Diastereoselective and Enantioselective Photoredox Pinacol Coupling Promoted by Titanium Complexes with a Red-Absorbing Organic Dye

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Abstract: The pinacol coupling reaction, a reductive coupling of carbonyl compounds that proceeds through the formation of ketyl radicals in presence of an electron donor, affords the corresponding 1,2-diols in one single step. The photoredox version of this transformation has been accomplished using different organic dyes or photoactive metal complexes in presence of sacrificial donors such as tertiary amines or Hantzsch's ester. Normally, the homo-coupling of such reactive ketyl radicals is neither diastero- nor enantio-selective. Herein, we report a highly diastereoselective pinacol coupling reaction of aromatic aldehydes promoted by 5 mol% of non-toxic, inexpensive, and available Cp2TiCl2 complex. The key feature that allows the complete control of the diasteroselectivity is the employment of a red-absorbing organic dye in the presence of a redox-active titanium complex. Taking advantage of the well-tailored photoredox potentials of this organic dye, the selective reduction of Ti(IV) to Ti(III) is achieved. These conditions enable the formation of the d,l (syn) diasteroisomer as the favored product of the pinacol coupling (d.r. > 20:1 in most of the cases). Moreover, employing a simply prepared chiral SalenTi complex, the new photoredox reaction gave a complete diastereoselection for the d,l diastereoisomer, and high enantiocontrol (up to 92% of enantiomeric excess).

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Experimental Procedures

General methods and materials

^{1}H-NMR spectra were recorded on Varian Mercury 400 MHz spectrometer. The chemical shifts (δ) for ^{1}H are given in ppm relative to residual signals of the solvents and tetramethylsilane (TMS) at 0 ppm ($CDCl_3$: δ = 7.27 ppm, DMSO-d_6: δ = 2.50 ppm, CD_3CN: δ = 1.94 ppm, CD_3OD: δ = 3.31 ppm). Data are reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz). ^{13}C-NMR spectra were recorded on Varian Mercury 400 MHz spectrometer. The chemical shifts (δ) for ^{13}C are given in ppm relative to residual signals of the solvents and tetramethylsilane (TMS) at 0 ppm ($CDCl_3$: δ = 77.0 ppm, DMSO-d_6: δ = 39.5 ppm, CD_3OD: δ = 49.0 ppm). GC-MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. Analytical high-performance liquid chromatograph (HPLC) was performed on a HP 1090 liquid chromatograph equipped with a variable wavelength UV detector (deuterium lamp 190-600 nm), using either Daicel Chiralcel™ or Phenomenex™ columns (0.46 cm I.D. x 25 cm). HPLC grade isopropanol and hexane were used as the eluting solvents. Chromatographic purifications were done with 240-400 mesh silica gel. All reactions were set up under an argon atmosphere in oven-dried glassware using standard Schlenk techniques.
Anhydrous solvents were supplied by Aldrich in Sureseal® bottles. Anhydrous tetrahydrofuran was freshly distilled before the use to remove the radical inhibitor BHT present as stabilizer. Unless specified, other anhydrous solvents were used without further purifications. All the reagents were purchased from commercial sources (Sigma-Aldrich, Alfa Aesar, Fluorochem, Strem Chemicals, TCI) and used without further purification unless specified.
Reaction mixtures were irradiated with Kessil® PR160L@595 nm. [1]

Irradiation Sources

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

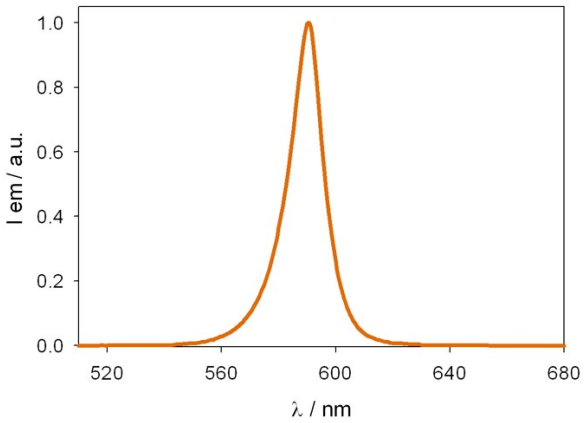
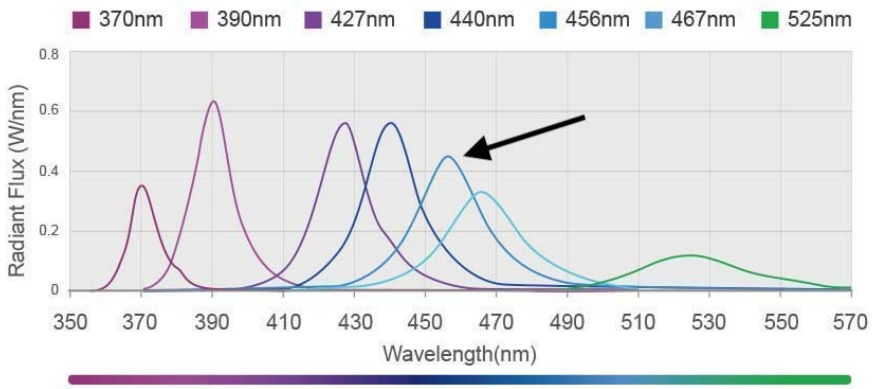


Figure S2. Emission profile of the Kessil® PR160L@456 nm used to irradiate the reaction mixture, table 1 entries 5-10 (from Kessil® website https://www.kessil.com/science/PR160L.php).



Reaction Set-up

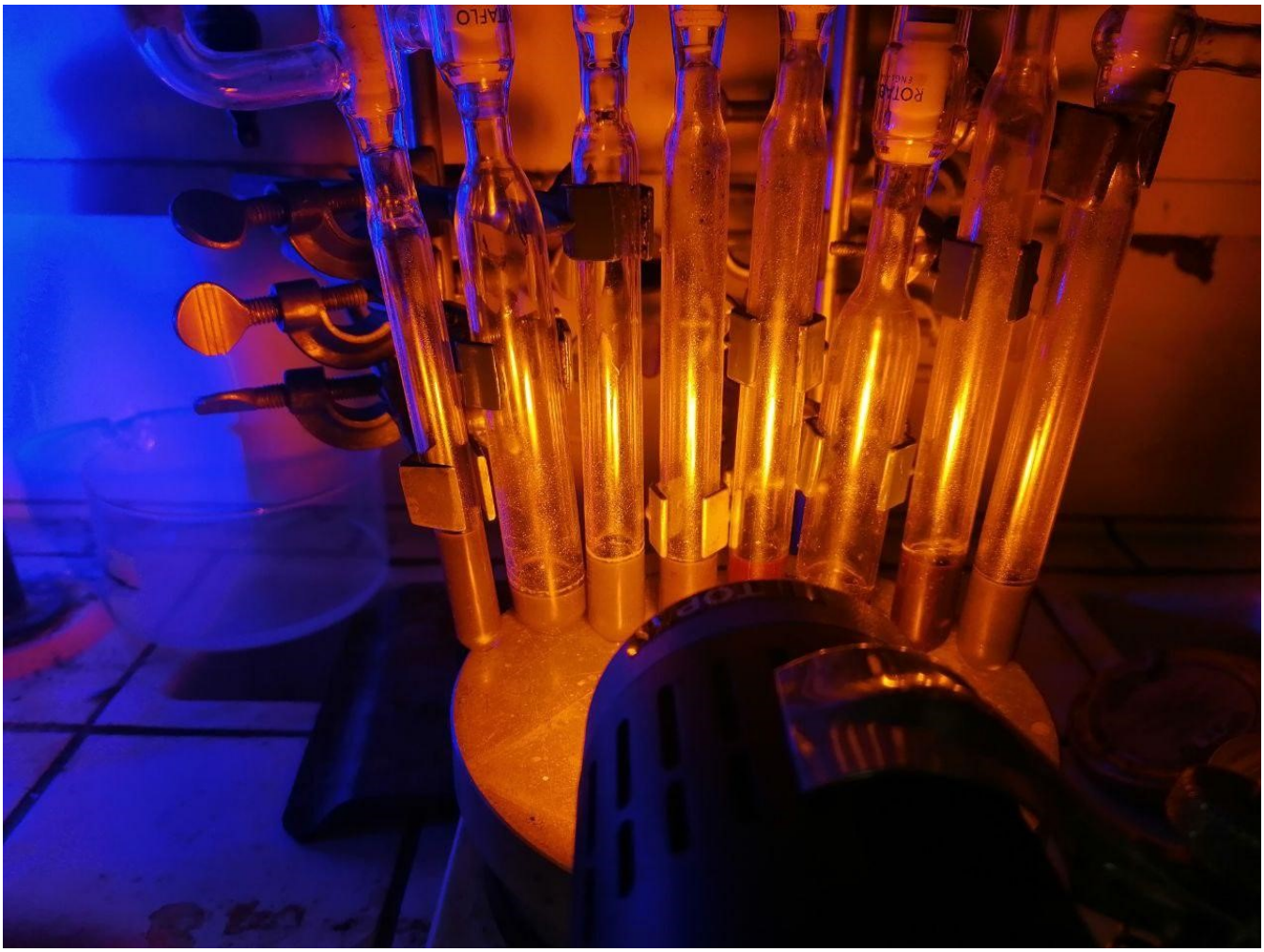
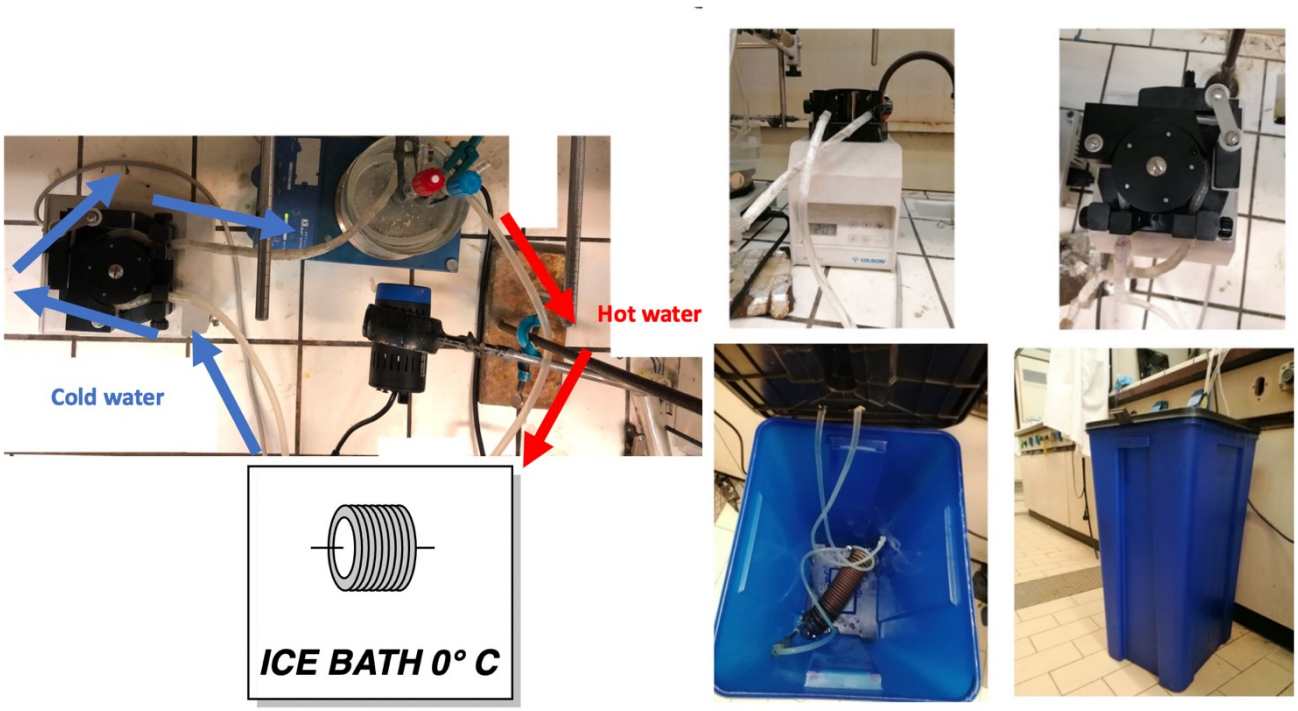


Figure S3. Reaction set-up for diastereoselective pinacol coupling with Kessil® PR160L@595 nm lamp.

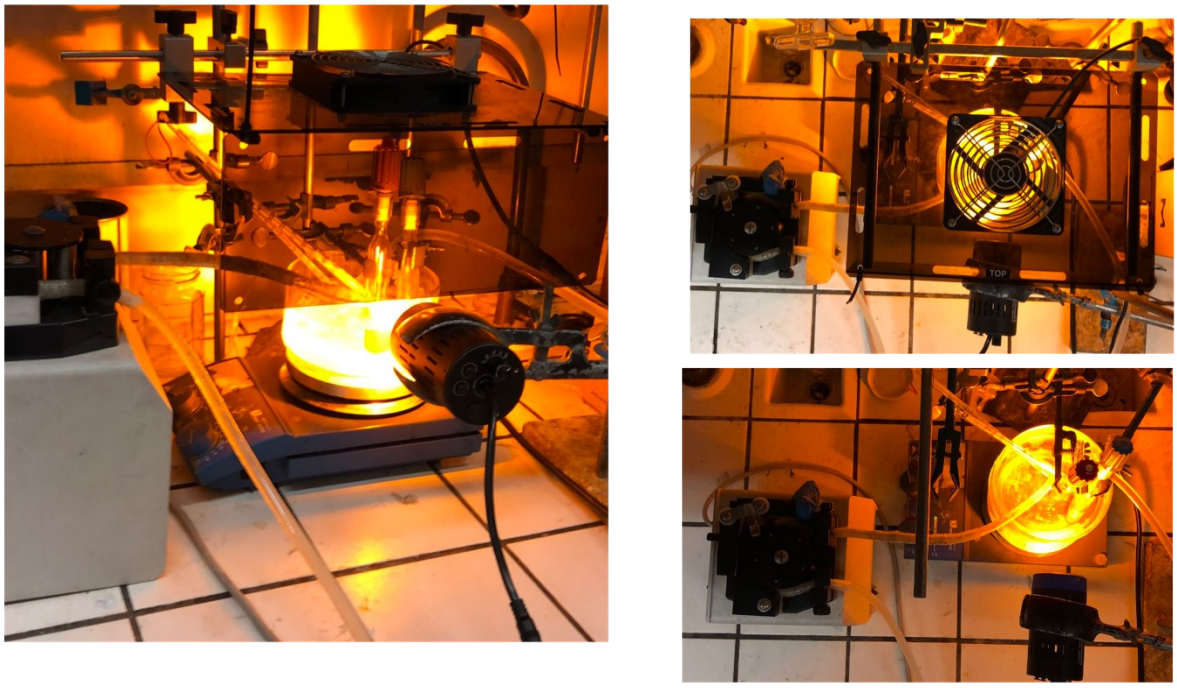
The reaction flasks were positioned approximatively at 10 cm from the light source and Kessil® PR160@595 nm. The reaction temperature was 25 °C during the irradiation as measured with a thermometer at 2 cm from reaction flask.

Figure S4. Home-made cryostat system.



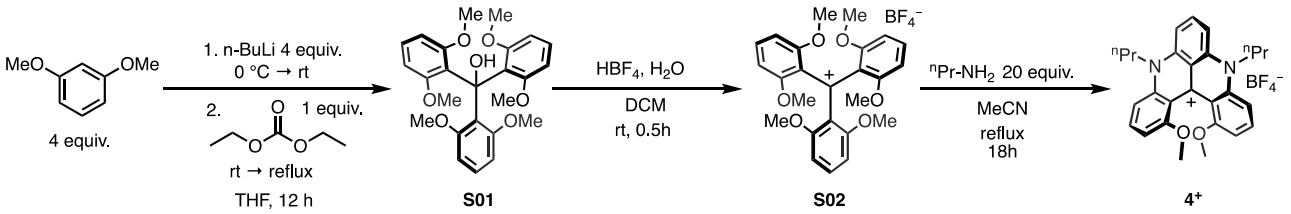
The home–made cryostat system was filled with ice allowing the control of the temperature. The reaction temperature was 10 °C during the irradiation as measured with a thermometer at 2 cm from reaction flask. The blue container was filled with ice to allow the refrigeration of the running water.

Figure S5. Reaction set-up for enantioselective pinacol coupling with Kessil® PR160L@595 nm lamp.



The reaction flasks were positioned approximatively at 10 cm from the light source and Kessil® PR160 Rig with Fan Kit.

Synthesis of *N,N'*-di-*n*-propyl-1,13-dimethoxyquinacridinium 4^+



*Synthesis of **S01***

Carbinol **S01** was synthetized modifying the procedure reported by Martin and Smith.[2] In a flame dried 250 mL three-necked round bottom flask equipped with a magnetic stirring bar, under argon atmosphere, 1,3-dimethoxybenzene (16 mmol, 2.2 g, 2.1 mL, 4 equiv.) was dissolved in dry THF (8 mL). The solution was cooled to 0 °C, and *n*-BuLi (2.5 M in hexane, 16 mmol, 6.4 mL, 4 equiv.) was added dropwise. The solution was allowed to stir 4 h at room temperature, then diethyl carbonate (4 mmol, 473 mg, 487 µL, 1 equiv.) was added and the reaction mixture was refluxed for 8 h. Water (20 mL) was added dropwise at 0 °C, volatiles were removed under reduced pressure and the resulting mixture was extracted with DCM (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, and concentrated under reduced pressure to yield a black solid which was employed in the next step without further purifications.

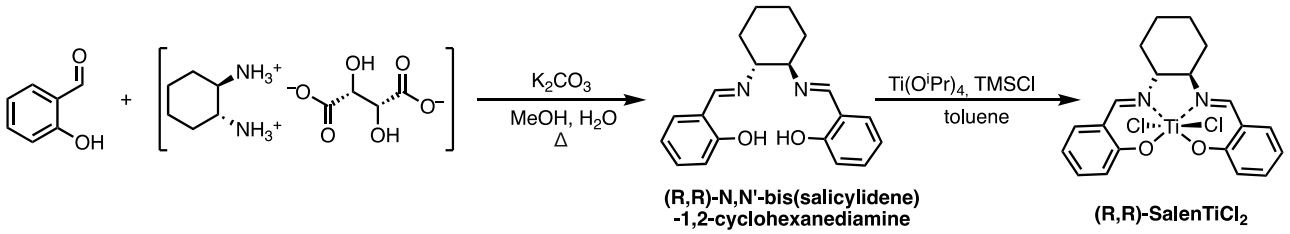
*Synthesis of **S02***

Compound **S02** was synthetized adapting the procedure reported by Laursen and co–workers.[3] In a one-necked round bottom flask equipped with a magnetic stir bar, the carbinol **S01** was dissolved in absolute EtOH (30 mL), and HBF_4 (48% wt. in H_2O, 12 mmol, 1.57 mL, 3 equiv.) was added dropwise. After 0.5 h a mixture of diethyl ether and hexane (1:1, 60 mL) was added, and the formation of a purple precipitate was observed. **S02** was allowed to precipitate overnight from the reaction mixture. The solid was filtered and washed with hexane (*ca.* 20 mL). Compound **S02** was isolated as a dark purple solid (1.11 g, 2.2 mmol, 54% yield over two steps). Spectroscopic data matched those previously reported in the literature.[3]

*Synthesis of **4**$^+$*

Following the procedure reported by Giannetti and co-workers,[4] in a flame dried 250 mL Schlenk tube equipped with a magnetic stirring bar, under argon atmosphere **S02** (2.15 mmol, 1.1 g, 1 equiv.) was dissolved in dry and degassed MeCN (25 mL). Propylamine (53.7 mmol, 3.18 g, 4.42 mL, 25 equiv.) was added, and the reaction mixture was heated at 80 °C under stirring for 18 h. Complete conversion of the starting material **S02** was revealed by HPLC-MS. Volatiles were removed under reduced pressure and the residue was washed with diethyl ether (20 mL), then it was dissolved in the minimum volume of DCM (*ca.* 10 mL) and reprecipitated with EtOAc (*ca.* 100 mL). **4**$^+$ was isolated after filtration of the mixture as a dark green solid (1.4 mmol, 700 mg, 65%). Spectroscopic data matched those previously reported in the literature.[4]

Synthesis of (1*R*,2*R*)-SalenTiCl$_2$ (11)



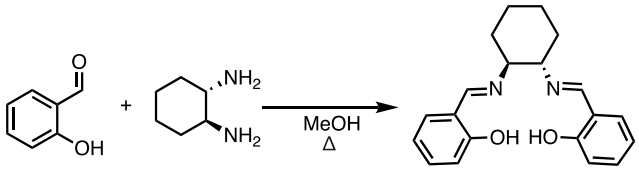
(R,R)-N,N'-bis(salicylidene)-1,2-cyclohexanediamine

Chiral ligand was obtained following the procedure reported by Chusov and co-workers.[5] Under argon atmosphere, a flame-dried 50 mL Schlenk tube, equipped with a magnetic stirring bar, was charged with (1*R*,2*R*)-*trans*-cyclohexane-1,2-diammonium *L*-tartrate (2 mmol, 528 mg, 1.0 equiv.), K_2CO_3 (2 mmol, 276 mg, 1.0 equiv.) and H_2O (1.5 mL), and the reaction mixture was stirred for 30 min. Then MeOH (5 mL) was added and, after 15 min, a solution of 2-hydroxybenzaldehyde (488 mg, 4 mmol, 2 equiv.) in MeOH (2 mL) was added dropwise. The reaction mixture was refluxed until TLC analysis showed a full conversion of the starting material. The solvents were evaporated under *vacuum* and the residue was dissolved in EtOAc, washed with water (10 mL), dried (Na_2SO_4) and concentrated to afford the desired product in 75% yield (1.5 mmol, 485 mg). The crude product was employed in the next step without further purifications.

(R,R)-SalenTiCl$_2$

Titanium complex was obtained following the procedure reported by Joshi and co-workers.[6] Under argon atmosphere, in a flame-dried 5 mL Schlenk tube, equipped with a magnetic stirring bar, a solution of (*R*,*R*)-*N*,*N'*-bis(salicylidene)-1,2-cyclohexanediamine (1 mmol, 322 mg, 1 equiv.) in toluene (0.5 mL) was added to a solution of Ti(O^{i}Pr)$_4$ (1.0 M in toluene, 1 mmol, 1 mL, 1 equiv.). The solution was stirred at room temperature for 12 h and the reaction mixture was diluted with 2 mL of toluene and treated dropwise with TMSCl (2.4 mmol, 300 µL, 2.4 equiv.). Immediately, the complex precipitating as a red solid. After the mixture was stirred for 4 h, the solid was filtered through a sintered funnel and dried under reduced pressure to afford the desired (*R*,*R*)SalenTiCl$_2$ as a bright red solid (0.82 mmol, 360 mg, 82% yield).

Synthesis of (*S*,*S*)-*N*,*N*'-bis(salicylidene)-1,2-cyclohexanediamine



(S,S)-N,N'-bis(salicylidene)
-1,2-cyclohexanediamine

Under argon atmosphere, a flame-dried 50 mL Schlenk tube, equipped with a magnetic stirring bar, was charged with mixture of (1*S*,2*S*)-*trans*-cyclohexane-1,2-diammine (2 mmol, 228 mg, 1.0 equiv.) in MeOH (5 mL) After 15 min a solution of 2-hydroxybenzaldehyde (4 mmol, 488 mg, 2 equiv.) in MeOH (2 mL) was added dropwise. The reaction mixture was refluxed until TLC analysis showed a full conversion of the starting material. The solvents were evaporated under vacuum and the residue was dissolved in EtOAc, washed with water (10 mL), dried (Na_2SO_4) and concentrated to afford the desired product in 65% yield (420 mg, 1.3 mmol). The crude product was employed in the synthesis of the corresponding titanium complex following the procedure reported above for the (*R*,*R*)-enantiomer.

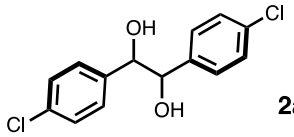
General procedure A: diastereoselective photoredox pinacol coupling

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, aldehyde **1a–s** (0.2 mmol), Cp_2TiCl_2 (0.01 mmol, 2.5 mg, 5 mol%), photocatalyst $\mathbf{4}^+$ (0.01 mmol, 5.0 mg, 5 mol%) and diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (Hantzsch's ester) (0.22 mmol, 55 mg, 1.1 equiv.) were added in the Schlenk tube. Dry trifluorotoluene (2 mL) was then added, 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 72 h at room temperature. The solvent was evaporated under reduced pressure and the reaction crude was analyzed by ^{1}H NMR to evaluate the diastereomeric ratio of the products. The crude was subject of flash column chromatography (SiO_2) to afford products **2a–s** in the stated yields.

General procedure B: enantioselective photoredox pinacol coupling

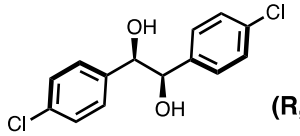
All the reactions were performed on 0.2 mmol of aldehyde in a flame dried 10 mL Schlenk tube, equipped with a Rotaflo stopcock, magnetic stirring bar, and an argon supply tube.
Under vigorous argon flux, aldehyde (0.2 mmol), (*R,R*)-SalenTiCl$_2$ (0.02 mmol, 8.4 mg, 10 mol%), photocatalyst $\mathbf{4}^+$ (0.01 mmol, 5.0 mg, 5 mol%) and diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (Hantzsch's ester) (0.22 mmol, 55 mg, 1.1 equiv.) were added in the Schlenk tube. Dry trifluorotoluene (4 mL) was then added, the reaction mixture was further subjected to a freeze-pump-thaw procedure (four cycles), and the vessel was then refilled with argon. The reaction was irradiated under vigorous stirring for 48 h at 6–12°C. The solvent was evaporated under reduced pressure, and the reaction crude was analyzed by ^{1}H NMR to evaluate the conversion and the diastereomeric ratio of the products and was analyzed by HPLC to evaluate enantiomeric excess. The crude was subject of flash column chromatography (SiO_2) to afford the final products in the stated yields. The absolute configuration of the final products was determined by comparison of HPLC retention time reported in literature.[7]

Characterization of pinacol coupling products



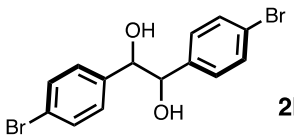
2a

1,2-bis(4-chlorophenyl)ethane-1,2-diol (2a) white solid; 89% (0.089 mmol, 25 mg); d.r. > 20:1 (*d/l*-**2a**:*meso*-**2a**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using **1a** (0.2 mmol, 28 mg). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in hexane). Spectroscopic data matched those previously reported in the literature.[8]



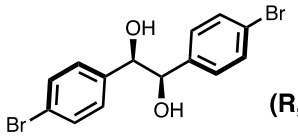
(R,R)-2a

(1*R*,2*R*)-1,2-bis(4-chlorophenyl)ethane-1,2-diol (*R*,*R*-2a) white solid; 67% (0.067 mmol, 19 mg); d.r. > 20:1 (*d/l*-**2a**:*meso*-**2a**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure B was applied using **1a** (0.2 mmol, 28 mg). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in hexane). Spectroscopic data matched those previously reported in the literature.[8] HPLC analysis (LUX CELLULOSE 3, *n*-Hexane: *i*-PrOH = 95:5, 1 mL/min, 30 °C, 224 nm) indicated 96:4 e.r. (*t*-major = 31.83 min, *t*-minor = 35.19 min).



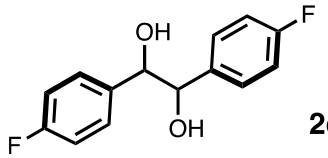
2b

1,2-bis(4-bromophenyl)ethane-1,2-diol (2b) white solid; 60% (0.06 mmol, 22 mg); d.r. > 20:1 (*d/l*-**2b**:*meso*-**2b**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using **1b** (0.2 mmol, 37 mg). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in hexane). Spectroscopic data matched those previously reported in the literature.[9]



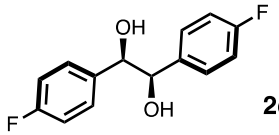
(R,R)-2b

(1*R*,2*R*)-1,2-bis(4-bromophenyl)ethane-1,2-diol (*R*,*R*-2b) white solid; 70% (0.07 mmol, 26 mg); d.r. > 20:1 (*d*/*l*-**2b**:*meso*-**2b**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure B was applied using **1b** (0.2 mmol, 37 mg). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in hexane). Spectroscopic data matched those previously reported in the literature. HPLC analysis (LUX CELLULOSE 3, *n*-Hexane: *i*-PrOH = 95:5, 1 mL/min, 30 °C, 220 nm) indicated 96:4 e.r. (*t*-minor = 25.98 min, *t*-major = 27.19 min).[9]



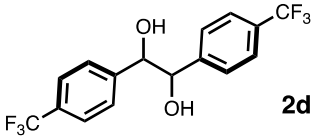
2c

1,2-bis(4-fluorophenyl)ethane-1,2-diol (2c) white solid; 74% (0.074 mmol, 18 mg); d.r. = 15:1 (*d*/*l*-**2c**:*meso*-**2c**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using previously distilled **1c** (0.2 mmol, 25 mg, 22 µL). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in hexane). Spectroscopic data matched those previously reported in the literature.[10]



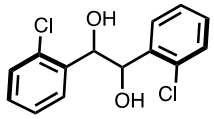
2c

(1*R*,2*R*)-1,2-bis(4-fluorophenyl)ethane-1,2-diol (*R*,*R*-2c) white solid; 85% (0.085 mmol, 21 mg); d.r. > 20:1 (*d*/*l*-**2c**:*meso*-**2c**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure B was applied using previously distilled **1c** (0.2 mmol, 25 mg, 22 µL). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in hexane). Spectroscopic data matched those previously reported in the literature. HPLC analysis (LUX CELLULOSE 3, *n*-Hexane: *i*-PrOH = 95:5, 1 mL/min, 30 °C, 224 nm) indicated 95.5:4.5 e.r. (*t*-major = 12.09 min, *t*-minor = 13.92 min).[10]



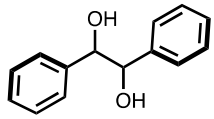
2d

1,2-bis(4-(trifluoromethyl)phenyl)ethane-1,2-diol (2d) white solid; 81% (0.081 mmol, 28 mg); d.r. = 8:1 (*d*/*l*-**2d**:*meso*-**2d**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using previously distilled **1d** (0.2 mmol, 35 mg, 27 µL). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in hexane). Spectroscopic data matched those previously reported in the literature.[11]



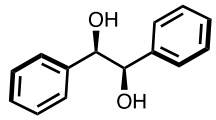
2e

1,2-bis(2-chlorophenyl)ethane-1,2-diol (2e) pale yellow oil; 78% (0.078 mmol, 22 mg); d.r. = 3:1 (*d*/*l*-**2e**:*meso*-**2e**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using previously distilled **1e** (0.2 mmol, 28 mg, 23 µL). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in hexane). Spectroscopic data matched those previously reported in the literature.[12]



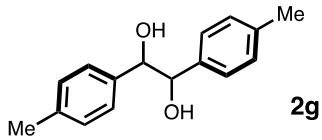
2f

1,2-diphenylethane-1,2-diol (2f) pale yellow solid; 77% (0.077 mmol, 16 mg); d.r. > 20:1 (*d*/*l*-**2f**:*meso*-**2f**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using previously distilled **1f** (0.2 mmol, 21 mg, 20 µL). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in hexane). Spectroscopic data matched those previously reported in the literature.[7]



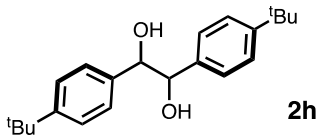
(R,R)-2f

(1*R*,2*R*)-1,2-diphenylethane-1,2-diol (*R*,*R*-2f) pale yellow solid; 42% (0.042 mmol, 9 mg); d.r. > 20:1 (*d*/*l*-**2f**:*meso*-**2f**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure B was applied using previously distilled **1f** (0.2 mmol, 21 mg, 20 μL). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in hexane). Spectroscopic data matched those previously reported in the literature. HPLC analysis (LUX CELLULOSE 3, *n*-Hexane: *i*-PrOH = 95:5, 1 mL/min, 30 °C, 214 nm) indicated 95.5:4.5 e.r. (*t*-minor = 12.43 min, *t*-major = 14.00 min).[12]



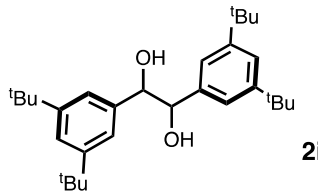
2g

1,2-di-p-tolylethane-1,2-diol (2g) pale yellow solid; 95% (0.095 mmol, 23 mg); d.r. = 16:1 (*d*/*l*-**2g**:*meso*-**2g**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using previously distilled **1g** (0.2 mmol, 24 mg, 24 μL). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in hexane). Spectroscopic data matched those previously reported in the literature.[13]



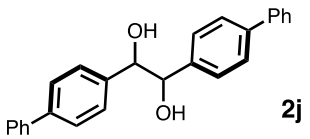
2h

1,2-bis(4-(tert-butyl)phenyl)ethane-1,2-diol (2h) white solid; 74% (0.074 mmol, 24 mg); d.r. > 20:1 (*d*/*l*-**2h**:*meso*-**2h**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using previously distilled **1h** (0.2 mmol, 32 mg, 33 μL). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in hexane). Spectroscopic data matched those previously reported in the literature.[14]



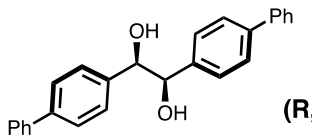
2i

1,2-bis(3,5-di-tert-butylphenyl)ethane-1,2-diol (2i) white solid; 97% (0.097 mmol, 42 mg); d.r. > 20:1 (*d*/*l*-**2i**:*meso*-**2i**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using **1i** (0.2 mmol, 44 mg). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 1.8 Hz, 2H), 6.87 (d, *J* = 1.9 Hz, 4H), 4.67 (s, 2H), 2.83 (s, 2H), 1.18 (d, *J* = 0.9 Hz, 36H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3 (2C), 138.9 (4C), 121.5 (2C), 121.1 (4C), 80.6 (2C), 34.7 (4C), 31.4 (12C).



