Fluorinated Acid Amplifiers for EUV Lithography

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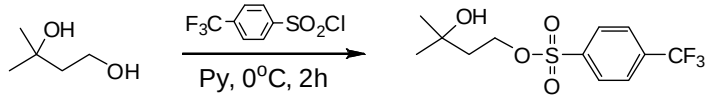
Supporting Information

General information	S-2
Synthesis of 3-Hydroxy-3-methylbutyl 4-(trifluoromethyl)benzenesulfonate **1a**	S-2
Synthesis of 3-hydroxy-3-methylbutyl 2-(trifluoromethyl)benzenesulfonate **1b**	S-2
Synthesis of 4-hydroxy-4-methylpentan-2-yl 4-(trifluoromethyl)benzenesulfonate **2**	S-2
Synthesis of 1-methylcyclohexane-1,2-diol	S-3
Synthesis of 2-hydroxy-2-methylcyclohexyl-4-(trifluoromethyl)benzenesulfonate **3a**	S-3
Synthesis of 1-methyl-2-(4-(trifluoromethyl)phenylsulfonyloxy)cyclohexyl acetate **3b**	S-3
Outgassing results	S-4
^{1}H NMR of 3-Hydroxy-3-methylbutyl 4-(trifluoromethyl)benzenesulfonate **1a**	S-4
^{13}C NMR of 3-Hydroxy-3-methylbutyl 4-(trifluoromethyl)benzenesulfonate **1a**	S-4
^{19}F NMR of 3-Hydroxy-3-methylbutyl 4-(trifluoromethyl)benzenesulfonate **1a**	S-5
IR of 3-Hydroxy-3-methylbutyl 4-(trifluoromethyl)benzenesulfonate **1a**	S-5
^{1}H NMR of 3-hydroxy-3-methylbutyl 2-(trifluoromethyl)benzenesulfonate **1b**	S-5
^{13}C NMR of 3-hydroxy-3-methylbutyl 2-(trifluoromethyl)benzenesulfonate **1b**	S-6
^{19}F NMR of 3-hydroxy-3-methylbutyl 2-(trifluoromethyl)benzenesulfonate **1b**	S-6
IR of 3-hydroxy-3-methylbutyl 2-(trifluoromethyl)benzenesulfonate **1b**	S-6
^{1}H NMR of 4-hydroxy-4-methylpentan-2-yl 4-(trifluoromethyl)benzenesulfonate **2**	S-7
^{13}C NMR of 4-hydroxy-4-methylpentan-2-yl 4-(trifluoromethyl)benzenesulfonate **2**	S-7
^{19}F NMR of 4-hydroxy-4-methylpentan-2-yl 4-(trifluoromethyl)benzenesulfonate **2**	S-7
IR of 4-hydroxy-4-methylpentan-2-yl 4-(trifluoromethyl)benzenesulfonate **2**	S-8
^{1}H NMR of 2-hydroxy-2-methylcyclohexyl-4-(trifluoromethyl)benzenesulfonate **3a**	S-8
^{13}C NMR of 2-hydroxy-2-methylcyclohexyl-4-(trifluoromethyl)benzenesulfonate **3a**	S-8
^{19}F NMR of 2-hydroxy-2-methylcyclohexyl-4-(trifluoromethyl)benzenesulfonate **3a**	S-9
IR of 2-hydroxy-2-methylcyclohexyl-4-(trifluoromethyl)benzenesulfonate **3a**	S-9
^{1}H NMR of 1-methyl-2-(4-(trifluoromethyl)phenylsulfonyloxy)cyclohexyl acetate **3b**	S-9
^{13}C NMR of 1-methyl-2-(4-(trifluoromethyl)phenylsulfonyloxy)cyclohexyl acetate **3b**	S-10
^{19}F NMR of 1-methyl-2-(4-(trifluoromethyl)phenylsulfonyloxy)cyclohexyl acetate **3b**	S-10
IR of 1-methyl-2-(4-(trifluoromethyl)phenylsulfonyloxy)cyclohexyl acetate **3b**	S-10
References	S-11

General Introduction and Materials.

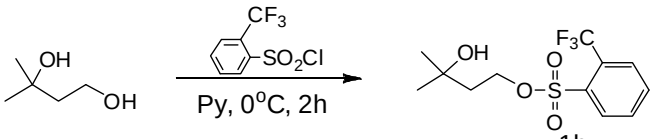
Nuclear Magnetic Resonance spectra were recorded on Bruker 400 Fourier transform NMR spectrometers. Spectra were recorded in solutions of deuterated chloroform ($CDCl_3$) or $CDCl_3/C_6F_6$ and were referenced to TMS (0.0 ppm) or the solvent residual peak in $CDCl_3$ (7.24 and 77.16 for ^1H and ^{13}C respectively) or C_6F_6 (-164.9 for ^{19}F). Flash chromatography was performed on Pharmaco silica gel (60-120 mesh). IR spectra were recorded on a Perkin Elmer.

Synthesis.



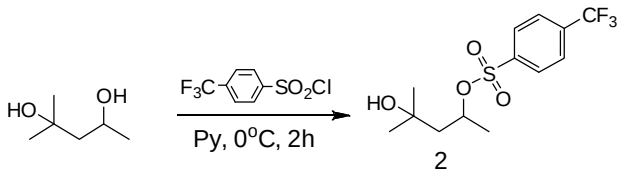
1 1a

3-Hydroxy-3-methylbutyl 4-(trifluoromethyl)benzenesulfonate (1a): A mixture of 3-methyl-1,3-methanebutane diol (1.495 g, 14.4 mmol), (4-trifluoromethyl)benzene sulfonyl chloride (5.403 g, 22.1 mmol) in dry pyridine (20 mL) was stirred at 0 °C for 2 hours, poured into the cold HCl (50 mL, 2 N), and extracted with ethyl acetate. The organic phase was washed with HCl (4 X 50 mL, 2 N), brine (1 X 25 mL), dried over Na_2SO_4, and evaporated to dryness. The product is a low melting point solid. (2.585 g, 57 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4, 2H, Ar-H), 7.81 (d, J = 8.4, 2H, Ar-H), 4.27 (t, J = 7.2, 2H, CH_2), 1.87 (t, J = 6.4, 2H, CH_2), 1.21 (s, 6H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$) δ 139.77, 135.5 (q), 128.53, 126.61(q), 124.54, 121.81, 69.60, 68.68, 41.77, 29.74. ^{19}F NMR (400 MHz, $CDCl_3/C_6F_6$) δ -66.25. IR (ATR) 3323, 2969, 1319, 1131, 1061 cm.$^{-1}$ Anal. Calcd for $C_{12}H_{15}SO_4F_3$: C, 46.1; H, 4.8. Found: C, 46.1; H, 4.9.



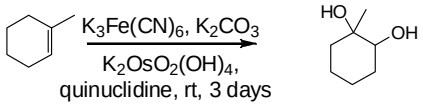
1 1b

3-hydroxy-3-methylbutyl 2-(trifluoromethyl)benzenesulfonate (1b): A mixture of 3-methyl-1,3-methanebutane diol (0.725 g, 7 mmol), (2-trifluoromethyl)benzene sulfonyl chloride (0.974 g, 4 mmol) in dry pyridine (5 mL) was stirred at 0 °C for 3 hours, poured into the cold HCl (50 mL, 2 N), and extracted with ethyl acetate. The organic phase was washed with HCl (4 X 25 mL, 2 N), brine (1 X 25 mL), dried over Na_2SO_4, and evaporated to dryness. (0.931 g, 71 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 7.0, 1H, Ar - H), 7.86 (d, J = 7.0, 1H, Ar - H), 7.72 (m, 2H, Ar - H), 4.26 (t, J = 7.1, 2H, CH_2), 2.11 (s, 1H, OH), 1.85 (t, J = 7.1, 2H, CH_2), 1.15 (s, 6H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$) δ 134.59, 134.08, 132.65, 132.08, 128.76(q), 128.42, 123.82, 69.60, 68.88, 41.71, 29.62. ^{19}F NMR (400 MHz, $CDCl_3/C_6F_6$) δ -61.48. IR (ATR) 3544, 3419, 2970, 1735, 1370, 1309, 1172, 1141, 1181, 1038, 931, 770 cm.$^{-1}$ Anal. Calcd for $C_{12}H_{15}SO_4F_3$: C, 46.1; H, 4.8. Found C, 45.7; H, 4.9.

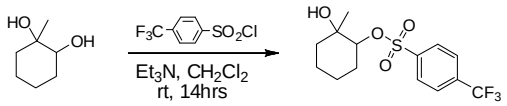


2

4-hydroxy-4-methylpentan-2-yl 4-(trifluoromethyl)benzenesulfonate (2): A mixture of 2-methyl-2,4-pentane diol (0.952 g, 8 mmol), (4-trifluoromethyl)benzene sulfonyl chloride (0.975 g, 4 mmol) in dry pyridine (6 mL) was stirred at room temperature for 7 hours, poured into the cold HCl (25 mL, 2 N), and extracted with ethyl acetate. The organic phase was washed with HCl (2 X 25 mL, 2 N), brine (1 X 25 mL), dried over Na_2SO_4, and evaporated to dryness. (0.927 g, 71 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.4, 2H, Ar - H), 7.77 (d, J = 8.4, 2H, Ar - H), 5.12 – 4.98 (m, 1H, C<u>H</u>-O-SO_2 C_6H_4-CF_3), 3.14 (s, 1H, OH), 1.92 (dd, J = 7.6, 15.2, 1H, CH_2), 1.66 (dd, J = 4.8, 15.2, 1H, CH_2), 1.28 (d, J = 6.4, 3H, CH_3), 1.17 (s, 6H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$) δ 141.31, 135.6 (q), 128.39, 126.50 (d), 124.58, 121.87, 79.53, 69.85, 49.56, 30.39, 29.48, 22.78. ^{19}F NMR (400 MHz, $CDCl_3/C_6F_6$) δ -66.28. IR (ATR) 3519, 3410, 2967, 1734, 1319, 1309, 1127, 1061, 880 cm.$^{-1}$ Anal. Calcd for $C_{13}H_{17}SO_4F_3$: C, 47.8; H, 5.2. Found C, 47.5; H, 5.4.

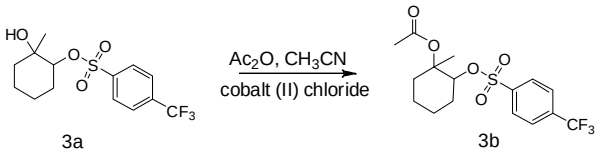


1-methylcyclohexane-1,2-diol:[1] Potassium ferricyanide, $K_3Fe(CN)_6$, (20.5 g, 62.4 mmol), potassium carbonate, K_2CO_3, (8.62 g, 62.4 mmol), potassium osmate, $K_2OsO_2(OH)_4$, (0.092 g, 0.312 mmol), and quinuclidine, $C_7H_{13}N$, (0.139g, 1.56 mmol) were placed into a round bottom flask. Water (25 mL) and tert-butanol (25 mL) were added and the mixture was heated with a heat gun until two distinct layers were formed. Subsequently, 1-methylcyclohexene (3.00 g, 31.2 mmol) was added dropwise. The reaction was stirred in the dark for three days. Sodium sulfite, $NaSO_3$, (15.7 g, 124.8 mmol) was added slowly, followed by water (35 mL) and the resulting solution was stirred for an additional hour. The solution was extracted with dichloromethane (3x50 mL) and the organic phase was dried over $MgSO_4$. The solvent was removed via rotary evaporation followed by drying *in vacuo*. The product was isolated as a white solid, yielding 2.83 g, (69.6%). mp 69-70 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz) 1.24 (3H, s, H^{10-12}), 1.26-1.81 (8H, m, H^{2-9}), 1.85 (1H, s, H^{13}), 1.93 (1H, d, J = 5.5, H^{14}), 3.39 (1H, ddd, J1 = 9.15, J2 = 5.37, J3 = 4.13, H^1)



3a

2-hydroxy-2-methylcyclohexyl-4-(trifluoromethyl)benzenesulfonate (3a): 1-methyl-1,2-cyclohexanediol (1.00 g, 7.68 mmol) was placed into a three-necked round bottom flask equipped with a stir bar and N_2 inlet. Dichloromethane (ca. 20 mL) was added. Triethylamine (3.89 g, 38.4 mmol) was added to the flask through a ca. 5 cm column of activated alumina. 4-triflouromethylbenzenesufonyl chloride (2.07 g, 8.45 mmol) was added to the flask and the reaction was stirred for 14 hours. The solution was washed with saturated sodium bicarbonate (2x30 mL) and a 10% aqueous triethylamine solution (25 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed via rotary evaporation which yielded a yellow oil. Column chromatography on silica, eluting with 50/50 hexane/ethyl acetate gave the product as yellow solid (1.74 g, 67%). mp 59-60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4, 2H, Ar - H), 7.79 (d, *J* = 8.4, 2H, Ar - H), 4.49 – 4.42 (m, 1H, C<u>H</u>-OH), 1.90 – 1.47 (m, 6H, CH_2), 1.49 – 1.19 (m, 3H, CH_2, OH), 1.15 (s, 3H, CH_3) ^{13}C NMR (400 MHz, $CDCl_3$) δ 141.28, 135.60 (q), 128.40, 126.52, 124.61, 122.01, 88.53, 70.88, 37.88, 28.44, 27.12, 23.68, 20.82. ^{19}F NMR (400 MHz, $CDCl_3/C_6F_6$) δ -66.37. IR (ATR) 3544, 3453, 2936, 2863, 1736, 1365, 1319, 1170, 1129, 1062, 879, 838, 712 cm.$^{-1}$ Anal. Calcd for $C_{14}H_{17}SO_4F_3$: C, 49.7; H, 5.0. Found C, 49.7; H, 5.0.



3a 3b

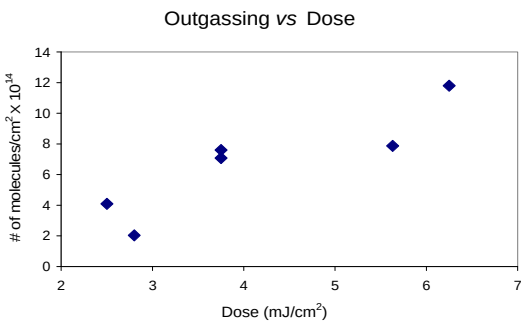
1-methyl-2-(4-(trifluoromethyl)phenylsulfonyloxy)cyclohexyl acetate (3b) : Compound **3a** (0.588 g, 1.74 mmol) was placed into a three-necked flask equipped with a stir bar and a N_2 inlet. Acetonitrile (25 mL), acetic anhydride (0.355 g, 3.48 mmol) and cobalt (II) chloride (0.0113 g, 0.087 mmol) were added and the reaction was refluxed for 3 hours. The solvent was removed via rotary evaporation to give oil. Column chromatography on silica gel, eluting with 50/50 hexane/ethyl acetate gave a white solid (0.61 g, 31.3%). mp 110-111 °C. IR (ATR) $\nu_{C=O}$ = 1736 cm^{-1}. %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0, 2H, Ar - H), 7.80 (d, *J* = 8.4, 2H, Ar - H), 4.62 – 4.51 (m, 1H, C<u>H</u>), 2.61-2.49 (m, 1H, CH_2), 2.02 – 1.86 (m, 4H, CH_2, CH_3-CO), 1.75 – 1.62 (m, 2H, CH_2), 1.48-1.26 (m, 8H, CH_3, CH_2) ^{13}C NMR (400 MHz, $CDCl_3$) δ 169.95, 141.39, 135.44 (q), 128.28, 126.60, 124.47, 121.81, 86.85, 81.37, 33.08, 28.49, 22.80, 22.34, 20.94. ^{19}F NMR (400 MHz, $CDCl_3/C_6F_6$) δ -66.42. IR (ATR) 2937, 2860, 1735, 1366, 1321, 1230, 1178, 1132, 1064, 714 cm.$^{-1}$ Anal. Calcd for $C_{16}H_{19}SO_5F_3$: C, 50.5; H, 5.0. Found C, 50.6; H, 5.0.

Resist Outgassing

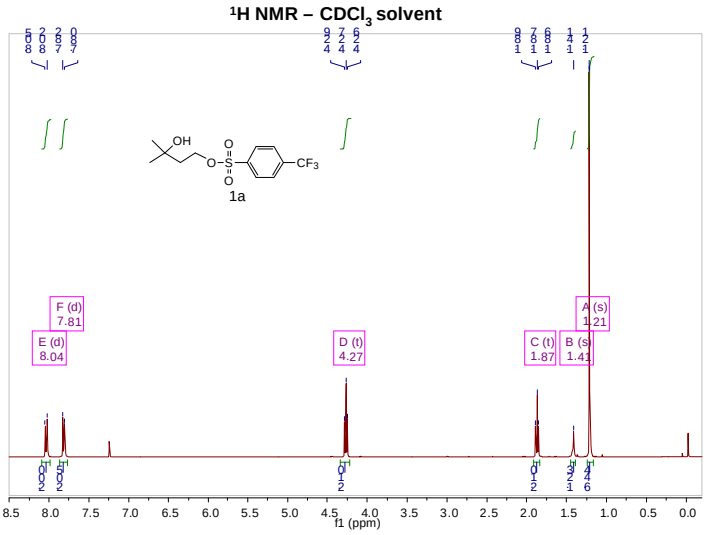
6 resists were evaluated for EUV outgassing according to previously published results:[3] 1 control and 5 with 70 mM added acid amplifier. Using the established methods clearing doses were determined using soft bake and post exposure bake of 90 °C, as expected **2** and **3a** thermally decomposed. Nonetheless outgassing was the same within experimental error.

Outgassing Results		
AA	Dose (mJ/cm^2)	# of molecules/cm^2 35-200 amu excluding 44 amu
No AA	5.63	7.87×10^{14}
1a	3.75	7.08×10^{14}
1b	3.75	7.60×10^{14}
2	2.8*	2.03×10^{14}
3a	2.5*	4.09×10^{14}
3b	6.25	1.18×10^{15}

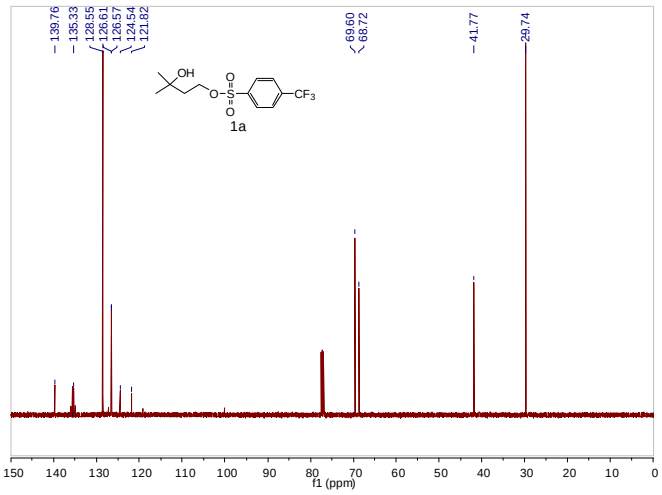
* AA thermally decomposed during the soft bake.



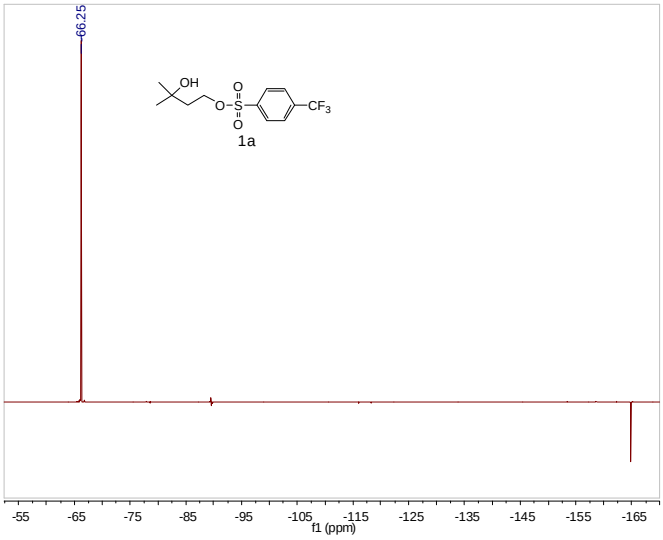
^{1}H NMR – $CDCl_3$ solvent



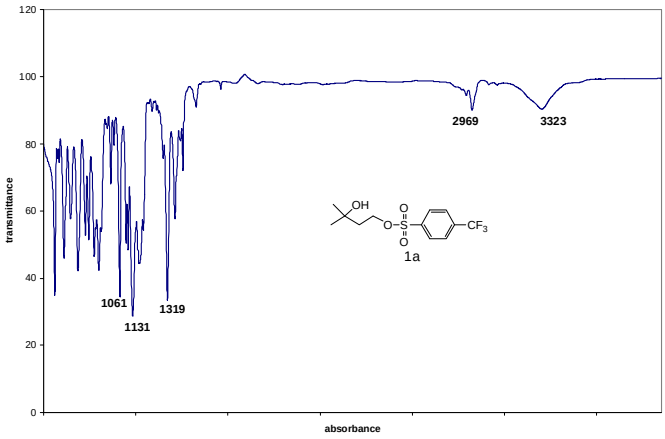
^{13}C NMR – $CDCl_3$ solvent



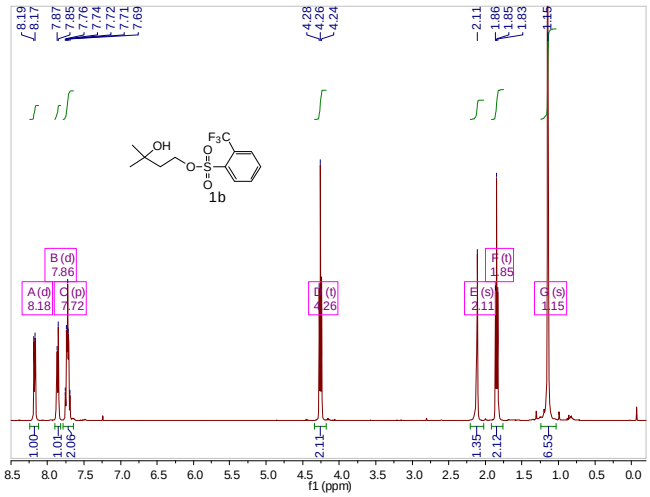
^{19}F NMR – $CDCl_3$ / C_6F_6 solvent



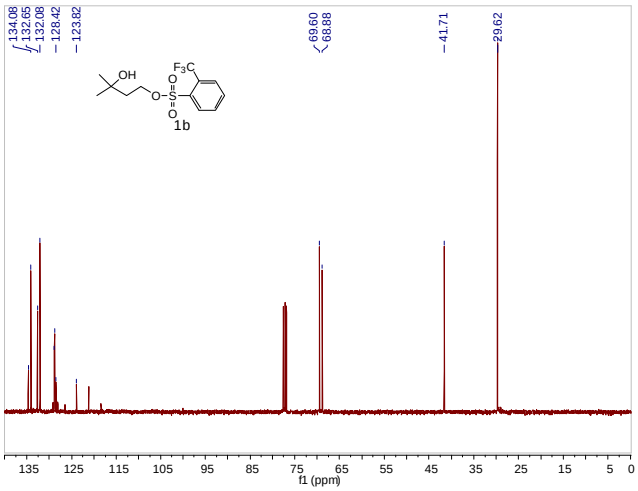
IR spectrum



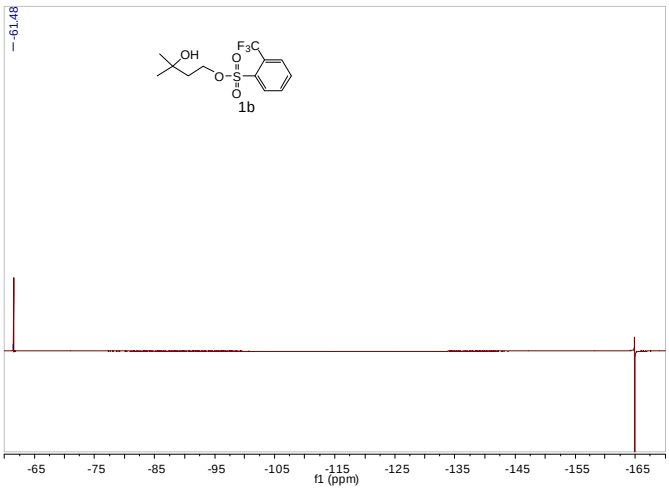
^{1}H NMR – $CDCl_3$ solvent



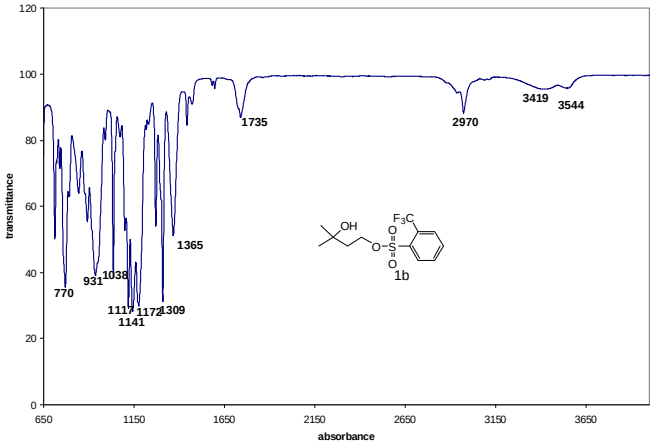
^{13}C NMR – $CDCl_3$ solvent



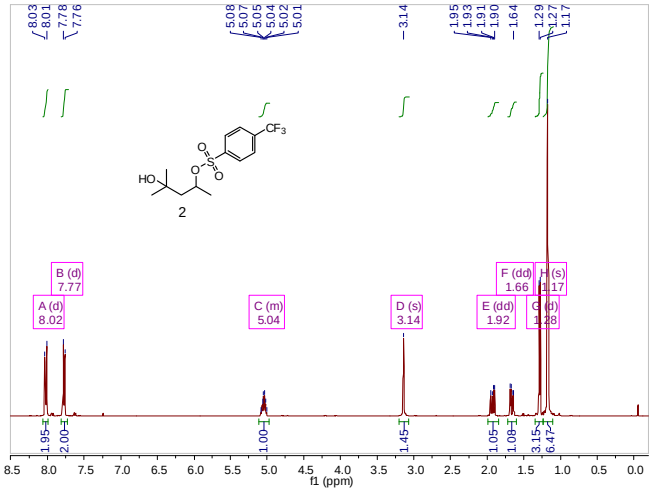
^{19}F NMR – $CDCl_3$ Solvent / C_6F_6 Reference



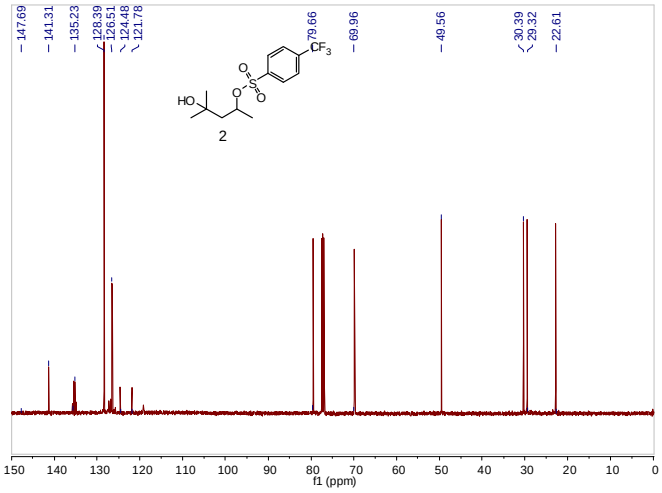
IR spectrum



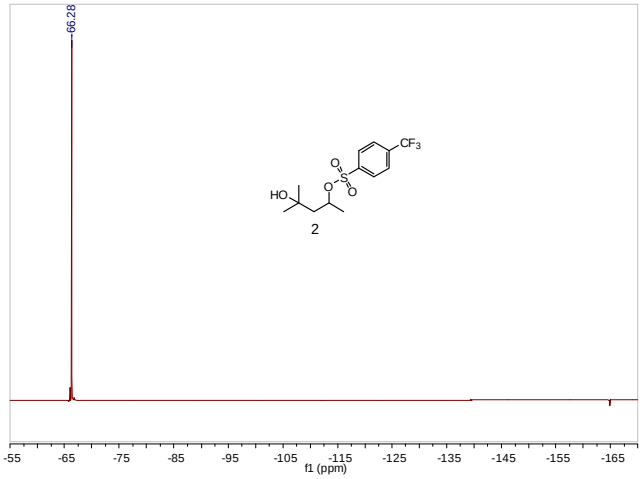
^{1}H NMR – $CDCl_3$ solvent



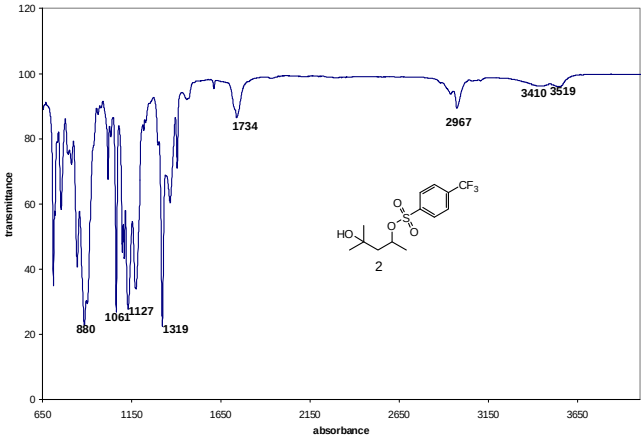
^{13}C NMR – $CDCl_3$ solvent



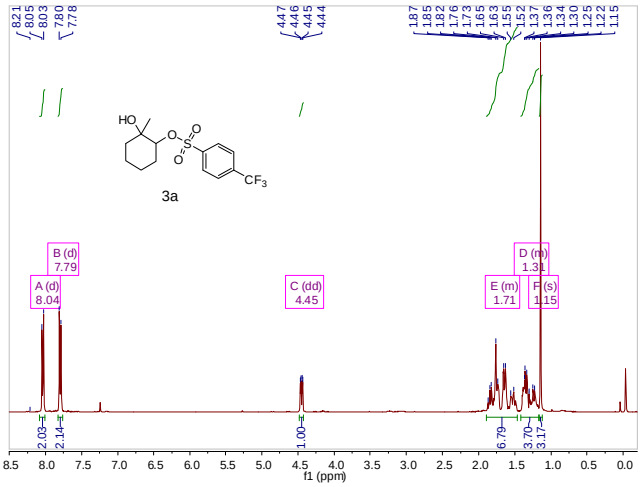
^{19}F NMR – $CDCl_3$ Solvent / C_6F_6 Reference



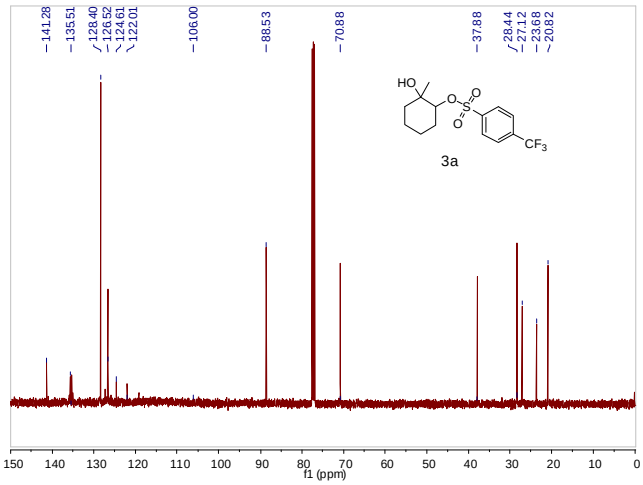
IR spectrum



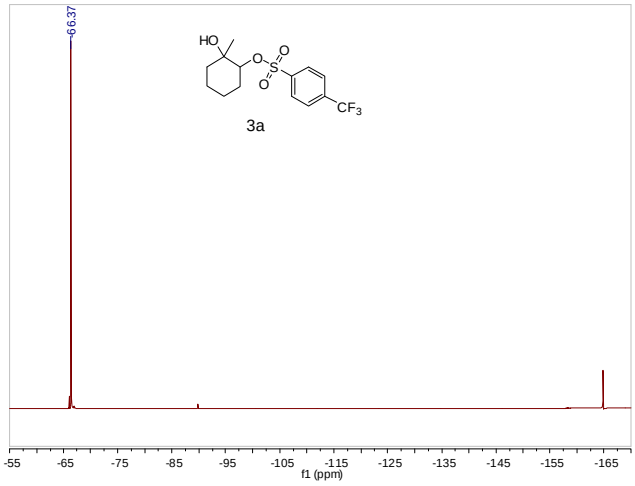
^{1}H NMR – $CDCl_3$ solvent



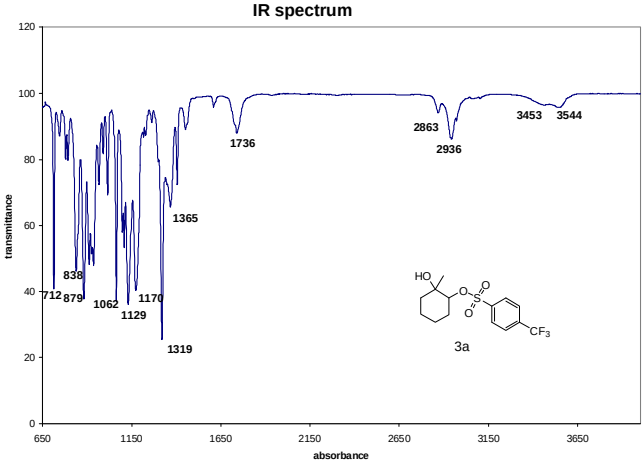
^{13}C NMR – $CDCl_3$ solvent



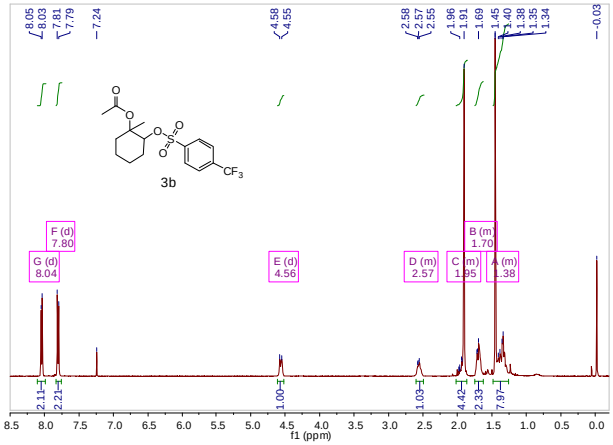
^{19}F NMR – $CDCl_3$ Solvent / C_6F_6 Reference



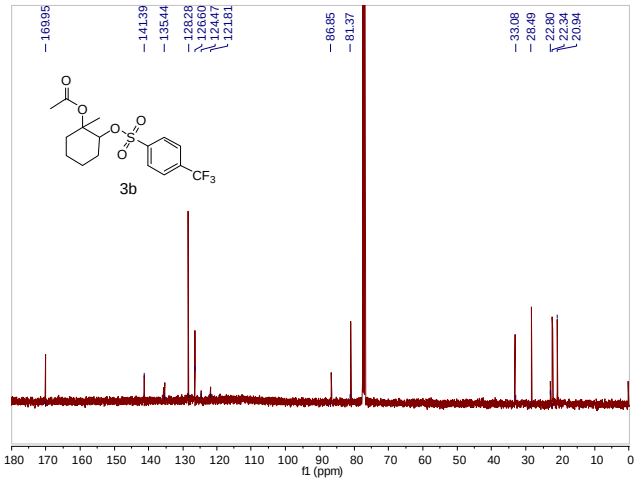
IR spectrum



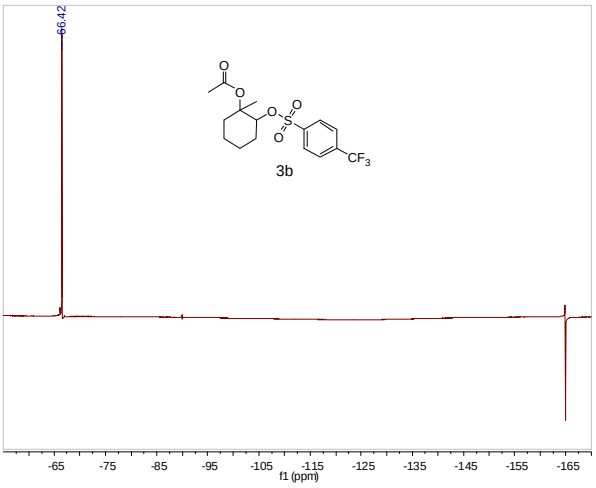
^{1}H NMR – $CDCl_3$ solvent



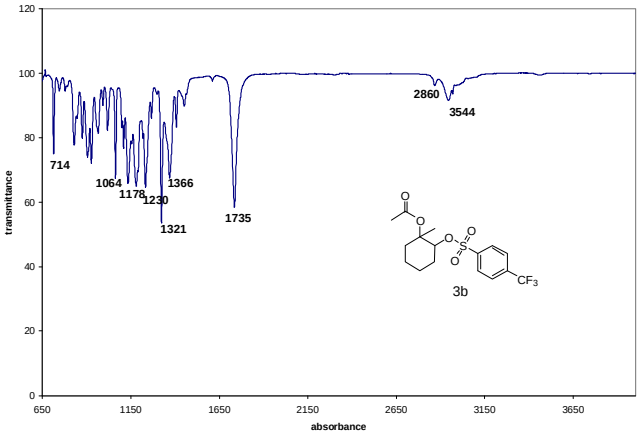
^{13}C NMR – $CDCl_3$ solvent



^{19}F NMR – $CDCl_3$ Solvent / C_6F_6 Reference



IR spectrum



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2. For comparison, the lithographic performance of 193 nm resists that use AAs is found in the following references. (a) Naito, T.; Ohfuji, T.; Endo, M.; Arimitsu, K.; Ichimura, K. *J. Photopoly. Sci. and Tech.* **1999,** 12, 509-514. (b) Ohfui, T., Takahashi, M.; Kuhara, K.; Ogawa, T.; Ohtsuka, H.; Sasago, M.; Ichimura, K. *Proc. SPIE* **1997,** 3049, 76-82.

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