SUPPLEMENTARY INFORMATION

Decarboxylative sulfation by persulfates

Zhen Xia, Ting Deng, Chunlan Song and Jiakun Li*

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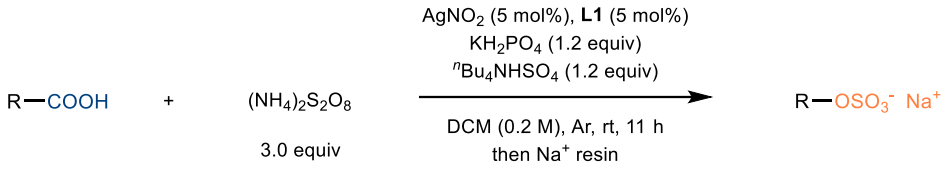
MATERIALS AND METHODS

All glasswares were oven dried at 110 °C for several hours and cooled down under vacuum. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The sulfation reactions were performed in 4.0 mL (15 x 45 mm) glass vials on Synthware H221520 heating block (15.3 x 20 mm) for heat transmission. Flash chromatography columns were packed with 200 mesh silica gel in petroleum (bp. 60-90 °C). Na^+ resin (Dowex® 50WX8 200-400 mesh, cas: 11119-67-8) were obtained from commercial suppliers. ^1H, ^{13}C and ^{19}F NMR data were recorded with Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. Chemical shifts are reported in ppm with the solvent resonance as the internal standard. For ^1H NMR: $CDCl_3$, 7.26; CD_3OD, 3.31; DMSO-*d*$_6$, 2.50; D_2O, 4.79; For ^{13}C NMR: $CDCl_3$, 77.16; CD_3OD, 49.00; DMSO-*d*$_6$, 39.52. Data is reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentamer, h = hexamer, m = multiplet, br = broad; coupling constants in Hz. High resolution mass spectra (HRMS) were measured on a Finnigan-MAT95XP equipped with EI ion source and double-focusing mass analyzer, or a Bruker APEX III 7.0 Tesla FTMS with ESI ion source.

EXPERIMENTAL DATA

1 General procedure for decarboxylative sulfation



To a 4 mL borosilicate vial equipped with a stir bar was added carboxylic acid (0.2 mmol, 1.0 equiv), $AgNO_2$ (1.5 mg, 0.01 mmol, 5 mol%), 4,7-diphenyl-1,10-phenanthroline **L1** (3.3 mg, 0.01 mmol, 5 mol%), ammonium persulfate (136.9 mg, 0.6 mmol, 3.0 equiv), tetrabutylammonium hydrogen sulfate (81.5 mg, 0.24 mmol, 1.2 equiv) and potassium phosphate monobasic (32.6 mg, 0.24 mmol, 1.2 equiv). The vial was evacuated and backfilled with argon for three times. 1 mL CH_2Cl_2 was added, and the reaction mixture was stirred at room temperature for 11 h. 200 mg $NaHCO_3$ was added to quench the reaction and filtered with CH_2Cl_2 (3 × 30 mL) as eluent. The filtrate was collected and concentrated by rotary evaporation. The residue was purified by flash chromatography on

silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford the product in the form of tetrabutylammonium sulfate salt.

The tetrabutylammonium sulfate salt product was dissolved in a small amount of MeOH, and then passed through an activated Na^+ resin (Dowex® 50WX8 200-400 mesh, cas: 11119-67-8) using MeOH as the eluent at a flow rate of about 1 drop per second. The resulting organic phase was collected and evaporated under vacuum, then diluted with CH_2Cl_2 (50 mL). The desired product organosulfate sodium precipitated in CH_2Cl_2 solution. These solids were separated from the liquid phase through a sand core funnel equipped with a short cotton pad, and then the solid were washed repeatedly with CH_2Cl_2. The solid product and organic phase containing tetrabutylammonium sulfate salt were collected separately. The unexchanged tetrabutylammonium sulfate salt solution was concentrated by rotary evaporation and re-dissolved in a small amount of MeOH. It was then passed through an activated Na^+ resin using MeOH as the eluent. This process was continued until no desired product precipitated from CH_2Cl_2 solution. Finally, the pure product was obtained after each ion exchange step was combined.

Note:

Organosulfate is labile to acid and temperature.[1] In most cases, two rounds of flash chromatography are necessary to isolate tetrabutylammonium sulfate salt, resulting in some loss of product. Additionally, five to ten rounds of ion exchange are required, with a small amount of primary tetrabutylammonium sulfate remaining exchanged. Due to the higher solubility of the secondary product in CH_2Cl_2 compared to the primary product, 10% to 20% of the secondary product remains soluble in CH_2Cl_2 as the tetrabutylammonium sulfate salt. This portion of the mixture containing sodium salt and tetrabutylammonium salt will establish a dynamic equilibrium during ion exchange, making it unattainable as final product. These various factors collectively contribute to a decrease in the overall isolated yield.

2 Physicochemical properties between carboxylic acids and organosulfates.

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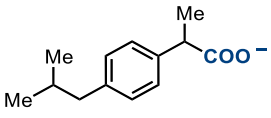
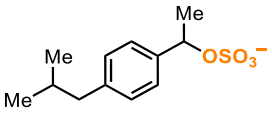
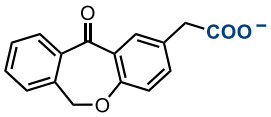
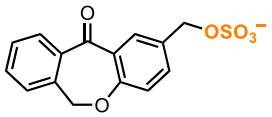
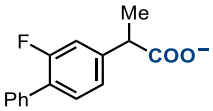
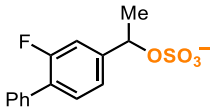
		
logD$_{7.4}$	1.01	1.31
logP$_{app}$	3.46	2.25
p*K*a	4.39	0.12

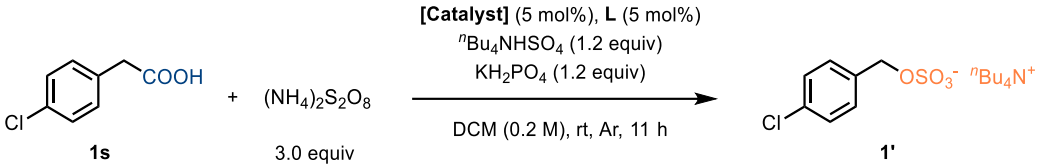
	isoxepac	
		
logD$_{7.4}$	0.29	0.54
logP$_{app}$	2.54	1.42
p*K*a	4.32	0.06

	flurbiprofen	
		
logD$_{7.4}$	1.07	1.25
logP$_{app}$	3.44	2.25
p*K*a	4.36	0.12

Calculated p*K*$_a$, logD$_{7.4}$ and P$_{app}$ values were obtained with ChemAxon. https://chemaxon.com/calculators-and-predictors.

3 Screening reaction conditions for decarboxylative sulfation

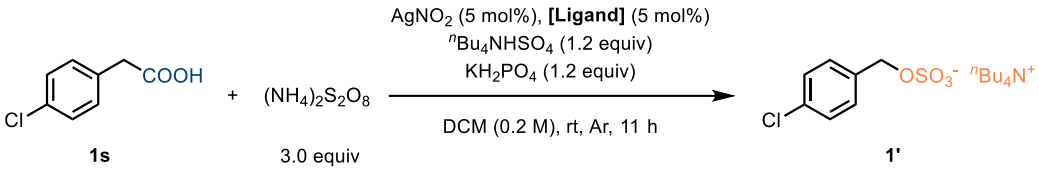
3.1 Optimization of catalysts

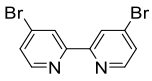
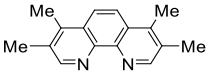
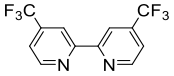
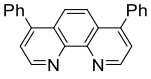
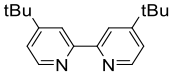
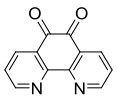
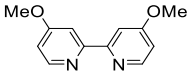
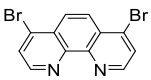
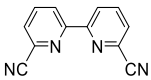


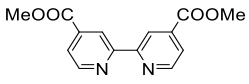
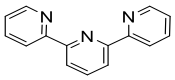
Entry	Catalysts	Yield (%)
1	AgOAc	25
2	$AgNO_2$	27
3	AgOTf	24
4	CuCl	trace
5	$Cu(OAc)_2$	trace
6	$FeCl_2$	trace
7	$FeCl_3$	trace
8	$NiCl_2$	trace
9	$Pd(OAc)_2$	trace
10	20 mol % $AgNO_2$+20 mol% L	30

L = 3,4,7,8-tetramethyl-1,10-phenanthroline, yields were determined by ^1H NMR using 0.2 mmol dibromomethane as an internal standard.

3.2 Optimization of ligands

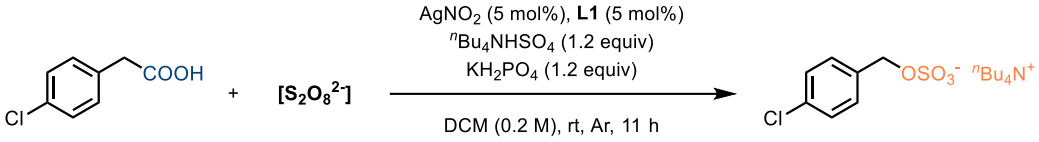


Entry	Ligand	Yield (%)	Entry	Ligand	Yield (%)
1	Without ligand	trace	7		trace
2		27	8		29
3		75	9		trace
4		27	10		13
5		49	11		6

6		trace	12		6

Yields were determined by ^{1}H NMR using 0.2 mmol dibromomethane as an internal standard.

3.3 Optimization of persulfates

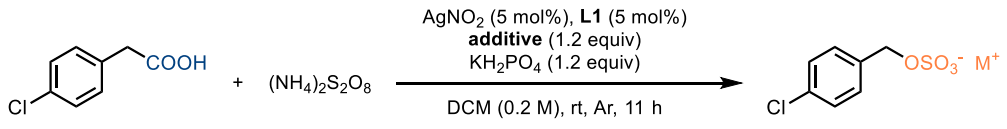


1s 3.0 equiv **1'**

Entry	Persulfates (3.0 equiv)	Yield (%)
1	$K_2S_2O_8$	59
2	$Na_2S_2O_8$	47
3	$(NH_4)_2S_2O_8$	75
4	without $^nBu_4NHSO_4$	trace
5	$(^nBu_4N)_2S_2O_8$ instead of $(NH_4)_2S_2O_8$, $^nBu_4NHSO_4$	28
6	$(NH_4)_2S_2O_8$ (1.0 equiv)	47
7	$(NH_4)_2S_2O_8$ (2.0 equiv)	66
8	$(NH_4)_2S_2O_8$ (4.0 equiv)	72

L1 = 4,7-diphenyl-1,10-phenanthroline, yields were determined by ^{1}H NMR using 0.2 mmol dibromomethane as an internal standard.

3.4 Optimization of additives



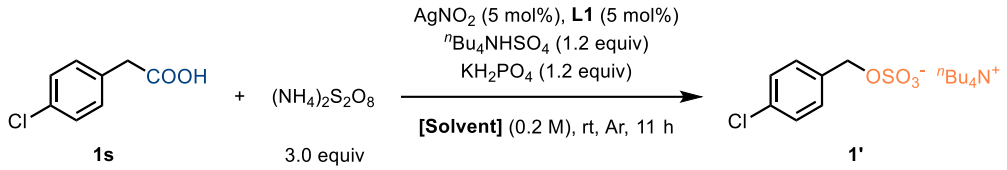
1s 3.0 equiv **1'**

Entry	Additives	Yield (%)
1	without additive	trace
2[a]	Et_3N ($M^+ = Et_3NH^+$)	48
3	Et_4NCl ($M^+ = Et_4N^+$)	12
4	Et_4NOAc ($M^+ = Et_4N^+$)	trace
5	Et_4NBF_4 ($M^+ = Et_4N^+$)	33
6	$^nBu_4NCl$ ($M^+ = {}^nBu_4N^+$)	trace
7	$^nBu_4NOAc$ ($M^+ = {}^nBu_4N^+$)	26
8	$^nBu_4NBF_4$ ($M^+ = {}^nBu_4N^+$)	24
9	Me_4NHSO_4 ($M^+ = Me_4N^+$)	<10
10	Et_4NHSO_4 ($M^+ = Et_4N^+$)	16
11	$^nPr_4NHSO_4$ ($M^+ = {}^nPr_4N^+$)	48
12	$^nBu_4NHSO_4$ ($M^+ = {}^nBu_4N^+$)	75
13	$^nHex_4NHSO_4$ ($M^+ = {}^nHex_4N^+$)	51

L1 = 4,7-diphenyl-1,10-phenanthroline, yields were determined by ^{1}H NMR using 0.2 mmol dibromomethane as an internal standard.

a: without KH_2PO_4

3.5 Optimization of solvents



1s 3.0 equiv **1'**

Entry	Solvents	Yield (%)
1	DCM	75
2	DCE	64
3	MeCN	9
4	Acetone	trace
5	PhCl	trace
6	Toluene	trace
7	HFIP	trace
8	1,4-Dioxane	trace
9	DMF	trace
10	DMSO	trace

L1 = 4,7-diphenyl-1,10-phenanthroline, yields were determined by ^{1}H NMR using 0.2 mmol dibromomethane as an internal standard.

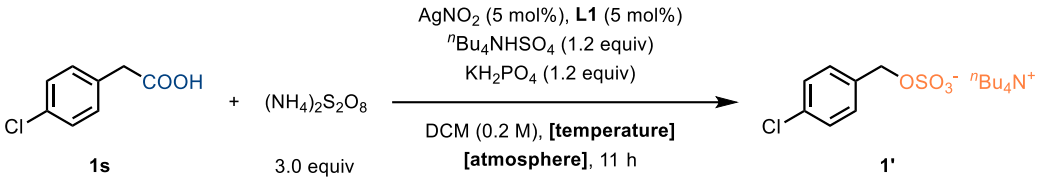
3.6 Optimization of bases

1s 3.0 equiv **1'**

Entry	Bases	Yield (%)
1	K_2HPO_4	55
2	KH_2PO_4	75
3	CH_3COOK	46
4	PhCOOK	44
5	K_2CO_3	49
6	*t*-BuOK	59
7	Na_2HPO_4	69
8	Na_2CO_3	47
9	CH_3COONa	36
10	Li_2CO_3	59
11	Cs_2CO_3	27
12	KH_2PO_4 (0.6 equiv.)	69
13	KH_2PO_4 (1.8 equiv.)	67
14	KH_2PO_4 (2.4 equiv.)	66
15	KH_2PO_4 (3.0 equiv.)	60

L1 = 4,7-diphenyl-1,10-phenanthroline, yields were determined by ^{1}H NMR using 0.2 mmol dibromomethane as an internal standard.

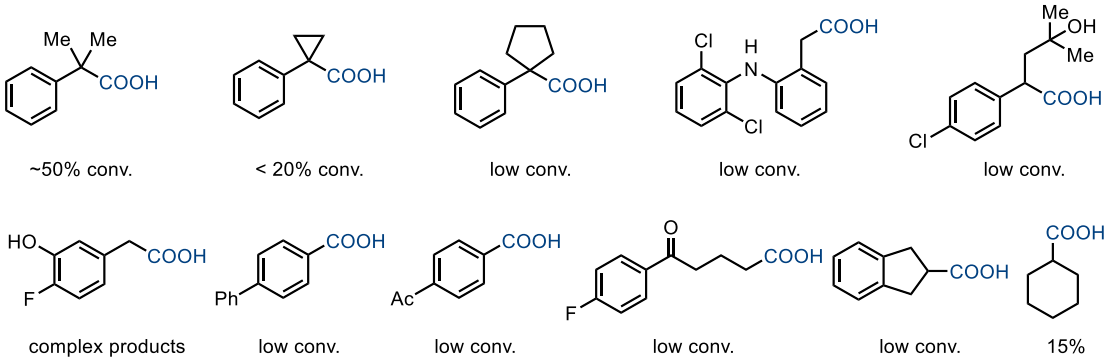
3.7 Optimization of temperatures and atmospheres



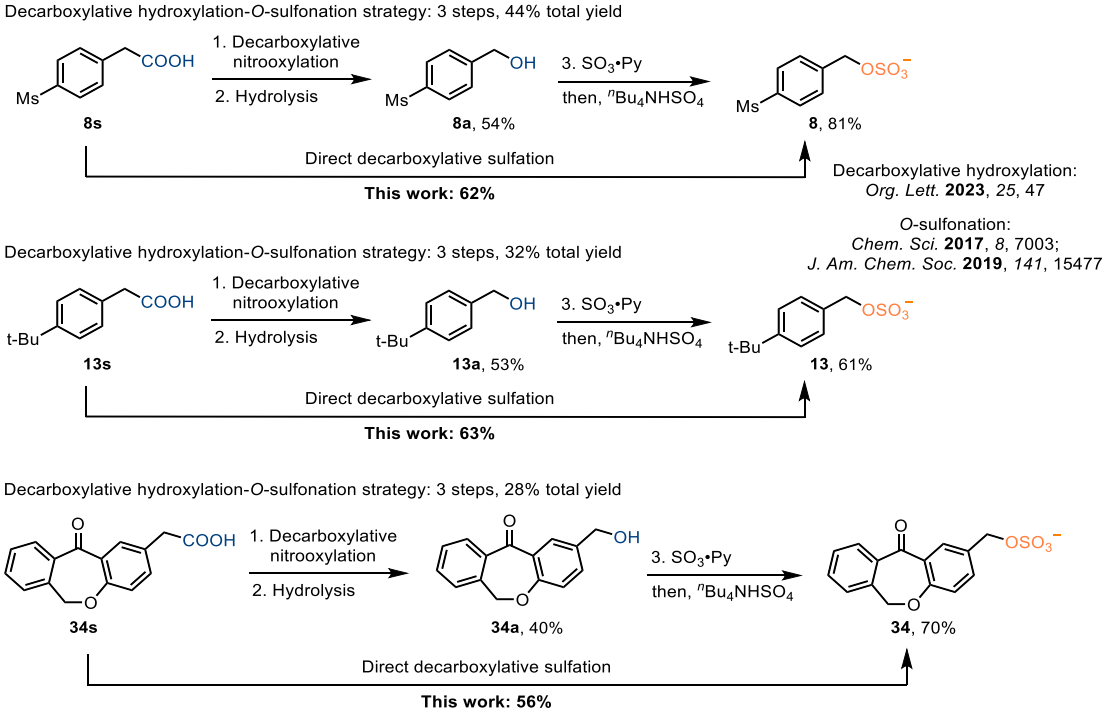
Entry	Temperature (°C)	Yield (%)	Entry	Atmosphere	Yield (%)
1	r.t.	75	4	Ar	75
2	0	30	5	Air	52
3	50	50	6	O_2	trace

L1 = 4,7-diphenyl-1,10-phenanthroline, yields were determined by ^{1}H NMR using 0.2 mmol dibromomethane as an internal standard.

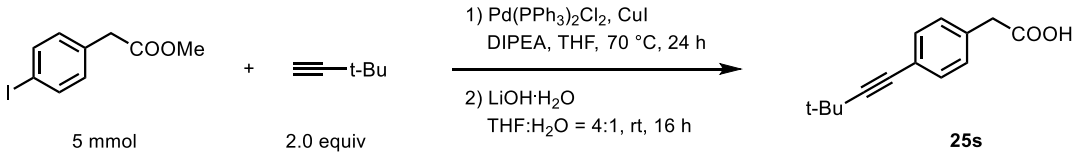
3.8 Unsuccessful substrates or poor results for sulfation



3.9 Comparative analysis of this method with traditional methods



4 Preparation of starting materials



5 mmol 2.0 equiv **25s**

To a THF solution (9 mL) of $Pd(PPh_3)_2Cl_2$ (210.6 mg, 0.30 mmol, 0.06 equiv), CuI (95.3 mg, 0.50 mmol, 0.1 equiv) and DIPEA (3.5 mL, 20 mmol, 4.0 equiv) was added methyl 4-iodophenylacetate (1.38 g, 5 mmol, 1.0 equiv) and stirred for 5 min. Subsequently, 3,3-dimethyl-1-butyne (1.25 mL, 10 mmol, 2.0 equiv) was added dropwise and the mixture was stirred at 70 °C for 24 hours. Upon completion of the reaction, the mixture was filtered through a short celite bed and concentrated under reduced pressure. The residue was then eluted through a silica column (PE/EA=15:1) to afford sonogashira coupling product (1.23 g, 99%) as a dark brown liquid oil. This product was further hydrolyzed with 6 equivalents of $LiOH{\cdot}H_2O$ to yield **25s** (833.3 mg, 72%).

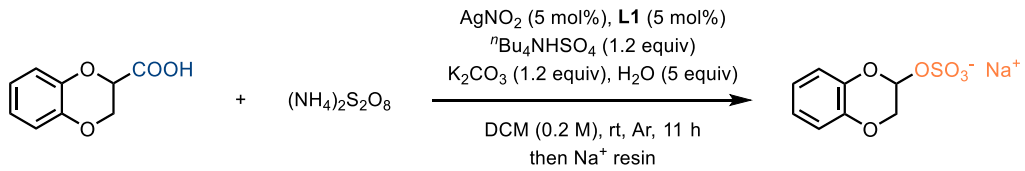
NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ): 7.34 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 3.62 (s, 2H), 1.31 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, 298 K, δ): 177.0, 132.5, 131.9, 129.3, 123.4, 99.0, 78.8, 40.9, 31.2, 28.1 ppm.

HRMS (ESI+) calculated for $C_{14}H_{16}O_2Na^+$, 239.1043; found, 239.1036 $[M + Na]^+$.

5 Gram-scale reaction



28s (6 mmol) 3.0 equiv **28** (1.02 g, 67%)

To a 50 mL schlenk bottle equipped with a stir bar was added 1,4-benzodioxan-2-carboxylic acid **28s** (1.08 g, 6 mmol, 1.0 equiv), $AgNO_2$ (46 mg, 0.3 mmol, 5 mol%), 4,7-diphenyl-1,10-phenanthroline **L1** (100 mg, 0.3 mmol, 5 mol%), ammonium persulfate (4.11 g, 18 mmol, 3.0 equiv), tetrabutylammonium hydrogen sulfate (2.44 g, 7.2 mmol, 1.2 equiv), H_2O (540 μL, 30 mmol, 5.0 equiv) and K_2CO_3 (1.00 g, 7.2 mmol, 1.2 equiv). The schlenk bottle was evacuated and backfilled with Argon for three times. 30 mL CH_2Cl_2 was added, and the reaction mixture was stirred at room temperature for 11 h. After reaction, 6 g $NaHCO_3$ was added to quench the reaction and filtered using CH_2Cl_2 (200 mL) as eluent.

The filtrate was collected and concentrated by rotary evaporation. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium 1,4-benzodioxan-2-sulfate **28'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 1,4-benzodioxan-2-sulfate **28** (1.02 g, 4.02 mmol, 67%) as white solid.

NMR Spectroscopy:

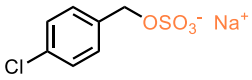
^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 6.94 – 6.88 (m, 1H), 6.88 – 6.81 (m, 3H), 6.04 (t, *J* = 1.8 Hz, 1H), 4.29 (dd, *J* = 11.5, 2.1 Hz, 1H), 4.11 (dd, *J* = 11.5, 1.5 Hz, 1H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 144.6, 142.1, 123.1, 122.8, 118.7, 117.8, 92.8, 66.9 ppm.

HRMS (ESI-) calculated for $C_8H_7O_6S^-$, 230.9969; found, 230.9960 [M - Na]$^-$.

6 Compound characterization

Sodium 4-chlorobenzyl sulfate (1)



The reaction was carried out according to general procedure. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium 4-chlorobenzyl sulfate **1'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 4-chlorobenzyl sulfate **1** (33.6 mg, 0.138 mmol, 69%) as a white solid.

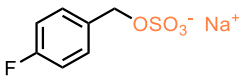
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.42 – 7.37 (m, 2H), 7.37 – 7.32 (m, 2H), 4.99 (s, 2H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 136.8, 134.8, 130.6, 129.5, 69.8 ppm.

HRMS (ESI-) calculated for $C_7H_6ClO_4S^-$, 220.9681; found, 220.9669 [M - Na]$^-$.

Sodium 4-fluorobenzyl sulfate (2)



The reaction was carried out according to general procedure. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium4-fluorobenzyl sulfate **2'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 4-fluorobenzyl sulfate **2** (34.5 mg, 0.151 mmol, 76%) as a white solid.

NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.46 – 7.40 (m, 2H), 7.11 – 7.03 (m, 2H), 4.99 (s, 2H) ppm.

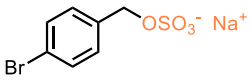
^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 164.0 (d, *J* = 244.7 Hz), 134.0 (d, *J* = 3.1 Hz), 131.2 (d, *J* = 8.3 Hz), 116.0 (d, *J* = 21.8 Hz), 70.0 ppm.

^{19}F NMR (376 MHz, CD_3OD, 298 K, δ): -116.67 (ddd, *J* = 14.4, 9.2, 5.4 Hz) ppm.

^{19}F{^{1}H } NMR (376 MHz, CD_3OD, 298 K, δ): -116.64 ppm.

HRMS (ESI-) calculated for $C_8H_7O_6S^-$, 204.9976; found, 204.9960 [M - Na]-.

Sodium 4-bromobenzyl sulfate (3)



The reaction was carried out according to general procedure, and potassium phosphate monobasic was replaced by potassium phosphate dibasic (41.8 mg, 0.24 mmol, 1.2 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium 4-bromobenzyl sulfate **3'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 4-bromobenzyl sulfate **3** (41.9 mg, 0.146 mmol, 73%) as a white solid.

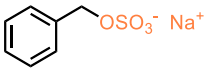
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.54 – 7.47 (m, 2H), 7.37 – 7.30 (m, 2H), 4.97 (s, 2H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 137.3, 132.5, 130.8, 122.8, 69.8 ppm.

HRMS (ESI-) calculated for $C_7H_6BrO_4S^-$, 264.9176; found, 264.9174 [M - Na]$^-$.

Sodium benzyl sulfate (4)



The reaction was carried out according to general procedure. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to

tetrabutylammonium benzyl sulfate **4'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium benzyl sulfate **4** (22.7 mg, 0.108 mmol, 54%) as a white solid.

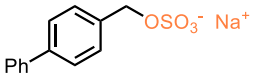
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.43 – 7.38 (m, 2H), 7.37 – 7.26 (m, 3H), 5.01 (s, 2H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 137.8, 129.3, 129.0(2), 129.0(1), 70.7 ppm.

HRMS (ESI+) calculated for $C_7H_6FO_4SNa_2^+$, 232.9855; found, 232.9853 $[M + Na]^+$.

Sodium 4-phenylbenzyl sulfate (5)



The reaction was carried out according to general procedure, and potassium phosphate monobasic and tetrabutylammonium hydrogen sulfate were replaced by triethylamine (30.4 mg, 0.3 mmol, 1.5 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford quaternary ammonium 4-phenylbenzyl sulfate **5'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 4-phenylbenzyl sulfate **5** (17.2 mg, 0.06 mmol, 30%) as a white solid.

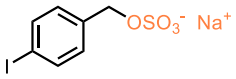
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.64 – 7.59 (m, 4H), 7.51 – 7.47 (m, 2H), 7.45 – 7.40 (m, 2H), 7.36 – 7.30 (m, 1H), 5.06 (s, 2H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 142.2, 142.1, 136.9, 129.8, 129.6, 128.4, 128.0, 70.5 ppm.

HRMS (ESI-) calculated for $C_{13}H_{11}O_4S^-$, 263.0384; found, 263.0377 $[M - Na]^-$.

Sodium 4-iodobenzyl sulfate (6)



The reaction was carried out according to general procedure, and potassium phosphate monobasic and tetrabutylammonium hydrogen sulfate were replaced by triethylamine (30.4 mg, 0.3 mmol, 1.5 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford quaternary ammonium 4-iodobenzyl sulfate **6'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 4-iodobenzyl sulfate **6** (35.5 mg, 0.106 mmol, 53%) as a yellow solid.

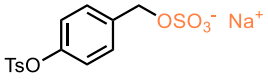
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.70 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 4.96 (s, 2H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 138.6, 137.9, 130.9, 94.0, 69.9 ppm.

HRMS (ESI+) calculated for $C_7H_6O_4INa_2S^+$, 358.8821; found, 358.8827 $[M + Na]^+$.

Sodium 4-(tosyloxy)benzyl sulfate (7)



The reaction was carried out according to general procedure, and potassium phosphate monobasic was replaced by potassium phosphate dibasic (41.8 mg, 0.24 mmol, 1.2 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium 4-(tosyloxy)benzyl sulfate **7'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 4-(tosyloxy)benzyl sulfate **7** (35.7 mg, 0.094 mmol, 47%) as a white solid.

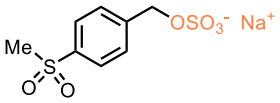
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.72 – 7.67 (m, 2H), 7.46 – 7.34 (m, 4H), 7.00 – 6.93 (m, 2H), 4.99 (s, 2H), 2.46 (s, 3H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 150.7, 147.2, 137.3, 133.5, 131.0, 130.2, 129.6, 123.3, 69.6, 21.6 ppm.

HRMS (ESI+) calculated for $C_{14}H_{13}O_7Na_2S^+$, 402.9893; found, 402.9889 $[M + Na]^+$.

Sodium 4-(methylsulfonyl)benzyl sulfate (8)



The reaction was carried out according to general procedure. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium 4-(methylsulfonyl)benzyl sulfate **8'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 4-(methylsulfonyl)benzyl sulfate **8** (35.7 mg, 0.124 mmol, 62%) as a white solid.

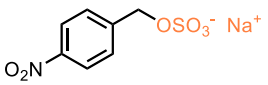
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.95 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 5.13 (s, 2H), 3.12 (s, 3H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 144.7, 141.3, 129.3, 128.5, 69.4, 44.4 ppm.

HRMS (ESI-) calculated for $C_8H_9O_6S_2^-$, 264.9846; found, 264.9841 $[M - Na]^-$.

Sodium 4-nitrobenzyl sulfate (9)



The reaction was carried out according to general procedure, and potassium phosphate monobasicwas replaced by potassium phosphate dibasic (41.8 mg, 0.24 mmol, 1.2 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium 4-nitrobenzyl sulfate **9'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 4-nitrobenzyl sulfate **9** (31.6 mg, 0.124 mmol, 62%) as a white solid.

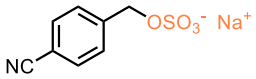
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 8.27 – 8.19 (m, 2H), 7.70 – 7.62 (m, 2H), 5.14 (s, 2H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 148.9, 145.9, 129.3, 124.4, 69.1 ppm.

HRMS (ESI-) calculated for $C_7H_6NO_6S^-$, 231.9921; found, 231.9917 [M - Na]$^-$.

Sodium 4-cyanobenzyl sulfate (10)



The reaction was carried out according to general procedure. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium 4-cyanobenzyl sulfate **10'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 4-cyanobenzyl sulfate **10** (24.5 mg, 0.104 mmol, 52%) as a white solid.

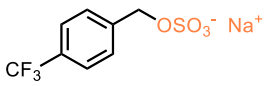
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.74 – 7.68 (m, 2H), 7.63 – 7.57 (m, 2H), 5.09 (s, 2H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 144.0, 133.3, 129.3, 119.7, 112.5, 69.4 ppm.

HRMS (ESI-) calculated for $C_8H_6NO_4S^-$, 212.0023; found, 212.0016 [M - Na]$^-$.

Sodium 4-(trifluoromethyl)benzyl sulfate (11)



The reaction was carried out according to general procedure. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium 4-(trifluoromethyl)benzyl sulfate **11'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 4-(trifluoromethyl)benzyl sulfate **11** (18.9 mg, 0.068 mmol, 34%) as a white solid.

NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.65 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H),

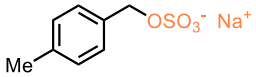
5.10 (s, 2H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 142.6, 130.95 (q, *J* = 32.2 Hz), 129.1, 126.2 (q, *J* = 3.8 Hz), 125.7 (q, *J* = 272.1 Hz), 69.6 ppm.

^{19}F NMR (376 MHz, CD_3OD, 298 K, δ): -64.05 ppm.

HRMS (ESI+) calculated for $C_8H_6O_4F_3Na_2S^+$, 300.9729; found, 300.9725 $[M + Na]^+$.

Sodium 4-methylbenzyl sulfate (12)



The reaction was carried out according to general procedure. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium 4-methylbenzyl sulfate **12'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 4-methylbenzyl sulfate **12** (25.0 mg, 0.112 mmol, 56%) as a white solid.

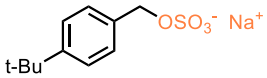
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.28 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 4.96 (s, 2H), 2.33 (s, 3H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 138.9, 134.8, 130.0, 129.2, 70.7, 21.2 ppm.

HRMS (ESI-) calculated for $C_8H_9O_4S^-$, 201.0227; found, 201.0223 $[M - Na]^-$.

Sodium 4-(*tert*-butyl)benzyl sulfate (13)



The reaction was carried out according to general procedure, and potassium phosphate monobasic was replaced by potassium phosphate dibasic (41.8 mg, 0.24 mmol, 1.2 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium 4-(*tert*-butyl)benzyl sulfate **13'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 4-(*tert*-butyl)benzyl sulfate **13** (33.5 mg, 0.126 mmol, 63%) as a white solid.

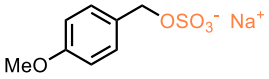
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.41 – 7.36 (m, 2H), 7.36 – 7.31 (m, 2H), 4.98 (s, 2H), 1.31 (s, 9H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 152.2, 134.8, 129.0, 126.2, 70.6, 35.4, 31.7 ppm.

HRMS (ESI-) calculated for $C_{11}H_{15}O_4S^-$, 243.0697; found, 243.0690 $[M - Na]^-$.

Sodium 4-methoxybenzyl sulfate (14)



The reaction was carried out according to general procedure, and potassium phosphate monobasic was replaced by potassium phosphate dibasic (41.8 mg, 0.24 mmol, 1.2 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium 4-methoxybenzyl sulfate **14'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 4-methoxybenzyl sulfate **14** (20.2 mg, 0.084 mmol, 42%) as a white solid.

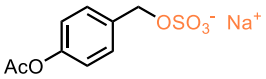
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.36 – 7.30 (m, 2H), 6.94 – 6.86 (m, 2H), 4.94 (s, 2H), 3.79 (s, 3H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 161.1, 130.9, 129.8, 114.7, 70.7, 55.7 ppm.

HRMS (ESI+) calculated for $C_8H_9O_5Na_2S^+$, 262.9961; found, 262.9966 $[M + Na]^+$.

Sodium 4-acetoxybenzyl sulfate (15)



The reaction was carried out according to general procedure, and potassium phosphate monobasic was replaced by potassium phosphate dibasic (41.8 mg, 0.24 mmol, 1.2 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium 4-acetoxybenzyl sulfate **15'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 4-acetoxybenzyl sulfate **15** (29.5 mg, 0.110 mmol, 55%) as a white solid.

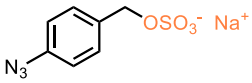
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.47 – 7.41 (m, 2H), 7.12 – 7.05 (m, 2H), 5.01 (s, 2H), 2.27 (s, 3H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 171.1, 152.0, 135.6, 130.1, 122.6, 70.1, 20.9 ppm.

HRMS (ESI+) calculated for $C_9H_9O_6Na_2S^+$, 290.9910; found, 290.9907 $[M + Na]^+$.

Sodium 4-azidobenzyl sulfate (16)



The reaction was carried out according to general procedure, and potassium phosphate monobasic and tetrabutylammonium hydrogen sulfate were replaced by triethylamine (30.4 mg, 0.3 mmol, 1.5 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford quaternary ammonium 4-

azidobenzyl sulfate **16'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 4-azidobenzyl sulfate **16** (25.1 mg, 0.100 mmol, 50%) as a white solid.

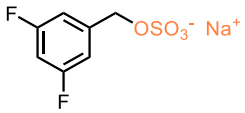
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.44 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 4.99 (s, 2H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 141.2, 134.9, 130.8, 119.9, 70.1 ppm.

HRMS (ESI+) calculated for $C_7H_6O_4N_3Na_2S^+$, 273.9869; found, 273.9868 $[M + Na]^+$.

Sodium 3,5-difluorobenzyl sulfate (17)



The reaction was carried out according to general procedure. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium 3,5-difluorobenzyl sulfate **17'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 3,5-difluorobenzyl sulfate **17** (22.6 mg, 0.092 mmol, 46%) as a white solid.

NMR Spectroscopy:

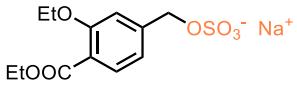
^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.06 – 7.00 (m, 2H), 6.85 (tt, *J* = 9.2, 2.4 Hz, 1H), 5.01 (s, 2H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 164.4 (dd, *J* = 247.9, 12.7 Hz), 142.8 (t, *J* = 9.3 Hz), 111.2 (dd, *J* = 19.0, 7.0 Hz), 103.7 (t, *J* = 25.8 Hz), 69.0 ppm.

^{19}F NMR (376 MHz, CD_3OD, 298 K, δ): -112.03 (t, *J* = 8.2 Hz) ppm.

HRMS (ESI+) calculated for $C_7H_5O_4F_2Na_2S^+$, 268.9667; found, 268.9664 $[M + Na]^+$.

Sodium 3-ethoxy-4-(ethoxycarbonyl)benzyl sulfate (18)



The reaction was carried out according to general procedure, and potassium phosphate monobasic and tetrabutylammonium hydrogen sulfate (81.5 mg, 0.24 mmol, 1.2 equiv) were replaced by triethylamine (30.4 mg, 0.3 mmol, 1.5 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford quaternary ammonium 4-iodobenzyl sulfate **18'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 4-iodobenzyl sulfate **18** (27.2 mg, 0.083 mmol, 42%) as a white solid.

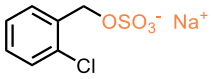
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.68 (d, *J* = 7.9 Hz, 1H), 7.17 (s, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 5.04 (s, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 4.14 (q, *J* = 7.0 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H), 1.36 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 168.3, 159.8, 144.2, 132.2, 121.3, 120.0, 113.5, 69.9, 65.8, 61.9, 15.0, 14.6 ppm.

HRMS (ESI+) calculated for $C_{12}H_{15}O_7Na_2S^+$, 349.0328; found, 349.0326 $[M + Na]^+$.

Sodium 2-chlorobenzyl sulfate (19)



The reaction was carried out according to general procedure, and potassium phosphate monobasic was replaced by potassium carbonate (33.2 mg, 0.24 mmol, 1.2 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium 2-chlorobenzyl sulfate **19'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 2-chlorobenzyl sulfate **19** (26.3 mg, 0.108 mmol, 54%) as a white solid.

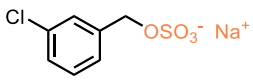
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.60 – 7.56 (m, 1H), 7.41 – 7.36 (m, 1H), 7.35 – 7.26 (m, 2H), 5.13 (s, 2H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 135.6, 133.8, 130.4, 130.3, 130.2, 128.1, 67.6 ppm.

HRMS (ESI-) calculated for $C_7H_6O_4ClS^-$, 220.9681; found, 220.9678 $[M - Na]^-$.

Sodium 3-chlorobenzyl sulfate (20)



The reaction was carried out according to general procedure, potassium phosphate monobasic was replaced by potassium carbonate (33.2 mg, 0.24 mmol, 1.2 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium 3-chlorobenzyl sulfate **20'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 3-chlorobenzyl sulfate **20** (31.6 mg, 0.130 mmol, 65%) as a white solid.

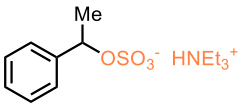
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.44 (s, 1H), 7.35 – 7.28 (m, 3H), 5.00 (s, 2H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 140.4, 135.2, 130.9, 128.9, 128.8, 127.1, 69.7 ppm.

HRMS (ESI-) calculated for $C_7H_6O_4ClS^-$, 220.9681; found, 220.9671 $[M - Na]^-$.

Quaternary ammonium α-methylbenzyl sulfate (21')



The reaction was carried out according to general procedure, potassium phosphate monobasic and tetrabutylammonium hydrogen sulfate (81.5 mg, 0.24 mmol, 1.2 equiv) were replaced by triethylamine (30.4 mg, 0.3 mmol, 1.5 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford quaternary ammonium α-methylbenzyl sulfate **21'** (36.4 mg, 0.12 mmol, 60%) as a yellow oil**.**

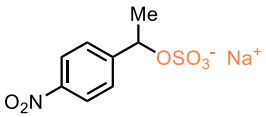
NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ): 9.18 (br, 1H), 7.39 – 7.33 (m, 2H), 7.29 – 7.22 (m, 2H), 7.21 – 7.16 (m, 1H), 5.44 (q, *J* = 6.6 Hz, 1H), 2.94 (qd, *J* = 7.3, 4.8 Hz, 6H), 1.57 (d, *J* = 6.6 Hz, 3H), 1.17 (t, *J* = 7.4 Hz, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, 298 K, δ): 142.9, 128.1, 127.4, 126.2, 76.4, 46.5, 23.3, 8.7 ppm.

HRMS (ESI-) calculated for $C_8H_9O_4S^-$, 201.0228; found, 201.0227 $[M - HNEt_3]^-$.

Sodium α-methyl-4-nitrobenzyl sulfate (22)



The reaction was carried out according to general procedure. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium α-methyl-4-nitrobenzyl sulfate **22'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium α-methyl-4-nitrobenzyl sulfate **22** (26.9 mg, 0.100 mmol, 50%) as a white solid.

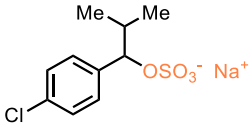
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 8.25 – 8.16 (m, 2H), 7.69 – 7.63 (m, 2H), 5.55 (q, *J* = 6.6 Hz, 1H), 1.60 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 151.9, 148.6, 128.1, 124.4, 76.6, 23.7 ppm.

HRMS (ESI+) calculated for $C_8H_8O_6NNa_2S^+$, 291.9862; found, 291.9861 $[M + Na]^+$.

Sodium α-isopropyl-4-chlorobenzyl sulfate (23)



The reaction was carried out according to general procedure, potassium phosphate monobasic was replaced by potassium phosphate dibasic (41.8 mg, 0.24 mmol, 1.2 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium α-isopropyl-4-chlorobenzyl sulfate **23'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium α-isopropyl-4-chlorobenzyl sulfate **23** (37.2 mg, 0.130 mmol, 65%) as a white solid.

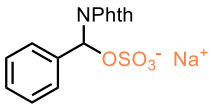
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.34 – 7.26 (m, 4H), 5.00 (d, *J* = 6.4 Hz, 1H), 2.11 – 1.97 (m, *J* = 6.7 Hz, 1H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 140.9, 133.9, 129.8, 128.8, 85.8, 35.8, 18.9, 18.5 ppm.

HRMS (ESI-) calculated for $C_{10}H_{12}O_4ClS^-$, 263.0150; found, 263.0149 [M - Na]$^-$.

Sodium α-(1,3-dioxoisoindolin-2-yl)benzyl sulfate (24)



The reaction was carried out according to general procedure. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium α-(1,3-dioxoisoindolin-2-yl)benzyl sulfate **24'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium α-(1,3-dioxoisoindolin-2-yl)benzyl sulfate **24** (47.6 mg, 0.134 mmol, 67%) as a white solid.

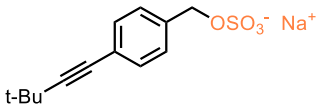
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.92 – 7.82 (m, 2H), 7.85 – 7.76 (m, 2H), 7.57 – 7.52 (m, 2H), 7.40 – 7.30 (m, 3H), 7.29 (s, 1H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 168.3, 137.8, 135.7, 133.1, 129.4, 129.3, 127.1, 124.5, 78.7 ppm.

HRMS (ESI+) calculated for $C_{15}H_{10}O_6NNa_2S^+$, 378.0019; found, 378.0015 [M + Na]$^+$.

Sodium 4-(3,3-dimethyl-1-yne)benzyl sulfate (25)



The reaction was carried out according to general procedure, potassium phosphate monobasic and tetrabutylammonium hydrogen sulfate were replaced by triethylamine (30.4 mg, 0.3 mmol, 1.5 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford quaternary ammonium 4-(3,3-dimethyl-1-yne)benzyl sulfate **25'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 4-(3,3-dimethyl-1-yne)benzyl sulfate **25** (20.3 mg, 0.08 mmol, 35%) as a white solid.

