Catalytic, Regioselective Friedel-Crafts Alkylation of Beta-Naphthol

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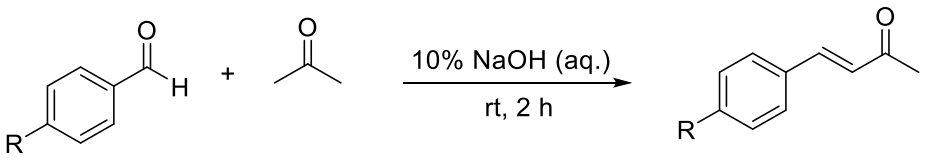
1. General information

All reactions were carried out under air atmosphere in oven-dried glassware with a magnetic stirring bar. Anhydrous solvents (DCM) were obtained by solvent purification system under argon. All commercially available reagents were used as received without further purification. The tubes used for the reaction are shown in **Figure S1**. Purification of reaction products was carried out by flash column chromatography using silica gel 60 (230-400 mesh). Analytical thin-layer chromatography was performed on 0.25 mm aluminum-backed silica gel 60-F plates. Visualization was accompanied by UV light and $KMnO_4$ solution. Concentration under reduced pressure refers to the removal of volatiles using a rotary evaporator attached to a dry diaphragm pump (10-15 mm Hg) followed by pumping to a constant weight with an oil pump (<300 mTorr). Infrared (IR) spectra were recorded on an IR spectrometer with KBr wafers or a film on a KBr plate. High-resolution mass spectra (HRMS) were recorded on an LCMS-IT-TOF mass spectrometer using ESI (electrospray ionization) or APCI (Atmospheric Pressure Chemical Ionization). ^1H NMR spectra were recorded in $CDCl_3$ on 400 MHz NMR spectrometer. The ^1H chemical shifts are referenced to residual solvent signals at δ 7.26 ($CHCl_3$). ^1H NMR coupling constants (*J*) are reported in Hertz (Hz) and multiplicities are indicated as follows: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), td (triplet of doublets), tt (triplet of triplets). ^{13}C NMR spectra were proton decoupled and recorded in $CDCl_3$ on a 100.5 MHz NMR spectrometer. The ^{13}C chemical shifts are referenced to solvent signals at δ 77.16 ($CDCl_3$). ^{31}P NMR spectra were proton decoupled and recorded in $CDCl_3$ on 162 MHz NMR spectrometer. ^{31}P chemical shifts are reported relative to 85% H_3PO_4 (0.00 ppm) as an external standard. ^{19}F NMR spectra were recorded on 376 MHz NMR spectrometer and chemical shifts are reported relative to the external standard (contained in a coaxial capillary) trifluoroacetic acid in CDCl3 (δF = -76.55 ppm).

Figure S1. A pictorial description of reaction tubes for the reaction.

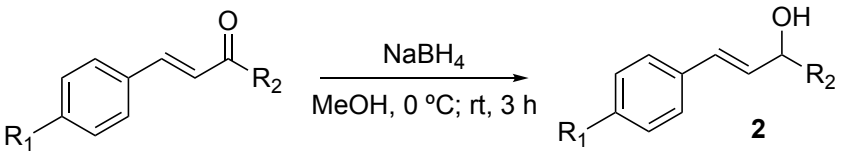
2. General experimental procedure and characterization data

2.1. General procedure for the synthesis of enone



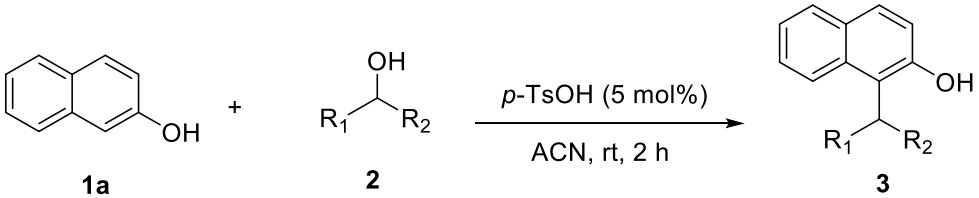
To a solution of benzaldehyde (2.0 mmol, 1.0 equiv) in acetone (5.12 mmol, 2.56 equiv) was added 10% NaOH (1.0 mL). The reaction was stirred until completion monitored by thin layer chromatography. H_2O (5.0 mL) was then added, and extraction was performed with DCM (3 X 5 mL). The organic extract was washed with brine and dried over Na_2SO_4. The sodium sulfate was filtered off, and the dried organic extract was concentrated under reduced pressure and directly purified by column chromatography to give the enone product.

2.2 General procedure for the synthesis of allylic alcohol 2



A solution of enone (1.0 mmol, 1.0 equiv) in MeOH (5.0 mL) was cooled to 0°C and $NaBH_4$ (2.0 mmol, 4.0 equiv) was slowly added. The reaction was stirred until completion monitored by thin layer chromatography. H_2O (5.0 mL) was then added, and extraction was performed with DCM (3 X 5 mL). The organic extract was washed with brine and dried over Na_2SO_4. The sodium sulfate was filtered off, and the dried organic extract was concentrated under reduced pressure and directly purified by column chromatography to give the allylic alcohol product **2**.

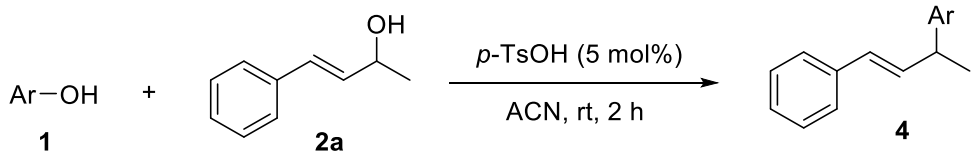
2.3 Synthesis of α-functionalized naphthol 3



To a solution of alcohol (0.2 mmol, 1.0 equiv) and beta naphthol (0.2 mmol, 1.0 equiv) in acetonitrile (1.0

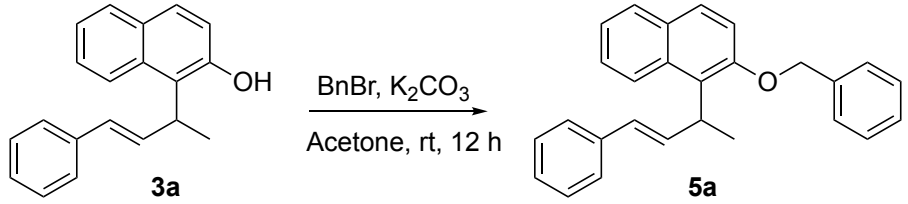
mL) was added *p*-TsOH catalyst (1.7 mg, 0.01 mmol). The solution was stirred for 2 hours and then directly purified by column chromatography to give alkylated naphthol product **3**.

2.4 Synthesis of functionalized phenol/naphthol 4

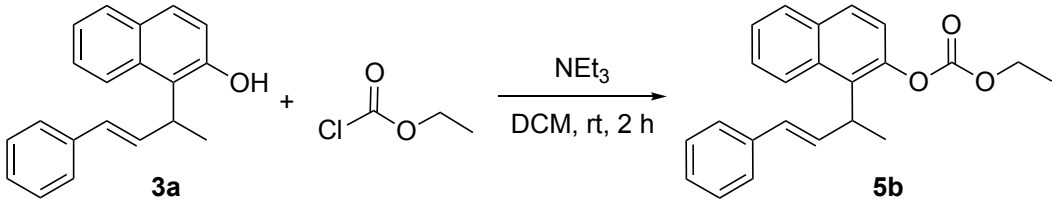


To a solution of allylic alcohol (0.2 mmol, 1.0 equiv) and aryl alcohol (0.2 mmol, 1.0 equiv) in acetonitrile (1.0 mL) was added *p*-TsOH (1.7 mg, 0.01 mmol). The solution was stirred for 2 hours and then directly purified by column chromatography to give the product **4**.

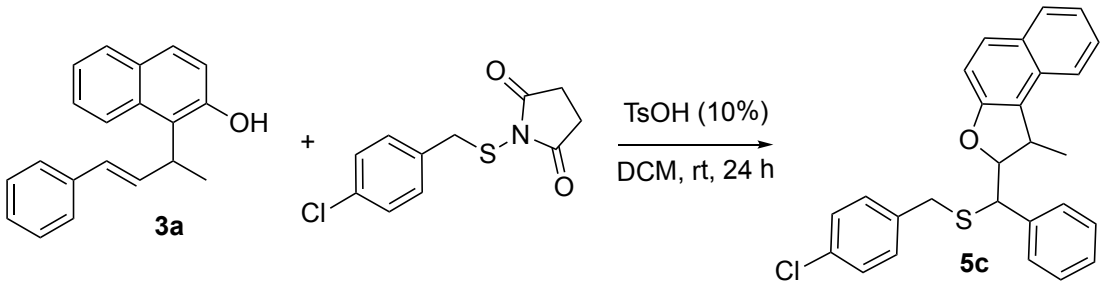
2.5 Synthesis of 5



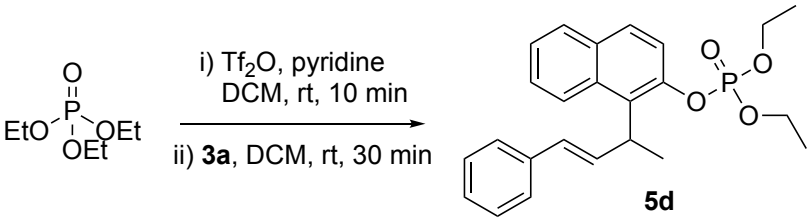
To a solution of **3a** (27.5 mg, 0.10 mmol, 1.0 equiv) and K_2CO_3 (41.5 mg, 0.30 mmol, 3.0 equiv) in acetone (0.25 mL) was added benzyl bromide (18 µL, 0.15 mmol, 1.5 equiv). The solution was stirred for 12 hours. The crude reaction mixture was filitered and then directly purified by column chromatography (85:15 hexane/DCM) to give **5a** (30.6 mg, 84%) as a clear oil.



To a solution of **3a** (27.4 mg, 0.1 mmol, 1.0 equiv) and ethyl chloroformate (14 µL, 0.15 mmol, 1.5 equiv) was slowly added triethyl amine (28 µL, 0.20 mmol, 2.0 equiv). The solution was stirred for 2 hours, and then directly purified by column chromatography (6:4 Hexane/DCM) to give **5b** (33.0 mg, 92%) as a yellow oil.

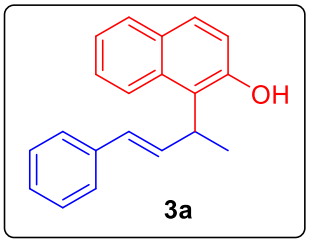


To a solution of **3a** (27.6 mg, 0.1 mmol, 1.0 equiv) and n-thiosuccinimide (38.7 mg, 0.15 mmol, 1.5 equiv) was added TsOH (1.7 mg, 0.01 mmol, 0.01 equiv). The reaction was stirred for 24 hours and then directly purified by column chromatography (7:3 hexane/ DCM) to give **5c** (28.2 mg, 65%) as a white solid.

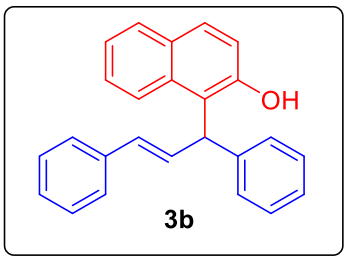


To a solution of triethyl phosphate (18.2 mg, 0.1 mmol, 1.0 equiv) was added Tf_2O (26 µL, 0.15 mmol, 1.5 equiv) and pyridine (16 µL, 0.20 mmol, 2.0 equiv). After stirring for 10 minutes, a solution of **3a** (55.0 mg, 0.2 mmol, 2.0 equiv) in DCM (200 µL) was added. After stirring for 30 minutes, the reaction was directly purified by column chromatography (7:3 hexane/ethyl acetate) to give phosphate **5d** (29.1 mg, 71%) as a clear oil.

3. Characterization data 3, 4, and 5

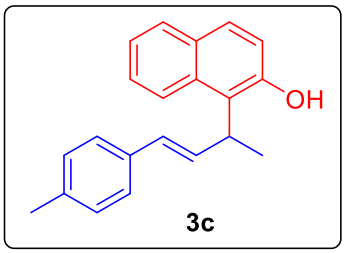


(E)-1-(4-phenylbut-3-en-2-yl)naphthalen-2-ol (3a).[1] 49.6 mg, 91%; as an oil; **IR** ν (thin film, cm^{-1}) 3452, 3056, 2964, 1666, 1620, 1511, 1258, 965, 815, 746, 695; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 MHz, 1H), 7.79 (d, J = 8.4 MHz, 1H), 7.67 (d, J = 8.8 MHz, 1H), 7.50 (t, J = 8.4 MHz, 1H), 7.40-7.39 (m, 2H), 7.36-7.28 (m, 3H), 7.25-7.21 (m, 1H), 7.06 (d, J = 8.8 MHz, 1H), 6.75-6.74 (m, 2H), 5.84 (s, 1H), 4.63 (q, J = 6.8 MHz, 1H), 1.63 (d, J = 6.8 MHz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 152.3, 136.6, 133.5, 132.5, 130.5, 129.6, 128.9, 128.8, 128.7, 127.7, 126.5, 126.3, 123.0, 122.3, 121.2, 119.2, 33.4, 17.2.

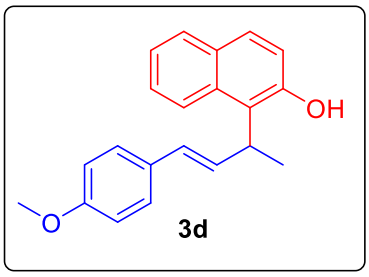


(E)-1-(1,3-diphenylallyl)naphthalen-2-ol (3b).[2] 58.9 mg, 88%; as a solid; mp 48-50 °C; **IR** ν (thin film, cm^{-1}) 3498, 3056, 1620, 1511, 1258, 965, 815, 746; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 MHz, 1H), 7.80 (d, J = 8.0 MHz, 1H), 7.73 (d, J = 8.8 MHz, 1H), 7.43 (t, J = 6.8 MHz, 1H), 7.38-7.19 (m, 11H), 7.10 (d, J = 8.8 MHz, 1H), 6.94 (dd, J = 15.6, 6.4 MHz, 1H), 6.50 (d, J = 16.4 MHz, 1H), 5.87 (d, J = 6.8 MHz, 1H), 5.48 (s, 1H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 152.3, 141.4, 136.7, 133.2, 132.9, 129.9, 129.7, 129.4, 128.9, 128.8, 128.5, 128.0, 127.6, 126.9, 126.7, 126.4, 123.2, 122.9,

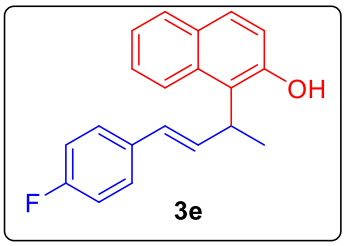
119.5, 119.2, 45.2.



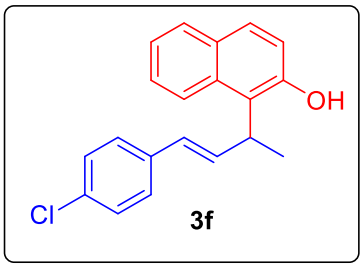
(E)-1-(4-(p-tolyl)but-3-en-2-yl)naphthalen-2-ol (3c).[1] 48.1 mg, 84%, as an oil; **IR** ν (thin film, cm^{-1}) 3412, 2964, 1602, 1511, 1246, 1172, 959, 815, 746; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.4 MHz, 1H), 7.77 (d, J = 8.4 MHz, 1H), 7.65 (d, J = 8.8 MHz, 1H), 7.46 (t, J = 6.8 MHz, 1H), 7.34-7.30 (m, 1H), 7.27 (d, J = 8.4 MHz, 2H), 7.10 (d, J = 8.0 MHz, 2H), 7.05 (d, J = 8.8 MHz, 1H), 6.70-6.69 (m, 2H), 5.94 (s, 1 H), 4.60 (q, J = 7.2 MHz, 1H), 2.31 (s, 3H), 1.60 (d, J = 7.2 MHz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 152.4, 137.6, 133.8, 132.5, 132.4, 130.5, 129.6, 129.4, 128.9, 128.7, 126.5, 126.3, 123.0, 122.4, 121.3, 119.3, 33.4, 21.2, 17.2.



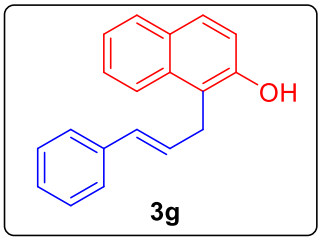
(E)-1-(4-(4-methoxyphenyl)but-3-en-2-yl)naphthalen-2-ol (3d).[1] 42.3 mg, 70%; as an oil; **IR** ν (thin film, cm^{-1}) 3435, 2964, 1602, 1298, 1252, 1177, 999, 815, 741; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 MHz, 1H), 7.78 (d, J = 8.0 MHz, 1H), 7.66 (d, J = 8.8 MHz, 1H), 7.47 (t, J = 6.8 MHz, 1H), 7.35-7.30 (m, 3H), 7.06 (d, J = 8.8 MHz, 1H), 6.85-6.82 (m, 2H), 6.70 (dd, J = 16.4, 2.0 MHz, 1H), 6.60 (dd, J = 16.4, 3.6 MHz, 1H), 6.01 (s, 1H), 4.62-4.58 (m, 1H), 3.79 (s, 3H), 1.60 (d, J = 7.2 MHz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 159.3, 152.4, 132.5, 131.0, 130.1, 129.6, 129.3, 128.9, 128.7, 127.5, 126.5, 123.0, 122.3, 121.3, 119.3, 114.1, 55.3, 33.3, 17.2.



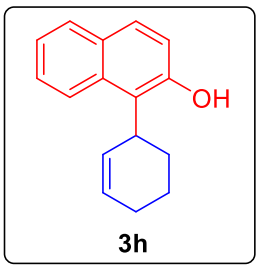
(E)-1-(4-(4-fluorophenyl)but-3-en-2-yl)naphthalen-2-ol (3e).[1] 52.7 mg, 89%; as an oil; **IR** ν (thin film, cm^{-1}) 3452, 2970, 1620, 1511, 1258, 970, 815, 746; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 MHz, 1H), 7.79 (d, J = 8.0 MHz, 1H), 7.67 (d, J = 8.8 MHz, 1H), 7.48 (t, J = 7.2 MHz, 1H), 7.36-7.31 (m, 3H), 7.05 (d, J = 8.8 MHz, 1H), 7.00-6.96 (m, 2H), 6.67-6.66 (m, 2H), 5.77 (s, 1H), 4.62 (q, J = 6.8 MHz, 1H), 1.32 (d, J = 7.2 MHz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 162.1 (d, J = 245.6 MHz), 152.1, 133.4, 132.8 (d, J = 3.7 MHz), 132.4, 129.6, 129.2, 128.9, 128.8, 127.9 (d, J= 8.2 MHz), 126.5, 123.1, 122.4, 121.2, 119.2, 115.5 (d, J = 21.6 MHz), 33.4, 17.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.3.



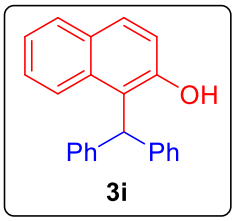
(E)-1-(4-(4-chlorophenyl)but-3-en-2-yl)naphthalen-2-ol (3f).[1] 54.6 mg, 89%; as an oil; **IR** ν (thin film, cm^{-1}) 3452, 2964, 1666, 1258, 1149, 965, 810, 746; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.8 MHz, 1H), 7.80 (d, J = 7.6 MHz, 1H), 7.68 (d, J = 9.2 MHz, 1H), 7.50-7.48 (t, J = 7.2 MHz, 1H), 7.36-7.24 (m, 5H), 7.06 (d, J = 8.8 MHz, 1H), 6.73 (dd, J = 16.4, 4.0 MHz, 1H), 6.65 (dd, J = 16.4, 2.0 MHz, 1H), 5.67 (s, 1H), 4.64-4.61 (m, 1H), 1.63 (d, J = 7.2 MHz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 152.0, 135.2, 134.4, 133.2, 132.4, 129.6, 129.1, 128.9, 128.8, 128.7, 127.5, 126.5, 123.1, 122.4, 121.1, 119.1, 33.5, 17.3.



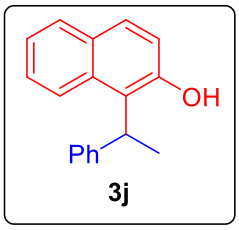
1-cinnamylnaphthalen-2-ol (3g).[1] 28.6 mg, 55%; as an oil; **IR** ν (thin film, cm^{-1}) 3539, 3056, 2918, 1625, 1511, 1263, 956, 810, 741; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 MHz, 1H), 7.78 (d, *J* = 8.4 MHz, 1H), 7.67 (d, *J* = 8.8 MHz, 1H), 7.48 (t, *J* = 6.8 MHz, 1H), 7.35-7.31 (m, 1H), 7.29-7.21 (m, 4H), 7.17-7.15 (m, 1H), 7.09 (d, *J* = 8.8 MHz, 1H), 6.43-6.42 (m, 2H), 5.05 (s, 1H), 3.97 (d, *J* = 3.2 MHz, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 151.1, 137.1, 133.2, 130.9, 129.4, 128.6, 128.5, 128.4, 127.5, 127.1, 126.6, 126.1, 123.2, 123.0, 117.9, 117.1, 28.4.



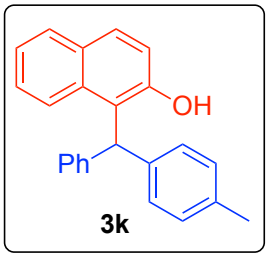
1-(cyclohex-2-en-1-yl)naphthalen-2-ol (3h).[1] 37.7 mg, 84%; as an oil; **IR** ν (thin film, cm^{-1}) 3441, 3056, 2930, 1620, 1258, 1154, 982, 815, 741; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 MHz, 1H), 7.76 (d, *J* = 8.0 MHz, 1H), 7.64 (d, *J* = 8.8 MHz, 1H), 7.45 (t, *J* = 7.2 MHz, 1H), 7.32-7.28 (m, 1H), 7.08 (d, *J* = 8.8 MHz, 1H), 6.58 (s, 1H), 6.24 (s, 1H), 6.07 (d, *J* = 9.2 MHz, 1H), 4.39-4.26 (m, 1H), 2.27-2.19 (m, 2H), 2.12-2.08 (m, 1H), 1.96-1.90 (m, 1H), 1.81-1.72 (m, 2H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 153.1, 133.3, 132.6, 130.3, 129.3, 128.8, 128.5, 126.4, 122.9, 121.9, 120.6, 119.4, 34.4, 28.7, 25.1, 22.0.



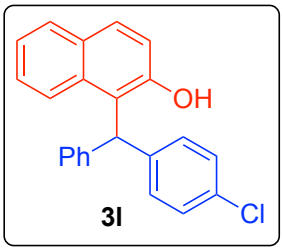
1-benzhydrylnaphthalen-2-ol (3i).[2] 50.2 mg, 81%, as a solid; mp 109-111 °C; **IR** ν (thin film, cm^{-1}) 3493, 3062, 2918, 1620, 1465, 1252, 1177, 1057, 907, 856, 741; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.8 MHz, 1H), 7.77 (d, *J* = 7.6 MHz, 1H), 7.73 (d, *J* = 8.8 MHz, 1H), 7.40 (t, *J* = 6.8 MHz, 1H), 7.34-7.27 (m, 11H), 7.06 (d, *J* = 8.8 MHz, 1H), 6.40 (s, 1H), 5.13 (s, 1H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 152.8, 141.5, 133.4, 129.7, 129.6, 129.1, 129.0, 128.7, 127.2, 126.8, 123.2, 122.7, 120.1, 119.8, 48.6.



1-(1-phenylethyl)naphthalen-2-ol (3j).[3] 26.4 mg, 53%; as an oil; **IR** ν (thin film, cm^{-1}) 3498, 3027, 2970, 1620, 1493, 1258, 930, 810, 746; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 MHz, 1H), 7.79 (d, *J* = 8.4 MHz, 1H), 7.66 (d, *J* = 8.8 MHz, 1H), 7.46 (t, *J* = 7.2 MHz, 1H), 7.39-7.31 (m, 5H), 7.26-7.21 (m, 1H), 6.99 (d, *J* = 8.8 MHz, 1H), 5.18 (q, *J* = 7.6 MHz, 1H), 4.83 (s, 1H), 1.78 (d, *J* = 6.8 MHz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 151.5, 143.6, 132.8, 129.7, 129.0, 128.8, 128.7, 127.1, 126.8, 126.6, 123.8, 123.1, 122.6, 119.4, 34.8, 17.1.

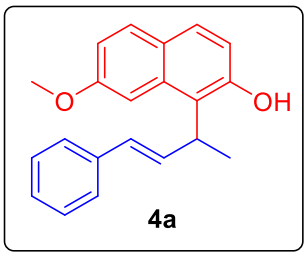


1-(phenyl(p-tolyl)methyl)naphthalen-2-ol (3k). 59.7 mg, 92%; as a semisolid compound; **IR** ν (thin film, cm^{-1}) 3487, 3056, 3027, 1620, 1493, 1396, 1252, 1206, 1137, 959, 741; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 9.2 Hz, 1H), 7.39 (t, *J* = 7.2 MHz, 1H), 7.33-7.21 (m, 6H), 7.23-7.21 (m, 4H), 7.06 (d, *J* = 8.8 Hz, 1H), 6.35 (s, 1H), 5.21 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 152.8, 141.6, 138.5, 137.0, 133.4, 129.9, 129.7, 129.6, 129.1, 129.0, 128.8, 128.7, 127.1, 126.8, 123.2, 122.7, 120.2, 119.9, 48.3, 21.0; HRMS(ESI): m/z calculated for $C_{24}H_{20}O$ ([M+Na]+): 347.1412; found 347.1411.



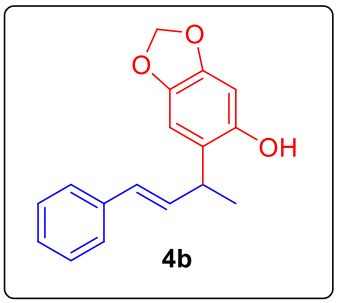
3l

1-((4-chlorophenyl)(phenyl)methyl)naphthalen-2-ol (3l).[4] 52.9 mg, 77%; as a semisolid compound; **IR** ν (thin film, cm^{-1}) 3498, 3062, 3027, 1620, 1488, 1396, 1252, 1206, 1091, 907, 735; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 7.2 MHz, 1H), 7.33-7.17 (m, 10H), 7.04 (d, J = 8.8 Hz, 1H), 6.36 (s, 1H), 5.05 (s, 1H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 152.6, 141.4, 140.0, 133.3, 132.9, 130.5, 129.9, 129.7, 129.2, 129.1, 128.9, 128.8, 127.4, 126.9, 123.3, 122.7, 119.8, 119.7, 47.9.



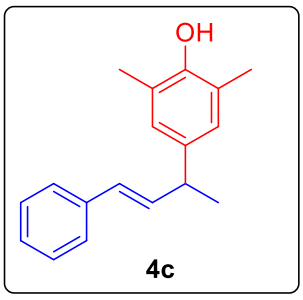
4a

(E)-7-methoxy-1-(4-phenylbut-3-en-2-yl)naphthalen-2-ol (4a).[1] 51.3 mg, 84%; as an oil; **IR** ν (thin film, cm^{-1}) 3447, 3022, 2964, 1625, 1516, 1459, 1258, 1034, 970, 833, 746; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.8 MHz, 1H), 7.57 (d, J = 8.4 MHz, 1H), 7.39-7.36 (m, 3H), 7.29 (t, J = 7.6 MHz, 2H), 7.23-7.20 (m, 1H), 7.01 (dd, J = 8.8, 2.4 MHz, 1H), 6.91 (d, J = 8.4 MHz, 1H), 6.74-6.73 (m, 2H), 5.80 (s, 1H), 4.55 (q, J = 7.2 MHz, 1H), 3.88 (s, 3H), 1.63 (d, J = 7.2 MHz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 158.3, 152.7, 136.7, 133.9, 133.8, 130.4, 130.2, 128.6, 128.4, 127.6, 126.3, 125.0, 120.4, 116.6, 114.9, 102.2, 55.2, 33.6, 17.0.



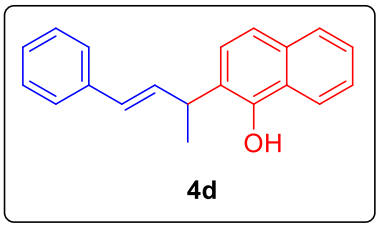
4b

(E)-4-(4-phenylbut-3-en-2-yl)benzo[d][1,3]dioxol-5-ol (4b).[1] 51.6 mg, 96%; as an oil; **IR** ν (thin film, cm^{-1}) 3481, 3022, 2964,1631, 1488, 1292, 1172, 1039, 936, 856, 752; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 1.6 MHz, 1H), 7.35 (s, 1H), 7.33-7.26 (m, 2H), 7.25-7.18 (m, 1H), 6.68 (s, 1H), 6.48 (dd, J = 16.0, 1.2 MHz, 1H), 6.41 (s, 1H), 6.35 (dd, J = 16.0, 6.4 MHz, 1H), 5.87 (s, 2H), 4.81 (s, 1H), 3.80-3.77 (m, 1H), 1.43 (d, J = 7.2 MHz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 148.0, 146.3, 141.7, 136.9, 133.9, 129.3, 128.5, 127.3, 126.2, 122.6, 107.1, 101.0, 98.8, 36.4, 19.6.



4c

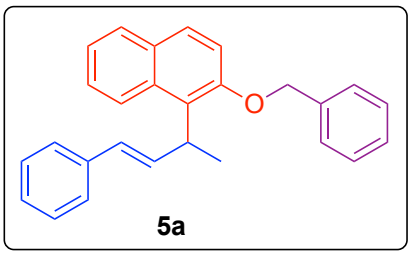
(E)-2,6-dimethyl-4-(4-phenylbut-3-en-2-yl)phenol (4c).[5] 40.9 mg, 81%; as an oil; **IR** ν (thin film, cm^{-1}) 3573, 3022, 2964, 1602, 1488, 1195, 956, 746, 695; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.34 (m, 2H), 7.29-7.24 (m, 2H), 7.20-7.16 (m, 1H), 6.86 (s, 2H), 6.41-6.32 (m, 2H), 4.47 (s, 1H), 3.52-3.49 (m, 1H), 2.23 (s, 6H), 1.41 (d, J = 7.2 MHz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 150.5, 137.6, 137.2, 135.7, 128.4, 127.9, 127.3, 126.9, 126.1, 122.9, 41.7, 21.3, 15.9.



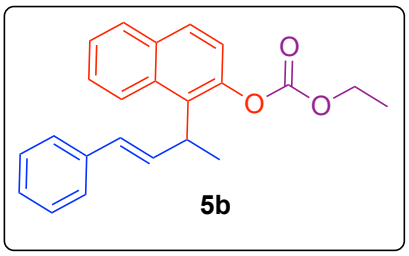
4d

(E)-2-(4-phenylbut-3-en-2-yl)naphthalen-1-ol (4d).[1] 28.6 mg, 60%; as an oil; **IR** ν (thin film, cm^{-1}) 3481, 3056, 2964, 1654, 1575, 1263, 970, 810, 752; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15-8.13 (m, 1H), 7.79-7.77 (m, 1H), 7.48-7.42 (m, 3H), 7.37-7.20 (m, 6H), 6.61 (dd, J = 16.0, 1.2 MHz, 1H), 6.51 (dd, J = 16.0, 5.6 MHz, 1H), 5.67 (s, 1H), 3.98-3.95 (m, 1H), 1.59 (d, J = 6.8 MHz, 3H); ^{13}C NMR

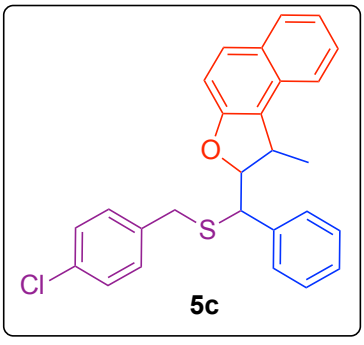
(100.5 MHz, $CDCl_3$) δ 148.8, 136.6, 133.5, 133.4, 130.0, 128.6, 127.6, 127.5, 126.3, 125.9, 125.8, 125.3, 125.0, 123.2, 121.3, 120.5, 37.7, 19.3.



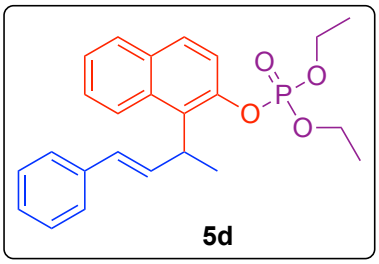
(E)-2-(benzyloxy)-1-(4-phenylbut-3-en-2-yl)naphthalene (5a). 30.6 mg, 84%; as an oil; **IR** ν (thin film, cm^{-1}) 3056, 3027, 2964, 1620, 1597, 1453, 1258, 1022, 804, 746, 695; ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.8 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.41 (t, J = 7.6 MHz, 1H), 7.40-7.21 (m, 11H), 7.16-7.12 (m, 1H), 6.73 (dd, J = 16.0, 5.2 Hz, 1H), 6.42 (dd, J = 16.0, 2.0 Hz, 1H), 5.20 (d, J = 4.0 Hz, 2H), 4.81-4.78 (m, 1H), 1.63 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 153.6, 138.0, 137.3, 135.8, 132.6, 130.0, 128.7, 128.5, 128.4, 128.3, 128.0, 127.9, 127.6, 127.5, 126.6, 126.0, 125.9, 124.3, 123.3, 115.6, 71.8, 33.8, 19.1; HRMS(ESI): m/z calculated for $C_{27}H_{24}O$ ([M+Na]+): 387.1725; found 387.1759.



(E)-ethyl(1-(4-phenylbut-3-en-2-yl)naphthalen-2-yl) carbonate (5b). 33.0 mg, 92%; as an oil; **IR** ν (thin film, cm^{-1}) 3055, 3024, 2978, 2931, 2873, 2137, 1759, 1242, 1215; ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 9.2 Hz, 1H), 7.52-7.44 (m, 2H), 7.37-7.33 (m, 2H), 7.28-7.23 (m, 3H), 7.18-7.14 (m, 1H), 6.63 (dd, J = 16.0, 4.4 Hz, 1H), 6.51 (dd, J = 16.0, 1.6 Hz, 1H), 4.58-4.54 (m, 1H), 4.16-4.10 (m, 1H), 3.97-3.92 (m, 1H), 1.67 (d, J = 7.6 Hz, 3H), 1.21 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 153.8, 146.6, 137.5, 133.6, 132.5, 132.1, 131.6, 128.9, 128.5, 128.4, 128.3, 126.9, 126.3, 126.0, 125.3, 124.5, 121.9, 64.8, 34.0, 18.5, 14.0; HRMS(ESI): m/z calculated for $C_{23}H_{22}O_3$ ([M+Na]+): 369.1461; found 369.1411.



2-(((4-chlorobenzyl)thio)(phenyl)methyl)-1-methyl-1,2-dihydronaphtho[2,1-b]furan (5c). 28.2 mg, 65%; as a white solid; mp 142-144°C; **IR** ν (thin film, cm^{-1}) 3062, 2968, 1623, 1600, 1489, 1400, 1229, 1088, 1014, 814, 741; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 9.2 Hz, 1H), 7.58-7.56 (m, 2H), 7.50-7.42 (m, 4H), 7.33 (t, J = 8.0 MHz, 1H), 7.15 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.8 Hz, 1H), 6.95 (d, J = 8.4 Hz, 2H), 5.27 (d, J = 11.2 Hz, 1H), 3.68 (q, J = 4.4 Hz, 1H), 3.11 (dd, J = 10.8, 4.8 Hz, 1H), 2.85 (d, J = 13.2 Hz, 1H), 2.67 (d, J = 13.2 Hz, 1H), 1.50 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 150.6, 139.7, 136.0, 132.8, 131.5, 130.1, 129.2, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 126.6, 123.2, 121.7, 118.7, 118.6, 77.8, 48.3, 35.4, 32.2, 17.5; HRMS(ESI): m/z calculated for $C_{27}H_{23}ClOS$ ([M+H]+): 453.1056; found 453.1056.

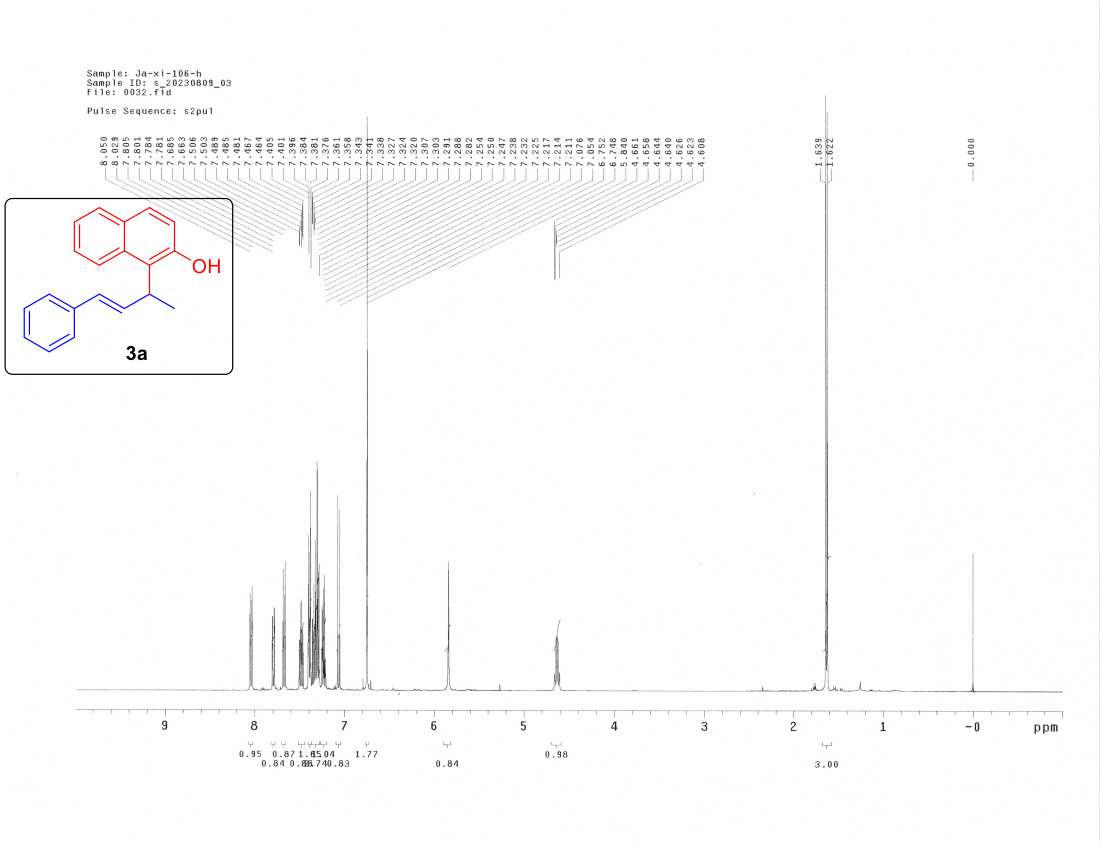


5d

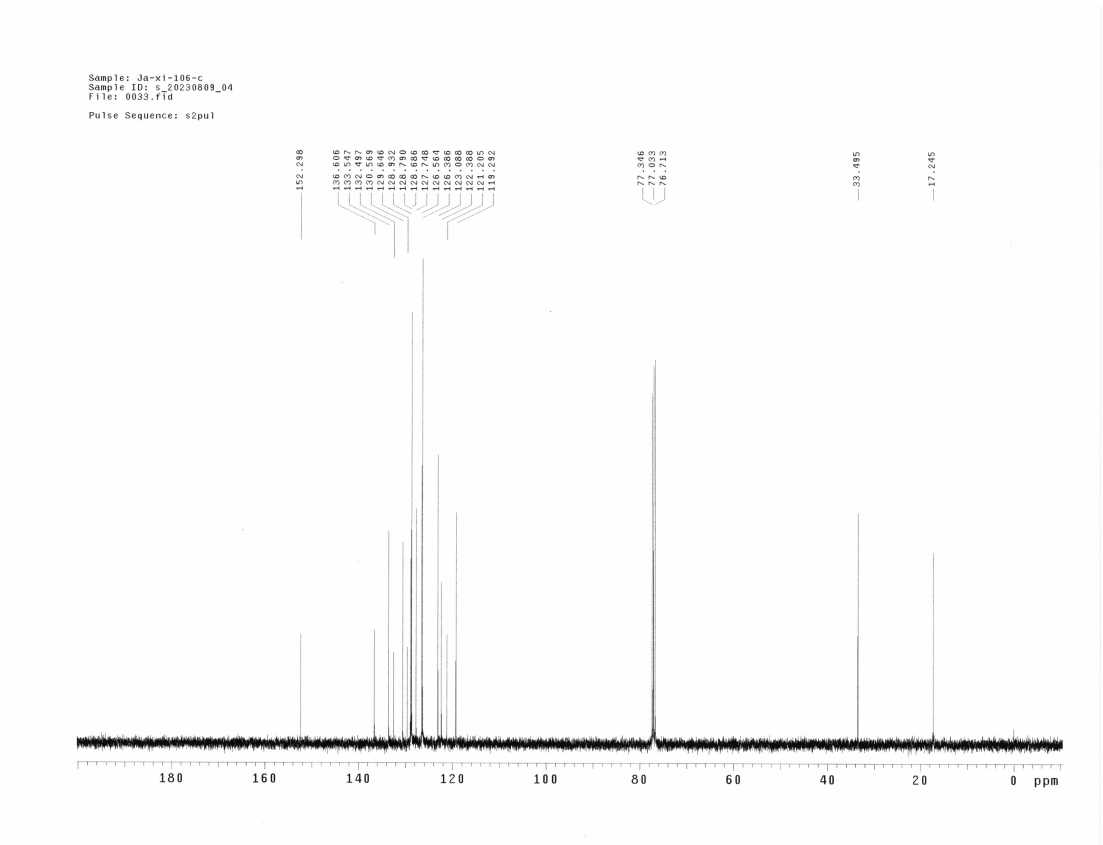
(E)-diethyl (1-(4-phenylbut-3-en-2-yl)naphthalen-2-yl) phosphate (5d). 29.1 mg, 71%; as an oil; **IR** ν (thin film, cm^{-1}) 3024, 2981, 1597, 1495, 1276, 1216, 1031, 976, 815, 749; ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.46-7.39 (m, 2H), 7.34 (d, *J* = 6.8 Hz, 2H), 7.28-7.24 (m, 2H), 7.19-7.17 (t, *J* = 7.6 MHz, 1H), 6.72 (dd, *J* = 16.0, 4.8 Hz, 1H), 6.50 (dd, *J* = 16.4, 2.0 Hz, 1H), 4.75-4.72 (m, 1H), 4.27-4.17 (m, 4H), 1.71 (d, *J* = 6.8 Hz, 3H), 1.35-1.30 (m, 6H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 146.0, 137.6, 134.7, 132.3, 131.9, 130.0 (d, *J* = 7.4 Hz), 128.8, 128.7, 128.5, 128.4, 126.9, 126.1, 126.0, 125.2, 124.8, 119.8 (d, *J* = 1.5 Hz), 64.6 (d, *J* = 6.0 Hz), 33.8, 19.0, 16.2 (d, *J* = 3.7 Hz), 16.1 (d, *J* = 3.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ -5.68; HRMS(ESI): m/z calculated for $C_{24}H_{27}O_4P$ ([M+H]+): 411.1725; found 411.1725.

4. ^1H, ^{13}C, and ^{19}F NMR Spectra

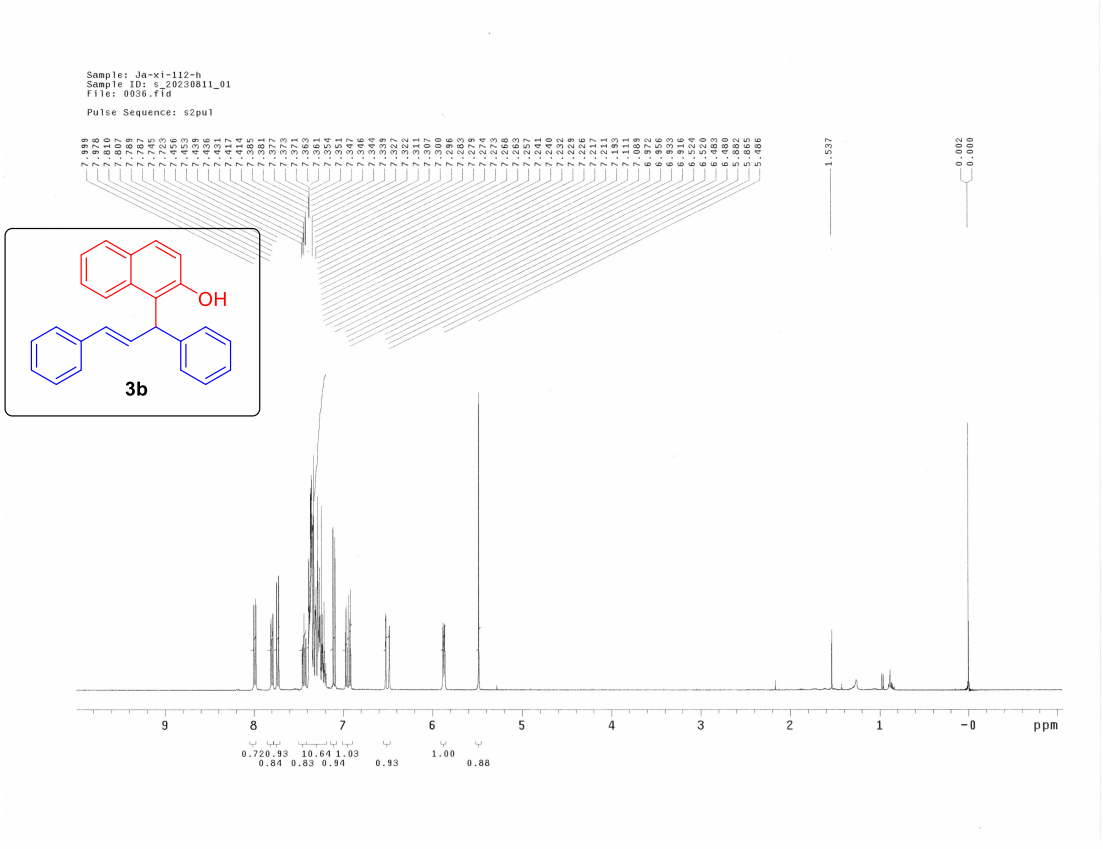
^{1}H NMR (400 MHz) in $CDCl_3$



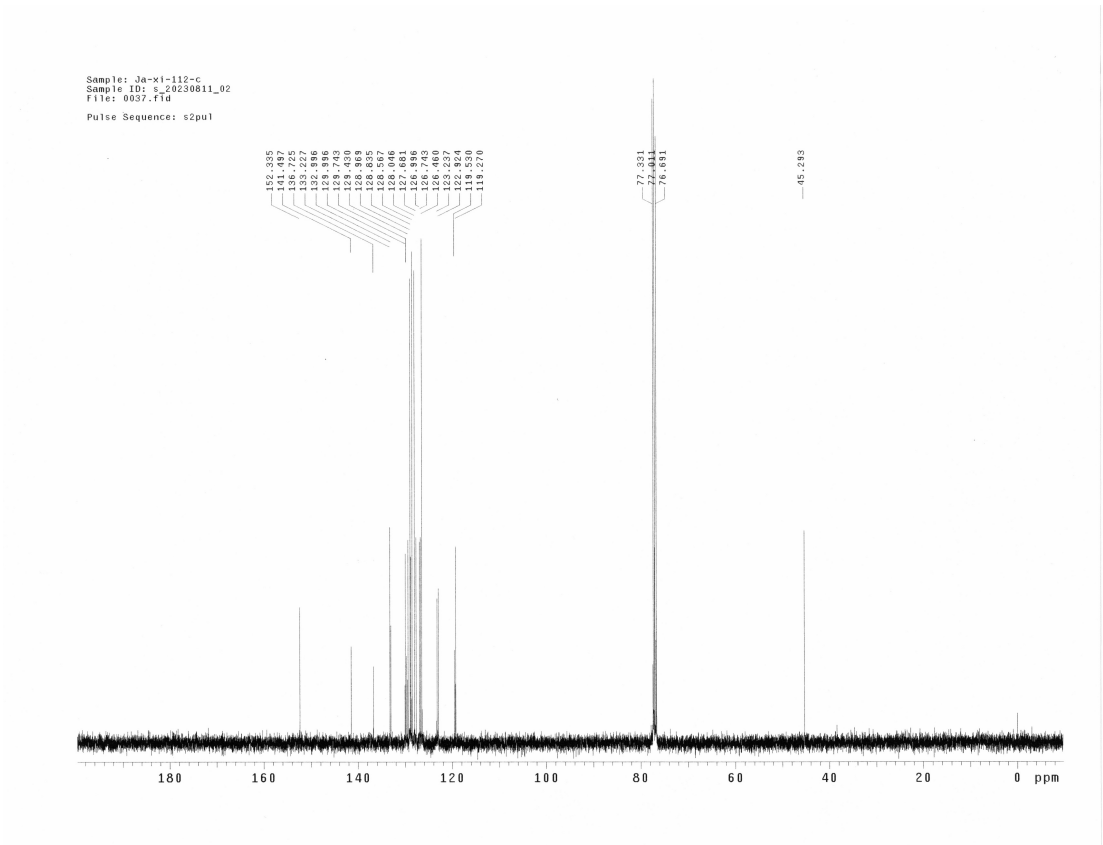
^{13}C NMR (100.5 MHz) in $CDCl_3$



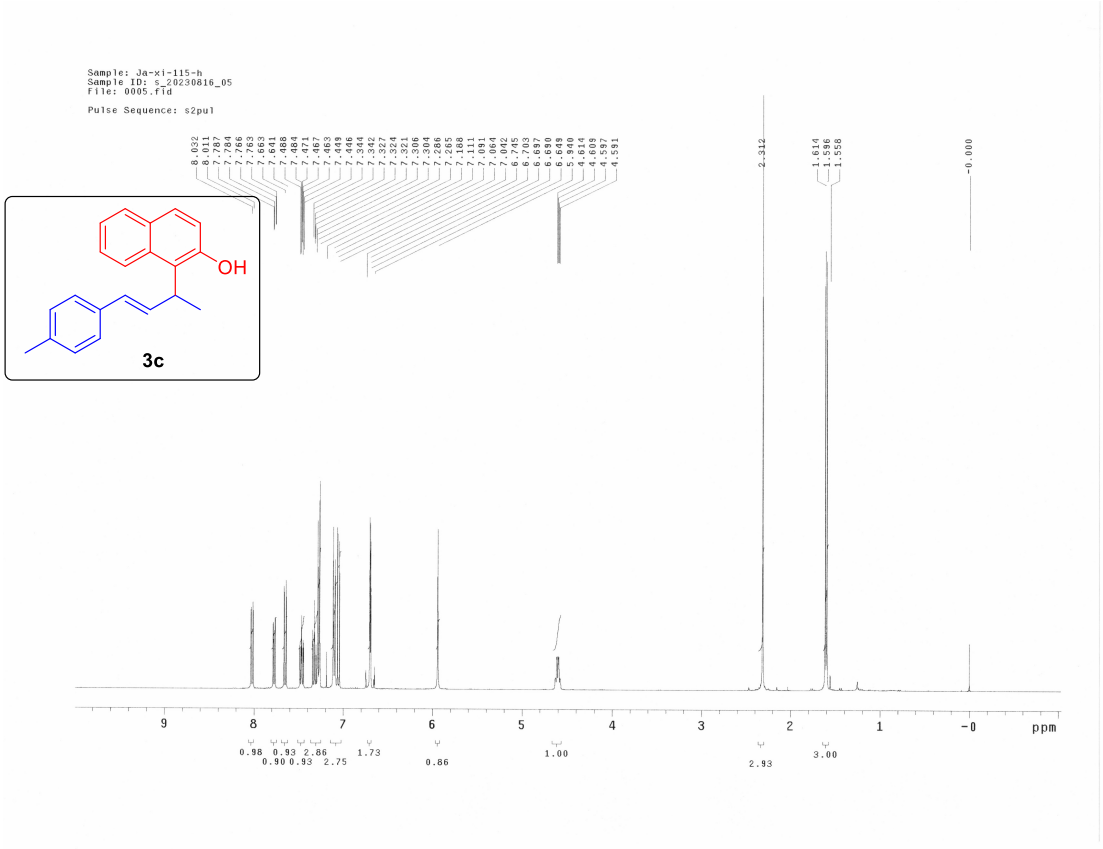
^{1}H NMR (400 MHz) in $CDCl_3$



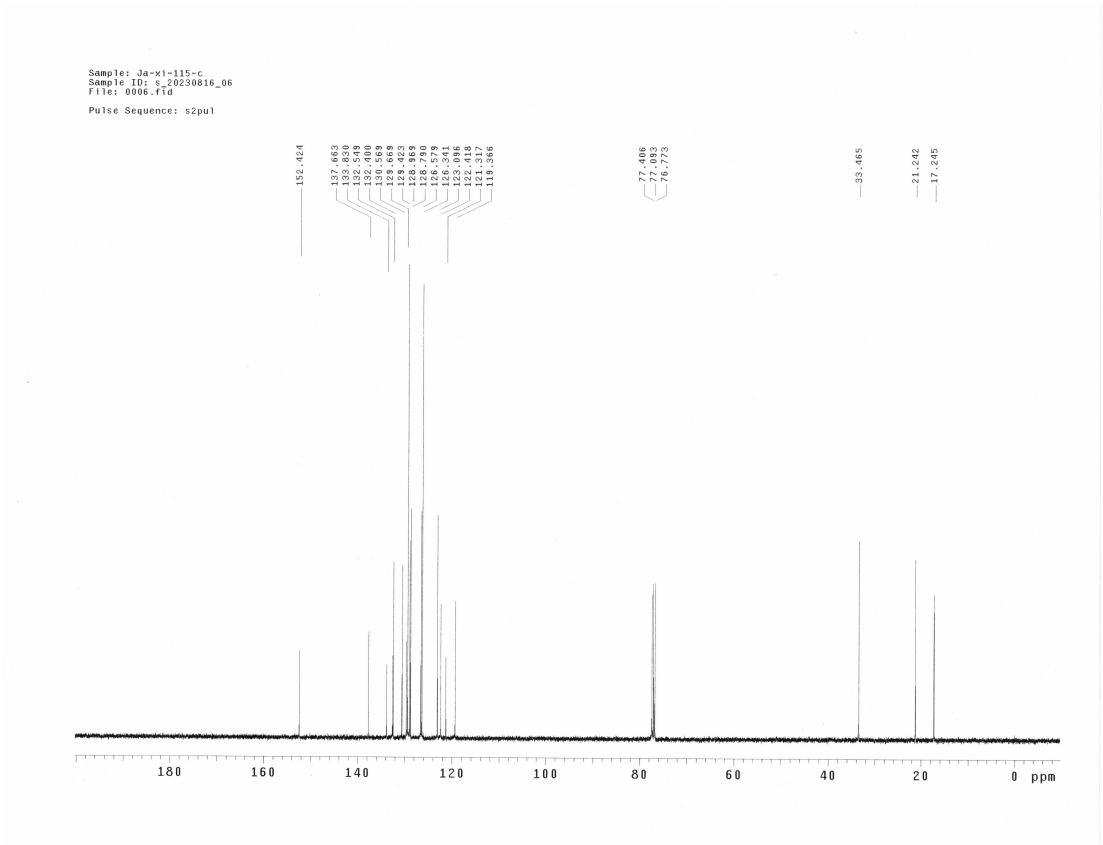
^{13}C NMR (100.5 MHz) in $CDCl_3$



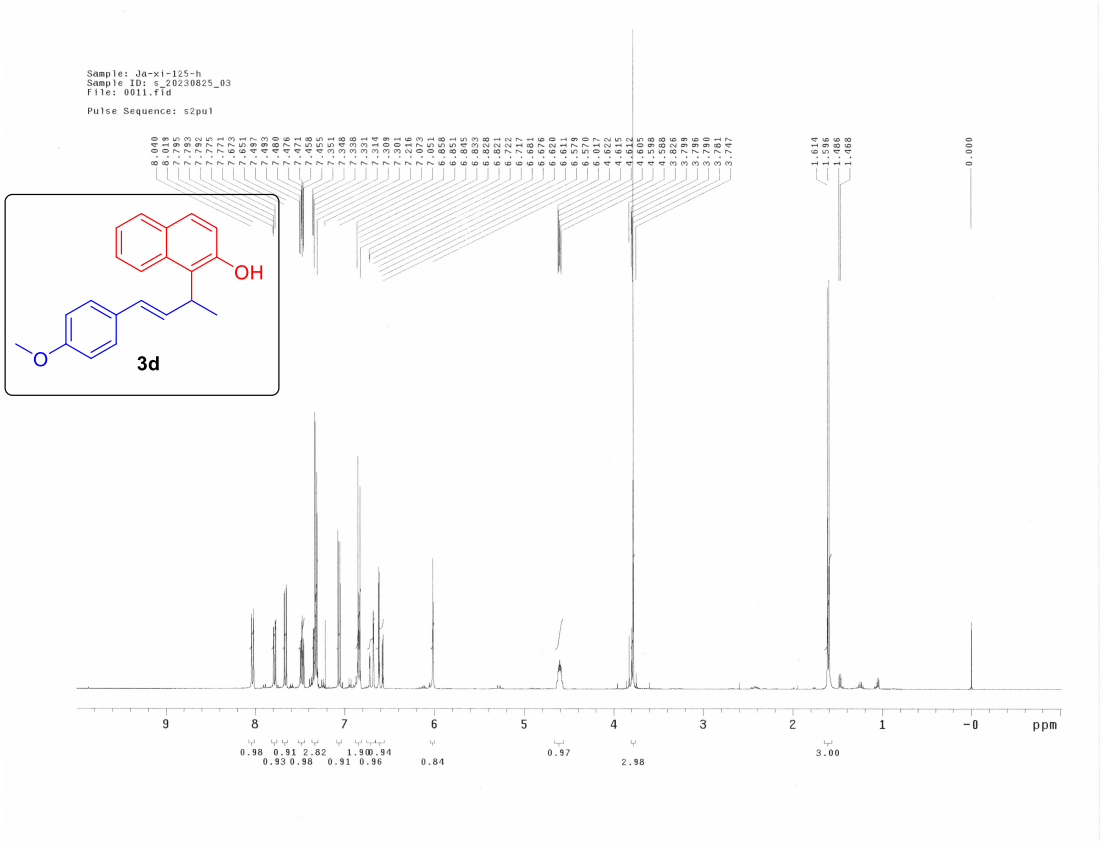
^{1}H NMR (400 MHz) in $CDCl_3$



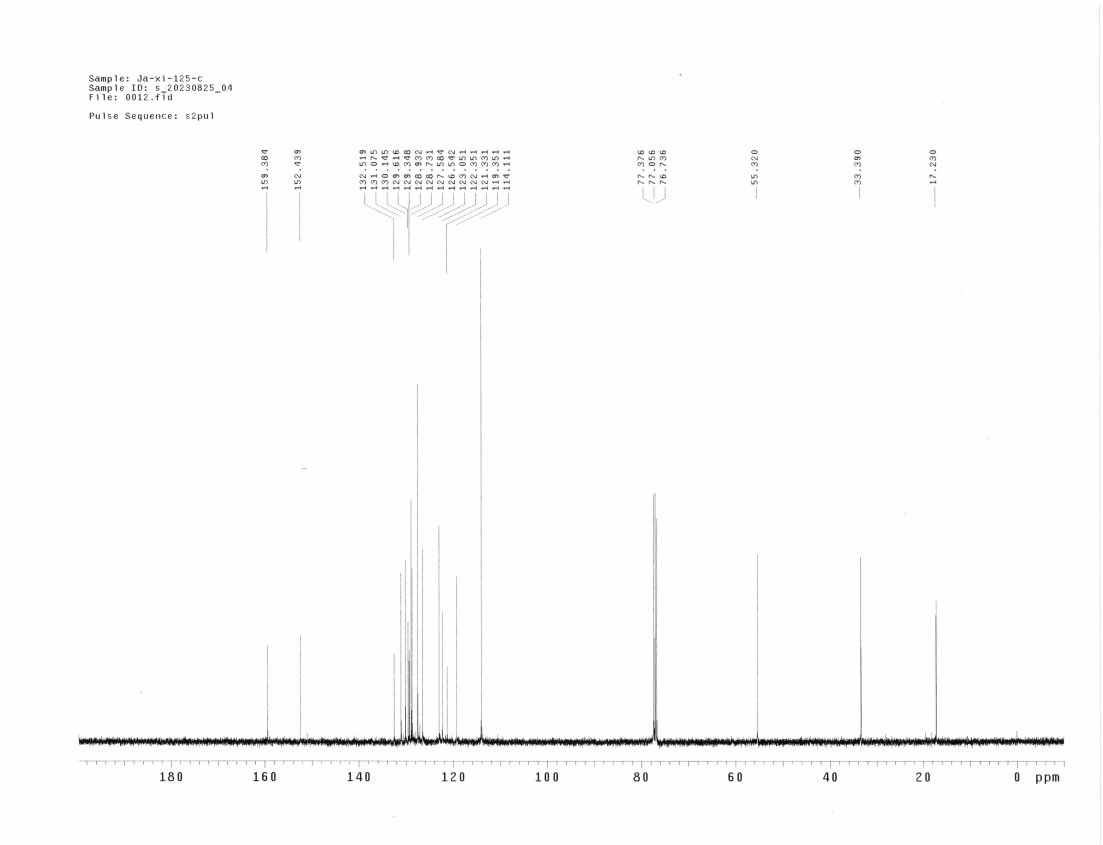
^{13}C NMR (100.5 MHz) in $CDCl_3$



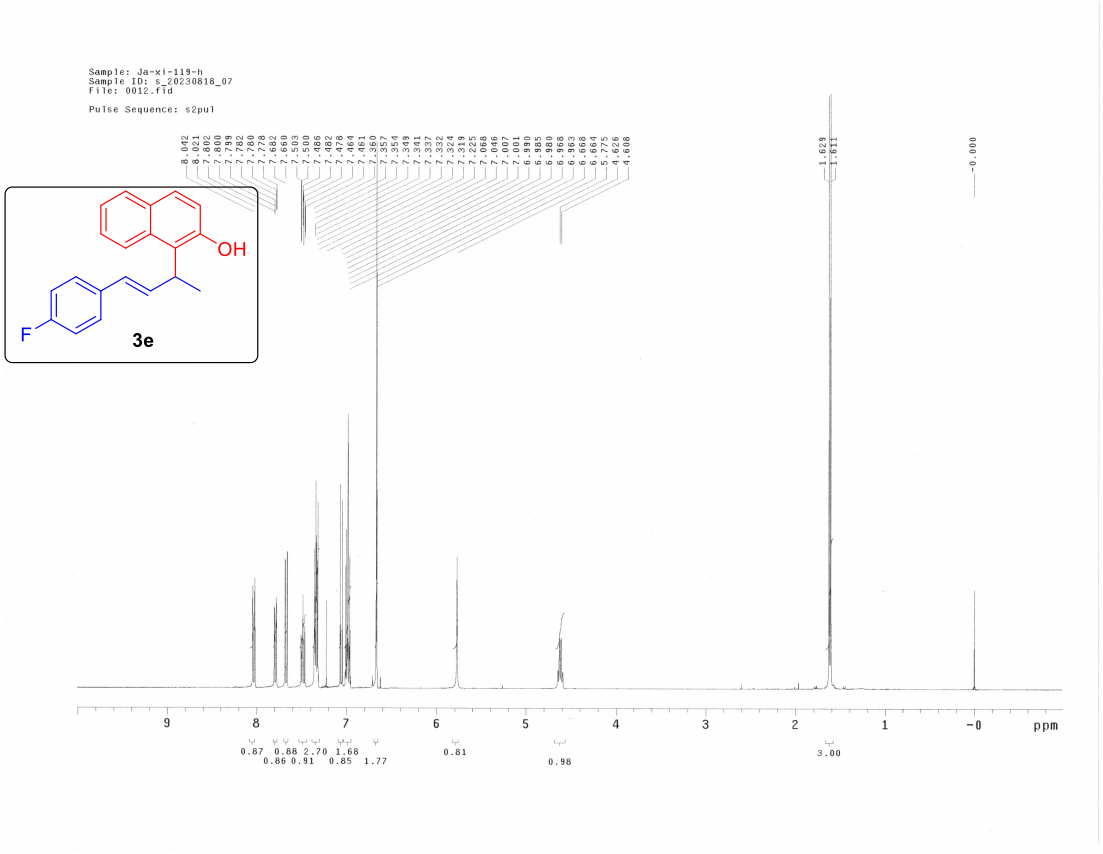
^{1}H NMR (400 MHz) in $CDCl_3$



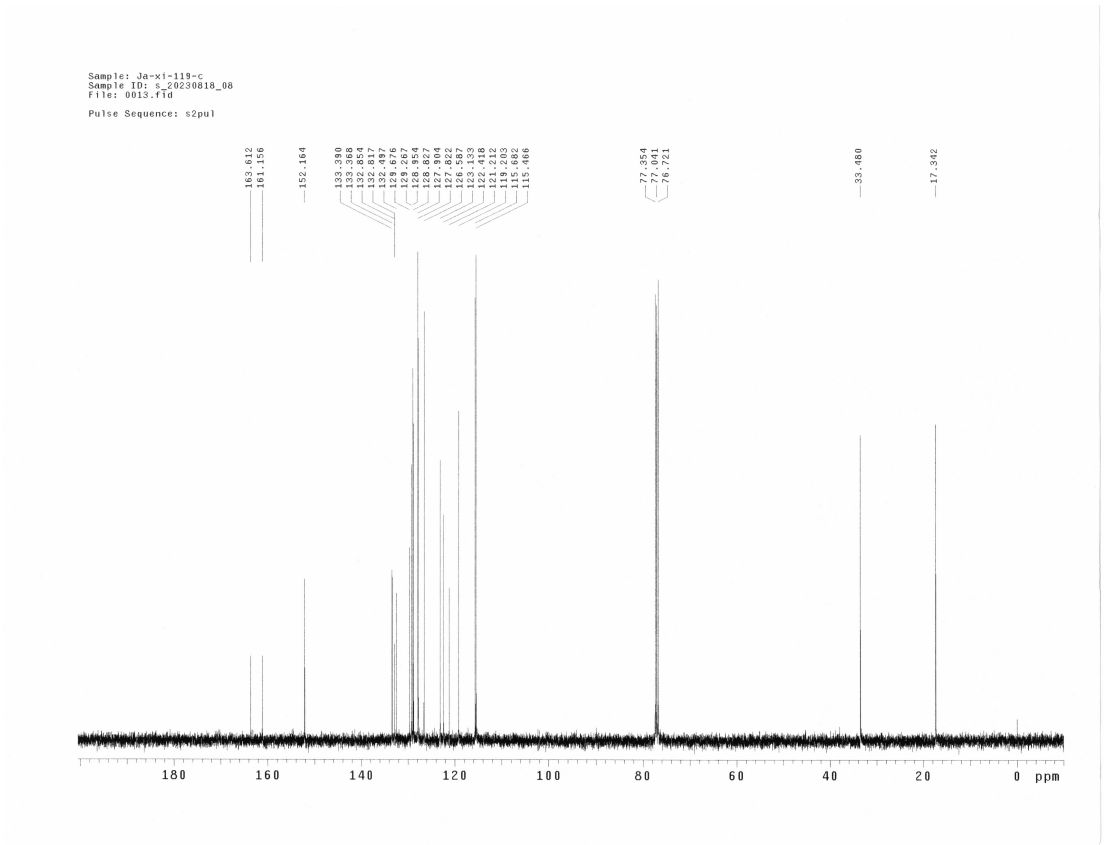
^{13}C NMR (100.5 MHz) in $CDCl_3$



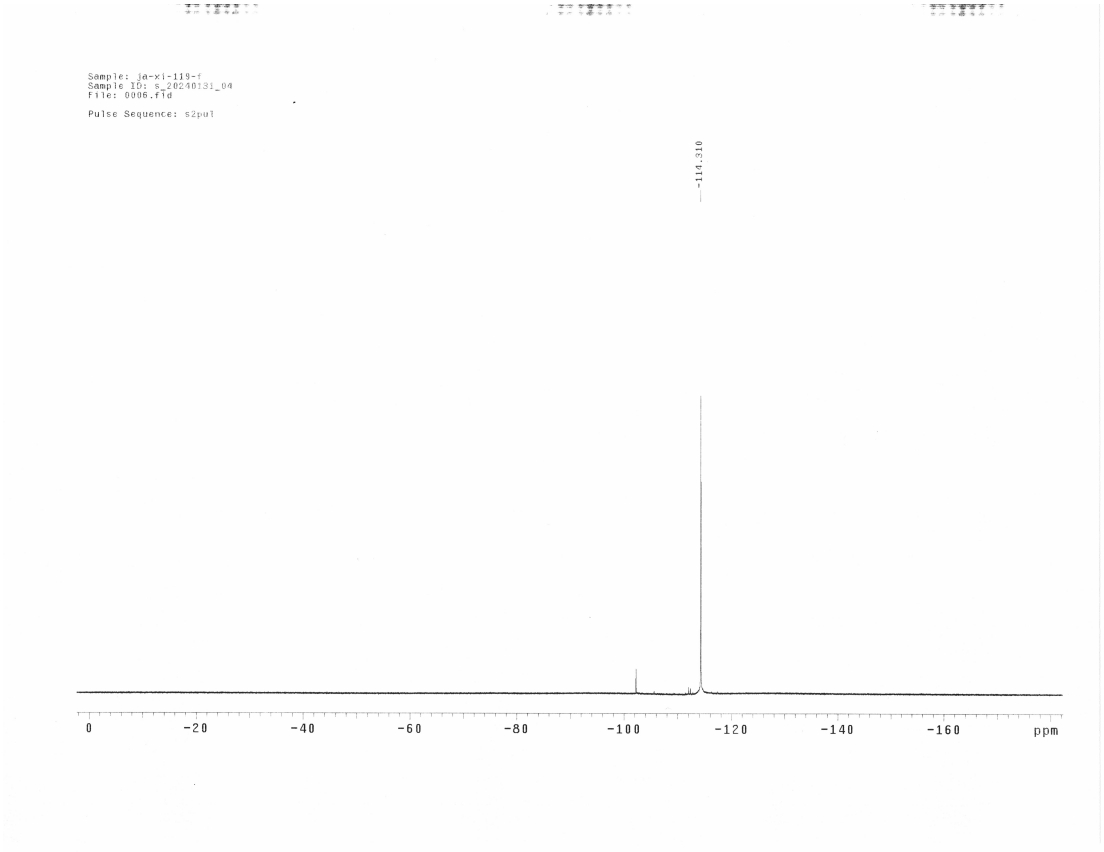
^{1}H NMR (400 MHz) in $CDCl_3$



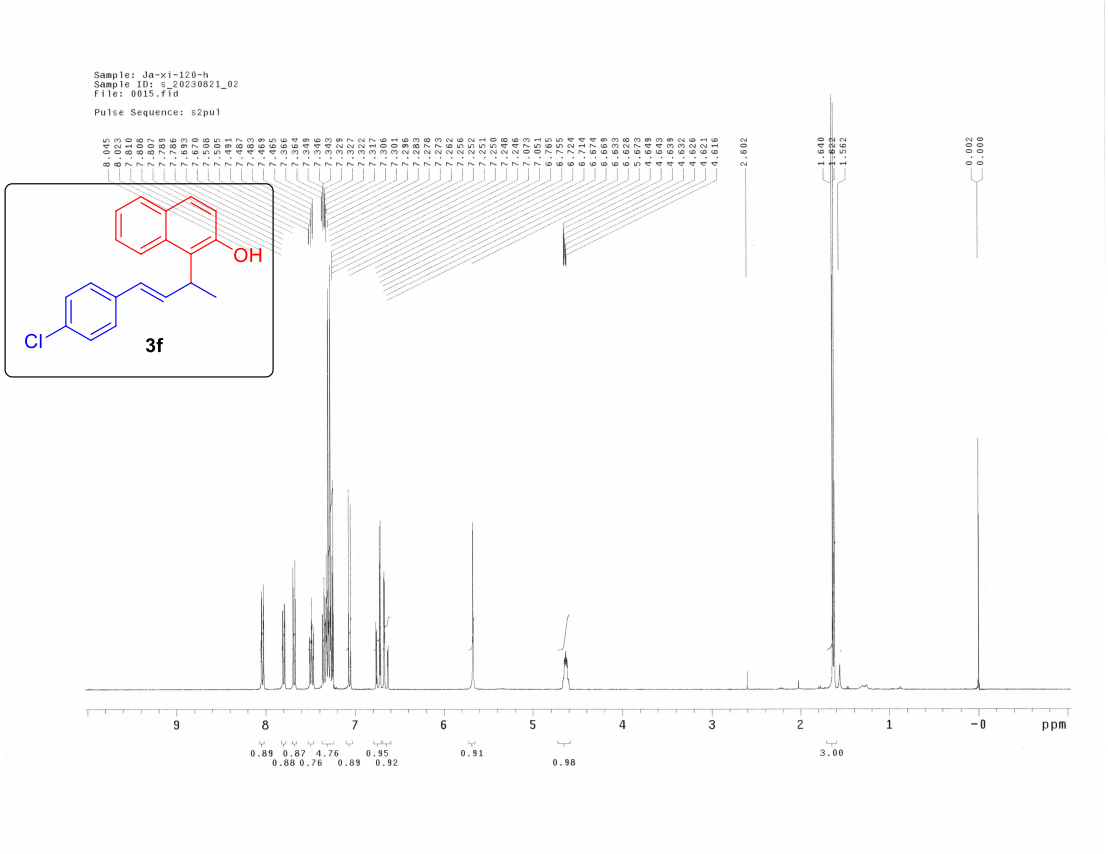
^{13}C NMR (100.5 MHz) in $CDCl_3$



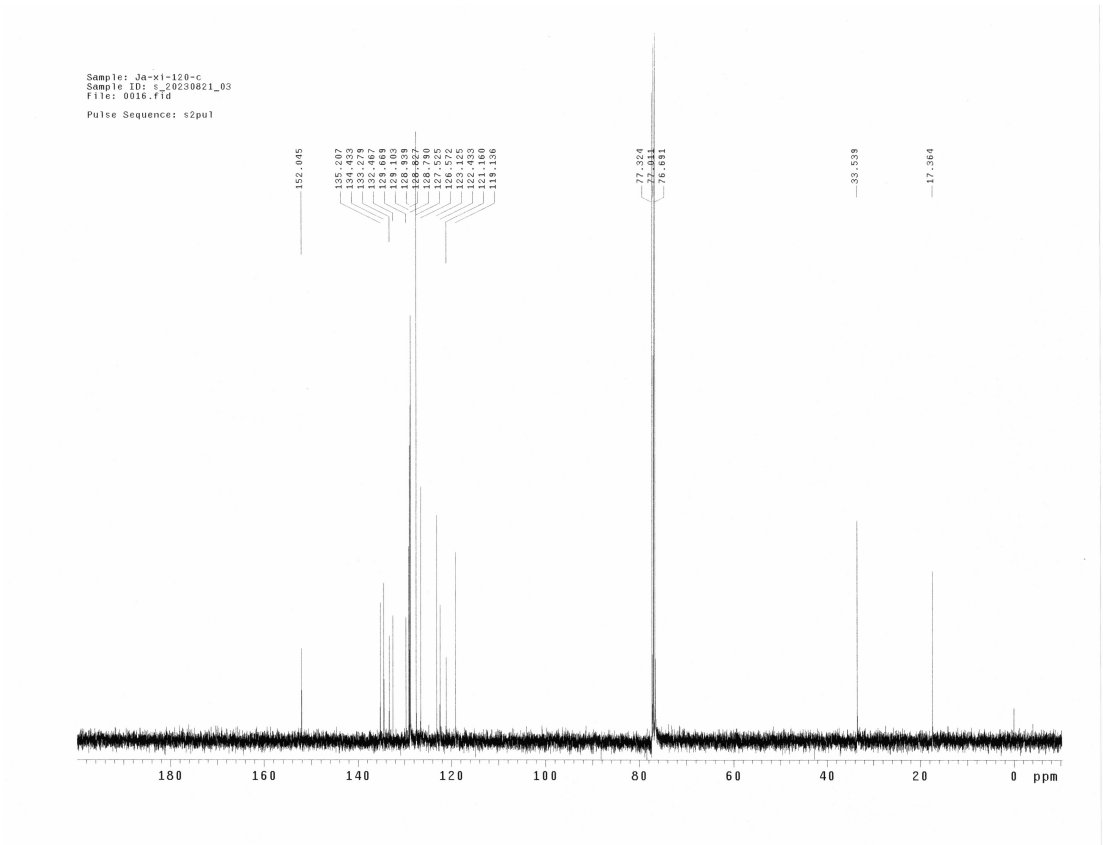
^{19}F NMR (376 MHz) in $CDCl_3$



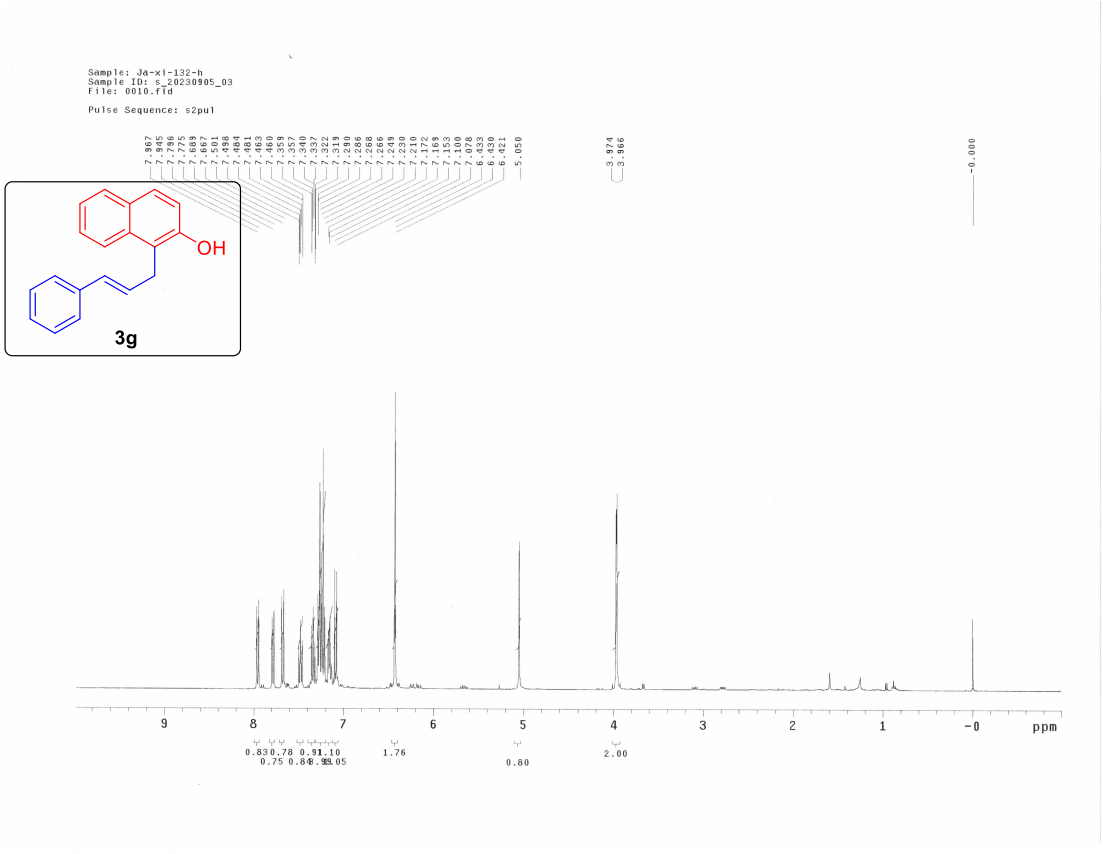
^{1}H NMR (400 MHz) in $CDCl_3$



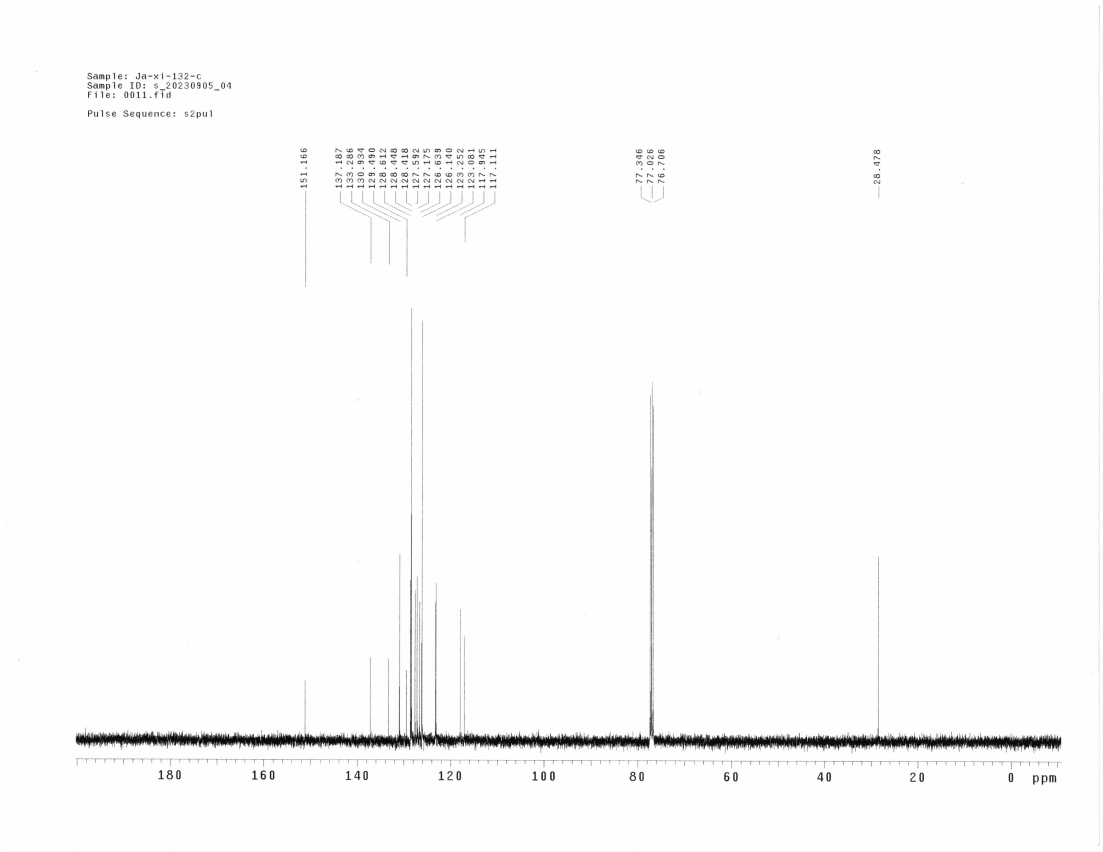
^{13}C NMR (100.5 MHz) in $CDCl_3$



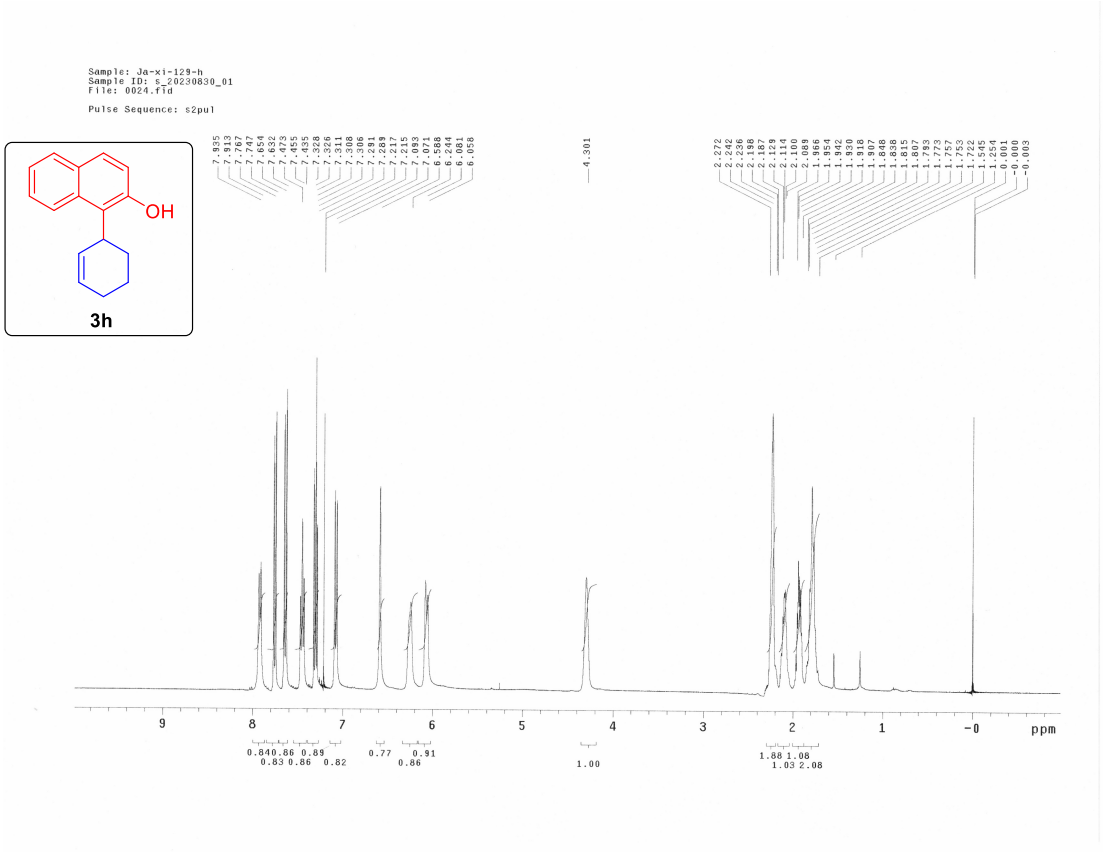
^{1}H NMR (400 MHz) in $CDCl_3$



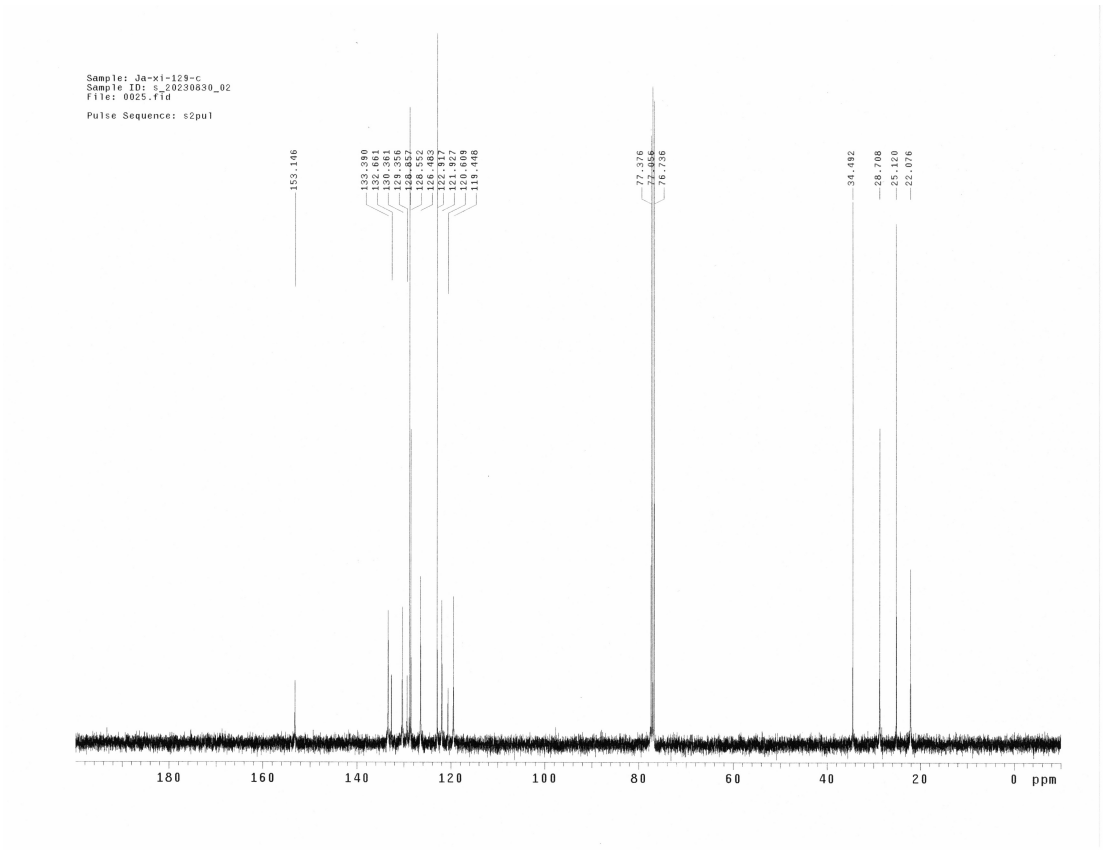
^{13}C NMR (100.5 MHz) in $CDCl_3$



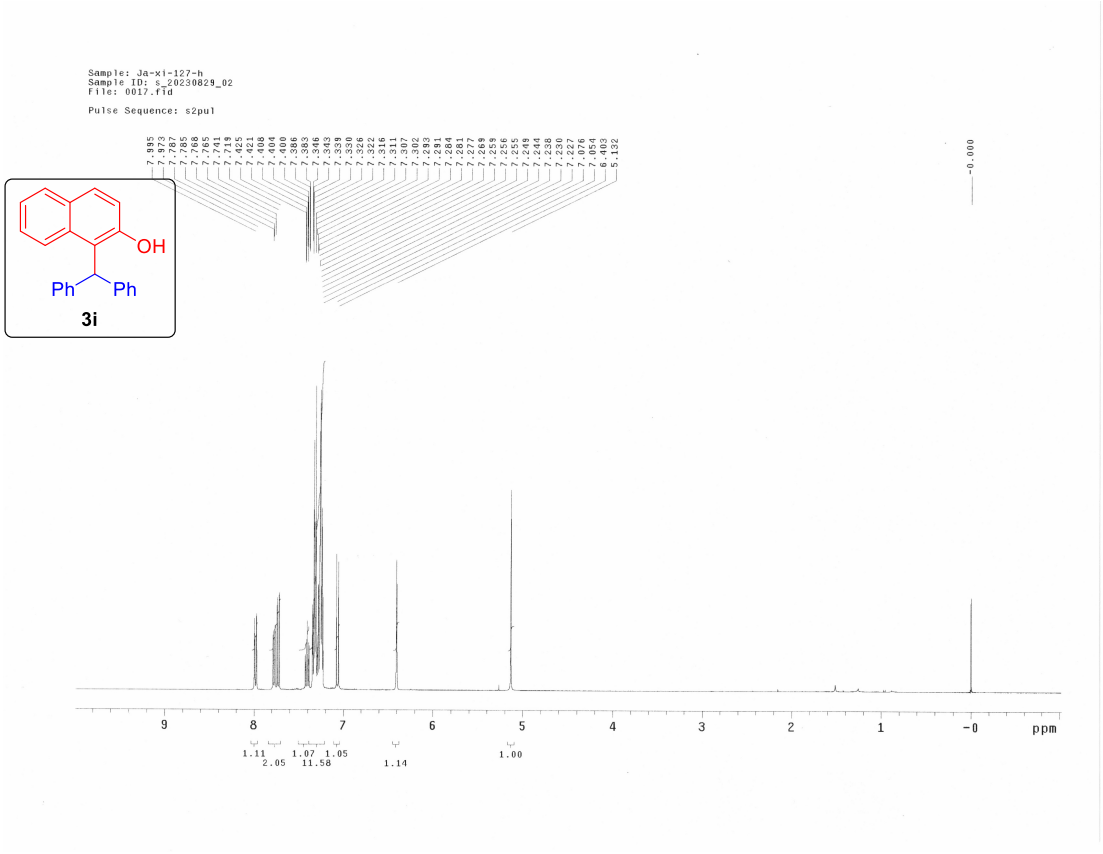
^{1}H NMR (400 MHz) in $CDCl_3$



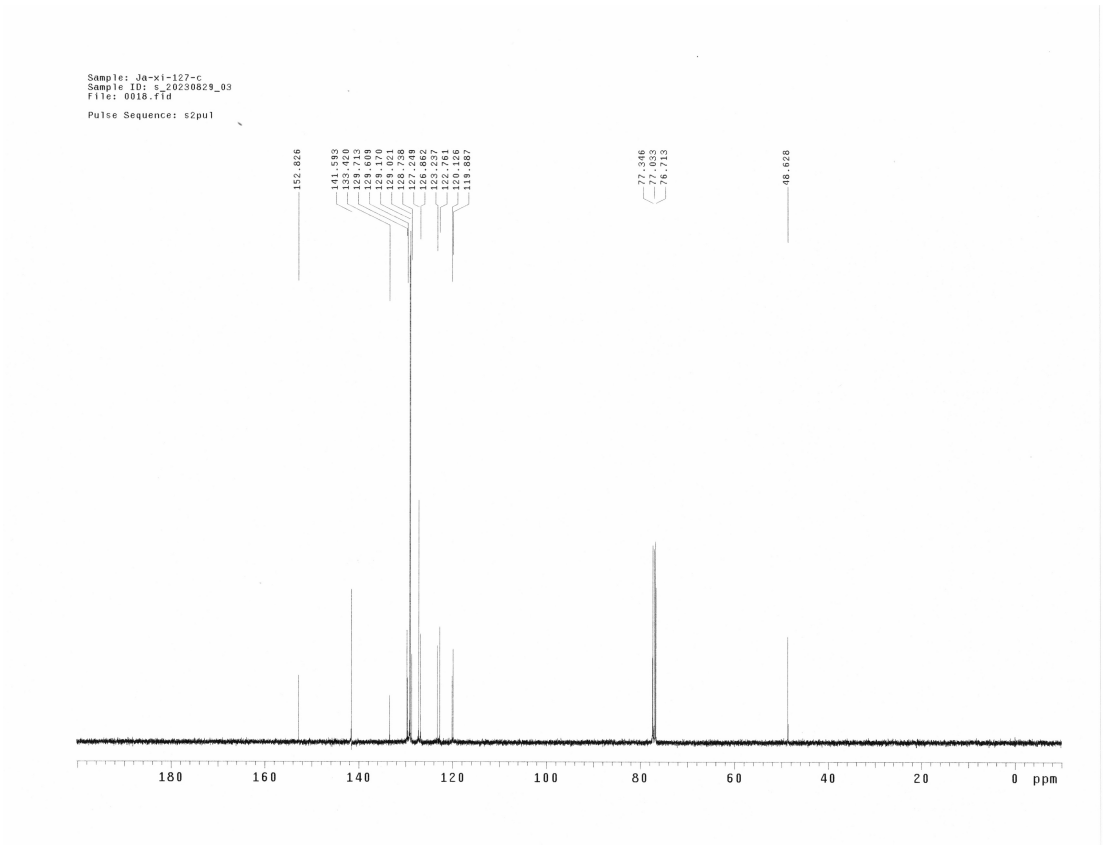
^{13}C NMR (100.5 MHz) in $CDCl_3$



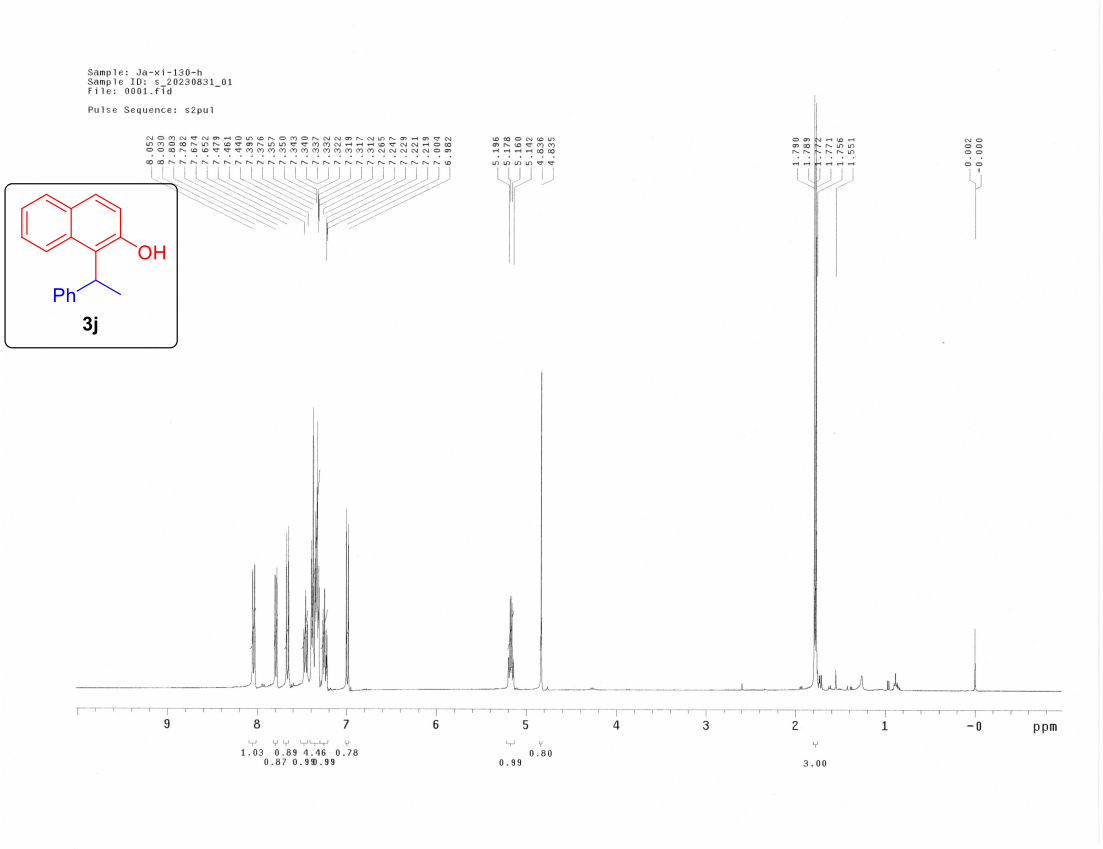
^{1}H NMR (400 MHz) in $CDCl_3$



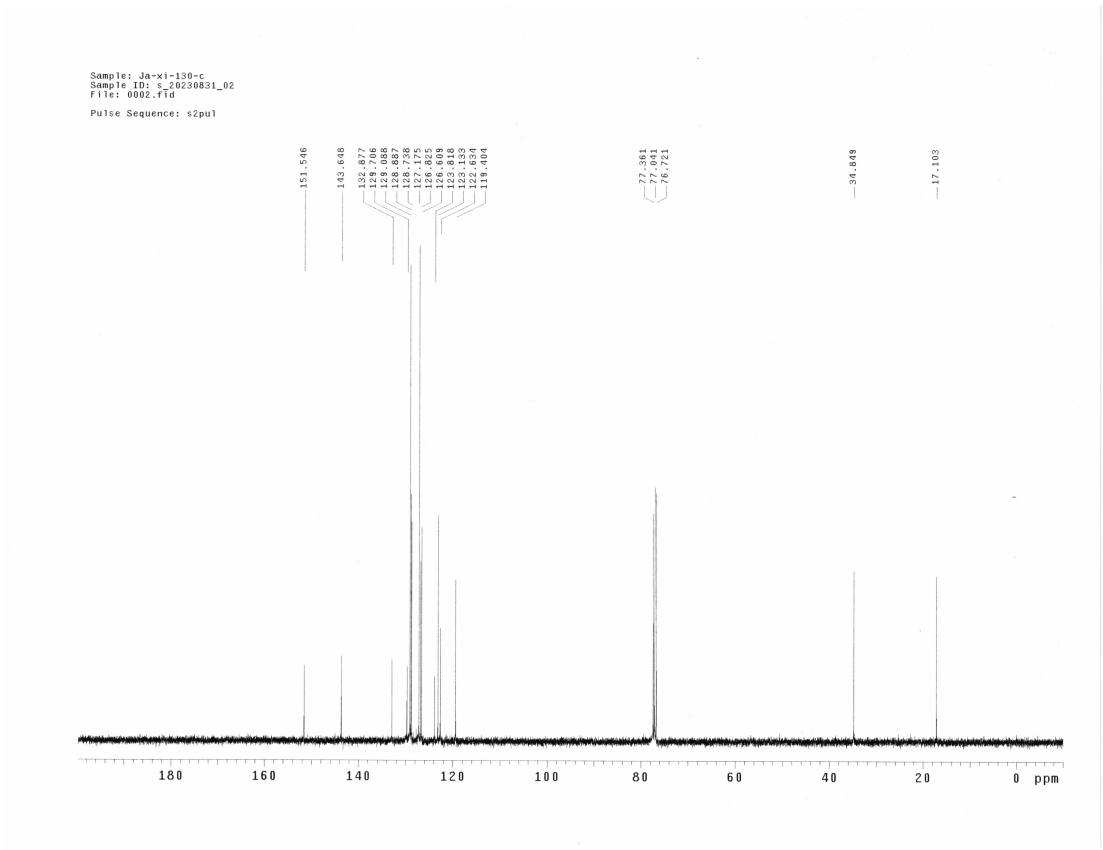
^{13}C NMR (100.5 MHz) in $CDCl_3$



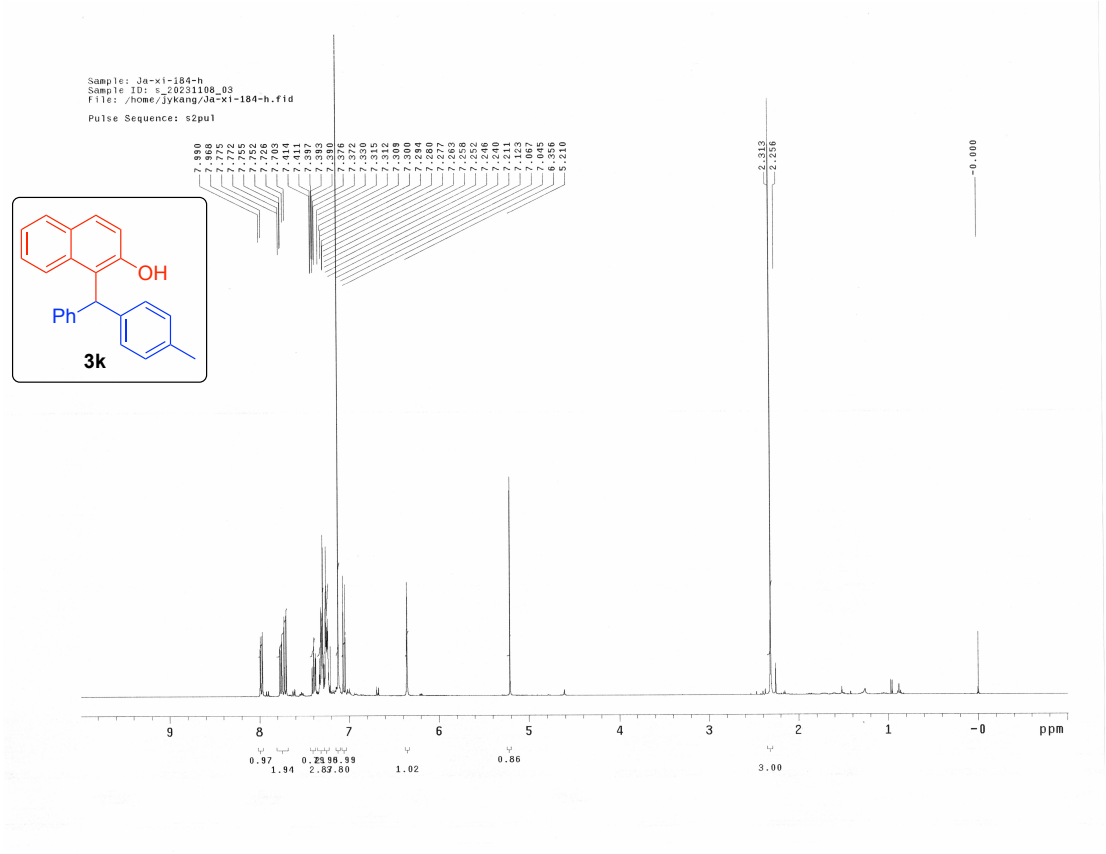
^{1}H NMR (400 MHz) in $CDCl_3$



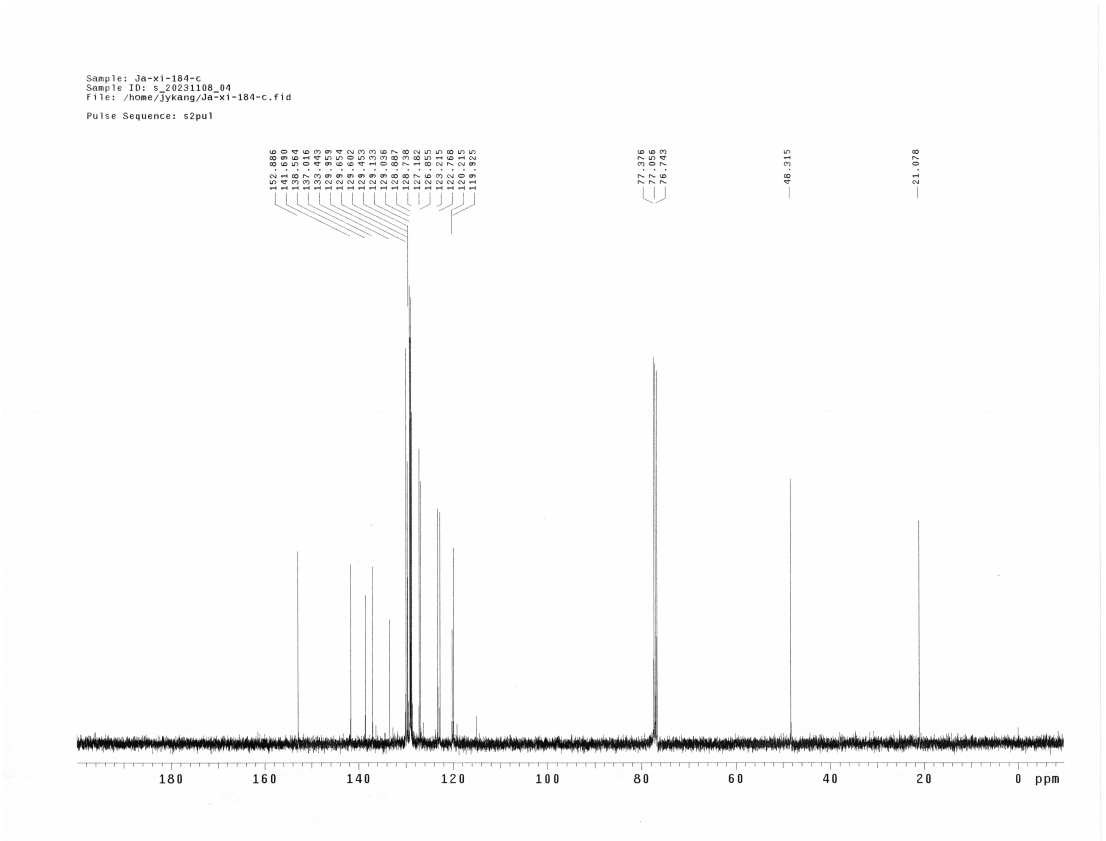
^{13}C NMR (100.5 MHz) in $CDCl_3$



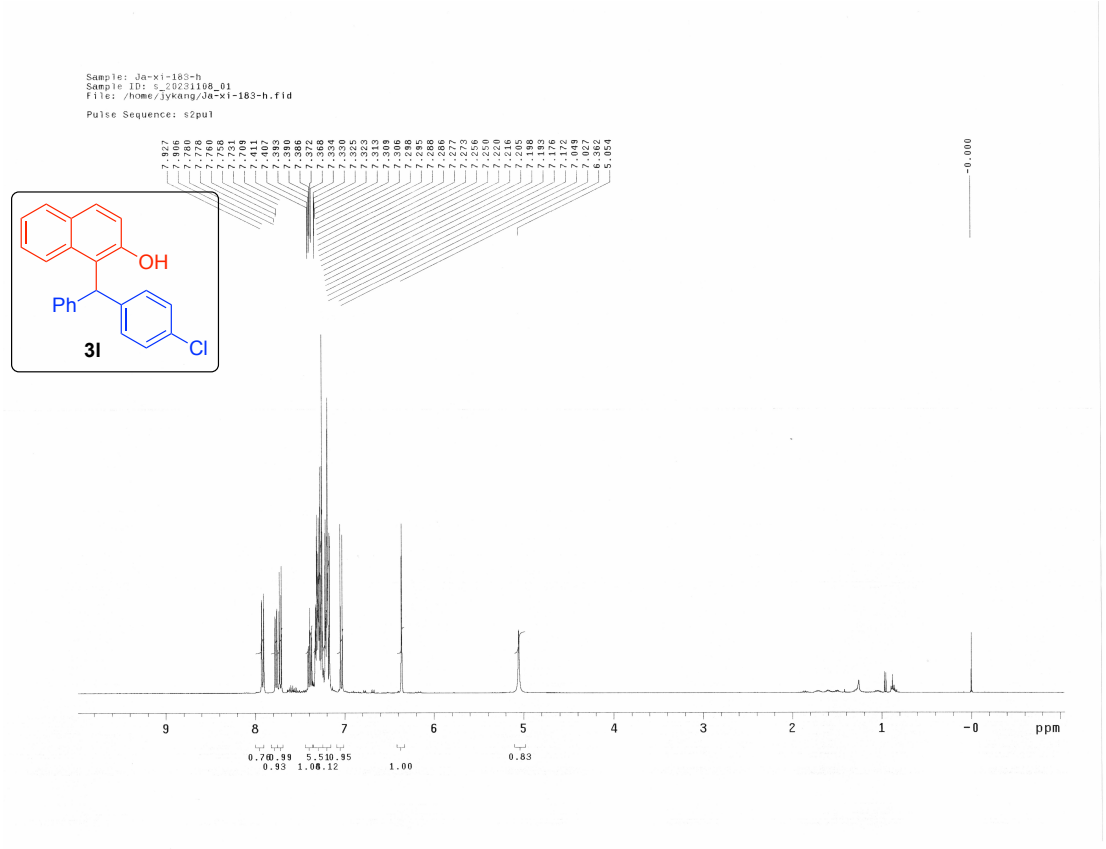
^{1}H NMR (400 MHz) in $CDCl_3$



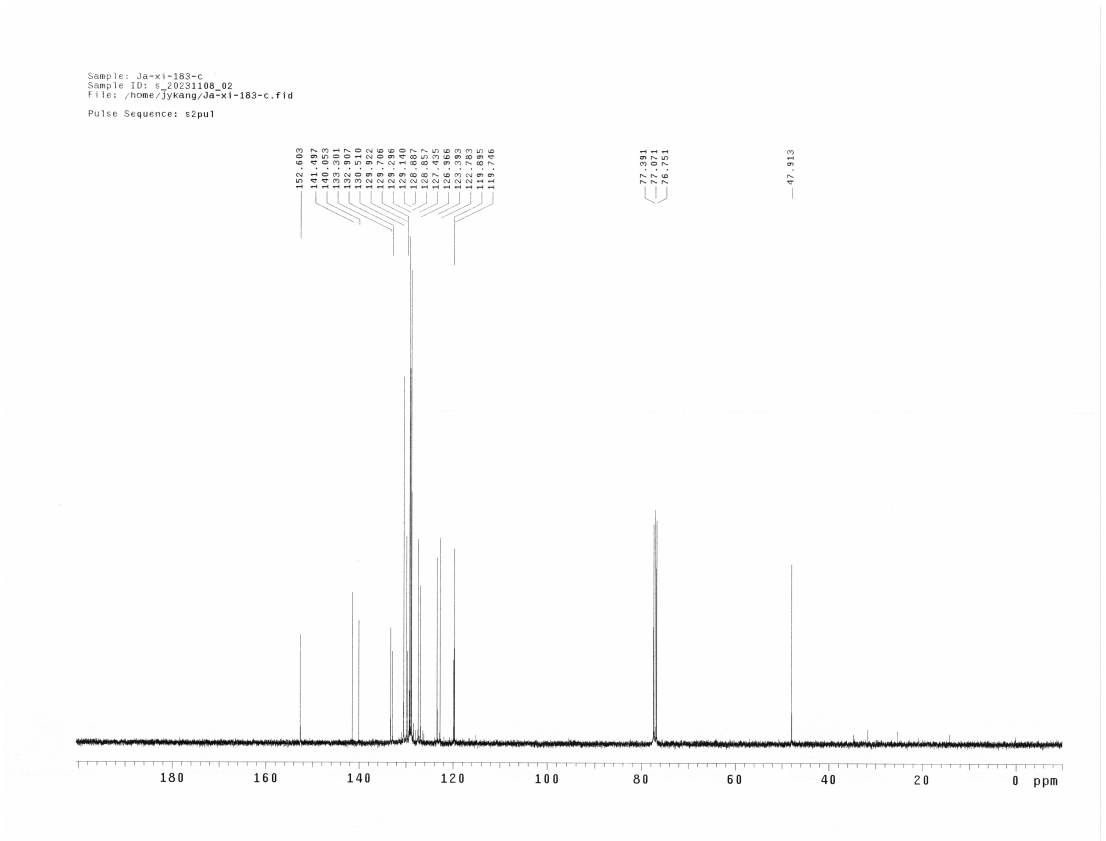
^{13}C NMR (100.5 MHz) in $CDCl_3$



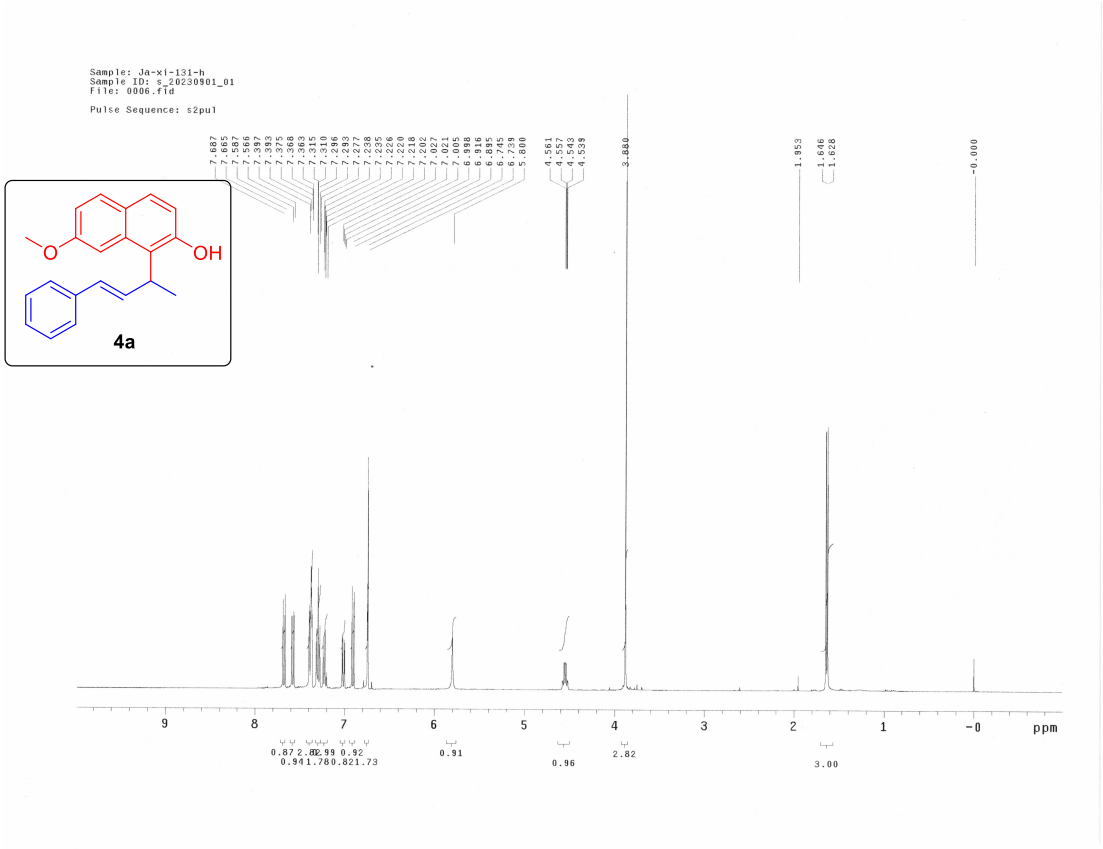
^{1}H NMR (400 MHz) in $CDCl_3$



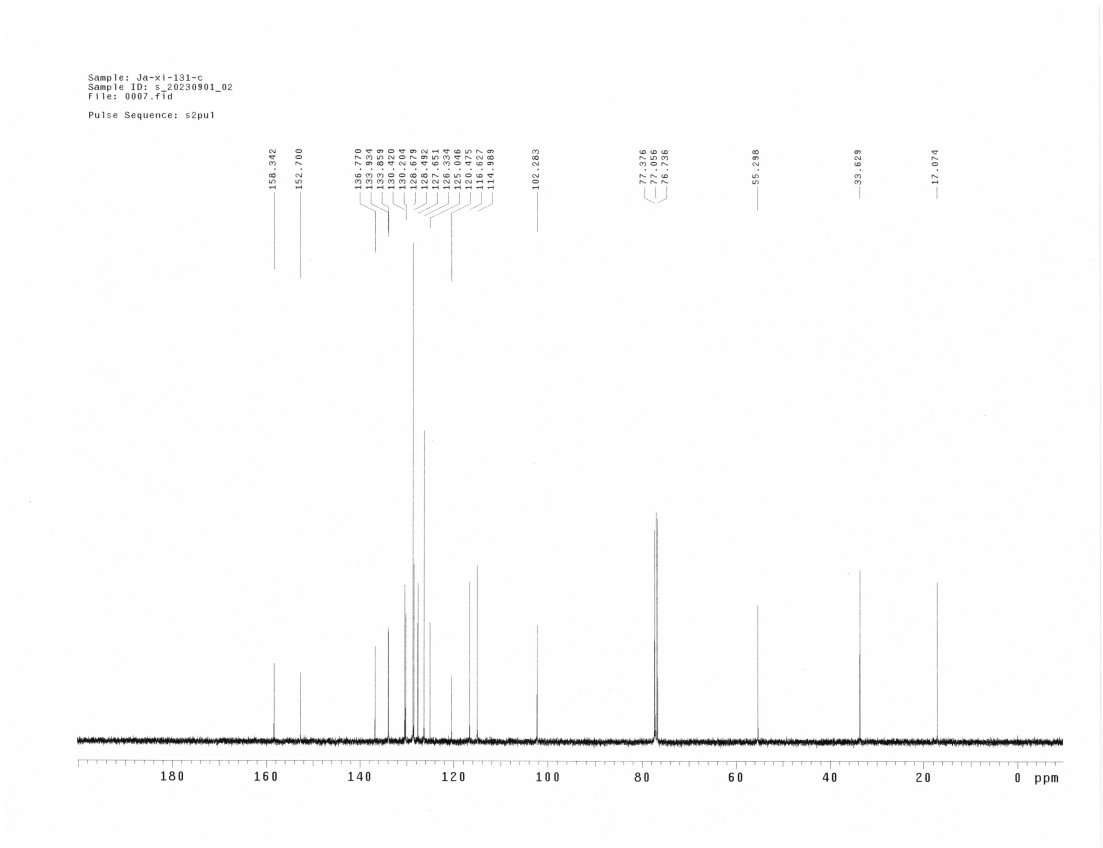
^{13}C NMR (100.5 MHz) in $CDCl_3$



^{1}H NMR (400 MHz) in $CDCl_3$



^{13}C NMR (100.5 MHz) in $CDCl_3$



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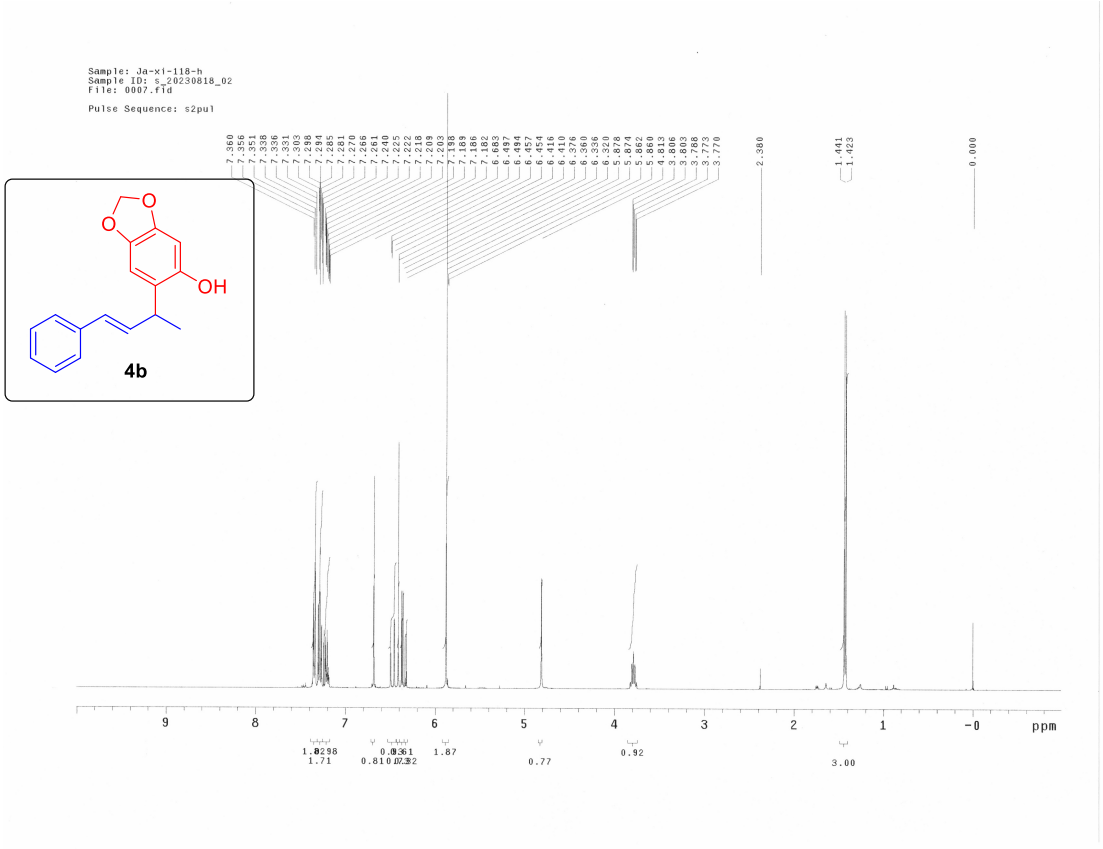
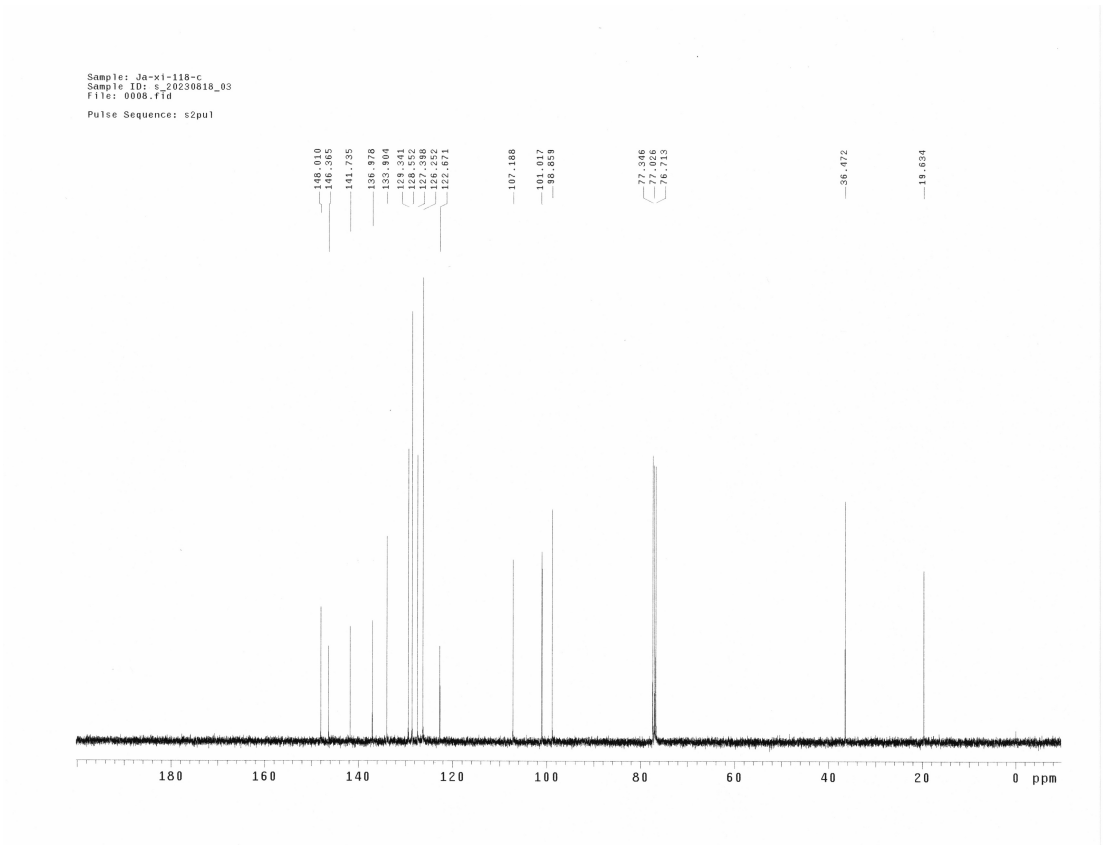


^{13}C NMR (100.5 MHz) in $CDCl_3$



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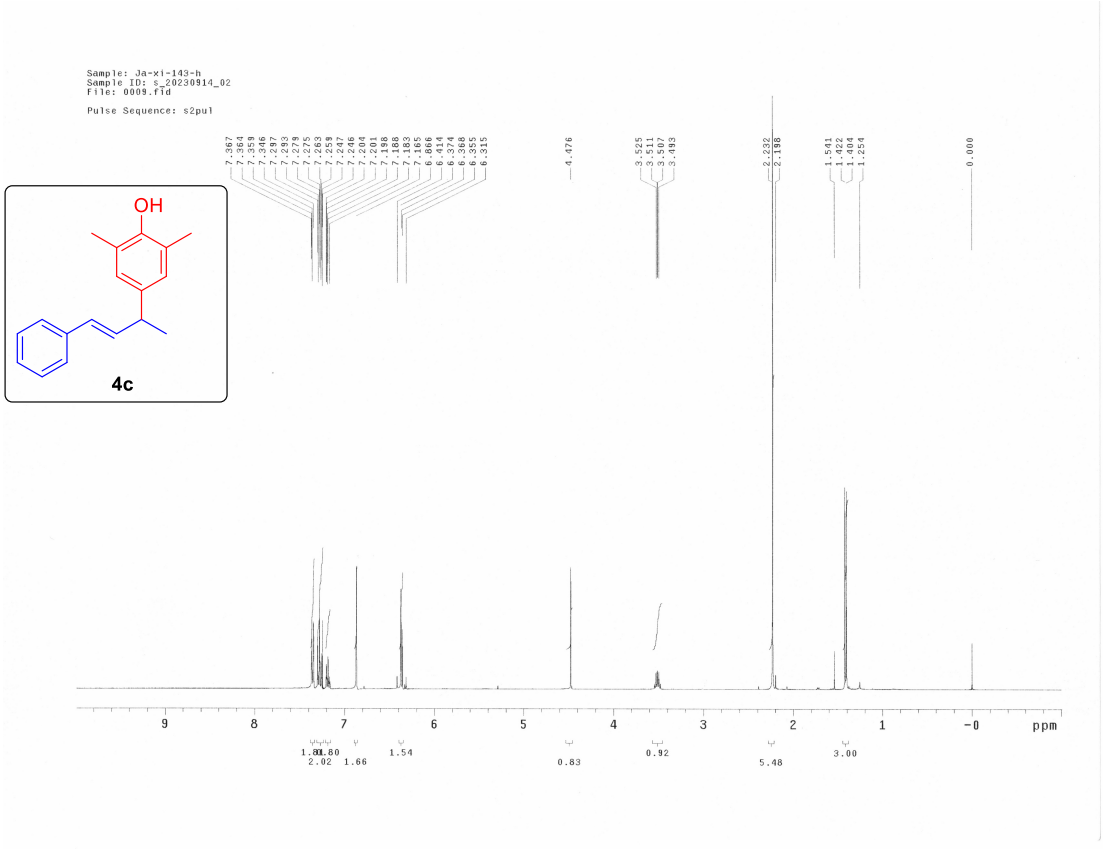
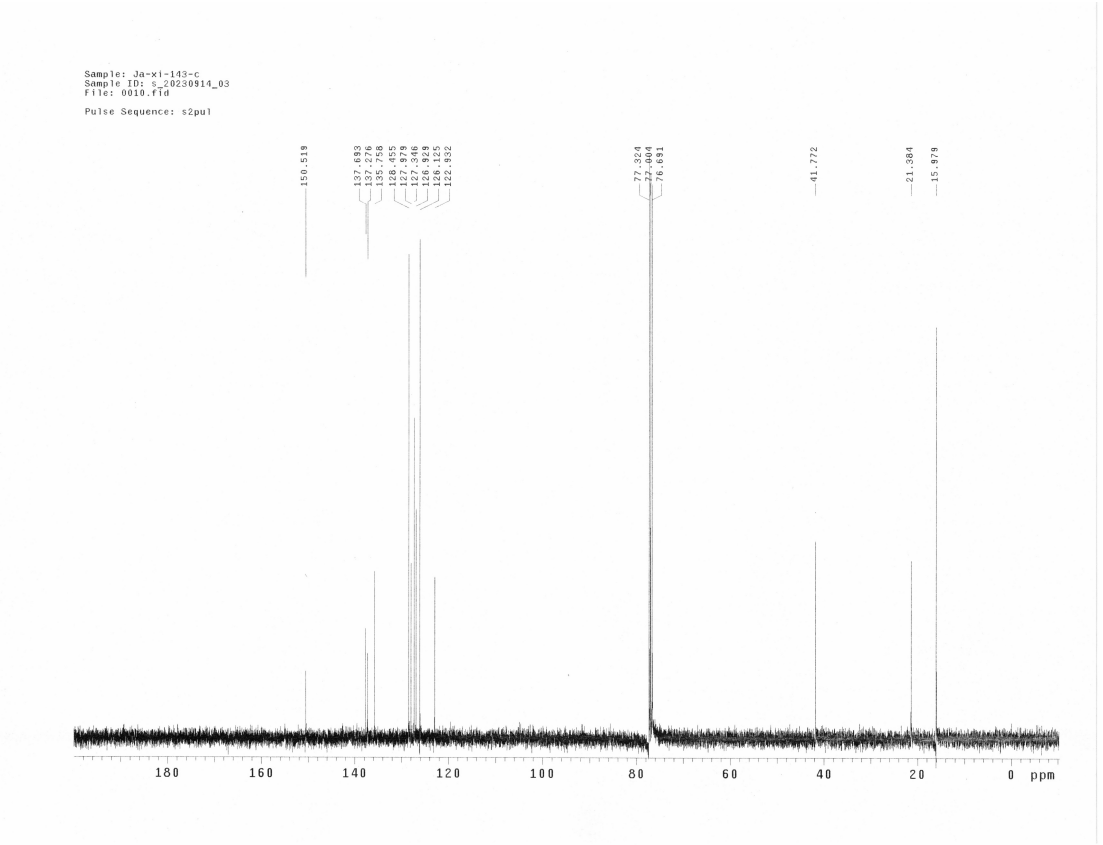
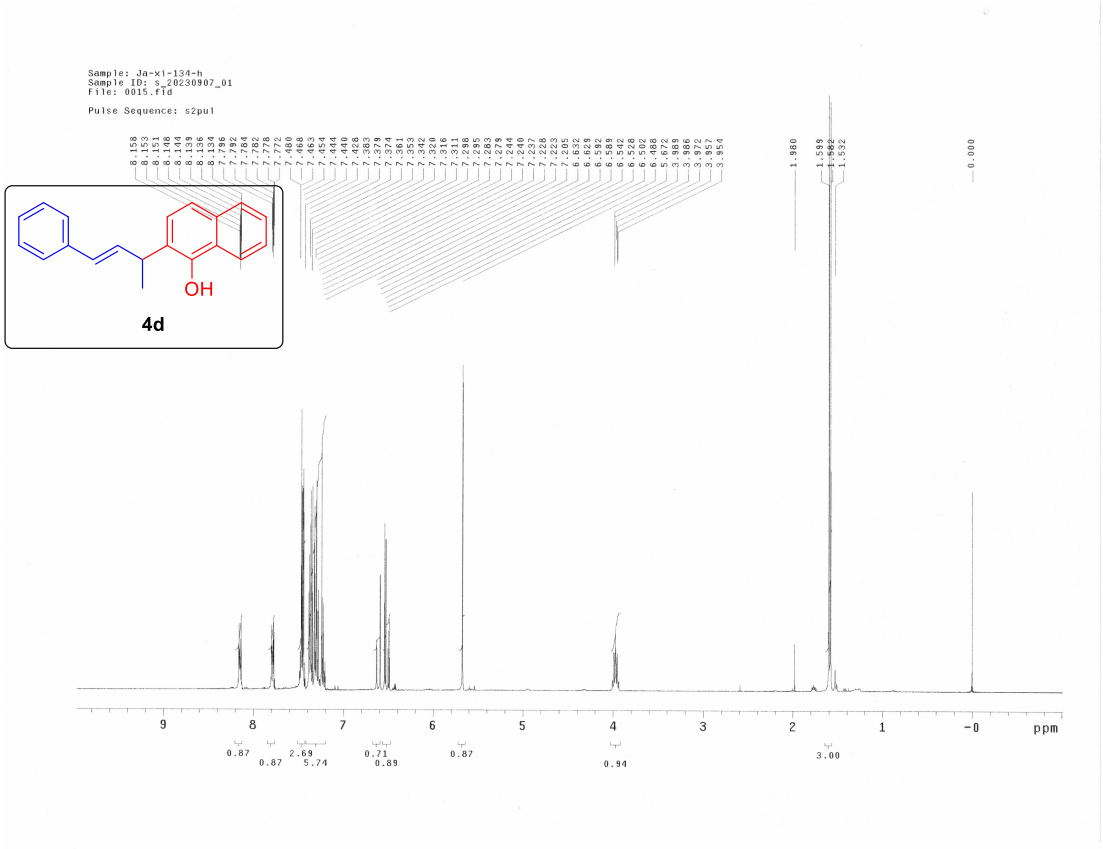


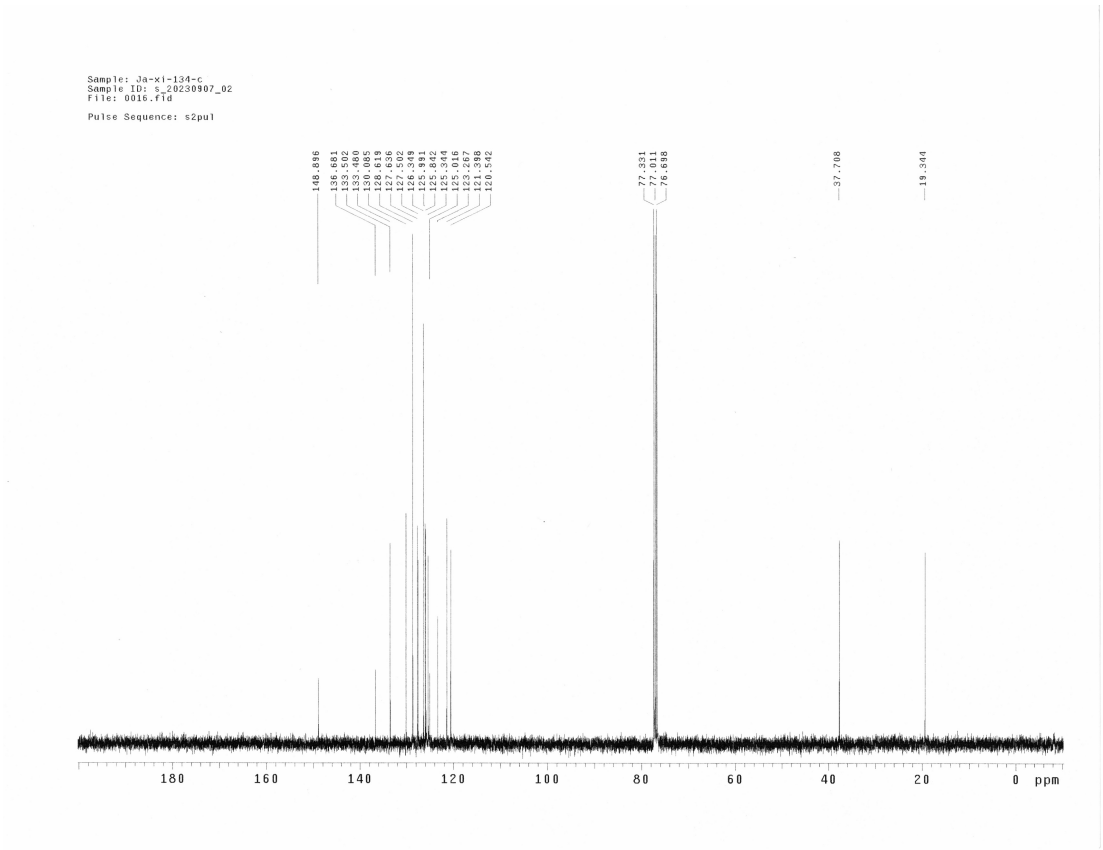
^{13}C NMR (100.5 MHz) in $CDCl_3$



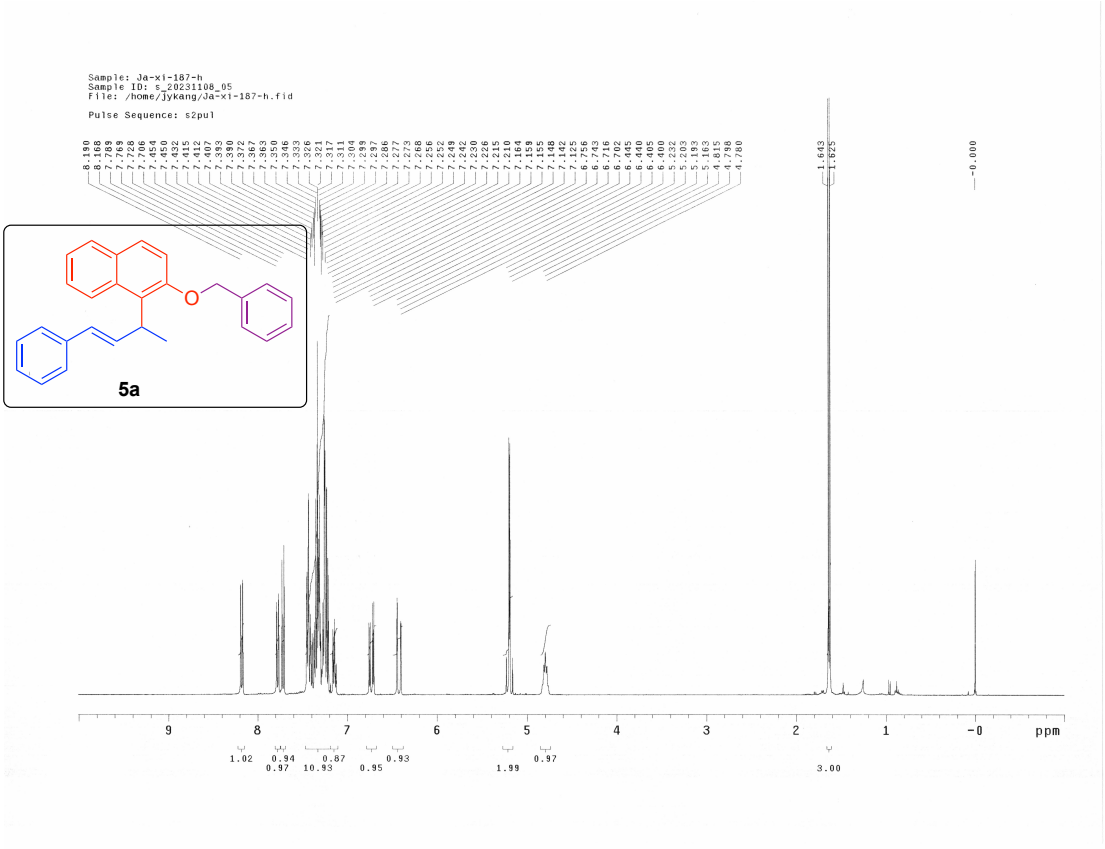
^{1}H NMR (400 MHz) in $CDCl_3$



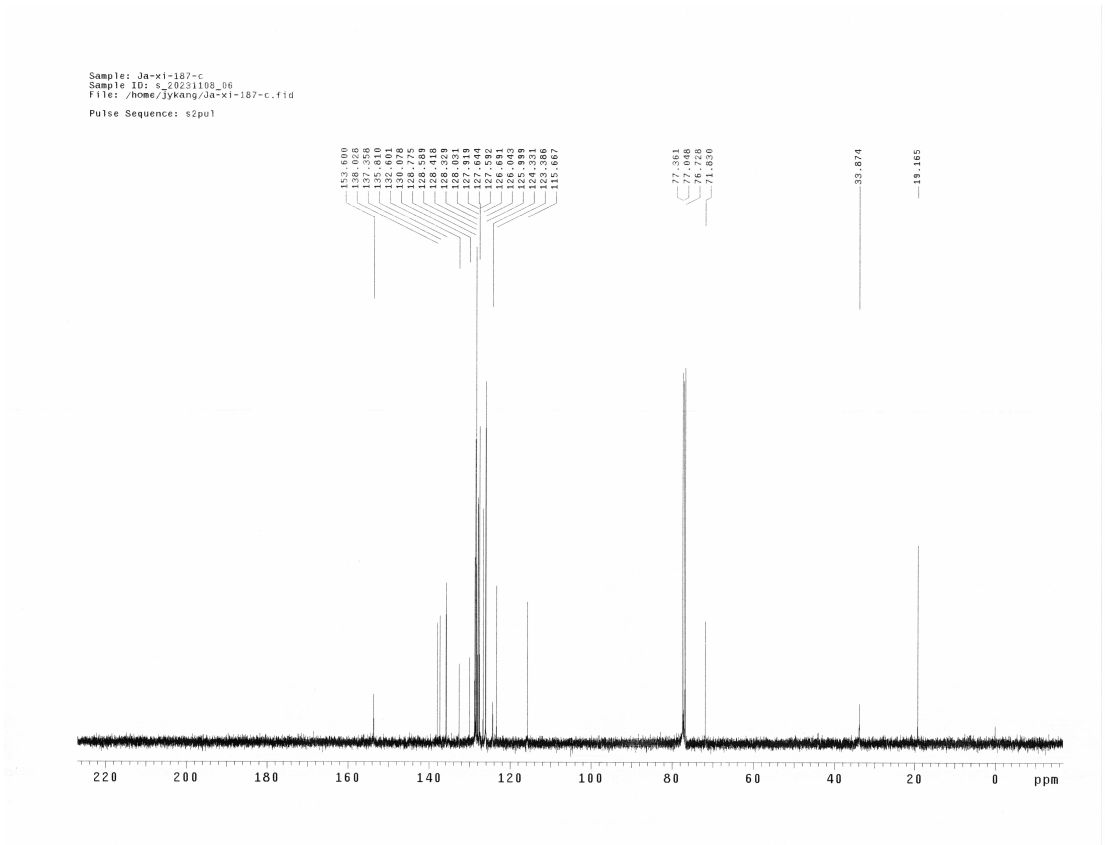
^{13}C NMR (100.5 MHz) in $CDCl_3$



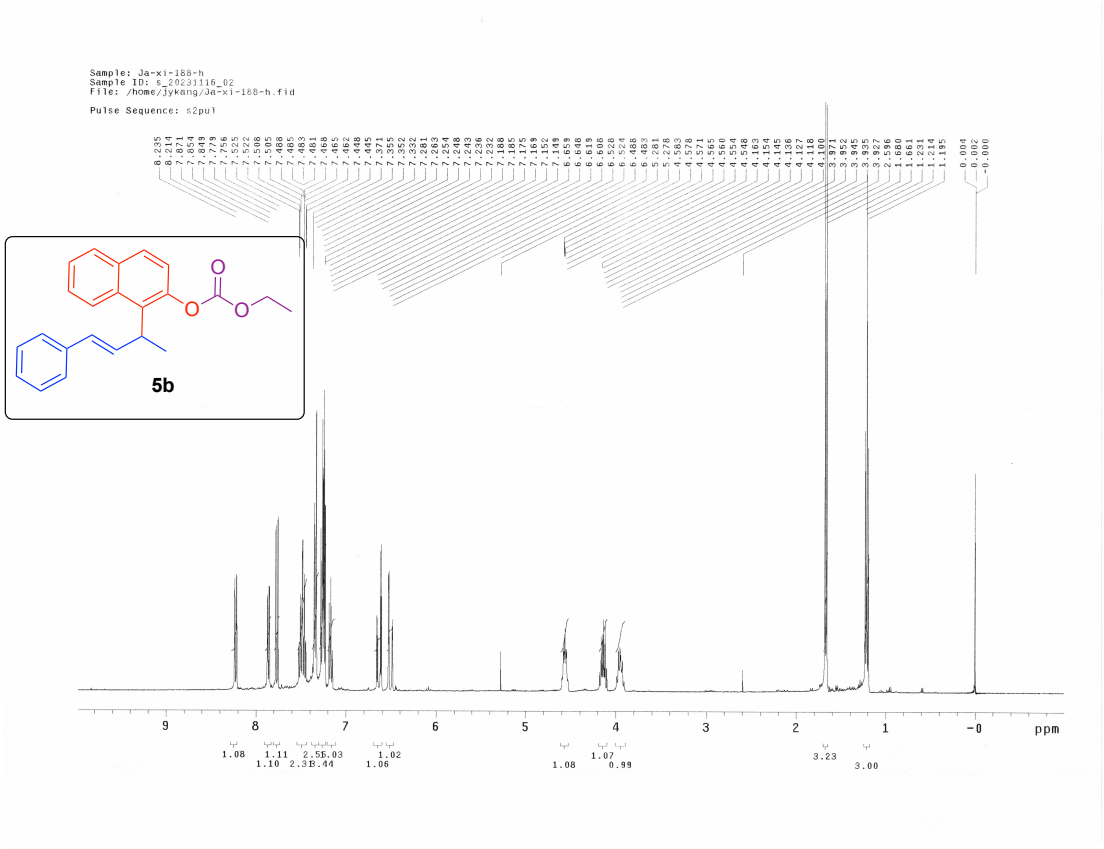
^{1}H NMR (400 MHz) in $CDCl_3$



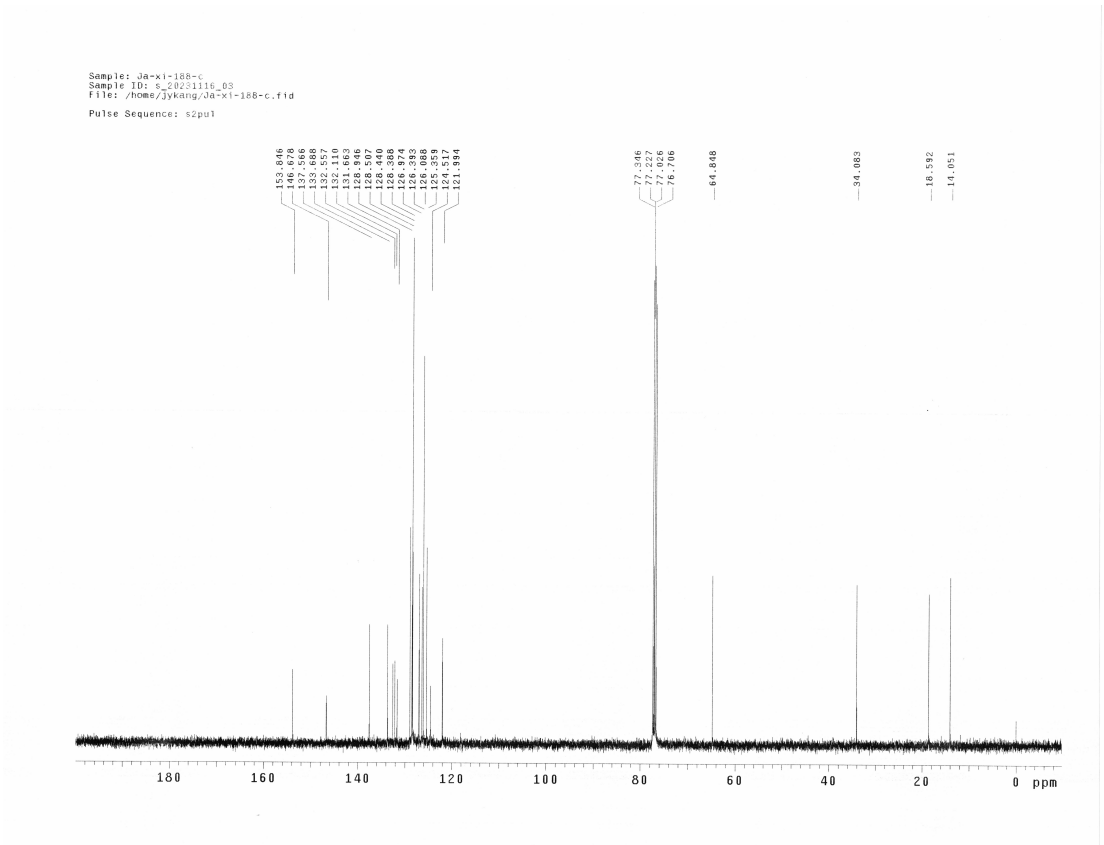
^{13}C NMR (100.5 MHz) in $CDCl_3$



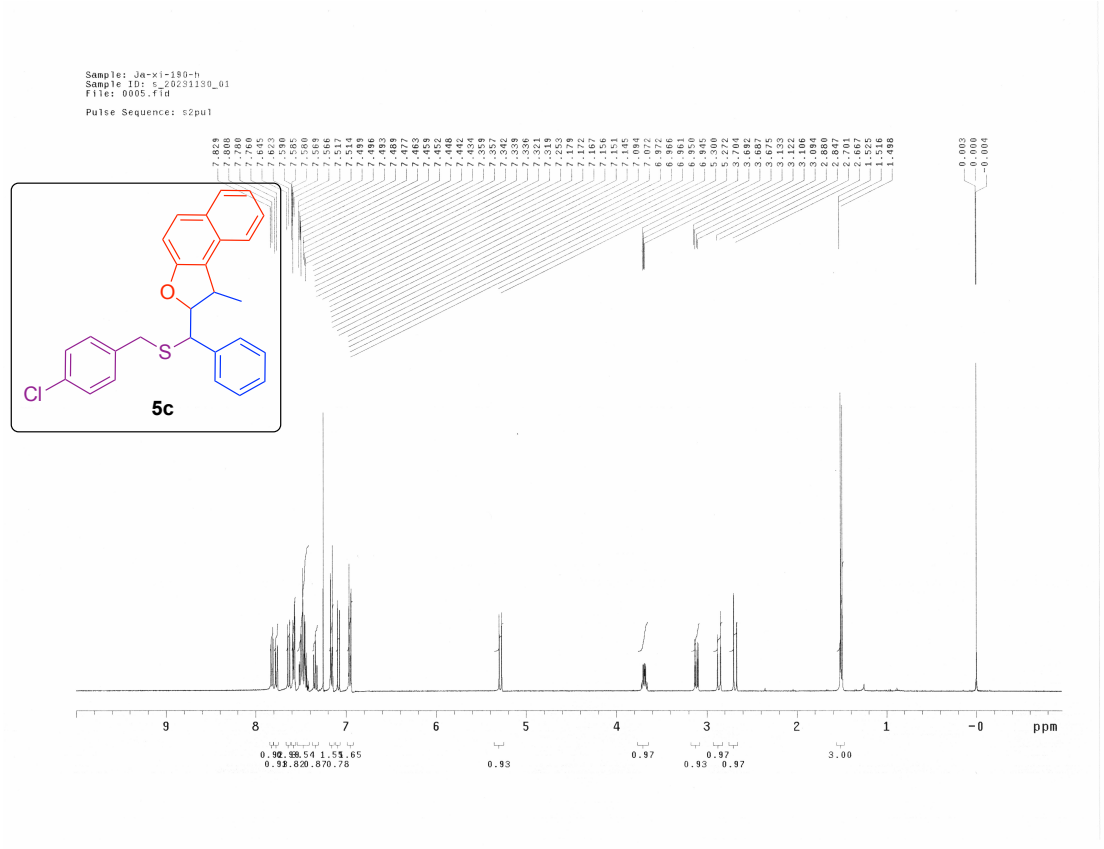
^{1}H NMR (400 MHz) in $CDCl_3$



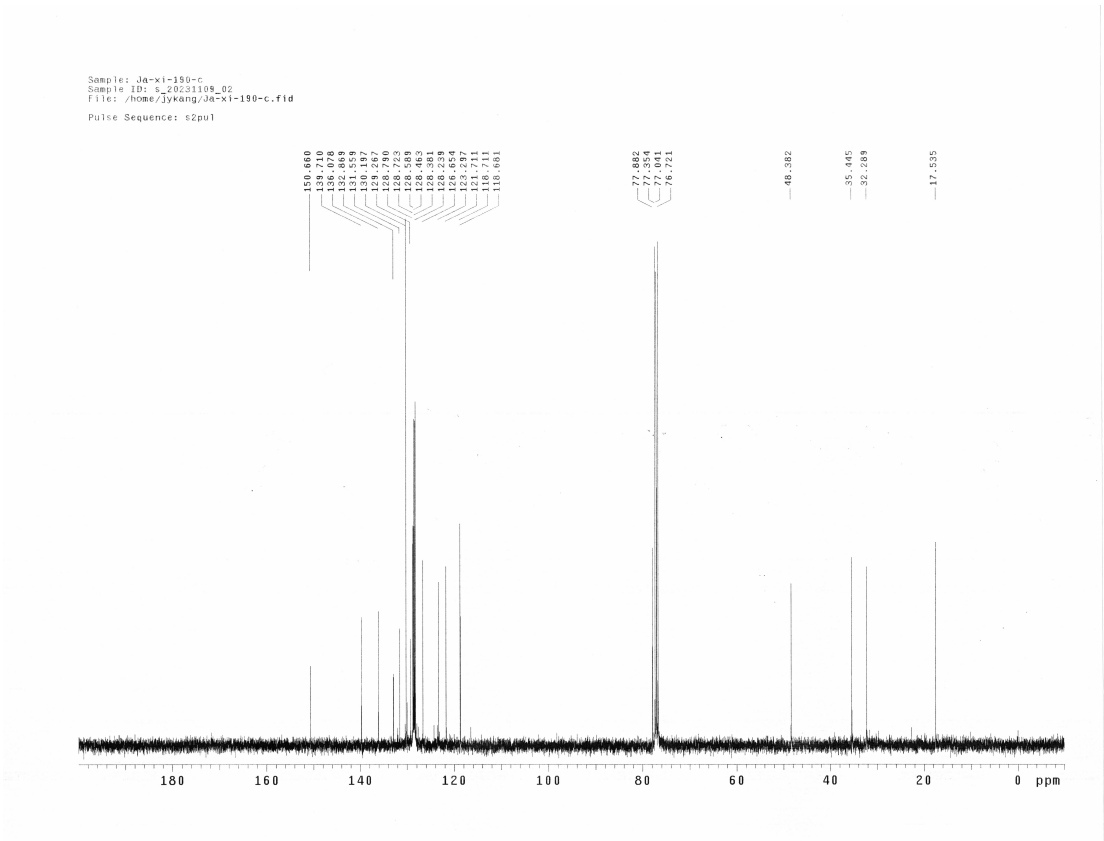
^{13}C NMR (100.5 MHz) in $CDCl_3$



^{1}H NMR (400 MHz) in $CDCl_3$



^{13}C NMR (100.5 MHz) in $CDCl_3$



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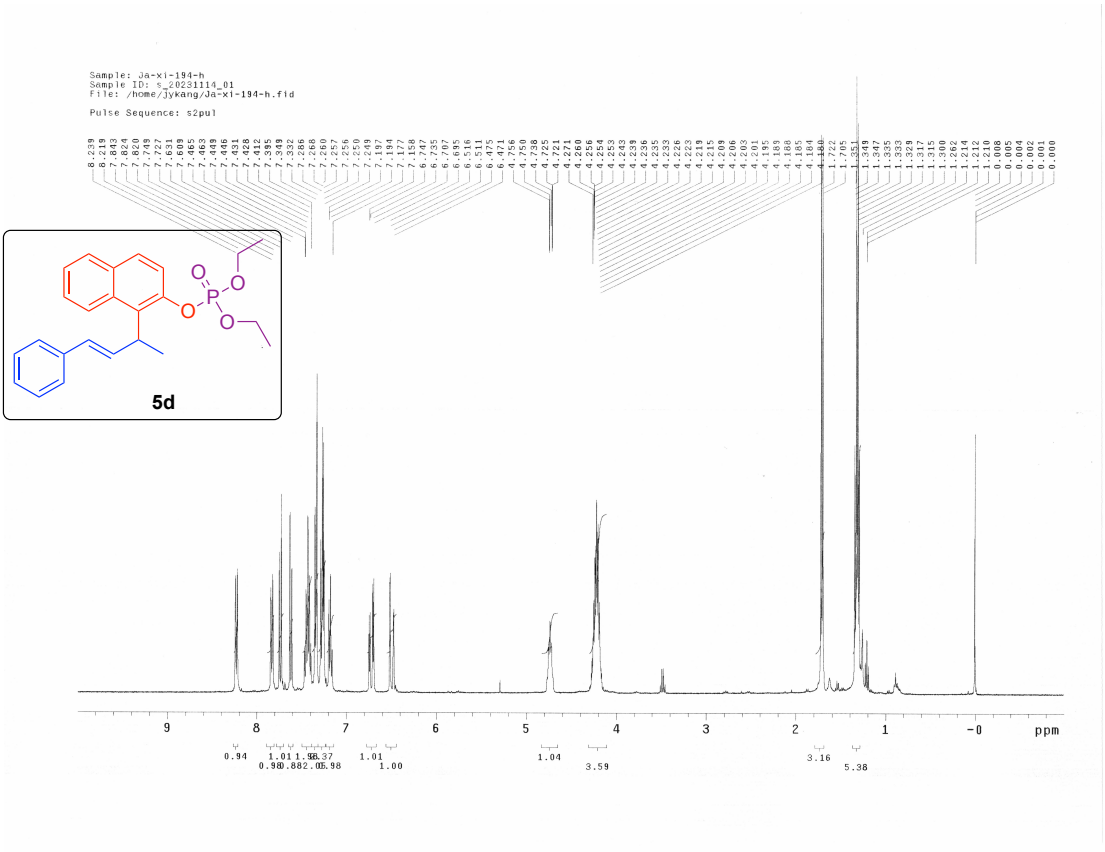
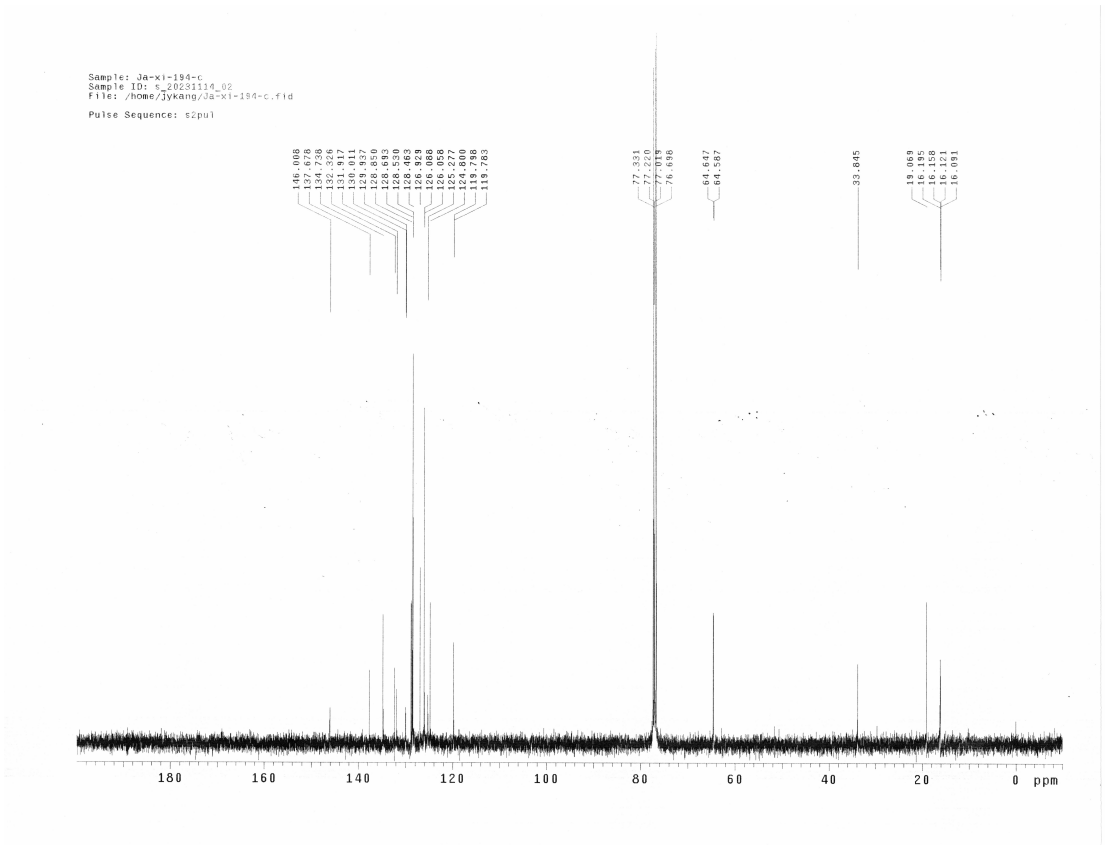
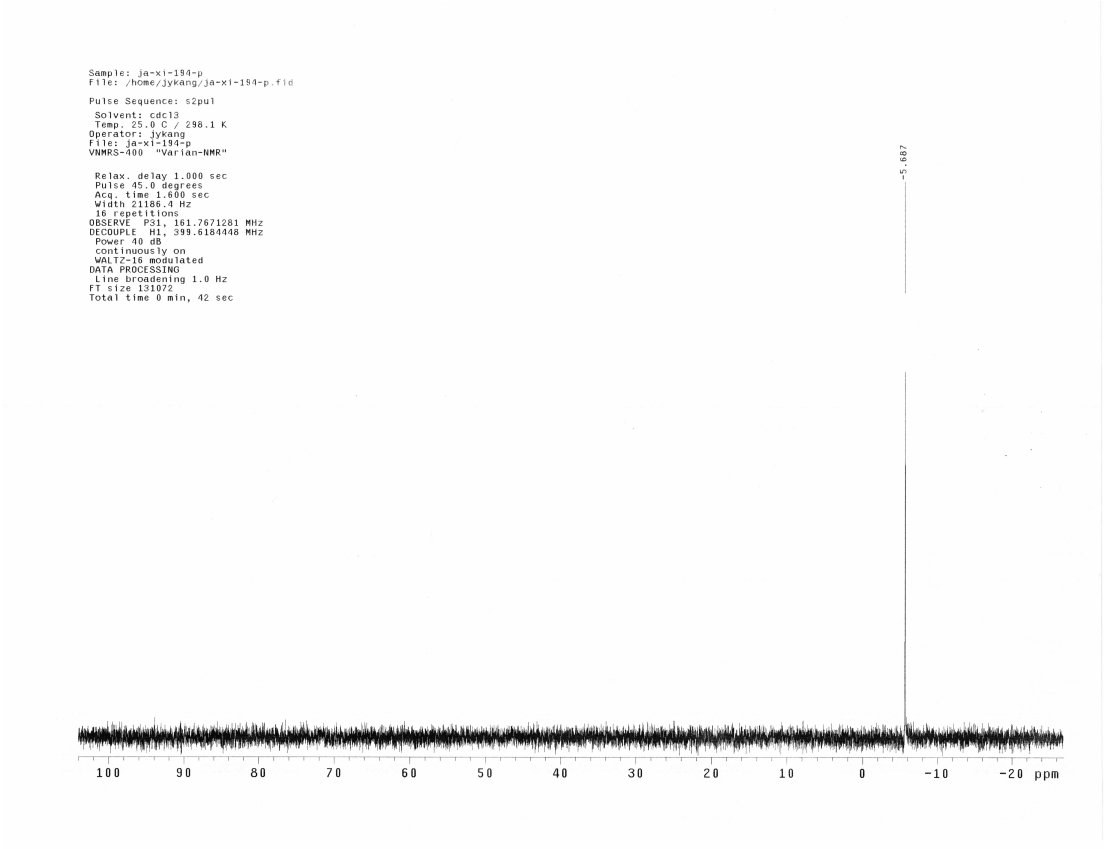


^{13}C NMR (100.5 MHz) in $CDCl_3$



^{31}P NMR (162 MHz) in $CDCl_3$



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