2a Yield[b]
1	TMED (0.75)	64%	26%
2	DBU (1.5)	100%	50%
3	Et_2NH (1.5).	50%	<5%
4	L-Arg (1.5)	100%	9%

TMED = *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine; DBU = 1,8-Diazabicyclo(5.4.0)undec-7-ene. [a]Reaction conditions: iodobenzene **1a** (0.5 mmol), $Pd(OAc)_2$ (0.5 mol%), base, $Mo(CO)_6$ (0.25 mmol), MTPBr/EG (1.0 mL), 80 °C, 2 h. [b]Calculated via ^1H NMR analysis of the crude reaction mixture using the internal standard technique (NMR internal standard: dimethyl sulfone).

4 Graph S1: Investigation on CO Equivalents Released by $Mo(CO)_6$

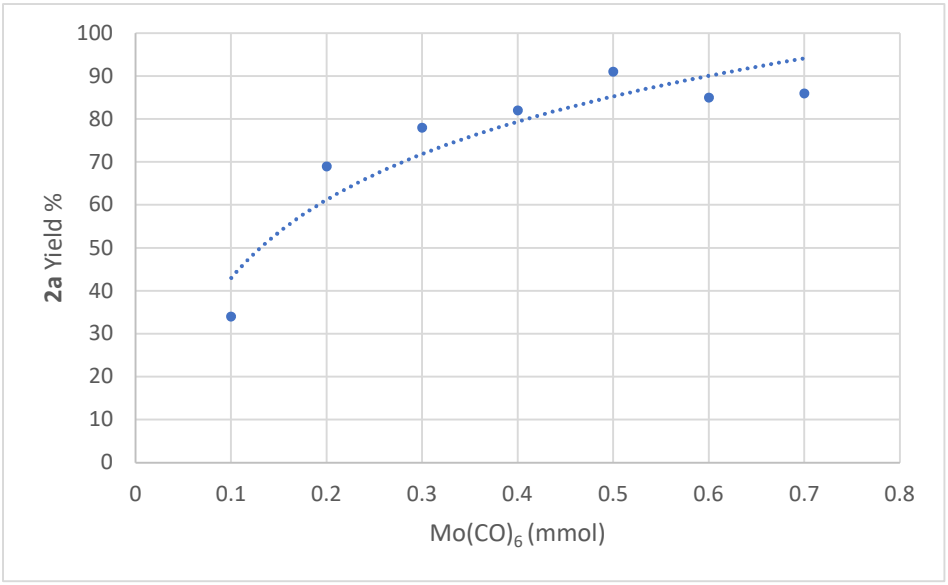


1a
0.5 mmol

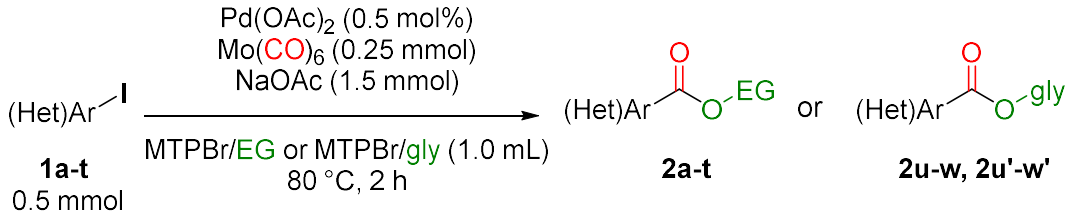
2a

Entry	1a (mmol)	$Mo(CO)_6$ (mmol)	2a Yield[b]
1	1	0.1	34%
2	1	0.2	69%
3	1	0.3	78%
4	1	0.4	82%
5	**1**	**0.5**	**91%**
6	1	0.6	85%
7	1	0.7	86%

[a]Reaction conditions: iodobenzene **1a** (1.0 mmol), $Pd(OAc)_2$ (0.5 mol%), $Mo(CO)_6$ (0.1-0.7 mmol), MTPBr/EG (2.0 mL), 80 °C, 2 h. [b]Calculated via ^1H NMR analysis of the crude reaction mixture using the internal standard technique (NMR internal standard: dimethyl sulfone).



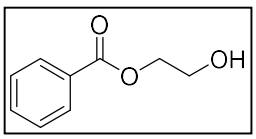
5 Experimental Procedure for the Alkoxycarbonylation Reaction of (Hetero)Aryl Iodide 1a-t in MTPBr/EG or MTPBr/gly Eutectic Mixture



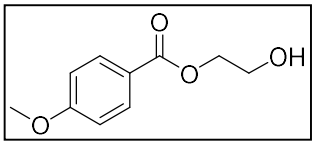
In a 10 mL round bottom flask, (hetero)aryl iodide (**1a-r**, 0.5 mmol), $Mo(CO)_6$ (66.0 mg, 0.25 mmol), $NaOAc{\cdot}3H_2O$ (204.0 mg, 1.5 mmol), $Pd(OAc)_2$ (trimeric, FW = 673.46, 0.5 mol%, 0.0025 mmol, 1.6 mg) and MTPBr/EG or MTPBr/gly DES (1.0 mL) were sequentially added. The reaction was stirred for 2 hours at 80 °C. After this time, the reaction mixture was cooled to room temperature and water (2.5 ml) and HCl solution (10% v/v) up to pH = 2 were sequentially added. The mixture was then extracted with AcOEt (5 ml x 3) and the reunited organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered through a celite pad and evaporated under reduced pressure. The crude was purified by flash column chromatography on silica gel (using as eluent petroleum ether/AcOEt 80/20 to pure AcOEt), obtaining the desired 2-hydroxyethyl esters as pure compounds **2a-r** or the desired glycerol esters as mixture of isomers (**2u-w**, **2u'-w'**).

When the diiodo arenes **1s-t** were used as the substrates, the following procedure was employed: in a 10 mL round bottom flask, diiodo arene (**1s-t**, 0.5 mmol), $Mo(CO)_6$ (132.0 mg, 0.5 mmol), $NaOAc{\cdot}3H_2O$ (408.0 mg, 3.0 mmol), $Pd(OAc)_2$ (trimeric, FW = 673.46, 1.0 mol%, 0.005 mmol, 3.12 mg) and MTPBr/EG DES (2.0 mL). The reaction was stirred for 2 hours at 80 °C. The work-up procedure and purification process are similar to those ones described above for the substrates **1a-r**.

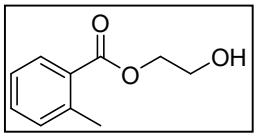
6 Characterization Data for Compounds 2a-t, 2u-w and 2u'-w'



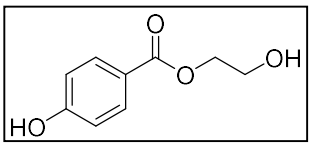
2-hydroxyethyl benzoate 2a[1]: pale yellow oil, 92%. ^{1}H NMR (400.12 MHz, $CDCl_3$): δ 8.07–8.04 (m, 2H), 7.58–7.54 (m, 1H), 7.45–7.41 (m, 2H), 4.46–4.44 (m, 2H), 3.96 – 3.93 (m, 2H), 2.42 (br s, 1H); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 167.0, 133.2, 129.7, 128.4, 126.8, 66.6, 61.3; FT-IR (Film, cm^{-1}): 3430, 2951, 1719, 1602, 1455, 1120. GC/MS (70 eV) *m/z* (%): 166 (M^+, 5), 123 (90), 105 (100), 77 (85), 51 (40). HRMS (ESI) *m/z* calc. for $[C_9H_{10}O_3 + Na]^+$: 189.0522; found: 189.0525.



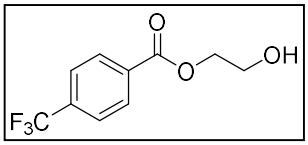
2-hydroxyethyl 4-methoxybenzoate 2b[1]: pale yellow oil, 88%. ^{1}H NMR (400.12 MHz, $CDCl_3$): δ 8.01–7.98 (m, 2H), 6.92–6.88 (m, 2H), 4.43–4.40 (m, 2H), 3.94–3.91 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 166.7, 163.5, 131.7, 122.1, 113.6, 66.3, 61.3, 55.4; FT-IR (Film, cm-1): 3440, 2936, 1719, 1599, 1455, 1110. GC/MS (70 eV) m/z (%): 196 (M^+, 20), 152 (80), 135 (100), 92 (30), 77 (45), 51 (10). HRMS (ESI) m/z calc. for $[C_{10}H_{12}O_4 + Na]^+$: 219.0628; found: 219.0631.



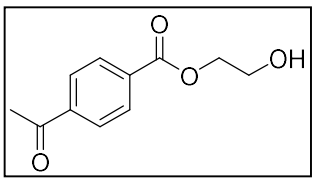
2-hydroxyethyl 2-methylbenzoate 2c[2]: orange oil, 88%. ^{1}H NMR (400.12 MHz, CDCl3): *δ* 7.92–7.90 (m, 1H), 7.38–7.34 (m, 1H), 7.21–7.17 (m, 2H), 4.39–4.36 (m, 2H), 3.90–3.88 (m, 2H), 3.03 (br s, 1H), 2.57 (s, 3H); ^{13}C NMR (100.62 MHz, $CDCl_3$): *δ* 167.9, 140.2, 132.1, 131.6, 130.6, 129.2, 125.6, 66.2, 61.0, 21.7; FT-IR (Film, cm^{-1}): 3319, 3008, 1718, 1602, 1568, 1379, 1261, 1120, 735. GC/MS (70 eV) *m/z* (%): 180 (M^+, 26), 137 (19) 119 (100), 118 (98), 91 (77), 65 (41). HRMS (ESI) *m/z* calc. for $[C_{10}H_{12}O_3 + Na]^+$: 203.0679; found: 203.0677.



2-hydroxyethyl 4-hydroxybenzoate 2d[3]: white cristal, m.p. 133-135 °C, 99%. ^{1}H NMR (400.12 MHz, Acetone-d_6): *δ* 9.15 (br s, 1H), 7.93–7.91 (m, 2H), 6.92–6.90 (m, 2H), 4.32–4.29 (m, 2H), 3.85–3.82 (m, 2H), 2.88 (br s, 1H); ^{13}C NMR (100.62 MHz, Acetone-d_6): *δ* 165.7, 161.6, 131.6, 121.7, 115.0, 66.0, 60.0; FT-IR (KBr, cm^{-1}): 3402, 2915, 1709, 1217, 809. GC/MS (70 eV) *m/z* (%): 182 (M^+, 12), 133 (27), 132 (30), 121 (100), 93 (31), 65 (29). HRMS (ESI) *m/z* calc. for $[C_9H_{10}O_4 + Na]^+$: 205.0471; found: 205.0475.

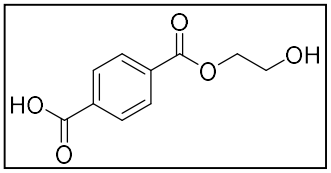


2-hydroxyethyl 4-(trifluoromethyl)benzoate 2e[6]: yellow oil, 99%. ^{1}H NMR (400.12 MHz, $CDCl_3$): *δ* 8.18–8.15 (m, 2H), 7.71–7.69 (m, 2H), 4.51–4.48 (m, 2H), 3.99–3.97 (m, 2H), 2.55 (br s, 1H); ^{13}C NMR (100.62 MHz, $CDCl_3$): *δ* 165.6, 134.6 (q, *J* = 32.7 Hz), 133.0 (q, *J* = 1.2 Hz), 130.0, 125.4 (q, *J* = 3.8 Hz) 123.5 (q, *J* = 272.7), 67.0, 61.1; FT-IR (Film, cm^{-1}): 3440, 1726, 1465, 1692, 1463, 1285, 775; GC/MS (70 eV) *m/z* (%): 234 (M^+, 2), 215 (4), 191 (38), 173 (100), 145 (57), 95 (9), 77 (7), 51 (5). HRMS (ESI) *m/z* calc. for $[C_{10}H_9F_3O_3 + Na]^+$: 257.0396; found: 257.0399.

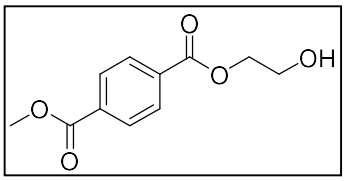


2-hydroxyethyl 4-acetylbenzoate 2f: pale yellow oil, 75%. ^{1}H NMR (400.12 MHz, $CDCl_3$): δ 8.08–8.06 (m, 2H), 7.92–7.90 (m, 2H), 4.43–4.41 (m, 2H), 3.93–3.90 (m, 2H), 3.11 (br s, 1H), 2.58 (s, 3H); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 197.7, 165.9, 140.1, 133.6, 129.8, 128.1, 66.9, 60.8, 26.8;

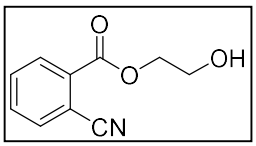
FT-IR (Film, cm-1): 3436, 2894, 1732, 1698, 1599, 1455, 1137. GC/MS (70 eV) m/z (%): 208 (M^+, 2), 193 (55), 165 (90), 147 (100), 119 (20), 104 (20), 91 (20), 76 (15), 51 (40). HRMS (ESI) m/z calc. for $[C_{11}H_{12}O_4 + Na]^+$: 231.0628; found: 231.0631.



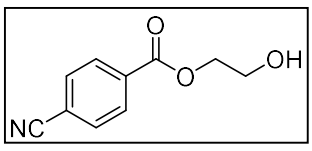
4-((2-hydroxyethoxy)carbonyl)benzoic acid 2g: white solid, m.p. 180-182 °C, 76%. ^{1}H NMR (400 MHz, Acetone-d_6): δ 8.18–8.13 (m, 4H), 4.43–4.41 (m, 2H), 3.91–3.89 (m, 2H); ^{13}C NMR (100 MHz, Acetone-d_6): δ 166.9, 166.2, 135.3, 135.1, 130.5, 130.4, 67.9, 60.8; FT-IR (KBr, cm^{-1}): 3431, 3050–2501 (multiple peak), 1715, 1686, 1275, 1120, 819. HRMS (ESI) *m/z* calc. for $[C_{10}H_{10}O_5 + Na]^+$: 233.0420; found: 233.0423.



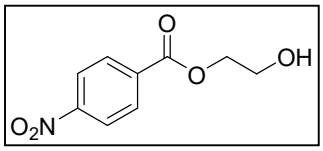
2-hydroxyethyl methyl terephthalate 2h[4]: white solid, m.p. 80-82 °C, 94%. ^{1}H NMR (400.12 MHz, $CDCl_3$): δ 8.13–8.07 (m, 4H), 4.49–4.47 (m, 2H), 3.98–3.96 (m, 2H), 3.94 (s, 3H), 2.25 (br s, 1H); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 166.2, 166.0, 134.0, 133.6, 129.6, 129.5, 66.9, 61.1, 52.4; FT-IR (KBr, cm^{-1}): 3453, 2961, 2883, 1715, 1695, 1580, 1432, 1275, 1106, 791. GC/MS (70 eV) *m/z* (%): 224 (M^+, 4), 193 (27), 181 (88), 163 (100), 149 (28), 135 (36), 104 (21), 76 (20), 51 (8). HRMS (ESI) *m/z* calc. for $[C_{11}H_{12}O_5 + Na]^+$: 247.0577; found: 247.0579.



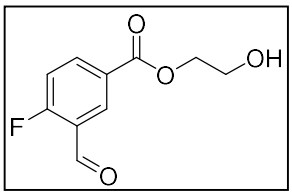
2-hydroxyethyl 2-cyanobenzoate 2i: pale yellow oil, 76%. ^{1}H NMR (400.12 MHz, $CDCl_3$): δ 8.18–8.16 (m, 1H), 7.77–7.75 (m, 1H), 7.70–7.63 (m, 2H), 4.48–4.46 (m, 2H), 3.97–3.95 (m, 2H), 2.90 (br s, 1H); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 163.9, 134.5, 132.9, 132.8, 132.4, 131.6, 118.6, 112.4, 68.0, 60.6; FT-IR (Film, cm^{-1}): 3430, 3010, 2966, 2226, 1724, 1256, 1069, 1012, 793, 759; GC/MS (70 eV) *m/z* (%): 191 (M^+, 5), 161 (33), 148 (19), 130 (100), 103 (72), 76 (24), 51 (10). HRMS (ESI) *m/z* calc. for $[C_{10}H_9NO_3 + Na]^+$: 214.0475; found: 214.0478.



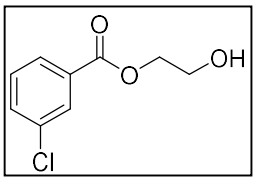
2-hydroxyethyl 4-cyanobenzoate 2j[5]: pale yellow oil, 84%. ^{1}H NMR (400.12 MHz, $CDCl_3$): δ 8.16–8.13 (m, 2H), 7.72–7.70 (m, 2H), 4.48–4.45 (m, 2H), 3.96–3.93 (m, 2H), 2.47 (br s, 1H); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 165.1, 133.8, 132.2, 130.2, 117.9, 116.3, 67.2, 60.7; FT-IR (Film, cm^{-1}): 3433, 3012, 2967, 2228, 1723, 1258, 1070, 1013, 812, 759; GC/MS (70 eV) *m/z* (%): 191 (M^+, 3), 160 (16), 148 (73), 130 (100), 102 (82), 75 (29), 51 (22). HRMS (ESI) *m/z* calc. for $[C_{10}H_9NO_3 + Na]^+$: 214.0475; found: 214.0479.



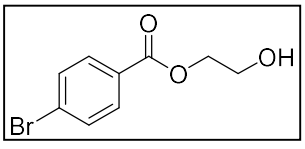
2-hydroxyethyl 4-nitrobenzoate 2k[6]: pale yellow wax, 53%. ^{1}H NMR (400.12 MHz, $CDCl_3$): δ 8.27–8.20 (m, 4H), 4.50–4.48 (m, 2H), 3.98–3.96 (m, 2H); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 164.9, 150.5, 135.2, 130.8, 123.5, 67.3, 60.8; FT-IR (KBr, cm^{-1}): 3334, 3115, 1724, 1530, 1461, 1361, 1285, 823. GC/MS (70 eV) *m/z* (%): 211 (M^+, 1), 181 (5), 168 (85), 164 (20), 150 (100), 104 (50), 76 (45), 50 (20). HRMS (ESI) *m/z* calc. for $[C_9H_9NO_5 + Na]^+$: 234.0373; found: 234.0378.



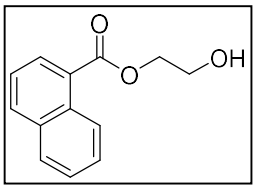
2-hydroxyethyl 4-fluoro-3-formylbenzoate 2l: pale red oil, 65%. ^{1}H NMR (400.12 MHz, $CDCl_3$): δ 10.28 (s, 1H), 8.50–8.48 (m, 1H), 8.28–8.25 (m, 1H), 7.23–7.19 (m, 1H), 4.44–4.42 (m, 2H), 3.94–3.92 (m, 2H), 2.99 (br s, 1H); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 186.4 (d, J = 6.0 Hz), 167.0 (d, J = 266.0 Hz), 164.9, 137.6 (d, J = 10.5 Hz), 130.9 (d, J = 3.0 Hz), 127.0 (d, J = 3.4 Hz), 123.9 (d, J = 9.0 Hz), 117.0 (d, J = 21.4 Hz), 67.1, 60.8; FT-IR (Film, cm^{-1}): 3454, 3066, 2957, 2876, 1709, 1672, 1609, 1265, 1218, 759; GC/MS (70 eV) *m/z* (%): 212 (M^+, 2), 169 (86), 151 (100), 123 (49) 95 (36), 75 (43); HRMS (ESI) *m/z* calc. for $[C_{10}H_9FO_4 + Na]^+$: 235.0377; found: 235.0380.



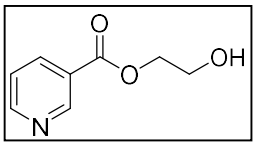
2-hydroxyethyl 3-chlorobenzoate 2m[7]: pale yellow oil, 75%. ^{1}H NMR (400.12 MHz, $CDCl_3$): δ 8.02–8.01 (m, 1H), 7.93–7.91 (m, 1H), 7.53–7.50 (m, 1H), 7.38–7.34 (m, 1H), 4.46–4.43 (m, 2H), 3.95–3.93 (m, 2H), 2.49 (br s, 1H); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 165.7, 134.5, 133.1, 131.5, 129.7, 129.6, 127.8, 66.9, 61.0; FT-IR (Film, cm^{-1}): 3418, 3004, 2897, 1722, 1192, 1183, 782. GC/MS (70 eV) *m/z* (%):202 (M^++2, 2), 200 (M^+, 5), 169 (8) 157 (63), 139 (100), 111 (62), 75 (47), 51 (20). HRMS (ESI) *m/z* calc. for $[C_9H_9ClO_3 + Na]^+$: 223.0132; found: 223.0134.



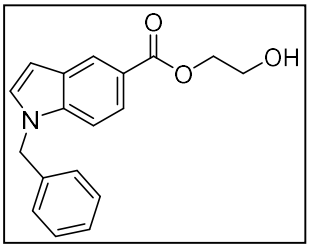
2-hydroxyethyl 4-bromobenzoate 2n[5]: yellow oil, 76%. ^{1}H NMR (400.12 MHz, $CDCl_3$): δ 7.88–7.86 (m, 2H), 7.54–7.51 (m, 2H), 4.42–4.39 (m, 2H), 3.92–3.90 (m, 2H), 2.84 (br s, 1H); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 166.1, 131.6, 131.1, 128.7, 128.2, 66.7, 60.8; FT-IR (Film, cm^{-1}): 3441, 3099, 1723, 1609, 1451, 1275, 757. GC/MS (70 eV) *m/z* (%): 246 (M^++2, 2), 244 (M^+, 2), 201 (58), 183 (100), 157 (43), 104 (12), 76 (32), 51 (8). HRMS (ESI) *m/z* calc. for $[C_9H_9BrO_3 + Na]^+$: 266.9627; found: 266.9630.



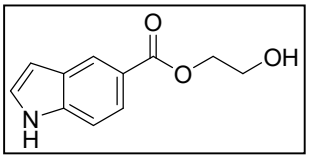
2-hydroxyethyl 1-naphtoate 2o[1]: yellow oil, 81%. ^{1}H NMR (400.12 MHz, $CDCl_3$): δ 8.91–8.89 (m, 1H), 8.21–8.19 (m, 1H), 8.01–7.99 (m, 1H), 7.88–7.85 (m, 1H), 7.63–7.44 (m, 3H), 4.52–4.50 (m, 2H), 3.98–3.96 (m, 2H), 2.65 (s, 1H); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 167.8, 133.8, 133.5, 131.2, 130.3, 128.5, 127.8, 126.7, 126.2, 125.6, 124.4, 66.6, 61.2; FT-IR (Film, cm^{-1}): 3499, 2978, 1710, 1601, 1518, 1118, 693. GC/MS (70 eV) *m/z* (%): 216 (M^+, 50), 172 (75), 155 (100), 127 (90), 101 (10), 77 (15), 51 (10). HRMS (ESI) *m/z* calc. for $[C_{13}H_{12}O_3 + Na]^+$: 239.0679; found: 239.0683.



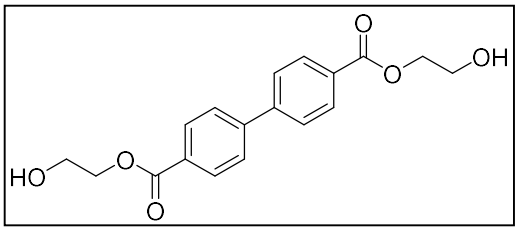
2-hydroxyethyl nicotinate 2p: yellow oil, 63%. ^{1}H NMR (400.12 MHz, $CDCl_3$): δ 9.183–9.176 (m, 1H), 8.72–8.70 (m, 1H), 8.30–8.27 (m, 1H), 7.39-7.36 (m, 1H), 4.47–4.45 (m, 2H), 3.96–3.93 (m, 2H); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 165.2, 152.9 150.4, 137.5, 126.1, 123.5, 67.0, 60.6; FT-IR (Film, cm^{-1}): 3401, 1726, 1587, 1293, 1250, 1075, 801. GC/MS (70 eV) *m/z* (%): 167 (M^+, 3), 136 (18), 124 (89), 106 (100), 78 (77), 51 (38). HRMS (ESI) *m/z* calc. for $[C_8H_9NO_3 + Na]^+$: 190.0475; found: 190.0477.



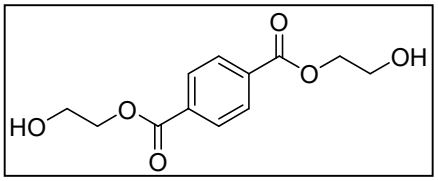
2-hydroxyethyl 1-benzyl-1H-indole-5-carboxylate 2q: yellow oil, 64%. ^{1}H NMR (400.12 MHz, $CDCl_3$): δ 8.45–8.44 (m, 1H), 7.91–7.88 (m, 1H), 7.33–7.27 (m, 4H), 7.193–7.186 (m, 1H), 7.10–7.08 (m, 2H), 6.66–6.65 (m, 1H), 5.34 (s, 2H), 4.49–4.46 (m, 2H), 3.98–3.95 (m, 2H), 2.36 (br s, 1H); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 168.0, 138.8, 136.8, 129.7, 128.8, 128.2, 127.8, 126.7, 124.2, 123.1, 121.2, 109.4, 103.3, 66.4, 61.6, 50.2; FT-IR (Film, cm^{-1}): 3234, 3033, 2957, 2880, 1696, 1609, 1275, 754; GC/MS (70 eV) *m/z* (%): 295 (M^+, 2), 292 (100), 275 (6), 251 (11), 201 (28), 158 (76), 132 (19), 106 (36), 91 (92), 77 (15), 65 (22), 51 (12). HRMS (ESI) *m/z* calc. for $[C_{18}H_{17}NO_3 + Na]^+$: 318.1101; found: 318.1104.



