Electronic Supplementary Information

Multiply-Twinned Intermetallic AuCu Pentagonal Nanorods*

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Experimental

Chemicals: Tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.9%), copper(II) acetylacetonate ($Cu(acac)_2$, 99%), oleylamine (technical grade, 70%), methanol (98%), and toluene (99%) were purchased from Sigma-Aldrich and used as received. All glassware and Teflon-coated magnetic stir bars were cleaned with *aqua regia*, followed by copious rinsing with de-ionized water before drying in an oven.

Silica gel 60 (230–400 mesh, Merck) was used for column chromatography. Ni grids (Ni-400CN, Pacific Grid Tech) were used for the TEM studies. All other reagents were purchased from Aldrich, Fluka and Merck, and used as received. All synthesized compounds were characterized with ^1H and ^{13}C NMR spectroscopy.

Physical characterization: FEI Tecnai G^2 F20 electron microscope was used to obtain the TEM, HRTEM and HAADF-STEM images. The catalyst composition was determined by an EDX attachment to the microscope. XRD patterns were recorded on a Rigaku D/Max-3B diffractometer using Cu K_α radiation (λ = 1.54056 Å). XPS spectra were obtained with an ESCALAB MKII spectrometer (VG Scientific) using Al-K_α radiation (1486.71 eV). Samples for XRD and XPS measurements were precipitated from a toluene solution of the nanoparticles using methanol, recovered via centrifugation, and washed with methanol several times to remove non-specifically bonded oleylamine. The nanoparticles were then dried at room temperature in vacuum.

^1H and ^{13}C NMR spectra were collected in $CDCl_3$ using a Bruker AV-400 (400 MHz) spectrometer at 25°C. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. Mass spectra were recorded on a Shimadzu

GCMS-QP2010 spectrometer. ICP-MS analyses were performed on a Perkin-Elmer Elan DRC II.

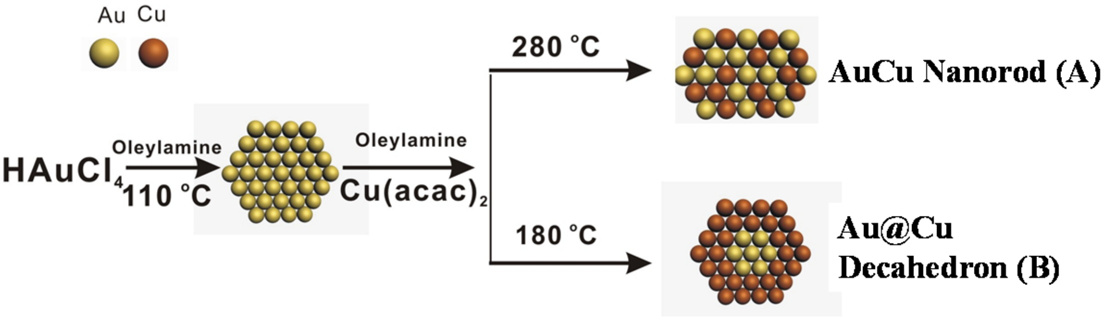
Synthesis of Au, AuCu and $AuCu_2$ pentagonal nanorods: In a typical synthesis of Au decahedra, a solution of 93 mg of $HAuCl_4{\cdot}3H_2O$ in 10 mL of oleylamine was heated at 110°C in a nitrogen atmosphere under magnetic stirring for 4 h. These Au nanoparticles were then used as seeds for the formation of AuCu and $AuCu_2$ nanorods. For the synthesis of AuCu nanorods with different lengths, 60 mg of $Cu(acac)_2$ was immediately added to the 10 ml of Au nanoparticles solution with different amounts of Au nanoparticles (Au/Cu atomic ratios = 1:1 and 2:1 for AuCu and $AuCu_2$, respectively), and the mixture was heated at 280°C for 1 h under the nitrogen flow with rapid magnetic stirring. The above solution was then cooled to 160°C for 1 h of aging. The resulting pentagonal nanorods were then cooled to room temperature. The nanorods in the solution were precipitated by methanol, and washed twice with methanol to remove the free ligands, followed by re-dispersion in hexane.

Synthesis of Cu nanoparticles, $AuCu_3$ nanorods and Au@Cu nanoparticles: For the synthesis of Cu nanoparticles, a solution of 60 mg of $Cu(acac)_2$ in 10 mL of oleylamine was heated at 200°C in a nitrogen atmosphere under magnetic stirring for 1 h. For the synthesis of $AuCu_3$ nanorods with different lengths, 60 mg of $Cu(acac)_2$ was immediately added to the 10 ml of Au nanoparticles solution (Au/Cu atomic ratio = 1:3) and the mixture was heated at 280°C for 1 h under the nitrogen flow with rapid magnetic stirring. The above solution was then cooled to 160°C for 1 h of aging. For the synthesis of spherical Au@Cu nanoparticles, 60 mg of $Cu(acac)_2$ was immediately added to the 10 ml Au nanoparticles solution with different amounts of Au nanoparticle (Au/Cu atomic ratios = 1:1 for AuCu at 180°C), and the mixture was heated at 180°C for 1 h under the nitrogen flow with rapid magnetic stirring. The resulting nanoparticles were then cooled to room temperature. The nanorods in the solution were precipitated by methanol, and washed twice with methanol to remove the free ligands, followed by re-dispersion in hexane.

Loading of AuCu onto carbon: A dispersion of AuCu nanorods (containing 1.96 mg Cu) in 10 mL of hexane was added dropwise to a suspension of 61 mg of Vulcan XC-72 carbon in hexane (60 mL) with vigorous stirring. The resulting suspension was stirred at room temperature under air for 1 day. The AuCu/C nanomaterial was collected *via* centrifugation and washed once with hexane/methanol (1:2) and twice with hexane/methanol (1:4). The nanomaterial was then dried at room temperature under vacuum overnight. The nanomaterial was characterized by TEM and ICP-MS.

General procedure for coupling reaction: A mixture of the AuCu/C nanomaterial (1 mol% Cu), K_2CO_3 (20 mol%), sulfonamide (0.2 mmol) and benzyl alcohol (1 mmol) were added to a 8-mL glass vial equipped with a screw cap. The reaction mixture was heated at 120°C under air for 15 h. The mixture was centrifuged at 7000 rpm for 15 min. The organic layer containing the product was separated, and the solids were washed with dichloromethane (2 × 3 mL). The solvent was removed by rotary evaporation, followed by purification using column chromatography (silica gel, dichloromethane or hexanes/ethyl acetate (2:1)).

For the recycling experiments, the solid catalyst recovered *via* centrifugation was dried at room temperature under vacuum for 5 h before it was used in the next run.



Scheme S1. Seed-mediated growth synthesis of nanocrystalline particles of (A) AuCu pentagonal nanorod, and (B) Au@Cu decahedron.

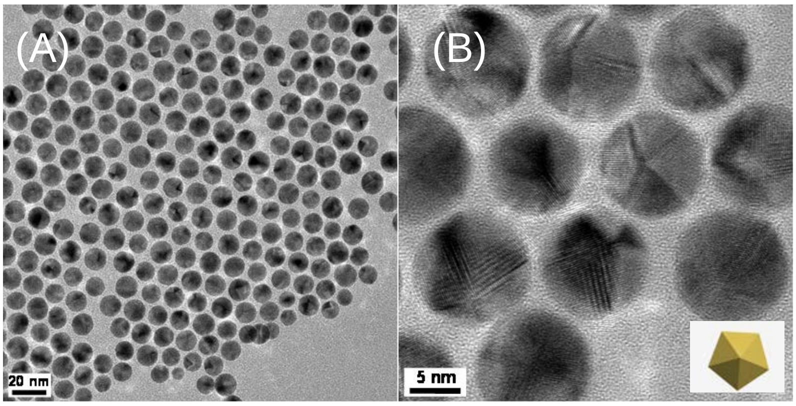


Figure S1. (A) TEM and (B) HRTEM images of decahedral Au nanoparticles. The average particle diameter was 10.0 ± 0.8 nm.

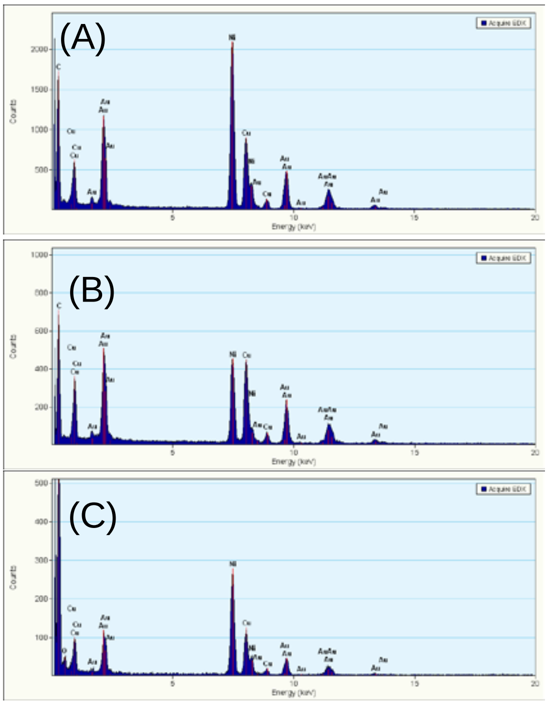


Figure S2. EDX spectra of (A) AuCu, (B) $AuCu_2$ and (C) $AuCu_3$ pentagonal nanorods, corresponding to Au/Cu atomic ratios of 47:53, 35:65 and 26:74, respectively.

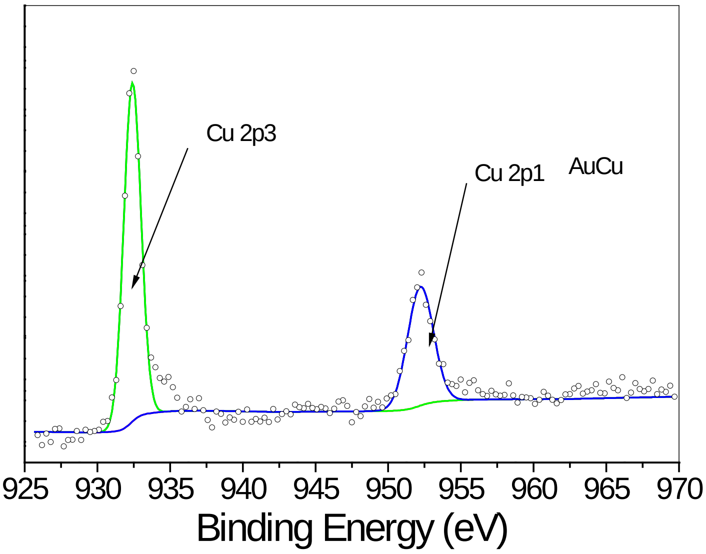


Figure S3. Cu XPS spectrum of AuCu nanorods.

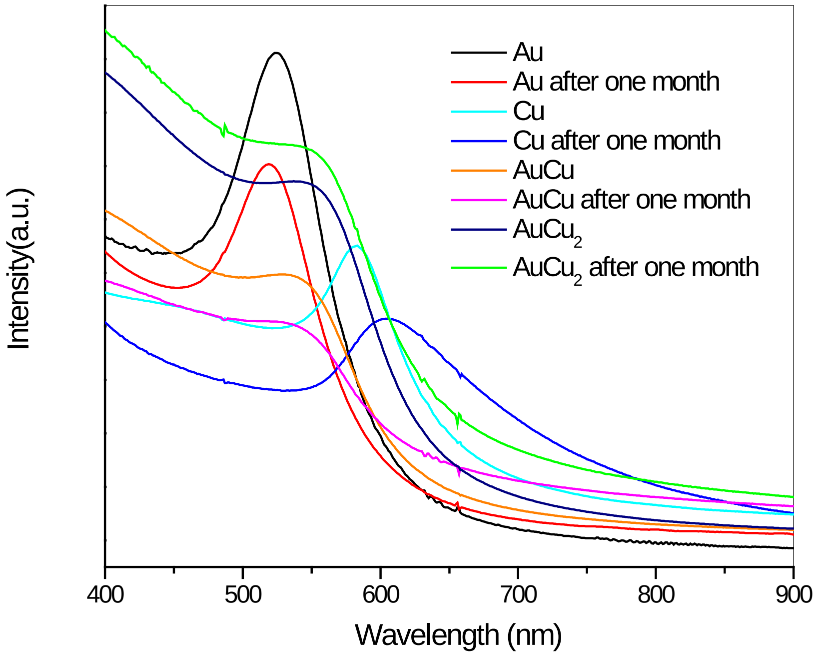


Figure S4. UV-vis spectra of Au decahedral nanoparticles, Cu nanoparticles, AuCu nanorods and AuCu$_2$ nanorods dispersed in hexane.

