Electronic Supplementary Material (ESI) for Green Chemistry.

Selective reductive amination of aldehydes from nitro compounds catalyzed by molybdenum sulfide clusters

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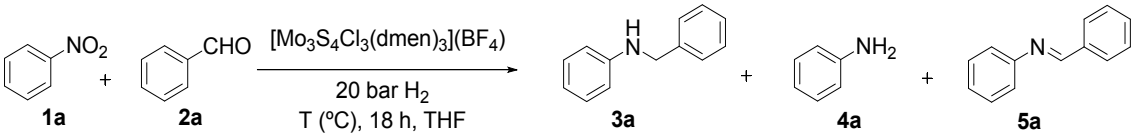
1. Materials and Methods.

Nitro compounds, aldehydes and internal standards were obtained from commercial sources and used as received. Organic solvents were dried by standard methods before use. The ^{1}H-NMR and ^{13}C-NMR spectra of the isolated anilines were recorded on a Bruker AV 300 or Bruker AV 400 spectrometer. All chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (J) in Hz. For ^{1}H-NMR all chemical shifts are reported relative to tetramethylsilane (δ 0.0 ppm in $CDCl_3$) or d-solvent peaks (δ 77.16 ppm $CDCl_3$) for ^{13}C-NMR. All measurements were carried out at room temperature unless otherwise stated. The GC yields were determined by GC-FID using *n*-hexadecane as an internal standard. Gas chromatography analyses were performed on an Agilent 7820A GC System equipped with a FID and a capillary column Agilent (HP-5, 30m x 0.32 mm x 0.25 μm). Mass determination was carried out on a GC-Mass Agilent 5973 Network equipped with a mass selective detector.

Electrospray mass spectrum of the catalyst after the catalytic reaction was recorded with a Quattro LC (quadrupole-hexapole-quadrupole) mass spectrometer with an orthogonal Z-spray electrospray interface (Micromass, Manchester, UK). The cone voltage was set at 20 V using CH_3CN as the mobile phase solvent. Sample solutions have been infused via syringe pump directly connected to the ESI source at a flow rate of 10 μL/min and a capillary voltage of 3.5 kV was used in the positive scan mode. Nitrogen was employed as drying and nebulizing gas. Isotope experimental patterns were compared with theoretical patterns obtained using the MassLynx 4.1 program.[2] ^{1}H spectrum of the reaction mixture was recorded on a Bruker Avance III HD 300 MHz using CD_3CN as solvent.

2. Advanced experimental details for the optimization of the reaction conditions.

Table SI1. Influence of the temperature.[a]

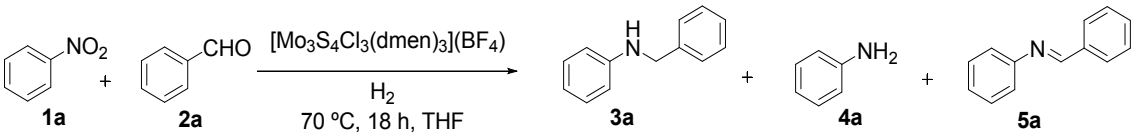


1a **2a** **3a** **4a** **5a**

Entry	Temperature [ºC]	Conversion [%][b]	Yield **3a** [%][b]	Yield **4a** [%][b]	Yield **5a** [%][b]
1	100	>99	99	1	0
2	70	>99	99	0	0
3	60	>99	42	17	38

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), H_2 (20 bar), catalyst (5 mol%), THF (2 mL), 18 h. [b] Determined by GC analysis using *n*-hexadecane as an internal standard.

Table SI2. Variation of the pressure of H_2.[a]

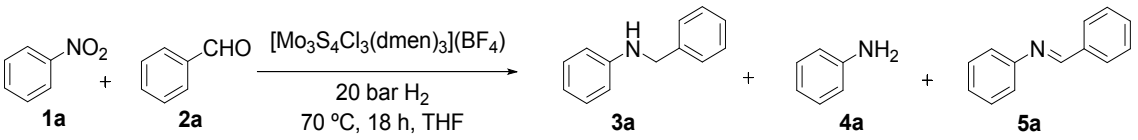


1a **2a** **3a** **4a** **5a**

Entry	Pressure [bar]	Conversion [%][b]	Yield **3a** [%][b]	Yield **4a** [%][b]	Yield **5a** [%][b]
1	20	>99	99	0	0
2	15	>99	65	16	17

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), catalyst (5 mol%), THF (2 mL), 18 h, 70ºC. [b] Determined by GC analysis using *n*-hexadecane as an internal standard.

Table SI3. Catalyst loading variation.[a]



Entry	Catalyst loading [mol%]	Conversion [%][b]	Yield **3a** [%][b]	Yield **4a** [%][b]	Yield **5a** [%][b]
1	0	0	0	0	0
2	1	73	0	20	51
3	2	>99	48	18	30
4	3	>99	92	2	5
5	4	>99	95	0	3
6	5	>99	99	0	0
7[c]	5	48	0	7	38

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), H_2 (20 bar), THF (2 mL), 18 h, 70 ºC. [b] Determined by GC analysis using *n*-hexadecane as an internal standard. [c] Reaction time: 4 h.

3. Characterization of the catalyst after the catalytic reaction.

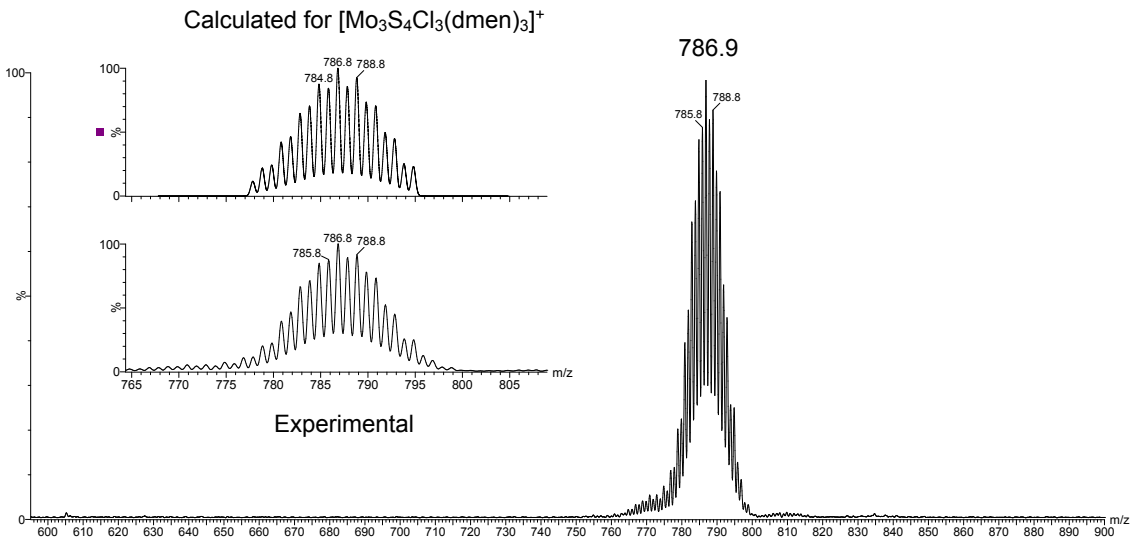


Figure SI1. ESI mass spectrum of the catalyst in CH_3CN at 20 V after the catalytic reaction between **1a** and **2a**.

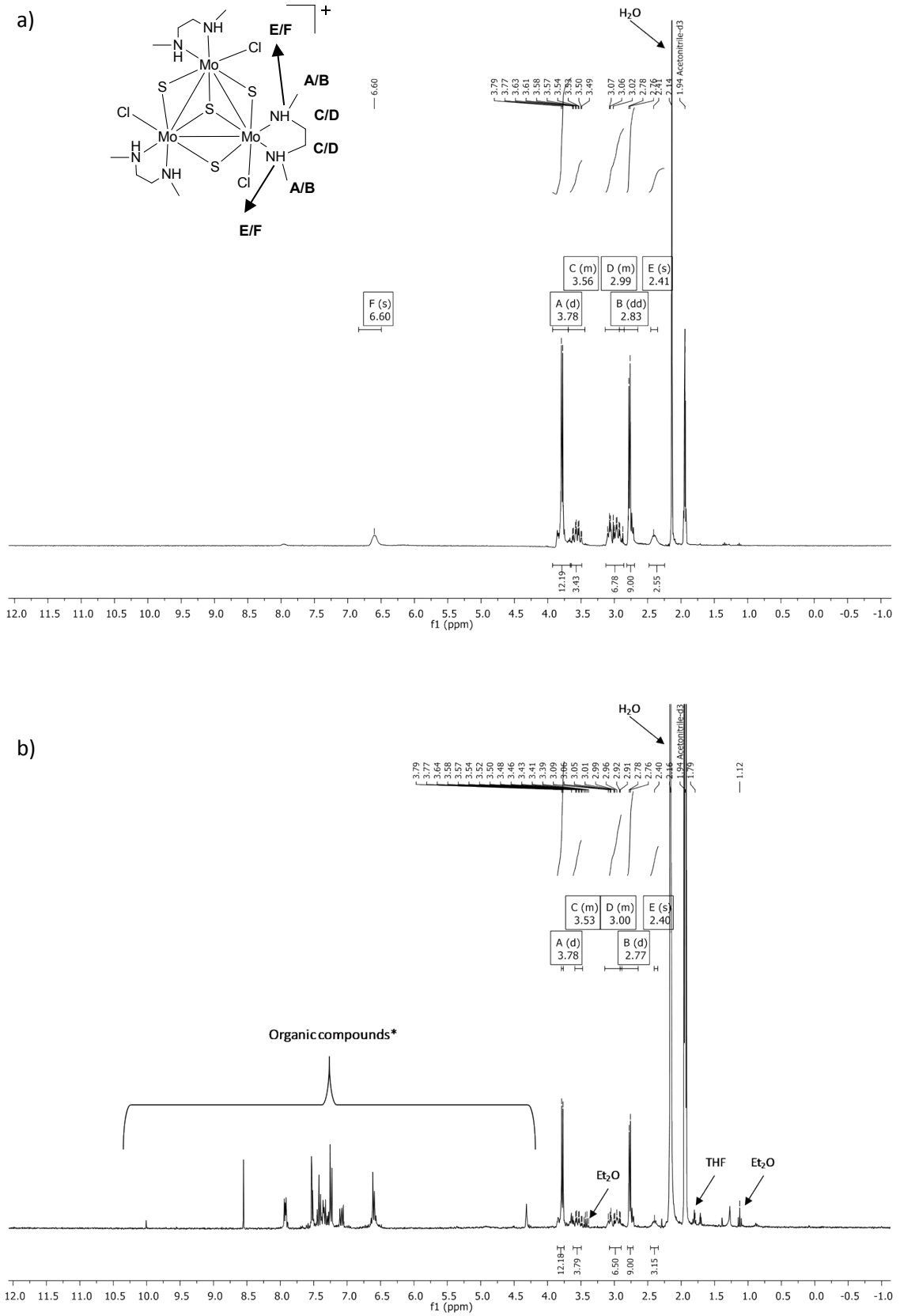
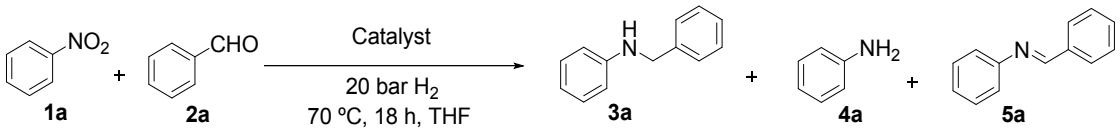


Figure SI2. (a) ^{1}H NMR spectrum of the $[Mo_3S_4Cl_3(dmen)_3](BF_4)$ cluster in CD_3CN; (b) ^{1}H NMR spectrum of the reaction mixture after the catalytic process. For this last experiment, the mixture was taken to dryness, washed with diethyl ether, dried and redissolved in CD_3CN. *Organic compounds: *N*-benzylaniline (**3a**), benzaldehyde (**2a**) and aniline (**4a**).

4. Catalyst recycling experiments for the reductive amination between nitrobenzene and benzaldehyde.



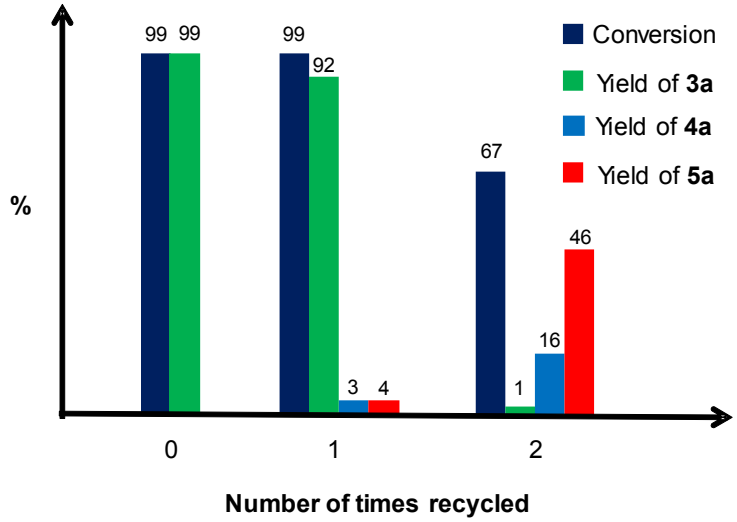
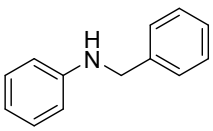
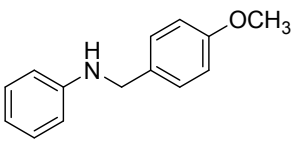


Figure SI3. Recycling of the catalyst for the reductive amination reaction.
Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), catalyst, H_2 (20 bar), THF (2 mL), 18 h, 70 ºC. Conversions of **1a** and yields of **3a** were determined by GC using *n*-hexadecane as standard (15 µL).

5. Characterization data of isolated products.

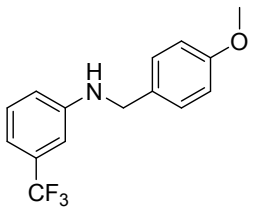


N-Benzylaniline[3]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 5H), 7.24 – 7.18 (m, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 2H), 4.36 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.01, 138.66, 129.43, 128.76, 127.97, 127.55, 118.79, 114.03, 49.18; MS (EI): m/z (rel. Int) 183.

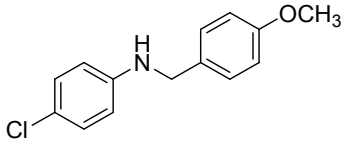


N-(4'-Methoxybenzyl)aniline[3]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.6 Hz, 2H), 7.21 – 7.11 (m, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.64 – 6.58 (m, 1H), 4.22 (s, 2H),

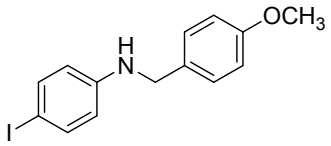
3.92 (br s, 1H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.96, 148.32, 131.53, 129.35, 128.90, 117.59, 114.13, 112.94, 55.39, 47.89; MS (EI): m/z (rel. Int) 213.



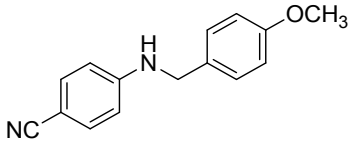
N-(4-methoxybenzyl)-3-(trifluoromethyl)aniline: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 – 7.10 (m, 3H), 6.90 – 6.72 (m, 4H), 6.67 – 6.61 (m, 1H), 4.16 (s, 2H), 4.04 (br s, 1H), 3.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.18, 148.39, [132.28, 131.86, 131.44, 131.02 (q, $^{2}J_{C-F}$ = 32 Hz)], 130.67, [129.90, 126.29, 122.68, 119.14 (q, $^{1}J_{C-F}$ = 272 Hz)], 129.75, 128.96, 115.84, 114.27, [114.02, 113.97, 113.92, 113.87 (q, $^{3}J_{C-F}$ = 4 Hz)], [109.21, 109.16, 109.11, 109.06 (q, $^{3}J_{C-F}$ = 4 Hz)], 55.40, 47.71; MS (EI): m/z (rel. int.) 281.



