Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Thioether-directed acetoxylation of C(sp^2)−H bond of arenes by palladium catalysis

Binjie Wang,[a] Cong Lin,[a] Yue Liu,[a] Zili Fan,[a] Zhanxiang Liu[a,*] and Yuhong Zhang[a,b,*]

ZJU-NHU United R&D Center, Department of Chemistry, Zhejiang University, Hangzhou 310027, China.

State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China.

***E-mail**: yhzhang@ zju.edu.cn*

Content

General Information The materials and solvents were purchased from common commercial sources and used without additional purification, if there is no special version. ^{1}H NMR spectra were recorded at 400 MHz using TMS as internal standard. ^{13}C NMR spectra were recorded at 100 MHz using TMS as internal standard. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), and broad resonances (br). Mass spectroscopy data were collected on an HRMS-EI and HRMS-ESI instrument.

Preparation and Characterization of Starting Material:

Method A: The procedure for the synthesis of $ArCH_2SAr'$: A 100 mL flask was charged with thiophenol (11.0 mmol) and dry THF (50 mL) in an ice-water bath, then NaH (11 mmol, 0.388 g) was added in portions carefully. Five minutes later, benzyl bromide (10.0 mmol) was dropwised with constantly stirring. This mixture was kept at this temperature for 4 hours. And then 30 mL of water was added to this reaction mixture. At the same time, ethyl acetate (50 mL) was also added and stirring for 5 minutes. The obtained upper layer washed with brine for 3 times, which was dried with anhydrous magnesium sulfate. After that, the solvent was evaporated under reduced pressure and the residue was subjected to flash column chromatography (petroleum ether as eluent) to obtain the thioether.

Characterization Data of the Benzyl(phenyl)sulfane Derivatives:

Benzyl(*p*-tolyl)sulfane[1a] **(1a):** White solid (1.71 g, 80% yield); mp 30-31 ^oC (uncorrected); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.87-7.25 (m, 5H), 7.23 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 4.06 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 137.7, 136.5, 132.4, 130.6, 129.5, 128.7, 128.3, 127.0, 39.7, 20.9.

Benzyl(4-methoxyphenyl)sulfane[3] **(1b):** White solid (2.00 g, 87% yield); mp 41-42 ^oC (uncorrected); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-6.80 (m, 9H), 4.02 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 138.1, 134.2, 129.0, 128.6, 128.5, 127.1, 126.0, 114.4, 55.4, 414.

(2-methylbenzyl)(*p*-tolyl)sulfane[1a] (**1c):** Colorless liquid (1.94 g, 85% yield); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.23-7.21 (m, 2H), 7.15-7.06 (m, 6H), 4.05 (s, 2H), 2.37 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 136.6 (2C), 135.3, 132.7, 131.0, 130.4, 129.7, 129.6, 127.4, 125.9, 38.1, 21.0, 19.1.

(3-methylbenzyl)(*p*-tolyl)sulfane[1a] **(1d):** Colorless liquid (1.96 g, 86% yield); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.21-7.00 (m, 8H), 4.01 (s, 2H), 2.29 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 137.6, 136.4, 132.8, 130.5, 129.6, 128.3, 127.8, 125.9, 39.7, 21.3, 21.0.

(4-methylphenethyl)(*p*-tolyl)sulfane[1c] **(1e):** White solid (1.94 g, 85% yield); mp 35-36 ^oC (uncorrected); ^1H NMR (400 MHz, $CDCl_3$) δ 7.23-7.20 (m, 2H), 7.16-7.14 (m, 2H), 7.08-7.04 (m, 4H), 4.03 (s, 2H), 2.31 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 136.4, 134.6, 132.7, 130.5, 129.6, 129.1, 128.7, 39.4, 21.1, 21.0.

(3-methoxybenzyl)(p-tolyl)sulfane[1b] **(1f):** Colorless liquid (1.95 g, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.23-7.20 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.80 (s, 1H), 6.76 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 4.03 (s, 2H), 3.74 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 139.3, 136.5, 132.4, 130.7, 129.6, 129.4, 121.1, 114.1, 112.8, 55.1, 39.4, 21.0.

(2-fluorobenzyl)(*p*-tolyl)sulfane[1b] **(1g):** Colorless liquid (1.95 g, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.24-7.18 (m, 4H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.04-6.99 (m, 2H), 4.09 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1 (*J* = 245 Hz), 136.4，131.2，130.8，130.3 (*J* = 2.2 Hz), 129.0，128.2 (*J* = 8.2 Hz), 124.5 (*J* = 15.2 Hz), 123.4 (*J* = 4.3 Hz), 114.8 (*J* = 22.4 Hz), 32.3 (*J* = 1.9 Hz), 20.5.

(3, 4-dichlorobenzyl)(*p*-tolyl)sulfane[1a] **(1h):** White solid (2.54 g, 90% yield); mp 47-48 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.08-7.03 (m, 3H), 3.95 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 138.3, 137.2, 132.2, 131.3, 131.1, 130.9, 130.6, 130.2, 129.7, 128.0, 38.9, 21.0.

(3-bromobenzyl)(*p*-tolyl)sulfane (1i): Colorless liquid (2.53 g, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.37 (s, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.13-7.10 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 3.98 (s, 2H), 2.30 (s, 3H), ^{13}C NMR (100MHz, $CDCl_3$) δ 140.3, 137.1, 131.9,131.7, 131.2, 130.2, 130.0, 129.8, 127.5, 122.4, 39.5, 21.1. IR (neat, cm^{-1}) 3018, 2732, 1594, 1492, 1425, 1091, 1070, 802, 780, 686; HRMS (EI) Calcd for $C_{14}H_{13}BrS$ (M^+), 291.9921; Found, 291.9916.

***p*-tolyl(2-(trifluoromethyl)benzyl)sulfane (1j):** Colorless liquid (2.14 g, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.62 (d, *J* = 7.6Hz, 1H), 7.42 (d, *J* = 6.4 Hz, 2H), 7.30 (dd, J_1 = 7.2 Hz, J_2 =7.2Hz, 2H), 7.23 (m, 2H), 7.07 (d, *J* = 8.0Hz, 2H), 4.23 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 137.1, 136.4, 132.0, 131.9, 131.3, 129.8, 128.3, 127.2, 126.1(q, *J* = 22 Hz), 125.8, 123.0, 36.5, 21.1. IR (neat, cm^{-1}) 2923, 1606, 1492, 1452, 1313, 1240, 1116, 1059, 1036, 804, 766, 652. HRMS (EI) Calcd for $C_{15}H_{13}F_3S$ (M^+), 282.0690; Found, 282.0687.

***p*-tolyl(4-(trifluoromethoxy)benzyl)sulfane**[2] **(1k):** White solid (2.56 g, 86% yield); mp 42-43 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.24 (d, *J* = 8.8, 2H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.05-7.11 (m, 4H), 4.03 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 148.2, 137.1, 136.7, 131.7, 131.2, 130.2, 130.0, 120.9, 39.2, 21.1.

4-(*p*-tolylthiomethyl)benzonitrile[1c] **(1l):** Light yellow solid (2.03 g, 85% yield); mp 45-46 °C (uncorrected); ^{1}H NMR (400MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 4.03 (s, 2H), 2.30 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 137.5, 132.2, 131.7, 130.9, 129.8, 129.5, 118.8, 110.8, 39.8, 21.1.

Methyl 4-(p-tolylthiomethyl)benzoate (1m): Colorless liquid (2.42g, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.30-7.23 (m, 2H), 7.20-7.17 (m, 2H), 7.13-7.11 (m, 2H), 7.02-6.99 (m, 2H), 4.03 (s, 2H), 2.33 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 169.6, 149.2, 137.9, 136.3, 130.2, 129.8, 129.5, 121.6, 35.8, 35.7, 21.2, 21.1. IR (neat, cm^{-1}) 3031, 2917, 1746, 1651, 1438, 1371, 1223, 1197, 1095, 913, 846, 745. HRMS (EI) Calcd for $C_{16}H_{16}O_2S$ (M^+), 272.0871; Found, 272.0869.

Method B: The procedure for the synthesis of $ArCH_2CH_2SOAr'$:

A mixture of thiophenol (11.0 mmol) and styrene (10.0 mmol) in H_2O (50 mL) was stirred at 50 °C for 12 h. This mixture was kept at this temperature for 4 hours. And then 30 mL aqueous solution of NaOH (20 mmol, 800 mg) was added to this reaction mixture. After that, ethyl acetate (50 mL) was also added and stirring for 5 minutes, the obtained upper layer washed with brine for 3 times, which was dried with anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure and the residue was subjected to flash column chromatography (petroleum ether as eluent) to obtain the thioether.

Characterization Data of the Phenethyl(phenyl)sulfane Derivatives:

Phenethyl(*p*-tolyl)sulfane[1a] **(3a):** Colorless liquid (2.17 g, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.30-7.26 (m, 4H), 7.22-7.16 (m, 3H),7.10 (d, *J* = 8.0 Hz, 2H), 3.11 (t, *J* = 8.0 Hz, 2H), 2.88 (t, *J* = 8.0 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 140.3, 136.1, 132.4, 130.1, 129.7, 128.5, 128.4, 126.3, 35.8, 35.7, 21.0.

(2-methylphenethyl)(*p*-tolyl)sulfane (3b): Colorless liquid (2.30 g, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.29-7.27 (m, 2H), 7.11-7.08 (m, 6H), 3.03 (t, *J* = 8.0 Hz, 2H), 2.89 (t, *J* = 8.0 Hz, 2H), 2.30 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 138.6, 136.3, 136.0, 132.6, 130.4, 130.2, 129.8, 129.1, 126.6, 126.2, 34.7, 33.4, 21.2, 19.3. IR (neat, cm^{-1}) 2920, 1491, 1455, 1093, 1018, 803, 743. HRMS (EI) Calcd for $C_{16}H_{18}S$ (M^+), 242.1129; Found, 242.1130.

(3-methylphenethyl)(*p*-tolyl)sulfane (3c): Colorless liquid (2.30 g, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.25 (d, *J* = 8.0 Hz, 2H), 7.00-6.96 (m, 6H), 3.07 (t, *J* = 8.0 Hz, 2H), 2.83 (t, *J* = 8.4

Hz, 2H), 2.30 (s, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ 140.4, 138.2, 136.2, 132.8, 130.2, 130.0, 129.5, 128.6, 127.3, 125.7, 35.9, 35.9, 21.6, 21.2. IR (neat, cm^{-1}) 2910, 1491, 14665, 1103, 1015, 801, 733. HRMS (EI) Calcd for $C_{16}H_{18}S$ (M^+), 242.1129; Found, 242.1126.

(4-methylphenethyl)(*p*-tolyl)sulfane (3d): Colorless liquid (2.18 g, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.08-7.05 (m, 6H), 3.09-3.05 (m, 2H), 2.85-2.82 (m, 2H), 2.29 (s, 2H), 2.30 (s, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ 137.4, 136.2, 136.0, 132.7, 130.1, 129.8, 129.3, 128.5, 36.0, 35.4, 21.2, 21.2. IR (neat, cm^{-1}) 3018, 2920, 1700, 1606, 1513, 1446, 1042, 802. HRMS (EI) Calcd for $C_{16}H_{18}S$ (M^+), 242.1129; Found, 242.1126.

(2-phenylpropyl)(*p*-tolyl)sulfane[2] **(3e):** olorless liquid (2.25 g, 93% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.29 (m, 2H), 7.24-7.21 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.16-3.20 (d, *J* = 6.5 Hz, 1H), 2.99-3.03 (d, *J* = 8.5 Hz, 1H), 2.94 (sext, *J* = 7.0 Hz, 1H), 2.31 (s, 3H), 1.38 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6. 136.0, 132.9, 129.9, 129.6, 128.5, 126.9, 126.5, 42.8, 39.4, 21.0, 20.9.

(3-fluorophenethyl)(*p*-tolyl)sulfane[2] **(3f):** olorless liquid (2.07 g, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.24-7.22 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.89-6.86 (m, 2H), 3.12-3.08 (m, 2H), 2.88 (t, *J* = 7.8 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 162.9 (*J* = 245.5 Hz), 142.8 (*J* = 7.3 Hz), 136.5, 132.2, 130.4, 130.0 (*J* = 8.4 Hz), 129.8, 124.2 (*J* = 2.8 Hz), 115.4 (*J* = 20.7 Hz), 113.3 (*J* = 20.5 Hz), 35.6, 35.5, 21.1.

(3-chlorophenethyl)(*p*-tolyl)sulfane[2] **(3g):** olorless liquid (2.04 g, 78% yield) ; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.21-7.19 (m, 2H), 7.16 (s, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.06-7.04 (m, 1H), 3.13-3.07 (m, 2H), 2.86 (t, *J* = 8.0 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 142.3, 136.5, 134.2, 132.1, 130.4, 129.8, 129.7, 128.7, 126.8, 126.6, 35.7, 35.4, 21.1.

(3-bromophenethyl)(*p*-tolyl)sulfane (3h) : Colorless liquid (2.69 g, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.31 (d, *J* = 9.6 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.12-7. 06 (m, 4H), 3.06 (t, *J* = 7.8 Hz, 2H), 2.83 (t, *J* = 7.8 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 142.6, 136.5, 132.1, 131.7, 130.5, 130.1, 130.0, 129.6, 127.3, 122.6, 35.7, 35.4, 21.2. IR (neat, cm^{-1}) 3018, 2919, 2732, 1594, 1567, 1492, 1473, 1452, 1091, 1070,802, 780. HRMS (EI) Calcd for $C_{15}H_{15}BrS$ (M^+), 306.0078; Found, 306.0075.

(2-(naphthalen-2-yl)ethyl)(*p*-tolyl)sulfane (3i): olorless liquid (2.47 g, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.78 (m, 3H), 7.64 (s, 1H), 7.49-7.45 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 3H), 7.14 (d,

J = 8.0 Hz, 2H), 3.25-3.21 (m, 2H), 3.10-3.06 (t, *J* = 7.6 Hz, 2H), 2.35 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 136.3. 135.6, 132.5, 132.2, 130.3, 129.8, 128.1, 127.7, 127.5, 127.1, 126.8, 126.1, 125.5, 36.0, 35.8, 21.1; IR (neat, cm^{-1}): 2909, 1711, 1436, 1271, 1171, 1047, 741; HRMS (EI) Calcd for $C_{19}H_{18}S$ (M+) 278.1129; Found, 278.1126.

Preparation and Characterization of Products:

A mixture of benzyl sulfide derivative (0.2 mmol), $PhI(OAc)_2$ (0.3 mmol), $Pd(OAc)_2$ (4 mg, 10 mol%), AgOAc (33 mg, 0.2 mmol) in 2 mL DCE/Ac_2O (1:1) was stirred at 110 ^oC for 24 h. Afterward, the reaction mixture was allowed to cool to room temperature and filtered through a pad of celite. The solvent was evaporated under reduced pressure and the residue was subjected to flash column chromatography (silica gel, ethyl acetate / petroleum ether = 1: 10, v/v) to obtain the desired products.

2-(*p*-tolylthiomethyl)phenyl acetate (2a): Yellow liquid (43 mg, 79% yield);^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.23-7.26 (m, 1H), 7.17-7.20 (m, 3H), 7.11 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.06 (t, *J* = 8.0 Hz, 3H), 3.97 (s, 2H), 2.30 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 169.3, 148.9, 137.0, 132.0, 131.4, 130.6, 129.8, 129.7, 128.3, 125.9, 122.7, 35.0, 21.1, 21.0; IR (neat, cm^{-1}) 3023, 2923, 1765, 1490, 1368, 1203, 1171, 1040, 1012, 915, 805, 757; HRMS (EI) Calcd for $C_{16}H_{16}O_2S$ (M^+), 272.0871; Found, 272.0872.

2-((4-methoxyphenylthio)methyl)phenyl acetate (2b): White liquid (38 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.21-7.24 (m, 3H), 7.04-7.08 (m, 3H), 6.76 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 2H), 3.76 (m, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 169.3, 159.5, 148.8, 134.7, 130.8, 130.1, 128.2, 125.8, 125.5, 122.8, 114.5, 55.3, 36.3, 21.1; IR (neat, cm^{-1}) 2938, 2836, 1763, 1590, 1491, 1243, 1202, 1171, 1029, 826; HRMS (EI) Calcd for $C_{16}H_{16}O_3S$ (M^+), 288.0820; Found, 288.0822.

3-methyl-2-(*p*-tolylthiomethyl)phenyl acetate (2c): Light yellow liquid (37 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.26 (d, *J* = 8.4 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8 Hz, 1H), 4.00 (s, 2H), 2.32 (s, 3H), 2.27 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 169.4, 149.3, 138.9, 137.2, 132.5, 132.0, 129.6, 128.0, 127.9, 127.7, 120.3, 32.1,21.1,21.0,19.3. IR (neat, cm^{-1}) 3021, 2920, 1766, 1469, 1367, 1203,

1181, 960, 792; HRMS (EI) Calcd for $C_{17}H_{18}O_2S$ (M^+), 286.1028; Found, 286.1027.

4-methyl-2-(*p*-tolylthiomethyl)phenyl acetate (2d): Light yellow liquid (38 mg, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.20 (d, *J* = 8.4 Hz, 2H), 7.04-7.07 (m, 3H),7.02 (s, 1H), 6.95 (d, *J* = 8 Hz, 1H), 3.94 (s, 2H), 2.31 (s, 3H), 2.27 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 169.5, 146.6, 136.8, 135.6, 132.3, 131.2, 131.2, 129.6, 129.2, 128.9, 122.4, 34.9, 21.1, 21.0, 20.8; IR (neat, cm^{-1}) 2926, 1772, 1460, 1198, 1119, 879, 766; HRMS (EI) Calcd for $C_{17}H_{18}O_2S$ (M^+), 286.1028; Found, 286.1031.

5-methyl-2-(*p*-tolylthiomethyl)phenyl acetate (2e): Colorless liquid (41 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.20 (d, *J* = 8.4 Hz, 2H), 7.05-7.09 (m, 3H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.88 (s, 1H), 3.94(s, 2H), 2.32 (s, 3H), 2.30 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 169.4, 148.7, 138.6, 136.8, 132.3, 131.1, 130.4, 129.6, 126.8, 126.6, 123.2, 34.7, 21.1, 21.0; IR (neat, cm^{-1}) 2922, 1767, 1495, 1368, 1194, 1140, 1015, 805; HRMS (EI) Calcd for $C_{17}H_{18}O_2S$ (M^+), 286.1028; Found, 286.1028.

4-methoxy-2-((p-tolylthio)methyl)phenyl acetate (2f): Colorless liquid (48 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.20 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 1H), 6.77 (dd, J_1 = 8.8 Hz, J_2 = 3.2 Hz, 1H), 6.70 (d, *J* = 3.2 Hz), 3.92 (s, 2H), 3.68 (s, 3H), 2.30 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 169.8, 157.1, 142.3, 137.0, 131.9, 131.4, 130.7, 130.5, 129.7, 123.4, 115.3, 113.7, 55.5, 35.0, 21.1, 21.0; IR (neat, cm^{-1}) 2929, 1777, 1495, 1360, 1198, 1141, 815; HRMS (EI) Calcd for $C_{17}H_{18}O_3S$ (M^+), 302.0977; Found, 302.0975.

3-fluoro-2-(*p*-tolylthiomethyl)phenyl acetate (2g): Light yellow liquid (26 mg, 45% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.25 (d, *J* = 7.6 Hz, 2H), 7.20-7.22 (m, 1 H), 7.06 (d, *J* = 8 Hz, 2H), 6.86-6.91 (m, 2H), 4.00 (s, 2H), 2.31(s, 3H,), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 168.8, 161.2 (d, *J* = 246 Hz, C-F), 149.8 (d, *J* = 6.4 Hz), 137.5, 132.6, 131.4, 129.6, 128.3 (d, *J* = 10 Hz), 118.8 (d, *J* = 17.2 Hz), 118.6 (d, *J* = 3.0 Hz), 112.8 (d, *J* = 22 Hz), 28.6 (d, *J* = 3 Hz), 21.1, 20.9; IR (neat, cm^{-1}) 2923, 1770, 1587, 1466, 136, 1167, 1018, 806, 749; HRMS (EI) Calcd for $C_{16}H_{15}FO_2S$ (M^+), 290.0777; Found, 290.0778.

4,5-dichloro-2-(*p*-tolylthiomethyl)phenyl acetate (2h): Light yellow liquid (31 mg, 46% yield); ^{1}H NMR (400MHz, $CDCl_3$, TMS): δ 7.21 (d, *J* = 6.0 Hz, 2H), 7.18 (s, 1H), 7.17 (s, 1H), 7.08 (d, *J* = 8Hz, 2H), 3.86 (s, 2H), 2.31 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 168.6, 147.3, 137.7, 132.0, 131.5, 131.4, 130.8, 130.5, 129.8, 129.5, 124.8, 34.5, 21.1, 20.9; IR (neat, cm^{-1})

2922, 1760, 1494, 1367, 1215, 1094, 942, 805, 635; HRMS (EI) Calcd for $C_{16}H_{14}Cl_2O_2S$ (M^+), 340.0092; Found, 340.0090.

4-bromo-2-(*p*-tolylthiomethyl)phenyl acetate (2i): Colorless liquid (38 mg, 54% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS):δ 7.36 (dd, J_1 = 7.2 Hz, J_2 = 2.4 Hz, 1H), 7.27 (d, J = 2.4 Hz, 1H), 7.18 (d, J = 8 Hz, 2H), 7.07 (d, J = 8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 1H),3.89 (s, 2H), 2.32 (s, 3H), 2.28 (s, 3H). ^{13}CNMR (100 MHz, $CDCl_3$, TMS): δ 168.9, 147.8, 137.5, 133.4, 132.2, 131.9, 131.2, 131.2, 129.8,124.4, 118.8, 34.8, 21.1,21.0; IR (neat, cm^{-1}) 2950, 1774, 1460, 1355, 1233, 1200, 890; HRMS (EI) Calcd for $C_{16}H_{15}BrO_2S$ (M^+), 349.9976; Found, 349.9981.

2-(*p*-tolylthiomethyl)-3-(trifluoromethyl)phenyl acetate (2j): Colorless liquid (31 mg, 46 yield); ^{1}H NMR (400MHz, $CDCl_3$, TMS): δ 7.53 (d, J = 7.6 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.26-7.32 (m, 3H), 7.10 (d, J = 8 Hz, 2H), 4.17 (s, 2H), 2.33 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 168.9, 150.3, 137.5, 132.4, 132.1, 129.7, 129.4, 129.1, 128.1, 127.7, 127.0, 123.6 (q, J = 25.6 Hz), 32.0, 32.3 21.1, 21.0; IR (neat, cm^{-1}) 2922, 1760, 1494, 1367, 1187, 1094, 1011, 905, 805; HRMS (EI) Calcd for $C_{17}H_{15}F_3O_2S$ (M^+), 340.0745; Found, 340.0748.

2-(*p*-tolylthiomethyl)-5-(trifluoromethoxy)phenyl acetate (2k): Light yellow liquid (34 mg, 48 yield); ^{1}H NMR (400MHz, $CDCl_3$, TMS): δ 7.17 (t, J = 8.0 Hz, 3H), 7.06 (d, J = 8.0 Hz, 2H), 6.57-7.00 (m, 2H), 3.9 (s, 2H), 2.31 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 168.6, 149.2, 148.3, 137.4, 131.8, 131.3, 131.2, 129.7, 128.8, 118.1, 116.0, 34.6, 21.1, 20.9; IR (neat, cm^{-1}) 2927, 1773, 1497, 1370, 1163, 986, 909, 806, 699; HRMS (EI) Calcd for $C_{17}H_{15}F_3O_3S$ (M^+), 356.0694; Found, 356.0692.

