Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Visible-Light TiO_2-Catalyzed Synthesis of Dihydrobenzofurans by Oxidative [3+2] Annulation of Phenols with Alkenyl Phenols

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General Considerations

Reactions were performed in round-bottom flasks with a IKA C-MAG HS7 stir plates. When necessary, solvents were dried and purified before use via a solvent purification system (THF). Other commercial reagents were used without additional purification. For light irradiation, a Kessil PR160L blue LED lamp (λmax = 440 nm, 100% intensity, max 45 W, 5 cm from wall of flask) was employed with a commercial blade fan for cooling and a commercial mirror for light reflection.

Titanium dioxide (TiO_2) (anatase) used in this reaction was purchased from Fisher (Acros organics): Titanium(IV) oxide, 98.0-100.5% TiO_2 (⩽10 μm), Code 277370010; Lot A0422338.

Analytical thin layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica-gel 254-F plates. Visualization of the TLC plates was accomplished with UV light. Automated flash chromatography was performed using a Teledyne ISCO CombiFlash® (254 nm & 280 nm UV detector) with RediSep Rf Gold® disposable silica columns (60 Å porosity, 20–40 μm) or flash chromatography with forced flow of the indicated solvent system on Silica-P flash silica gel (50-63 μm mesh particle size). NMR spectra (^1H, ^{13}C) were recorded on a Fourier transform NMR spectrometer equipped with an autosampler at 298 K using field strengths of 400/600 MHz and 151 MHz, respectively. Chemical shifts are reported relative to the solvent resonance peak δ 7.26 ($CDCl_3$) for ^1H NMR spectra and δ 77.16 ($CDCl_3$) for ^{13}C NMR spectra. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, b = broad singlet, m = multiplet, qd = quartet of doublet, hept = heptet), coupling constants, and number of protons. Accurate mass measurement analyses were acquired using an LCMS with electrospray ionization (ESI). The software calibrates the instruments, and reports measurements, by use of neutral atomic masses; the mass of the electron is not subtracted (positive ions) or added (negative ions). Unless otherwise noted, yields refer to isolated material following silica gel chromatography and purity is determined by ^1H NMR spectroscopy.

General Procedure A: Preparation of Alkenyl Phenols

To a flame-dried round-bottom flask, KO*t*Bu (2.0 equiv.) and ethyltriphenylphosphonium bromide (2.0 equiv) were added. The flask was sealed and charged with an atmosphere of argon after three cycles of evacuation/backfill using a Schlenk manifold. Sufficient dry THF (see individual procedures for amounts) was added to give an ylide solution, which was orange or yellow colored. After stirring for 2 h at room temperature, the mixture was cooled to 0 °C and benzaldehyde (1.0 equiv) in dry THF (12 mL) was added dropwise. The reaction mixture was stirred and allowed to slowly warm to room temperature. After stirring 12 h, the mixture was quenched with 2 N HCl. Saturated sodium bicarbonate solution was added, and the resultant mixture was extracted using EtOAc three times. The combined organic layers were washed with brine and deionized water, dried over anhydrous Na_2SO_4, and concentrated. Chromatography (EtOAc/hexanes) afforded the product as a yellow oil.

General Procedure B: Reaction Optimization

To a 100 mL round-bottom flask, 2-*tert*-butyl-4-methoxyphenol (200 mg, 2.0 equiv), isoeugenol (93 mg, 1.0 equiv), TiO_2 (448 mg, 10.0 equiv), and 1:1 ratio of hexafluoroisopropanol and trifluorotoluene (4 mL) were added. The round bottom flask was capped with a rubber septum. An air balloon was inserted to the round bottom flask above the

solvent level using a hypodermic needle. During the reaction the round bottom flask was irradiated with two 440 nm blue Kessil lamps on 100% power and five cm from the round bottom flask. A glass mirror was placed below the round bottom flask and a commercial fan was placed next to the round bottom flask for cooling. The reaction mixture was sampled during the reaction to monitor the conversion.

General Procedure C: Reaction Scope

To a 100 mL round-bottom flask, phenol (1.12 mmol, 2.0 equiv), alkenyl phenol (0.56 mmol, 1.0 equiv), TiO_2 (5.6 mmol, 10.0 equiv), and 1:1 ratio of hexafluoroisopropanol and trifluorotoluene (0.14 M, 4 mL) were added. The round bottom flask was capped with a rubber septum, and an air balloon was inserted to the round bottom flask above the solvent level using a hypodermic needle. During the reaction the round bottom flask was irradiated with one 440 nm blue Kessil lamps on 100% power and five cm from the round bottom flask for the indicated time. A glass mirror was placed below the round bottom flask and a commercial fan was placed next to the round bottom flask for cooling.

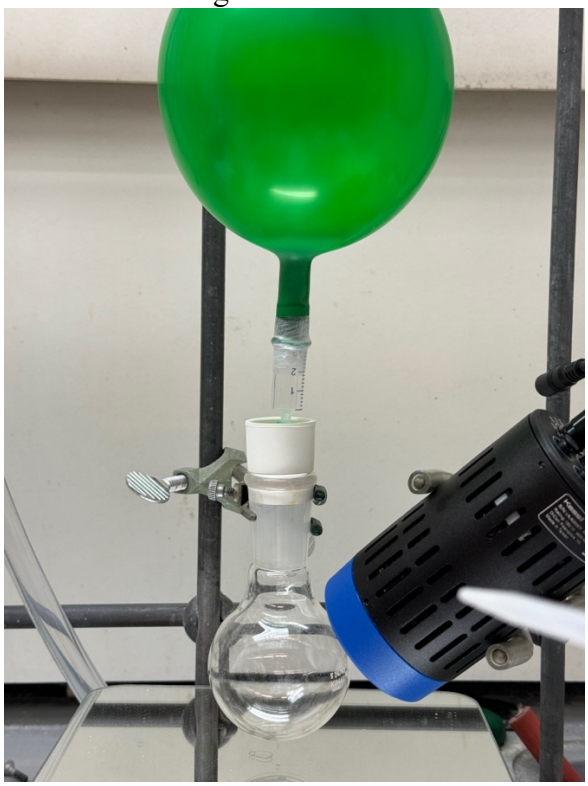
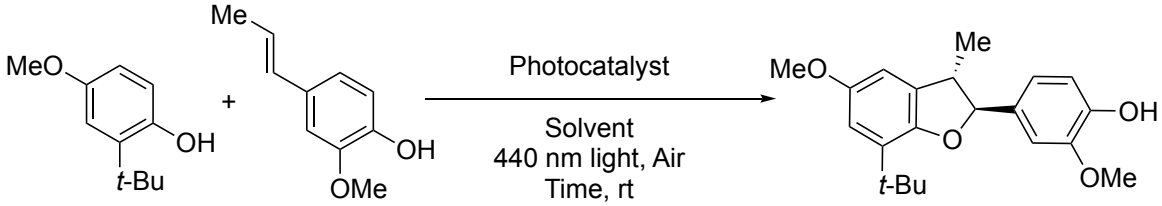


Figure S1: Example reaction assembly.

General Procedure D: Purification

The unpurified reaction mixture was added to a 50 mL plastic Falcon centrifuge tube together with methanol rinses from the round bottom flask. The resultant reaction mixture was centrifuged at 4000 rpm for five min. The top liquid layer was collected, the bottom solid residual (TiO_2) was collected and washed with 25 mL methanol and centrifuged at 4000 rpm for 5 min again. The TiO_2 residual was washed two further times. The reaction mixture and the methanol from washing the residual TiO_2 were combined and concentrated. The resultant material was purified by silica gel column chromatography to afford pure products as determined by ^{1}H- and ^{13}C-NMR spectroscopy.

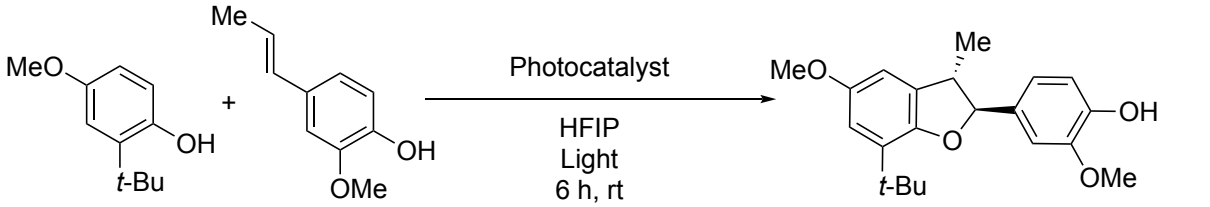
Table S1. Optimization of reaction conditions



Entry[a]	Time (h)	Isoeugenol (equiv)	BHA (equiv)	TiO_2 (equiv)	Solvent	Yield (%)[a]
1	12	1.5	1.0	10	HFIP	38
2	6	1.5	1.0	10	HFIP	32
3	6	1.0	1.0	10	HFIP	42
4	6	1.0	2.0	10	HFIP	59
5	6	3.0	1.0	10	HFIP	2
6	6	1.0	1.0	10	HFIP/TFT (1:1)	54
7	6	1.0	2.0	10	HFIP/TFT (1:1)	66
8	6	1.0	5.0	10	HFIP/TFT (1:1)	35
9	6	1.0	2.0	10	HFIP/MeCN (1:1)	51

[a] Reaction conditions: general procedure C was followed using *iso*-eugenol (**2a**) (0.56 mmol, 1.00 equiv), 2-*tert*-butyl-4-methoxyphenol (1.12 mmol, 2.00 equiv), TiO_2 (x equiv) and solvent (4.00 mL, 0.14 M) for x h. [b] yield after chromatography.