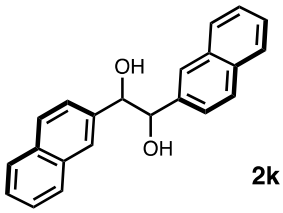
2j

1,2-di([1,1'-biphenyl]-4-yl)ethane-1,2-diol (2j) white solid; 80% (0.080 mmol, 29 mg); d.r. > 20:1 (*d*/*l*-**2j**:*meso*-**2j**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using **1j** (0.2 mmol, 36 mg). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in hexane). Spectroscopic data matched those previously reported in the literature.[15]



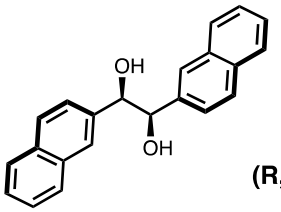
(R,R)-2j

(1*R*,2*R*)-1,2-di([1,1'-biphenyl]-4-yl)ethane-1,2-diol (*R*,*R*-2j) white solid; 30% (0.03 mmol, 11 mg); d.r. > 20:1 (*d*/*l*-**2j**:*meso*-**2j**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure B was applied using **1j** (0.2 mmol, 36 mg). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in hexane). Spectroscopic data matched those previously reported in the literature.[15] HPLC analysis (ID, *n*-Hexane: *i*-PrOH = 70:30, 1.5 mL/min, 40 °C, 254 nm) indicated 73.5:26.5 e.r. (*t*-major = 4.83 min, *t*-minor = 6.52 min).



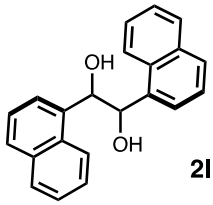
2k

1,2-di(naphthalen-2-yl)ethane-1,2-diol (2k) white solid; 70% (0.070 mmol, 22 mg); d.r. > 20:1 (*d*/*l*-**2k**:*meso*-**2k**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using **1k** (0.2 mmol, 31 mg). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in *n*-Hexane). Spectroscopic data matched those previously reported in the literature.[12]



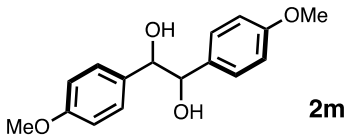
(R,R)-2k

(1*R*,2*R*)-1,2-di(naphthalen-1-yl)ethane-1,2-diol (*R*,*R*-2k) white solid; 61% (0.061 mmol, 19 mg); d.r. > 20:1 (*d*/*l*-**2k**:*meso*-**2k**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure B was applied using **1k** (0.2 mmol, 31 mg). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in *n*-Hexane). Spectroscopic data matched those previously reported in the literature. HPLC analysis (LUX CELLULOSE 3, *n*-Hexane: *i*-PrOH = 50:50, 1mL/min, 30 °C, 224 nm) indicated 96:4 e.r. (*t*-major = 11.33 min, *t*-minor = 19.25 min).[12]



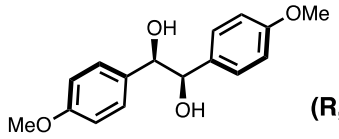
2l

1,2-di(naphthalen-1-yl)ethane-1,2-diol (2l) white solid; 77% (0.077 mmol, 24 mg); d.r. > 20:1 (*d*/*l*-**2l**:*meso*-**2l**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using **1l** (0.2 mmol, 31 mg, 27 µL). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in *n*-Hexane). Spectroscopic data matched those previously reported in the literature.[12]



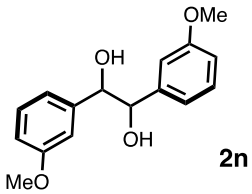
2m

1,2-bis(4-methoxyphenyl)ethane-1,2-diol (2m) white solid; 95% (0.095 mmol, 26 mg); d.r. = 18:1 (*d*/*l*-**2m**:*meso*-**2m**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using previously distilled **1m** (0.2 mmol, 27 mg, 24 µL). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in *n*-Hexane). Spectroscopic data matched those previously reported in the literature.[7]



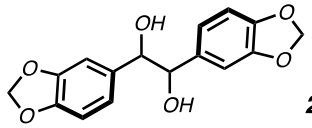
(R,R)-2m

(1*R*,2*R*)-1,2-bis(4-methoxyphenyl)ethane-1,2-diol (*R*,*R*-2m) white solid; 77% (0.077 mmol, 21 mg); d.r. > 20:1 (*d*/*l*-**2m**:*meso*-**2m**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure B was applied using previously distilled **1m** (0.2 mmol, 27 mg, 24 µL). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in *n*-Hexane). Spectroscopic data matched those previously reported in the literature. HPLC analysis (ID, *n*-Hexane: *i*-PrOH = 70:30, 1.5 mL/min, 40 °C, 214 nm) indicated 95:5 e.r. (*t*-major = 12.09 min, *t*-minor = 13.92 min).[7]



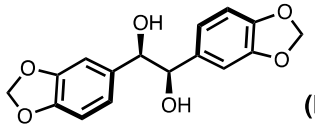
2n

1,2-bis(3-methoxyphenyl)ethane-1,2-diol (2n) white solid; 99% (0.099 mmol, 27 mg); d.r. > 20:1 (*d/l*-**2n**:*meso*-**2n**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using previously distilled **1n** (0.2 mmol, 27 mg, 24 µL). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in *n*-Hexane). Spectroscopic data matched those previously reported in the literature.[16]



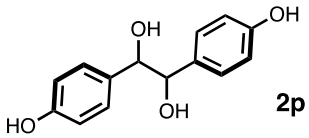
2o

1,2-bis(benzo[d][1,3]dioxol-5-yl)ethane-1,2-diol (2o) white solid; 92% (0.092 mmol, 27 mg); d.r. > 20:1 (*d/l*-**2o**:*meso*-**2o**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using **1o** (0.2 mmol, 30 mg). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in *n*-Hexane). ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.73 – 6.62 (m, 4H), 6.50 (dd, *J* = 8.0, 1.7 Hz, 2H), 5.90 (q, *J* = 1.1 Hz, 4H), 5.21 (s, 1.5 Hz, 2H), 4.41 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.9 (2C), 146.2 (2C), 136.9 (2C), 120.8 (2C), 107.9 (2C), 107.6 (2C), 101.0(2C), 77.7 (2C).



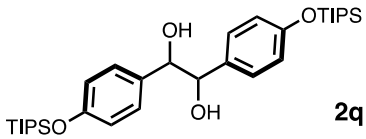
(R,R)-2o

(1*R*,2*R*)-1,2-bis(benzo[d][1,3]dioxol-5-yl)ethane-1,2-diol (*R*,*R*-2o) white solid; 79% (0.079 mmol, 24 mg); d.r. > 20:1 (*d/l*-**2o**:*meso*-**2o**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure B was applied using **1o** (0.2 mmol, 30 mg). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in *n*-Hexane).). ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.73 – 6.62 (m, 4H), 6.50 (dd, *J* = 8.0, 1.7 Hz, 2H), 5.90 (q, *J* = 1.1 Hz, 4H), 5.21 (s, 1.5 Hz, 2H), 4.41 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.9 (2C), 146.2 (2C), 136.9 (2C), 120.8 (2C), 107.9 (2C), 107.6 (2C), 101.0 (2C), 77.7 (2C). HPLC analysis (LUX CELLULOSE 3, *n*-Hexane: *i*-PrOH = 50:50, 1mL/min, 30 °C, 230 nm) indicated 95:5 e.r. (*t*-major = 7.26 min, *t*-minor = 8.34 min).



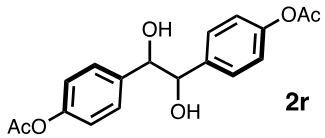
2p

1,2-bis(4-hydroxyphenyl)ethane-1,2-diol (2p) white solid; 77% (0.077 mmol, 19 mg); d.r. = 3:1 (*d/l*-**2p**:*meso*-**2p**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using **1p** (0.2 mmol, 24 mg). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in *n*-Hexane). Spectroscopic data matched those previously reported in the literature.[17]



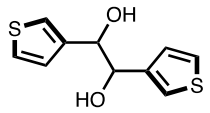
2q

1,2-bis(4-((triisopropylsilyl)oxy)phenyl)ethane-1,2-diol (2q) white solid; 57% (0.057 mmol, 32 mg); d.r. > 20:1 (*d/l*-**2q**:*meso*-**2q**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using **1q** (0.2 mmol, 56 mg). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in *n*-Hexane). ^{1}H NMR (400 MHz, DMSO-d_6) 6.76 (d, J = 8.4 Hz, 4H), 6.57 (d, J = 8.4 Hz, 4H), 5.30 (s, 2H), 4.39 (s, 2H), 1.22 – 1.13 (m, 6H), 1.03 (d, J = 7.2 Hz, 36H).^{13}C NMR (101 MHz, DMSO-d_6) δ 154.5 (2C), 135.1 (2C), 128.7 (4C), 118.7 (4C), 78.3 (2C), 18.1 (6C), 12.4 (12C).



2r

(1,2-dihydroxyethane-1,2-diyl)bis(4,1-phenylene) diacetate (2r) white solid; 70% (0.070 mmol, 23 mg); d.r. > 20:1 (*d/l*-**2r**:*meso*-**2r**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using **1r** (0.2 mmol, 33 mg, 28 µL). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in *n*-Hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.04 (m, 4H), 7.04 – 6.79 (m, 4H), 4.63 (s, 2H), 2.24 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5 (2C), 150.4 (2C), 137.6 (2C), 128.1 (4C), 121.4 (4C), 78.6 (2C), 21.3 (2C).



2s

1,2-di(thiophen-3-yl)ethane-1,2-diol (2s) white solid; 87% (0.087 mmol, 20 mg); d.r. > 20:1 (*d*/*l*-**2s**:*meso*-**2s**) was determined by integration of benzylic CH ^{1}H NMR signals. The general procedure A was applied using previously distilled **1s** (0.2 mmol, 22 mg, 18 µL). The title compound was isolated by flash column chromatography (10–50% ethyl acetate in *n*-Hexane). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.29 (dd, *J* = 5.0, 3.0 Hz, 2H), 7.06 (dd, *J* = 3.0, 1.2 Hz, 2H), 6.83 (dd, *J* = 5.0, 1.2 Hz, 2H), 5.26 (s, 2H), 4.64 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.4 (2C), 127.4 (2C), 125.1 (2C), 121.9 (2C), 74.0 (2C).

Non-linear effect studies

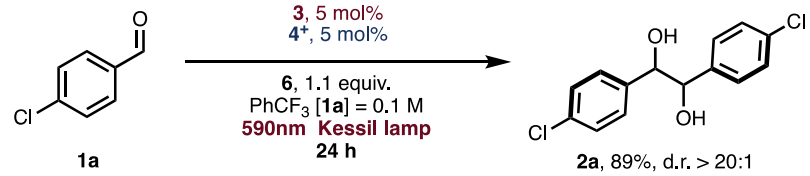
Non-linear effect experiments were performed adapting general procedure B on 0.1 mmol of **1a**. Two freshly prepared stock solutions of (*R*,*R*)- and (*S*,*S*)-SalenTiCl$_2$ **11** were used to obtain the desired enantiomeric excess. In order to obtain limpid solutions, the two complexes were dissolved in anhydrous DCM (20 μM). A flame-dried Schlenk tube was first charged with the required aliquots of the two stock solutions (0.5 mL overall), and the solvent was carefully evaporated under vacuum. The vessel was then refilled with argon, and charged with all the other reaction partners under vigorous argon flux. Then, general procedure B was followed as usual, and the reaction was irradiated under vigorous stirring for 16 h at 6–12°C. The solvent was evaporated under reduced pressure, and the reaction crude was analyzed by ^{1}H NMR to evaluate the conversion and the diastereomeric ratio of the products and was analyzed by HPLC to evaluate enantiomeric excess.

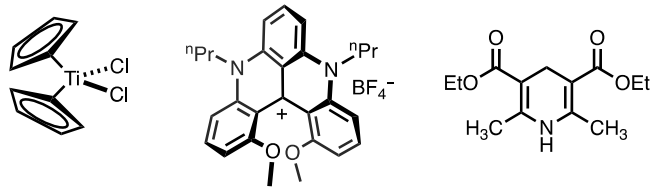
Table S1. Results of non-linear effect study, data reported in Figure 5.

e.e.% **11**[a]	e.e.% **2a**
0	1
10	19
25	49
40	68
60	84
75	88
99	92

Results and Discussion

Table S2. Further optimization of the pinacol coupling reaction mediated by Cp_2TiCl_2.



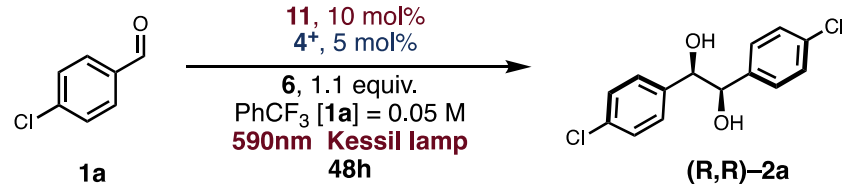


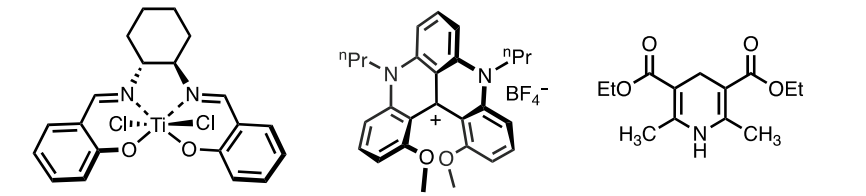
3 Cp_2TiCl_2 | **4**$^+$ $[^nPr\text{-}DMQA]^+[BF_4]^-$ | **6** Hantzsch's ester

Entry[a]	Deviations from standard conditions	Yield (%)[b]	d.r. (*d,l:meso*)[c]
1	None	>99(89)[d]	>20:1
2	10 mol% of **3** and [**1a**] = 0.05 M	>99	>20:1
3	2 equivalents of **6**	>99	10:1
4	1.5 equivalents of **6**	>99	>20:1
5	2.5 mol% of **3** and [**1a**] = 0.2 M	61	> 20:1

[a] Reactions performed on 0.1 mmol scale. [b] Determined by 1H NMR analysis using internal standard method. [c] Determined by ^{1}H NMR analysis of reaction crude. [d] Reaction performed on 0.2 mmol scale; the value in parenthesis is the isolated yield after chromatographic purification; the photocatalyst **4**$^+$ could be recovered (>90 %) after chromatographic purification using first ethyl acetate as eluent then DCM:MeOH 9:1.

Table S3. Further optimization of the pinacol coupling reaction mediated by Cp_2TiCl_2.





Entry[a]	Deviations from standard conditions	Yield (%)[b]	d.r. (*d,l:meso*)[c]	*R,R:S,S*[d]
1	None	74(67)[e]	>20:1	96:4
2	Reaction time 24h	57	>20:1	96:4
3	5 mol% of 4 and [1a] = 0.1 M	64	>20:1	96:4
4[f]	5 mol% of 4 and [1a] = 0.1 M	91	9:1	96:4

[a] Reactions performed on 0.1 mmol scale. [b] Determined by ^{1}H NMR analysis. [c] Determined on the reaction crude by integration of benzylic CH ^{1}H NMR signals. [d] Determined by HPLC analysis on column with chiral stationary phase column. [e] Reaction performed on 0.2 mmol scale; The value in parenthesis is the isolated yield after chromatographic purification. [f] Reaction time 96 h; Decomposition was observed.

Figure S6. Unreactive substrates.

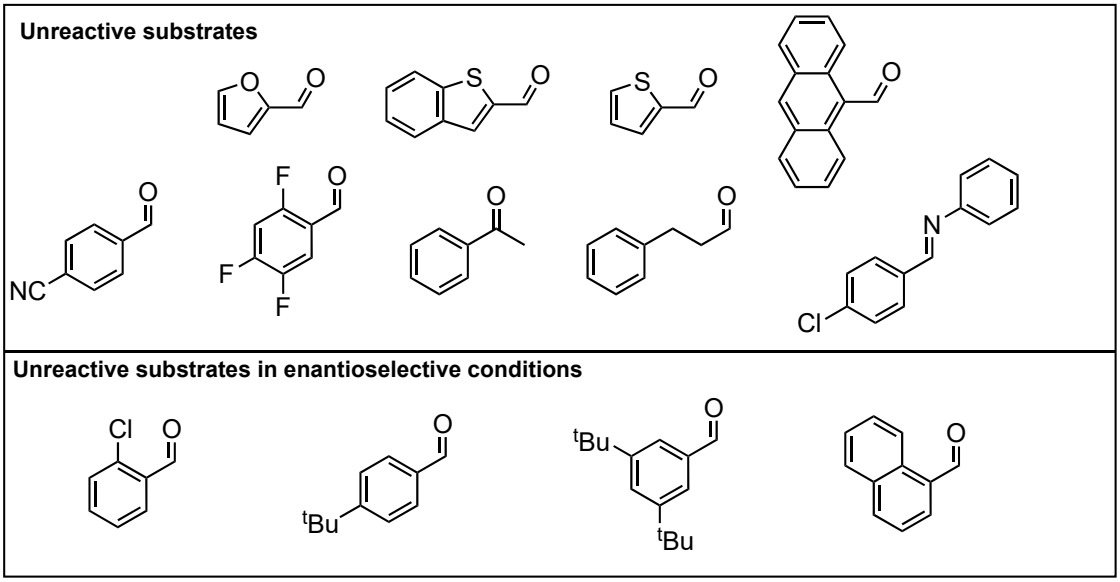
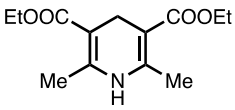
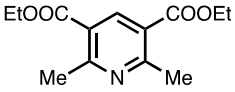


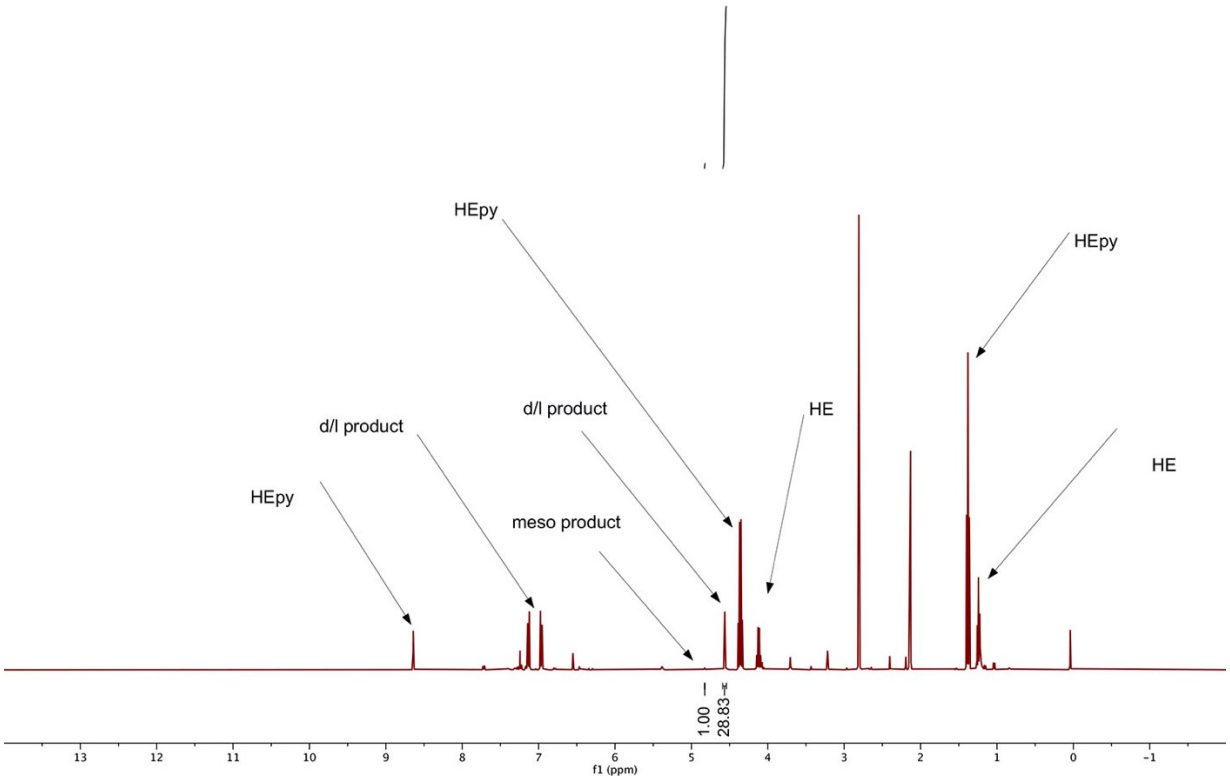
Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of reaction crude. Reaction of aldehyde **1a** to give product **2a** (Table 1 entry 1).

HE =



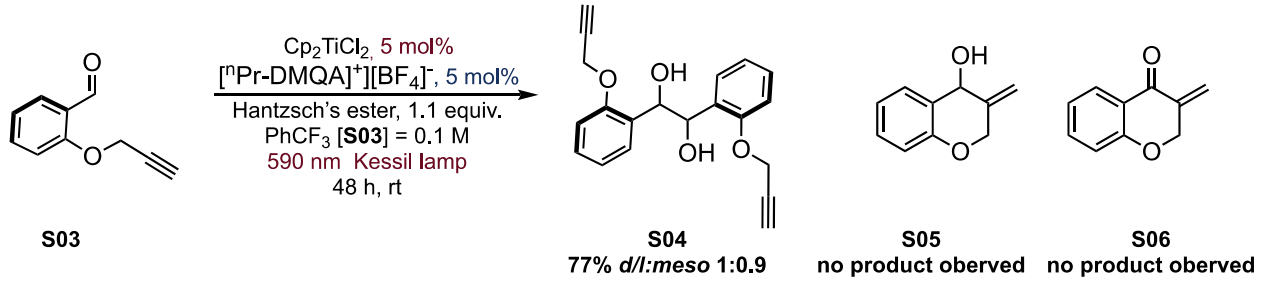
HEpy =

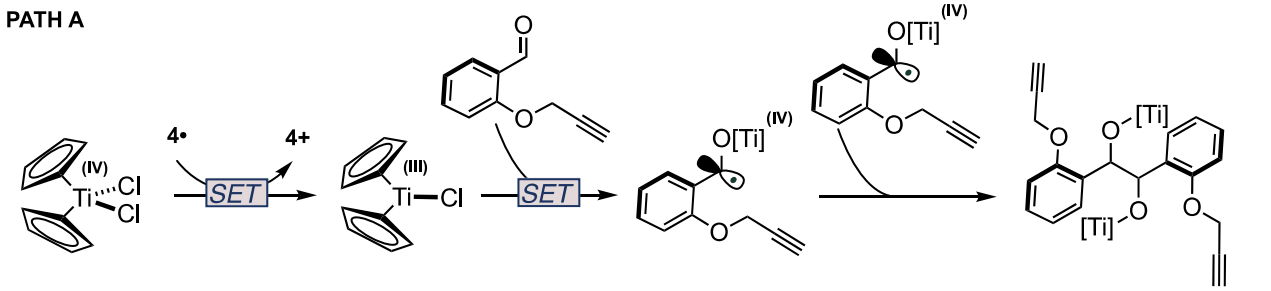


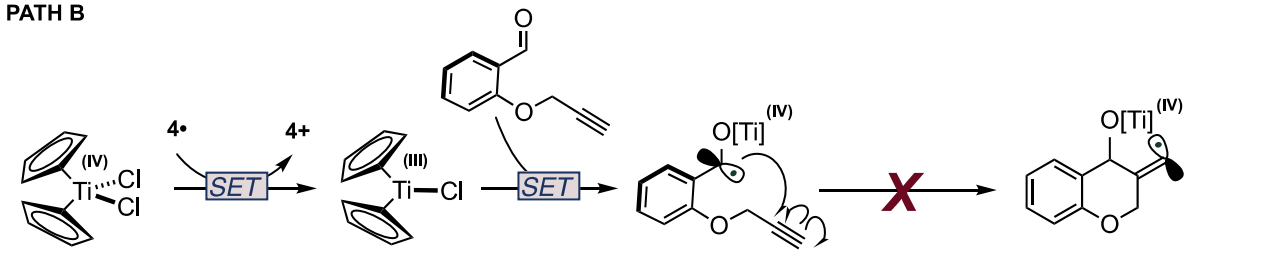


Further mechanistic experiments

Two model substrates were selected for additional information on the reaction mechanism: S03 and S07.
Employing the substrate **S03** (2-(prop-2-yn-1-yloxy)benzaldehyde) under the optimized reaction conditions, it was possible to verify whether simultaneously multiple mechanisms were involved in the process.
To our delight only the pinacol coupling product was detected, suggesting the radical–radical coupling involving two ketyl radicals mediated by two molecules of titanium complex was observed. (Path **A**) The low diastereoselectivity registered is consistent with the data obtained with *ortho*-substituted aldehydes.
No traces of products deriving from a intramolecular radical trapping of the ketyl radical by the alkyne moiety (Path **B**) were detected. At the same time, since the presence in the reaction crude of **S06** was not observed, a possible HAT process involving the photogeneration of a chlorine radical from the titanium reduction was excluded (Path **C**).







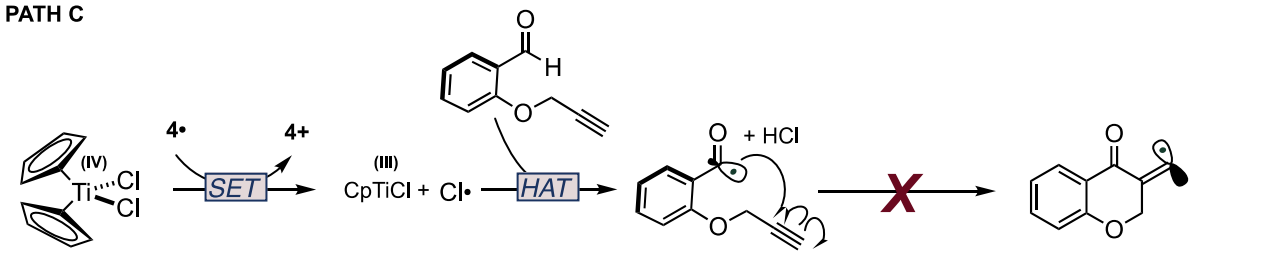


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of reaction crude. Reaction of aldehyde **S03** to give product **S04**.

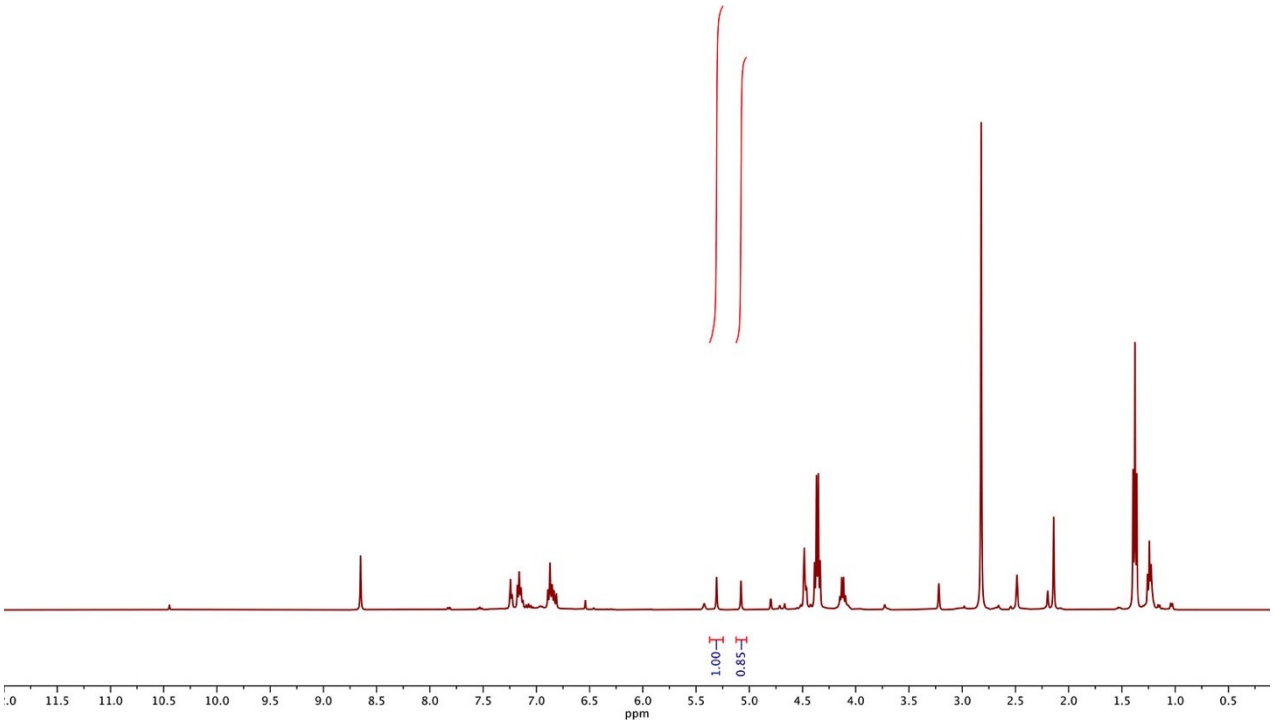


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S04**.

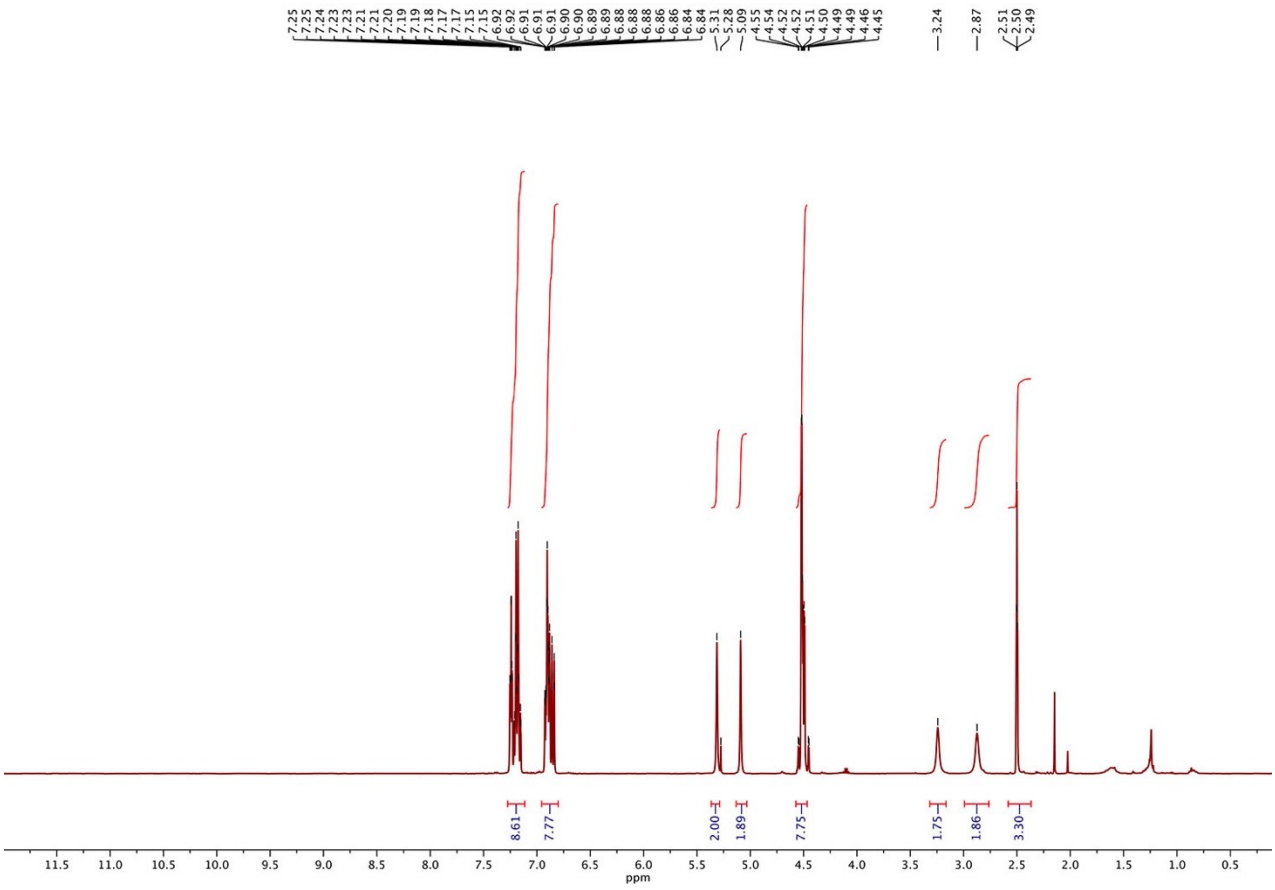
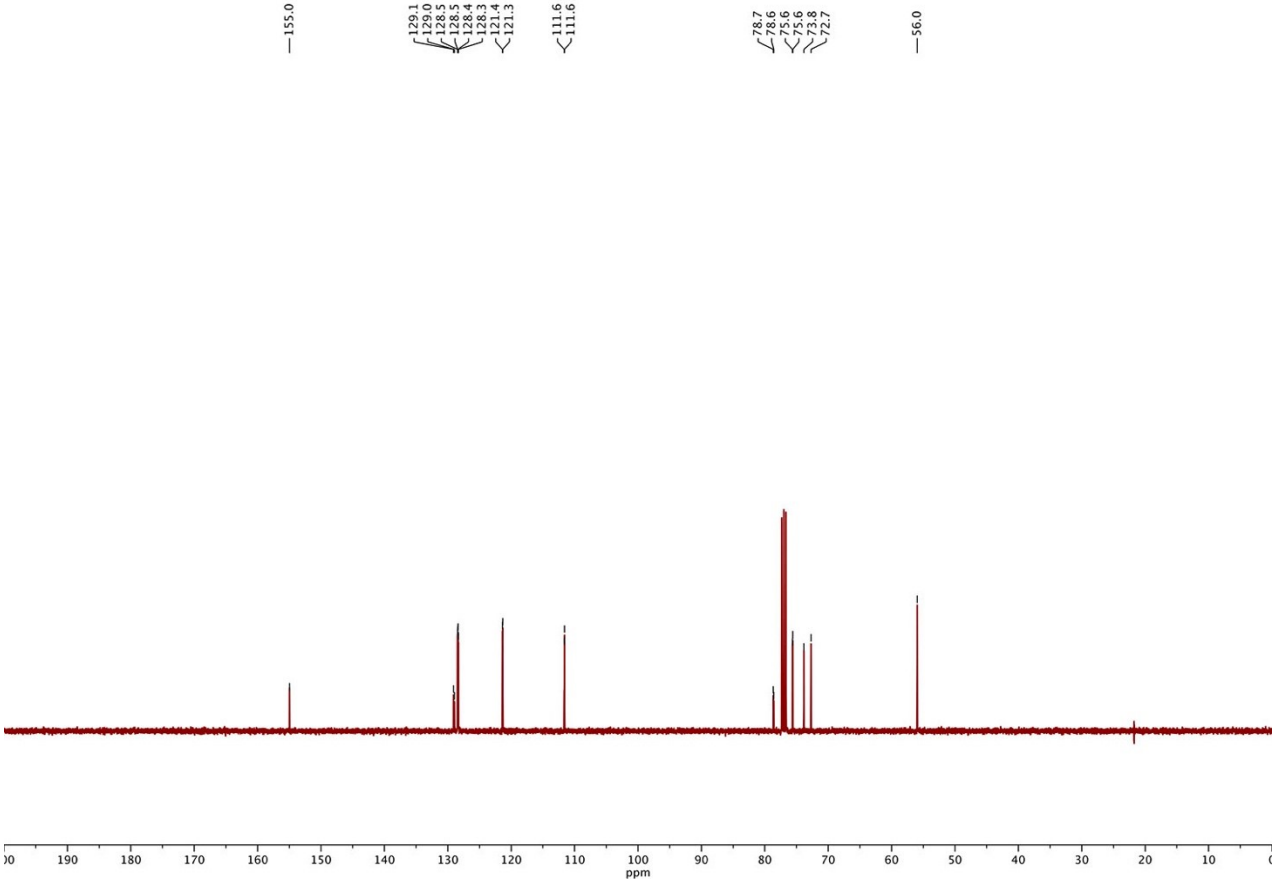
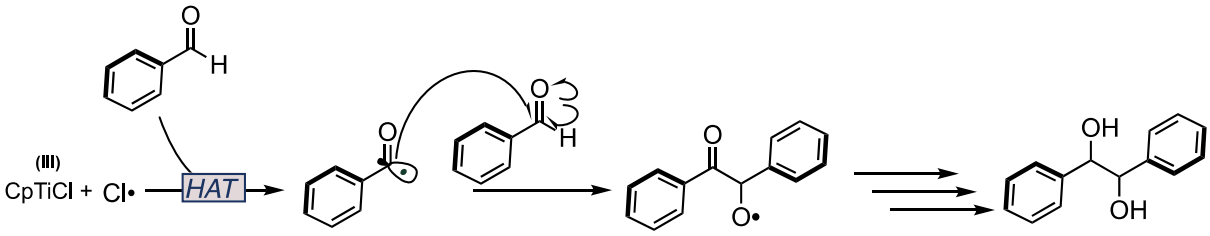


Figure S10. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **S04**.



