– Supporting Information –

Mechanism of solvolyses of substituted benzyl bromides in 80 % ethanol

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Table of contents

1. Procedures for the synthesis of benzyl bromides

General procedure for the synthesis of 4-methoxybenzyl bromide and 2,4,6-trimethylbenzyl bromide

A similar procedure was previously used for the preparation of benzhydryl bromides.[S1]

The appropriate benzyl alcohol was stirred with acetyl bromide (8-10 equiv) about 30 min. Byproducts and excess of acetyl bromide were evaporated under vacuum to give the substituted benzyl bromide.

4-Methoxybenzyl bromide: from 4-methoxybenzyl alcohol (1.0 g; 7.24 mmol) and acetyl bromide (8.9 g; 72.4 mmol) light yellow oil was obtained; yield 0.75 g, 51.4 %; ^{1}H NMR (300 MHz; $CDCl_3$; 20 °C): δ/ppm = 3.81 (s; 3H; Ar-OCH_3); 4.53 (s; 2H; ArCH_2Br); 6.90 (d; 2H; *J* = 7.4 Hz; ArH); 7.35 (d; 2H; *J* = 7.4 Hz; ArH). ^{13}C NMR (75 MHz; $CDCl_3$; 20 °C): δ/ppm = 34.1 (ArCH_2Br); 55.4 (Ar-OCH_3); 114.2; 130.0; 130.5; 159.7 (Ar).

2,4,6-Trimethylbenzyl bromide: from 2,4,6-tri-methylbenzyl alcohol (0.5 g; 3.33 mmol) and acetyl bromide (3.27 g; 26.6 mmol) white crystals were obtained; yield 0.62 g, 87.3 %; ^{1}H NMR (300 MHz; $CDCl_3$; 20 °C): δ/ppm = 2.36 (s; 3H; Ar-CH_3); 2.46 (s; 6H; Ar-CH_3); 4.64 (s; 2H; ArCH_2Br); 6.94 (s; 2H; ArH). ^{13}C NMR (75 MHz; $CDCl_3$; 20 °C): δ/ppm = 19.2 (Ar-CH_3), 21.1 (Ar-CH_3); 29.7 (ArCH_2Br); 129.3; 131.1; 137.4; 138.5 (Ar).

General procedure for the synthesis of 4-(methylthio)benzyl bromide, 4-phenoxybenzyl bromide, 2-methoxybenzyl bromide, 2,4-dimethylbenzyl bromide, 3,4-dimethylbenzyl bromide, 4-methylbenzyl bromide, 2-methylbenzyl bromide, 4-*tert*-butylbenzyl bromide, 4-phenylbenzyl bromide, 3,5-dimethylbenzyl bromide, benzyl bromide, 3,5-dimethoxy benzyl bromide, 4-nitrobenzyl bromide and 4-(trifluoromethyl)benzyl bromide

A similar procedure was previously used for the preparation of benzhydryl bromides.[S2]

The appropriate benzyl alcohol was dissolved in CH_2Cl_2 (15 ml) and placed in an ice bath. After cooling (10 min), a solution of PBr_3 in CH_2Cl_2 was added dropwise and the reaction mixture was stirred for 1 hours, and then another two hours at room temperature. The organic layer was washed with dilute Na_2CO_3 (3 × 20 ml) and water (3 × 20 ml), and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* to give the substituted benzyl bromide.

4-(Methylthio)benzyl bromide: from 4-(methylthio)benzyl alcohol (0.50 g; 3.24 mmol) and PBr_3 (1.05 g; 3.89 mmol) white crystals were obtained; yield 0.51 g, 72.9 %; ^{1}H NMR (300 MHz; $CDCl_3$; 20 °C): δ/ppm = 2.45 (s; 3H; Ar-SCH_3); 4.45 (s; 2H; ArCH_2Br); 7.19 (d; 2H; *J* = 8,4 Hz; ArH); 7.28 (d; 2H; *J* = 8.5 Hz; ArH). ^{13}C NMR (75 MHz; $CDCl_3$; 20 °C): δ/ppm = 15,6 (Ar-SCH_3); 33,5 (ArCH_2Br); 126,5; 129,5; 134,3; 139,2 (Ar).

4-Phenoxybenzyl bromide: from 4-phenoxybenzyl alcohol (0.30 g; 1.50 mmol) and PBr_3 (0.49 g; 1.80 mmol) yellow oil was obtained; yield 0.39 g, 79.6 %; ^{1}H NMR (300 MHz; $CDCl_3$; 20 °C): δ/ppm = 4.47 (s; 2H; $ArCH_2Br$); 6.94 (d; 2H; *J* = 8.6 Hz; ArH); 7.01 (d; 2H; *J* = 8.9 Hz; ArH); 7.11 (t; 1H; *J* = 7.3 Hz); 7.31–7.35 (m; 4H; ArH). ^{13}C NMR (75 MHz; $CDCl_3$; 20 °C): δ/ppm = 33.4 ($ArCH_2Br$); 118.7; 119.4; 123.8; 129.9; 130.7; 132.4; 156.6; 157.6 (Ar).

2-Methoxybenzyl bromide: from 2-methoxybenzyl alcohol (0.5 g; 3.62 mmol) and PBr_3 (1.18 g; 4.34 mmol) pale yellow oil was obtained; yield 0.31 g, 42.5 %; ^{1}H NMR (300 MHz; $CDCl_3$; 20 °C): δ/ppm = 3.86 (s; 3H; Ar-OCH_3); 4.56 (s; 2H; $ArCH_2Br$); 6.85-6.92 (m; 2H; ArH); 7.25-7.32 (m; 2H; ArH). ^{13}C NMR (75 MHz; $CDCl_3$; 20 °C): δ/ppm = 29.2 ($ArCH_2Br$); 55.6 (Ar-OCH_3); 111.0; 120.7; 126.1; 130.3; 130.9; 157.5 (Ar).

2,4-Dimethylbenzyl bromide: from 2,4-di-methylbenzyl alcohol (0.5 g; 3.67 mmol) and PBr_3 (1.19 g; 4.40 mmol) pale yellow oil was obtained; yield 0.54 g, 74.0 %; ^{1}H NMR (300 MHz; $CDCl_3$; 20 °C): δ/ppm = 2.29 (s; 3H; Ar-CH_3); 2.35 (s; 3H; Ar-CH_3); 4.47 (s; 2H; $ArCH_2Br$); 6.95-6.98 (m; 2H; ArH); 7.16 (d; 1H; *J* = 7.7 Hz; ArH). ^{13}C NMR (75 MHz; $CDCl_3$; 20 °C): δ/ppm = 18.7 (Ar-CH_3), 21.2 (Ar-CH_3); 32.7 ($ArCH_2Br$); 127.1; 130.0; 131.7; 132.8; 137.1; 139.0 (Ar).

3,4-Dimethylbenzyl bromide: from 3,4-dimethylbenzyl alcohol (0.25 g; 1.84 mmol) and PBr_3 (0.60 g; 2.21 mmol) pale yellow oil was obtained; yield 0.26 g, 70.3 %; ^{1}H NMR (300 MHz; $CDCl_3$; 20 °C): δ/ppm = 2.24 (s; 6H; Ar-CH_3); 4.45 (s; 2H; $ArCH_2Br$); 7.07-7.15 (m; 3H; ArH). ^{13}C NMR (75 MHz; $CDCl_3$; 20 °C): δ/ppm = 19.6 (Ar-CH_3); 19.8 (Ar-CH_3); 34.0 ($ArCH_2Br$); 126.5; 130.1; 130.3; 135.3; 137.1; 137.2 (Ar).

4-Methylbenzyl bromide: from 4-methylbenzyl alcohol (0.50 g; 4.09 mmol) and PBr_3 (1.33 g; 4.91 mmol) white crystals were obtained; yield 0.49 g, 64.5 %; ^{1}H NMR (300 MHz; $CDCl_3$; 20 °C): δ/ppm = 2.43 (s; 3H; Ar-CH_3); 4.55 (s; 2H; $ArCH_2Br$); 7.22 (d; 2H; *J* = 8.1 Hz; ArH); 7.36 (d; 2H; *J* = 8.1 Hz; ArH). ^{13}C NMR (75 MHz; $CDCl_3$; 20 °C): δ/ppm = 21.3 (Ar-CH_3); 33.8 ($ArCH_2Br$); 129.0; 129.5; 135.6; 140.1 (Ar).

2-Methylbenzyl bromide: from 2-methylbenzyl alcohol (0.5 g; 4.09 mmol) and PBr_3 (1.33 g; 4.91 mmol) pale yellow oil was obtained; yield 0.50 g, 65.8 %; ^{1}H NMR (300 MHz; $CDCl_3$; 20 °C): δ/ppm = 2.40 (s; 3H; Ar-CH_3); 4.49 (s; 2H; $ArCH_2Br$); 7.13-7.22 (m; 2H; ArH); 7.28 (d; 1H; *J* = 7.8 Hz; ArH). ^{13}C NMR (75 MHz; $CDCl_3$; 20 °C): δ/ppm = 18.8 (Ar-CH_3), 32.4 ($ArCH_2Br$); 126.4; 129.0; 130.0; 130.8; 135.8; 137.3 (Ar).

4-tert-Butylbenzyl bromide: from 4-*tert*-butylbenzyl alcohol (0.50 g; 3.04 mmol) and PBr_3 (0.99 g; 3.65 mmol) colorless oil was obtained; yield 0.35 g, 50.7 %; ^{1}H NMR (300 MHz; $CDCl_3$; 20 °C): δ/ppm = 1.39 (s; 9H; Ar-$(CH_3)_3$); 4.55 (s; 2H; $ArCH_2Br$); 7.39 (d; 2H; *J* = 8.5

Hz; ArH); 7.34 (d; 2H; *J* = 8.3 Hz; ArH). ^{13}C NMR (75 MHz; $CDCl_3$; 20 °C): δ/ppm = 31.3 (Ar-C($\underline{C}H_3$)); 33.7 ($ArCH_2Cl$); 34.7 (Ar-$\underline{C}(CH_3)$); 125.8; 128.8; 134.8; 151.6 (Ar).

4-Phenylbenzyl bromide: from 4-phenylbenzyl alcohol (0.50 g; 2.71 mmol) and and PBr_3 (0.88 g; 3.25 mmol) white crystals were obtained; yield 0.51 g, 76.1 %; ^{1}H NMR (300 MHz; $CDCl_3$; 20 °C): δ/ppm = 4.51 (s; 2H; $ArCH_2Br$); 7.31–7.44 (m; 5H; ArH); 7.53–7.57 (m; 4H; ArH). ^{13}C NMR (75 MHz; $CDCl_3$; 20 °C): δ/ppm = 33.5 ($ArCH_2Br$); 127.1; 127.6; 127.6; 128.9; 129.5; 136.8; 140.4; 141.4 (Ar).

3,5-dimethylbenzyl bromide: from 3,5-dimethylbenzyl alcohol (0.5 g; 3.67 mmol) and PBr_3 (1.19 g; 4.40 mmol) white crystals were obtained; yield 0.45 g, 61.6 %; ^{1}H NMR (300 MHz; $CDCl_3$; 20 °C): δ/ppm = 2.35 (s; 6H; Ar-CH_3); 4.47 (s; 2H; $ArCH_2Br$); 6.97-7.05 (m; 3H; ArH). ^{13}C NMR (75 MHz; $CDCl_3$; 20 °C): δ/ppm = 21.2 (Ar-CH_3); 33.9 ($ArCH_2Br$); 126.9; 130.2; 137.6; 138.4 (Ar).

Benzyl bromide: from benzyl alcohol (0.50 g; 4.62 mmol) and PBr_3 (1.50 g; 5.54 mmol) pale yellow oil was obtained; yield 0.32 g, 40.5 %; ^{1}H NMR (300 MHz; $CDCl_3$; 20 °C): δ/ppm = 4.47 (s; 2H; $ArCH_2Br$); 7.26-7.38 (m; 5H; ArH). ^{13}C NMR (75 MHz; $CDCl_3$; 20 °C): δ/ppm = 33.6 ($ArCH_2Br$); 128.4; 128.8; 129.1; 137.8.

3,5-dimethoxybenzyl bromide: from 3,5-dimethylbenzyl alcohol (0.5 g; 2.97 mmol) and PBr_3 (0.96 g; 3.56 mmol) white crystals were obtained; yield 0.39 g, 56.5 %; ^{1}H NMR (300 MHz; $CDCl_3$; 20 °C): δ/ppm = 3.79 (s; 6H; Ar-OCH_3); 4.42 (s; 2H; $ArCH_2Br$); 6.40 (s; 1H; Ar); 6.54-6.56 (m; 2H; ArH). ^{13}C NMR (75 MHz; $CDCl_3$; 20 °C): δ/ppm = 33.6 ($ArCH_2Br$); 55.4 (Ar-OCH_3); 100.6; 106.9; 139.7; 160.9 (Ar).

4-nitrobenzyl bromide: from 4-nitrobenzyl alcohol (0.50 g; 3.27 mmol) and PBr_3 (1.06 g; 3.92 mmol) white crystals were obtained; yield 0.32 g, 45.1 %; ^{1}H NMR (300 MHz; $CDCl_3$; 20 °C): δ/ppm = 4.53 (s; 2H; $ArCH_2Br$); 7.57 (d; 2H; *J* = 8.7 Hz; ArH); 8.20 (d; 2H; *J* = 8.8 Hz; ArH). ^{13}C NMR (75 MHz; $CDCl_3$; 20 °C): δ/ppm = 31.0 ($ArCH_2Br$); 124.0; 129.9; 144.8; 147.6.

4-(trifluoromethyl)benzyl bromide: from benzyl alcohol (0.50 g; 2.84 mmol) and PBr_3 (0.92 g; 3.41 mmol) white crystals were obtained; yield 0.27 g, 39.8 %; ^{1}H NMR (300 MHz; $CDCl_3$; 20 °C): δ/ppm = 4.48 (s; 2H; Ar$\underline{C}H_2$Br); 7.50 (d; 2H; *J* = 8.2 Hz; ArH); 7.60 (d; 2H; *J* = 8.4 Hz; ArH). ^{13}C NMR (75 MHz; $CDCl_3$; 20 °C): δ/ppm = 31.8 ($ArCH_2Br$); 123.9 (d; *J* = 272.5 Hz; F_3C-Ar); 125.6 (q; *J* = 3.8 Hz; F_3C-Ar); 129.4; 130.5 (d; *J* = 32.6 Hz; F_3C-Ar); 141.6. ^{19}F NMR (282 MHz; $CDCl_3$; 20 °C): δ/ppm = −62.7.

2. Tables

Table S1. Rate constants for solvolyses of X-substituted benzyl bromides in 80 % ethanol (v/v) at 25 °C

No.	X	k / s^{-1} [a]
1Br	4-OMe	$(1.06 \pm 0.03) \times 10^{-2}$
2Br	4-SMe	$(6.15 \pm 0.02) \times 10^{-4}$
3Br	4-OPh	$(1.32 \pm 0.01) \times 10^{-4}$
4Br	2,4,6-tri-Me	$(4.07 \pm 0.03) \times 10^{-4}$
5Br	2-OMe	$(8.76 \pm 0.02) \times 10^{-5}$
6Br	2,4-di-Me	$(7.91 \pm 0.04) \times 10^{-5}$
7Br	2-Me	1.51×10^{-5} [b]
8Br	3,4-di-Me	2.43×10^{-5} [b]
9Br	4-Me	1.75×10^{-5} [b]
10Br	4-*tert*-But	1.29×10^{-5} [b]
11Br	4-Ph	8.84×10^{-6} [b]
12Br	3,5-di-Me	7.18×10^{-6} [b]
13Br	H	3.94×10^{-6} [b]
14Br	3,5-di-OMe	2.05×10^{-6} [b]
15Br	4-CF_3	5.34×10^{-7} [b]
16Br	4-NO_2	3.53×10^{-7} [b]

[a] Errors shown are standard deviations.

[b] Extrapolated from data at higher temperatures (Table S2).

Table S2. Rate constants for solvolyses of X-substituted benzyl bromides in 80 % ethanol (v/v) at higher temperatures and corresponding activation parameters

No.	X	*t*/°C	k/s^{-1}	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}
7Br	2-Me	70	$(1.03 \pm 0.02) \times 10^{-3}$		
		60	$(4.43 \pm 0.01) \times 10^{-4}$	77.1	−78.5
		50	$(1.82 \pm 0.02) \times 10^{-4}$		
8Br	3,4-di-Me	70	$(1.76 \pm 0.01) \times 10^{-3}$		
		60	$(7.54 \pm 0.03) \times 10^{-4}$	78.3	−70.5
		50	$(3.03 \pm 0.05) \times 10^{-4}$		
9Br	4-Me	70	$(1.19 \pm 0.01) \times 10^{-3}$		
		60	$(5.17 \pm 0.03) \times 10^{-4}$	72.2	−77.1
		50	$(2.10 \pm 0.01) \times 10^{-4}$		
10Br	4-*tert*-But	70	$(9.10 \pm 0.02) \times 10^{-4}$		
		60	$(3.98 \pm 0.03) \times 10^{-4}$	78.0	−77.0
		50	$(1.58 \pm 0.04) \times 10^{-4}$		
11Br	4-Ph	70	$(6.21 \pm 0.06) \times 10^{-4}$		
		60	$(2.73 \pm 0.02) \times 10^{-4}$	77.9	−80.4
		50	$(1.08 \pm 0.01) \times 10^{-4}$		
12Br	3,5-di-Me	70	$(5.02 \pm 0.10) \times 10^{-4}$		
		60	$(2.18 \pm 0.02) \times 10^{-4}$	77.7	−82.7
		50	$(8.76 \pm 0.10) \times 10^{-5}$		
13Br	H	70	$(2.95 \pm 0.02) \times 10^{-4}$		
		60	$(1.26 \pm 0.02) \times 10^{-4}$	79.0	−83.5
		50	$(5.01 \pm 0.02) \times 10^{-5}$		
14Br	3,5-di-OMe	70	$(1.84 \pm 0.04) \times 10^{-4}$		
		60	$(7.57 \pm 0.10) \times 10^{-5}$	82.4	−77.4
		50	$(2.90 \pm 0.03) \times 10^{-5}$		
15Br	4-CF_3	70	$(5.35 \pm 0.04) \times 10^{-5}$		
		60	$(2.15 \pm 0.03) \times 10^{-5}$	84.5	−81.7
		50	$(1.32 \pm 0.02) \times 10^{-5}$		
16Br	4-NO_2	70	$(3.59 \pm 0.05) \times 10^{-5}$		
		60	$(1.42 \pm 0.03) \times 10^{-5}$	84.7	−84.3
		50	$(8.85 \pm 0.20) \times 10^{-6}$		

Table S3. Calculated relative stabilities of X-benzyl carbocations

No.	X	$G°$ [calc] / kcal mol^{-1} [a]
1$^+$	4-OMe	−11.89 [b]
2$^+$	4-SMe	−10.59 [b]
3$^+$	4-OPh	−9.99 [b]
4$^+$	2,4,6-tri-Me	−9.47 [b]
5$^+$	2-OMe	−8.18 [b]
6$^+$	2,4-di-Me	−7.04 [b]
7$^+$	2-Me	−2.46 [b]
8$^+$	3,4-di-Me	−5.68 [b]
9$^+$	4-Me	−5.00 [b]
10$^+$	4-*tert*-But	−4.43 [b]
11$^+$	4-Ph	−4.10 [b]
12$^+$	3,5-di-Me	−2.51 [b]
13$^+$	H	0.00 [b]
14$^+$	3,5-di-OMe	0.79
15$^+$	4-CF_3	7.14
16$^+$	4-NO_2	11.13

[a] Relative stabilities of X-benzyl carbocations were determined as the standard free energies for the isodesmic reactions shown in Scheme 2. Free energies of benzyl chlorides (**1Cl**–**16Cl**) and corresponding carbocations (**1**$^+$–**16**$^+$) were calculated at the IEFPCM-M06-2X/6-311+G(3df,3pd) level of theory.

[b] Taken from reference [S3].