5-cyano-2-(*p*-tolylthiomethyl)phenyl acetate (2l): Colorless liquid (29 mg, 39% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.40 (d, J = 1.2 Hz, 1H), 7.30 (dd, J_1 = 8 Hz, J_2 = 3.2 Hz, 1H), 7.14-7.18 (m, 3H), 7.06 (d, J = 8 Hz, 2H), 3.85 (s, 2H), 2.32 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 168.5, 148.8, 137.9, 136.1, 132.3, 131.4, 130.4, 129.9, 129.4, 126.6,117.9, 111.9, 35.2, 21.1, 20.9; IR (neat, cm^{-1}) 2924, 1771, 1567, 1493, 1408, 1368, 1184, 1043, 1014, 838; HRMS (EI) Calcd for $C_{17}H_{15}NO_2S$ (M^+), 297.0823; Found, 297.0829.

Methyl 3-acetoxy-4-(*p*-tolylthiomethyl)benzoate (2m): Light yellow liquid (38 mg, 58% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.94 (dd, J_1 = 8.4 Hz, $J2$ = 2.0 Hz, 1H), 7.87 (d, J = 2 Hz, 1H), 7.15-7.20 (m, 3H), 7.06 (d, J = 8 Hz, 2H), 3.99 (s, 2H), 3.88 (s, 3H), 2.31(s, 3H), 2.29 (s, 3H). ^{13}C NMR(100 MHz, $CDCl_3$, TMS): δ 168.7, 166.2, 152.4, 137.4, 132.3, 131.8, 131.3, 130.3, 129.8,

129.7, 127.7, 122.9, 52.2, 35.1, 21.1, 21.1; IR (neat, cm^{-1}) 3001, 2910, 1760, 1460, 1377, 1103, 930, 782; HRMS (EI) Calcd for $C_{18}H_{18}O_4S$ (M^+), 330.0926; Found, 330.0926.

2-(2-(*p*-tolylthio)ethyl)phenyl acetate (4a): Light yellow liquid (42 mg, 74% yield); ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.22-7.25 (m, 2H), 7.17-7.19 (m, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 6.70-7.02 (m, 1H), 3.01-3.05 (m, 2H,), 2.77-2.81 (m, 2H), 2.32 (s, 3H), 2.17(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 169.5, 148.9, 136.5, 132.2, 130.7, 130.5, 129.8, 129.7, 127.7, 126.3, 122.5, 34.6, 30.7, 21.0, 20.8; IR (neat, cm^{-1}) 2923, 2855, 1764, 1683, 1491, 1369, 1206, 1171, 1013, 946, 806; HRMS (EI) Calcd for $C_{17}H_{18}O_2S$ (M^+), 286.1028; Found, 286.1032.

3-methyl-2-(2-(*p*-tolylthio)ethyl)phenyl acetate (4b): Colorless liquid (48 mg, 80 yield); ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.26 (d, *J* = 8 Hz, 2H), 7.03-7.06 (m, 3H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 8 Hz, 1H), 2.82-2.84 (m, 2H), 2.71-2.74 (m, 2H), 2.26(s, 3H), 2.20 (s, 3 H), 2.05(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 168.7, 148.2, 137.2, 135.6, 131.1, 130.0, 129.6, 128.7, 127.1, 126.0, 119.0, 32.4, 26.8, 20.0, 19.7, 18.4; IR (neat, cm^{-1})2922, 1763, 1579, 1493, 1464, 1368, 1205, 1087, 1032, 806; HRMS (EI) Calcd for $C_{18}H_{20}O_2S$ (M^+), 300.1184; Found, 300.1182.

4-methyl-2-(2-(*p*-tolylthio)ethyl)phenyl acetate (4c): Light yellow liquid (45 mg, 75% yield); ^1H NMR (400MHz, $CDCl_3$, TMS):δ 7.30 (d, *J* = 8 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.03 (s, 2H), 6.88 (d, *J* = 8.8 Hz, 1H), 3.00-3.04 (m, 2H), 2.72-2.76 (m, 2H), 2.35 (s, 3H), 2.32 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 169.7, 146.7, 136.5, 135.9, 132.2, 131.8, 131.0, 130.7, 129.8, 128.3, 122.1, 34.7, 30.7, 21.0, 20.9, 20.8; IR (neat, cm^{-1}) 2922, 1758, 1494, 1446, 1368, 1215, 1189, 1144, 943, 806; HRMS (EI) Calcd for $C_{18}H_{20}O_2S$ (M^+), 300.1184; Found, 300.1183.

5-methyl-2-(2-(*p*-tolylthio)ethyl)phenyl acetate (4d): Colorless liquid (50 mg, 84% yield);^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.30 (d, *J* = 8 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 3H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.83 (s, 1H), 2.99-3.03 (m, 2H), 2.72-2.77 (m, 2H), 2.32 (s, 3H), 2.31 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 169.6, 148.7, 137.9, 136.4, 132.2, 130.6, 130.2, 129.7, 129.0, 127.1, 122.9, 34.7, 30.3, 21.0, 21.0, 20.8; IR (neat, cm^{-1})2921, 1762, 1621, 1572, 1493, 1368, 1199, 1131, 1096, 804; HRMS (EI) Calcd for $C_{18}H_{20}O_2S$ (M^+), 300.1184; Found, 300.1178.

2-(1-(*p*-tolylthio)propan-2-yl)phenyl acetate (4e): Colorless liquid (24 mg, 40% yield); ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.27-7.29 (m, 3H), 7.21-7.25 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.98-7.00 (m, 1H), 3.12-3.17 (m, 1H), 3.04-3.06 (m, 1H), 2.86-2.91 (m, 1H), 2.31 (s, 3H), 2.08 (s, 3H), 1.35 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 169.5, 148.2, 137.3, 136.3, 132.5,

130.6, 129.7, 127.3, 127.2, 126.4 122.5, 42.0, 32.3, 21.0, 20.7, 19.6; IR (neat, cm^{-1}) 2968, 1760, 1490, 1449, 1369, 1191, 1044, 805; HRMS (EI) Calcd for $C_{18}H_{20}O_2S$ (M^+), 300.1184; Found, 300.1188.

4-fluoro-2-(2-(*p*-tolylthio)ethyl)phenyl acetate (4f): Light yellow liquid (28 mg, 46% yield); ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8 Hz, 2H), 6.91-6.93 (m, 3H), 2.99-2.30 (m, 2H), 2.75-2.78 (m, 2H), 2.33 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$, TMS) :δ 169.4, 160.3 (d, *J* = 243.1 Hz, C-F), 144.7, 144.7, 136.8, 134.2 (d, *J* = 8.3 Hz), 131.8, 130.9, 129.8, 123.7 (d, *J* = 8.6 Hz), 116.9 (d, *J* = 22.8 Hz), 114.3 (d, *J* = 22.3 Hz), 34.4, 30.6, 21.0, 20.7; IR (neat, cm^{-1}) 2924, 1760, 1620, 1492, 1369, 1209, 1171, 1012, 872, 805; HRMS (EI) Calcd for $C_{17}H_{17}FO_2S$ (M^+), 304.0933; Found, 304.0936.

4-chloro-2-(2-(*p*-tolylthio)ethyl)phenyl acetate (4g): Light yellow liquid (38 mg, 60% yield); ^1H NMR (400 MHz, $CDCl_3$, TMS):δ 7.30 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 7.2 Hz, 2H), 7.13 (d, *J* = 8Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 1H), 2.99-3.03 (m, 2H), 2.73-2.77 (m, 2H), 2.33 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 169.2, 147.4, 136.8, 134.0, 131.8, 131.4, 130.9, 130.3, 129.8, 127.7, 123.7, 34.4, 30.5, 21.0, 20.7; IR (neat, cm^{-1}) 2955, 1704, 1470, 1350, 805; HRMS (EI) Calcd for $C_{17}H_{17}ClO_2S$ (M^+), 320.0638; Found, 320.0635.

4-bromo-2-(2-(*p*-tolylthio)ethyl)phenyl acetate (4h): Light yellow liquid (47 mg, 65% yield); ^1H NMR (400MHz, $CDCl_3$, TMS): δ 7.29-7.35 (m, 4H), 7.13 (d, *J* = 8 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 2.99-3.03 (m, 2H), 2.73-2.77 (m, 2H), 2.33(s, 3H), 2.16 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$,TMS): δ 169.1, 147.9, 136.8, 134.4, 133.3, 131.8, 131.0, 130.7, 129.8, 124.2, 119.2, 34.5, 30.5, 21.1, 20.7; IR (neat, cm^{-1}) 2930, 1764, 1488, 1453, 1205, 1171, 1044, 915, 809; HRMS (EI) Calcd for $C_{17}H_{17}BrO_2S$(M^+), 364.0133; Found, 364.0128.

3-(2-(*p*-tolylthio)ethyl)naphthalen-2-yl acetate (4i): Light yellow liquid (42 mg, 63 yield); ^1H NMR (400MHz, $CDCl_3$, TMS): δ 7.73-3.78 (m, 2H), 7.68 (s, 1H), 7.50 (s, 1H), 7.42-7.44 (m, 2H), 7.33 (d, *J* = 8 Hz, 2H), 7.13 (d, *J* = 8 Hz, 2H), 3.11-3.15 (m, 2H), 2.93-2.97 (m, 2H), 2.32 (d, *J* = 7.2 Hz, 3H), 2.22 (s, 3H).^{13}C NMR (100MHz, $CDCl_3$, TMS): δ 169.6, 147.3, 136.6, 132.8, 132.1, 131.8, 131.5, 130.9, 129.8, 129.3, 127.4, 127.3, 126.2, 125.9, 119.7, 34.9, 31.3, 21.1, 20.9; IR (neat, cm^{-1}): 2939, 1771, 1426, 12701, 1171, 1047, 741; HRMS (EI) Calcd for $C_{21}H_{20}O_2S$ (M^+), 336.1184; Found, 336.1188.

Transformation of Thioethers:

General Procedure for the Oxidation of 2-(*p*-tolylthiomethyl)phenyl acetate 2a to 2-(*p*-tolylsulfinylmethyl)phenyl acetate 5: To a solution of **2a** (54 mg, 0.2 mmol) in DCM (2 mL) was stirred at room temperature. The *m*-CPBA (34 mg, 0.2 mmol) was dissolved in 1 mL of DCM and added drop wise into the reaction mixture. Then it was stirred at room temperature for 10 minutes. Afterward, 20 mL of DCM was added to the reaction mixture, and the solution was wash with 2 mL 40% of NaOH (aq). The obtained upper layer was washed with brine and dried over anhydrous magnesium sulfate, evaporated under reduced pressure to obtain the solid crude product, which was washed with petroleum ether for 3 times to get the white powder in 91% yield,

2-(4-methylbenzylsulfinyl)phenyl acetate (5): Colorless liquid (41 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.26-7.30 (m, 3H), 7.21 (d, J = 8 Hz, 2H), 7.07-7.12 (m, 2H), 6.87 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 2H), 4.24 (d, J = 12.4 Hz,1H), 3.86 (d, J = 12.4 Hz, 1H), 2.39 (s, 3H), 2.29 (s, 3H). ^{13}C NMR(100 MHz, $CDCl_3$, TMS): δ 169.0, 149.4, 141.9, 139.7, 132.2, 129.6, 129.5, 125.9, 124.4, 122.7, 122.0, 59.2, 21.5, 21.1;IR (neat, cm^{-1}) 2912, 1743, 1559, 1483, 1461, 1366, 1201, 1055, 1032, 806; HRMS (EI) Calcd for $C_{16}H_{16}O_3S$ (M^+), 228.0820; Found, 228.0813.

General Procedure for the Transformation of 2-(*p*-tolylthiomethyl)phenyl acetate 2a to 2-(4-methylbenzyl)phenyl acetate 6: To a solution of **2a** (54 mg, 0.2 mmol) in DCM (2 mL) was stirred at room temperature. The *m*-CPBA (68 mg, 0.4 mmol) was dissolved in 1 mL of DCM and dropwised to the reaction mixture. Then it was stirred at 40 ^{o}C for 2 h. Afterward, 20 mL of DCM was added to the reaction mixture, then the solution was wash with 2 mL 40% of NaOH (aq). The obtained upper layer was washed with brine and dried over anhydrous magnesium sulfate, evaporated under reduced pressure to obtain the solid crude product, which was washed with petroleum ether for 3 times to get the white powder in 95% yield.

2-(tosylmethyl)phenyl acetate 6: Colorless liquid (57 mg, 95% yield); ^{1}H NMR (400MHz, $CDCl_3$, TMS): δ 7.31-7.20 (m, 5H), 7.12-7.06 (m, 2H), 7.86 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 4.25 (d, J = 12.4 Hz, 1H), 3.86 (d, J = 12.4 Hz, 1H), 2.39 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 169.0, 149.4, 141.9, 139.6, 132.2, 129.6, 125.9, 124.4, 122.7, 121.9, 59.2, 21.5, 21.1. IR (neat, cm^{-1}) 2925, 1765, 1594, 1490, 1453, 1369, 1201, 1171, 1087, 1040, 916, 835, 760; HRMS (EI) Calcd for $C_{16}H_{16}O_4S$ (M^+), 304.0769; Found, 304.0771.

General Procedure for the Transformation of 2-(*p*-tolylthiomethyl)phenyl acetate 2a to 2-formylphenyl acetate 7: To a solution of **2a** (54 mg, 0.2 mmol) in DCM (2 mL) was stirred at room temperature. The *m*-CPBA (34 mg, 0.2 mmol) was dissolved in 1 mL of DCM and dropwised to the reaction mixture. Then it was stirred at 40 ^{o}C for 2 h. Afterward, 20 mL of DCM was added to the reaction mixture, then the solution was wash with 2 mL 40% of NaOH (aq) and the obtained upper layer was washed with brine and dried over anhydrous magnesium sulfate, filtered through a pad of celite. The solvent was evaporated under reduced pressure. Trifluoroacetic anhydride (0.28 mL, 2 mol) was added to a solution of the solid in DME at room temperature. After 1 h, the solution was poured into saturated aq $NaHCO_3$ and extracted with EtOAc. The organic layer was washed with saturated aq NaCl, dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was subjected to flash column chromatography (silica gel, ethyl acetate / petroleum ether = 3:1, v/v) to obtain desire product in 95% yield as colorless liquid.

2-formylphenyl acetate[4] **7:** Colorless liquid (26 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 10.1 (s, 1H), 7.87 (dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.65-7.60 (m, 1H), 7.40 (d, J = 0.8 Hz, 1H), 7.18 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, CDCl3, TMS): δ 188.8, 169.3, 151.5, 135.4, 131.3, 128.0, 126.4, 123.5, 20.9.

General Procedure for the Transformation of 2-(*p*-tolylthiomethyl)phenyl acetate 2a to o-tolyl acetate 8: To a solution of 2-(*p*-tolylthiomethyl)phenyl acetate **2a** (54 mg, 0.2 mmol) in ethanol (5 mL), The Raney-Nickel (50 μm, saved in water) was added partly at 40 ^{o}C until little of the substrate exist (monitored by TLC). The reaction mixture was filtered through a pad of celite, the solven was evaporated under reduced pressure and the residue was subjected to flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1: 30, v/v) to obtain the desired product.

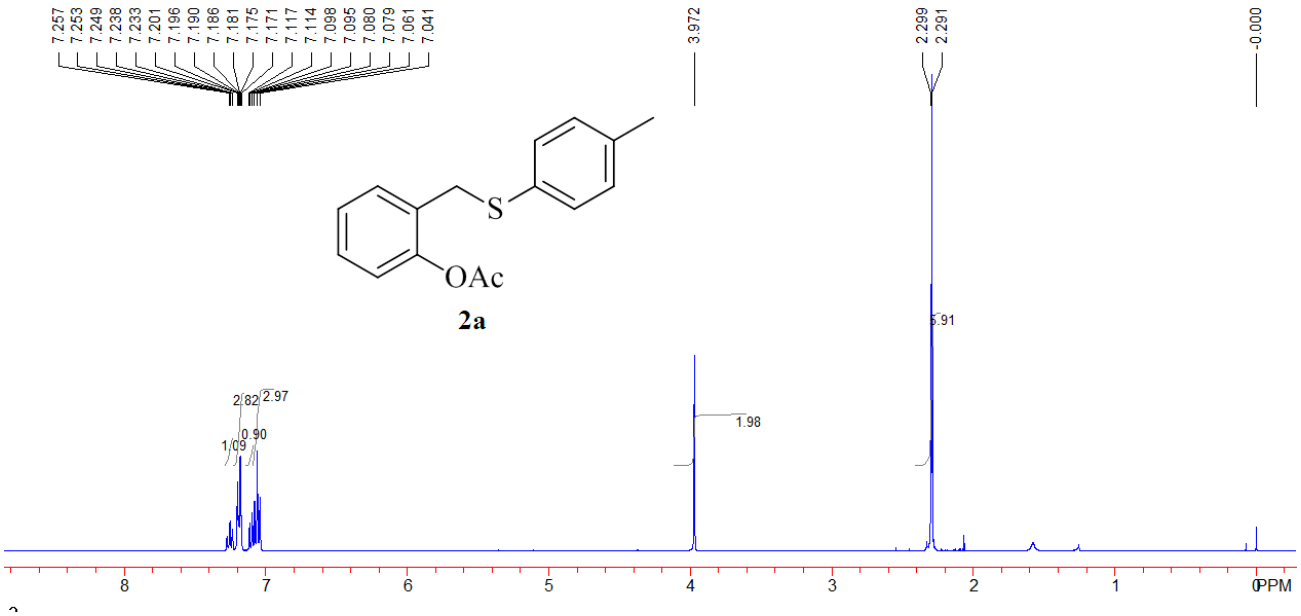
o-tolyl acetate[5] **8:** Colorless liquid (21 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.22-7.16 (m, 2H), 7.12 (t, J = 7.2 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 2.28 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, CDCl3, TMS): δ 169.3, 149.4, 131.2, 130.1, 127.0, 126.1, 121.9, 20.8, 16.2.

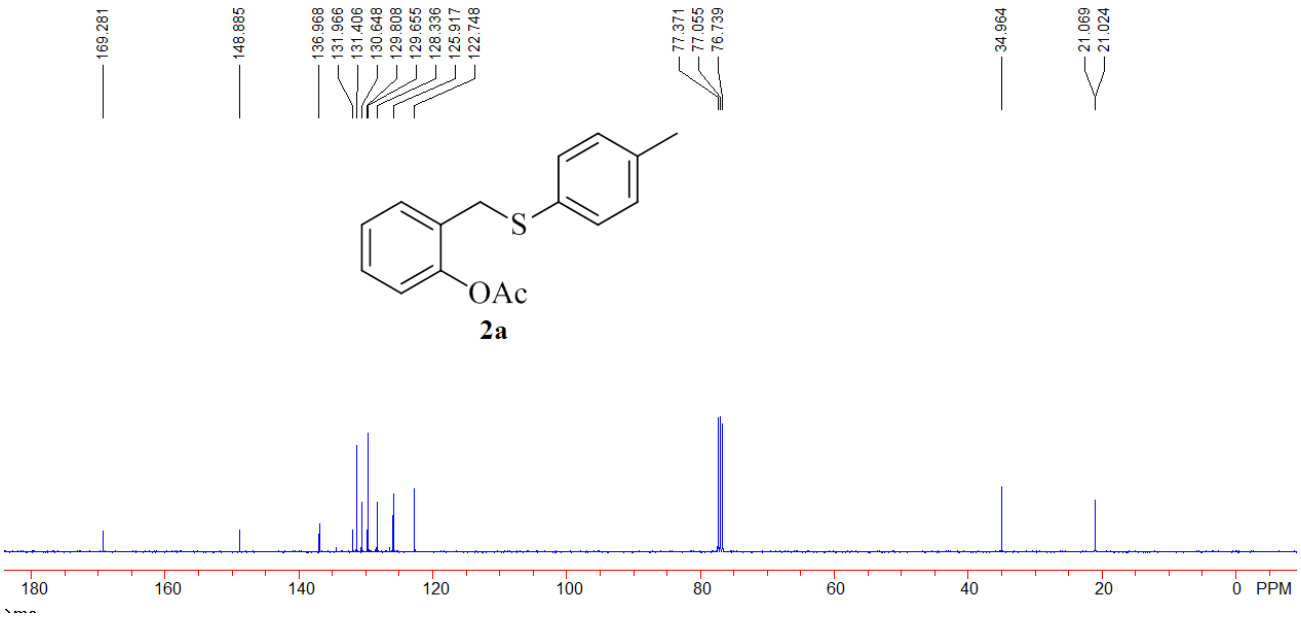
General Procedure for the Transformation of 2-(*p*-tolylthiomethyl)phenyl acetate 2a to 2-((p-tolylsulfinyl)methyl)phenol 9: To a solution of 2-(*p*-tolylthiomethyl)phenyl acetate **2a** (54 mg, 0.2 mmol) in a mixture of EtOH/H_2O (3/0.5 mL), NaOH (48 mg,1.2 mmol, 4.0 equiv) was added. The mixture was heated to 80 °C and stirred for 24 h. Water was added, and the mixture was extracted

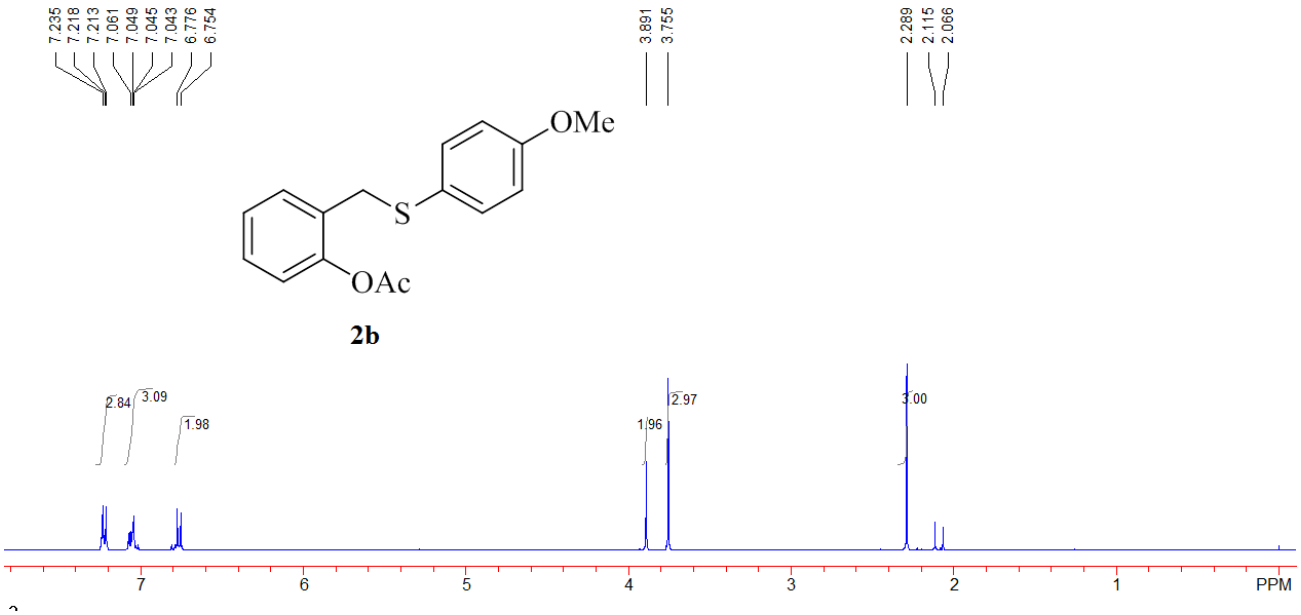
with DCM. The combined organic layers were washed with brine water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel flash chromatography to give the desired product **9** in 85% yields.

2-((p-tolylsulfinyl)methyl)phenol 9: Colorless liquid (39 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.22 (d, *J* = 2.0 Hz, 2H), 7.14 (t, *J* = 0.4 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 1.2 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.78-6.77 (m ,1H), 6.10 (s, 1H), 4.10 (s, 2H), 2.29 (s, 3H).^{13}C NMR (100 MHz, CDCl3, TMS): δ 153.7, 137.4, 131.6, 130.7, 130.0, 129.8, 122.9, 120.8, 116.8, 36.4, 21.1. IR(neat, cm^{-1}) 3610, 2925, 1490, 1453, 1211, 1179, 1080, 916, 760; HRMS (EI) Calcd for $C_{14}H_{14}OS$ (M^+), 230.0765; Found, 230.0768.