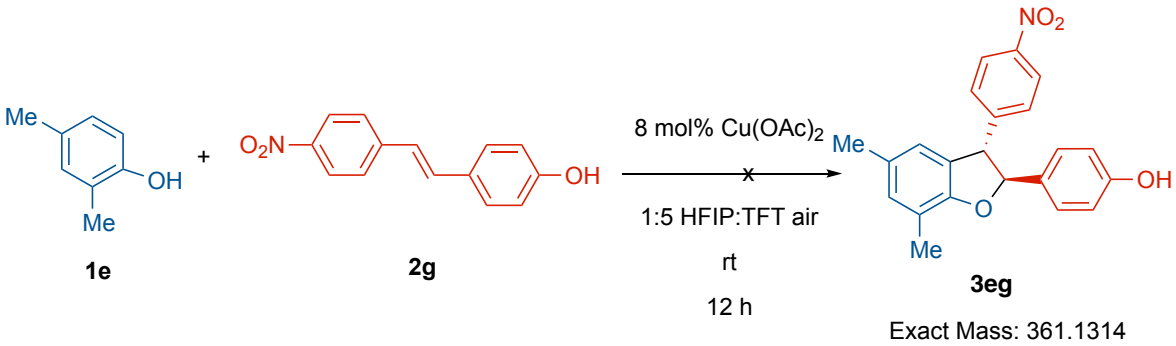
Table S2. Control reactions



Entry[c]	Photocatlyst	Light	Oxidant	Yield
1	10 equiv TiO_2	dark[d]	Air	/
2	10 equiv TiO_2	440 nm light	Argon	/
3	/	440 nm light	Air	/

[a] Reaction conditions: 0.56 mmol *iso*-eugenol (**2a**), 1.12 mmol 2-*tert*-butyl-4-methoxyphenol, x equiv TiO_2, 4.0 mL HFIP, irradiation 440 nm Kessil lamp; five cm distance for 6 h under 1 atm Air (unless otherwise mentioned in the reaction conditions). For reactions in the dark, the round bottom flasks were covered with aluminium foil.

$Cu(OAc)_2$ catalyzed[1] reaction for model substrate 3eg:



Scheme S1. $Cu(OAc)_2$ catalyzed reaction for the synthesis of **3eg**

To a 100 mL round-bottom flask, $Cu(OAc)_2$ (0.048 mmol, 0.08 equiv), and 1:5 ratio of hexafluoroisopropanol and trifluorotoluene (0.10 M, 6 mL) were added. $Cu(OAc)_2$ would not dissolve in 6 mL HFIP:TFT (1:5). The $Cu(OAc)_2$ solution was then sonicated for 10 minutes, no change in $Cu(OAc)_2$ dissolution. Then 2,4-dimethylphenol (0.60 mmol, 1.0 equiv), 4-(4-nitrostyryl)phenol (0.66 mmol, 1.1 equiv), were added to the $Cu(OAc)_2$ solution. The round bottom flask was capped with a rubber septum, and an air balloon was inserted to the round bottom flask above the solvent level using a hypodermic needle. Aliquots (10 µL) were withdrawn from the flask at 12 h. The aliquots were diluted to 0.001 M with MeOH (990 µL). This solution (2 µL) was injected into the UPLCMS for crude analysis. No conversion of either substrate was observed on UPLCMS result.

UPLC: C18 column (2.1 mm x 5 cm). Flow rate = 0.5 mL/min. Mobile phase gradient: 50% MeCN/H_2O with 0.1% formic acid for 0.5 min, changed to 95% MeCN/H_2O with 0.1% formic over 2 min and held for 0.5 min, reduced to 5% MeCN/H_2O with 0.1% formic acid over 5 s and held for an additional 25 s. Detection = UV-Vis (TWC)

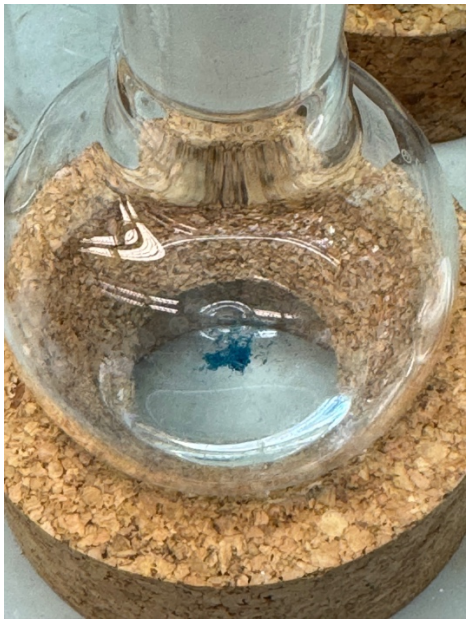


Figure S2: $Cu(OAc)_2$.in 6 mL (1:5 HFIP:TFT) after sonicating for 10 minutes.

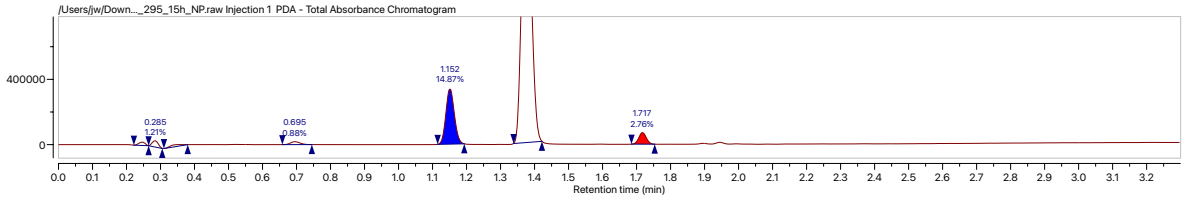


Figure S3: UPLC trace for crude reaction mixture after 12 h. t_R (**2g**) =1.15 min, t_R (**1e**) =1.72 min, t_R (TFT) =1.37 min

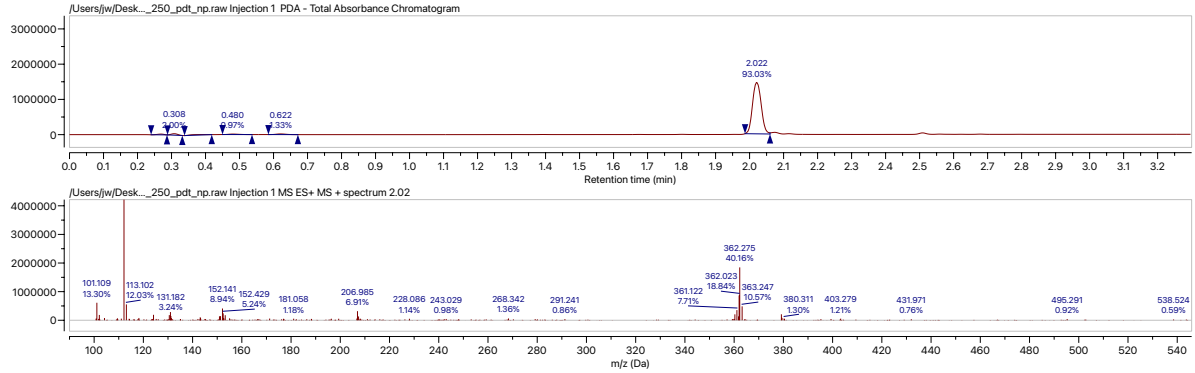
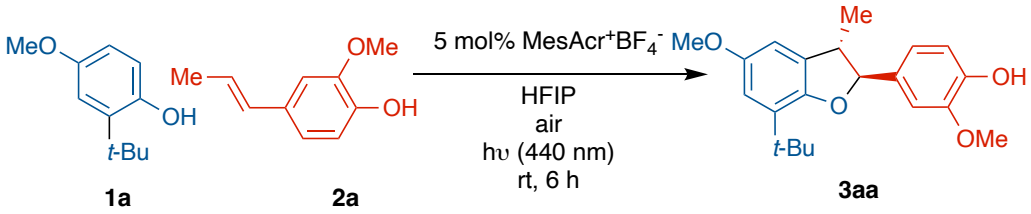


Figure S4: UPLCMS-ESI$^-$ trace for **3eg**. t_R (**3eg**) =2.02 min. ESI$^+$MS: t_R (**3eg**) =2.02 min, m/z=362.275.