Table S4. Total energies (E_{tot}), zero-point corrected total energies [E (ZPVE)], enthalpies [H (298)] and free energies [G (298) and G^Q (298)] of conformers of benzyl chlorides (**14Cl**–**16Cl**) and corresponding benzyl cations (**14**$^+$–**16**$^+$) calculated at the M062X/6-311+G(3df,3pd) level of theory with the IEFPCM solvation model for water along with statistical weights of the conformers according to the Boltzmann distribution (χ_i) and averaged free energies [$\langle G_{298}\rangle$ and $\langle G^Q_{298}\rangle$] at 25 °C

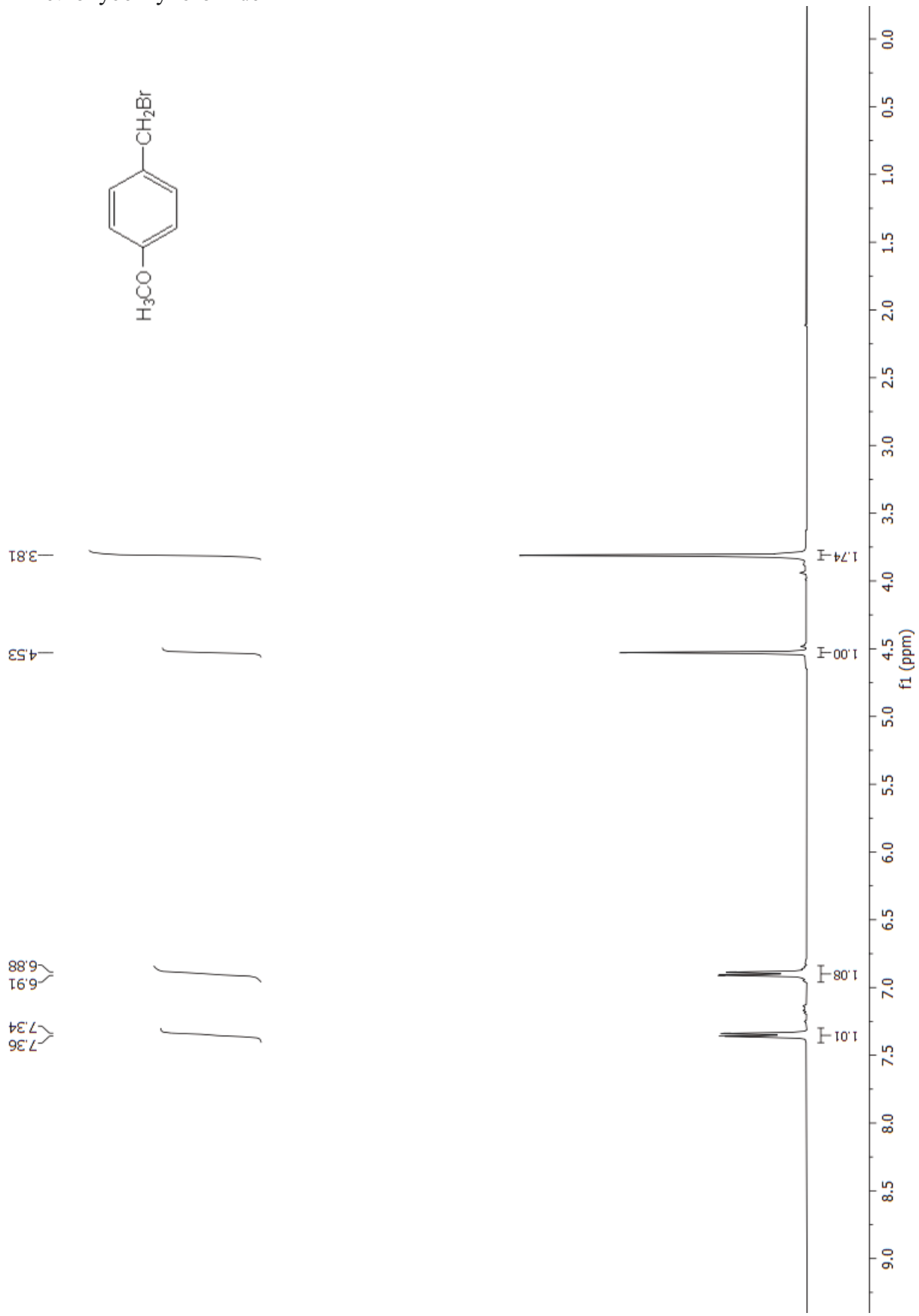
Conformer	E_{tot} [a]	E (ZPVE) [a]	H (298) [a]	G (298) [a]	weight (χ_i)	G^Q (298) [a,b]	weight^Q (χ_i^Q) [c]	$\langle G_{298}\rangle$ [a] $\langle G^Q_{298}\rangle$ [a,c]
3,5-Dimethoxybenzyl chloride (**14Cl**)								
1	-960.1847549	-959.998248	-959.985456	-960.037477	0.3029	-960.035951	0.3161	-960.037317 -960.035765 [c]
2	-960.1847549	-959.998248	-959.985456	-960.037477	0.3029	-960.035951	0.3161	
3	-960.1842110	-959.997777	-959.984949	-960.037087	0.2004	-960.035535	0.2035	
4	-960.1840940	-959.997681	-959.984836	-960.037056	0.1939	-960.035333	0.1643	
3,5-Dimethoxybenzyl cation (**14**$^+$)								
1	-499.7327456	-499.549335	-499.537705	-499.585520	0.8570	-499.584990	0.7999	-499.585229 -499.584667 [c]
2	-499.7314026	-499.547860	-499.536325	-499.583711	0.1262	-499.583583	0.1802	
3	-499.728984	-499.545775	-499.534155	-499.581808	0.0168	-499.581501	0.0199	
4-(Trifluoromethyl)benzyl chloride (**15Cl**)								
1	-1068.2100418	-1068.084631	-1068.073252	-1068.124046	0.3049	-1068.120776	0.3108	-1068.124135 -1068.120843 [c]
2	-1068.2100378	-1068.084726	-1068.073321	-1068.124258	0.3817	-1068.120884	0.3484	
3	-1068.2100335	-1068.074256	-1068.073312	-1068.124072	0.3134	-1068.120863	0.3408	
4-(Trifluoromethyl)benzyl cation (**15**$^+$)								
1	-607.7478453	-607.625571	-607.615445	-607.661425	0.4089	-607.659702	0.5399	-607.661631 -607.659633 [c]
2	-607.7478438	-607.625468	-607.615349	-607.661773	0.5911	-607.659551	0.4601	
4-Nitrobenzyl chloride (**16Cl**)								

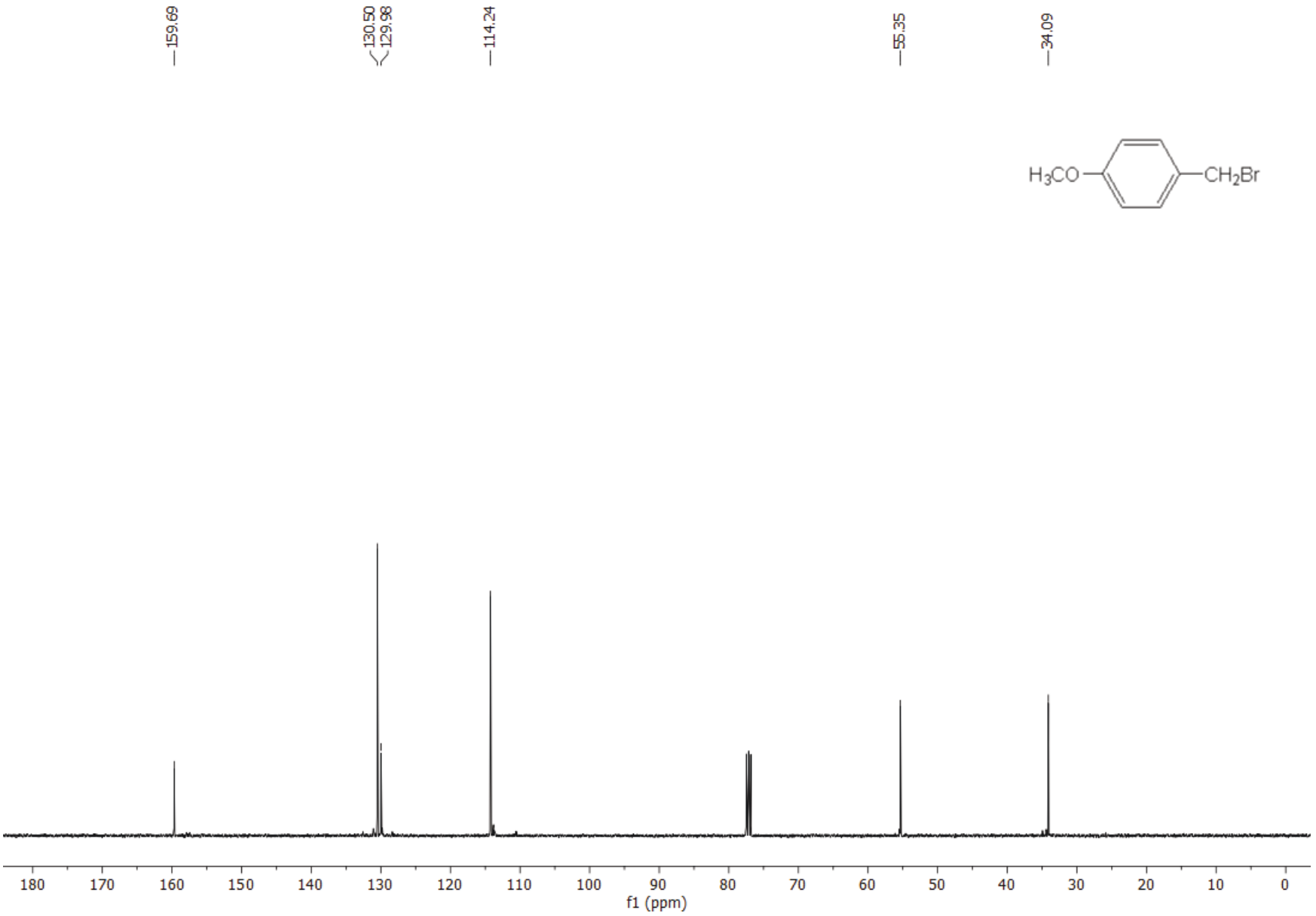
Conformer	E_{tot} [a]	E (ZPVE) [a]	H (298) [a]	G (298) [a]	weight (χ_i)	G^Q (298) [a,b]	weight^Q (χ_i^Q) [c]	$\langle G_{298} \rangle$ [a] $\langle G^Q_{298} \rangle$ [a,c]
1	-935.6449768	-935.521561	-935.511234	-935.558990	1.0000	-935.556538	1.0000	-935.558990 -935.556538 [c]
4-Nitrobenzyl cation (**16**$^+$)								
1	-475.1761047	-475.056092	-475.046988	-475.090475	1.0000	-475.088957	1.0000	-475.090475 -475.088957 [c]

[a] in Hartrees. [b] Free energy with quasiharmonic correction. [c] Obtained from free energies with quasiharmonic correction, G^Q (298).

3. NMR spectra of substituted benzyl bromides

4-Methoxybenzyl bromide

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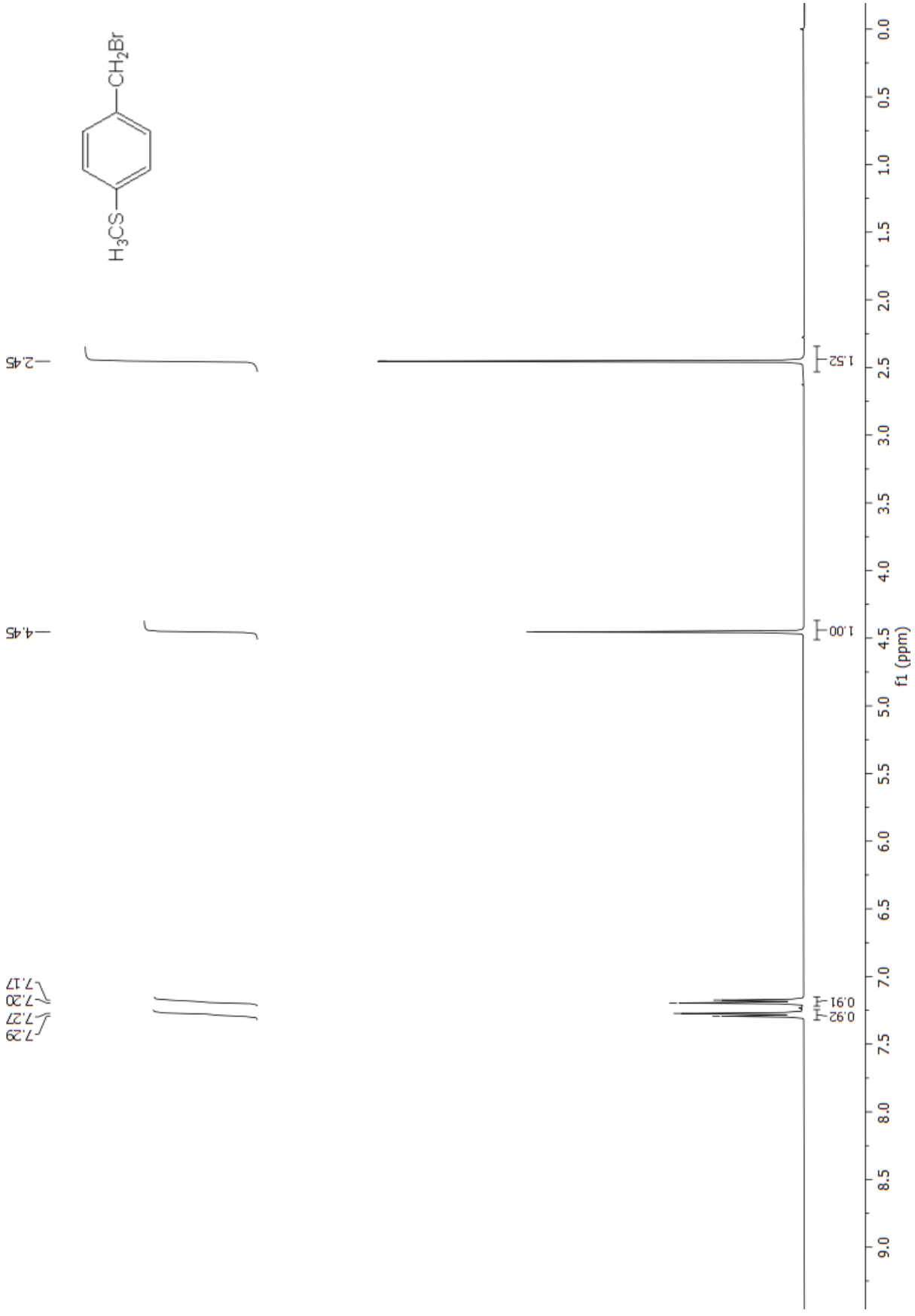
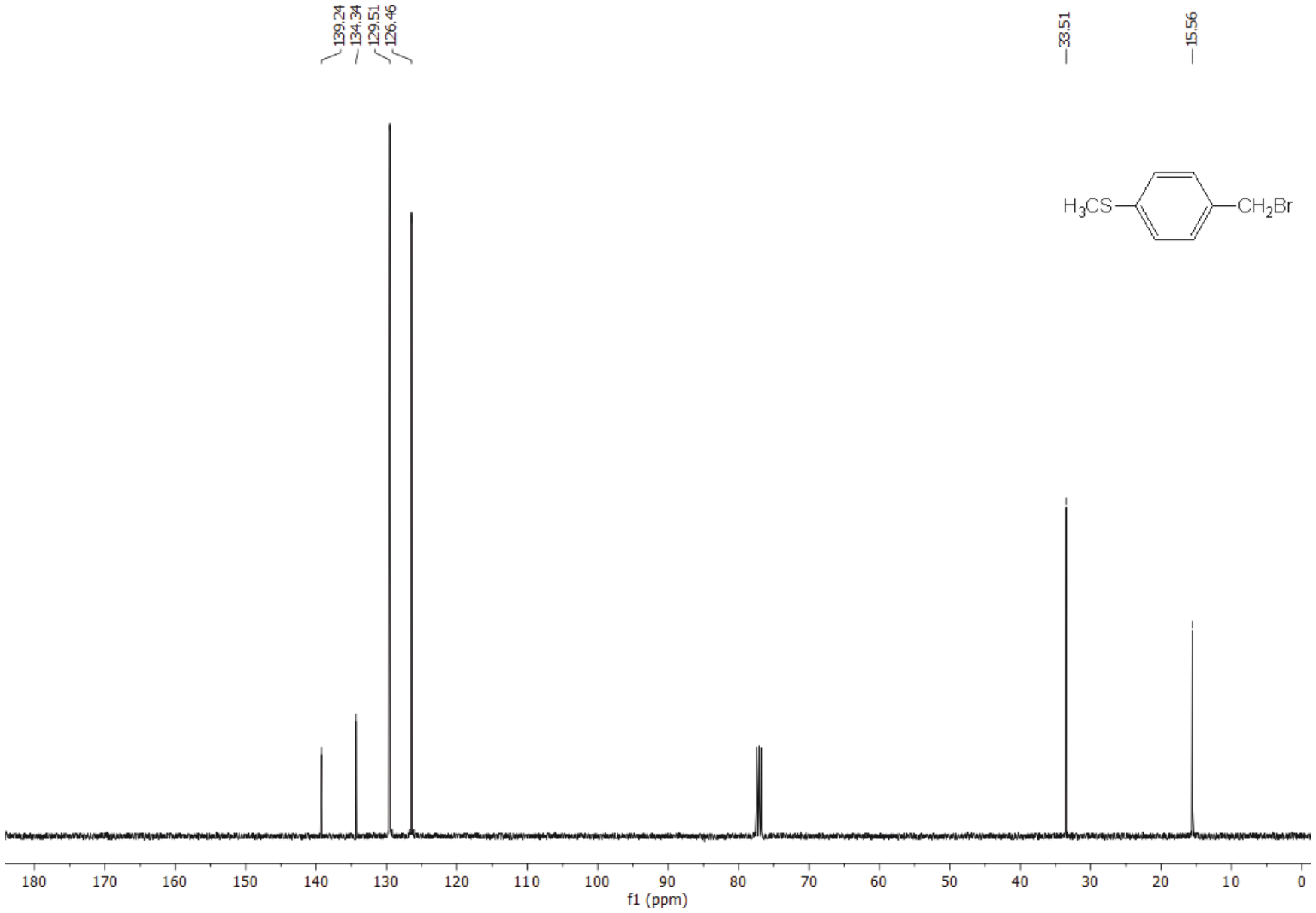
f1 (ppm)

