



Supporting Information

Dual Photoredox Catalysis with Vanadium Complexes in Low Oxidation State: Diastereoselective Pinacol Coupling

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Andrea Gualandi,* Andrea Fermi, Paola Ceroni, and Pier Giorgio Cozzi*

Dual photoredox catalysis with vanadium complexes in low oxidation state: a diastereoselective pinacol coupling

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Experimental Procedures

General methods and materials

¹H-NMR spectra were recorded on Varian Mercury 400 spectrometer or Bruker 600 spectrometer. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (CDCl₃: δ = 7.26 ppm, DMSO-*d*₆: δ = 2.50 ppm, CD₃CN: δ = 1.94 ppm, CD₃OD: δ = 3.31 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, m = multiplet), coupling constants (Hz), number of protons. ¹³C-NMR spectra were recorded on Varian Mercury 400 spectrometer or Bruker 600 spectrometer. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (CDCl₃: δ = 77.2 ppm, DMSO-*d*₆: δ = 39.5 ppm, CD₃CN: δ = 118.3, CD₃OD: δ = 49.0 ppm). ¹⁹F-NMR spectra were recorded on Varian Mercury 400 spectrometer or Bruker 600. Chemical shifts are reported in ppm from CFC₃. HRMS was performed on a Waters Xevo G2-XS QToF, ESI+, cone voltage 40 V, Capillary 3KV, with a source temperature of 120 °C. Chromatographic purifications were done with 240-400 mesh silica gel. All reactions were setup under an argon atmosphere in oven-dried glassware using standard Schlenk techniques. All the reagents were purchased from commercial sources (Sigma-Aldrich, Alfa Aesar, Fluorochem, Strem Chemicals, TCI) and used without further purification unless specified. Liquid aldehydes were purified by distillation prior to use. Ligands **5**, **8**, **13**, **14**, **19-24** were purchased from commercial sources. All reactions requiring inert atmosphere were setup under an argon in heat gun-dried glassware using standard Schlenk techniques. Anhydrous solvents were supplied by Aldrich in Sureseal[®] bottles and, unless specified, were used without further treatment. Trichlorotris(tetrahydrofuran)vanadium 0.5 M solution in dichloromethane was purchased from Thermo Scientific. To perform all the catalysis some milliliters were cannulated from the bottle in a heat gun-dried Schlenck tube and stored under argon atmosphere. Kessil[®] PR160L@595 nm¹ were used as light source for the photocatalytic reactions. N,N'-di-*N*-propyl-1,13-dimethoxyquinacridinium **1**⁺ was prepared according to published literature procedures.² Synthesis of Hantzsch's ethyl ester was achieved following the reported literature procedure.³ Ligands **7**,⁴ **9**,⁵ **12**,⁶ **13**,⁷ **15**,⁸ **16-18**⁹ and **25**¹⁰ were achieved following standard literature procedures. Ligands **10** and **11** were supplied by Prof. Marco Bandini's group.

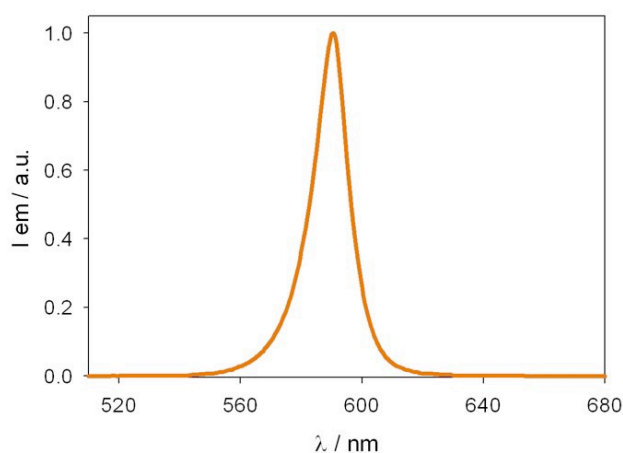


Figure S1. Emission spectrum collected from the Kessil lamp (PR160L@595 nm) used in the experimental setup (λ_{max} = 590 nm; FWHM = 13 nm).

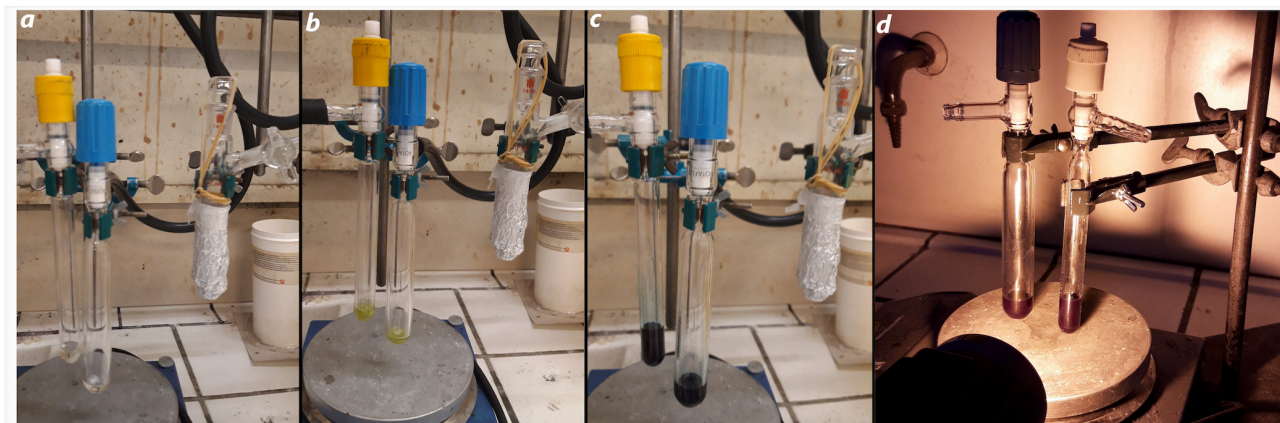
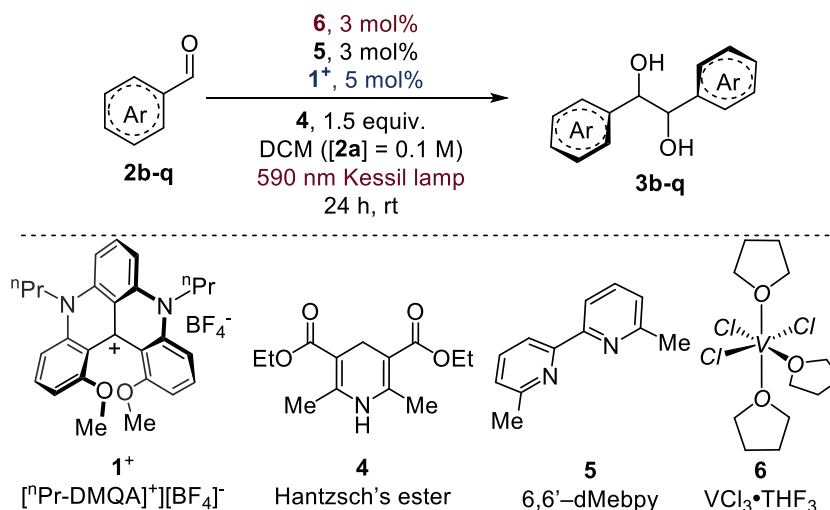


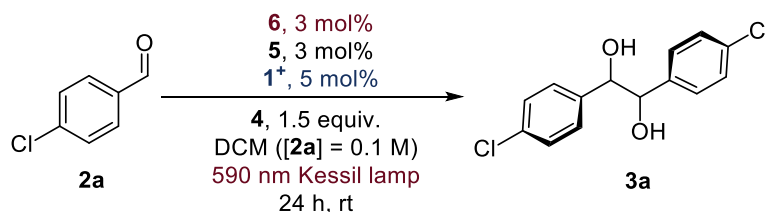
Figure S2. **a)** Solution of the ligand in DCM. **b)** Formation of the complex between **5** and $\text{VCl}_3 \cdot \text{THF}_3$. **c)** Reaction mixture after the addition of all the reagents. **d)** Reaction mixture under irradiation with Kessil® PR160L@595 nm lamp. The reaction flasks were positioned approximately at 10 cm from the light source and Kessil® PR160. The reaction temperature was close to room temperature (25-28°C) during the irradiation.

General procedure for the diastereoselective photoredox pinacol coupling promoted by vanadium complexes with a red-absorbing organic dye



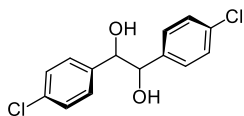
All the reactions were performed on 0.2 mmol of aldehyde. In a flame dried 10 mL Schlenk tube, equipped with a Rotaflo stopcock, magnetic stirring bar, and an argon supply tube. Under vigorous argon flux, 6,6'-dimethyl-2,2'-dipyridyl **5** (1.1 mg, 0.006 mmol, 3 mol%) was dissolved in anhydrous dichloromethane (0.6 mL), then trichlorotris(tetrahydrofuran)vanadium (0.5 M in DCM, 12 μ L, 0.006 mmol, 3 mol%) was added. Reaction mixture turned instantly into green color. The mixture was let stirring at room temperature for one hour, then the aldehyde **2a-q** (0.2 mmol), the photocatalyst **1⁺** (0.01 mmol, 5.0 mg, 5 mol%) and the diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (Hantzsch's ester) **4** (0.3 mmol, 76 mg, 1.5 equiv) were added in the Schlenk tube. Anhydrous dichloromethane (1.4 mL) was then added, and the reaction mixture was further subjected to a freeze-pump-thaw procedure (three cycles), and the vessel was then refilled with argon. The reaction was irradiated under vigorous stirring for 24 h at room temperature. The crude reaction was filtered over a pad of silica, the solvent was evaporated under reduced pressure and the reaction crude was analyzed by ¹H NMR to evaluate the diastereomeric ratio of the products. The crude was subject to flash column chromatography (SiO₂, Hexane/AcOEt) to afford products **3a-q** in the stated yields.

General procedure for 1 mmol scale

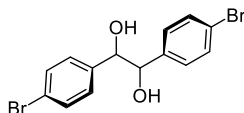


In a flame dried 30 mL Schlenk tube, equipped with a Rotaflo stopcock, magnetic stirring bar, and an argon supply tube, under vigorous argon flux, 6,6'-dimethyl-2,2'-dipyridyl **5** (5.5 mg, 0.03 mmol, 3 mol%) was dissolved in anhydrous dichloromethane (3 mL), then trichlorotris(tetrahydrofuran)vanadium (0.5 M in DCM, 60 μ L, 0.03 mmol, 3 mol%) was added. Reaction mixture turned instantly into green colour. The mixture was let stirring at room temperature for one hour, then the aldehyde **2a** (1.0 mmol, 140 mg), the photocatalyst **1⁺** (0.05 mmol, 25 mg, 5 mol%) and the diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (Hantzsch's ester) **4** (1.5 mmol, 380 mg, 1.5 equiv) were added in the Schlenk tube. Anhydrous dichloromethane (7 mL) was then added, and the reaction mixture was further subjected to a freeze-pump-thaw procedure (three cycles), and the vessel was then refilled with argon. The reaction was irradiated under vigorous stirring for 24 h at room temperature. A small portion of the crude reaction was filtered over a pad of silica, the solvent was evaporated under reduced pressure and the reaction crude was analyzed by ¹H NMR to evaluate the diastereomeric ratio of the product. The crude was subject to flash column chromatography (SiO₂, 5:1 Hexane/AcOEt, then 4:1, then 1:1) to afford products **3a** in quantitative yield (0.49 mmol, 139 mg).

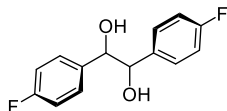
Characterization of the products



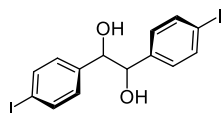
1,2-bis(4-chlorophenyl)ethane-1,2-diol (3a). White solid; Yield >95% (0.099 mmol, 28 mg); d.r._{d/l-meso} > 20:1 calculated considering the ¹H NMR spectrum of the reaction crude and comparing the integral of the benzylic CH. The general procedure was applied using **2a** (0.2 mmol, 28 mg). The title compound was isolated by flash column chromatography (SiO₂, 5:1 Hexane/AcOEt). Spectroscopic data matched those previously reported in the literature.²



1,2-bis(4-bromophenyl)ethane-1,2-diol (3b). White solid; Yield 89% (0.089 mmol, 33 mg); d.r._{d/l-meso} > 20:1 calculated considering the ¹H NMR spectrum of the reaction crude and comparing the integral of the benzylic CH. The general procedure was applied using **2b** (0.2 mmol, 37 mg). The title compound was isolated by flash column chromatography (SiO₂, 5:1 Hexane/AcOEt). Spectroscopic data matched those previously reported in the literature.²



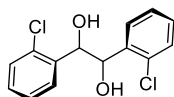
1,2-bis(4-fluorophenyl)ethane-1,2-diol (3c). White solid; Yield 95% (0.095 mmol, 24 mg); d.r._{d/l-meso} > 20:1 calculated considering the ¹H NMR spectrum of the reaction crude and comparing the integral of the benzylic CH. The general procedure was applied using **2c** (0.2 mmol, 22 μL). The title compound was isolated by flash column chromatography (SiO₂, 5:1 Hexane/AcOEt). Spectroscopic data matched those previously reported in the literature.²



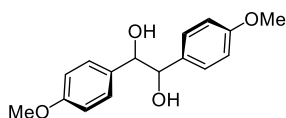
1,2-bis(4-iodophenyl)ethane-1,2-diol (3d). White solid; Yield 86% (0.086 mmol, 40 mg); d.r._{d/l-meso} = 17:1 calculated considering the ¹H NMR spectrum of the reaction crude and comparing the integral of the benzylic CH. The general procedure was applied using **2d** (0.2 mmol, 47 mg). The title compound was isolated by flash column chromatography (SiO₂, 4:1 Hexane/AcOEt).

d/l-3d. ¹H NMR (600 MHz, d₆-DMSO) δ = 7.60-7.55 (m, 4H), 6.87-6.83 (m, 4H), 4.60 (s, 2H). ¹³C NMR (151 MHz, d₆-DMSO) δ = 139.2 (2C), 137.3 (4C), 128.9 (4C), 93.8 (2C), 78.6 (2C).

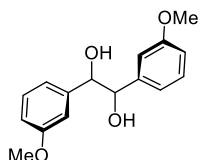
HRMS (ESI/Q-TOF) m/z: [M + Na]⁺ calcd for C₁₄H₁₂I₂NaO₂, 488.8819; found 488.8812.



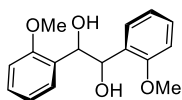
1,2-bis(2-chlorophenyl)ethane-1,2-diol (3e). White solid; Yield >95% (0.099 mmol, 28 mg); d.r._{d/l-meso} = 17:1 calculated considering the ¹H NMR spectrum of the reaction crude and comparing the integral of the benzylic CH. The general procedure was applied using **2e** (0.2 mmol, 23 μL). The title compound was isolated by flash column chromatography (SiO₂, 7:1 Hexane/AcOEt, then 5:1 Hexane/AcOEt). Spectroscopic data matched those previously reported in the literature.²



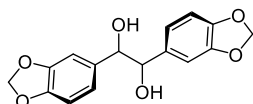
1,2-bis(4-methoxyphenyl)ethane-1,2-diol (3f). White solid; Yield 91% (0.091 mmol, 25 mg); d.r._{d/l-meso} > 20:1 calculated considering the ¹H NMR spectrum of the reaction crude and comparing the integral of the benzylic CH. The general procedure was applied using **2f** (0.2 mmol, 24 μL). The title compound was isolated by flash column chromatography (SiO₂, 5:1 Hexane/AcOEt). Spectroscopic data matched those previously reported in the literature.²



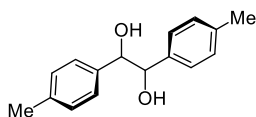
1,2-bis(3-methoxyphenyl)ethane-1,2-diol (3g). White solid; Yield 95% (0.095 mmol, 26 mg); d.r._{d/l-meso} > 20:1 calculated considering the ¹H NMR spectrum of the reaction crude and comparing the integral of the benzylic CH. The general procedure was applied using **2g** (0.2 mmol, 25 μL). The title compound was isolated by flash column chromatography (SiO₂, 4:1 Hexane/AcOEt). Spectroscopic data matched those previously reported in the literature.²



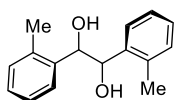
1,2-bis(2-methoxyphenyl)ethane-1,2-diol (3h). White solid; Yield >95% (0.099 mmol, 27 mg); d.r._{d/l-meso} > 20:1 calculated considering the ¹H NMR spectrum of the reaction crude and comparing the integral of the benzylic CH. The general procedure was applied using **2h** (0.2 mmol, 27 mg). The title compound was isolated by flash column chromatography (SiO₂, 4:1 Hexane/AcOEt). Spectroscopic data matched those previously reported in the literature.¹¹



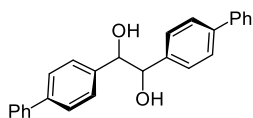
1,2-bis(benzo[d][1,3]dioxol-5-yl)ethane-1,2-diol (3i). White solid; Yield 90% (0.090 mmol, 27 mg); d.r._{d/l-meso} > 20:1 calculated considering the ¹H NMR spectrum of the reaction crude and comparing the integral of the benzylic CH. The general procedure was applied using **2i** (0.2 mmol, 30 mg). The title compound was isolated by flash column chromatography (SiO₂, 5:1 Hexane/AcOEt). Spectroscopic data matched those previously reported in the literature.²



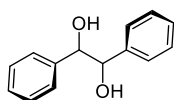
1,2-di-p-tolyethane-1,2-diol (3j). White solid; Yield 85% (0.085 mmol, 21 mg); d.r._{d/l-meso} > 20:1 calculated considering the ¹H NMR spectrum of the reaction crude and comparing the integral of the benzylic CH. The general procedure was applied using **2j** (0.2 mmol, 24 μL). The title compound was isolated by flash column chromatography (SiO₂, 5:1 Hexane/AcOEt). Spectroscopic data matched those previously reported in the literature.²



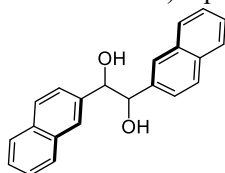
1,2-di-o-tolyethane-1,2-diol (3k). White solid; Yield 95% (0.095 mmol, 23 mg); d.r._{d/l-meso} > 20:1 calculated considering the ¹H NMR spectrum of the reaction crude and comparing the integral of the benzylic CH. The general procedure was applied using **2k** (0.2 mmol, 23 μL). The title compound was isolated by flash column chromatography (SiO₂, 10:1 Hexane/AcOEt). Spectroscopic data matched those previously reported in the literature.¹¹



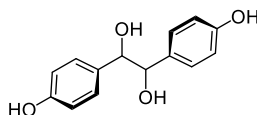
1,2-di([1,1'-biphenyl]-4-yl)ethane-1,2-diol (3l). White solid; Yield >95% (0.096 mmol, 35 mg); d.r.*d/l*-*meso* > 20:1 calculated considering the ¹H NMR spectrum of the reaction crude and comparing the integral of the benzylic CH. The general procedure was applied using **2l** (0.2 mmol, 37 mg). The title compound was isolated by flash column chromatography (SiO₂, 10:1 Hexane/AcOEt, then 5:1 Hexane/AcOEt). Spectroscopic data matched those previously reported in the literature.²



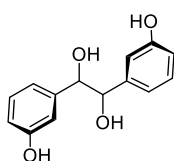
1,2-diphenylethane-1,2-diol (3m). White solid; Yield 74% (0.074 mmol, 16 mg); d.r.*d/l*-*meso* > 20:1 calculated considering the ¹H NMR spectrum of the reaction crude and comparing the integral of the benzylic CH. The general procedure was applied using **2m** (0.2 mmol, 21 μL). The title compound was isolated by flash column chromatography (SiO₂, 5:1 Hexane/AcOEt). Spectroscopic data matched those previously reported in the literature.²



1,2-di(naphthalen-2-yl)ethane-1,2-diol (3n). White solid; Yield 52% (0.052 mmol, 31 mg); d.r.*d/l*-*meso* > 20:1 calculated considering the ¹H NMR spectrum of the reaction crude and comparing the integral of the benzylic CH. The general procedure was applied using **2n** (0.2 mmol, 24.8 mg). The title compound was isolated by flash column chromatography (SiO₂, 6:1 Hexane/AcOEt). Spectroscopic data matched those previously reported in the literature.²



1,2-bis(4-hydroxyphenyl)ethane-1,2-diol (3o). White solid; Yield 61% (0.061 mmol, 15 mg); d.r.*d/l*-*meso* > 20:1 calculated considering the ¹H NMR spectrum of the reaction crude and comparing the integral of the benzylic CH. The general procedure was applied using **2o** (0.2 mmol, 24.8 mg). The title compound was isolated by flash column chromatography (SiO₂, 3:1 Hexane/AcOEt, then 100% AcOEt). Spectroscopic data matched those previously reported in the literature.²

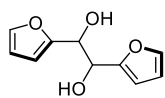


1,2-bis(3-hydroxyphenyl)ethane-1,2-diol (3p). Colorless oil; Yield > 95% (0.098 mmol, 24 mg); d.r.*d/l*-*meso* = 3:1 calculated considering the ¹H NMR spectrum of the reaction crude and comparing the integral of the benzylic CH. The general procedure was applied using **2p** (0.2 mmol, 24.8 mg). The title compound was isolated by flash column chromatography (SiO₂, 3:1 Hexane/AcOEt, then 1:1 Hexane/AcOEt).

***d/l*-3n.** ¹H NMR (600 MHz, CD₃OD) δ = 6.99 (t, *J* = 7.8 Hz, 2H), 6.77-6.73 (m, 1H *d/l* + 1H *meso*), 6.64 (dd, *J* = 2.4, 1.5 Hz, 2H), 6.61-6.57 (m, 3H *dl* + 3H *meso*), 4.55 (s, 2H), 3.35 (s, 2H). ¹³C NMR (151 MHz, CD₃OD) δ = 157.9 (2C), 144.1 (2C), 129.7 (2C), 119.7 (2C), 115.3 (2C), 115.2 (2), 80.1 (2C).

***meso*-3n.** ¹H NMR (600 MHz, CD₃OD) δ = 7.08 (t, *J* = 7.8 Hz, 2H), 6.77-6.73 (m, 1H *meso* + 1H *d/l*), 6.66 (ddd, *J* = 8.1, 2.6, 1.1 Hz, 2H), 6.61-6.57 (m, 3H *meso* + 3H *dl*), 4.68 (s, 2H). ¹³C NMR (151 MHz, CD₃OD) δ = 157.9 (2C), 144.4 (2C), 129.7 (2C), 119.9 (2C), 115.4 (2C), 115.2 (2C), 78.9 (2C).