MesAcr$^+$BF$_4^-$ catalyzed reaction for model substrate 3eg:



Scheme S2. Acridinium catalyzed reaction for the synthesis of **3aa**

To a 100 mL round-bottom flask, 2-*tert*-butyl-4-methoxyphenol (1.20 mmol, 2.0 equiv), *iso*-eugenol (0.60 mmol, 1.0 equiv) 9-mesityl-10-methylacridinium tetrafluoroborate (0.030 mmol, 0.05 equiv), and hexafluoroisopropanol (0.10 M, 6 mL) were added. The round bottom flask was capped with a rubber septum, and an air balloon was inserted to the round bottom flask above the solvent level using a hypodermic needle. During the reaction the round bottom flask was irradiated with one 440 nm blue Kessil lamps on 100% power and five cm from the round bottom flask for the indicated time. A glass mirror was placed below the round bottom flask and a commercial fan was placed next to the round bottom flask for cooling. Aliquots (10 µL) were withdrawn from the flask at 6 h. The aliquots were diluted to 0.001 M with MeOH (990 µL). This solution (2 µL) was injected into the UPLCMS for crude analysis.

The reaction mixture was concentrated on silica gel and purified by silica gel column chromatography (*n*-hexane/EtOAc 85:15) to afford **3aa** (29 mg, 0.084 mmol) in 14% isolated yield.

UPLC: C18 column (2.1 mm x 5 cm). Flow rate = 0.5 mL/min. Mobile phase gradient: 50% MeCN/H_2O with 0.1% formic acid for 0.5 min, changed to 95% MeCN/H_2O with 0.1% formic over 2 min and held for 0.5 min, reduced to 5% MeCN/H_2O with 0.1% formic acid over 5 s and held for an additional 25 s. Detection = UV-Vis (TWC)

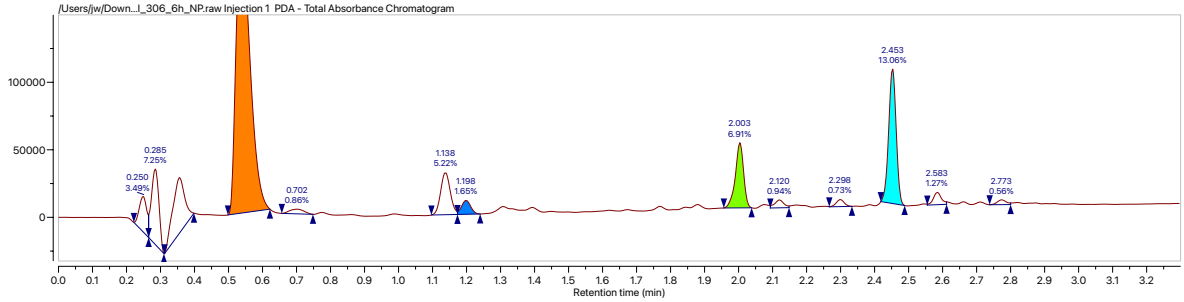


Figure S5: UPLC spectrum for the reaction of **3aa** after 6 hours. t_R (**MesAcr$^+$BF$_4^-$**) =0.55 min, t_R (**1a**) =1.20 min, t_R (**3aa**) =2.00 min, t_R (**over oxidized adduct**) =2.45 min

Additional studies:

Mechanism studies:

Kinetic study:

To a 100 mL round-bottom flask, isoeugenol (0.56 mmol, 1.0 equiv), TiO_2 (5.6 mmol, 5.0 equiv), HFIP (0.1 M, 6 mL) were added. The round bottom flask was capped with a rubber septum, and an air balloon was inserted to the round bottom flask above the solvent level using a hypodermic needle. During the reaction the round bottom flask was irradiated with one 440 nm blue Kessil lamps on 100% power and 3 cm from the round bottom flask for the indicated time. A glass mirror was placed below the round bottom flask and a commercial fan was placed next to the round bottom flask for cooling. Aliquots (10 µL) were withdrawn from the flask at intervals. The aliquots were diluted to 0.001 M with 0.001 M 4-ethyl anisole as an internal standard in MeOH (990 µL). The sample was passed through a PTFE 0.45 µm syringe filter to remove titanium dioxide. This solution (2 µL) was injected into the UPLC and the concentration of *iso*-eugenol was determined by UPLC using UV-Vis (TWC) relative to the 4-ethyl anisole with a response factor of 28.83.

UPLC: C18 column (2.1 mm x 5 cm). Flow rate = 0.5 mL/min. Mobile phase gradient: 50% MeCN/H_2O with 0.1% formic acid for 0.5 min, changed to 95% MeCN/H_2O with 0.1% formic over 2 min and held for 0.5 min, reduced to 5% MeCN/H_2O with 0.1% formic acid over 5 s and held for an additional 25 s. Detection = UV-Vis (TWC). t_R (*iso*-eugenol) = 0.9 min, t_R (4-ethyl anisole) = 1.56 min. The response factor was determined to be 22513834/780882=28.83 from a solution of 1:1 *iso*-eugenol:4-ethyl anisole.

To a 100 mL round-bottom flask, 2-*tert*-butyl-4-methoxyphenol (0.56 mmol, 1.0 equiv), TiO_2 (5.6 mmol, 5.0 equiv), HFIP (0.1 M, 6 mL) were added. The round bottom flask was capped with a rubber septum, and an air balloon was inserted to the round bottom flask above the solvent level using a hypodermic needle. During the reaction the round bottom flask was irradiated with one 440 nm blue Kessil lamps on 100% power and 3 cm from the round bottom flask for the indicated time. A glass mirror was placed below the round bottom flask and a commercial fan was placed next to the round bottom flask for cooling. Aliquots (10 µL) were withdrawn from the flask at x h intervals. The aliquots were diluted to 0.001 M with 0.001 M 1,3,5-trimethoxybenzene as an internal standard in MeOH (990

μL). The sample was passed through a PTFE 0.45 μm syringe filter to remove titanium dioxide. This solution (2 μL) was injected into the UPLC and the concentration of 2-*tert*-butyl-4-methoxyphenol was determined by UPLC using UV-Vis (TWC) relative to the 1,3,5-trimethoxybenzene with a response factor of 0.482.

UPLC: C18 column (2.1 mm x 5 cm). Flow rate = 0.5 mL/min. Mobile phase gradient: 50% MeCN/H_2O with 0.1% formic acid for 0.5 min, changed to 95% MeCN/H_2O with 0.1% formic over 2 min and held for 0.5 min, reduced to 5% MeCN/H_2O with 0.1% formic acid over 5 s and held for an additional 25 s. Detection = UV-Vis (TWC). t_R (2-*tert*-butyl-4-methoxyphenol) = 1.26 min, t_R (1,3,5-trimethoxybenzene) = 0.939 min. The response factor was determined to be 22513834/780882=28.83 from a solution of 1: 2-*tert*-butyl-4-methoxyphenol: 1,3,5-trimethoxybenzene.

To a 100 mL round-bottom flask, 3-*tert*-butyl-4-hydroxyanisole (0.56 mmol, 1.0 equiv), TiO_2 (5.6 mmol, 5.0 equiv), HFIP (0.1 M, 6 mL) were added. The round bottom flask was capped with a rubber septum, and an air balloon was inserted to the round bottom flask above the solvent level using a hypodermic needle. During the reaction the round bottom flask was irradiated with one 440 nm blue Kessil lamps on 100% power and 3 cm from the round bottom flask for the indicated time. A glass mirror was placed below the round bottom flask and a commercial fan was placed next to the round bottom flask for cooling. Aliquots (10 μL) were withdrawn from the flask at x h intervals. The aliquots were diluted to 0.001 M with 0.001 M 1,3,5-trimethoxybenzene as an internal standard in MeOH (990 μL). The sample was passed through a PTFE 0.45 μm syringe filter to remove titanium dioxide. This solution (2 μL) was injected into the UPLC and the concentration of 3-*tert*-butyl-4-methoxyphenol was determined by UPLC using UV-Vis (TWC) relative to the 1,3,5-trimethoxybenzene with a response factor of 0.527.