4-(Methylthio)benzyl bromide

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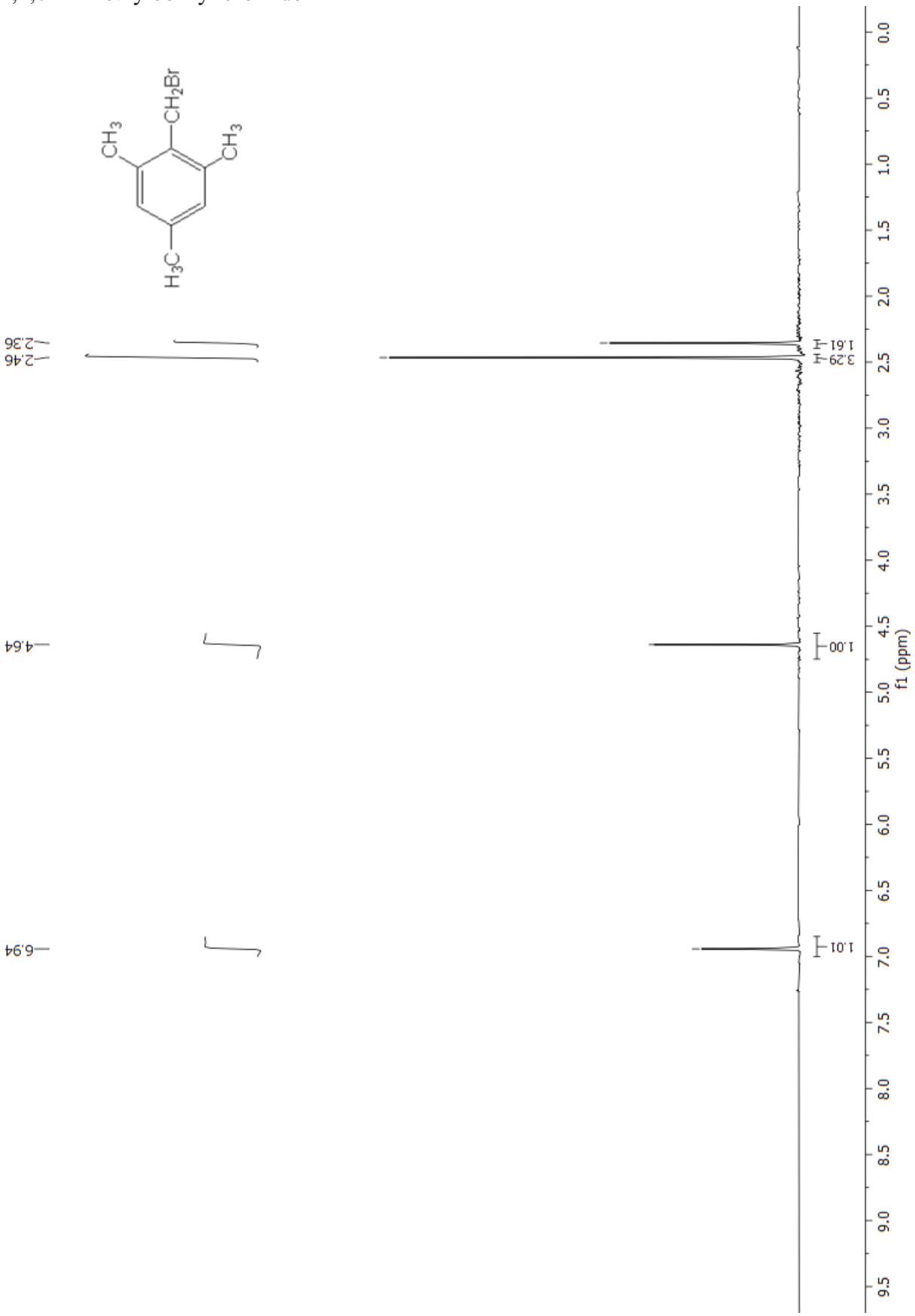
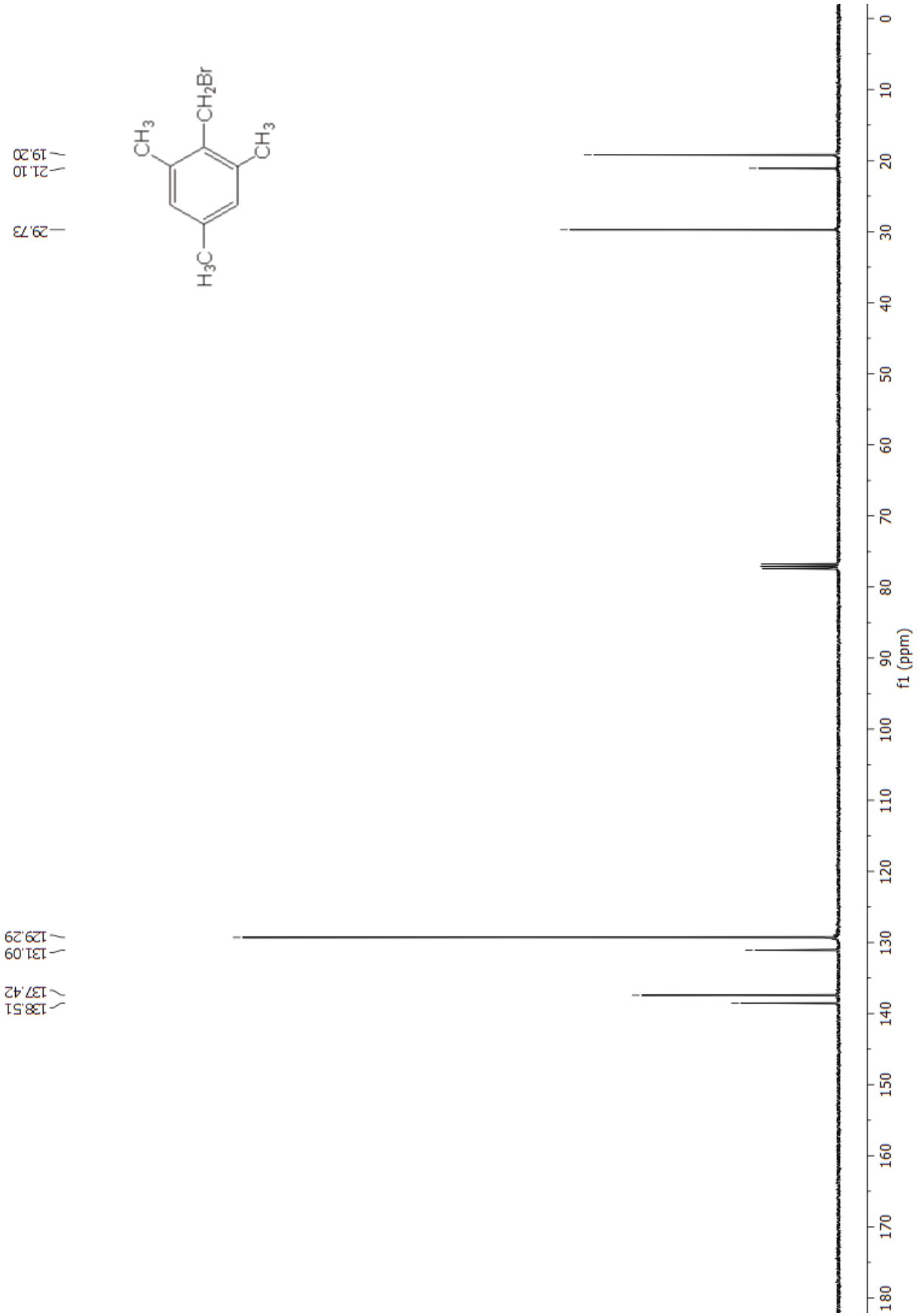
0
f1 (ppm)

2,4,6-Trimethylbenzyl bromide

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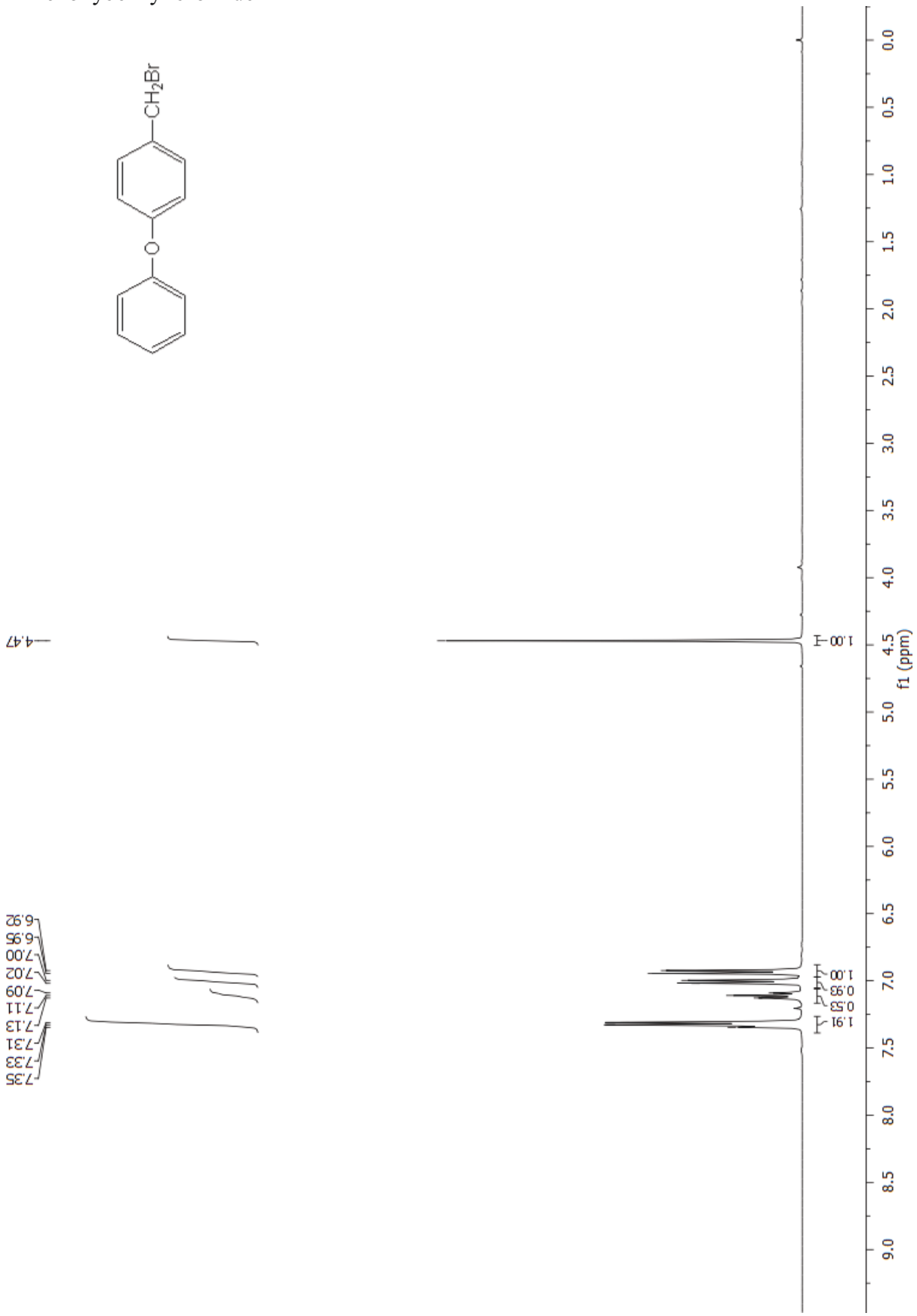
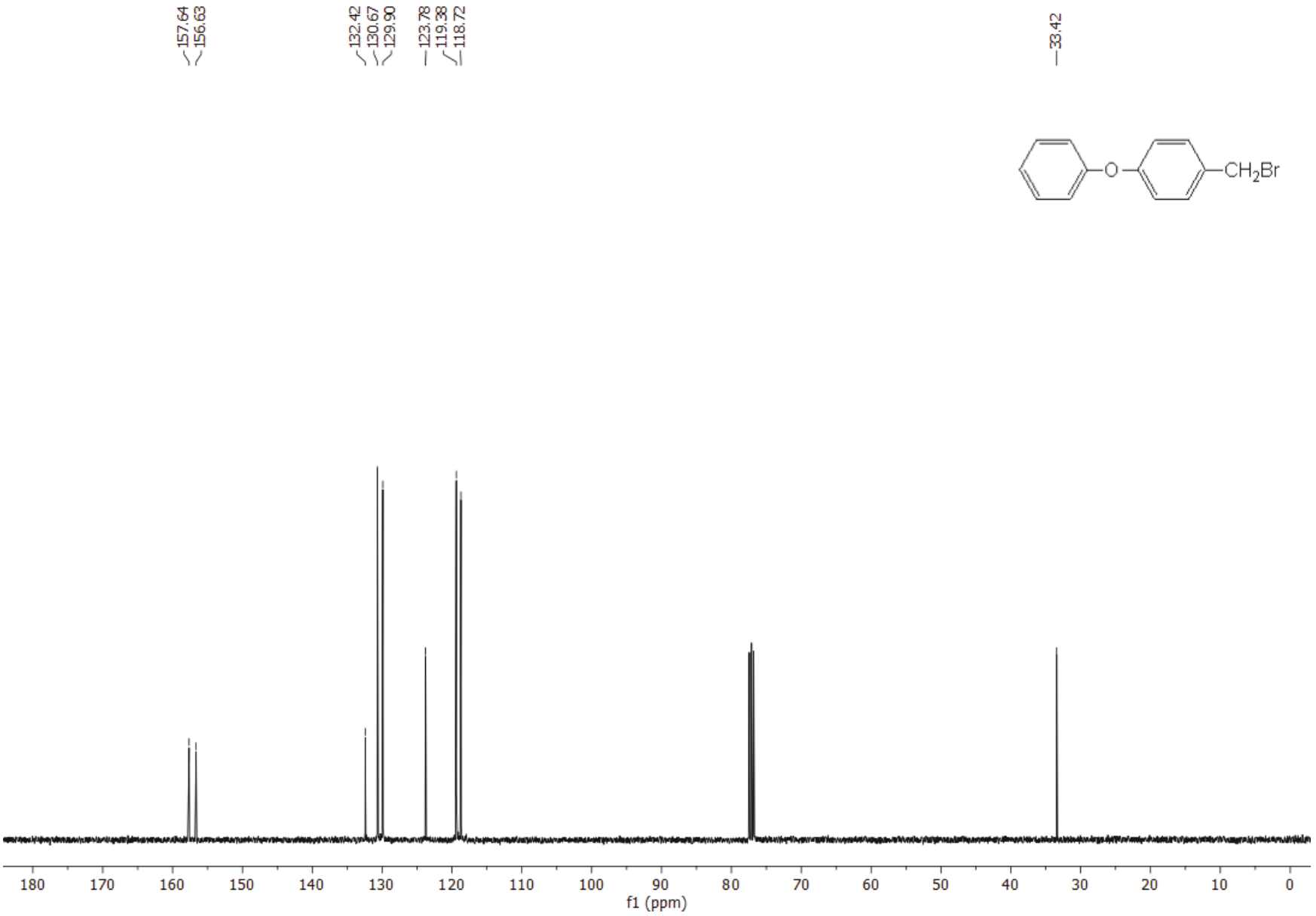
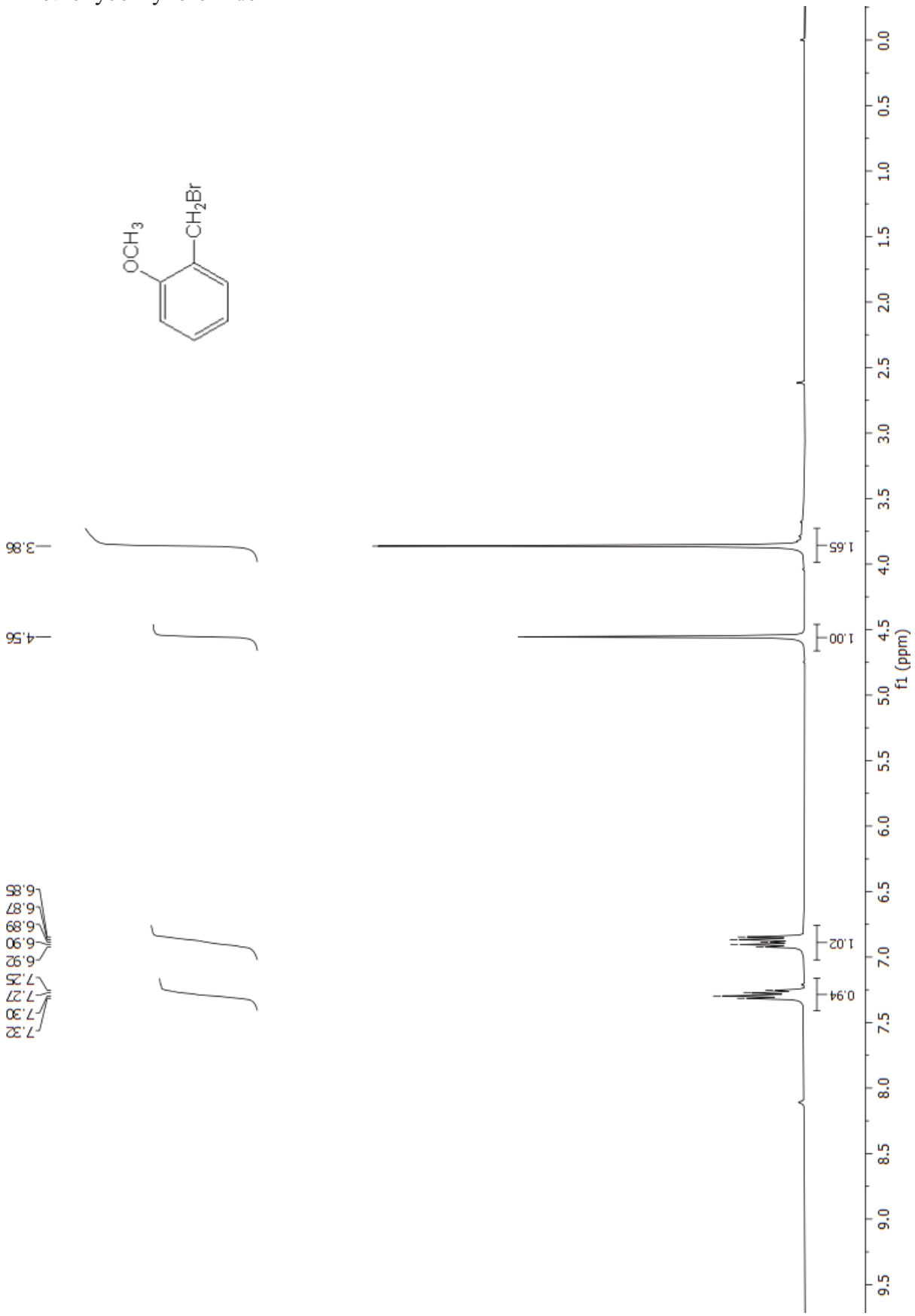
f1 (ppm)