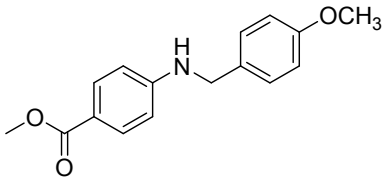
N-(4'-Methoxybenzyl)-4-Chloroaniline: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.6 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 6.45 (d, *J* = 8.8 Hz, 2H), 4.13 (s, 2H), 3.93 (s, 1H), 3.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.06, 146.82, 131.01, 129.16, 128.84, 122.12, 114.20, 114.02, 55.42, 47.95; MS (EI): m/z (rel. int.) 247.



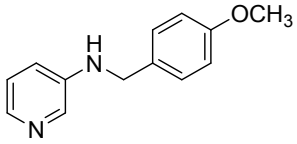
N-(4'-Methoxybenzyl)-4-Iodoaniline[3]: Isolated yield: X %. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.41 (d, *J* = 8.8 Hz, 2H), 4.22 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.10, 147.81, 137.91, 130.91, 128.84, 115.20, 114.23, 78.17, 55.45, 47.70; MS (EI): m/z (rel. int.) 339.



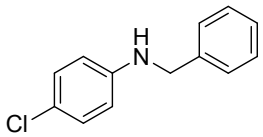
4-(4-Methoxybenzylamino) benzonitrile: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 2H), 7.24 – 7.12 (m, 2H), 6.86 – 6.76 (m, 2H), 6.55 – 6.45 (m, 2H), 4.49 (s, 1H), 4.21 (s, 2H), 3.72 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.27, 151.22, 133.80, 129.84, 128.79, 120.53, 114.35, 112.47, 99.02, 55.42, 47.09; MS (EI): m/z (rel. int.) 238.



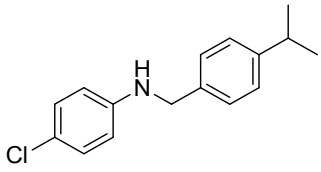
Methyl 4-((4-methoxybenzyl)amino)benzoate[4]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.49 (d, *J* = 8.8 Hz, 2H), 4.38 (br s, 1H), 4.21 (s, 2H), 3.75 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.40, 159.15, 151.90, 131.64, 130.43, 128.85, 118.61, 114.25, 111.70, 55.40, 51.61, 47.23; MS (EI): m/z (rel. int.) 271.



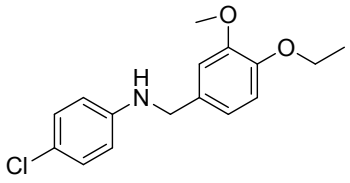
N-(4-methoxybenzyl)pyridin-3-amine[5]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J = 2 Hz, 1H), 7.95 (dd, *J* = 4.7, 1.3 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.06 (dd, *J* = 8.0 Hz, 4.7 Hz, 1H), 6.91 – 6.85 (m, 3H), 4.26 (s, 2H), 4.04 (br s, 1H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.13, 144.18, 138.90, 136.21, 130.57, 128.86, 123.83, 118.69, 114.25, 55.42, 47.46; MS (EI): m/z (rel. int.) 214.



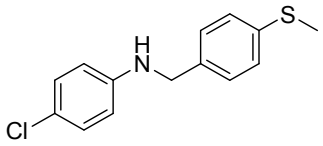
N-benzyl-4-chloroaniline[6]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 4H), 7.33 – 7.29 (m, 1H), 7.17 – 7.09 (m, 2H), 6.60 – 6.52 (m, 2H), 4.32 (s, 2H), 4.08 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.77, 139.06, 129.18, 128.82, 127.53, 127.48, 122.20, 114.03, 48.45; MS (EI): m/z (rel. int.) 217.



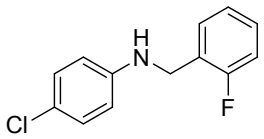
4-chloro-N-(4-isopropylbenzyl)aniline[7]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 – 7.07 (m, 4H), 7.07 – 6.95 (m, 2H), 6.50 – 6.39 (m, 2H), 4.15 (s, 2H), 3.90 (br s, 1H), 3.05 – 2.45 (m, 1H), 1.16 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.23, 146.88, 136.36, 129.16, 127.64, 126.86, 122.08, 113.98, 48.23, 33.92, 24.14; MS (EI): m/z (rel. int.) 259.



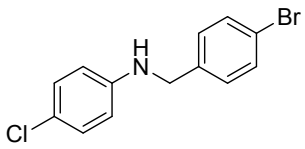
4-chloro-N-(4-ethoxy-3-methoxybenzyl)aniline: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 – 6.92 (m, 2H), 6.86 – 6.67 (m, 3H), 6.54 – 6.36 (m, 2H), 4.11 (s, 2H), 4.05 – 3.94 (m, 2H), 3.82 (s, 1H), 3.75 (s, 3H), 1.36 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.55, 147.68, 146.84, 131.44, 129.08, 122.07, 119.70, 113.99, 112.81, 111.06, 64.44, 55.97, 48.32, 14.89; MS (EI): m/z (rel. int.) 291.



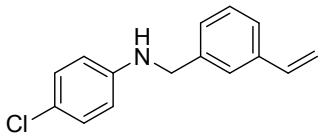
4-chloro-N-(4-(methylthio)benzyl)aniline: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 – 7.09 (m, 4H), 7.10 – 6.89 (m, 2H), 6.61 – 6.35 (m, 2H), 4.18 (s, 2H), 3.96 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.68, 137.56, 135.99, 129.21, 128.07, 127.14, 122.29, 114.08, 48.03, 16.13; MS (EI): m/z (rel. int.) 263.



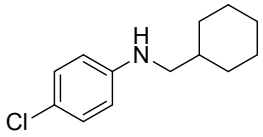
4-chloro-N-(2-fluorobenzyl)aniline: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.21 (m, 1H), 7.22 – 7.12 (m, 1H), 7.06 – 6.99 (m, 3H), 6.99 – 6.93 (m, 1H), 6.52 – 6.44 (m, 2H), 4.29 (s, 2H), 4.00 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ [162.64, 159.38 (d, $^{1}J_{C\text{-}F}$ = 246.0 Hz)], 146.43, [129.48, 129.42 (d, $^{3}J_{C\text{-}F}$ = 4.4 Hz)], 129.21, [129.16, 129.06 (d, $^{3}J_{C\text{-}F}$ = 8.2 Hz)], [126.06, 125.86 (d, $^{2}J_{C\text{-}F}$ = 14.4 Hz)], [124.39, 124.34 (d, $^{4}J_{C\text{-}F}$ = 3.5 Hz)], 122.44, [115.69, 115.41 (d, $^{2}J_{C\text{-}F}$ = 21.3 Hz)], 114.33, [42.10, 42.04 (d, $^{3}J_{C\text{-}F}$ = 4.3 Hz)]; MS (EI): m/z (rel. int.) 235.



N-(4-bromobenzyl)-4-chloroaniline: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.9 Hz, 2H), 6.52 (d, *J* = 8.9 Hz, 2H), 4.27 (s, 2H), 4.10 (s, 1H).^{13}C NMR (75 MHz, $CDCl_3$) δ 146.42, 138.14, 131.89, 129.22, 129.08, 122.49, 121.19, 114.09, 77.16, 47.79; MS (EI): m/z (rel. int.) 296.



4-chloro-N-(3-vinylbenzyl)aniline: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (qd, *J* = 7.5, 3.7 Hz, 4H), 7.02 – 6.94 (m, 2H), 6.58 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.48 – 6.37 (m, 2H), 5.63 (d, *J* = 18.4 Hz, 1H), 5.14 (d, *J* = 10.9 Hz, 1H), 4.16 (s, 2H), 3.93 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.66, 139.26, 138.04, 136.64, 129.12, 128.95, 126.91,125.30, 122.18, 114.31, 113.96, 48.35; MS (EI): m/z (rel. int.) 243.



4-chloro-N-(cyclohexylmethyl)aniline: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 – 7.07 (m, 2H), 6.54 – 6.47 (m, 2H), 3.68 (br s, 1H), 2.92 (d, *J* = 6.7 Hz, 2H), 1.83 – 1.70 (m, 4H), 1.62 – 1.49 (m, 1H), 1.34 – 1.12 (m, 4H), 1.04 – 0.88 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.31, 129.12, 121.45, 113.76, 50.81, 37.61, 31.38, 26.66, 26.07; MS (EI): m/z (rel. int.) 223.

5. References.

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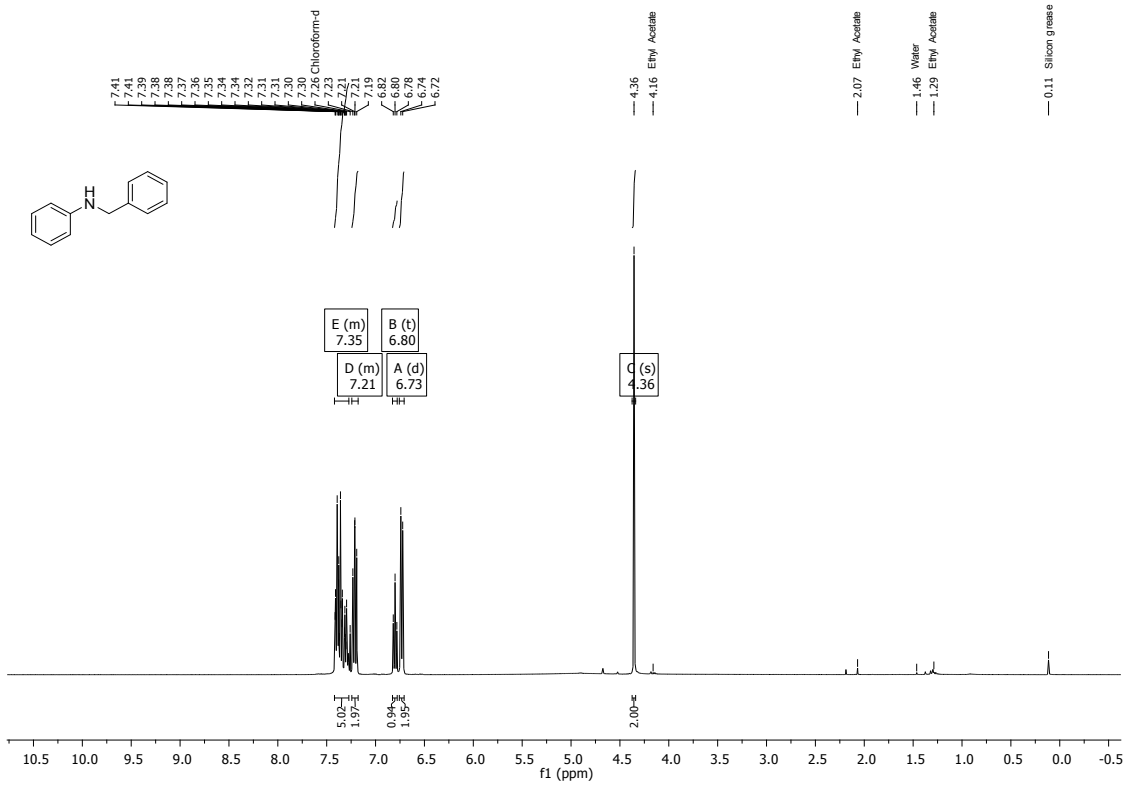
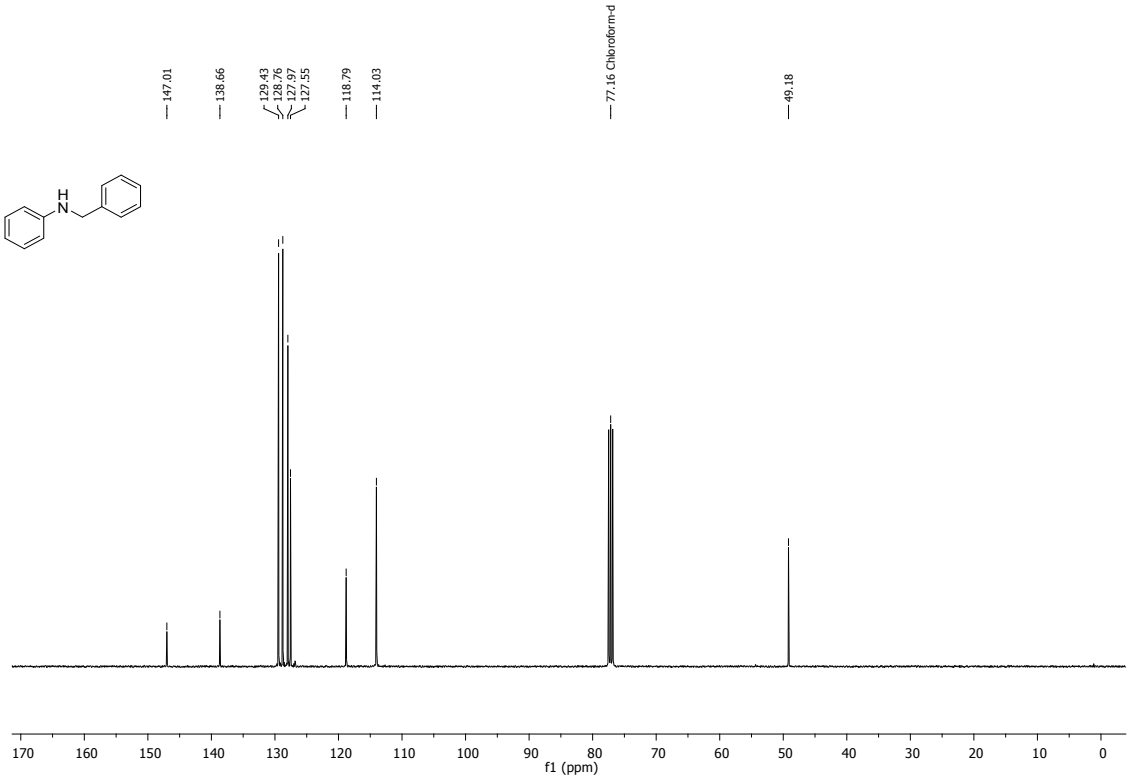
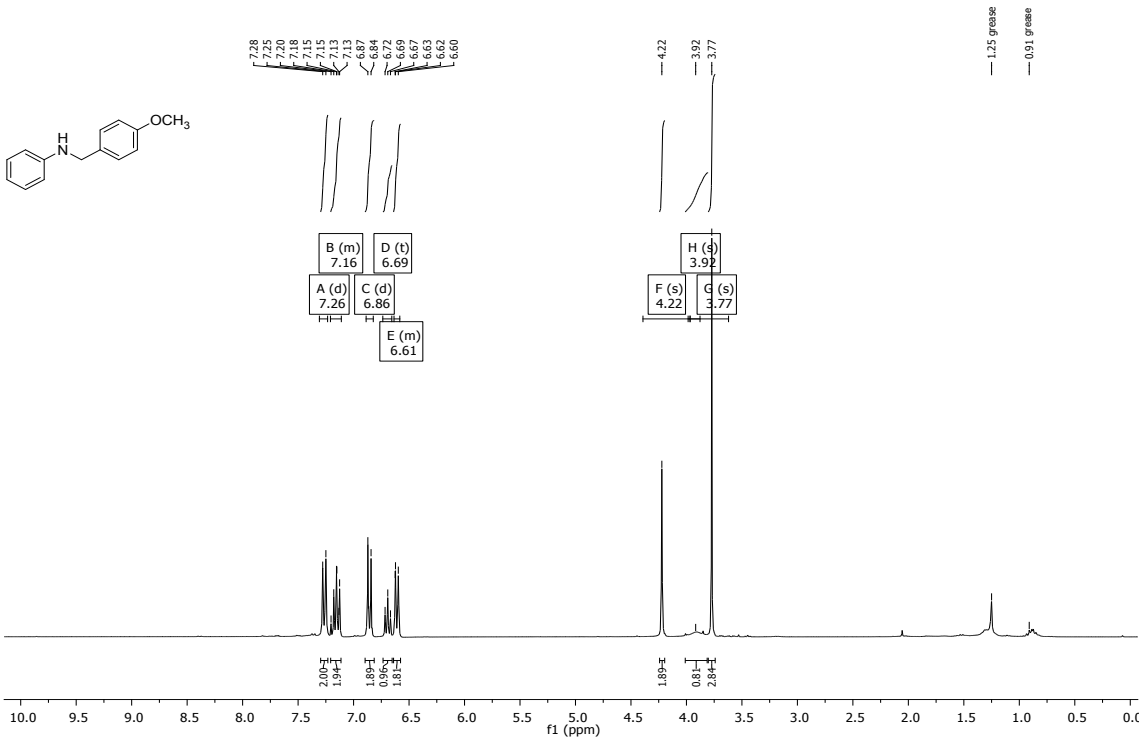
6. ^{1}H NMR and ^{13}C NMR spectra of isolated products.