UPLC: C18 column (2.1 mm x 5 cm). Flow rate = 0.5 mL/min. Mobile phase gradient: 50% MeCN/H_2O with 0.1% formic acid for 0.5 min, changed to 95% MeCN/H_2O with 0.1% formic over 2 min and held for 0.5 min, reduced to 5% MeCN/H_2O with 0.1% formic acid over 5 s and held for an additional 25 s. Detection = UV-Vis (TWC). t_R (3-*tert*-butyl-4-methoxyphenol) = 1.21 min, t_R (1,3,5-trimethoxybenzene) = 0.94 min. The response factor was determined to be 431099/818504=0.527 from a solution of 1: 3-*tert*-butyl-4-methoxyphenol: 1,3,5-trimethoxybenzene.

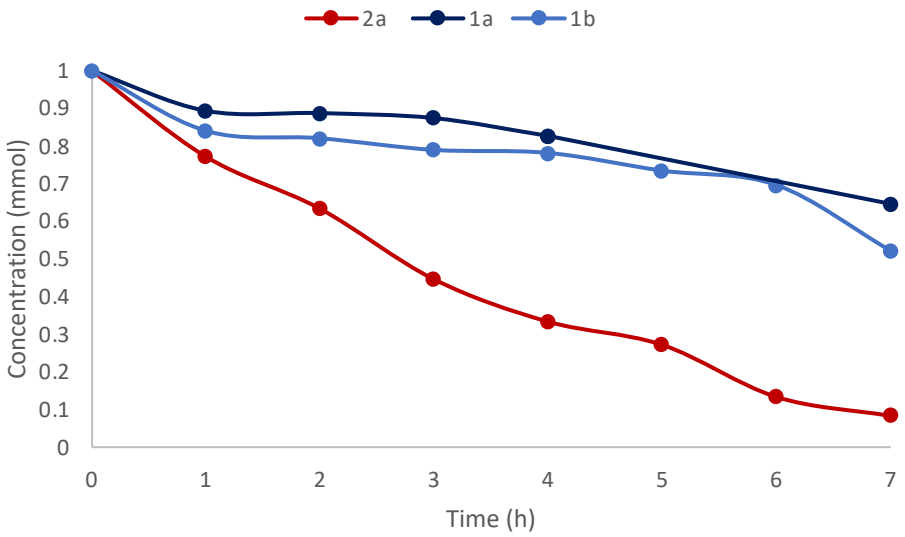
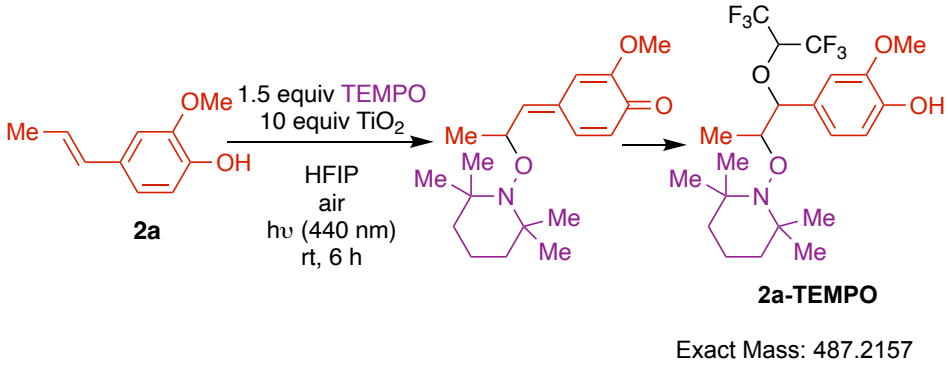


Figure S6: Concentration of **2a** vs **1b** vs **1a** over 6 hours of reaction.

Radical trapping experiment with TEMPO:



Exact Mass: 487.2157

Scheme S3. radical trapping study

To a 100 mL round-bottom flask, isoeugenol (0.56 mmol, 1.00 equiv), TiO_2 (5.60 mmol, 10.0 equiv), TEMPO (0.84 mmol, 1.50 equiv), and hexafluoroisopropanol (0.09 M, 6 mL) were added. The round bottom flask was capped with a rubber septum, and an air balloon was inserted to the round bottom flask above the solvent level using a hypodermic needle. During the reaction the round bottom flask was irradiated with one 440 nm blue Kessil lamps on 100% power and five cm from the round bottom flask for the indicated time. A glass mirror was placed below the round bottom flask and a commercial fan was placed next to the round bottom flask for cooling. The unpurified reaction mixture was added to a 50 mL plastic Falcon centrifuge tube together with methanol rinses from the round bottom flask. The resultant reaction mixture was centrifuged at 4000 rpm for 5 min. The top liquid layer was collected, the bottom solid residual (TiO_2) was collected and washed with methanol (25 mL) and centrifuged at 4000 rpm for 5 min again. The residual TiO_2 was washed two further times. The reaction mixture and the methanol from washing the residual TiO_2 were combined and concentrated on Celite. The mixture on Celite was then purified using a 42 g C18 column. Mobile phase gradient: 10% MeCN/H_2O with 0.1% formic acid for 5 min, changed to 95% MeCN/H_2O with 0.1% formic over 15 min and held for 5 min. The isolated fractions containing **2a-TEMPO** were combined, and acetonitrile was subsequently removed. The mixture was then extracted with 100 mL of ethyl acetate and

dried over sodium sulfate. **2a-TEMPO** (74 mg, 0.15 mmol) was obtained in 25% isolated yield.

UPLC: C18 column (2.1 mm x 5 cm). Flow rate = 0.5 mL/min. Mobile phase gradient: 50% MeCN/H_2O with 0.1% formic acid for 0.5 min, changed to 95% MeCN/H_2O with 0.1% formic over 2 min and held for 0.5 min, reduced to 5% MeCN/H_2O with 0.1% formic acid over 5 s and held for an additional 25 s. Detection = UV-Vis (TWC)

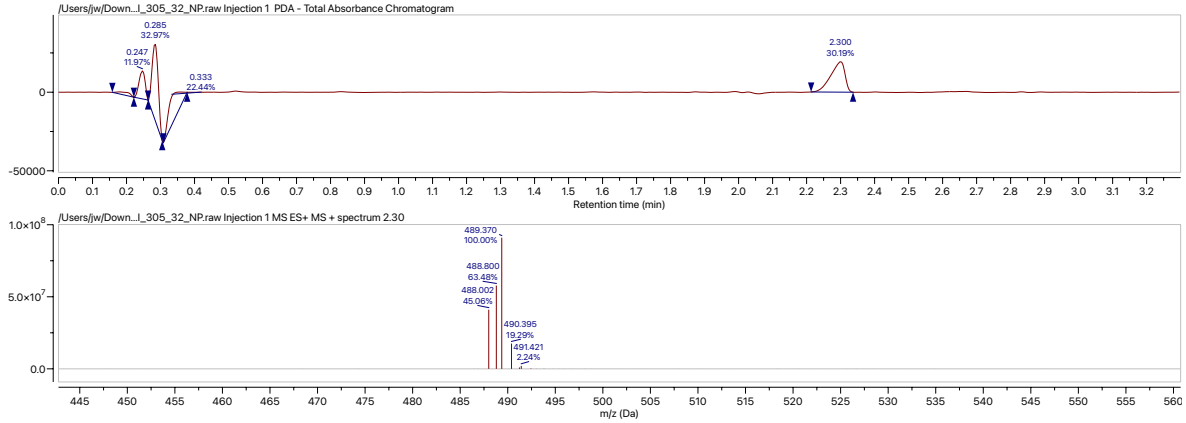


Figure S7: UPLCMS spectrum **2a-TEMPO**. t_R (**2a-TEMPO**) =2.27 min. ESI^+MS: t_R (**2a-TEMPO**) =2.30 min, m/z=489.370.

Oxidation potential measurements:

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV)

Experiments were performed using a CHI-620D potentiostat/galvanostat using a standard three-electrode configuration. The working electrode was a polished glassy carbon electrode (GCE, 3.0 mm diameter, CH Instruments) and the counter electrode was a Pt wire (0.5 mm diameter). Electrochemical potentials were measured against silver pseudo reference electrode (Ag/10 mM $AgNO_3$ in MeCN). Reported electrochemistry data are calibrated and reported versus the Fc/Fc^+ couple. The supporting electrolyte employed for CV and DPV experiments was 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$), dissolved in dry HFIP (1,1,1,3,3,3-Hexaflouropropan-2-ol). The analyte concentration was 1.0 mM, and all CV experiments were carried out at scan rate of 100 mV/s. Before starting a new CV experiment, the WE was polished and the solution was stirred at least 30 s to ensure complete homogeneity at the electrode/electrolyte interface. The solution was then allowed to rest for at least 2 min to ensure voltammetry was performed on quiescent solutions. All the CV and DPV experiments were performed under an inert atmosphere of Ar.