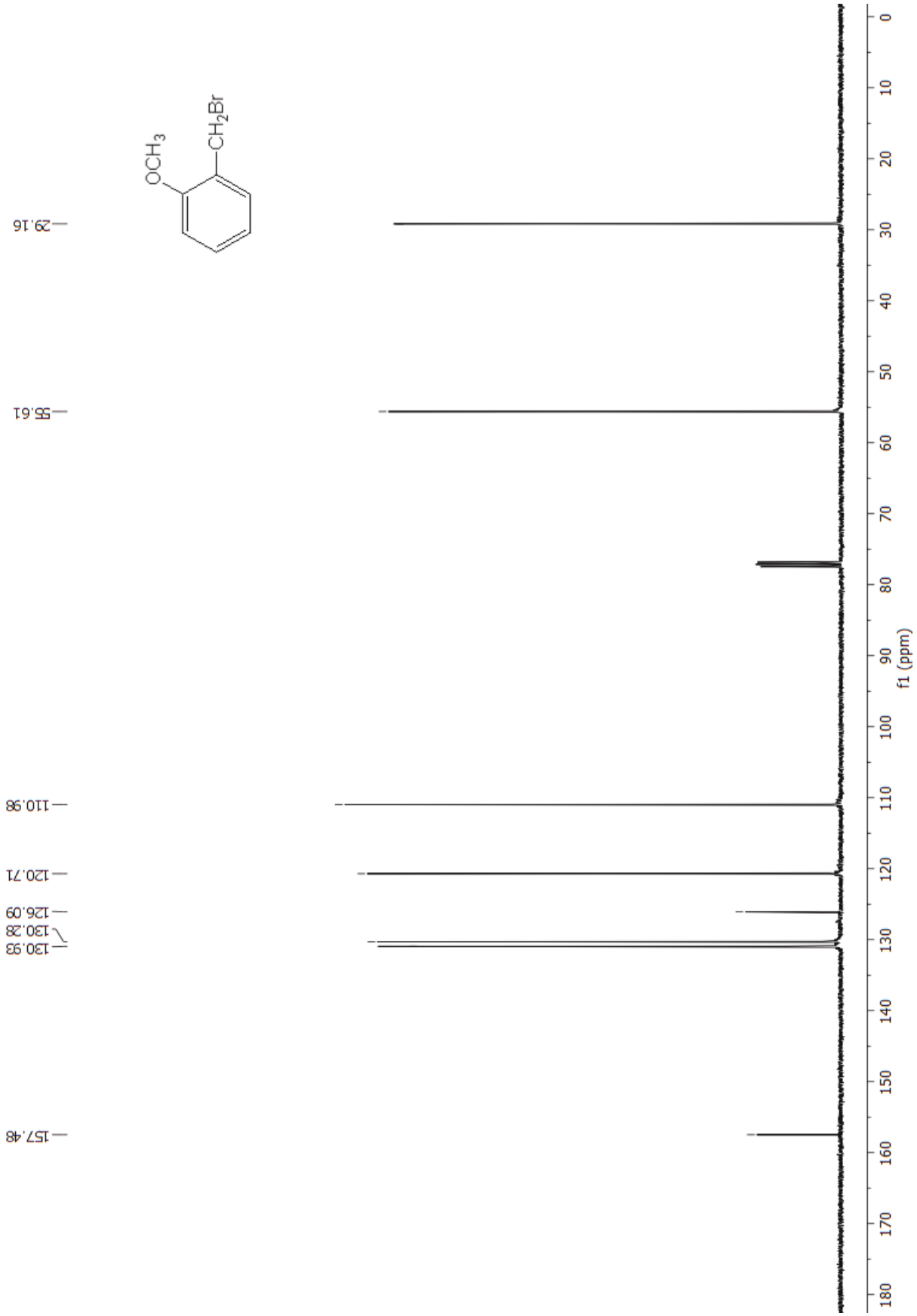
4-Phenoxybenzyl bromide



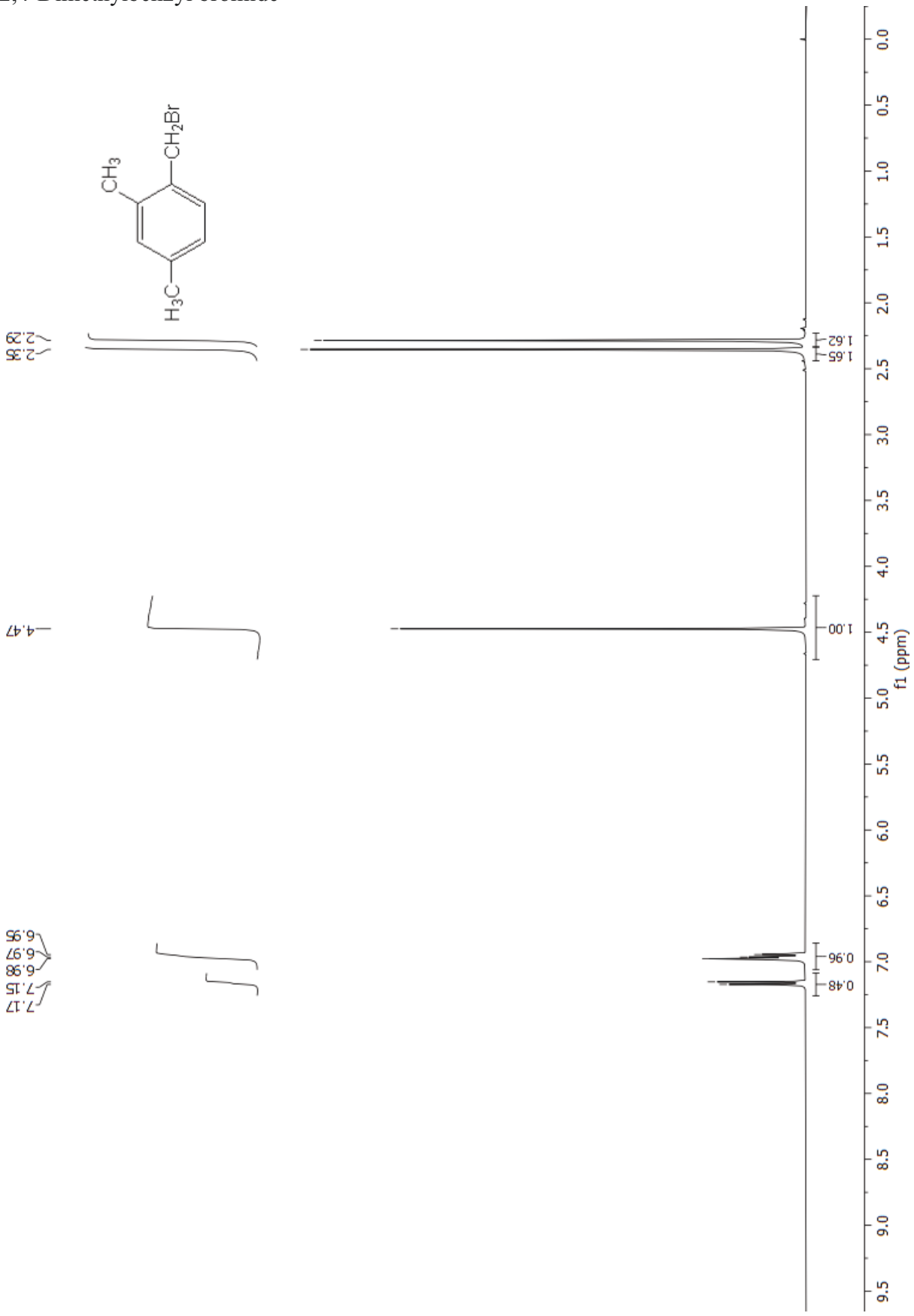

157.64
156.63
132.42
130.67
129.90
123.78
119.38
118.72
33.42
O
CH2Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

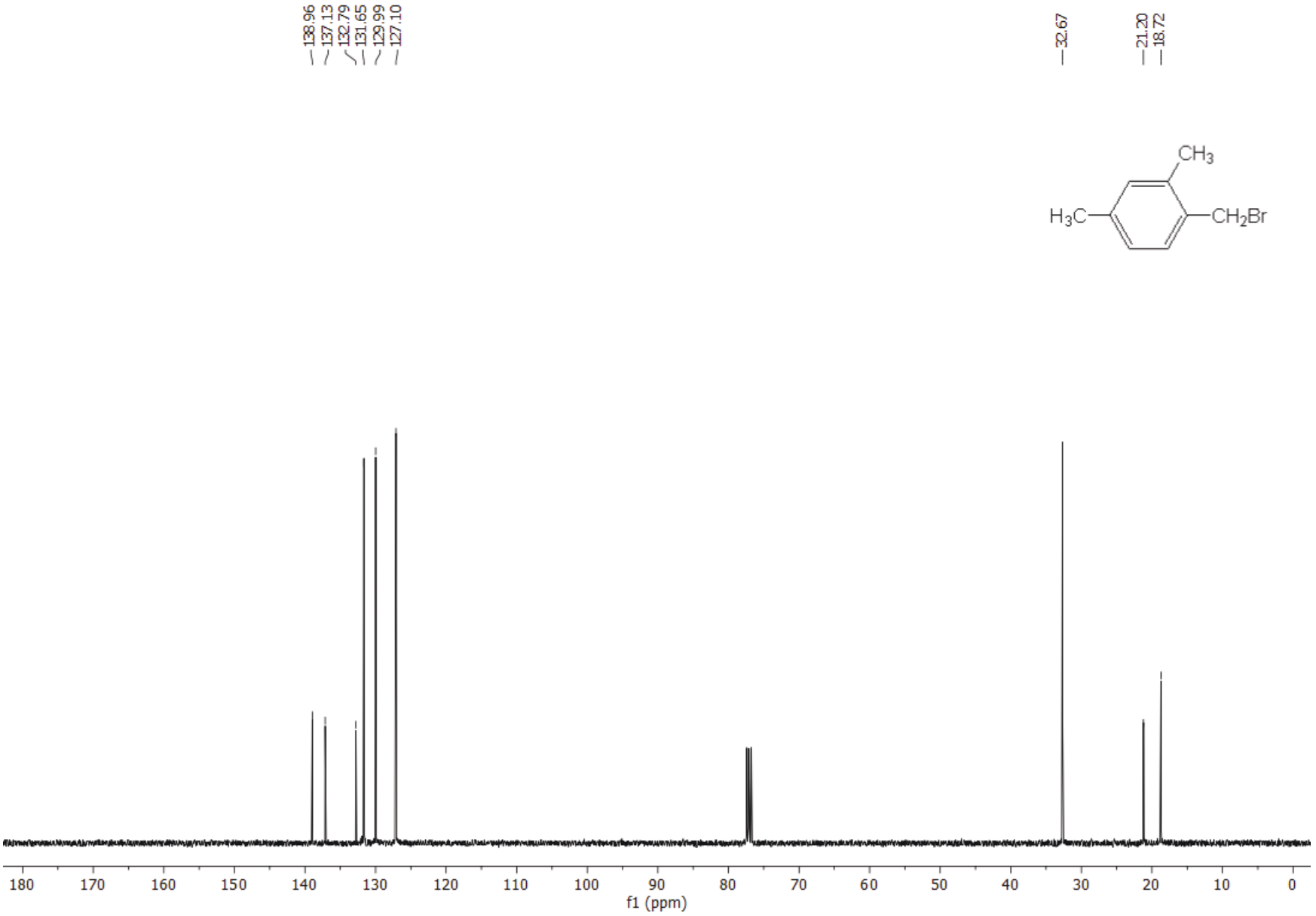
2-Methoxybenzyl bromide



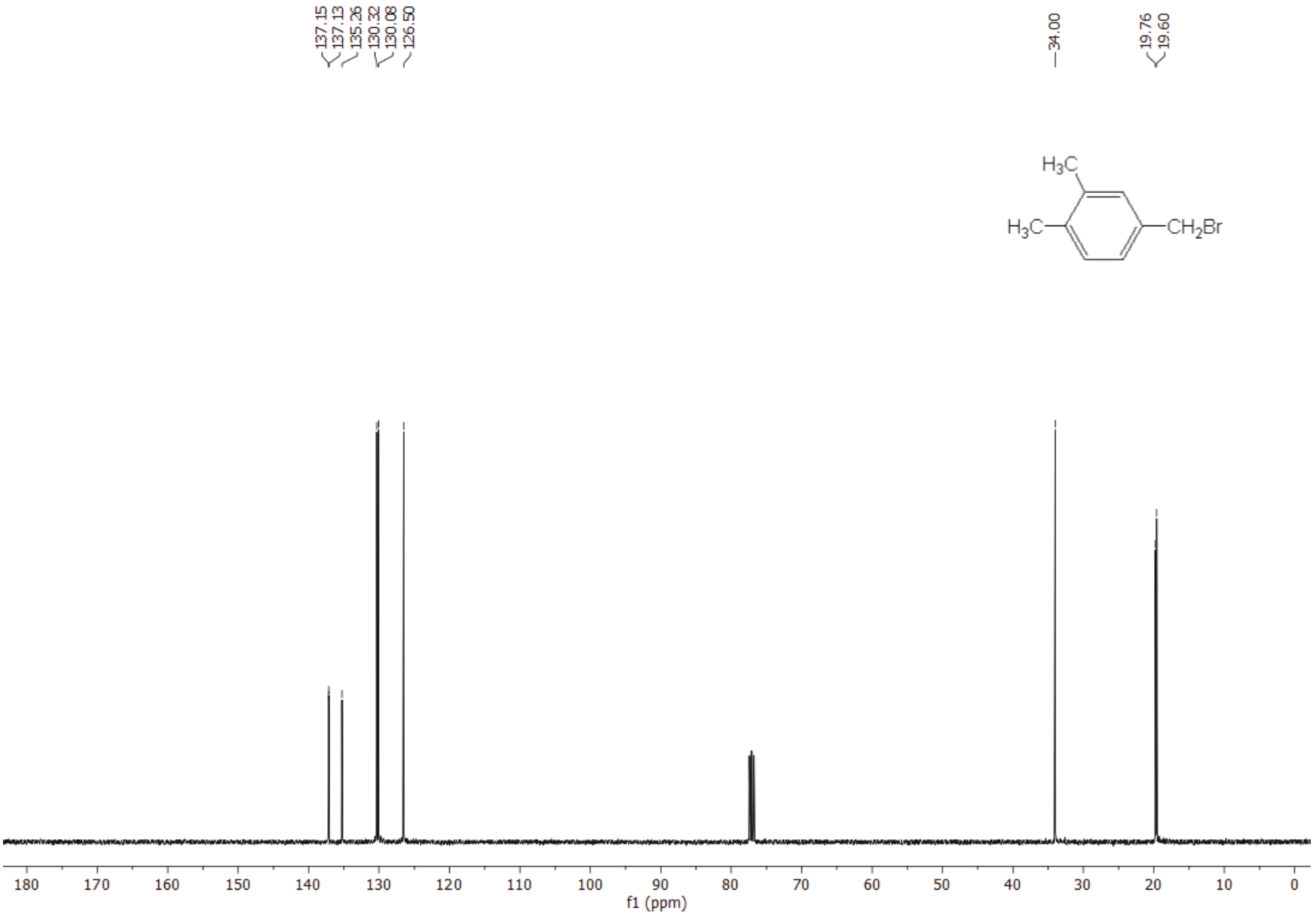

OCH3
CH2Br
29.16
55.61
110.98
120.71
126.09
130.28
130.93
157.48
f1 (ppm)

2,4-Dimethylbenzyl bromide

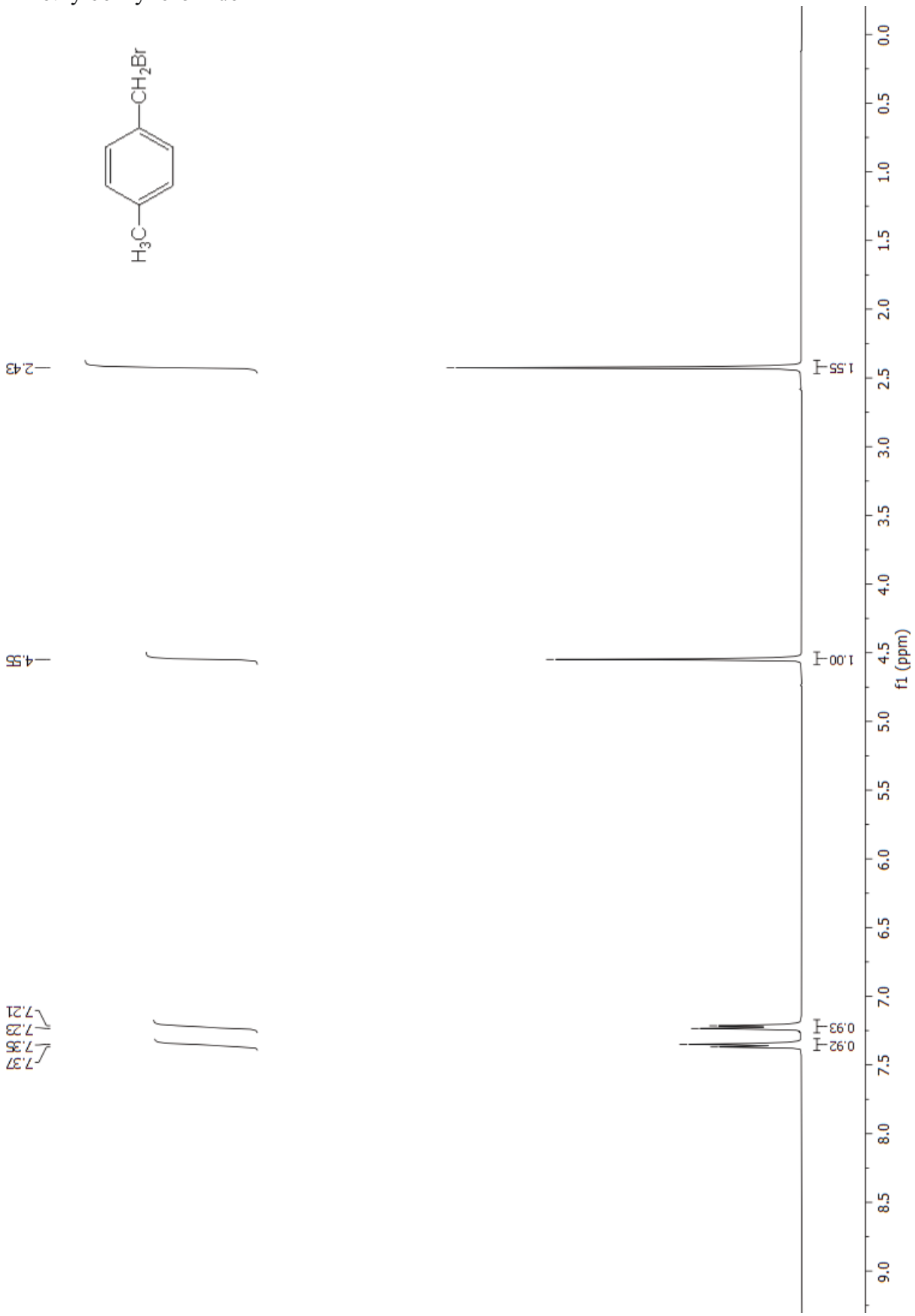


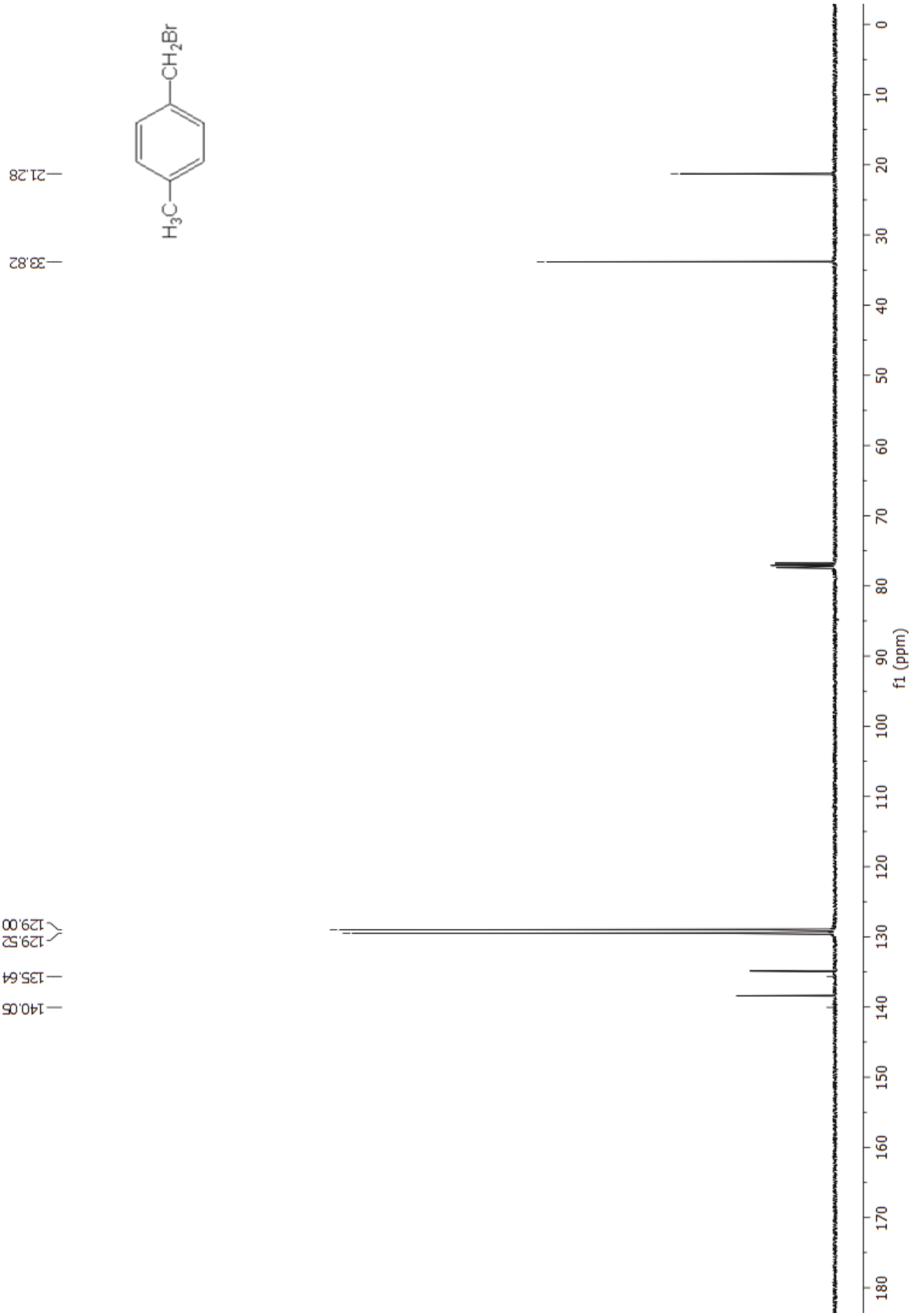

138.96
137.13
132.79
131.65
129.99
127.10
32.67
21.20
18.72
CH3
H3C
CH2Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3,4-Dimethylbenzyl bromide