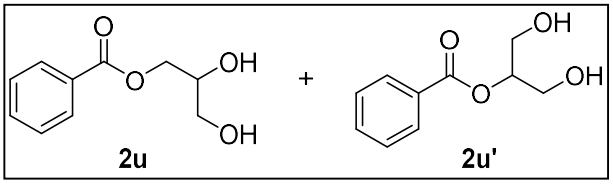
2-hydroxyethyl 1*H*-indole-5-carboxylate 2r: pale red oil, 55%. ^{1}H NMR (400.12 MHz, $CDCl_3$): δ 8.64 (br s, 1H), 8.43 (s, 1H), 7.91–7.89 (m, 1H), 7.40–7.38 (m, 1H), 7.27–7.26 (m, 1H), 6.64–6.63 (m, 1H), 4.49–4.47 (m, 2H), 3.99–3.97 (m, 2H), 2.40 (br s, 1H); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 168.2, 138.6, 127.5, 125.7, 123.9, 123.4, 121.4, 110.8, 104.0, 66.4, 61.7; FT-IR (Film, cm^{-1}): 3401, 3267, 3100, 2971, 2928, 1662, 1237, 749; GC/MS (70 eV) *m/z* (%): 205 (M^+, 9), 161 (56), 144 (100), 116 (62), 89 (34), 63 (13). HRMS (ESI) *m/z* calc. for $[C_{11}H_{11}NO_3 + Na]^+$: 228.0631; found: 228.0634.



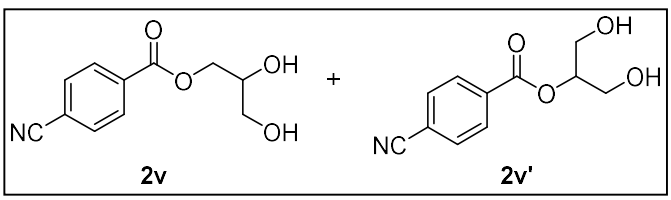
Bis(2-hydroxyethyl) [1,1'-biphenyl]-4,4'-dicarboxylate 2s: pale yellow solid, m.p. 115-116 °C, 99%. ^{1}H NMR (400.12 MHz, Acetone-d_6): δ 8.18–8.15 (m, 4H), 7.90–7.87 (m, 4H), 4.42–4.40 (m, 4H), 3.92–3.88 (m, 4H); ^{13}C NMR (100.62 MHz, Acetone-d_6): δ 166.6, 144.9, 131.02, 130.98, 128.1, 67.6, 60.9; FT-IR (Film, cm^{-1}): 3428, 2941, 2880, 1716, 1699, 1412, 1291, 1077, 875, 718. HRMS (ESI) *m/z* calc. for [$C_{18}H_{18}O_6$ + Na]$^+$: 353.0996; found: 353.0999.



Bis(2-hydroxyethyl) terephthalate 2t[8]: withe solid, m.p. 106-109 °C, 93%. ^{1}H NMR (400.12 MHz, DMSO-d_6): δ 8.12 (s, 4H), 4.98 (bs s, 2H), 4.33–4.30 (m, 4H), 3.73–3.71 (m, 4H); ^{13}C NMR (100.62 MHz, DMSO-d_6): δ 165.2, 133.8, 129.6, 67.1, 59.1; FT-IR (Film, cm^{-1}): 3431, 2950, 2877, 1704, 1721, 1412, 1299, 1102, 851, 718; HRMS (ESI) *m/z* calc. for [$C_{12}H_{14}O_6$ + Na]$^+$: 277.0683; found: 277.0685.

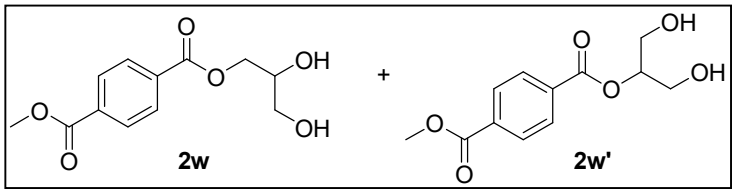


Mixture of 2,3-dihydroxypropyl benzoate (2u)[9] and 1,3-dihydroxypropan-2-yl benzoate (2u')[10]: 84%, **2u**:**2u'** = 88:12, pale yellow liquid. ^{1}H NMR (400.12 MHz, $CDCl_3$): δ 8.03–7.99 (m, 2H **2u**, 2H **2u'**), 7.55–7.50 (m, 1H **2u**, 1H **2u'**), 7.42–7.37 (m, 2H **2u**, 2H **2u'**), 5.14 (quin, *J* = 4.9 Hz, 1H **2u'**), 4.36 (d, *J* = 5.5 Hz, 2H **2u**), 4.08–4.02 (m, 1H **2u**), 3.92–3.90 (m, 4H **2u'**), 3.78 (br s, 1H **2u**), 3.77–3.73 (m, 1H **2u**), 3.68–3.63 (m, 1H **2u**), 3.42 (bs s, 1H **2u**), 2.66 (br s, 2H **2u'**). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 166.9 (**2u**), 166.7 (**2u'**), 133.28 (**2u'**), 133.25 (2u), 129.7 (**2u'**), 129.6 (**2u**, **2u'**), 129.4 (**2u**), 128.38 (**2u**), 128.36 (**2u'**), 75.6 (**2u'**), 70.2 (**2u**), 65.6 (**2u**), 63.4(**2u**), 61.8 (**2u'**). FT-IR (Film, cm^{-1}): 3415 (br), 3065, 2950, 2886, 1715, 1452, 1275, 1116, 1070, 710. HRMS (ESI) *m/z* calc. for [$C_{10}H_{12}O_4$ + Na]$^+$: 219.0628; found: 219.0631.



Mixture of 2,3-dihydroxypropyl 4-cyanobenzoate (2v) and 1,3-dihydroxypropan-2-yl 4-cyanobenzoate (2v'): 76%, **2v**:**2v'** = 86:14, pale yellow waxy solid. ^{1}H NMR (400.12 MHz, $CDCl_3$): δ 8.18–8.13 (m, 2H **2v**, 2H **2v'**), 7.76–7.72 (m, 2H **2v**, 2H **2v'**), 5.20 (quin, *J* = 4.8 Hz, 1H **2v'**), 4.48–4.40 (m, 2H **2v**), 4.12–4.07 (m, 1H **2v**), 3.98 (d, *J* = 4.8 Hz, 4H **2v'**), 3.81–3.77 (m, 1H **2v**), 3.71–3.67 (m, 1H **2v**), 2.93 (br s, 1H **2v**), 2.49 (br s, 1H **2v**), 1.88 (br s, 2H **2v'**). ^{13}C NMR

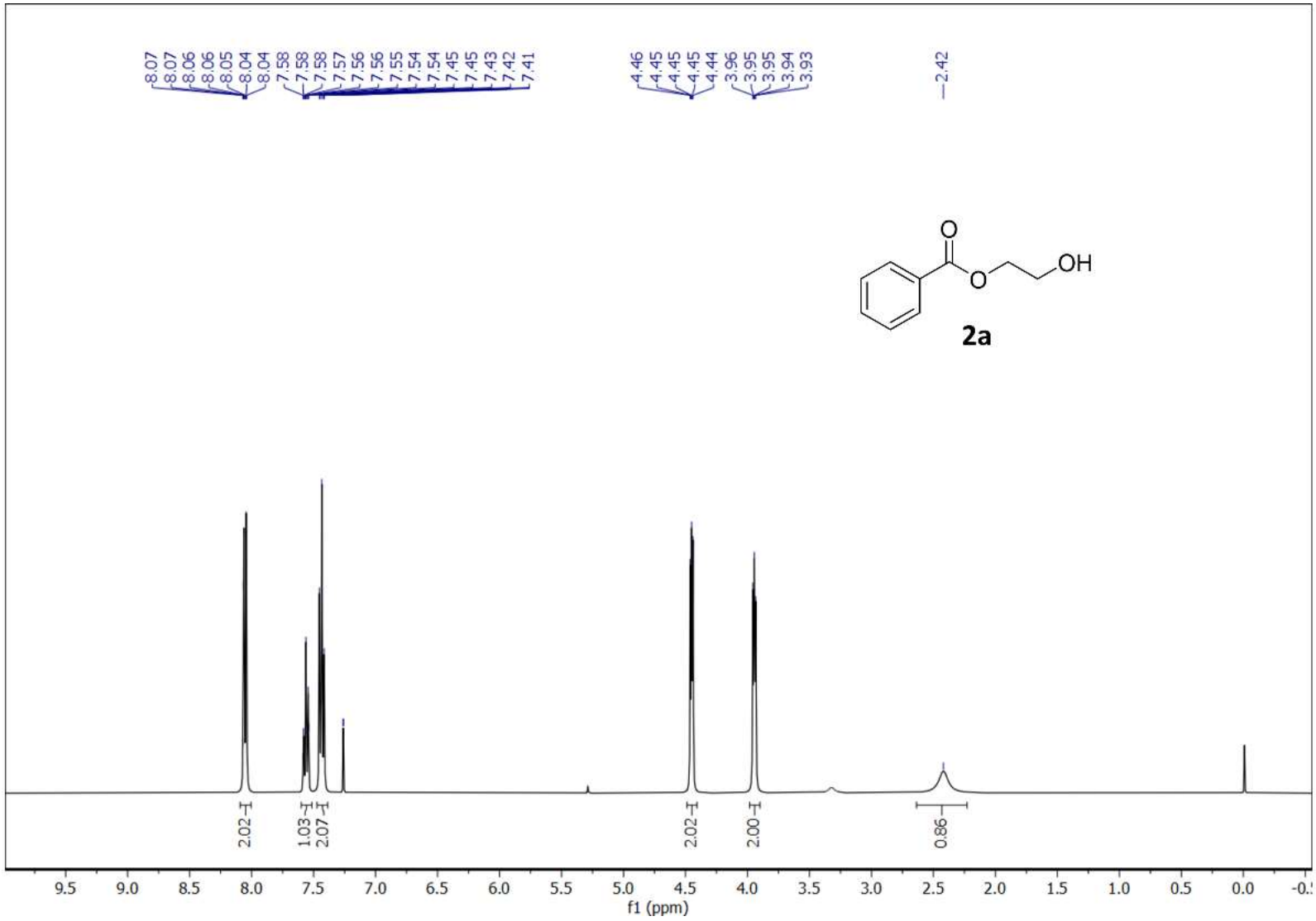
(100.62 MHz, $CDCl_3$): δ 165.2 (**2v**), 164.9 (**2v'**), 133.6 (**2v'**), 133.4 (**2v'**), 132.25 (**2v**), 132.22 (**2v'**), 130.23 (**2v**), 130.16 (**2v**), 129.7 (**2v'**), 128.4 (**2v'**), 117.8 (**2v**), 116.6 (**2v**), 76.2 (**2v'**), 70.0 (**2v**), 66.3 (**2v**), 63.3 (**2v**), 62.2 (**2v'**). FT-IR (KBr, cm^{-1}): 3253 (br), 3045, 2940, 2887, 2238, 1716, 1271, 1118, 1046, 859, 766. HRMS (ESI) *m/z* calc. for $[C_{11}H_{11}NO_4 + Na]^+$: 244.0580; found: 244.0584.



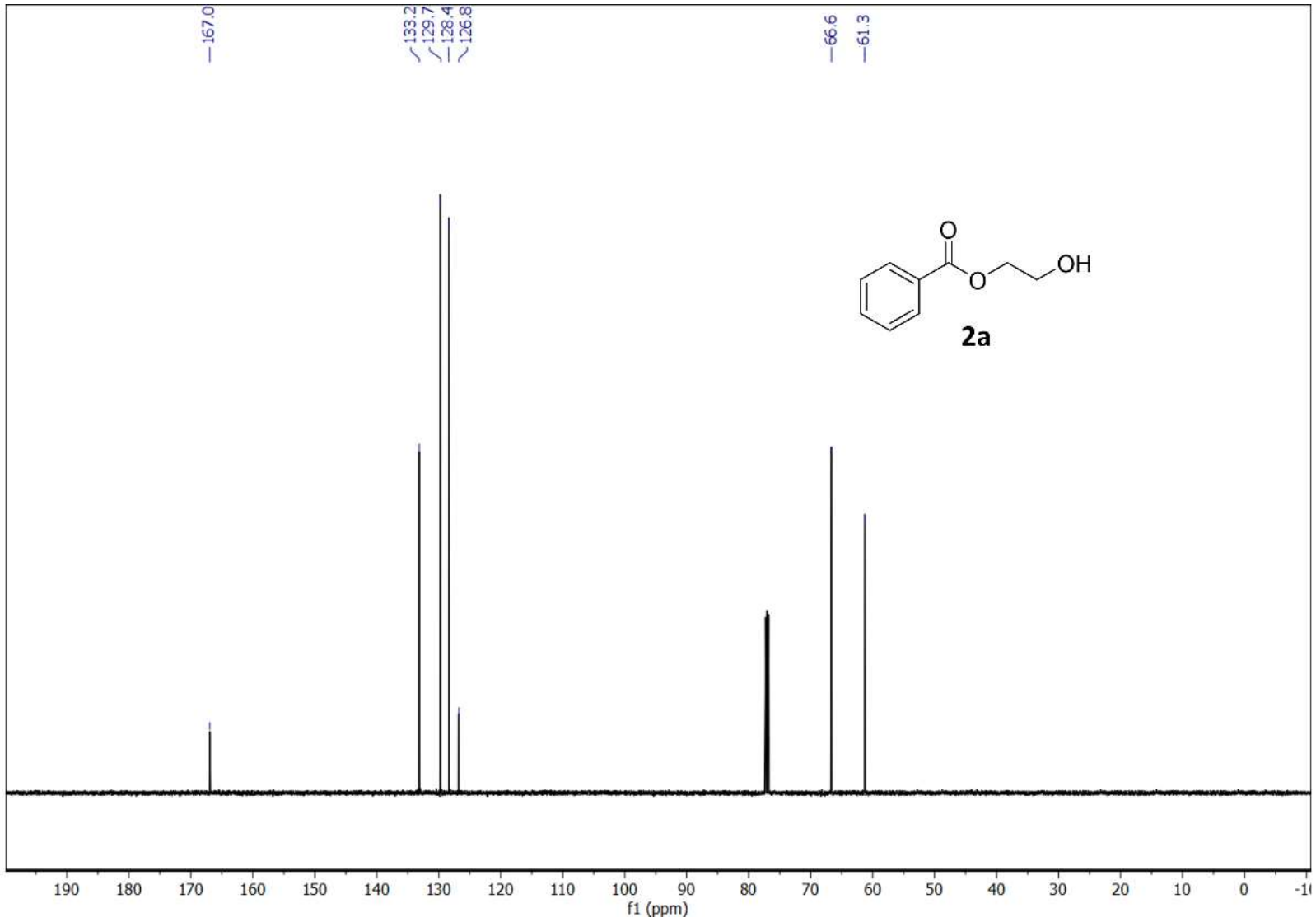
Mixture of 2,3-dihydroxypropyl methyl terephthalate (2w) and 1,3-dihydroxypropan-2-yl methyl terephthalate (2w'): 71%, **2w**:**2w'** = 87:13, white waxy solid. ^{1}H NMR (400.12 MHz, $CDCl_3$): δ 8.13–8.07 (m, 4H **2w**, 4H **2w'**), 5.19 (quin, *J* = 4.7 Hz, 1H **2w'**), 4.48–4.40 (m, 2H **2w**), 4.13–4.40 (m, 1H **2w**), 3.99 (d, *J* = 4.6 Hz, 4H **2w'**), 3.95 (s, 3H **2w**, 3H **2w'**), 3.81–3.78 (m, 1H **2w**), 3.72–3.68 (m, 1H **2w**), 2.88 (br s, 1H **2w**), 2.41 (br s, 1H **2w**), 1.77 (br s, 2H **2w'**). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 166.2 (**2w**), 166.1 (**2w**), 165.8 (2C **2w'**), 134.3 (**2w**), 133.5 (2C **2w'**), 133.4 (**2w**), 129.74 (**2w'**), 129.70 (**2w**), 129.63 (**2w**), 129.60 (**2w'**), 76.1 (**2w'**), 70.3 (**2w**), 66.1 (**2w**), 63.4 (**2w**), 62.4 (**2w'**), 52.5 (**2w**, **2w'**). FT-IR (KBr, cm^{-1}): 3368 (br), 2959, 2904, 1719, 1449, 1408, 1262, 1104, 1019, 802, 727. HRMS (ESI) *m/z* calc. for $[C_{12}H_{14}O_6 + Na]^+$: 277.0683; found: 277.0681.

7 ^{1}H NMR and ^{13}C NMR Spectra for Compounds 2a-t, 2u-w and 2u'-w'

