Synthesis of Aryl-Substituted 2-Methoxyphenol Derivatives from Maltol-Derived Oxidopyrylium Cycloadducts through an Acid-Mediated Ring Contraction Cascade

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Supplementary Information

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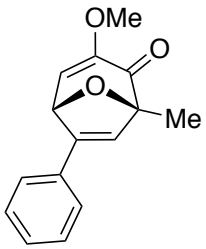
I. General Information:

All starting materials and reagents were purchased from commercially available sources and used without further purification, with the exception of CH_2Cl_2, which was purified on a solvent purification system prior to reactions. ^{1}H, and ^{13}C NMR shifts were measured using the solvent residual peak as the internal standard and reported as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, dd = doublet of doublets, q = quartet, m = multiplet), coupling constant (Hz), integration. Infrared (IR) spectral bands are characterized as broad (br), strong (s), medium (m), and weak (w). Mass spectra were recorded on a spectrometer by the electrospray ionization (ESI) technique with a time-of-flight (TOF) mass analyzer. Microwave reactions were performed via the Biotage Initiator EXP US 400W(no. 355302, external IR temperature sensor) in a sealed vessel. Where noted, reaction products were purified via silica gel chromatography using a Biotage Isolera Prime, SiliCycle Silia*Sep* 12 g or 25 g cartridges, in a solvent system of ethyl acetate (EtOAc) in hexane.

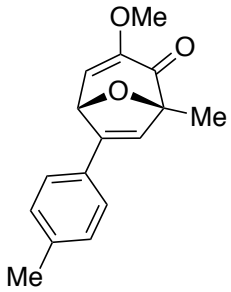
II. Synthesis of 8 oxabicyclo [3.2.1] octenes

Synthesis of (1*S*,5*S*)-3-methoxy-1-methyl-6-phenyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (4a):



To a solution of **11/12** (250 mg, 0.89 mmol, 1 eq) was added phenylacetylene (966 µL, 8.9 mmol, 10 equiv). The reaction was subjected to microwave irradiation at 120 °C for 3 h, and immediately purified by chromatography (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 µm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL)). Product fractions were concentrated *en vacuo* to yield **4b** as a yellow oil (107.7 mg, 25% yield). Characterization described previously.[1]

Synthesis of (1*S*,5*S*)-3-methoxy-1-methyl-6-(*p*-tolyl)-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (4b):

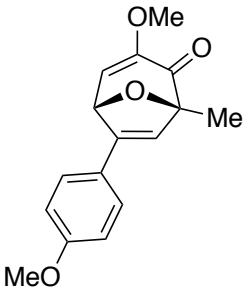


To a solution of **11/12** (50 mg, 0.18 mmol, 1 eq) was added 4-Ethynyltoluene (228 µL, 1.8 mmol, 10 equiv). The reaction was subjected to microwave irradiation at 120 °C for 2 h, and immediately purified by chromatography (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 µm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL)). Product fractions were concentrated *en vacuo* to yield **4b** as a yellow oil (36 mg, 39% yield).

Characterization for **4b** is as follows: R_f = 0.4 in 20% ethyl acetate. IR (thin film, KBr): 2934 (br), 2361 (m), 1707 (s), 1613 (m), 1511 (m), 1450 (w), 1375 (m), 1342 (m), 1295 (m), 1249 (m), 1180 (m), 1133 (m), 1063 (m), 935 (m), 906 (m), 852 (w), 804 (w), 764 (w), 724 (w), 674 (w) cm $^{-1}$. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{16}H_{17}O_4^+$: 257.1172. Found: 257.1136. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 7H), 7.20 (d, *J* = 8.0 Hz, 6H), 6.28 (d, *J* = 4.9 Hz, 3H), 6.20 (s, 3H), 5.56 (d, *J* = 4.8 Hz, 3H), 3.54 (s, 9H), 2.37 (s, 9H), 1.62 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6 (s), 155.8 (s), 147.4 (s), 139.6 (s), 129.8 (s), 129.1 (s), 126.0 (s), 122.7 (s), 115.0 (s), 93.0 (s), 79.1 (s), 54.9 (s), 21.5 (s), 17.6 (s).

[1] Bejcek, L. P.; Garimallaprabhakaran, A. K.; Suyabatmaz, D. M.; Greer, A.; Hersh, W. H.; Greer, E. M.; Murelli, R. P. Maltol- and Allomaltol-Derived Oxidopyrylium Ylides: Methyl Substitution Pattern Kinetically Influences [5+ 3] Dimerization versus [5+ 2] Cycloaddition Reactions. *J. Org. Chem.*,**2019**, *84* (22), 14670–14678.

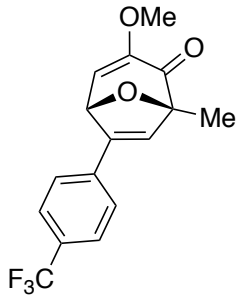
Synthesis of (1*S*,5*S*)-3-methoxy-6-(4-methoxyphenyl)-1-methyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (4c):



To a solution of **11/12** (50 mg, 0.18 mmol, 1 eq) was added 4-Ethynylanisole (237 μL, 1.8 mmol, 10 equiv). The reaction was subjected to microwave irradiation at 120 °C for 2 h, and immediately purified by chromatography (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 μm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL)). Product fractions were concentrated *en vacuo* to yield **4c** as a yellow oil (39 mg, 40% yield).

Characterization data for **4c** is as follows: R_f = 0.25 in 20% ethyl acetate. IR (thin film, KBr): 2935 (br), 2838 (m), 1707 (s), 1610 (m), 1511 (m), 1462 (m), 1030 (m), 935 (m), 906 (m), 839 (w), 795 (w), 70 (m), 590 (m) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{16}H_{17}O_4^+$: 273.1121. Found: 273.1121. ^{381}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.9 Hz, 2H), 6.96 – 6.85 (m, 2H), 6.27 (d, *J* = 4.9 Hz, 1H), 6.10 (s, 1H), 5.53 (d, *J* = 4.8 Hz, 1H), 3.83 (s, 3H), 3.54 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6 (s), 160.6 (s), 155.4 (s), 147.5 (s), 127.5 (s), 124.7 (s), 121.1 (s), 114.8 (s), 114.5 (s), 93.0 (s), 79.1 (s), 55.5 (s), 54.9 (s), 17.6 (s).

Synthesis of (1*S*,5*S*)-3-methoxy-1-methyl-6-(4-(trifluoromethyl)phenyl)-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (4d):

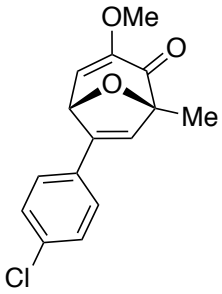


To a solution of **11/12** (50 mg, 0.18 mmol, 1 eq) was added 4-Ethynyl-α,α,α–tifluorotoluene (293 μL, 1.8 mmol, 10 equiv). The reaction was subjected to microwave irradiation at 120 °C for 2 h, and immediately purified by chromatography (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 μm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL)). Product fractions were concentrated *en vacuo* to yield **4d** as a yellow oil (33 mg, 30% yield).

Characterization for **4d** is as follows: R_f = 0.32 in 20% ethyl acetate. IR (thin film, KBr): 2930 (br), 2361 (m), 1709 (s), 1614 (m), 1455 (m), 1412 (m), 1377 (m), 1325 (m), 1250 (m), 1167 (m), 1124 (m), 1068 (m), 1016 (m), 935 (m), 907 (m), 850 (w), 815 (m), 786 (m), 741 (m), 718 (m), 668 (w) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{16}H_{14}F_3O_3^+$: 311.0890. Found:

311.0845.: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 6.42 (s, 1H), 6.28 (d, *J* = 4.9 Hz, 1H), 5.58 (d, *J* = 4.8 Hz, 1H), 3.56 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1 (s), 154.6 (s), 147.5 (s), 135.2 (s), 131.0 (q, J = 33.3 Hz), 127.1 (s), 126.2 (s), 126.1 (s) (q, J = 4 Hz), 123.9 (q, J = 272.7 Hz), 114.4 (s), 93.2 (s), 79.0 (s), 55.0 (s), 17.5 (s)

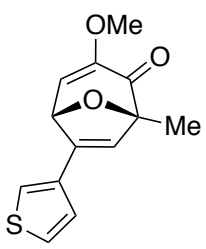
Synthesis of (1*S*,5*S*)-6-(4-chlorophenyl)-3-methoxy-1-methyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (4e):



To a solution of **11/12** (50 mg, 0.18 mmol, 1 eq) in $CDCl_3$ (1 mL, 0.4 M) was added 1-chloro-4-ethynylbenzene (323 mg, 2.4 mmol, 6.7 equiv). The reaction was subjected to microwave irradiation at 120 °C for 2 h, and immediately purified by chromatography (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 μm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL)). Product fractions were concentrated *en vacuo* to yield **4e** as a yellow oil (30 mg, 30% yield).

Characterization data for **4e** is as follows: R_f = 0.16 in 20% ethyl acetate. IR (thin film, KBr): 3453 (br), 2940 (w), 1708 (s), 1615 (m), 1441 (w), 1369 (w), 1305 (w), 1241 (w), 1062 (m), 934 (w), 907 (w), 917 (m), 863 (w), 836 (w), 723 (s) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{15}H_{14}ClO_3^+$: 277.0626. Found: 277.0601. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 2H), 6.28 – 6.24 (m, 2H), 5.53 (d, *J* = 4.8 Hz, 1H), 3.55 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3 (s), 154.8 (s), 147.5 (s), 135.3 (s), 130.4 (s), 129.4 (s), 127.3 (s), 124.7 (s), 114.5 (s), 93.1 (s), 79.0 (s), 55.0 (s), 17.5 (s).

Synthesis of (1*S*,5*S*)-3-methoxy-1-methyl-6-(thiophen-3-yl)-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (4f):

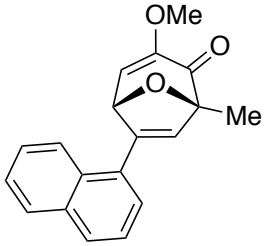


To a solution of **11/12** (100 mg, 0.36 mmol, 1 eq) in $CDCl_3$ (1 mL, 0.4 M) was added 3-Ethynylthiophene (354 μL, 3.6 mmol, 10 equiv). The reaction was subjected to microwave irradiation at 120 °C for 2 h, and immediately purified by chromatography (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-

63 μm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL)). Product fractions were concentrated *en vacuo* to yield **4e** as a yellow oil (46 mg, 26% yield).

Characterization data for **4e** is as follows: R_f = 0.22 in 20% ethyl acetate. IR (thin film, KBr): 3096 (w), 2934 (m), 1704 (s), 1612 (m), 1450 (m), 1374 (m), 1268 (m), 1244 (m), 1150 (m), 1128 (m), 1062 (m), 917 (m), 857 (w), 845 (w), 777 (m), 713 (m) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{13}H_{13}O_3S^+$: 249.0580. Found: 249.0563. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.24 – 7.17 (m, 2H), 6.26 (d, *J* = 4.9 Hz, 1H), 6.07 (s, 1H), 5.47 (d, *J* = 4.9 Hz, 1H), 3.55 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4 (s), 150.8 (s), 127.3 (s), 126.0 (s), 122.6 (s), 114.7 (s), 92.8 (s), 79.5 (s), 55.0 (s), 17.6 (s).

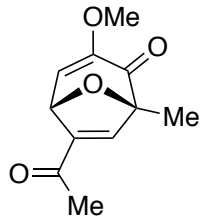
Synthesis of (1*S*,5*S*)-3-methoxy-1-methyl-6-(naphthalen-1-yl)-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (4g):



To a solution of **11/12** (175 mg, 0.63 mmol, 1 eq) was added 1-Ethynylnapthalene (887 μL, 6.3 mmol, 10 equiv). The reaction was subjected to microwave irradiation at 120 °C for 2 h, and immediately purified by chromatography (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 μm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL)). Product fractions were concentrated *en vacuo* to yield **4g** as an orange oil (106 mg, 29% yield).

Characterization data for **4g** is as follows: R_f = 0.19 in 20% ethyl acetate. IR (thin film, KBr): 3057 (w), 2934 (w), 1707 (s), 1614 (m), 1507 (w), 1450 (w), 1395 (w), 1342 (m), 1240 (m), 1139 (m), 1062 (s), 930 (m), 904 (w), 853 (w), 799 (m), 776 (m), 723 (m) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{19}H_{17}O_3^+$: 293.1172. Found: 293.1147. ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 6.2, 3.5 Hz, 1H), 7.92 – 7.80 (m, 2H), 7.58 – 7.51 (m, 2H), 7.47 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.32 (dd, *J* = 7.1, 1.1 Hz, 1H), 6.27 (s, 1H), 6.22 (d, *J* = 4.9 Hz, 1H), 5.54 (d, *J* = 4.9 Hz, 1H), 3.58 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7 (s), 155.1 (s), 147.2 (s), 133.9 (s), 131.0 (s), 130.7 (s), 129.4 (s), 129.1 (s), 128.8 (s), 127.0 (s), 126.5 (s), 125.2 (s), 125.1 (s), 124.8 (s), 115.8 (s), 93.4 (s), 82.1 (s), 55.1 (s), 17.7 (s).

Synthesis of (1*S*,5*S*)-6-acetyl-3-methoxy-1-methyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (14):

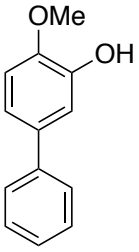


To a solution of **11/12** (100 mg, 0.36 mmol, 1 eq) in $CDCl_3$ (700 µL, 0.5 M) was added 3-butyn-2-one (281 µL, 3.6 mmol, 10 equiv). The reaction was subjected to microwave irradiation at 120 °C for 2 h, and immediately purified by chromatography (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 µm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL)). Product fractions were concentrated *en vacuo* to yield **14** as a yellow oil (58 mg, 39% yield).

Characterization data for **14** is as follows: R_f = 0.13 in 20% ethyl acetate. IR (thin film, KBr): 3445 (br), 2937 (w), 1709 (s), 1740 (s), 1613 (m), 1491 (s), 1442 (w), 1403 (w), 1376 (w), 1344 (w), 1249 (m), 1064 (s), 1013 (m), 936 (w), 906 (w), 840 (w), 814 (w), 784 (m) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{11}H_{13}O_4^+$: 209.0808. Found: 209.0783. ^1H NMR (400 MHz, $CDCl_3$) δ 6.79 (s, 1H), 6.23 (d, *J* = 4.9 Hz, 1H), 5.43 (d, *J* = 4.9 Hz, 1H), 3.55 (s, 3H), 2.37 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0 (s), 190.7 (s), 155.6 (s), 146.4 (s), 141.8 (s), 115.9 (s), 93.7 (s), 78.0 (s), 55.0 (s), 27.1 (s), 17.2 (s).

III. Synthesis of 2-methoxy-5-arylphenols

Synthesis of 4-methoxy-[1,1'-biphenyl]-3-ol (5a):

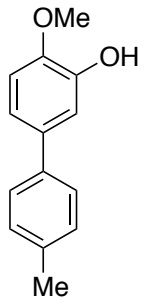


To a solution of **4a** (9 mg, 0.04 mmol, 1 eq) in CH_2Cl_2 (0.5 mL, 0.07 M) at 0°C, a 1M solution of boron trichloride in CH_2Cl_2 (148 µL, 0.15 mmol, 4 eq) was added. The reaction stirred at room temp for 15 minutes, at which point the reaction was quenched with pH 5 phosphate buffer to a final pH of 3. The reaction mixture was then extracted with DCM (5 x 10 mL). The combined organics were dried over Na_2SO_4 and concentrated *en vacuo* to a yellow oil. The crude product was purified by chromatography (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 µm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL). Product fractions were concentrated *en vacuo* to yield **5a** as a clear oil (6 mg, 71% yield).

^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.40 (dd, *J* = 10.8, 4.5 Hz, 2H), 7.31 (dt, *J* = 9.2, 4.3 Hz, 1H), 7.20 (d, *J* = 2.2 Hz, 1H), 7.09 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 3H).

Characterization consistent with previously published data.[2]

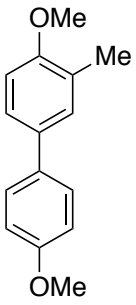
Synthesis of 4-methoxy-4'-methyl-[1,1'-biphenyl]-3-ol (5b):



To a solution of **4b** (27 mg, 0.11 mmol, 1 eq) in CH_2Cl_2 (1.0 mL, 0.1 M) at 0 °C, a 1M solution of boron trichloride in CH_2Cl_2 (420 µL, 0.42 mmol, 4 eq) was added. The reaction stirred at room temp for 15 minutes, at which point the reaction was quenched with pH 5 phosphate buffer to a final pH of 3. The reaction mixture was then extracted with DCM (5 x 10 mL). The combined organics were dried over Na_2SO_4 and concentrated *en vacuo* to a yellow oil. The crude product was purified by chromatography (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 µm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL). Product fractions were concentrated *en vacuo* to yield **5b** as a white solid (12 mg, 51% yield).

Characterization for **5b** is as follows: Mp: 120-122 °C. R_f = 0.35 in 20% ethyl acetate. IR (thin film, KBr): 3536 (br), 3332 (br), 2966 (m), 2934 (m), 1589 (m), 1506 (m), 1441 (m), 2011 (m), 1301 (m), 1265 (m), 1213 (m), 1193 (m), 1137 (m), 1040 (m), 1016 (m), 989 (m), 871 (w), 823 (w), 801 (m), 737 (w), 704 (w) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{14}H_{15}O_2^+$: 215.1067. Found: 215.0101. ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 2.2 Hz, 1H), 7.08 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 5.63 (s, 1H), 3.93 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 146.1 (s), 145.9 (s), 138.0 (s), 136.7 (s), 134.9 (s), 129.6 (s), 126.8 (s), 118.7 (s), 113.4 (s), 111.0 (s), 56.2 (s), 21.2 (s).

Synthesis of 4,4'-dimethoxy-[1,1'-biphenyl]-3-ol (5c):



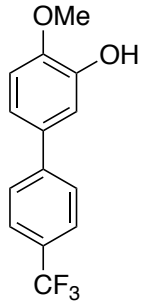
To a solution of **4c** (40 mg, 0.15 mmol, 1 eq) in CH_2Cl_2 (1.5 mL, 0.1 M) at 0° C, a 1M solution of boron trichloride in CH_2Cl_2 (600 µL, 0.60 mmol, 4 eq) was added. The reaction stirred at room temp for 15 minutes, at which point the reaction was quenched with pH 5 phosphate buffer to a final pH of 3. The reaction mixture was then extracted with DCM (5 x 10 mL).

[2] Pilevar, A.; Hosseini, A.; Šekutor, M.; Hausmann, H.; Becker, J.; Turke, K.; Schreiner, P. R. Tuning the Reactivity of Peroxo Anhydrides for Aromatic C–H Bond Oxidation. *J. Org. Chem*. **2018**, *83* (17), 10070–10079.

The combined organics were dried over Na_2SO_4 and concentrated en vacuo to a yellow oil.
The crude product was purified by chromatography (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 µm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL). Product fractions were concentrated *en vacuo* to yield **5c** as a yellow solid (26 mg, 75% yield).

Characterization data for **5c** is as follows: Mp: 136-139 °C. (75%).: R_f = 0.25 in 20% ethyl acetate. IR (thin film, KBr): 2964 (br), 2838 (m), 1505 (m), 1440 (m), 1279 (m), 1246 (m), 1183 (m), 1042 (m), 1014 (m), 835 (w), 801 (w) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{14}H_{15}O_3^+$: 231.1016. Found: 231.0992. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 2H), 7.15 (d, *J* = 2.2 Hz, 1H), 7.04 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.90 (d, *J* = 8.3 Hz, 1H), 3.92 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 158.9 (s), 145.9 (s), 145.8 (s), 134.6 (s), 133.5 (s), 127.9 (s), 118.4 (s), 114.3 (s), 113.2 (s), 111.1 (s), 56.2 (s), 55.5 (s).

Synthesis of 4-methoxy-4'-(trifluoromethyl)-[1,1'-biphenyl]-3-ol (5d):

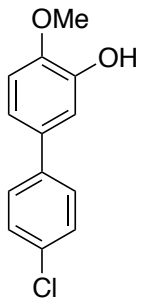


To a solution of **4d** (40 mg, 0.13 mmol, 1eq) in CH_2Cl_2 (1.3 mL, 0.13 M) at 0 °C, a 1M solution of boron trichloride in CH_2Cl_2 (520 µL, 0.52 mmol, 4 eq) was added. The reaction stirred at room temp for 15 minutes, at which point the reaction was quenched with pH 5 phosphate buffer to a final pH of 3. The reaction mixture was then extracted with DCM (5 x 10 mL). The combined organics were dried over Na_2SO_4 and concentrated *en vacuo* to a yellow oil. The crude product was purified by chromatography (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 µm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL). Product fractions were concentrated *en vacuo* to yield **5d** as a white solid (18.2 mg, 50% yield)

Characterization for **5d** is as follows: Mp: 113-116 °C. R_f = 0.33 in 20% ethyl acetate. IR (thin film, KBr): 3648 (br), 3545 (br), 1610 (m), 1590 (m), 1573 (m), 1457 (m), 1340 (m), 1289 (m), 1275 (m), 1265 (m), 1206 (m), 1165 (m), 1178 (m), 1141 (m), 1112 (m), 1074 (m), 1041 (m), 1016 (m), 837 (w), 804 (m) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{14}H_{12}F_3^+O_2^+$: 269.0784. Found: 269.0742. ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.61 (m, 4H), 7.20 (d, *J* = 2.2 Hz, 1H), 7.11 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 5.69 (s, 1H), 3.95 (s, 3H). ^{13}C NMR (101

MHz, $CDCl_3$) δ 147.0 (s), 146.1 (s), 133.3 (s), 129.0 (q, J = 32.3 Hz), 127.1 (s), 125.8 (q, J = 4.0 Hz), 125.1 (q, J = 392.0 Hz), 119.2 (s), 113.6 (s), 111.1 (s), 56.2 (s).