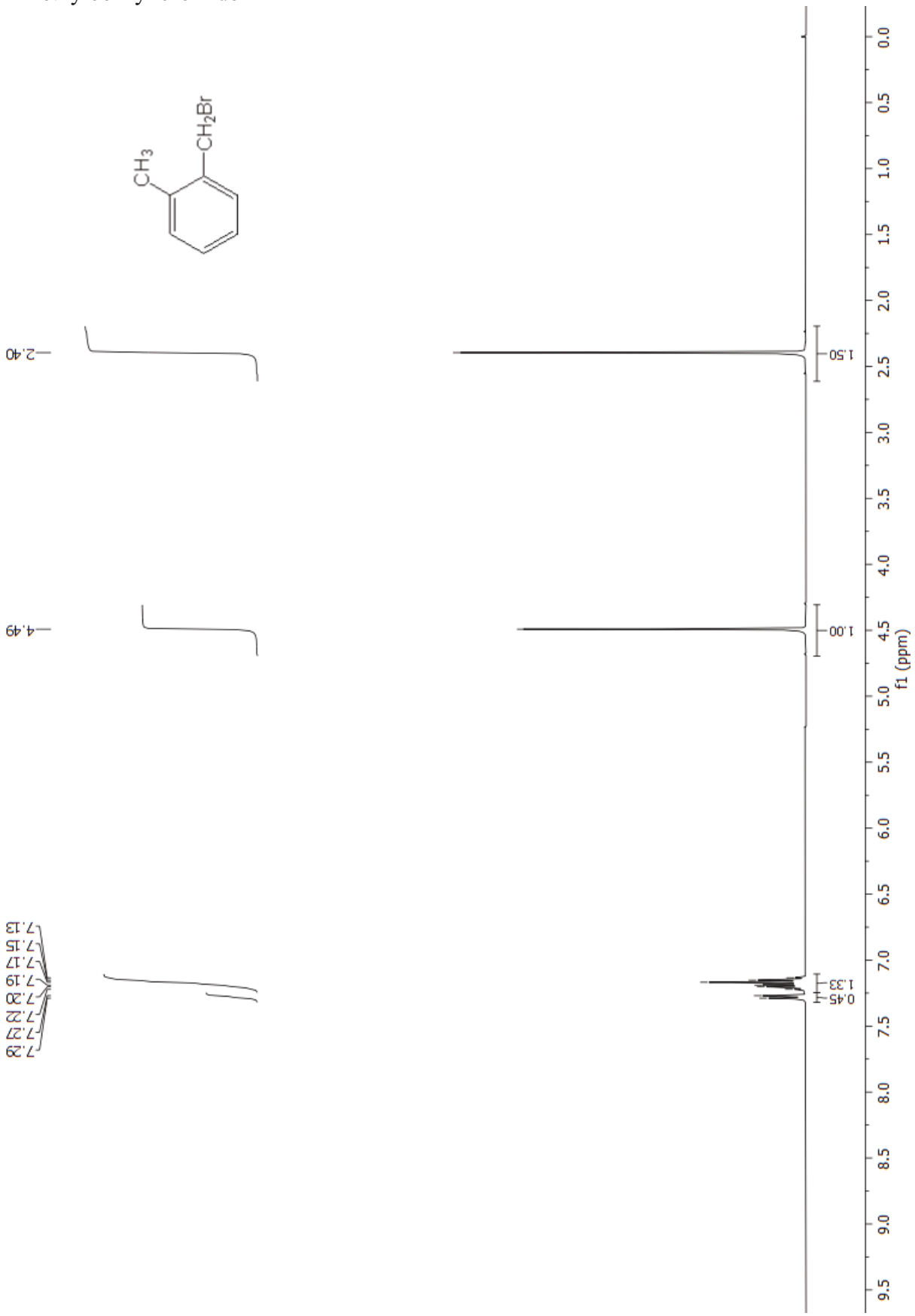

137.15
137.13
135.26
130.32
130.08
126.50
34.00
19.76
19.60
H3C
H3C
CH2Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

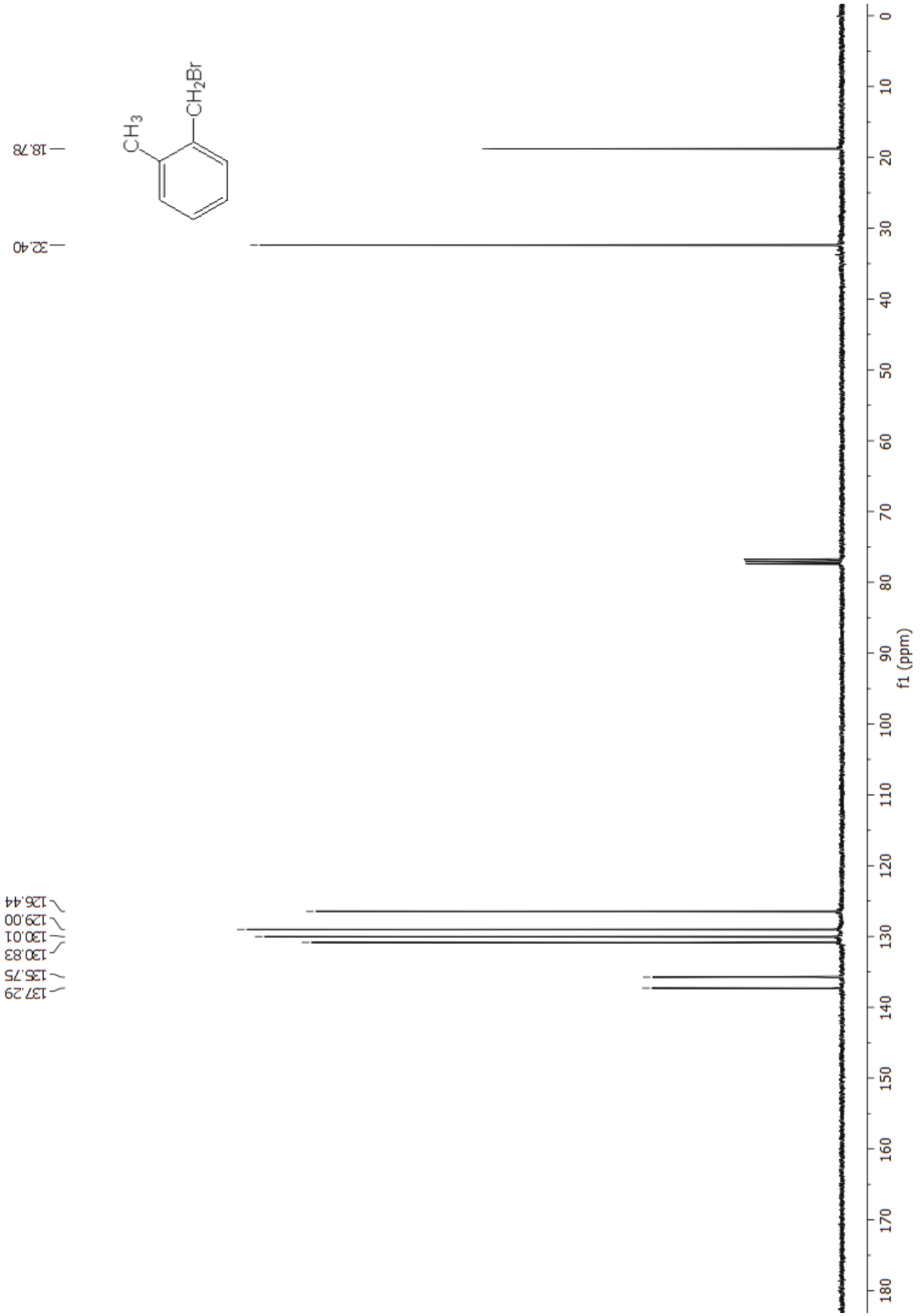
4-Methylbenzyl bromide



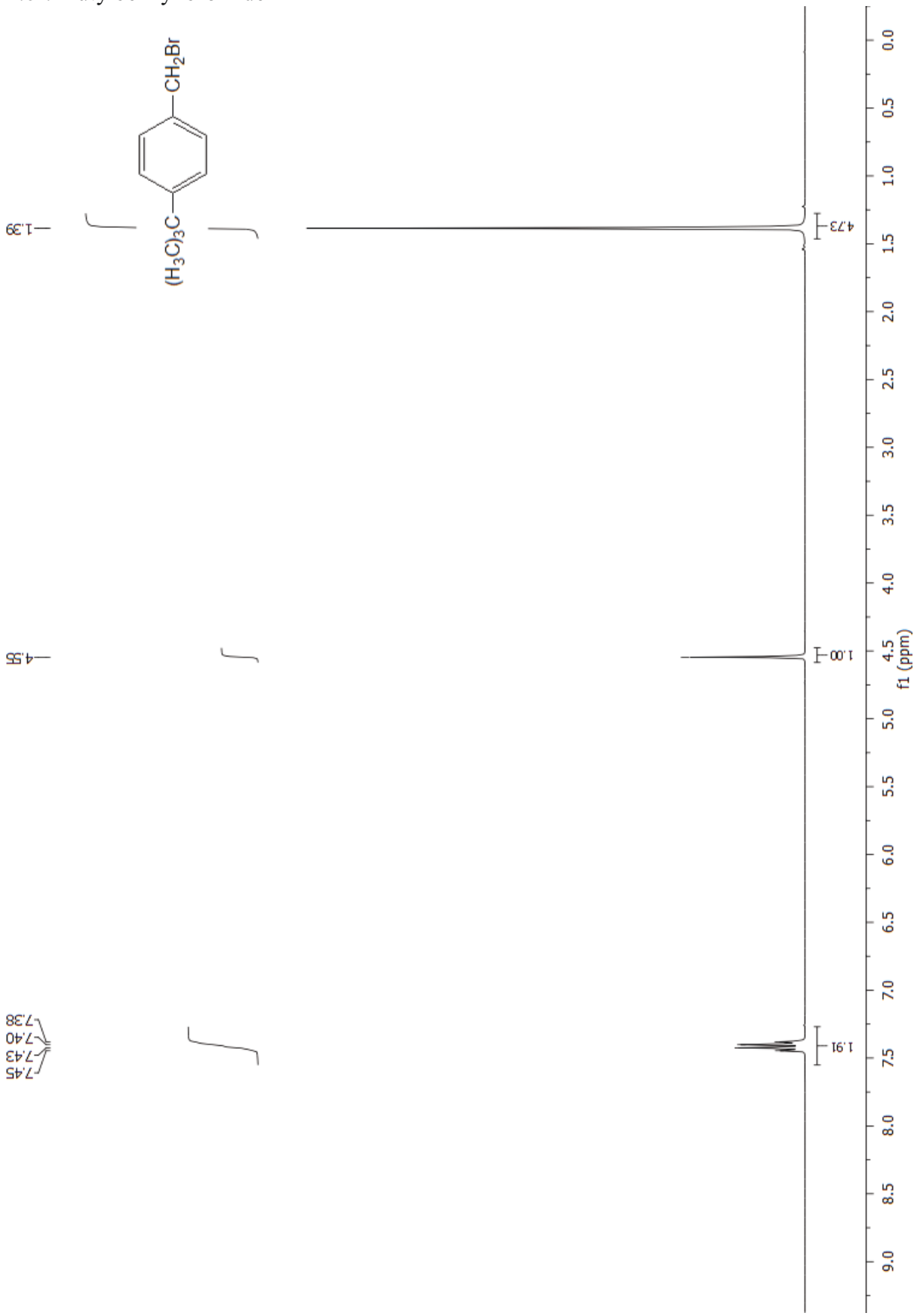

21.28
33.82
129.00
129.52
135.64
140.05
CH_2Br
H_3C
f1 (ppm)

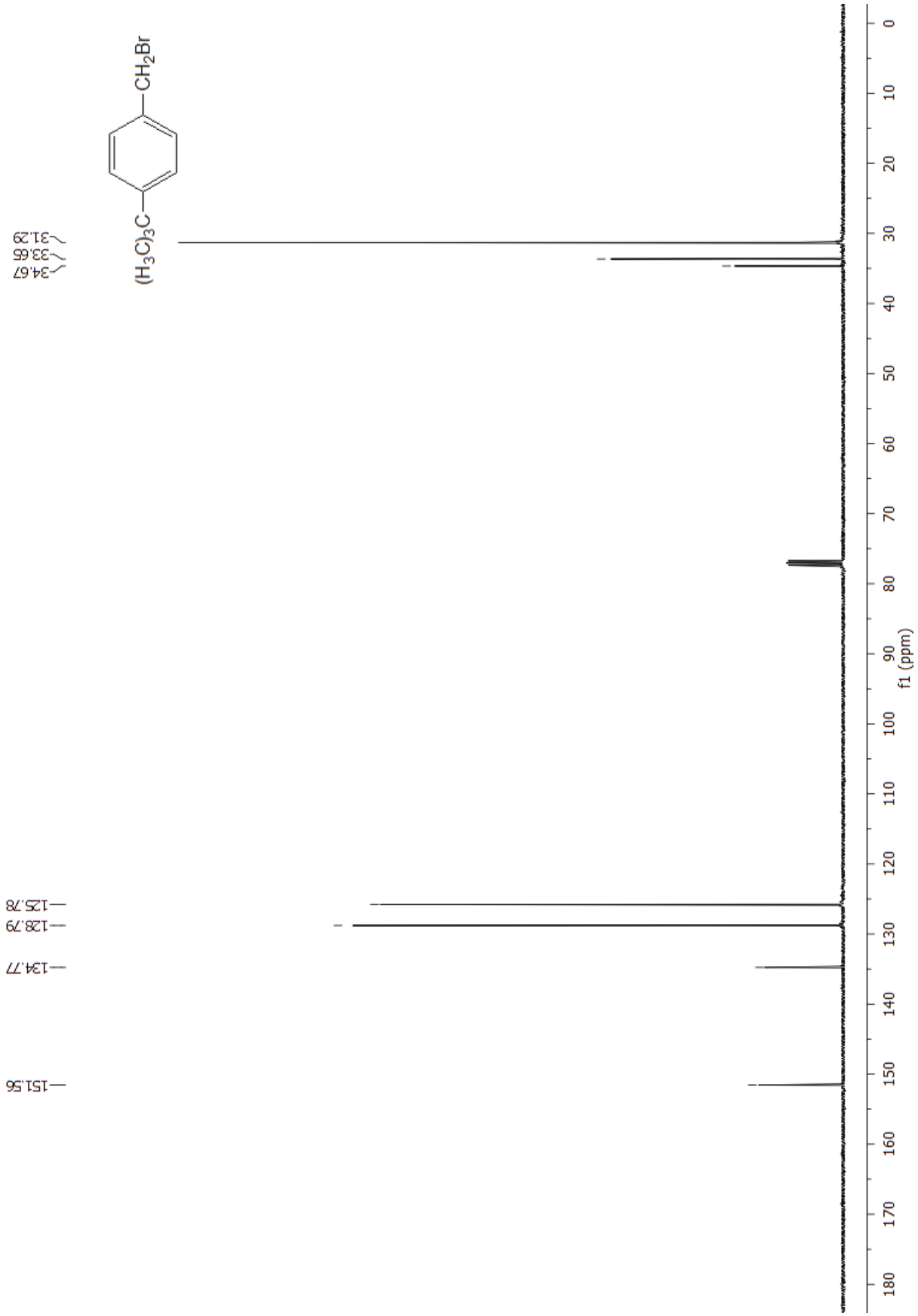
2-Methylbenzyl bromide



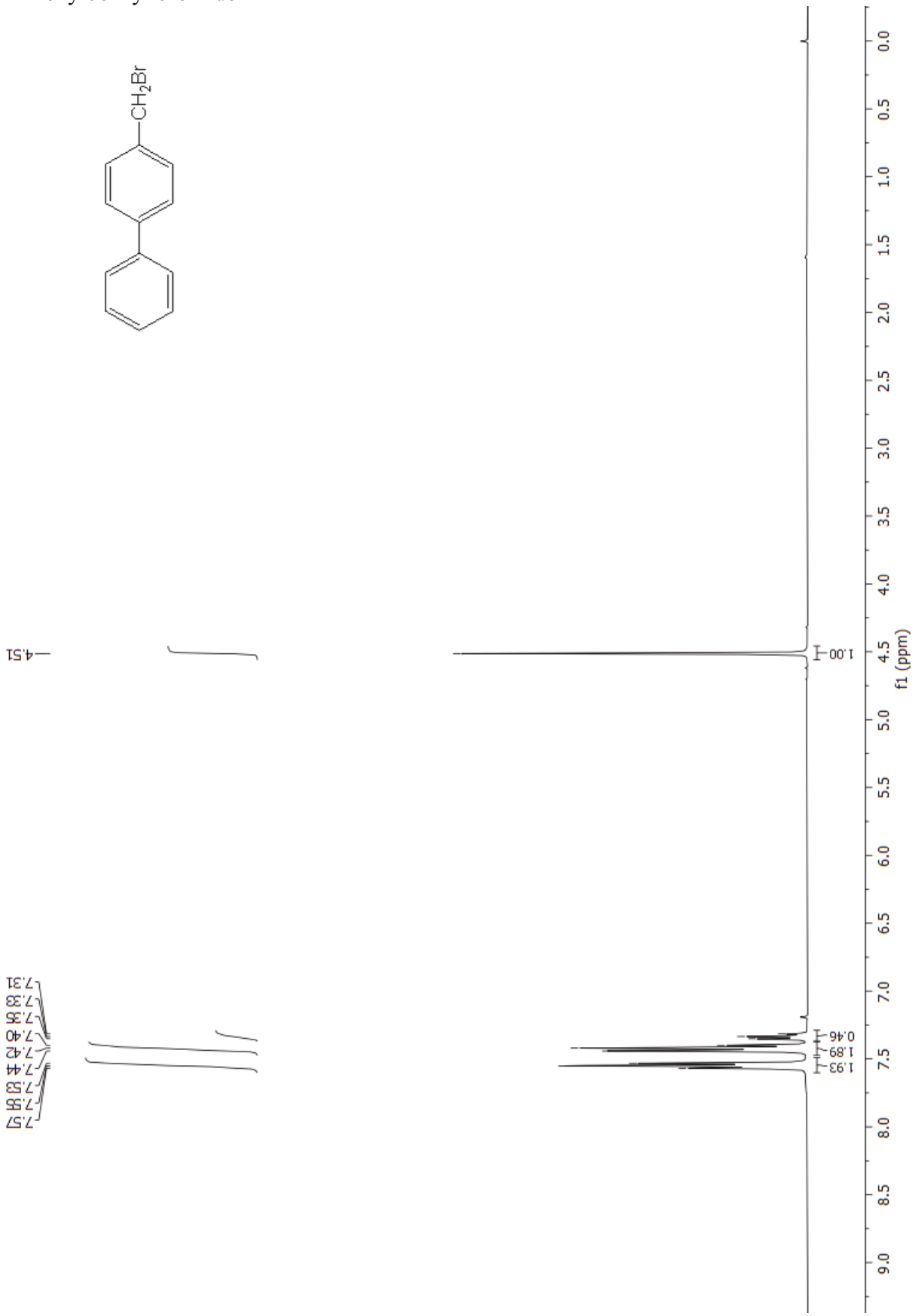

18.78
32.40
137.29
135.75
130.83
130.01
129.00
126.44
CH3
CH2Br
f1 (ppm)