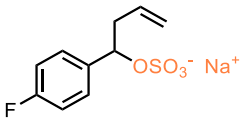
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.36 – 7.28 (m, 4H), 4.99 (s, 2H), 1.31 (s, 9H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 137.3, 132.3, 128.9, 125.1, 99.2, 80.0, 70.3, 31.4, 28.9 ppm.

HRMS (ESI+) calculated for $C_{13}H_{15}O_4Na_2S^+$, 313.0481; found, 313.0476 $[M + Na]^+$.

Sodium 1-(4-fluorophenyl)but-3-en-1-yl sulfate (26)



The reaction was carried out according to general procedure, potassium phosphate monobasic and tetrabutylammonium hydrogen sulfate were replaced by triethylamine (30.4 mg, 0.3 mmol, 1.5 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford quaternary ammonium 1-(4-fluorophenyl)but-3-en-1-yl sulfate **26'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 1-(4-fluorophenyl)but-3-en-1-yl sulfate **26** (25.7 mg, 0.096 mmol, 48%) as a white solid.

NMR Spectroscopy:

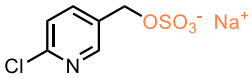
^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.41 – 7.34 (m, 2H), 7.07 – 6.99 (m, 2H), 5.72 (ddt, *J* = 17.2, 10.3, 7.0 Hz, 1H), 5.31 (t, *J* = 6.6 Hz, 1H), 5.04 – 4.93 (m, 2H), 2.79 – 2.69 (m, 1H), 2.65 – 2.54 (m, 1H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 163.6 (d, *J* = 243.9 Hz), 138.3 (d, *J* = 3.2 Hz), 134.7, 129.7 (d, *J* = 8.1 Hz), 118.1, 115.6 (d, *J* = 21.7 Hz), 80.5, 42.7 ppm.

^{19}F NMR (376 MHz, CD_3OD, 298 K, δ): -117.54 ppm.

HRMS (ESI+) calculated for $C_{10}H_{10}O_4FNa_2S^+$, 291.0074; found, 291.0073 $[M + Na]^+$.

Sodium (6-chloropyridin-3-yl)methyl sulfate (27)



The reaction was carried out according to general procedure, potassium phosphate monobasic was replaced by potassium phosphate dibasic (41.8 mg, 0.24 mmol, 1.2 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium (6-chloropyridin-3-yl)methyl sulfate **27'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium (6-chloropyridin-3-yl)methyl sulfate **27** (24.5 mg, 0.100 mmol, 50%) as a white solid.

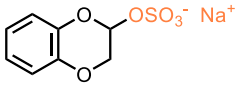
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 8.41 (d, *J* = 2.4 Hz, 1H), 7.89 (dd, *J* = 8.2, 2.5 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 5.05 (s, 2H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 151.7, 150.0, 140.6, 133.7, 125.4, 67.1 ppm.

HRMS (ESI+) calculated for $C_6H_5O_4ClNNa_2S^+$, 267.9418; found, 267.9412 $[M + Na]^+$.

Sodium 1,4-benzodioxan-2-sulfate (28)



The reaction was carried out according to general procedure, potassium phosphate monobasic was replaced by potassium carbonate (33.2 mg, 0.24 mmol, 1.2 equiv) and H_2O (18.0 mg, 1 mmol, 5 equiv.). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium 1,4-benzodioxan-2-sulfate sulfate **28'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium 1,4-benzodioxan-2-sulfate **28** (40.2 mg, 0.158 mmol, 79%) as a white solid.

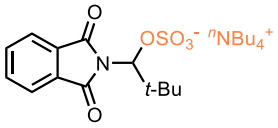
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 6.94 – 6.88 (m, 1H), 6.88 – 6.81 (m, 3H), 6.04 (t, *J* = 1.8 Hz, 1H), 4.29 (dd, *J* = 11.5, 2.1 Hz, 1H), 4.11 (dd, *J* = 11.5, 1.5 Hz, 1H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 144.6, 142.1, 123.1, 122.8, 118.7, 117.8, 92.8, 66.9 ppm.

HRMS (ESI-) calculated for $C_8H_7O_6S^-$, 230.9969; found, 230.9960 $[M - Na]^-$.

Tetrabutylammonium α-(1,3-dioxoisoindolin-2-yl)benzyl sulfate (29')



The reaction was carried out according to general procedure. The residue was purified by

flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium α-(1,3-dioxoisoindolin-2-yl)benzyl sulfate **29'** (77.6 mg, 0.140 mmol, 70%) as a white solid.

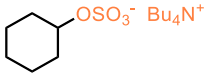
NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ): 7.76 – 7.71 (m, 2H), 7.68 – 7.61 (m, 2H), 5.91 (s, 1H), 3.29 – 3.15 (m, 8H), 1.69 – 1.53 (m, 8H), 1.40 – 1.28 (m, 8H), 1.06 (s, 9H), 0.91 (t, J = 7.3 Hz, 12H). ppm.

^{13}C NMR (101 MHz, $CDCl_3$, 298 K, δ): 169.0, 167.0, 133.8, 133.5, 133.0, 131.8, 123.2, 123.0, 85.7, 58.4, 37.2, 26.4, 23.9, 19.7, 13.8 ppm.

HRMS (ESI-) calculated for $C_{13}H_{14}O_6NS^-$, 312.0547; found, 312.0542 $[M - NBu_4]^+$.

Tetrabutylammonium cyclohexyl sulfate (30')



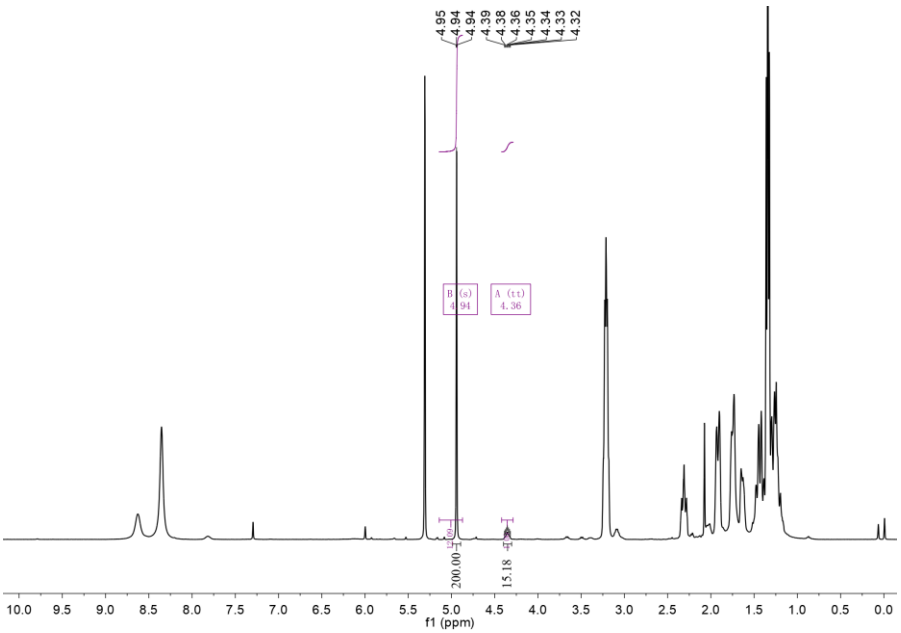
The reaction was carried out according to general procedure. and potassium phosphate monobasic and tetrabutylammonium hydrogen sulfate were replaced by triethylamine (30.4 mg, 0.3 mmol, 1.5 equiv), **L1** was replaced by 3,8-dibromo-1,10-phenanthroline. The yield of cyclohexyl sulfate was determined by ^{1}H NMR integration relative to the internal standard (15% yield, standard: δ 4.94 ppm, cyclohexyl sulfate: δ 4.36 (tt, *J* = 9.4, 4.0 Hz) ppm, $CDCl_3$). Tetrabutylammonium hydrogen sulfate (81.5 mg, 0.24 mmol, 1.2 equiv) was added to the residue and stir for 5 minutes. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium cyclohexyl sulfate **30'** as a light yellow oil.

NMR Spectroscopy:

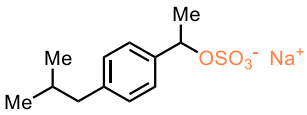
^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ): 4.29 (tt, *J* = 9.4, 4.0 Hz, 1H), 3.29 – 3.23 (m, 8H), 2.11 – 2.02 (m, 2H), 1.73 – 1.58 (m, 10H), 1.42 (p, *J* = 7.1 Hz, 11H), 1.33 – 1.21 (m, 2H), 1.19 – 1.10 (m, 1H), 0.97 (t, *J* = 7.3 Hz, 12H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, 298 K, δ): 76.0, 58.8, 33.3, 25.7, 24.4, 24.1, 19.8, 13.8 ppm.

HRMS (ESI-) calculated for $C_6H_{11}O_4S^-$, 179.0384; found, 179.0392 $[M – NBu_4]^–$.



Sodium ibuprofen-sulfate (32)



The reaction was carried out according to general procedure, potassium phosphate monobasic was replaced by potassium carbonate (33.2 mg, 0.24 mmol, 1.2 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium ibuprofen-sulfate **32'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium ibuprofen-sulfate **32** (24.5 mg, 0.087 mmol, 44%) as a white solid.

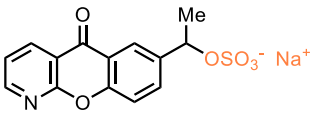
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.34 – 7.28 (m, 2H), 7.14 – 7.08 (m, 2H), 5.44 (q, *J* = 6.5 Hz, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.89 – 1.79 (m, 1H), 1.59 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 6H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 142.1, 141.4, 129.9, 126.9, 78.0, 46.1, 31.5, 23.5, 22.7 ppm.

HRMS (ESI-) calculated for $C_{12}H_{17}O_4S^-$, 257.0853; found, 257.0853 [M - Na]$^-$.

Sodium pranoprofen derivative-sulfate (33)



The reaction was carried out according to general procedure, potassium phosphate

monobasic was replaced by potassium phosphate dibasic (41.8 mg, 0.24 mmol, 1.2 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium pranoprofen derivative-sulfate **33'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium pranoprofen derivative-sulfate **33** (46.7 mg, 0.137 mmol, 68%) as a white solid.

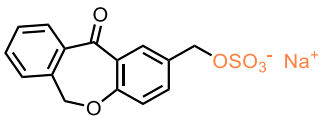
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 8.72 (dd, *J* = 4.7, 2.1 Hz, 1H), 8.65 (dd, *J* = 7.8, 2.1 Hz, 1H), 8.24 (d, *J* = 2.3 Hz, 1H), 7.96 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.66 – 7.51 (m, 2H), 5.62 (q, *J* = 6.6 Hz, 1H), 1.69 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 177.5, 160.1, 154.9, 154.1, 139.9, 137.2, 134.2, 123.2, 121.3, 120.7, 118.2, 116.3, 75.4, 22.2 ppm.

HRMS (ESI+) calculated for $C_{14}H_{10}O_6NNa_2S^+$, 366.0019; found, 366.0017 $[M + Na]^+$.

Sodium isoxepac-sulfate (34)



The reaction was carried out according to general procedure. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium isoxepac-sulfate **34'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium isoxepac-sulfate **34** (38.3 mg, 0.112 mmol, 56%) as a white solid.

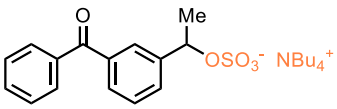
NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 8.20 (d, *J* = 2.3 Hz, 1H), 7.83 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.53 – 7.44 (m, 2H), 7.07 (d, *J* = 8.5 Hz, 1H), 5.23 (s, 2H), 5.02 (s, 2H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 192.2, 162.6, 141.5, 137.4, 136.6, 134.1, 132.3, 131.8, 130.2, 130.1, 129.1, 126.1, 122.0, 74.5, 69.9 ppm.

HRMS (ESI+) calculated for $C_{15}H_{11}O_6Na_2S^+$, 365.0066; found, 365.0059 $[M + Na]^+$.

Tetrabutylammonium ketoprofen-sulfate (35')



The reaction was carried out according to general procedure, potassium phosphate monobasic was replaced by potassium carbonate (33.2 mg, 0.24 mmol, 1.2 equiv). The

residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium ketoprofen-sulfate **35'** (53.5 mg, 0.098 mmol, 49%) as a yellow oil.

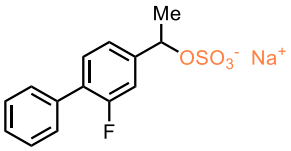
NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ): 7.81 (s, 1H), 7.77 – 7.72 (m, 2H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 1H), 5.53 (q, *J* = 6.5 Hz, 1H), 3.23 – 3.13 (m, 8H), 1.60 (d, *J* = 6.6 Hz, 3H), 1.59 – 1.50 (m, 8H), 1.33 (h, *J* = 7.3 Hz, 8H), 0.91 (t, *J* = 7.3 Hz, 12H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, 298 K, δ): 196.9, 144.7, 137.6, 137.3, 132.5, 130.8, 130.1, 128.7, 128.3, 127.9, 127.5, 74.6, 58.6, 23.9, 23.6, 19.7, 13.7 ppm.

HRMS (ESI-) calculated for $C_{15}H_{13}O_5S^-$, 305.0489; found, 305.0486 $[M - NBu_4]^-$.

Sodium flurbiprofen-sulfate (36)



The reaction was carried out according to general procedure. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium flurbiprofen-sulfate **36'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium flurbiprofen-sulfate **36** (41.6 mg, 0.131 mmol, 65%) as a white solid.

NMR Spectroscopy:

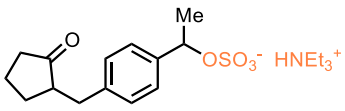
^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.54 – 7.49 (m, 2H), 7.46 – 7.39 (m, 3H), 7.38 – 7.31 (m, 1H), 7.31 – 7.22 (m, 2H), 5.49 (q, *J* = 6.6 Hz, 1H), 1.62 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, 298 K, δ): 160.9 (d, *J* = 246.2 Hz), 146.1 (d, *J* = 7.5 Hz), 137.0 (d, *J* = 1.2 Hz), 131.6 (d, *J* = 3.8 Hz), 130.0 (d, *J* = 2.9 Hz), 129.4, 129.2 (d, *J* = 13.8 Hz), 128.6, 123.1 (d, *J* = 3.4 Hz), 114.6 (d, *J* = 24.3 Hz), 76.8 (d, J = 1.4 Hz), 23.6 ppm.

^{19}F NMR (376 MHz, $CDCl_3$, 298 K, δ): -120.24 ppm.

HRMS (ESI-) calculated for $C_{14}H_{12}O_4FS^-$, 295.0446; found, 295.0445 $[M - Na]^-$.

Quaternary ammonium loxoprofen-sulfate (37')



The reaction was carried out according to general procedure, potassium phosphate

monobasic and tetrabutylammonium hydrogen sulfate were replaced by triethylamine (30.4 mg, 0.3 mmol, 1.5 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford quaternary ammonium loxoprofen-sulfate **37'** (49.5 mg, 0.124 mmol, 62%) as a colorless oil.

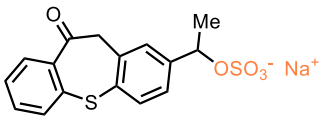
NMR Spectroscopy:

^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ): 9.58 (br, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 5.46 (q, *J* = 6.6 Hz, 1H), 3.08 – 2.97 (m, 7H), 2.47 (dd, *J* = 13.9, 9.3 Hz, 1H), 2.35 – 2.22 (m, 2H), 2.12 – 1.99 (m, 2H), 1.97 – 1.87 (m, 1H), 1.76 – 1.64 (m, 1H), 1.59 (d, *J* = 6.5 Hz, 3H), 1.55 – 1.46 (m, 1H), 1.23 (t, *J* = 7.4 Hz, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, 298 K, δ): 220.4, 140.9, 139.2, 128.7, 126.6, 76.7, 51.1, 46.5, 38.3, 35.4, 29.3, 23.2, 20.7, 8.7 ppm.

HRMS (ESI-) calculated for $C_{14}H_{17}O_5S^-$, 297.0802; found, 297.0802 [M - $HNEt_3$]$^-$.

Sodium zaltoprofen-sulfate (38)



The reaction was carried out according to general procedure, potassium phosphate monobasic was replaced by potassium carbonate (33.2 mg, 0.24 mmol, 1.2 equiv). The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford the product in the form of tetrabutylammonium sulfate **36'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium **38** (40.9 mg, 0.110 mmol, 55%) as a white solid.

NMR Spectroscopy:

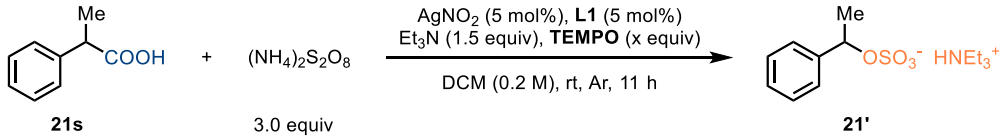
^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 8.13 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.53 (d, *J* = 1.9 Hz, 1H), 7.49 (td, J = 7.6, 1.6 Hz, 1H), 7.39 – 7.29 (m, 2H), 5.49 – 5.43 (m, 1H), 4.36 (s, 2H), 1.58 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 193.1, 146.8, 141.7, 138.9, 137.2, 134.6, 133.9, 132.3, 132.1, 131.9, 128.0, 126.2, 77.1, 51.7, 23.7 ppm.

HRMS (ESI+) calculated for $C_{16}H_{13}O_5Na_2S_2^+$, 394.9994; found, 394.9998 [M + Na]$^+$.

7 Mechanistic experiments

7.1 Radical quenching experiments for decarboxylative sulfation



21s 3.0 equiv **21'**

Entry	TEMPO (x equiv)	Conv.(%)	Yield (%, ^{1}H NMR)
1	0.2	100	72
2	1.0	80	50
3	2.0	<10	trace

L1 = 4,7-diphenyl-1,10-phenanthroline, yields were determined by ^{1}H NMR using 0.2 mmol dibromomethane as an internal standard.

The reaction was found to be inhibited by TEMPO, suggesting that decarboxylative sulfation involves a radical process. The TEMPO adduct **21a** was detected by LC-MS.

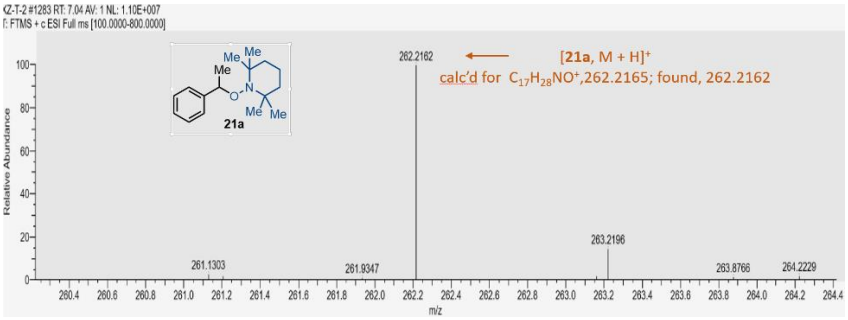
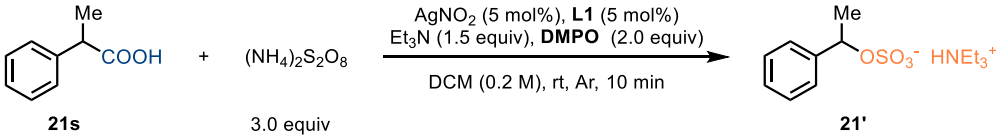


Figure S1. Benzylic TEMPO adduct trapping



21s 3.0 equiv **21'**

To a 4 mL borosilicate vial equipped with a stir bar was added carboxylic acid **21s** (0.2 mmol, 1.0 equiv), $AgNO_2$ (1.5 mg, 0.01 mmol, 5 mol%), 4,7-diphenyl-1,10-phenanthroline **L1** (3.3 mg, 0.01 mmol, 5 mol%), ammonium persulfate (136.9 mg, 0.6 mmol, 3.0 equiv), and triethylamine (30.4 mg, 0.3 mmol, 1.5 equiv). The vial was evacuated and backfilled with argon for three times. 1 mL CH_2Cl_2 was added, and the reaction mixture was stirred at room temperature for 10 min, then added DMPO (45.2 mg, 0.40 mmol, 2.0 equiv). The system was taken out by a capillary (borosilicate glass, 0.8-1.1×100 mm) and analyzed by EPR at room temperature. The samples were EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.823 GHz. Typical spectrometer

parameters are shown as follows, scan range: 200 mT; center field set: 330.00 mT; time constant: 0.0300 s; scan time: 30.00 s; modulation amplitude: 800 mT; modulation frequency: 100 kHz; mod width: 1.00×0.1; microwave power: 0.99800 mW.

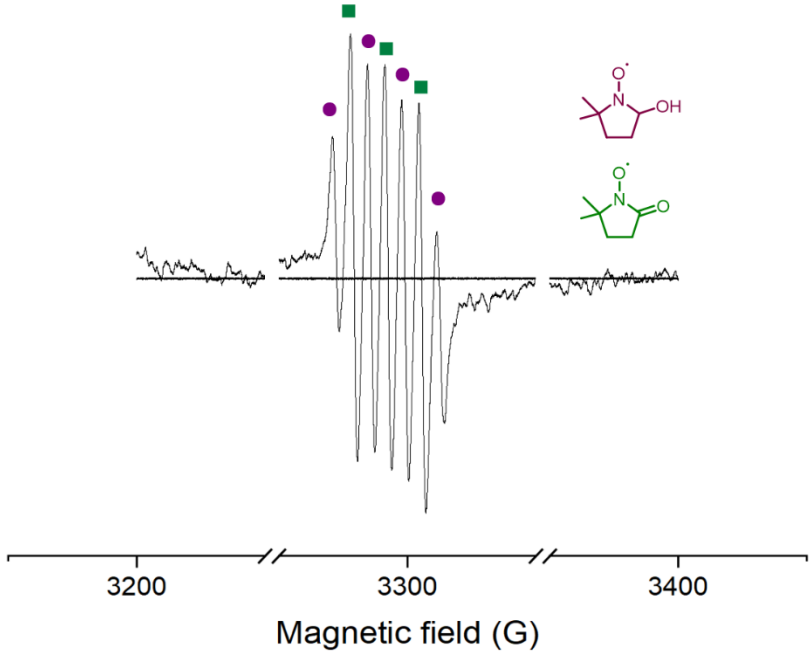
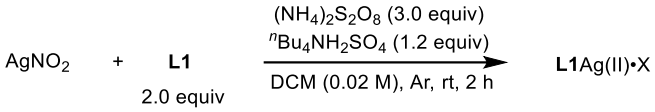


Figure S2. EPR of sulfate radical signal trapped by DMPO



To a 25 mL borosilicate vial equipped with a stir bar was added $AgNO_2$ (30.8 mg, 0.20 mmol,), **L1** (4,7-diphenyl-1,10-phenanthroline) (133.0 mg, 0.40 mmol, 2.0 equiv.) and $(NH_4)_2S_2O_8$ (136.9 mg, 0.60 mmol, 3.0 equiv.). The vial was evacuated and backfilled with argon. 10 ml CH_2Cl_2 were added respectively. The reaction mixture was stirred at room temperature for 2 h and a brown solid precipitated during the reaction. Filtration with CH_2Cl_2 (3 × 5 mL) and H_2O (3 × 5 mL) gave a brown solid, which was dried in vacuo for 6 h. The brown solid was taken out by a capillary (borosilicate glass, 0.8-1.1×100 mm) and analyzed by EPR at room temperature. The samples were EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.823 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 mT; center field set: 325.00 mT; time constant: 0.0300 s; scan time: 30.00 s; modulation amplitude: 100 mT; modulation frequency: 91.97 kHz; microwave power: 0.998 mW; g = 2.0248.

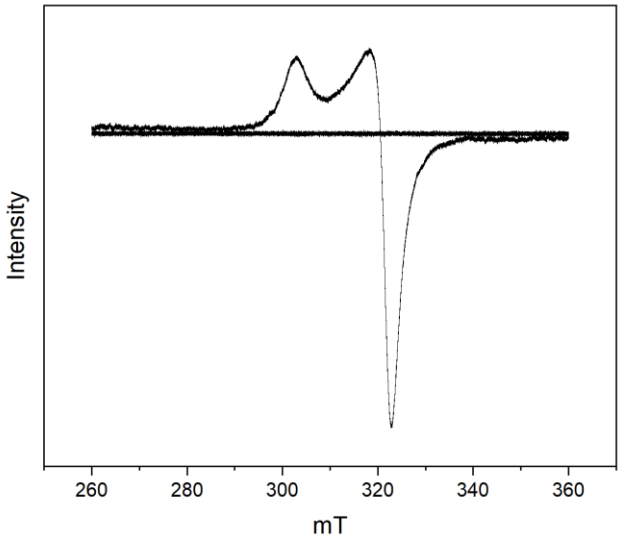
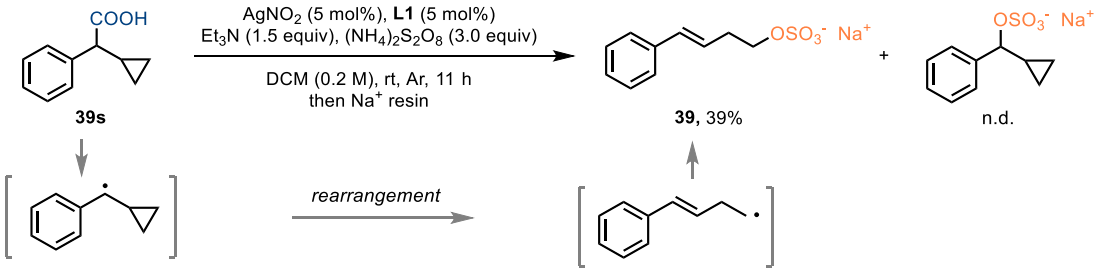


Figure S3. EPR of silver species

7.2 Radical clock experiments



To a 4 mL borosilicate vial equipped with a stir bar was added α-cyclopropylphenylacetic acid **39s** (35.2 mg, 0.2 mmol, 1.0 equiv), $AgNO_2$ (1.5 mg, 0.01 mmol, 5 mol%), 4,7-diphenyl-1,10-phenanthroline **L1** (3.3 mg, 0.01 mmol, 5 mol%), ammonium persulfate (136.9 mg, 0.6 mmol, 3.0 equiv), Et_3N (41.7 μL, 0.30 mmol, 1.5 equiv). The vial was evacuated and backfilled with Argon for three times. 1 mL CH_2Cl_2 was added, and the reaction mixture was stirred at room temperature for 11 h. 200 mg $NaHCO_3$ was added to quench the reaction and filtered using CH_2Cl_2 (30 mL) as eluent. The filtrate was collected and concentrated by rotary evaporation. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→20:1, v/v) to afford tetrabutylammonium sulfate **39'**. Subsequently, it underwent ion-exchanged with Na^+ resin to yield sodium (E)-4-phenylbut-3-en-1-yl sulfate **39** (19.5 mg, 0.078 mmol, 39%) as a white solid.

NMR Spectroscopy:

^{1}H NMR (400 MHz, CD_3OD, 298 K, δ): 7.39 – 7.33 (m, 2H), 7.29 – 7.23 (m, 2H), 7.20 – 7.13 (m, 1H), 6.51 (dt, *J* = 15.9, 1.5 Hz, 1H), 6.28 (dt, *J* = 15.9, 6.9 Hz, 1H), 4.11 (t, *J* = 6.6 Hz, 2H), 2.58 (qd, *J* = 6.8, 1.5 Hz, 2H) ppm.

^{13}C NMR (101 MHz, CD_3OD, 298 K, δ): 139.0, 133.3, 129.4, 128.1, 127.1, 126.6, 68.5, 34.1 ppm.

HRMS (ESI+) calculated for $C_{10}H_{11}O_4Na_2S^+$, 273.0168; found, 273.0168 $[M + Na]^+$.

7.3 Hammett plot experiment

To a 4 mL borosilicate vial equipped with a stir bar was added substituted phenylacetic acid (0.10 mmol, 0.5 equiv), phenylacetic acid (13.6 mg, 0.10 mmol, 0.5 equiv), $AgNO_2$ (1.5 mg, 0.01 mmol, 5 mol%), 4,7-diphenyl-1,10-phenanthroline **L1** (3.3 mg, 0.01 mmol, 5 mol%), ammonium persulfate (136.9 mg, 0.6 mmol, 3.0 equiv), tetrabutylammonium hydrogen sulfate (81.5mg, 0.24 mmol, 1.2 equiv) and KH_2PO_4 (32.7 mg, 0.24 mmol, 1.2 equiv). The vial was evacuated and backfilled with Argon for three times. 1 mL CH_2Cl_2 was added, and the reaction mixture was stirred at room temperature for 1 h. $NaHCO_3$ (200 mg) was added to quench the reaction and filtered using CH_2Cl_2 (3 × 30 mL) as eluent. The filtrate was collected and concentrated by rotary evaporation. The residue was analyzed by ^{1}H-NMR spectroscopy in $CDCl_3$. The resulting ^{1}H resonances of the benzylic protons of the *para*-substituted product (or **12** in case of X = Me) were integrated relative to the benzylic ^{1}H proton resonances of tolyl sulfate (δ = 5.06 ppm) to calculate the ratio of products.

Table S1. Reaction rate ratio for competition reactions (k: reaction rate for or para substituted phenylacetic acid; k_0: reaction rate for phenylacetic acid).

Para-Substituent (X)	σ_p^+ - effect	k/k_0				k/k_0 average	$\log(k/k_0)$
		Entry 1	Entry 2	Entry 3	Entry 4		
Me	-0.31	2.1182	2.5920	2.4315	2.3292	2.3677	0.3743
t-Bu	-0.26	1.6230	1.7380	1.6745	1.7907	1.7065	0.2321
F	-0.07	1.0198	1.0163	1.0110	1.0215	1.0172	0.0074
H	0						
Cl	0.11	0.8854	0.9297	0.9311	0.9268	0.9183	-0.0370
Br	0.15	0.8305	0.8634	0.8850	0.9192	0.8745	-0.0582
CF_3	0.61	0.2097	0.2477	0.2472	0.2022	0.2267	-0.6445
CN	0.66	0.1514		0.1580		0.1547	-0.8105
NO_2	0.79	0.0773	0.0517	0.0950	0.0628	0.0717	-1.1445

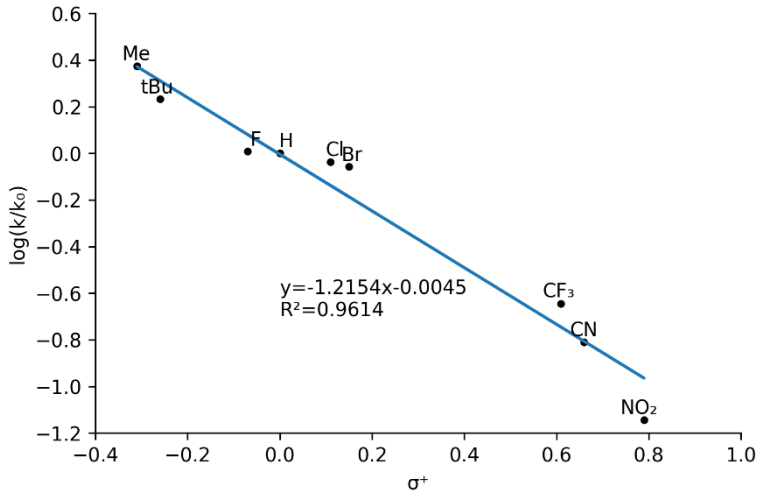


Figure S4. Hammett-plot for the decarboxylation of arylacetic acids

7.4 Different oxidants in decarboxylative sulfation

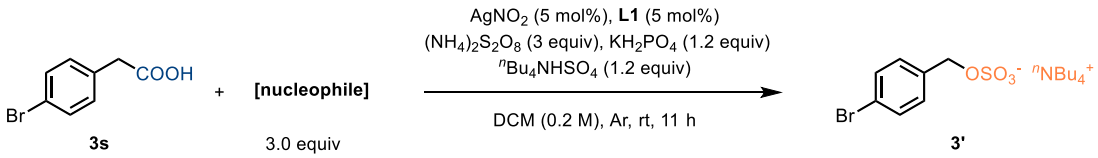
21s 3.0 equiv 3.0 equiv **21'**

Entry	Oxidants	Conv. (%)	Yield **21'** (%, ^{1}H NMR)	Byproducts
1	PIDA	22	n.d.	--
2	PIFA	8	n.d.	--
3	DDQ	34	n.d.	--
4	CAN	100	n.d.	R—ONO_2 (21%)
5	mCPBA	0	n.d.	--
6	Dess-Martin	69	n.d.	R—OAc (4%)
7	H_2O_2	14	n.d.	--
8	BPO	18	n.d.	--
9	DTBP	8	n.d.	--

L1 = 4,7-diphenyl-1,10-phenanthroline, yields were determined by ^{1}H NMR using 0.2 mmol dibromomethane as an internal standard.

When persulfate was replaced by other oxidants with sulfate anion, **21s** partially consumed. However, no sulfate product **21'** was observed. This suggests that persulfate serves as more than just an oxidant in the reaction system, and it is unlikely to undergo nucleophilic substitution of sulate anion towards carboncation.

7.5 Exogenous nucleophiles in decarboxylative sulfation



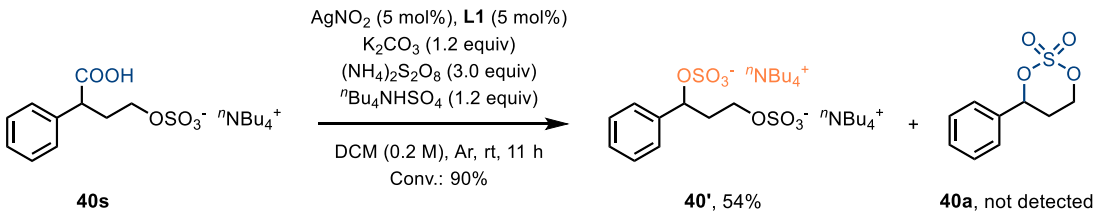
3s 3.0 equiv **3'**

Entry	Nucleophilic reagents	Conv.(%)	Yield **3'** (%, ^{1}H NMR)	Yield R—X (%, ^{1}H NMR)
1	NH_4F	100	49	--
2	NH_4Cl	27	26	R—Cl (3%)
3	NH_4OAc	95	56	R—OAc (9%)
4	$^nBu_4NF$	100	49	--
5	$^nBu_4NCl$	0	0	--
6	$^nBu_4NOAc$	100	53	R—OAc (9%)

L1 = 4,7-diphenyl-1,10-phenanthroline, yields were determined by ^{1}H NMR using 0.2 mmol dibromomethane as an internal standard.

Even when other nucleophilic reagents with stronger nucleophilicity than sulfate anion were present in the reaction system, sulfation products remained dominant. This observation suggests that the decarboxylative sulfation process might not involve nucleophilic attack as the primary mechanism.

7.6 Intramolecular competition experiments



40s **40'**, 54% **40a**, not detected

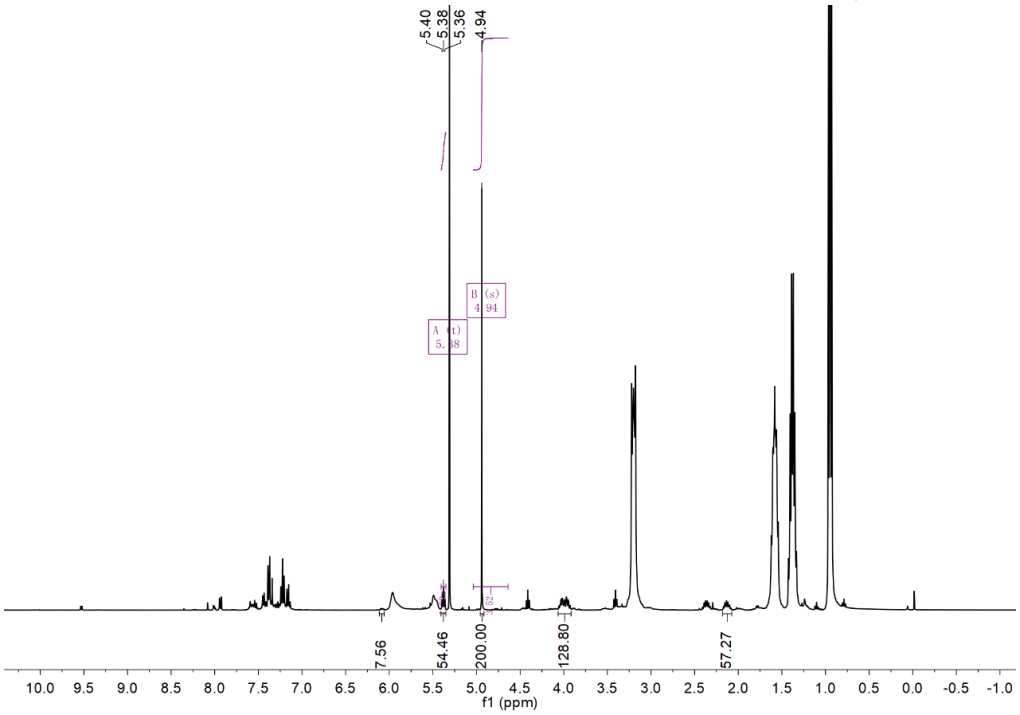
Compound **40s** was synthesized from the reported literature. [2] To a 4 mL borosilicate vial equipped with a stir bar was added **40s** (100.3 mg, 0.2 mmol, 1.0 equiv), $AgNO_2$ (1.5 mg, 0.01 mmol, 5 mol%), 4,7-diphenyl-1,10-phenanthroline **L1** (3.3 mg, 0.01 mmol, 5 mol%), ammonium persulfate (136.9 mg, 0.6 mmol, 3.0 equiv), tetrabutylammonium hydrogen sulfate (81.5 mg, 0.24 mmol, 1.2 equiv) and potassium carbonate (33.2 mg, 0.24 mmol, 1.2 equiv). The vial was evacuated and backfilled with argon for three times. 1 mL CH_2Cl_2 was added, and the reaction mixture was stirred at room temperature for 11 h. The sulfate salts were diluted with $CDCl_3$ (2 mL), and 0.2 mmol of dibromomethane was added as the internal standard. The yield of **40'** was determined by ^{1}H NMR integration relative to the internal standard (54%, standard: δ = 4.94 ppm, and **40'**: δ = 5.38 (t, *J* = 6.7 Hz) ppm, $CDCl_3$,). The filtrate was collected and concentrated by rotary evaporation. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (100:1→50:1→15:1, v/v) to afford tetrabutylammonium 1-phenylpropane-1,3-disulfate **40'** as a colorless oil.

NMR Spectroscopy of 40':

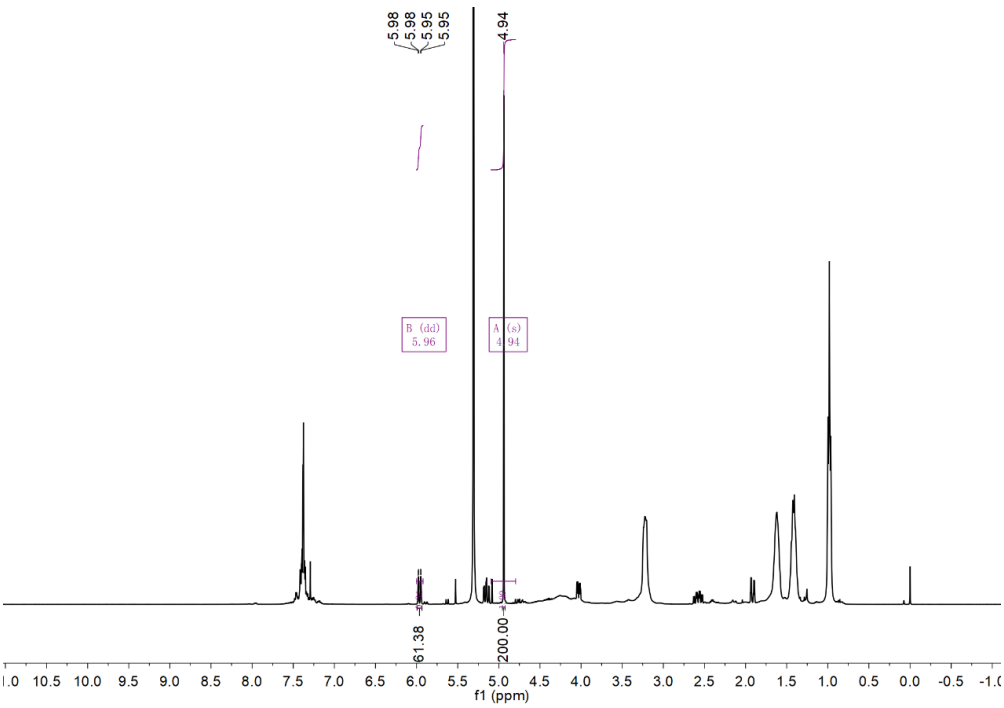
^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ): 7.34 (d, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 5.37 (t, *J* = 6.7 Hz, 1H), 4.12 – 4.02 (m, 1H), 3.96 – 3.87 (m, 1H), 3.21 – 3.07 (m, 16H), 2.33 – 2.21 (m, 1H), 2.12 – 2.02 (m, 1H), 1.59 – 1.46 (m, 16H), 1.33 (h, *J* = 7.5 Hz, 16H), 0.90 (t, *J* = 7.3 Hz, 24H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, 298 K, δ): 142.3, 127.9, 126.9, 126.6, 76.1, 63.9, 58.5, 37.6, 23.9, 19.6, 13.7 ppm.

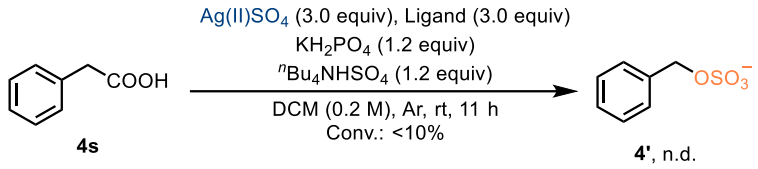
HRMS (ESI-) calculated for $[C_9H_{10}O_8S_2^{2-}]/2$, 154.9914; found, 154.9906 $\{[M - 2NBu_4]/2\}^-$.



Compound **40a** was synthesized from the reported literature.[3] To a 4 mL borosilicate vial equipped with a stir bar was added **40a** (42.8 mg, 0.2 mmol, 1.0 equiv), $AgNO_2$ (1.5 mg, 0.01 mmol, 5 mol%), 4,7-diphenyl-1,10-phenanthroline **L1** (3.3 mg, 0.01 mmol, 5 mol%), ammonium persulfate (136.9 mg, 0.6 mmol, 3.0 equiv), tetrabutylammonium hydrogen sulfate (81.5 mg, 0.24 mmol, 1.2 equiv) and potassium phosphate monobasic (32.6 mg, 0.24 mmol, 1.2 equiv). The vial was evacuated and backfilled with argon for three times. 1 mL CH_2Cl_2 was added, and the reaction mixture was stirred at room temperature for 11 h. 0.2 mmol of dibromomethane was added as the internal standard. Based on ^{1}H NMR analysis, a conversion of 38% was observed, and no traces of sulfation product **40'** was detected.



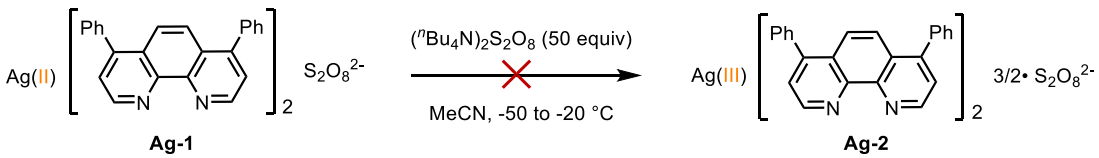
7.7 The reactivity of Ag(II)SO_4



4s **4'**, n.d.

$Ag(II)SO_4$ was synthesized from the reported literature.[4] To a 4 mL borosilicate vial equipped with a stir bar was added **4s** (27.2 mg, 0.2 mmol, 1.0 equiv), $Ag(II)SO_4$ (122.3 mg, 0.6 mmol, 3.0 equiv), 4,7-Diphenyl-1,1-phenanthroline (199.4 mg, 0.6 mmol, 3.0 equiv), potassium phosphate monobasic (32.7 mg, 0.24 mmol, 1.2 equiv), tetrabutylammonium hydrogen sulfate (81.5 mg, 0.24 mmol, 1.2 equiv). The vial was evacuated and backfilled with argon for three times. 1 mL CH_2Cl_2 was added, and the reaction mixture was stirred at room temperature for 11 h. 0.2 mmol of dibromomethane was added as the internal standard. The yield of **4'** was less than 1% by ^1H NMR integration relative to the internal standard.