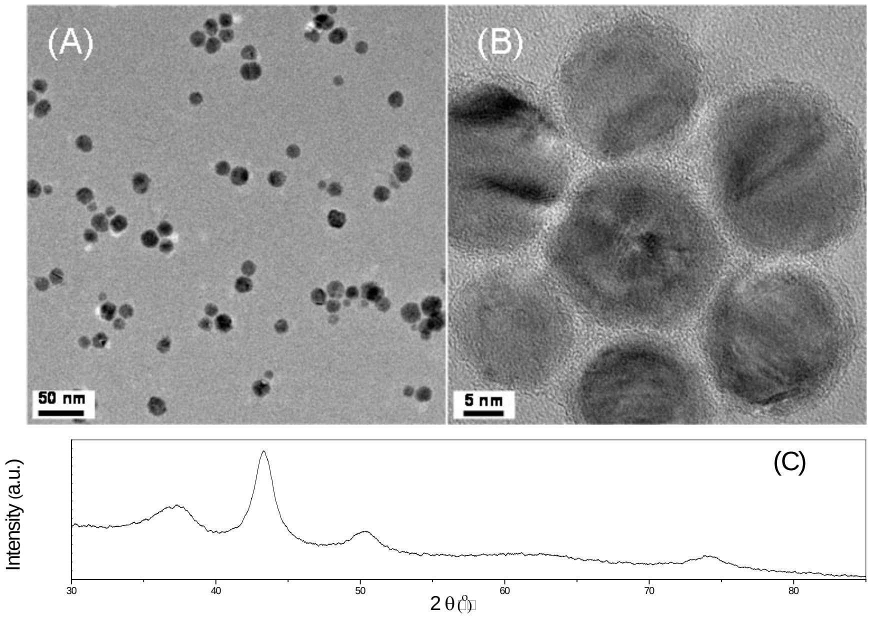


Figure S5. (A) TEM and (B) HRTEM images of Cu nanopaticles. The average particle diameter was 19.0 ± 3.0 nm. (C) XRD pattern of Cu nanoparticles, which indicated the presence of Cu and CuO phases.

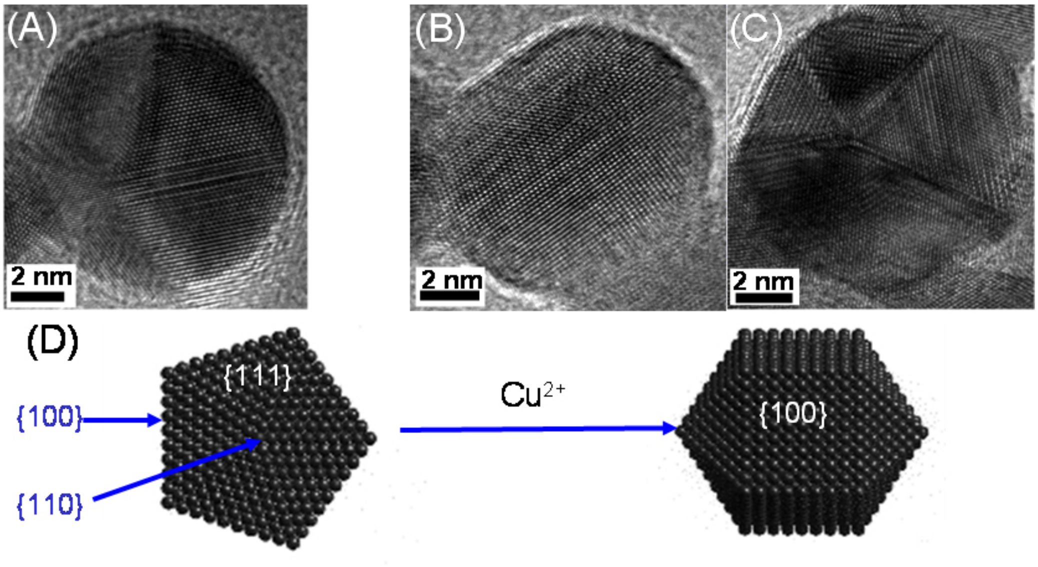


Figure S6. HRTEM images of (A) Au decahedron, and (B, C) AuCu pentagonal nanorod – (B) side view and (C) end view. (D) Mechanism of growth of AuCu pentagonal nanorod.

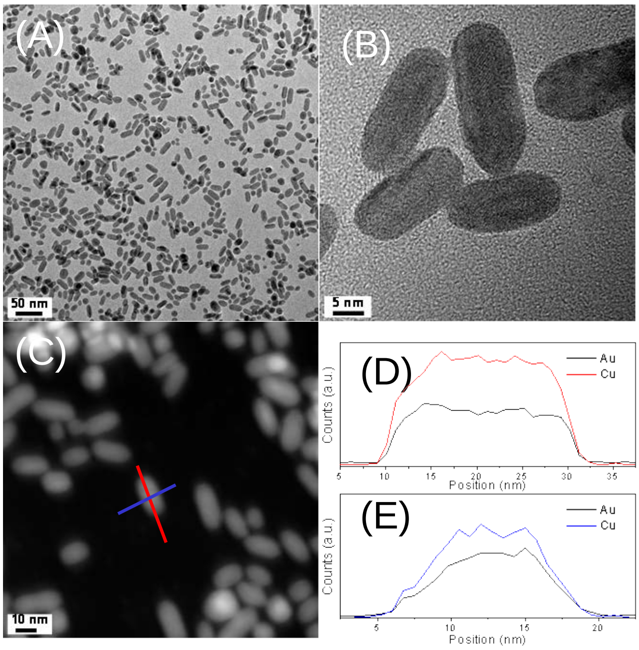


Figure S7. (A) TEM, (B) HRTEM, and (C) HAADF-STEM images of $AuCu_3$ nanorods. Au and Cu elemental profiles along the (D) red and (E) blue lines, respectively, across the $AuCu_3$ nanorod shown in (C).

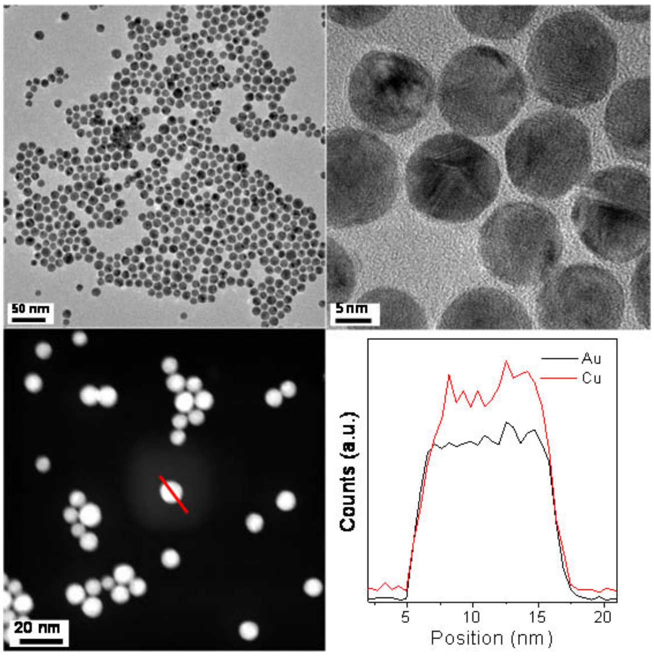


Figure S8. (A) TEM, (B) HRTEM, and (C) HAADF-STEM images of AuCu nanoparticles synthesized in oleic acid/tri-n-octylamine solution. (D) Au and Cu elemental profiles along the red line across the AuCu nanoparticle shown in (C).

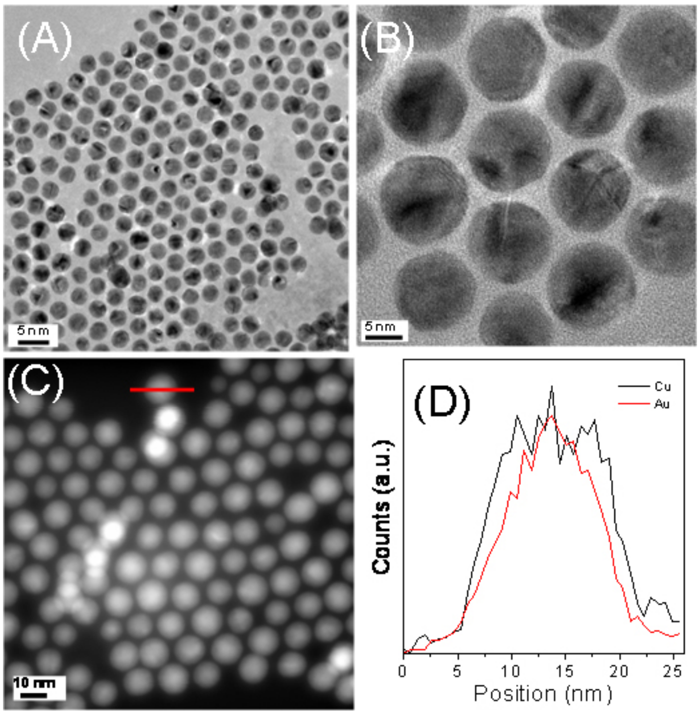


Figure S9. (A) TEM, (B) HRTEM, and (C) HAADF-STEM images of Au@Cu nanoparticles synthesized at 180°C. (D) Au and Cu elemental profiles along the red line across the AuCu nanoparticle shown in (C).

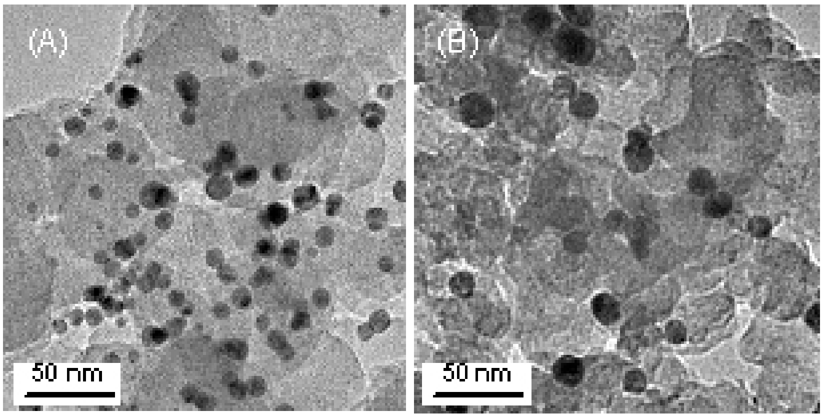
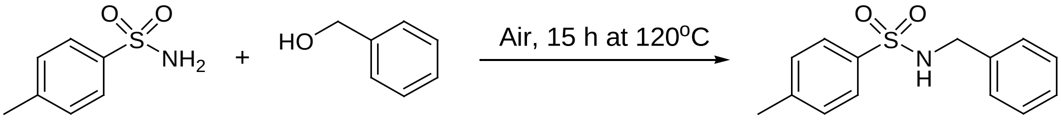


Figure S10. TEM images of AuCu/C (a) before and (b) after the coupling reaction.

Table S1. Alkylation of sulfonamide with benzyl alcohol.[a]



Entry	Catalyst	Cu loading [wt%][b]	Cu used [mol%]	K_2CO_3 [mol%]	Yield [%][c]
1	AuCu/C	2.8	1	20	88
2	AuCu/C	2.8	1	0	0
3	C	0	0	20	< 1
4	None	0	0	20	4

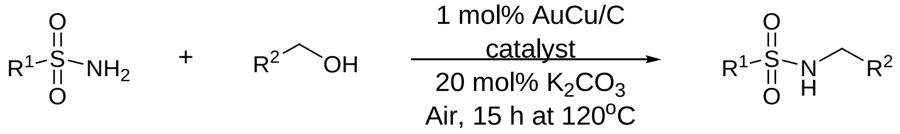
[a] Reaction conditions: *p*-toluenesulfonamide (0.2 mmol), benzyl alcohol (1 mmol), 120°C, 15 h under air. [b] Cu content in nanomaterial was determined from ICP-MS analysis. [c] Isolated and unoptimized yield based on *p*-toluenesulfonamide.