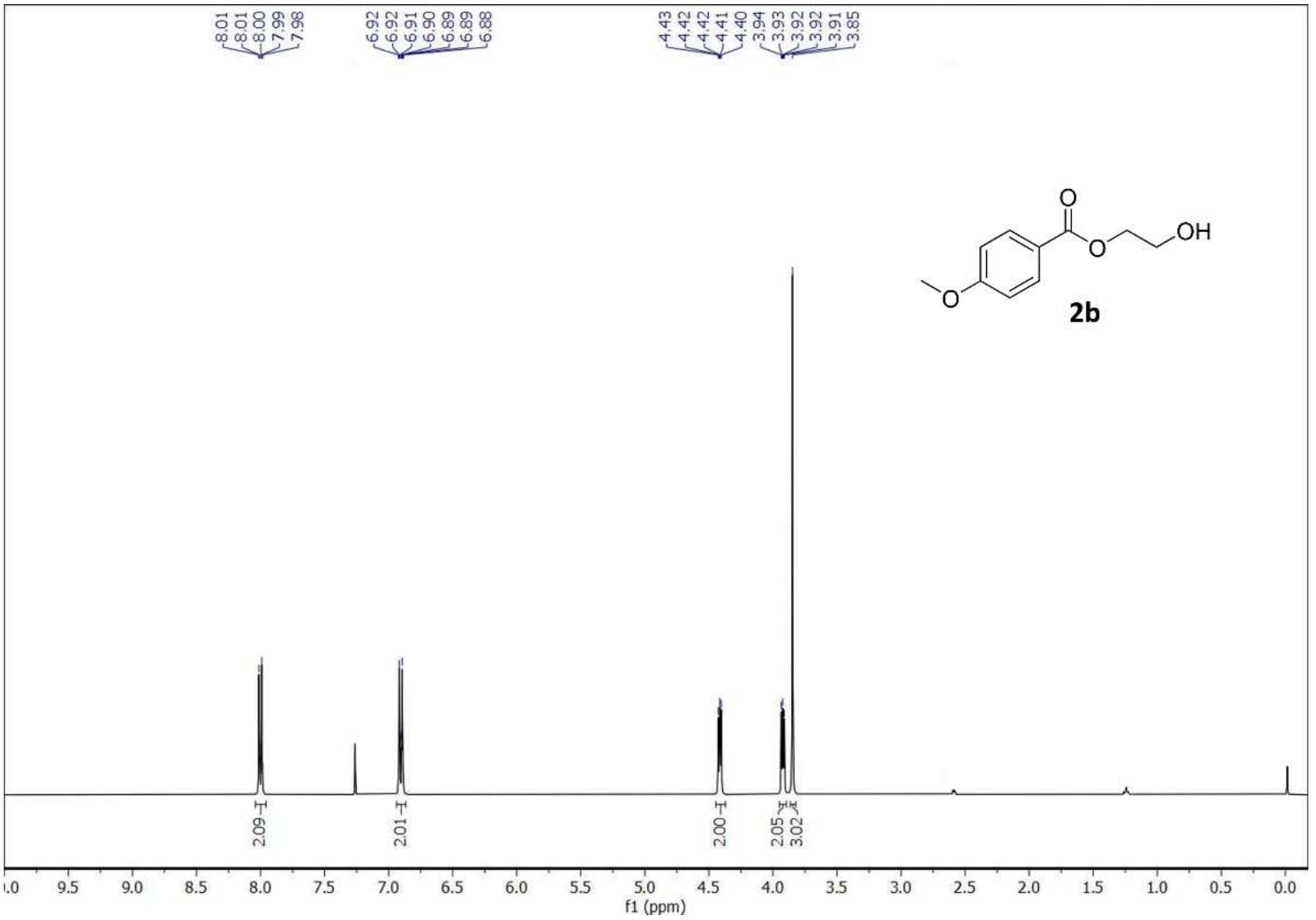
^{1}H NMR 400.12 MHz, $CDCl_3$



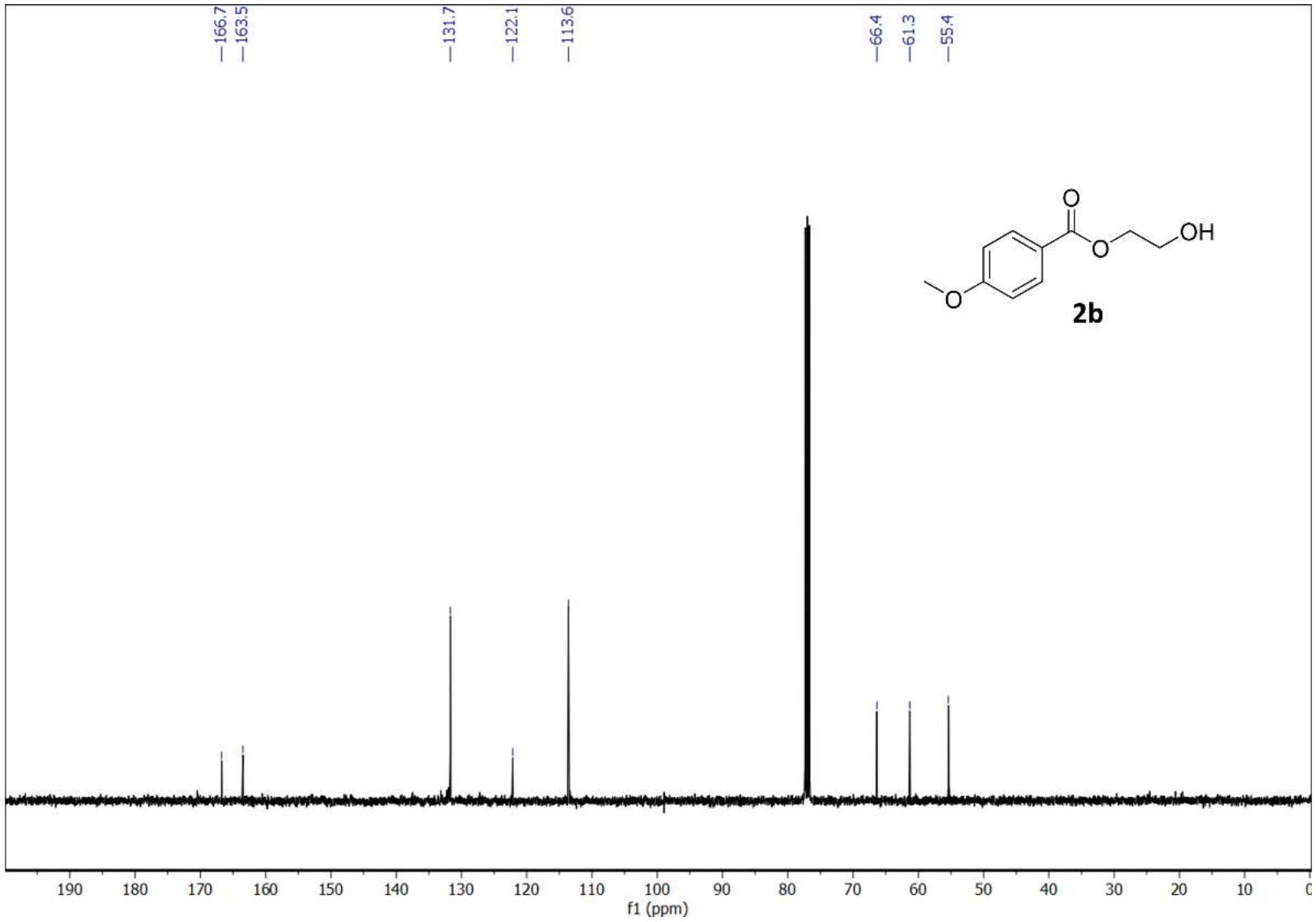
^{13}C NMR 100.62 MHz, $CDCl_3$



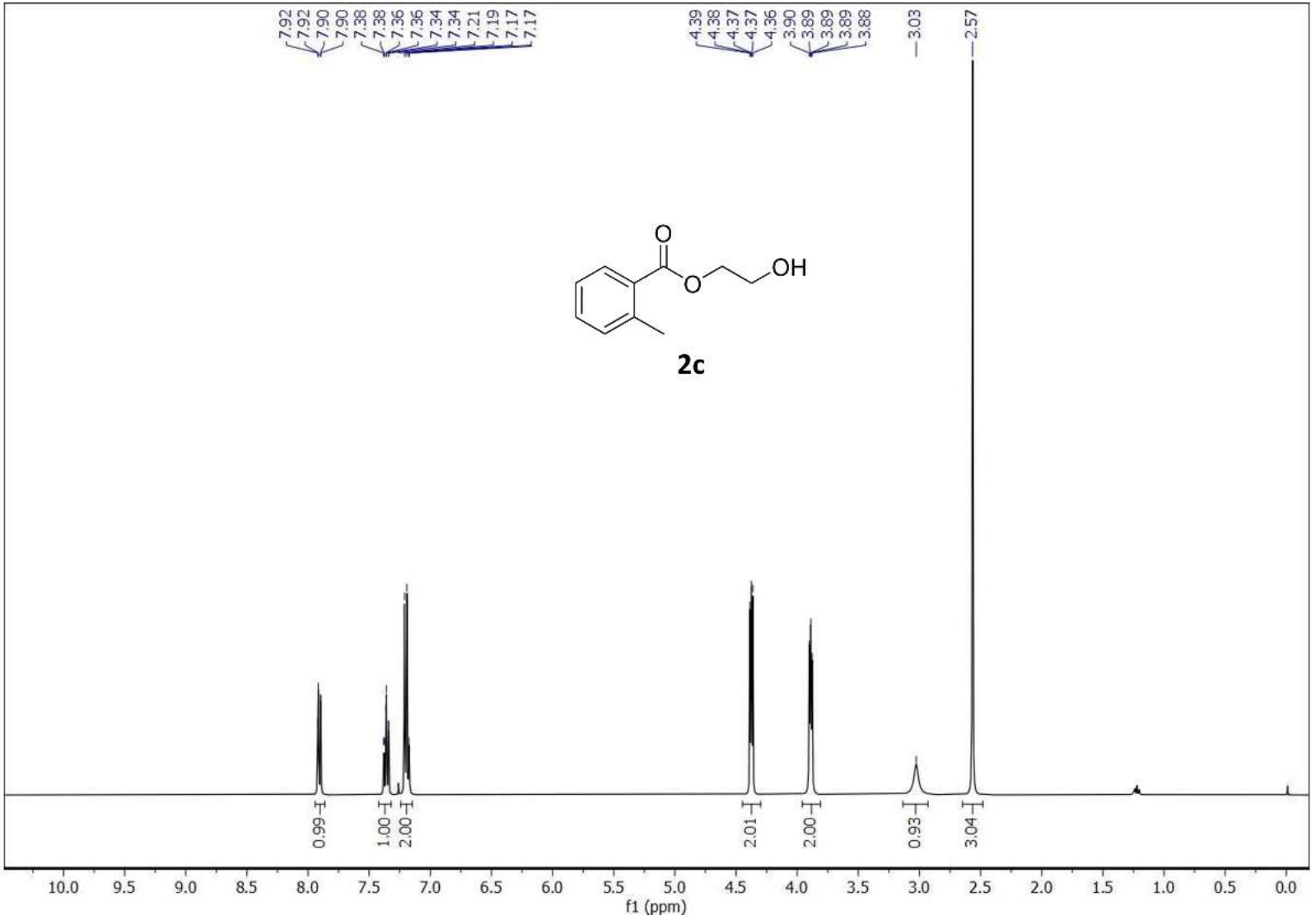
^{1}H NMR 400.12 MHz, $CDCl_3$



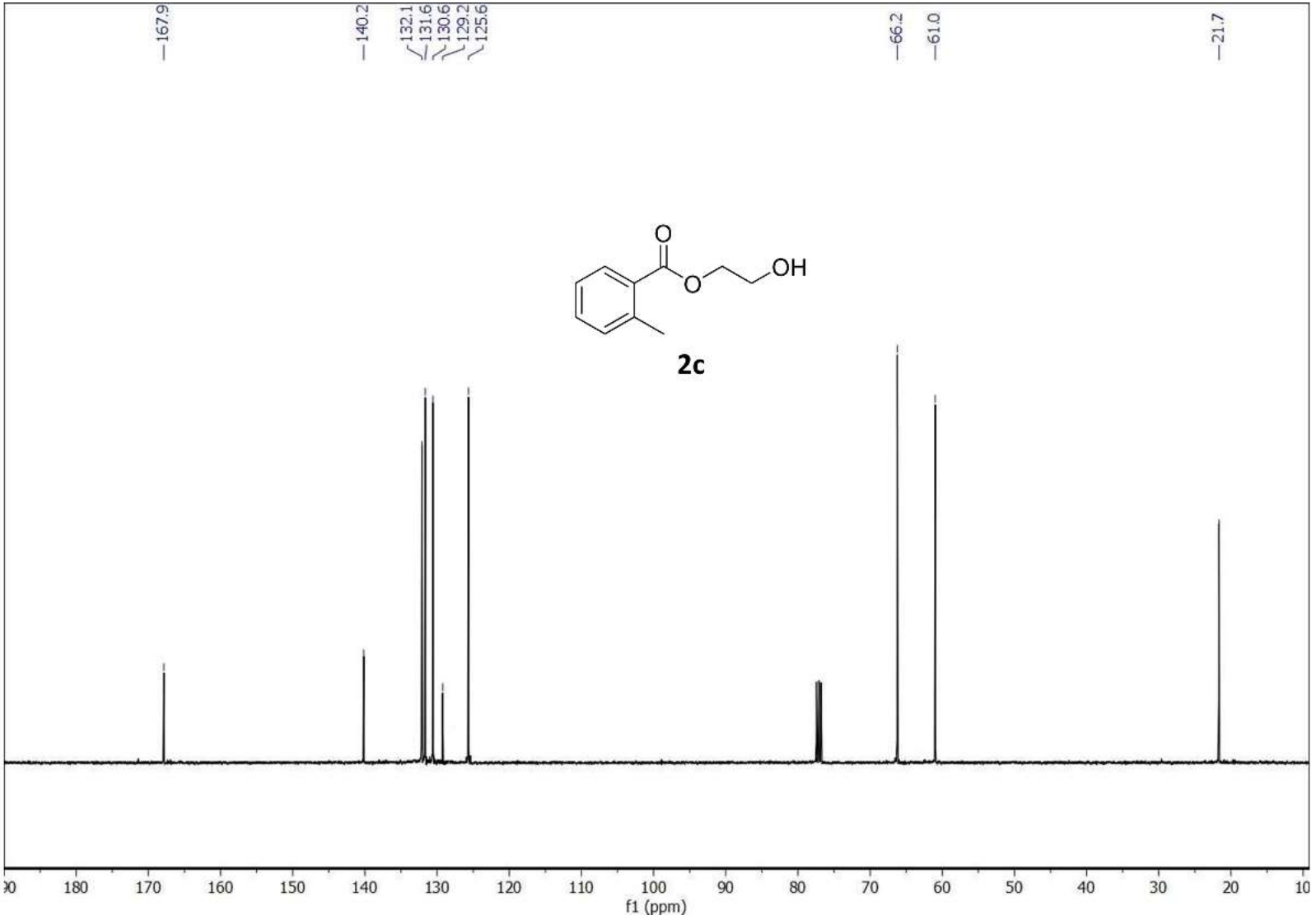
^{13}C NMR 100.62 MHz, $CDCl_3$



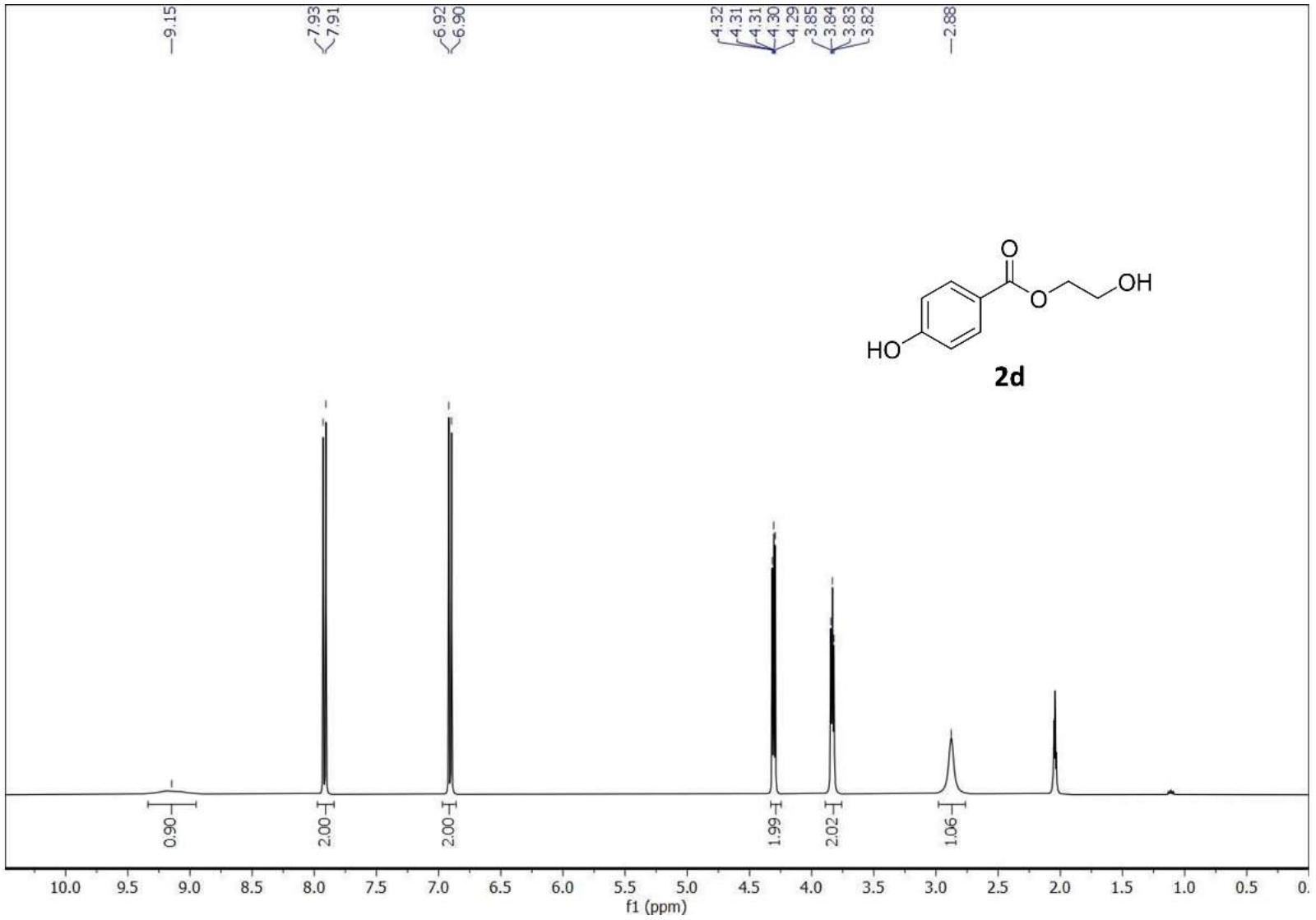
^{1}H NMR 400.12 MHz, $CDCl_3$



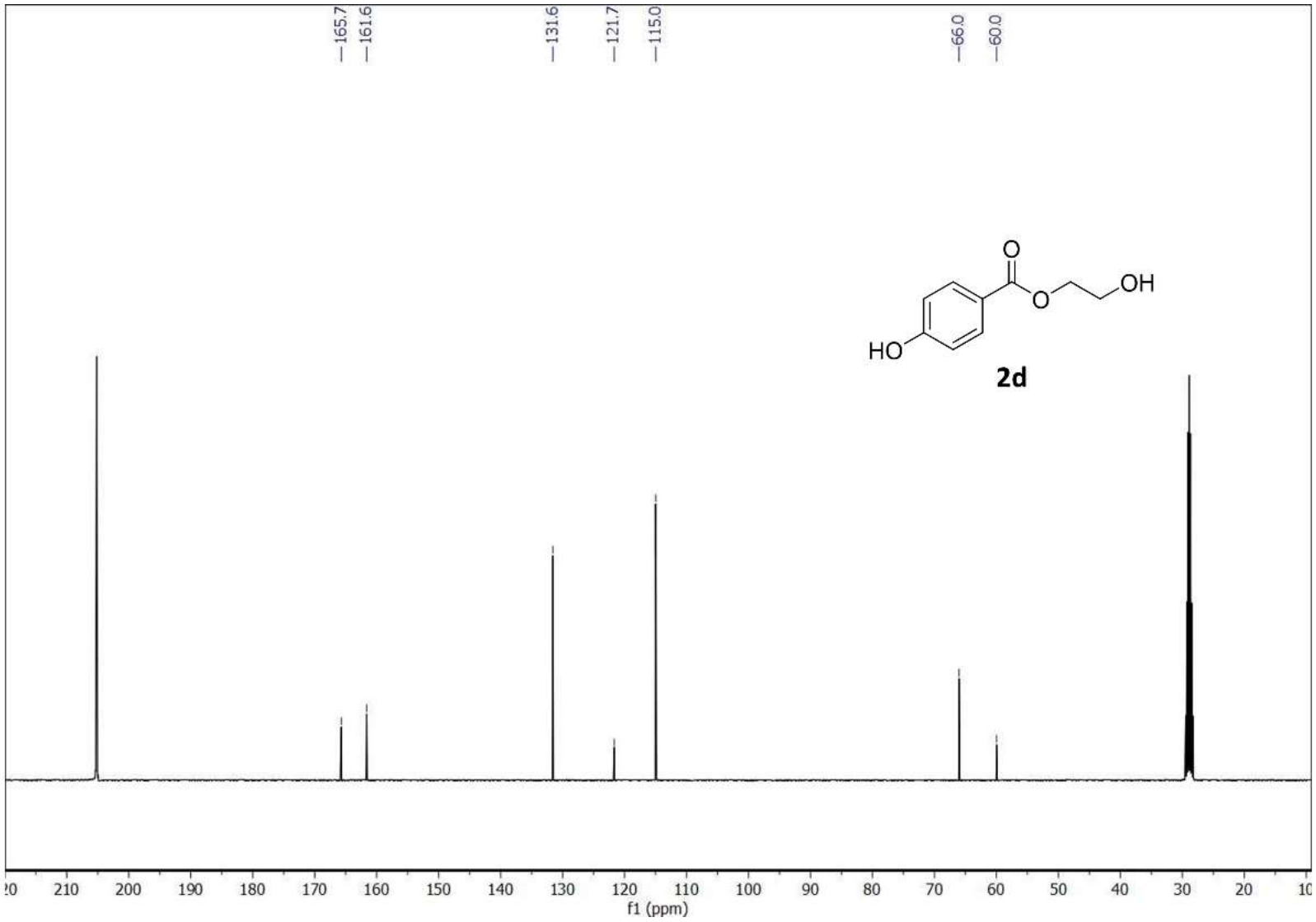
^{13}C NMR 100.62 MHz, $CDCl_3$



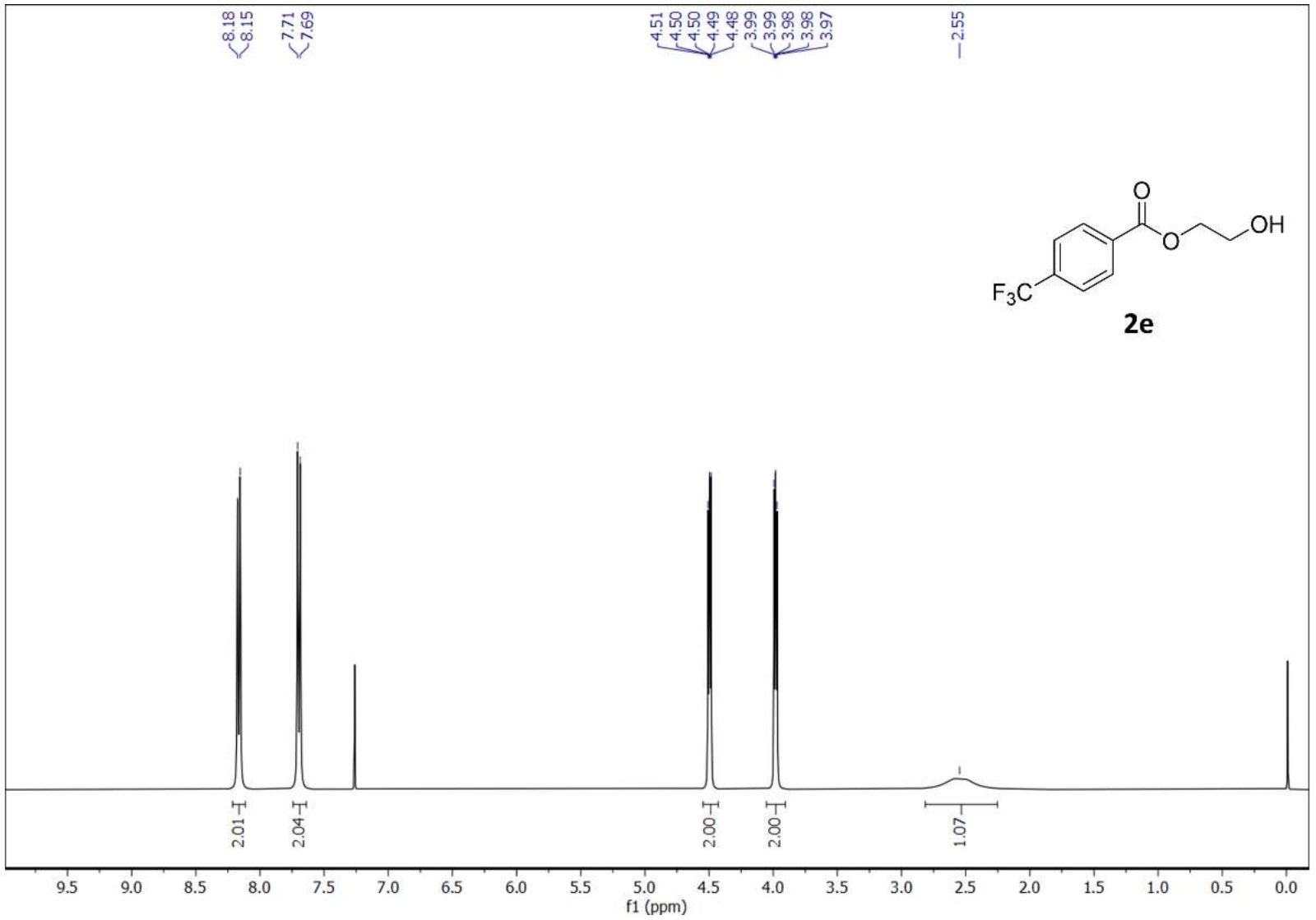
^{1}H NMR 400.12 MHz, Acetone-d_6



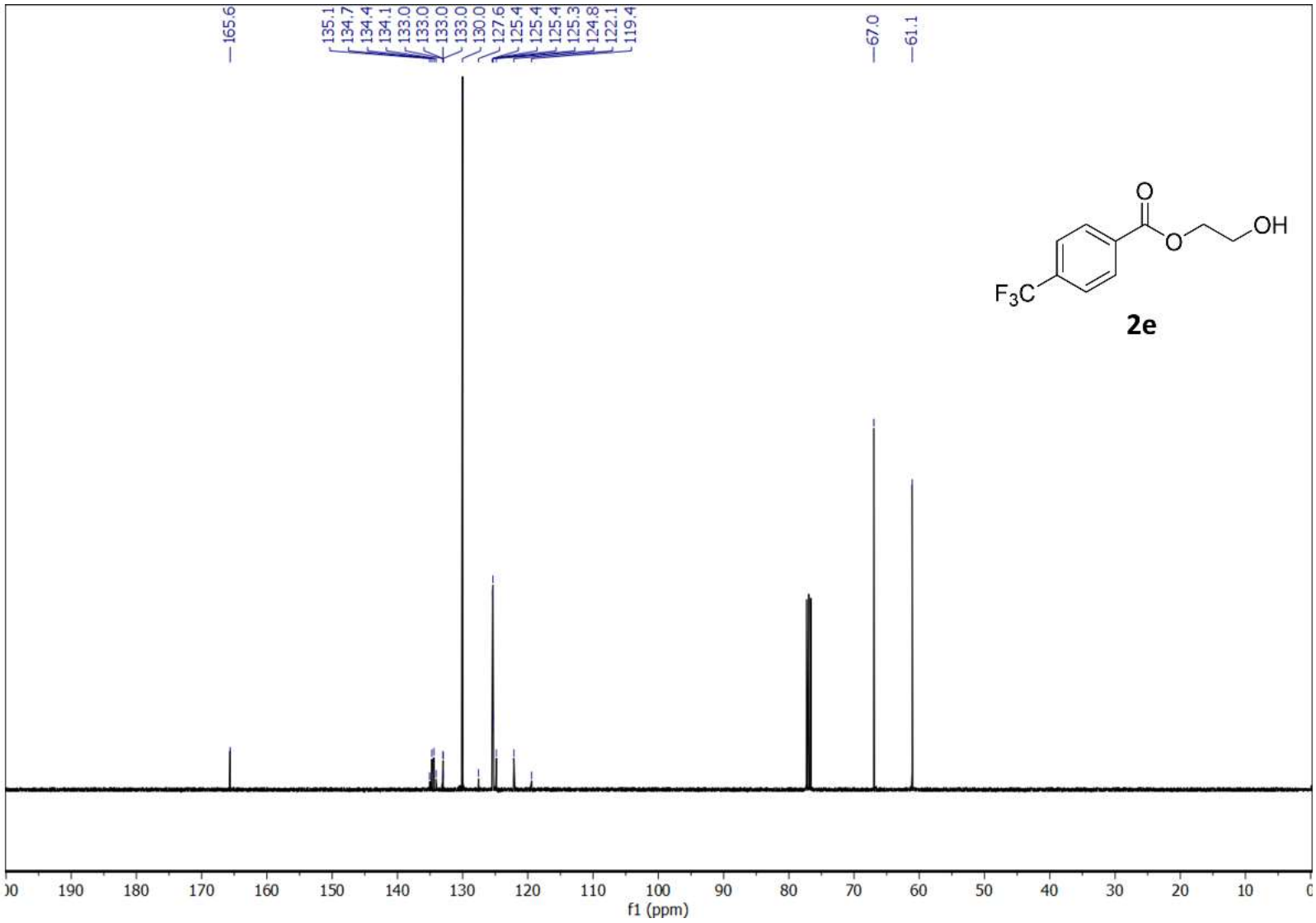
^{13}C NMR 100.62 MHz, Acetone-d_3



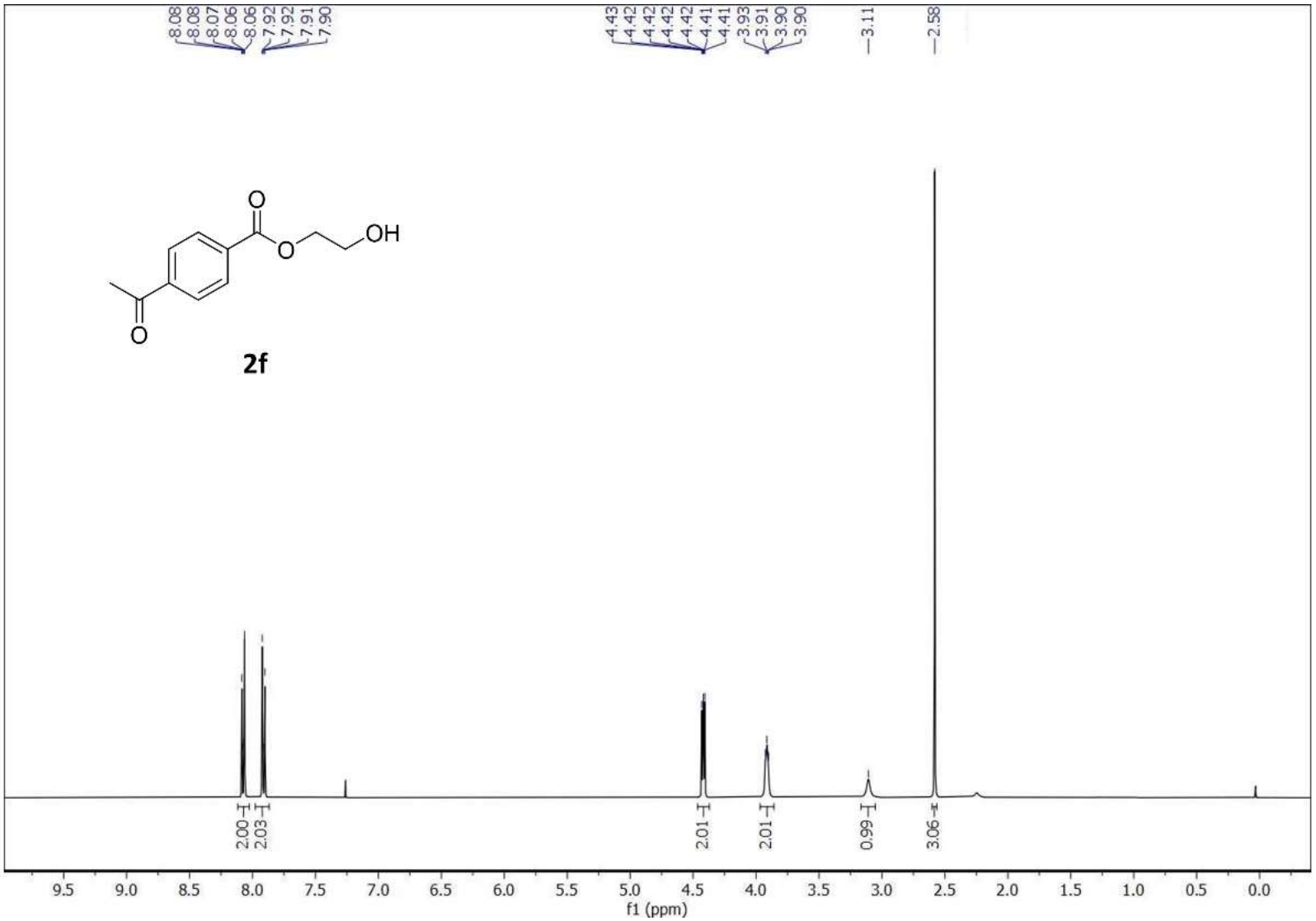
^{1}H NMR 400.12 MHz, $CDCl_3$