7.8 Ag(III) trapping experiment



Ag-1 **Ag-2**

(**L1**)$_2$Ag(II)S_2O_8 **Ag-1** was synthesized following the reported literature,[5] and the synthesis of **Ag-2** was based on known procedure as well.[6] To a 4 mL borosilicate vial equipped with a stir bar was added **Ag-1** (19.3 mg, 0.02 mmol, 1.0 equiv), CH_3CN (1 mL) and CD_3CN (1 mL). The brown reaction mixture was then transferred to a vial containing excess tetrabutylammonium persulfate (676.5 mg, 1 mmol, 50 equiv) and swirled for 10 min, resulting in an immediate color change to pale yellow. The reaction mixture was then chilled to –50 °C, and transferred to a pre-chilled J. Young NMR tube. The tube was sealed, rapidly transported out of the dry box, and flash-frozen by immersion in a dry ice/ethanol bath. The conversion of **Ag-1** in the system was monitored by ^{1}H NMR spectra at –20 °C to capture **Ag-2**. The ^{1}H NMR spectra at various timepoints were combined to generate the spectrum presented above, which visualizes the conversion of **Ag-1**. As **Ag-2** is diamagnetic and **Ag-1** is paramagnetic, **Ag-2** may exhibit characteristic chemical shifts of the ligand on ^{1}H NMR spectra. However, the absence of characteristic chemical shifts of the ligand indicates that **Ag-2** was not formed.

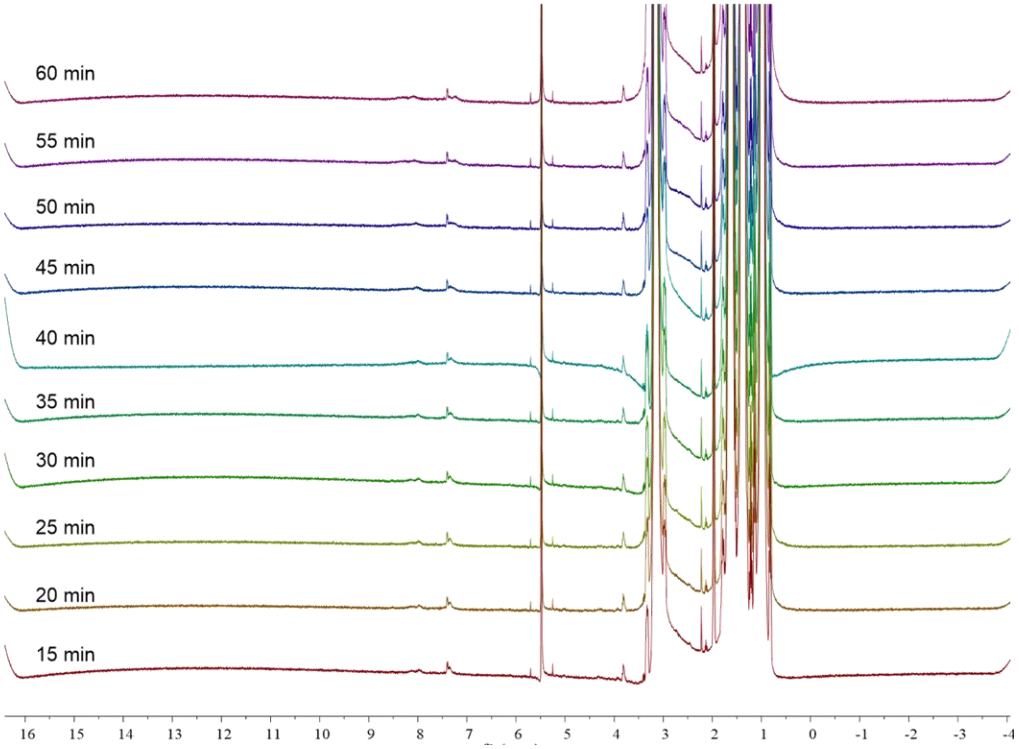


Figure S5. ^{1}H spectrum monitors of reaction mixture at –20 °C

CRYSTAL DATA

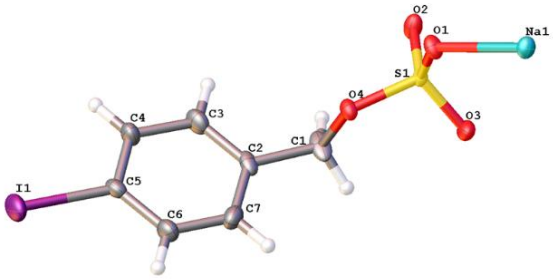


Table S2. Crystal Data and Structure Refinement for Sodium 4-Iodobenzyl Sulfate（**6**）

Identification code	CCDC 2255772
Empirical formula	C7H6INaO4S
Formula weight	336.07
Temperature	213.0 K
Wavelength	1.34139 Å
Crystal system	Monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 20.6719(4) Å α= 90° b = 6.04090(10) Å β= 97.7750(10)° c = 8.4029(2) Å γ = 90°
Volume	1039.68(4) $Å^3$
Z	4
Density (calculated)	2.147 Mg/m^3
Absorption coefficient	17.653 mm^{-1}
F(000)	640
Crystal size	0.07 x 0.07 x 0.05 mm^3
Theta range for data collection	5.638 to 54.907°.
Index ranges	-24<=h<=25, -7<=k<=4, -10<=l<=10
Reflections collected	6074
Independent reflections	1931 [R(int) = 0.0494]
Completeness to theta = 53.594°	97.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.4155
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1931 / 0 / 127
Goodness-of-fit on F^2	1.161
Final R indices [I>2sigma(I)]	R1 = 0.0866, wR2 = 0.2460
R indices (all data)	R1 = 0.0893, wR2 = 0.2520
Extinction coefficient	n/a
Largest diff. peak and hole/2.074 and -2.072 e.$Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	597(1)	11870(1)	6956(1)	59(1)
S(1)	4144(1)	6086(2)	5156(2)	20(1)
Na(1)	4754(1)	1205(4)	6771(3)	28(1)
O(1)	4308(2)	4647(7)	6530(5)	30(1)
O(2)	4563(2)	8025(6)	5260(6)	33(1)
O(3)	4099(2)	4997(8)	3627(6)	37(1)
O(4)	3444(2)	6901(6)	5391(6)	28(1)
C(1)	3128(4)	8405(15)	4148(9)	48(2)
C(2)	2513(3)	9216(12)	4763(8)	34(1)
C(3)	2530(4)	11236(14)	5525(10)	42(2)
C(4)	1978(4)	11984(11)	6180(11)	40(2)
C(5)	1424(3)	10723(12)	6014(8)	33(1)
C(6)	1408(4)	8678(13)	5239(10)	41(2)
C(7)	1951(4)	7949(11)	4629(10)	43(2)

Table S4. Bond lengths [Å] and angles [°]

I(1)-C(5)	2.096(7)
S(1)-Na(1)#1	3.206(3)
S(1)-Na(1)#2	3.390(3)
S(1)-O(1)	1.449(4)
S(1)-O(2)	1.453(4)
S(1)-O(3)	1.435(5)
S(1)-O(4)	1.567(5)
Na(1)-Na(1)#1	3.365(2)
Na(1)-Na(1)#3	3.365(2)
Na(1)-Na(1)#4	3.582(5)
Na(1)-O(1)#3	2.437(5)
Na(1)-O(1)	2.272(4)
Na(1)-O(2)#3	2.911(6)
Na(1)-O(2)#5	2.307(5)
Na(1)-O(2)#2	2.403(5)
Na(1)-O(3)#6	2.316(5)
O(4)-C(1)	1.469(8)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-C(2)	1.516(10)
C(2)-C(3)	1.376(11)
C(2)-C(7)	1.384(12)
C(3)-H(3)	0.9400
C(3)-C(4)	1.407(11)
C(4)-H(4)	0.9400
C(4)-C(5)	1.367(10)

C(5)-C(6)	1.395(11)
C(6)-H(6)	0.9400
C(6)-C(7)	1.368(12)
C(7)-H(7)	0.9400
Na(1)#1-S(1)-Na(1)#2	85.60(7)
O(1)-S(1)-Na(1)#2	124.8(2)
O(1)-S(1)-Na(1)#1	46.12(19)
O(1)-S(1)-O(2)	111.2(3)
O(1)-S(1)-O(4)	102.1(2)
O(2)-S(1)-Na(1)#2	37.4(2)
O(2)-S(1)-Na(1)#1	65.2(2)
O(2)-S(1)-O(4)	107.0(2)
O(3)-S(1)-Na(1)#1	133.2(2)
O(3)-S(1)-Na(1)#2	76.1(2)
O(3)-S(1)-O(1)	114.7(3)
O(3)-S(1)-O(2)	112.9(3)
O(3)-S(1)-O(4)	107.9(3)
O(4)-S(1)-Na(1)#2	126.93(17)
O(4)-S(1)-Na(1)#1	117.36(19)
S(1)#3-Na(1)-S(1)#2	86.84(7)
S(1)#3-Na(1)-Na(1)#1	65.13(9)
S(1)#3-Na(1)-Na(1)#4	114.14(11)
S(1)#2-Na(1)-Na(1)#4	60.94(7)
S(1)#3-Na(1)-Na(1)#3	62.57(8)
Na(1)#1-Na(1)-S(1)#2	63.30(7)
Na(1)#3-Na(1)-S(1)#2	114.66(11)
Na(1)#1-Na(1)-Na(1)#4	124.13(13)
Na(1)#3-Na(1)-Na(1)#4	80.32(8)
Na(1)#1-Na(1)-Na(1)#3	127.66(15)
O(1)-Na(1)-S(1)#2	78.82(13)
O(1)#3-Na(1)-S(1)#2	86.16(13)
O(1)-Na(1)-S(1)#3	109.12(14)
O(1)#3-Na(1)-S(1)#3	25.37(10)
O(1)#3-Na(1)-Na(1)#1	87.44(14)
O(1)-Na(1)-Na(1)#4	117.09(16)
O(1)#3-Na(1)-Na(1)#4	92.10(14)
O(1)#3-Na(1)-Na(1)#3	42.45(11)
O(1)-Na(1)-Na(1)#3	162.34(17)
O(1)-Na(1)-Na(1)#1	46.37(12)
O(1)-Na(1)-O(1)#3	133.35(18)
O(1)-Na(1)-O(2)#2	91.69(16)
O(1)-Na(1)-O(2)#3	82.78(15)
O(1)#3-Na(1)-O(2)#3	52.28(13)

O(1)-Na(1)-O(2)#5	132.6(2)
O(1)-Na(1)-O(3)#6	94.60(19)
O(2)#5-Na(1)-S(1)#2	102.41(14)
O(2)#3-Na(1)-S(1)#2	86.99(11)
O(2)#3-Na(1)-S(1)#3	26.93(9)
O(2)#2-Na(1)-S(1)#3	98.88(16)
O(2)#5-Na(1)-S(1)#3	118.32(15)
O(2)#2-Na(1)-S(1)#2	21.53(11)
O(2)#5-Na(1)-Na(1)#4	41.50(13)
O(2)#2-Na(1)-Na(1)#4	39.49(11)
O(2)#5-Na(1)-Na(1)#3	58.24(13)
O(2)#3-Na(1)-Na(1)#3	86.50(13)
O(2)#2-Na(1)-Na(1)#3	104.74(15)
O(2)#5-Na(1)-Na(1)#1	165.59(18)
O(2)#3-Na(1)-Na(1)#1	42.35(10)
O(2)#2-Na(1)-Na(1)#1	84.65(13)
O(2)#3-Na(1)-Na(1)#4	134.90(15)
O(2)#2-Na(1)-O(1)#3	89.62(18)
O(2)#5-Na(1)-O(1)#3	93.66(17)
O(2)#5-Na(1)-O(2)#3	144.39(16)
O(2)#5-Na(1)-O(2)#2	80.99(17)
O(2)#2-Na(1)-O(2)#3	105.78(19)
O(2)#5-Na(1)-O(3)#6	92.17(19)
O(3)#6-Na(1)-S(1)#2	164.78(16)
O(3)#6-Na(1)-S(1)#3	82.35(13)
O(3)#6-Na(1)-Na(1)#4	133.63(18)
O(3)#6-Na(1)-Na(1)#1	102.22(17)
O(3)#6-Na(1)-Na(1)#3	69.45(15)
O(3)#6-Na(1)-O(1)#3	88.60(18)
O(3)#6-Na(1)-O(2)#3	78.52(16)
O(3)#6-Na(1)-O(2)#2	172.81(19)
S(1)-O(1)-Na(1)	132.0(3)
S(1)-O(1)-Na(1)#1	108.5(2)
Na(1)-O(1)-Na(1)#1	91.18(15)
S(1)-O(2)-Na(1)#7	139.5(3)
S(1)-O(2)-Na(1)#1	87.9(2)
S(1)-O(2)-Na(1)#2	121.1(3)
Na(1)#7-O(2)-Na(1)#1	79.41(16)
Na(1)#7-O(2)-Na(1)#2	99.01(17)
Na(1)#2-O(2)-Na(1)#1	114.7(2)
S(1)-O(3)-Na(1)#8	140.7(3)
C(1)-O(4)-S(1)	115.7(4)
O(4)-C(1)-H(1A)	110.6

O(4)-C(1)-H(1B)	110.6
O(4)-C(1)-C(2)	105.6(5)
H(1A)-C(1)-H(1B)	108.7
C(2)-C(1)-H(1A)	110.6
C(2)-C(1)-H(1B)	110.6
C(3)-C(2)-C(1)	118.4(7)
C(3)-C(2)-C(7)	119.7(7)
C(7)-C(2)-C(1)	121.8(7)
C(2)-C(3)-H(3)	120.1
C(2)-C(3)-C(4)	119.8(7)
C(4)-C(3)-H(3)	120.1
C(3)-C(4)-H(4)	120.2
C(5)-C(4)-C(3)	119.6(6)
C(5)-C(4)-H(4)	120.2
C(4)-C(5)-I(1)	119.4(5)
C(4)-C(5)-C(6)	120.5(7)
C(6)-C(5)-I(1)	120.1(5)
C(5)-C(6)-H(6)	120.3
C(7)-C(6)-C(5)	119.5(7)
C(7)-C(6)-H(6)	120.3
C(2)-C(7)-H(7)	119.6
C(6)-C(7)-C(2)	120.9(6)
C(6)-C(7)-H(7)	119.6

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y+1/2,-z+3/2 #2 -x+1,-y+1,-z+1 #3 -x+1,y-1/2,-z+3/2

#4 -x+1,-y,-z+1 #5 x,y-1,z #6 x,-y+1/2,z+1/2

#7 x,y+1,z #8 x,-y+1/2,z-1/2

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*b^*U^{12}\ ]$

U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	U^{11}
I(1)	34(1)	91(1)	54(1)	-17(1)	16(1)	12(1)
S(1)	21(1)	20(1)	20(1)	0(1)	7(1)	1(1)
Na(1)	33(2)	21(1)	30(1)	2(1)	10(1)	1(1)
O(1)	29(2)	32(2)	31(2)	12(2)	8(2)	10(2)
O(2)	35(3)	24(2)	43(3)	-2(2)	21(2)	-5(2)
O(3)	31(2)	51(2)	31(3)	-15(2)	5(2)	7(2)
O(4)	24(3)	35(2)	25(2)	4(2)	7(2)	7(2)
C(1)	46(5)	79(5)	20(3)	22(3)	9(3)	31(4)
C(2)	29(3)	50(3)	25(3)	11(3)	6(2)	18(3)
C(3)	28(4)	56(4)	45(4)	4(3)	13(3)	1(3)
C(4)	25(4)	43(4)	52(5)	-8(3)	8(3)	3(3)
C(5)	21(3)	46(3)	31(3)	1(3)	1(2)	1(3)

C(6)	26(4)	54(4)	44(4)	-5(3)	7(3)	0(3)
C(7)	49(5)	40(4)	39(4)	-10(3)	2(3)	11(3)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3).

	x	y	z	U(eq)
H(1A)	3019	7621	3125	57
H(1B)	3416	9650	3987	57
H(3)	2908	12113	5607	51
H(4)	1990	13343	6729	48
H(6)	1028	7808	5137	49
H(7)	1942	6567	4111	51

Table S7. Torsion angles [°].

I(1)-C(5)-C(6)-C(7)	180.0(6)
S(1)-O(4)-C(1)-C(2)	-171.8(5)
Na(1)#2-S(1)-O(1)-Na(1)	-72.1(4)
Na(1)#2-S(1)-O(1)-Na(1)#1	37.1(3)
Na(1)#1-S(1)-O(1)-Na(1)	-109.3(4)
Na(1)#2-S(1)-O(2)-Na(1)#1	-117.8(3)
Na(1)#1-S(1)-O(2)-Na(1)#7	-71.0(4)
Na(1)#2-S(1)-O(2)-Na(1)#7	171.2(7)
Na(1)#1-S(1)-O(2)-Na(1)#2	117.8(3)
Na(1)#2-S(1)-O(3)-Na(1)#8	39.2(4)
Na(1)#1-S(1)-O(3)-Na(1)#8	-30.9(7)
Na(1)#1-S(1)-O(4)-C(1)	134.3(5)
Na(1)#2-S(1)-O(4)-C(1)	28.0(6)
O(1)-S(1)-O(2)-Na(1)#7	-68.8(5)
O(1)-S(1)-O(2)-Na(1)#1	2.1(3)
O(1)-S(1)-O(2)-Na(1)#2	119.9(3)
O(1)-S(1)-O(3)-Na(1)#8	-83.0(6)
O(1)-S(1)-O(4)-C(1)	-179.1(5)
O(2)-S(1)-O(1)-Na(1)	-111.9(4)
O(2)-S(1)-O(1)-Na(1)#1	-2.7(3)
O(2)-S(1)-O(3)-Na(1)#8	45.9(6)
O(2)-S(1)-O(4)-C(1)	63.9(6)
O(3)-S(1)-O(1)-Na(1)#1	127.1(3)
O(3)-S(1)-O(1)-Na(1)	17.8(5)
O(3)-S(1)-O(2)-Na(1)#1	-128.5(2)
O(3)-S(1)-O(2)-Na(1)#2	-10.7(4)
O(3)-S(1)-O(2)-Na(1)#7	160.5(4)
O(3)-S(1)-O(4)-C(1)	-57.9(6)
O(4)-S(1)-O(1)-Na(1)	134.2(3)
O(4)-S(1)-O(1)-Na(1)#1	-116.5(2)

O(4)-S(1)-O(2)-Na(1)#1	112.8(2)
O(4)-S(1)-O(2)-Na(1)#7	41.9(5)
O(4)-S(1)-O(2)-Na(1)#2	-129.4(3)
O(4)-S(1)-O(3)-Na(1)#8	164.0(4)
O(4)-C(1)-C(2)-C(3)	97.4(8)
O(4)-C(1)-C(2)-C(7)	-80.3(9)
C(1)-C(2)-C(3)-C(4)	-176.8(7)
C(1)-C(2)-C(7)-C(6)	177.8(7)
C(2)-C(3)-C(4)-C(5)	-1.8(12)
C(3)-C(2)-C(7)-C(6)	0.2(12)
C(3)-C(4)-C(5)-I(1)	-178.9(6)
C(3)-C(4)-C(5)-C(6)	1.7(12)
C(4)-C(5)-C(6)-C(7)	-0.7(12)
C(5)-C(6)-C(7)-C(2)	-0.3(12)
C(7)-C(2)-C(3)-C(4)	0.9(11)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y+1/2,-z+3/2 #2 -x+1,-y+1,-z+1 #3 -x+1,y-1/2,-z+3/2

#4 -x+1,-y,-z+1 #5 x,y-1,z #6 x,-y+1/2,z+1/2

#7 x,y+1,z #8 x,-y+1/2,z-1/2

Table S8. Hydrogen bonds [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

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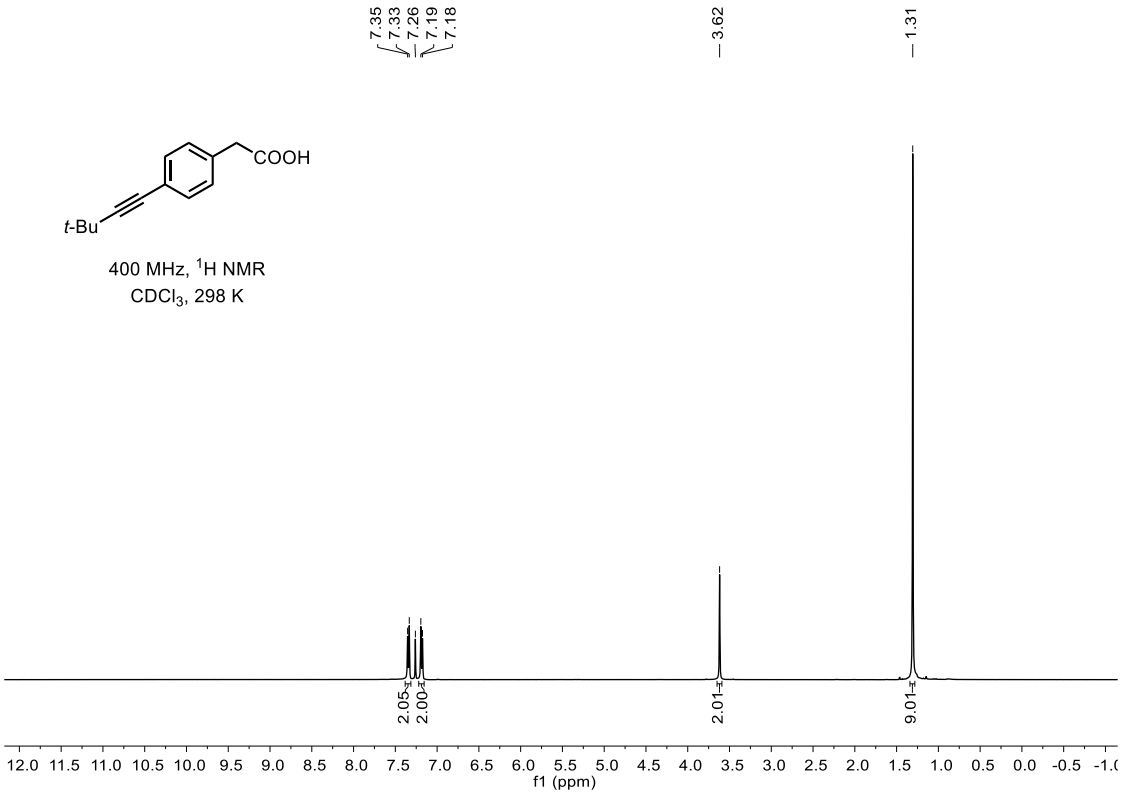
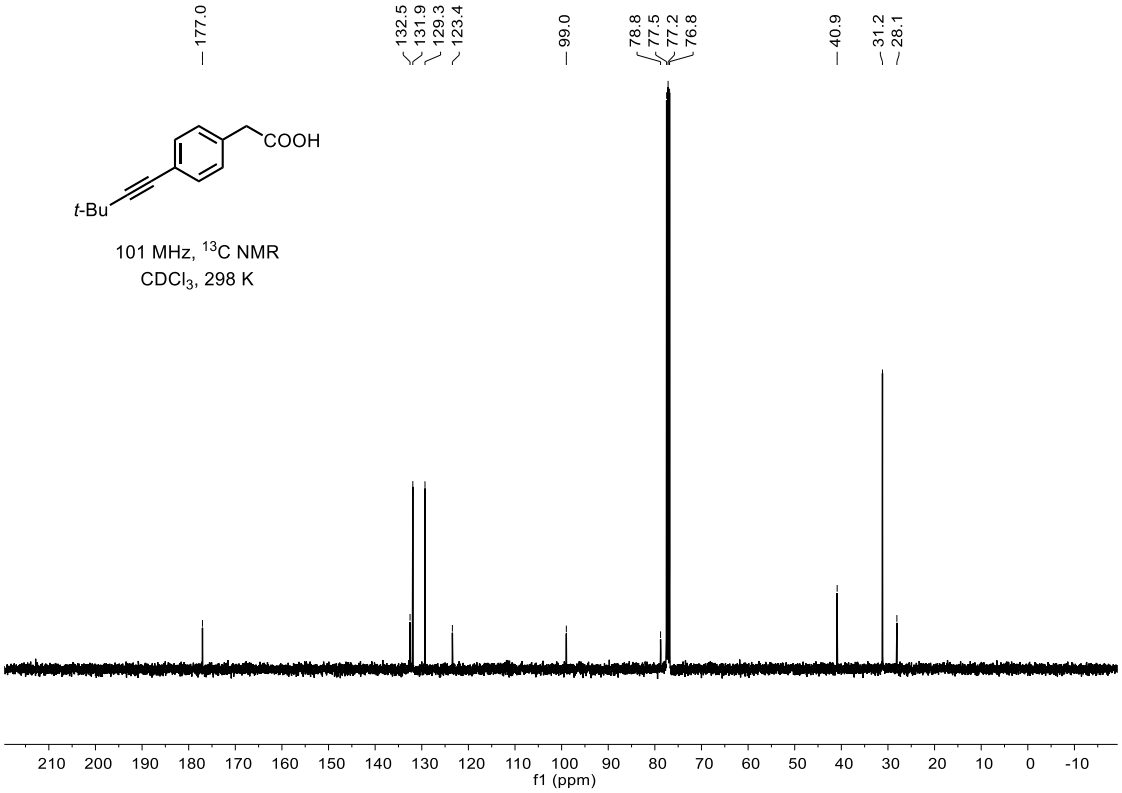
SPECTROSCOPIC DATA

4-(3,3-dimethyl-1-yne)benzyl carboxylic acid (25s)

^{1}H NMR of 4-(3,3-dimethyl-1-yne)benzyl carboxylic acid (25s)

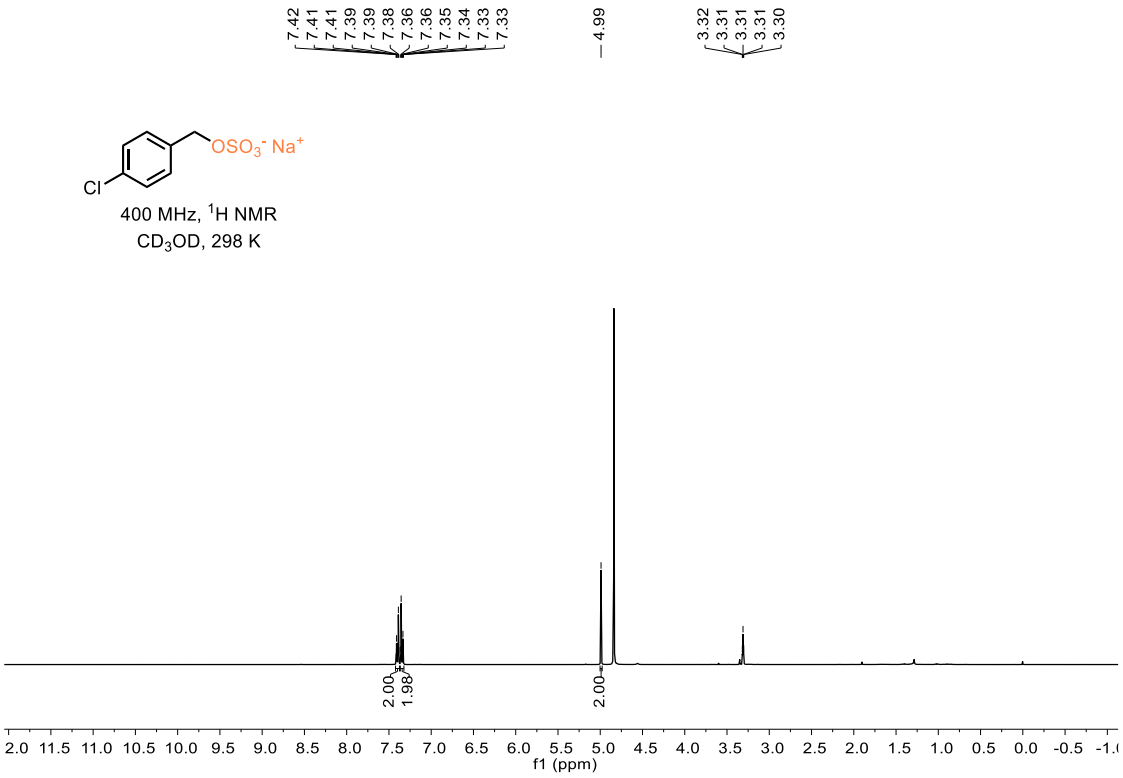


^{13}C NMR of 4-(3,3-dimethyl-1-yne)benzyl carboxylic acid (25s)

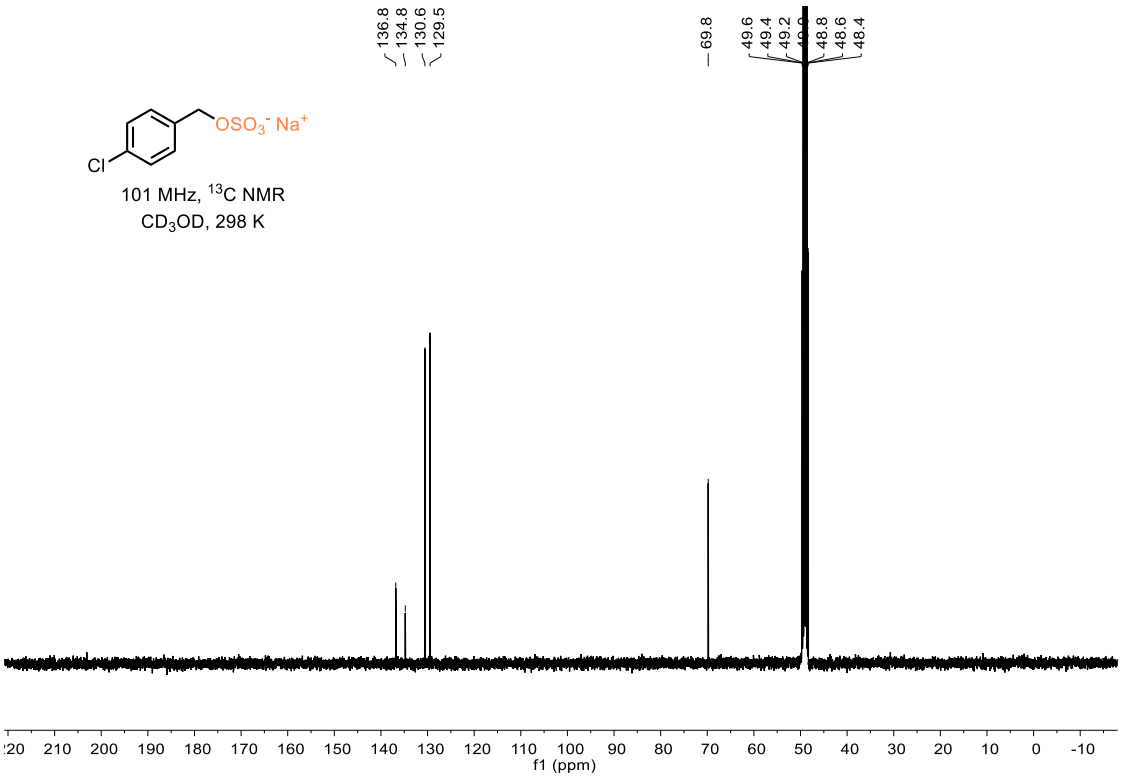


Sodium 4-chlorobenzyl sulfate (1)

^{1}H NMR of sodium 4-chlorobenzyl sulfate (1)

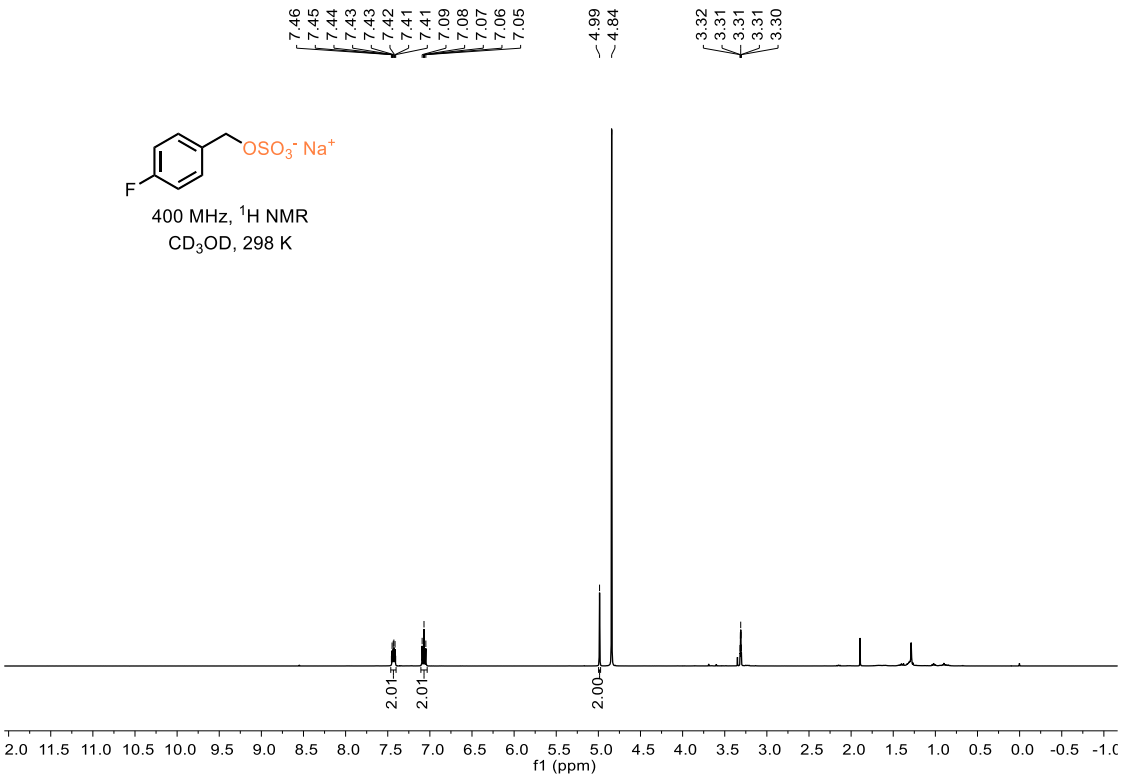


^{13}C NMR of sodium 4-chlorobenzyl sulfate (1)

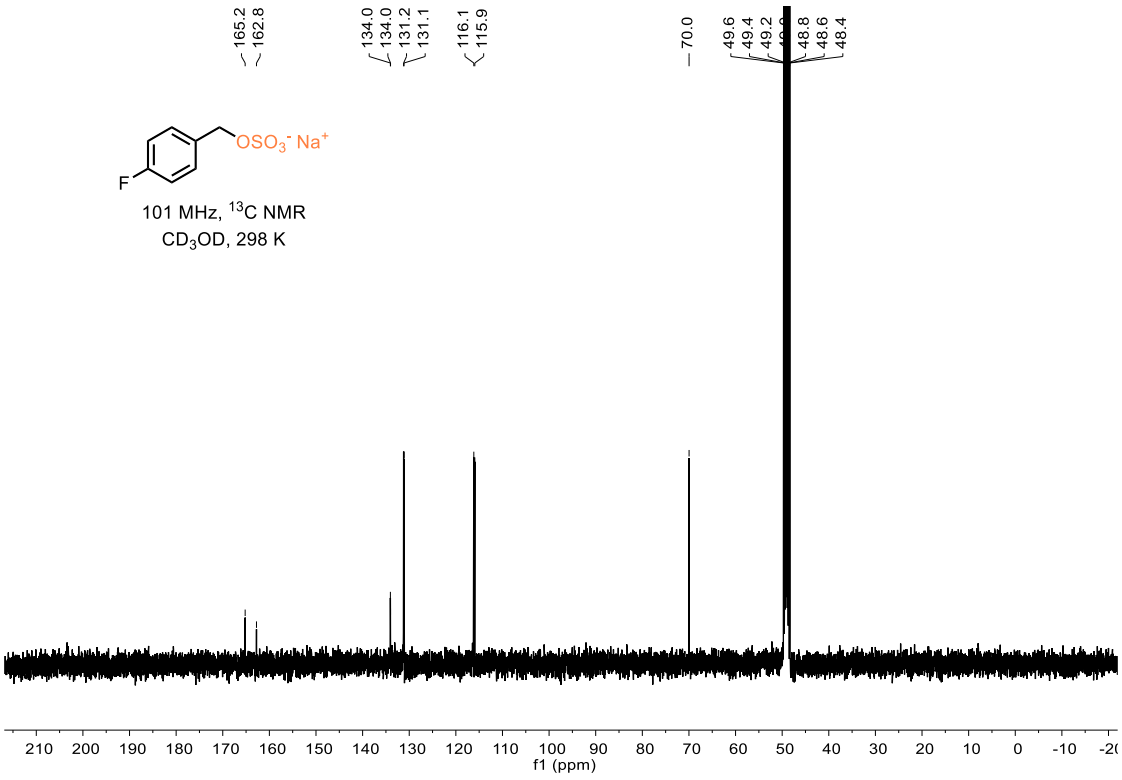


Sodium 4-fluorobenzyl sulfate (2)

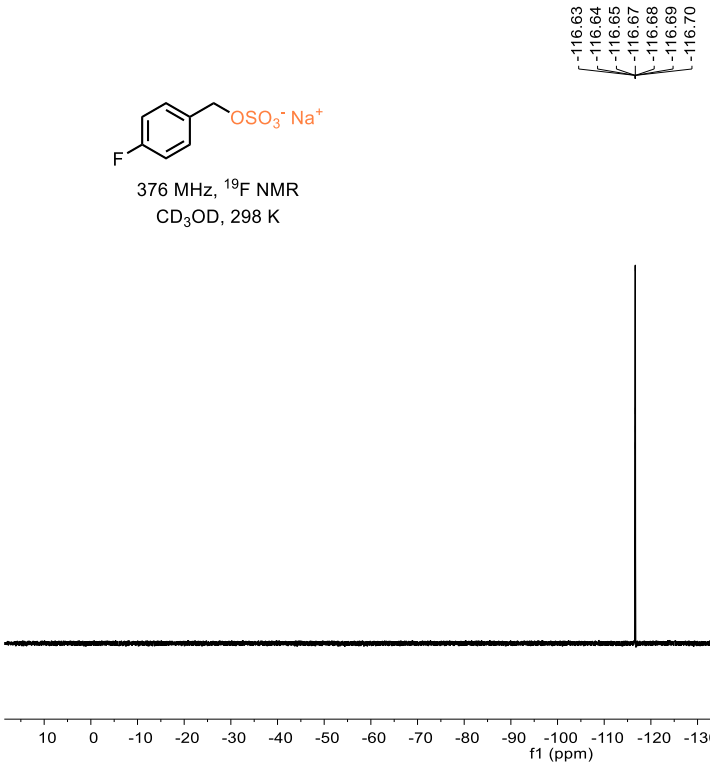
^{1}H NMR of sodium 4-fluorobenzyl sulfate (2)



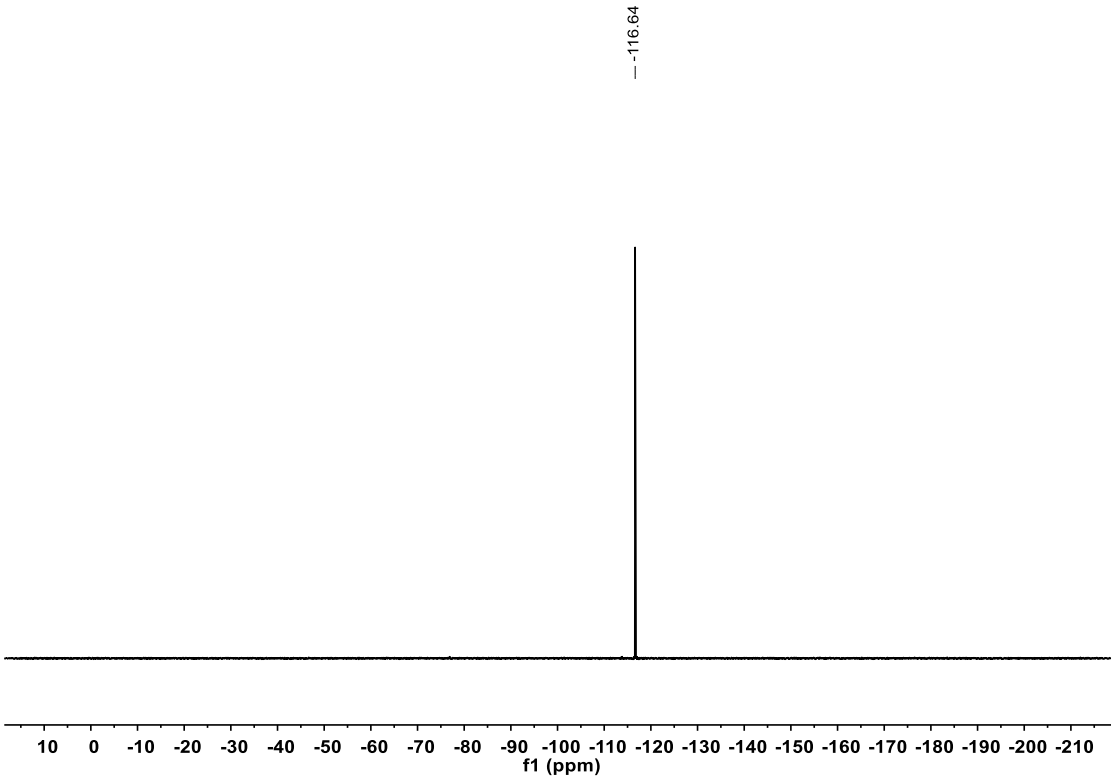
^{13}C NMR of sodium 4-fluorobenzyl sulfate (2)



^{19}F NMR of sodium 4-fluorobenzyl sulfate (2)

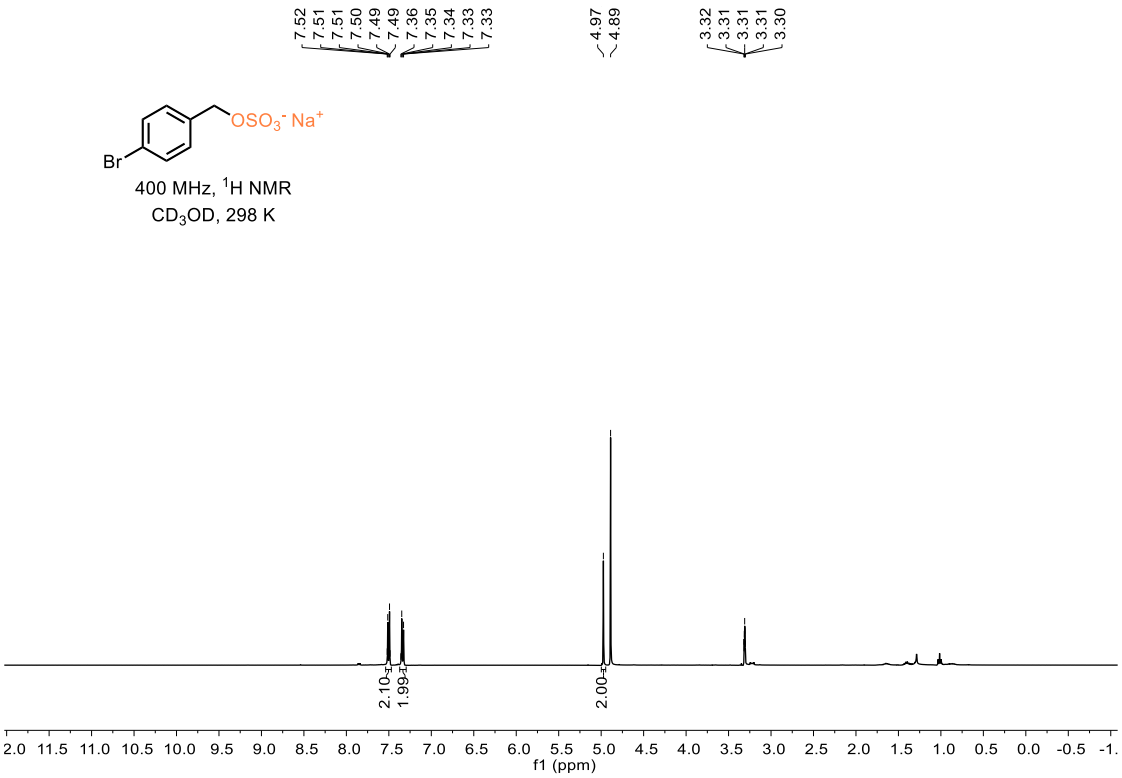


^{19}F{^{1}H} NMR of sodium 4-fluorobenzyl sulfate (2)