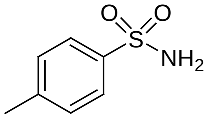
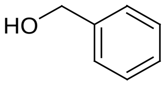
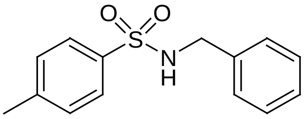
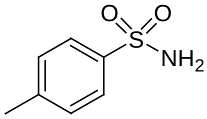
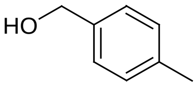
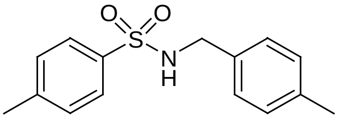
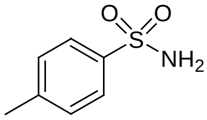
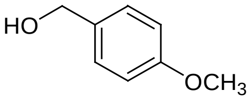
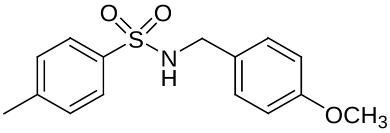
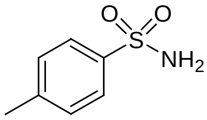
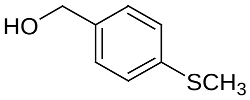
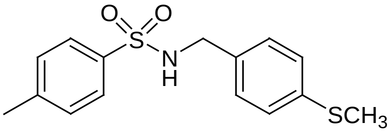
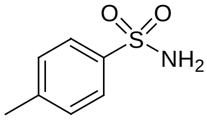
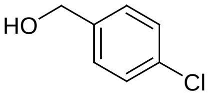
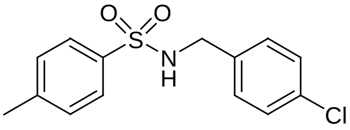
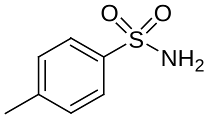
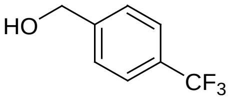
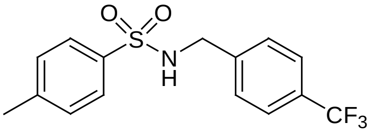
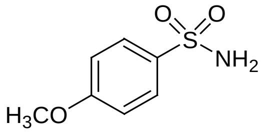
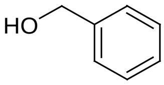
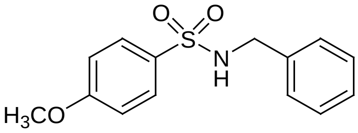
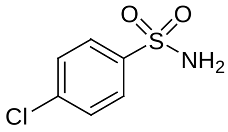
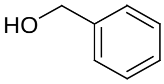
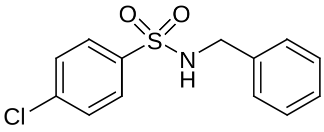
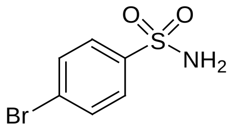
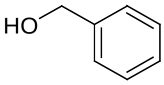
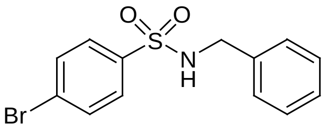
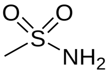
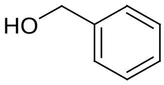
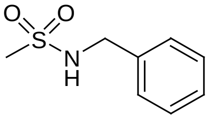
Table S2. Recycling of AuCu/C nanomaterial for the alkylation of sulfonamide with benzyl alcohol.[a]

Run #	1	2	3	4	5
Yield (%)[b]	88	88	86	90	91

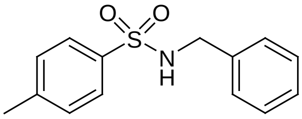
[a] Reaction conditions: AuCu/C catalyst (1 mol% Cu), *p*-toluenesulfonamide (0.2 mmol), benzyl alcohol (1 mmol), K_2CO_3 (20 mol%), 120°C, 15 h under air. [b] Isolated and unoptimized yield based on *p*-toluenesulfonamide.

Table S3. Scope of sulfonamide alkylation with alcohol.[a]

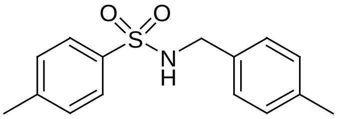


Entry	Sulfonamide	Alcohol	Product	Yield [%][b]
1				88, 97[c]
2				90
3				98
4				98
5				89
6				95
7				92
8				80, 96[c]
9				71, 99[c]
10				93

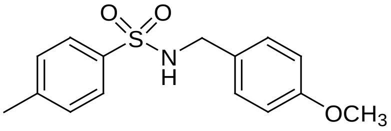
[a] Reaction conditions: AuCu/C catalyst (1 mol% Cu), sulfonamide (0.2 mmol), alcohol (1 mmol), K_2CO_3 (20 mol%), 120°C, 15 h under air. [b] Isolated and unoptimized yield based on sulfonamide. [c] 150°C, 15 h under air.



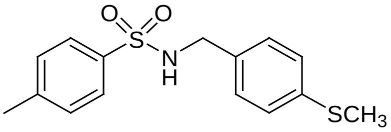
N-benzyl-4-methylbenzenesulfonamide. Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.80–7.79 (t, 1H), 7.77–7.76 (t, 1H), 7.35–7.27 (m, 5H), 7.22–7.20 (m, 2H), 4.64 (t, *J* = 5.98 Hz, 1H), 4.14 (d, *J* = 6.24 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 143.60, 136.75, 136.20, 129.78, 128.73, 127.98, 127.89, 127.20, 47.31, 21.58. GC-MS: 260 $(M-H)^+$, 106 (base).



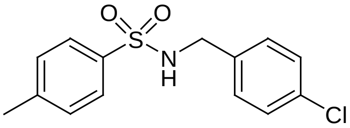
N-(4-methylbenzyl)-4-methylbenzenesulfonamide. Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.79–7.78 (t, 1H), 7.77–7.76 (t, 1H), 7.34–7.32 (m, 2H), 7.12–7.07 (m, 4H), 4.58 (t, *J* = 5.98 Hz, 1H), 4.09 (d, *J* = 6.12 Hz, 2H), 2.46 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 143.55, 137.77, 136.77, 133.14, 129.76, 129.38, 127.87, 127.21, 47.08, 21.57, 21.10. GC-MS: 275 (M^+), 120 (base).



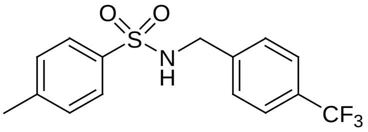
N-(4-methoxybenzyl)-4-methylbenzenesulfonamide. Yield: 98%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.79–7.78 (t, 1H), 7.77–7.76 (t, 1H), 7.34–7.32 (m, 2H), 7.14–7.10 (m, 2H), 6.84–6.82 (t, 1H), 6.81–6.80 (t, 1H), 4.55 (t, *J* = 5.90 Hz, 1H), 4.07 (d, *J* = 6.08 Hz, 2H), 3.79 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 159.31, 143.53, 136.81, 129.76, 129.29, 128.20, 127.20, 114.06, 55.30, 46.82, 21.57. GC-MS: 291 (M^+), 135 (base).



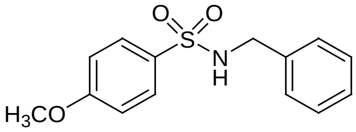
N-(4-methylthiobenzyl)-4-methylbenzenesulfonamide. Yield: 98%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.78–7.77 (t, 1H), 7.75–7.74 (t, 1H), 7.34–7.33 (m, 1H), 7.32–7.31 (m, 1H), 7.18–7.15 (m, 2H), 7.13–7.10 (m, 2H), 4.68 (t, *J* = 6.10 Hz, 1H), 4.09 (d, *J* = 6.20 Hz, 2H), 2.47 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 143.61, 138.38, 136.77, 132.94, 129.78, 128.42, 127.18, 126.64, 46.86, 21.57, 15.75. GC-MS: 307 (M^+), 151 (base).



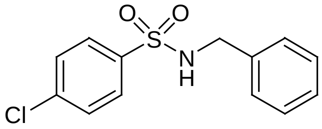
N-(4-chlorobenzyl)-4-methylbenzenesulfonamide. Yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.77–7.76 (t, 1H), 7.75–7.74 (t, 1H), 7.33–7.31 (m, 2H), 7.28–7.26 (t, 1H), 7.25–7.24 (t, 1H), 7.17–7.13 (m, 2H), 4.73 (t, J = 6.21 Hz, 1H), 4.11 (d, J = 6.32 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 143.74, 136.72, 134.80, 133.79, 129.81, 129.22, 128.84, 127.16, 46.59, 21.57. GC-MS: 294 $(M-H)^+$, 140 (base).



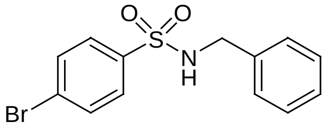
N-(4-trifluoromethylbenzyl)-4-methylbenzenesulfonamide. Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.75–7.74 (t, 1H), 7.73–7.72 (t, 1H), 7.53 (d, J = 8.09 Hz, 2H), 7.35–7.33 (m, 2H), 7.31–7.29 (m, 2H), 4.89 (t, J = 6.30 Hz, 1H), 4.21 (d, J = 6.44 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 143.82, 140.40, 140.38, 140.36, 136.70, 130.26, 129.95, 129.81, 128.05, 127.14, 125.64, 125.60, 125.56, 125.53, 125.29, 122.58, 46.71, 21.53. GC-MS: 329 (M^+), 174 (base).



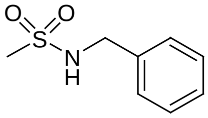
N-benzyl-4-methoxybenzenesulfonamide. Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.85–7.83 (t, 1H), 7.82–7.81 (t, 1H), 7.33–7.27 (m, 3H), 7.22–7.20 (m, 2H), 7.01–7.00 (t, 1H), 6.99–6.97 (t, 1H), 4.62 (t, J = 6.10 Hz, 1H), 4.13 (t, J = 6.20 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 162.95, 136.24, 131.33, 129.34, 128.74, 127.96, 127.89, 114.29, 55.66, 47.27. GC-MS: 277 (M^+), 106 (base).



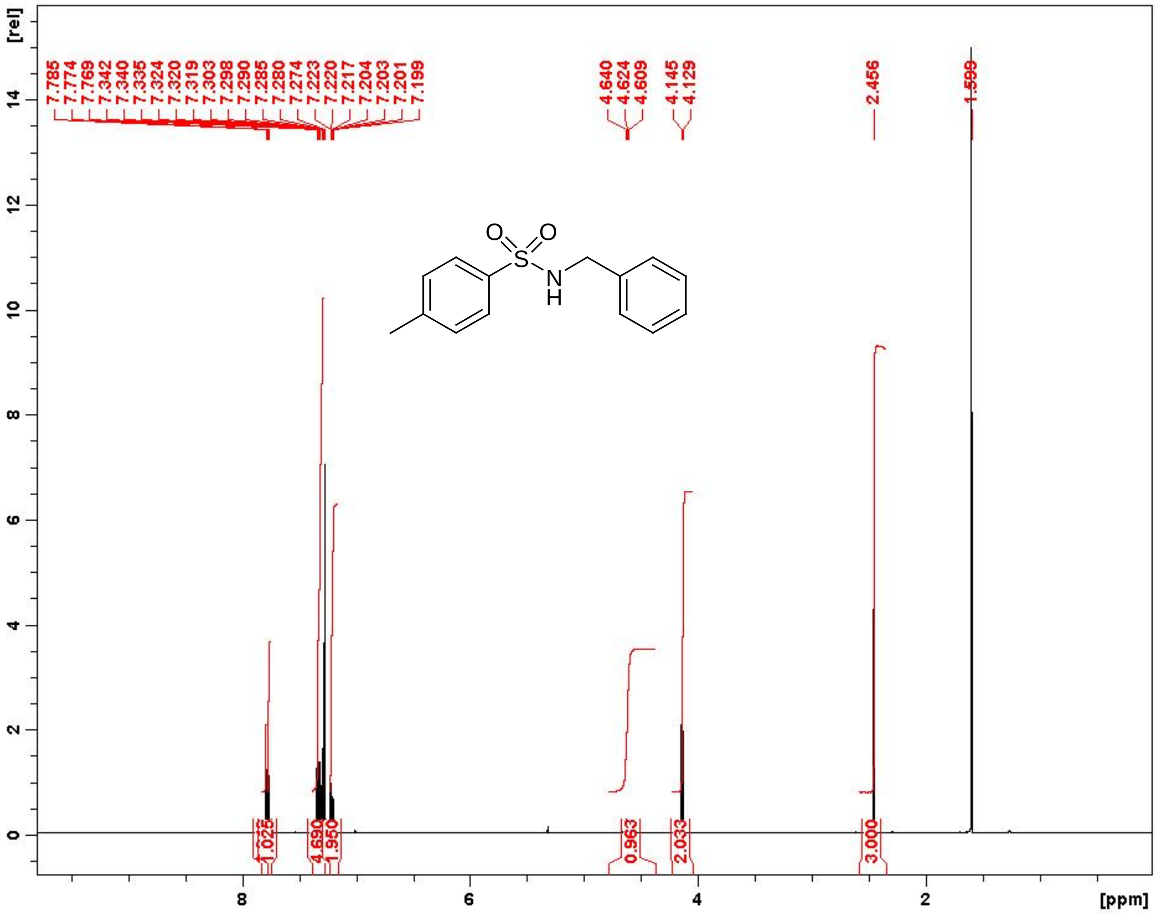
N-benzyl-4-chlorobenzenesulfonamide. Yield: 80 %. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.82–7.81 (t, 1H), 7.80–7.78 (t, 1H), 7.50–7.49 (t, 1H), 7.48–7.47 (t, 1H), 7.31–7.28 (m, 3H), 7.21–7.18 (m, 2H), 4.77 (t, J = 5.94 Hz, 1H), 4.17 (d, J = 6.12 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 139.23, 138.45, 135.83, 129.43, 128.80, 128.59, 128.12, 127.88, 47.32. GC-MS: 280 $(M\text{-}H)^+$, 106 (base).



N-benzyl-4-bromobenzenesulfonamide. Yield: 71 %. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.74–7.71 (m, 2H), 7.67–7.63 (m, 2H), 7.33–7.28 (m, 3H), 7.22–7.18 (m, 2H), 4.77 (t, J = 5.96 Hz, 1H), 4.17 (d, J = 6.12 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 138.99, 135.82, 132.41, 128.81, 128.68, 128.12, 127.89, 127.71, 47.33. GC-MS: 326 (M^+), 106 (base).