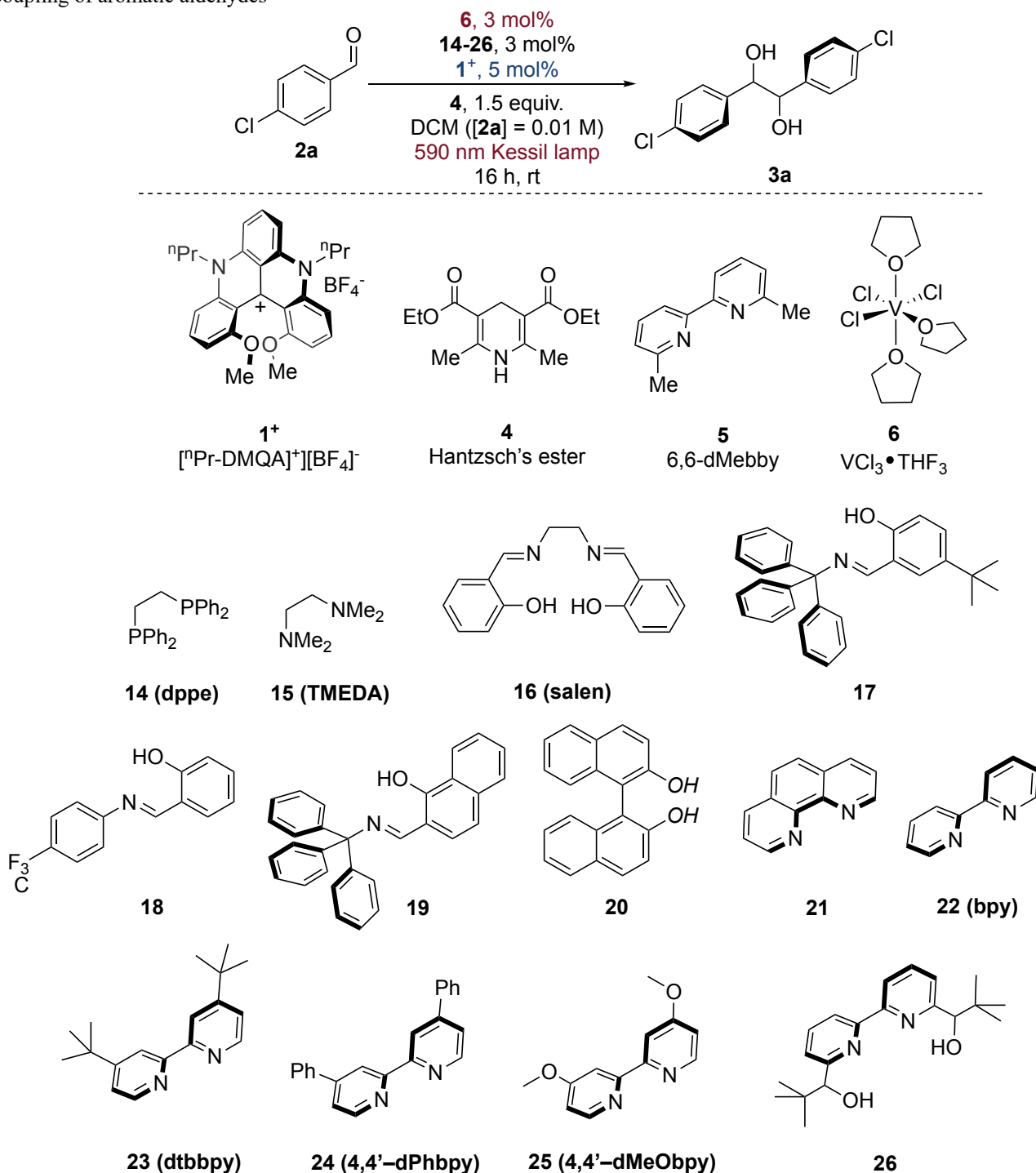
HRMS (ESI/Q-TOF) *m/z*: [M + Na]⁺ calcd for C₁₄H₁₄NaO₄, 269.0784; found 269.0780.



1,2-di(furan-2-yl)ethane-1,2-diol (3q). White solid; Yield 73% (0.073 mmol, 14 mg); d.r.*d/l*-*meso* = 11:1 calculated considering the ^1H NMR spectrum of the reaction crude and comparing the integral of the aromatic CH at 7.44 ppm for the *meso*-diastereoisomer and at 7.38 ppm for the *d/l*-diastereoisomer. The general procedure was applied using **2q** (0.2 mmol, 17 μL). The title compound was isolated by flash column chromatography (SiO_2 , 5:1 Hexane/AcOEt). Spectroscopic data matched those previously reported in the literature.¹²

Optimization Studies

Table S1. Further optimization of the reaction conditions for the diastereoselective dual vanadium-photoredox pinacol coupling of aromatic aldehydes

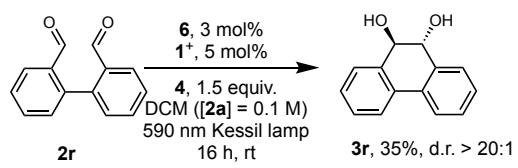


Entry ^[a]	Deviation from standard conditions	Conversion% ^[b]	d.r. 3a (<i>dl:meso</i>) ^[c]
1	none	99 (94)	>20:1
2	14 instead of 5		NR
3	15 instead of 5		NR
4 ^[d]	16 instead of 5		NR
5 ^[e]	17 instead of 5	99	2.3:1
6 ^[e]	18 instead of 5	99	2.4:1
7 ^[e]	19 instead of 5	99	2.3:1
8 ^[d]	20 instead of 5	99	2.5:1
9	21 instead of 5	74	6:1
10	22 instead of 5	90	6.3:1
11	23 instead of 5	92	6:1
12	24 instead of 5		NR
13	25 instead of 5		NR
14	26 instead of 5	99	3:1

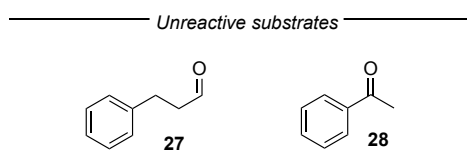
^[a] Reaction performed on a 0.1 mmol scale. ^[b] Conversion determined by ¹H-NMR analysis of the reaction crude. Isolated yield after chromatographic purification is reported in brackets. ^[c] Determined by ¹H-NMR analysis of the reaction crude and reported as *dl:meso* ratio. ^[d] The vanadium complex was obtained by the addition of 2 equiv. of Et₃N in the reaction mixture. ^[e] The vanadium complex was obtained by the addition of 1 equiv of Et₃N in the reaction mixture.

NR = no reaction.

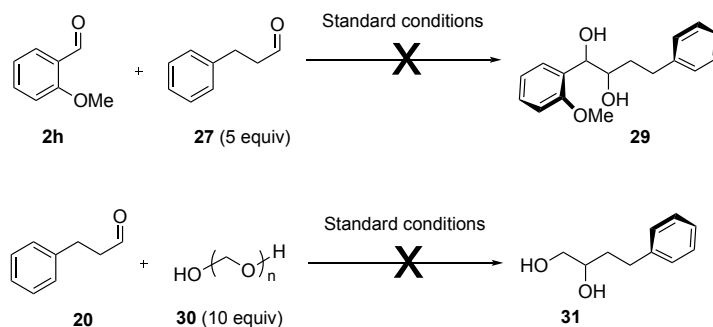
Intramolecular variant



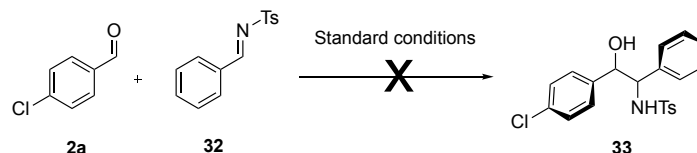
Unsuccessful substrates tested



Applying the standard conditions for dual vanadium and photoredox pinacolization of aromatic aldehydes to substrate **27** and **28** no conversion of the starting material was observed. Only degradation of the photocatalyst was observed.



Attempts to apply the standard conditions for dual vanadium and photoredox pinacolization of aromatic aldehydes to the cross-coupling reaction between **2h** and **27**¹³ and between **27** and **30**¹⁴ did not lead to the desired product (**29** and **31** respectively). In the first case neither the homocoupling product **3h** was observed. In both cases only the degradation of the photocatalyst was observed.



Attempts to apply the standard conditions for dual vanadium and photoredox pinacolization of aromatic aldehydes to the cross-coupling reaction between **2a** and **32** (0.1 mmol, **2a:32** = 2:1 or **2a:32** = 4:1) did not lead to the desired product **33**. Only the diastereoselective homo-pinacol product **3a** (**3a_d**/**3a_{meso}** > 20:1) was observed.

Photophysical analyses

General Methods

All the photophysical analyses were carried out in dichloromethane CH_2Cl_2 at 298 K, unless otherwise specified. UV-vis absorption spectra were recorded with a PerkinElmer λ 40 spectrophotometer using quartz cells with path length of 1.0 cm. Luminescence spectra were performed with a PerkinElmer LS-50, an Edinburgh FS5 spectrofluorometer equipped with a Hamamatsu Photomultiplier R928P phototube or on an Edinburgh FLS920 equipped with a Ge detector for NIR emissions. Lifetimes were measured by the same Edinburgh FLS920 spectrofluorometer by time-correlated single-photon counting (TCSPC) technique. Quantum yields are determined with the method of Demas and Crosby¹⁵ using Cresyl Violet in air-equilibrated methanol as a standard ($\Phi = 0.54$). Experiments in absence of oxygen were carried out in sealed custom-made quartz cuvettes and the samples were prepared inside a nitrogen filled glovebox. The estimated experimental errors are 2 nm on the band maximum, 5% on the molar absorption coefficient and luminescence lifetime.

Quenching Experiments

1^+ vs $2a$

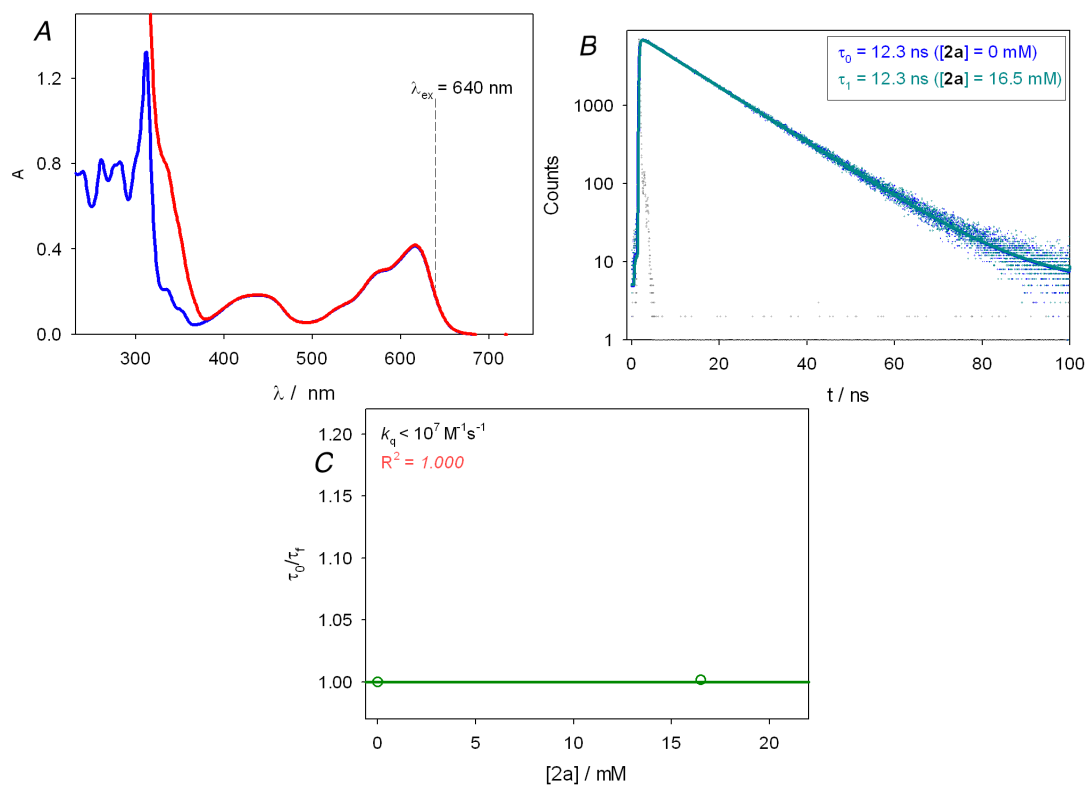


Figure S3. Absorption spectra of solutions of 1^+ in air-equilibrated CH_2Cl_2 at r.t. (ca. $37 \mu M$, blue line) obtained upon addition of increasing amounts of p-chlorobenzaldehyde ($2a$, up to ca. 16.5 mM , red line). **b.** fluorescence decays of 1^+ obtained from the same solutions at $\lambda_{em} = 680 \text{ nm}$ ($\lambda_{ex} = 640 \text{ nm}$). The instrument response function (IRF) is also shown (grey dots). **c.** Stern-Volmer diagram relative to the fluorescence lifetimes.

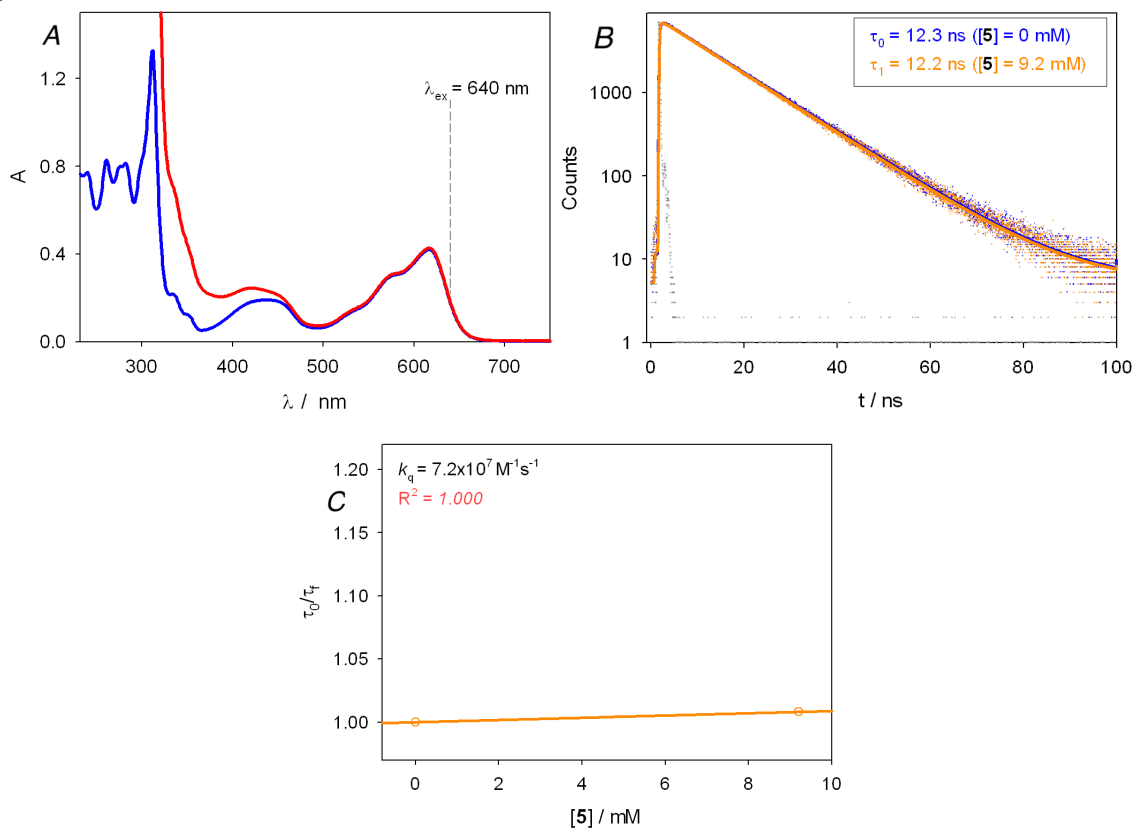
1⁺ vs 5

Figure S4. a. Absorption spectra of solutions of **1⁺** in air-equilibrated CH₂Cl₂ at r.t. (ca. 37 μM, blue line) obtained upon addition of increasing amounts of 2,2'-dimethyl bi pyridine (**5**, up to ca. 9.2 mM, red line). **b.** fluorescence decays of **1⁺** obtained from the same solutions at λ_{em} = 680 nm (λ_{ex} = 640 nm). The instrument response function (IRF) is also shown (grey dots). **c.** Stern-Volmer diagram relative to the fluorescence lifetimes.

1⁺ vs 4

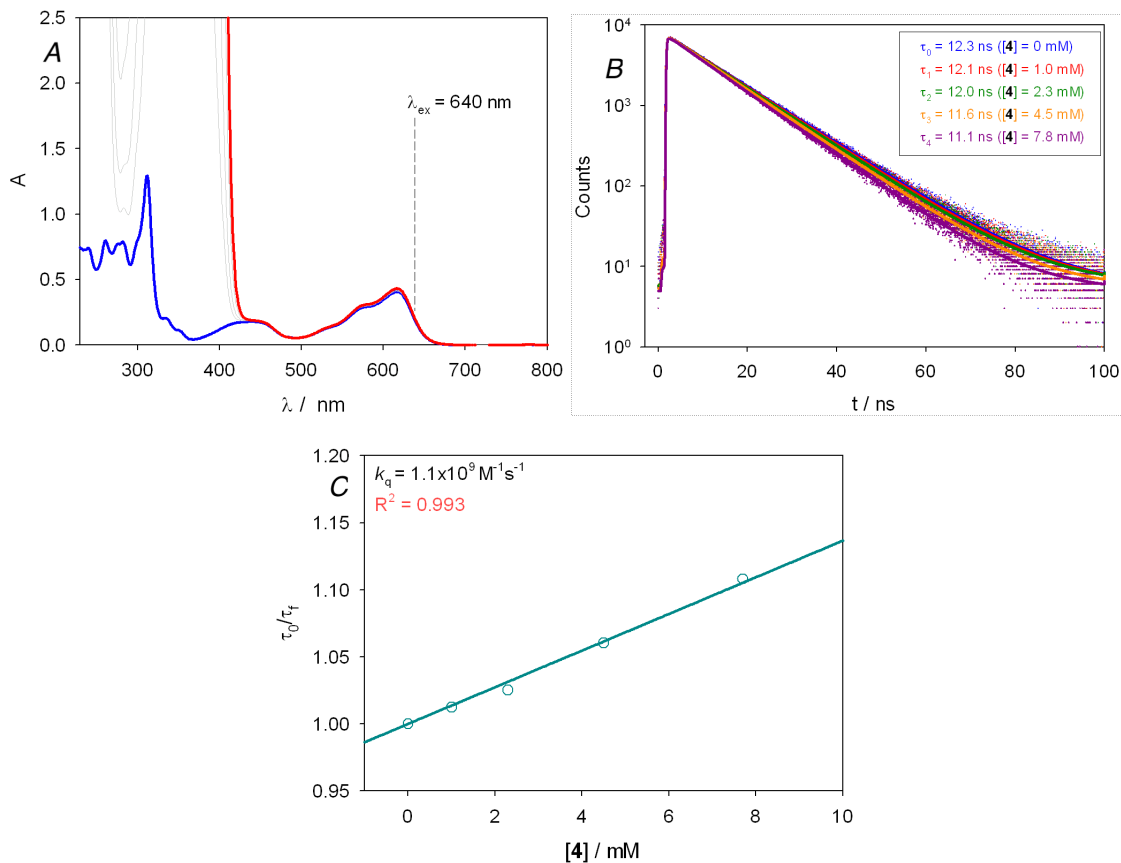


Figure S5. a. Absorption spectra of solutions of 1⁺ in air-equilibrated CH₂Cl₂ at r.t. (ca. 37 μM, blue line) obtained upon addition of increasing amounts of Hantzsch's ester (4, up to ca. 7.8 mM, red line). **b.** fluorescence decays of 1⁺ obtained from the same solutions at λ_{em} = 680 nm (λ_{ex} = 640 nm). The instrument response function (IRF) is also shown (grey dots). **c.** Stern-Volmer diagram relative to the fluorescence lifetimes.

1⁺ vs equimolar 5 + 6

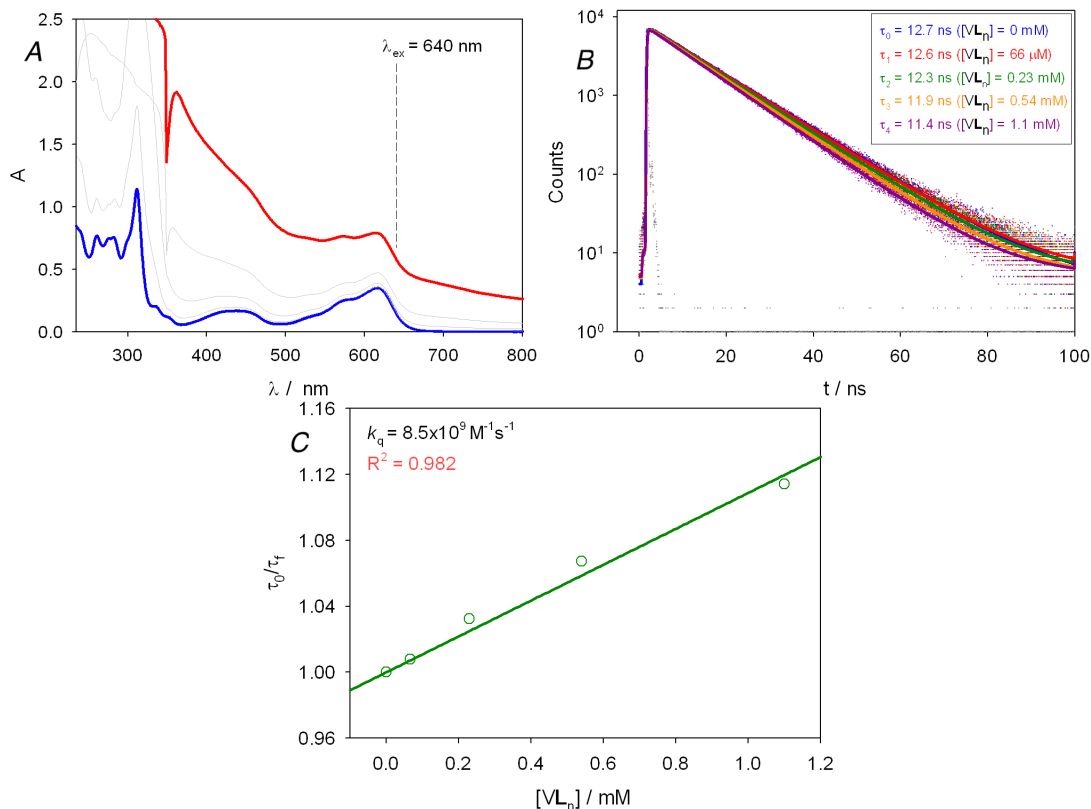


Figure S6. a. Absorption spectra of solutions of 1⁺ in degassed CH₂Cl₂ at r.t. (ca. 32 μM, blue line) obtained upon addition of increasing amounts of the complex obtained between equimolar amounts of 5 + 6 (up to ca. 1.1 mM, red line). **b.** fluorescence decays of 1⁺ obtained from the same solutions at λ_{em} = 680 nm (λ_{ex} = 640 nm). The instrument response function (IRF) is also shown (grey dots). **c.** Stern-Volmer diagram relative to the fluorescence lifetimes.

Note for the preparation of the complex between 6 and 5: Inside a nitrogen filled glovebox was prepared a solution containing 5 + 6 reproducing the concentration obtained running the photocatalytic reaction. To ensure the formation of the desired complex the solution was allowed to stir 30 minutes prior to use.

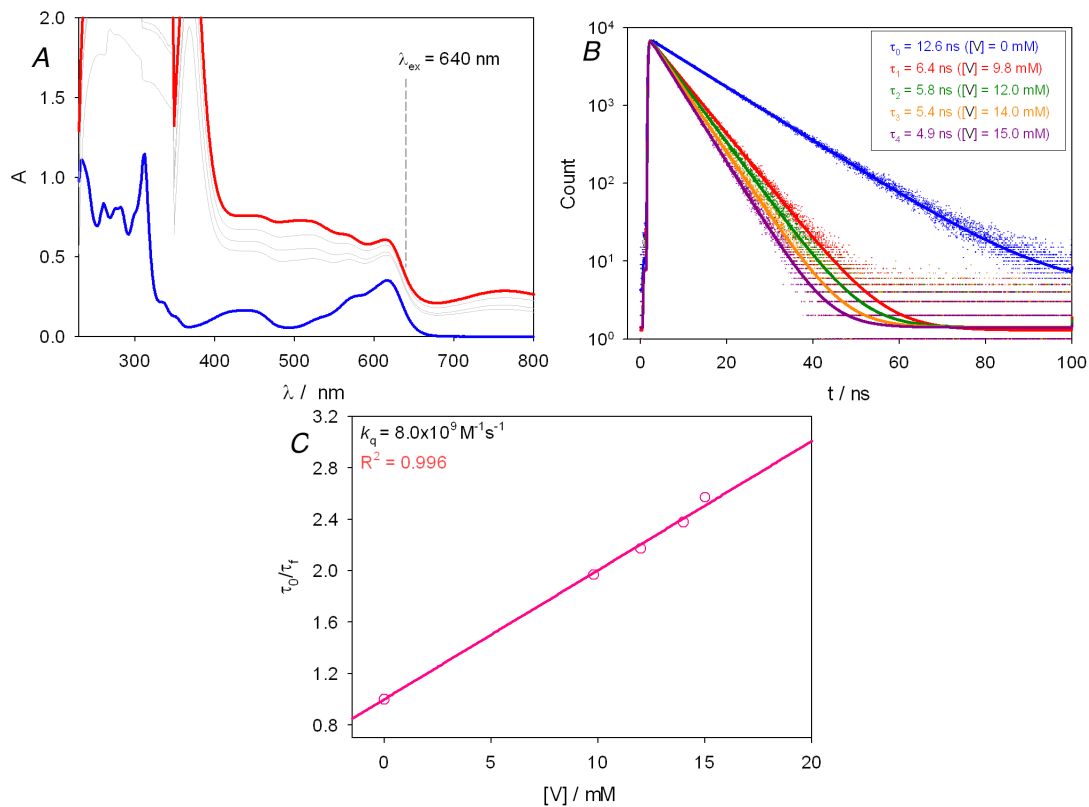
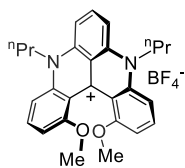
1^+ vs 6

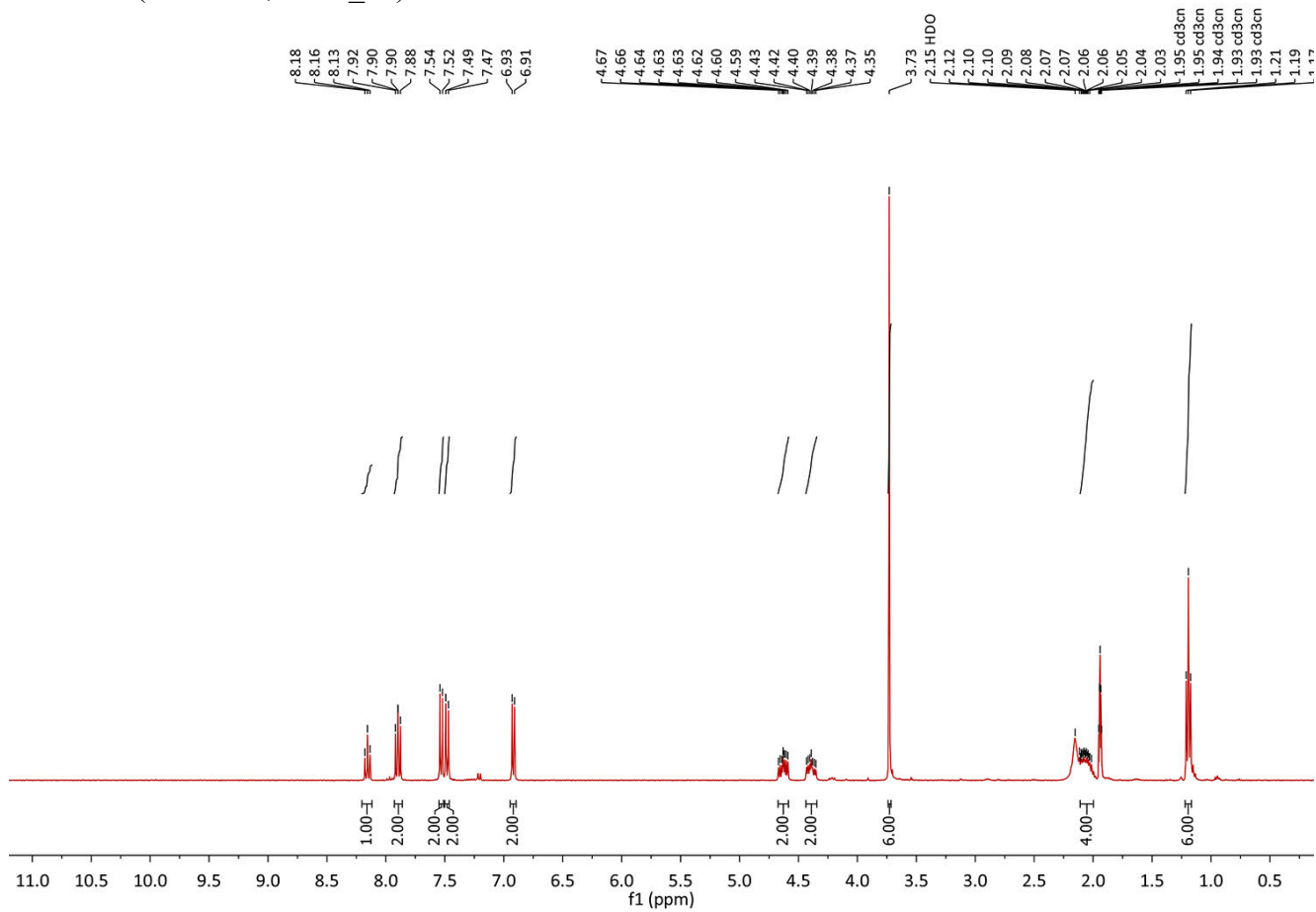
Figure S7. a. Absorption spectra of solutions of 1^+ in degassed CH_2Cl_2 at r.t. (ca. $32 \mu\text{M}$, blue line) obtained upon addition of increasing amounts of 6 (up to ca. 15 mM, red line). **b.** fluorescence decays of 1^+ obtained from the same solutions at $\lambda_{\text{em}} = 680 \text{ nm}$ ($\lambda_{\text{ex}} = 640 \text{ nm}$). The instrument response function (IRF) is also shown (grey dots). **c.** Stern-Volmer diagram relative to the fluorescence lifetimes.

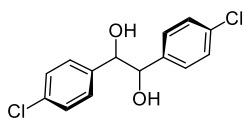
Copies of NMR spectra



(1⁺) *N,N'*-di-*n*-propyl-1,13-dimethoxyquinacridinium

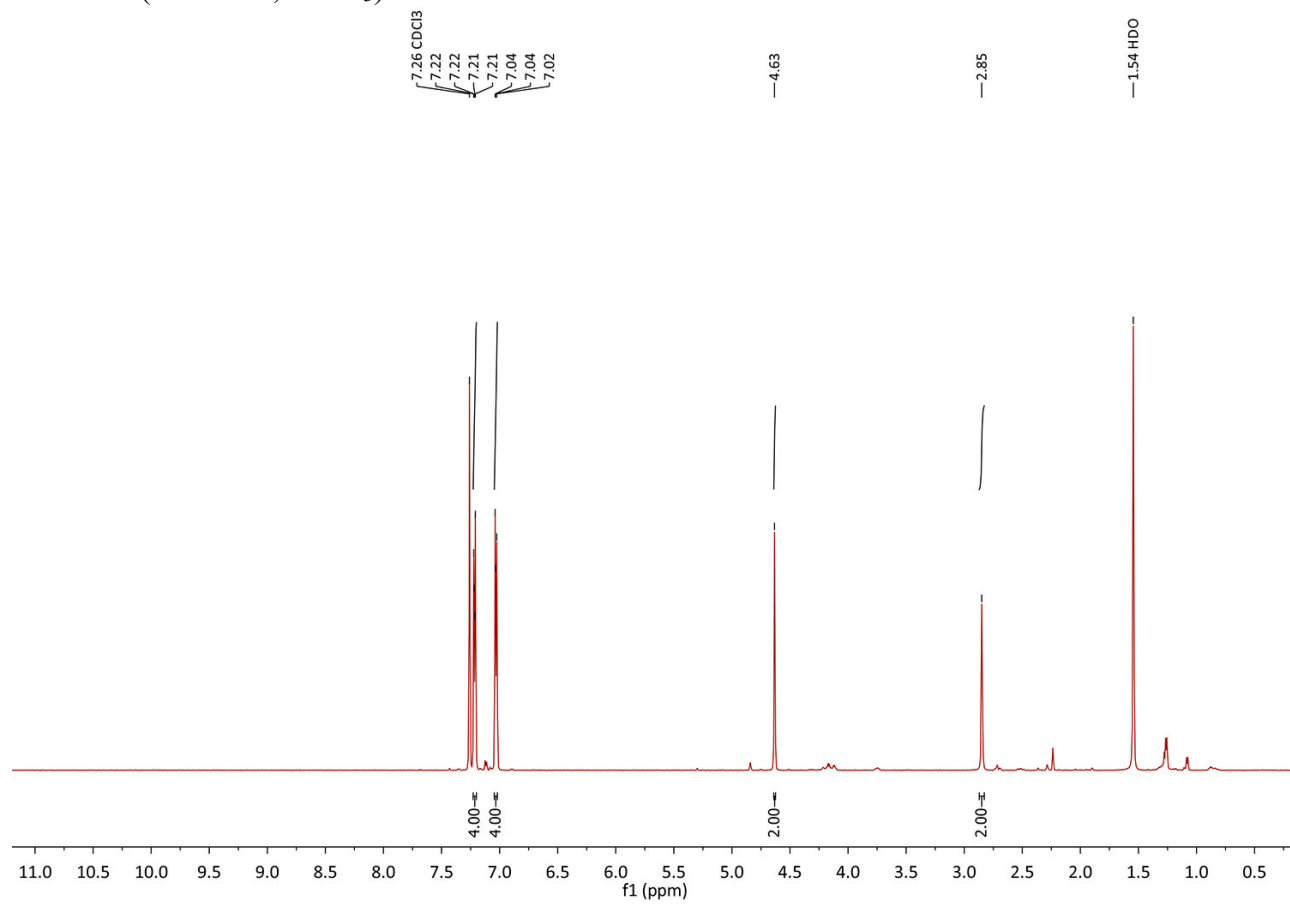
¹H NMR (400 MHz, ACN-*d*3)



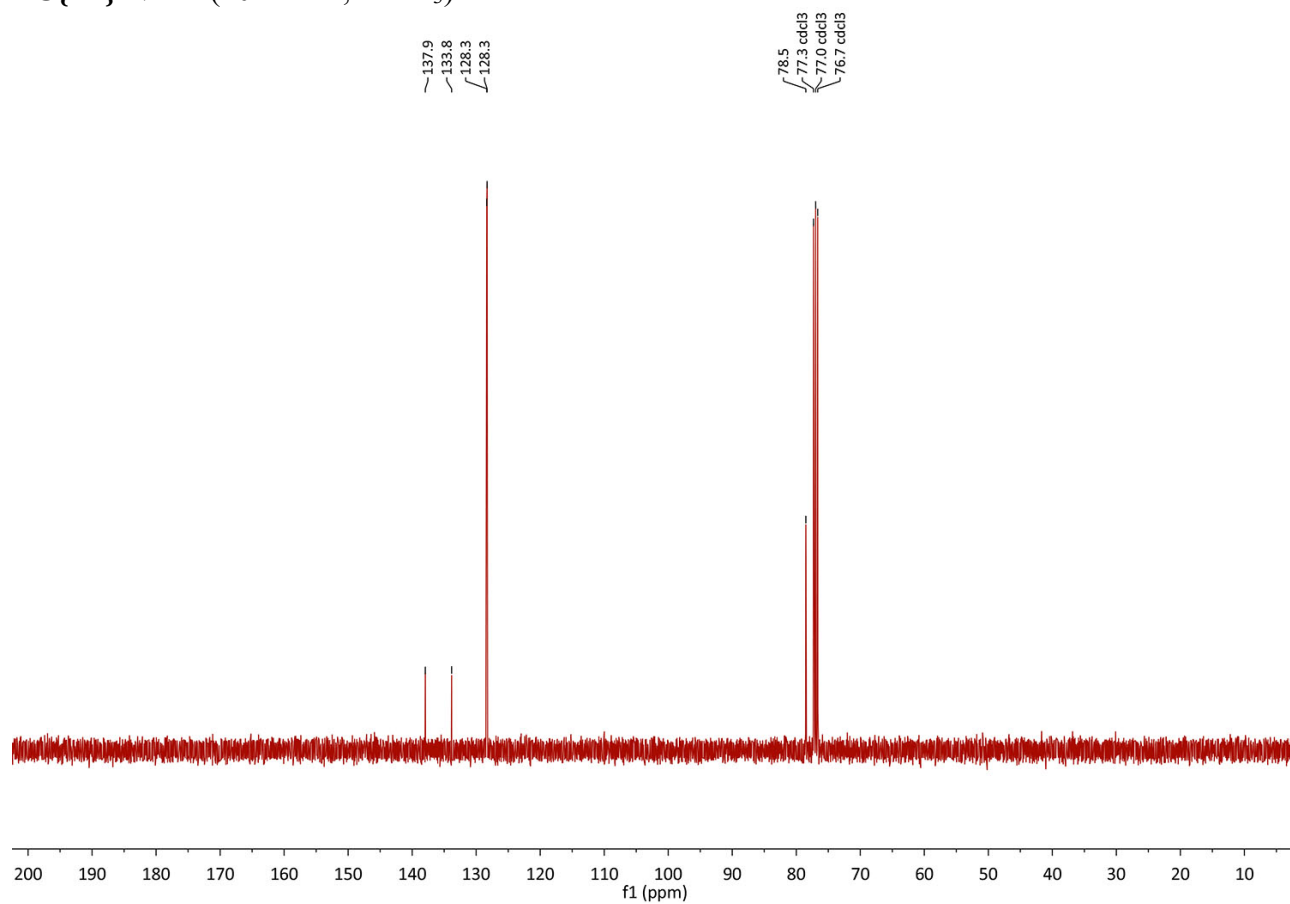


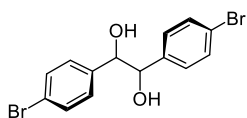
(**3a_d**/**1** : **3a_{meso}** > 20:1) 1,2-bis(4-chlorophenyl)ethane-1,2-diol

¹H NMR (600 MHz, CDCl₃)



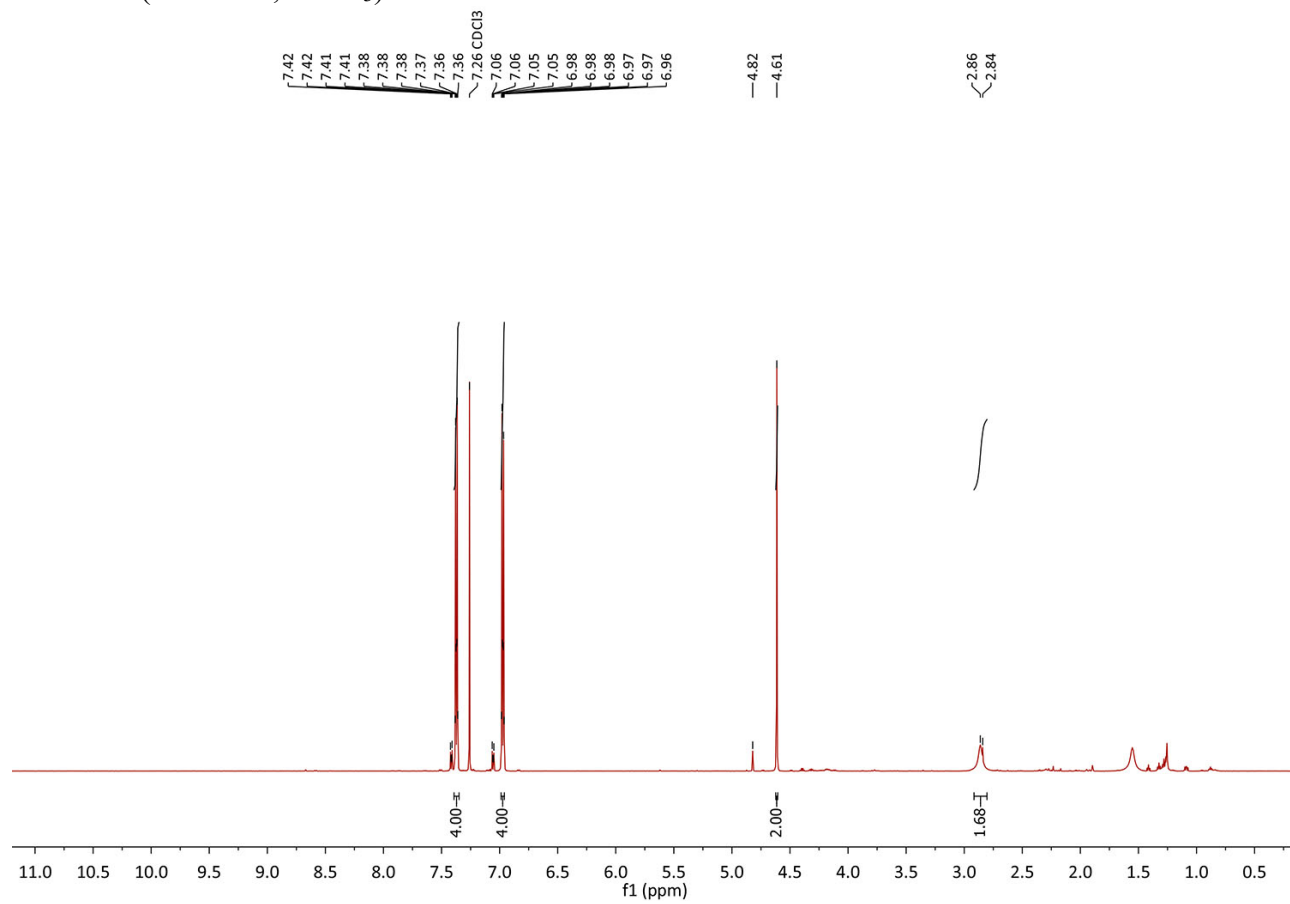
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3)



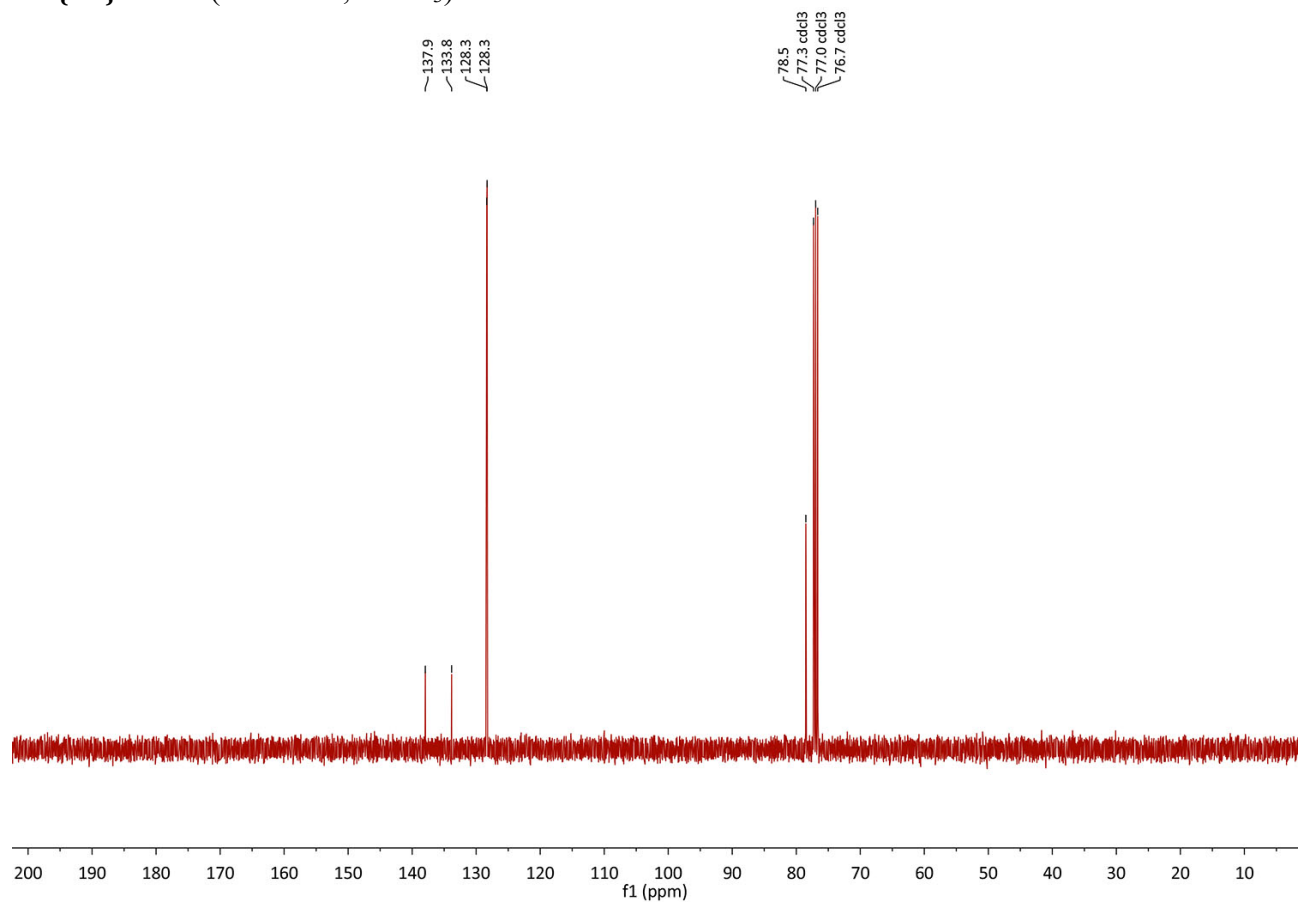


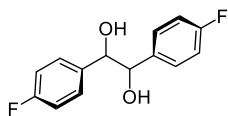
(**3b_d** / **3b_{meso}** > 20:1) 1,2-bis(4-bromophenyl)ethane-1,2-diol

¹H NMR (600 MHz, CDCl₃)



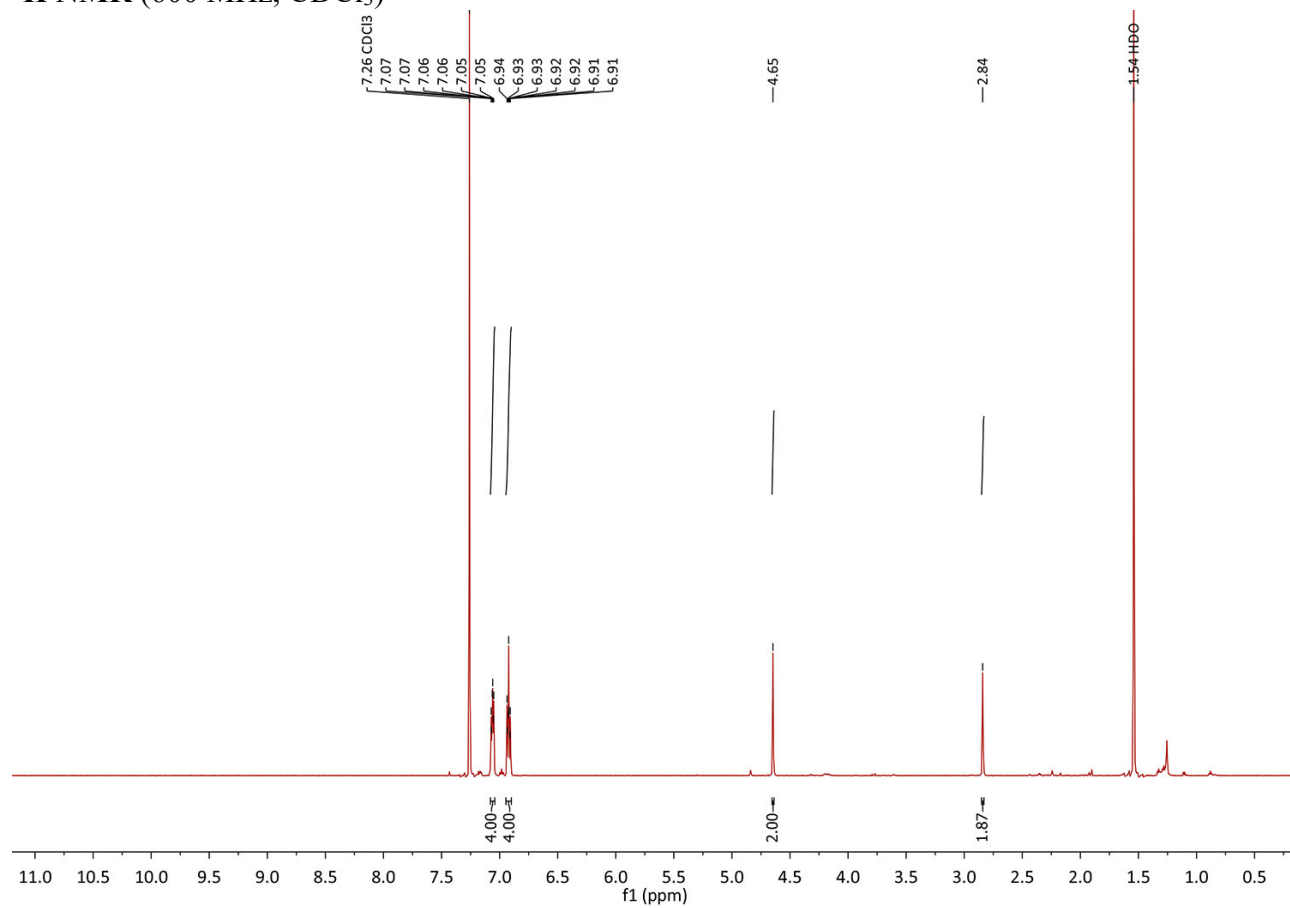
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3)



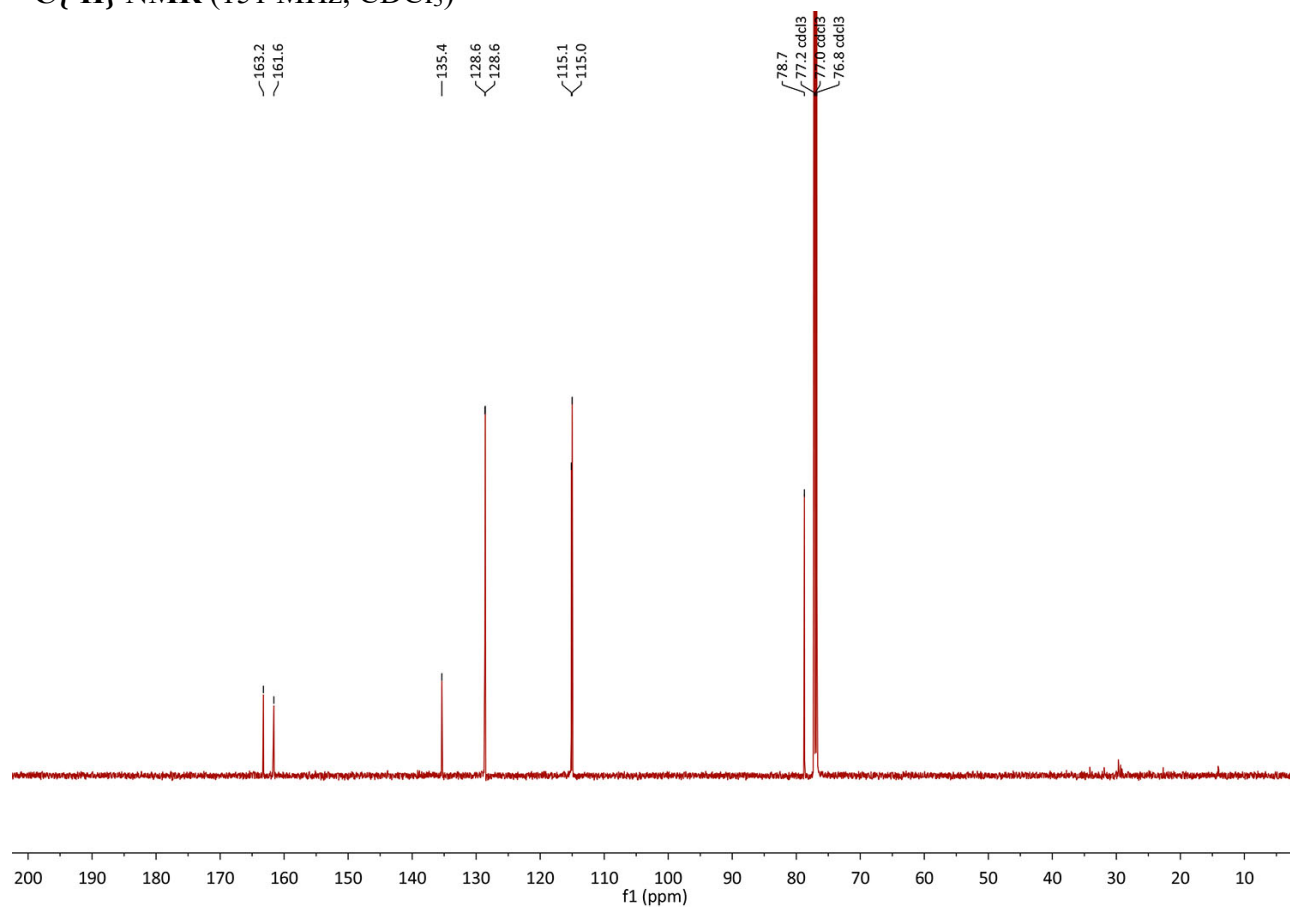


(**3c_{d/l}** : **3c_{meso}** > 20:1) 1,2-bis(4-fluorophenyl)ethane-1,2-diol

¹H NMR (600 MHz, CDCl₃)

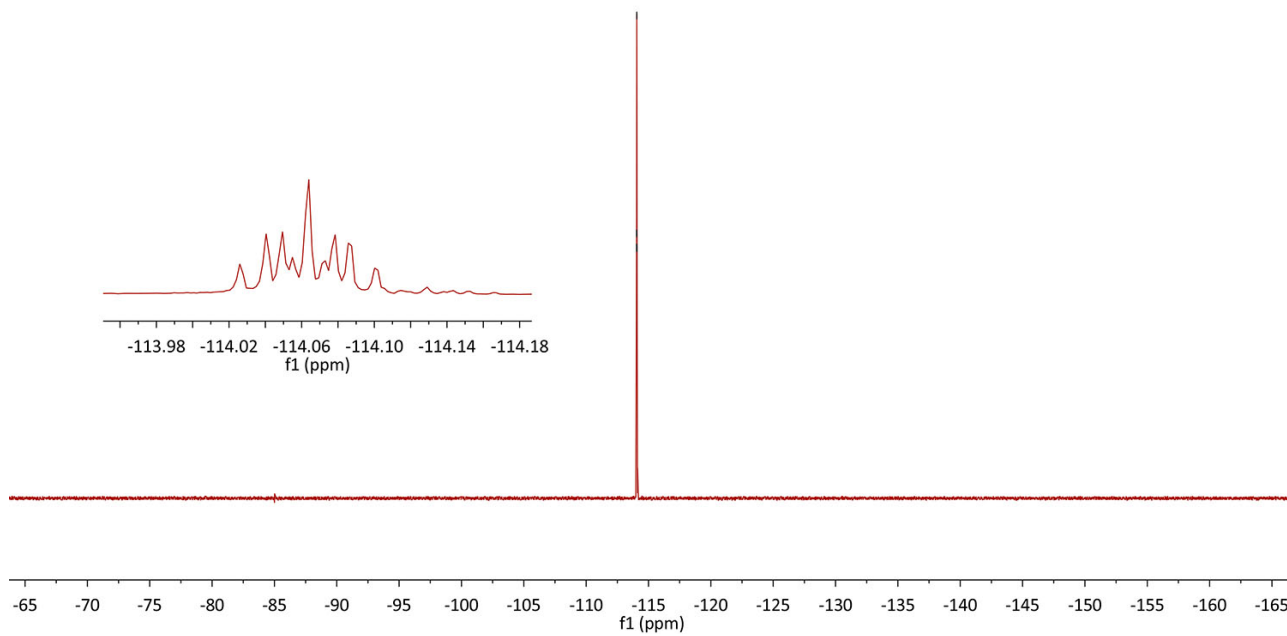


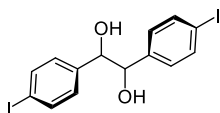
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

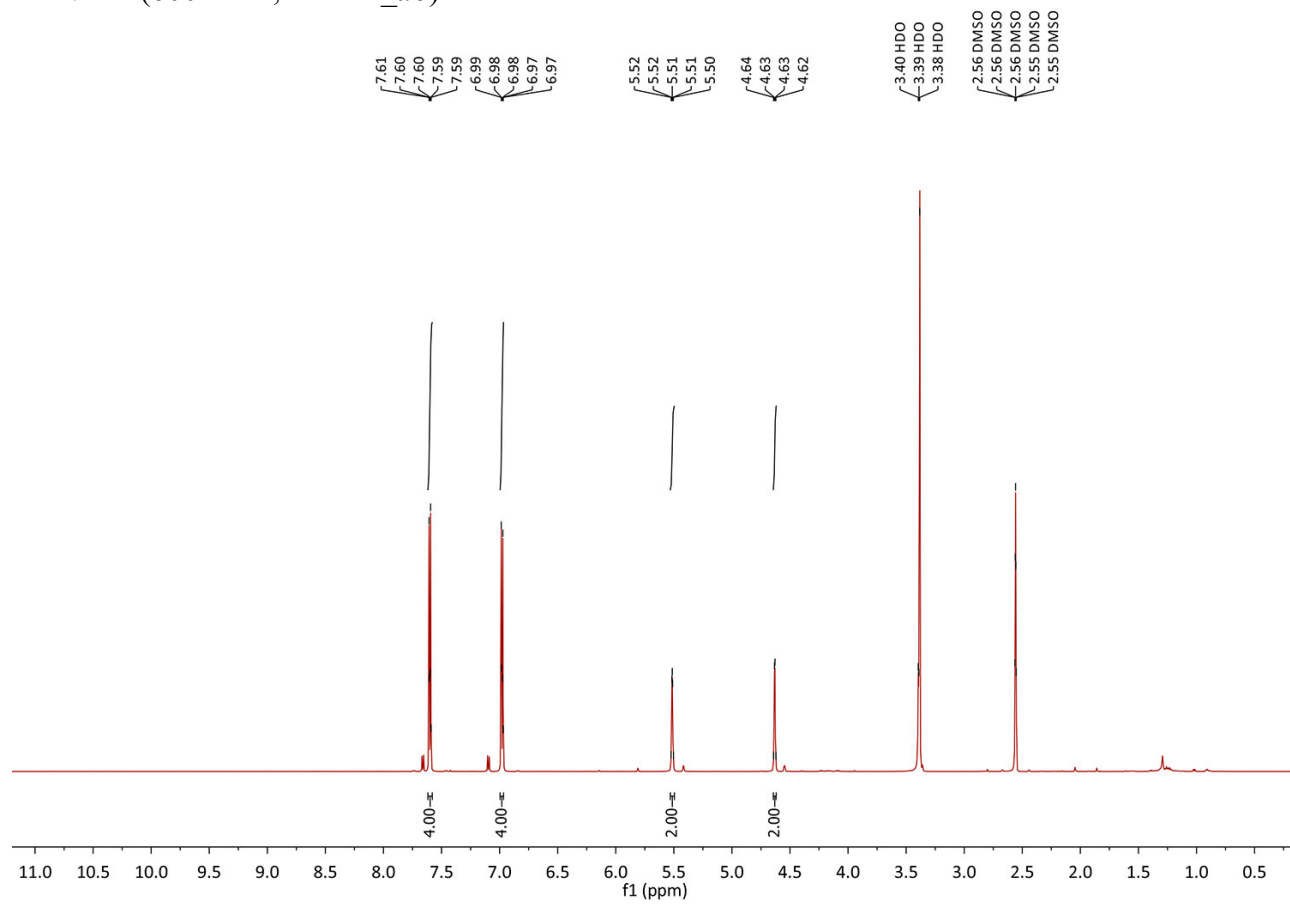
{
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}



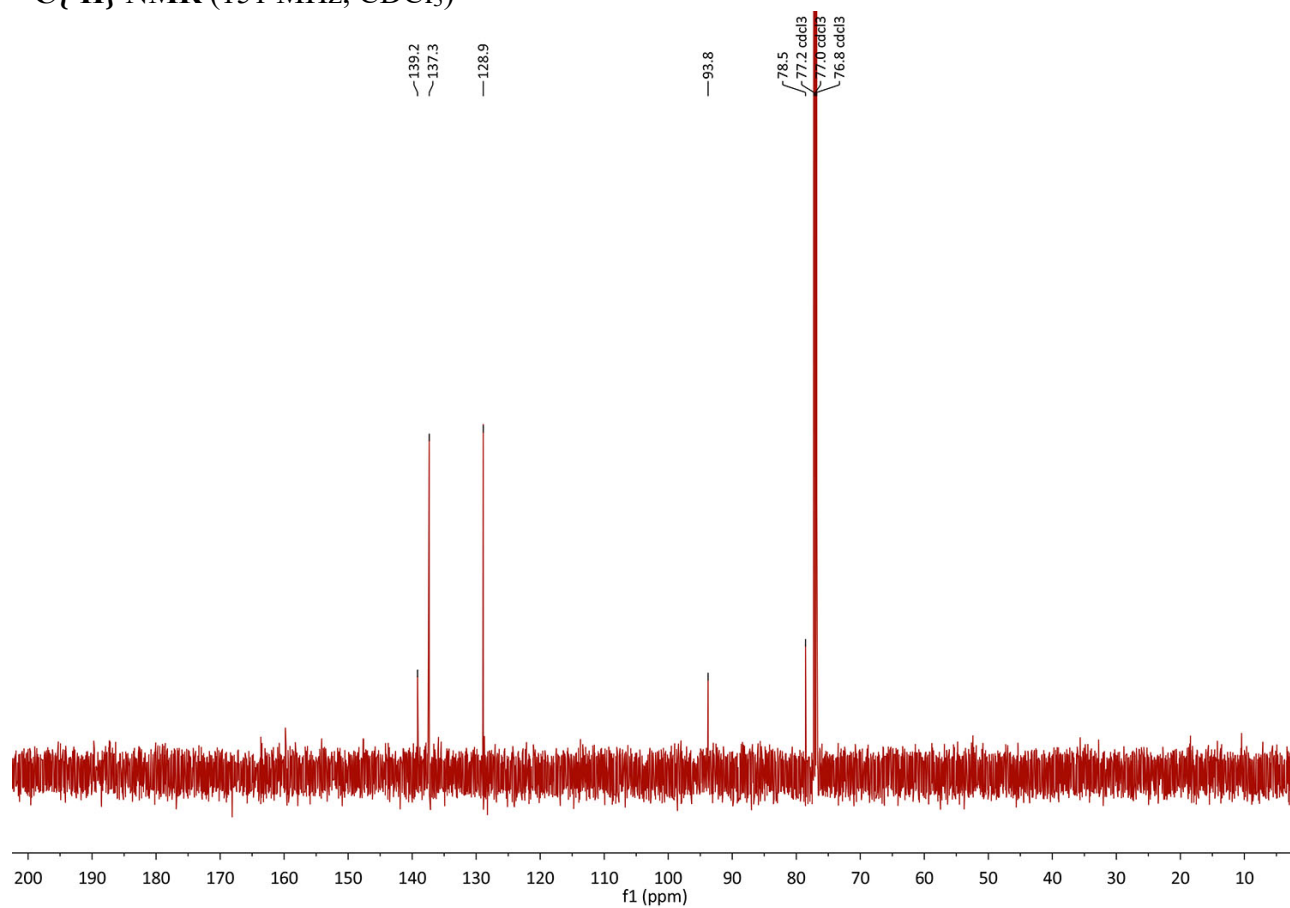


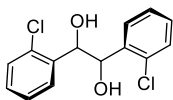
(**3d_d**/**3d_{meso}** = 17:1) 1,2-bis(4-iodophenyl)ethane-1,2-diol

¹H NMR (600 MHz, DMSO-*d*₆)



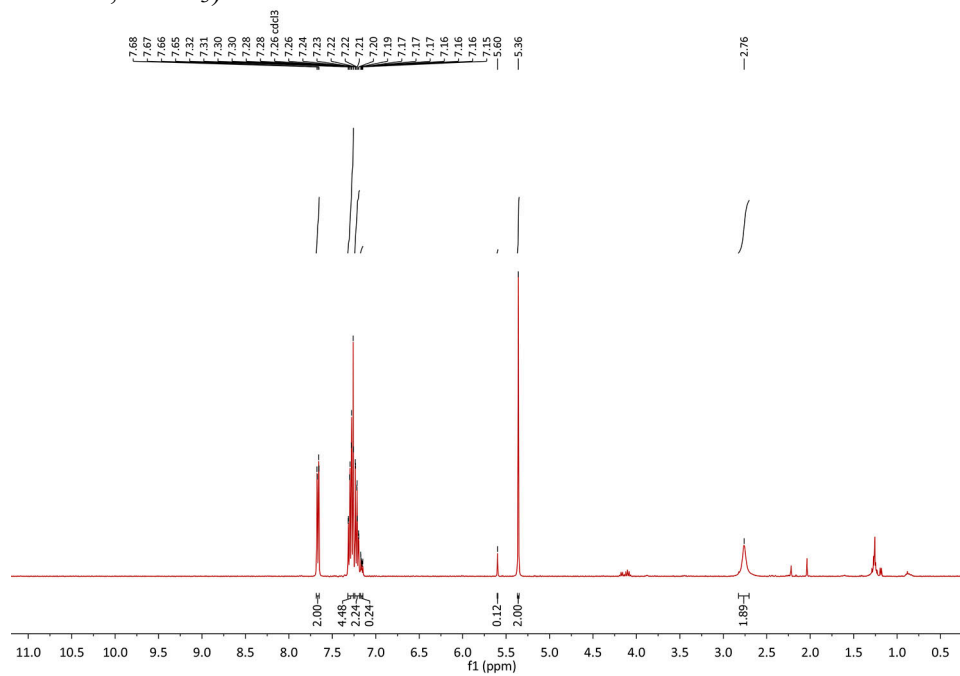
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)



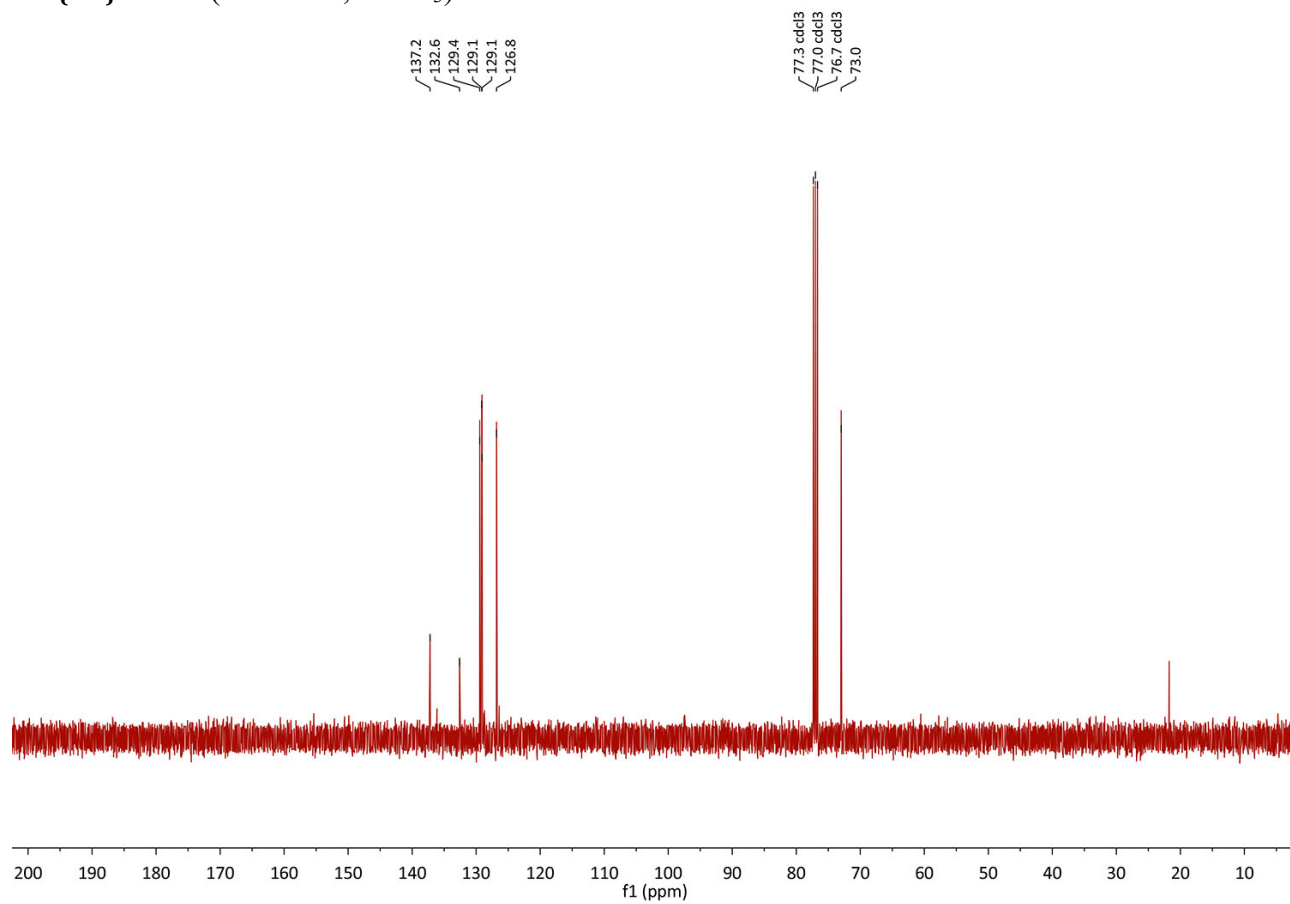


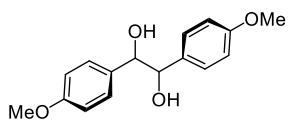
($3e_d$: $3e_{meso}$ = 17:1) 1,2-bis(2-chlorophenyl)ethane-1,2-diol

^1H NMR (400 MHz, CDCl_3)



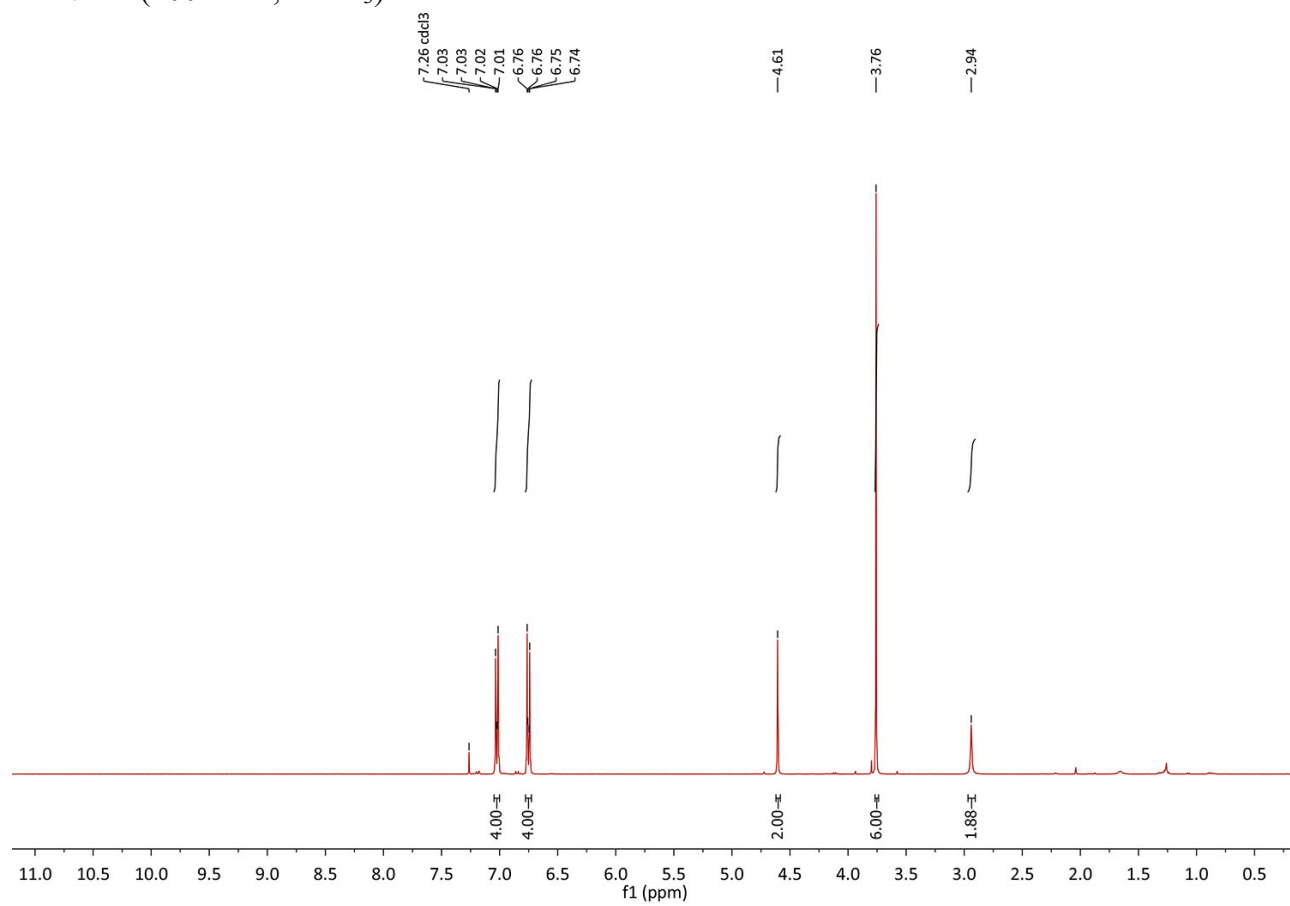
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3)



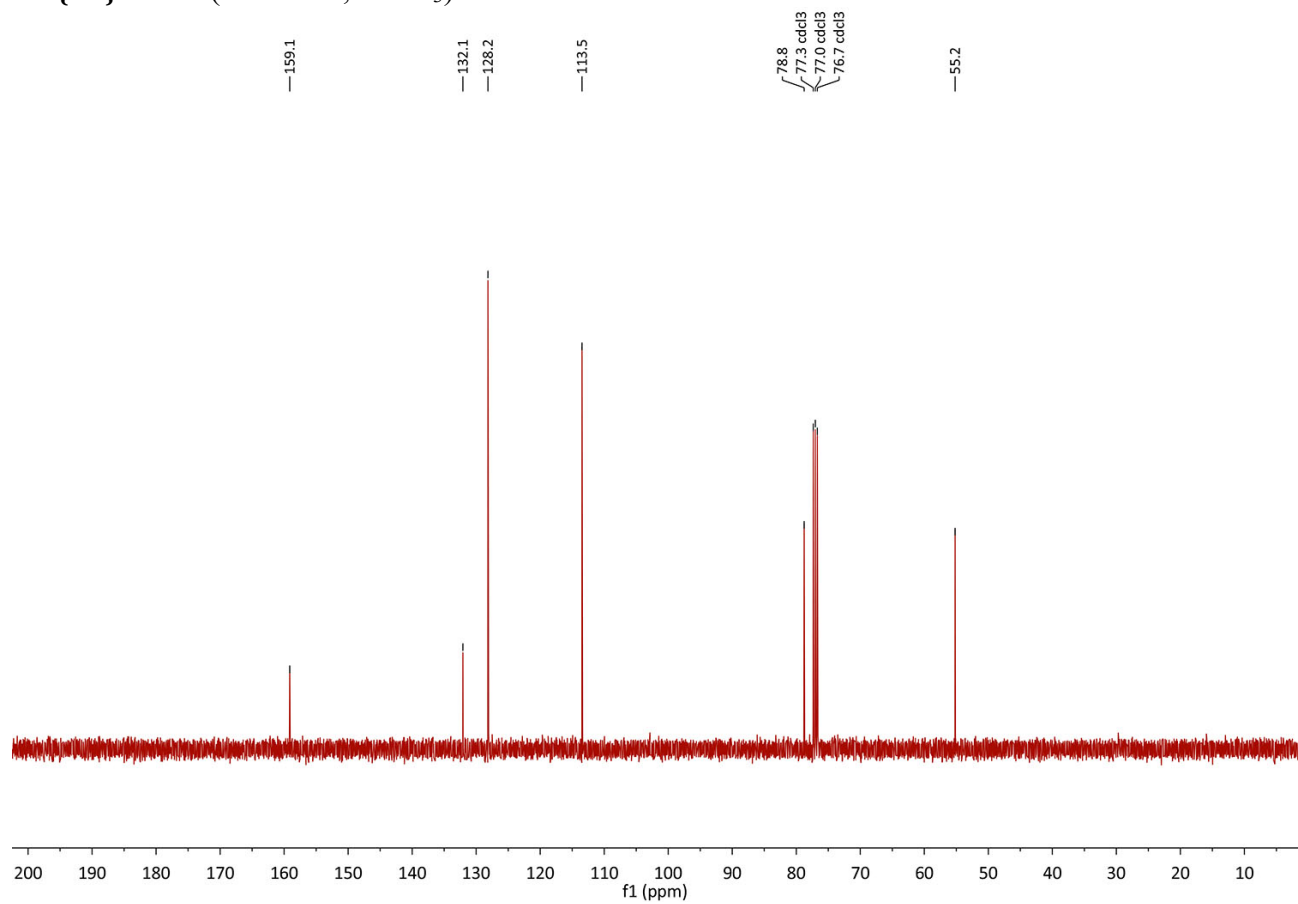


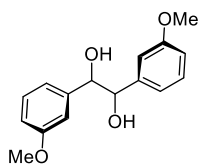
(**3f_d** : **3f_{meso}** > 20:1) 1,2-bis(4-methoxyphenyl)ethane-1,2-diol

¹H NMR (400 MHz, CDCl₃)



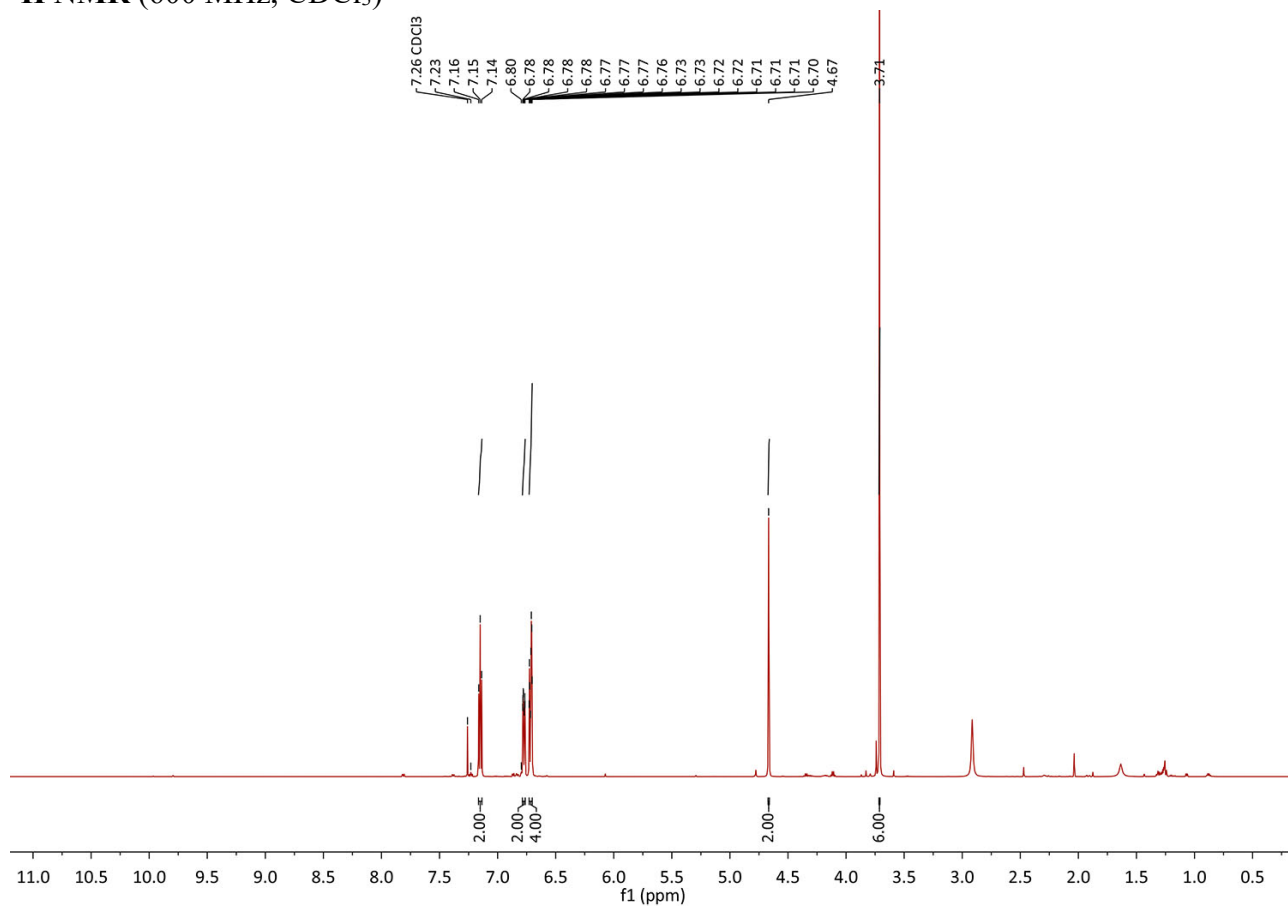
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3)



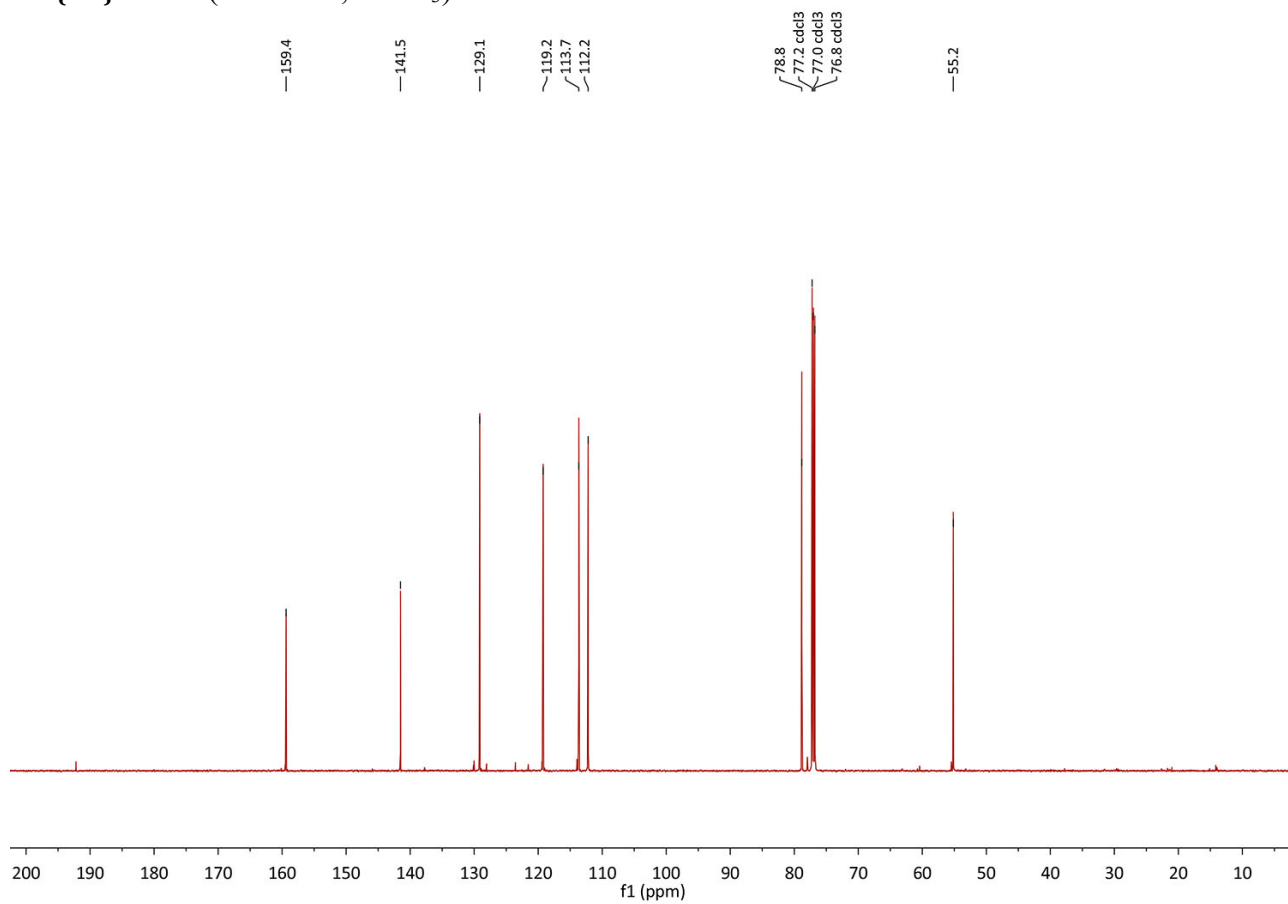


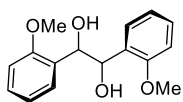
(**3g_{d/l}** : **3g_{meso}** > 20:1) 1,2-bis(3-methoxyphenyl)ethane-1,2-diol

¹H NMR (600 MHz, CDCl₃)



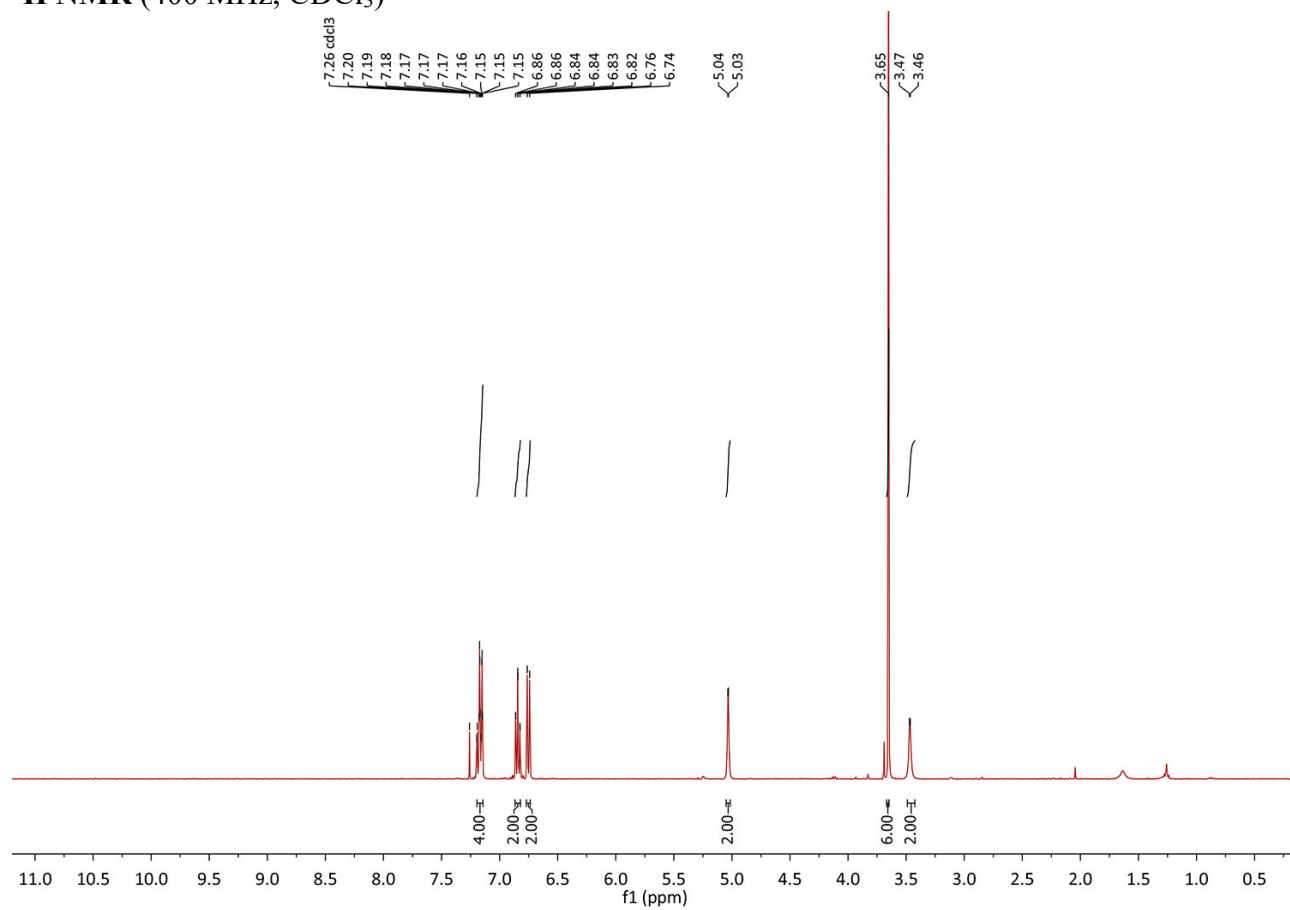
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)



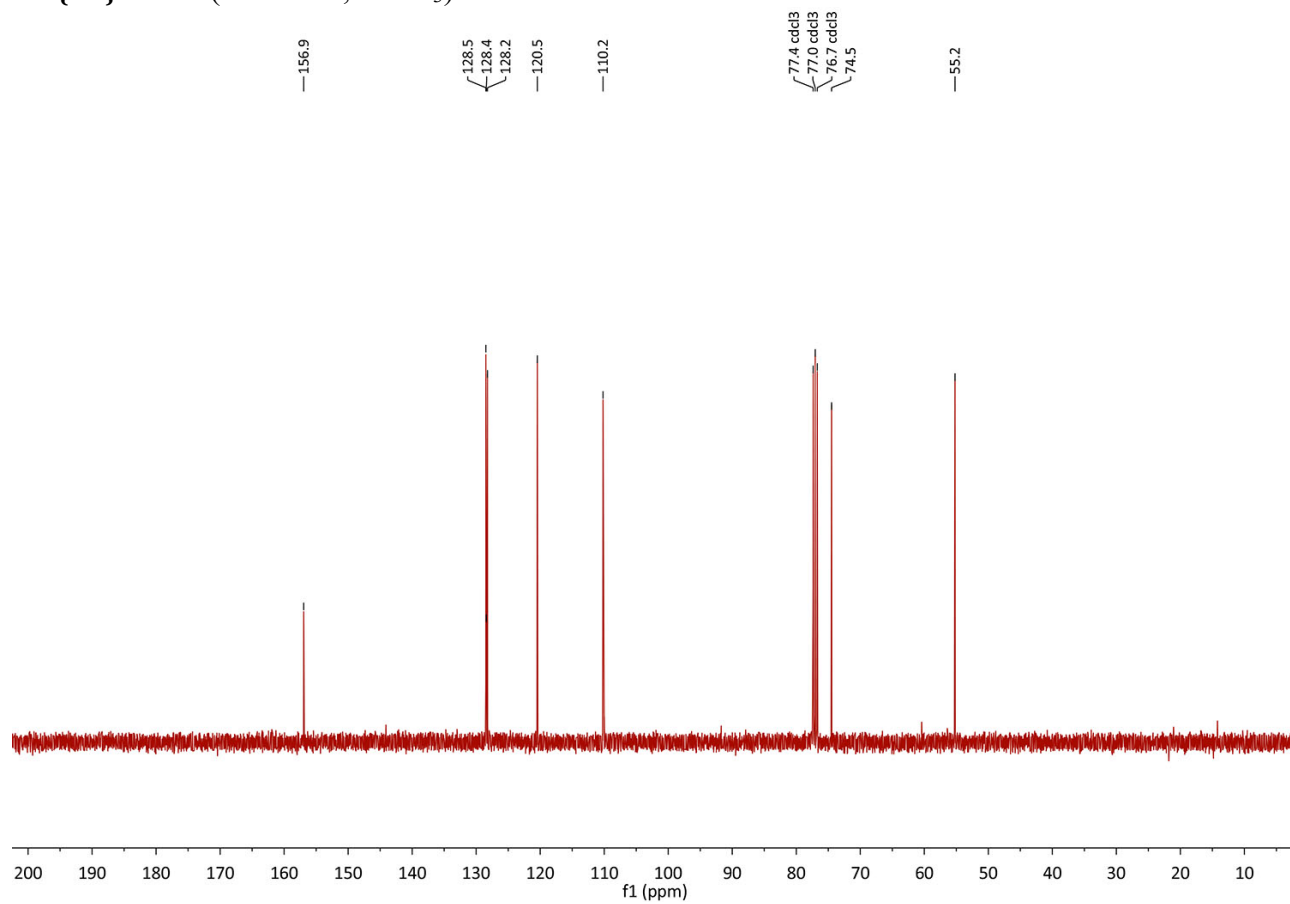


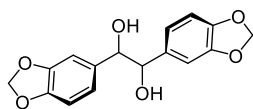
(**3h_{d/l}** : **3h_{meso}** > 20:1) 1,2-bis(2-methoxyphenyl)ethane-1,2-diol

¹H NMR (400 MHz, CDCl₃)



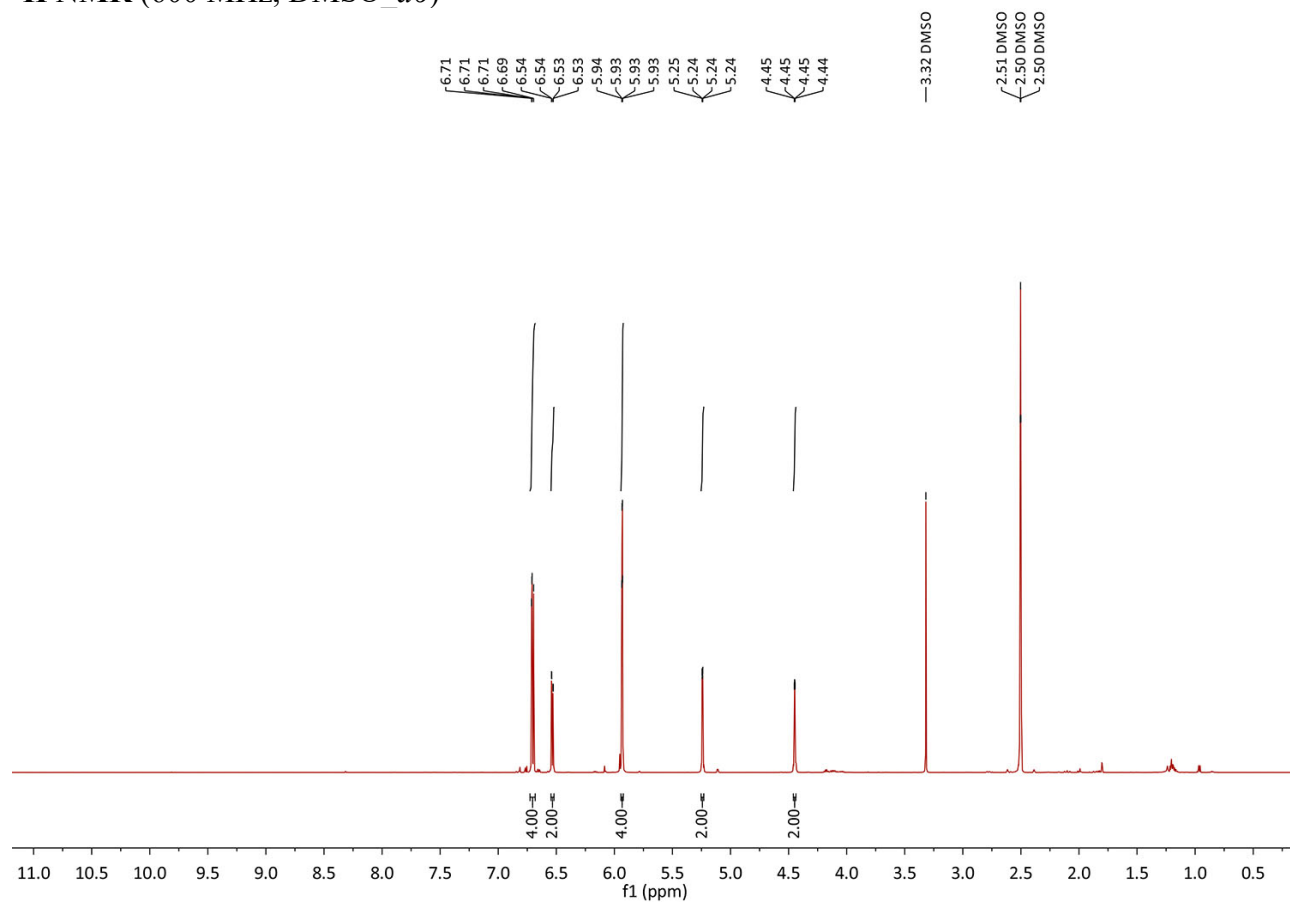
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3)



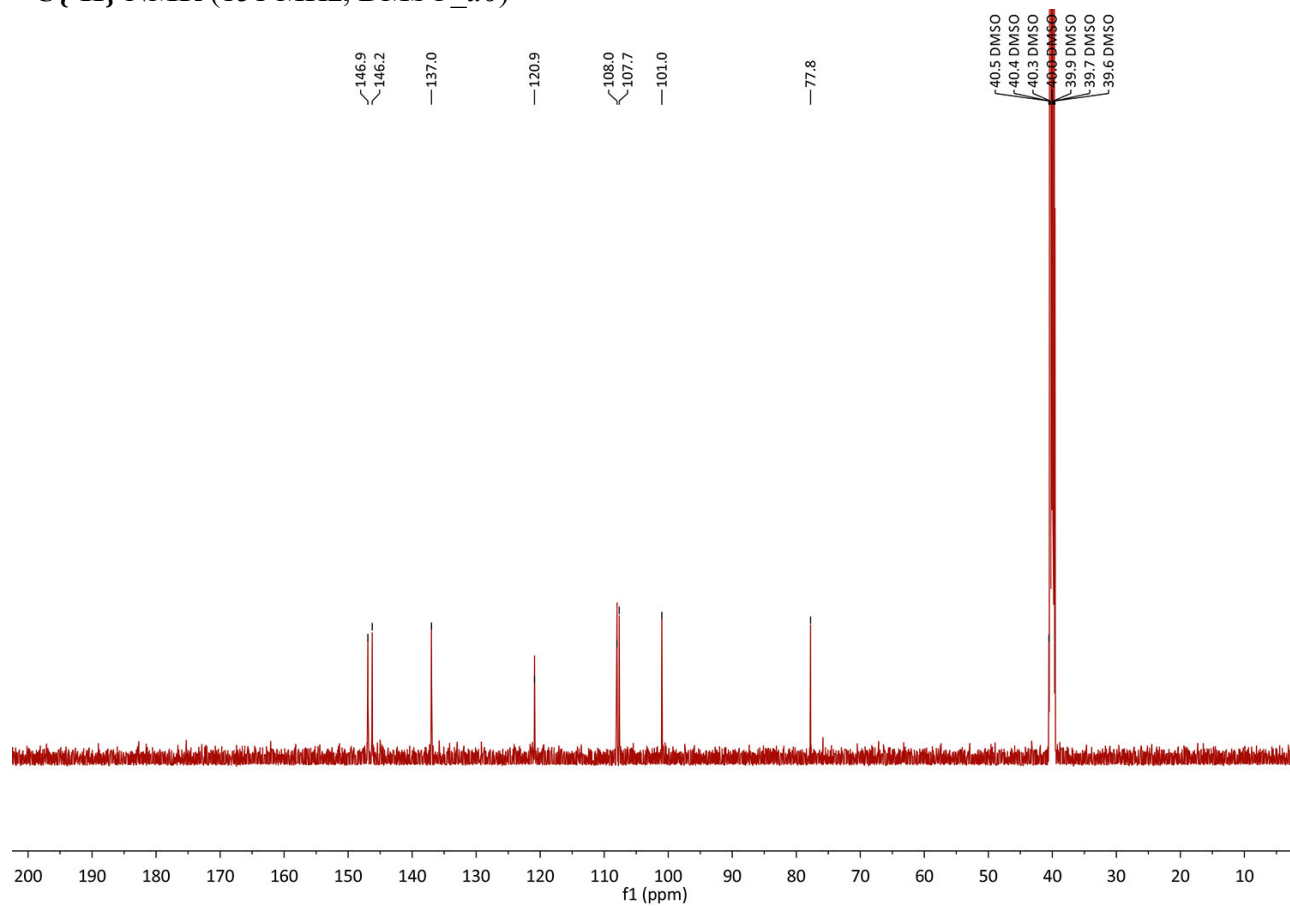


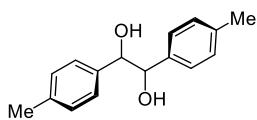
(**3i_d**1 : **3i_{meso}** > 20:1) 1,2-bis(benzo[d][1,3]dioxol-5-yl)ethane-1,2-diol

¹H NMR (600 MHz, DMSO-*d*₆)



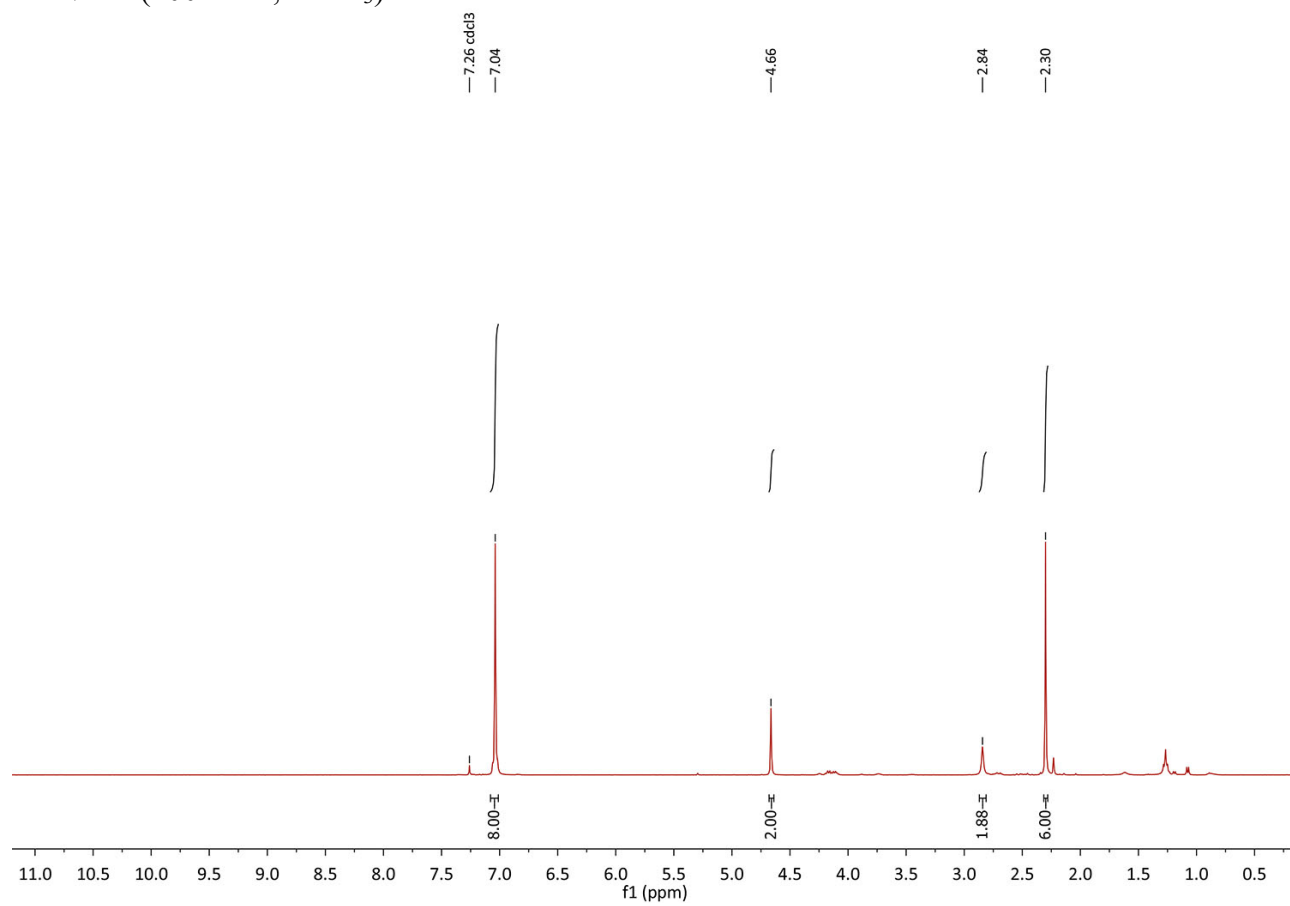
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO-*d*₆)



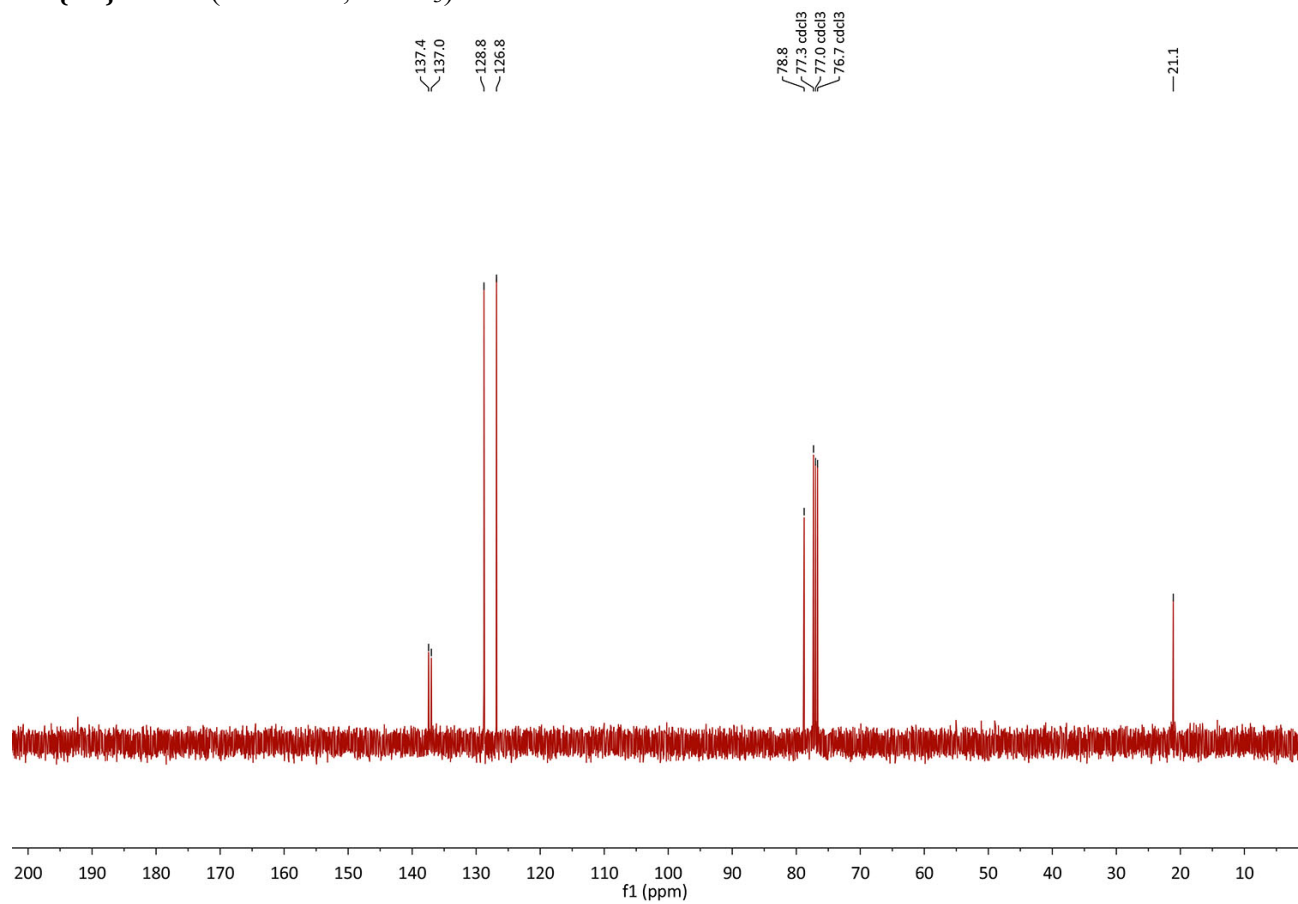


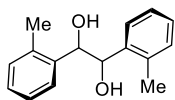
(**3j_d** / **3j_{meso}** > 20:1) 1,2-di-p-tolyethane-1,2-diol

¹H NMR (400 MHz, CDCl₃)



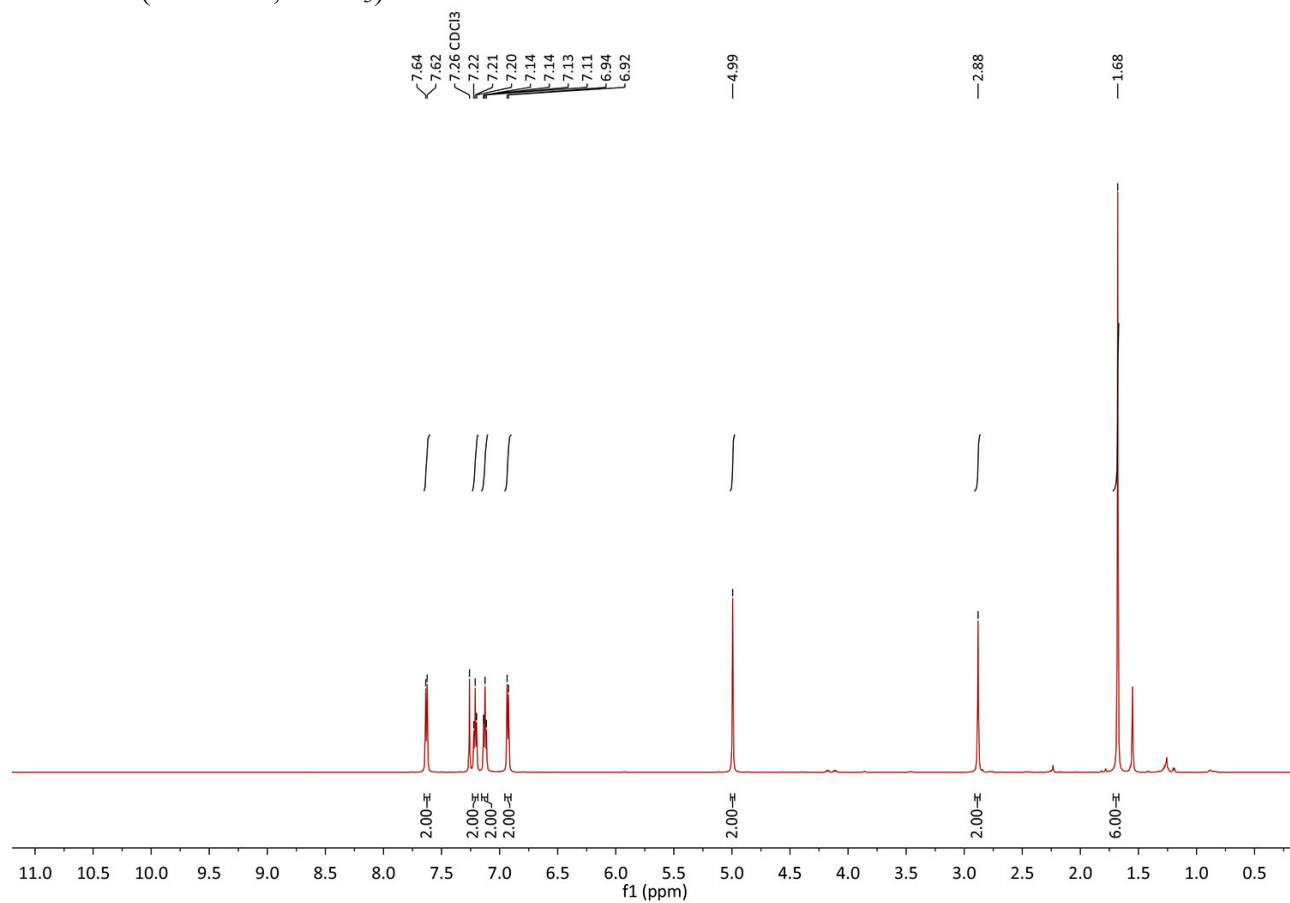
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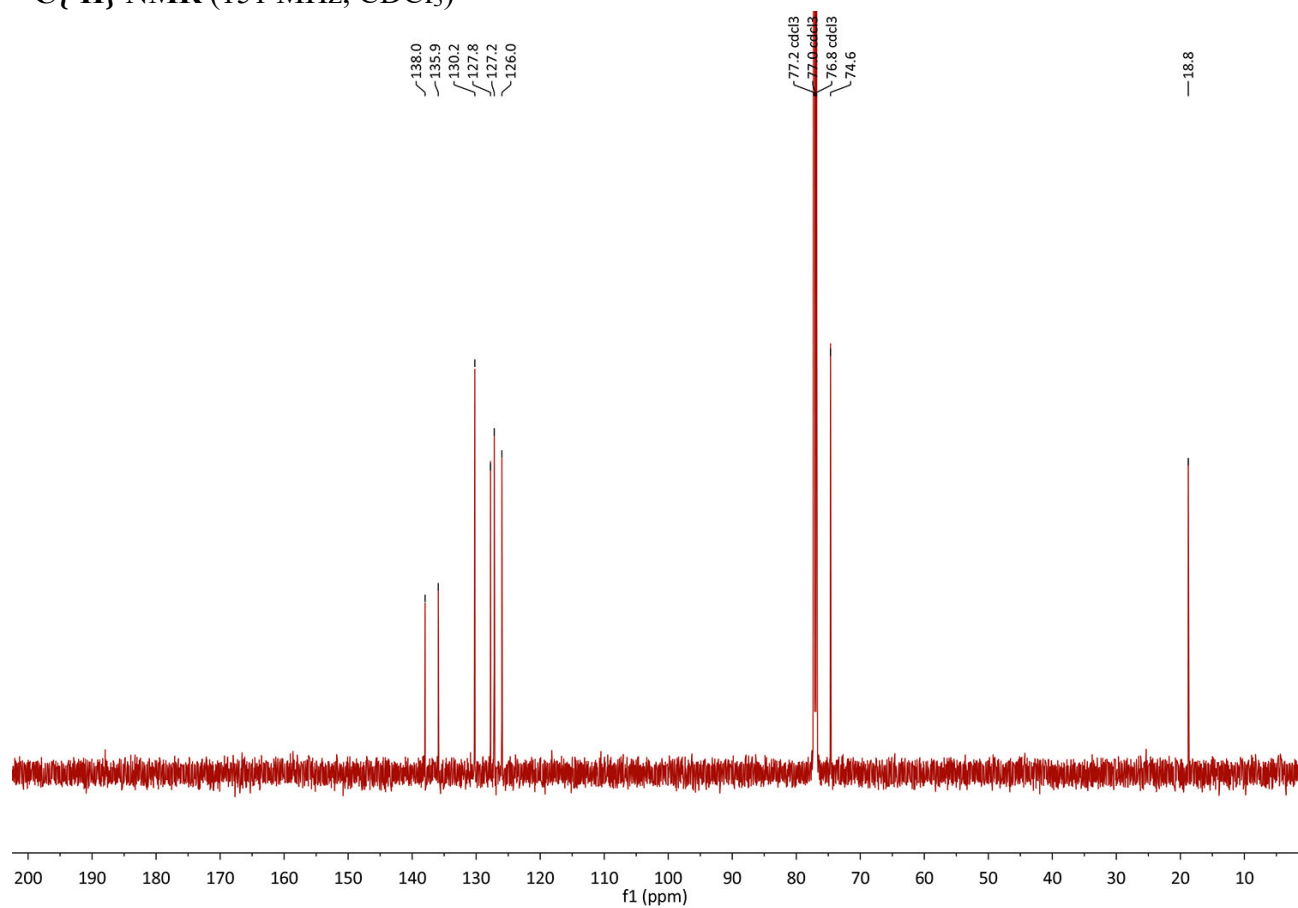


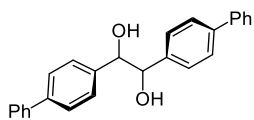
(**3k_d**/**3k_{meso}** > 20:1) 1,2-di-*o*-tolylethane-1,2-diol

¹H NMR (600 MHz, CDCl₃)



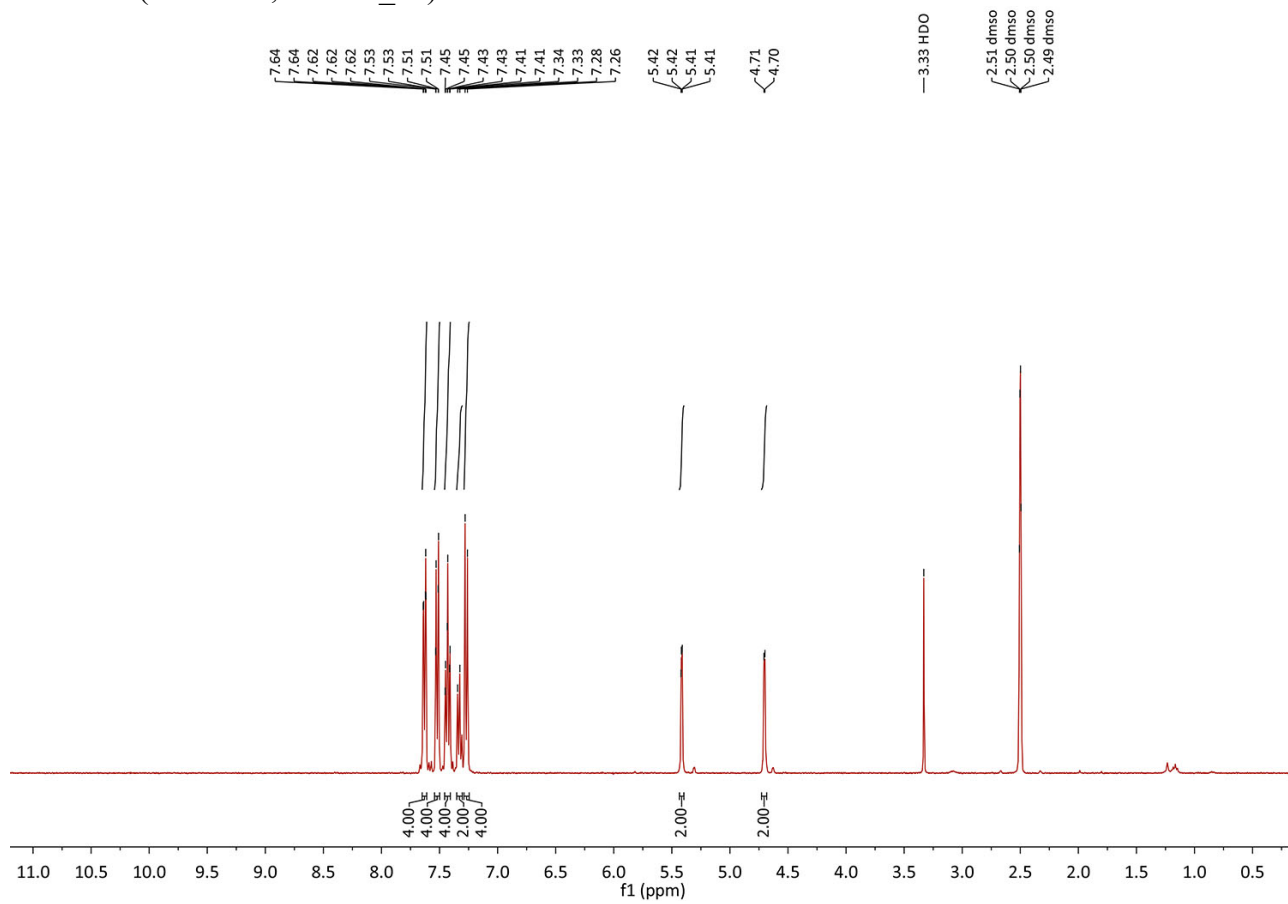
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)



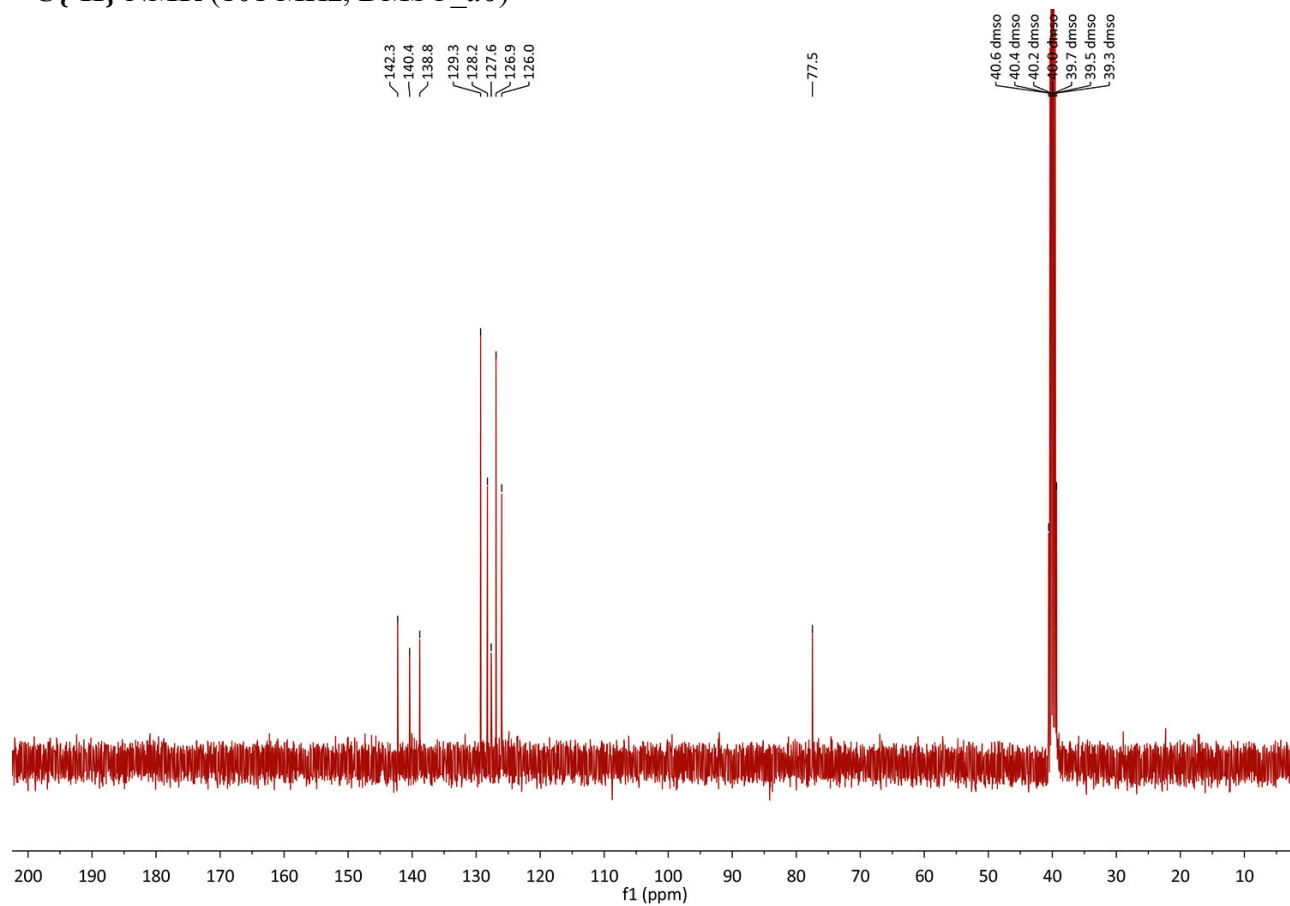


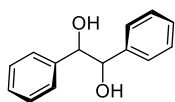
(**3l_d** : **3l_{meso}** > 20:1) 1,2-di([1,1'-biphenyl]-4-yl)ethane-1,2-diol

¹H NMR (400 MHz, DMSO-*d*₆)



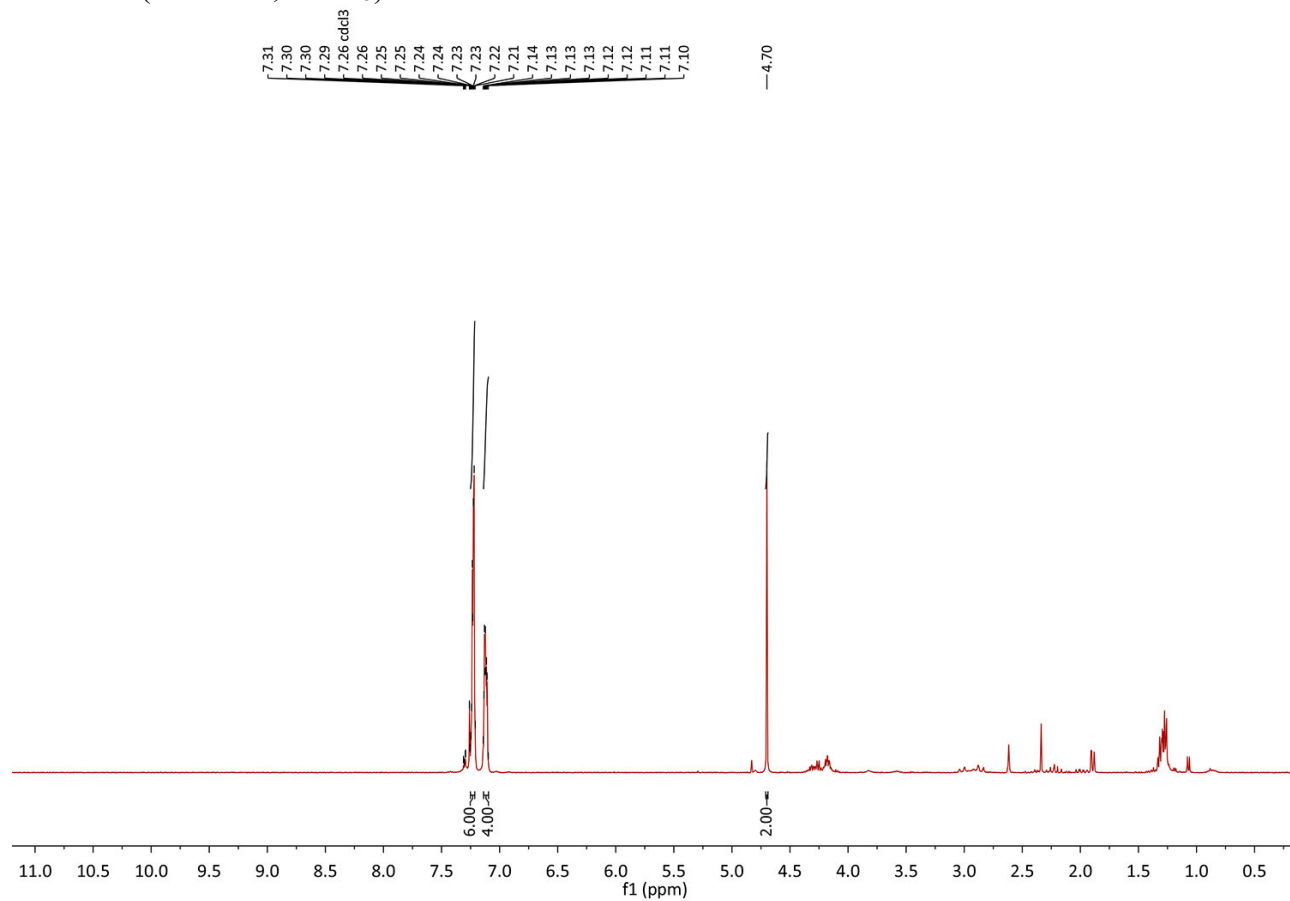
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO-*d*₆)



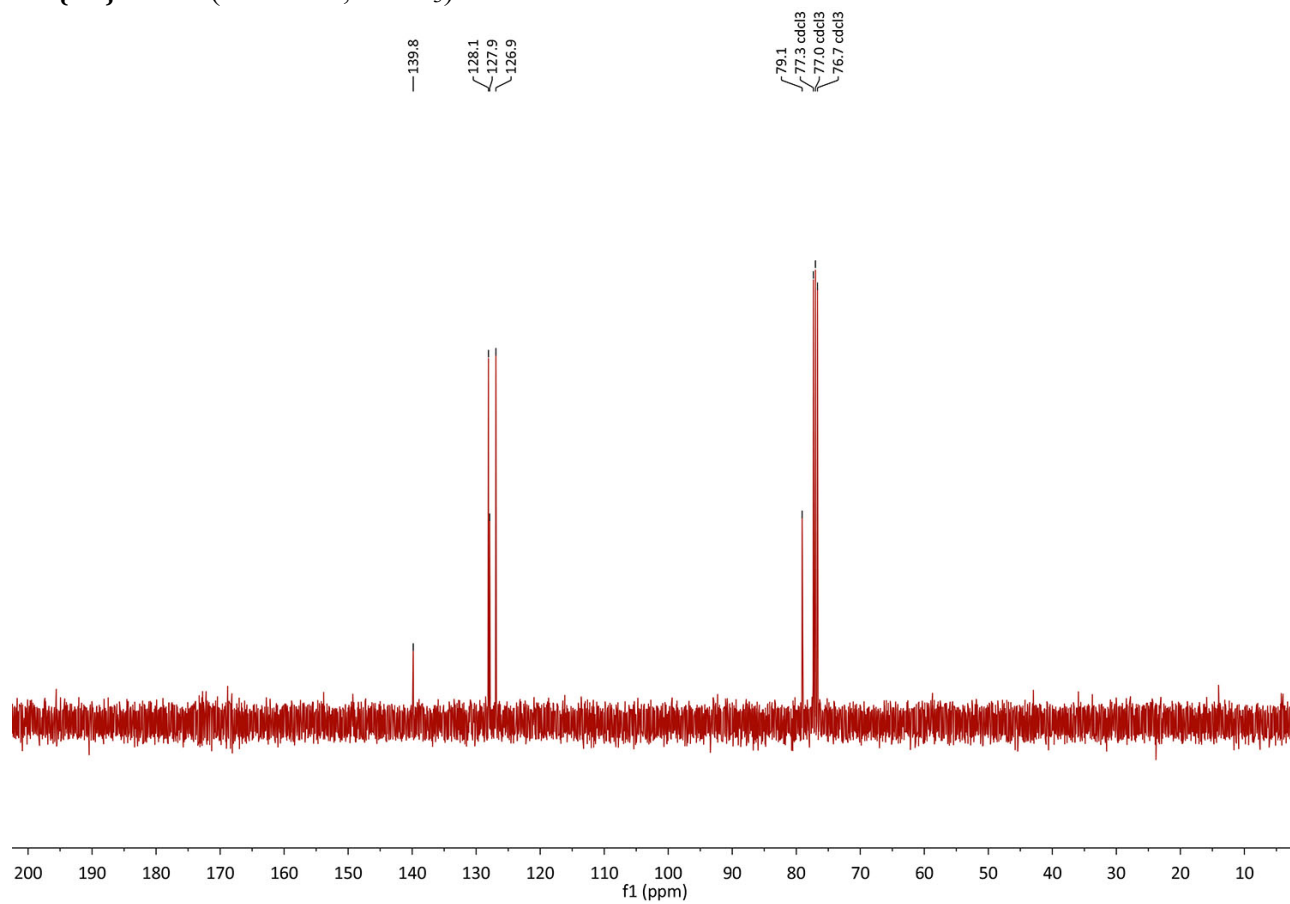


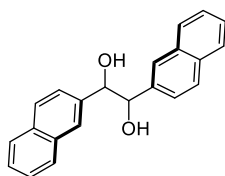
(**3m_{d/l}** : **3m_{meso}** > 20:1) 1,2-diphenylethane-1,2-diol

¹H NMR (400 MHz, CDCl₃)



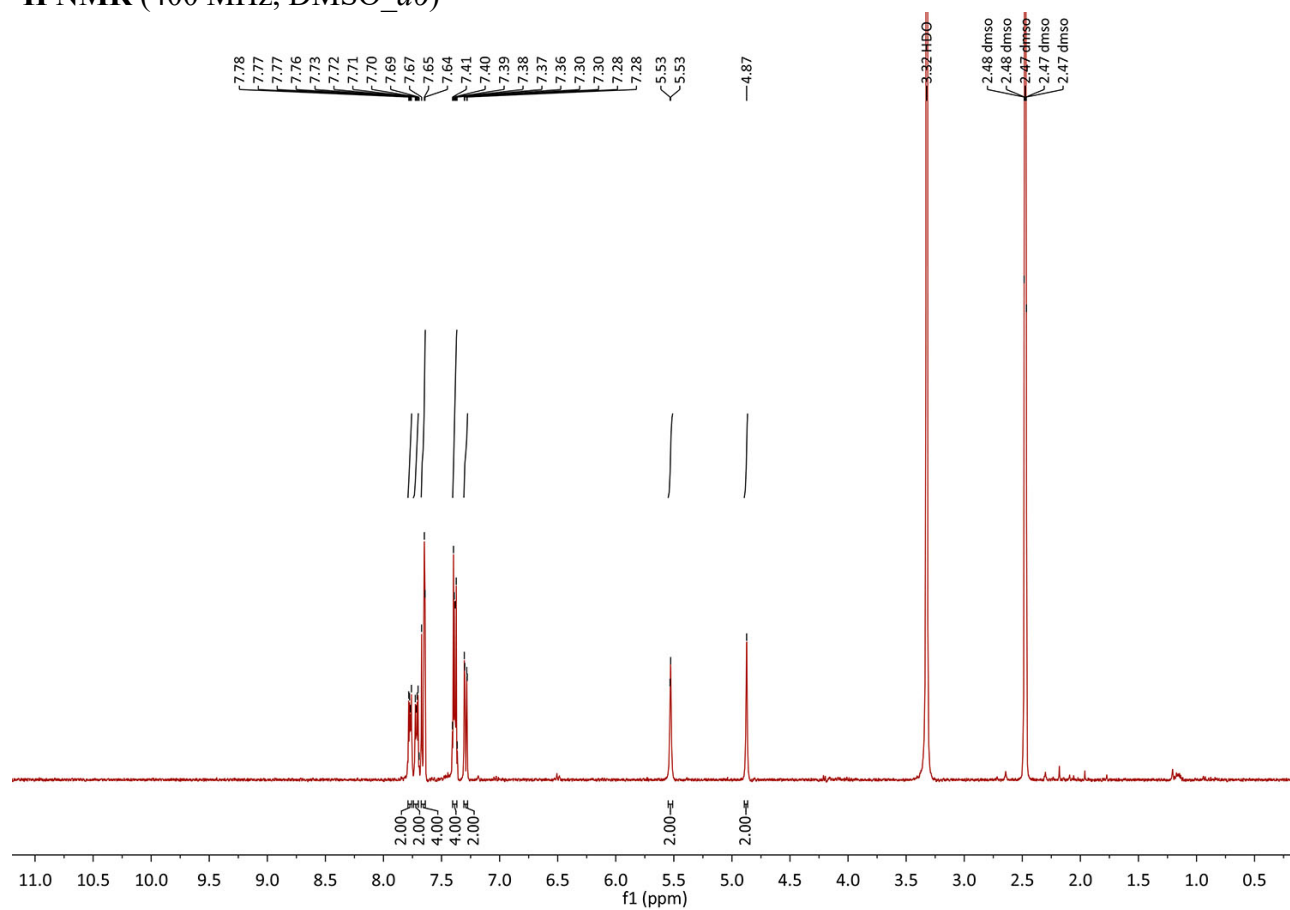
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3)



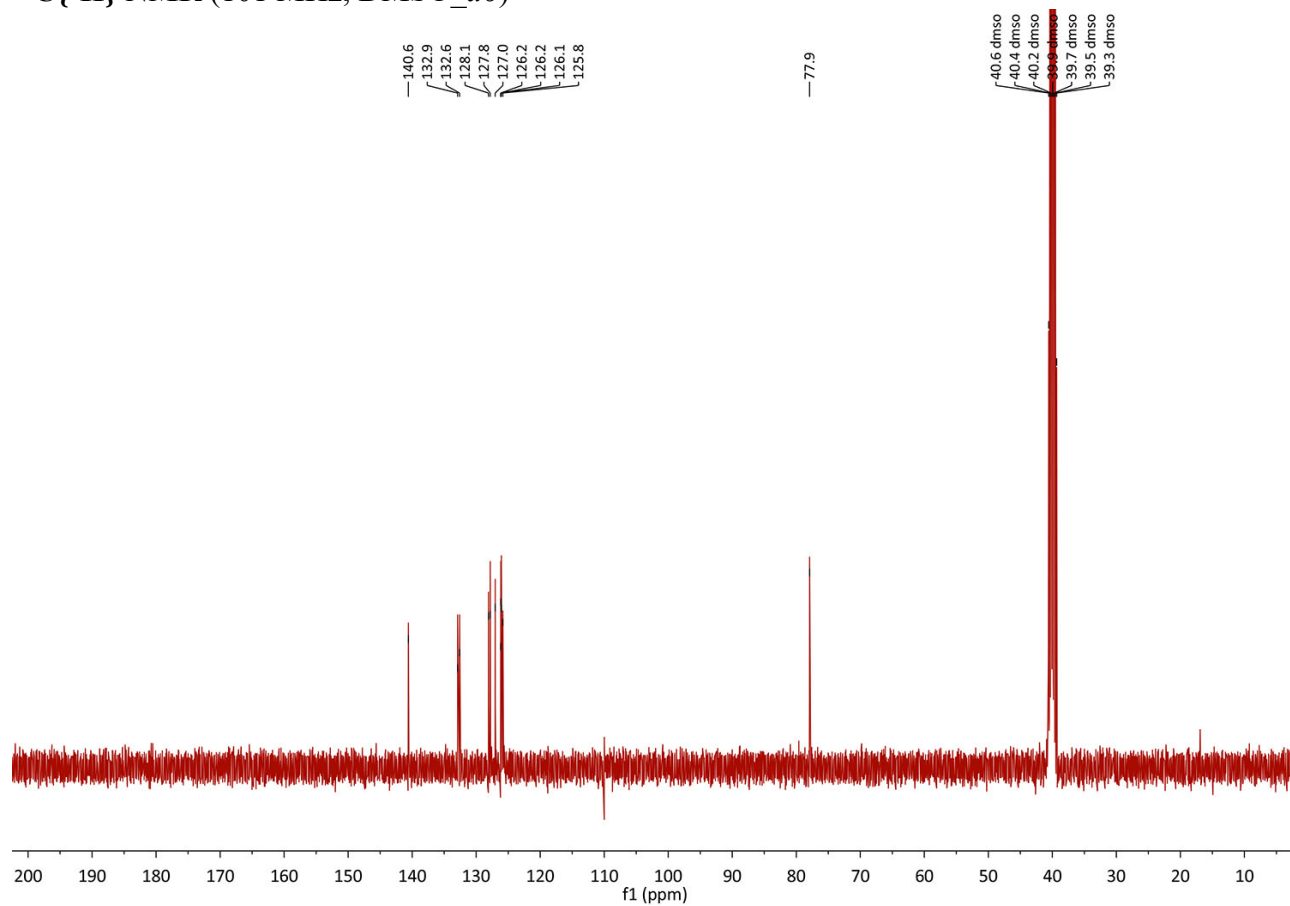


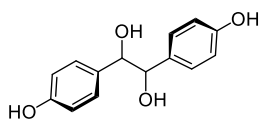
(**3n_d** / **3n_{meso}** > 20:1) 1,2-di(naphthalen-2-yl)ethane-1,2-diol

¹H NMR (400 MHz, DMSO-*d*₆)



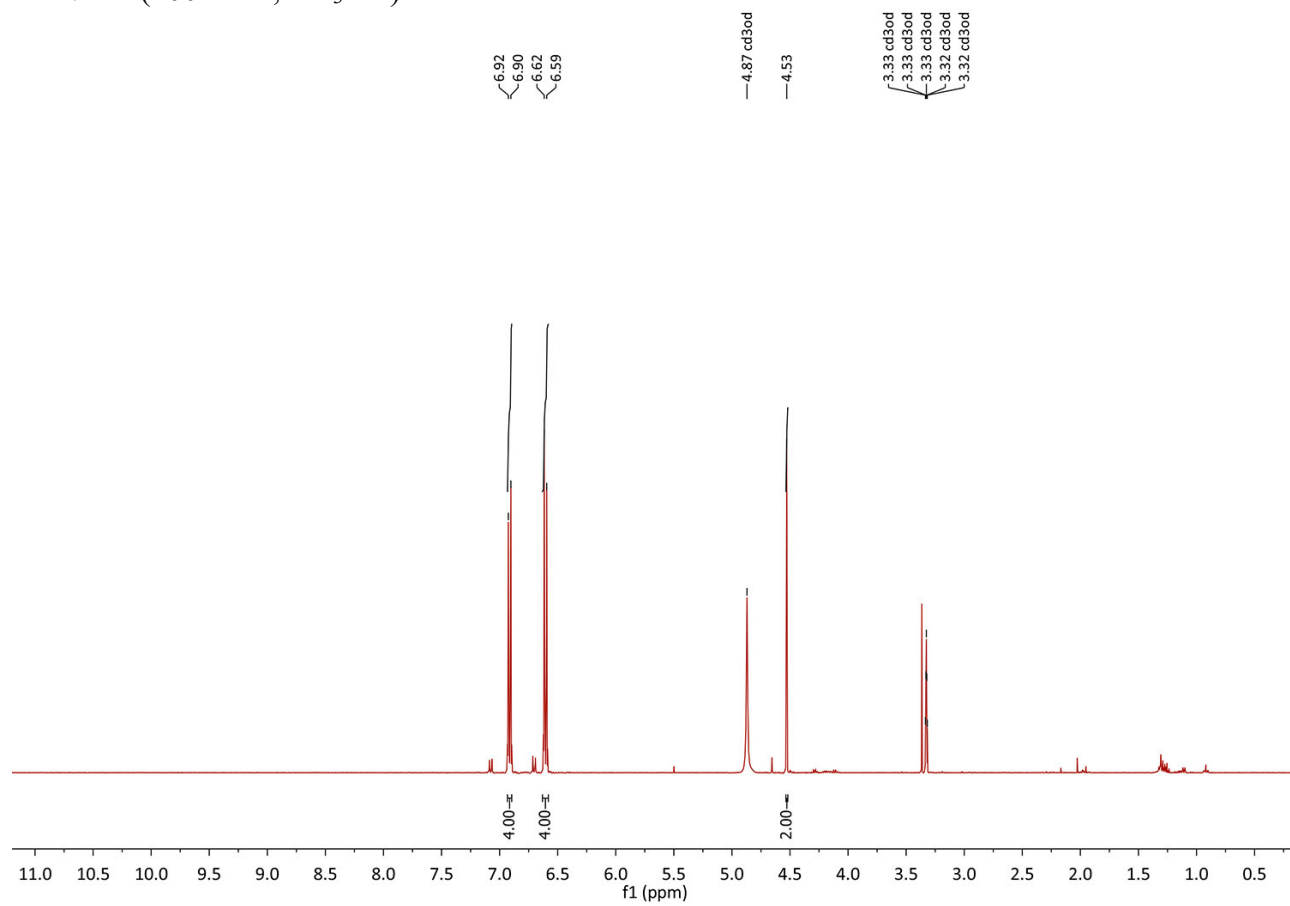
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO-*d*₆)



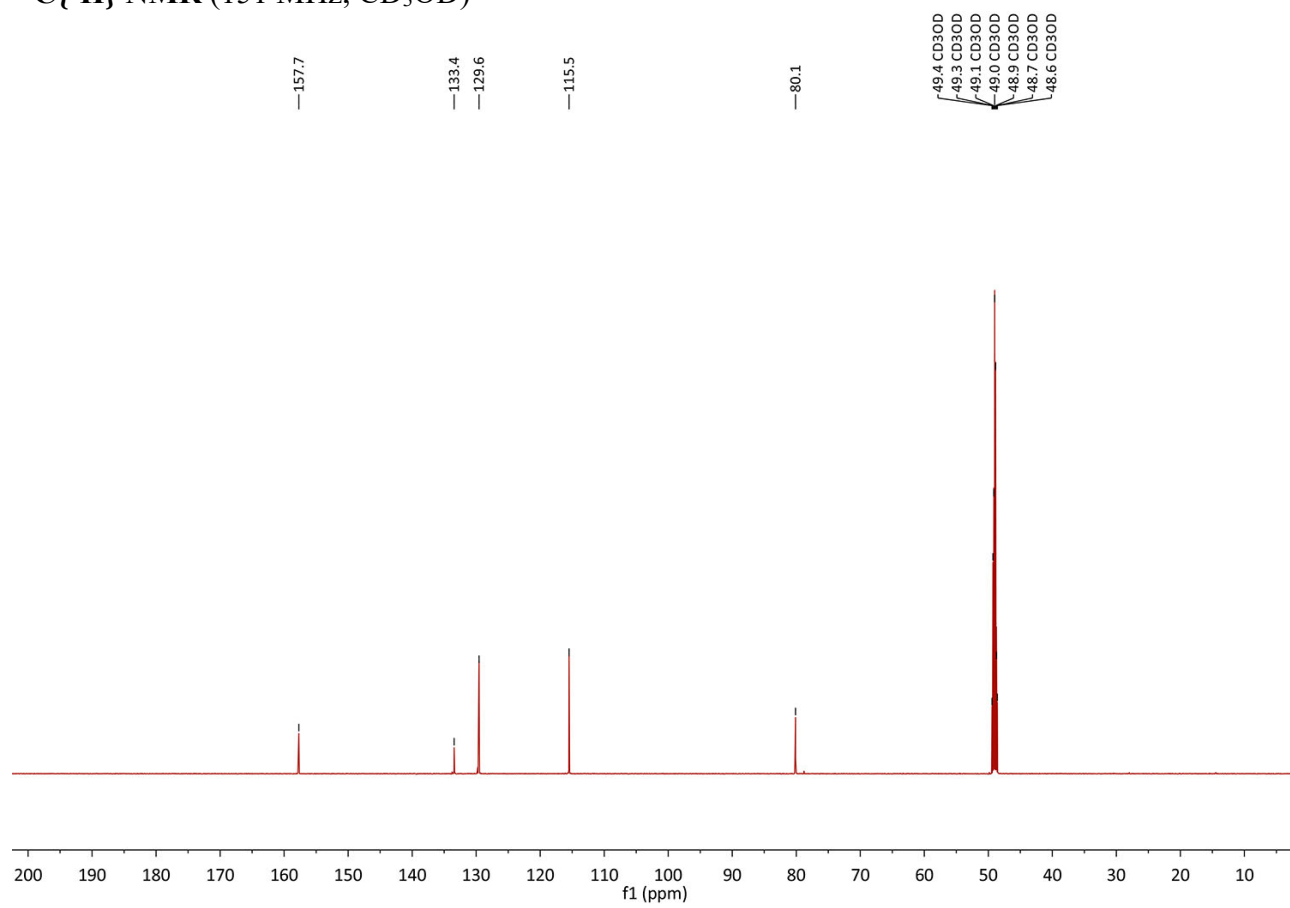


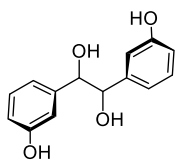
(**30_{d/l}** : **30_{meso}** > 20:1) 1,2-bis(4-hydroxyphenyl)ethane-1,2-diol

¹H NMR (400 MHz, CD₃OD)



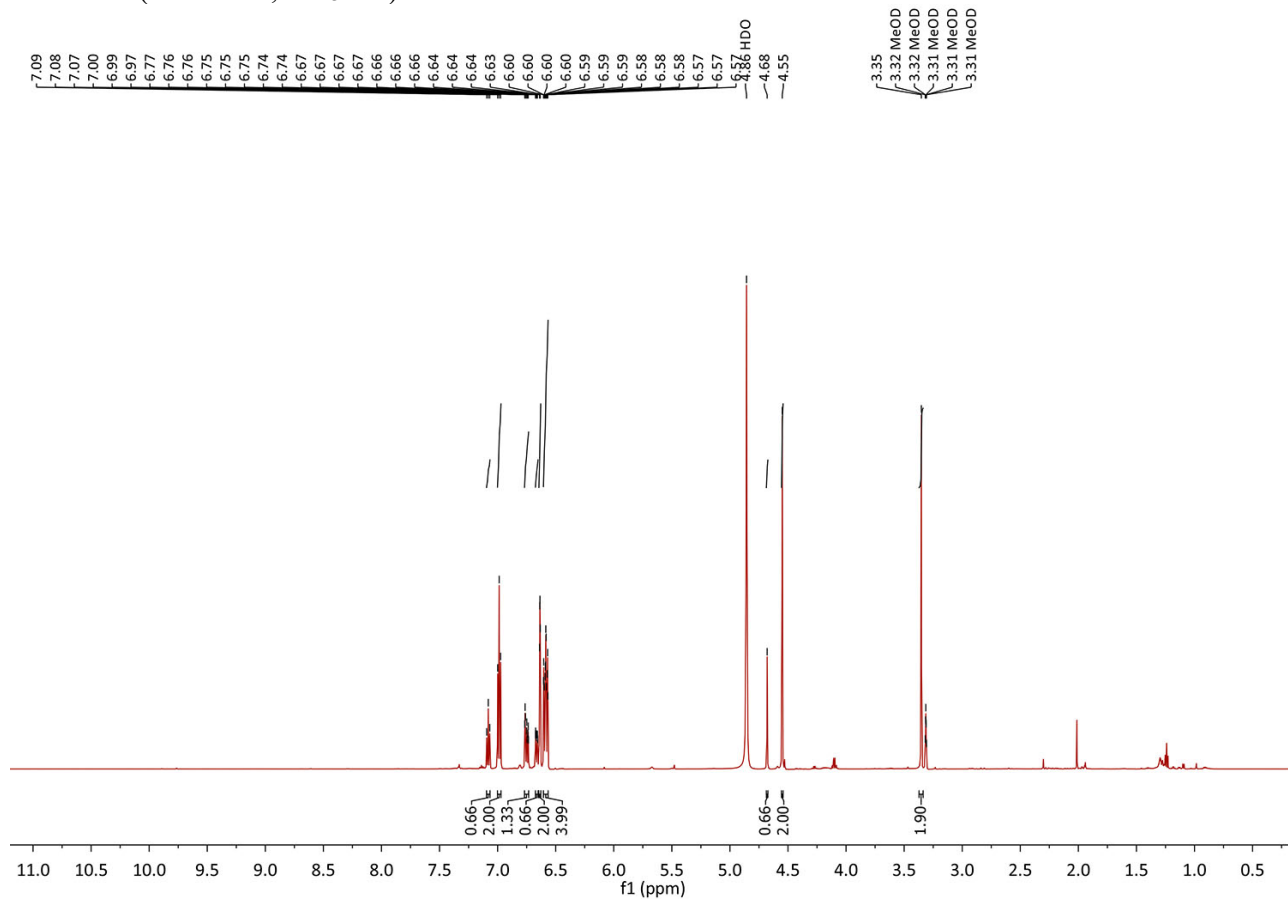
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CD_3OD)



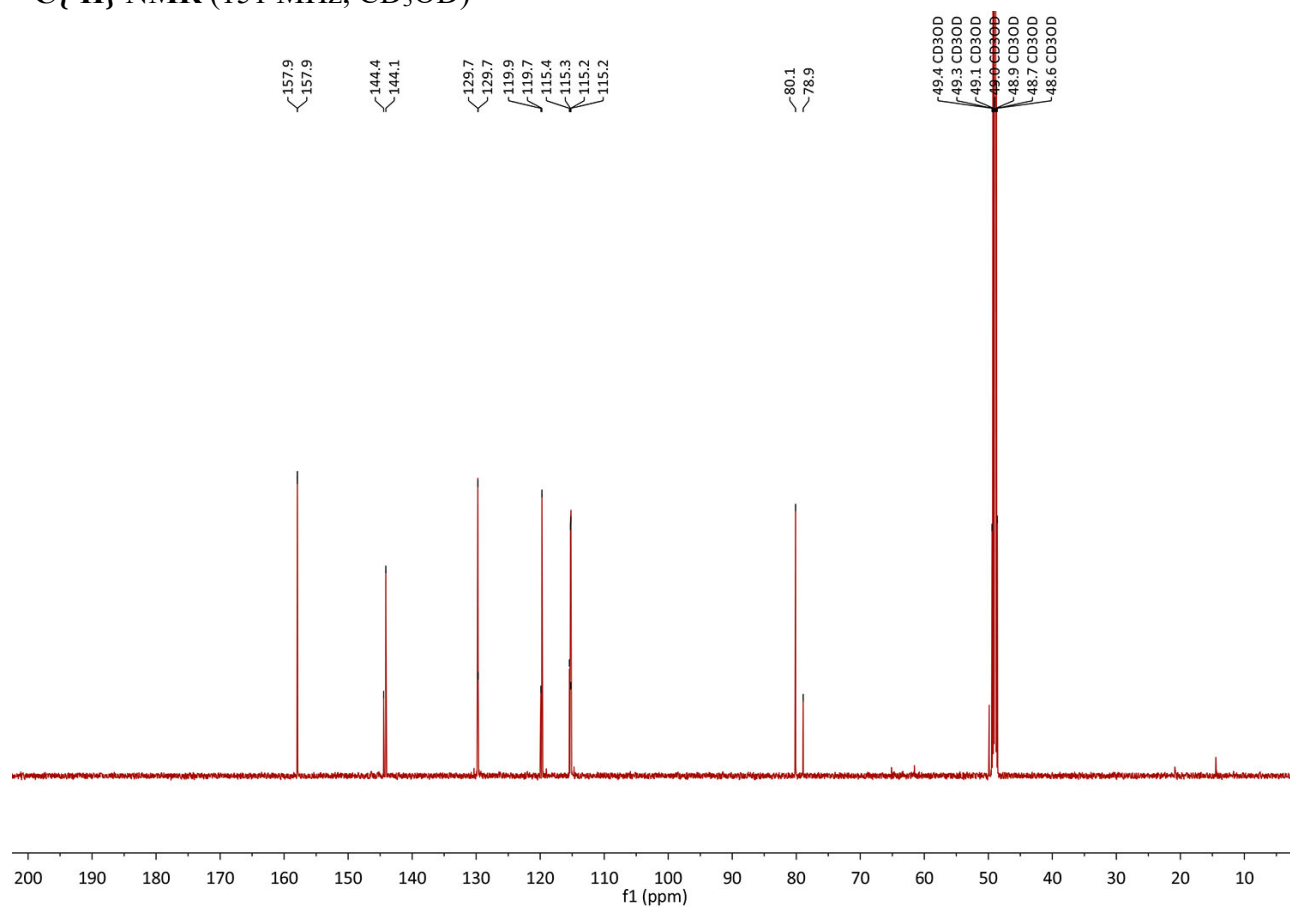


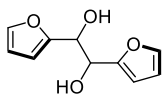
(**3p_{d/l}** : **3p_{meso}** = 3:1) 1,2-bis(3-hydroxyphenyl)ethane-1,2-diol

¹H NMR (600 MHz, CD₃OD)



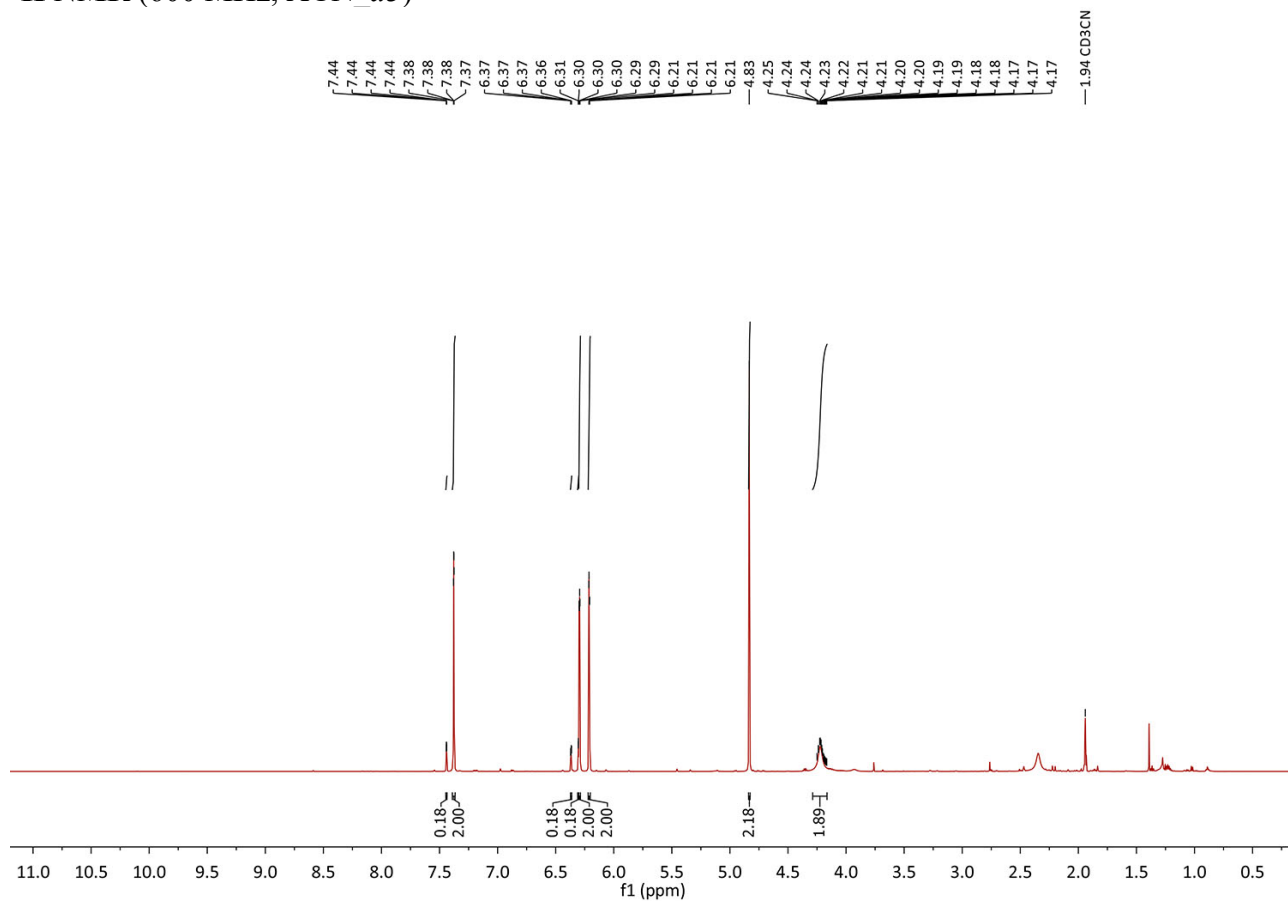
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CD_3OD)



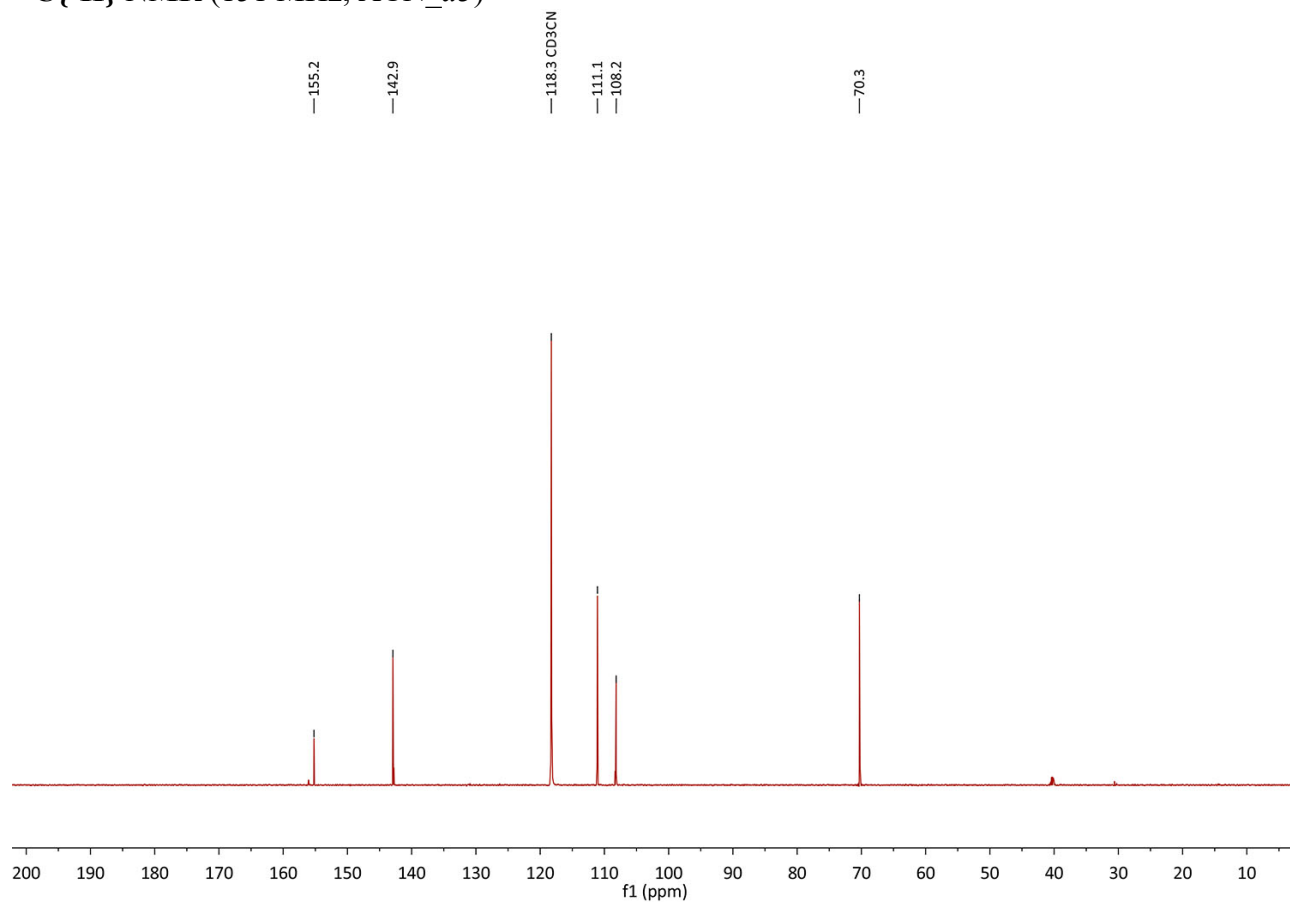


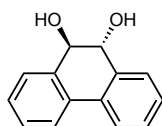
(**3q_d** / **3q_{meso}** = 11:1) 1,2-di(furan-2-yl)ethane-1,2-diol

¹H NMR (600 MHz, ACN-*d*3)

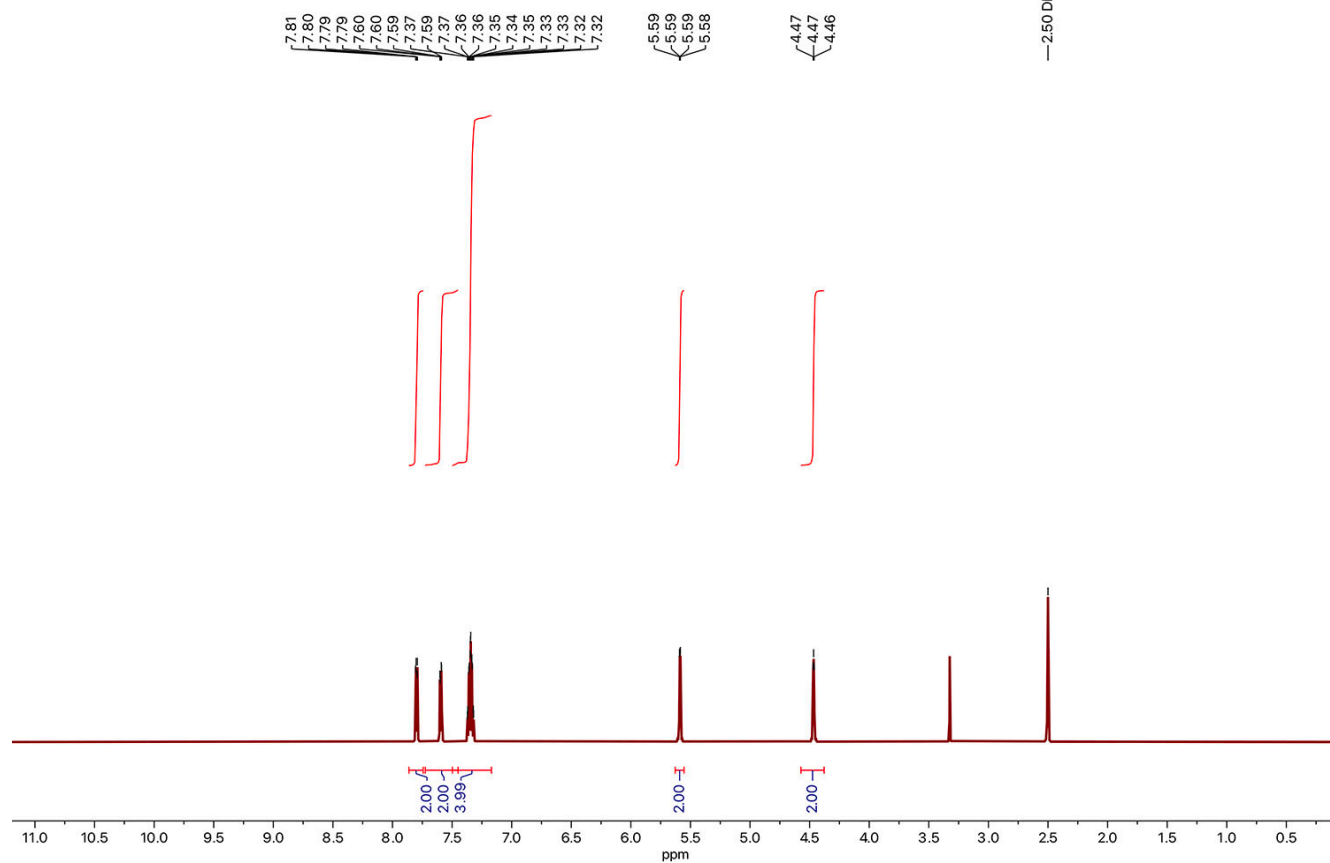


$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, ACN_d3)

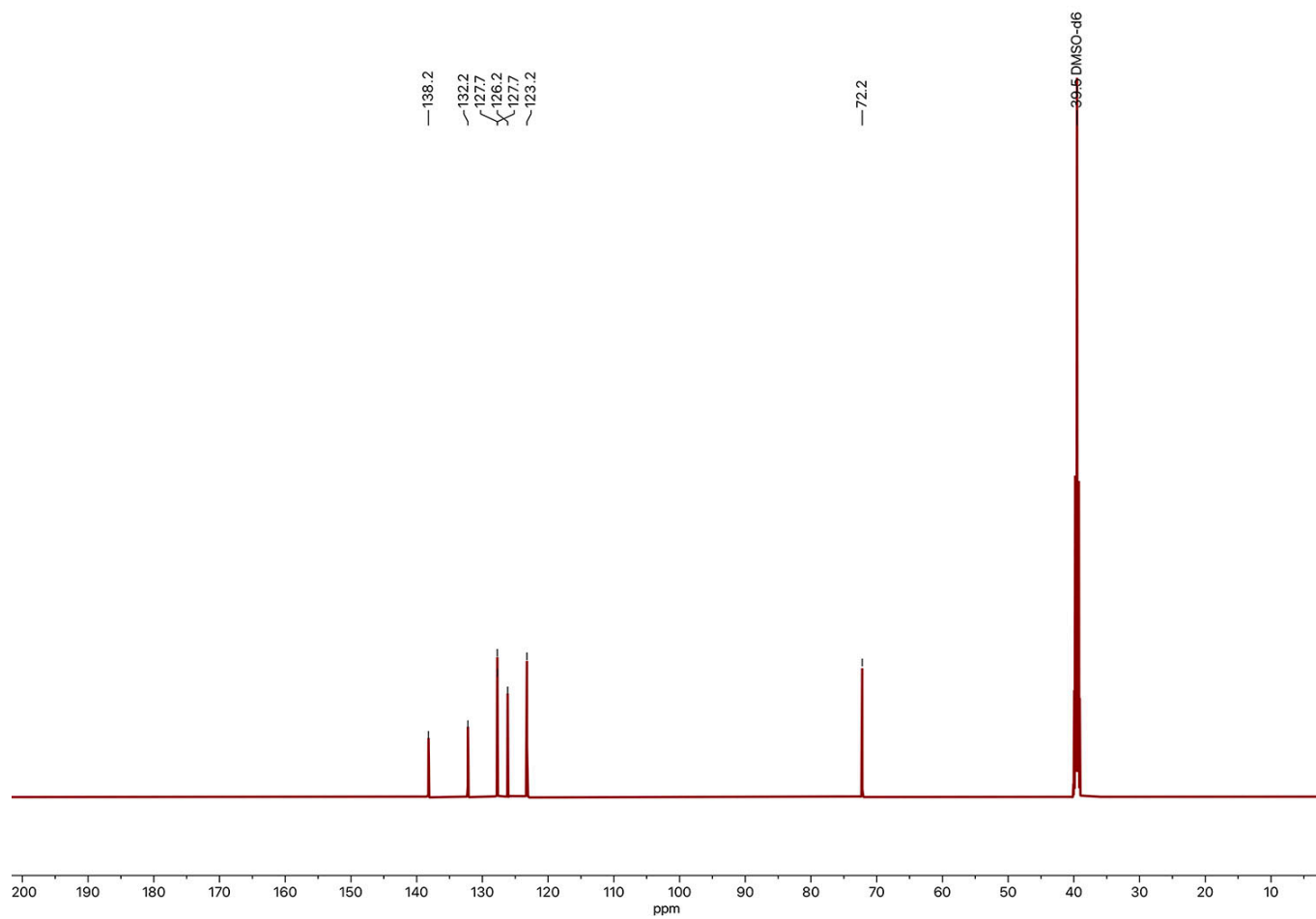




($3r_{dl} : 3r_{meso} > 20:1$) 9,10-dihydrophenanthrene-9,10-diol
 ^1H NMR (600 MHz, DMSO- d_6)



$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, DMSO-*d*₆)



References

-
- ¹ <https://www.kessil.com/photoreaction/PR160L.php>.
- ² F. Calogero, G. Magagnano, S. Potenti, F. Pasca, A. Fermi, A. Gualandi, P. Ceroni, G. Bergamini, P. G. Cozzi, *Chem. Sci.* **2022**, *13*, 5973-5981.
- ³ E. Tatunashvili, B. Chan, P. E. Nashar, C. S. P. McErlean, *Org. Biomol. Chem.* **2020**, *18*, 1812-1819.
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