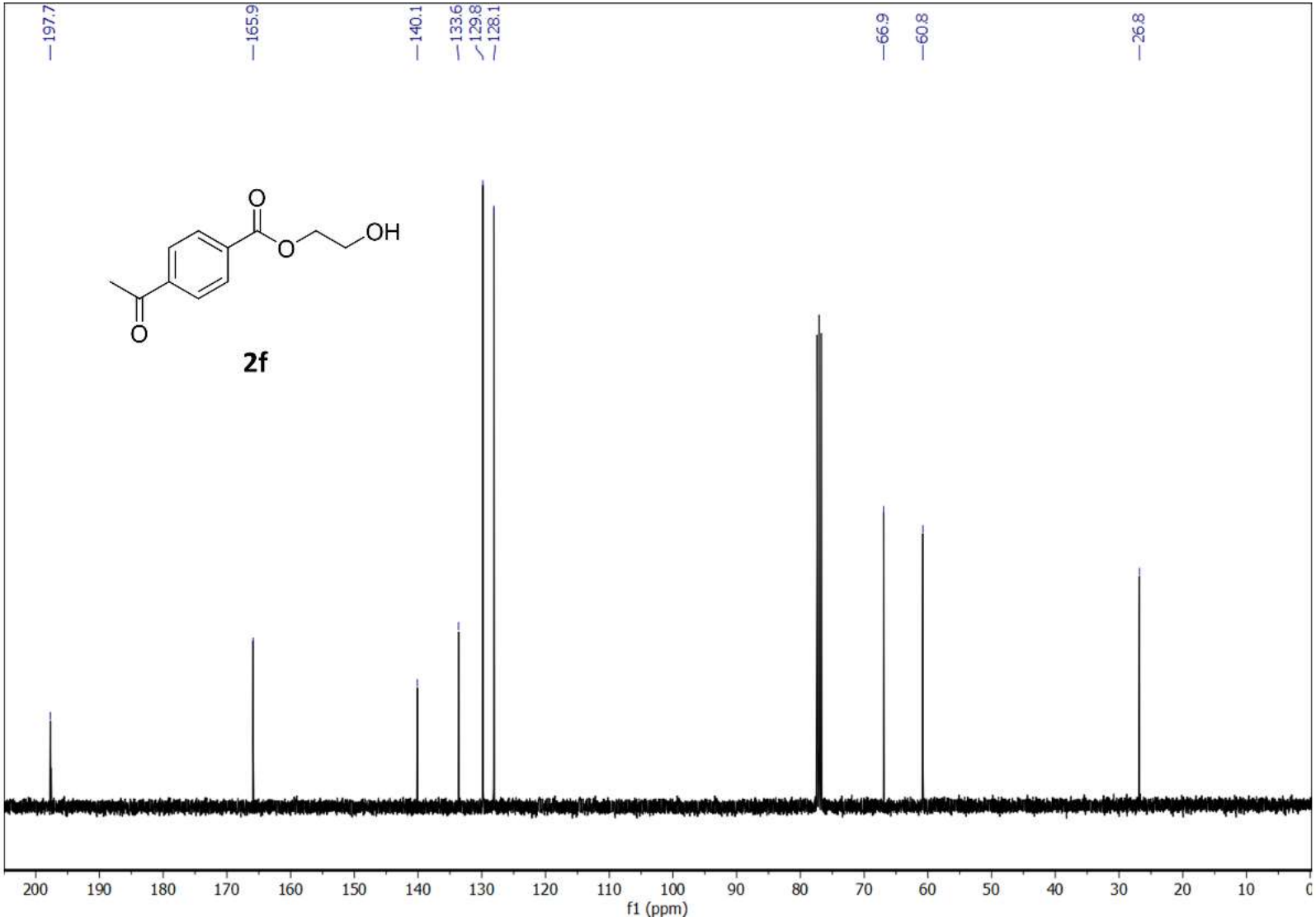
^{13}C NMR 100.62 MHz, $CDCl_3$



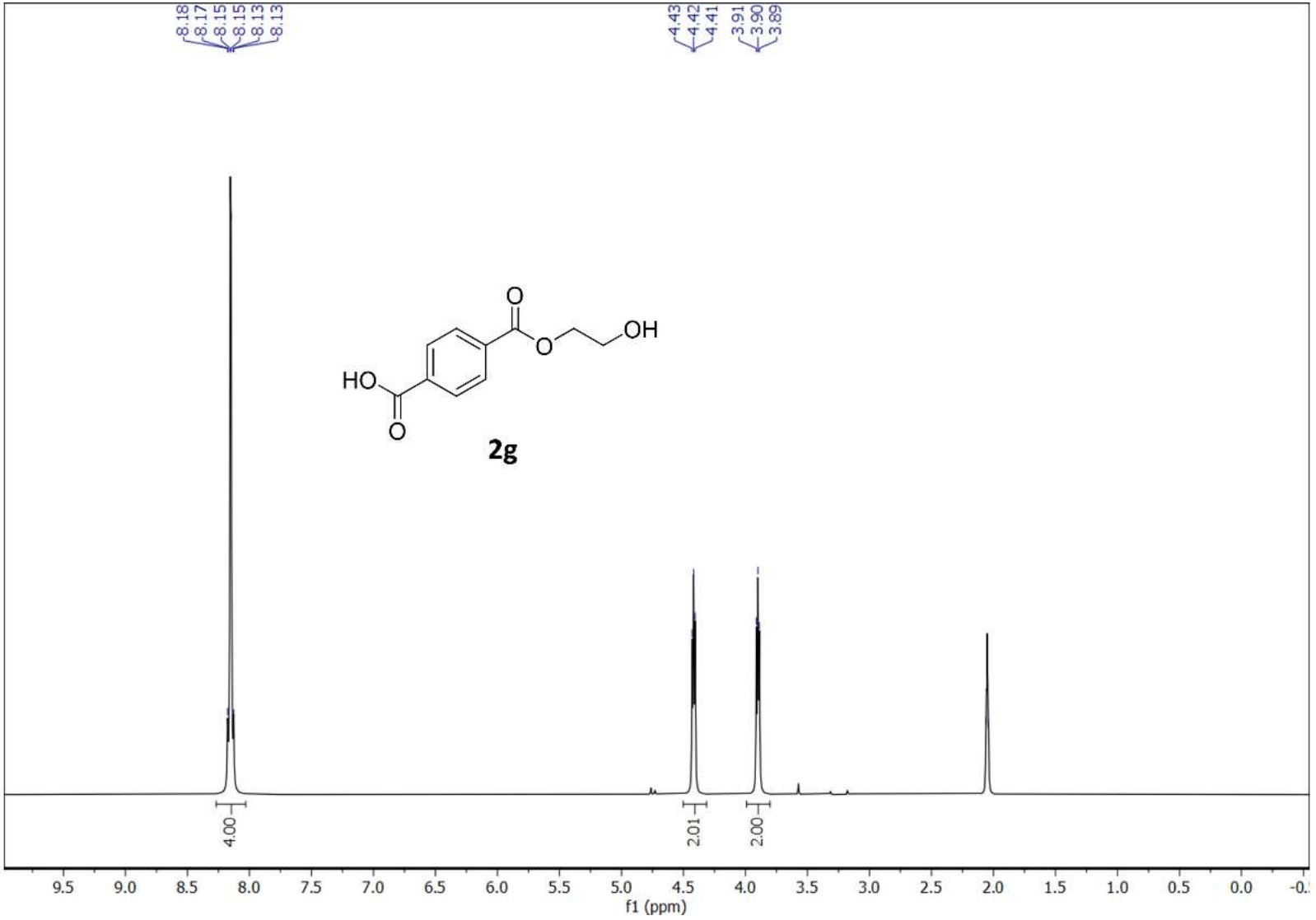
^{1}H NMR 400.12 MHz, $CDCl_3$



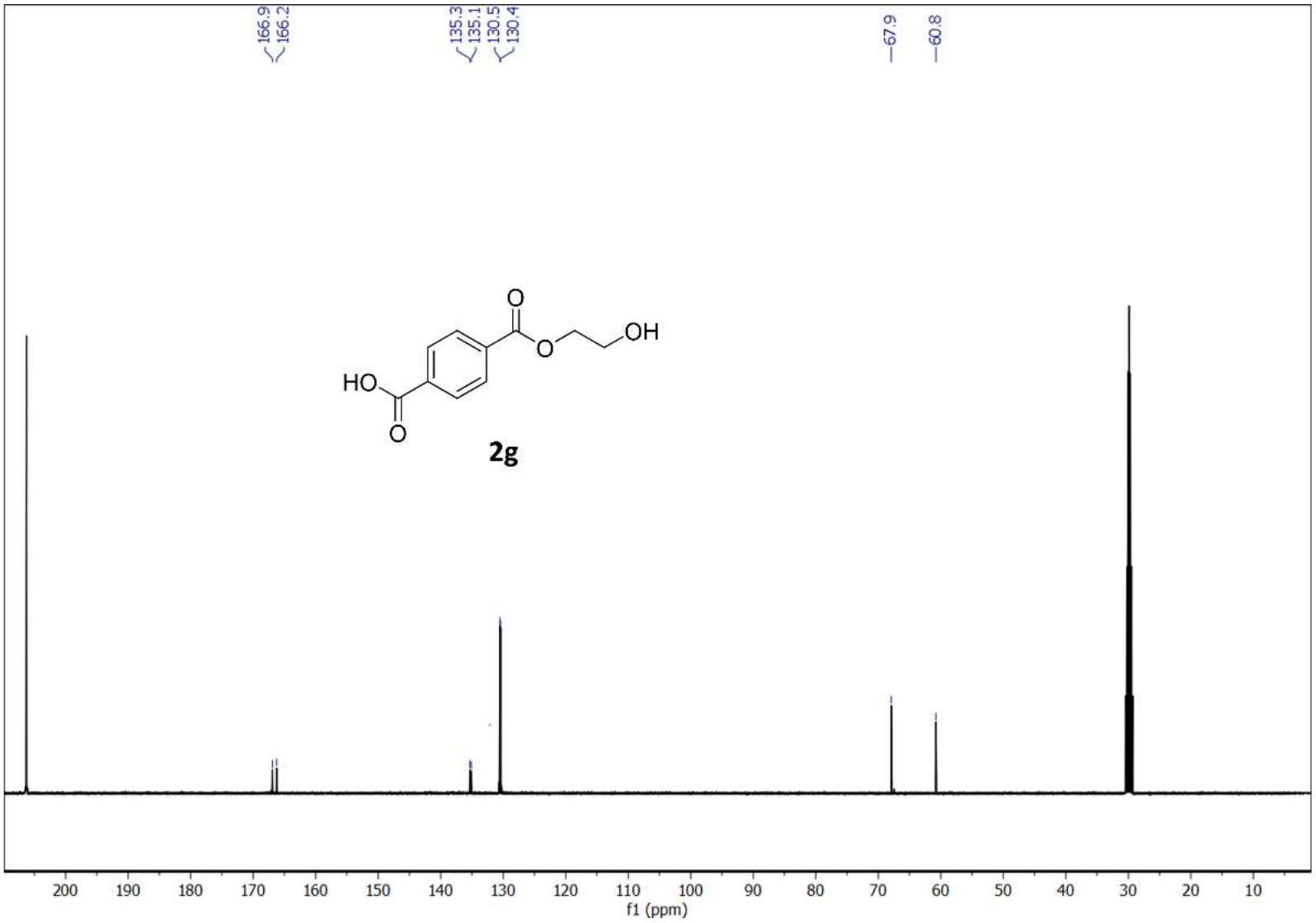
^{13}C NMR 100.62 MHz, $CDCl_3$



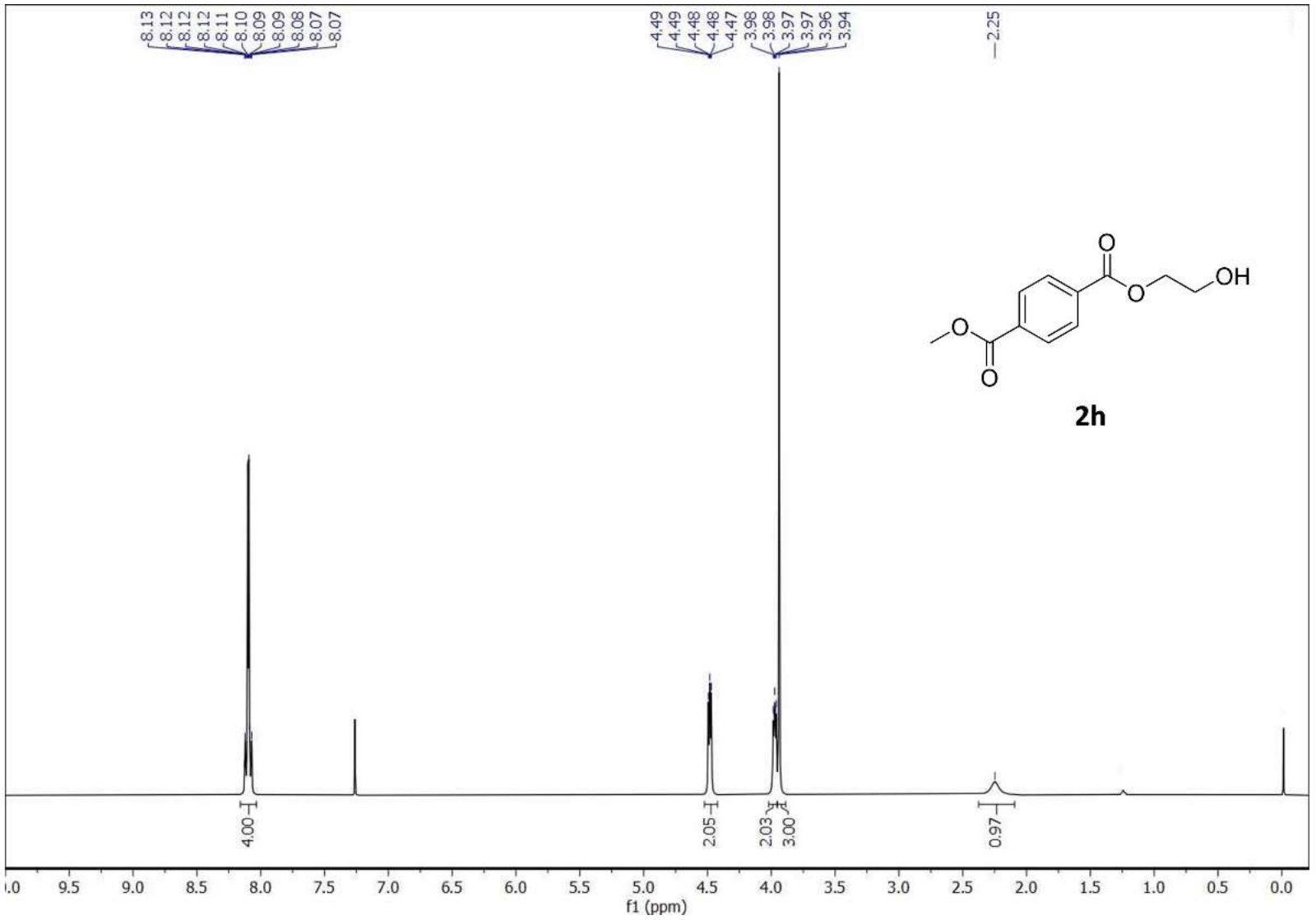
^{1}H NMR 400.12 MHz, Acetone-d_6



^{13}C NMR 100.62 MHz, Acetone-d_6



^{1}H NMR 400.12 MHz, $CDCl_3$



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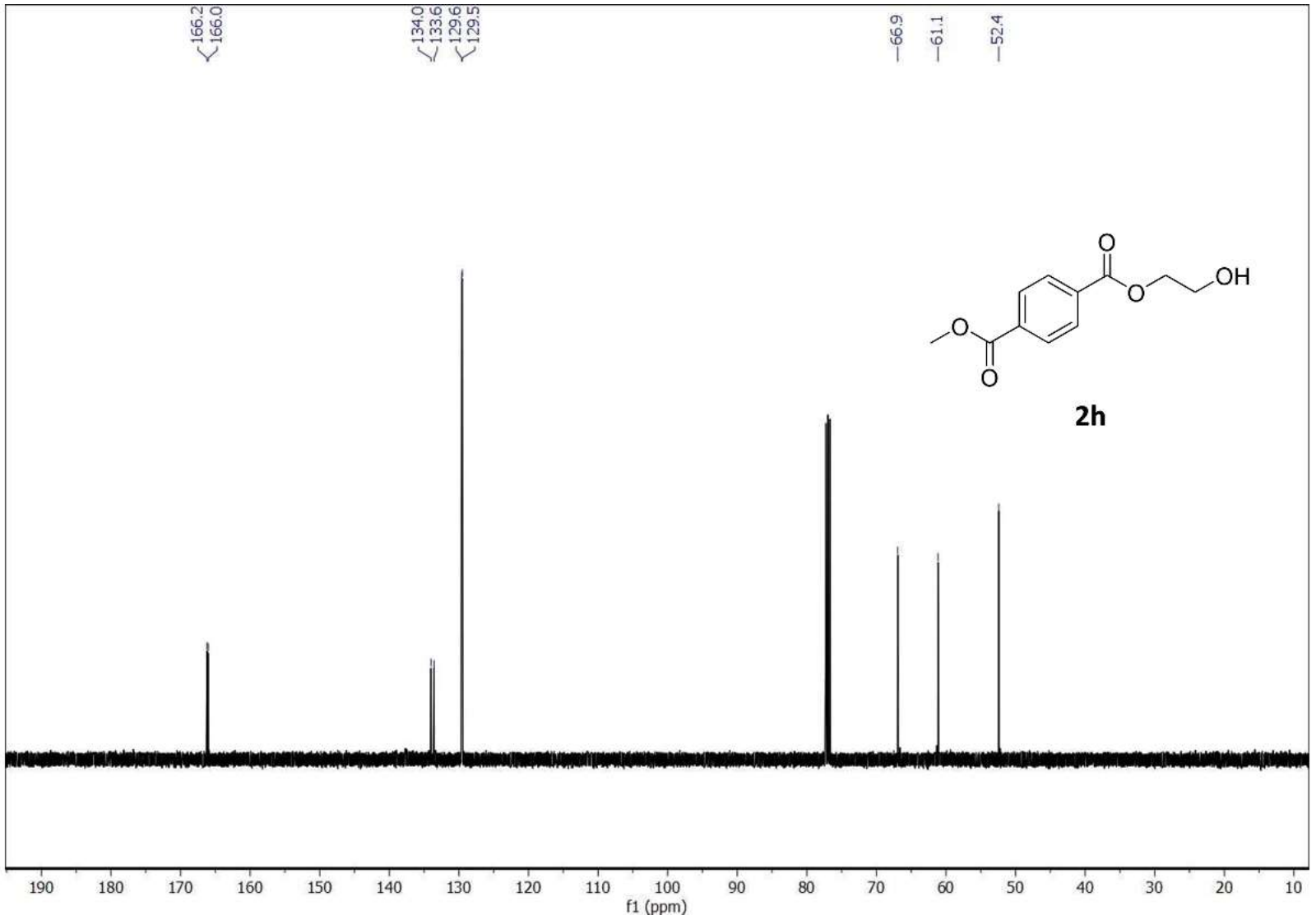

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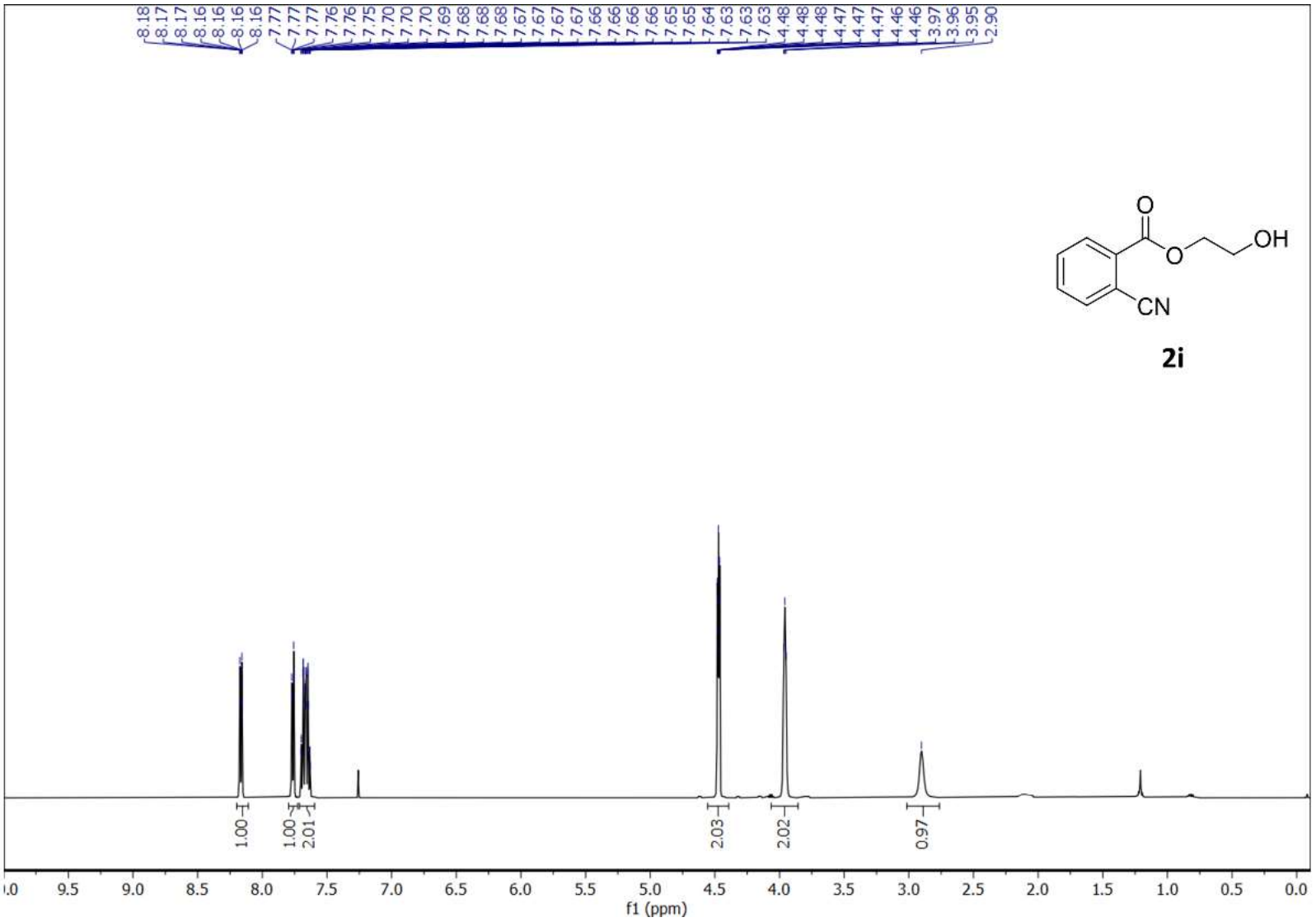

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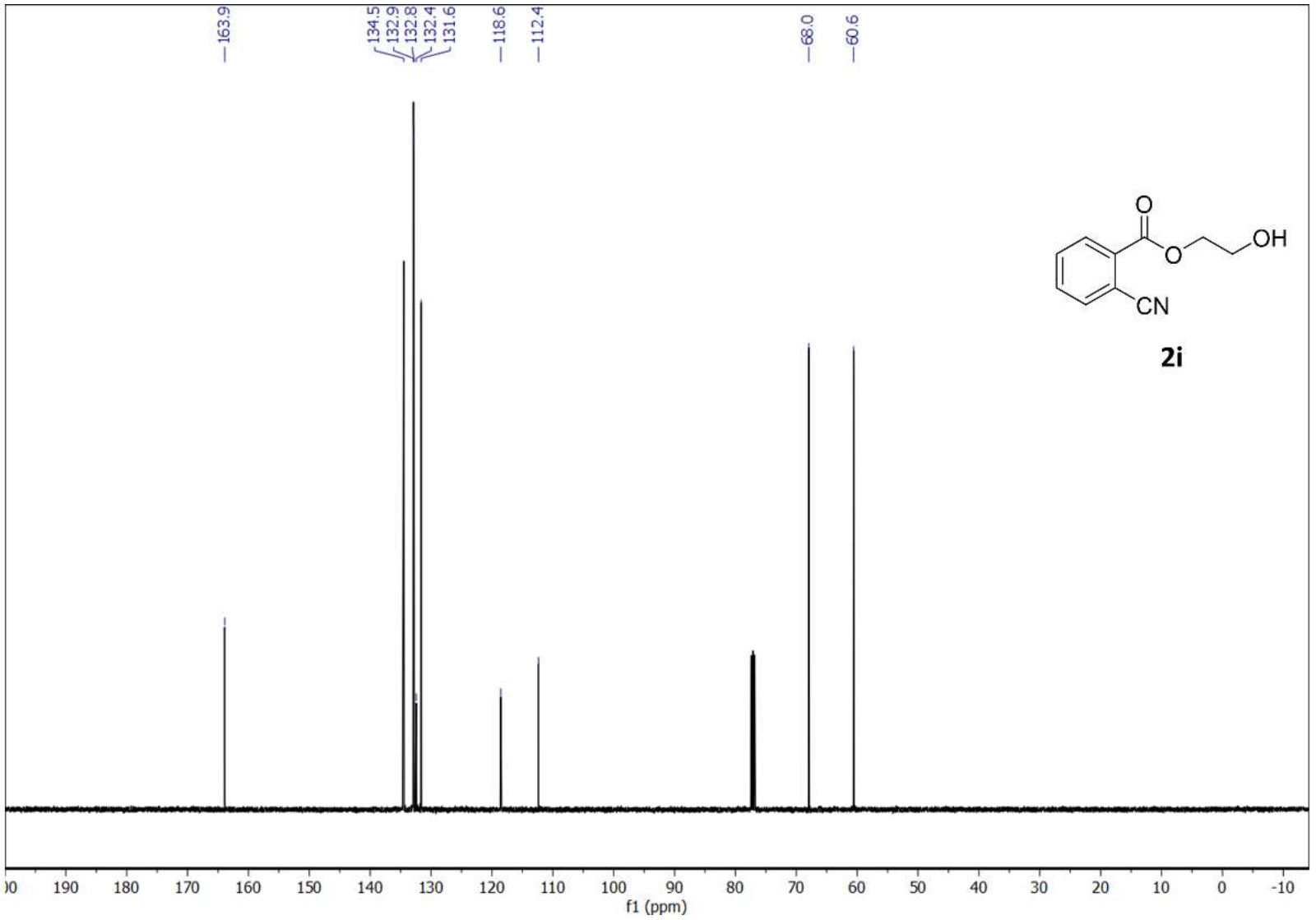