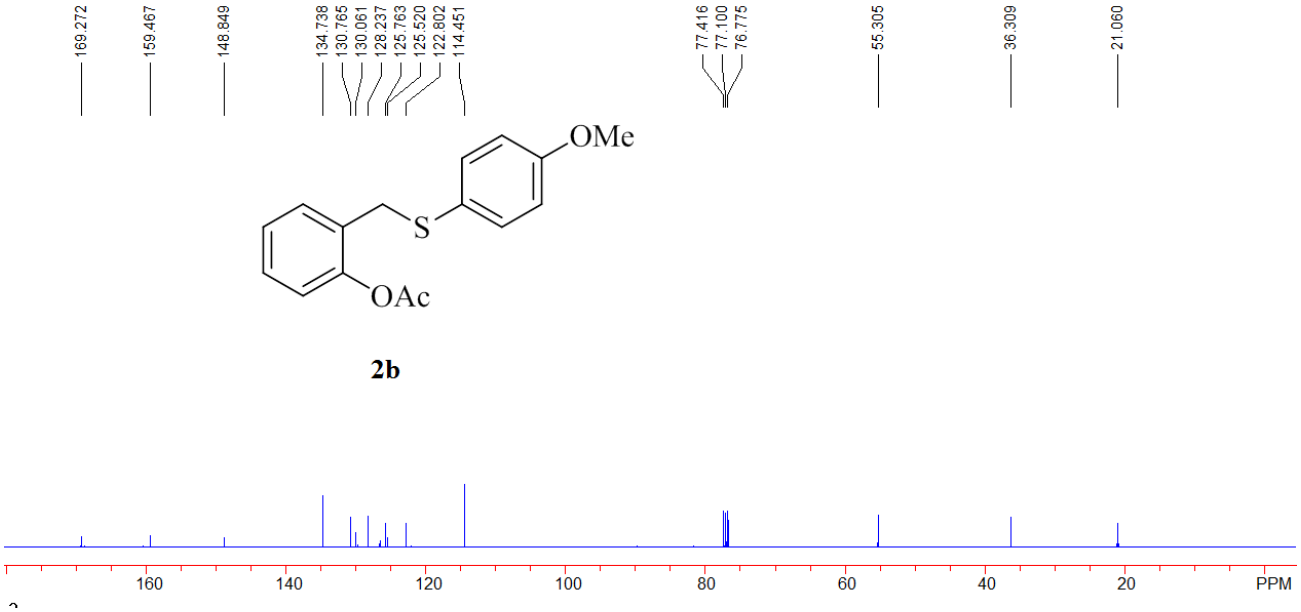
^{1}H NMR and ^{13}C NMR Spectra



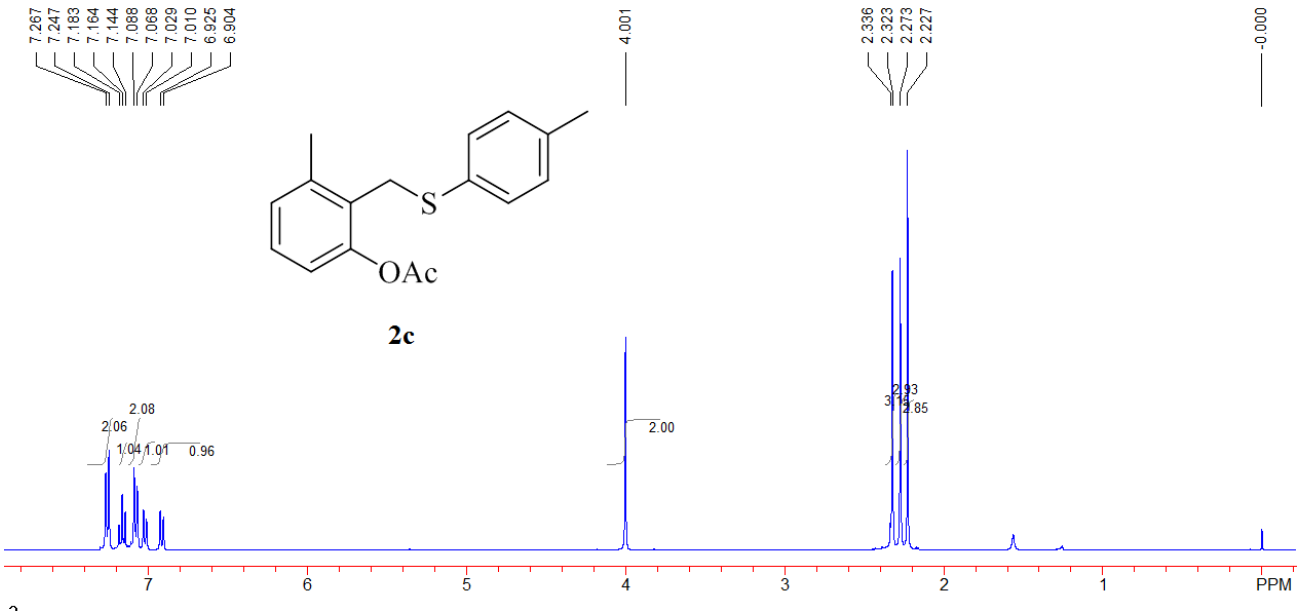



7.235
7.218
7.213
7.061
7.049
7.045
7.043
6.776
6.754
3.891
3.755
2.289
2.115
2.066
OMe
S
OAc
2.84
3.09
1.98
1.96
2.97
3.00
7
6
5
4
3
2
1
PPM

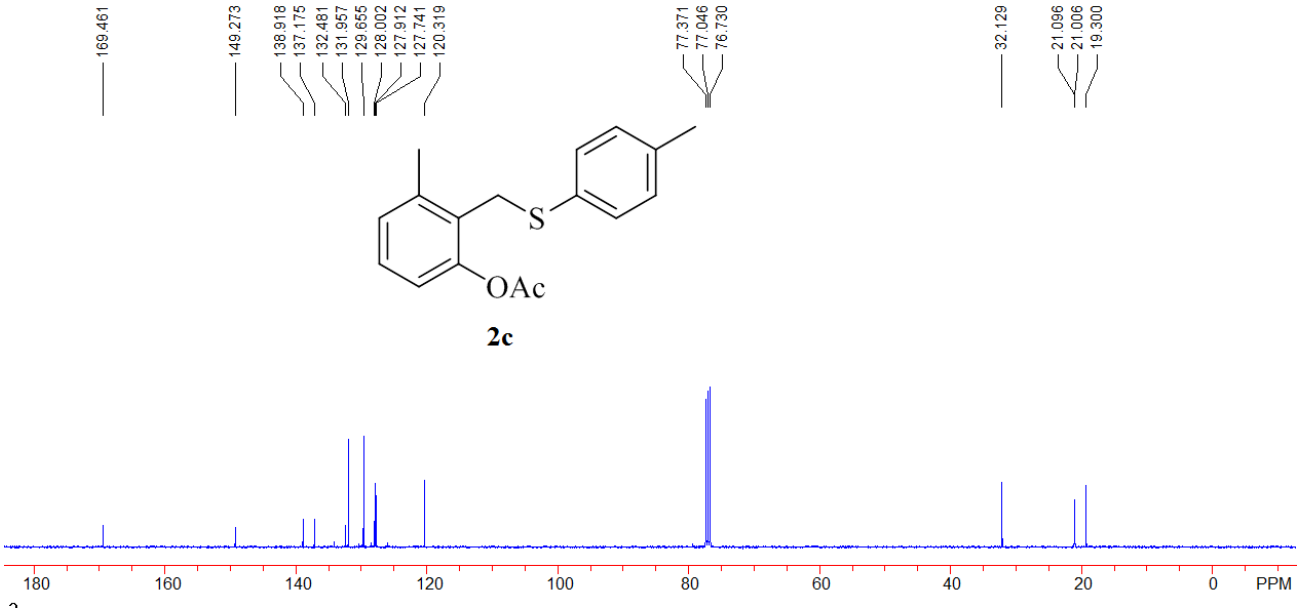
2b


169.272
159.467
148.849
134.738
130.765
130.061
128.237
125.763
125.520
122.802
114.451
77.416
77.100
76.775
55.305
36.309
21.060
OMe
S
OAc
160
140
120
100
80
60
40
20
PPM

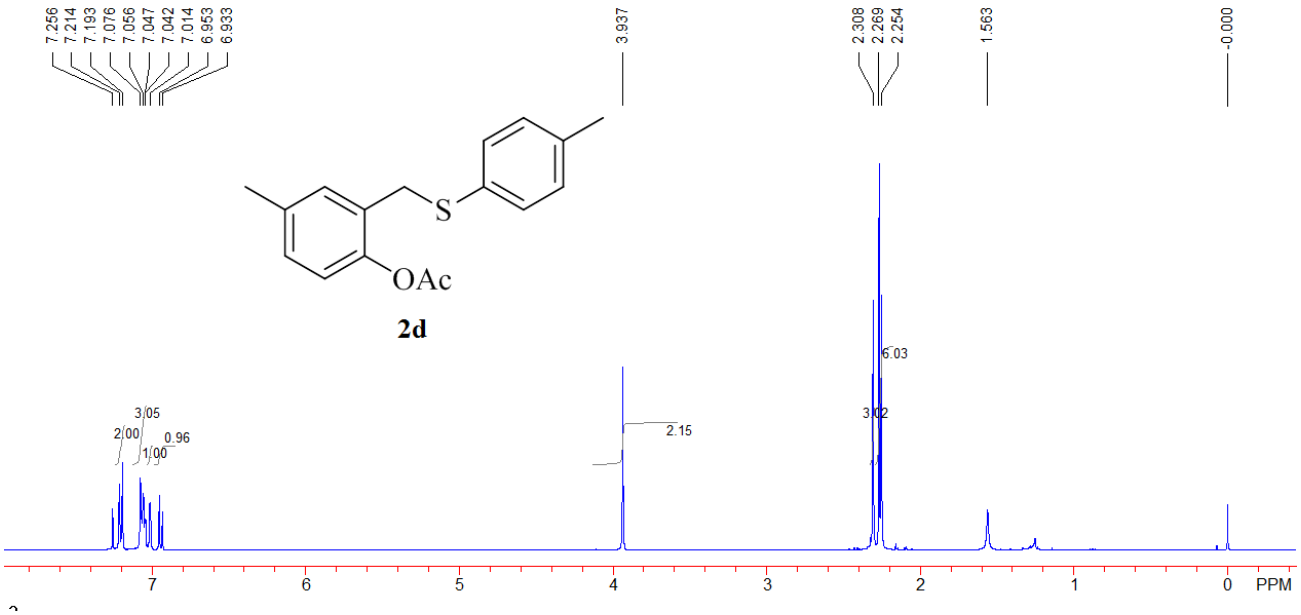
2b

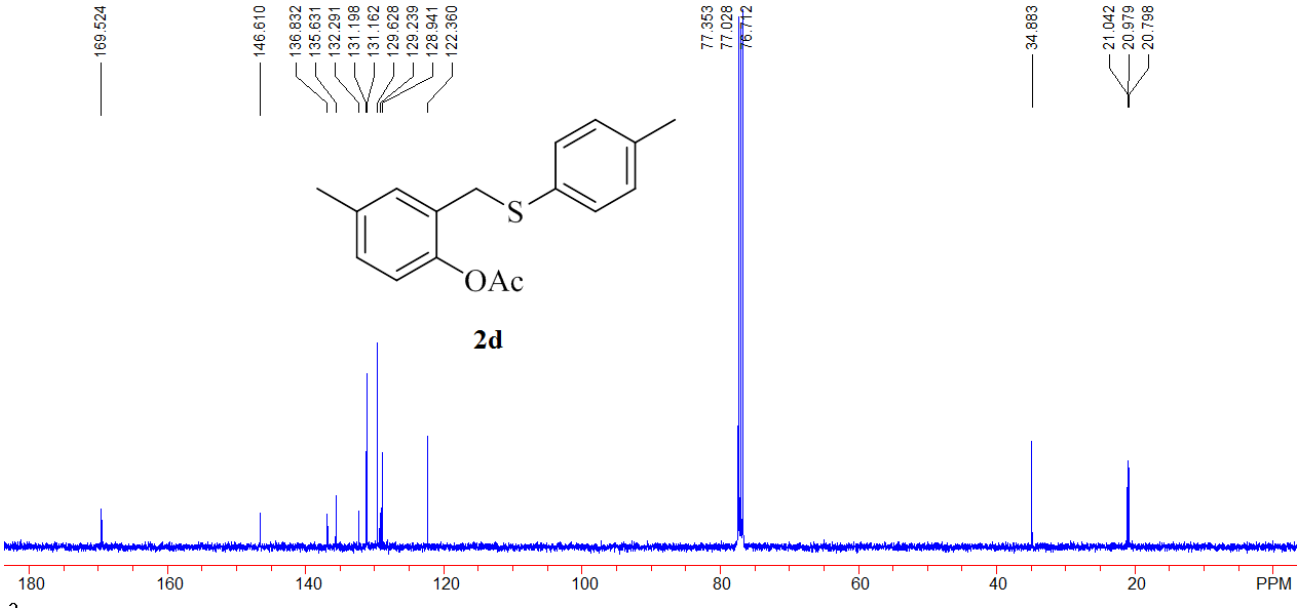

7.267
7.247
7.183
7.164
7.144
7.088
7.068
7.029
7.010
6.925
6.904
4.001
2.336
2.323
2.273
2.227
-0.000
S
OAc
2.08
2.06
1.04
1.01
0.96
2.00
2.93
2.85
7
6
5
4
3
2
1
PPM

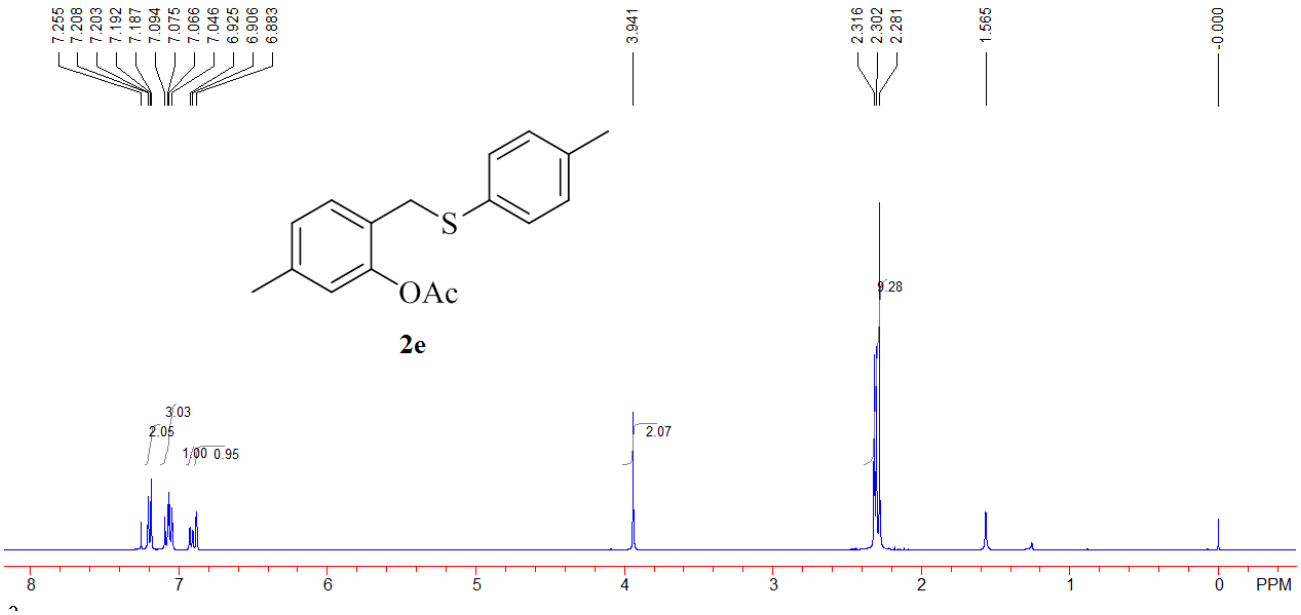
2c

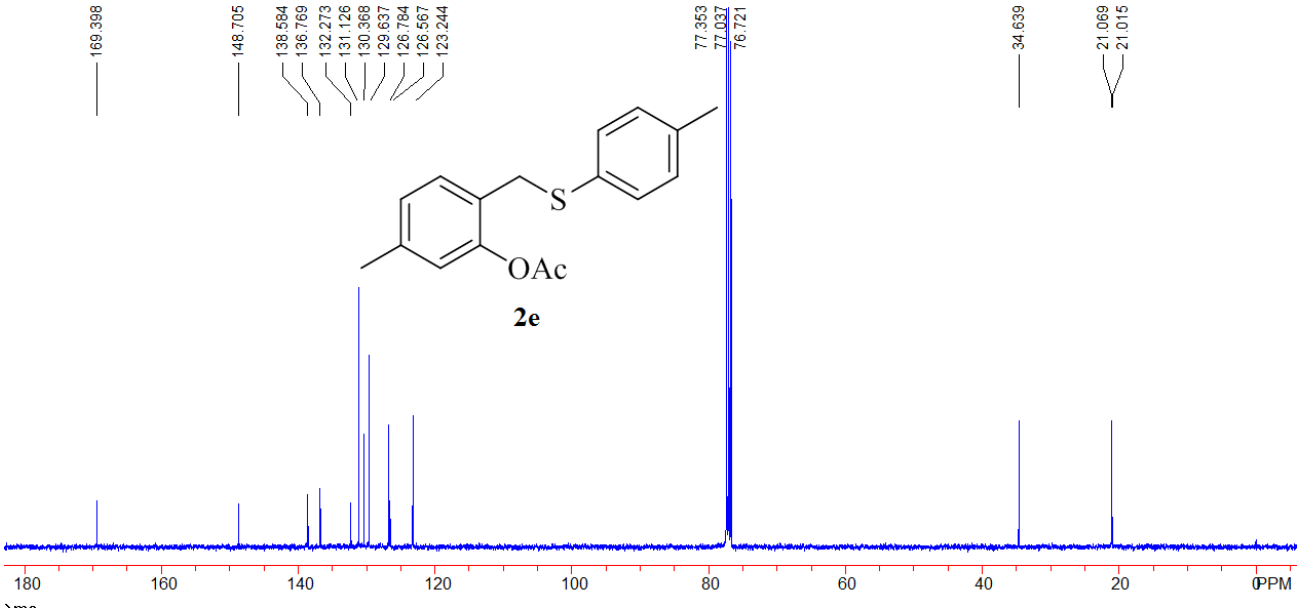

169.461
149.273
138.918
137.175
132.481
131.957
129.655
128.002
127.912
127.741
120.319
77.371
77.046
76.730
32.129
21.096
21.006
19.300
S
OAc
180
160
140
120
100
80
60
40
20
0
PPM

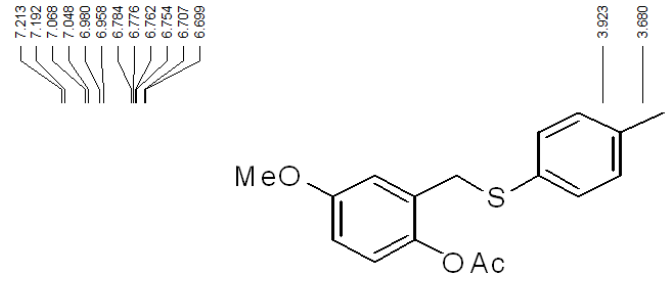
2c


7.256
7.214
7.193
7.076
7.056
7.047
7.042
7.014
6.953
6.933
3.937
2.308
2.269
2.254
1.563
-0.000
S
OAc
2d
3.05
2.00
0.96
1.00
2.15
6.03
3.02
7
6
5
4
3
2
1
0
PPM

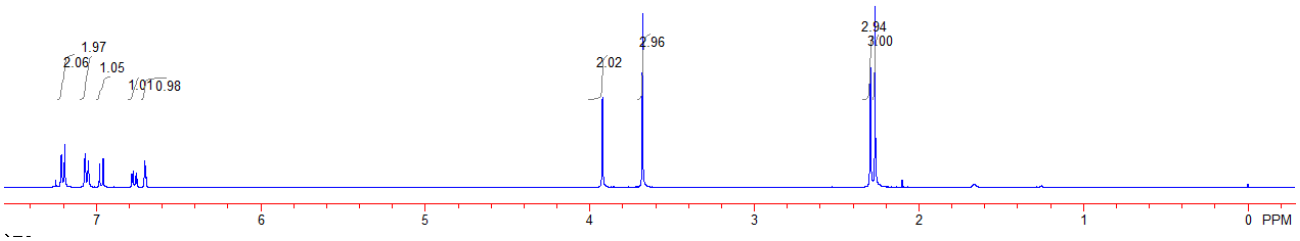

169.524
146.610
136.832
135.631
132.291
131.198
131.162
129.628
129.239
128.941
122.360
77.353
77.028
76.712
34.883
21.042
20.979
20.798
S
OAc
2d
180
160
140
120
100
80
60
40
20
PPM

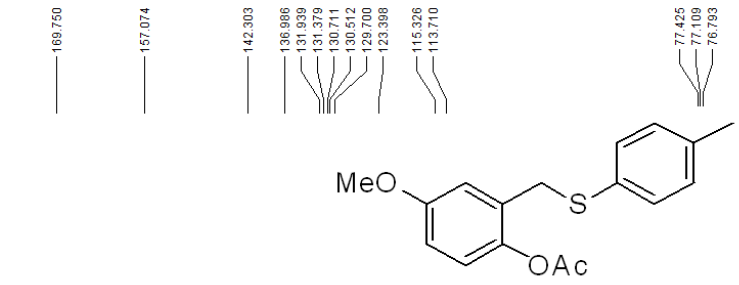

7.255
7.208
7.203
7.192
7.187
7.094
7.075
7.066
7.046
6.925
6.906
6.883
3.941
2.316
2.302
2.281
1.565
0.000
S
OAc
2e
9.28
3.03
2.05
1.00
0.95
2.07
8
7
6
5
4
3
2
1
0
PPM


169.398
148.705
138.584
136.769
132.273
131.126
130.368
129.637
126.784
126.567
123.244
77.353
77.037
76.721
34.639
21.069
21.015
S
OAc
2e
180
160
140
120
100
80
60
40
20
0
PPM

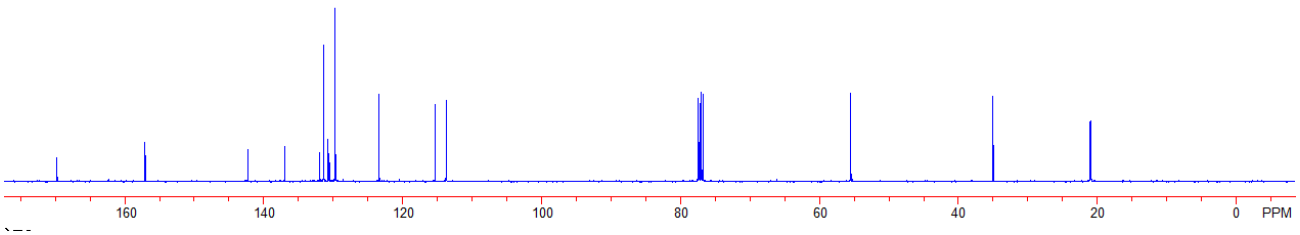

7.213
7.192
7.068
7.048
6.980
6.958
6.784
6.776
6.762
6.754
6.707
6.699
3.923
3.680
2.295
2.266
MeO
S
OAc