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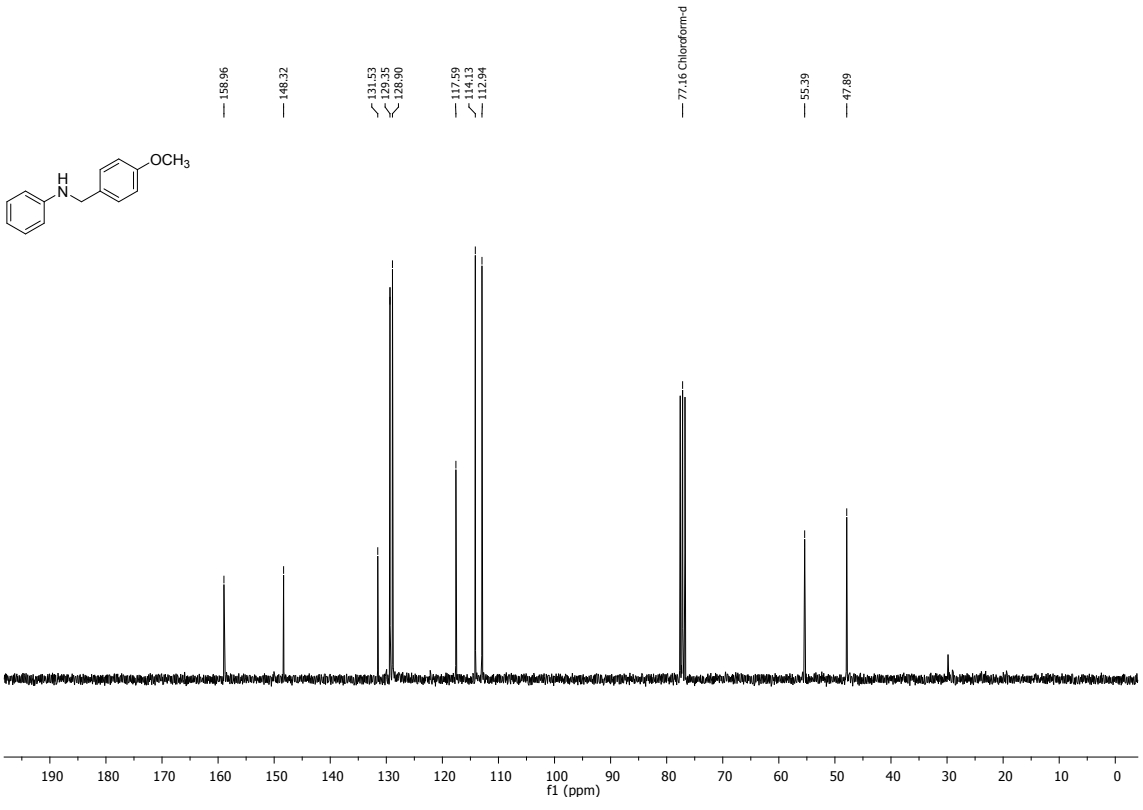
7.25
7.20
7.18
7.15
7.15
7.13
7.13
6.87
6.84
6.72
6.69
6.67
6.63
6.62
6.60
4.22
3.92
3.77
1.25 grease
0.91 grease
OCH3
H
N
B (m)
7.16
D (t)
6.69
H (s)
3.92
A (d)
7.26
C (d)
6.86
F (s)
4.22
G (s)
3.77
E (m)
6.61
2.00
1.94
1.89
0.96
1.81
1.89
0.81
2.84
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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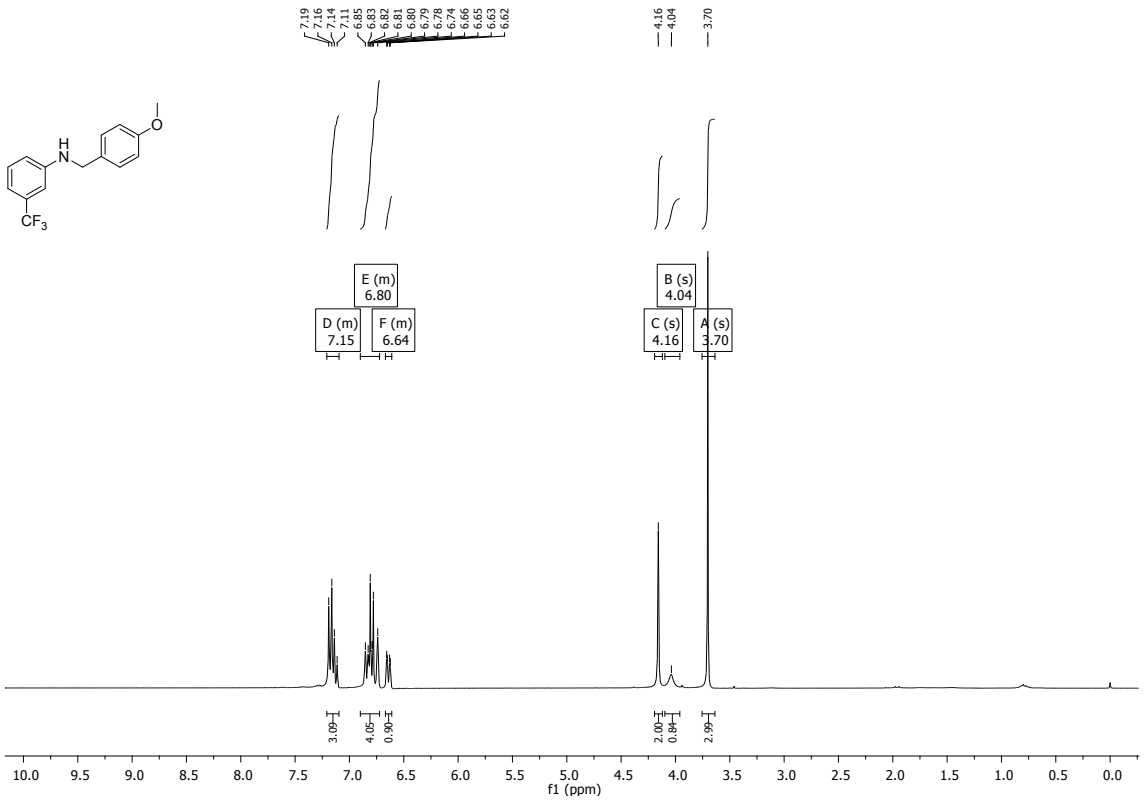
148.32
131.53
129.35
128.90
117.59
114.13
112.94
77.16 Chloroform-d
55.39
47.89
OCH3
H
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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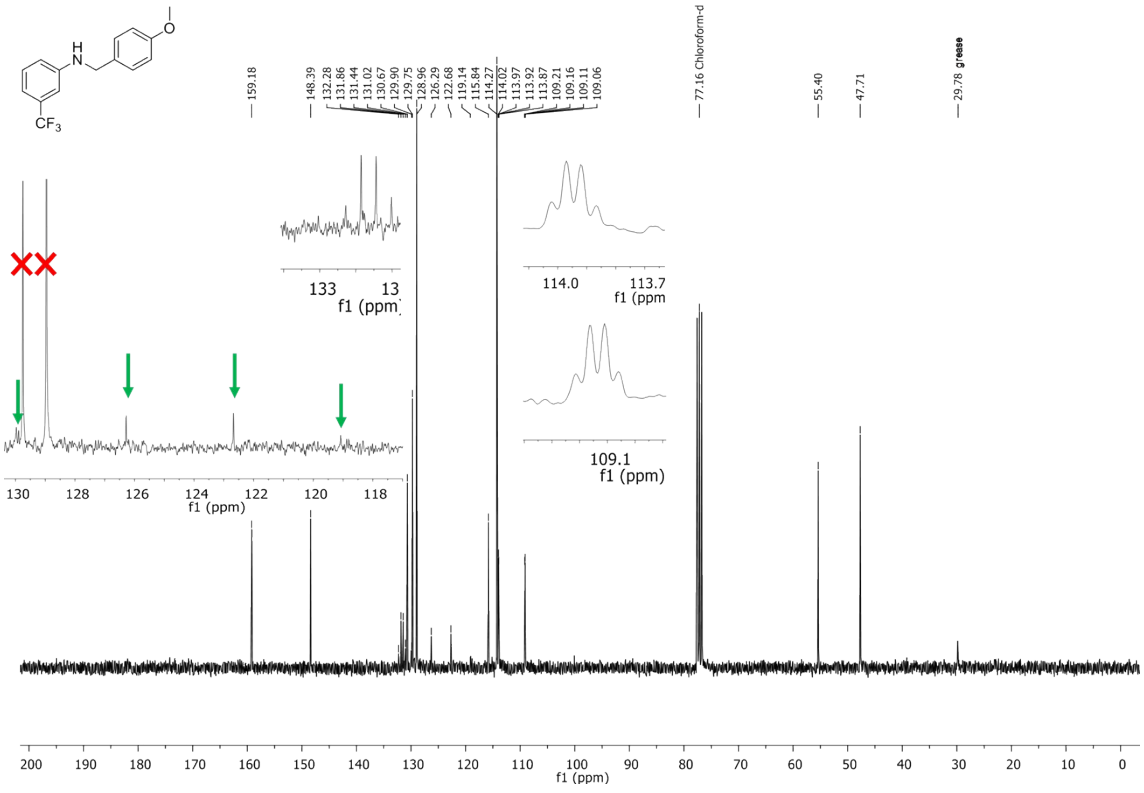
7.16
7.14
7.11
6.85
6.83
6.82
6.81
6.80
6.79
6.78
6.74
6.66
6.65
6.63
6.62
4.16
4.04
3.70
E (m)
6.80
D (m)
7.15
F (m)
6.64
B (s)
4.04
C (s)
4.16
A (s)
3.70
3.09
4.05
0.90
2.00
0.84
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.90
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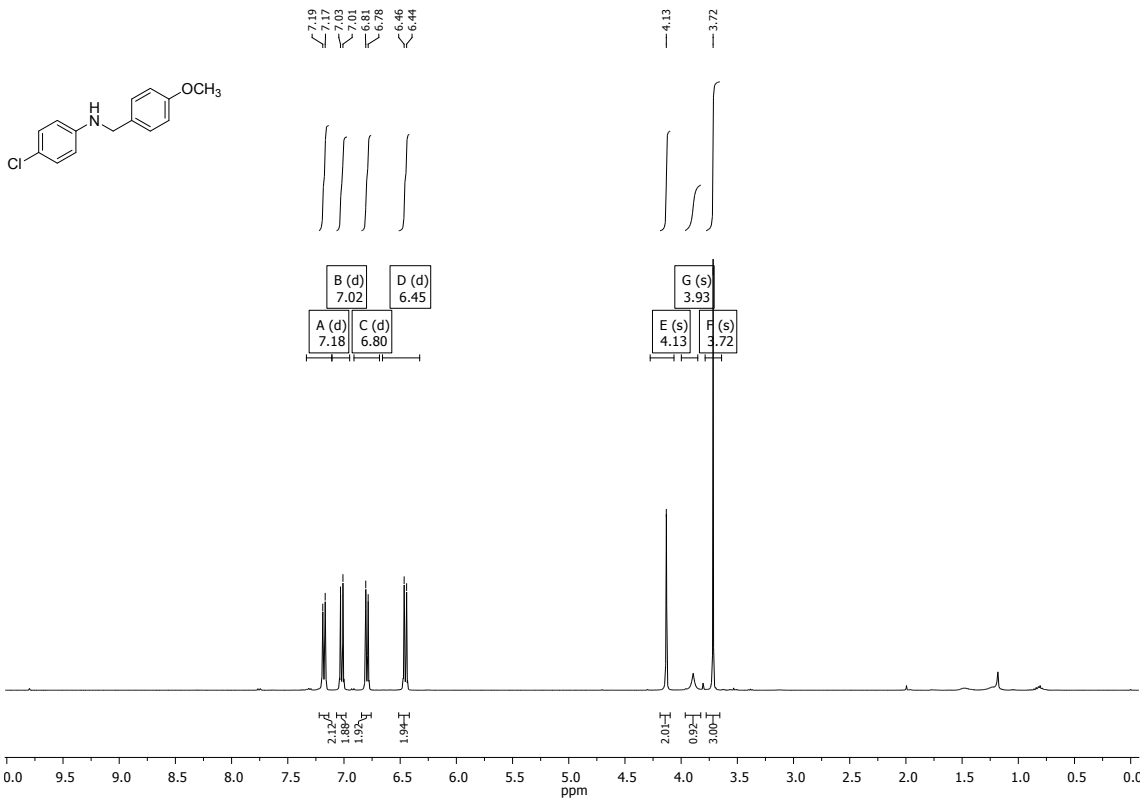
122.68
119.14
115.84
114.27
114.02
113.97
113.92
113.87
109.21
109.16
109.11
109.06
77.16 Chloroform-d
55.40
47.71
29.78 grease
133
13
f1 (ppm)
114.0
113.7
f1 (ppm)
109.1
f1 (ppm)
130 128 126 124 122 120 118
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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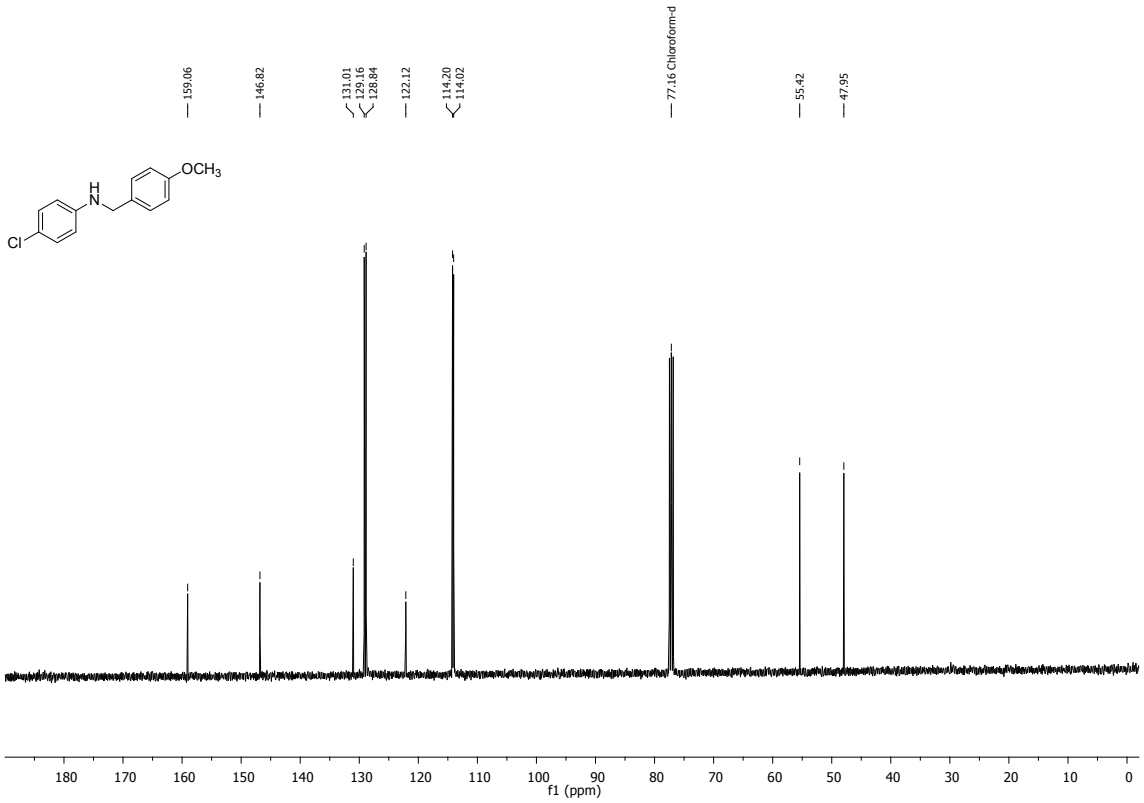
7.17
7.03
7.01
6.81
6.78
6.46
6.44
4.13
3.72
OCH3
H
N
Cl
B (d)
7.02
D (d)
6.45
G (s)
3.93
A (d)
7.18
C (d)
6.80
E (s)
4.13
F (s)
3.72
2.12
1.88
1.92
1.94
2.01
0.92
3.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm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146.82
131.01
129.16
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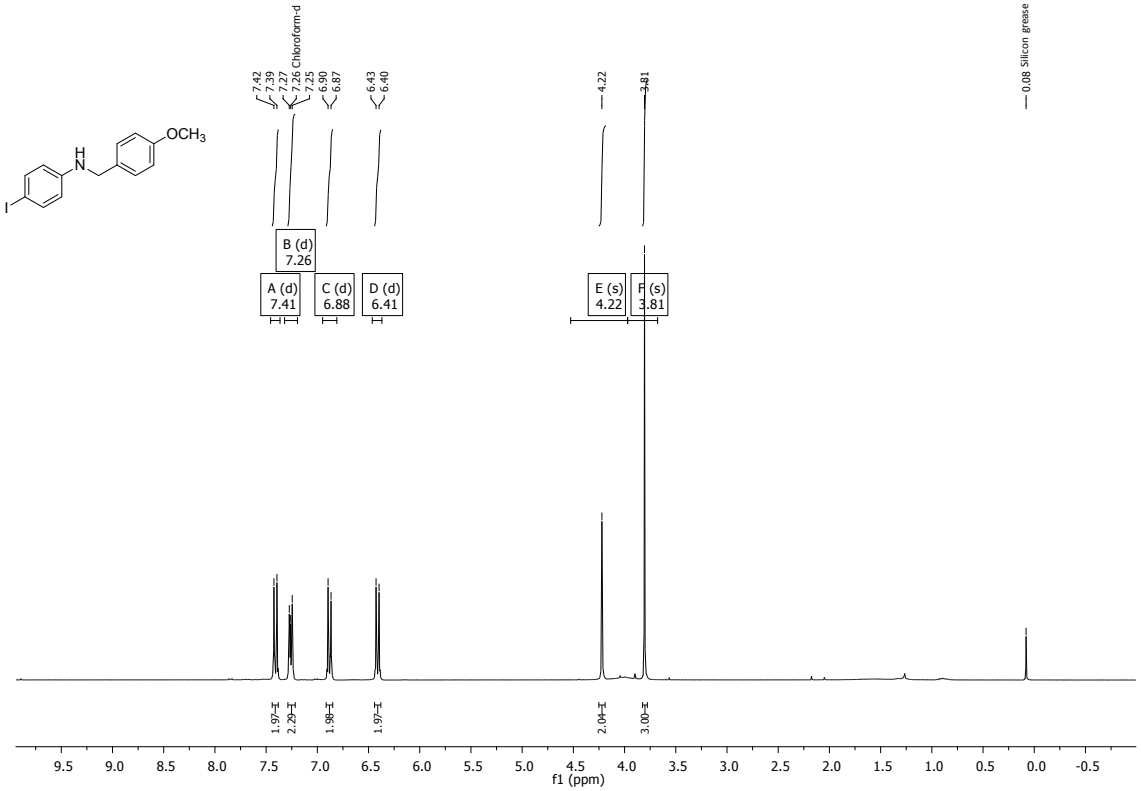
122.12
114.20
114.02
77.16 Chloroform-d
55.42
47.95
OCH3
H
N
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.25
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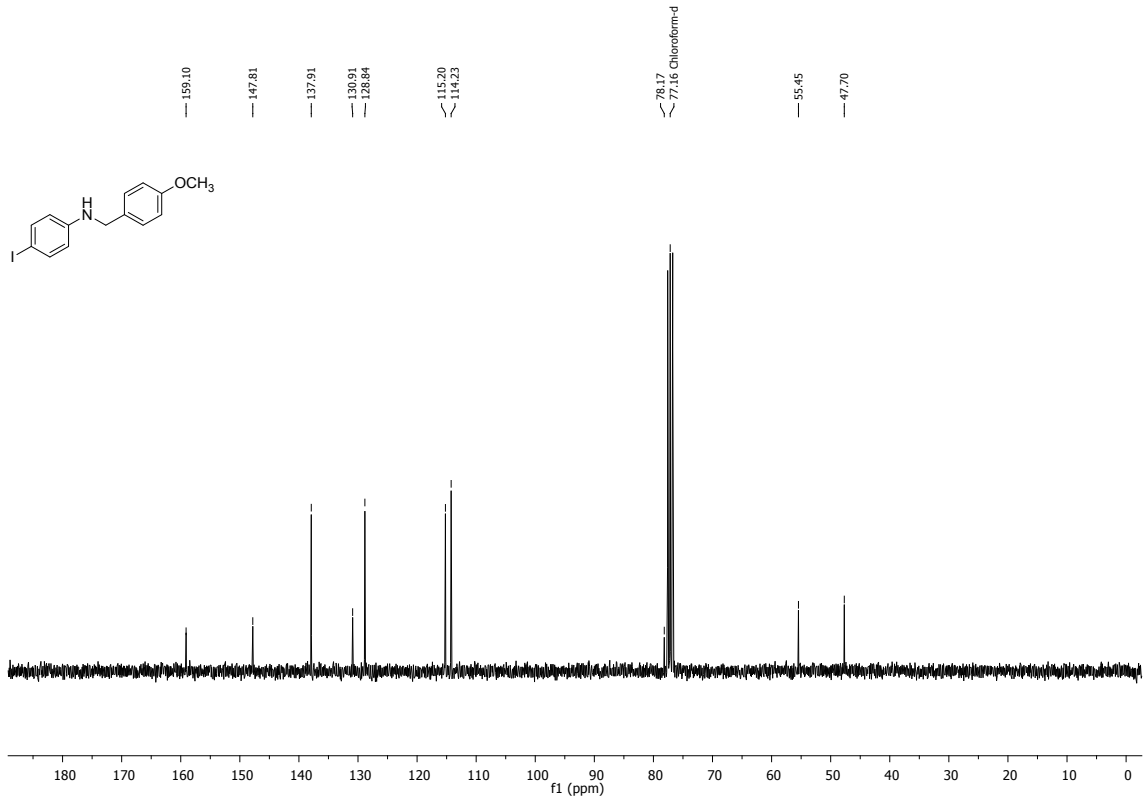
6.43
6.40
4.22
3.81
0.08 Silicon grease
OCH3
H
N
I
B (d)
7.26
A (d)
7.41
C (d)
6.88
D (d)
6.41
E (s)
4.22
F (s)
3.81
1.97
2.29
1.98
1.97
2.04
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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114.23
78.17
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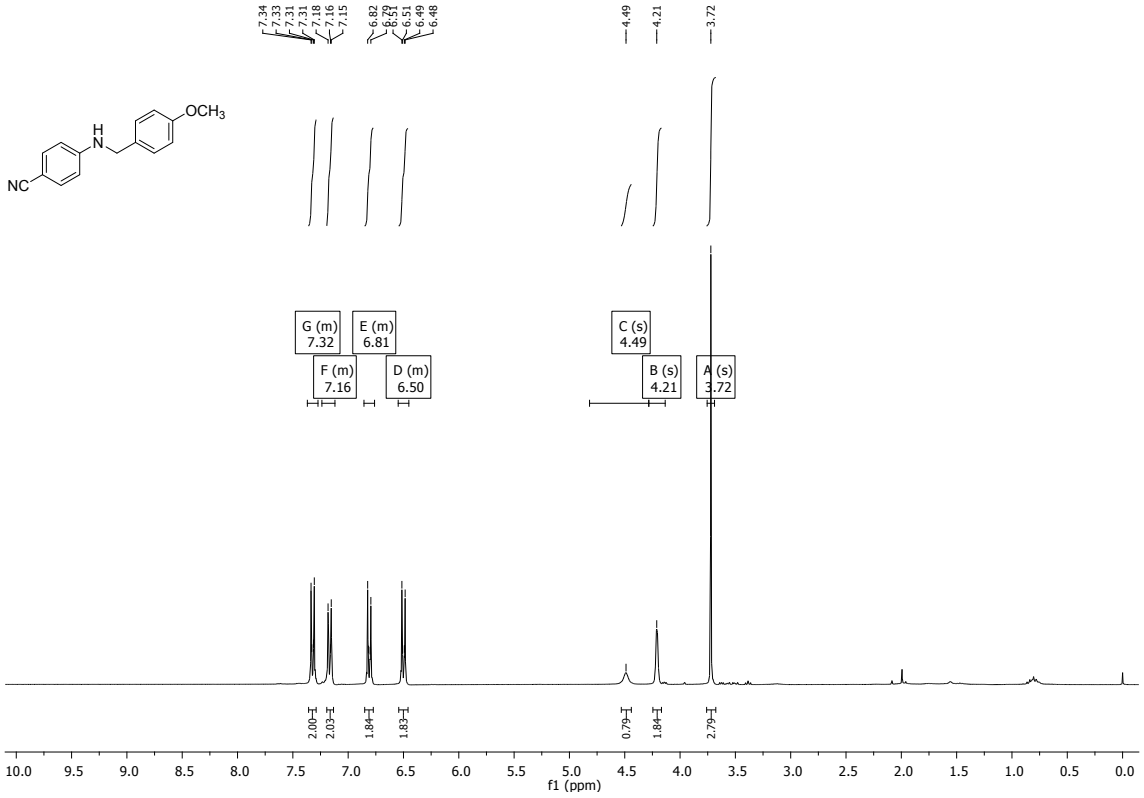
H
N
I
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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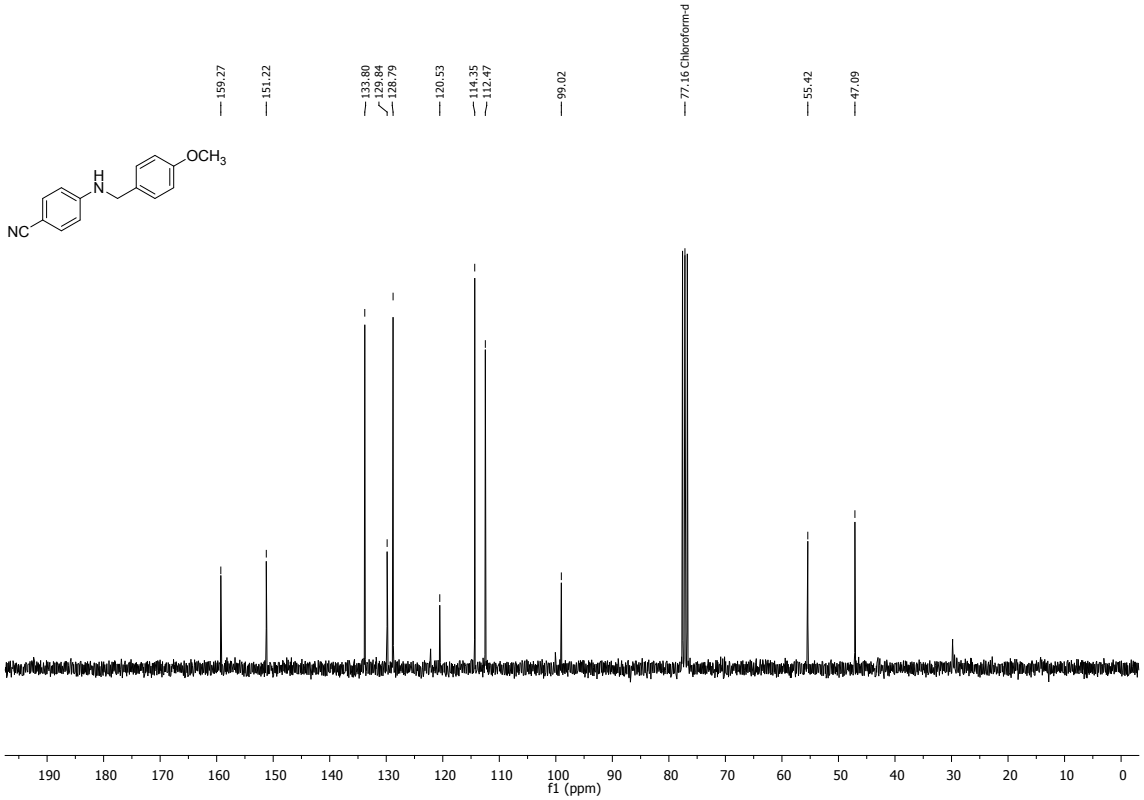
7.31
7.31
7.18
7.16
7.15
6.82
6.79
6.51
6.49
6.48
4.49
4.21
3.72
OCH3
H
N
NC
G (m)