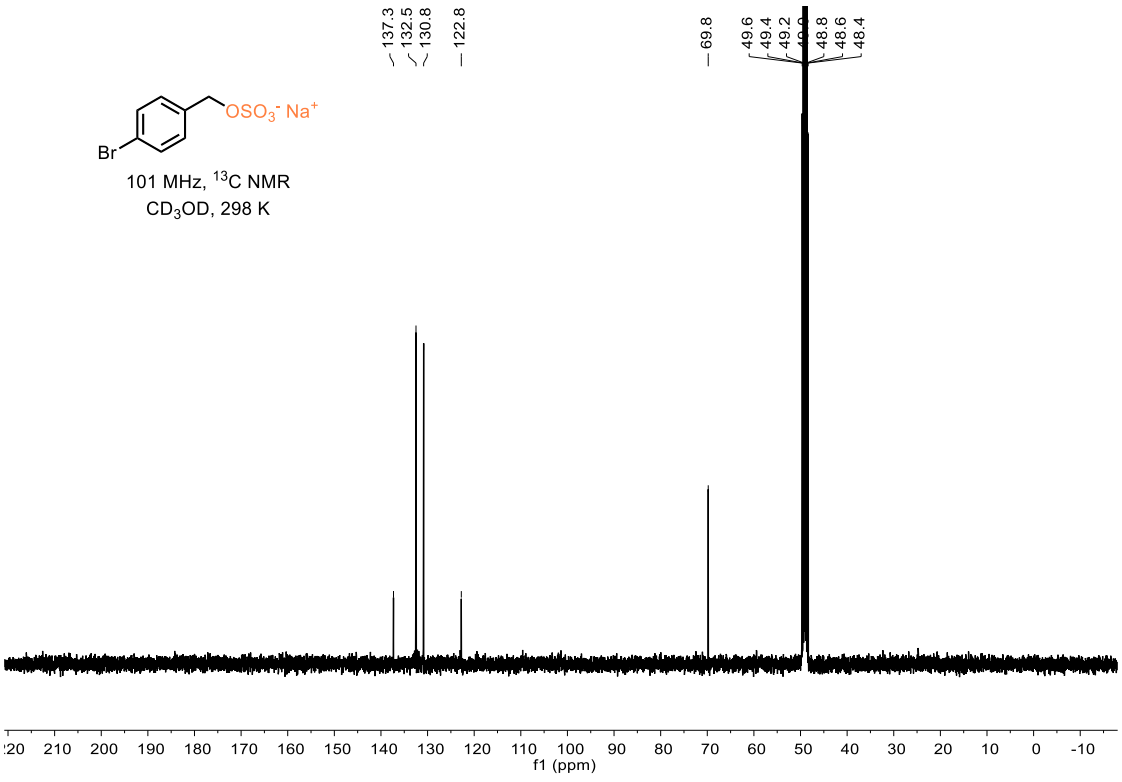


Sodium 4-bromobenzyl sulfate (3)

^{1}H NMR of sodium 4-bromobenzyl sulfate (3)

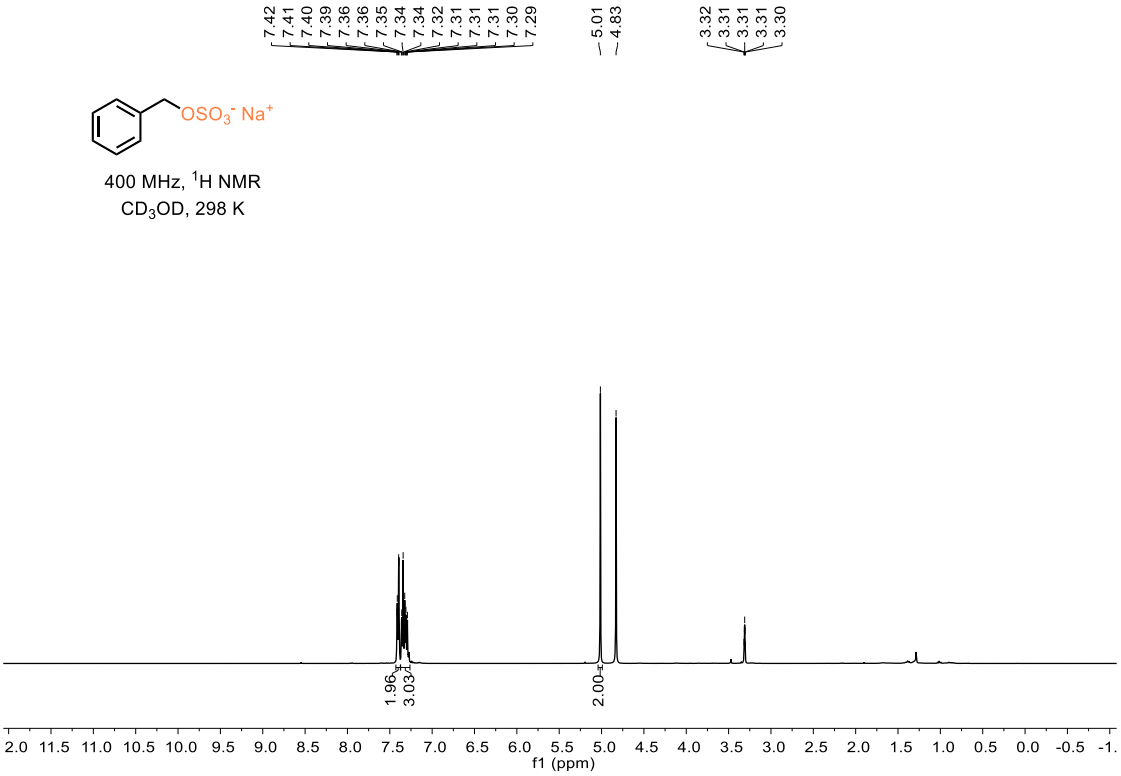


^{13}C NMR of sodium 4-bromobenzyl sulfate (3)

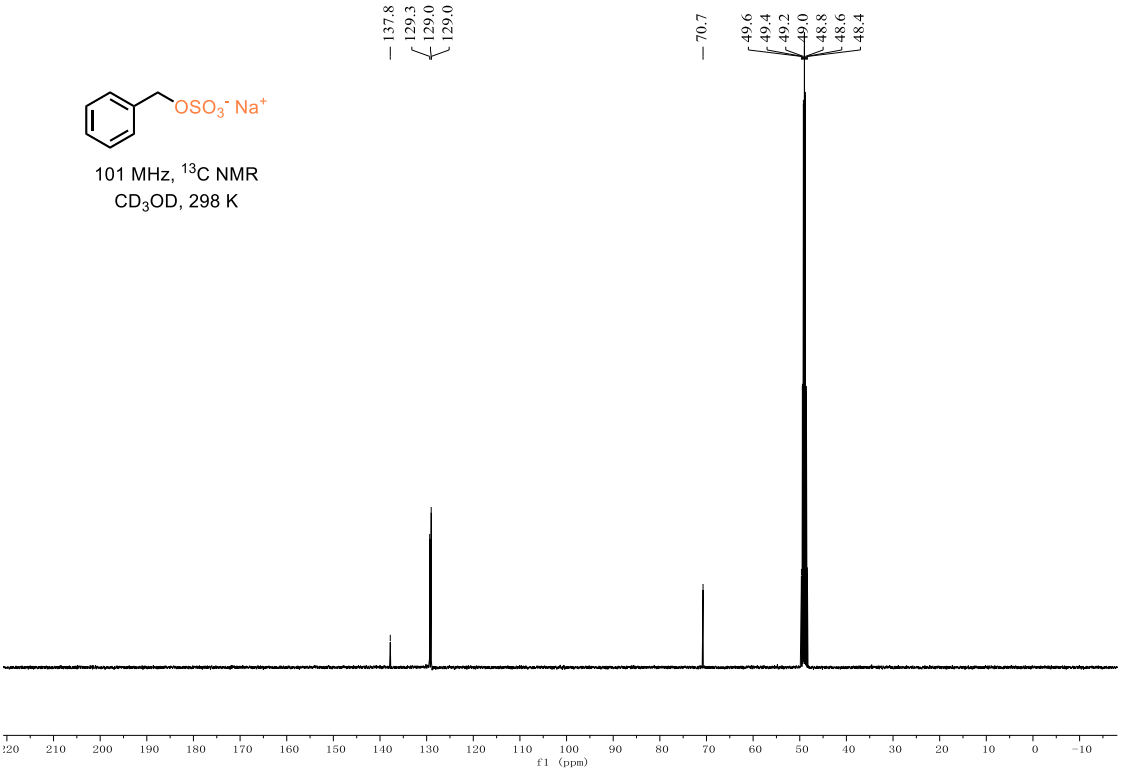


Sodium benzyl sulfate (4)

^{1}H NMR of sodium benzyl sulfate (4)

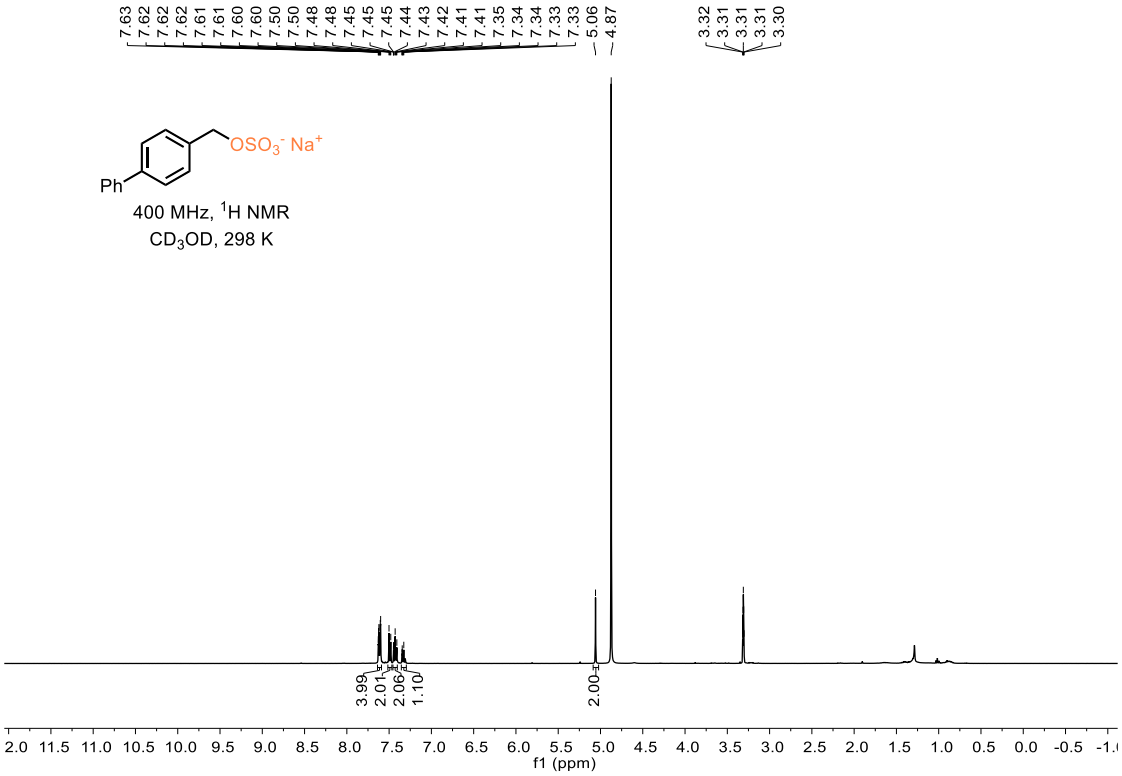


^{13}C NMR of sodium benzyl sulfate (4)

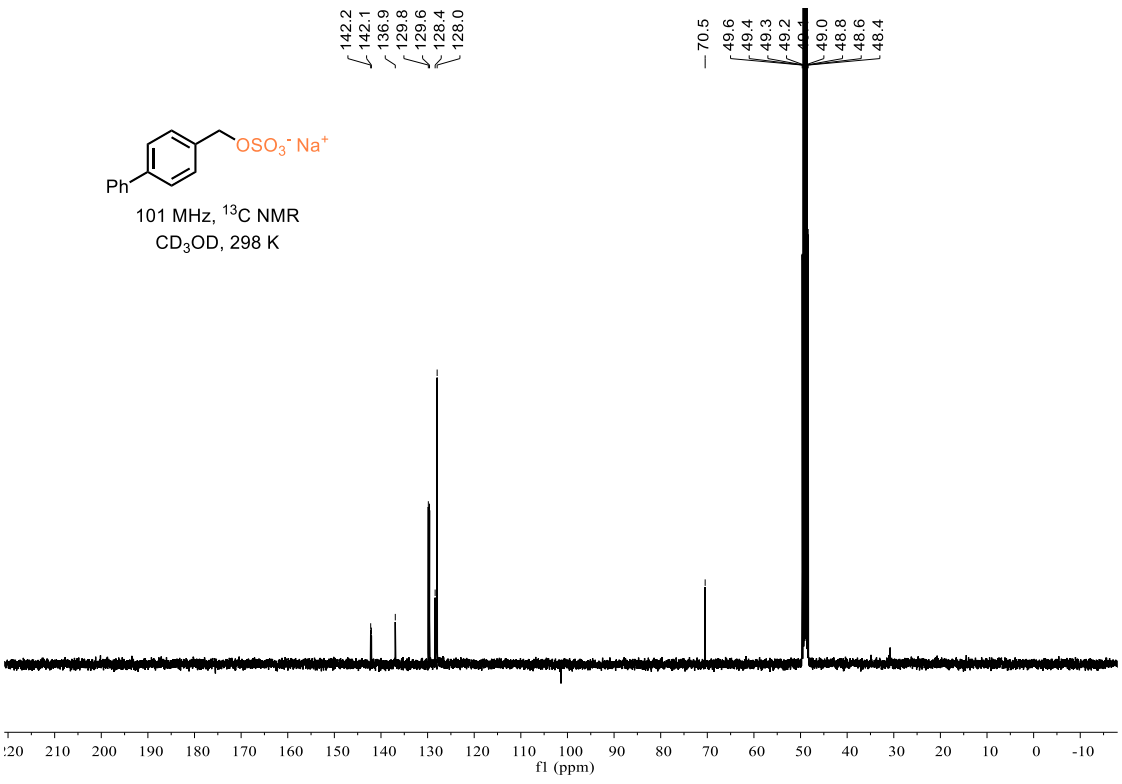


Sodium 4-phenylbenzyl sulfate (5)

^{1}H NMR of sodium 4-phenylbenzyl sulfate (5)

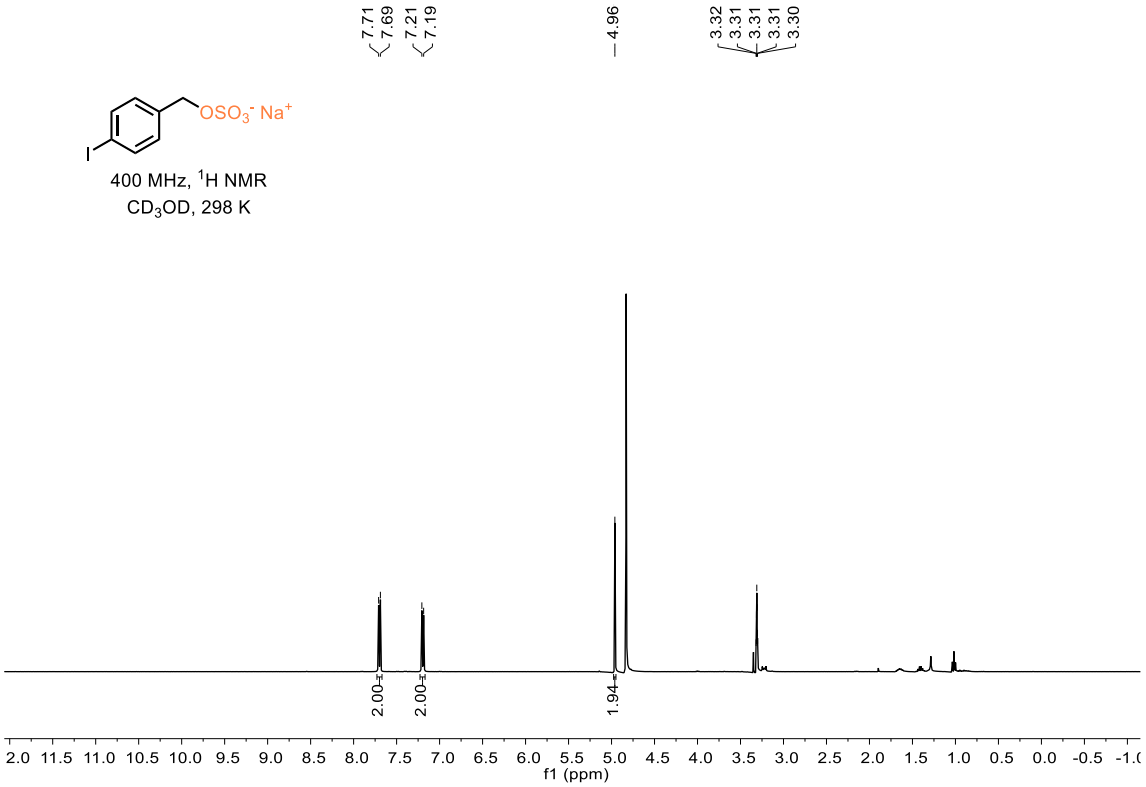


^{13}C NMR of sodium 4-phenylbenzyl sulfate (5)

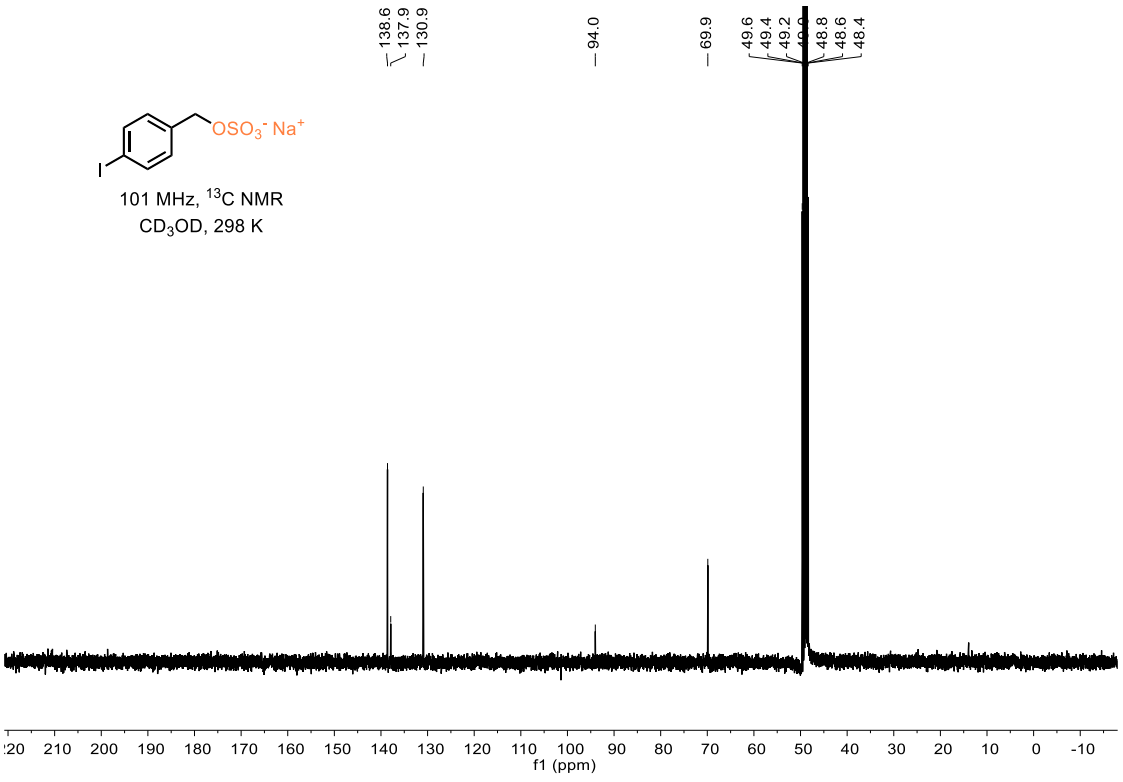


Sodium 4-iodobenzyl sulfate (6)

^{1}H NMR of sodium 4-iodobenzyl sulfate (6)

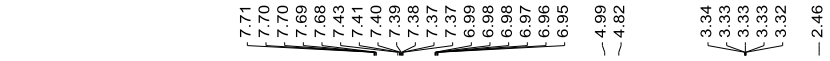


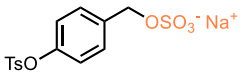
^{13}C NMR of sodium 4-iodobenzyl sulfate (6)



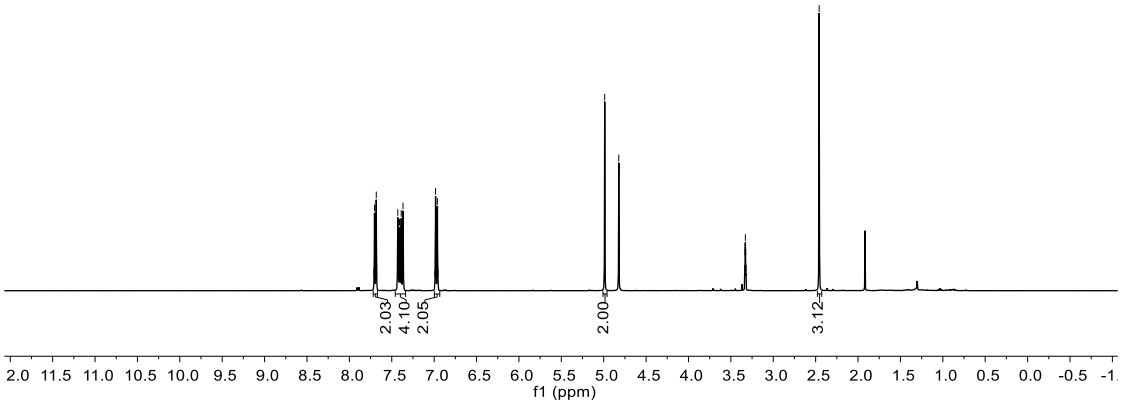
Sodium 4-(tosyloxy)benzyl sulfate (7)

^{1}H NMR of sodium 4-(tosyloxy)benzyl sulfate (7)

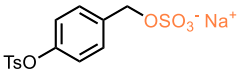




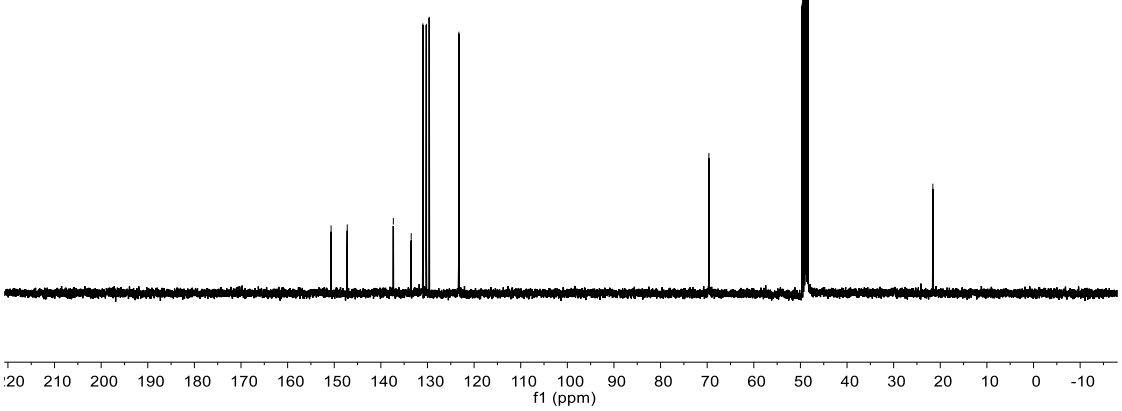
400 MHz, ^{1}H NMR
CD_3OD, 298 K



^{13}C NMR of sodium 4-(tosyloxy)benzyl sulfate (7)

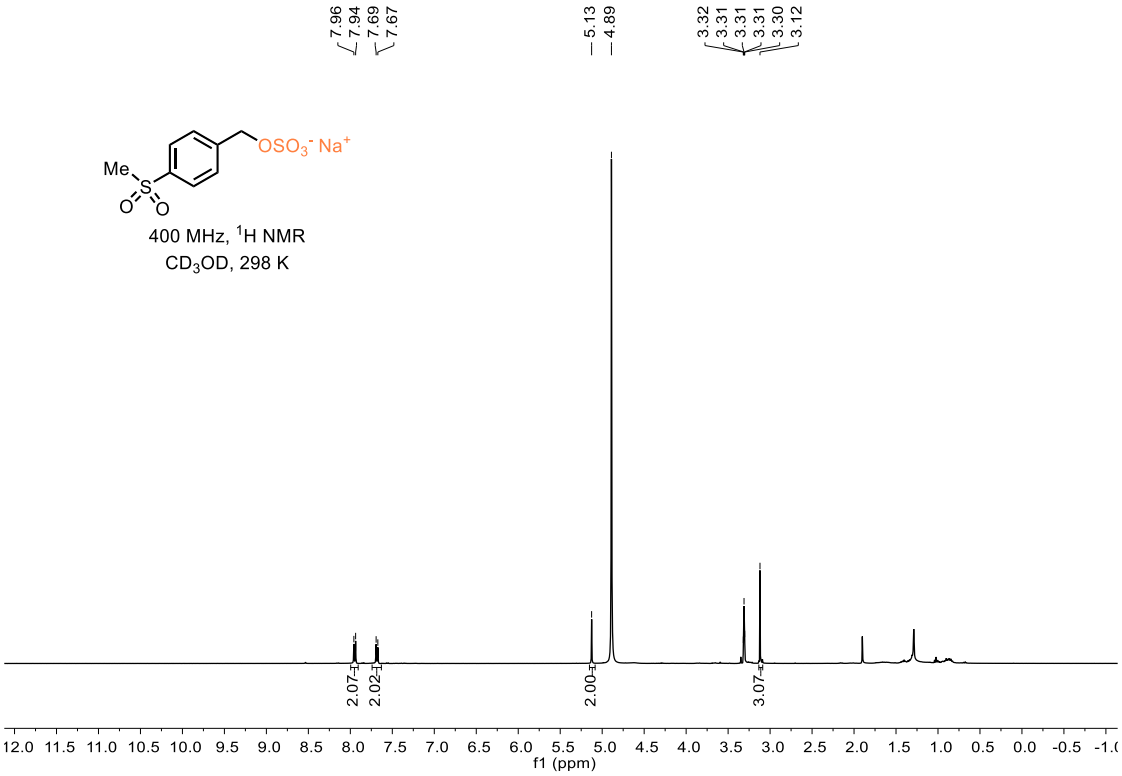


101 MHz, ^{13}C NMR
CD_3OD, 298 K

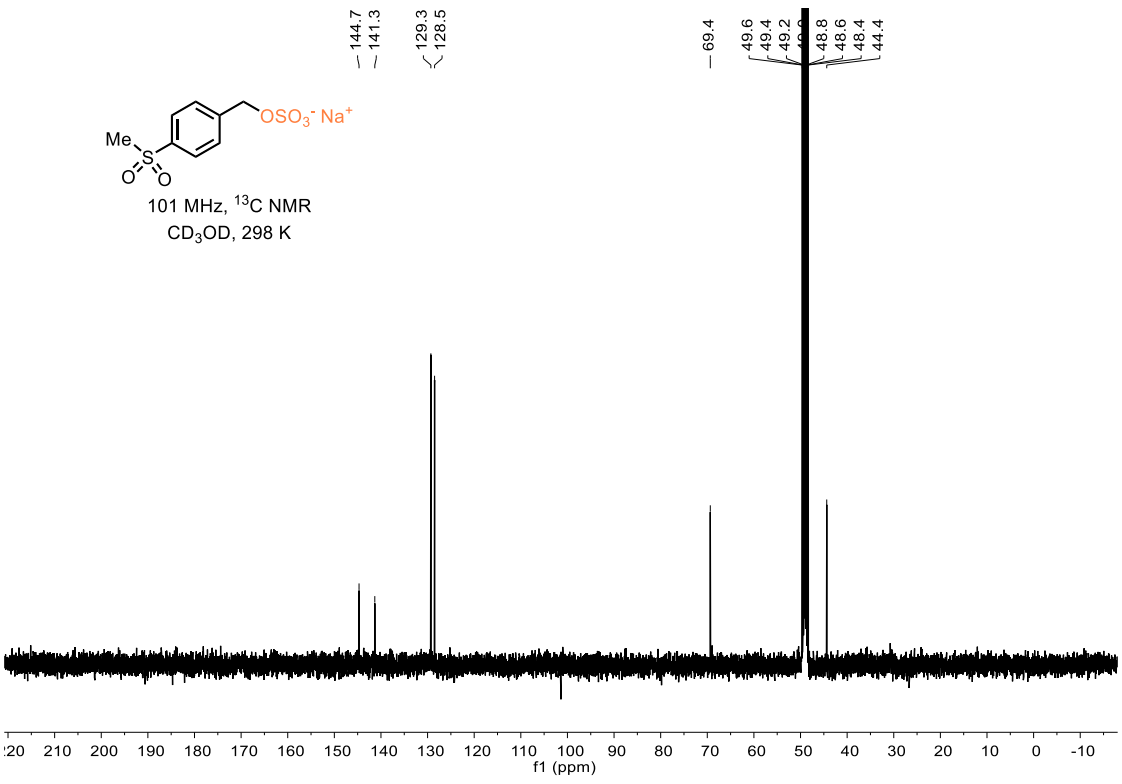


Sodium 4-(methylsulfonyl)benzyl sulfate (8)

^{1}H NMR of sodium 4-(methylsulfonyl)benzyl sulfate (8)

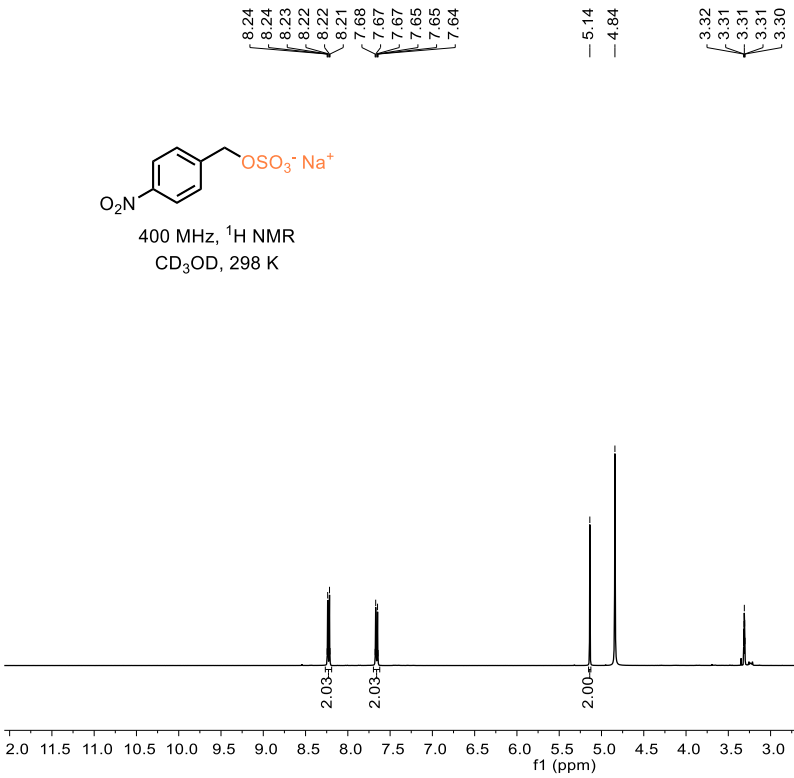


^{13}C NMR of sodium 4-(methylsulfonyl)benzyl sulfate (8)

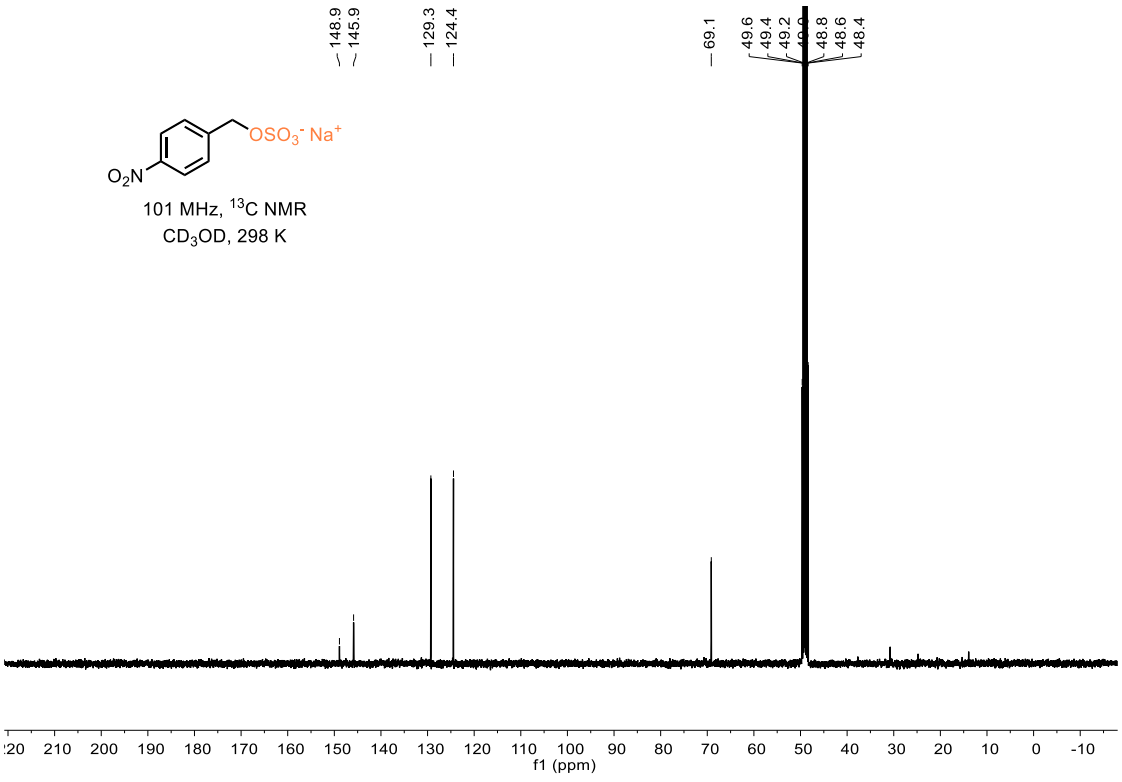


Sodium 4-nitrobenzyl sulfate (9)

^{1}H NMR of sodium 4-nitrobenzyl sulfate (9)

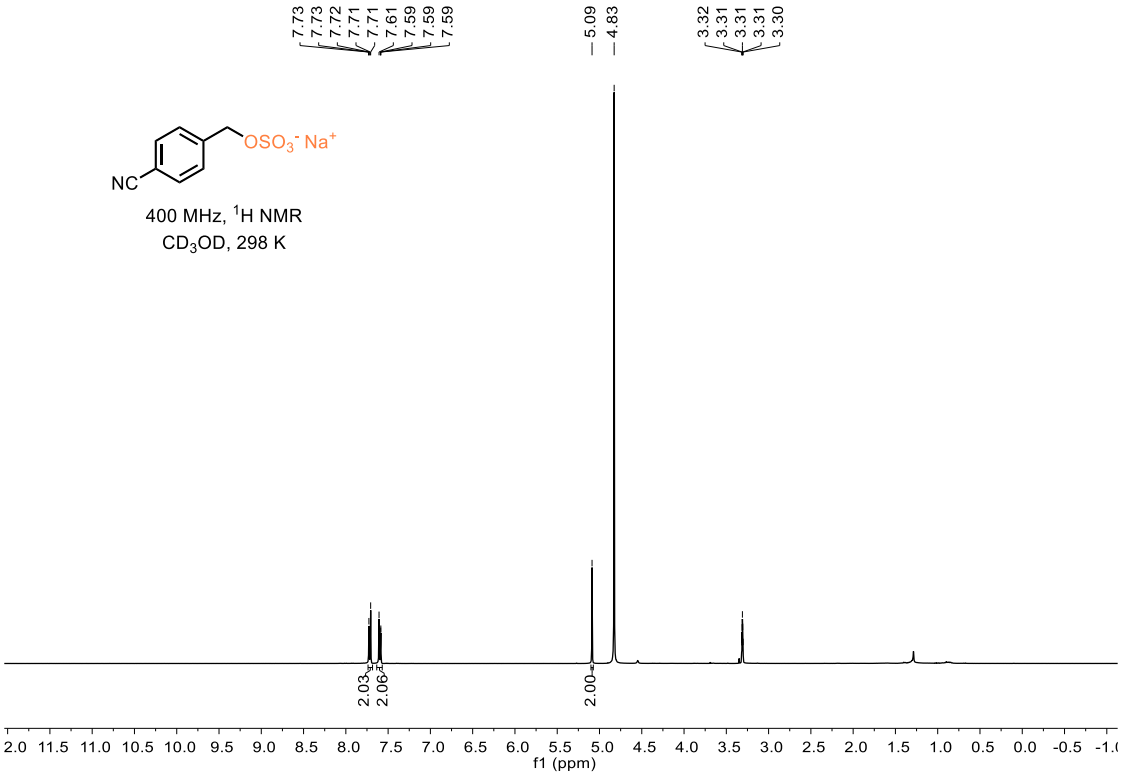


^{13}C NMR of sodium 4-nitrobenzyl sulfate (9)

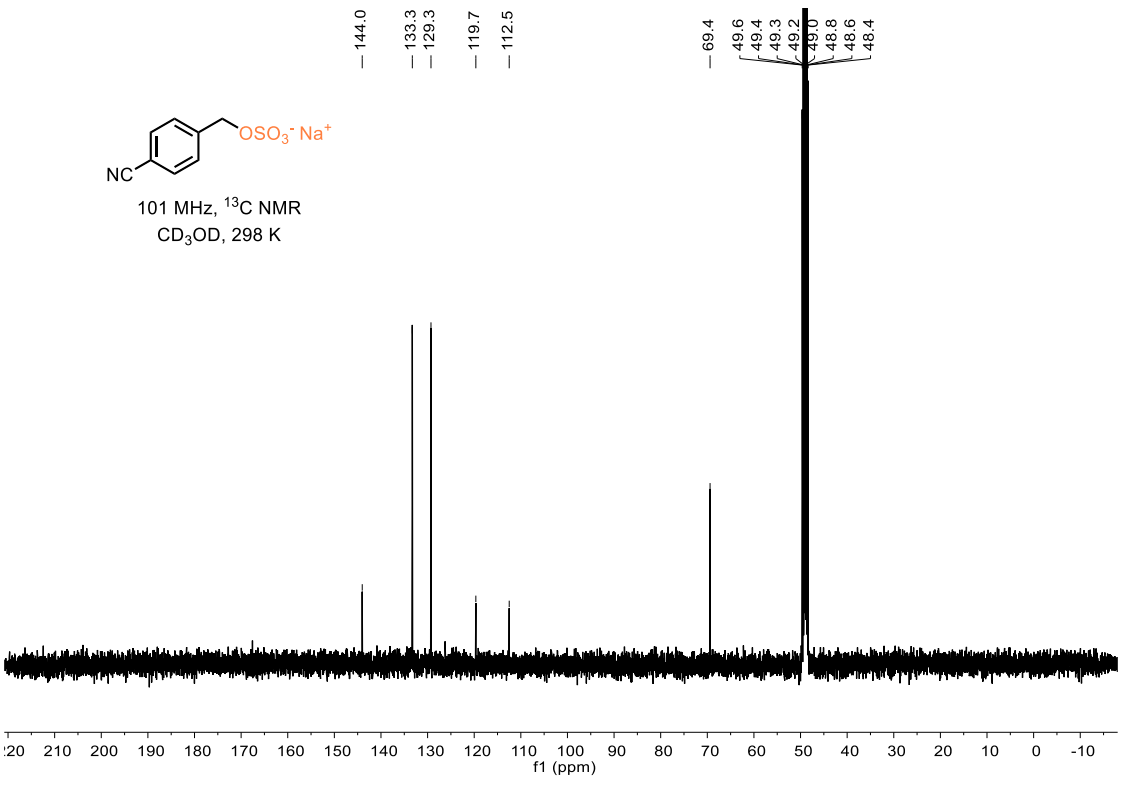


Sodium 4-cyanobenzyl sulfate (10)

^{1}H NMR of sodium 4-cyanobenzyl sulfate (10)

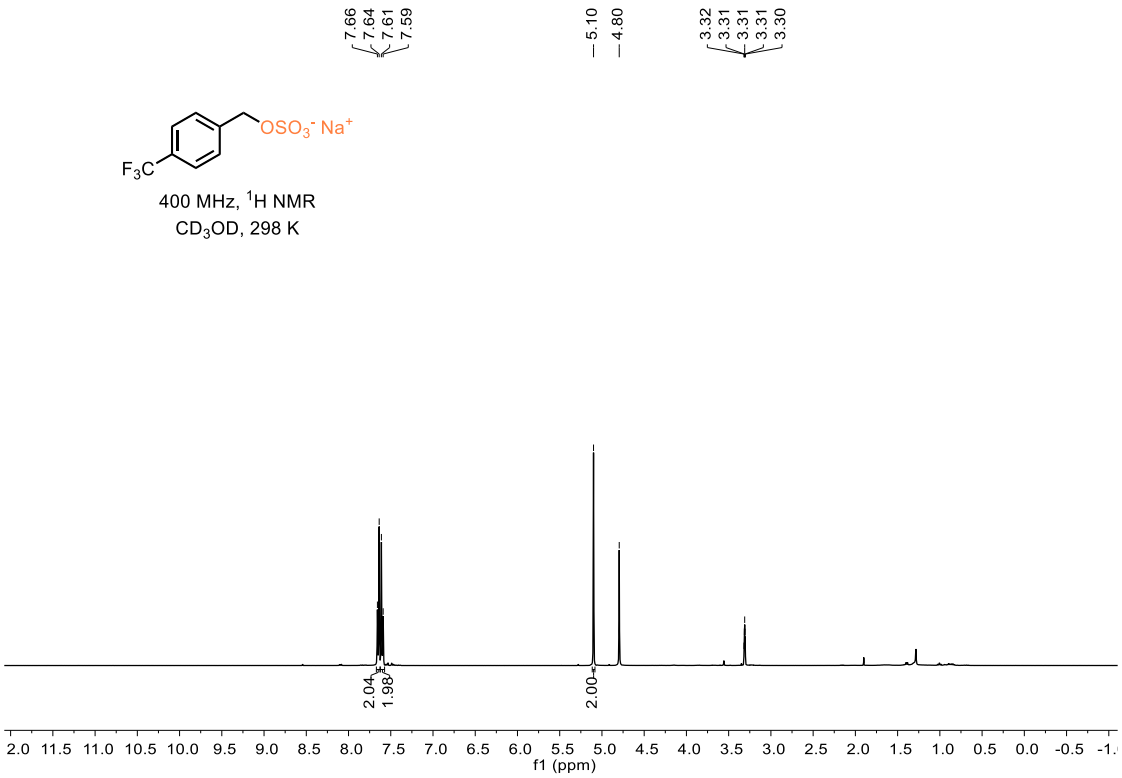


^{13}C NMR of sodium 4-cyanobenzyl sulfate (10)

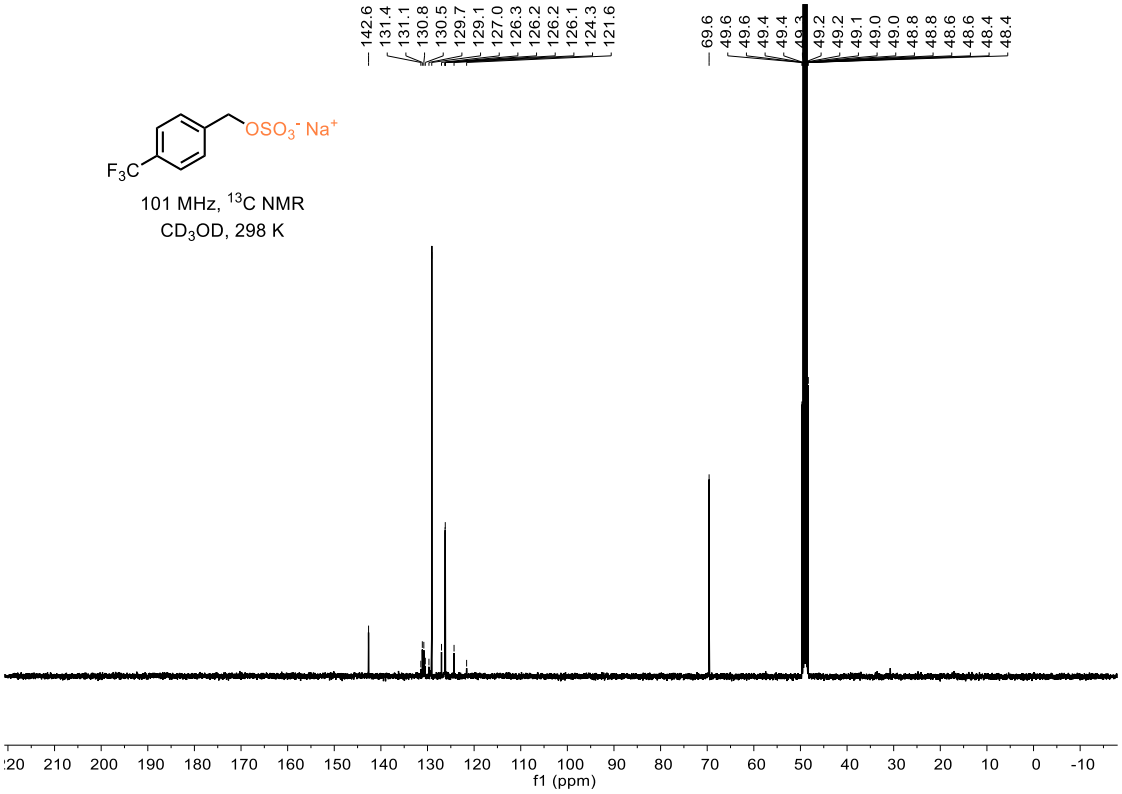


Sodium 4-(trifluoromethyl)benzyl sulfate (11)

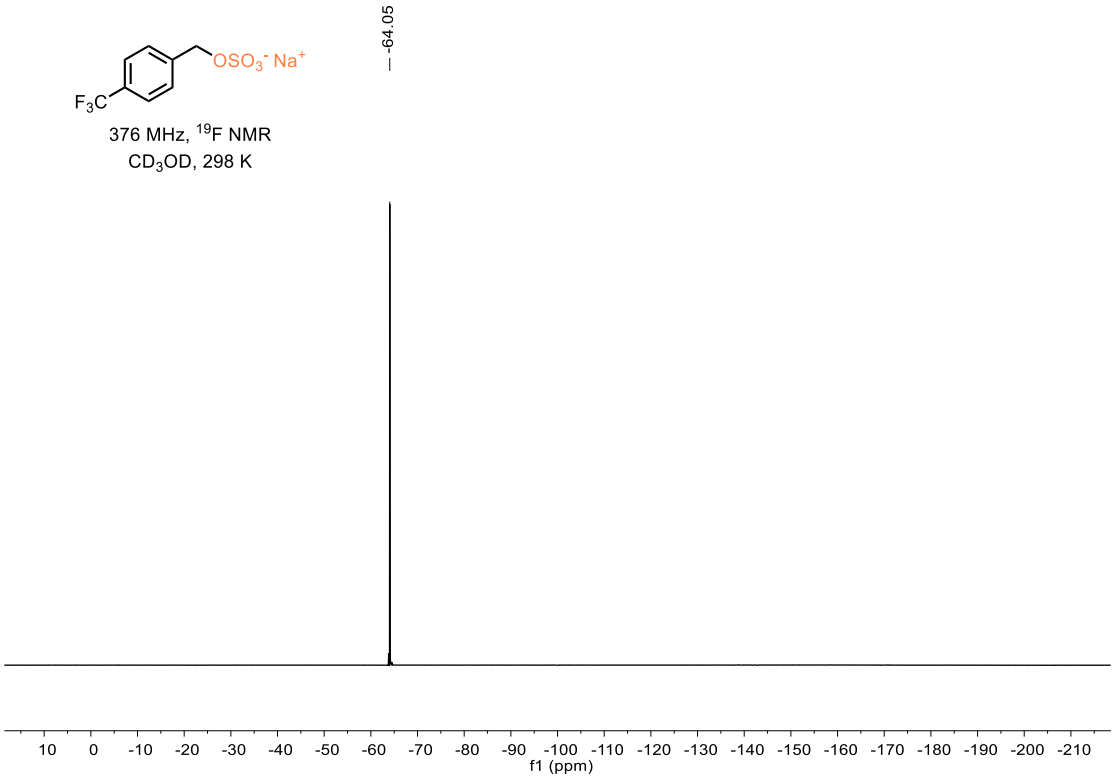
^{1}H NMR of sodium 4-(trifluoromethyl)benzyl sulfate (11)



^{13}C NMR of sodium 4-(trifluoromethyl)benzyl sulfate (11)

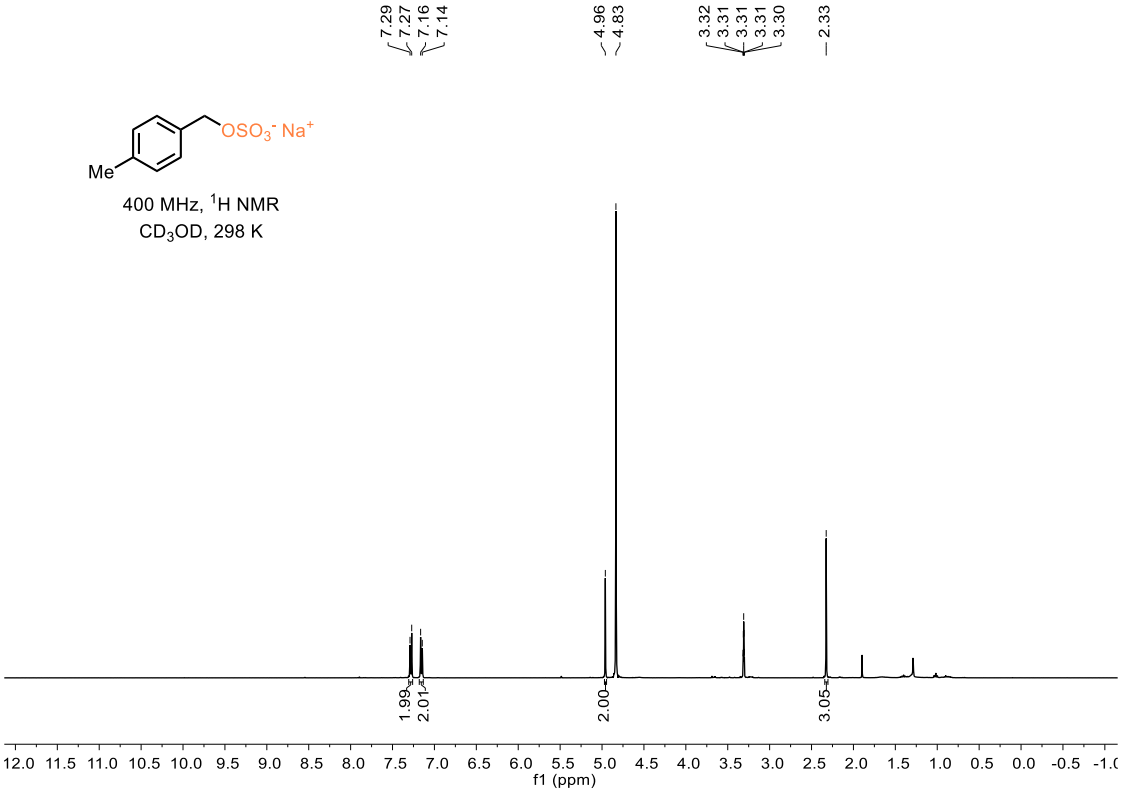


^{19}F NMR of sodium 4-(trifluoromethyl)benzyl sulfate (11)

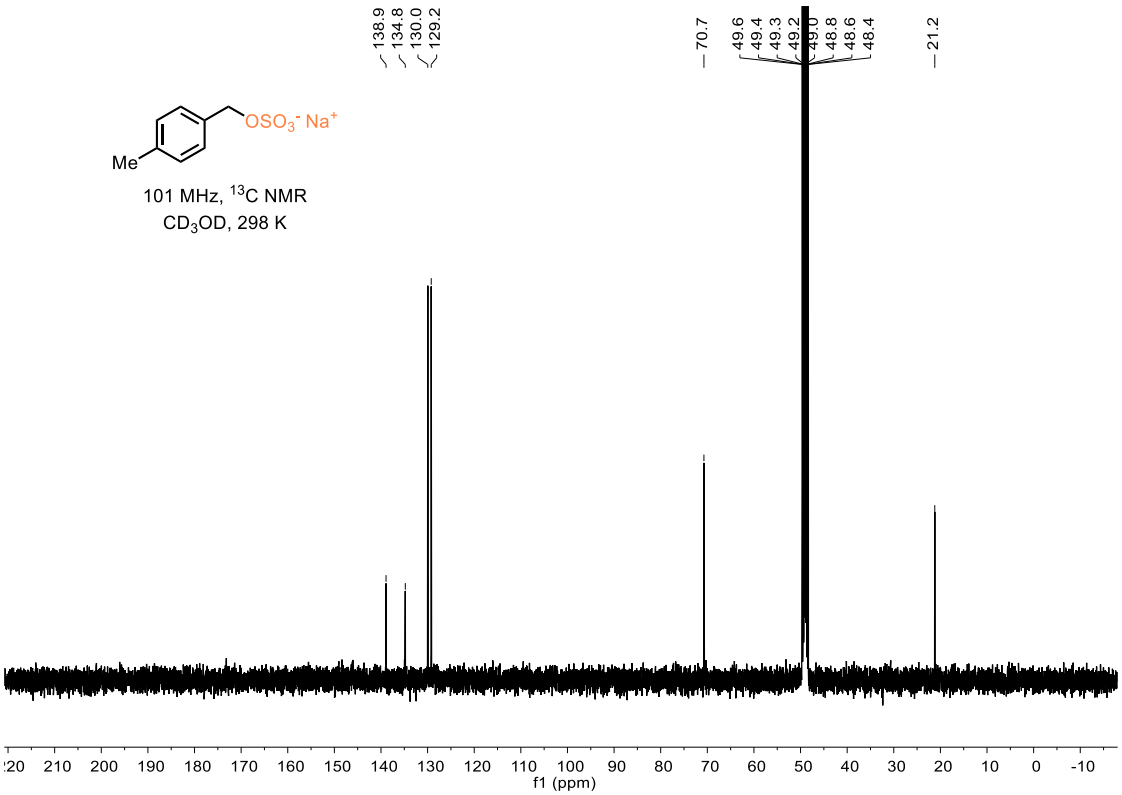


Sodium 4-methylbenzyl sulfate (12)

^{1}H NMR of sodium 4-methylbenzyl sulfate (12)

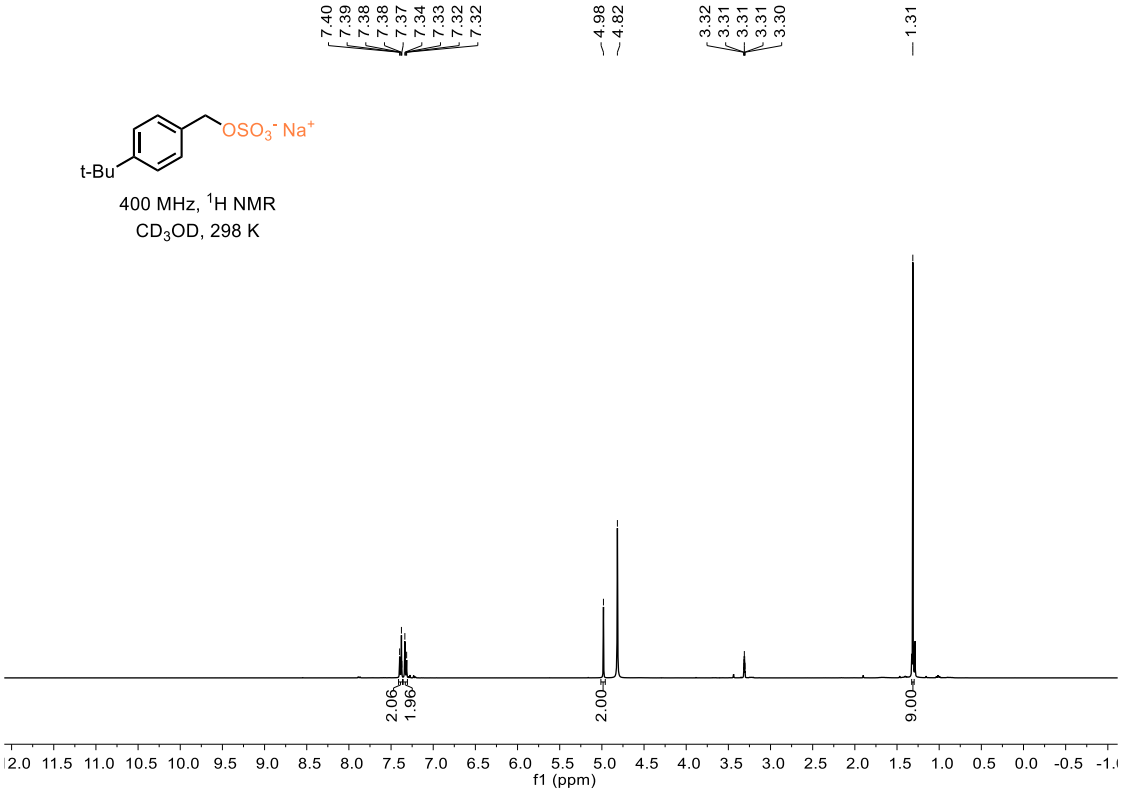


^{13}C NMR of sodium 4-methylbenzyl sulfate (12)

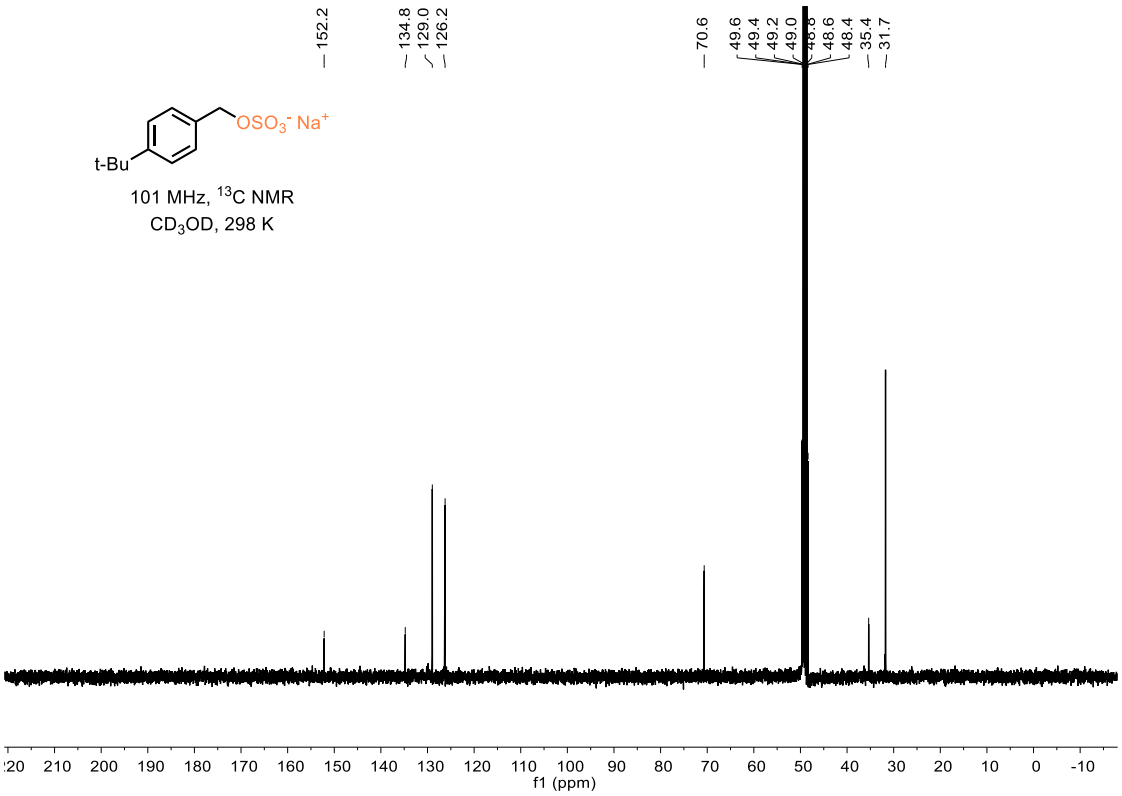


Sodium 4-(*tert*-butyl)benzyl sulfate (13)

^{1}H NMR of sodium 4-(*tert*-butyl)benzyl sulfate (13)

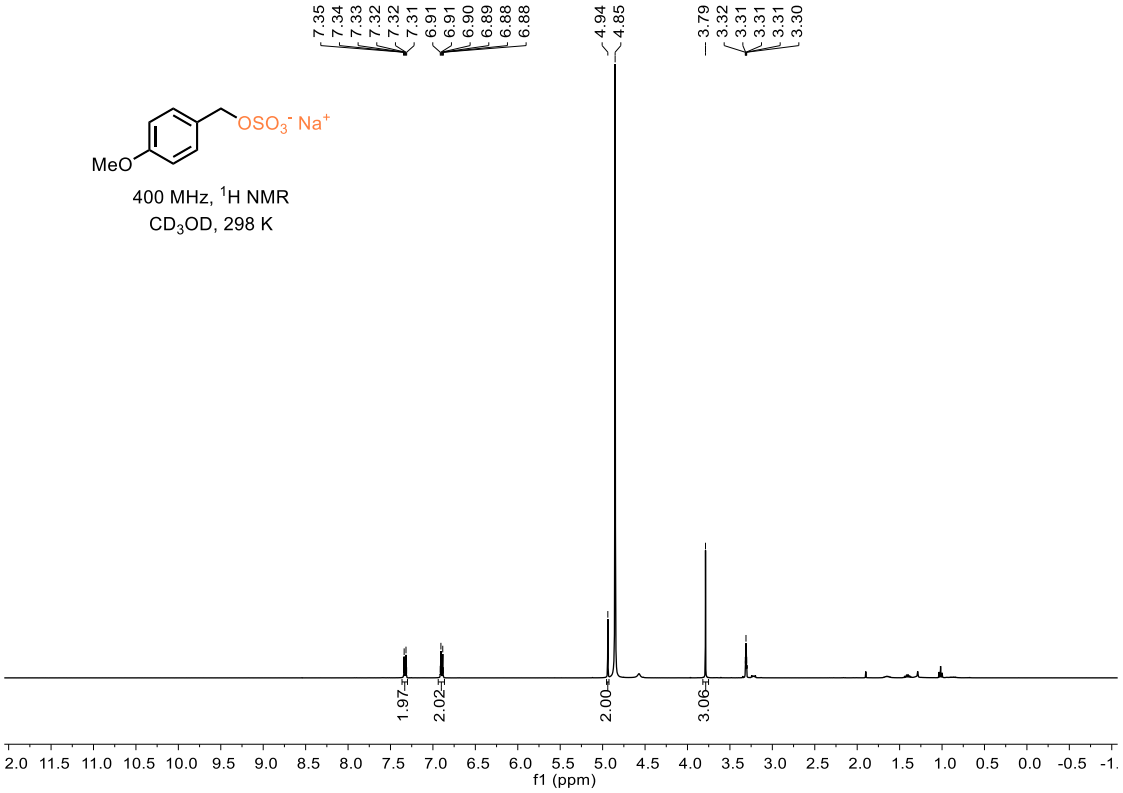


^{13}C NMR of sodium 4-(*tert*-butyl)benzyl sulfate (13)

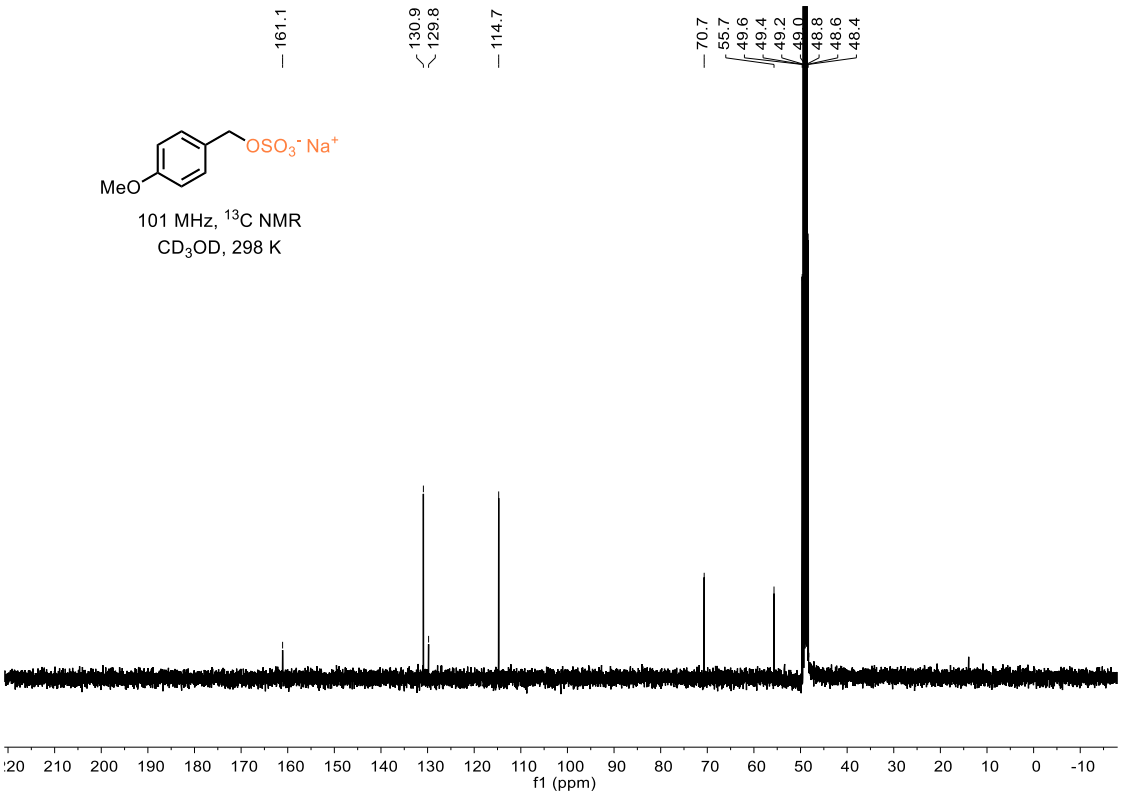


Sodium 4-methoxybenzyl sulfate (14)

^{1}H NMR of sodium 4-methoxybenzyl sulfate (14)

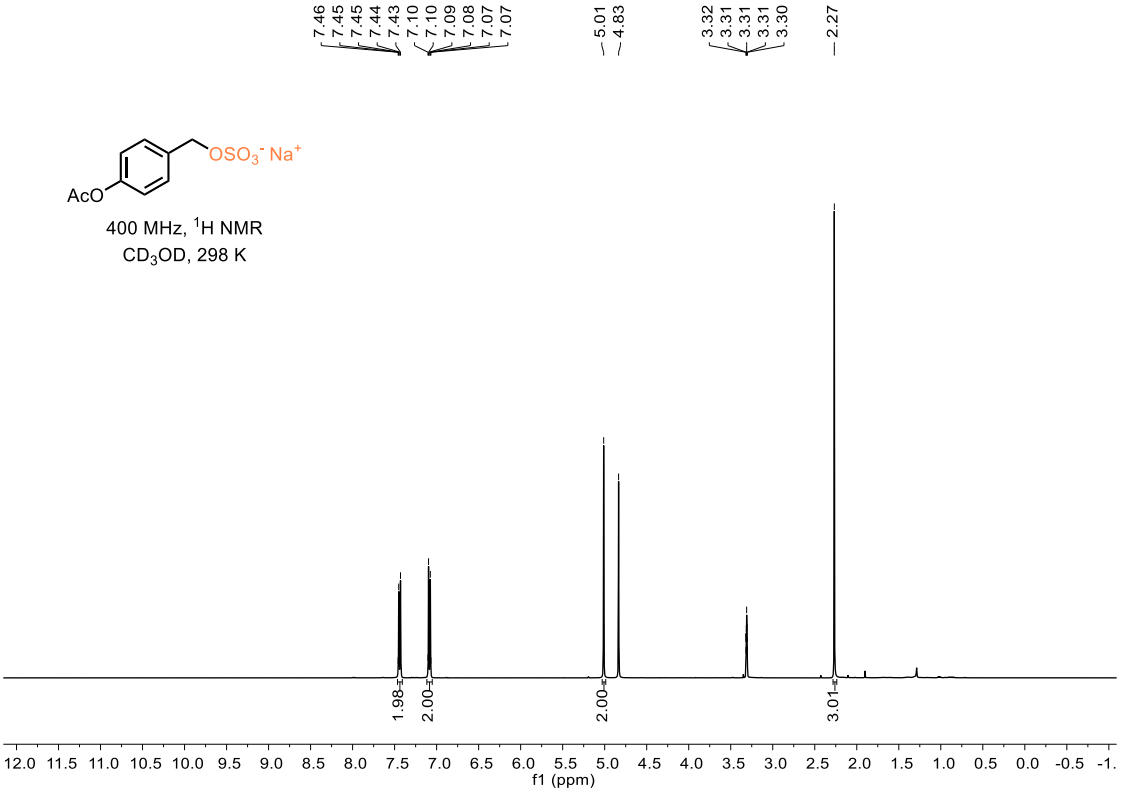


^{13}C NMR of sodium 4-methoxybenzyl sulfate (14)

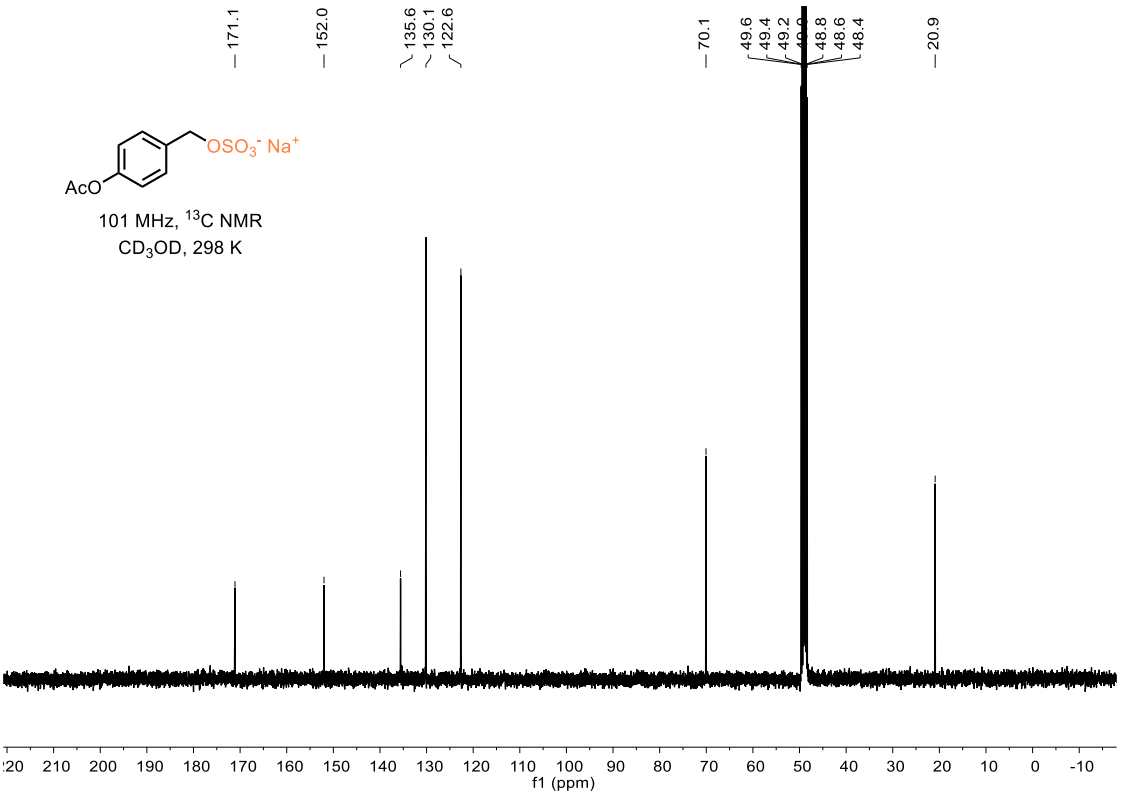


Sodium 4-acetoxybenzyl sulfate (15)

^{1}H NMR of sodium 4-acetoxybenzyl sulfate (15)

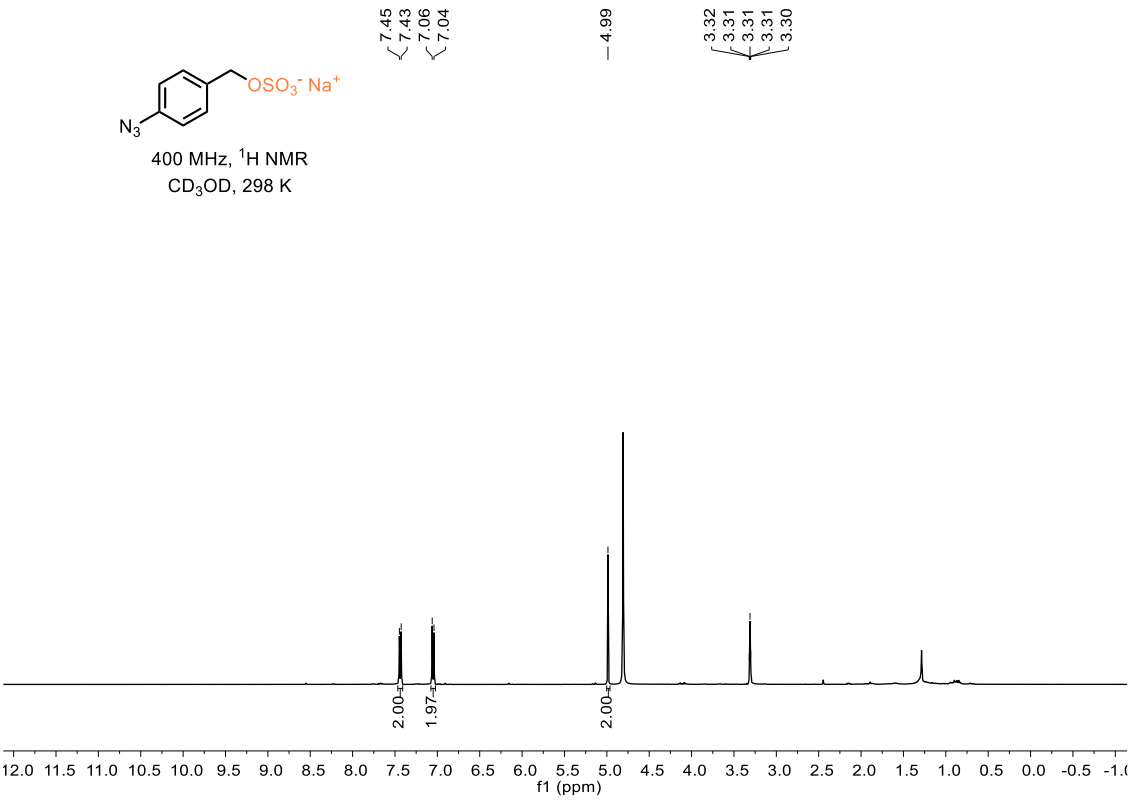


^{13}C NMR of sodium 4-acetoxybenzyl sulfate (15)

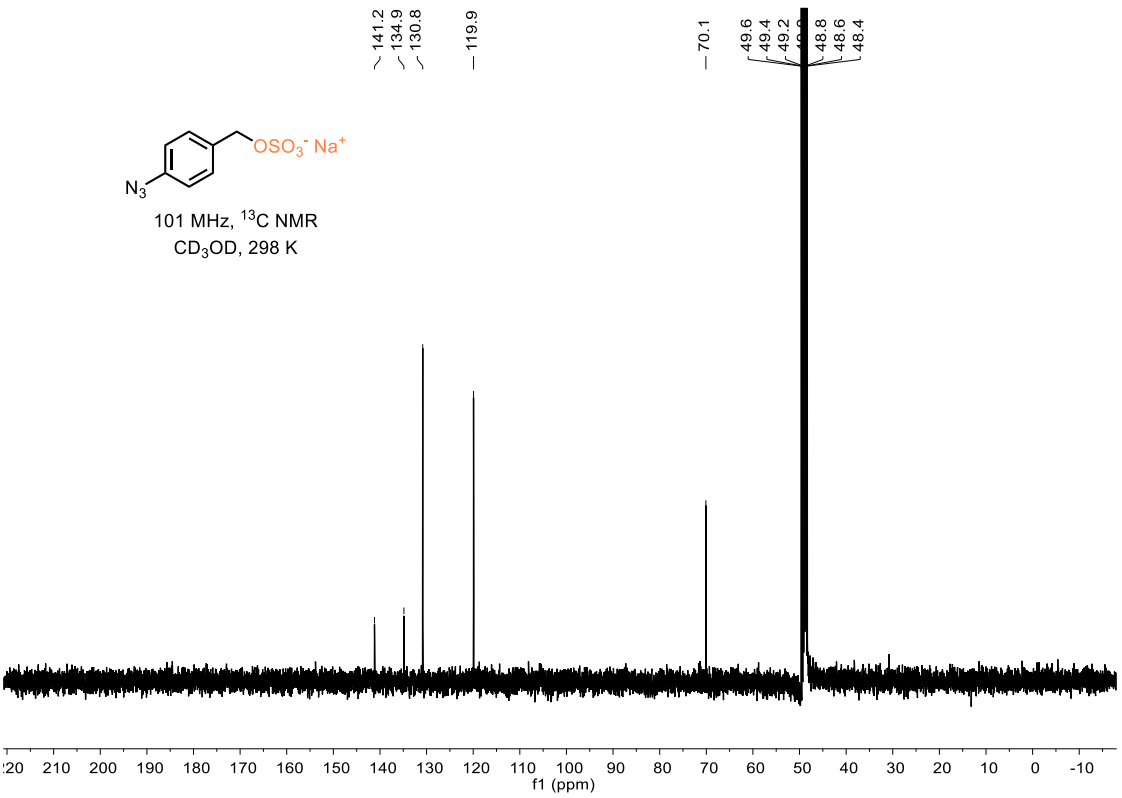


Sodium 4-azidobenzyl sulfate (16)

^{1}H NMR of sodium 4-azidobenzyl sulfate (16)

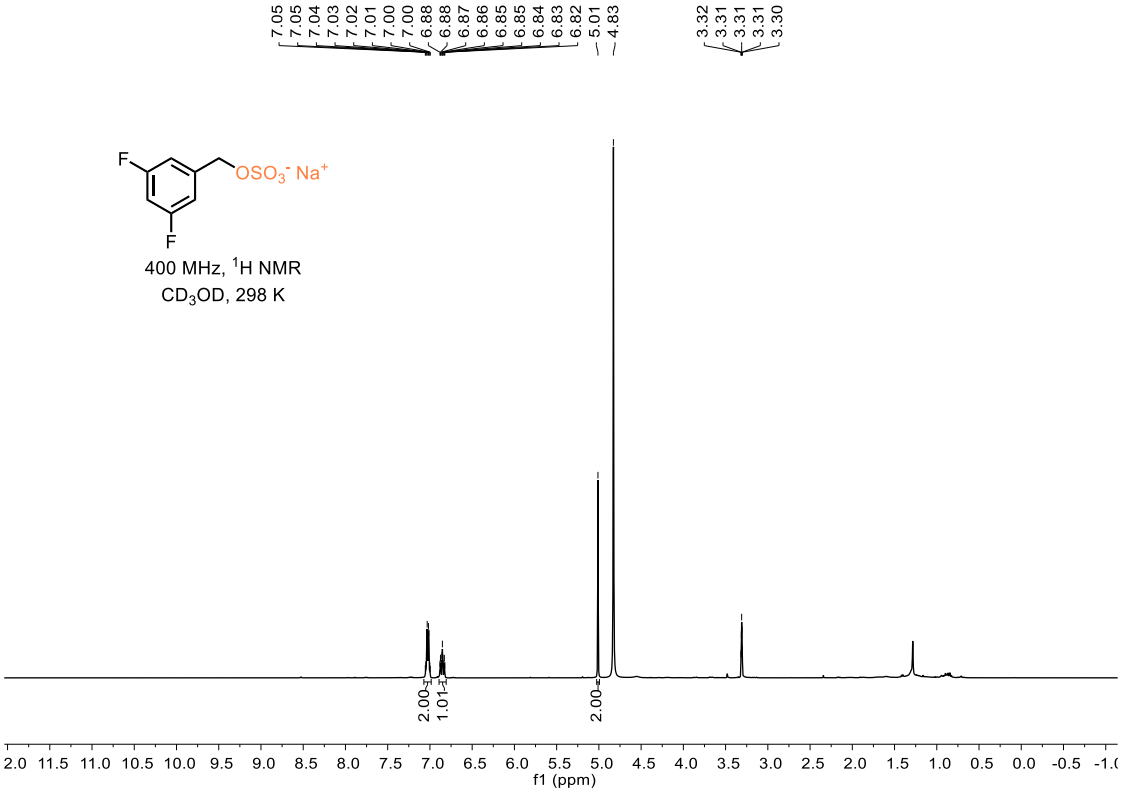


^{13}C NMR of sodium 4-azidobenzyl sulfate (16)

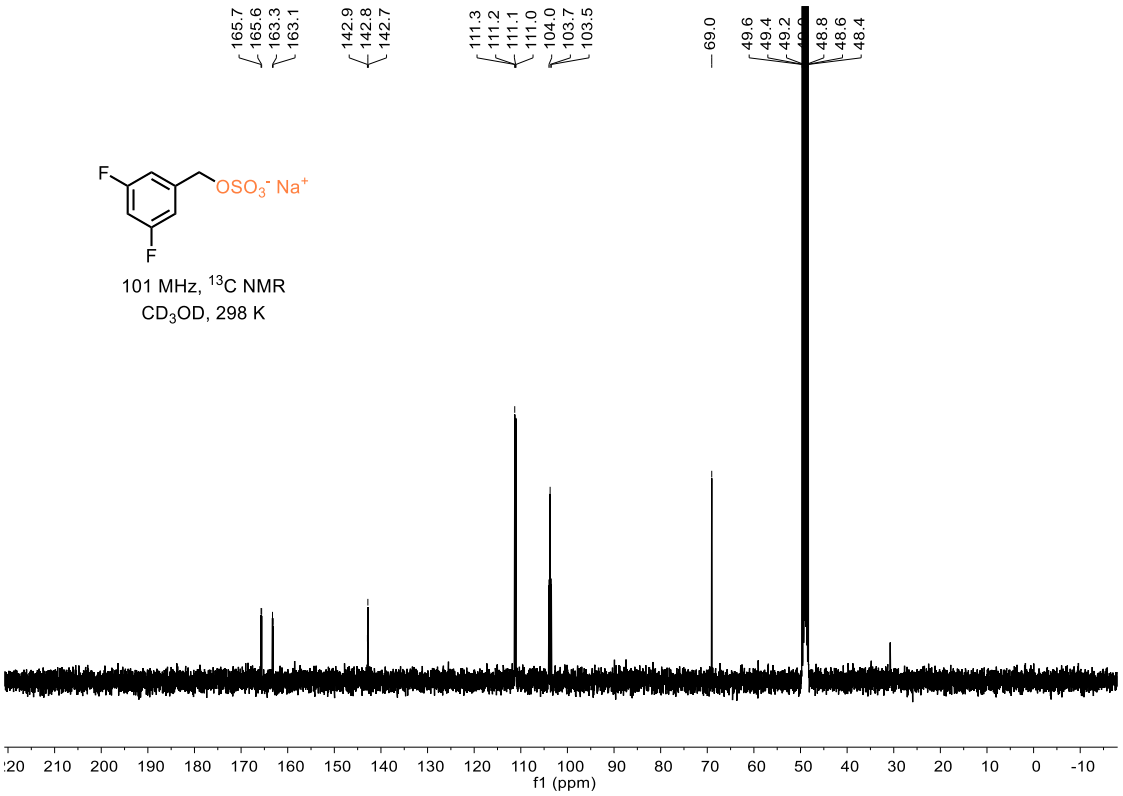


Sodium 3,5-difluorobenzyl sulfate (17)

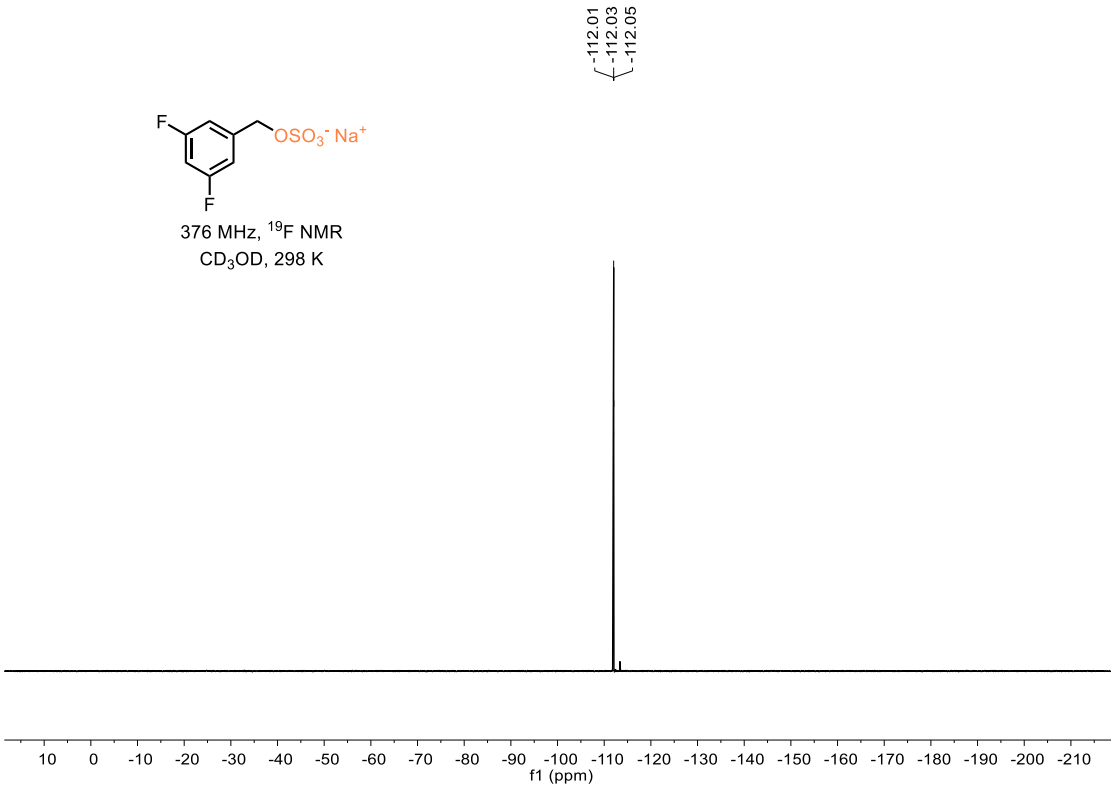
^{1}H NMR of sodium 3,5-difluorobenzyl sulfate (17)



^{13}C NMR of sodium 3,5-difluorobenzyl sulfate (17)

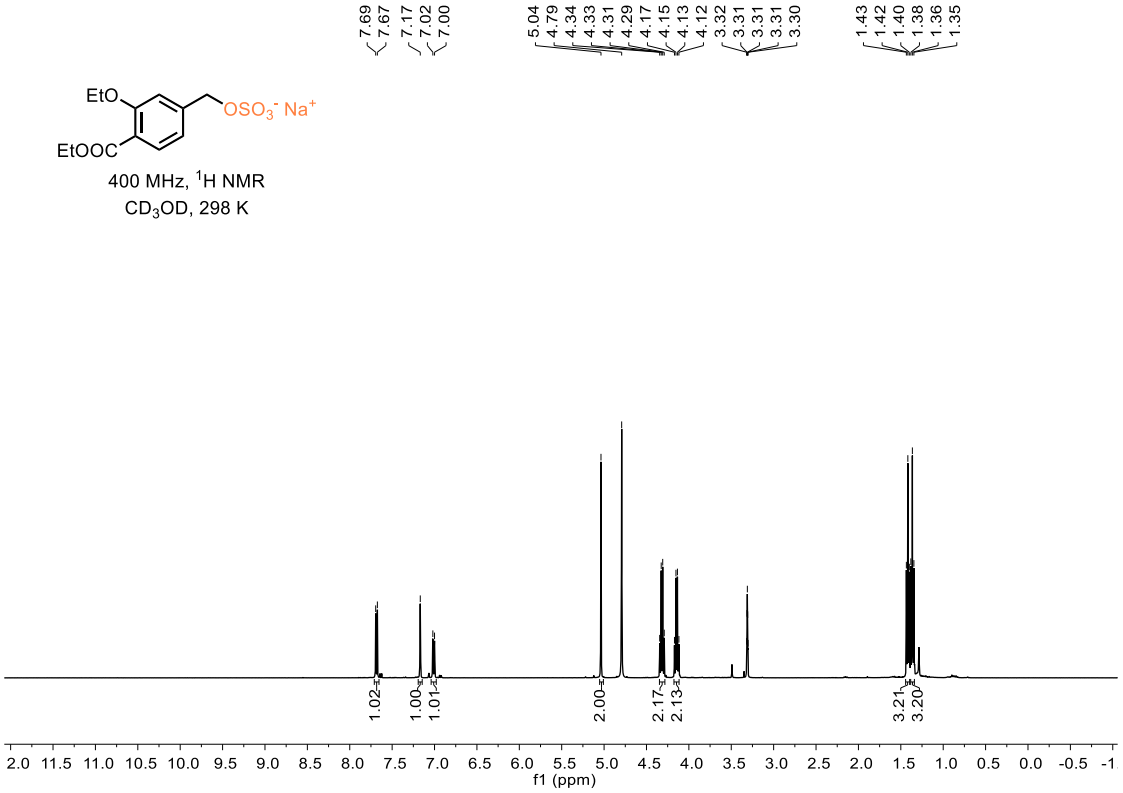


^{19}F NMR of sodium 3,5-difluorobenzyl sulfate (17)

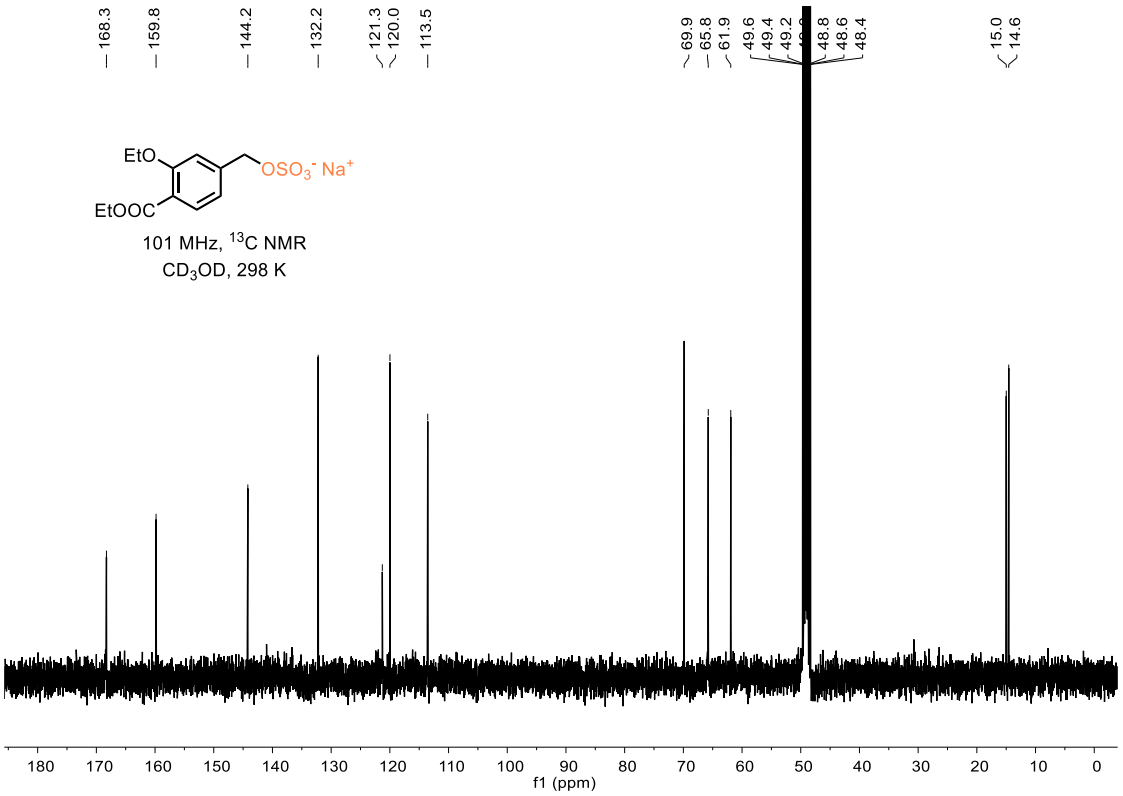


Sodium 3-ethoxy-4-(ethoxycarbonyl)benzyl sulfate (18)

^{1}H NMR of sodium 3-ethoxy-4-(ethoxycarbonyl)benzyl sulfate (18)

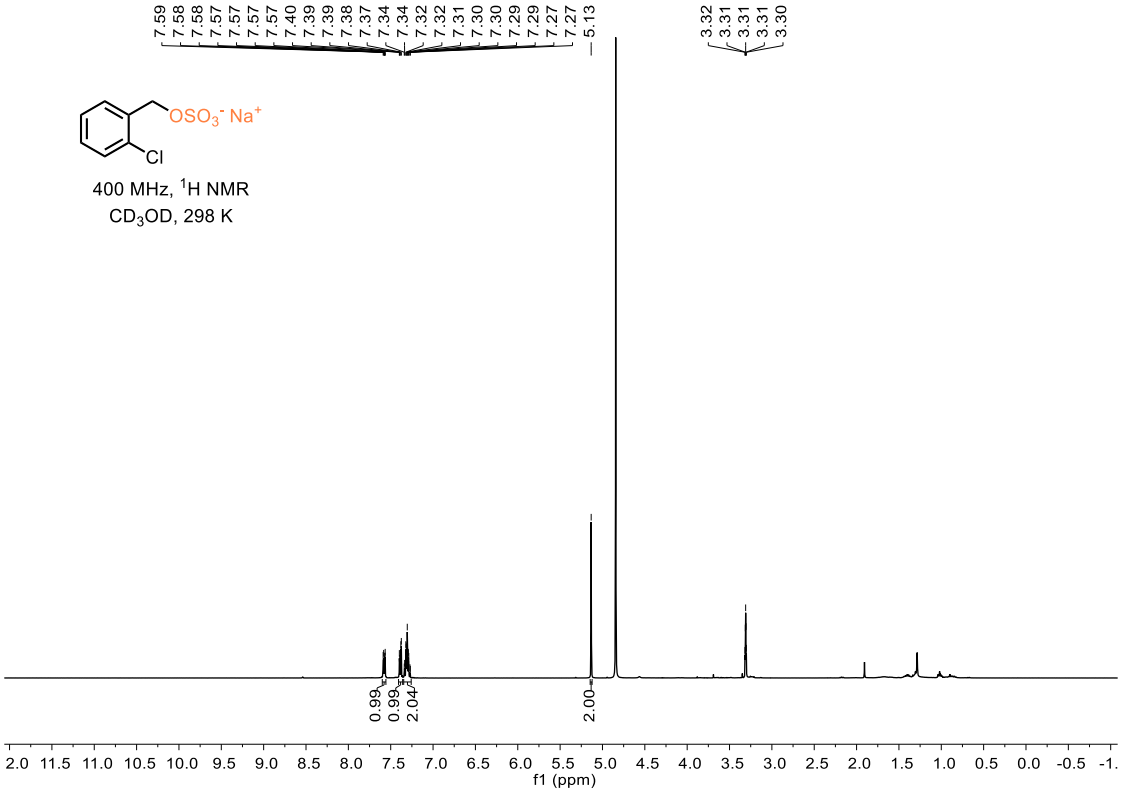


^{13}C NMR of sodium 3-ethoxy-4-(ethoxycarbonyl)benzyl sulfate (18)

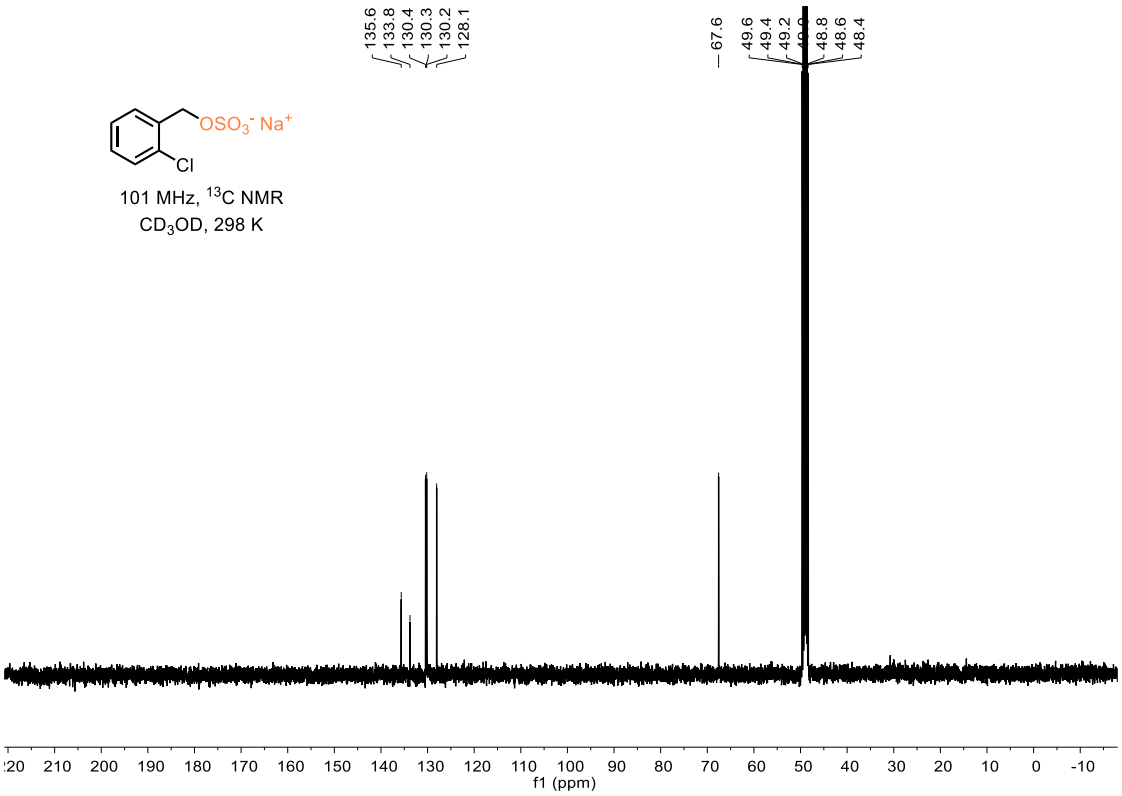


Sodium 2-chlorobenzyl sulfate (19)

^{1}H NMR of sodium 2-chlorobenzyl sulfate (19)

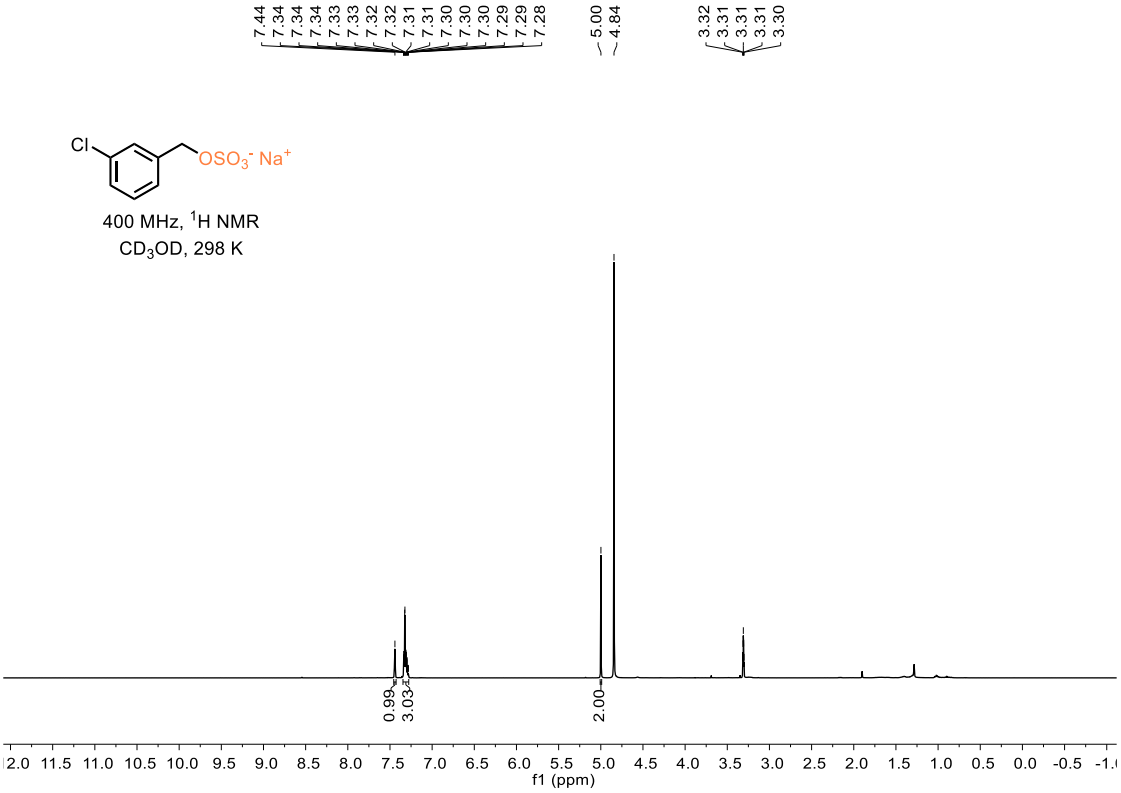


^{13}C NMR of sodium 2-chlorobenzyl sulfate (19)

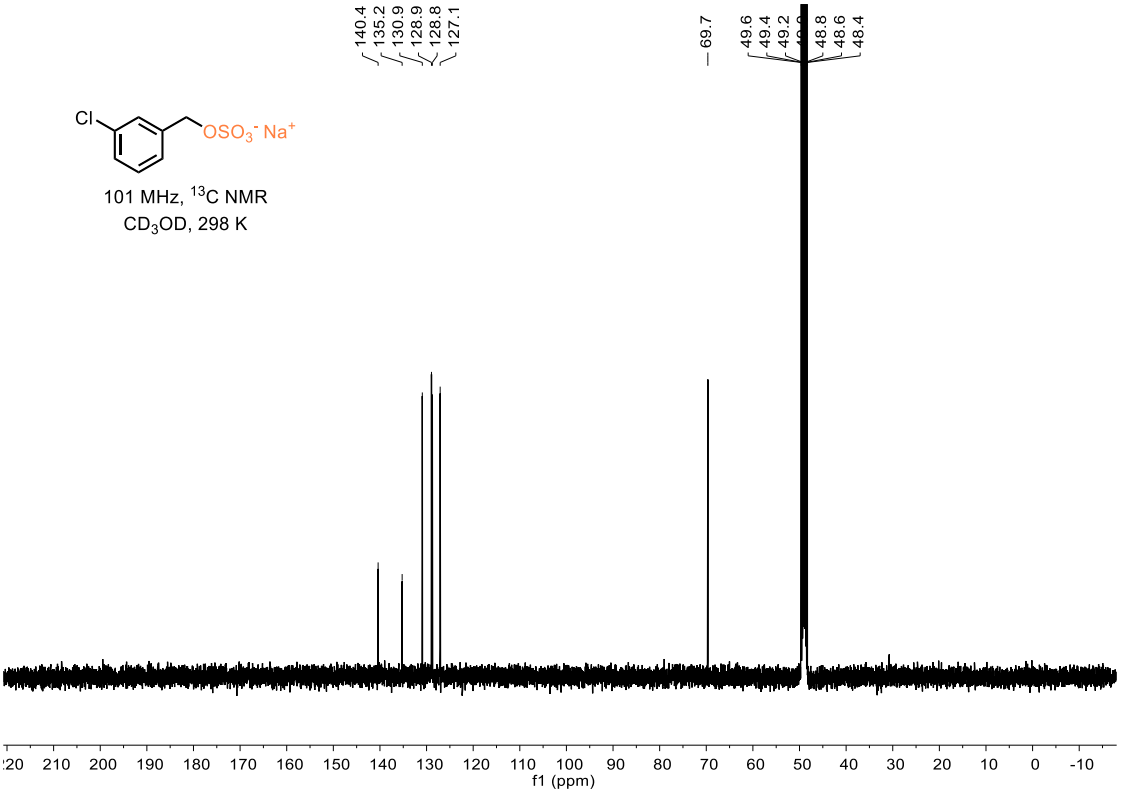


Sodium 3-chlorobenzyl sulfate (20)

^{1}H NMR of sodium 3-chlorobenzyl sulfate (20)

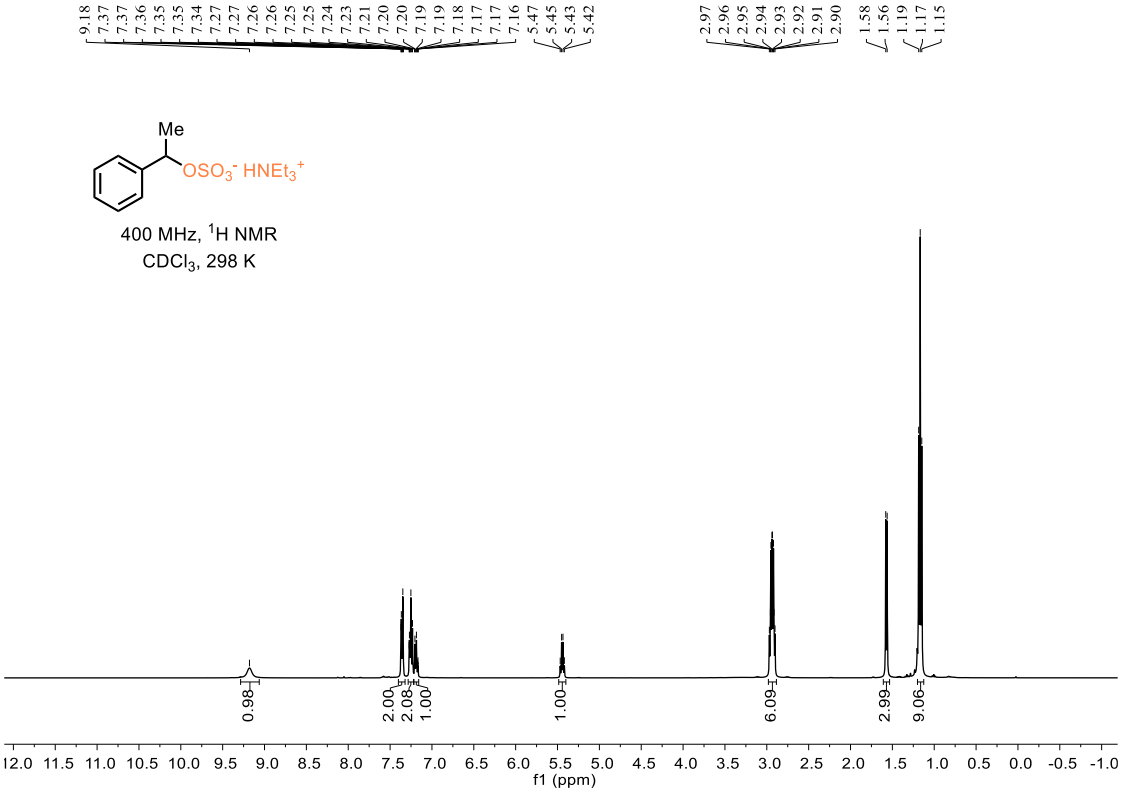


^{13}C NMR of sodium 3-chlorobenzyl sulfate (20)

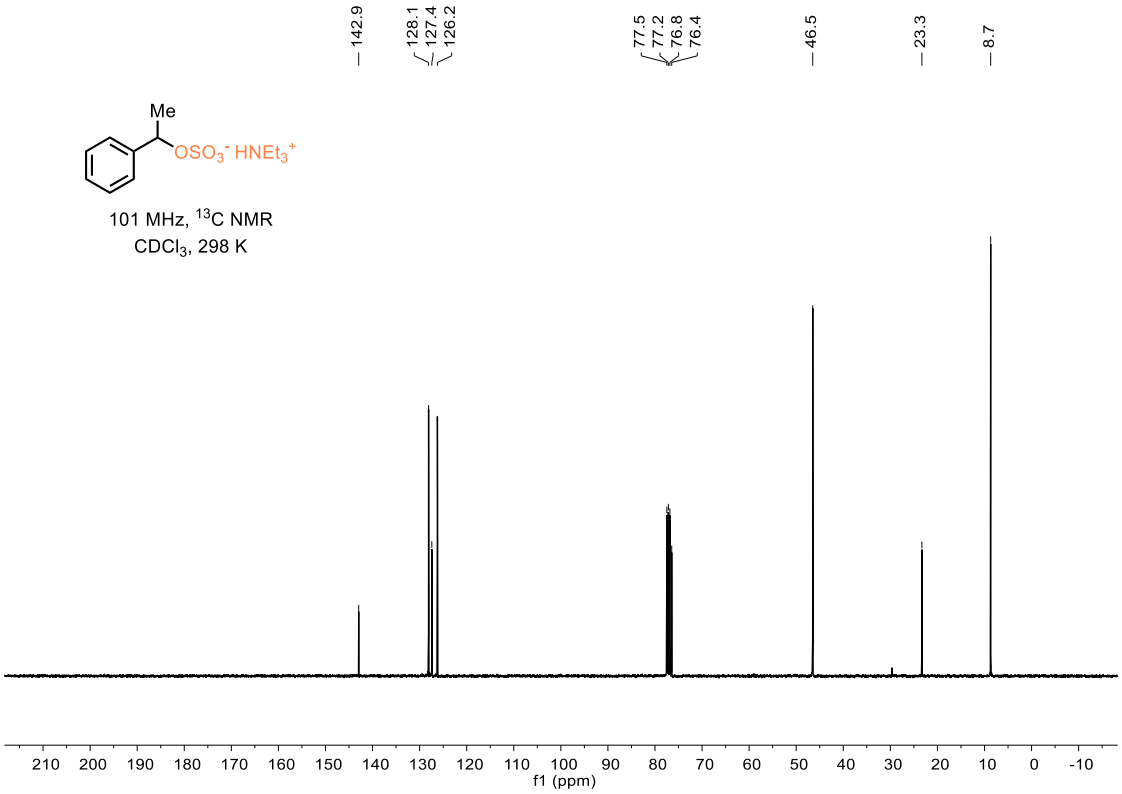


Quaternary ammonium α-methylbenzyl sulfate (21')

^{1}H NMR of quaternary ammonium α-methylbenzyl sulfate (21')

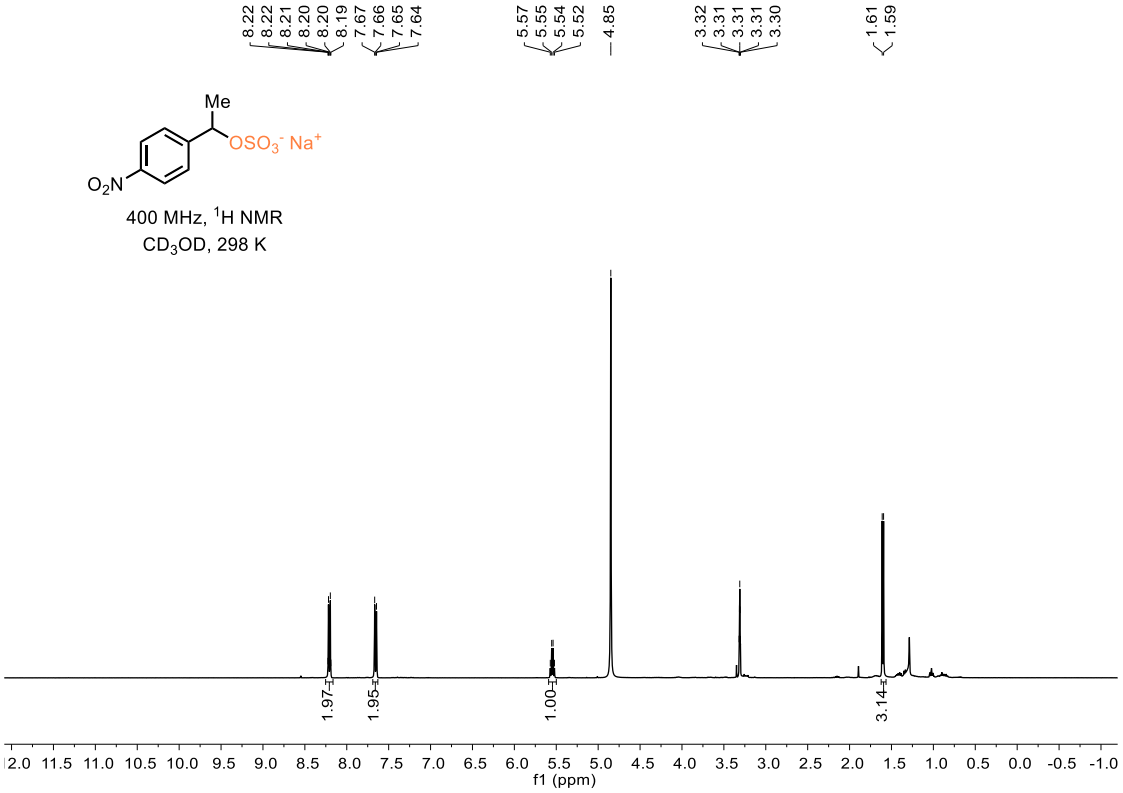


^{13}C NMR of quaternary ammonium α-methylbenzyl sulfate (21')

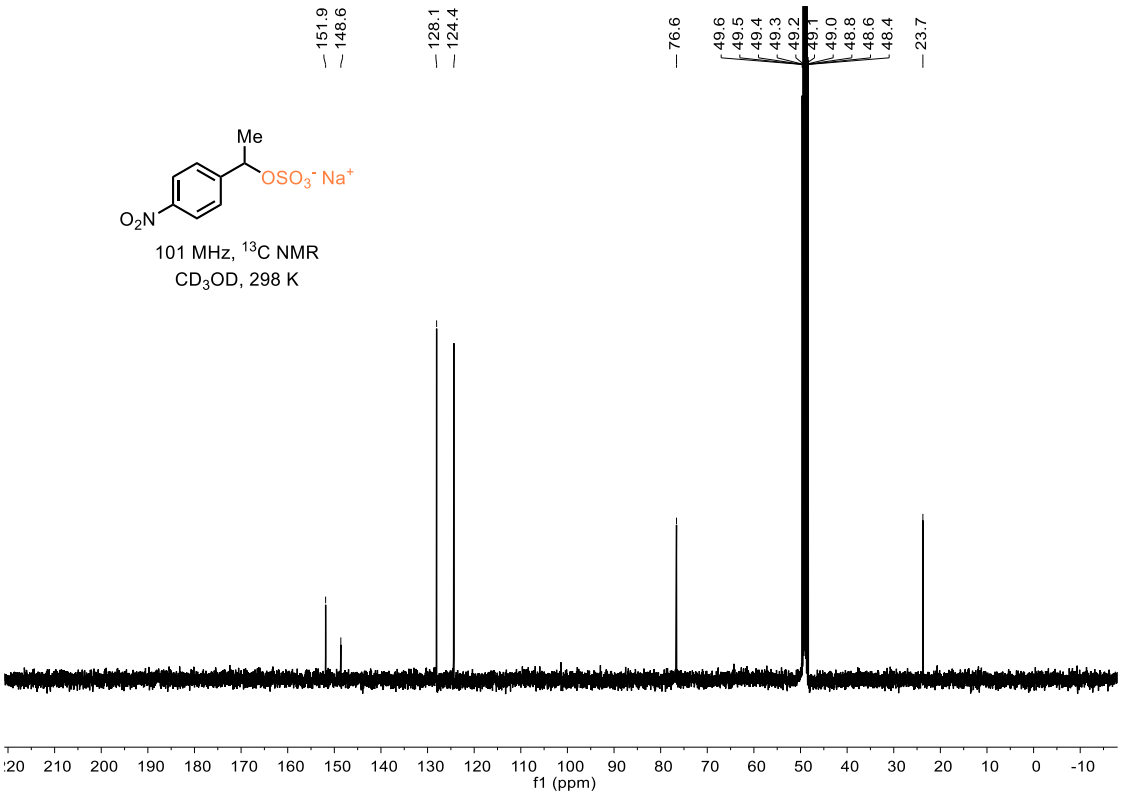


Sodium α-methyl-4-nitrobenzyl sulfate (22)

^{1}H NMR of sodium α-methyl-4-nitrobenzyl sulfate (22)

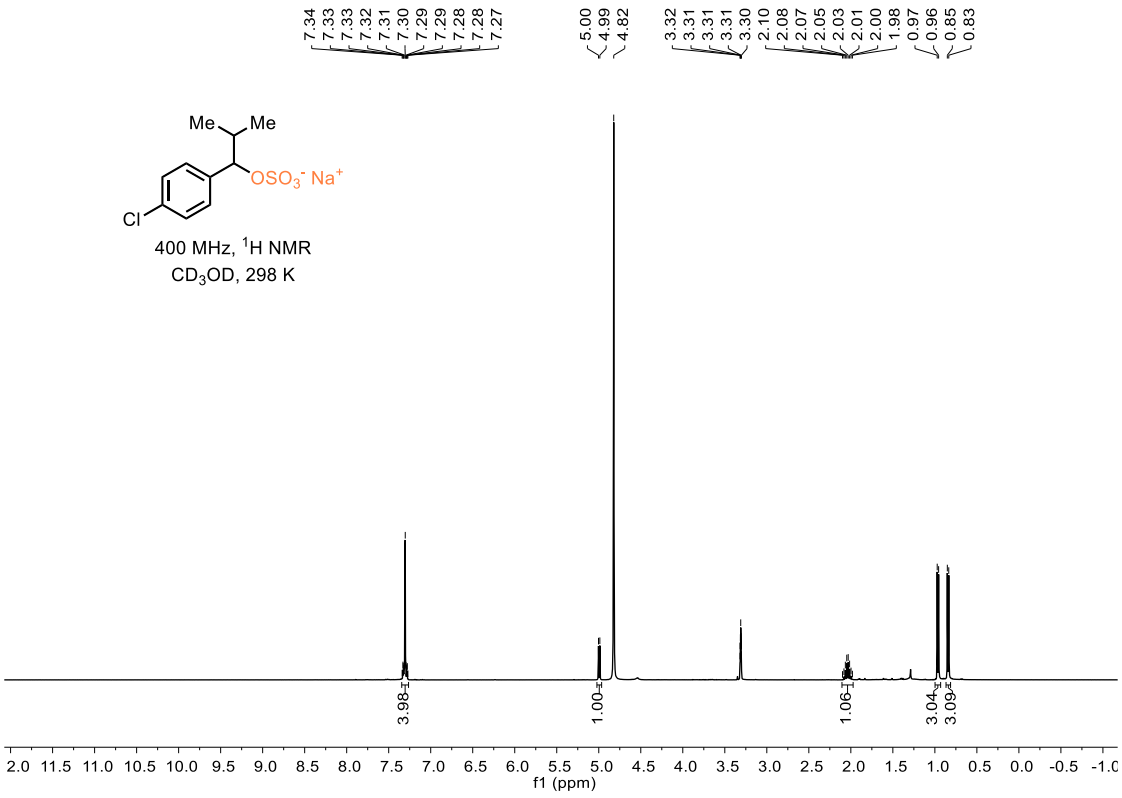


^{13}C NMR of sodium α-methyl-4-nitrobenzyl sulfate (22)

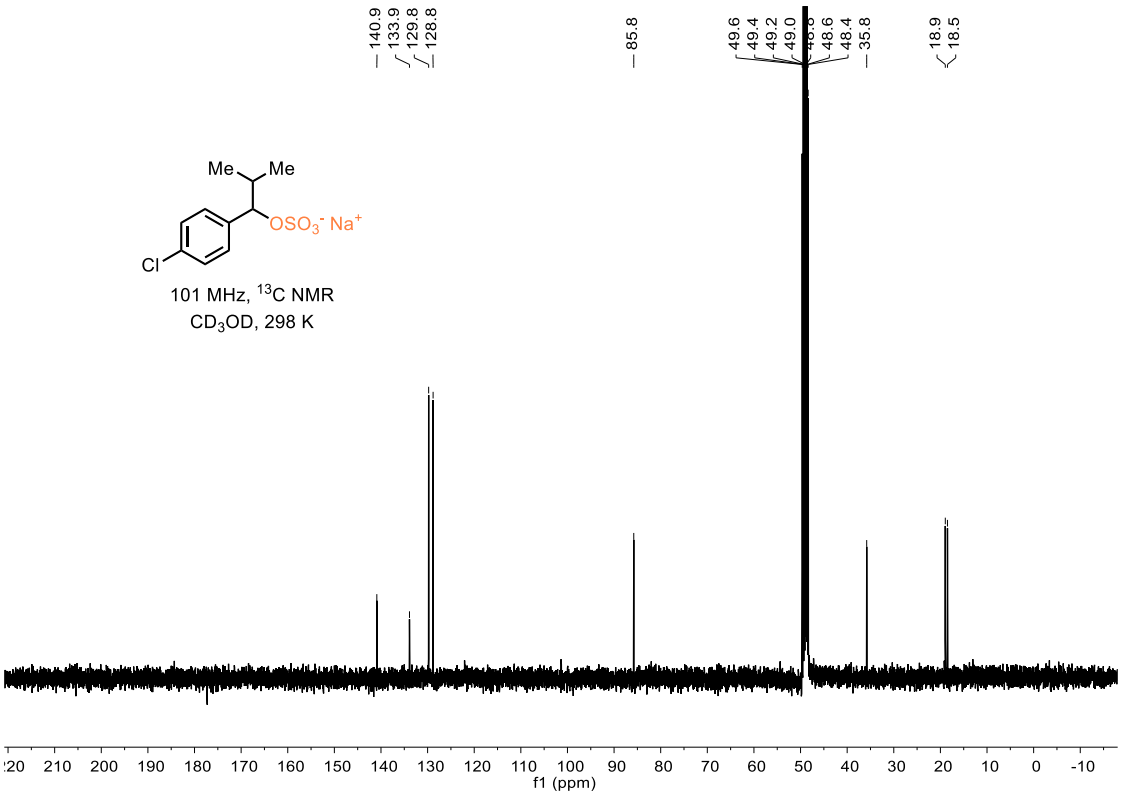


Sodium α-isopropyl-4-chlorobenzyl sulfate (23)

^{1}H NMR of sodium α-isopropyl-4-chlorobenzyl sulfate (23)

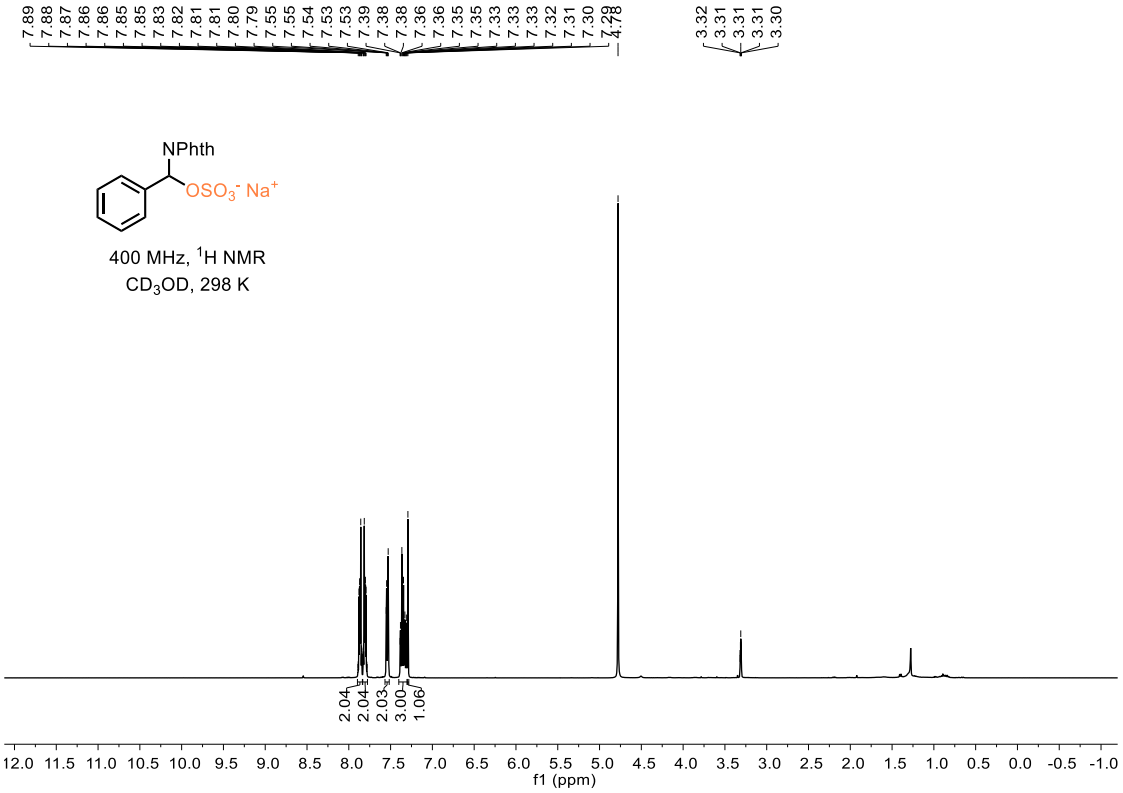


^{13}C NMR of sodium α-isopropyl-4-chlorobenzyl sulfate (23)

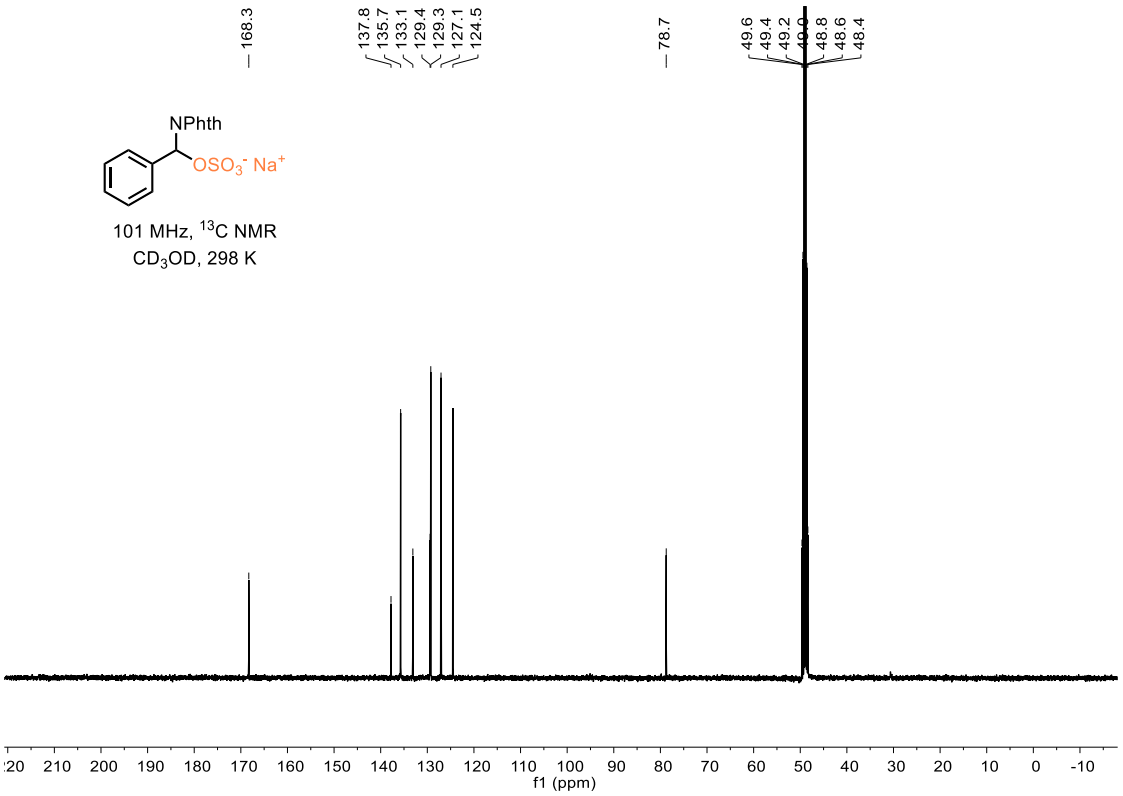


Sodium α-(1,3-dioxoisoindolin-2-yl)benzyl sulfate (24)

^{1}H NMR of sodium α-(1,3-dioxoisoindolin-2-yl)benzyl sulfate (24)

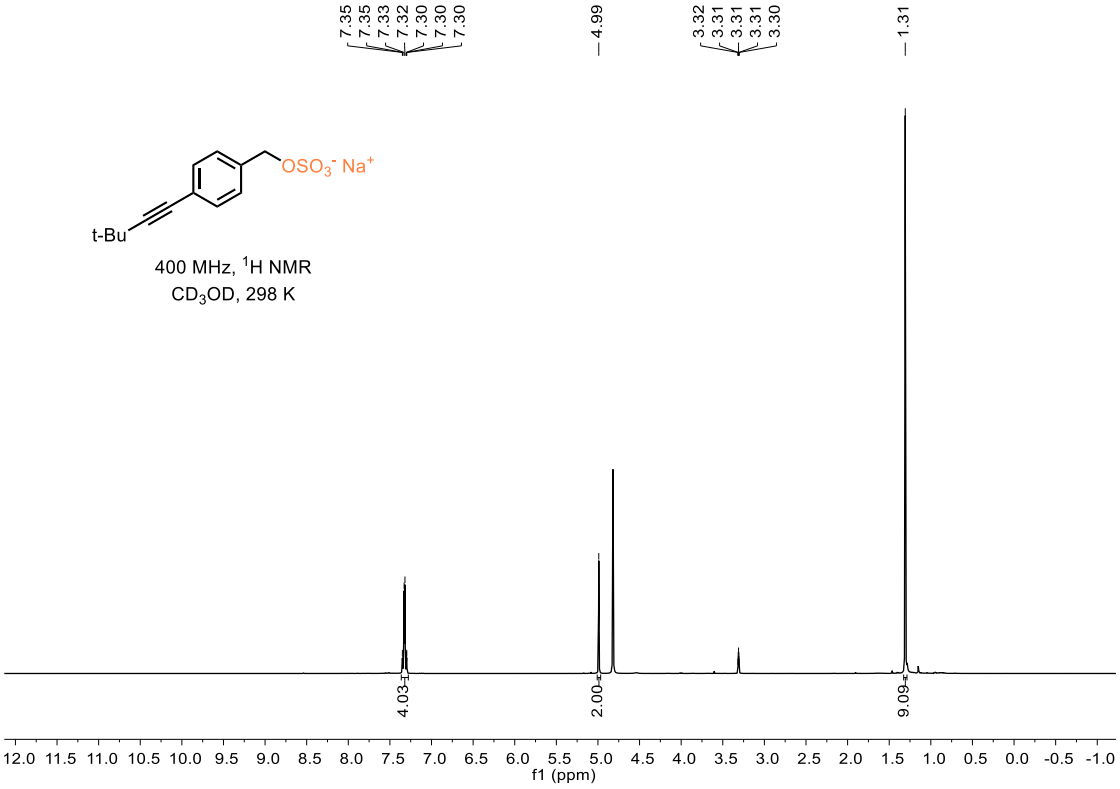


^{13}C NMR of sodium α-(1,3-dioxoisoindolin-2-yl)benzyl sulfate (24)