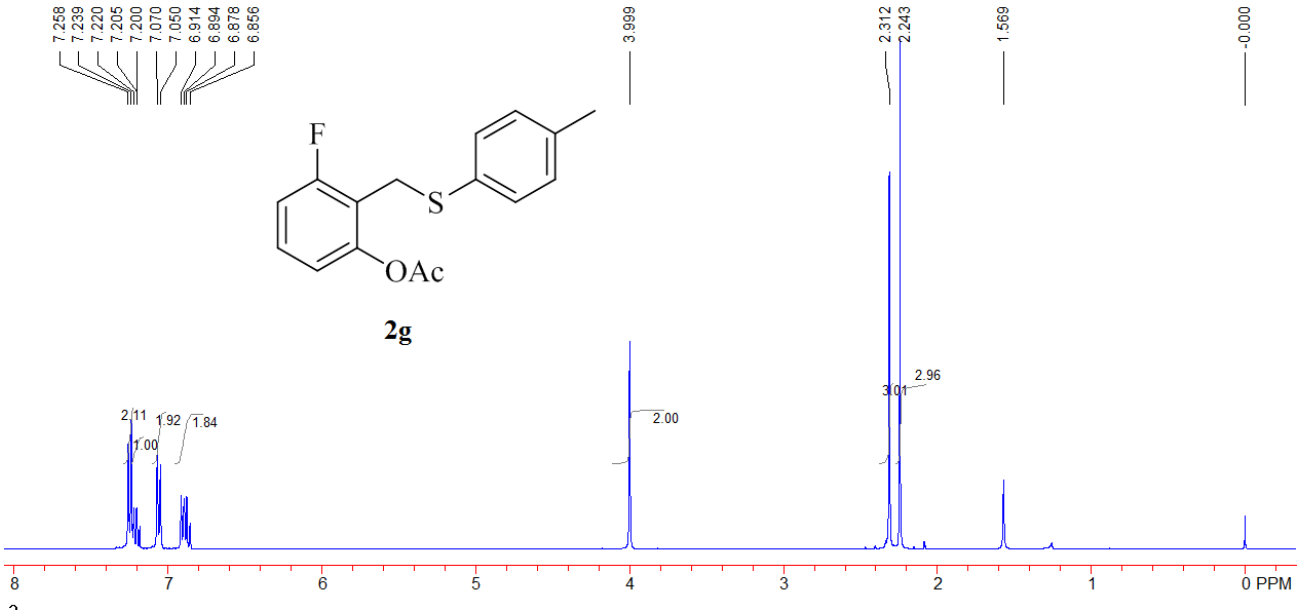
2f

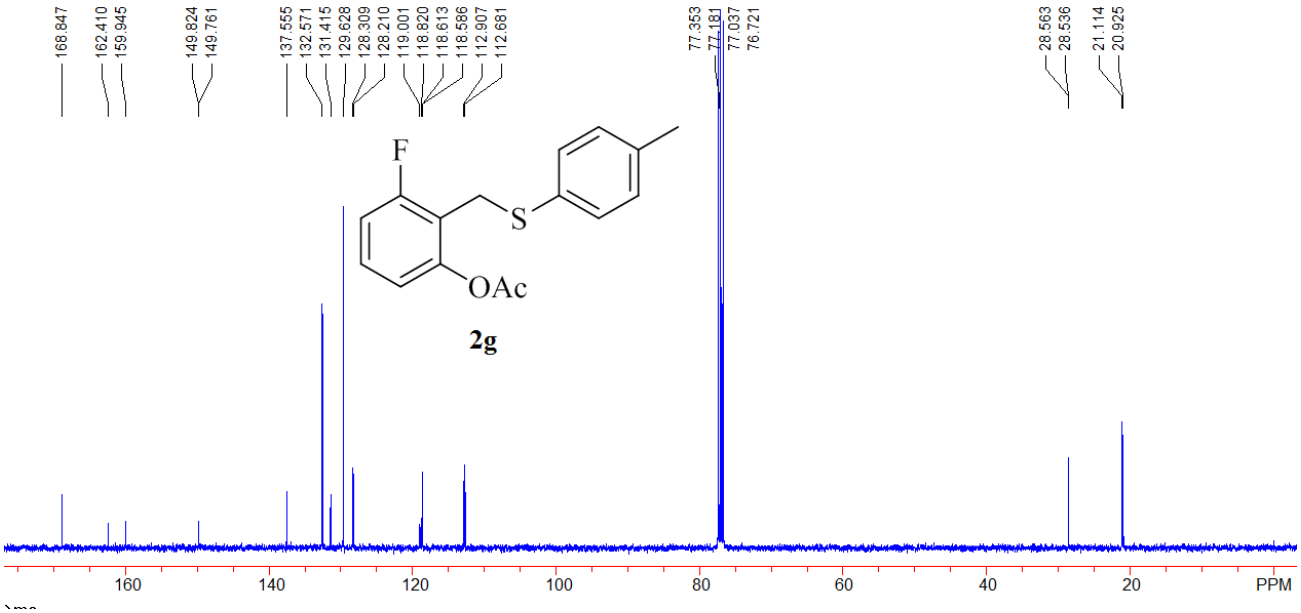

1.97
2.06
1.05
1.01
0.98
2.02
2.96
2.94
3.00
7
6
5
4
3
2
1
0
PPM

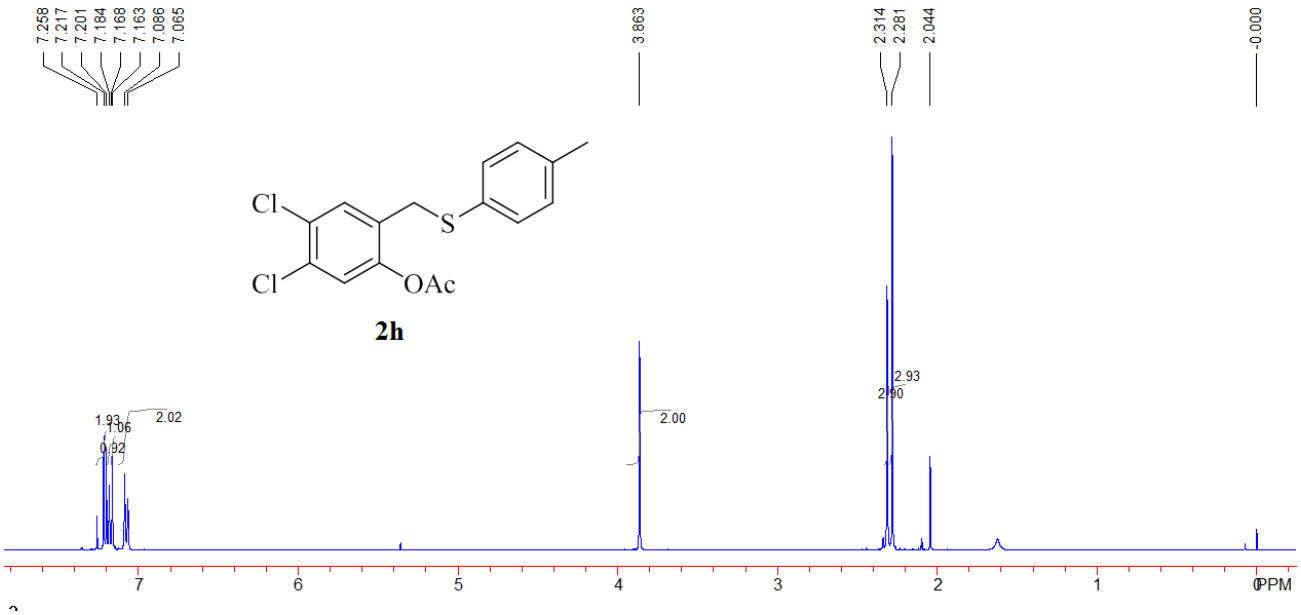

169.750
157.074
142.303
136.986
131.939
131.379
130.711
130.512
129.700
123.398
115.326
113.710
77.425
77.109
76.793
55.513
35.036
21.078
20.961
MeO
S
OAc

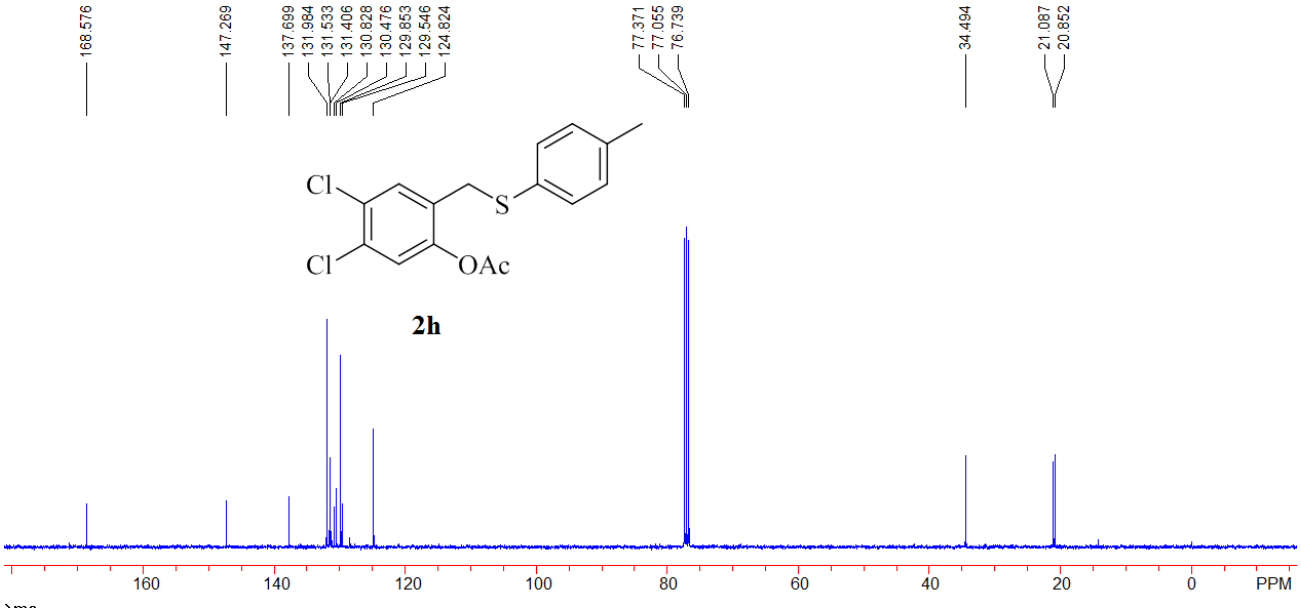
2f

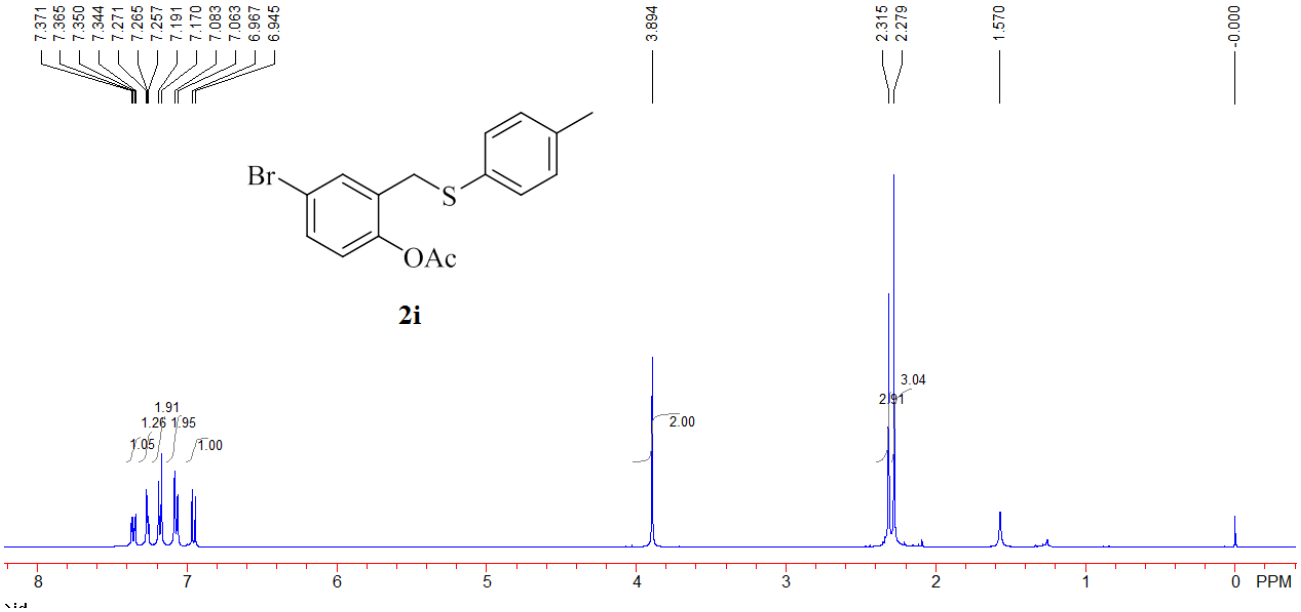

160
140
120
100
80
60
40
20
0
PPM

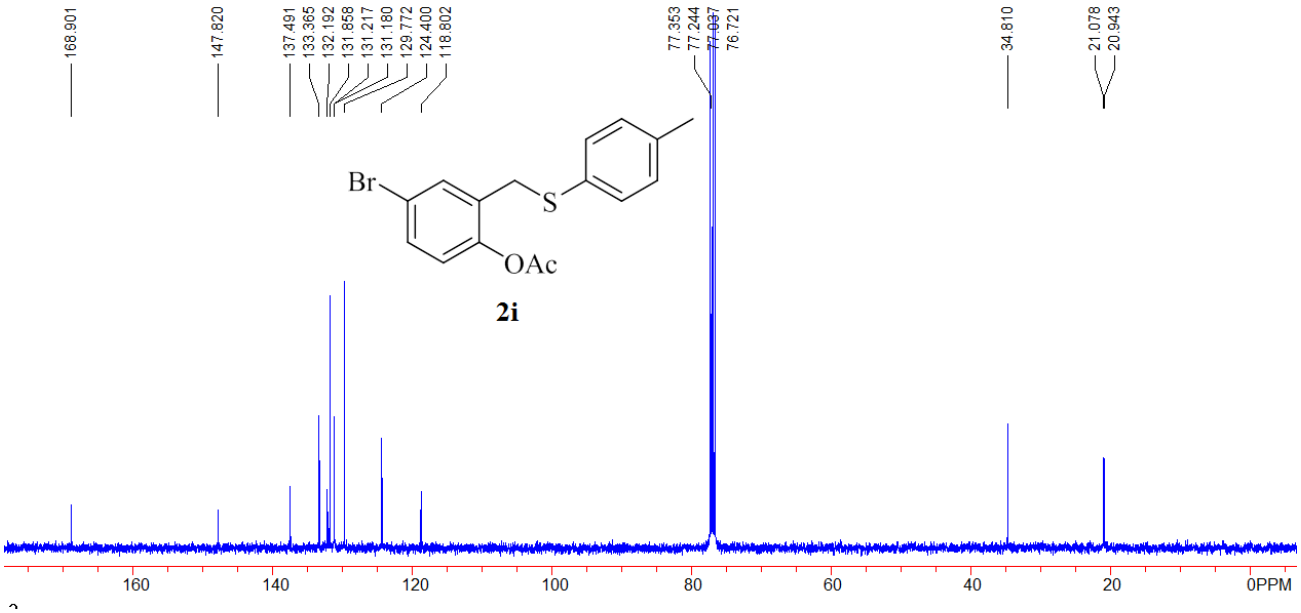

7.258
7.239
7.220
7.205
7.200
7.070
7.050
6.914
6.894
6.878
6.856
3.999
2.312
2.243
1.569
0.000
F
S
OAc
2g
2.11
1.92
1.84
1.00
2.00
3.01
2.96
8
7
6
5
4
3
2
1
0 PPM

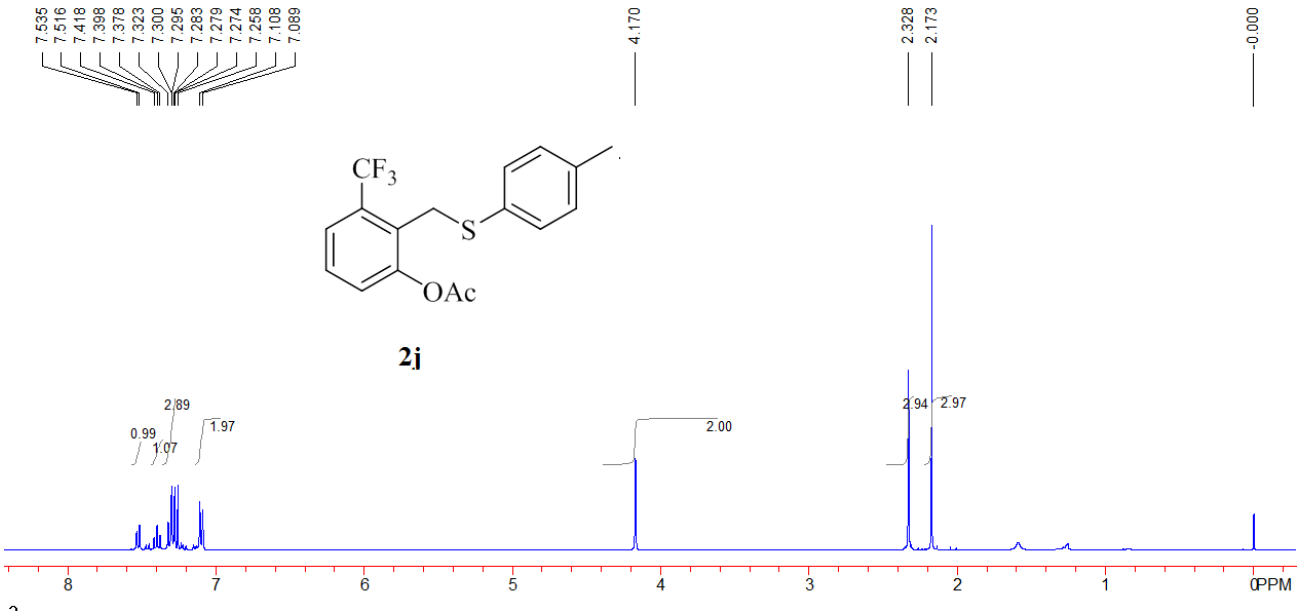

168.847
162.410
159.945
149.824
149.761
137.555
132.571
131.415
129.628
128.309
128.210
119.001
118.820
118.613
118.586
112.907
112.681
77.353
77.181
77.037
76.721
28.563
28.536
21.114
20.925
F
S
OAc
2g
160
140
120
100
80
60
40
20
PPM

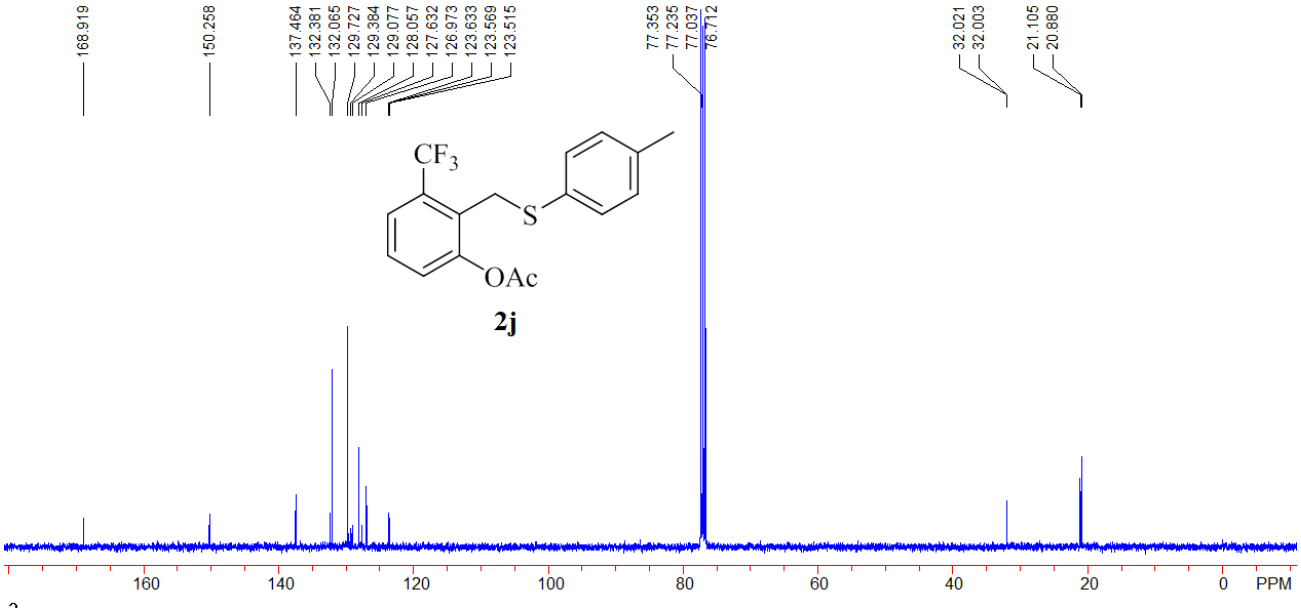

7.258
7.217
7.201
7.184
7.168
7.163
7.086
7.065
3.863
2.314
2.281
2.044
-0.000
Cl
Cl
S
OAc
2h
1.93
1.06
0.92
2.02
2.00
2.93
2.90
7
6
5
4
3
2
1
0
PPM

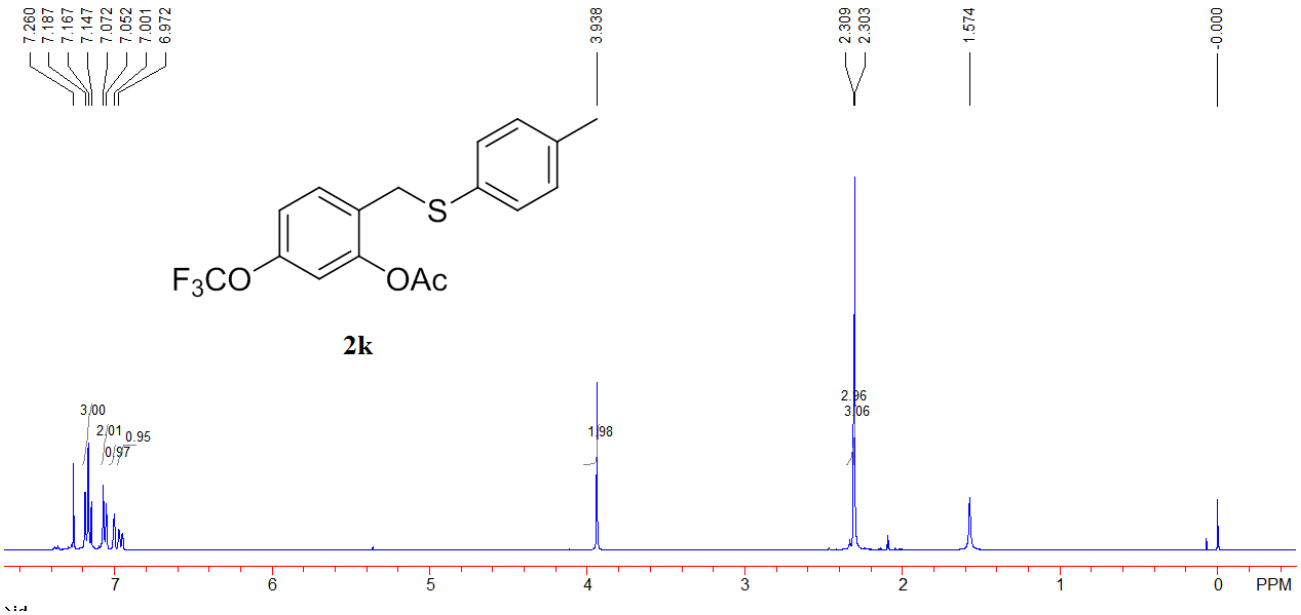

168.576
147.269
137.699
131.984
131.533
131.406
130.828
130.476
129.853
129.546
124.824
77.371
77.055
76.739
34.494
21.087
20.852
Cl
Cl
S
OAc
2h
160
140
120
100
80
60
40
20
0
PPM


7.371
7.365
7.350
7.344
7.271
7.265
7.257
7.191
7.170
7.083
7.063
6.967
6.945
3.894
2.315
2.279
1.570
-0.000
Br
S
OAc
2i
1.91
1.26
1.95
1.05
1.00
2.00
3.04
2.91
8
7
6
5
4
3
2
1
0 PPM