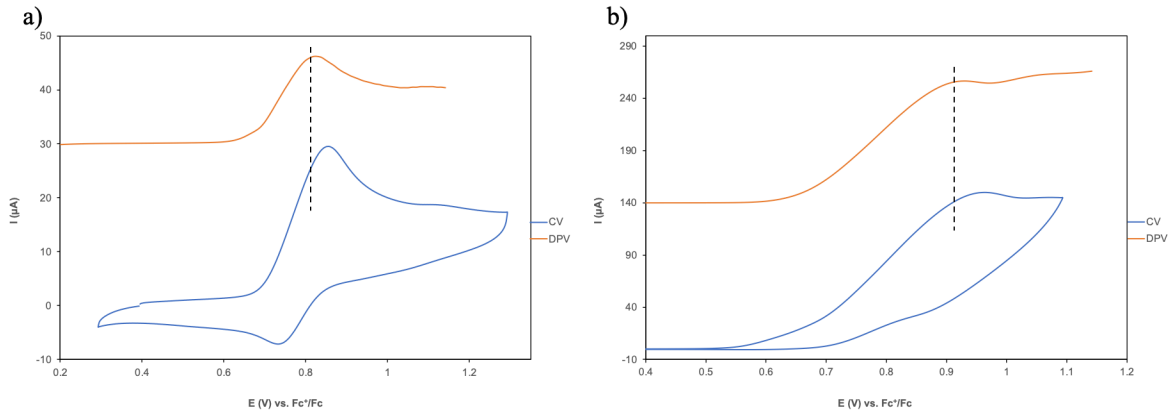


Figure S8. a) CV and DPV measurements of **1a**, measured E_{ox} = 0.83V, b) CV and DPV measurements of **2a**, measured E_{ox} = 0.92V.

Potassium iodide test for the presence of H_2O_2:

A solution of freshly-prepared 10% aqueous potassium iodide solution (5 mL) was added to the reaction mixture (4 mL) and allowed to stir for 5 min. Stirring was halted. After the TiO_2 settled, the supernatant had turned from colorless to bright yellow, indicating the presence of H_2O_2.

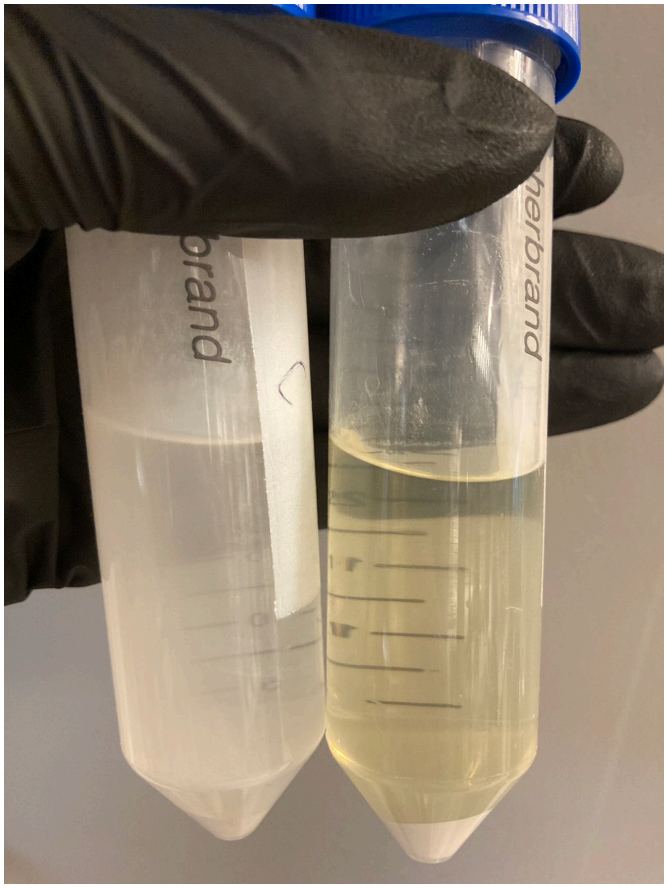
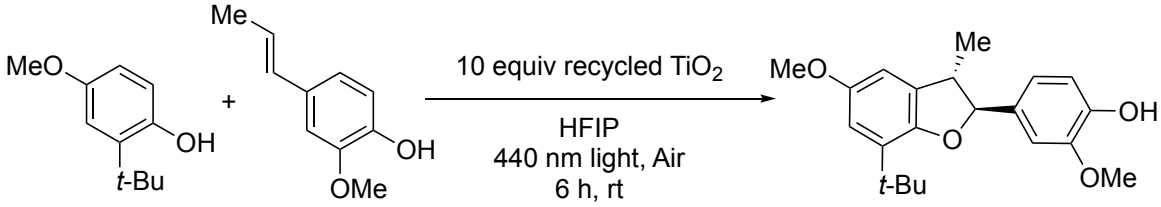


Figure S9. KI test on TiO_2 catalyzed phenol-alkenyl phenol coupling (right), control test without KI solution (left).

TiO_2 recyclability study:



Scheme S4. Recycled TiO_2 study

A 100 mL round bottom flask with a stirbar was charged with *iso*-eugenol (0.56 mmol, 1 equiv), 2-*tert*-butyl-4-methoxyphenol (1.12 mmol, 2 equiv) recycled TiO_2 (5.6 mmol, 10 equiv), HFIP:trifluorotoluene (4 mL, 1:1 mixture). The round bottom flask was capped with a rubber septum. An air balloon was inserted to the round bottom flask above the solvent level using a hypodermic needle. During the reaction the round bottom flask was irradiated with two 440 nm blue Kessil lamps on 100% power and 5 cm from the round bottom flask. A glass mirror was placed below the round bottom flask and a commercial fan was placed next to the round bottom flask for cooling. General procedure B was used followed by flash column chromatography (*n*-hexane/EtOAc 85:15).

TiO_2 characterization and recycle procedure:

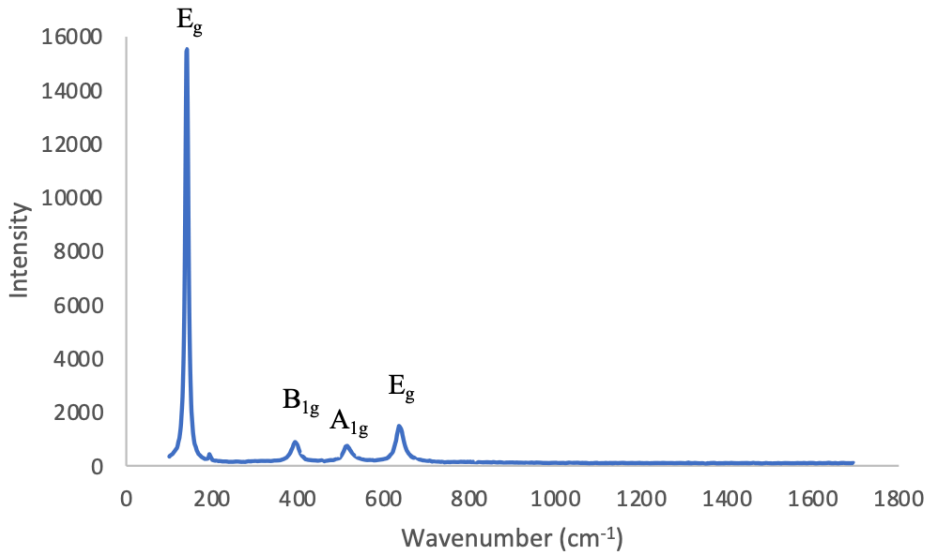


Figure S10. Raman spectrum of TiO_2 sample used in the reaction. Raman active modes were assigned and compared to *Sci. Rep*. **2017**, *7*, 8783[2].