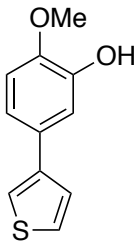
Synthesis of 4'-chloro-4-methoxy-[1,1'-biphenyl]-3-ol (5e):



To a solution of **4e** (10 mg, 0.04 mmol, 1eq) in CH_2Cl_2 (283 µL, 0.13 M) at 0 °C, a 1M solution of boron trichloride in CH_2Cl_2 (160 µL, 0.16 mmol, 4 eq) was added. The reaction stirred at room temp for 15 minutes, at which point the reaction was quenched with pH 5 phosphate buffer to a final pH of 3. The reaction mixture was then extracted with DCM (5 x 10 mL). The combined organics were dried over Na_2SO_4 and concentrated *en vacuo* to a yellow oil. The crude product was purified by chromatography (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 µm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL). Product fractions were concentrated *en vacuo* to yield **5e** as a clear oil (4.6 mg, 50% yield).

Characterization for **5d** is as follows: R_f = 0.30 in 20% ethyl acetate. IR (thin film, KBr): 3338 (br), 1588 (m), 1522 (m), 1488 (s), 1462 (m), 1442 (w), 1323 (w), 1295 (s), 1255 (m), 1232 (w), 1200 (m), 1136 (m), 1095 (w), 1039 (w), 1016 (m), 897 (w), 833 (w), 802 (m) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{13}H_{12}ClO_2^+$: 235.0520. Found: 235.0495. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 2.2 Hz, 1H), 7.05 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 5.65 (s, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5 (s), 146.1 (s), 139.4 (s), 133.7 (s), 133.0 (s), 129.0 (s), 128.2 (s), 118.8 (s), 113.3 (s), 111.1 (s), 56.2 (s).

Synthesis of 2-methoxy-5-(thiophen-3-yl) phenol (5f):

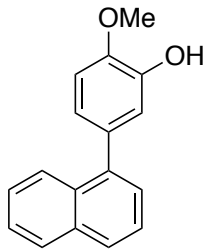


To a solution of **4f** (22 mg, 0.09 mmol, 1 eq) in CH_2Cl_2 (1.0 mL, 0.1 M) at 0° C, a 1M solution of boron trichloride in CH_2Cl_2 (360 µL, 0.36 mmol, 4 eq) was added. The reaction stirred at room temp for 15 minutes, at which point the reaction was quenched with pH 5 phosphate buffer to a final pH of 3. The reaction mixture was then extracted with DCM (5 x 10 mL). The combined organics were dried over Na_2SO_4 and concentrated *en vacuo* to a yellow oil. The crude product was purified by chromatography (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 µm 60 Å, solvent gradient: 0-25% EtOAc

in hexanes (500 mL). Product fractions were concentrated *en vacuo* to yield **5e** as a brown solid (14 mg, 74% yield).

Characterization of **5e** is as follows: R_f = 0.34 in 20% ethyl acetate. IR (thin film, KBr): 3326 (br), 3103 (m), 2933 (m), 1586 (m), 1539 (m), 1507 (m), 1462 (m), 1441 (m), 1282 (m), 1251 (m), 1216 (m), 1170 (m), 1132 (m), 1045 (w), 1018 (w), 867 (m), 848 (m), 779 (w) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{11}H_{11}O_2S^+$: 207.0474. Found: 207.0469. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{16}H_{17}O_4^+$: 257.1172. Found: 257.1136. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.41 (dd, *J* = 8.2, 7.0 Hz, 2H), 7.34 – 7.28 (m, 1H), 7.09 (d, *J* = 2.2 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 5.64 (s, 1H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 146.3 (s), 145.9 (s), 140.9 (s), 135.0 (s), 128.8 (s), 127.0 (s), 126.9 (s), 118.9 (s), 113.5 (s), 111.0 (s), 56.2 (s).

Synthesis of 2-methoxy-5-(naphthalen-1-yl) phenol (5g):



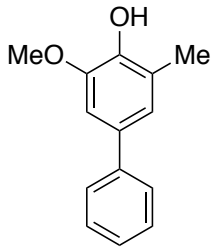
To a solution of **4g** (35.3 mg, 0.11 mmol, 1eq) in CH_2Cl_2 (845 µL, 0.13 M) at 0 °C, a 1M solution of boron trichloride in CH_2Cl_2 (444 µL, 0.44 mmol, 4 eq) was added. The reaction stirred at room temp for 15 minutes, at which point the reaction was quenched with pH 5 phosphate buffer to a final pH of 3. The reaction mixture was then extracted with DCM (5 x 10 mL). The combined organics were dried over Na_2SO_4 and concentrated *en vacuo* to a yellow oil. The crude product was purified by chromatography (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 µm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL). Product fractions were concentrated *en vacuo* to yield **5g** as a clear oil (18.2 mg, 66% yield)

Characterization for **5d** is as follows: R_f = 0.37 in 20% ethyl acetate. IR (thin film, KBr): 3512 (br), 3045 (w), 2934 (w), 2838 (w), 1581 (m), 1504 (s), 1461 (m), 1440 (m), 1393 (m), 1288 (s), 1257 (s), 1245 (m), 1213 (m), 1172 (w), 1026 (m), 993 (w), 901 (m), 798 (s), 777 (s), 735 (w) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{17}H_{15}O_2^+$: 251.1067. Found: 251.1040. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.92 – 7.87 (m, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.54 – 7.39 (m, 9H), 7.11 (d, *J* = 0.7 Hz, 2H), 6.99 (d, *J* = 1.5 Hz, 4H), 5.70 (s, 2H), 3.98 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1 (s), 145.5 (s), 134.0 (s), 134.3 (s), 133.9 (s), 131.9 (s), 128.4 (s),

127.5 (s), 127.0 (s), 126.3 (s), 126.1 (s), 125.8 (s), 125.5 (s), 122.0 (s), 116.6 (s), 110.6 (s), 56.2 (s).

IV. Synthesis and characterization of 2-methoxy-4-aryl-6-methylphenols

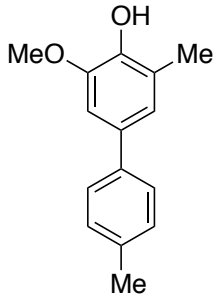
Synthesis of 3-methoxy-5-methyl-[1,1'-biphenyl]-4-ol (19a):



To a solution of **4a** (8 mg, 0.03 mmol, 1 eq) in CH_2Cl_2 (1 mL, 0.03 M) methane sulfonic acid (12 μL, 0.13 mmol, 4 eq) was added. The reaction stirred at room temp for 30 minutes, at which point the reaction was quenched with pH 5 phosphate buffer to a final pH of 3. The reaction mixture was then extracted with DCM (5 x 10 mL). The combined organics were dried over Na_2SO_4 and concentrated *en vacuo* to a yellow oil. The oil was purified by (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 μm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL). Product fractions were concentrated *en vacuo* to yield **19a** as a clear oil (2.7 mg, 41% yield).

Characterization for **19a** is as follows: R_f = 0.595 in 20% ethyl acetate. IR (thin film, KBr): 3524 (br), 3031 (br), 2942 (m), 1510 (m), 1486 (m), 1464 (m), 1444 (m), 1318 (m), 1248 (m), 1203 (m), 1180 (m), 1092 (w), 1072 (w), 760 (w), 698 (w) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{14}H_{15}O_2^+$: 215.1067. Found: 215.1060. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.40 (dd, *J* = 10.8, 4.5 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.02 – 6.98 (m, 1H), 6.94 (d, *J* = 2.0 Hz, 1H), 5.70 (s, 1H), 3.95 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6 (s), 143.5 (s), 141.6 (s), 132.9 (s), 128.8 (s), 127.0 (s), 126.8 (s), 124.2 (s), 122.2 (s), 107.4 (s), 56.3 (s), 15.7 (s). See page s35 for NOESY spectrum. NMR data consistent with similar molecule, 3-(*tert*-butyl)-5-methoxy-[1,1'-biphenyl]-4-ol.[3]

Synthesis of 3-methoxy-4',5-dimethyl-[1,1'-biphenyl]-4-ol (19b):



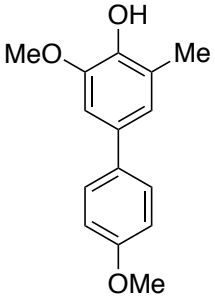
To a solution of **4b** (34 mg, 0.13 mmol, 1 eq) in CH_2Cl_2 4 mL, 0.03 M) methane sulfonic acid (40 μL, 0.53 mmol, 4 eq) was added. The reaction stirred at room temp for 30 minutes, at which point the reaction was quenched with pH 5 phosphate buffer to a final pH of 3. The reaction mixture was then extracted with DCM (5 x 10 mL).

[3]Moore, G. G. I.; Kirk, A. R. An Unusual Dienone-Phenol Rearrangement of a p-Quinol. *The Journal of Organic Chemistry*. **1979**, *44* (6), 925–930.

The combined organics were dried over Na_2SO_4 and concentrated *en vacuo* to a yellow oil. The oil was purified by (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 μm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL). Product fractions were concentrated *en vacuo* to yield **19b** as a yellow oil (7.5 mg, 25% yield).

Characterization for **19b** is as follows: R_f = 0.57. IR (thin film, KBr): 3523 (br), 2919 (br), 1604 (m), 1493 (n), 1463 (m), 1426 (m), 1397 (m), 1318 (m), 1306 (m), 1249 (m), 1213 (m), 1201 (m), 1179 (m), 1092 (w), 1071 (w), 996 (w), 924 (m), 813 (m), 757 (m) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{15}H_{17}O_2^+$: 229.1223. Found: 229.1219. ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.00 – 6.94 (m, 1H), 6.92 (d, *J* = 2.0 Hz, 1H), 5.67 (s, 1H), 3.94 (s, 3H), 2.38 (s, 3H), 2.31 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5 (s), 143.3 (s), 138.7 (s), 136.5 (s), 132.8 (s), 129.5 (s), 126.8 (s), 124.1 (s), 122.0 (s), 107.3 (s), 56.2 (s), 21.2 (s), 15.7 (s).

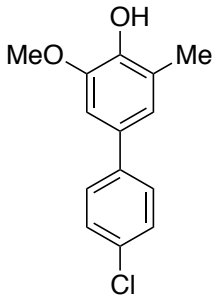
Synthesis of 3,4'-dimethoxy-5-methyl-[1,1'-biphenyl]-4-ol (19c):



To a solution of **19c** (80 mg, 0.29 mmol, 1 eq) in CH_2Cl_2 10 mL, 0.03 M) methane sulfonic acid (76 μL, 1.18 mmol, 4 eq) was added. The reaction stirred at room temp for 30 minutes, at which point the reaction was quenched with pH 5 phosphate buffer to a final pH of 3. The reaction mixture was then extracted with DCM (5 x 10 mL). The combined organics were dried over Na_2SO_4 and concentrated *en vacuo* to a yellow oil. The oil was purified by (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 μm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL). Product fractions were concentrated *en vacuo* to yield **19c** as a white solid (25.1 mg, 36% yield).

Characterization for **19c** is as follows: Mp = 122-124 °C. R_f = 0.44. IR (thin film, KBr): 3419 (br), 2948 (m), 2838 (m), 1608 (m), 1495 (m), 1466 (m), 1319 (m), 1290 (m), 1240 (w), 1193 (w), 1179 (m), 1088 (m), 1070 (m), 1033 (w), 823 (w) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{15}H_{17}O_3^+$: 245.1172. Found: 245.1169. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 6.98 – 6.92 (m, 3H), 6.89 (d, *J* = 2.0 Hz, 1H), 5.66 (s, 1H), 3.94 (s, 3H), 3.85 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8 (s), 146.5 (s), 143.1 (s), 134.2 (s), 132.6 (s), 128.0 (s), 124.1 (s), 121.7 (s), 114.2 (s), 107.1 (s), 56.2 (s), 55.5 (s), 15.7 (s).

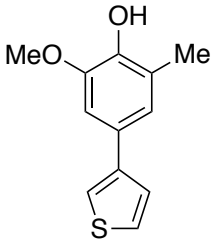
Synthesis of 4'-chloro-3-methoxy-5-methyl-[1,1'-biphenyl]-4-ol (19e):



To a solution of **4e** (10 mg, 0.04 mmol, 1 eq) in CH_2Cl_2 (1.3 mL, 0.03 M) methane sulfonic acid (10.4 µL, 0.16 mmol, 4 eq) was added. The reaction stirred at room temp for 30 minutes, at which point the reaction was quenched with pH 5 phosphate buffer to a final pH of 3. The reaction mixture was then extracted with DCM (5 x 10 mL). The combined organics were dried over Na_2SO_4 and concentrated *en vacuo* to a yellow oil. The oil was purified by (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 µm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL). Product fractions were concentrated *en vacuo* to **19e** as a yellow oil (2.8 mg, 28% yield).

Characterization for **19e** is as follows: R_f = 0.52 in 20% ethyl acetate. IR (thin film, KBr): 3462 (br), 2920 (w), 1603 (m), 1512 (m), 1487 (w), 1392 (m), 1319 (m), 1205 (w), 1181 (m), 1088 (m), 1068 (m), 819 (w), 750 (w) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{14}H_{14}ClO_2^+$: 2491.0677. Found: 249.0652. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 1.9 Hz, 1H), 6.89 (d, *J* = 2.0 Hz, 1H), 5.71 (s, 1H), 3.94 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6 (s), 143.8 (s), 140.0 (s), 132.7 (s), 131.6 (s), 128.9 (s), 128.2 (s), 124.3 (s), 122.1 (s), 107.2 (s), 56.3 (s), 15.7 (s).

Synthesis of 2-methoxy-6-methyl-4-(thiophen-3-yl) phenol (19f):

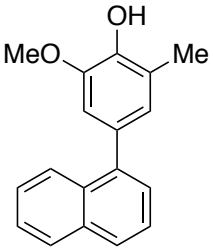


To a solution of **4f** (22 mg, 0.09 mmol, 1 eq) in CH_2Cl_2 (3 mL, 0.03 M) methane sulfonic acid (30 µL, 0.35 mmol, 4 eq) was added. The reaction stirred at room temp for 30 minutes, at which point the reaction was quenched with pH 5 phosphate buffer to a final pH of 3. The reaction mixture was then extracted with DCM (5 x 10 mL). The combined organics were dried over Na_2SO_4 and concentrated *en vacuo* to a yellow oil. The oil was purified by (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 µm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL). Product fractions were concentrated *en vacuo* to yield **19f** as a yellow oil (4.2 mg, 21% yield).

Characterization for **19f** is as follows: R_f = 0.53 in 20% ethyl acetate. IR (thin film, KBr): 3509 (br), 2937 (m), 1604 (m), 1536 (m), 1496 (w), 1463 (m), 1410 (m), 1361 (m), 1344 (m), 1299 (w),

1247 (m), 1211 (m), 1170 (m), 1087 (m), 1067 (m), 947 (w), 845 (w), 778 (m), 729 (m) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{12}H_{13}O_2S^+$: 221.0631. Found: 221.0629.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, *J* = 5.1, 2.8 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.03 – 6.97 (m, *J* = 1.3, 0.5 Hz, 1H), 6.94 (m, 1H), 5.67 (s, 1H), 3.93 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5 (s), 143.3 (s), 142.8 (s), 127.7 (s), 126.6 (s), 126.1 (s), 124.2 (s), 121.7 (s), 119.0 (s), 106.9 (s), 56.3 (s), 15.7 (s).

Synthesis of 2-methoxy-6-methyl-4-(naphthalen-1-yl)phenol (19g):



To a solution of **4g** (35.3 mg, 0.11 mmol, 1 eq) in CH_2Cl_2 (3.6 mL, 0.03 M) methane sulfonic acid (28.8 μL, 0.44 mmol, 4 eq) was added. The reaction stirred at room temp for 1 hour, at which point the reaction was quenched with pH 5 phosphate buffer to a final pH of 3. The reaction mixture was then extracted with DCM (5 x 10 mL). The combined organics were dried over Na_2SO_4 and concentrated *en vacuo* to a yellow oil. The oil was purified by (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 μm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL). Product fractions were concentrated *en vacuo* to yield **19g** as a clear oil (1.8 mg, 6% yield).

Characterization for **15e** is as follows: R_f = 0.56 in 20% ethyl acetate. IR (thin film, KBr): 3676 (br), 2347 (m), 1653 (m), 1559 (m), 1507 (s), 1490 (m), 1399 (m), 1315 (m), 1270 (w), 1233 (m), 1186 (m), 1117 (m), 1091 (m), 1008 (m), 785 (s), 712 (w), 639 (m) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{18}H_{17}O_2^+$: 265.1223. Found: 265.1198. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.92 – 7.87 (m, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.46 (dddd, *J* = 13.9, 8.3, 7.6, 4.1 Hz, 4H), 6.89 (d, *J* = 1.9 Hz, 1H), 6.86 (d, *J* = 1.8 Hz, 1H), 5.74 (s, 1H), 3.90 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1 (s), 143.2 (s), 140.6 (s), 134.0 (s), 132.1 (s), 132.0 (s), 128.4 (s), 127.4 (s), 127.0 (s), 126.3 (s), 126.0 (s), 125.8 (s), 125.5 (s), 124.9 (s), 123.7 (s), 110.4 (s), 56.3 (s), 15.7 (s).

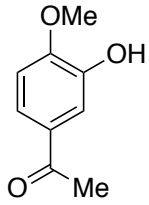
V. Synthesis of 3-hydroxy-4-methoxyphenyl ethanones

Procedure for the Synthesis of 1-(3-hydroxy-4-methoxyphenyl)ethan-1-one (15) and 1,1'-(3-hydroxy-4-methoxy-1,2-phenylene)bis(ethan-1-one) (16):

To a solution of **14** (23 mg, 0.11 mmol, 1 eq) in CH_2Cl_2 (3.6 mL, 0.03 M) at 0 °C, a 1M solution of boron trichloride in CH_2Cl_2 (440 μL, 0.44 mmol, 4 eq) was added. The reaction stirred at room

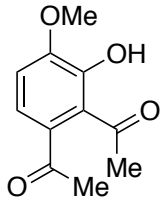
temp for 15 minutes, at which point the reaction was quenched with pH 5 phosphate buffer to a final pH of 3. The reaction mixture was then extracted with DCM (5 x 10 mL). The combined organics were dried over Na_2SO_4 and concentrated *en vacuo* to a yellow oil. The oil was purified by (Biotage Isolera Prime, SiliCycle Silia*Sep* 25 g silica gel, 40-63 µm 60 Å, solvent gradient: 0-25% EtOAc in hexanes (500 mL). Product fractions were concentrated *en vacuo* to yield **15** (2.0 mg, 10%) and **16** (6.4 mg, 28% yield) as yellow oils.

Characterization for **15** has been described previously.[4]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 2.1 Hz, 1H), 7.53 (s, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 5.65 (s, 1H), 3.96 (s, 3H), 2.54 (s, 3H).

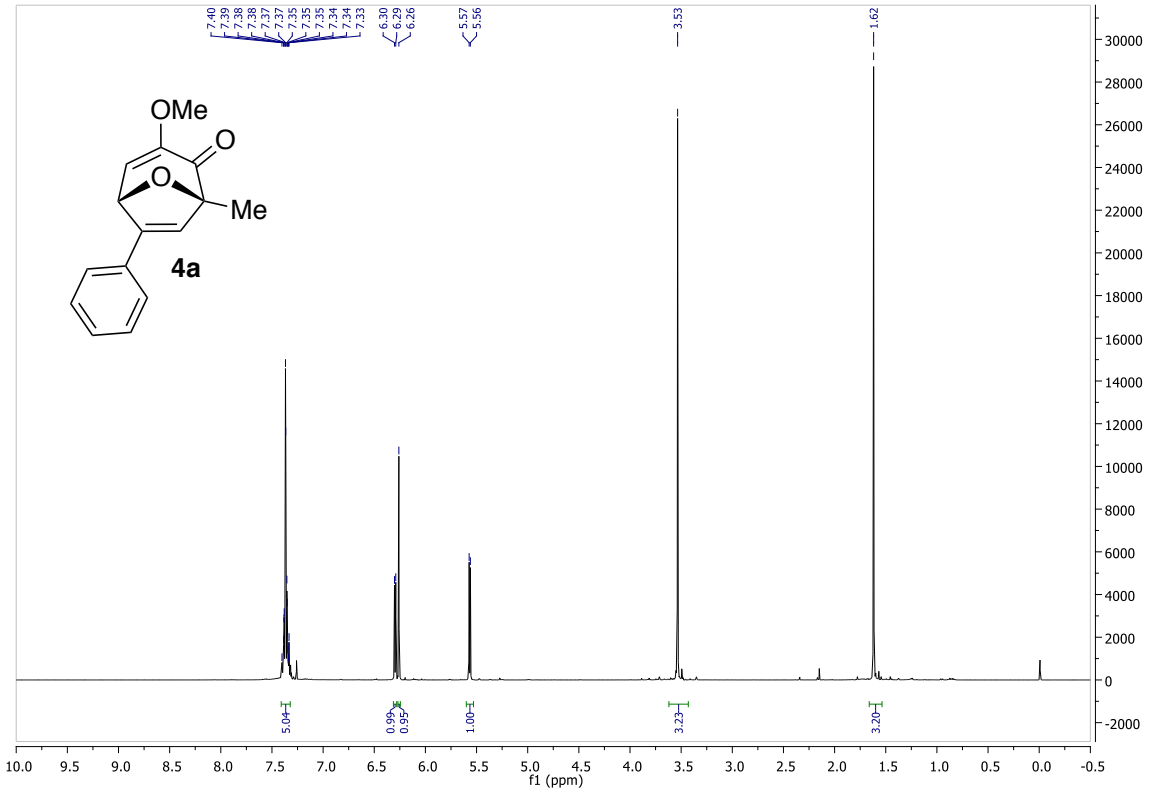
Characterization for **16** is as follows: R_f = 0.53 in 20% ethyl acetate. IR (thin film, KBr): 3355 (br), 2940 (m), 2360 (w), 1701 (s), 1670 (m), 1576 (m), 1490 (w), 1458 (w), 1438 (w), 1359 (m), 1278 (s), 1254 (m), 1137 (w), 1073 (w), 1046 (w), 970 (w), 847 (w), 808 (w) cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ calc'd for $C_{11}H_{13}O_4^+$: 209.0808. Found: 209.0793. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.50 (s, 1H), 3.97 (s, 3H), 2.53 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.9 (s), 197.6 (s), 150.9 (s), 143.3 (s), 129.7 (s), 128.9 (s), 122.9 (s), 109.8 (s), 56.5 (s), 31.4 (s), 26.9 (s).