N-benzylmethanesulfonamide. Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.41–7.31 (m, 5H), 4.72 (m, 1H), 4.34 (d, J = 6.12 Hz, 2H), 2.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 136.61, 128.95, 128.17, 127.91, 47.22, 41.14. GC-MS: 185 (M^+), 106 (base).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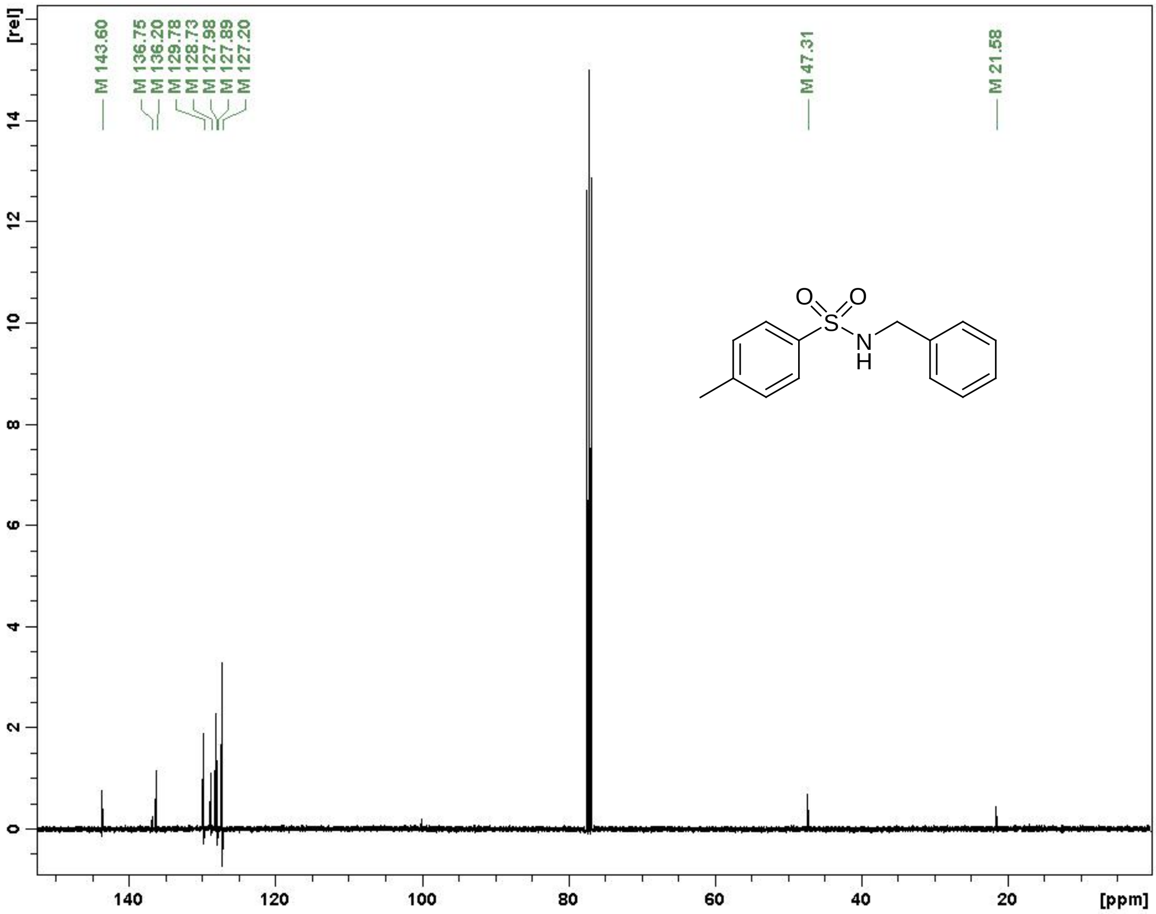
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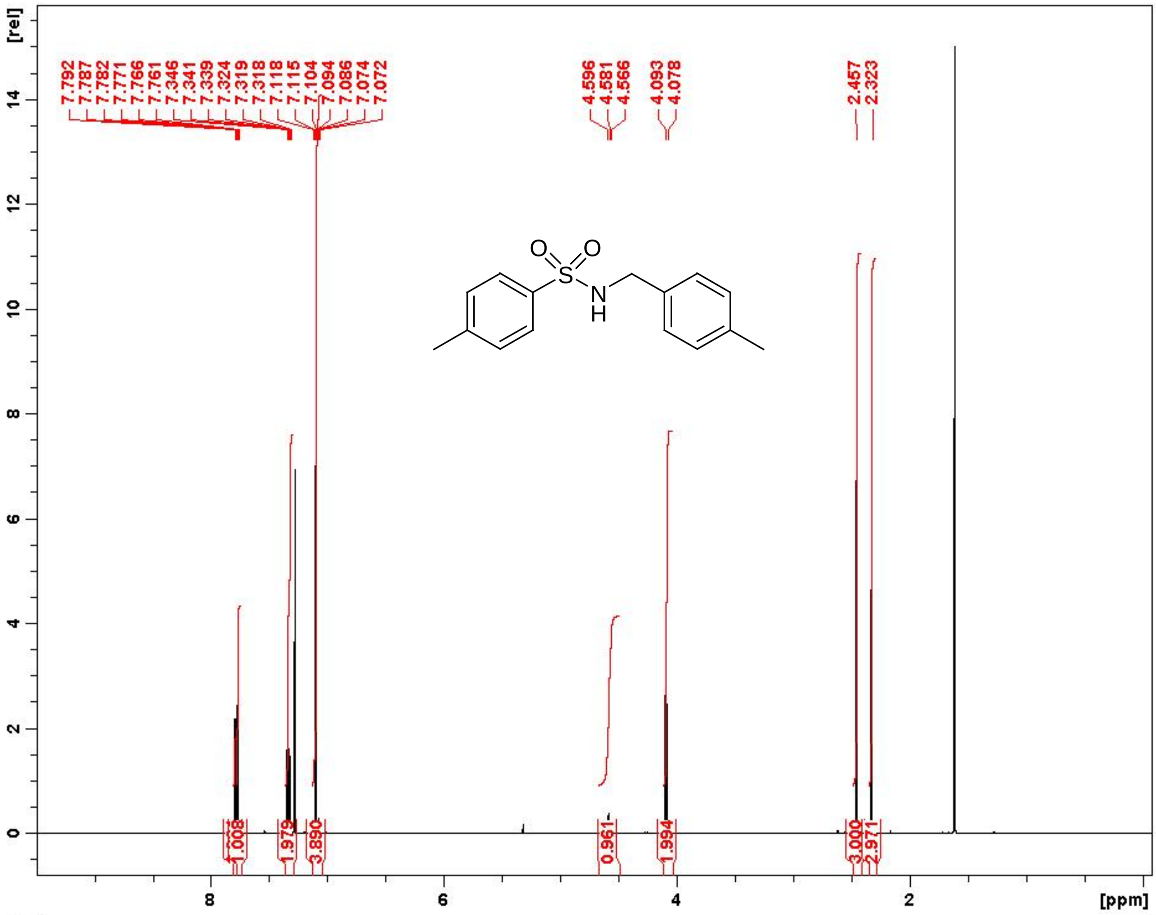