7.32
E (m)
6.81
C (s)
4.49
F (m)
7.16
D (m)
6.50
B (s)
4.21
A (s)
3.72
2.00
2.03
1.84
1.83
0.79
1.84
2.79
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.84
128.79
120.53
114.35
112.47
99.02
77.16 Chloroform-d
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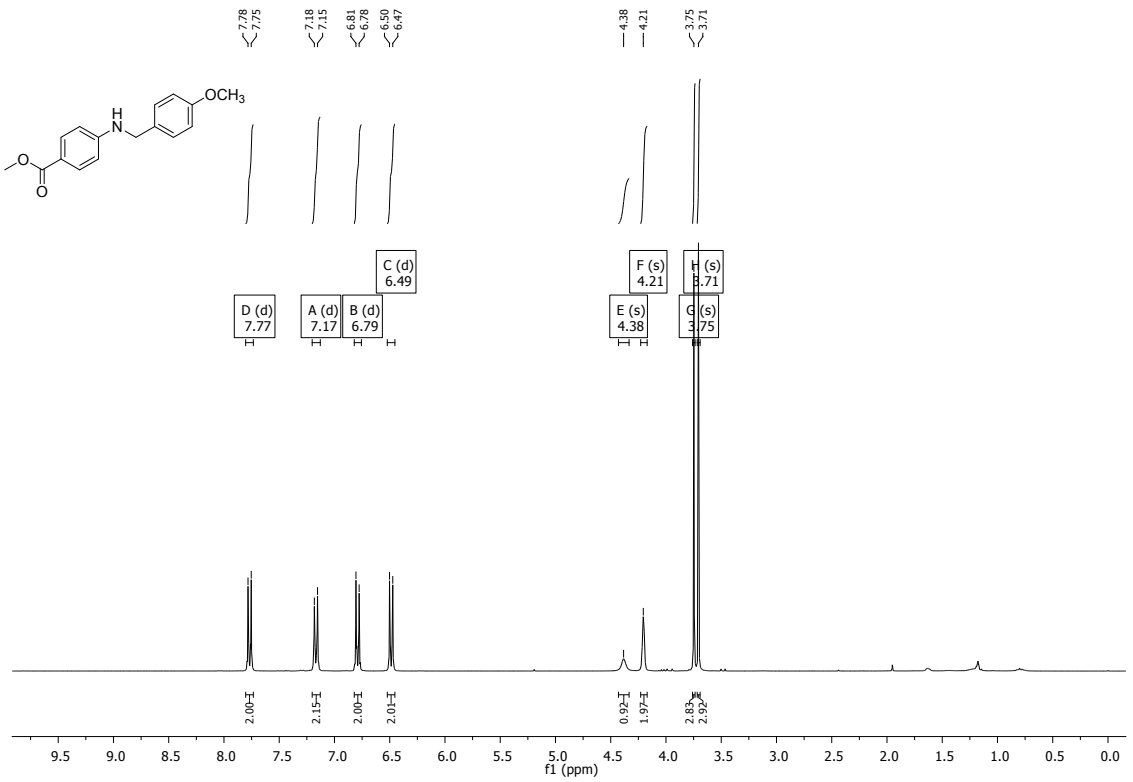
47.09
OCH3
H
N
NC
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.18
7.15
6.81
6.78
6.50
6.47
4.38
4.21
3.75
3.71
OCH3
H
N
O
O
D (d) 7.77
A (d) 7.17
B (d) 6.79
C (d) 6.49
E (s) 4.38
F (s) 4.21
G (s) 3.75
H (s) 3.71
2.00
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2.00
2.01
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1.97
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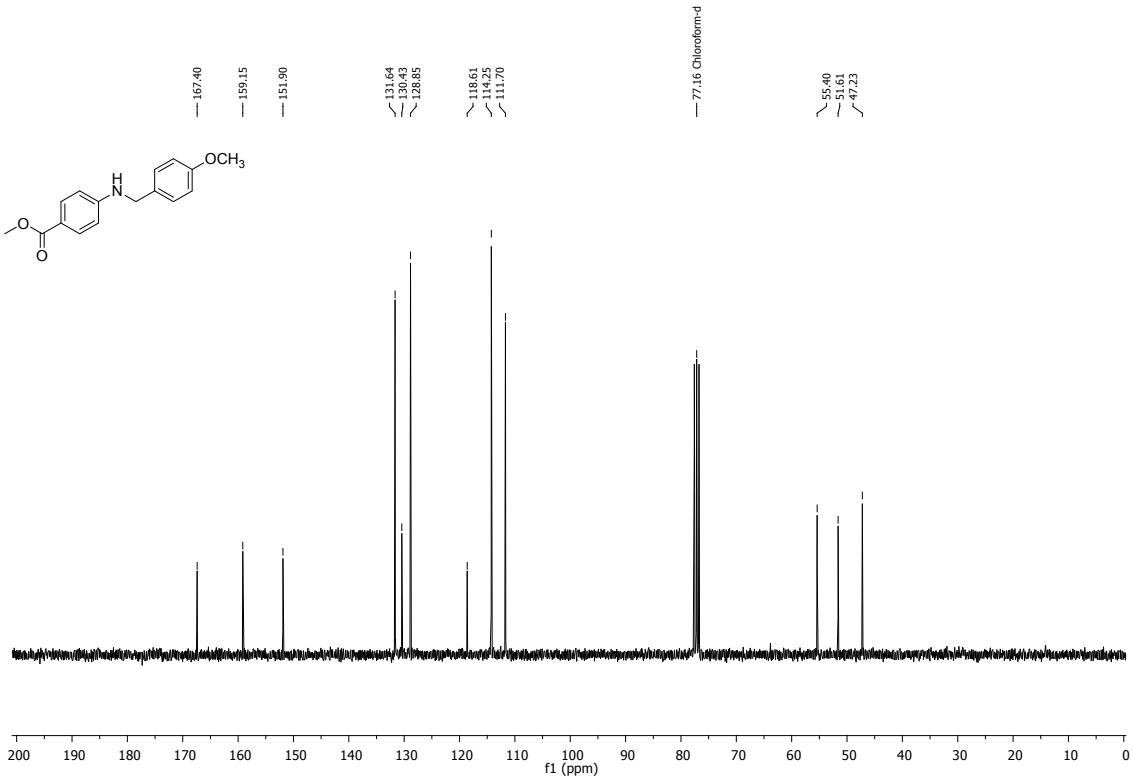
2.92
f1 (ppm)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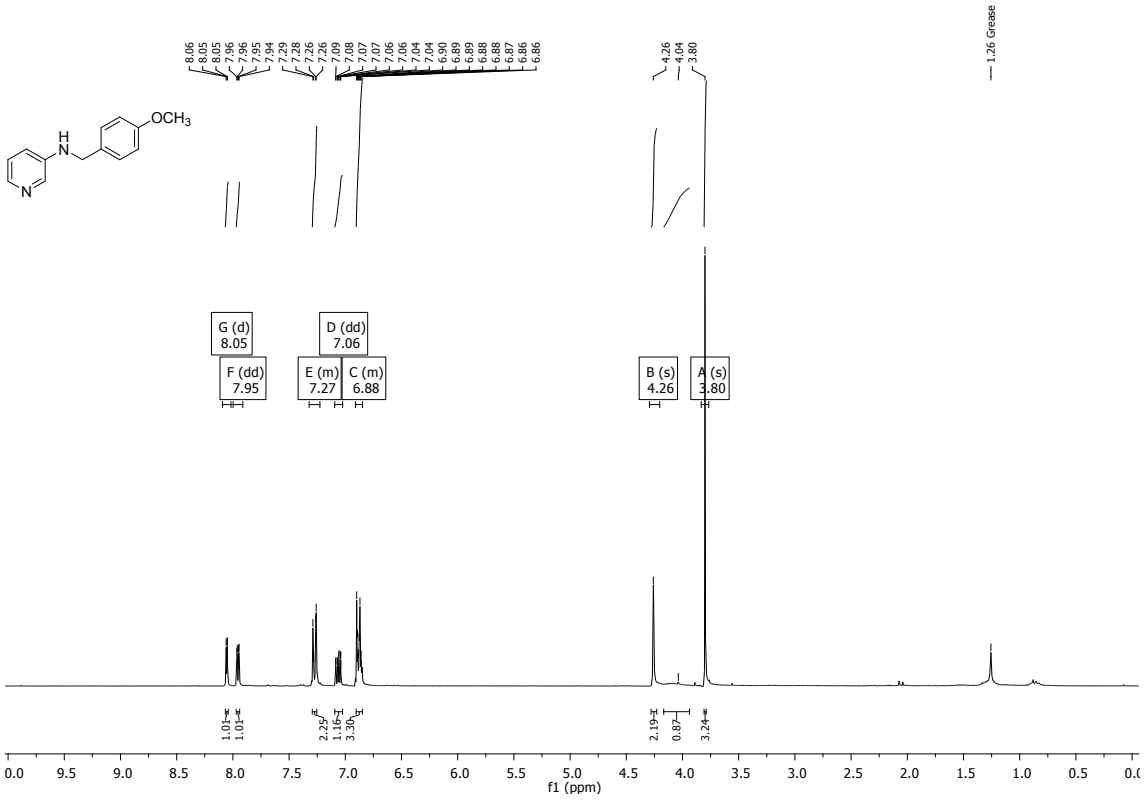
114.25
111.70
77.16 Chloroform-d
55.40
51.61
47.23
OCH3
H
N
O
O
f1 (ppm)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8.05
8.05
7.96
7.96
7.95
7.94
7.29
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7.26
7.26
7.09
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7.07
7.07
7.06
7.06
7.04
7.04
6.90
6.89
6.89
6.88
6.88
6.87
6.86
6.86
4.26
4.04
3.80
1.26 Grease
OCH3
H
N
N
G (d)
8.05
F (dd)
7.95
E (m)
7.27
D (dd)
7.06
C (m)
6.88
B (s)
4.26
A (s)
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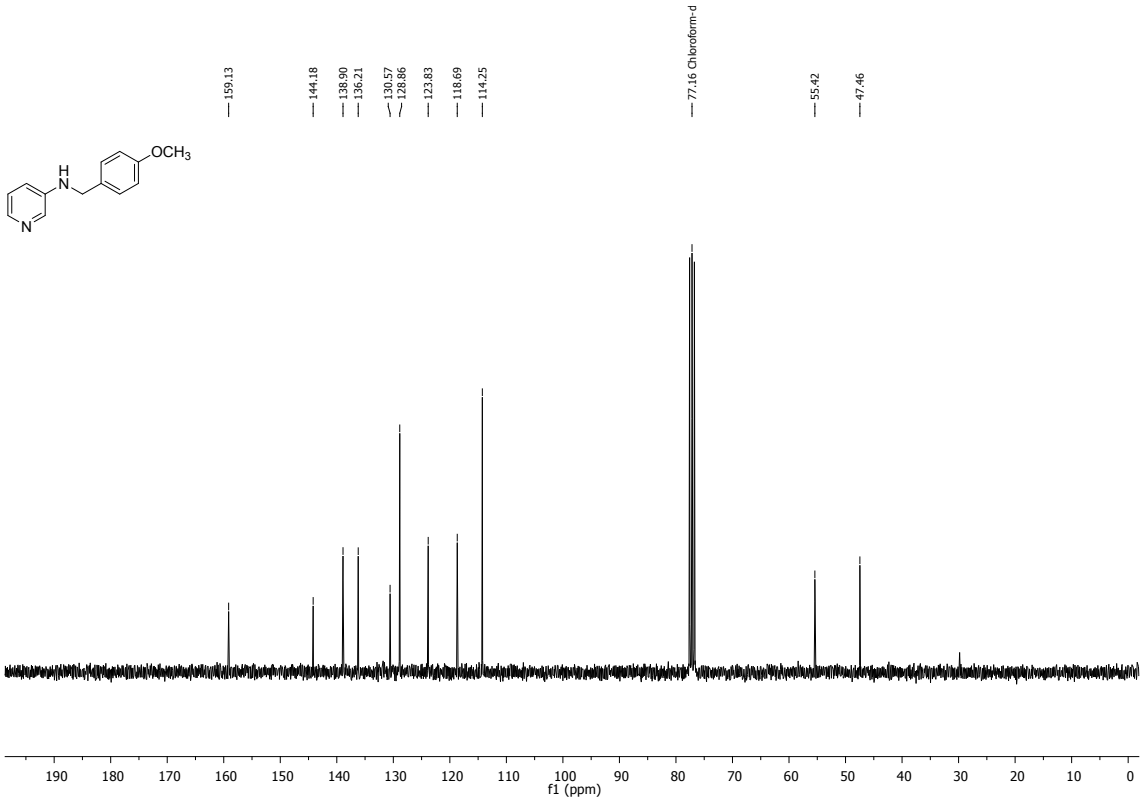
3.24
f1 (ppm)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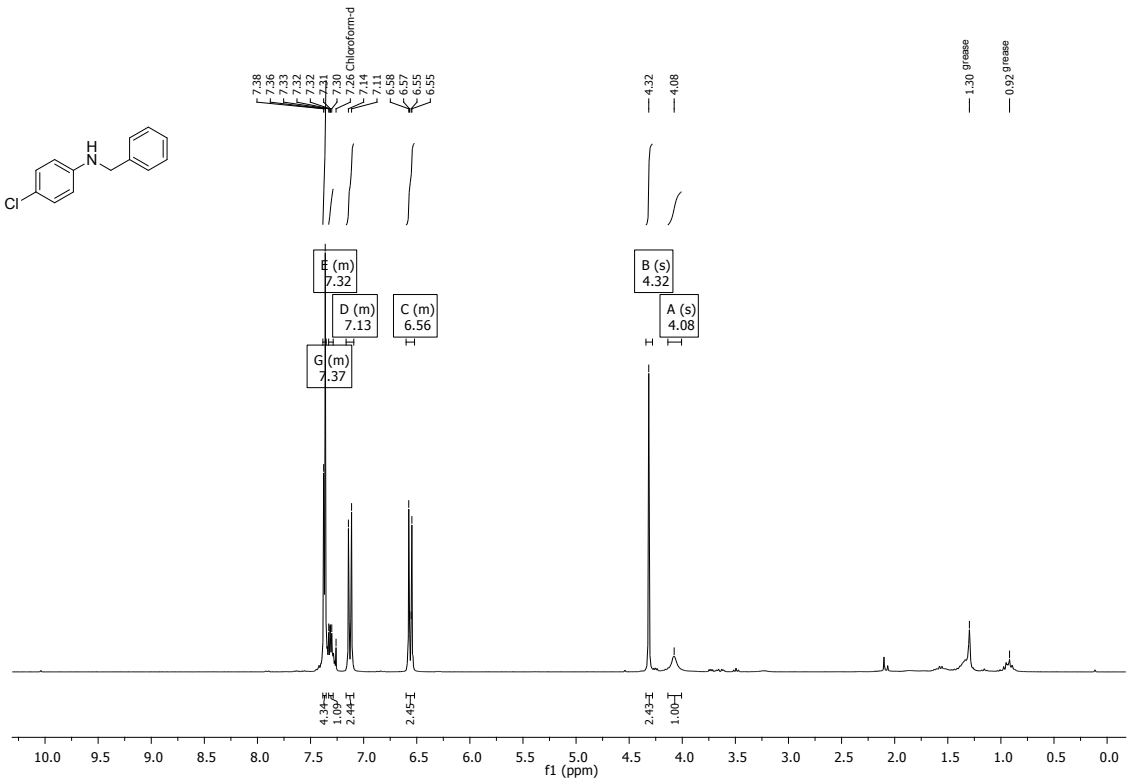
118.69
114.25
77.16 Chloroform-d
55.42
47.46
OCH3
H
N
N
f1 (ppm)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7.26 Chloroform-d
7.14
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6.58
6.57
6.55
6.55
4.32
4.08
1.30 grease
0.92 grease
E (m) 7.32
D (m) 7.13
C (m) 6.56
G (m) 7.37
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A (s) 4.08
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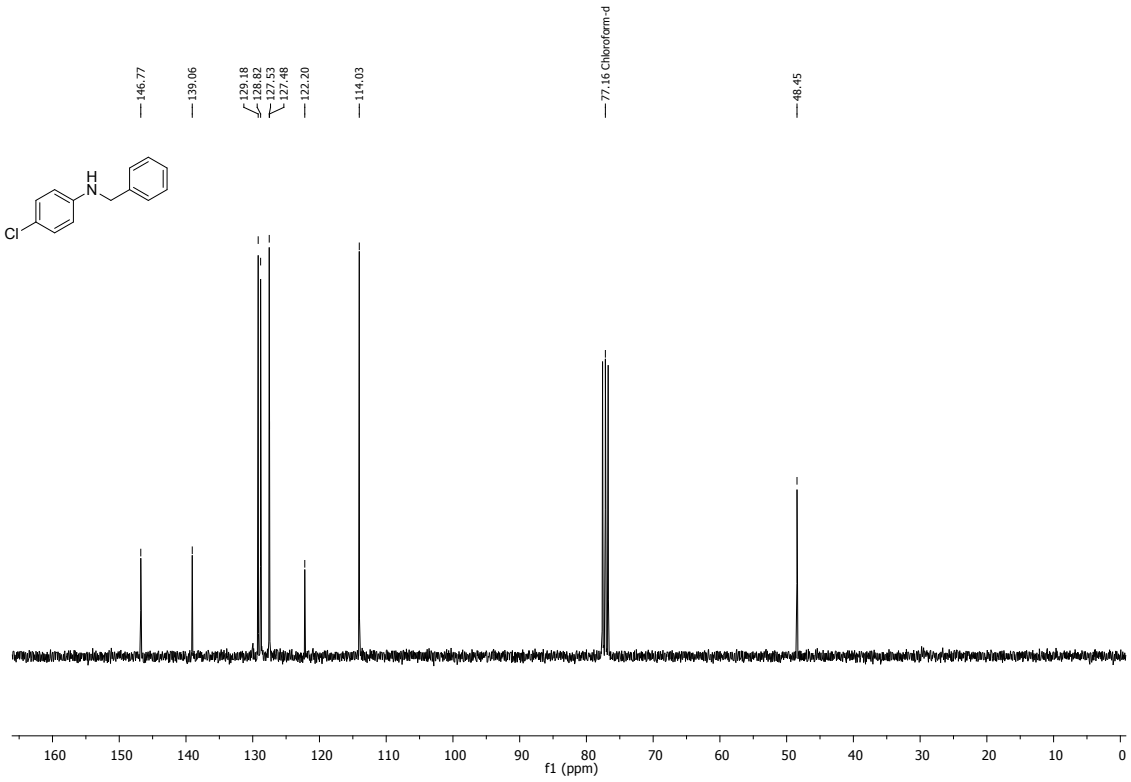
1.09
2.44
2.45
2.43
1.00
f1 (ppm)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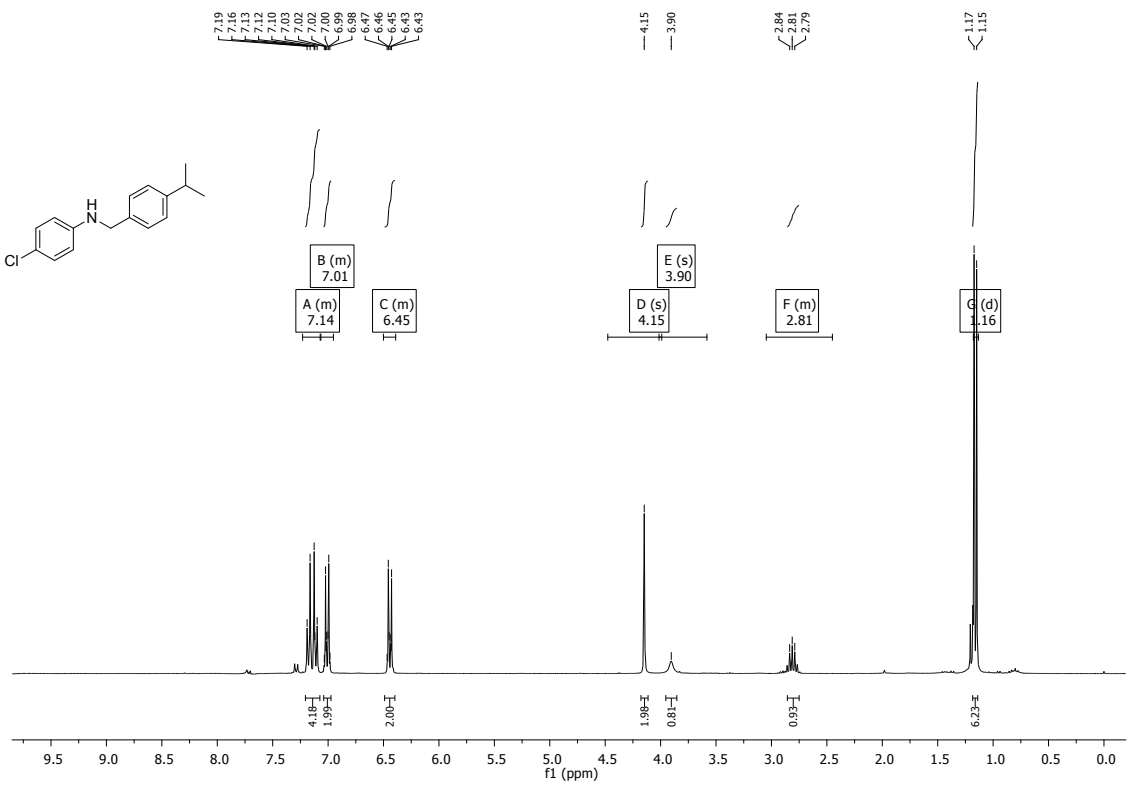
114.03
77.16 Chloroform-d
48.45
f1 (ppm)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7.03
7.02
7.02
7.02
7.00
6.99
6.98
6.47
6.46
6.45
6.43
6.43
4.15
3.90
2.84
2.81
2.79
1.17
1.15
Cl
H
N
B (m)
7.01
A (m)
7.14
C (m)
6.45
E (s)
3.90
D (s)
4.15
F (m)
2.81
G (d)
1.16
4.18
1.99
2.00
1.98
0.81
0.93
6.23
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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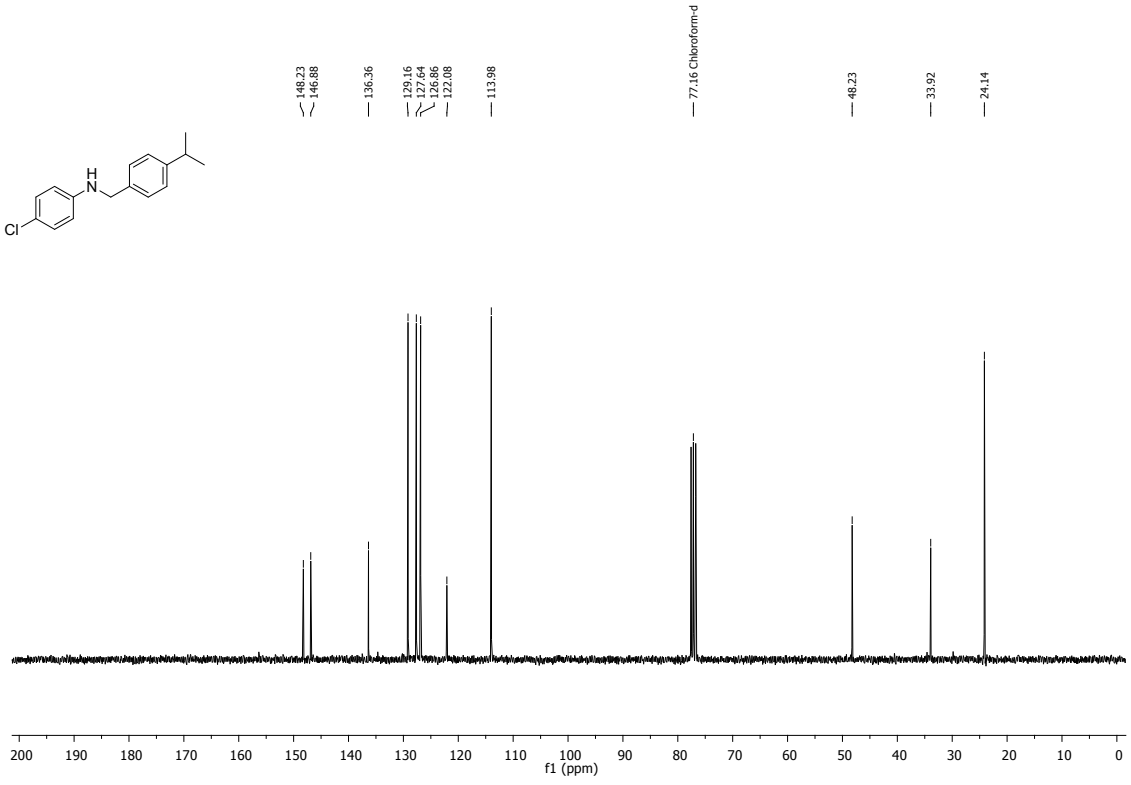
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


148.23
146.88
136.36
129.16
127.64
126.86
122.08
113.98
77.16 Chloroform-d
48.23
33.92
24.14
Cl
H
N
200
190
180
170
160
150
140
130
120
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100
90
80
70
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50
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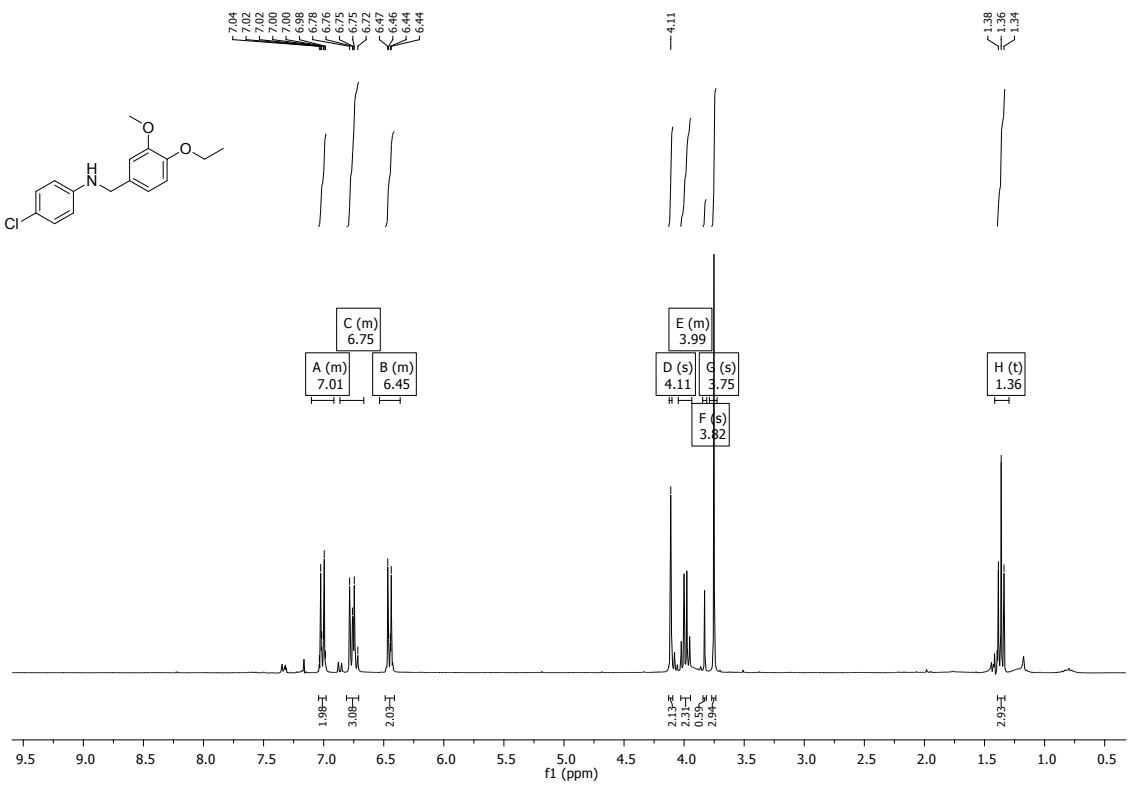
30
20
10
0
f1 (ppm)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7.02
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7.00
6.98
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6.76
6.75
6.75
6.72
6.47
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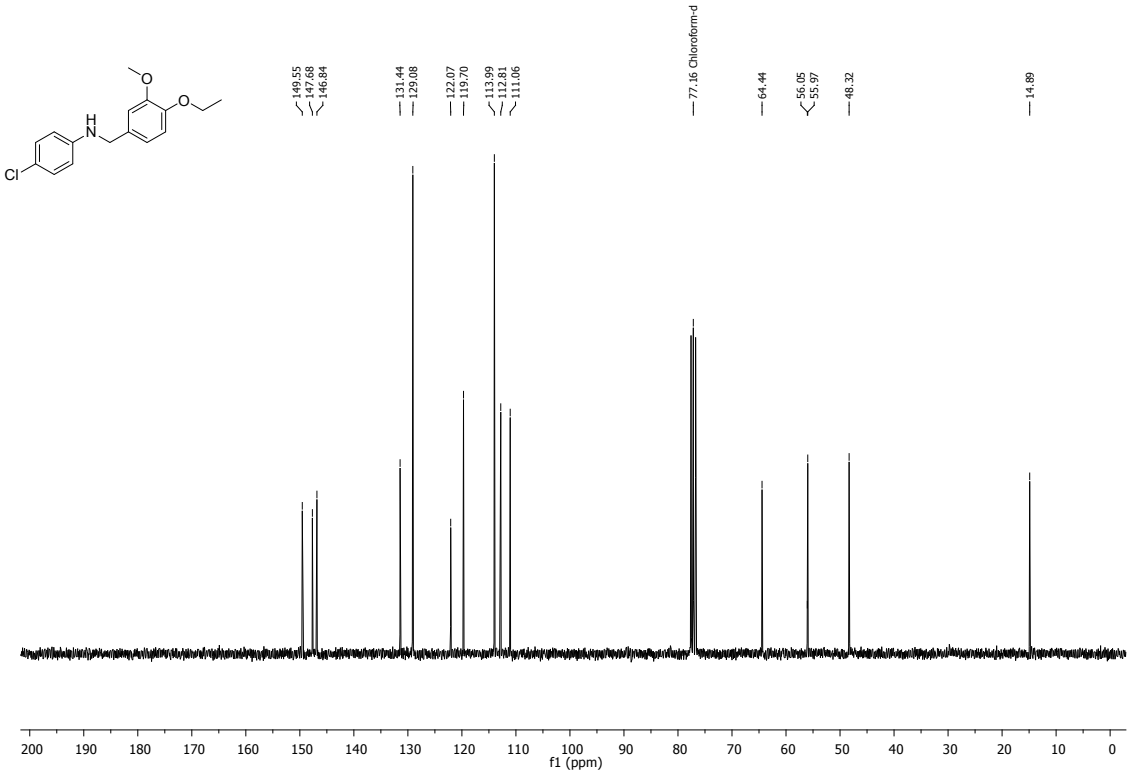
6.44
6.44
4.11
1.38
1.36
1.34
O
O
H
N
Cl
C (m)
6.75
A (m)
7.01
B (m)
6.45
E (m)
3.99
D (s)
4.11
G (s)
3.75
F (s)
3.82
H (t)
1.36
1.98
3.08
2.03
2.13
2.31
0.59
2.94
2.93
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