A transient acyl radical, formed under the reaction conditions, could be trapped by aldehyde to give the corresponding benzoin derivative, that after reduction give the pinacol coupling product:



To exclude this pathway, we submitted to the optimised reaction conditions the benzoin **S07** and no reduction of carbonyl was detected.

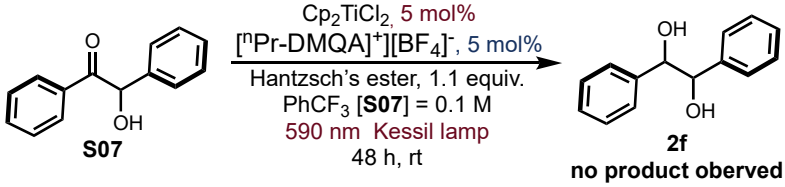


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S07**.

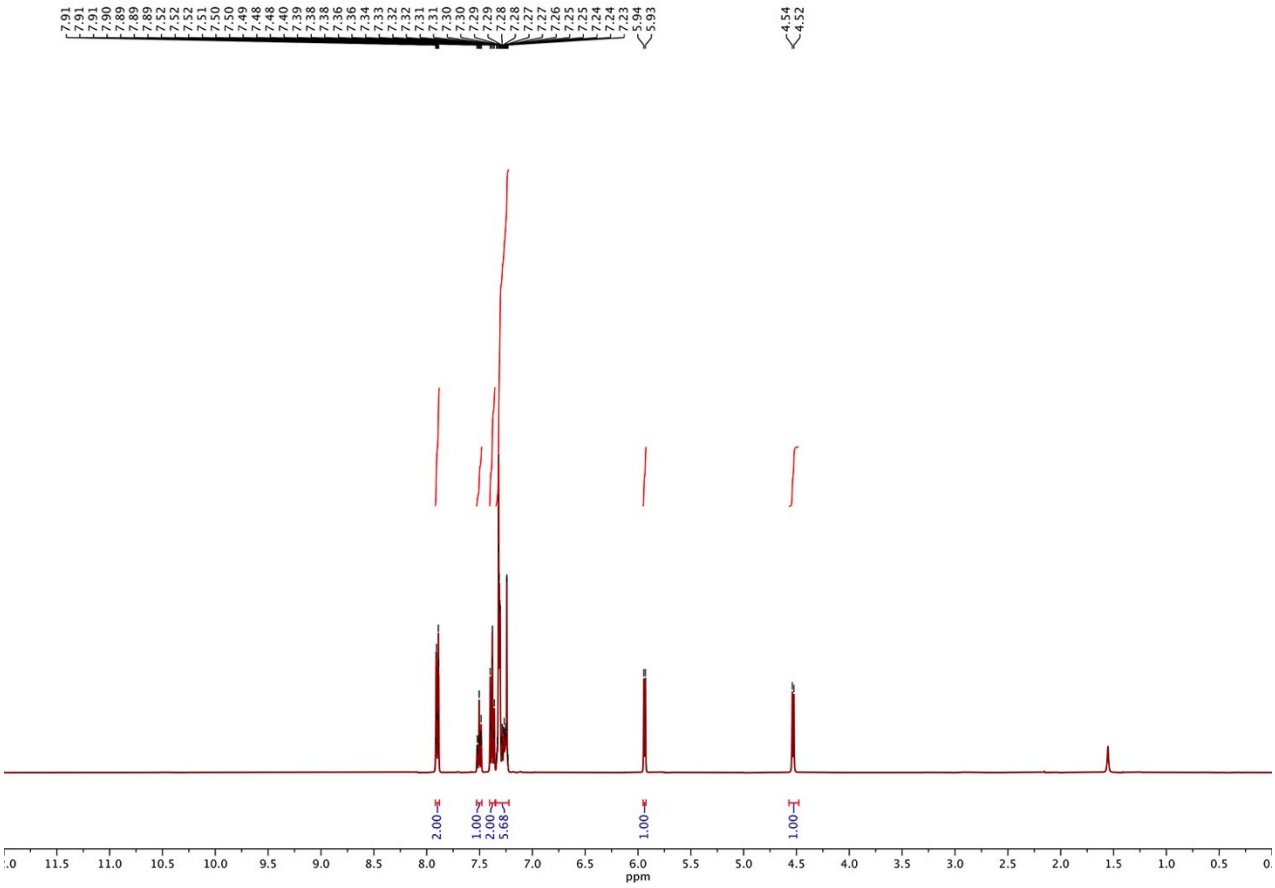
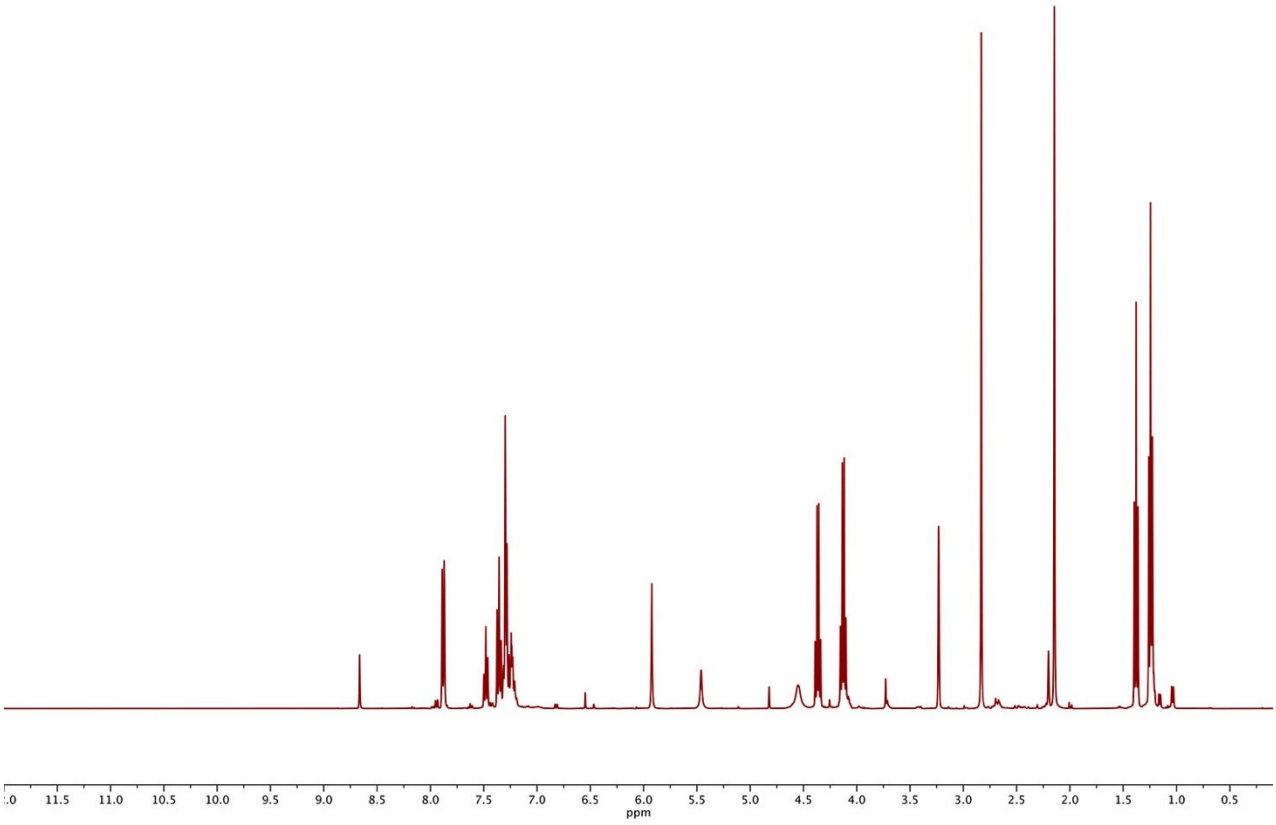


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of reaction crude. Reaction of benzoin **S07** under optimized reaction conditions.



Photophysical and Electrochemical Studies

All the photophysical analyses were carried out in α,α,α-trifluorotoluene at 298 K, unless otherwise specified. UV–vis absorption spectra were recorded with a PerkinElmer λ40 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 shorter than 10 μs 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 Crosby[18] 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, upon degassing with repeated pump-freeze-thaw cycles in high vacuum. The estimated experimental errors are 2 nm on the band maximum, 5% on the molar absorption coefficient and luminescence lifetime.
Cyclic voltammetry (CV) experiments were carried out in argon-purged dichloromethane solutions with tetrabutylammonium hexafluorophosphate as supporting electrolyte at room temperature with an Autolab 30 potentiostat interfaced to a personal computer. The working electrode was a glassy carbon electrode (0.08 cm^2, Amel); its surface was routinely polished with 0.3 mm alumina-water slurry on a felt surface, immediately prior to use. In all cases, the counter electrode was a Pt spiral and an Ag wire was used as a quasi-reference electrode. Ferrocene ($E_{1/2}$ = +0.46 V vs. SCE) was introduced as an internal standard.

Figure S13. Absorption (blue) and emission (red) spectra of a solution of $\mathbf{4}^+$ in air equilibrated CH_2Cl_2 at r.t. (λ_{ex} = 550 nm). The emission (red) and excitation (blue, λ_{em} = 690 nm) spectra recorded in $PhCF_3$ are also shown as dashed lines, for the sake of comparison.

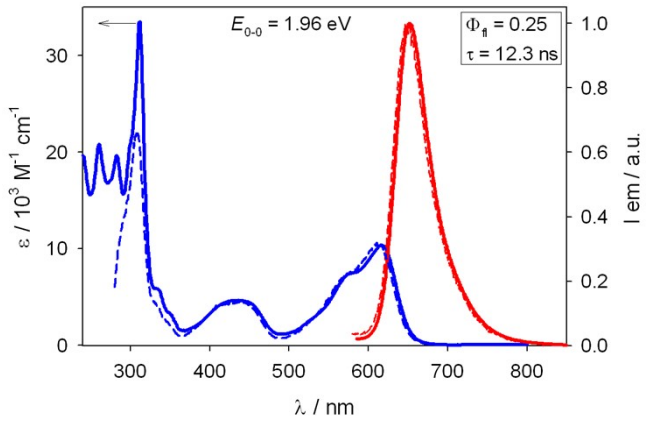


Figure S14. Emission spectra collected on a diluted solution of $\mathbf{4}^+$ in air-equilibrated $PhCF_3$ at r.t. (ca. 10 μM) upon 30 minutes of continuous irradiation at λ_{ex} = 570 nm. Inset: profile of the variations on emission maxima.

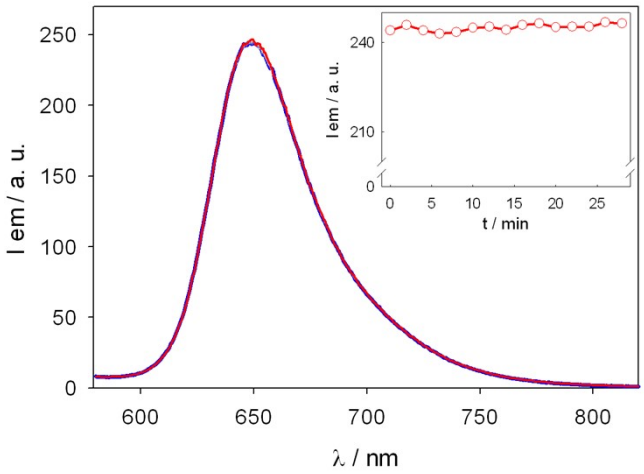


Figure S15. A: absorption spectra of solutions of $\mathbf{4}^+$ in air-equilibrated $PhCF_3$ at r.t. (ca. 32 μM, blue line) obtained upon addition of increasing amounts of *p*-chlorobenzaldehyde (**1a**, up to ca. 0.06 M, red line). **B**: fluorescence decays of $\mathbf{4}^+$ obtained from the same solutions at λ_{em}= 690 nm (λ_{ex}= 640 nm). The instrument response function (IRF) is also shown (grey dots). **C**: Stern-Volmer diagram relative to the fluorescence lifetimes shown in **B**.

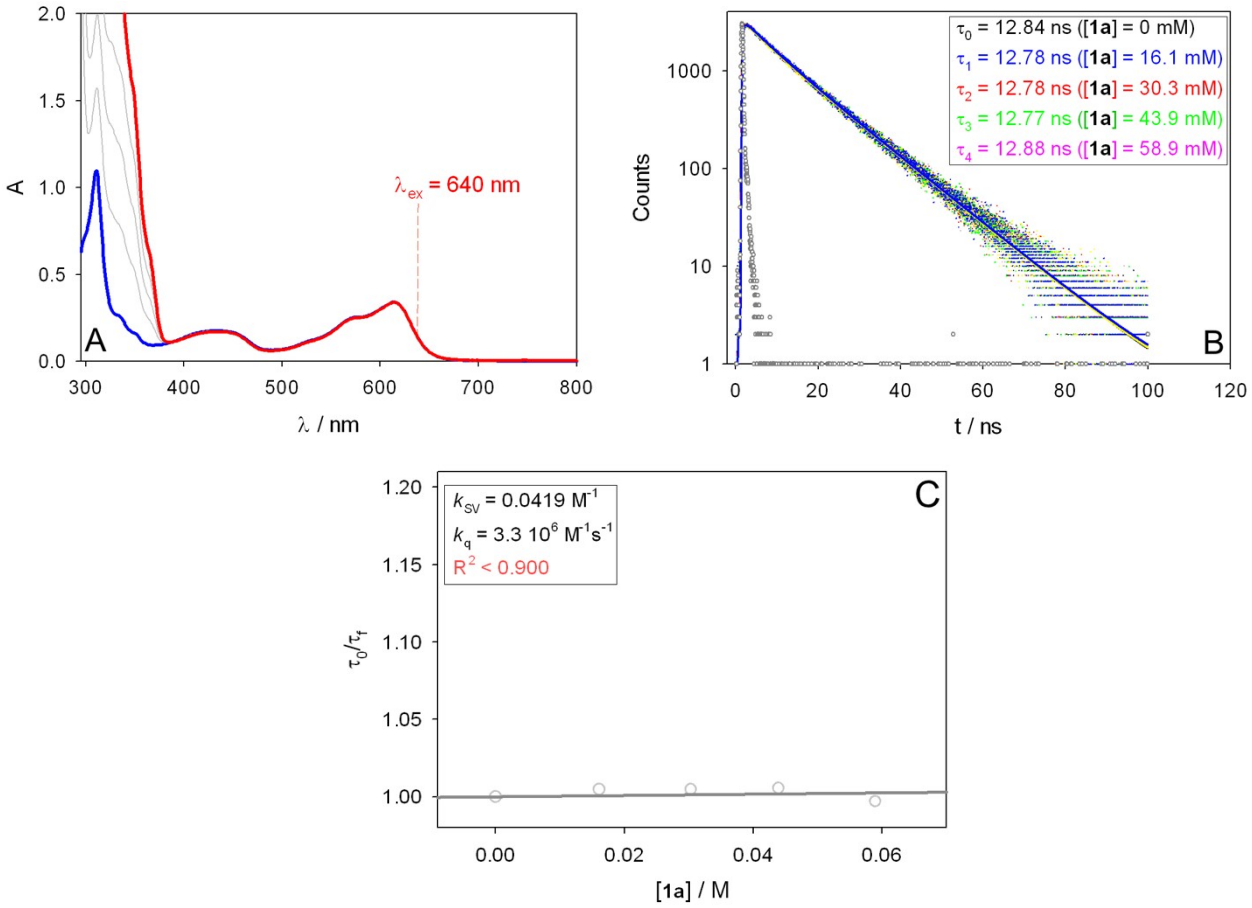


Figure S16. A: absorption spectra of solutions of $\mathbf{4}^+$ in air-equilibrated $PhCF_3$ at r.t. (ca. 6.2 μM, blue line) obtained upon addition of **3** (5.4 mM, red line). The baseline is affected by the low solubility of **3**. **B**: fluorescence decays of $\mathbf{4}^+$ obtained from the same solutions at λ_{em}= 690 nm (λ_{ex}= 640 nm). The instrument response function (IRF) is also shown (grey dots).

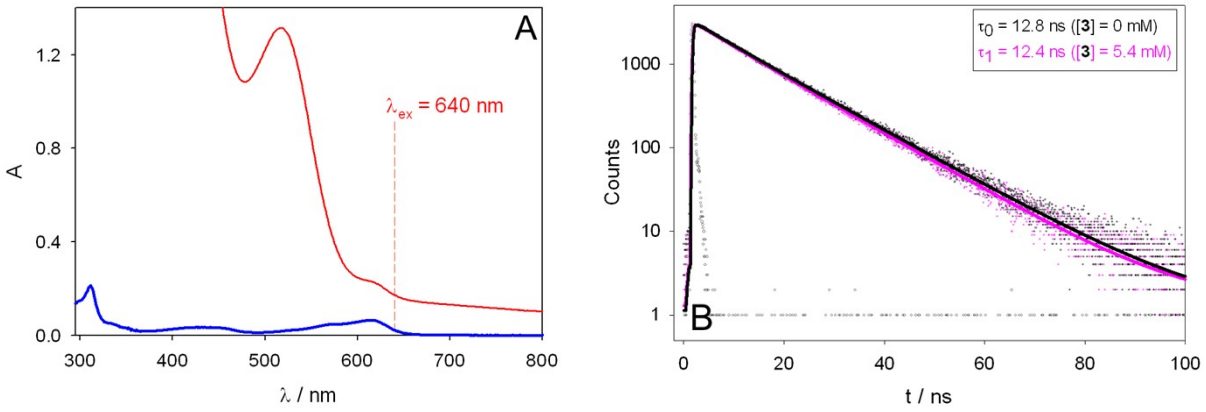


Figure S17. **A**: absorption spectra of solutions of $\mathbf{4}^+$ in air-equilibrated $PhCF_3$ at r.t. (ca. 16 μM, blue line) obtained upon addition of **11** (up to 3.3 mM, red line). The baseline is affected by the low solubility of $\mathbf{4}^+$. **B**: fluorescence decays of $\mathbf{4}^+$ obtained from the same solutions at λ_{em}= 690 nm (λ_{ex}= 640 nm). The instrument response function (IRF) is also shown (grey dots). Lifetimes are obtained from multiexponential fitting, taking into account the longest component (whose contribution to the fitting is expressed in percentage).

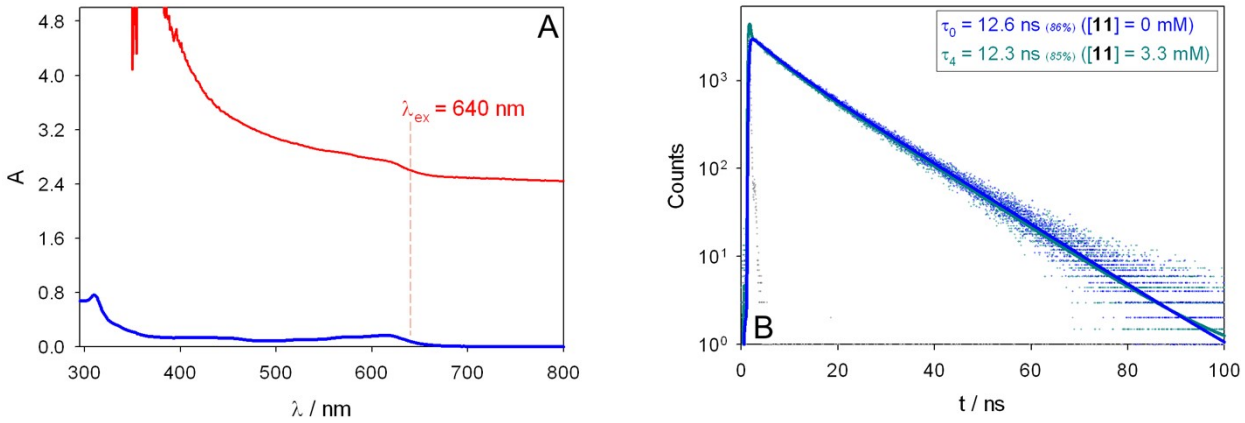


Figure S18. A: absorption spectra of solutions of $\mathbf{4}^{+}$ in air-equilibrated $PhCF_3$ at r.t. (ca. 7.5 μM, blue line) obtained upon addition of increasing amounts of **6** (**HE**, up to 6.7 mM, red line). **B**: fluorescence decays of $\mathbf{4}^{+}$ obtained from the same solutions at λ_{em}= 690 nm (λ_{ex}= 640 nm). The instrument response function (IRF) is also shown (grey dots). **C**: Stern-Volmer diagram relative to the fluorescence lifetimes shown in **B**.

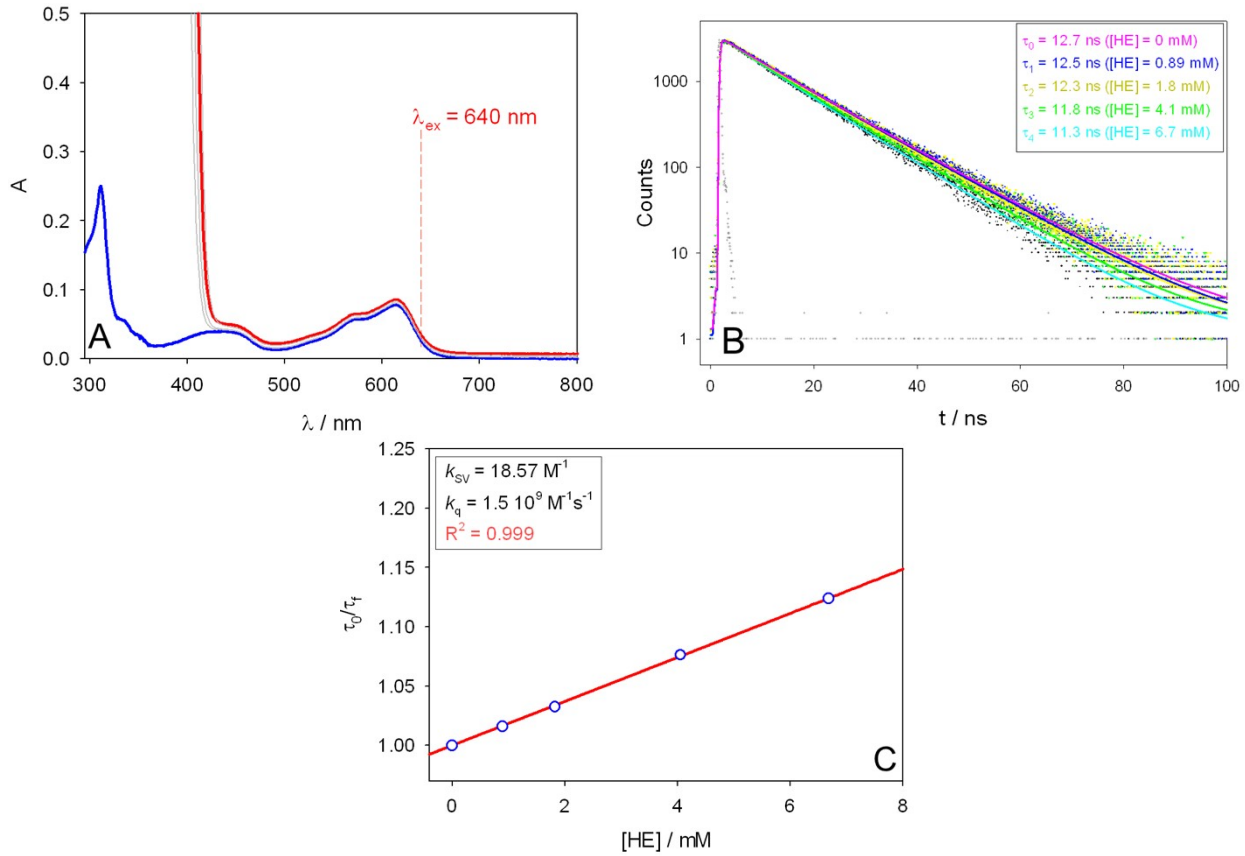


Figure S19. Comparison between Stern-Volmer kinetics determined for the quenching of the luminescence of $\mathbf{4}^+$ in air-equilibrated $PhCF_3$ in the presence of the different quenchers (**Q**) in the reaction mixture (**6**: blue line; **1a**: grey line; the corresponding quenching constants have been made explicit). The quenching efficiencies η are calculated considering, for each quencher, a concentration close to that used in the reaction medium (for **6**: data are extrapolated by using the relative quenching constant).

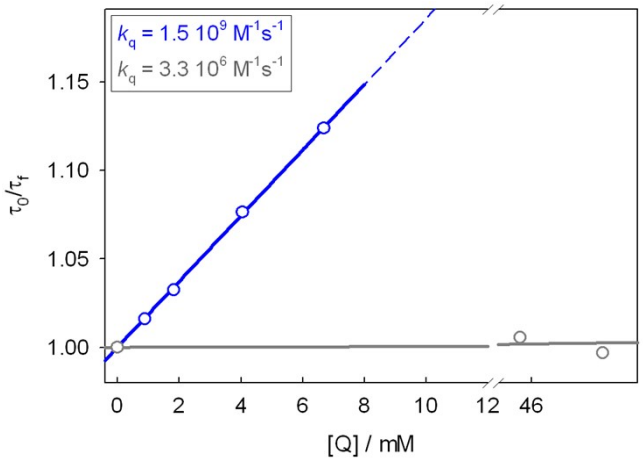


Table S4.

Quencher	[quencher] / mM	τ_0 / τ_q	η_q / %
6	*110*	*3.04*	67
3	5.4	1.03	< 3
11	3.3	1.02	< 2
1a	59	~ 1.0	negligible

Discussion on alternative quenching mechanisms. The absorption spectra of **3** and **11** (λ_{onset} ~600 nm, see figure S15) are not compatible with a singlet-singlet EnT from the excited singlet excited state of $\mathbf{4}^+$ ($^1\mathbf{4}^{+}$*, λ_{max} = 648 nm). Triplet-triplet EnT from $\mathbf{4}^+$ to **3** are also most unlikely due to the proximity in energy of $^1\mathbf{4}^{+}$* and $^3\mathbf{3}$* ($\lambda_{max,ph}$ = 660 nm. In addition, no significative information on the virtually accessible excited states of **11** is available, since the complex does not show any fluorescence or phosphorescence emission in deoxygenated solvents at r.t. or in rigid matrix (CH_2Cl_2:CH_3OH, 1:1 v/v) at 77 K.

Figure S20. Comparison between qualitative absorption spectra of solutions of **3** (dark red line) and **11** (orange line) in CH_2Cl_2 at r.t. Inset: the portions in the visible spectrum are enlarged 5 times.

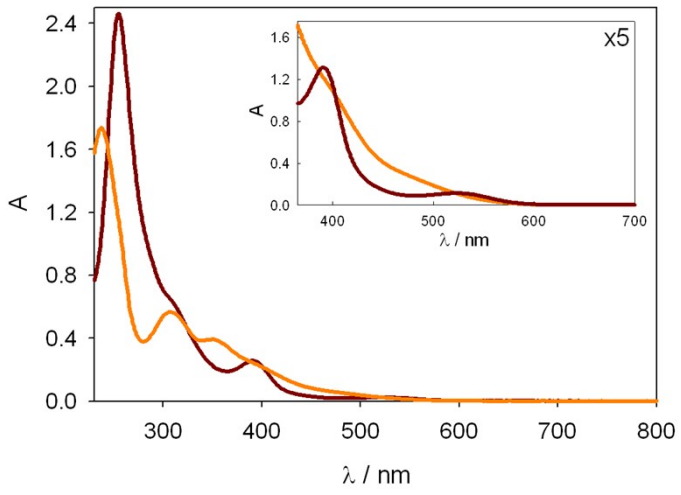
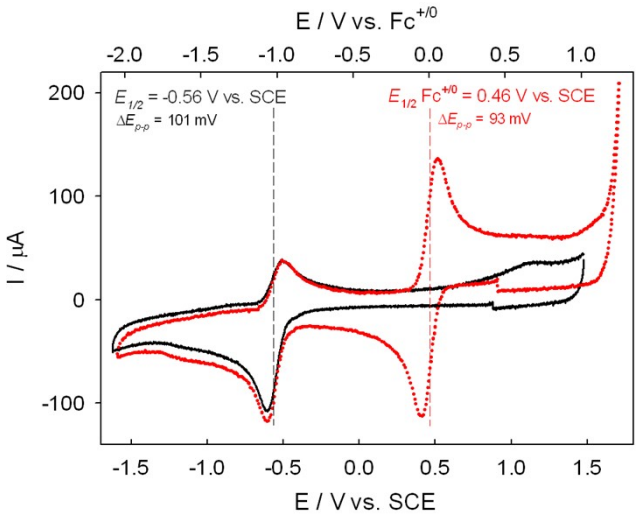
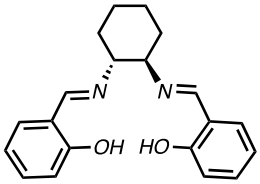


Figure S21. Cyclic voltammogram (scan rate: 1 V/s) of a solution containing **11** in CH_2Cl_2 (black line, 1.6 mM; tetrabutylammonium hexafluorophosphate 0.1 M is introduced as supporting electrolyte). For comparison purposes, the voltammogram of the same solution containing ferrocene as internal standard is also shown (red line; $Fc^{+/0}$ = 0.46 V vs. SCE).

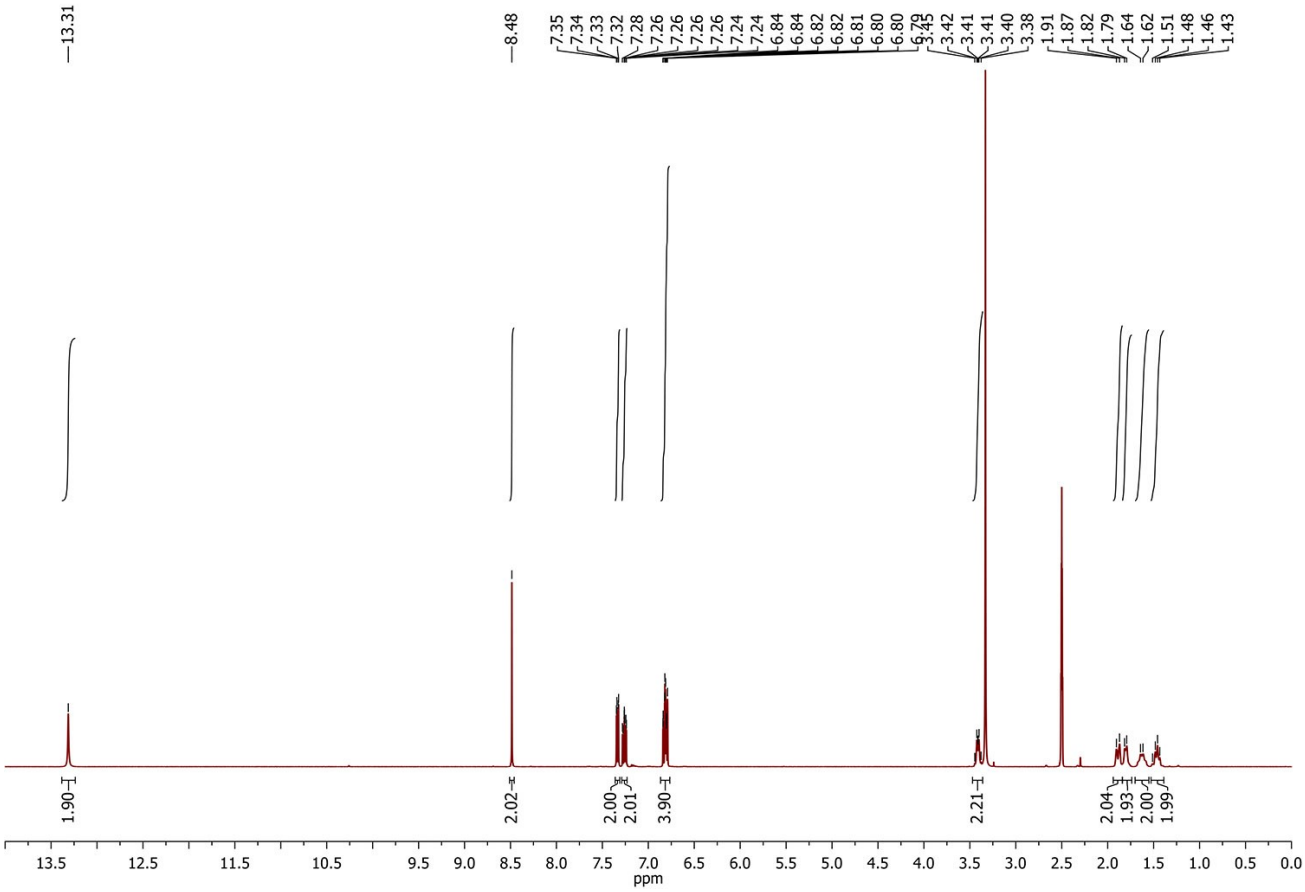


Copies of NMR spectra for racemic substrates



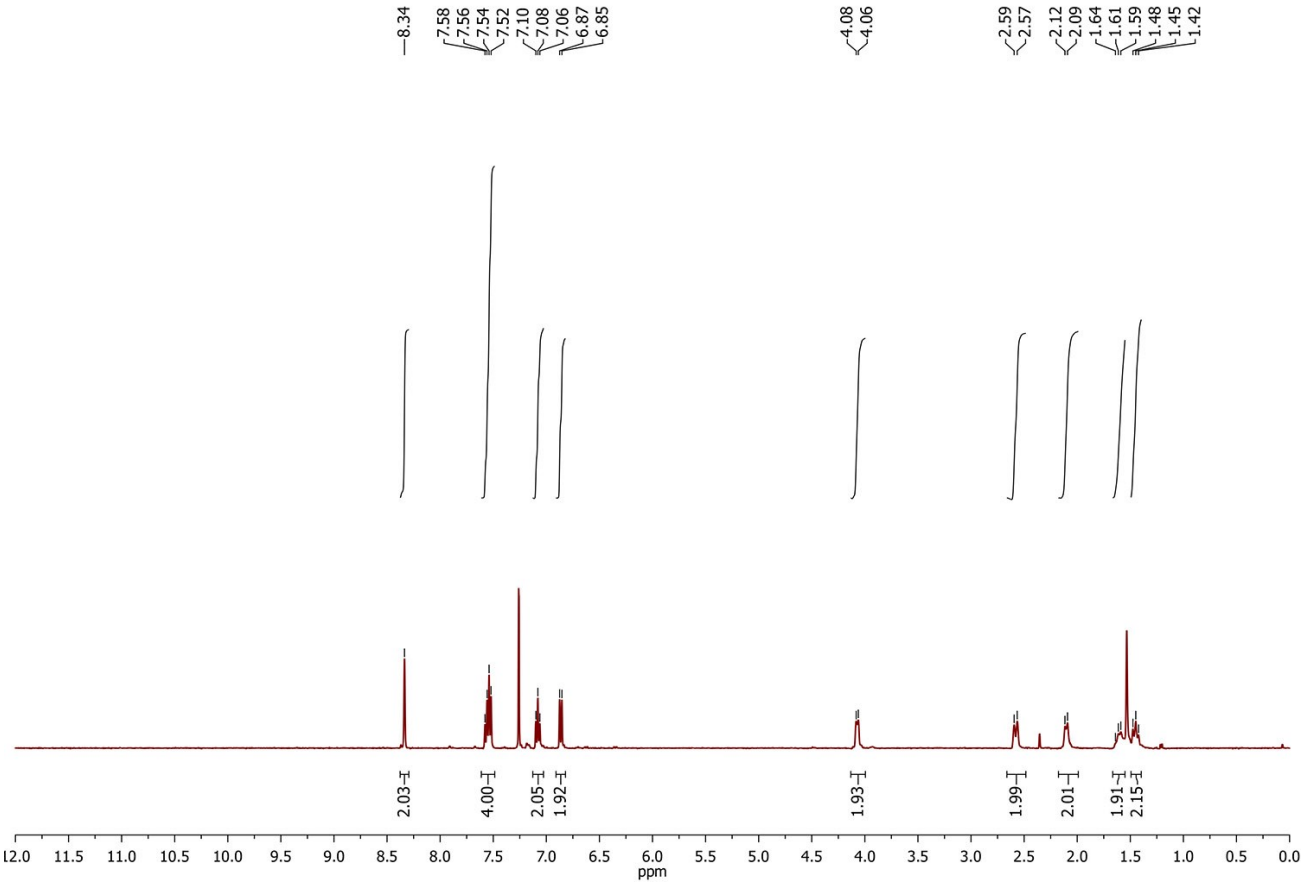
(R,R)-N,N'-bis(salicylidene)-1,2-cyclohexanediamine

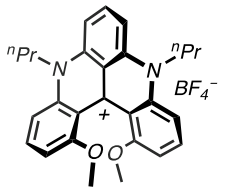
^{1}H NMR (400 MHz, DMSO-d_6)



SalenTiCl$_2$

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

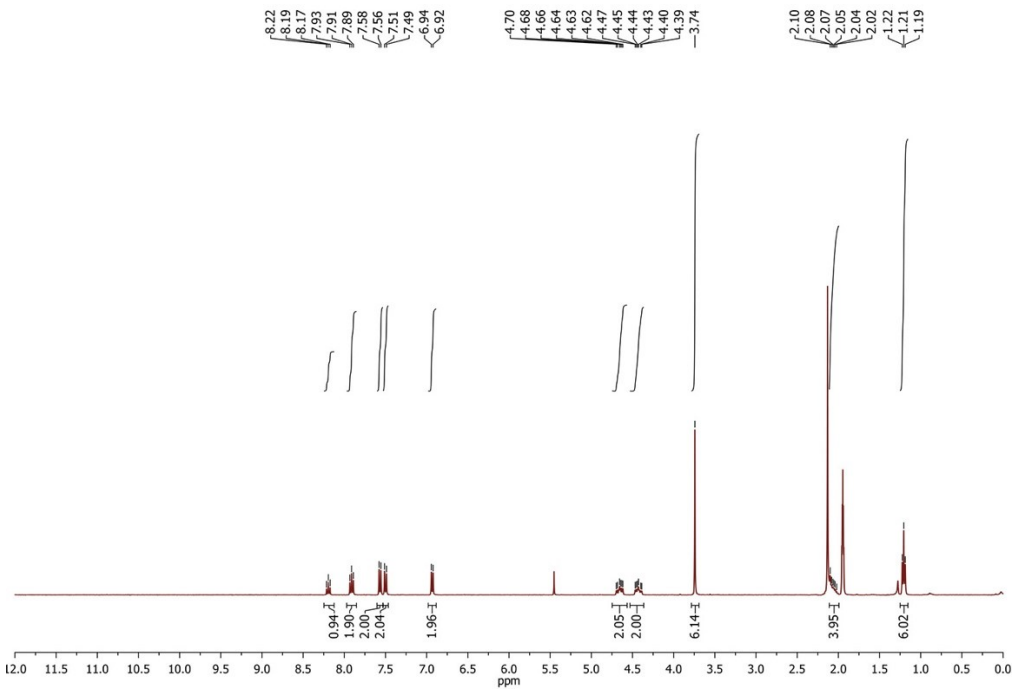




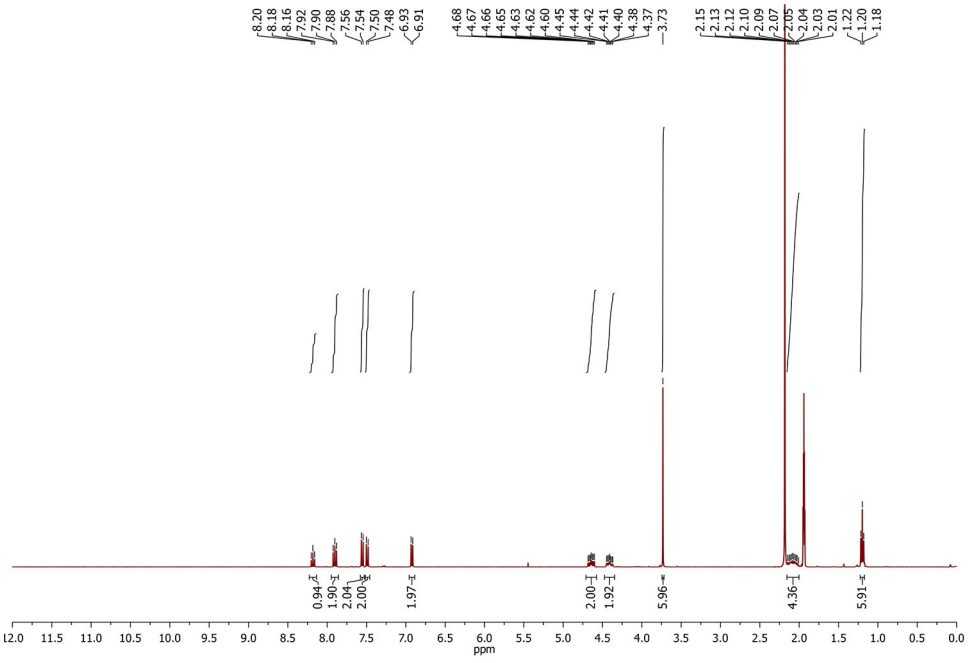
4⁺

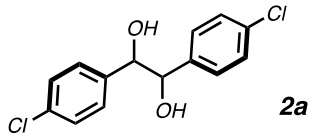
[^{n}Pr-DMQA]⁺[BF$_4$]⁻

^{1}H NMR (400 MHz, CD_3CN)



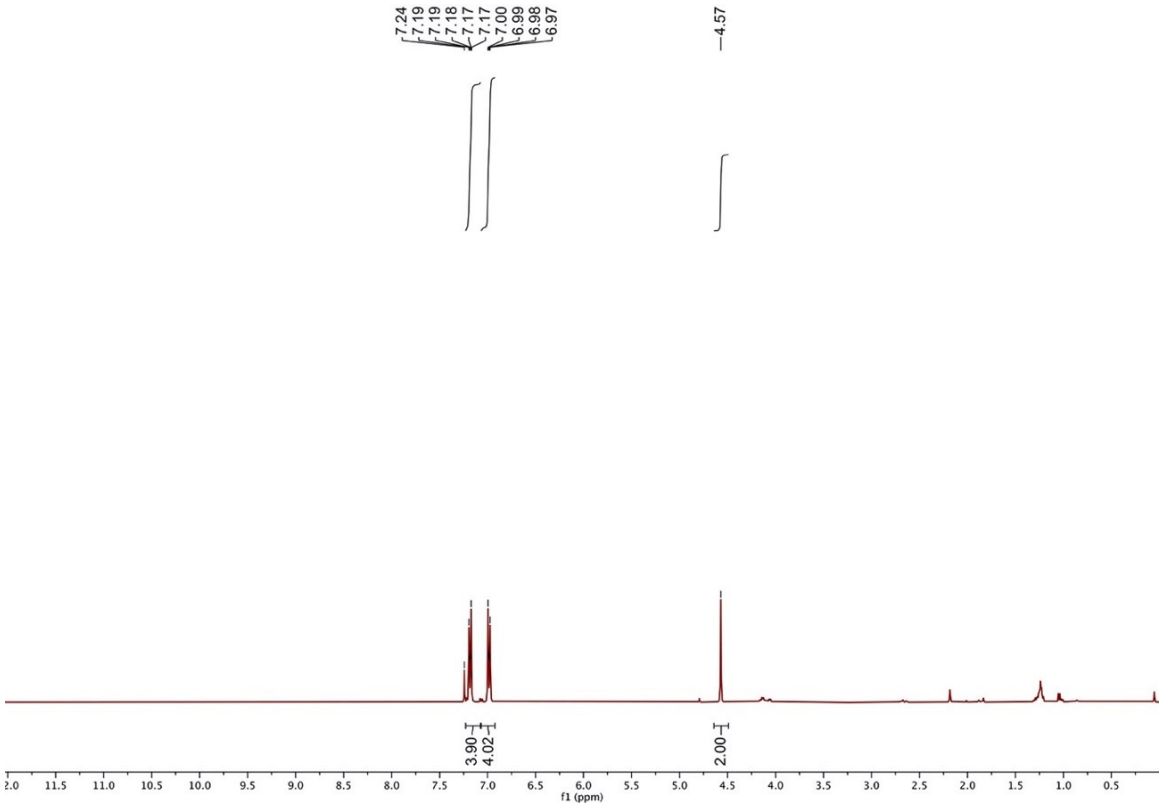
^{1}H NMR (400 MHz, CD_3CN) of **4**$^+$ after 24 h of irradiation with Kessil® PR160L@595 lamp in solution of $PhCF_3$.



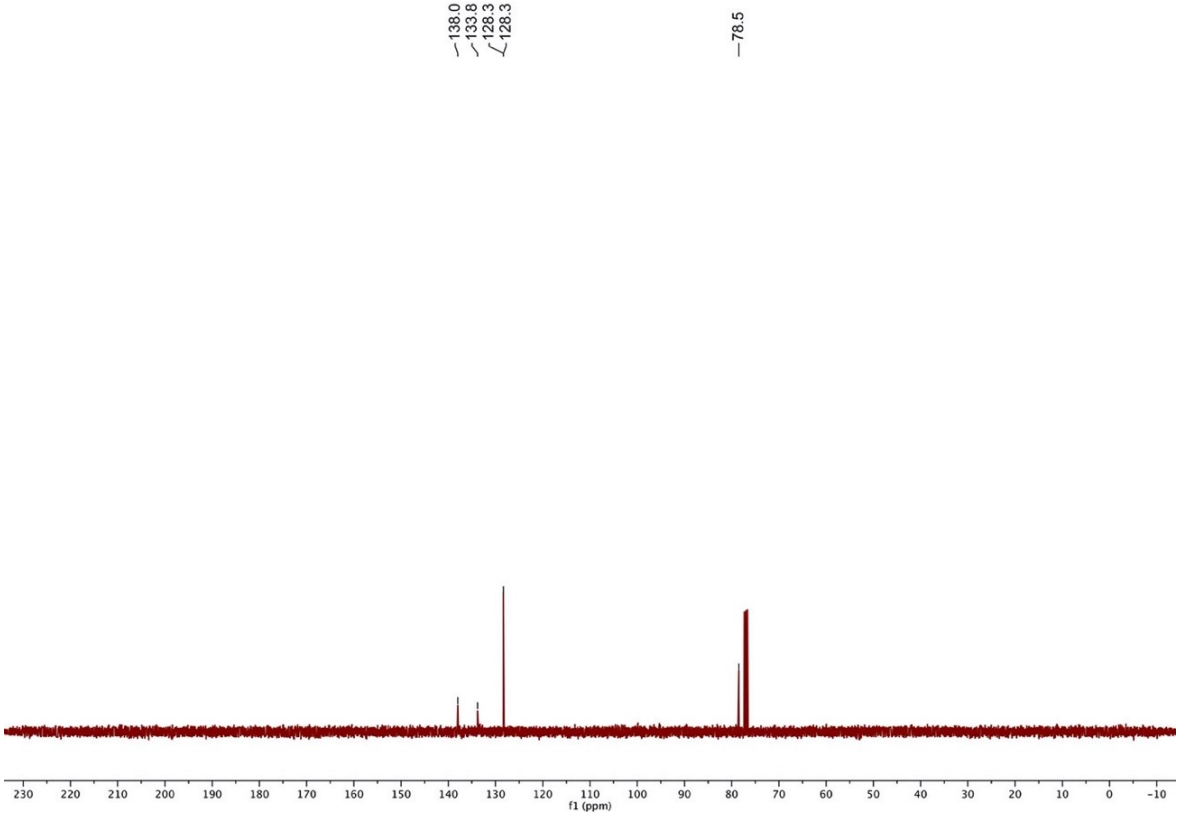


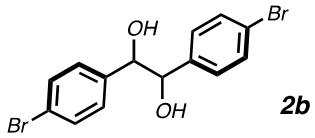
2a

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



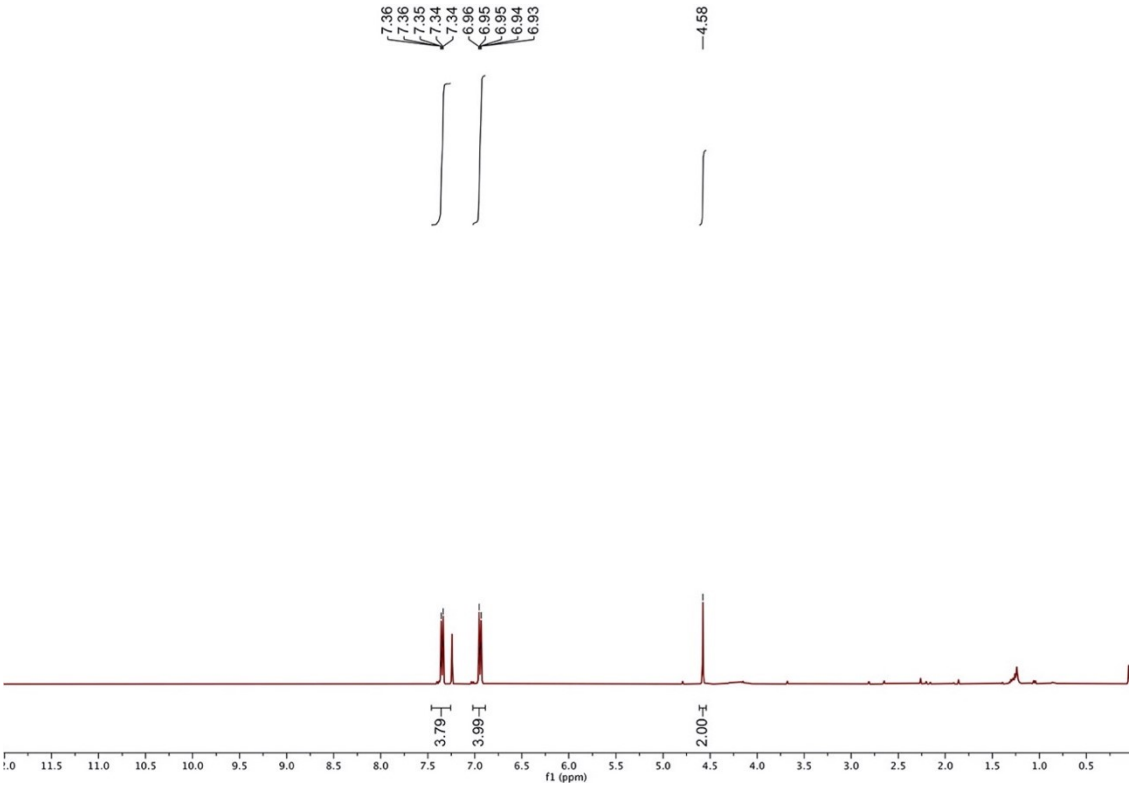
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



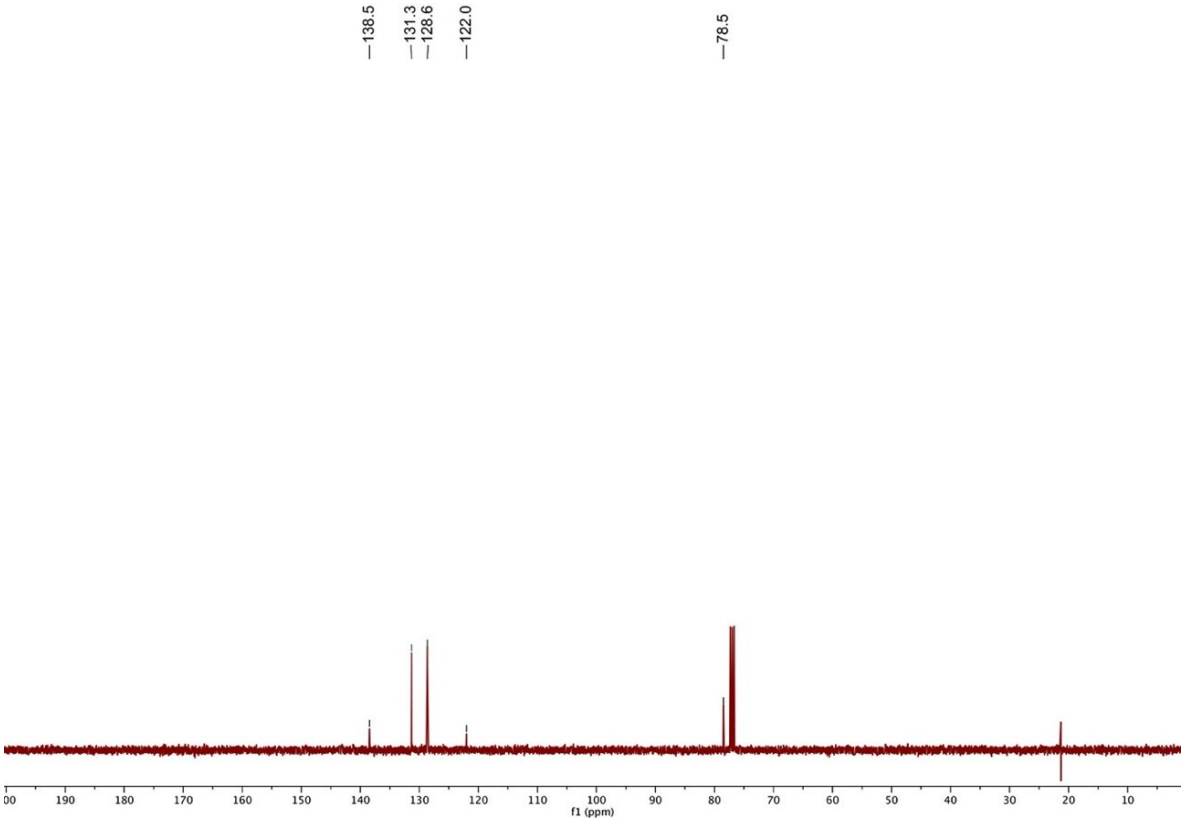


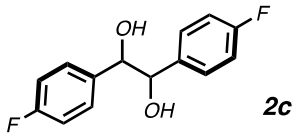
2b

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



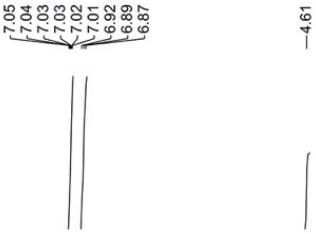
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

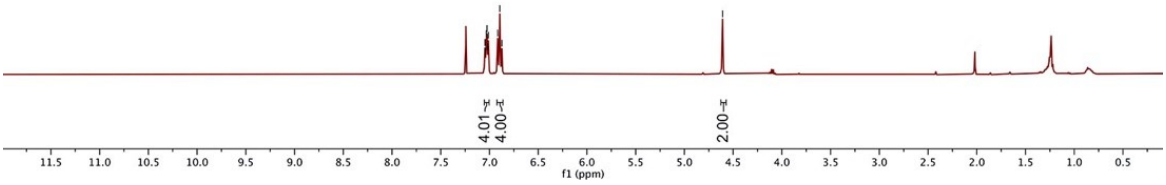




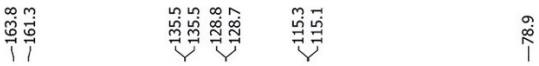
2c

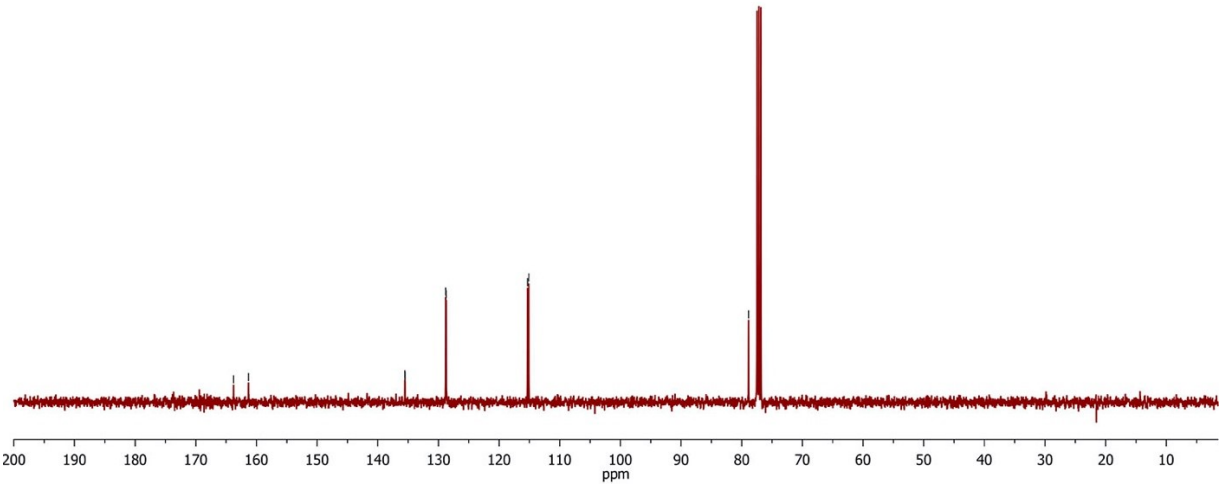
^{1}H NMR (400 MHz, $CDCl_3$)



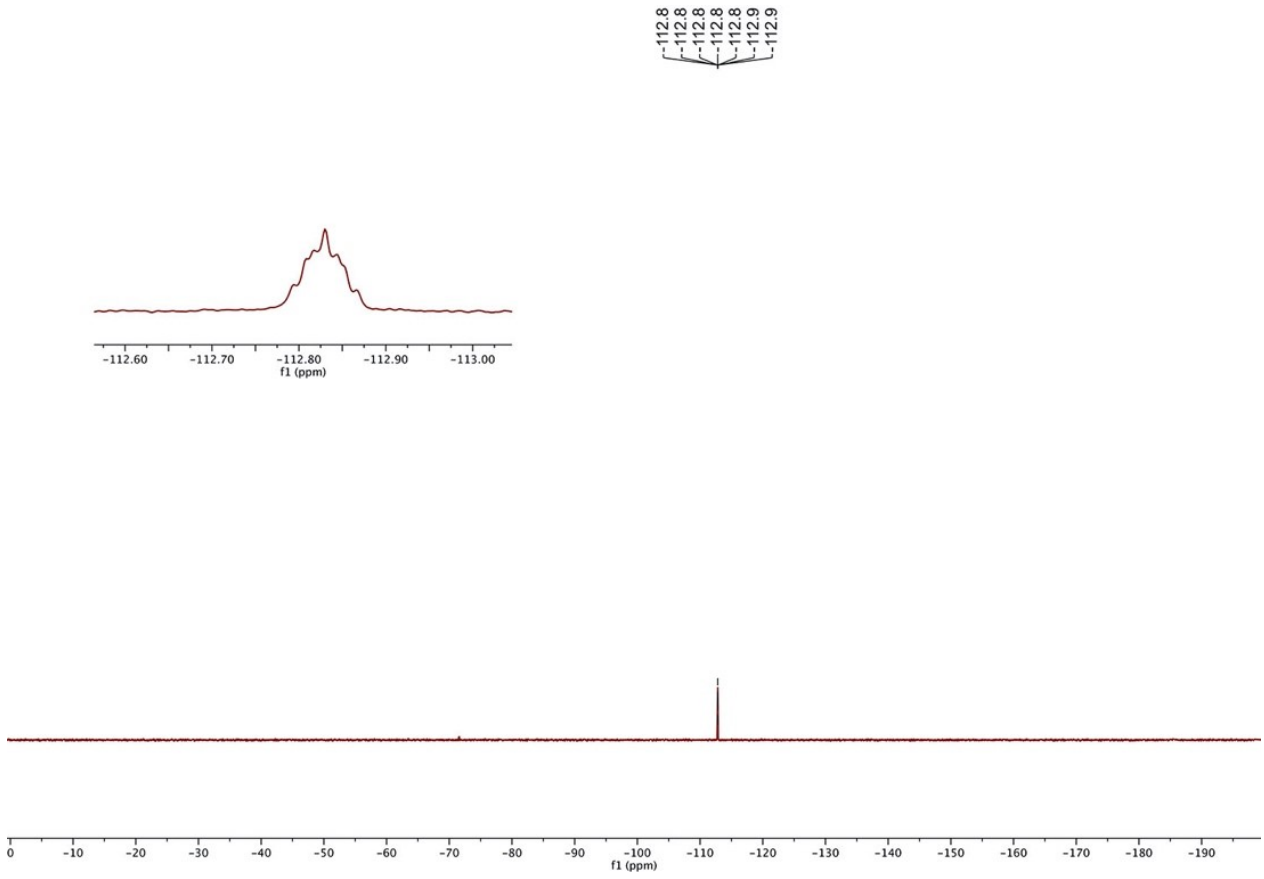


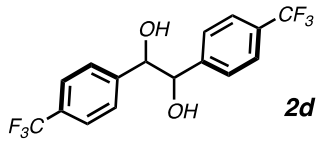
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)





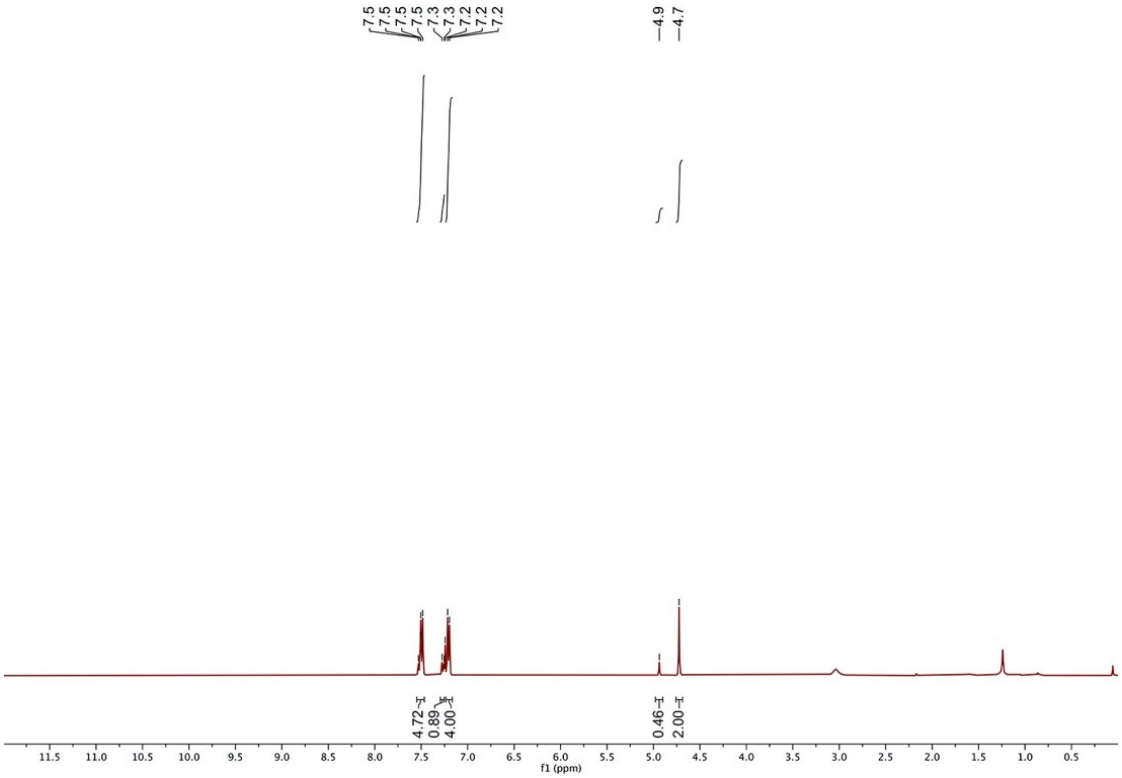
^{19}F NMR (376.5 Hz, $CDCl_3$)



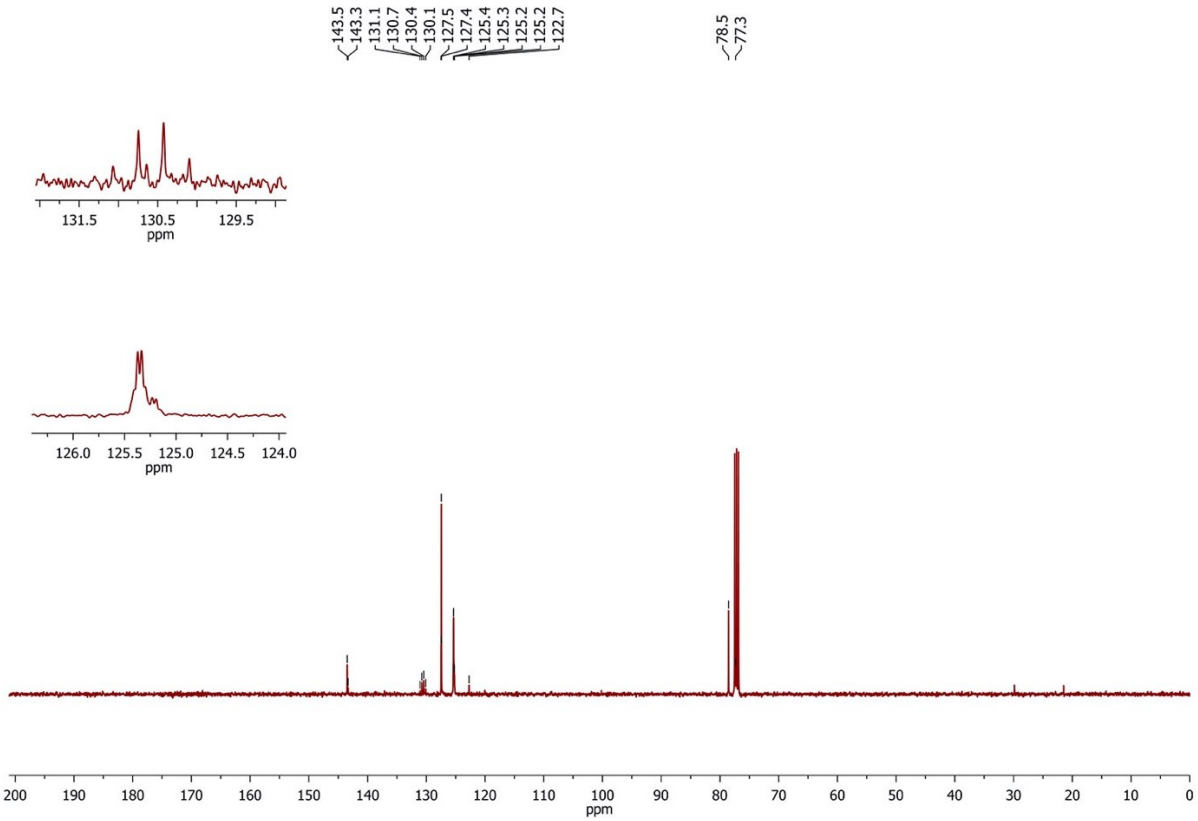


2d

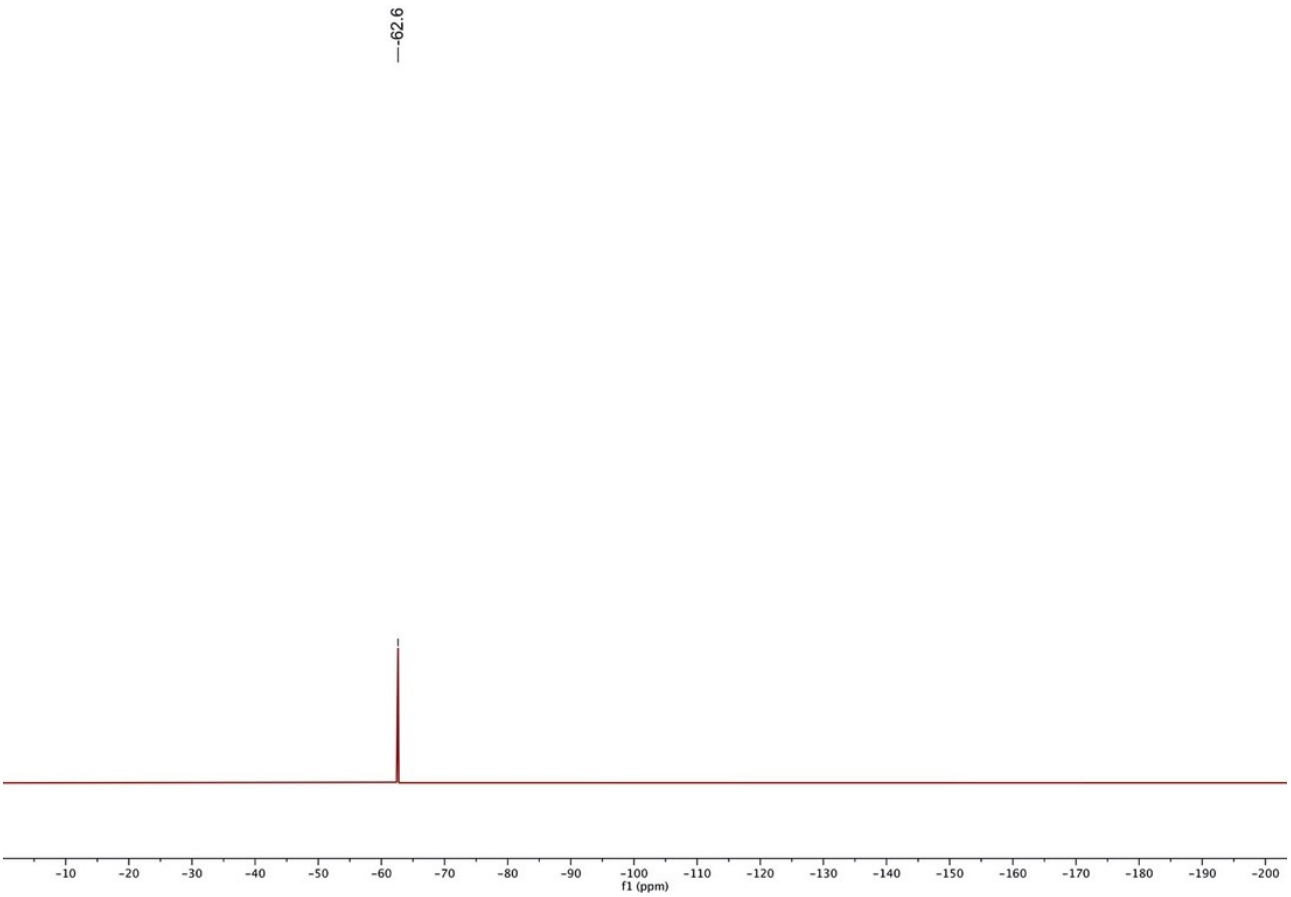
^{1}H NMR (400 MHz, $CDCl_3$)

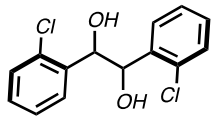


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



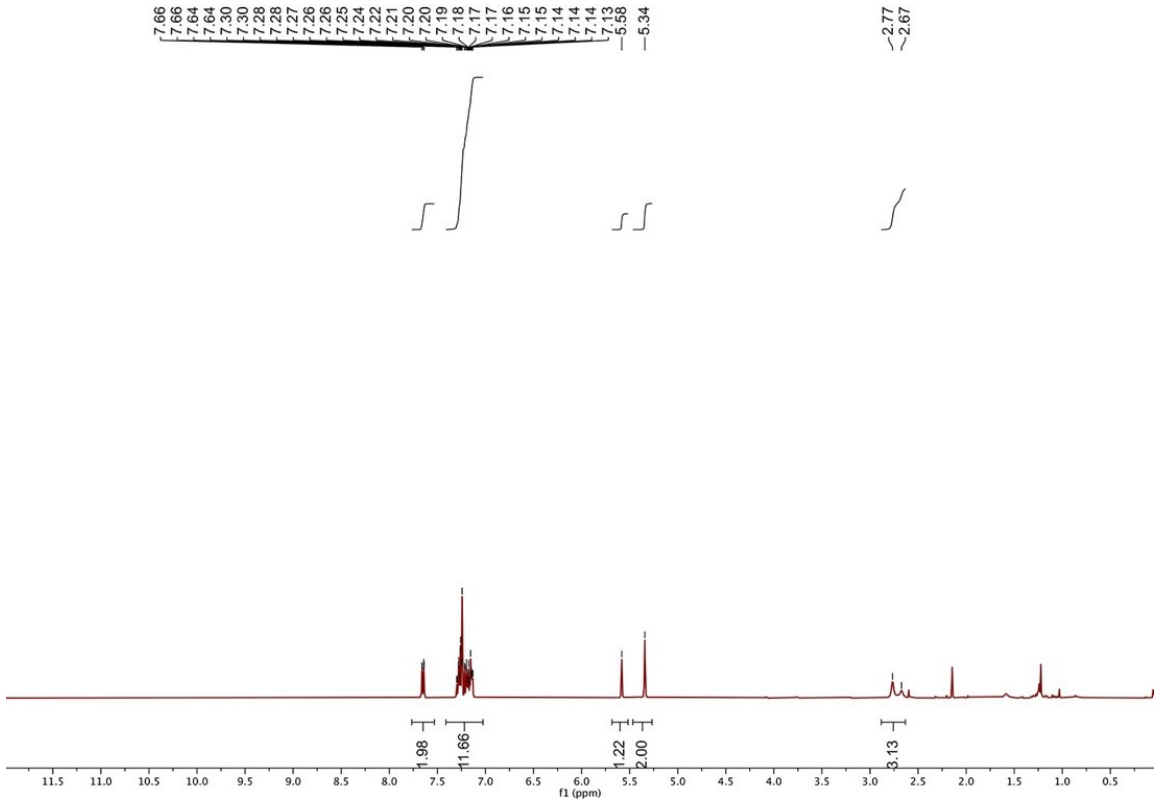
^{19}F NMR (376.5 Hz, $CDCl_3$)



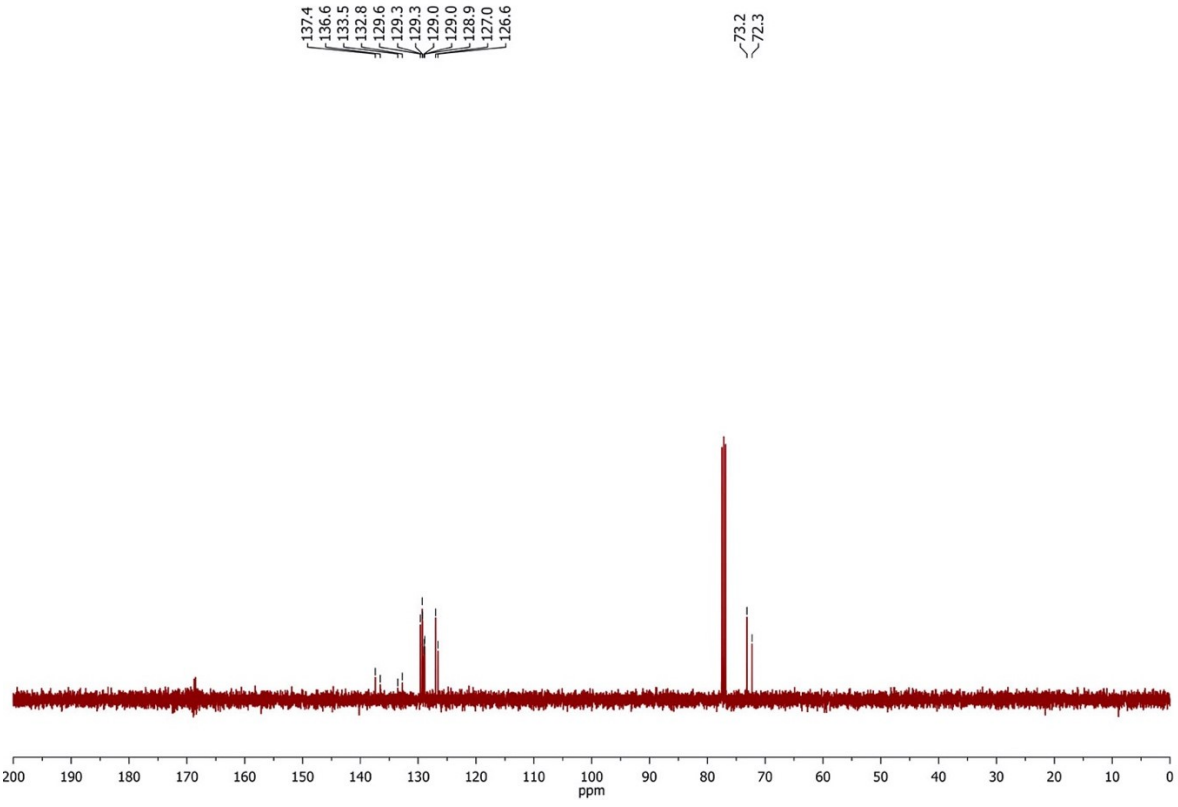


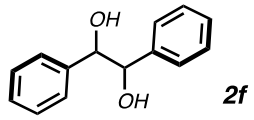
2e

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



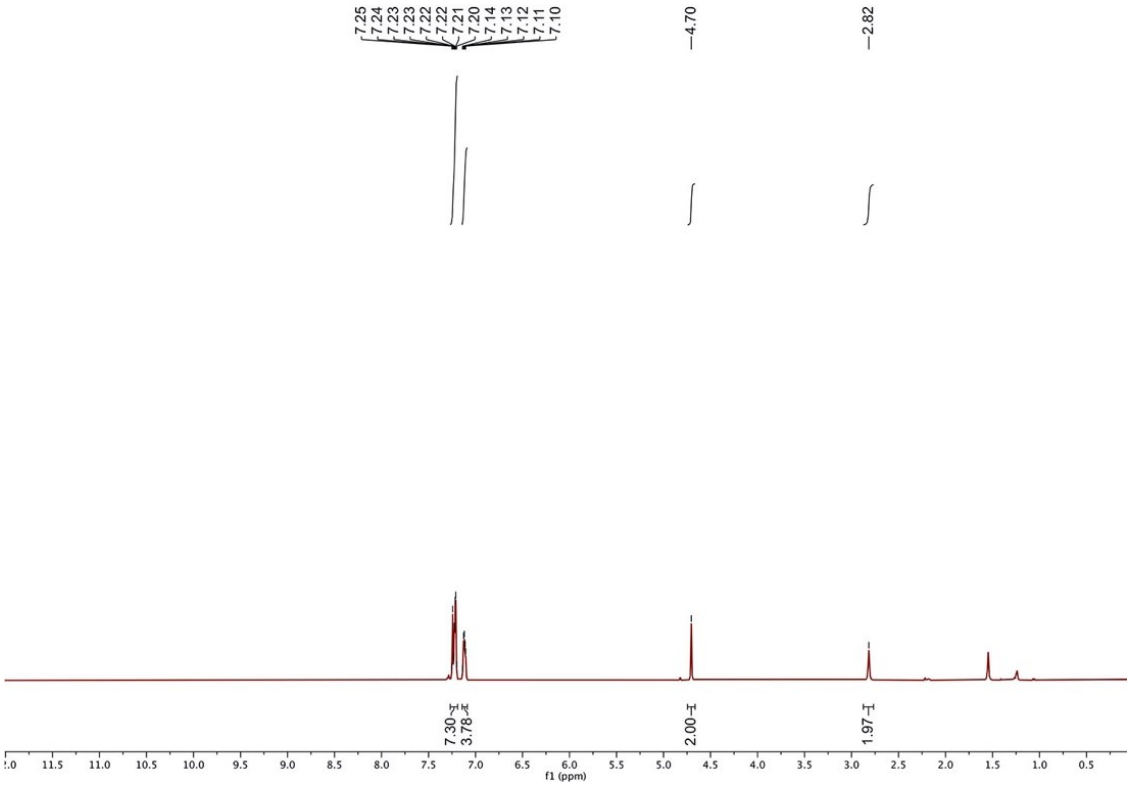
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



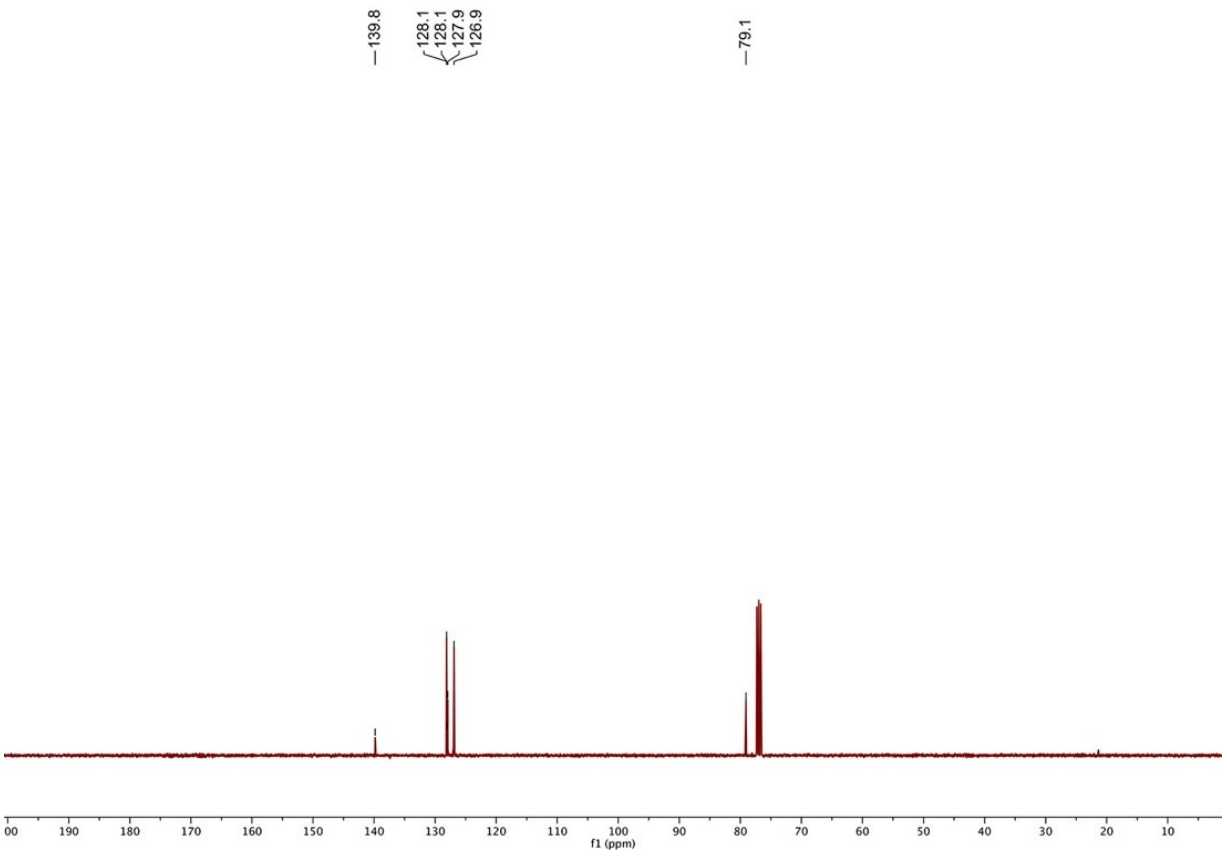


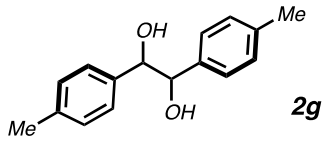
2f

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



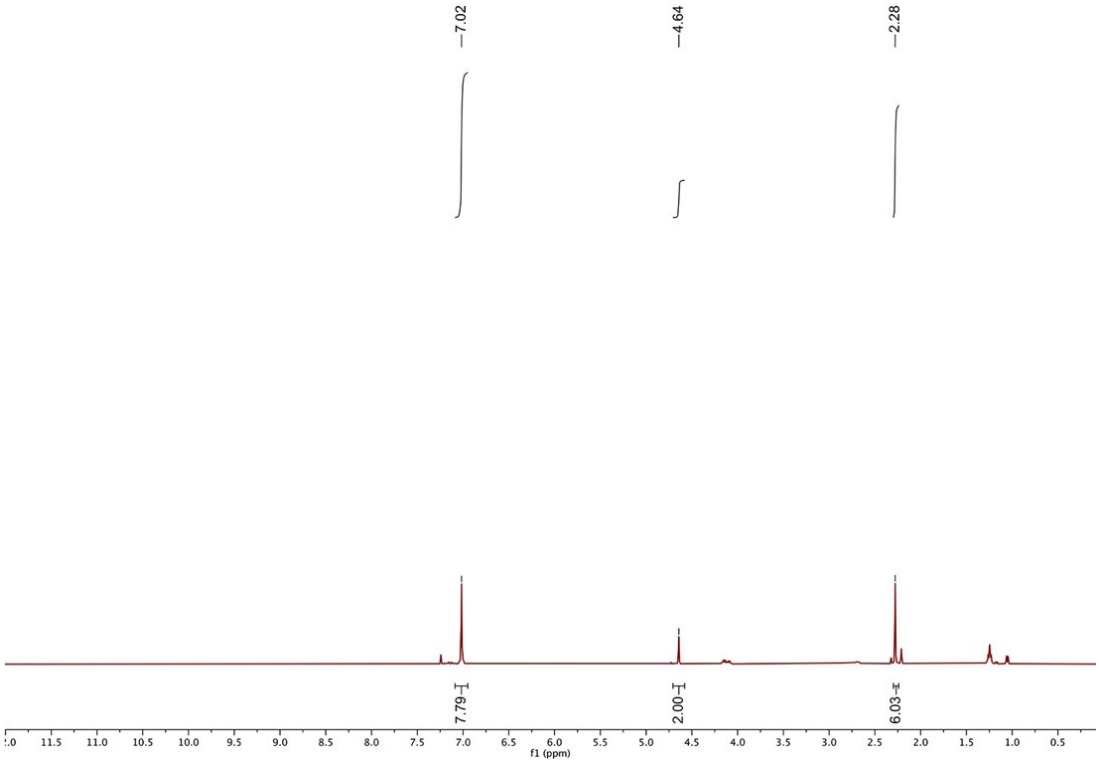
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



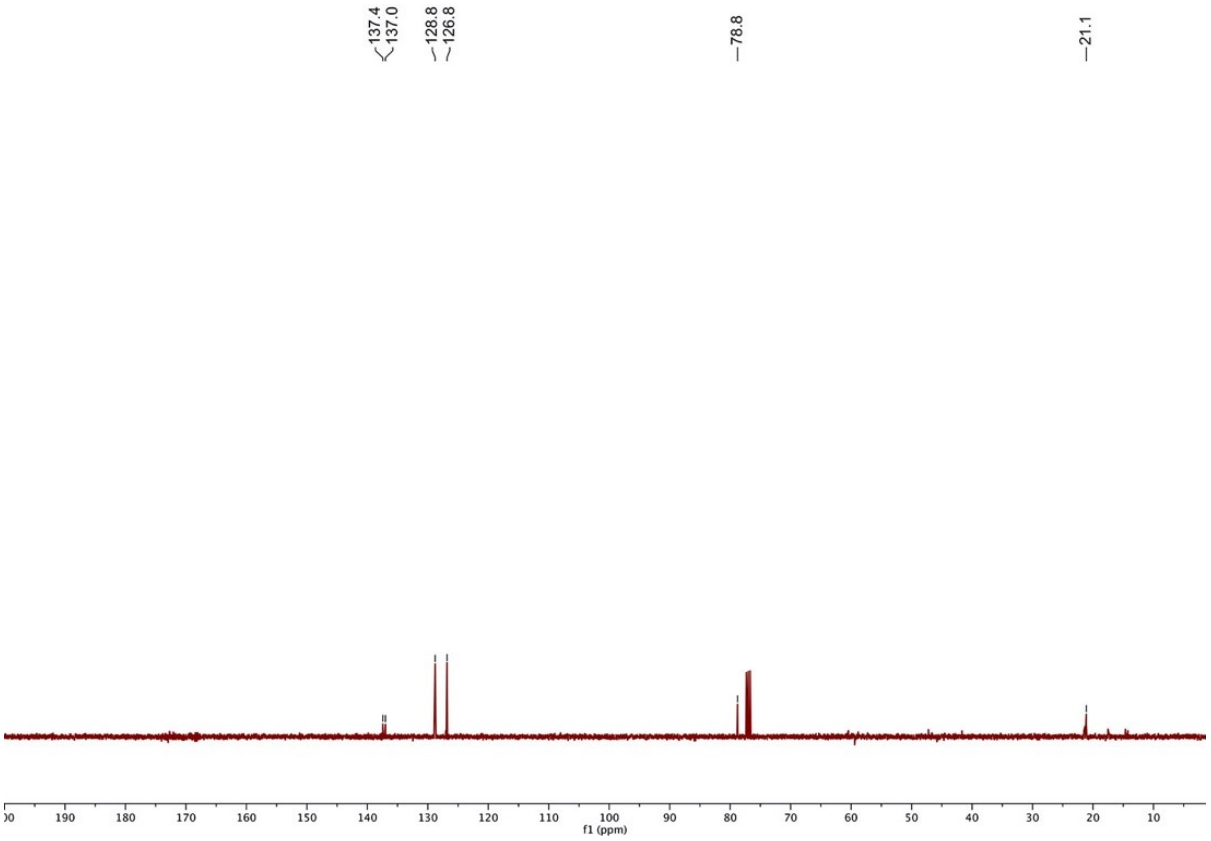


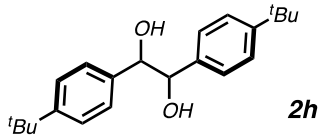
2g

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



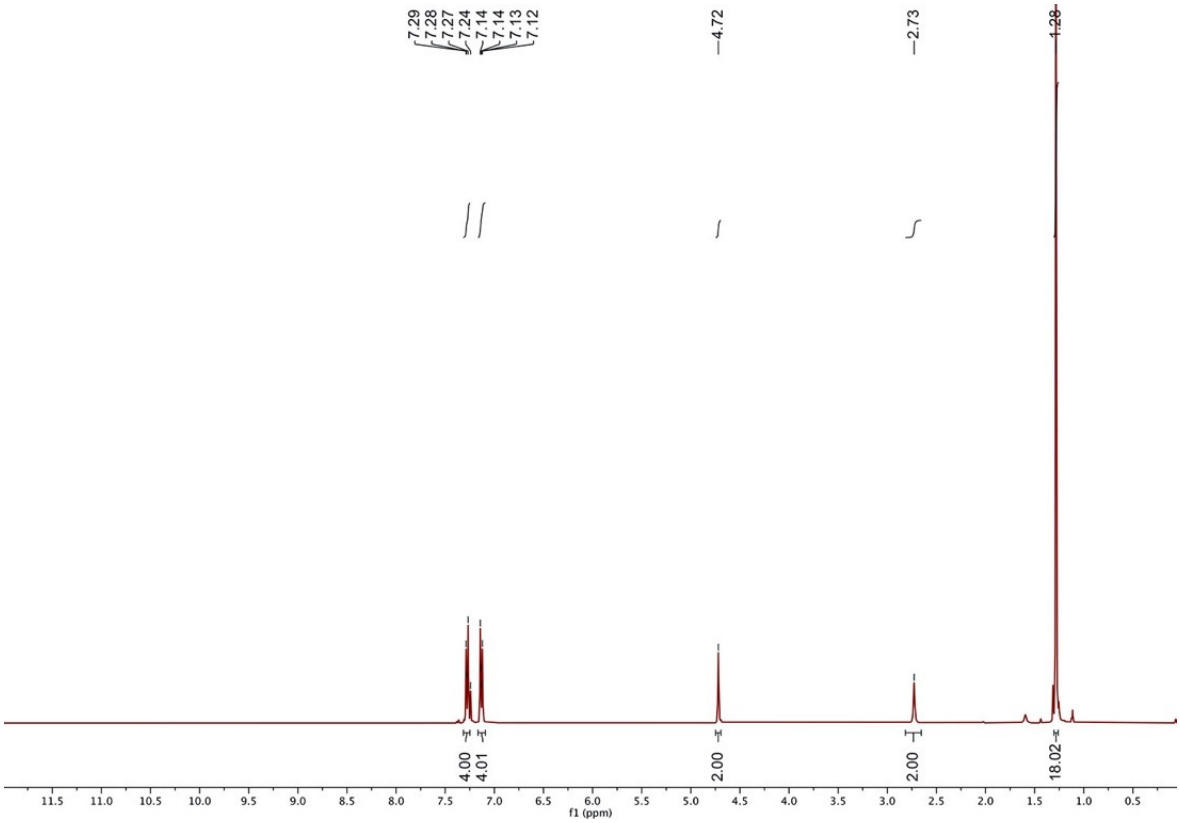
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



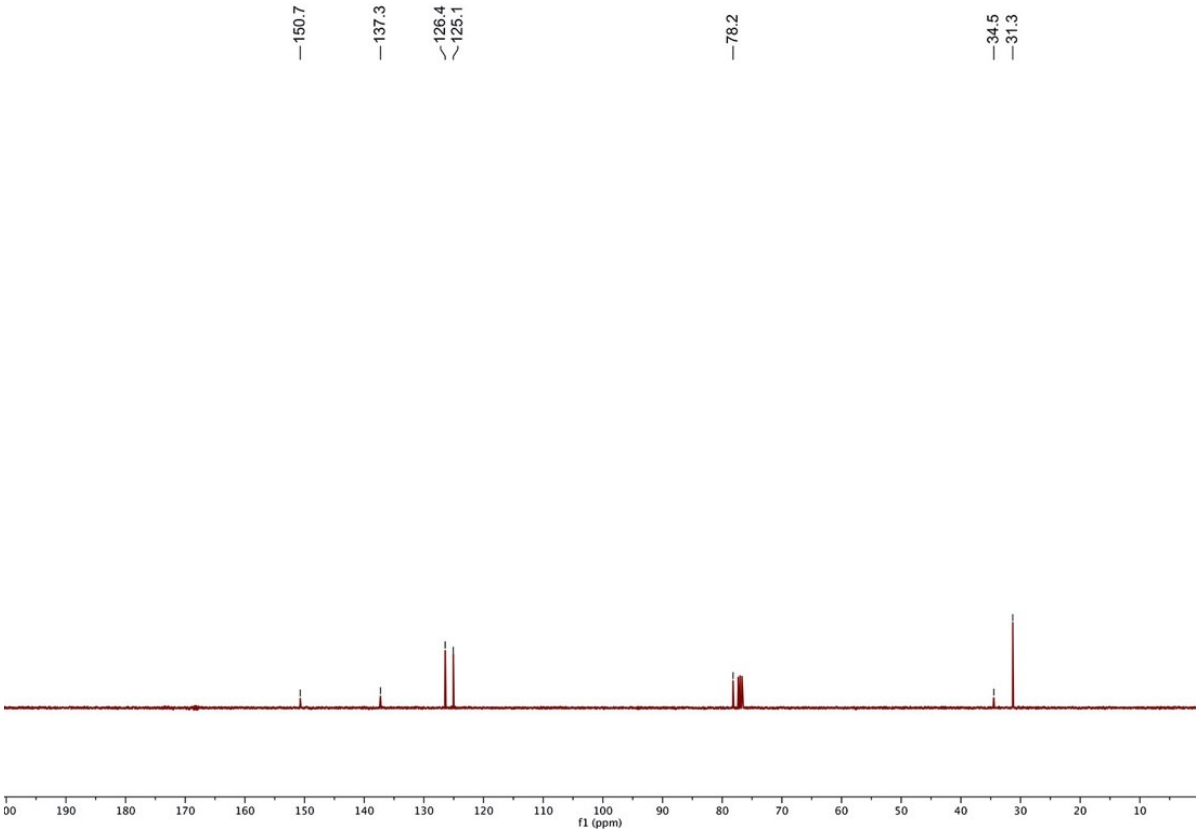


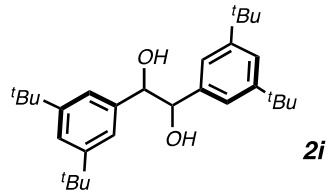
2h

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



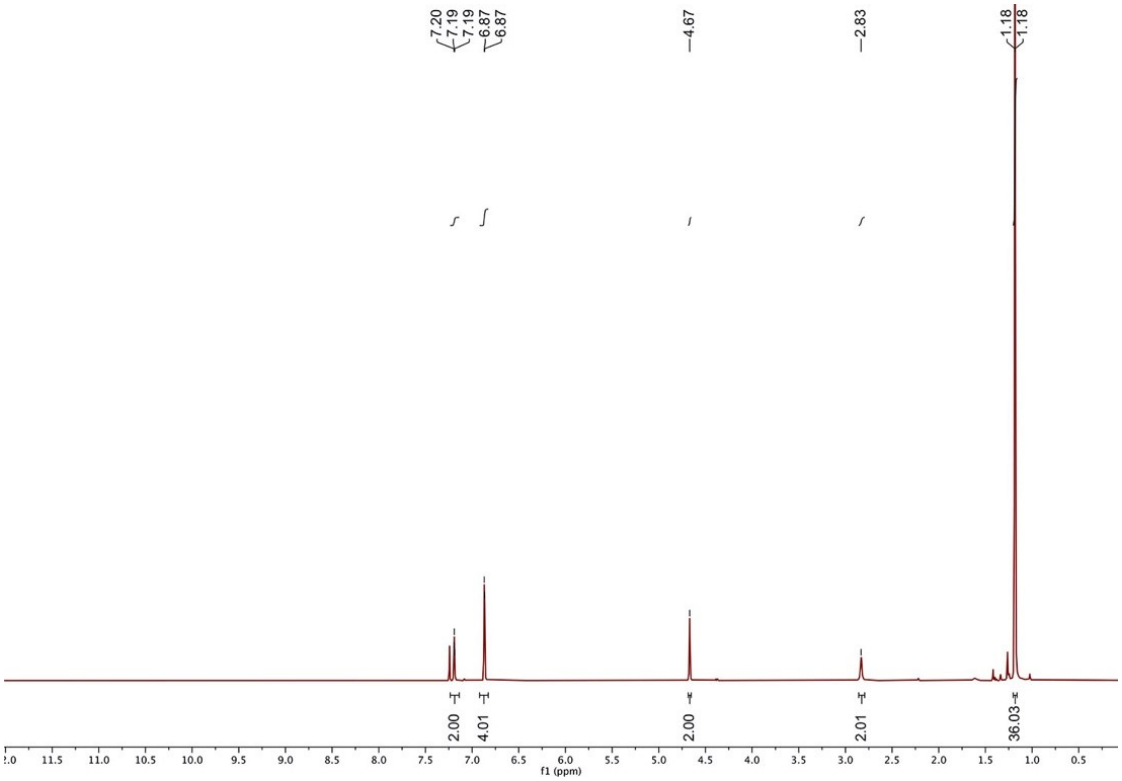
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



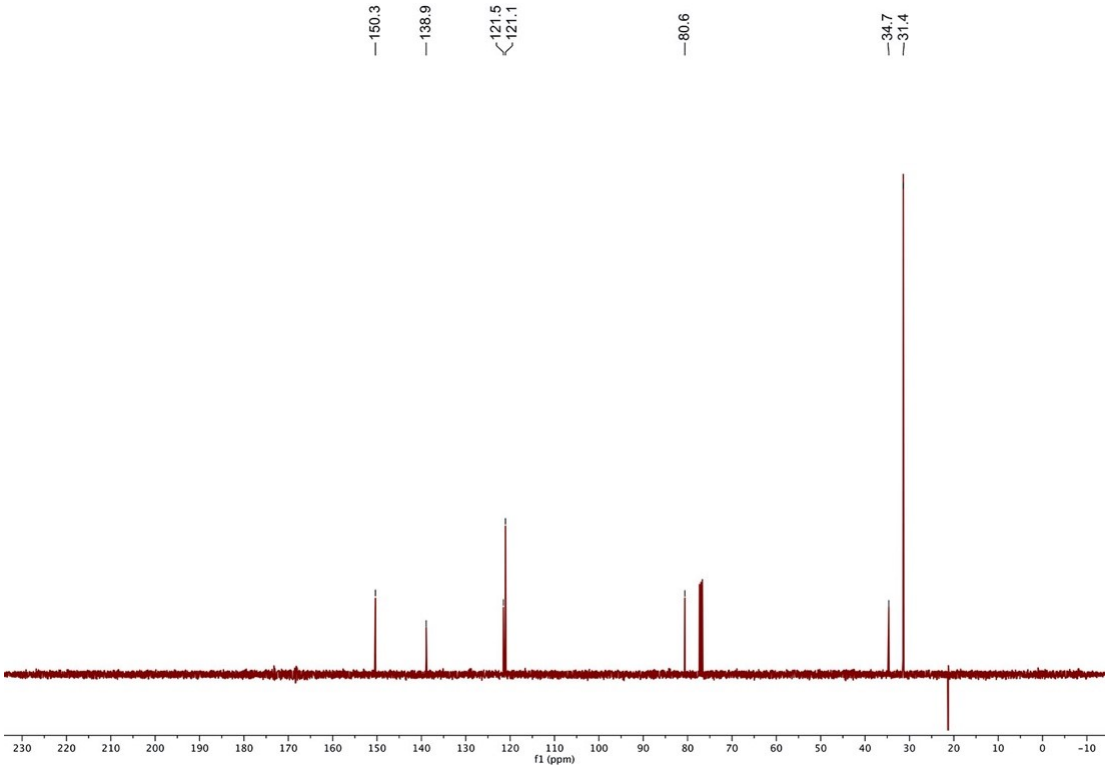


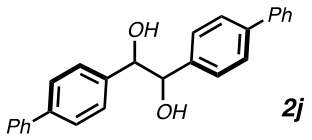
2i

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



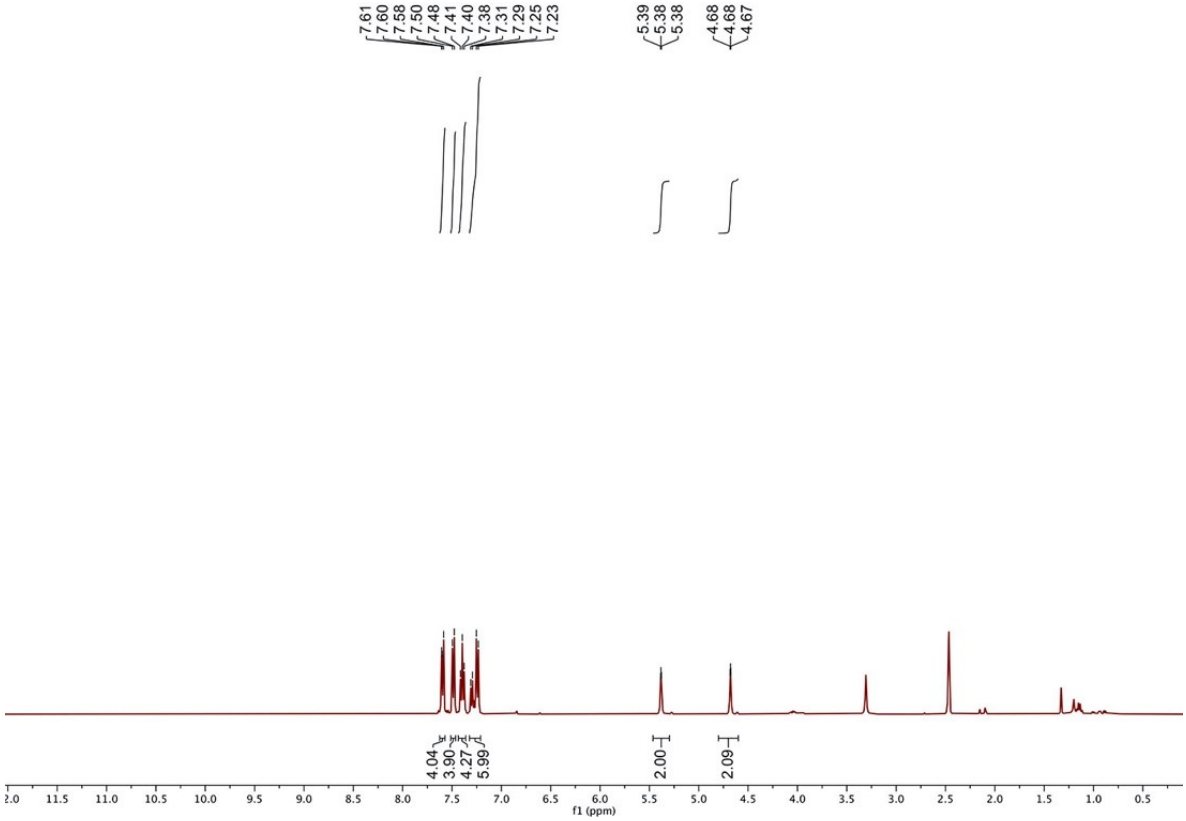
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



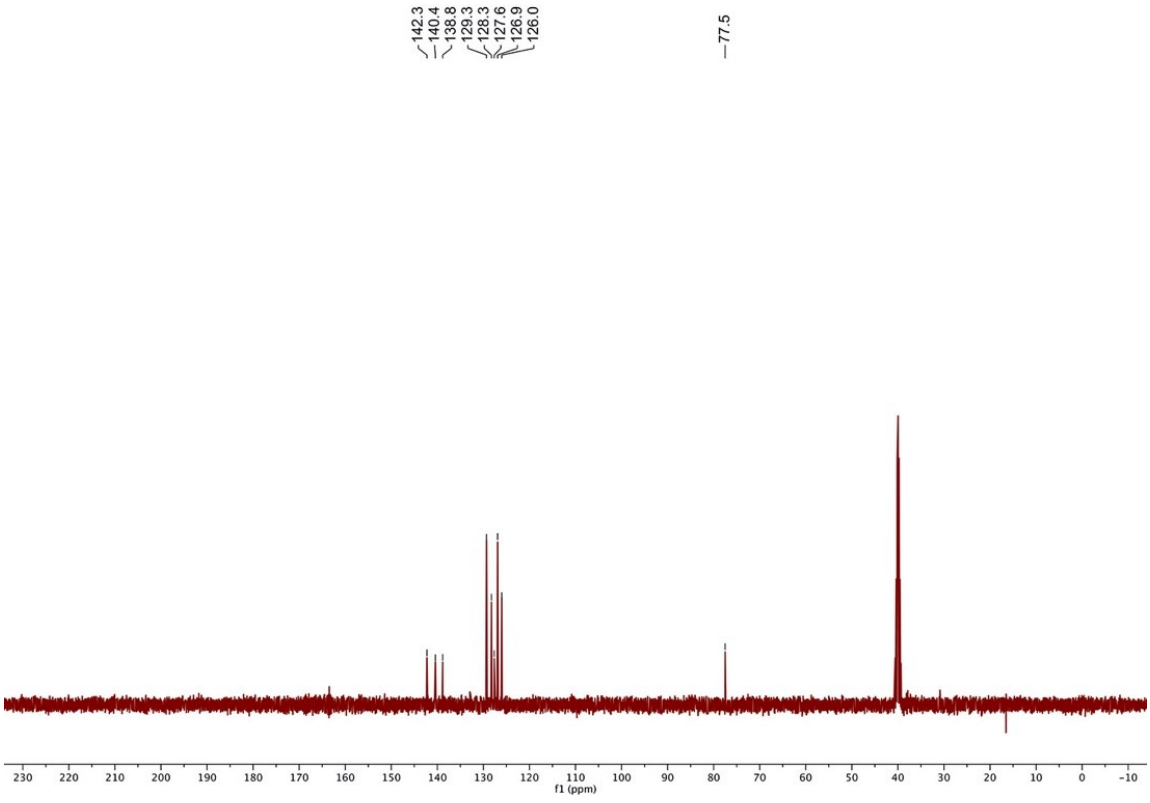


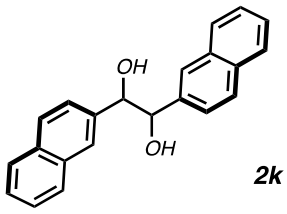
2j

^{1}H NMR (400 MHz, DMSO-d_6)



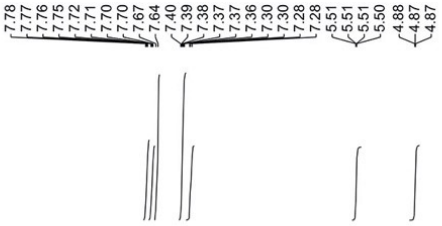
^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)

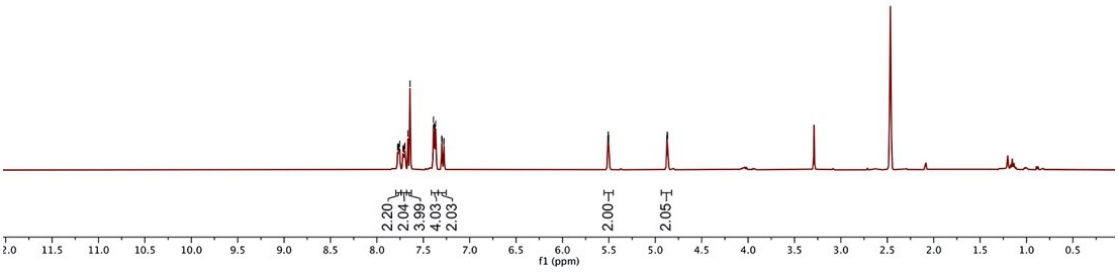




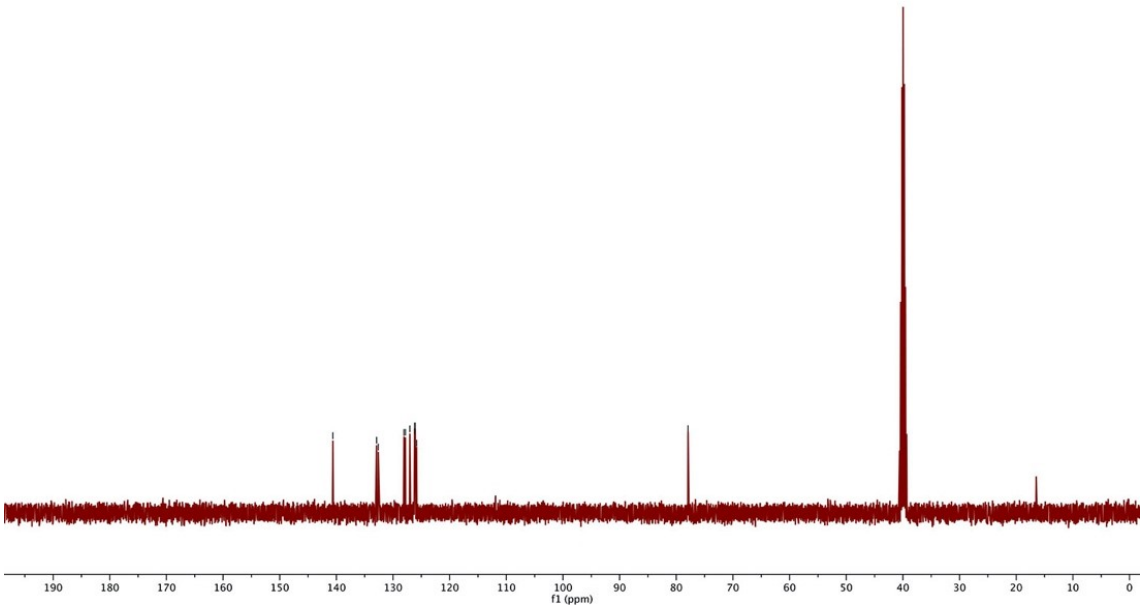
2k

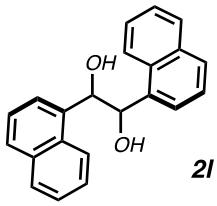
^{1}H NMR (400 MHz, DMSO-d_6)





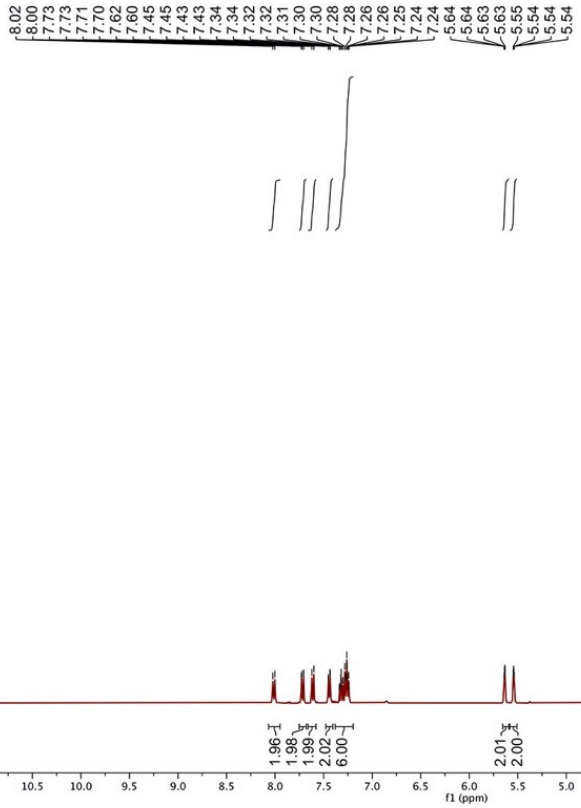
^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)



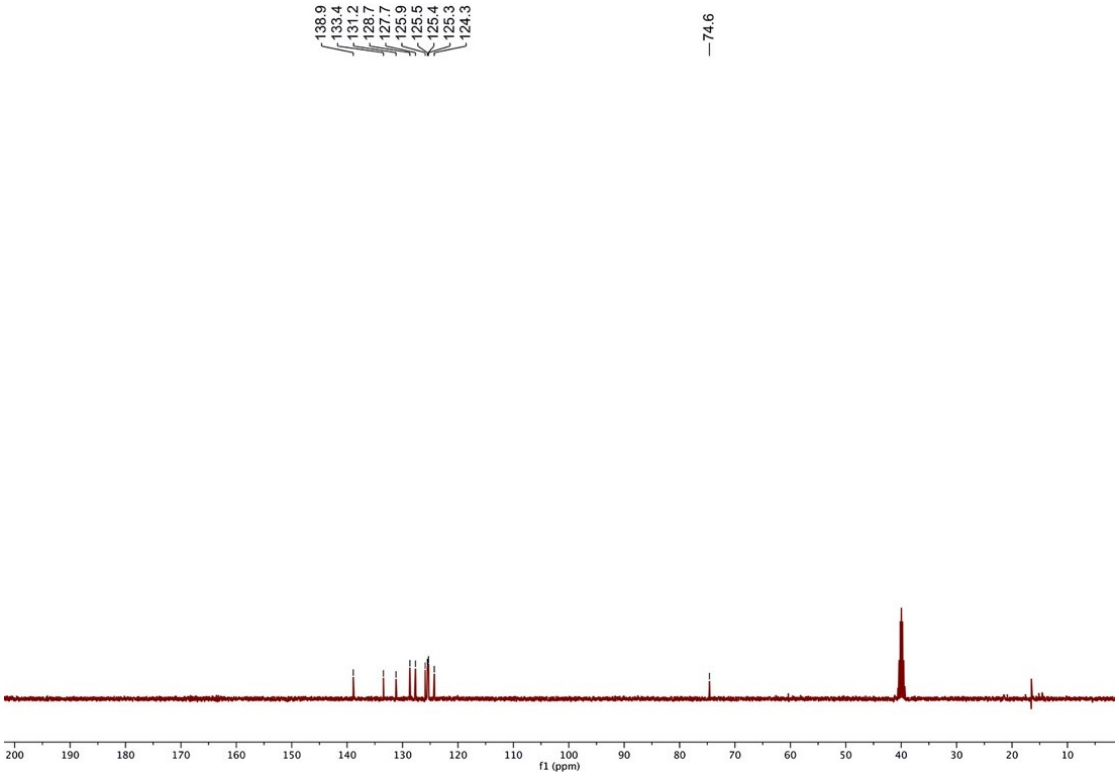


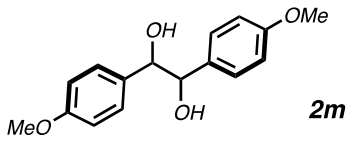
2l

^{1}H NMR (400 MHz, DMSO-d_6)



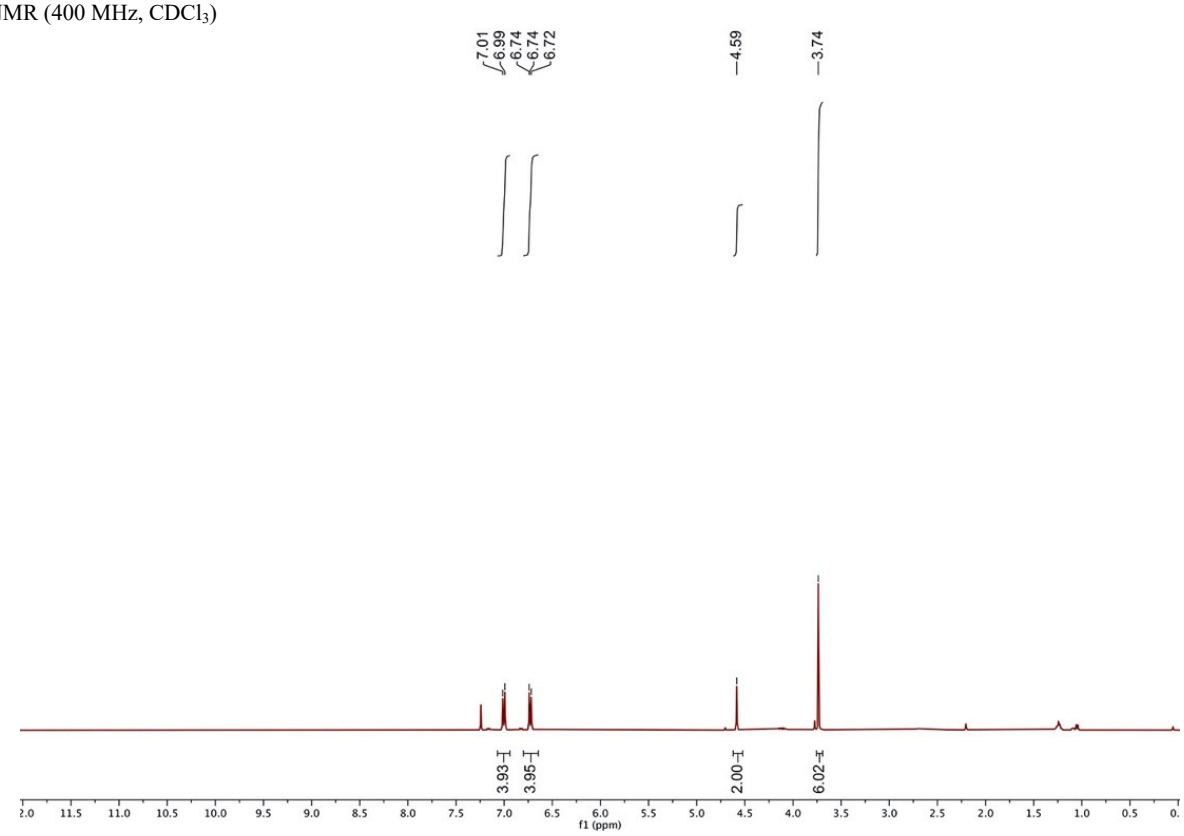
^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)



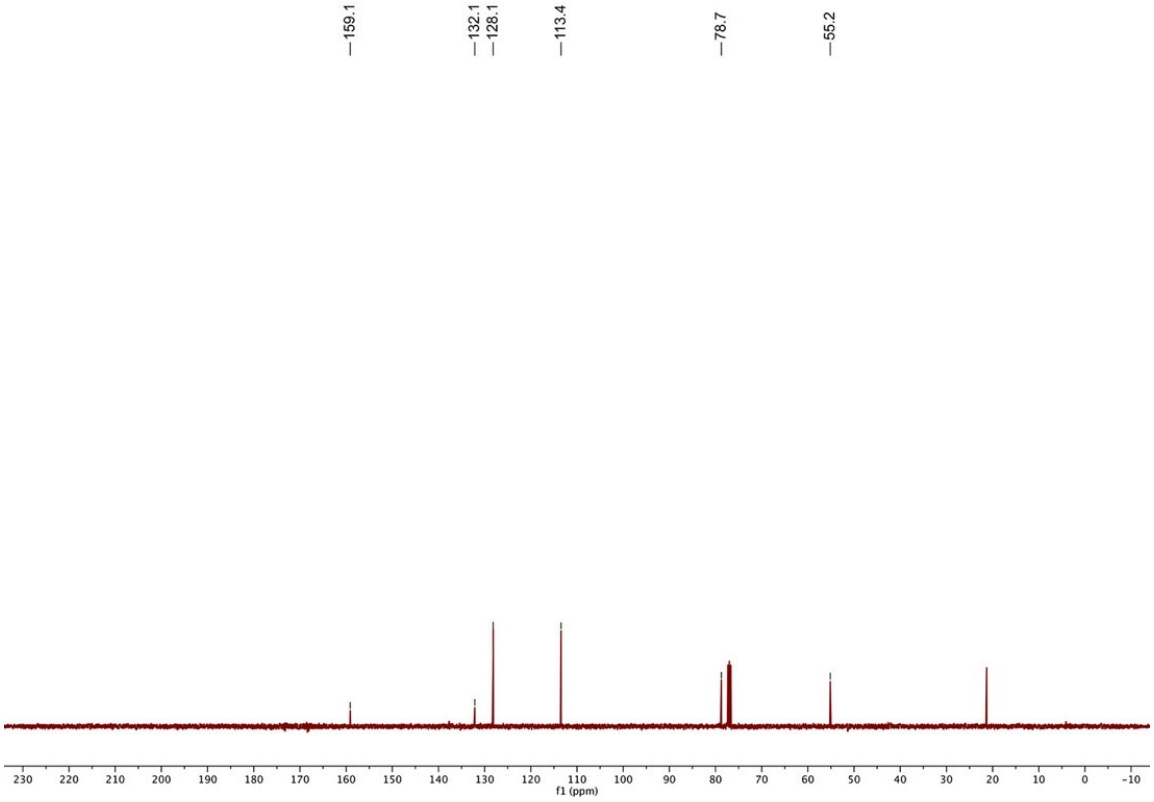


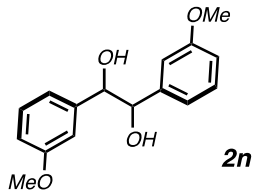
2m

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



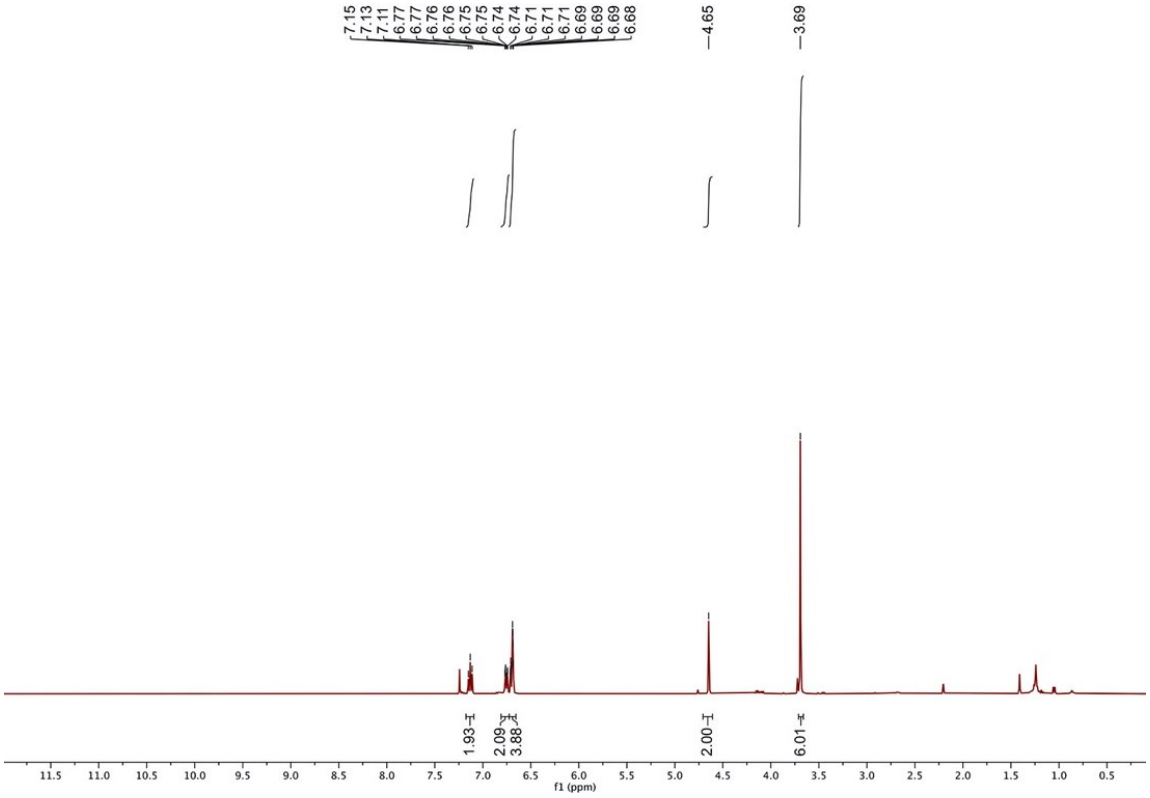
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



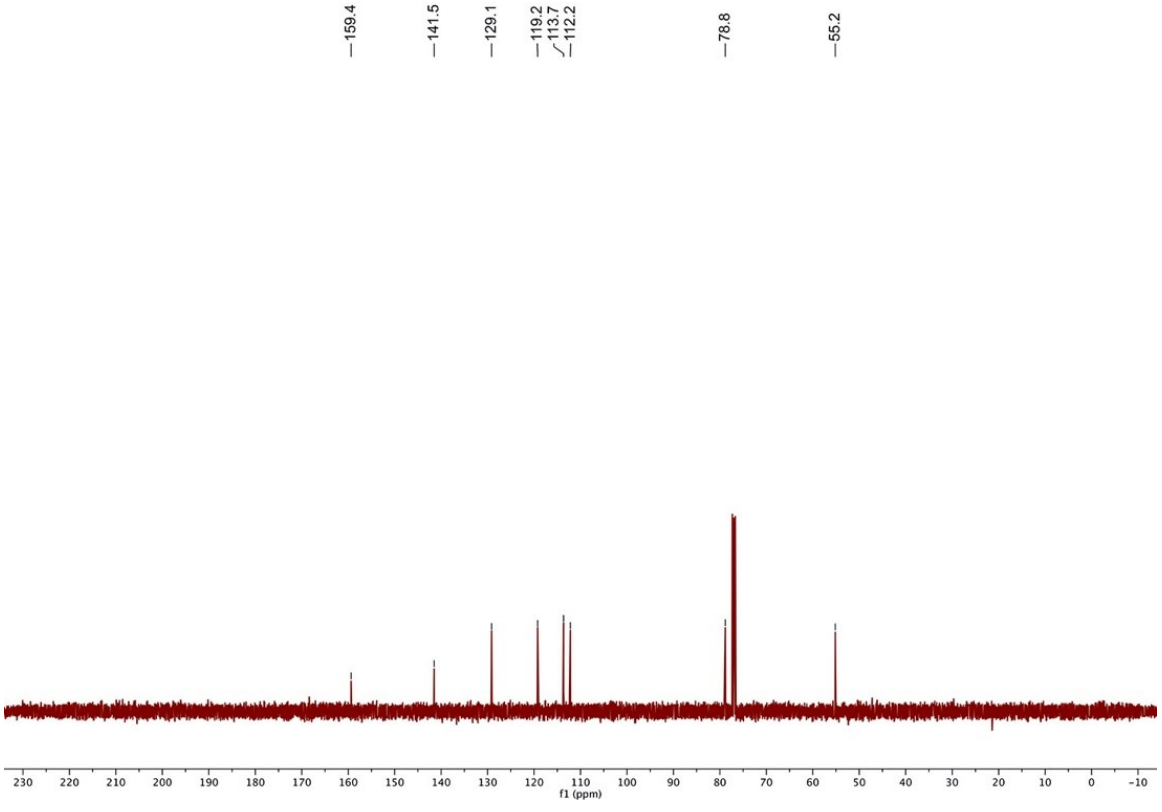


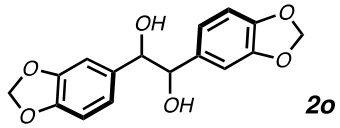
2n

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



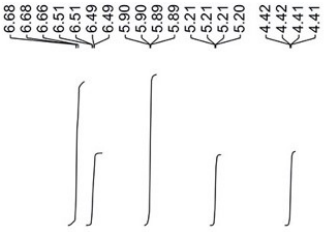
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

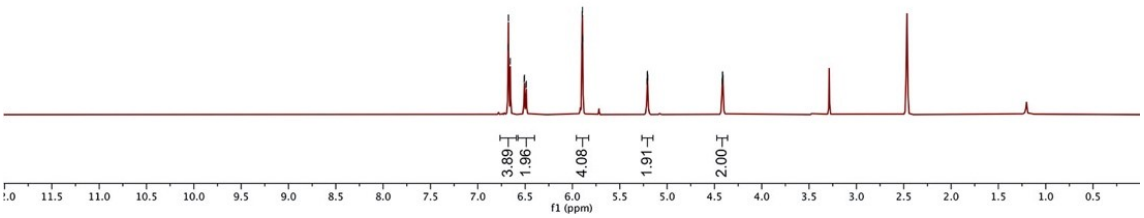




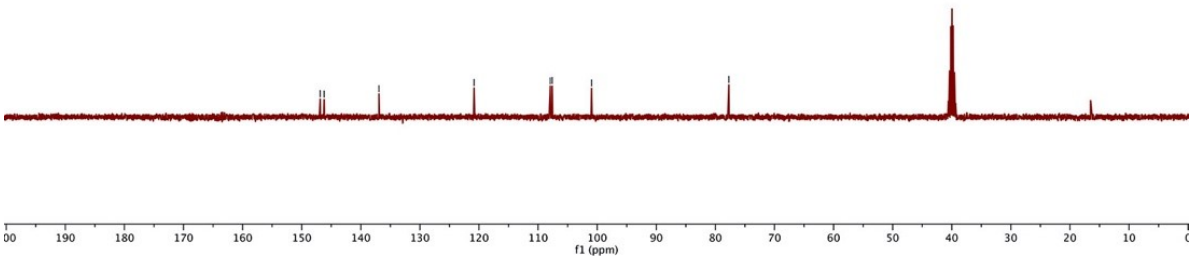
2o

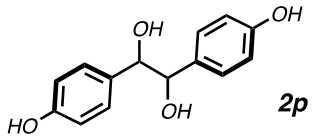
^{1}H NMR (400 MHz, DMSO-d_6)





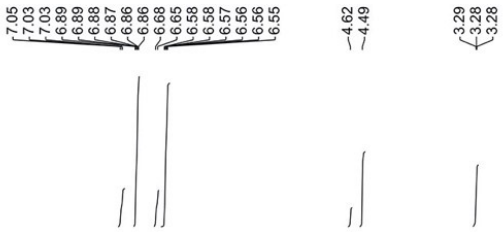
^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)

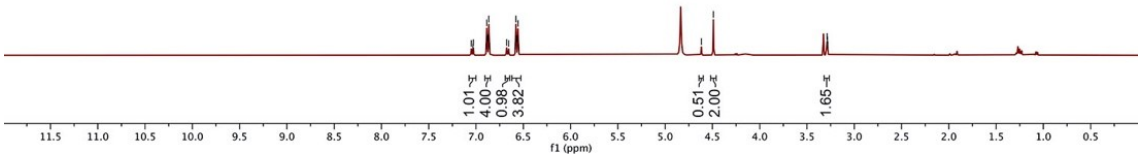




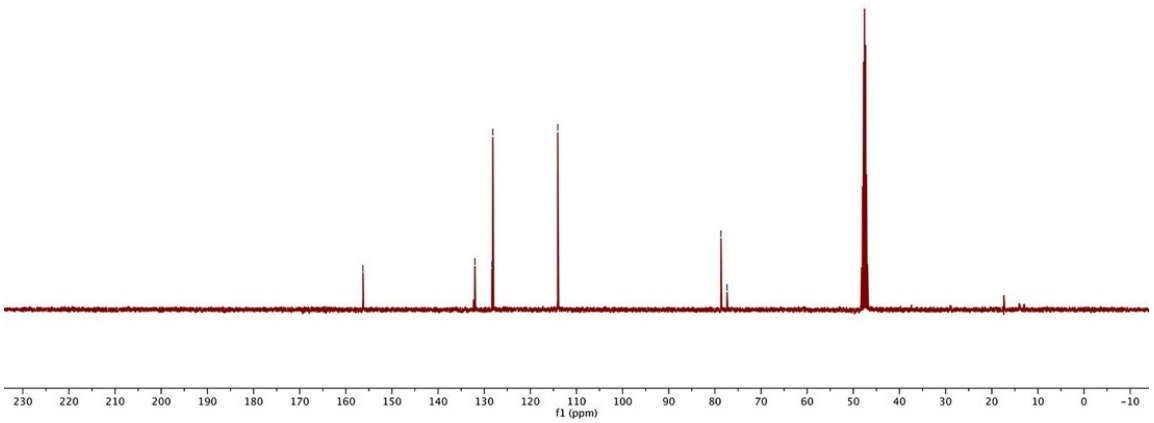
2p

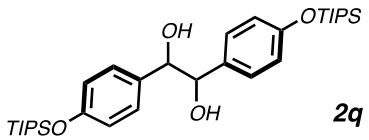
^{1}H NMR (400 MHz, CD_3OD)





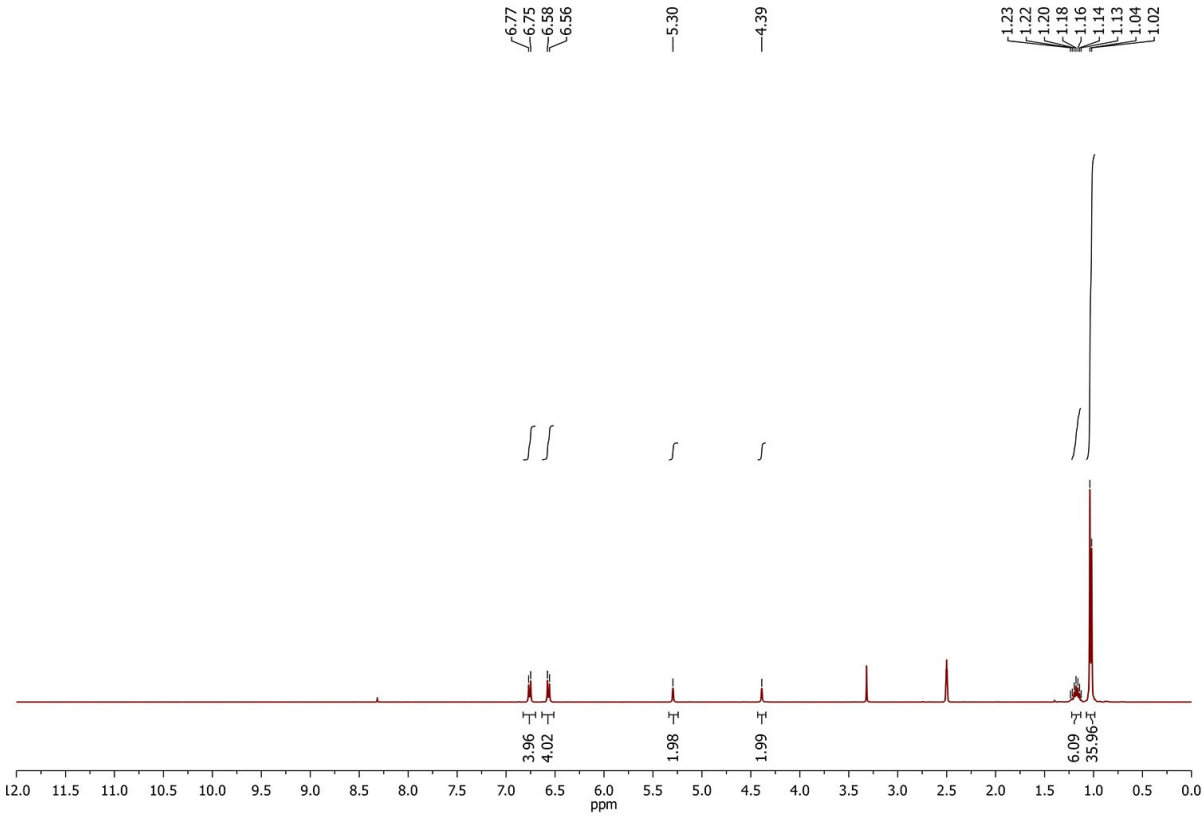
^{13}C{^{1}H} NMR (101 MHz, CD_3OD)



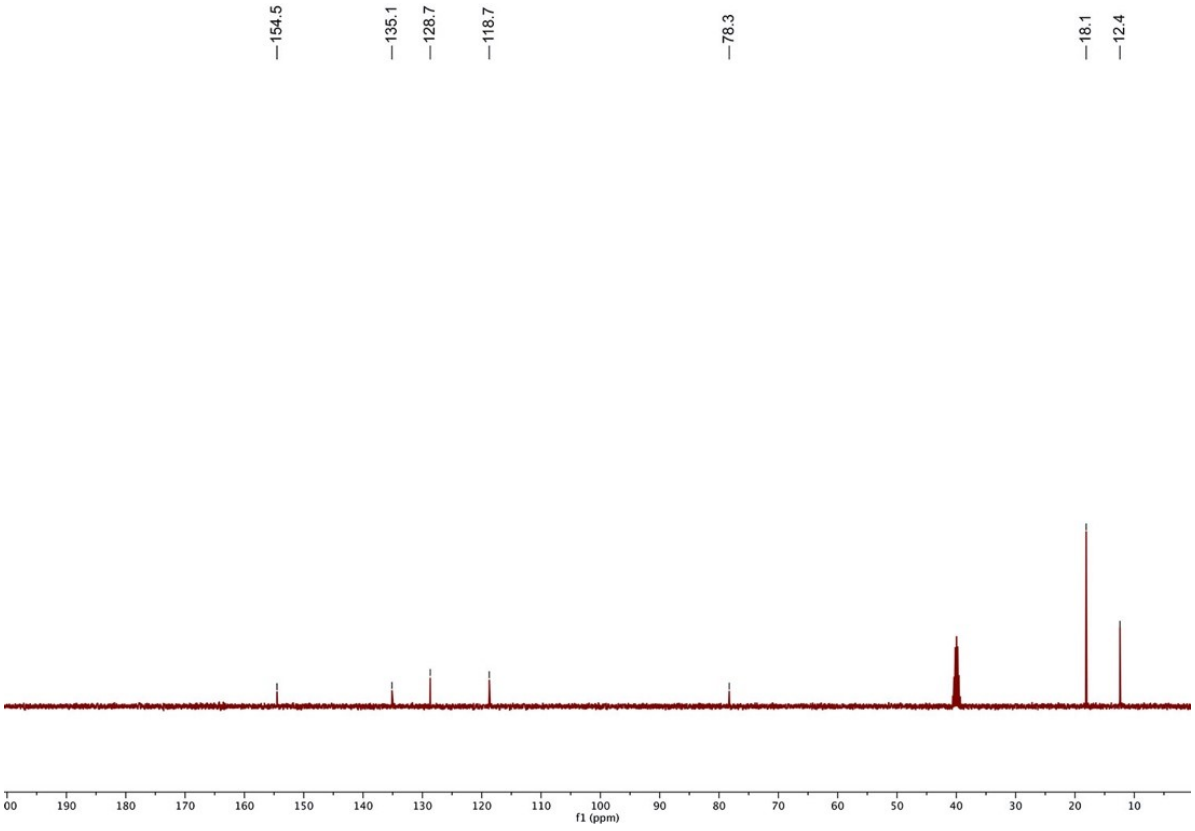


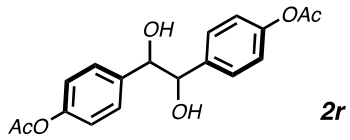
2q

^{1}H NMR (400 MHz, DMSO-d_6)



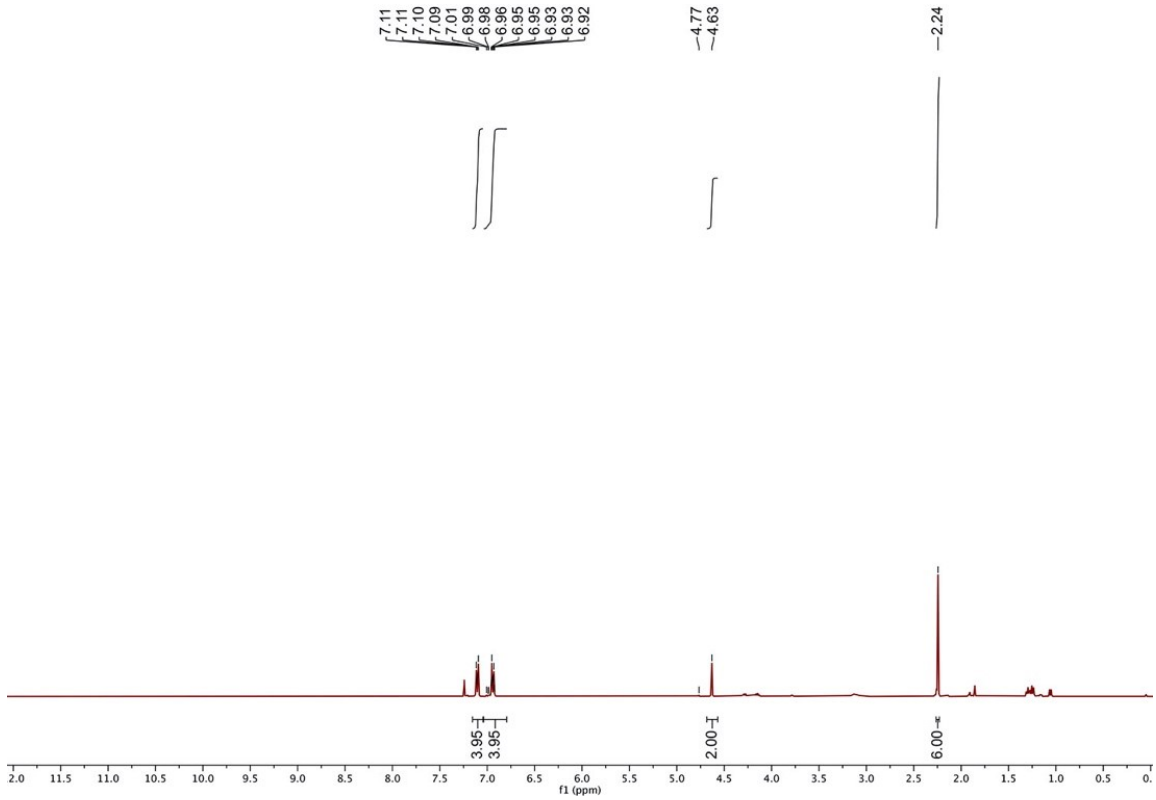
^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)



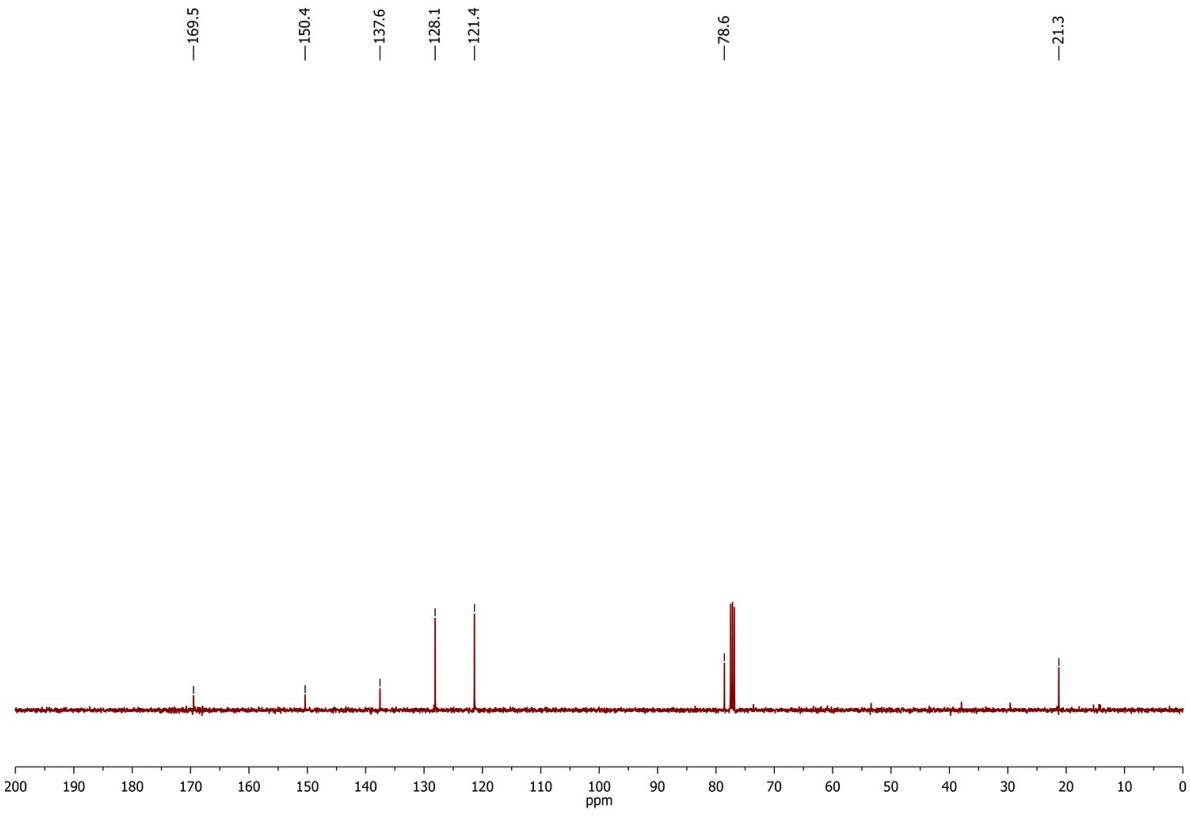


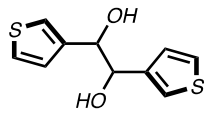
2r

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



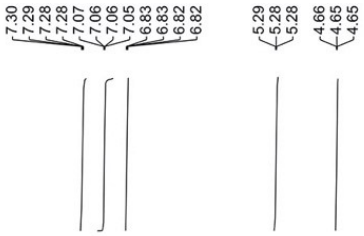
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

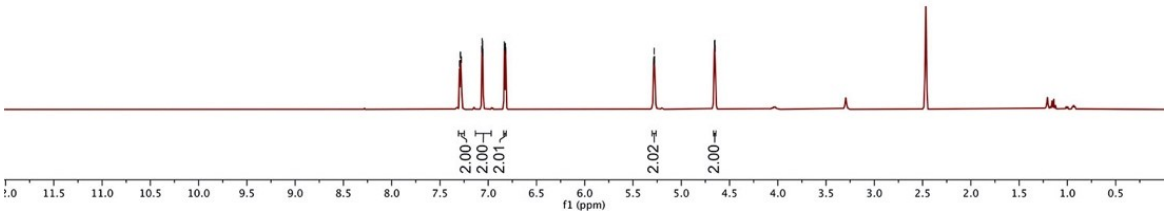




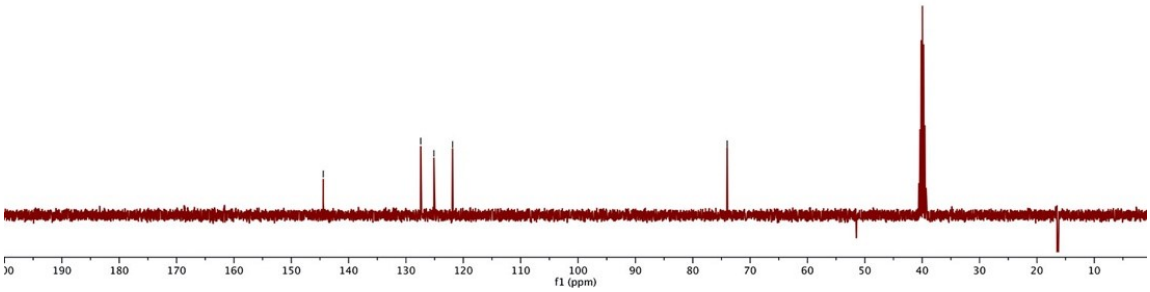
2s

^{1}H NMR (400 MHz, DMSO-d_6)

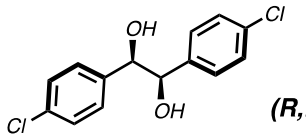




^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)

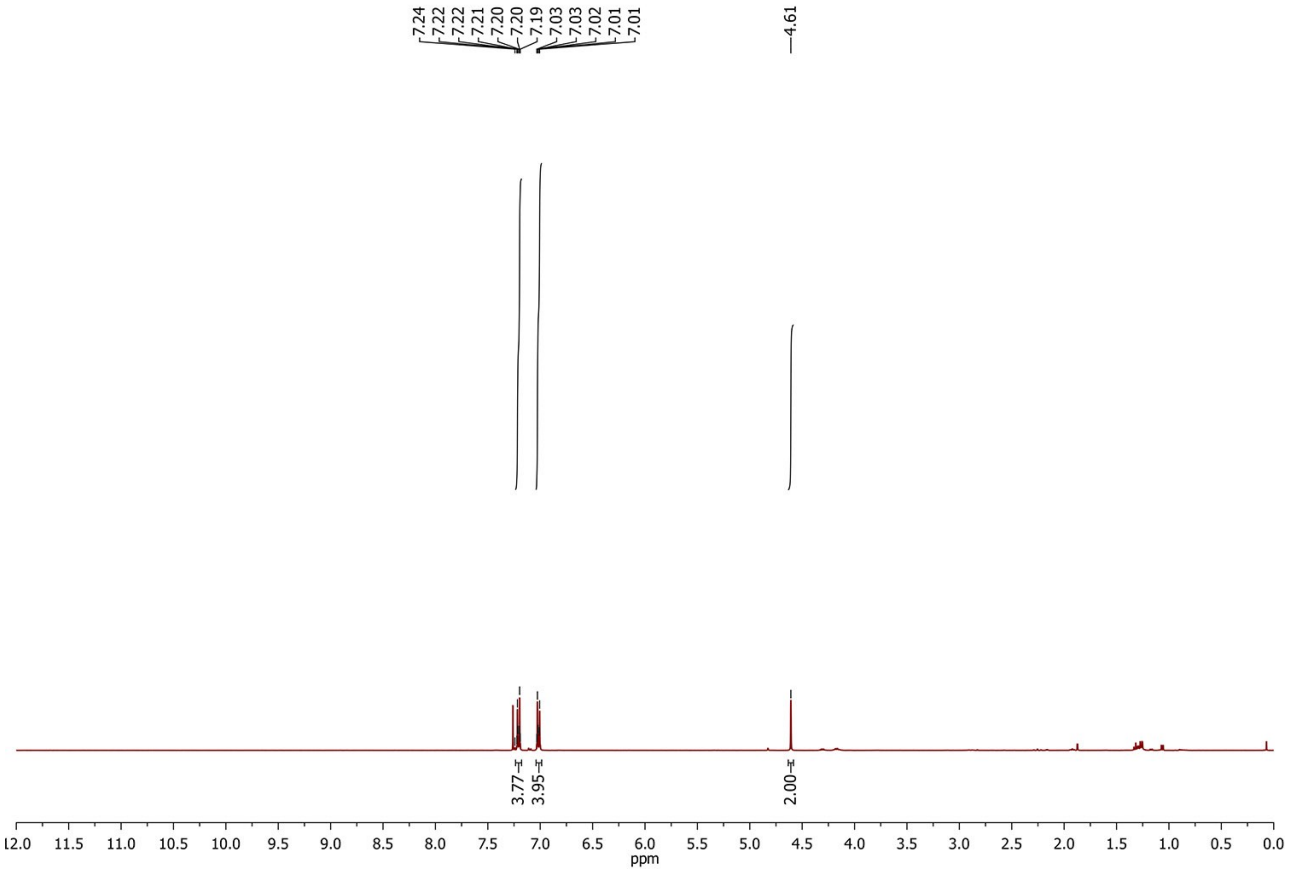


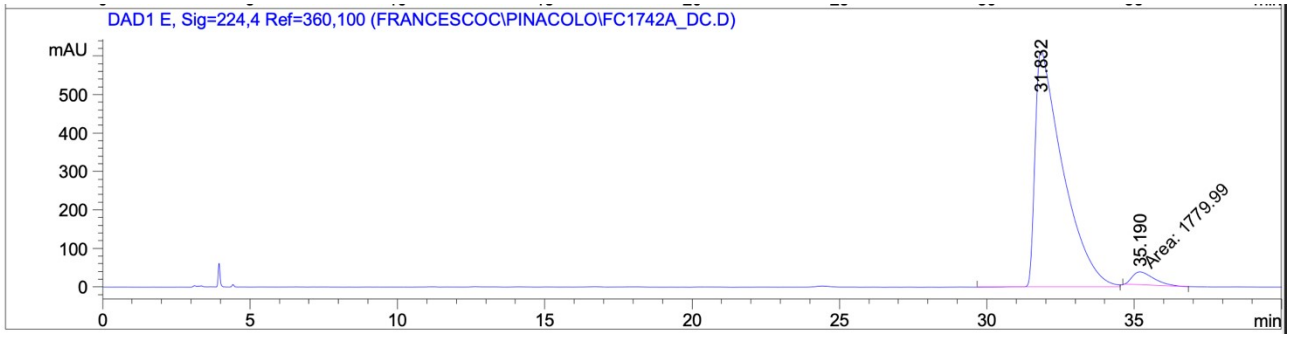
Copies of 1H NMR and HPLC traces for enantioenriched substrates



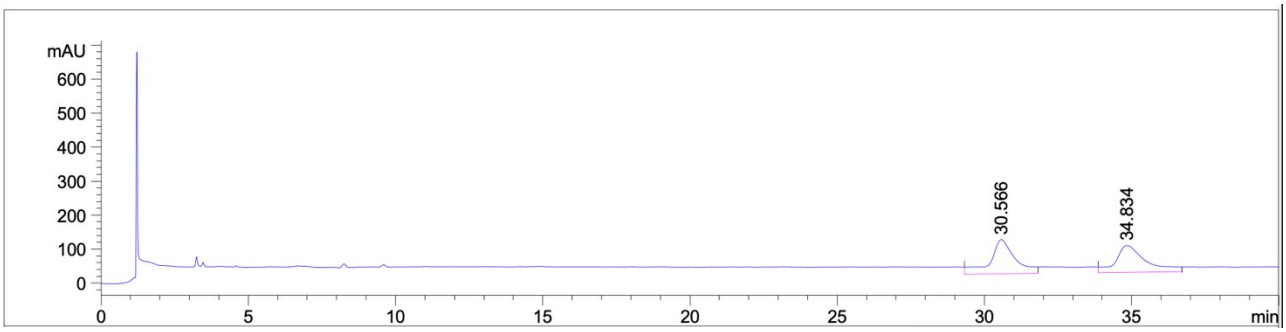
(R,R)-2a

67% Y, dr > 20:1, er 96:4

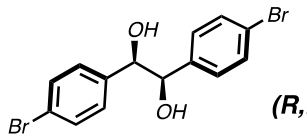




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.832	VV	0.8993	4.02516e4	613.60266	95.7651
2	35.190	MM	0.8792	1779.99146	33.74203	4.2349

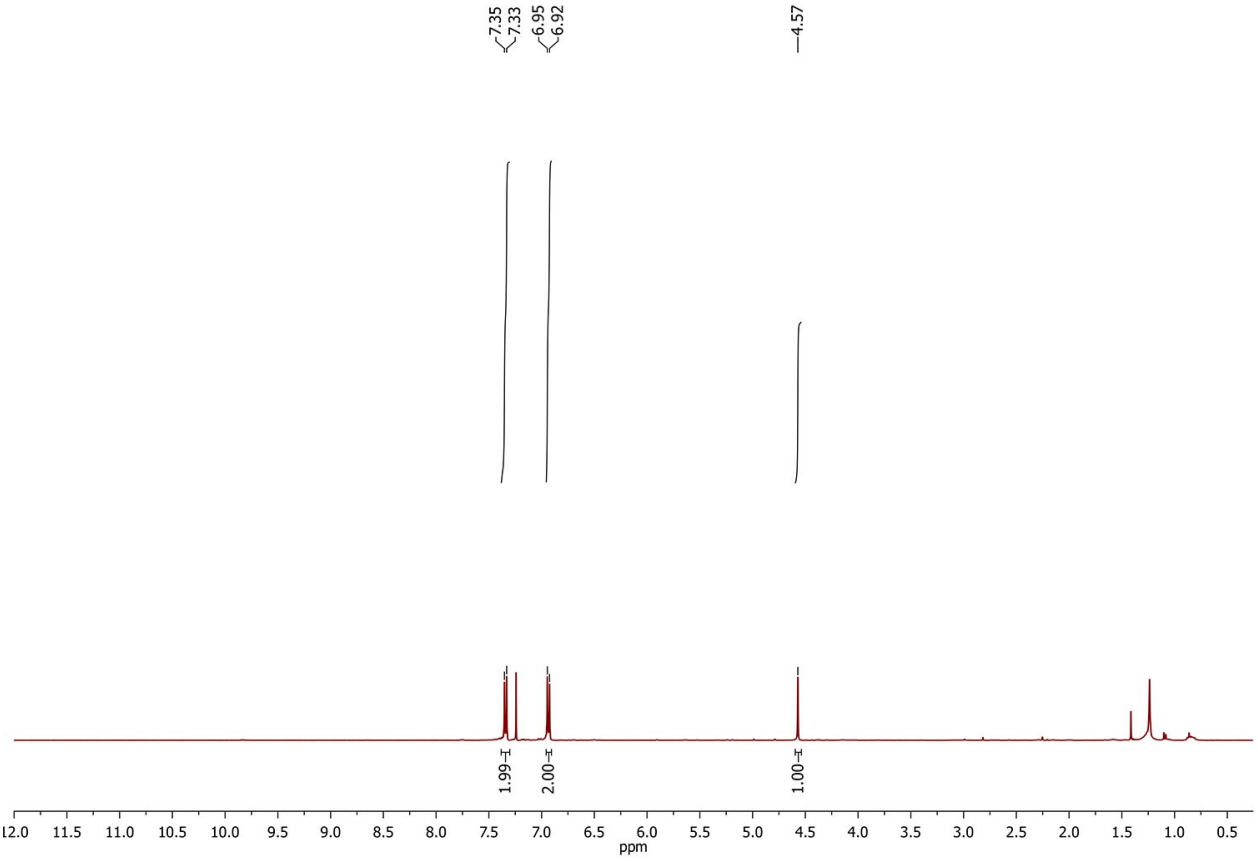


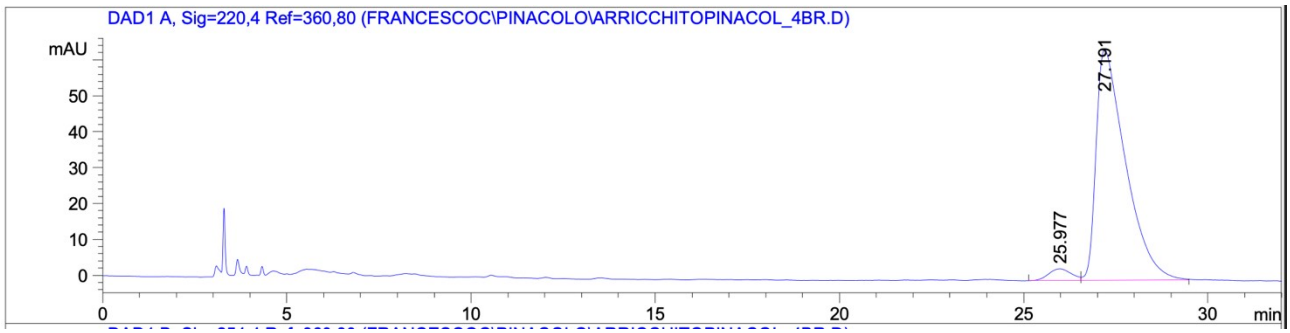
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.566	VV	0.8322	6113.87891	101.28490	51.2478
2	34.834	VV	1.0335	5816.15820	79.87313	48.7522



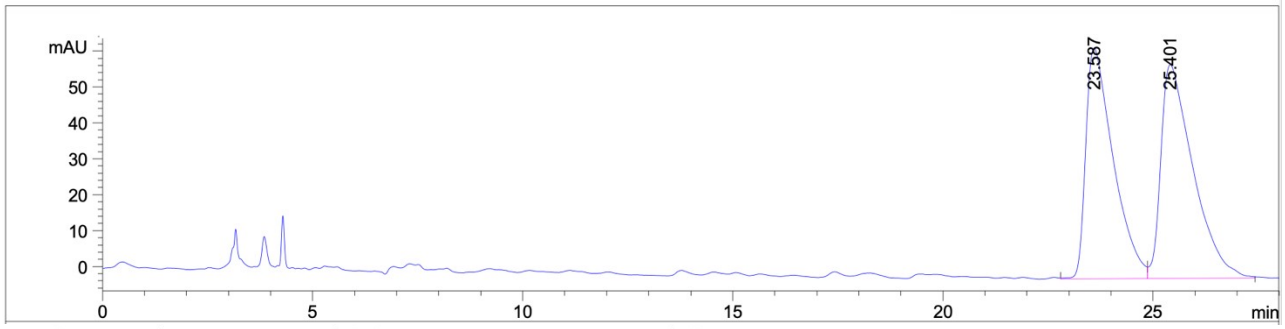
(R,R)-2b

70% Y, dr > 20:1, er 96:4

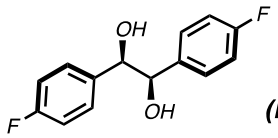




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.977	BV	0.5789	139.34477	3.25856	3.7586
2	27.191	VB	0.8117	3567.96436	64.26516	96.2414

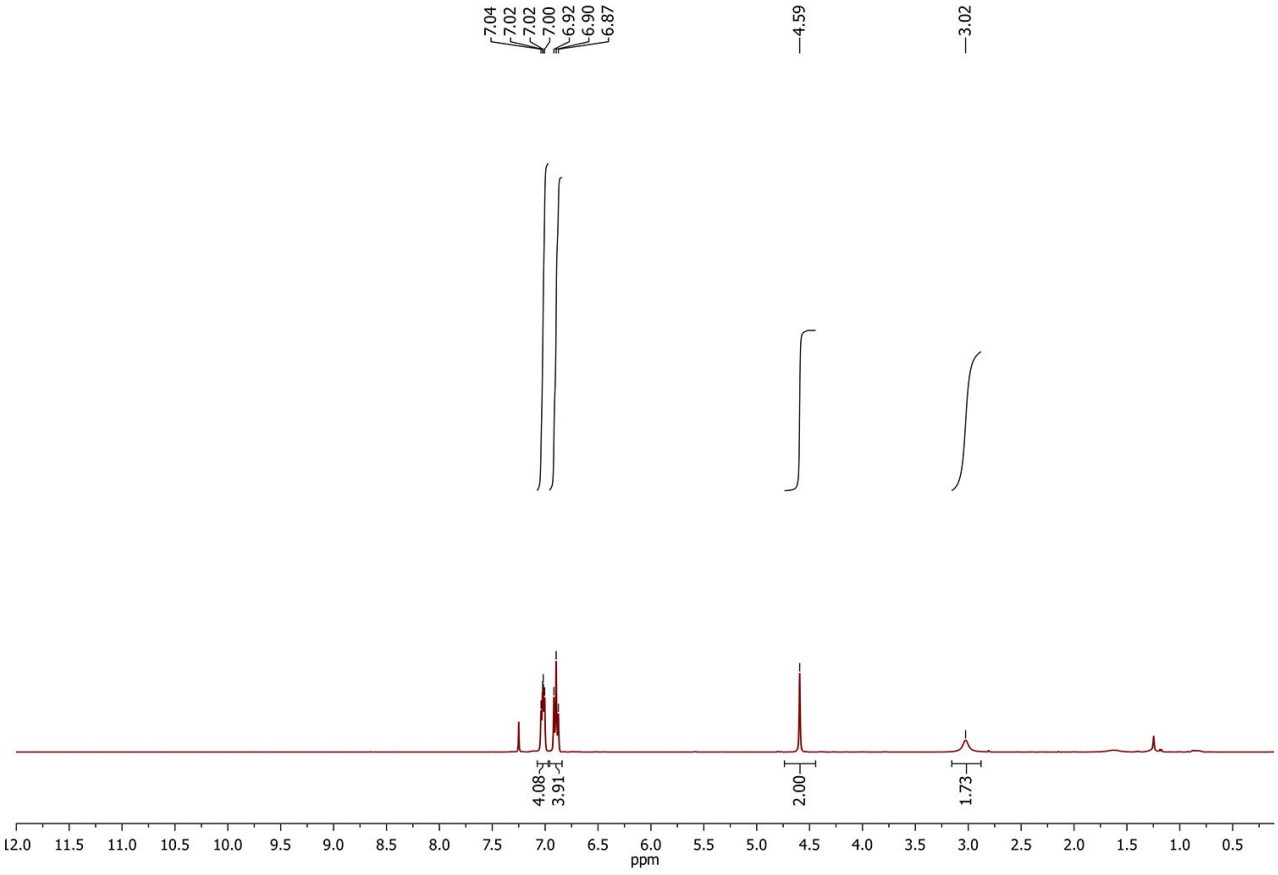


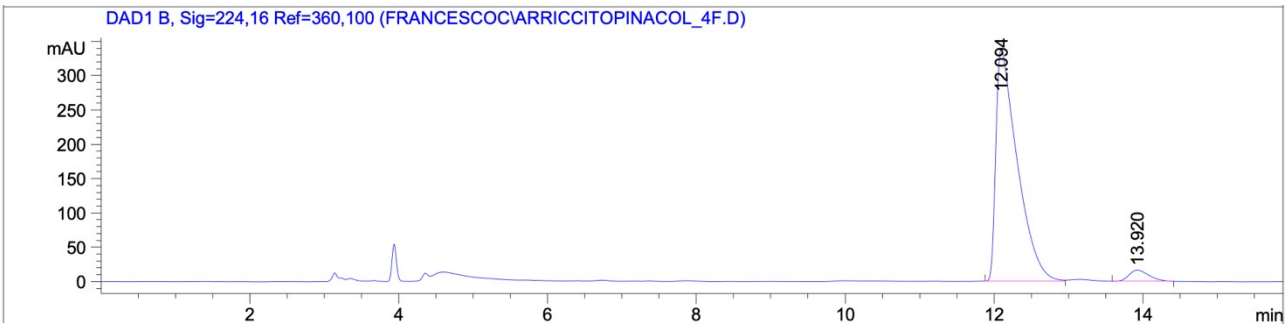
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.587	VV	0.6715	2929.68872	64.30592	48.0114
2	25.401	VB	0.7575	3172.37427	59.55227	51.9886



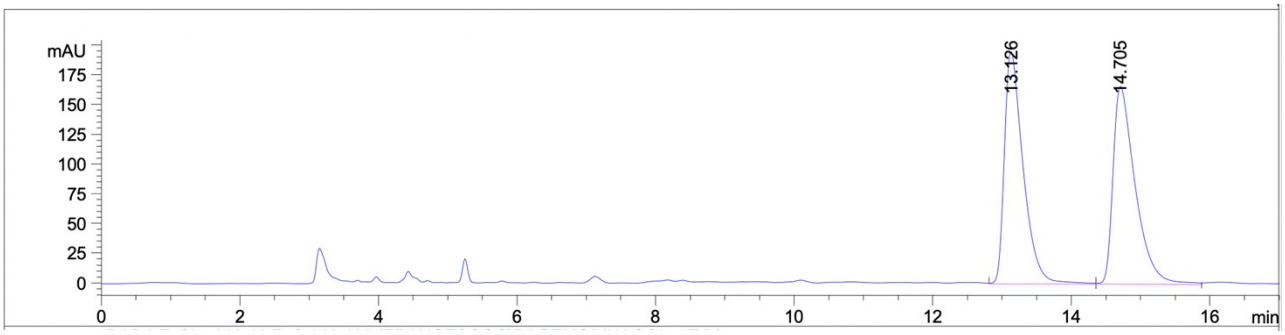
(R,R)-2c

85% Y, dr > 20:1, er 95.5:4.5

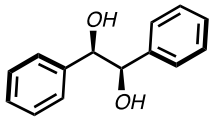




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.094	BB	0.2898	6773.72461	338.08020	95.6043
2	13.920	VB	0.2912	311.44299	16.42501	4.3957

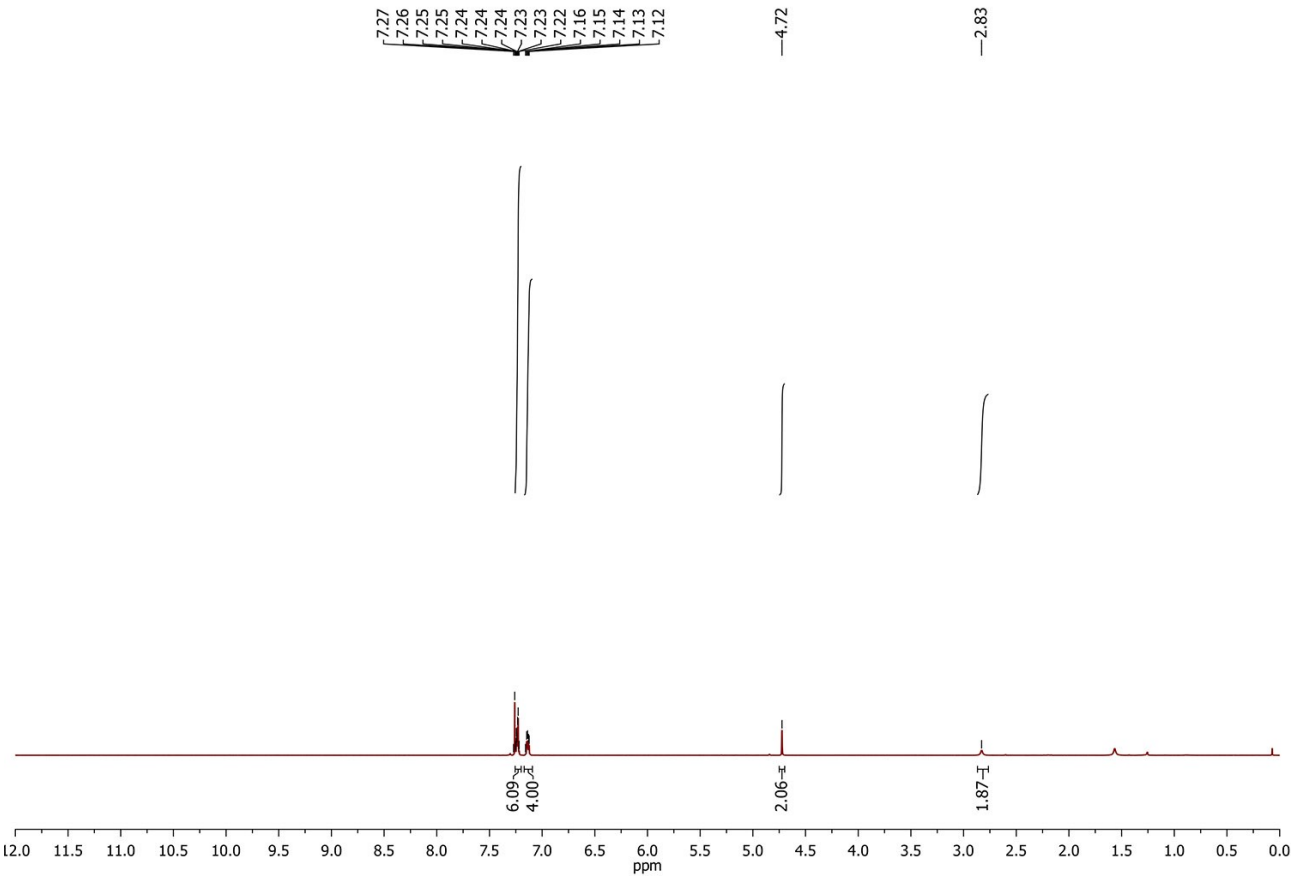


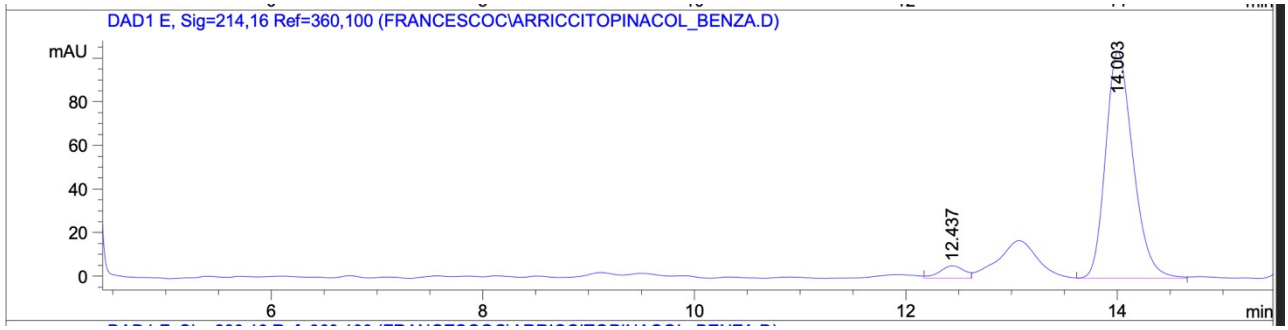
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.126	VV	0.2841	3725.70557	195.72293	49.9872
2	14.705	VV	0.3331	3727.61523	166.55109	50.0128



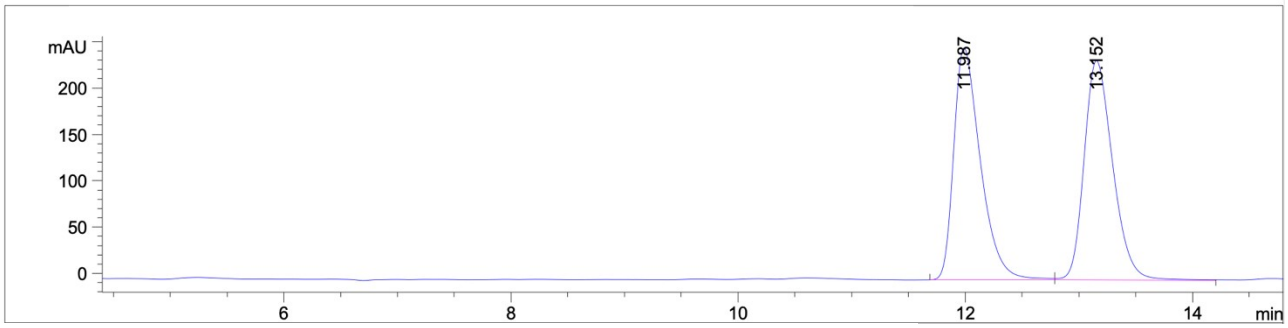
(R,R)-2f

42% Y, dr > 20:1, er 95.5:4.5

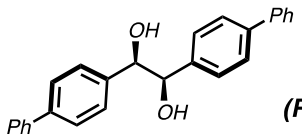




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.435	VV	0.2494	111.00645	6.69483	4.4730
2	14.004	VV	0.2794	2370.71362	130.81329	95.5270

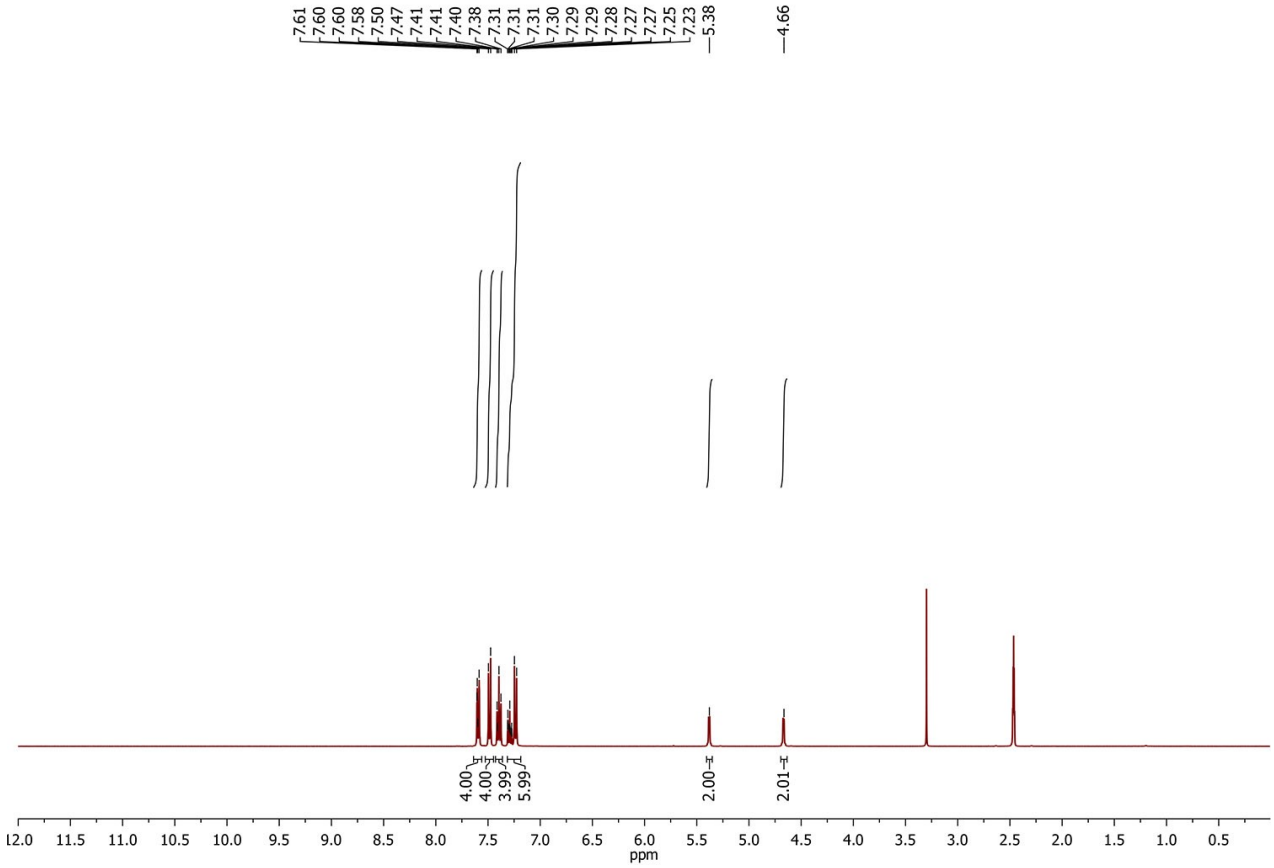


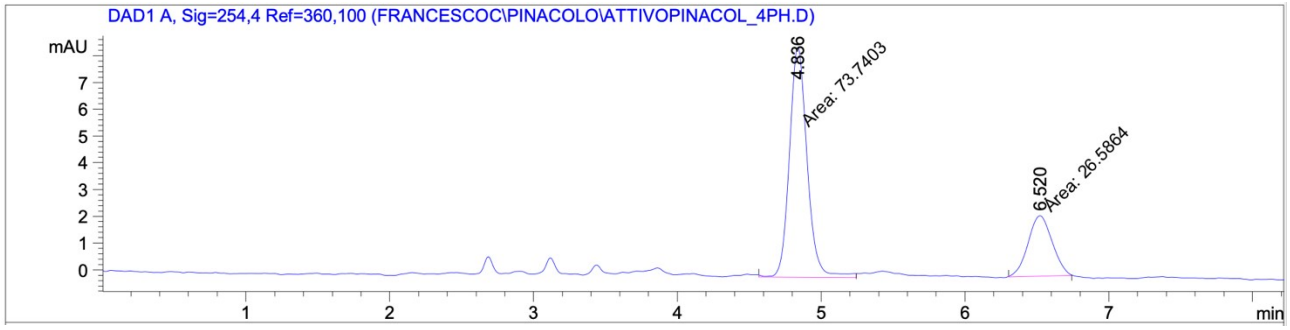
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.987	BV	0.2516	4110.92969	250.28018	49.6809
2	13.152	VB	0.2731	4163.74023	236.86893	50.3191



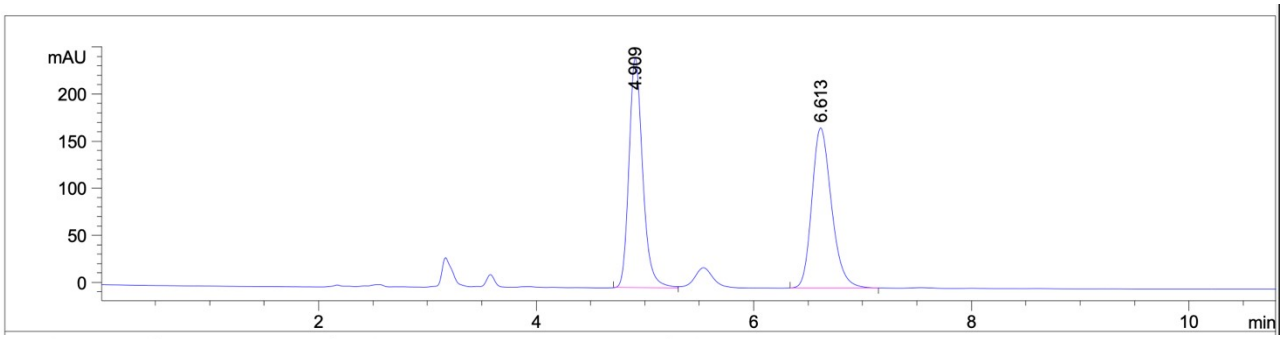
(R,R)-2j

30% Y, dr > 20:1, er 73.5:26.5

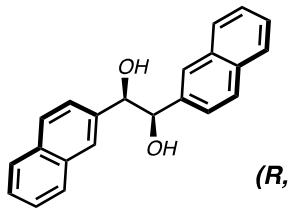




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.836	MM	0.1428	73.74026	8.60620	73.5002
2	6.520	MM	0.1951	26.58639	2.27089	26.4998

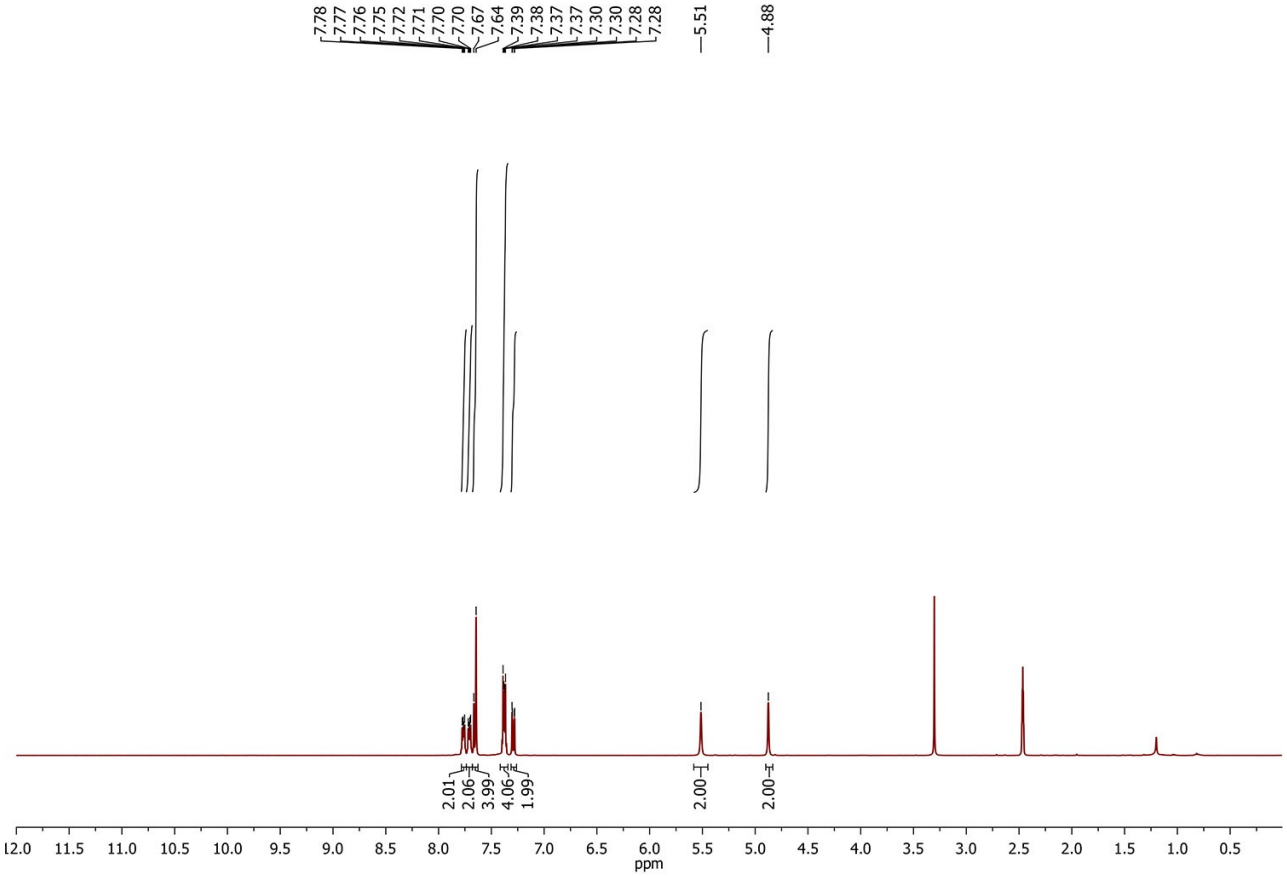


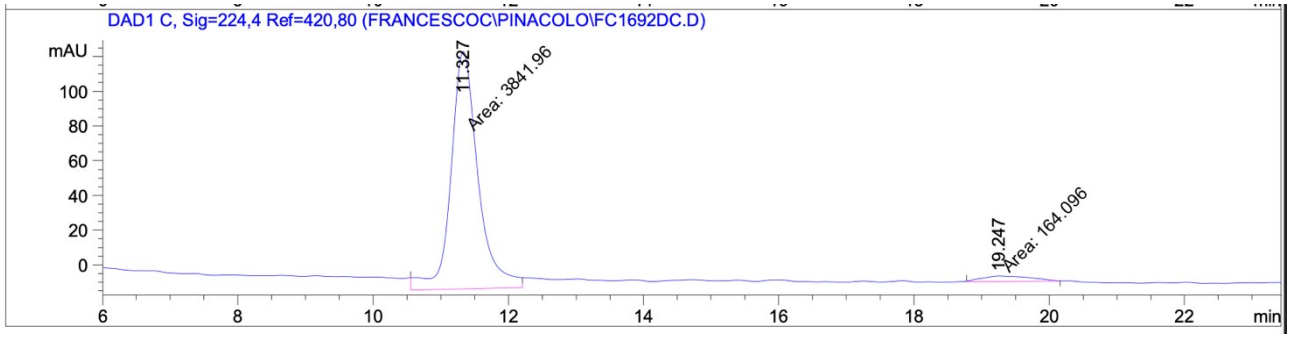
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.909	BV	0.1342	2141.13330	244.44960	50.0185
2	6.613	BB	0.1927	2139.55371	170.18555	49.9815



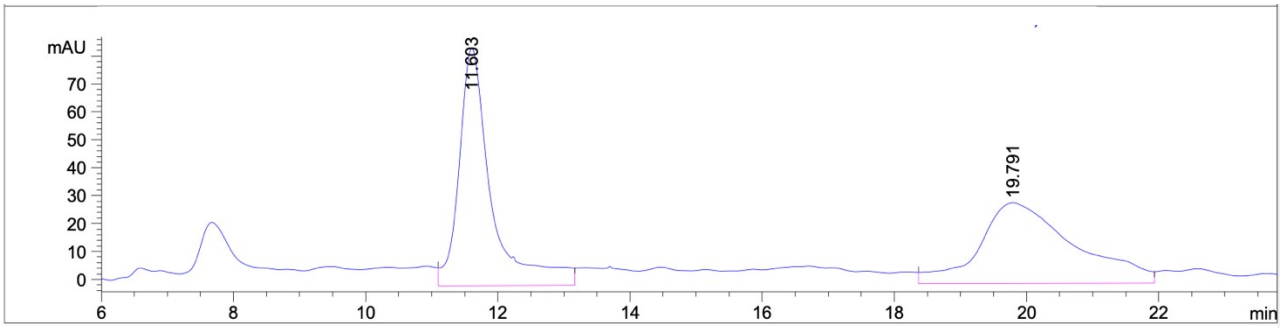
(R,R)-2k

61% Y, dr > 20:1, er 96:4

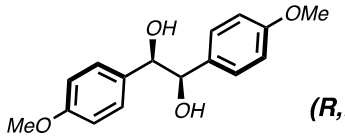




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.327	MM	0.4669	3841.96411	137.13683	95.9038
2	19.247	MM	0.8589	164.09592	3.18429	4.0962

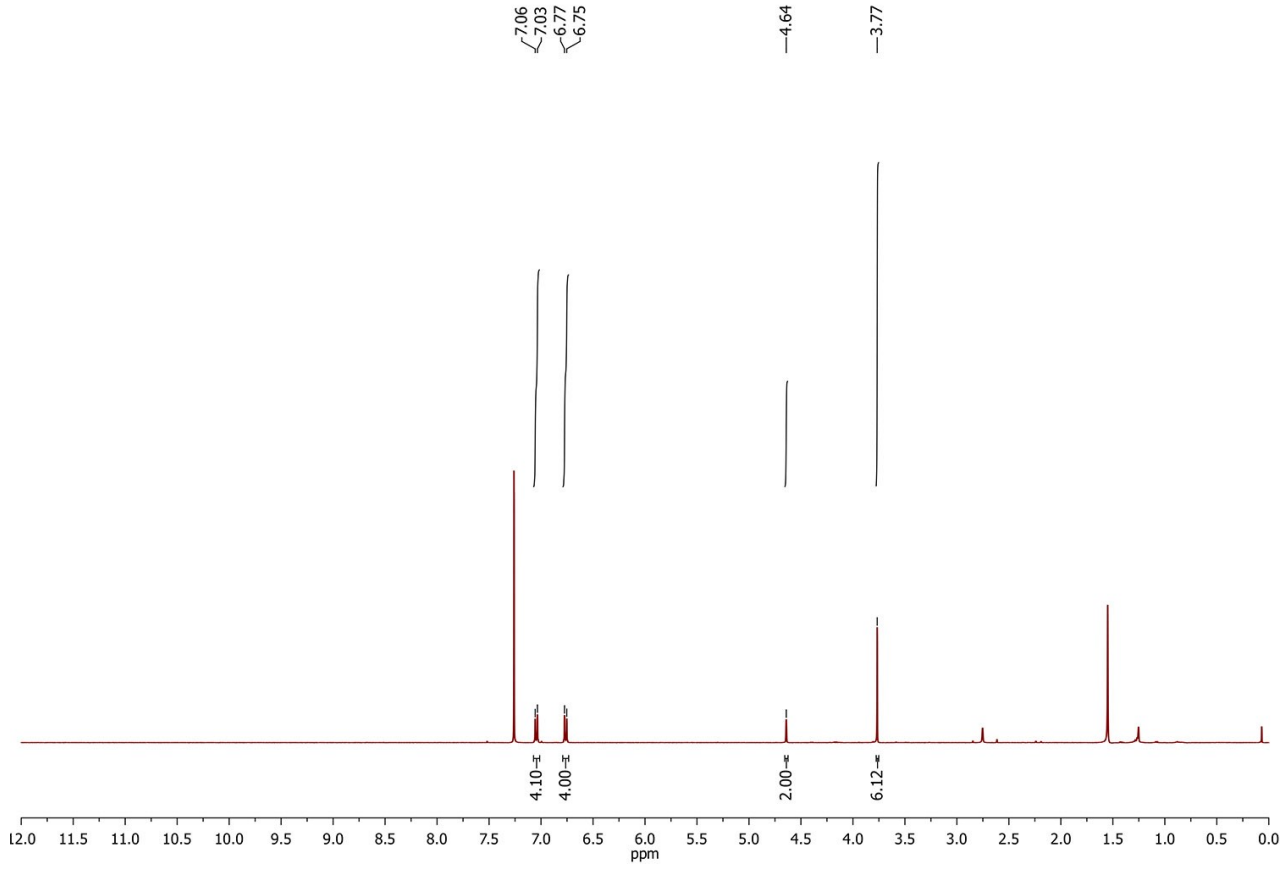


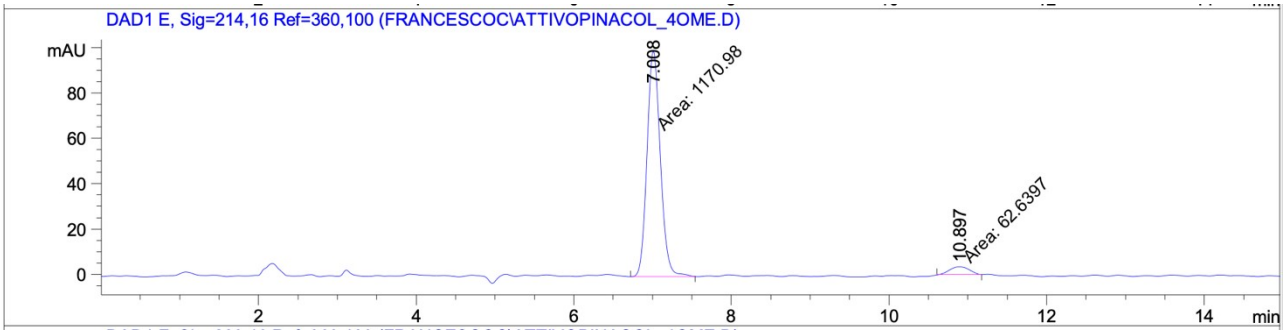
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.603	VV	0.4918	2883.87817	85.01467	49.8445
2	19.791	VV	1.3983	2901.86670	29.02757	50.1555



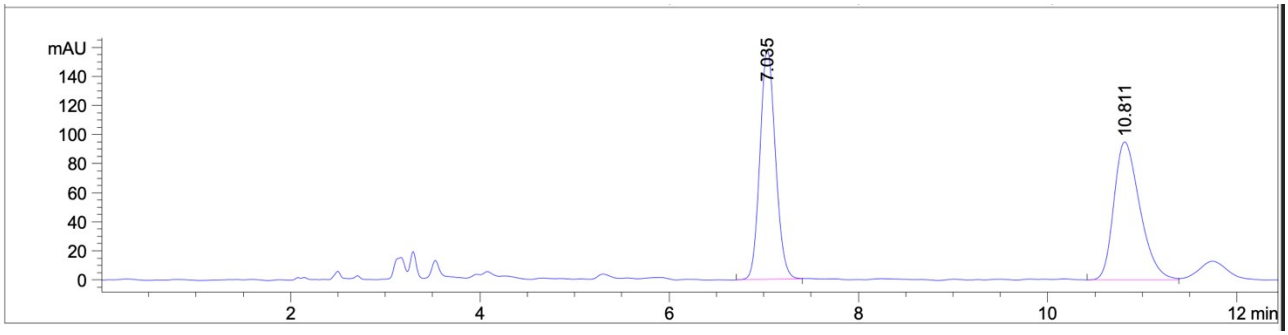
(R,R)-2m

77% Y, dr > 20:1, er 95:5

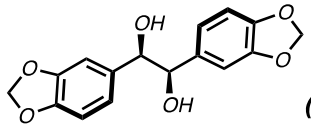




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.008	MM	0.1962	1170.98303	99.49201	94.9223
2	10.897	MM	0.2969	62.63968	3.51626	5.0777

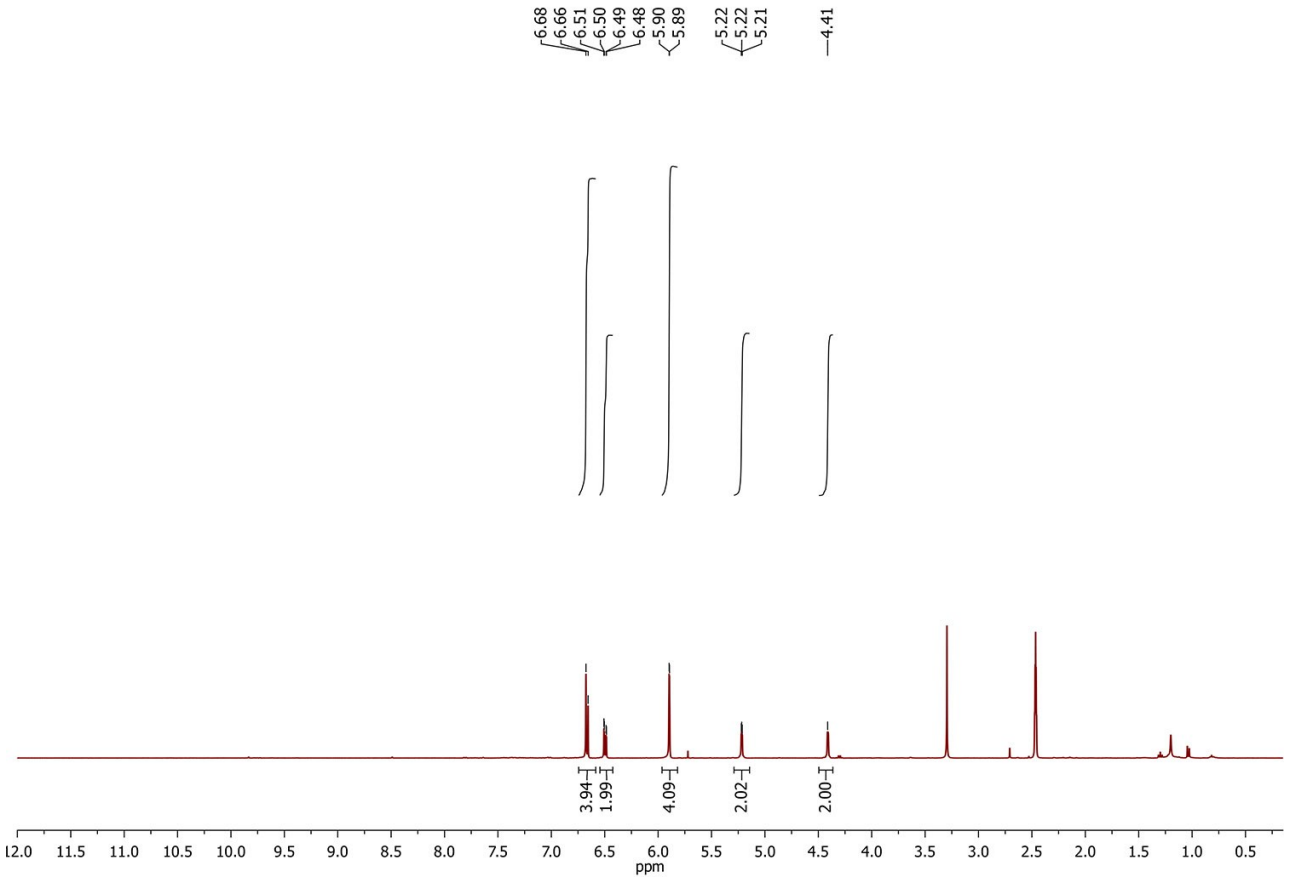


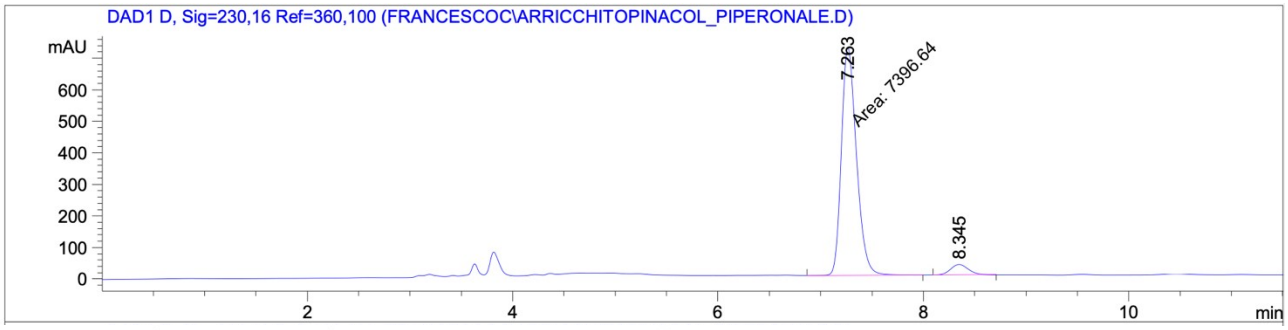
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.035	BB	0.1770	1803.51257	158.25554	49.8518
2	10.811	VV	0.2929	1814.23694	94.96841	50.1482



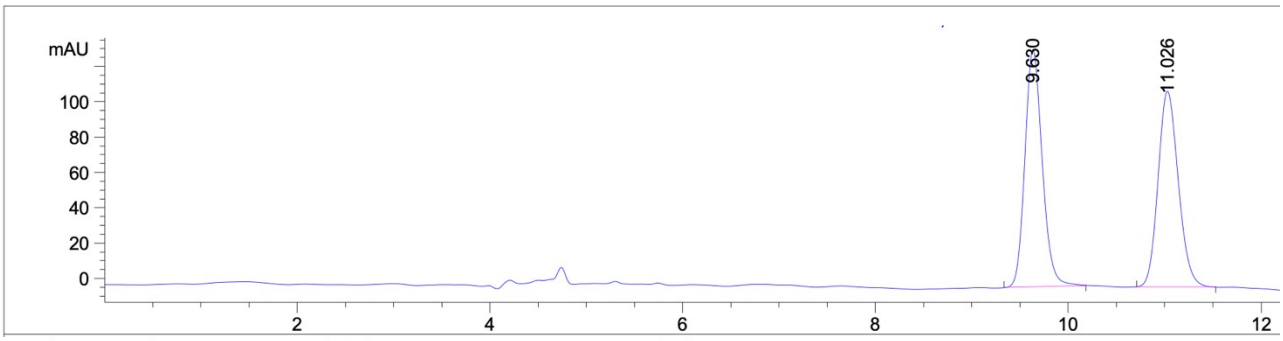
(R,R)-2o

79% Y, dr > 20:1, er 95:5





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.263	MM	0.1705	7396.64014	723.12823	94.8271
2	8.345	BB	0.1873	403.49286	33.30582	5.1729



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.630	BB	0.1945	1685.87683	134.26591	50.9481
2	11.026	BB	0.2268	1623.13403	110.83760	49.0519

Author Contributions

P. G. C. and A. G. conceived the study. Photoredox reactions and preparation of chiral SalenTiCl$_2$ were carried out by F. P., F. C., G. M., S. P.. The latter three authors contributed equally to the experimental studies. Photophysical analysis and interpretation of photophysical data were carried out by A.F., P.C. and G.B. The manuscript was written with the contributions of all authors. All authors have given approval to the final version of the manuscript.

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