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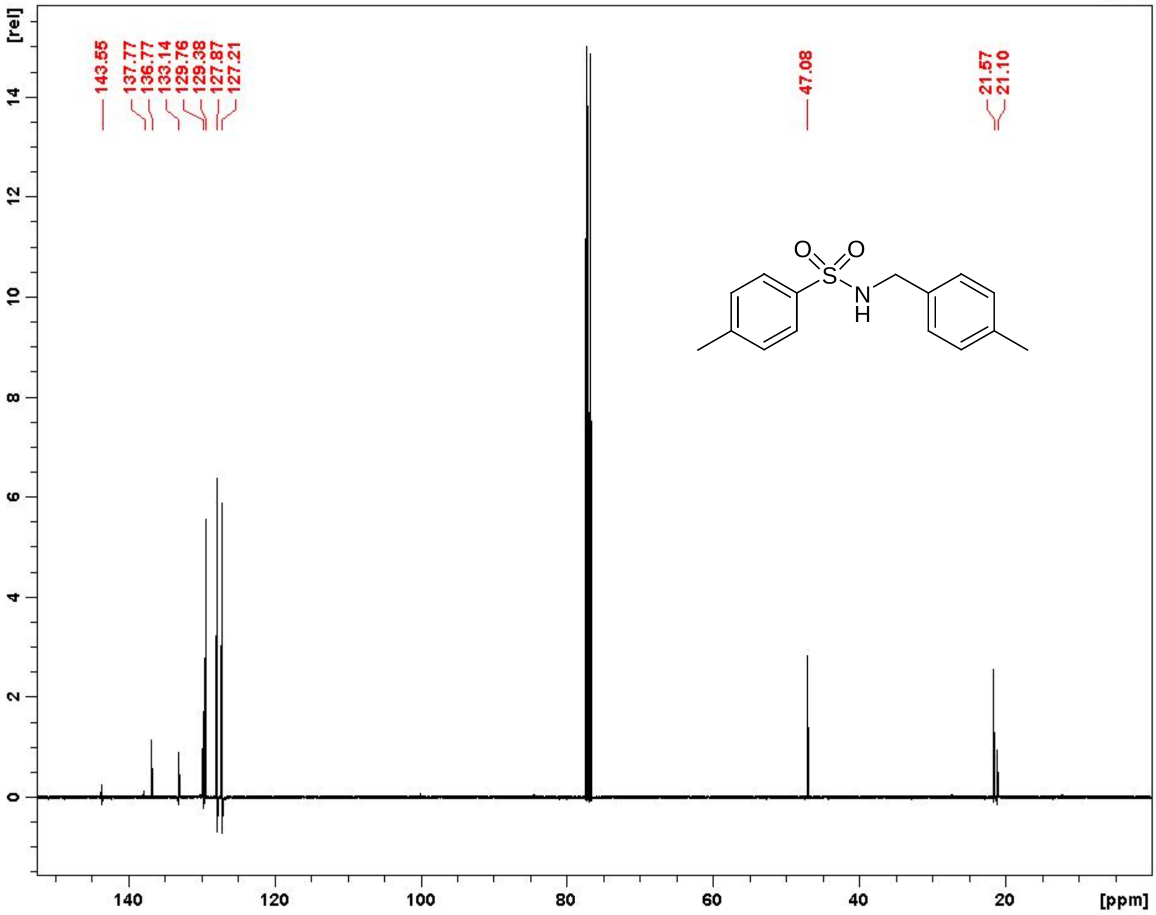
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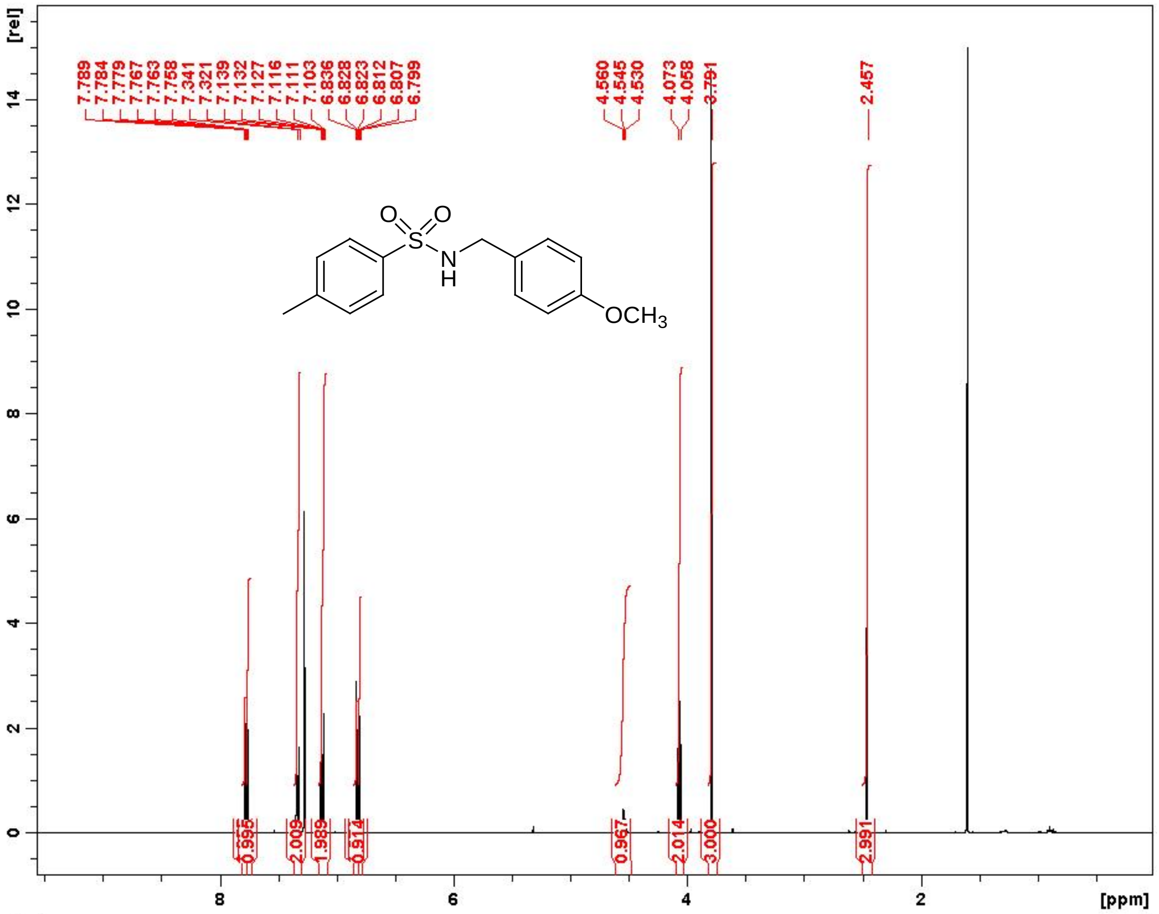
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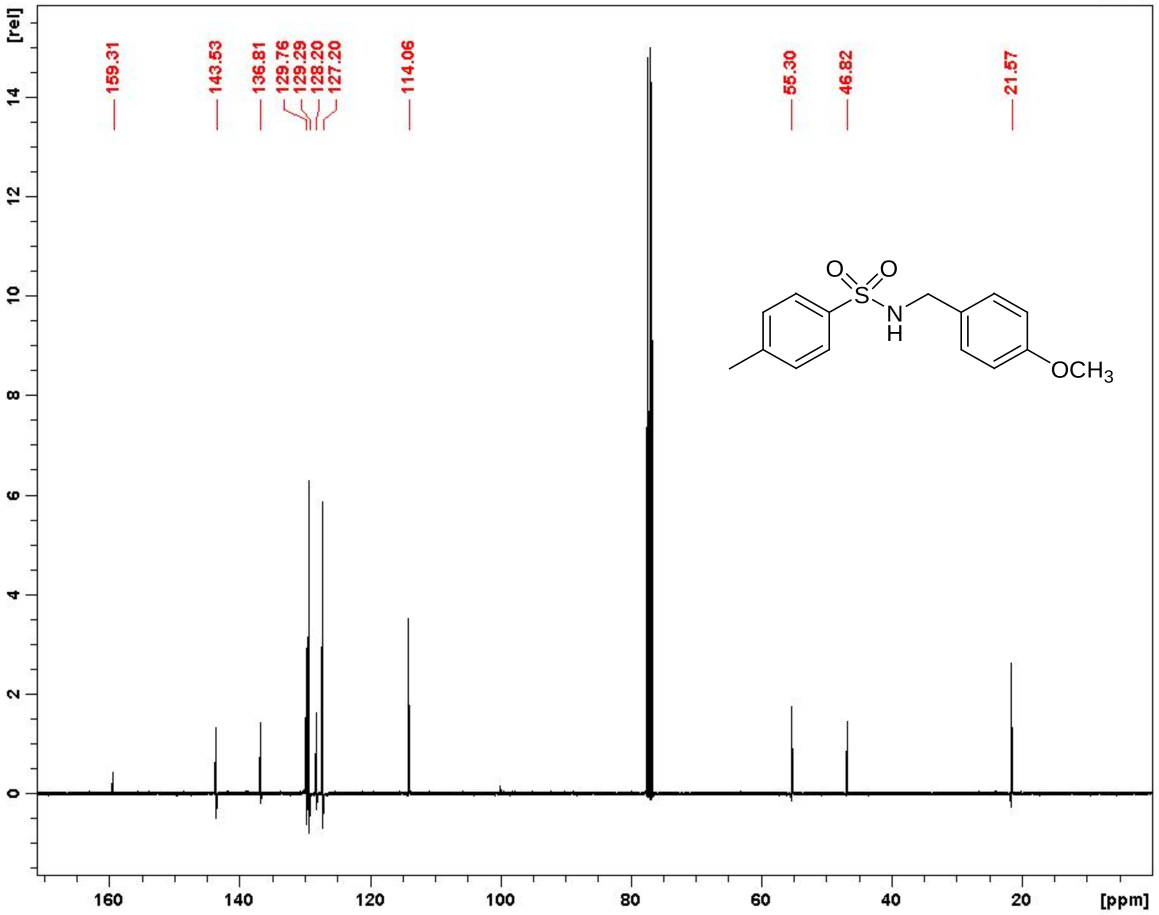
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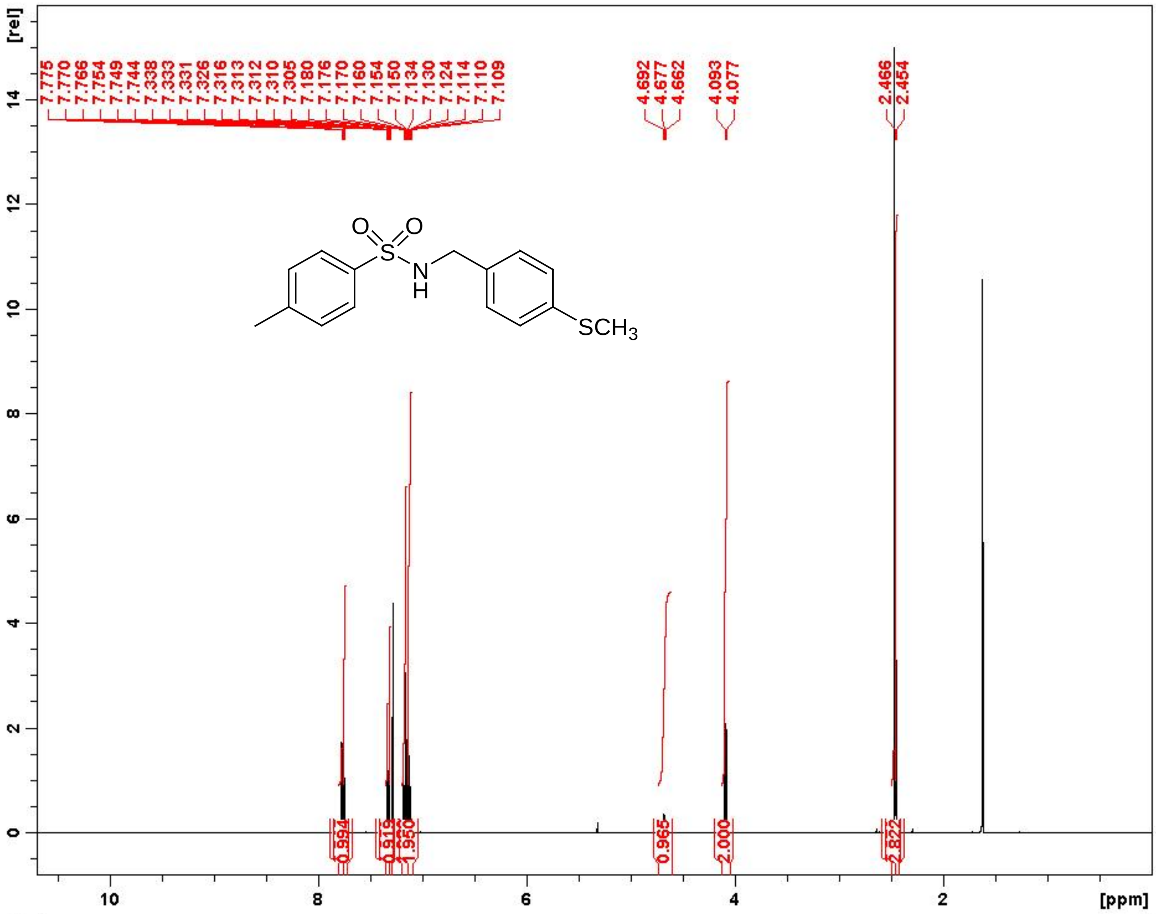