149.55
147.68
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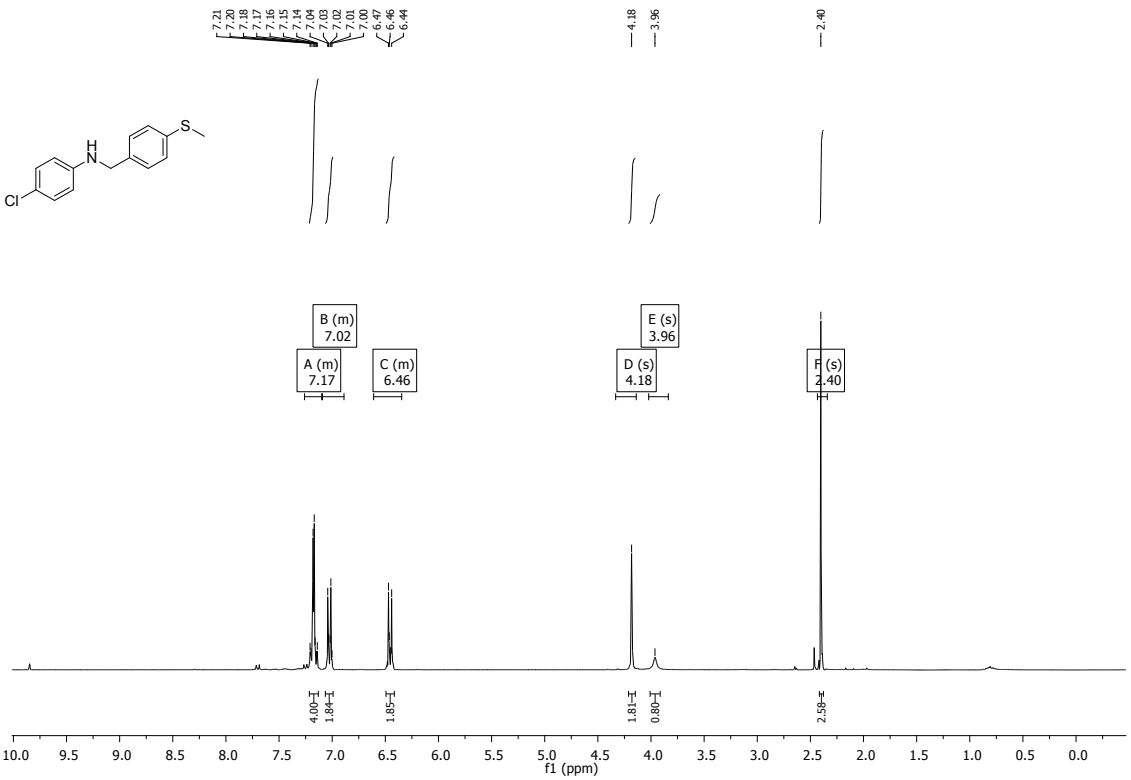
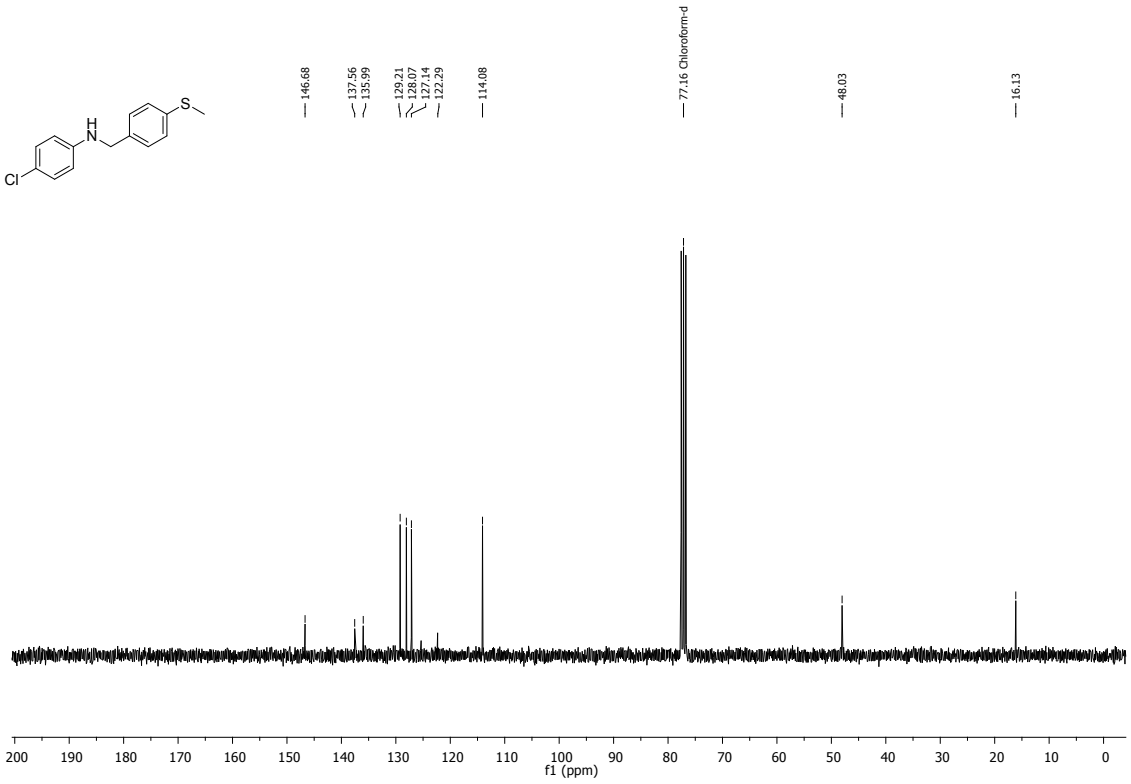
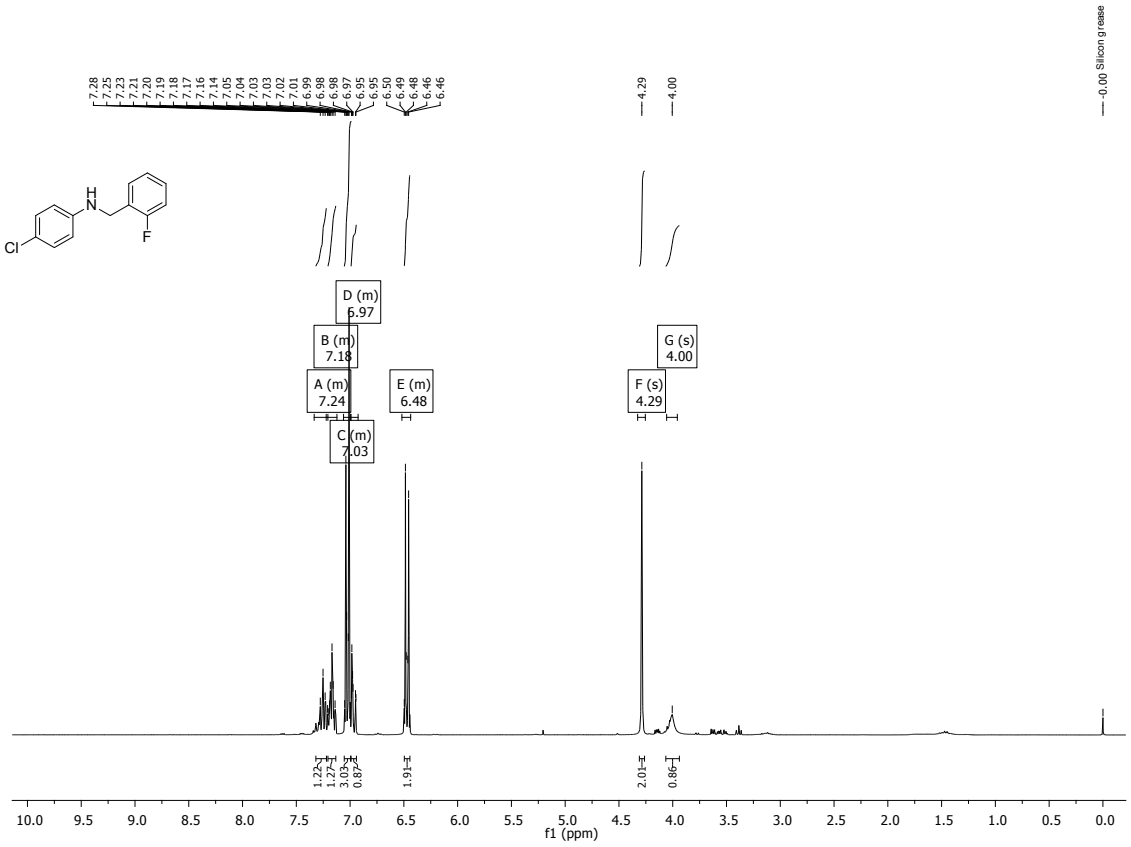
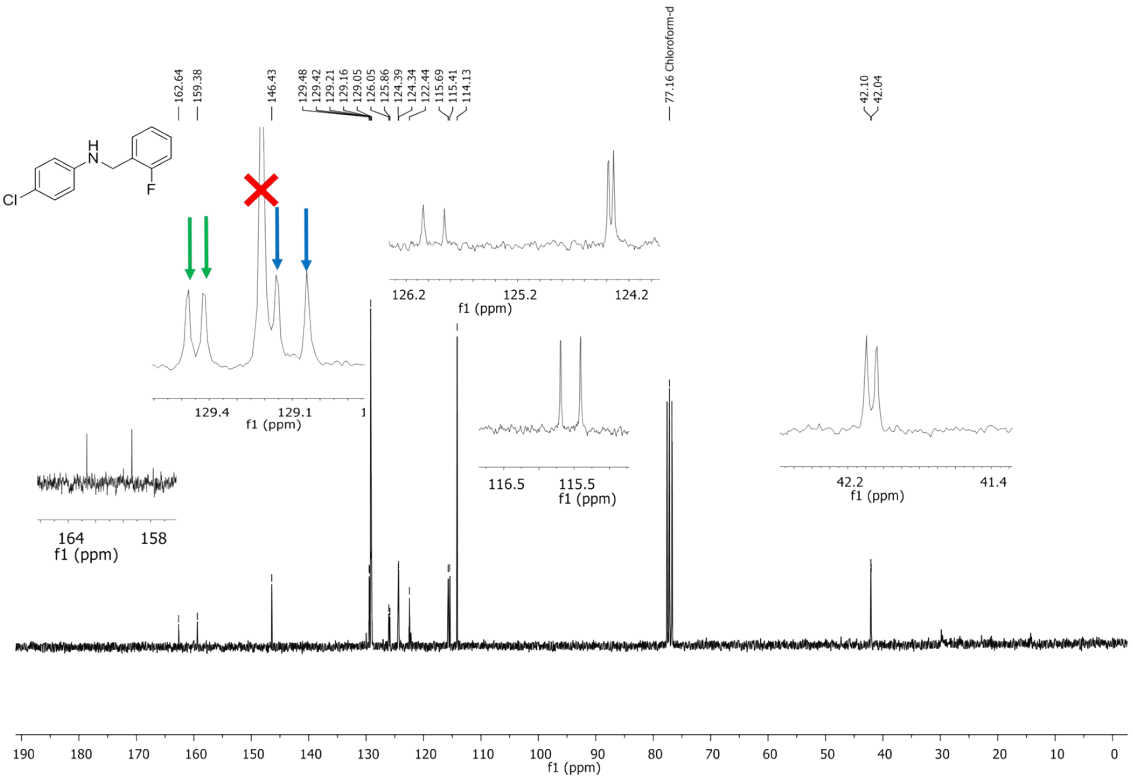
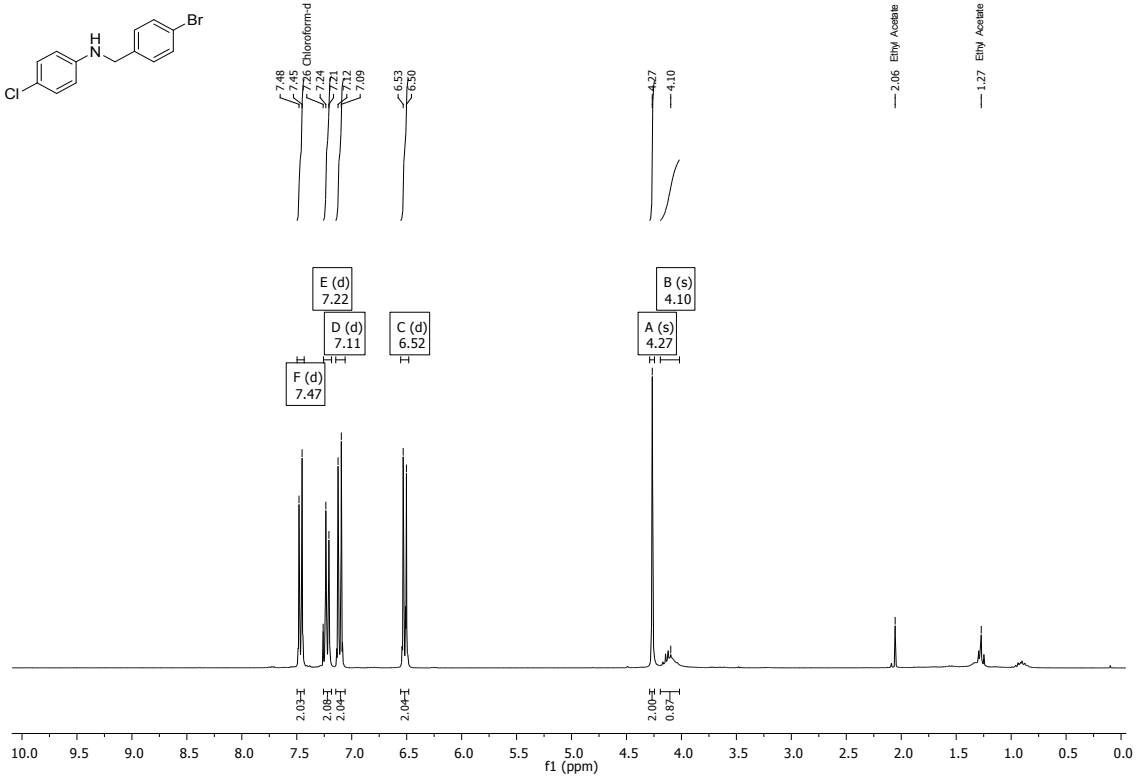
131.44
129.08
122.07
119.70
113.99
112.81
111.06
77.16 Chloroform-d
64.44
56.05
55.97
48.32
14.89
O
O
H
N
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

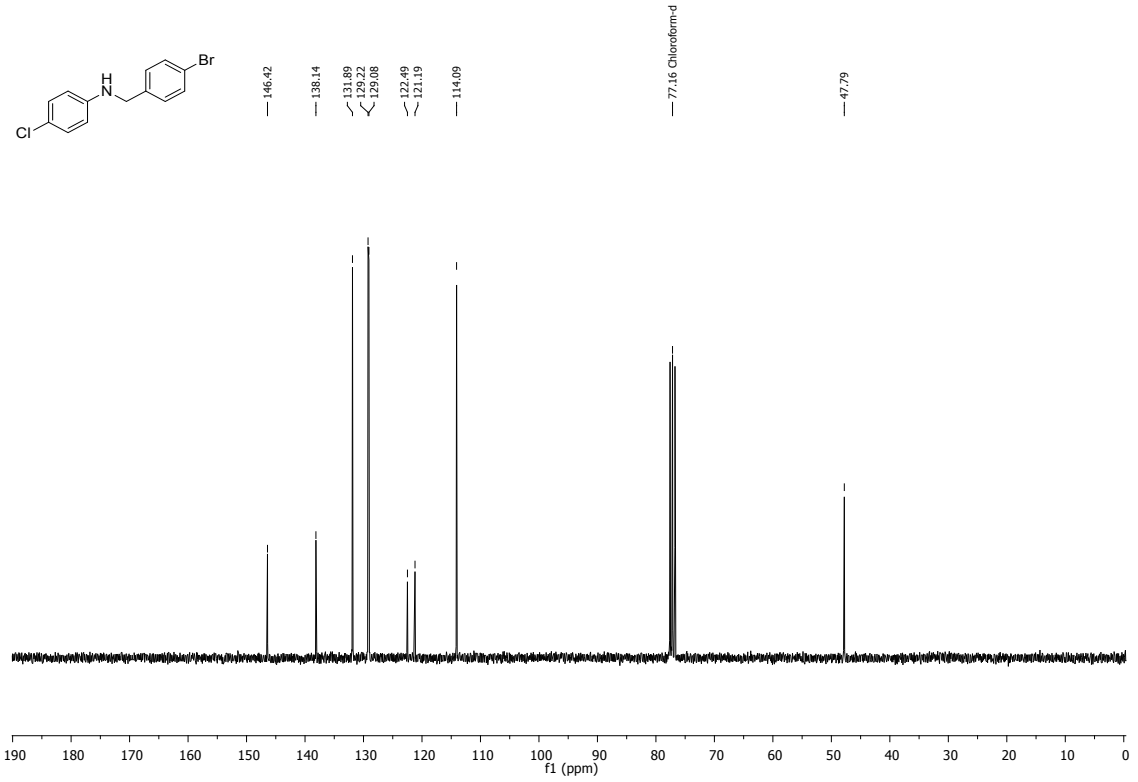

7.21
7.20
7.18
7.17
7.16
7.15
7.14
7.04
7.03
7.02
7.01
7.00
6.47
6.46
6.44
4.18
3.96
2.40
S
H
N
Cl
B (m)
7.02
A (m)
7.17
C (m)
6.46
E (s)
3.96
D (s)
4.18
F (s)
2.40
4.00
1.84
1.85
1.81
0.80
2.58
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

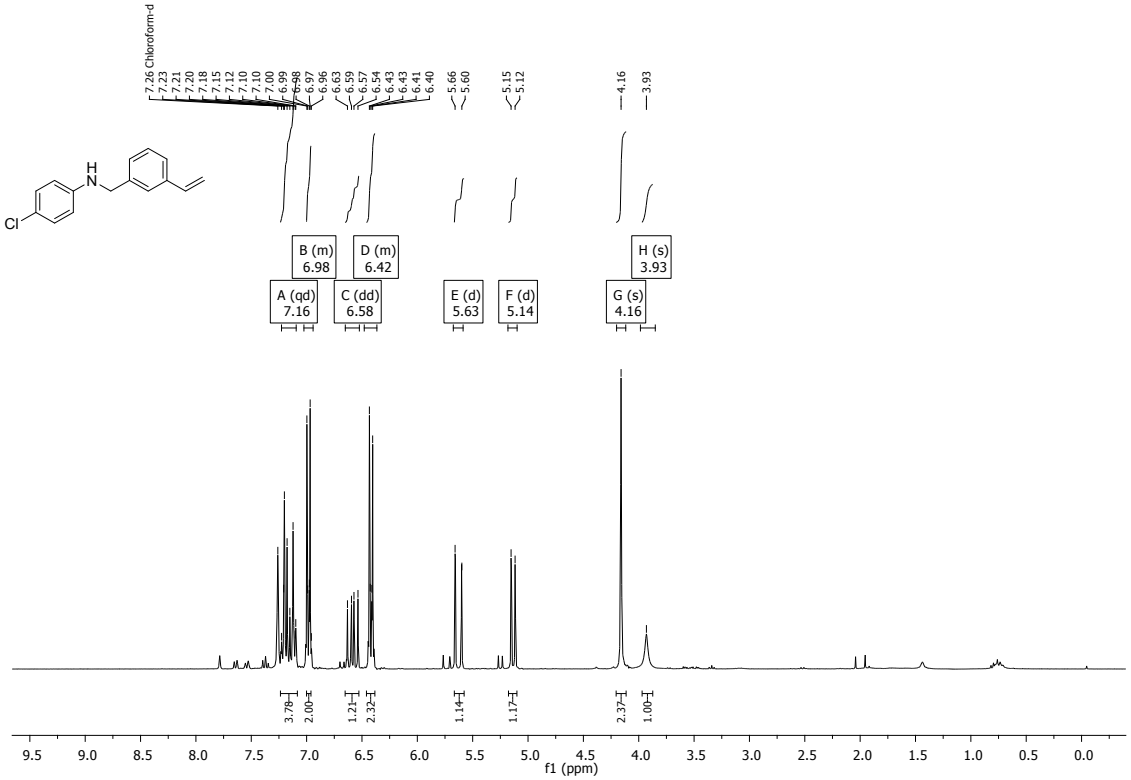

146.68
137.56
135.99
129.21
128.07
127.14
122.29
114.08
77.16 Chloroform-d
48.03
16.13
S
H
N
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

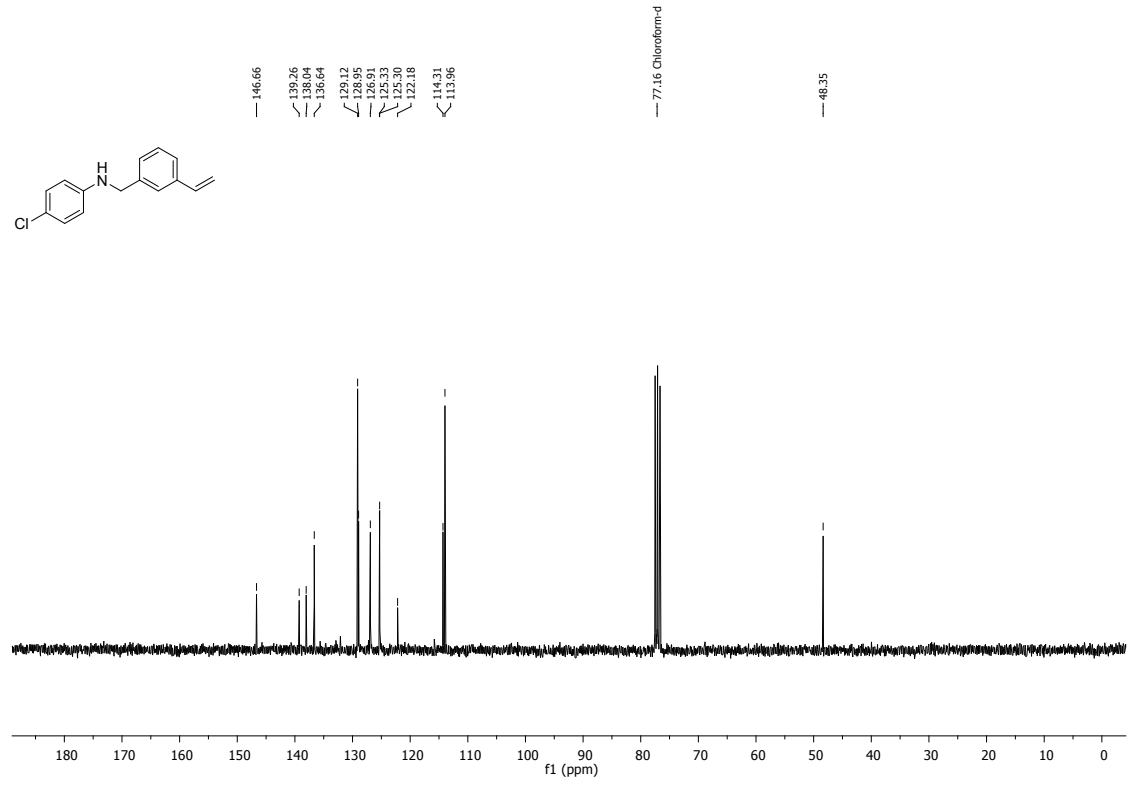

7.28
7.25
7.23
7.21
7.20
7.19
7.18
7.17
7.16
7.14
7.05
7.04
7.03
7.03
7.02
7.01
6.99
6.98
6.97
6.95
6.50
6.49
6.48
6.46
6.46
4.29
4.00
0.00 Silicon grease
Cl
H
N
F
D (m)
6.97
B (m)
7.18
A (m)
7.24
C (m)
7.03
E (m)
6.48
F (s)
4.29
G (s)
4.00
1.22
1.27
3.03
0.87
1.91
2.01
0.86
10.0 9.5 9.0 8.5 8.0 7.5 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)

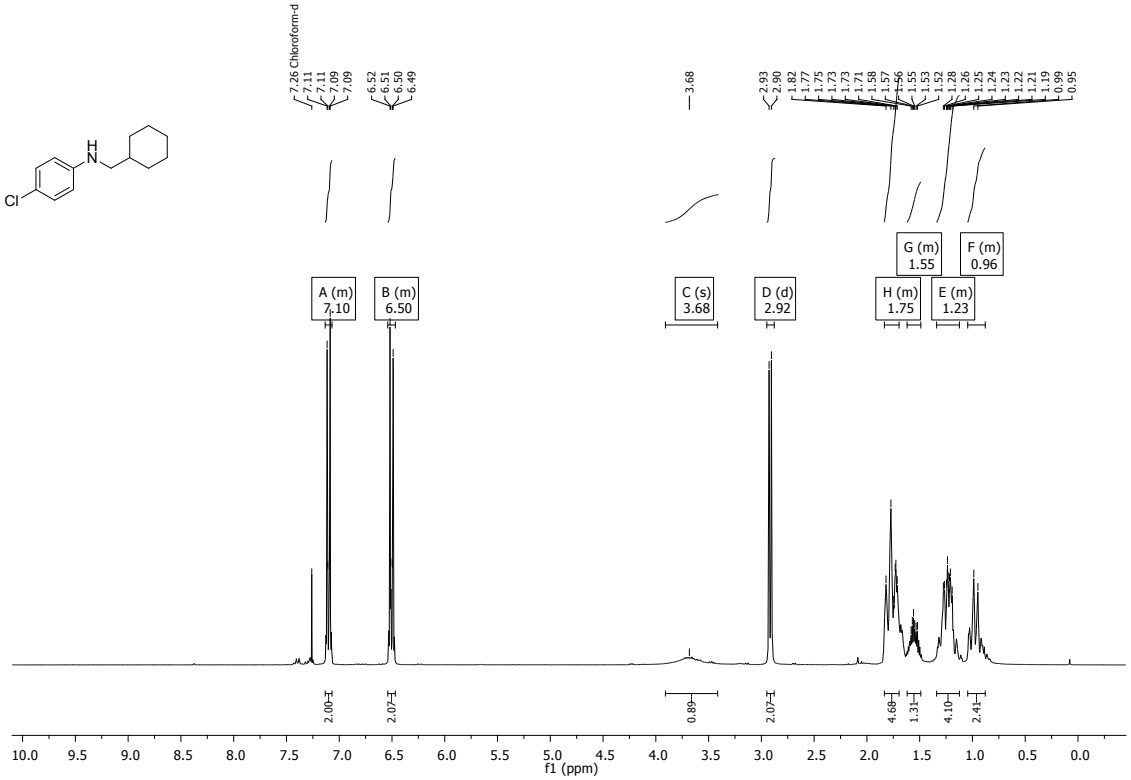

162.64
159.38
146.43
129.48
129.42
129.21
129.16
129.05
126.05
125.86
124.39
124.34
122.44
115.69
115.41
114.13
77.16 Chloroform-d
42.10
42.04
Cl
H
N
F
126.2
125.2
124.2
f1 (ppm)
129.4
129.1
f1 (ppm)
164
158
f1 (ppm)
116.5
115.5
f1 (ppm)
42.2
41.4
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

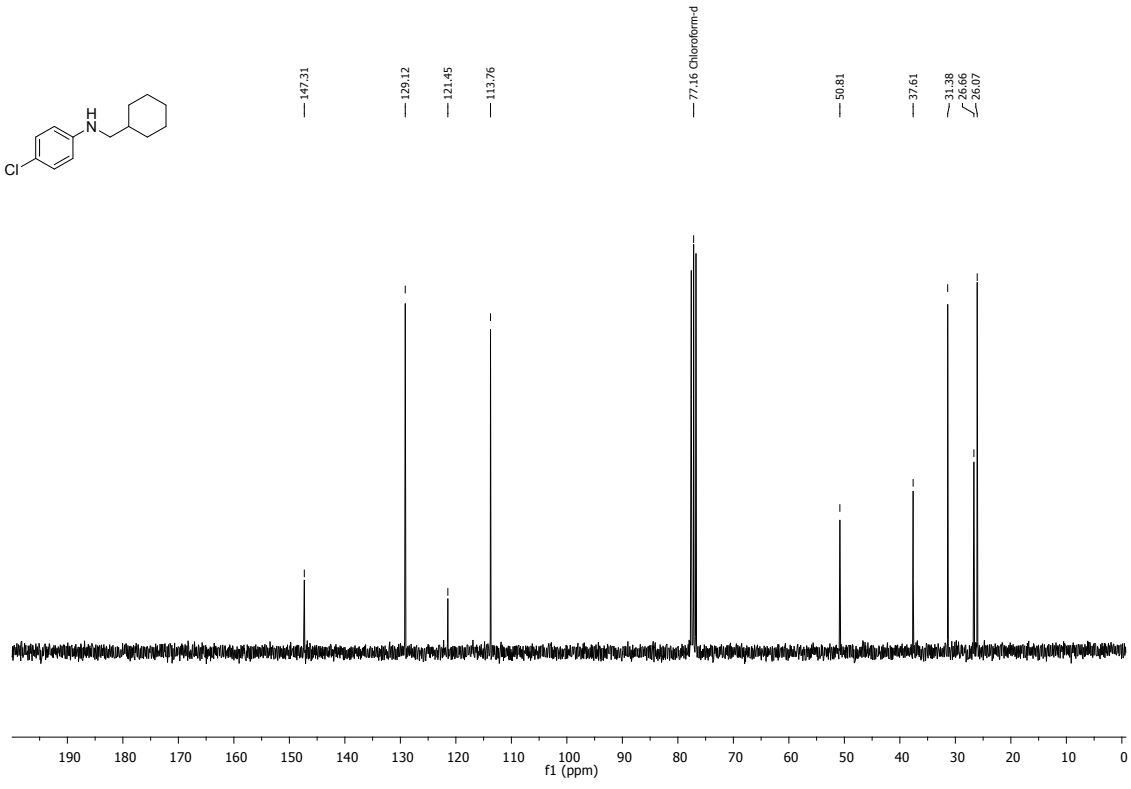

Br
H
N
Cl
7.48
7.45
Chloroform-d
7.24
7.24
7.21
7.12
7.09
6.53
6.50
4.27
4.10
2.06 Ethyl Acetate
1.27 Ethyl Acetate
E (d)
7.22
D (d)
7.11
C (d)
6.52
B (s)
4.10
A (s)
4.27
F (d)
7.47
2.03
2.08
2.04
2.04
2.00
0.87
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Br
H
N
Cl
146.42
138.14
131.89
129.22
129.08
122.49
121.19
114.09
77.16 Chloroform-d
47.79
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26 Chloroform-d
7.23
7.21
7.20
7.18
7.15
7.12
7.10
7.10
7.00
6.99
6.98
6.97
6.96
6.63
6.59
6.57
6.54
6.43
6.41
6.40
5.66
5.60
5.15
5.12
4.16
3.93
H
N
Cl
B (m) 6.98
D (m) 6.42
H (s) 3.93
A (qd) 7.16
C (dd) 6.58
E (d) 5.63
F (d) 5.14
G (s) 4.16
3.78
2.00
1.21
2.32
1.14
1.17
2.37
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)


146.66
139.26
138.64
136.64
129.12
128.95
126.91
125.33
125.30
122.18
114.31
113.96
77.16 Chloroform-d
48.35
H
N
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26 Chloroform-d
7.11
7.11
7.09
7.09
6.52
6.51
6.50
6.49
3.68
2.93
2.90
1.82
1.77
1.75
1.73
1.73
1.71
1.58
1.57
1.56
1.55
1.53
1.52
1.28
1.26
1.25
1.24
1.23
1.22
1.21
1.19
0.99
0.95
A (m) 7.10
B (m) 6.50
C (s) 3.68
D (d) 2.92
G (m) 1.55
F (m) 0.96
H (m) 1.75
E (m) 1.23
2.00
2.07
0.89
2.07
4.68
1.31
4.10
2.41
f1 (ppm)


147.31
129.12
121.45
113.76
77.16 Chloroform-d
50.81
37.61
31.38
26.66
26.07
f1 (ppm)