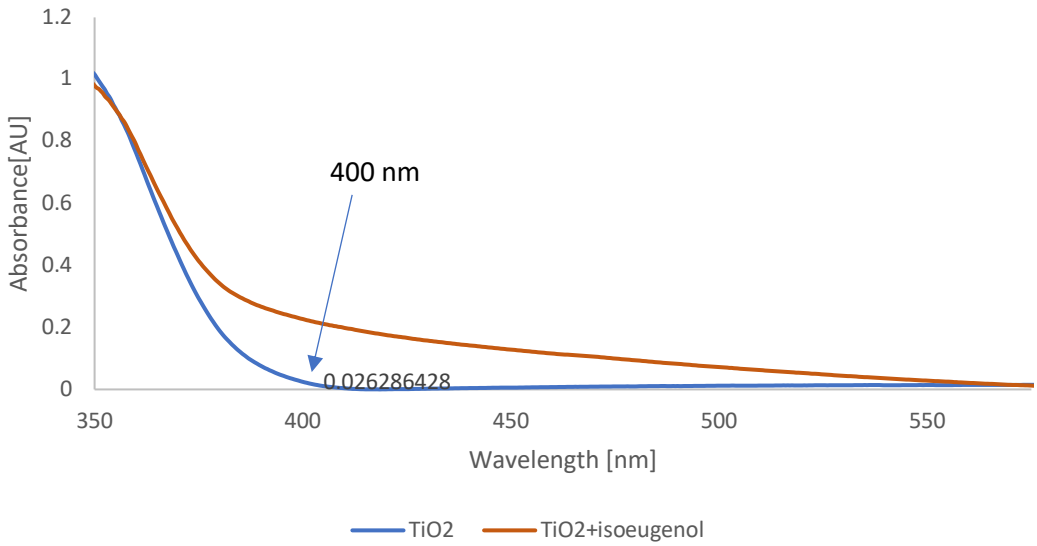


Figure S11. Diffuse reflectance spectroscopy (DRS) UV-Vis of new TiO_2, and TiO2-**2a** mixture for band gap measurement.

TiO_2 band gap is being calculated using the following equation: (E)=(h*C)/λ
where h=6.63E-34, C=3.00E+8, λ =4.00E-07, E=4.84E-19, and 1eV=1.6E-19 J

The TiO_2 band gap being used in this reaction is calculated to be 3.11 eV.

Recycled TiO_2 from the reaction was collected, centrifuged, and washed with a mixture of MeOH (methanol) and acetone. After centrifugation, the liquid was discarded, and the residual TiO_2 was washed again with MeOH/acetone. This process was repeated three times. Subsequently, the solid TiO_2 residual was transferred to a 100 mL round-bottom flask and treated with 25 mL of a 30% H_2O_2 (hydrogen peroxide) aqueous solution. After stirring for 6 h under 370 nm light, the mixture was centrifuged to collect the washed TiO_2. The washed TiO_2 was then dried in a 180 °C oven overnight. Scanning electron microscopy (SEM) and powder X-ray diffraction (powder XRD) were performed to evaluate the structural integrity and particle surface.

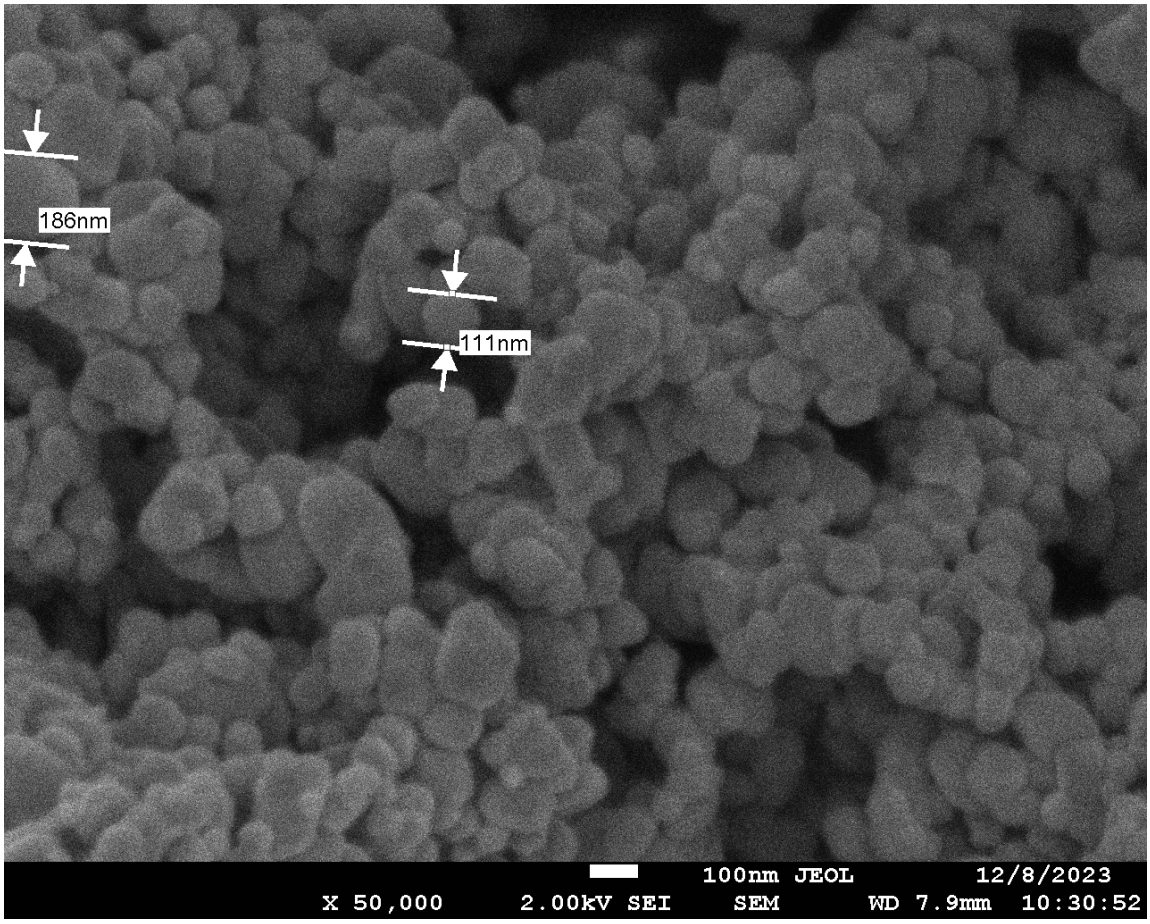


Figure S12. SEM imaging of new TiO_2, average particle size is estimated to be around 150 nm.

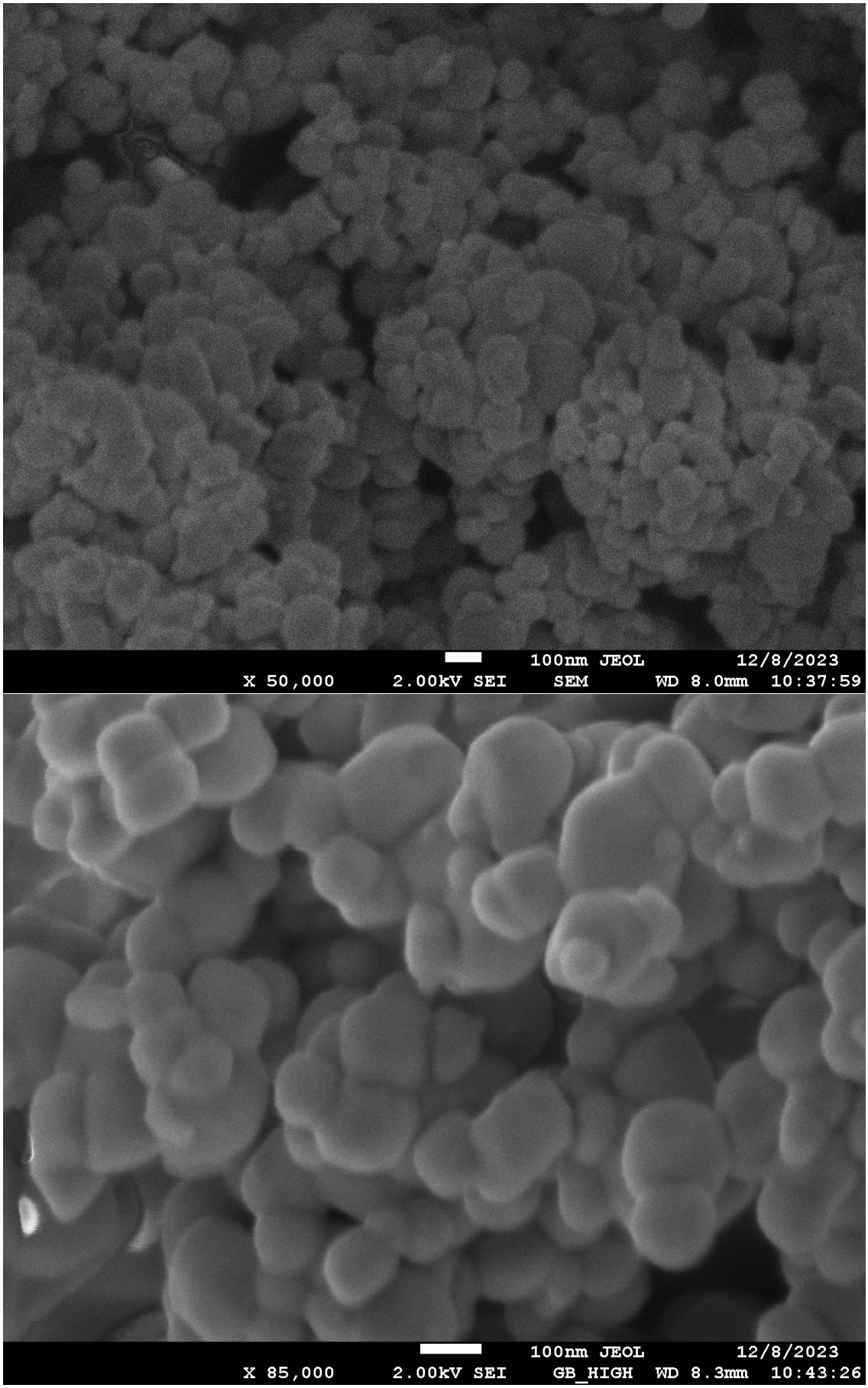


Figure S13. SEM imaging of TiO_2 after one use (no H_2O_2 treatment).