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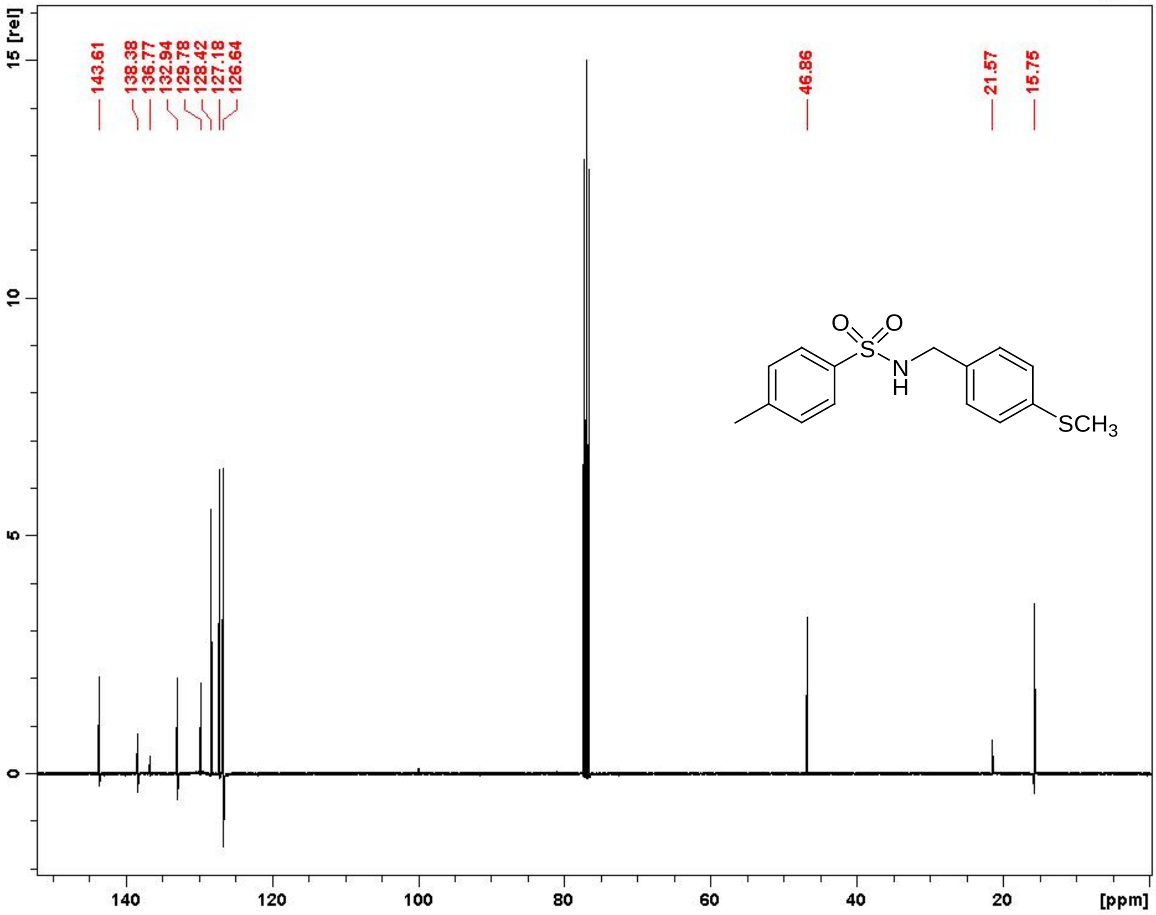
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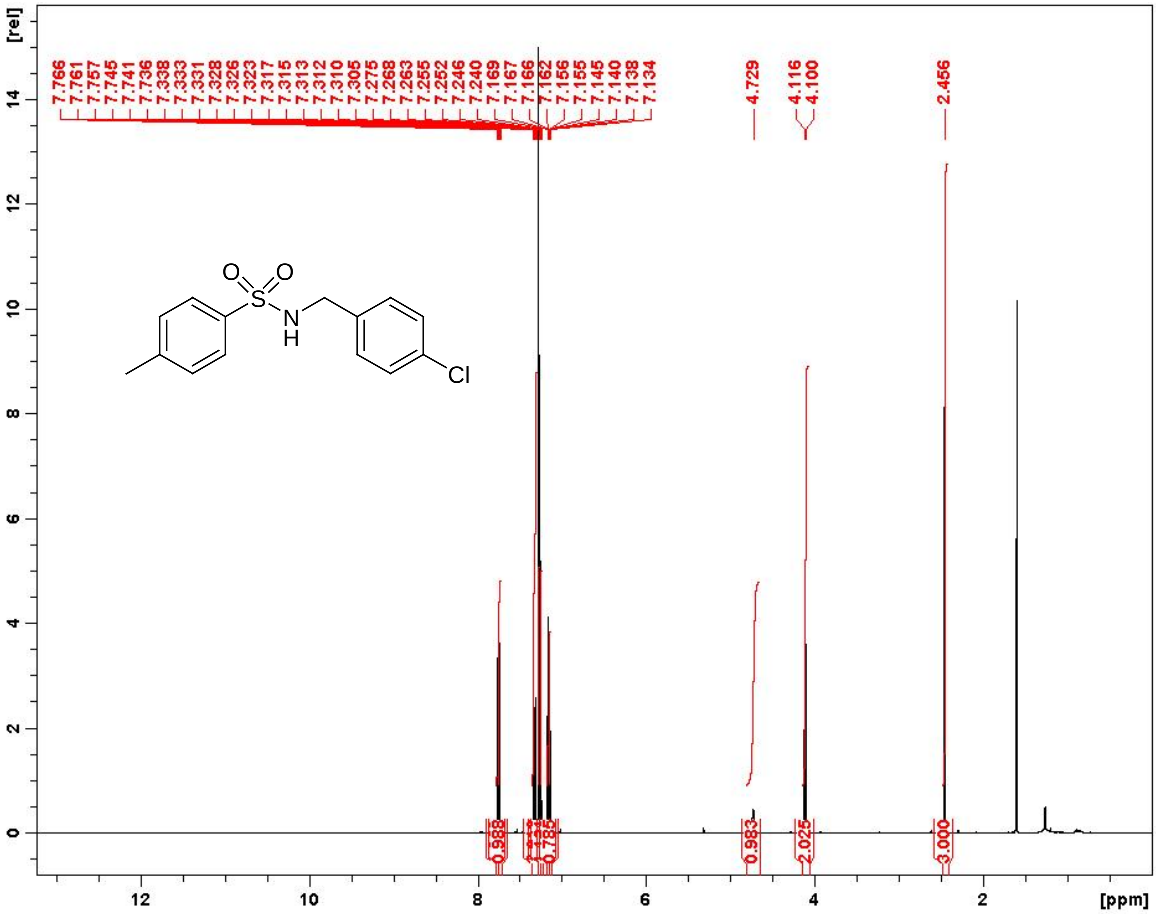
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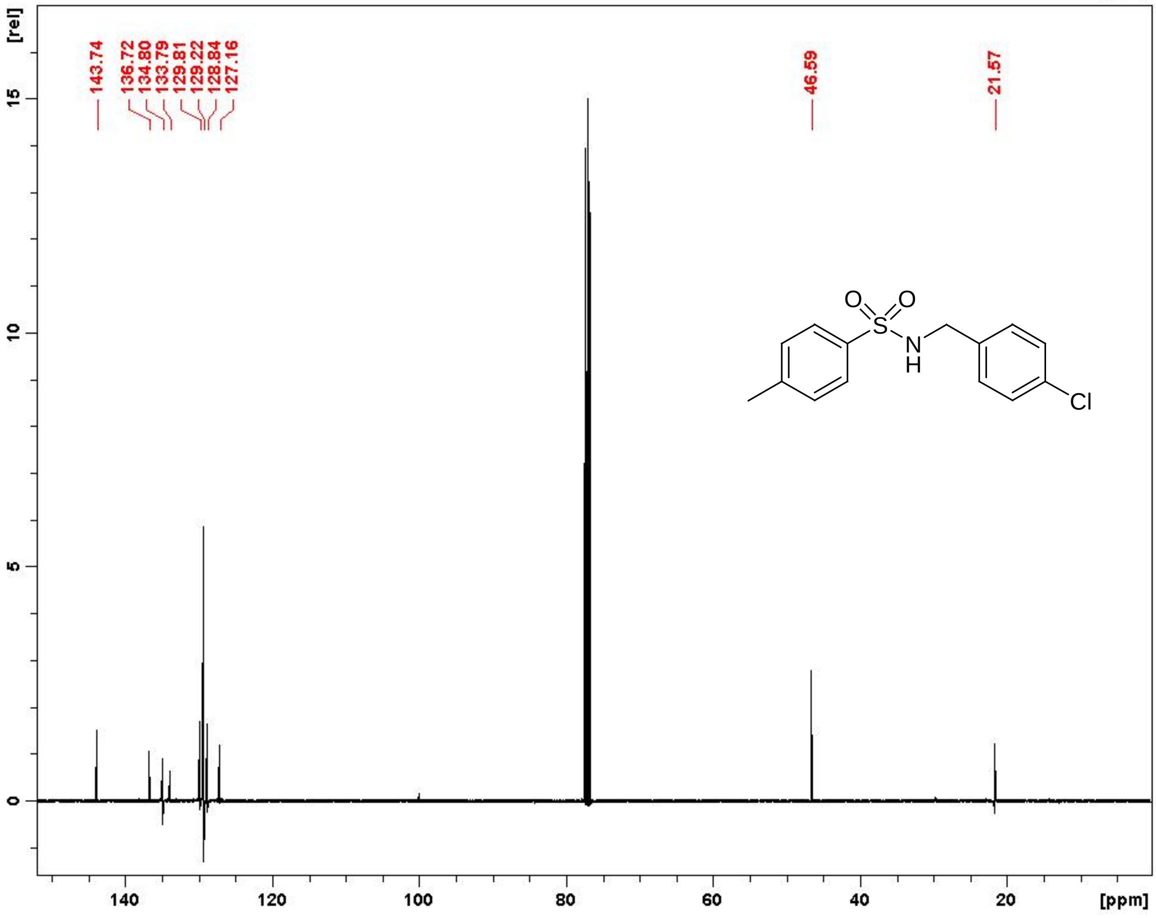
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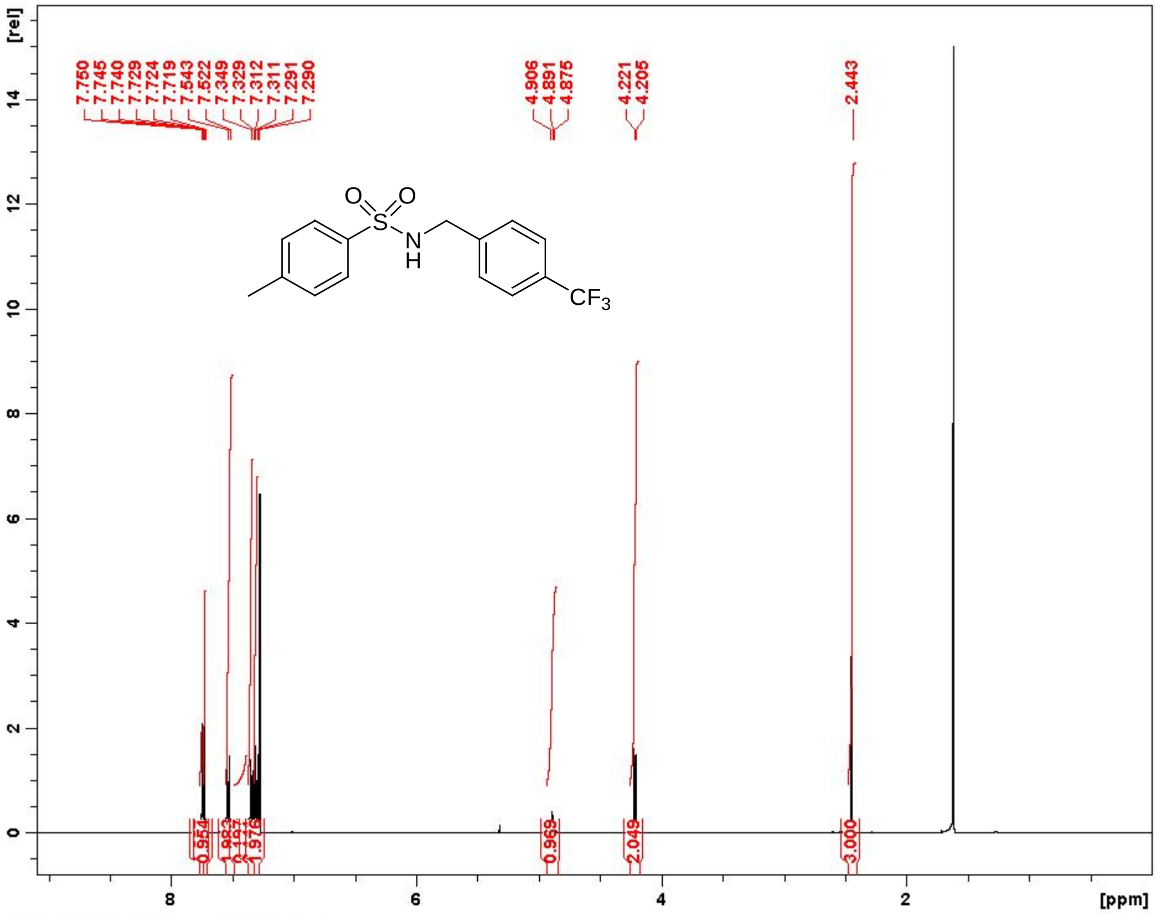
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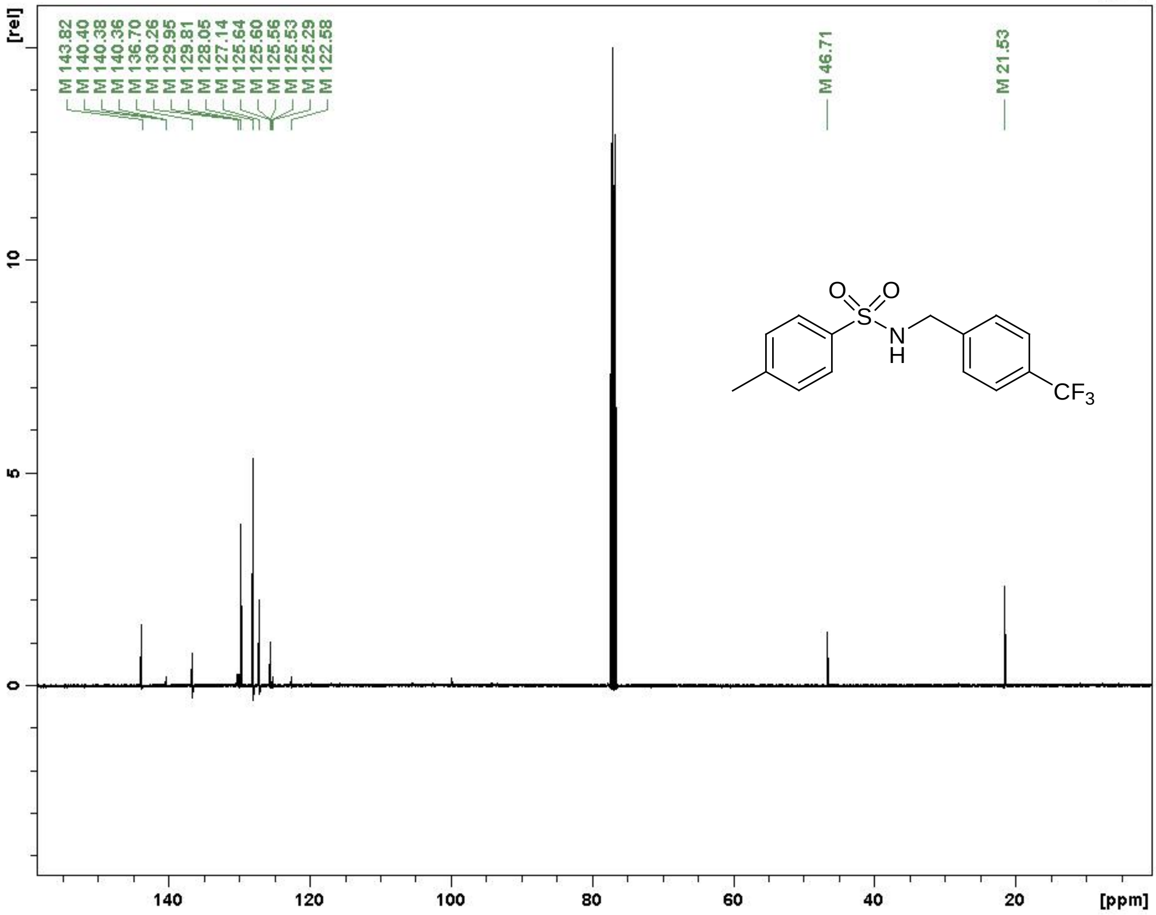