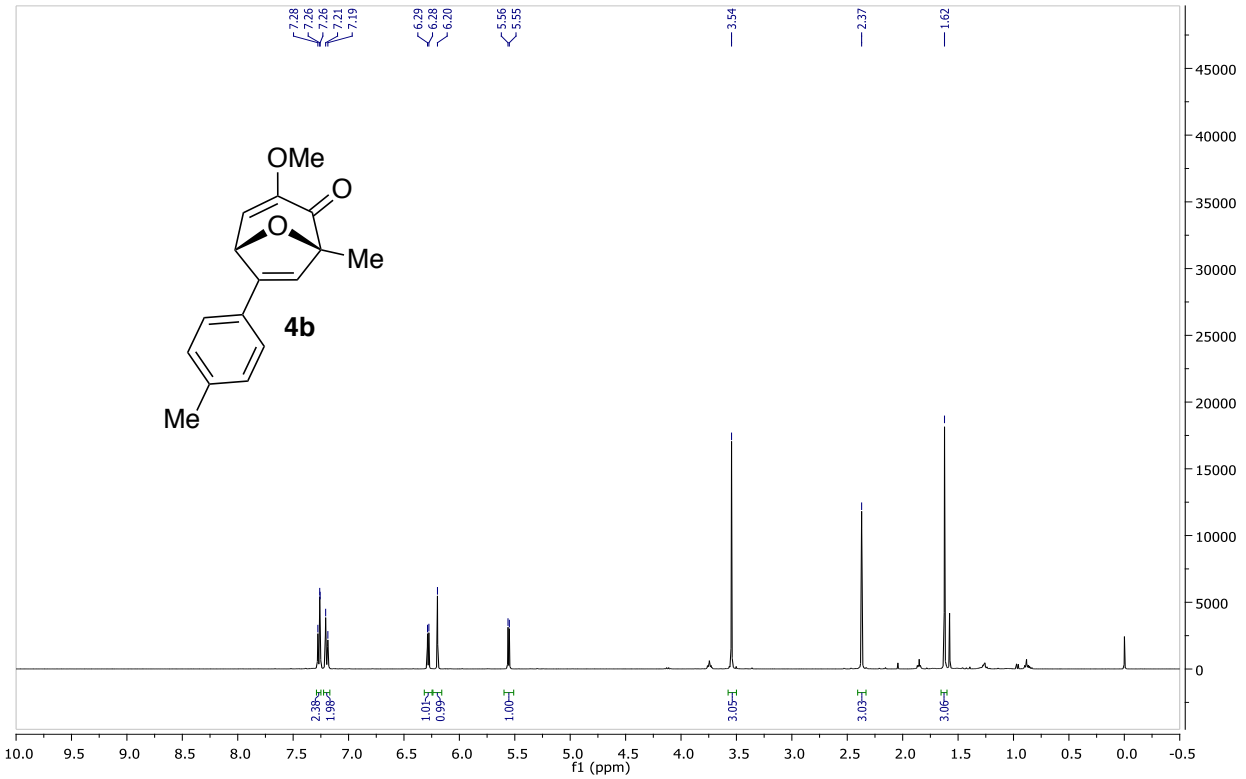
[4]Kobayashi, S.; Okimoto, K.; Imakura, Y. Cleavage of the Methylenedioxy Ring. III. Cleavage with Sodium Benzyloxide in Dimethyl Sulfoxide. *Chemical & Pharmaceutical Bulletin.* **1982**, *30* (5), 1567–1573.

VI. NMR Data

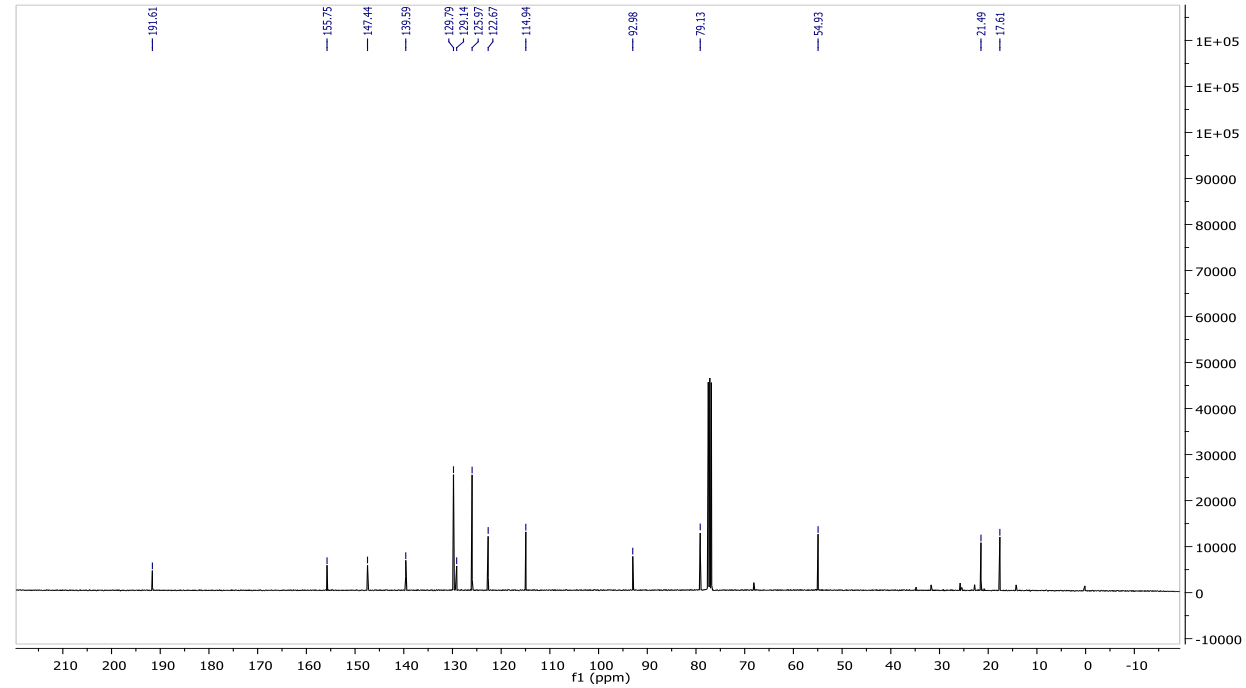
^{1}H NMR spectrum of 4a:



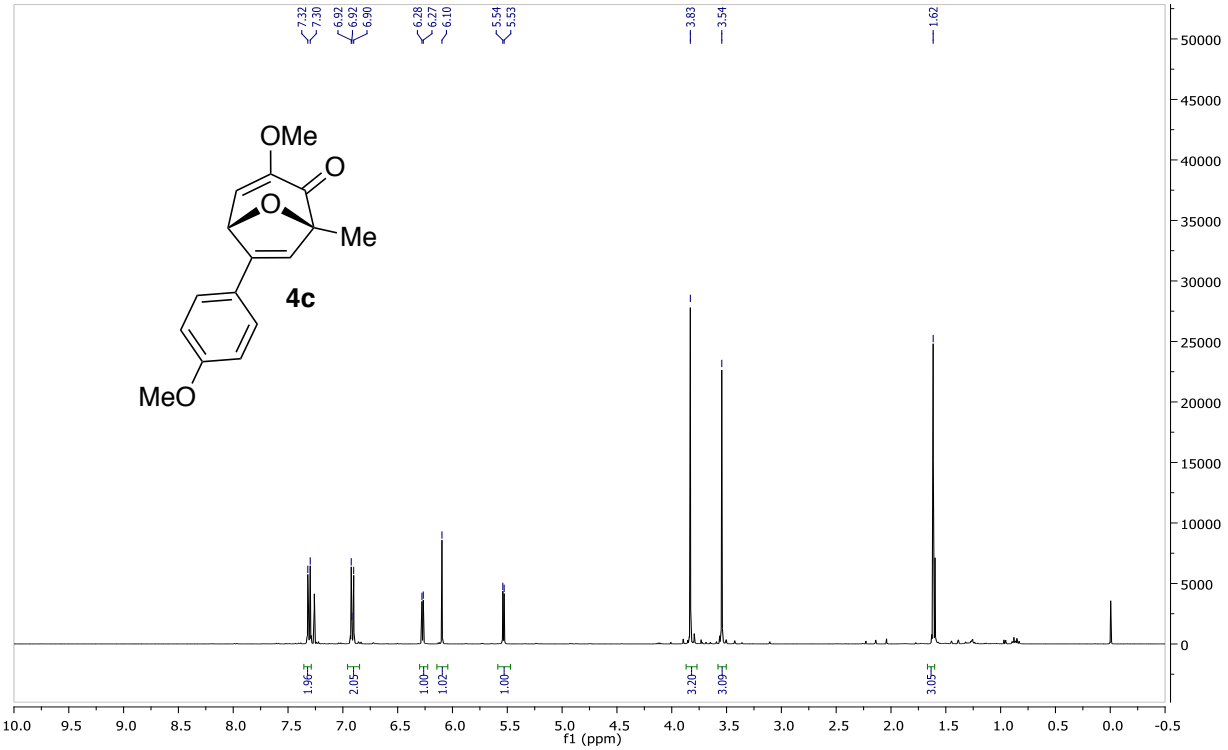
^{1}H NMR spectrum of 4b:



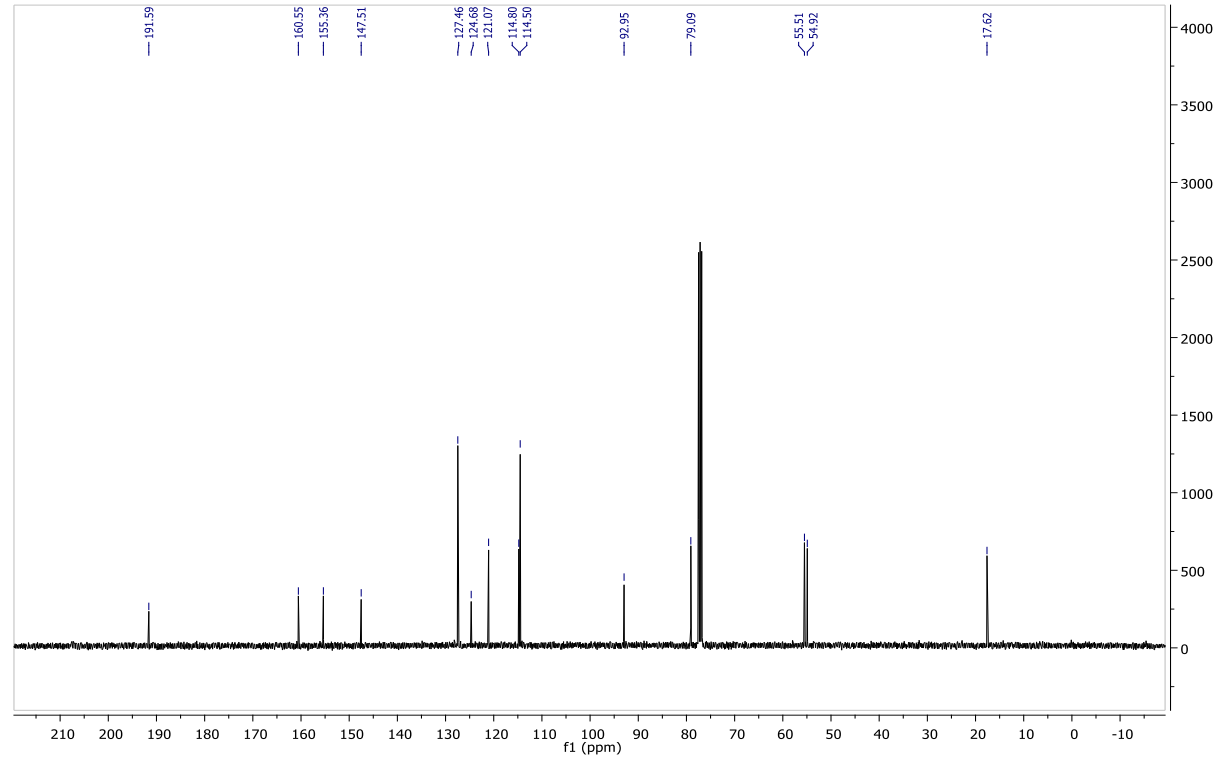
^{13}C NMR spectrum of 4b:



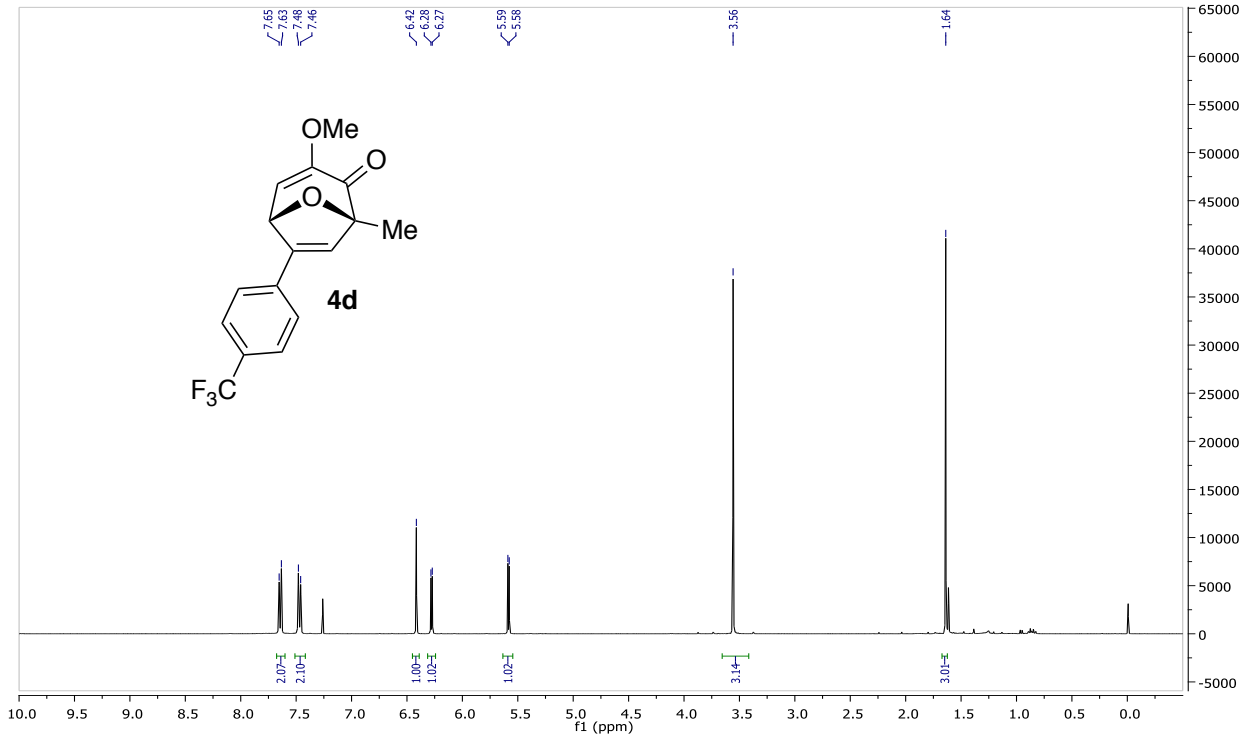
^{1}H NMR spectrum of 4c:



^{13}C NMR spectrum of 4c:



^{1}H NMR spectrum of 4d:



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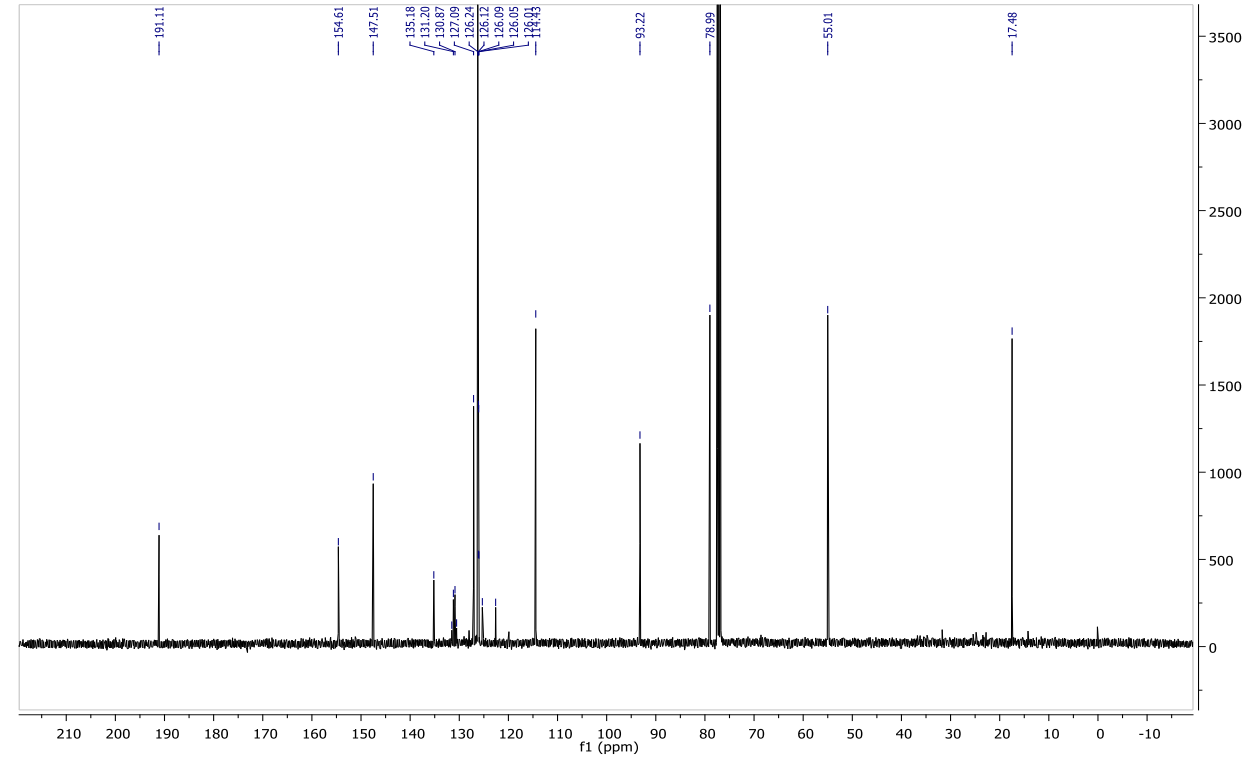