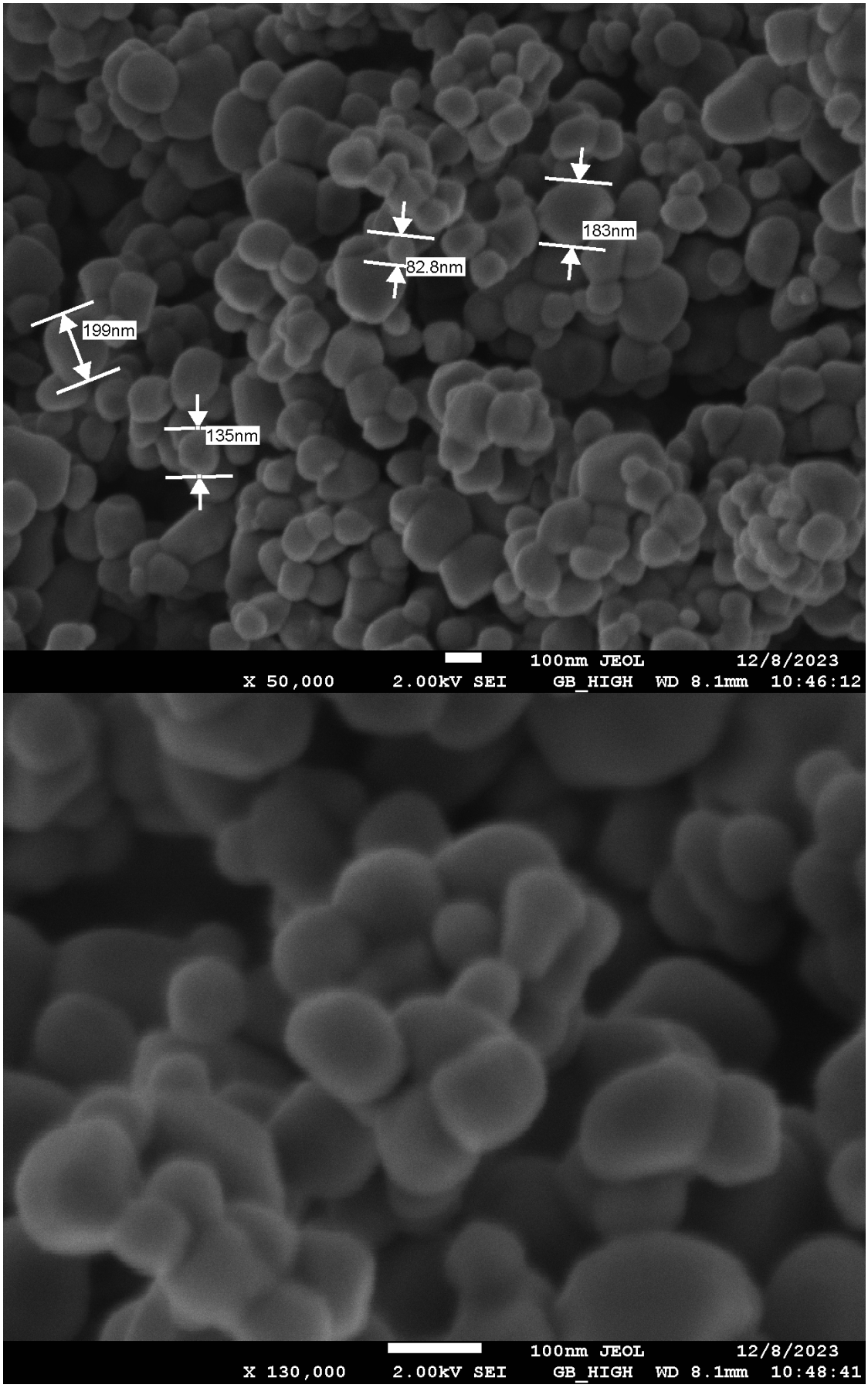


Figure S14. SEM imaging of TiO_2 after one use and treatment with H_2O_2.

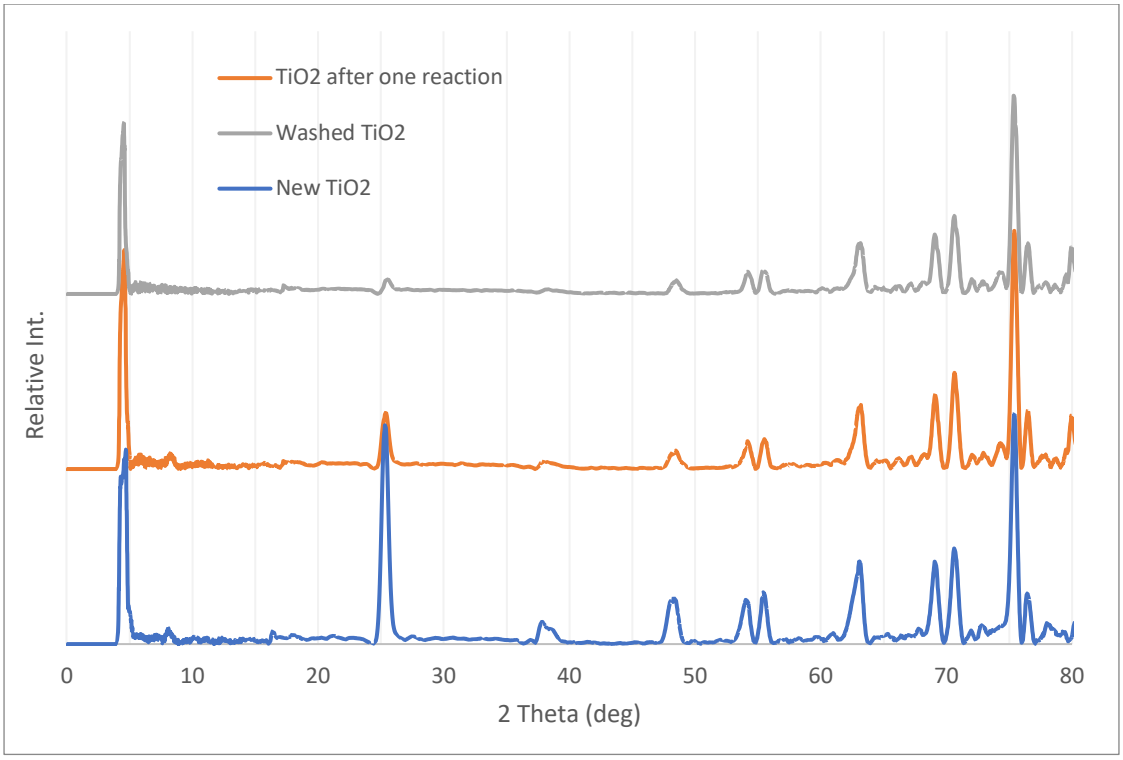


Figure S15. PXRD new, recycled, and washed TiO_2.

TiO_2 substrate (2a) surface interaction study:

Figure S16. New TiO_2 vs TiO_2-**2a** mixture.

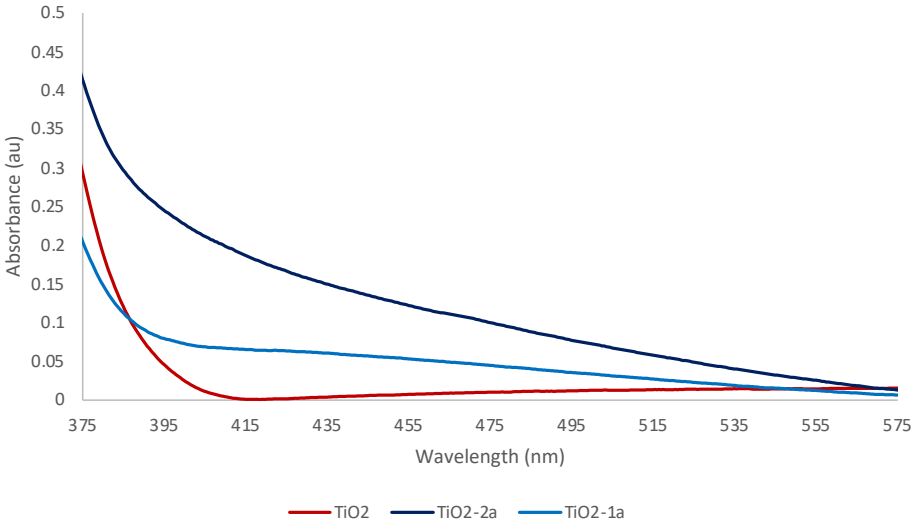


Figure S17. Diffuse reflectance spectroscopy (DRS) UV-Vis of new TiO_2, TiO_2-**1a**, and TiO2-**2a** mixture.