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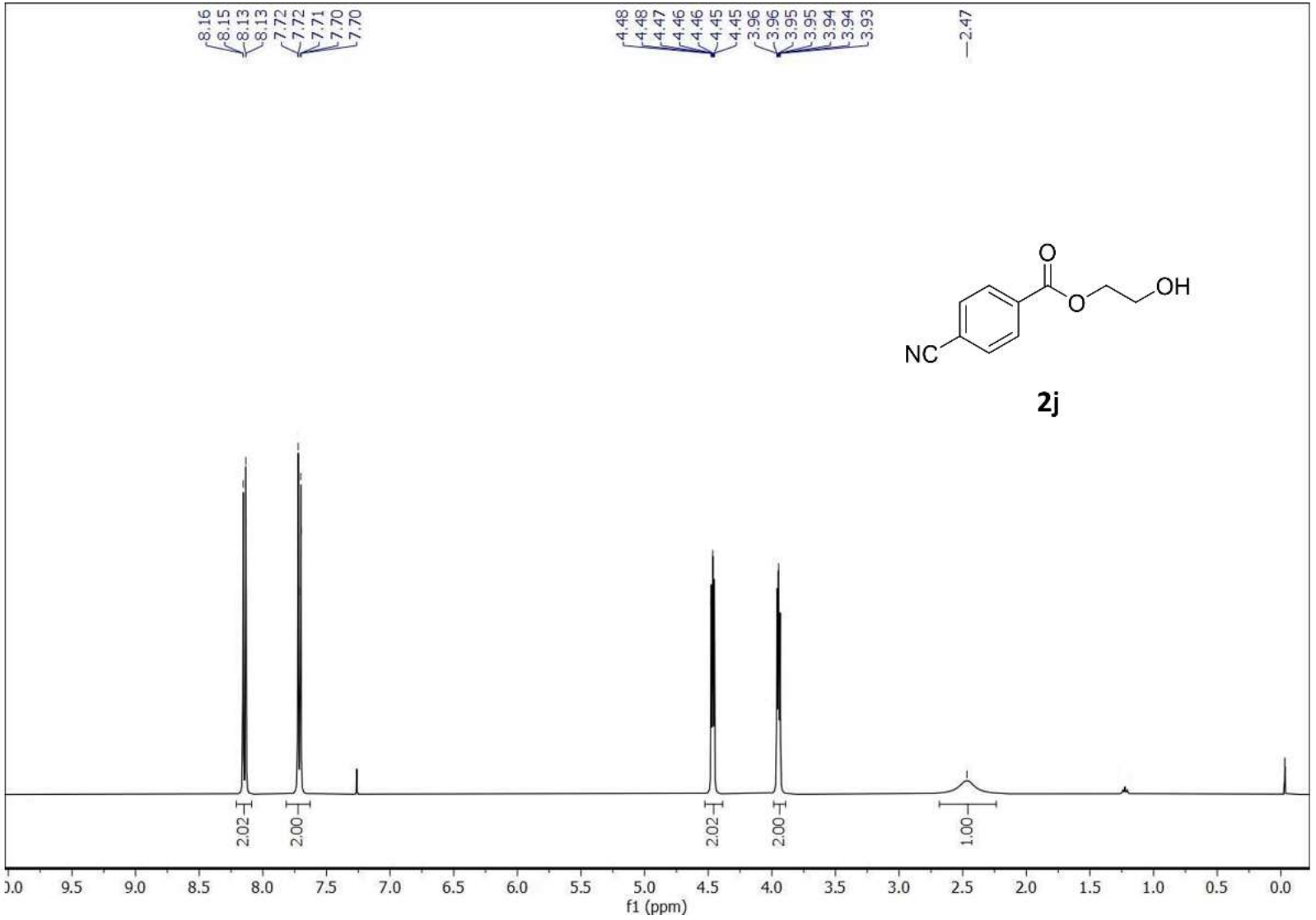

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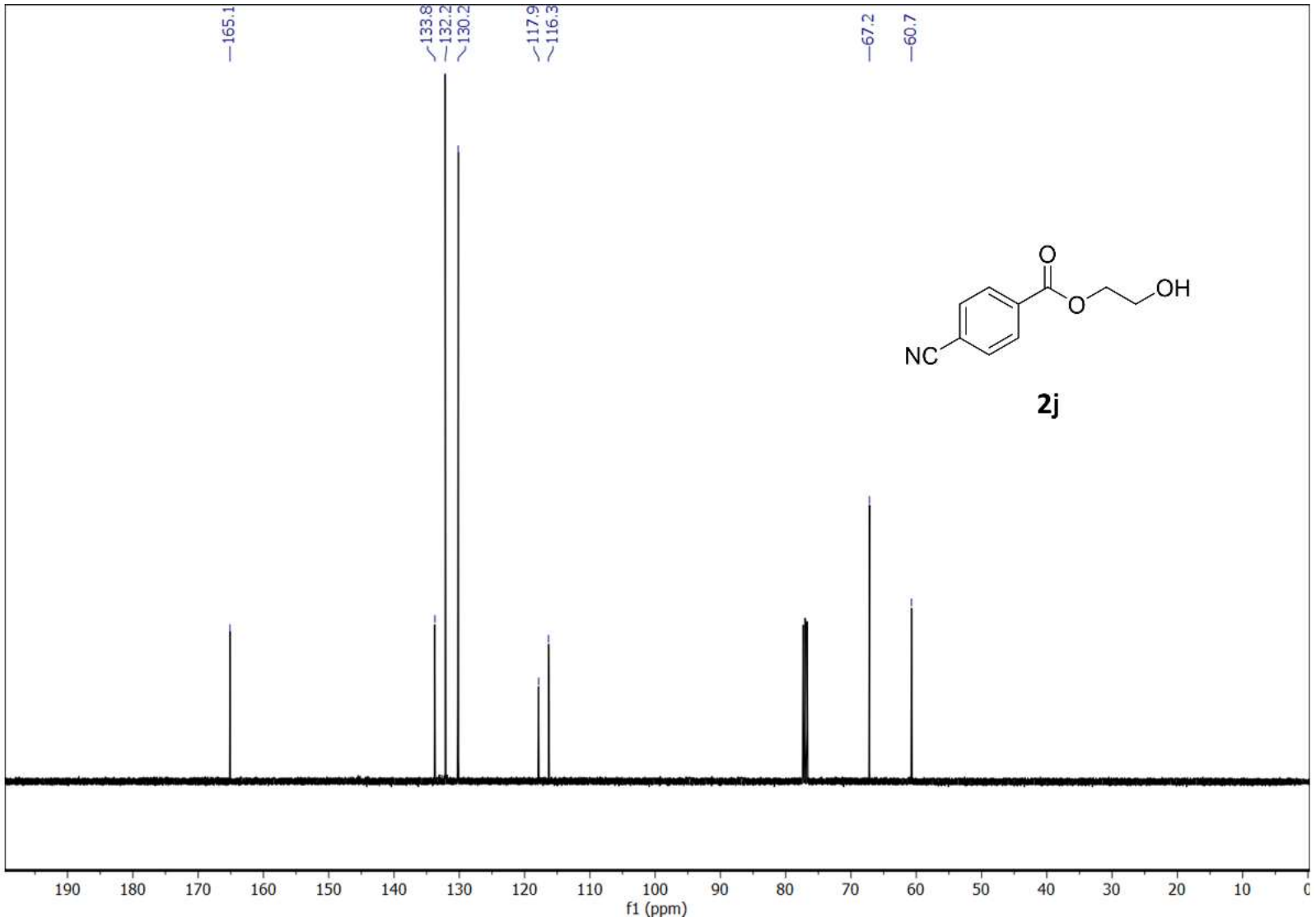

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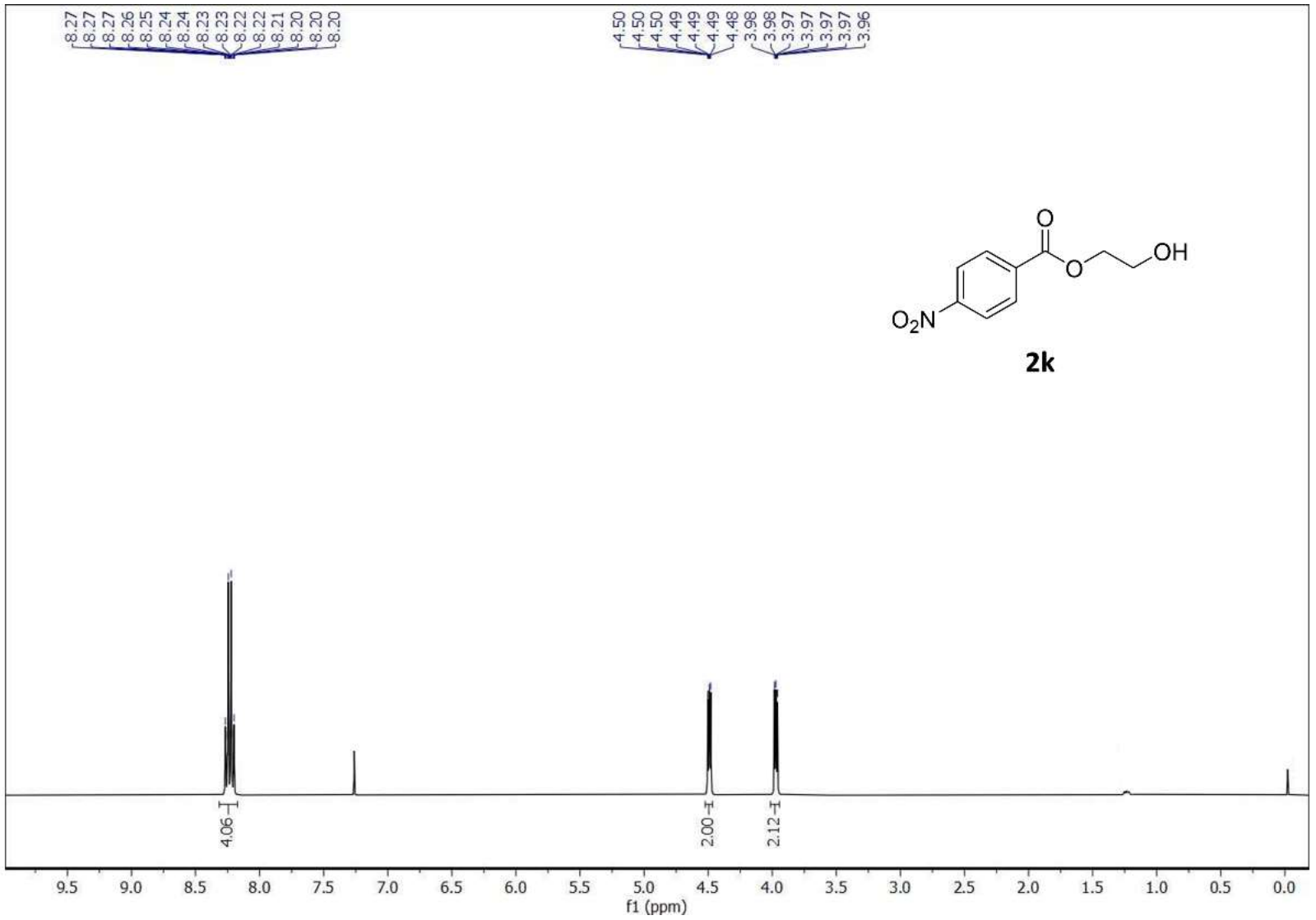

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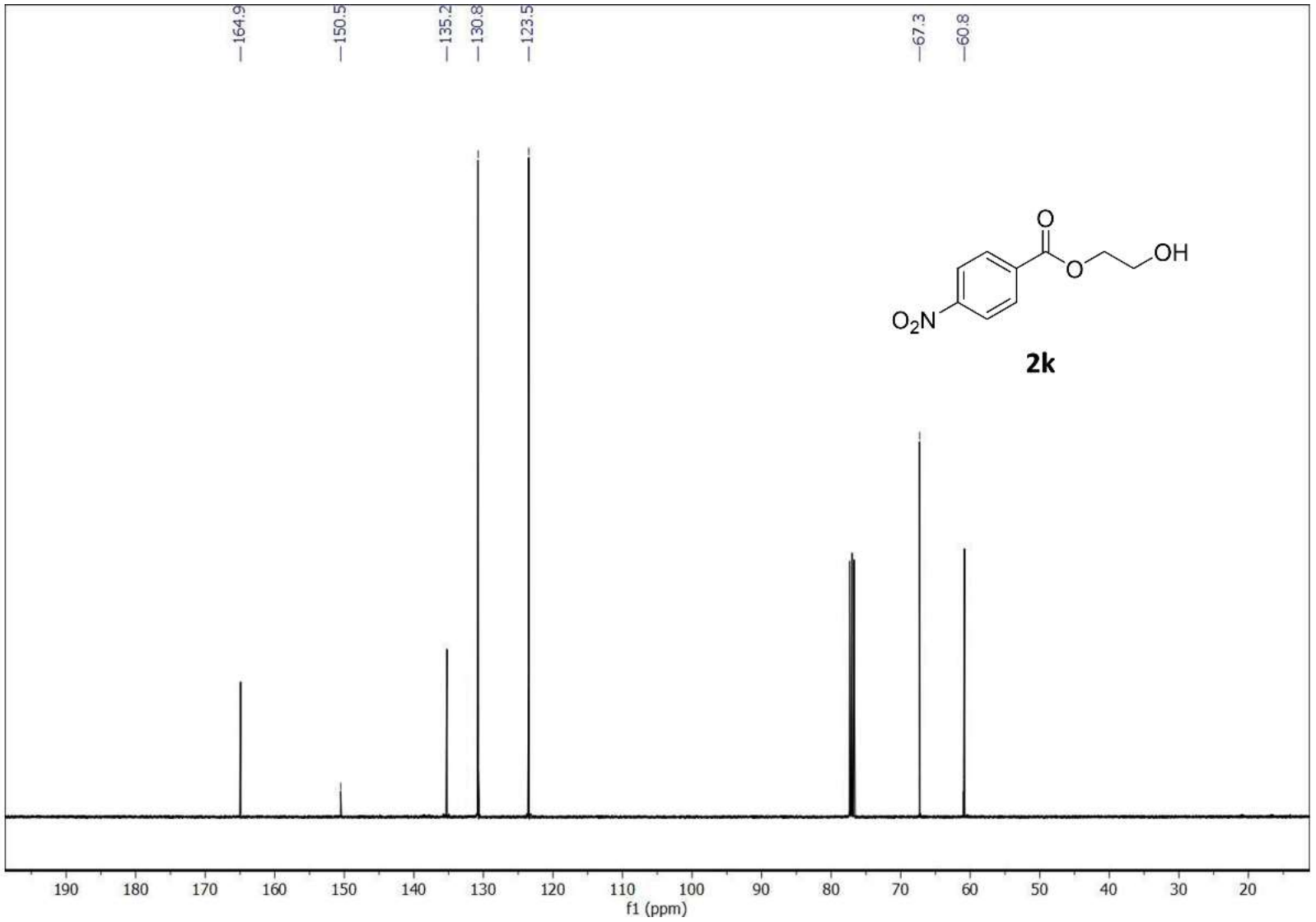
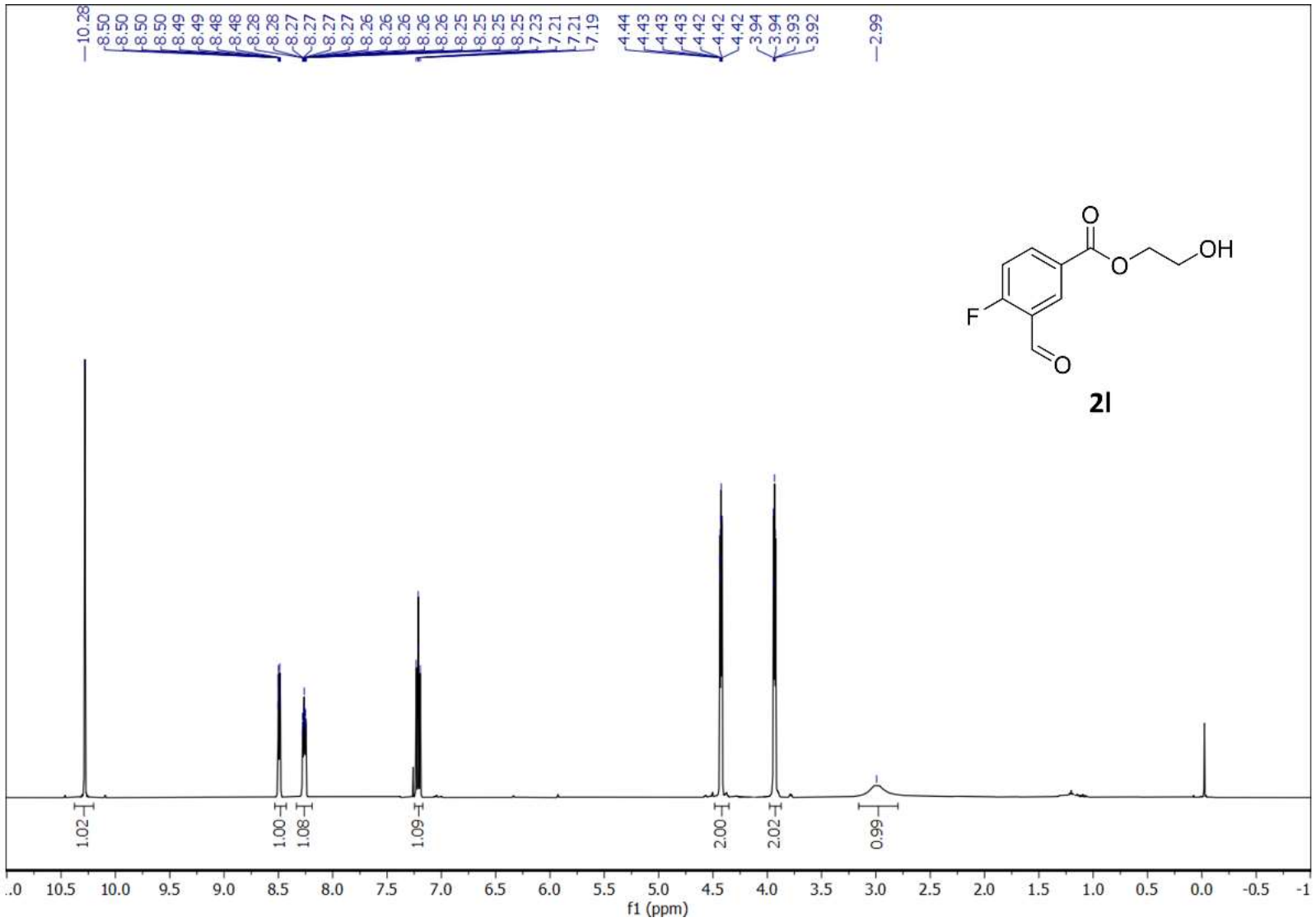


^{1}H NMR 400.12 MHz, $CDCl_3$



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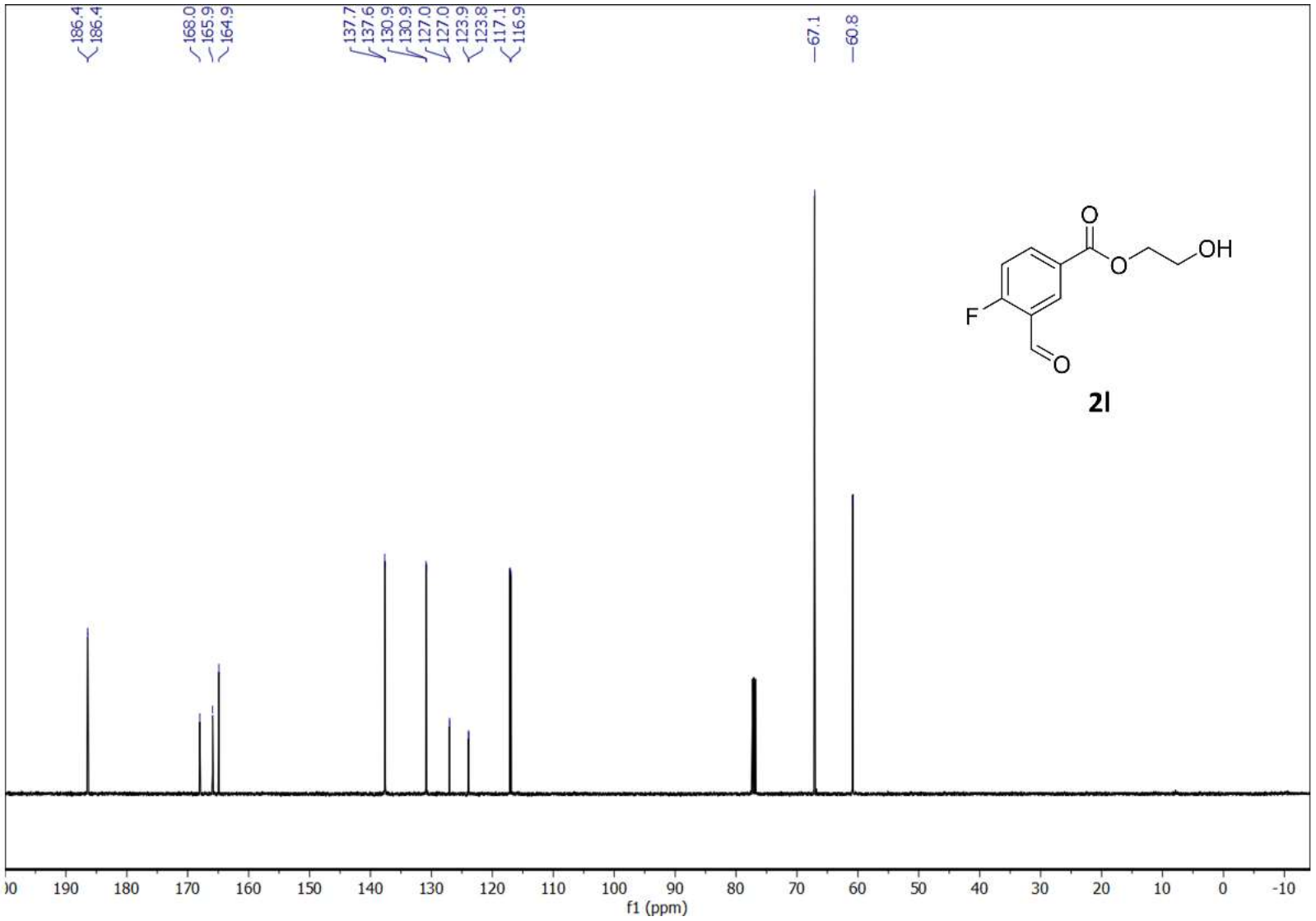

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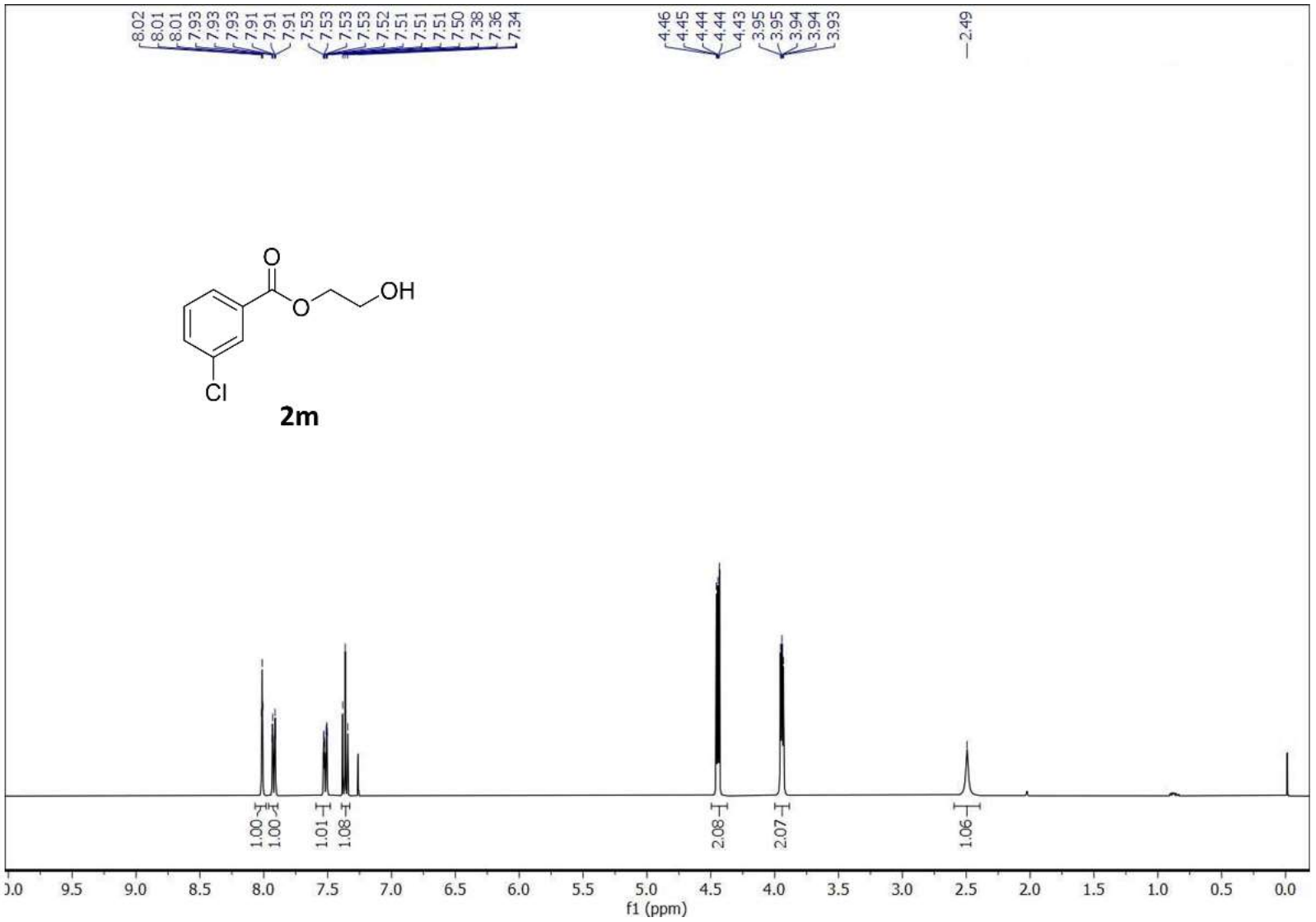

