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Singlet/Triplet Phenyl Cation and Benzyne from the Photodehalogenation of some silylated and stannylated Phenyl Halides

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ELECTRONIC SUPPLEMENTARY INFORMATIONS

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1. Experimental details

Computational investigations. Optimizations were carried out by using the (U)B3LYP DFT method with LANL2DZ basis set and added solvation correction (Gaussian 2003 package).[S1] Frequency calculations were evaluated at the same level of theory to certify structures as minima. Energies of the solvated cation was evaluated with CPCM method on the optimized geometries by using acetonitrile as solvent and adding Gaussian's keywords radii=UAHF and SCFVAC in order to evaluate, respectively, the volume of the molecule through United Atom Topological Model Hartree Fock method and the ΔG_{solv}. Energy (values in hartree) and cartesian coordinates (values in Angstrom) of the obtained minima are reported below. As described in figures S1-S6, the presence of either a Sn or a Si atom involves a modification in the charge distribution of both the singlet and triplet cations, with a significant increase of the negative charge in C_3 and C_6.

General. NMR spectra were recorded on a 300 MHz spectrometer. The attributions were made on the basis of ^{1}H and ^{13}C NMR, as well as DEPT-135 experiments; chemical shifts are reported in ppm downfield from TMS. The photochemical reactions were performed by using nitrogen-purged solutions in quartz tubes and a multilamp reactor fitted with six 15 W phosphor coated lamps (maximum of emission 310 nm) for the irradiation. Quantum yields were measured at 254 nm for compounds **1a,c** and at 317 nm for compounds **2-3**. 4-Chloroanisole (**1a**), allyltrimethylsilane (ATMS), *N*,*N*-dimethylaniline (**5a**), benzene and furan were commercially available and freshly distilled before use. 4-Chloro-*N*,*N*-dimethylaniline (**2a**) and 4-fluoro-*N*,*N*-dimethylaniline (**3a)** have been synthesized from the corresponding anilines.[S2] 4-*N*,*N*-Dimethylaminobiphenyl (**9a**), 4-(2-propenyl)-*N*,*N*-dimethylaniline (**11a**) and 3-trimethylsilylanisole (**4b**) have been previously synthesized and fully characterized.[S3,S4] 4-Chloro-3-trimethylsilylanisole (**1b**) and 4-chloro-3-trimethylsilyl-*N*,*N*-dimethylaniline (**2b**) have been prepared starting from 3-bromoanisole.[S4] The GC yields of compounds **5a, 9a**, **11a** and **4b** were determined by comparison with authentic samples. (2-(2,2,2-Trifluoroethoxy)-5-(4-*N*,*N*-dimethylaminophenyl)-(*2H*,*5H*)-dihydrofuran (**14a**) has been detected and characterized only by GC-MS analyses due to its low stability during the purification upon silica gel column. 4-(Propen-2-yl)-3-trimethylsilyl-*N*,*N*-dimethylaniline (**11b)** was identified by GC-MS analyses since the corresponding desilylated product (4-propen-2-yl-*N*,*N*-dimethylaniline (**11a)** was isolated upon purification by column chromatography (see table S2).

14a: MS (m/z): 288 (15), 287 (100), 286 (15), 258 (15), 187 (40), 186 (30), 160 (25), 158 (55), 148 (40), 144 (30), 121 (75), 115 (25).

11b: MS (m/z): 233 (100), 218 (15), 160 (65), 158 (45), 73 (35).

Emission measurements have been carried out by means of a LS-55 spectrofluorimeter (Perkin Elmer) whereas fluorescence lifetimes have been measured by using an Edimburgh Single Photon Counter.

Synthesis of 3-bromo-4-chloroanisole. For the preparation of the title compound we modified the procedure reported for the synthesis of 3-methyl-4-chloroanisole.[S5] A solution of 3-bromoanisole (1 mL, 8 mmol), *N*-chlorosuccinimide (1.1 g, 8 mmol) in acetonitrile (60 mL) was refluxed overnight and then the solvent was removed in vacuo. Treatment of the resulting residue with carbon tetrachloride (20 mL) afforded a white solid that was removed by filtration. Elimination of the solvent and distillation in vacuo of the resulting crude oil afforded 680 mg of pure 3-bromo-4-chloroanisole (oil, 38 % yield).[S6]

^{1}H NMR ($CDCl_3$), δ: 7.40-7.30 (d, 1 H, *J* = 8 Hz); 7.20-7.15 (d, 1 H, *J* = 3 Hz), 6.85-6.80 (dd, 1 H, *J* = 8 and 3 Hz), 3.80 (s, 3 H). Calcd for C_7H_6BrClO: C 37.96, H 2.73; Found: C 37.9, H 2.8.

Synthesis of 3-bromo-4-fluoro-*N,N*-dimethylaniline. Following a known procedure,[S7] 2-bromo-1-fluoro-4-nitrobenzene[S8] (9.7 g, 41.8 mmol) was treated with $SnCl_2{\cdot}2H_2O$ (48.5 g, 215 mmol) in ethyl acetate (220 mL), at room temperature for 18 hours. The resulting mixture was treated with 10% aqueous NaOH and extracted with ethyl acetate (3×50 mL). Organic phases were then reunited, washed with water (3×50 mL) and dried over Na_2SO_4. The solvent was removed in vacuo and the resulting raw 3-bromo-4-fluoroaniline (yellow oil, 8.2 g, 100% yield) was methylated with $NaBH_4$ and formaldehyde in THF[S9] to afford 5.8 g of 3-bromo-4-fluoro-*N*,*N*-dimethylaniline (oil, 5.8 g, 61% yield). The product was dried in vacuo and used for the next steps without any further purification.

Synthesis of 3-bromo-4-chloro-*N,N*-dimethylaniline. Following a known procedure[S7] a mixture of di 3-bromo-4-chloro-nitrobenzene[S10] (5.5 g, 23.3 mmol) and $SnCl_2$*$2H_2O$ (25 g, 111 mmol) in ethyl acetate (25 mL) was stirred overnight at room temperature. The resulting mixture was treated with NaOH 10% aq and extracted with ethyl acetate (3×30 mL); the organic phases reunited were then dried over $MgSO_4$, and the solvent evaporated. The resulting raw 3-bromo-4-chloro-aniline (2.70 g, 13.07 56% yield) was treated with $NaBH_4$ and formaldehyde in THF, [S9] to give 2.6 g of 3-bromo-4-chloro-*N,N*-dimethylaniline (84% yield). The product was dried in vacuo and used for the synthesis of **2c** without any further purification.

General procedure for the synthesis of 1c, 2c, 3b,c and 4c. A mixture of the chosen aryl bromide, Magnesium turnings and trimethylchlorosilane (Me_3SiCl) or trimethyltin chloride (Me_3SnCl) in dry THF was refluxed under nitrogen atmosphere. The resulting mixture was filtrated (to remove the unreacted Mg), poured in a saturated NH_4Cl aq. solution and then extracted with ether (3×20 mL). The organic phases were reunited, washed with brine (2×20 mL) and neat water (1×20 mL) and dried over $MgSO_4$. Solvent was removed by evaporation and the resulting residue purified by column chromatography or by distillation in vacuo.

Synthesis of 4-chloro-3-trimethyltin anisole (1c). From 3-bromo-4-chloro-anisole (1.2 g, 5.4 mmol), magnesium (400 mg, 16.5 gatom) and trimethyltin chloride (3 g, 15 mmol) in anhydrous THF (40 mL) refluxed overnight. Purification by column chromatography (eluant: neat cyclohexane with 0.5 % v/v triethylamine) afforded 0.6 g of **1c** (oil, 36% yield).

1c: ^{1}H NMR ($CDCl_3$), δ: 7.30-7.25 (d, 1H, J = 8.5 Hz), 6.95-6.90 (d, 1H, J = 3 Hz), 6.80-6.75 (dd, 1H, J = 8.5 and 3 Hz), 3.80 (s, 3H), 0.35 (s, 9H, J_{Sn-H} = 27 Hz); ^{13}C NMR ($CDCl_3$), δ: 155.7, 143.7, 133.8, 128.7 (CH), 122.4 (CH), 114.9 (CH), 55.3 (CH_3), -8.5 (CH_3); IR (neat) ν/cm^{-1}: 2918, 1588, 1459, 1285, 1234, 1042, 722. MS (m/z): 306 (5), 295 (20), 293 (30), 291 (100), 289 (80), 287 (40), 286 (15), 261 (15), 240 (20), 185 (10), 157 (15), 155 (30), 121 (55). Calcd for $C_{10}H_{15}ClOSn$: C 39.33, H 4.95; Found: C 39.9, H 4.9.

Synthesis of 4-chloro-3-trimethylstannyl-*N,N*-dimethylaniline (2c). From 3-bromo-4-chloro-*N*,*N*-dimethylaniline (1.7 g, 7.2 mmol), Mg (400 mg, 16.5 gatom) and Me_3SnCl (4 g, 20 mmol) in anhydrous THF (50 mL) refluxed overnight. Purification by column chromatography afforded 450 mg of 4-chloro-3-trimethylstannyl-*N*,*N*-dimethylaniline (**2c**, oil, 29 % yield).

2c: ^{1}H NMR ($CDCl_3$), δ: 7.20-7.10 (d, 1H, J = 9 Hz), 6.75-6.70 (d, 1H, J = 3 Hz), 6.65-6.55 (dd, 1 H, J = 3 and 11 Hz), 2.95 (s, 6H), 0.40 (s, 9H, J_{Sn-H} = 27 Hz); ^{13}C NMR ($CDCl_3$), δ: 148.6, 142.5, 130.1, 128.3 (CH), 120.5 (CH), 114.3 (CH), 40.6, -8.5; IR (neat) ν/cm^{-1}: 2981, 2913, 2805, 1578, 1482, 1347, 1173, 796, 770. MS (m/z): 321 (15), 319 (25), 317 (20), 304 (40), 302 (35), 300 (25), 289 (20), 134 (100), 118 (20). Anal. Calcd for $C_{11}H_{18}ClNSn$: C 41.49, H 5.70, N 4.40; Found: C 41.5, H 5.7, N 4.4.

Synthesis of 4-fluoro-3-trimethylsilyl-*N,N*-dimethylaniline (3b). From 3-bromo-4-fluoro-*N*,*N*-dimethylaniline (2.9 g, 13.6 mmol), Mg (330 mg, 13.6 gatom) and Me_3SiCl (3.6 mL, 28.4 mmol) in anhydrous THF (90 mL) refluxed for 24 hours. Purification by bulb-to-bulb distillation gave 4-fluoro-3-trimethylsilyl-*N*,*N*-dimethylaniline (**3b**) as a colorless oil (946 mg, 33% yield).

3b: ^{1}H NMR ($CDCl_3$), δ: 7.00-6.85 (m, 1H), 6.80-6.70 (m, 2H), 2.90 (s, 6H), 0.35 (s, 9H); ^{13}C NMR ($CDCl_3$), δ: 160.3 (d, J = 230 Hz), 147.1, 125.9 (d, J = 30 Hz), 118.9 (d, CH, J = 11 Hz), 115.6 (d, CH, J = 8 Hz), 114.7 (d, CH, J = 27 Hz), 41.5 (CH_3), -1.1 (CH_3); IR (neat) ν/cm^{-1}: 2956, 2897, 2799, 1212, 864, 840. Anal. Calcd for $C_{11}H_{18}FNSi$: C 62.51, H 8.58, N 6.63; Found: C 62.5, H 8.6, N 6.6.

Synthesis of 4-fluoro-3-trimethylstannyl-*N,N*-dimethylaniline (3c). From 3-bromo-4-fluoro-*N*,*N*-dimethylaniline (2.2 g, 9.9 mmol), Mg (470 mg, 19.5 gatom) and Me_3SnCl (3.3 g, 16.5 mmol) in anhydrous THF (45 mL). The mixture was refluxed for 24 hours. Bulb-to-bulb distillation gave **3c** as a colorless oil (670 mg, 36.1% yield).

3c: ^{1}H NMR ($CDCl_3$), δ: 6.95-6.90 (m, 1H), 6.75-6.70 (m, 2H), 2.95 (s, 6H), 0.35 (s, 9H, J_{Sn-H} = 27 Hz); ^{13}C NMR ($CDCl_3$), δ: 160.4 (d, CF, J = 224 Hz), 147.5, 127.1 (d, J = 45 Hz), 120.3 (d, CH, J = 14 Hz), 115.1 (d, CH, J = 8 Hz), 113.9 (d, CH, J = 12 Hz), 41.5 (CH_3), -9.3 (CH_3); IR (neat) ν/cm^{-1}: 2981, 2799, 1577, 1485, 1212, 836, 772. MS (m/z): 303 (30), 301 (25), 299 (20), 288 (50), 286 (40), 284 (25), 258 (25), 134 (100), 118 (25) Anal. Calcd for $C_{11}H_{18}FNSn$: C 43.75, H 6.01, N 4.64; Found: C 43.7, H 6.0, N 4.6.

Synthesis of 3-trimethylstannyl anisole (4c) From 3-bromoanisole (1.27 mL, 10 mmol), magnesium (490 mg, 20 gatom) and trimethyltin chloride (3.3 g, 30 mmol) in dry THF refluxed overnight under nitrogen atmosphere. Purification by vacuum distillation afforded 1.56 g of **4c** (oil, 58 % yield).

4c:[S11] ^{1}H NMR ($CDCl_3$), δ: 7.35-7.30 (m, 1H); 7.15-7.10 (m, 2H), 6.80-6.90 (m, 1H), 3.80 (s, 3H), 0.30 (s, 9H, J_{Sn-H} = 27 Hz); ^{13}C NMR ($CDCl_3$), δ: 159.0, 143.7, 128.9 (CH), 127.9 (CH), 121.3 (CH), 113.3 (CH), 55.0 (CH_3), -9.6 (CH_3); IR (neat) ν/cm^{-1}: 2912, 2834, 1579, 1567, 1459, 1285, 1235, 1098, 1042, 878. MS (m/z): 261 (15), 257 (100), 255 (80), 253 (50), 227 (30), 225 (20), 223 (15), 135 (10). Calcd for $C_{10}H_{16}OSn$: C 44.33, H 5.95; Found: C 44.4, H 5.9.

General procedure for the irradiation of halides 1-3. A solution of the chosen halide (**1-3**, 0.05M), in 2,2,2-trifluoroethanol or MeCN-Water 5:1 in the presence of cesium carbonate (Cs_2CO_3, 0.025 M) and the chosen nucleophile (allyltrimethylsilane (ATMS, 0.5 M), benzene (1.0 M) or furan (1.0 M)) was poured in a quartz tube and purged for 10 min with Nitrogen. When MeCN-Water 5:1 has been used as the solvent no Cs_2CO_3 was required. Irradiations were carried out by means of a multilamp reactor (Rayonet) equipped with twelve 15W phosphor coated lamps (λ_{em} = 310 nm). The progress of the reaction was followed by GC analyses. In the case of anilines **3b,c** consumption was determined through HPLC analysis (AQUASIL C-18 (250×4.6 mm) column, eluant: MeCN/water mixtures) with UV detection at λ = 270 nm. Work-up of the photolytes involved concentration in vacuo and chromatographic separation using Millipore (60 Å, 35-70 μm) silica gel.

Irradiation of 1b in TFE in the presence of furan. Halide **1b** (320 mg, 1.5 mmol, 0.05 M), cesium carbonate (244 mg, 0.75 mmol, 0.025 M) and furan (2.2 mL, 30 mmol, 1 M) were dissolved in TFE (30 mL) and irradiated for 8h. Purification by column chromatography (eluant: neat cyclohexane) afforded 15 mg of (2-(2,2,2-trifluoroethoxy)-5-methoxyphenyl)trimethylsilane **(6b)** along with a mixture of **6b** (123 mg, 33% overall**)** and of (2-(2,2,2-trifluoroethoxy)-5-(4-methoxy-

2-trimethylsilylphenyl)-(*2H,5H*)-dihydrofuran **12b** (104 mg, 20%**)** present as a mixture of diasteroisomers in a 3:2 ratio.

6b: ^{1}H NMR ($CDCl_3$), δ: 7.00-6.95 (d, 1H, *J* = 3 Hz), 6.85-6.80 (dd, 1H, *J* = 3 and 8 Hz), 6.75-6.70 (d, 1H, *J* = 8 Hz), 4.30-4.20 (q, 2H, *J* = 8 Hz), 3.80 (s, 3 H), 0.30 (s, 9 H); ^{13}C NMR ($CDCl_3$), δ: 155.5, 154.3, 130.1, 130.0 (CF_3, q, *J* = 275 Hz), 121.6 (CH), 114.2 (CH), 110.5 (CH), 65.5 (CH_2, q, *J* = 35 Hz), 55.6 (CH_3), -1.3 (CH_3); IR (neat) ν/cm^{-1}: 2955, 1482, 1269, 1216, 1165, 839. Anal. Calcd for $C_{12}H_{17}F_3O_2Si$: C 51.78, H 6.16; Found: C 51.8, H 6.1.

12b: ^{1}H NMR (from the mixture, $CDCl_3$), δ: 7.45-7.40 (d, 1H minor, *J* = 8 Hz), 7.20-7.15 (d, 1H, *J* = 8 Hz, major); 7.10-7.05 (d, 1H major , *J* = 3 Hz), 7.05-7.00 (d, 1H minor, *J* = 3 Hz), 6.95-6.90 (m, 1H + 1H), 6.35-6.30 (dt, 1H, *J* = 1 and 6 Hz, major), 6.25-6.20 (dt, 1H, *J* = 1 and 6 Hz minor), 6.15-6.10 (m, 1H + 1H), 6.05-6.00 (m, 1H, major), 6.00 (m, 1H, minor), 5.95-5.90 (m, 1H + 1H), 3.90-3.85 (m, 2H minor), 4.05-4.00 (m, 2H major), 3.80 (s, 3H + 3H), 0.35 (s, 9H + 9H); ^{13}C NMR (from the mixture, $CDCl_3$), δ: 158.8 (major), 158.5 (minor), 140.7 (major), 139.6 (minor), 137.3 (CH major), 136.6 (CH minor), 130.1 (major), 129.6 (CH minor), 128.8 (minor), 128.1 (CH major), 120.1 (CH major), 119.8 (CH, minor), 119.0 (q, CF_3+CF_3, *J* = 235 Hz), 114.4 (CH +CH), 108.7 (CH minor), 108.5 (CH major), 87.1 (CH minor), 86.0 (CH major), 64.3 (q, CH_2+CH_2, *J* = 35 Hz), 55.1 (CH_3+CH_3), 0.4 (CH_3+CH_3). IR (of the mixture) ν/cm^{-1}: 2954, 1482, 1346, 1228, 837

Irradiation of 1b in acetonitrile/water 5/1 mixture in the presence of furan. Halide **1b** (320 mg, 1.5 mmol, 0.05 M), and furan (2.2 mL, 30 mmol, 1 M) were dissolved in acetonitrile/water 5/1 mixture (30 mL) and irradiated for 18h causing a 80% consumption of **1b**. Purification by column chromatography (eluant: neat cyclohexane) afforded 4-methoxy-2-trimethylsilylphenyl furan (**13b**, 106 mg, oil, 36% yield based on the consumption of **1b**).

13b: ^{1}H NMR ($CDCl_3$), δ: 7.80-7.75 (m, 1H), 7.45-7.40 (d, 1H, *J* = 8.5 Hz), 7.20-7.15 (d, 1H, *J* = 3Hz), 6.90-6.85 (dd, 1H, *J* = 8.5 and 3 Hz), 6.50-6.45 (m, 1H), 6.35-6.40 (dd, 1H, *J* = 4 and 1 Hz), 3.85 (s, 3H), 0.15 (s, 9H). ^{13}C NMR ($CDCl_3$), δ: 158.5, 156.0, 142.5, 140.7 (CH), 140.5, 129.9 (CH), 121.1 (CH), 113.2 (CH), 111.5 (CH), 106.1 (CH), 55.1 (CH_3), 0.0 (CH_3); IR (neat) ν/cm^{-1} : 2960, 2851, 1987, 1286, 1170, 830; Anal. Calcd for $C_{14}H_{18}O_2Si$: C 68.25, 7.36; Found: C 68.2, H 7.4.

Irradiation of 1c in TFE in the presence of benzene. Anisole **1c** (458 mg, 0.05 M, 1.5 mmol), cesium carbonate (244 mg, 0.75 mmol, 0.025M) and benzene (2.7 mL, 30 mmol, 1.0 M) were dissolved in TFE (30 mL) and irradiated for 6h. Purification by column chromatography (eluant: neat cyclohexane) afforded 138 mg of 2-(2,2,2-trifluoroethoxy)-5-methoxyphenyl trimethylstannane (**6c**, oil, 25% yield) and 78 mg of 4-methoxy-2-trimethylstannyl-biphenyl (**8c**, oil, 15% yield).

6c ^{1}H NMR ($CDCl_3$), δ: 7.00-6.95 (d, 1H, J = 3 Hz), 6.85-.6.80 (dd, 1H, *J* = 3 and 9 Hz), 6.75-6.70 (d, 1H, J = 9 Hz), 4.35-4.25 (q, 2H, J = 9 Hz), 3.80 (s, 3H), 0.30 (s, 9H, J_{Sn-H} = 27 Hz). ^{13}C NMR ($CDCl_3$), δ: -9.4 (CH3), 55.6 (CH_3), 66.0 (q, CH_2, J = 35 Hz), 110.0 (CH), 113.7 (CH), 122.7 (CH), 122.8, 130.0 (q, CF_3, *J* = 250 Hz), 154.7, 155.4. IR (neat) ν/cm^{-1}: 2938, 1508, 1476, 1214, 1163, 975. MS (m/z): 370 (10), 359 (15), 355 (100), 353 (80), 351 (40), 335 (30), 272 (15), 257 (15). Anal. Calcd for $C_{12}H_{17}F_3O_2Sn$: C 39.06, H 4.64; Found: C 39.1, H 4.7

8c: ^{1}H NMR ($CDCl_3$), δ: 7.50-7.35 (m, 5H), 7.30-7.25 (m, 1H), 7.15-7.10 (d, 1H *J* = 3Hz), 6.95-6.90 (dd, 1H, *J* = 8 and 3 Hz), 3.80 (s, 3H), 0.05 (s, 9H, J_{Sn-H} = 27 Hz). ^{13}C NMR ($CDCl_3$), δ: 158.0, 142.8, 129.3 (CH), 128.9 (CH), 128.6, 128.1 (CH), 126.7 (CH), 121.9 (CH), 114.1, 113.0 (CH), 55.1 (CH_3), -8.0 (CH_3); IR (neat) ν/cm^{-1}: 3940, 1563, 1208, 1150, 1045, 970. MS (m/z): 348 (2), 337 (20), 333 (100), 331 (70), 329 (50), 303 (45), 301 (40), 299 (25), 259 (10), 256 (10), 168 (5), 165 (10), 152 (10), 132 (10). Anal. Calcd for $C_{16}H_{20}OSn$: C 55.37, H 5.81; Found: C 55.4, H 5.8

Irradiation of 1c in TFE in the presence of ATMS. A solution of the anisole **1c** (305 mg, 0.05 M, 1.0 mmol), cesium carbonate (165 mg, 0.5 mmol, 0.025M) and ATMS (1.6 mL, 10 mmol, 0.5 M) in TFE (20 mL) was irradiated for 6h. The photolyzed solution was then evaporated. Purification by column chromatography (eluant neat cyclohexane + 0.5% triethylamine, stationary phase: silica gel or neutral Al_2O_3) caused the decomposition of the photoproduct. GC-analysis of the photolyzed solution evidenced the presence of 4-(2-propenyl)-3-trimethyltin anisole (**10c**, (m/z) : 312 (5), 297 (100), 295 (70), 293 (45), 151 (15), 147 (65), 91 (15)). The presence of **10c** has been further confirmed by ^{1}H NMR analysis of the crude residue (previously filtrated to remove cesium carbonate).

10c: ^{1}H NMR ($CDCl_3$), δ: 7.15-7.05 (m, 1H), 7.00-6.95 (m, 1H), 6.80-6.60 (m, 1H), 5.90-6.00 (m, 1H), 4.95-5.10 (m, 2H), 3.20-3.25 (d, 2H, *J* = 5 Hz), 0.35 (s, 9H).

Irradiation of 1c in TFE in the presence of furan. Halide **1c** (458 mg, 1.5 mmol, 0.05 M), cesium carbonate (244 mg, 0.75 mmol, 0.025M), and furan (2.2 mL, 30 mmol, 1 M) were dissolved in TFE (30 mL) and irradiated for 8h. Purification by column chromatography (eluant: neat cyclohexane) afforded 2-(2,2,2-trifluoroethoxy)-5-(4-methoxy-2-trimethylstannylphenyl)-(*2H,5H*)-dihydrofuran **(12c**, 268 mg, 41% yield) as a mixture of diasteroisomers in a roughly 1:1 ratio.

12c: ^{1}H NMR (of the mixture, $CDCl_3$), δ: 7.25-7.20 (d, 1H minor, *J* = 8 Hz), 7.15-7.10 (d, 1H major, *J* = 8 Hz), 6.95-6.85 (m, 1H + 1H), 6.40-6.35 (m, 1H major), 6.35-6.30 (m, 1H minor), 6.25-6.20 (m, 1H major), 6.15 (m, 1H minor), 6.10-5.90 (m, 2H + 2H), 4.10-4.00 (m, 2H, major), 4.00-3.85 (m, 2H minor), 3.80 (s, 3H + 3H), 0.40 (s, 9H + 9H, J_{Sn-H} = 27 Hz); ^{13}C NMR ($CDCl_3$ from the mixture), δ: 158.8 (major + minor), 143.9 (major + minor), 136.9 (CH major), 136.2 (CH minor), 128.5 (CH major), 128.0 (CH minor), 125.9 (CH major), 126.0 (q, CF_3 + CF_3, *J* = 235 Hz), 125.0

(CH minor), 121.7 (CH+CH), 114.0 (CH minor), 113.8 (CH major), 108.5 (CH minor), 108.4 (CH major), 88.7 (CH major) 88.0 (CH minor), 64.6 (q, $CH_2 + CH_2$, J = 35 Hz), 55.2 (CH_3, minor), 55.1 (CH_3, major), -8.0 (CH_3 + CH_3). IR of the mixture (neat) ν/cm^{-1}: 2936, 1590, 1280, 1162, 1052, 824; Anal. Calcd for $C_{16}H_{21}F_3O_3Sn$: C 43.97, H 4.84; Found: C 44.0, H 4.8.

Irradiation of 3c in MeCN-Water 5-1 in the presence of ATMS. Aniline **3c** (453 mg, 1.5 mmol) and ATMS (2.4 mL, 15 mmol, 0.5 M) were dissolved in 30 mL of a MeCN/water mixture 5/1, and irradiated for 2h. The photolyzed solution was then evaporated and purification by column chromatography afforded 190 mg of 3-trimethylstannyl-*N,N*-dimethylaniline (**5c**, oil, 50 % yield) and a mixture of **5c** (23 mg) and of 4-(2-propenyl)-3-trimethylstannyl-*N,N*-dimethylaniline (**11c**, 34 mg, 7 % yield).

5c ^{1}H NMR ($CDCl_3$) δ: 7.30-7.25 (m, 1H), 6.85-6.75 (m, 2H), 6.75-6.70 (m, 1H), 2.95 (s, 6H), 0.20 (s, 9H, J_{Sn-H} = 27 Hz); ^{13}C NMR ($CDCl_3$): 150.1, 142.6, 128.5 (CH), 124.0 (CH), 119.6 (CH), 112.8 (CH), 40.5 (CH_3), -9.7 (CH_3) IR: (neat) ν/cm^{-1}: 2917, 1502, 1489, 1345, 988, 770; MS (m/z): 285 (40), 270 (95), 240 (70), 134 (45); Anal. Calcd for $C_{11}H_{19}NSn$: C 46.52, H 6.74, N 4.93; Found: C 46.5, H 6.7, N 4.9.

11c ^{1}H NMR (from the mixture, $CDCl_3$) δ: 7.15-7.05 (m, 1H), 6.90-6.80 (m, 2H), 6.05-5.95 (m, 1H), 5.10-5.05 (m, 2H), 3.35-3.30 (d, 2H, J = 6 Hz), 3.00 (s, 6H), 0.30 (s, 9H). ^{13}C NMR (from the mixture, $CDCl_3$) δ: 145.0, 142.4, 138.4 (CH), 138.2, 129.4 (CH_2), 120.4 (CH), 115.2 (CH), 114.9 (CH), 41.6 (CH_2), 40.8 (CH_3), -8.2 (CH_3); IR of the mixture: (neat) ν/cm^{-1}: 2977, 1582, 1490, 1345, 988, 770; MS (m/z): 329 (10), 325 (25), 321 (15), 325 (25), 310 (50), 308 (40), 306 (30), 160 (100), 158 (70), 145 (40).

Irradiation of 4-chloro-3-trimethylstannyl-*N,N*-dimethylaniline (2c) in TFE. A solution of **2c** (239 mg, 1.5 mmol, 0.05 M) and cesium carbonate (244 mg, 0.75 mmol, 0.025 M) in TFE (15 mL) was irradiated for 3 hours. Purification by column chromatography (eluant: neat hexane) afforded a mixture of *N,N*-dimethylaniline (**5a**, 16 mg, 18% yield) and 3-trimethylstannyl-*N,N*-dimethylaniline (**5c**, 32 mg, 15% yield) and a mixture of 4-(2,2,2-trifluoethoxy)-*N,N*-dimethylaniline (**17a**, 25 mg, 15% yield) and 3-(2,2,2-trifluoethoxy)-*N,N*-dimethylaniline (**17'a**, 8 mg, 5% yield). GC/MS analysis has likewise revealed the presence of 3-trimethylstannyl-4-(2,2,2-trifluoroethoxy)-*N,N*-dimethylaniline (**17c**, 4 % yield).

17a: ^{1}H NMR (from the mixture, $CDCl_3$), δ: 6.95-6.75 (AA'BB', 4H), 4.30-4.20 (q, 2 H, J = 8 Hz), 2.95 (s, 6 H); ^{13}C NMR (from the mixture, $CDCl_3$), δ: 149.5, 146.9, 125 (q, CF_3, J = 275 Hz), 116.4 (CH), 114.1 (CH), 67 (q, CH_2, J = 34.5 Hz), 41.2 (CH_3). MS (m/z): 220 (5), 219 (65), 218 (5), 136 (100), 108 (10), 74 (5).

17'a: ^{1}H NMR (from the mixture, $CDCl_3$), δ: 7.25-7.15 (t, 1 H, *J* = 8 Hz), 6.50-6.45 (dd, 1 H, *J* = 8 and 2 Hz), 6.35-6.30 (t, 1 H, *J* = 2 Hz), 6.25-6.20 (d, 1 H, *J* = 8 and 2 Hz); 4.40-4.30 (q, 2 H, *J* = 8 Hz), 3.00 (s, 6H); ^{13}C NMR (from the mixture, $CDCl_3$), δ: 158.5, 151.9, 129.8 (CH), 125 (q, CF_3, *J* = 275 Hz), 107.0 (CH), 101.4 (CH), 99.9 (CH), 65 (CH_2, *J* = 35 Hz), 40.3 (CH_3). MS (m/z): 220 (10), 219 (80), 218 (100), 156 (20), 155 (35), 154 (45), 135 (30).

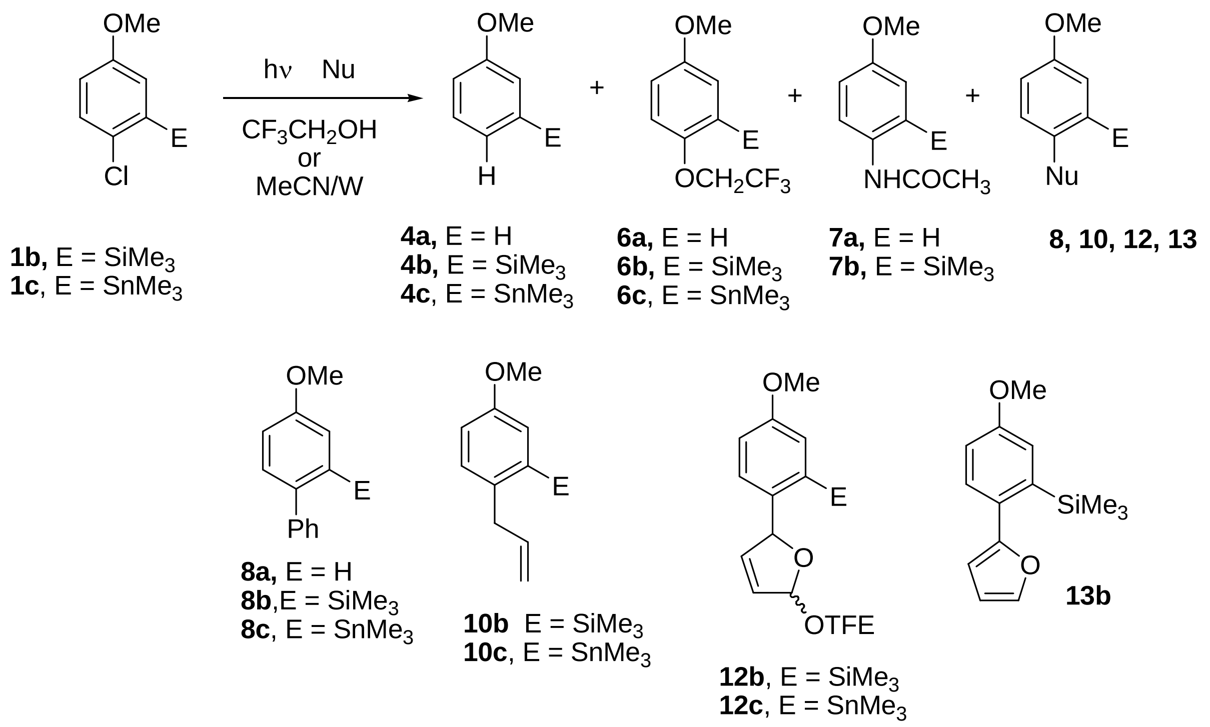
IR of the mixture (neat) ν/cm^{-1}: 2920, 1614, 1514, 1281, 1227, 1157, 972, 817.

17c: MS (m/z): 381 (60), 379 (40), 368 (80), 366 (50), 364 (30), 304 (45), 285 (100), 283 (50), 281 (40), 255 (50), 253 (40), 251 (30), 174 (25), 150 (30), 135 (35).

2. Product distribution in the irradiation of compounds 1-3

Table S1. Product distribution in the irradiation of chloroanisoles 1b,c in neat solvent and in the presence of π bond nucleophiles.

Nu = ATMS, Benzene, Furan



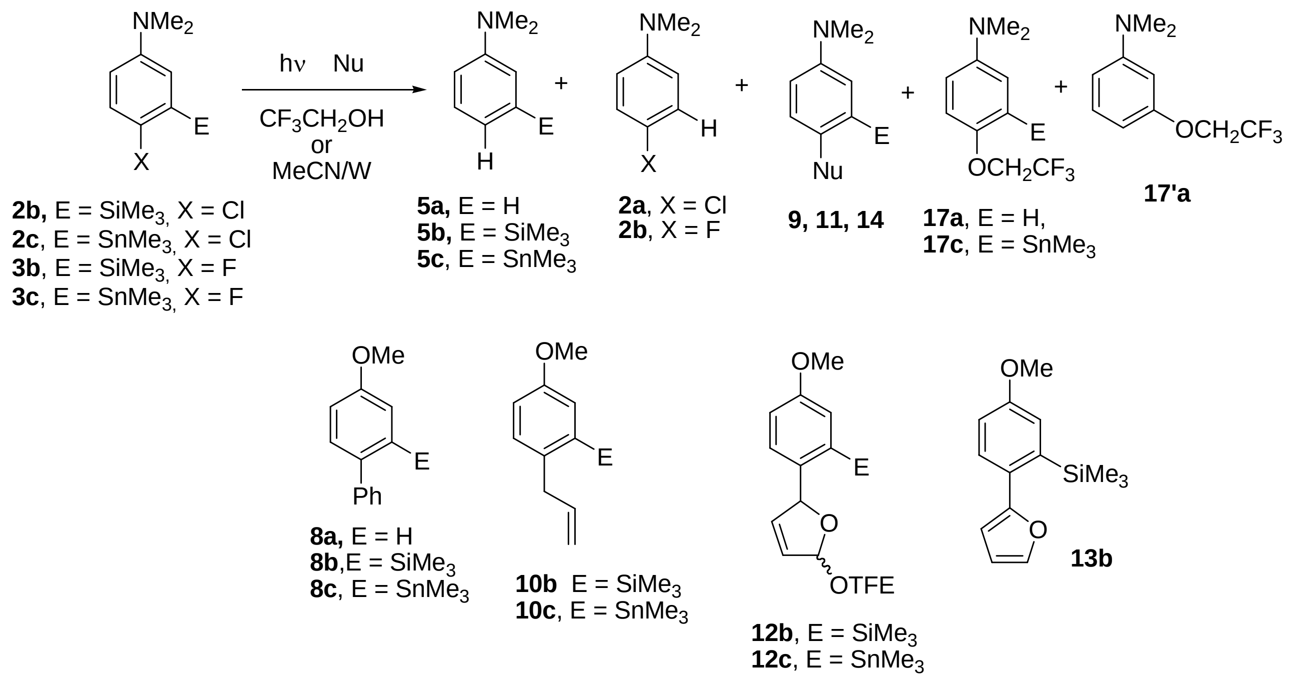
Aryl stannane	Solvent	Nu	t_{irr}, h (conversion, %)	Products (yield %)[a]		
				R_D	S_L	A_R
1b	TFE [b,c]	None	7 (100)	**4b** (23) **4a** (18)	**6a** (44)	-
1b	TFE [b,c]	C_6H_6 1M	7 (100)	**4a** (3)	**6a** (25)	**9a** (60)
1b	TFE [b,c]	ATMS 0.5M	12 (100)	**4b** (22)	**6a**(53)	**10b** (11) **10a** (8)
1b	TFE[b]	Furan 1 M	6 (100)	**4b** (3)	**6b** (33)	**12b** (20)
1b	W[c]	None	23 (90)	**4b** (23)	**7b** (74)	-
1b	W[c]	C_6H_6 1M	20 (86)	**4b** (14)	**7b** (65)	-
1b	W	ATMS 0.5M	25 (87)	**4b** (22)	**7b** (36)	**10b** (31)

1b	W	Furan 1M	24 (80)	**4b** (11)	**7b** (34)	**13b** (36)
1c	TFE [b]	None	5 (100)	**4c** (43) **4a** (9)	**6c** (46)	
1c	TFE [b]	C_6H_6 1M	5 (95)	**4c** (11)	**6c** (23)	**8c** (25)
1c	TFE [b]	ATMS 0.5M	5 (100)	**4c** (20) **4a** (3)	**6c** (23)	**10c** (25)[d]
1c	TFE [b]	Furan 1 M	6 (100)	**4c** (7)	**6c** (13)	**12c** (41)
1c	W	None	1 (14)	**4c** (35)	**7a** (traces)	
1c	W	None	4 (78)	**4c** (15) **4a** (10)	**7a** (26)	-
1c	W	None	8 (100)	**4c** (8) **4a** (16)	**7a** (31)	-
1c	W	C_6H_6 1M	8 (76)	**4c** (18) **4a** (15)	**7a** (15)	-
1c	W	ATMS 0.5M	8 (68)	**4c** (18) **4a** (6)	**7a** (23)	-
1c	W	Furan 1 M	8 (75)	**4c** (12) **4a** (3)	**7a** (19)	-

[a] Yields were based on the consumed aryl ester and determined by GC; TFE = 2,2,2-trifluoroethanol, W = MeCN/water 5.1. [b] Cesium carbonate (0.025 M) added. [c] See ref S4. [d] Compound not isolated but the structure was assigned according to GC-MS analyses and by NMR measurements performed on the raw photolysate.

Table S2. Product distribution in the irradiation of anilines 2-3 in neat solvent and in the presence of π bond nucleophiles.

Nu = ATMS, Benzene, Furan



Aryl fluoride	Solvent	Nu	t_{irr}, h (conversion, %)	Products (yield %)[a]			
				RD	DM	AR	SL + BE
2b	TFE [b,c]	None	3 (90)	**5b** (44) **5a** (11)	-	-	-
2b	TFE [b,c]	C_6H_6 1M	3 (100)	**5b** (16) **5a** (32)	-	**9a** (7)	-
2b	TFE [b,c]	ATMS 0.5M	6(100)	**5a** (10)	-	**11a** (62)	-
2b	W	None	2 (100)	**5b** (60)	-	-	-
2b	W	C_6H_6 1M	2 (100)	**5b** (86)	-	-	-
2b	W	ATMS 0.5M	2 (100)	**5b** (57)	-	**11a** (10)	-
2b	W	Furan 1M	2 (79)	**5b** (36)			
2c	TFE [b]	None	1 (100)	**5b** (15), **5a** (18)	-	-	**17a** (15), **17'a** (5), **17c** (4)[d]

2c	TFE [b]	C_6H_6 1M	1 (88)	**5b,** (18) **5a** (10)	-	**9a** (8)	**17a** (8), **17'a** (5), **17c** (4)[d]
2c	TFE [b]	ATMS 0.5M	1 (89)	**5c** (4) **5a** (4)	-	**11c** (28), **11a** (34	**17a** (6), **17'a** (3)
2c	TFE [b]	Furan 1M	1 (81)	**5c** (5) **5a** (3)	-	**14a** (6)	**17a** (7), **17'a** (5)
2c	W	None	1 (63)	**5c** (62)	-	-	-
2c	W	C_6H_6 1M	1 (78)	**5c** (34)	-	-	-
2c	W	ATMS 0.5M	1 (71)	**5c** (22)	-	**11c** (42)	-
2c	W	Furan 1M	1 (63)	**5c** (23)	-	-	-
3b	TFE [b]	None	0.25 (28)	**5b** (13) **5a** (2.5)	**3a** (7)	-	-
3b	TFE [b]	None	1 (59)	**5b** (14) **5a** (10)	**3a** (6)	-	-
3b	TFE [b]	None	2 (76)	**5b** (16) **5a** (15)	**3a** (7)	-	-
3b	TFE [b]	None	4 (100)	**5a** (24)	**3a** (6)	-	-
3b	TFE [b]	None	20 (100)	**5a** (30)	-	-	-
3b	TFE [b]	C_6H_6 1M	1 (67)	**5b** (20) **5a** (16)	**3a** (17)	**9a** (8)	-
3b	TFE [b]	C_6H_6 1M	4 (100)	**5b** (15) **5a** (9)	**3a** (13)	**9a** (18)	-
3b	TFE [b]	C_6H_6 1M	20 (100)	**5a** (10)		**9a** (16)	-
3b	TFE [b]	ATMS 0.5M	1 (49)	**5b** (8), **5a** (7)	**3a** (7)	**11a** (21)	-
3b	TFE [b]	ATMS 0.5M	2 (73)	**5b** (11) **5a** (12)	**3a** (8)	**11a** (40)	-
3b	TFE [b]	ATMS 0.5M	20 (100)	**5a** (11)		**11a** (45)	-
3b	TFE [b]	Furan 1M	16 (71)	**5a** (25)	**3a** (15)	-	-
3b	W	None	16 (95)	**5b** (49)	**3a** (tr.)	-	-
3b	W	ATMS 0.5M	16 (100)	**5b** (63)	**3a** (tr.)	-	-
3b	W	C_6H_6 1M	16 (100)	**5b** (33)	-	-	-
3b	W	Furan 1M	16 (100)	**5b** (62) **5a** (tr.)	**3a** (tr.)	-	-

3c	TFE [b]	None	0.15 (32)	-	**3a** (25)	-	-
3c	TFE [b]	None	0.3 (50)	**5a** (2)	**3a** (37)	-	-
3c	TFE [b]	None	0.5 (66)	**5a** (12)	**3a** (50)	-	-
3c	TFE [b]	None	1 (85)	**5a** (22)	**3a** (47)	-	-
3c	TFE [b]	C_6H_6 1M	4 (100)	**5a** (4)	**3a** (15)	**9a** (31)	-
3c	TFE [b]	ATMS 0.5M	4 (90)	**5a** (2)	**3a** (7)	**11b** (80)	-
3c	TFE [b]	Furan 1M	4 (100)	**5a** (4)	**3a** (11)	**14a** (10) [d]	-
3c	W	-	0.5 (47)	**5c** (33)	-	-	-
3c	W	-	2 (100)	**5c** (44) **5a** (2)	-	-	-
3c	W	C_6H_6 1M	2 (100)	**5c** (46) **5a** (1)	-	-	-
3c	W	C_6H_6 1M	16 (100)	**5c** (5) **5a** (18)	-	-	-
3c	W	ATMS 05	2 (100)	**5c** (50)	-	**11c** (7)	-
3c	W	Furan 1M	2 (100)	**5c** (46)	-	-	-

[a] Yields were based on the consumed aryl fluoride and chloride determined by GC; TFE = 2,2,2-trifluoroethanol, W = MeCN/water 5.1. [b] Cesium carbonate (0.025 M) added. [c] See ref. S4. [d] Compound not isolated but the structure was assigned according to GC-MS analyses

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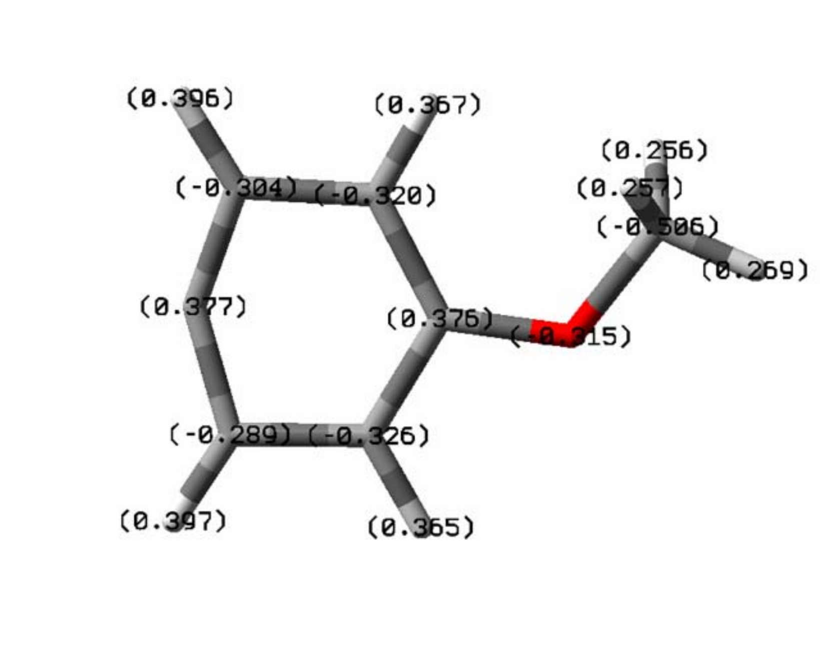
3. Calculated geometries and charge distribution for cations 4a,c$^+$ and 5a,c$^+$.

Figure S1. Calculated geometries and charge distribution for methoxyphenyl cations **4a**$^+$

^{1}**4a**$^+$



^{3}**4a**$^+$

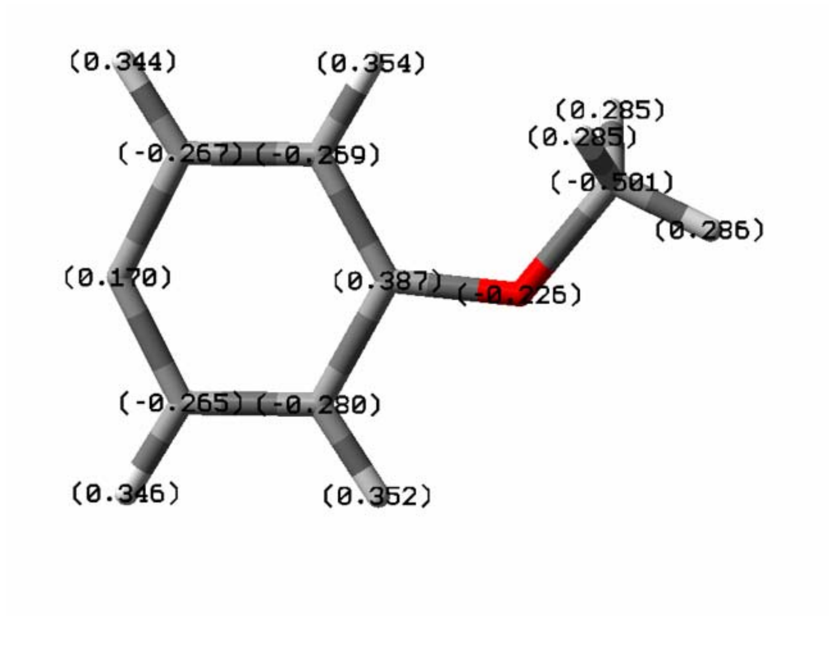
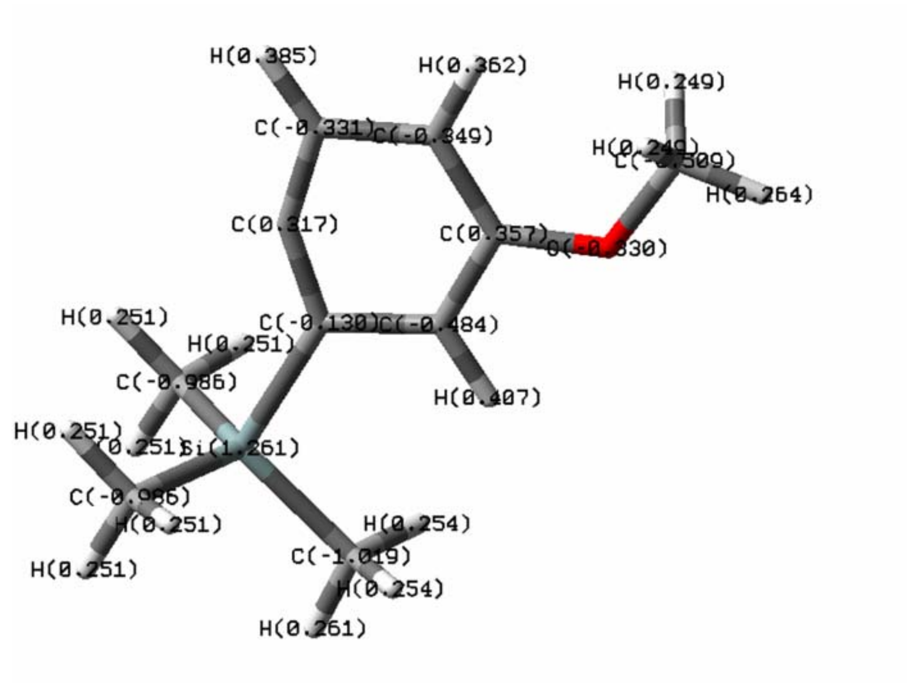


Figure S2. Calculated geometries and charge distribution for methoxyphenyl cations **4b**$^+$

^{1}**4b**$^+$



^{3}**4b**$^+$

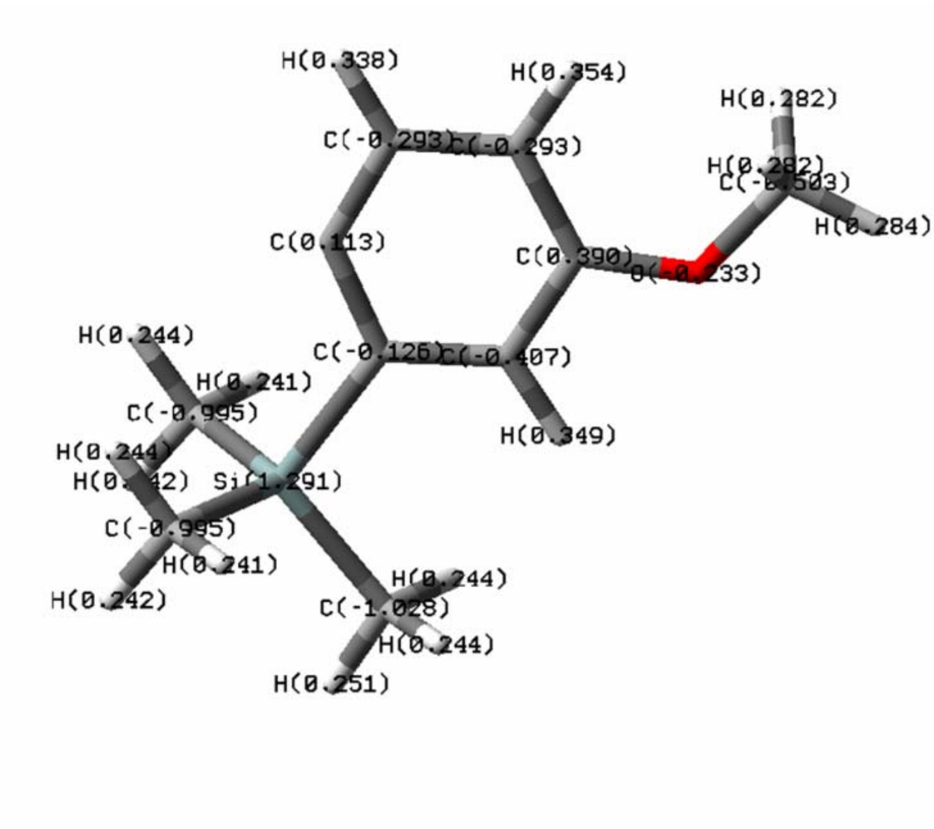
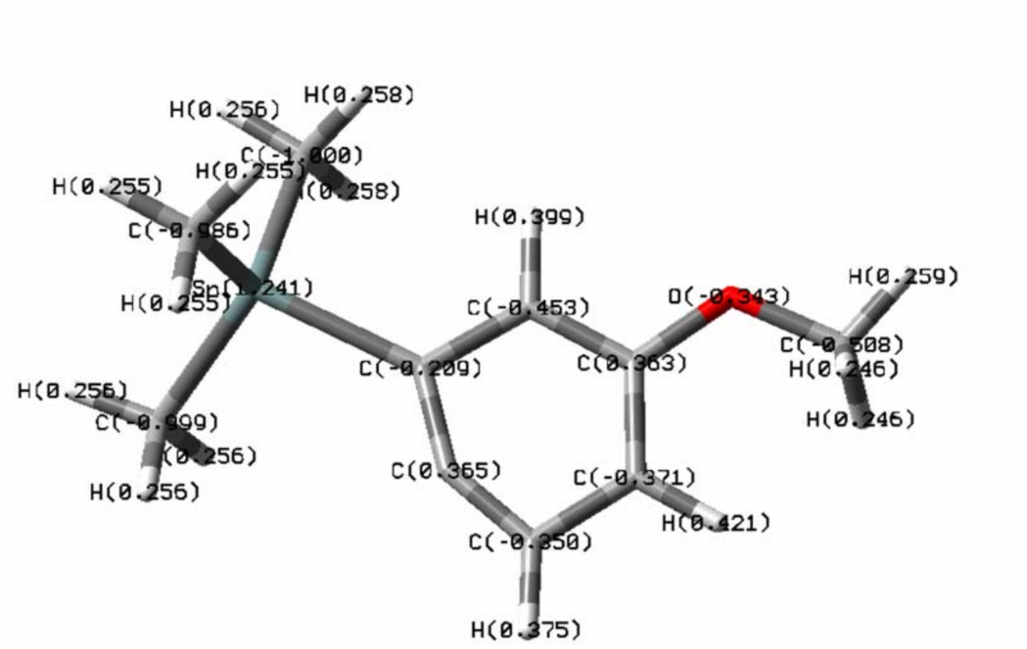


Figure S3. Calculated geometries and charge distribution for methoxyphenyl cations **4c**$^+$

^{1}**4c**$^+$



^{3}**4c**$^+$

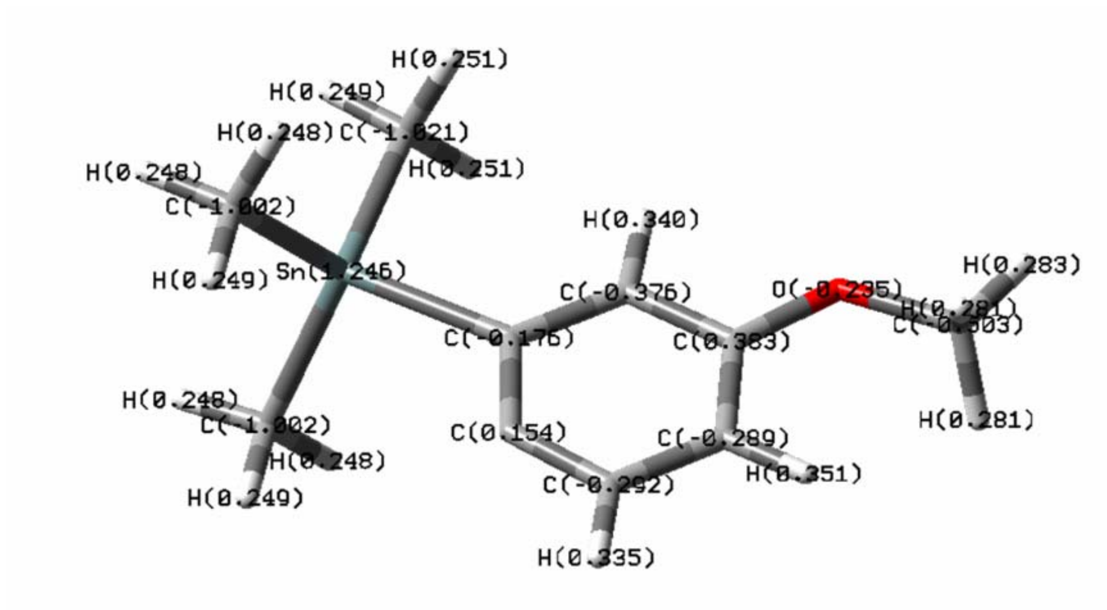
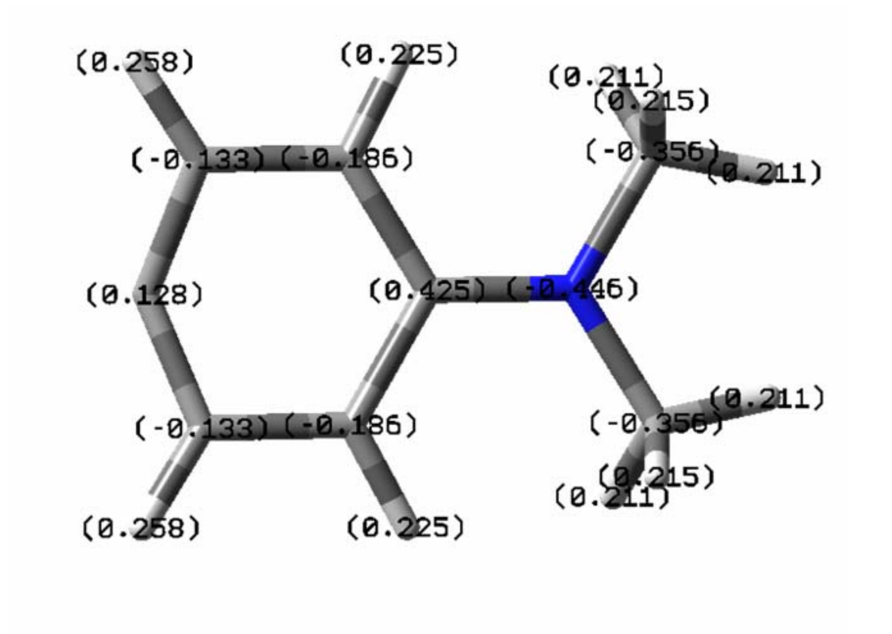


Figure S4. Calculated geometries and charge distribution for *N*,*N*-dimethylaminophenyl cations **5a**$^+$

^{1}**5a**$^+$



^{3}**5a**$^+$

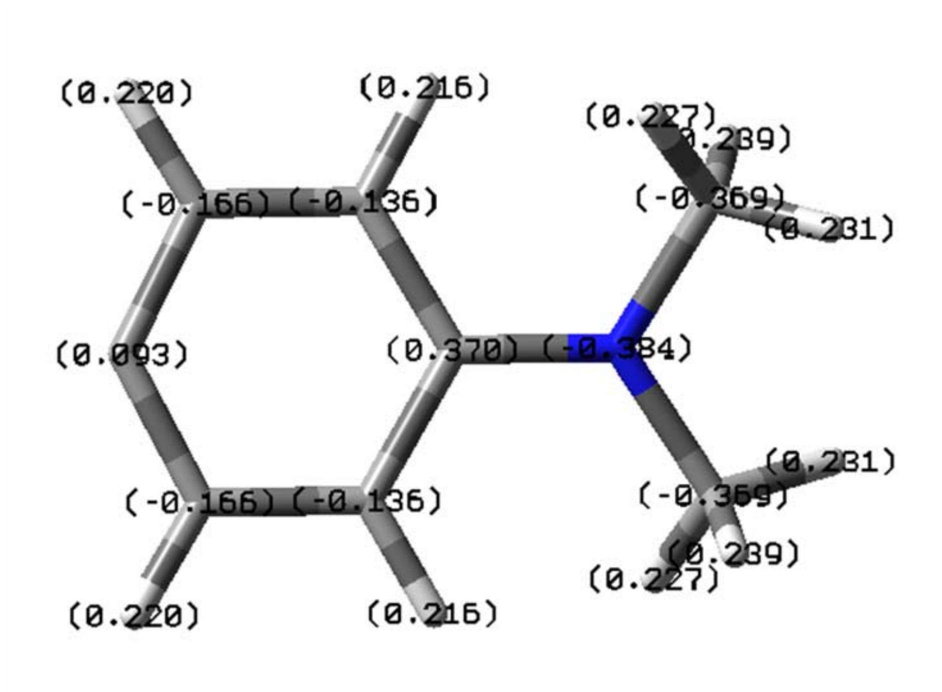
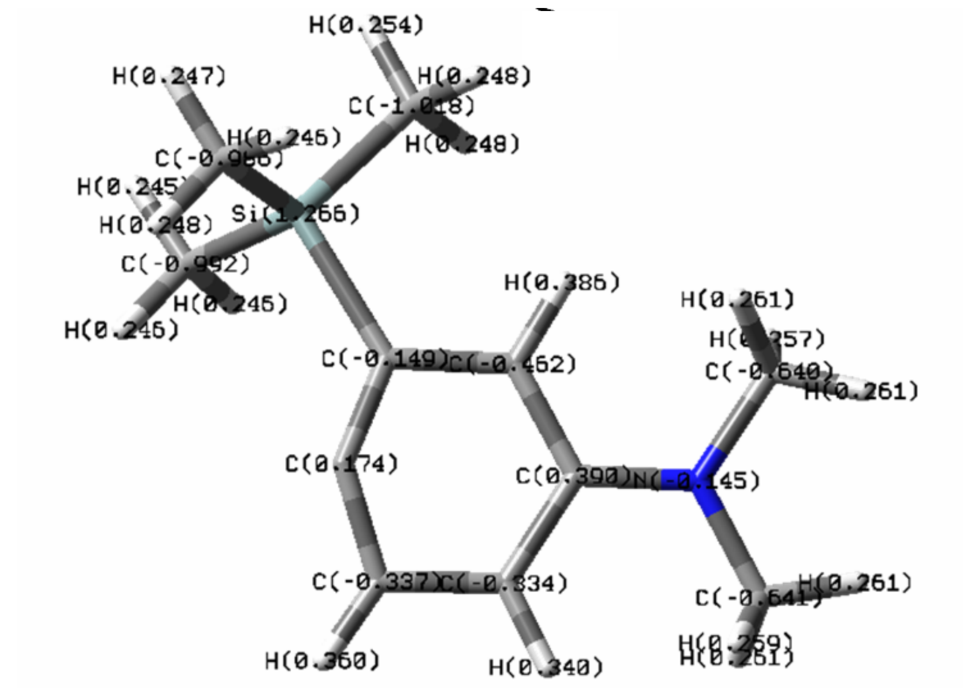


Figure S5. Calculated geometries and charge distribution for *N*,*N*-dimethylaminophenyl cations **5b**$^+$

^{1}**5b**$^+$



^{3}**5b**$^+$

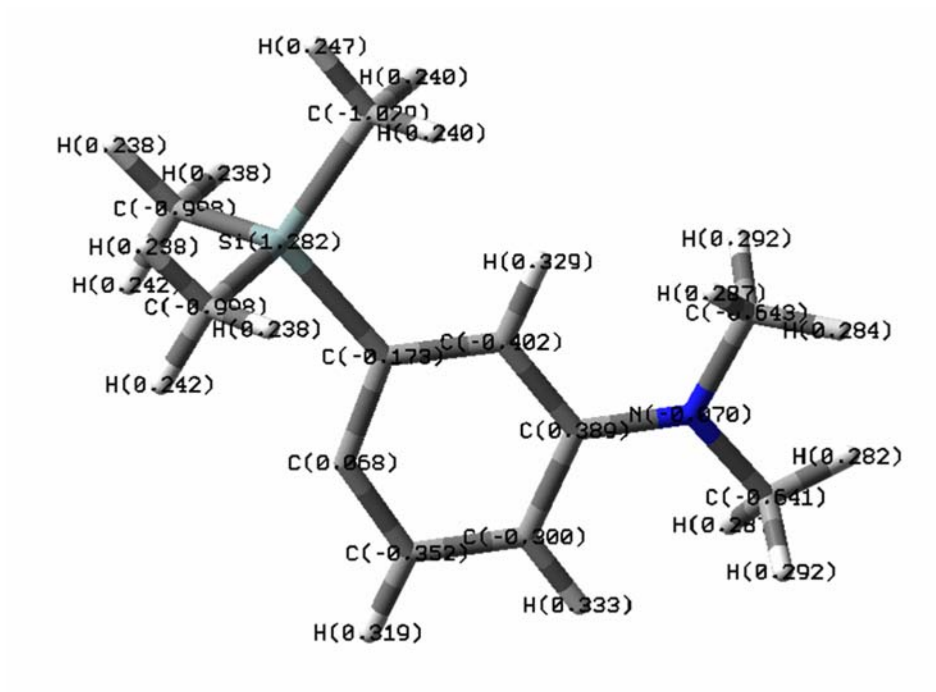
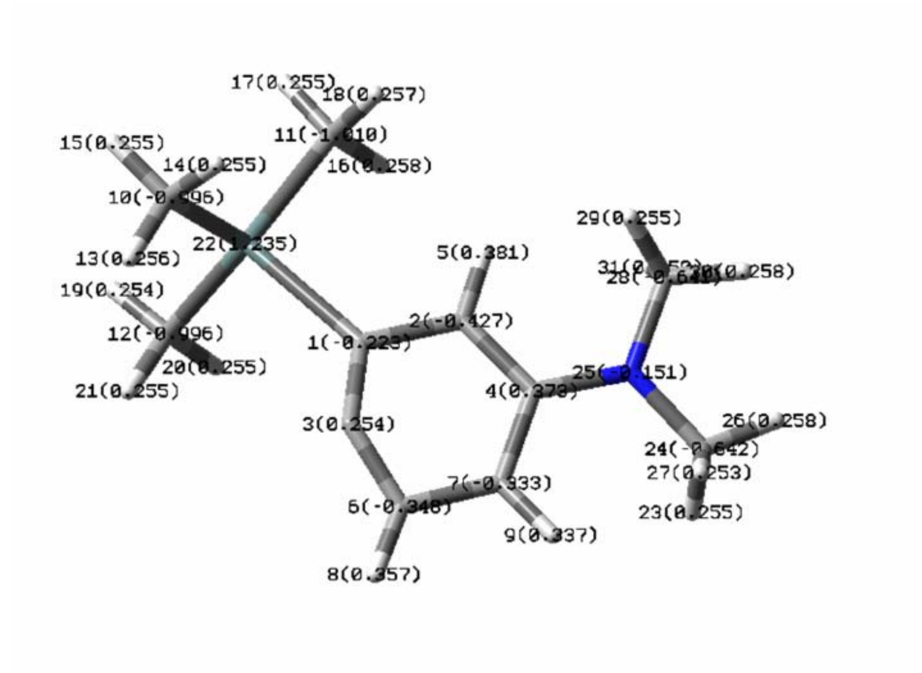
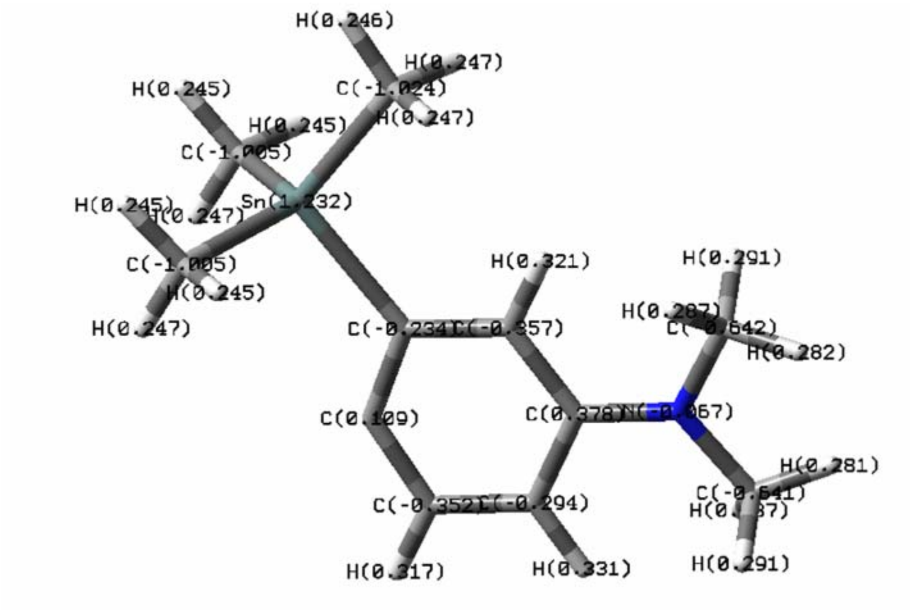


Figure S6. Calculated geometries and charge distribution for *N*,*N*-dimethylaminophenyl cations **5c**$^{+}$

^{1}**5c**$^{+}$

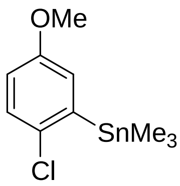


^{3}**5c**$^{+}$



4. Cartesian coordinates and energies for selected excited states and cations

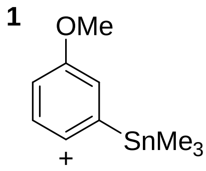
3



[3]1c

E (MeCN) = -483.4688707 Ha

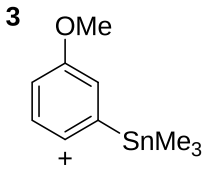
C	-0.37582300	-0.05701800	-0.31218700
C	-1.39510700	-0.89179300	0.16834900
C	-0.80509300	1.15955900	-0.91397900
C	-2.76791400	-0.55087500	-0.01782100
H	-1.18692500	-1.82582000	0.68533400
C	-2.15863300	1.47170600	-1.22091000
C	-3.15429000	0.62610600	-0.72055400
H	-2.41155500	2.36865400	-1.77834300
H	-4.20109400	0.86818800	-0.87474900
C	2.17828700	-0.17371200	2.04554400
C	2.07637100	-2.47228600	-0.60822300
C	2.80864100	0.92681400	-1.27655400
H	1.84243500	0.82003500	2.36175900
H	1.66199200	-0.92864500	2.65179900
H	3.25716600	-0.26126000	2.22781700
H	1.79808900	-2.63293300	-1.65750000
H	3.13705300	-2.73056200	-0.49053200
H	1.48864800	-3.16050700	0.01327300
H	3.89155900	0.81233000	-1.14073600
H	2.57254300	0.75904900	-2.33477400
H	2.52616600	1.95299800	-1.01527800
Sn	1.73729200	-0.43305200	-0.03107100
O	-3.66639100	-1.46033500	0.50344600
C	-5.10504000	-1.23228600	0.36237400
H	-5.57532000	-2.07480100	0.87118600
H	-5.39966100	-0.29197100	0.84518700
H	-5.39831800	-1.22305900	-0.69508900
Cl	-0.19674400	2.82625100	0.75414100



^{1}**4c**$^{+}$

E (MeCN) = -468.286285 Ha

C	0.39850300	0.44909300	-0.00004000
C	1.43779000	-0.55504600	-0.00009600
C	1.00043500	1.61425400	0.00000000
C	2.80809200	-0.16072700	-0.00010000
H	1.19026200	-1.61140000	-0.00009100
C	2.20081900	2.25129800	0.00000000
C	3.18719500	1.21393900	-0.00003300
H	2.43016400	3.30907800	0.00006100
H	4.22719100	1.52230700	0.00002000
C	-2.51817800	0.73965200	-1.79999800
C	-1.64142600	-2.25473800	-0.00010900
C	-2.51804900	0.73946200	1.80016000
H	-2.49858100	1.83382500	-1.74098900
H	-1.91763400	0.42092000	-2.65913200
H	-3.55537500	0.42796600	-1.97595700
H	-1.12091900	-2.61886200	0.89293300
H	-2.64837800	-2.69110100	-0.00009600
H	-1.12098400	-2.61876900	-0.89322600
H	-3.55523400	0.42775900	1.97615800
H	-1.91744600	0.42063700	2.65921700
H	-2.49845400	1.83364100	1.74126600
Sn	-1.80157200	-0.13639200	0.00000900
O	3.69705100	-1.20435400	-0.00002500
C	5.14574900	-0.94784700	0.00009000
H	5.60245300	-1.93708600	0.00011700
H	5.43984200	-0.40025200	-0.90386600
H	5.43971000	-0.40026500	0.90409600

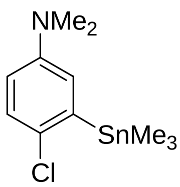


³**4c**⁺

E (MeCN) = -468.2719793 Ha

C	0.39399100	0.38008700	0.00000000
C	1.42442800	-0.56874400	0.00000800
C	0.84702000	1.71554300	0.00000700
C	2.81259800	-0.15207800	-0.00002600
H	1.23762800	-1.63963300	0.00000900
C	2.18578500	2.19913400	0.00000900
C	3.19407700	1.24365400	-0.00001300
H	2.40828400	3.26188700	0.00000600
H	4.23886400	1.53721800	-0.00000800
C	-2.53757500	0.74072200	-1.78034100
C	-1.75225800	-2.26651000	-0.00000100
C	-2.53757200	0.74072000	1.78034300
H	-2.39791000	1.82815100	-1.77608700
H	-2.05135500	0.32781600	-2.67171500
H	-3.61289500	0.53724500	-1.85318500
H	-1.25581200	-2.66724000	0.89241600
H	-2.78381100	-2.63940300	0.00000200
H	-1.25581600	-2.66723900	-0.89242000
H	-3.61289400	0.53724800	1.85318300
H	-2.05135700	0.32780700	2.67171600
H	-2.39790100	1.82814800	1.77609400
Sn	-1.75500300	-0.13535400	0.00000000
O	3.69462300	-1.16220300	-0.00000600
C	5.17203700	-0.97332500	0.00001300
H	5.57004200	-1.98643100	0.00002600
H	5.47145400	-0.43774600	-0.90612000
H	5.47143300	-0.43773200	0.90614300

3

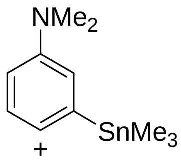


32c

E (MeCN) = -483.4688707 Ha

C	-0.19399200	0.15565800	-0.34128000
C	-1.32762700	-0.59462600	-0.01163200
C	-0.40886000	1.50198200	-0.76424600
C	-2.65928900	-0.06314600	-0.16828800
H	-1.20997600	-1.61019900	0.35573700
C	-1.70458800	2.01088200	-1.07701000
C	-2.81793600	1.25261500	-0.73428700
H	-1.81787400	3.00007200	-1.51151200
H	-3.80906900	1.66388800	-0.89364300
C	2.33070200	-0.48941300	2.00230200
C	1.85967100	-2.57738500	-0.76621700
C	3.12083400	0.68896900	-1.25465700
H	2.19267000	0.53248800	2.37179300
H	1.68262300	-1.16269300	2.57789500
H	3.37384100	-0.79284700	2.16038600
H	1.53767100	-2.63947000	-1.81380500
H	2.87389800	-2.99229600	-0.69405600
H	1.19399000	-3.20877200	-0.16202300
H	4.17105000	0.39953300	-1.12159600
H	2.87131400	0.61258600	-2.32035900
H	2.99640700	1.73129200	-0.94027300
Sn	1.83423900	-0.53889100	-0.07790500
Cl	0.53492200	2.84920600	0.95737300
H	-5.31797800	-0.12434600	-1.11303400
C	-5.12964700	-0.29519400	-0.04435700
N	-3.76852700	-0.81071200	0.18862600
H	-5.85893500	-1.02345300	0.31702600
H	-5.29453100	0.64842200	0.49285500
C	-3.61384000	-2.14904700	0.78552900
H	-2.96102600	-2.11265400	1.66678800
H	-4.59147500	-2.51853800	1.10302200
H	-3.19108700	-2.86773500	0.06920900

1

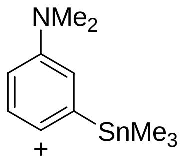


[1]**5c**$^+$

E (MeCN) = -487.7360948 Ha

C	0.14658900	-0.57219800	0.10918200
C	1.26281300	0.32857100	0.10051700
C	0.58954500	-1.81327700	0.24747700
C	2.60767400	-0.19387200	0.05383600
H	1.07825800	1.39525100	0.09863000
C	1.72709400	-2.54323300	0.01585600
C	2.80711700	-1.62564500	0.00386100
H	1.85469600	-3.61833000	-0.00093200
H	3.80512200	-2.04728800	0.03723200
C	-2.83591700	-0.44314900	1.82871700
C	-1.68969200	2.25651100	-0.24648000
C	-2.75819100	-0.82092800	-1.74287400
H	-2.88254000	-1.53568900	1.90078000
H	-2.25240200	-0.06095700	2.67362800
H	-3.85725000	-0.05134600	1.91268600
H	-1.08441100	2.48603700	-1.13116700
H	-2.66455700	2.74382700	-0.37443400
H	-1.21338600	2.69269500	0.63929600
H	-3.76932300	-0.45301500	-1.95690800
H	-2.13343100	-0.62742100	-2.62218300
H	-2.81950300	-1.90414100	-1.58617500
Sn	-1.97998600	0.16015500	-0.02327300
H	5.11541400	-0.40473000	-1.17346200
C	5.05053100	0.12881000	-0.21622800
N	3.69044500	0.65440800	0.02245700
H	5.75703900	0.95958400	-0.24542700
H	5.36208100	-0.54843200	0.59151600
C	3.50427500	2.11403700	0.13456300
H	2.87333300	2.36063500	0.99814700
H	4.47483800	2.58943400	0.28587300
H	3.05117200	2.54151600	-0.77122200

3

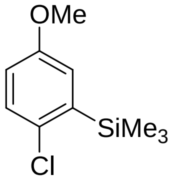


^{3}**5c**$^{+}$

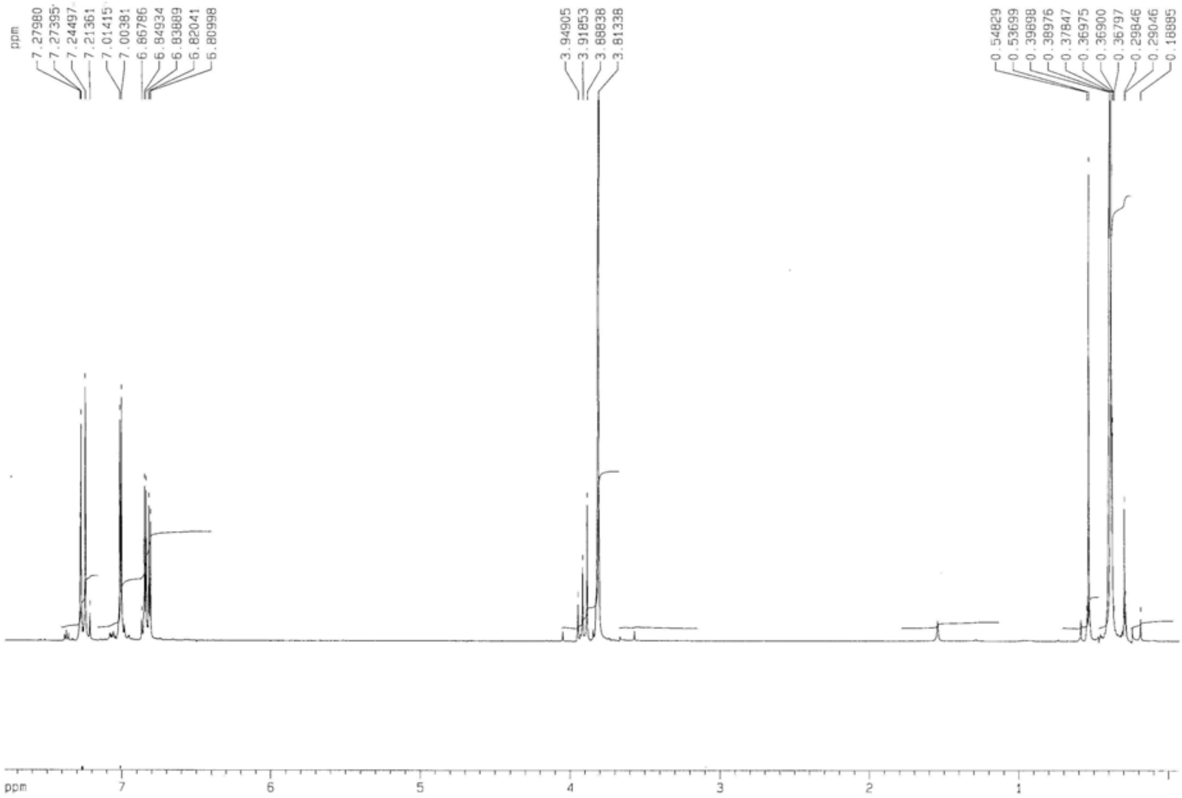
E (MeCN) = -487.7452322 Ha

C	0.13961400	-0.54668700	0.01947500
C	1.25251000	0.31018600	0.00416800
C	0.45305400	-1.91434400	0.04858100
C	2.60676400	-0.20857400	0.01202500
H	1.09891800	1.38360800	-0.03917000
C	1.73181700	-2.50598700	0.05907200
C	2.82324000	-1.64027600	0.03661100
H	1.86942900	-3.58250600	0.09056000
H	3.82697700	-2.04868500	0.06295700
C	-2.81780500	-0.54201300	1.80528700
C	-1.77110200	2.28440300	-0.10290500
C	-2.82717500	-0.69888600	-1.75051600
H	-2.77127200	-1.63604900	1.86273200
H	-2.30337600	-0.12570800	2.67934700
H	-3.87225700	-0.24420600	1.85603500
H	-1.23961500	2.60677900	-1.00734500
H	-2.77124200	2.73427500	-0.13119900
H	-1.25444800	2.68674100	0.77782200
H	-3.87874600	-0.39690100	-1.82854400
H	-2.31002600	-0.37080100	-2.65984000
H	-2.79135100	-1.79393700	-1.70573100
Sn	-1.94334800	0.15719900	-0.00952100
H	5.13837000	-0.60371200	-0.93789500
C	5.07520300	0.14927700	-0.14830300
N	3.68181200	0.64700800	-0.00386900
H	5.72433400	0.98370600	-0.41651500
H	5.42924500	-0.28077400	0.79736300
C	3.51140000	2.11753700	0.12263800
H	2.79639800	2.35858500	0.91303000
H	4.47226000	2.56555300	0.37917000
H	3.16597400	2.54723500	-0.82643200

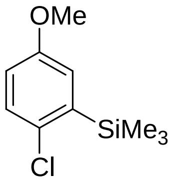
4. ^{1}H NMR and ^{13}C NMR spectra



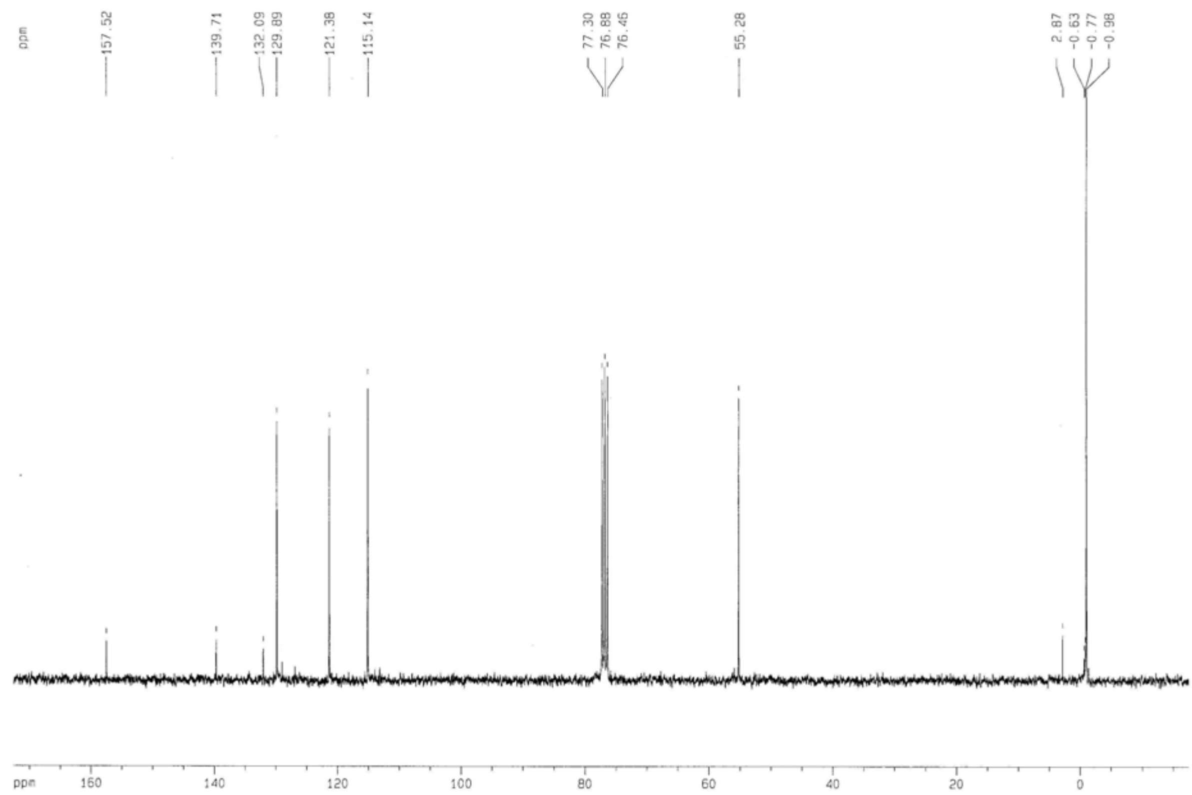
1b, ^{1}H NMR

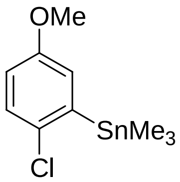


Electronic Supplementary Material (ESI) for Chemical Science

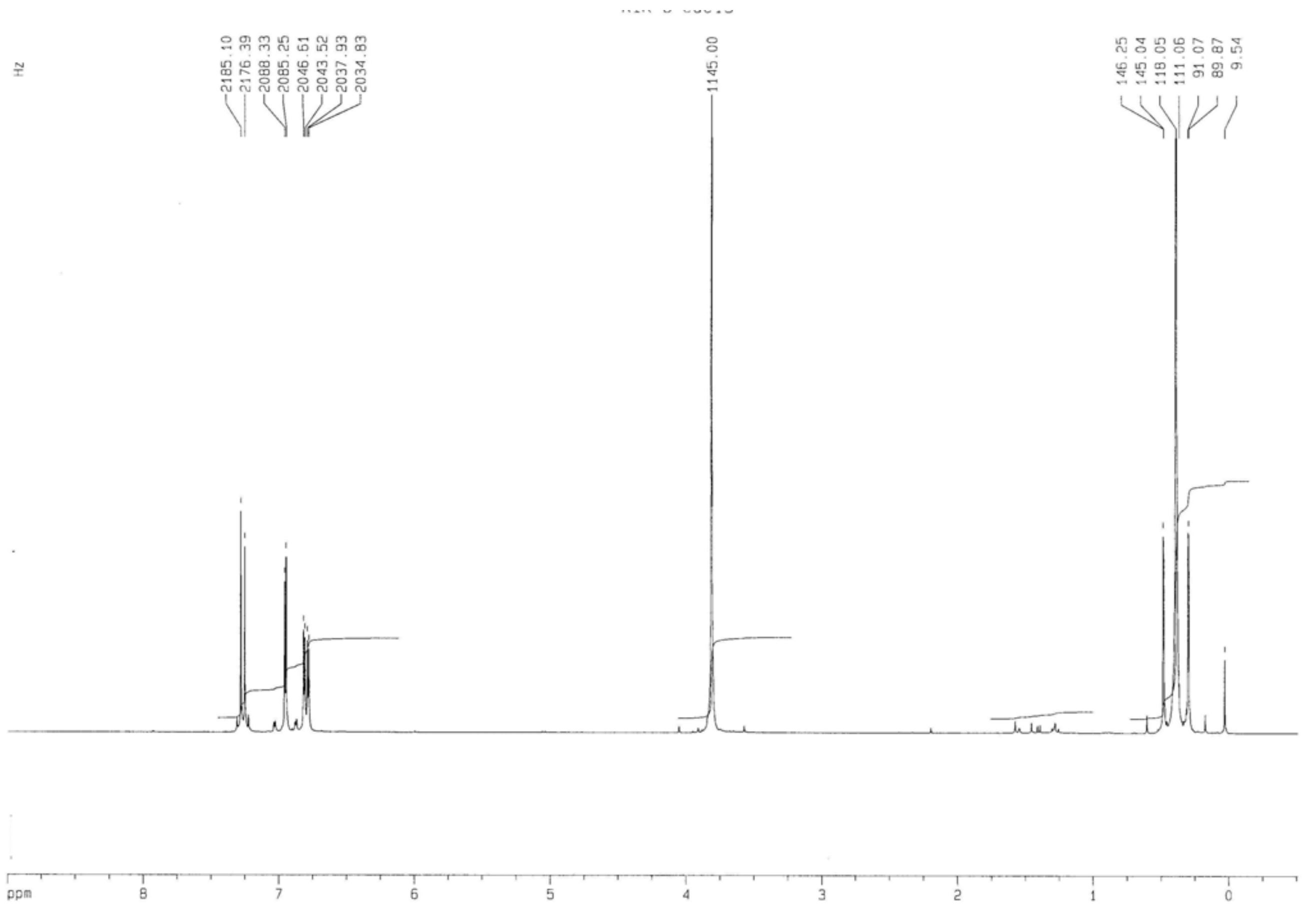


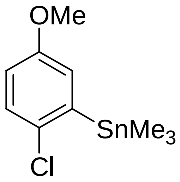
1b, ^{13}C NMR



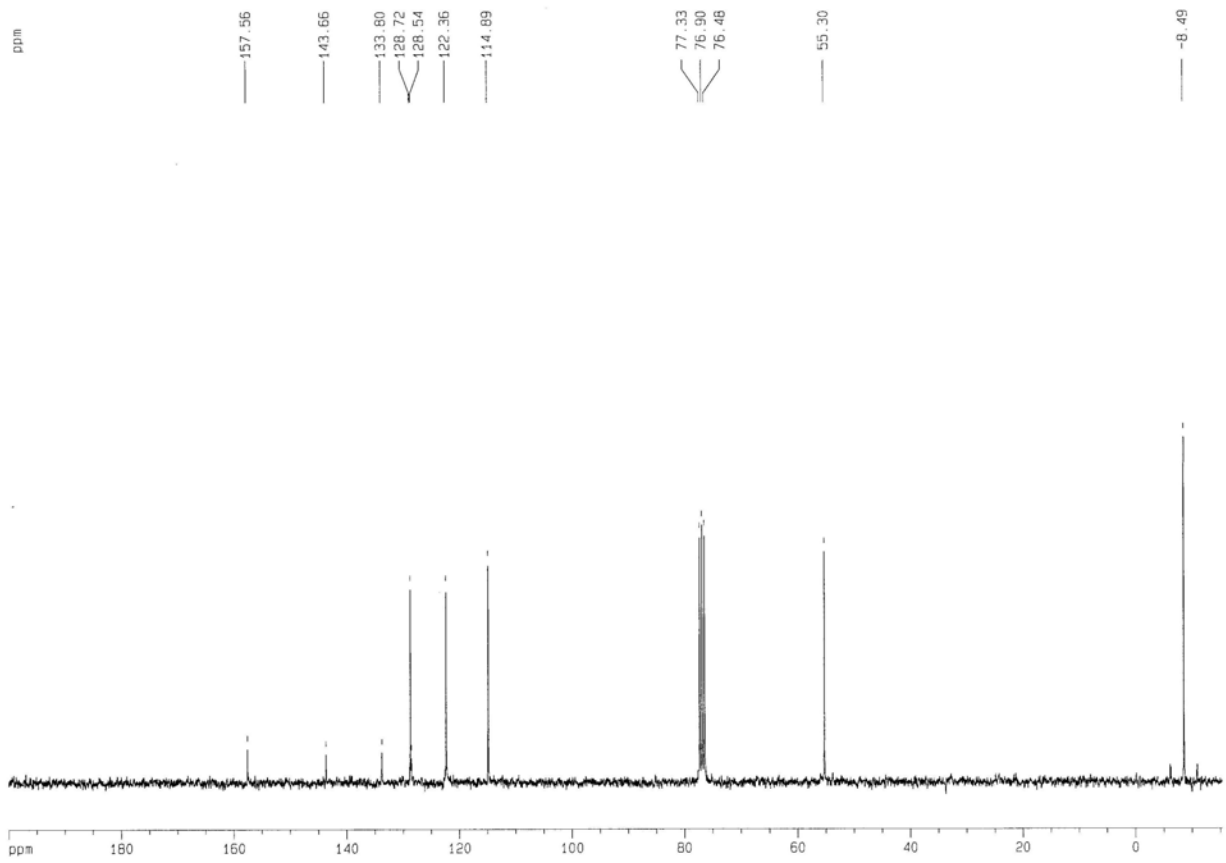

OMe
SnMe3
Cl

1c, [1]H NMR


Hz
2185.10
2176.39
2088.33
2085.25
2046.61
2043.52
2037.93
2034.83
1145.00
146.25
145.04
118.05
111.06
91.07
89.87
9.54
ppm
8
7
6
5
4
3
2
1
0


OMe
SnMe3
Cl

1c, ^{13}C NMR


ppm
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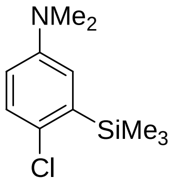
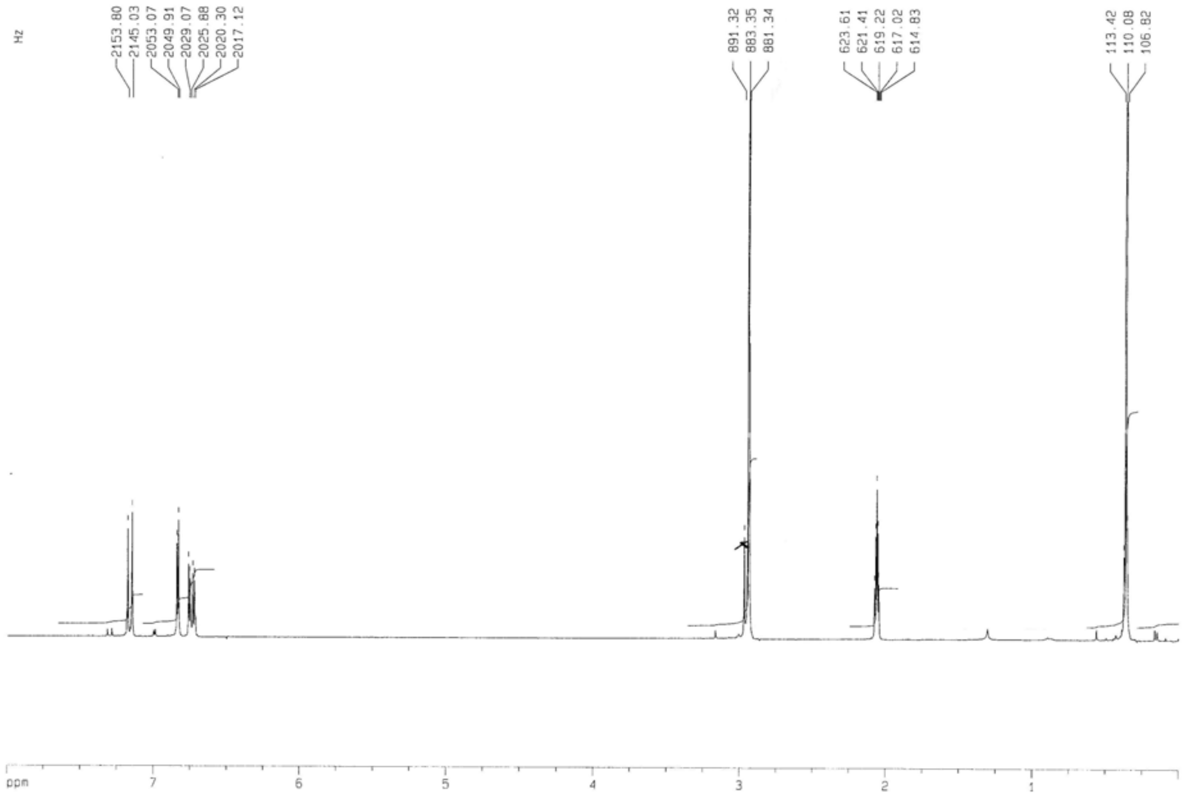
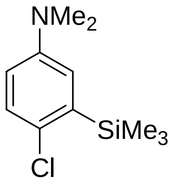
133.80
128.72
128.54
122.36
114.89
77.33
76.90
76.48
55.30
-8.49
ppm
180
160
140
120
100
80
60
40
20
0

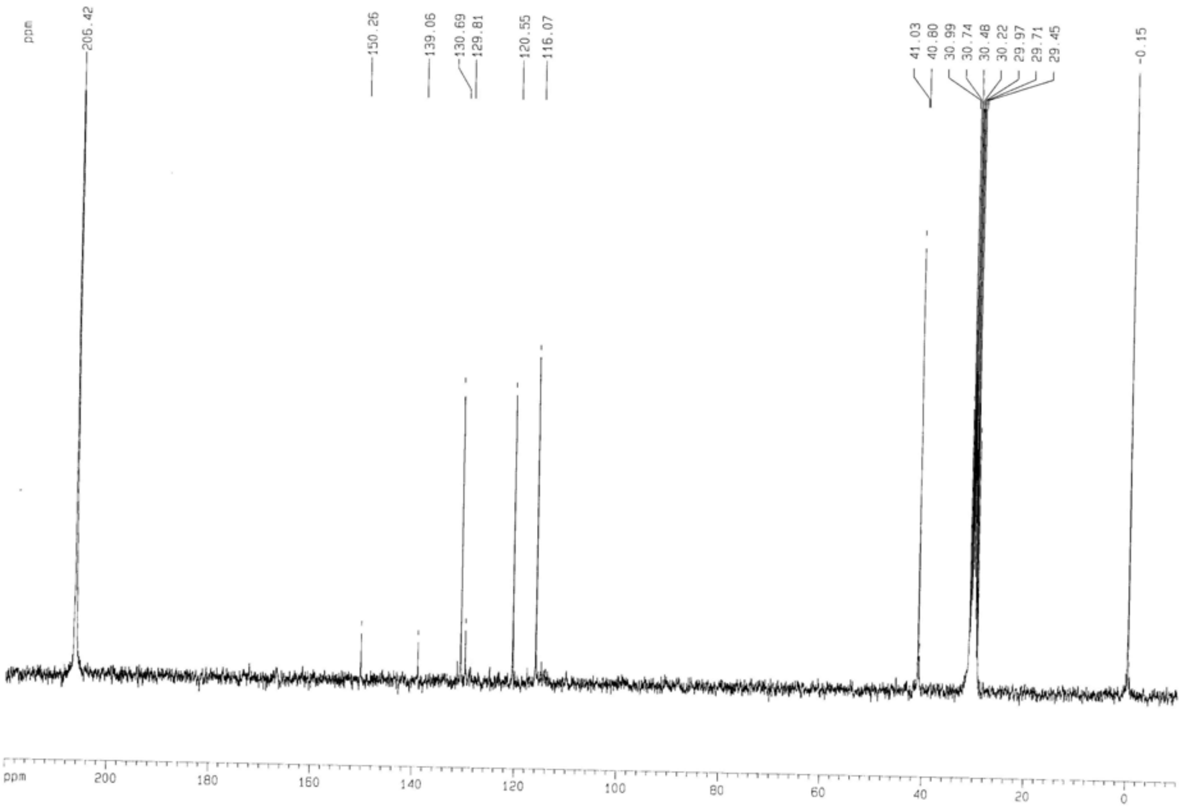

NMe2
SiMe3
Cl

2b, [1]H NMR


Hz
2153.80
2145.03
2053.07
2049.91
2029.07
2025.88
2020.30
2017.12
891.32
883.35
881.34
623.61
621.41
619.22
617.02
614.83
113.42
110.08
106.82
ppm
7
6
5
4
3
2
1


NMe2
SiMe3
Cl

2b, ^{13}C NMR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205.42
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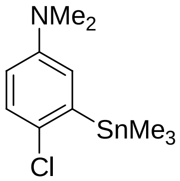
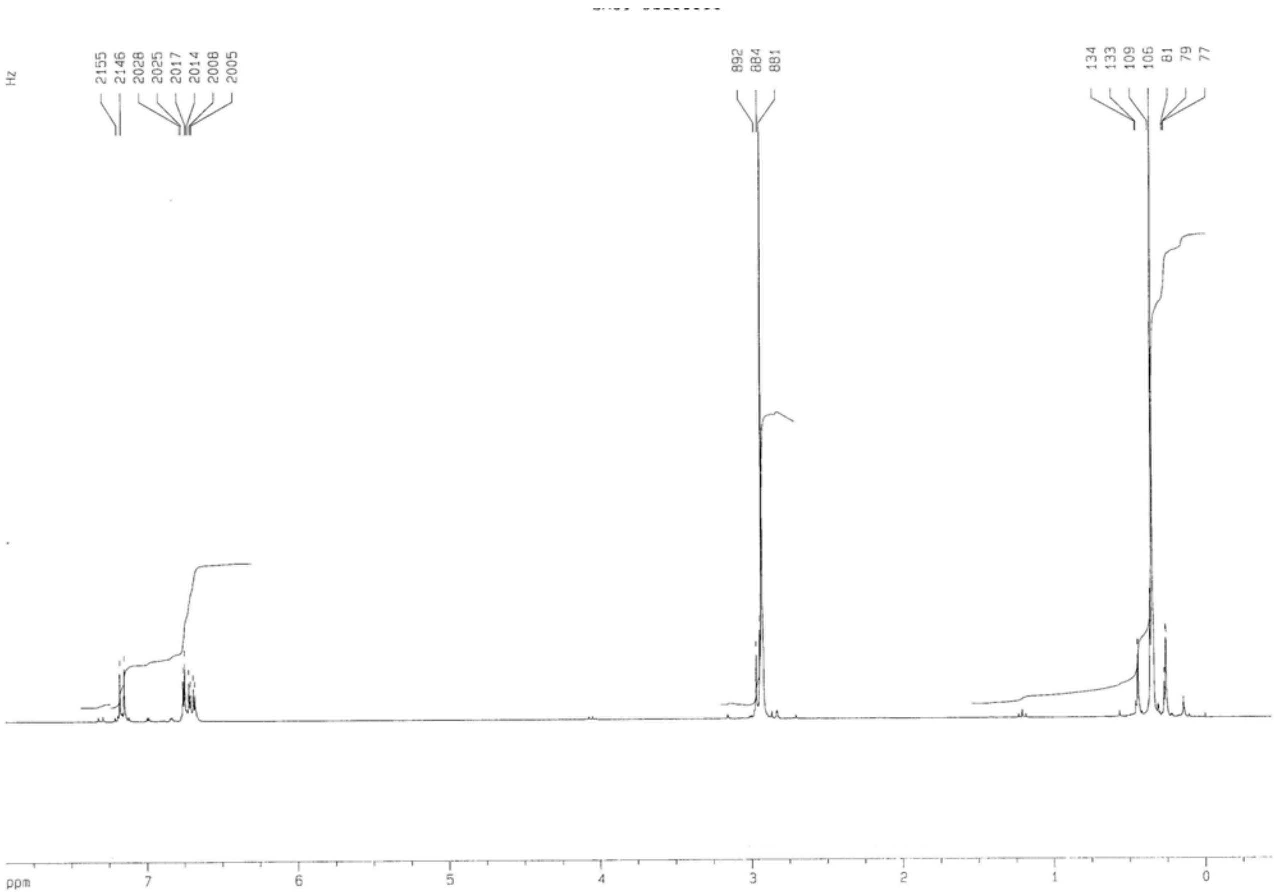
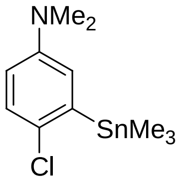
139.06
130.69
129.81
120.55
116.07
41.03
40.80
30.99
30.74
30.48
30.22
29.97
29.71
29.45
-0.15
ppm
200
180
160
140
120
100
80
60
40
20
0

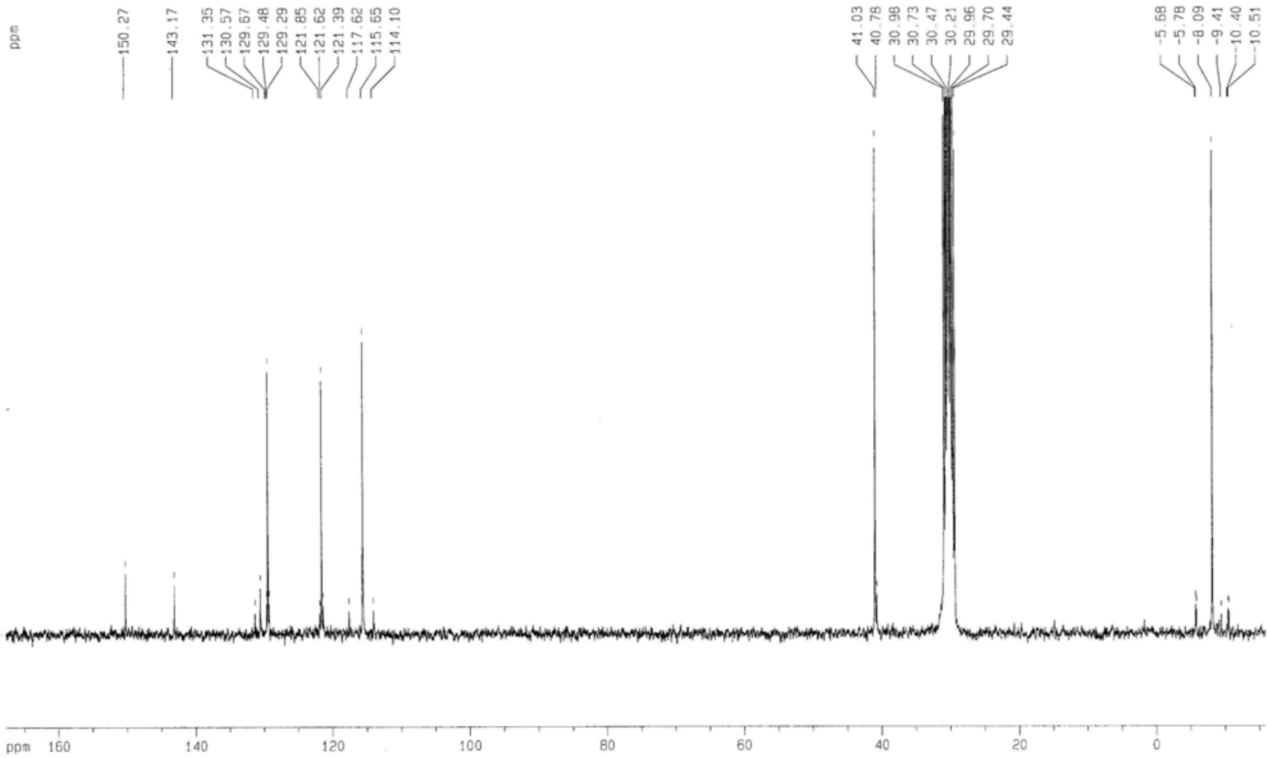

NMe2
SnMe3
Cl

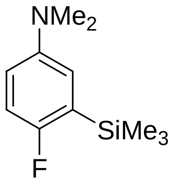
2c, 1H NMR


Hz
2155
2146
2028
2025
2017
2014
2008
2005
892
884
881
134
133
109
106
81
79
77
ppm
7
6
5
4
3
2
1
0

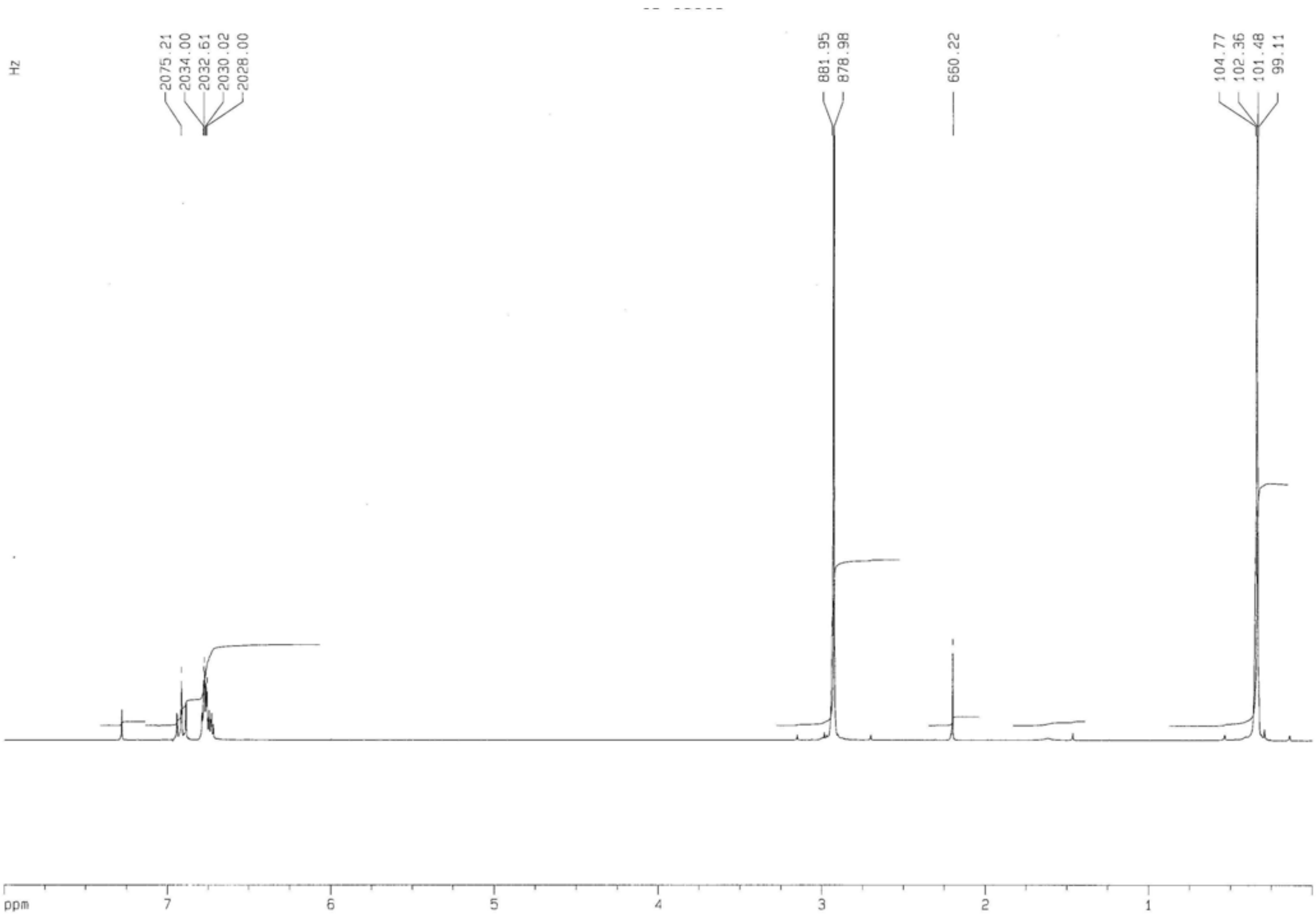


2c, ^{13}C NMR




NMe2
SiMe3
F

3b, ¹H NMR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2034.00
2032.61
2030.02
2028.00
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660.22
104.77
102.36
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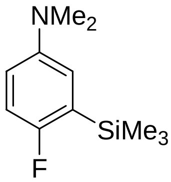
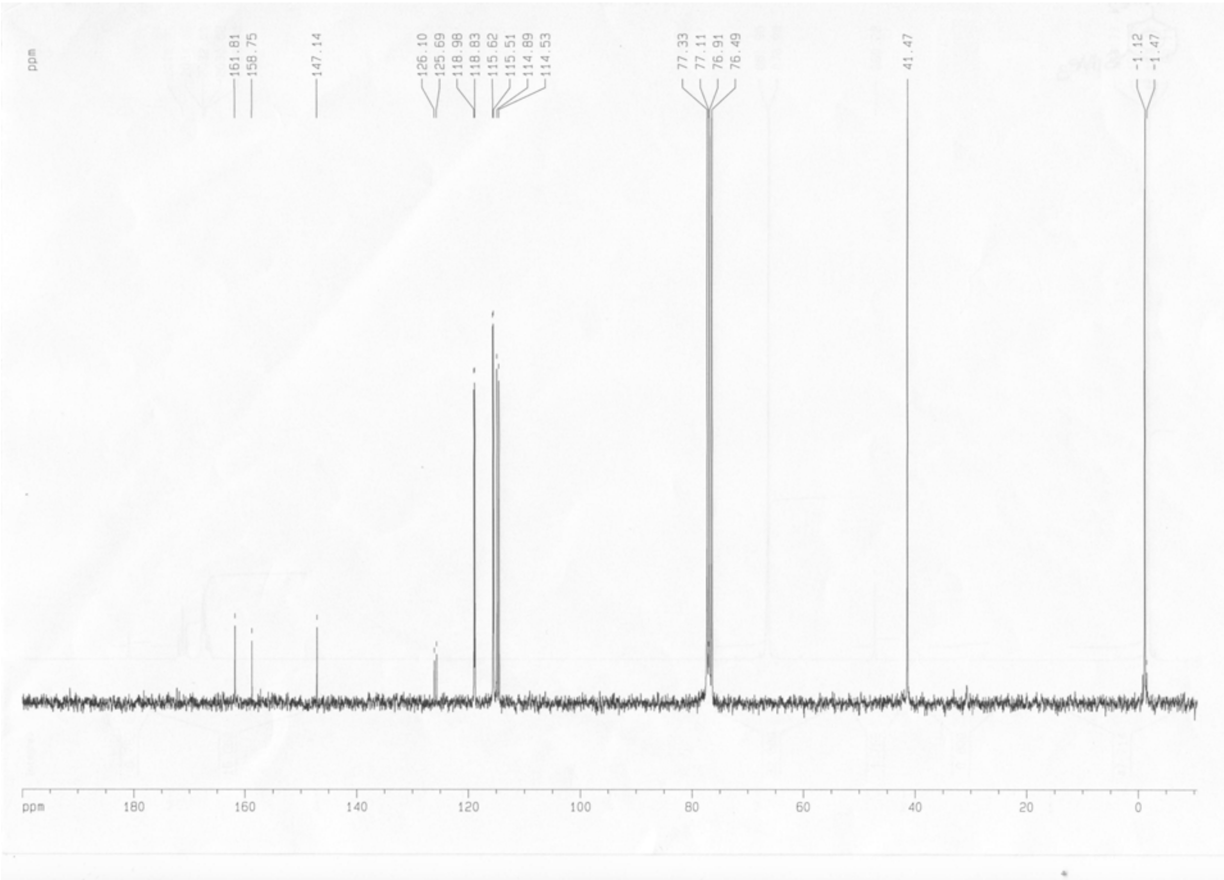
5
4
3
2
1


NMe2
SiMe3
F

3b, ^{13}C NMR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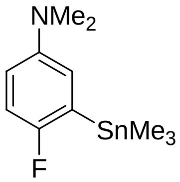
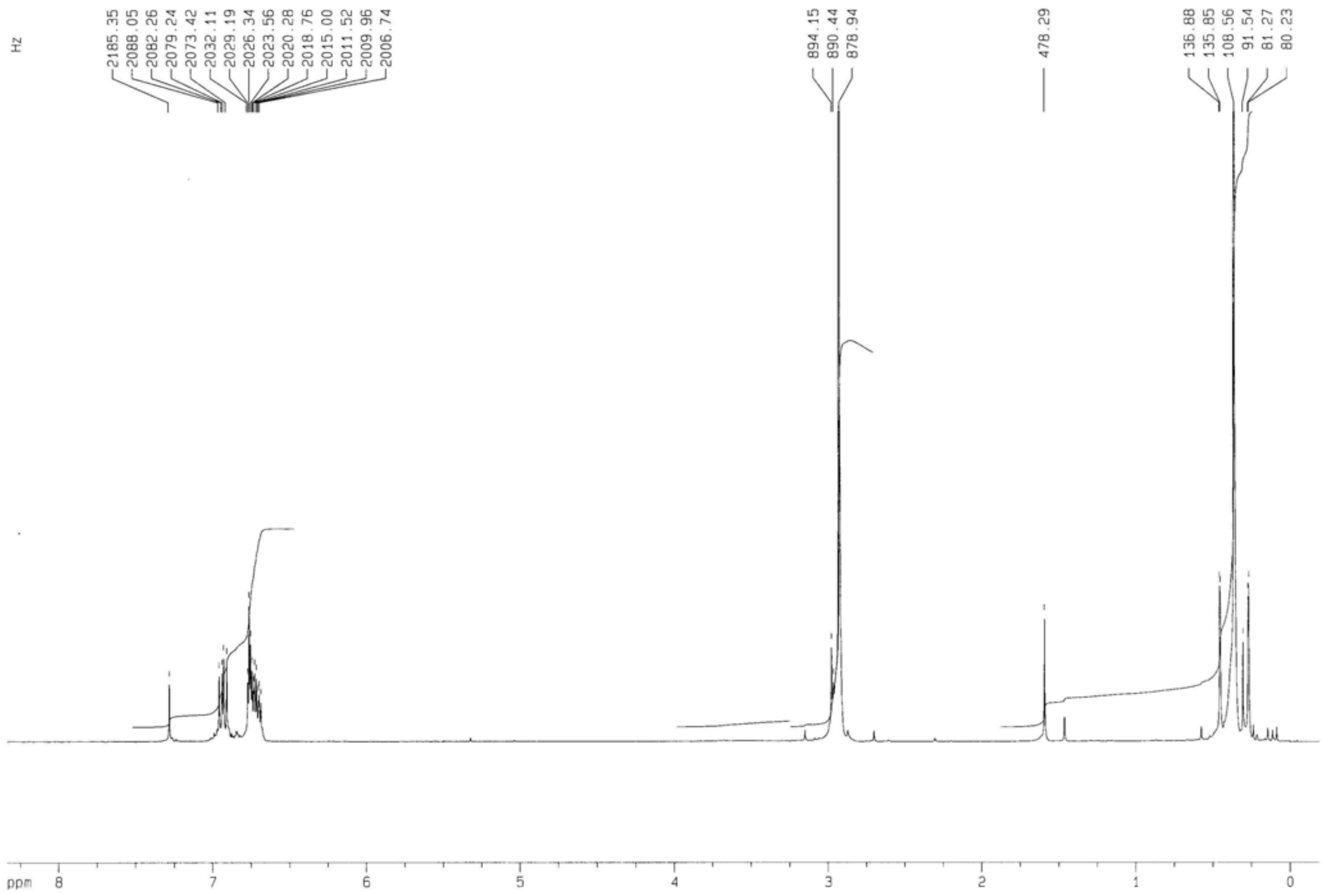
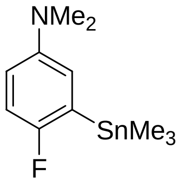
147.14
126.10
125.69
118.98
118.83
115.62
115.51
114.89
114.53
77.33
77.11
76.91
76.49
41.47
-1.12
-1.47
ppm
180
160
140
120
100
80
60
40
20
0

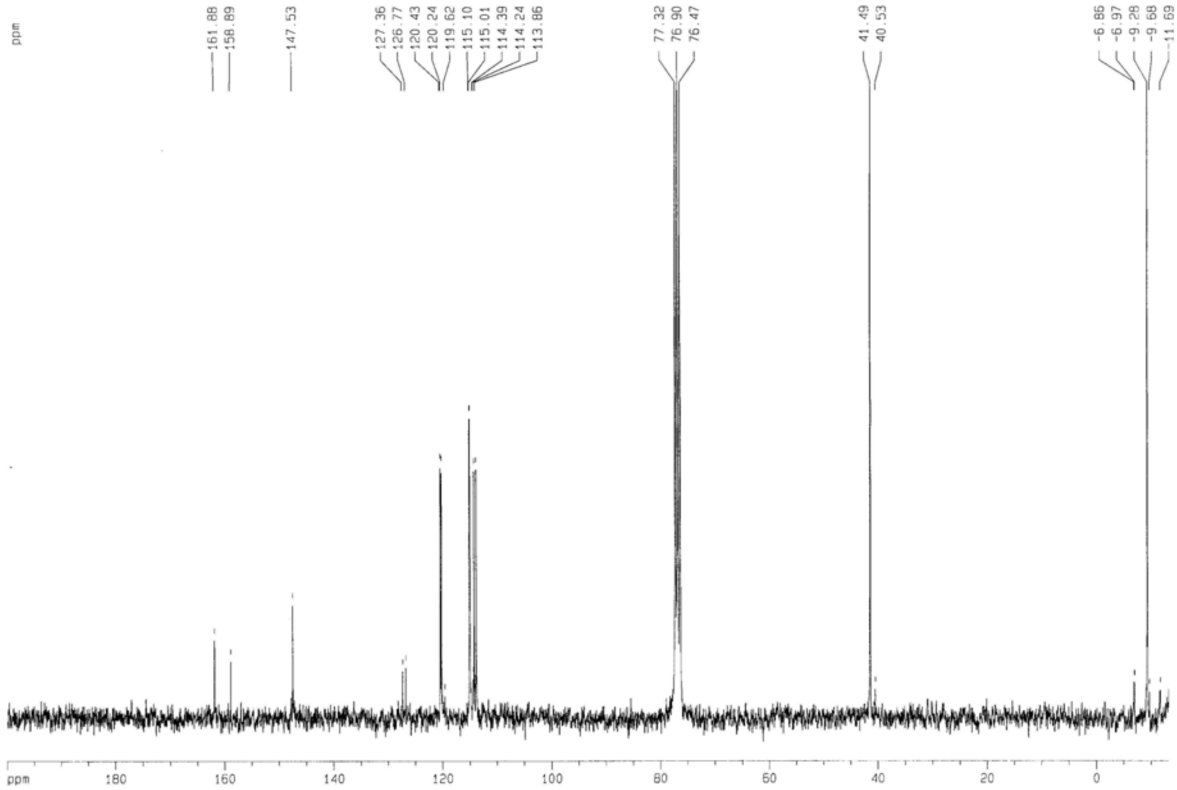

NMe2
SnMe3
F

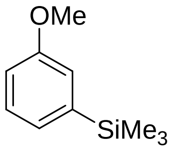
3c, ^{1}H NMR


Hz
2185.35
2088.05
2082.26
2079.24
2073.42
2032.11
2029.19
2026.34
2023.56
2020.28
2018.76
2015.00
2011.52
2009.96
2006.74
894.15
890.44
878.94
478.29
136.88
135.85
108.56
91.54
81.27
80.23
ppm
8
7
6
5
4
3
2
1
0

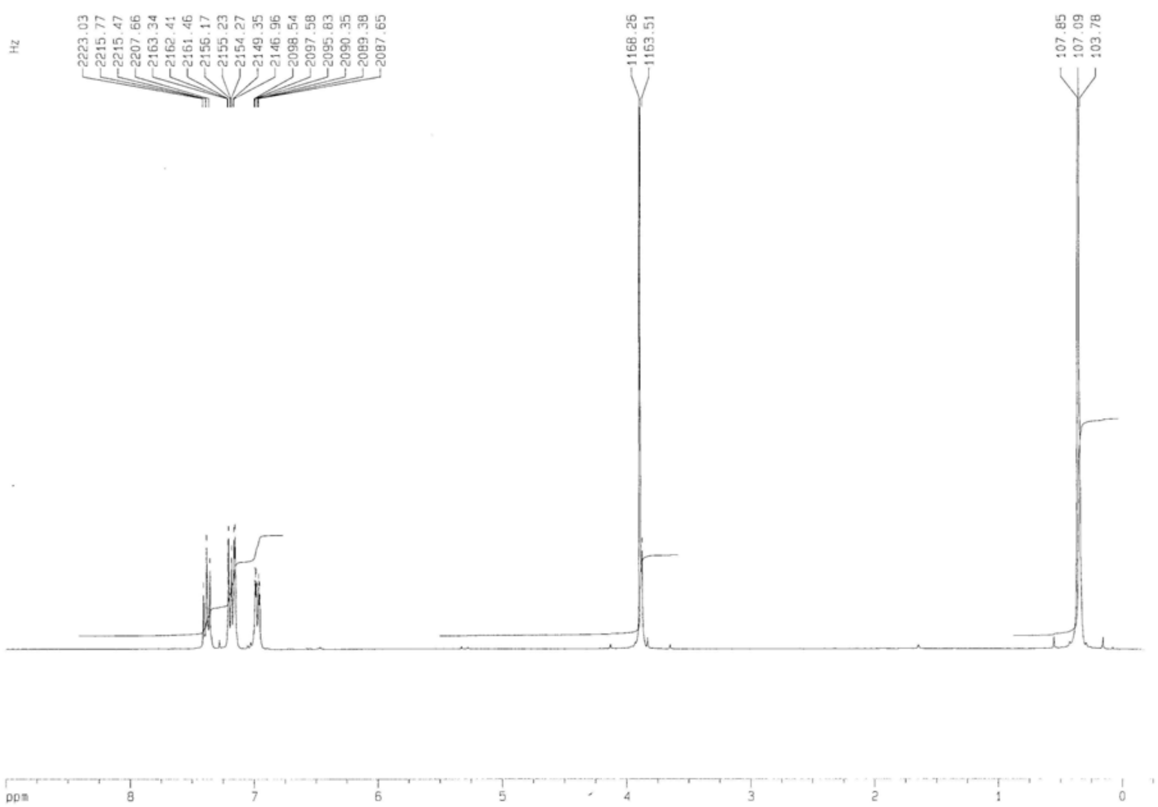

NMe2
SnMe3
F

3c, ^{13}C NMR


161.88
158.89
147.53
127.36
126.77
120.43
120.24
119.62
115.10
115.01
114.39
114.24
113.86
77.32
76.90
76.47
41.49
40.53
-6.86
-6.97
-9.28
-9.68
-11.69
ppm
180
160
140
120
100
80
60
40
20
0


OMe
SiMe3

4b, [1]H NMR.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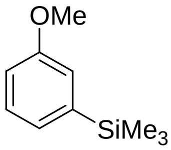
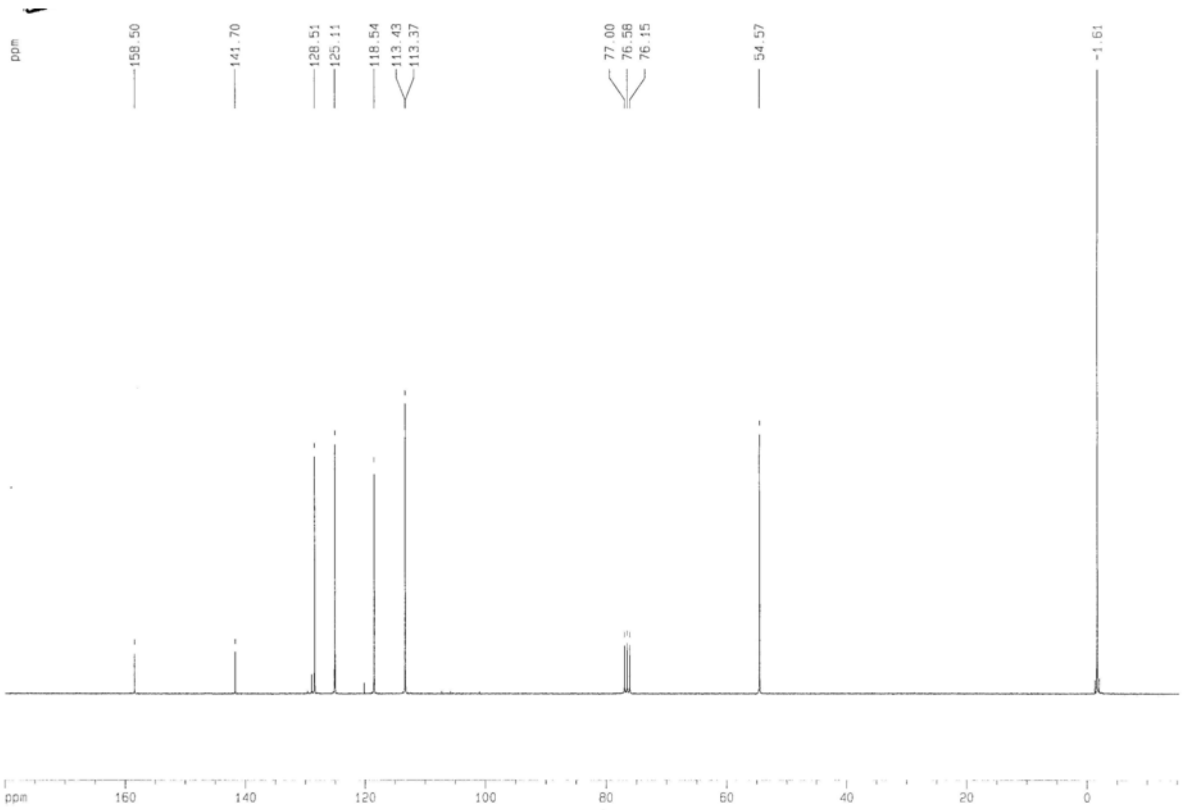
2223.03
2215.77
2215.47
2207.66
2163.34
2162.41
2161.46
2156.17
2155.23
2154.27
2149.35
2146.96
2098.54
2097.58
2095.83
2090.35
2089.38
2087.65
1168.26
1163.51
107.85
107.09
103.78
ppm
8
7
6
5
4
3
2
1
0


OMe
SiMe3

4b, ^{13}C NMR.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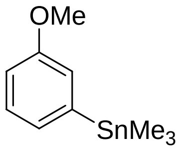
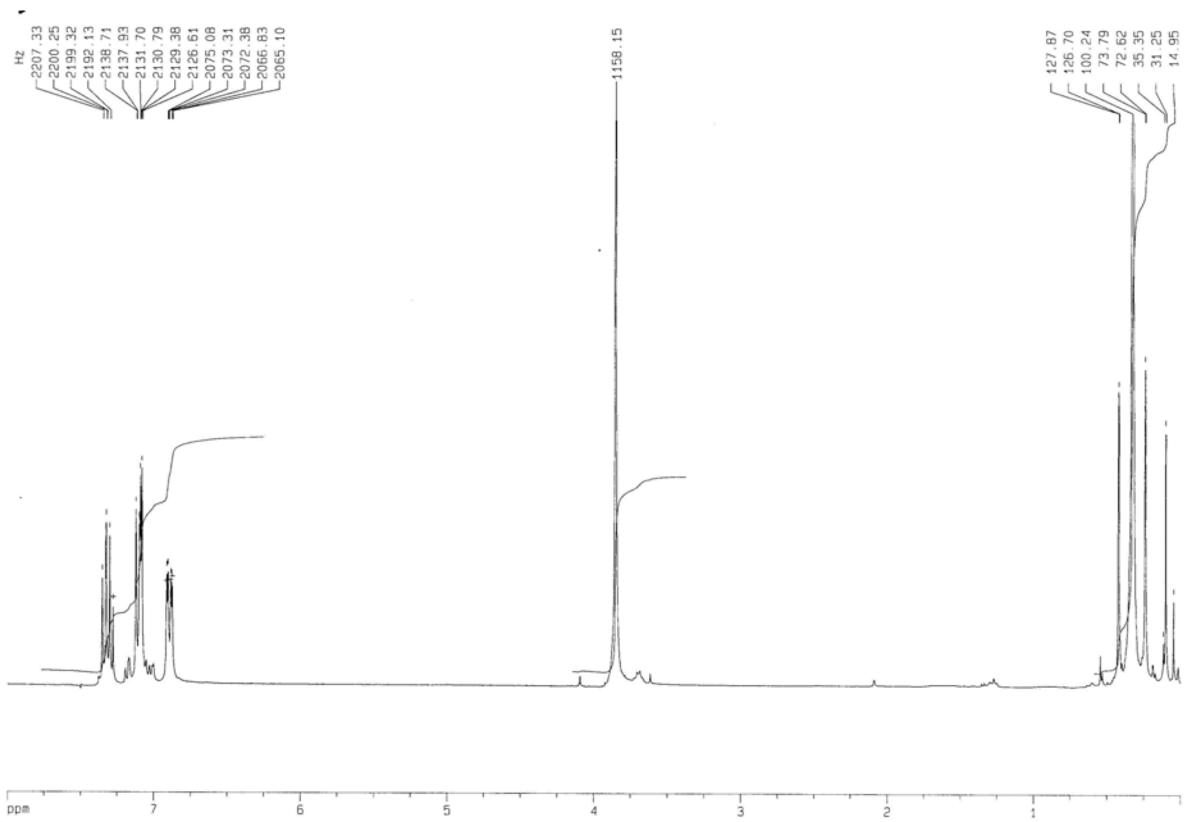
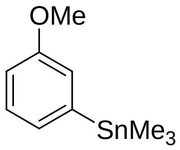
128.51
125.11
118.54
113.43
113.37
77.00
76.58
76.15
54.57
-1.61
ppm
160
140
120
100
80
60
40
20
0

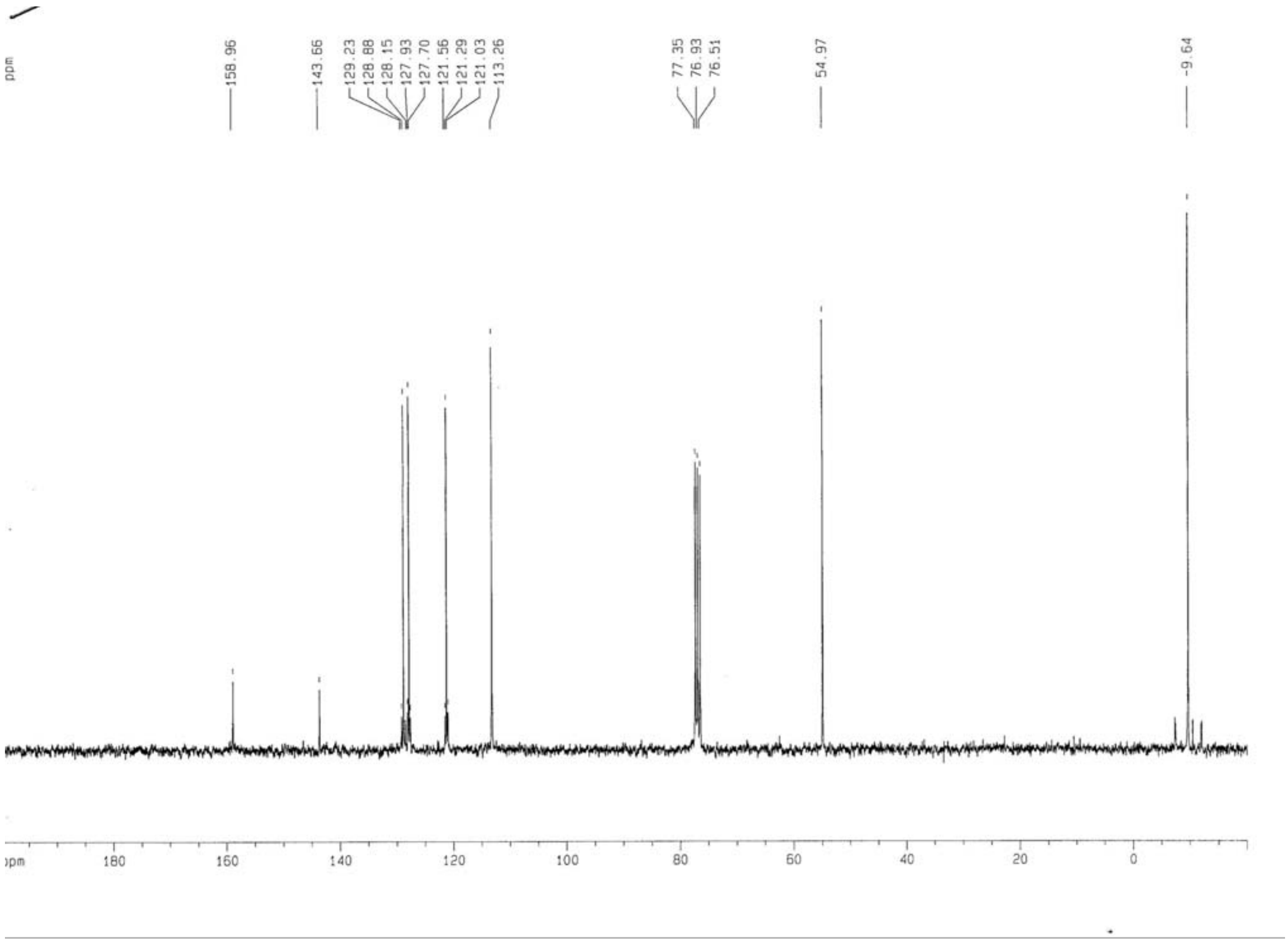


4c, [1]H NMR





4c, ^{13}C NMR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127.70
121.56
121.29
121.03
113.26
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76.93
76.51
54.97
-9.64
ppm
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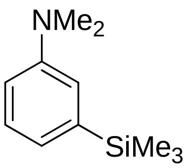
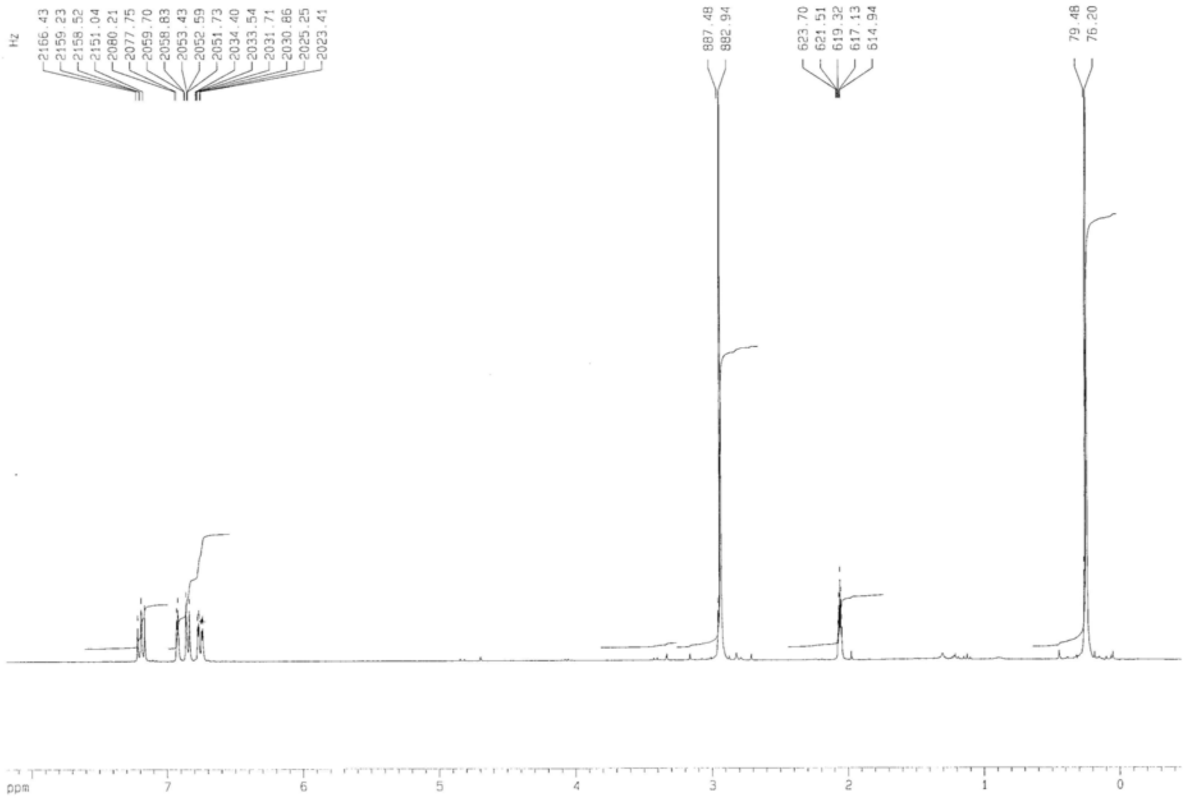
140
120
100
80
60
40
20
0


NMe2
SiMe3

5b [1]H NMR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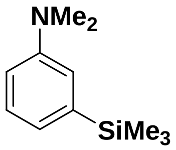
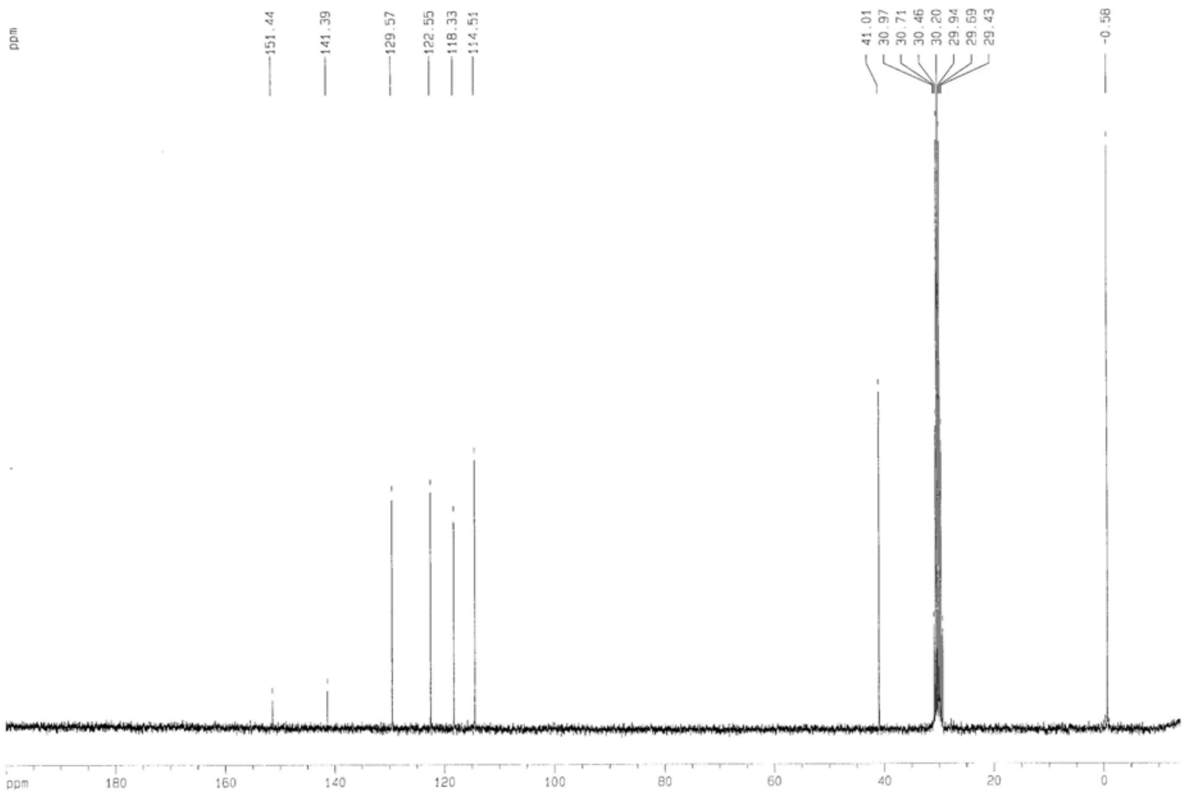
2151.04
2080.21
2077.75
2059.70
2058.83
2053.43
2052.59
2051.73
2034.40
2033.54
2031.71
2030.86
2025.25
2023.41
887.48
882.94
623.70
621.51
619.32
617.13
614.94
79.48
76.20
ppm
7
6
5
4
3
2
1
0


NMe2
SiMe3

5b ^{13}C NMR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122.55
118.33
114.51
41.01
30.97
30.71
30.46
30.20
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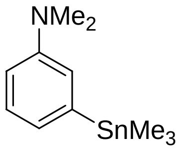
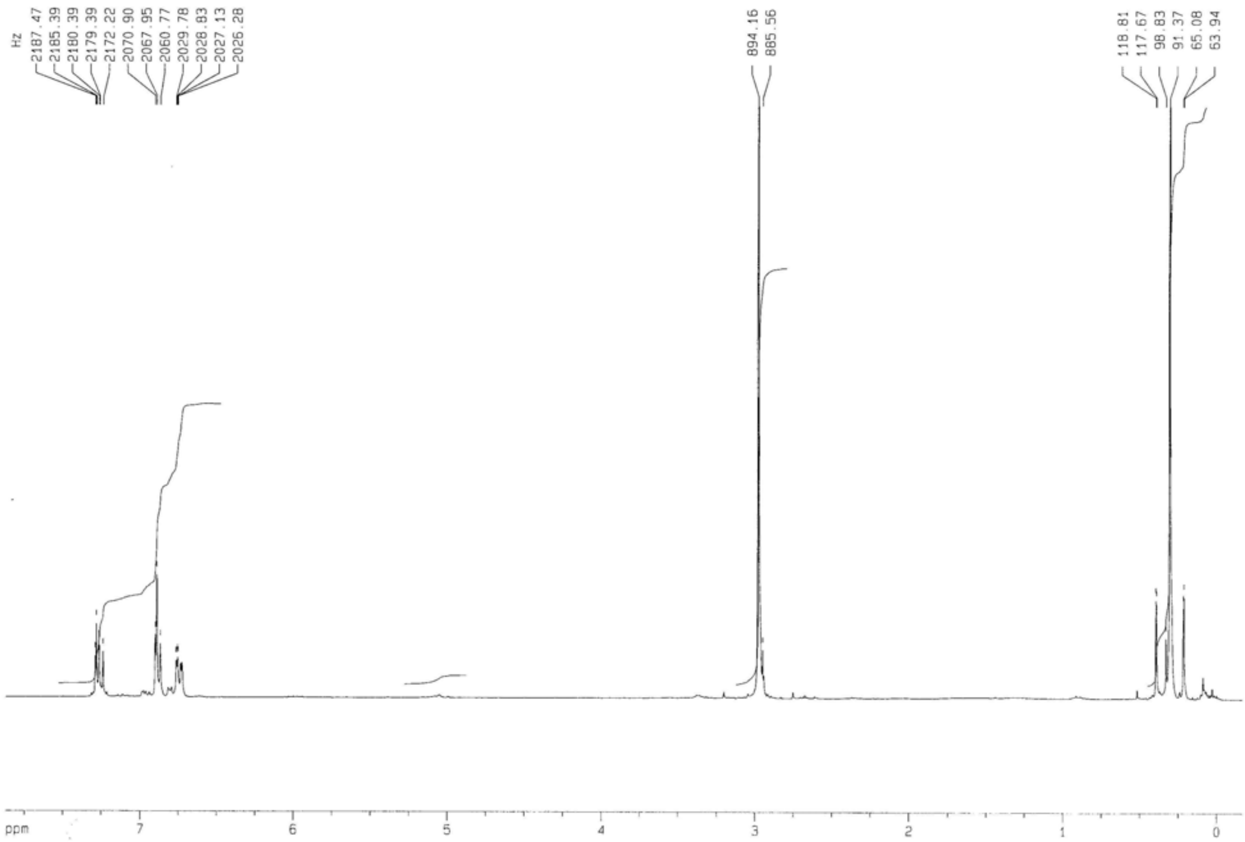
80
60
40
20
0


NMe2
SnMe3

5c [1]H NMR


Hz
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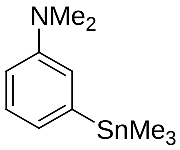
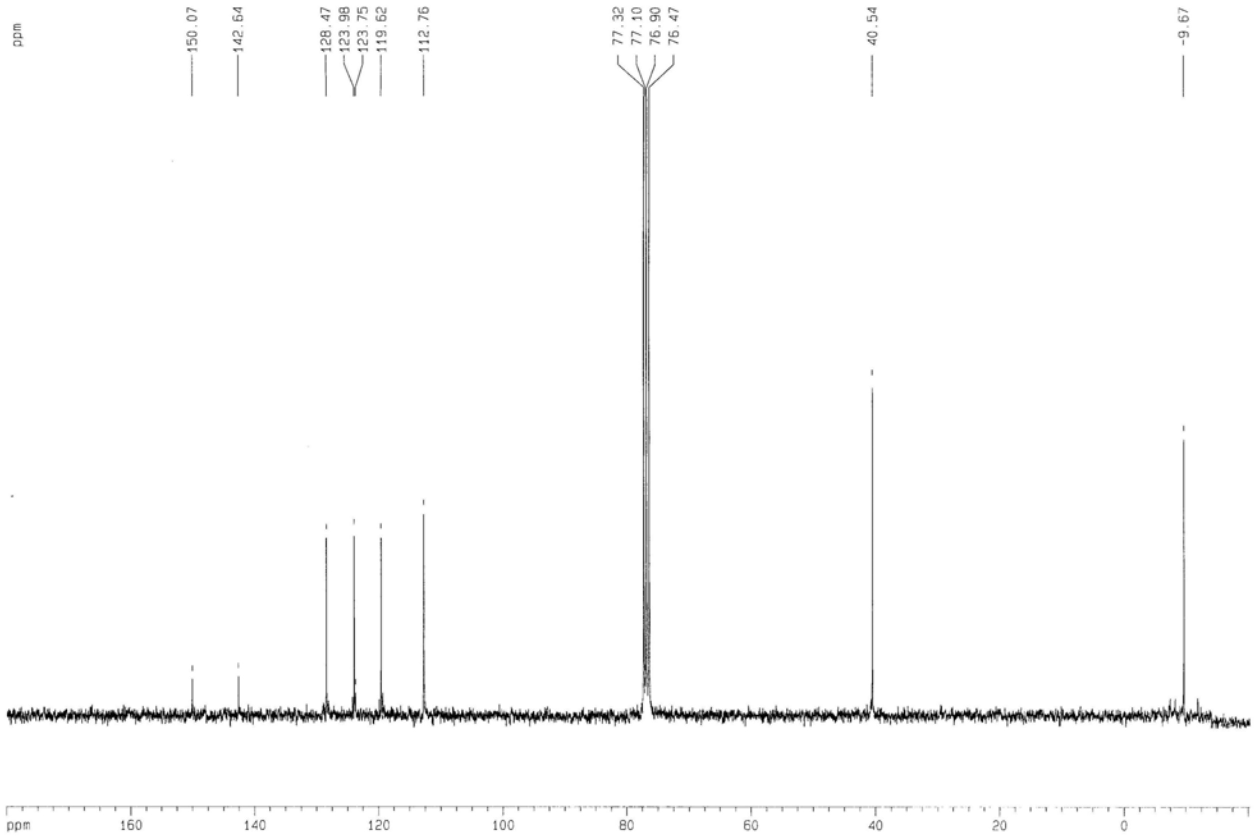
2185.39
2180.39
2179.39
2172.22
2070.90
2067.95
2060.77
2029.78
2028.83
2027.13
2026.28
894.16
885.56
118.81
117.67
98.83
91.37
65.08
63.94
ppm
7
6
5
4
3
2
1
0


NMe2
SnMe3

5c ^{13}C NMR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128.47
123.98
123.75
119.62
112.76
77.32
77.10
76.90
76.47
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140
120
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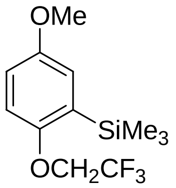
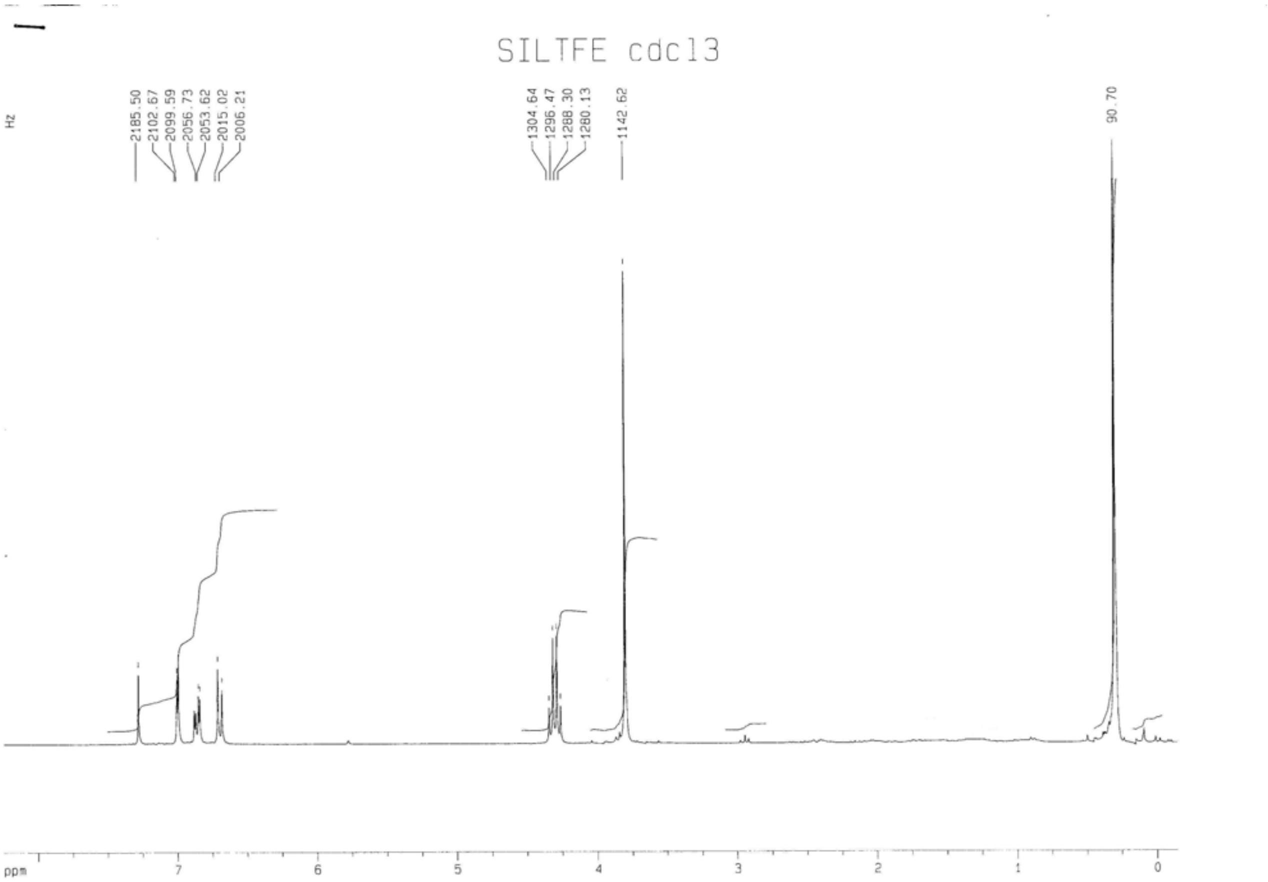
80
60
40
20
0


OMe
SiMe3
OCH2CF3

6b [1]H NMR


SILTFE cdcl3
Hz
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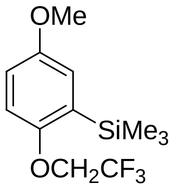
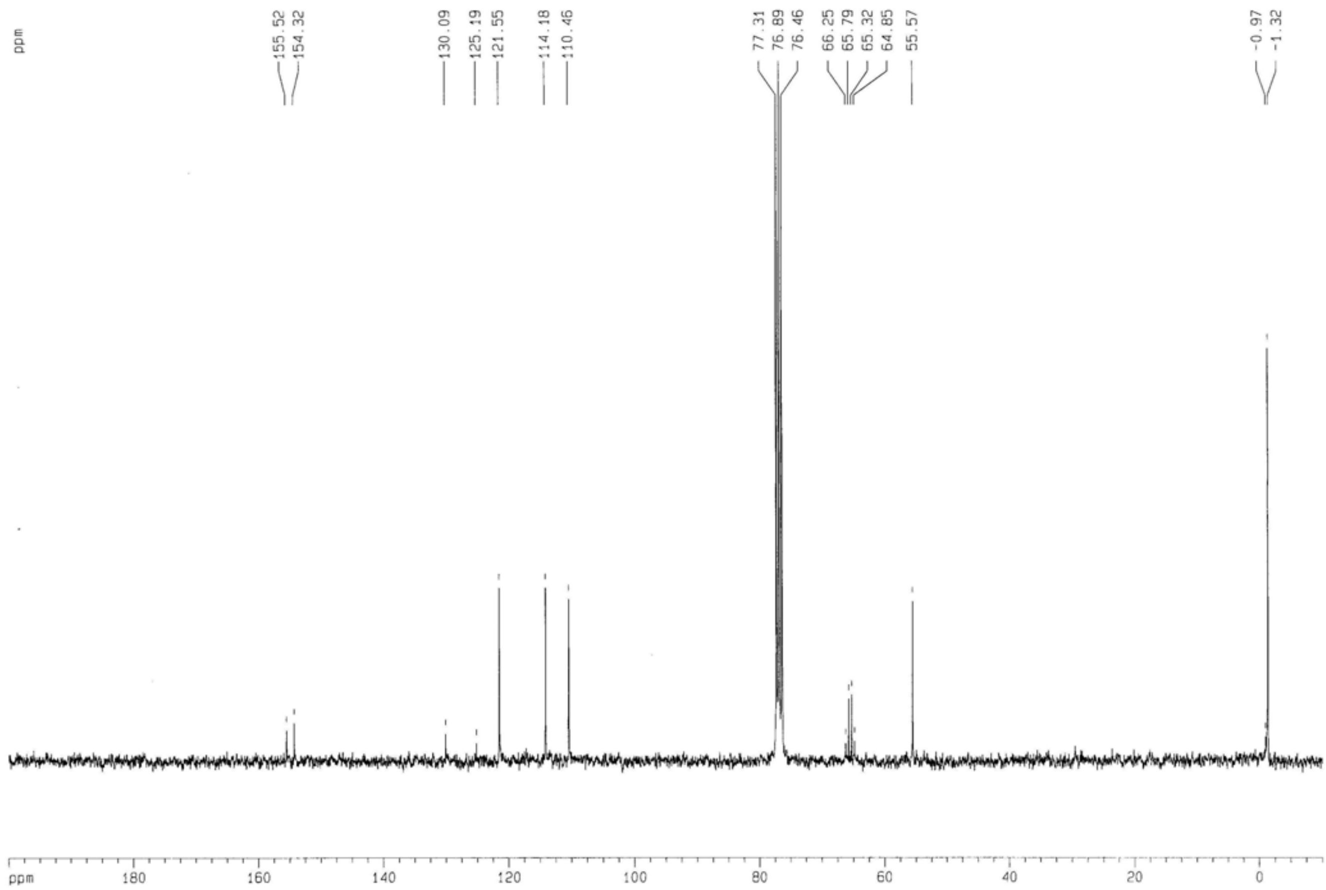
2102.67
2099.59
2056.73
2053.62
2015.02
2006.21
1304.64
1296.47
1288.30
1280.13
1142.62
90.70
ppm
7
6
5
4
3
2
1
0


OMe
SiMe3
OCH2CF3

6b ^{13}C NMR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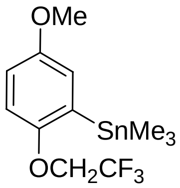
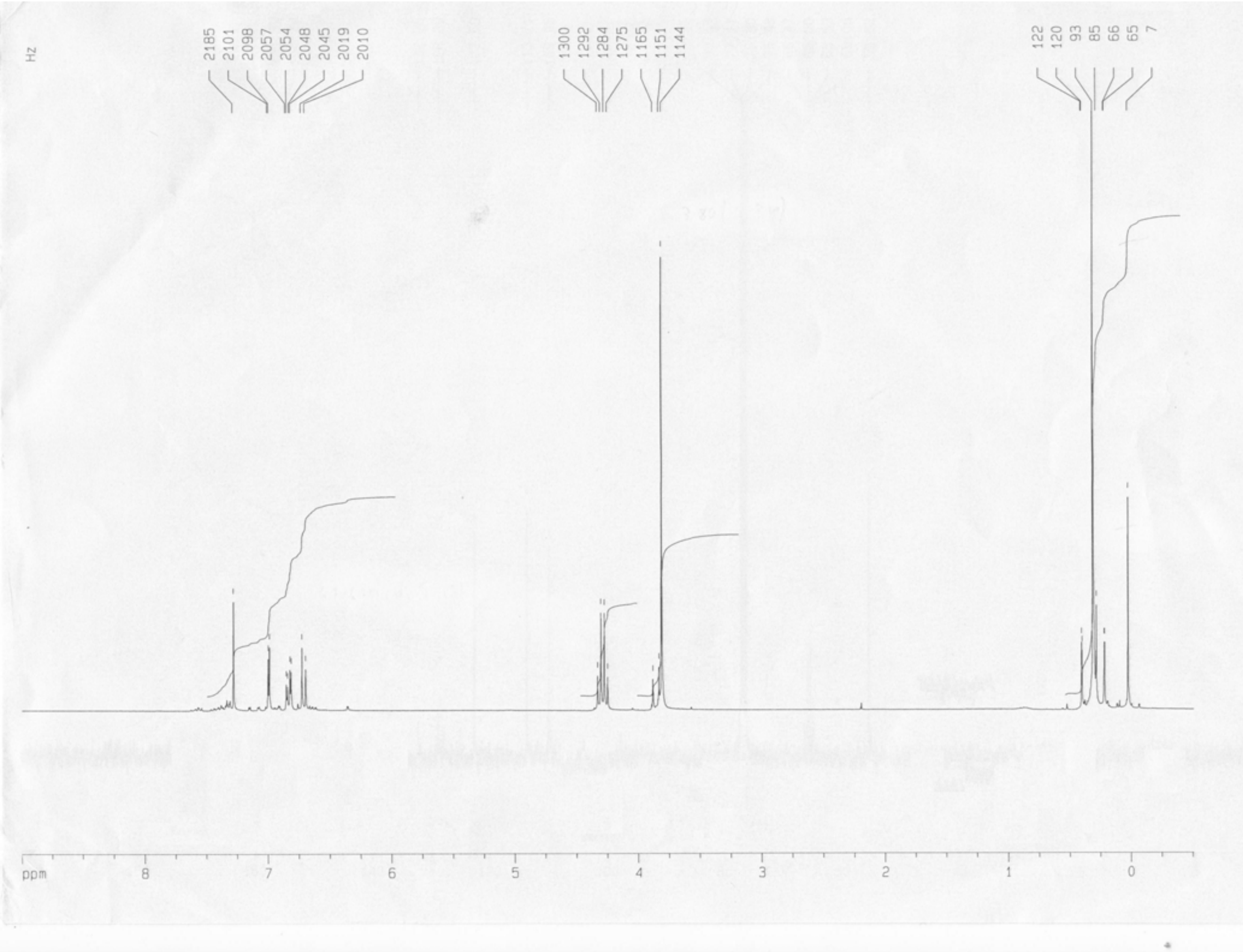
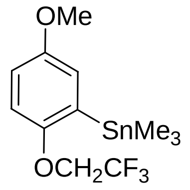
130.09
125.19
121.55
114.18
110.46
77.31
76.89
76.46
66.25
65.79
65.32
64.85
55.57
-0.97
-1.32
ppm
180
160
140
120
100
80
60
40
20
0

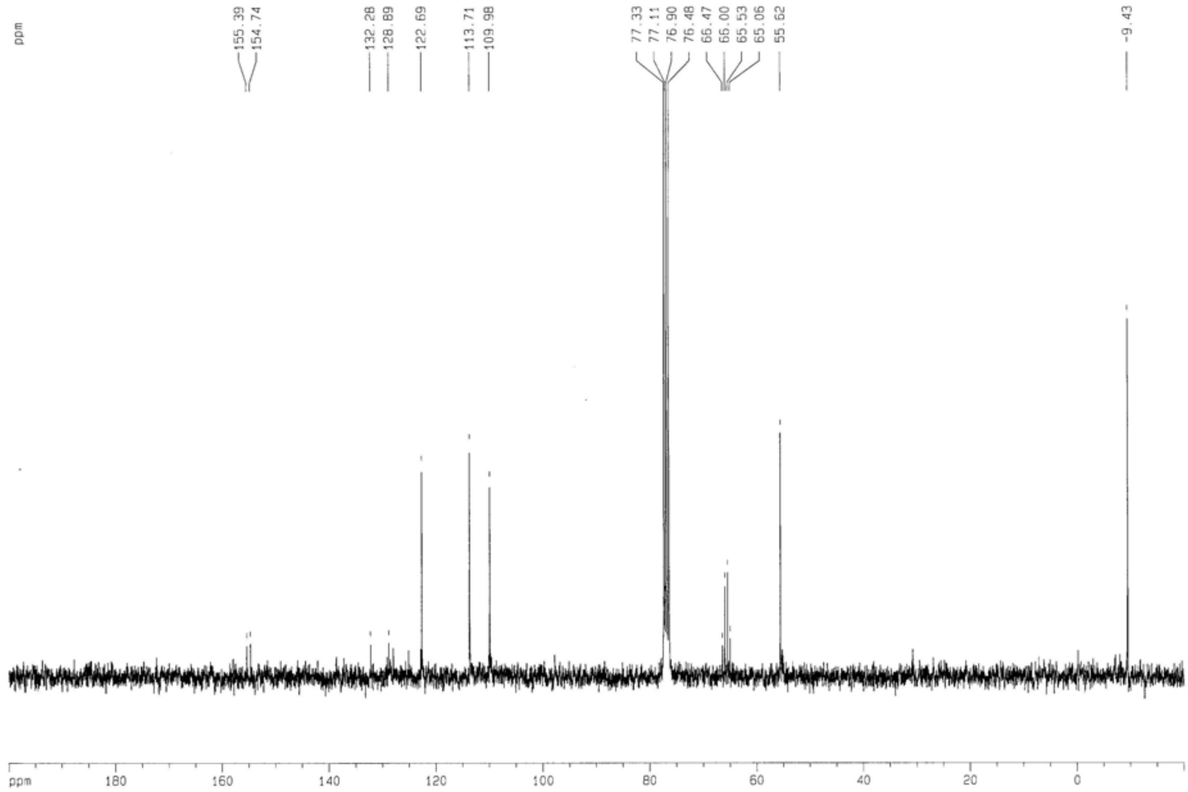

OMe
SnMe3
OCH2CF3

6c [1]H NMR


Hz
2185
2101
2098
2057
2054
2048
2045
2019
2010
1300
1292
1284
1275
1165
1151
1144
122
120
93
85
66
65
7
ppm
8
7
6
5
4
3
2
1
0


OMe
SnMe3
OCH2CF3

6c ^{13}C NMR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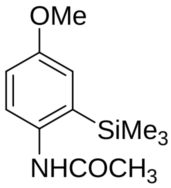
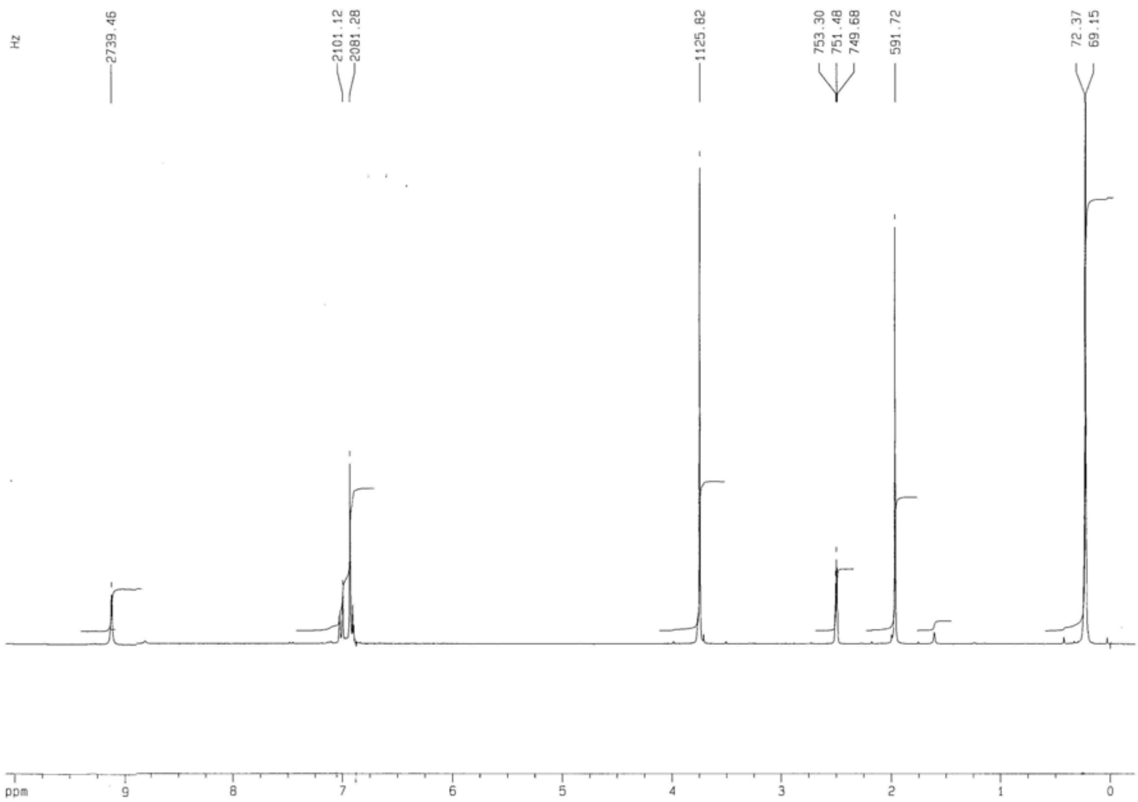
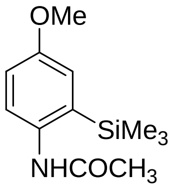
128.89
122.69
113.71
109.98
77.33
77.11
76.90
76.48
66.47
66.00
65.53
65.06
55.62
-9.43
ppm
180
160
140
120
100
80
60
40
20
0

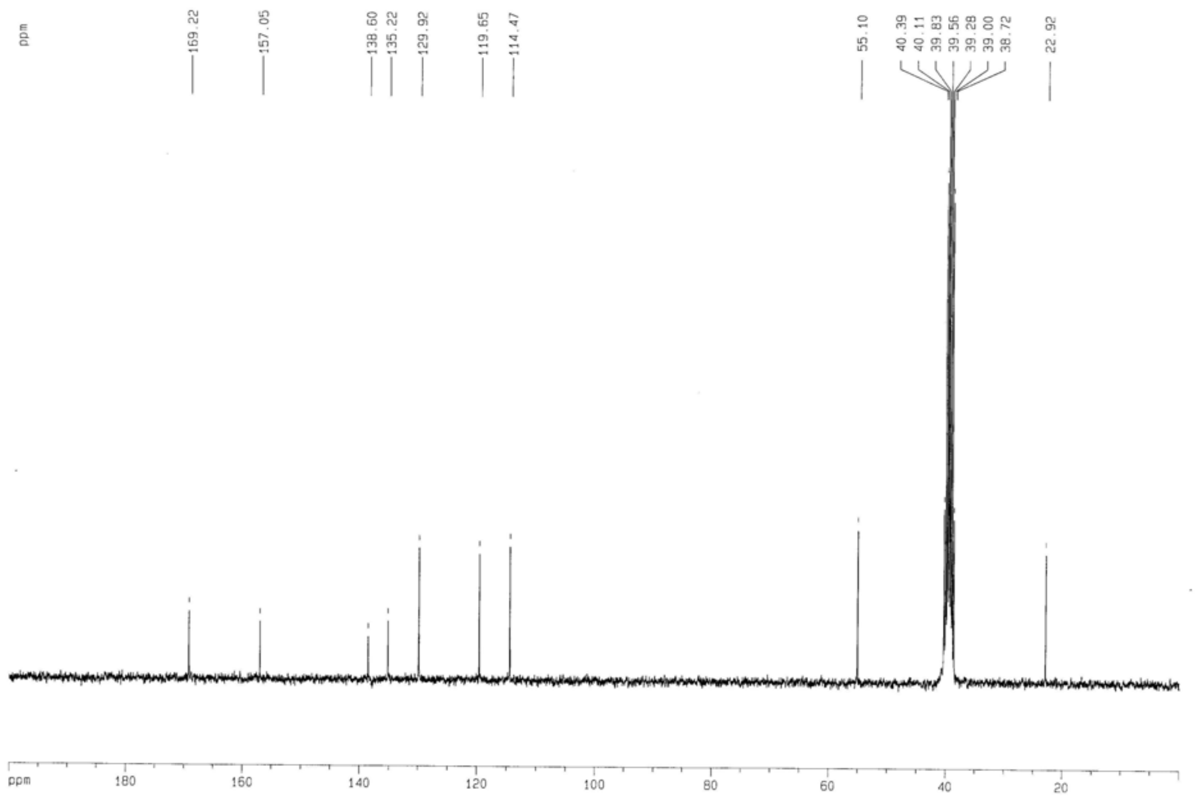

OMe
SiMe3
NHCOCH3

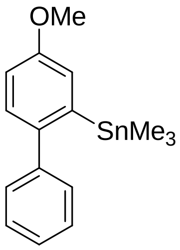
7b, ¹H NMR.


Hz
2739.46
2101.12
2081.28
1125.82
753.30
751.48
749.68
591.72
72.37
69.15
ppm
9
8
7
6
5
4
3
2
1
0

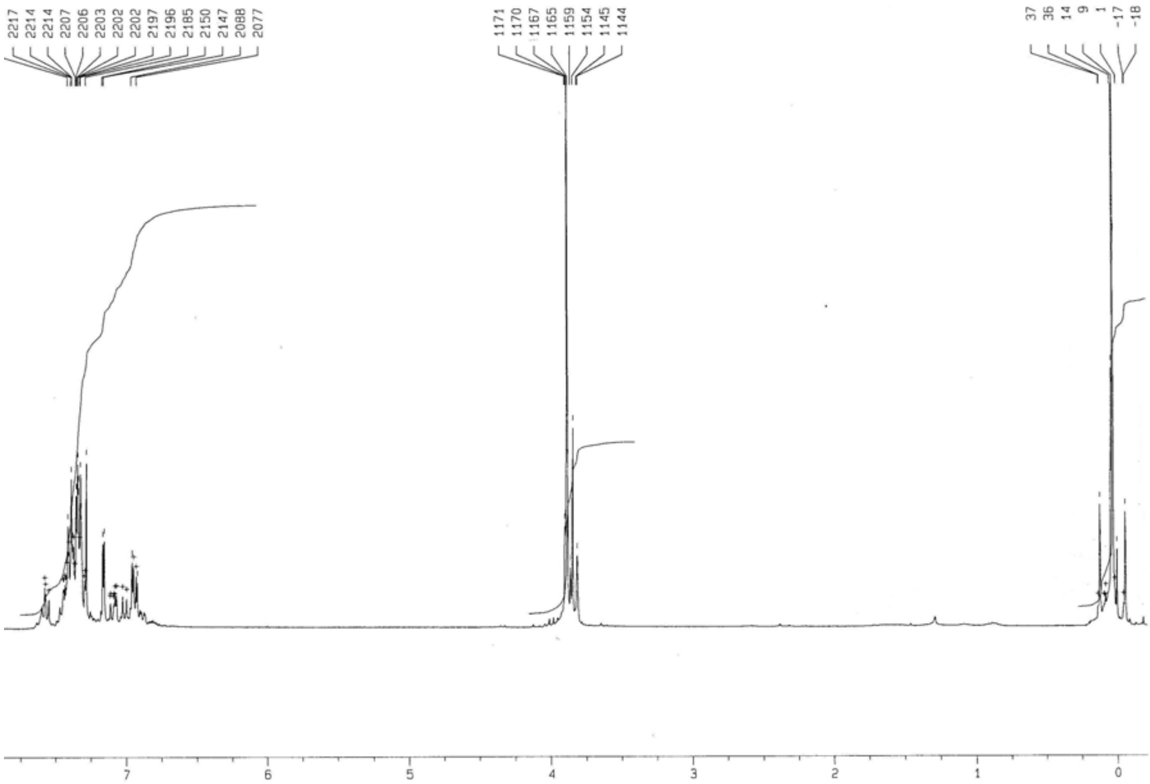

OMe
SiMe3
NHCOCH3

7b, ^{13}C NMR.

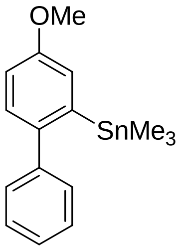

ppm
169.22
157.05
138.60
135.22
129.92
119.65
114.47
55.10
40.39
40.11
39.83
39.56
39.28
39.00
38.72
22.92
ppm
180
160
140
120
100
80
60
40
20



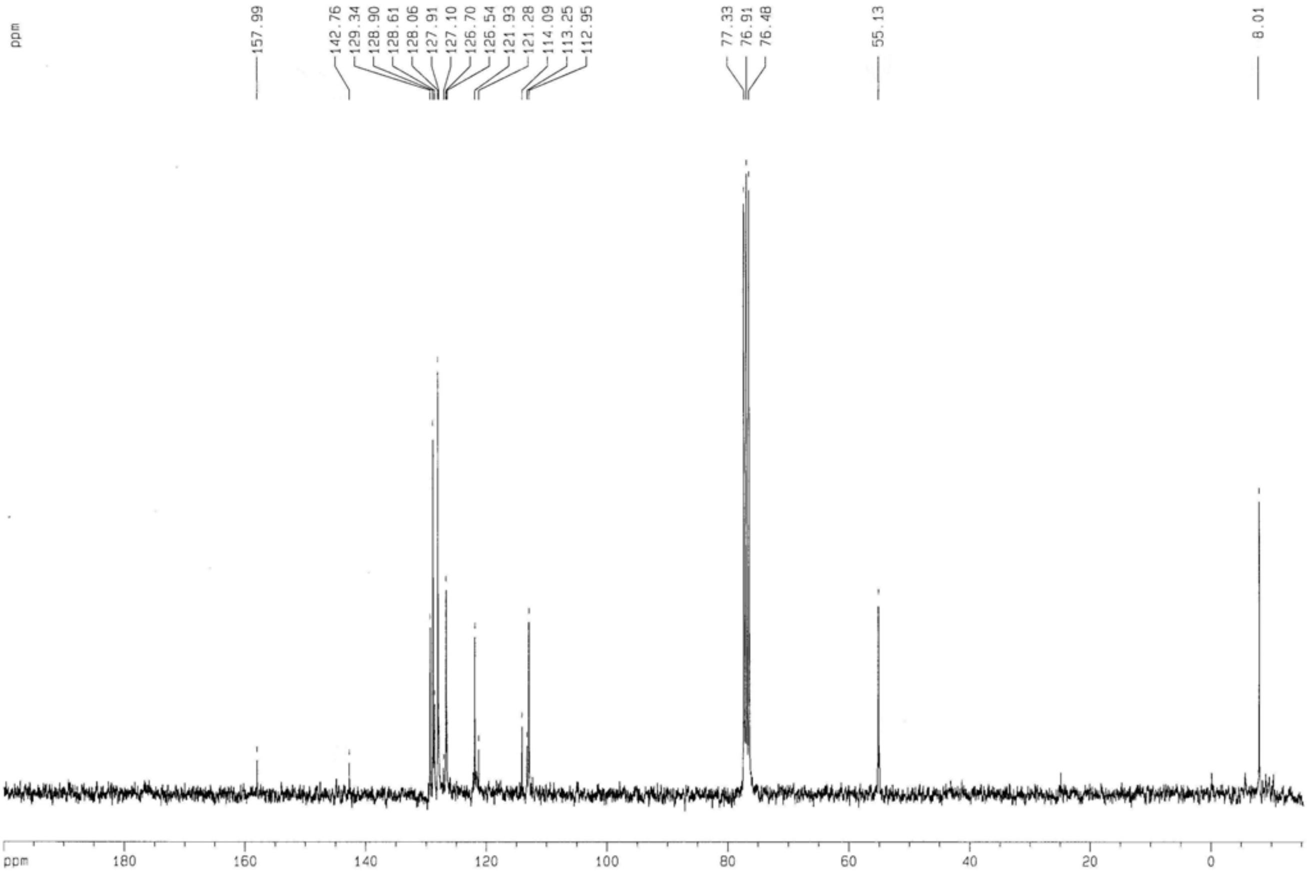
8c [1]H NMR



In this case, a partial destannylation took place during the analysis.


OMe
SnMe3

8c ^{13}C NMR


ppm
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128.90
128.61
128.06
127.91
127.10
126.70
126.54
121.93
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113.25
112.95
77.33
76.91
76.48
55.13
8.01
ppm
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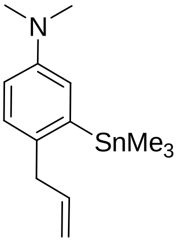
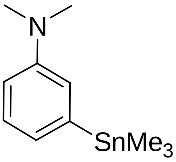
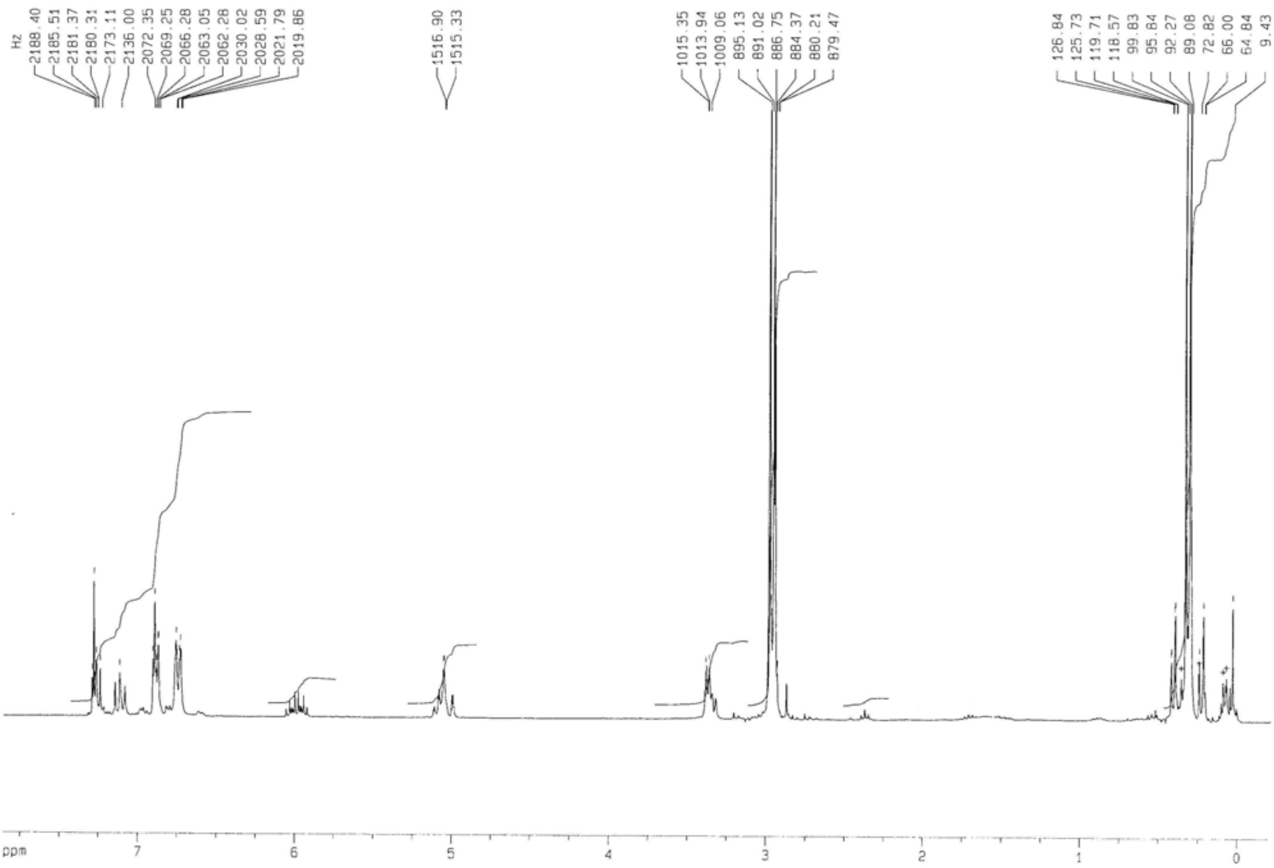
140
120
100
80
60
40
20
0


N
SnMe3

11c +


N
SnMe3

5c [1]H NMR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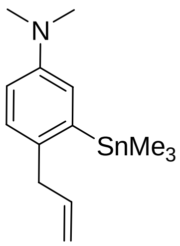
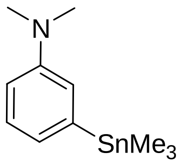
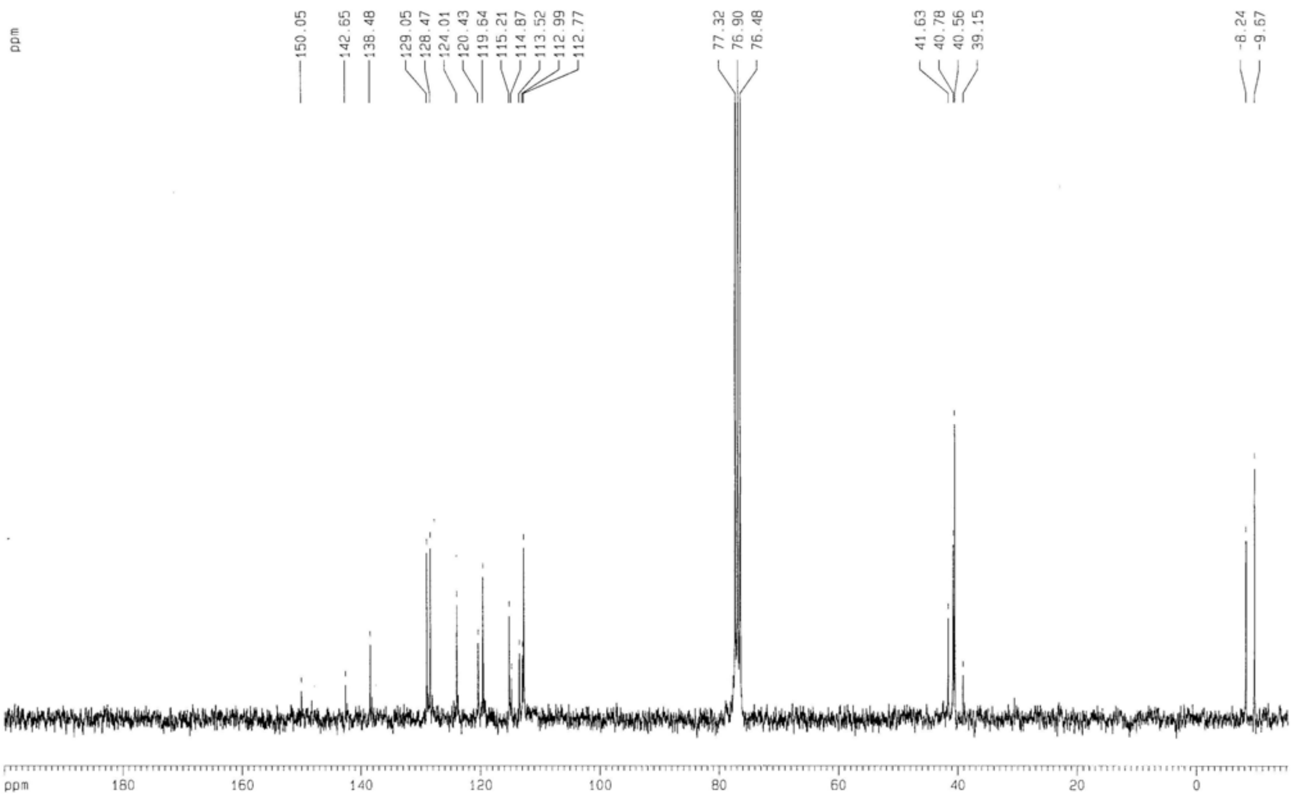
2185.51
2181.37
2180.31
2173.11
2136.00
2072.35
2069.25
2066.28
2063.05
2062.28
2030.02
2028.59
2021.79
2019.86
1516.90
1515.33
1015.35
1013.94
1009.06
895.13
891.02
886.75
884.37
880.21
879.47
126.84
125.73
119.71
118.57
99.83
95.84
92.27
89.08
72.82
66.00
64.84
9.43
ppm
7
6
5
4
3
2
1
0

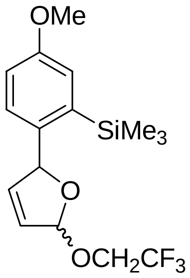


11c +

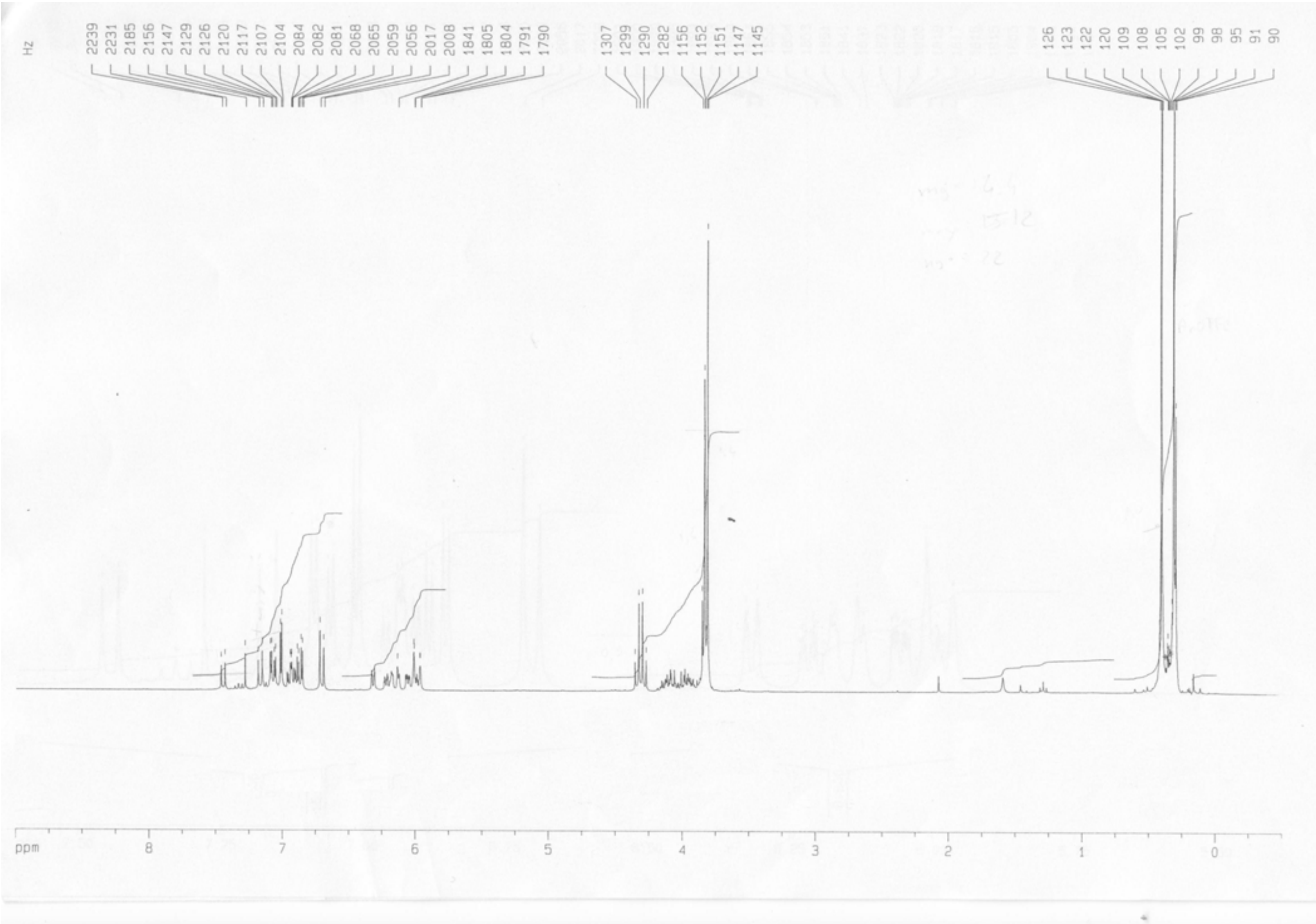


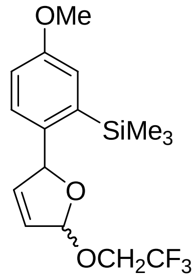
5c ^{13}C NMR



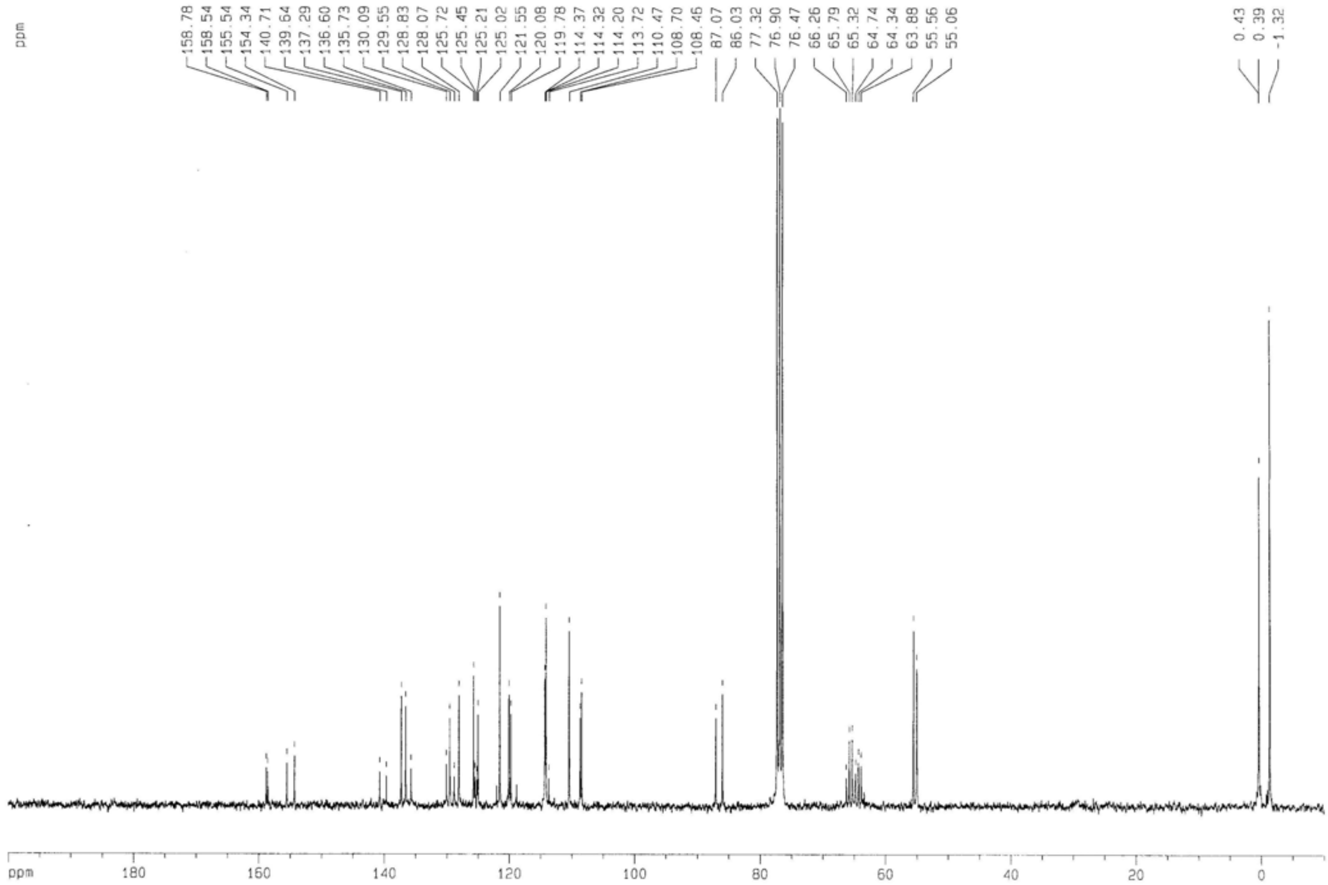


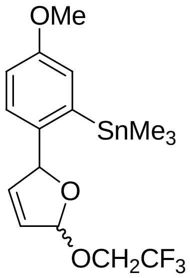
12b + 6b [1]H NMR



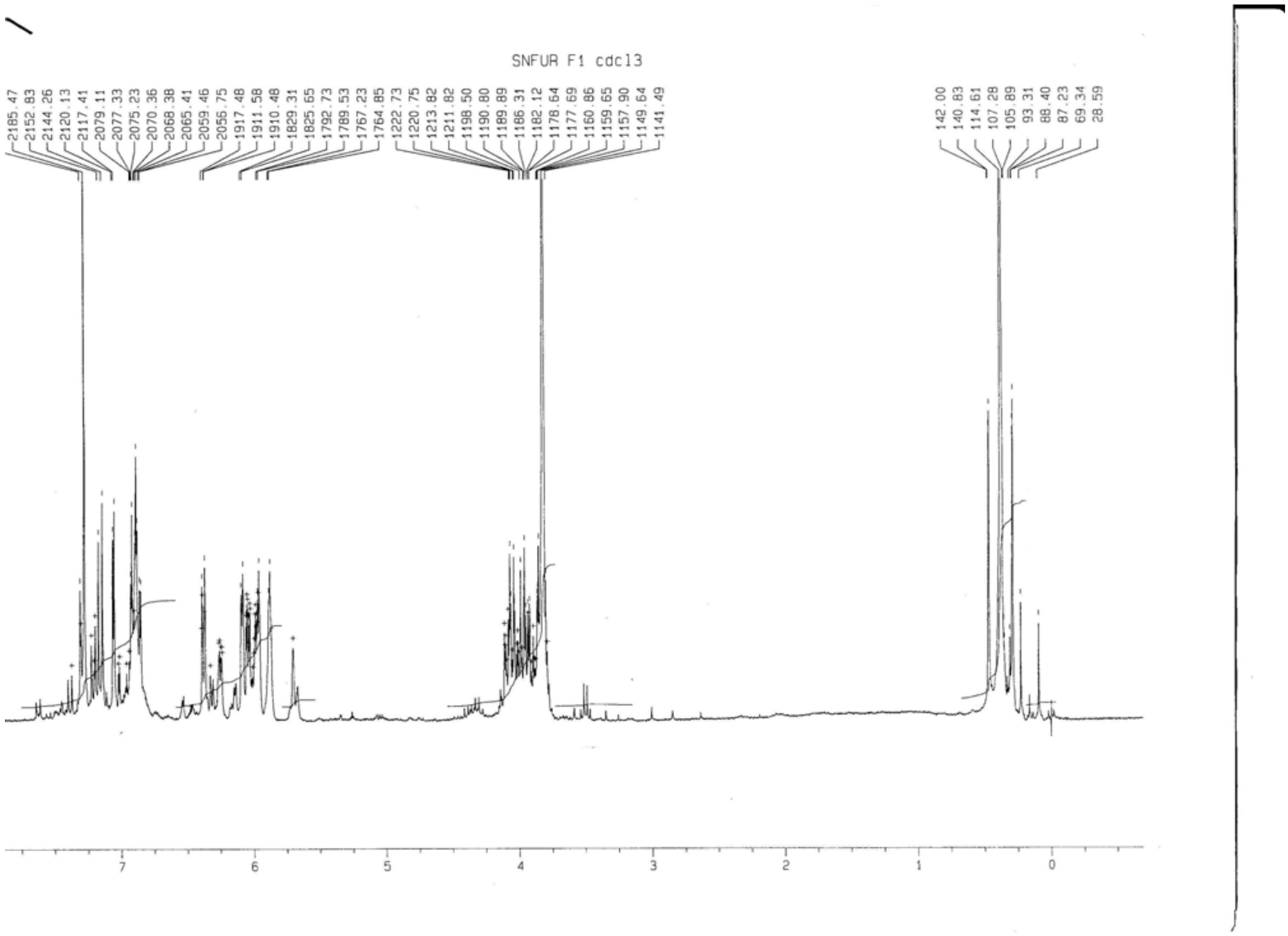


12b+ 6b ^{13}C NMR




OMe
SnMe3
O
OCH2CF3

12c ^{1}H NMR


SNFUR F1 cdcl3
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2144.26
2120.13
2117.41
2079.11
2077.33
2075.23
2070.36
2068.38
2065.41
2059.46
2056.75
1917.48
1911.58
1910.48
1829.31
1825.65
1792.73
1789.53
1767.23
1764.85
1222.73
1220.75
1213.82
1211.82
1198.50
1190.80
1189.89
1186.31
1182.12
1178.64
1177.69
1160.86
1159.65
1157.90
1149.64
1141.49
142.00
140.83
114.61
107.28
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88.40
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69.34
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7
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3
2
1
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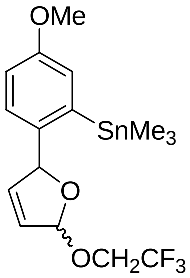
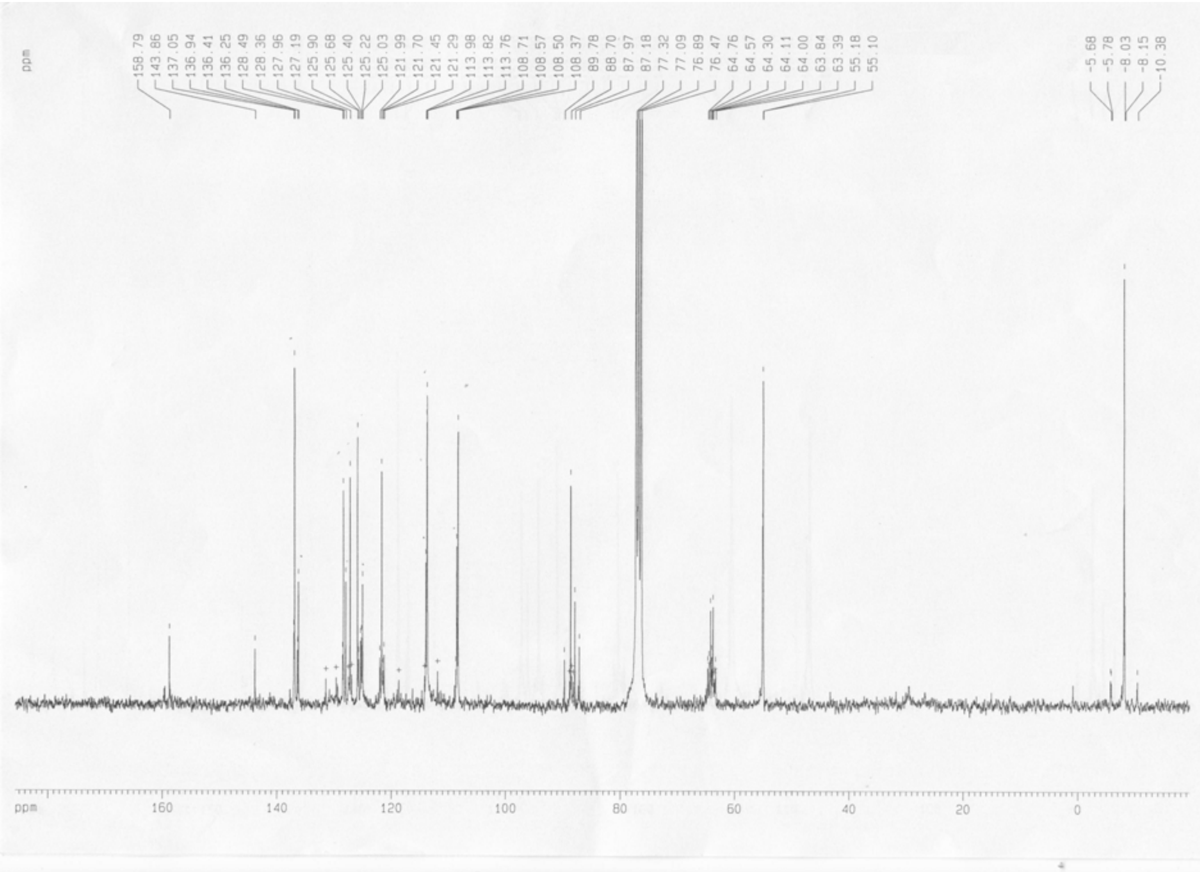

OMe
SnMe3
O
OCH2CF3

12c [13]C NMR


ppm
158.79
143.86
137.05
136.94
136.41
136.25
128.49
128.36
127.96
127.19
125.90
125.68
125.40
125.22
125.03
121.99
121.70
121.45
121.29
113.98
113.82
113.76
108.71
108.57
108.50
108.37
89.78
88.70
87.97
87.18
77.32
77.09
76.89
76.47
64.76
64.57
64.30
64.11
64.00
63.84
63.39
55.18
55.10
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-5.78
-8.03
-8.15
-10.38
ppm
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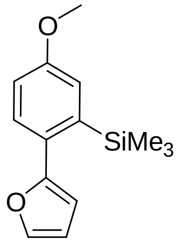
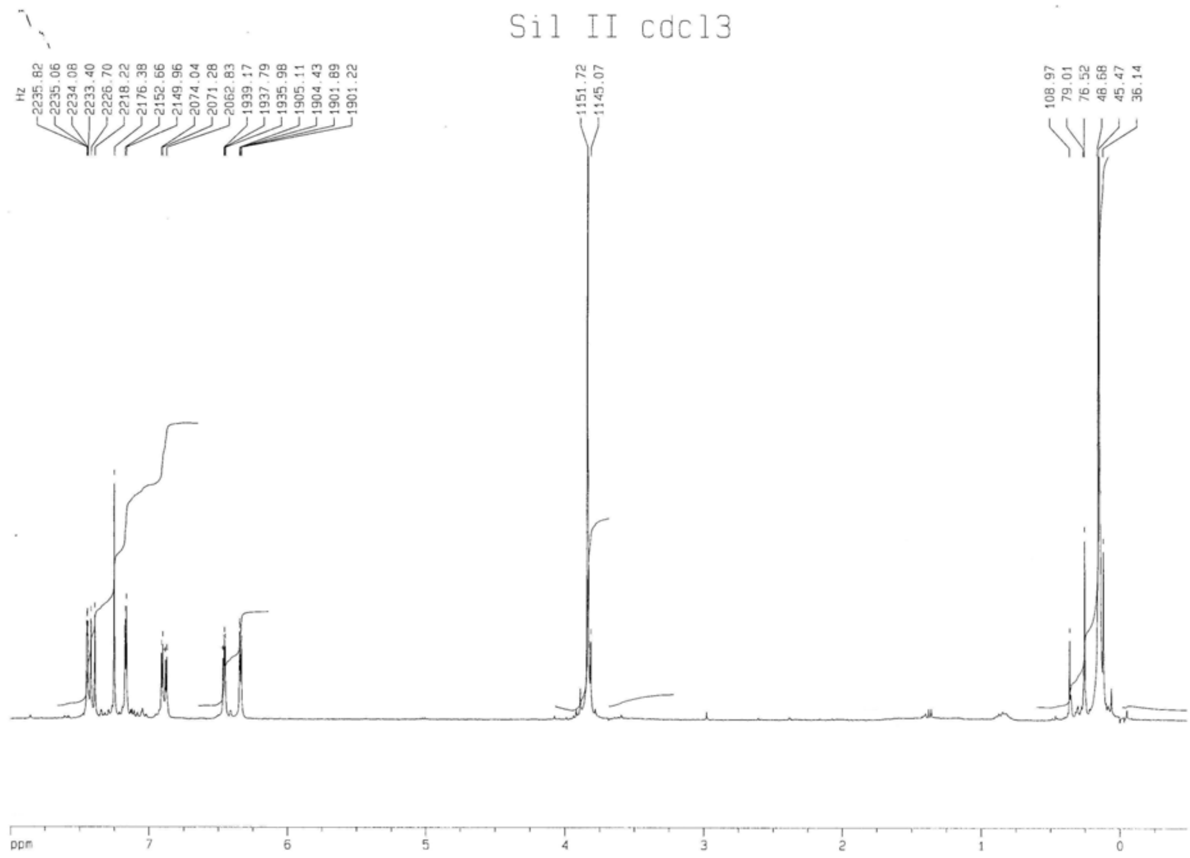
140
120
100
80
60
40
20
0



13b ^{1}H NMR


Sil II cdcl3
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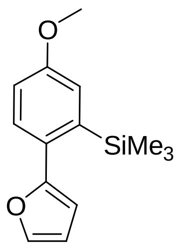
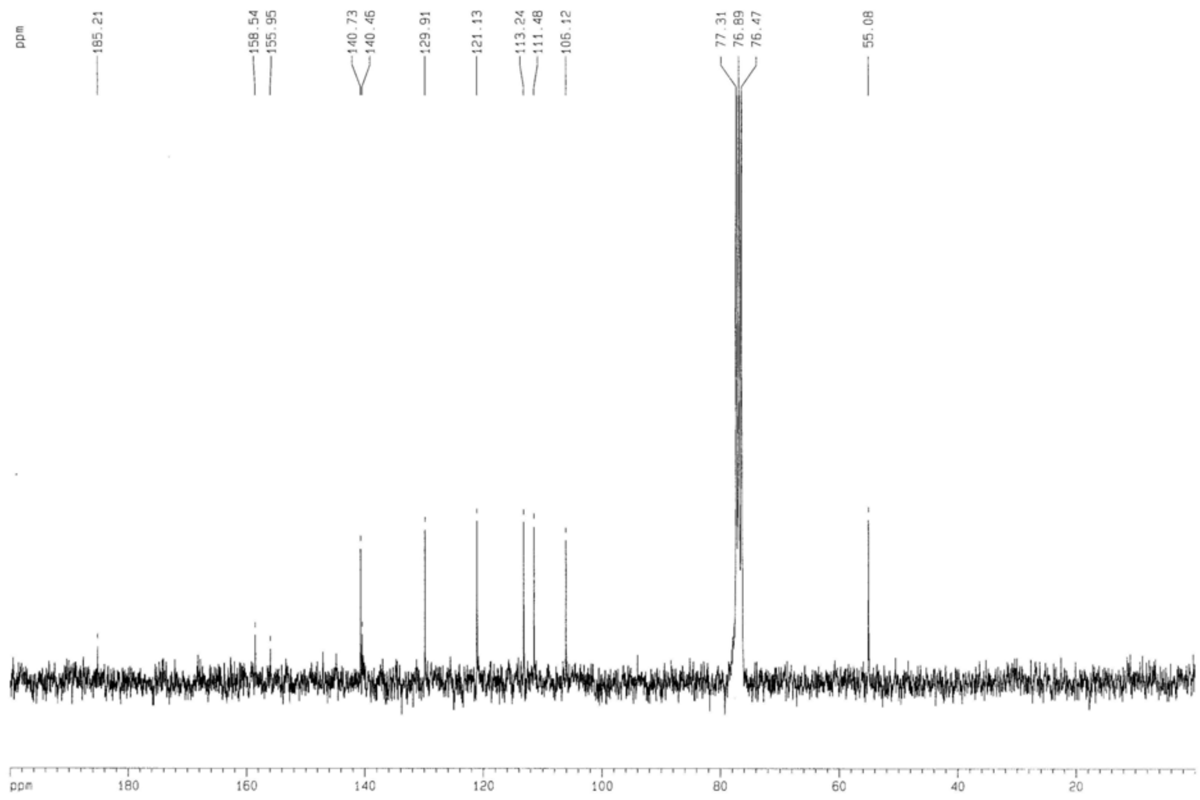
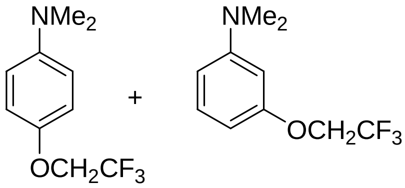
2235.06
2234.08
2233.40
2226.70
2218.22
2176.38
2152.66
2149.96
2074.04
2071.28
2062.83
1939.17
1937.79
1935.98
1905.11
1904.43
1901.89
1901.22
1151.72
1145.07
108.97
79.01
76.52
48.68
45.47
36.14
ppm
7
6
5
4
3
2
1
0

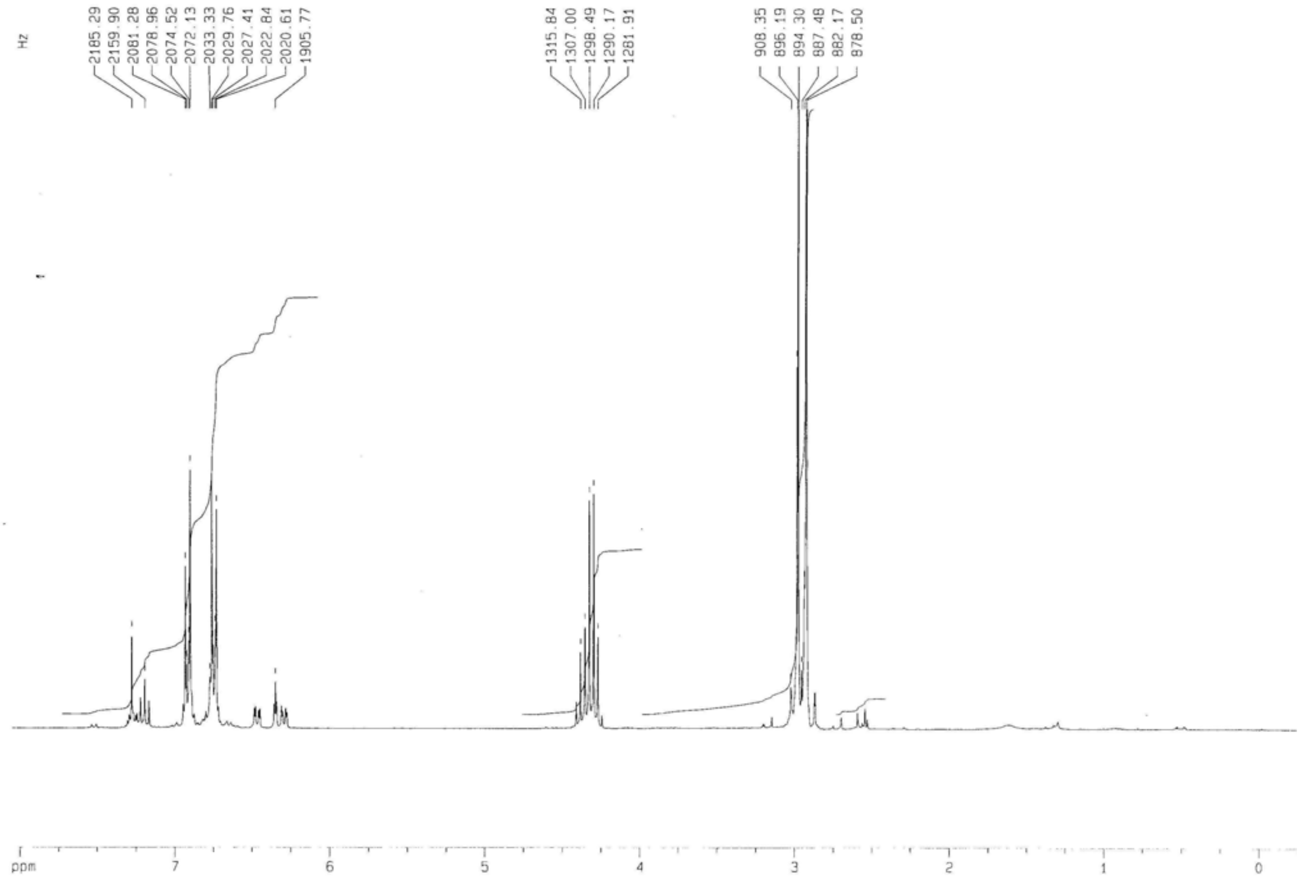

O
SiMe3
O

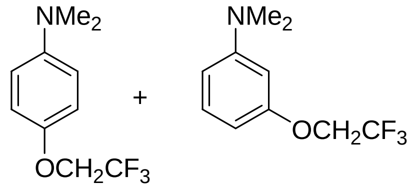
13b ^{13}C NMR


ppm
185.21
158.54
155.95
140.73
140.46
129.91
121.13
113.24
111.48
106.12
77.31
76.89
76.47
55.08
ppm
180
160
140
120
100
80
60
40
20



17a + 17'a ^{1}H NMR





17a + 17'a [13]C NMR