理 學 碩 士 學 位 論 文

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Visible-light Photoredox Catalyzed Pinacol coupling in Water

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1. Abstract

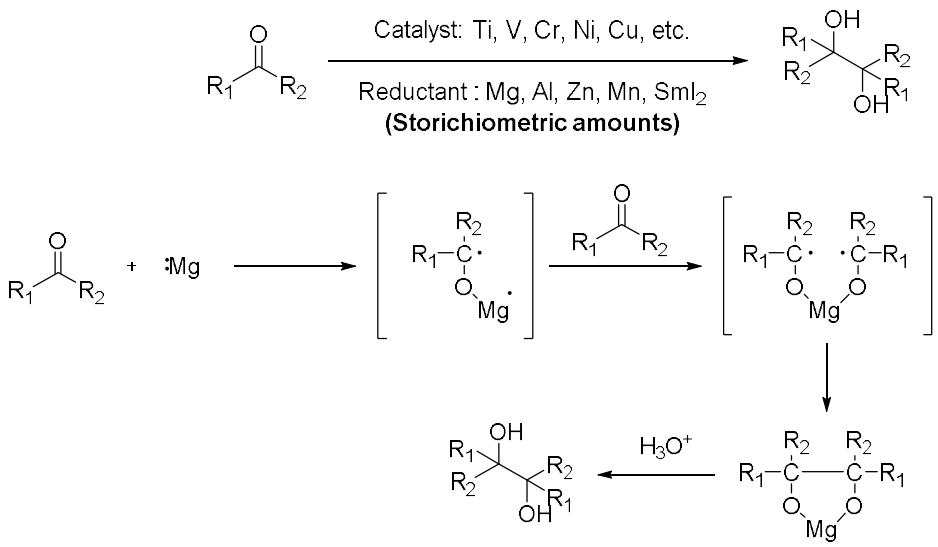
We developed the visible-light mediated photoredox-catalyzed Pinacol coupling in water. This reaction is eco-friendly and economical because it uses water as a solvent and 4CzIPN, an organic photocatalyst that is cheap and easy to make. Various functional groups were tolerated under mild and metal-free conditions to provide good to excellent yields.

Keywords.

Photoredox-catalysis, Pinacol coupling, 4CzIPN, Water, Green chemistry, Diol.

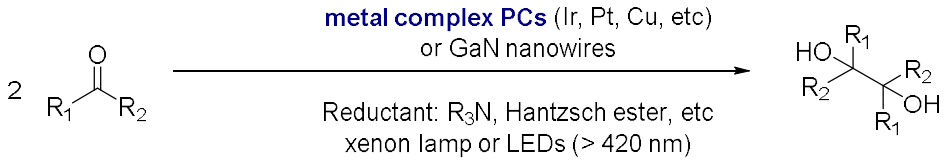
2. Introduction

Vicinal diols or diamines are important substrates in organic synthesis. These are used in pharmaceuticals, agrochemicals, and natural products.[1, 2] The most representative reaction for preparation of diols and diamines is Pinacol coupling reaction. The Pinacol coupling reaction is a powerful synthetic method for constructing vicinally funtionalized carbon-carbon bonds. Basically, traditional method of pinacol coupling reaction require more than stoichiometric amount of metal reductants such as Mg, Al, Zn, Mn, etc. (**Scheme 1.**)[3-9] Metal containing Pinacol coupling process produce large amounts of metal wastes. Therefore, these types of synthetic methods can cause economical and environmental issues in a long-term perspective.

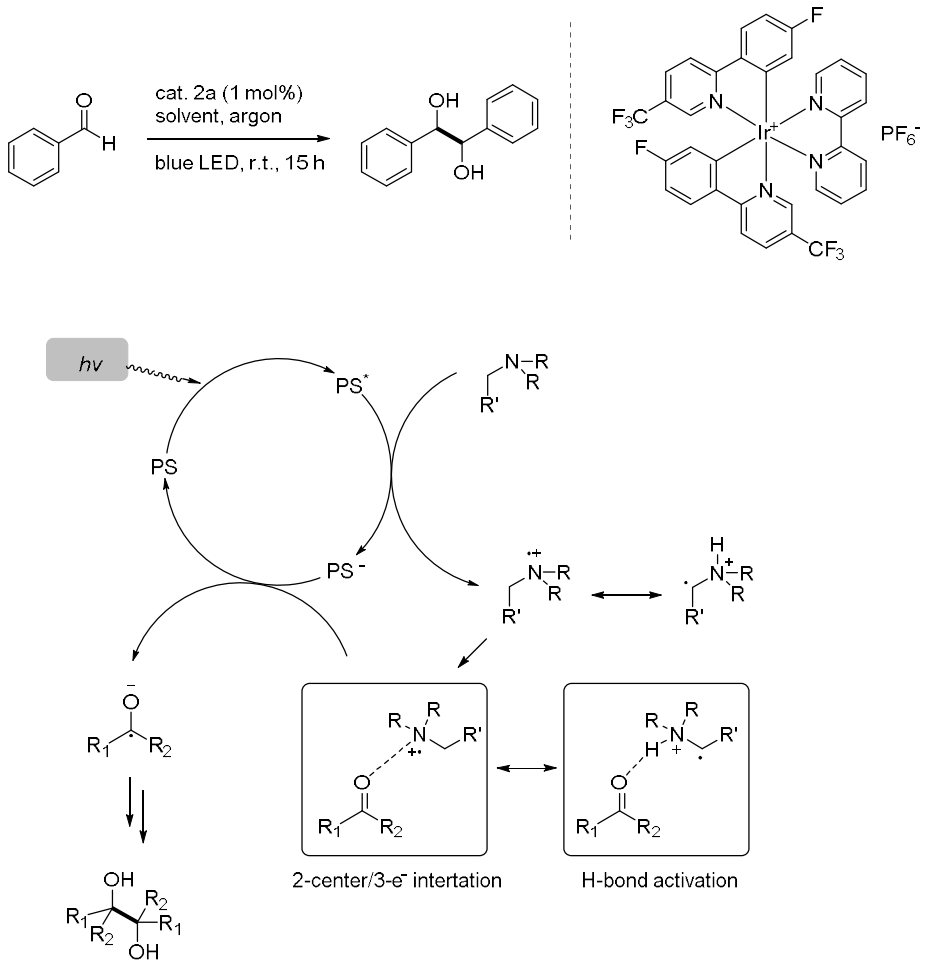


Scheme 1. Classical Pinacol coupling reactions using Metal compounds

To resolve this problems, alternative Pinacol coupling reactions using photoreaction have been developed. The photocatalytic reaction has the advantage of using a small amount of metal source reagents and the reaction proceeds under mild conditions. There are variety photocatalytic reactions of Pinacol reactions published so far, using metal complexes (Ir, Pt, Cu, etc.)[9-11], GaN nanowires[12], supramolecules, coumarin dyes[13] and perylene[14] as photocatalysts (**Scheme 2a and 3**.) One of the representative photoredox catalysed Pinacol coupling reaction was carried out by Rueping groups used Ir-containing photocatalyst and tri-n-butylamine as a reductant.[10] (**Scheme 2b**.). First, tri-n-butylamine is oxidized by activated photocatalyst. Second, oxidized tri-n-butylamine promoted to transform aldehyde or ketone into ketyl radical. But iriduim based catalyst source also need the use of novel metal, so it still has an economical issue and environmental problem.



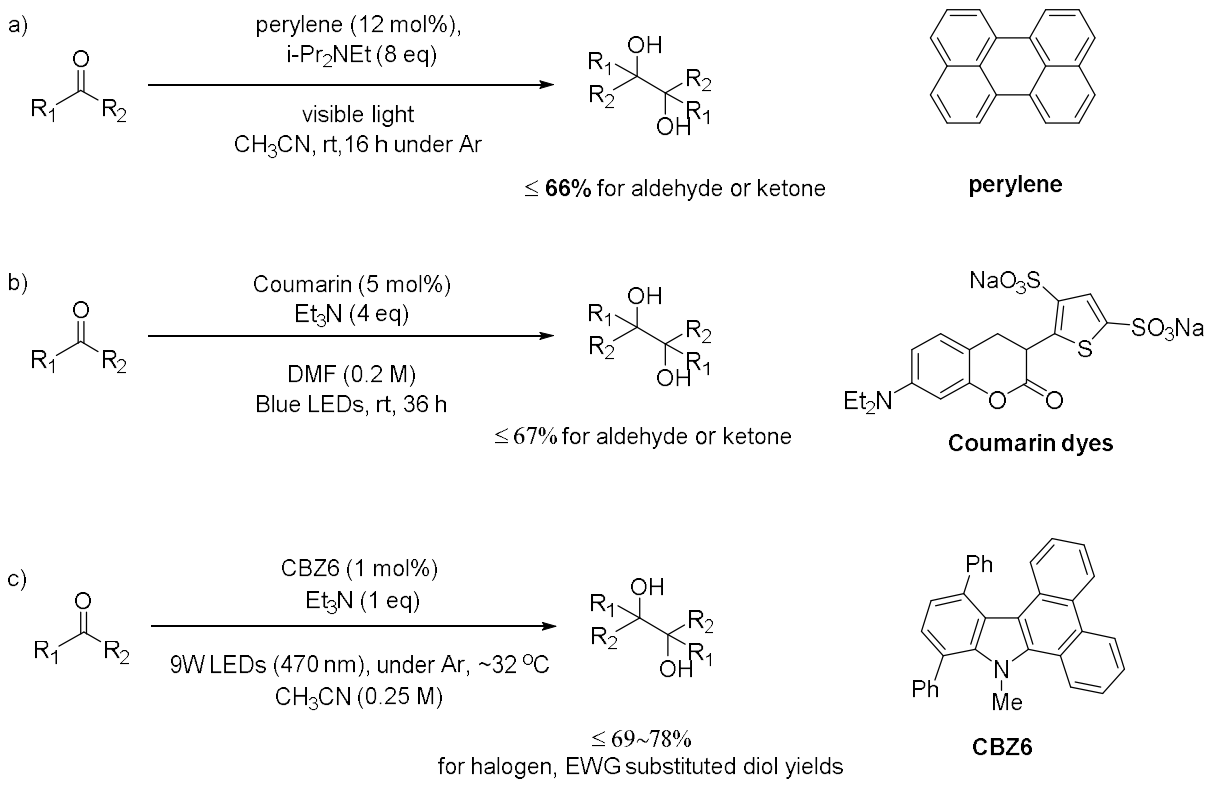
Scheme 2a. Metal-containing photoredox catalysts-promoted Pinacol coupling



Scheme 2b. Reaction mechanism of photoredox catalyzed Pinacol coupling

Several Pinacol coupling reactions have been developed using organic dyes as photocatalysts to compensate for these disadvantages **(Scheme 3).** In Atsushi Sudo group and Pier Giorgio Cozzi group, they tried to use perylene and coumarin as photocatalysts, but overall yield was up to 66~67%. Although Yan-Biao Kang group, which used CBZ6 as a catalyst, has achieved excellent yields up to 99%. Halogen and EWG substituted substrates were afforded in yield of 69~78%. Moreover, these

reactions use toxic solvents such as DMF, THF, MeCN, etc. that can cause health problems.



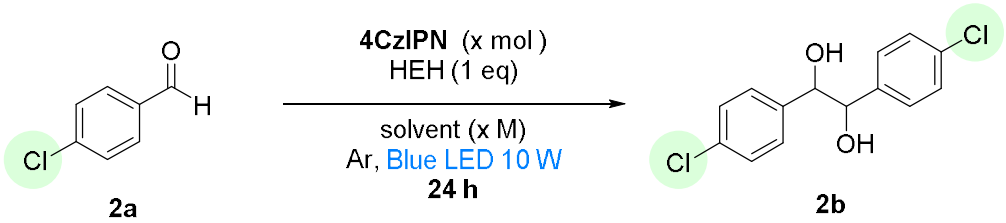
Scheme 3. Organic photoredox catalyzed Pinacol coupling

In a drug synthesis solvents represent at least half of the material used in a chemical process. Therefore, reducing their amount and selecting the "greenest" solvents[15-19] are the most efficient levers to reduce the environmental impact of an active pharmaceutical ingredient. So, we focused on finding appropriate green solvents for eco-friendly Pinacol coupling reaction. This eco-friendly reaction uses water as a solvent and organic photoredox catalyst to achieve eco-friendly and economical reaction.

3. Result and Discussions

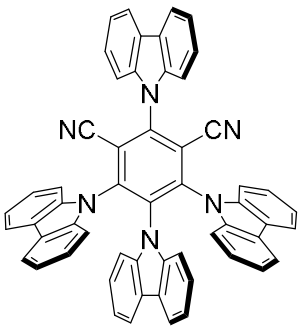
a. Optimization of Pinacol coupling with Electron deficient benzaldehyde.

Table 1. Optimization of the reaction conditions with electron-deficient aldehyde

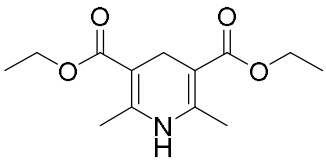


Entry	SM (mmol)	catalyst	solvent	solvent (x M)	yield[a]
1	0.2	4CzIPN (1 mol%)	THF	0.1 M	>99%
2	0.2	4CzIPN (1 mol%)	EtOH	0.1 M	64%
3	0.2	4CzIPN (1 mol%)	i-PrOH	0.1 M	86%
4	0.2	4CzIPN (1 mol%)	EtOAc	0.1 M	90%
5	**0.2**	**4CzIPN (1 mol%)**	**H_2O**	**0.1 M**	**82%**
6	0.2	4CzIPN (0.5 mol%)	H_2O	0.1 M	63%
7	0.2	4OMeCzIPN(1 mol%)	H_2O	0.1 M	trace
8	0.2	PDI-S (1 mol%)	H_2O	0.1 M	trace

[a]NMR yield with Internal standard (Mesitylene)
[b]isolated yield by column chromatography



4CzIPN



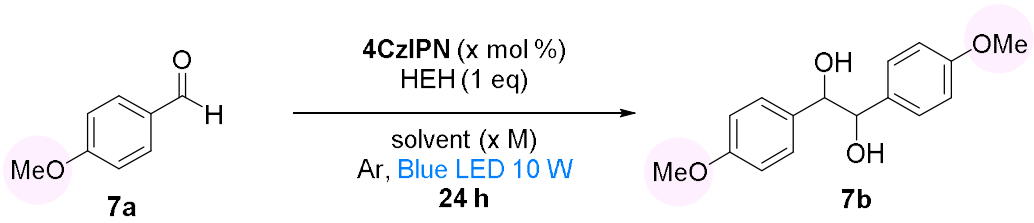
Hantzsch ester
[HEH]

We started the optimization of photocatalytic Pinacol coupling reaction with 4-chloro-benzaldehyde which has a characteristic of electron-deficiency and easy to available. Fortunately, we afforded desired diol product as excellent yield in initial study. The 4-chloro-benzaldehyde **1a** (0.2 mmol) was converted to corresponding diol in > 99% yield using 4-CzIPN (1 mol%) as photocatalyst in THF (0.1 M) under irradiation of 450 nm 10 W Blue LEDs for 24 h **(Table 1,** entry 1**).**

Although we had a good yield, we tried further examination to develop an economical and environmentally friendly reaction. Therefore, we searched several solvents which are evaluated as "green-solvent" from a health & environmental criterion.[20] After several solvent optimization with green solvent such as EtOH, *i*-PrOH, EtOAc and H_2O (**Table 1**, entry 2-5**)**, we got good result in *i*-PrOH, EtOAc and H_2O (**Table 1,** entry 3-5). We have chosen water the most environmentally friendly solvent in the photoredox catalyzed Pinacol coupling reaction. When we reduced amount of photocatalyst from 1 mol% to 0.5 mol%, yield was decreased (**Table 1,** entry 6). Although we studied optimization with another photocatalysts such as 4-OMeCzIPN and PDI-S, the result was not good (**Table 1,** entry 7-8).

b. Optimization of Pinacol coupling with Electron rich benzaldehyde

Table 2. Optimization of the reaction conditions with electron-rich aldehyde



Entry	SM (mmol)	catalyst	solvent	solvent (x M)	yield[a]
1	0.2	4CzIPN (1 mol%)	H_2O	0.1 M	48%
2	0.2	4CzIPN (1 mol%)	i-PrOH	0.1 M	32%
3	0.2	4CzIPN (1 mol%)	EtOAc	0.1 M	>99%
4	0.2	4CzIPN (1 mol%)	H_2O:i-PrOH (3:1)	0.1 M	45%
5	0.2	4CzIPN (1 mol%)	H_2O:EtOAc (1:1)	0.1 M	86%
6	0.2	4CzIPN (1 mol%)	H_2O:EtOAc (5:1)	0.1 M	87%
7	**0.4**	**4CzIPN (1 mol%)**	**H_2O:EtOAc (5:1)**	**0.2 M**	**94%[b]**

[a]NMR yield with Internal standard (Mesitylene)
[b]isolated yield by column chromatography

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Recommended	Water, EtOH, i-PrOH, EtOAc, *i*-PrOAc, *n*-BuOAc. anisole, sulfolane.
Recommended or problematic?	MeOH, *t*-BuOH, benzyl alcohol, ethylene glycol, acetone, MEK,MIBK,cyclohexanone, MeOAc, AcOH, Ac_2O.
Problematic	Me-THF, heptane, Me-cyclohexane, toluene, xylenes, chlorobenzene, acetonitrile, DMPU, DMSO.
Problematic or harzardrous?	MTBE, THF, cyclohexane, DCM, formic acid, pyridine.
Harzardrous	Diisopropyl ether, 1,4-dioxane, DME, pentane, hexane, DMF, DMAc, NMP, methoxy-ethanol, TEA.
Highly hazardrous	Diethyl ether, benzene, chloroform, CCl_4, DCE, nitromthane, CS_2, HMPA.

With optimized reaction condition, we tested electron rich aldehydes (**Table 2**). Unfortunately, it was not possible to obtain a high yield of electron-rich aldehyde under the optimized reaction conditions (**Table 2**, entry 1). Therefore, we examined further optimization for electron rich carbonyl compounds. First, we tried optimization with green solvents (**Table 2**, entries 1-3). We got excellent yield in EtOAc as solvent (**Table 2**, entry 3). We still considered using water as reaction solvent Therefore, we

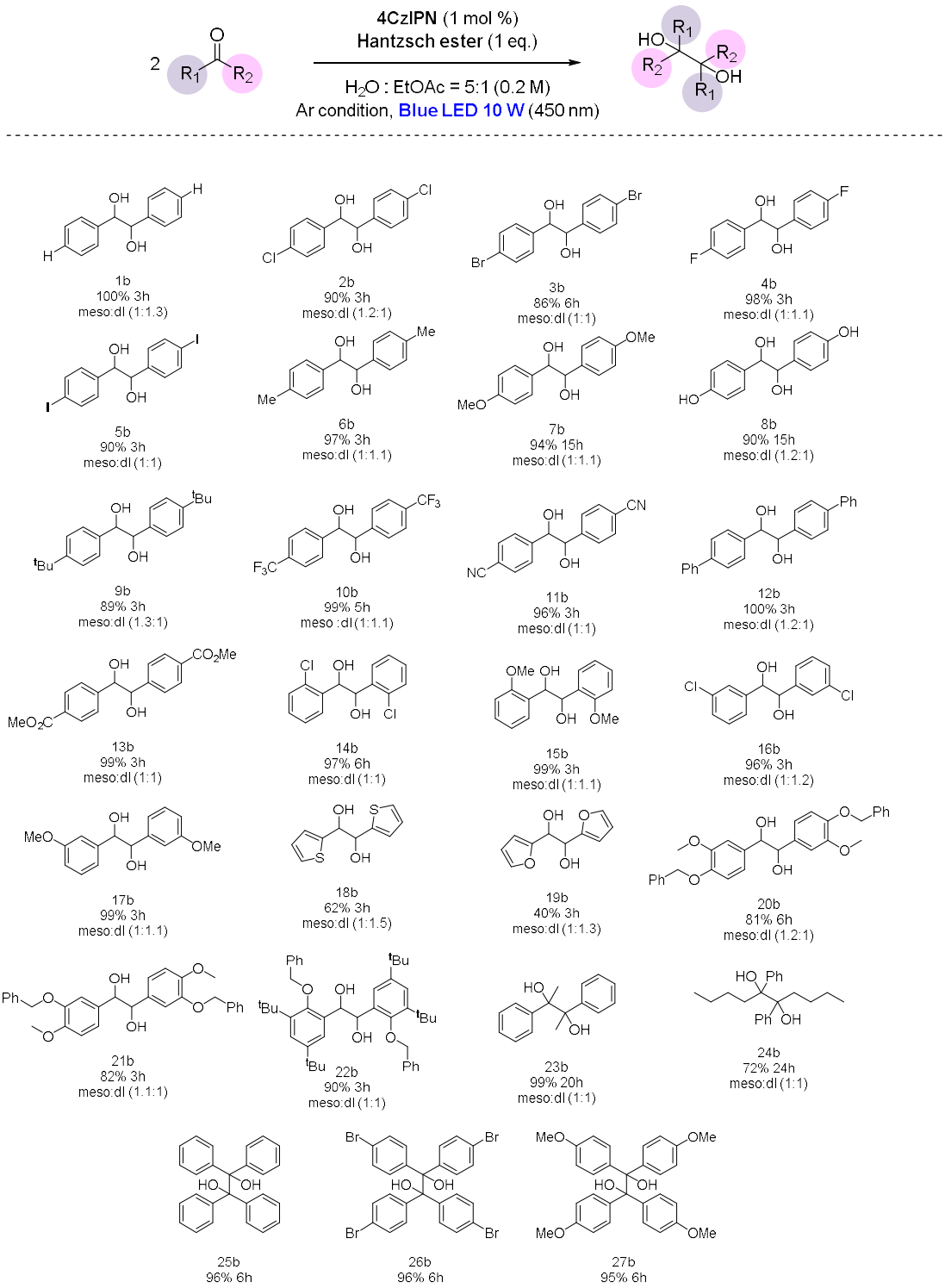
examined co-solvent using water with green organic solvents such as isopropyl alcochol and ethyl acetate (**Table 2**, entries 4-5). We found good co-solvent system for Pinacol coupling reaction using water with ethyl acetate (**Table 2**, entry 5). Finally, we established optimization conditions change ratio and concentration of co-solvent (**Table 2**, entry 7).

c. Substrate Scope

Next, we explored the substrate with various benzaldehydes and ketones to examine the photoredox catalyzed pinacol coupling under optimized condition. (**Scheme 1.**) We examined a variety of substituents on benzaldehyde including halogens (*p*-F, Cl, Br and I), electron-rich groups (*p*-Me, OMe, *t*Bu, Ph and OH), electron deficient groups (*p*-CF_3, CN, CO_2Me), disubstituted groups and trisubstituted groups (**20b – 22b**), heteroaryl aldehydes (**18b-19b**), and ketone groups (**23b-27b**) that gave vicinal diol products in good to excellent yields (72% ~ 99%) except heteroaryl aldehydes (40% ~ 62%). Since the reaction completion time was different for each substrate, time optimization was also carried out, and the diastereomer (meso:*dl*) ratio was also measured through ^{1}H NMR. In the reaction with halogen-substituted benzaldehydes, the corresponding vicinal diol products were obtained in excellent yields (86% ~ 97%) in time from 3h to 6h, and the ratio were overall closed to meso:*dl* = 1:1 (**2b - 5b**). The photocatalyzed Pinacol coupling with electron-rich groups-substituted benzaldehydes produced pinacol coupling products in excellent yields (90% ~ 100%)

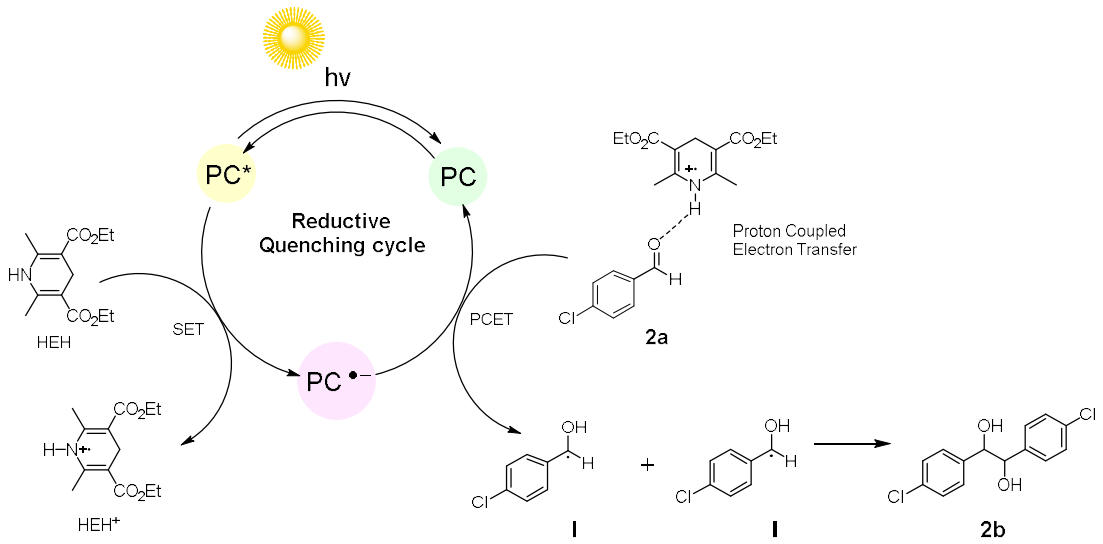
and, the ratio were overall closed to meso:dl = 1:1 (**6b - 9b**). However, In the case of *p*-OH and *p*-OMe substituted benzaldehydes were taken longer time than other (15h ~ 16h) and we assume that because they have high reduction potential (**7b - 8b**). In case of electron deficient groups, yields were excellent (96% ~ 99%) in time from 3h to 5h, and the ratio were overall closed to meso:dl = 1:1 (**10b - 13b**). Not only *para* substituted benzaldehyde but also *ortho*, *meta* substituted benzaldehydes were proceeded well (**14b - 17b**). The yields were still excellent (96% ~ 99%) in reaction time from 3h to 6h, and the ratio were overall closed to meso:*dl* = 1:1. Unfortunately, In the case of heteroaryl aldehydes, the yield was decreased and reactions were completed in 3h, and the ratio were overall closed to meso:*dl* = 1:1 (**18b - 19b**). In conclusion of TLC monitoring, we were noticed that starting materials were decomposed. Di- or tri-substituted benzaldehyde also provided vicinal diol products in good yields (**20b – 22b**) Acetophenone and valerophenone, which are ketone moieties, provided vicinal diol products in good yields (**23b - 24b**), but took a longer reaction time than the benzaldehyde substitutes cases (20h ~ 24h). Benzophenone moieties were provided excellent yields of vicinal diol products in time from 6h to 9h (**25b - 27b**).

Scheme 1. Substrate scope of photoredox catalyzed Pinacol coupling



d. Plausible mechanism for a photoredox catalyzed Pinacol coupling.

A plausible mechanism has been postulated in **Scheme 2**. Initially, the photocatalyst is excited by blue LEDs irradiation. Then, oxidation of Hantzsch ester by the excited photoredox catalyst (4CzIPN*) produces cation radical species ($HEH^{\bullet+}$) and at the same time photoredox catalyst is reduced to $4CzIPN^{\bullet-}$. This cation radical species ($HEH^{\bullet+}$) helps to generate ketyl radical species **I** by proton coupled electron transfer (PCET) from benzaldehyde **2a**. Generating ketyl radical **I**, photoredox catalyst ($4CzIPN^{\bullet-}$) is oxidized to its original state (4CzIPN) and reductive quenching cycle is completed. Then, generated ketyl radical **I** proceeds radical homocoupling by themselves and provide vicinal diol products **2b.**



Scheme 2. The plausible mechanism for a photoredox catalyzed Pinacol coupling

4. Conclusion

In conclusion, we have developed photoredox catalyzed pinacol coupling with 4CzIPN in water. The radical coupling reaction tolerates various functional groups and provides good to excellent yields under metal-free conditions. We proposed a reaction mechanism that involves proton coupled electron transfer (PCET) that generates ketyl radicals. The vicinal diol products are obtained by homocoupling ketyl radicals. The developed reaction is efficient, economical and environmentally friendly method because of using cheap and safe water as solvent.

5. Experiment section

a. General Information

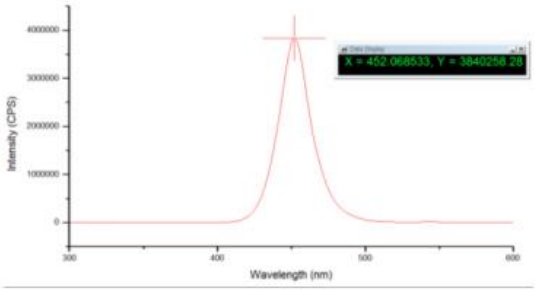
All reactions were run under an atmosphere of argon under anhydrous conditions unless otherwise indicated. Tertiary distilled water is used as a solvent. Ethyl acetates were purchased from Dae-jung chemical company and degassed by the bubbling of nitrogen gas for 30 minutes. Pressure tubes (13 x 100 mm, PYREXPLUS, and 50 mL flask, purchased from Chem Glass) were dried in an oven for overnight and cooled under a stream of nitrogen prior to use. All commercial reagents were used directly without further purification.

The progress of the reaction was checked on TLC plates (Merck 5554 Kiesel gel 60 F254), and the spots were visualized under 254 nm UV light and/or charring after dipping the TLC plate into a PMA (Phosphomolybdic Acid) stain solution (10 g of phosphomolybdic acid in 100 mL of absolute ethanol). Column chromatography was performed on silica gel (Merck 9385 Kiesel gel 60) using hexanes: EtOAc (v/v).

b. Reaction Setup

Irradiation of photochemical reactions was carried out using two MR16 5W blue LED spotlight lamp for milligram scale reaction. The pictures utilized spotlight lamps and their description are given below:

MR16 5W blue LED spotlight lamp



Emission spectrum of 5W blue LED

	Specification
Power	5 W
Voltage	12 V
Wavelength	452 nm

Figure S1A. Description for 5 W blue LED spotlight lamp

For milligram scale reactions, two MR16 10W blue LEDs spotlight lamp are positioned 3 cm away from the reaction vial using a customized reactor that was made by acrylic plate.

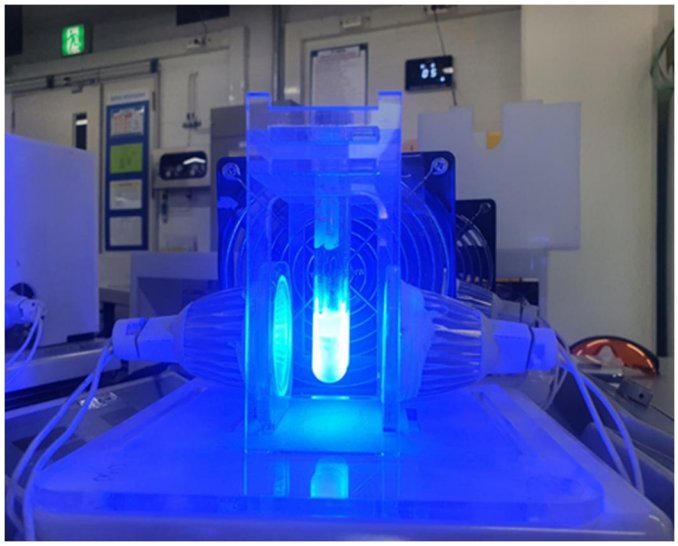


Figure S2. Milligram scale reaction set up

In the optimized reaction conditions, the reaction is not significantly affected by temperature. The fan was used or not used according to the external temperature to maintain 20 ~ 30 ºC in the reactor.

c. Reagent

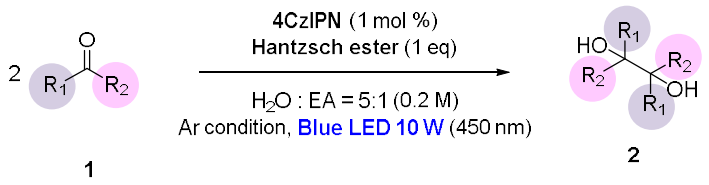
All reactions were run under an atmosphere of argon under anhydrous conditions unless otherwise indicated. Tertiary distilled water is used as a solvent. Ethyl acetates were purchased from Dae-jung chemical company and degassed by the bubbling of nitrogen gas for 30 minutes. Pressure tubes (13 x 100 mm, PYREXPLUS, and 50 mL

flask, purchased from Chem Glass) were dried in an oven for overnight and cooled under a stream of nitrogen prior to use. All commercial reagents were used directly without further purification.

The progress of the reaction was checked on TLC plates (Merck 5554 Kiesel gel 60 F254), and the spots were visualized under 254 nm UV light and/or charring after dipping the TLC plate into a PMA (Phosphomolybdic Acid) stain solution (10 g of phosphomolybdic acid in 100 mL of absolute ethanol). Column chromatography was performed on silica gel (Merck 9385 Kiesel gel 60) using hexanes: EtOAc (v/v).

d. Synthesis of compound.

- General procedure and data for a photoredox catalyzed Pincol coupling reaction



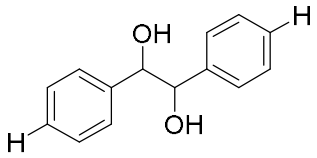
To a re-sealable pressure tube (13 x 100 mm) with a tiny magnetic stir bar was charged with **1** (0.4 mmol, 1.0 equiv.) and 4CzIPN (0.004 mmol, 1.0 mol %) under argon atmosphere. Then, degassed solvents (2 mL, 0.1 M for **1**) of Tertiary distilled water/EtOAc in a ratio of 5:1 was added to that pressure tube. The resultant light yellow heterogenious mixture was irradiating with 2 x 5 W blue LEDs using our customized milligram scale reaction set up under constant stirring condition at room

for optimal time (3h ~ 24h). After finishing the stipulated time, the solvent was removed under reduced pressure and residue was purified by flash column chromatography on silica gel to afford the corresponding vicinal diol product **2**.

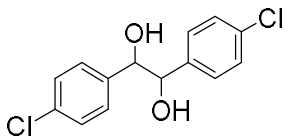
If there is the case that TLC spots of Hantzsch ester and vicinal diol product are the same or similar, we dissolved crude in acetonitrile and kept it in photoreactor again for minutes until it gets transparent. Then, the Hantzsch ester would be oxidized to Hantzsch pyridine and the spot move to the upper side to get easily separated from the vicinal diol product.

e. ^{1}H, ^{13}C NMR Spectrum analysis

1,2-diphenylethane-1,2-diol (1b)



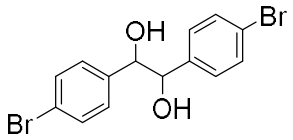
Following the general procedure using 25% ethyl acetate in hexanes as eluant, **1b** was obtained as a white solid (42.4 mg, 100% yield) meso:dl (1:1.3) ; R_f = 0.4 (ethyl acetate:hexanes, 1:2); 1H NMR (300 MHz, Chloroform-d) δ 7.38 – 7.23 (m, 16H, *meso* and *dl*), 7.19 – 7.12 (m, 1.3 x 4H, *dl*), 4.86 (s, 2H, *meso*), 4.73 (s, 1.3x 2H, *dl*).; 13C NMR (75 MHz, CDCl3) δ 139.83, 139.76, 128.27, 128.15, 127.96, 127.10, 126.95, 79.13, 78.12.



1,2-bis(4-chlorophenyl)ethane-1,2-diol (2b).

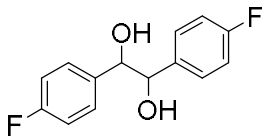
Following the general procedure using 25% ethyl acetate in hexanes as eluant, **2b** was obtained as a yellowish white solid (51mg, 90% yield) meso:dl (1.2:1) ; R_f= 0.4 (ethyl acetate:hexanes, 1:2); 1H NMR (300 MHz, Chloroform-d) δ 7.31 – 7.18 (m, 8H, meso : dl = 1.2:1), 7.12 – 7.05 (m, 4H, meso), 7.04 – 6.97 (m, 4H, dl), 4.81 (s, 2H, meso),

4.59 (s, 2H, dl).; 13C NMR (75 MHz, CDCl3) δ 137.94, 137.79, 133.88, 128.41, 128.38, 128.35, 78.57, 77.17.



1,2-bis(4-bromophenyl)ethane-1,2-diol (3b).

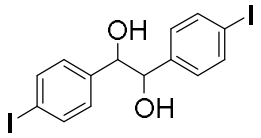
Following the general procedure using 25% ethyl acetate in hexanes as eluant, **3b** was obtained as a white solid (64 mg, 86% yield) meso:dl (1:1) ; Rf = 0.2 (ethyl acetate : hexanes, 1:3); 1H NMR (300 MHz, Chloroform-d) δ 7.47 – 7.42 (m, 4H, meso), 7.42 – 7.36 (m, 4H, dl), 7.10 – 7.04 (m, 4H, meso), 7.02 – 6.95 (m, 4H, dl), 4.84 (s, 2H, meso), 4.62 (s, 2H, dl).; 13C NMR (75 MHz, CDCl3) δ 138.44, 138.29, 131.36, 131.29, 128.72, 128.69, 122.07, 78.52, 77.16.



1,2-bis(4-fluorophenyl)ethane-1,2-diol (4b).

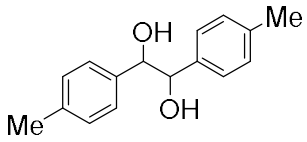
Following the general procedure using 30% ethyl acetate in hexanes as eluant, **4b** was obtained as a colorless liquid (49 mg, 98% yield) meso:dl (1:1.1); R_f = 0.3 (ethyl acetate : hexanes, 1:2).; 1H NMR (300 MHz, Chloroform-d) δ 7.22 – 7.13 (m, 4H, meso), 7.11 – 7.03 (m, 4H, dl), 7.03 – 6.97 (m, 4H, meso), 6.97 – 6.89 (m, 4H, dl),

4.85 (s, 2H, meso), 4.64 (s, 2H, dl), 3.00 (s, 2H, meso), 2.40 (s, 2H, dl).; 13C NMR (75 MHz, CDCl3) δ 164.12, 164.04, 160.86, 160.78, 135.36, 135.32, 135.20, 135.16, 128.75, 128.69, 128.64, 128.58, 115.23, 114.95, 78.74, 77.26.



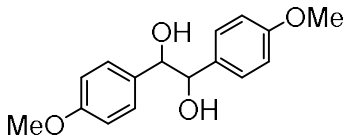
1,2-bis(4-iodophenyl)ethane-1,2-diol (5b).

Following the general procedure using 25% ethyl acetate in hexanes as eluant and acetone, **5b** was obtained as a white solid (84 mg, 90% yield) meso:dl (1:1) ; R_f= 0.35 (ethyl acetate : hexanes, 1:5); 1H NMR (300 MHz, Acetone-d6) δ 7.66 – 7.61 (m, 4H, meso), 7.61 – 7.57 (m, 4H, dl), 7.14 – 7.06 (m, 4H, meso), 7.05 – 6.97 (m, 4H, dl), 4.78 (dd, J = 2.8, 1.3 Hz, 2H, meso), 4.75 – 4.72 (m, 2H, dl), 4.70 (dd, J = 2.8, 1.3 Hz, 2H, meso), 4.60 – 4.54 (m, 2H, dl).; 13C NMR (75 MHz, Acetone-d6) δ 142.09, 141.60, 136.61, 136.46, 129.65, 129.49, 92.13, 91.94, 77.70, 76.95.



1,2-di-p-tolylethane-1,2-diol (6b).

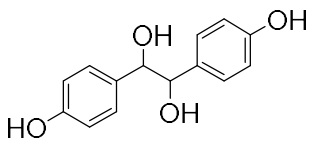
Following the general procedure using 20% ethyl acetate in hexanes as eluant, **6b** was obtained as a white solid (47 mg, 97% yield, meso:dl = 1:1.1) ; R_f= 0.35 (ethyl acetate : hexanes, 1:2); 1H NMR (300 MHz, Chloroform-d) δ 7.22 – 7.11 (m, 8H, meso), 7.10 – 6.99 (m, 1.1 x 8H, dl), 4.74 (s, 2H, meso), 4.64 (s, 1.1 x 2H, dl), 2.37 (s, 6H, meso), 2.33 (s, 1.1 x 6H, dl).; 13C NMR (75 MHz, CDCl3) δ 137.78, 137.46, 137.02, 137.00, 128.99, 128.82, 127.08, 126.90, 78.79, 78.02, 21.22, 21.19.



1,2-bis(4-methoxyphenyl)ethane-1,2-diol (7b).

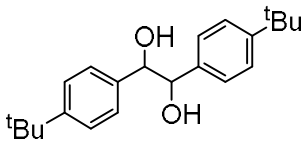
Following the general procedure using 20% ethyl acetate in hexanes as eluant, **7b** was obtained as a white solid (52 mg, 94% yield, meso:dl = 1:1.1); R_f = 0.20 (ethyl acetate:hexanes, 1:3); 1H NMR (300 MHz, Chloroform-d) δ 7.26 – 7.20 (m, 4H, meso), 7.09 – 7.03 (m,1.1 x 4H, dl), 6.91 – 6.85 (m, 4H, meso), 6.82 – 6.75 (m, 1.1 x 4H, dl), 4.76 (s, 2H, meso), 4.65 (s, 1.1 x 2H, dl), 3.83 (s, 6H, meso), 3.81 – 3.77 (m, 1.1 x 6H,

dl), 2.85 (s, 2H), 2.14 (s, 1.1 x 2H, dl).; 13C NMR (75 MHz, CDCl3) δ 159.44, 159.16, 132.06, 132.01, 128.35, 128.17, 113.71, 113.50, 78.81, 77.81, 55.29, 55.21.



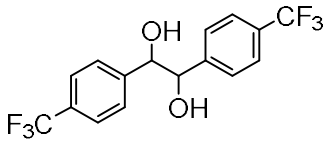
1,2-bis(4-hydroxyphenyl)ethane-1,2-diol (8b)

Following the general procedure using 40% acetone in hexanes as eluant, **8b** was obtained as a white solid (44 mg, 90% yield, meso:dl=1:1.2); R_f = 0.15 (acetone:hexanes, 1:1); 1H NMR (300 MHz, DMSO-d6) δ 9.16 (s, meso and dl 4H), 7.04 – 6.96 (m, 1.2 x 4H, meso), 6.86 – 6.79 (m, 4H, dl), 6.66 – 6.58 (m, 1.2 x 4H, meso), 6.57 – 6.49 (m, 4H, dl), 5.12 (s, 2H, dl), 4.91 (s, 2H, meso), 4.40 (s, 2H, meso), 4.36 (s, 2H, dl).; 13C NMR (75 MHz, DMSO) δ 156.41, 134.16, 133.09, 128.81, 128.70, 114.56, 114.47, 78.17, 77.22.



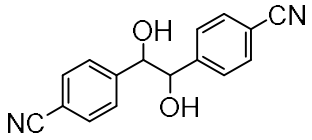
1,2-bis(4-(tert-butyl)phenyl)ethane-1,2-diol (9b).

Following the general procedure using 15% ethyl acetate in hexanes as eluant, **9b** was obtained as a white solid (58 mg, 89% yield, meso:dl = 1.3:1); R_f = 0.30 (ethyl acetate:hexanes, 1:3); 1H NMR (300 MHz, Chloroform-d) δ 7.45 – 7.39 (m, 4H), 7.38 – 7.29 (m, 8H, meso and dl), 7.22 – 7.15 (m, 4H), 4.78 (s, 1.3 x 2H, meso), 4.74 (s, 2H,dl), 1.35 (s, 18H), 1.32 (s, 18H).; 13C NMR (75 MHz, CDCl3) δ 151.30, 150.79, 137.34, 137.28, 126.91, 126.43, 125.45, 125.14, 78.19, 78.12, 34.61, 34.52, 31.35.



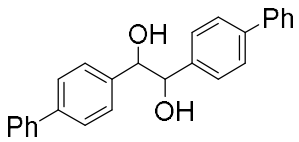
1,2-bis(4-(trifluoromethyl)phenyl)ethane-1,2-diol (10b).

Following the general procedure using 25% ethyl acetate in hexanes as eluant, **10b** was obtained as a colorless liquid (69 mg, 99% yield, meso:dl=1:1.1); 1H NMR (300 MHz, Chloroform-d) δ 7.54 (m, J = 8.0 Hz, 4H meso and 4H dl), 7.30 (d, J = 6.9 Hz, 4H, meso), 7.23 (d, J = 8.0 Hz, 4H, dl), 4.97 (s, 2H, meso), 4.75 (s, 2H, dl).; ^{13}C NMR (75 MHz, Chloroform-*d*) δ 143.29, 143.13, 130.63 (C-F, $2J_{C\text{-}F}$ = 32.4 Hz), 130.51 (C-F, $2J_{C\text{-}F}$ = 32.3 Hz), 127.33, 127.28, 125.26 (C-F, $3J_{C\text{-}F}$ =3.8 Hz), 125.06 (C-F, $3J_{C\text{-}F}$ = 3.7 Hz), 122.20 (C-F, $1J_{C\text{-}F}$ = 272.2 Hz), 122.17 (d, J = 4.7 Hz), 118.88 (d, J = 43.8 Hz), 78.38, 77.15.



4,4'-(1,2-dihydroxyethane-1,2-diyl)dibenzonitrile (11b).

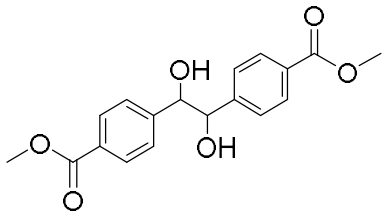
Following the general procedure using 50% acetone in hexanes as eluant, **11b** was obtained as a yellowish solid (51 mg, 96% yield, meso:dl=1:1); R_f = 0.50 (ethyl acetate:hexanes, 1:1); 1H NMR (300 MHz, DMSO-d6) δ 7.74 (d, J = 8.2 Hz, 6H, dl), 7.69 (d, J = 8.2 Hz, 6H, meso), 7.42 (d, J = 8.2 Hz, 4H, dl), 7.34 (d, J = 8.2 Hz, 4H, meso), 5.78 (s, 2H, meso), 5.73 (s, 2H, dl), 4.82 (s, 2H, meso), 4.68 (s, 2H, dl).; 13C NMR (75 MHz, DMSO) δ 148.91, 148.22, 131.86, 131.70, 128.75, 128.43, 119.54, 119.52, 110.08, 109.95, 76.59, 76.39.



1,2-di([1,1'-biphenyl]-4-yl)ethane-1,2-diol (12b).

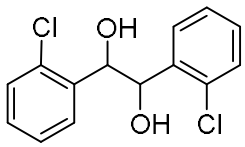
Following the general procedure using 20% ethyl acetate in hexanes and acetone as eluents, **12b** was obtained as a white solid (73 mg, 100% yield, meso:dl = 1.2:1); R_f= 0.2 (ethyl acetate:hexanes, 1:2); 1H NMR (300 MHz, DMSO-d6) δ 7.77 – 7.24 (m, 18H meso and 1.2 x 18H dl), 5.50 (s, 2H, meso), 5.39 (s, 1.2 x 2H, dl), 4.75 (s, 2H, meso), 4.69 (s, 1.2 x 2H, dl).; 13C NMR (75 MHz, DMSO) δ 143.28, 142.26, 140.65,

140.43, 139.01, 138.90, 129.40, 129.37, 128.53, 128.32, 127.70, 127.00, 126.95, 126.16, 126.08, 77.60, 77.28.



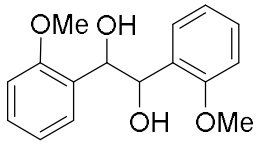
dimethyl 4,4'-(1,2-dihydroxyethane-1,2-diyl)dibenzoate (13b).*

Following the general procedure using 50% ethyl acetate in hexanes and MeOH as solvents, **13b** was obtained as a white solid (65 mg, 99% yield, meso:dl=1:1); R_f= 0.1 (ethyl acetate:hexanes, 1:1); 1H NMR (300 MHz, DMSO-d6) δ 7.86 (d, J = 8.0 Hz, 4H, dl), 7.79 (d, J = 8.1 Hz, 4H, meso), 7.38 (d, J = 8.1 Hz, 4H, dl), 7.26 (d, J = 8.1 Hz, 4H, meso), 5.69 (s, 2H, meso), 5.58 (s, 2H, dl), 4.78 (s, 2H, meso), 4.71 (s, 2H, dl), 3.84 (s, 6H, dl), 3.82 (s, 6H, meso).; 13C NMR (75 MHz, DMSO) δ 166.74, 166.69, 148.94, 148.17, 128.77, 128.66, 128.55, 128.48, 128.08, 127.82, 77.11, 76.90, 52.46, 52.44.



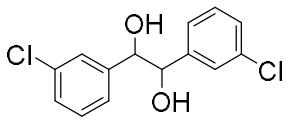
1,2-bis(2-chlorophenyl)ethane-1,2-diol (14b).

Following the general procedure using 20% ethyl acetate in hexanes as eluant, **14b** was obtained as a transparent yellow liquid (55 mg, 97% yield, meso:dl=1:1); R_f = 0.35 (ethyl acetate:hexanes, 1:2); 1H NMR (300 MHz, Chloroform-d) δ 7.69 (dd, J = 7.6, 1.7 Hz, 2H, dl), 7.36 – 7.15 (m, 6H meso and 8H dl), 5.62 (s, 2H, meso), 5.38 (s, 2H, dl), 2.52 (br s, 2H meso and 2H dl).; 13C NMR (75 MHz, CDCl3) δ 137.24, 136.39, 133.40, 132.63, 129.49, 129.20, 129.13, 128.91, 128.84, 128.76, 126.86, 126.47, 73.01, 72.12.



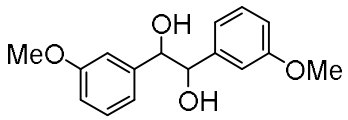
1,2-bis(2-methoxyphenyl)ethane-1,2-diol (15b).

Following the general procedure using 20% ethyl acetate in hexanes as eluant, **15b** was obtained as a colorless liquid (54 mg, 99% yield); R_f= 0.30 (ethyl acetate:hexanes, 1:2); 1H NMR (300 MHz, Chloroform-d) δ 7.27 – 7.16 (m, 4H meso and 1.1 x 4H dl), 6.94 – 6.74 (m, 4H meso and 1.1 x 4H dl), 5.28 (s, 2H, meso), 5.06 (s, 1.1 x 2H, dl), 3.69 (s, 6H, meso), 3.66 (s, 1.1 x 6H dl), 3.60 (s, 1.1 x 2H, dl), 3.25 (s, 2H, meso).; 13C NMR (75 MHz, CDCl3) δ 156.95, 156.89, 128.58, 128.53, 128.49, 128.43, 128.26, 120.46, 110.20, 74.44, 73.54, 55.27, 55.23.



1,2-bis(3-chlorophenyl)ethane-1,2-diol (16b).

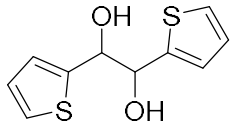
Following the general procedure using 25% ethyl acetate in hexanes as eluant, **16b** was obtained as a yellowish solid (54 mg, 96% yield meso:dl=1:1.2); R_f= 0.30 (ethyl acetate:hexanes, 1:4); 1H NMR (300 MHz, Chloroform-d) δ 7.32 – 7.14 (m, 6H meso and 1.2 x 6H dl), 7.06 (dt, J = 7.3, 1.6 Hz, 2H, meso), 6.92 (dt, J = 7.6, 1.4 Hz, 1.2 x 2H, dl), 4.81 (s, 2H, meso), 4.64 (s, 1.2 x 2H, dl), 2.59 (s, 2H meso and 1.2 x 2H dl).; 13C NMR (75 MHz, CDCl3) δ 141.57, 141.49, 134.27, 134.24, 129.45, 129.44, 128.33, 127.18, 126.95, 125.27, 125.22, 78.32, 77.21.



1,2-bis(3-methoxyphenyl)ethane-1,2-diol (17b).

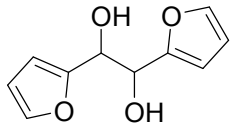
Following the general procedure using 25% ethyl acetate in hexanes as eluant, **17b** was obtained as a colorless liquid (54 mg, 99% yield, meso:dl=1:1.1); R_f= 0.25 (ethyl acetate:hexanes, 1:2); 1H NMR (300 MHz, Chloroform-d) δ 7.27 (t, J = 7.7 Hz, 2H, meso), 7.19 (t, J = 8.2 Hz, 1.1 x 2H, dl), 6.96 – 6.70 (m, 6H meso and 1.1 x 6H dl), 4.81 (s, 2H, meso), 4.72 (s, 1.1 x 2H, dl), 3.78 (s, 6H, meso), 3.75 (s, 6H, dl), 2.83 (s, 2H, dl), 2.22 (s, 2H, meso).; 13C NMR (75 MHz, CDCl3) δ 159.41, 159.30, 141.61,

141.42, 129.15, 129.09, 119.49, 119.34, 113.86, 113.61, 112.33, 112.27, 78.85, 77.86, 55.19, 55.17.



1,2-di(thiophen-2-yl)ethane-1,2-diol (18b).

Following the general procedure using 20% acetone in hexanes as eluant, **18b** was obtained as a brown liquid (28 mg, 62% yield, meso:dl=1:1.2); R_f = 0.25 (acetone:hexanes, 2:1); 1H NMR (300 MHz, Chloroform-d) δ 7.31 (dd, J = 5.0, 1.4 Hz, 2H, meso), 7.27 (dd, J = 5.0, 1.2 Hz, 1.5 x 2H, dl), 7.04 (dd, J = 3.5, 1.3 Hz, 2H, meso), 7.00 (dd, J = 5.0, 3.5 Hz, 2H, meso), 6.93 (dd, J = 5.0, 3.5 Hz, 1.5 x 2H, dl), 6.83 (dd, J = 3.5, 1.2 Hz, 1.5 x 2H, dl), 5.13 (s, 2H, meso), 5.05 (s, 1.5 x 2H, dl), 3.21 (s, 1.5 x 2H, dl), 2.68 (s, 2H, meso).; 13C NMR (75 MHz, CDCl3) δ 142.85, 142.47, 126.66, 126.63, 126.09, 125.92, 125.70, 125.45, 74.96, 74.41.

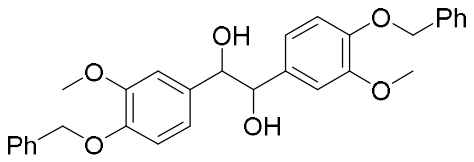


1,2-di(furan-2-yl)ethane-1,2-diol (19b).

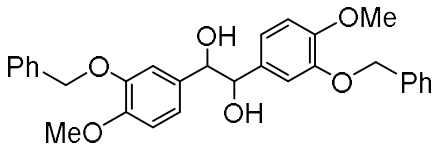
Following the general procedure using 15% ethyl acetate in hexanes as eluant, **19b** was obtained as a transparent yellow liquid (15.5 mg, 40% yield, meso:dl=1:1.3); R_f=

0.5 (ethyl acetate:hexanes, 1:2); 1H NMR (300 MHz, Chloroform-d) δ 7.42 (dd, J = 1.9, 0.8 Hz, 2H, meso), 7.38 (dd, J = 1.8, 0.9 Hz, 1.3 x 2H, dl), 6.36 (dd, J = 3.3, 1.8 Hz, 2H, meso), 6.34 – 6.30 (m, 1.3 x 2H dl and 2H meso), 6.28 (dd, J = 3.3, 0.9 Hz, 1.3 x 2H, dl), 5.05 (s, 2H, meso), 5.03 (s, 1.3 x 2H, dl), 2.93 (s, 1.3 x 2H, dl), 2.59 (s, 2H, meso).; 13C NMR (75 MHz, CDCl3) δ 152.72, 152.53, 142.51, 142.45, 110.44, 110.34, 108.29, 108.03, 70.10, 69.86.

1,2-bis(4-(benzyloxy)-3-methoxyphenyl)ethane-1,2-diol (20b)



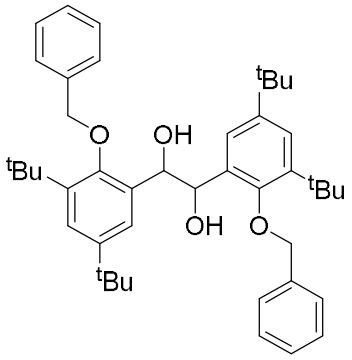
Following the general procedure using 50% ethyl acetate in hexanes as eluant, **20b** was obtained as white solid (79 mg, 81% yield, meso:dl=1.2:1); R_f = 0.35 (ethyl acetate:hexanes, 1:1); 1H NMR (300 MHz, Chloroform-d) δ 7.50 – 7.29 (m, 1.2 x 10H meso and 10H dl), 6.90 – 6.54 (m, 1.2 x 6H meso and 6H dl), 5.17 (s, 1.2 x 4H, meso), 5.13 (s, 4H, dl), 4.71 (s, 1.2 x 2H, meso), 4.59 (s, 2H, dl), 3.82 (s, 1.2 x 6H, meso), 3.76 (s, 6H, dl), 2.85 (br s, 1H, dl), 2.16 (br s, 1.2 x 1H, meso).; 13C NMR (75 MHz, CDCl3) δ 149.46, 149.16, 147.90, 147.58, 137.05, 133.00, 132.88, 128.59, 128.55, 127.89, 127.87, 127.25, 119.51, 119.21, 113.41, 113.37, 110.49, 78.95, 77.89, 70.93, 70.89, 55.93, 55.92.



1,2-bis(3-(benzyloxy)-4-methoxyphenyl)ethane-1,2-diol (21b).

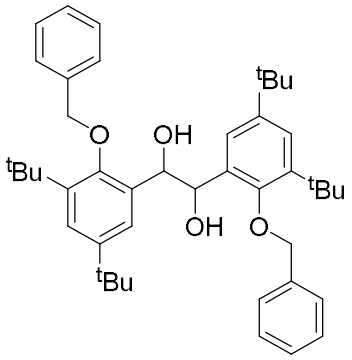
Following the general procedure using 50% ethyl acetate in hexanes as eluant, **21b** was obtained as transparent solid (79 mg, 82% yield, meso:dl=1.1:1); R_f= 0.35 (ethyl acetate:hexanes, 1:1); 1H NMR (300 MHz, Chloroform-d) δ 7.50 – 7.24 (m, 1.1 x 10H meso and 10H dl), 6.87 – 6.74 (m, 1.1 x 2H meso and 4H dl), 6.69 (d, J = 8.2 Hz, 1.1 x 2H, meso), 6.63 (d, J = 2.0 Hz, 2H, dl), 6.51 (dd, J = 8.2, 2.0 Hz, 1.1 x 2H, dl), 5.10 – 4.93 (m, 1.1 x 4H meso and 4H dl), 4.63 (s, 1.1 x 2H, meso), 4.43 (s, 2H, dl), 3.86 (s, 1.1 x 6H, meso), 3.83 (s, 6H, dl).; 13C NMR (75 MHz, CDCl3) δ 149.47, 149.21, 147.94, 147.64, 137.05, 136.99, 132.32, 132.25, 128.54, 127.90, 127.87, 127.47, 127.36, 120.10, 120.05, 112.78, 112.68, 111.26, 111.07, 78.94, 77.71, 70.98, 70.89, 56.02, 55.94

1,2-bis(2-(benzyloxy)-3,5-di-tert-butylphenyl)ethane-1,2-diol, upper spot (meso) (22b)

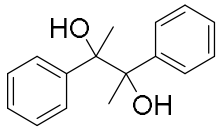


Following the general procedure using 5% Acetone in hexanes as eluant, **22b** was obtained as white solid (58mg, 45% yield, meso); R_f = 0.65 (ethyl acetate:hexanes, 4:1); 1H NMR (300 MHz, Chloroform-d) δ 7.56 (d, J = 6.7 Hz, 4H), 7.50 – 7.32 (m, 10H), 5.33 (s, 2H), 5.19 – 4.96 (m, 4H), 2.24 (s, 2H), 1.46 (s, 18H), 1.25 (s, 18H).; 13C NMR (75 MHz, CDCl3) δ 154.43, 146.76, 142.11, 137.67, 133.52, 128.62, 127.69, 126.60, 124.82, 122.46, 76.71, 72.01, 35.57, 34.65, 31.51, 31.47.

1,2-bis(2-(benzyloxy)-3,5-di-tert-butylphenyl)ethane-1,2-diol, down spot (dl) (22b)

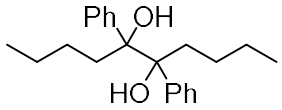


Following the general procedure using 5% Acetone in hexanes as eluant, **22b** was obtained as white solid (58mg, 45% yield, dl); R_f = 0.4 (ethyl acetate:hexanes, 4:1); 1H NMR (300 MHz, Chloroform-d) δ 7.56 (d, J = 6.6 Hz, 4H), 7.50 – 7.34 (m, 6H), 7.24 (d, J = 2.4 Hz, 2H), 7.18 (d, J = 2.4 Hz, 2H), 5.35 (s, 2H), 5.10 – 4.81 (m, 4H), 3.14 (s, 2H), 1.28 (s, 18H), 1.20 (s, 18H).; 13C NMR (75 MHz, CDCl3) δ 153.52, 145.87, 141.37, 137.65, 132.19, 128.51, 127.75, 127.25, 124.34, 122.73, 77.13, 72.93, 35.27, 34.48, 31.41, 31.16.



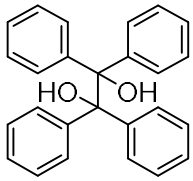
2,3-diphenylbutane-2,3-diol (23b).

Following the general procedure using 10% ethyl acetate in hexanes as eluant, **23b** was obtained as a white solid (48 mg, 99% yield meso:dl=1:1.1); R_f = 0.5 (ethyl acetate:hexanes, 1:4); 1H NMR (300 MHz, Chloroform-d) δ 7.34 – 7.18 (m, 10H meso and 10H dl), 2.59 (br s, 2H, dl), 2.30 (br s, 2H, meso), 1.61 (s, 6H, meso), 1.53 (s, 6H, dl).; 13C NMR (75 MHz, CDCl3) δ 143.76, 143.40, 127.37, 127.31, 127.18, 127.08, 126.92, 78.86, 78.60, 25.13, 24.97.



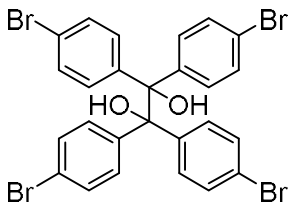
5,6-diphenyldecane-5,6-diol (24b).

Following the general procedure using 5% ethyl acetate in hexanes as eluant, **24b** was obtained as a transparent yellowish sticky liquid (47 mg, 72% yield meso:dl=1:1); R_f = 0.4 (ethyl acetate:hexanes, 1:10); 1H NMR (300 MHz, Chloroform-d) δ 7.35 – 7.11 (m, 10H meso and 10H dl), 2.65 (s, 2H, dl), 2.44 – 2.21 (m, 2H, meso and 2H meso), 2.17 – 1.97 (m, 2H, dl), 1.78 – 1.59 (m, 2H meso and 2H dl), 1.34 – 1.07 (m, 4H meso, 4H dl and 4H meso), 0.94 – 0.71 (m, 4H dl, 4H meso and 4H dl); 13C NMR (75 MHz, CDCl3) δ 141.68, 140.79, 128.21, 127.51, 127.32, 127.11, 126.84, 126.64, 81.70, 81.67, 35.24, 34.81, 25.78, 25.63, 23.25, 23.23, 14.12, 14.10.



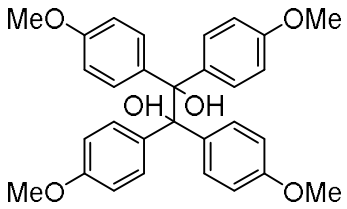
1,1,2,2-tetraphenylethane-1,2-diol (25b).

Following the general procedure using 5% ethyl acetate in hexanes as eluant, **25b** was obtained as a white solid (73 mg, % yield); R_f= 0.35 (ethyl acetate:hexanes, 1:10); 1H NMR (300 MHz, Chloroform-d) δ 7.41 – 7.32 (m, 8H), 7.28 – 7.18 (m, 12H), 3.11 (s, 2H).; 13C NMR (75 MHz, CDCl3) δ 144.21, 128.67, 127.37, 127.02, 83.07.



1,1,2,2-tetrakis(4-bromophenyl)ethane-1,2-diol (26b).

Following the general procedure using 3% ethyl acetate in hexanes as eluant, **26b** was obtained as a white solid (131 mg, 96% yield); R_f = 0.5 (ethyl acetate:hexanes, 1:5); 1H NMR (300 MHz, Chloroform-d) δ 7.37 – 7.30 (m, 8H), 7.20 – 7.13 (m, 8H), 2.92 (s, 2H).; 13C NMR (75 MHz, CDCl3) δ 142.47, 130.73, 130.22, 121.83, 82.53.

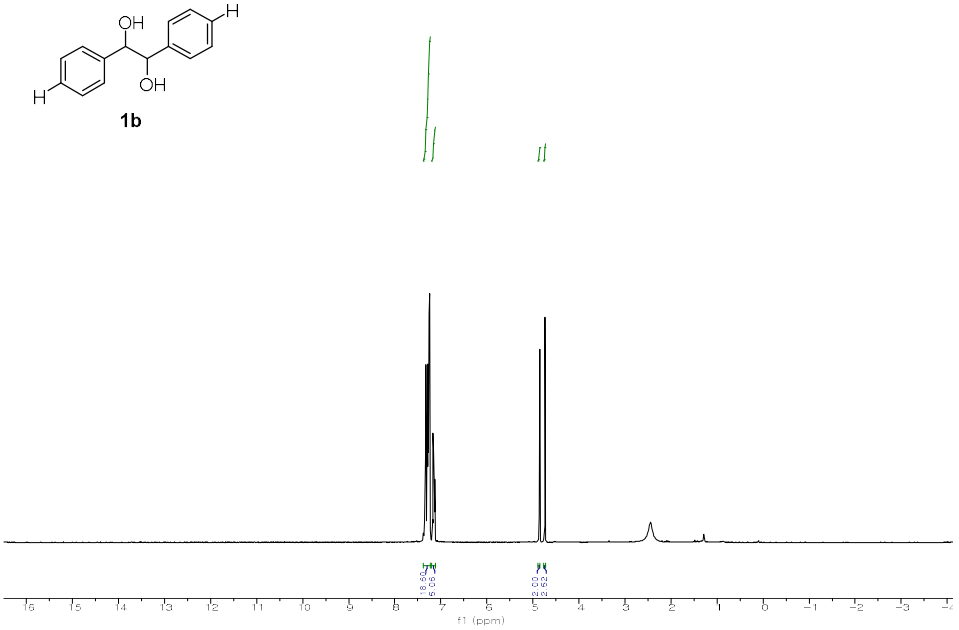


1,1,2,2-tetrakis(4-methoxyphenyl)ethane-1,2-diol (27b).

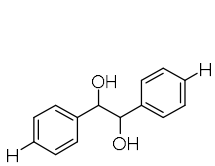
Following the general procedure using 10% ethyl acetate in hexanes as eluant, **27b** was obtained as a yellow solid (92 mg, 95% yield); R_f = 0.50 (ethyl acetate:hexanes, 1:2); 1H NMR (300 MHz, Chloroform-d) δ 7.23 (d, J = 8.4 Hz, 8H), 6.73 (d, J = 8.5 Hz, 8H), 3.78 (s, 12H), 2.99 (s, 2H).; 13C NMR (75 MHz, CDCl3) δ 158.21, 136.75, 129.87, 112.51, 82.73, 55.15.

.e. ^{1}H, ^{13}C NMR Spectrum

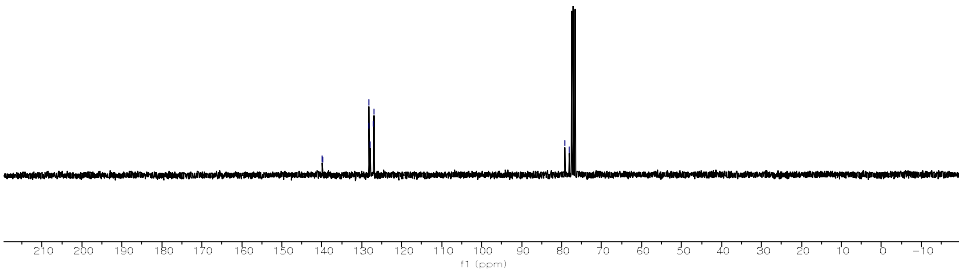
1b



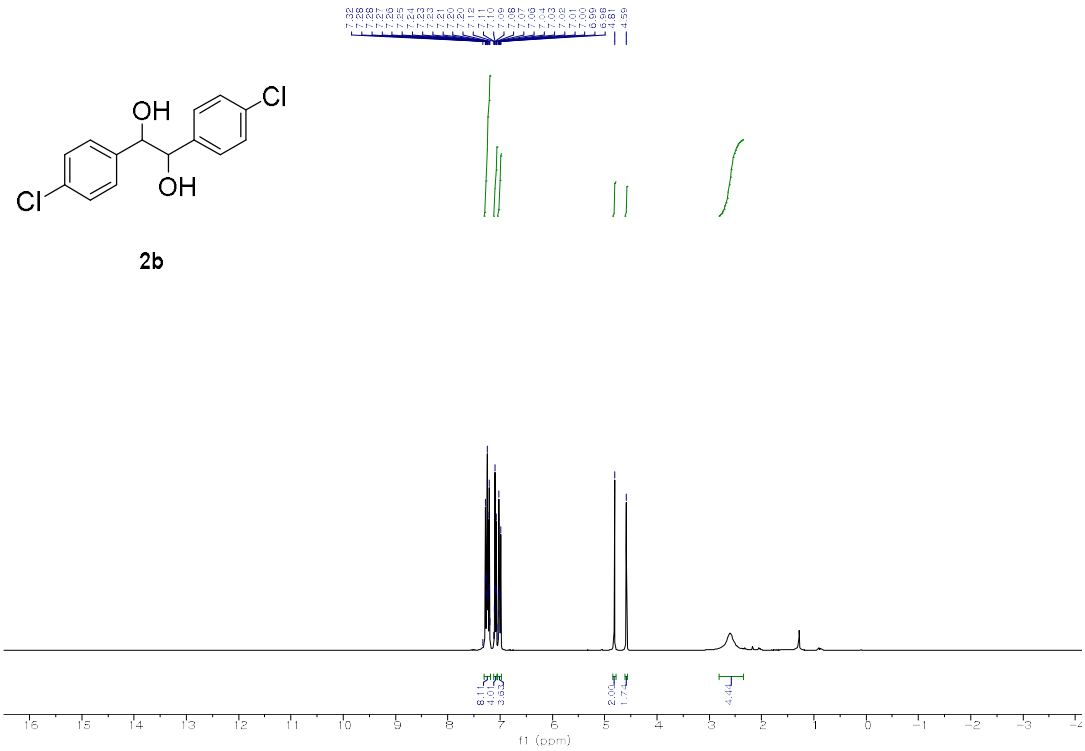
^{1}H-NMR (300 MHz, $CDCl_3$) of **1b**



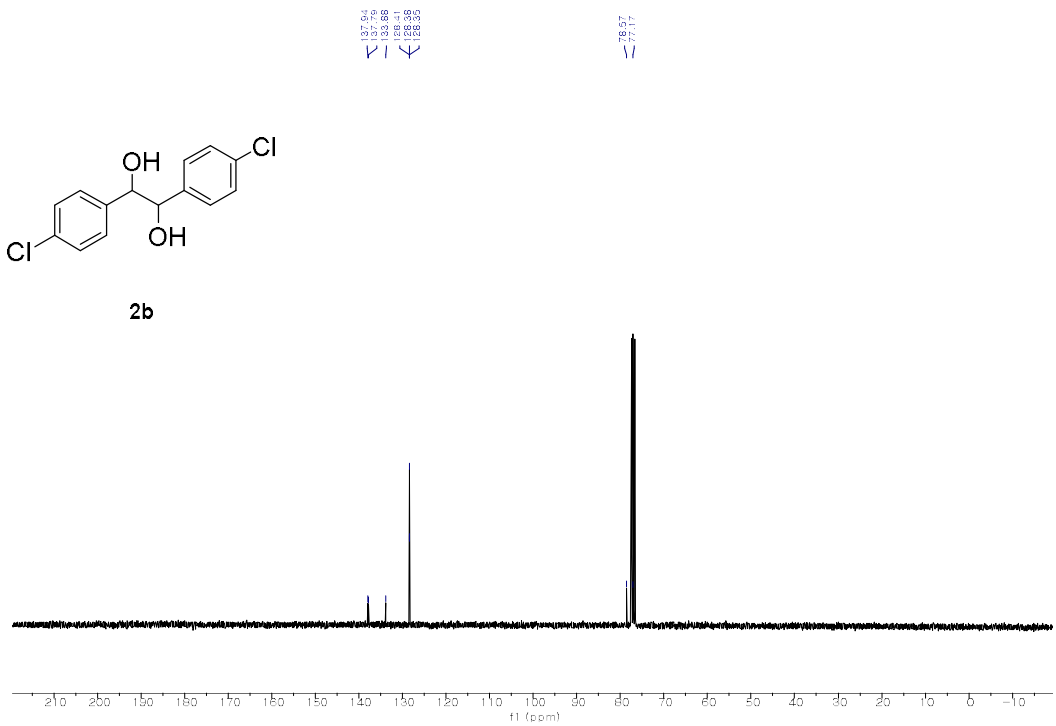
1b



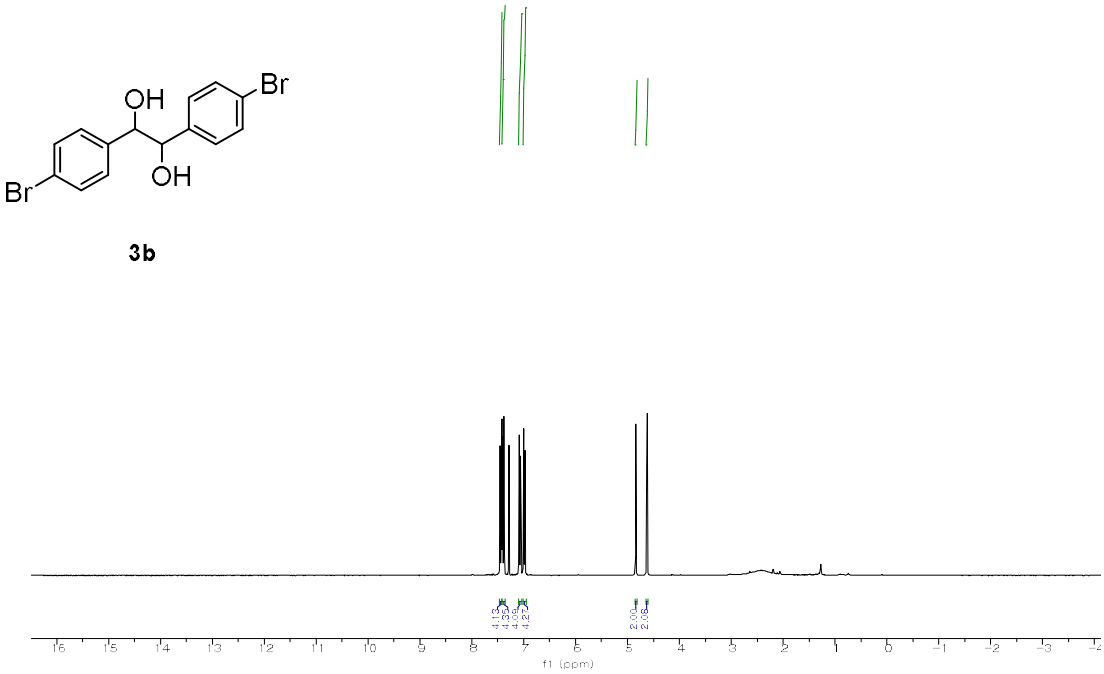
^{13}C-NMR (75Hz, $CDCl_3$) of **1b**



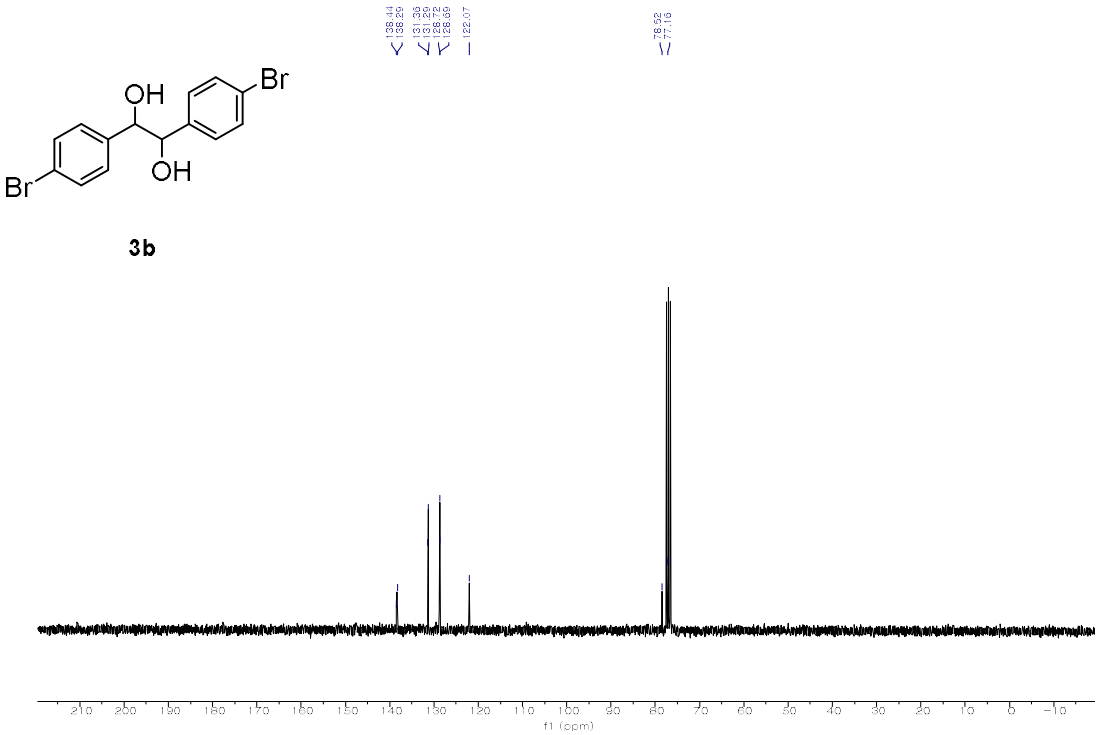
^{1}H-NMR (300 MHz, $CDCl_3$) of **2b**



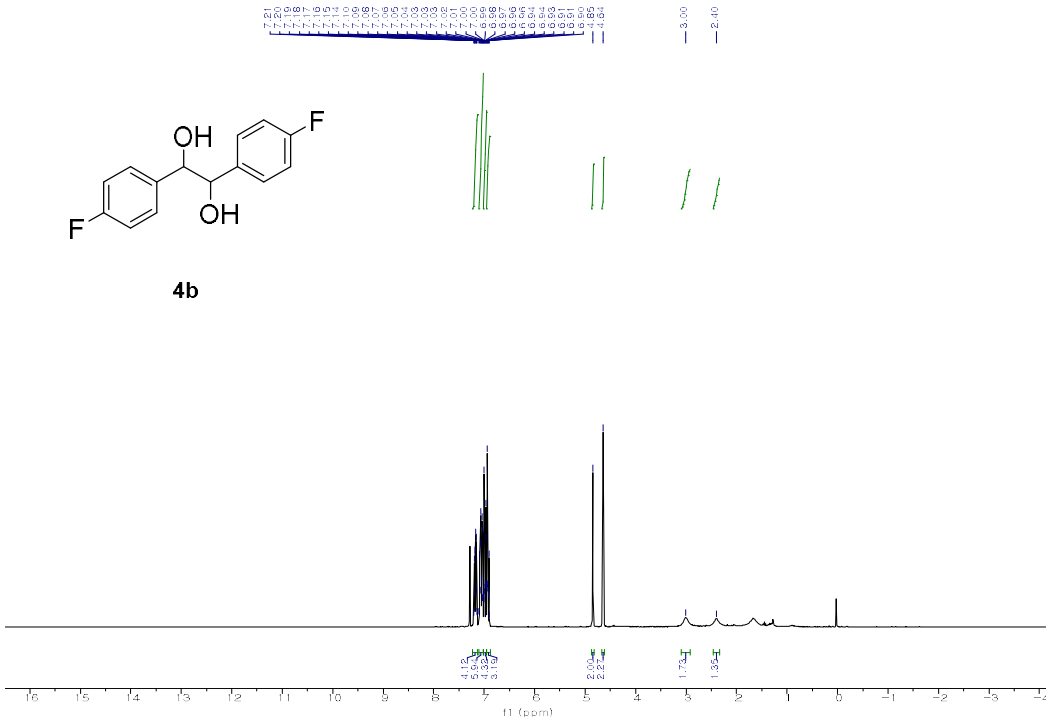
^{13}C-NMR (75Hz, $CDCl_3$) of **2b**



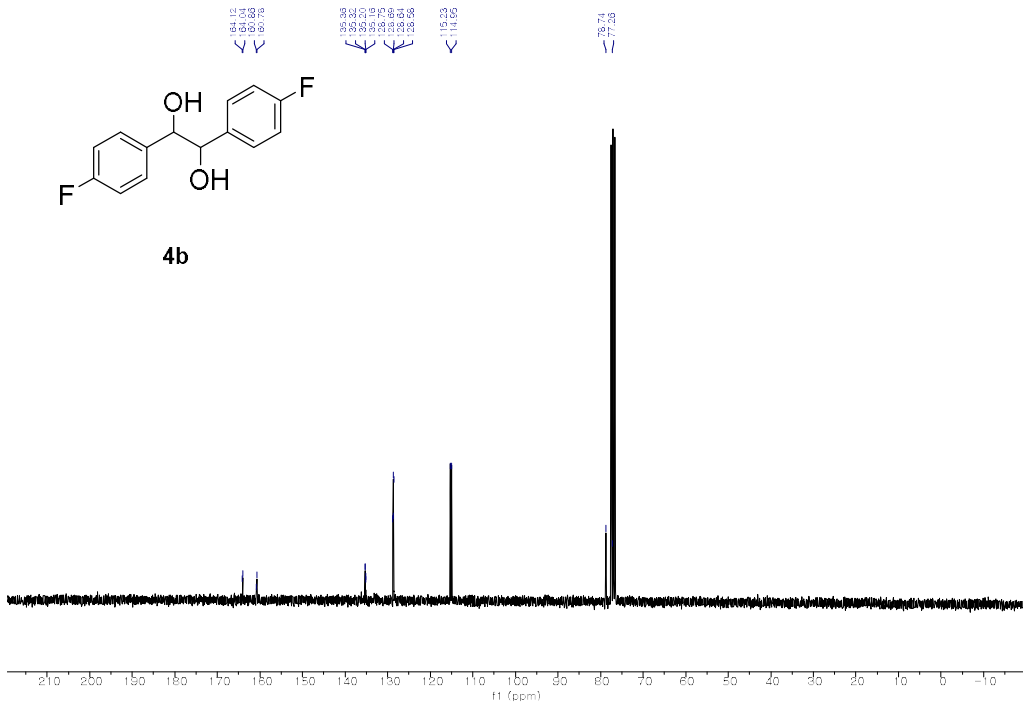
^{1}H-NMR (300 MHz, $CDCl_3$) of **3b**



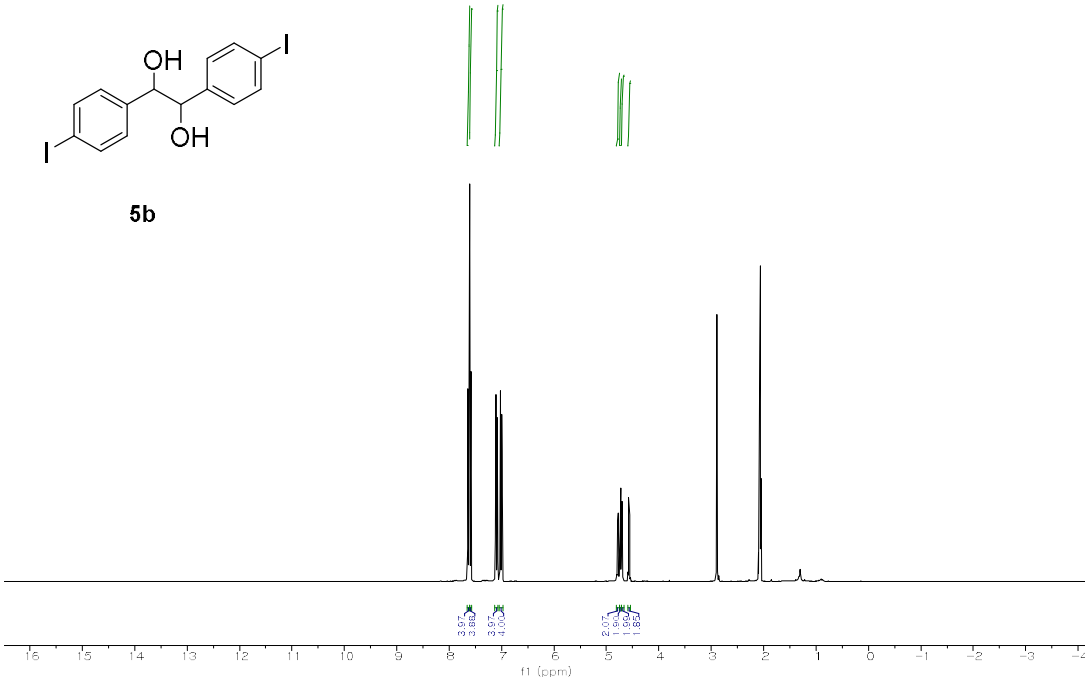
^{13}C-NMR (75Hz, $CDCl_3$) of **3b**



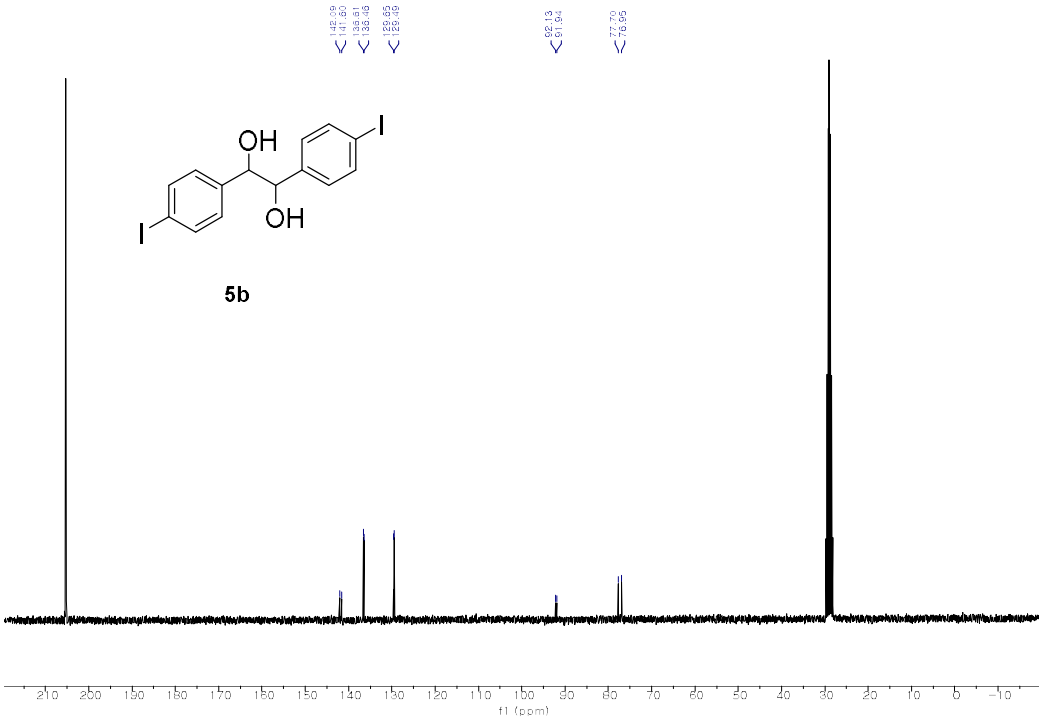
^{1}H-NMR (300 MHz, $CDCl_3$) of **4b**



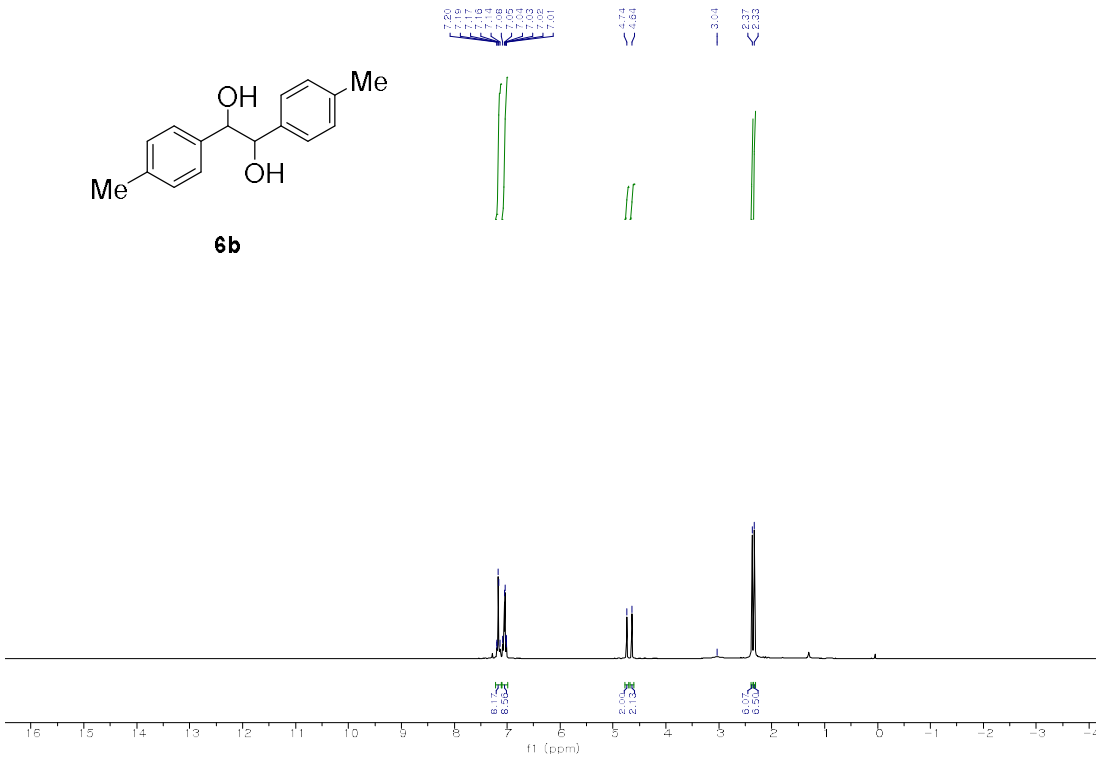
^{13}C-NMR (75Hz, $CDCl_3$) of **3b**



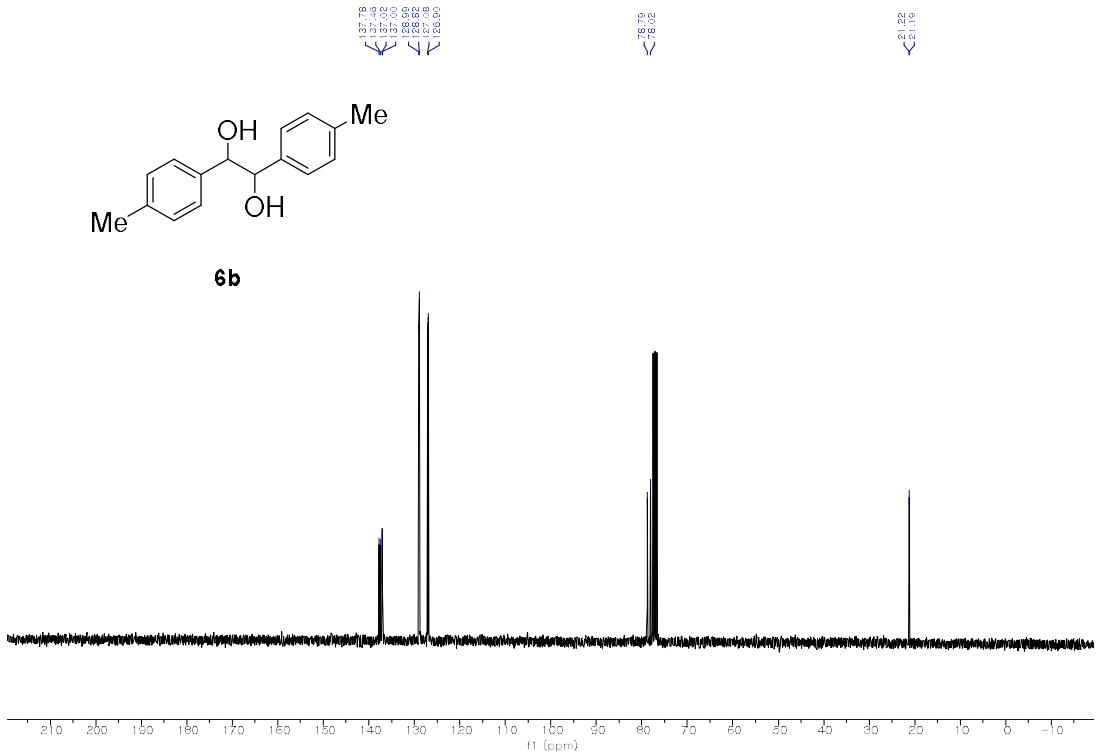
^{1}H-NMR (300 MHz, Acetone-d6) of **5b**



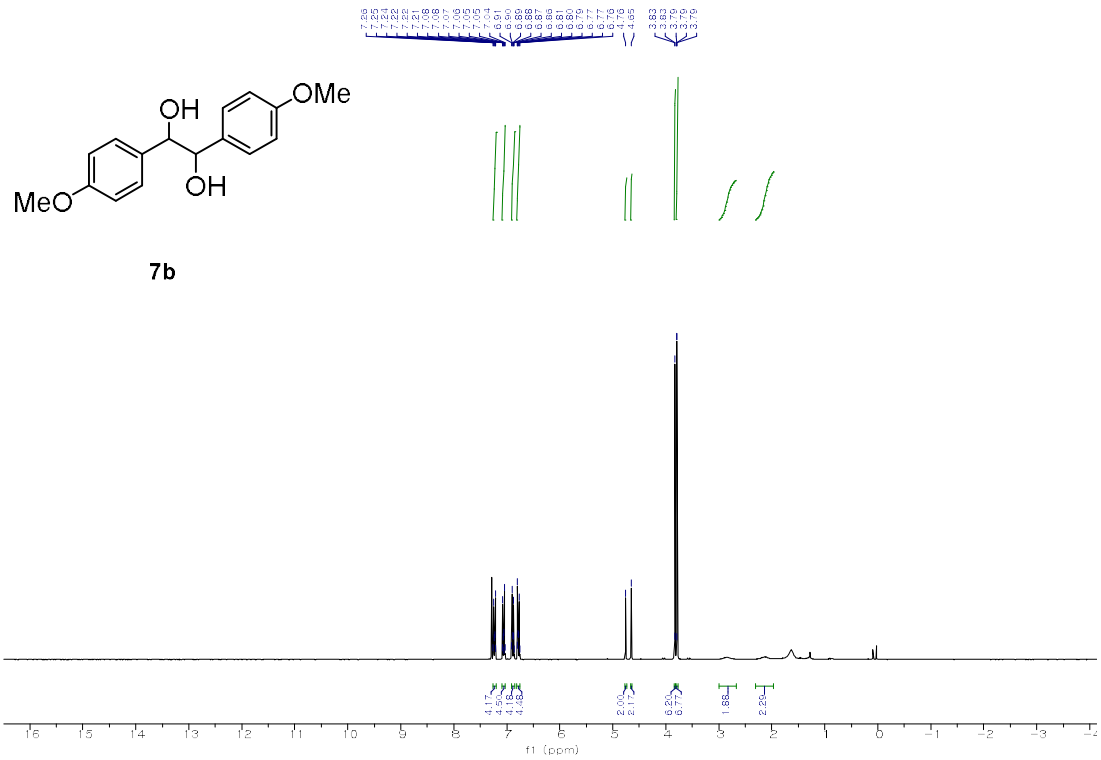
^{13}C-NMR (75Hz, Acetone-d6) of **5b**



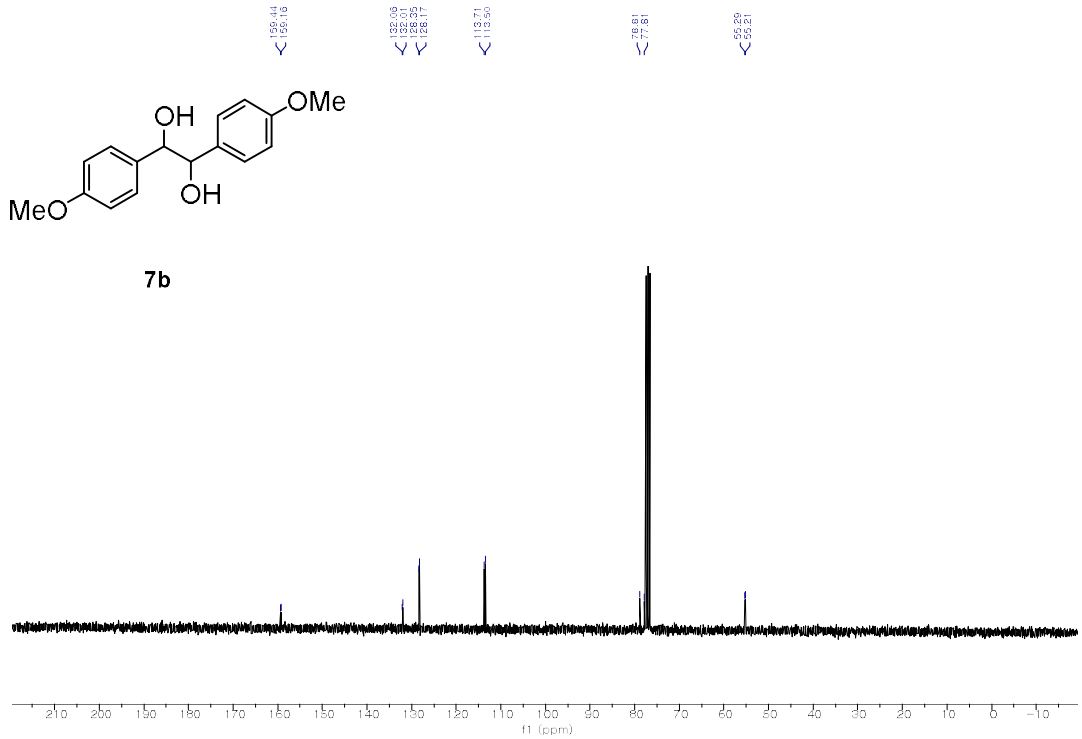
^{1}H-NMR (300 MHz, $CDCl_3$) of 6**b**



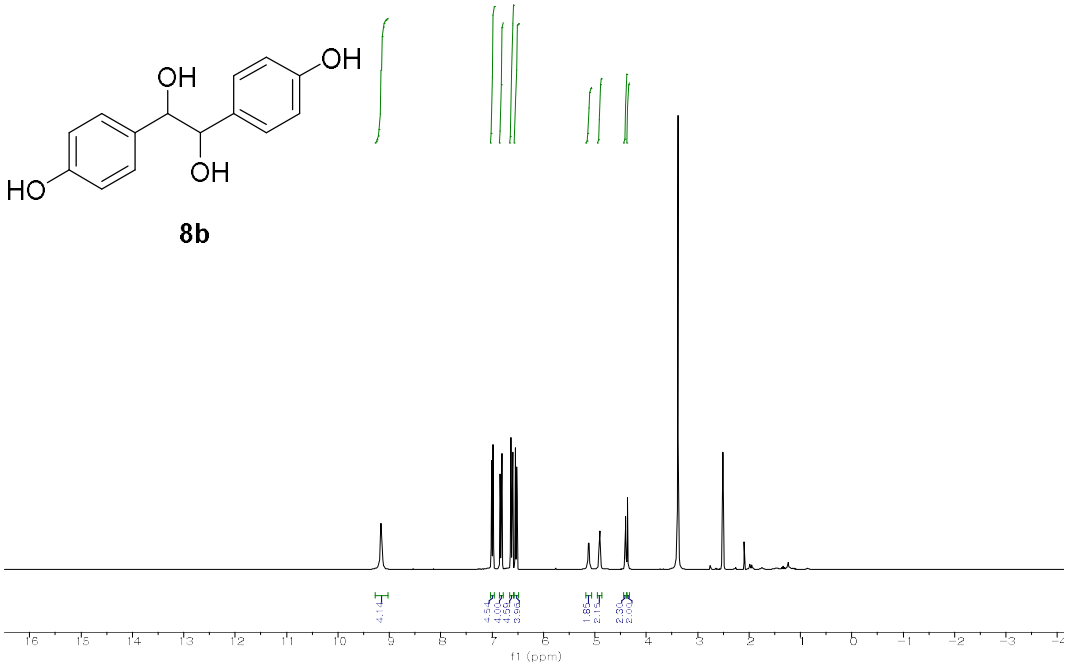
^{13}C-NMR (75Hz, $CDCl_3$) of 6**b**



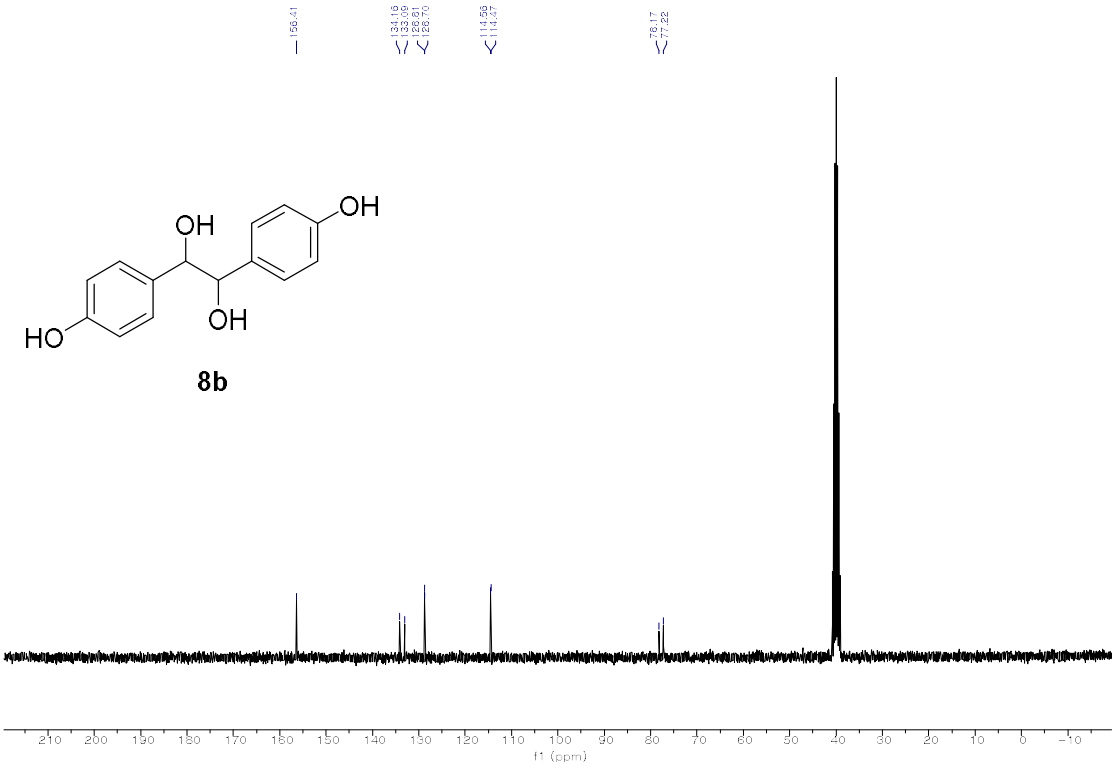
^{1}H-NMR (300 MHz, $CDCl_3$) of **7b**



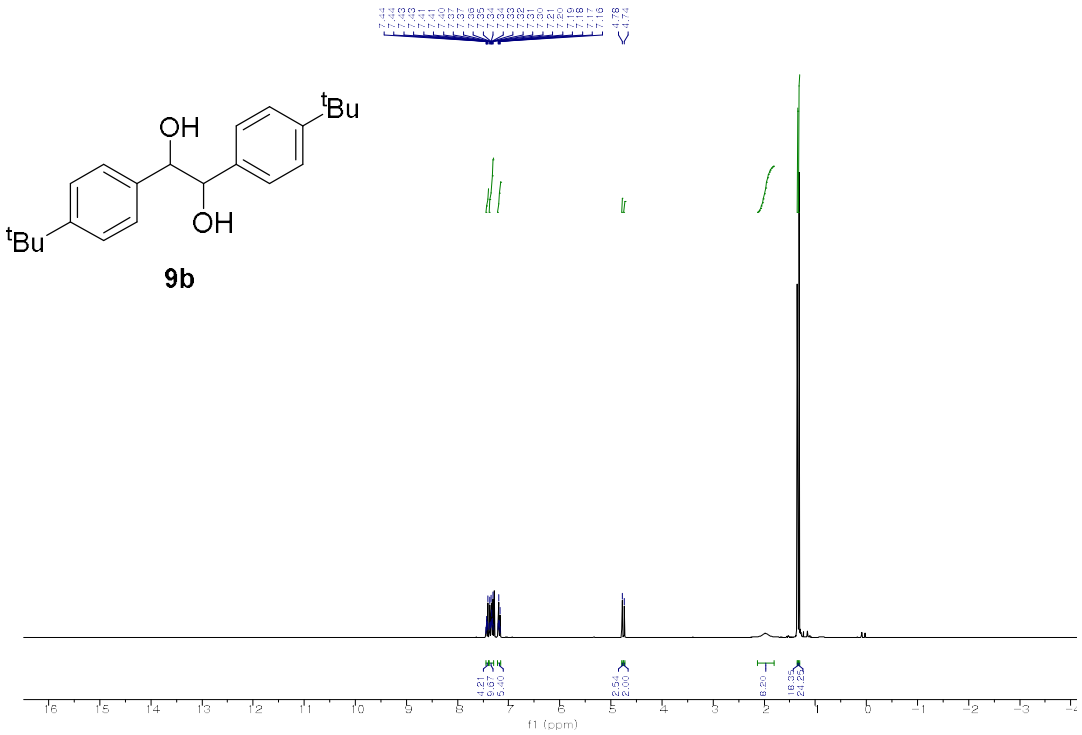
^{13}C-NMR (75Hz, $CDCl_3$) of **7b**



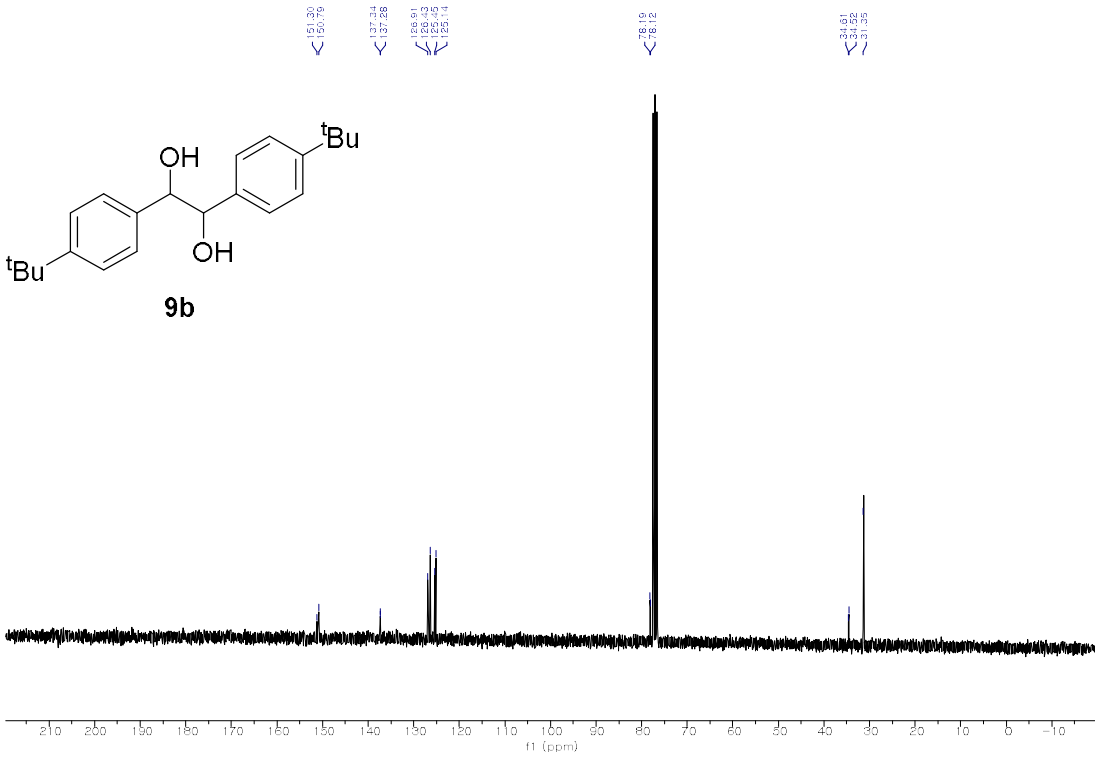
^{1}H-NMR (300 MHz, DMSO-d6) of **8b**



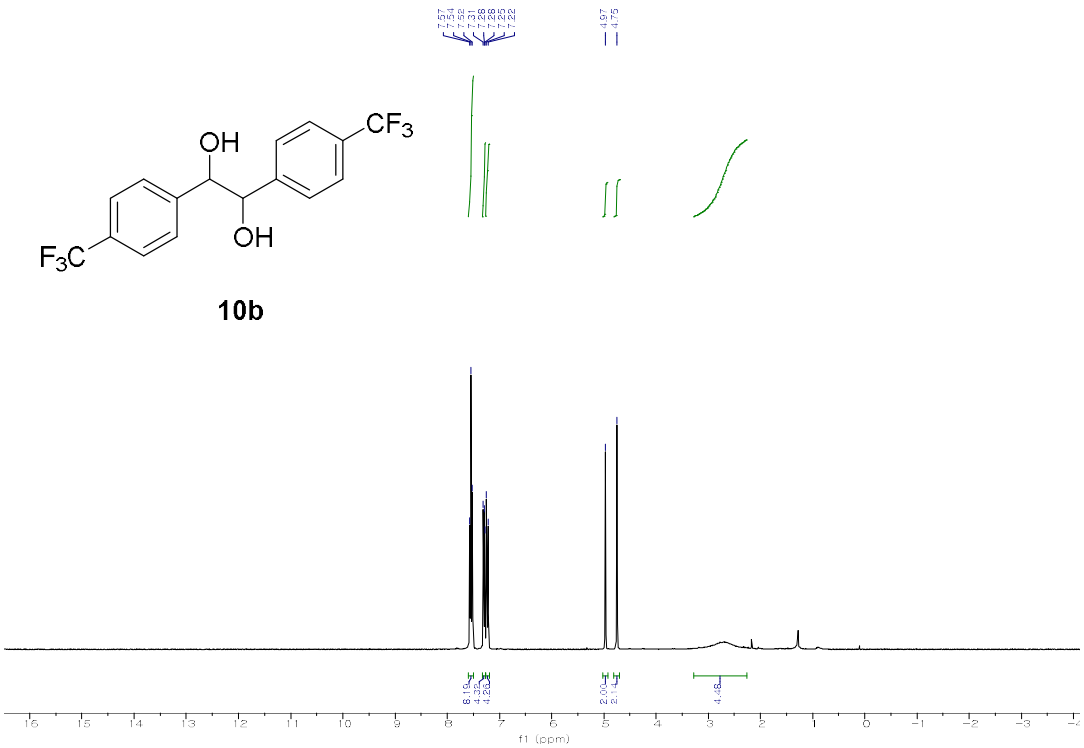
^{13}C-NMR (75Hz, DMSO-d6) of **8b**



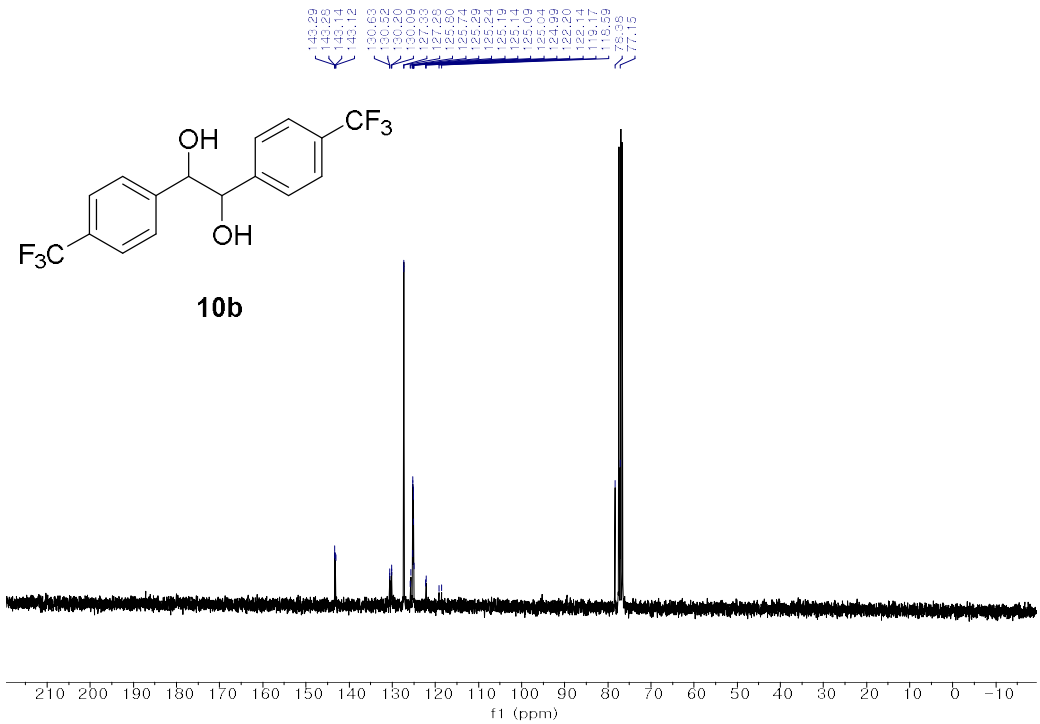
^{1}H-NMR (300 MHz, $CDCl_3$) of **9b**



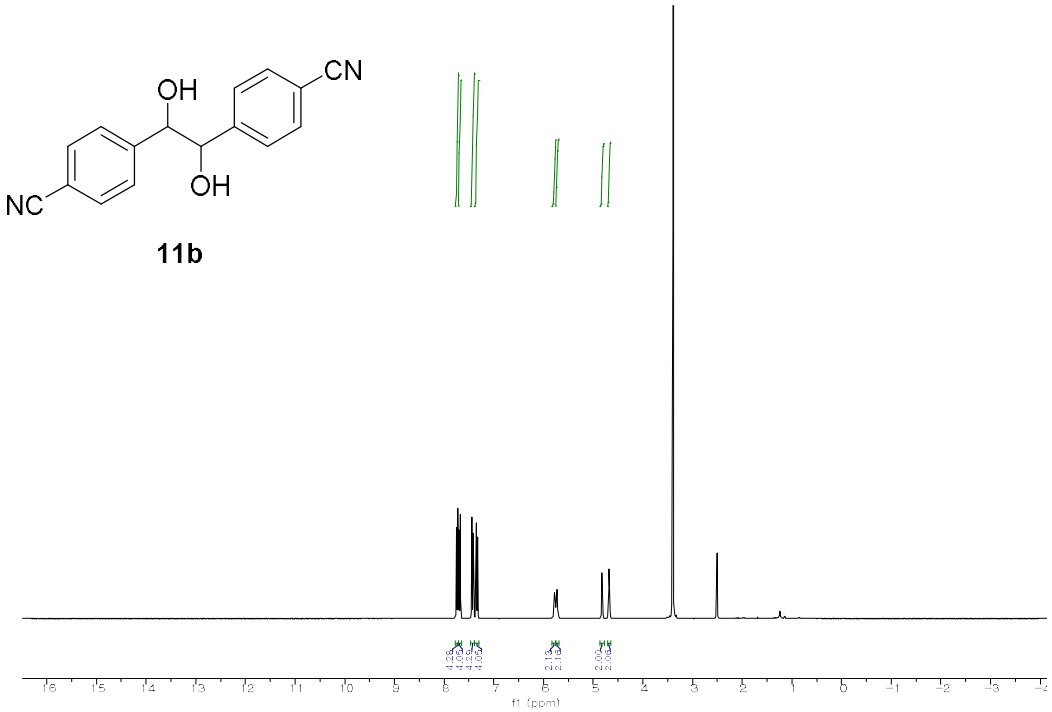
^{13}C-NMR (75Hz, $CDCl_3$) of 9**b**



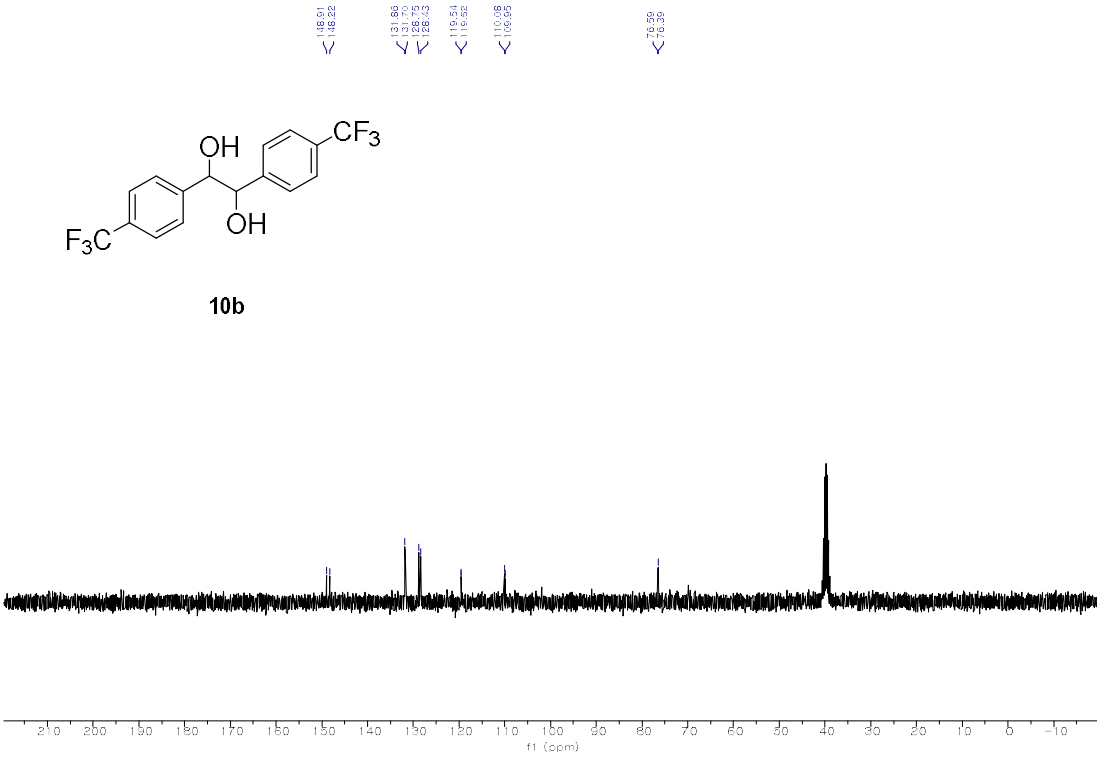
^{1}H-NMR (300 MHz, $CDCl_3$) of **10b**



^{13}C-NMR (75Hz, $CDCl_3$) of **10b**



^{1}H-NMR (300 MHz, DMSO-d6) of **11b**



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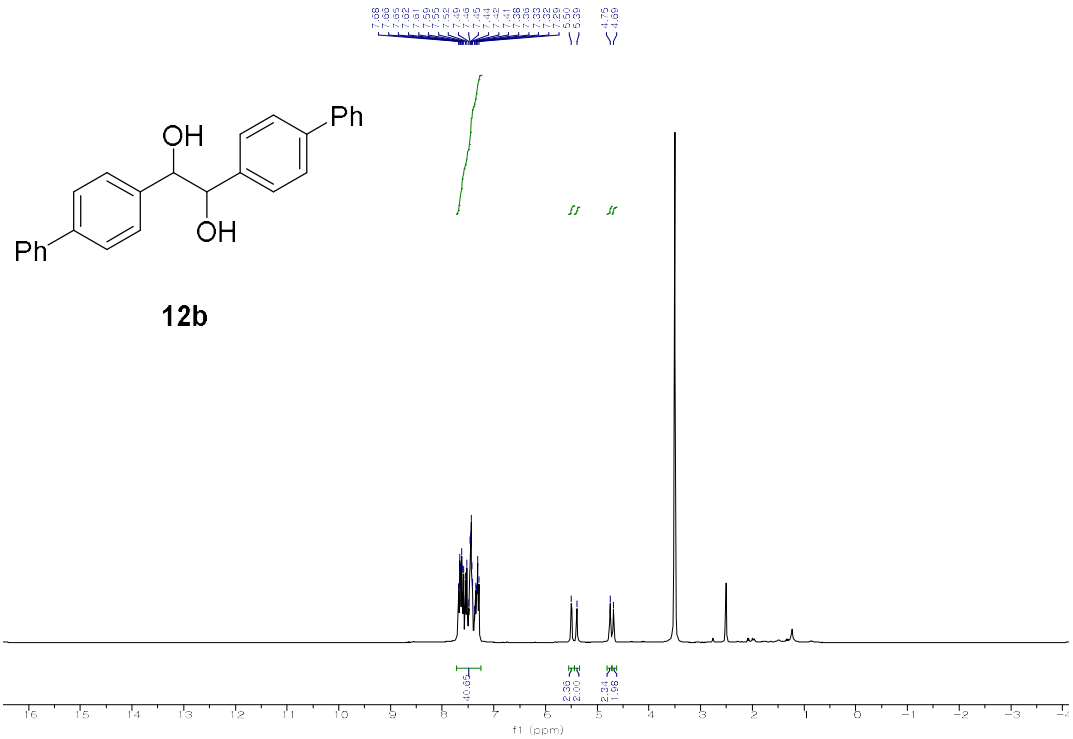
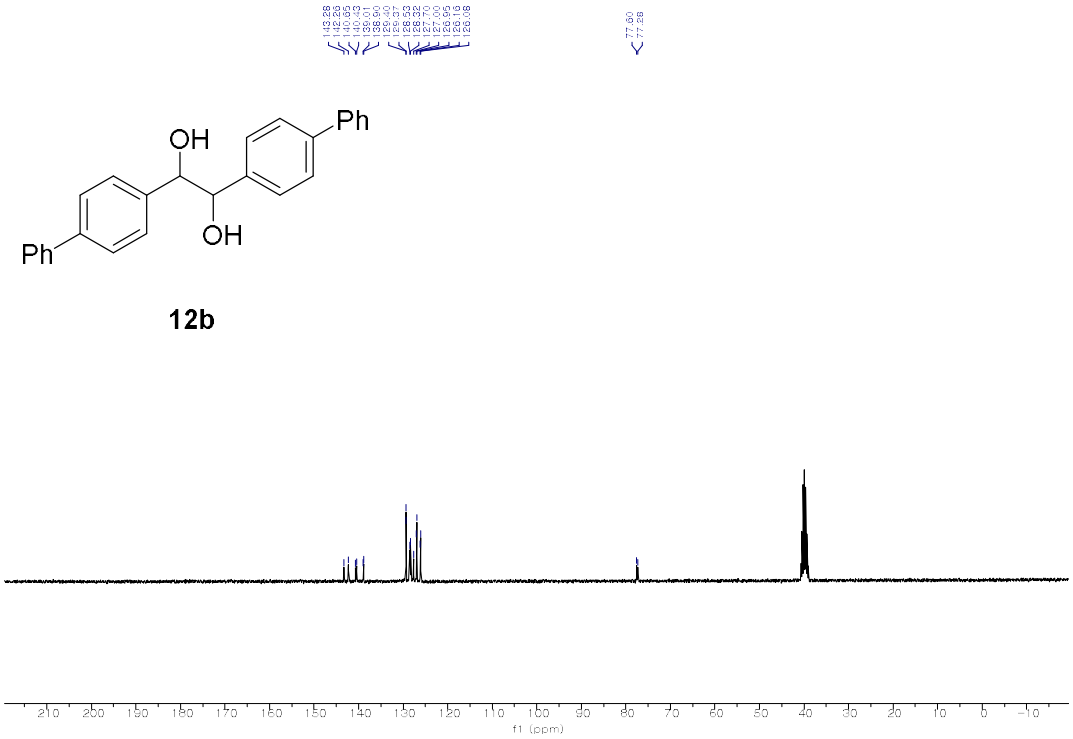


^{1}H-NMR (300 MHz, DMSO-d6) of **12b**



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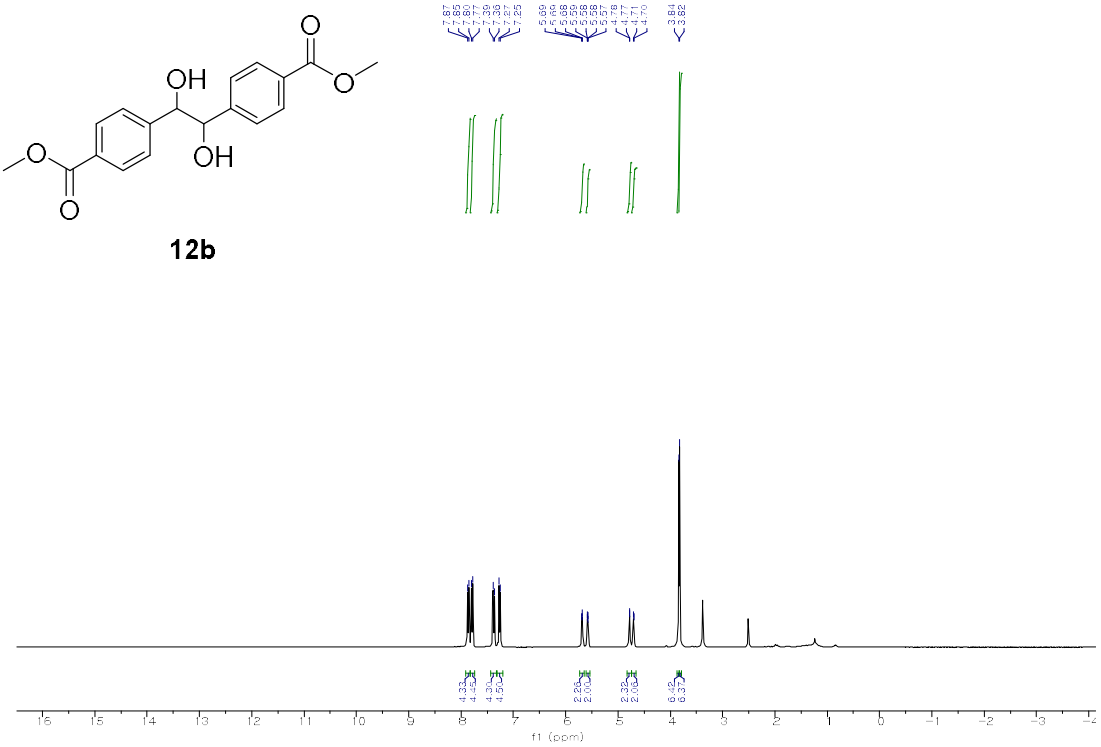

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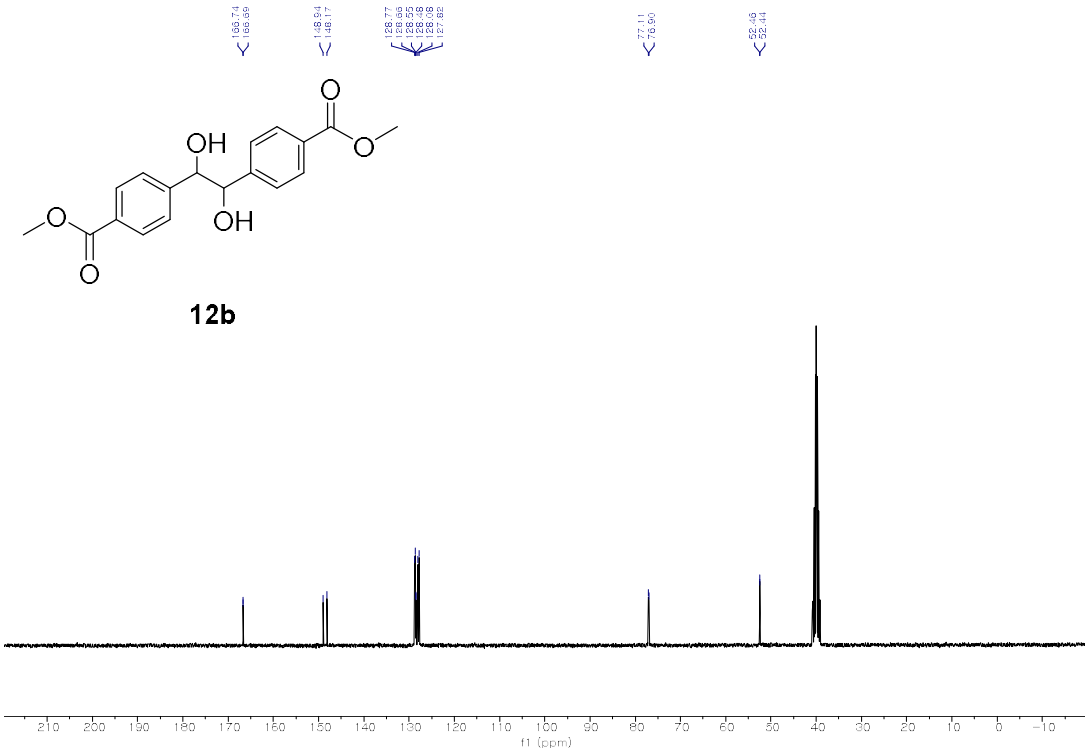
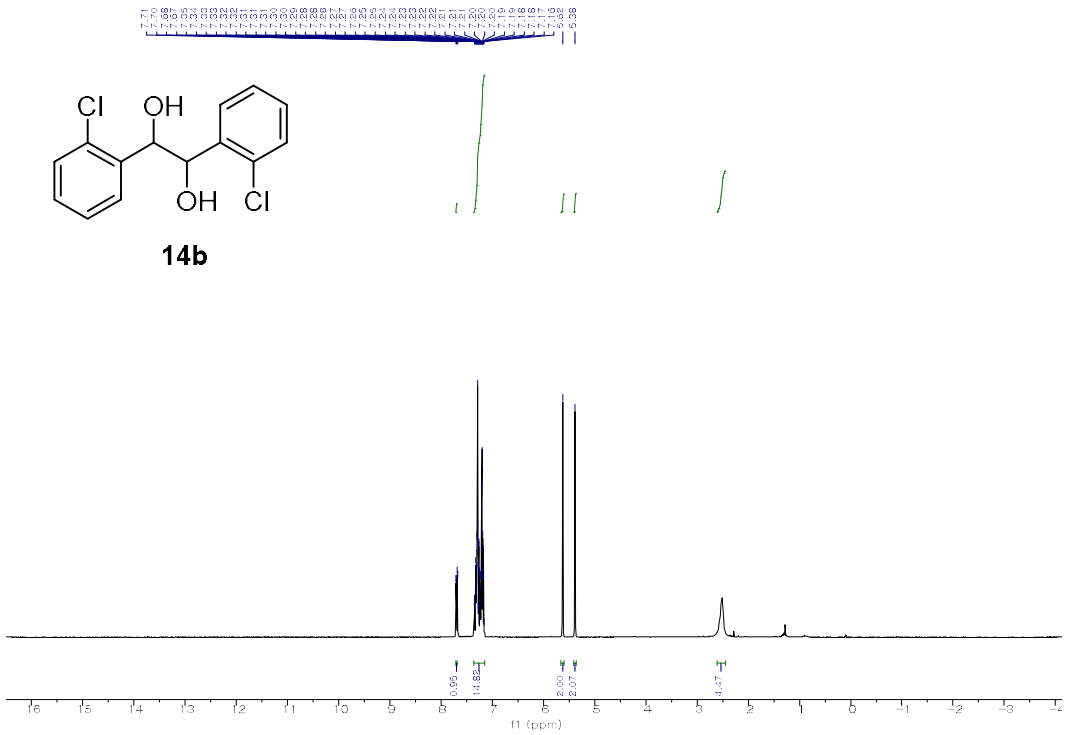
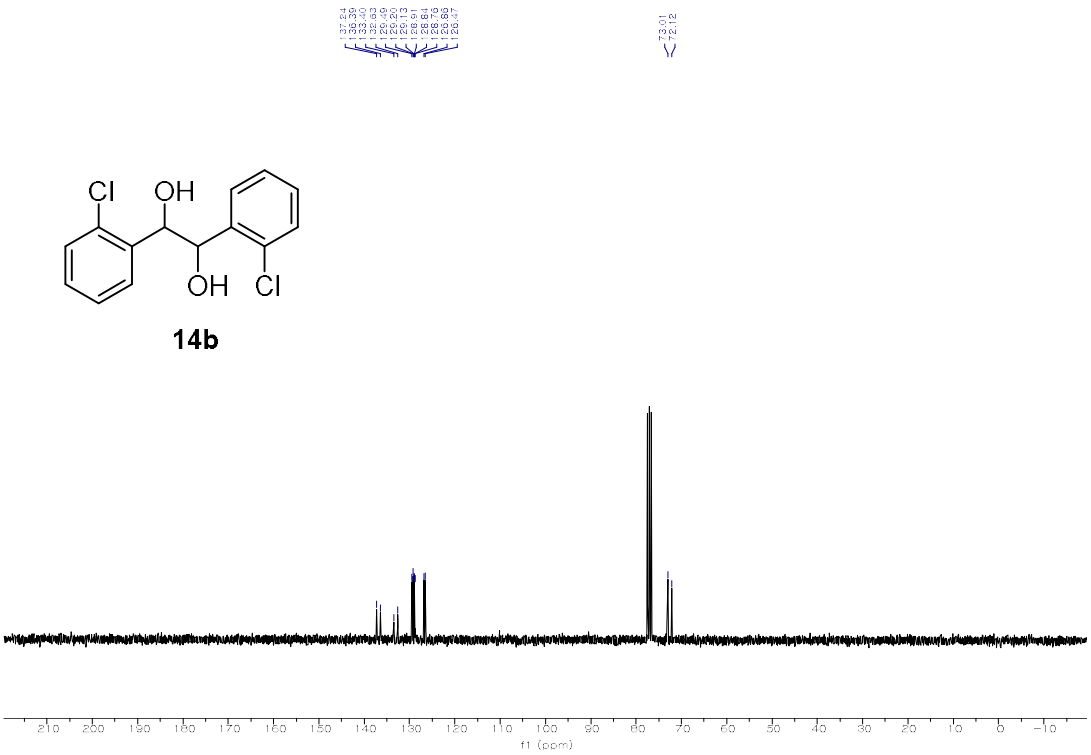


^{13}C-NMR (75Hz, DMSO-d6) of **13b**



^{1}H-NMR (300 MHz, $CDCl_3$) of **14b**



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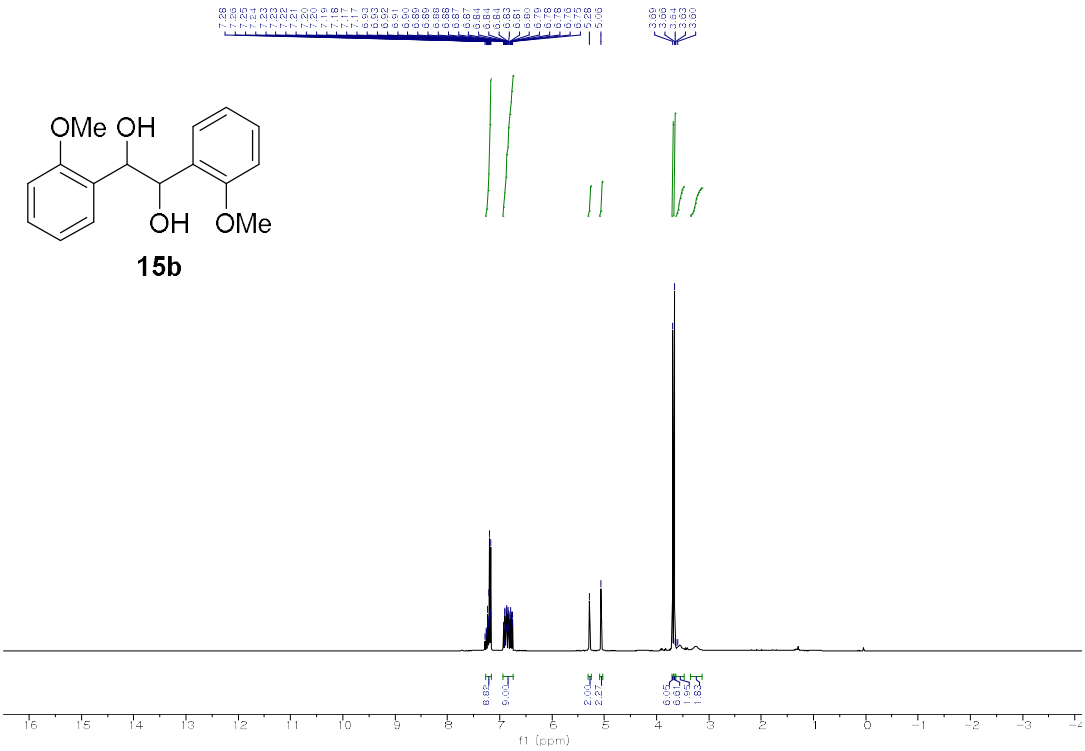
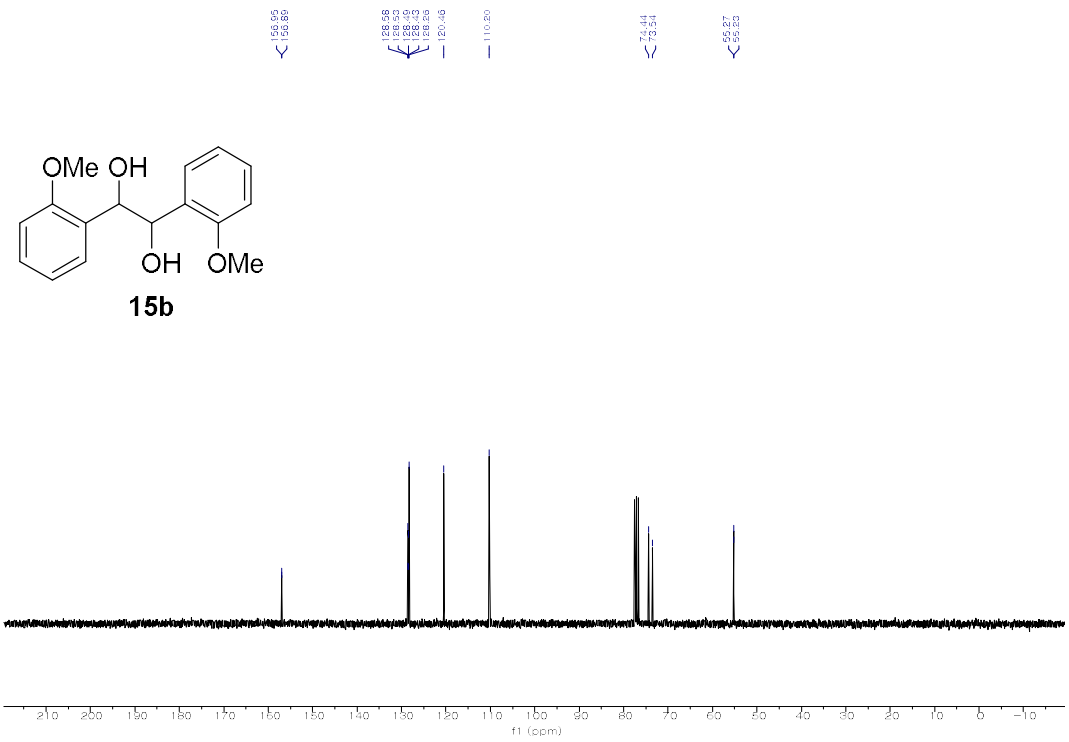
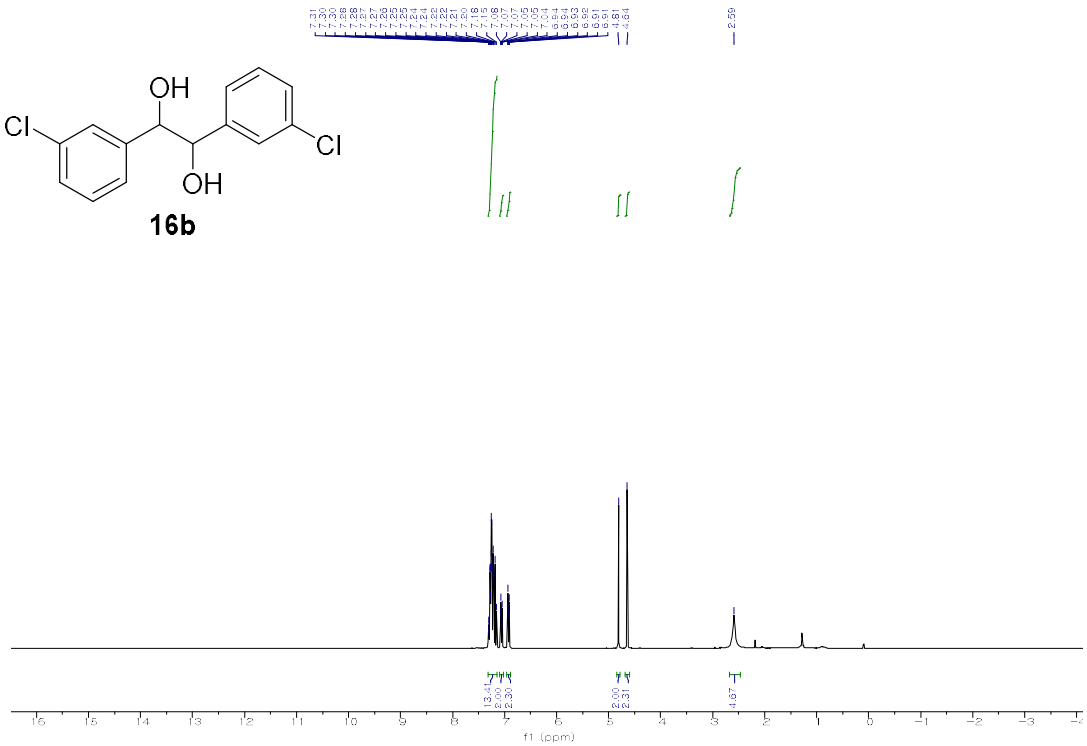


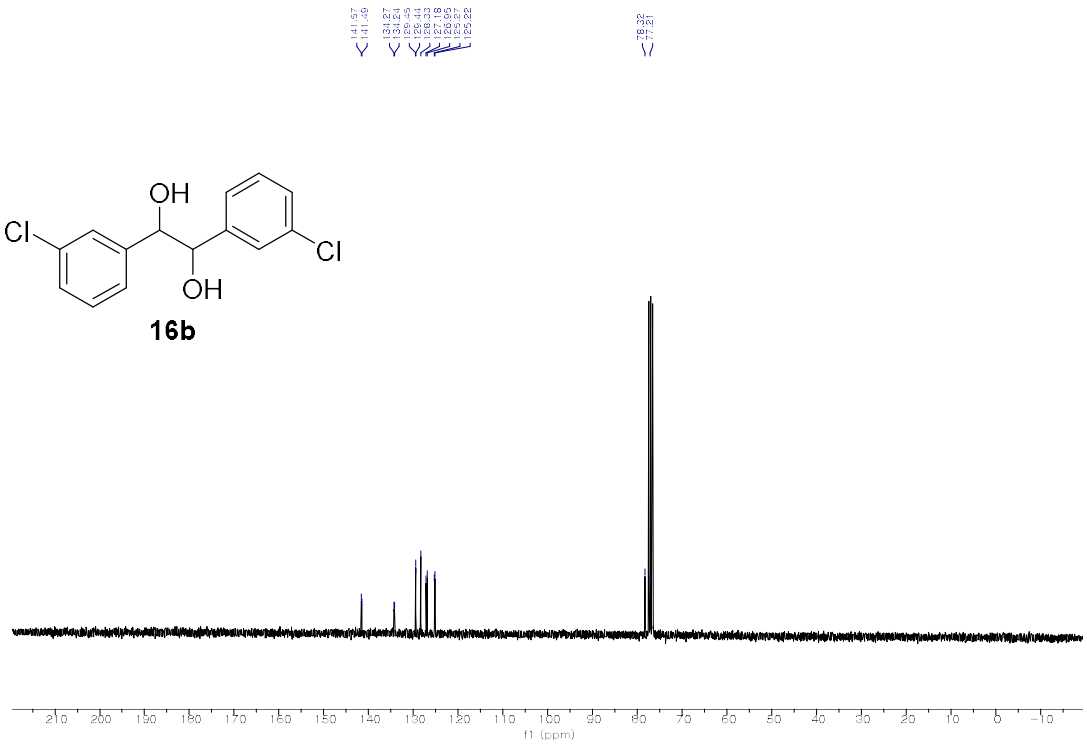
^{1}H-NMR (300 MHz, $CDCl_3$) of **15b**



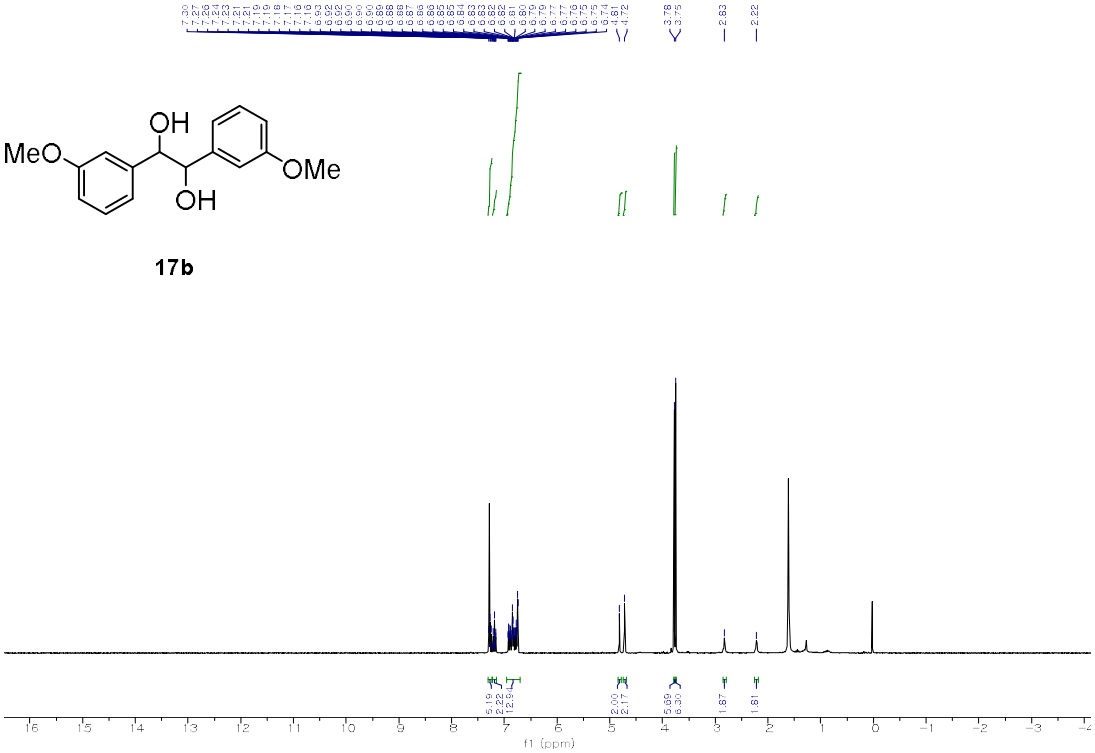
^{13}C-NMR (75Hz, $CDCl_3$) of **15b**



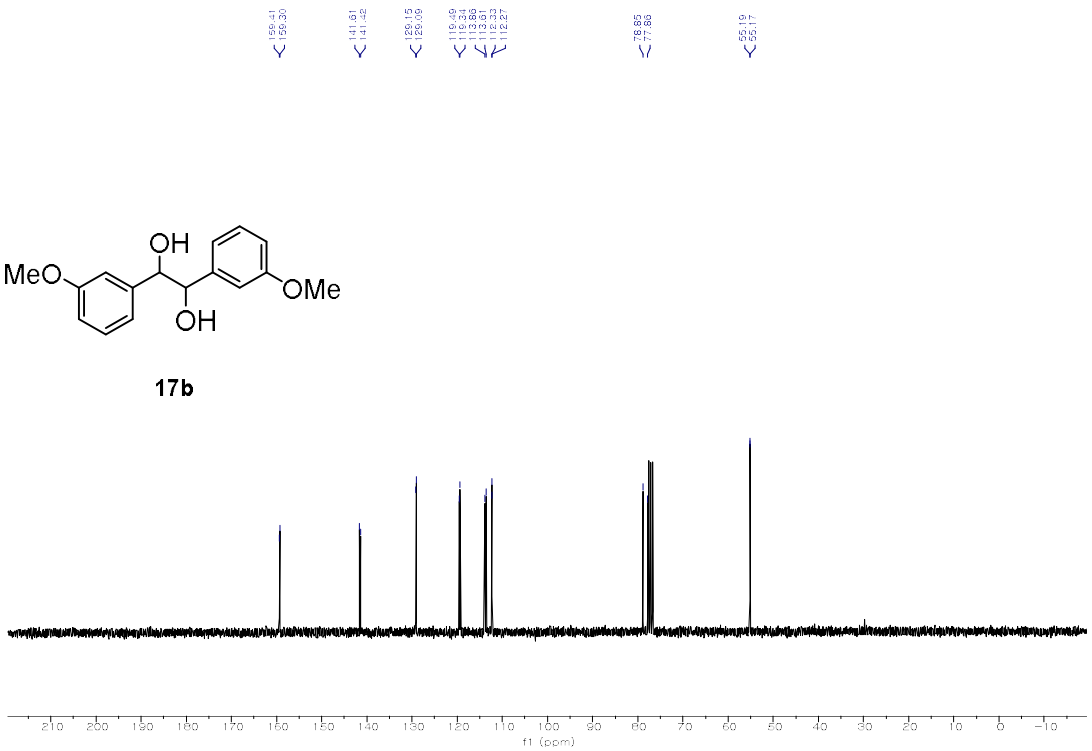
^{1}H-NMR (300 MHz, $CDCl_3$) of **16b**



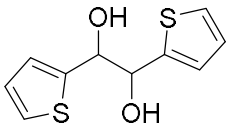
^{13}C-NMR (75Hz, $CDCl_3$) of **16b**



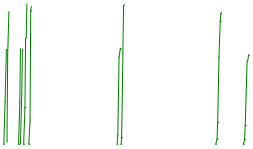
^{1}H-NMR (300 MHz, $CDCl_3$) of **17b.**

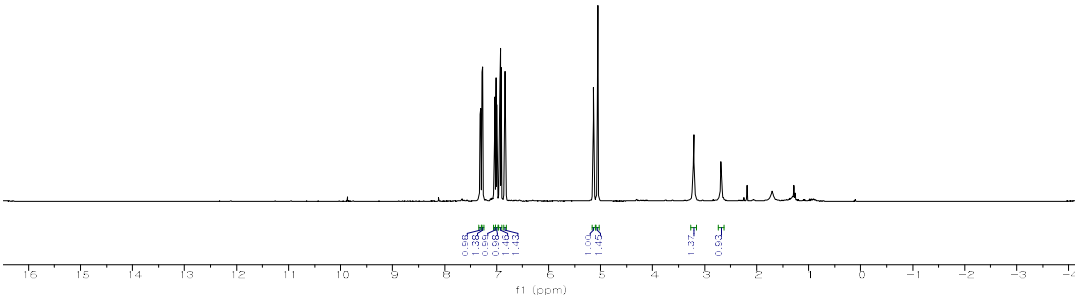


^{13}C-NMR (75Hz, $CDCl_3$) of **17b**

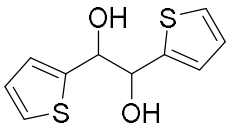


18b

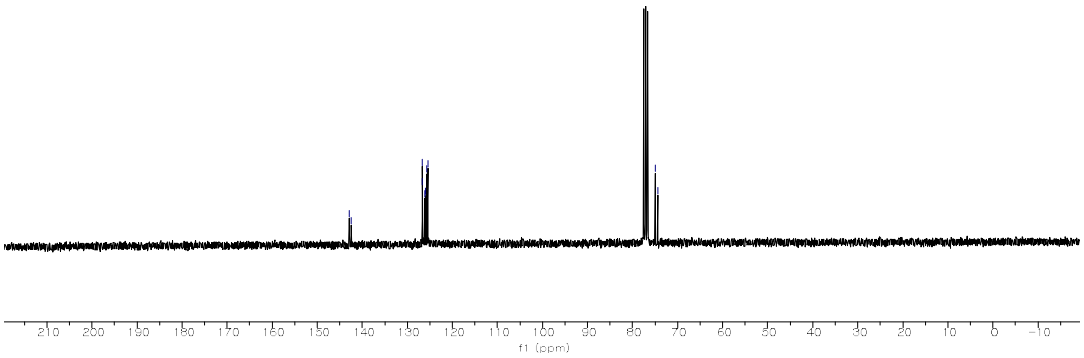




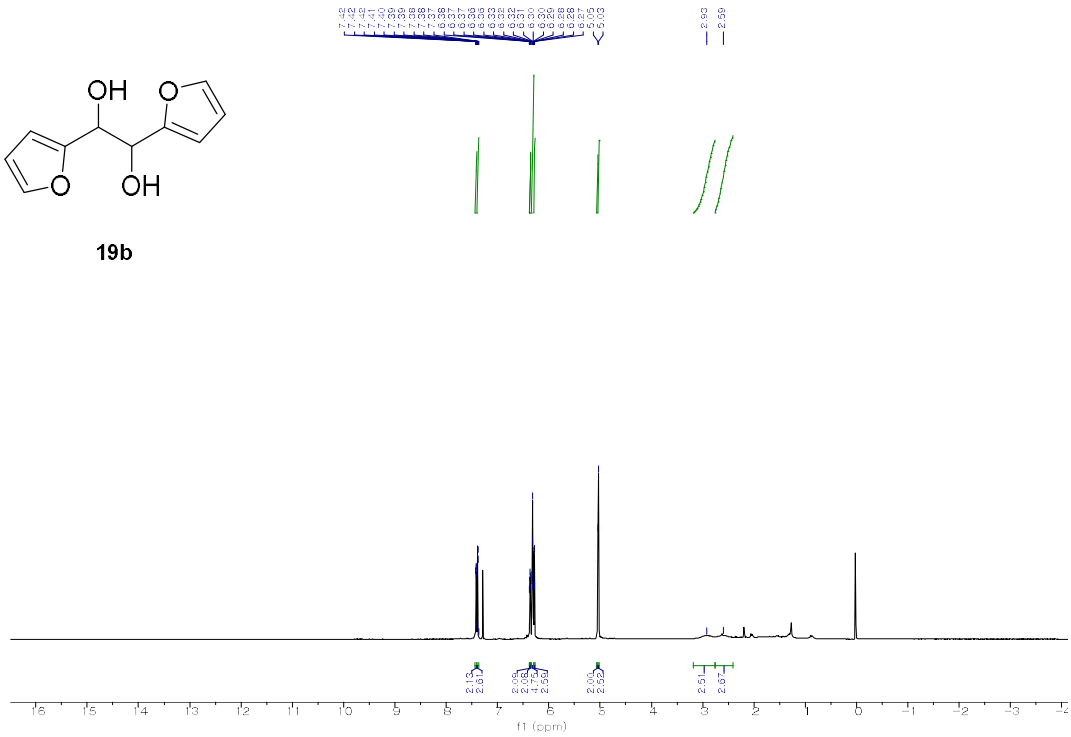
^{1}H-NMR (300 MHz, $CDCl_3$) of **18b**



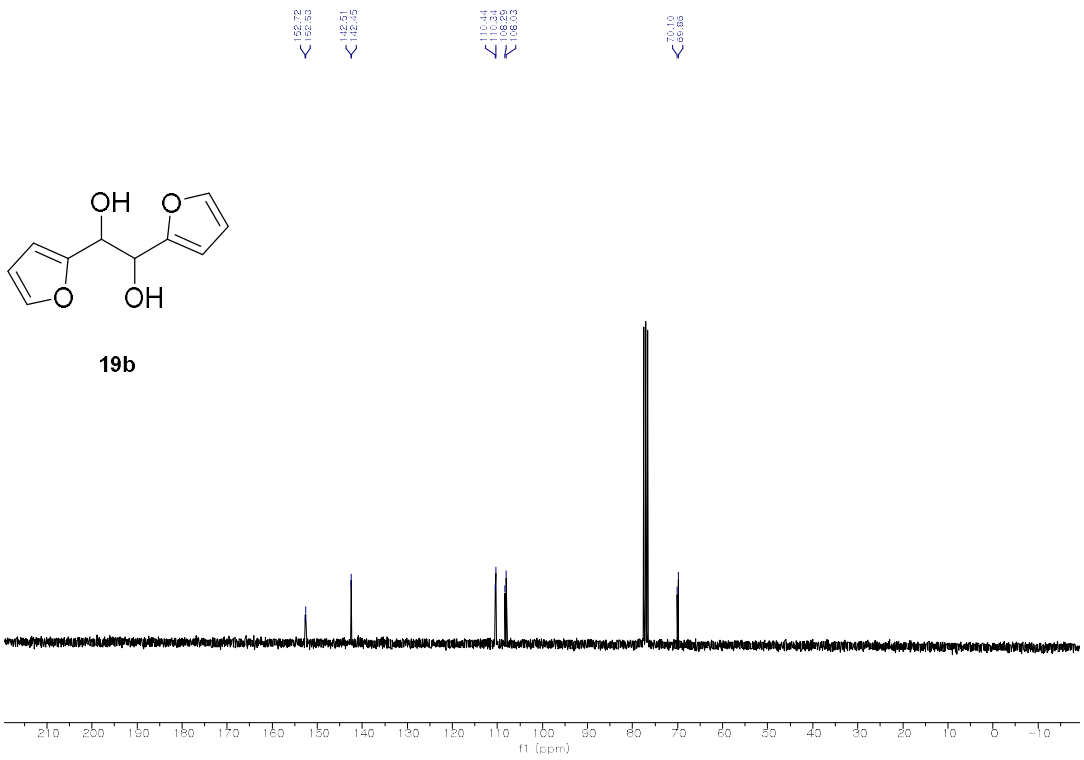
18b



^{13}C-NMR (75Hz, $CDCl_3$) of **18b**



^{1}H-NMR (300 MHz, $CDCl_3$) of **19b**



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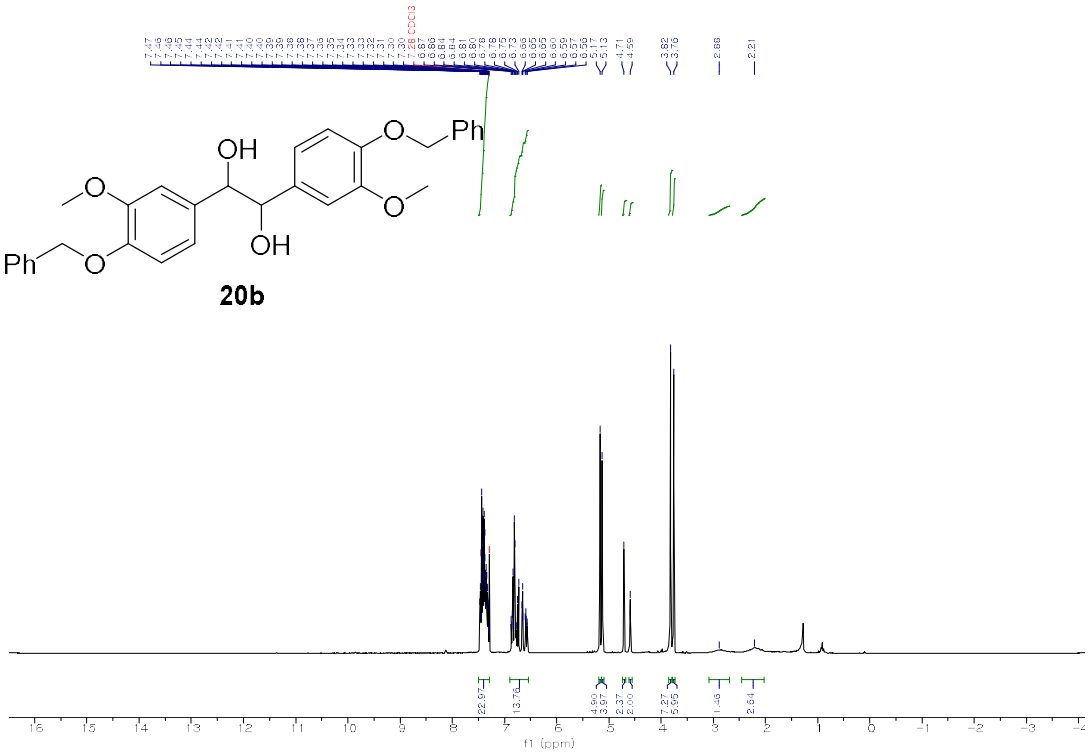

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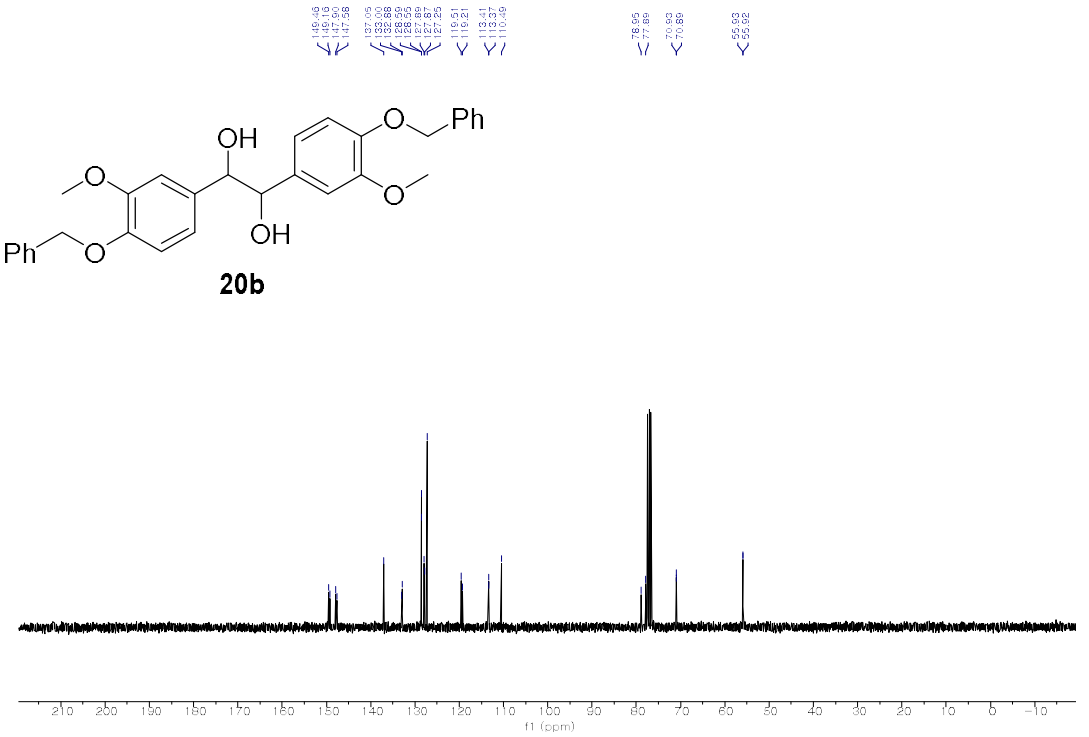

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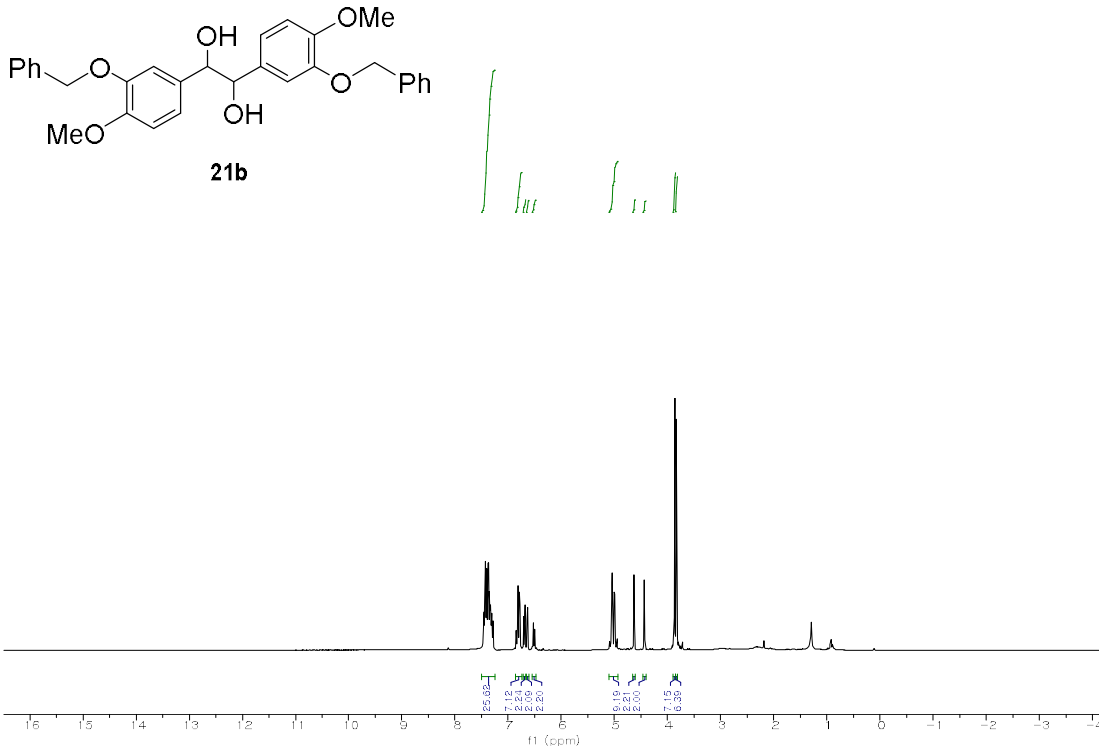
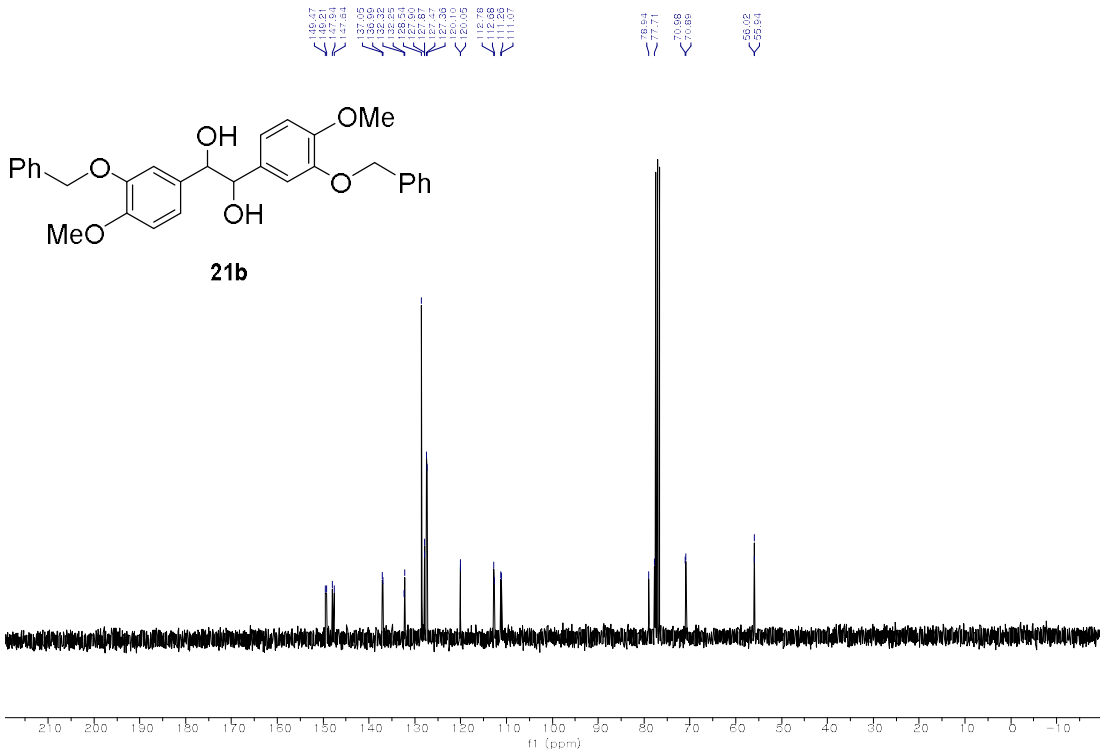


^{1}H-NMR (300 MHz, $CDCl_3$) of **21b**



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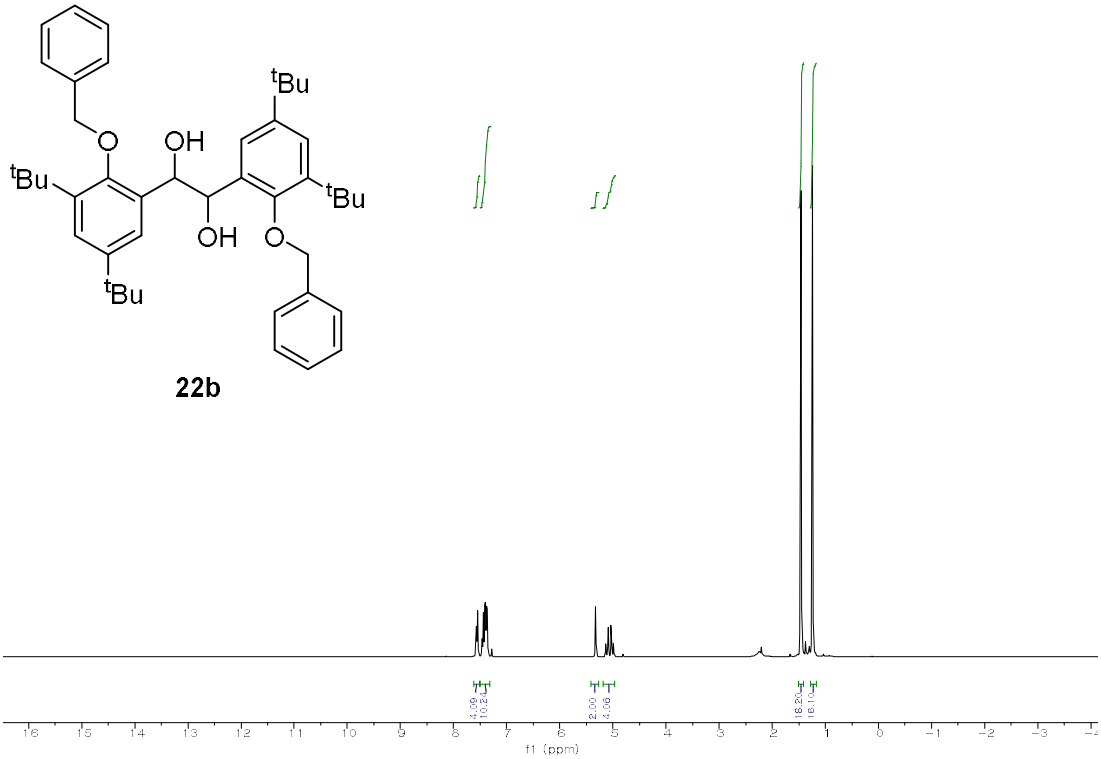
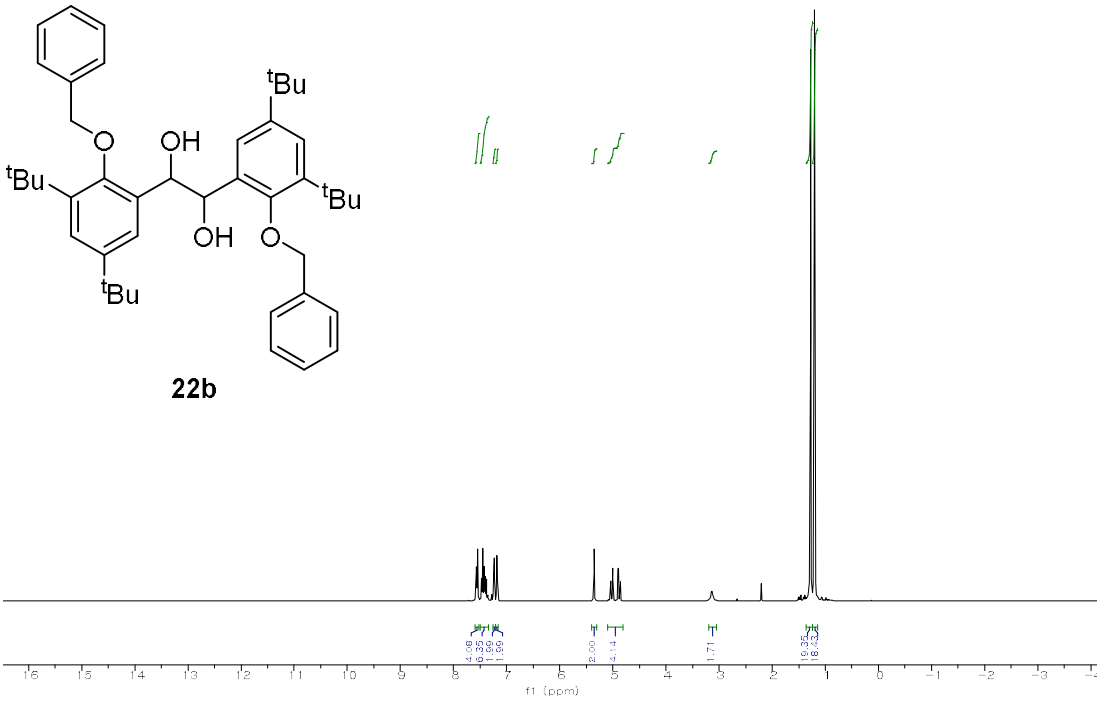
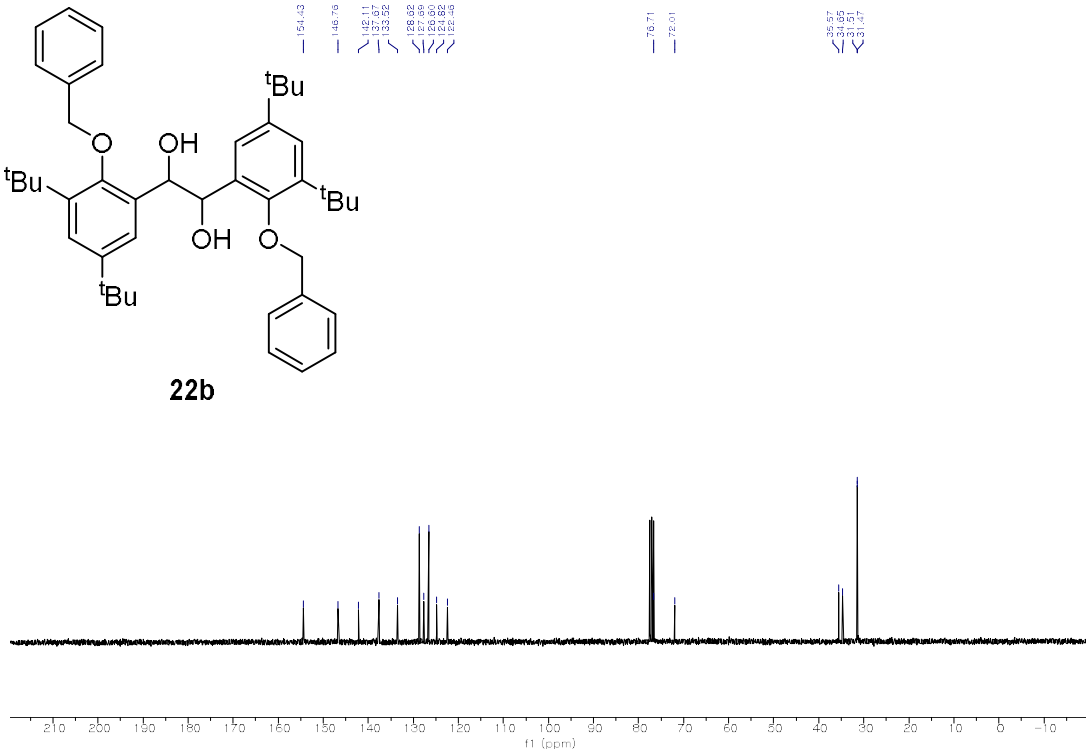


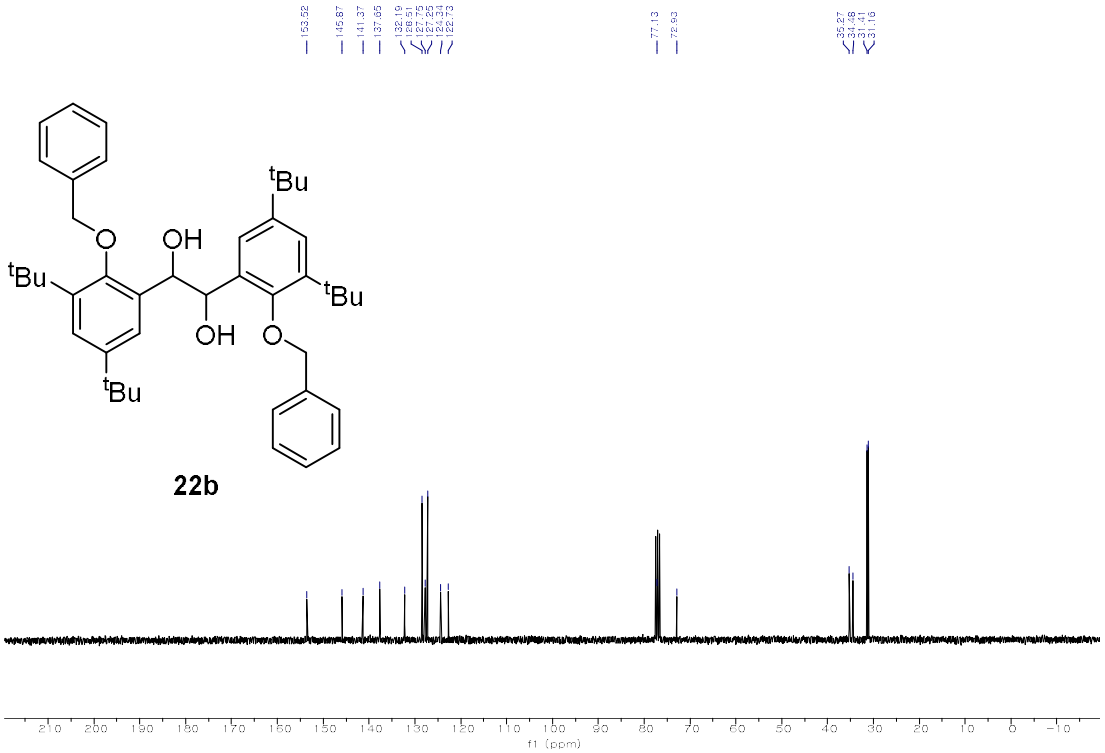
^{1}H-NMR (300 MHz, $CDCl_3$) of **22b(meso)**



NMR (300 MHz, $CDCl_3$) of **22b(dl)**



^{13}C-NMR (75Hz, $CDCl_3$) of **21b(meso)**



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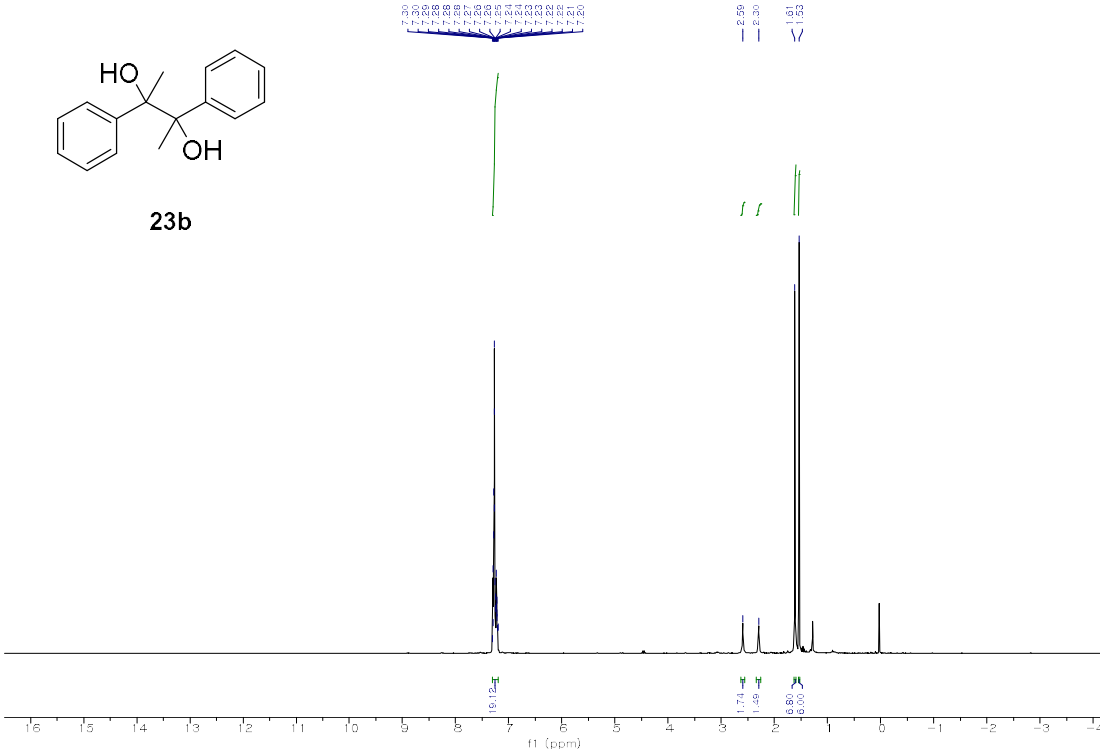

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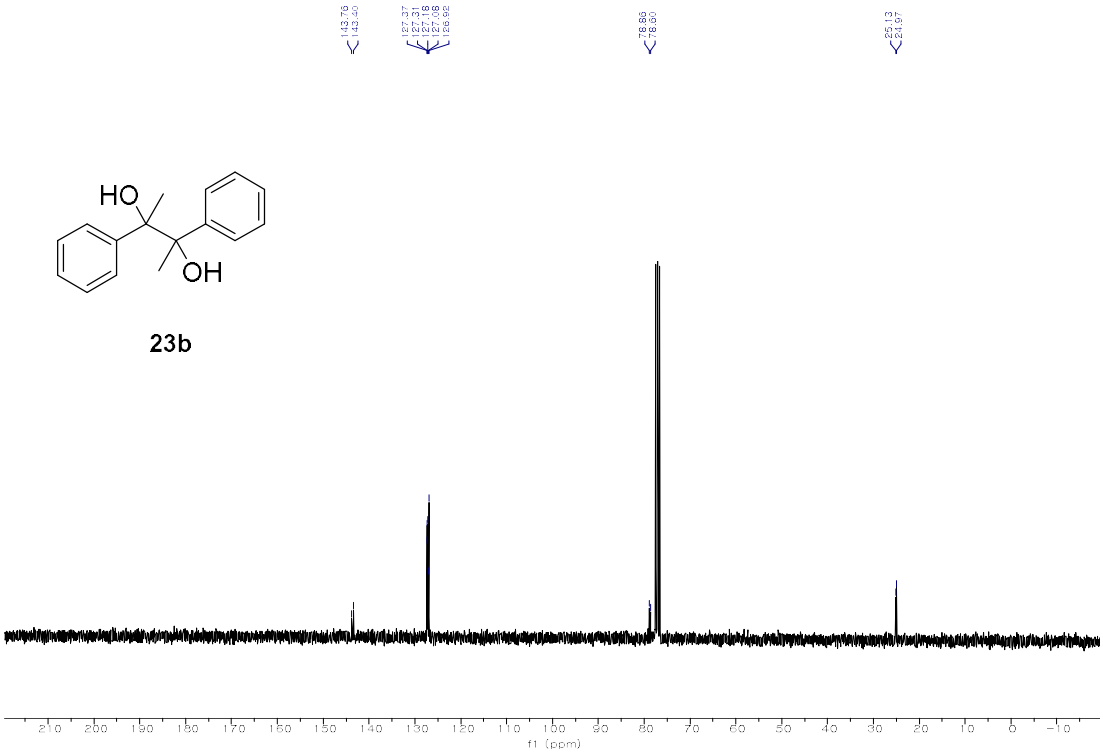

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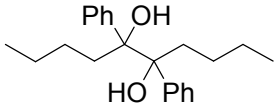
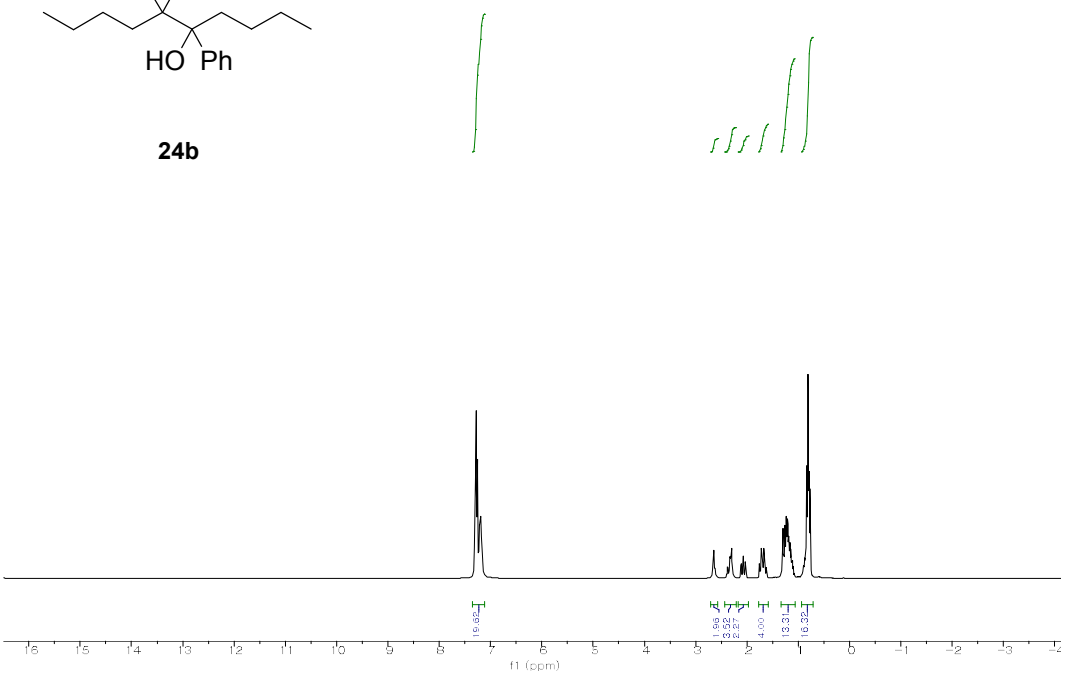


24b



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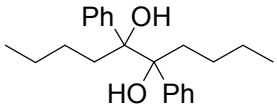
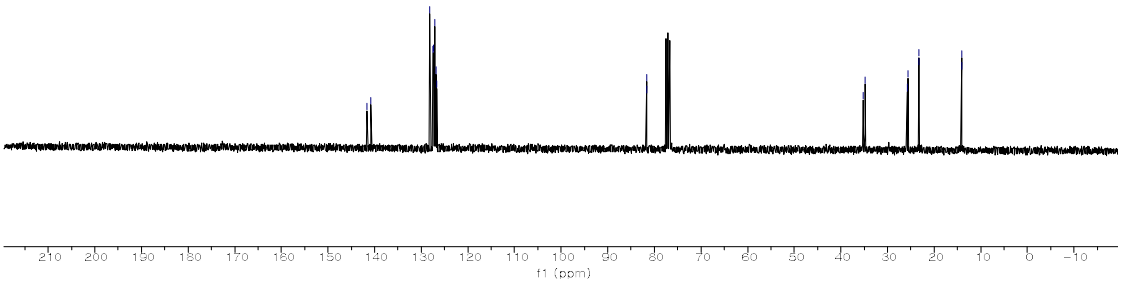


24b



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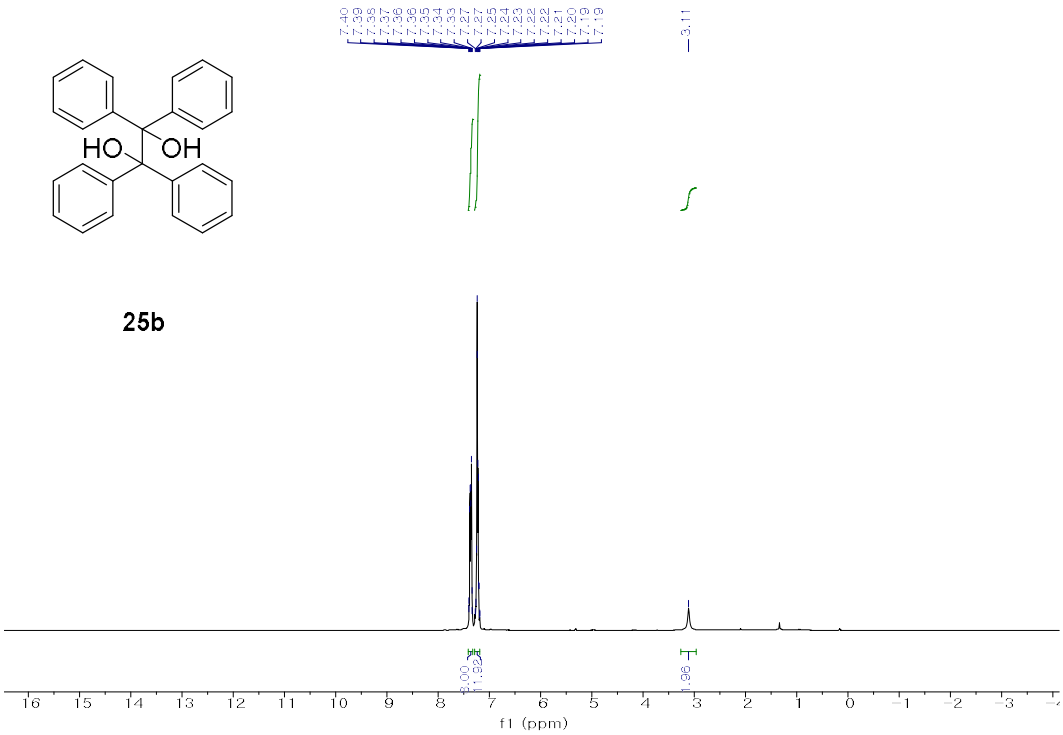
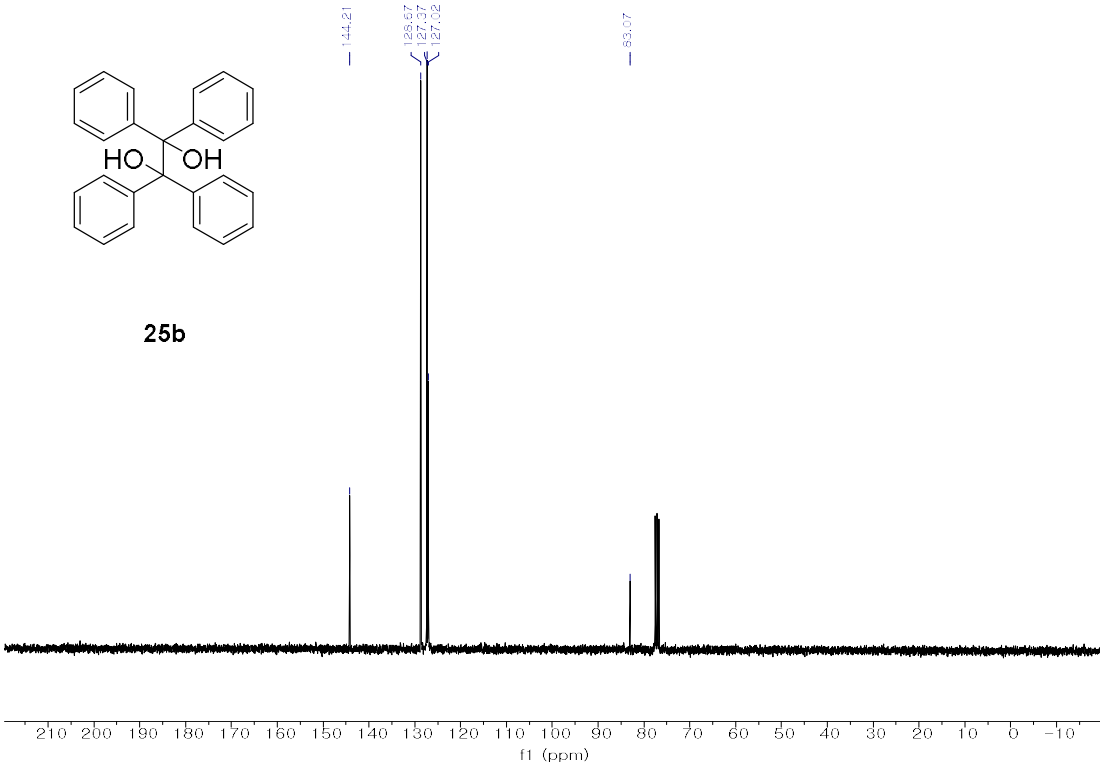


^{1}H-NMR (300 MHz, $CDCl_3$) of **25b**



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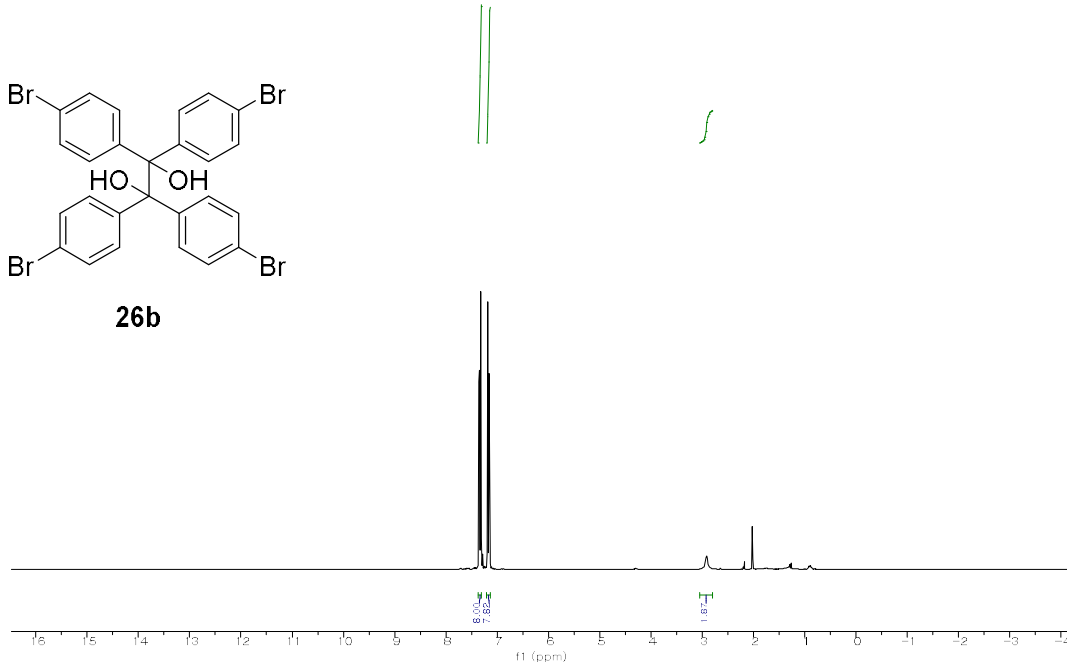
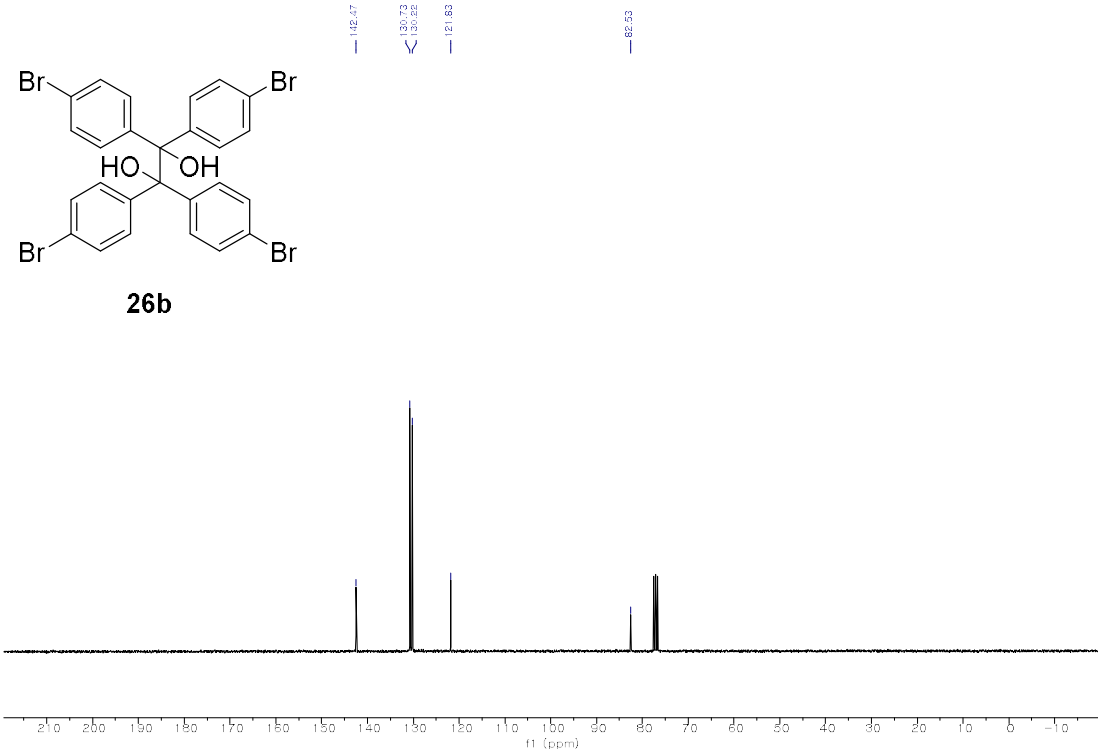
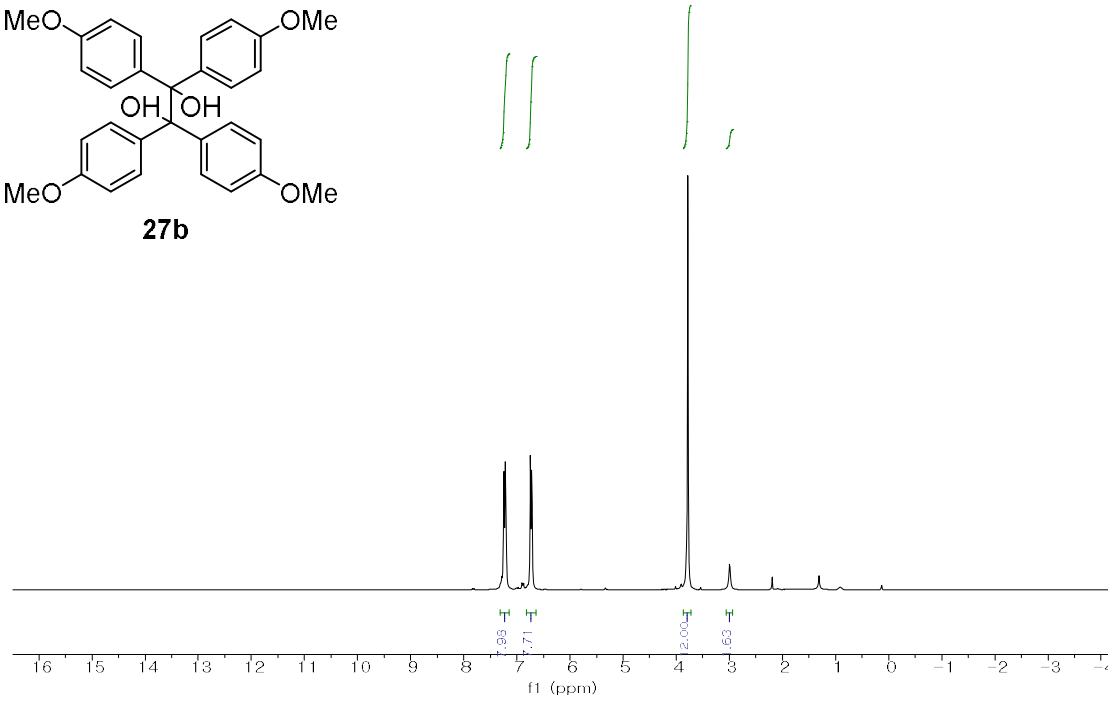


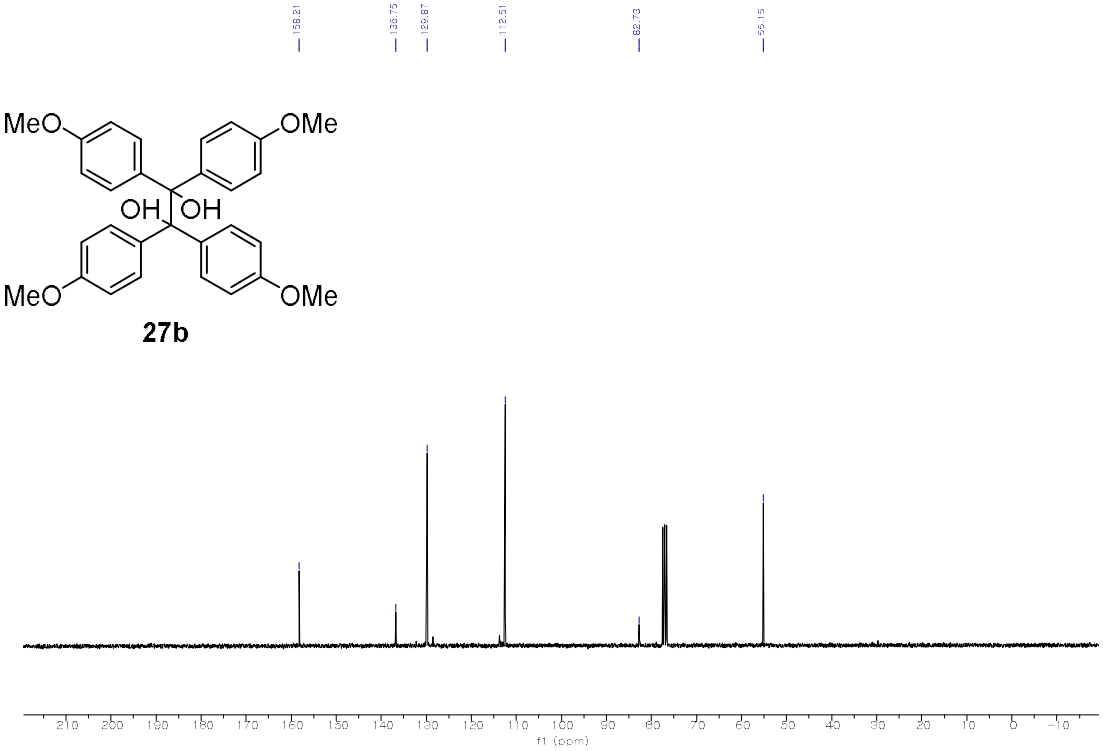
^{1}H-NMR (300 MHz, $CDCl_3$) of **26b**



^{13}C-NMR (75Hz, $CDCl_3$) of **26b**



^{1}H-NMR (300 MHz, $CDCl_3$) of **27b**



^{13}C-NMR (75Hz, $CDCl_3$) of **27b**

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288-296.

7. Korean abstract

물에서 가시광선을 이용한, 광 산화 환원 촉매 Pinacol 커플링을 개발했습니다. 이 반응은 물을 용매로 사용하고 저렴하고 쉽게 제조할 수 있는 유기 광촉매인 4CzIPN을 사용하기 때문에 친환경적이고 경제적입니다. 다양한 치환기를 사용해 반응을 진행해 보았으며, 금속이 없는 조건에서 높은 수율의 vicinal diol 생성물들을 얻을 수 있었습니다.