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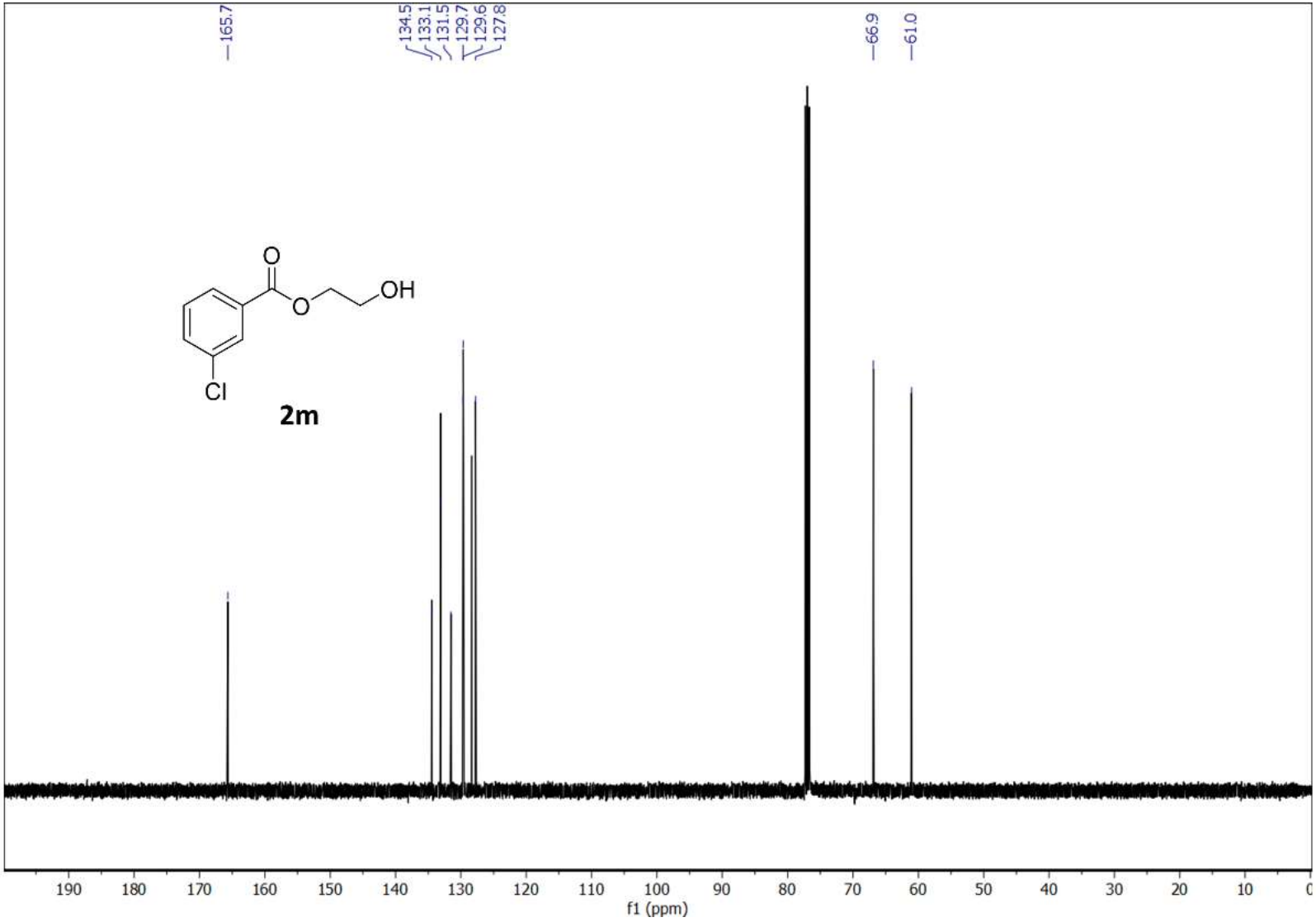

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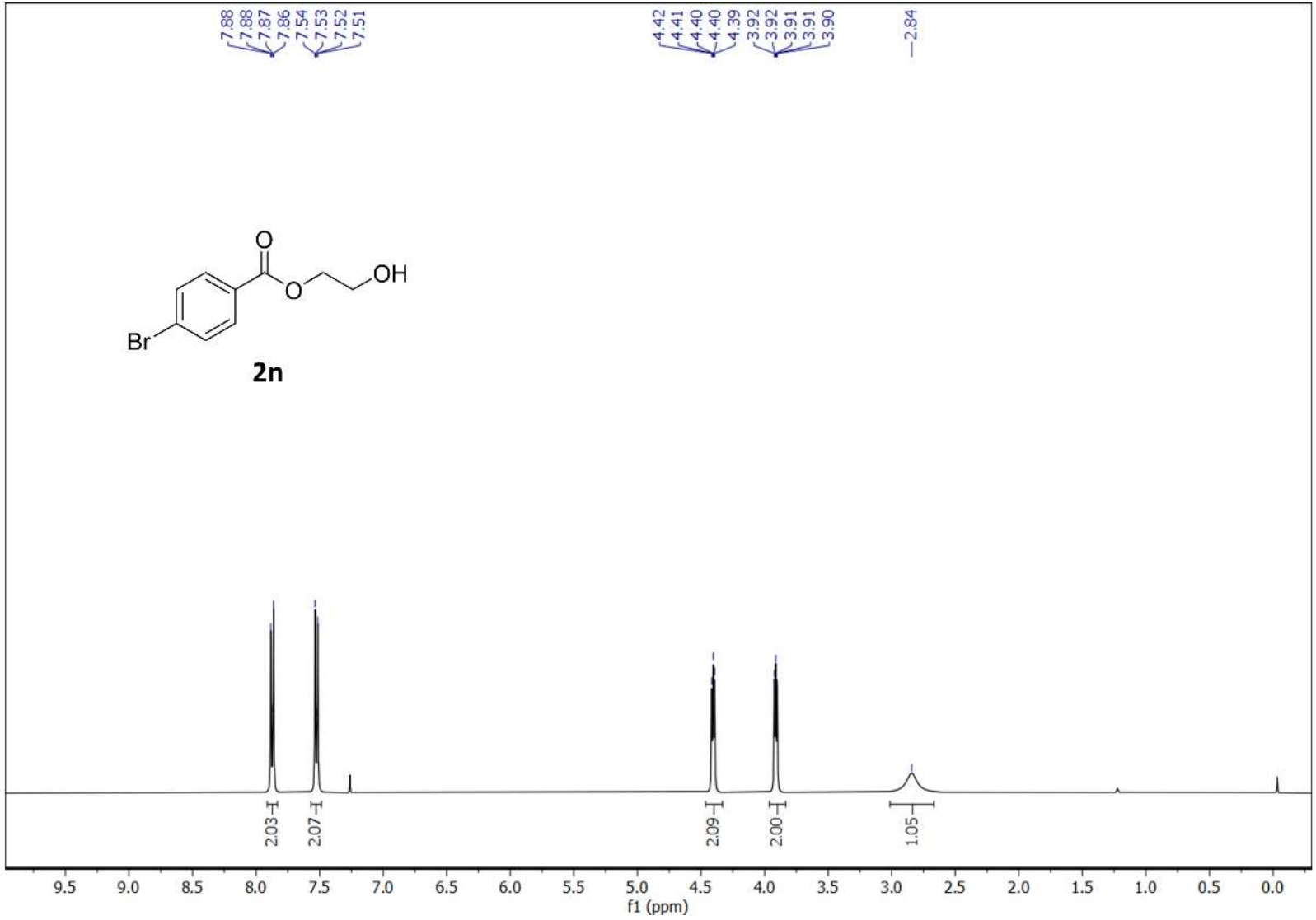

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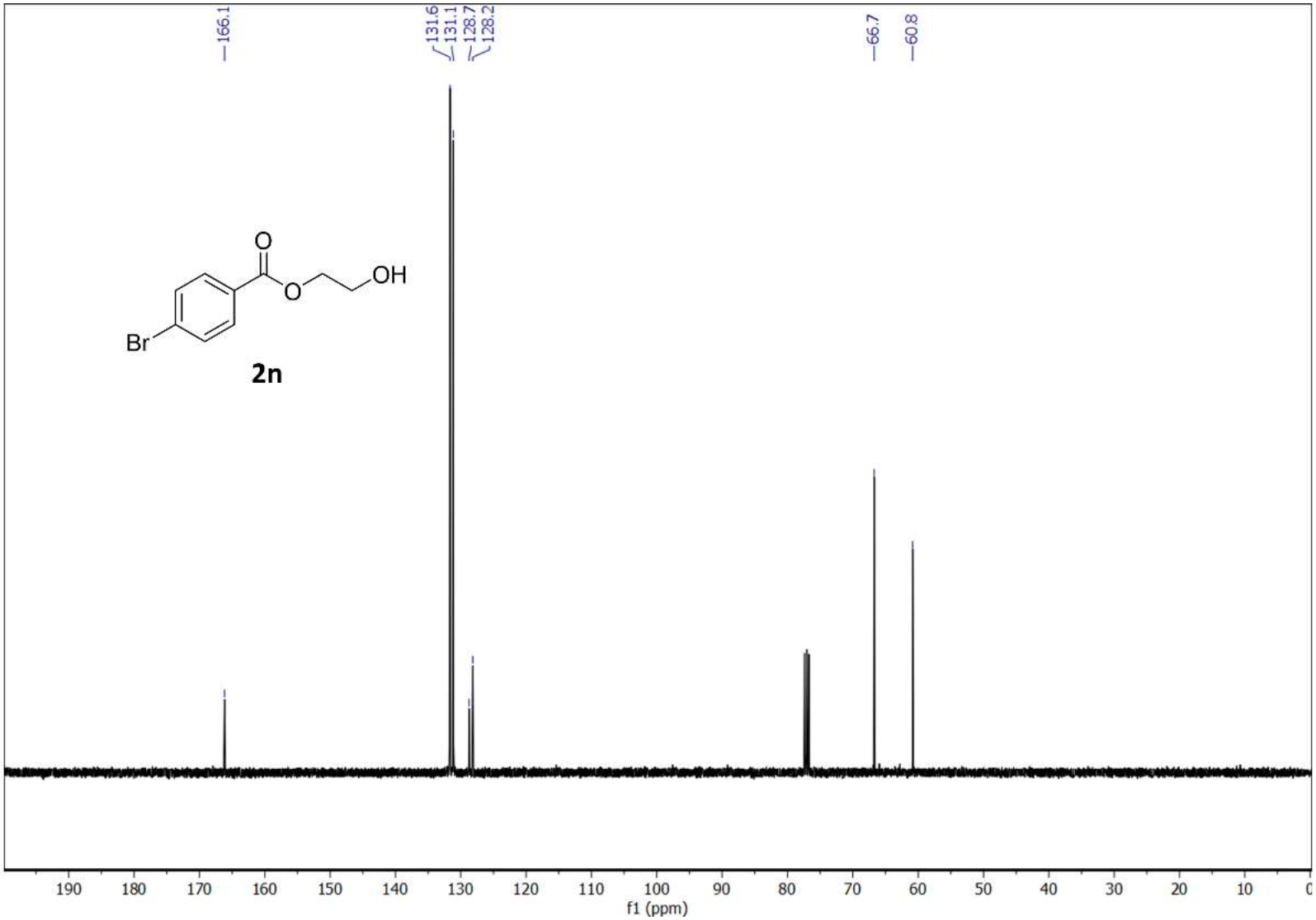

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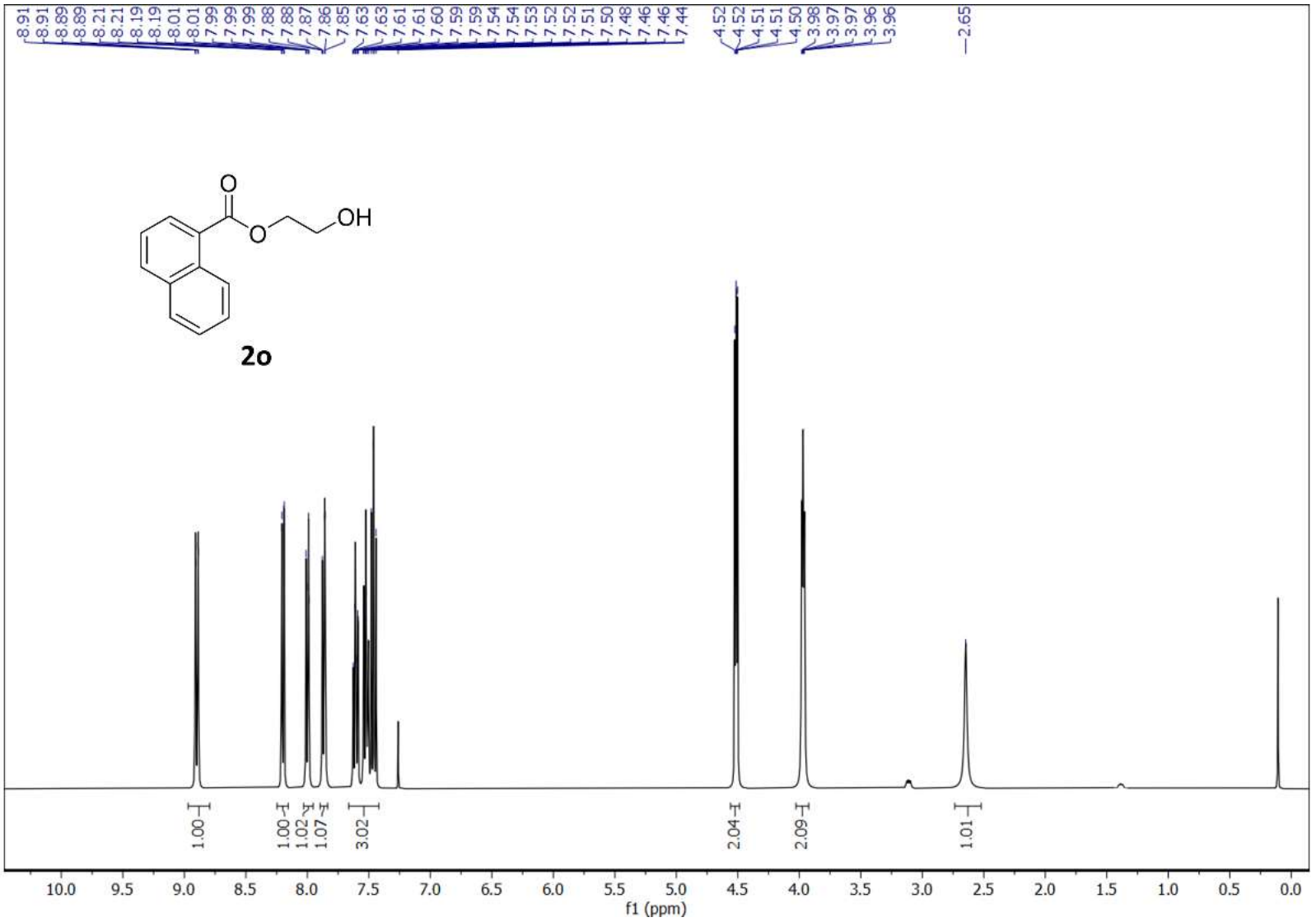

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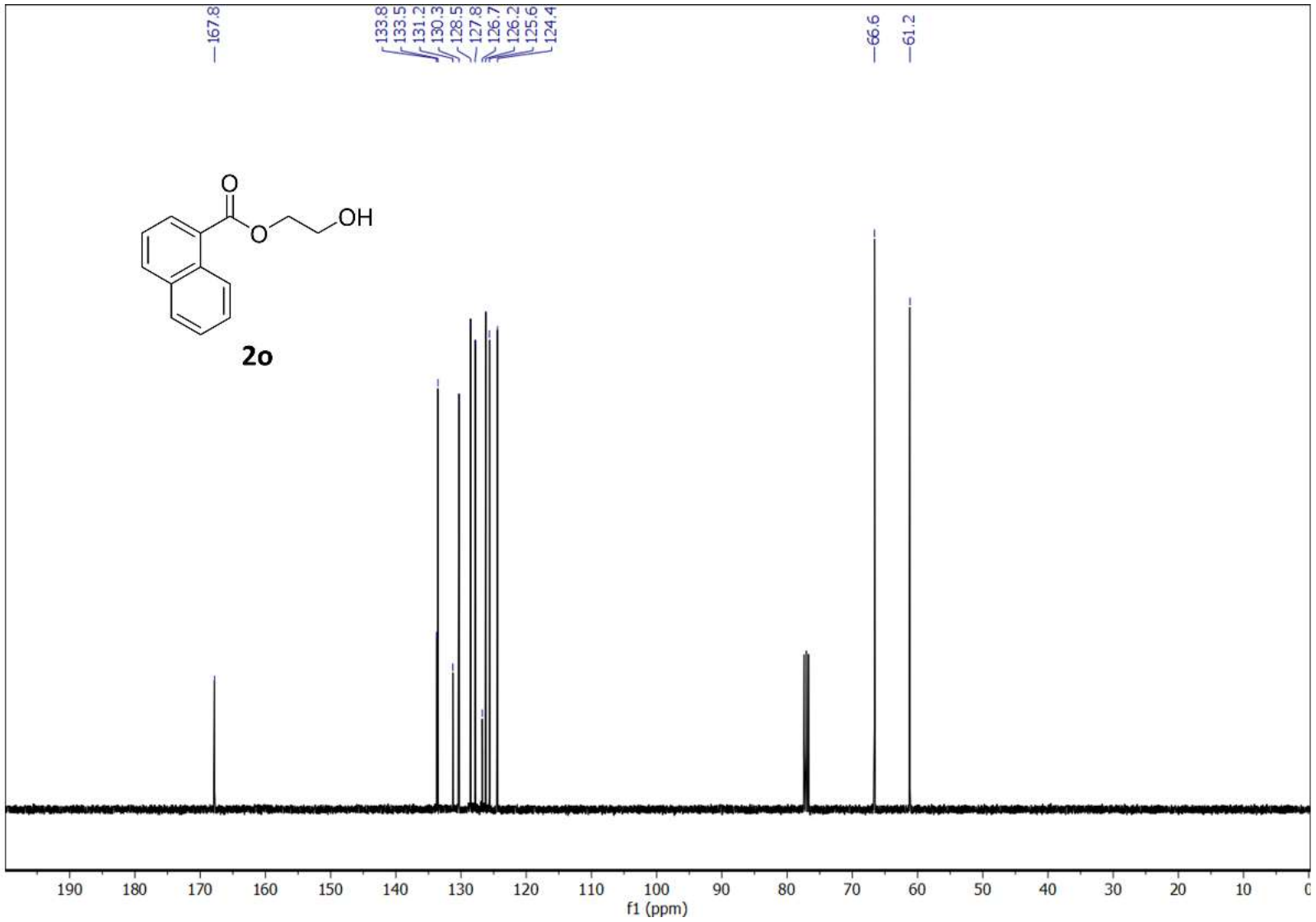

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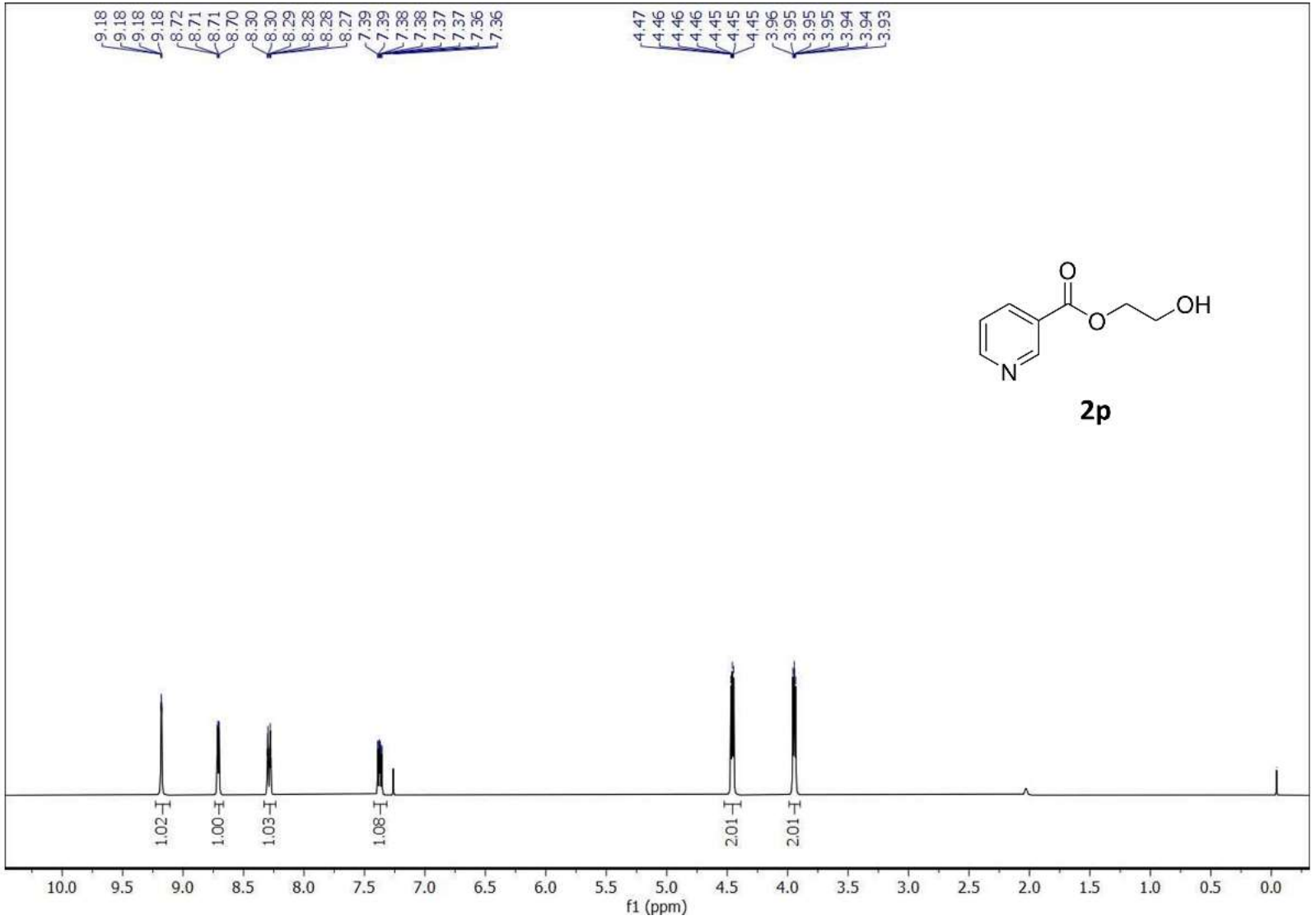

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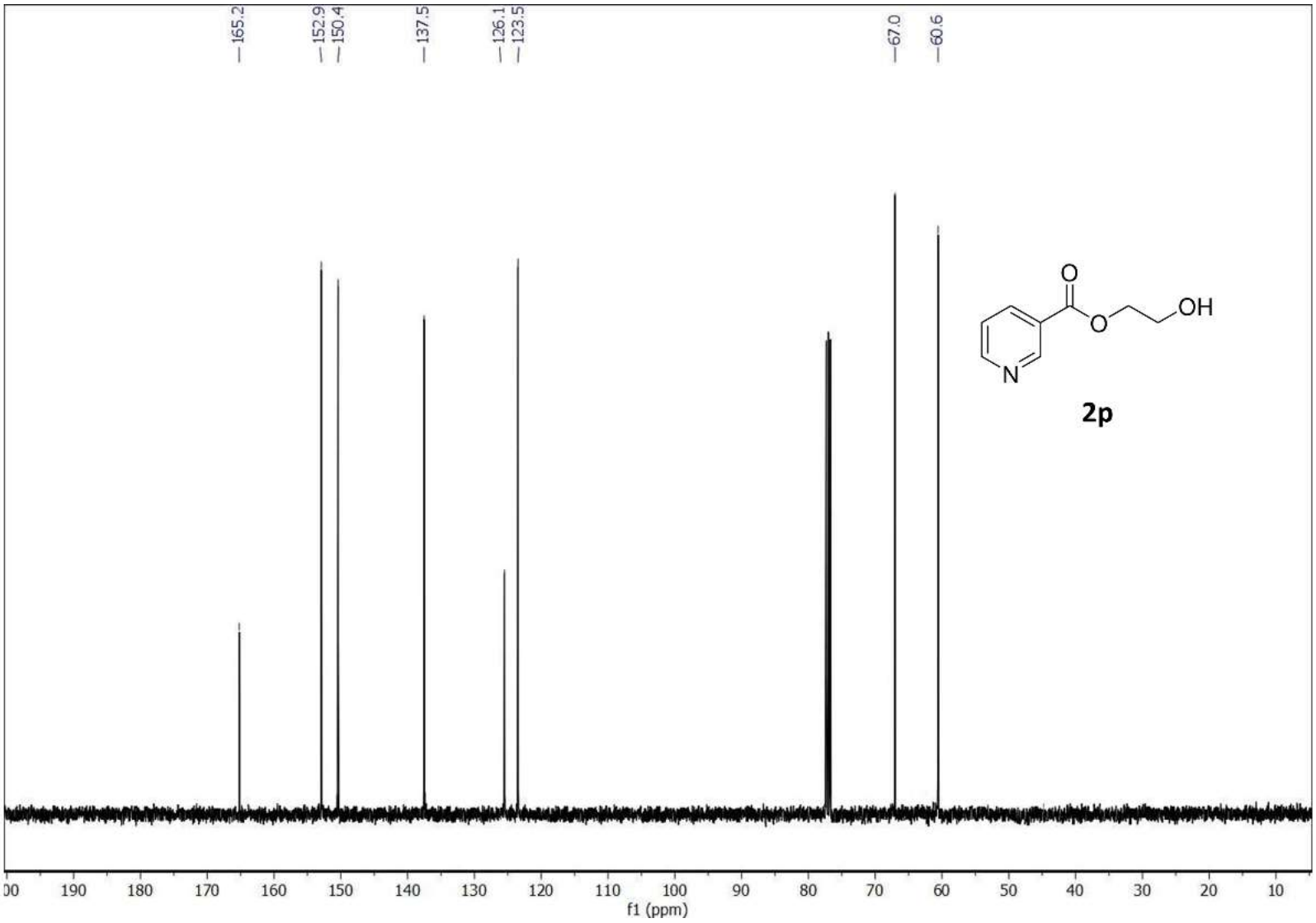

