Supporting Information

Cobalt-Catalyzed Direct α-hydroxymethylation of Amide with Methanol as a C1 Source

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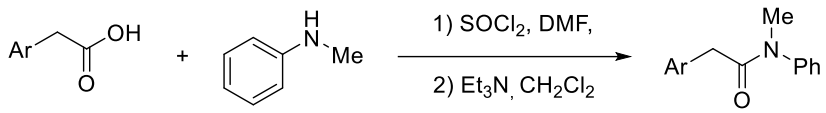
1. General information

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury-400 Plus or Agilent Technologies DD2 (600 MHz) spectrometer in $CDCl_3$ or CD_3OD. Chemical shifts (δ) for NMR were quoted in ppm relative to the solvent peak (7.26 ppm for ^{1}H and 77.00 ppm for ^{13}C in $CDCl_3$, 3.31 ppm for 1H and 49.00 ppm for ^{13}C in CD_3OD). High-resolution mass spectra (HRMS) (ESI) were obtained with Bruker Daltonics APEXII 47 e FT-ICR, Agilent QTOF 700 or Agilent 1200 spectrometer. Melting points were measured on an XT4A apparatus (uncorrected). The reactions were monitored by TLC on silica gel plates (GF254). Reagents and solvents were commercially available, and were used without further purification. The reaction mixtures were purified by column chromatography over silica gel (PE-EtOAc).

2. Experimental Procedures

2.1 General experimental procedure for synthesis of 1.[1]



1a-1q

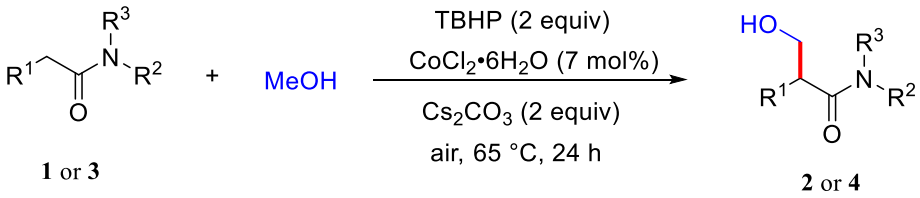
Arylacetic acid (5.0 mmol) was dissolved in dry CH_2Cl_2 (4.0 mL) and thionyl chloride (0.5 mL) were added at 0 °C. Add DMF (36.5 mg, 0.5 mmol, 10 mol%) dropwise to the reaction mixture. Stir the reaction mixture for 10 minutes. The resulting solution was decompressed to remove the solvent, and the residue was dissolved in dry CH_2Cl_2 (40 mL). Amine (5.0 mmol) and Et_3N (6.0 mmol) were slowly added to the mixture. The reaction was stirred overnight at room temperature. TLC was used to detect the reaction. After the reaction was completed, the reaction mixture was washed with ethyl acetate (20 mL) and saturated $NaHCO_3$ (3×30 mL), and the organic phase was dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the coarse residue was purified by silica gel chromatography (PE : EtOAc = 10:1) to get the pure compounds **1a-1q**.

2.2 General experimental procedure for synthesis of 3.[2]

3a-3q

Amine (10.0 mmol) and Et_3N (6.0 mmol) were dissolved in CH_2Cl_2 (30 mL) and aryl chloride (5.0 mmol) was slowly added at 0 °C. The mixture reacts overnight at room temperature. TLC was used to determine the reaction. After the reaction was completed, the reaction mixture was respectively extracted three times by HCl (1M) and DCM. Dry the organic phase with sodium sulfate, and concentration of organic phases under reduced pressure. The crude product was purified by column chromatography (PE : EtOAc = 10:1) to get the pure compounds **3a-3q**.

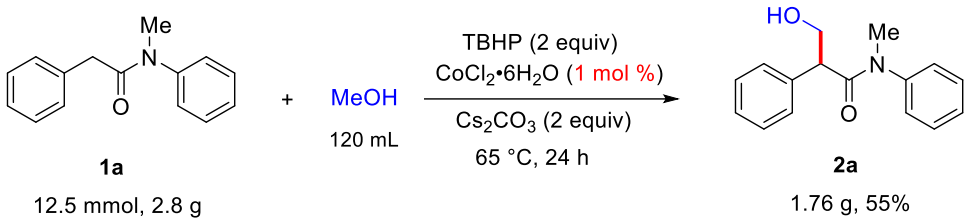
2.3 General procedure for α-hydroxymethylation of amide



1 or **3** **2** or **4**

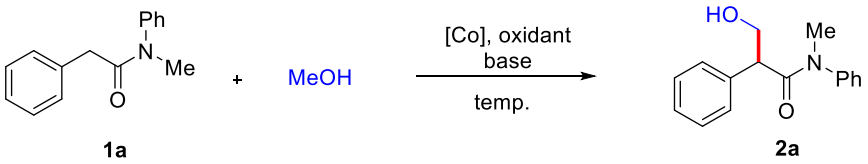
$CoCl_2 \cdot 6H_2O$ (5.0 mg, 0.021 mmol, 7 mol%), Cs_2CO_3 (231.5 mg, 0.6 mmol), amide (**1** or **3**, 0.3 mmol) and MeOH:*n*-Hexane 10 : 1 (3 mL) were sequentially added into a 25 mL Schleck tube. Then TBHP (70 wt% in H_2O) (83 μL, 0.6 mmol) was added to the stirred reaction system. The reaction mixture was stirred at 65 °C until the reaction was complete (monitored by TLC). The reaction solution was cooled at room temperature and quenched with NH_4Cl (2 mL), extracted with ethyl acetate (3×5 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 5:1-3:1) to afford the pure products (**2** or **4**).

2.4 Procedure for gram-scale hydroxymethylation of amide 1a



$CoCl_2·6H_2O$ (32.1 mg, 0.125 mmol, 1.0 mol%), Cs_2CO_3 (8.1 g, 25.0 mmol, 2 equiv), MeOH:*n*-Hexane 10 : 1 (120 mL) and amide (12.5 mmol) were sequentially added into a 200 mL round-bottom flask. Then TBHP (70 wt% in H_2O) (2.1 mL, 25.0 mmol) was added to the stirred reaction system. The reaction mixture was stirred at 65 °C for 1 h. The reaction solution was cooled at room temperature and quenched with NH_4Cl (20 mL), extracted with EtOAc (3×30 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 5:1) to afford the pure product **2a** (1.76 g, 55%).

3. Table S1. Optimization of reaction conditions.

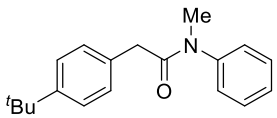


Entry	[Co] (mol%)	Oxidation (eq)	Base (eq)	Temp. (°C)	Yield 2a (%)
1	$CoCl_2·6H_2O$ (7)	TBHP (2)	Cs_2CO_3 (2)	65	77
2	$CoCl_2·6H_2O$ (7)	H_2O_2 (2)	Cs_2CO_3 (2)	65	<1
3	$CoCl_2·6H_2O$ (7)	O_2	Cs_2CO_3 (2)	65	NR
4	$Co(PO_4)_2$ (7)	TBHP (2)	Cs_2CO_3 (2)	65	73
5	$Co(OAc)_2$ (7)	TBHP (2)	Cs_2CO_3 (2)	65	75
6	$CoCO_3$ (7)	TBHP (2)	Cs_2CO_3 (2)	65	74
7	$Co(NO_3)_2·6H_2O$ (7)	TBHP (2)	Cs_2CO_3 (2)	65	47
8	$CoCl_2·6H_2O$ (7)	TBHP (2)	K_2CO_3 (2)	65	22
9	$CoCl_2·6H_2O$ (7)	TBHP (2)	K_3PO_4 (2)	65	26
10	$CoCl_2·6H_2O$ (7)	TBHP (2)	Na_2CO_3 (2)	65	<1

11	$CoCl_2·6H_2O$ (7)	TBHP (2)	DABCO (2)	65	NR
12	$CoCl_2·6H_2O$ (7)	TBHP (2)	NEt_3 (2)	65	NR
13	$CoCl_2·6H_2O$ (7)	TBHP (2)	DBU (2)	65	NR
14	$CoCl_2·6H_2O$ (7)	TBHP (2)	CsF (2)	65	67
15	$CoCl_2·6H_2O$ (7)	TBHP (2)	CsOH (2)	65	32
16	$CoCl_2·6H_2O$ (3)	TBHP (2)	Cs_2CO_3 (2)	65	54
17	$CoCl_2·6H_2O$ (5)	TBHP (2)	Cs_2CO_3 (2)	65	66
18	$CoCl_2·6H_2O$ (10)	TBHP (2)	Cs_2CO_3 (2)	65	40
19	$CoCl_2·6H_2O$ (7)	TBHP (1.0)	Cs_2CO_3 (2)	65	30
20	$CoCl_2·6H_2O$ (7)	TBHP (1.5)	Cs_2CO_3 (2)	65	39
21	$CoCl_2·6H_2O$ (7)	TBHP (2.2)	Cs_2CO_3 (2)	65	74
22	$CoCl_2·6H_2O$ (7)	TBHP (2)	Cs_2CO_3 (1.6)	65	61
23	$CoCl_2·6H_2O$ (7)	TBHP (2)	Cs_2CO_3 (1.8)	65	68
24	$CoCl_2·6H_2O$ (7)	TBHP (2)	Cs_2CO_3 (2.2)	65	75
25	$CoCl_2·6H_2O$ (7)	TBHP (2)	Cs_2CO_3 (2)	50	52
26	$CoCl_2·6H_2O$ (7)	TBHP (2)	Cs_2CO_3 (2)	100	23
27[c]	$CoCl_2·6H_2O$ (7)	TBHP (2)	Cs_2CO_3 (2)	65	90(88)
28[d]	$CoCl_2·6H_2O$ (7)	TBHP (2)	Cs_2CO_3 (2)	65	70
29[e]	$CoCl_2·6H_2O$ (7)	TBHP (2)	Cs_2CO_3 (2)	65	75
30	—	TBHP (2)	Cs_2CO_3 (2)	65	NR
31	$CoCl_2·6H_2O$ (7)	—	Cs_2CO_3 (2)	65	NR

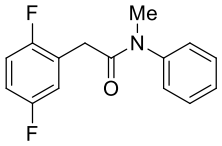
[a] reaction condition: **1a** (0.1 mmol), MeOH (3 mL). [b] NMR yield, the number in parenthesis is isolated yield. [c] MeOH:hexane (10:1) ; [d]MeOH:Toluene (10:1); [e] MeOH:DCM (10:1) 3 mL as solvent.

4. Characterization data for all compounds

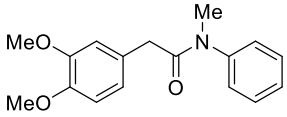


***(4-(tert-butyl)phenyl)-N-methyl-N-phenylacetamide (1h)*:** 1.3 g, 92% yield. Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 3H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.2 Hz, 2H), 7.01 (d, *J* = 7.6 Hz,

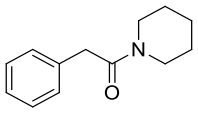
2H), 3.42 (s, 2H), 3.27 (s, 3H), 1.28 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.6, 148.7, 143.6, 131.9, 129.2, 128.3, 127.4, 127.1, 124.7, 39.8, 37.1, 33.9, 30.9.



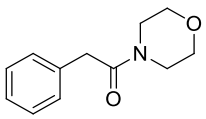
2-(2,5-difluorophenyl)-N-methyl-N-phenylacetamide (1o)**:** 1.1 g, 86% yield. Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.2 Hz, 2H), 7.28 – 7.26 (m, 1H), 7.13 (d, *J* = 7.2 Hz, 2H), 6.87 (br, 1H), 6.83 – 6.76 (m, 2H), 3.35 (s, 2H), 3.21 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.8, 158.8, 157.2 (d, *J* = 2.57 Hz), 155.6 (d, *J* = 2.42 Hz), 143.3, 129.5, 127.7, 126.9, 124.3 (d, *J* = 8.15 Hz), 124.1 (d, *J* = 8.31 Hz), 117.6 (d, *J* = 4.53 Hz), 117.4 (d, *J* = 4.38 Hz), 115.6 (d, *J* = 8.76 Hz), 115.4 (d, *J* = 8.76 Hz), 114.4 (d, *J* = 8.47 Hz), 114.3 (d, *J* = 8.47 Hz), 37.1, 33.7.



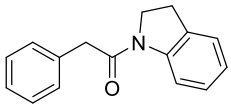
2-(3,4-dimethoxyphenyl)-N-methyl-N-phenylacetamide (1p)**:** 1.2 g, 84% yield. Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 3H), 7.06 (d, *J* = 6.4 Hz, 2H), 6.78 – 6.72 (m, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.53 (s, 1H), 6.46 (d, *J* = 7.4 Hz, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 3.34 (s, 2H), 3.19 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.9, 148.4, 147.4, 143.7, 129.4, 127.6, 127.6, 127.4, 120.8, 112.1, 110.8, 55.6, 55.4, 40.2, 37.3.



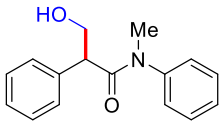
2-phenyl-1-(piperidin-1-yl)ethan-1-one (3n)**:** 1.8 g, 89% yield. Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.25 (m, 5H), 7.19 (q, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 4.06 (t, *J* = 8.5 Hz, 2H), 3.81 (s, 2H), 3.16 (t, *J* = 8.4 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.9, 135.1, 128.3, 128.2, 126.3, 46.9, 42.5, 40.8, 25.8, 25.2, 24.1.



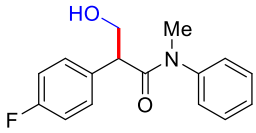
***1-morpholino-2-phenylethan-1-one (3o)*:** 1.7 g, 84% yield. Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 7.16 – 7.14 (m, 3H), 3.63 (s, 2H), 3.52 (s, 4H), 3.34 (d, *J* = 11.2 Hz, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.1 (d, *J* = 1.5 Hz), 134.5, 128.3 (d, *J* = 1.5 Hz), 128.2, 126.4 (d, *J* = 1.2 Hz), 66.3, 66.0, 46.1, 41.7, 40.3.



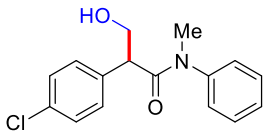
***1-(indolin-1-yl)-2-phenylethan-1-one (3p)*:** 1.9 g, 80% yield. Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.37– 7.25 (m, 5H), 7.19 (q, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 4.06 (t, *J* = 8.6 Hz, 2H), 3.81 (s, 2H), 3.16 (t, *J* = 8.4 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.0, 143.0, 134.2, 131.0, 129.0, 128.7, 127.5, 126.9, 124.5, 123.7, 117.1, 48.1, 43.5, 28.0.



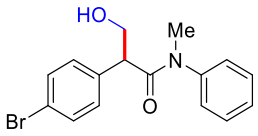
***3-hydroxy-N-methyl-N,2-diphenylpropanamide (2a)*:** 68 mg, 88% yield. White solid; mp: 122-123 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (s, 3H), 7.19 – 7.15 (m, 3H), 6.93 – 6.90 (m, 4H), 4.08 (t, *J* = 9.6 Hz, 1H), 3.76 (dd, *J* = 8.6, 4.6 Hz, 1H), 3.65 (d, *J* = 9.6 Hz, 1H), 3.26 (s, 3H), 3.11 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.5, 142.8, 136.5, 129.3, 129.0, 128.3, 128.0, 127.1, 127.0, 65.5, 51.9, 37.5. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{18}NO_2^+$: 256.1332; found: 256.1325.



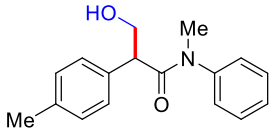
2-(4-fluorophenyl)-3-hydroxy-N-methyl-N-phenylpropanamide (2b): 56 mg, 68% yield. White solid; mp: 101-102 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 3H), 6.88 – 6.86 (m, 6H), 4.01 (t, *J* = 9.6 Hz, 1H), 3.74 (dd, *J* = 8.2, 4.6 Hz, 1H), 3.65 (dd, *J* = 10.8, 4.4 Hz, 1H), 3.26 (s, 3H), 2.99 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.5, 162.0 (d, *J* = 244.5 Hz), 142.8, 132.3 (d, *J* = 3.15 Hz), 129.7 (d, *J* = 8.1 Hz), 129.5, 128.0, 127.8, 115.3 (d, *J* = 21.0 Hz), 65.6, 51.0, 37.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -115.68 – 115.75. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{17}FNO_2^+$: 274.1238; found: 274.1232.



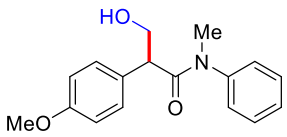
***2-(4-chlorophenyl)-3-hydroxy-N-methyl-N-phenylpropanamide (2c)*:** 69 mg, 80% yield. White solid; mp: 117-118 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.89 – 6.84 (m, 4H), 4.04 – 3.98 (m, 1H), 3.73 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.66 – 3.60 (m, 1H), 3.25 (s, 3H), 3.10 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.3, 142.8, 135.1, 133.1, 129.5, 129.5, 128.6, 128.1, 127.8, 65.5, 51.2, 37.6. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{17}ClNO_2^+$: 290.0942; found: 290.0937.



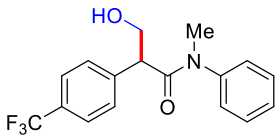
***2-(4-bromophenyl)-3-hydroxy-N-methyl-N-phenylpropanamide (2d)*:** 85 mg, 85% yield. White solid; mp:128-129 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 5H), 6.89 (br, 2H), 6.81 – 6.78 (m, 2H), 4.00 (dd, *J* = 9.6, 8.8 Hz, 1H), 3.71 (dd, *J* = 8.0, 4.4 Hz, 1H), 3.66 (d, *J* = 10.6 Hz, 1H), 3.26 (s, 3H), 2.95 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.2, 142.7, 135.6, 131.6, 129.9, 129.5, 128.1, 127.8, 121.2, 65.4, 51.2, 37.6. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{18}BrNO_2^+$: 334.0437; found: 334.0429.



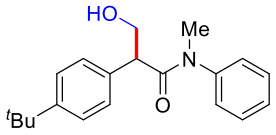
***3-hydroxy-N-methyl-N-phenyl-2-(p-tolyl)propanamide (2e)*:** 71 mg, 88% yield. White solid; mp: 111-112 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 4.4 Hz, 3H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.89 (br, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 4.03 (dd, *J* = 10.4, 8.4 Hz, 1H), 3.72 (dd, *J* = 8.2, 4.6 Hz, 1H), 3.64 (dd, *J* = 10.8, 4.4 Hz, 1H), 3.26 (s, 3H), 2.83 (s, 1H), 2.29 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.8, 143.0, 136.8, 133.5, 129.4, 129.1, 128.0, 127.9, 127.9, 65.8, 51.5, 37.6, 21.0. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{20}NO_2^+$: 270.1488; found: 270.1482.



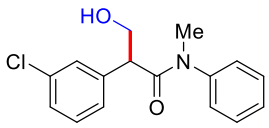
***3-hydroxy-2-(4-methoxyphenyl)-N-methyl-N-phenylpropanamide (2f)*:** 68 mg, 80% yield. White solid; mp: 94-95 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.28 (m, 3H), 6.89 (br, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 4.05 – 3.99 (m, 1H), 3.76 (s, 3H), 3.69 (dd, *J* = 8.2, 4.6 Hz, 1H), 3.67 – 3.58 (m, 1H), 3.25 (s, 3H), 2.89 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.9, 158.7, 143.0, 129.4, 129.2, 128.6, 127.9, 127.9, 113.9, 65.7, 55.2, 51.0, 37.5. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{20}NO_3^+$: 286.1437; found: 286.1431.



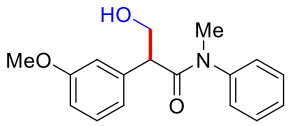
***(4-(trifluoromethyl)-3-hydroxy-N-methyl-N-phenylpropenamide (2g)*:** 44 mg, 45% yield. White solid; mp: 83-84 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.28 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.88 (br, 2H), 4.06 – 4.00 (m, 1H), 3.82 (dd, *J* = 8.0, 4.4 Hz, 1H), 3.74 – 3.67 (m, 1H), 3.27 (s, 3H), 3.06 (br, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.0, 142.7, 140.7, 129.6, 129.5 (dd, *J* = 32.3 Hz), 128.5, 128.2, 127.8, 125.4 (dd, *J* = 3.6 Hz), 124.0 (d, *J* = 270.5 Hz), 65.4, 51.6, 37.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.9. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{17}F_3NO_2^+$: 324.1206; found: 324.1199.



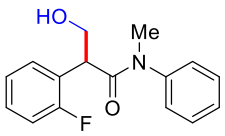
***2-(4-(tert-butyl)phenyl)-3-hydroxy-N-methyl-N-phenylpropanamide (2h)*:** 49 mg, 52% yield. White solid; mp: 109-110 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 1.2 Hz, 3H), 7.19 – 7.17 (m, 2H), 6.90 (br, 2H), 6.85 – 6.83 (m, 2H), 4.10 – 4.06 (m, 1H), 3.75 – 3.72 (m, 1H), 3.65 – 3.62 (m, 1H), 3.24 (d, *J* = 1.6 Hz, 3H), 1.26 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.9, 149.9, 142.9, 133.3, 129.3, 127.8, 127.8, 127.7, 125.2, 65.5, 51.4, 37.6, 34.3, 31.3. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{26}NO_2^+$: 312.1958; found: 312.1954.



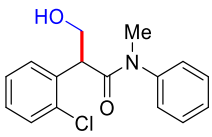
***2-(3-chlorophenyl)-3-hydroxy-N-methyl-N-phenylpropanamide (2i)*:** 41 mg, 47% yield. White solid; mp: 96-97 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.87 (t, *J* = 1.6 Hz, 3H), 6.79 (d, *J* = 7.6 Hz, 1H), 4.02 (t, *J* = 7.8 Hz, 1H), 3.72 (dd, *J* = 8.0, 4.4 Hz, 1H), 3.67 – 3.64 (m, 1H), 3.26 (s, 3H), 3.03 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.0, 142.7, 138.5, 134.2, 129.6, 129.5, 128.3, 128.1, 127.8, 127.4, 126.3, 65.4, 51.5, 37.6. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{17}ClNO_2^+$: 290.0942; found: 290.0937.



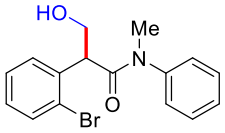
***3-hydroxy-2-(3-methoxyphenyl)-N-methyl-N-phenylpropanamide (2j)*:** 62 mg, 72% yield. White solid; mp:91-92 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 3H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.91 (s, 2H), 6.73 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 6.45 (d, *J* = 2.0 Hz, 1H), 4.10 – 4.04 (m, 1H), 3.74 – 3.70 (m, 1H), 3.70 (s, 3H), 3.67 – 3.62 (m, 1H), 3.26 (s, 3H), 2.94 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.4, 159.5, 142.9, 138.0, 129.30, 127.9, 127.8, 120.5, 113.5, 112.8, 65.6, 55.1, 52.0, 37.5. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{20}NO_3^+$: 286.1437; found: 286.1431.



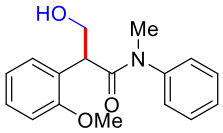
***(2-fluorophenyl)-3-hydroxy-N-methyl-N-phenylpropanamide (2k)*:** 46 mg, 56% yield. White solid; mp:100-101 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 4H), 7.19 – 7.13 (m, 1H), 7.06 – 7.02 (m, 1H), 6.84 – 6.78 (m, 3H), 4.11 (q, *J* = 4.0 Hz, 1H), 3.96 (dd, *J* = 10.8, 8.0 Hz, 1H), 3.72 – 3.68 (m, 1H), 3.27 (d, *J* = 2.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.6, 160.04 (d, *J* = 245.4 Hz), 142.4, 129.48 (d, *J* = 3.5 Hz) 129.4, 128.80 (d, *J* = 8.3 Hz), 128.0, 127.4, 124.10 (d, *J* = 3.6 Hz), 123.74 (d, *J* = 15.2 Hz), 115.10 (d, *J* = 22.4 Hz), 64.3, 43.9, 37.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -119.38 – -119.44 (m). **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{17}FNO_2^+$: 274.1238; found: 274.1232.



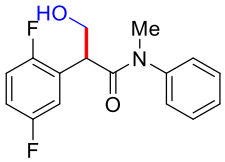
***2-(2-chlorophenyl)-3-hydroxy-N-methyl-N-phenylpropanamide (2l)*:** 55 mg, 63% yield. White solid; mp:107-108 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.6 Hz, 1H), 7.23 – 7.15 (m, 4H), 7.12 (d, *J* = 4.8 Hz, 2H), 6.77 (br, 2H), 4.25 (q, *J* = 3.9 Hz, 1H), 3.92 – 3.86 (m, 1H), 3.74 – 3.68 (m, 1H), 3.31 (t, *J* = 7.0 Hz, 1H), 3.27 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.8, 142.3, 134.3, 133.9, 129.5, 129.4, 129.3, 128.4, 128.0, 127.5, 126.8, 63.8, 48.1, 37.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{17}ClNO_2^+$: 290.0942; found: 290.0937.



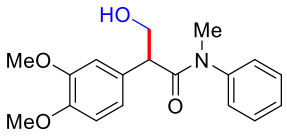
***2-(2-bromophenyl)-3-hydroxy-N-methyl-N-phenylpropanamide (2m)*:** 74 mg, 74% yield. White solid; mp: 128-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.33 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.27 – 7.21 (m, 4H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.77 (s, 2H), 4.23 (q, *J* = 3.9 Hz, 1H), 3.90 – 3.84 (m, 1H), 3.76 – 3.70 (m, 1H), 3.30 (br, 1H), 3.27 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.8, 142.3, 136.0, 132.7, 129.6, 129.4, 128.6, 128.0, 127.6, 127.5, 124.7, 63.8, 50.9, 37.7. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{17}BrNO_2^+$: 334.0437; found: 334.0429.



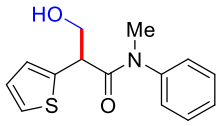
***2-(2-methoxyphenyl)-3-hydroxy--N-methyl-N-phenylpropanamide (2n)*:** 56 mg, 66% yield. White solid; mp: 110-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.12 (m, 5H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 6.4 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 1H), 4.27 (q, *J* = 4.1 Hz, 1H), 3.91 (t, *J* = 9.2 Hz, 1H), 3.64 – 3.61 (m, 1H), 3.36 (s, 3H), 3.25 (s, 3H), 3.22 (br, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.9, 156.2, 142.7, 128.9, 128.6, 128.2, 127.8, 127.3, 125.0, 120.4, 109.9, 64.2, 54.7, 44.3, 37.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{20}NO_3^+$: 286.1437; found: 286.1431.



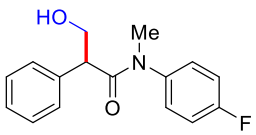
***(2,5-difluorophenyl)-3-hydroxy-N-methyl-N-phenylpropanamide (2o)*:** 45 mg, 51% yield. White solid; mp: 124-125 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.13 (m, 5H), 6.85 – 6.75 (m, 3H), 4.05 – 4.01 (m, 1H), 3.69 (dd, *J* = 8.2, 4.6 Hz, 1H), 3.64 – 3.60 (m, 1H), 3.23 (s, 3H), 3.18 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.0, 159.3 (d, *J* = 2.42 Hz), 157.7 (d, *J* = 2.27 Hz), 156.8 (d, *J* = 2.27 Hz), 155.2 (d, *J* = 2.57 Hz), 142.4, 129.6, 128.1, 127.4, 125.5 (d, *J* = 8.15 Hz), 125.4 (d, *J* = 8.00 Hz), 116.2 (d, *J* = 1.51 Hz), 116.1 (d, *J* = 11.02 Hz), 116.0, 115.9 (d, *J* = 11.93 Hz), 115.3 (d, *J* = 8.61 Hz), 115.2 (d, *J* = 8.61 Hz), 64.1, 43.8, 37.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -118.64 – -118.75 (m), -125.12 – -125.22 (m). **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{16}F_2NO_2^+$: 292.1143; found: 292.1142.



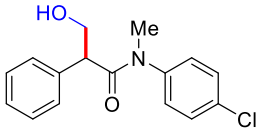
***2-(3,4-dimethoxyphenyl)-3-hydroxy-N-methyl-N-phenylpropanamide (2p)*:** 68 mg, 72% yield. White solid; mp: 135-136 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.26 (m, 3H), 6.89 (br, 2H), 6.67 (d, *J* = 8.4 Hz, 1H), 6.46 (d, *J* = 8.4 Hz, 1H), 6.36 (d, *J* = 1.6 Hz, 1H), 4.05 (dd, *J* = 10.8, 8.4 Hz, 1H), 3.85 – 3.80 (m, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 3.67 (q, *J* = 4.4 Hz, 1H), 3.63 – 3.57 (m, 1H), 3.23 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.7, 148.7, 148.0, 142.9, 129.3, 128.9, 127.9, 127.8, 120.2, 111.3, 111.0, 65.5, 55.8, 55.6, 51.4, 37.5. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{22}NO_4^+$: 316.1543; found: 316.1537.



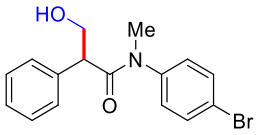
***3-hydroxy-N-methyl-N-phenyl-2-(thiophen-2-yl)propenamide (2q)*:** 70 mg, 89% yield. White solid; mp: 117-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 3H), 7.12 (d, *J* = 5.2 Hz, 1H), 7.07 – 7.06 (m, 2H), 6.85 (dd, *J* = 5.0, 3.4 Hz, 1H), 6.64 (d, *J* = 3.2 Hz, 1H), 4.10 – 4.02 (m, 2H), 3.75 – 3.68 (m, 1H), 3.29 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.9, 142.9, 138.3, 129.6, 128.0, 127.6, 126.4, 125.8, 124.7, 65.8, 46.3, 37.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{16}NO_2S^+$: 262.0896; found: 262.0896.



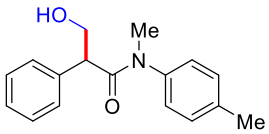
***N-(4-fluorophenyl)-3-hydroxy-N-methyl-2-phenylpropanamide (4a)*:** 48 mg, 58% yield. White solid; mp: 105-106 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 – 7.17 (m, 3H), 6.91 – 6.89 (m, 4H), 6.84 (s, 2H), 4.10 – 4.05 (m, 1H), 3.71 (q, *J* = 4.4 Hz, 1H), 3.62 (d, *J* = 10.6 Hz, 1H), 3.22 (s, 3H), 3.17 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.6, 161.7 (d, *J* = 246.0 Hz), 138.8 (d, *J* = 3.0 Hz), 136.3, 129.7 (d, *J* = 7.5 Hz), 128.5, 128.0, 127.2, 116.2 (d, *J* = 22.5 Hz), 65.6, 52.1, 37.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -113.40 – -113.47 (m). HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{17}FNO_2^+$: 274.1238; found: 274.1232.



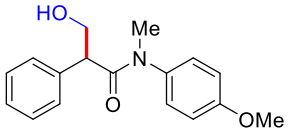
***N-(4-chlorophenyl)-3-hydroxy-N-methyl-2-phenylpropanamide (4b)*:** 77 mg, 89% yield. White solid; mp:91-92 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 5H), 6.93 – 6.91 (m, 2H), 6.80 (d, *J* = 6.0 Hz, 2H), 4.07 (t, *J* = 9.8 Hz, 1H), 3.72 (dd, *J* = 8.6, 4.6 Hz, 1H), 3.64 (dd, *J* = 10.6, 3.8 Hz, 1H), 3.24 (s, 3H), 2.87 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.5, 141.4, 136.3, 133.8, 129.6, 129.3, 128.6, 128.1, 127.3, 65.7, 52.2, 37.6. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{17}ClNO_2^+$: 290.0942; found: 290.0937.



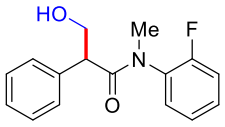
***N-(4-bromophenyl)-3-hydroxy-N-methyl-2-phenylpropanamide (4c)*:** 80 mg, 80% yield. White solid; mp:129-130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.19 (m, 3H), 6.92 (dd, *J* = 6.2, 3.0 Hz, 2H), 6.75 (d, *J* = 5.6 Hz, 2H), 4.07 (dd, *J* = 11, 9.0 Hz, 1H), 3.72 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.63 (dd, *J* = 11.0, 4.7 Hz, 1H), 3.23 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.4, 141.9, 136.2, 132.5, 129.6, 128.6, 128.0, 127.3, 121.7, 65.6, 52.1, 37.5. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{17}BrNO_2^+$: 334.0437; found: 334.0429.



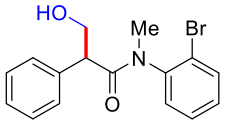
3-hydroxy-N-methyl-2-phenyl-N-(p-tolyl)propenamide (4d): 70 mg, 87% yield. White solid; mp: 118-119 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 – 7.18 (m, 3H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.00 – 6.93 (m, 2H), 6.76 (s, 2H), 4.12 – 4.03 (m, 1H), 3.76 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.67 – 3.64 (m, 1H), 3.23 (s, 3H), 3.07 (s, 1H), 2.34 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.7, 140.3, 137.7, 136.7, 129.9, 128.4, 128.1, 127.5, 127.0, 65.7, 51.7, 37.6, 21.0. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{20}NO_2^+$: 270.1488; found: 270.1482.



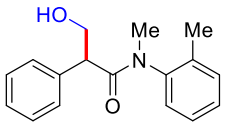
***3-hydroxy-N-(4-methoxyphenyl)-N-methyl-2-phenylpropanamide (4e)*:** 53 mg, 62% yield. White solid; mp:97-98 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 – 7.18 (m, 3H), 6.94 – 6.92 (m, 2H), 6.76 (br, 3H), 4.08 – 4.02 (m, 1H), 3.79 (s, 3H), 3.75 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.70 – 3.60 (m, 1H), 3.22 (s, 3H), 3.02 (t, *J* = 6.5 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.0, 158.9, 136.6, 135.7, 128.9, 128.4, 128.1, 127.1, 114.4, 65.7, 55.4, 51.8, 37.7. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{20}NO_3^+$: 286.1437; found: 286.1431.



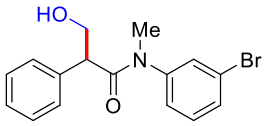
***N-(2-fluorophenyl)-3-hydroxy-N-methyl-2-phenylpropanamide (4f)*:** 54 mg, 66% yield. White solid; mp:110-112 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 1H), 7.30 – 7.22 (m, 1H), 7.20 – 7.18 (m, 3H), 7.15 – 7.08 (m, 1H), 6.91 (q, *J* = 3.1Hz, 1H), 6.88 – 6.84 (m, 1H), 6.79 – 6.75 (m, 1H), 6.48 – 6.43 (m, 1H), 4.14 – 4.01 (m, 1H), 3.84 – 3.80 (m, 1H), 3.70 – 3.65 (m, 1H), 3.62 – 3.56 (m, 1H), 3.26 – 3.20 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.9 (d, *J* = 19.5 Hz), 158.0 (dd, *J* = 249.8, 96.8 Hz) , 135.8 (d, *J* = 196.5 Hz) , 130.2 (dd, *J* = 13.5, 7.5 Hz), 129.9 (t, *J* = 6.8 Hz), 128.3 (dd, *J* = 143.3, 80.3 Hz), 128.4 (d, *J* = 30.0 Hz), 127.9 (d, *J* = 19.5 Hz), 127.1 (d, *J* = 13.5 Hz), 124.6 (dd, *J* = 21.8, 3.75 Hz), 116.6 (dd, *J* = 19.5, 3.0 Hz), 65.5 (d, *J* = 16.5 Hz), 52.3 (d, *J* = 15.0 Hz), 36.7 – 36.4 (m). **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{17}FNO_2^+$: 274.1238; found: 274.1232. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -119.23 (s), -121.92 (s).



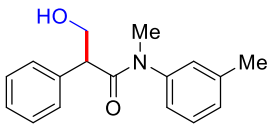
***N-(2-bromophenyl)-3-hydroxy-N-methyl-2-phenylpropanamide (4g)*:** 46 mg, 46% yield. White solid; mp:130-131 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.31 (m, 1H), 7.26 – 7.23 (m, 4H), 6.95 – 6.84 (m, 4H), 4.14 (dd, *J* = 10.8, 8.8 Hz, 1H), 3.77 (dd, *J* = 8.6, 4.6 Hz, 1H), 3.68 (dd, *J* = 11.0, 4.6 Hz, 1H), 3.28 (s, 3H), 3.20 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.3, 143.9, 136.2, 134.6, 130.2, 128.5, 128.4, 128.1, 128.1, 127.3, 126.1, 65.5, 52.3, 37.4. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{17}BrNO_2^+$: 334.0437; found: 334.0429.



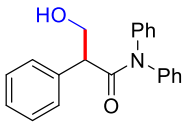
***3-hydroxy-N-methyl-2-phenyl-N-(o-tolyl)propanamide (4h)*:** 63 mg, 78% yield. White solid; mp: 115-116 °C. ^{1}H NMR (400 MHz, CDCl3) δ 7.49 – 7.43 (m, 0.5H), 7.31 – 7.12 (m, 5H), 7.02 (d, J = 7.2 Hz, 0.5H), 6.94 – 6.90 (m, 1.5H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.36 (d, *J* = 7.6 Hz, 0.5H), 4.09 (q, *J* = 11.1 Hz, 1H), 3.79 (dd, J = 8.4, 4.4 Hz, 0.5H), 3.65 – 3.59 (m, 1H), 3.40 (dd, *J* = 8.6, 4.6 Hz, 0.5H), 3.17 (d, *J* = 9.2 Hz, 3H), 2.32 (s, 1.5H), 1.36 (s, 1.5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.7, 172.6, 141.4, 141.3, 136.8, 136.3, 135.5, 135.3, 131.4, 131.2, 128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 127.3, 127.2, 127.1, 126.8, 65.6, 65.5, 52.5, 51.9, 36.2, 36.1, 17.5, 16.4. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{20}NO_2^+$: 270.1488; found: 270.1482.



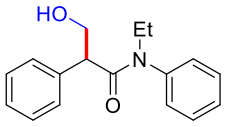
***N-(3-bromophenyl)-3-hydroxy-N-methyl-2-phenylpropanamide (4i)*:** 52 mg, 52% yield. White solid; mp:125-127 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 5H), 6.95 – 6.85 (m, 4H), 4.10 – 4.06 (m, 1H), 3.71 (dd, *J* = 5.6, 3.2 Hz, 1H), 3.67 – 3.63 (m, 1H), 3.24 (s, 3H), 2.89 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.4, 144.0, 136.2, 131.3, 131.1, 130.5, 128.6, 128.0, 127.3, 126.6, 122.5, 65.5, 52.4, 37.5. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{17}BrNO_2^+$: 334.0437; found: 334.0429.



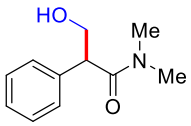
***3-hydroxy-N-methyl-2-phenyl-N-(m-tolyl)propenamide (4j)*:** 61 mg, 76% yield. White solid; mp:112-113 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 – 7.07 (m, 3H), 7.11 (dd, *J* = 24.2, 7.6 Hz, 2H), 6.92 – 6.90 (m, 2H), 6.70 (s, 1H), 6.58 (s, 1H), 4.05 (t, *J* = 9.4 Hz, 1H), 3.73 (dd, *J* = 8.2, 4.6 Hz, 1H), 3.66 (d, *J* = 10.4 Hz, 1H), 3.24 (s, 3H), 2.99 (s, 1H), 2.21 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.6, 142.7, 139.3, 136.8, 129.1, 128.6, 128.6, 128.3, 128.1, 127.0, 124.6, 65.6, 52.0, 37.5, 21.0. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{20}NO_2^+$: 270.1488; found: 270.1482.



***3-hydroxy-N,N,2-triphenylpropanamide (4k)*:** 95 mg, 83% yield. colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.19 (m, 11H), 7.00 – 6.98 (m, 4H), 4.19 – 4.13 (m, 1H), 4.00 (q, *J* = 4.4 Hz, 1H), 3.73 – 3.70 (m, 1H), 2.97 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.0, 142.4, 141.6, 136.1, 129.3, 129.2, 128.9, 128.6, 128.1, 127.9, 127.3, 126.4, 126.3, 65.7, 52.9. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{20}NO_2^+$: 318.1489; found: 318.1488.

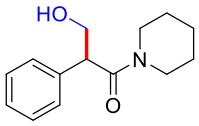


***N-ethyl-3-hydroxy-N,2-diphenylpropanamide (4l)*:** 81 mg, 76% yield. White solid; mp:115-116 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.14 (m, 7H), 6.89 (dd, *J* = 6.4, 3.2 Hz, 2H), 6.83 (br, 1H), 4.07 – 4.00 (m, 1H), 3.82 – 3.62 (m, 4H), 3.01 (br, 1H), 1.09 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.0, 141.1, 136.7, 129.2, 128.9, 128.4, 128.1, 127.9, 127.0, 65.7, 52.3, 44.3, 12.9. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{20}NO_2^+$: 285.1598; found: 270.1482.

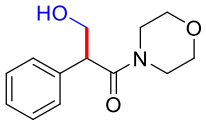


***3-hydroxy-N,N-dimethyl-2-phenylpropanamide (4m)*:** 30 mg, 52% yield. White solid; mp:81-82 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 2H), 4.05 – 4.00 (m, 1H), 3.94 (dd, *J* = 8.4, 4.0 Hz, 1H), 3.74 (dd, *J* = 11.6, 3.8 Hz, 1H), 3.27 (s, 1H), 2.98 (s, 3H), 2.80

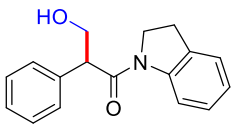
(s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.7, 136.2, 129.0, 128.0, 127.4, 66.0, 52.0, 36.3 (d, *J* = 207.0 Hz). **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{11}H_{16}NO_2^+$: 194.1176; found: 194.1171.



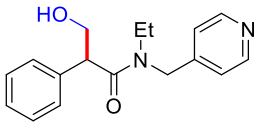
***3-hydroxy-2-phenyl-1-(piperidin-1-yl)propan-1-one (4n)*:** 32 mg, 46% yield. White solid; mp: 136-137 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.21 (m, 5H), 4.06 – 4.00 (m, 1H), 3.93 (dd, *J* = 8.4, 4.0 Hz, 1H), 3.80 – 3.71 (m, 2H), 3.41 – 3.32 (m, 2H), 3.26 – 3.15 (m, 2H), 1.56 – 1.41 (m, 4H), 1.34 – 1.26 (m, 1H), 0.90 (br, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.7, 136.6, 128.9, 128.0, 127.3, 66.0, 51.8, 46.4, 42.9, 25.6, 25.4, 24.3. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{20}NO_2^+$: 234.1489; found: 234.1489.



***3-hydroxy-1-morpholino-2-phenylpropan-1-one (4o)*:** 38 mg, 54% yield. White solid; mp:139-140 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 2H), 7.29 – 7.25 (m, 1H), 7.21 – 7.19 (m, 2H), 4.06 (dd, *J* = 11.0, 8.6 Hz, 1H), 3.91 (dd, *J* = 8.6, 4.2 Hz, 1H), 3.85 – 3.79 (m, 1H), 3.76 – 3.63 (m, 2H), 3.56 – 3.43 (m, 3H), 3.35 – 3.29 (m, 1H), 3.23 – 3.19 (m, 2H), 3.07 – 3.02 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.1, 136.0, 129.1, 127.9, 127.6, 66.6, 66.0, 65.7, 51.8, 45.8, 42.1. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{13}H_{18}NO_3^+$: 236.1281; found: 236.1275.



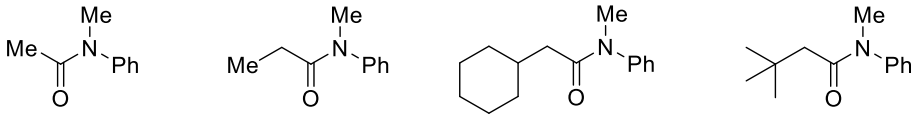
***3-hydroxy-1-(indolin-1-yl)-2-phenylpropan-1-one (4p)*:** 49 mg, 61% yield. yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.4 Hz, 1H), 7.37 – 7.21 (m, 6H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 4.22 – 4.17 (m, 1H), 4.08 – 3.98 (m, 2H), 3.84 – 3.78 (m, 1H), 3.65 – 3.58 (m, 1H), 3.15 – 3.07 (m, 2H), 3.00 – 2.91 (br, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.8, 142.8, 135.3, 131.2, 129.1, 128.2, 127.7, 127.5, 124.6, 124.1, 117.3, 65.7, 54.7, 47.5, 27.9. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{18}NO_2^+$: 268.1331; found: 268.1332.



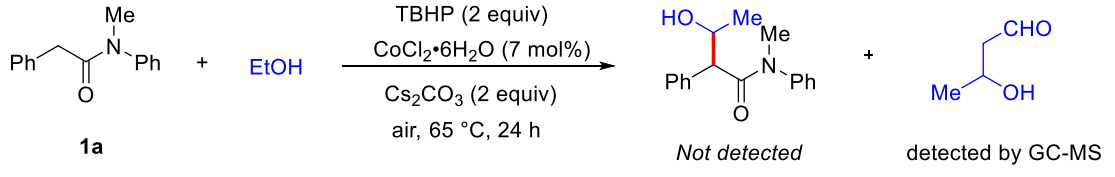
N-ethyl-3-hydroxy-2-phenyl-N-(pyridin-4-ylmethyl)propanamide (4q)[3]**:** 55 mg, 65% yield. White solid; mp:96-97 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 – 8.45 (m, 2H), 7.36 – 7.16 (m, 5H), 6.98 (dd, *J* = 40.8, 5.4 Hz, 2H), 4.72 (d, *J* = 16.0 Hz, 1H), 4.44 (dd, *J* = 16.0, 9.2 Hz, 1H), 4.23 – 4.02 (m, 2H), 3.80 – 3.68 (m, 2H), 3.36 – 3.27 (m, 1H), 3.18 – 3.06 (m, ,1H), 1.08 (t, *J* = 7.1 Hz, 1H), 0.92 (t, *J* = 7.1 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.5, 172.6, 150.1, 149.8, 146.7, 145.9, 136.1, 135.8, 129.1, 129.0, 128.0, 127.8, 127.7, 127.6, 122.1, 121.3, 65.8, 52.0, 51.9, 49.2, 47.3, 42.2, 41.2, 13.4, 12.3. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{21}N_2O_2^+$: 285.1598; found: 285.1597.

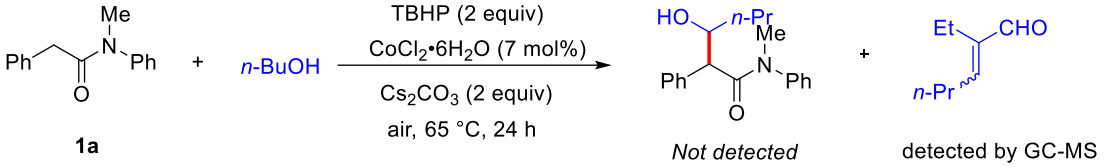
5. Unsuccessful substrates

5.1 Scope of 2-alkyl-*N*-methyl-*N*-phenylacetamides



5.2 Scope of alcohols





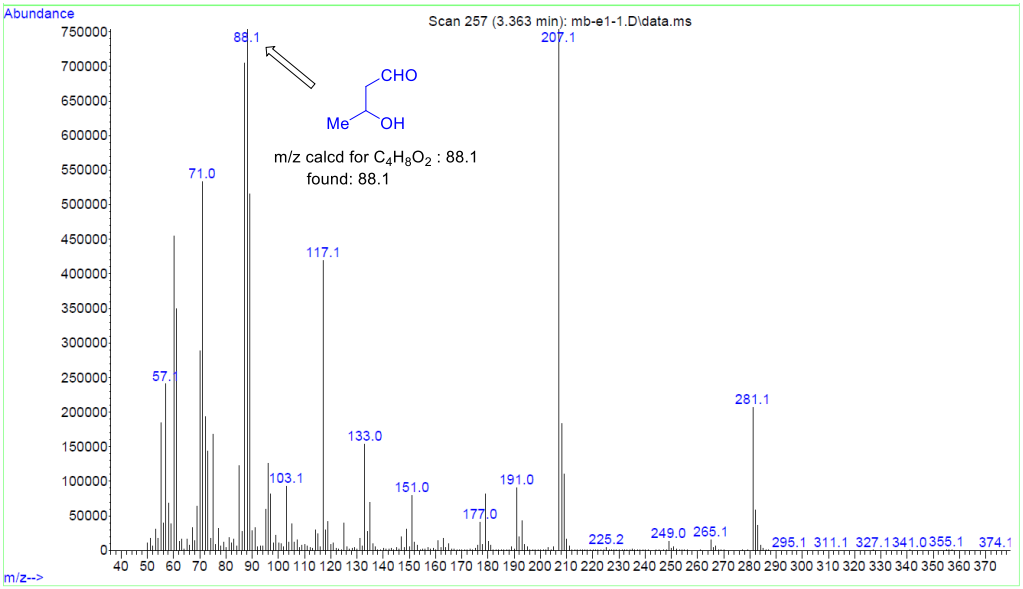


Figure S1

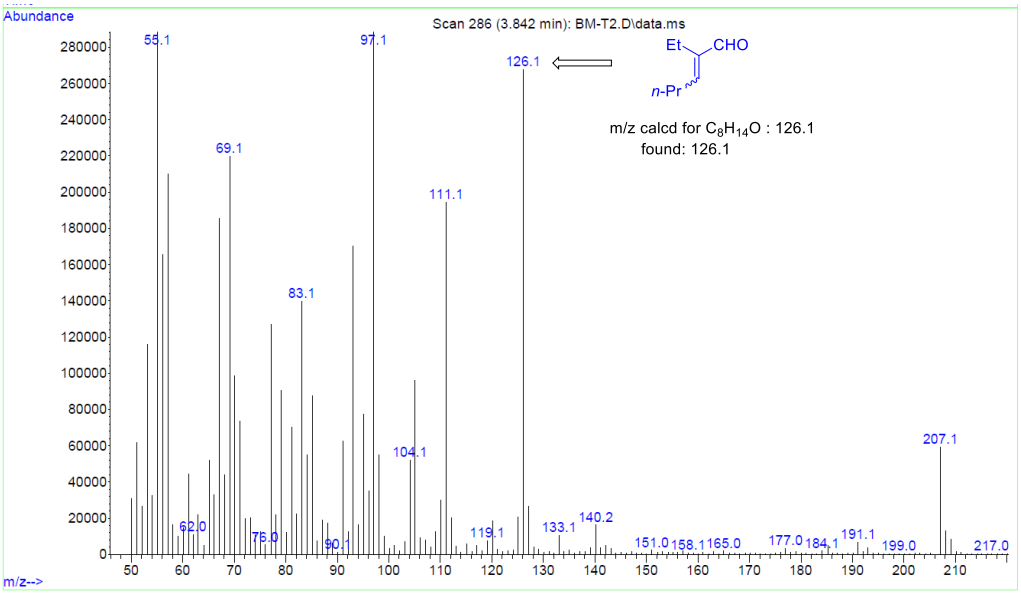
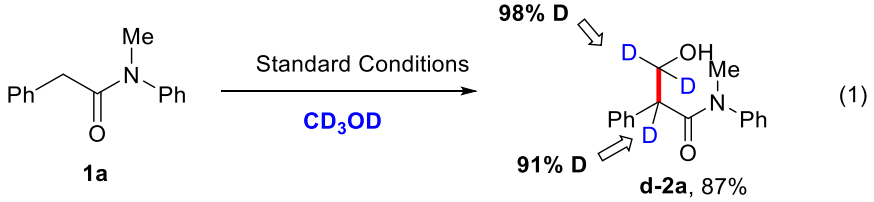


Figure S2

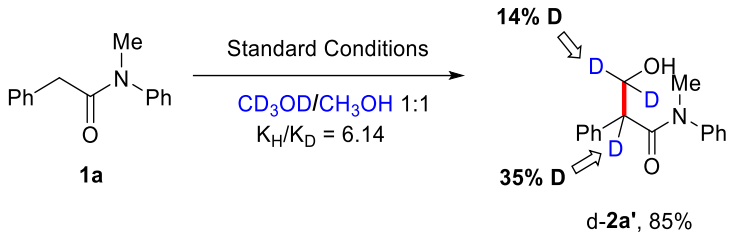
6. Mechanistic Studies

6.1 Kinetic isotopic effect experiments



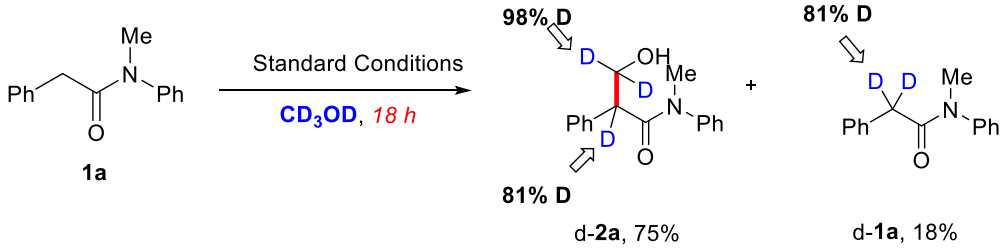
(1)

$CoCl_2·6H_2O$ (2.5 mg, 0.0105 mmol, 7 mol%), Cs_2CO_3 (97.7 mg, 0.30 mmol, 2 equiv), CD_3OD (3.0 mL) and amide **1a** (23.5 μL, 0.15 mmol) were sequentially added into a 25 mL Schleck tube. Then TBHP (70 wt% in H_2O) (41.2 μL, 0.3 mmol, 2 equiv) was added to the stirred reaction system. The reaction mixture was stirred at 65 °C for 24 h. The reaction solution was cooled at room temperature and quenched with saturated NH_4Cl (2 mL), extracted with EtOAc (3×5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 5:1) to afford the pure product d-**2a** (33.2 mg, 87%).



(2)

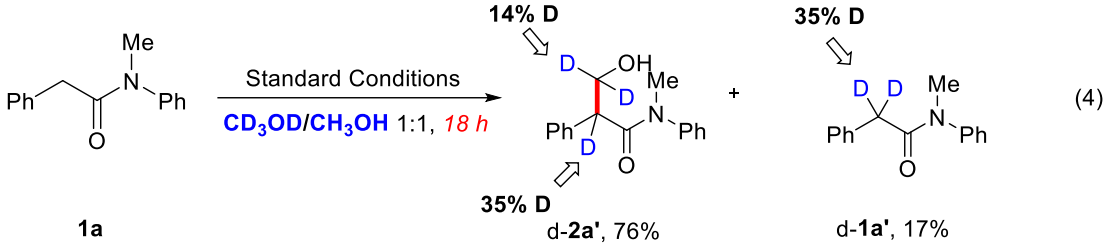
$CoCl_2·6H_2O$ (2.5 mg, 0.0105 mmol, 7 mol%), Cs_2CO_3 (97.7 mg, 0.30 mmol, 2 equiv), CD_3OD (1.5 mL), CH_3OH (1.5 mL) and amide **1a** (23.5 μL, 0.15 mmol) were sequentially added into a 25 mL Schleck tube. Then TBHP (70 wt% in H_2O) (41.2 μL, 0.3 mmol, 2 equiv) was added to the stirred reaction system. The reaction mixture was stirred at 65 °C for 24 h. The reaction solution was cooled at room temperature and quenched with saturated NH_4Cl (2 mL), extracted with EtOAc (3×5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 5:1) to afford the pure product d-2a' (28.7 mg, 85%).



(3)

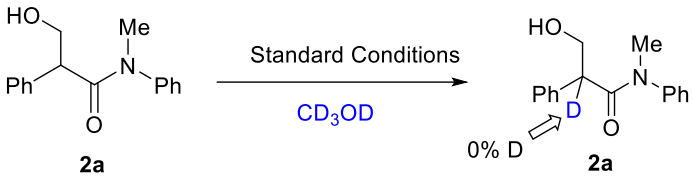
$CoCl_2·6H_2O$ (2.5 mg, 0.0105 mmol, 7 mol%), Cs_2CO_3 (97.7 mg, 0.30 mmol, 2 equiv), CD_3OD (1.5 mL), and amide **1a** (23.5 μL, 0.15 mmol) were sequentially added into a 25 mL Schleck tube. Then TBHP (70 wt% in H_2O) (41.2 μL, 0.3 mmol, 2 equiv) was added to the stirred reaction system. The reaction

mixture was stirred at 65 °C for 18 h. The reaction solution was cooled at room temperature and quenched with saturated NH_4Cl (2 mL), extracted with EtOAc (3×5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 5:1) to afford the pure product d-**2a** (28.6 mg, 75%), and d-**1a** (6.1 mg, 18%).



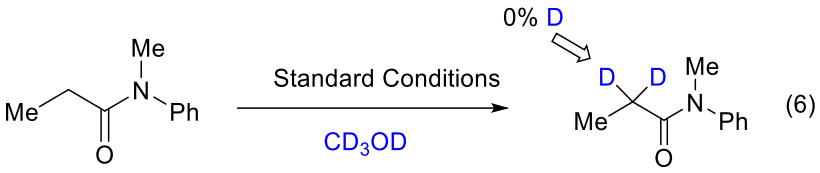
(4)

$CoCl_2·6H_2O$ (2.5 mg, 0.0105 mmol, 7 mol%), Cs_2CO_3 (97.7 mg, 0.30 mmol, 2 equiv), CD_3OD/CH_3OH 1:1 (3 mL), and amide **1a** (23.5 µL, 0.15 mmol) were sequentially added into a 25 m Schleck tube. Then TBHP (70 wt% in H_2O) (41.2 µL, 0.3 mmol, 2 equiv) was added to the stirred reaction system. The reaction mixture was stirred at 65 °C for 18 h. The reaction solution was cooled at room temperature and quenched with saturated NH_4Cl (2 mL), extracted with EtOAc (3×5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 5:1) to afford the pure product d-**2a'** (29.1 mg, 76%), and d-**1a** (5.7 mg, 17%).



(5)

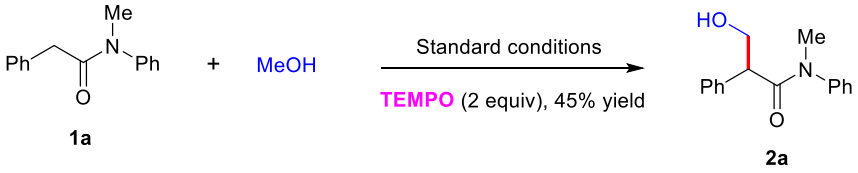
$CoCl_2·6H_2O$ (2.5 mg, 0.0105 mmol, 7 mol%), Cs_2CO_3 (97.7 mg, 0.30 mmol, 2 equiv), CD_3OD (3.0 mL) and **2a** (38.3 mg, 0.15 mmol) were sequentially added into a 25 mL Schleck tube. Then TBHP (70 wt% in H_2O) (41.2 µL, 0.3 mmol, 2 equiv) was added to the stirred reaction system. The reaction mixture was stirred at 65 °C for 24 h. The reaction solution was cooled at room temperature and quenched with saturated NH_4Cl (2 mL), extracted with EtOAc (3×5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 5:1) to afford the pure product.



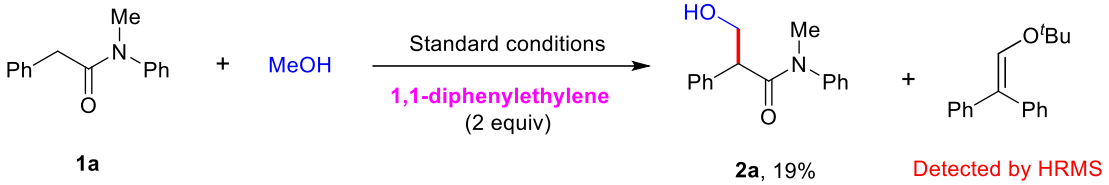
(6)

$CoCl_2·6H_2O$ (2.5 mg, 0.0105 mmol, 7 mol%), Cs_2CO_3 (97.7 mg, 0.30 mmol, 2 equiv), CD_3OD (3.0 mL) and *N*-methyl-*N*-phenylpropionamide (24.5 mg, 0.15 mmol) were sequentially added into a 25 mL Schleck tube. Then TBHP (70 wt% in H_2O) (41.2 μL, 0.3 mmol, 2 equiv) was added to the stirred reaction system. The reaction mixture was stirred at 65 °C for 24 h. The reaction solution was cooled at room temperature and quenched with saturated NH_4Cl (2 mL), extracted with EtOAc (3×5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 5:1) to afford the pure product.

6.2 Radical Inhibiting Experiment with TEMPO



$CoCl_2·6H_2O$ (5.0 mg, 0.021 mmol, 7 mol%), Cs_2CO_3 (231.5 mg, 0.6 mmol), MeOH/Hexane 10:1 (3 mL), TEMPO (93.8 mg, 0.6 mmol, 2.0 equiv) and **1a** (67.5 mg, 0.3 mmol) were sequentially added into a 25 mL Schleck tube. Then TBHP (70 wt% in H_2O) (83 μL, 0.6 mmol) was added to the stirred reaction system. The reaction mixture was stirred at 65 °C until the reaction was complete (monitored by TLC). The reaction solution was cooled at room temperature and quenched with NH_4Cl (2 mL), extracted with ethyl acetate (3×5 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 5:1-3:1) to afford the pure products **2a** (34.4 mg), 45% yield.



$CoCl_2·6H_2O$ (5.0 mg, 0.021 mmol, 7 mol%), Cs_2CO_3 (231.5 mg, 0.6 mmol), MeOH/Hexane 10:1 (3 mL), 1,1-diphenylethylene (108.2 mg, 0.6 mmol, 2.0 equiv) and **1a** (67.5 mg, 0.3 mmol) were sequentially added into a 25 mL Schleck tube. Then TBHP (70 wt% in H_2O) (83 μL, 0.6 mmol) was added to the stirred reaction system. The reaction mixture was stirred at 65 °C until the reaction was complete (monitored by TLC). Then, the reaction mixture was analyzed by HRMS, and the oxygen radical trapped by 1,1-diphenylethylene was detected (**Figure S1**, data of $[M+H]^+$ are showed). In addition, after concentration under reduced pressure, **2a** was obtained in 19% yield by column chromatography isolation on silica gel (PE:EtOAc = 5:1).

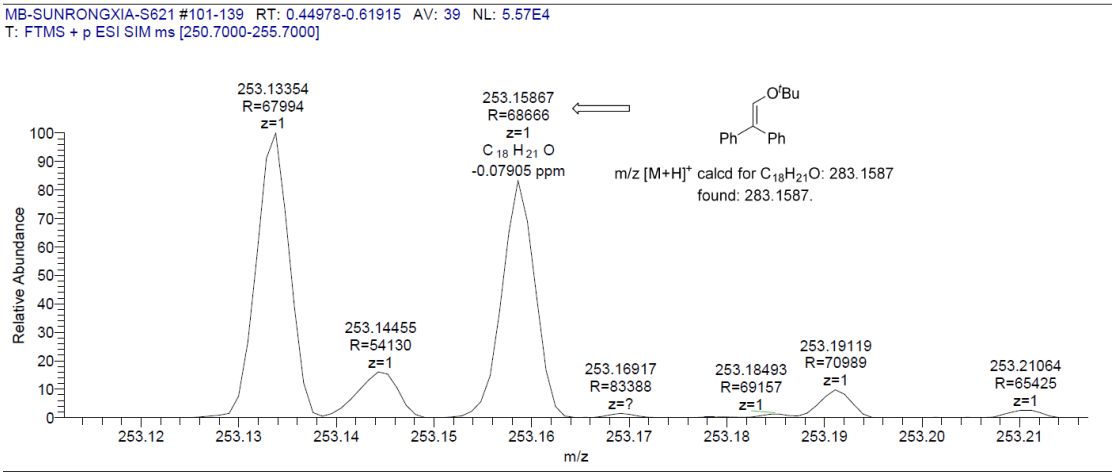
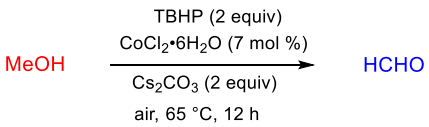


Figure S3

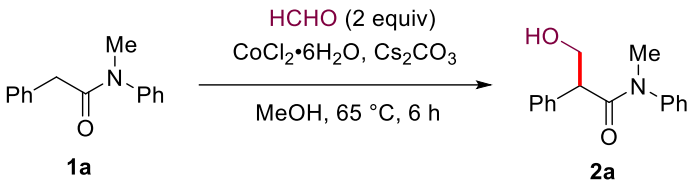
6.3 Procedure for control experiments

Using silver mirror reaction to detect the *in situ* formed formaldehyde:

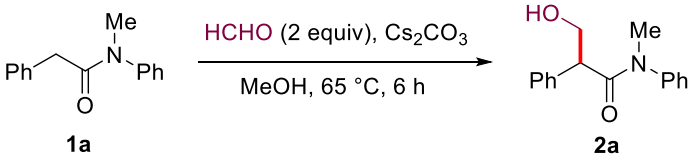


To a solution of $CoCl_2·6H_2O$ (5.0 mg, 0.005 mmol) and Cs_2CO_3 (195.5 mg, 0.6 mmol) in MeOH (3 mL), TBHP (70 wt% in H_2O) (83 μL, 0.6 mmol) was added. After stirring for 30 min, a small amount of the

reaction mixture was dropped into the fresh silver ammonia solution in test tube. After shaking, the test tube was warmed in hot water and a layer of metallic silver was found adhering to the inner wall of the test tube. The picture of this phenomenon is shown in follow：



$CoCl_2·6H_2O$ (2.5 mg, 0.0105 mmol, 7 mol%), Cs_2CO_3 (97.7 mg, 0.30 mmol, 2 equiv), CH_3OH (3 mL) and amide **1a** (23.5 μL, 0.15 mmol) were sequentially added into a 25 mL Schleck tube. Then HCHO (22.1 μL, 0.6 mmol, 2 equiv) was added to the stirred reaction system. The reaction mixture was stirred at 65 °C for 1 h. The reaction solution was cooled at room temperature and quenched with saturated NH_4Cl (2 mL), extracted with EtOAc (3×5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 5:1) to afford the pure product **2a** (32 mg, 84%).

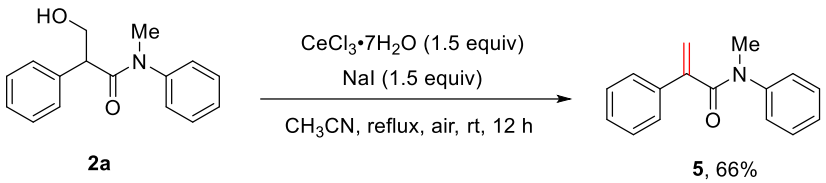


Cs_2CO_3 (97.7 mg, 0.30 mmol, 2 equiv), CH_3OH (3 mL) and amide **1a** (23.5 μL, 0.15 mmol) were sequentially added into a 25 mL Schleck tube. Then HCHO (22.1 μL, 0.6 mmol, 2 equiv) was added to

the stirred reaction system. The reaction mixture was stirred at 65 °C for 1 h. The reaction solution was cooled at room temperature and quenched with saturated NH_4Cl (2 mL), extracted with EtOAc (3×5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 5:1) to afford the pure product **2a** (29 mg, 77%).

7. Late-stage modification

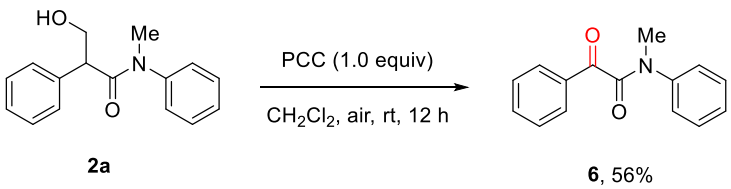
7.1 Experimental procedure for synthesis of 5



2a **5**, 66%

2a (76.5 mg, 0.3 mmol), cerium(III) chloride heptahydrate (167.7 mg, 1.5 equiv), sodium iodide (67.5 mg, 1.5 equiv) and acetonitrile (3 mL) were sequentially charged into a dry Schlenk tube. The reaction mixture was stirred at reflux temperature for 12 h. After cooled to room temperature, it was diluted with ether and treated with 0.5 mol/L HCl (10 mL). The organic layer was separated, and the aqueous layer was extracted with ether (3 × 20 mL). The combined organic layers were washed twice with an aqueous saturated $NaHCO_3$ solution and a saturated NaCl solution and dried over anhydrous Na_2SO4, concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE: EtOAc = 10:1) to afford the pure product. ***N-methyl-N,2-diphenylacrylamide (5)***: 56 mg, 66% yield. colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 8H), 6.93 (s, 2H), 5.46 (s, 1H), 5.36 (s, 1H), 3.38 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.5, 145.7, 143.6, 136.8, 128.7, 127.2, 127.8, 126.9, 126.8, 126.0, 117.7, 37.3. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{16}NO^+$: found: 238.1227.

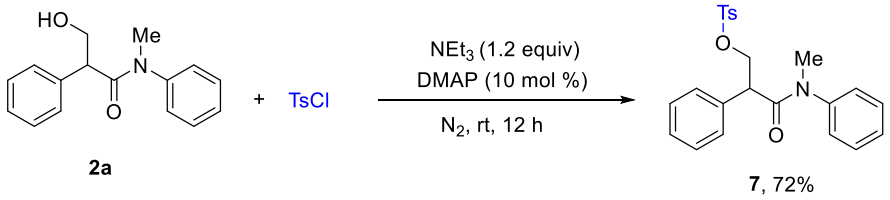
7.2 Experimental procedure for synthesis of 6



2a **6**, 56%

Pyridinium chlorochromate (129.3 mg, 0.6 mmol) and 1.0 g of silica gel were mixed in CH_2Cl_2 (5 mL), 3-hydroxy-N-methyl-N,2-diphenylpropanamide (**2a,** 153.1 mg, 0.6 mmol) dissolved in 5 mL dichloromethane was added, the resultant mixture was stirred for 5 hours. Following this, the reaction was filtered through a silica plug and washed through with diethyl ether, and the solvent was removed to give the crude product. Purify the product by column chromatography chromatography (PE:EtOAc = 10:1). ***N-methyl-2-oxo-N,2-diphenylacetamide (6)*****:** 134 mg, 56% yield. Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 2H), 7.56 – 7.52 (m, 1H), 7.44 – 7.38 (m, 2H), 7.23 – 7.16 (m, 3H), 7.13 – 7.10 (m, 2H), 3.46 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 190.8, 167.1, 141.1, 134.3, 133.5, 129.5, 129.3, 128.8, 128.1, 126.7, 77.4, 77.1, 76.9, 36.2. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{16}NO^+$: 240.1019; found: 240.1012.

7.3 Experimental procedure for synthesis of 7.[4]



p-Toluenesulfonyl chloride (137.3 mg, 1.2 equiv) and **2a** (153.6 mg, 0.6 mmol) were mixed under an atmosphere of nitrogen, then CH_2Cl_2 (5 ml) was added to the stirred system and cool the mixture to 0 °C. Add NEt_3 (1.4 equiv) dropwise over a period of 5 mins, warm the reaction mixture to room temperature and stir overnight. Add $NaHCO_3$ (10 mL/1M) and extract the solution with CH_2Cl_2 (3×10 mL/1M). Wash the combined extracts with brine (10 mL/1M), dry over Na_2SO4 and concentrate in vacuo. Purify the residue by flash column chromatography (PE:EtOAc = 10:1). ***3-(methyl(phenyl)amino)-3-oxo-2-phenylpropyl 4-methylbenzenesulfonate (7)*****:** 177 mg, 72% yield. Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.65 (m, 2H), 7.35 – 7.27 (s, 5H), 7.23 – 7.14 (m, 3H), 6.94 – 6.88 (m, 4H), 4.56 (t, *J* = 9.2 Hz, 1H), 4.03 (dd, *J* = 9.4, 5.8 Hz, 1H), 3.89 (dd, *J* = 9.2, 5.6 Hz, 1H), 3.21 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.6, 143.7 (d, *J* = 279.0 Hz), 133.7 (d, *J* = 306.0 Hz), 129.7, 129.6, 128.6, 128.2 (d, *J* = 4.5 Hz), 127.9 (d, *J* = 7.5 Hz), 127.8, 71.7, 48.5, 37.6, 21.6. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{16}NO^+$: 410.1421; found: 410.1415.

8. Crystallographic Structure Determination (4a)

The colorless single crystal of product **4a** was obtained by recrystallization using a $CHCl_3$/acetone solvent system at room temperature. The X-ray single-crystal diffraction was performed on an Agilent SuperNOVA instrument (**Figure S4**).

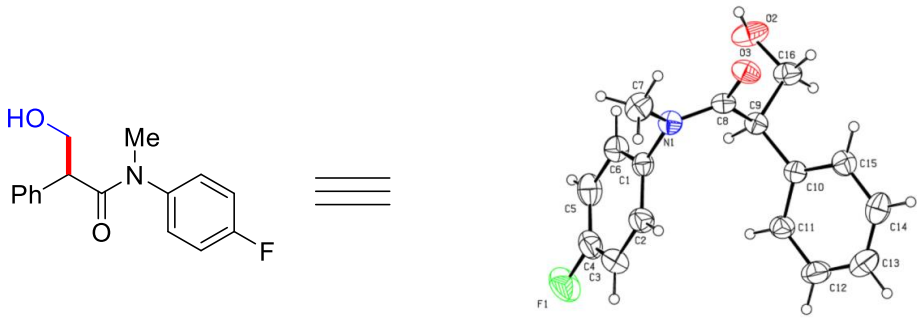


Figure S4. Thermal ellipsoid plot of compound **4a** at the 30% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

Table 1 Crystal data and structure refinement for sunrongxia_0428-1_auto

Identification code	sunrongxia_0428-1_auto
Empirical formula	$C_{16}H_{16}FNO_2$
Formula weight	273.30
Temperature/K	302.01(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	18.0338(3)
b/Å	11.15970(19)
c/Å	14.0652(3)
α/°	90
β/°	97.5402(18)
γ/°	90
Volume/Å^3	2806.18(9)
Z	8
ρ_{calc}mg/mm^3	1.294

μ/mm^{-1}	0.778
F(000)	1152.0
Crystal size/mm^3	0.13 × 0.11 × 0.07
2Θ range for data collection	9.342 to 151.388°
Index ranges	-22 ≤ h ≤ 22, -5 ≤ k ≤ 13, -17 ≤ l ≤ 17
Reflections collected	9716
Independent reflections	2801[R(int) = 0.0232]
Data/restraints/parameters	2801/0/184
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0416, wR_2 = 0.1168
Final R indexes [all data]	R_1 = 0.0443, wR_2 = 0.1195
Largest diff. peak/hole / e Å^{-3}	0.23/-0.21

Table 2. Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for sunrongxia_0428-1_auto. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	8637.8(6)	3596.8(12)	5480.2(11)	107.9(5)
O2	6239.2 (7)	7758.9(13)	2415.7(7)	80.5(4)
O3	4929.7(5)	6495.0(10)	3609.1(7)	60.9(3)
N1	5804.6(5)	5082.7(9)	3973.7(8)	49.9(3)
C1	6547.0(7)	4706.6(11)	4357.9(9)	48.1(3)
C2	6688.1(9)	4374.0(13)	5309.6(10)	61.5(4)
C3	7397.3(10)	3999.7(16)	5692.0(13)	74.3(5)
C4	7941.7(9)	3958.4(14)	5107.7(14)	70.0(4)
C5	7817.9(9)	4248.6(15)	4161.2(14)	71.5(4)
C6	7104.3(8)	4626.1(13)	3777.3(11)	59.2(3)
C7	5245.6(9)	4122.4(15)	3827.1(13)	68.9(4)
C8	5587.9(6)	6232.6(11)	3857.5(8)	45.0(3)
C9	6177.9(6)	7214.8(11)	4077.2(9)	45.9(3)

C10	6140.3(6)	7699.3(11)	5078.9(9)	46.3(3)
C11	6695.9(8)	7403.3(13)	5820.6(10)	56.6(3)
C12	6662.8(11)	7798.6(16)	6746.5(11)	73.7(5)
C13	6076.5(11)	8505.7(17)	6942.8(12)	78.2(5)
C14	5524.5(10)	8815.4(15)	6213.1(13)	72.9(4)
C15	5552.4(8)	8414.1(13)	5289.5(11)	58.1(3)
C16	6071.5(9)	8183.9(14)	3304.6(10)	61.0(4)

Table 3. Anisotropic Displacement Parameters (Å2×103) for sunrongxia_0428-1_auto. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	67.4(6)	102.0(8)	146.4(12)	2.8(7)	-16.1(7)	27.0(6)
O2	79.3(7)	112.9(10)	49.6(6)	3.1(5)	9.7(5)	-41.5(7)
O3	40.9(5)	72.6(6)	66.2(6)	12.2(5)	-4.4(4)	-3.9(4)
N1	44.0(5)	49.8(6)	55.6(6)	-0.3(4)	5.7(4)	-9.7(4)
C1	47.7(6)	42.1(6)	54.7(7)	-1.5(5)	7.5(5)	-3.0(5)
C2	65.8(8)	63.3(8)	56.4(8)	5.7(6)	12.0(6)	5.8(6)
C3	80.7(11)	70.6(10)	67.4(9)	8.4(7)	-5.2(8)	13.9(8)
C4	58.7(8)	54.8(8)	92.7(12)	-1.4(7)	-4.3(8)	8.5(6)
C5	55.6(8)	63.8(9)	99.0(12)	-5.8(8)	24.8(8)	3.7(7)
C6	59.4(8)	58.9(8)	61.4(8)	0.2(6)	15.7(6)	-0.8(6)
C7	62.5(8)	64.2(9)	79.7(10)	-6.0(7)	8.2(7)	-24.4(7)
C8	40.8(6)	54.7(7)	39.0(6)	4.0(5)	3.6(4)	-5.7(5)
C9	39.7(6)	48.7(6)	49.0(6)	2.7(5)	4.1(5)	-4.6(5)
C10	45.0(6)	44.3(6)	48.8(6)	3.1(5)	3.8(5)	-7.3(5)
C11	56.5(7)	54.6(7)	55.5(7)	1.3(6)	-4.5(6)	-4.8(6)
C12	89.9(11)	73.0(10)	52.9(8)	0.2(7)	-10.5(7)	-13.5(8)
C13	99.1(13)	80.4(11)	56.5(9)	-12.7(7)	15.3(8)	-20.6(9)
C14	73.5(10)	67.2(9)	82.8(11)	-14.2(8)	28.5(8)	-6.3(7)
C15	52.1(7)	58.1(8)	64.1(8)	0.8(6)	7.3(6)	0.0(6)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C16	67.5(8)	61.6(8)	52.2(7)	10.1(6)	1.2(6)	-18.0(6)

Table 4 Bond Lengths for sunrongxia_0428-1_auto.

Atom	Atom	Length/Å
F1	C4	1.3568(18)
O2	C16	1.407(2)
O3	C8	1.2279(15)
N1	C1	1.4391(16)
N1	C7	1.4672(16)
N1	C8	1.3451(17)
C1	C2	1.3803(19)
C1	C6	1.3785(19)
C2	C3	1.385(2)
C3	C4	1.361(3)
C4	C5	1.360(3)

Atom	Atom	Length/Å
C5	C6	1.394(2)
C8	C9	1.5306(16)
C9	C10	1.5189(17)
C9	C16	1.5273(18)
C10	C11	1.3883(18)
C10	C15	1.3894(19)
C11	C12	1.384(2)
C12	C13	1.376(3)
C17	C18	1.377(3)
C13	C14	1.381(2)

Table 5 Bond Angles for sunrongxia_0428-1_auto.

Atom	Atom	Atom	Angle/˚
C1	N1	C7	115.34(11)
C8	N1	C1	124.40(10)
C8	N1	C7	119.77(11)
C2	C1	N1	119.12(12)
C6	C1	N1	120.075(12)
C6	C1	C2	120.07(13)
C1	C2	C3	120.06(14)
C4	C3	C2	118.56(15)
F1	C4	C3	118.75(17)
F1	C4	C5	118.27(16)
C5	C4	C3	122.97(15)
C4	C5	C6	118.42(15)

Atom	Atom	Atom	Angle/˚
O3	C8	C9	120.47(11)
N1	C8	C9	118.39(19)
C10	C9	C8	109.13(11)
C10	C9	C16	113.03(10)
C16	C9	C8	110.14(11)
C11	C10	C9	119.78(12)
C11	C10	C15	118.17(13)
C15	C10	C9	122.03(11)
C12	C11	C10	121.02(15)
C13	C12	C11	120.06(15)
C12	C13	C14	119.59(15)
C13	C14	C15	120.51(16)

C1	C6	C5	119.87(14)	C14	C15	C10	110.64(14)
O3	C8	N1	121.11(11)	O2	C16	C9	111.84(13)

Table 6 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for sunrongxia_0428-1_auto.

Atom	x	y	z	U(eq)
H2	5871.83	7418.54	2132.73	121
H3	6306.69	4401.26	5694.59	74
H4	7499.31	3781.35	6333.91	89
H5	8200.23	4196.35	3779.13	86
H6	7004.32	4823.27	3130.73	71
H7	5156.75	3808.22	4437.48	103
H8	5426.79	3494.29	3452.17	103
H9	4787.36	4436.45	3495.91	103
H10	6671.98	6852.91	4067.28	55
H11	7096.67	6932.12	5693.22	68
H12	7037.15	7586.17	7236.57	88
H13	6053.23	8772.75	7564.49	94
H14	5129.74	9298.41	6343.12	87
H15	5174.01	8624.52	4803.84	70
H16	5557.59	8462.13	3233.06	73
H17	6392.96	8859.52	3504.5	73

9. Reference

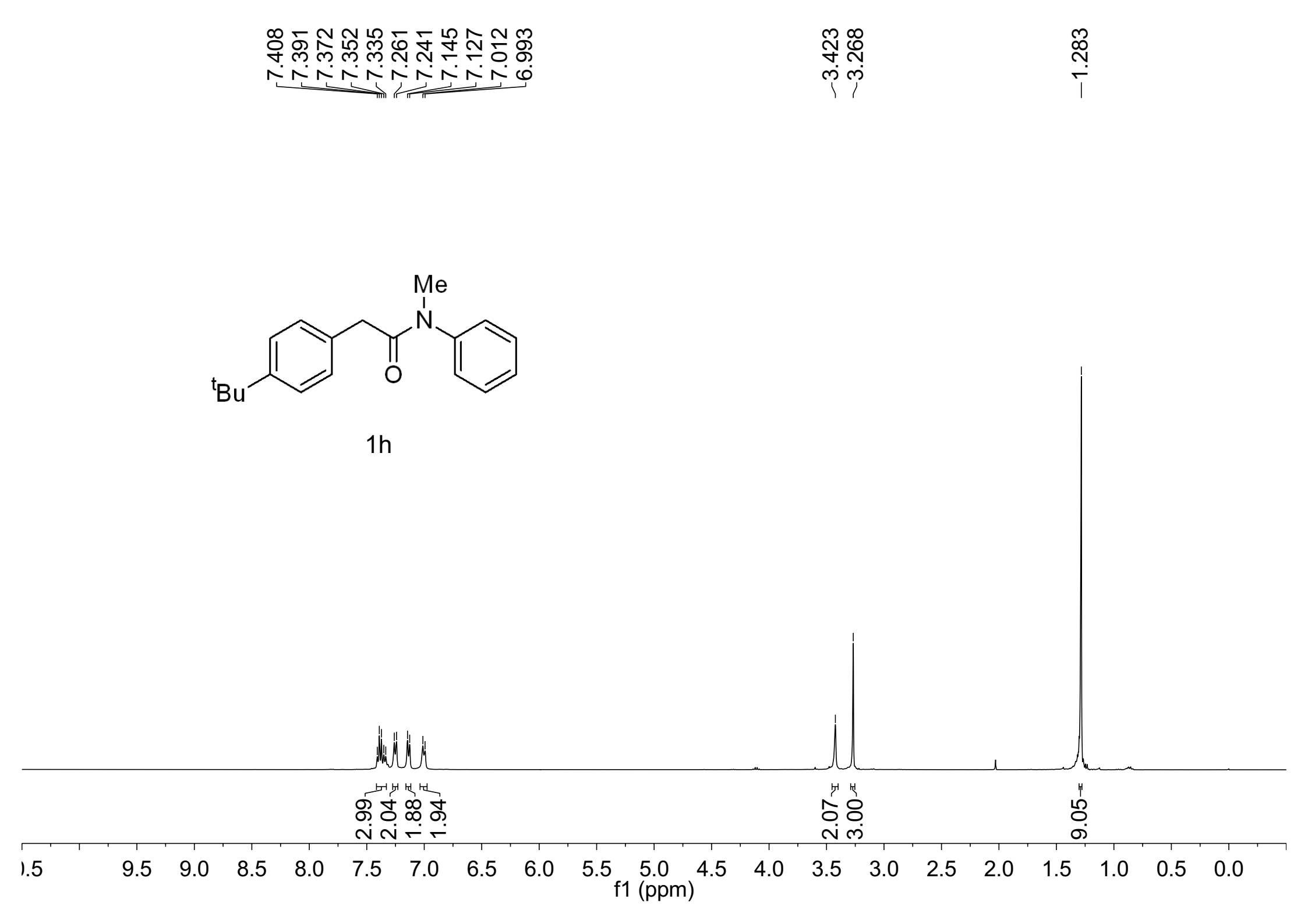
[1] C. Jin, J. Du, C. Zeng, X. Zhao, Y. Cao, X. Zhang, X. Lu, C. Fan, *Adv. Synth. Catal*. 2014, **356**, 2437.

[2] T. Slagbrand, G. Kervefors, F. Tinnis, H. Adolfsson, *Adv. Synth. Catal*. 2017, **359**, 1990.

[3] H. Yang, P. G. Dormer, N. R. Rivera, A. J. Hoover, *Angew. Chem., Int. Ed*. 2018, **57**, 1883.

[4] M. H. Shaw, N. G. McCreanor, W. G. Whittingham, J. F. Bower, *J. Am. Chem. Soc*. 2014, **137**, 463.

10. Cope of NMR Spectra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3.268
1.283
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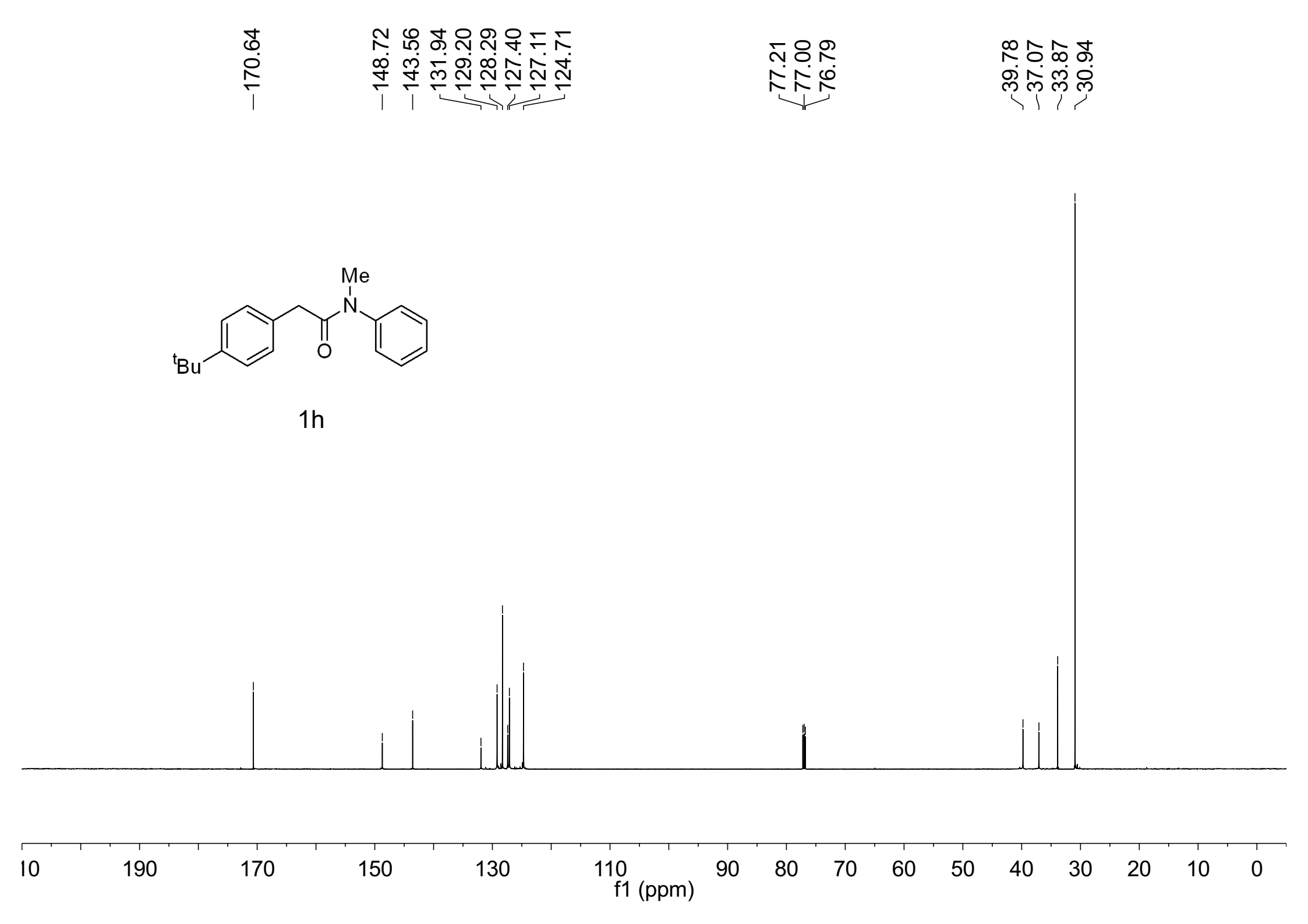
O
tBu
1h
2.99
2.04
1.88
1.94
2.07
3.00
9.05
f1 (ppm)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127.11
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39.78
37.07
33.87
30.94
Me
N
O
tBu
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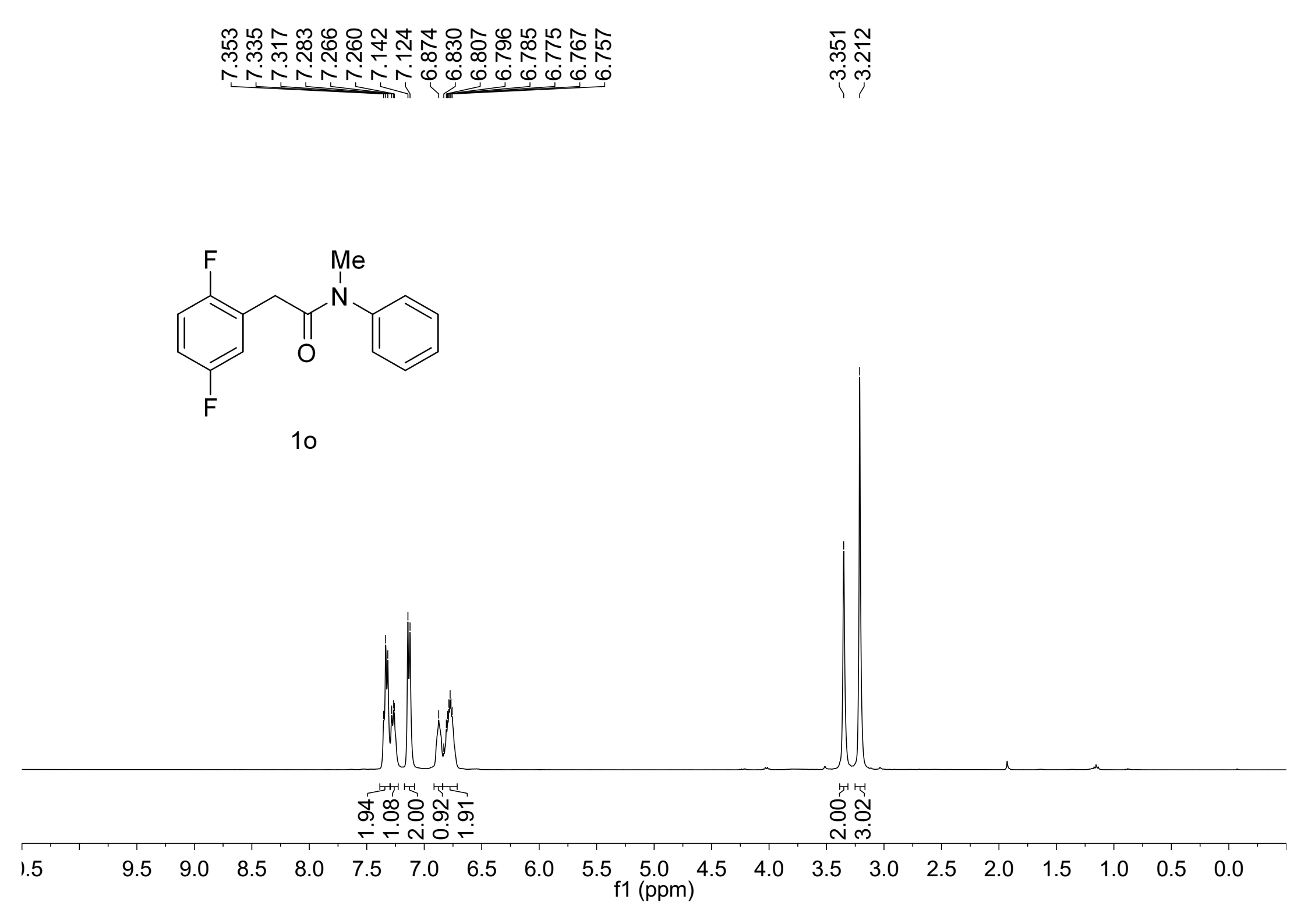
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.785
6.775
6.767
6.757
3.351
3.212
F
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N
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F
1o
1.94
1.08
2.00
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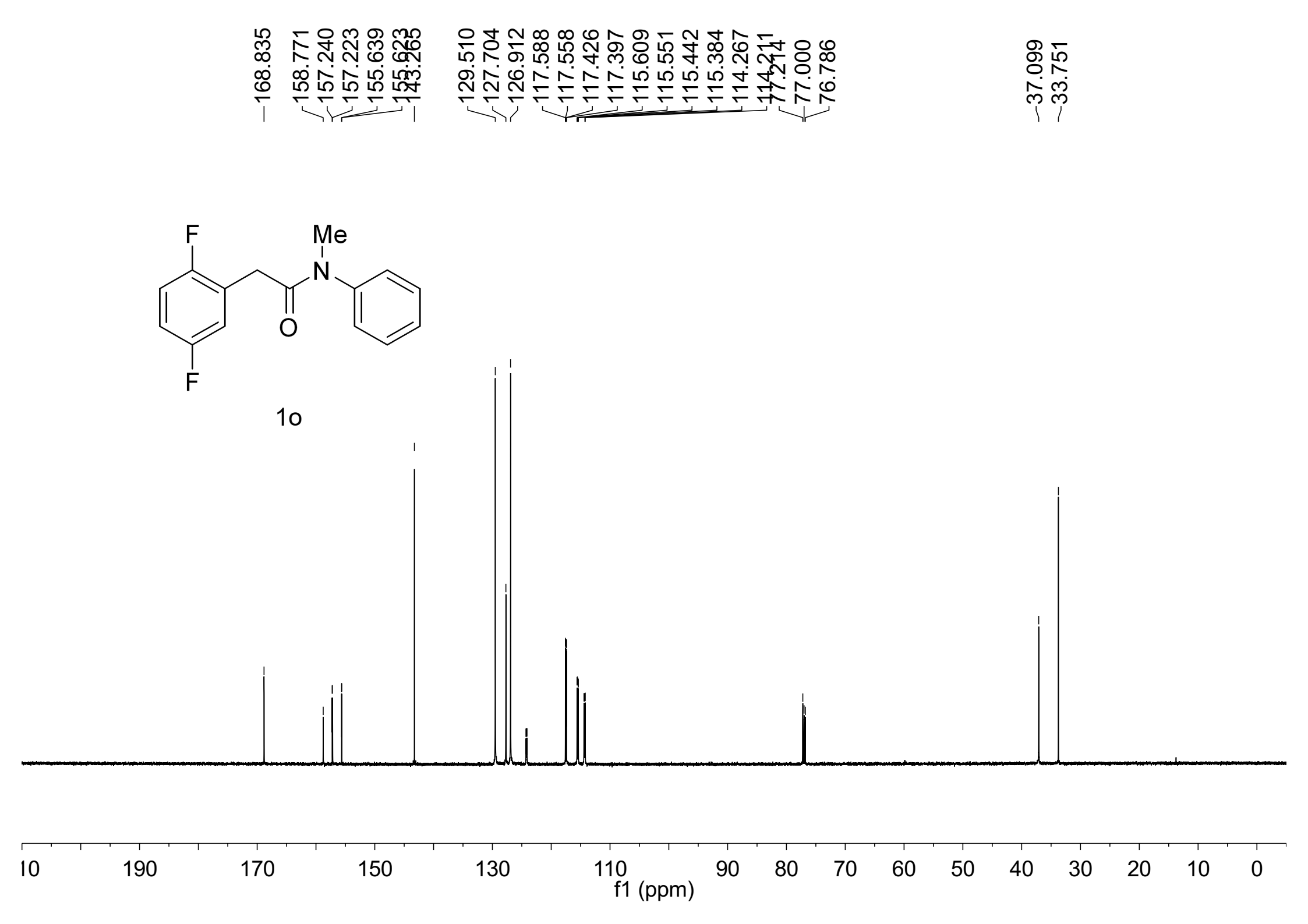
1.91
2.00
3.02
f1 (ppm)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117.426
117.397
115.609
115.551
115.442
115.384
114.267
114.211
77.214
77.000
76.786
37.099
33.751
F
Me
N
O
F
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150
130
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90
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50
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30
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10
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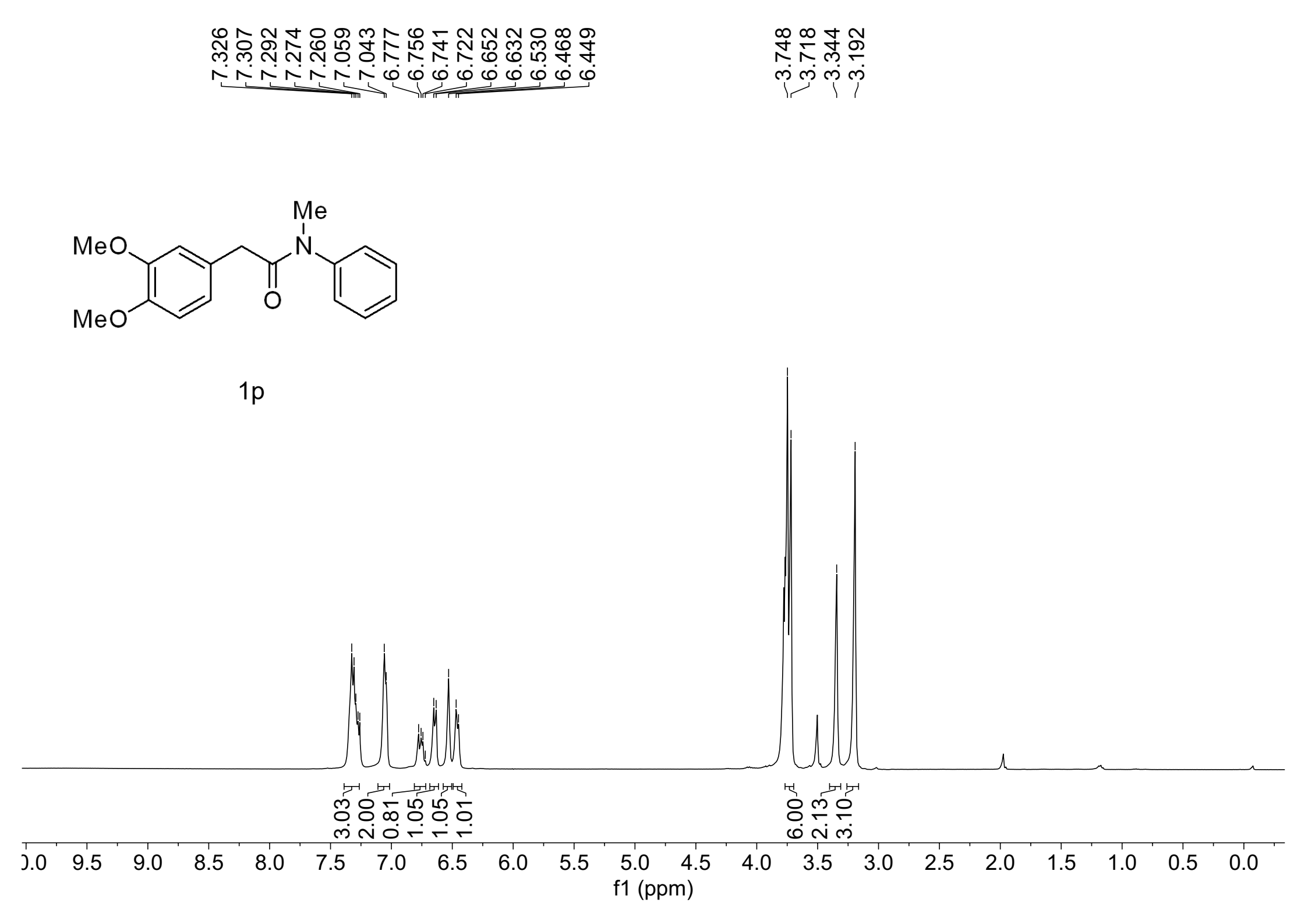
f1 (ppm)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6.530
6.468
6.449
3.748
3.718
3.344
3.192
Me
N
MeO
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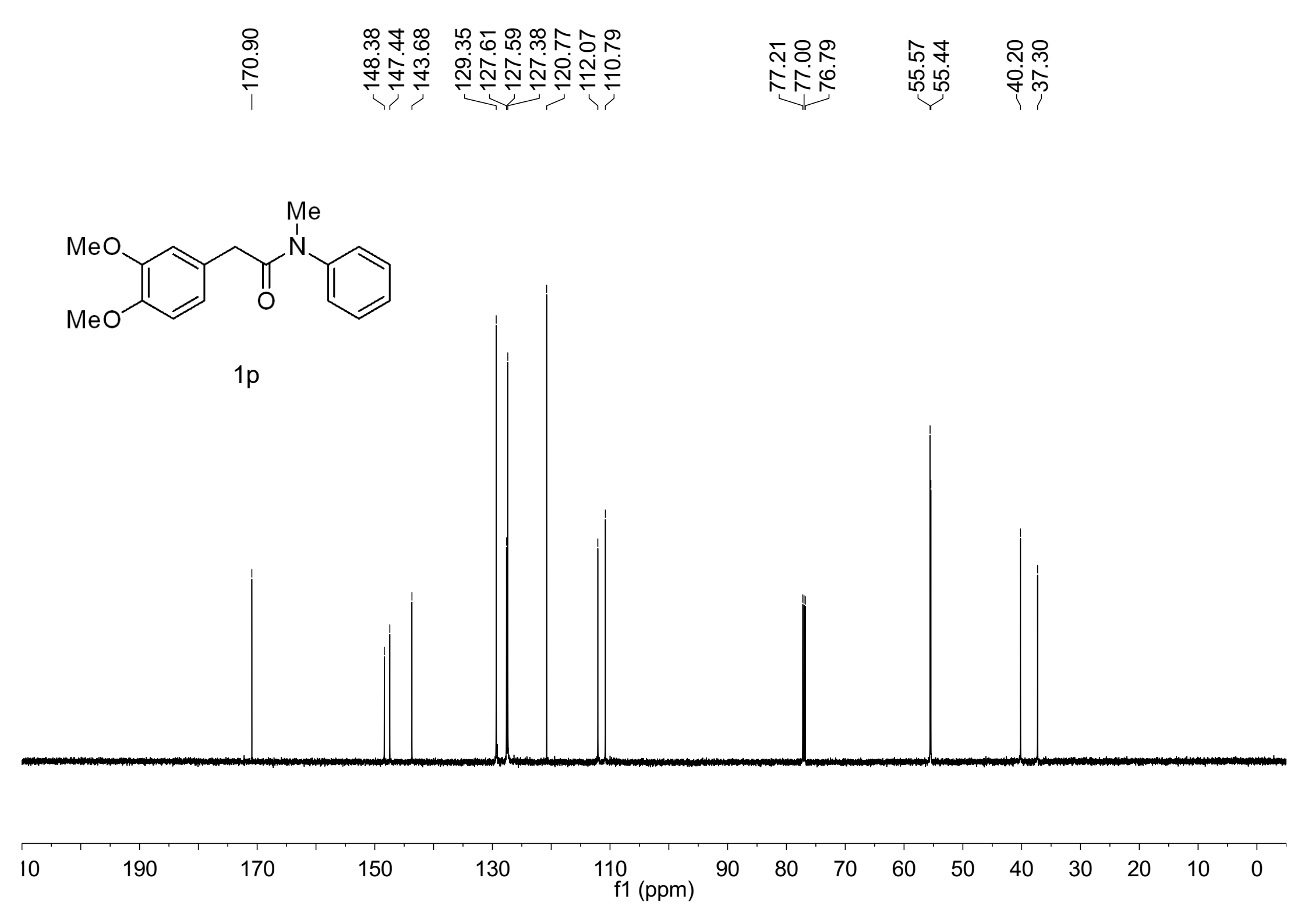
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76.79
55.57
55.44
40.20
37.30
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N
MeO
MeO
O
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150
130
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90
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70
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50
40
30
20
10
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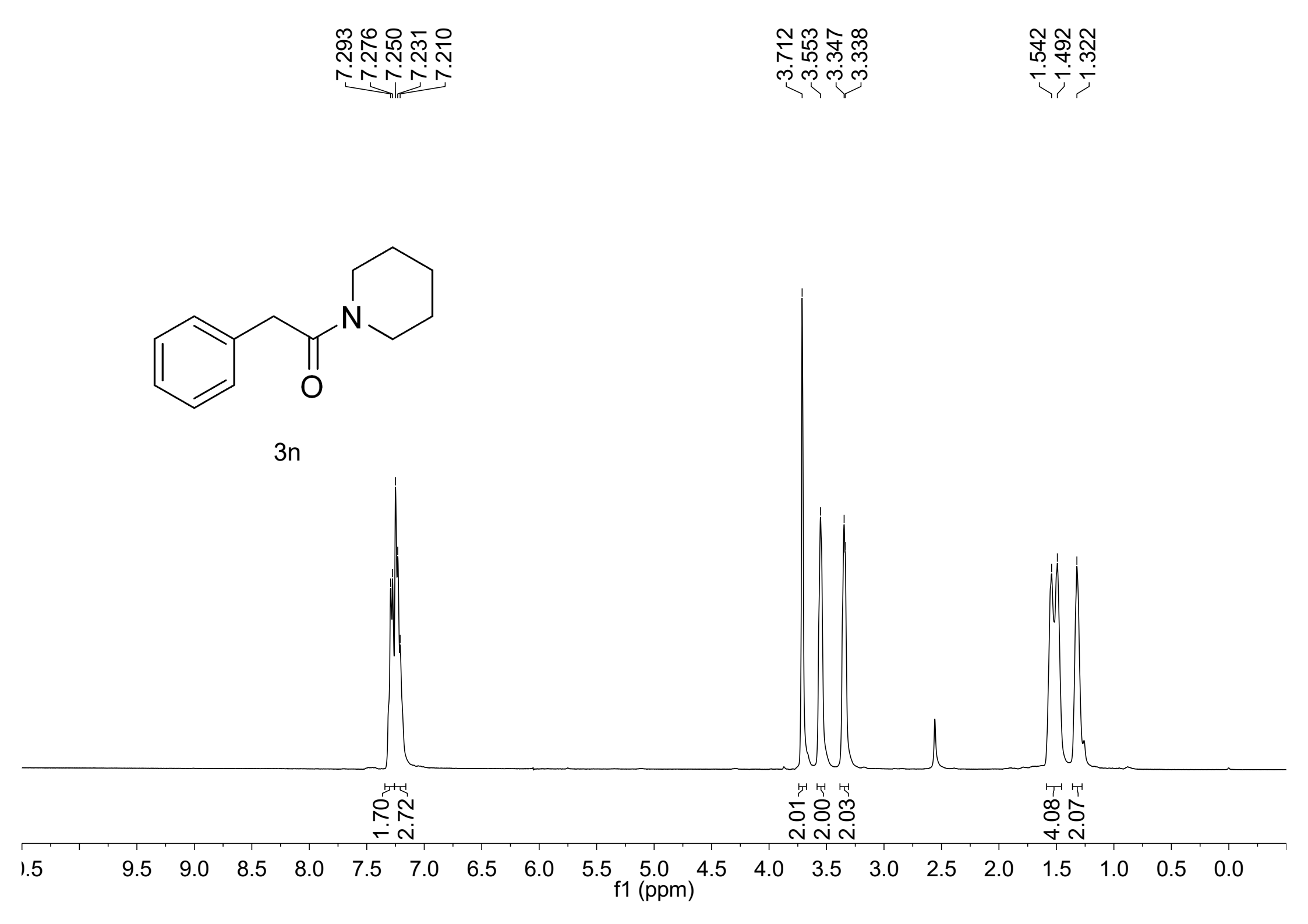
f1 (ppm)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O
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2.00
2.03
4.08
2.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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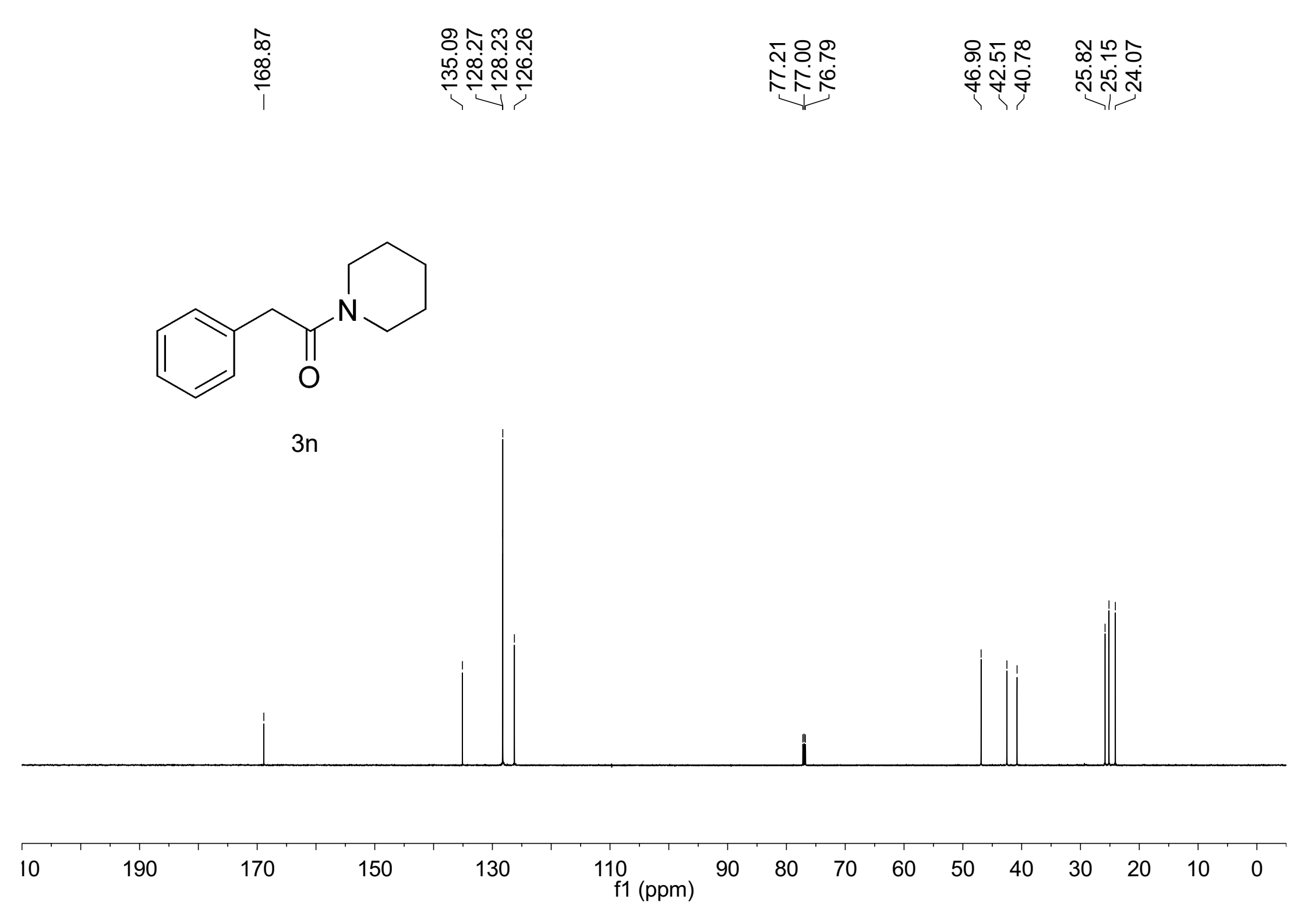
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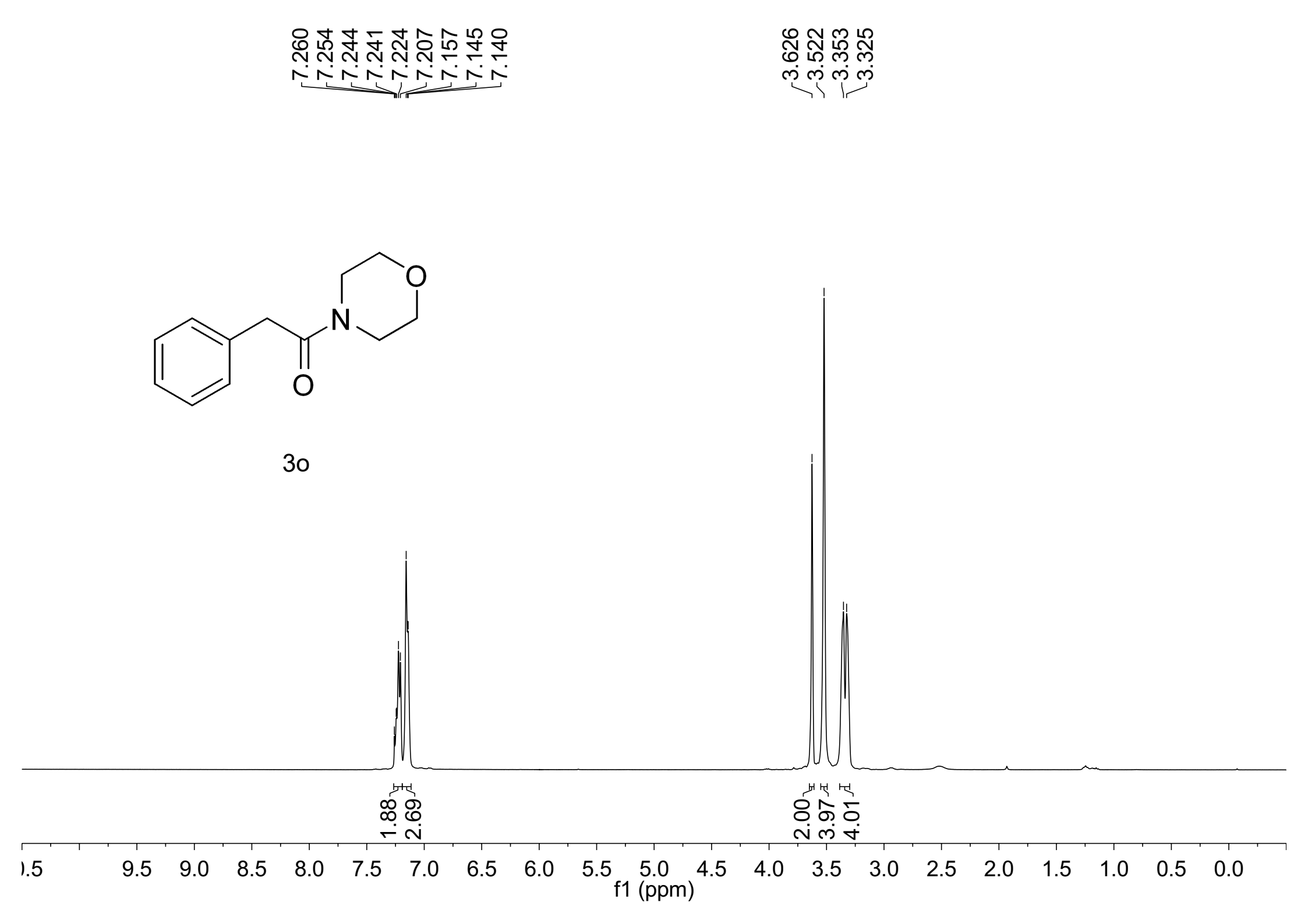
25.15
24.07
N
O
3n
f1 (ppm)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N
O
3o
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2.00
3.97
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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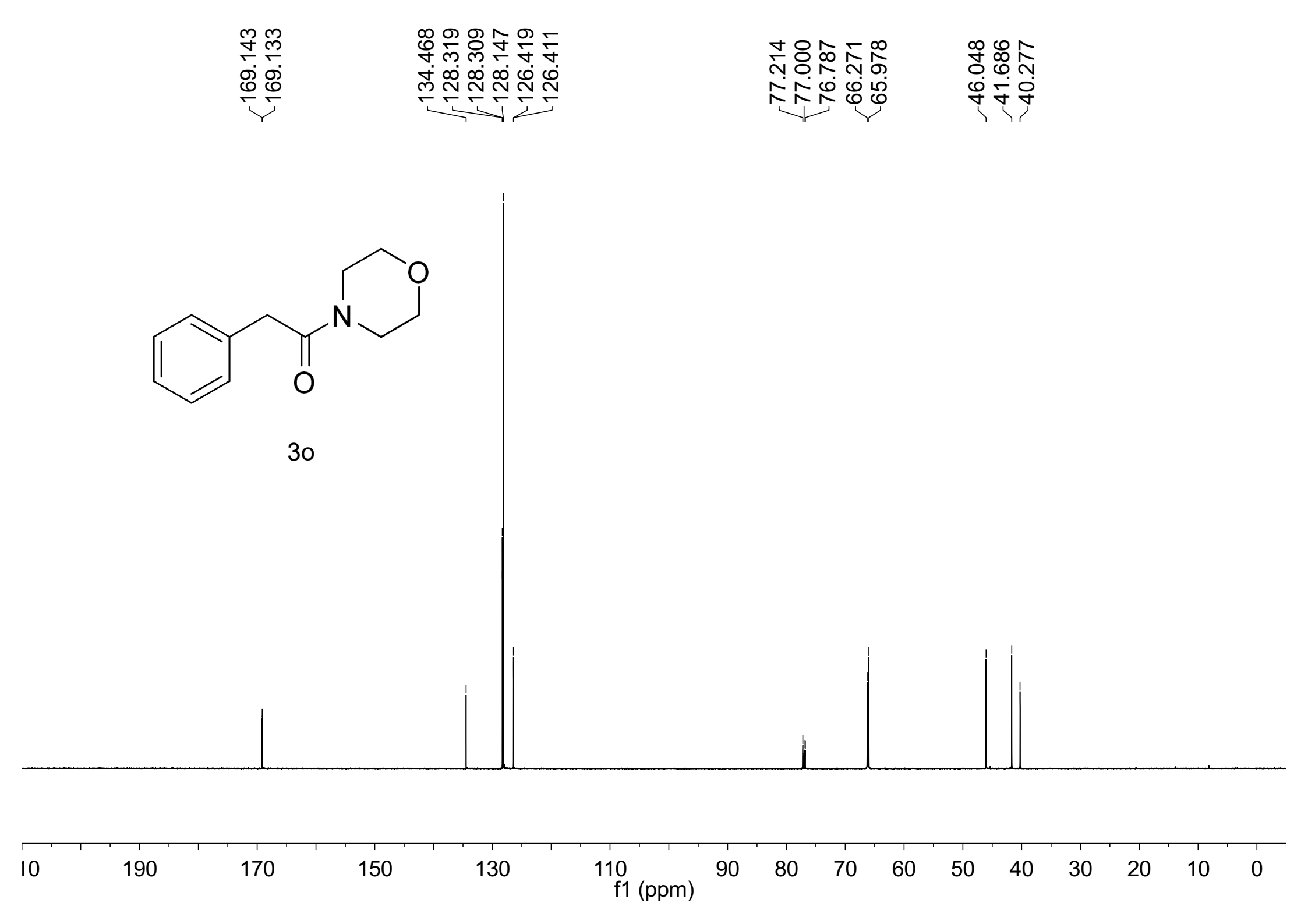
0.0
f1 (ppm)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46.048
41.686
40.277
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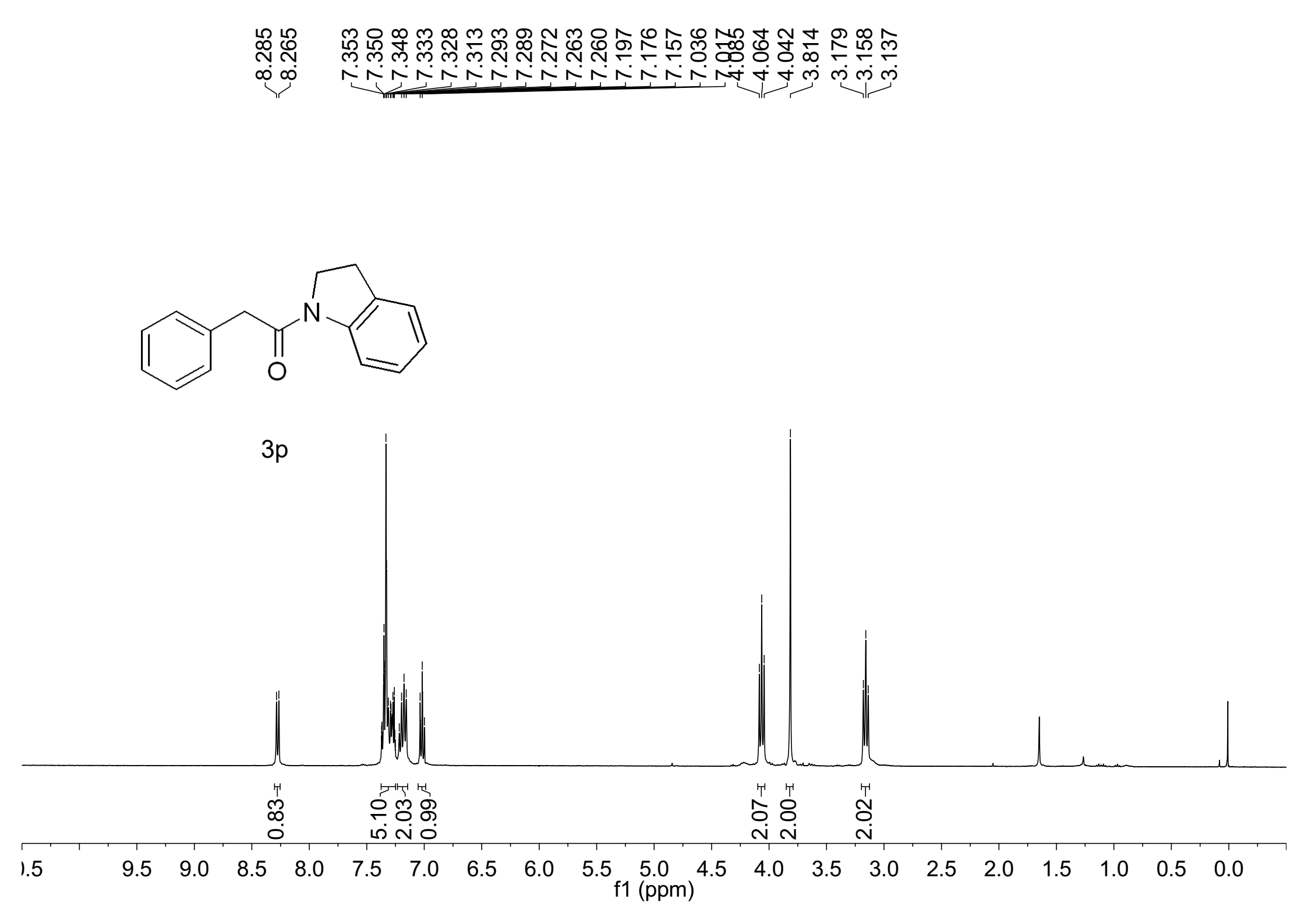
f1 (ppm)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7.036
4.064
4.042
3.814
3.179
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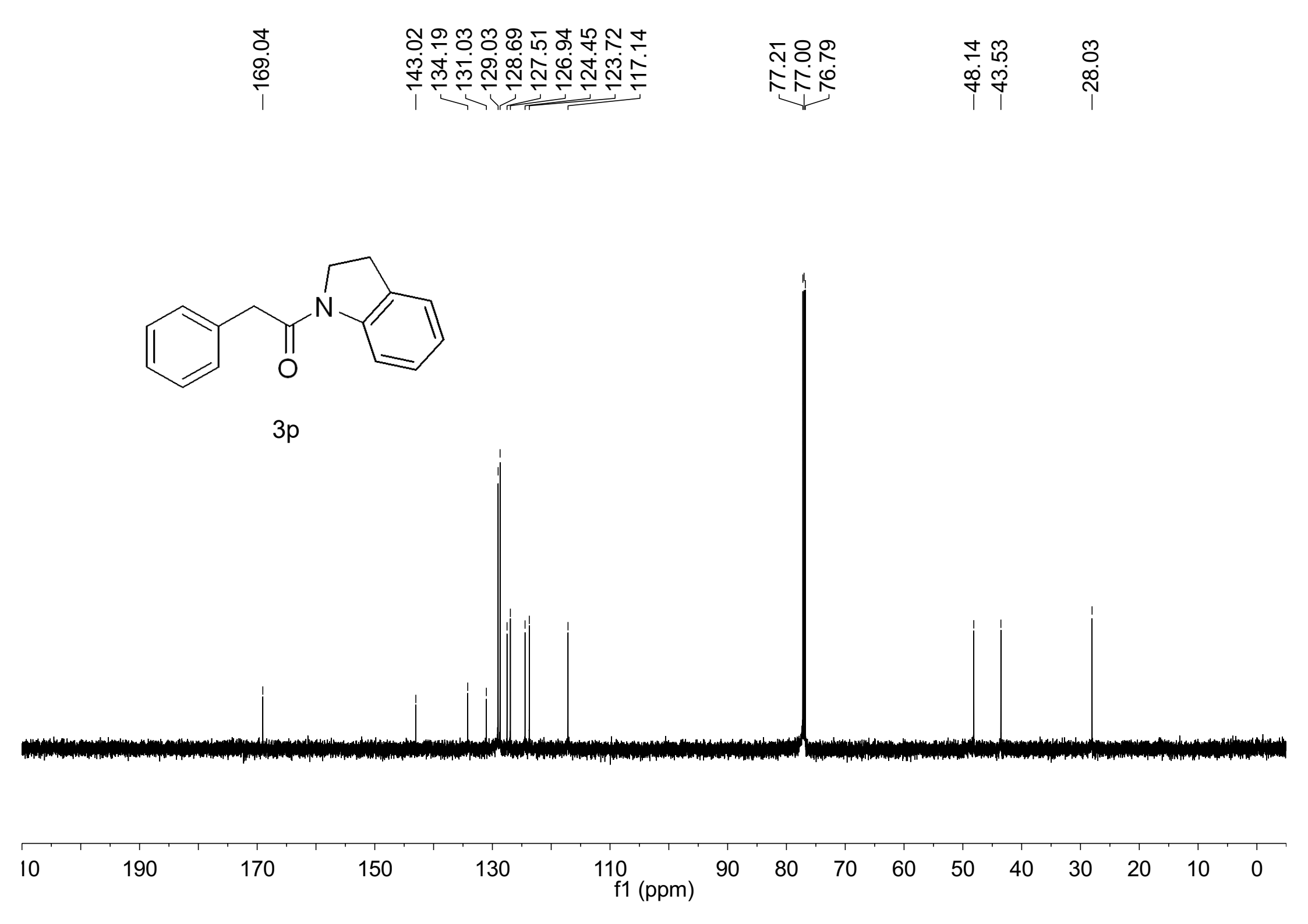
f1 (ppm)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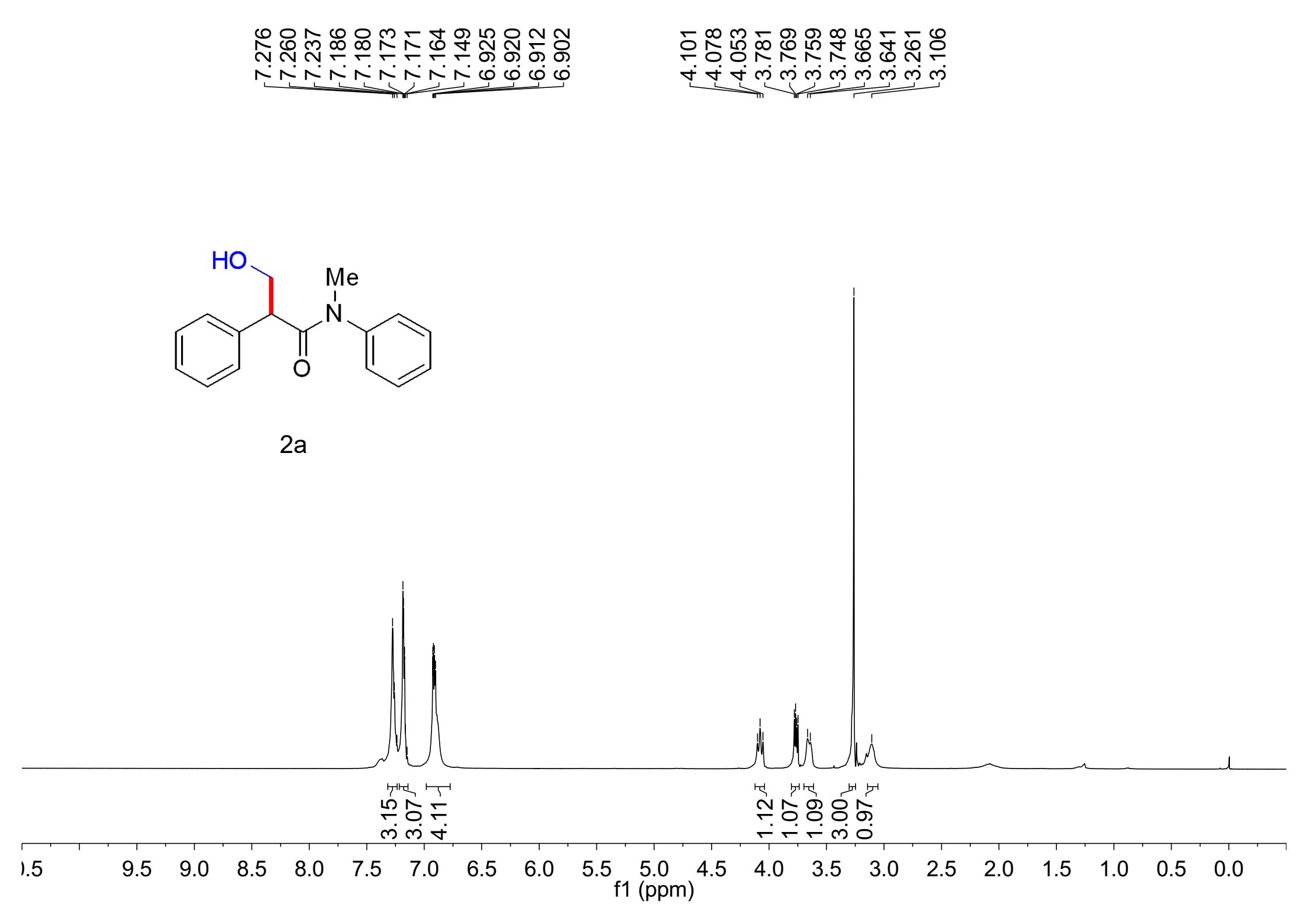
O
3p
f1 (ppm)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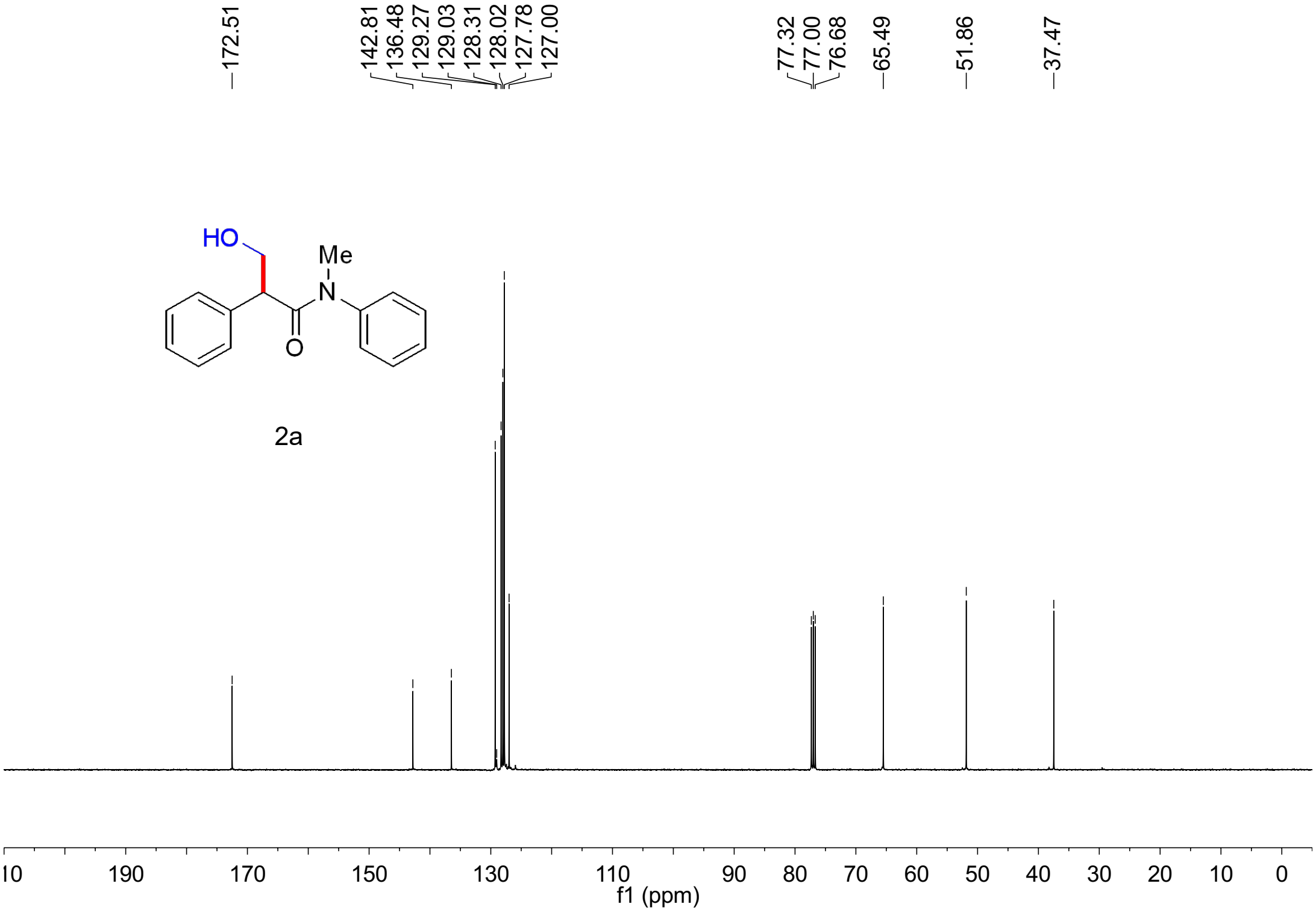
f1 (ppm)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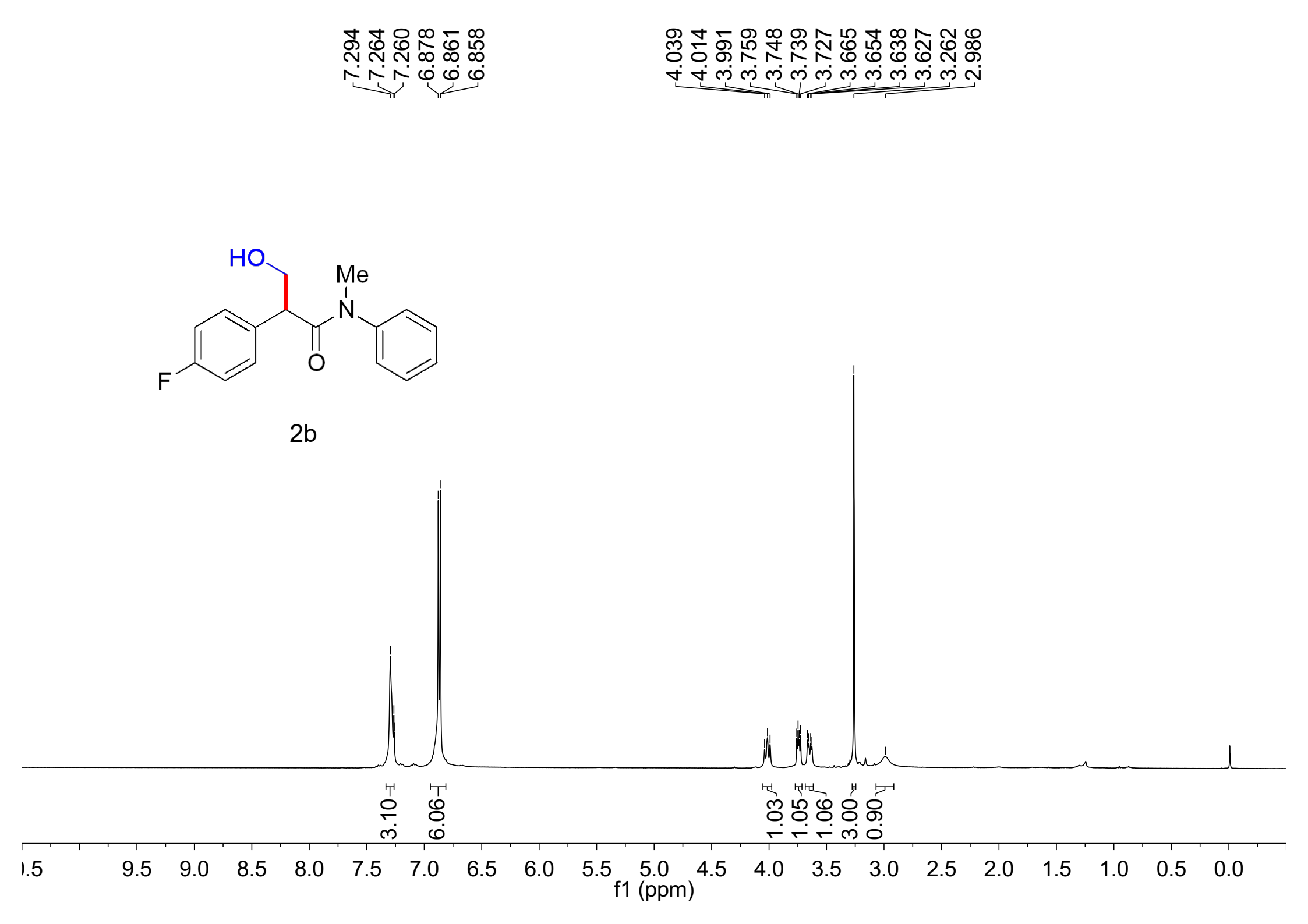
O
2a
f1 (ppm)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1.06
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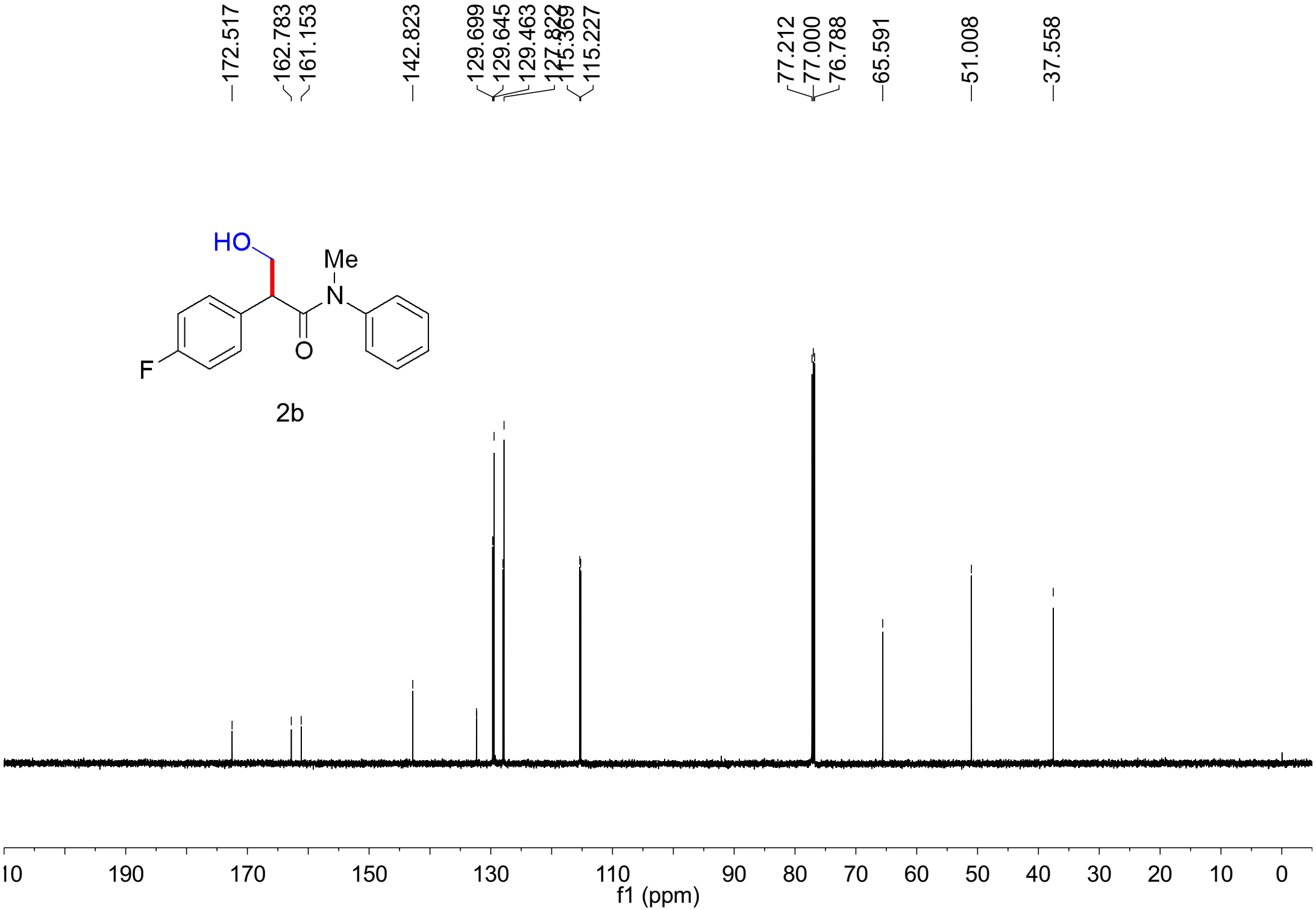
f1 (ppm)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HO
Me
N
O
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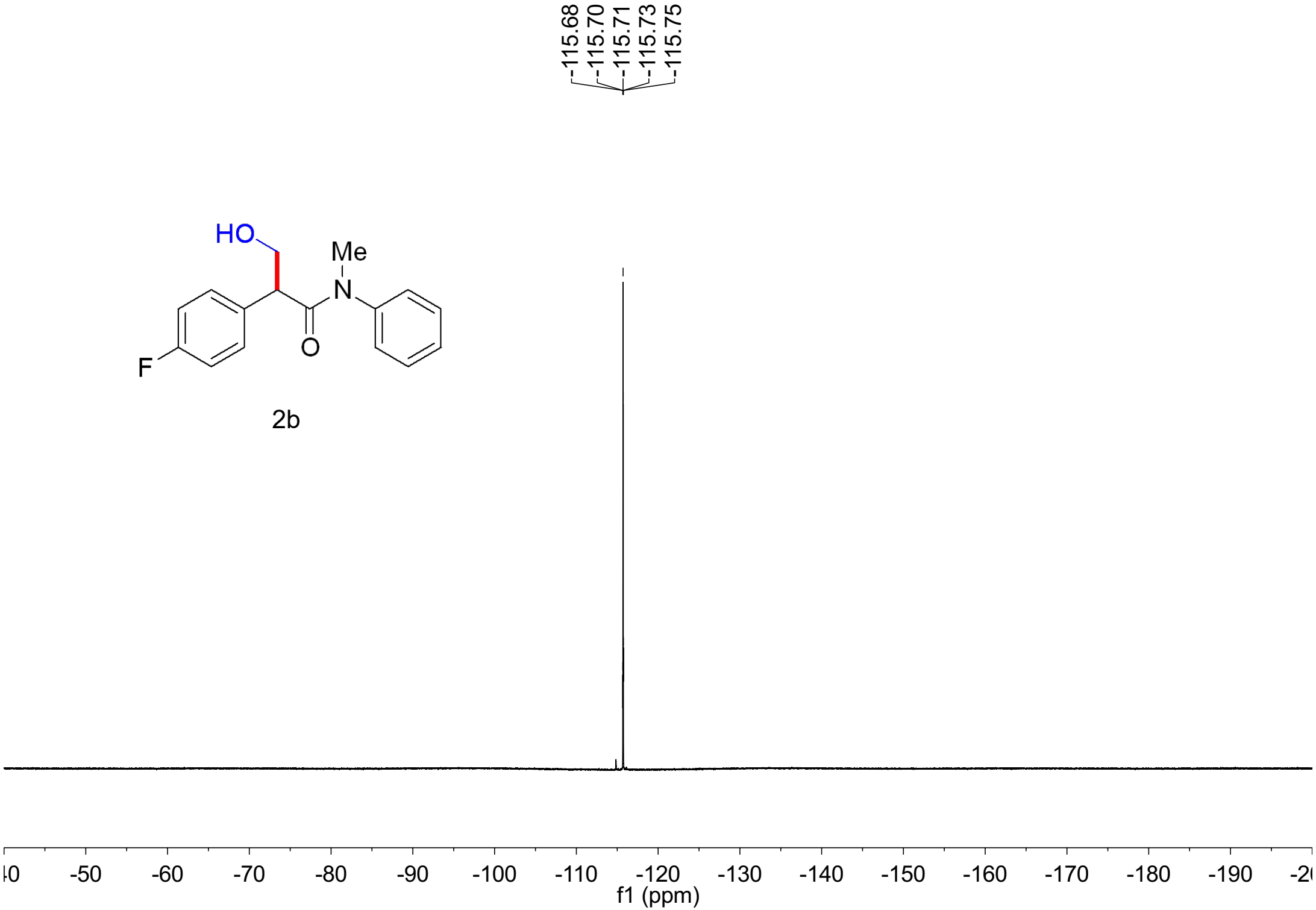
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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-110
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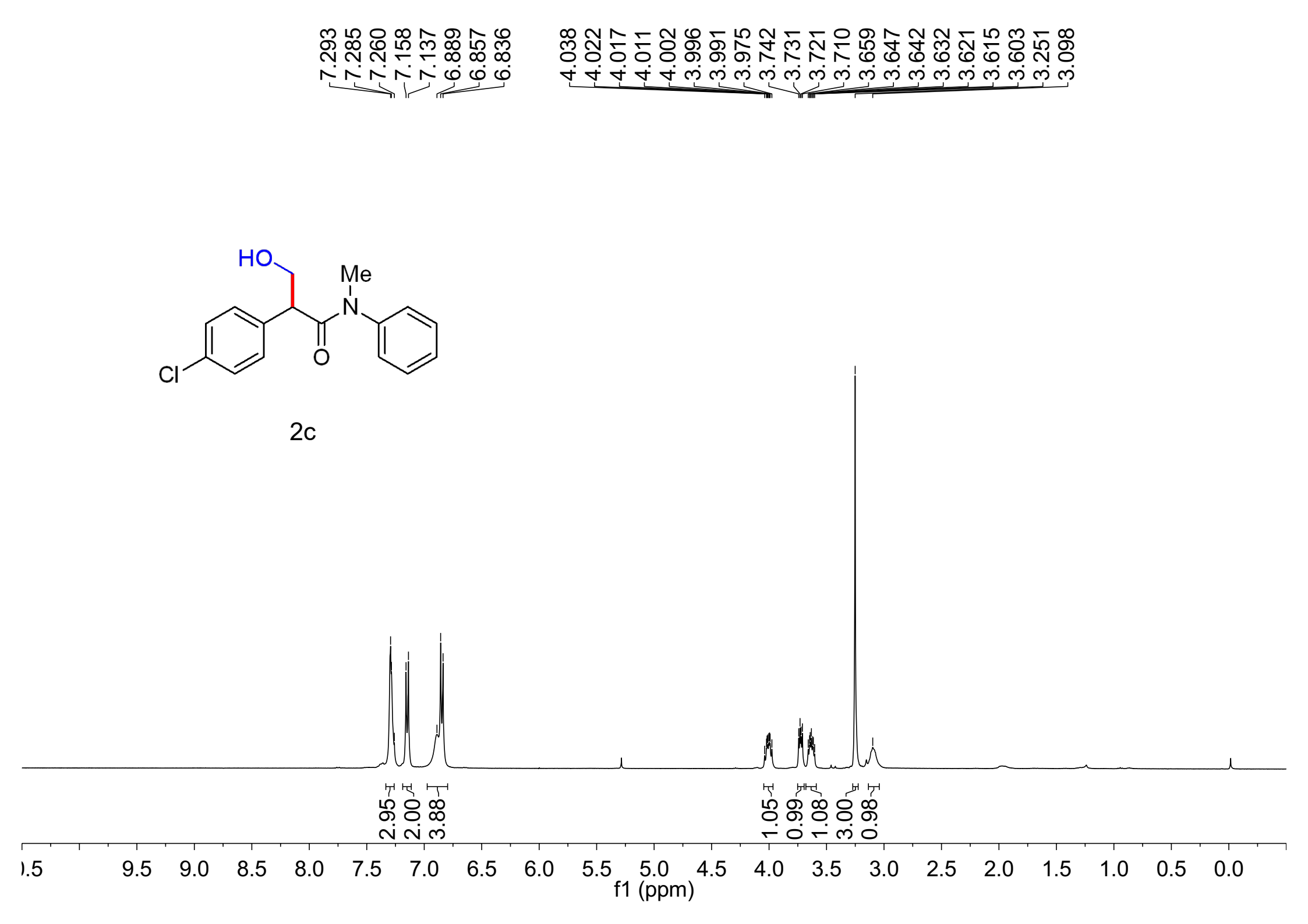
-180
-190
f1 (ppm)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3.991
3.975
3.742
3.731
3.721
3.710
3.659
3.647
3.642
3.632
3.621
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3.098
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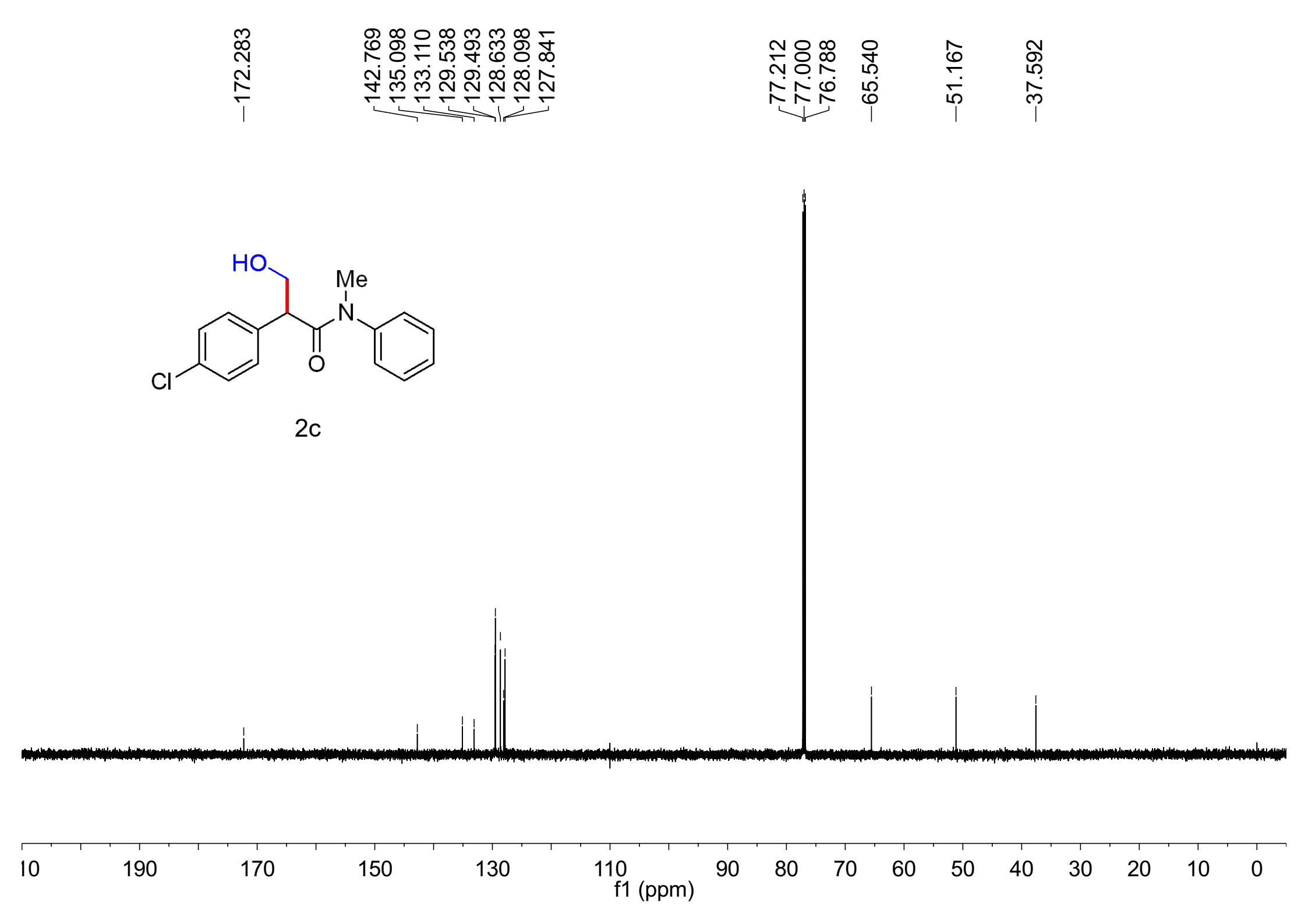
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O
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50
40
30
20
10
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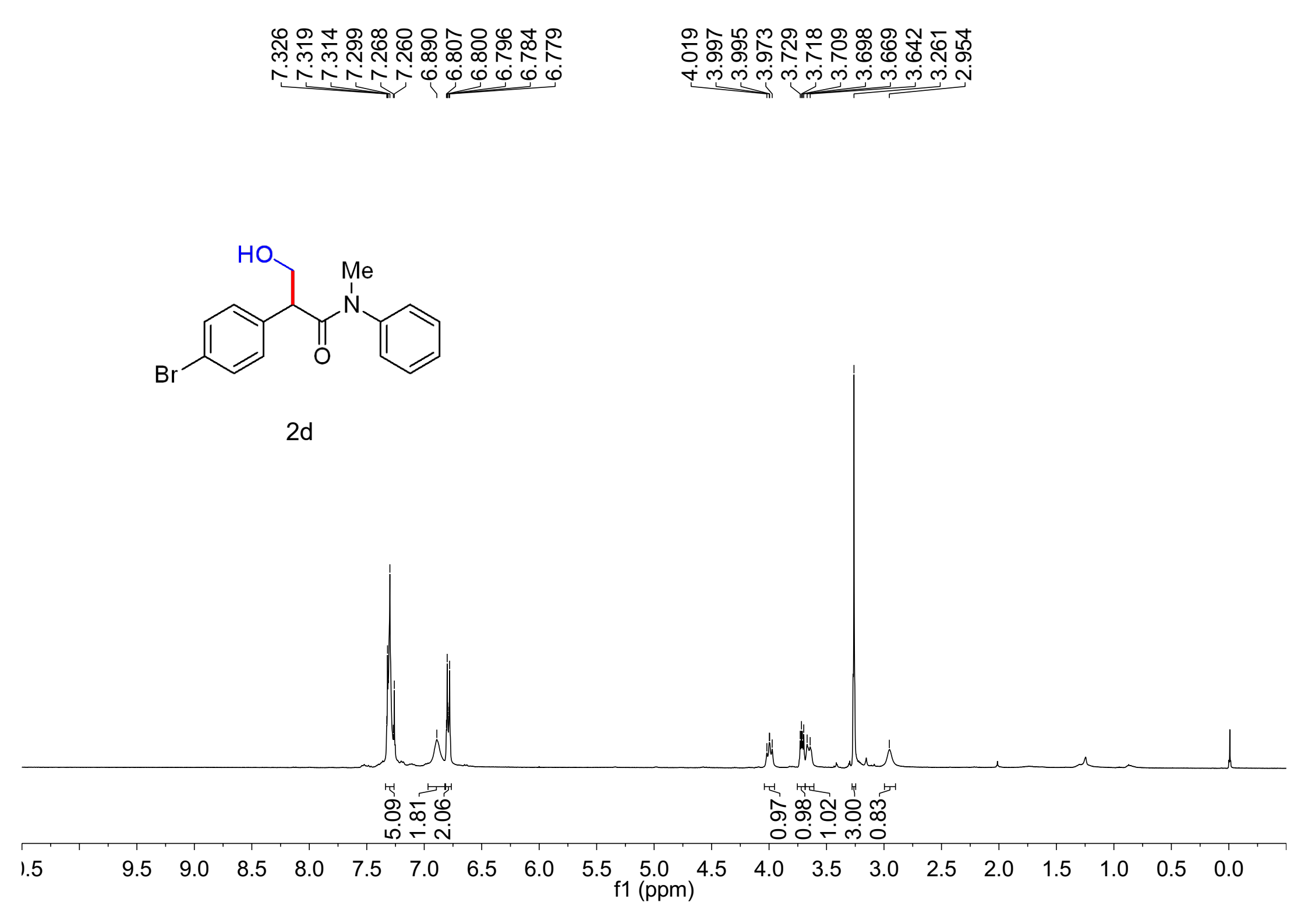
f1 (ppm)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3.973
3.729
3.718
3.709
3.698
3.669
3.642
3.261
2.954
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Br
2d
5.09
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2.06
0.97
0.98
1.02
3.00
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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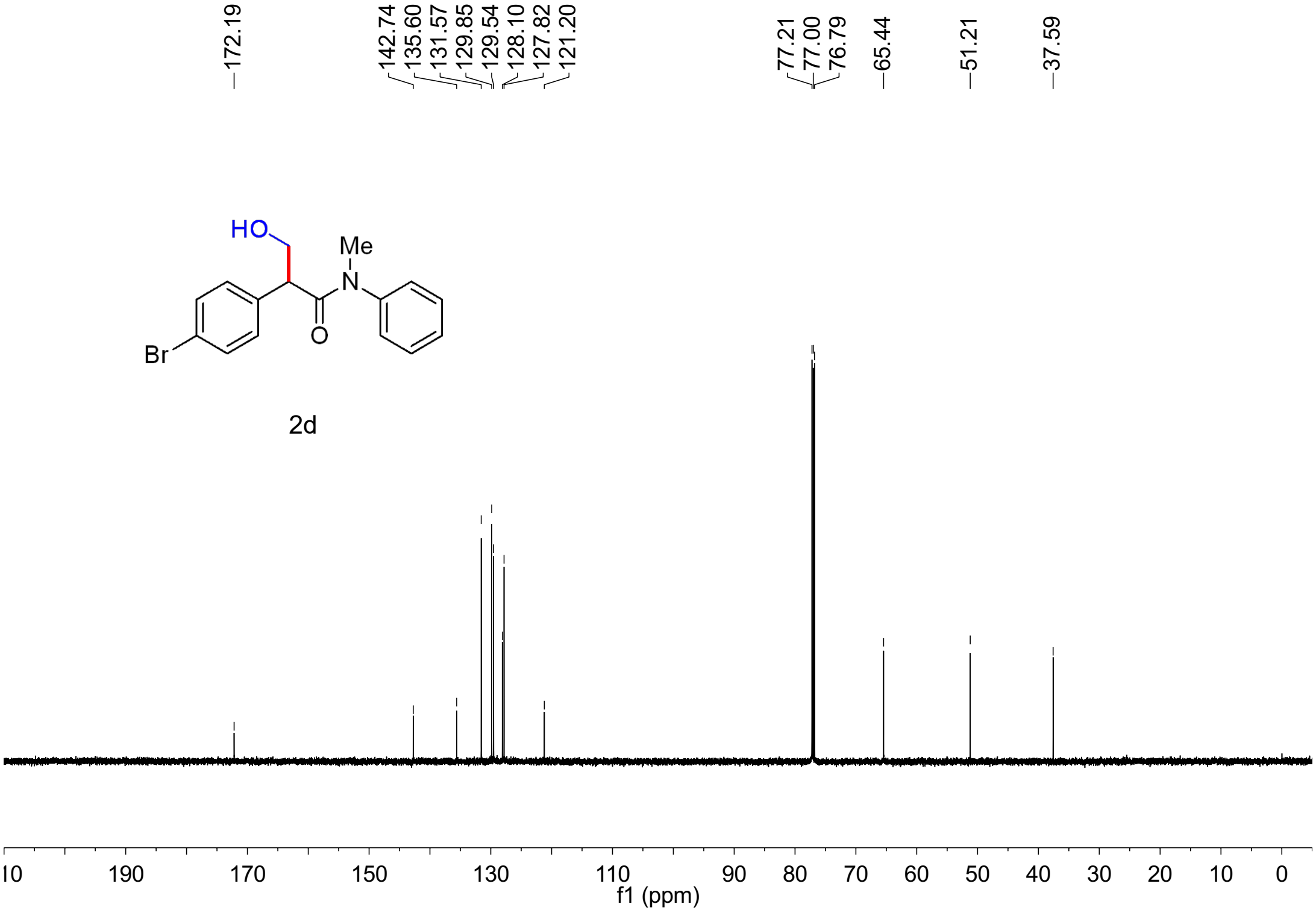
f1 (ppm)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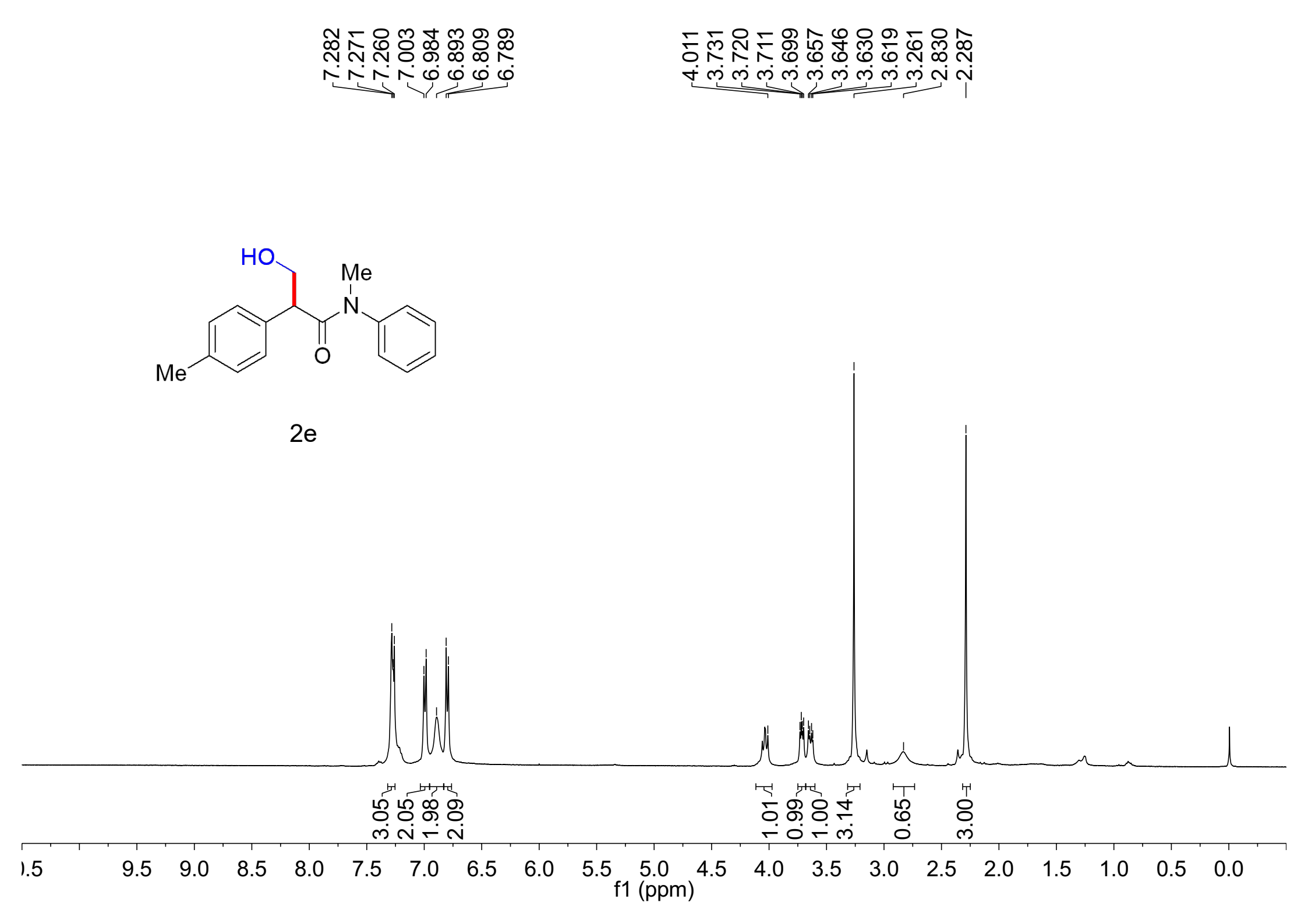
O
Br
2d
f1 (ppm)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3.630
3.619
3.261
2.830
2.287
HO
Me
N
O
Me
2e
3.05
2.05
1.98
2.09
1.01
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1.00
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9.0
8.5
8.0
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6.5
6.0
5.5
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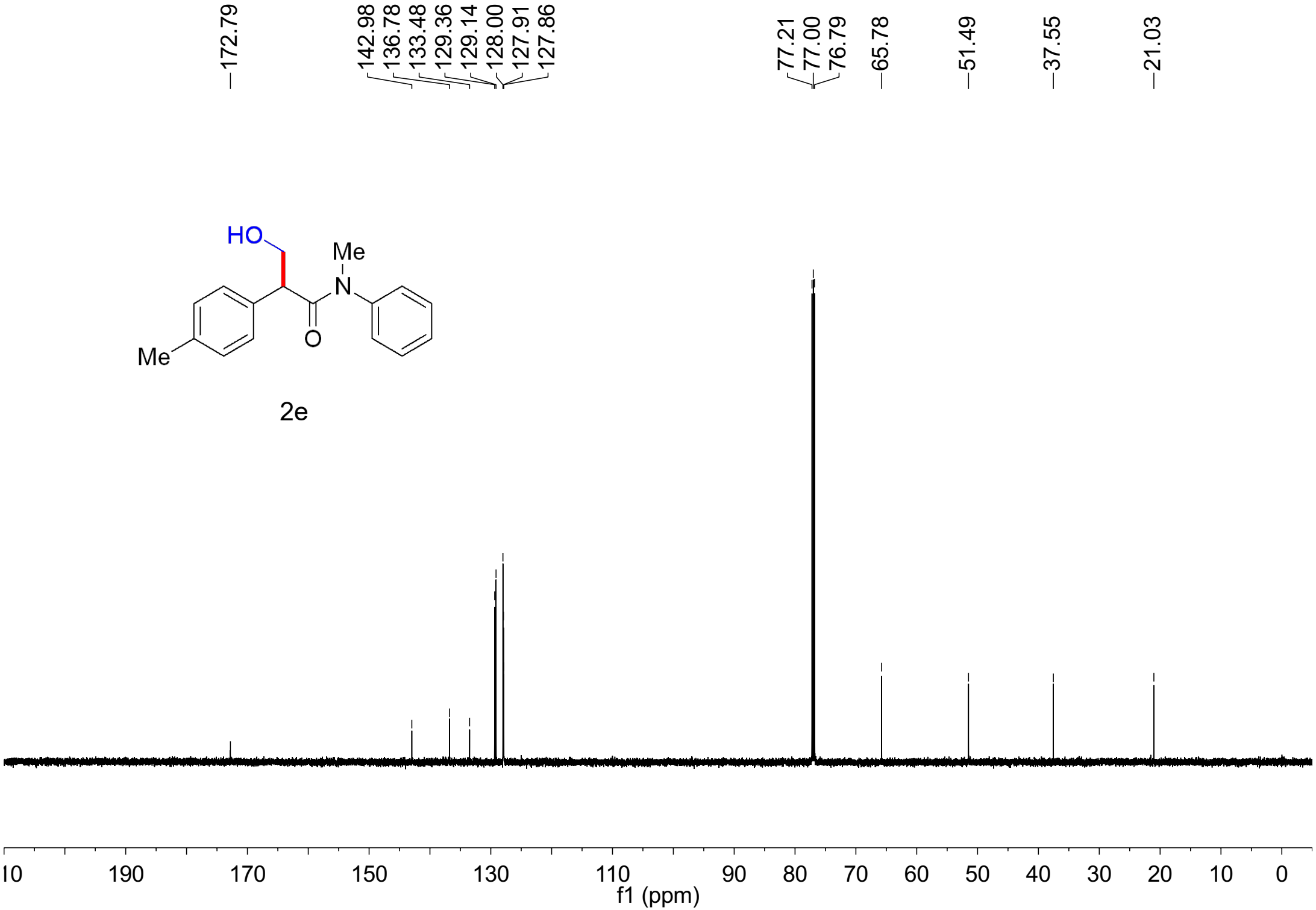
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51.49
37.55
21.03
HO
Me
N
O
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150
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90
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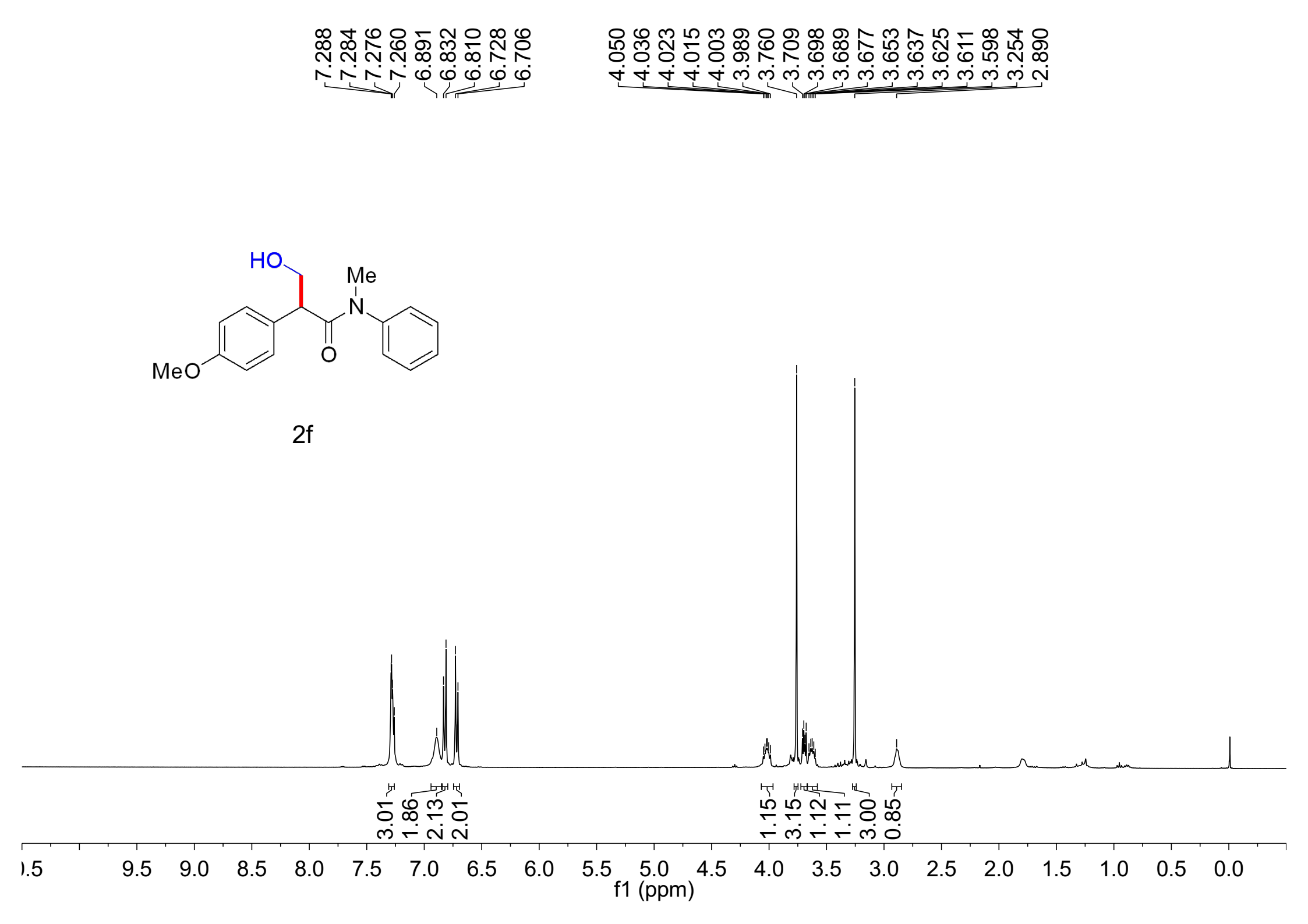
50
40
30
20
10
0
f1 (ppm)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4.023
4.015
4.003
3.989
3.760
3.709
3.698
3.689
3.677
3.653
3.637
3.625
3.611
3.598
3.254
2.890
HO
Me
N
O
MeO
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2.13
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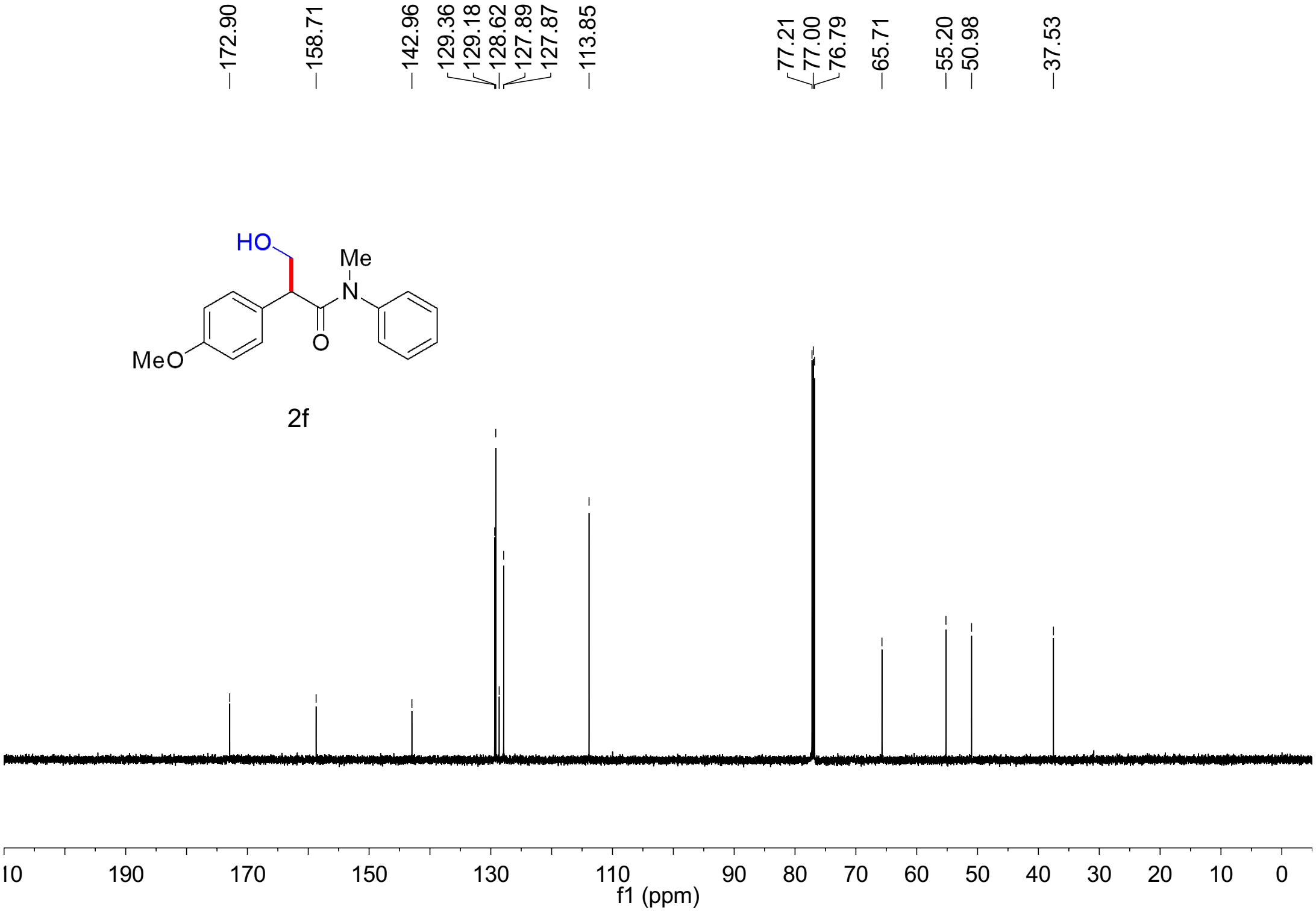
f1 (ppm)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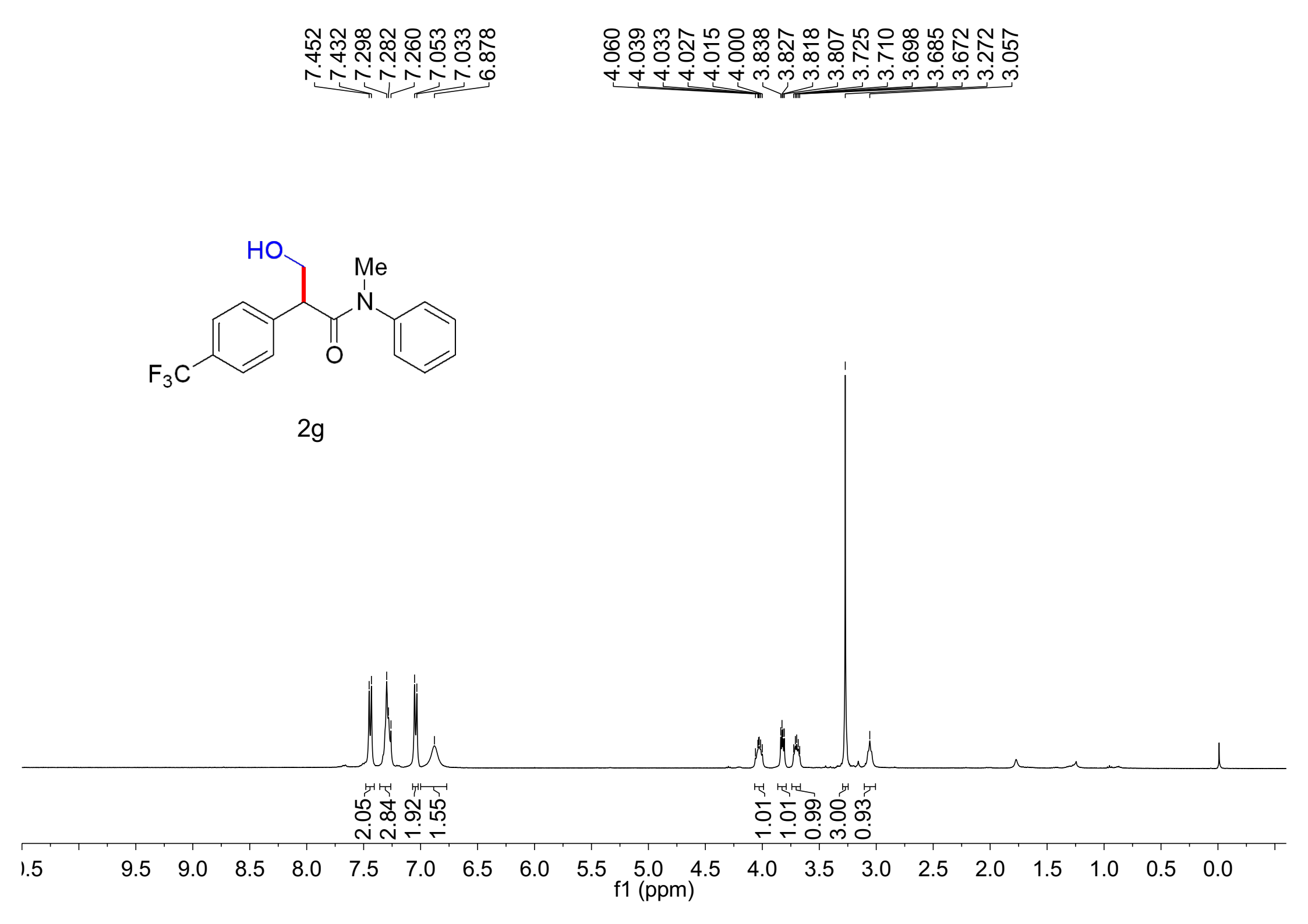
113.85
77.21
77.00
76.79
65.71
55.20
50.98
37.53
HO
Me
N
O
MeO
2f
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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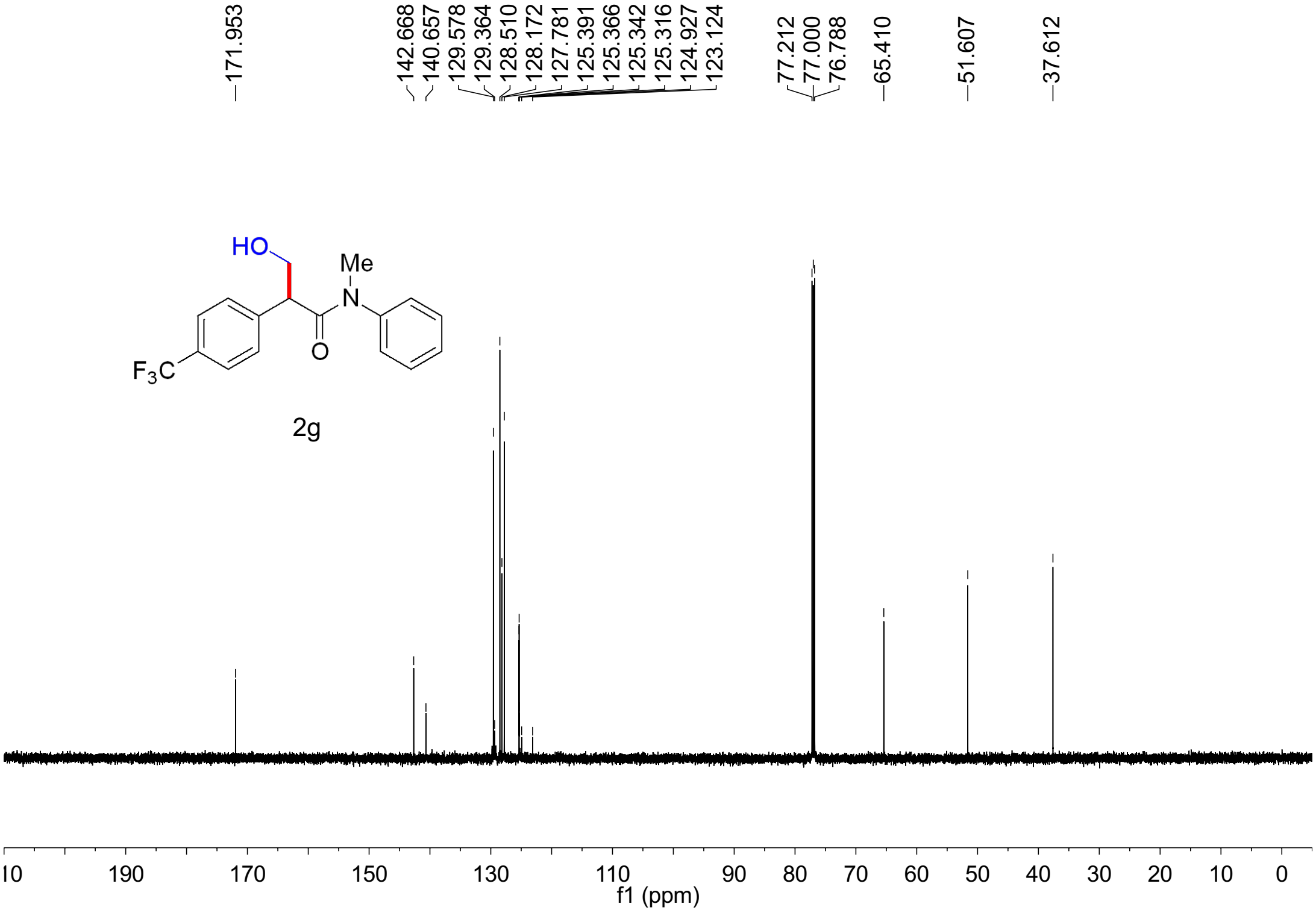
7.260
7.053
7.033
6.878
4.060
4.039
4.033
4.027
4.015
4.000
3.838
3.827
3.818
3.807
3.725
3.710
3.698
3.685
3.672
3.272
3.057
HO
Me
N
O
F3C
2g
2.05
2.84
1.92
1.55
1.01
1.01
0.99
3.00
0.93
f1 (ppm)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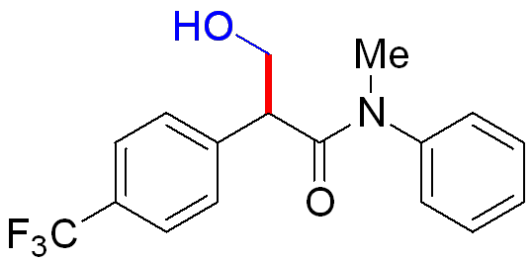
140.657
129.578
129.364
128.510
128.172
127.781
125.391
125.366
125.342
125.316
124.927
123.124
77.212
77.000
76.788
65.410
51.607
37.612
HO
Me
N
O
F3C
2g
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

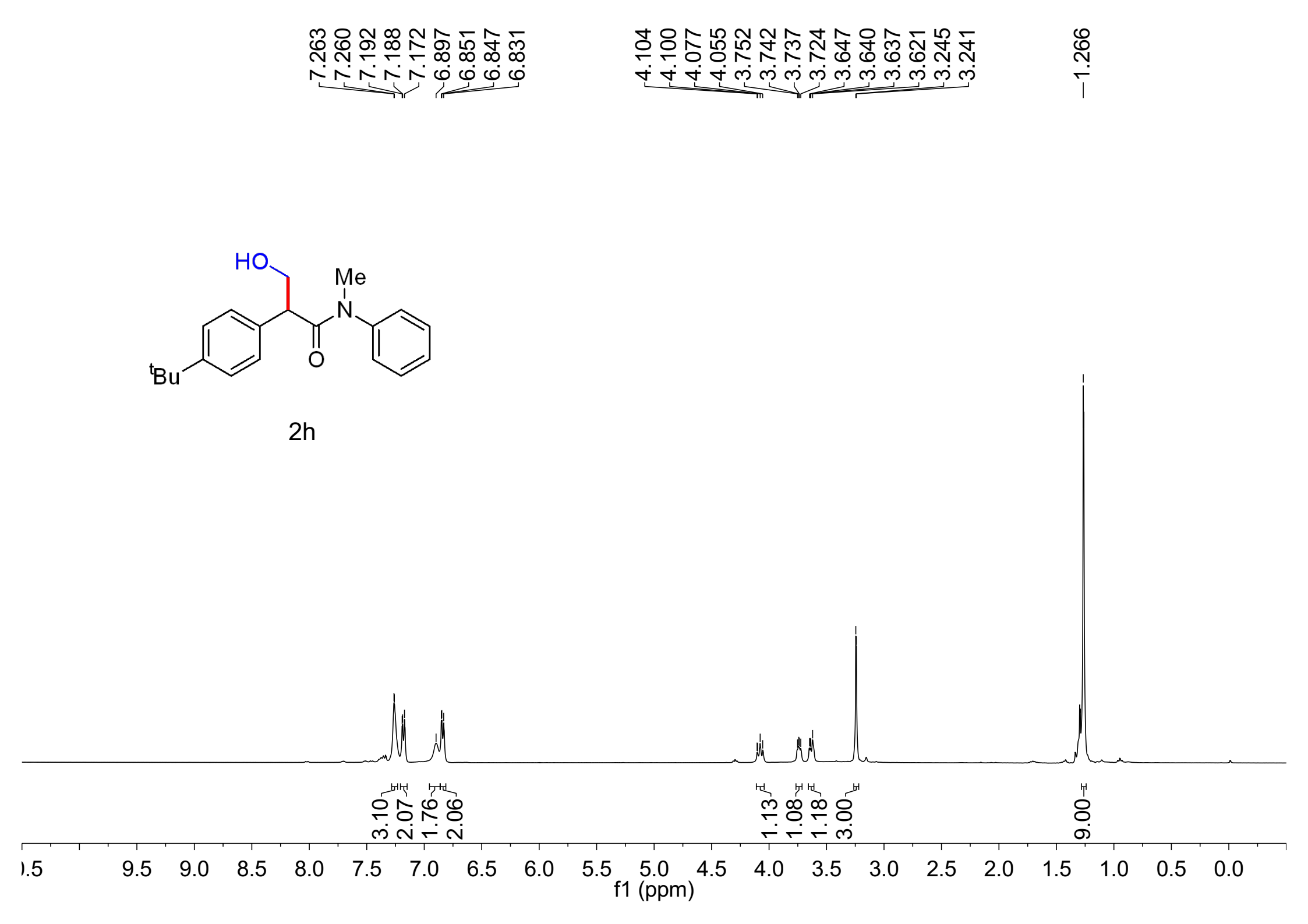


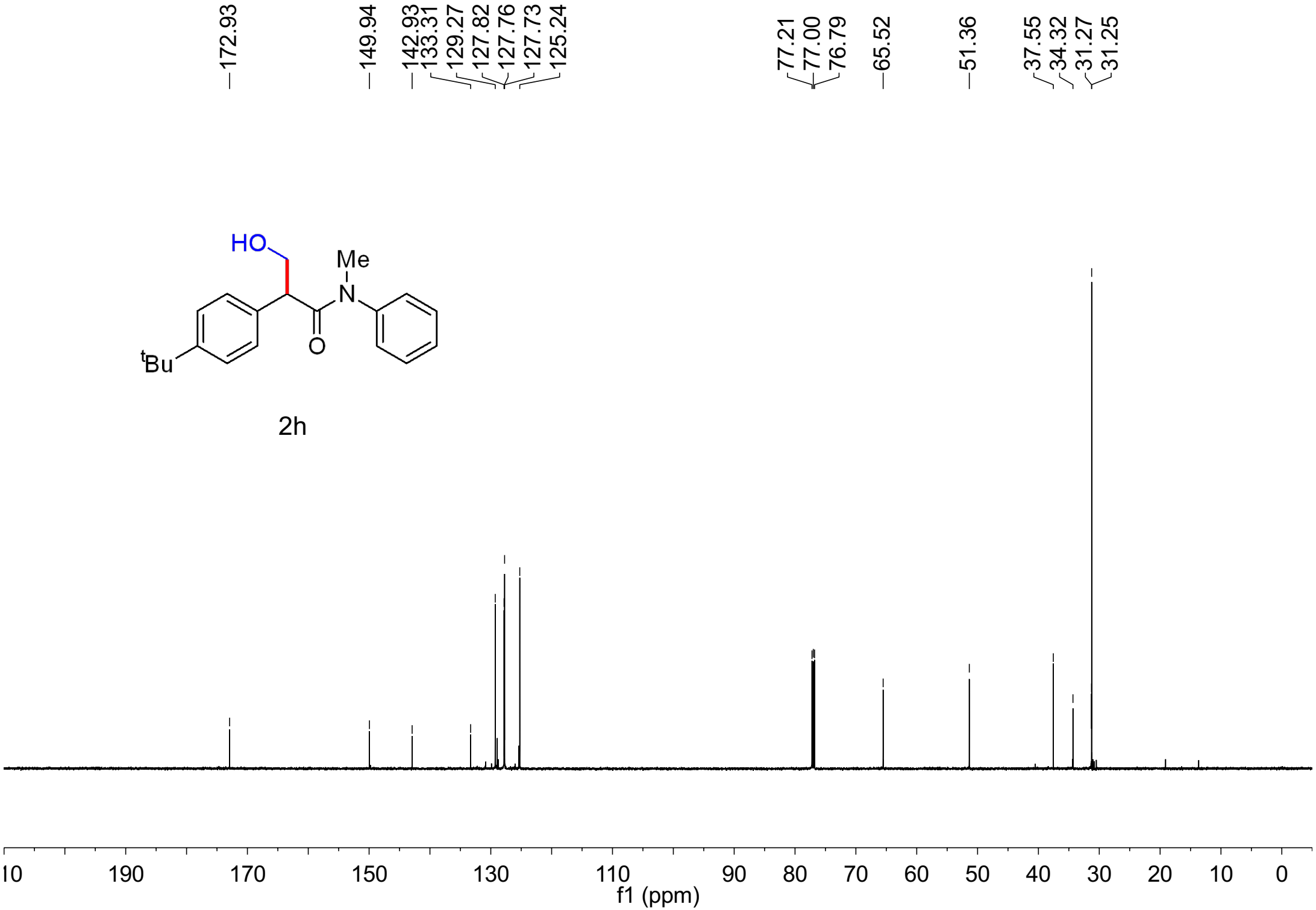
2g

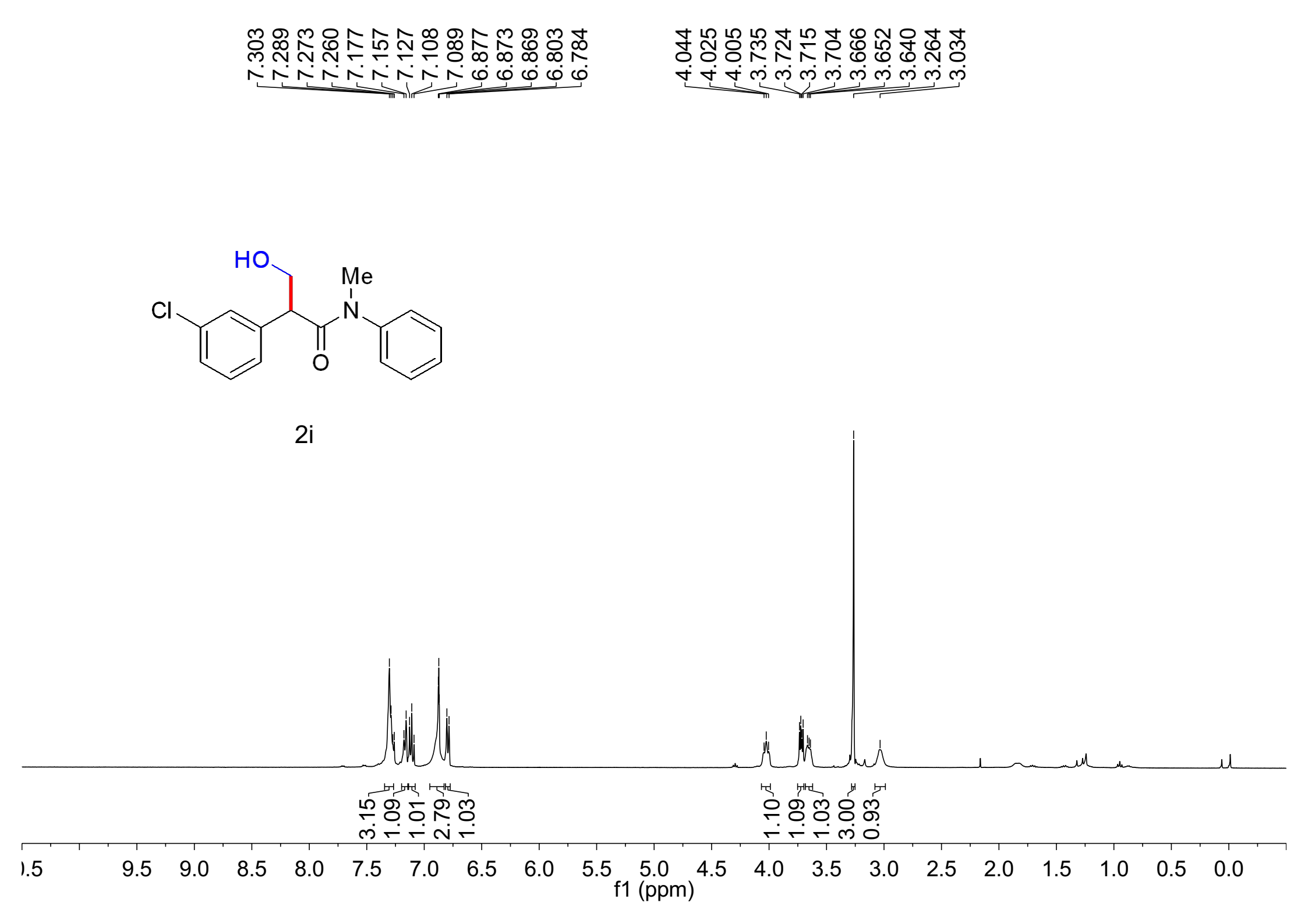
-62.907
-62.965

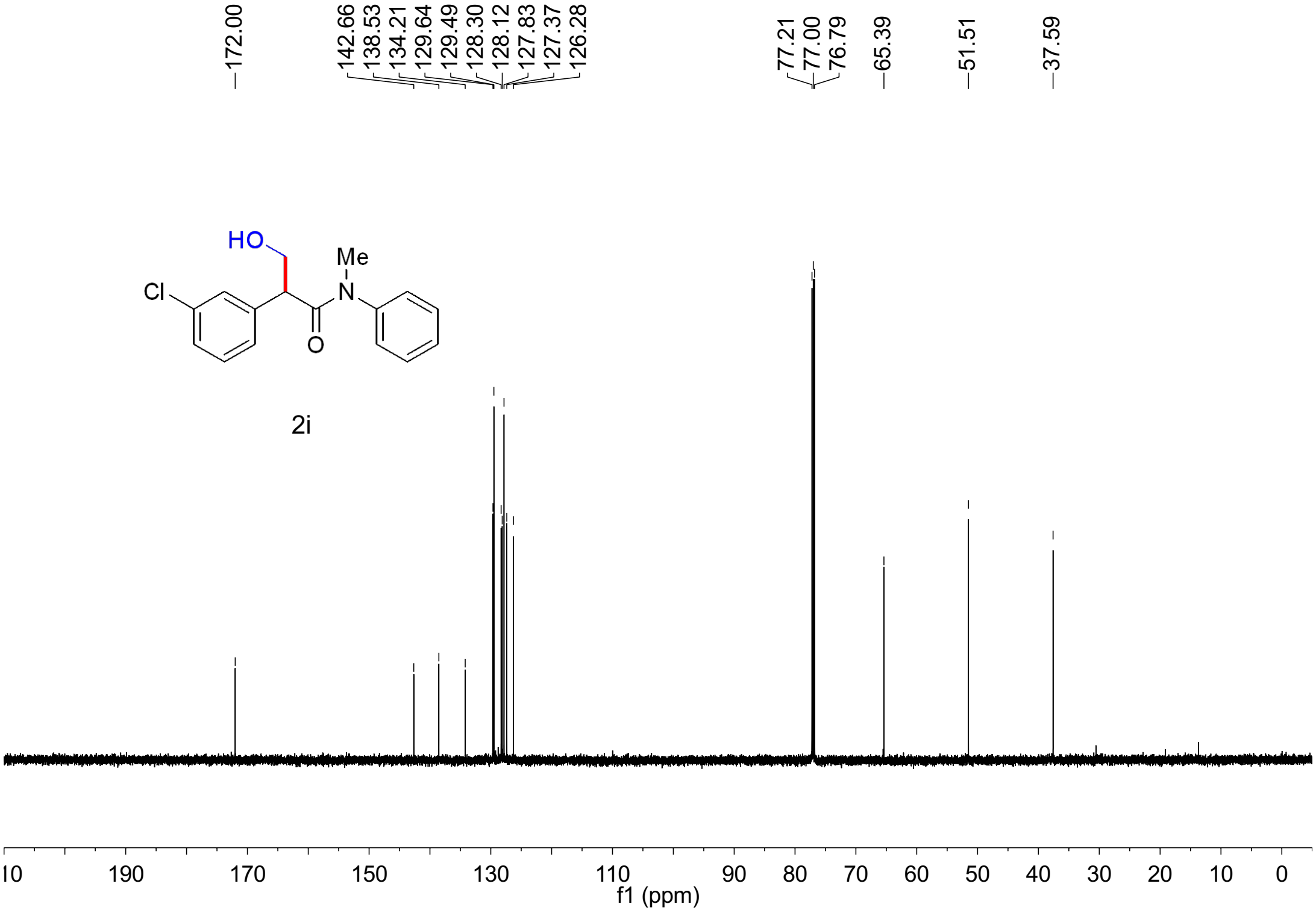
0 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105

f1 (ppm)


7.263
7.260
7.192
7.188
7.172
6.897
6.851
6.847
6.831
4.104
4.100
4.077
4.055
3.752
3.742
3.737
3.724
3.647
3.640
3.637
3.621
3.245
3.241
1.266
HO
Me
N
O
tBu
2h
3.10
2.07
1.76
2.06
1.13
1.08
1.18
3.00
9.00
f1 (ppm)


172.93
149.94
142.93
133.31
129.27
127.82
127.76
127.73
125.24
77.21
77.00
76.79
65.52
51.36
37.55
34.32
31.27
31.25
HO
Me
N
O
tBu
2h
f1 (ppm)


7.303
7.289
7.273
7.260
7.177
7.157
7.127
7.108
7.089
6.877
6.873
6.869
6.803
6.784
4.044
4.025
4.005
3.735
3.724
3.715
3.704
3.666
3.652
3.640
3.264
3.034
HO
Me
N
Cl
O
2i
3.15
1.09
1.01
2.79
1.03
1.10
1.09
1.03
3.00
0.93
f1 (ppm)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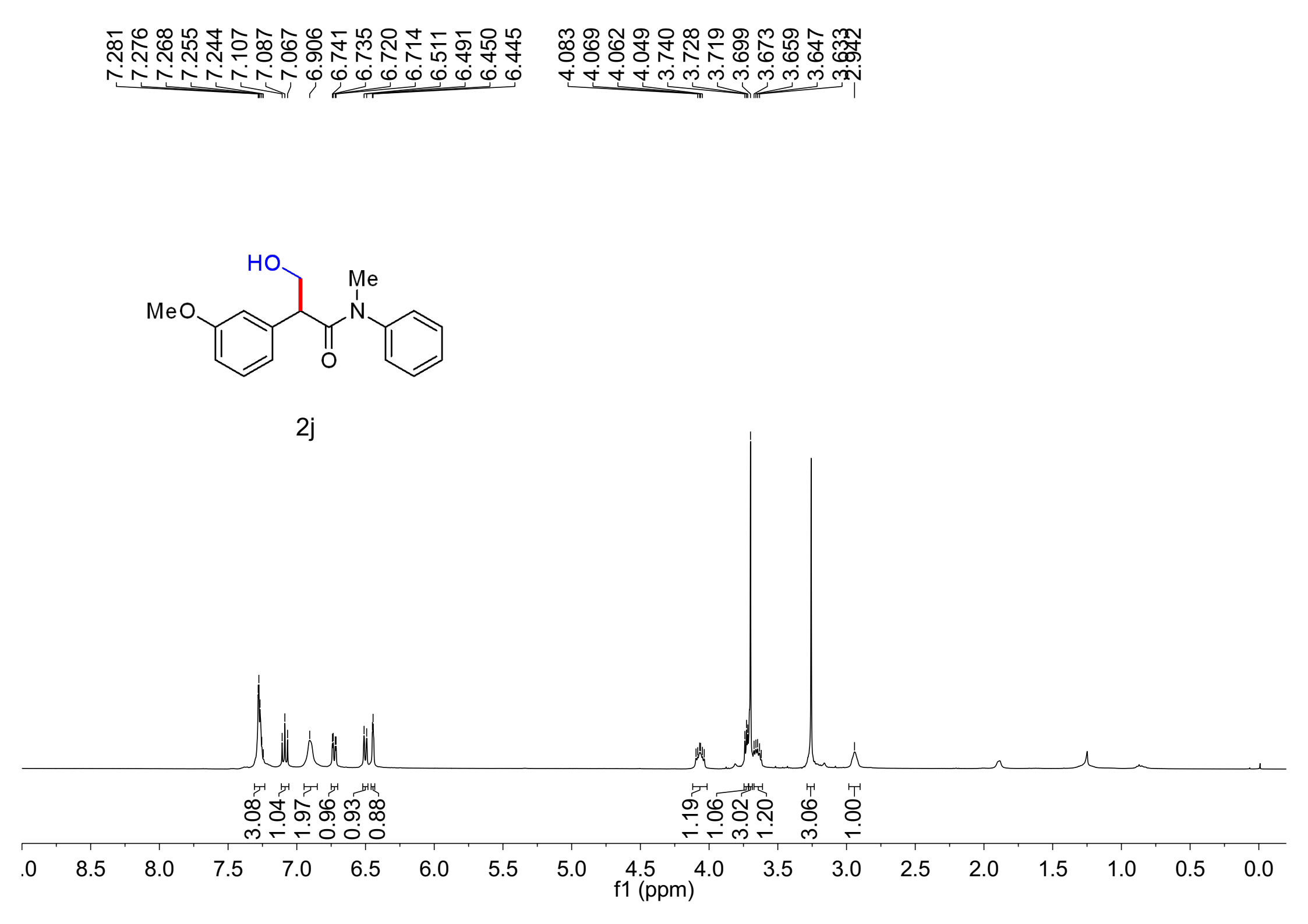
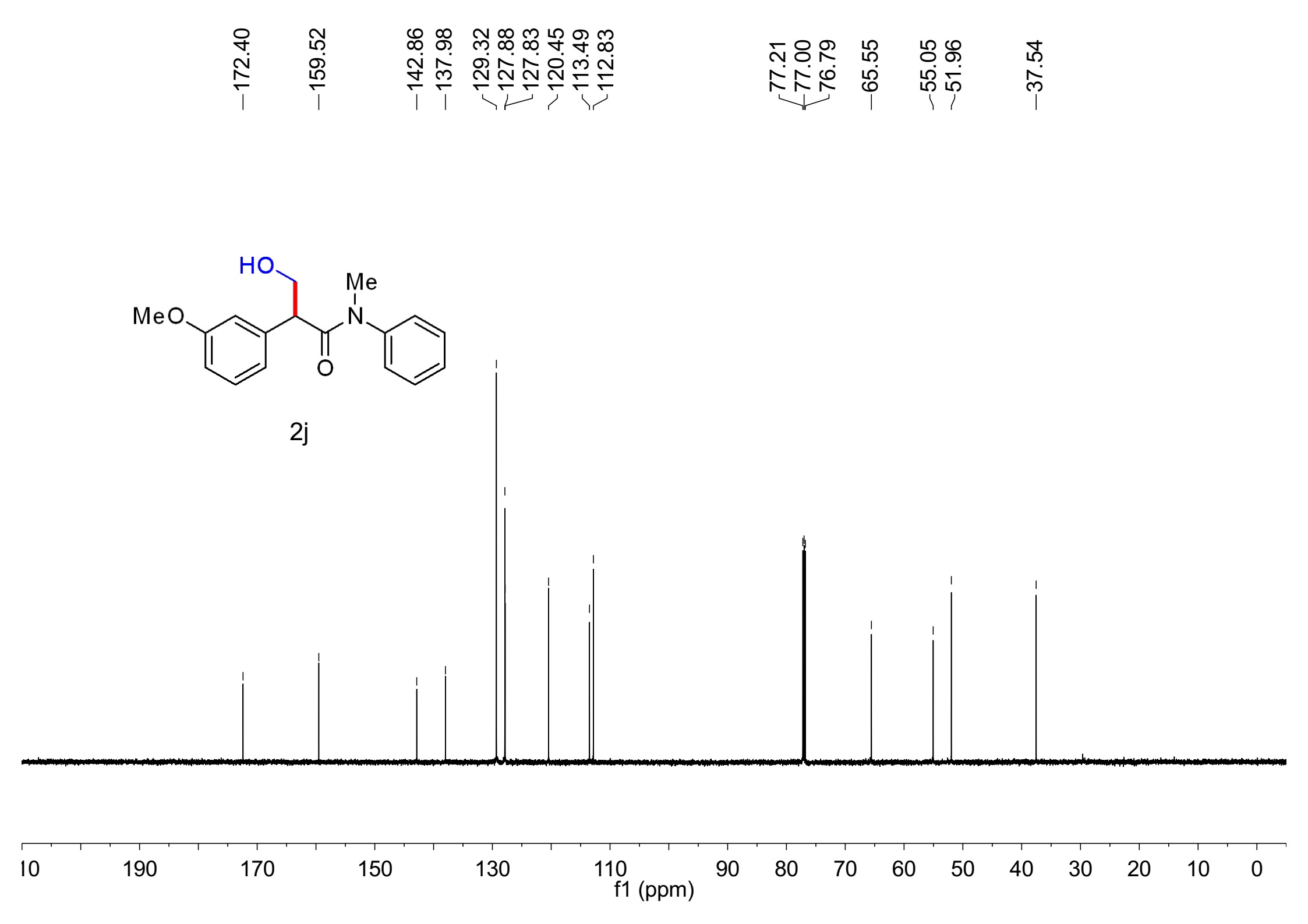
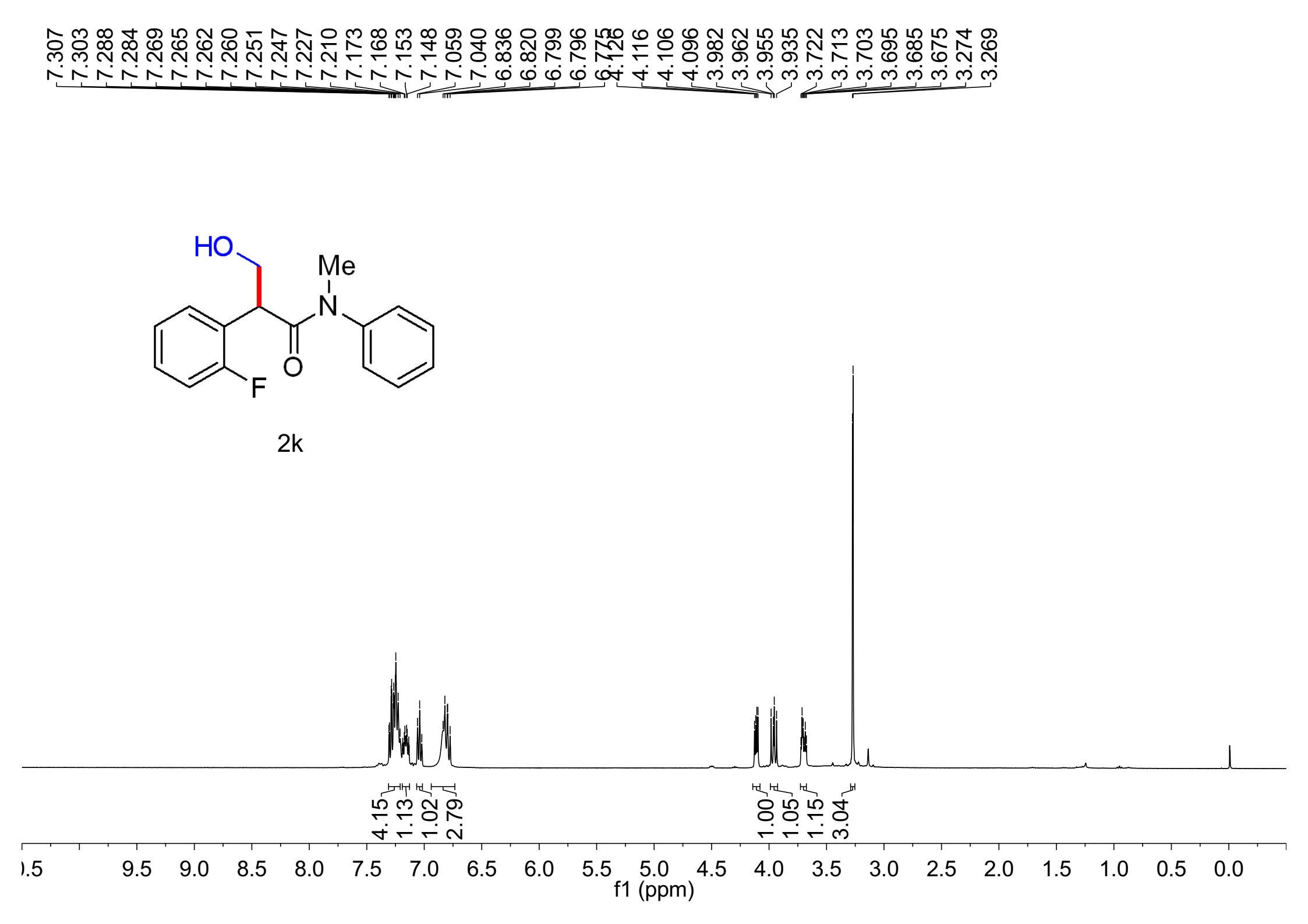
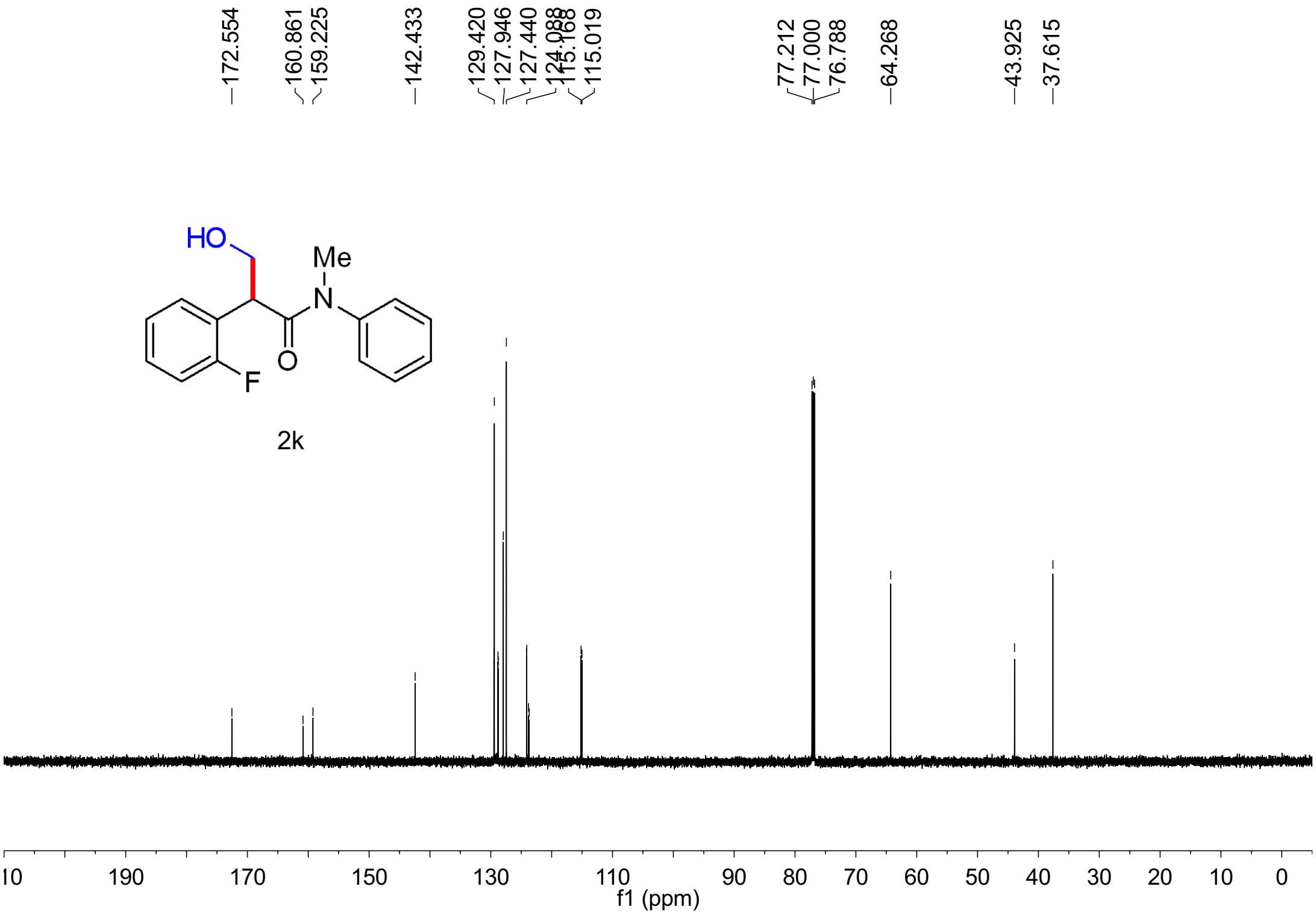
142.66
138.53
134.21
129.64
129.49
128.30
128.12
127.83
127.37
126.28
77.21
77.00
76.79
65.39
51.51
37.59
HO
Me
N
Cl
O
2i
f1 (ppm)


7.281
7.276
7.268
7.255
7.244
7.107
7.087
7.067
6.906
6.741
6.735
6.720
6.714
6.511
6.491
6.450
6.445
4.083
4.069
4.062
4.049
3.740
3.728
3.719
3.699
3.673
3.659
3.647
3.633
2.942
HO
Me
MeO
N
O
2j
3.08
1.04
1.97
0.96
0.93
0.88
1.19
1.06
3.02
1.20
3.06
1.00
f1 (ppm)


172.40
159.52
142.86
137.98
129.32
127.88
127.83
120.45
113.49
112.83
77.21
77.00
76.79
65.55
55.05
51.96
37.54
HO
Me
MeO
N
O
2j
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.307
7.303
7.288
7.284
7.269
7.265
7.262
7.260
7.251
7.247
7.227
7.210
7.173
7.168
7.153
7.148
7.059
7.040
6.836
6.820
6.799
6.796
6.775
4.126
4.116
4.106
4.096
3.982
3.962
3.955
3.935
3.722
3.713
3.703
3.695
3.685
3.675
3.274
3.269
HO
Me
N
O
F
2k
4.15
1.13
1.02
2.79
1.00
1.05
1.15
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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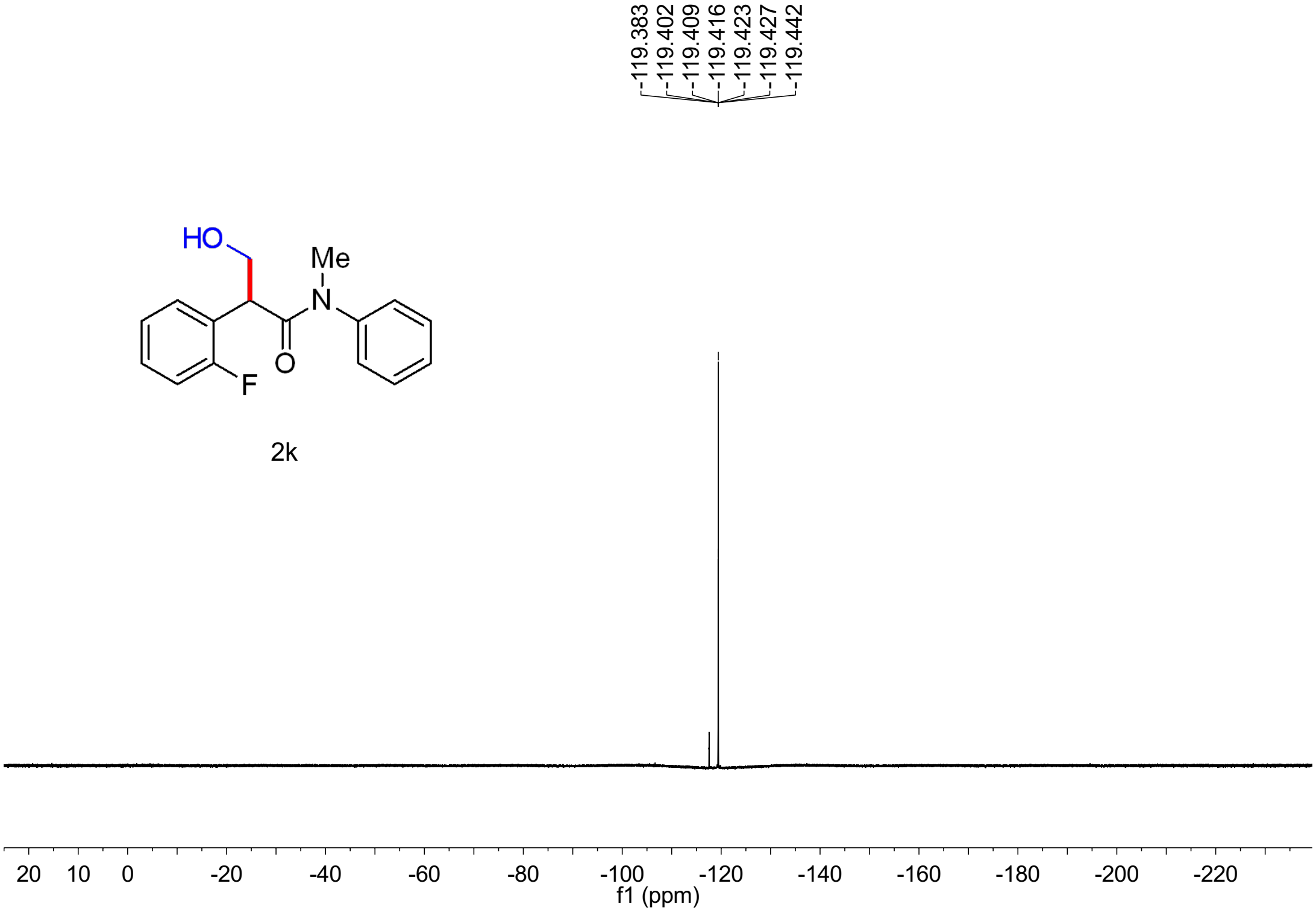
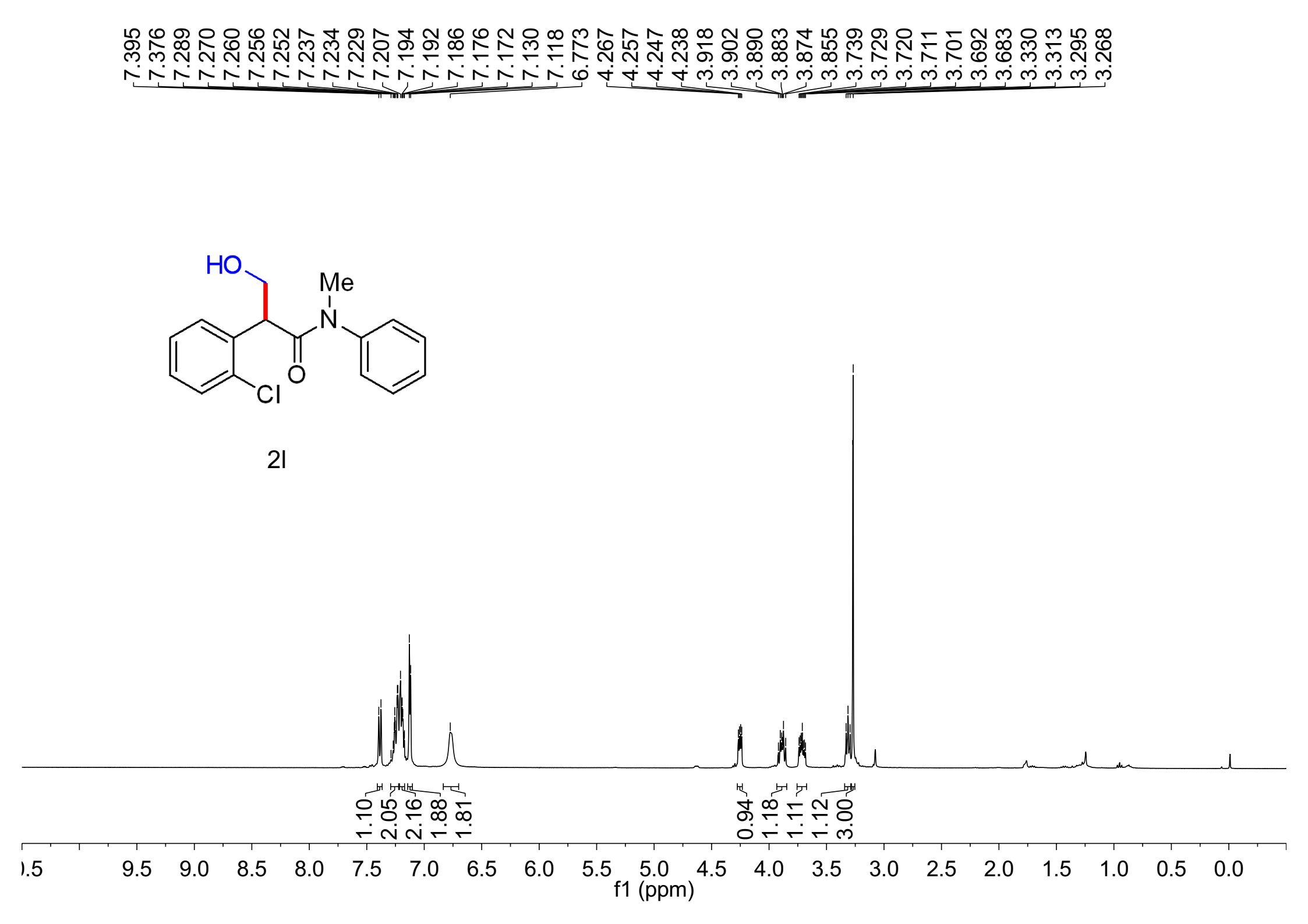
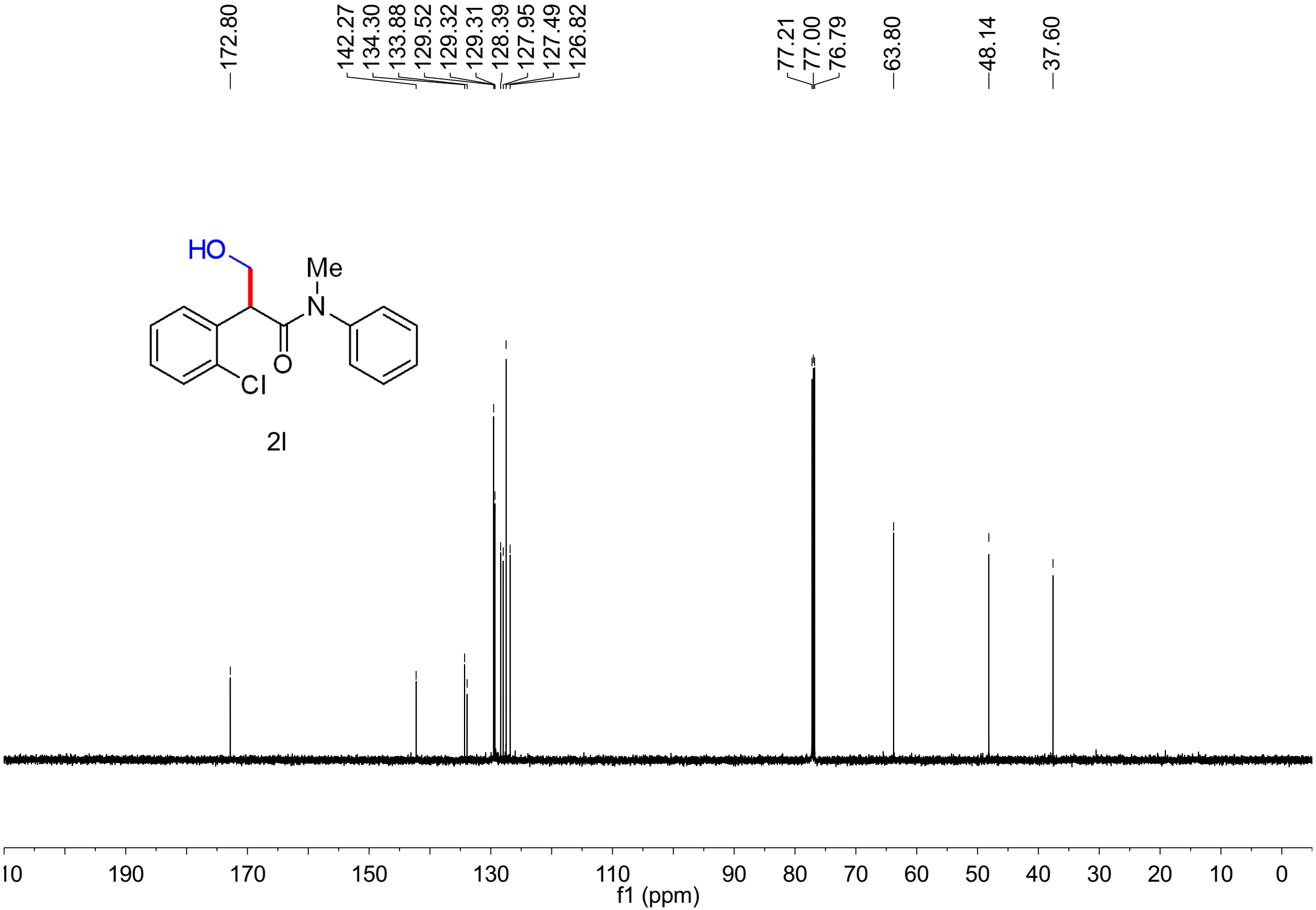
160.861
159.225
142.433
129.420
127.946
127.440
124.088
115.168
115.019
77.212
77.000
76.788
64.268
43.925
37.615
HO
Me
N
O
F
2k
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


119.383
119.402
119.409
119.416
119.423
119.427
119.442
HO
Me
N
O
F
2k
20
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
f1 (ppm)


7.395
7.376
7.289
7.270
7.260
7.256
7.252
7.237
7.234
7.229
7.207
7.194
7.192
7.186
7.176
7.172
7.130
7.118
6.773
4.267
4.257
4.247
4.238
3.918
3.902
3.890
3.883
3.874
3.855
3.739
3.729
3.720
3.711
3.701
3.692
3.683
3.330
3.313
3.295
3.268
HO
Me
N
O
Cl
2l
1.10
2.05
2.16
1.88
1.81
0.94
1.18
1.11
1.12
3.00
f1 (ppm)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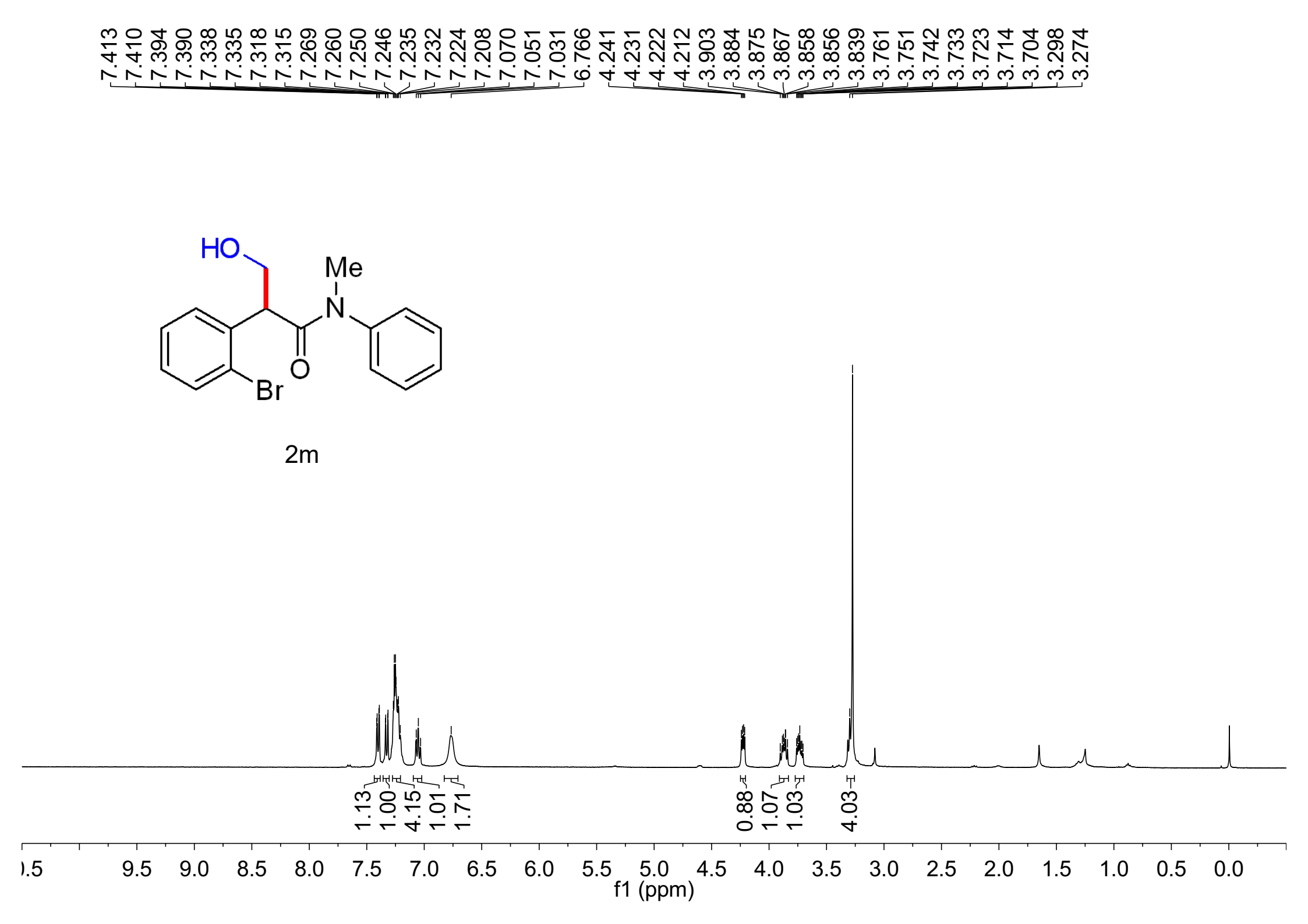
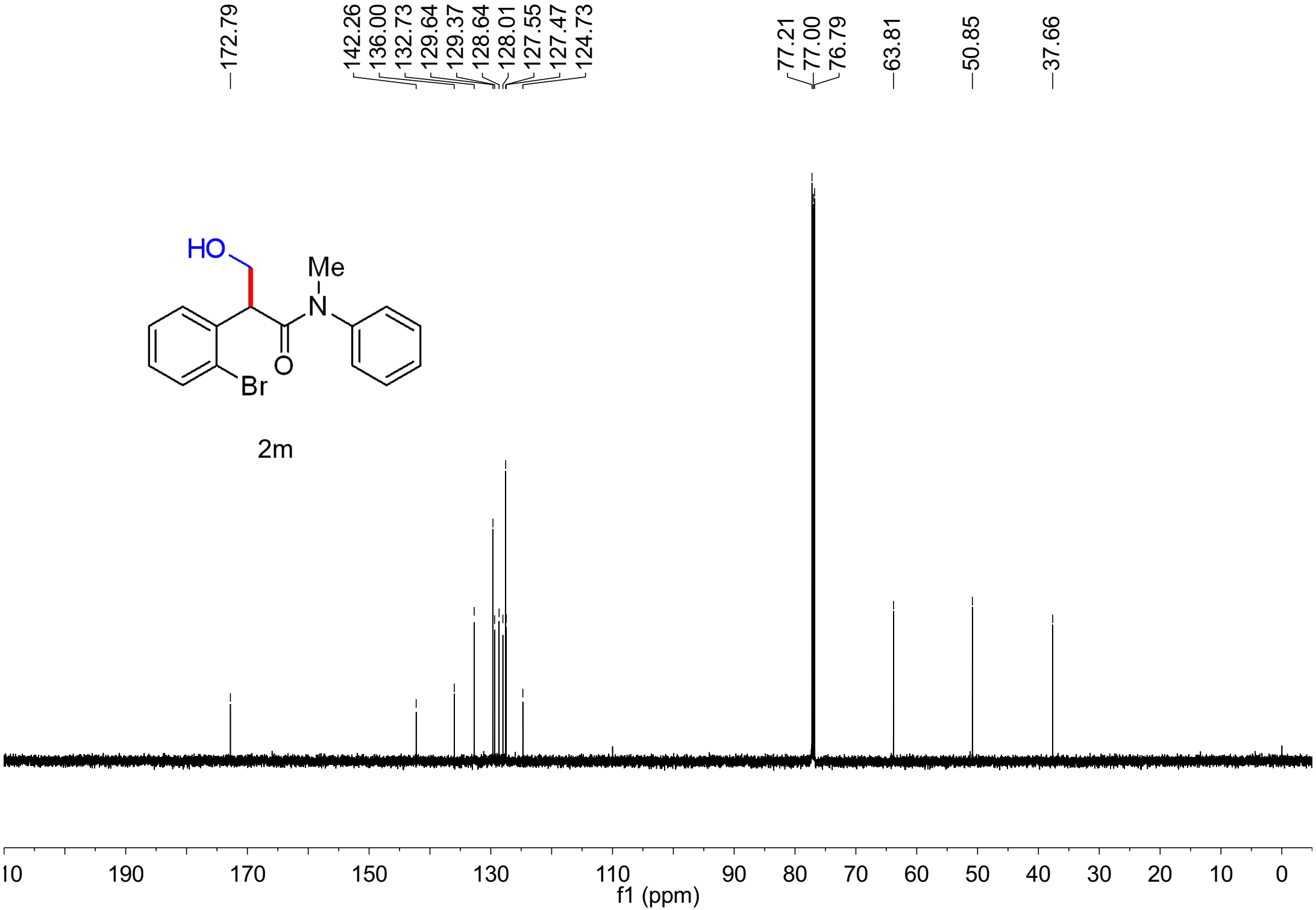
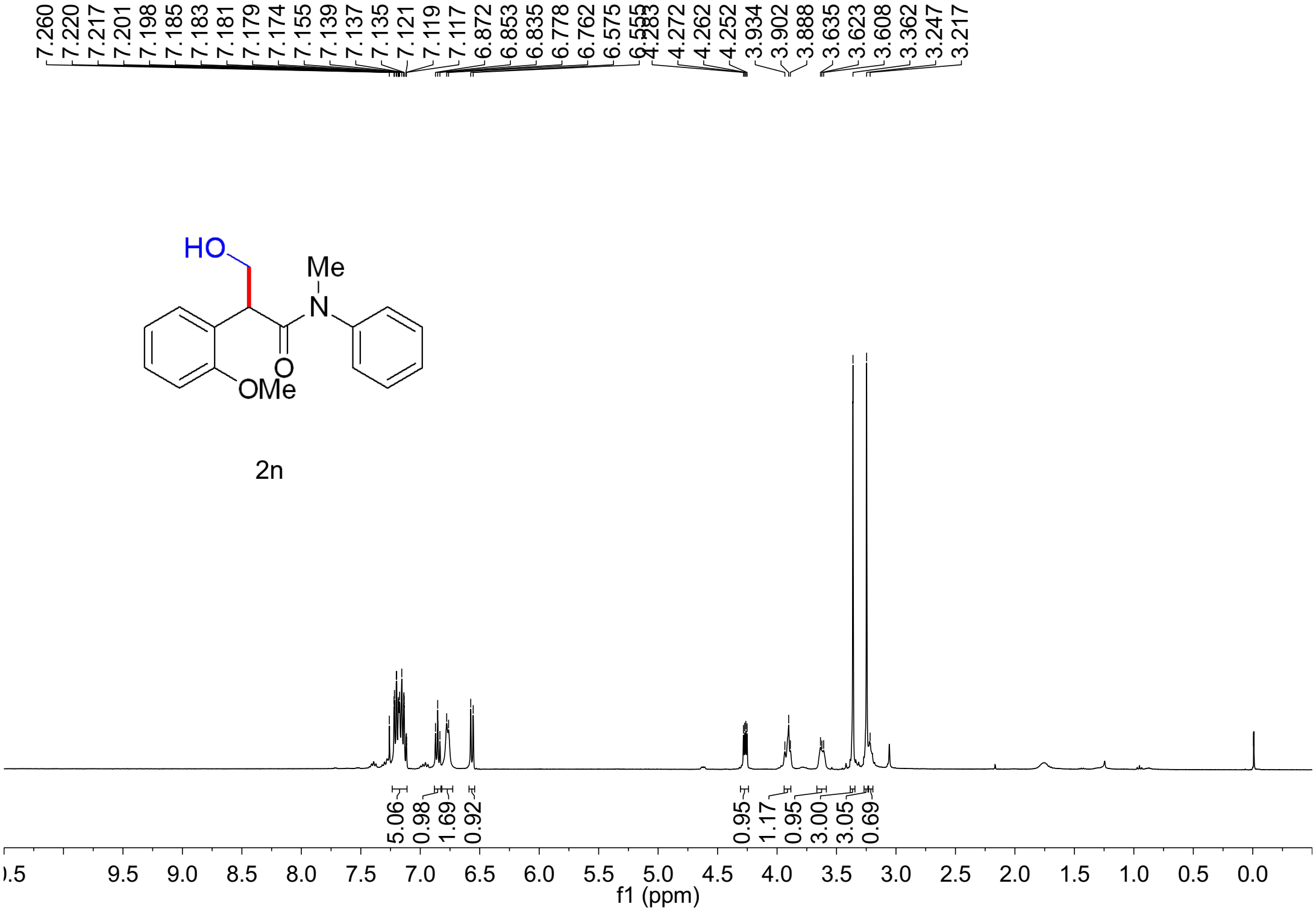
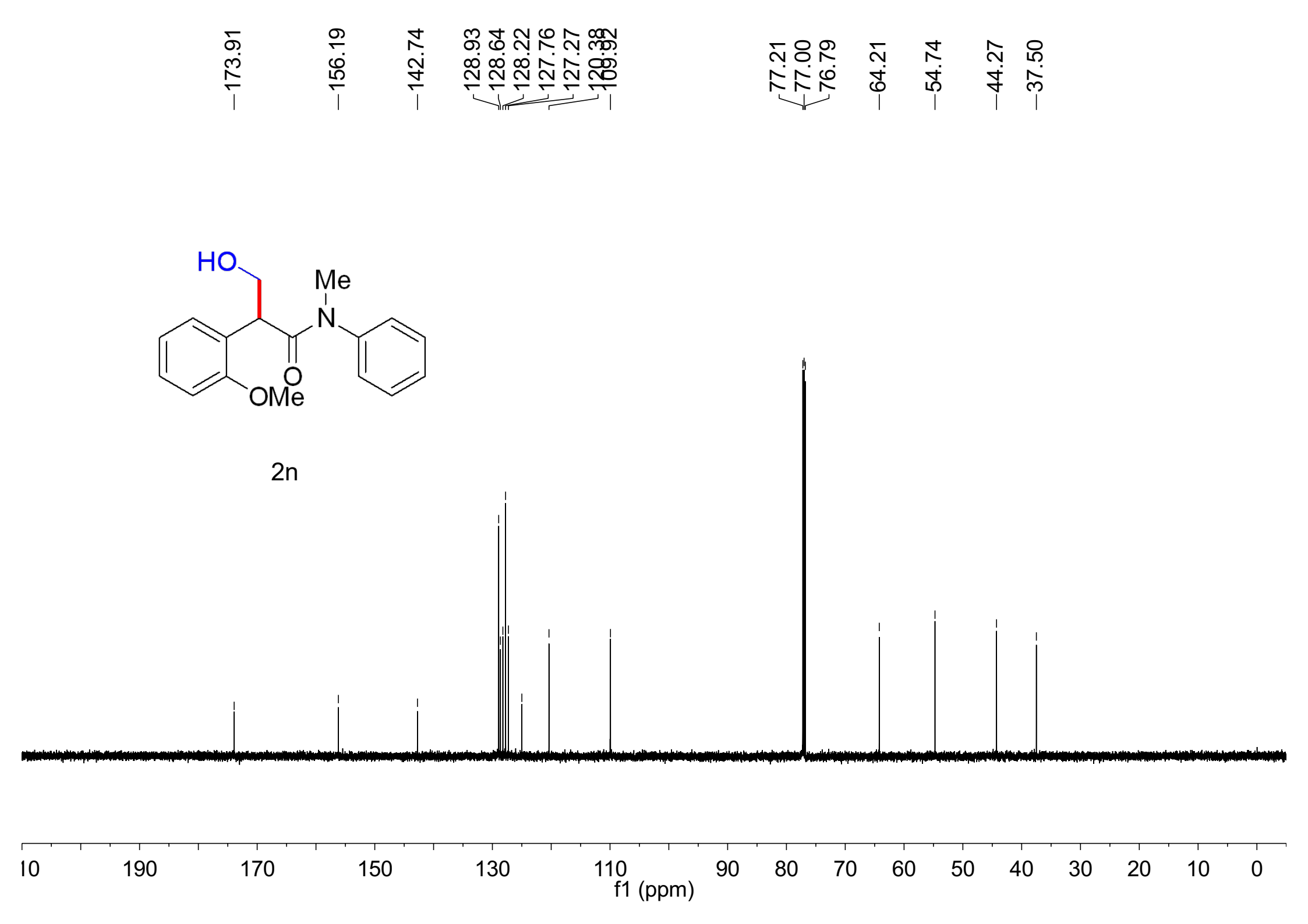
142.27
134.30
133.88
129.52
129.32
129.31
128.39
127.95
127.49
126.82
77.21
77.00
76.79
63.80
48.14
37.60
HO
Me
N
O
Cl
2l
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.413
7.410
7.394
7.390
7.338
7.335
7.318
7.315
7.269
7.260
7.250
7.246
7.235
7.232
7.224
7.208
7.070
7.051
7.031
6.766
4.241
4.231
4.222
4.212
3.903
3.884
3.875
3.867
3.858
3.856
3.839
3.761
3.751
3.742
3.733
3.723
3.714
3.704
3.298
3.274
HO
Me
N
O
Br
2m
1.13
1.00
4.15
1.01
1.71
0.88
1.07
1.03
4.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


172.79
142.26
136.00
132.73
129.64
129.37
128.64
128.01
127.55
127.47
124.73
77.21
77.00
76.79
63.81
50.85
37.66
HO
Me
N
O
Br
2m
f1 (ppm)


7.260
7.220
7.217
7.201
7.198
7.185
7.183
7.181
7.179
7.174
7.155
7.139
7.137
7.135
7.121
7.119
7.117
6.872
6.853
6.835
6.778
6.762
6.575
6.555
4.283
4.272
4.262
4.252
3.934
3.902
3.888
3.635
3.623
3.608
3.362
3.247
3.217
HO
Me
N
O
OMe
2n
5.06
0.98
1.69
0.92
0.95
1.17
0.95
3.00
3.05
0.69
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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142.74
128.93
128.64
128.22
127.76
127.27
120.38
109.92
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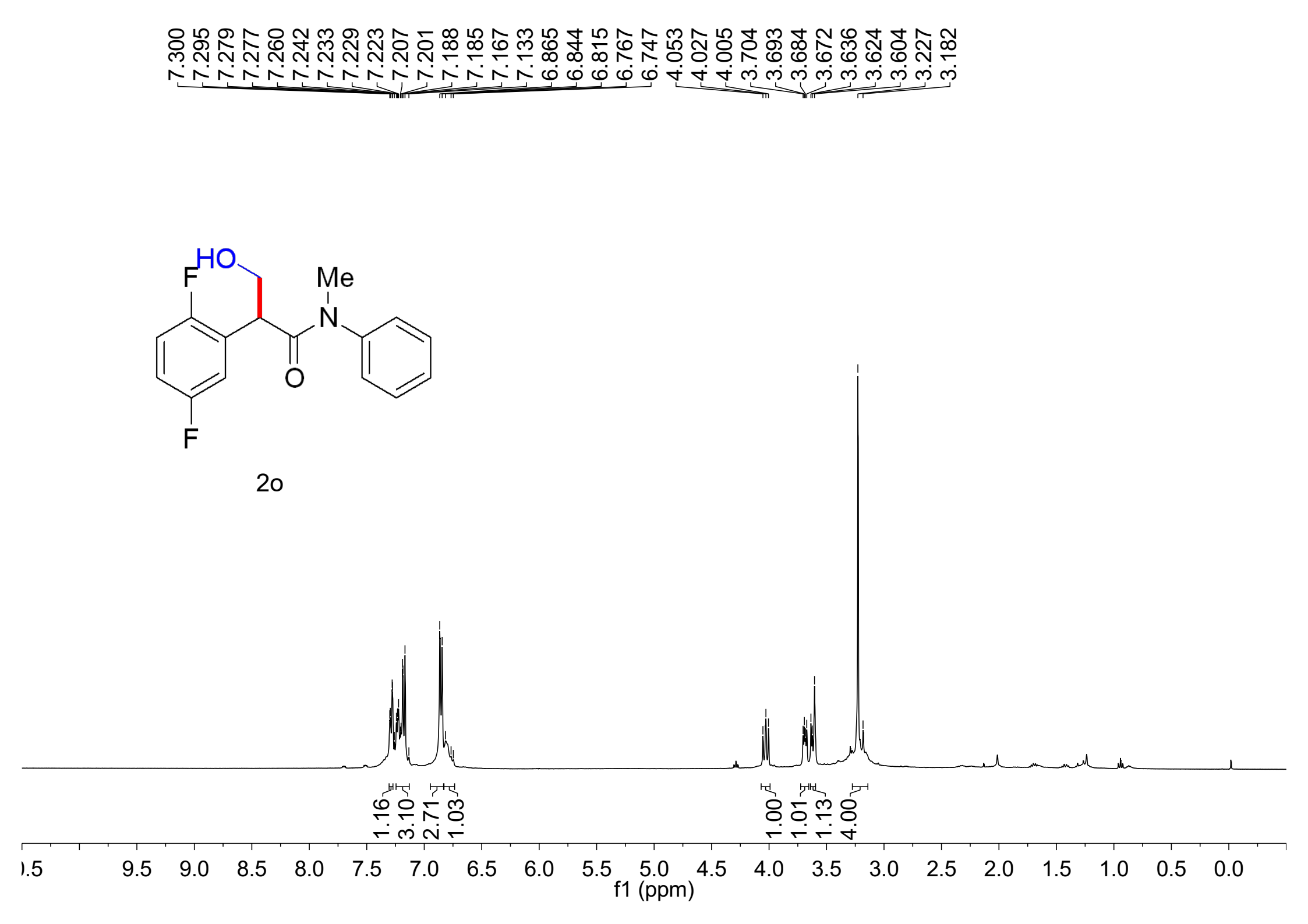
77.00
76.79
64.21
54.74
44.27
37.50
HO
Me
N
O
OMe
2n
f1 (ppm)


7.300
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7.279
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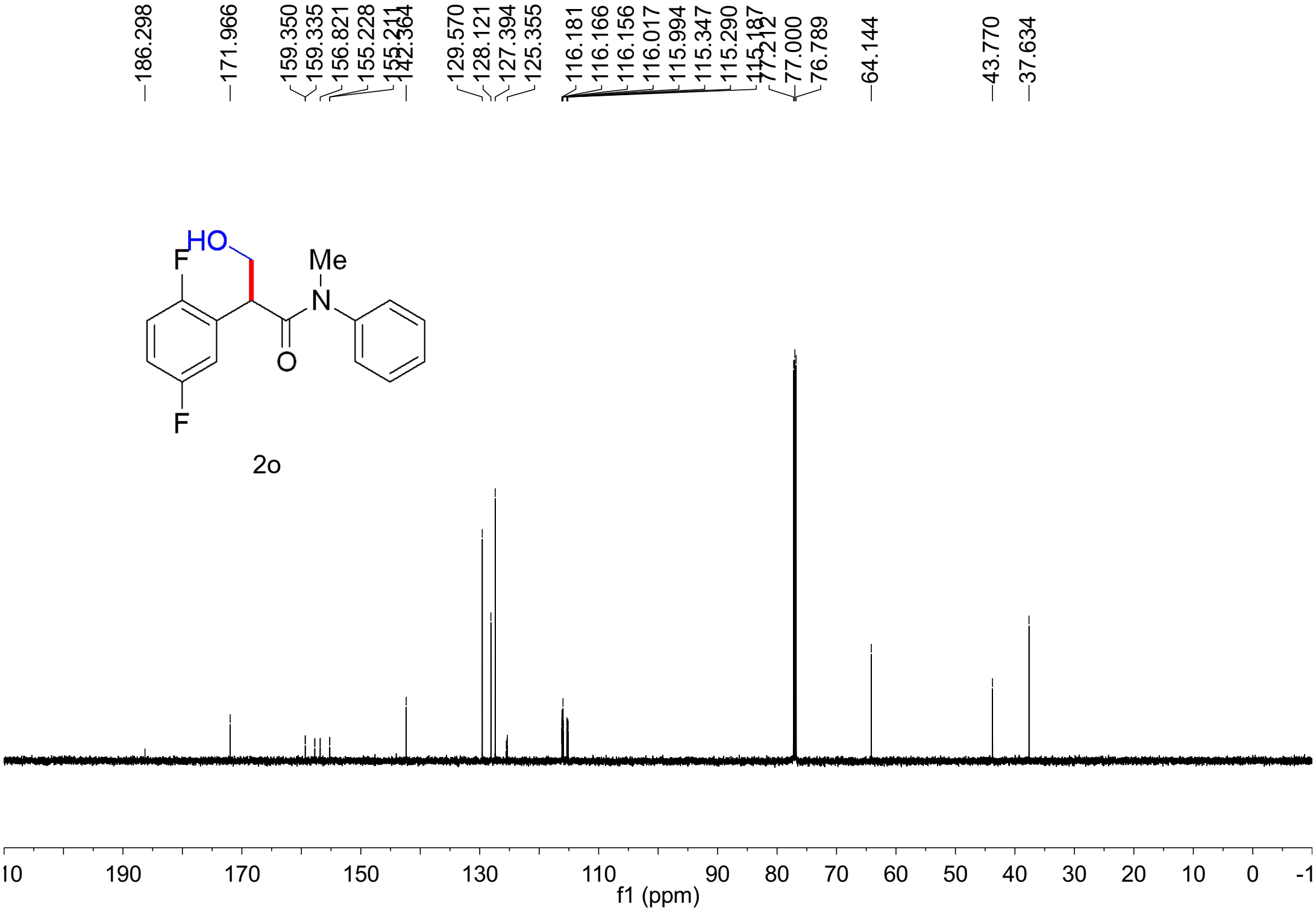
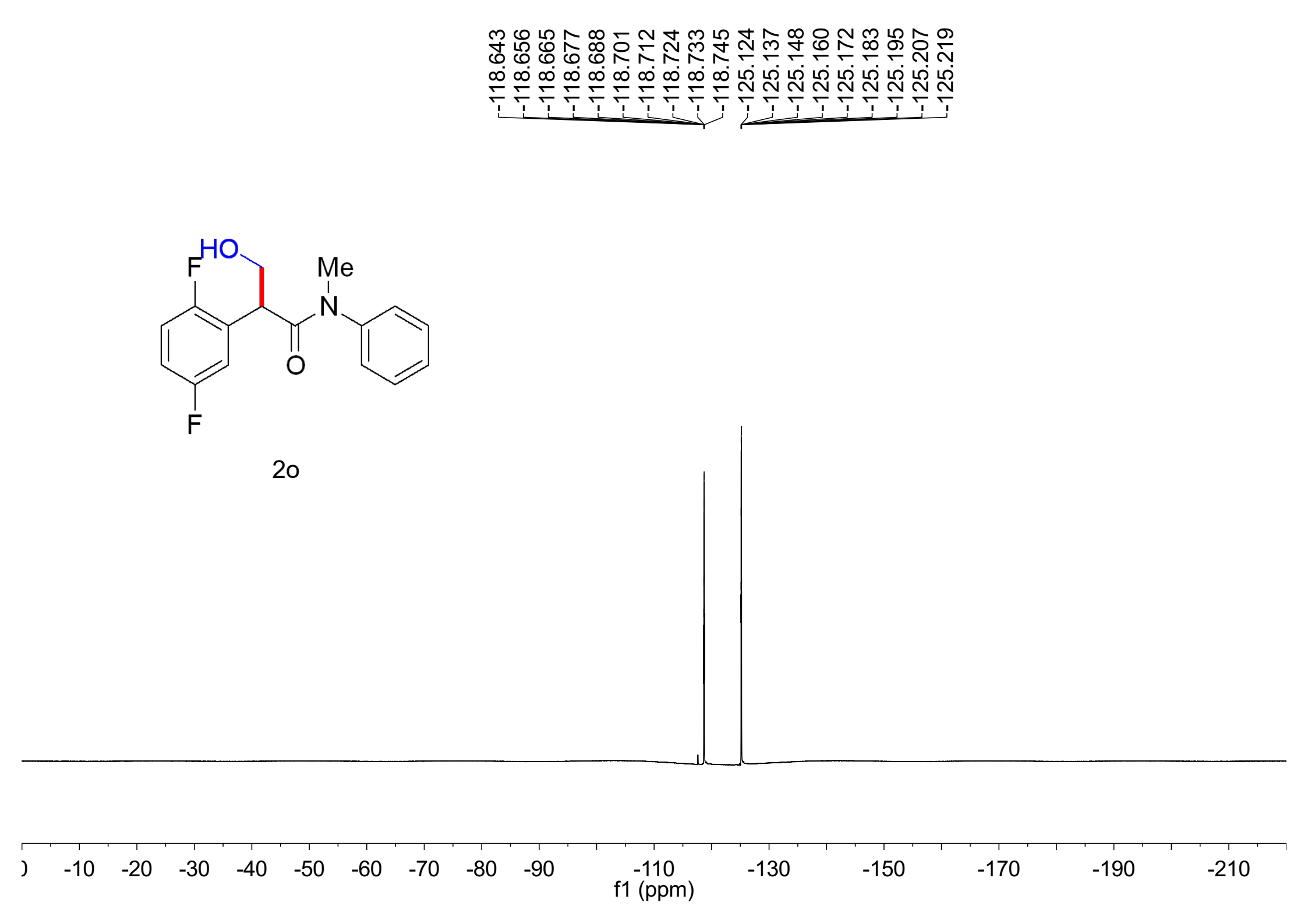
7.242
7.233
7.229
7.223
7.207
7.201
7.188
7.185
7.167
7.133
6.865
6.844
6.815
6.767
6.747
4.053
4.027
4.005
3.704
3.693
3.684
3.672
3.636
3.624
3.604
3.227
3.182
HO
F
Me
N
O
F
2o
1.16
3.10
2.71
1.03
1.00
1.01
1.13
4.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


186.298
171.966
159.350
159.335
156.821
155.228
155.211
142.364
129.570
128.121
127.394
125.355
116.181
116.166
116.156
116.017
115.994
115.347
115.290
115.187
77.212
77.000
76.789
64.144
43.770
37.634
HO
F
Me
N
O
F
2o
f1 (ppm)


118.643
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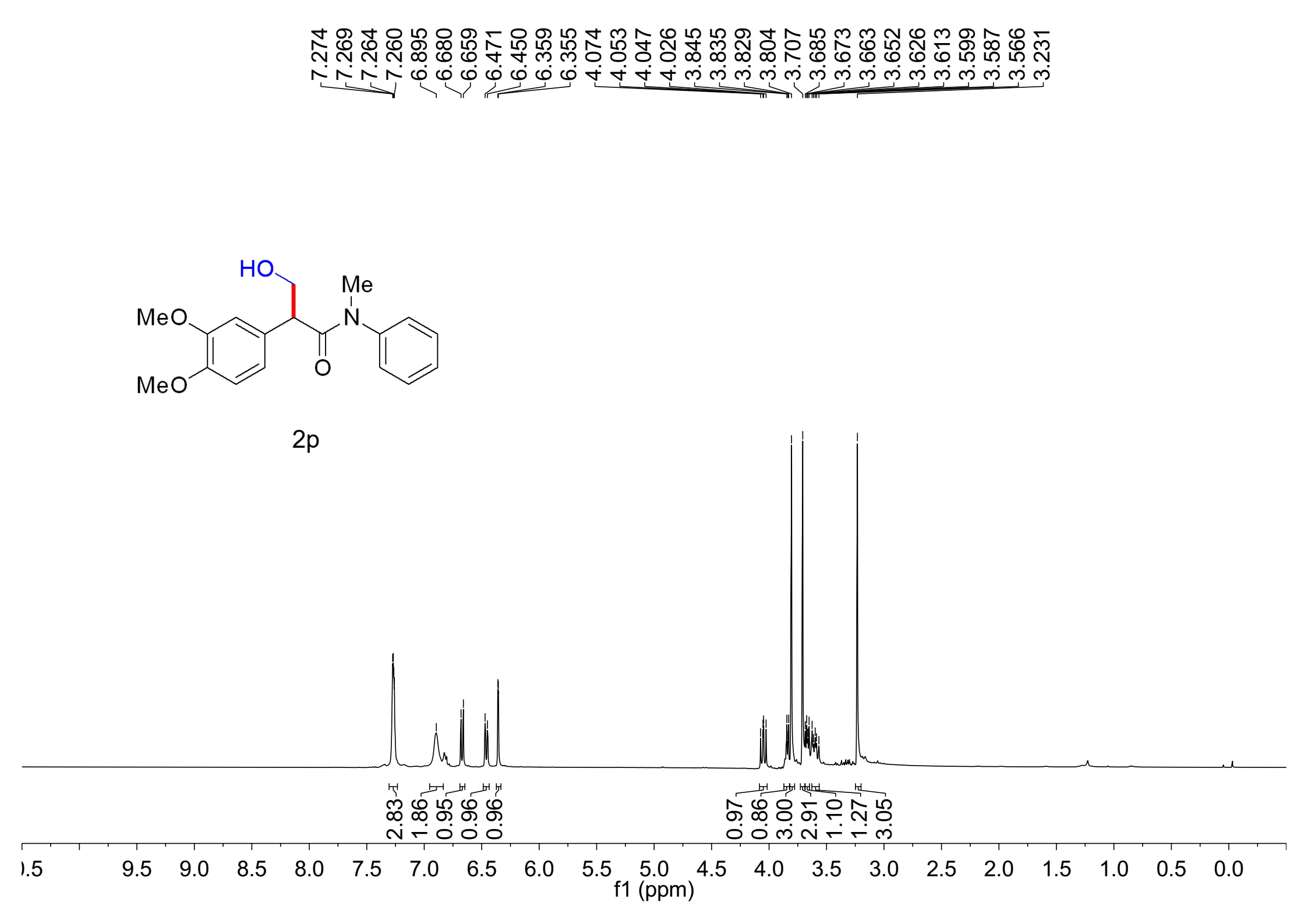
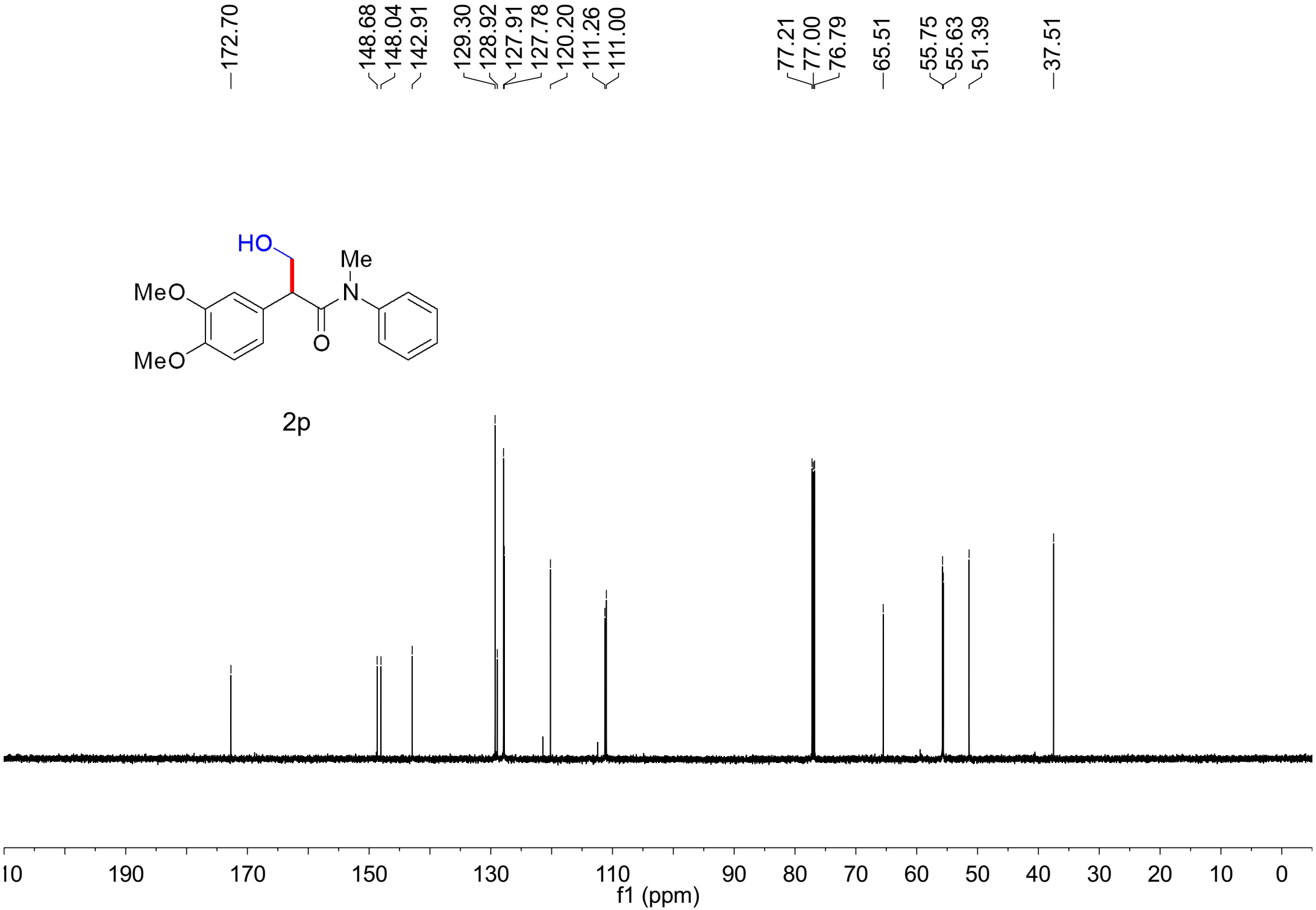
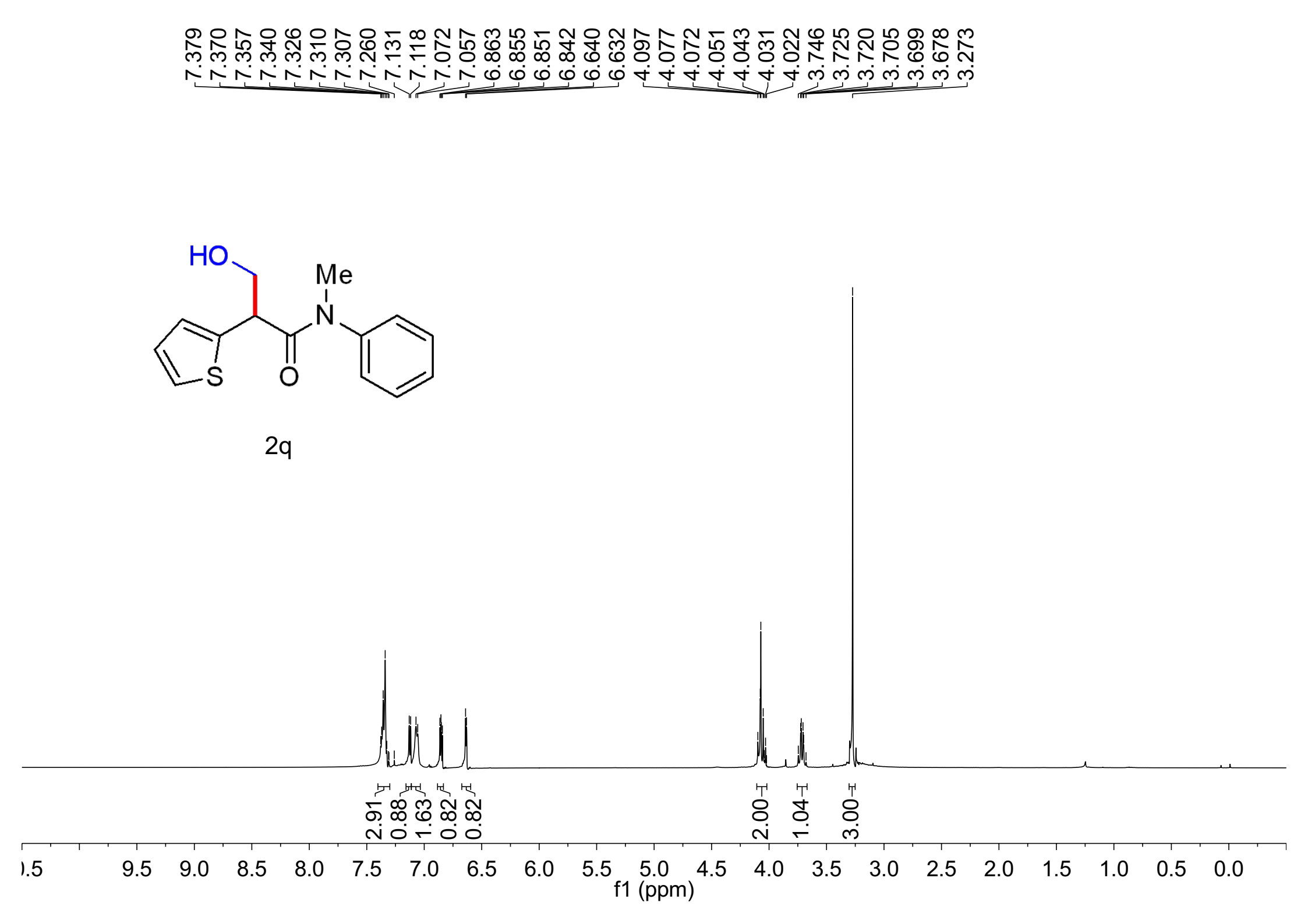
118.712
118.724
118.733
118.745
125.124
125.137
125.148
125.160
125.172
125.183
125.195
125.207
125.219
HO
F
Me
N
O
F
2o
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)


7.274
7.269
7.264
7.260
6.895
6.680
6.659
6.471
6.450
6.359
6.355
4.074
4.053
4.047
4.026
3.845
3.835
3.829
3.804
3.707
3.685
3.673
3.663
3.652
3.626
3.613
3.599
3.587
3.566
3.231
HO
Me
N
MeO
MeO
O
2p
2.83
1.86
0.95
0.96
0.96
0.97
0.86
3.00
2.91
1.10
1.27
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


172.70
148.68
148.04
142.91
129.30
128.92
127.91
127.78
120.20
111.26
111.00
77.21
77.00
76.79
65.51
55.75
55.63
51.39
37.51
HO
Me
N
MeO
MeO
O
2p
f1 (ppm)


7.379
7.370
7.357
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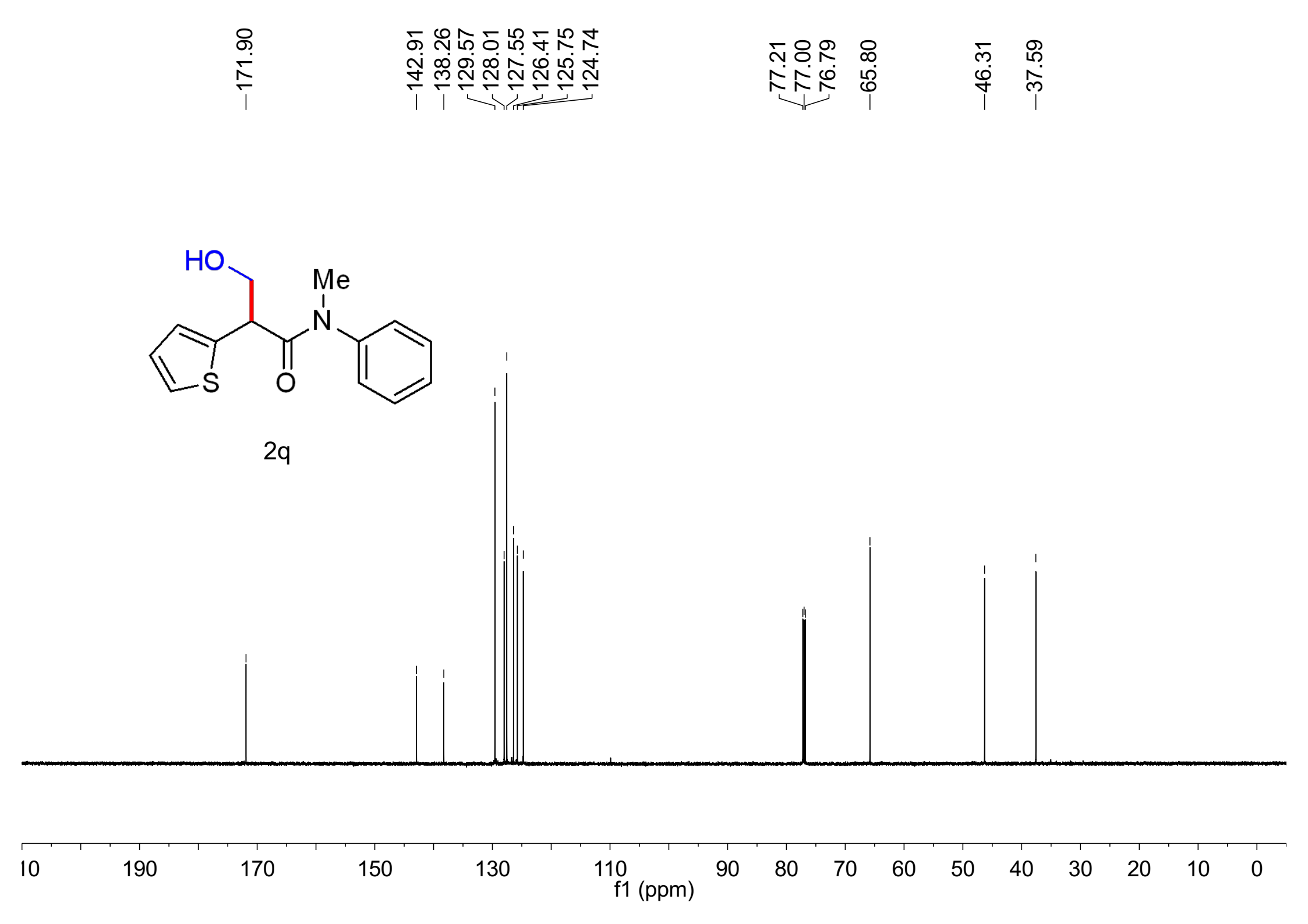
7.326
7.310
7.307
7.260
7.131
7.118
7.072
7.057
6.863
6.855
6.851
6.842
6.640
6.632
4.097
4.077
4.072
4.051
4.043
4.031
4.022
3.746
3.725
3.720
3.705
3.699
3.678
3.273
HO
Me
N
S
O
2q
2.91
0.88
1.63
0.82
0.82
2.00
1.04
3.00
f1 (ppm)


171.90
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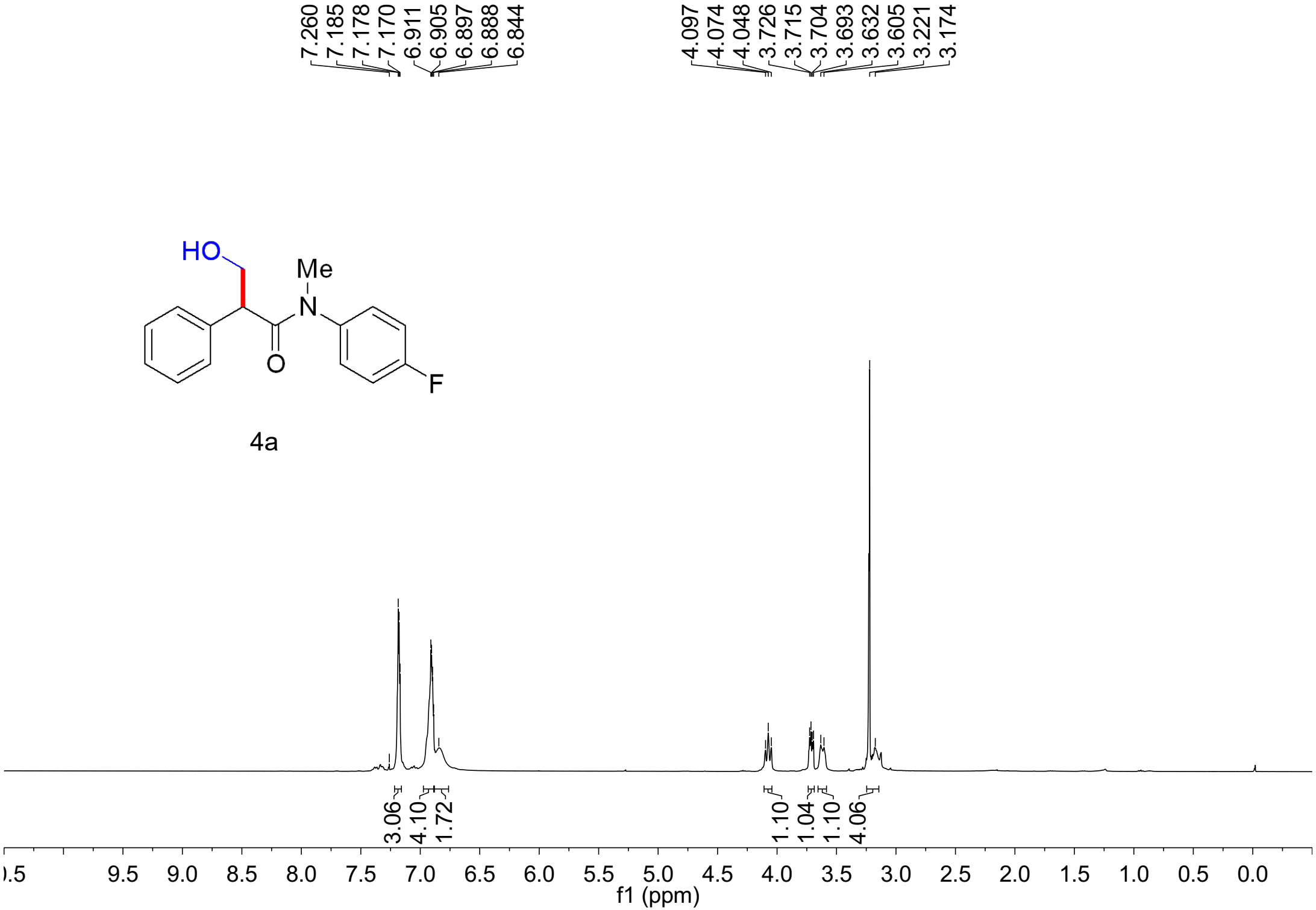
128.01
127.55
126.41
125.75
124.74
77.21
77.00
76.79
65.80
46.31
37.59
HO
Me
N
S
O
2q
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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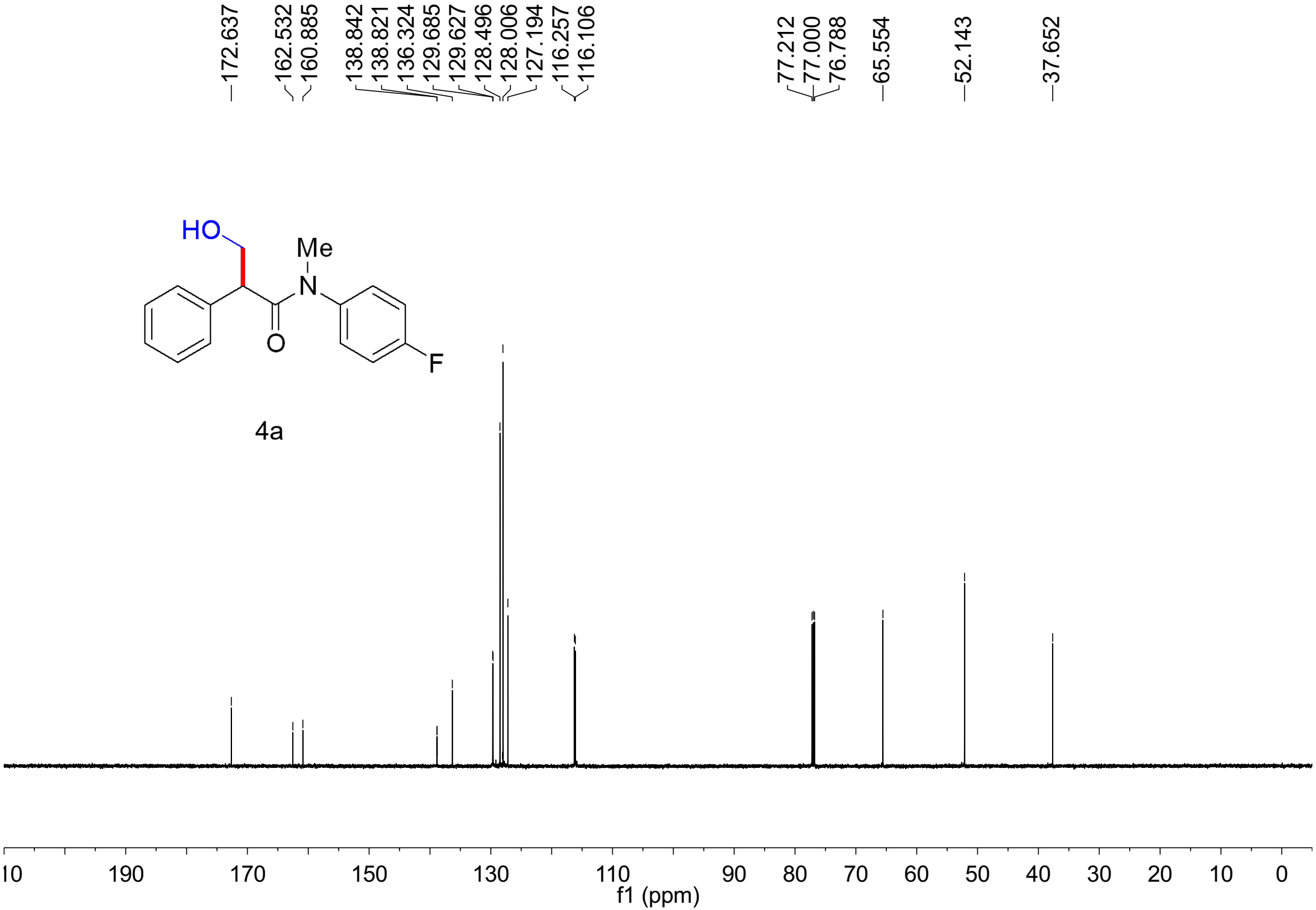
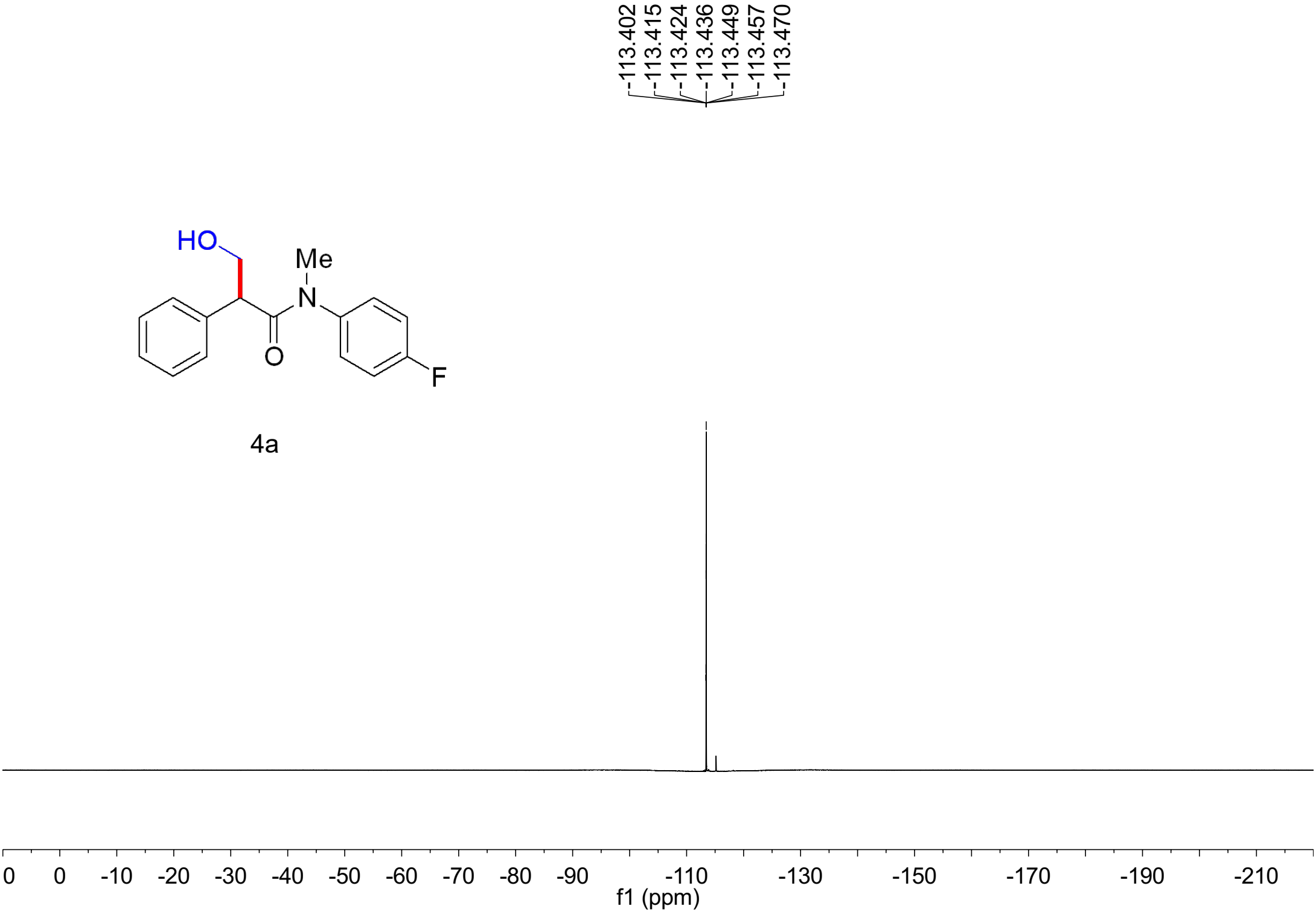
7.185
7.178
7.170
6.911
6.905
6.897
6.888
6.844
4.097
4.074
4.048
3.726
3.715
3.704
3.693
3.632
3.605
3.221
3.174
HO
Me
N
O
F
4a
3.06
4.10
1.72
1.10
1.04
1.10
4.06
f1 (ppm)


172.637
162.532
160.885
138.842
138.821
136.324
129.685
129.627
128.496
128.006
127.194
116.257
116.106
77.212
77.000
76.788
65.554
52.143
37.652
HO
Me
N
O
F
4a
f1 (ppm)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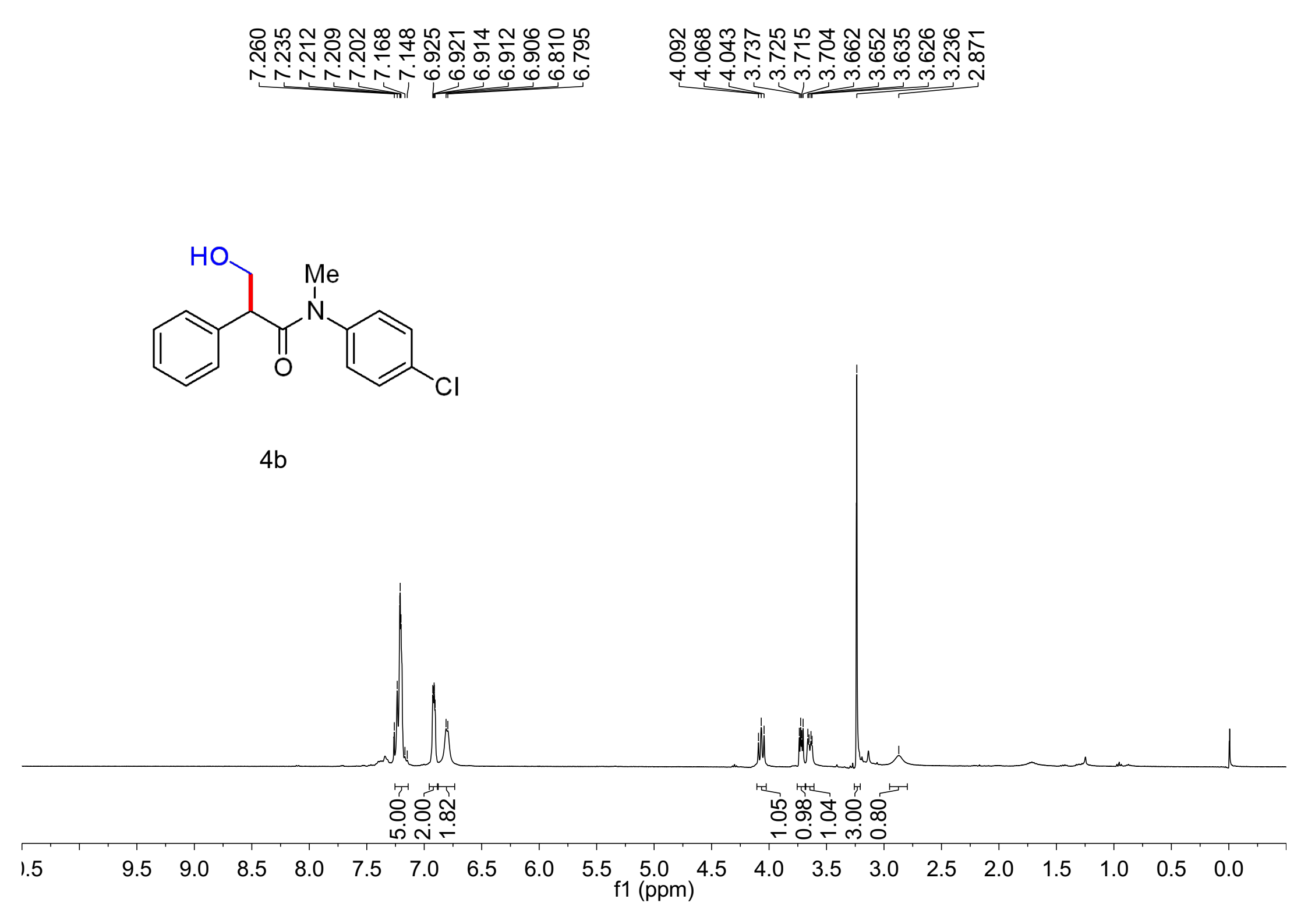
-113.415
-113.424
-113.436
-113.449
-113.457
-113.470
HO
Me
N
O
F
4a
0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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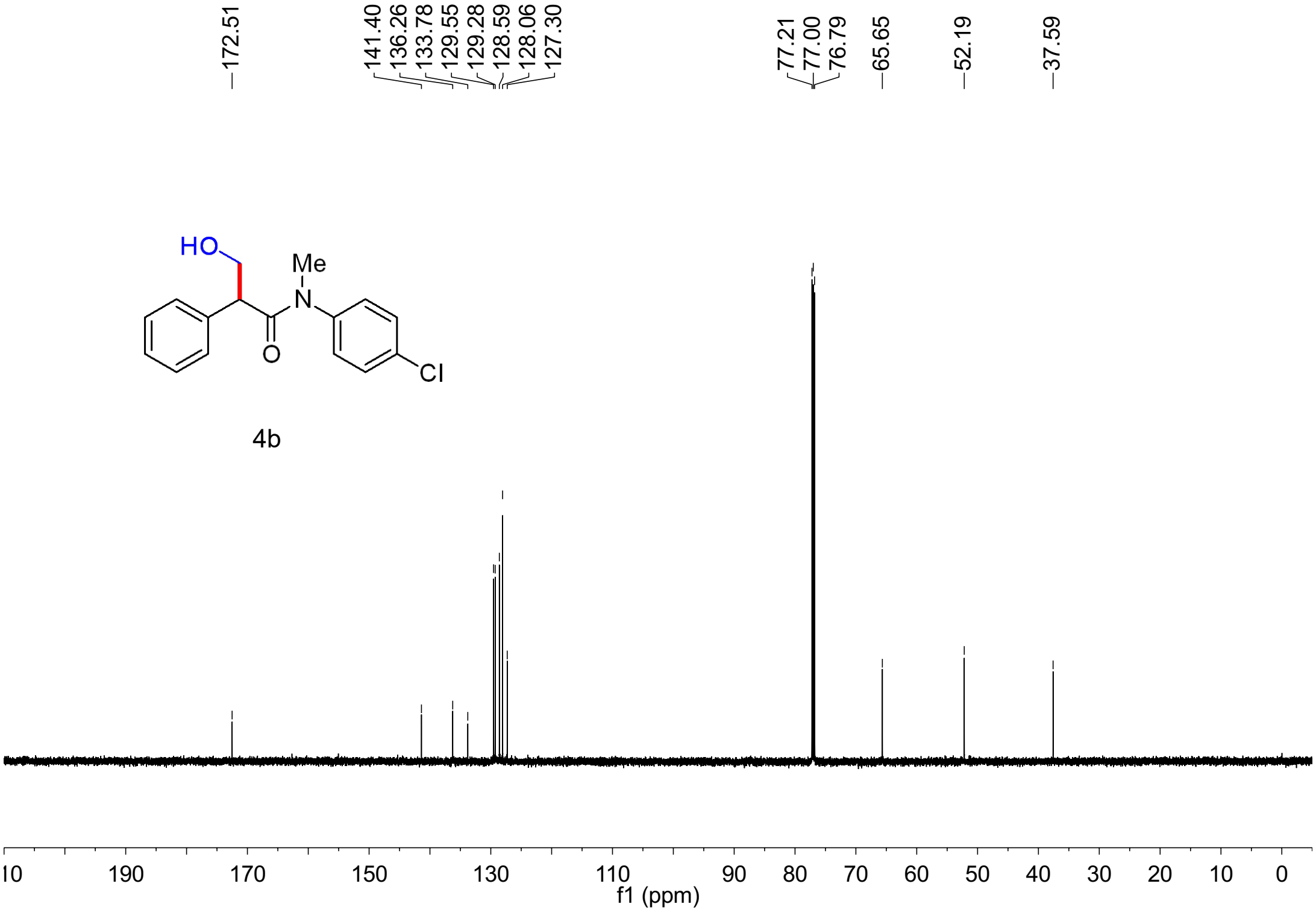
7.235
7.212
7.209
7.202
7.168
7.148
6.925
6.921
6.914
6.912
6.906
6.810
6.795
4.092
4.068
4.043
3.737
3.725
3.715
3.704
3.662
3.652
3.635
3.626
3.236
2.871
HO
Me
N
O
Cl
4b
5.00
2.00
1.82
1.05
0.98
1.04
3.00
0.80
f1 (ppm)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136.26
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129.55
129.28
128.59
128.06
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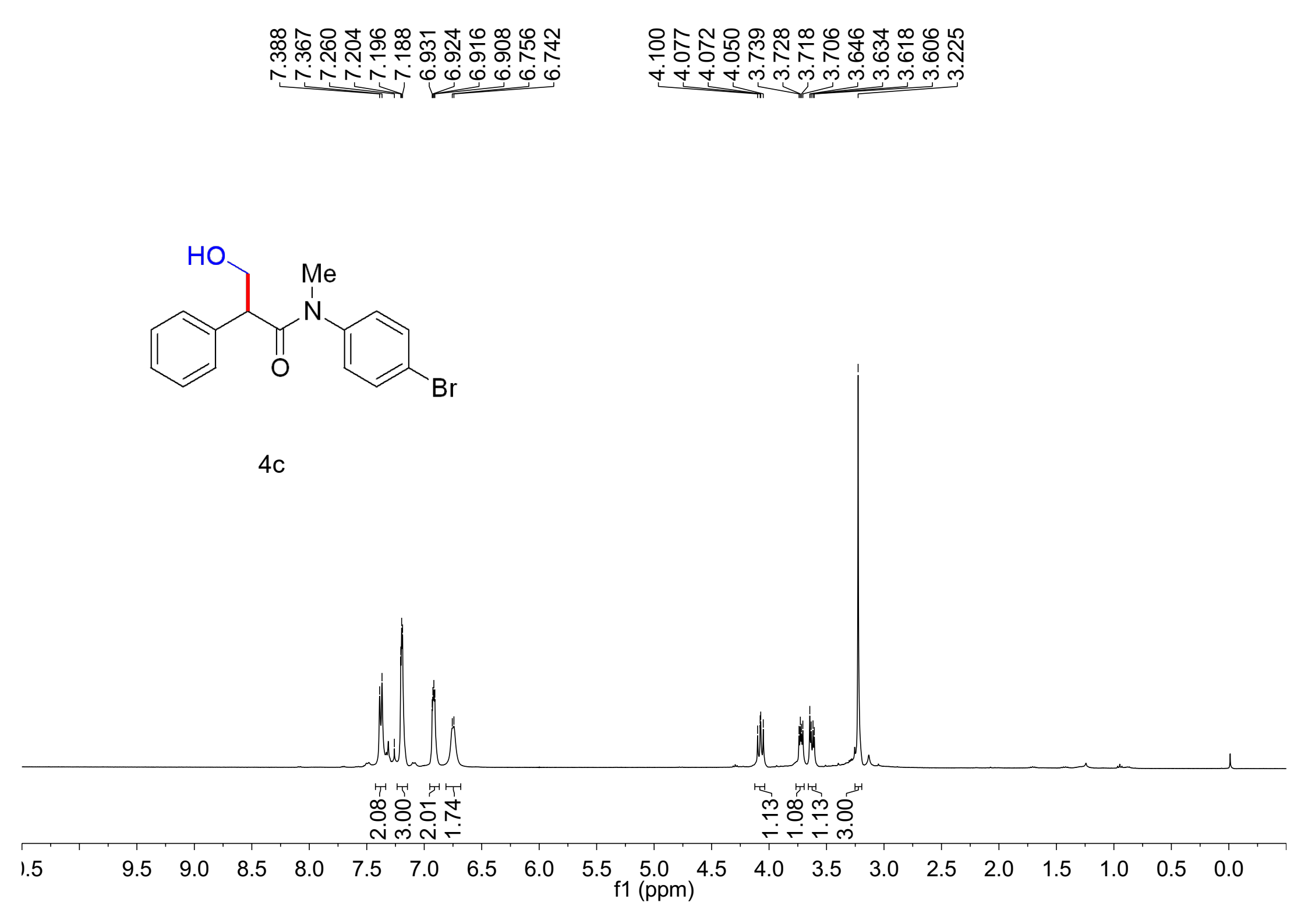
77.00
76.79
65.65
52.19
37.59
HO
Me
N
O
Cl
4b
f1 (ppm)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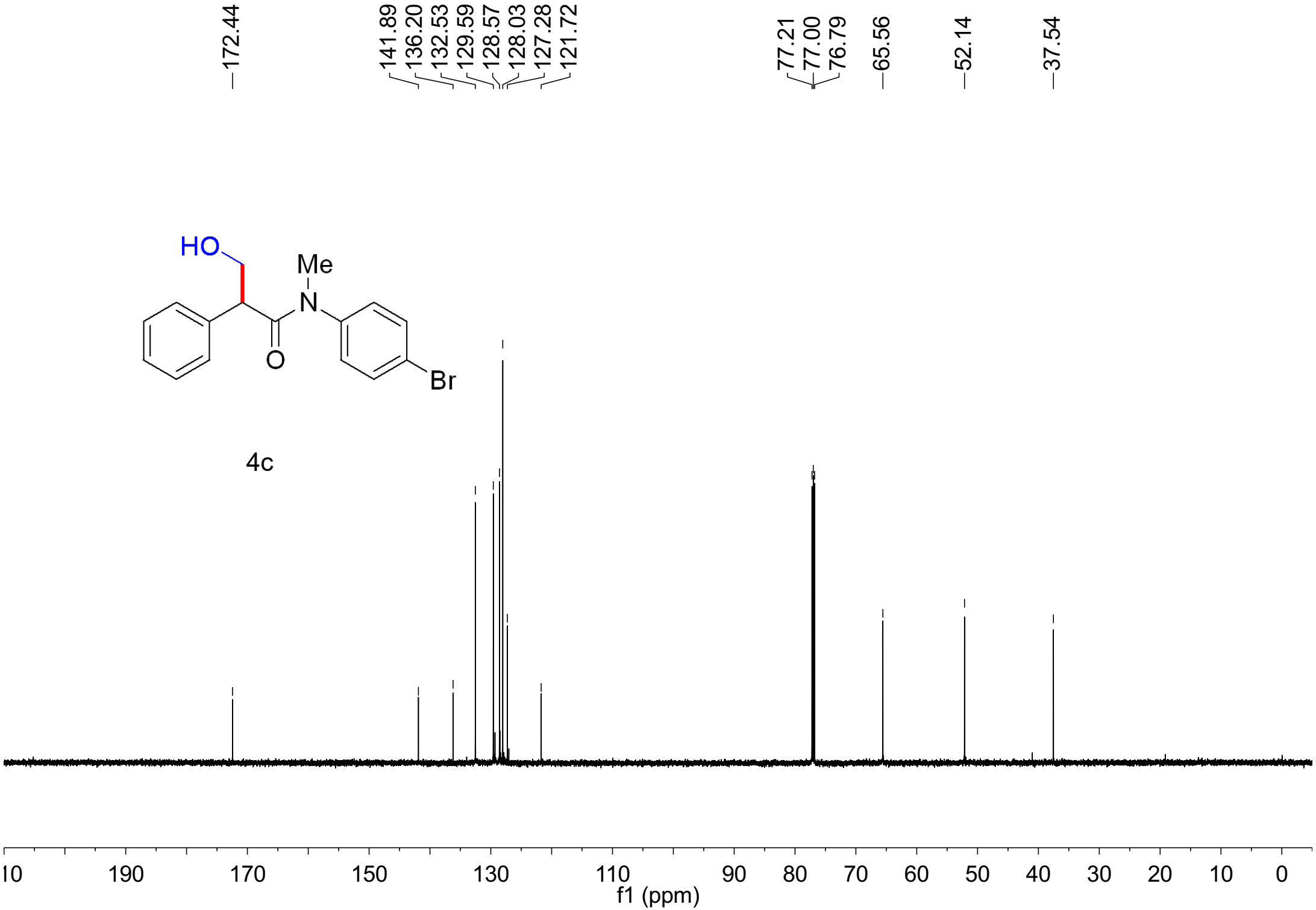
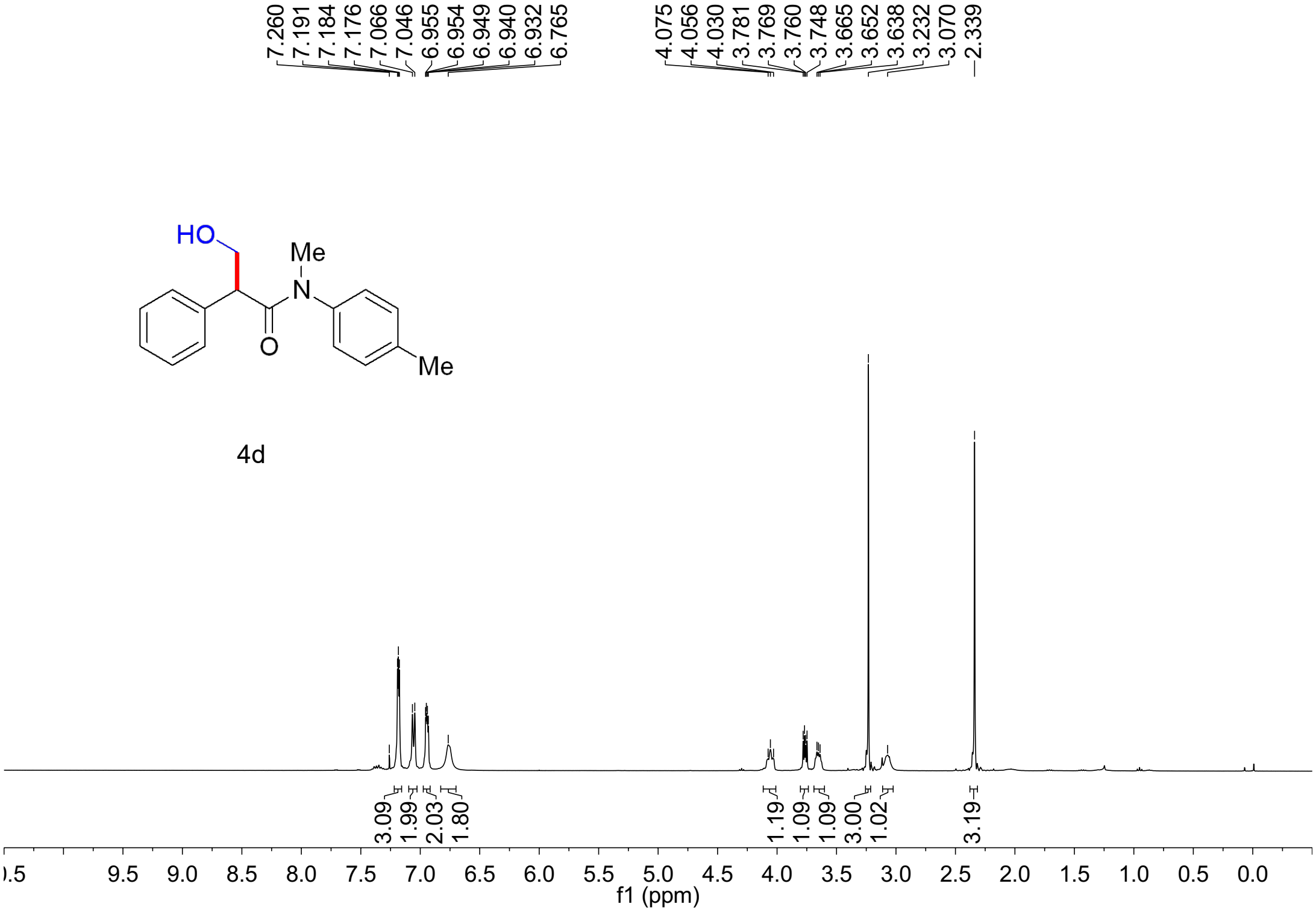
7.367
7.260
7.204
7.196
7.188
6.931
6.924
6.916
6.908
6.756
6.742
4.100
4.077
4.072
4.050
3.739
3.728
3.718
3.706
3.646
3.634
3.618
3.606
3.225
HO
Me
N
O
Br
4c
2.08
3.00
2.01
1.74
1.13
1.08
1.13
3.00
f1 (ppm)


172.44
141.89
136.20
132.53
129.59
128.57
128.03
127.28
121.72
77.21
77.00
76.79
65.56
52.14
37.54
HO
Me
N
O
Br
4c
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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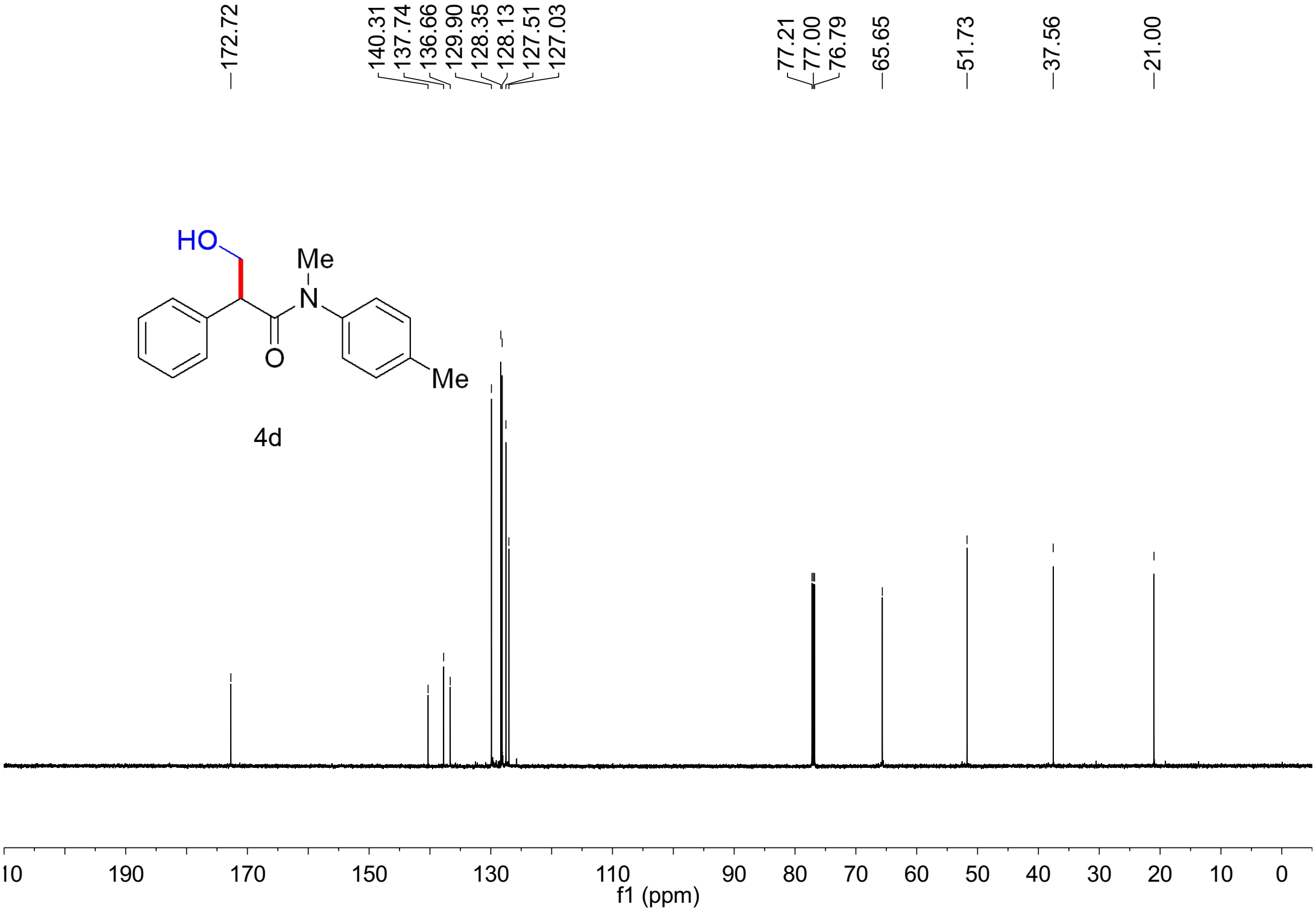
7.191
7.184
7.176
7.066
7.046
6.955
6.954
6.949
6.940
6.932
6.765
4.075
4.056
4.030
3.781
3.769
3.760
3.748
3.665
3.652
3.638
3.232
3.070
2.339
HO
Me
N
O
Me
4d
3.09
1.99
2.03
1.80
1.19
1.09
1.09
3.00
1.02
3.19
f1 (ppm)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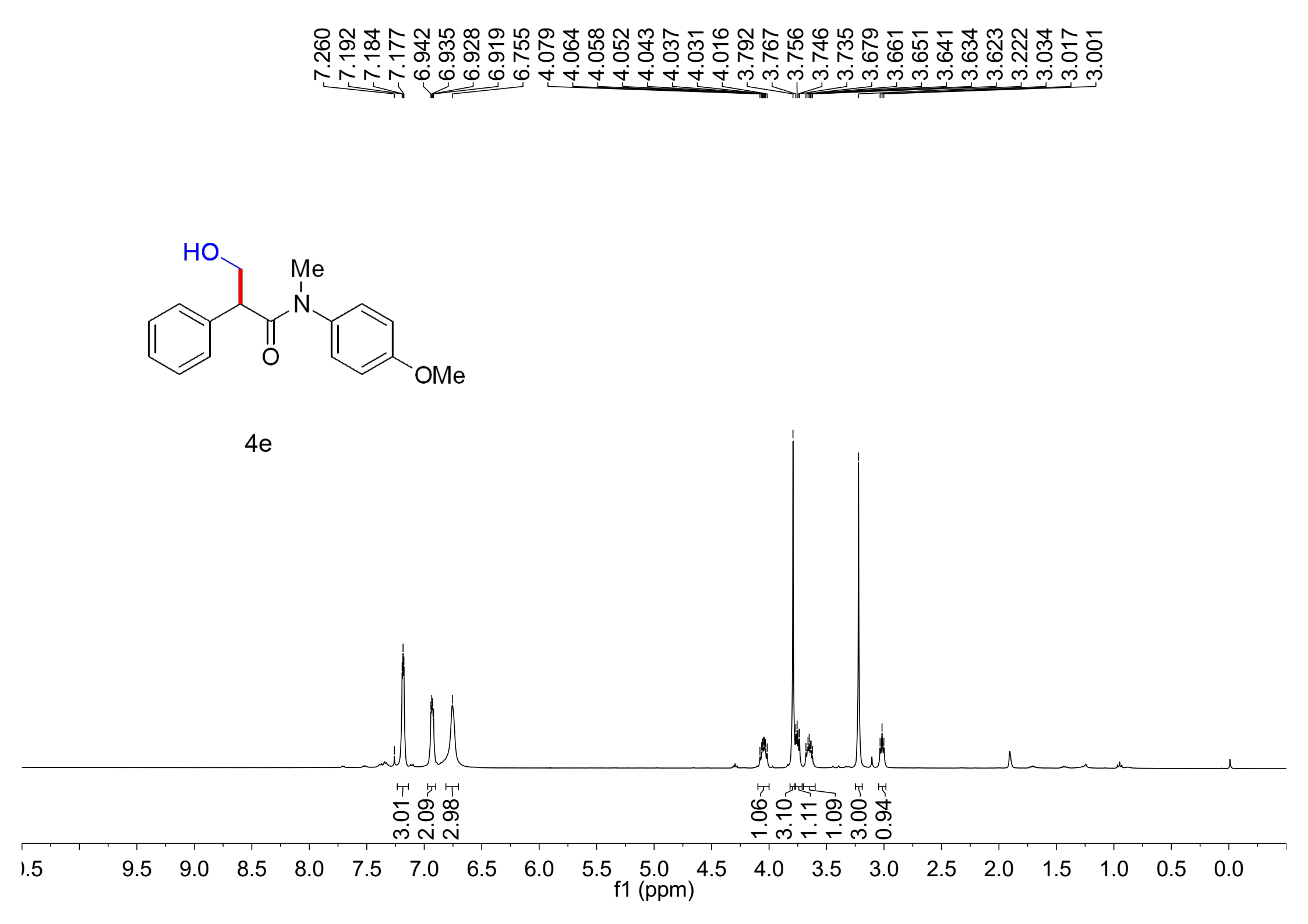
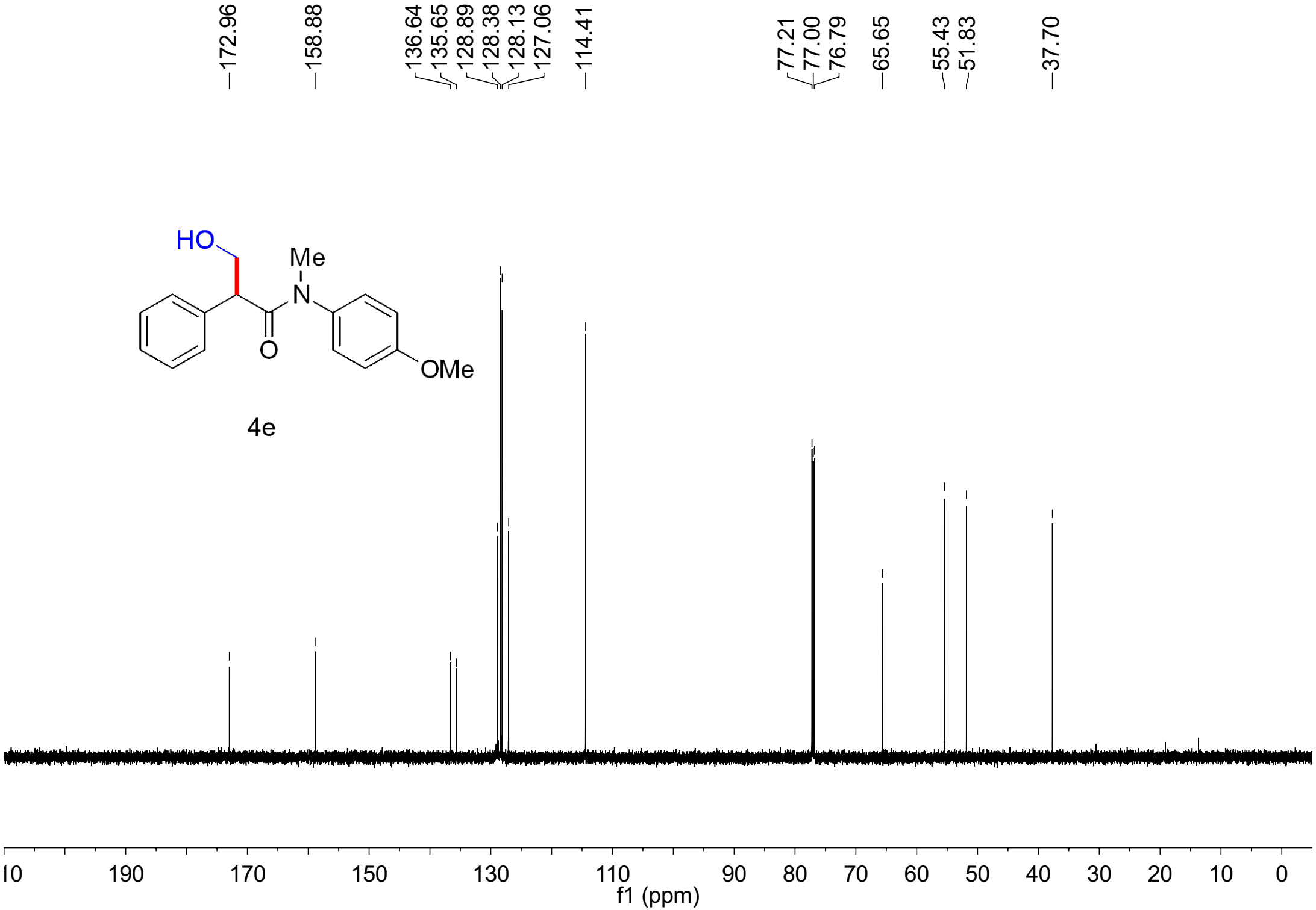
140.31
137.74
136.66
129.90
128.35
128.13
127.51
127.03
77.21
77.00
76.79
65.65
51.73
37.56
21.00
HO
Me
N
O
Me
4d
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.260
7.192
7.184
7.177
6.942
6.935
6.928
6.919
6.755
4.079
4.064
4.058
4.052
4.043
4.037
4.031
4.016
3.792
3.767
3.756
3.746
3.735
3.679
3.661
3.651
3.641
3.634
3.623
3.222
3.034
3.017
3.001
HO
Me
N
O
OMe
4e
3.01
2.09
2.98
1.06
3.10
1.11
1.09
3.00
0.94
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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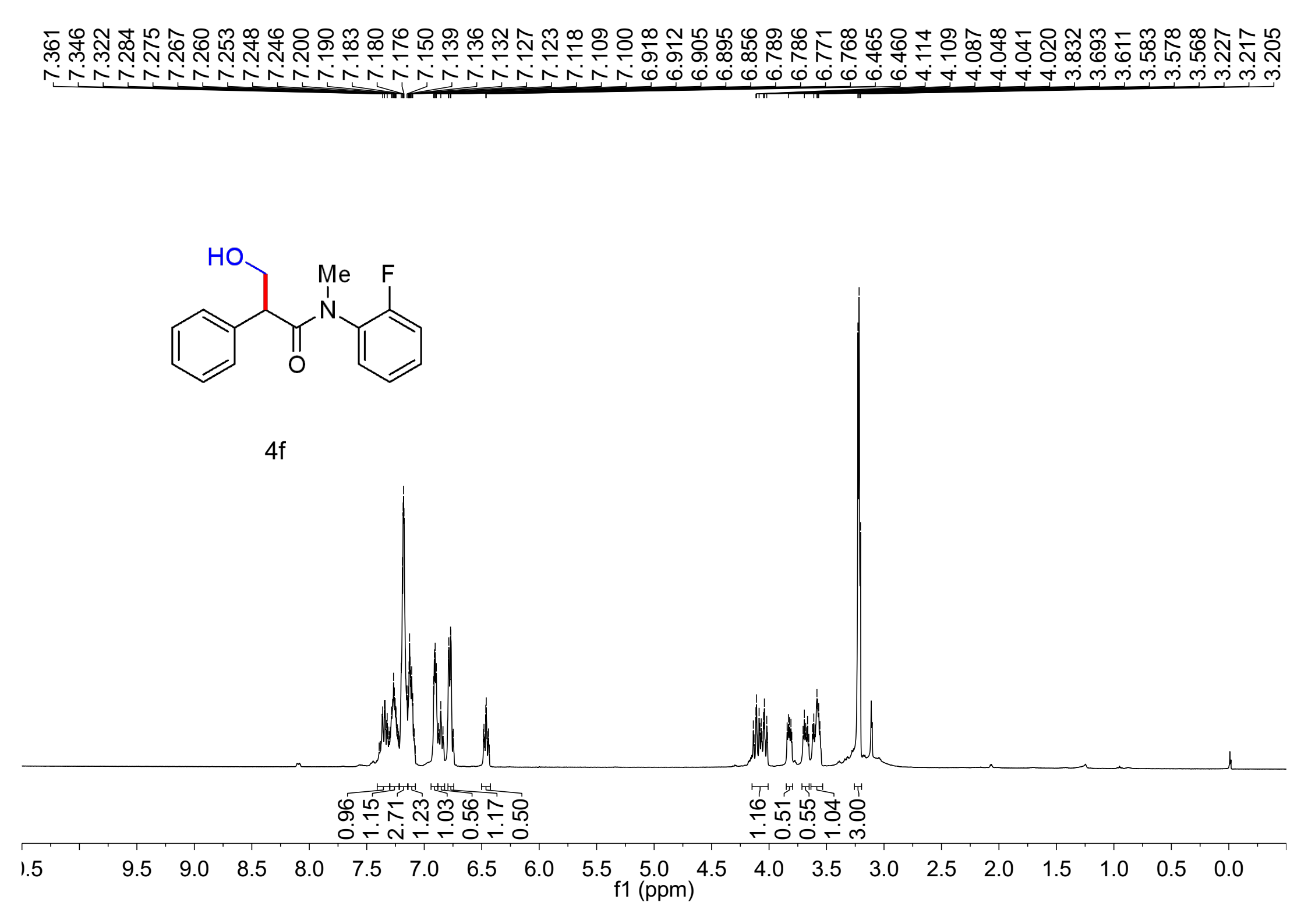
158.88
136.64
135.65
128.89
128.38
128.13
127.06
114.41
77.21
77.00
76.79
65.65
55.43
51.83
37.70
HO
Me
N
O
OMe
4e
f1 (ppm)


7.361
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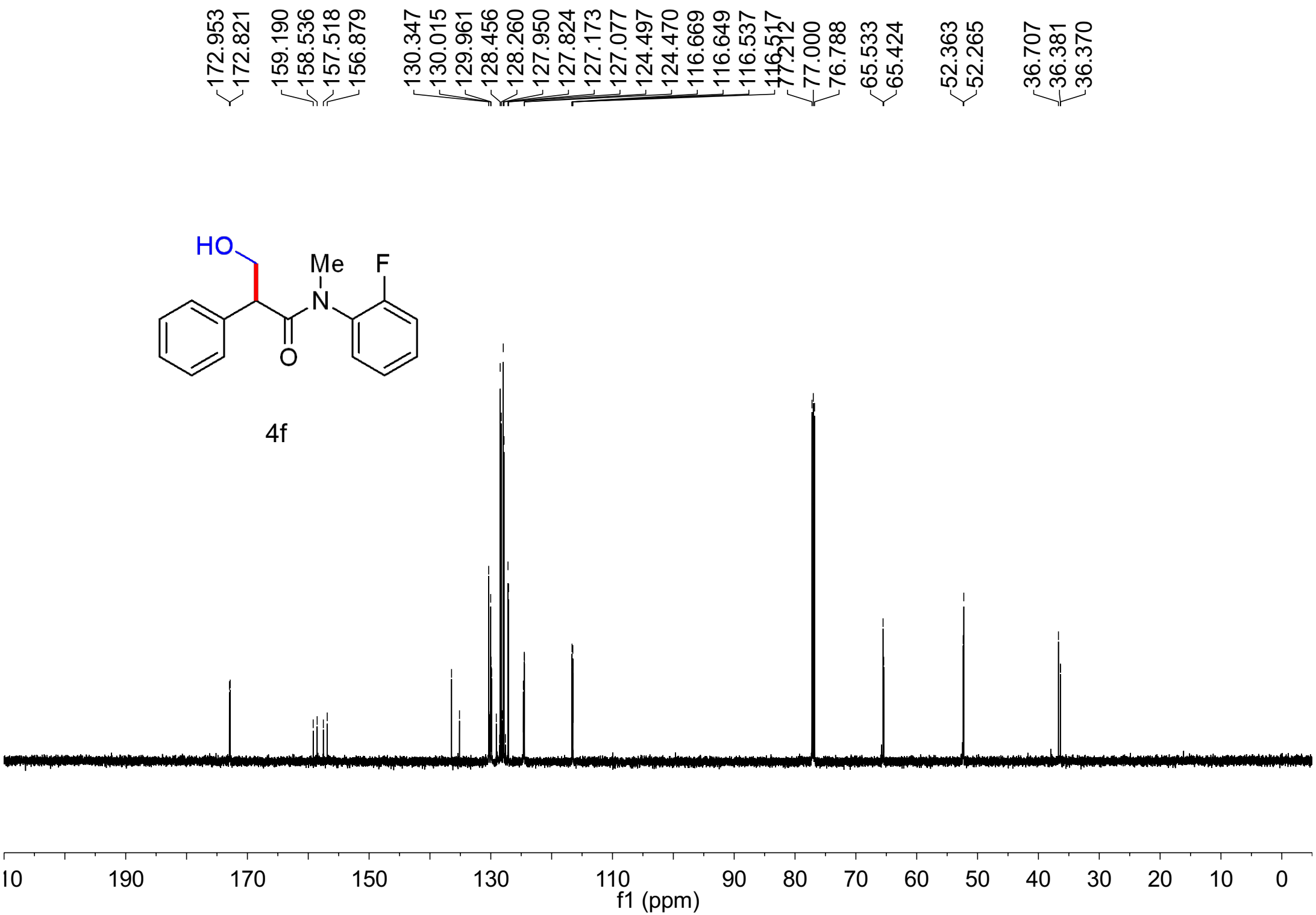
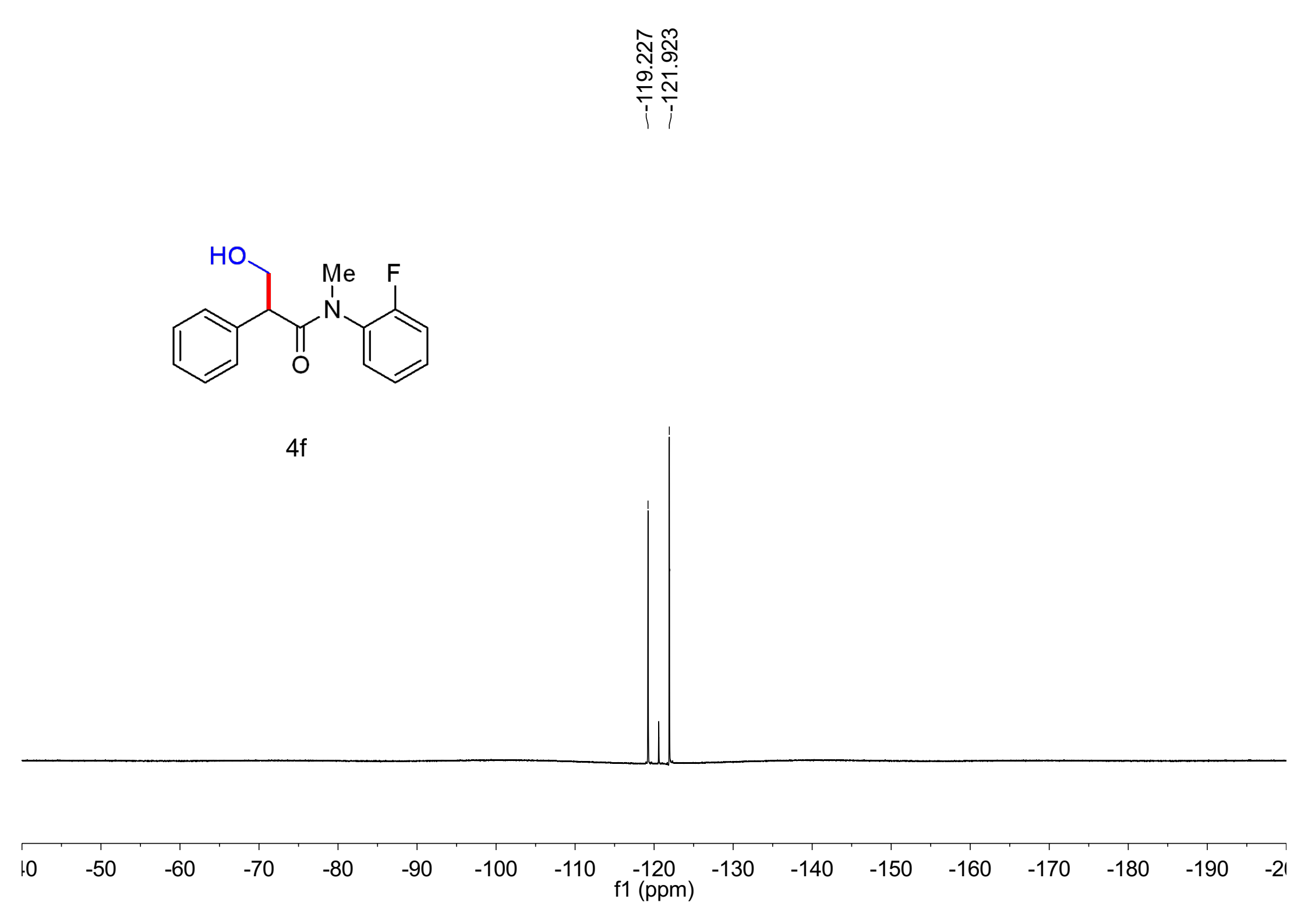
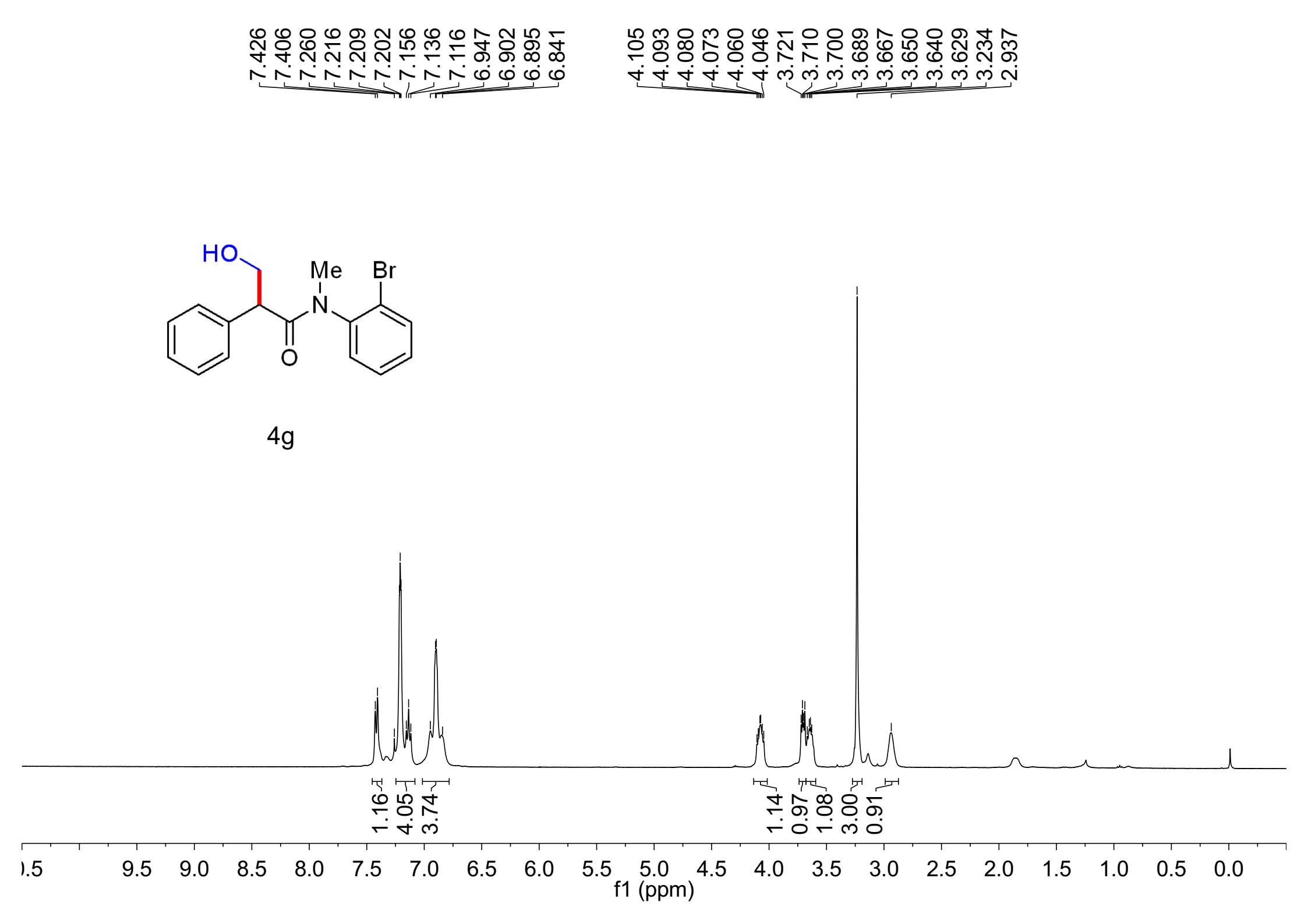
7.322
7.284
7.275
7.267
7.260
7.253
7.248
7.246
7.200
7.190
7.183
7.180
7.176
7.150
7.139
7.136
7.132
7.127
7.123
7.118
7.109
7.100
6.918
6.912
6.905
6.895
6.856
6.789
6.786
6.771
6.768
6.465
6.460
4.114
4.109
4.087
4.048
4.041
4.020
3.832
3.693
3.611
3.583
3.578
3.568
3.227
3.217
3.205
HO
Me
F
N
O
4f
0.96
1.15
2.71
1.23
1.03
0.56
1.17
0.50
1.16
0.51
0.55
1.04
3.00
f1 (ppm)


172.953
172.821
159.190
158.536
157.518
156.879
130.347
130.015
129.961
128.456
128.260
127.950
127.824
127.173
127.077
124.497
124.470
116.669
116.649
116.537
116.517
77.212
77.000
76.788
65.533
65.424
52.363
52.265
36.707
36.381
36.370
HO
Me
F
N
O
4f
f1 (ppm)


-119.227
-121.923
HO
Me
F
N
O
4f
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)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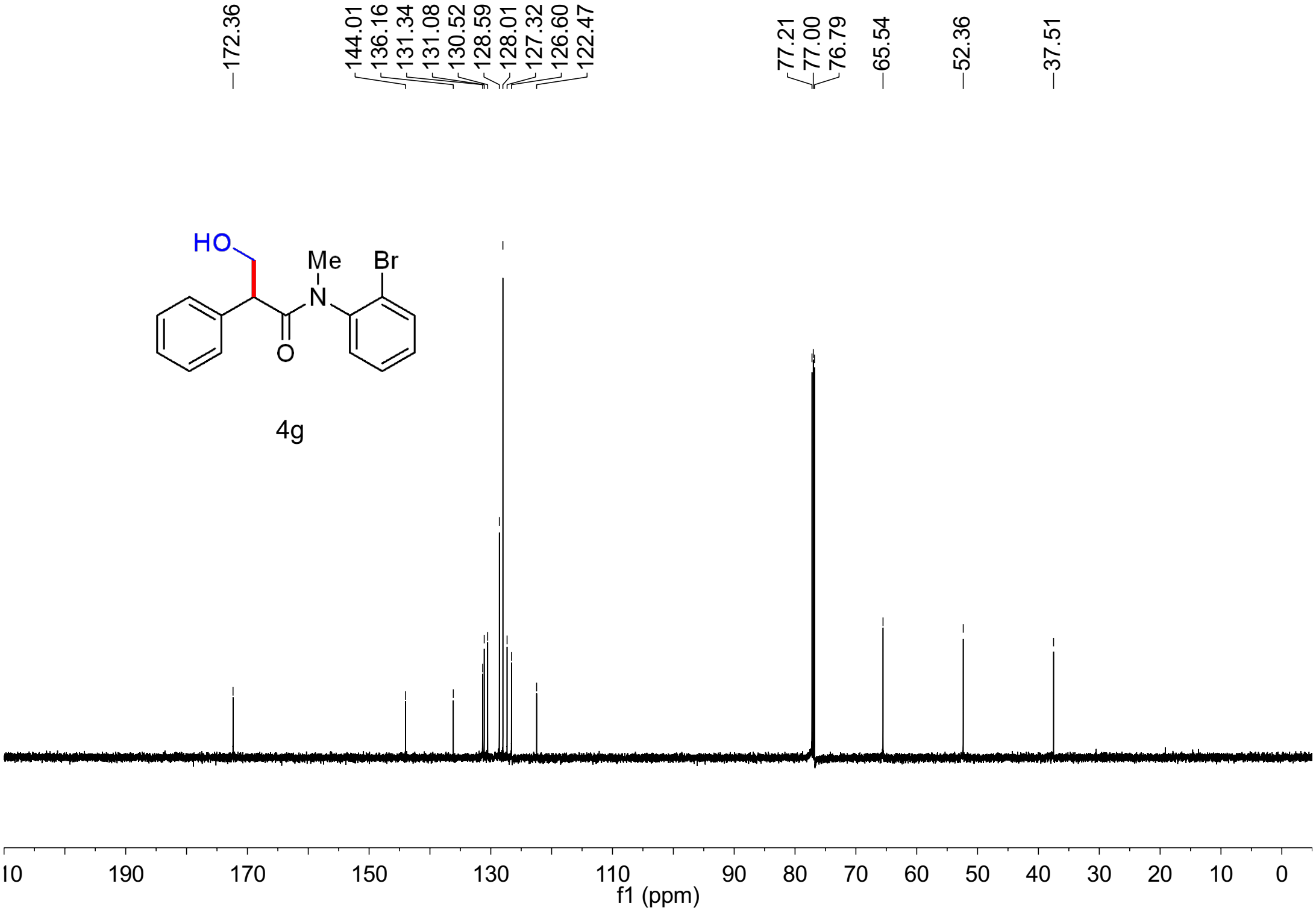
7.406
7.260
7.216
7.209
7.202
7.156
7.136
7.116
6.947
6.902
6.895
6.841
4.105
4.093
4.080
4.073
4.060
4.046
3.721
3.710
3.700
3.689
3.667
3.650
3.640
3.629
3.234
2.937
HO
Me
Br
N
O
4g
1.16
4.05
3.74
1.14
0.97
1.08
3.00
0.91
f1 (ppm)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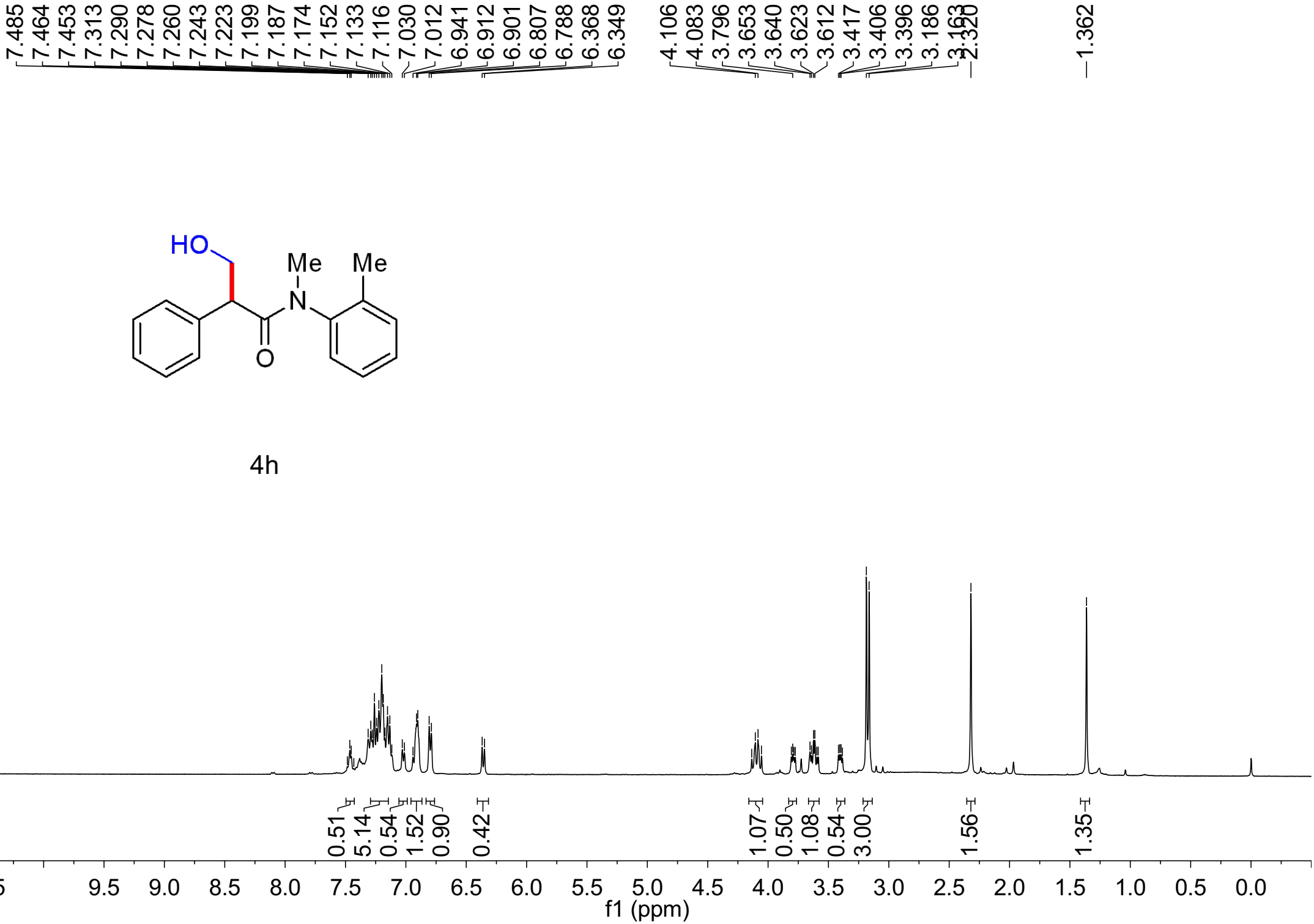
136.16
131.34
131.08
130.52
128.59
128.01
127.32
126.60
122.47
77.21
77.00
76.79
65.54
52.36
37.51
HO
Me
Br
N
O
4g
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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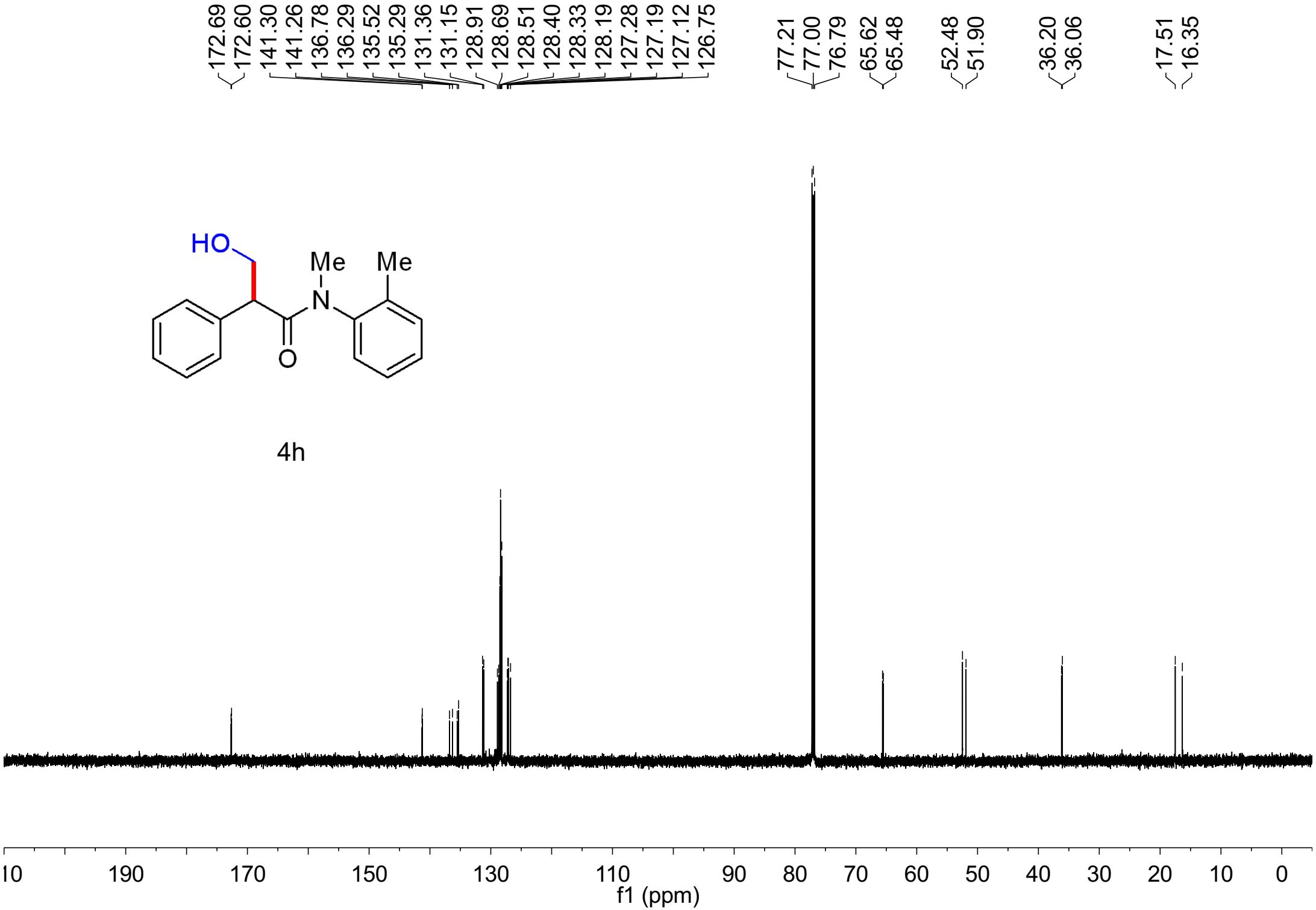
7.313
7.290
7.278
7.260
7.243
7.223
7.199
7.187
7.174
7.152
7.133
7.116
7.030
7.012
6.941
6.912
6.901
6.807
6.788
6.368
6.349
4.106
4.083
3.796
3.653
3.640
3.623
3.612
3.417
3.406
3.396
3.186
3.163
2.320
1.362
HO
Me
Me
N
O
4h
0.51
5.14
0.54
1.52
0.90
0.42
1.07
0.50
1.08
0.54
3.00
1.56
1.35
f1 (ppm)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172.60
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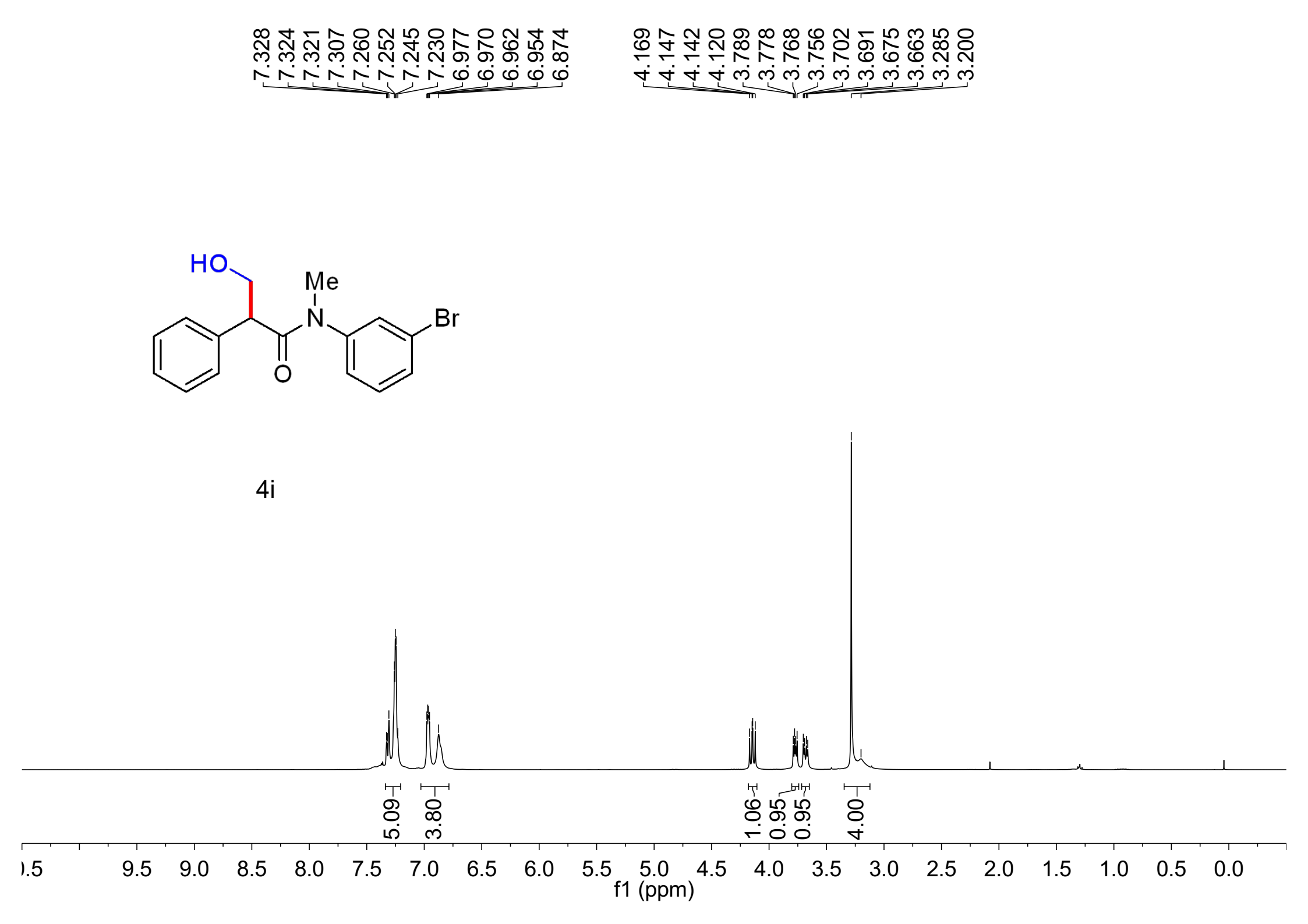
136.78
136.29
135.52
135.29
131.36
131.15
128.91
128.69
128.51
128.40
128.33
128.19
127.28
127.19
127.12
126.75
77.21
77.00
76.79
65.62
65.48
52.48
51.90
36.20
36.06
17.51
16.35
HO
Me
Me
N
O
4h
f1 (ppm)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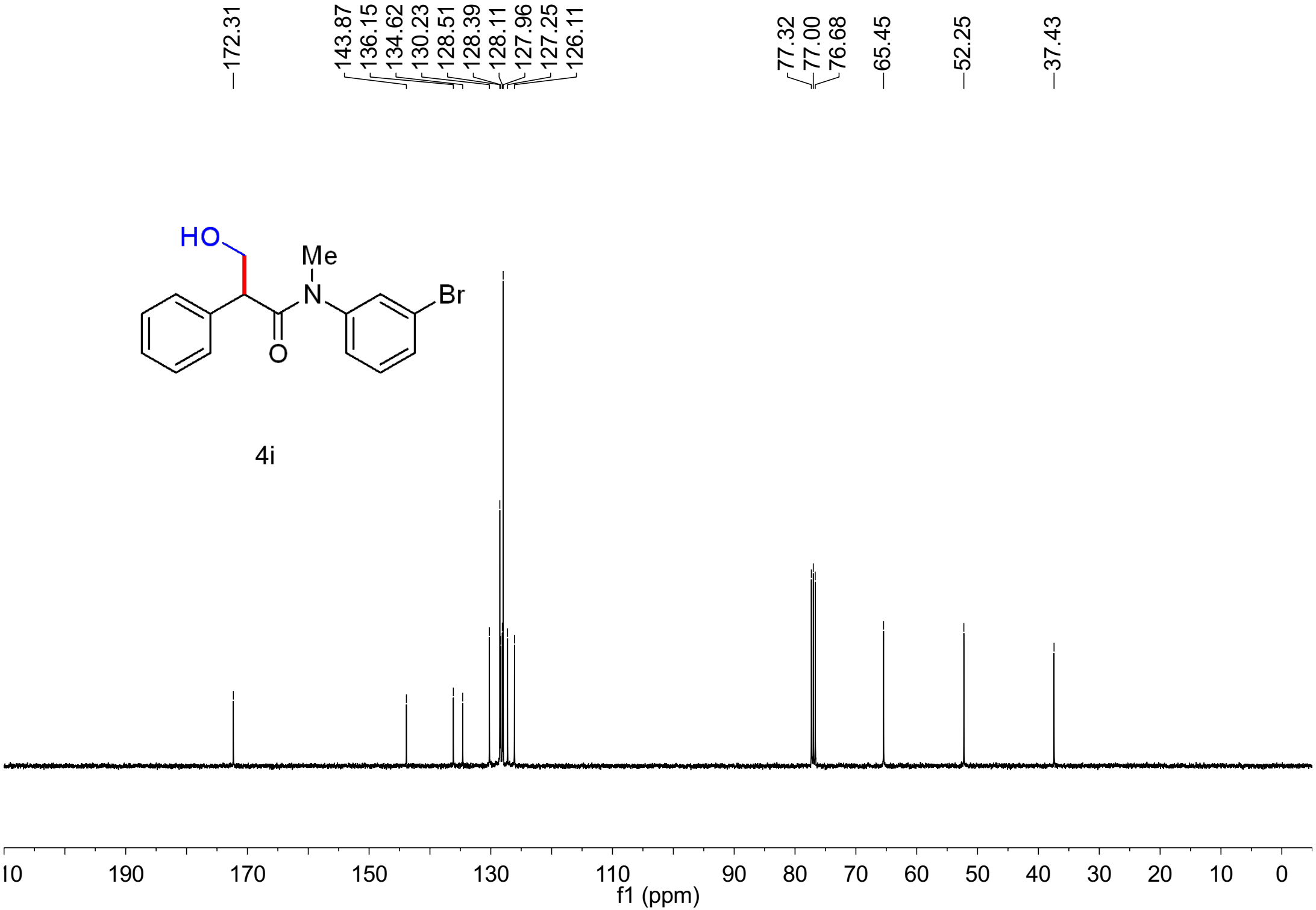
7.324
7.321
7.307
7.260
7.252
7.245
7.230
6.977
6.970
6.962
6.954
6.874
4.169
4.147
4.142
4.120
3.789
3.778
3.768
3.756
3.702
3.691
3.675
3.663
3.285
3.200
HO
Me
N
Br
O
4i
5.09
3.80
1.06
0.95
0.95
4.00
f1 (ppm)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128.51
128.39
128.11
127.96
127.25
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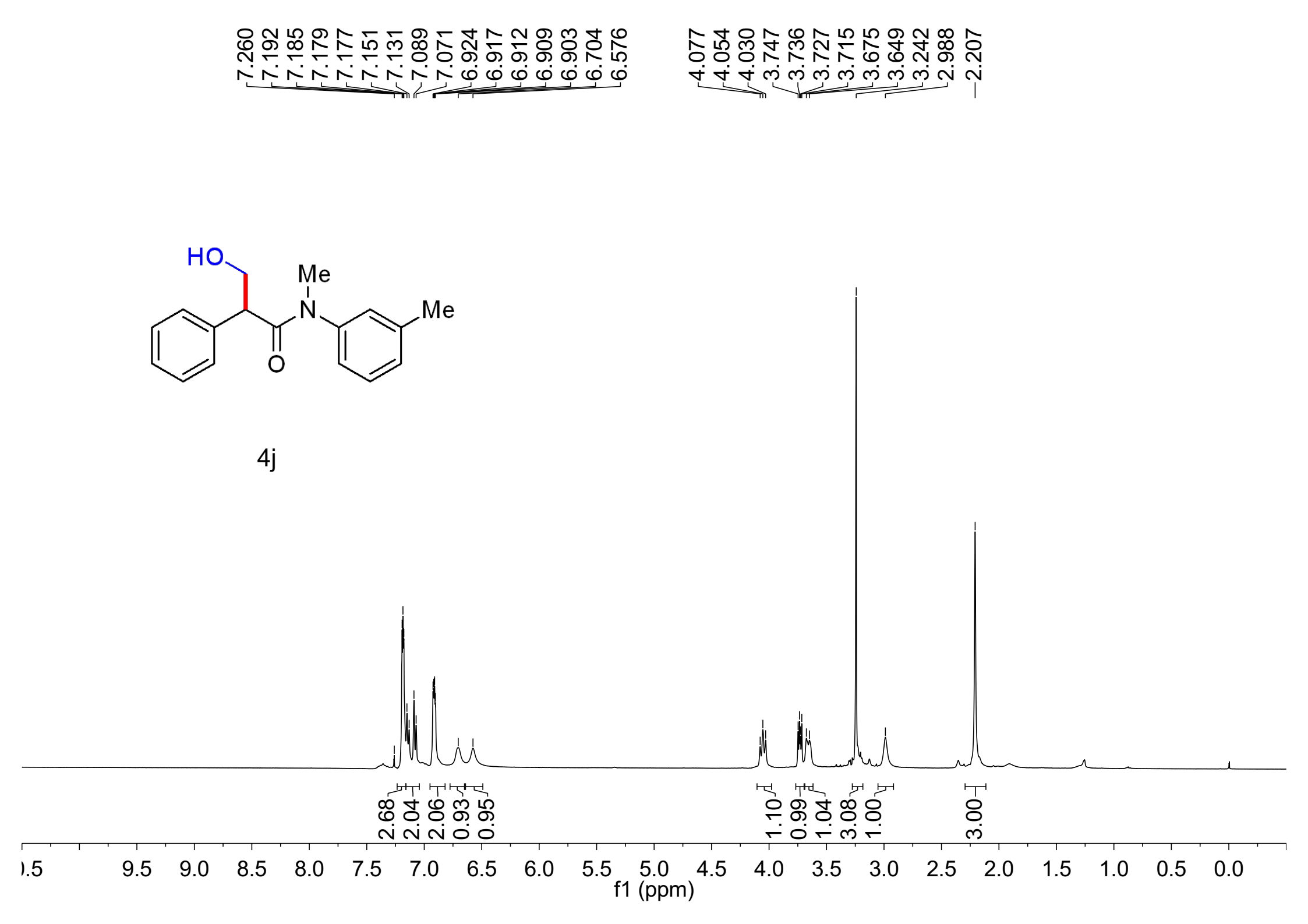
76.68
65.45
52.25
37.43
HO
Me
N
Br
O
4i
f1 (ppm)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7.192
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6.917
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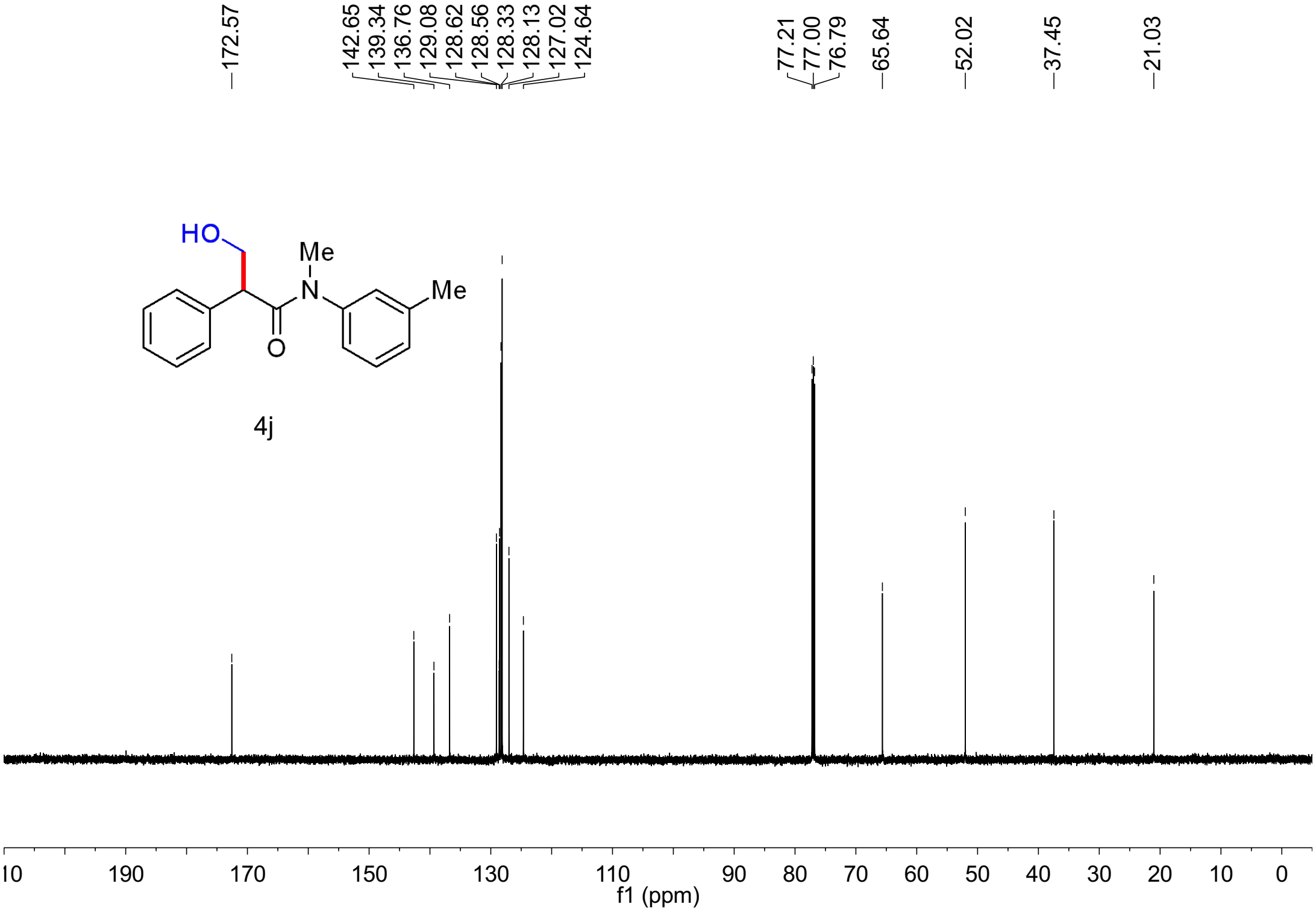
6.909
6.903
6.704
6.576
4.077
4.054
4.030
3.747
3.736
3.727
3.715
3.675
3.649
3.242
2.988
2.207
HO
Me
N
Me
O
4j
2.68
2.04
2.06
0.93
0.95
1.10
0.99
1.04
3.08
1.00
3.00
f1 (ppm)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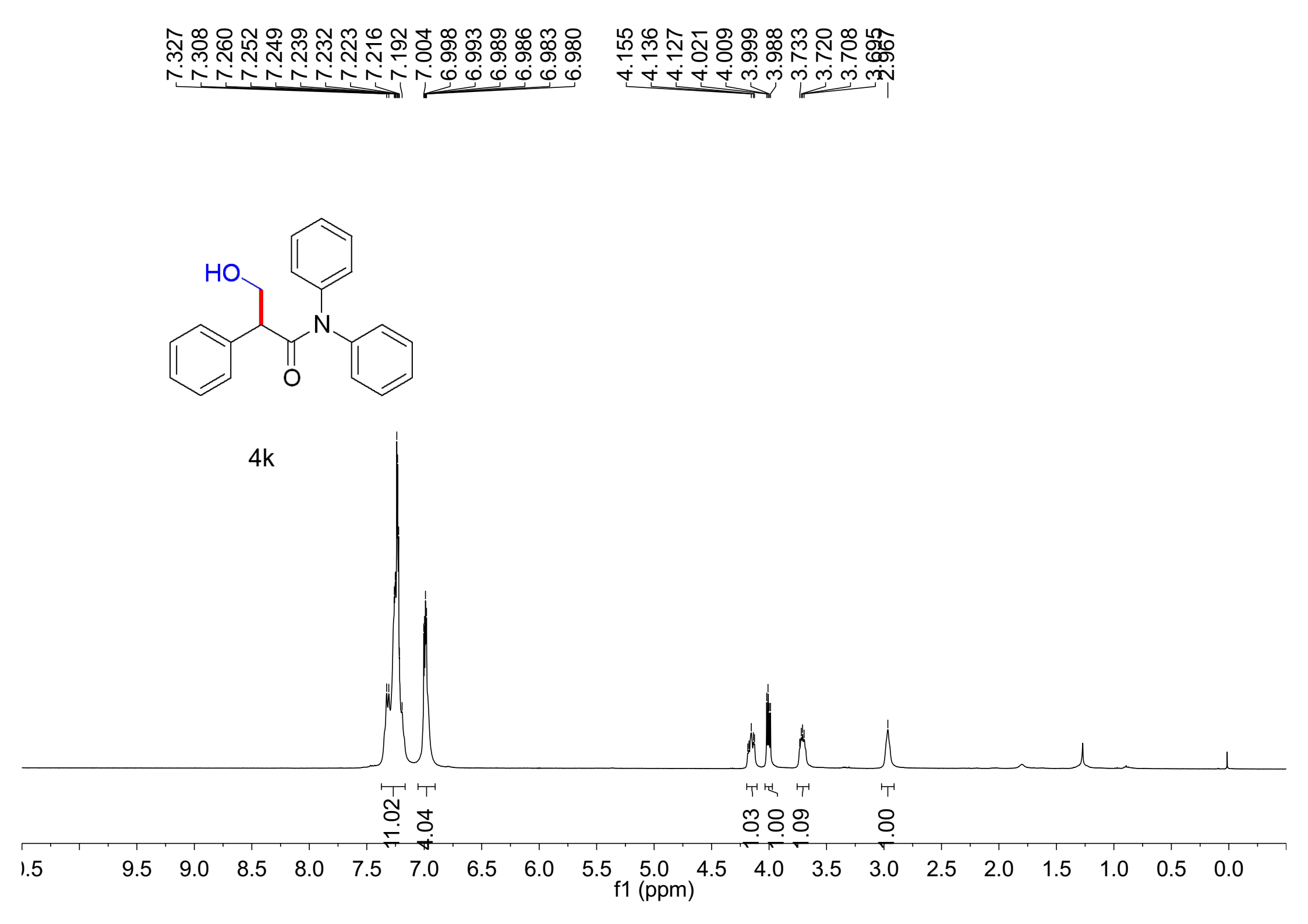
136.76
129.08
128.62
128.56
128.33
128.13
127.02
124.64
77.21
77.00
76.79
65.64
52.02
37.45
21.03
HO
Me
N
Me
O
4j
f1 (ppm)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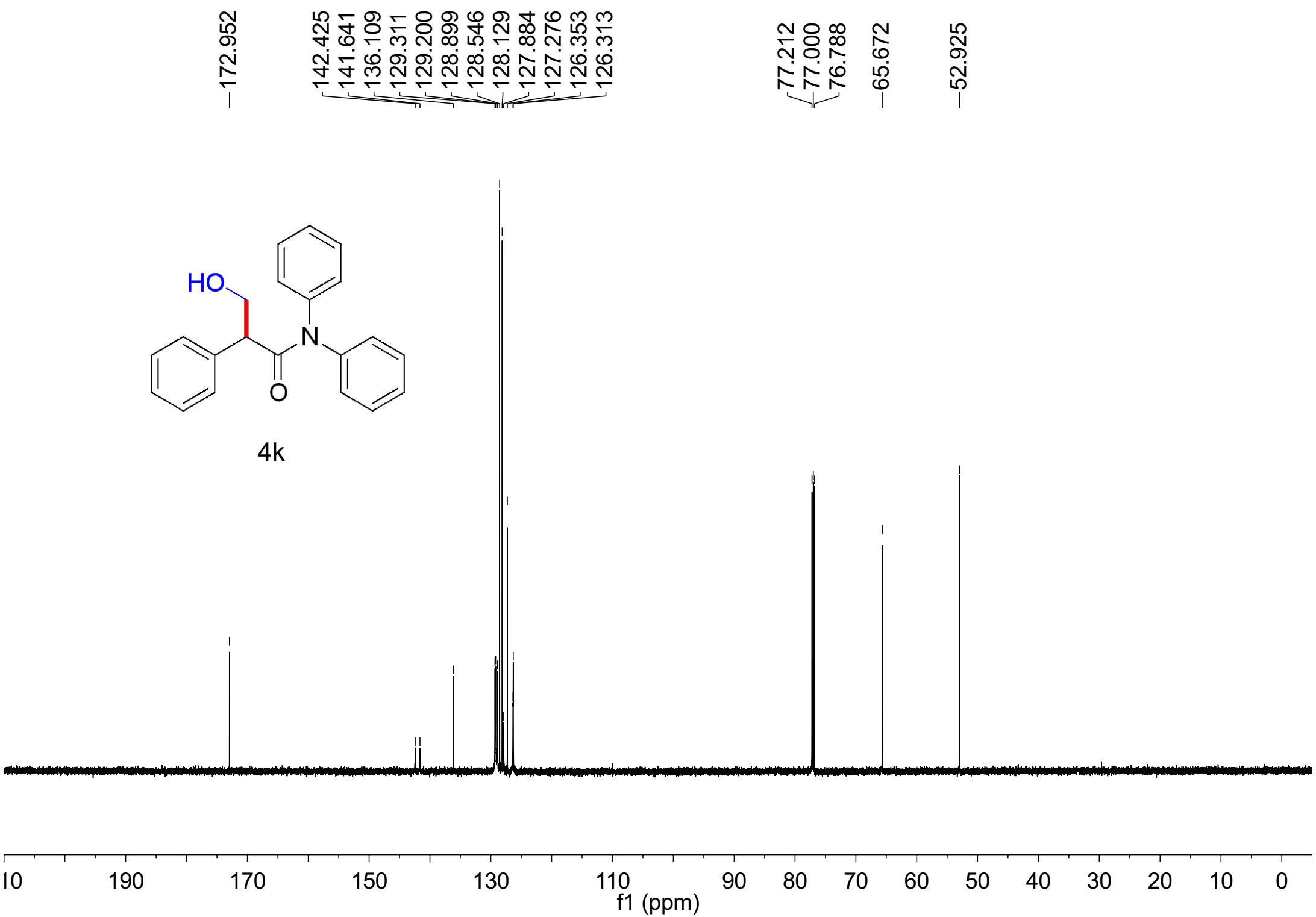
7.308
7.260
7.252
7.249
7.239
7.232
7.223
7.216
7.192
7.004
6.998
6.993
6.989
6.986
6.983
6.980
4.155
4.136
4.127
4.021
4.009
3.999
3.988
3.733
3.720
3.708
3.695
3.667
HO
N
O
4k
11.02
4.04
1.03
1.00
1.09
1.00
f1 (ppm)


172.952
142.425
141.641
136.109
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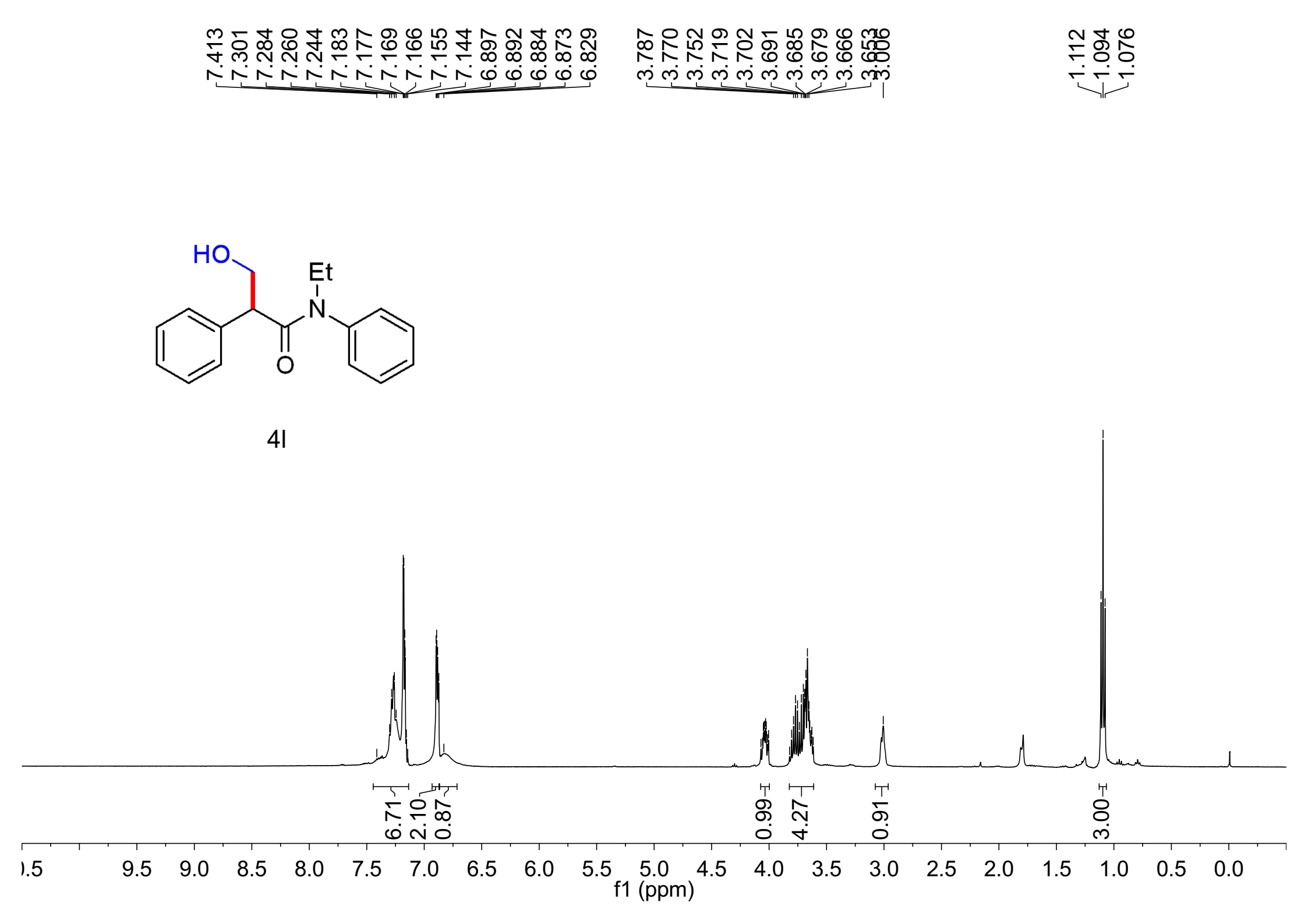
129.200
128.899
128.546
128.129
127.884
127.276
126.353
126.313
77.212
77.000
76.788
65.672
52.925
HO
N
O
4k
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.413
7.301
7.284
7.260
7.244
7.183
7.177
7.169
7.166
7.155
7.144
6.897
6.892
6.884
6.873
6.829
3.787
3.770
3.752
3.719
3.702
3.691
3.685
3.679
3.666
3.653
3.008
1.112
1.094
1.076
HO
Et
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O
4l
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2.10
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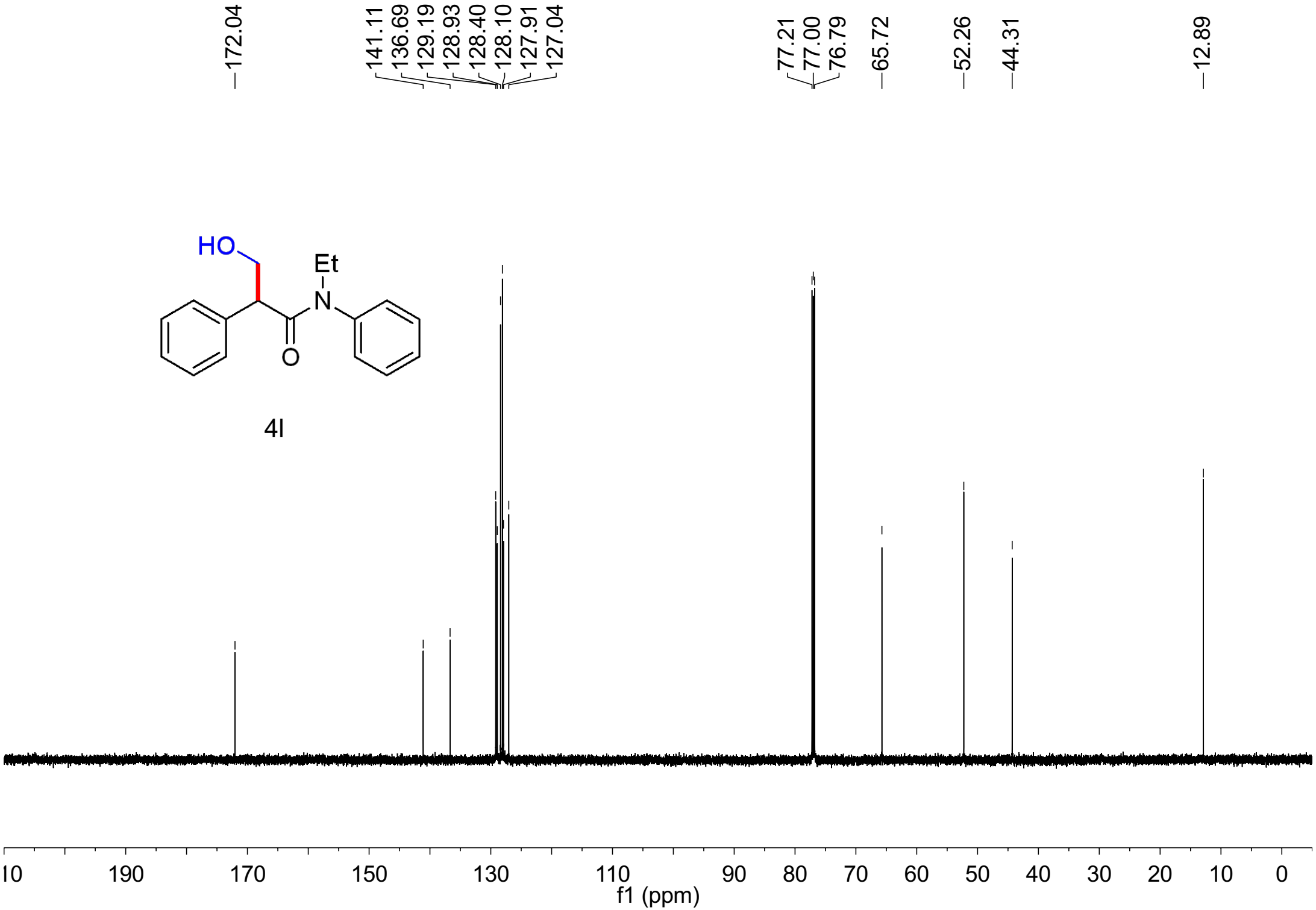
4.27
0.91
3.00
f1 (ppm)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129.19
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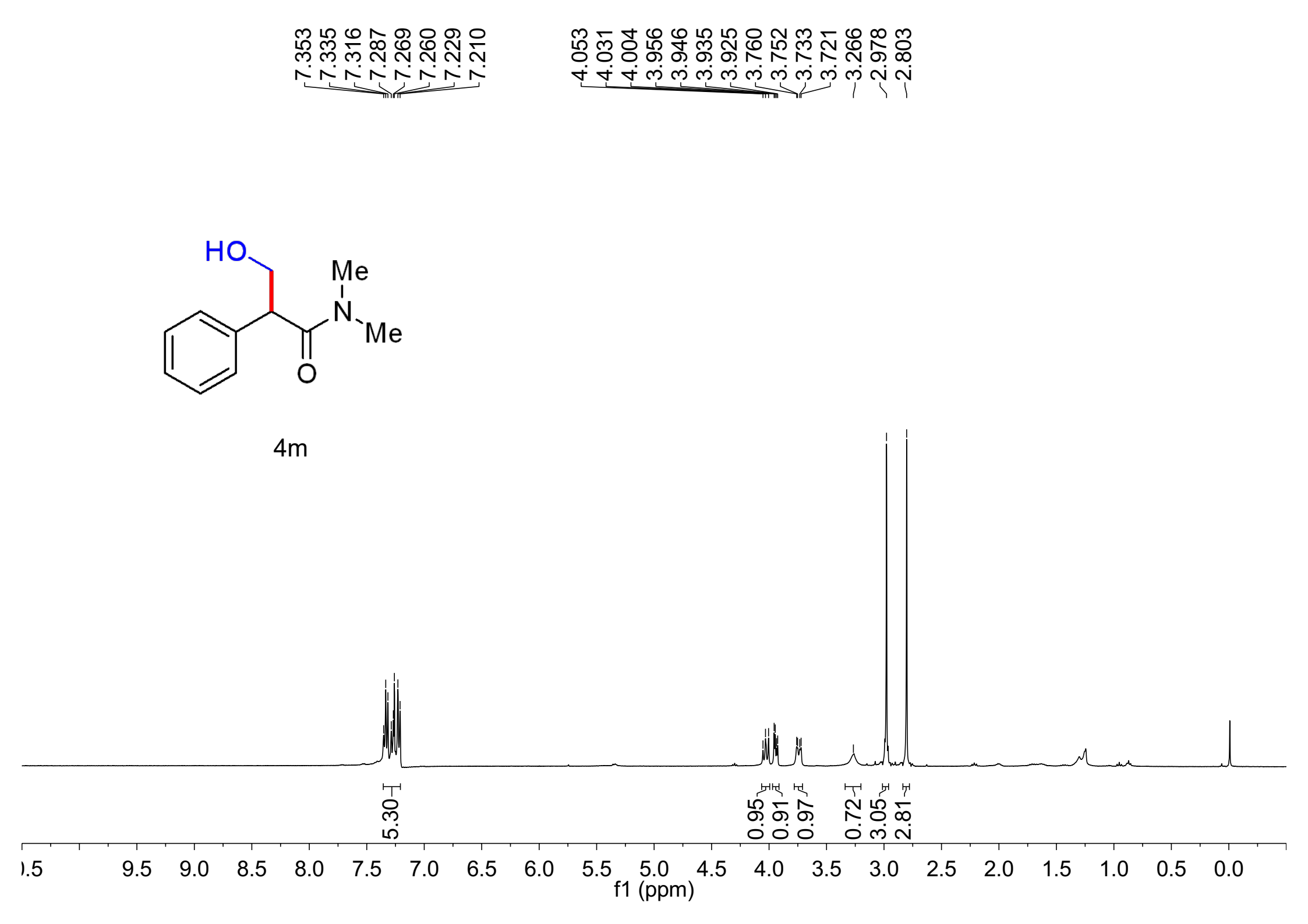
128.40
128.10
127.91
127.04
77.21
77.00
76.79
65.72
52.26
44.31
12.89
HO
Et
N
O
4l
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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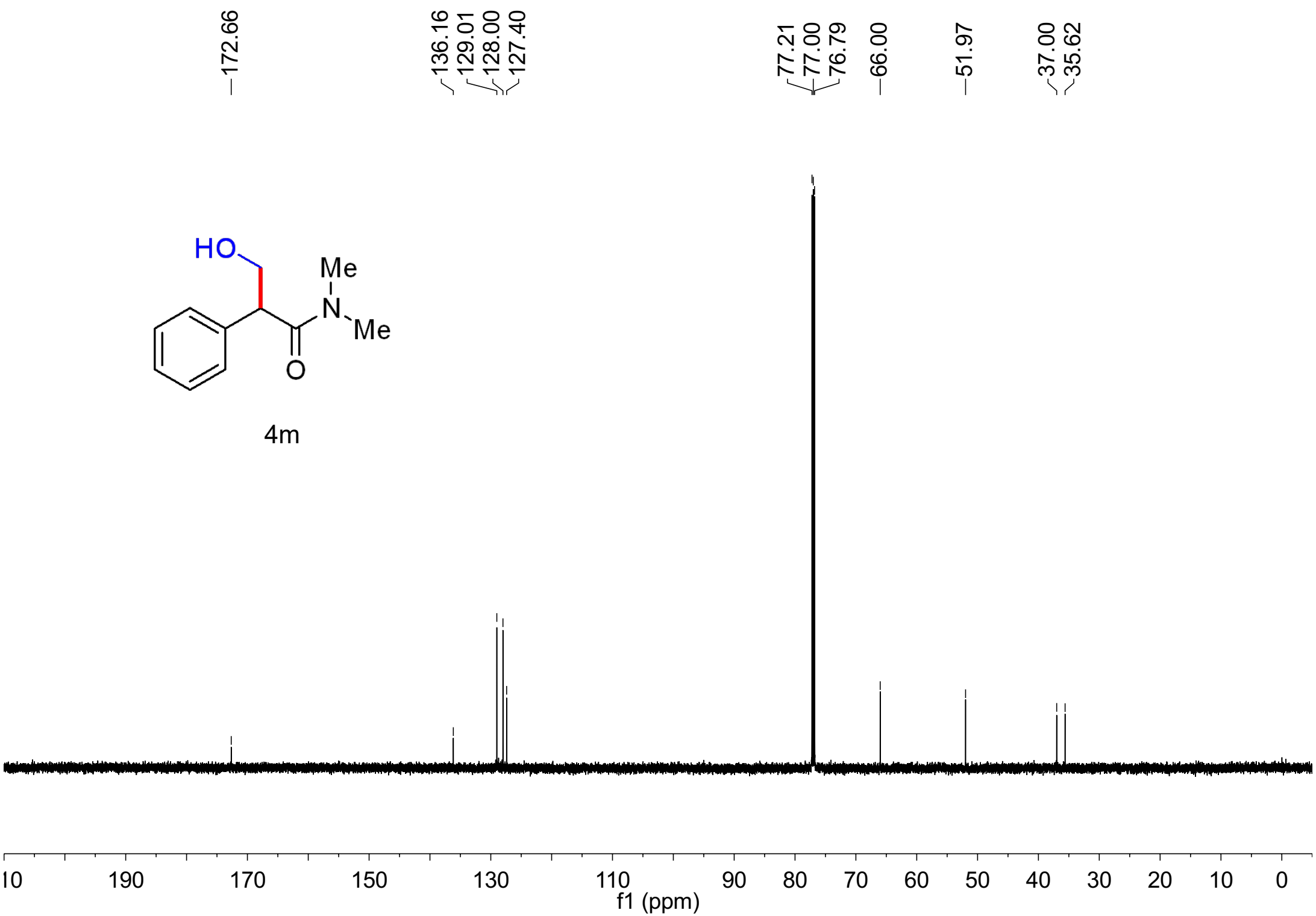
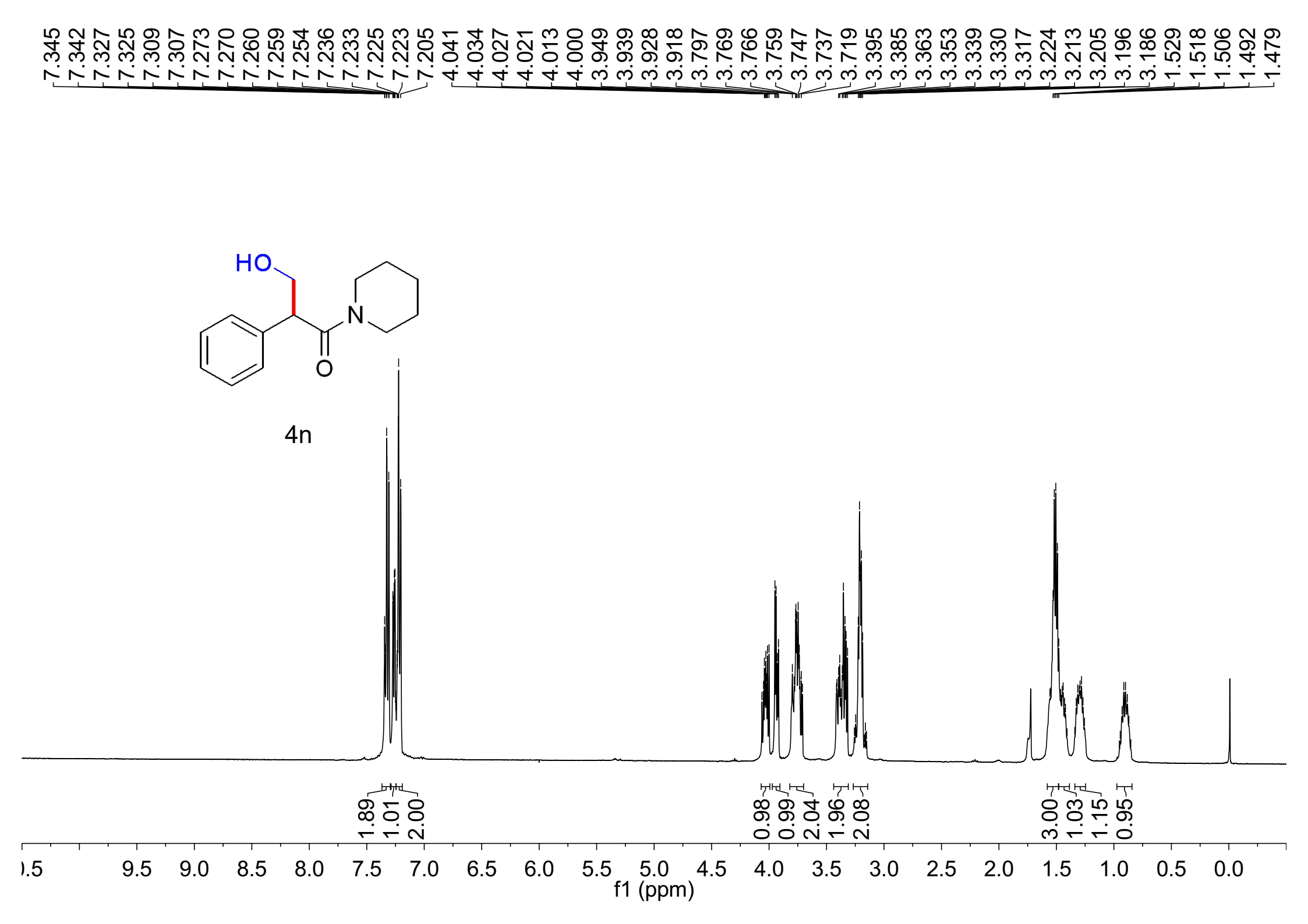
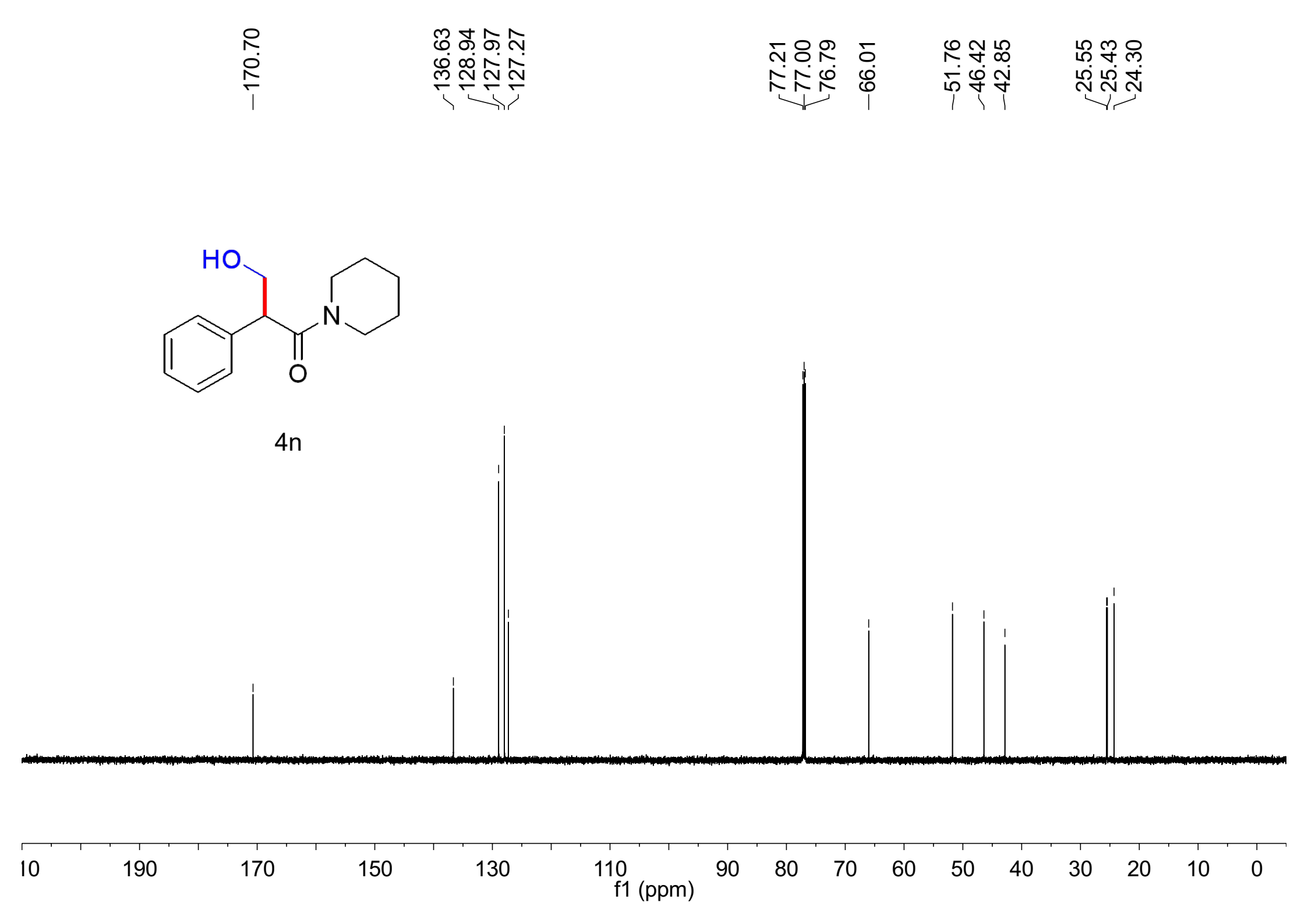
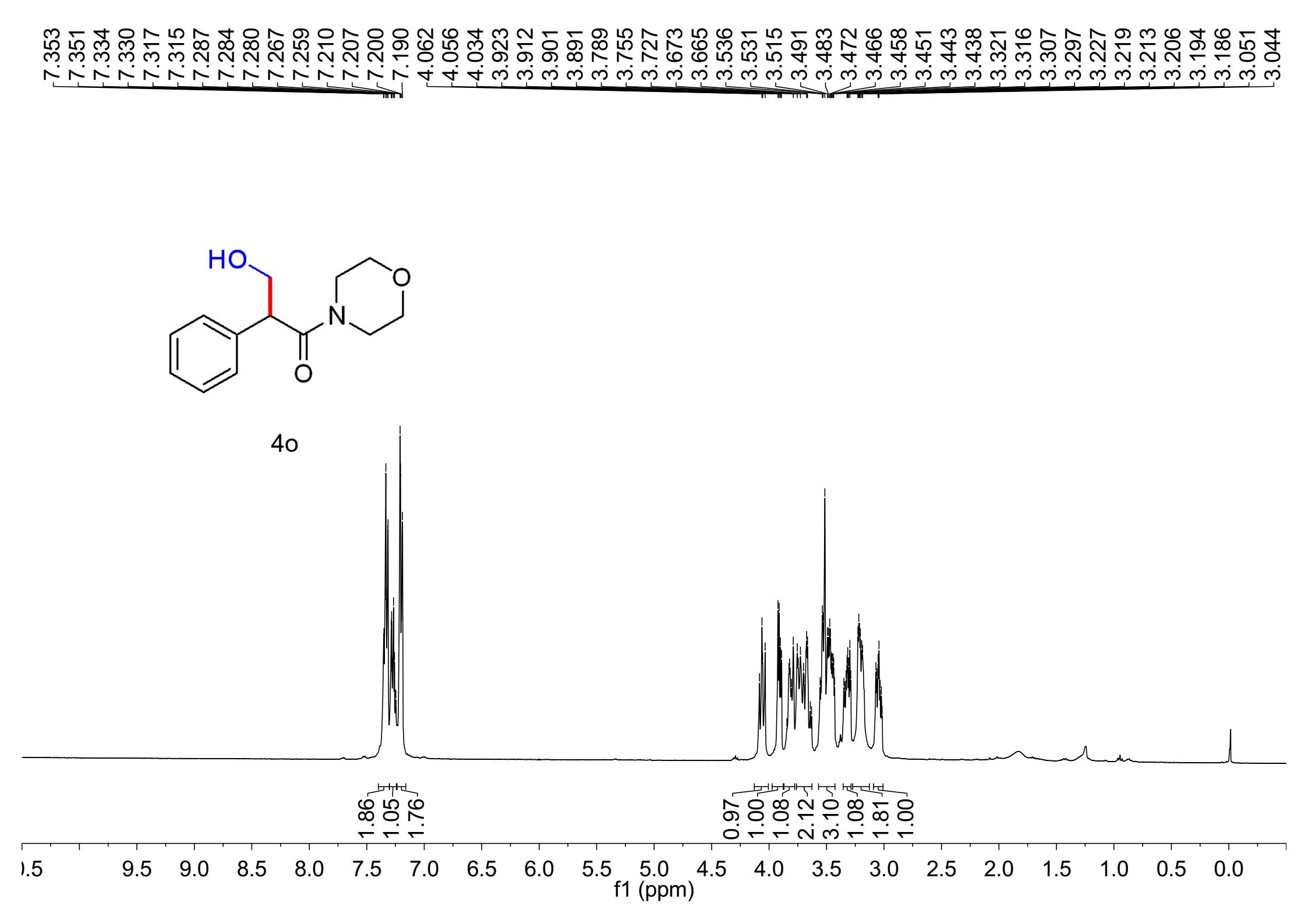
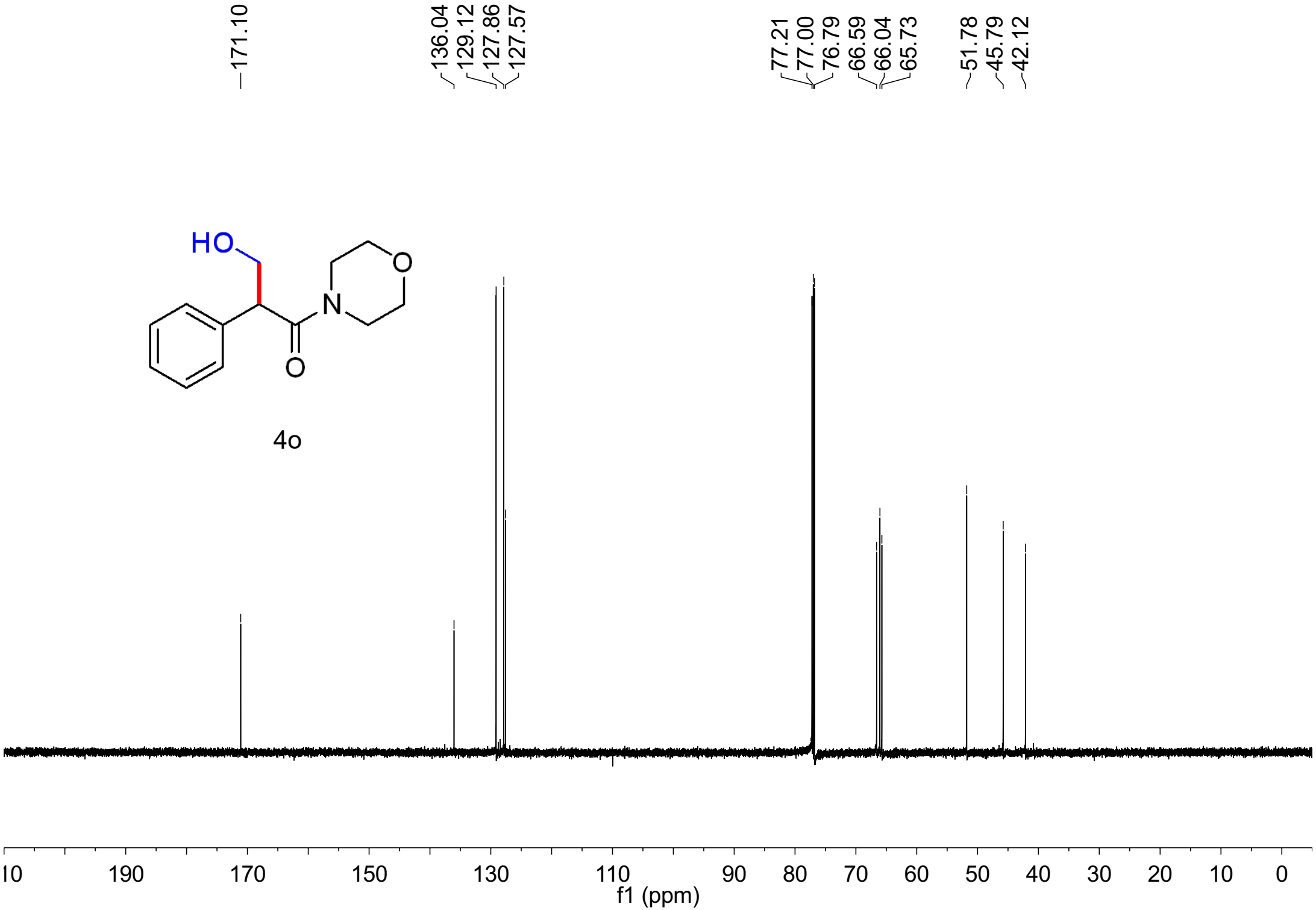
7.335
7.316
7.287
7.269
7.260
7.229
7.210
4.053
4.031
4.004
3.956
3.946
3.935
3.925
3.760
3.752
3.733
3.721
3.266
2.978
2.803
HO
Me
N
Me
O
4m
5.30
0.95
0.91
0.97
0.72
3.05
2.81
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


172.66
136.16
129.01
128.00
127.40
77.21
77.00
76.79
66.00
51.97
37.00
35.62
HO
Me
N
Me
O
4m
f1 (ppm)


7.345
7.342
7.327
7.325
7.309
7.307
7.273
7.270
7.260
7.259
7.254
7.236
7.233
7.225
7.223
7.205
4.041
4.034
4.027
4.021
4.013
4.000
3.949
3.939
3.928
3.918
3.797
3.769
3.766
3.759
3.747
3.737
3.719
3.395
3.385
3.363
3.353
3.339
3.330
3.317
3.224
3.213
3.205
3.196
3.186
1.529
1.518
1.506
1.492
1.479
HO
N
O
4n
1.89
1.01
2.00
0.98
0.99
2.04
1.96
2.08
3.00
1.03
1.15
0.95
f1 (ppm)


170.70
136.63
128.94
127.97
127.27
77.21
77.00
76.79
66.01
51.76
46.42
42.85
25.55
25.43
24.30
HO
N
O
4n
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.353
7.351
7.334
7.330
7.317
7.315
7.287
7.284
7.280
7.267
7.259
7.210
7.207
7.200
7.190
4.062
4.056
4.034
3.923
3.912
3.901
3.891
3.789
3.755
3.727
3.673
3.665
3.536
3.531
3.515
3.491
3.483
3.472
3.466
3.458
3.451
3.443
3.438
3.321
3.316
3.307
3.297
3.227
3.219
3.213
3.206
3.194
3.186
3.051
3.044
HO
O
N
O
4o
1.86
1.05
1.76
0.97
1.00
1.08
2.12
3.10
1.08
1.81
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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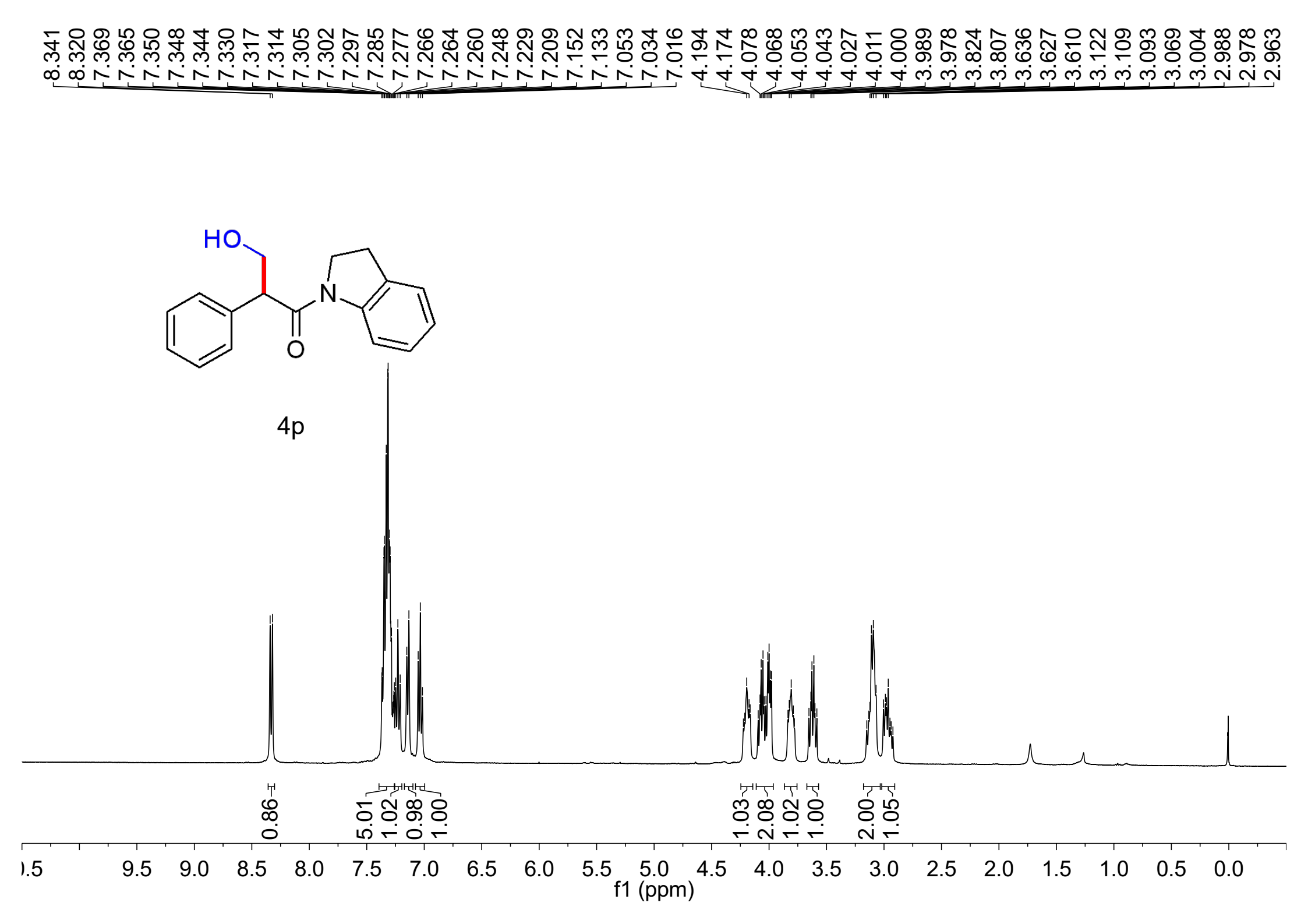
136.04
129.12
127.86
127.57
77.21
77.00
76.79
66.59
66.04
65.73
51.78
45.79
42.12
HO
O
N
O
4o
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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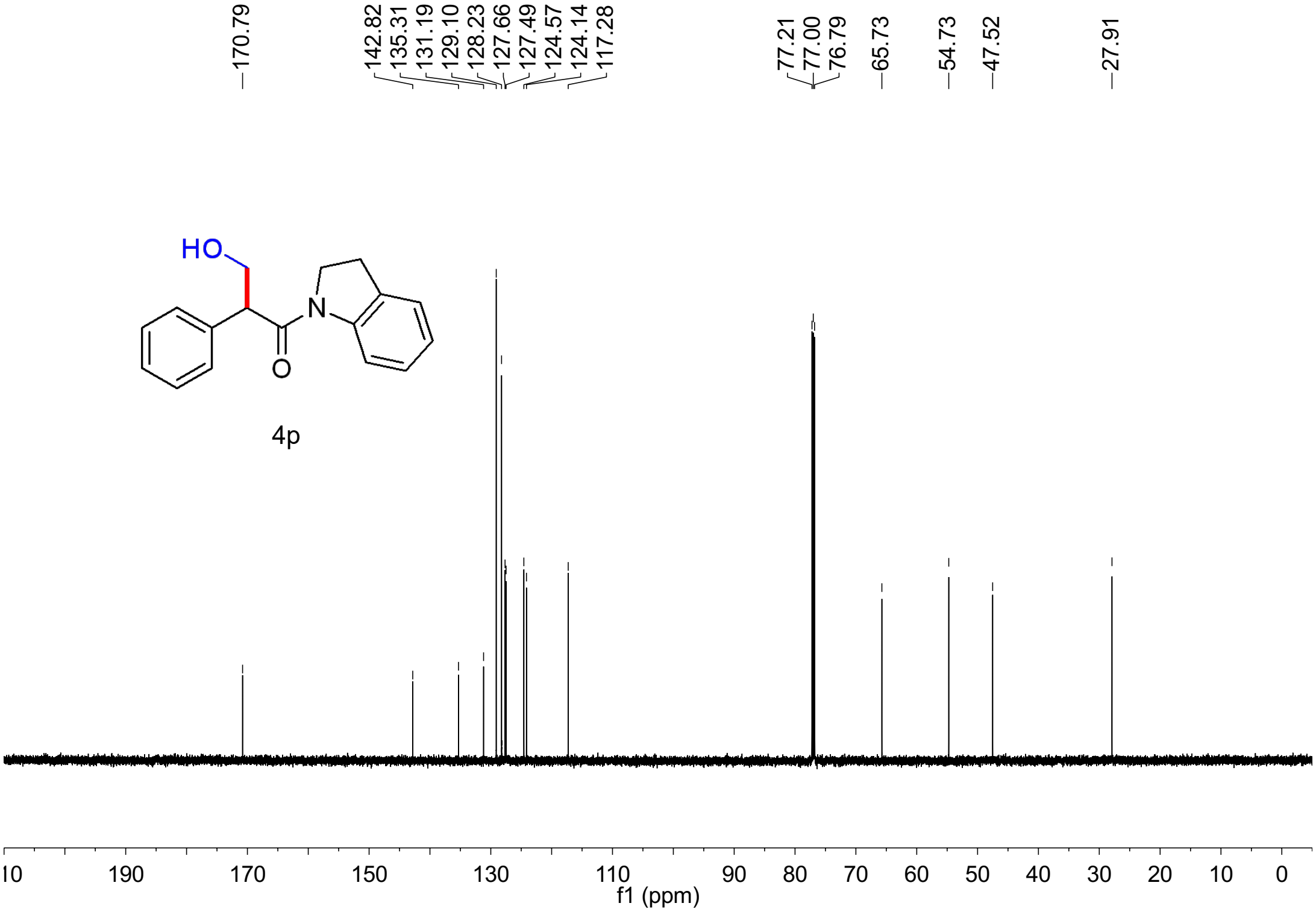
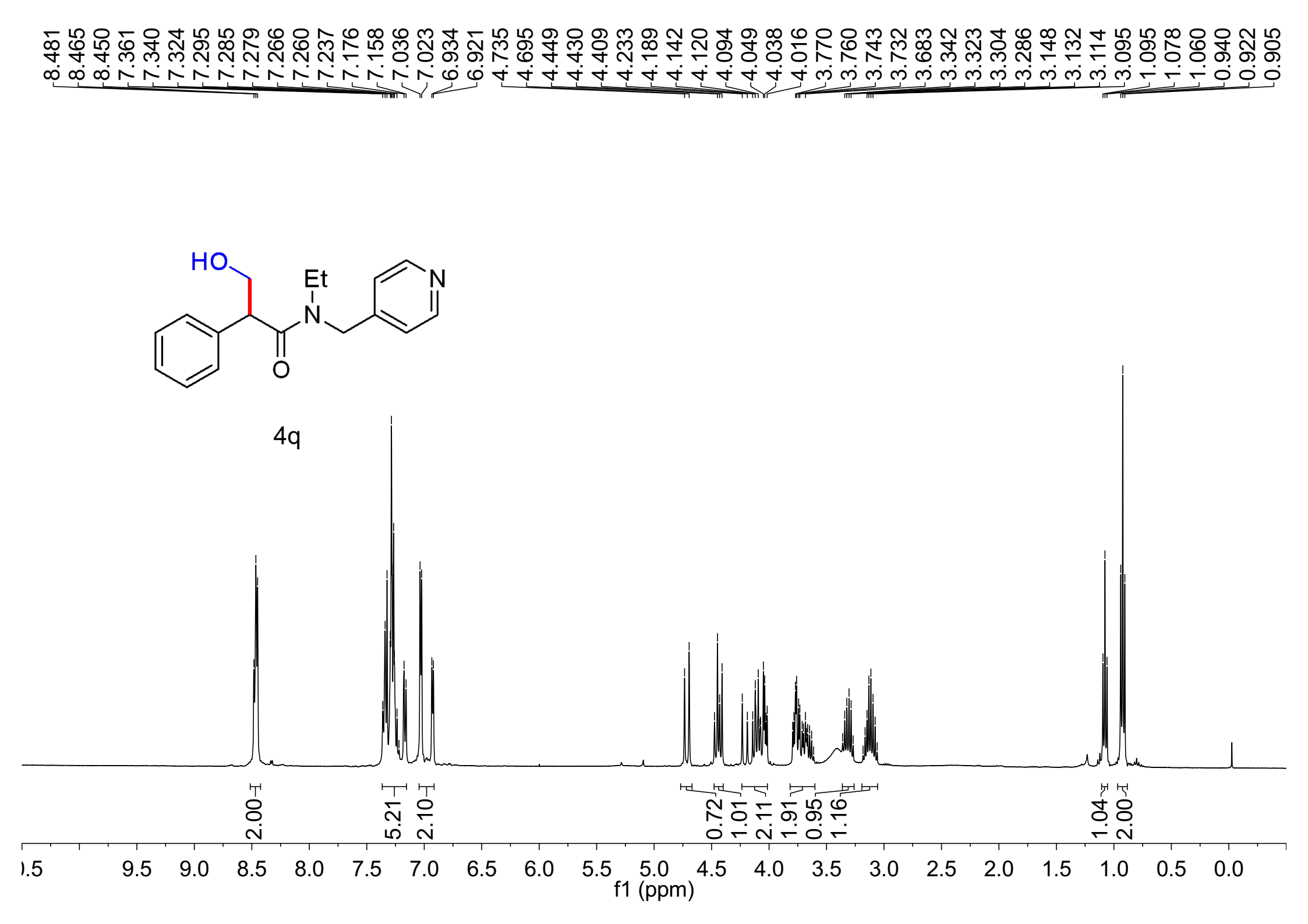
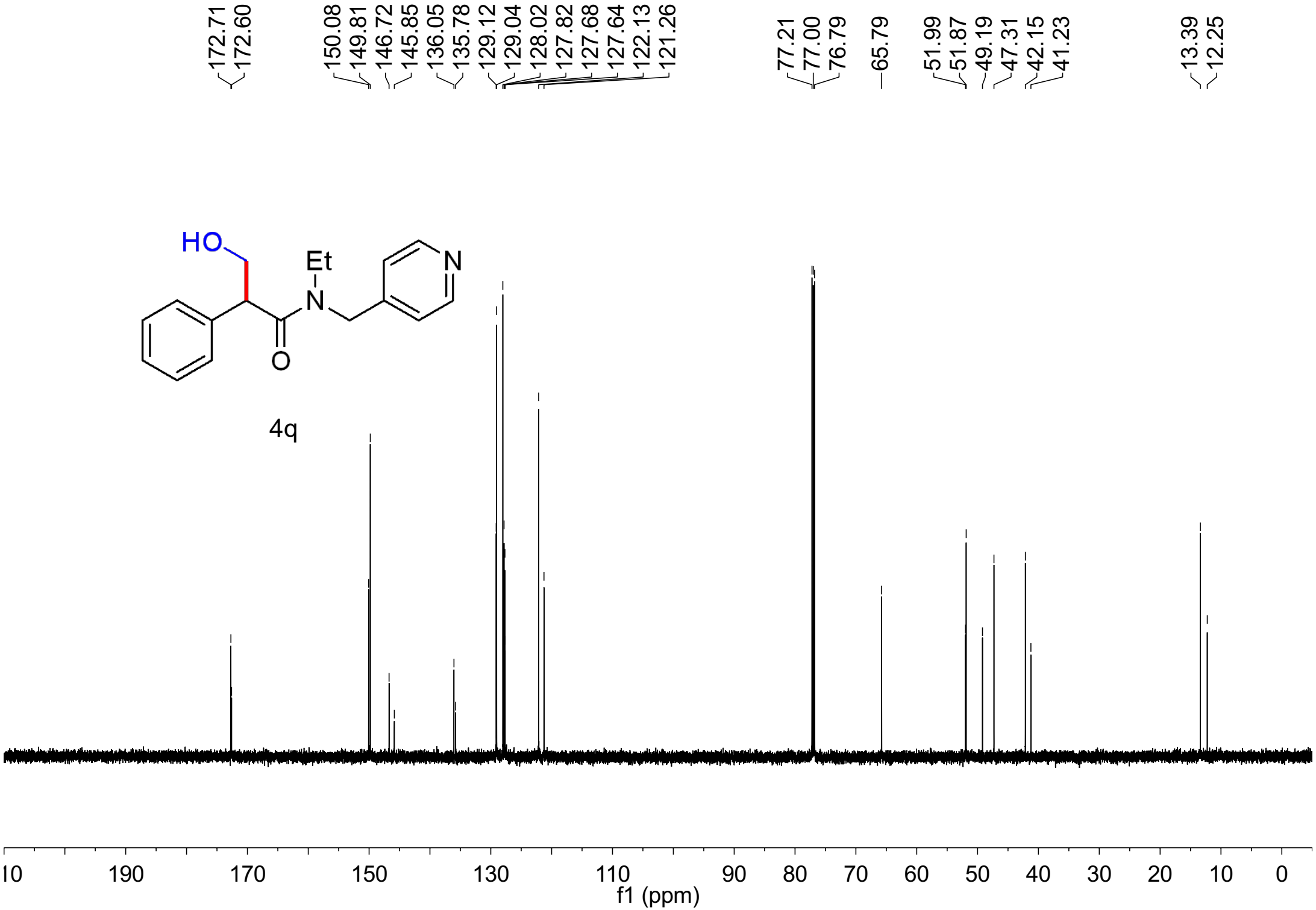
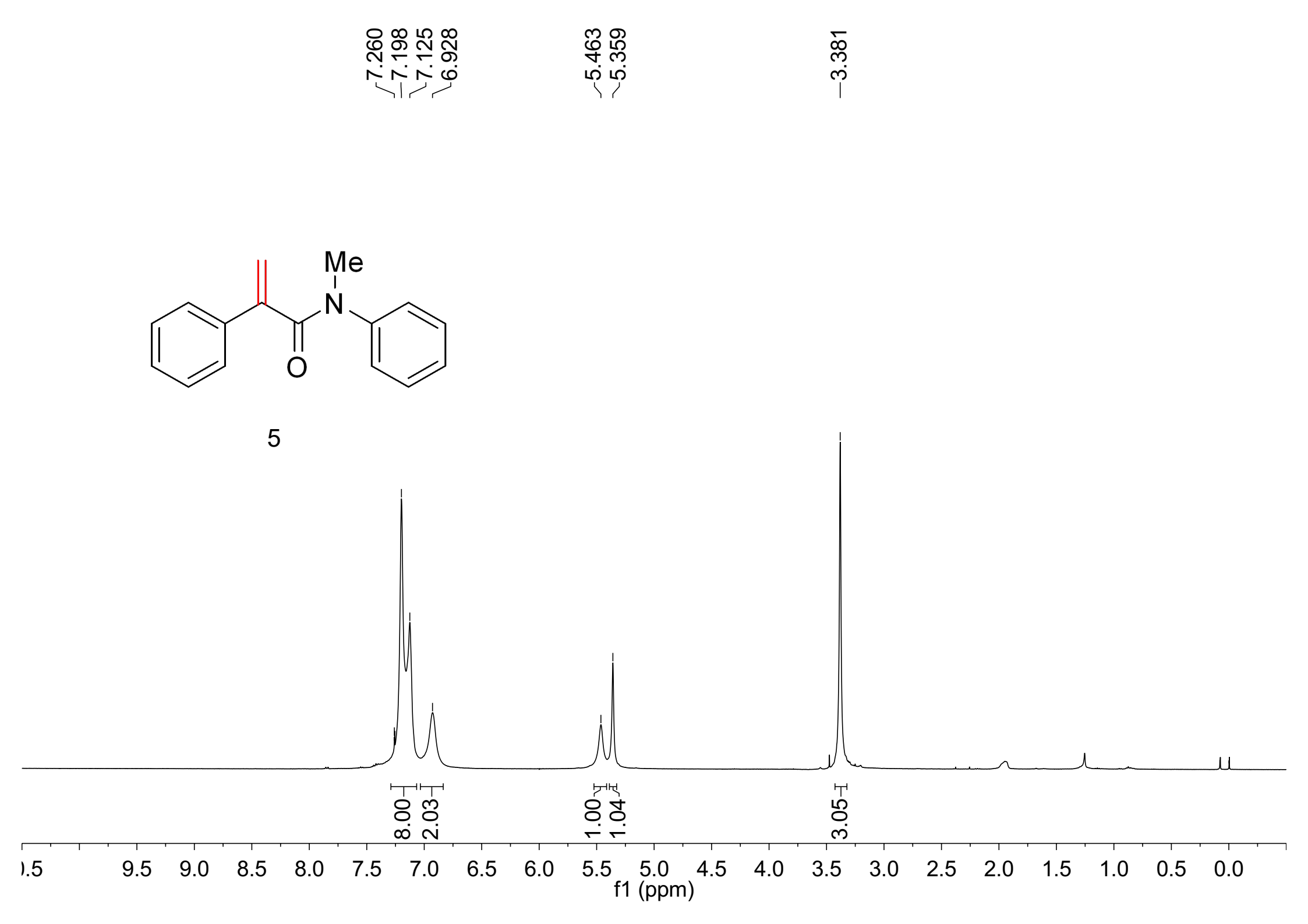
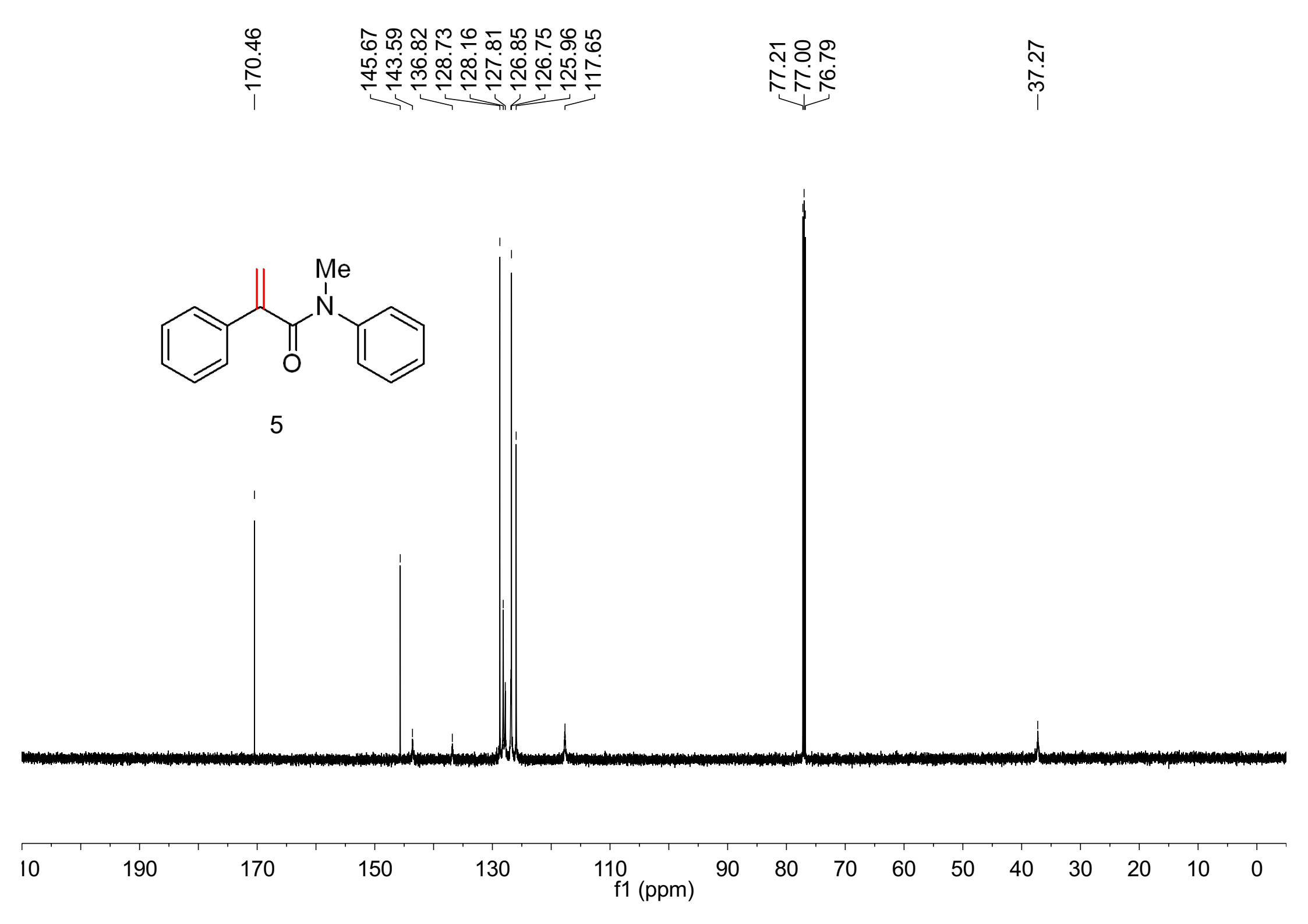
8.320
7.369
7.365
7.350
7.348
7.344
7.330
7.317
7.314
7.305
7.302
7.297
7.285
7.277
7.266
7.264
7.260
7.248
7.229
7.209
7.152
7.133
7.053
7.034
7.016
4.194
4.174
4.078
4.068
4.053
4.043
4.027
4.011
4.000
3.989
3.978
3.824
3.807
3.636
3.627
3.610
3.122
3.109
3.093
3.069
3.004
2.988
2.978
2.963
HO
N
O
4p
0.86
5.01
1.02
0.98
1.00
1.03
2.08
1.02
1.00
2.00
1.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

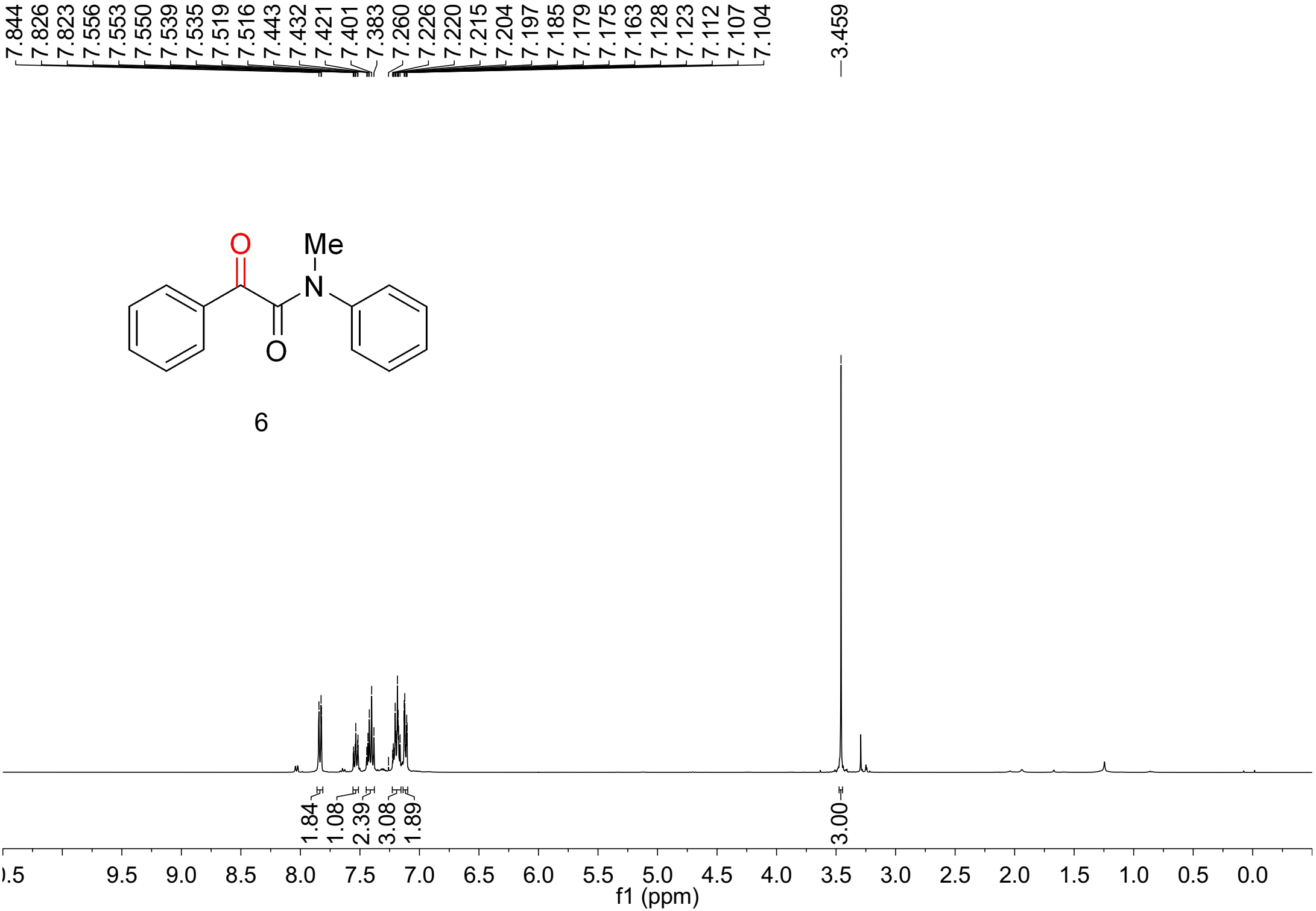

170.79
142.82
135.31
131.19
129.10
128.23
127.66
127.49
124.57
124.14
117.28
77.21
77.00
76.79
65.73
54.73
47.52
27.91
HO
N
O
4p
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

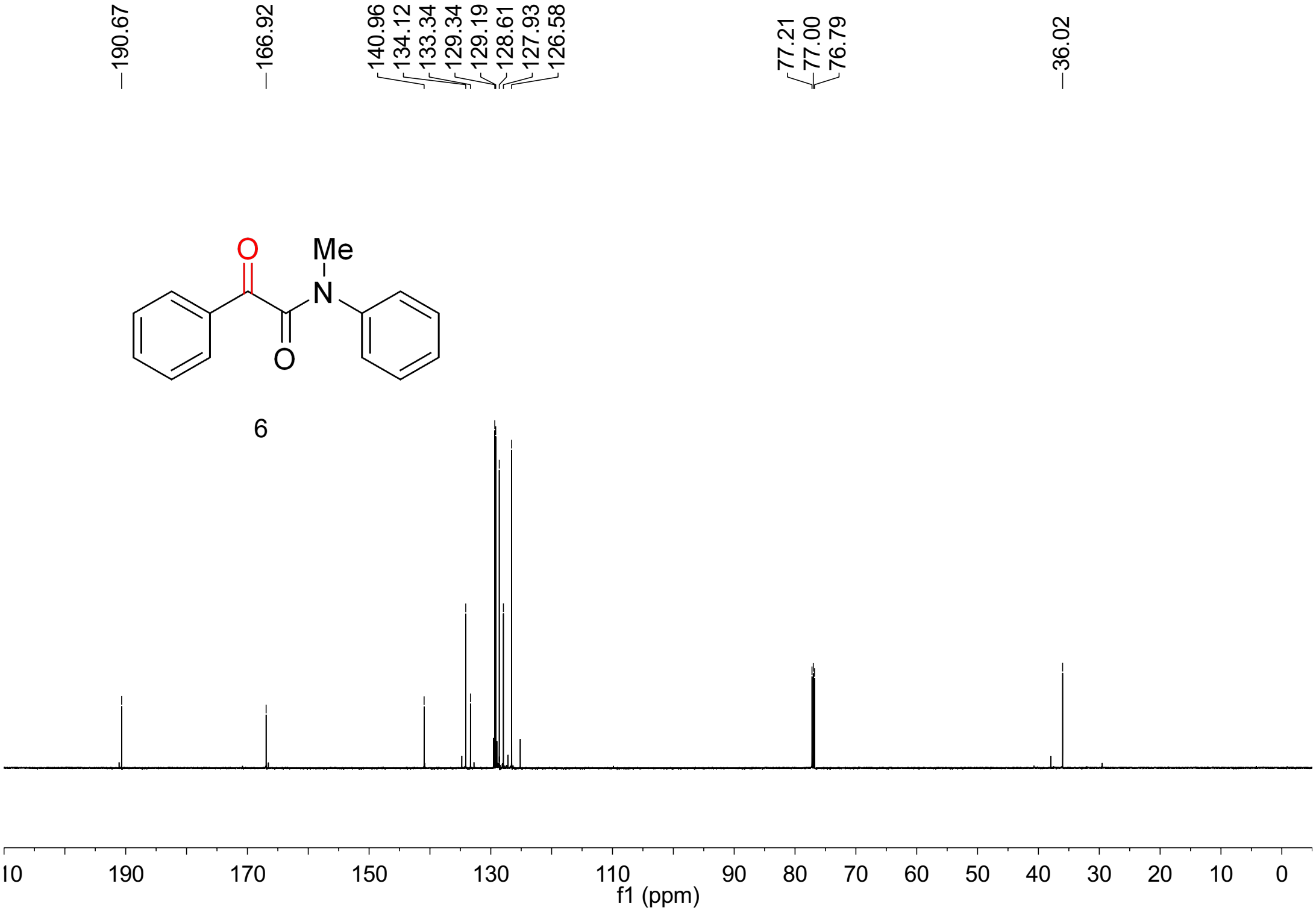

8.481
8.465
8.450
7.361
7.340
7.324
7.295
7.285
7.279
7.266
7.260
7.237
7.176
7.158
7.036
7.023
6.934
6.921
4.735
4.695
4.449
4.430
4.409
4.233
4.189
4.142
4.120
4.094
4.049
4.038
4.016
3.770
3.760
3.743
3.732
3.683
3.342
3.323
3.304
3.286
3.148
3.132
3.114
3.095
1.095
1.078
1.060
0.940
0.922
0.905
HO
Et
N
N
O
4q
2.00
5.21
2.10
0.72
1.01
2.11
1.91
0.95
1.16
1.04
2.00
f1 (ppm)

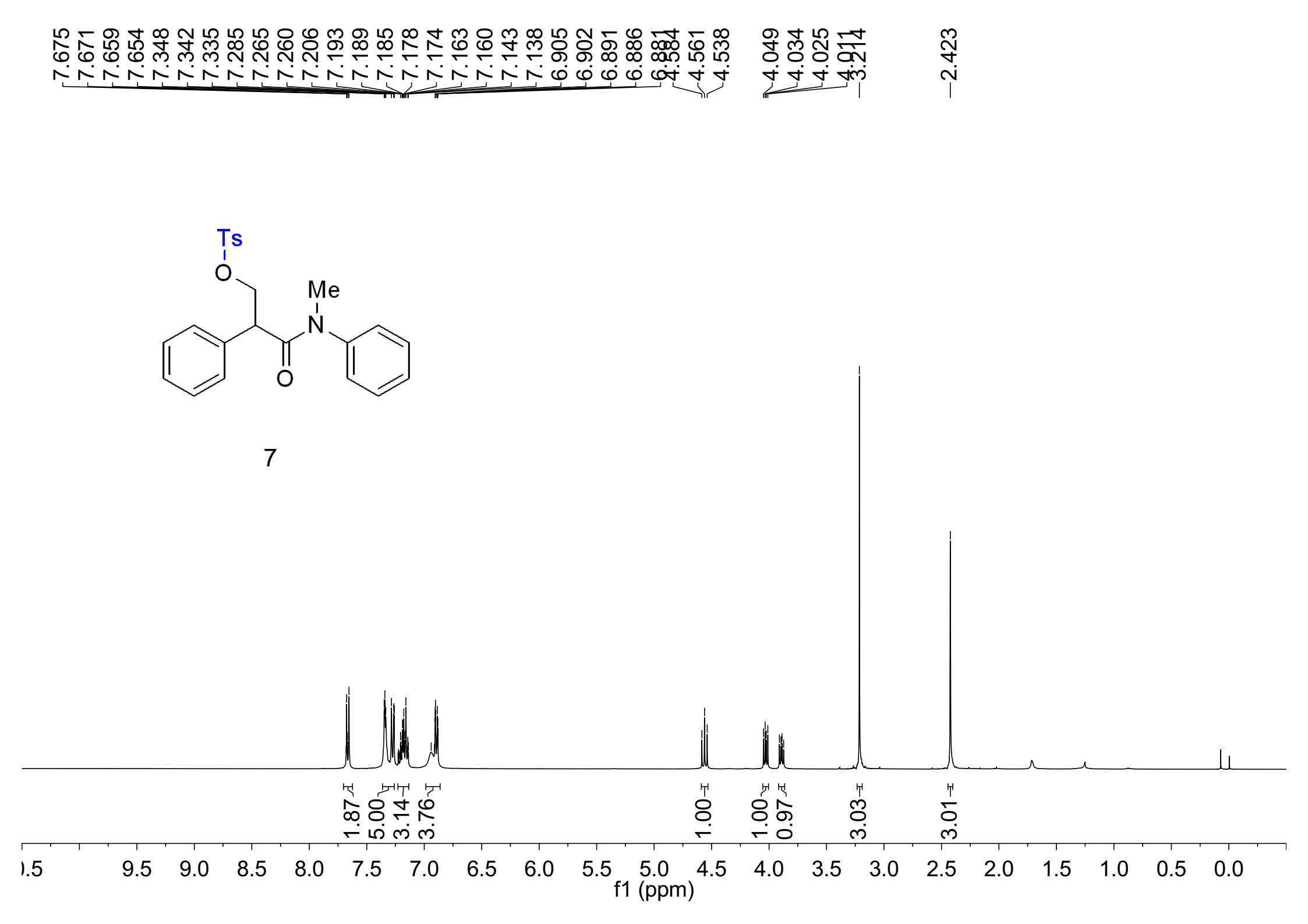

172.71
172.60
150.08
149.81
146.72
145.85
136.05
135.78
129.12
129.04
128.02
127.82
127.68
127.64
122.13
121.26
77.21
77.00
76.79
65.79
51.99
51.87
49.19
47.31
42.15
41.23
13.39
12.25
HO
Et
N
N
O
4q
f1 (ppm)

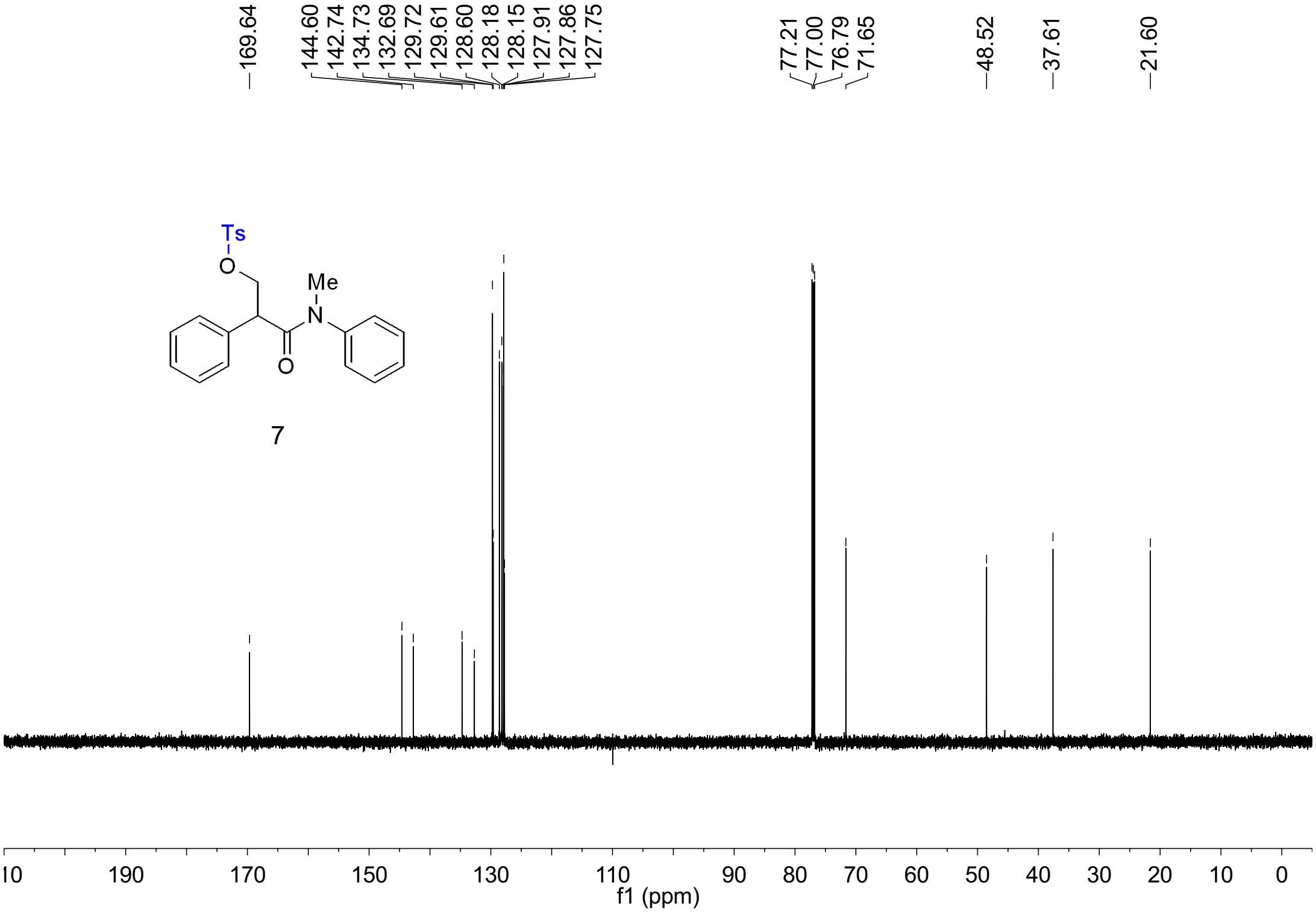

7.260
7.198
7.125
6.928
5.463
5.359
3.381
Me
N
O
5
8.00
2.03
1.00
1.04
3.05
f1 (ppm)

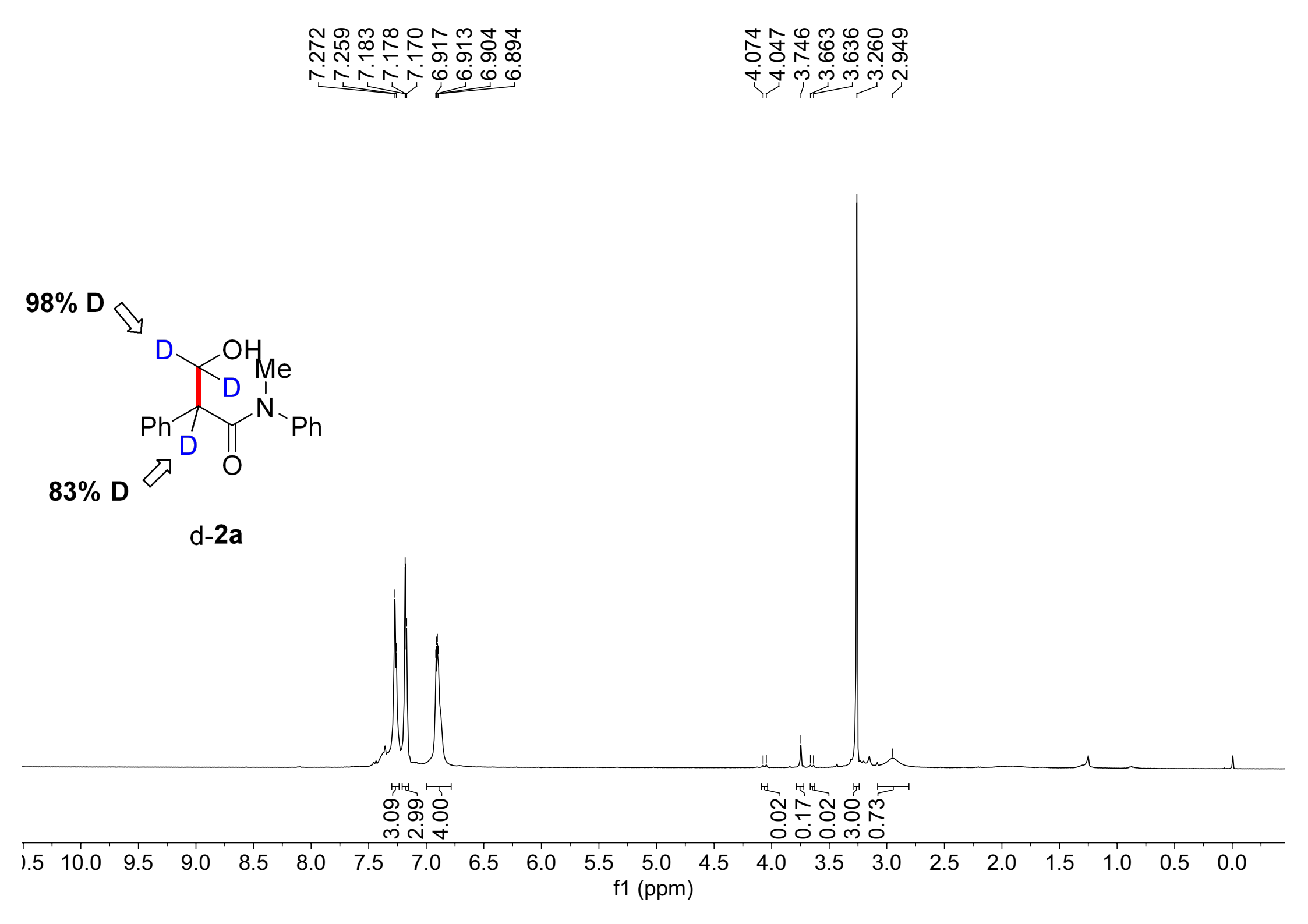

170.46
145.67
143.59
136.82
128.73
128.16
127.81
126.85
126.75
125.96
117.65
77.21
77.00
76.79
37.27
Me
N
O
5
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

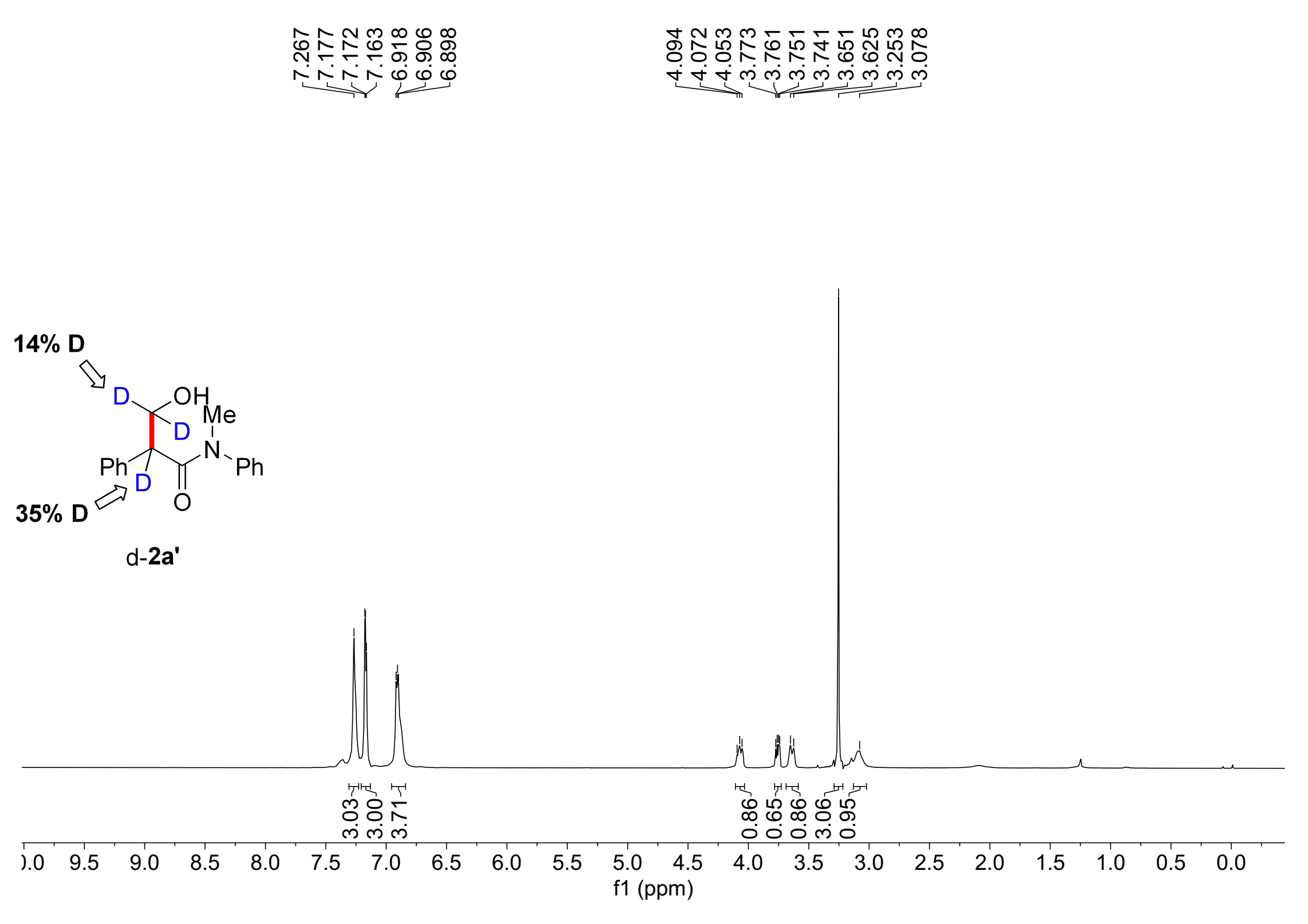

7.844
7.826
7.823
7.556
7.553
7.550
7.539
7.535
7.519
7.516
7.443
7.432
7.421
7.401
7.383
7.260
7.226
7.220
7.215
7.204
7.197
7.185
7.179
7.175
7.163
7.128
7.123
7.112
7.107
7.104
3.459
O
Me
N
O
6
1.84
1.08
2.39
3.08
1.89
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

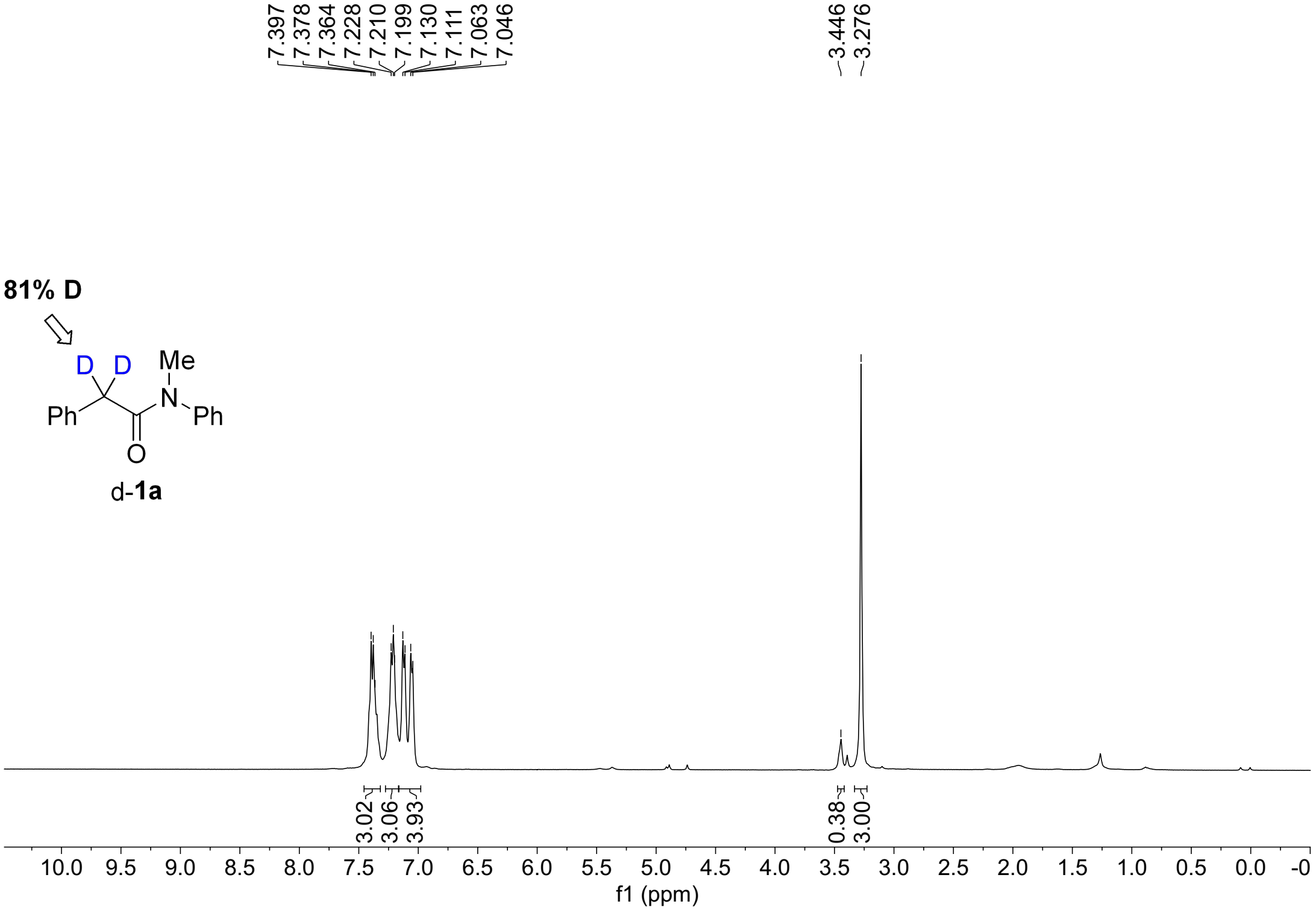

190.67
166.92
140.96
134.12
133.34
129.34
129.19
128.61
127.93
126.58
77.21
77.00
76.79
36.02
O
Me
N
O
6
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.675
7.671
7.659
7.654
7.348
7.342
7.335
7.285
7.265
7.260
7.206
7.193
7.189
7.185
7.178
7.174
7.163
7.160
7.143
7.138
6.905
6.902
6.891
6.886
4.561
4.538
4.049
4.034
4.025
3.214
2.423
Ts
O
Me
N
O
7
1.87
5.00
3.14
3.76
1.00
1.00
0.97
3.03
3.01
f1 (ppm)


169.64
144.60
142.74
134.73
132.69
129.72
129.61
128.60
128.18
128.15
127.91
127.86
127.75
77.21
77.00
76.79
71.65
48.52
37.61
21.60
Ts
O
Me
N
O
7
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.272
7.259
7.183
7.178
7.170
6.917
6.913
6.904
6.894
4.074
4.047
3.746
3.663
3.636
3.260
2.949
98% D
D
OH
Me
D
N
Ph
Ph
D
O
83% D
d-2a
3.09
2.99
4.00
0.02
0.17
0.02
3.00
0.73
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


7.267
7.177
7.172
7.163
6.918
6.906
6.898
4.094
4.072
4.053
3.773
3.761
3.751
3.741
3.651
3.625
3.253
3.078
14% D
D
OH
Me
D
N
Ph
Ph
D
O
35% D
d-2a'
3.03
3.00
3.71
0.86
0.65
0.86
3.06
0.95
f1 (ppm)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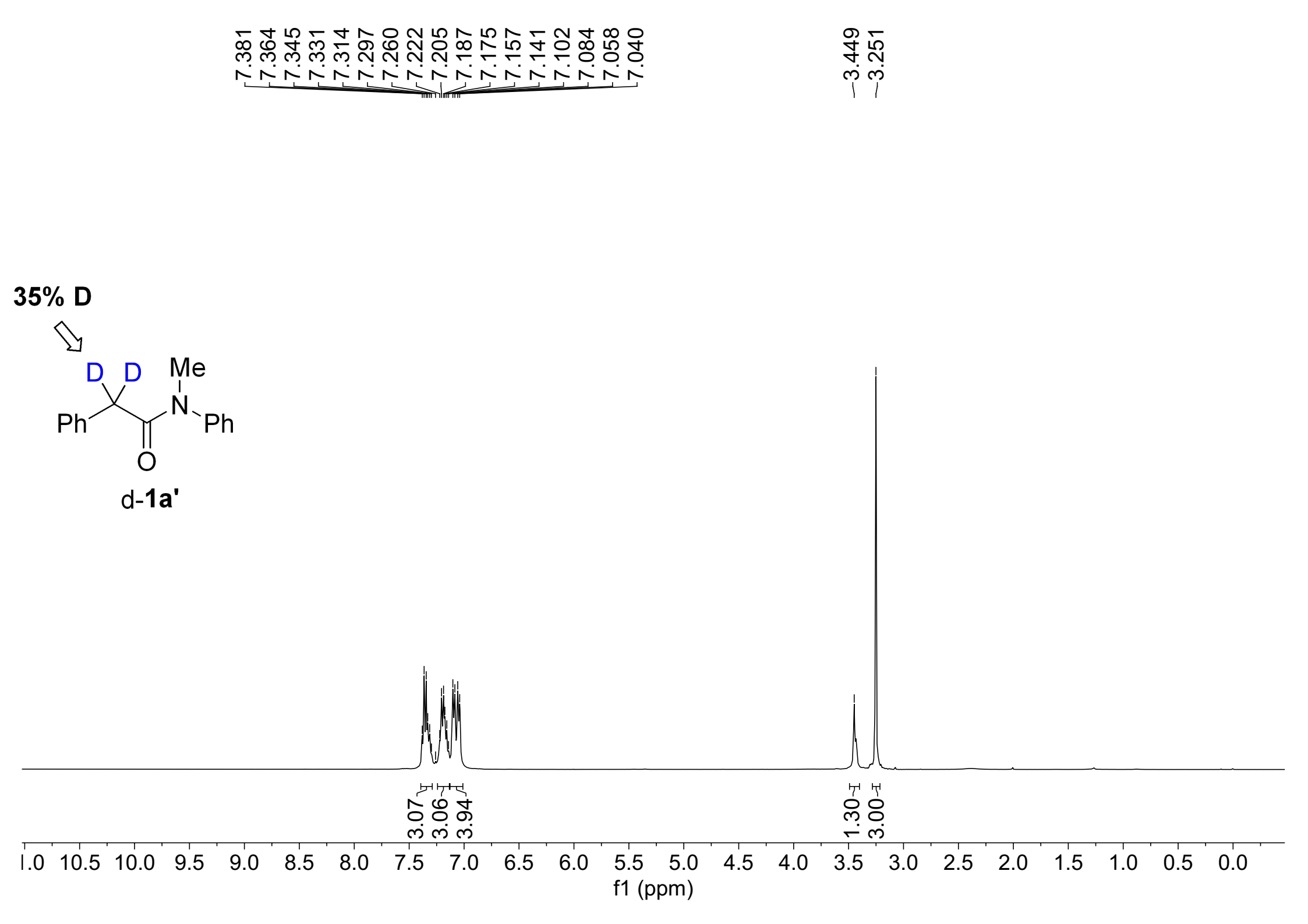
7.378
7.364
7.228
7.210
7.199
7.130
7.111
7.063
7.046
3.446
3.276
81% D
D D
Me
N
Ph
Ph
O
d-1a
3.02
3.06
3.93
0.38
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


7.381
7.364
7.345
7.331
7.314
7.297
7.260
7.222
7.205
7.187
7.175
7.157
7.141
7.102
7.084
7.058
7.040
3.449
3.251
35% D
D D
Me
N
Ph
Ph
O
d-1a'
3.07
3.06
3.94
1.30
3.00
f1 (ppm)