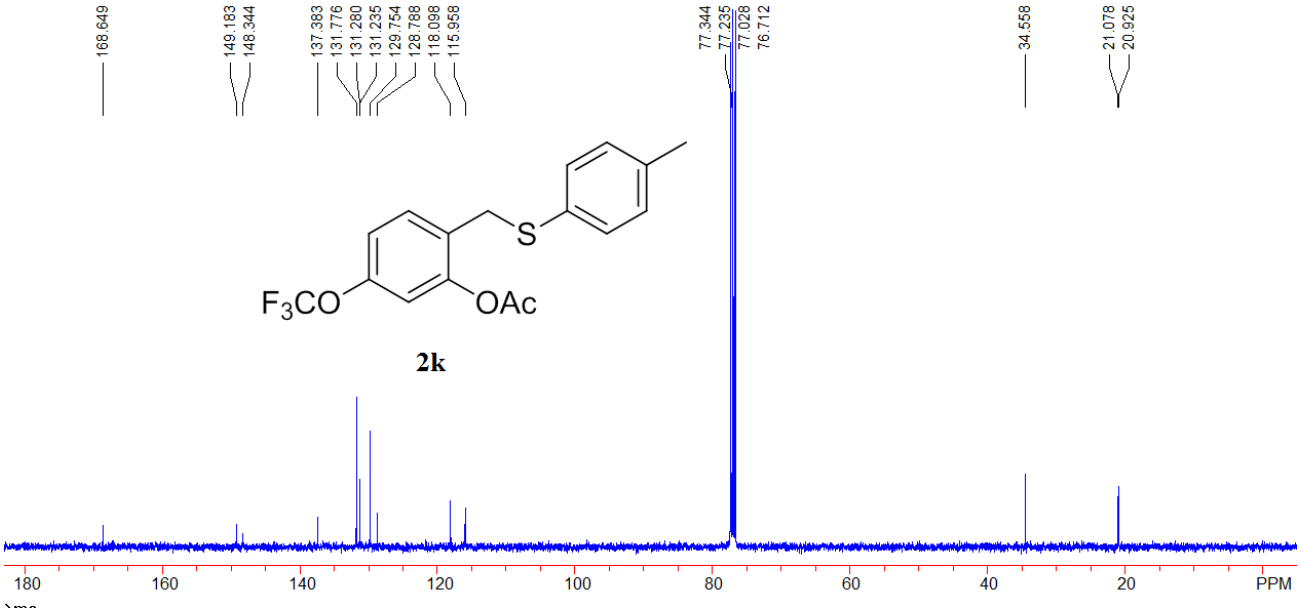

168.901
147.820
137.491
133.365
132.192
131.858
131.217
131.180
129.772
124.400
118.802
77.353
77.244
77.037
76.721
34.810
21.078
20.943
Br
S
OAc
2i
160
140
120
100
80
60
40
20
0PPM


7.535
7.516
7.418
7.398
7.378
7.323
7.300
7.295
7.283
7.279
7.274
7.258
7.108
7.089
4.170
2.328
2.173
-0.000
CF3
S
OAc
2j
2.89
1.97
0.99
1.07
2.00
2.94
2.97
8
7
6
5
4
3
2
1
0PPM

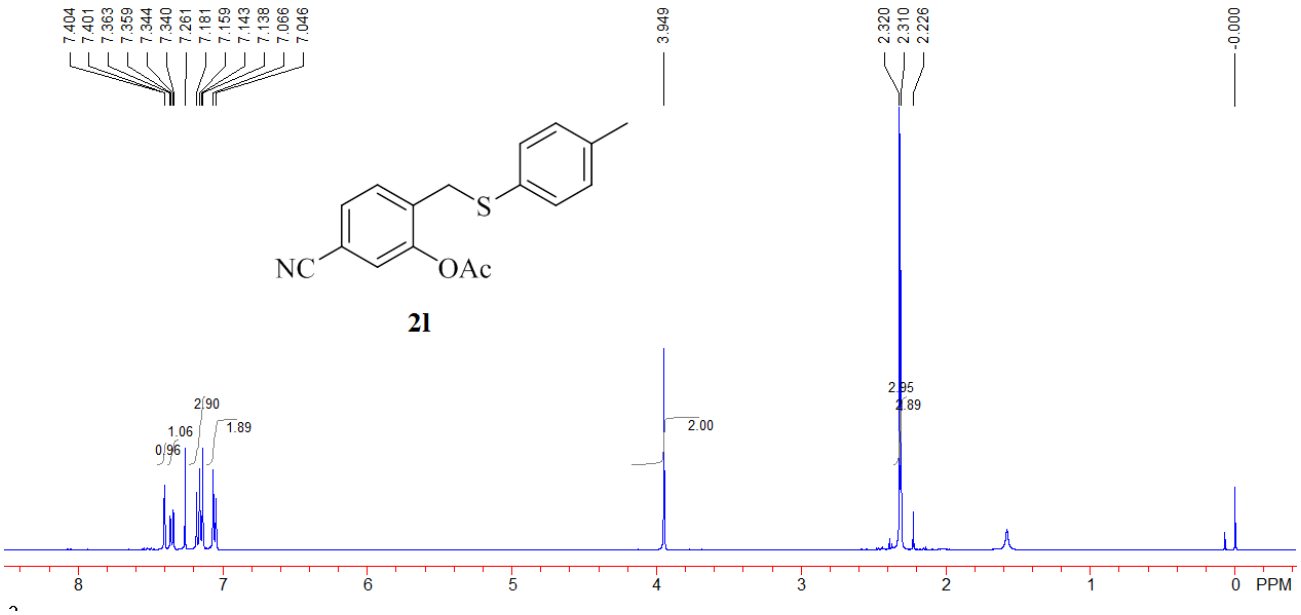

168.919
150.258
137.464
132.381
132.065
129.727
129.384
129.077
128.057
127.632
126.973
123.633
123.569
123.515
77.353
77.235
77.037
76.712
32.021
32.003
21.105
20.880
CF3
S
OAc
2j
160
140
120
100
80
60
40
20
0
PPM

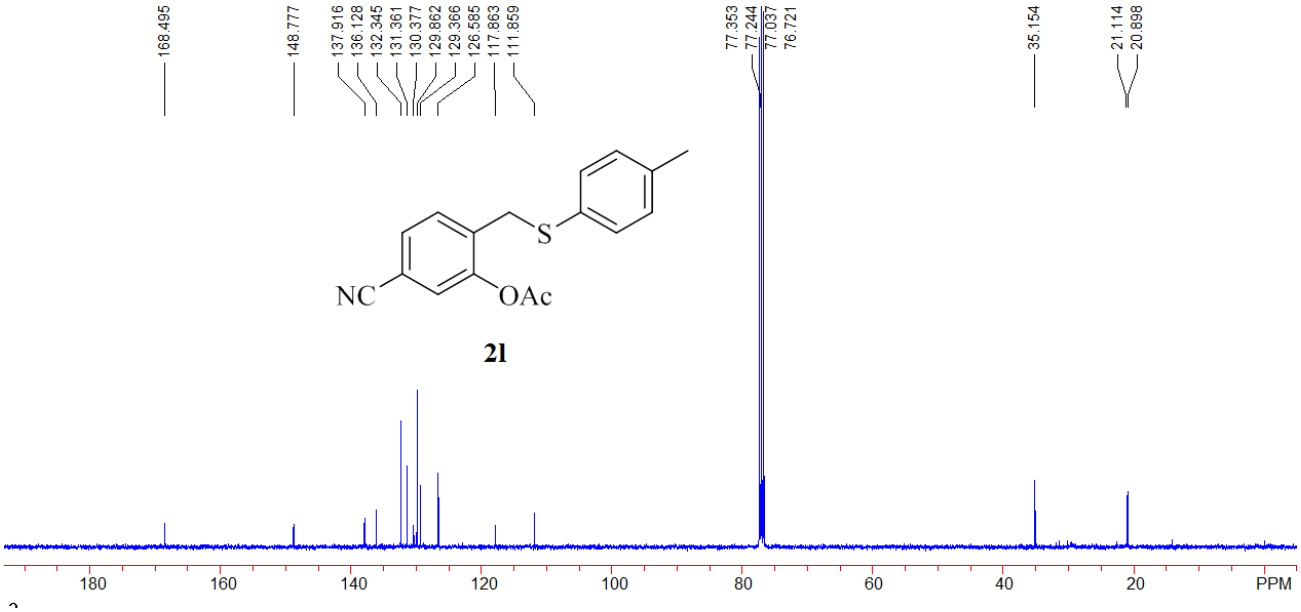

7.260
7.187
7.167
7.147
7.072
7.052
7.001
6.972
3.938
2.309
2.303
1.574
0.000
S
F3CO
OAc
3.00
2.01
0.95
0.97
1.98
2.96
3.06
7
6
5
4
3
2
1
0
PPM

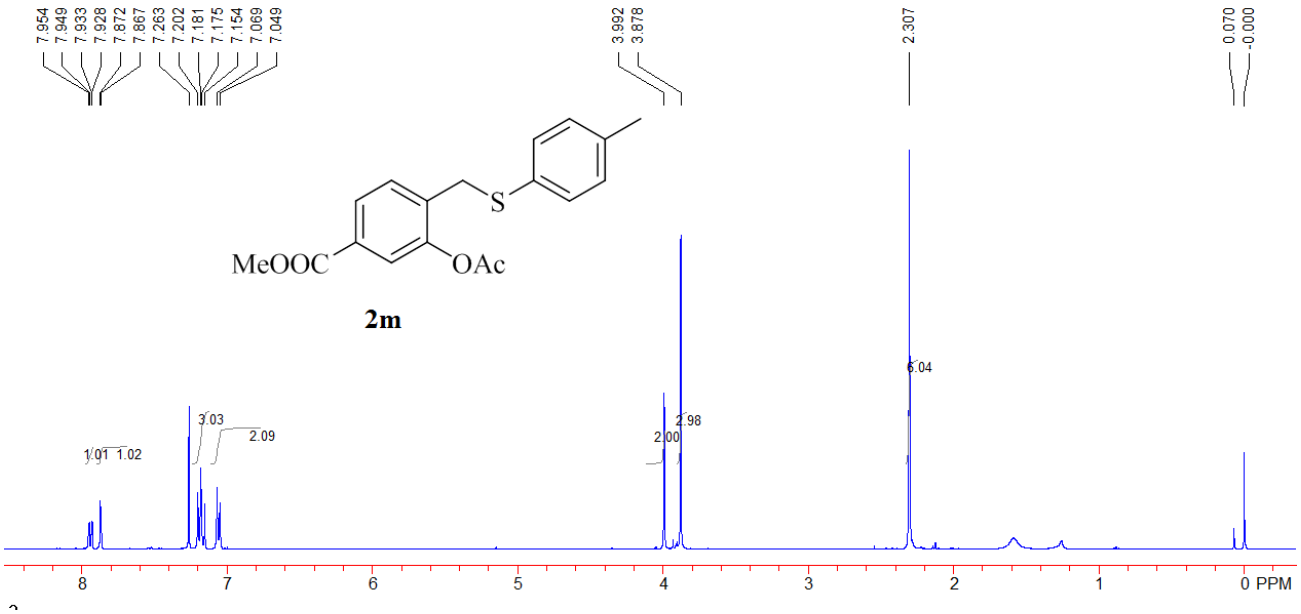
2k

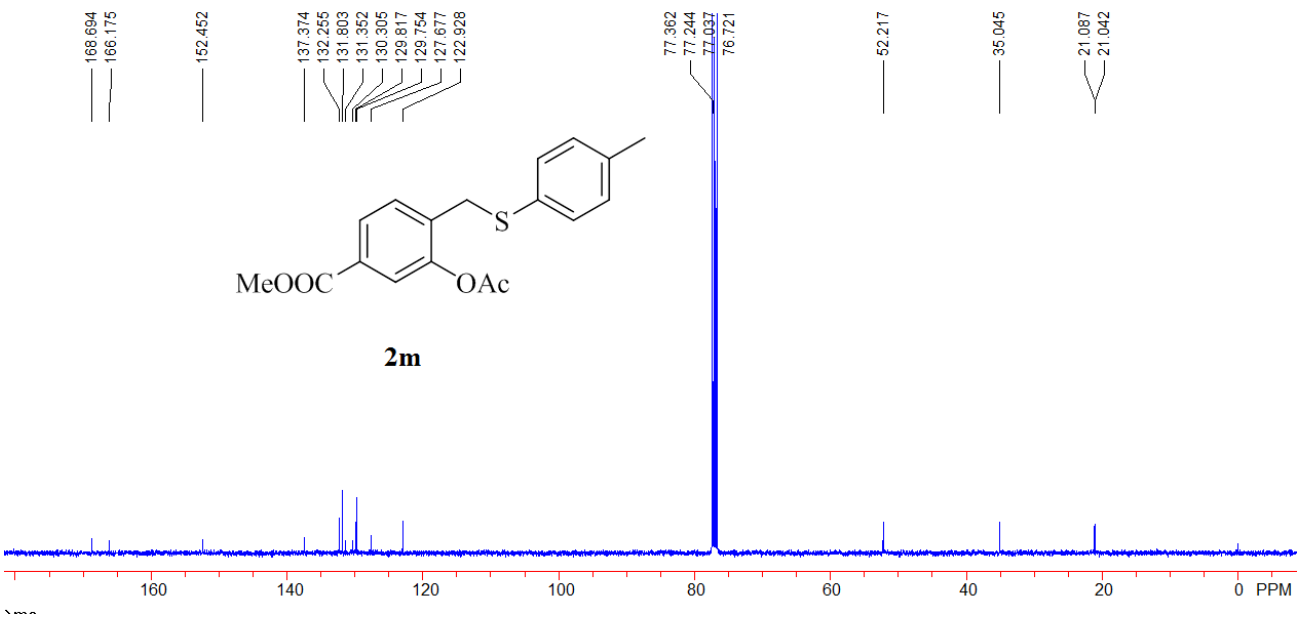

168.649
149.183
148.344
137.383
131.776
131.280
131.235
129.754
128.788
118.098
115.958
77.344
77.235
77.028
76.712
34.558
21.078
20.925
S
F3CO
OAc
180
160
140
120
100
80
60
40
20
PPM

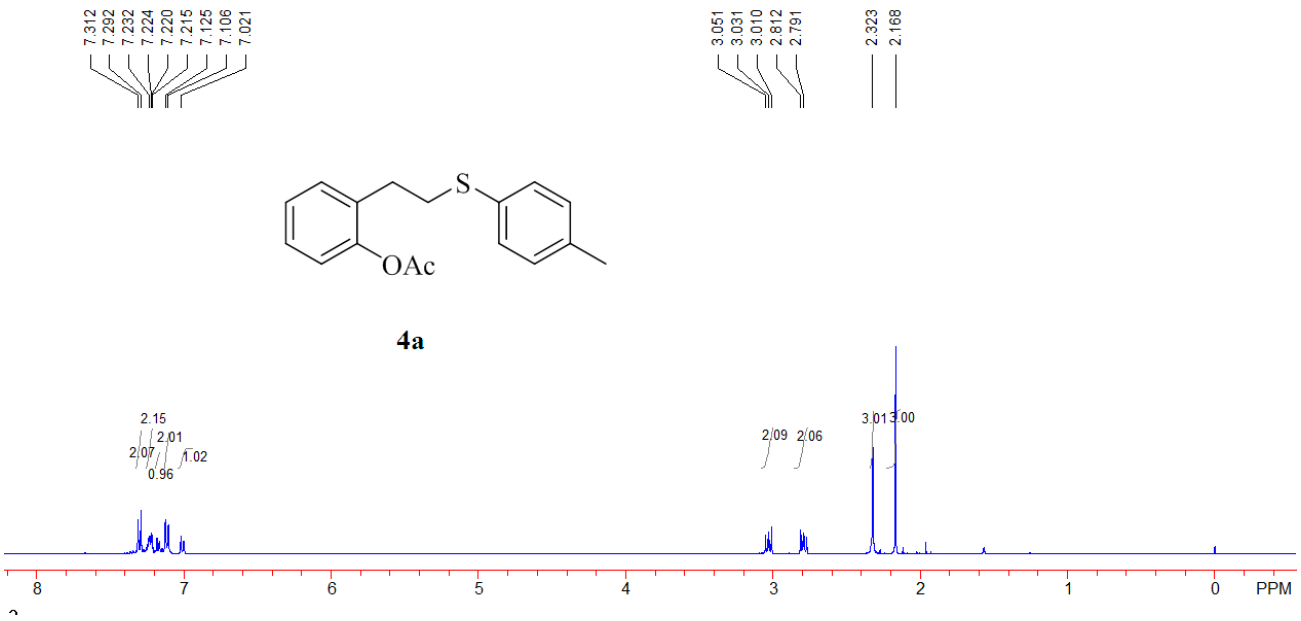
2k


7.404
7.401
7.363
7.359
7.344
7.340
7.261
7.181
7.159
7.143
7.138
7.066
7.046
3.949
2.320
2.310
2.226
-0.000
NC
OAc
S
21
2.90
1.89
1.06
0.96
2.00
2.95
2.89
8
7
6
5
4
3
2
1
0
PPM

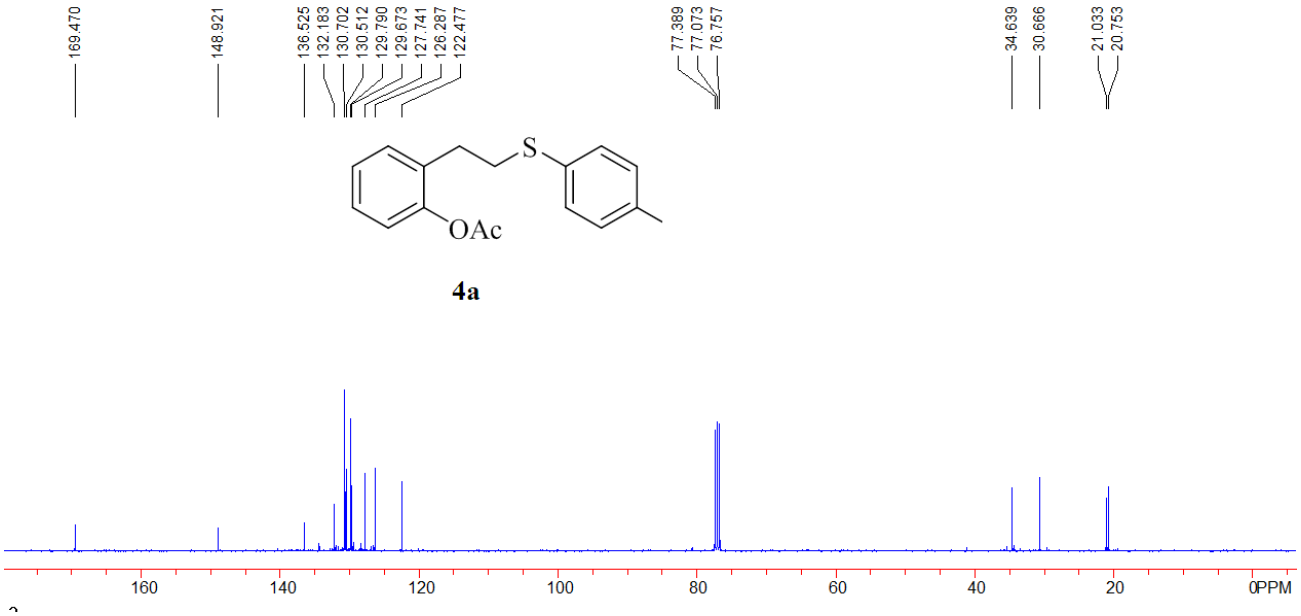

168.495
148.777
137.916
136.128
132.345
131.361
130.377
129.862
129.366
126.585
117.863
111.859
77.353
77.244
77.037
76.721
35.154
21.114
20.898
NC
OAc
S
21
180
160
140
120
100
80
60
40
20
PPM


7.954
7.949
7.933
7.928
7.872
7.867
7.263
7.202
7.181
7.175
7.154
7.069
7.049
3.992
3.878
2.307
0.070
-0.000
S
MeOOC
OAc
2m
6.04
3.03
2.09
1.01
1.02
2.00
2.98
8
7
6
5
4
3
2
1
0 PPM

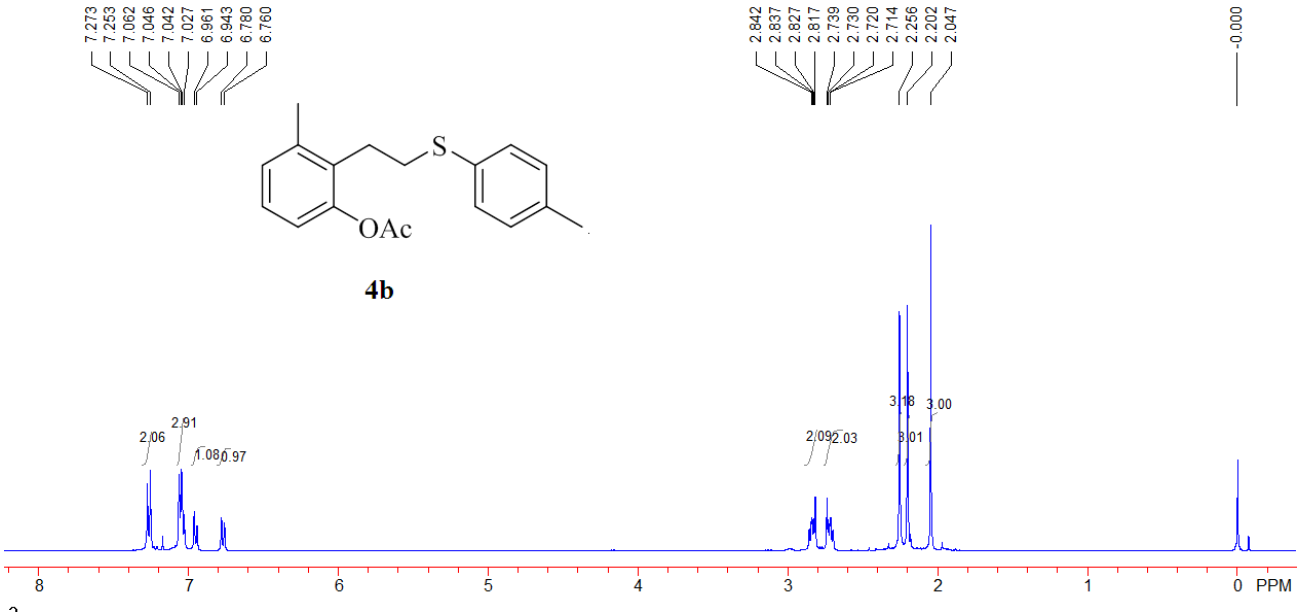

168.694
166.175
152.452
137.374
132.255
131.803
131.352
130.305
129.817
129.754
127.677
122.928
77.362
77.244
77.037
76.721
52.217
35.045
21.087
21.042
S
MeOOC
OAc
2m
160
140
120
100
80
60
40
20
0 PPM


7.312
7.292
7.232
7.224
7.220
7.215
7.125
7.106
7.021
3.051
3.031
3.010
2.812
2.791
2.323
2.168
S
OAc
2.15
2.01
2.07
1.02
0.96
2.09
2.06
3.01
3.00
8
7
6
5
4
3
2
1
0
PPM

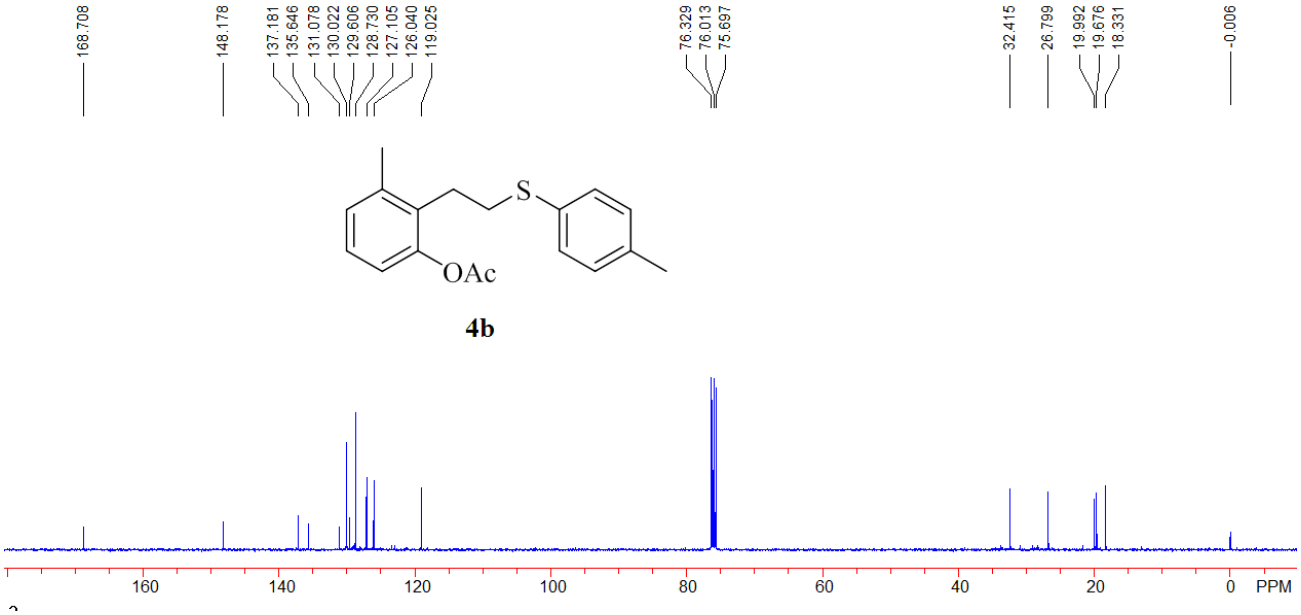
4a


169.470
148.921
136.525
132.183
130.702
130.512
129.790
129.673
127.741
126.287
122.477
77.389
77.073
76.757
34.639
30.666
21.033
20.753
S
OAc
160
140
120
100
80
60
40
20
0PPM

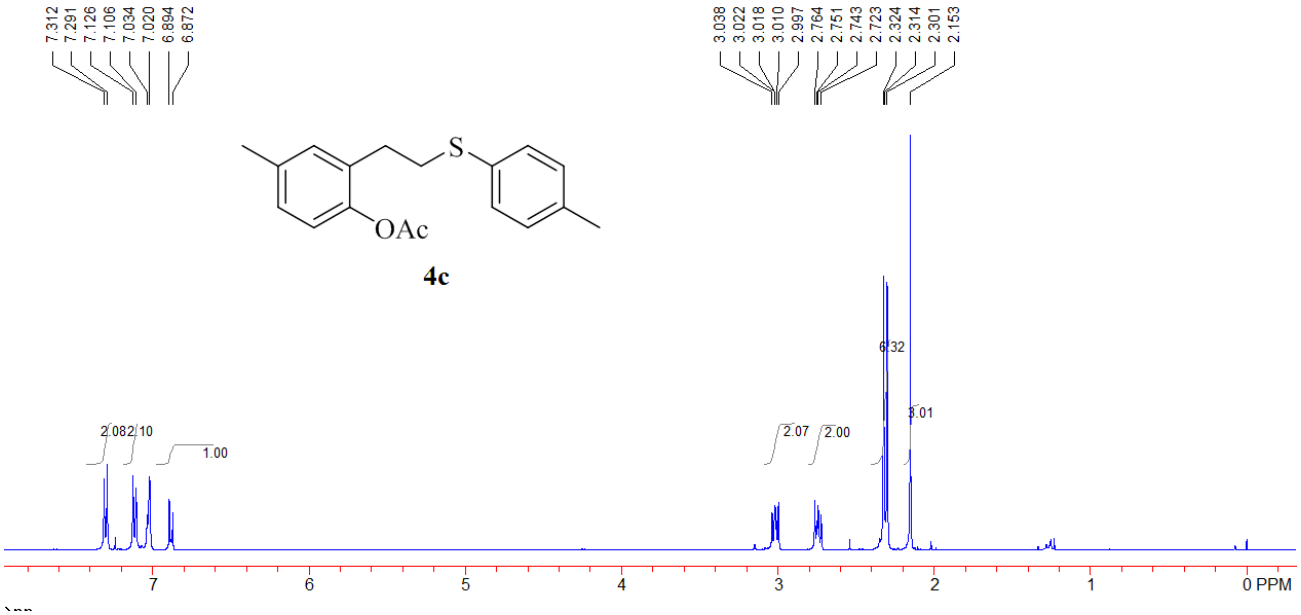
4a


7.273
7.253
7.062
7.046
7.042
7.027
6.961
6.943
6.780
6.760
2.842
2.837
2.827
2.817
2.739
2.730
2.720
2.714
2.256
2.202
2.047
-0.000
S
OAc
2.06
2.91
1.08
0.97
2.09
2.03
3.18
3.01
3.00
8
7
6
5
4
3
2
1
0
PPM

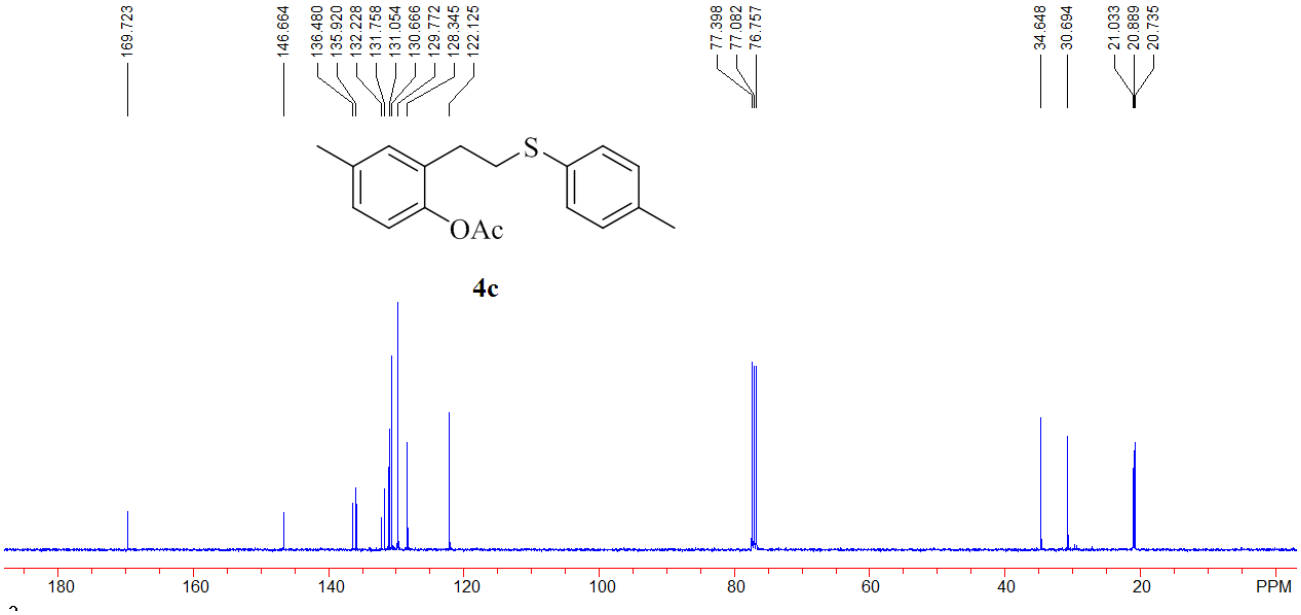
4b


168.708
148.178
137.181
135.646
131.078
130.022
129.606
128.730
127.105
126.040
119.025
76.329
76.013
75.697
32.415
26.799
19.992
19.676
18.331
-0.006
S
OAc
160
140
120
100
80
60
40
20
0
PPM

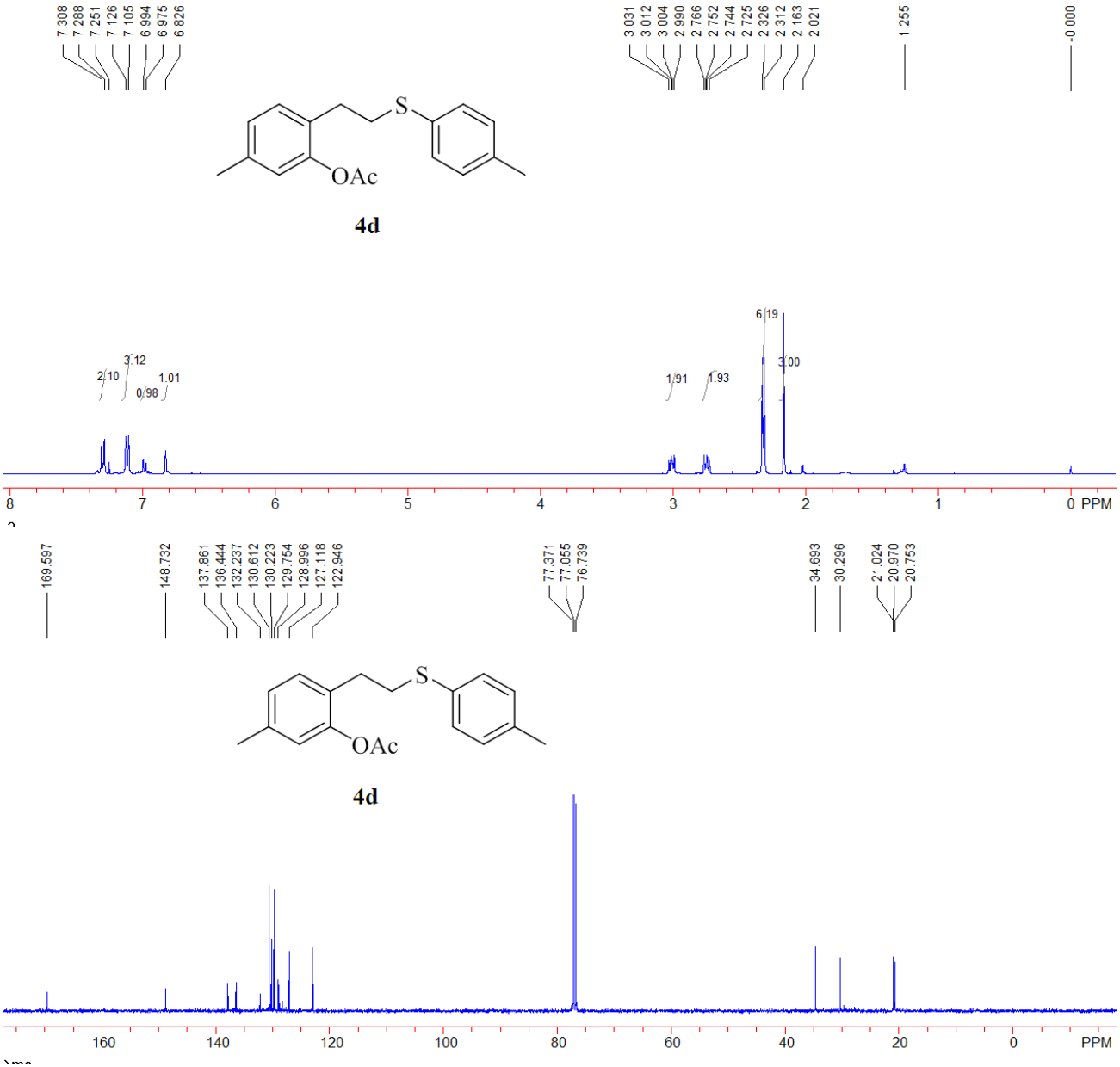
4b

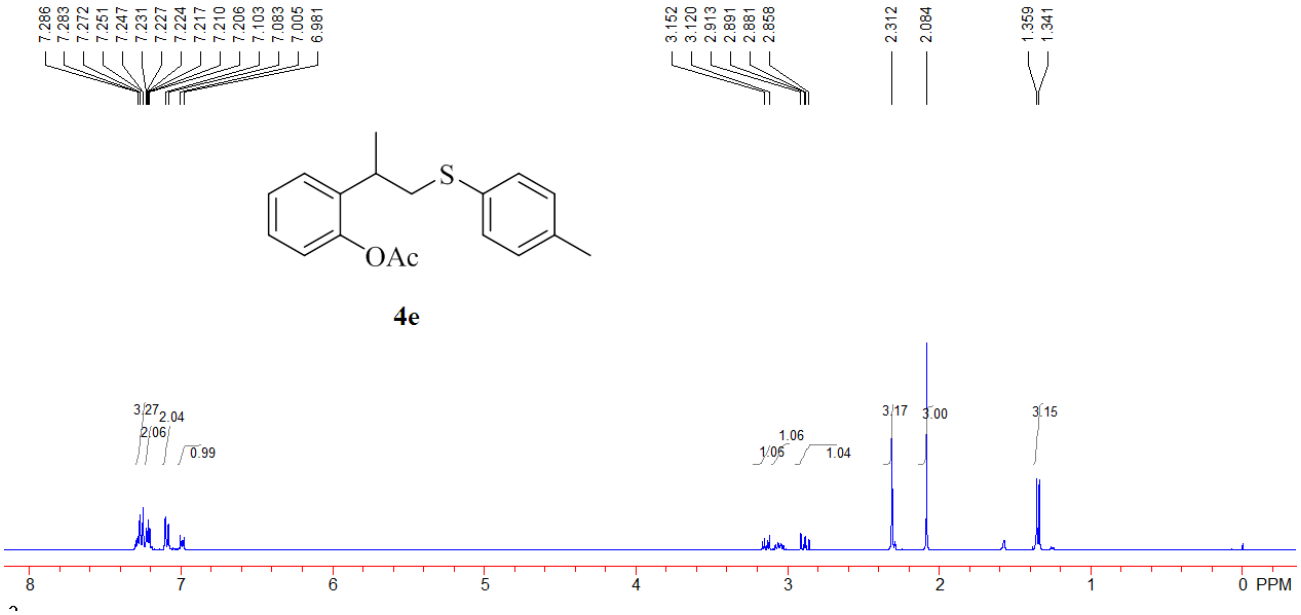

7.312
7.291
7.126
7.106
7.034
7.020
6.894
6.872
3.038
3.022
3.018
3.010
2.997
2.764
2.751
2.743
2.723
2.324
2.314
2.301
2.153
S
OAc
2.08
2.10
1.00
2.07
2.00
6.32
3.01
7
6
5
4
3
2
1
0 PPM

4c

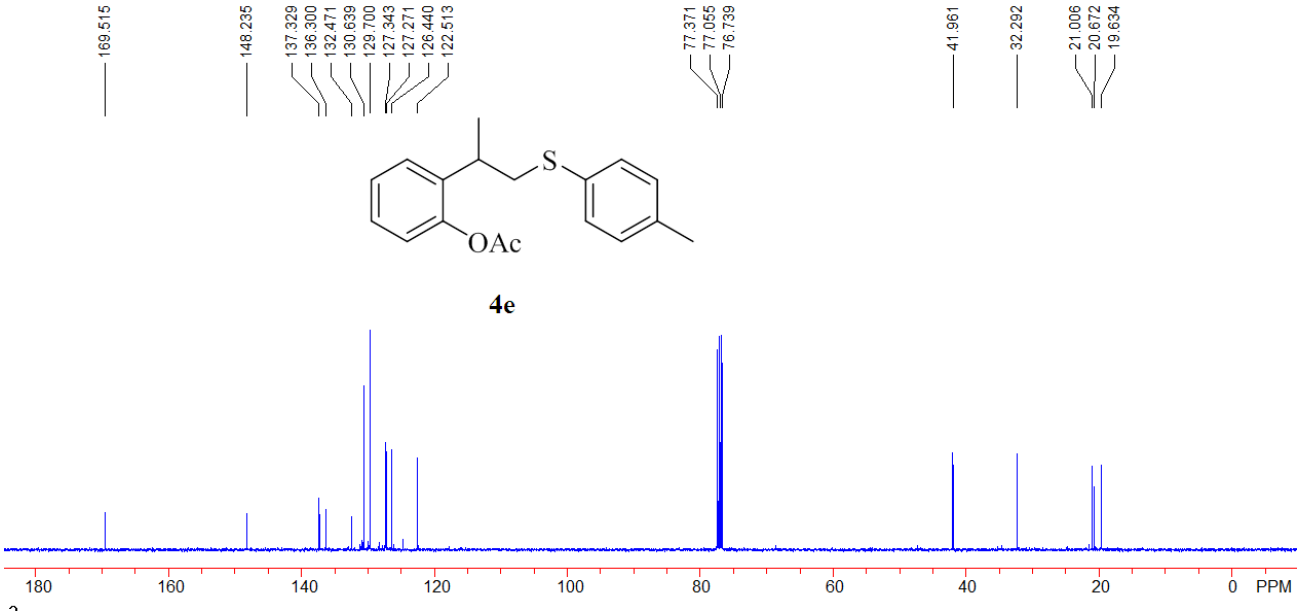

169.723
146.664
136.480
135.920
132.228
131.758
131.054
130.666
129.772
128.345
122.125
77.398
77.082
76.757
34.648
30.694
21.033
20.889
20.735
S
OAc
180
160
140
120
100
80
60
40
20
PPM

4c

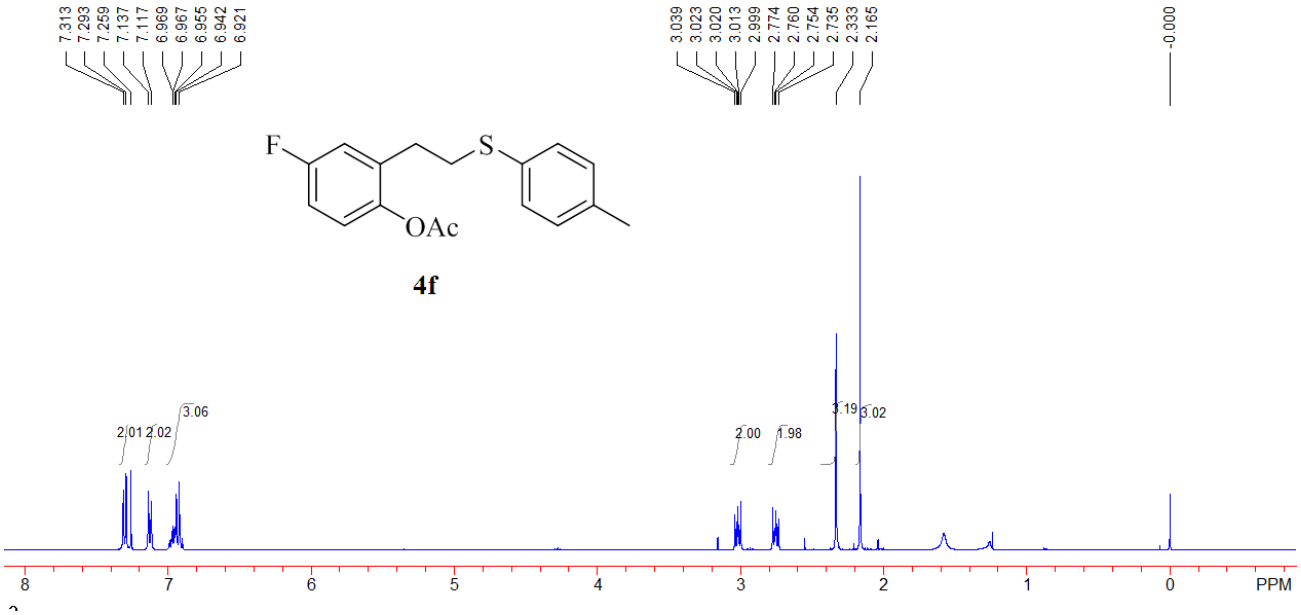

7.308
7.288
7.251
7.126
7.105
6.994
6.975
6.826
3.031
3.012
3.004
2.990
2.766
2.752
2.744
2.725
2.326
2.312
2.163
2.021
1.255
-0.000
S
OAc
4d
6.19
3.12
2.10
1.01
0.98
1.91
1.93
3.00
8
7
6
5
4
3
2
1
0 PPM
169.597
148.732
137.861
136.444
132.237
130.612
130.223
129.754
128.996
127.118
122.946
77.371
77.055
76.739
34.693
30.296
21.024
20.970
20.753
S
OAc
4d
160
140
120
100
80
60
40
20
0
PPM


7.286
7.283
7.272
7.251
7.247
7.231
7.227
7.224
7.217
7.210
7.206
7.103
7.083
7.005
6.981
3.152
3.120
2.913
2.891
2.881
2.858
2.312
2.084
1.359
1.341
S
OAc
3.27
2.04
2.06
0.99
1.06
1.05
1.04
3.17
3.00
3.15
8
7
6
5
4
3
2
1
0 PPM

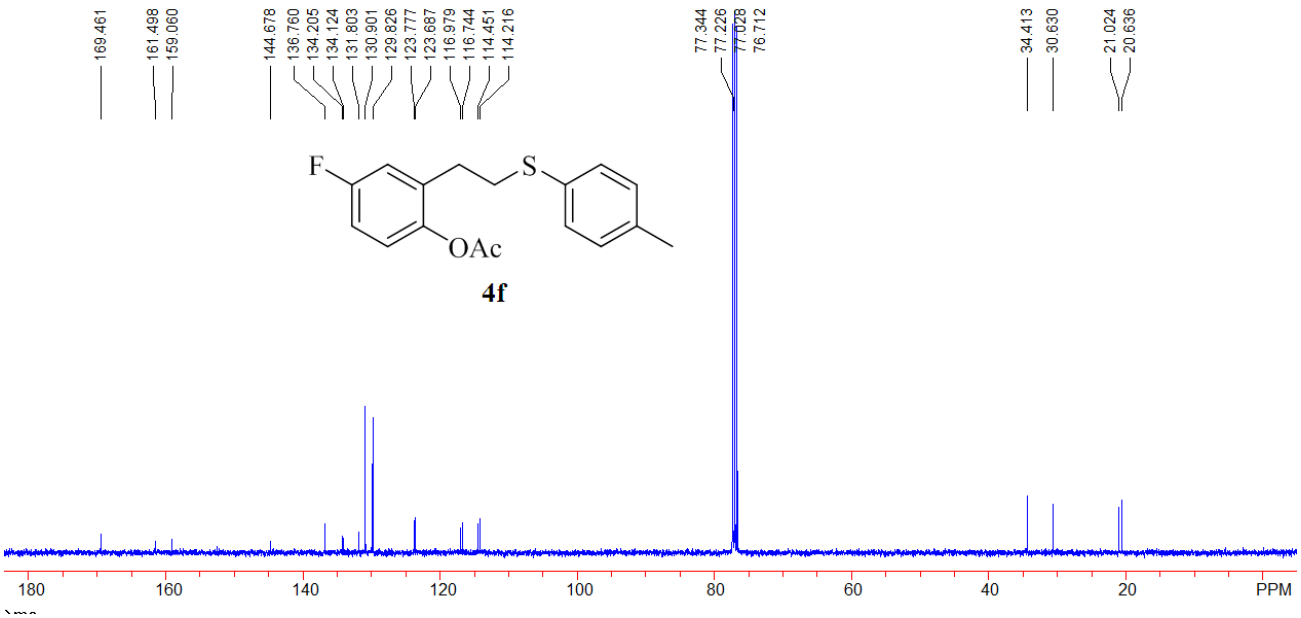
4e


169.515
148.235
137.329
136.300
132.471
130.639
129.700
127.343
127.271
126.440
122.513
77.371
77.055
76.739
41.961
32.292
21.006
20.672
19.634
S
OAc
180
160
140
120
100
80
60
40
20
0 PPM

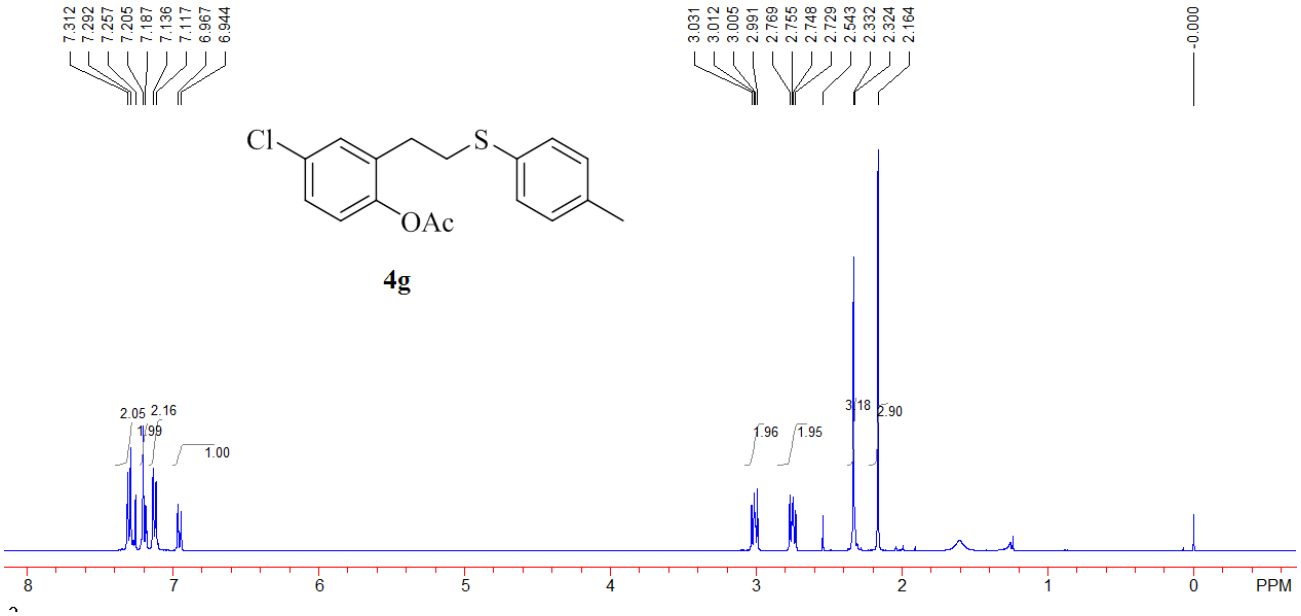
4e

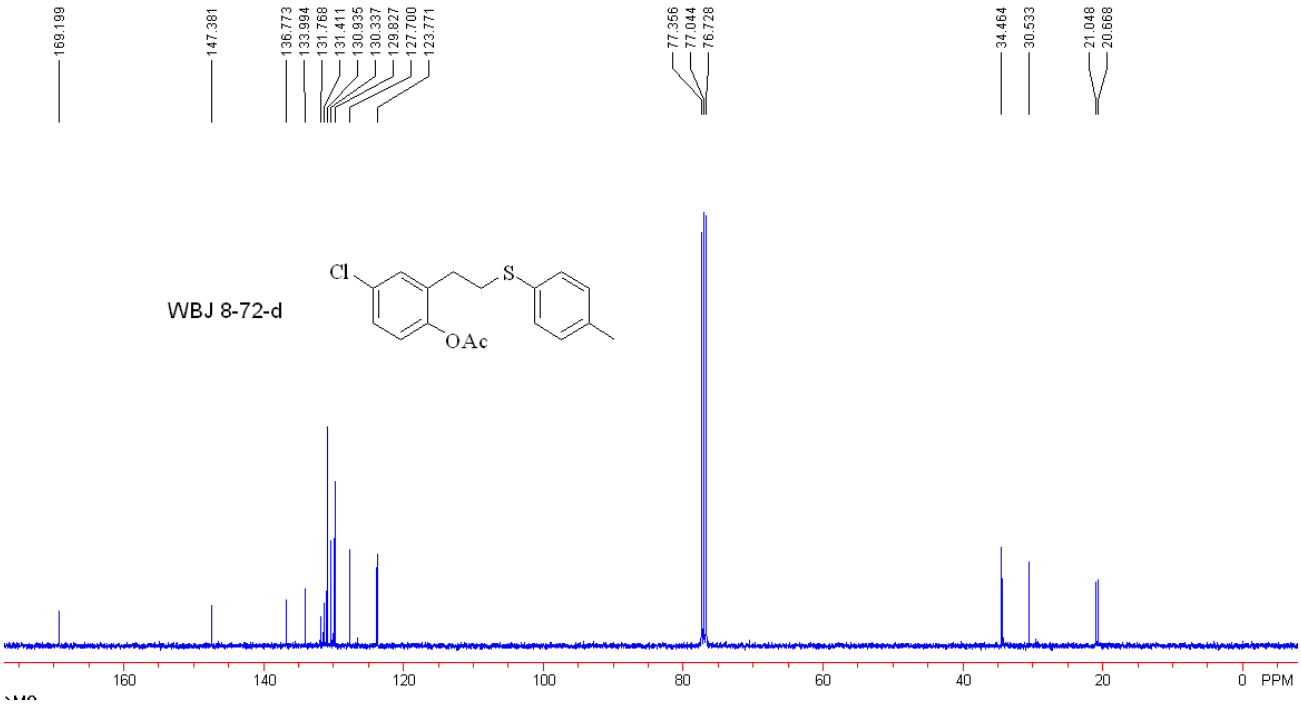

7.313
7.293
7.259
7.137
7.117
6.969
6.967
6.955
6.942
6.921
3.039
3.023
3.020
3.013
2.999
2.774
2.760
2.754
2.735
2.333
2.165
0.000
F
S
OAc
2.01
2.02
3.06
2.00
1.98
3.19
3.02
8
7
6
5
4
3
2
1
0
PPM

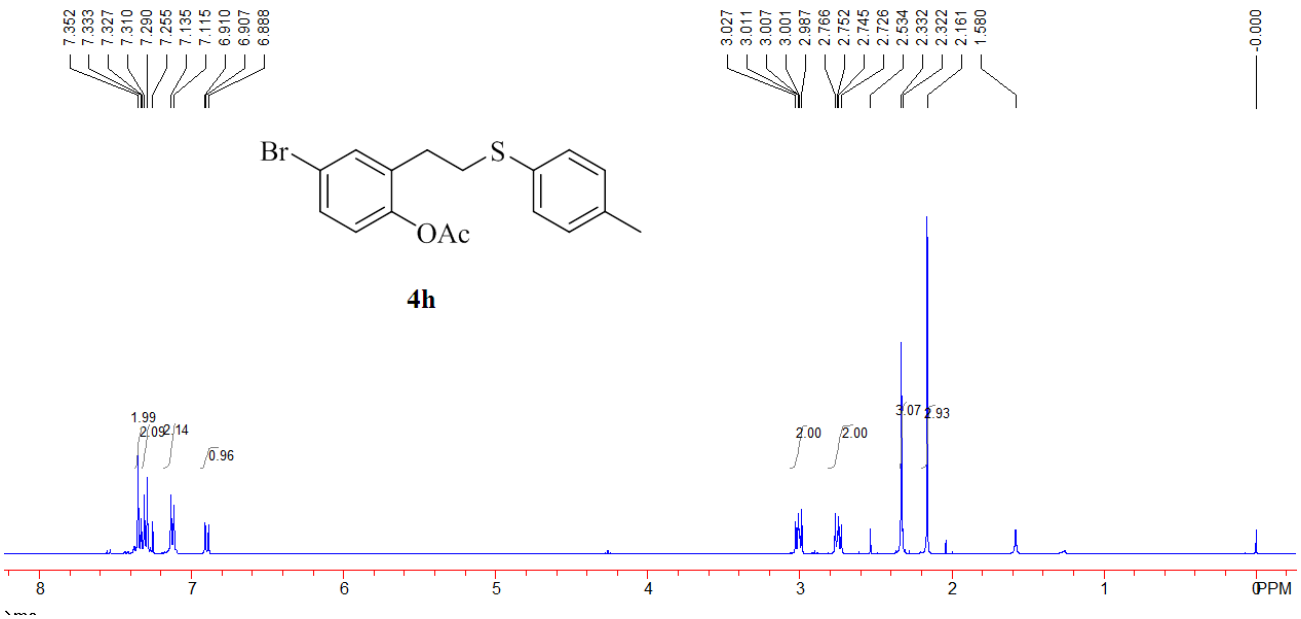
4f

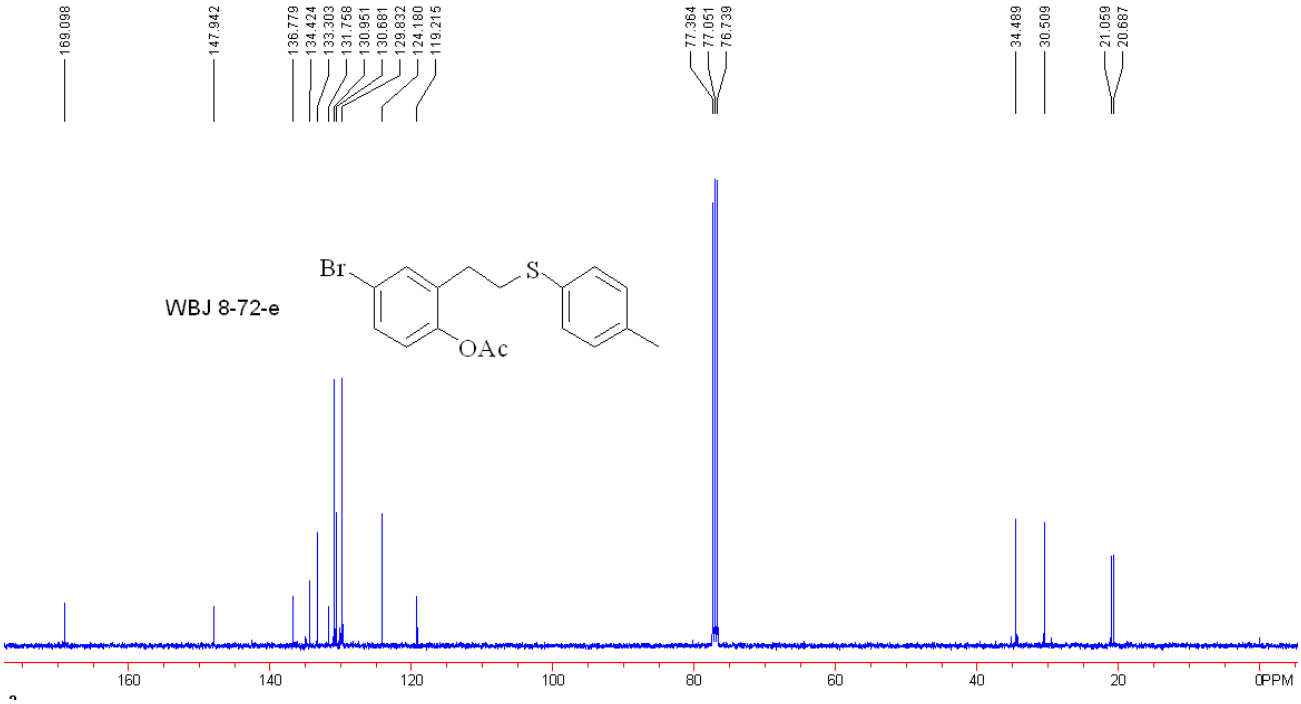

169.461
161.498
159.060
144.678
136.760
134.205
134.124
131.803
130.901
129.826
123.777
123.687
116.979
116.744
114.451
114.216
77.344
77.226
77.028
76.712
34.413
30.630
21.024
20.636
F
S
OAc
180
160
140
120
100
80
60
40
20
PPM

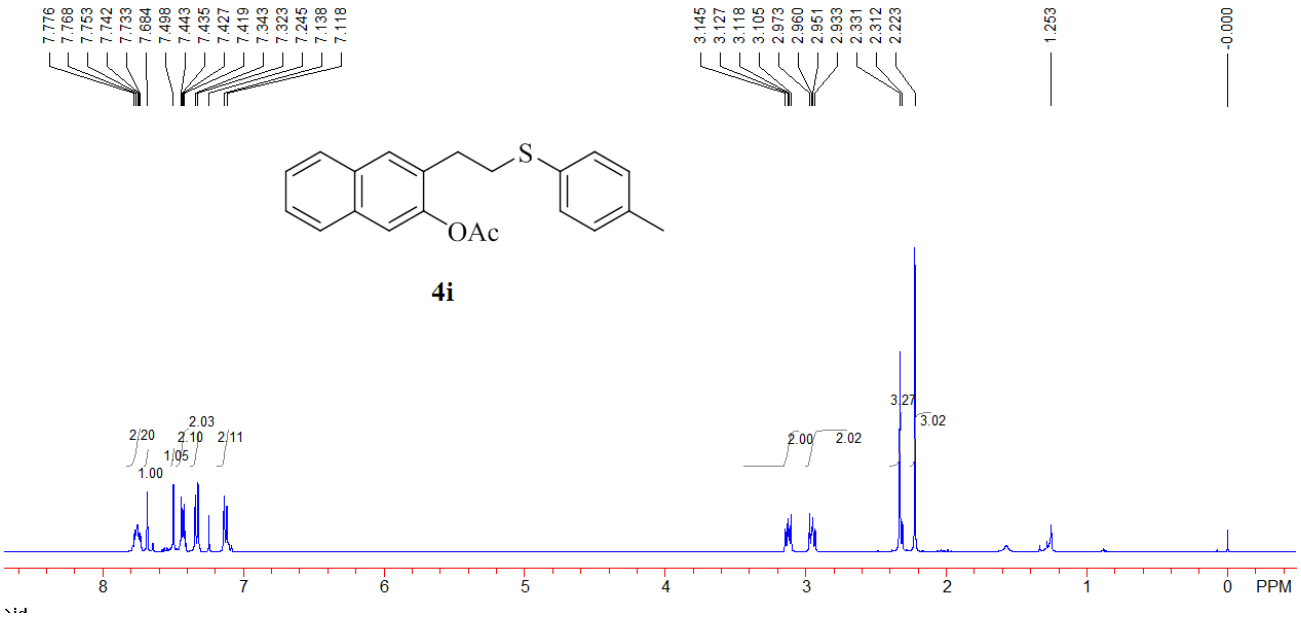
4f

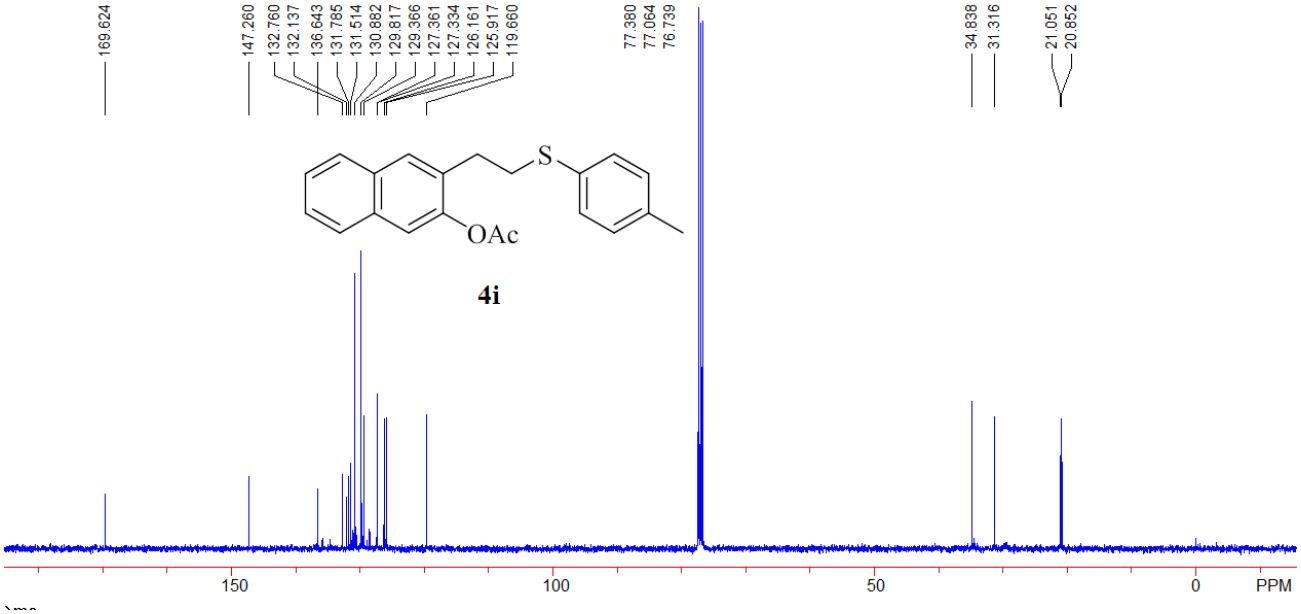

7.312
7.292
7.257
7.205
7.187
7.136
7.117
6.967
6.944
3.031
3.012
3.005
2.991
2.769
2.755
2.748
2.729
2.543
2.332
2.324
2.164
-0.000
Cl
S
OAc
4g
2.05
2.16
1.99
1.00
1.96
1.95
3.18
2.90
8
7
6
5
4
3
2
1
0
PPM

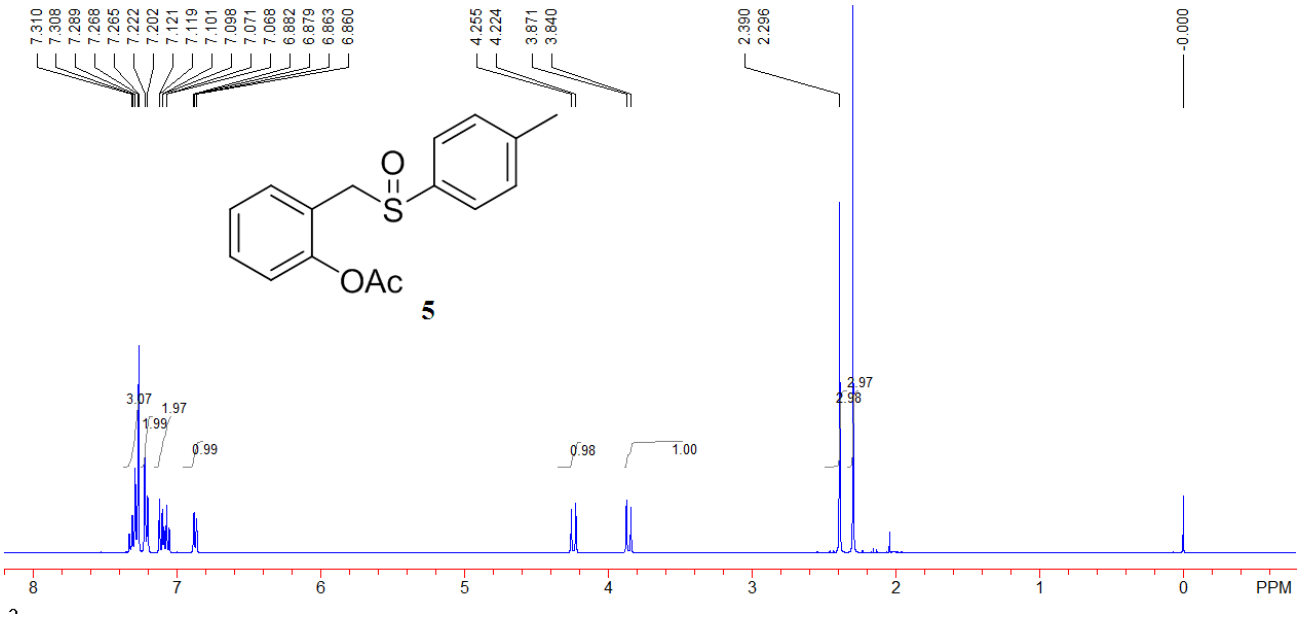

169.199
147.381
136.773
133.994
131.768
131.411
130.935
130.337
129.827
127.700
123.771
77.356
77.044
76.728
34.464
30.533
21.048
20.668
WBJ 8-72-d
Cl
S
OAc
160
140
120
100
80
60
40
20
0
PPM

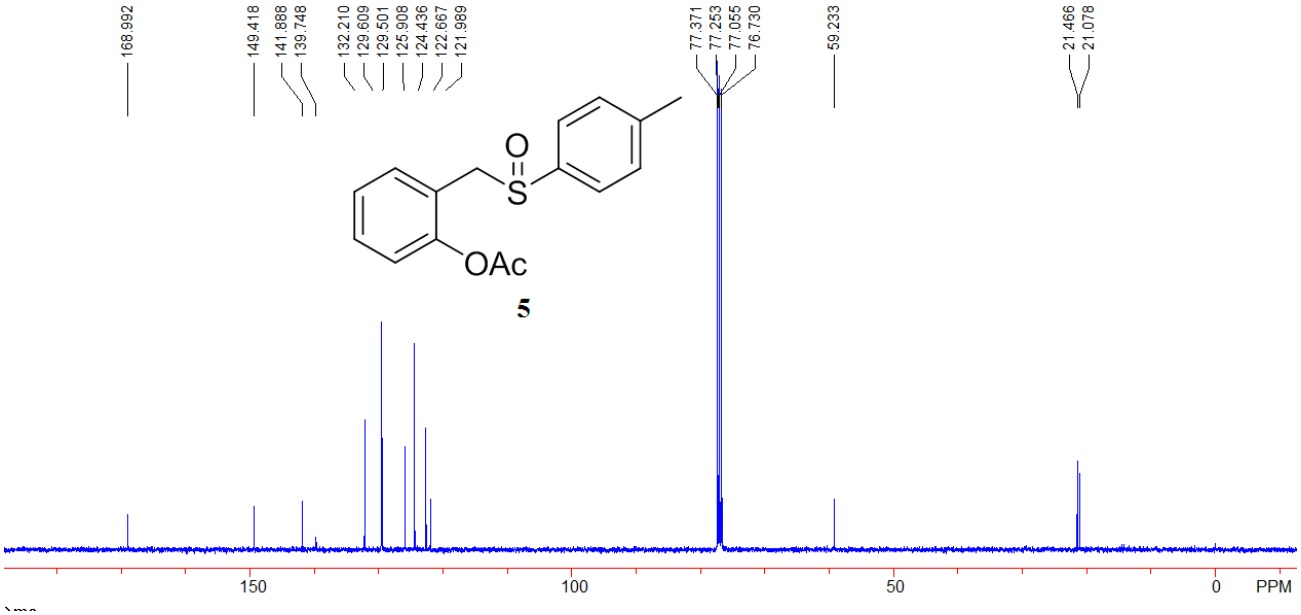

7.352
7.333
7.327
7.310
7.290
7.255
7.135
7.115
6.910
6.907
6.888
3.027
3.011
3.007
3.001
2.987
2.766
2.752
2.745
2.726
2.534
2.332
2.322
2.161
1.580
0.000
Br
S
OAc
4h
1.99
2.09
2.14
0.96
2.00
2.00
3.07
2.93
8
7
6
5
4
3
2
1
0PPM