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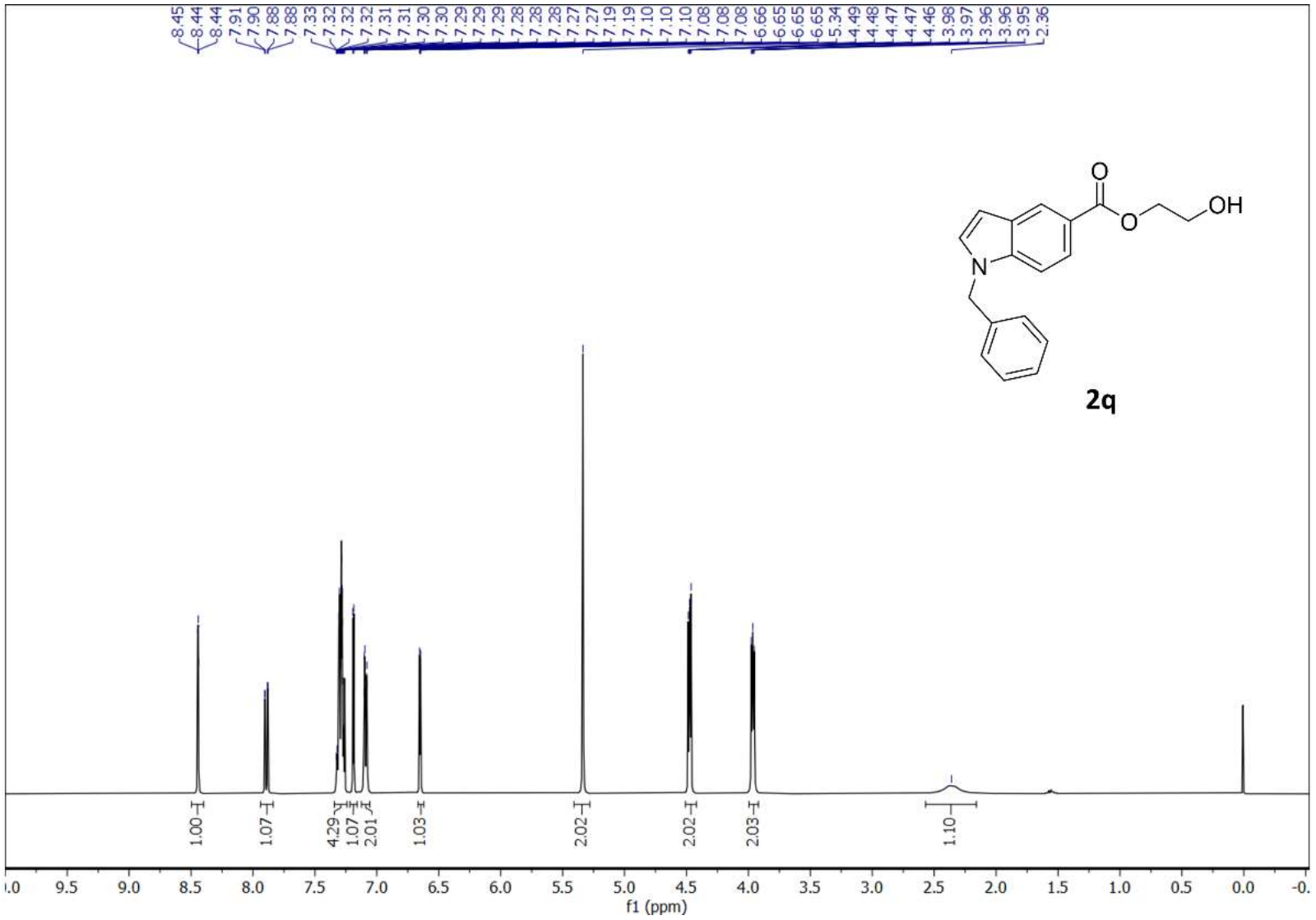

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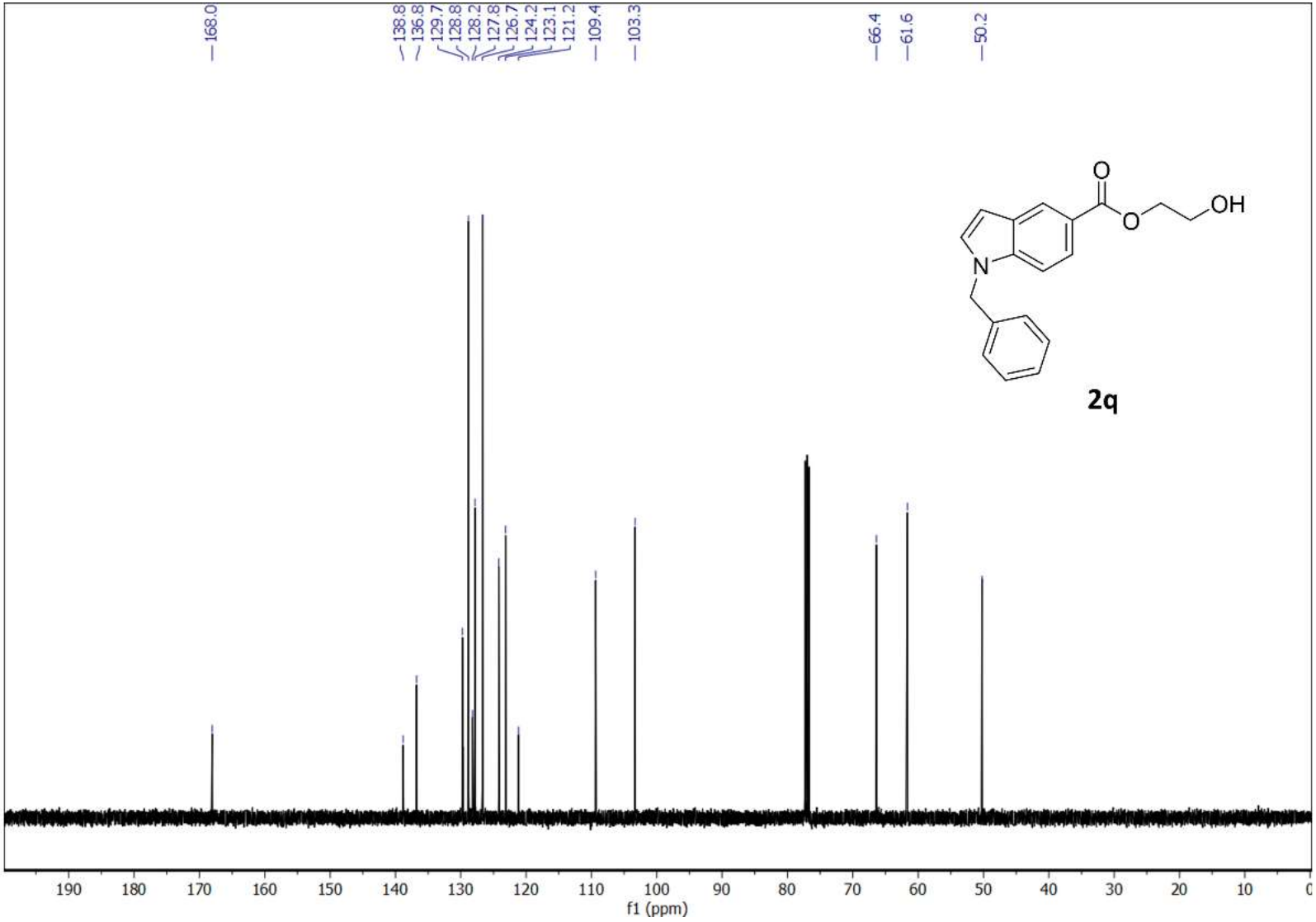

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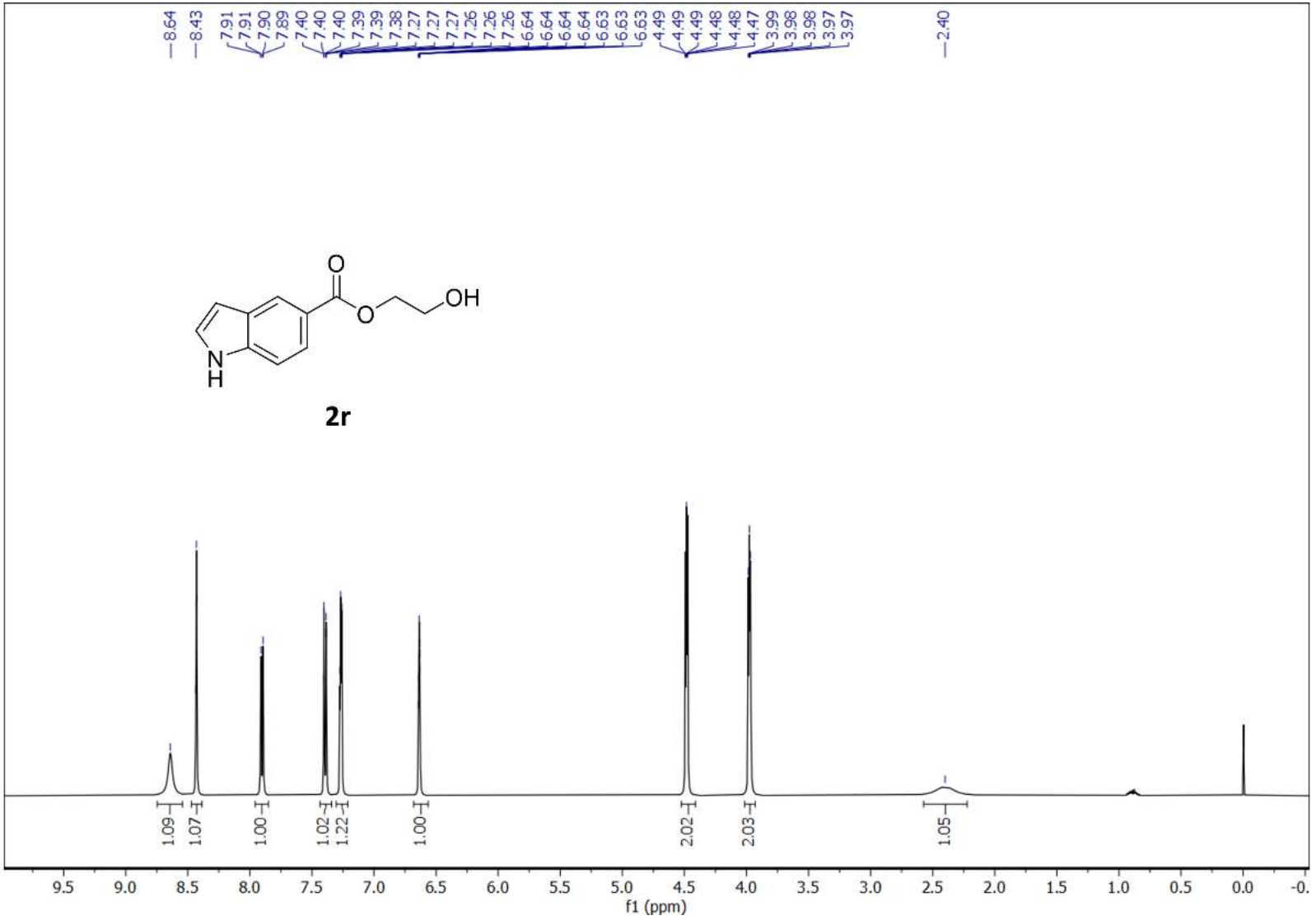

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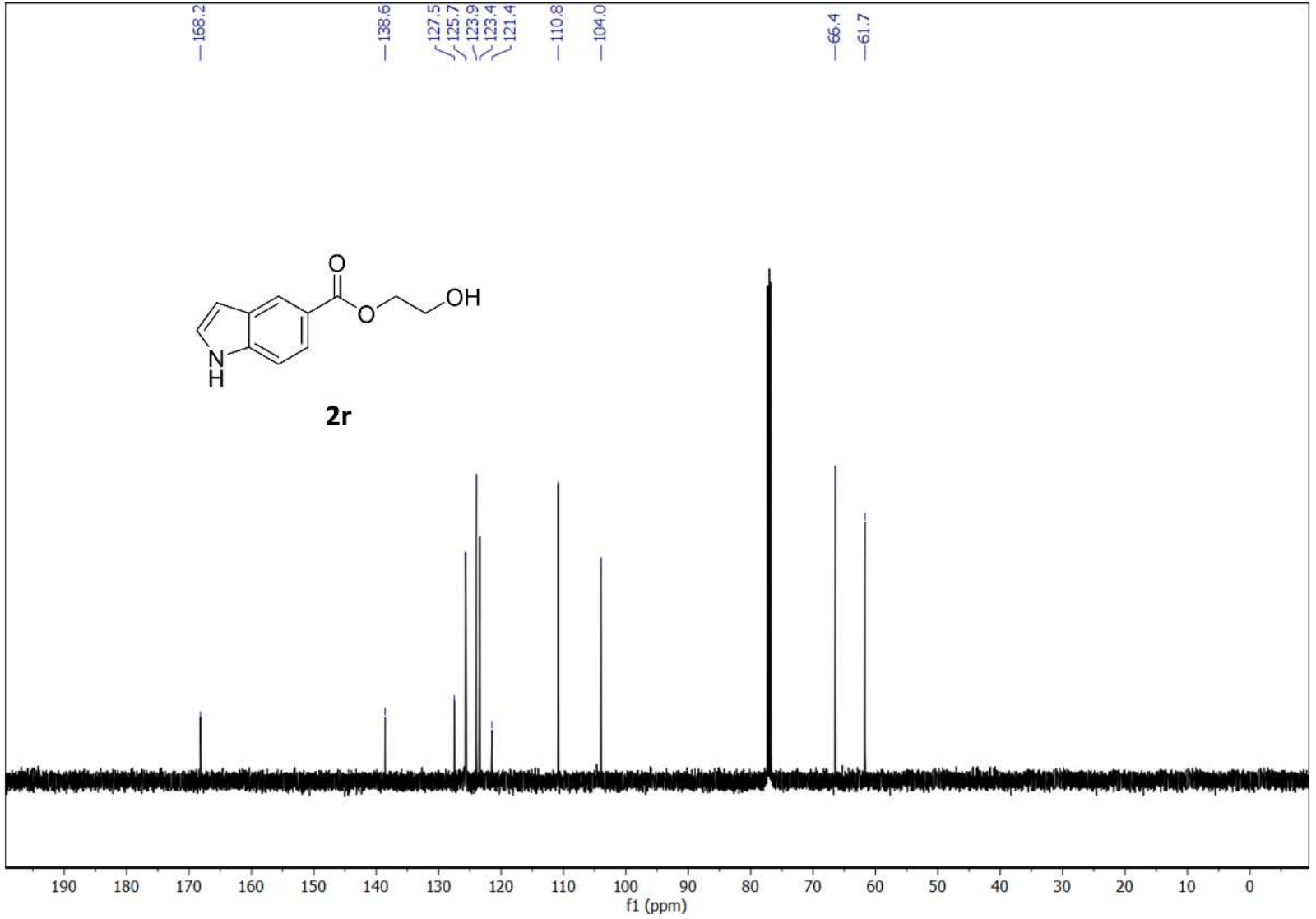
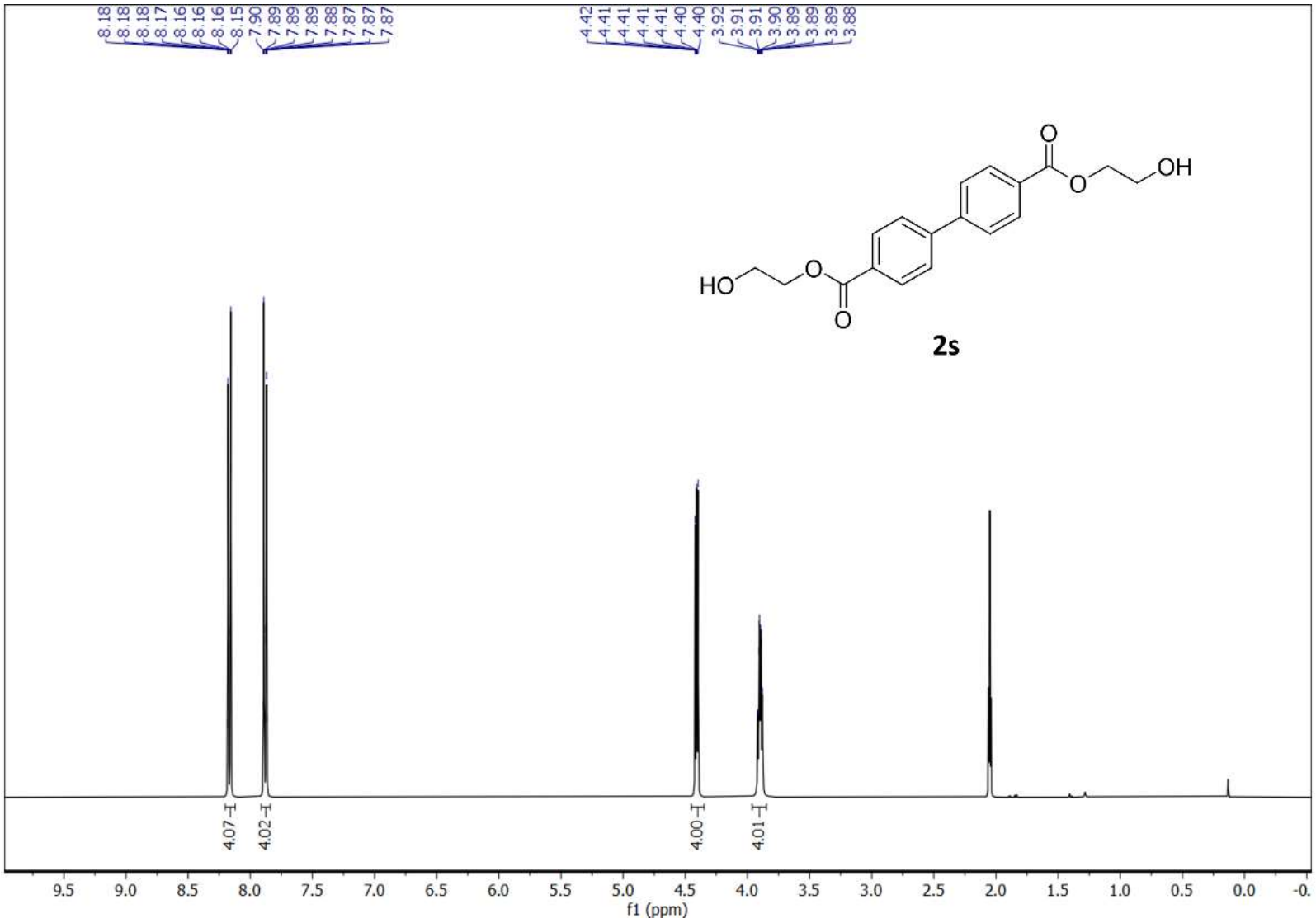


^{1}H NMR 400.12 MHz, Acetone-d_6



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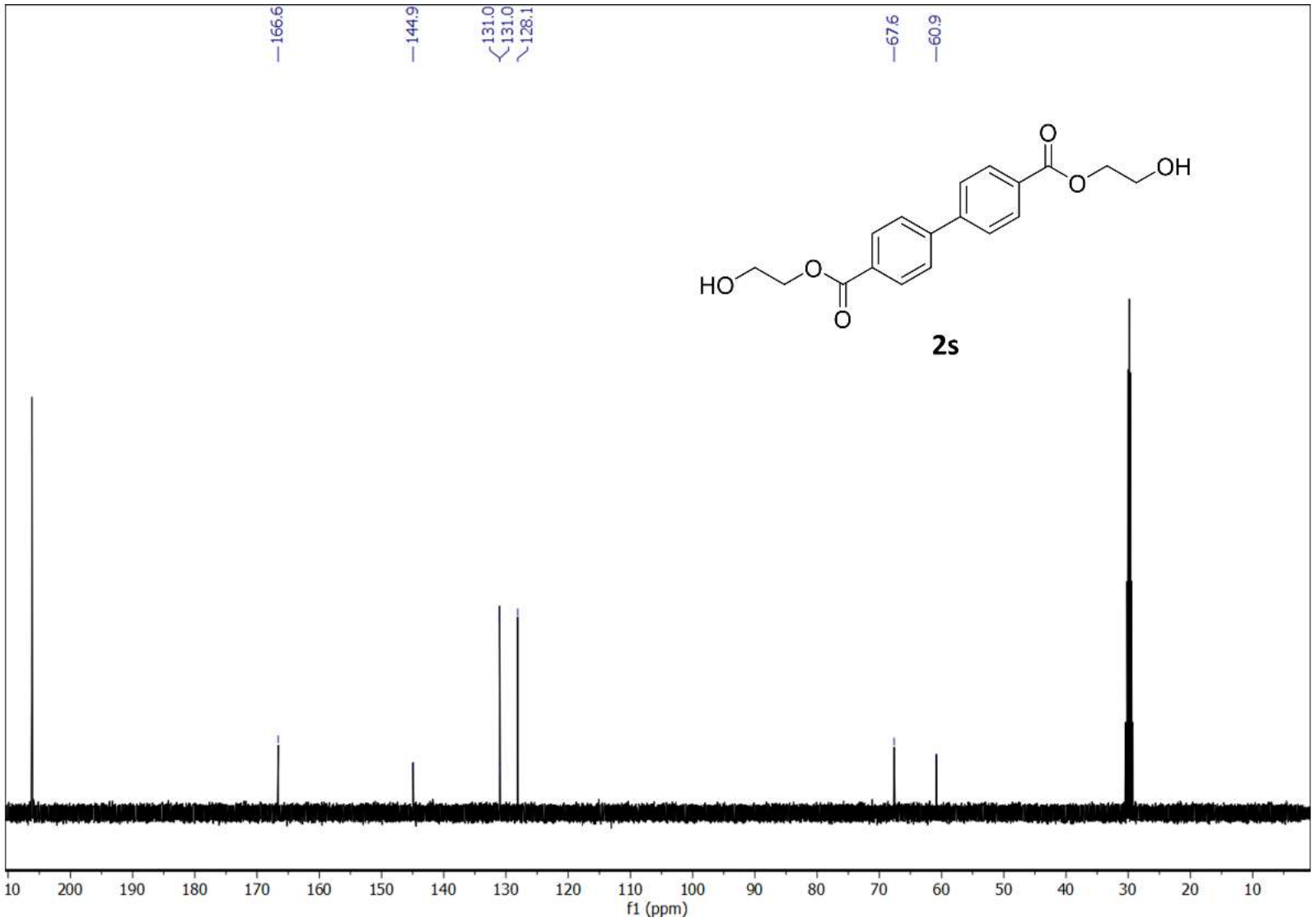
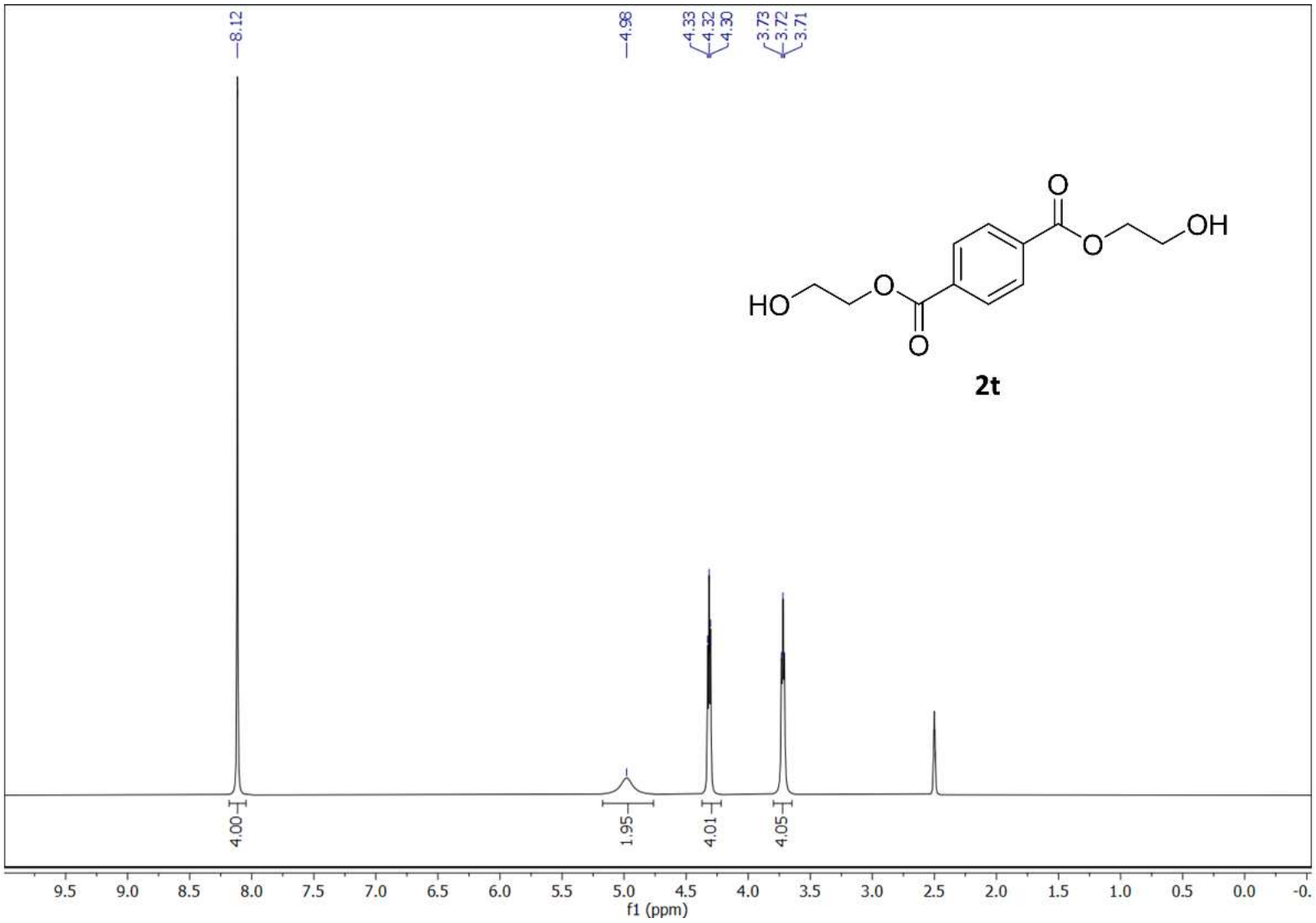
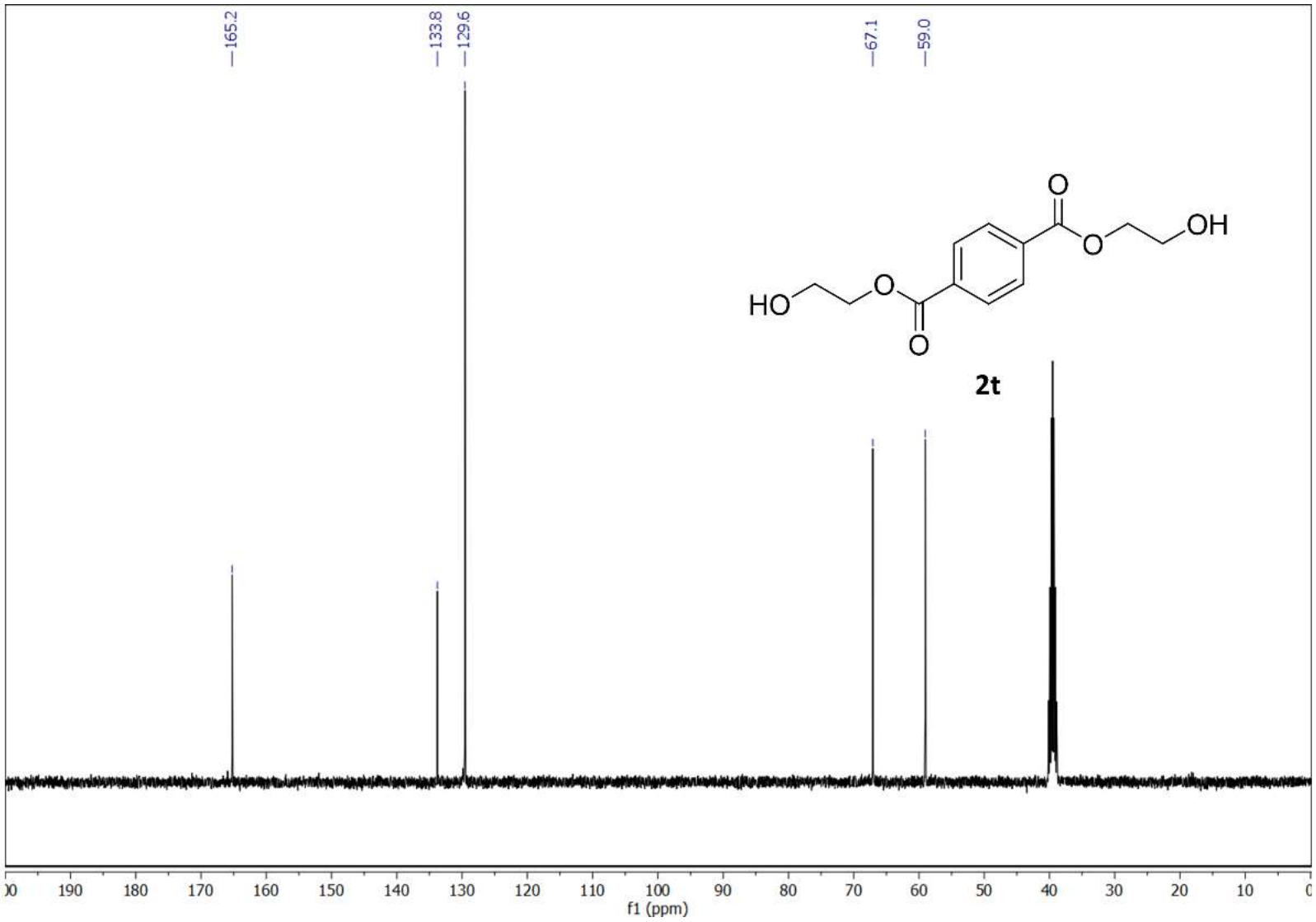