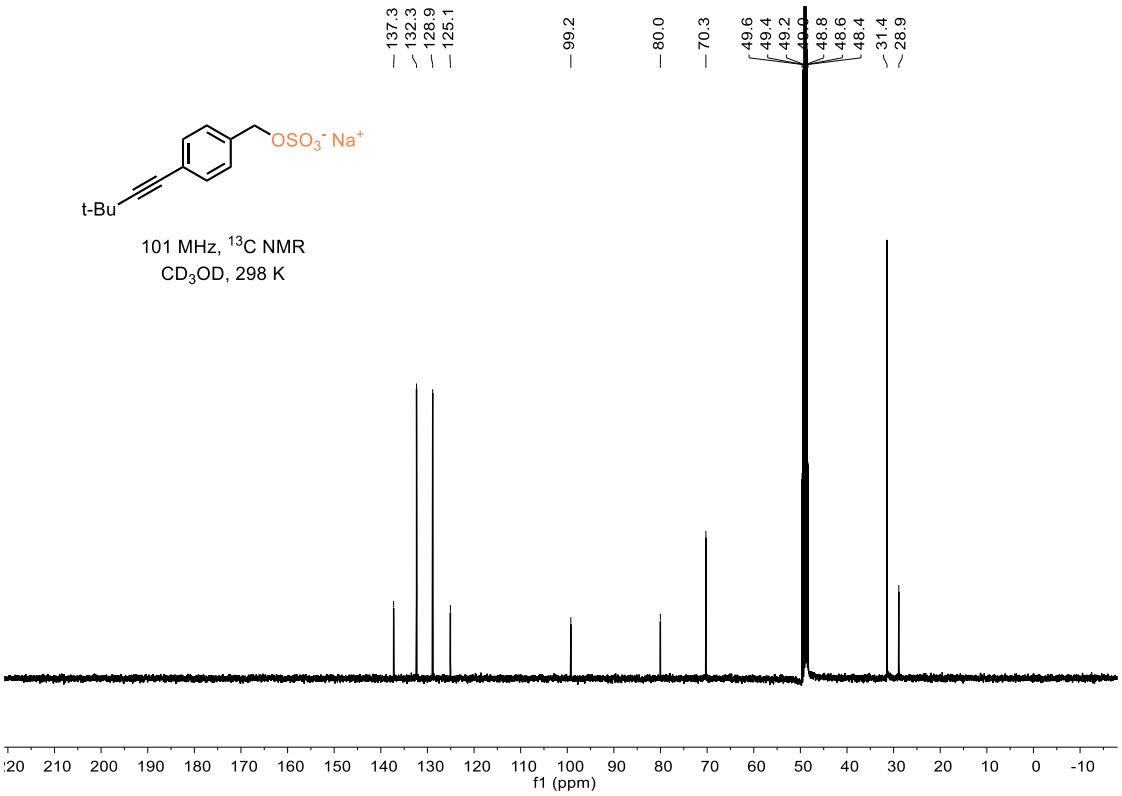


Sodium 4-(3,3-dimethyl-1-yne)benzyl sulfate (25)

^{1}H NMR of sodium 4-(3,3-dimethyl-1-yne)benzyl sulfate (25)

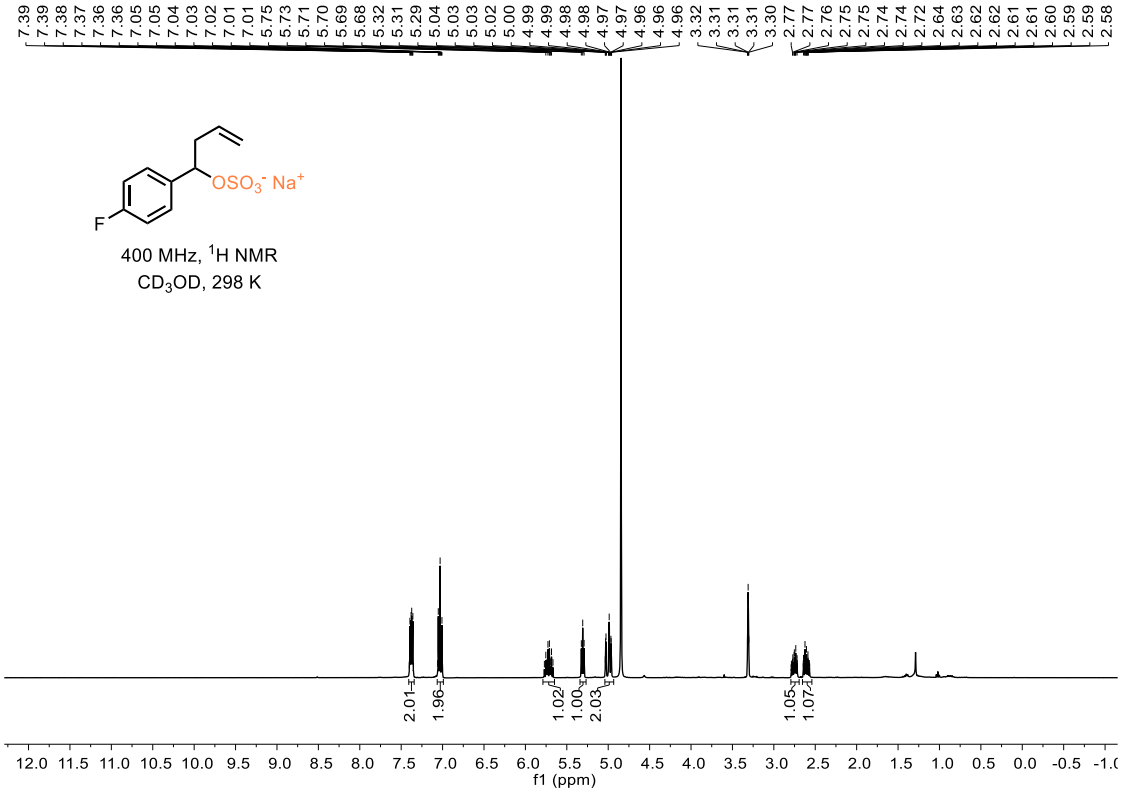


^{13}C NMR of sodium 4-(3,3-dimethyl-1-yne)benzyl sulfate (25)

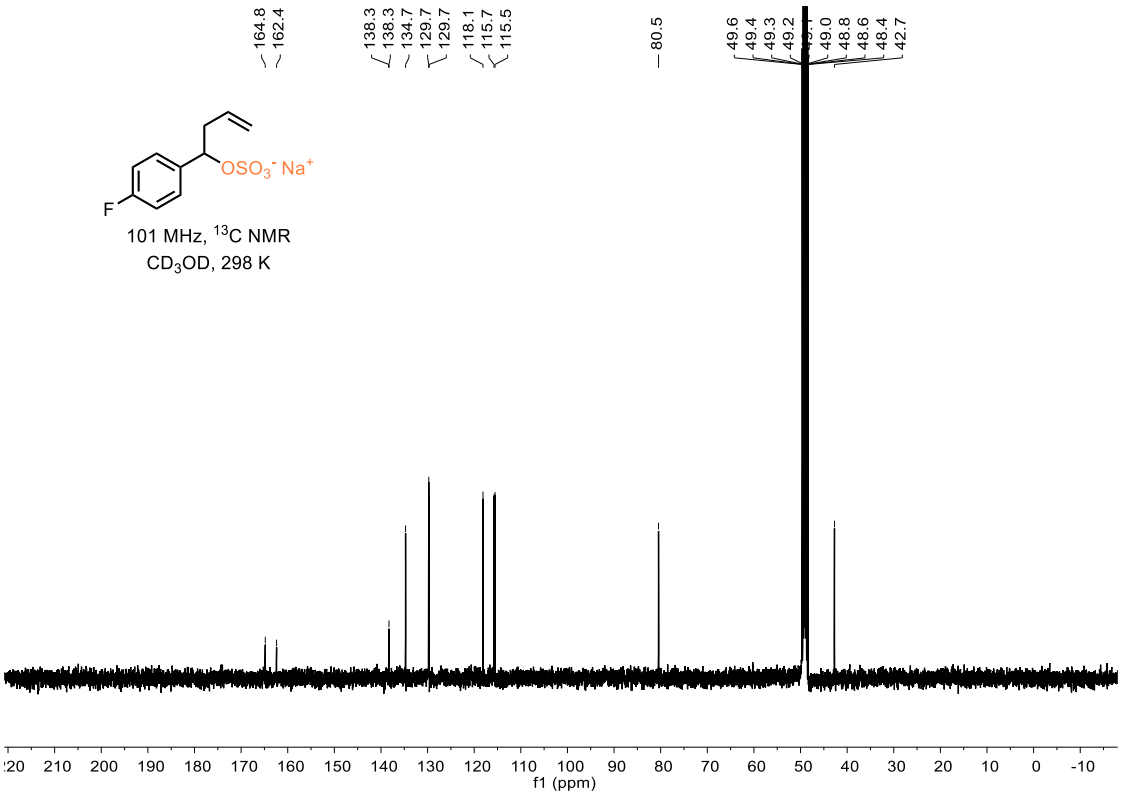


Sodium 1-(4-fluorophenyl)but-3-en-1-yl sulfate (26)

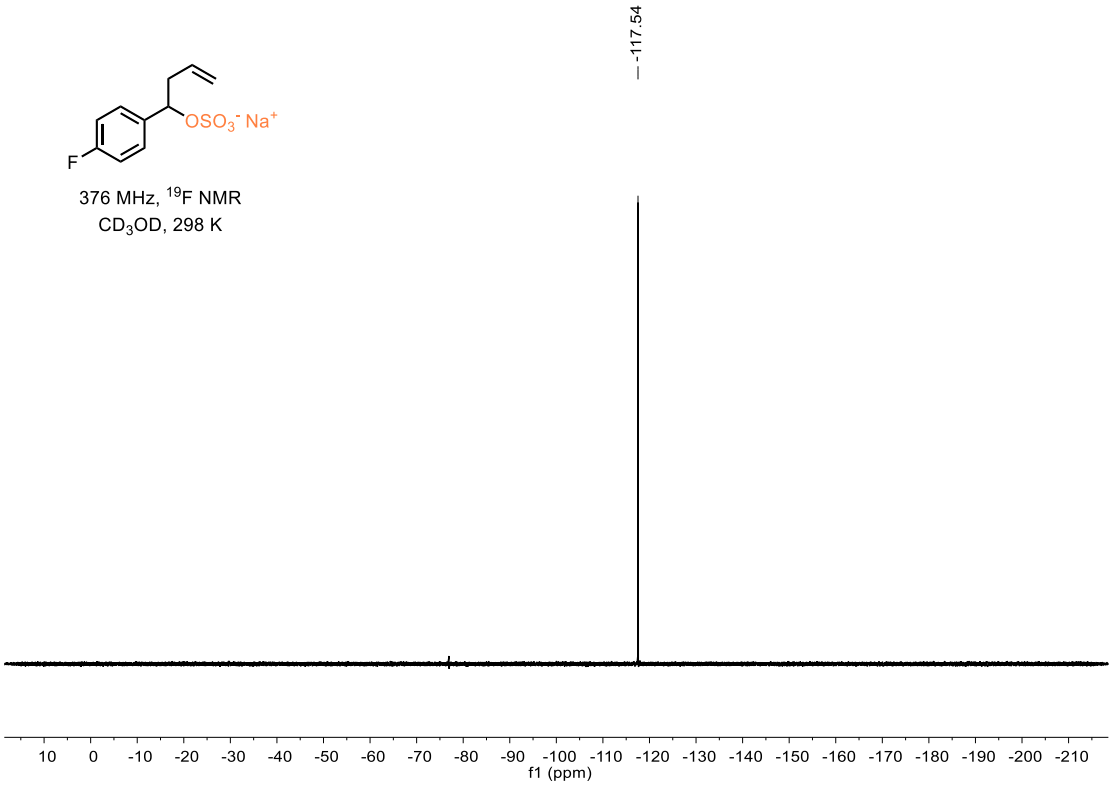
^{1}H NMR of sodium 1-(4-fluorophenyl)but-3-en-1-yl sulfate (26)



^{13}C NMR of sodium 1-(4-fluorophenyl)but-3-en-1-yl sulfate (26)

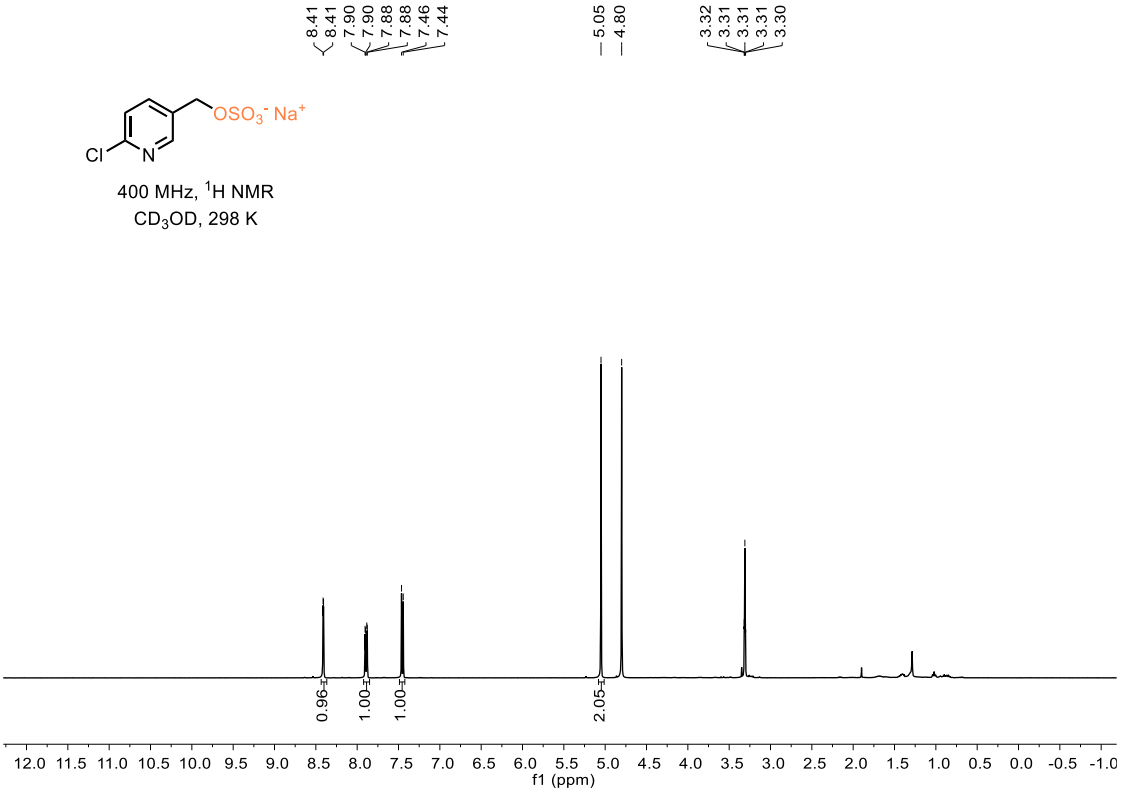


^{19}F NMR of sodium 1-(4-fluorophenyl)but-3-en-1-yl sulfate (26)



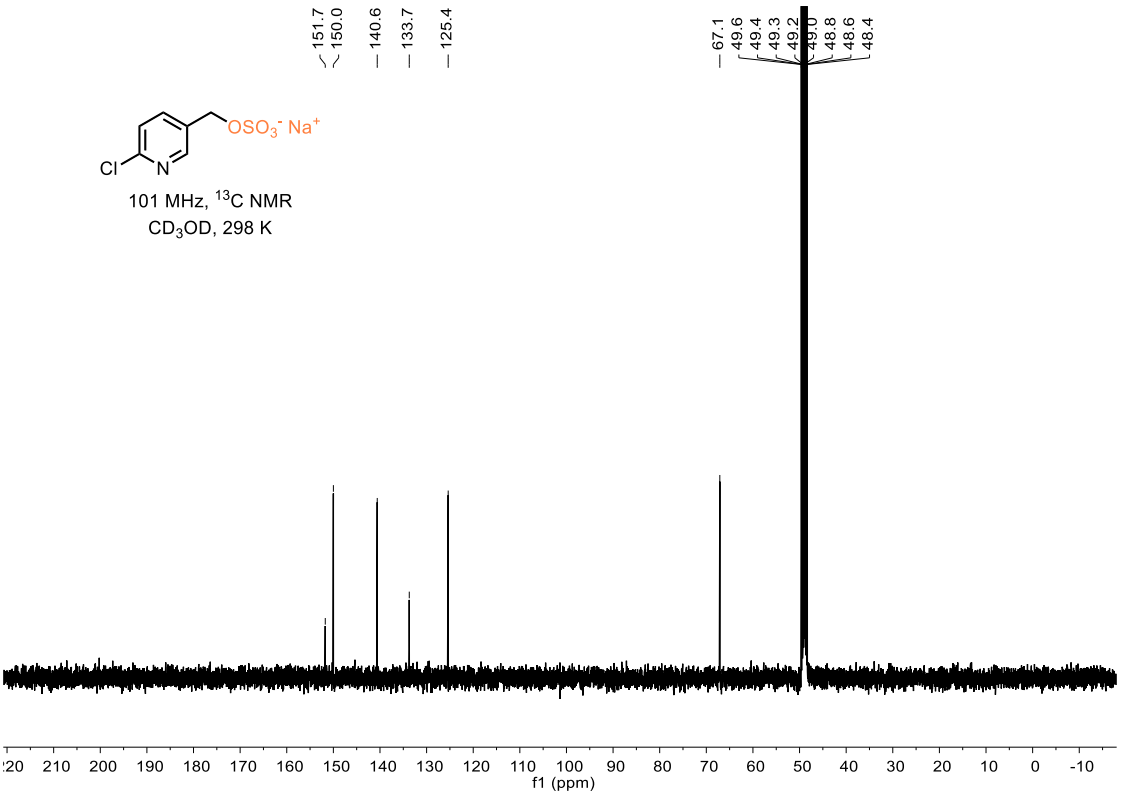
Sodium (6-chloropyridin-3-yl)methyl sulfate (27)

^{1}H NMR of sodium (6-chloropyridin-3-yl)methyl sulfate (27)



400 MHz, ^{1}H NMR
CD_3OD, 298 K

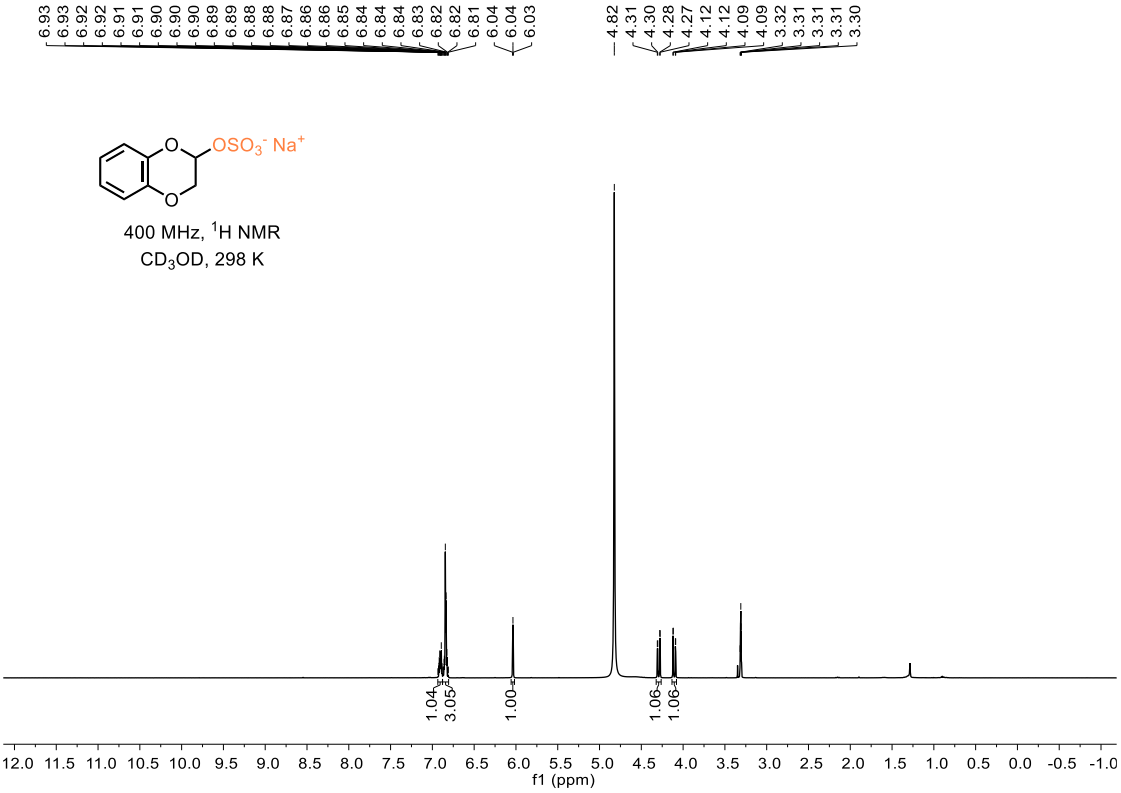
^{13}C NMR of sodium (6-chloropyridin-3-yl)methyl sulfate (27)



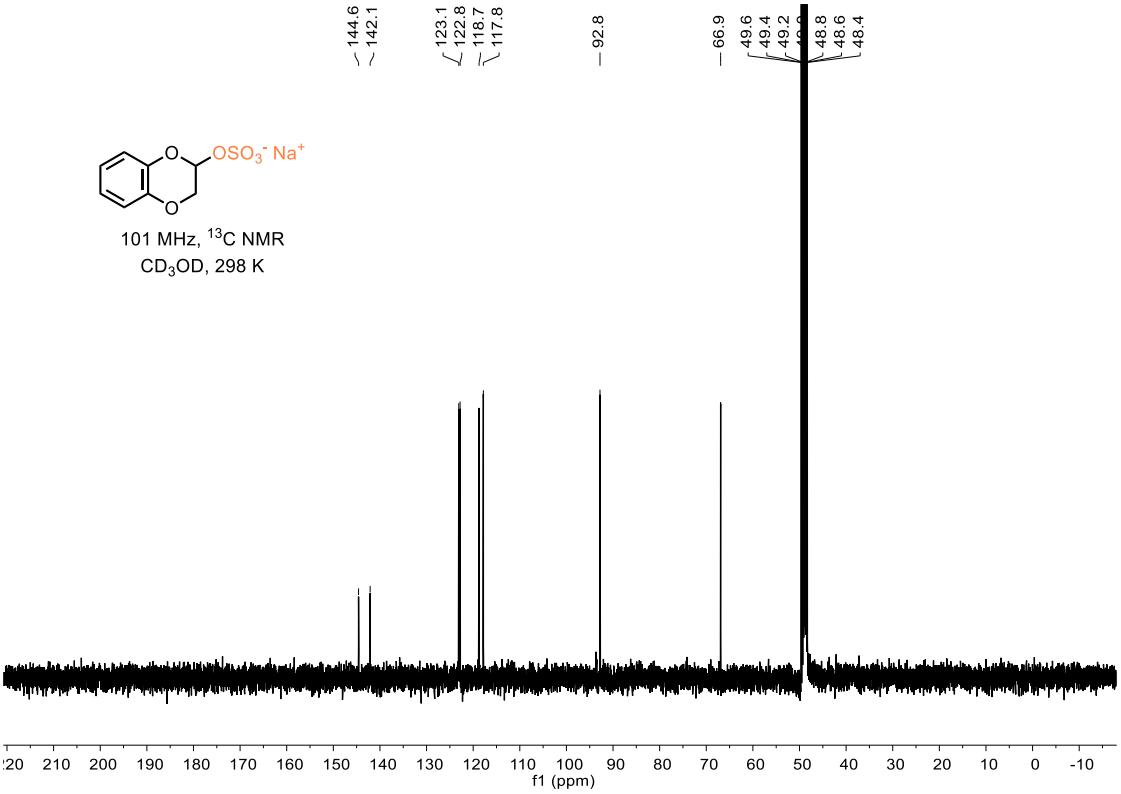
101 MHz, ^{13}C NMR
CD_3OD, 298 K

Sodium 1,4-benzodioxan-2-sulfate (28)

^{1}H NMR of sodium 1,4-benzodioxan-2-sulfate (28)

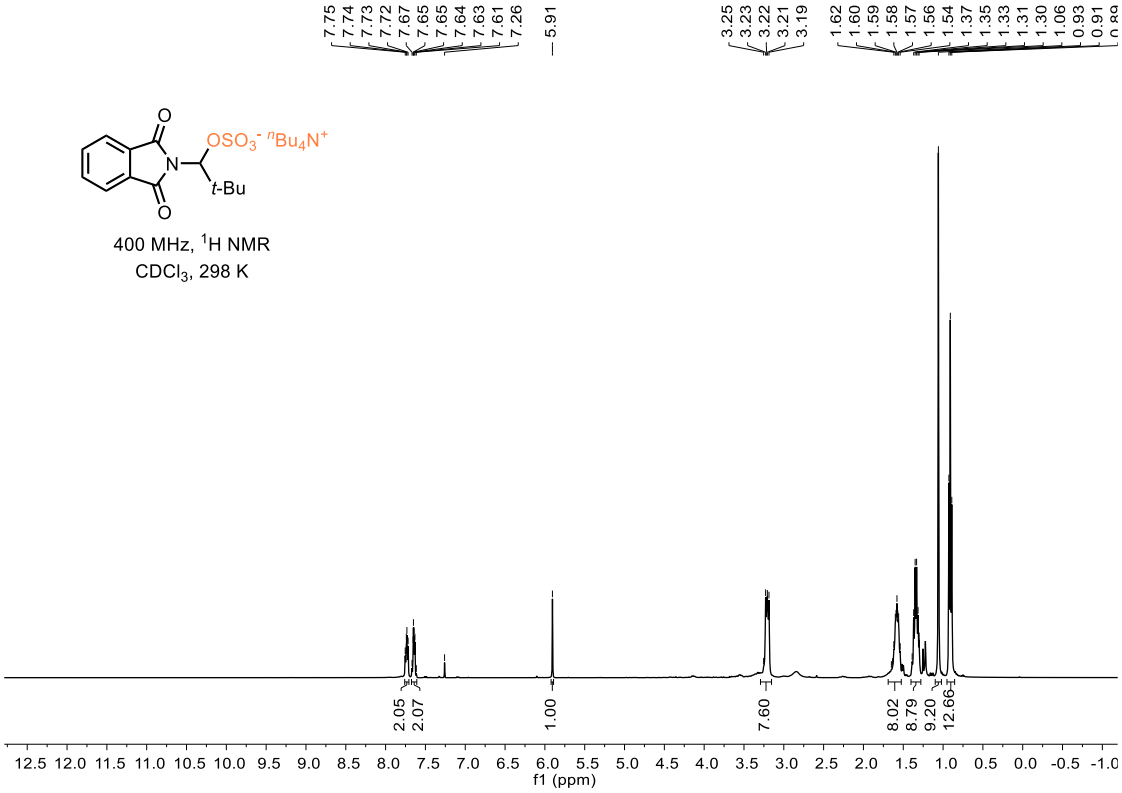


^{13}C NMR of sodium 1,4-benzodioxan-2-sulfate (28)

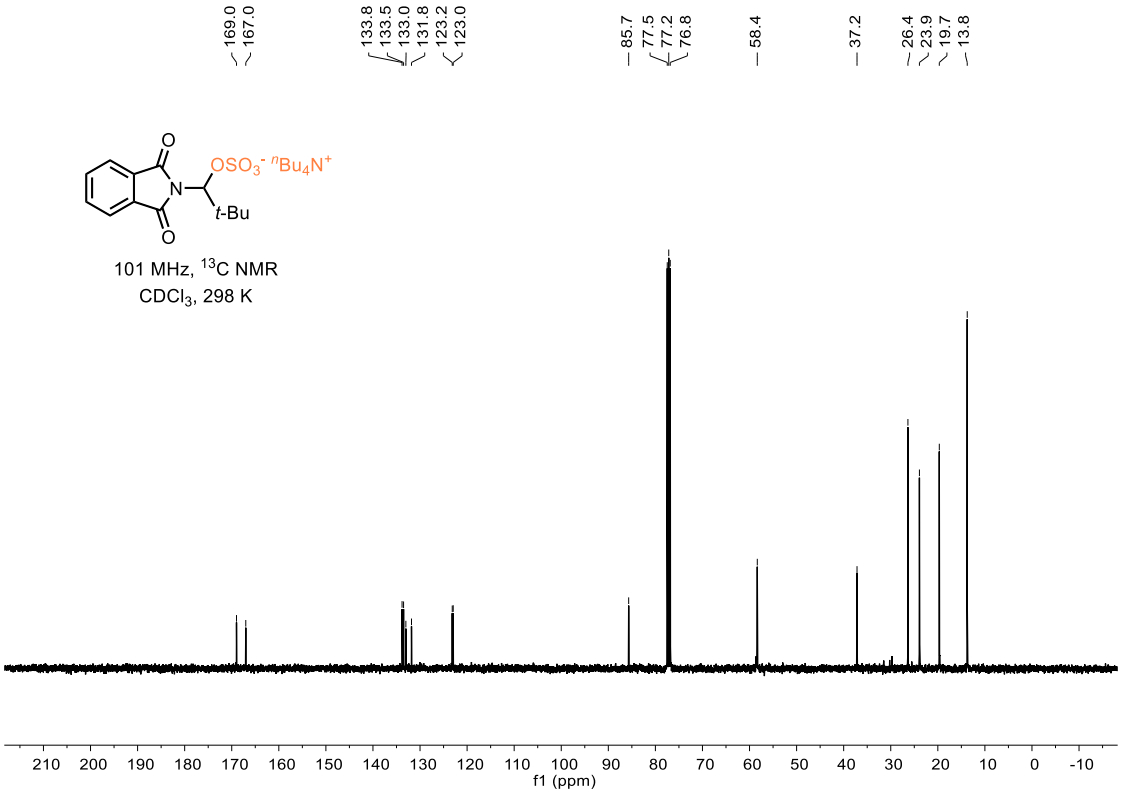


Tetrabutylammonium 1-(1,3-dioxoisoindolin-2-yl)-2,2-dimethylpropyl sulfate (29)

^{1}H NMR of tetrabutylammonium 1-(1,3-dioxoisoindolin-2-yl)-2,2-dimethylpropyl sulfate (29)

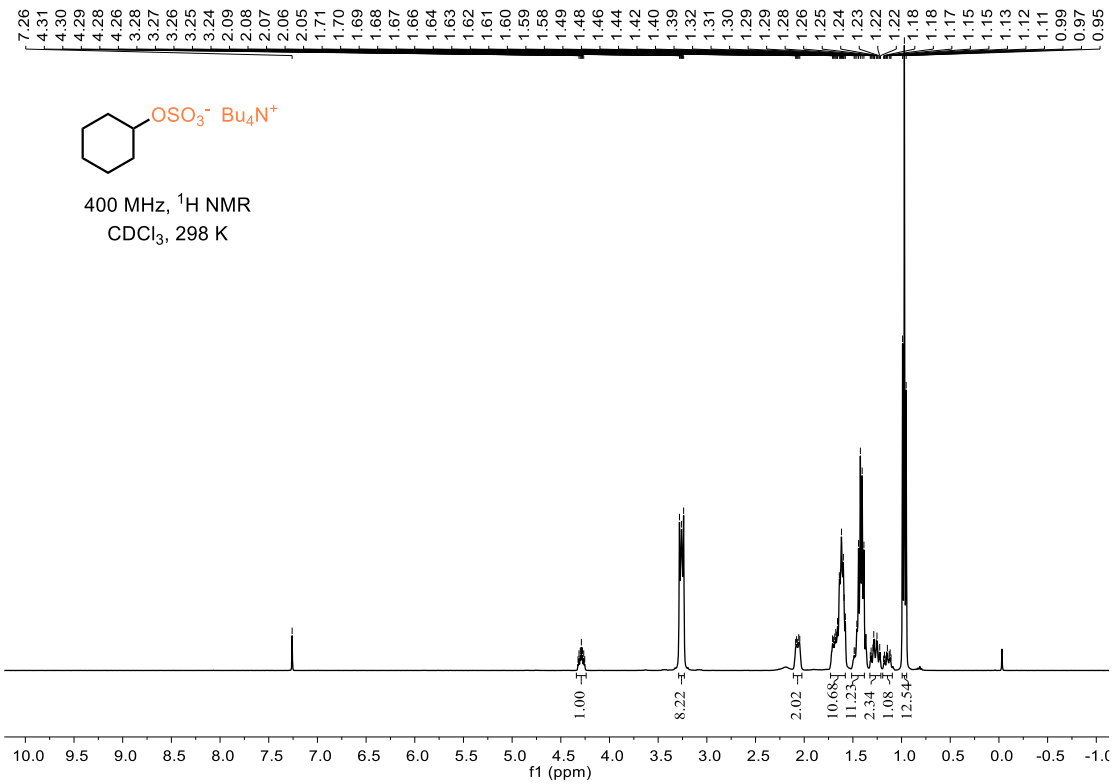


^{13}C NMR of tetrabutylammonium 1-(1,3-dioxoisoindolin-2-yl)-2,2-dimethylpropyl sulfate (29)

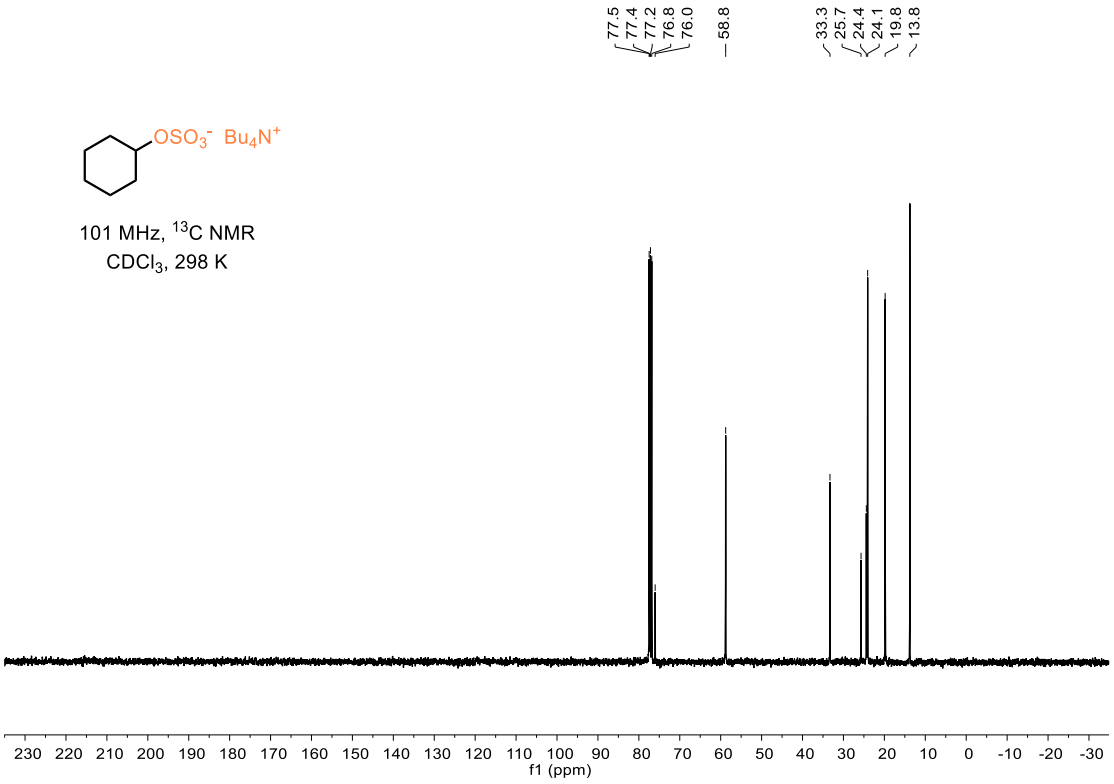


Tetrabutylammonium cyclohexyl sulfate (30')

^{1}H NMR of tetrabutylammonium cyclohexyl sulfate (30')

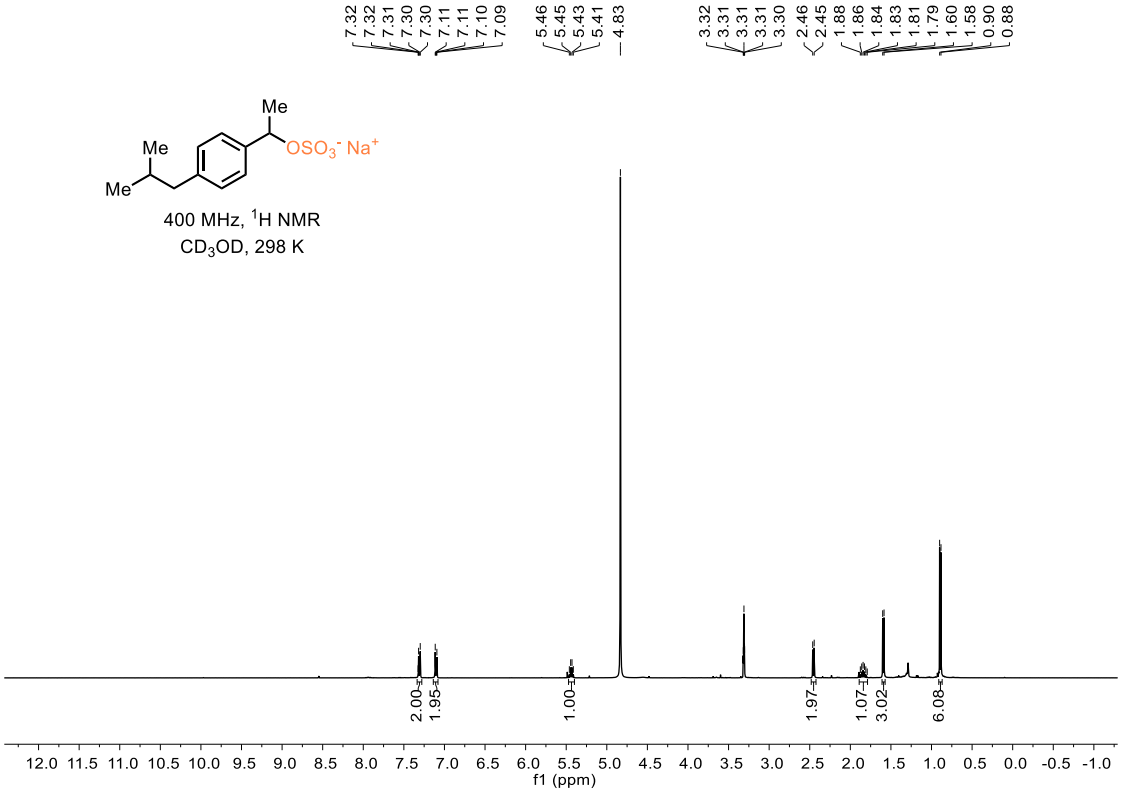


^{13}C NMR of tetrabutylammonium cyclohexyl sulfate (30')

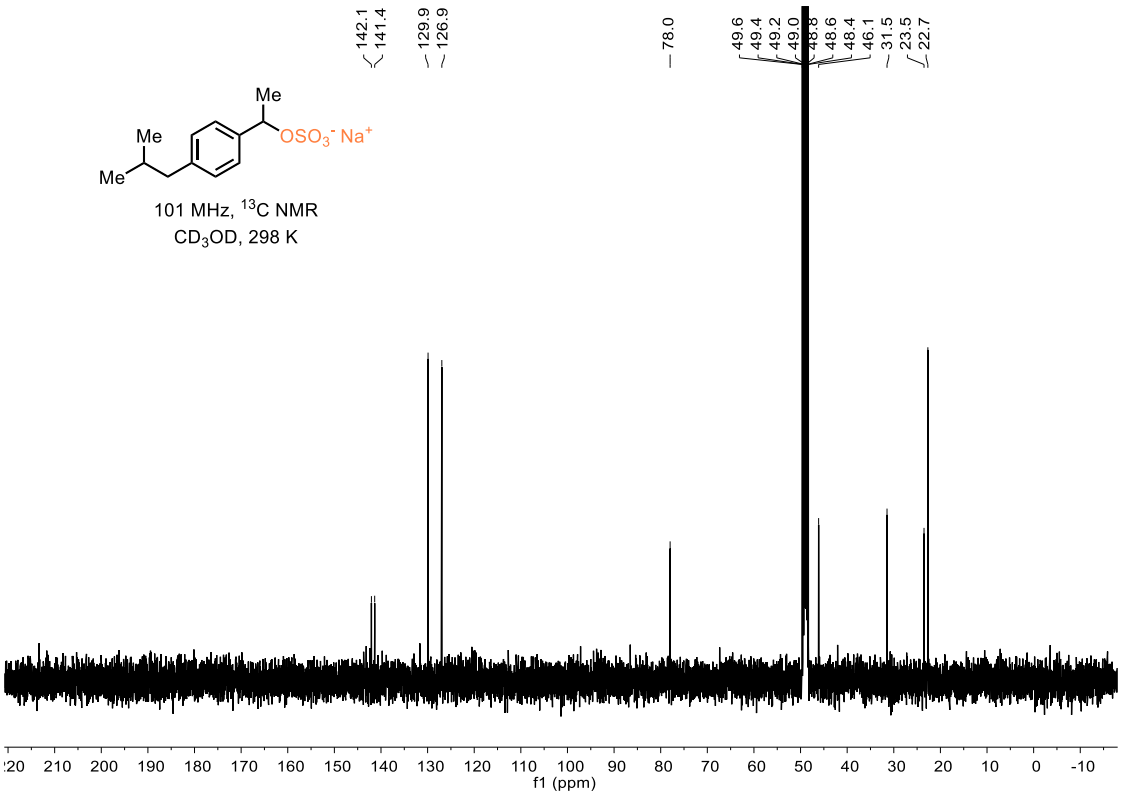


Sodium ibuprofen-sulfate (32)

^{1}H NMR of sodium ibuprofen-sulfate (32)

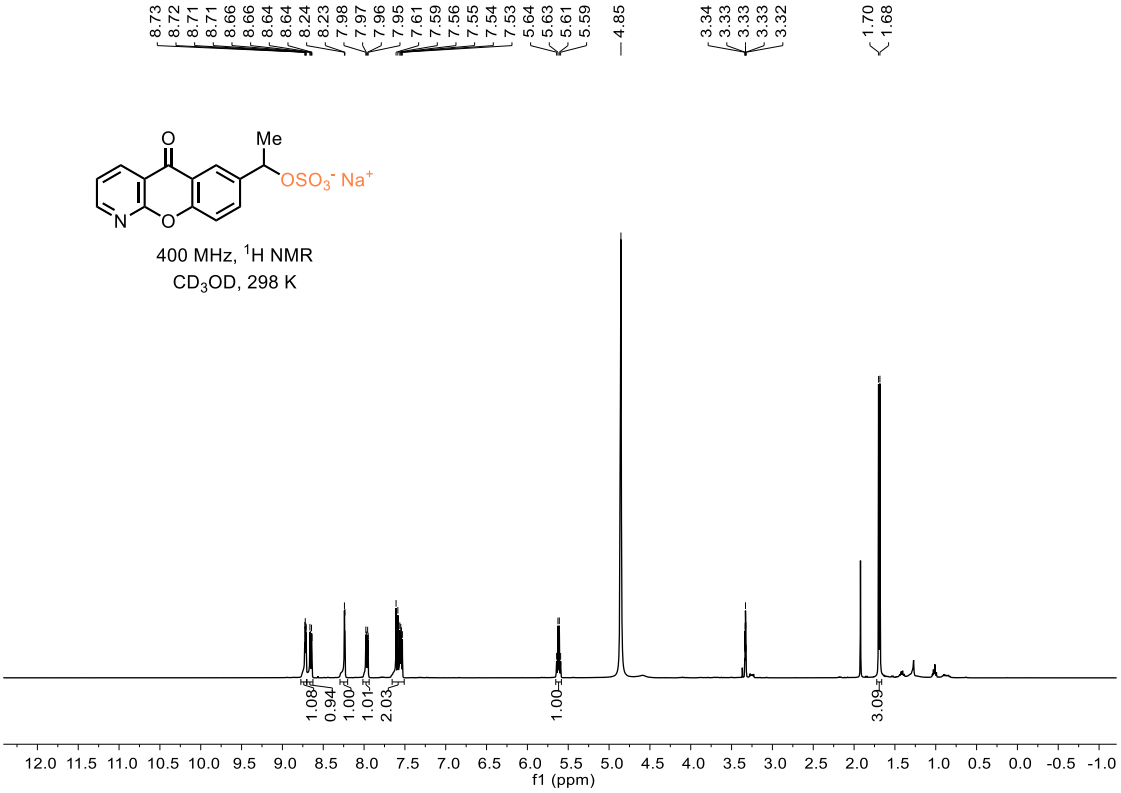


^{13}C NMR of sodium ibuprofen-sulfate (32)

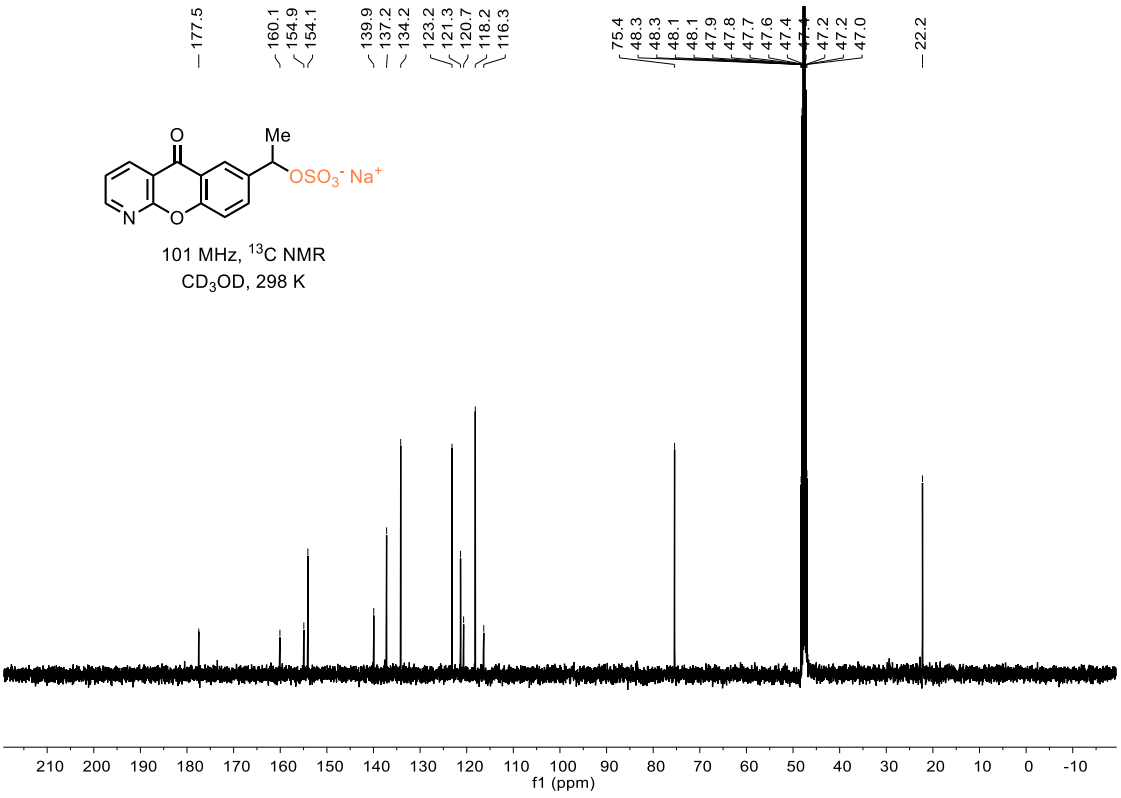


Sodium pranoprofen derivative-sulfate (33)

^{1}H NMR of sodium pranoprofen derivative-sulfate (33)

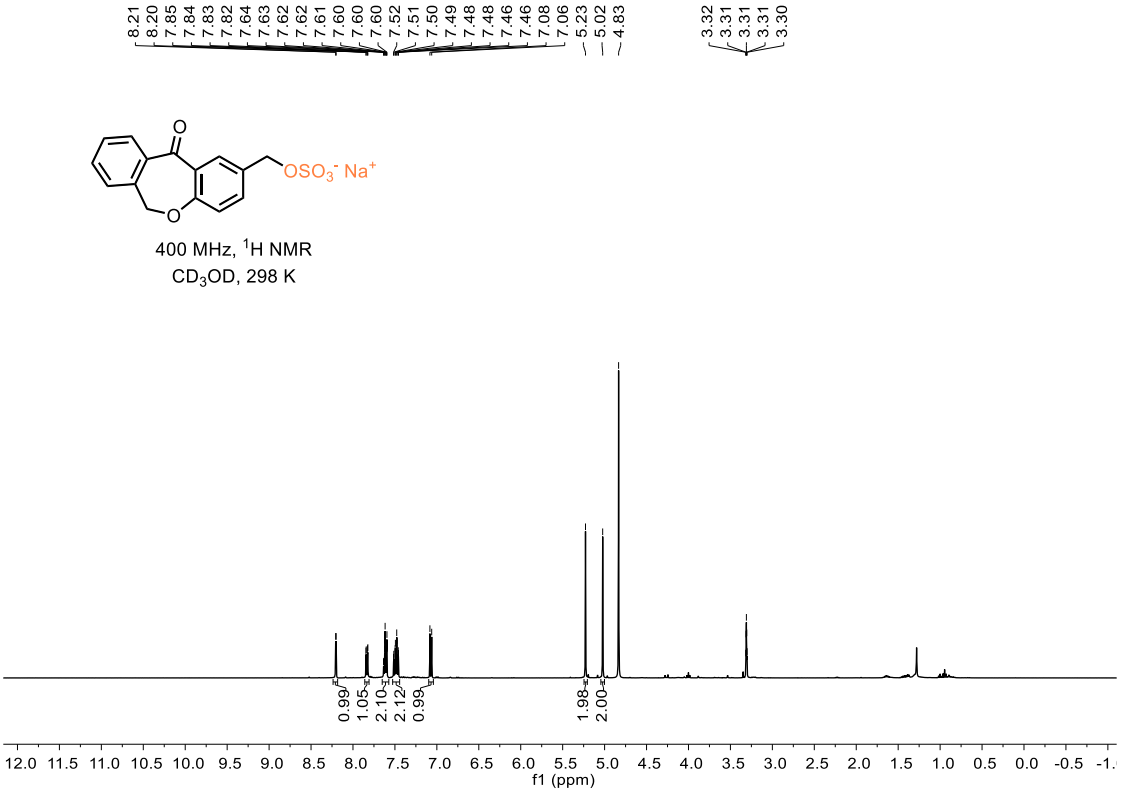


^{13}C NMR of sodium pranoprofen derivative-sulfate (33)

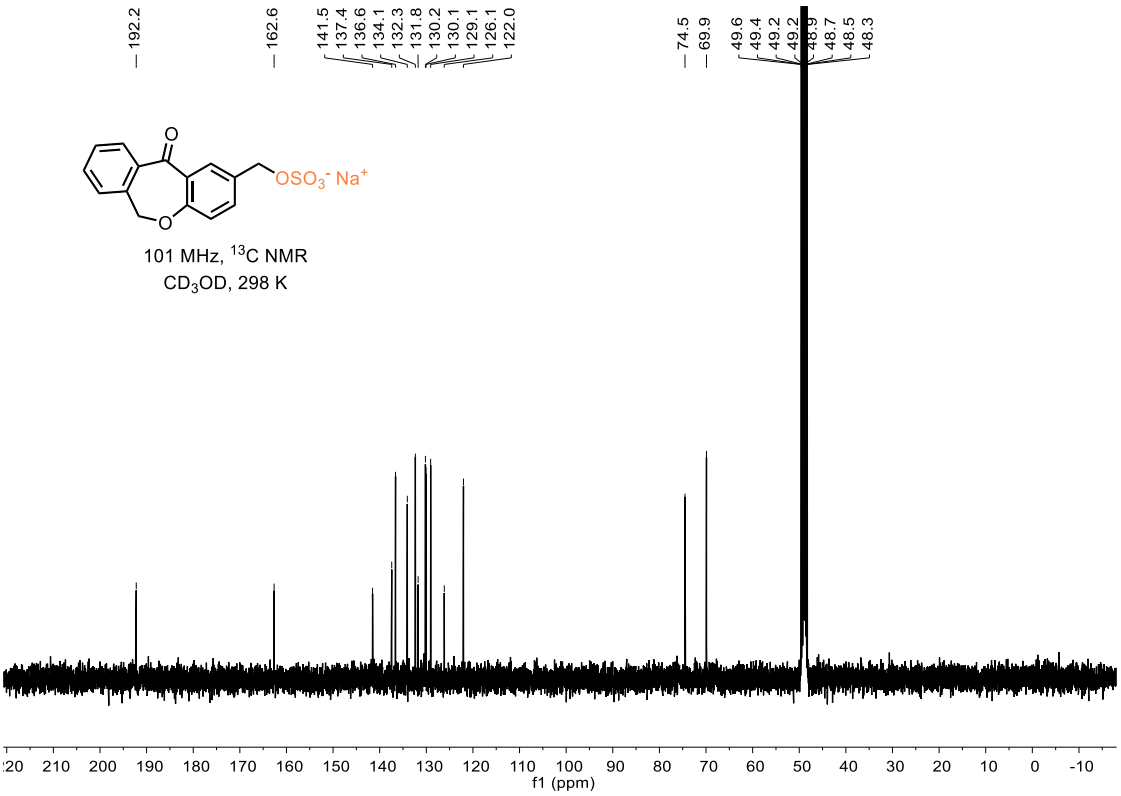


Sodium isoxepac-sulfate (34)

^{1}H NMR of sodium isoxepac-sulfate (34)

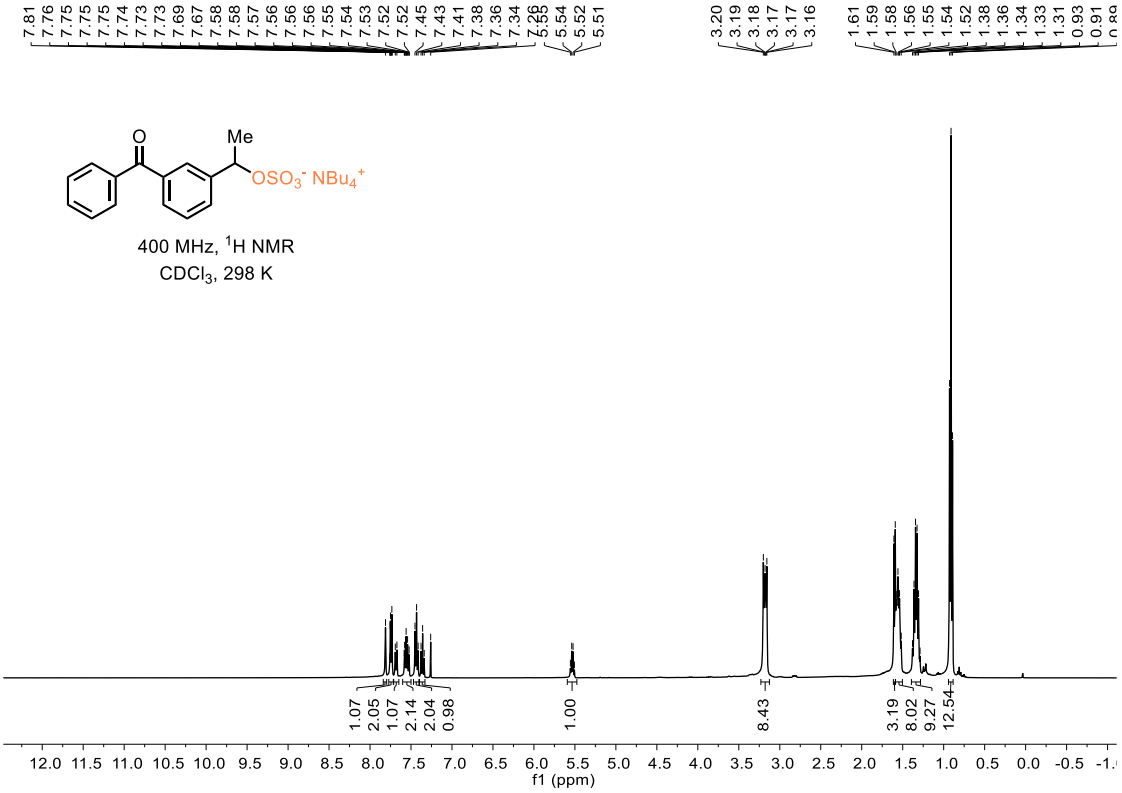


^{13}C NMR of sodium isoxepac-sulfate (34)

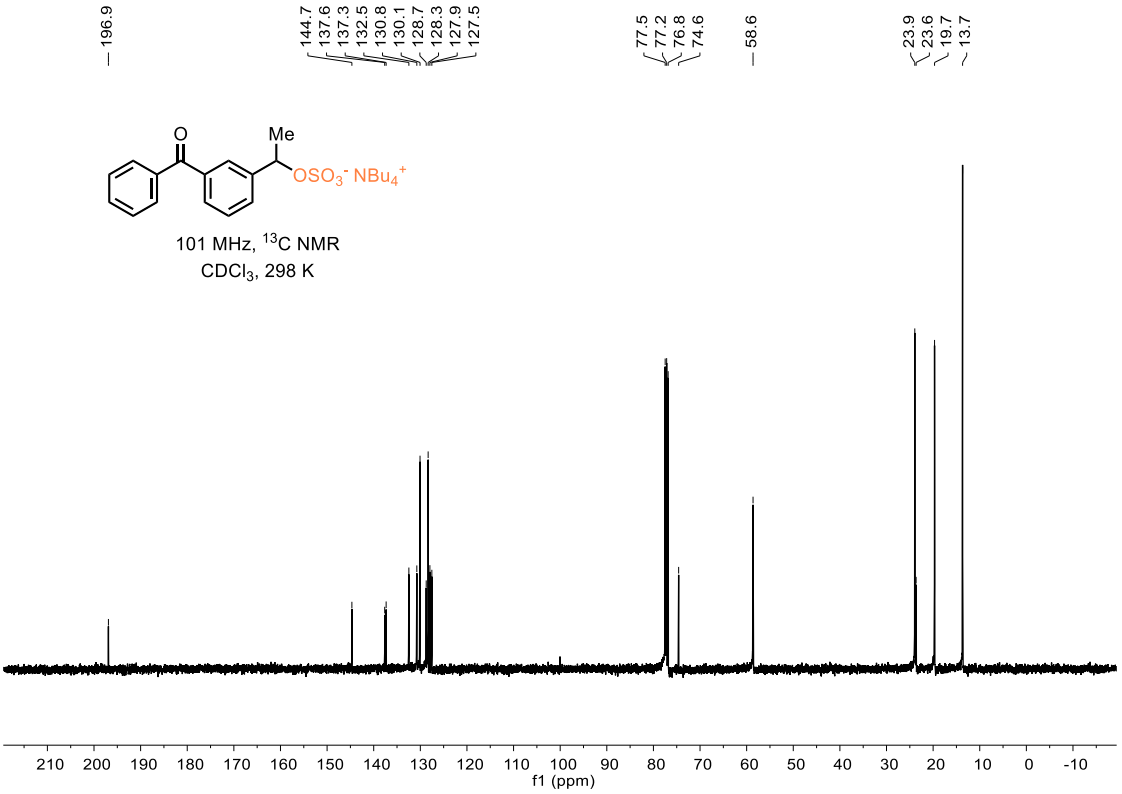


Tetrabutylammonium ketoprofen-sulfate (35')

^{1}H NMR of tetrabutylammonium ketoprofen-sulfate (35')

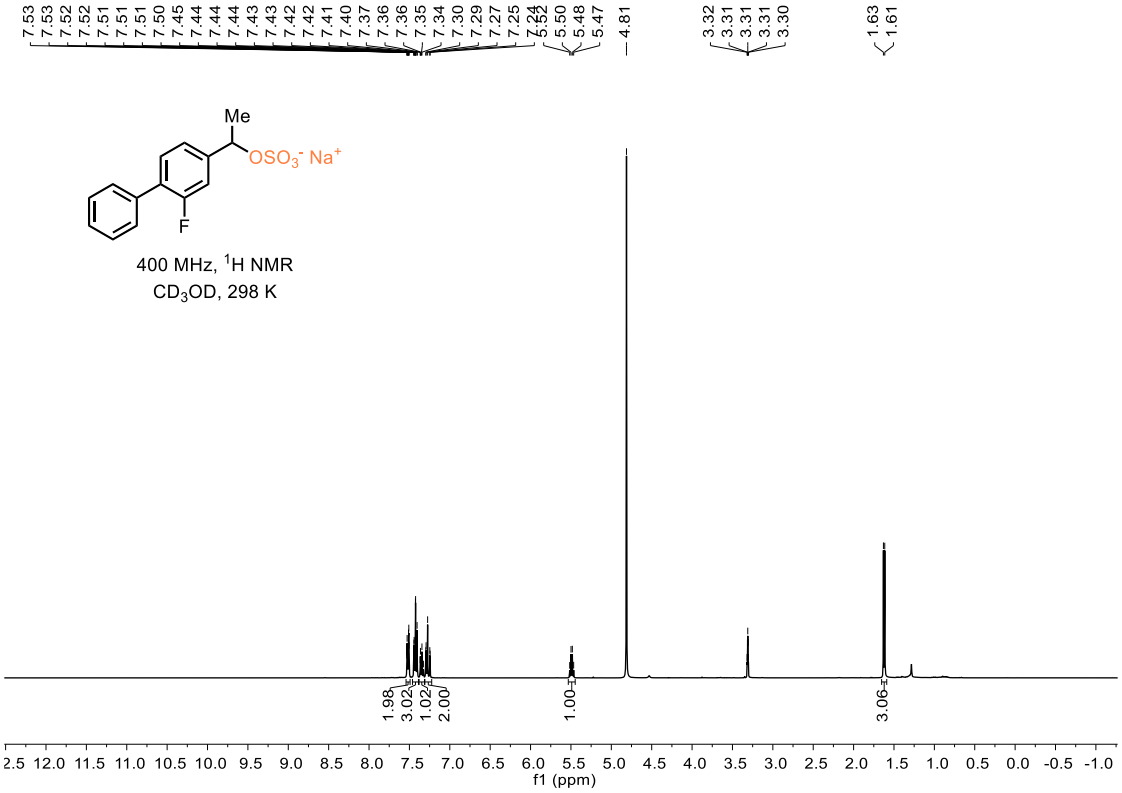


^{13}C NMR of tetrabutylammonium ketoprofen-sulfate (35')

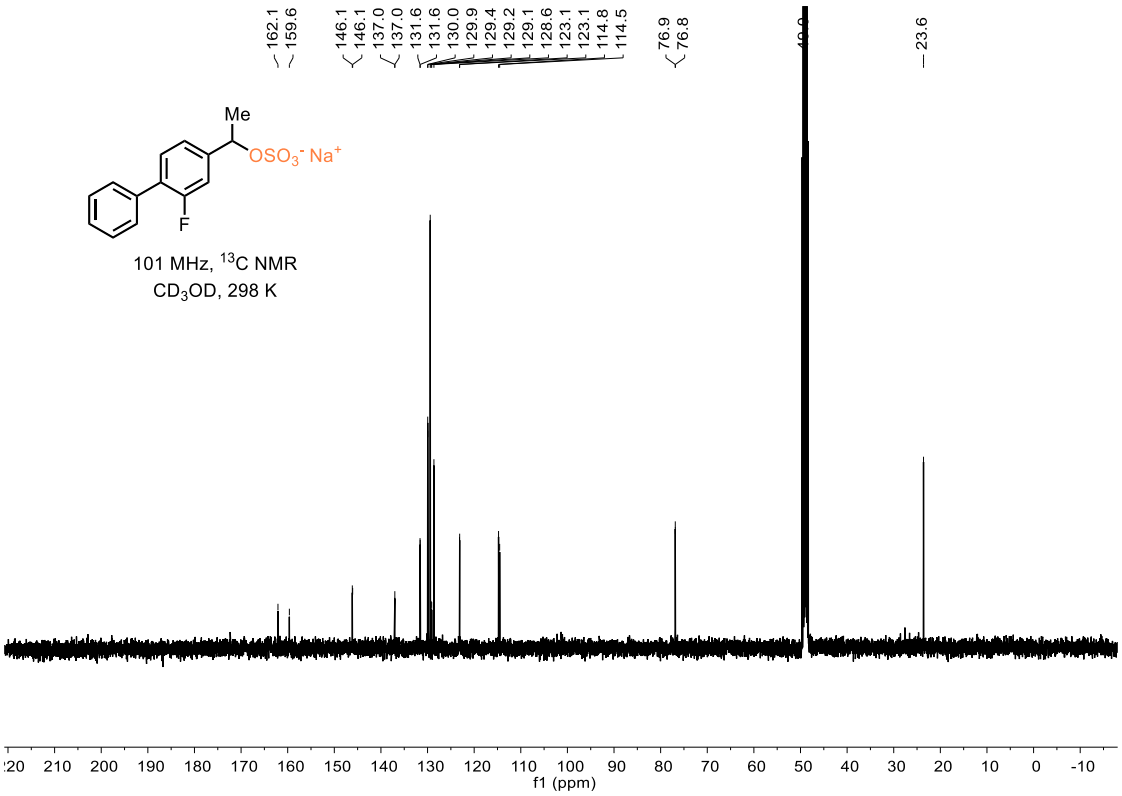


Sodium flurbiprofen-sulfate (36)

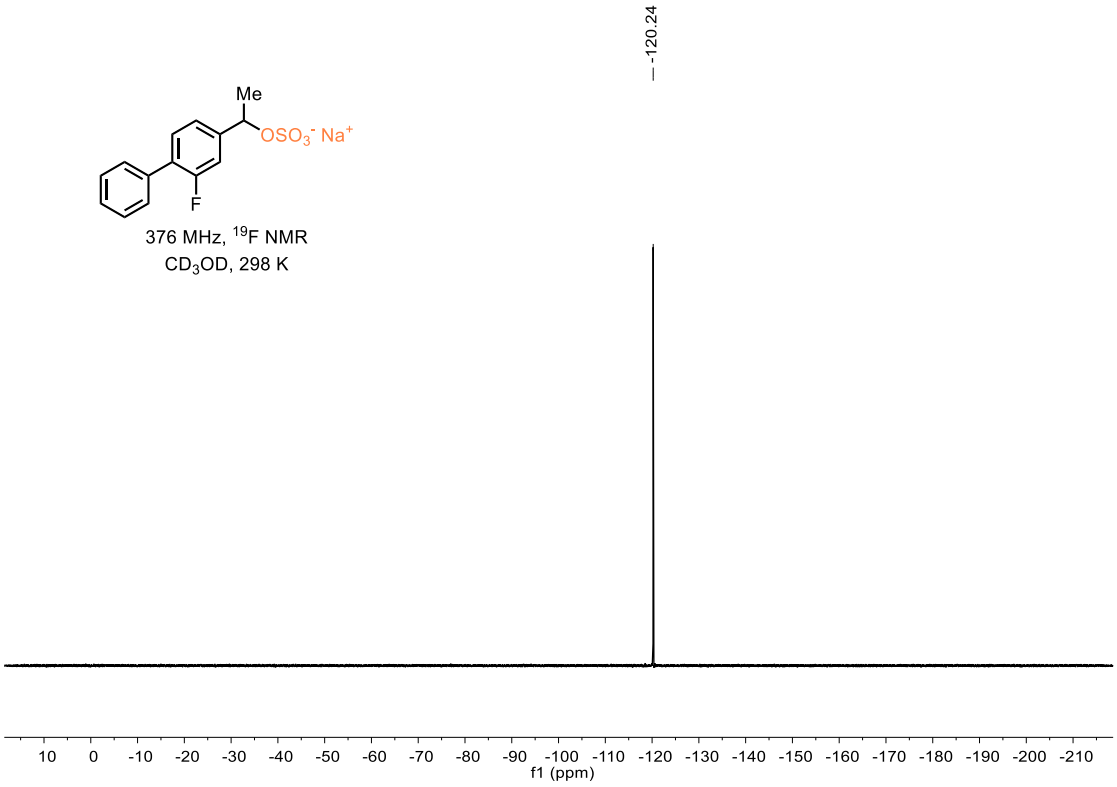
^{1}H NMR of sodium flurbiprofen-sulfate (36)



^{13}C NMR of sodium flurbiprofen-sulfate (36)

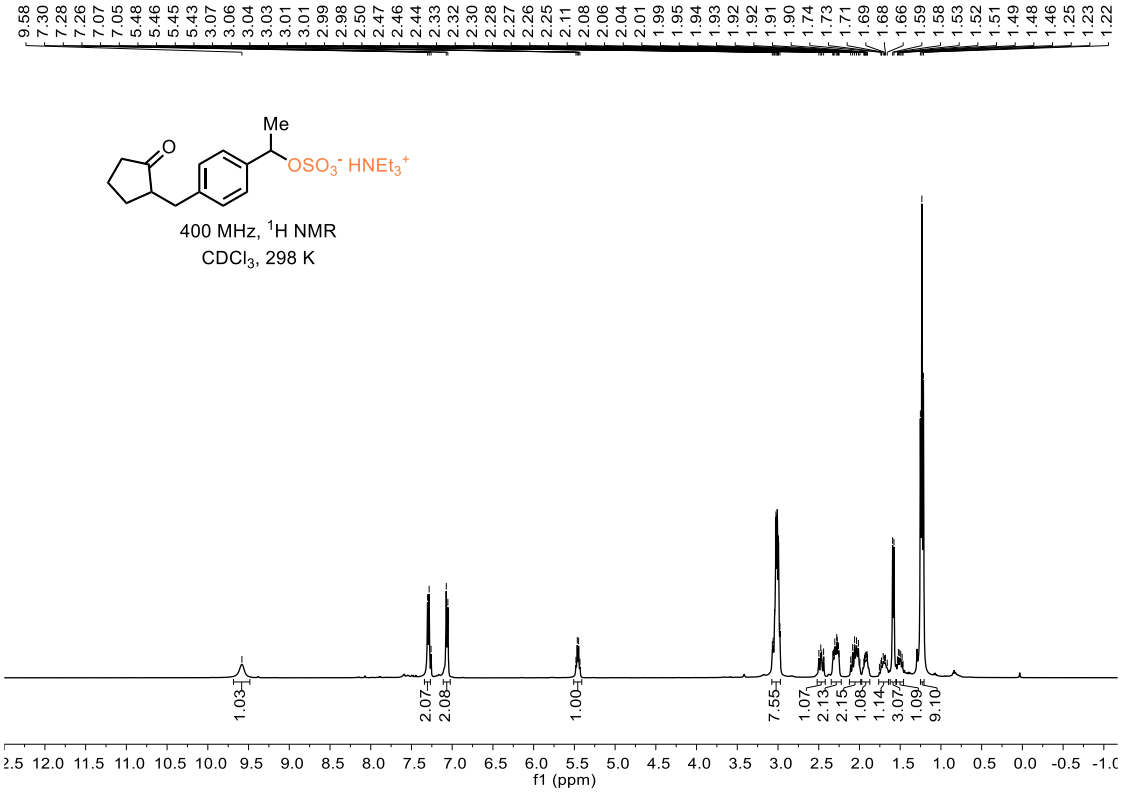


^{19}F NMR of sodium flurbiprofen-sulfate (36)

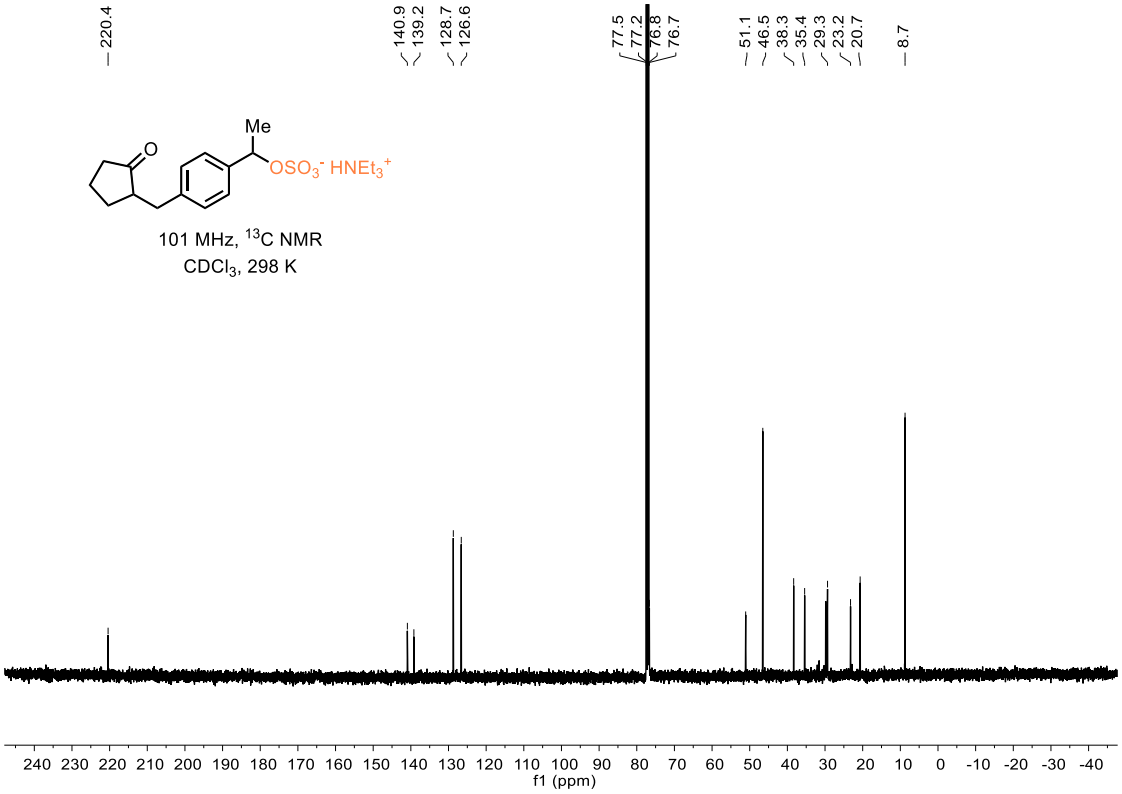


Quaternary ammonium loxoprofen-sulfate (37')

^{1}H NMR of quaternary ammonium loxoprofen-sulfate (37')

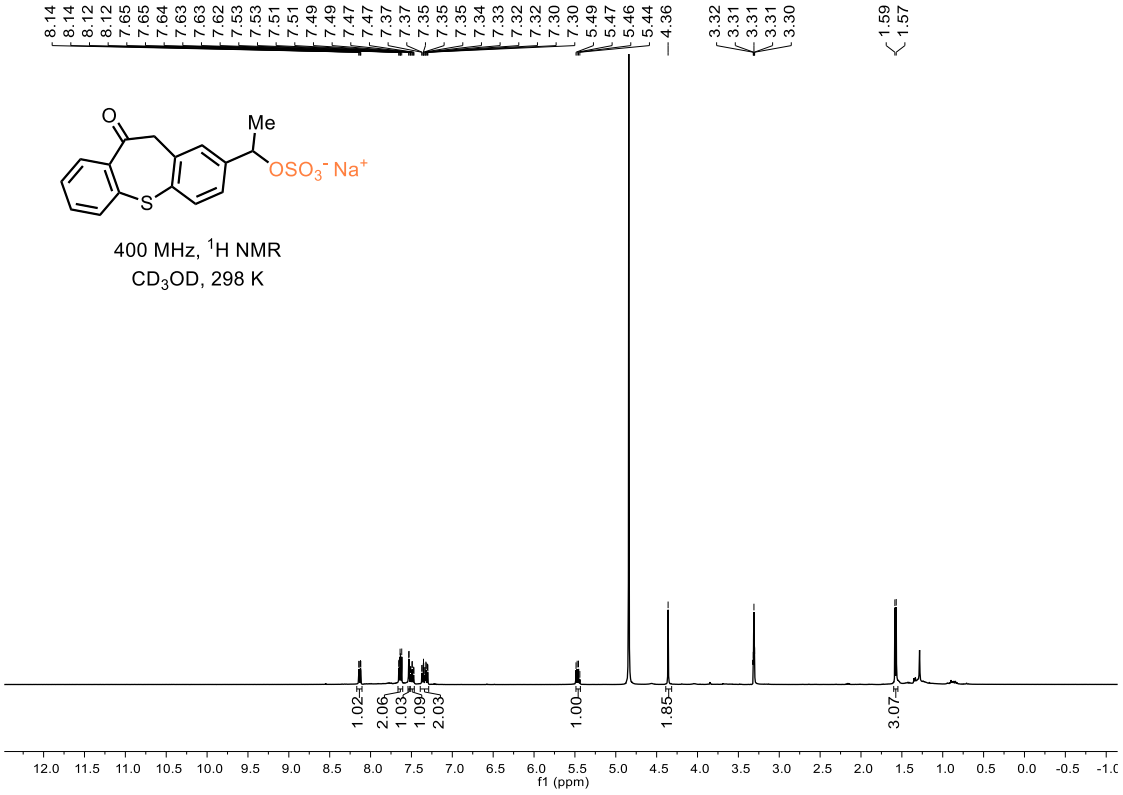


^{13}C NMR of quaternary ammonium loxoprofen-sulfate (37')

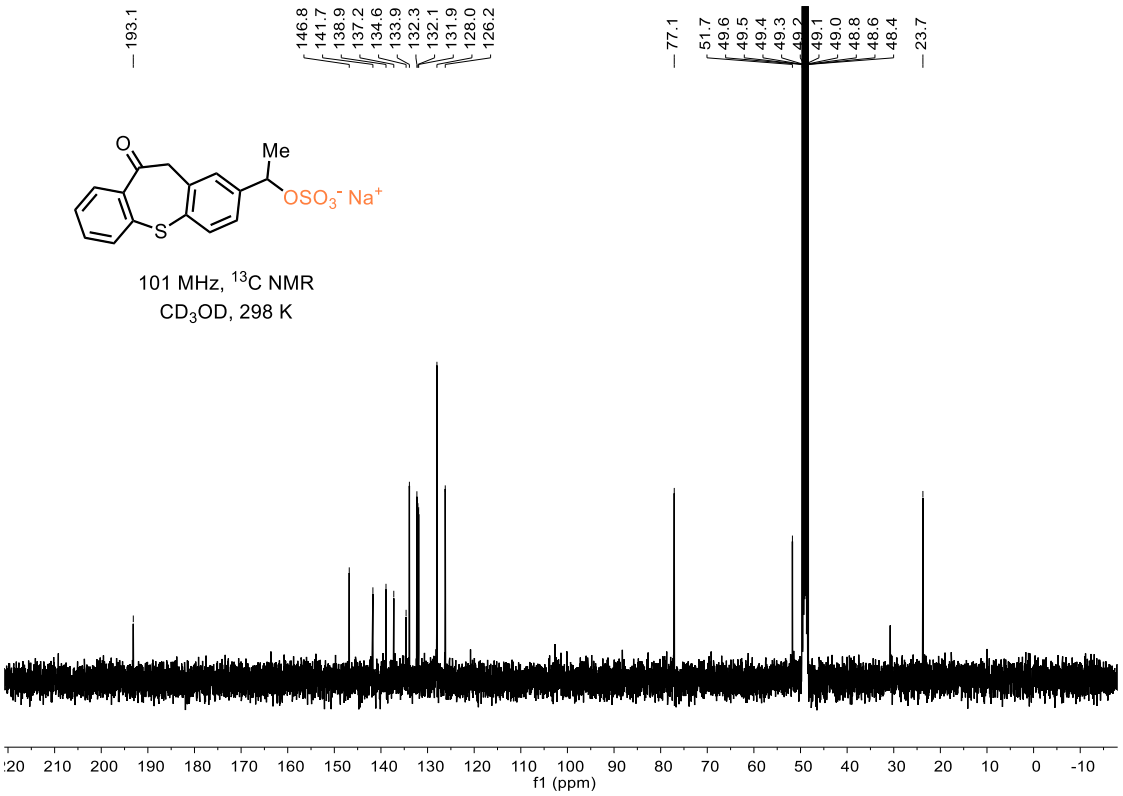


Sodium zaltoprofen-sulfate (38)

^{1}H NMR of sodium zaltoprofen-sulfate (38)

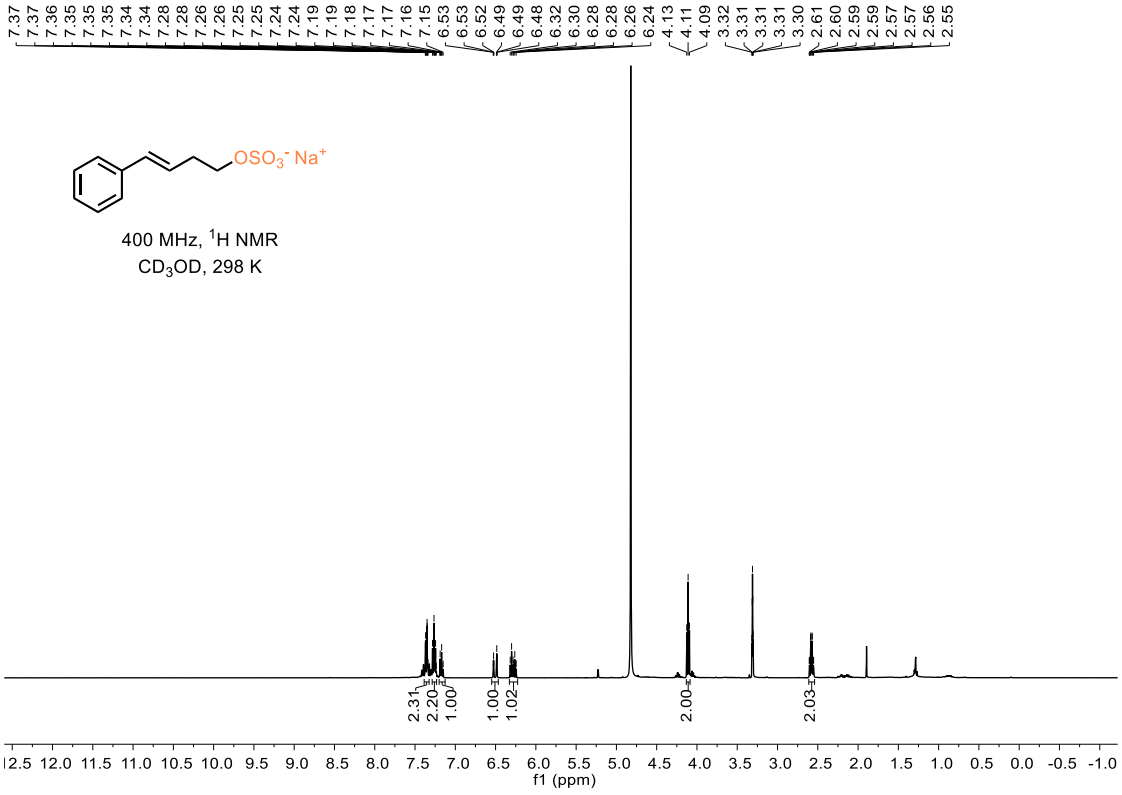


^{13}C NMR of sodium zaltoprofen-sulfate (38)

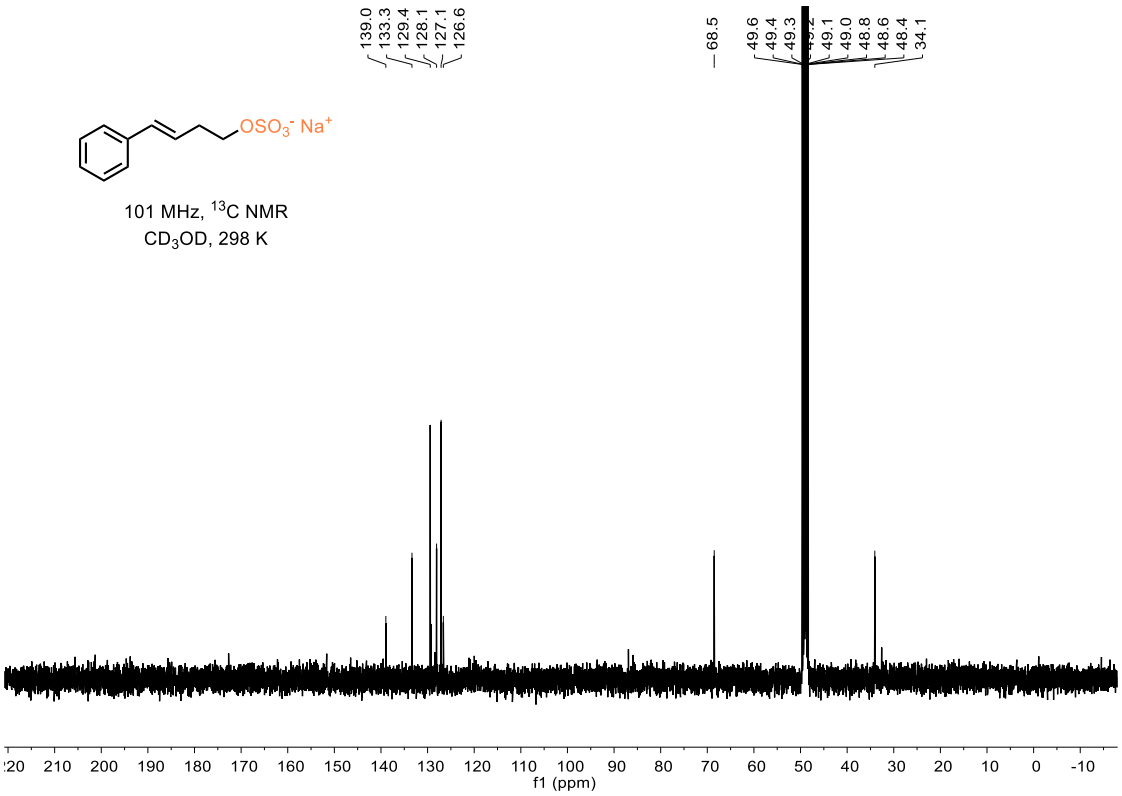


Sodium (E)-4-phenylbut-3-en-1-yl sulfate (39)

^{1}H NMR of sodium (E)-4-phenylbut-3-en-1-yl sulfate (39)

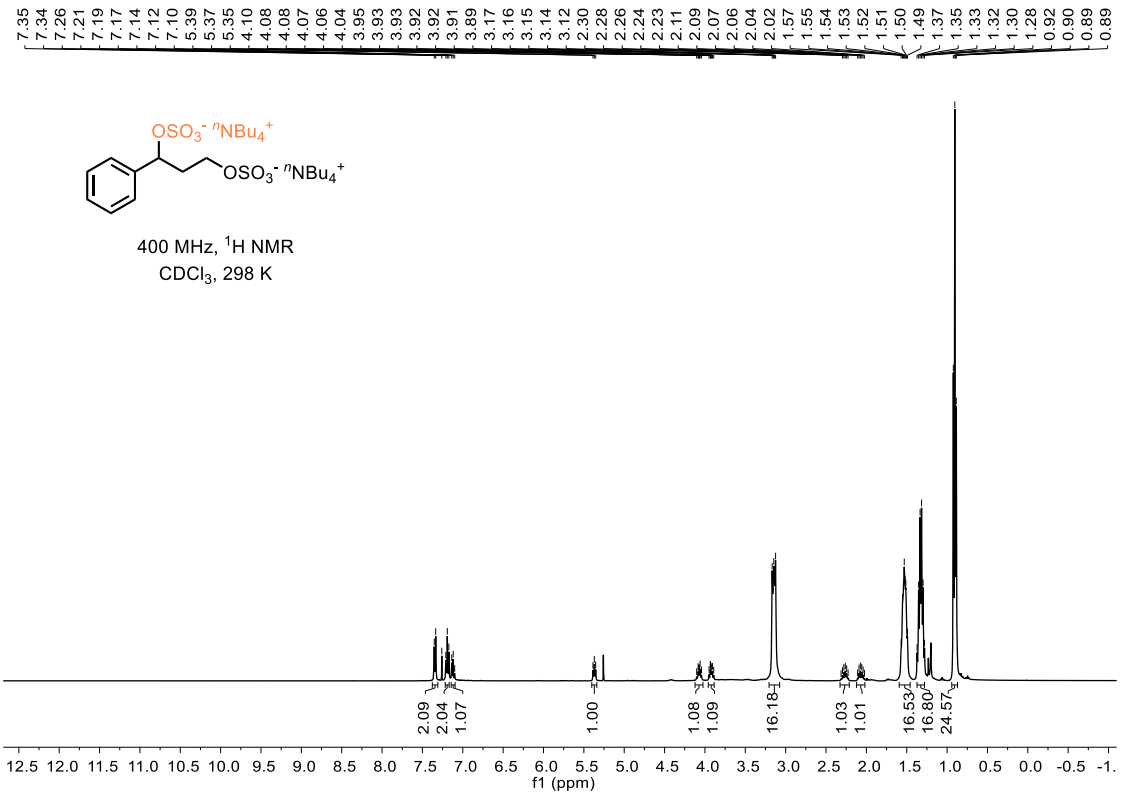


^{13}C NMR of sodium (E)-4-phenylbut-3-en-1-yl sulfate (39)



Tetrabutylammonium 1-phenylpropane-1,3-disulfate (40')

^{1}H NMR of tetrabutylammonium 1-phenylpropane-1,3-disulfate (40')



^{13}C NMR of tetrabutylammonium 1-phenylpropane-1,3-disulfate (40')