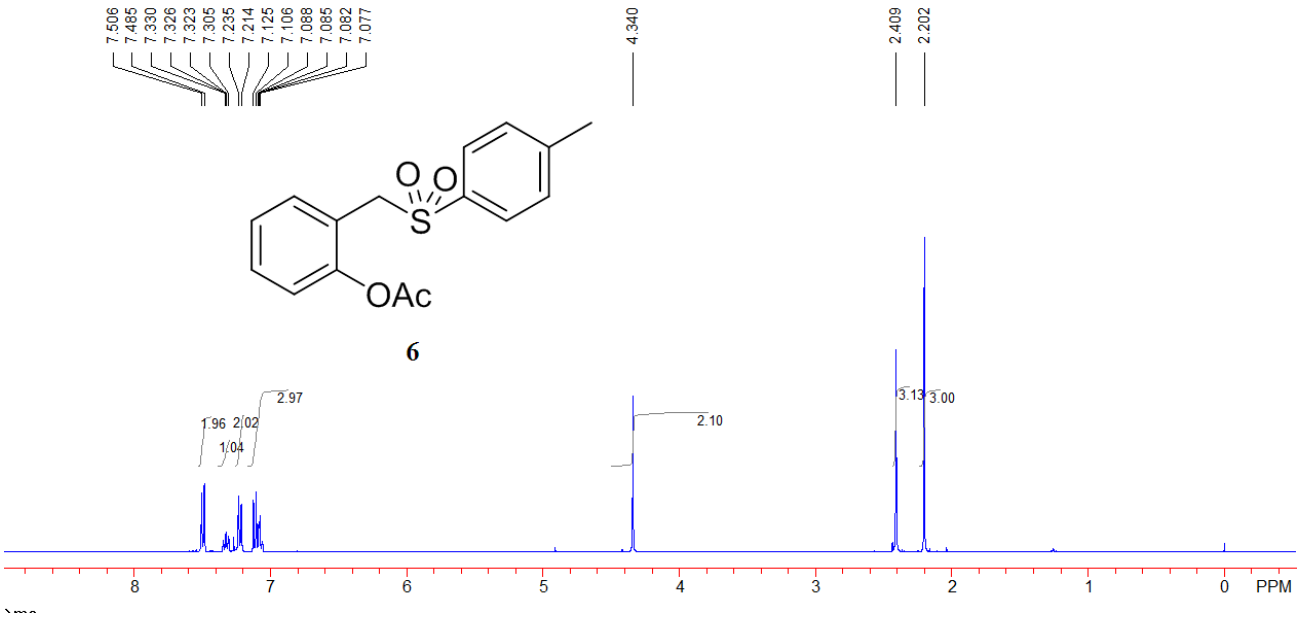

169.098
147.942
136.779
134.424
133.303
131.758
130.951
130.681
129.832
124.180
119.215
77.364
77.051
76.739
34.489
30.509
21.059
20.687
WBJ 8-72-e
Br
S
OAc
160
140
120
100
80
60
40
20
0PPM

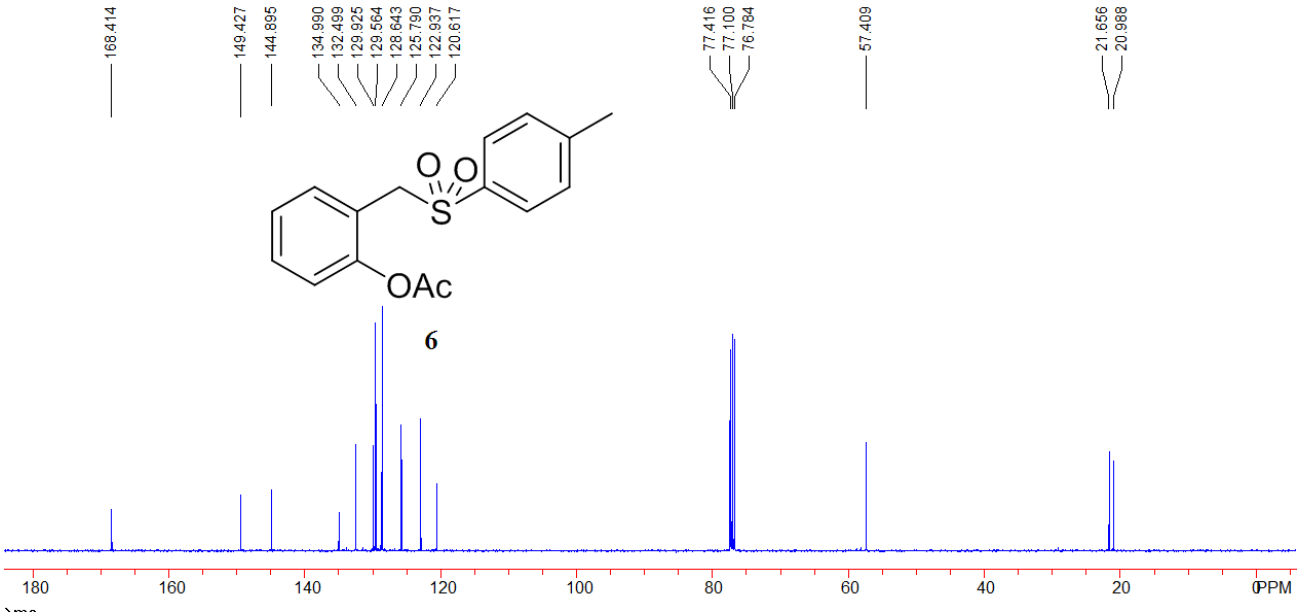

7.776
7.768
7.753
7.742
7.733
7.684
7.498
7.443
7.435
7.427
7.419
7.343
7.323
7.245
7.138
7.118
3.145
3.127
3.118
3.105
2.973
2.960
2.951
2.933
2.331
2.312
2.223
1.253
-0.000
S
OAc
4i
2.20
2.03
2.10
2.11
1.05
1.00
2.00
2.02
3.27
3.02
8
7
6
5
4
3
2
1
0
PPM

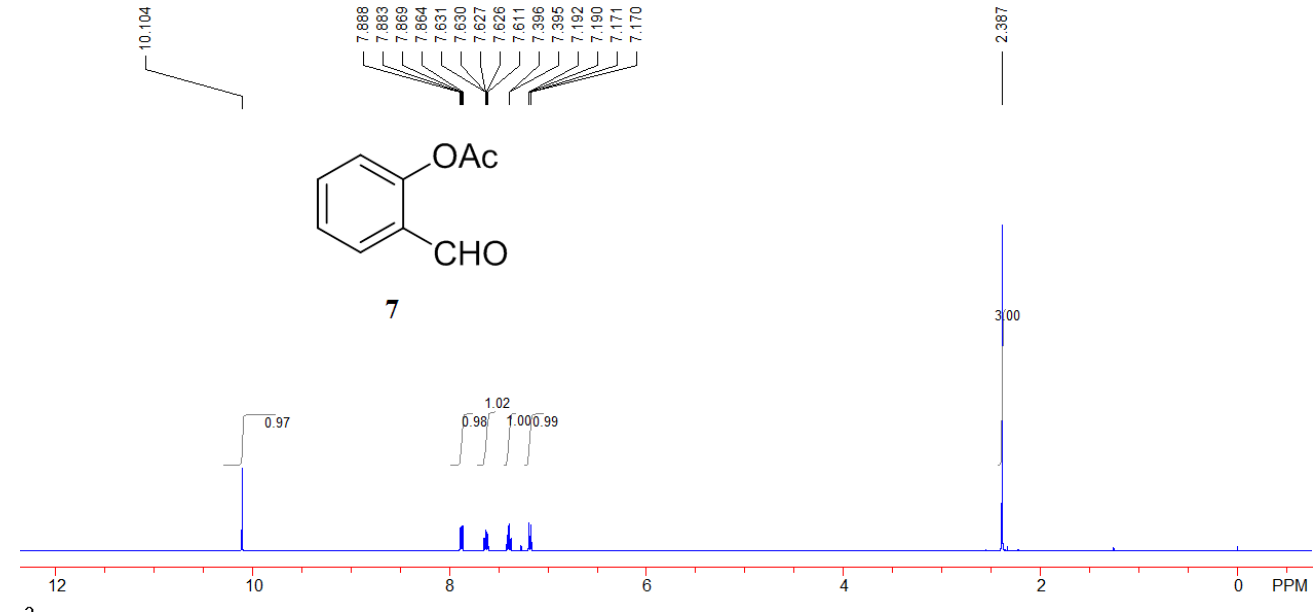

169.624
147.260
132.760
132.137
136.643
131.785
131.514
130.882
129.817
129.366
127.361
127.334
126.161
125.917
119.660
77.380
77.064
76.739
34.838
31.316
21.051
20.852
S
OAc
4i
150
100
50
0
PPM

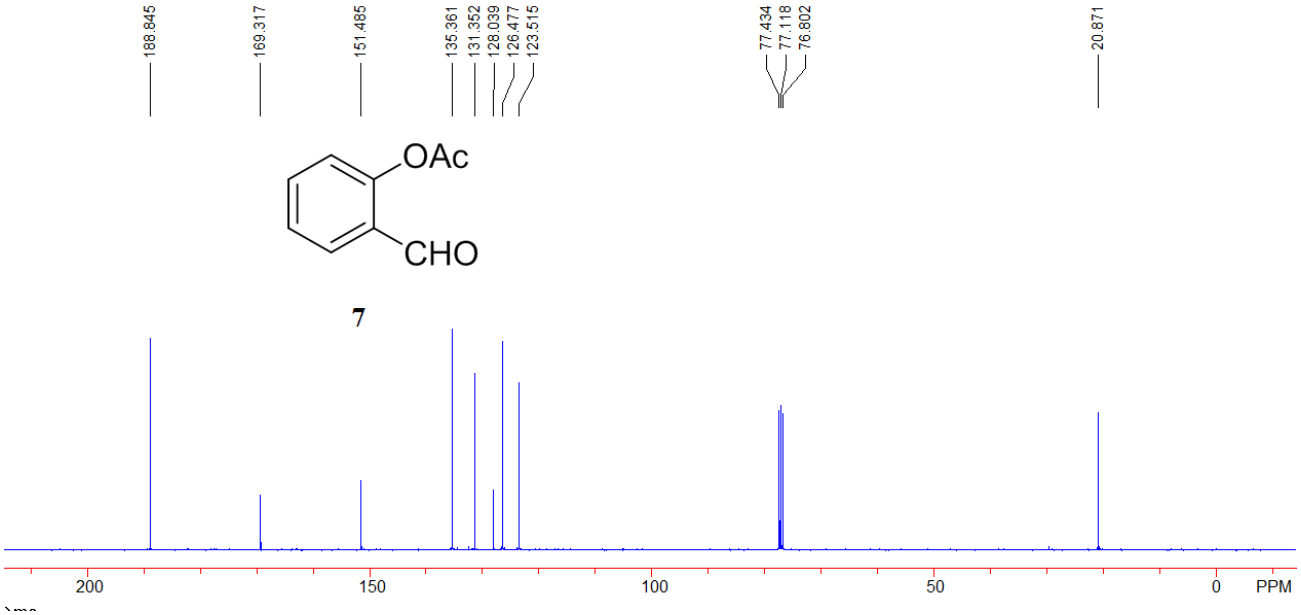

7.310
7.308
7.289
7.268
7.265
7.222
7.202
7.121
7.119
7.101
7.098
7.071
7.068
6.882
6.879
6.863
6.860
4.255
4.224
3.871
3.840
2.390
2.296
-0.000
O
S
OAc
5
3.07
1.99
1.97
0.99
0.98
1.00
2.97
2.98
8
7
6
5
4
3
2
1
0
PPM

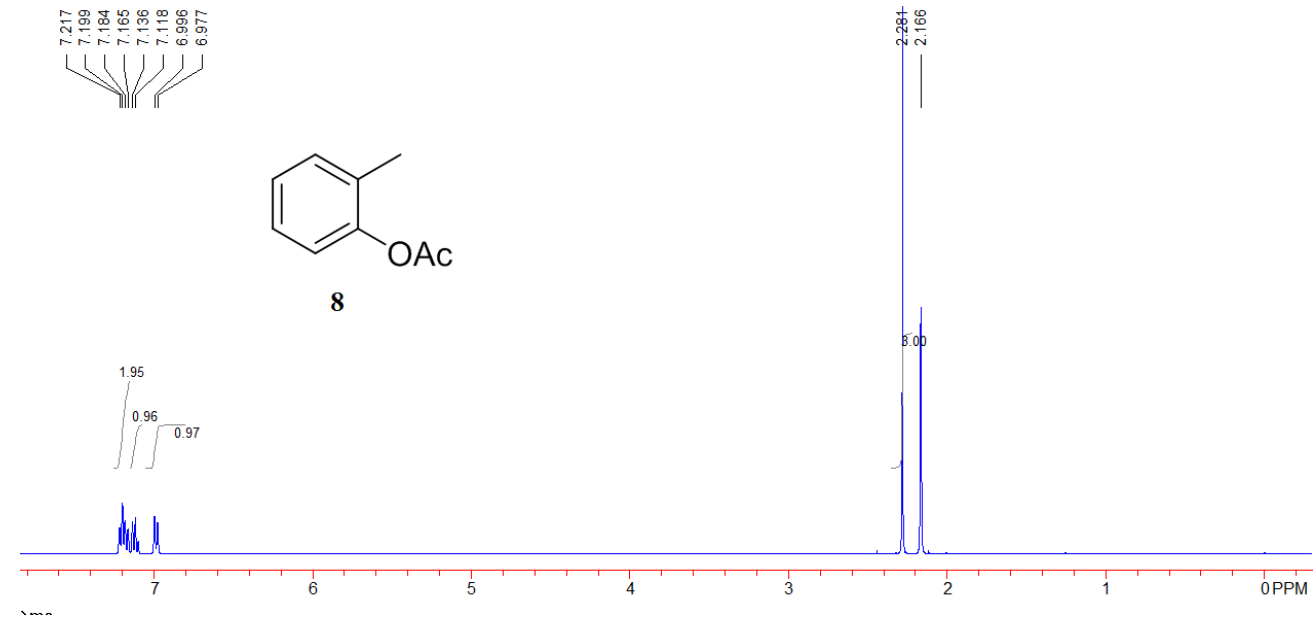

168.992
149.418
141.888
139.748
132.210
129.609
129.501
125.908
124.436
122.667
121.989
77.371
77.253
77.055
76.730
59.233
21.466
21.078
O
S
OAc
5
150
100
50
0
PPM

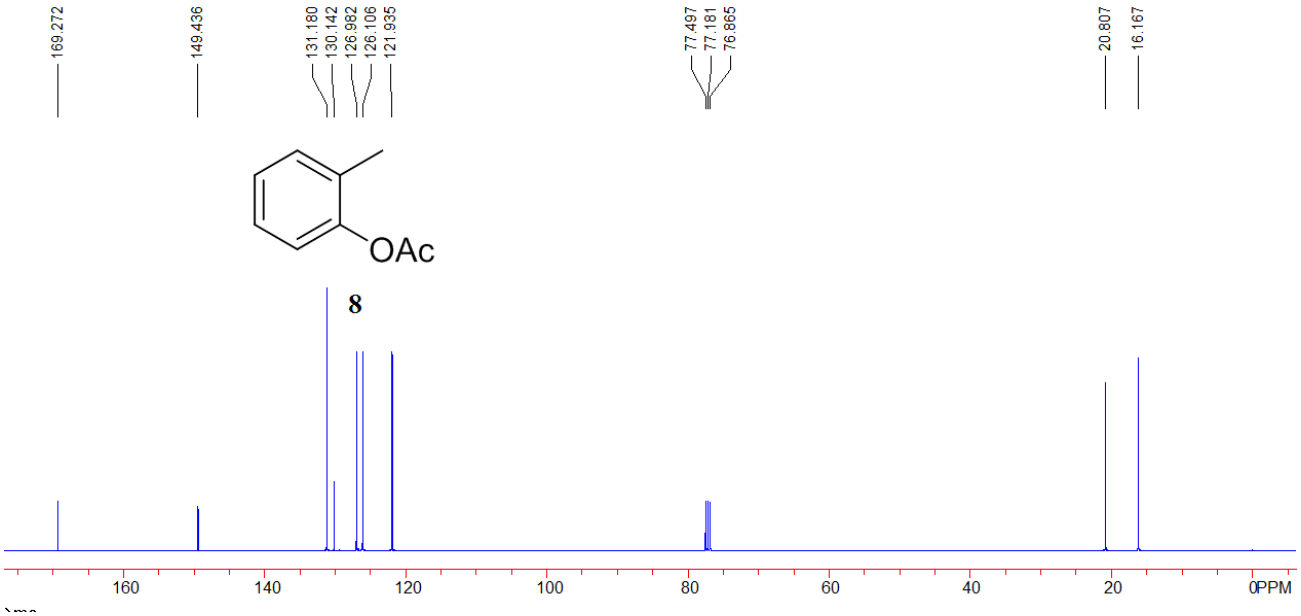

7.506
7.485
7.330
7.326
7.323
7.305
7.235
7.214
7.125
7.106
7.088
7.085
7.082
7.077
4.340
2.409
2.202
O
O
S
OAc
6
2.97
1.96
2.02
1.04
2.10
3.13
3.00
8
7
6
5
4
3
2
1
0
PPM

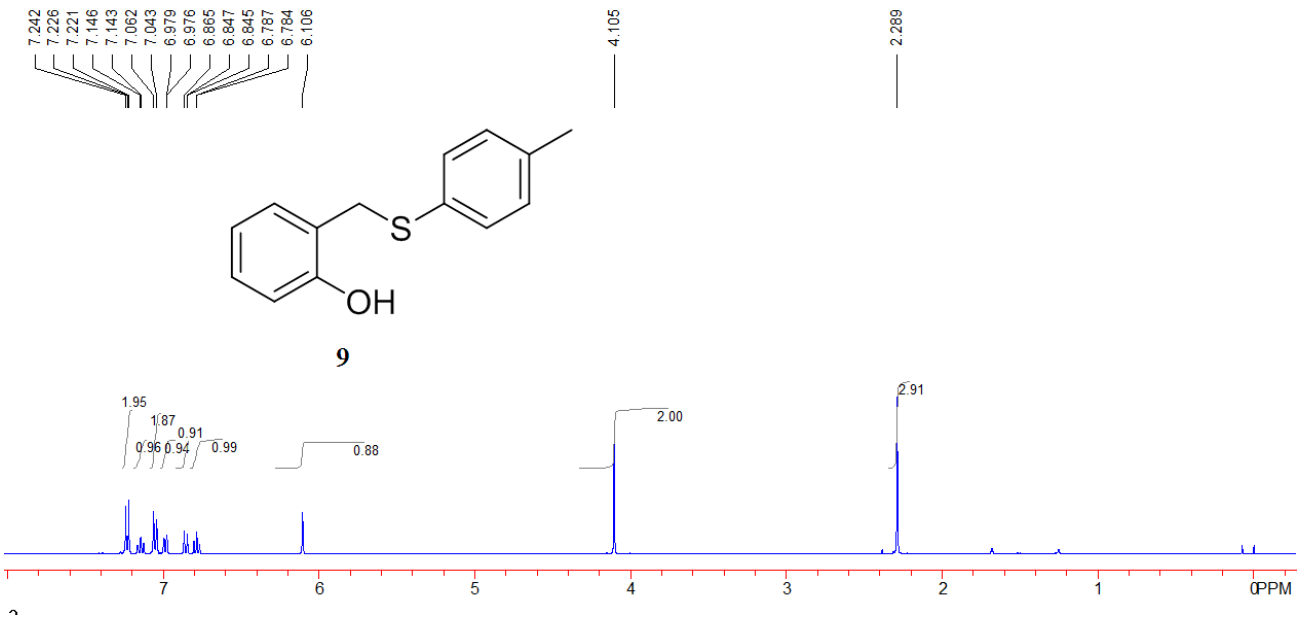

168.414
149.427
144.895
134.990
132.499
129.925
129.564
128.643
125.790
122.937
120.617
77.416
77.100
76.784
57.409
21.656
20.988
O
O
S
OAc
6
180
160
140
120
100
80
60
40
20
0
PPM


10.104
7.888
7.883
7.869
7.864
7.631
7.630
7.627
7.626
7.611
7.396
7.395
7.192
7.190
7.171
7.170
2.387
OAc
CHO
7
3.00
1.02
0.97
0.98
1.00
0.99
12
10
8
6
4
2
0
PPM

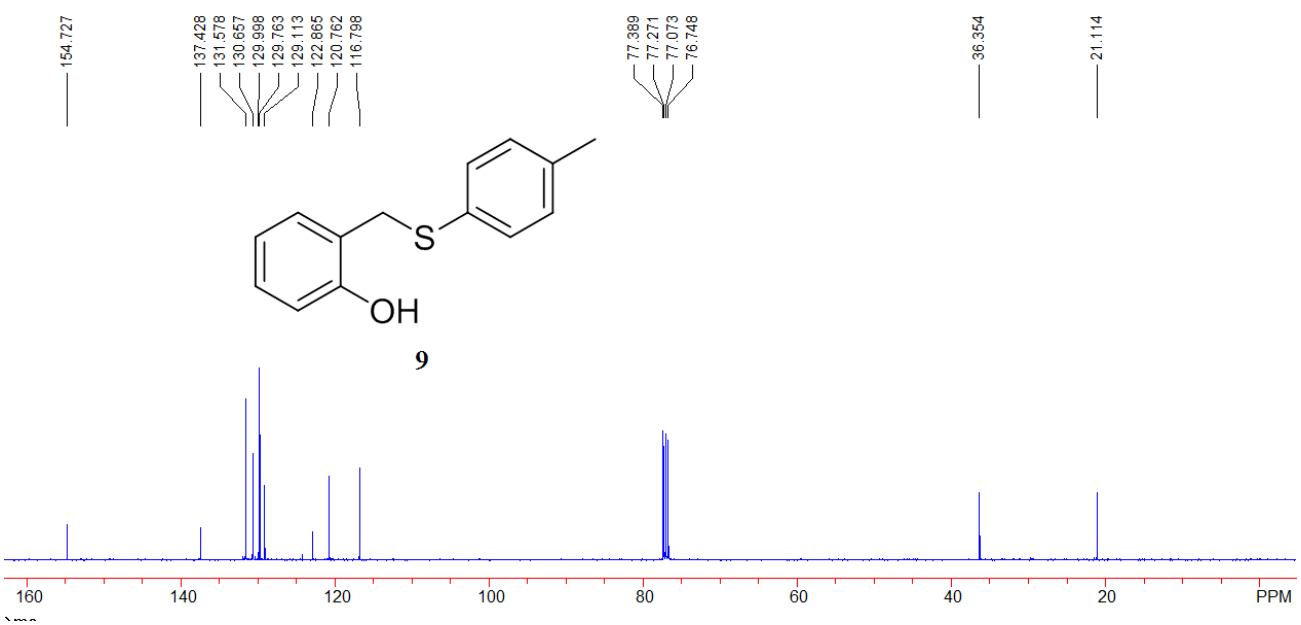

188.845
169.317
151.485
135.361
131.352
128.039
126.477
123.515
77.434
77.118
76.802
20.871
OAc
CHO
7
200
150
100
50
0
PPM


7.217
7.199
7.184
7.165
7.136
7.118
6.996
6.977
2.281
2.166
OAc
8
1.95
0.96
0.97
3.00
7
6
5
4
3
2
1
0 PPM


169.272
149.436
131.180
130.142
126.982
126.106
121.935
77.497
77.181
76.865
20.807
16.167
OAc
8
160
140
120
100
80
60
40
20
0PPM


7.242
7.226
7.221
7.146
7.143
7.062
7.043
6.979
6.976
6.865
6.847
6.845
6.787
6.784
6.106
4.105
2.289
S
OH
1.95
1.87
0.91
0.96
0.94
0.99
0.88
2.00
2.91
7
6
5
4
3
2
1
0
PPM

9


154.727
137.428
131.578
130.657
129.998
129.763
129.113
122.865
120.762
116.798
77.389
77.271
77.073
76.748
36.354
21.114
S
OH
160
140
120
100
80
60
40
20
PPM

9

References:

(1) (a) M. Yu, Y. Xie, C. Xie and Y. Zhang, *Org. Lett.,* 2012, **14**, 2164; (b) J. Yao, M. Yu and Y. Zhang, *Adv. Synth. Catal.,* 2012, **354**, 3205; (c) X.-S. Zhang, Q.-L. Zhu, Y.-F. Zhang, Y.-B. Li and Z.-J. Shi, *Chem. Eur. J.,* 2013, ***19***, 11898.

(2) N. Sakai, T. Miyazaki, T. Sakamoto, T. Yatsuda, T. Moriya, R. Ikeda and T. Konakahara, *Org. Lett.,* 2012, **14**, 4366.

(3) Nishimoto, A. Okita, M. Yasuda and A. Baba, *Org. Lett*., 2012, **14**, 1846.

(4) C. T. T. Wong, H. Y. Lam and X. Li, *Org. Biomol. Chem.,* 2013, **11**, 7616.

(5) H.-J. Yoona, S.-M. Leea, J.-H. Kima, H.-J. Choa, J.-W. Choia, S.-H. Leeb and Y.-S. Leea, *Tetrahedron. Lett.,* 2008, **49**, 3165.