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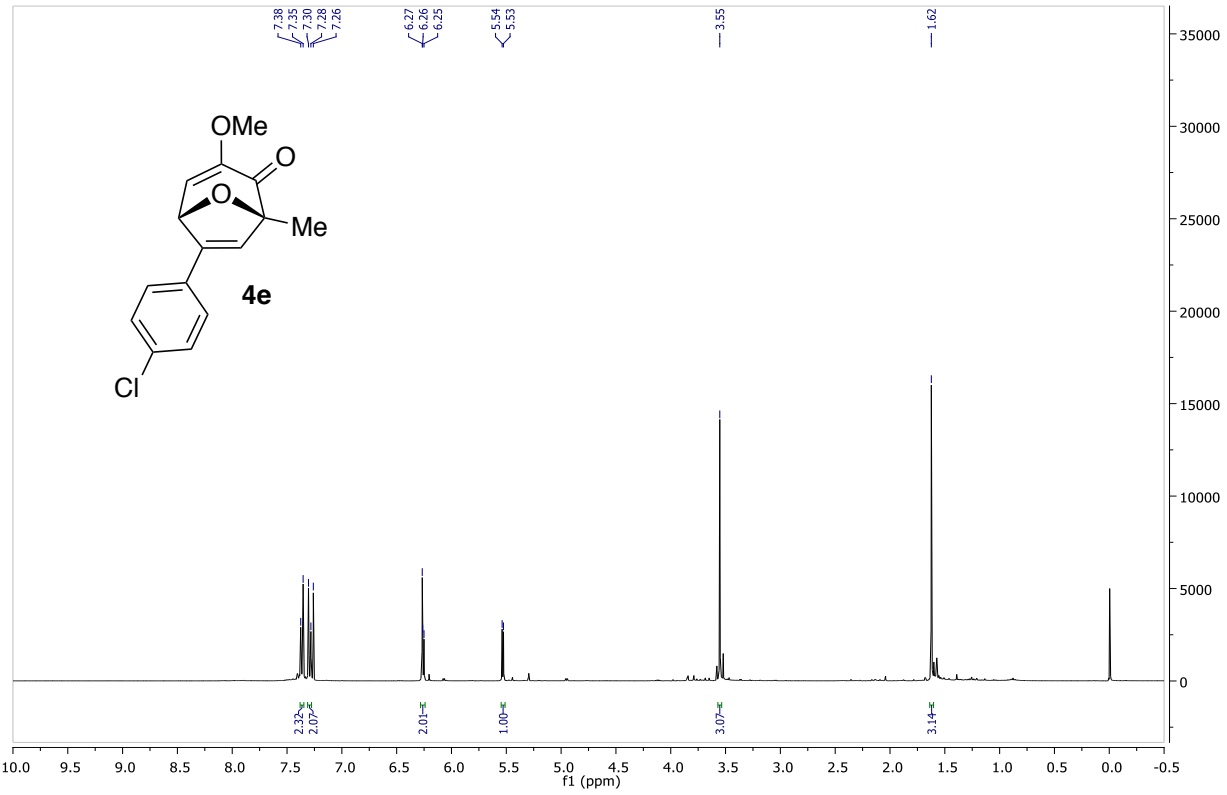
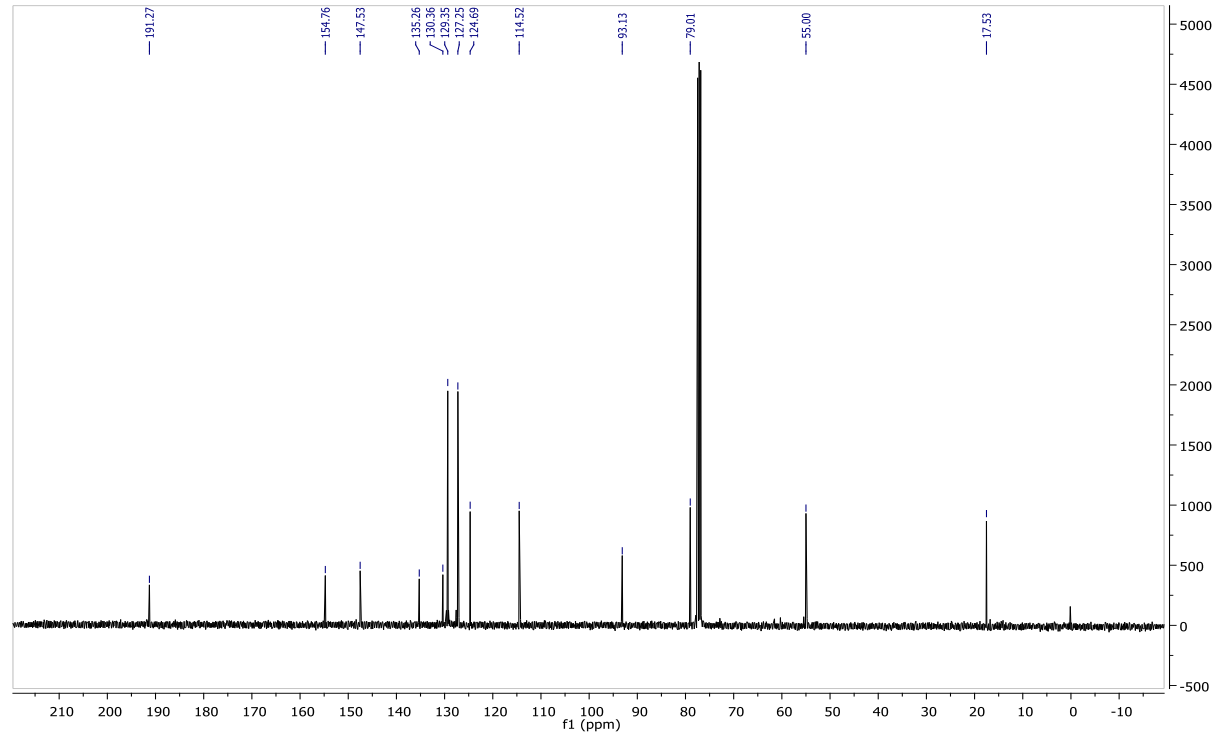
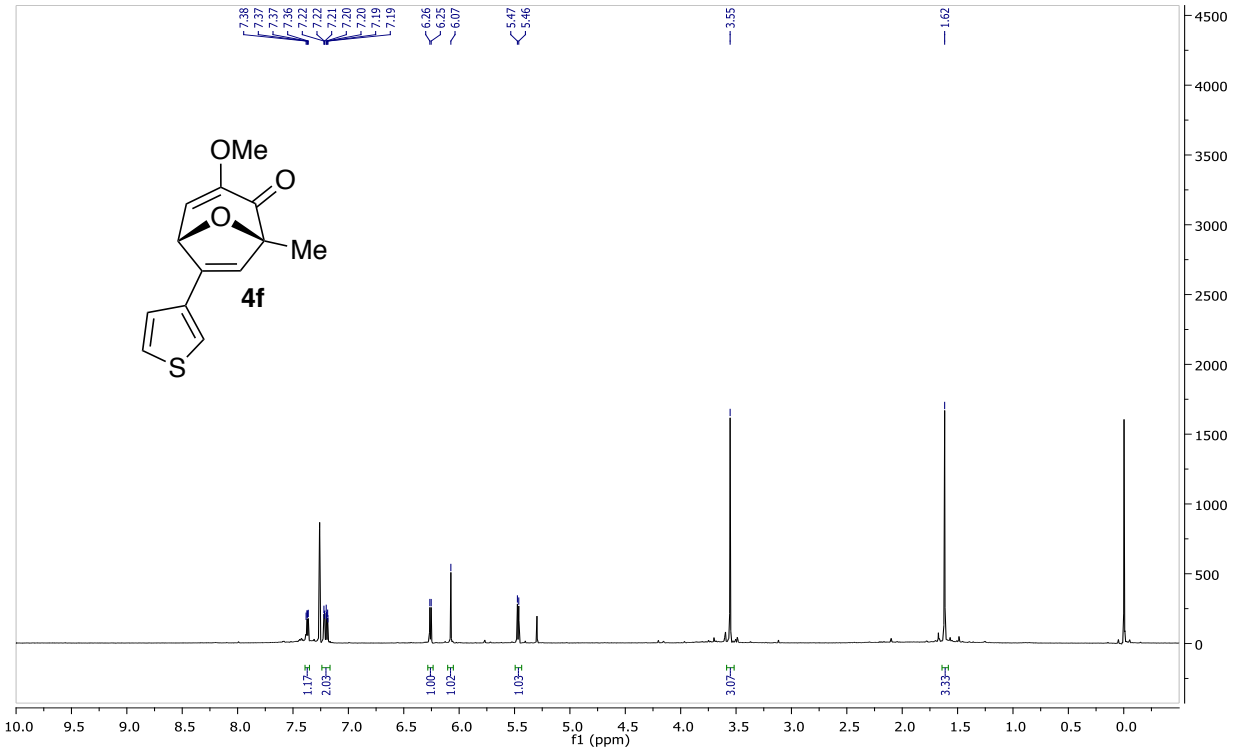


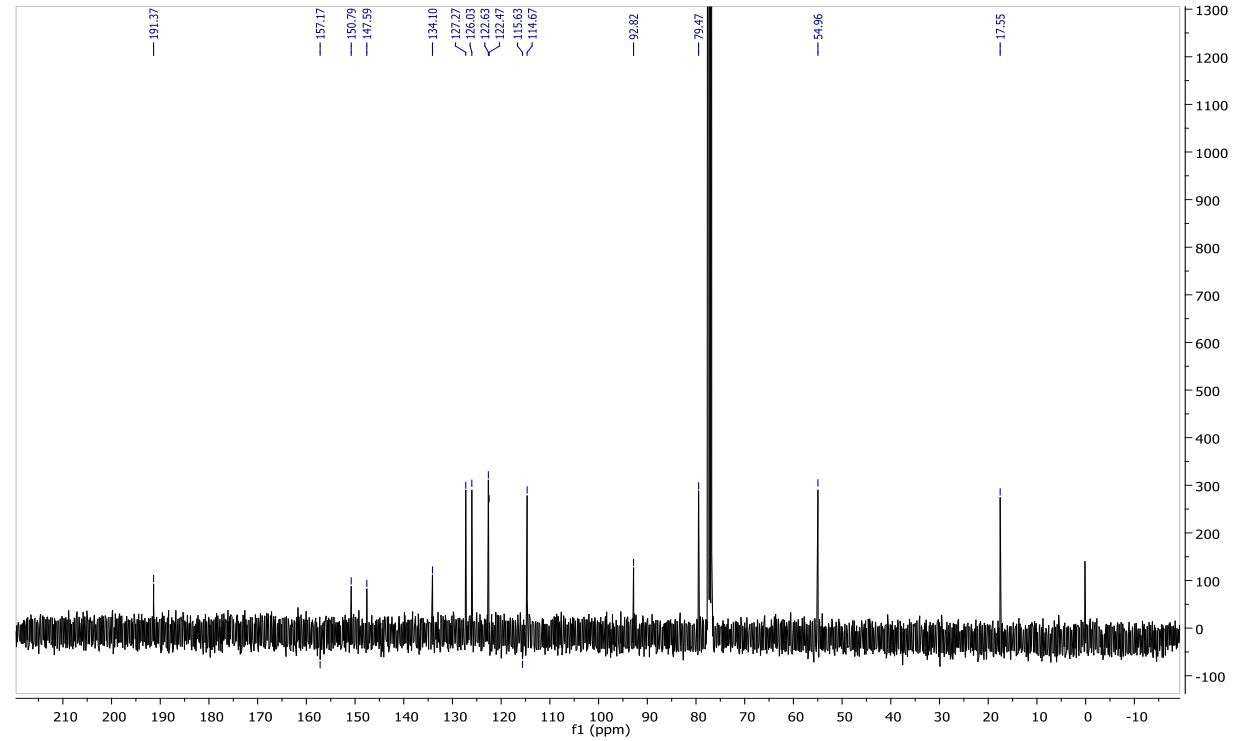
^{13}C NMR spectrum of 4e:



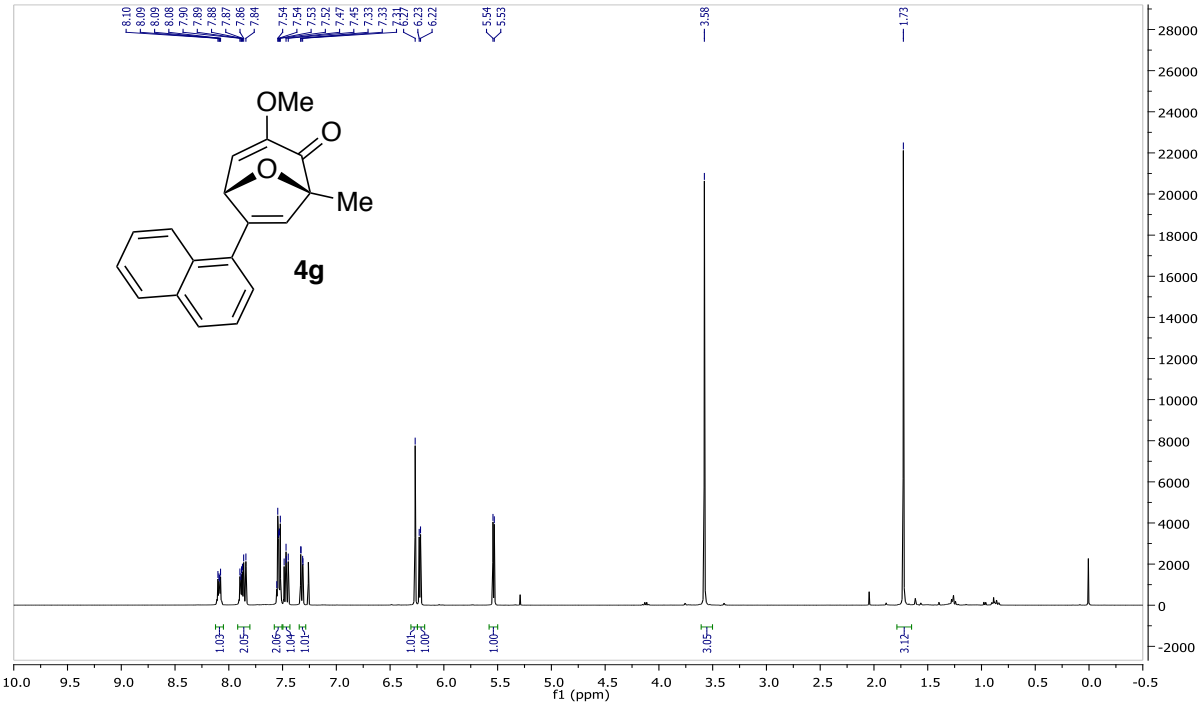
^{1}H NMR spectrum of 4f:



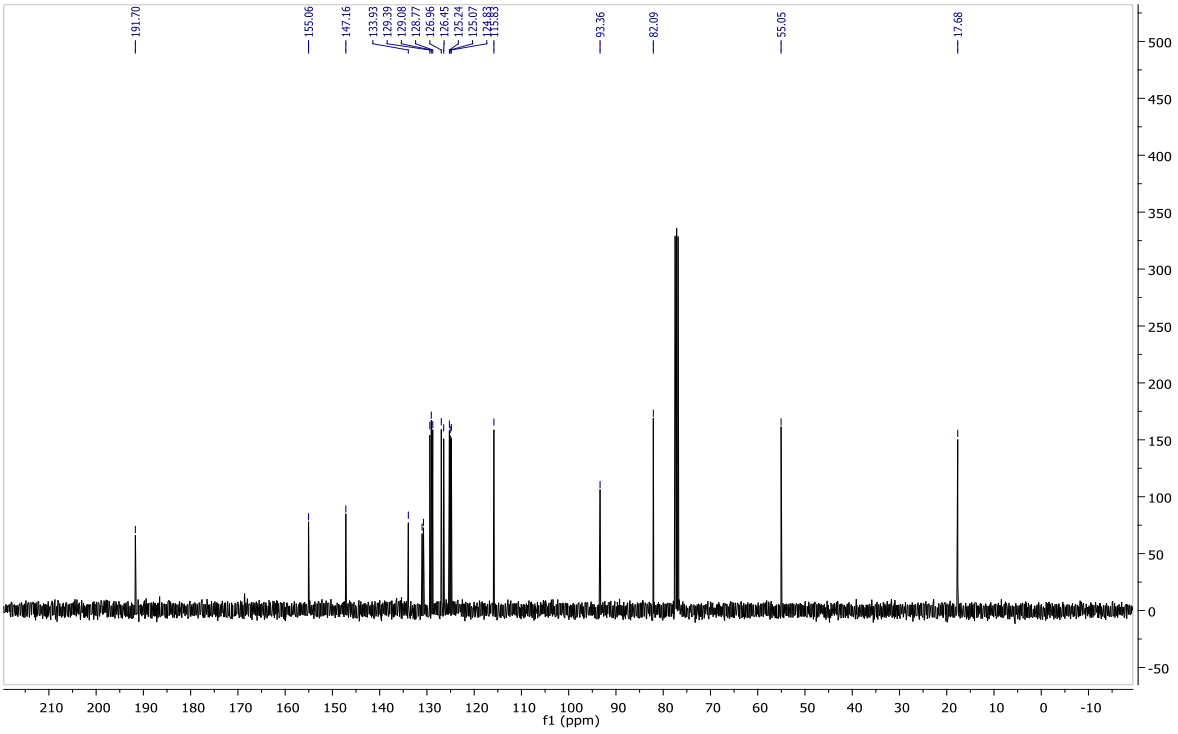
^{13}C NMR spectrum of 4f:



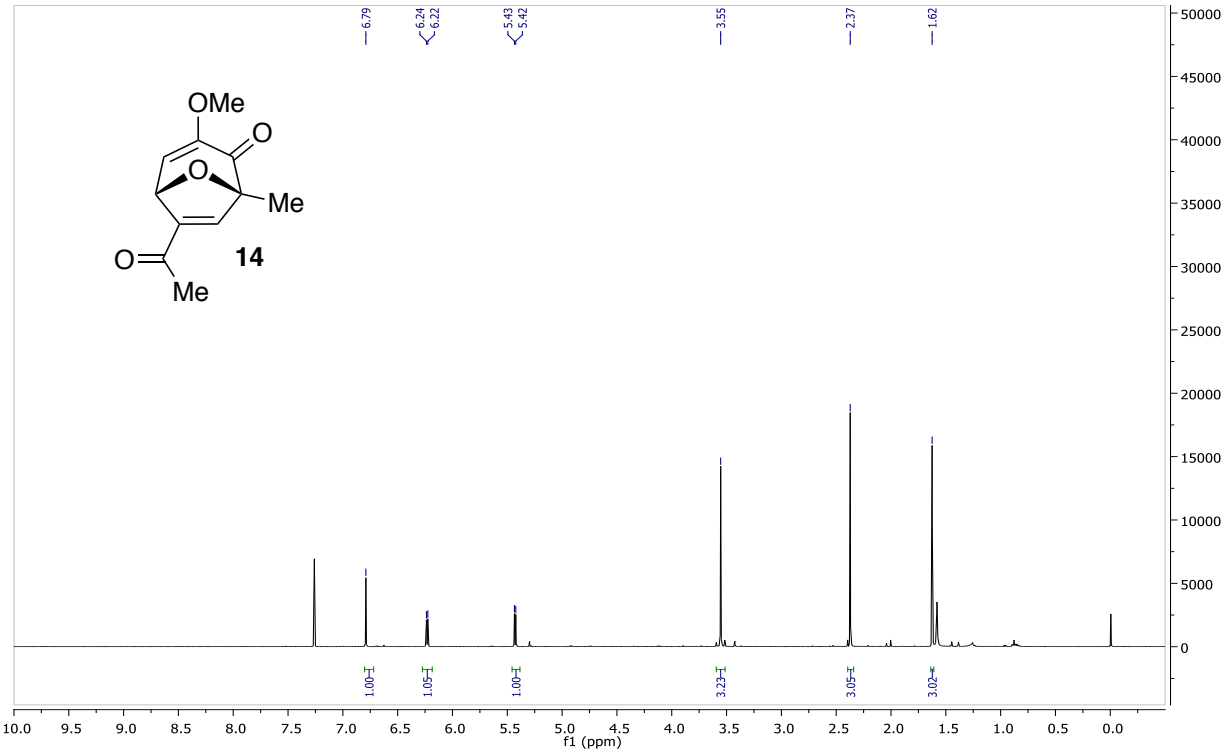
^{1}H NMR spectrum of 4g:



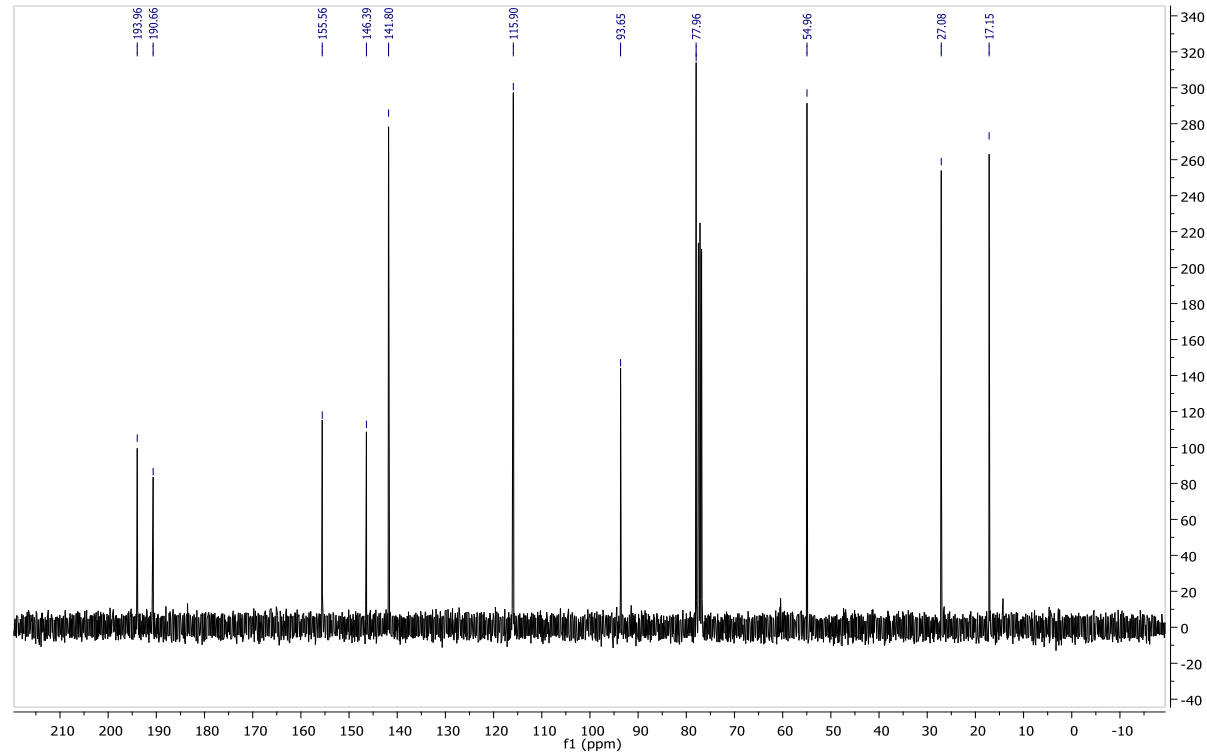
^{13}C NMR spectrum of 4g:



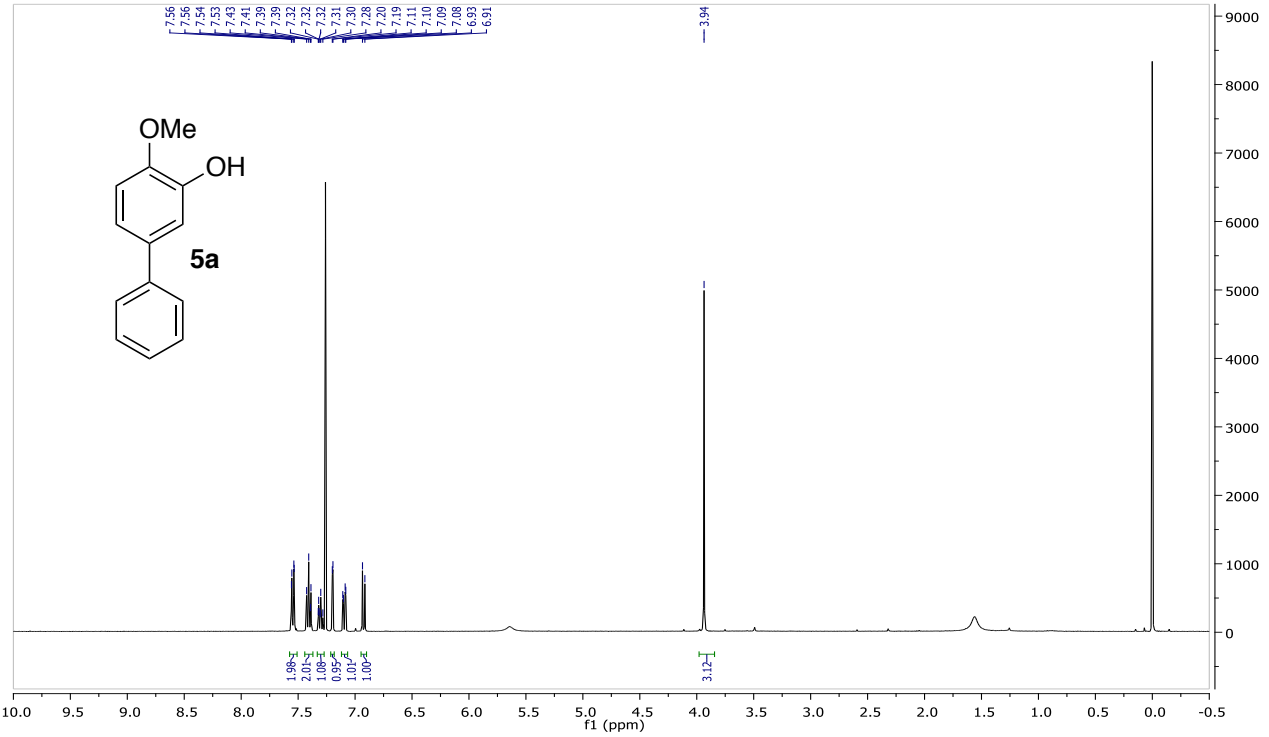
^{1}H NMR spectrum of 14:



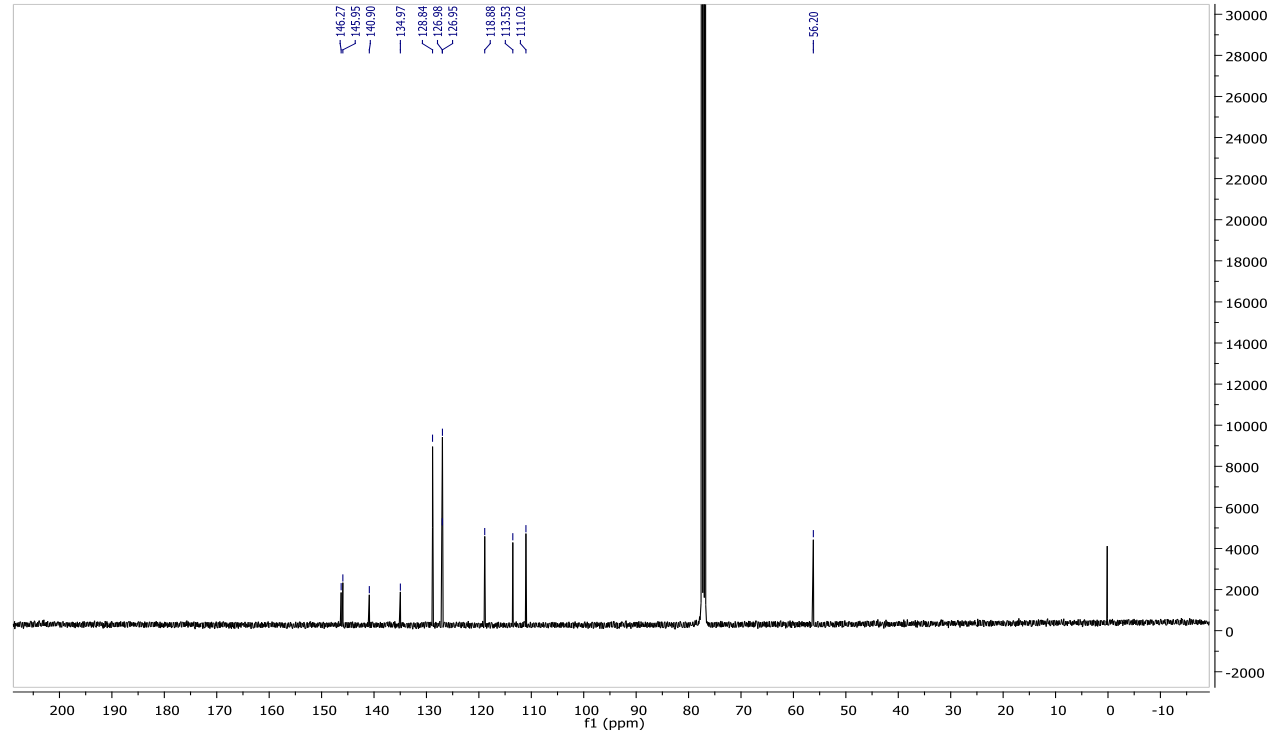
^{13}C NMR spectrum of 14:



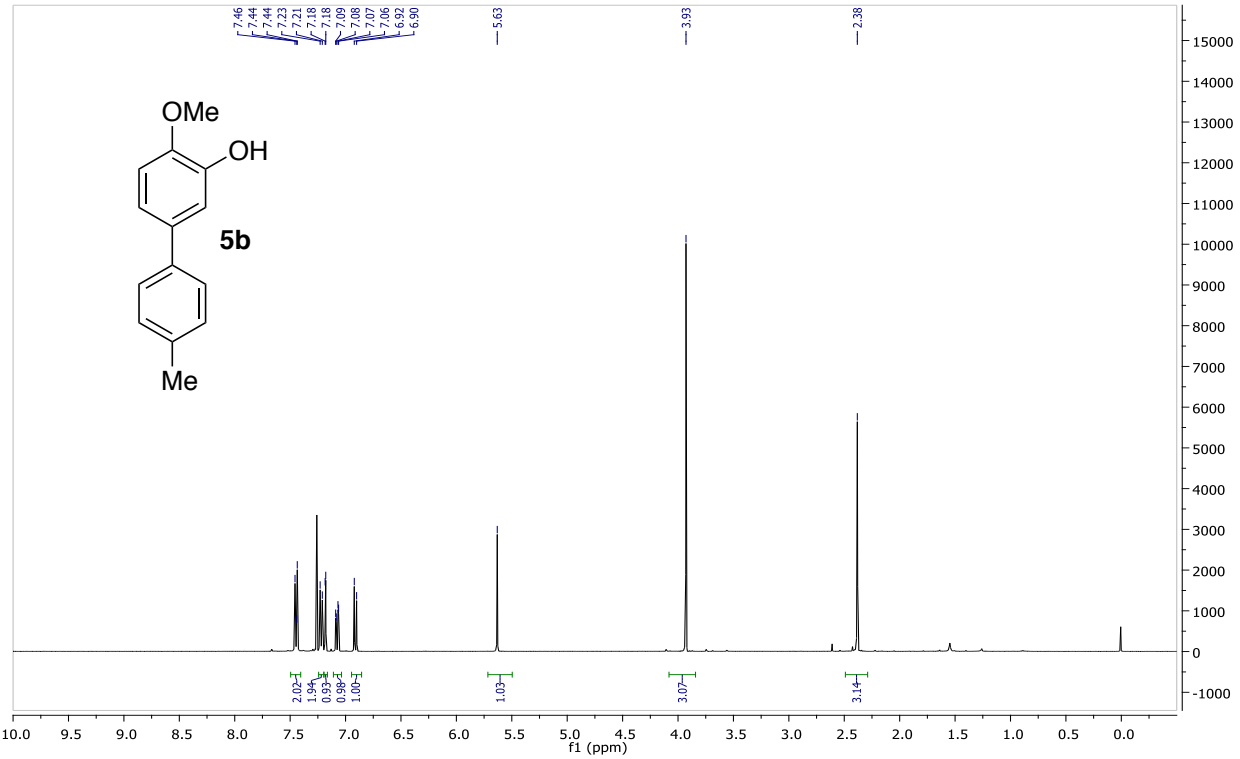
^{1}H NMR spectrum of 5a:



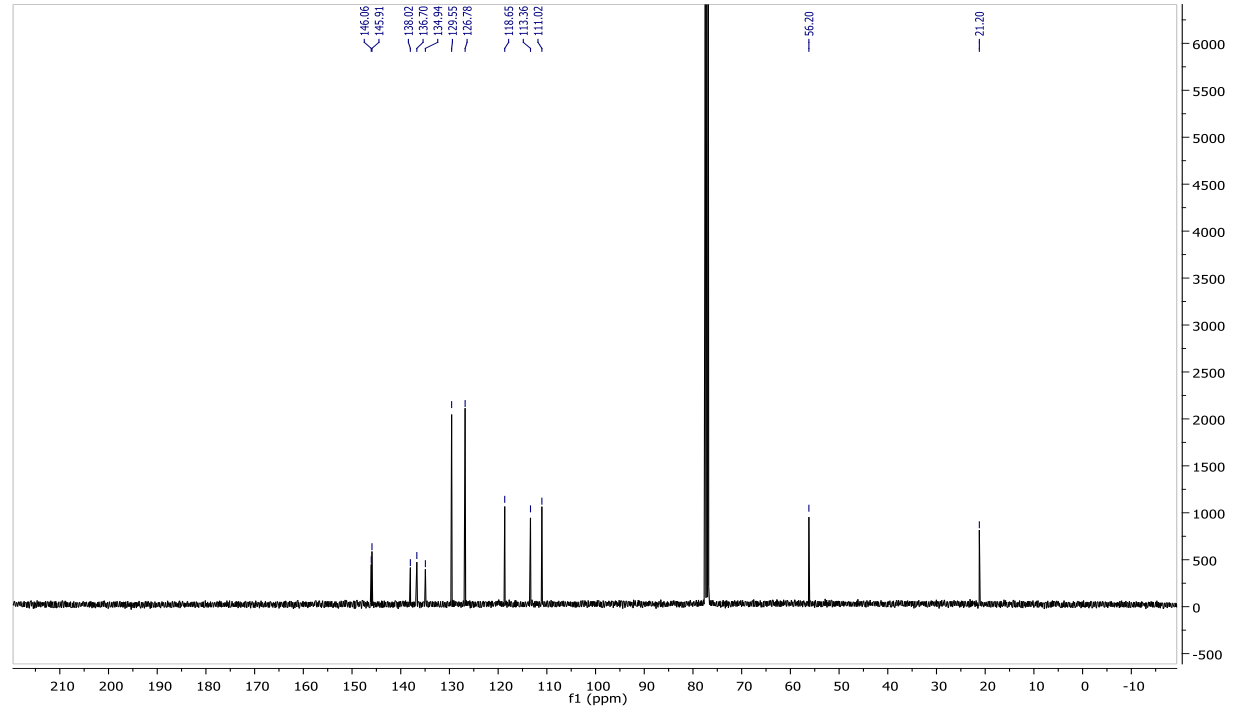
^{13}C NMR spectrum of 5a:



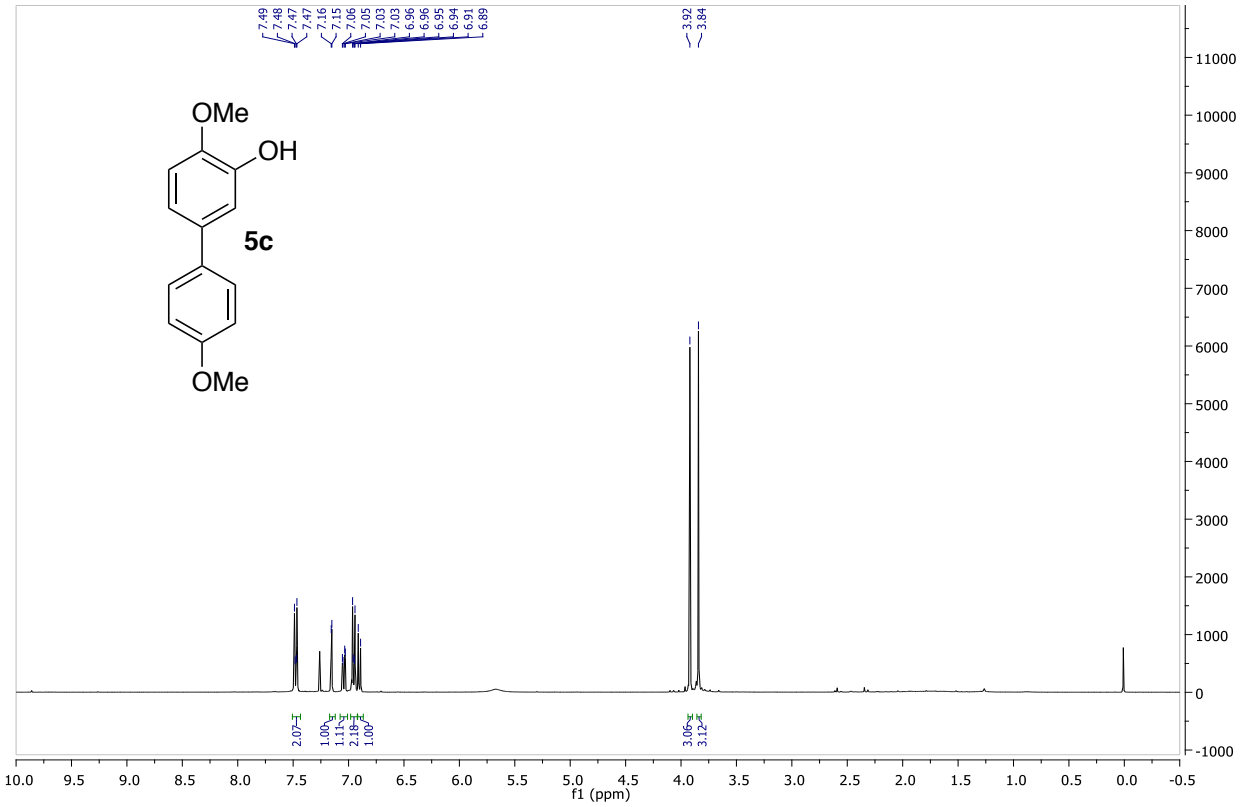
^{1}H NMR spectrum of 5b:



^{13}C NMR spectrum of 5b:



^{1}H NMR spectrum of 5c:



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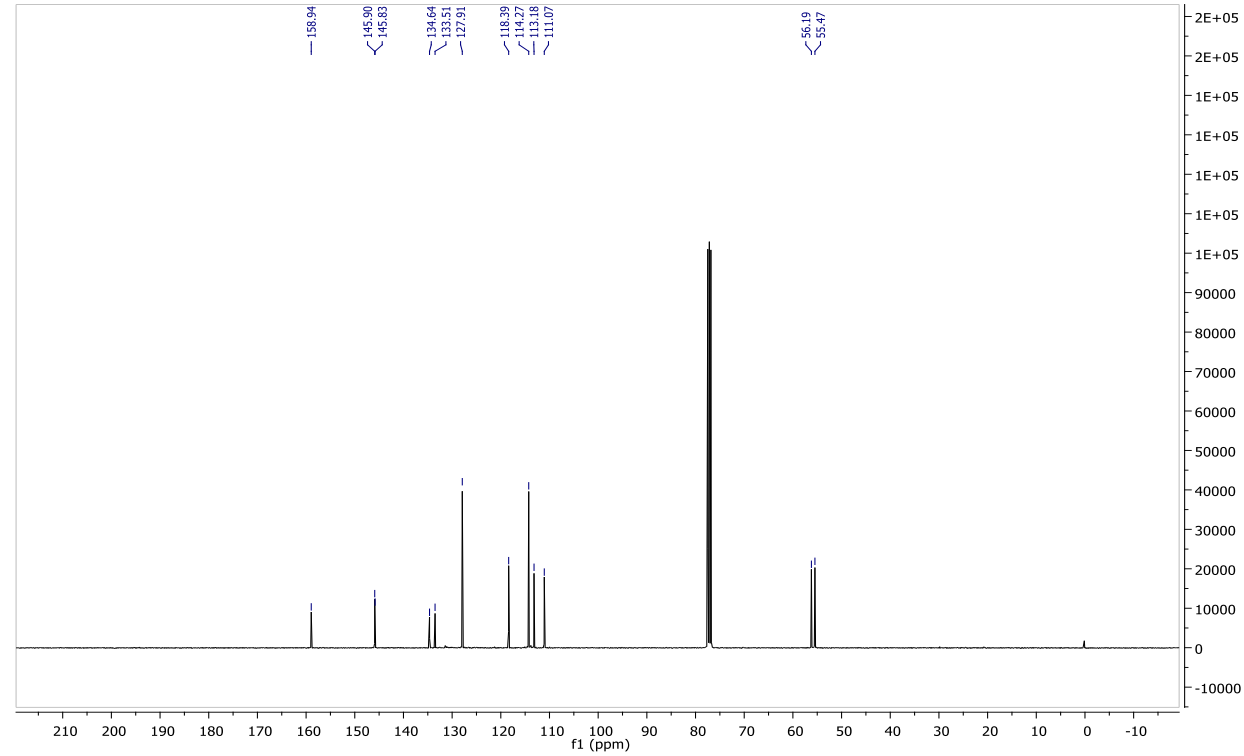
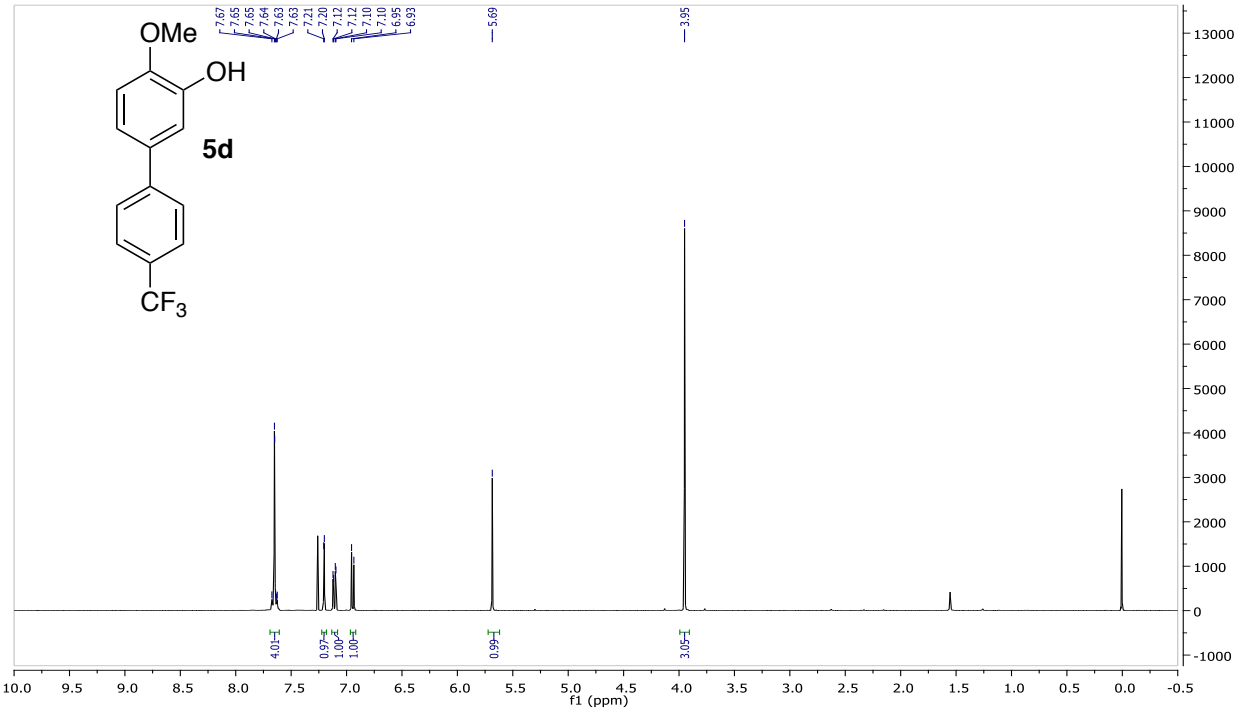
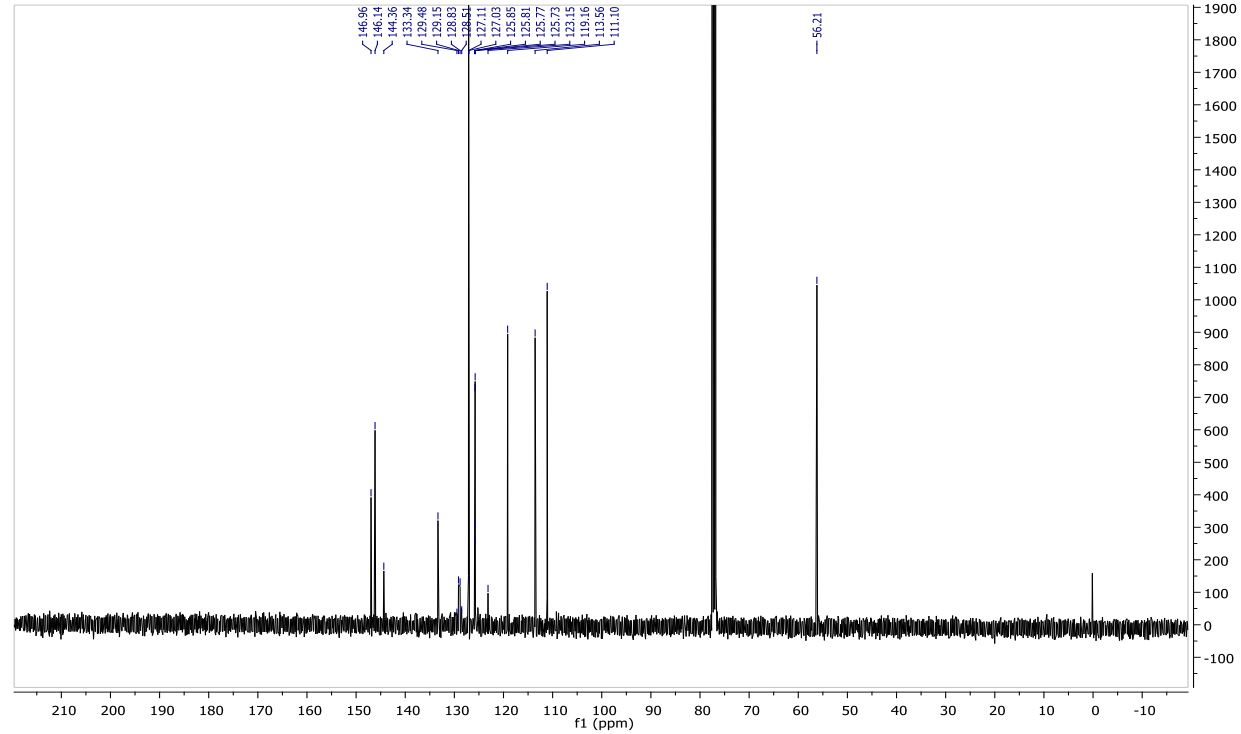