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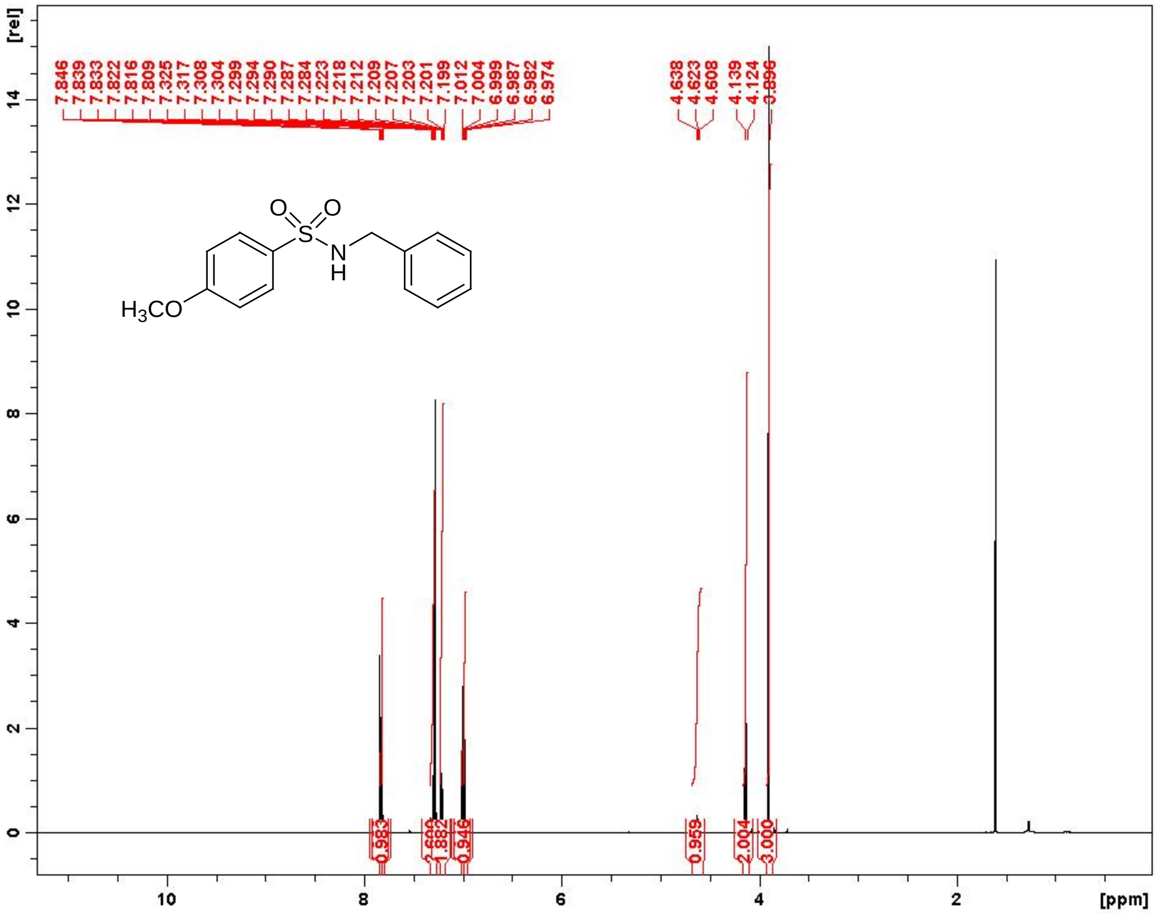
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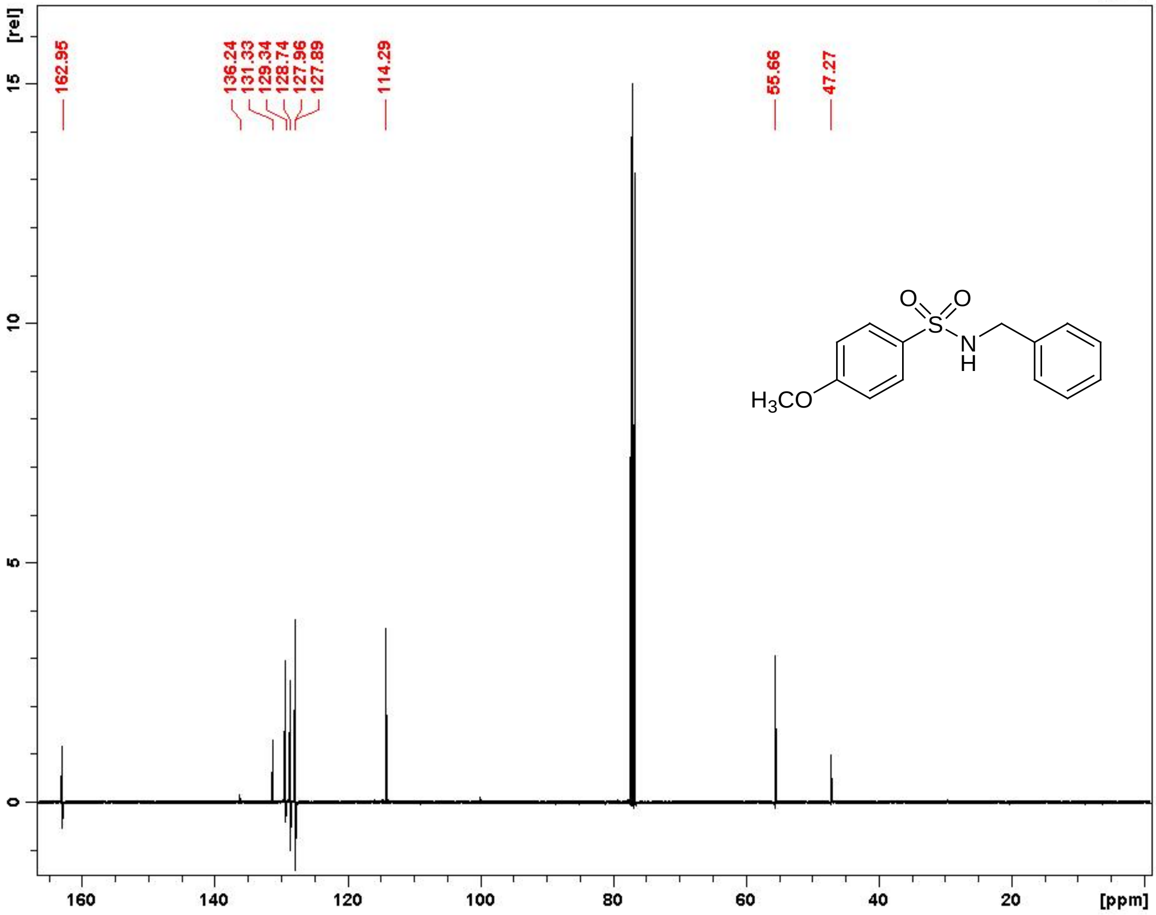
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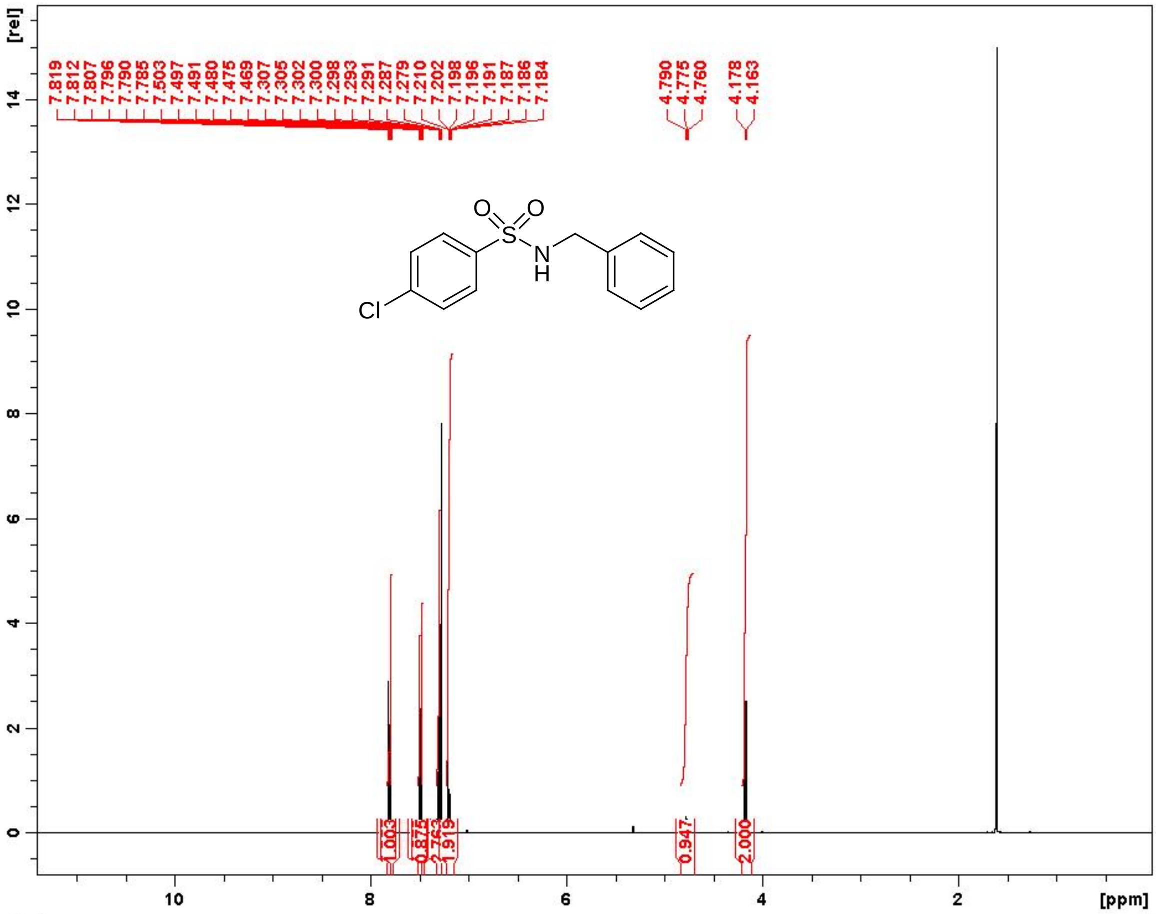
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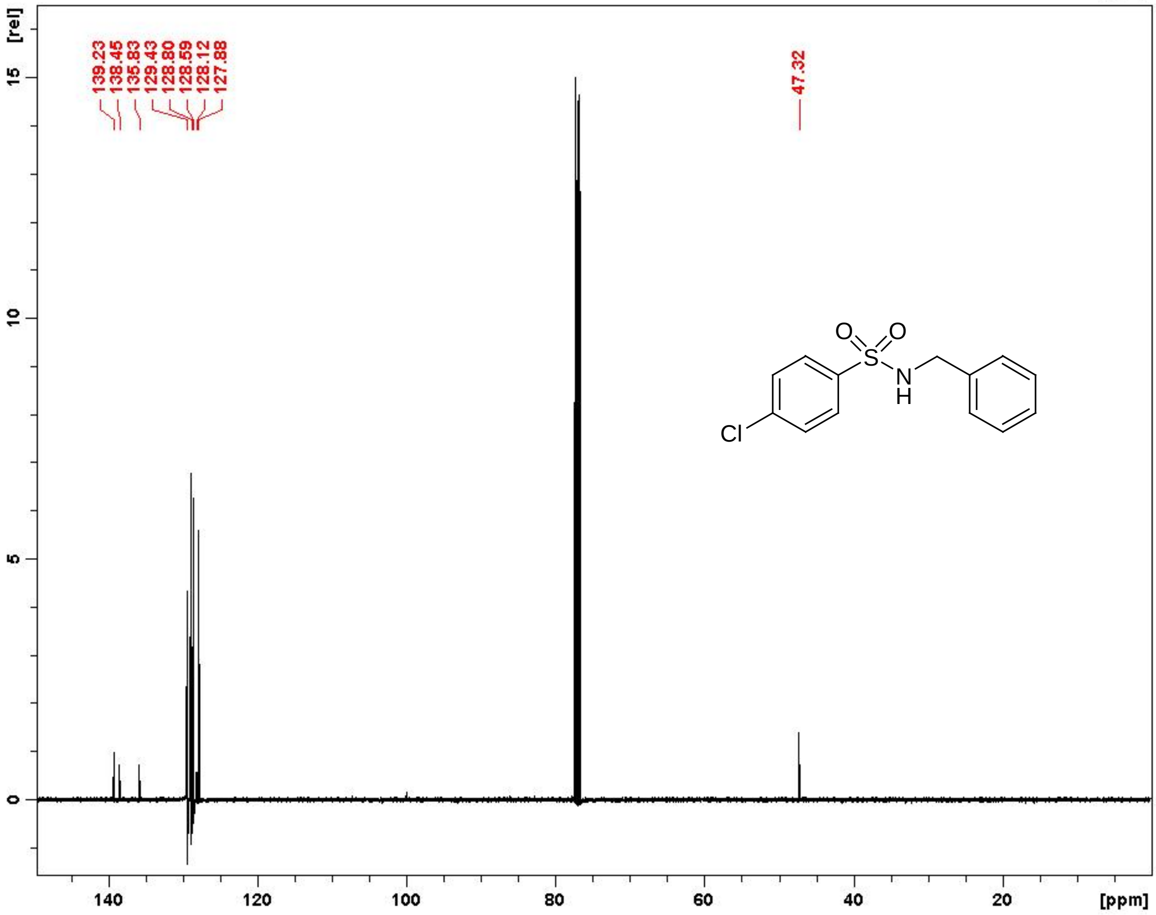
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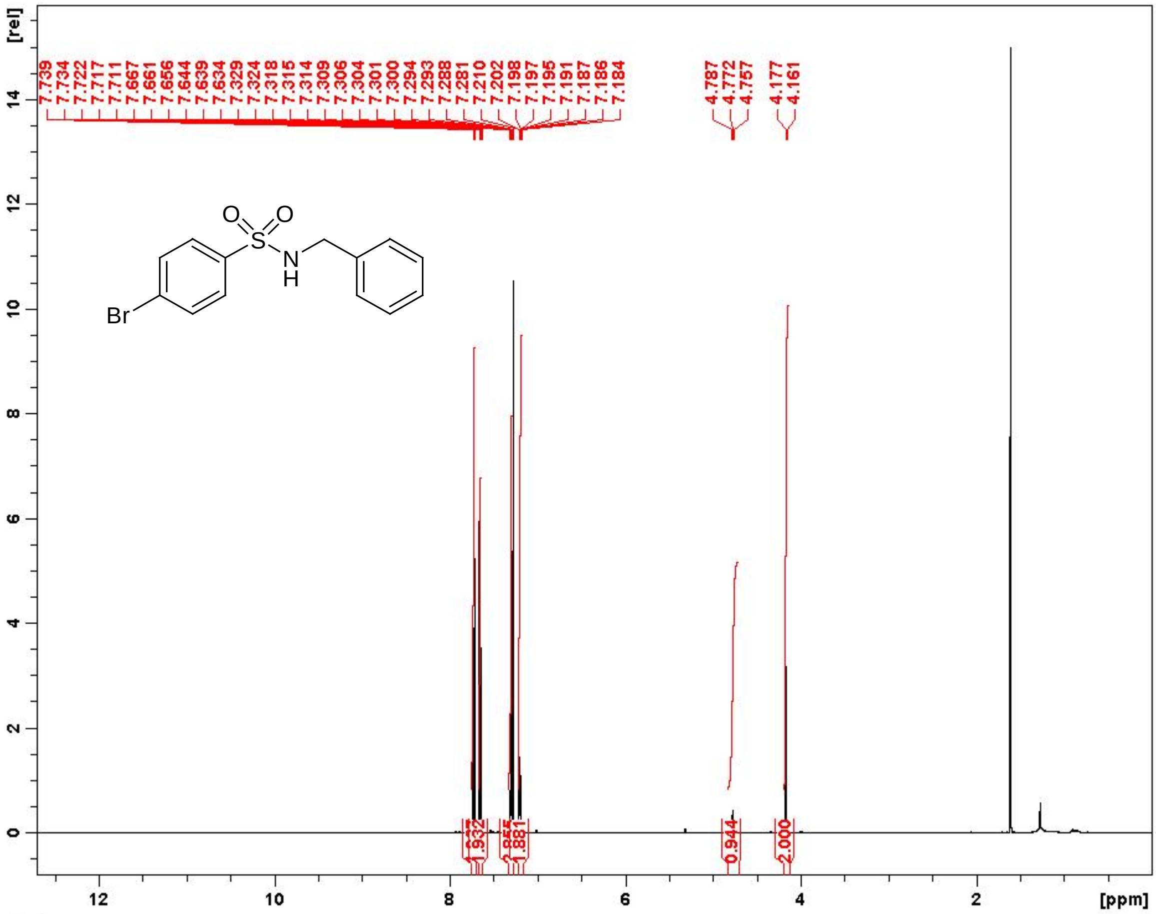
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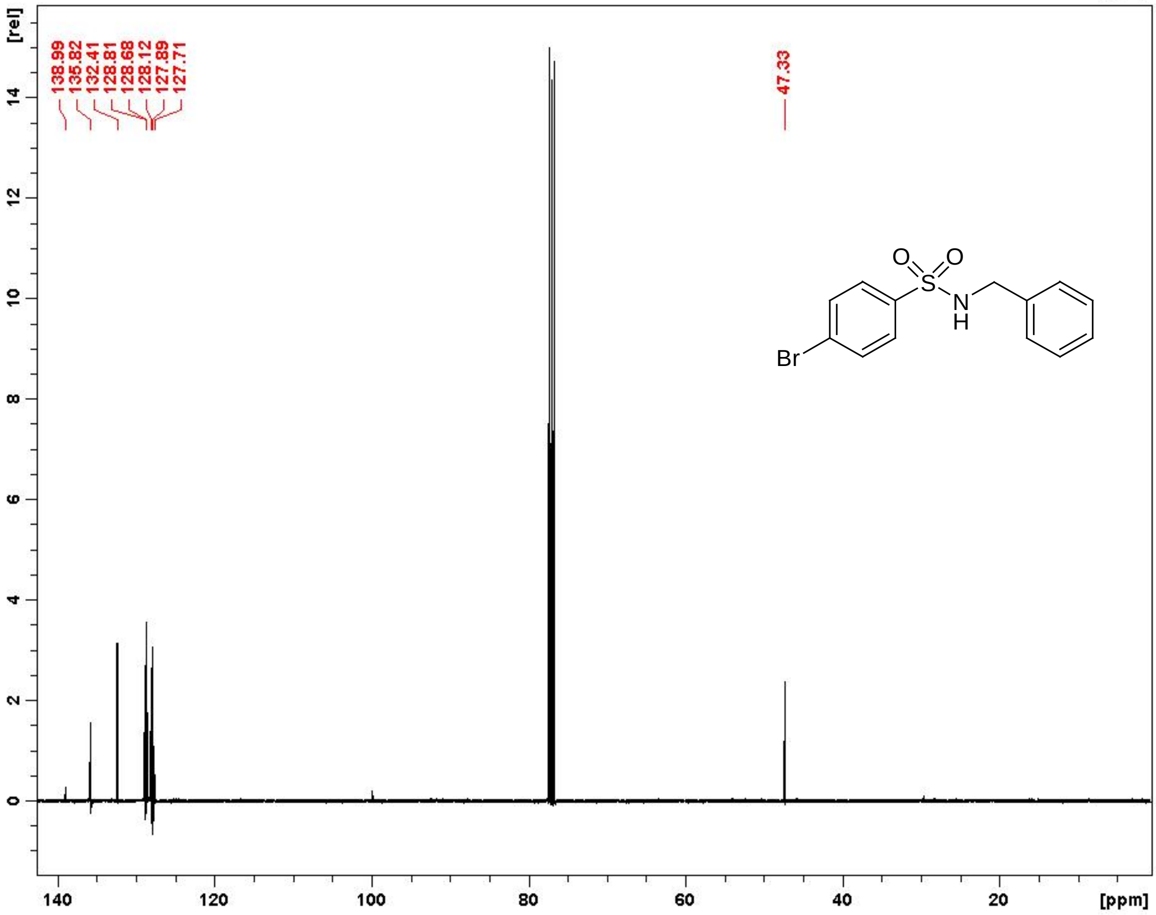
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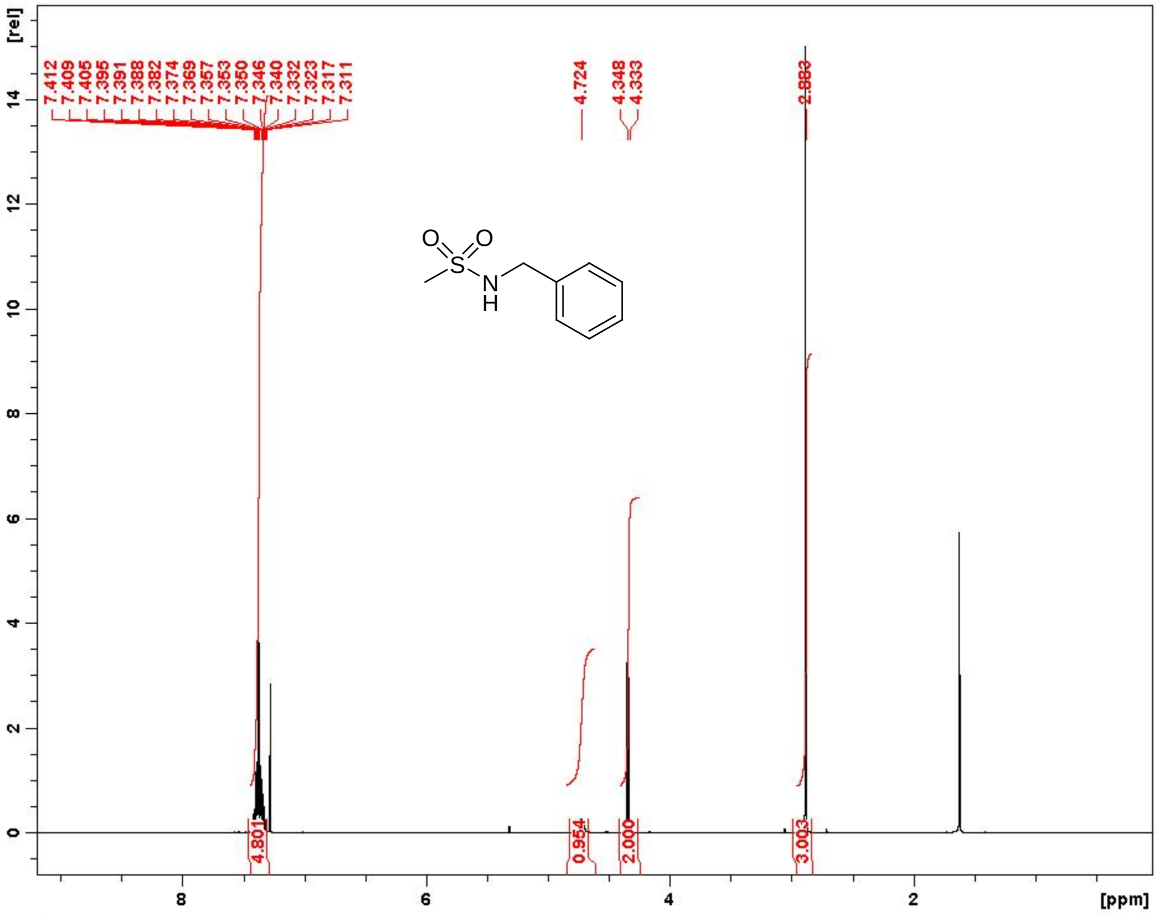
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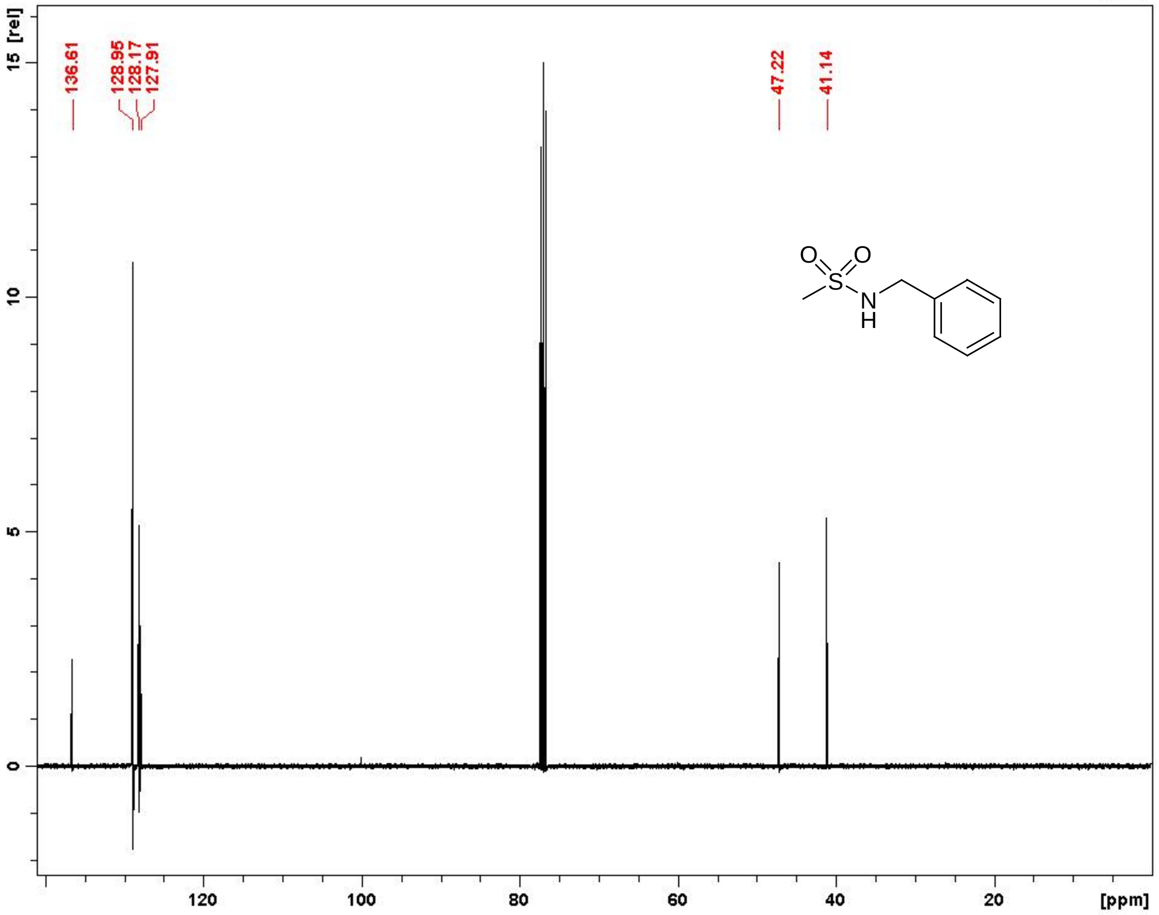
2
[ppm]


15 [rel]
136.61
128.95
128.17
127.91
47.22
41.14
O
S
O
N
H
10
5
0
120
100
80
60
40
20
[ppm]