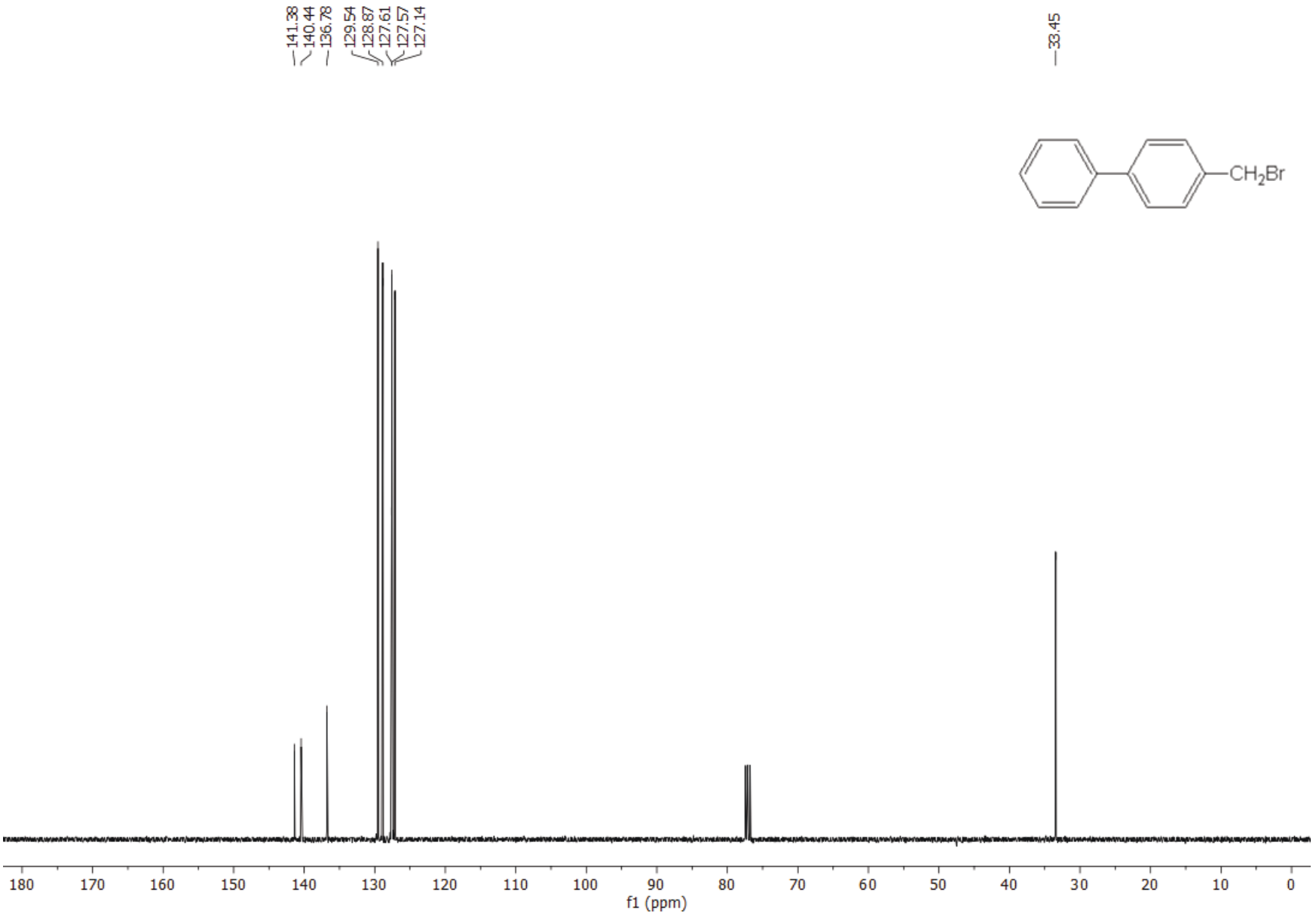
4-*tert*-Butylbenzyl bromide



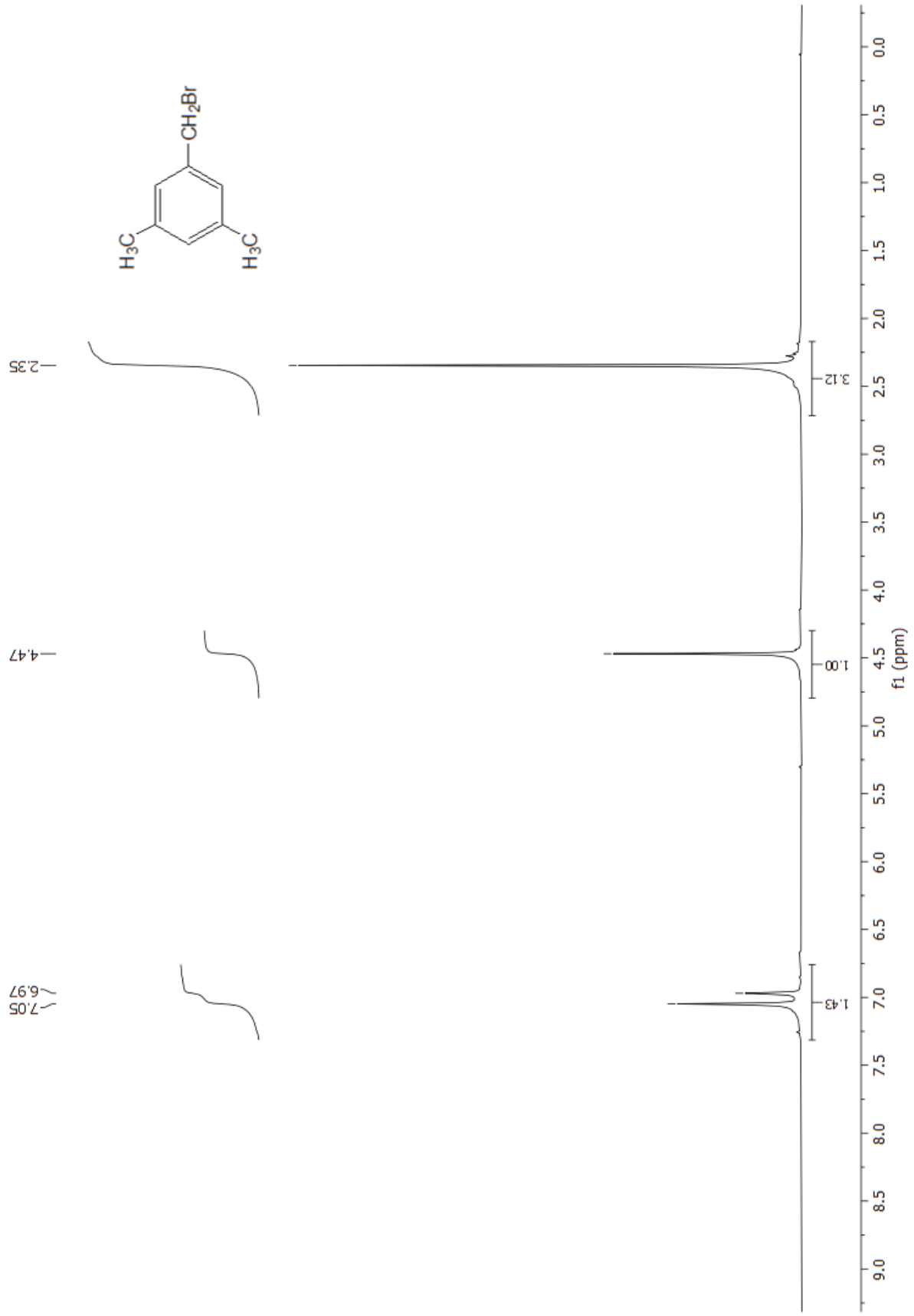

151.56
134.77
128.79
125.78
34.67
33.65
31.29
(H3C)3C
CH2Br
f1 (ppm)

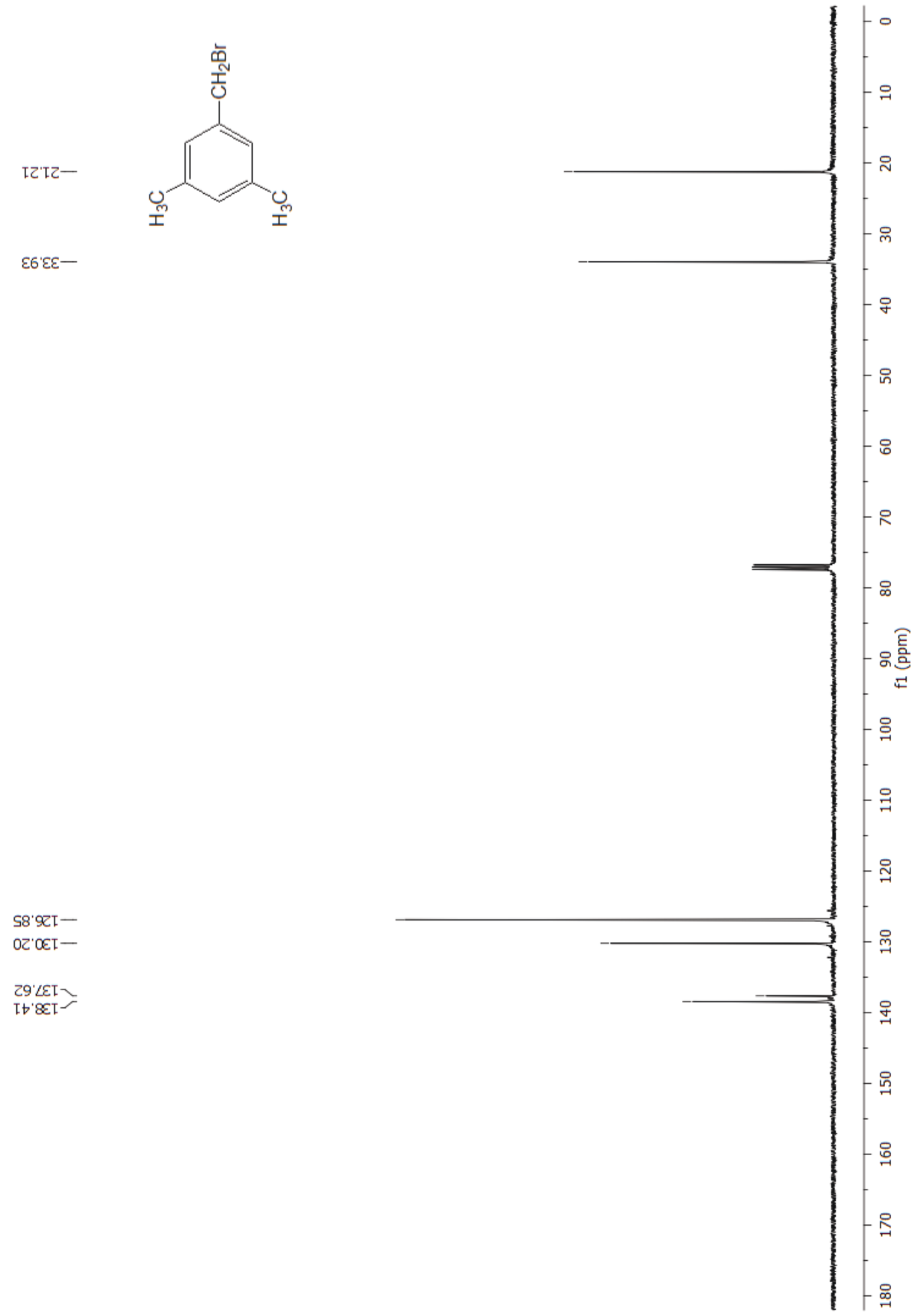
4-Phenylbenzyl bromide



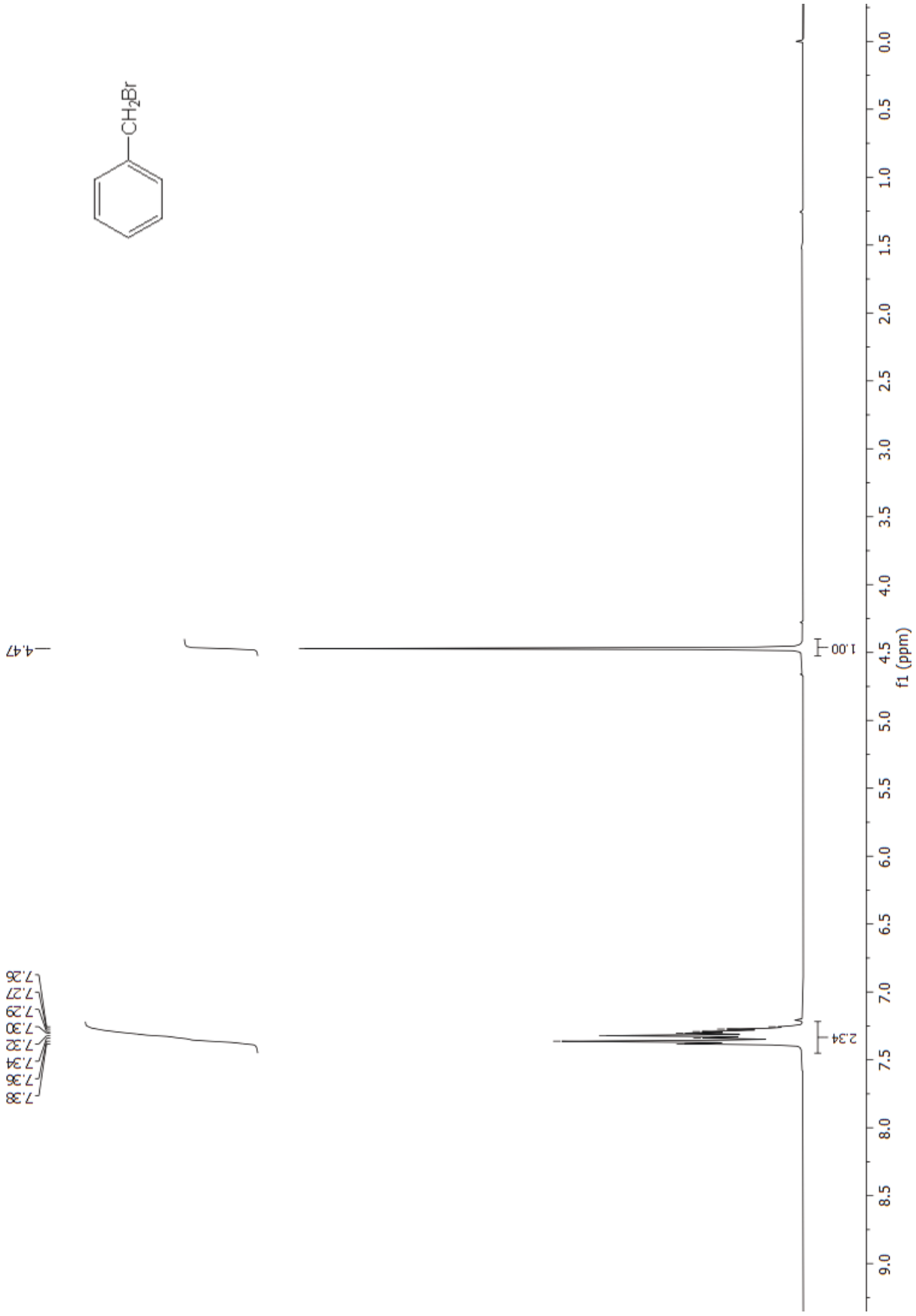

141.38
140.44
136.78
129.54
128.87
127.61
127.57
127.14
33.45
CH2Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

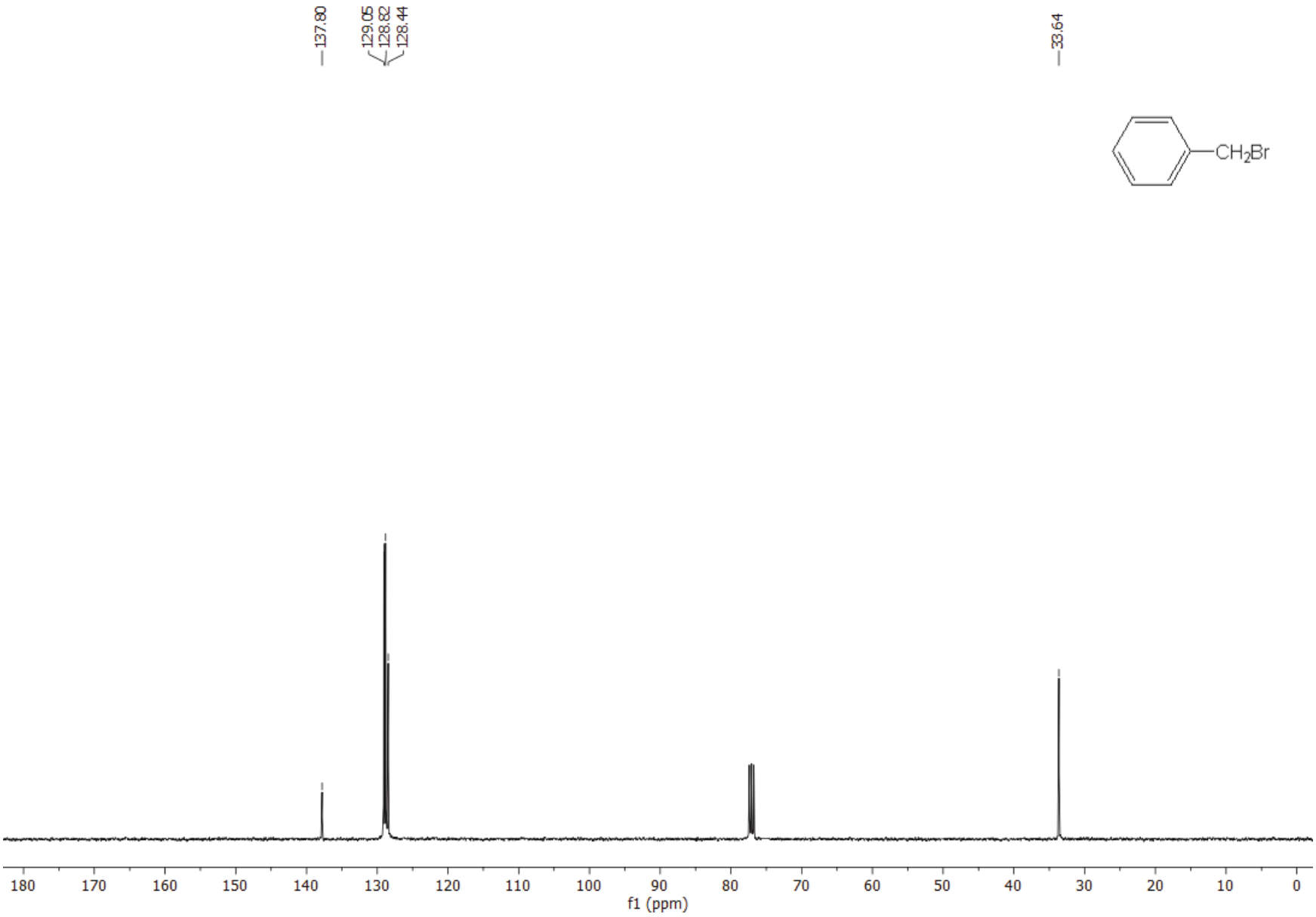
3,5-Dimethylbenzyl bromide



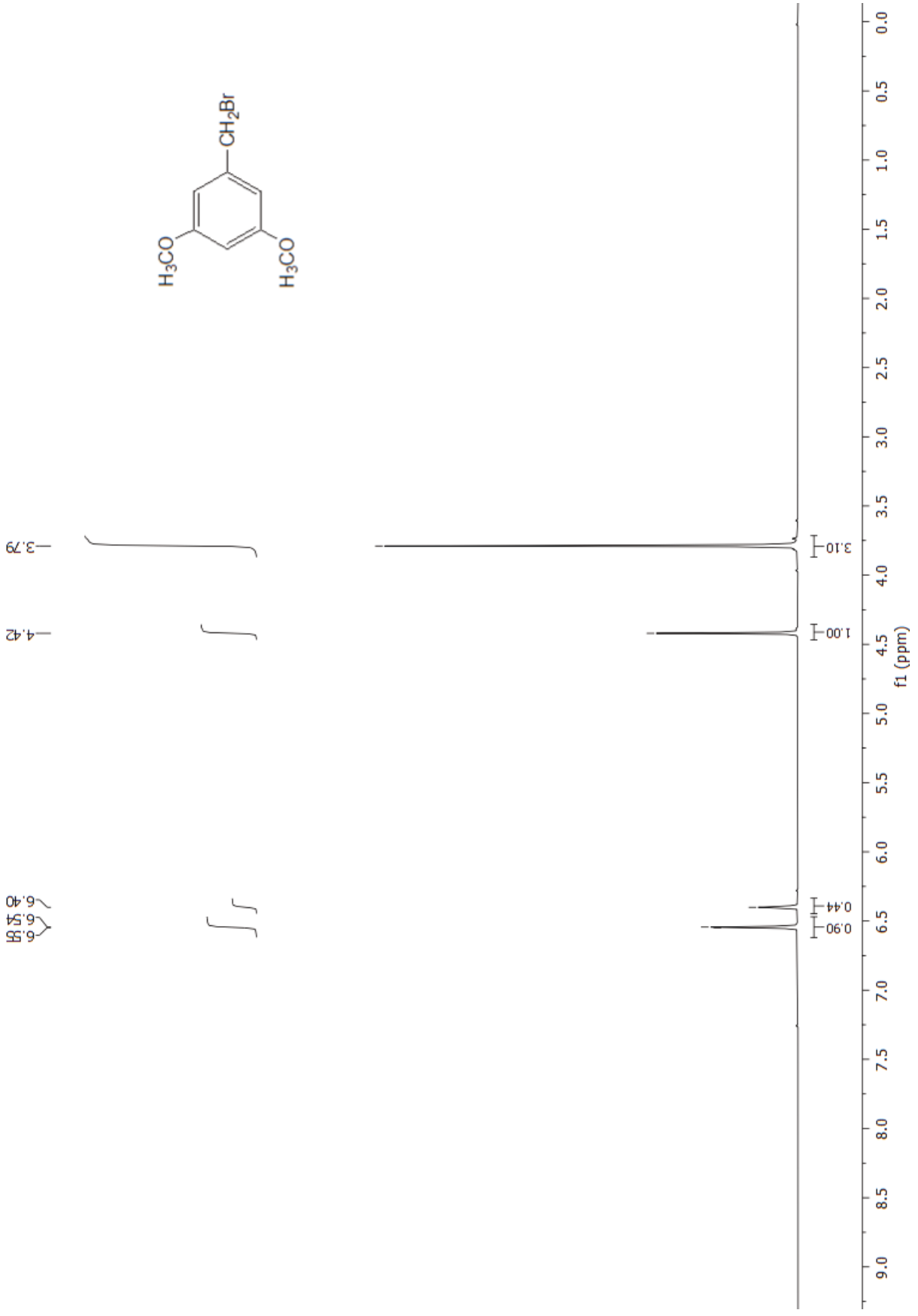

CH2Br
H3C
H3C
21.21
33.93
136.85
130.20
137.62
138.41
f1 (ppm)

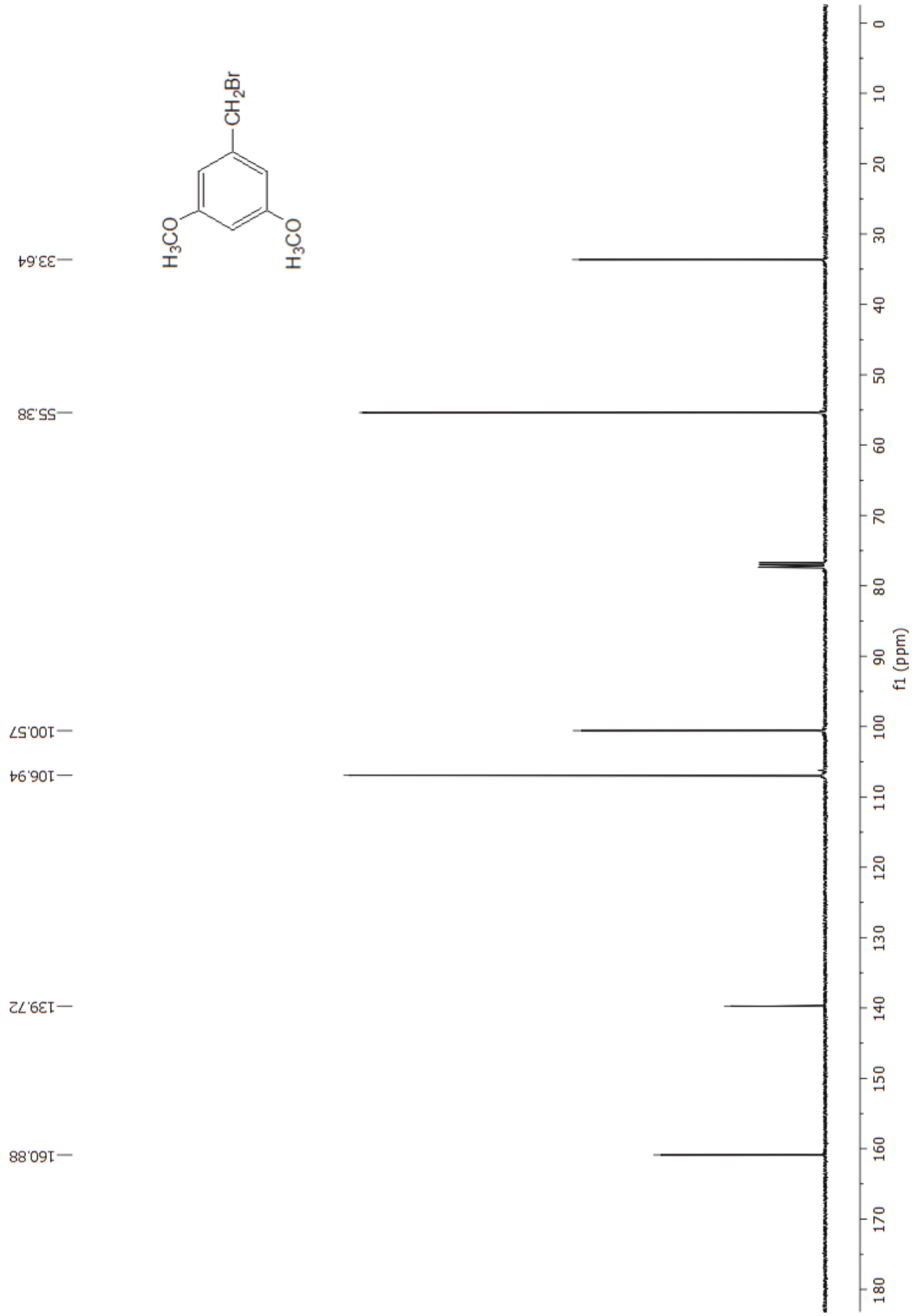
Benzyl bromide



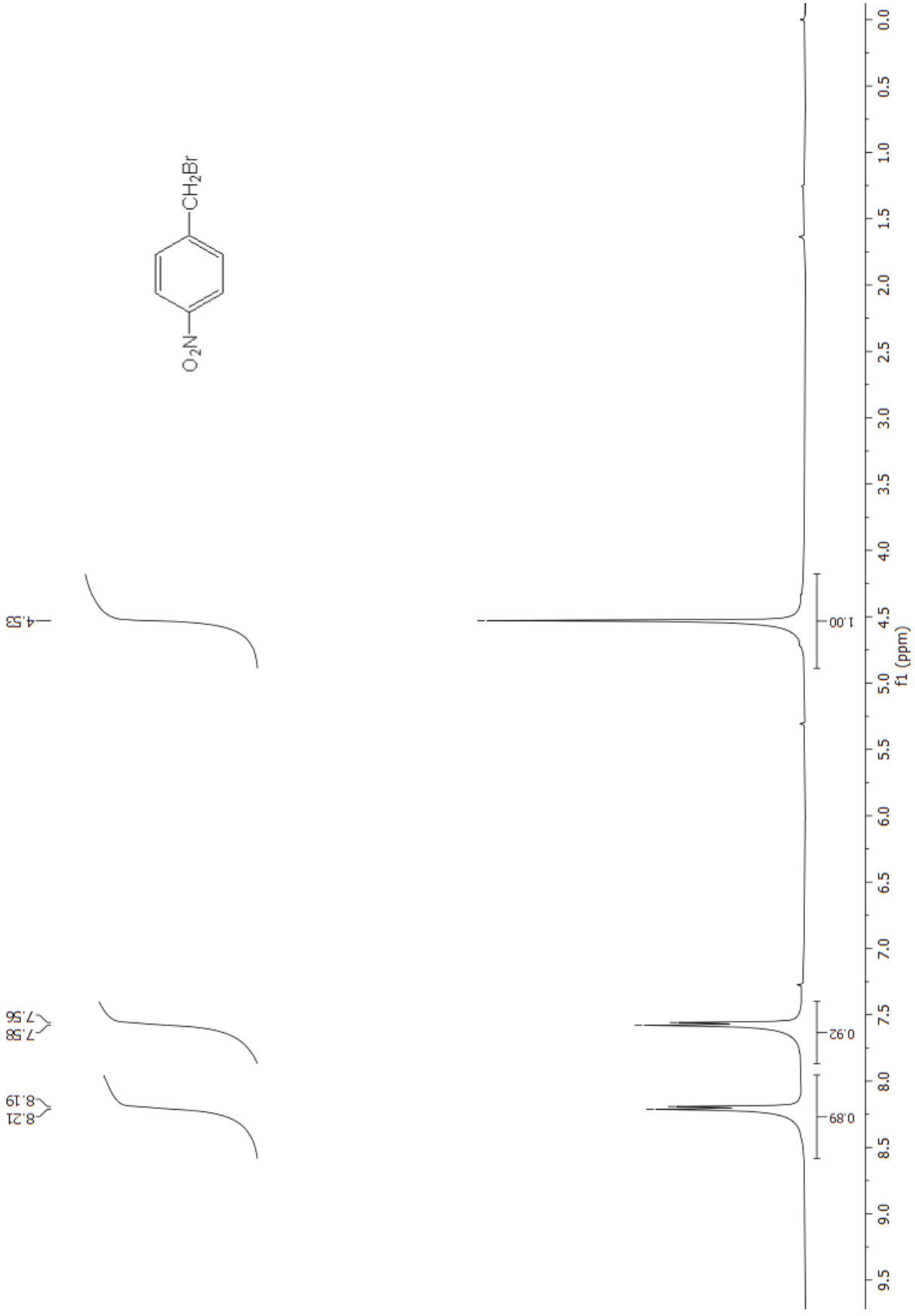

137.80
129.05
128.82
128.44
33.64
CH2Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

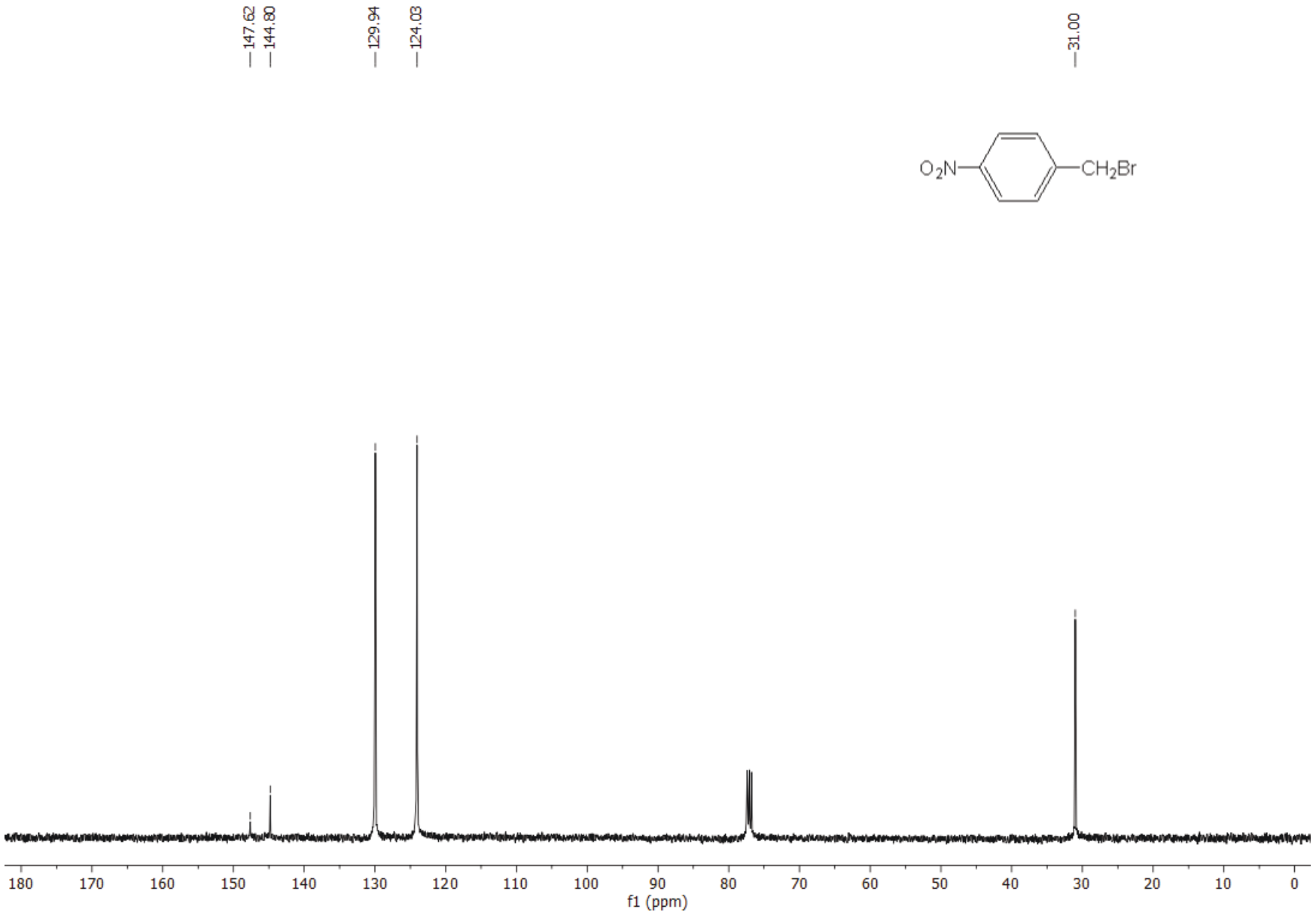
3,5-Dimethoxybenzyl bromide



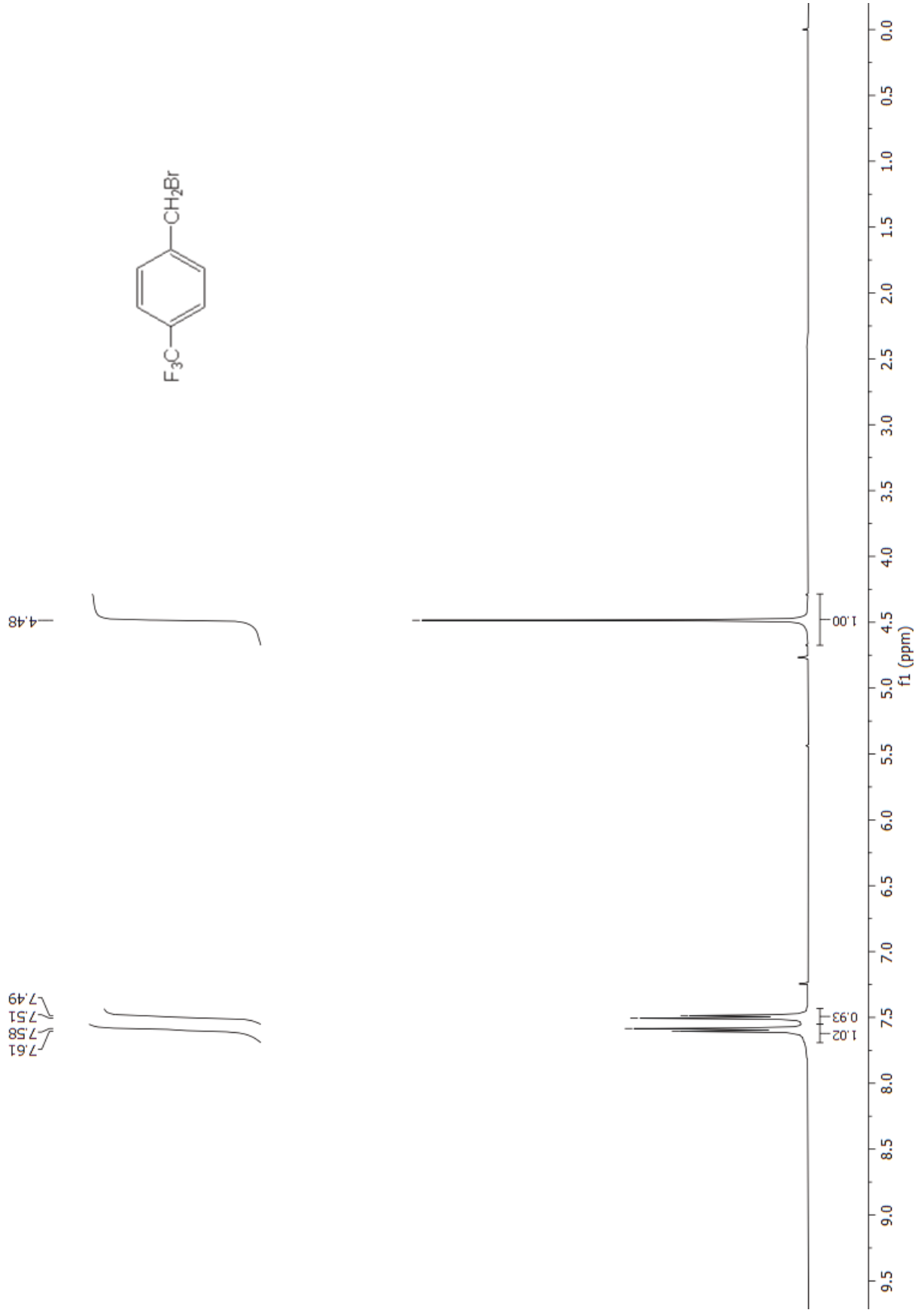

33.64
55.38
100.57
106.94
139.72
160.88
H3CO
H3CO
CH2Br
f1 (ppm)

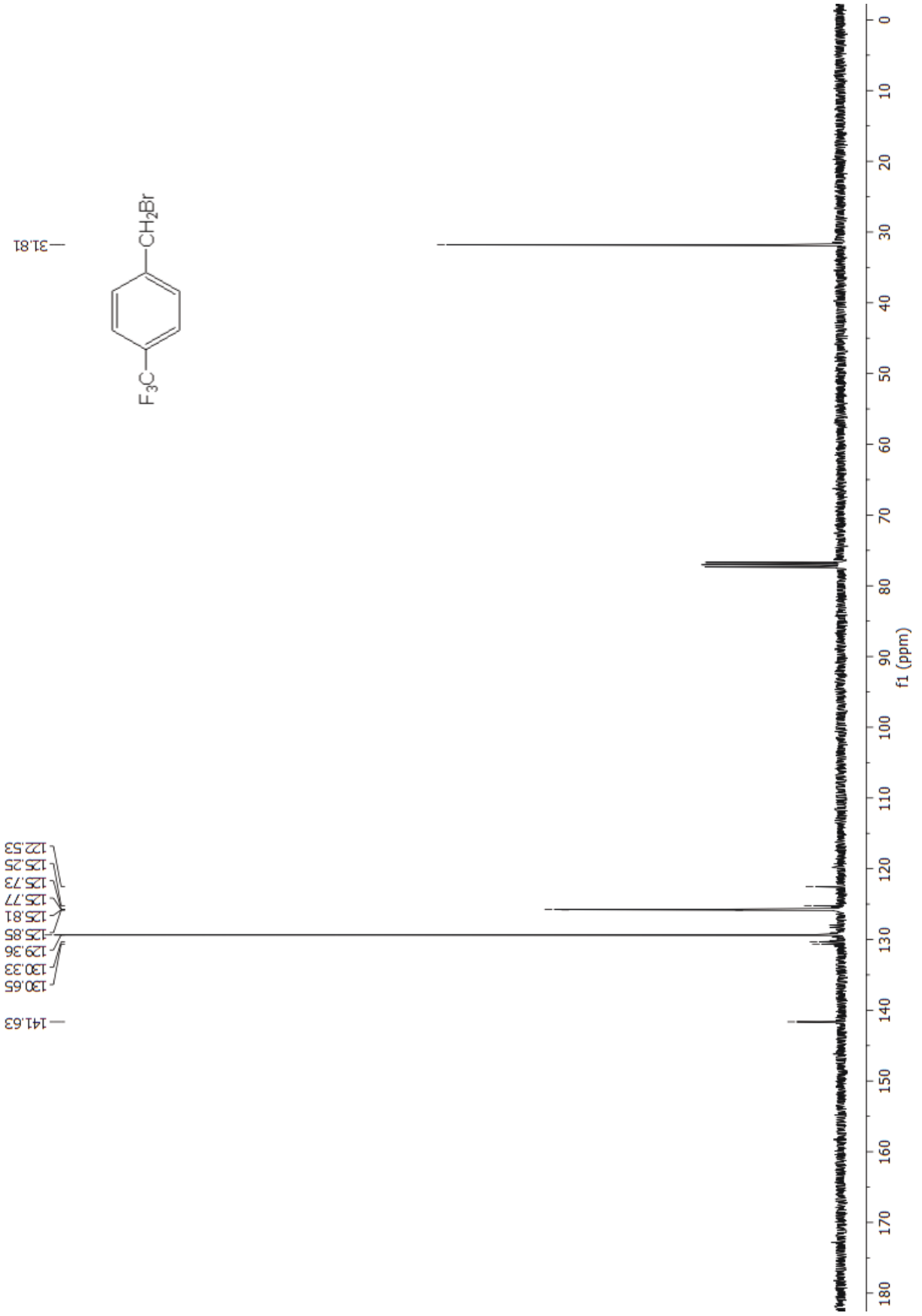
4-Nitrobenzyl bromide

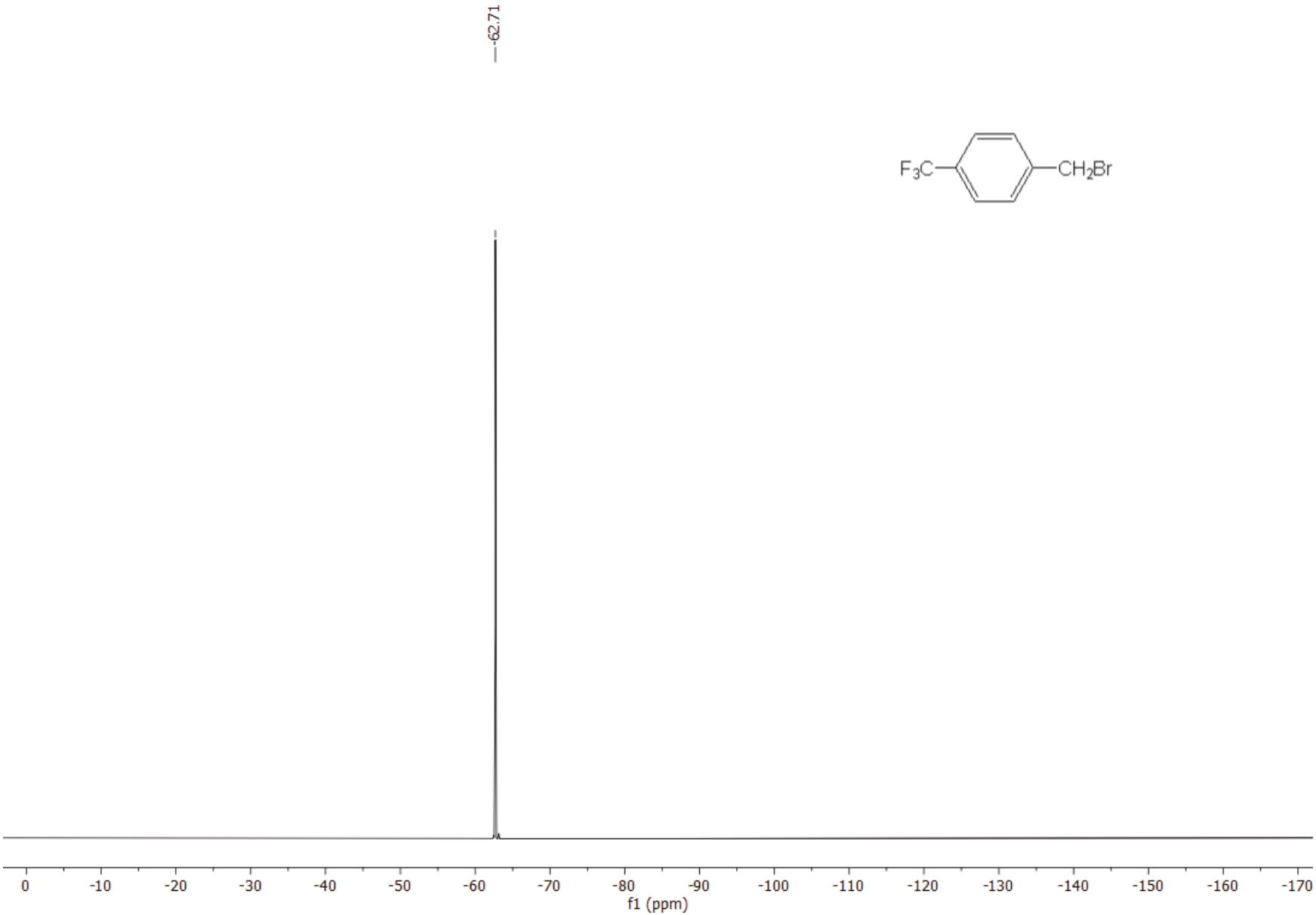



147.62
144.80
129.94
124.03
31.00
O2N
CH2Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4-(Trifluoromethyl)benzyl bromide




31.81
141.63
130.65
130.33
129.36
125.85
125.81
125.77
125.73
125.25
122.53
CH2Br
F3C
f1 (ppm)


-62.71
F3C
CH2Br
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

4. Coordinates

IEFPCM (water) - M062X/6-311+G(3df,3pd)

Benzyl chlorides (14Cl–16Cl)

3,5-Dimethoxybenzyl chloride (14Cl)

conformer 1
C,0,-1.2433513456,-0.249153505,0.2394540028
C,0,-1.0741076693,1.1178888815,0.3947550956
C,0,0.2049024664,1.6879894892,0.3842171366
C,0,1.3118617729,0.8743411715,0.2165065142
C,0,1.1538627389,-0.5084983903,0.0610010694
C,0,-0.1122788789,-1.0550206397,0.0733047212
C,0,-0.2835958925,-2.5339992924,-0.0781018723
Cl,0,-0.5074572792,-3.322844185,1.5321095945
O,0,2.58418369,1.3296815994,0.1888985769
O,0,-2.0910816381,1.9940640922,0.5595244607
C,0,2.7914951772,2.7223795544,0.3396534212
C,0,-3.4095017056,1.477937333,0.5823849206
H,0,-2.2225943425,-0.7028761893,0.2450879534
H,0,0.2864039111,2.7566606164,0.5047369584
H,0,2.0314465421,-1.1267344297,-0.0681377698
H,0,0.5898200841,-2.9989868114,-0.5199023108
H,0,-1.1685544828,-2.7843823467,-0.6524763051
H,0,2.4172357542,3.0696567792,1.3032577349
H,0,3.8635705357,2.8768182594,0.2889391539
H,0,2.3036204686,3.2776488452,-0.462176468
H,0,-4.0659678656,2.3293661592,0.7237408813
H,0,-3.6504929138,0.9829975056,-0.3589167145
H,0,-3.5387031275,0.7758775034,1.4067422449

conformer 2
C,0,-1.1511942097,-0.3571607557,-0.205753568
C,0,-1.0463705638,1.0213645087,-0.4295216153
C,0,0.1973340497,1.6125058319,-0.568299187
C,0,1.3495959672,0.8210223172,-0.4855938923
C,0,1.2585405866,-0.5447693177,-0.2667615585
C,0,-0.0071964369,-1.123335742,-0.1270334236
C,0,-0.1152601644,-2.5942985719,0.1264260951
Cl,0,0.1570295273,-2.9667393431,1.8735148082
O,0,2.5158767535,1.4884599346,-0.6385139883
O,0,-2.2141052945,1.6986482066,-0.4972179319
C,0,3.7175251531,0.7432991552,-0.5615916018
C,0,-2.1563338582,3.0951080414,-0.7249778857
H,0,-2.132065483,-0.7994826909,-0.0995047284
H,0,0.318073909,2.6698198538,-0.7436112734
H,0,2.1374510278,-1.1676690646,-0.2009954591
H,0,0.6381535277,-3.1566710291,-0.4138093337
H,0,-1.1024230625,-2.9737468616,-0.1097617898
H,0,3.755349118,-0.0166629498,-1.3426920733
H,0,4.5243037757,1.4533082788,-0.706006465
H,0,3.8192471332,0.2679405616,0.4145400047
H,0,-3.1834616534,3.4420737762,-0.7447792251
H,0,-1.6157870878,3.5984082384,0.0773331619
H,0,-1.6777267144,3.314322622,-1.6800470696

conformer 3
C,0,-1.1552321607,-0.5268589602,-0.1855252967
C,0,-1.1249963499,0.8479115276,-0.4201908848
C,0,0.0889444514,1.5040733066,-0.5805022581
C,0,1.2807893443,0.7939814331,-0.5085697027
C,0,1.2666000303,-0.5811487661,-0.2744940034
C,0,0.0448763122,-1.2240571439,-0.1153410789
C,0,0.0219289093,-2.6954854791,0.1578682006
Cl,0,0.0799866513,-3.0185953226,1.9358364322
O,0,2.4103137386,1.5176953988,-0.6814981279
O,0,-2.2306378095,1.621733379,-0.5110083458
C,0,3.6504926431,0.8372004884,-0.6114574378
C,0,-3.4915493706,0.9973093113,-0.3490840313
H,0,-2.086724658,-1.0564867443,-0.0572784045
H,0,0.1059925665,2.5683806711,-0.7658883422
H,0,2.1803528781,-1.1521395683,-0.2140341821
H,0,0.8840932784,-3.2006878117,-0.2621326325
H,0,-0.8904489118,-3.1609125692,-0.1969578685
H,0,3.7214626951,0.0739131787,-1.386947748
H,0,4.4166957596,1.5879063228,-0.7704091338
H,0,3.7883289872,0.376949952,0.367400636
H,0,-4.2329794112,1.7818139322,-0.4526513102
H,0,-3.6532905273,0.2392376537,-1.1160235556
H,0,-3.5776850466,0.5420818099,0.6380030759

conformer 4
C,0,-1.2359881377,-0.1859047738,-0.1564880503
C,0,-1.1039692211,1.1960484467,-0.252429851
C,0,0.1011504507,1.8204101781,0.0694442688
C,0,1.1758227794,1.0365347611,0.4893997829
C,0,1.0511983987,-0.3459358604,0.5877476925
C,0,-0.1558523935,-0.9486460243,0.263842867
C,0,-0.2992251448,-2.4333907643,0.3851954245
Cl,0,-0.8690047552,-2.8893141866,2.0382045976
O,0,2.3834378882,1.5493553796,0.818162763
O,0,-2.1987274301,1.8699627747,-0.6728442521
C,0,2.5640679062,2.9508921324,0.7287057885
C,0,-2.1143503842,3.2782341981,-0.7936214375
H,0,-2.1807384819,-0.6452011025,-0.4126735437
H,0,0.201422007,2.8890490414,-0.0089238367
H,0,1.8997433118,-0.9307064156,0.9150888977
H,0,0.6462884362,-2.9449303707,0.2465561932
H,0,-1.0393657827,-2.8269876914,-0.301945636
H,0,1.8819567176,3.4765722524,1.3977167659
H,0,3.5874750692,3.1433952334,1.0311113325
H,0,2.4148114268,3.2998214718,-0.2936676858
H,0,-3.086553937,3.6103672979,-1.1405747982
H,0,-1.8940291239,3.7407724932,0.1690352092
H,0,-1.3519126,3.5633735287,-1.5193354919

4-(Trifluoromethyl)benzyl chloride (15Cl)

conformer 1
C,0,0.1582637408,1.2022491442,0.3472465235
C,0,1.5069566287,1.2071930381,0.029874323
C,0,2.1733323385,0.0000012674,-0.1299715959
C,0,1.5069552914,-1.2071910182,0.0298679376
C,0,0.1582627217,-1.2022477785,0.3472400603
C,0,-0.5235990367,0.0000006984,0.5084424556
C,0,-1.9838383243,0.0000004094,0.8334471772
Cl,0,-2.9672451079,0.000003258,-0.6787949397
C,0,3.6454812793,-0.0000012156,-0.4213259853
H,0,-0.3692033156,2.1386522791,0.4705706488
H,0,2.0351563781,2.1414927063,-0.094883358
H,0,2.0351543473,-2.1414905005,-0.0948950288
H,0,-0.3692052837,-2.1386510519,0.4705590945

H,0,-2.2764233757,0.8880525058,1.3818859
H,0,-2.2764237331,-0.8880535419,1.3818827138
F,0,4.0239262209,1.0754948551,-1.1185846299
F,0,4.3749455406,-0.0000325566,0.7053738017
F,0,4.0239115399,-1.0754711084,-1.1186337583

conformer 2
C,0,-0.1621144927,1.222873385,0.3364498416
C,0,-1.5141911127,1.220489176,0.0239201658
C,0,-2.1757340144,0.0109767455,-0.1169717356
C,0,-1.5029025549,-1.1935631951,0.0543716587
C,0,-0.1552629726,-1.1815354408,0.3664466807
C,0,0.5237882143,0.0267250658,0.5096166366
C,0,1.9851584645,0.0344421591,0.8293812369
Cl,0,2.9627810295,-0.0335153127,-0.6852266864
C,0,-3.6424480858,-0.0313325981,-0.4315733276
H,0,0.3618194054,2.1627599307,0.4473252628
H,0,-2.0450037281,2.1515742127,-0.1078853775
H,0,-2.0301046113,-2.1312002035,-0.0557782413
H,0,0.3760255528,-2.1142832731,0.5007006723
H,0,2.2766712289,-0.8313109797,1.4130419145
H,0,2.2831992734,0.9432646392,1.339383724
F,0,-4.3593785491,-0.4933282993,0.6038668985
F,0,-3.9071904915,-0.8446947057,-1.4624864246
F,0,-4.1377575455,1.167975554,-0.7412288592

conformer 3
C,0,-0.493842423,-1.252901869,-0.9698428727
C,0,0.8472989122,-0.9564324314,-1.1325342249
C,0,1.5053791966,-0.2096376807,-0.1615246992
C,0,0.8349957005,0.2386017725,0.9651284681
C,0,-0.5107671513,-0.0636912453,1.1200394844
C,0,-1.1816635765,-0.8082534931,0.1576414333
C,0,-2.6362415425,-1.117173029,0.321010879
Cl,0,-3.6434912364,0.1516806428,-0.4727101035
C,0,2.9595784883,0.0980916761,-0.3681328894
F,0,3.1614993117,0.8166620981,-1.4819803327
F,0,3.4896886572,0.7886732059,0.6422914925
F,0,3.689151004,-1.0179539321,-0.5059427497
H,0,-1.013100288,-1.8342493487,-1.7199828828
H,0,1.3819469153,-1.3048739163,-2.0055582747
H,0,1.3544475697,0.814461736,1.7164409952
H,0,-1.0409627283,0.2811750286,1.9976117156
H,0,-2.9331772456,-1.1286793717,1.3633902201
H,0,-2.9071225636,-2.0540038431,-0.1524196584

4-Nitrobenzyl chloride (16Cl)

C,0,0.5600691096,0.2132398482,1.1696890611
C,0,-0.8103151507,0.0671155668,1.2965547178
C,0,-1.5685769039,-0.013610441,0.1413307581
C,0,-1.0135893787,0.0476467878,-1.1252616042
C,0,0.3585731935,0.1939413435,-1.2309412605
C,0,1.1516304749,0.2778383382,-0.089331703
C,0,2.6361635676,0.4184432348,-0.2150656349
Cl,0,3.4111797691,-1.2066939871,-0.2670466282
N,0,-3.0261424779,-0.1662539904,0.2648980867
O,0,-3.4993806276,-0.2168327522,1.3787971826
O,0,-3.6783615949,-0.2339730744,-0.75358515
H,0,1.1755268342,0.2794312843,2.0563523784
H,0,-1.2858608628,0.0187773903,2.2630681012
H,0,-1.6435195962,-0.0154777441,-1.9980912802
H,0,0.8175388705,0.2451445496,-2.2087296205
H,0,3.0666524142,0.9334407988,0.6359904894
H,0,2.9180823592,0.9192058469,-1.1340858937

Benzyl carbocations (14^+–16^+)

3,5-Dimethoxybenzyl cation (14^+)

conformer 1
C,0,-1.2388488277,-0.5494622035,0.136062987
C,0,-1.2555364374,0.8187331286,-0.0263182946
C,0,-0.0389547773,1.4935963799,-0.2003500832
C,0,1.2055155498,0.8480269147,-0.2185729931
C,0,1.2466167007,-0.519877844,-0.0580989996
C,0,0.0184126193,-1.222553277,0.1201511062
C,0,0.0470268779,-2.5773406401,0.2800136923
O,0,-2.3475434113,1.5885006067,-0.0346447424
O,0,2.264465479,1.6433971073,-0.3949301393
C,0,3.549317357,1.0323911611,-0.4203808914
C,0,-3.6059457435,0.9472218182,0.1385760255
H,0,-2.1383424082,-1.128576871,0.2743225881
H,0,-0.0616571779,2.5684771702,-0.3271842
H,0,2.1701147699,-1.0772935774,-0.0622498631
H,0,0.9824386867,-3.120633104,0.2732594338
H,0,-0.8649709477,-3.142622718,0.4175771753
H,0,4.2588989833,1.836736075,-0.571014994
H,0,3.7531334661,0.5319246193,0.5258872051
H,0,3.6175134155,0.320395382,-1.2424772131
H,0,-3.6484699878,0.443822716,1.104087341
H,0,-4.3491390018,1.734274116,0.1014287607
H,0,-3.7840931847,0.2322940399,-0.6642769027

conformer 2
C,0,-1.2404389464,-0.5188716901,0.1243145677
C,0,-1.3260490259,0.8459010117,0.0042608994
C,0,-0.1466444541,1.6123972252,-0.1169079131
C,0,1.1277062367,1.0419118803,-0.1209522011
C,0,1.2353187319,-0.3318211127,-0.0010484896
C,0,0.0574146413,-1.1146357492,0.1215330695
C,0,0.1847295436,-2.4693599121,0.2388473608
O,0,-2.4582269448,1.5557538037,-0.0105617925
O,0,2.2630585324,1.7379946966,-0.2338050173
C,0,2.182754648,3.1533267005,-0.3586752139
C,0,-3.6822939712,0.8406743875,0.1078996875
H,0,-2.1074436201,-1.1529152052,0.2197899639
H,0,-0.2747827164,2.6816749485,-0.2082946118
H,0,2.2070936236,-0.804313681,-0.0007340187
H,0,1.1590810238,-2.9394045987,0.2388344133
H,0,-0.6849080026,-3.1059972318,0.334680629
H,0,3.2056180105,3.5014231049,-0.4350333253
H,0,1.6325725447,3.429765754,-1.2575901769
H,0,1.7104071354,3.5910330024,0.5202263889
H,0,-3.7201893951,0.3040886593,1.0556016193

H,0,-4.4679574998,1.5855508106,0.0747306788
H,0,-3.7979820953,0.1429201959,-0.7211085156

conformer 3
C,0,-1.2192612715,-0.4388526746,0.0528352952
C,0,-1.3079247847,0.9242160532,-0.1280179129
C,0,-0.1305305906,1.6916593396,-0.1516746663
C,0,1.1427924633,1.116842848,0.0033099667
C,0,1.2488636335,-0.2448575725,0.18509615
C,0,0.0639829587,-1.0300182741,0.2105532595
C,0,0.1605774494,-2.3815957316,0.3904344929
O,0,-2.5309012712,1.446029383,-0.2729821684
O,0,2.2779356267,1.8240055465,-0.0152902771
C,0,2.206875852,3.232755856,-0.2008833256
C,0,-2.6608747494,2.8501464051,-0.4617519575
H,0,-2.1107456292,-1.0481208927,0.0743702361
H,0,-0.2067430124,2.7580465356,-0.2936001512
H,0,2.2169883779,-0.707960162,0.3062829819
H,0,1.122752897,-2.8609086632,0.5133263159
H,0,-0.7227204939,-3.0059623463,0.4144315997
H,0,3.2311458371,3.5846604482,-0.1808750827
H,0,1.7559282852,3.4728727354,-1.1633547376
H,0,1.6432323553,3.700289693,0.606011432
H,0,-2.1531912312,3.1655997301,-1.3728543794
H,0,-3.7237208708,3.0380002285,-0.5535956884
H,0,-2.2658878313,3.3930415149,0.3965086174

4-(Trifluoromethyl)benzyl cation (15^+)

conformer 1
C,0,0.6967959296,-0.5161233395,1.2088169955
C,0,-0.6743421292,-0.4669498112,1.2109832303
C,0,-1.3360761847,-0.3175532157,-0.0069480797
C,0,-0.673521876,-0.2148008099,-1.2352081238
C,0,0.6937062492,-0.2624918271,-1.2503889668
C,0,1.406927181,-0.4147033514,-0.0231447221
C,0,2.7735042732,-0.4637015345,-0.0254234617
C,0,-2.8526501193,-0.2594836912,-0.0402738212
F,0,-3.3349089455,-1.2457810753,-0.7930946861
F,0,-3.2579229672,0.8912774187,-0.5728128353
F,0,-3.3891349856,-0.364630159,1.1672976563
H,0,1.2505781966,-0.630992437,2.1295491486
H,0,-1.2329285943,-0.5416110136,2.1304201383
H,0,-1.2377289049,-0.1002868209,-2.1488509927
H,0,1.245279662,-0.1869075859,-2.1763277276
H,0,3.3344687314,-0.388817612,-0.947863068
H,0,3.3291524839,-0.5787141292,0.8960353168

conformer 2
C,0,1.2752067195,0.064962355,-0.6928501535
C,0,1.2565896664,-0.0262959898,0.6740832384
C,0,0.0230748475,-0.1396655014,1.3200298973
C,0,-1.198559691,-0.1645956322,0.6427910829
C,0,-1.1925731867,-0.0740460161,-0.7243018924
C,0,0.0476631501,0.0435884948,-1.4192222106
C,0,0.0597622031,0.137491464,-2.7834107023
C,0,0.0064480601,-0.1879976697,2.8379014404
F,0,-1.0368671851,-0.8708236328,3.2943910014
F,0,-0.0694722022,1.0494261842,3.3258492212
F,0,1.1078935425,-0.7500146644,3.3217315524
H,0,2.2070263977,0.1527207989,-1.2327762896
H,0,2.1717447956,-0.0160926726,1.2455791499
H,0,-2.1232945156,-0.2580337556,1.1908379149
H,0,-2.1143341768,-0.090697193,-1.287852495
H,0,-0.8605972972,0.1243385606,-3.3525130886
H,0,0.989939872,0.2285748702,-3.3289246668

4-Nitrobenzyl cation (16^+)

C,0,1.4178841014,-0.0772936234,0.1539225424
C,0,0.8730482043,0.6974101411,-0.8391035385
C,0,-0.5124920113,0.7310783108,-0.933916398
C,0,-1.3938147298,0.0457713665,-0.1071943328
C,0,-0.8515332742,-0.7296668491,0.8866563953
C,0,0.5638166206,-0.8036509864,1.0332060679
C,0,1.1068503577,-1.5779722975,2.0256860959
N,0,-1.1045950194,1.5753677851,-2.0160787851
O,0,-2.3065181778,1.6016709823,-2.0947446002
O,0,-0.3367131898,2.1679109294,-2.7307462351
H,0,2.4889245706,-0.144020608,0.2783008925
H,0,1.479489064,1.263511496,-1.526636397
H,0,-2.4575650075,0.131754899,-0.2554672958
H,0,-1.4852967491,-1.2864617911,1.5614700003
H,0,0.4771890292,-2.1380213896,2.70473337
H,0,2.1789602254,-1.648825361,2.1552772135

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