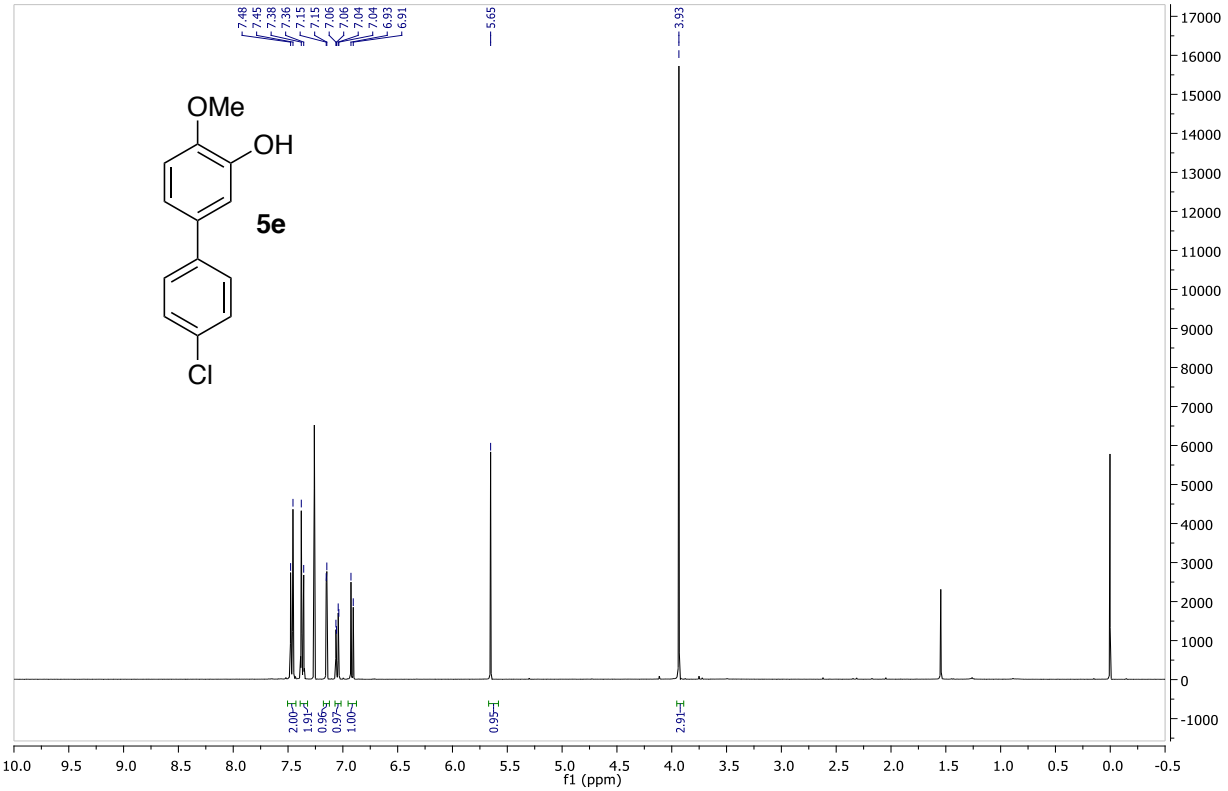
^{1}H NMR spectrum of 5d:



^{13}C NMR spectrum of 5d:



^{1}H NMR spectrum of 5e:



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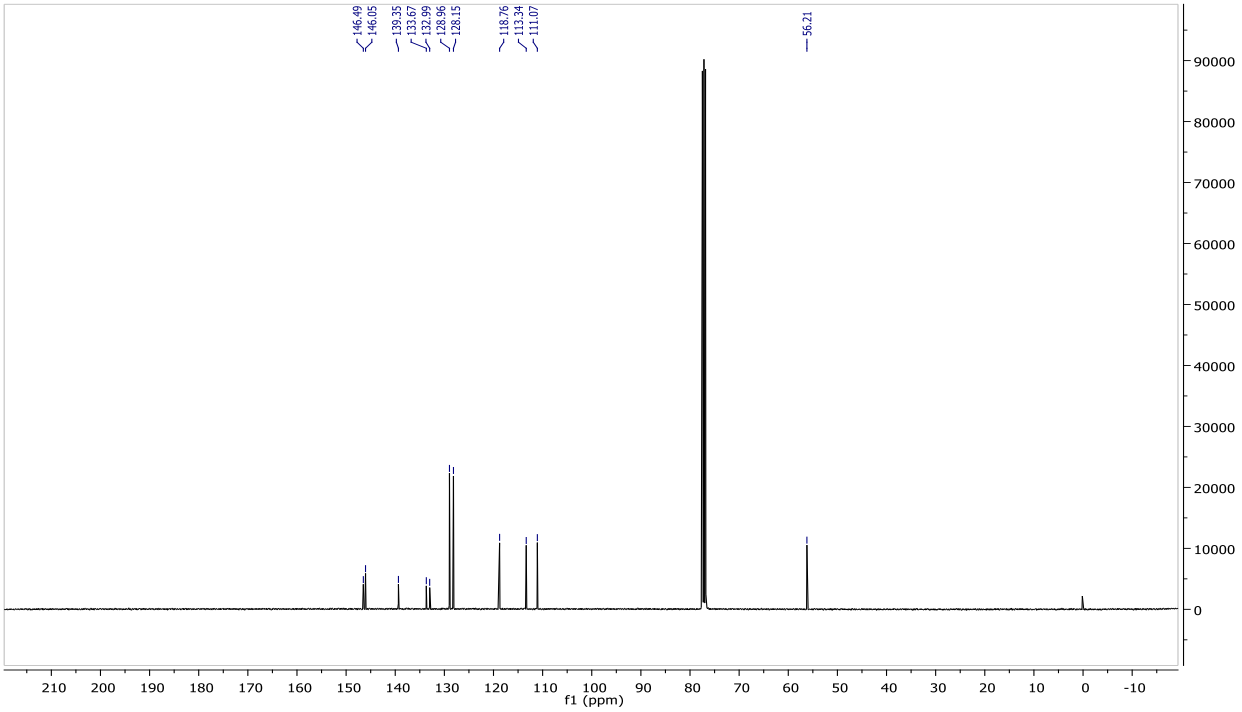
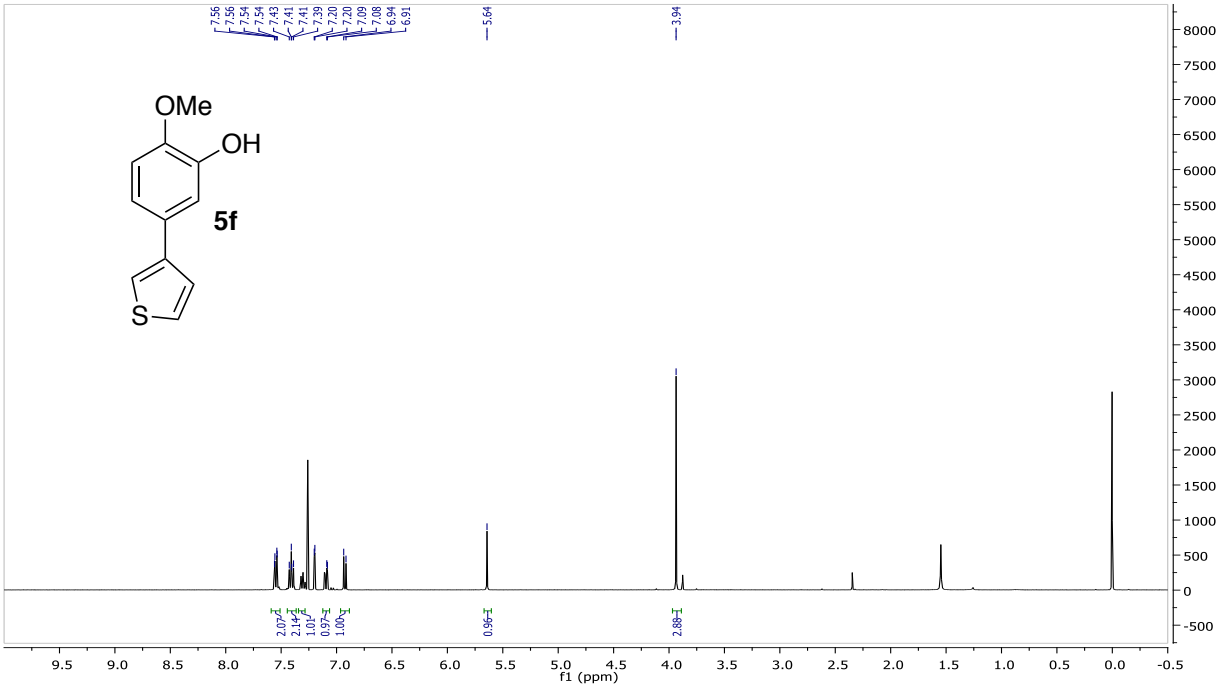
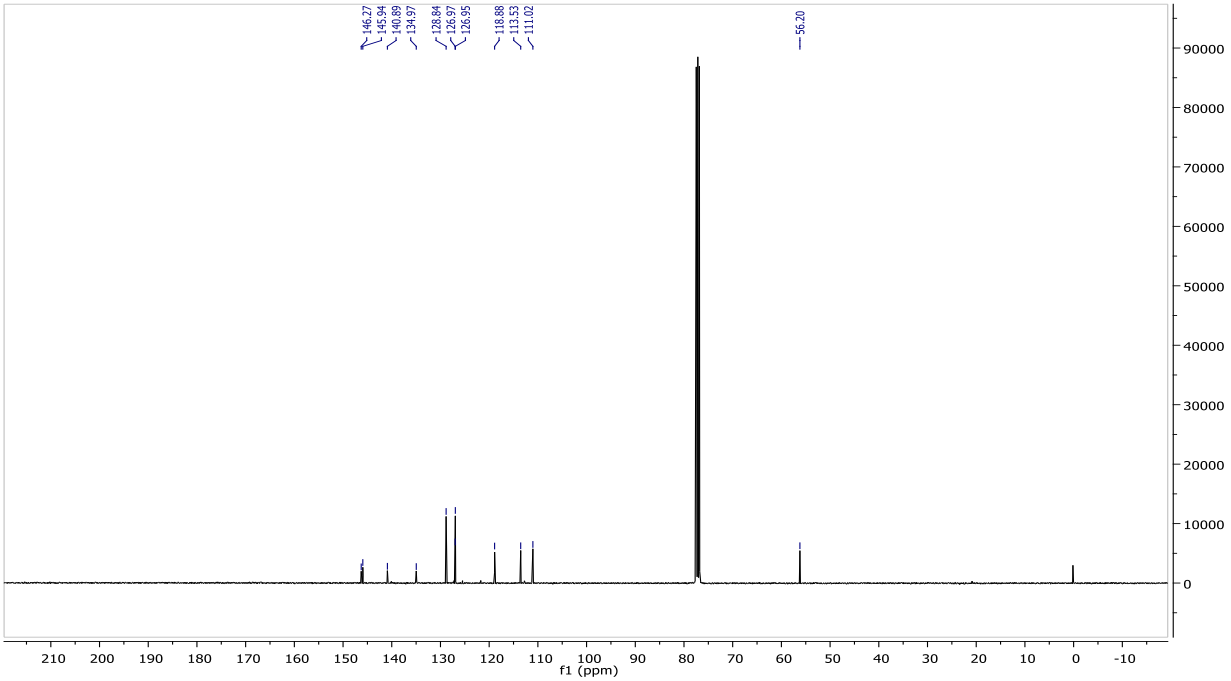


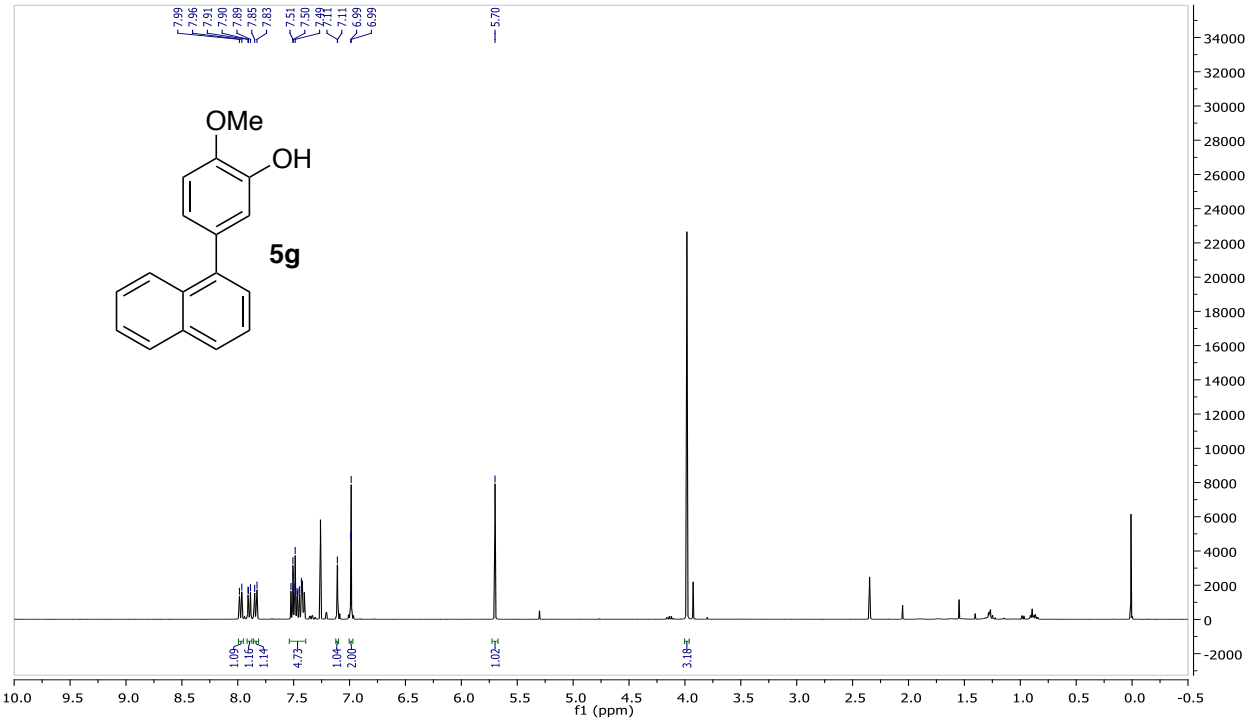
^{1}H NMR spectrum of 5f:



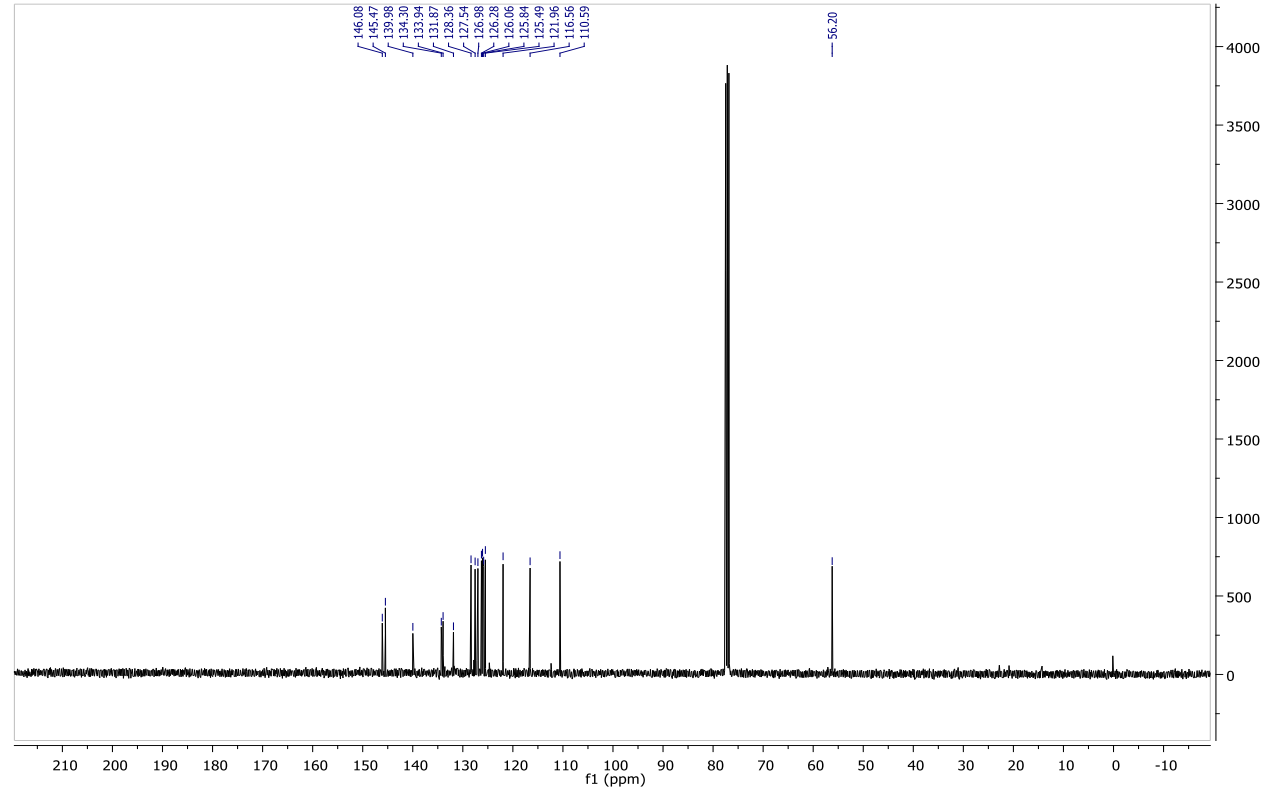
^{13}C NMR spectrum of 5f:



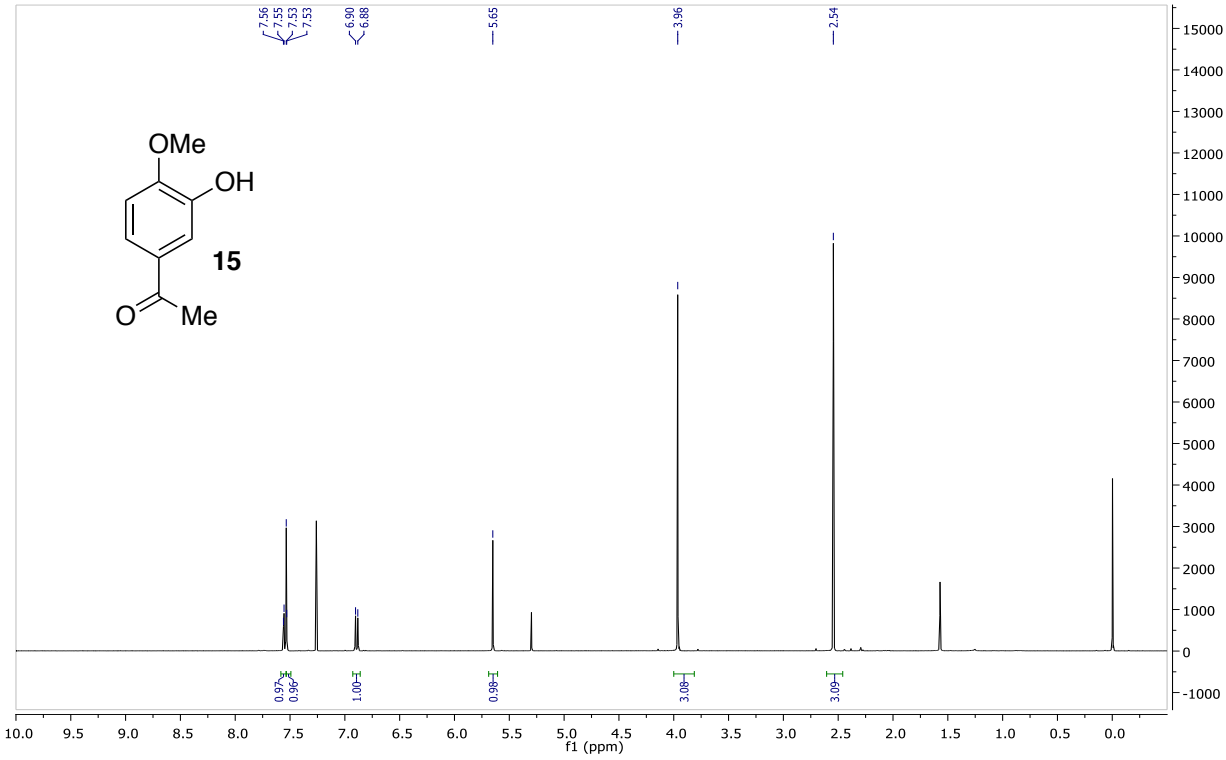
^{1}H NMR of 5g:



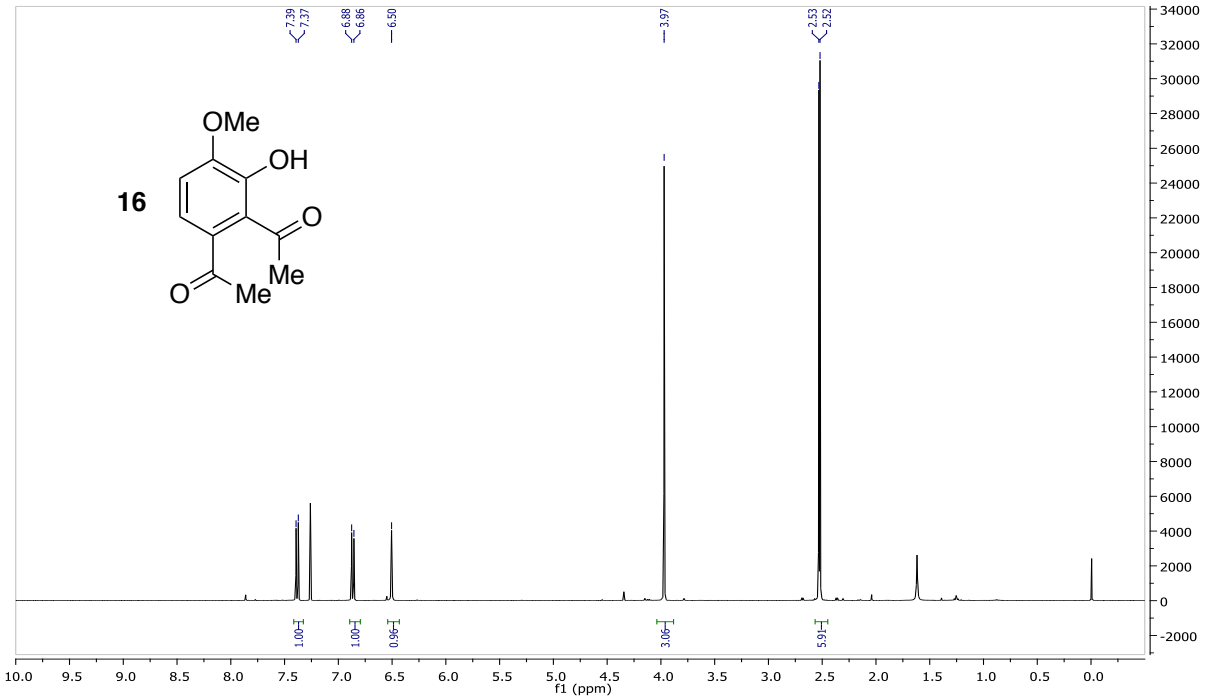
^{13}C NMR spectrum of 5g:



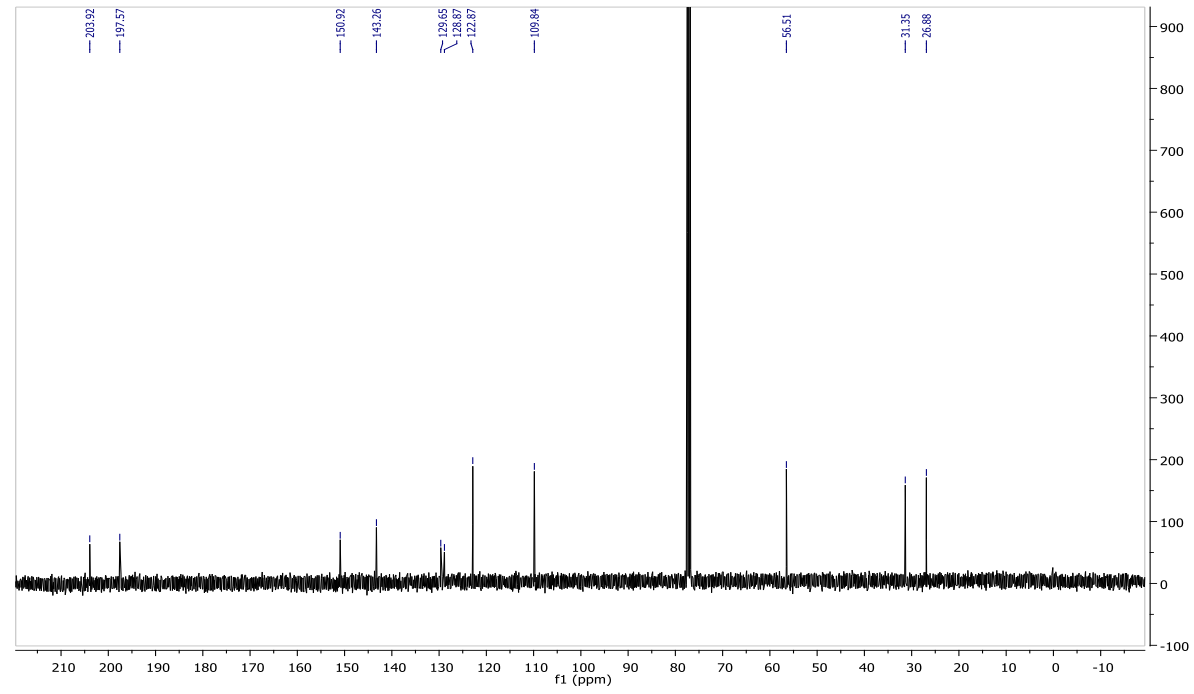
^{1}H NMR of 15:


7.56
7.55
7.53
7.53
6.90
6.88
5.65
3.96
2.54
OMe
OH
15
O
Me
0.97
0.96
1.00
0.98
3.08
3.09
f1 (ppm)

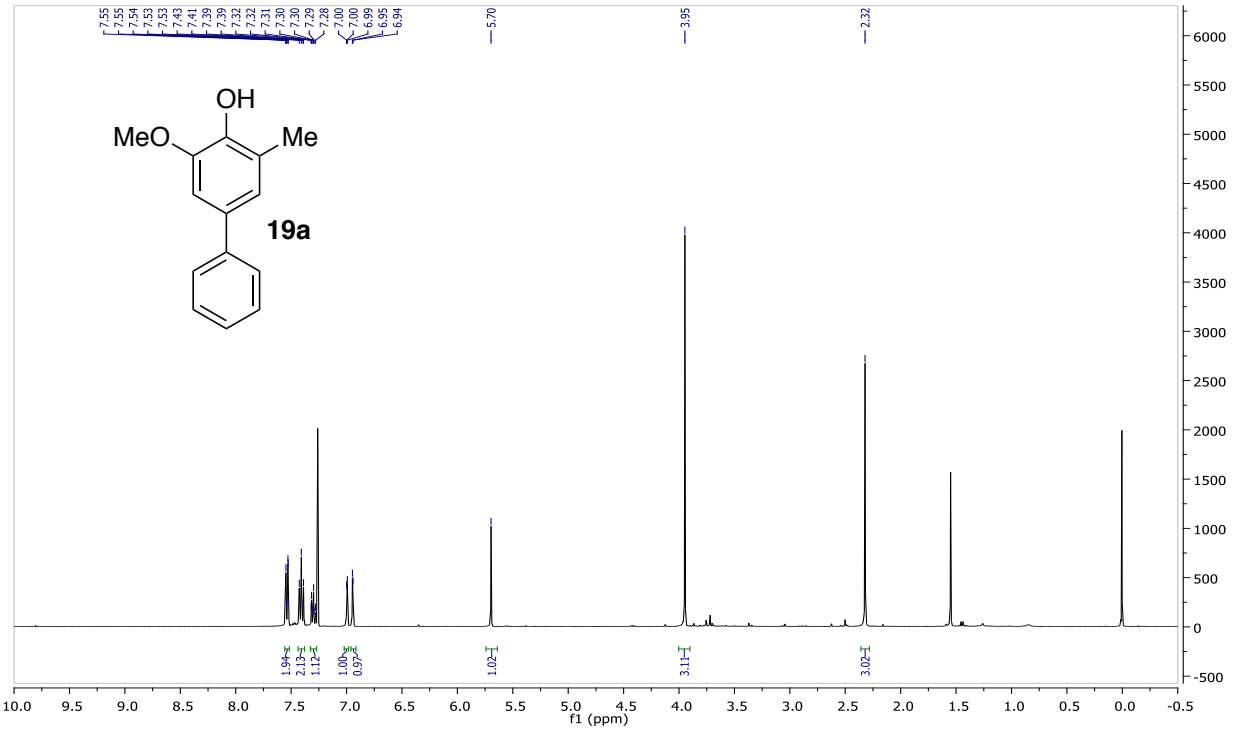
^{1}H NMR spectrum of 16:



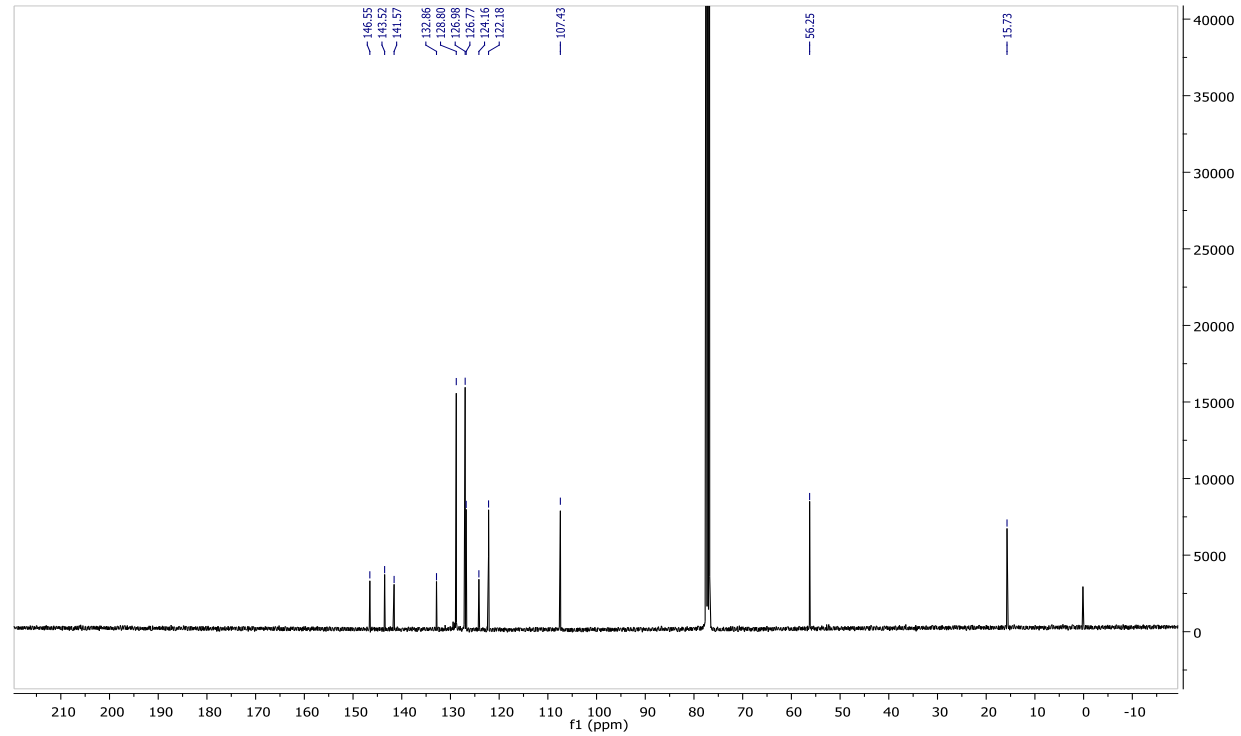
^{13}C NMR spectrum of 16:



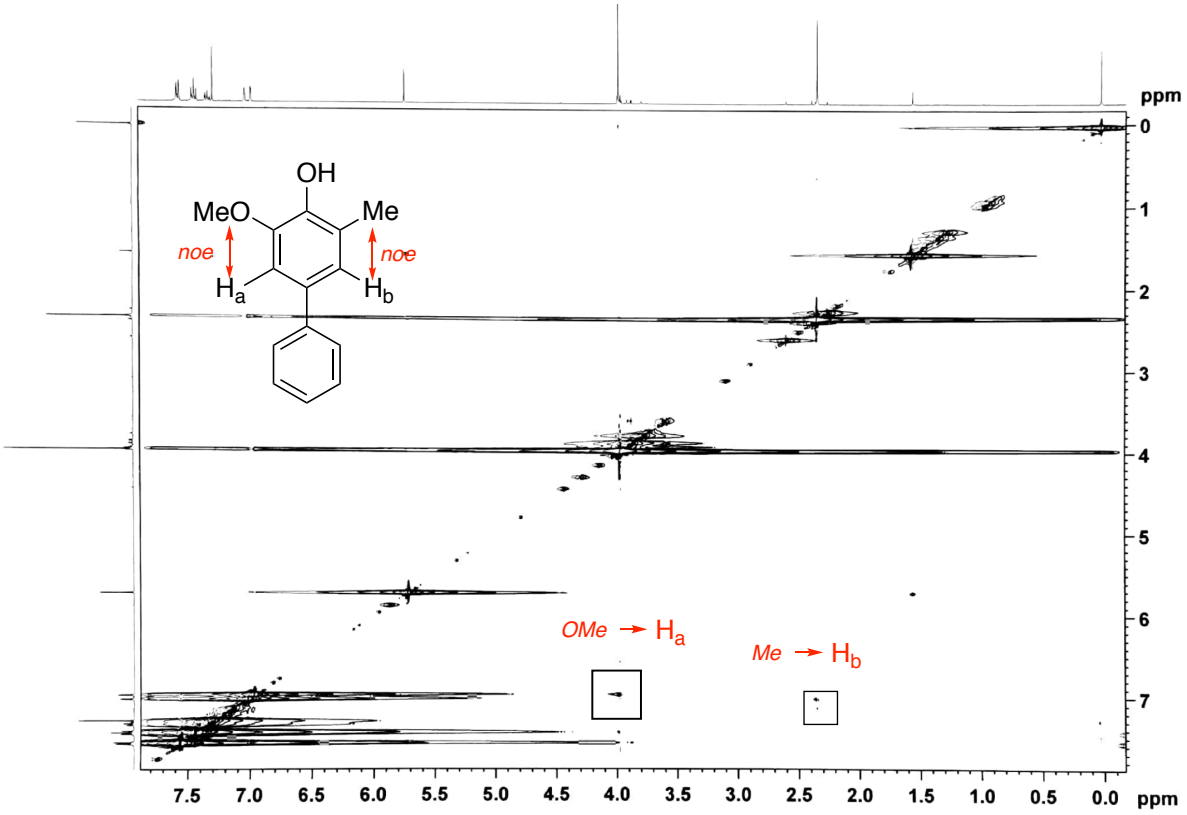
^{1}H NMR spectrum of 19a:



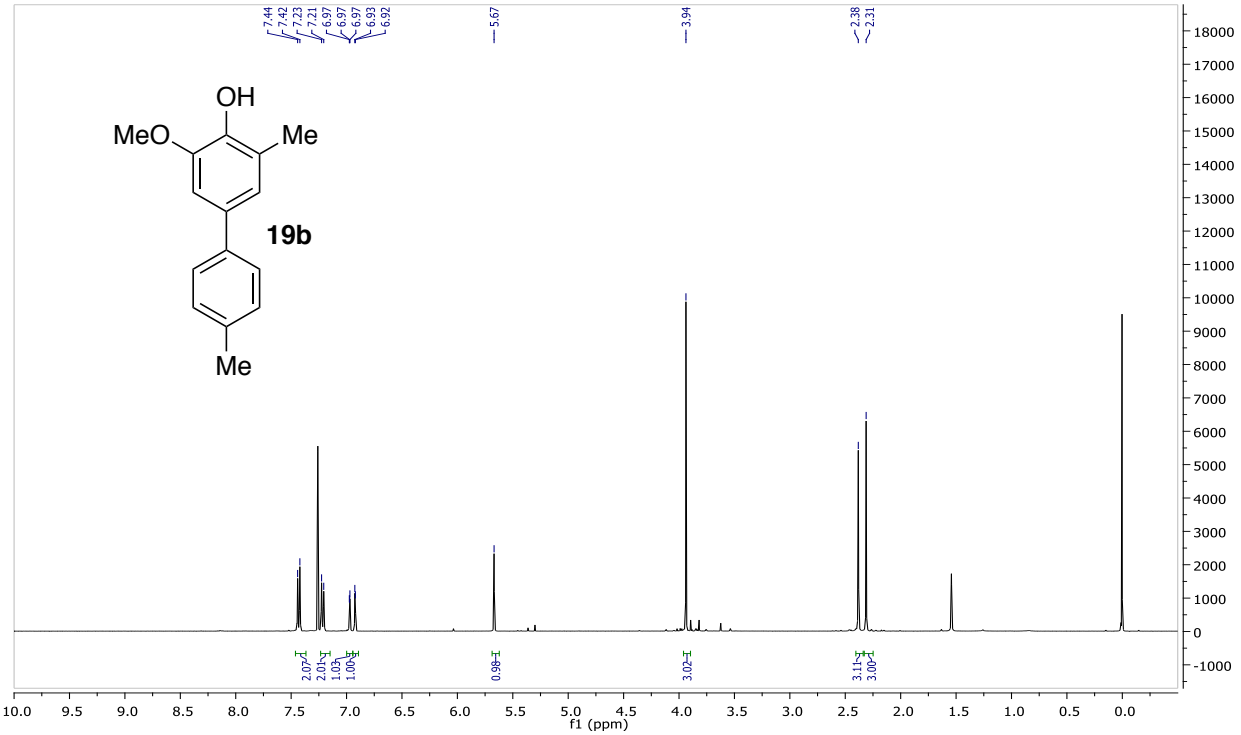
^{13}C NMR spectrum of 19a:



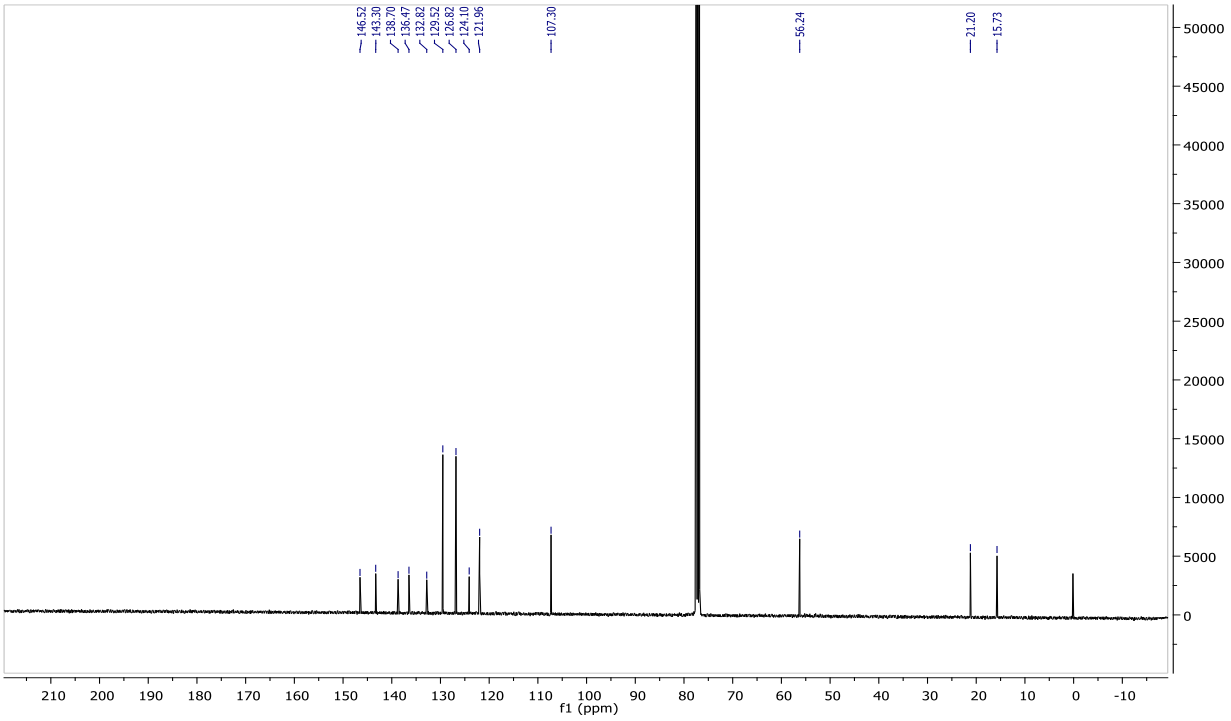
NOESY spectrum of 19a:



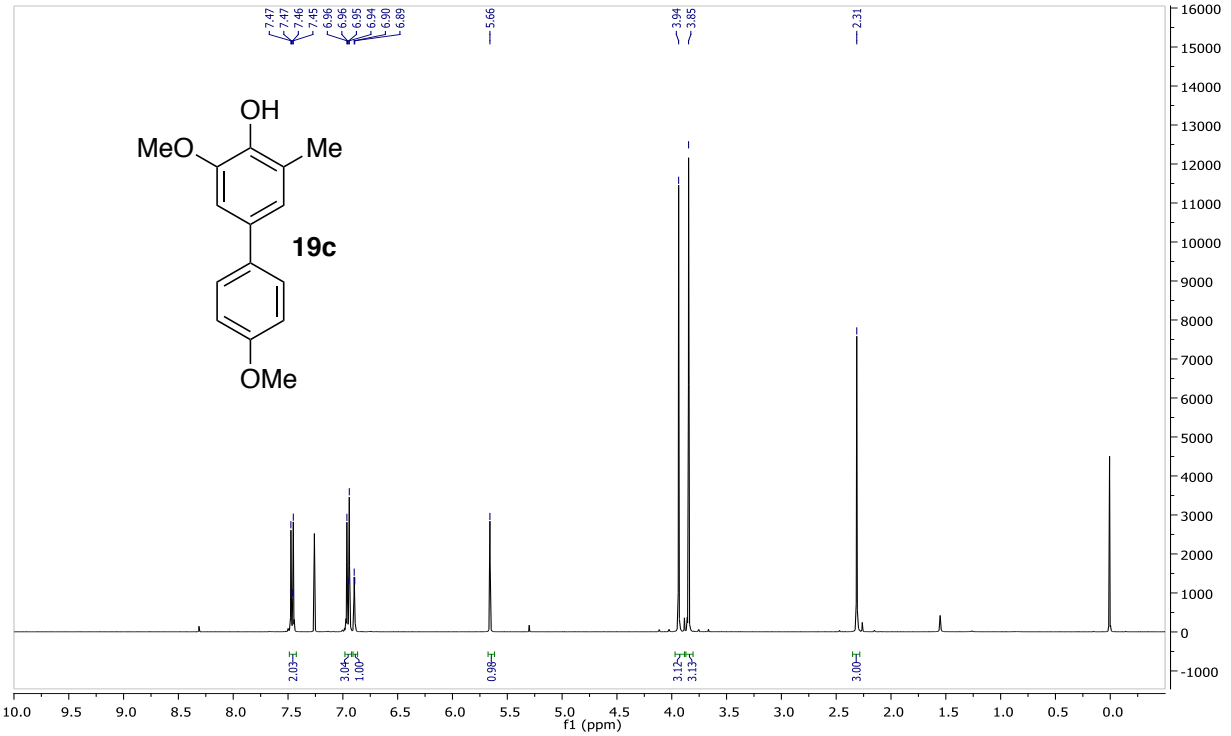
^{1}H NMR spectrum of 19b:



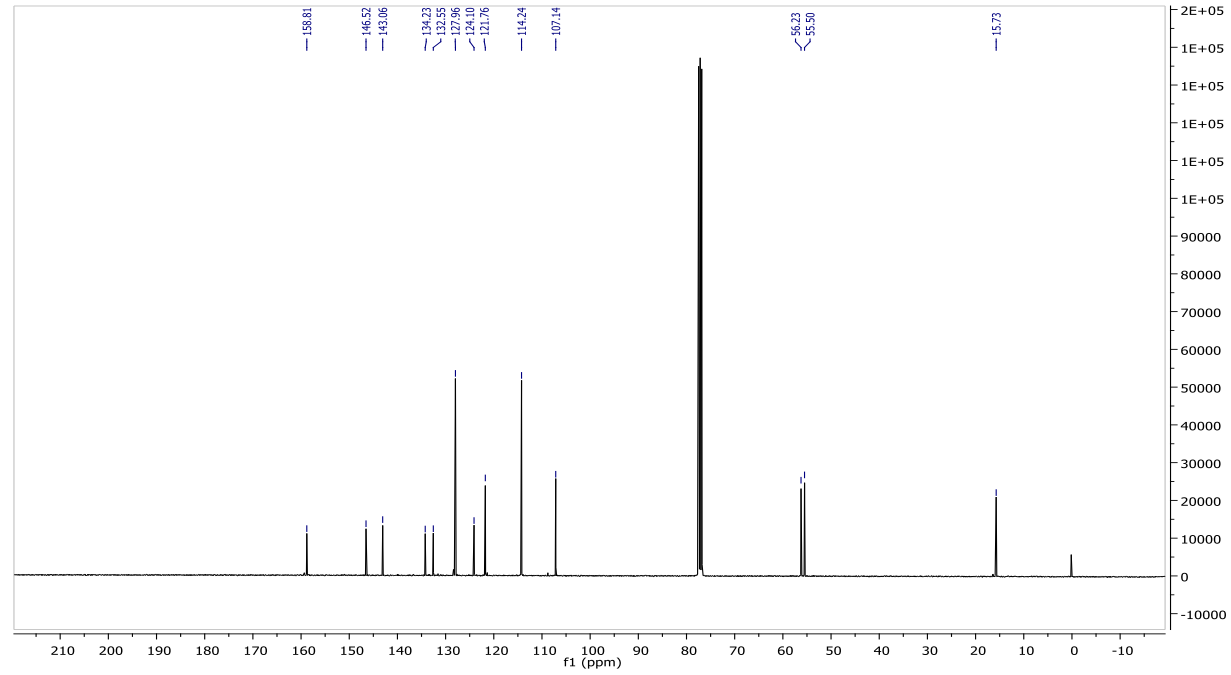
^{13}C NMR spectrum of 19b:



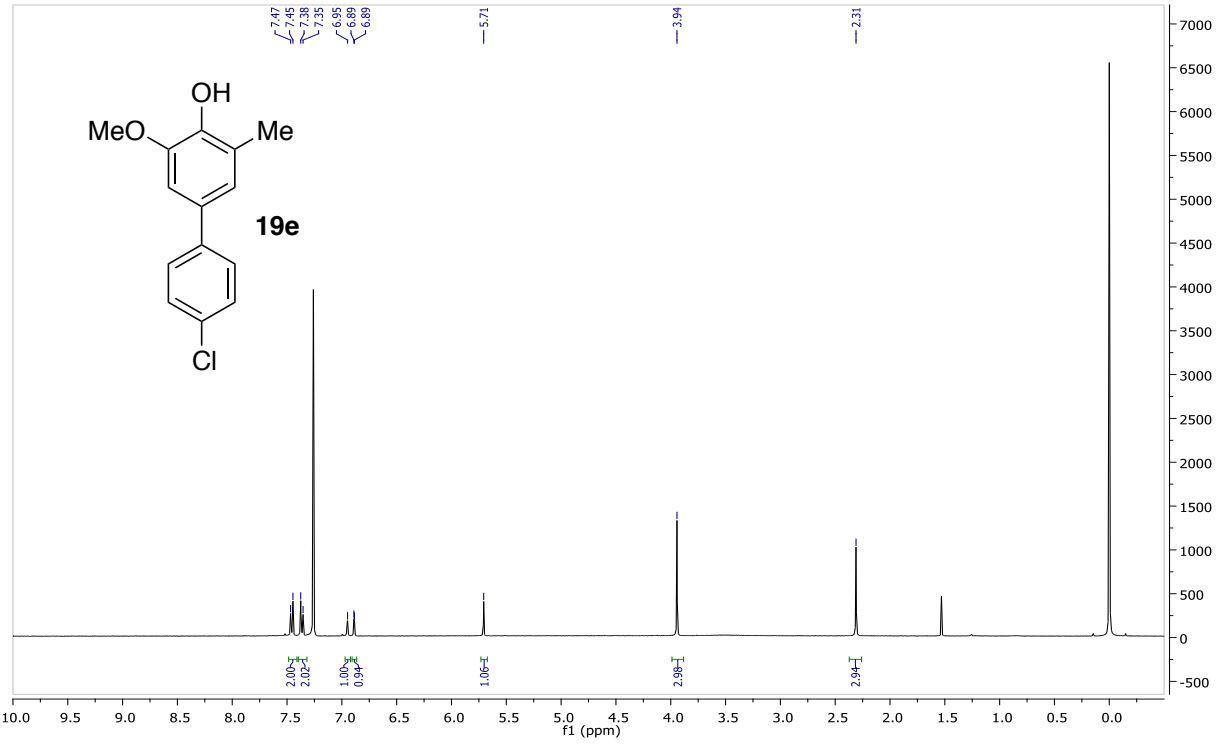
^{1}H NMR spectrum of 19c:



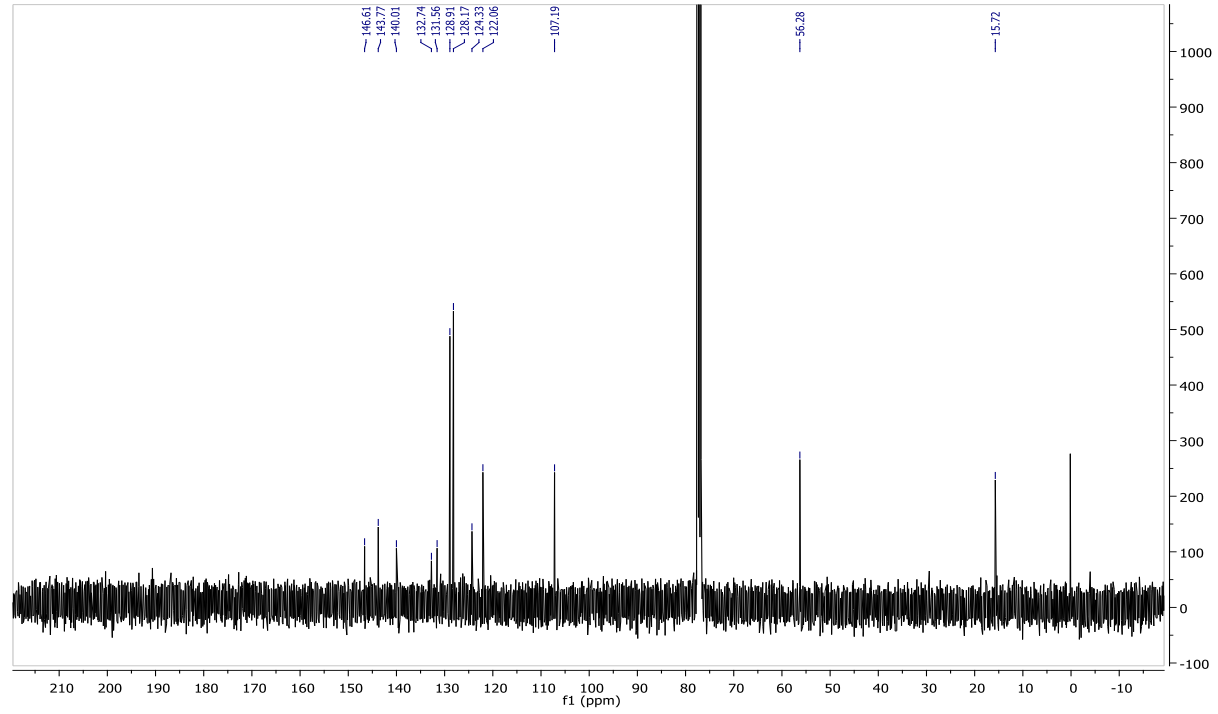
^{13}C NMR spectrum of 19c:



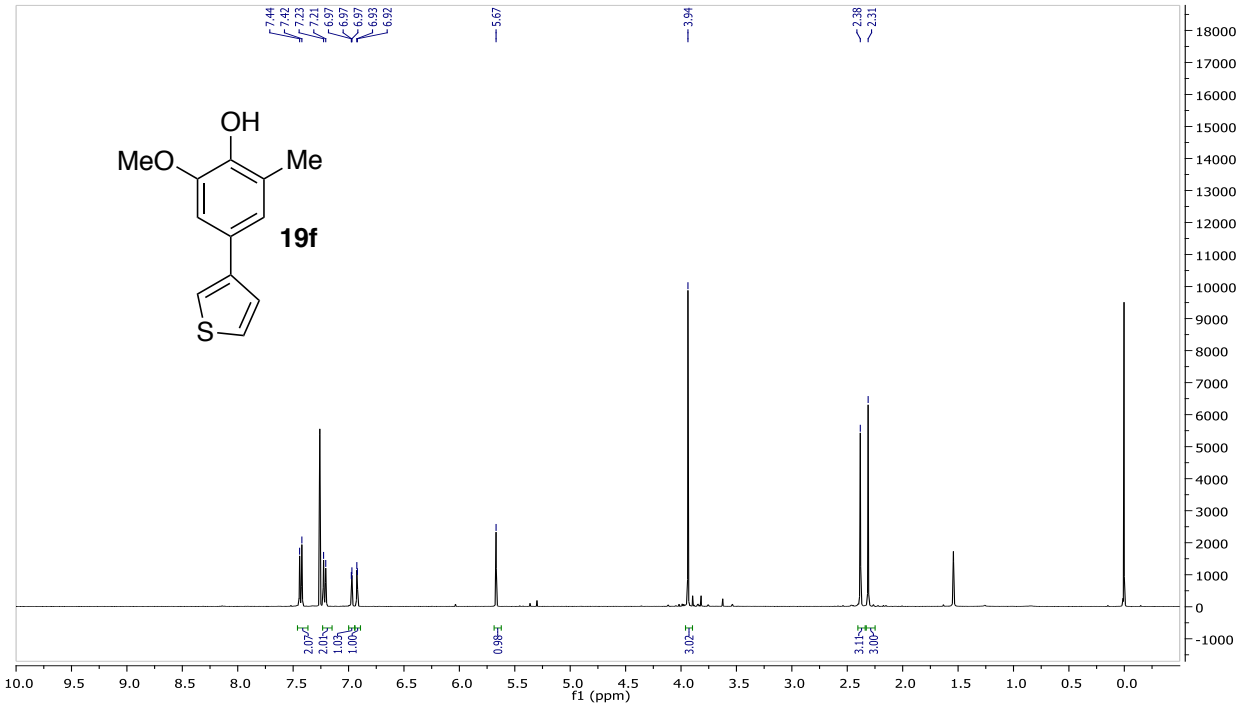
^{1}H NMR spectrum of 19e:



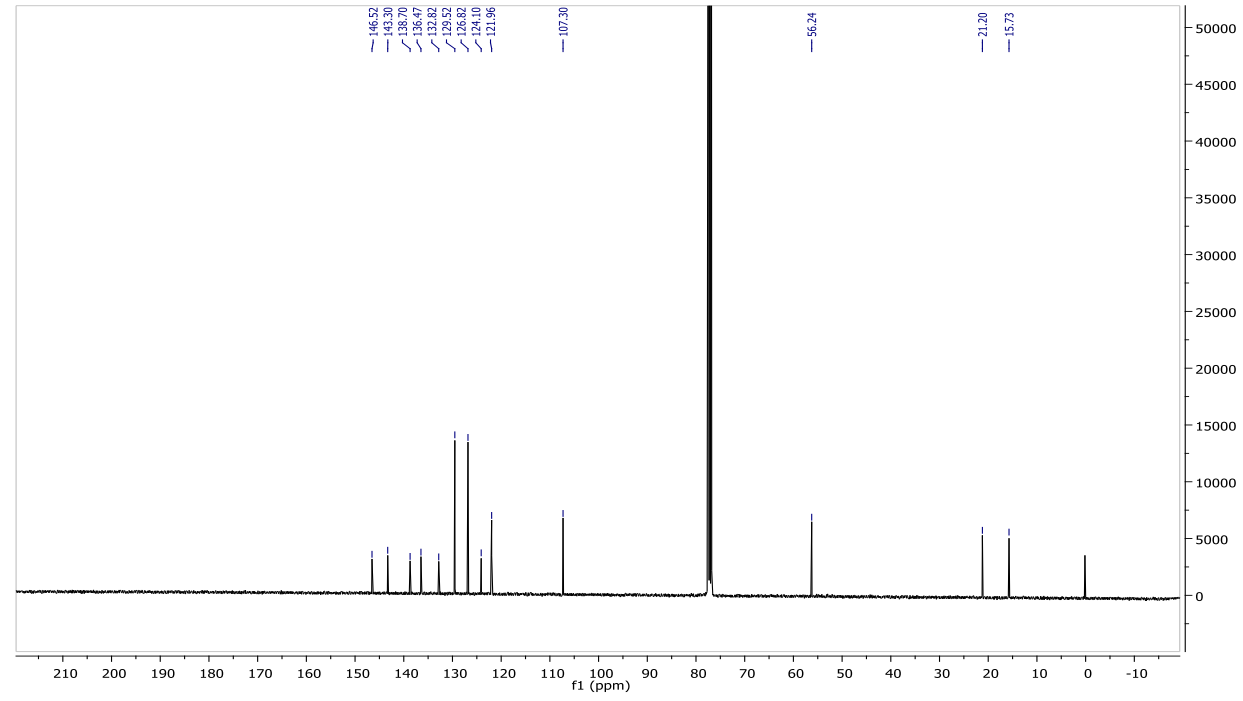
^{13}C NMR spectrum of 19e:



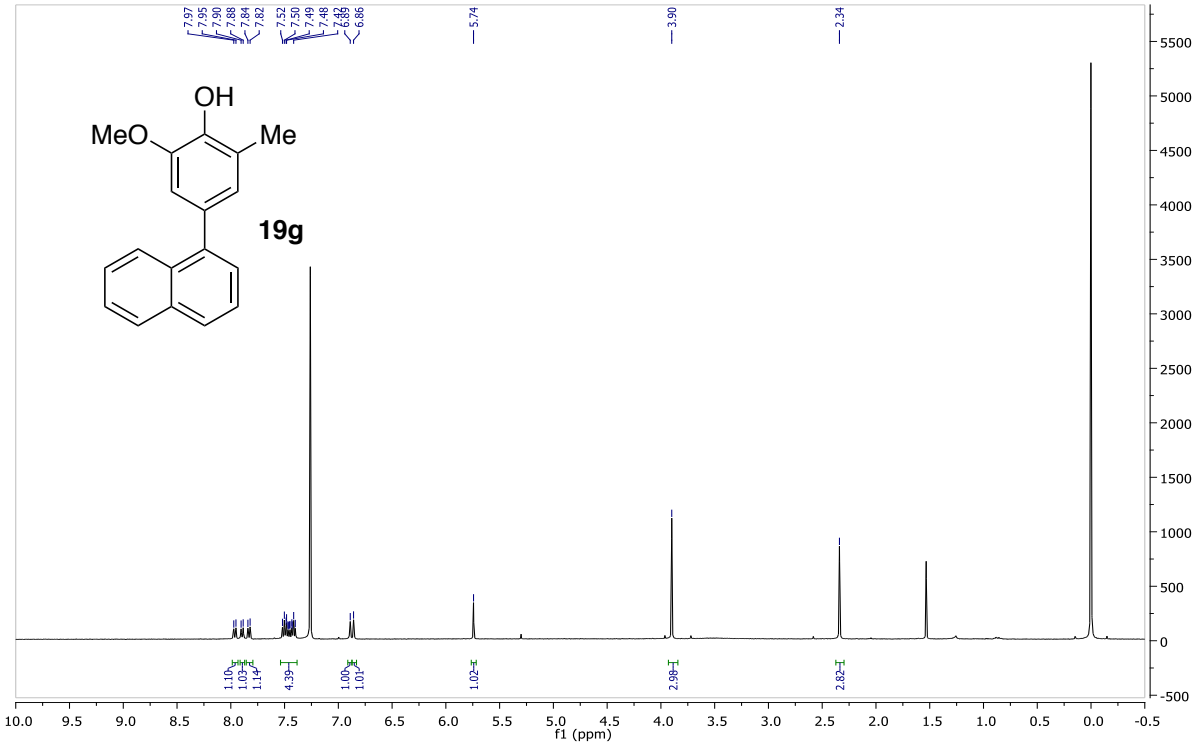
^{1}H NMR spectrum of 19f:



^{13}C NMR spectrum of 19f:



^{1}H NMR spectrum of 19g:



^{13}C NMR spectrum of 19g: