Supporting Information

A Heteroditopic NHC and Phosphine Ligand Supported Ruthenium(II)-Complex: Effective Catalyst for the N-alkylations of Amides using Alcohols

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General experimental details

All manipulations were performed under an argon/N_2 atmosphere using either standard Schlenk line or glovebox techniques. All glassware was oven-dried at 130 °C overnight prior to use. The solvents used were dried, distilled, and degassed by standard methods and stored over 4 Å molecular sieves. NMR measurements were performed using Bruker 400 and 500 MHz FT-NMR spectrometers. The chemical shifts in the ^{1}H NMR spectra were referenced to the residual proton signals of the deuterated solvents ($CDCl_3$, ^{1}H 7.26 ppm and $^{13}C\{^1H\}$ 77.16 ppm; DMSO-d_6, ^{1}H 2.50 ppm and $^{13}C\{^1H\}$ 39.52 ppm and CD_3CN, ^{1}H 1.94 ppm) and reported relative to tetramethylsilane. The coupling constants are expressed in hertz. All chemicals were purchased from the commercial sources and used as received without further purification. Primary alcohols were synthesized according to the literature procedures.[1] All of ruthenium (II) complexes used in catalytic studies were synthesised following reported procedures.[1-2]

General procedure for amide N-alkylation reaction: An oven dried Schlenk tube was charged with the stock solution (0.2 mol%) of catalyst (**2c**), prepared in CH_3CN and after that the volatiles were removed in vacuum. To this, dppe (0.8 mol%), amide (0.5 mmol), primary alcohol (1.0 mmol), and KO^{t}Bu (0.125 mmol) followed by *t*-amyl alcohol (1 mL) were added. The reaction tube was then kept in oil bath (bath temperature 130 °C) and heated for the specified time. After completion of the reaction, pure products were isolated *via* column chromatography using hexane/ethyl acetate as eluent.

General procedure for the selective N-monoalkylation of 4-aminobenzamide: An oven dried Schlenk tube was charged with the catalyst **2c** (1.0 mol%), dppe (2.0 mol%), 4-aminobenzamide (0.5 mmol), primary alcohol (0.75 mmol), and KO^{t}Bu (0.5 mmol) followed by *t*-amyl alcohol (1 mL). The reaction tube was then kept in oil bath (bath temperature 130 °C) and heated for the specified time. After the completion of reaction, the pure products were isolated *via* column chromatography using dichloromethane/methanol as eluent.

General procedure for the unsymmetrical N-dialkylation of 4-aminobenzamide: An oven dried Schlenk tube was charged with the catalyst **2c (**0.5-1.0 mol%), dppe (1.0-2.0 mol%), mono alkylated 4-aminobenzamide derivative (0.25 mmol), primary alcohol (0.5 mmol), and KO^{t}Bu (0.125 mmol) followed by *t*-amyl alcohol (1 mL). The reaction tube was then kept in oil bath (bath temperature 130 °C) and heated for the specified time. After the completion of

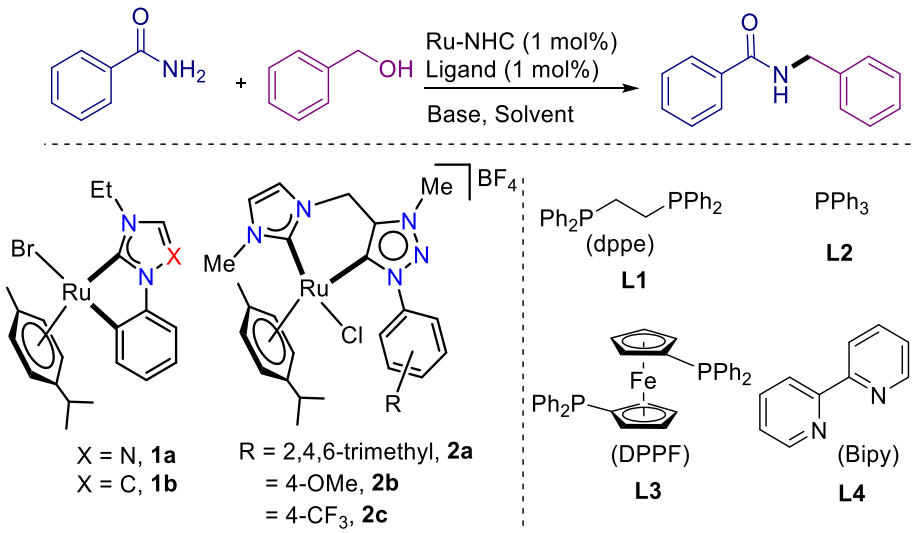
reaction, the pure products were isolated *via* column chromatography using dichloromethane/methanol as eluent.

Procedure for the calculation of TON for N-benzylation reaction:

An oven dried Schlenk tube was charged with a catalyst (**2c**) stock solution (0.002 mol%), prepared in CH_3CN and after that the volatiles were removed in vacuum. To this, dppe (1 mg, 0.5 mol%), amide (0.5 mmol), primary alcohol (1.0 mmol), and KO^{t}Bu (0.125 mmol) followed by *t*-amyl alcohol (1 mL) were added. The reaction tube was then kept in oil bath (bath temperature 130 °C) and heated for 24 h. After that the reaction mixture was cooled to room temperature and GC-MS analysis was performed using dodecane as an internal standard. The GC-MS data shows the formation of **5a** in 38% (0.01 mol%) yield which provides TON of 3800 at TOF = 158 h^{-1}.

Optimization studies

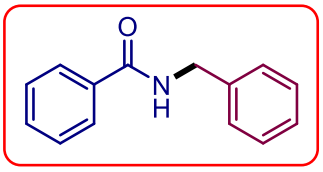
Table S1. Optimization data for benzamide alkylation using benzyl alcohol



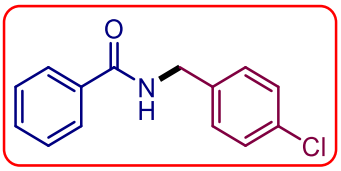
Entry	Base (eq.)	Catalyst	Ligand	Solvent	Conversion (%)
1	KO^{t}Bu (1.0)	**1a**	**L1**	^{t}AmOH	30%
2	KO^{t}Bu (1.0)	**1b**	**L1**	^{t}AmOH	57%
3	KO^{t}Bu (1.0)	**2a**	**L1**	^{t}AmOH	71%
4	KO^{t}Bu (1.0)	**2a**	**L1**	THF	10%
5	KO^{t}Bu (1.0)	**2a**	**L1**	Toluene	27%
6	KO^{t}Bu (1.0)	**2a**	**L1**	Dioxane	56%
7	KO^{t}Bu (1.0)	**2a**	**L1**	DMF	NR
8	NaO^{t}Bu (1.0)	**2a**	**L1**	^{t}AmOH	43%
9	KOH (1.0)	**2a**	**L1**	^{t}AmOH	6%
10	Cs_2CO_3 (1.0)	**2a**	**L1**	^{t}AmOH	9%
11	pyridine (1.0)	**2a**	**L1**	^{t}AmOH	NR
12	KO^{t}Bu (1.0)	**2b**	**L1**	^{t}AmOH	60%
13	KO^{t}Bu (1.0)	**2c**	**L1**	^{t}AmOH	85%
14	KO^{t}Bu (0.5)	**2c**	**L1**	^{t}AmOH	100% (94%)[b]
15	**KO^{t}Bu (0.25)**	**2c**[d]	**L1**	**^{t}AmOH**	**100% (95%)**[c]
16	KO^{t}Bu (0.25)	**2c**[d]	**L2**	^{t}AmOH	67%[c]
17	KO^{t}Bu (0.25)	**2c**[d]	**L3**	^{t}AmOH	67%[c]
18	KO^{t}Bu (0.25)	**2c**[d]	**L4**	^{t}AmOH	NR[c]
19	KO^{t}Bu (0.25)	**2c**[d]	-	^{t}AmOH	36%[c]
20	KO^{t}Bu (0.25)	-	-	^{t}AmOH	NR[c]
21	KO^{t}Bu (0.25)	-	**L4**	^{t}AmOH	NR[c]

[a]Reaction conditions: benzamide (0.5 mmol), benzyl alcohol (0.75 mmol), catalyst (0.005 mmol; 1 mol%), ligand (0.005 mmol; 1 mol%), 120 °C, 12 h, inert atmosphere. [b]2 equiv. alcohol, 130 °C, 18 h. [c]24 h. [d]**2c** (0.2 mol%), dppe (0.8 mol%). Isolated yields were given in parenthesis.

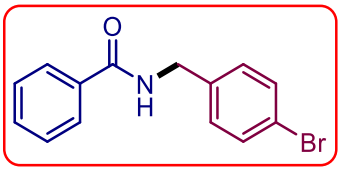
NMR characterization data of the isolated compounds



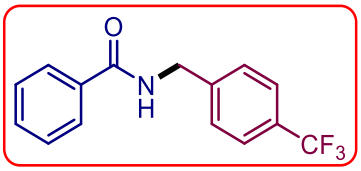
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, 2H), 7.51-7.26 (m, 8H), 6.54 (s, 1H), 4.64 (d, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 167.6, 138.4, 134.6, 131.7, 128.9, 128.7, 128.1, 127.8, 127.1, 44.3 ppm. HRMS (ESI): *m/z* = 212.1080, calcd. for $C_{14}H_{13}NOH$ $[M + H]^+$: 212.1075.



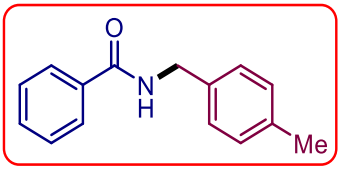
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, 2H), 7.50 (t, 1H), 7.41 (t, *2*H), 7.31-7.25 (m, 5H), 6.65 (s, 1H), 4.58 (d, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 167.6, 136.9, 134.3, 133.5, 131.8, 129.3, 129.0, 128.8, 127.1, 43.5 ppm. HRMS (ESI): *m/z* = 245.0689, calcd. for $C_{14}H_{12}ClNOH$ $[M + H]^+$: 246.0686.



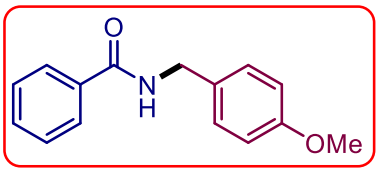
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, 2H), 7.52-7.41 (m, 5H), 7.22 (d, 2H), 6.52 (s, 1H), 4.58 (d, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 167.6 137.5, 134.3, 132.0, 131.8, 129.7, 128.8, 127.1, 121.6, 43.6 ppm. HRMS (ESI): *m/z* = 290.0179, calcd. for $C_{14}H_{12}BrNOH$ $[M + H]^+$: 290.0181.



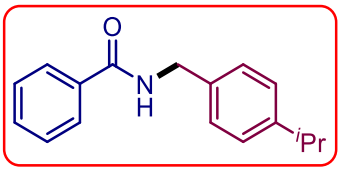
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, 2H), 7.56 (d, 2H), 7.50 (t, 1H), 7.42-7.38 (m, 4H), 6.91 (s, 1H), 4.64 (d, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 167.8, 142.6, 134.1, 131.9, 129.8 (d, *J* (C, F) = 32.5 Hz) 128.8, 128.0, 127.1, 125.7 (q, *J* (C, F) = 3.6 Hz), 125.5 (t, *J* (C, F) = 271.0 Hz), 122.8, 43.6 ppm. HRMS (ESI): *m/z* = 280.0947, calcd. for $C_{15}H_{12}F_3NOH$ $[M + H]^+$: 280.0949.



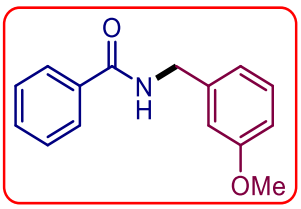
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79-7.77 (m, 2H), 7.50-7.46 (m, 1H), 7.41-7.38 (m, 2H), 7.23 (d, 2H), 7.15 (d, 2H), 6.60 (s, 1H), 4.58 (d, 2H), 2.34 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 167.5, 137.4, 135.4, 134.6, 131.5, 129.5, 128.6, 128.0, 127.1, 44.0, 21.2 ppm. HRMS (ESI): *m/z* = 226.1239, calcd. for $C_{15}H_{15}NOH$ $[M + H]^+$: 226.1232.



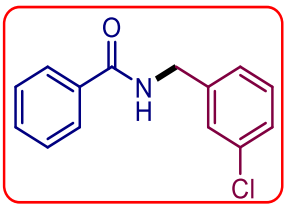
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, 2H), 7.42-7.32 (m, 3H), 7.20-7.18 (m, 2H), 6.80 (d, 2H), 6.38 (s, 1H), 4.48 (d, 2H), 3.72 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.4, 159.3, 134.6, 131.6, 130.4, 129.4, 128.7, 127.1, 114.3, 55.4, 43.8 ppm. HRMS (ESI): *m/z* = 242.1182, calcd. for $C_{15}H_{15}NO_2H$ $[M + H]^+$: 242.1181.



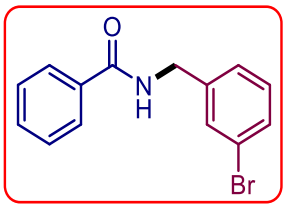
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, 2H), 7.47 (t, 1H), 7.38 (t, 2H), 7.27-7.18 (m, 4H), 6.62 (s, 1H), 4.58 (d, 2H), 2.94-2.84 (m, 1H), 1.24 (d, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.5, 148.4, 135.6, 134.5, 131.6, 128.6, 128.1, 127.1, 126.9, 126.8, 44.0, 33.9, 24.1 ppm. HRMS (ESI): *m/z* = 254.1544, calcd. for $C_{17}H_{19}NOH$ $[M + H]^+$: 254.1545.



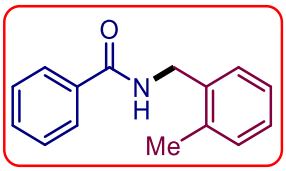
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, 2H), 7.48 (t, 1H), 7.38 (t, 2H), 7.24 (t, 1H), 6.92-6.80 (m, 3H), 6.76 (s,1H), 4.57 (d, 2H), 3.77 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.6, 160.0, 139.9, 134.4, 131.6, 129.8, 128.6, 127.1, 120.1, 113.5, 113.0, 55.3, 44.1 ppm. HRMS (ESI): *m/z* = 242.1181, calcd. for $C_{15}H_{15}NO_2H$ $[M + H]^+$: 242.1181.



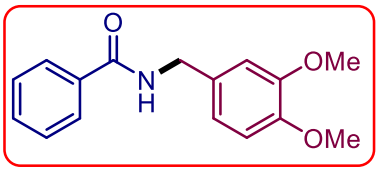
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, 2H), 7.42 (t, 1H), 7.33 (t, 2H), 7.22 (s,1H), 7.18-7.12 (m, 3H), 6.72 (s, 1H), 4.50 (d, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.7, 140.5, 134.6, 134.2, 131.8, 130.1, 128.7, 127.9, 127.8, 127.1, 126.0, 43.5 ppm. HRMS (ESI): *m/z* = 246.0677, calcd. for $C_{14}H_{12}NClOH$ $[M + H]^+$: 246.0686.



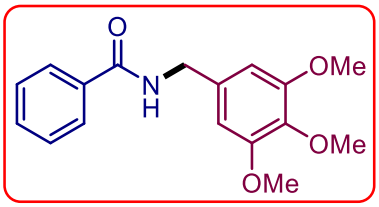
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, 2H), 7.45-7.32 (m, 5H), 7.19-7.09 (m, 2H), 6.69 (s, 1H), 4.50 (d, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 167.6, 140.8, 134.2, 131.8, 130.8, 130.7, 130.4, 128.7, 127.1, 126.5, 122.9, 43.5 ppm. HRMS (ESI): *m/z* = 290.0172, calcd. for $C_{14}H_{12}NBrOH$ $[M + H]^+$: 290.0181.



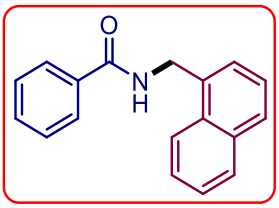
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, 2H), 7.49 (t, 1H), 7.41 (t, 2H), 7.29 (d, 1H), 7.25-7.17 (m, 3H), 6.38 (s, 1H), 4.63 (d, 2H), 2.36 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 167.4, 136.7, 135.9, 134.5, 131.6, 130.7, 128.8, 128.7, 128.0, 127.1, 126.4, 42.4, 19.2 ppm. HRMS (ESI): *m/z* = 226.1237, calcd. for $C_{15}H_{15}NOH$ $[M + H]^+$: 226.1232.



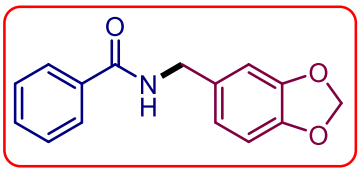
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, 2H), 7.50 (t, 1H), 7.43 (t, 2H), 6.91-6.88 (m, 2H), 6.84 (d, 1H), 6.38 (s, 1H), 4.59 (d, 2H), 3.87 (s, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 167.4, 149.5, 148.9, 134.7, 131.7, 131.0, 128.8, 127.1, 120.5, 111.7, 111.6, 56.2, 56.1, 44.2 ppm. HRMS (ESI): *m/z* = 272.1297, calcd. for $C_{16}H_{17}NO_3H$ $[M + H]^+$: 272.1287.



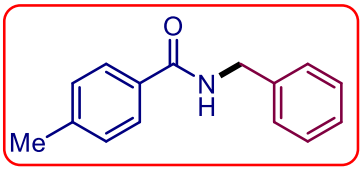
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, 2H), 7.52-7.41 (m, 3H), 6.67 (s, 1H), 6.56 (s, 2H), 4.56 (d, 2H), 3.83 (s, 9H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 167.4, 153.4, 137.3, 134.3, 134.0, 131.6, 128.6, 127.0, 105.0, 60.8, 56.1, 44.5 ppm. HRMS (ESI): *m/z* = 302.1387, calcd. for $C_{17}H_{19}NO_4H$ $[M + H]^+$: 302.1392.



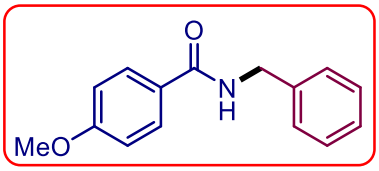
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, 1H), 7.89 (dd, 1H), 7.84 (d, H), 7.76-7.74 (m, 2H), 7.58-7.36 (m, 7H), 6.46 (s, 1H), 5.08 (d, 2H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.3, 134.5, 134.1,133.5,131.6, 128.9, 128.9,128.7, 127.1, 127.0, 126.9, 126.2, 125.6, 123.6, 42.5 ppm. HRMS (ESI): *m/z* = 262.1230, calcd. for $C_{18}H_{15}NOH$ $[M + H]^+$: 262.1232.



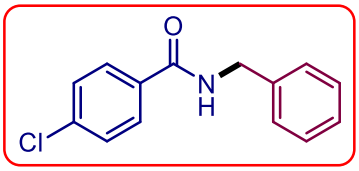
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78-7.76 (m, 2H), 7.51-7.47 (m, 1H), 7.43-7.40 (m, 2H), 6.84-6.76 (m, 3H), 6.45 (s, 1H), 5.94 (s, 2H), 4.53 (d, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.5, 148.2, 147.3, 134.5, 132.2, 131.7, 128.8, 127.1, 121.4, 108.7, 108.5, 101.3, 44.2 ppm. HRMS (ESI): *m/z* = 256.0976, calcd. for $C_{15}H_{13}NO_3H$ $[M + H]^+$: 256.0974.



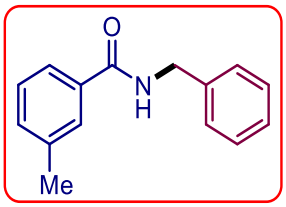
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, 2H), 7.35 (d, 4H), 7.31-7.27 (m, 1H), 7.22 (d, 2H), 6.44 (s, 1H), 4.63 (d, 2H), 2.39 (s, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.4, 142.1, 138.5, 131.7, 129.4, 128.9, 128.0, 127.7, 127.1, 44.2, 21.5 ppm. HRMS (ESI): *m/z* = 226.1237, calcd. for $C_{15}H_{15}NOH$ $[M + H]^+$: 226.1232.



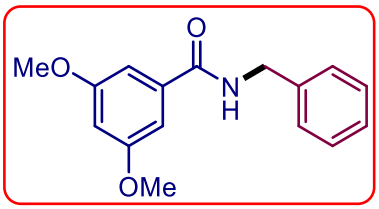
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, 2H), 7.35-7.29 (m, 5H), 6.92-6.87 (m, 2H), 6.55 (s, 1H), 4.62 (d, 2H), 3.85 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.0, 162.3, 138.6, 129.0, 128.9, 128.8, 128.0, 127.6, 126.8, 113.9, 55.5, 44.1 ppm. HRMS (ESI): *m/z* = 242.1182, calcd. for $C_{15}H_{15}NO_2H$ $[M + H]^+$: 242.1181.



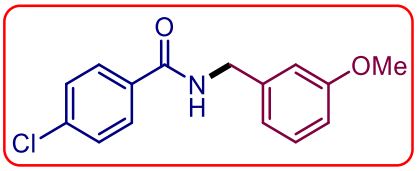
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, 2H), 7.38-7.29 (m, 7H), 6.60 (s, 1H), 4.60 (d, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 166.5, 138.1, 137.9, 132.8, 128.9, 128.6, 128.0, 127.8, 44.3 ppm. HRMS (ESI): *m/z* = 245.0689, calcd. for $C_{14}H_{12}NClOH$ $[M + H]^+$: 246.0686.



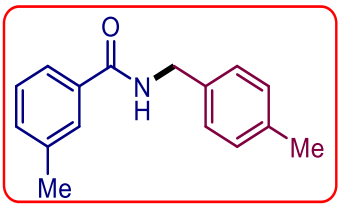
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.58-7.55 (m, 1H), 7.36-7.28 (m, 7H), 6.45 (s, 1H), 4.64 (d, 2H), 2.39 (s, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 167.7, 138.6, 138.4, 134.5, 132.4, 128.9, 128.6, 128.1, 127.9, 127.7, 124.0, 44.3, 21.5 ppm. HRMS (ESI): *m/z* = 226.1239, calcd. for $C_{15}H_{15}NOH$ $[M + H]^+$: 226.1232.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.28 (m, 5H), 6.91 (d, 2H), 6.57 (s, 1H), 6.47 (s, 1H), 4.62 (d, 2H), 3.80 (s, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 167.3, 161.0, 138.2, 136.7, 128.9, 128.0, 127.8, 105.1, 103.7, 55.7, 44.3 ppm. HRMS (ESI): *m/z* = 272.1292, calcd. for $C_{16}H_{17}NO_3H$ $[M + H]^+$: 272.1287.

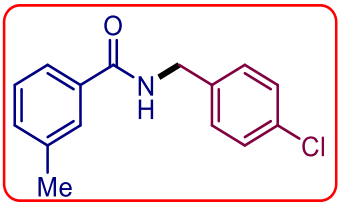


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, 2H), 7.38 (d, 2H), 7.28-7.24 (m, 2H), 6.92-6.82 (m, 3H), 6.53 (s, 1H), 4.58 (d, 2H), 3.79 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 166.5, 160.1, 139.6, 137.9, 132.8, 130.0, 129.0, 128.6, 120.2, 113.7, 113.2, 55.4, 44.3 ppm. HRMS (ESI): *m/z* = 276.0782, calcd. for $C_{15}H_{14}NClO_2H$ $[M + H]^+$: 276.0791.

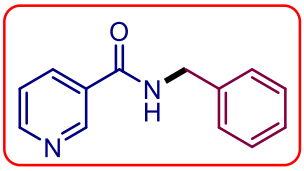


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.47-7.44 (m, 1H), 7.22-7.14 (m, 4H), 7.06 (d, 2H), 6.43 (s, 1H), 4.49 (d, 2H), 2.27 (d, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 167.6,

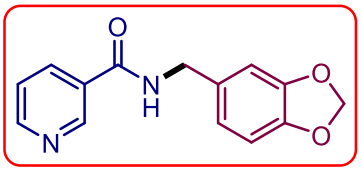
138.5, 137.4, 135.3, 134.5, 132.3, 129.5, 128.5, 128.0, 127.8, 124.0, 44.0, 21.4, 21.2 ppm. HRMS (ESI): *m/z* = 240.1392, calcd. for $C_{16}H_{17}NOH$ $[M + H]^+$: 240.1388.



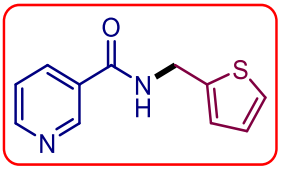
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.58-7.56 (m, 1H), 7.32-7.28 (m, 6H), 6.64 (s, 1H), 4.59 (d, 2H), 2.39 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.8, 138.6, 137.0, 134.3, 133.4, 132.5, 129.3, 129.0, 128.6, 127.9, 124.0, 43.4, 21.4 ppm. HRMS (ESI): *m/z* = 260.0849, calcd. for $C_{15}H_{14}NClOH$ $[M + H]^+$: 260.0842.



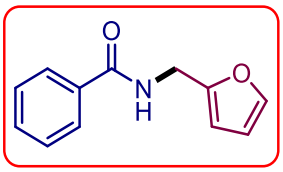
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.61 (t, 1H), 8.10 (d, 1H), 7.31-7.27 (m, 6H), 7.09 (s, 1H), 4.61 (d, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.7, 152.2, 148.0, 137.9, 135.4, 130.2, 128.9, 128.0, 127.8, 123.6, 44.2 ppm. HRMS (ESI): *m/z* = 213.1027, calcd. for $C_{13}H_{12}N_2OH$ $[M + H]^+$: 213.1028.



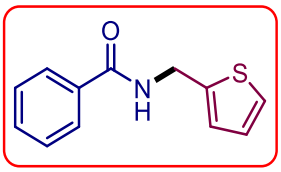
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.65 (d, 1H), 8.13 (d, 1H), 7.36 (dd, 1H), 6.92 (s, 1H), 6.82-6.73 (m, 3H), 5.92 (s, 2H), 4.52 (d, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.5, 152.1, 148.1, 147.8, 147.3, 135.6, 131.7, 130.3, 123.7, 121.4, 108.6, 108.5, 101.3, 44.1 ppm. HRMS (ESI): *m/z* = 257.0913, calcd. for $C_{14}H_{12}N_2O_3H$ $[M + H]^+$: 257.0926.



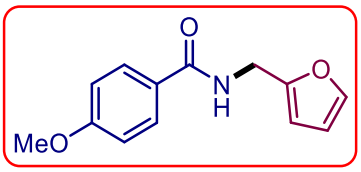
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.64 (d, 1H), 8.11 (d, 1H), 7.34 (dd, 1H), 7.22 (d, 1H), 7.11 (s, 1H), 7.01 (d, 1H), 6.95-6.93 (m, 1H), 4.79 (d, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.5, 152.3, 148.0, 140.4, 135.4, 130.0, 127.1, 126.6, 125.6, 123.6, 38.9 ppm. HRMS (ESI): *m/z* = 219.0581, calcd. for $C_{11}H_{10}N_2SOH$ $[M + H]^+$: 219.0592.



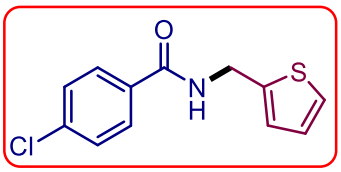
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, 2H), 7.52-7.38 (m, 4H), 6.48 (s, 1H), 6.32 (d, 2H), 4.64 (d, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 167.4, 151.3, 142.5, 134.3, 131.8, 128.7, 127.1, 110.7, 107.9, 37.2 ppm. HRMS (ESI): *m/z* = 202.0865, calcd. for $C_{12}H_{11}NO_2H$ $[M + H]^+$: 202.0868.



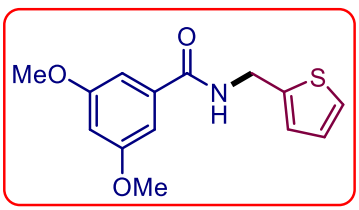
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79-7.76 (m, 2H), 7.49-7.46 (m, 1H), 7.41-7.38 (m, 2H), 7.22 (dd, 1H), 7.02-7.00 (m, 1H), 6.95 (dd, 1H), 6.75 (s, 1H), 4.79 (d, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 167.4, 141.0, 134.2, 131.7, 128.7, 127.1, 127.0, 126.3, 125.4, 38.9 ppm. HRMS (ESI): *m/z* = 218.0640, calcd. for $C_{12}H_{11}NSOH$ $[M + H]^+$: 218.0640.



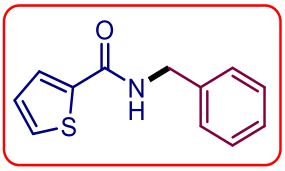
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, 2H), 7.34 (s, 1H), 6.87 (d, 2H), 6.63 (s, 1H), 6.31 (s, 1H), 6.25 (d, 1H), 4.59 (d, 2H), 3.81 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 166.9, 162.3, 151.6, 142.3, 129.0, 126.5, 113.8, 110.6, 107.6, 55.5, 37.0 ppm. HRMS (ESI): *m/z* = 232.09658, calcd. for $C_{13}H_{13}NO_3H$ $[M + H]^+$: 232.0974.



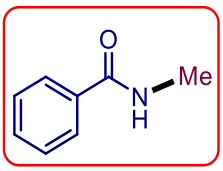
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, 2H), 7.33 (d, 2H), 7.19 (s, 1H), 6.97 (d, 1H), 6.90 (t, 1H), 6.37 (s, 1H), 4.73 (d, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 166.2, 140.6, 138.1, 132.6, 129.0, 128.6, 127.2, 126.6, 125.7, 39.0 ppm. HRMS (ESI): *m/z* = 252.0235, calcd. for $C_{12}H_{10}NClSOH$ $[M + H]^+$: 252.0250.



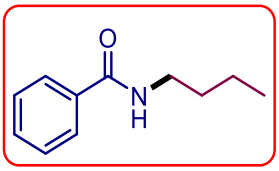
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, 1H), 7.02 (s, 1H), 6.97-6.94 (m, 1H), 6.90 (d, 2H), 6.56-6.54 (m, 1H), 4.78 (d, 2H), 3.79 (d, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.1, 161.0, 140.8, 136.5, 127.1, 126.3, 125.4, 105.1, 103.8, 55.7, 39.0 ppm. HRMS (ESI): *m/z* = 278.0839, calcd. for $C_{14}H_{15}NSO_3H$ $[M + H]^+$: 278.0851.



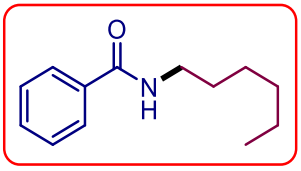
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.39 (m, 2H), 7.29-7.18 (m, 5H), 6.99-6.97 (m, 1H), 6.32 (s, 1H), 4.54 (d, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.9, 138.9, 138.2, 130.2, 128.9, 128.3, 128.1, 127.8, 44.1 ppm. HRMS (ESI): *m/z* = 218.0630, calcd. for $C_{12}H_{11}NSOH$ $[M + H]^+$: 218.0640.



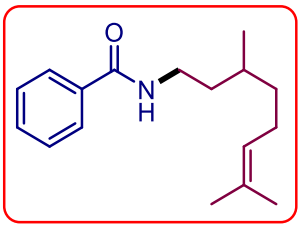
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.75 (m, 2H), 7.51-7.47 (m, 1H), 7.44-7.41 (m, 2H), 3.03 (d, 3H) ppm. GCMS: *m/z* = 135, calcd. for C_8H_9NO $[M]^+$: 135.17.



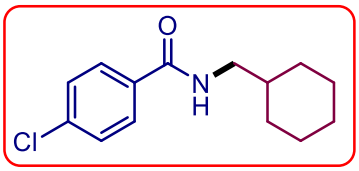
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, 2H), 7.41 (dt, 3H), 6.54 (s, 1H), 3.40 (q, 2H), 1.56 (p, 2H), 1.37 (m, 2H), 0.91 (t, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.7, 134.9, 131.3, 128.5, 127.0, 39.9, 31.8, 20.2, 13.8 ppm. HRMS (ESI): *m/z* = 178.1230, calcd. for $C_{11}H_{15}NOH$ $[M + H]^+$: 178.1232



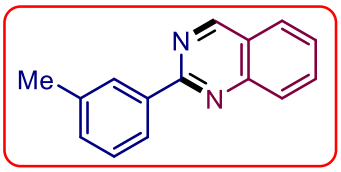
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, 2H), 7.46-7.35 (m, 3H), 6.54 (s, 1H), 3.39 (q, 2H), 1.61-1.54 (s, 2H), 1.35-1.24 (m, 6H), 0.86 (t, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.7, 134.9, 131.3, 128.5, 127.0, 40.2, 31.6, 29.7, 26.7, 22.6, 14.1 ppm. HRMS (ESI): *m/z* = 206.1534, calcd. for $C_{13}H_{19}NOH$ $[M + H]^+$: 206.1545.



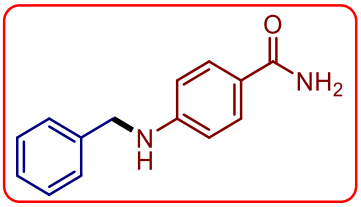
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, 2H), 7.49-7.38 (m, 3H), 6.22 (s, 1H), 5.10 (t, 1H), 3.53-3.39 (m, 2H), 2.06-1.90 (m, 2H), 1.66 (s, 3H), 1.64-1.49 (m, 5H), 1.46-1.32 (m, 2H), 1.25–1.15 (m, 1H), 0.94 (d, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.6, 135.0, 131.5, 131.4, 128.6, 126.9, 124.7, 38.3, 37.1, 36.7, 30.4, 25.8, 25.5, 19.5, 17.8 ppm. HRMS (ESI): *m/z* = 260.2014, calcd. for $C_{17}H_{25}NOH$ $[M + H]^+$: 260.2014.



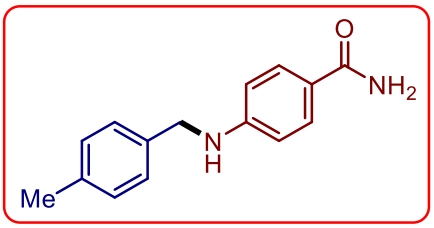
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, 2H), 7.39 (d, 2H), 6.21 (s, 1H), 3.28 (t, 2H), 1.78-1.67 (m, 6H), 1.30-1.15 (m, 3H), 1.03-0.93 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.7, 137.7, 133.4, 128.9, 128.4, 46.5, 38.1, 31.1, 26.5, 25.9 ppm. HRMS (ESI): *m/z* = 252.1162, calcd. for $C_{14}H_{18}NClOH$ $[M + H]^+$: 252.1155.



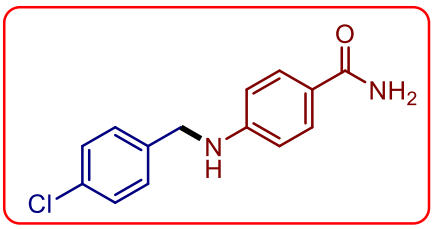
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 8.42 (d, 2H), 8.10 (d, 1H), 7.91 (t, 2H), 7.61 (t, 1H), 7.44 (t, 1H), 7.33 (d, 1H), 2.49 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.3, 160.6, 150.9, 138.4, 138.0, 134.3, 131.6, 129.3, 128.7, 127.4, 127.3, 125.9, 123.7, 21.7 ppm. HRMS (ESI): *m/z* = 221.1085, calcd. for $C_{15}H_{12}N_2H$ $[M + H]^+$: 221.1079.



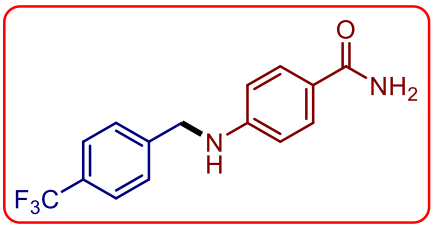
^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.60 (d, 2H), 7.52 (s, 1H), 7.36-7.30 (m, 4H), 7.25-7.20 (m, 1H), 6.84 (s, 1H), 6.77 (t, 1H), 6.55 (d, 2H), 4.32 (d, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-*d6*) δ 168.4, 151.6, 140.2, 129.4, 128.8, 127.6, 127.2, 121.6, 111.5, 46.5 ppm. HRMS (ESI): *m/z* = 227.1181, calcd. for $C_{14}H_{14}N_2OH$ $[M + H]^+$: 227.1184.



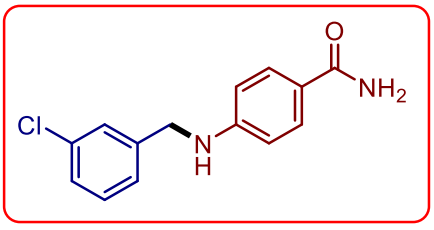
^{1}H NMR (500 MHz, DMSO-*d6*) δ 7.63-7.61 (m, 2H), 7.50 (s, 1H), 7.24-7.22 (m, 2H), 7.13-7.11 (m, 2H), 6.81(s, 1H), 6.69 (t, 1H), 6.57-6.54 (m, 2H), 4.27 (d, 2H), 2.27 (s, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, DMSO-*d6*) δ 168.5, 151.6, 137.1, 136.2, 129.4, 129.3, 127.6, 121.7, 111.5, 46.3, 21.1 ppm. HRMS (ESI): *m/z* = 241.1337, calcd. for $C_{15}H_{16}N_2OH$ $[M + H]^+$: 241.1341.



^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.61 (d, 2H), 7.52 (s, 1H), 7.42-7.35 (m, 4H), 6.86 (s, 1H), 6.82 (t, 1H), 6.54 (d, 2H), 4.32 (d, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-*d6*) δ 168.4, 151.3, 139.4, 131.7, 129.5, 129.4, 128.7, 121.8, 111.5, 45.7 ppm. HRMS (ESI): *m/z* = 261.0790, calcd. for $C_{14}H_{13}N_2ClOH$ $[M + H]^+$: 261.0795.

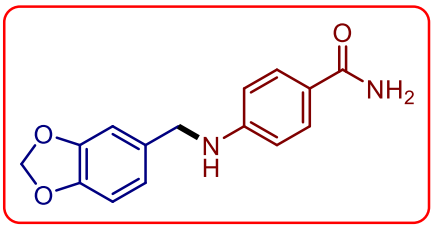


^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.67 (d, 2H), 7.60 (d, 2H), 7.55-7.50 (m, 3H), 6.90-6.84 (m, 2H), 6.54 (d, 2H), 4.42 (d, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-*d6*) δ 168.4, 151.3, 145.4, 129.5, 128.2, 128.1 (t, *J* (C, F) = 31.5 Hz), 125.7 (q, *J* (C, F) = 3.78 Hz), 123.5 (t, *J* (C, F) = 271.47 Hz), 122.0, 111.5, 46.0 ppm. HRMS (ESI): *m/z* = 295.1059, calcd. for $C_{15}H_{13}F_3N_2OH$ $[M + H]^+$: 295.1058.

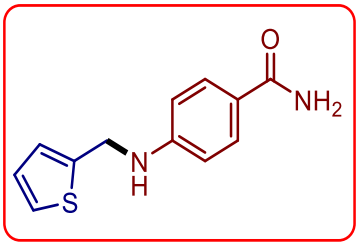


^{1}H NMR (500 MHz, DMSO-*d6*) δ 7.63 (d, 2H), 7.53 (s, 1H), 7.39-7.29 (m, 4H), 6.86-6.81 (m, 2H), 6.57 (d, 2H), 4.35 (d, 2H) ppm. ^{13}C{^{1}H} NMR (126 MHz, DMSO-*d6*) δ 168.5, 151.3,

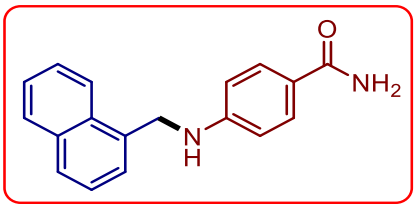
143.1, 133.6, 130.7, 129.5, 127.3, 127.1, 126.3, 122.0, 111.6, 45.9 ppm. HRMS (ESI): *m/z* = 261.0801, calcd. for $C_{14}H_{13}N_2ClOH$ $[M + H]^+$: 261.0795



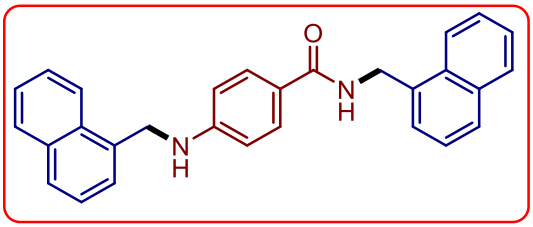
^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.63-7.60 (m, 2H), 7.53 (s, 1H), 6.91-6.81 (m, 4H), 6.71 (t, 1H), 6.56 (d, 2H), 5.97 (s, 1H), 4.22 (d, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-*d6*) δ 168.0, 151.0, 147.3, 146.0, 133.6, 129.0, 121.2, 120.3, 111.1, 108.1, 107.7, 100.8, 45.8 ppm. HRMS (ESI): *m/z* = 271.1085, calcd. for $C_{15}H_{14}N_2O_3H$ $[M + H]^+$: 271.1083.



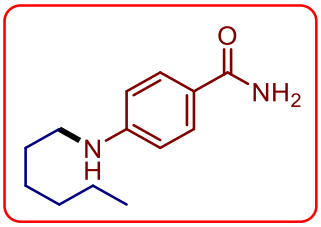
^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.62 (d, *2*H), 7.54 (s, 1H), 7.37 (d, 1H), 7.05 (d, 1H), 6.97-6.95 (m, 1H), 6.86 (s, 1H), 6.78 (t, 1H), 6.61 (d, 2H), 4.50 (d, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-*d6*) δ 168.4, 151.2, 144.1, 129.4, 127.2, 125.5, 125.1, 122.0, 111.7, 41.9 ppm. HRMS (ESI): *m/z* = 233.0743, calcd. for $C_{12}H_{12}N_2SOH$ $[M + H]^+$: 233.0749.



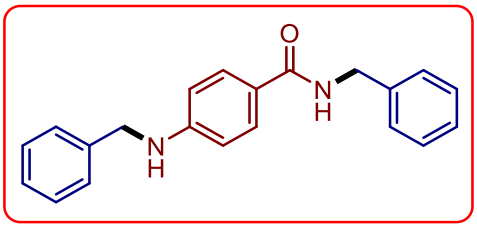
^{1}H NMR (400 MHz, DMSO-*d6*) δ 8.14 (d, 1H), 7.96 (d, 1H), 7.84 (d, 1H), 7.68 (d, 2H), 7.59-7.43 (m, 5H), 6.91 (s, 1H), 6.81 (t, 1H), 6.66 (d, 2H), 4.78 (d, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-*d6*) δ 168.6, 151.8, 134.9, 133.9, 131.6, 129.6, 129.0, 127.9, 126.6, 126.3, 125.9, 125.5, 124.0, 121.6, 111.4, 44.7 ppm. HRMS (ESI): *m/z* = 277.1342, calcd. for $C_{18}H_{16}N_2OH$ $[M + H]^+$: 277.1341.



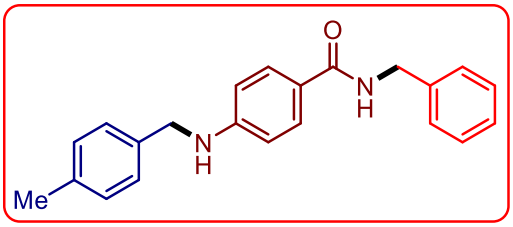
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, 1H), 8.00-7.97 (m, 1H), 7.89-7.86(m, 2H), 7.81 (t, 2H), 7.63 (d, 2H), 7.54-7.39 (m, 9H), 6.60 (d, 2H), 6.18 (t, 1H), 5.07 (d, 2H), 4.74 (d, 2H), 4.33 (s, 1H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.1, 151.0, 134.1, 133.6, 131.8, 131.6, 129.0, 129.0, 128.9, 128.7, 128.6, 126.9, 126.8, 126.6, 126.2, 126.1, 126.1, 126.1, 125.6, 125.6, 123.8, 123.4, 123.0, 112.0, 46.1, 42.4 ppm. HRMS (ESI): *m/z* = 417.1984, calcd. for $C_{29}H_{24}N_2OH$ [M + H]$^{+}$: 417.1967.



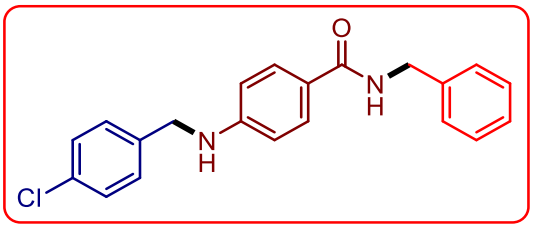
^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.63 (d, 2H), 7.52 (s, 1H), 6.83 (s, 1H), 6.52 (d, 2H), 6.11 (t, 1H), 3.03 (q, 2H), 1.52 (q, 2H), 1.37-1.27 (m, 6H), 0.87 (t, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-*d6*) δ 168.0, 151.5, 129.1, 120.5, 110.5, 42.4, 40.1, 39.9, 39.5, 39.3, 38.9, 31.1, 28.5, 26.3, 22.1, 13.9 ppm. HRMS (ESI): *m/z* = 221.1657, calcd. for $C_{13}H_{20}N_2OH$ [M + H]$^{+}$: 221.1654.



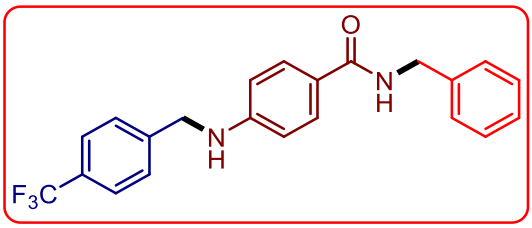
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, 2H), 7.34-7.27 (m, 10H), 6.61-6.57 (m, 2H), 4.61 (t, 2H), 4.36 (d, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.4, 150.9, 138.8, 138.7, 128.8, 128.8, 128.7, 128.7, 127.9, 127.5, 127.4, 122.6, 112.0, 47.7, 43.9 ppm. HRMS (ESI): *m/z* = 317.1657, calcd. for $C_{21}H_{20}N_2OH$ [M + H]$^{+}$: 317.1654.



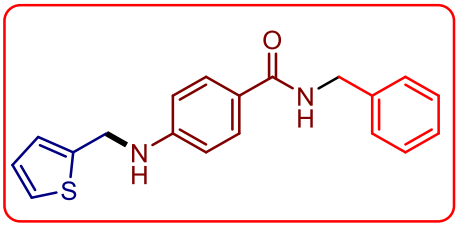
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, 2H), 7.25 (d, 4H), 7.21-7.17 (m, 1H), 7.15-7.05 (m, 4H), 6.52 (d, 2H), 6.21 (s, 1H), 4.53 (d, 2H), 4.23 (s, 2H), 2.26 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.3, 150.7, 138.8, 137.3, 135.4, 129.5, 128.8, 128.0, 127.6, 127.5, 123.0, 112.3, 47.8, 44.1, 21.2 ppm. HRMS (ESI): *m/z* = 331.1810, calcd. for $C_{22}H_{22}N_2OH$ [M + H]$^{+}$: 331.1810.



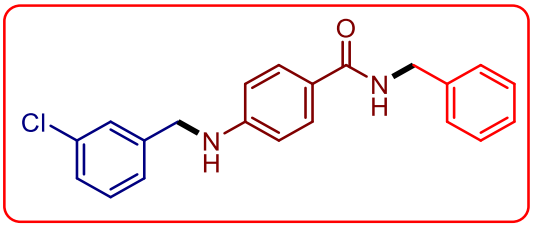
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, 2H), 7.23-7.05 (m, 8H), 6.49-6.47 (m, 2H), 6.22 (s, 1H), 4.52 (d, 2H), 4.26 (s, 2H) ppm. ^{13}C{^{1}H} (101 MHz, $CDCl_3$) δ 167.3, 150.6, 138.8, 137.2, 133.3, 129.0, 128.8, 128.7, 128.0, 127.6, 123.1, 112.2, 47.2, 44.1 ppm. HRMS (ESI): *m/z* = 351.1262, calcd. for $C_{21}H_{19}N_2ClOH$ $[M + H]^+$: 351.1264.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.50 (m, 4H), 7.37 (d, 2H), 7.28-7.17 (m, 6H), 6.50 (d, 2H), 6.20 (t, 1H), 4.52 (d, 2H), 4.37 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.2, 150.3, 142.9, 138.8, 128.9, 128.8, 128.0, 127.7, 127.5, 125.8 (q, *J* (C, F) = 3.72 Hz), 123.5, 112.4, 47.5, 44.1 ppm. HRMS (ESI): *m/z* = 385.1525, calcd. for $C_{22}H_{19}F_3N_2OH$ $[M + H]^+$: 385.1528.

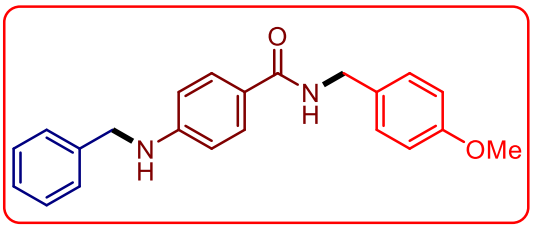


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, 2H), 7.29-7.13 (m, 6H), 7.14 (d, 1H), 6.94 (s, 1H), 6.88 (t, 1H), 6.57 (d, 2H), 6.21 (t, 1H), 4.53 (d, 2H), 4.46 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.3, 150.1, 141.8, 138.8, 128.8, 128.7, 128.0, 127.6, 127.1, 125.6, 125.0, 123.6, 112.6, 44.1, 43.2 ppm. HRMS (ESI): *m/z* = 323.1215, calcd. for $C_{19}H_{18}N_2SOH$ $[M + H]^+$: 323.1218.

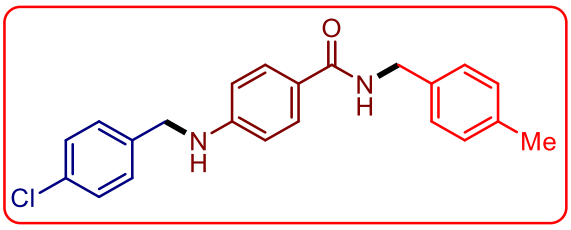


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, 2H), 7.27-7.13 (m, 10H), 6.51 (d, 2H), 6.19 (s, 1H), 4.54 (d, 2H), 4.28 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.2, 150.4, 140.9, 138.8,

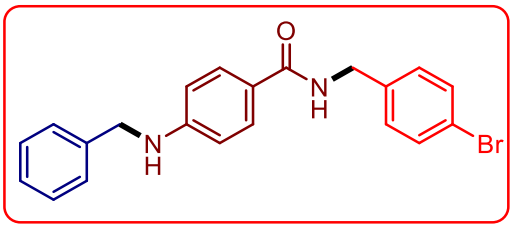
134.8, 130.2, 129.0, 129.0, 128.9, 128.9, 128.0, 127.8, 127.6, 127.5, 125.5, 123.5, 112.4, 47.5, 44.1 ppm. HRMS (ESI): *m/z* = 351.1263, calcd. for $C_{21}H_{19}N_2ClOH$ $[M + H]^+$: 351.1264.



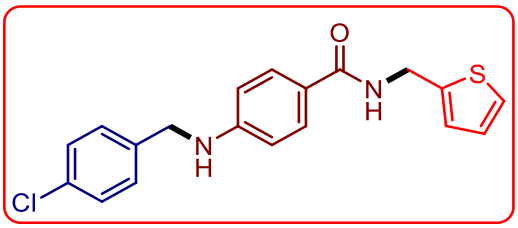
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, 2H), 7.24-7.15 (m, 7H), 6.76 (d, 2H), 6.51 (d, 2H), 6.13 (t, 1H), 4.43 (d, 2H), 4.26 (s, 2H), 3.69 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.2, 159.1, 150.2, 138.3, 130.9, 129.4, 128.9, 128.8, 127.7, 127.7, 123.5, 114.2, 112.6, 55.4, 48.2, 43.6 ppm. HRMS (ESI): *m/z* = 347.1760, calcd. for $C_{22}H_{22}N_2O_2H$ $[M + H]^+$: 347.1760.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 2H), 7.23-7.05 (m, 8H), 6.48 (d, 2H), 6.14 (s, 1H), 4.48 (d, 2H), 4.41 (s, 1H), 4.26 (s, 2H), 2.26 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.2, 150.5, 137.3, 137.2, 135.7, 133.3, 129.5, 129.0, 128.8, 128.7, 128.0, 123.2, 112.1, 47.2, 43.9, 21.2 ppm. HRMS (ESI): *m/z* = 365.1412, calcd. for $C_{22}H_{21}ClN_2OH$ $[M + H]^+$: 365.1421.

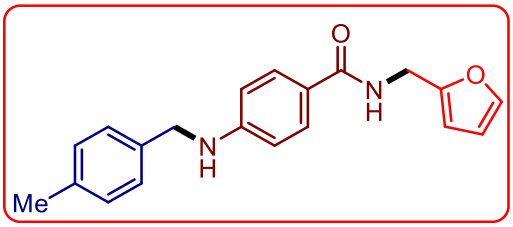


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, 2H), 7.35 (d, 2H), 7.27-7.18 (m, 5H), 7.11 (d, 2H), 6.51 (d, 2H), 6.29 (t, 1H), 4.46 (d, 2H), 4.29 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.4, 151.0, 138.6, 138.0, 131.8, 129.6, 128.9, 128.9, 127.6, 127.5, 122.6, 121.3, 112.1, 47.9, 43.3 ppm. HRMS (ESI): *m/z* = 395.0760, calcd. for $C_{21}H_{19}N_2BrOH$ $[M + H]^+$: 395.0759.

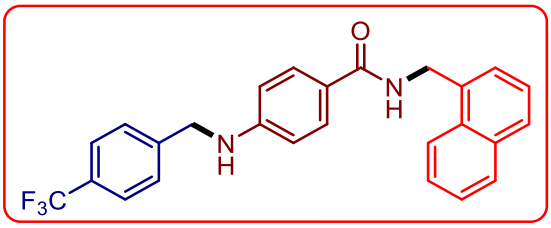


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 2H), 7.20 (q, 4H), 7.14 (d, 1H), 6.93 (d, 1H), 6.87 (t, 1H), 6.49 (d, 2H), 6.26 (s, 1H), 4.68 (d, 2H), 4.26 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz,

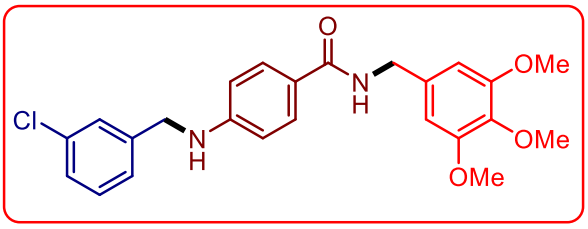
$CDCl_3$) δ 167.0, 150.5, 141.5, 137.1, 133.3, 129.0, 128.9, 128.7, 127.0, 126.1, 125.3, 123.0, 112.3, 47.2, 38.8 ppm. HRMS (ESI): *m/z* = 357.0823, calcd. for $C_{19}H_{17}N_2ClSOH$ $[M + H]^+$: 357.0828.



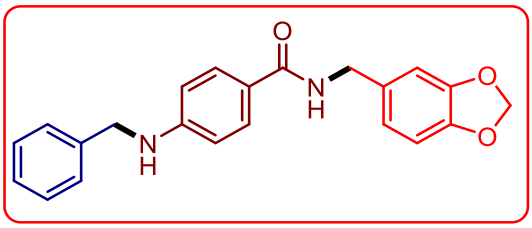
^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, 2H), 7.14-7.05 (m, 4H), 6.49 (d, 2H), 6.26 (t, 1H), 6.22 (d, 1H), 6.16 (s, 1H), 4.50 (d, 2H), 4.21 (s, 2H), 2.25 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.2, 151.9, 150.9, 142.2, 137.2, 135.6, 129.5, 128.9, 127.5, 122.5, 112.0, 110.6, 107.5, 47.6, 37.0, 21.2 ppm. HRMS (ESI): *m/z* = 321.1600, calcd. for $C_{20}H_{20}N_2O_2H$ $[M + H]^+$: 321.1603.



^1H NMR (500 MHz, $CDCl_3$) δ 8.08-8.06 (m, 1H), 7.88 (dd, 1H), 7.82 (d, 1H), 7.58 (t, 4H), 7.54-7.41 (m, 9H), 6.52 (d, 2H), 6.19 (t, 1H), 5.05 (d, 2H), 4.54 (s, 1H), 4.42 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 167.0, 150.4, 143.0, 134.1, 134.0, 131.7, 128.9, 128.8, 127.5, 126.9, 126.8, 126.1, 125.8 (q, *J* (C, F) = 3.7 Hz), 125.6, 123.8, 112.2, 47.4, 42.4 ppm. HRMS (ESI): *m/z* = 435.1701, calcd. for $C_{26}H_{21}N_2F_3OH$ $[M + H]^+$: 435.1684.

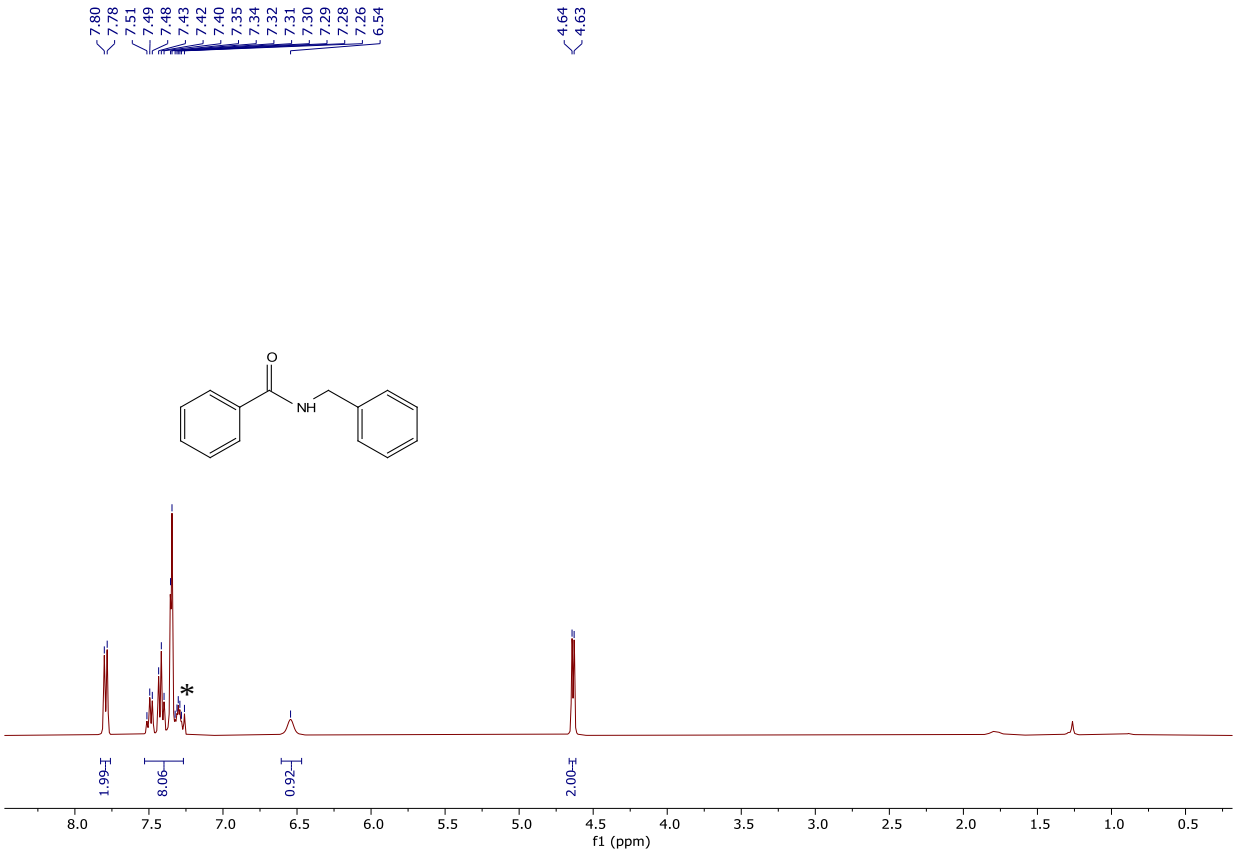


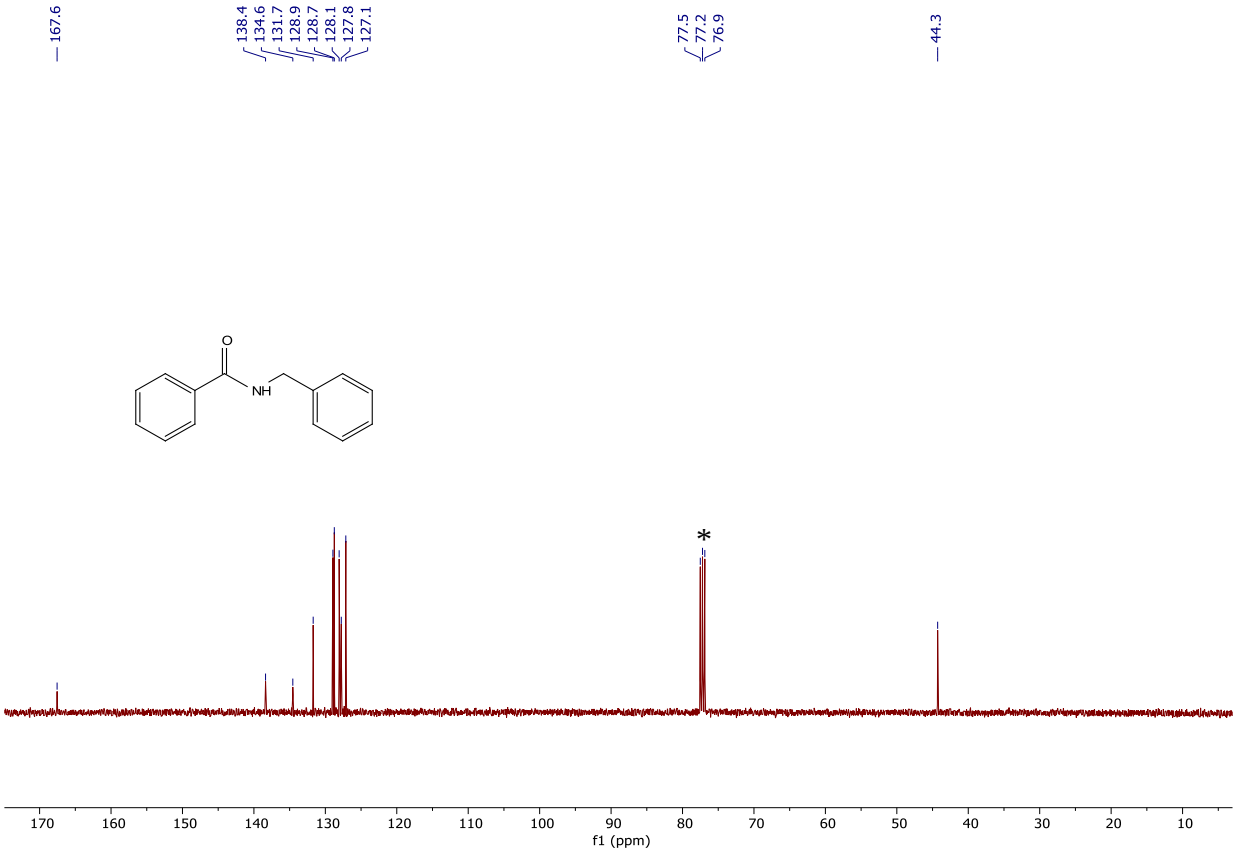
^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, 2H), 7.32 (s, 1H), 7.25-7.20 (m, 2H), 6.57 (d, 2H), 6.55 (s, 2H), 6.34 (t, 1H), 4.53 (d, 2H), 4.36 (s, 1H), 3.82 (d, 9H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.3, 153.5, 150.6, 140.9, 137.3, 134.7, 134.5, 130.1, 128.9, 127.7, 127.4, 125.4, 123.0, 112.1, 105.0, 61.0, 56.2, 47.3, 44.4 ppm. HRMS (ESI): *m/z* = 441.1578, calcd. for $C_{24}H_{25}N_2ClO_4H$ $[M + H]^+$: 441.1581.

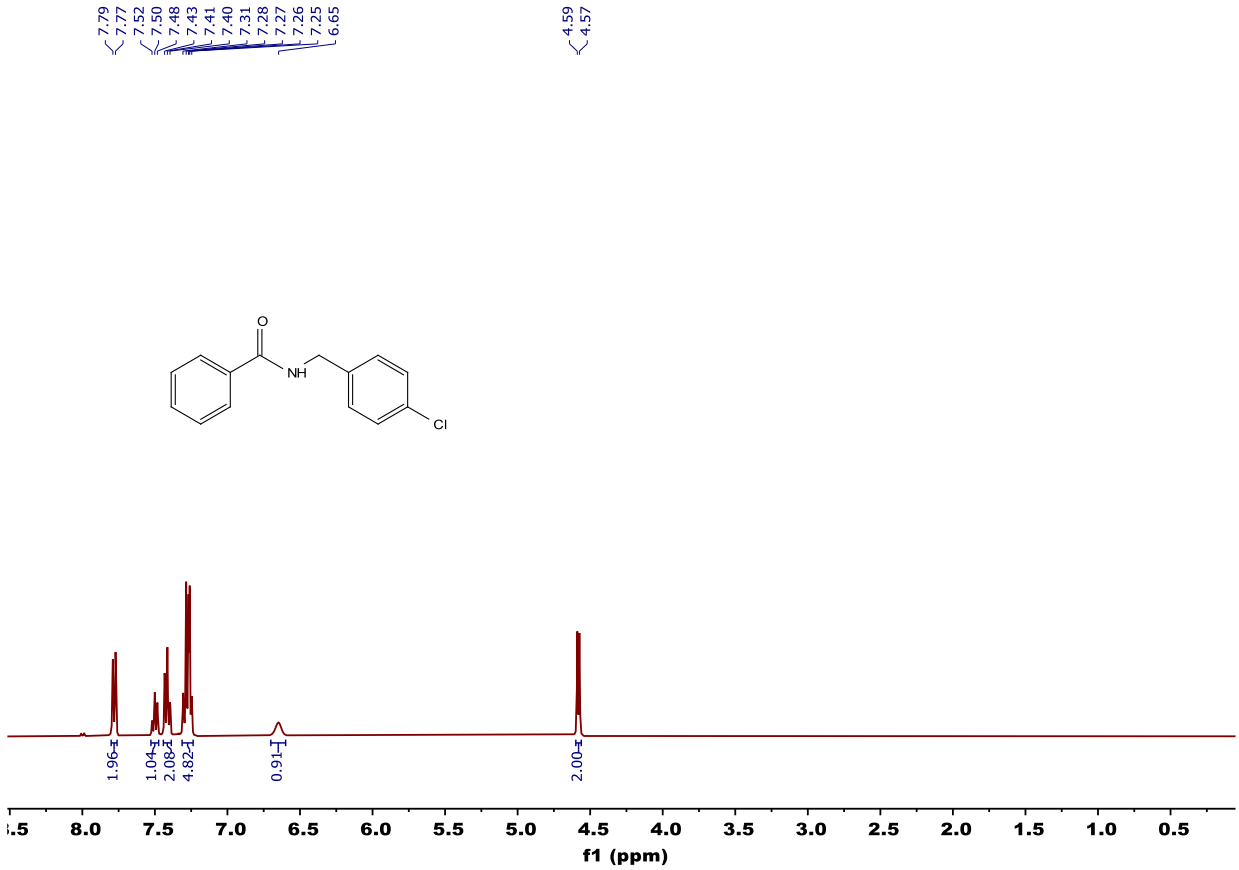


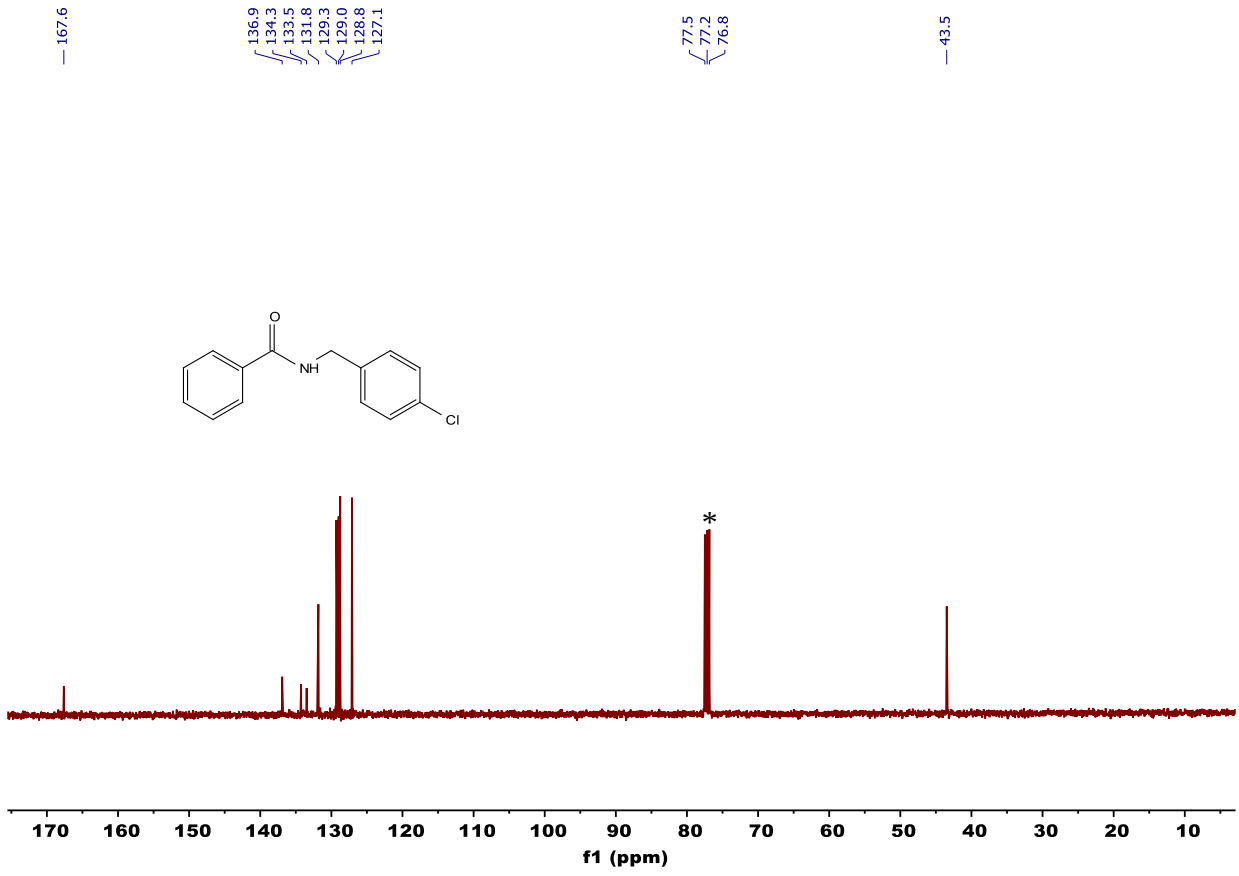
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, 2H), 7.35-7.25 (m, 6H), 6.80-6.71 (m, 3H), 6.56 (d, 2H), 6.35 (t, 1H), 5.90 (s, 2H), 4.47 (d, 2H), 4.34 (s, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 167.3, 150.9, 147.9, 146.9, 138.7, 132.7, 128.8, 127.5, 127.5, 122.7, 121.1, 112.0, 108.6, 108.4, 101.1, 47.8, 43.8 ppm. HRMS (ESI): *m/z* = 361.1554, calcd. for $C_{22}H_{20}N_2O_3H$ $[M + H]^+$: 361.1552.

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of isolated compounds 5a-5al in $CDCl_3$ (*) from catalytic reactions






7.79
7.77
7.52
7.50
7.48
7.43
7.41
7.40
7.31
7.28
7.27
7.26
7.25
6.65
4.59
4.57
O
NH
Cl
1.96
1.04
2.08
4.82
0.91
2.00
f1 (ppm)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133.5
131.8
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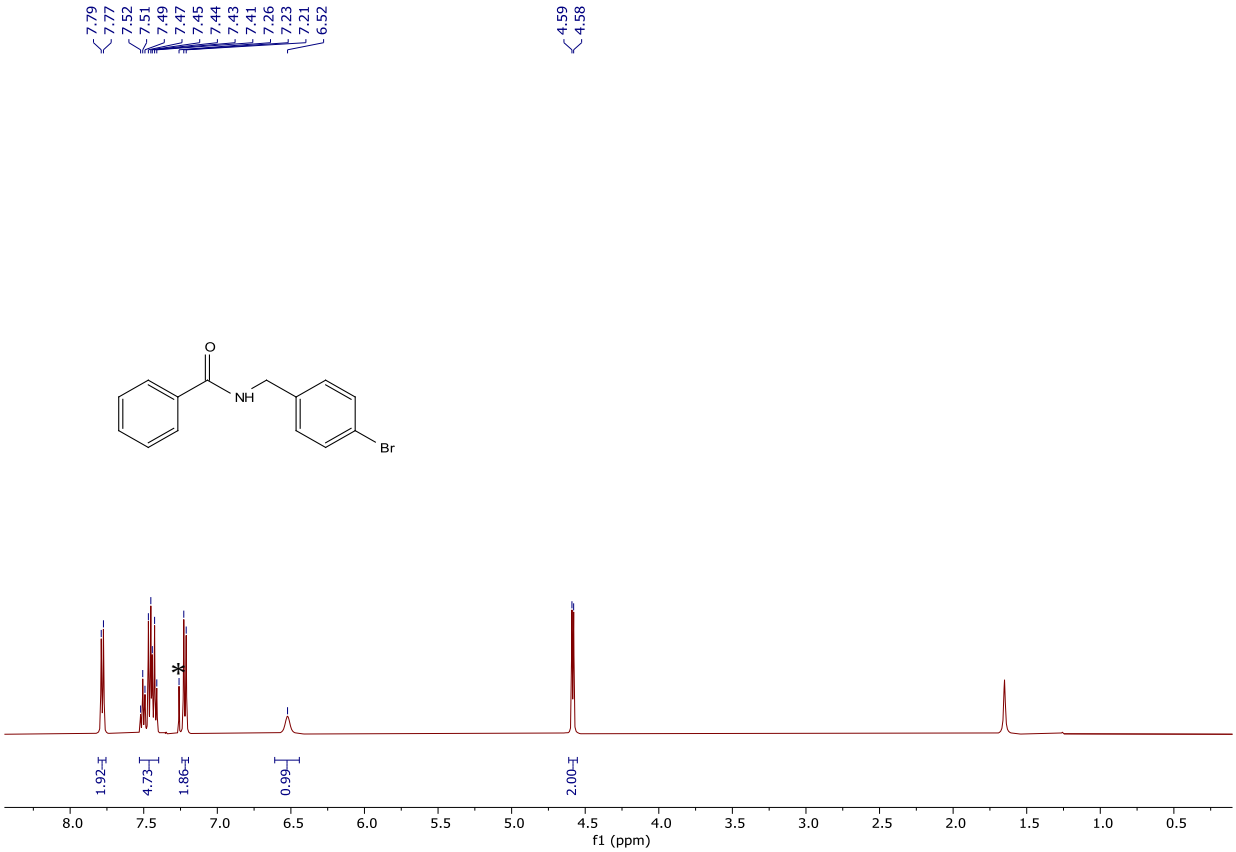
128.8
127.1
77.5
77.2
76.8
43.5
O
NH
Cl
*
f1 (ppm)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7.45
7.44
7.43
7.41
7.26
7.23
7.21
6.52
4.59
4.58
O
NH
Br
*
1.92
4.73
1.86
0.99
2.00
8.0
7.5
7.0
6.5
6.0
5.5
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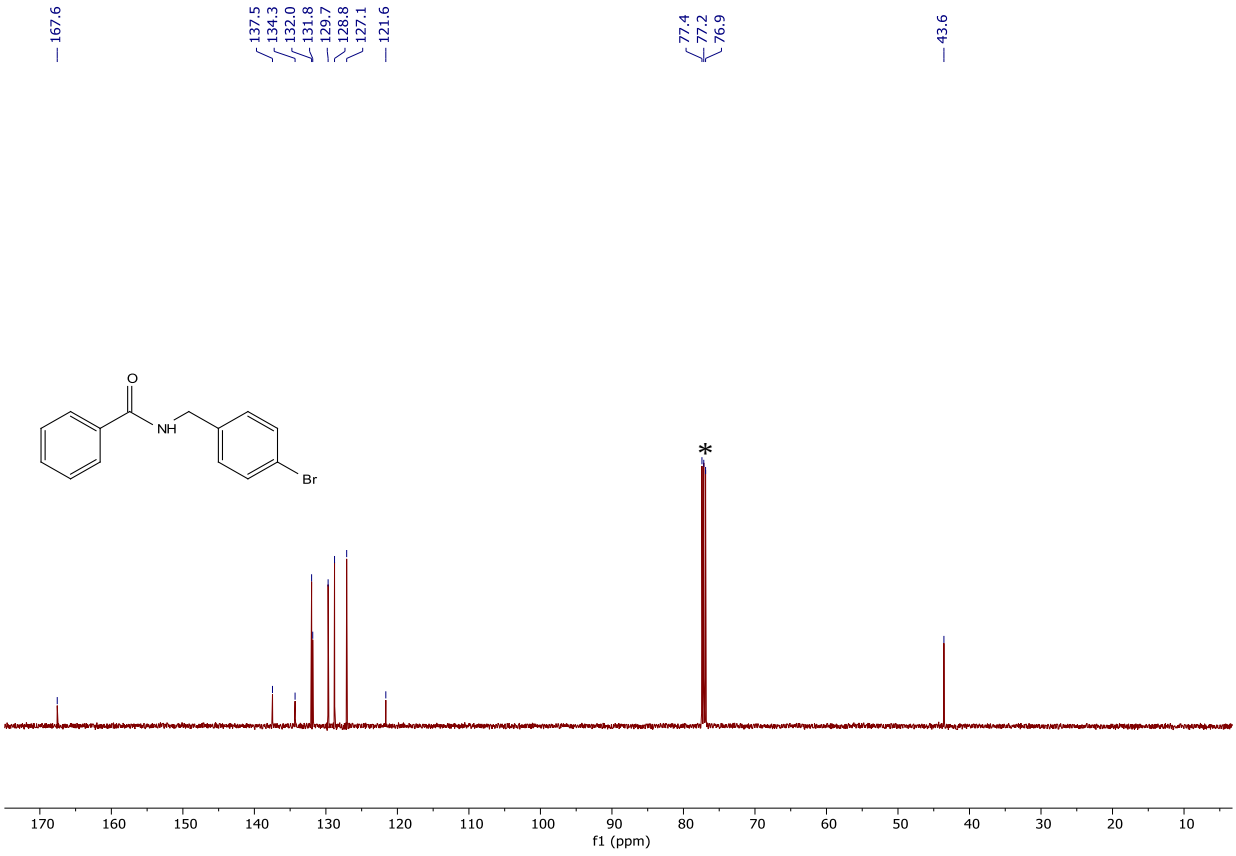
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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137.5
134.3
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131.8
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128.8
127.1
121.6
77.4
77.2
76.9
43.6
O
NH
Br
*
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160
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140
130
120
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100
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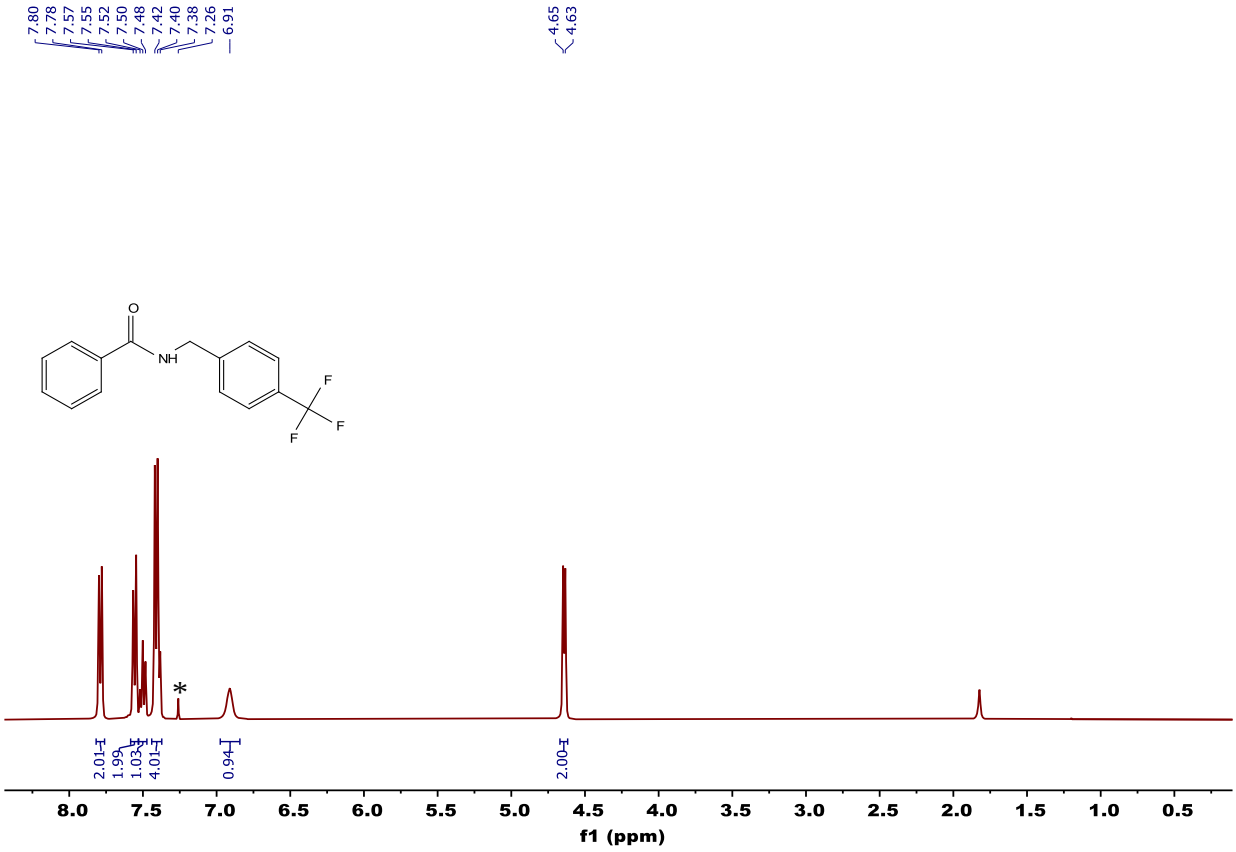
80
70
60
50
40
30
20
10
f1 (ppm)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7.38
7.26
6.91
4.65
4.63
O
NH
F
F
F
*
2.01
1.99
1.03
4.01
0.94
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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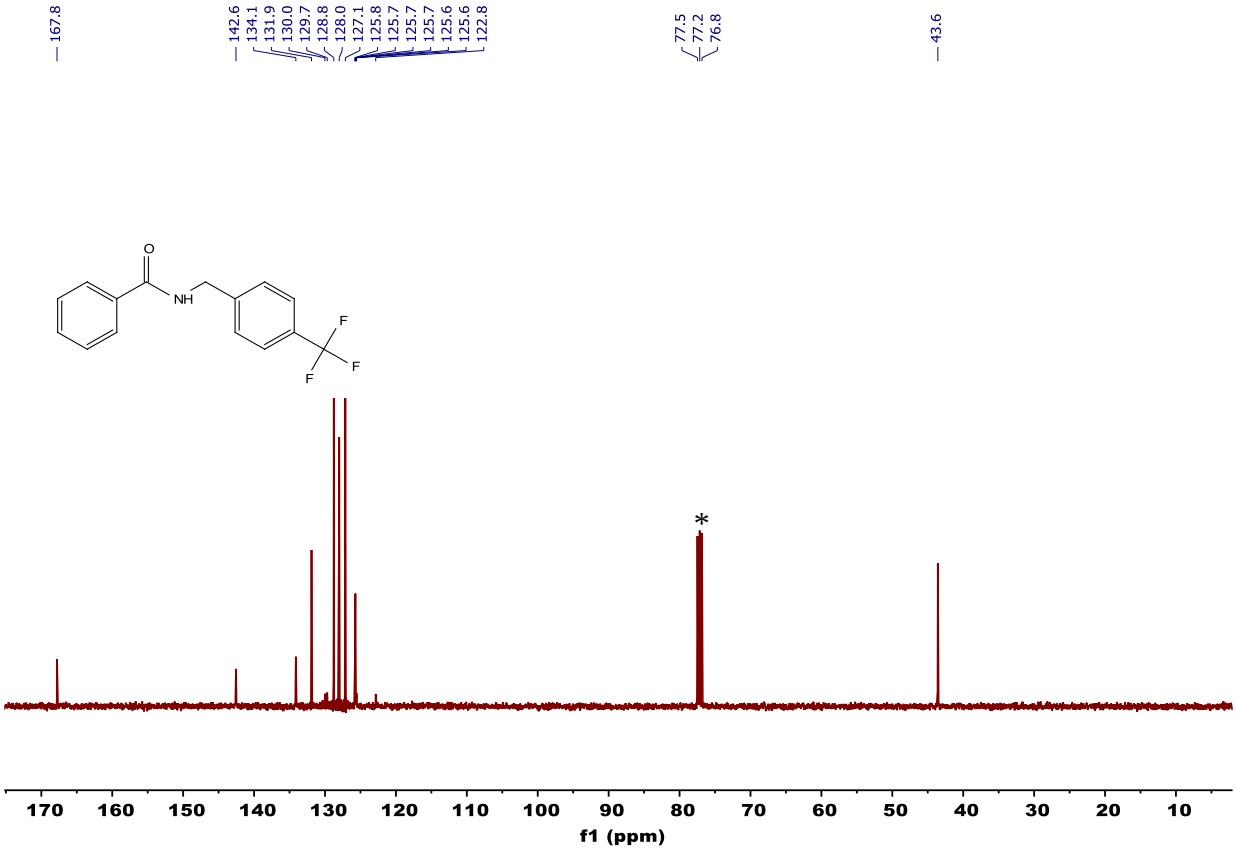
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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128.0
127.1
125.8
125.7
125.7
125.7
125.6
125.6
122.8
77.5
77.2
76.8
43.6
O
NH
F
F
F
*
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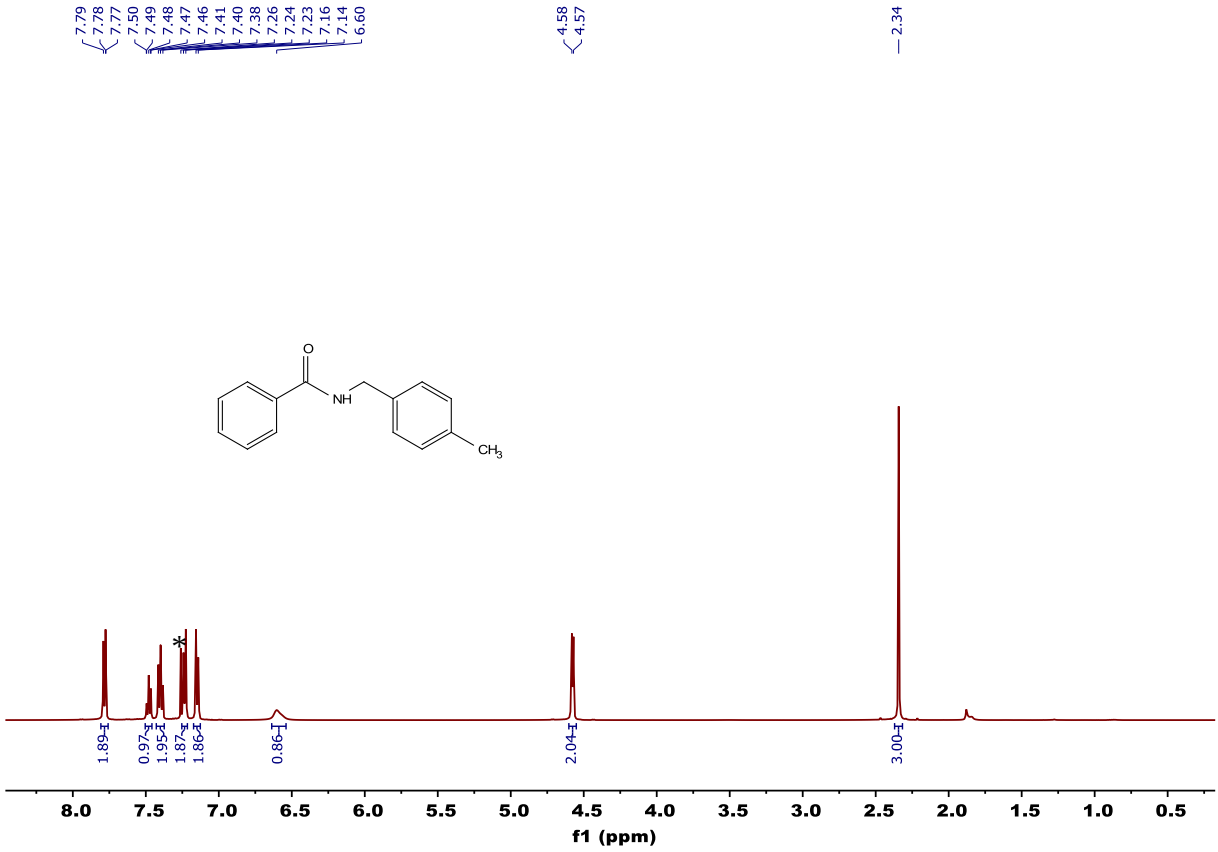
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.40
7.38
7.26
7.24
7.23
7.16
7.14
6.60
4.58
4.57
2.34
O
NH
CH3
*
1.89
0.97
1.95
1.87
1.86
0.86
2.04
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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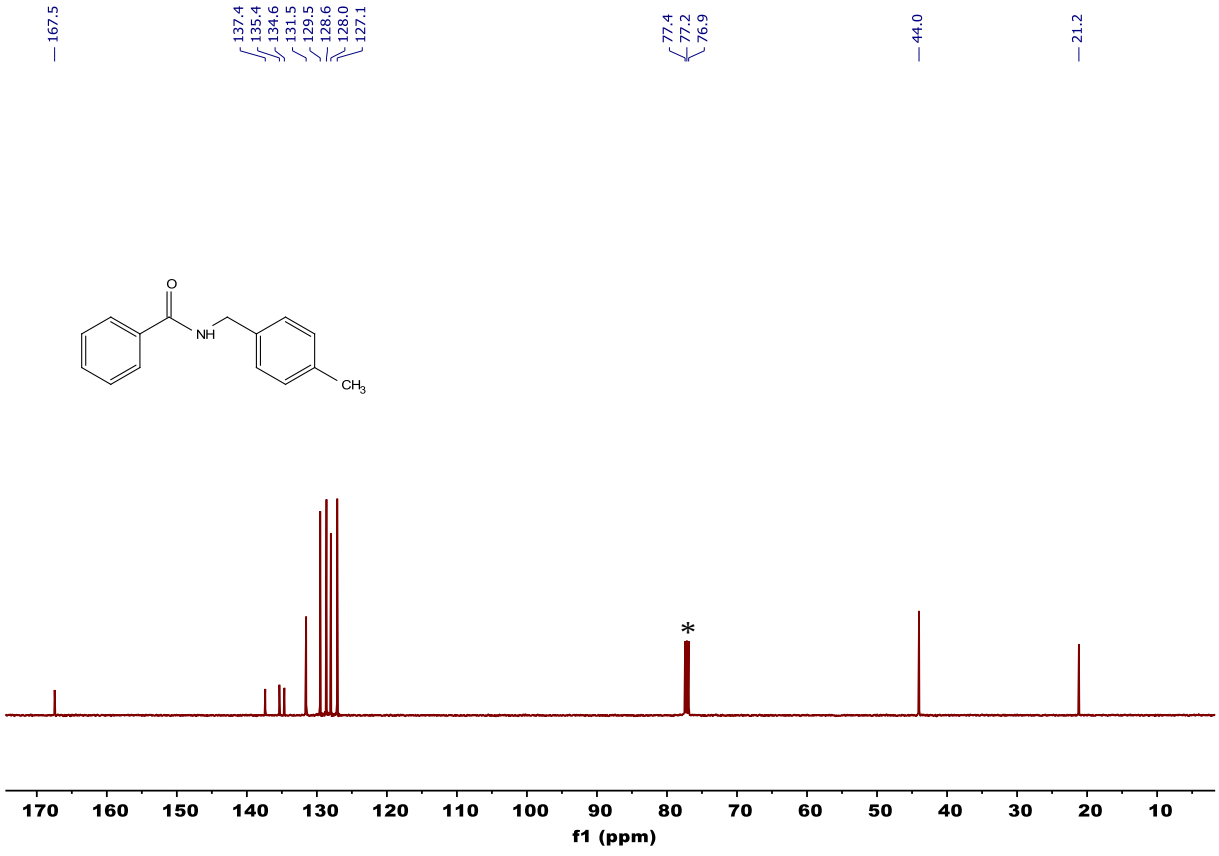
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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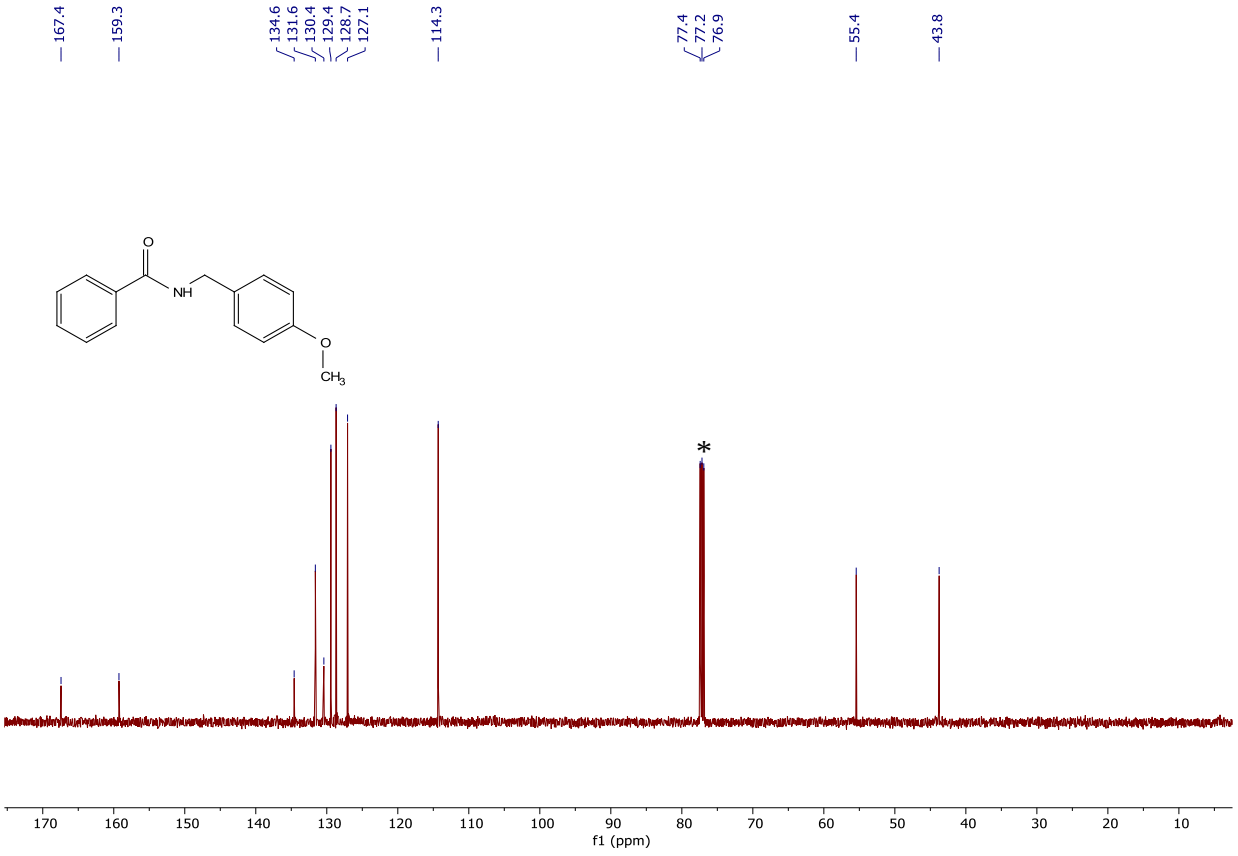
135.4
134.6
131.5
129.5
128.6
128.0
127.1
77.4
77.2
76.9
44.0
21.2
O
NH
CH3
*
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.70
7.69
7.42
7.41
7.39
7.35
7.33
7.32
7.20
7.19
7.18
6.81
6.79
6.38
4.49
4.48
3.72
O
NH
O
CH3
1.92
2.98
2.01
1.91
0.95
2.00
2.93
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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134.6
131.6
130.4
129.4
128.7
127.1
114.3
77.4
77.2
76.9
55.4
43.8
O
NH
O
CH3
*
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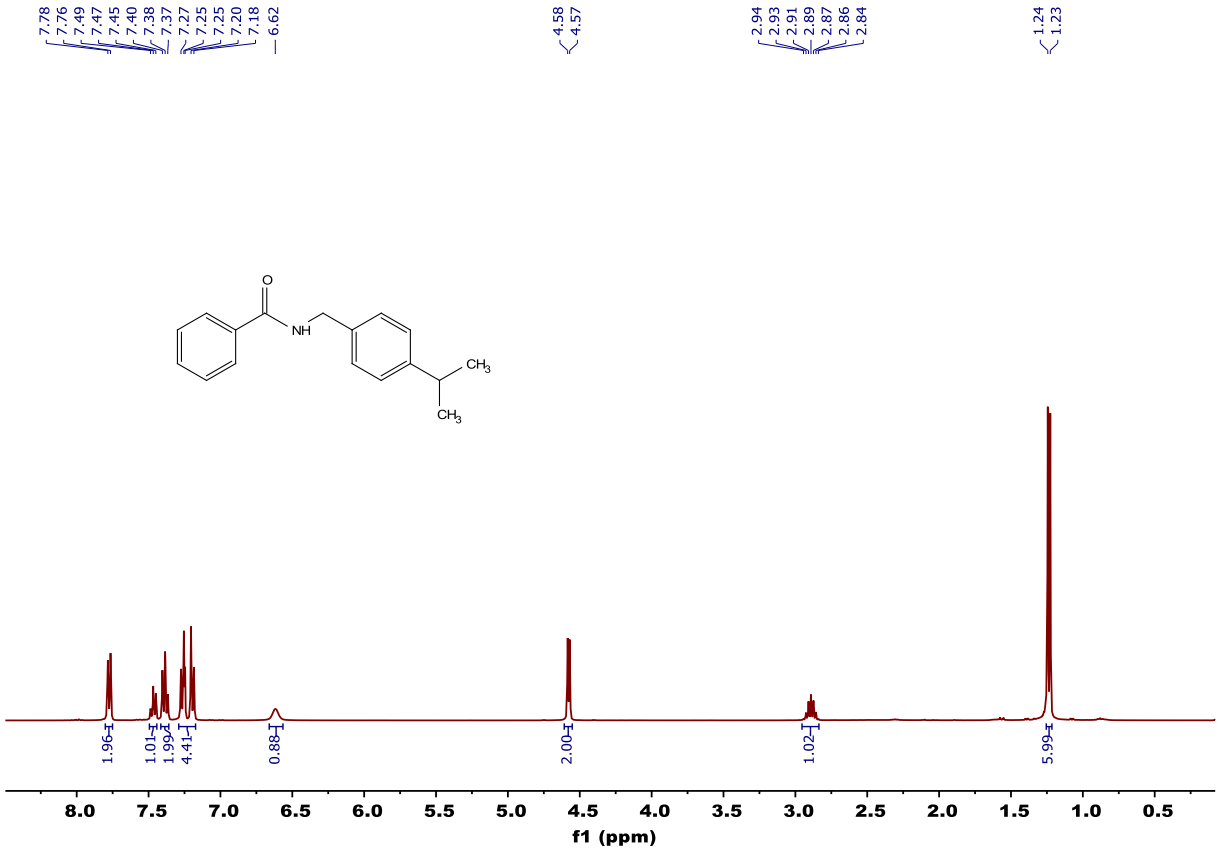
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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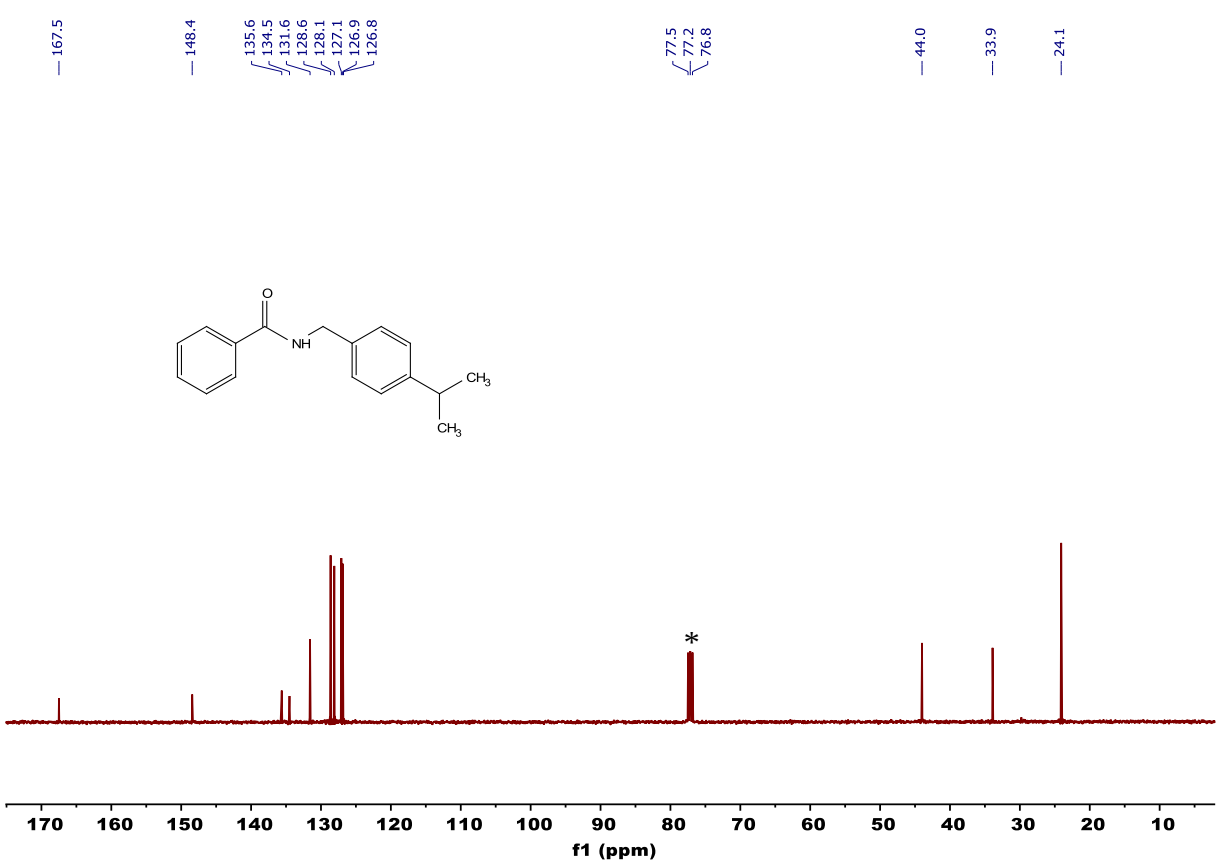
7.40
7.38
7.37
7.27
7.25
7.25
7.20
7.18
6.62
4.58
4.57
2.94
2.93
2.91
2.89
2.87
2.86
2.84
1.24
1.23
O
NH
CH3
CH3
1.96
1.01
1.99
4.41
0.88
2.00
1.02
5.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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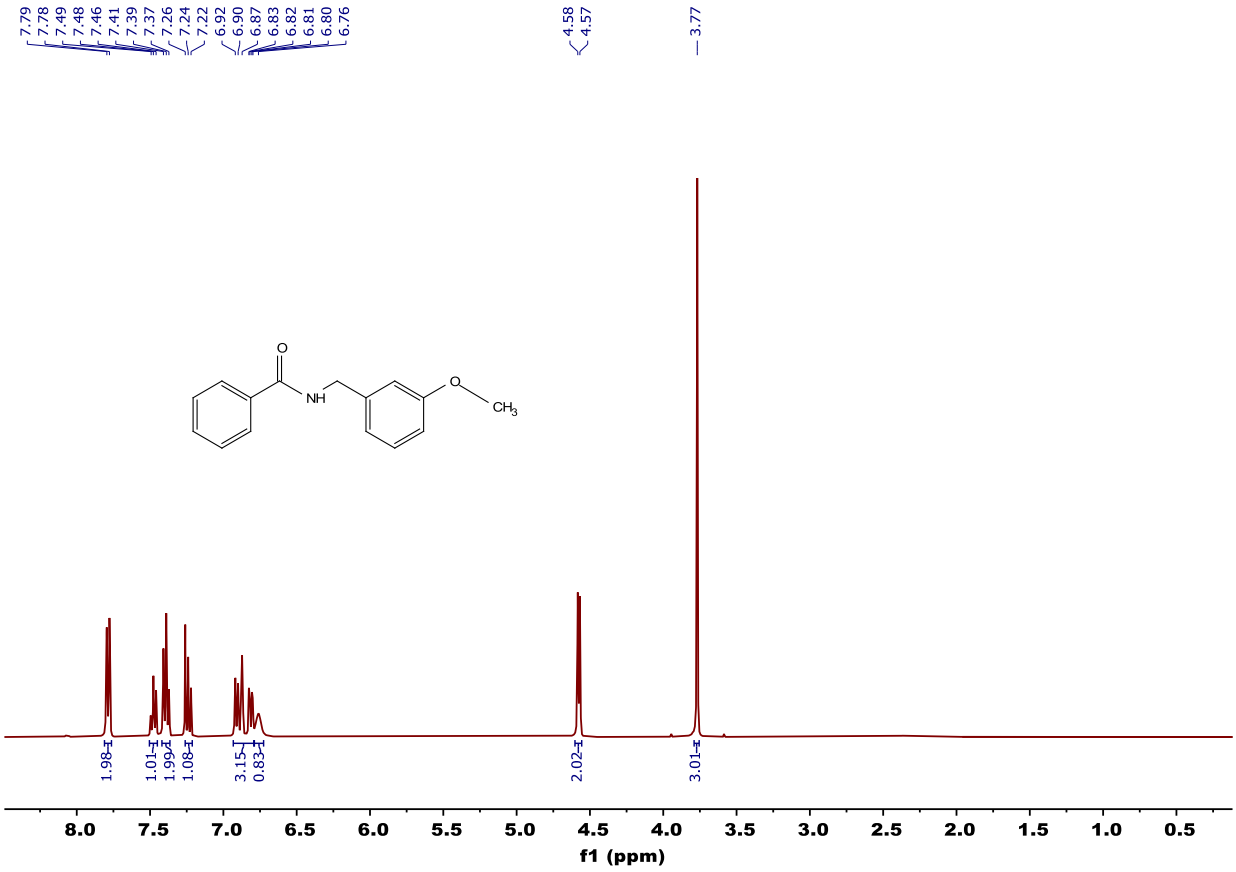
148.4
135.6
134.5
131.6
128.6
128.1
127.1
126.9
126.8
77.5
77.2
76.8
44.0
33.9
24.1
O
NH
CH3
CH3
*
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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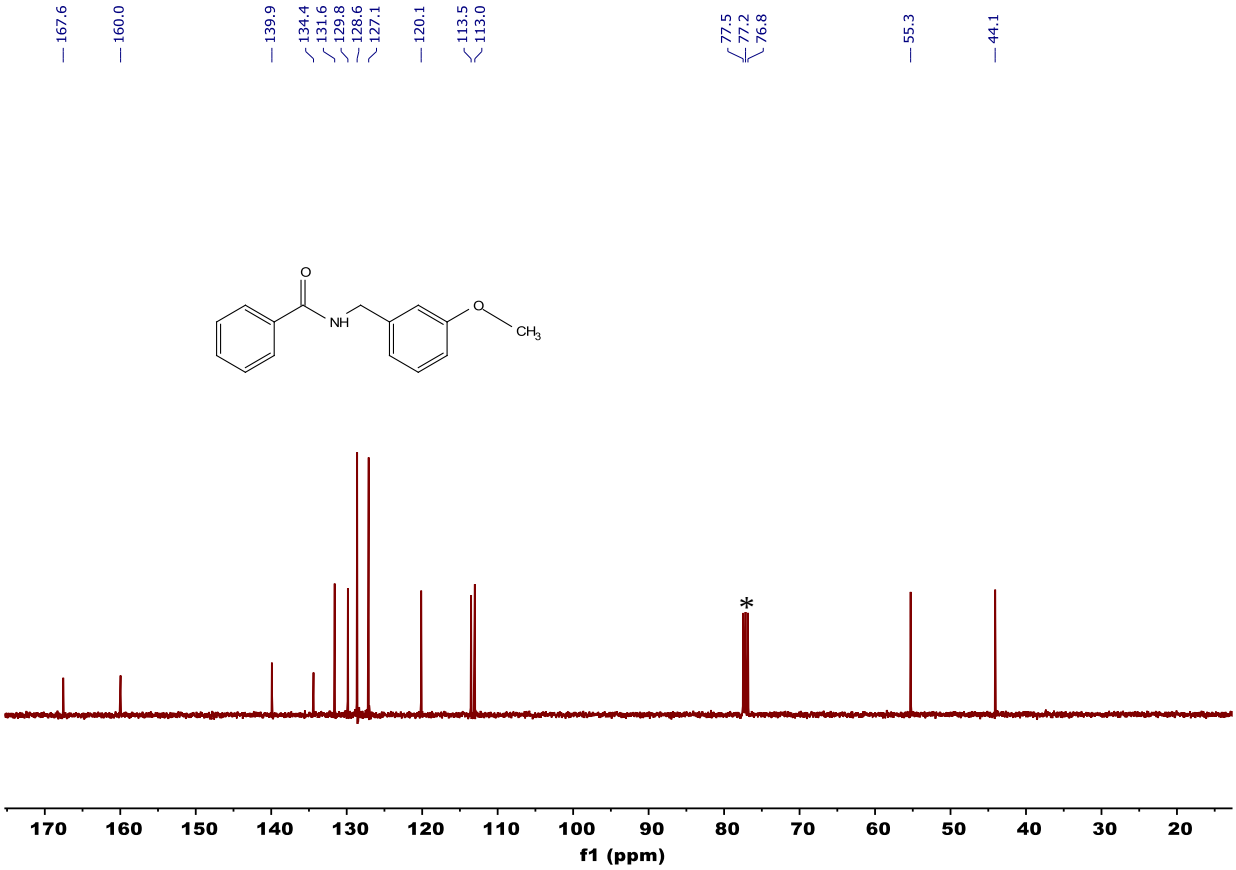
7.78
7.49
7.48
7.46
7.41
7.39
7.37
7.26
7.24
7.22
6.92
6.90
6.87
6.83
6.82
6.81
6.80
6.76
4.58
4.57
3.77
O
NH
O
CH3
1.98
1.01
1.99
1.08
3.15
0.83
2.02
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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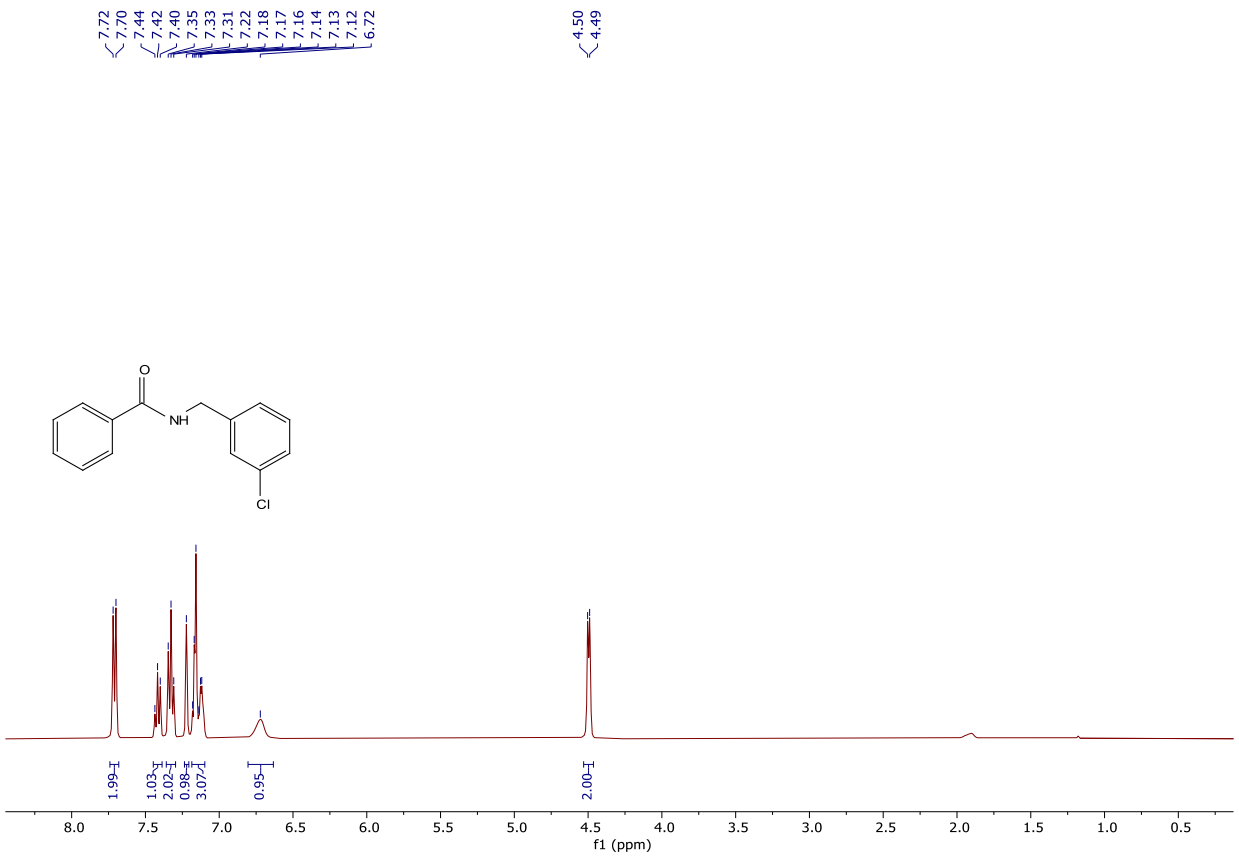
160.0
139.9
134.4
131.6
129.8
128.6
127.1
120.1
113.5
113.0
77.5
77.2
76.8
55.3
44.1
O
NH
O
CH3
*
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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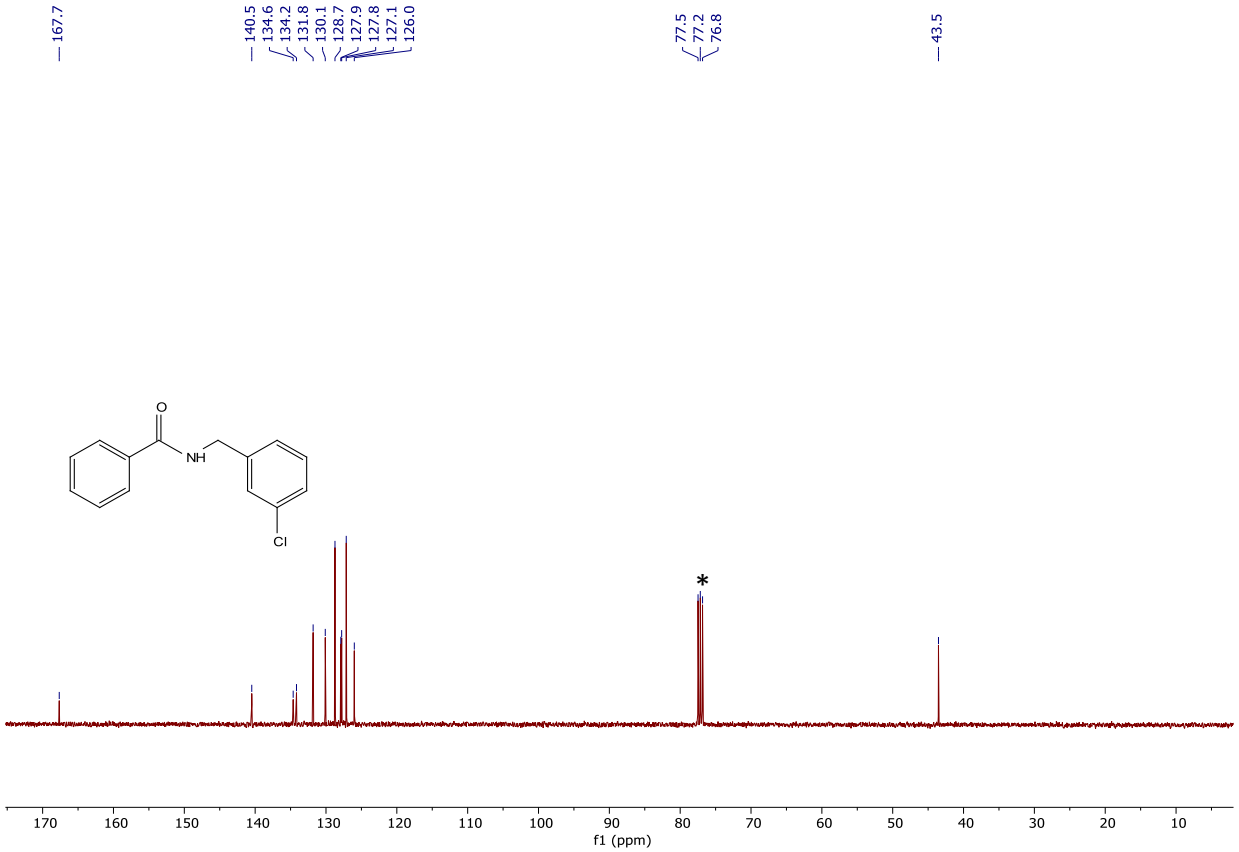
7.35
7.33
7.31
7.22
7.18
7.17
7.16
7.14
7.13
7.12
6.72
4.50
4.49
O
NH
Cl
1.99
1.03
2.02
0.98
3.07
0.95
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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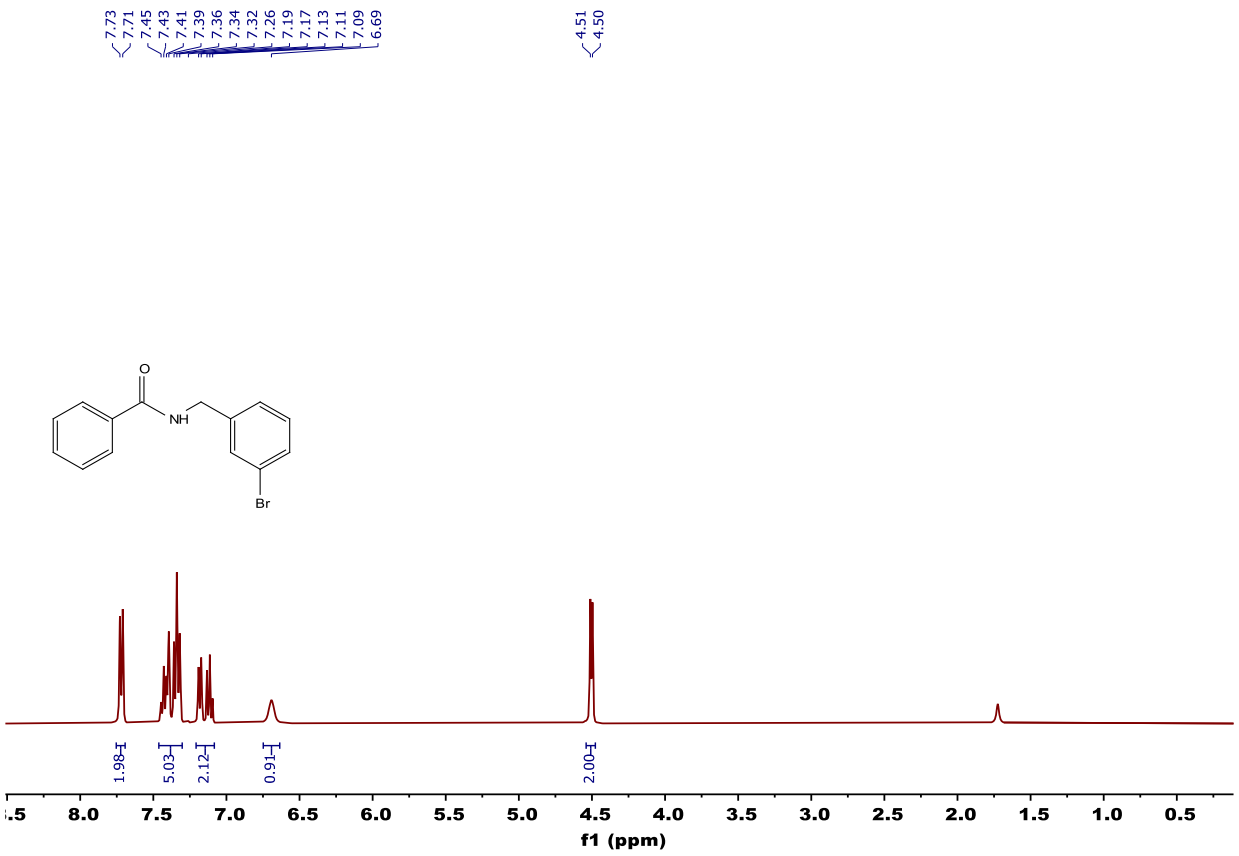
134.6
134.2
131.8
130.1
128.7
127.9
127.8
127.1
126.0
77.5
77.2
76.8
43.5
O
NH
Cl
*
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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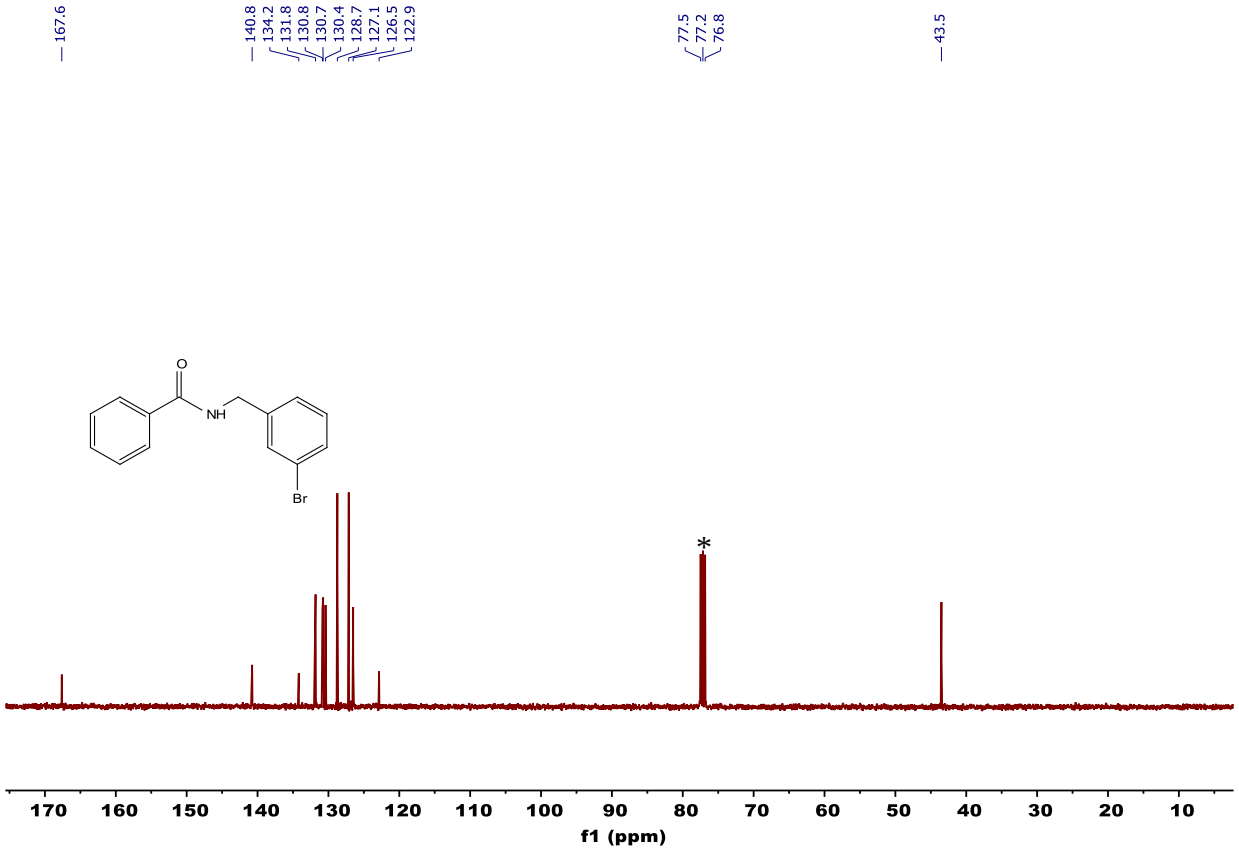
7.19
7.17
7.13
7.11
7.09
6.69
4.51
4.50
O
NH
Br
1.98
5.03
2.12
0.91
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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134.2
131.8
130.8
130.7
130.4
128.7
127.1
126.5
122.9
77.5
77.2
76.8
43.5
O
NH
Br
*
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.78
7.77
7.77
7.77
7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.43
7.43
7.42
7.40
7.40
7.26
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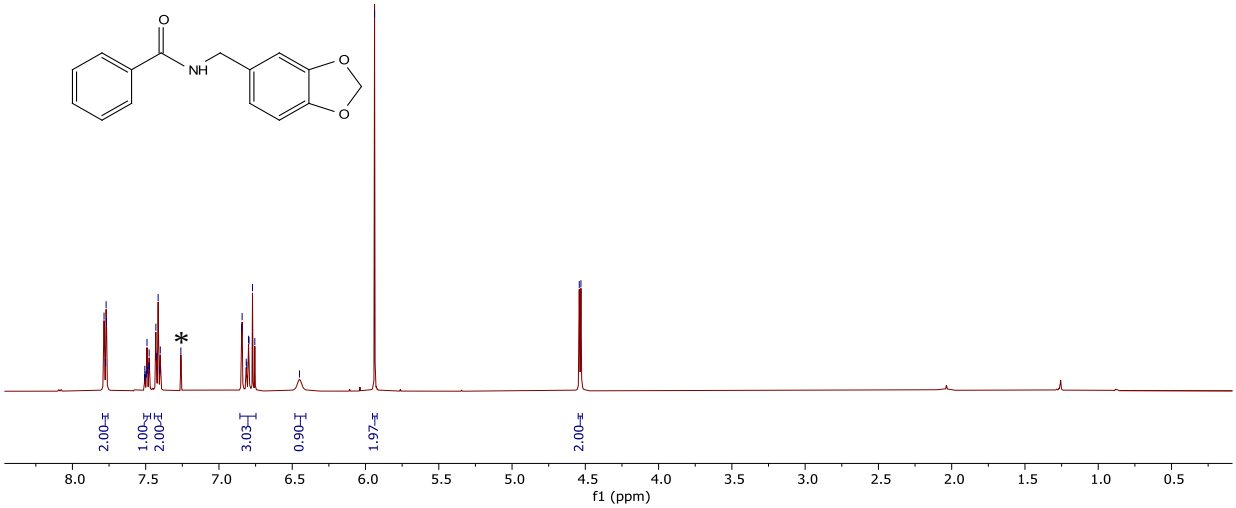
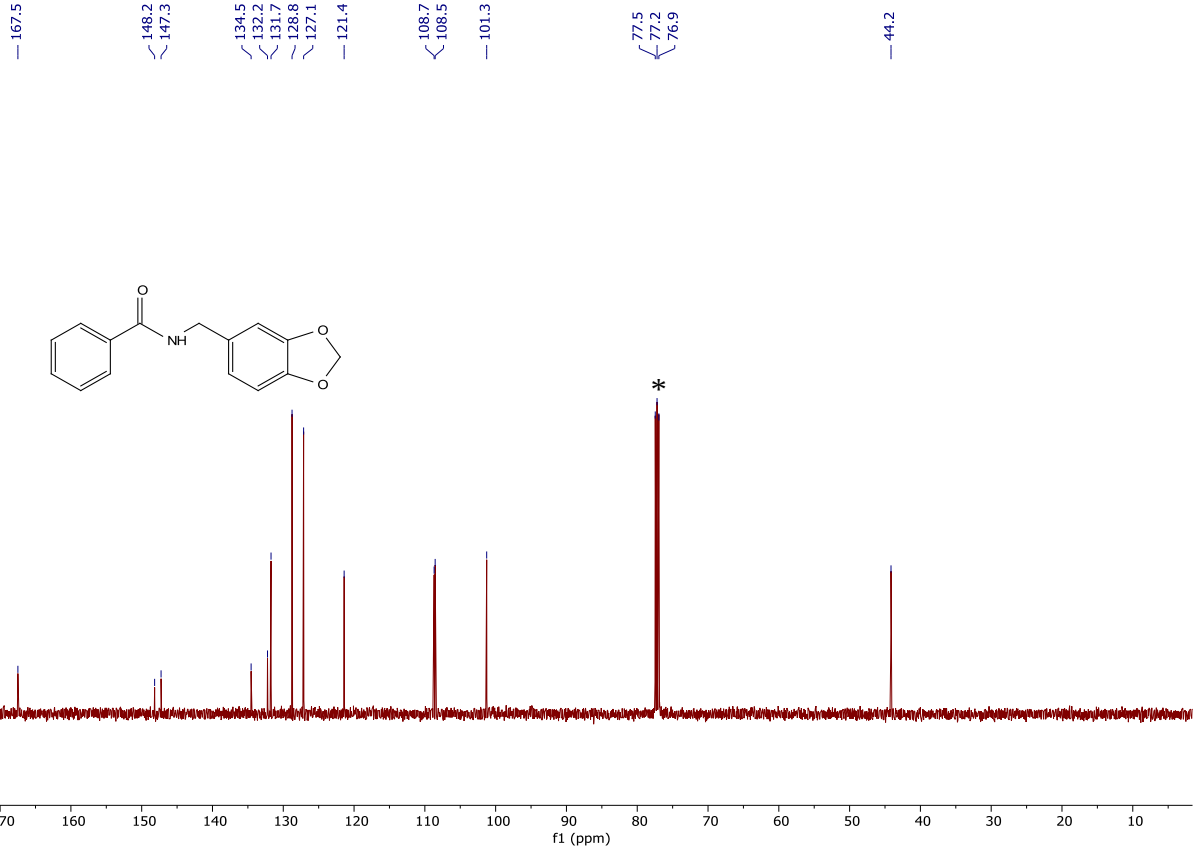
6.84
6.81
6.81
6.80
6.80
6.77
6.76
6.45
5.94
4.54
4.53


O
NH
O
O
*
2.00
1.00
2.00
3.03
0.90
1.97
2.00
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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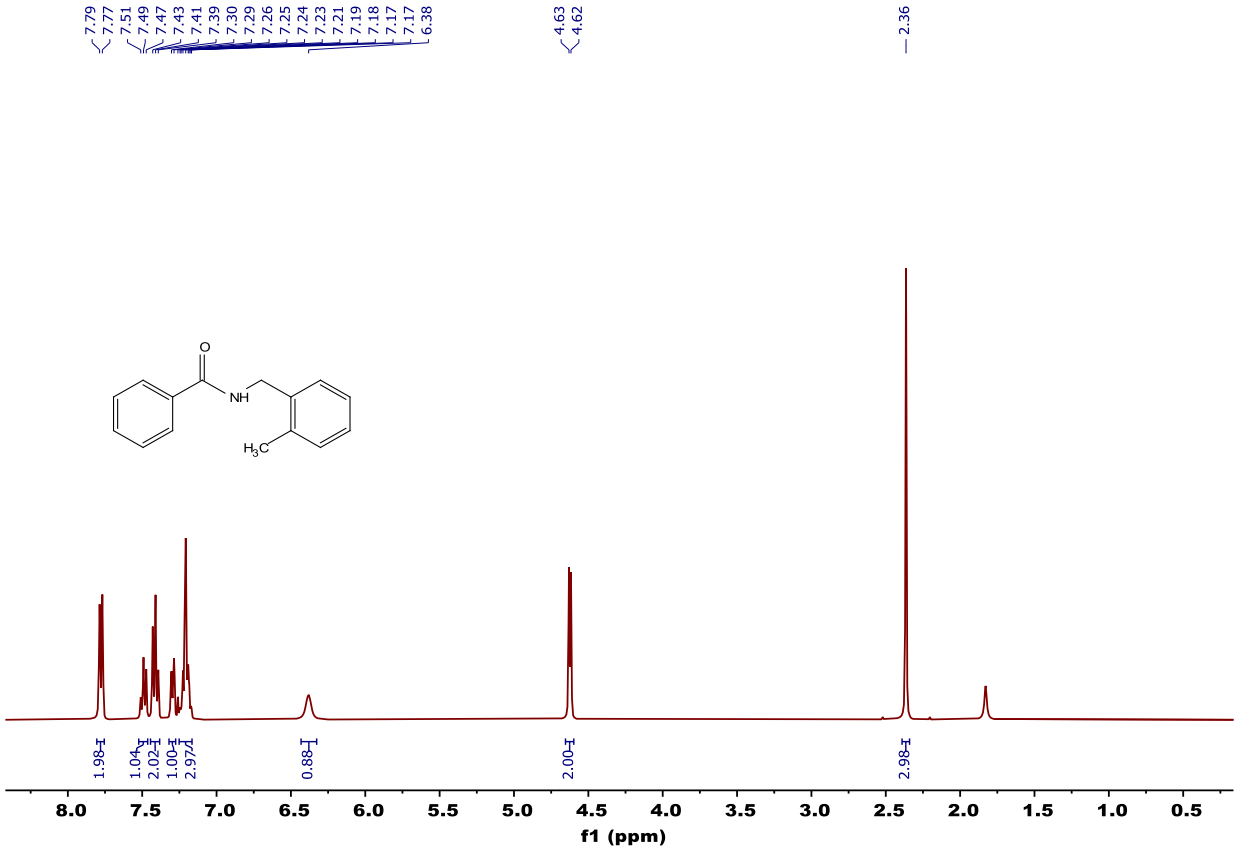
147.3
134.5
132.2
131.7
128.8
127.1
121.4
108.7
108.5
101.3
77.5
77.2
76.9
44.2
O
NH
O
O
*
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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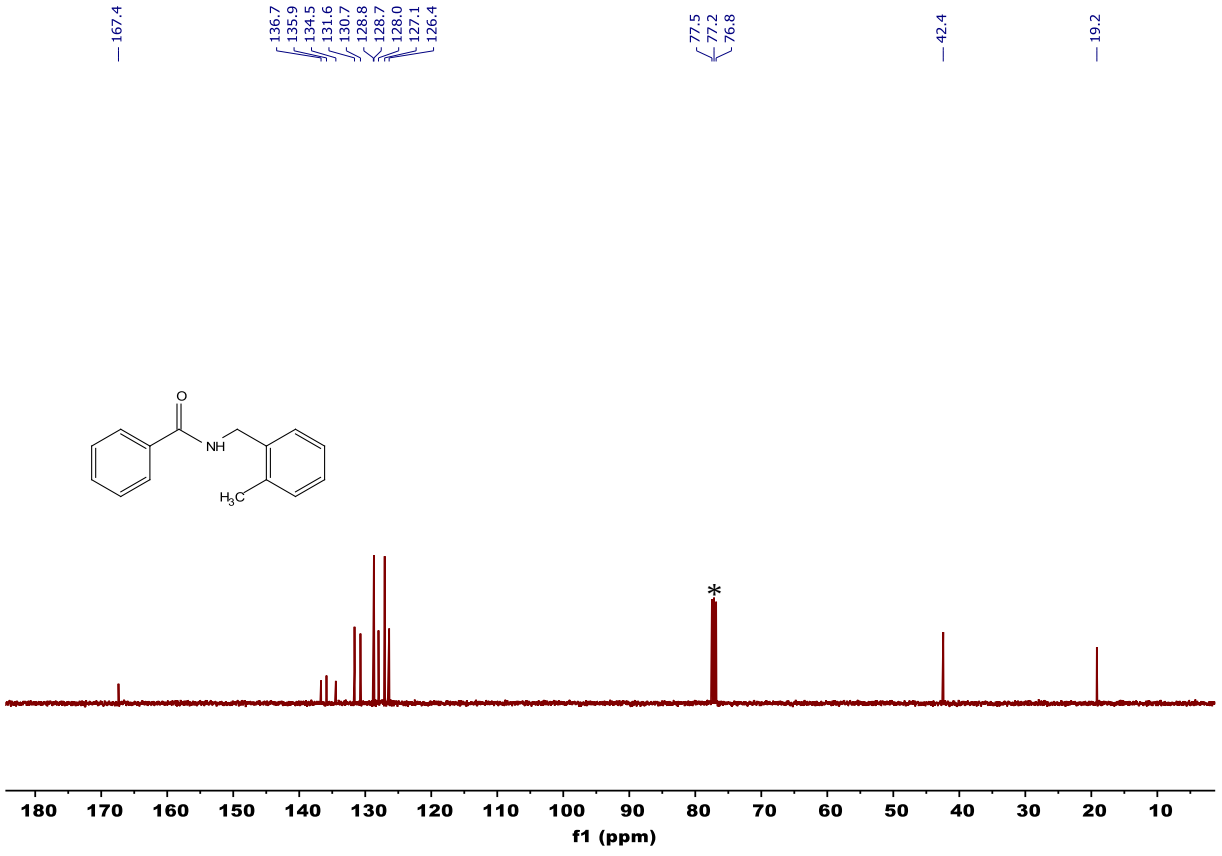
7.77
7.51
7.49
7.47
7.43
7.41
7.39
7.30
7.29
7.26
7.25
7.24
7.23
7.21
7.19
7.18
7.17
7.17
6.38
4.63
4.62
2.36
O
NH
H3C
1.98
1.04
2.02
1.00
2.97
0.88
2.00
2.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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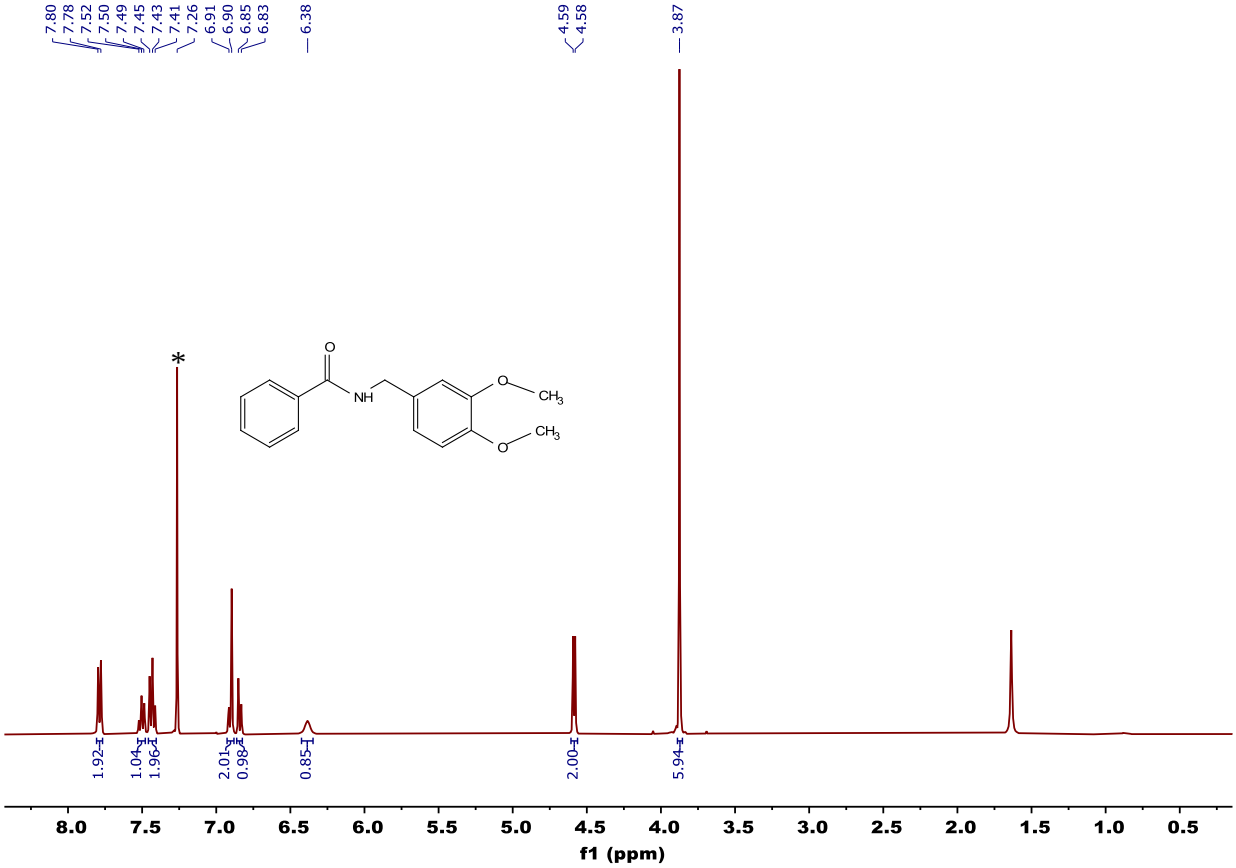
135.9
134.5
131.6
130.7
128.8
128.7
128.0
127.1
126.4
77.5
77.2
76.8
42.4
19.2
O
NH
H3C
*
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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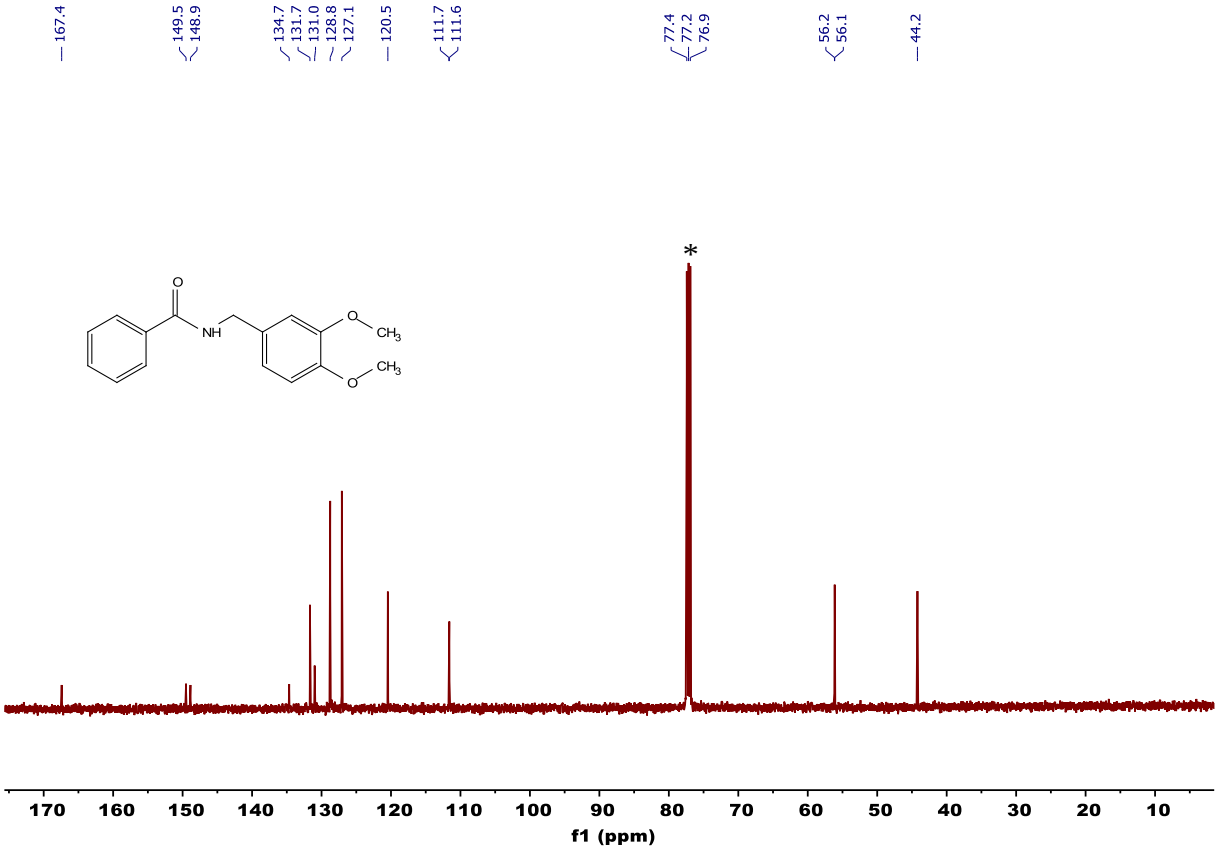
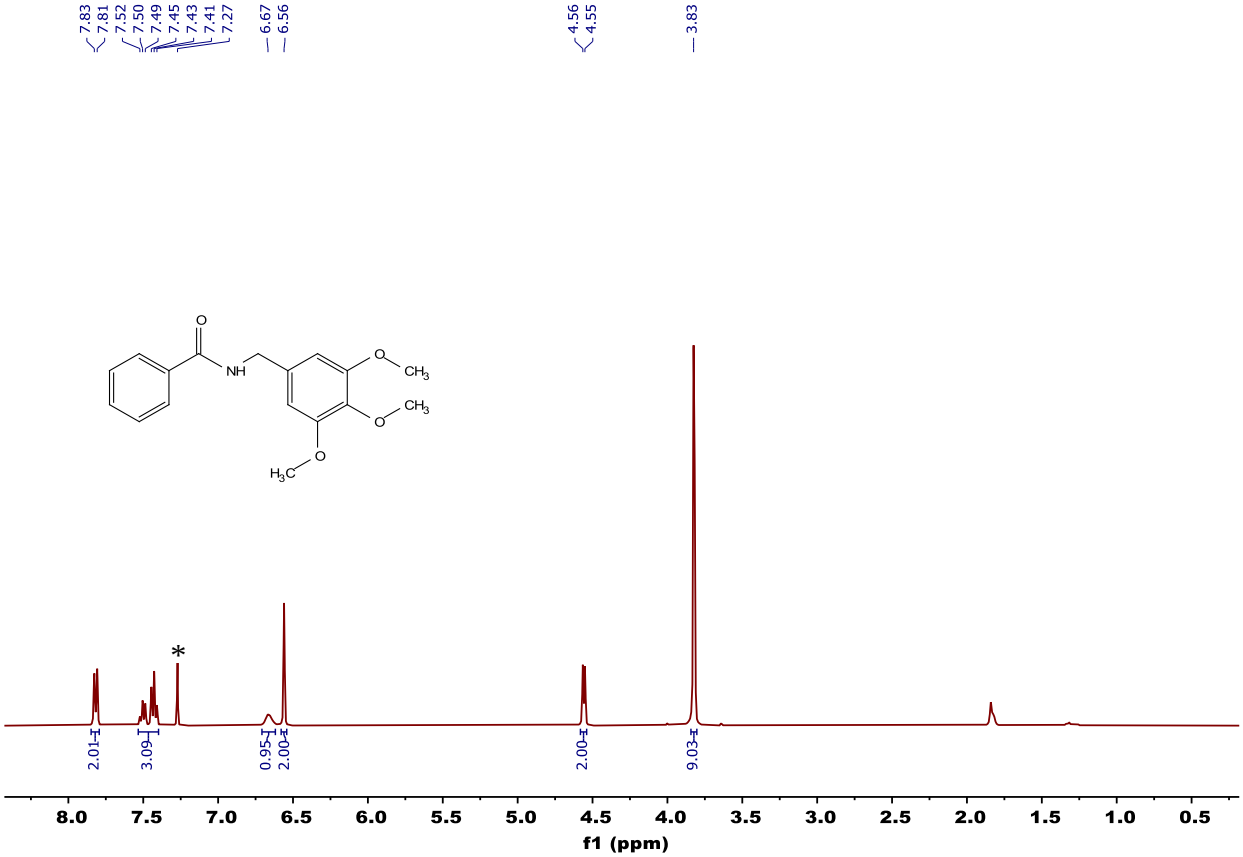
7.49
7.45
7.43
7.41
7.26
6.91
6.90
6.85
6.83
6.38
4.59
4.58
3.87
*
O
NH
O
CH3
O
CH3
1.92
1.04
1.96
2.01
0.98
0.85
2.00
5.94
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


167.4
149.5
148.9
134.7
131.7
131.0
128.8
127.1
120.5
111.7
111.6
77.4
77.2
76.9
56.2
56.1
44.2
*
O
NH
O
CH3
O
CH3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.81
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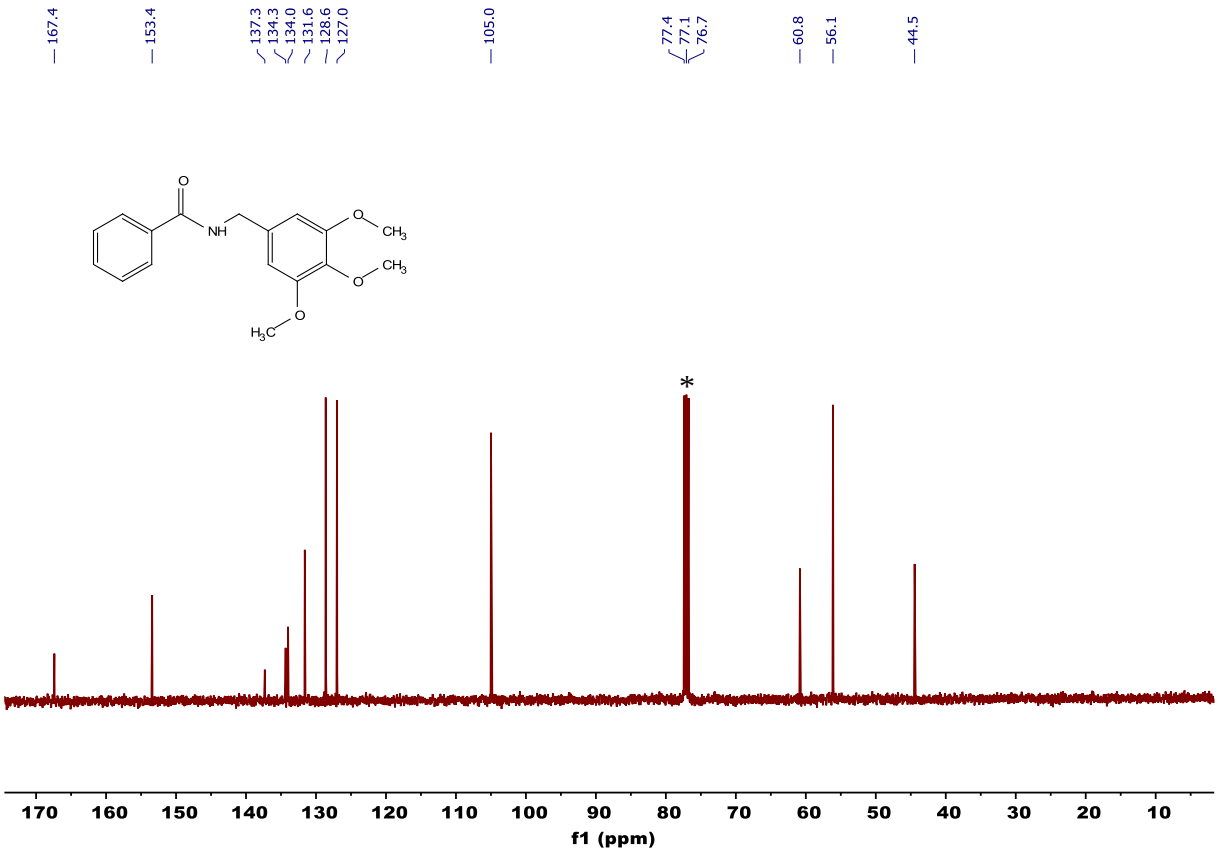
7.50
7.49
7.45
7.43
7.41
7.27
6.67
6.56
4.56
4.55
3.83
O
NH
O
CH3
O
CH3
O
H3C
*
2.01
3.09
0.95
2.00
2.00
9.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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153.4
137.3
134.3
134.0
131.6
128.6
127.0
105.0
77.4
77.1
76.7
60.8
56.1
44.5
O
NH
O
CH3
O
CH3
O
H3C
*
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.09
8.07
7.90
7.89
7.88
7.84
7.83
7.76
7.74
7.74
7.58
7.56
7.55
7.53
7.53
7.51
7.50
7.48
7.47
7.45
7.44
7.42
7.39
7.38
7.36
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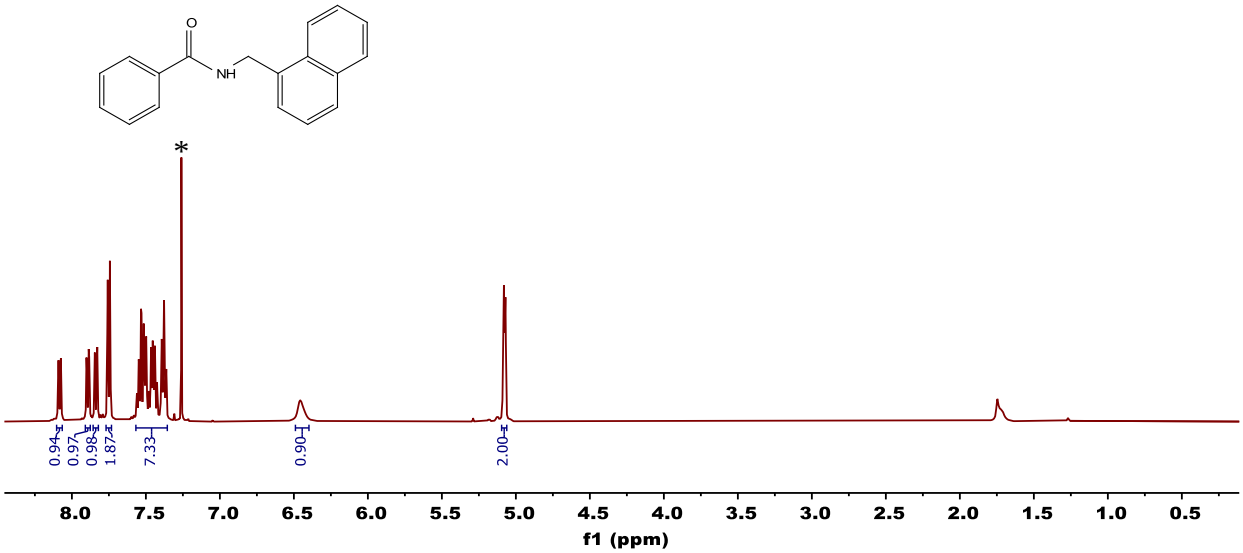
6.46
5.08
5.07


O
NH
*
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0.97
0.98
1.87
7.33
0.90
2.00
8.0
7.5
7.0
6.5
6.0
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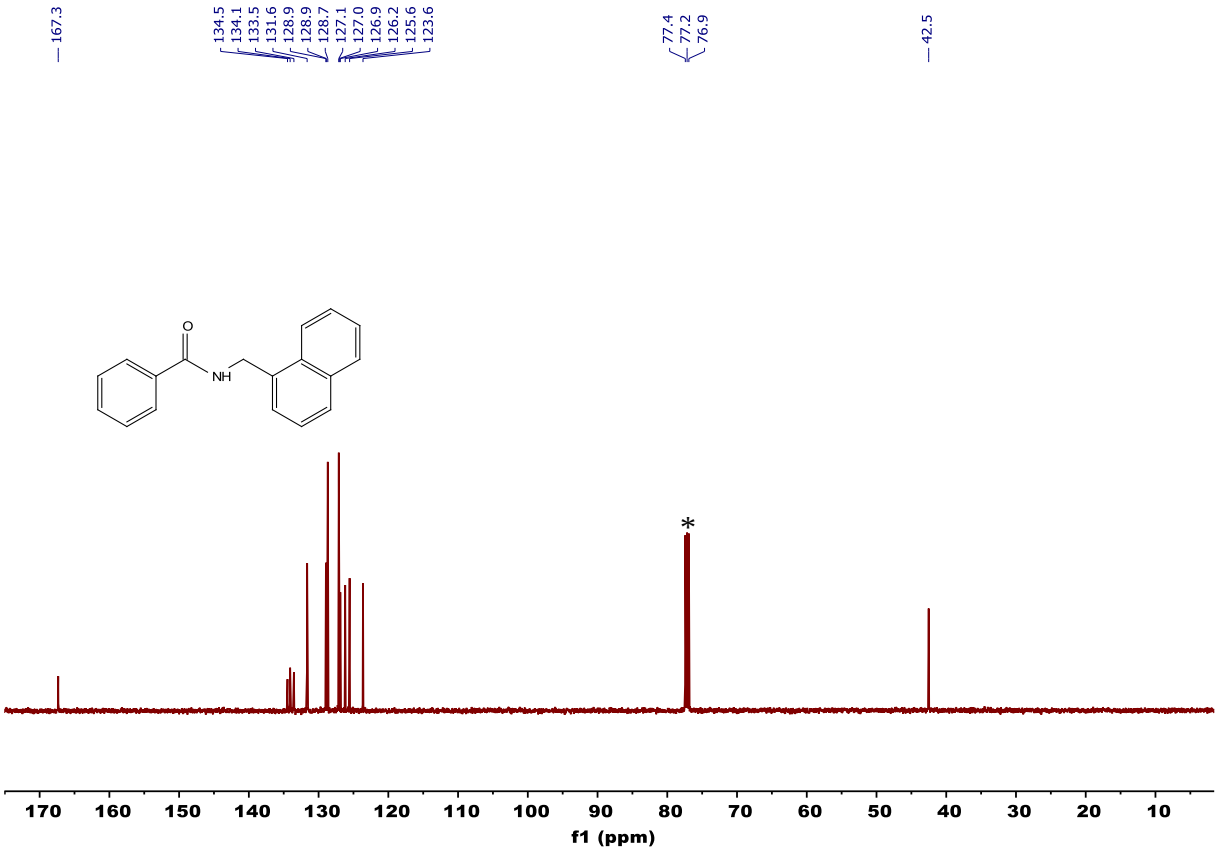
f1 (ppm)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128.9
128.7
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127.0
126.9
126.2
125.6
123.6
77.4
77.2
76.9
42.5
O
NH
*
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140
130
120
110
100
90
80
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60
50
40
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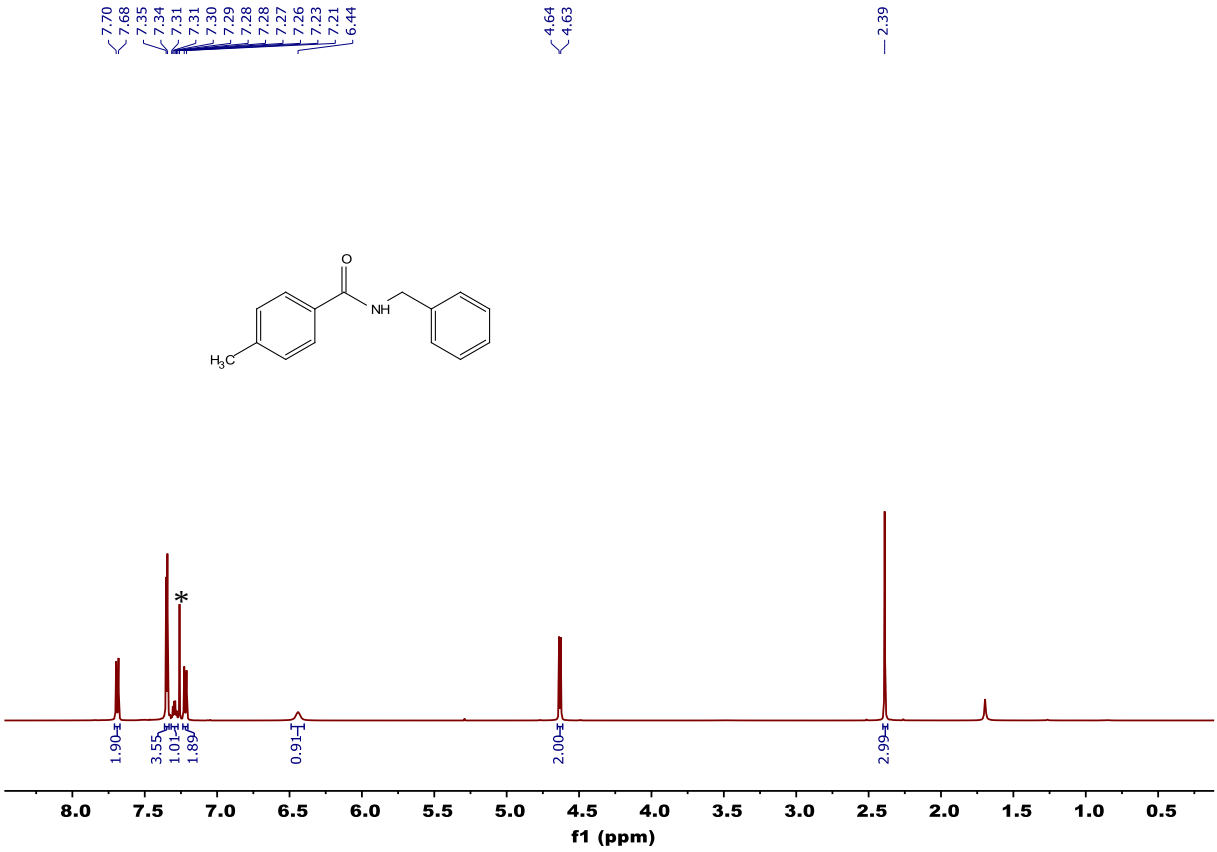
20
10
f1 (ppm)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7.21
6.44
4.64
4.63
2.39
O
NH
H3C
*
1.90
3.55
1.01
1.89
0.91
2.00
2.99
8.0
7.5
7.0
6.5
6.0
5.5
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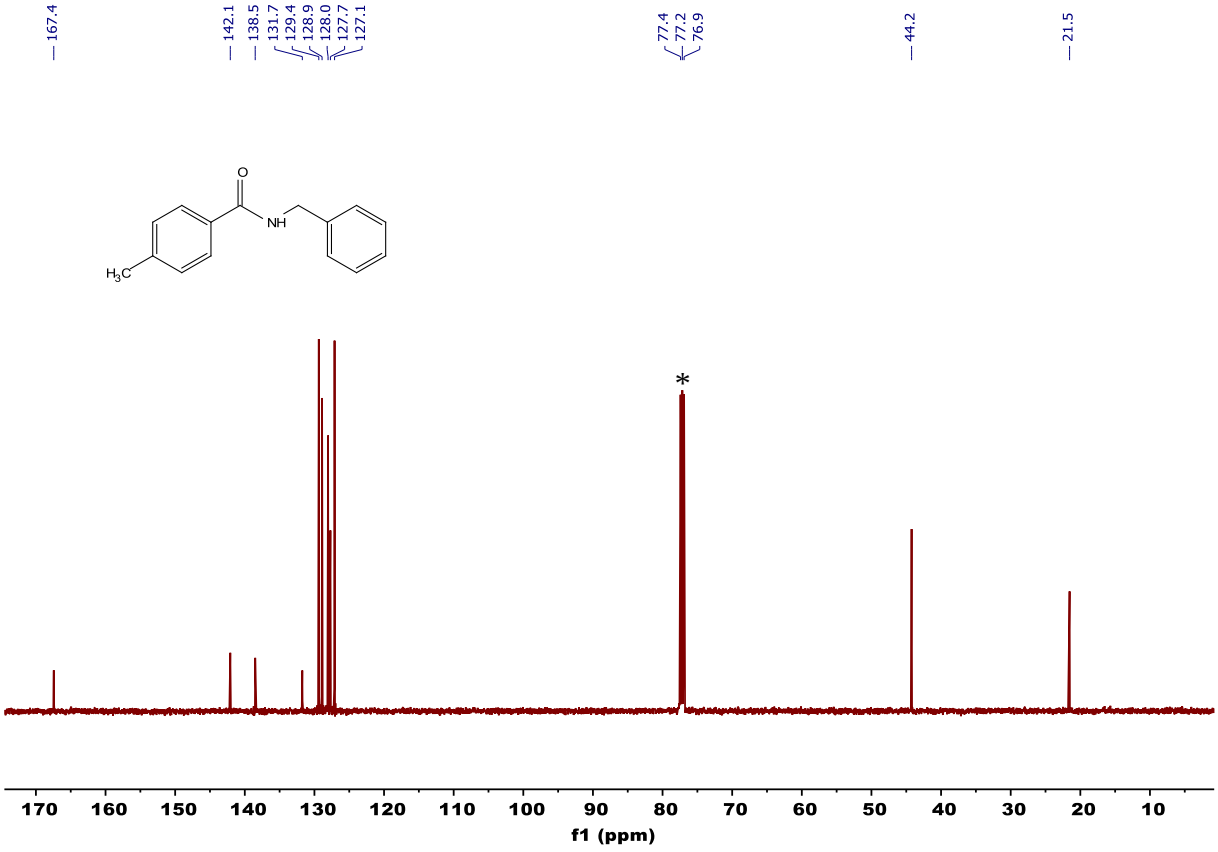
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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127.7
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77.4
77.2
76.9
44.2
21.5
O
NH
H3C
*
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120
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100
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80
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50
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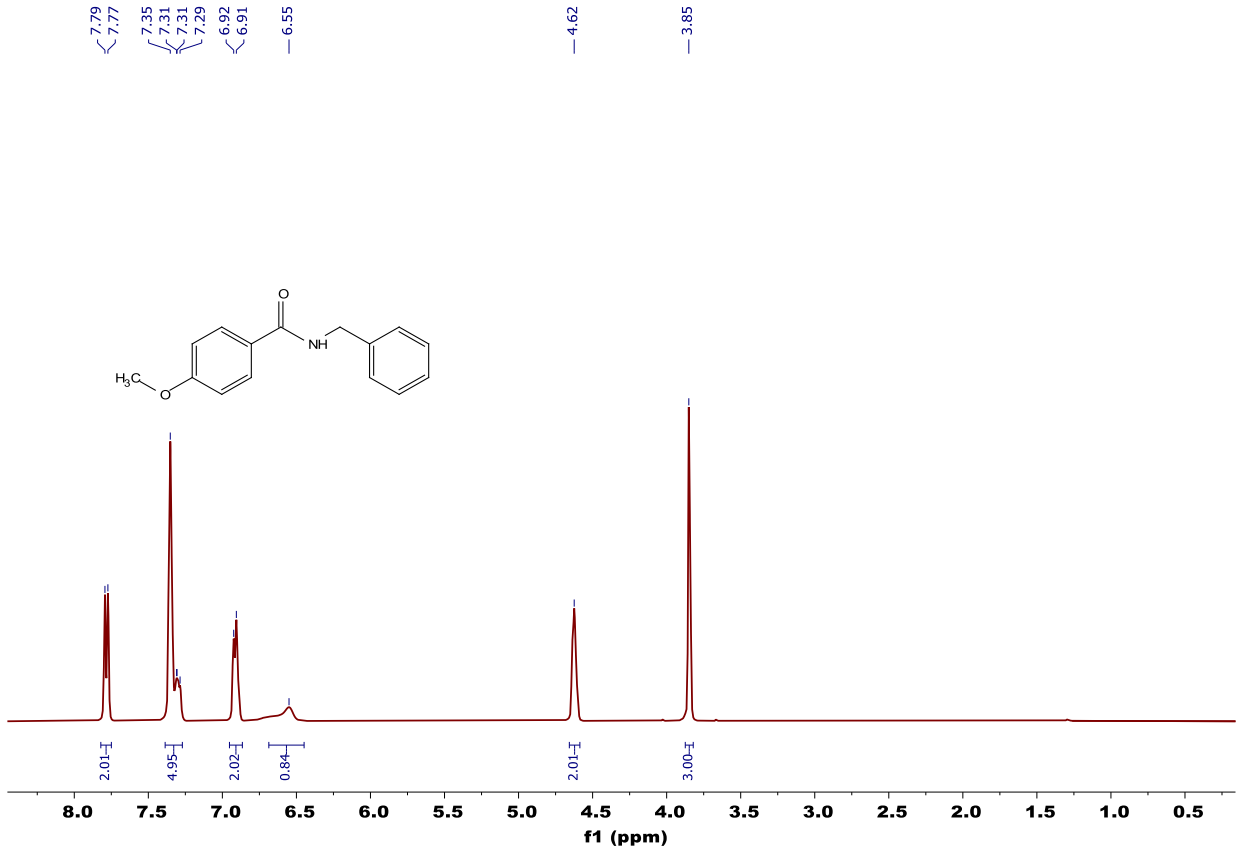
20
10
f1 (ppm)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6.91
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H3C
O
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4.95
2.02
0.84
2.01
3.00
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
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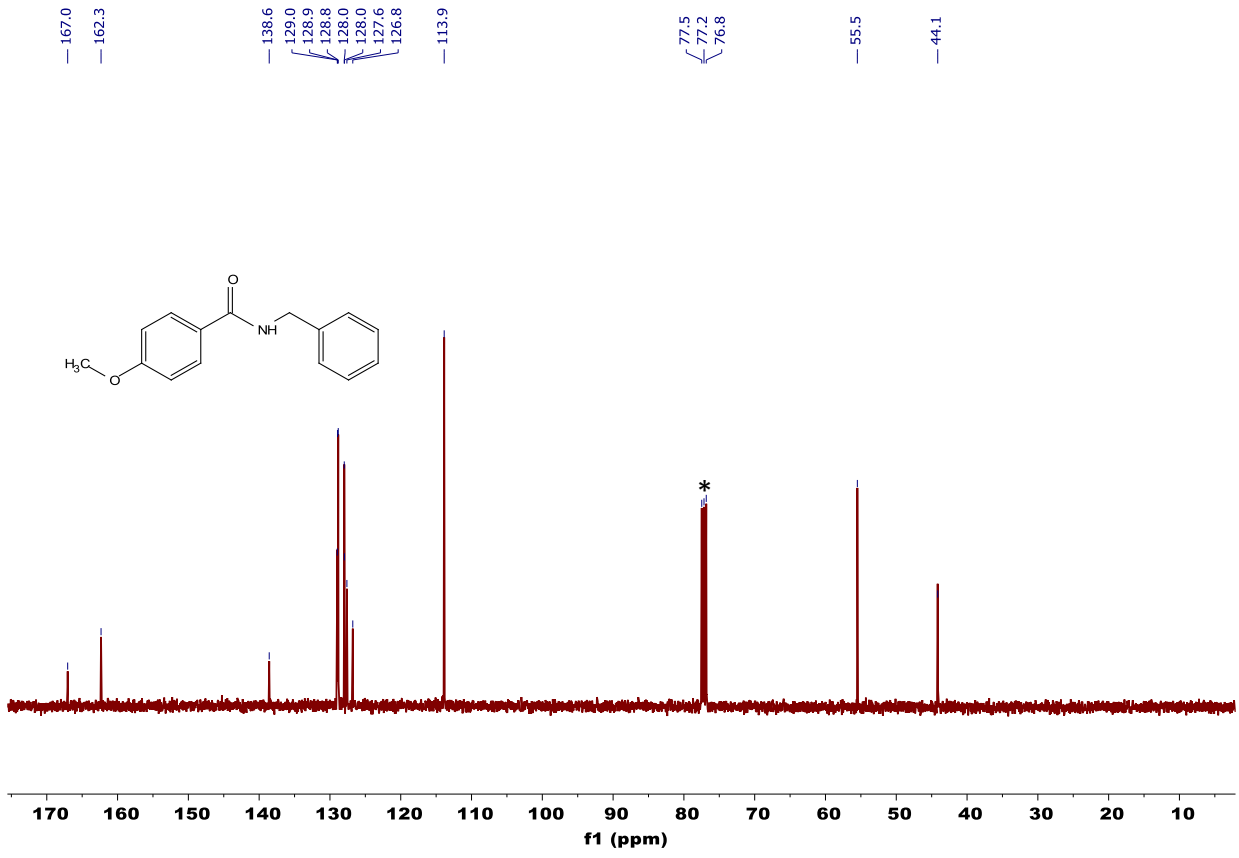
2.0
1.5
1.0
0.5
f1 (ppm)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128.0
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126.8
113.9
77.5
77.2
76.8
55.5
44.1
O
NH
H3C
O
*
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160
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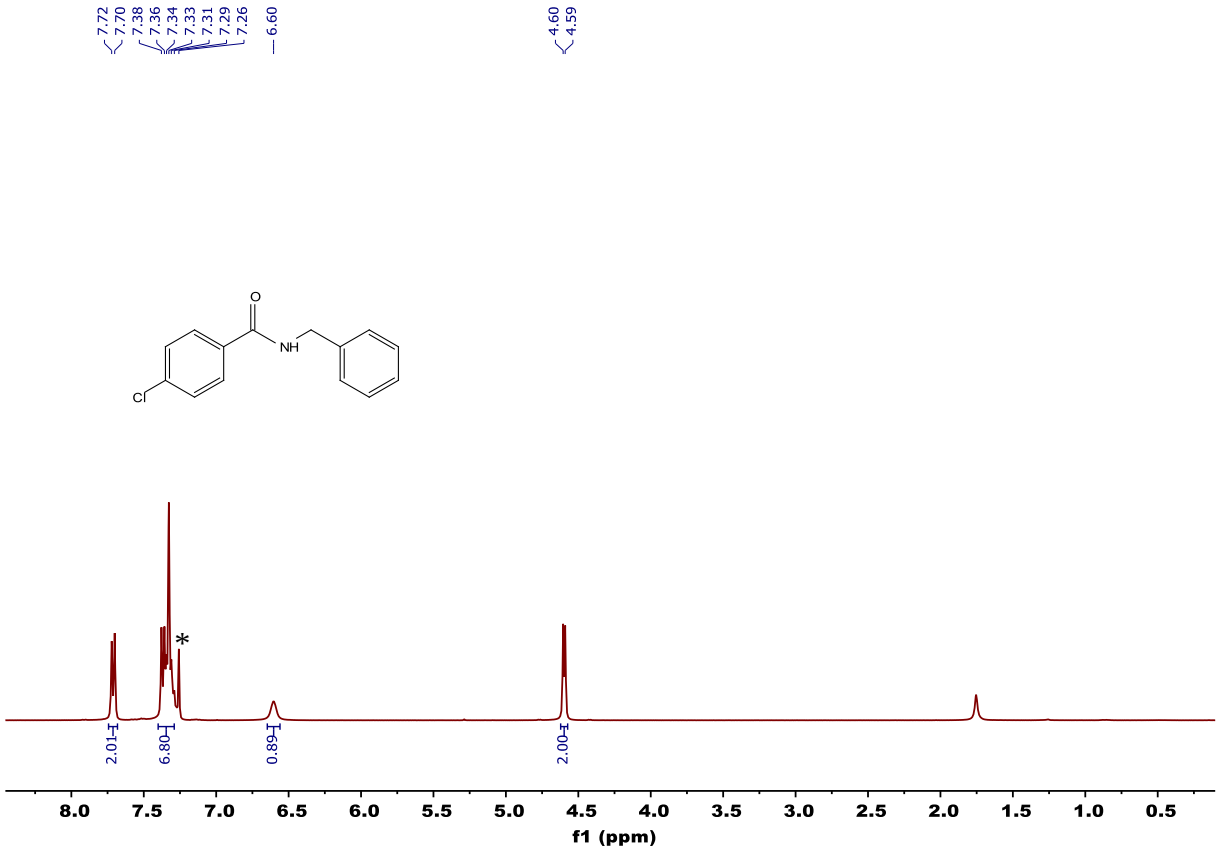
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.26
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4.59
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NH
Cl
*
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6.80
0.89
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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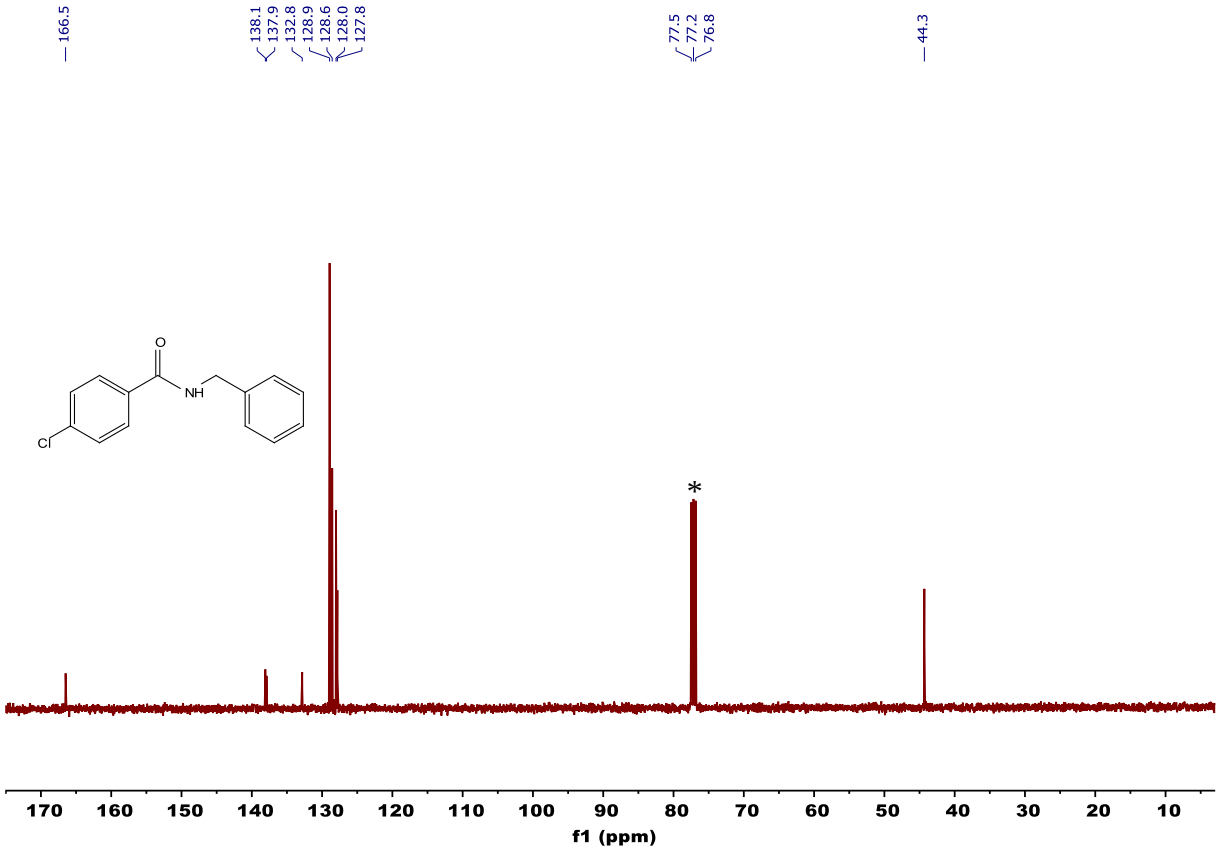
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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77.5
77.2
76.8
44.3
O
NH
Cl
*
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120
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100
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20
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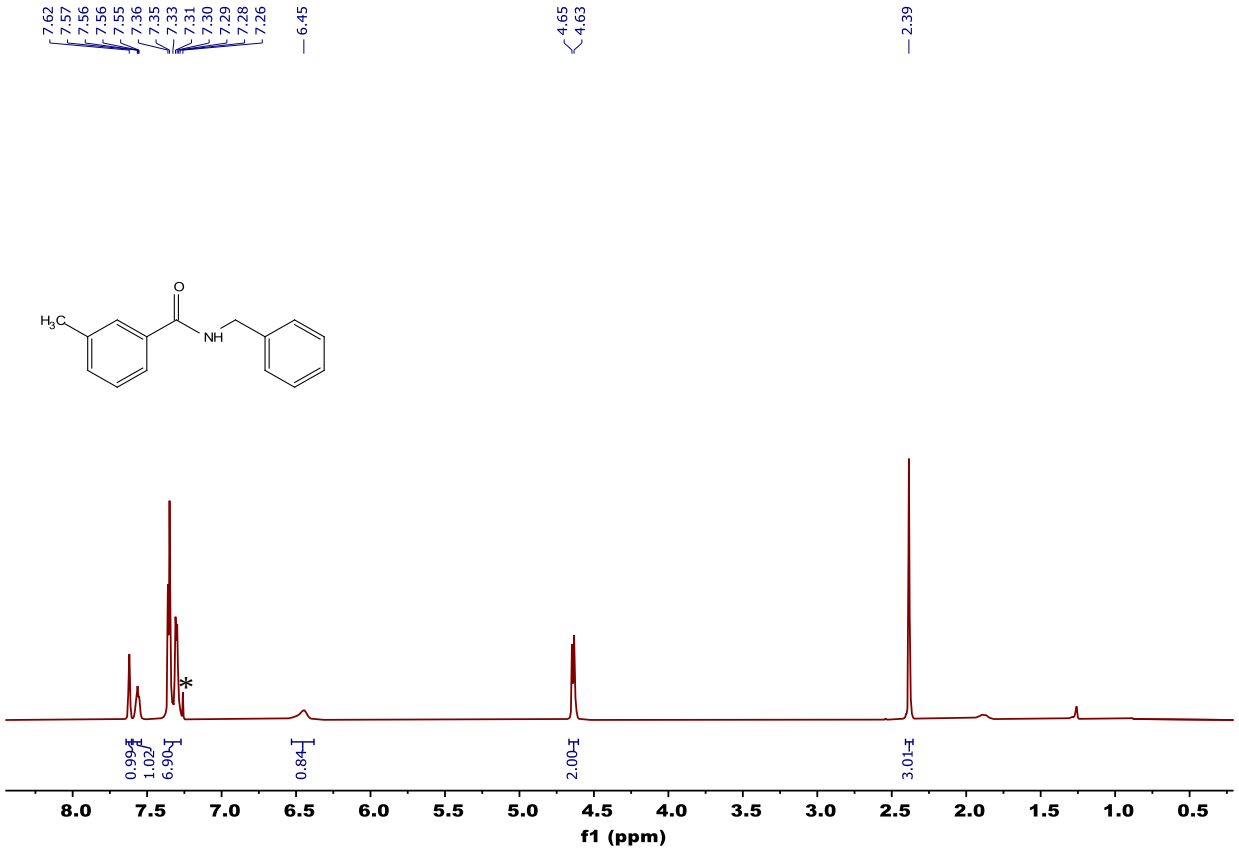
f1 (ppm)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7.56
7.55
7.36
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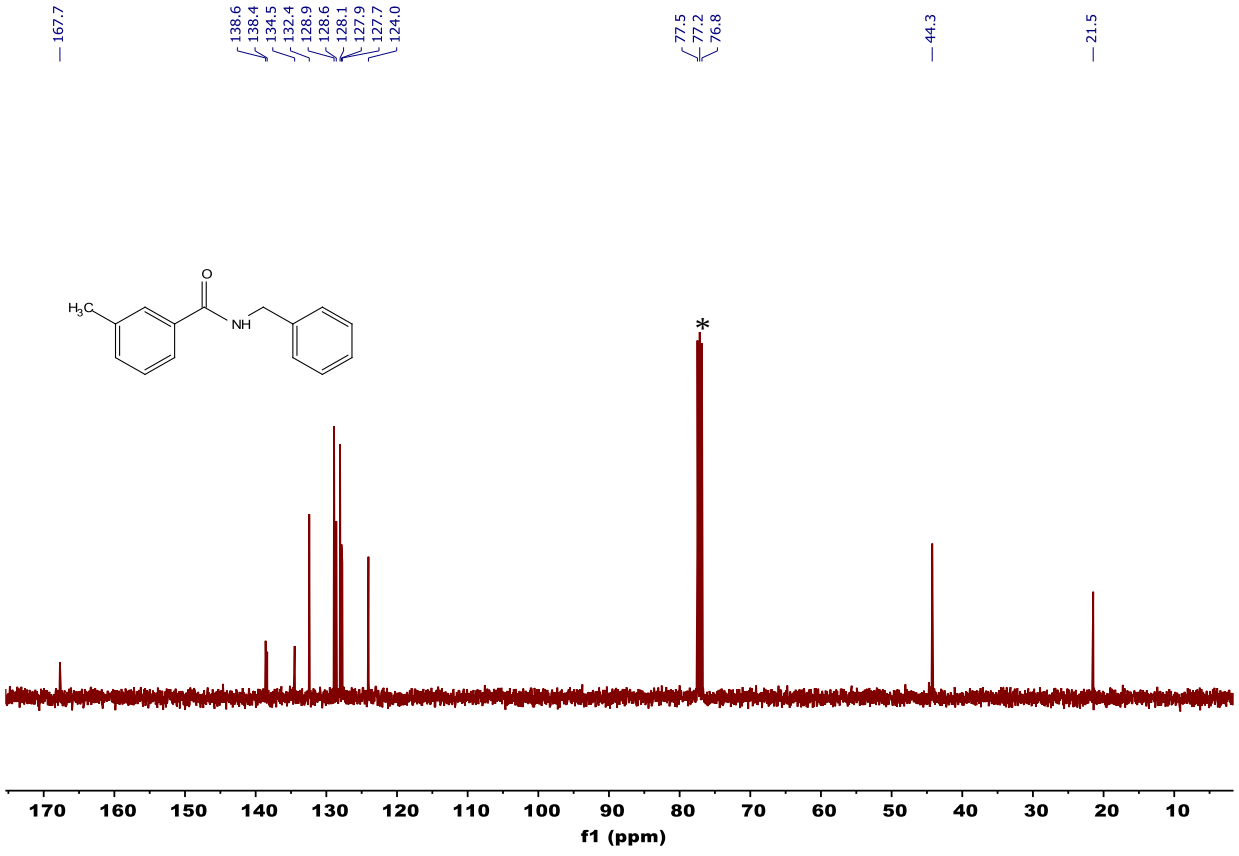
7.33
7.31
7.30
7.29
7.28
7.26
6.45
4.65
4.63
2.39
O
NH
H3C
*
0.99
1.02
6.90
0.84
2.00
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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134.5
132.4
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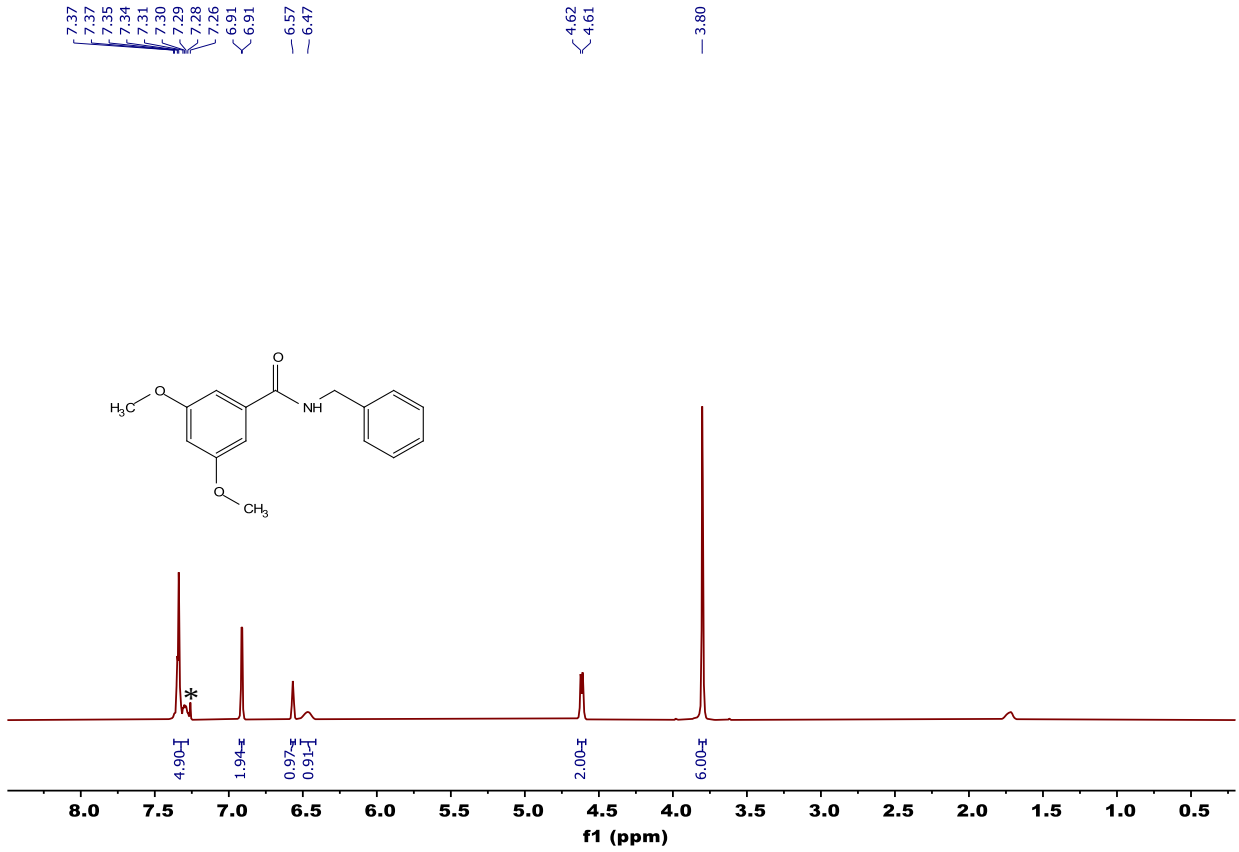
128.6
128.1
127.9
127.7
124.0
77.5
77.2
76.8
44.3
21.5
O
NH
H3C
*
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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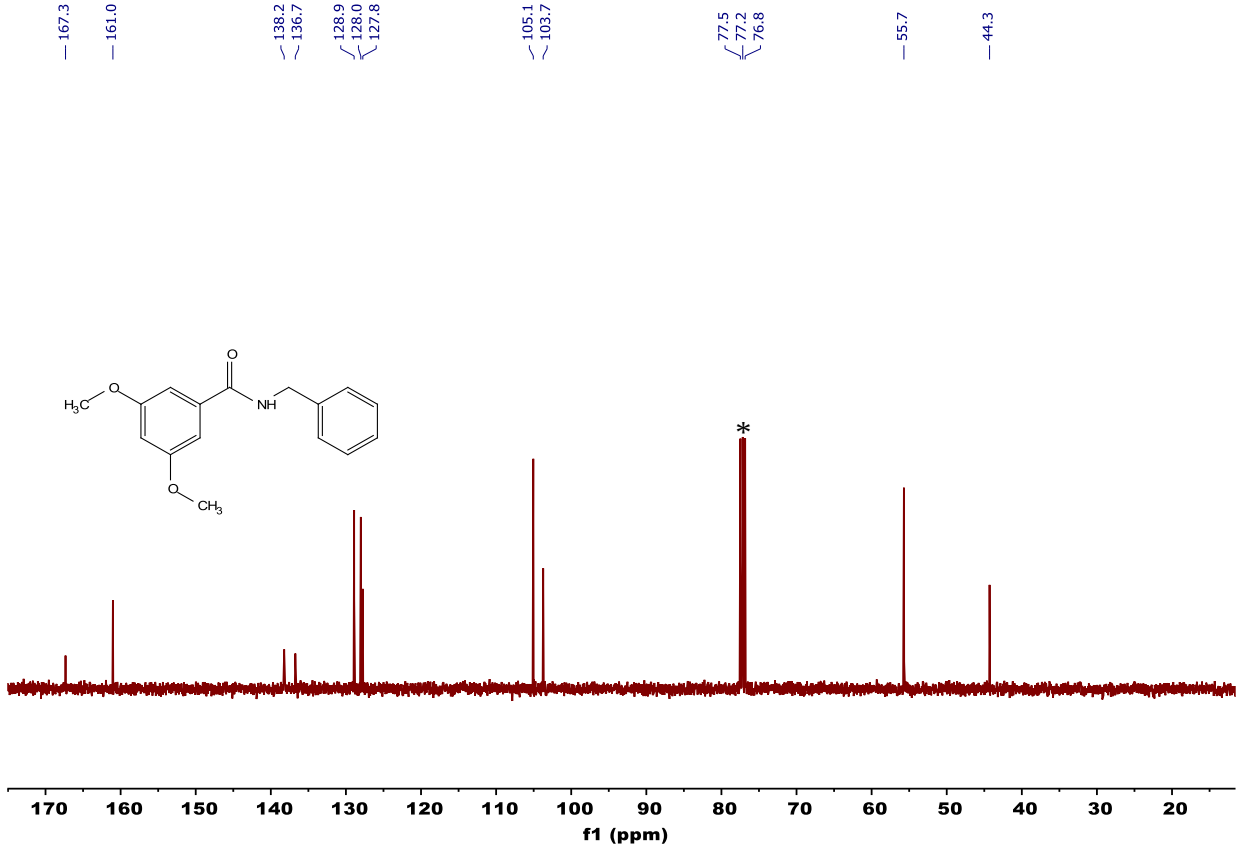
7.30
7.29
7.28
7.26
6.91
6.91
6.57
6.47
4.62
4.61
3.80
O
H3C
O
NH
O
CH3
*
4.90
1.94
0.97
0.91
2.00
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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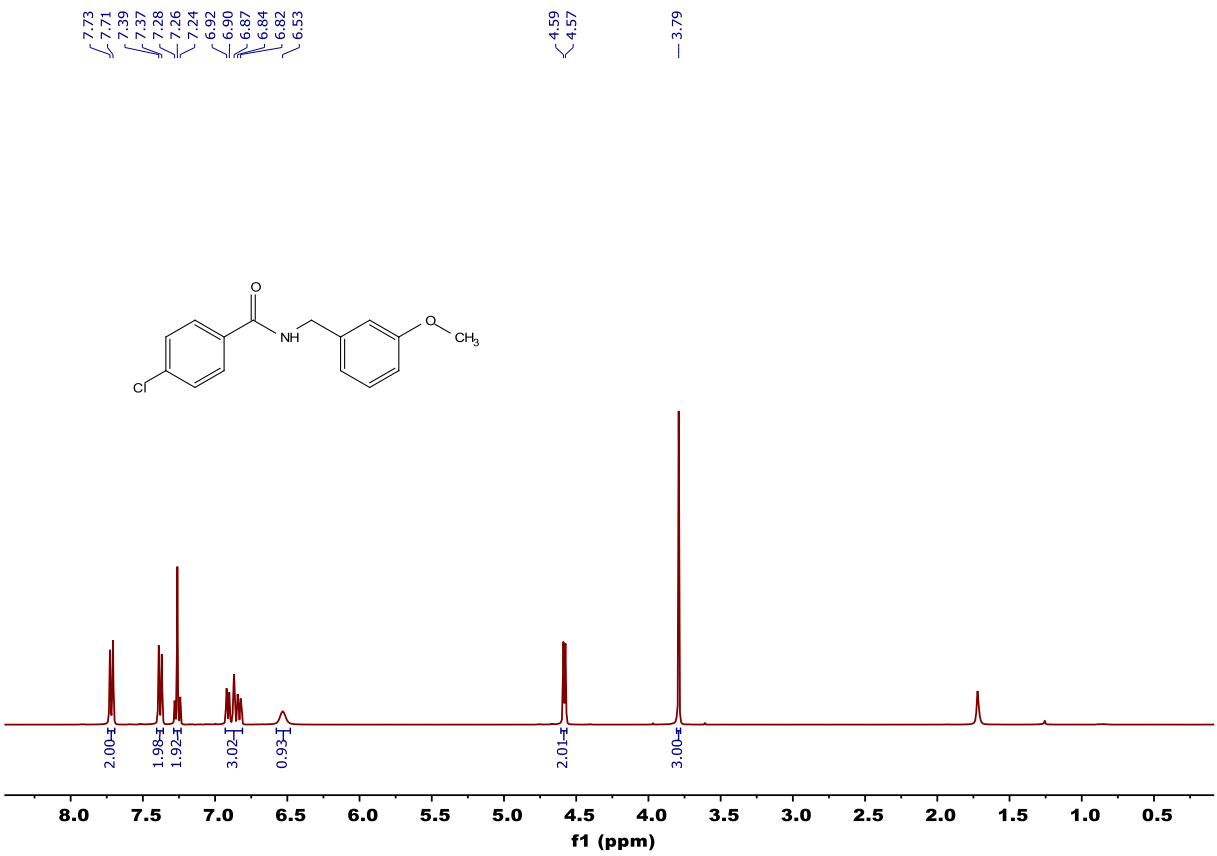
136.7
128.9
128.0
127.8
105.1
103.7
77.5
77.2
76.8
55.7
44.3
O
H3C
O
NH
O
CH3
*
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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7.71
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7.37
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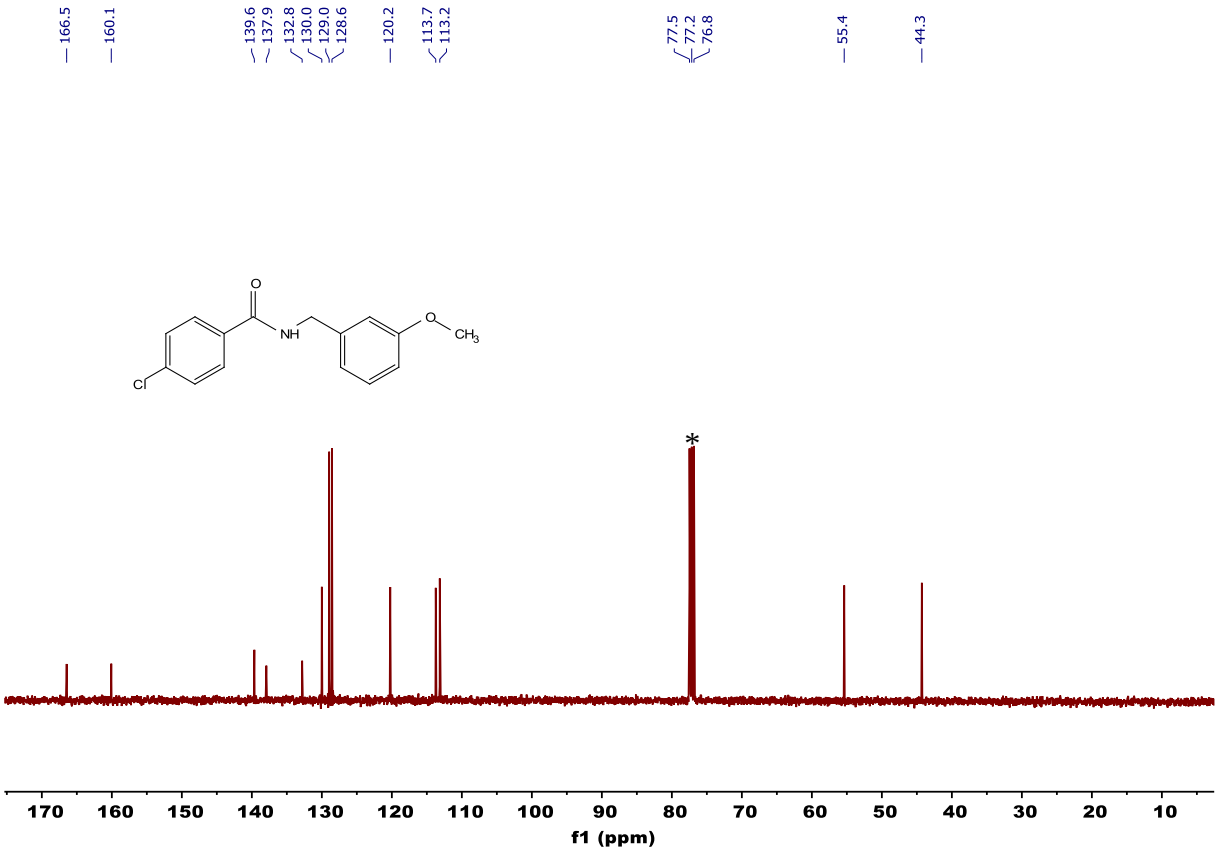
7.26
7.24
6.92
6.90
6.87
6.84
6.82
6.53
4.59
4.57
3.79
O
NH
O
CH3
Cl
2.00
1.98
1.92
3.02
0.93
2.01
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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139.6
137.9
132.8
130.0
129.0
128.6
120.2
113.7
113.2
77.5
77.2
76.8
55.4
44.3
O
NH
O
CH3
Cl
*
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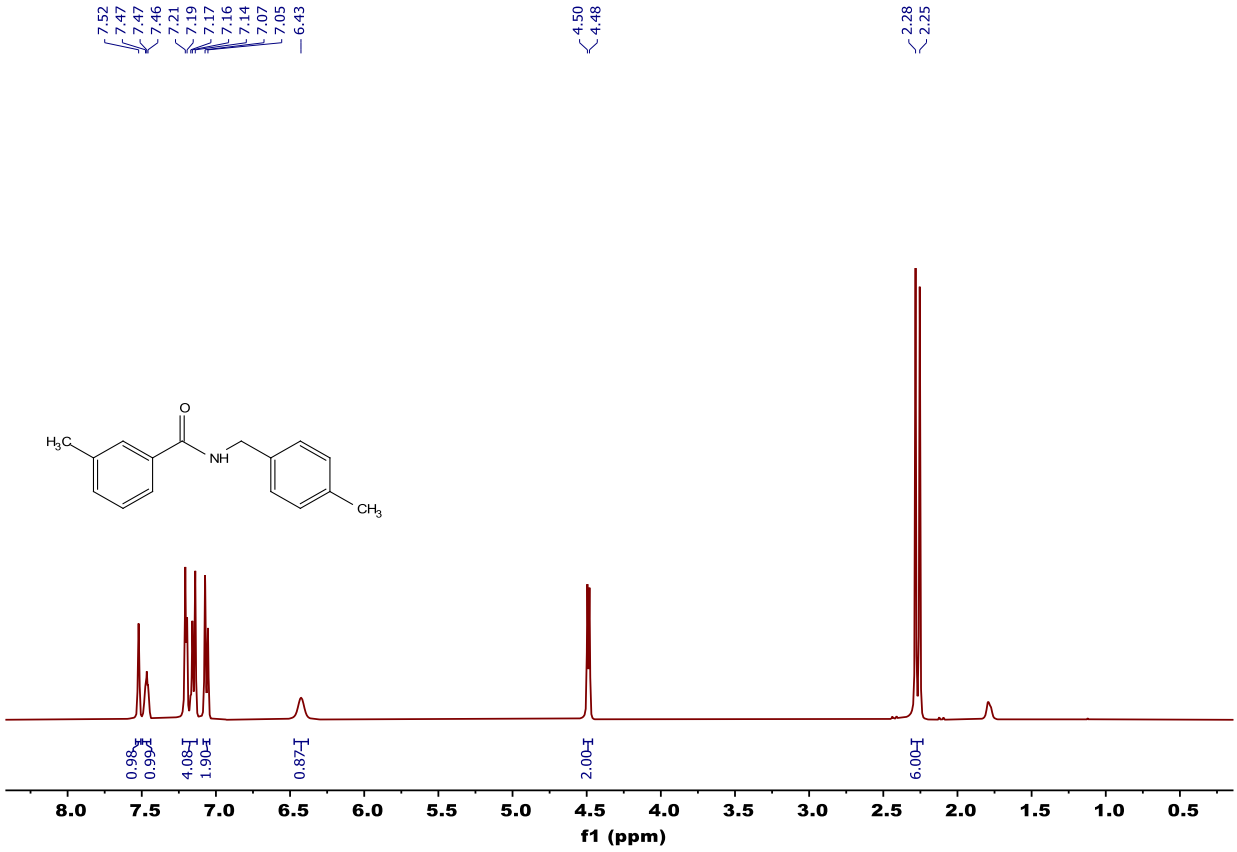
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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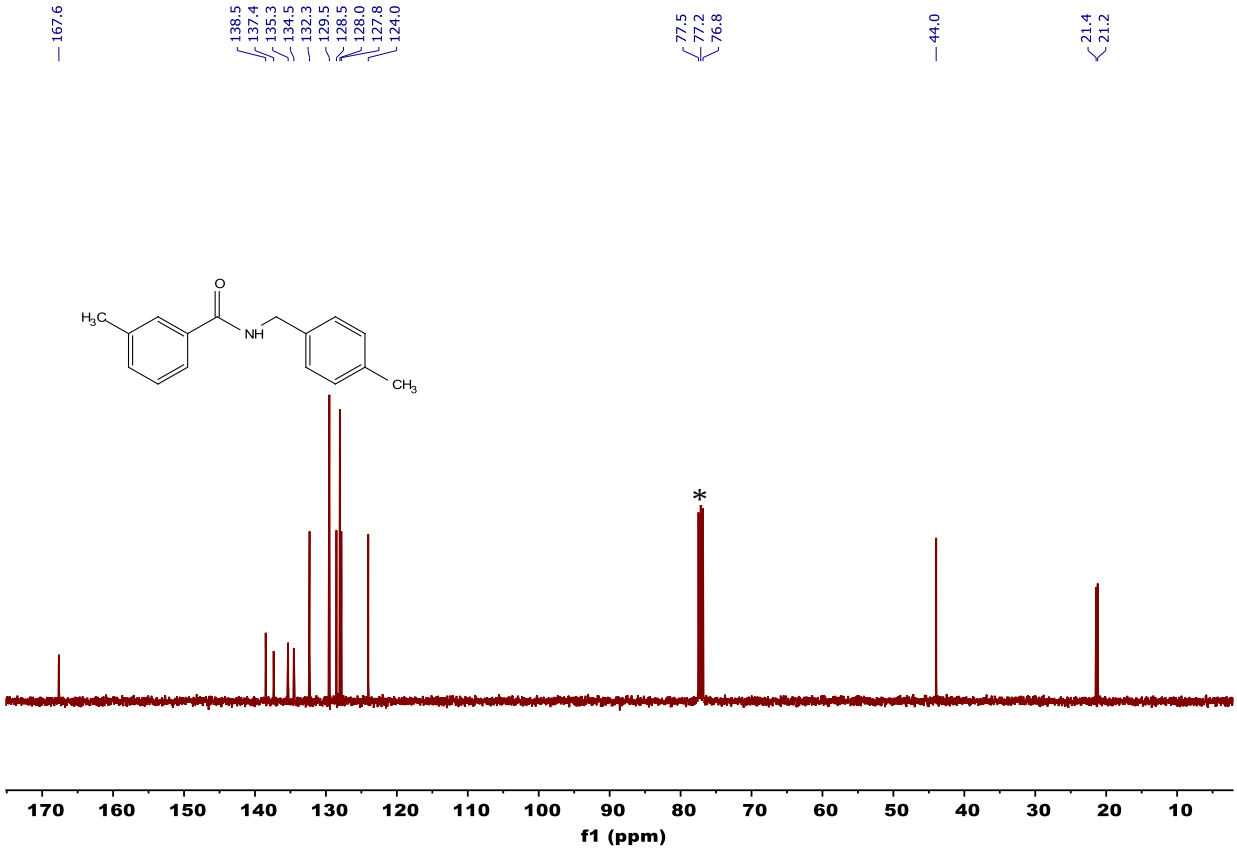
7.16
7.14
7.07
7.05
6.43
4.50
4.48
2.28
2.25
O
NH
H3C
CH3
0.98
0.99
4.08
1.90
0.87
2.00
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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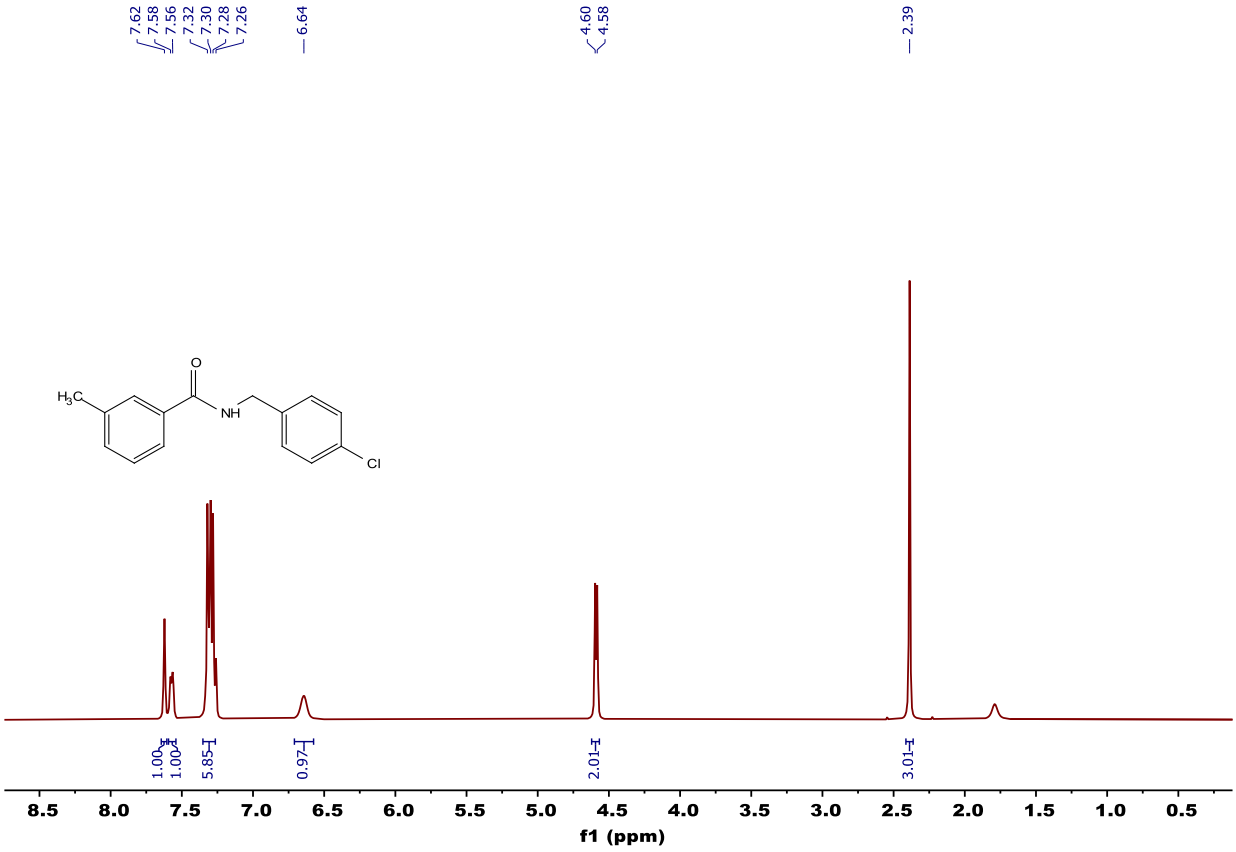
135.3
134.5
132.3
129.5
128.5
128.0
127.8
124.0
77.5
77.2
76.8
44.0
21.4
21.2
O
NH
H3C
CH3
*
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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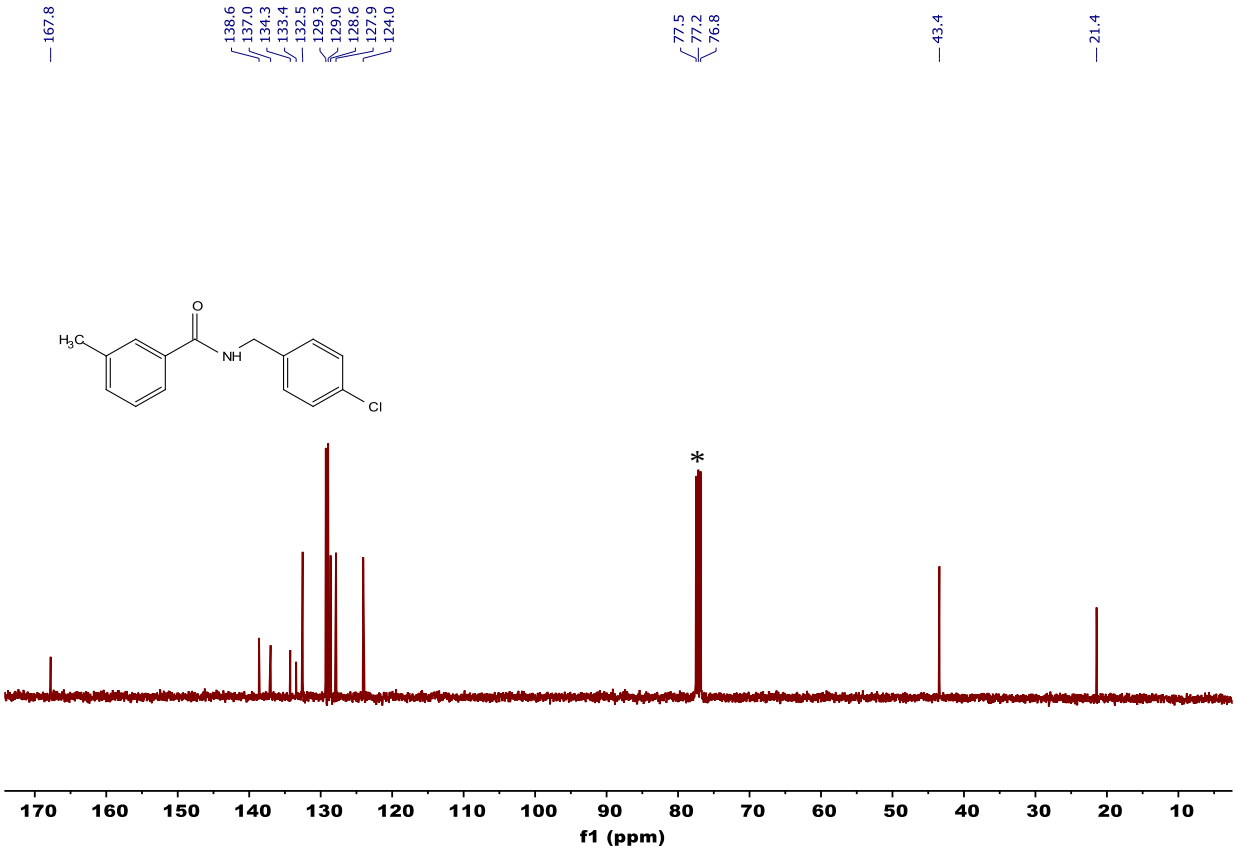
7.28
7.26
6.64
4.60
4.58
2.39
O
H3C
NH
Cl
1.00
1.00
5.85
0.97
2.01
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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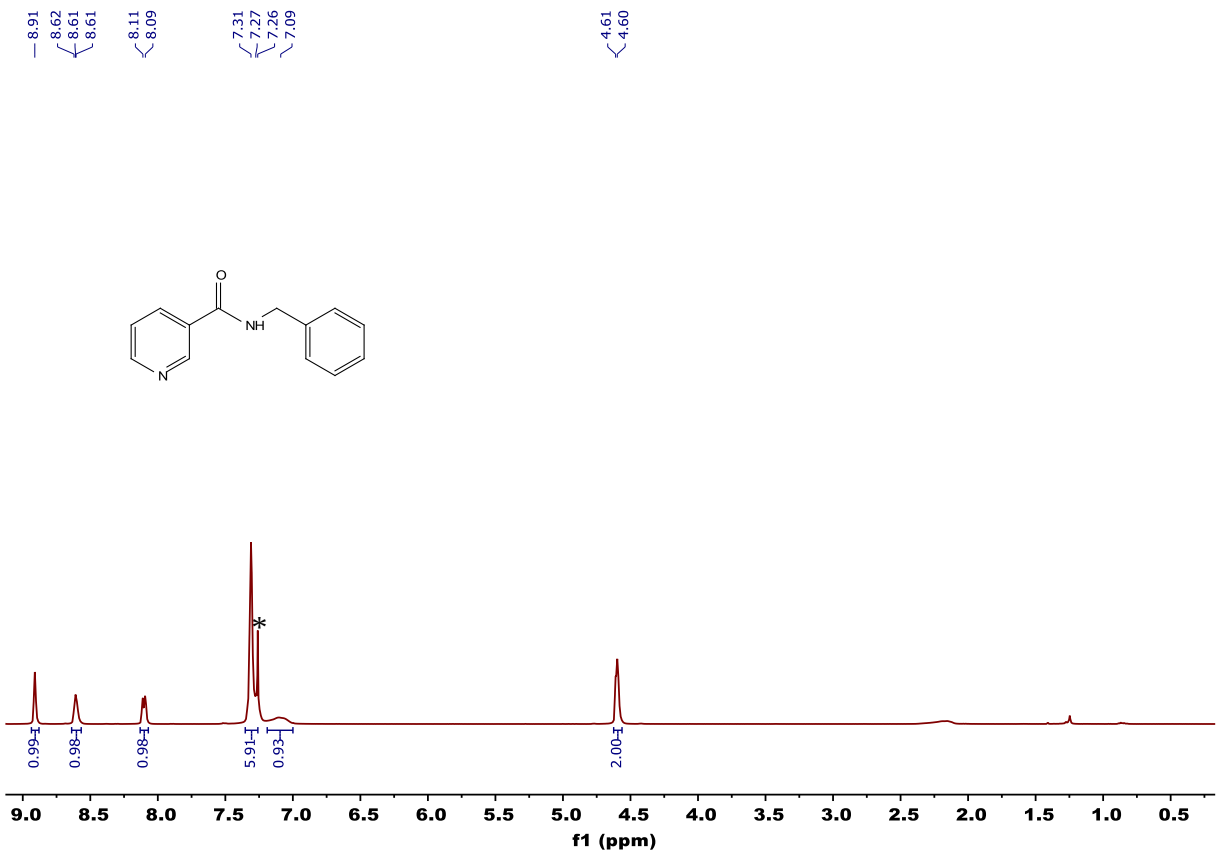
133.4
132.5
129.3
129.0
128.6
127.9
124.0
77.5
77.2
76.8
43.4
21.4
O
H3C
NH
Cl
*
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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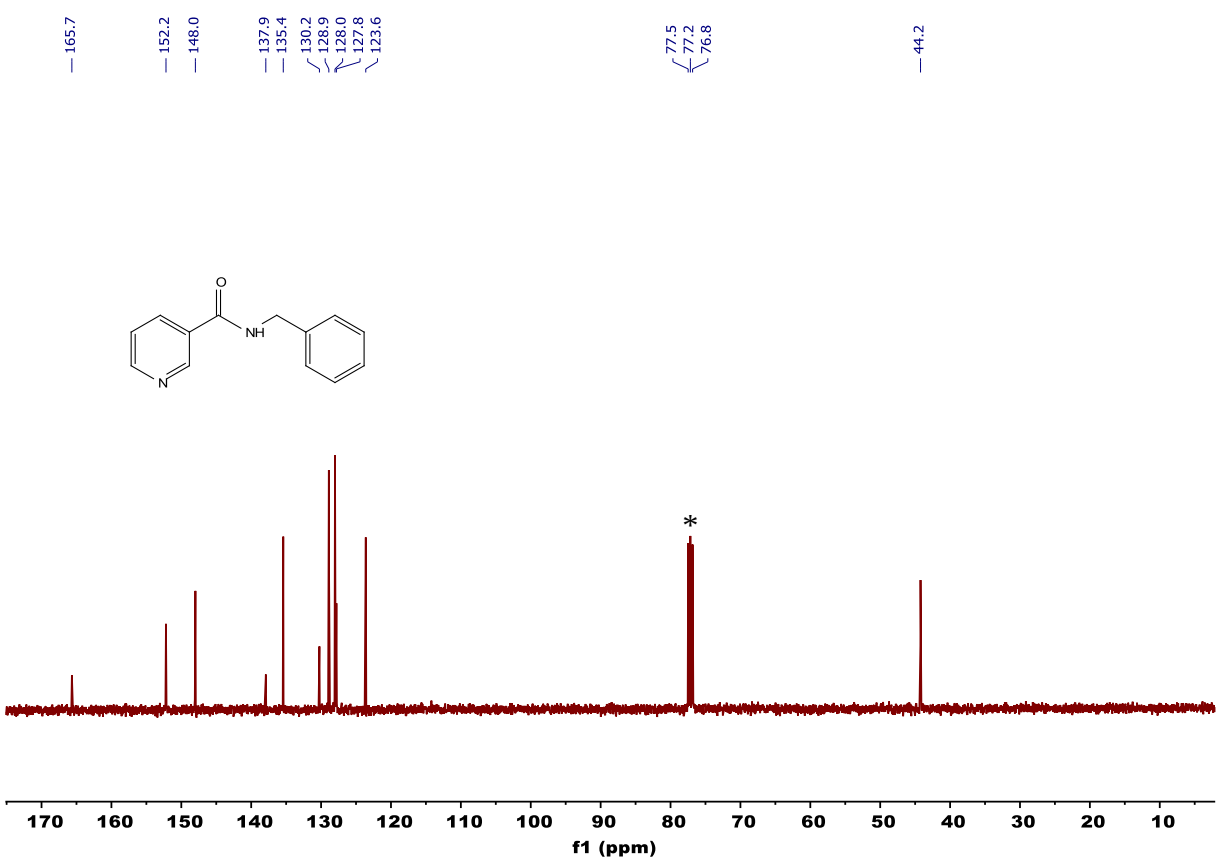
8.61
8.61
8.11
8.09
7.31
7.27
7.26
7.09
4.61
4.60
O
NH
N
*
0.99
0.98
0.98
5.91
0.93
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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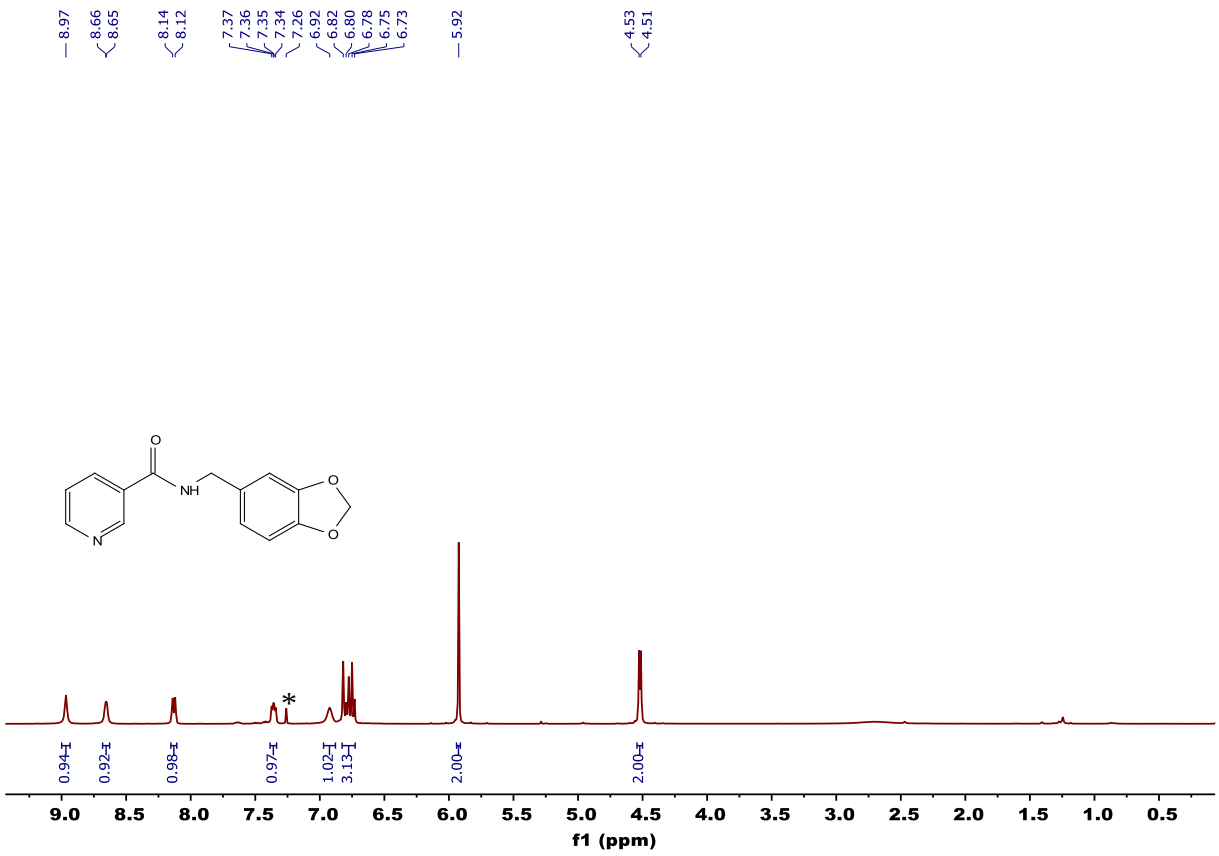
152.2
148.0
137.9
135.4
130.2
128.9
128.0
127.8
123.6
77.5
77.2
76.8
44.2
O
NH
N
*
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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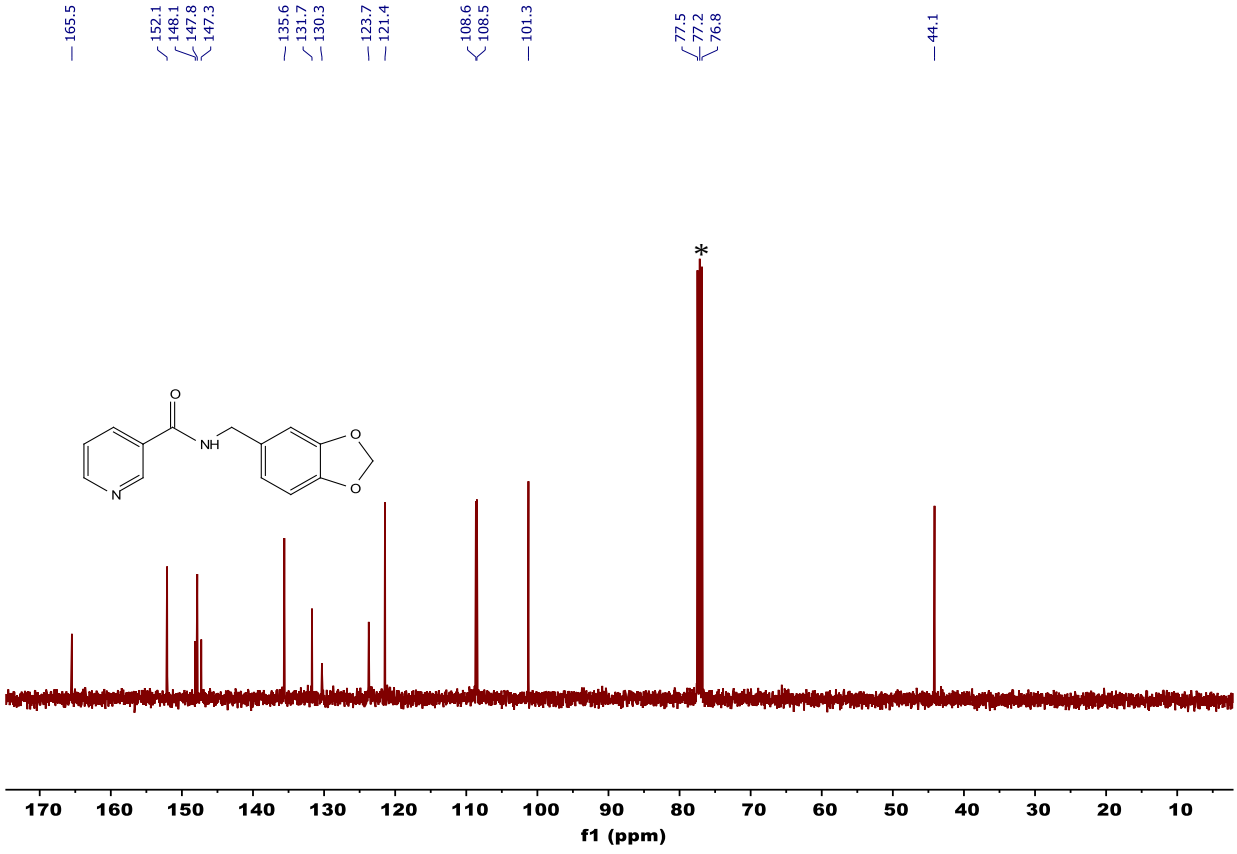
7.35
7.34
7.26
6.92
6.82
6.80
6.78
6.75
6.73
5.92
4.53
4.51
O
NH
N
O
O
*
0.94
0.92
0.98
0.97
1.02
3.13
2.00
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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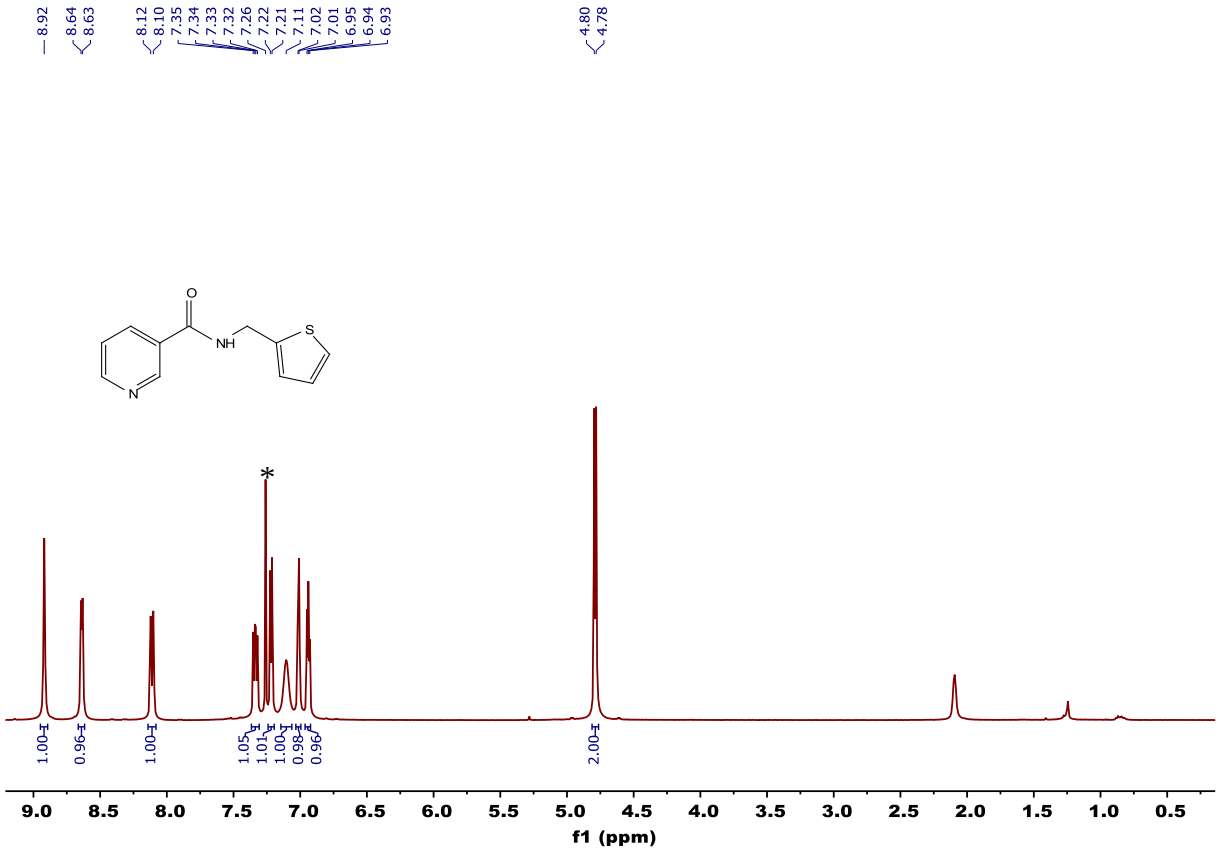
148.1
147.8
147.3
135.6
131.7
130.3
123.7
121.4
108.6
108.5
101.3
77.5
77.2
76.8
44.1
O
NH
N
O
O
*
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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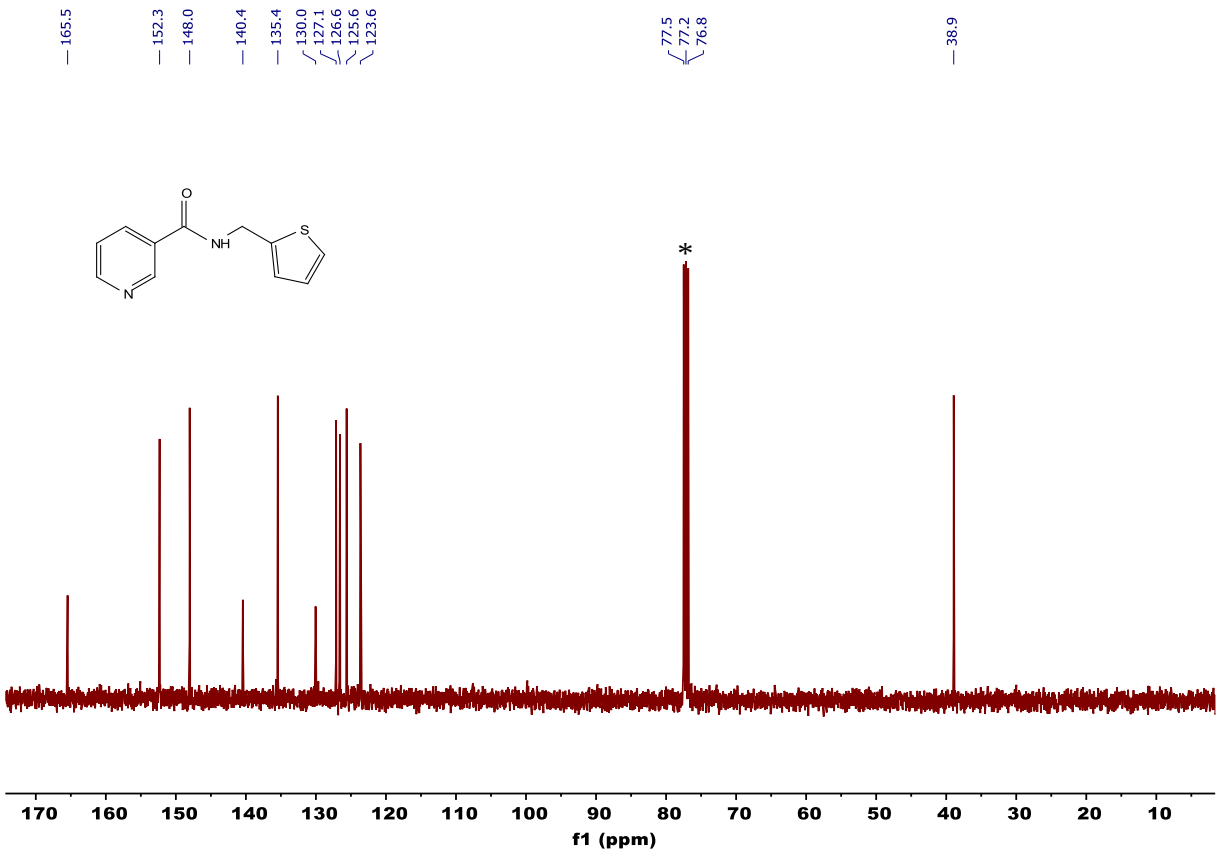
8.64
8.63
8.12
8.10
7.35
7.34
7.33
7.32
7.26
7.22
7.21
7.11
7.02
7.01
6.95
6.94
6.93
4.80
4.78
O
NH
S
N
*
1.00
0.96
1.00
1.05
1.01
1.00
0.98
0.96
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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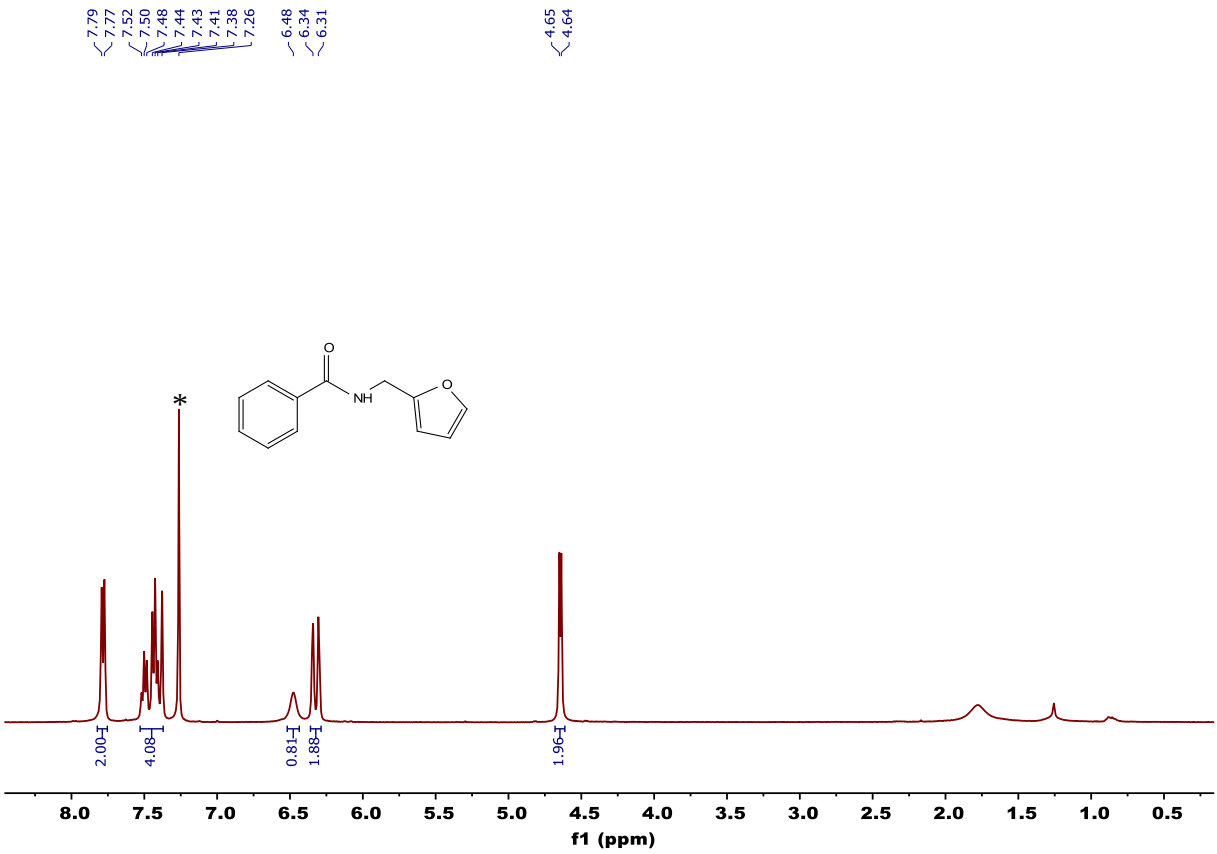
140.4
135.4
130.0
127.1
126.6
125.6
123.6
77.5
77.2
76.8
38.9
O
NH
S
N
*
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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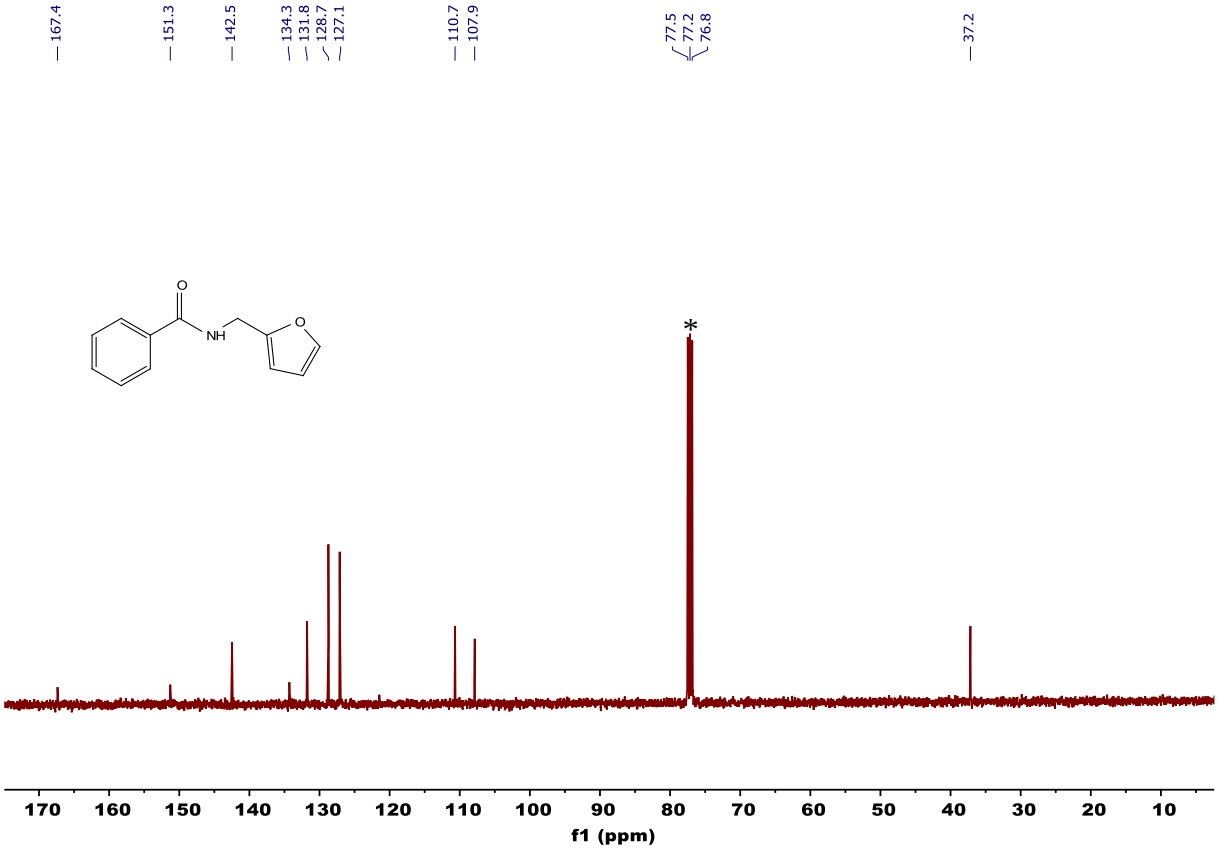
7.41
7.38
7.26
6.48
6.34
6.31
4.65
4.64
O
NH
O
*
2.00
4.08
0.81
1.88
1.96
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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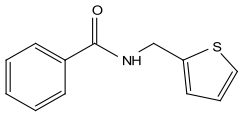
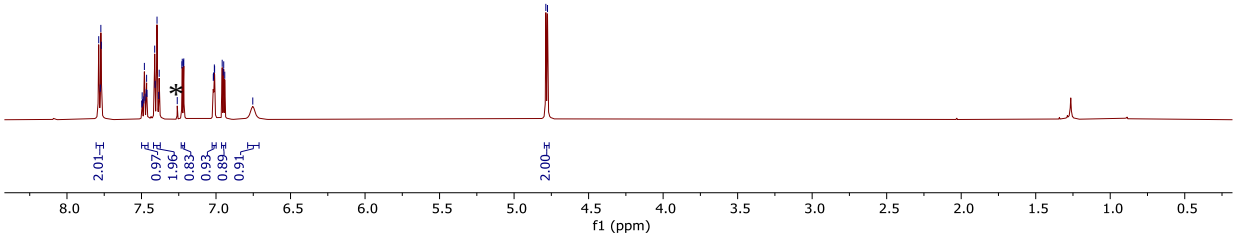
142.5
134.3
131.8
128.7
127.1
110.7
107.9
77.5
77.2
76.8
37.2
O
NH
O
*
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.79
7.78
7.77
7.77
7.50
7.50
7.49
7.48
7.48
7.48
7.47
7.47
7.46
7.41
7.41
7.40
7.38
7.38
7.26
7.23
7.23
7.22
7.22
7.02
7.02
7.01
7.01
6.96
6.95
6.94
6.75
4.79
4.78


O
NH
S


*
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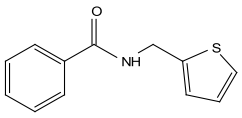
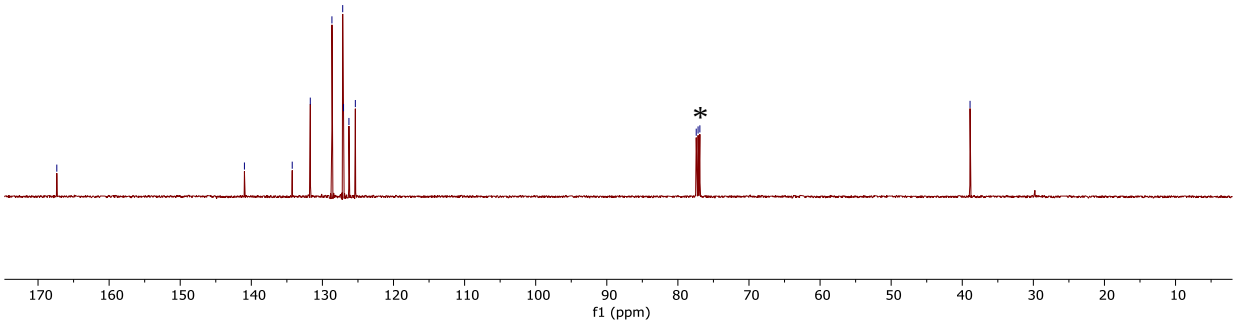
0.97
1.96
0.83
0.93
0.89
0.91
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


167.4
141.0
134.2
131.7
128.7
127.1
127.0
126.3
125.4
77.4
77.2
76.9
38.9


O
NH
S


*
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160
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140
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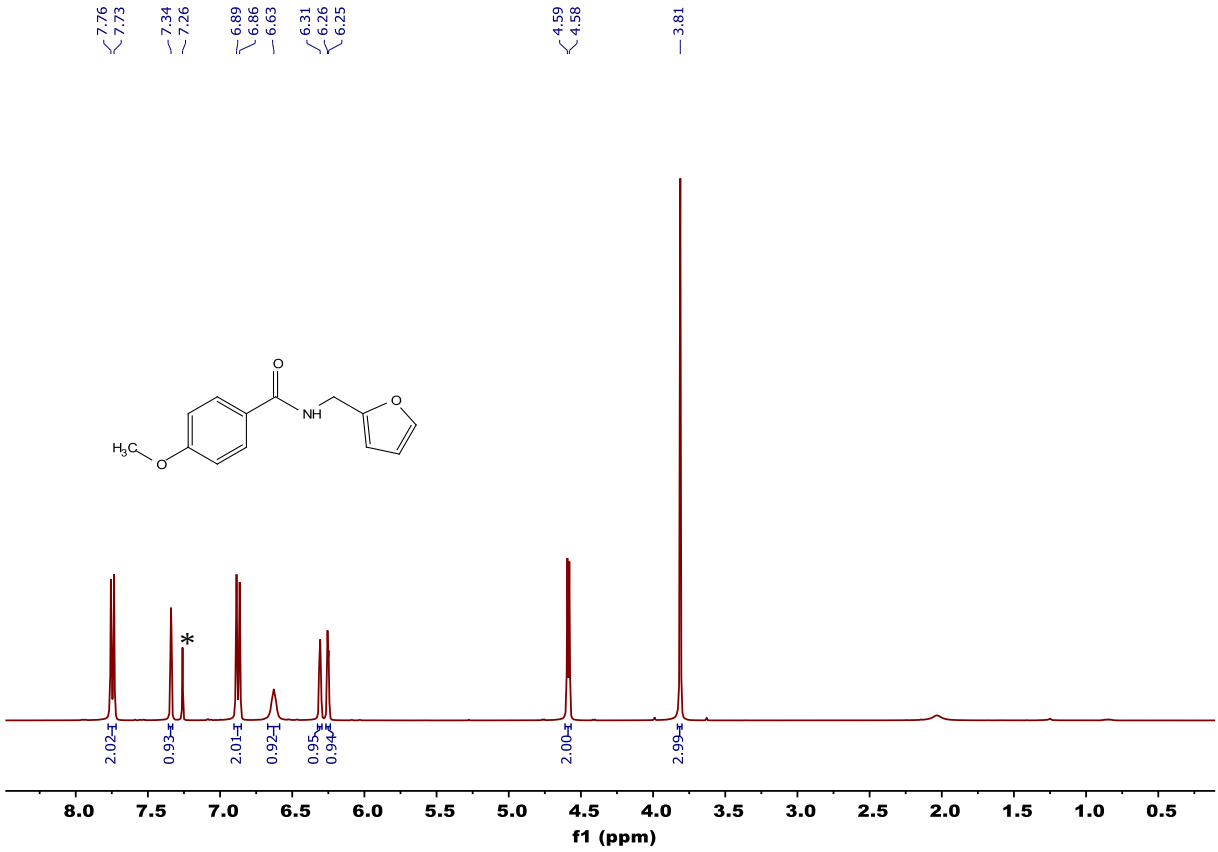
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.73
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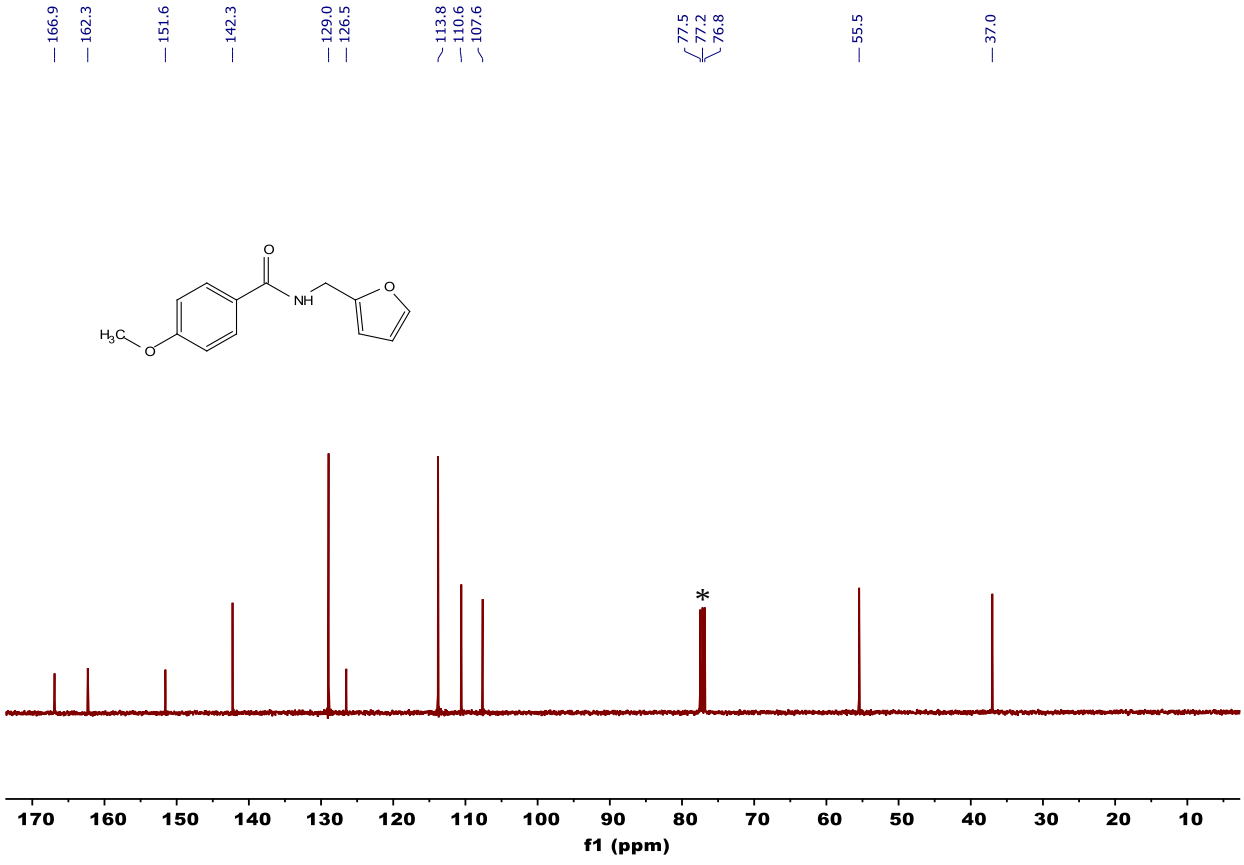
7.26
6.89
6.86
6.63
6.31
6.26
6.25
4.59
4.58
3.81
O
NH
O
H3C
O
*
2.02
0.93
2.01
0.92
0.95
0.94
2.00
2.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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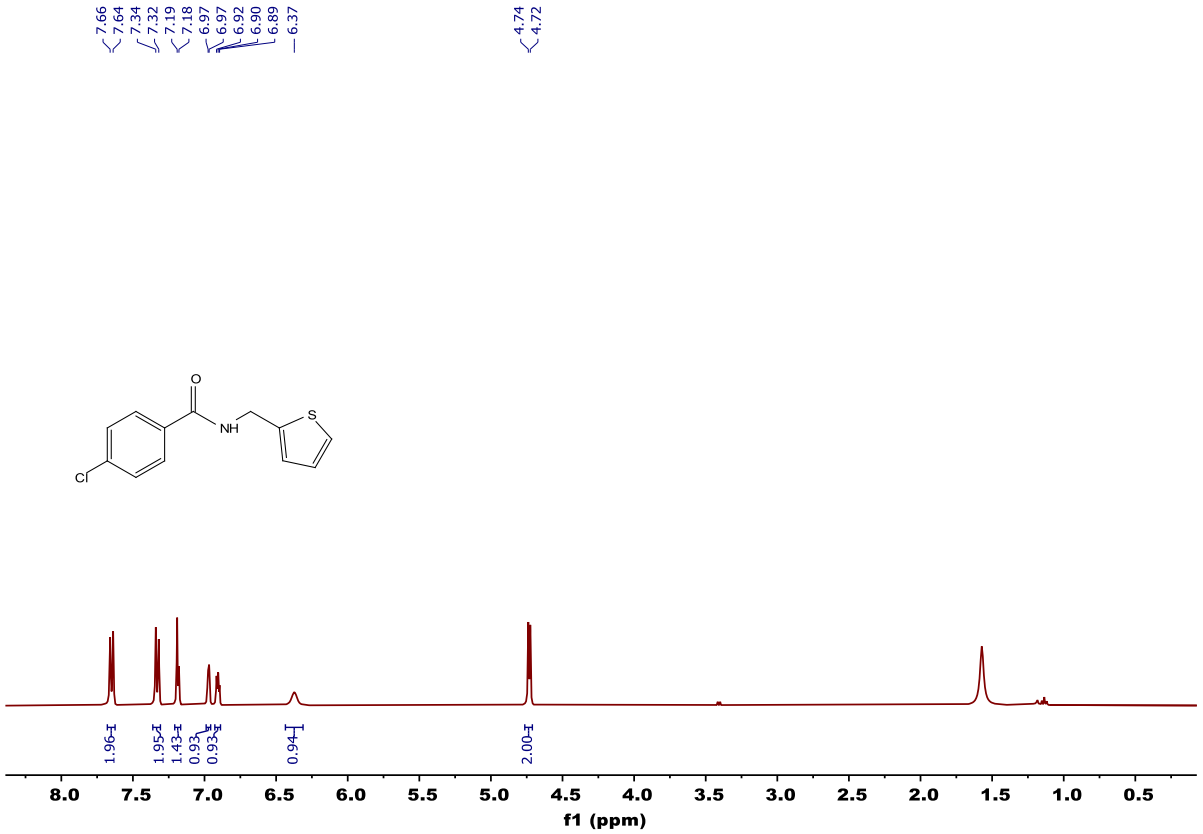
162.3
151.6
142.3
129.0
126.5
113.8
110.6
107.6
77.5
77.2
76.8
55.5
37.0
O
NH
O
H3C
O
*
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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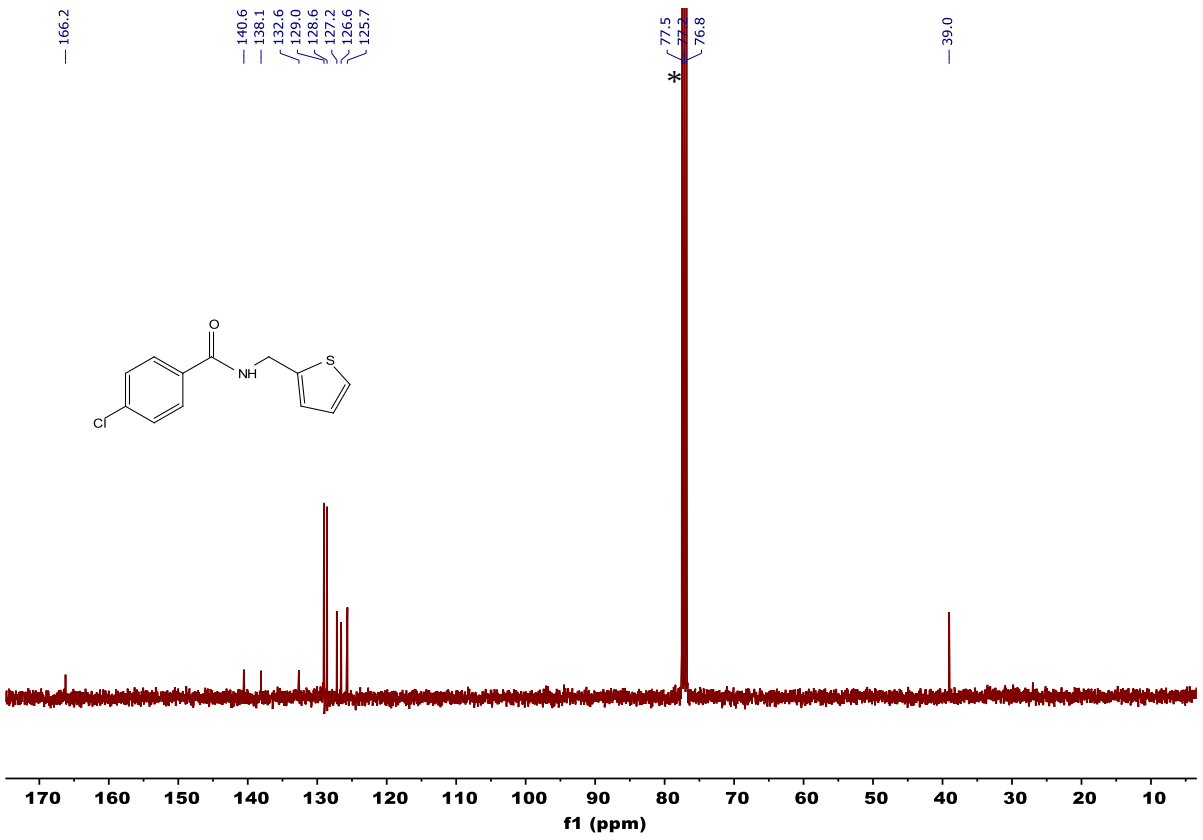
7.64
7.34
7.32
7.19
7.18
6.97
6.97
6.92
6.90
6.89
6.37
4.74
4.72
O
NH
S
Cl
1.96
1.95
1.43
0.93
0.93
0.94
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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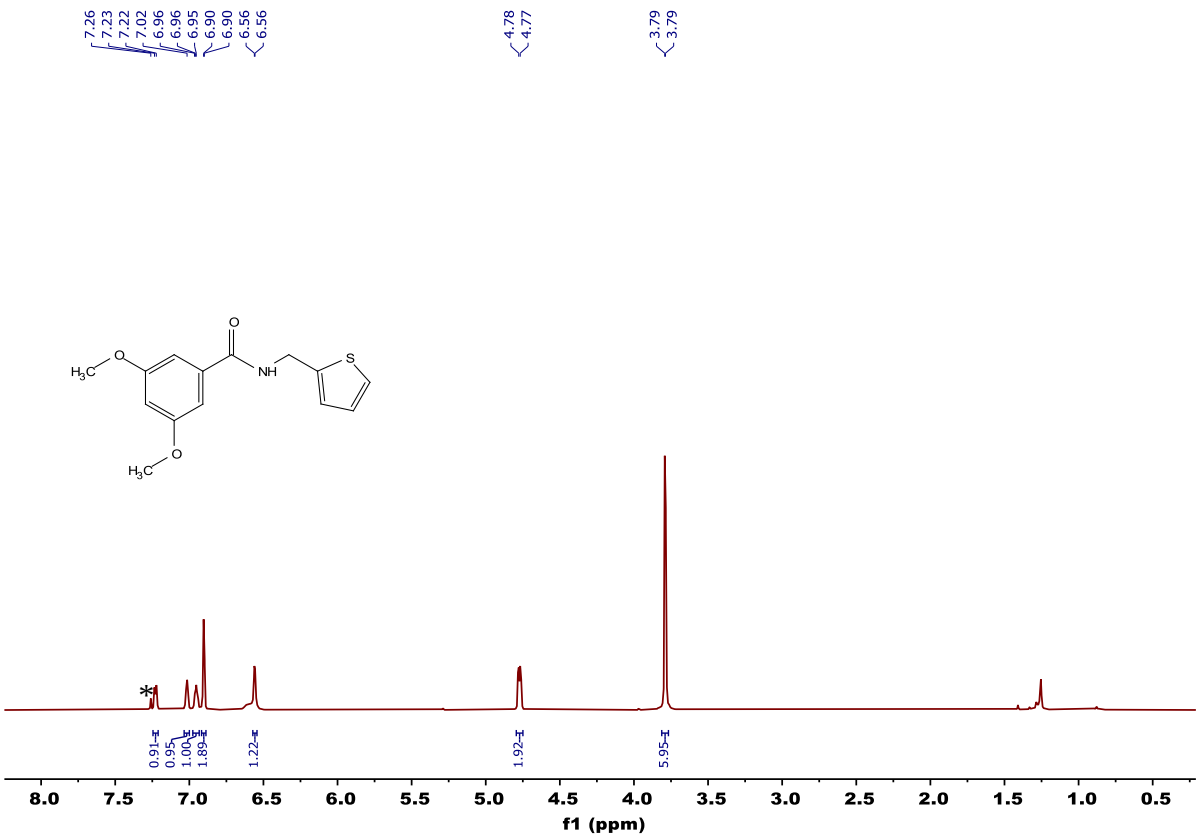
140.6
138.1
132.6
129.0
128.6
127.2
126.6
125.7
77.5
77.2
76.8
39.0
*
O
NH
S
Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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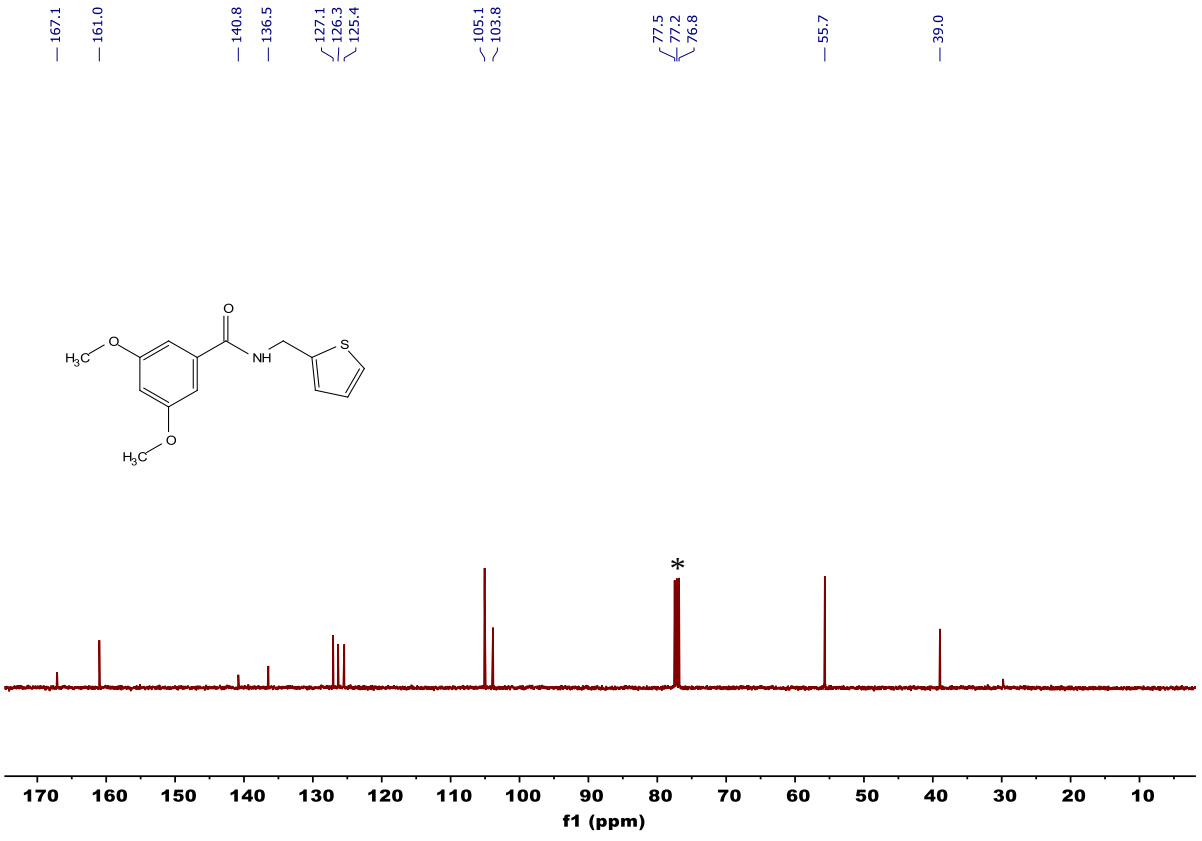
7.23
7.22
7.02
6.96
6.96
6.95
6.90
6.90
6.56
6.56
4.78
4.77
3.79
3.79
O
O
NH
S
O
0.91
0.95
1.00
1.89
1.22
1.92
5.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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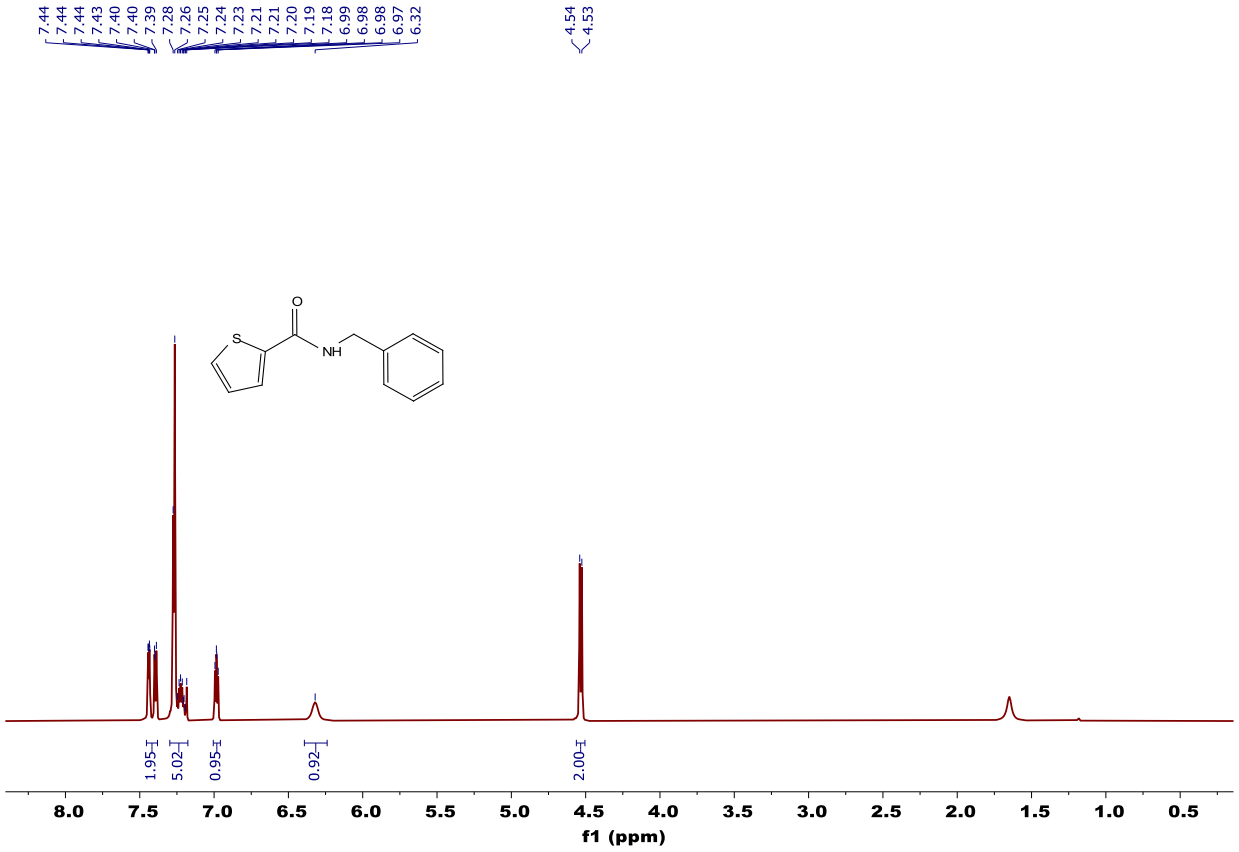
161.0
140.8
136.5
127.1
126.3
125.4
105.1
103.8
77.5
77.2
76.8
55.7
39.0
O
O
NH
S
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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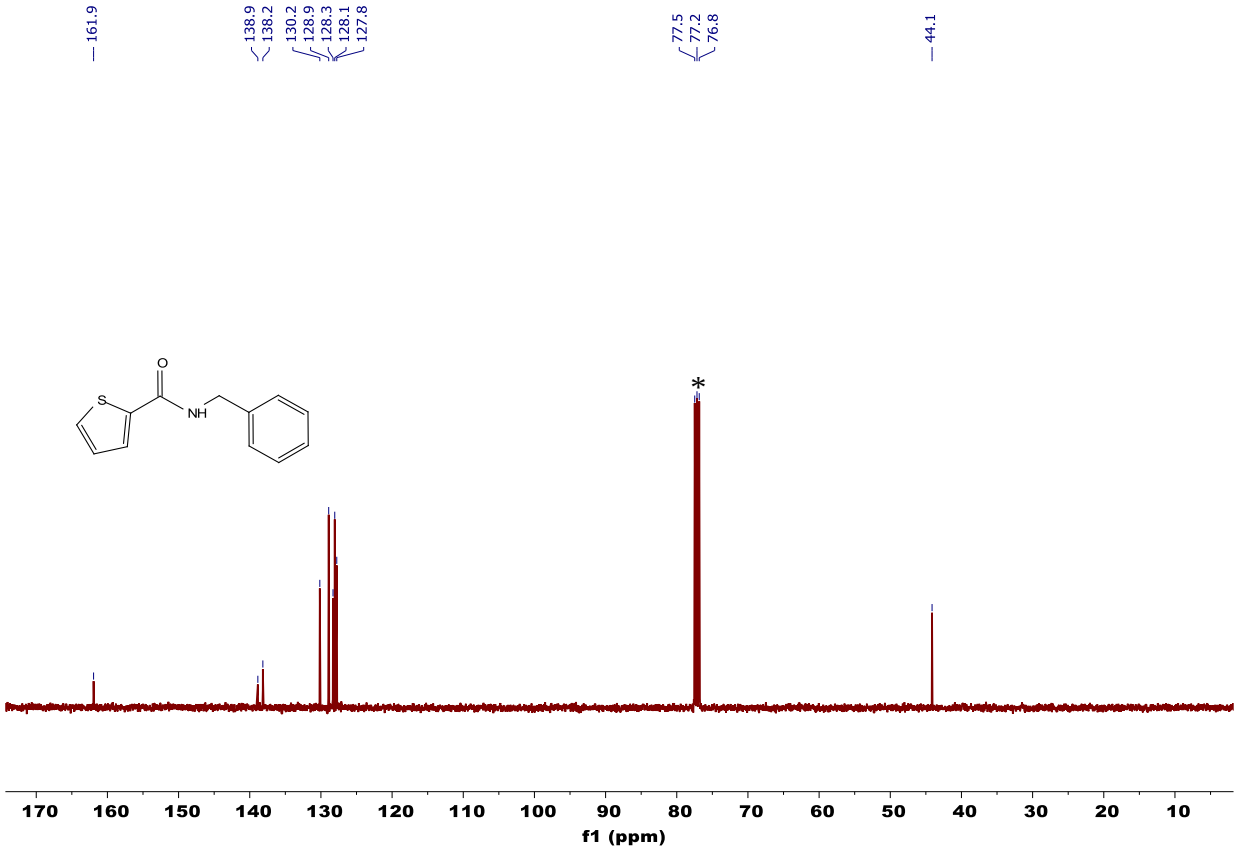
7.44
7.44
7.43
7.40
7.40
7.39
7.28
7.26
7.25
7.24
7.23
7.21
7.21
7.20
7.19
7.18
6.99
6.98
6.98
6.97
6.32
4.54
4.53
O
S
NH
1.95
5.02
0.95
0.92
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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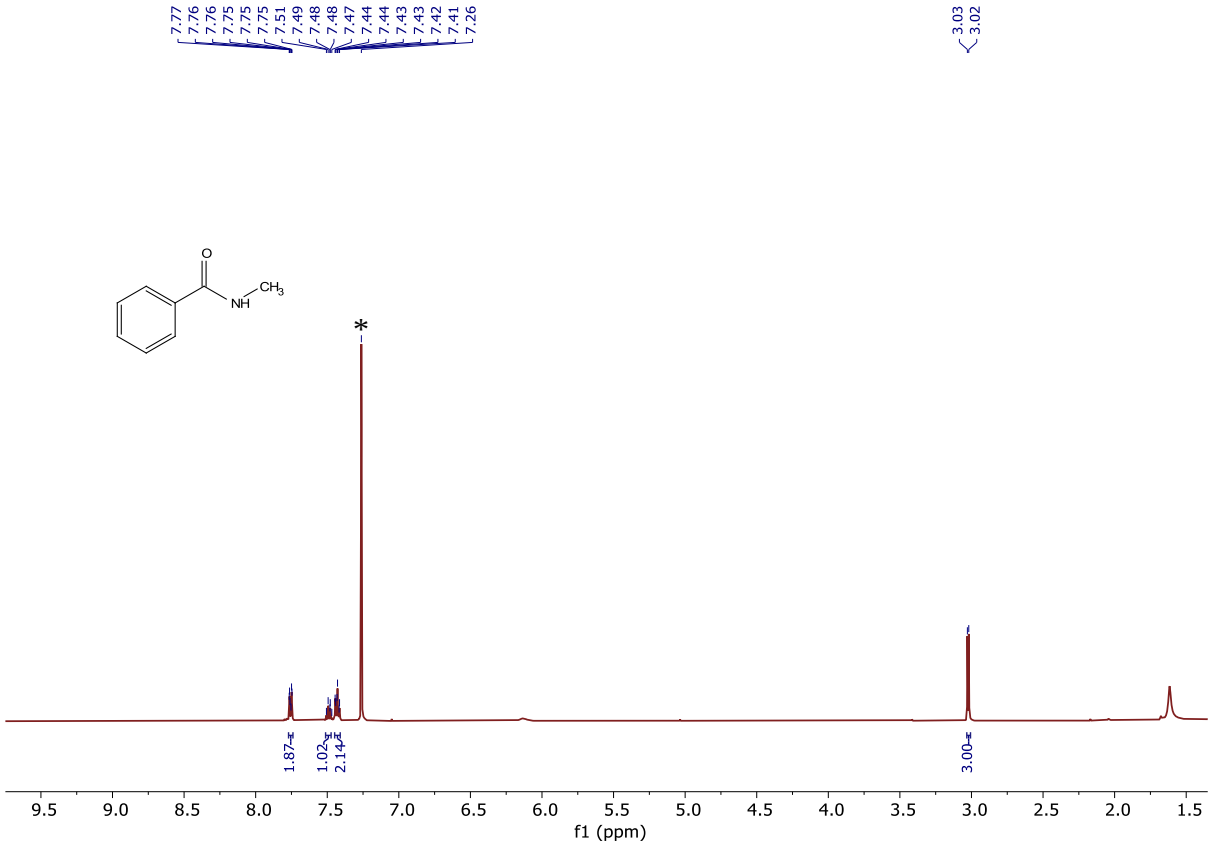
138.9
138.2
130.2
128.9
128.3
128.1
127.8
77.5
77.2
76.8
44.1
O
S
NH
*
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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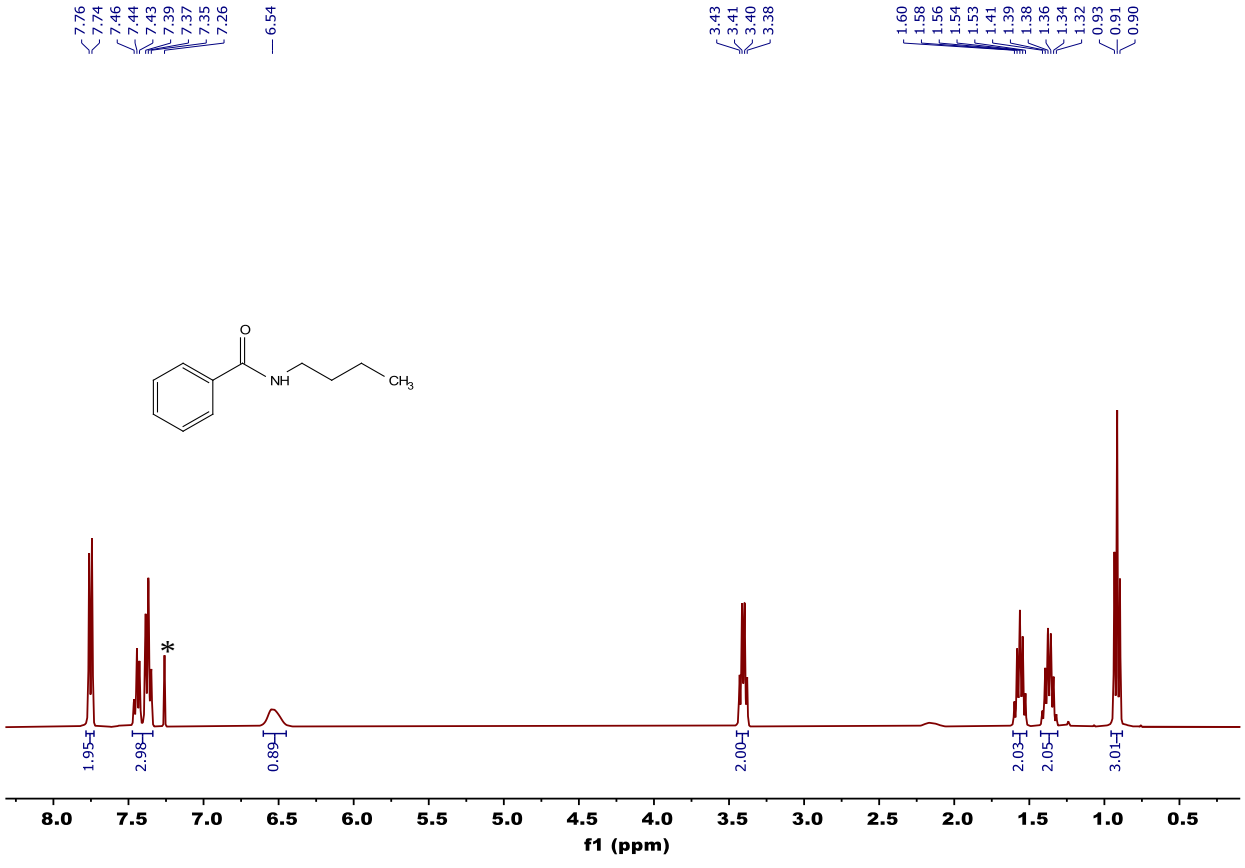
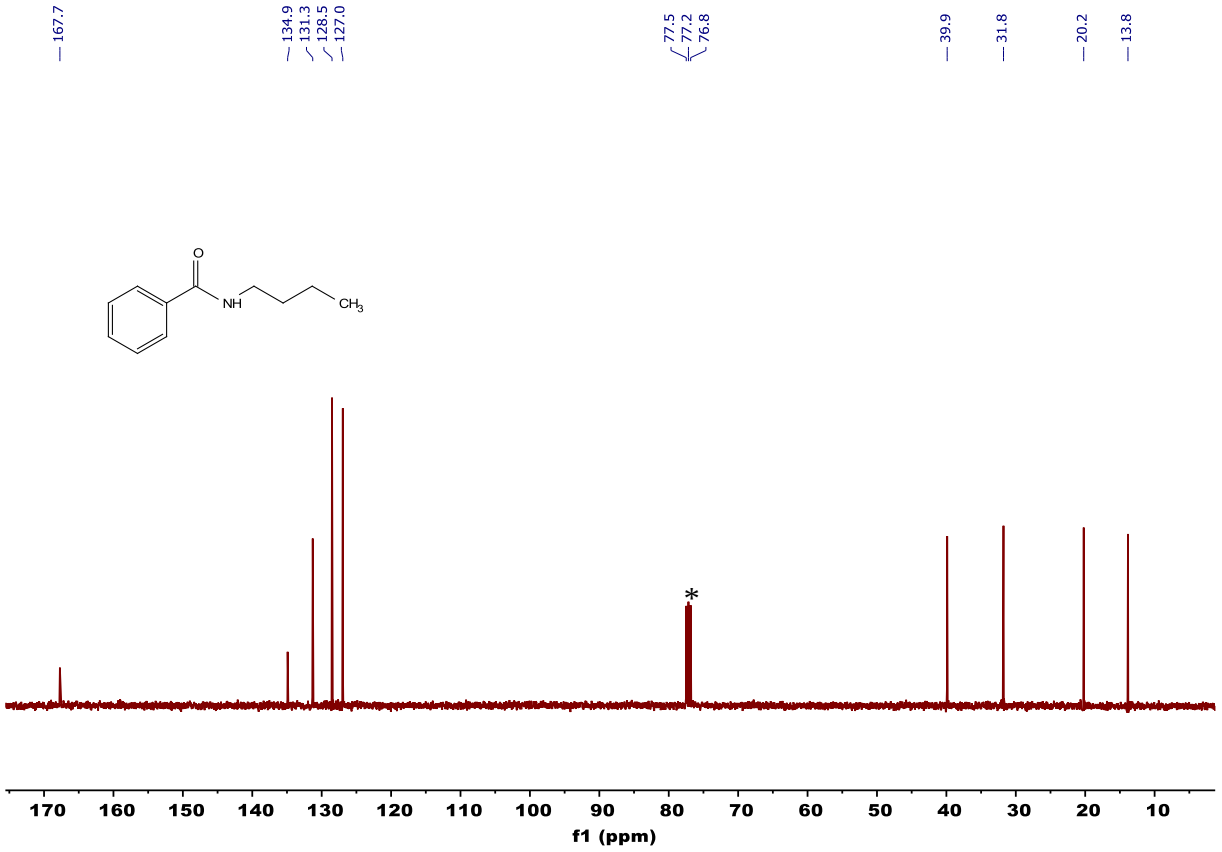
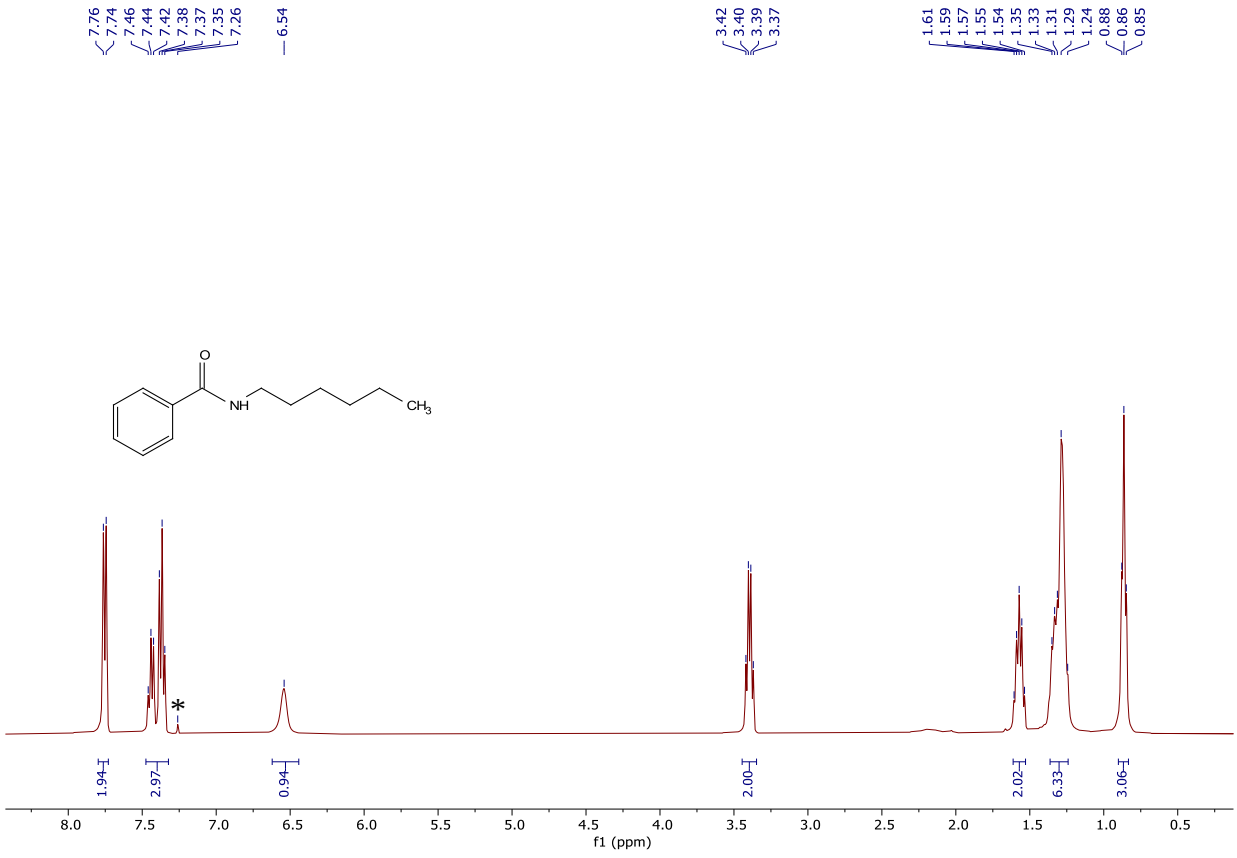
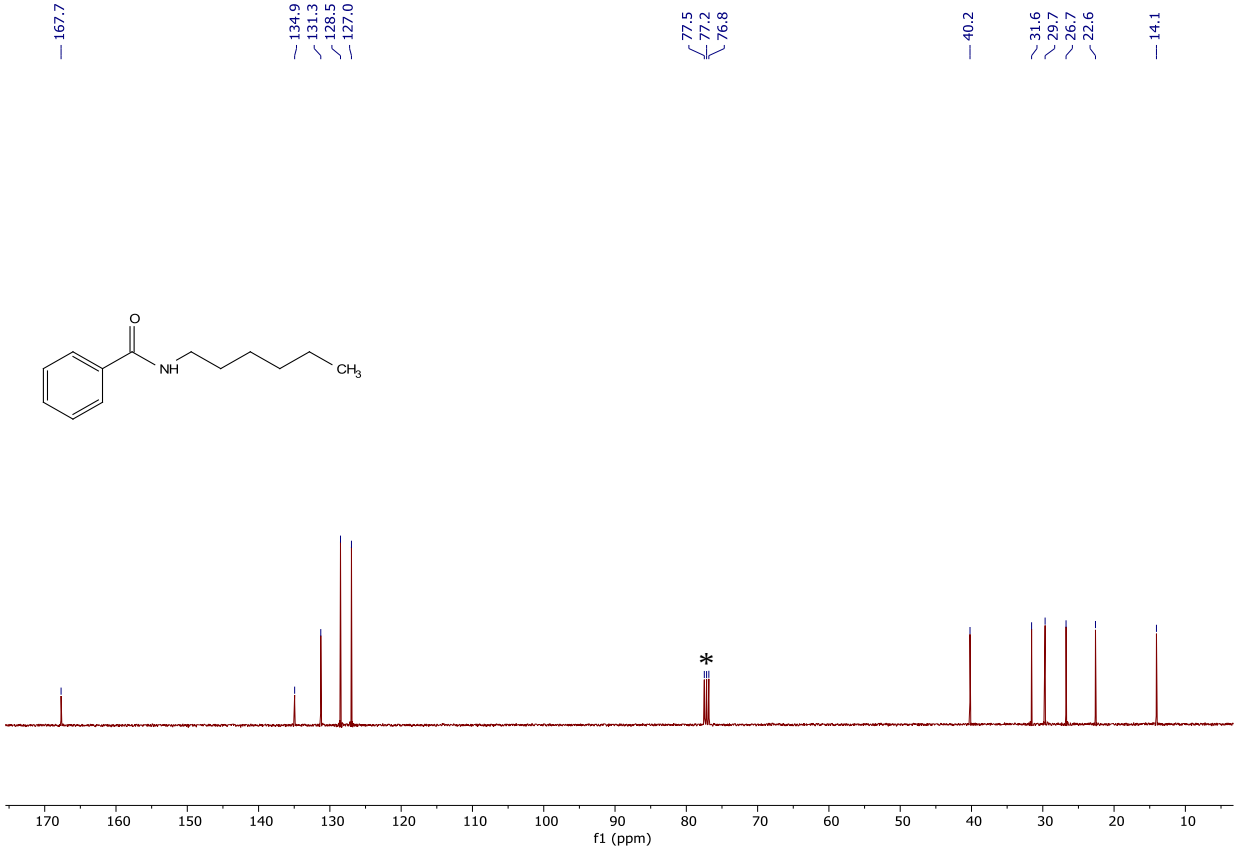
7.76
7.76
7.75
7.75
7.75
7.51
7.49
7.48
7.48
7.47
7.44
7.44
7.43
7.43
7.42
7.41
7.26
3.03
3.02
O
NH
CH3
*
1.87
1.02
2.14
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

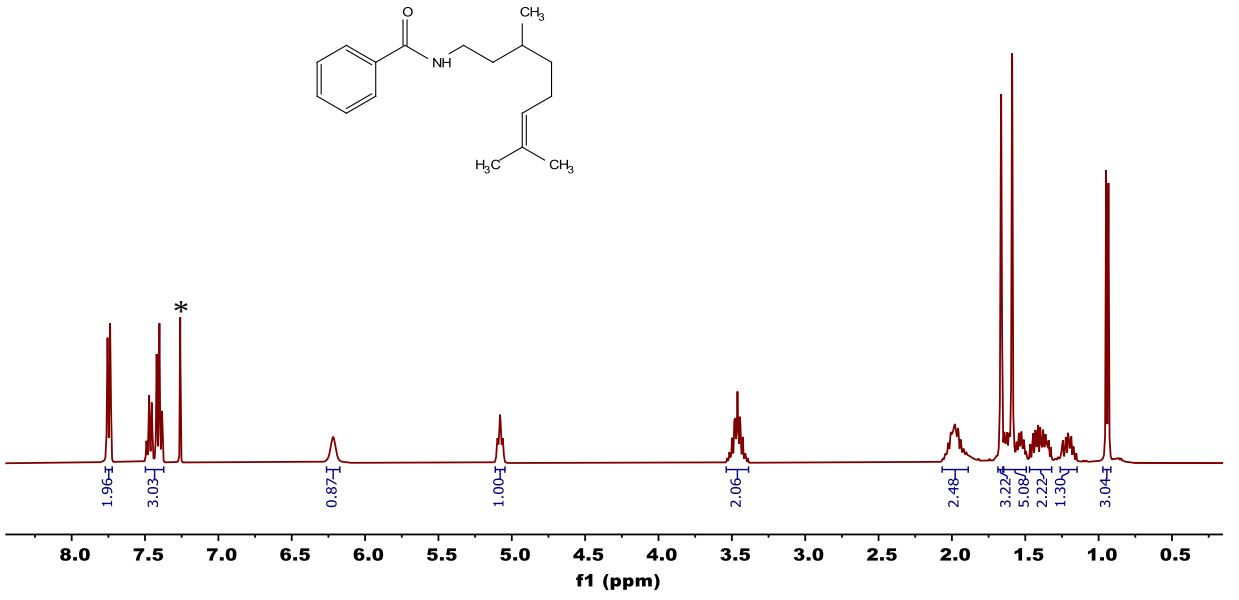

7.76
7.74
7.46
7.44
7.43
7.39
7.37
7.35
7.26
6.54
3.43
3.41
3.40
3.38
1.60
1.58
1.56
1.54
1.53
1.41
1.39
1.38
1.36
1.34
1.32
0.93
0.91
0.90
O
NH
CH3
*
1.95
2.98
0.89
2.00
2.03
2.05
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

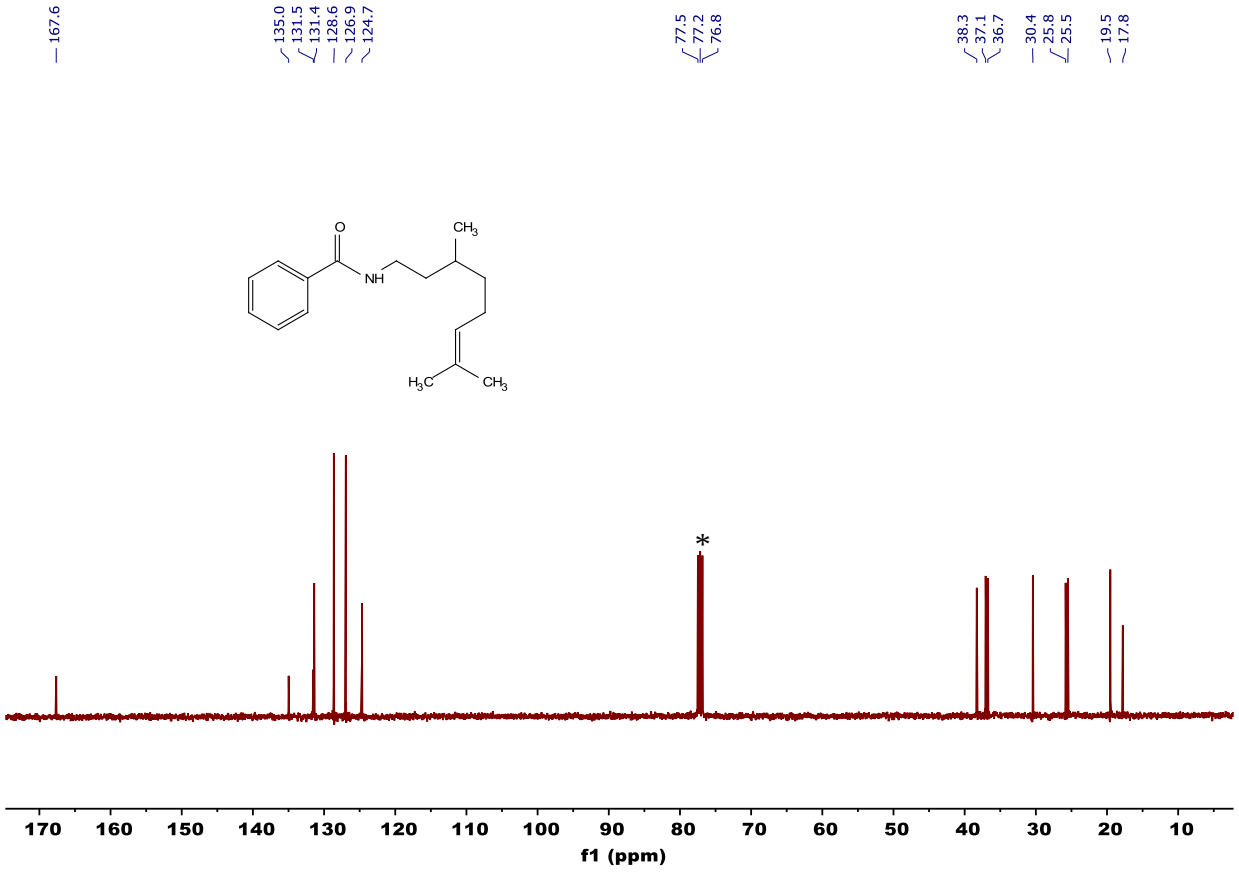

167.7
134.9
131.3
128.5
127.0
77.5
77.2
76.8
39.9
31.8
20.2
13.8
O
NH
CH3
*
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.76
7.74
7.46
7.44
7.42
7.38
7.37
7.35
7.26
6.54
3.42
3.40
3.39
3.37
1.61
1.59
1.57
1.55
1.54
1.35
1.33
1.31
1.29
1.24
0.88
0.86
0.85
O
NH
CH3
*
1.94
2.97
0.94
2.00
2.02
6.33
3.06
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)


167.7
134.9
131.3
128.5
127.0
77.5
77.2
76.8
40.2
31.6
29.7
26.7
22.6
14.1
O
NH
CH3
*
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.76 7.74 7.49 7.47 7.45 7.42 7.41 7.38 7.26 6.22 5.10 5.08 3.52 3.50 3.48 3.48 3.47 3.46 3.45 3.44 3.43 3.41 2.05 2.03 2.01 1.99 1.98 1.96 1.94 1.92 1.90 1.67 1.65 1.63 1.62 1.61 1.60 1.59 1.56 1.54 1.53 1.51 1.49 1.47 1.45 1.43 1.43 1.42 1.41 1.40 1.39 1.39 1.38 1.37 1.36 1.36 1.35 1.34 1.33 1.25 1.24 1.22 1.22 1.20 1.19 1.17 1.15 0.95 0.93


O
NH
CH3
H3C
CH3
*
1.96
3.03
0.87
1.00
2.06
2.48
3.22
5.08
2.22
1.30
3.04
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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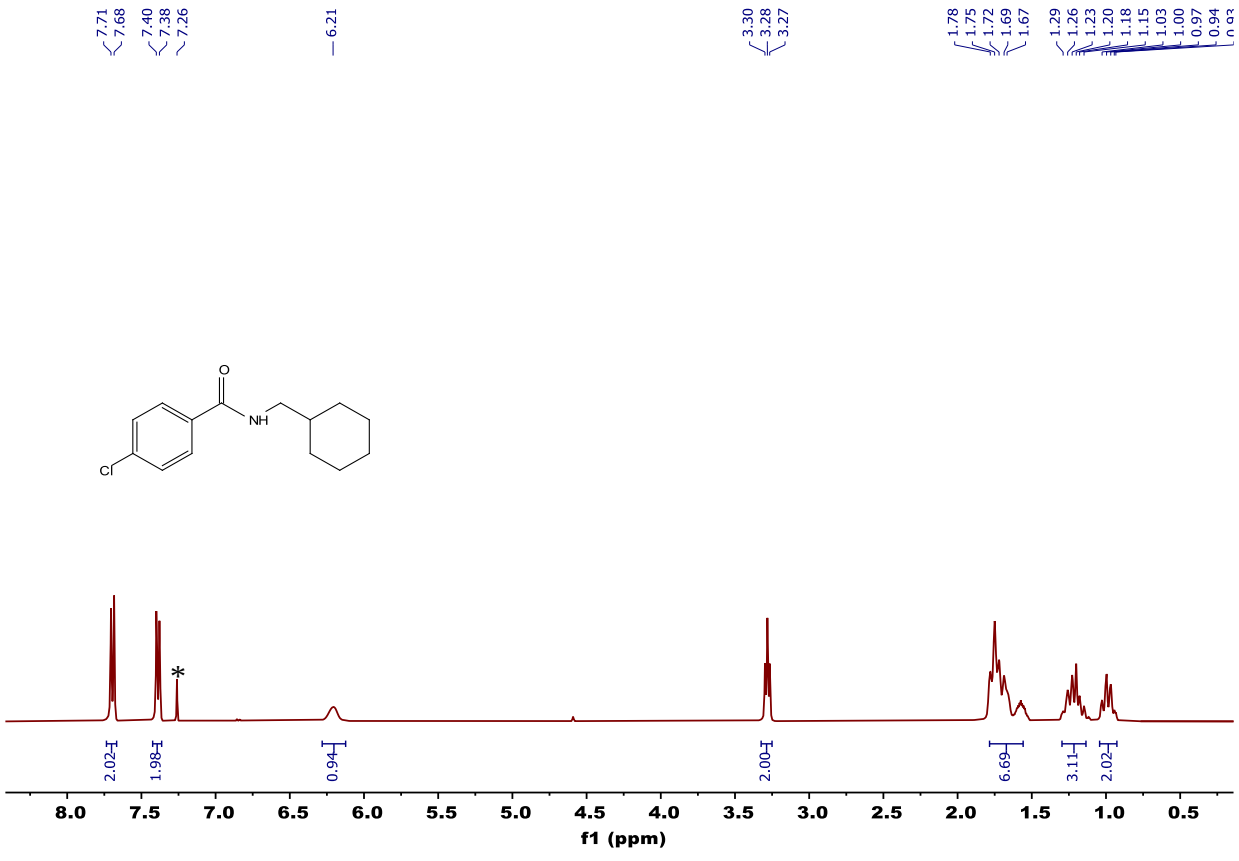
135.0
131.5
131.4
128.6
126.9
124.7
77.5
77.2
76.8
38.3
37.1
36.7
30.4
25.8
25.5
19.5
17.8
O
NH
CH3
H3C
CH3
*
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.71
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7.40
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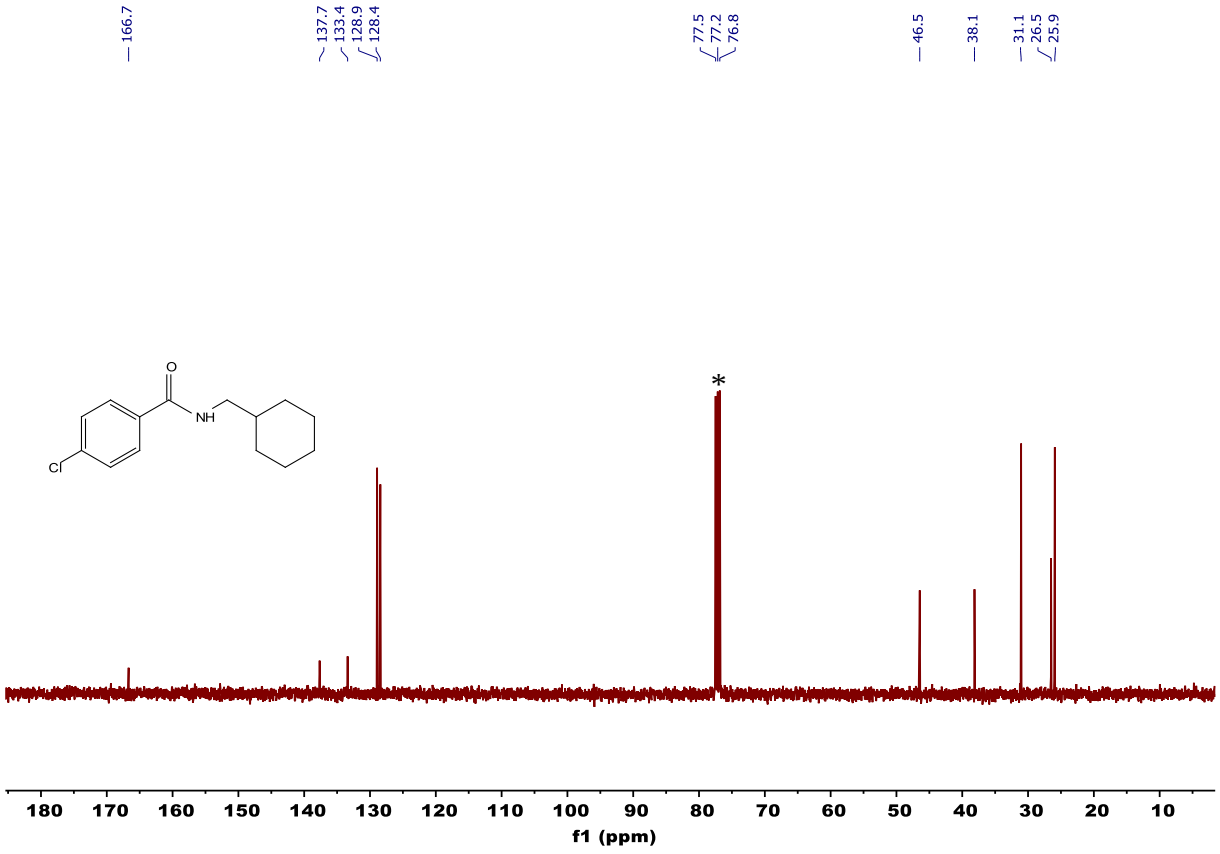
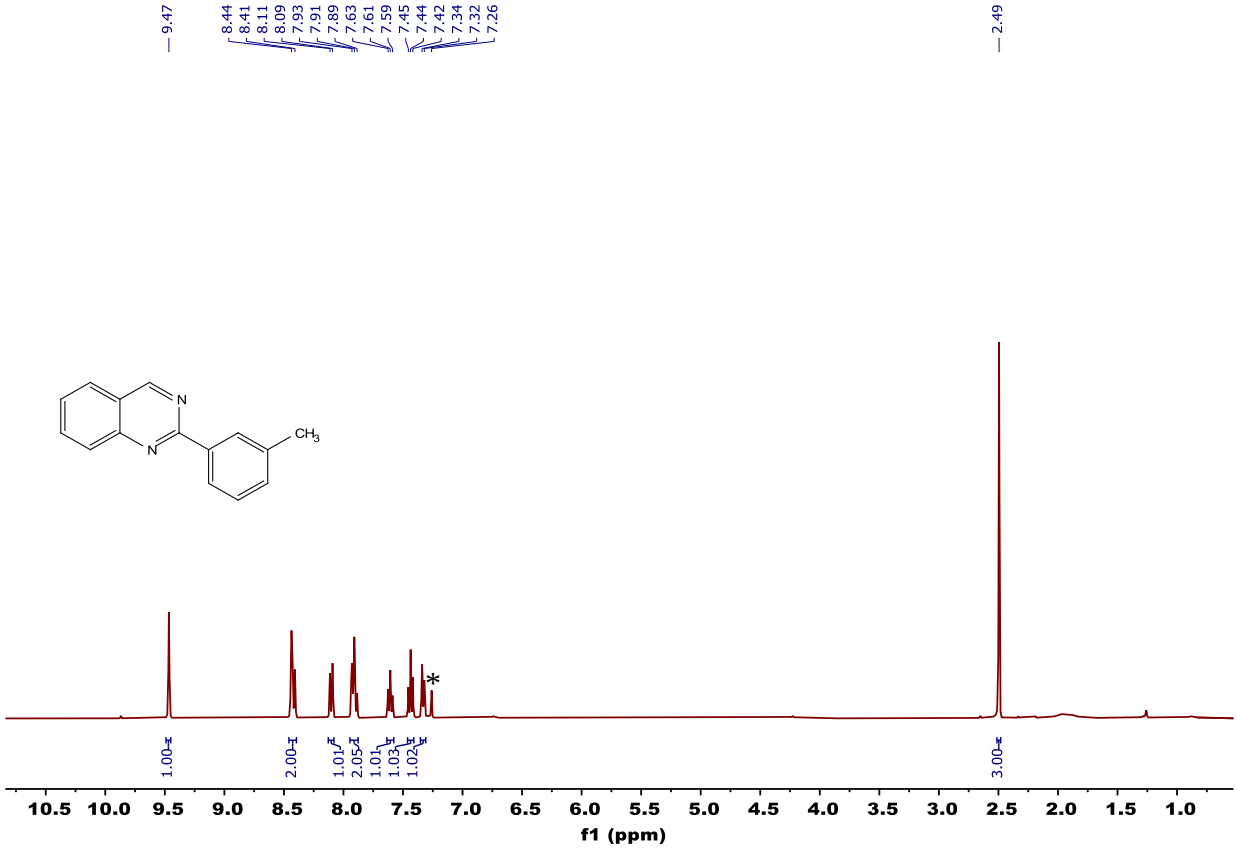
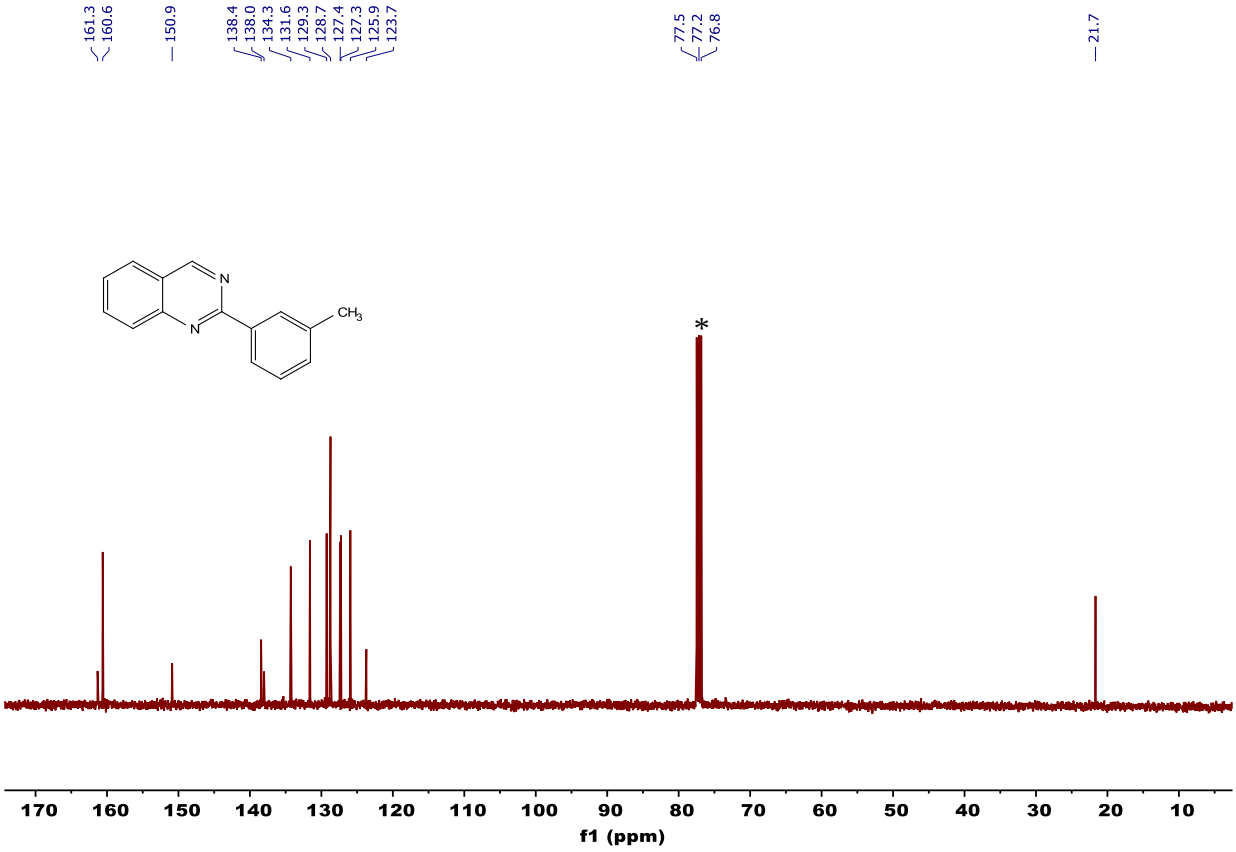
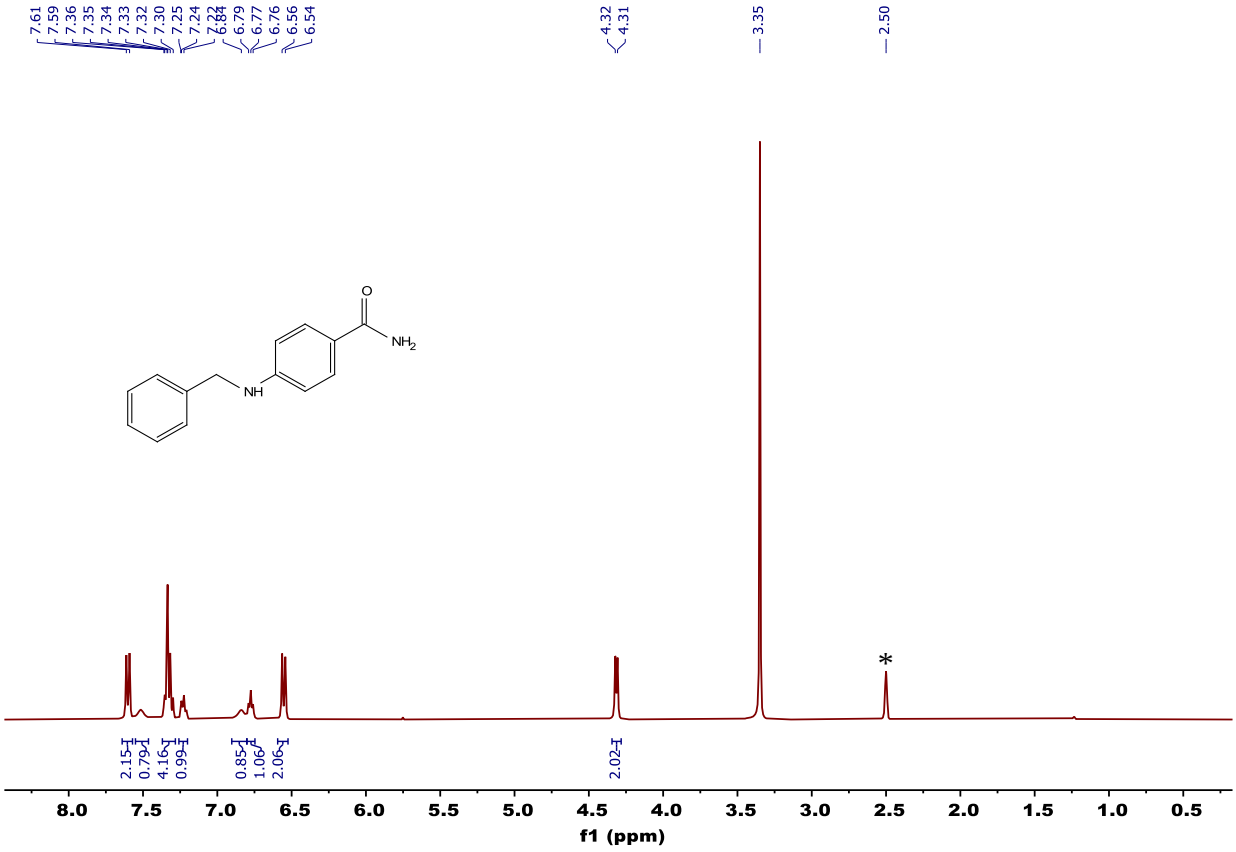
7.26
6.21
3.30
3.28
3.27
1.78
1.75
1.72
1.69
1.67
1.29
1.26
1.23
1.20
1.18
1.15
1.03
1.00
0.97
0.94
O
NH
Cl
*
2.02
1.98
0.94
2.00
6.69
3.11
2.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

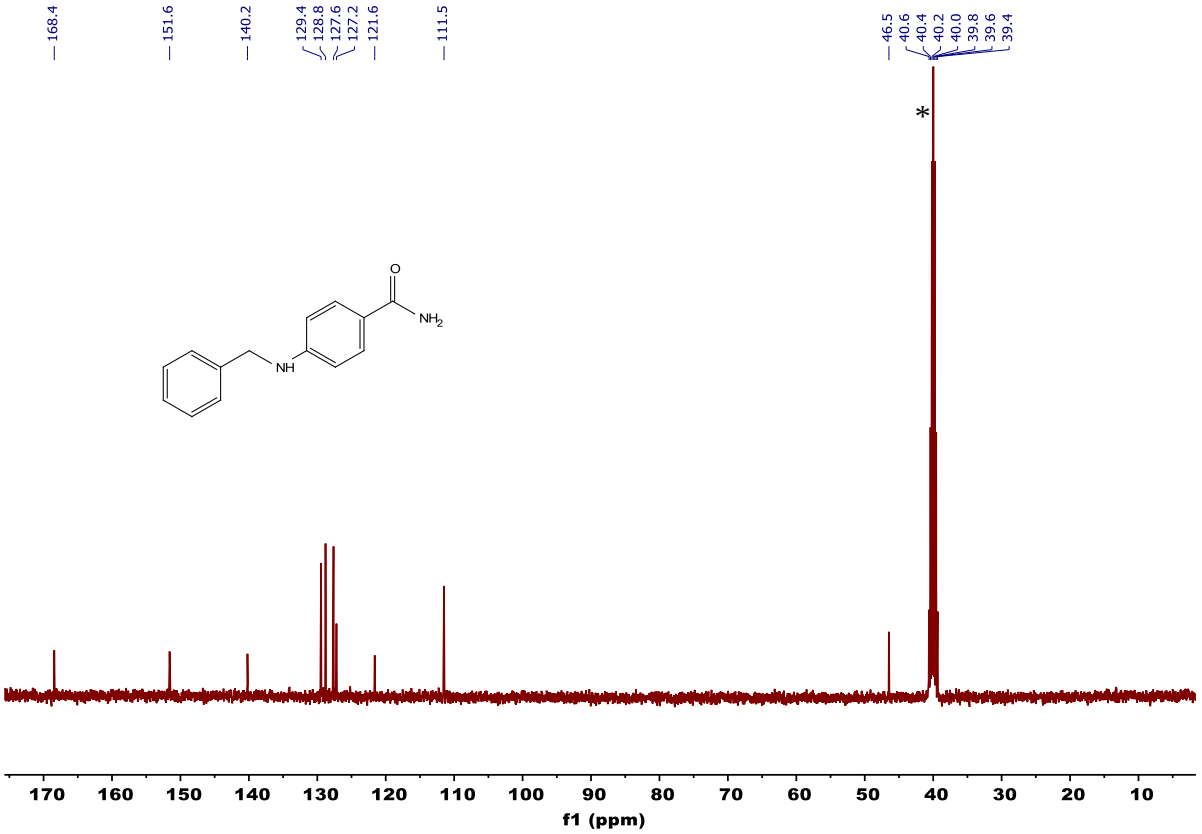

166.7
137.7
133.4
128.9
128.4
77.5
77.2
76.8
46.5
38.1
31.1
26.5
25.9
O
NH
Cl
*
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


9.47
8.44
8.41
8.11
8.09
7.93
7.91
7.89
7.63
7.61
7.59
7.45
7.44
7.42
7.34
7.32
7.26
2.49
N
N
CH3
*
1.00
2.00
1.01
2.05
1.01
1.03
1.02
3.00
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
f1 (ppm)



^{1}H and ^{13}C{^{1}H} NMR spectra of isolated compounds 6a-6i in DMSO-*d*$_6$ (*) from catalytic reactions

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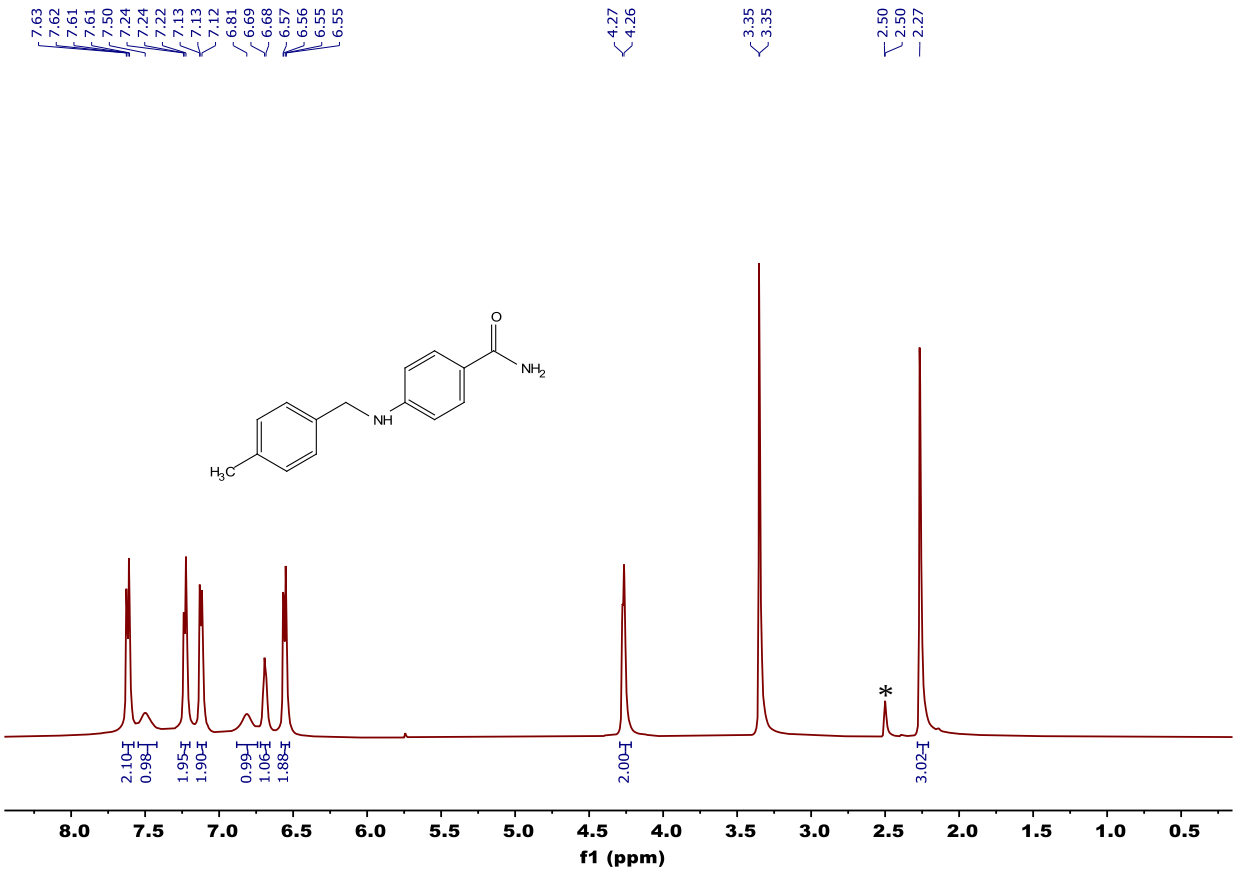
140.2
129.4
128.8
127.6
127.2
121.6
111.5
46.5
40.6
40.4
40.2
40.0
39.8
39.6
39.4
*
O
NH2
NH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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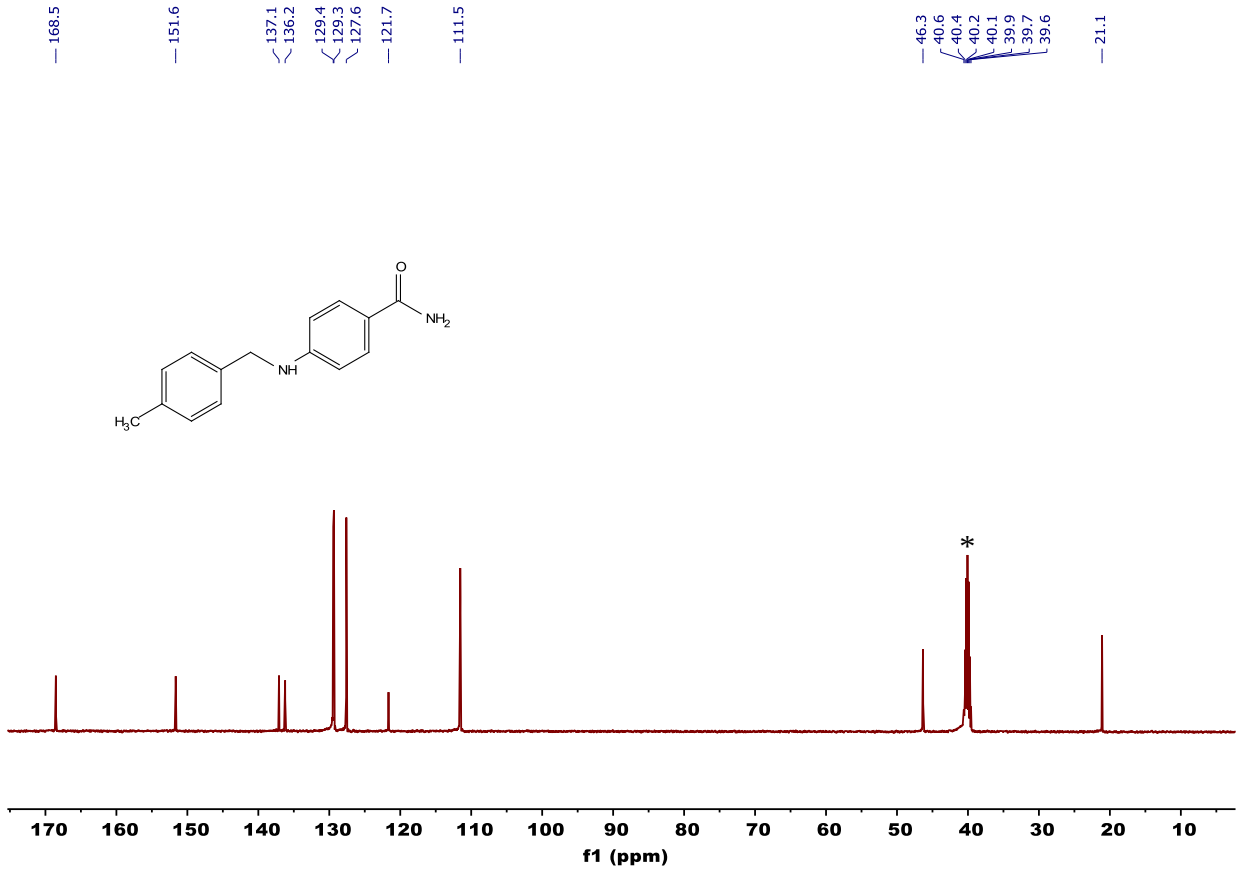
7.62
7.61
7.61
7.50
7.24
7.24
7.22
7.13
7.13
7.12
6.81
6.69
6.68
6.57
6.56
6.55
6.55
4.27
4.26
3.35
3.35
2.50
2.50
2.27
O
NH2
NH
H3C
*
2.10
0.98
1.95
1.90
0.99
1.06
1.88
2.00
3.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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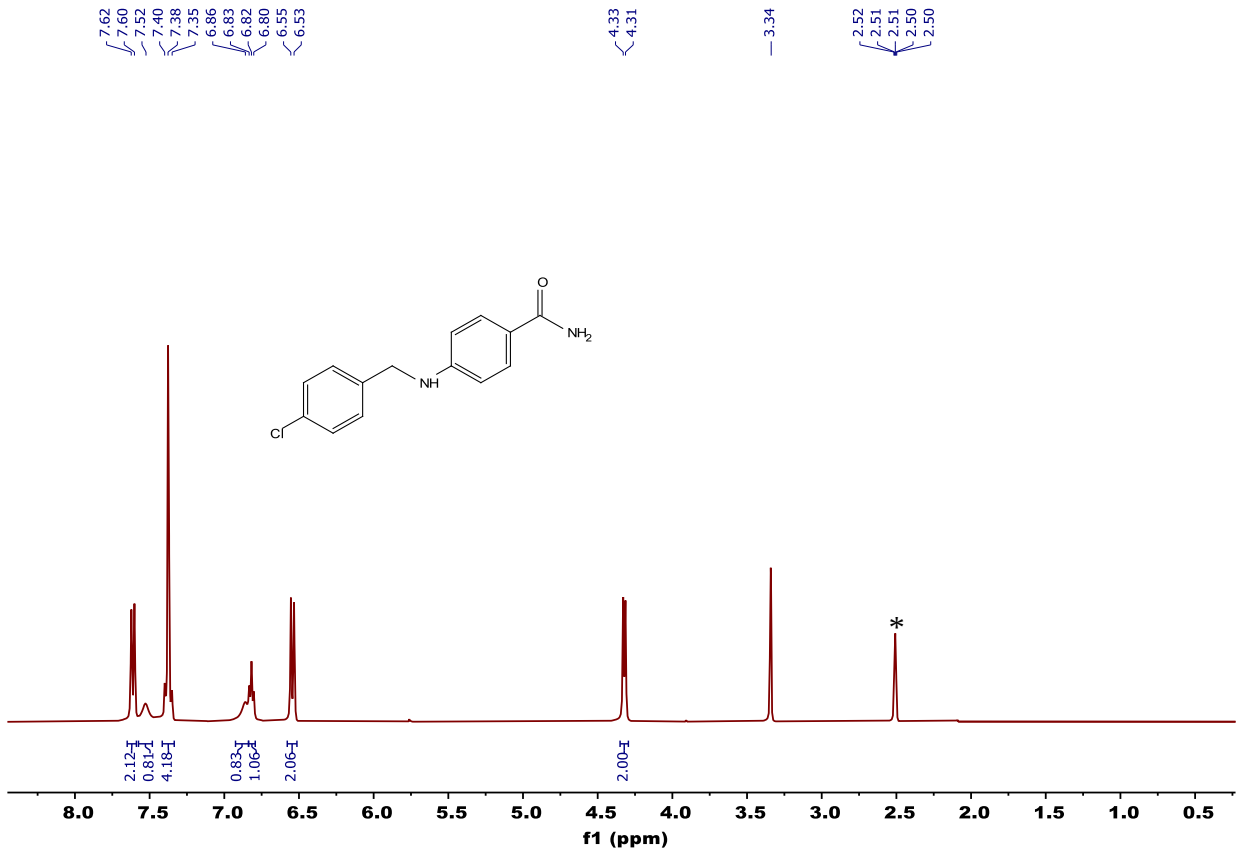
137.1
136.2
129.4
129.3
127.6
121.7
111.5
46.3
40.6
40.4
40.2
40.1
39.9
39.7
39.6
21.1
O
NH2
NH
H3C
*
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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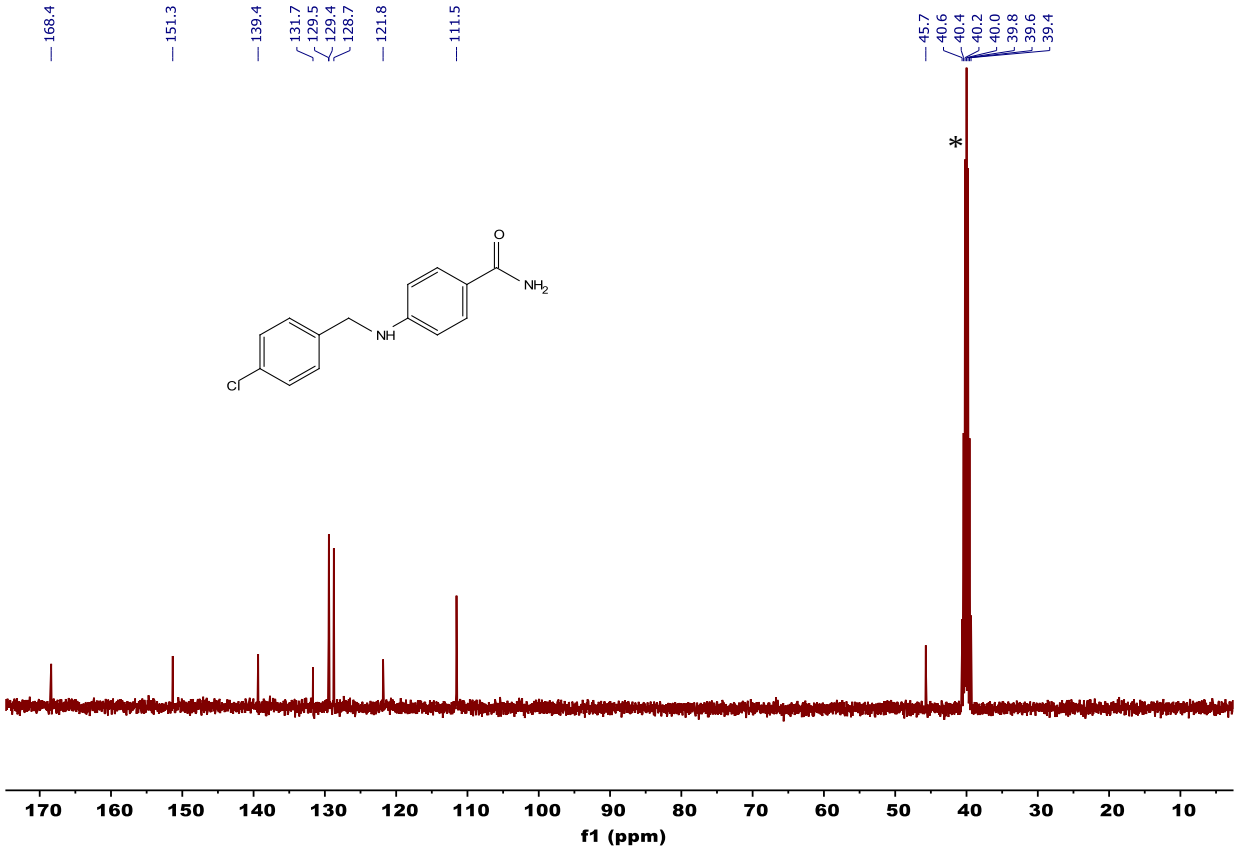
7.60
7.52
7.40
7.38
7.35
6.86
6.83
6.82
6.80
6.55
6.53
4.33
4.31
3.34
2.52
2.51
2.51
2.50
2.50
O
NH2
NH
Cl
*
2.12
0.81
4.18
0.83
1.06
2.06
2.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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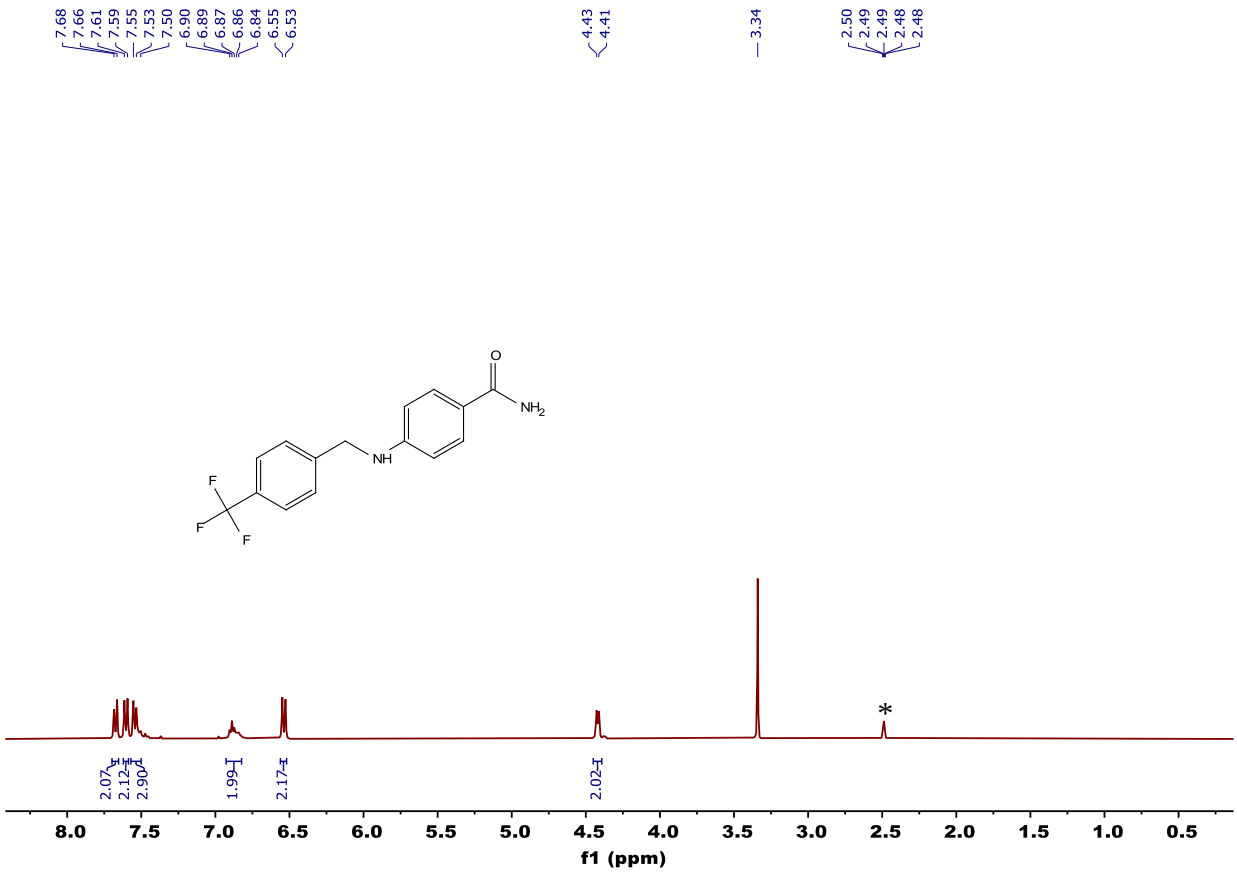
151.3
139.4
131.7
129.5
129.4
128.7
121.8
111.5
45.7
40.6
40.4
40.2
40.0
39.8
39.6
39.4
*
O
NH2
NH
Cl
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.66
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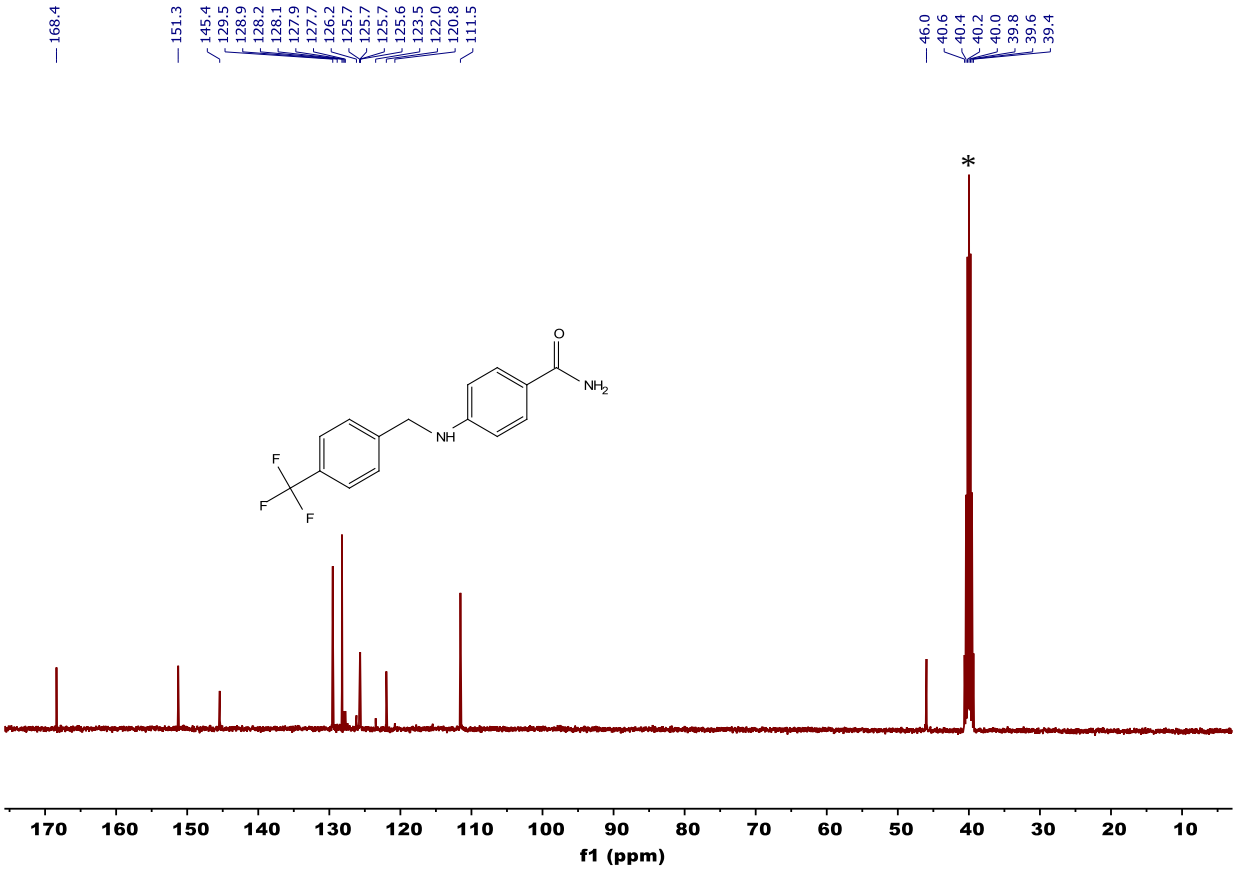
7.55
7.53
7.50
6.90
6.89
6.87
6.86
6.84
6.55
6.53
4.43
4.41
3.34
2.50
2.49
2.49
2.48
2.48
O
NH2
NH
F
F
F
*
2.07
2.12
2.90
1.99
2.17
2.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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145.4
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127.9
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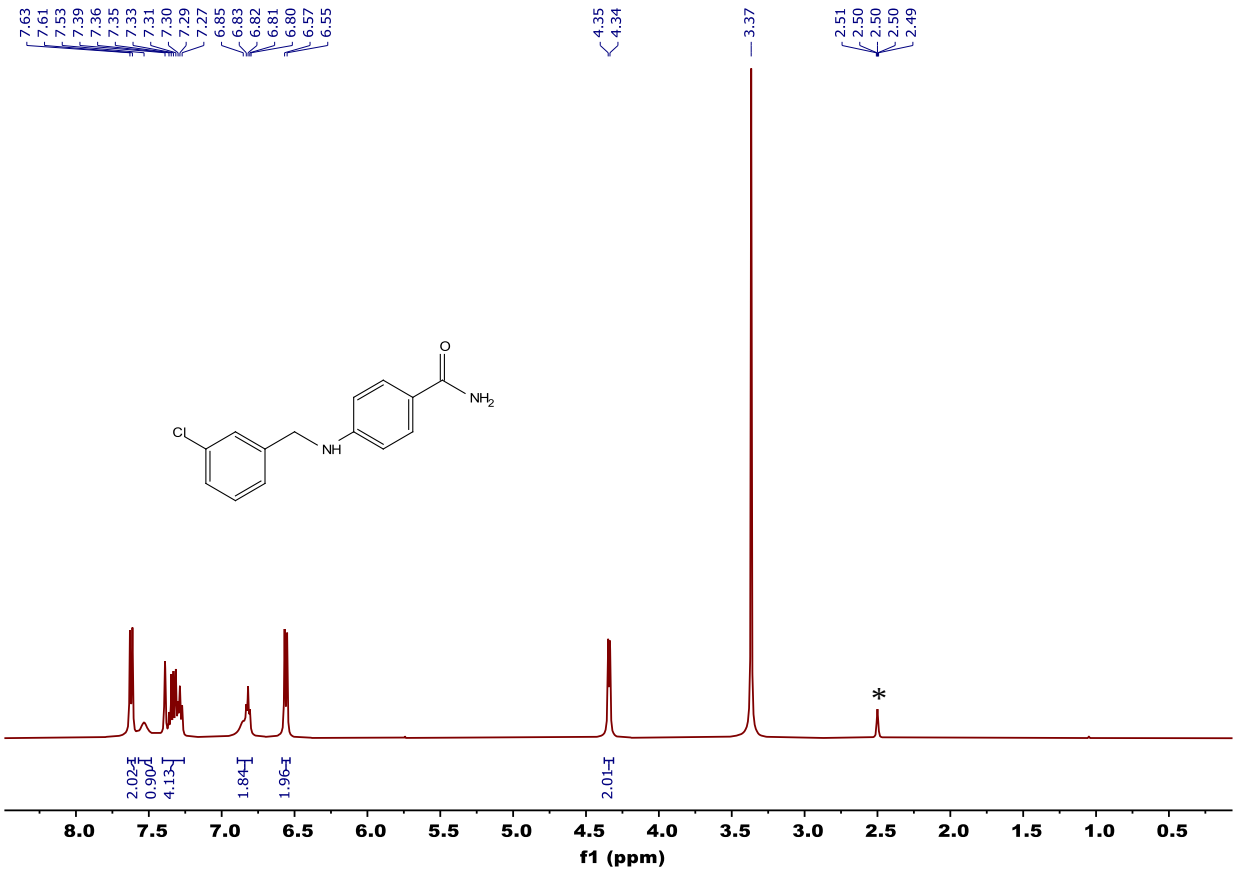
126.2
125.7
125.7
125.7
125.6
123.5
122.0
120.8
111.5
46.0
40.6
40.4
40.2
40.0
39.8
39.6
39.4
*
O
NH2
NH
F
F
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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6.83
6.82
6.81
6.80
6.57
6.55
4.35
4.34
3.37
2.51
2.50
2.50
2.50
2.49
*
O
NH2
Cl
NH
2.02
0.90
4.13
1.84
1.96
2.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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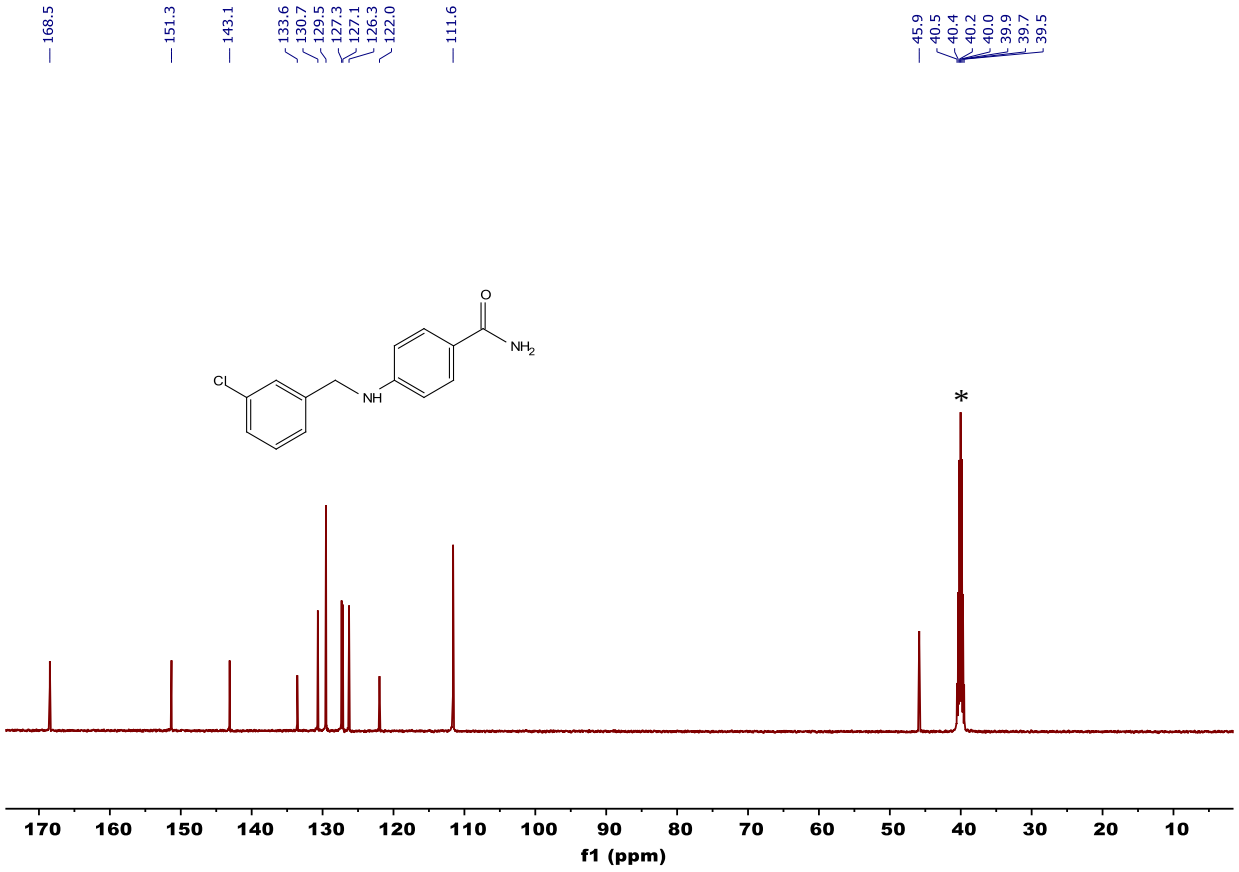
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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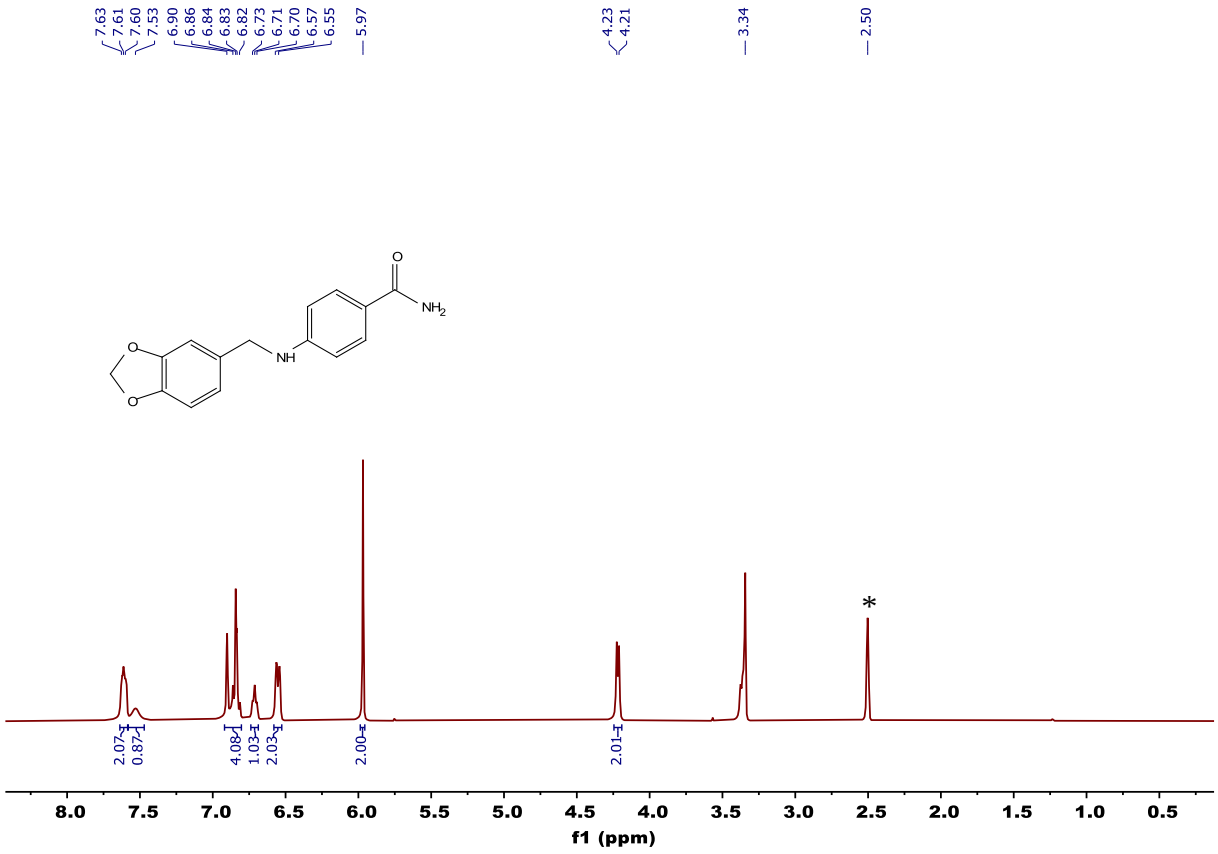
45.9
40.5
40.4
40.2
40.0
39.9
39.7
39.5
O
NH2
Cl
NH
*
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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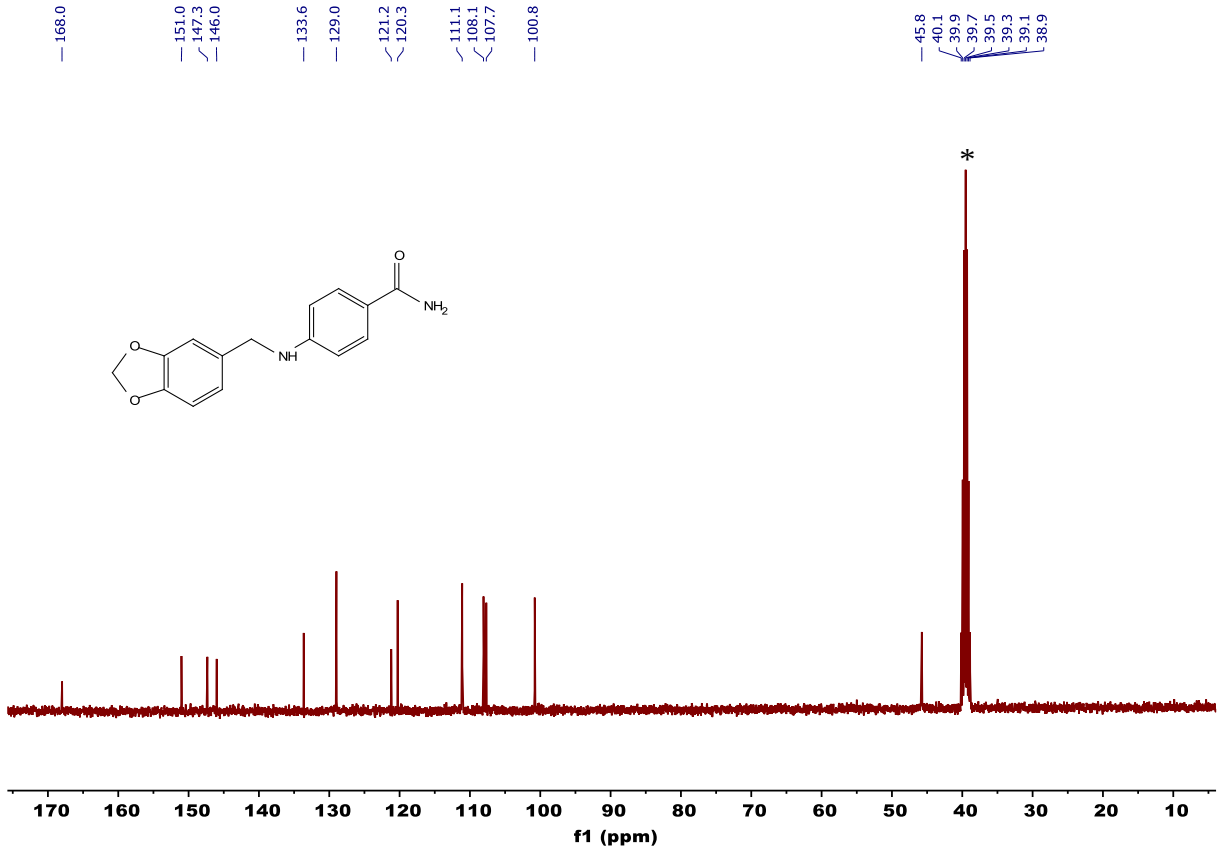
6.57
6.55
5.97
4.23
4.21
3.34
2.50
O
NH2
O
O
NH
*
2.07
0.87
4.08
1.03
2.03
2.00
2.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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121.2
120.3
111.1
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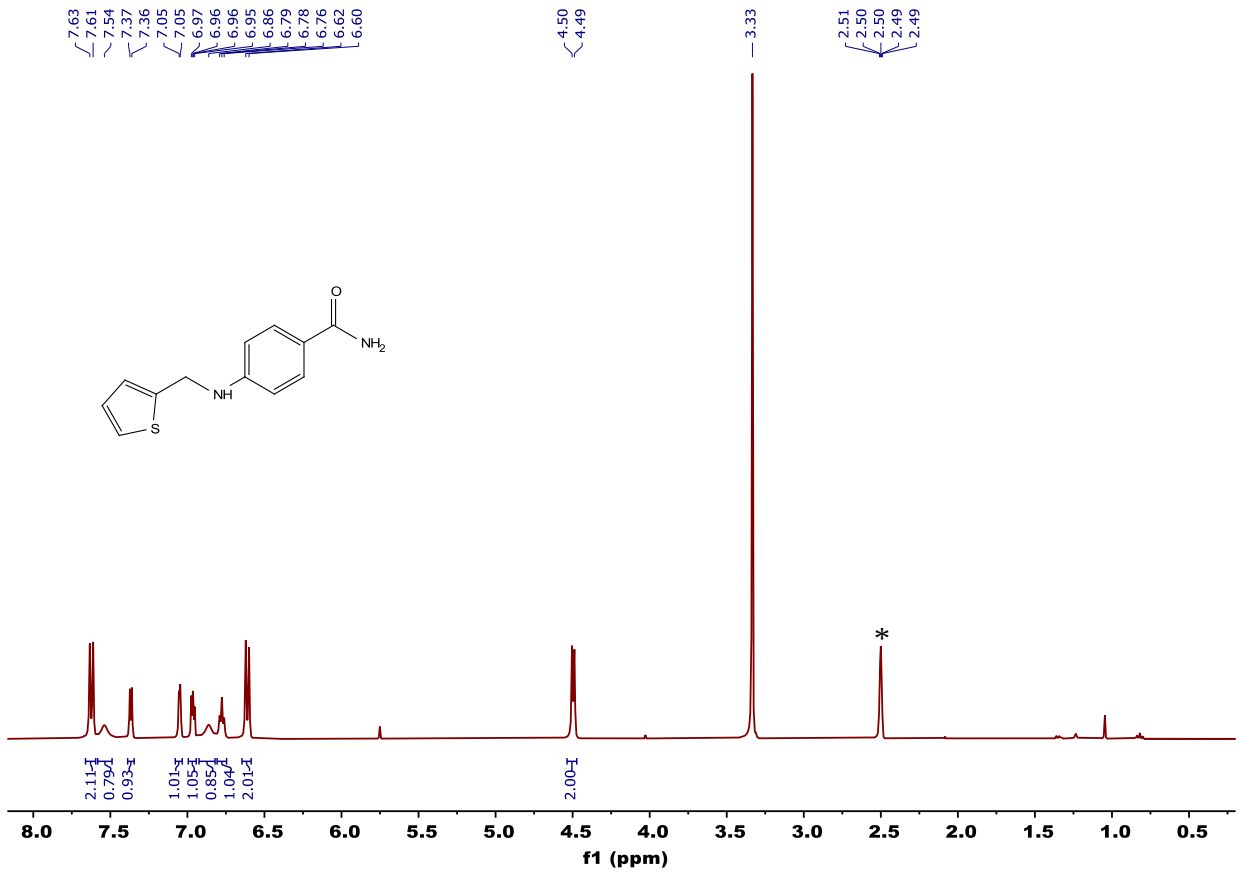
107.7
100.8
45.8
40.1
39.9
39.7
39.5
39.3
39.1
38.9
*
O
NH2
NH
O
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.05
6.97
6.96
6.96
6.95
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6.78
6.76
6.62
6.60
4.50
4.49
3.33
2.51
2.50
2.50
2.49
2.49
*
O
NH2
NH
S
2.11
0.79
0.93
1.01
1.05
0.85
1.04
2.01
2.00
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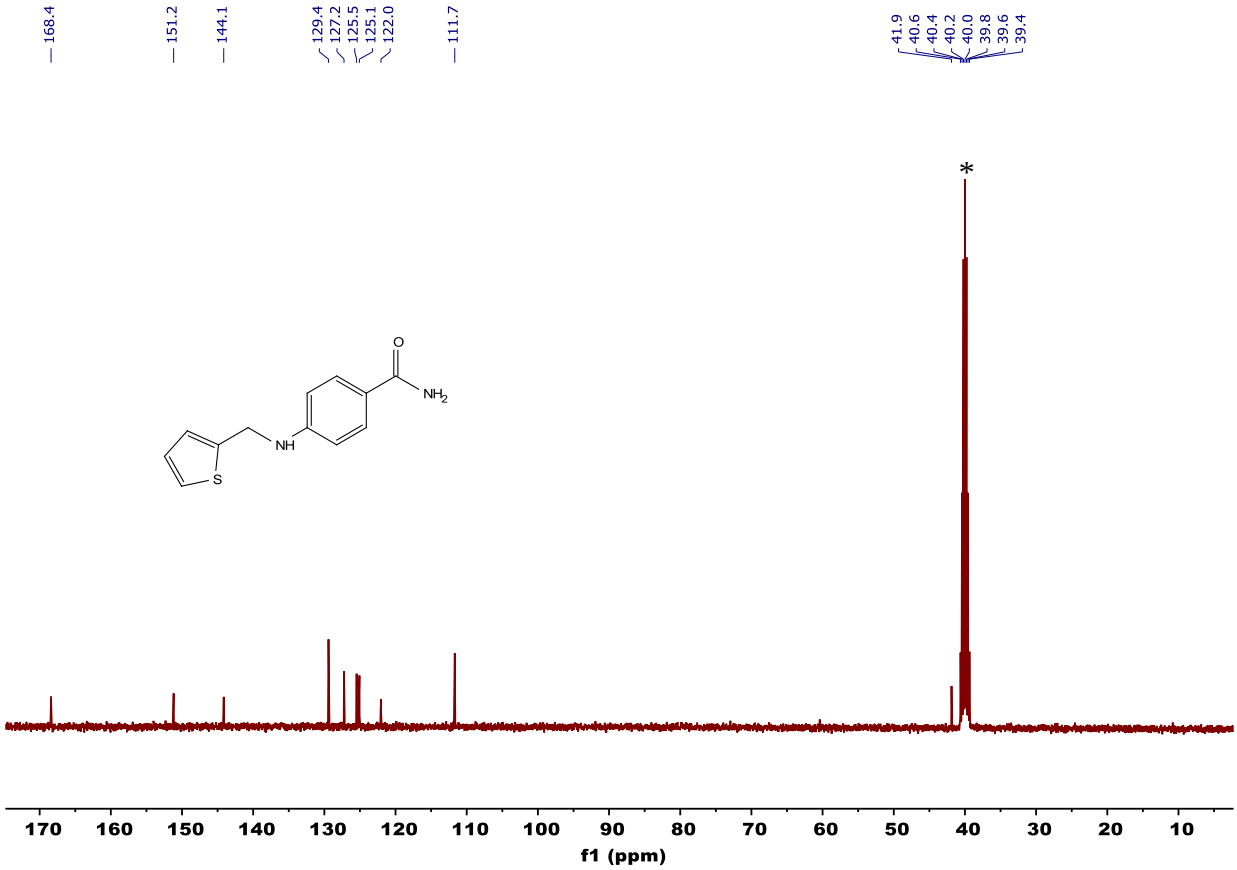
f1 (ppm)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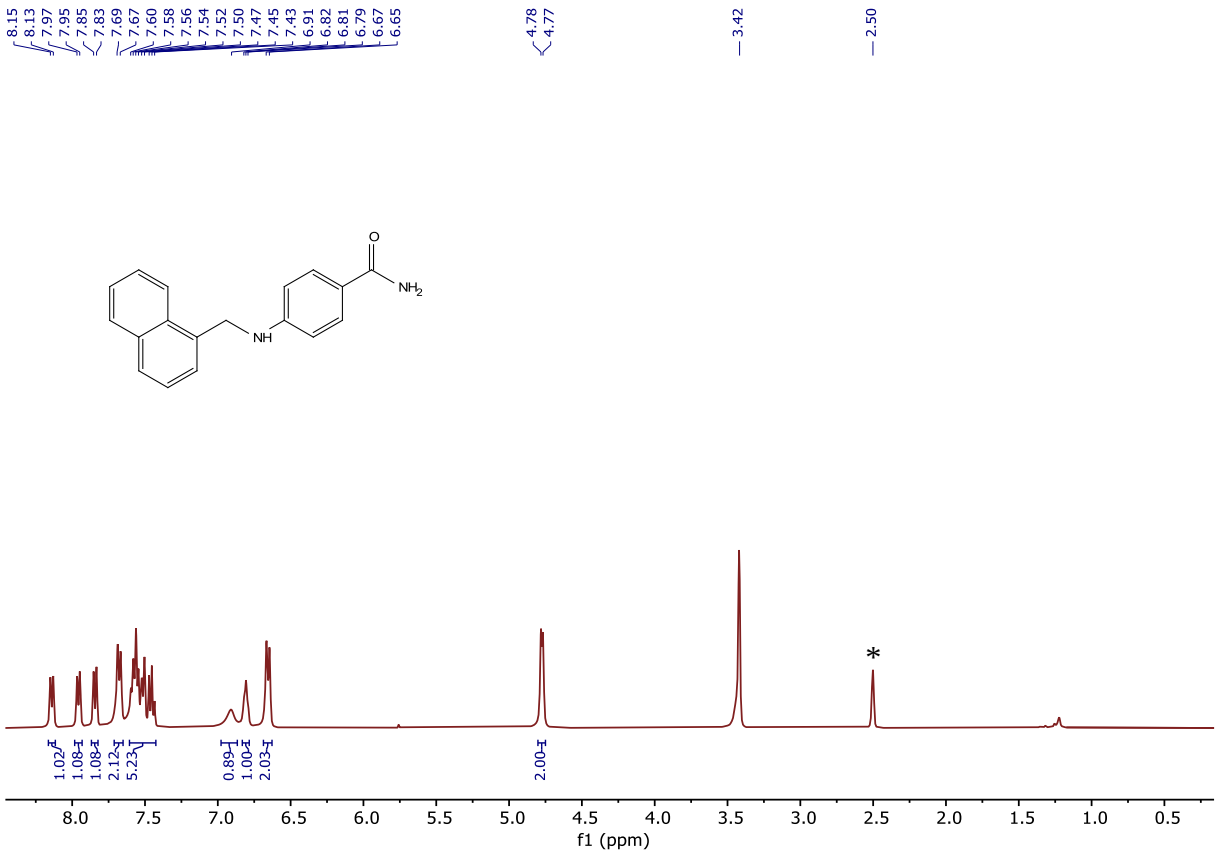
125.1
122.0
111.7
41.9
40.6
40.4
40.2
40.0
39.8
39.6
39.4
*
O
NH2
NH
S
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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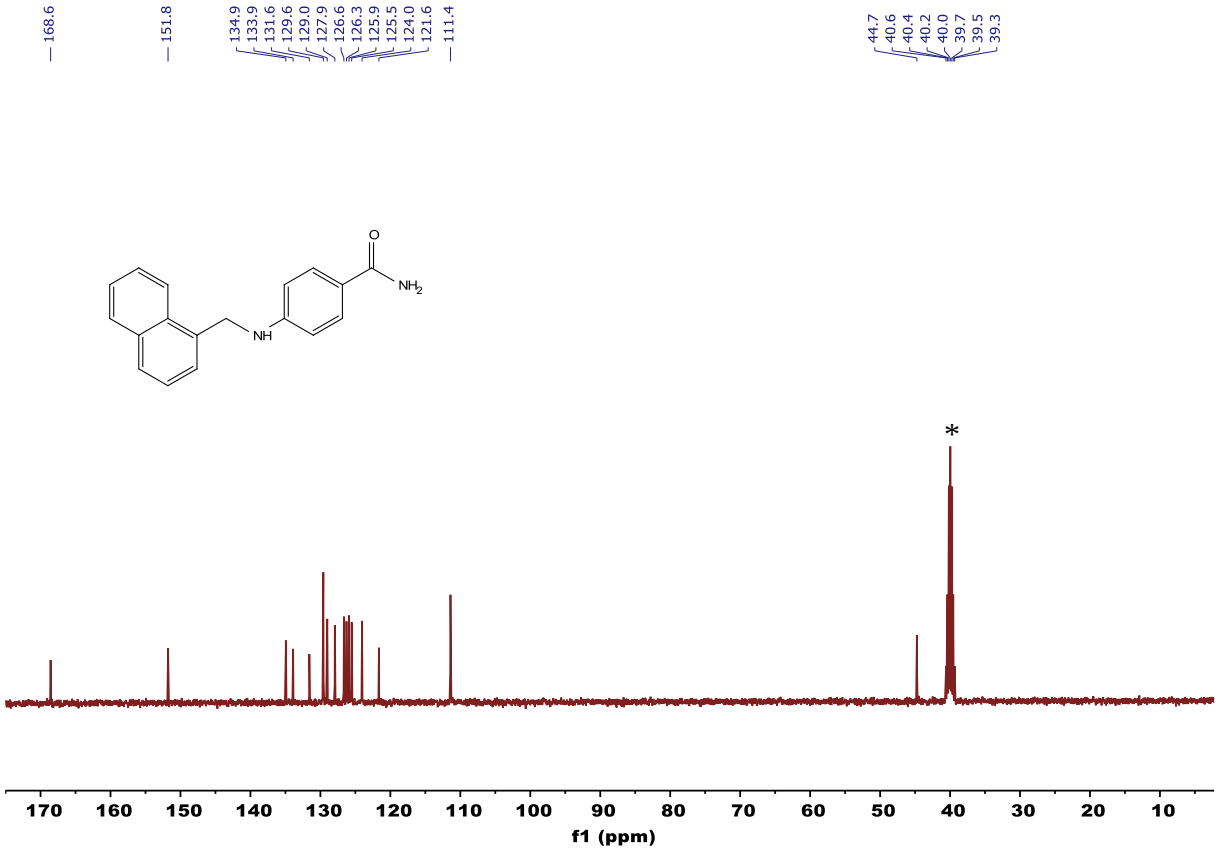
7.52
7.50
7.47
7.45
7.43
6.91
6.82
6.81
6.79
6.67
6.65
4.78
4.77
3.42
2.50
O
NH2
NH
*
1.02
1.08
1.08
2.12
5.23
0.89
1.00
2.03
2.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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126.3
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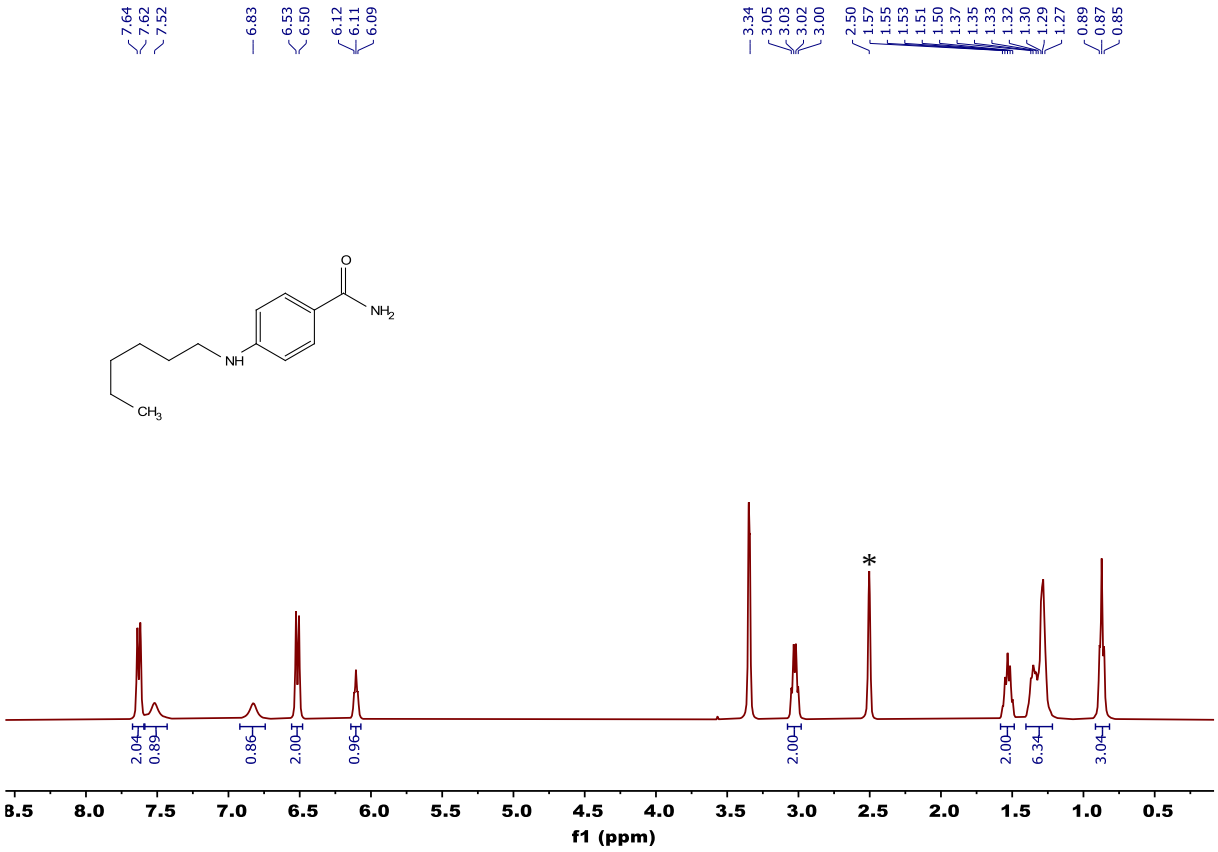
125.5
124.0
121.6
111.4
44.7
40.6
40.4
40.2
40.0
39.7
39.5
39.3
O
NH2
NH
*
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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6.83
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6.50
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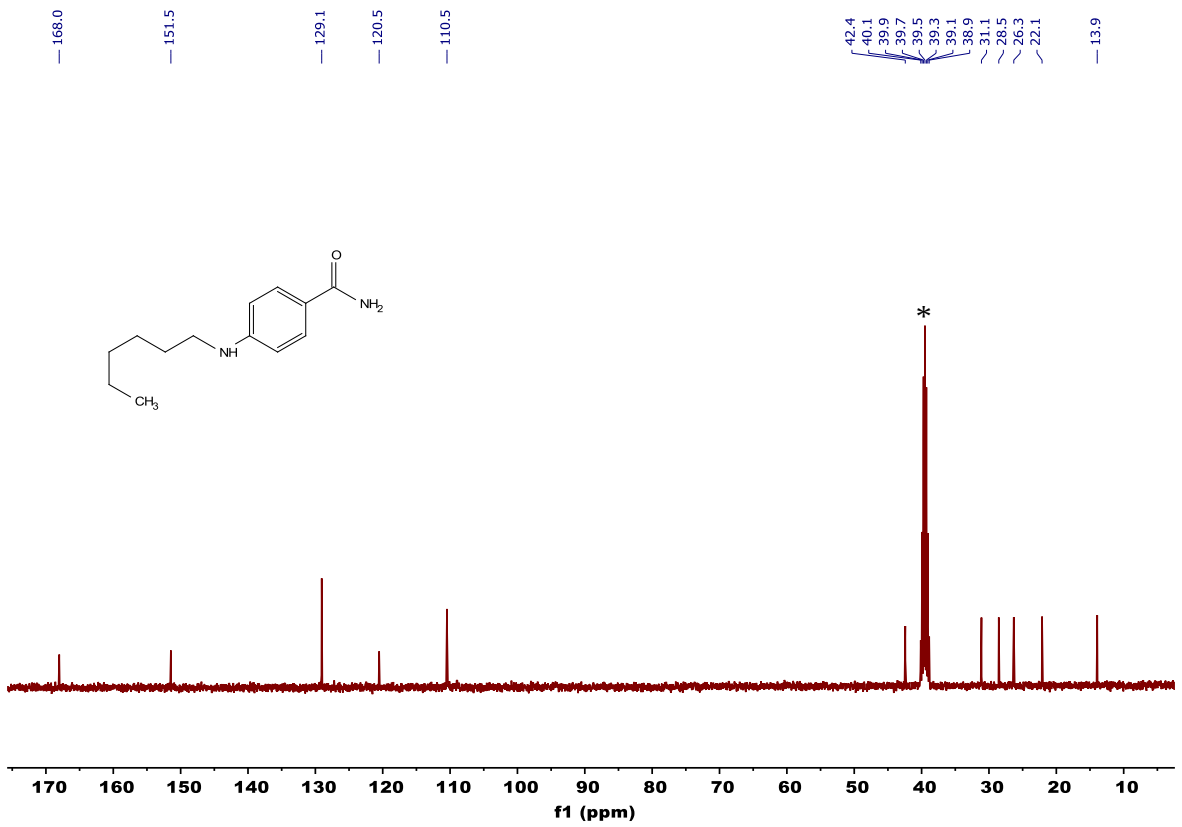
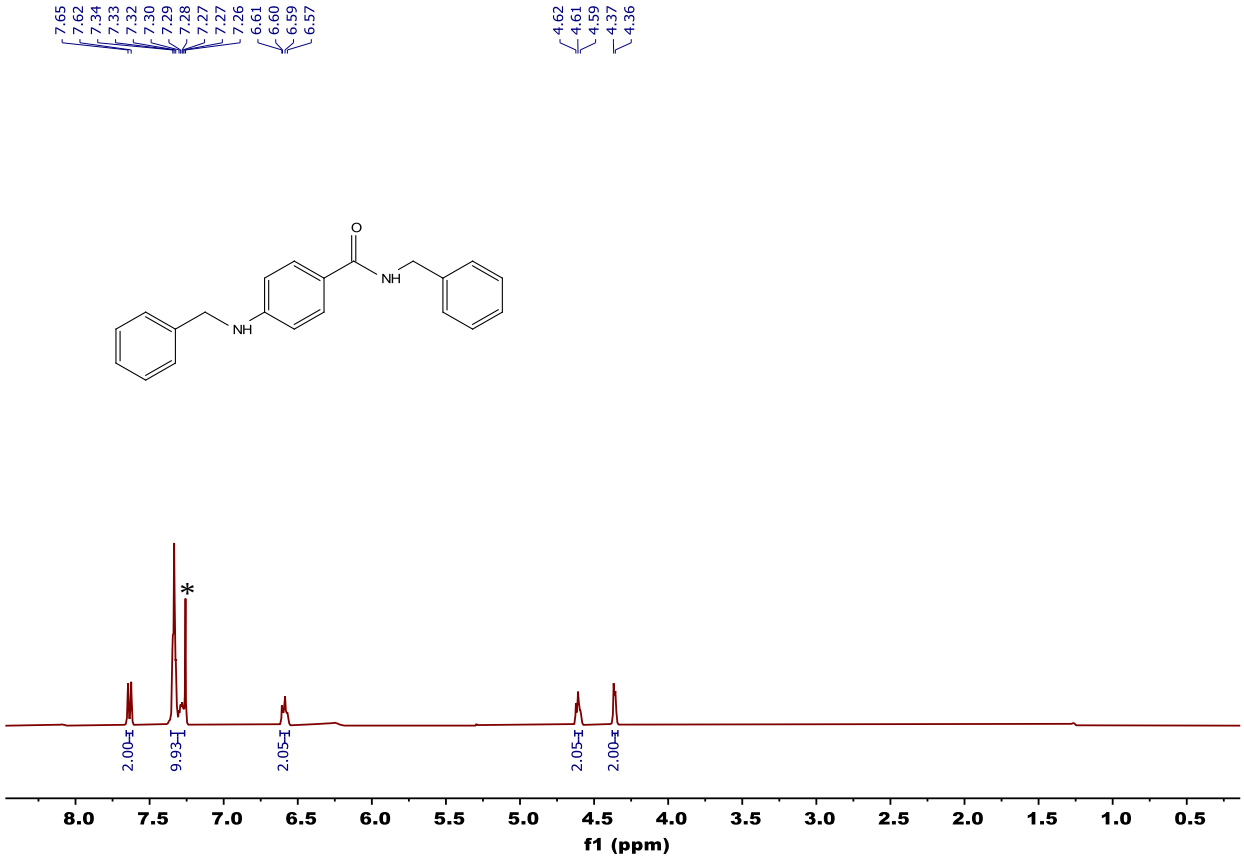
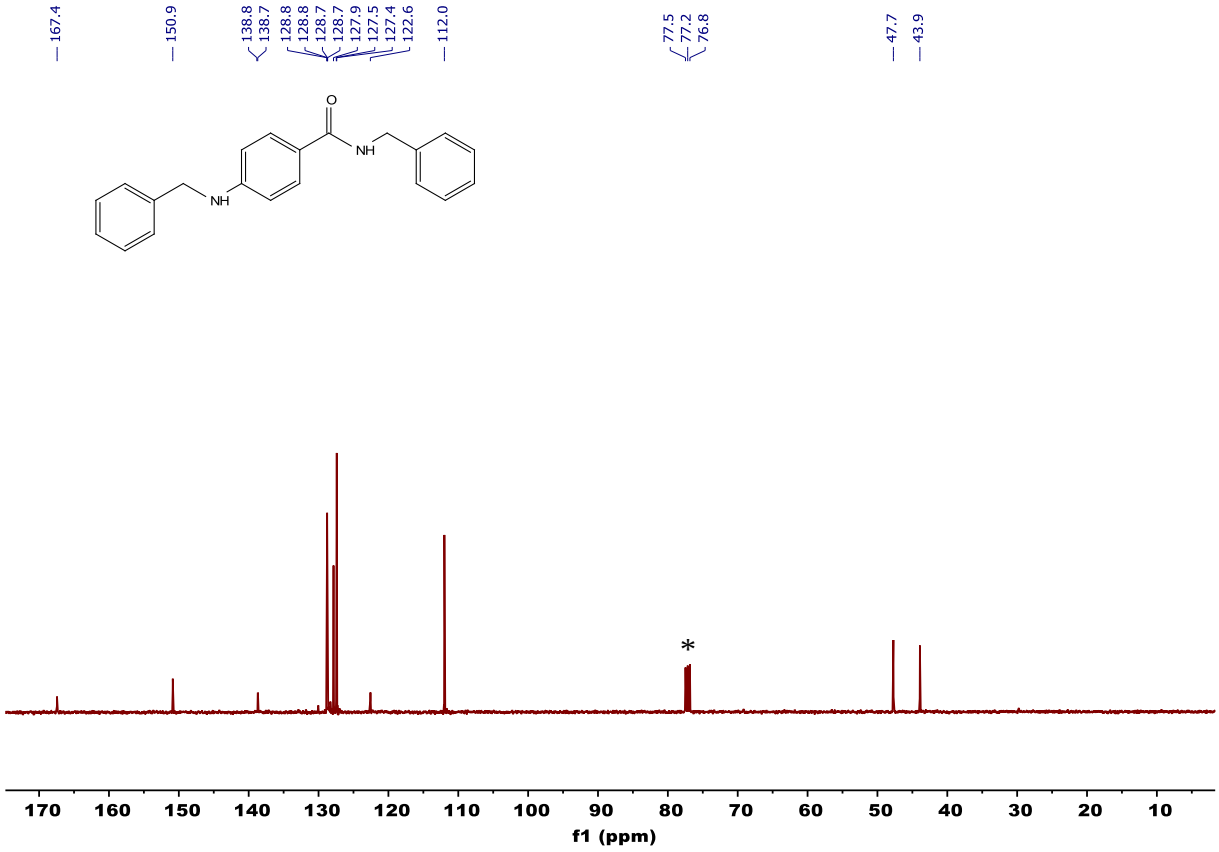
6.11
6.09
3.34
3.05
3.03
3.02
3.00
2.50
1.57
1.55
1.53
1.51
1.50
1.37
1.35
1.33
1.32
1.30
1.29
1.27
0.89
0.87
0.85
O
NH2
NH
CH3
*
2.04
0.89
0.86
2.00
0.96
2.00
2.00
6.34
3.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



^{1}H and ^{13}C{^{1}H} NMR spectra of isolated compounds 7a-7n in $CDCl_3$ (*) from catalytic reactions

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138.7
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128.8
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128.7
127.9
127.5
127.4
122.6
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77.5
77.2
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47.7
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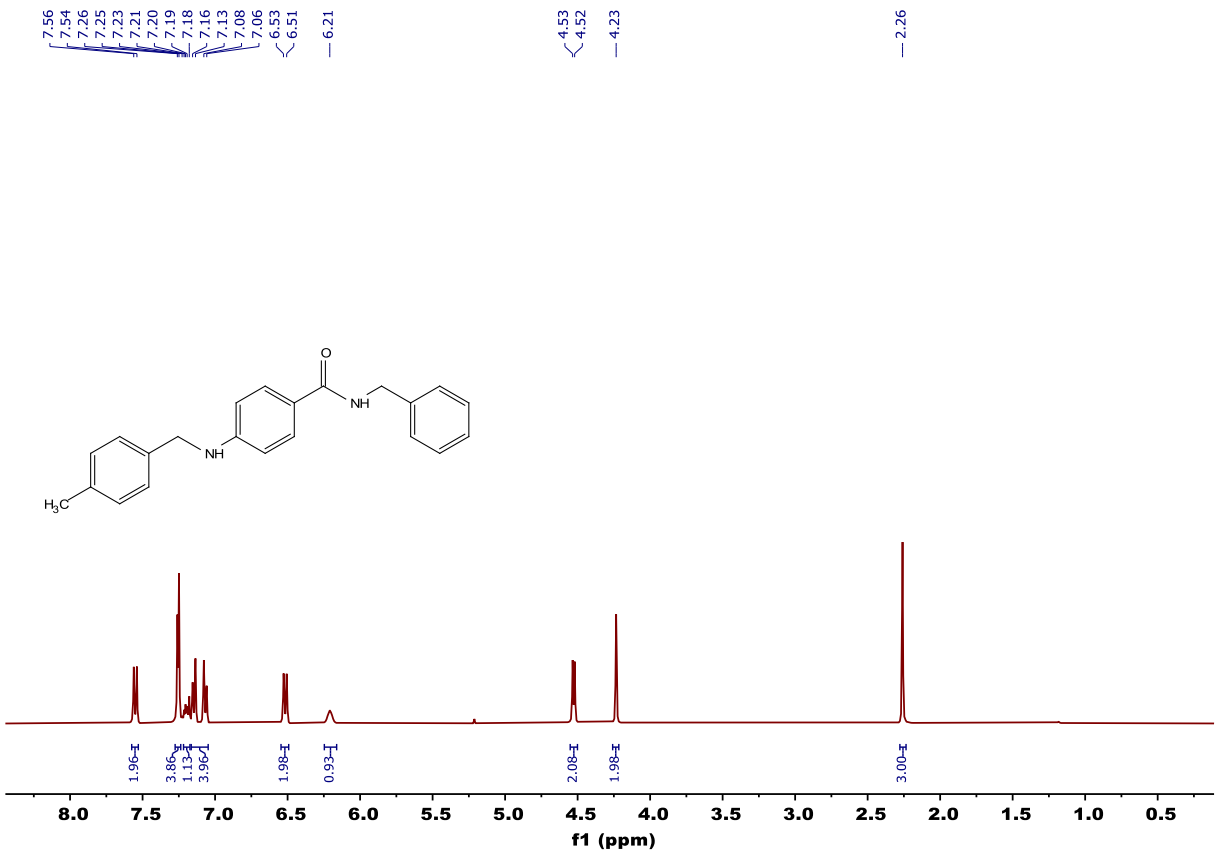
NH
*
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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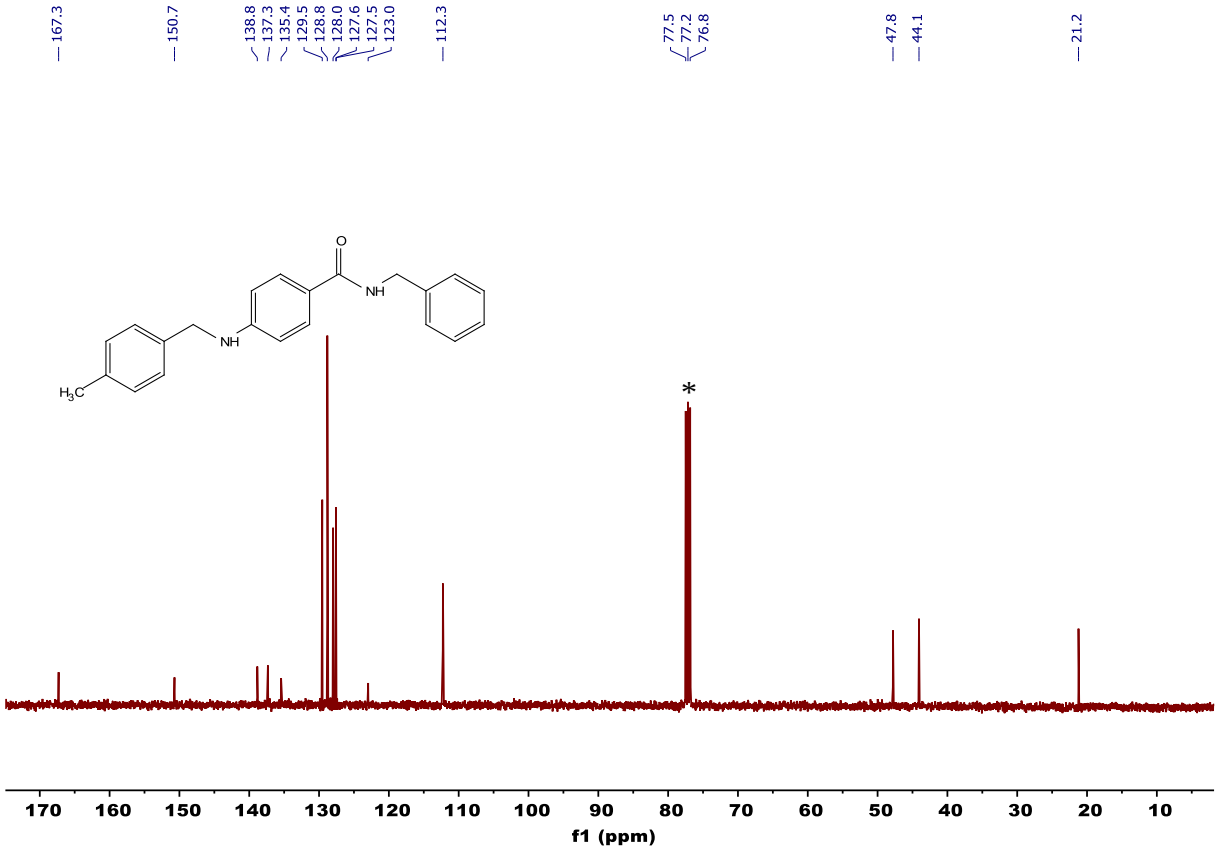
7.06
6.53
6.51
6.21
4.53
4.52
4.23
2.26
O
NH
NH
H3C
1.96
3.86
1.13
3.96
1.98
0.93
2.08
1.98
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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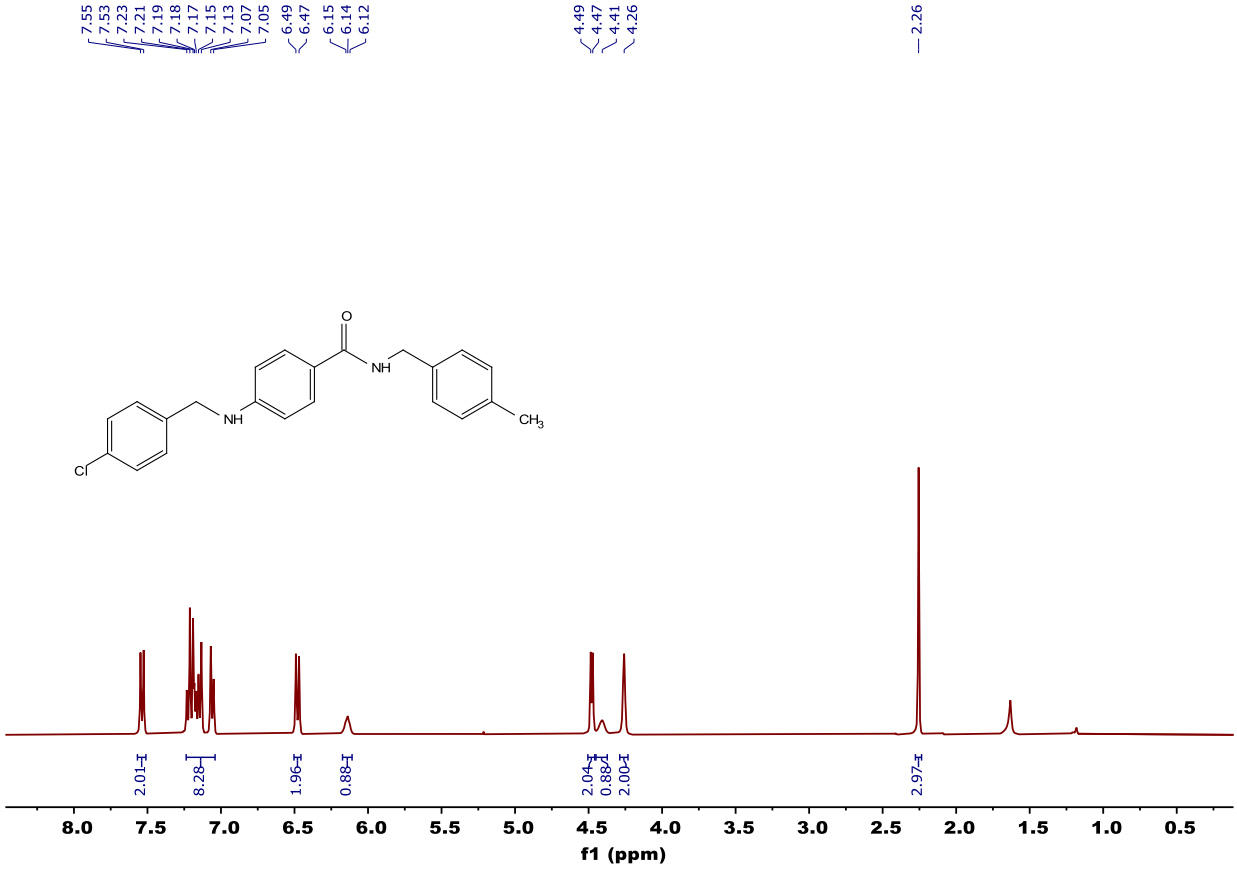
127.5
123.0
112.3
77.5
77.2
76.8
47.8
44.1
21.2
O
NH
NH
H3C
*
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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6.15
6.14
6.12
4.49
4.47
4.41
4.26
2.26
O
NH
NH
CH3
Cl
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8.28
1.96
0.88
2.04
0.88
2.00
2.97
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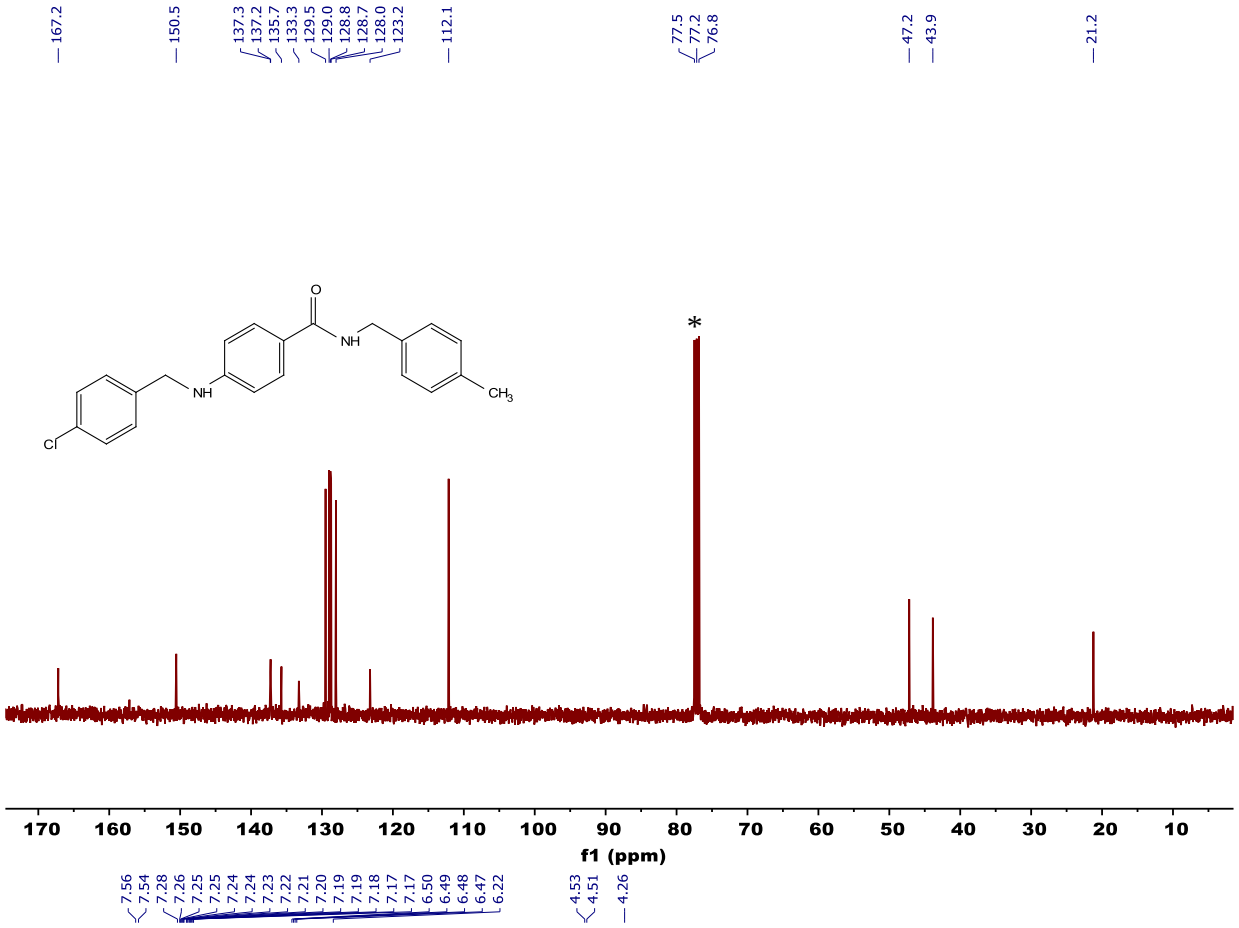
f1 (ppm)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129.0
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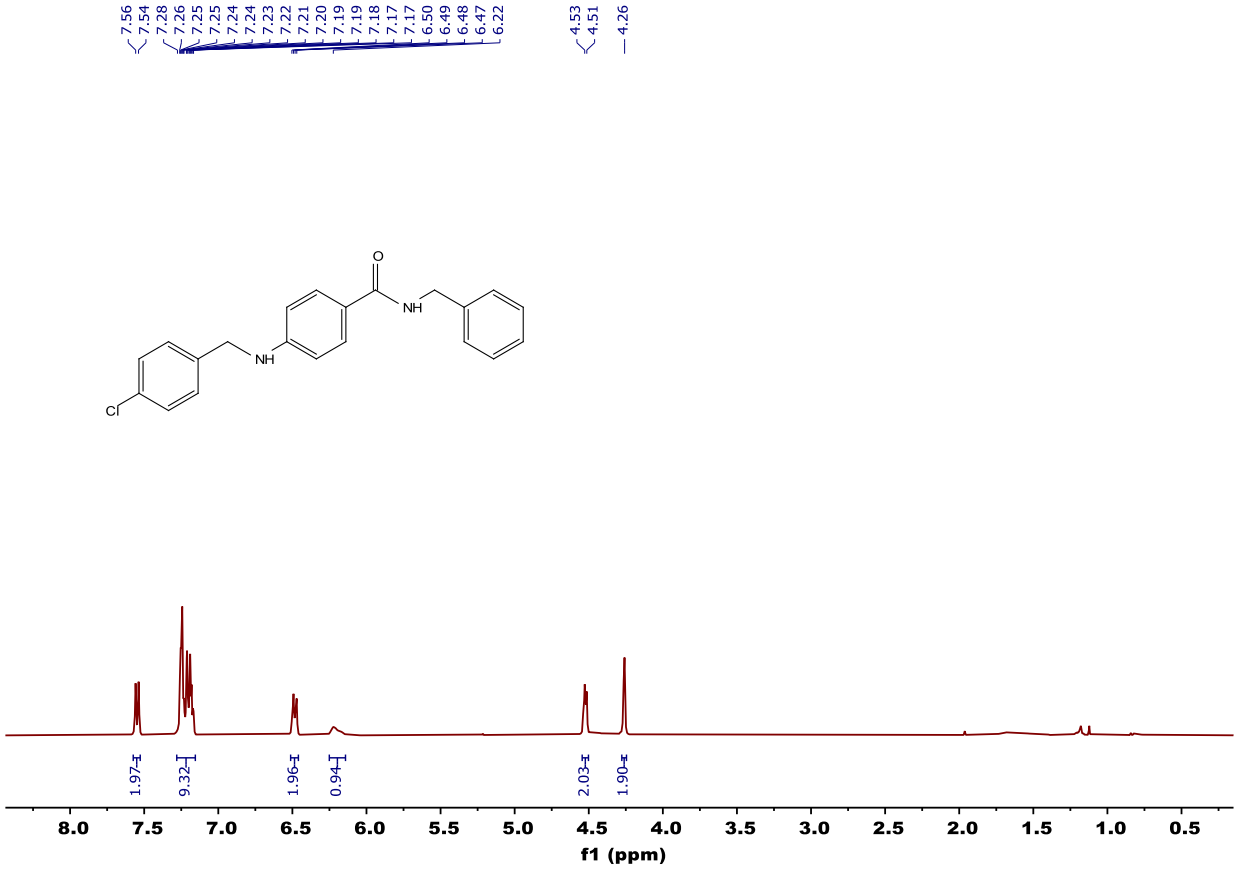
128.7
128.0
123.2
112.1
77.5
77.2
76.8
47.2
43.9
21.2
O
NH
NH
CH3
Cl
*
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.18
7.17
7.17
6.50
6.49
6.48
6.47
6.22
4.53
4.51
4.26
O
NH
NH
Cl
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1.96
0.94
2.03
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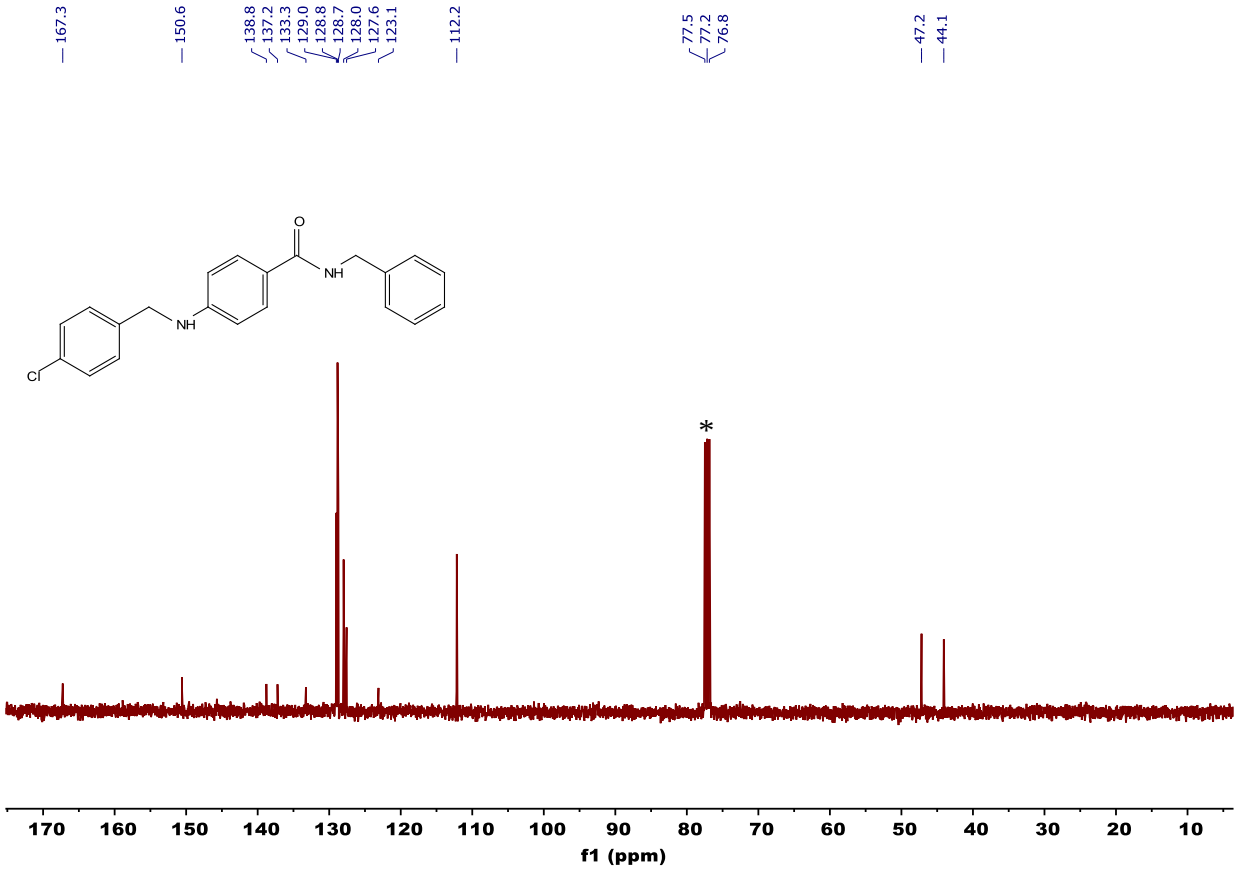
f1 (ppm)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128.0
127.6
123.1
112.2
77.5
77.2
76.8
47.2
44.1
O
NH
NH
Cl
*
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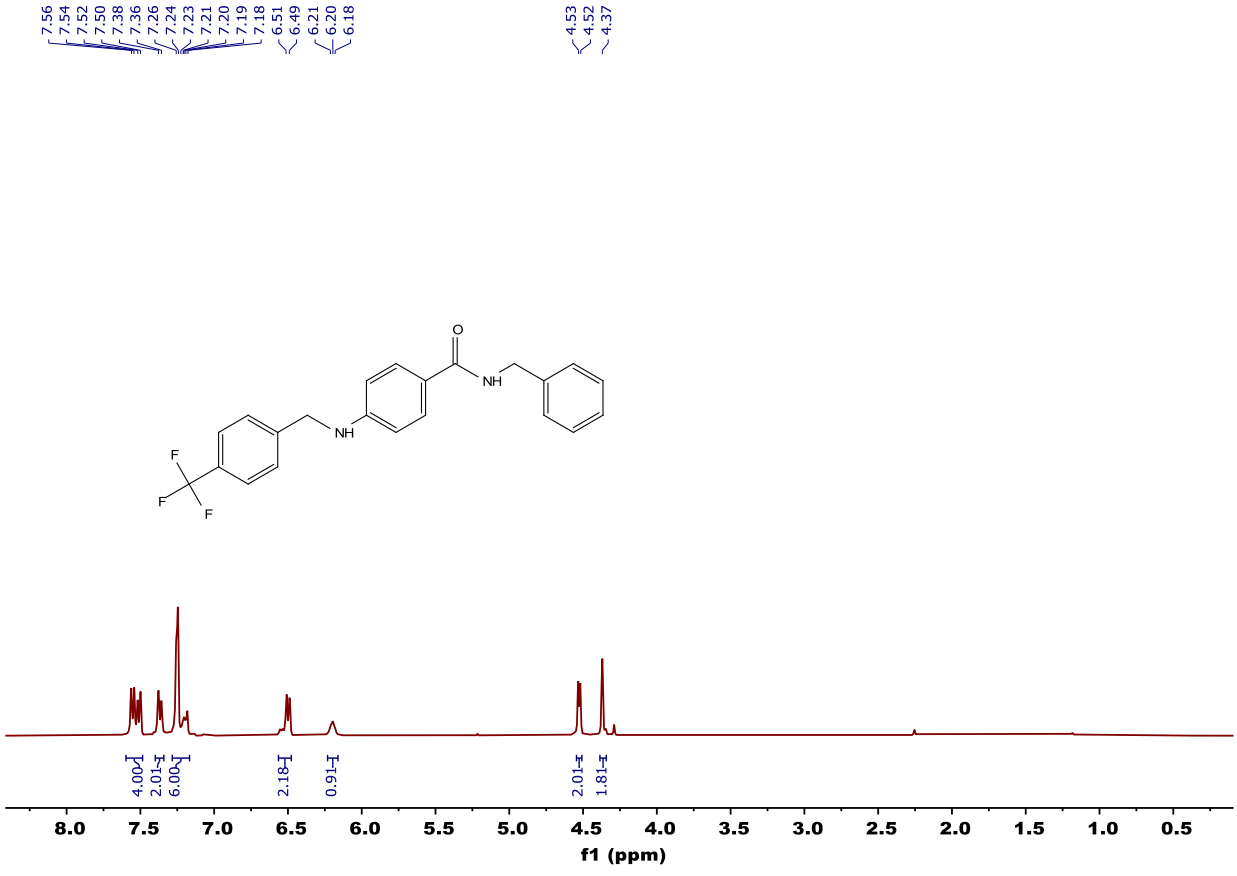
f1 (ppm)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7.18
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6.49
6.21
6.20
6.18
4.53
4.52
4.37
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NH
NH
F
F
F
4.00
2.01
6.00
2.18
0.91
2.01
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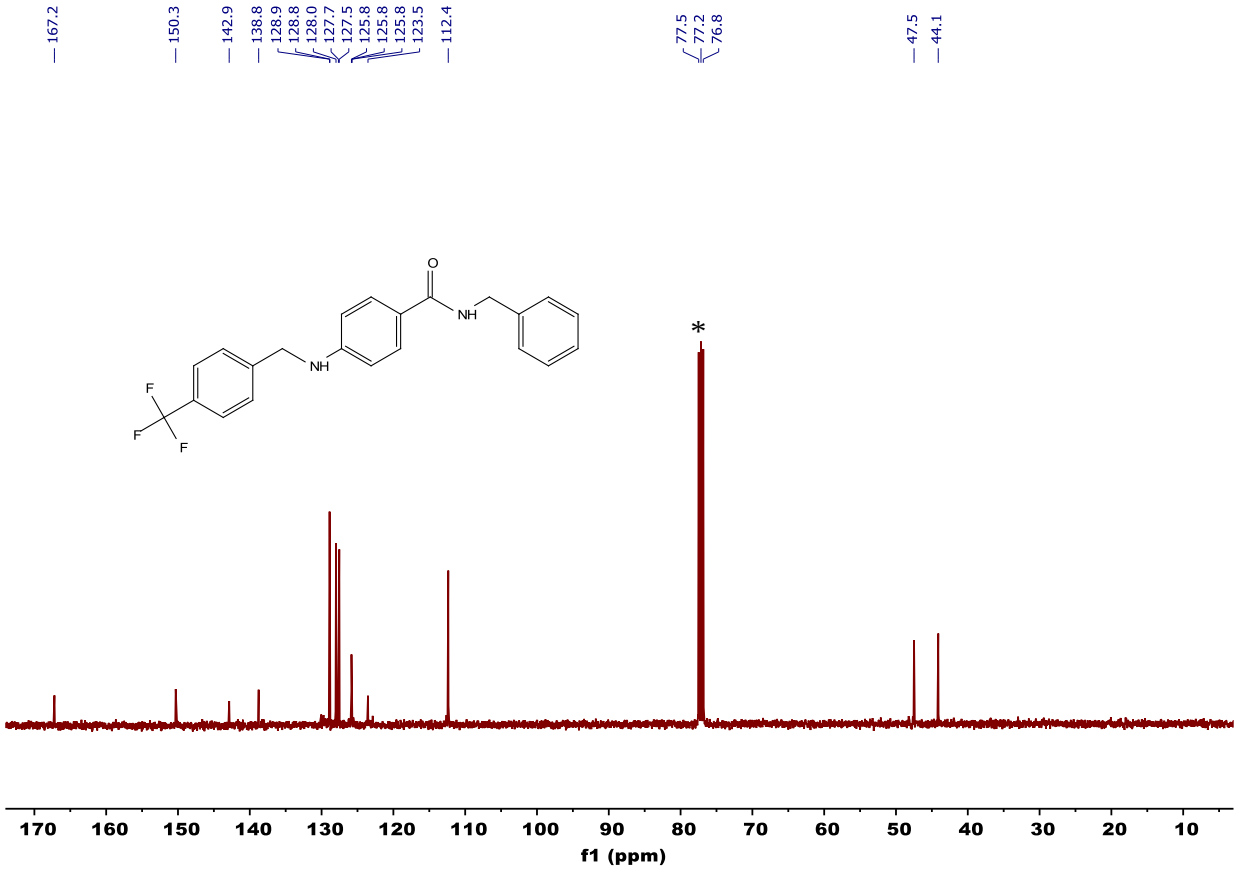
f1 (ppm)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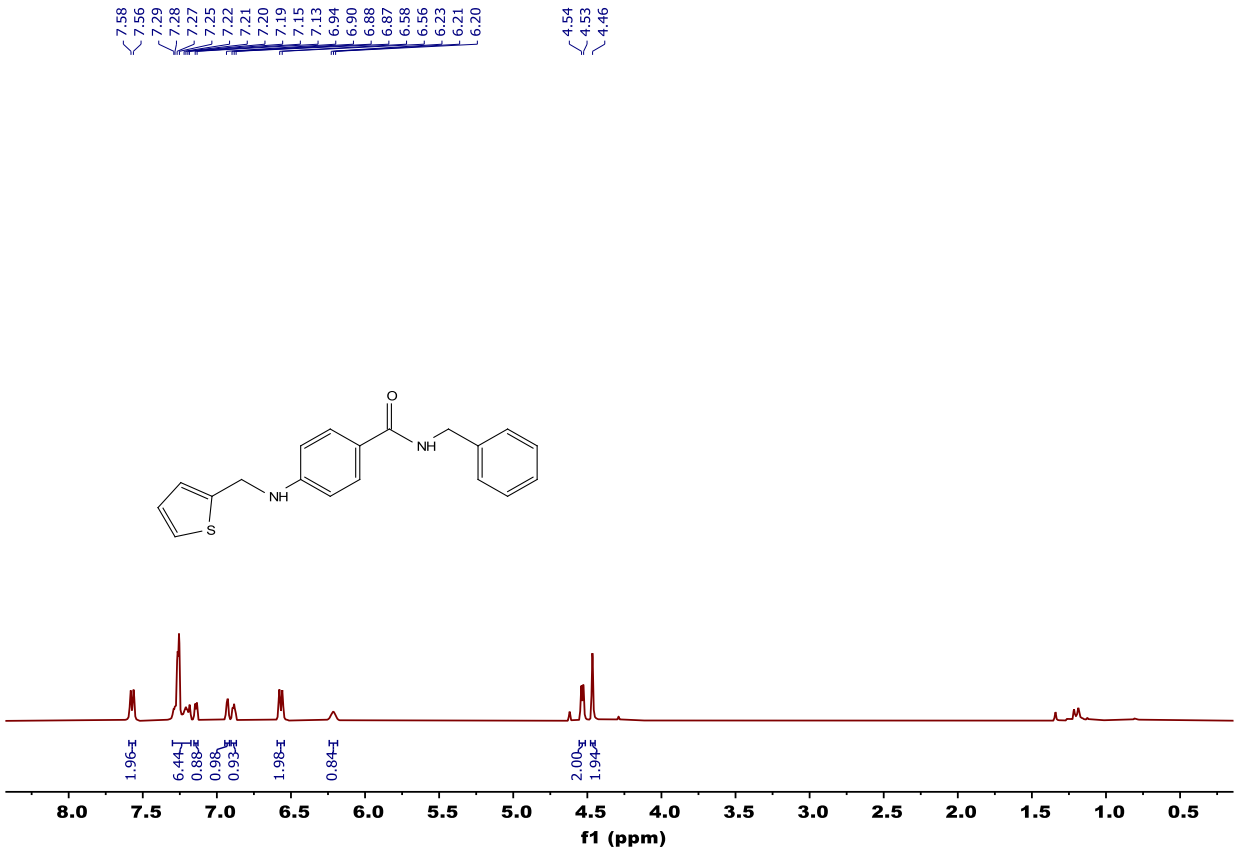
125.8
123.5
112.4
77.5
77.2
76.8
47.5
44.1
O
NH
NH
F
F
F
*
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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6.21
6.20
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4.53
4.46
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NH
S
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0.98
0.93
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7.0
6.5
6.0
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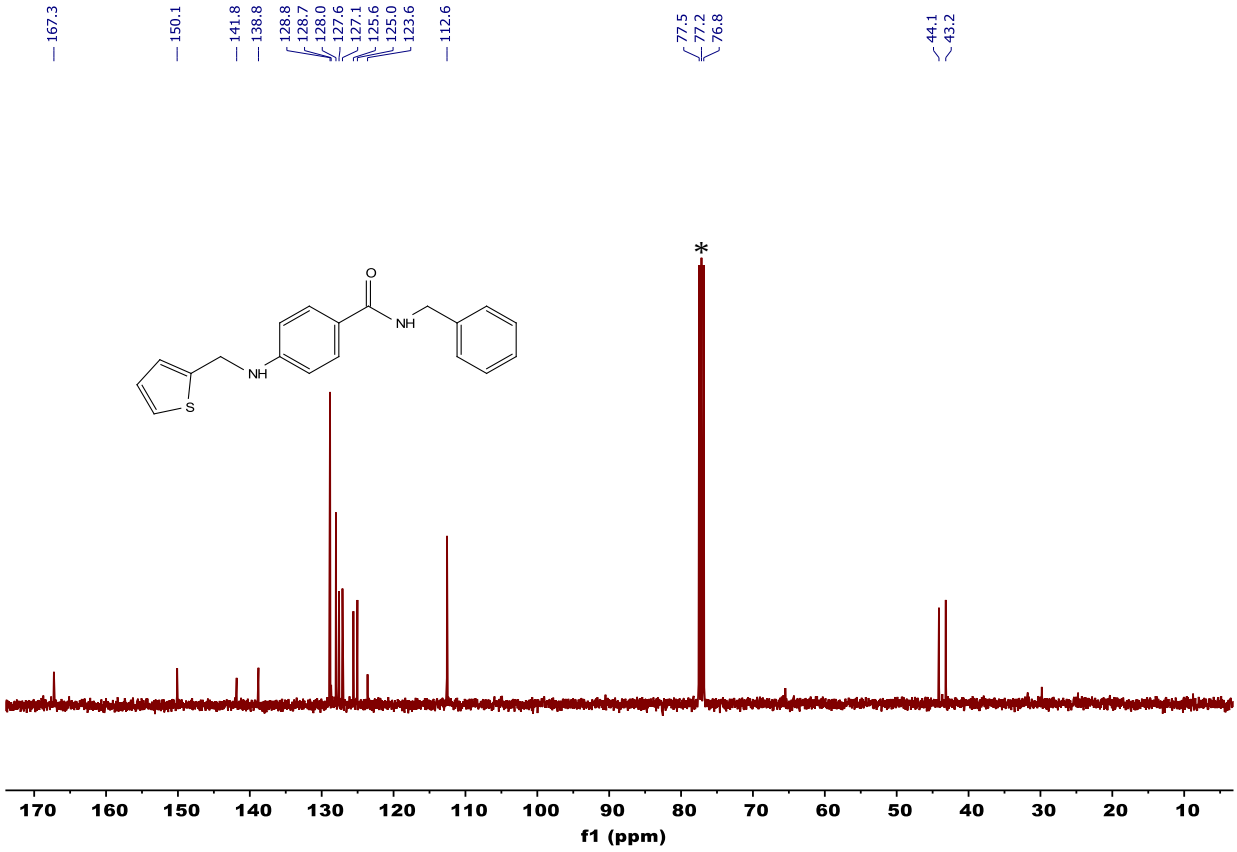
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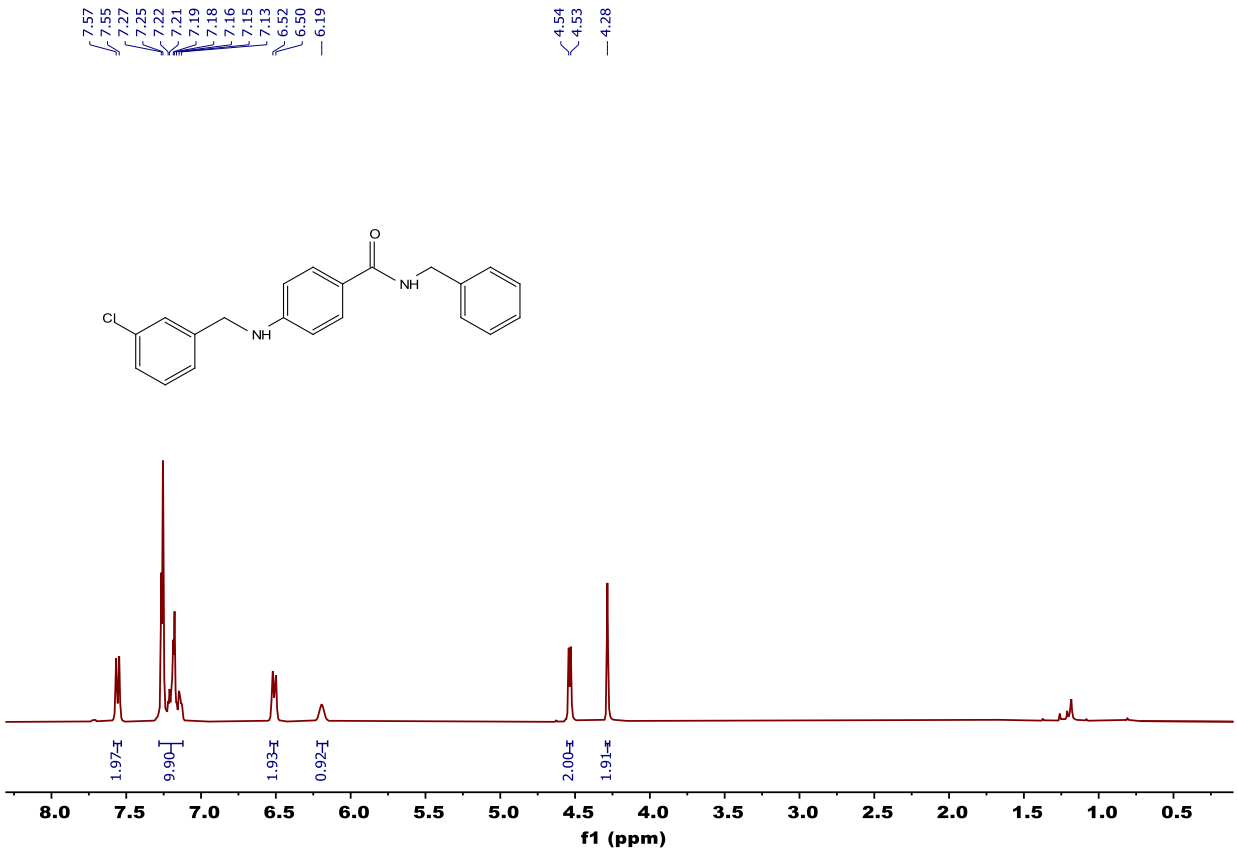
125.6
125.0
123.6
112.6
77.5
77.2
76.8
44.1
43.2
O
NH
NH
S
*
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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6.19
4.54
4.53
4.28
O
NH
Cl
NH
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1.93
0.92
2.00
1.91
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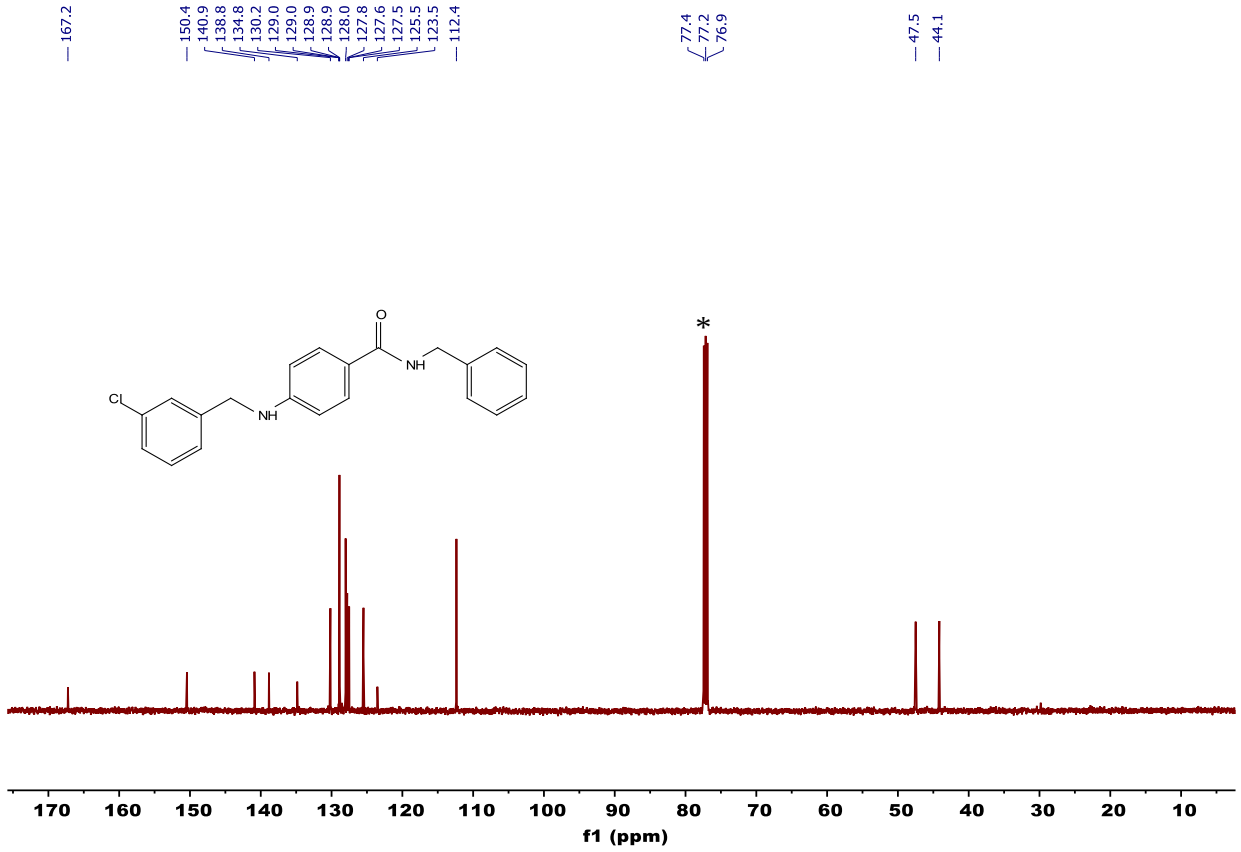
f1 (ppm)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127.5
125.5
123.5
112.4
77.4
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76.9
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44.1
O
NH
Cl
NH
*
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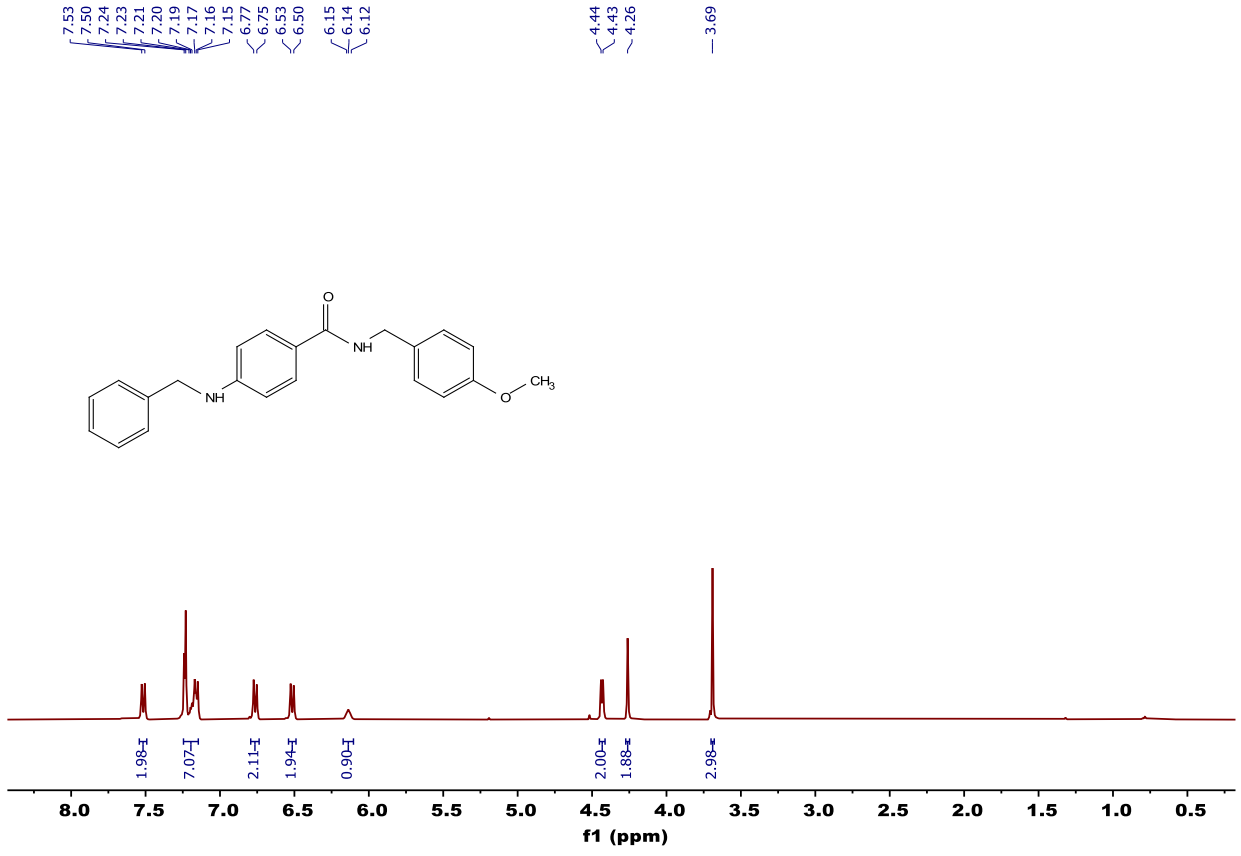
f1 (ppm)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6.15
6.14
6.12
4.44
4.43
4.26
3.69
O
NH
NH
O
CH3
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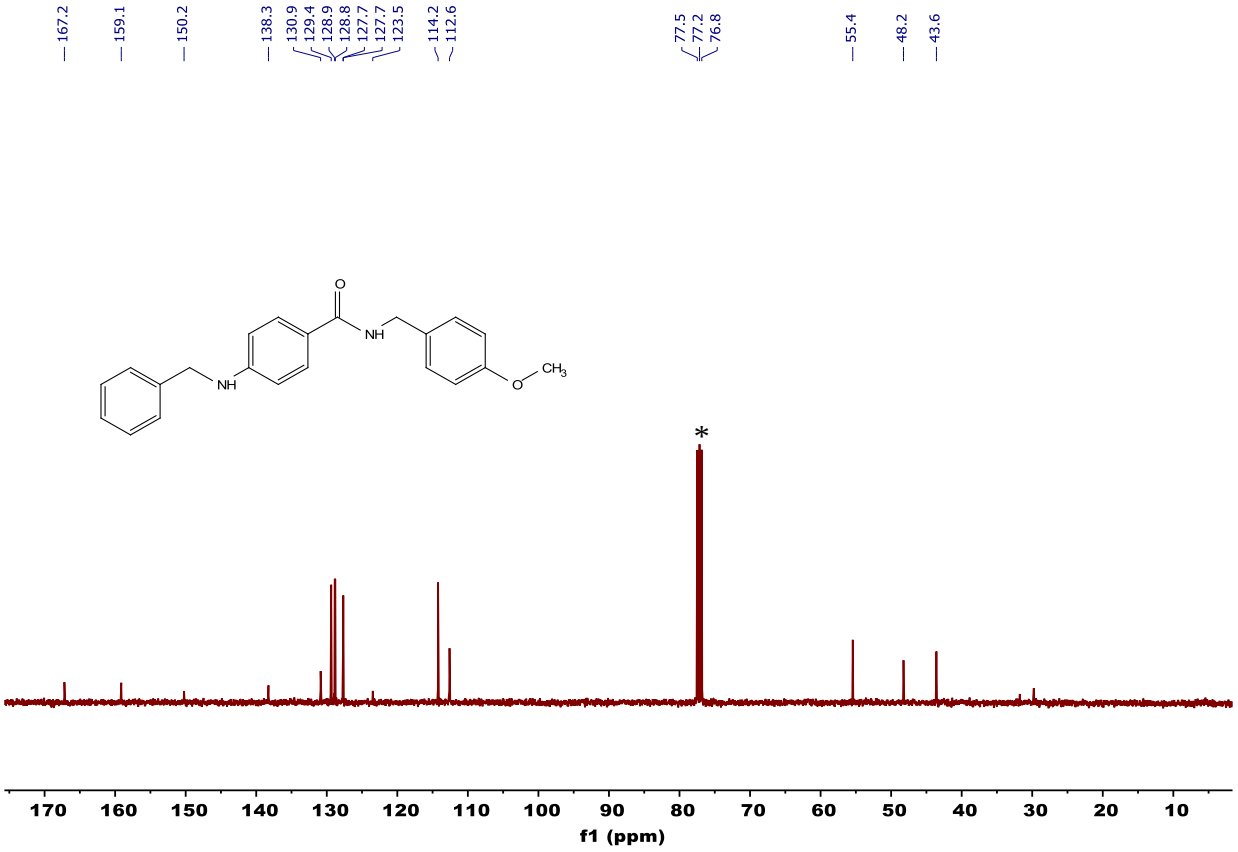
7.07
2.11
1.94
0.90
2.00
1.88
2.98
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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129.4
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127.7
123.5
114.2
112.6
77.5
77.2
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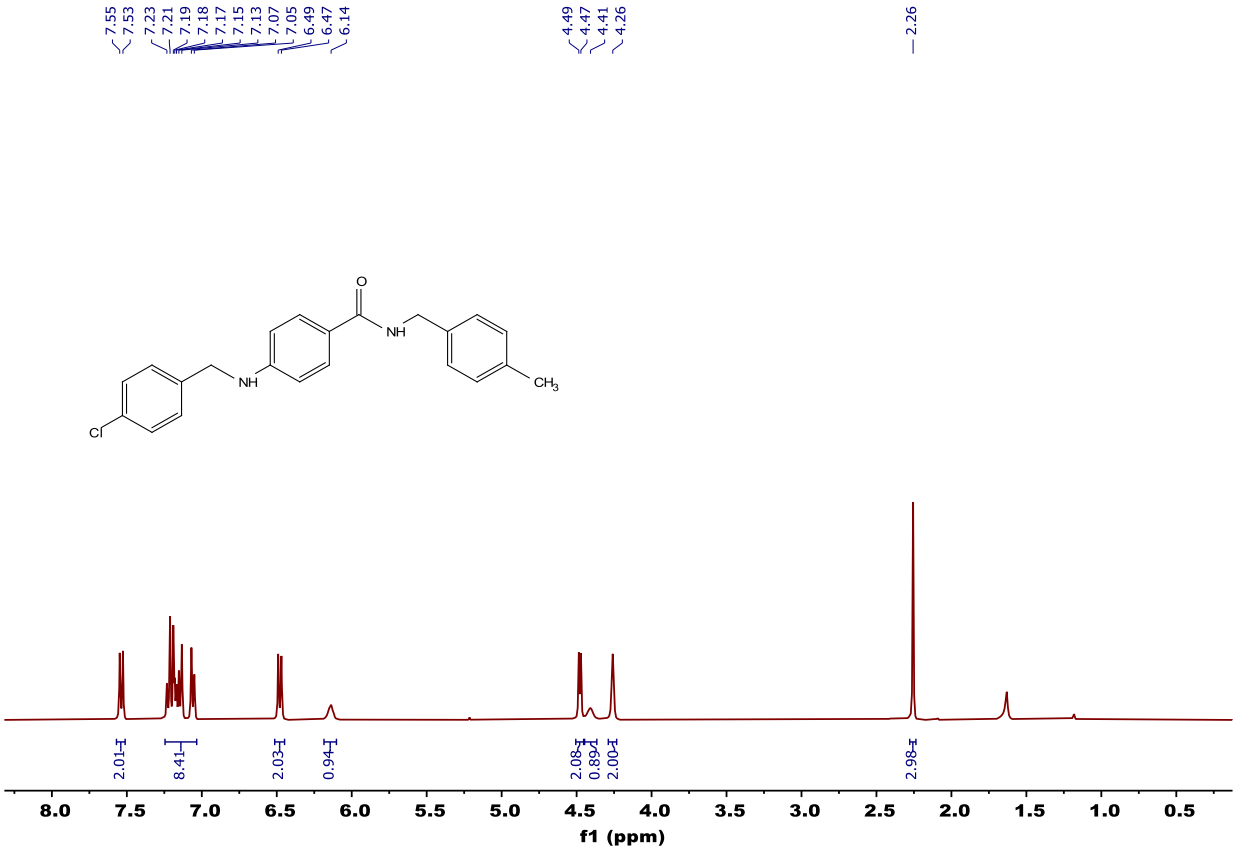
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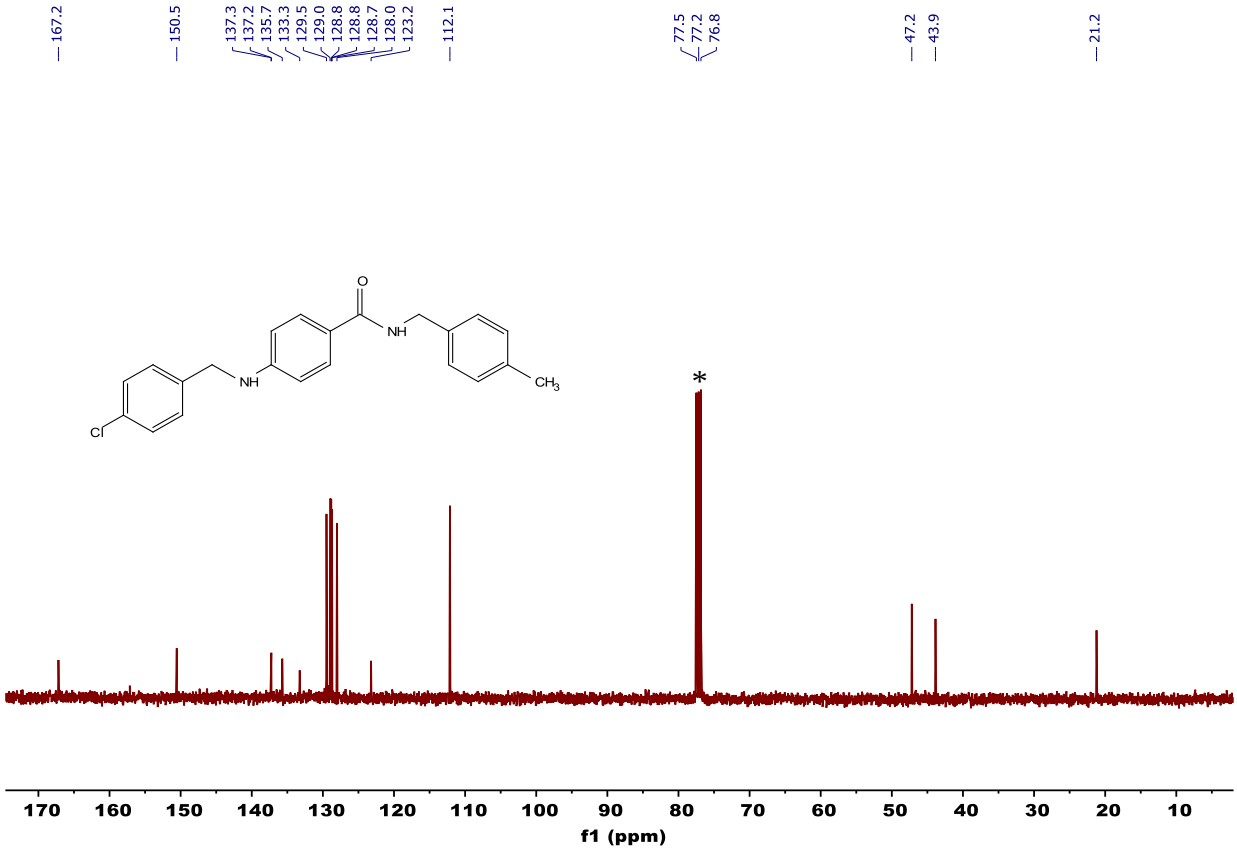
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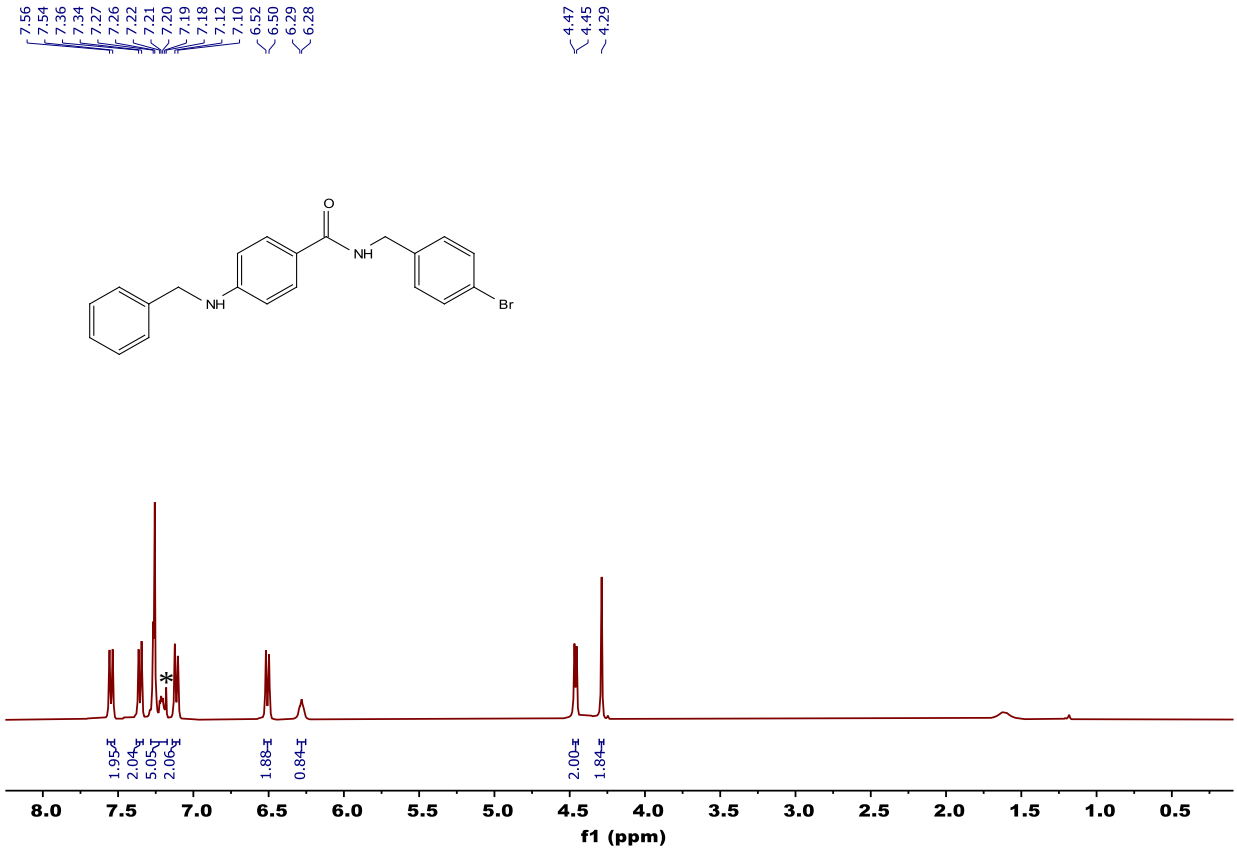
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2.00
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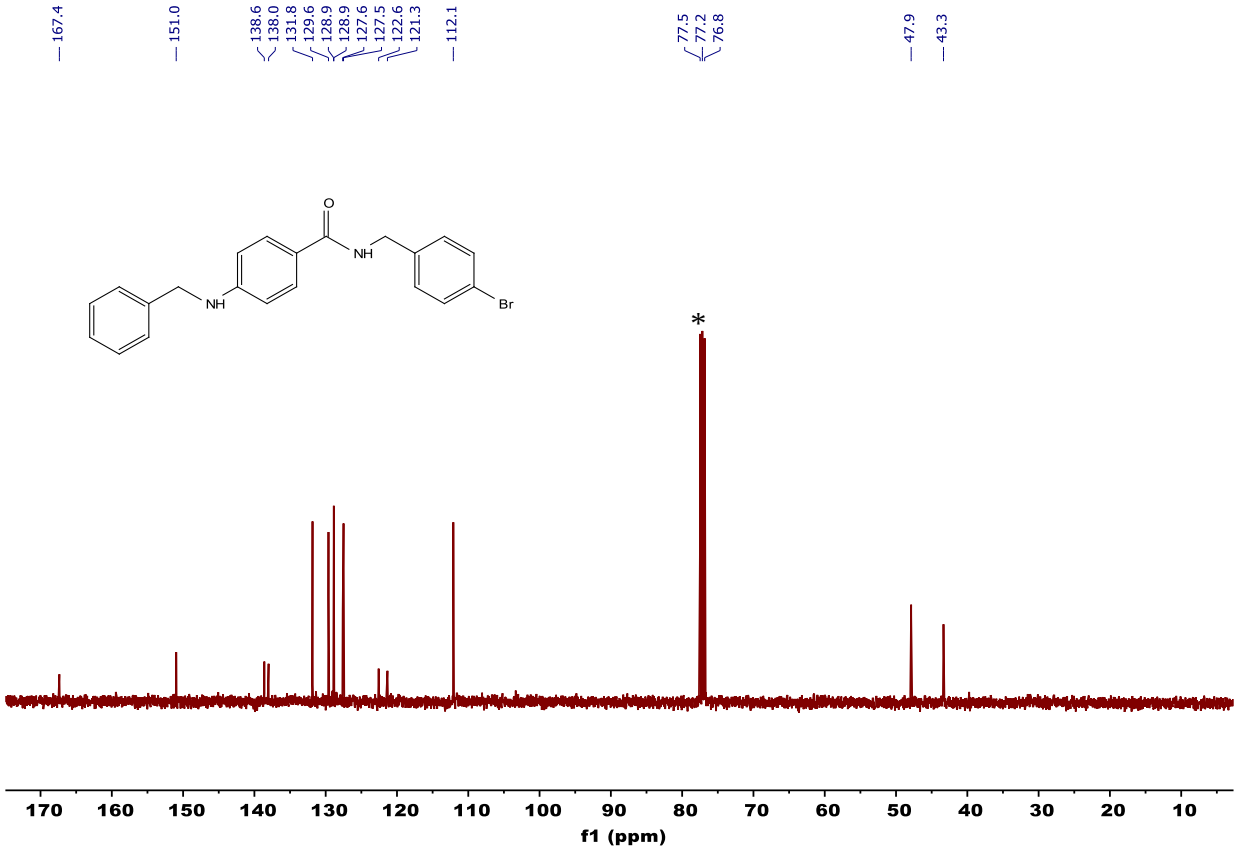
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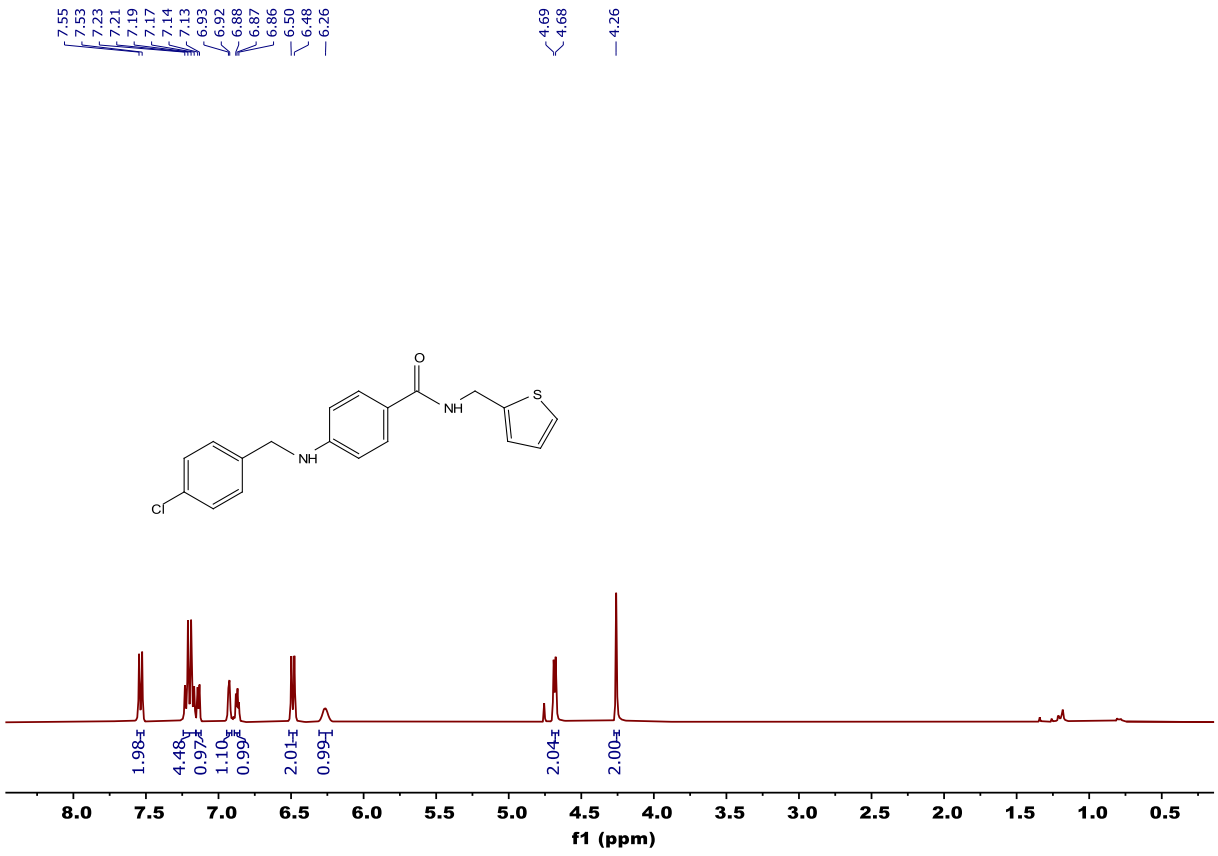
f1 (ppm)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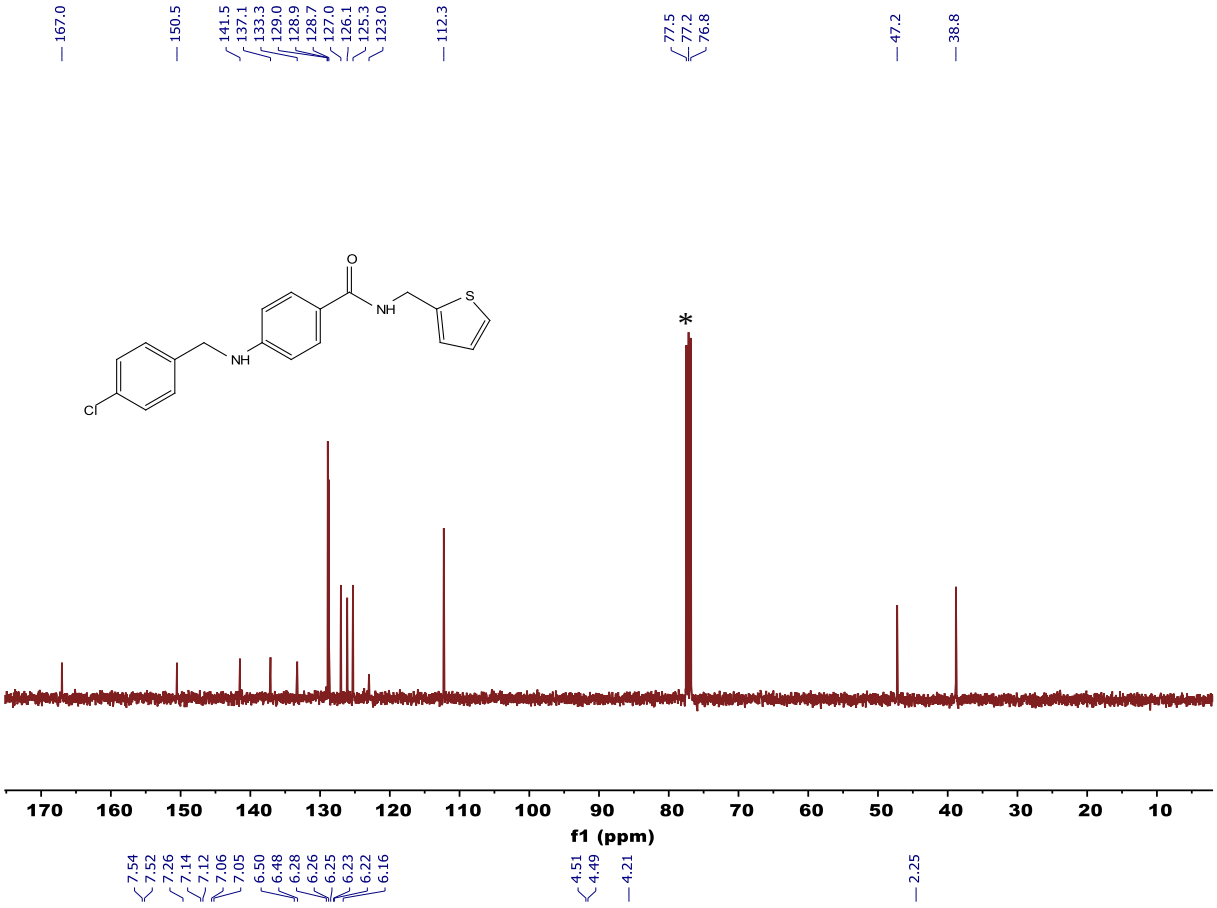
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S
NH
Cl
*
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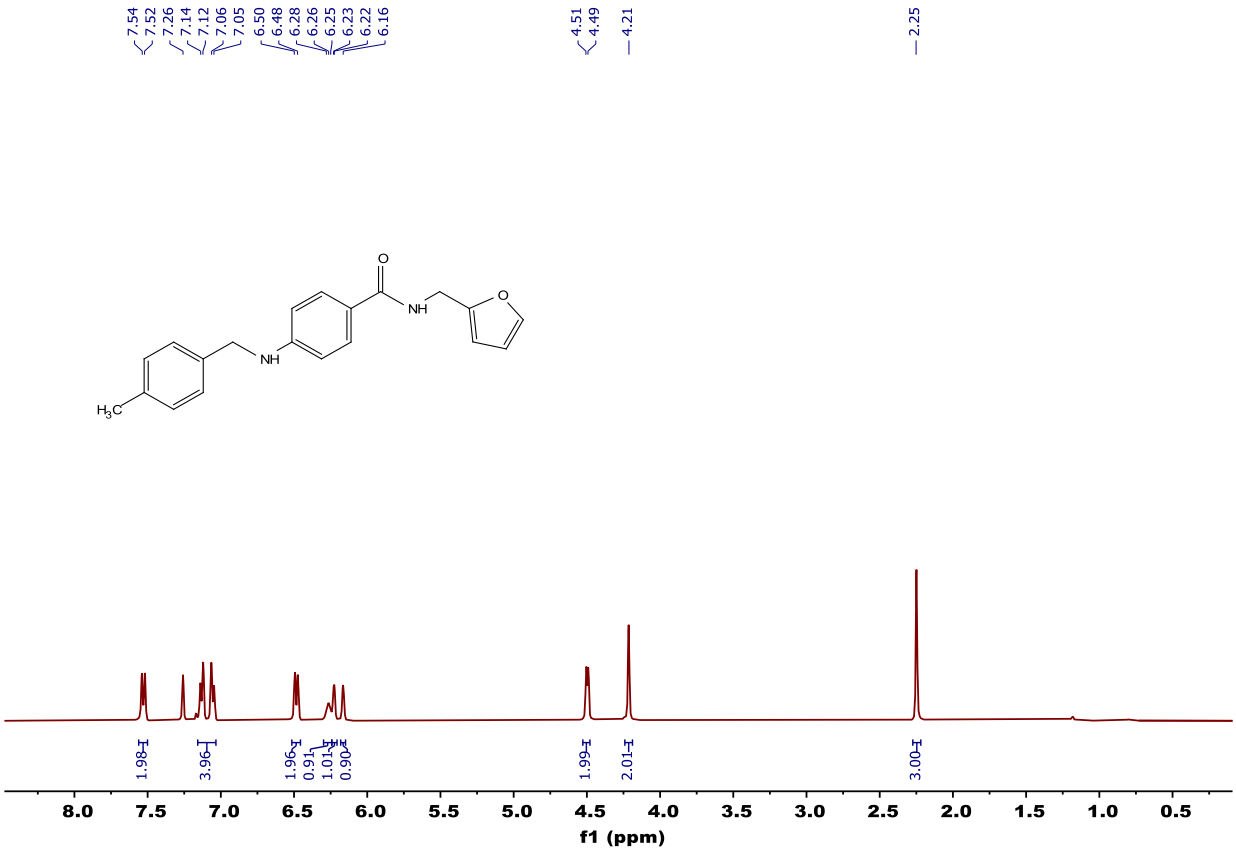
f1 (ppm)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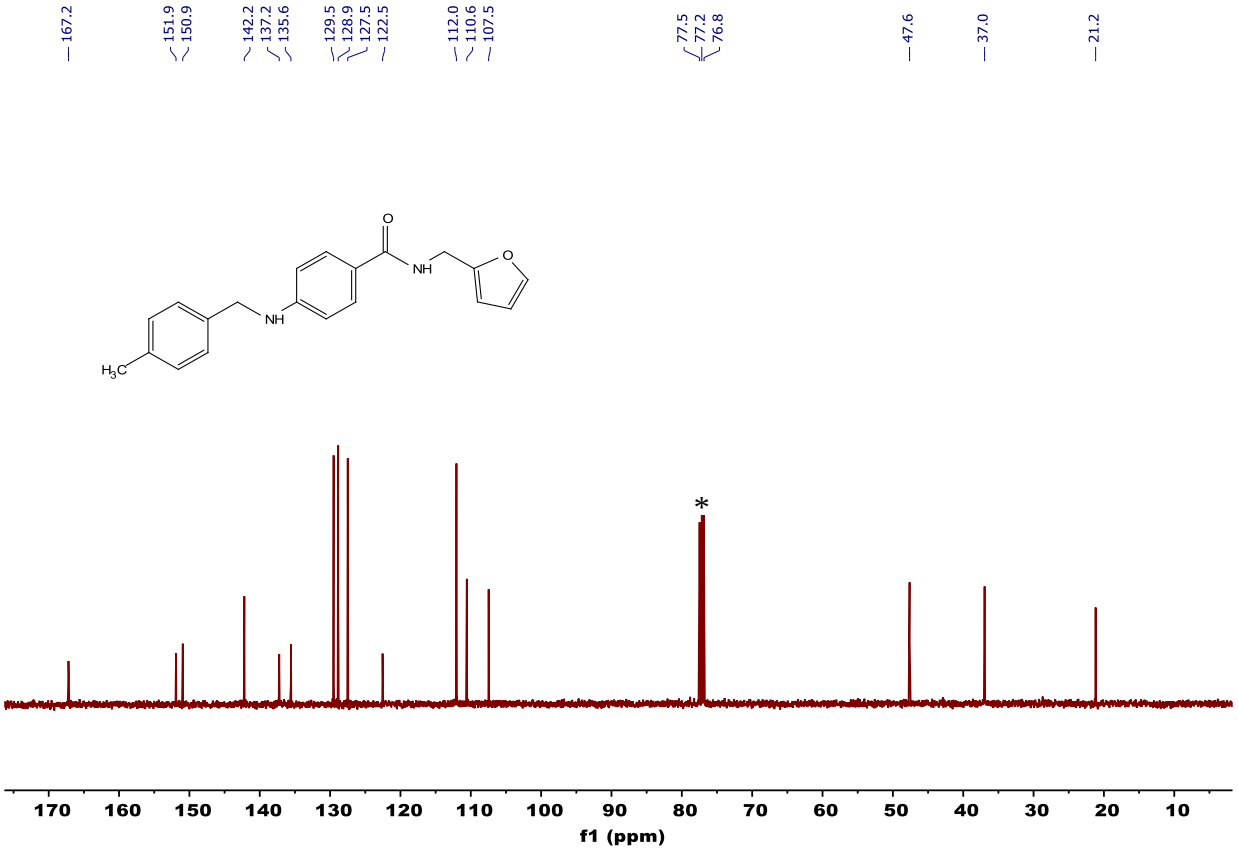
f1 (ppm)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76.8
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O
NH
H3C
*
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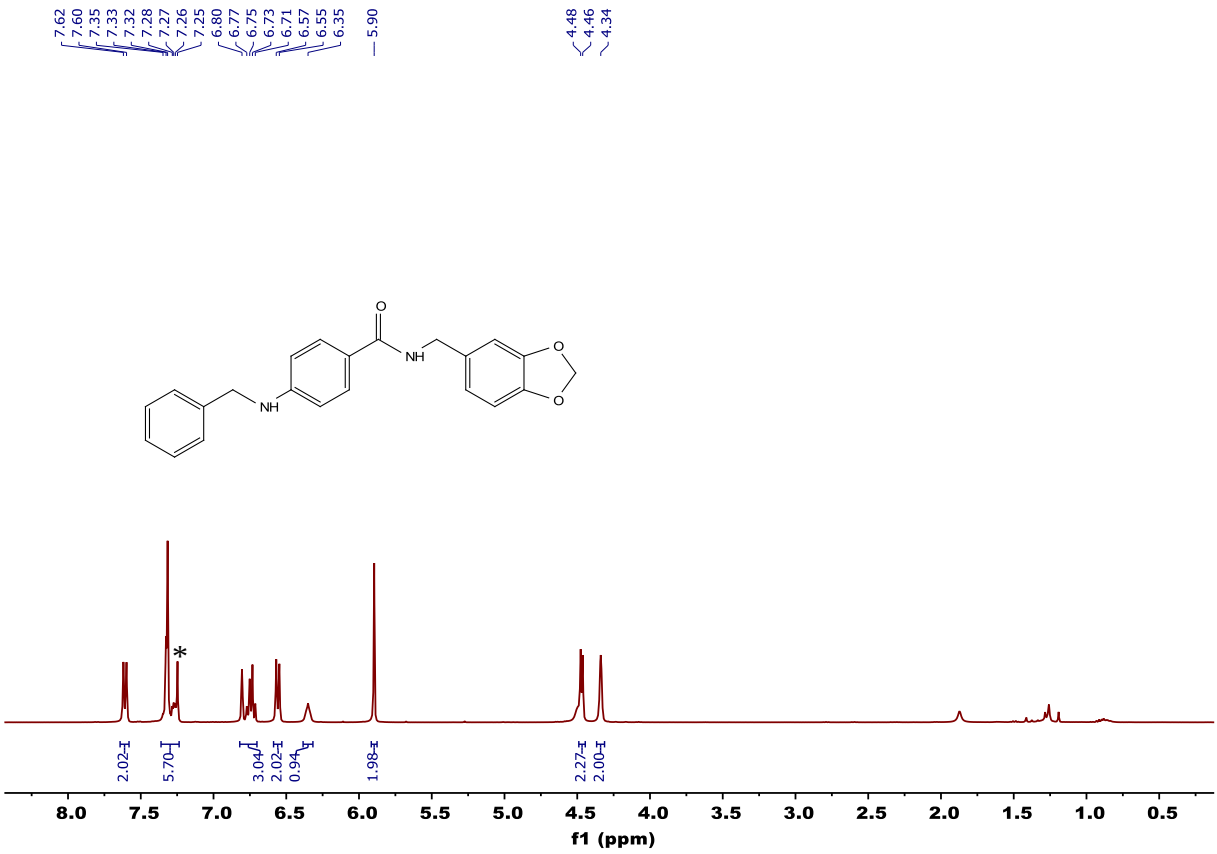
f1 (ppm)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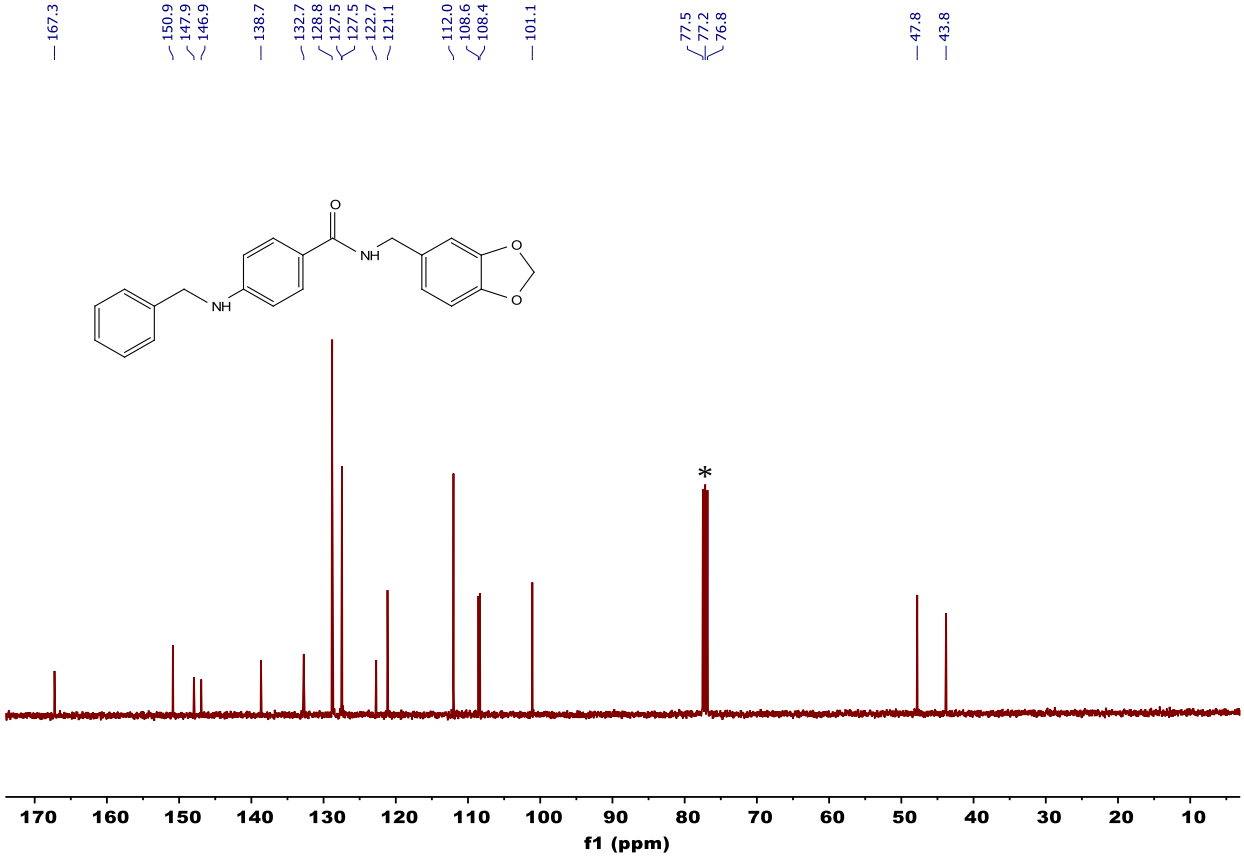
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NH
O
O
O
*
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f1 (ppm)


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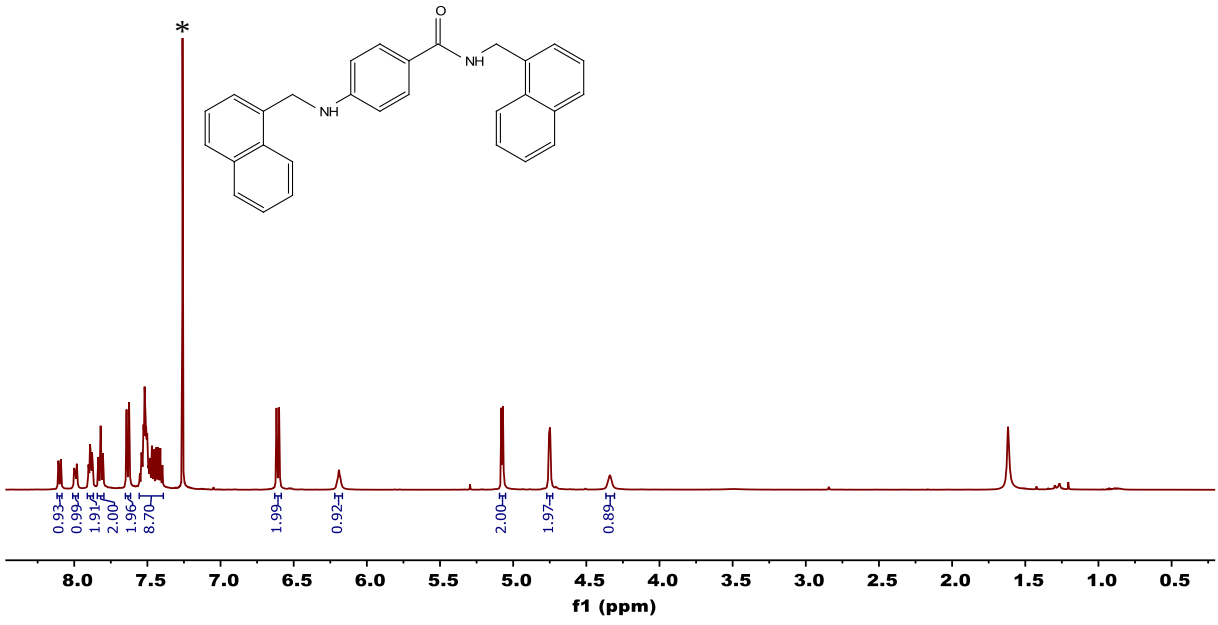
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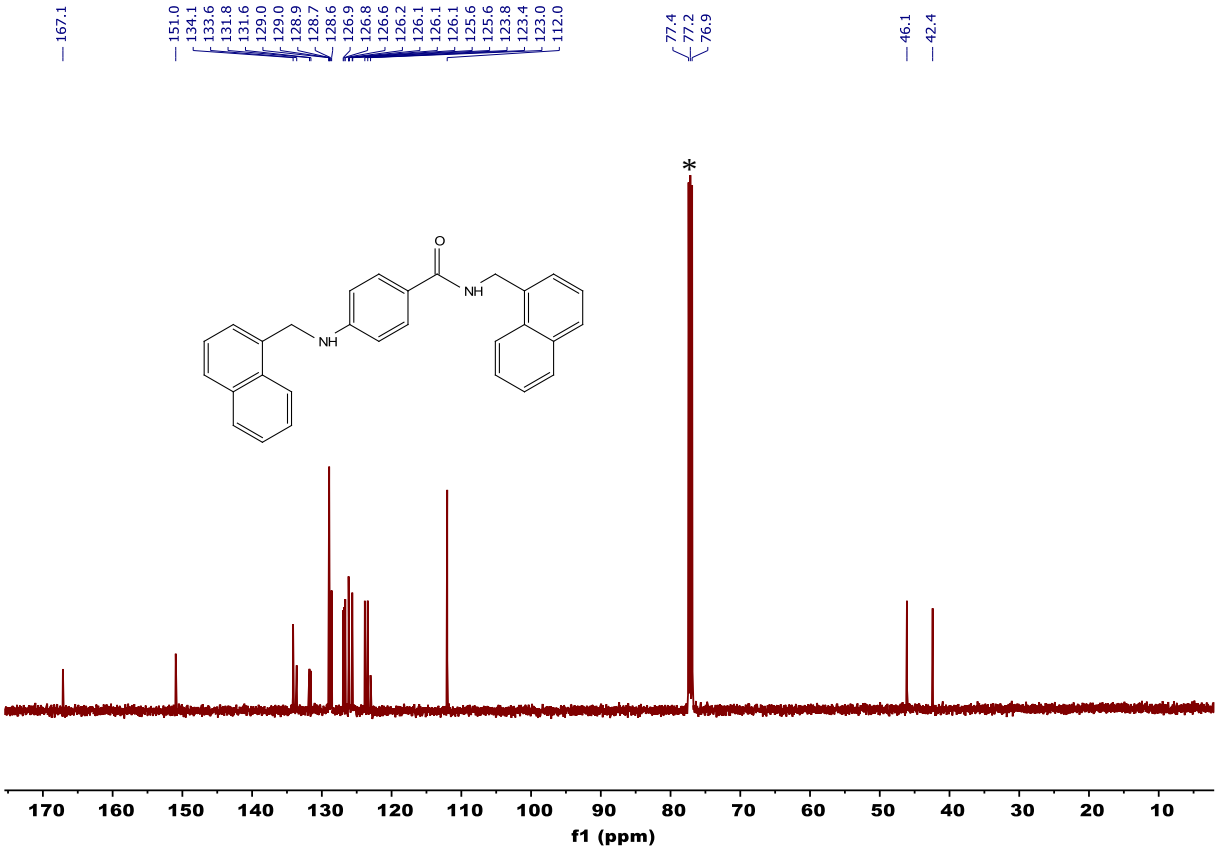
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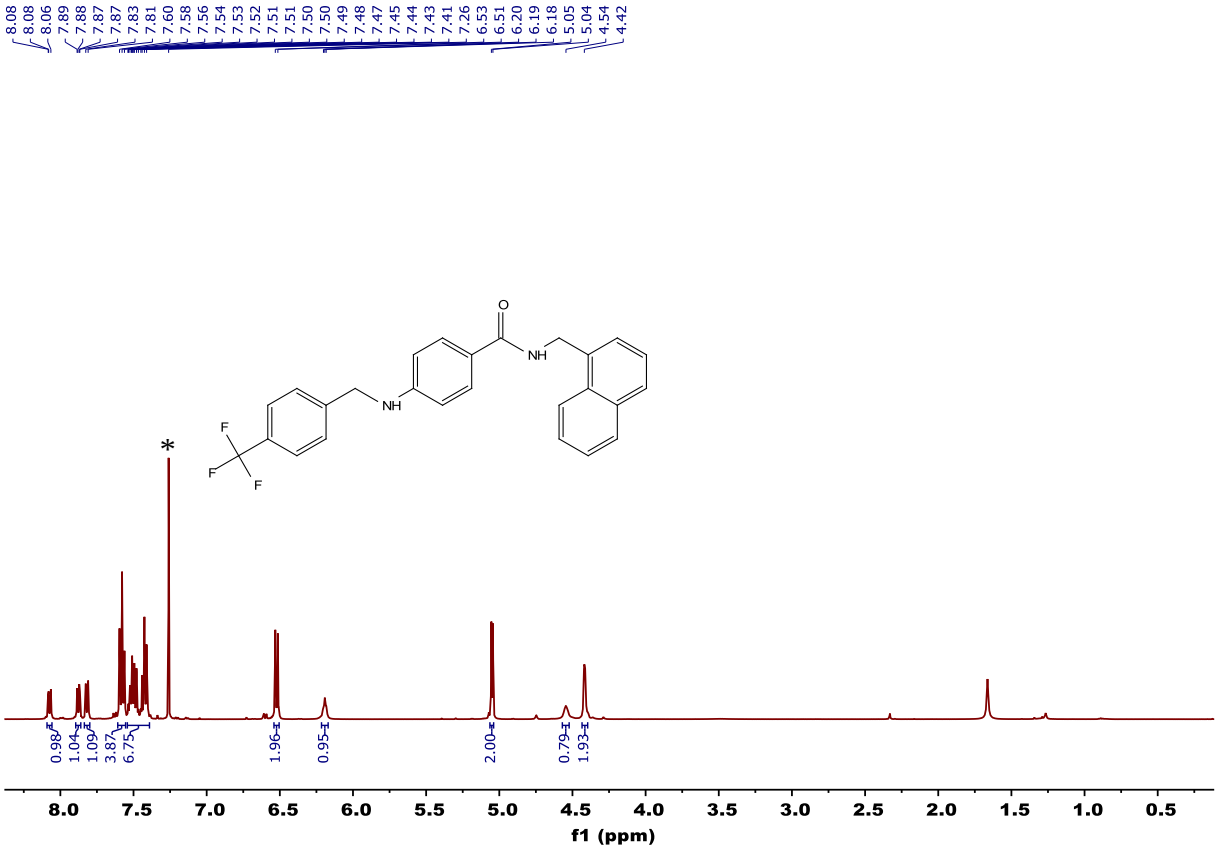
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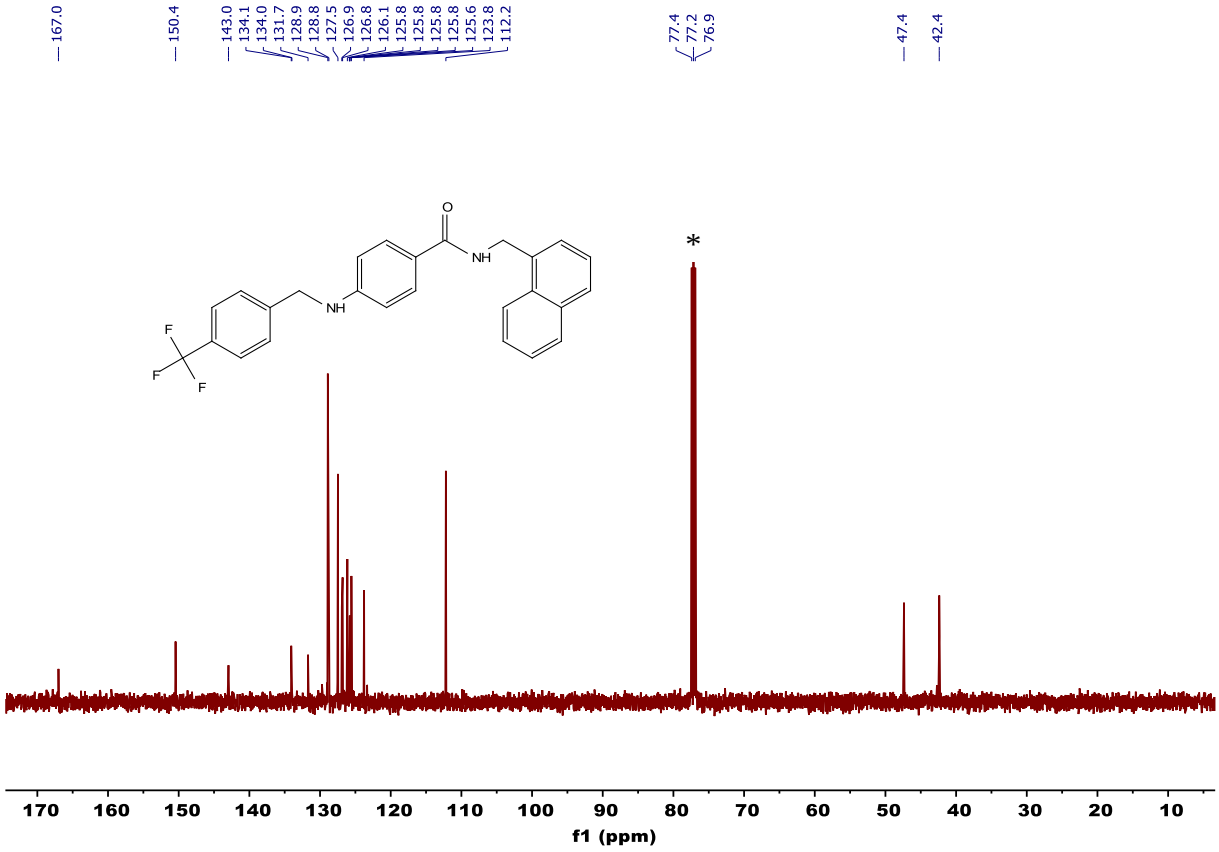
f1 (ppm)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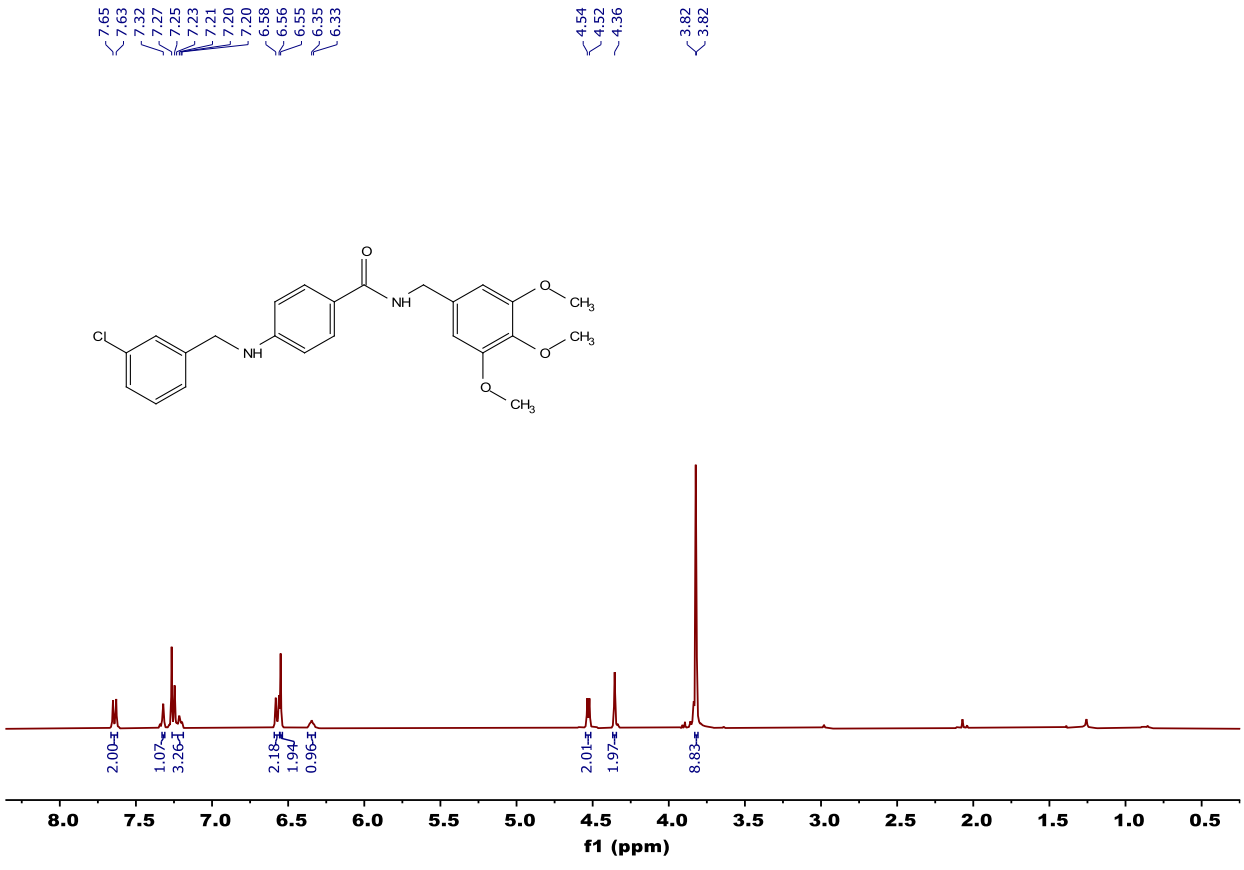
f1 (ppm)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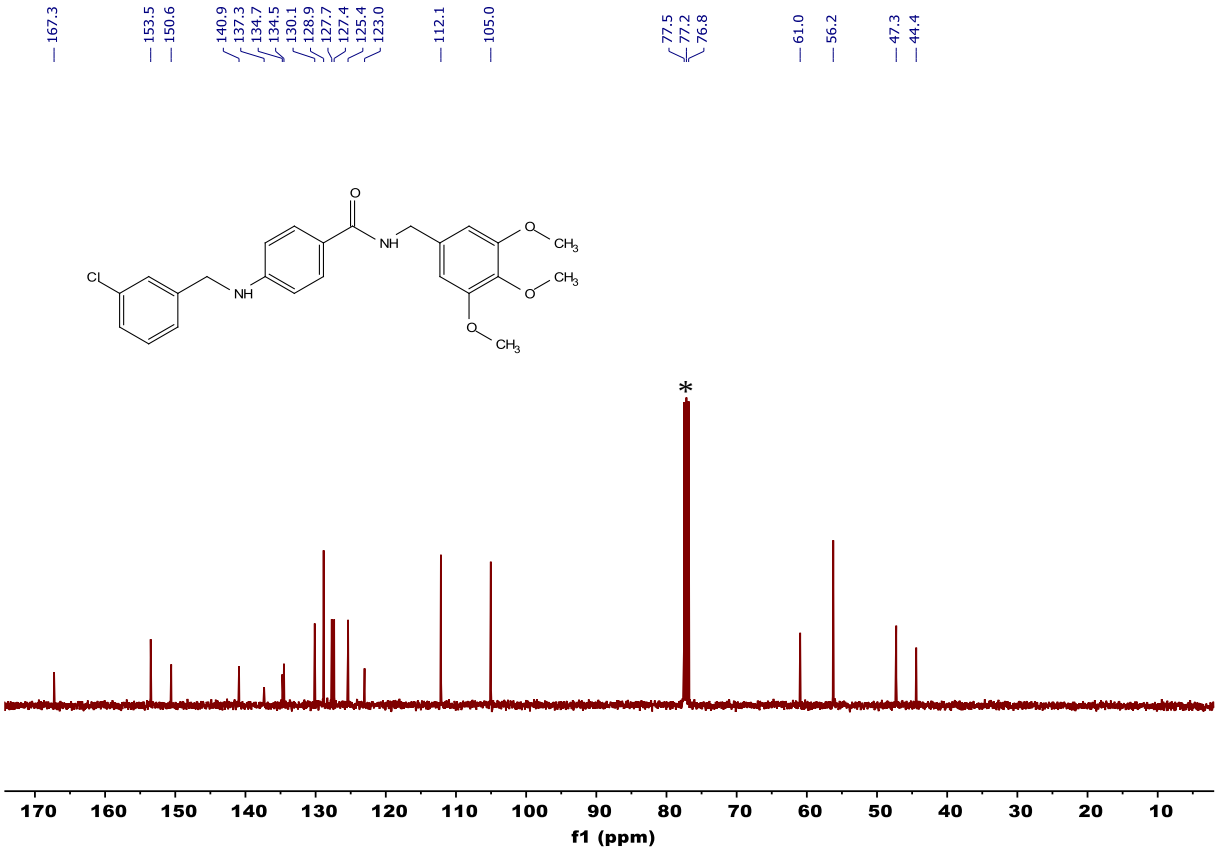

General procedure for deuterium labelling experiment. An oven dried Schlenk tube was charged with the catalyst (**2c**) stock solution (0.2 mol%), prepared in CH_3CN and then the volatiles were removed in vacuum. To this, dppe (0.8 mol%), benzamide (0.5 mmol), benzyl alcohol-d_2 (1.0 mmol), and KO^{t}Bu (0.125 mmol) followed by *t*-amyl alcohol (1 mL) were added. The reaction tube was then kept in oil bath (bath temperature 130 °C) and heated for the 24 h. After completion of the reaction, the pure products were isolated *via* column chromatography using hexane/ethyl acetate as eluent and deuterium incorporation was analysed from ^{1}H-NMR analysis as shown below.

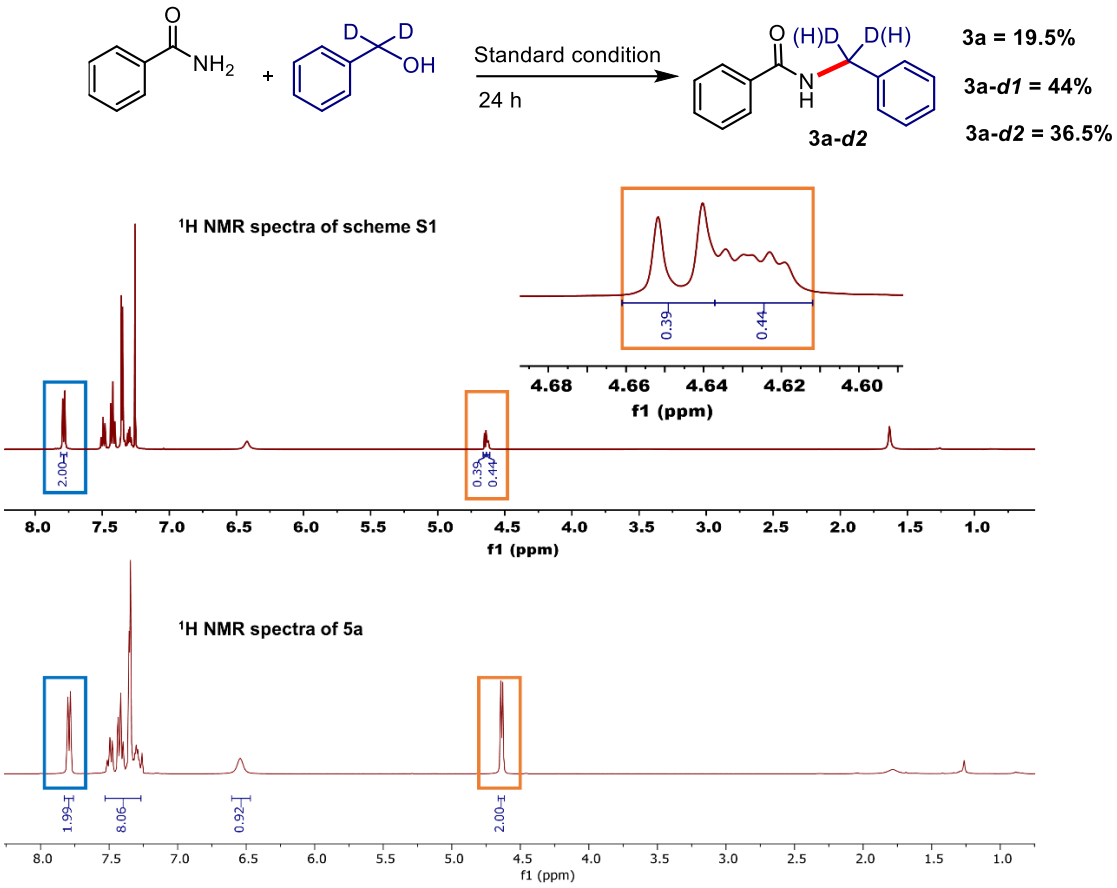

Figure S1. Deuterium labelling experiment.

Product distribution by ^{1}H NMR integration

	5a + **5a-*d*$_1$**	**5a**	**5a-*d*$_1$**	**5a-*d*$_2$**
Signal δ	7.79 [*ortho*-H, (2H)]	4.65 [*benzyl*-H (2H)]	4.63 [*benzyl*-H (1H)]	-
Integral Value	2.00	0.39/2	0.44	
Calculated ratio	-	**19.5%**	**44%**	**36.5%**

General procedure for the ESI-MS analysis of reaction mixture. An oven dried Schlenk tube was charged with the catalyst **2c** (6.8 mg, 2 mol%), dppe (8.0 mg, 4 mol%), benzamide (0.5 mmol), benzyl alcohol (1.0 mmol), and KO^{t}Bu (0.125 mmol) followed by *t*-amyl alcohol (1 mL). The reaction tube was then kept in oil bath (bath temperature 130 °C) and heated for 1 h. After that all volatiles were dried in high vacuum and the sample for ESI-MS analysis was prepared in CH_3CN.

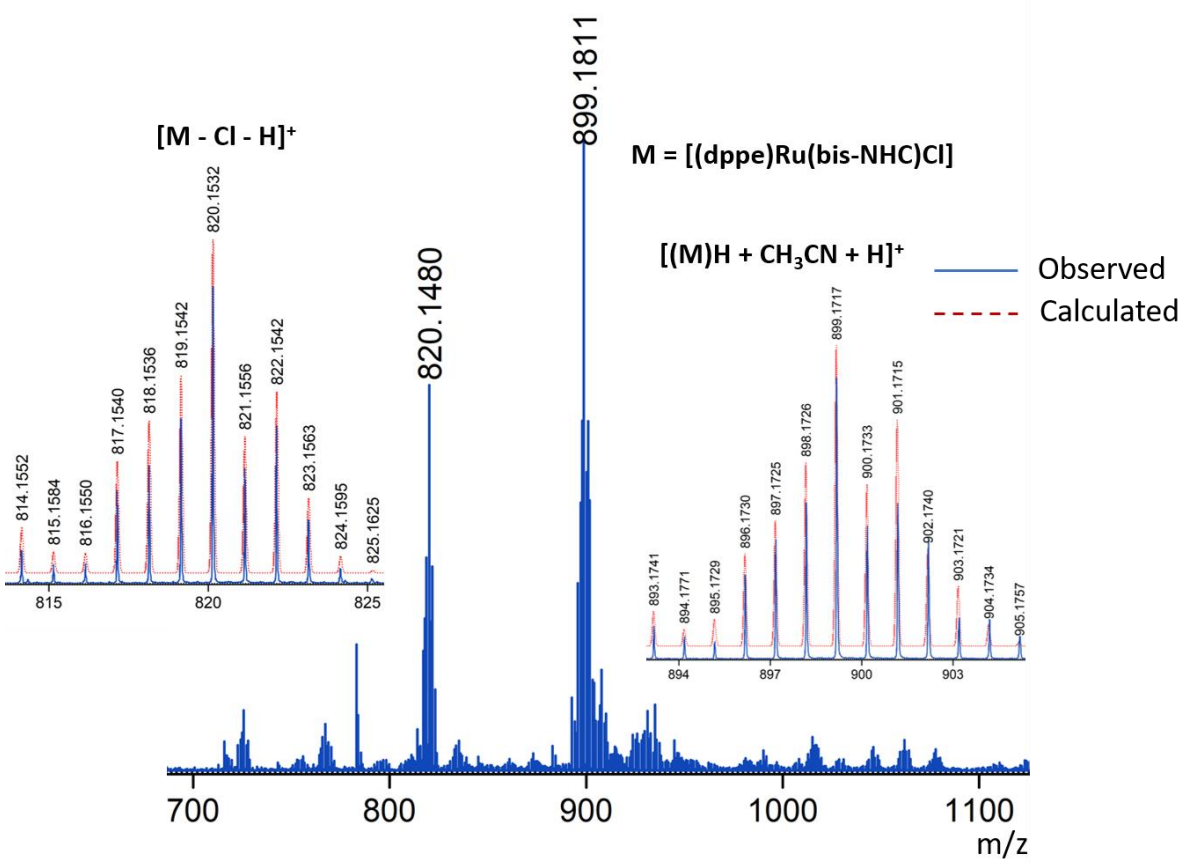

Figure S2. ESI-MS of a reaction mixture under standard condition.

General procedure for the generation of hydride species:

An oven dried Schlenk tube was charged with the catalyst **2c** (15 mg, 0.0229 mmol), dppe (18.2 mg, 0.0458 mmol), benzyl alcohol (24 µl, 0.229 mmol, 10 equiv w.r.t **2c**), and KO^{t}Bu (26 mg, 0.229 mmol, 10 equiv w.r.t **2c**) followed by *t*-amyl alcohol (1 mL). The reaction tube was then kept in oil bath (bath temperature 130 °C) and heated for 2 h. After that all the volatiles were dried in high vacuum and ^{1}H NMR and ^{31}P NMR were recorded in CD_3CN. The same sample was also submitted for ESI-MS analysis.

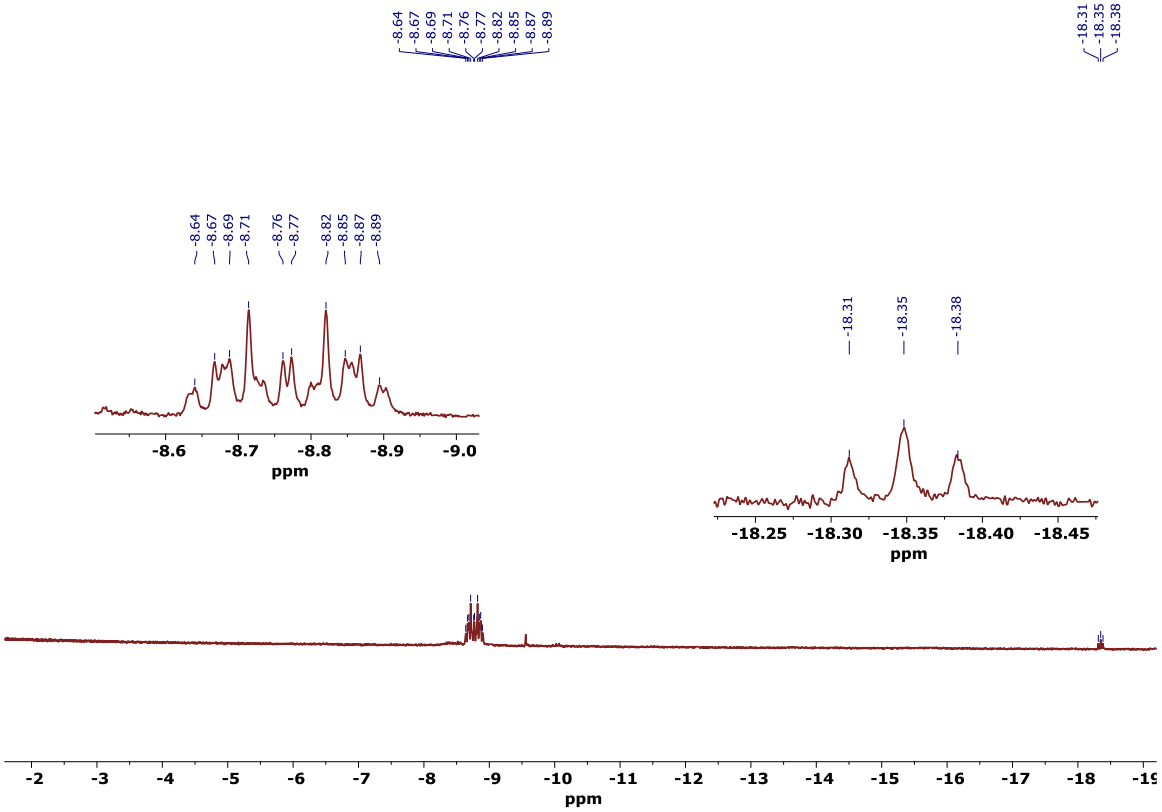

Figure S3. Selected region of the ^{1}H NMR spectrum of metal hydride species generated from benzyl alcohol dehydrogenation.

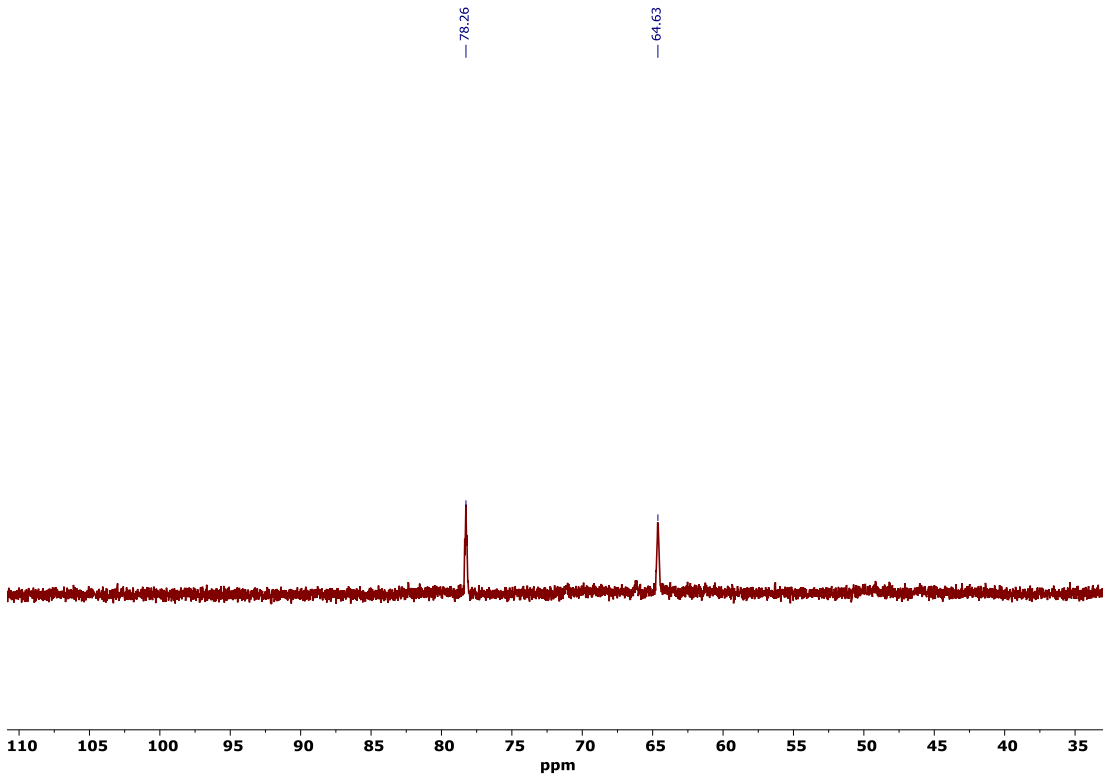

Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of metal hydride species generated from benzyl alcohol dehydrogenation.

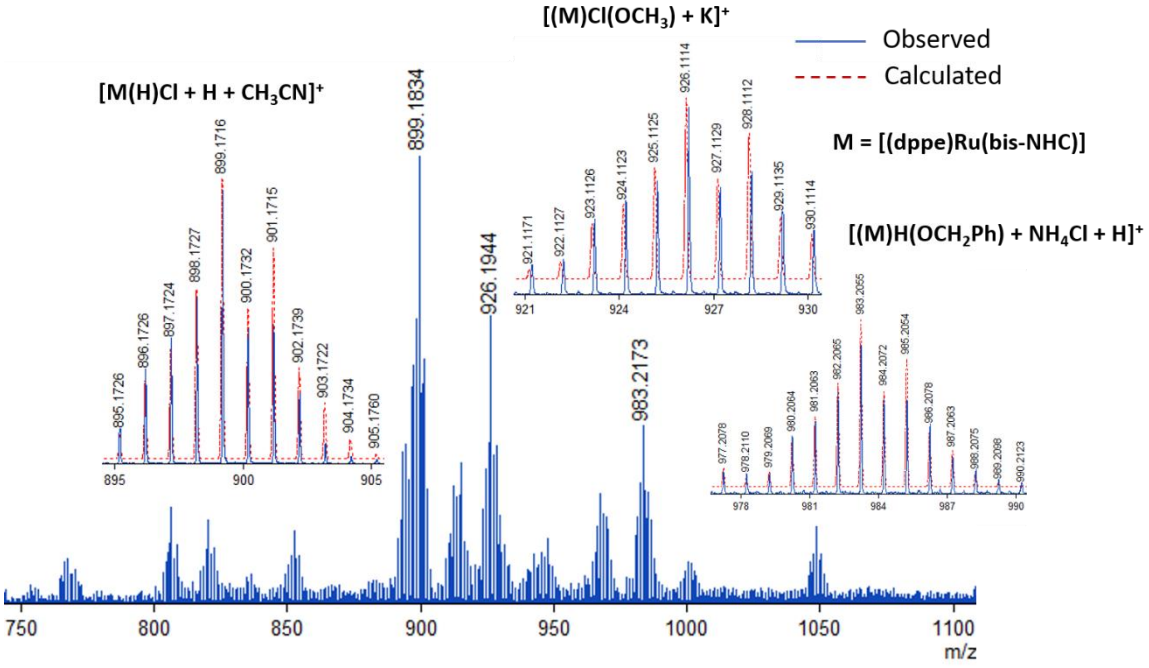

Figure S5. ESI-MS spectrum of benzyl alcohol dehydrogenation reaction.

Kinetic isotopic effect

Two separate oven dried Schlenk tubes were charged with the catalyst (**2c**) (0.5 mol%), dppe (1 mol%), amide (0.5 mmol), and KO^{t}Bu (0.125 mmol) followed by *t*-amyl alcohol (1 mL). To this benzyl alcohol **4a** (1 mmol) in one tube and deuterated benzyl alcohol **4a-*d*$_2$** in another tube were added. The reaction tube was then kept in oil bath (bath temperature 130 °C) and heated for 2 h. Then reaction mixture was cooled to room temperature and the formation of respective products were analysed by GC-MS using dodecane as an internal standard which provides KIE value k_H/k_D = 13/5 = 2.6.

Reaction progress and temperature effect

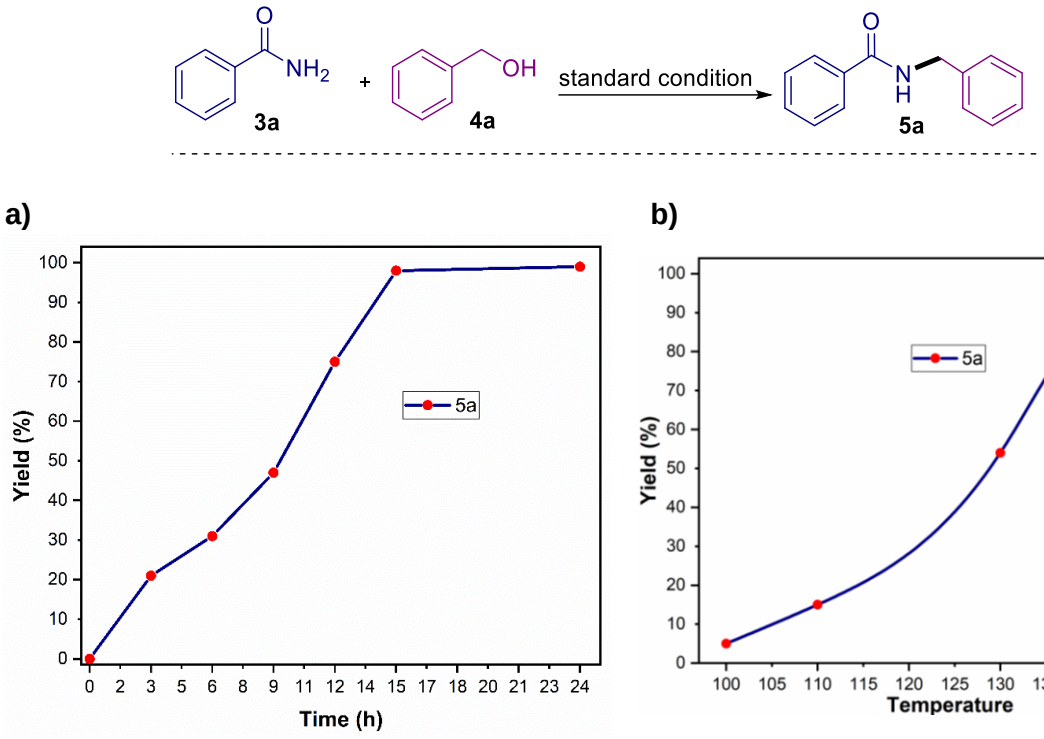

Figure S6. (a) Reaction progress for the formation of product **5a**; (b) Temperature effect on the formation of product **5a**.

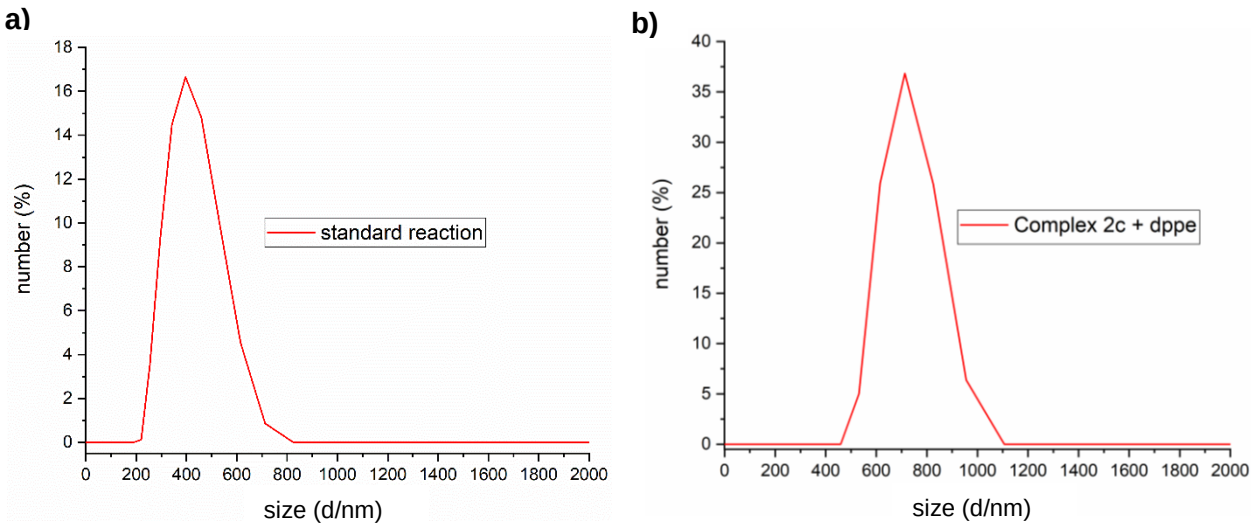

Figure S7. DLS plot for (a) the standard reaction mixture; (b) reaction mixture containing the complex **2c** and dppe.

References

1. S. N. R. Donthireddy, P. M. Illam and A. Rit, *Inorg. Chem.,* 2020, **59**, 1835-1847.
2. (*a*) P. M. Illam, V. K. Singh, Priya and A. Rit, *J. Organomet. Chem.,* 2021, **951**, 122008-122016. (*b*) P. M. Illam and A. Rit, *Catal. Sci. Technol.,* 2022, **12**, 67-74.