^{1}H NMR 400.12 MHz, DMSO-d_6



2t

^{13}C NMR 100.62 MHz, DMSO-d_6



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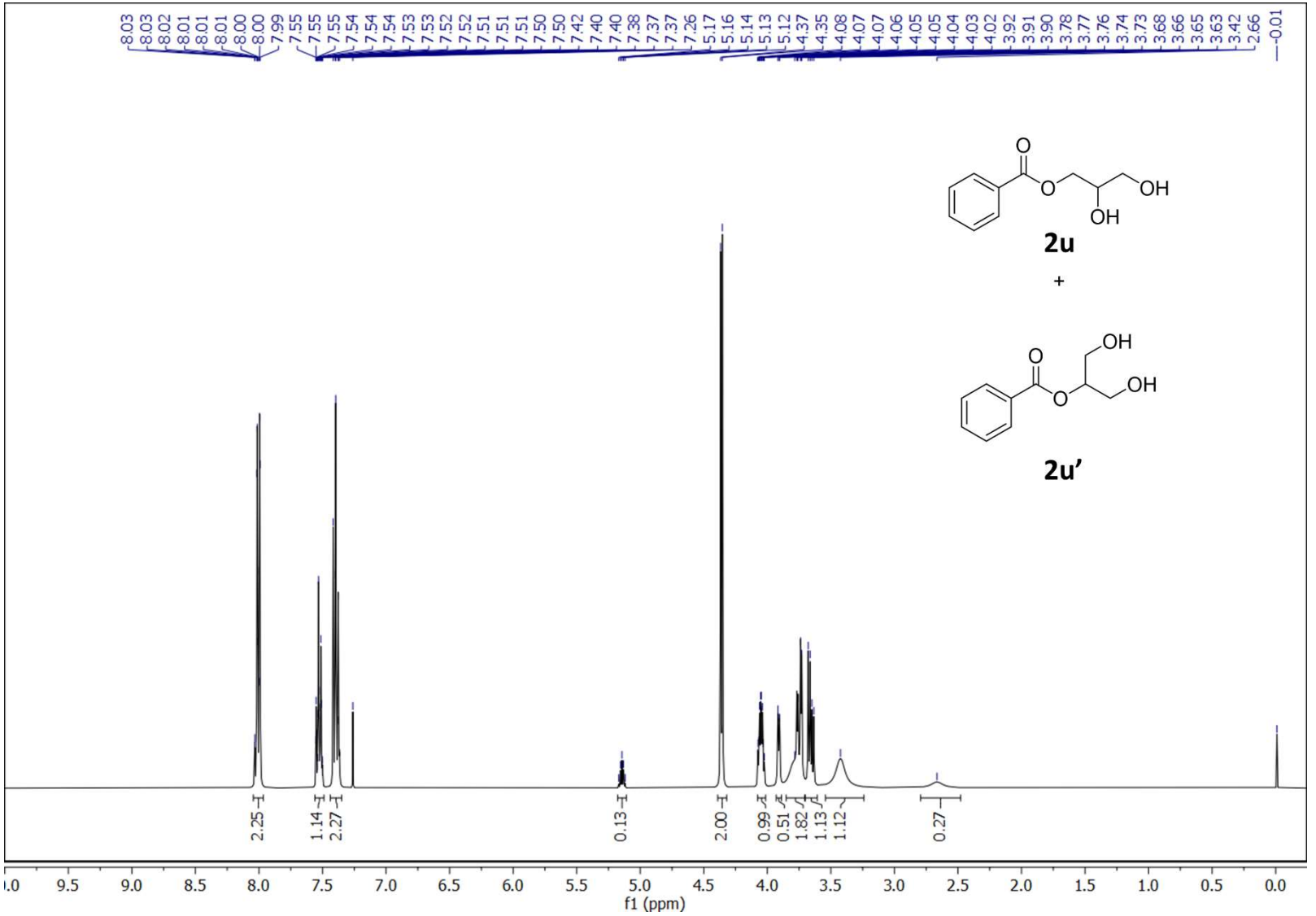

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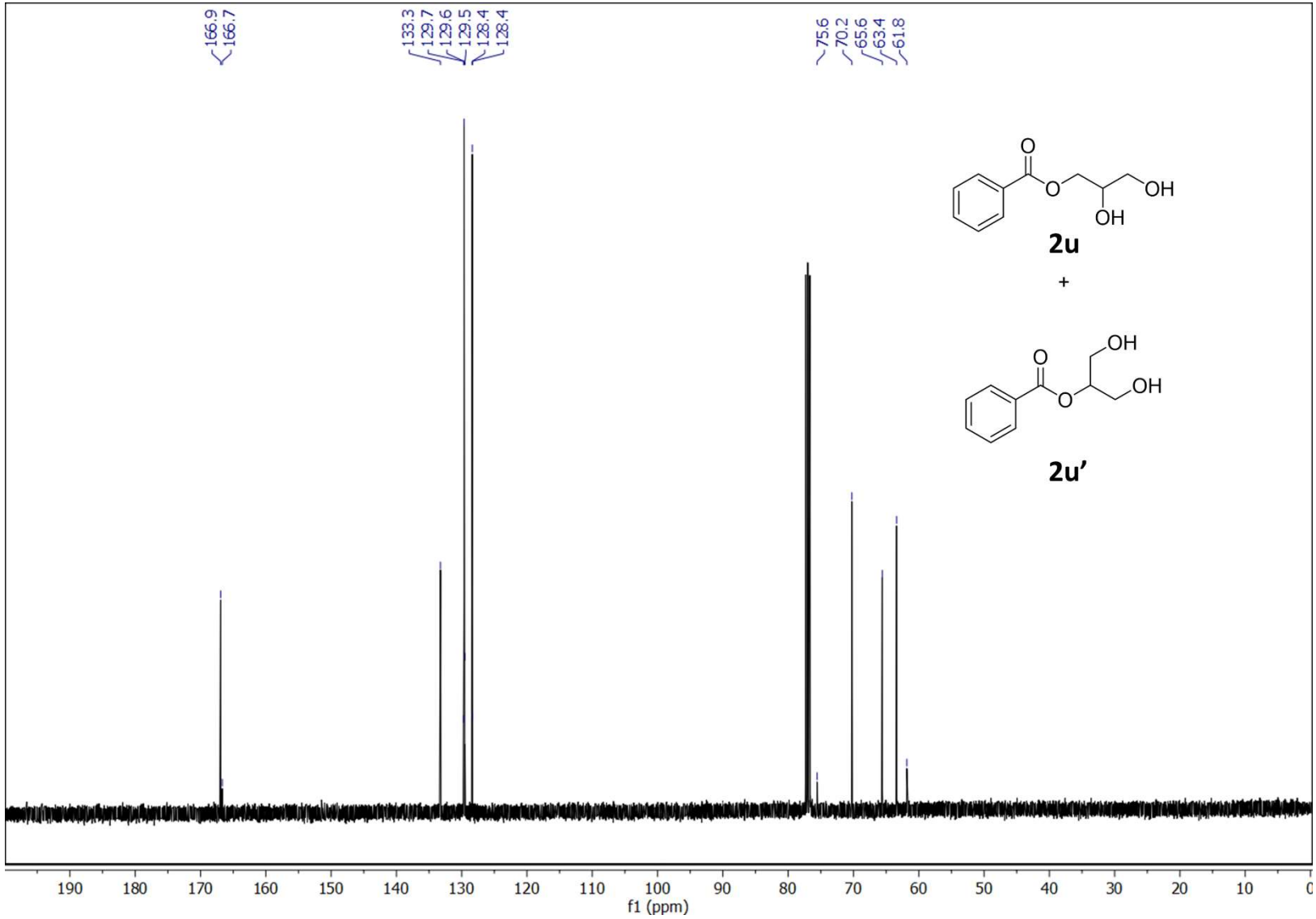

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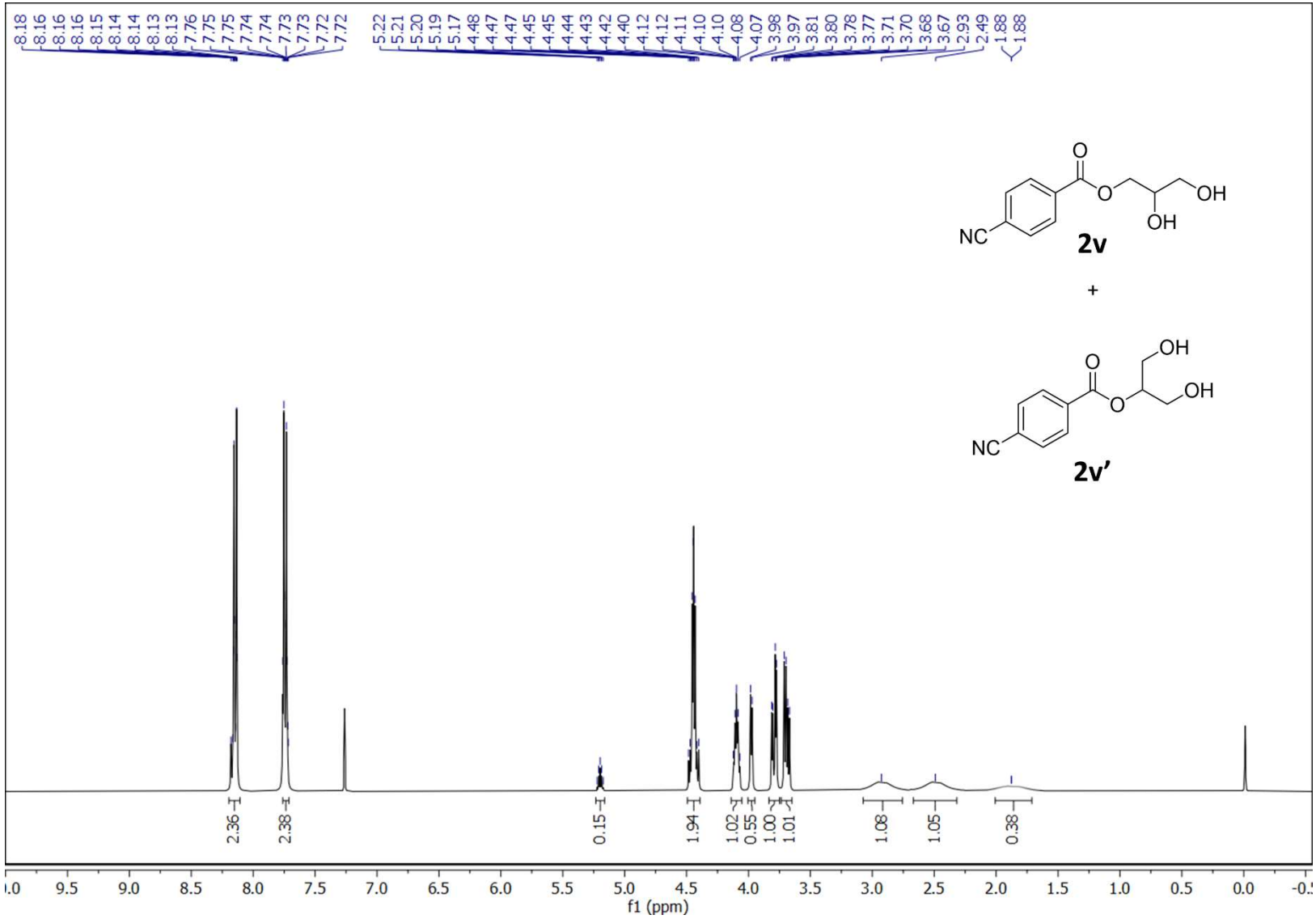

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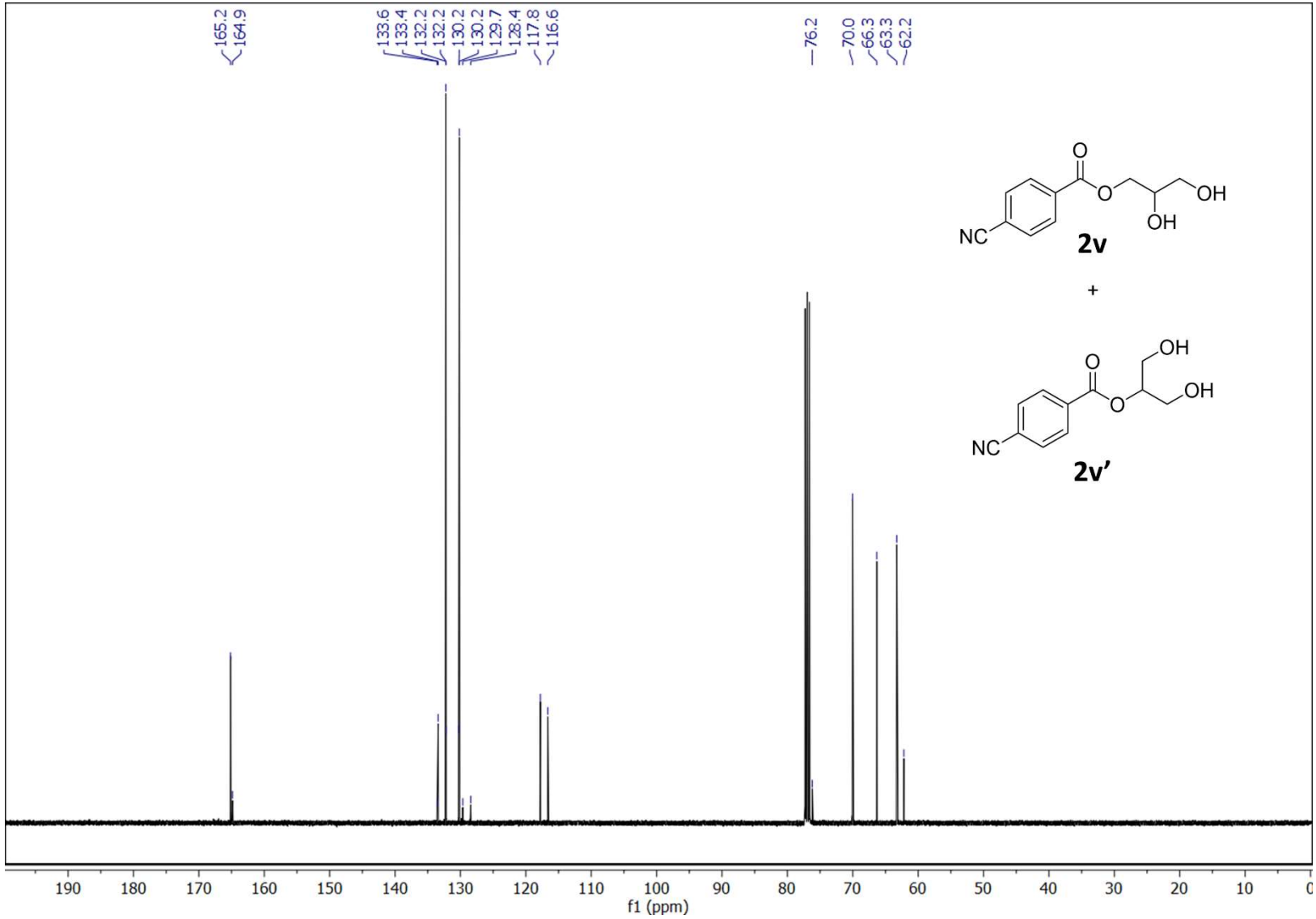

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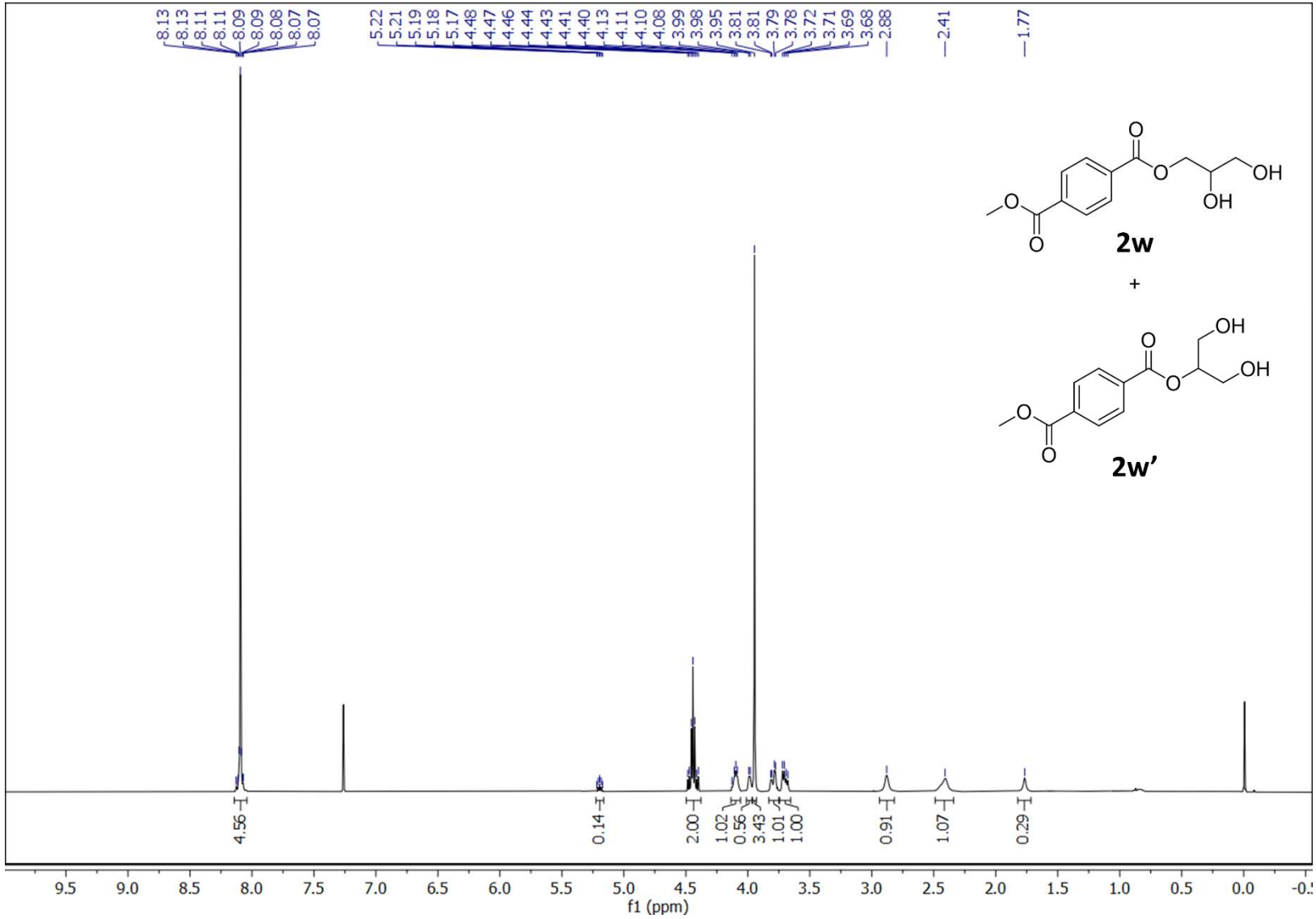

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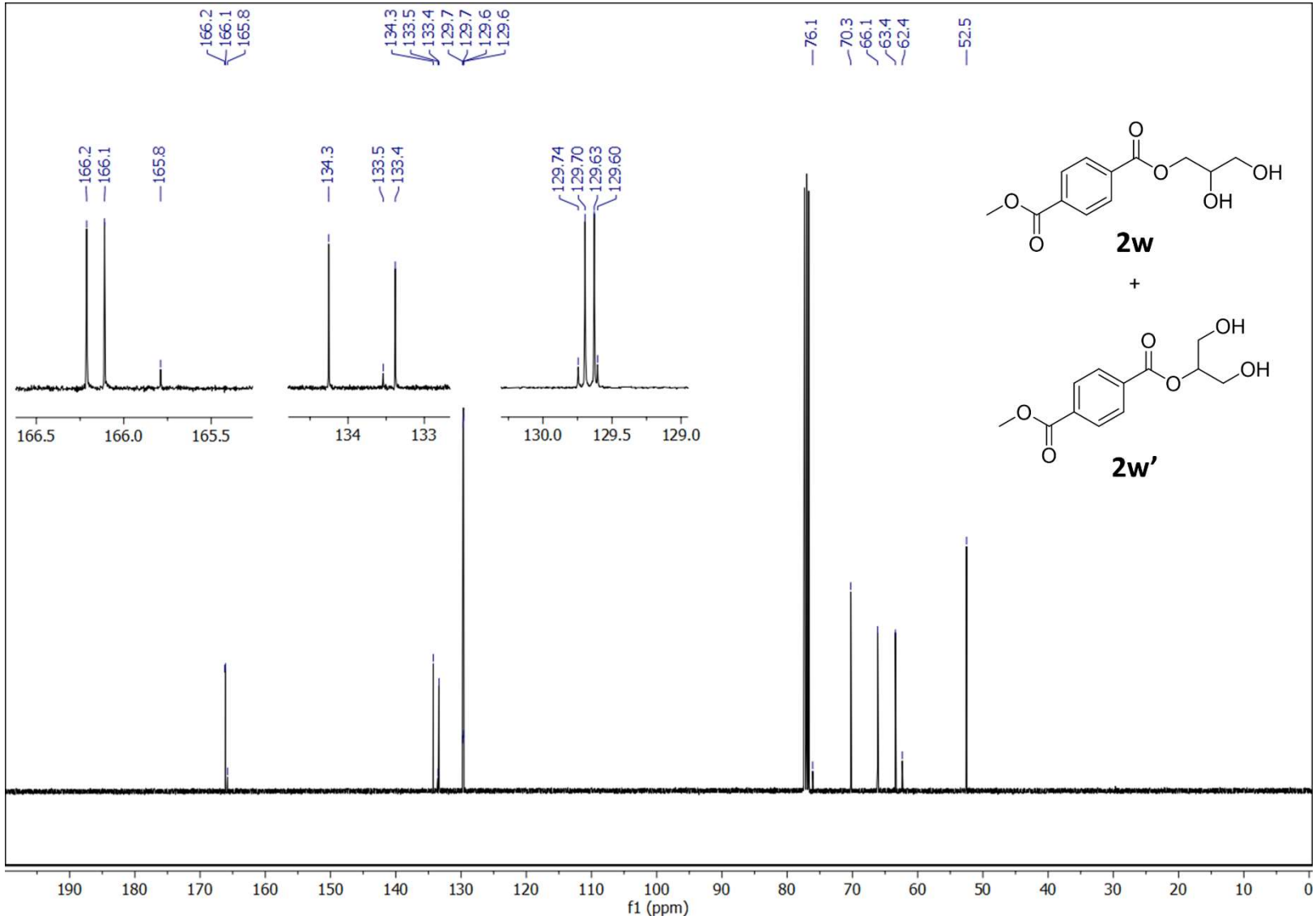

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