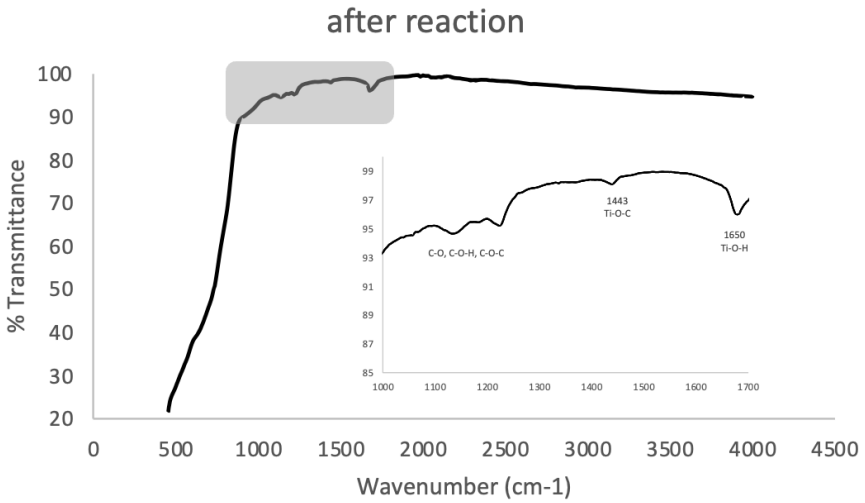


Figure S18. FT-IR spectrum of TiO_2 after reaction. The characteristic peaks centered at 1443 cm^{-1} and 1650 cm^{-1} were attributed to Ti-O-C bending and Ti-O-H vibrations, consistent with literature descriptions.[3,4]

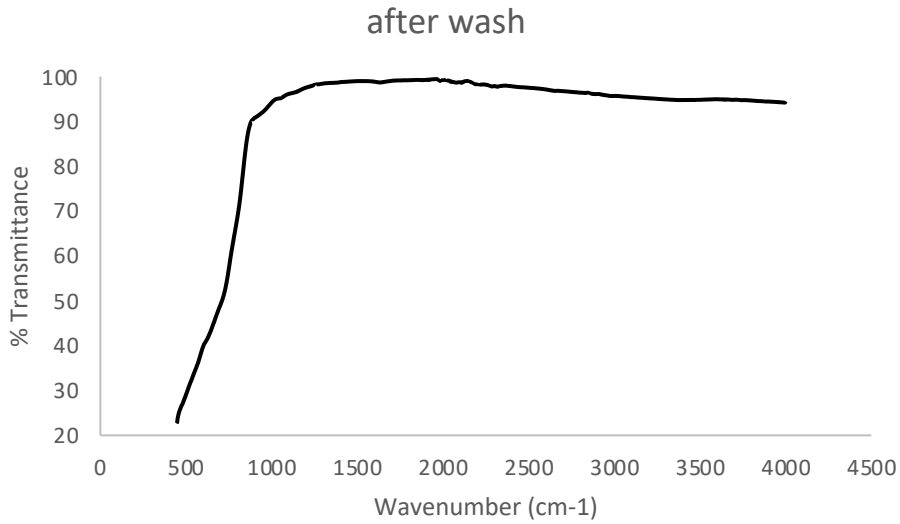


Figure S19. FT-IR spectrum of used TiO_2 after wash.

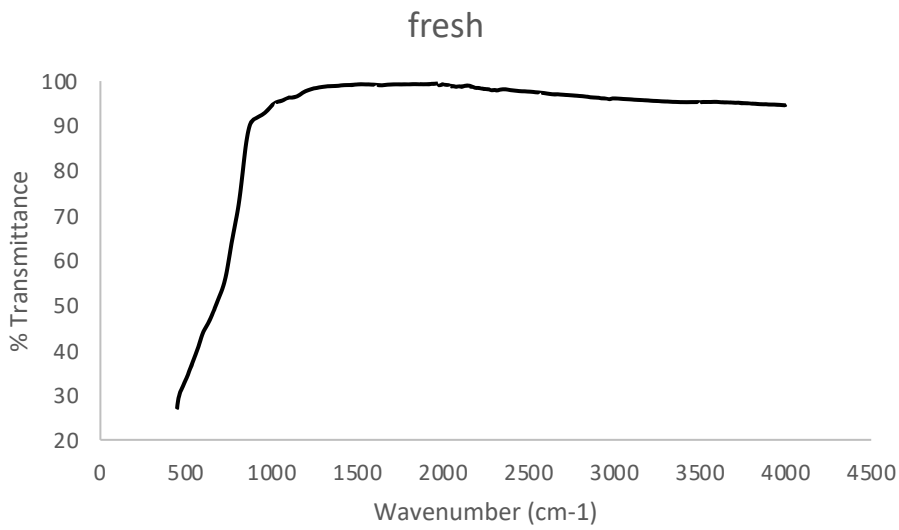


Figure S20. FT-IR spectrum of fresh TiO_2.

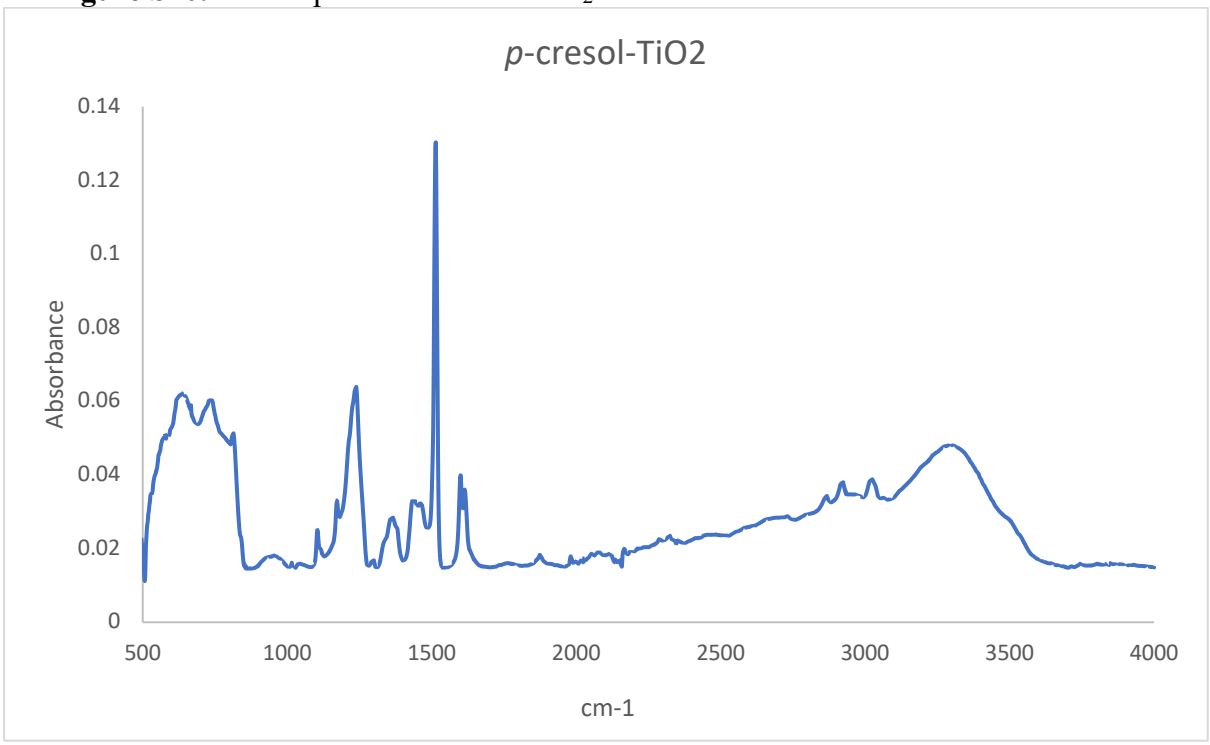


Figure S21. FT-IR spectrum of *p*-cresol(10 mol%)-TiO_2.

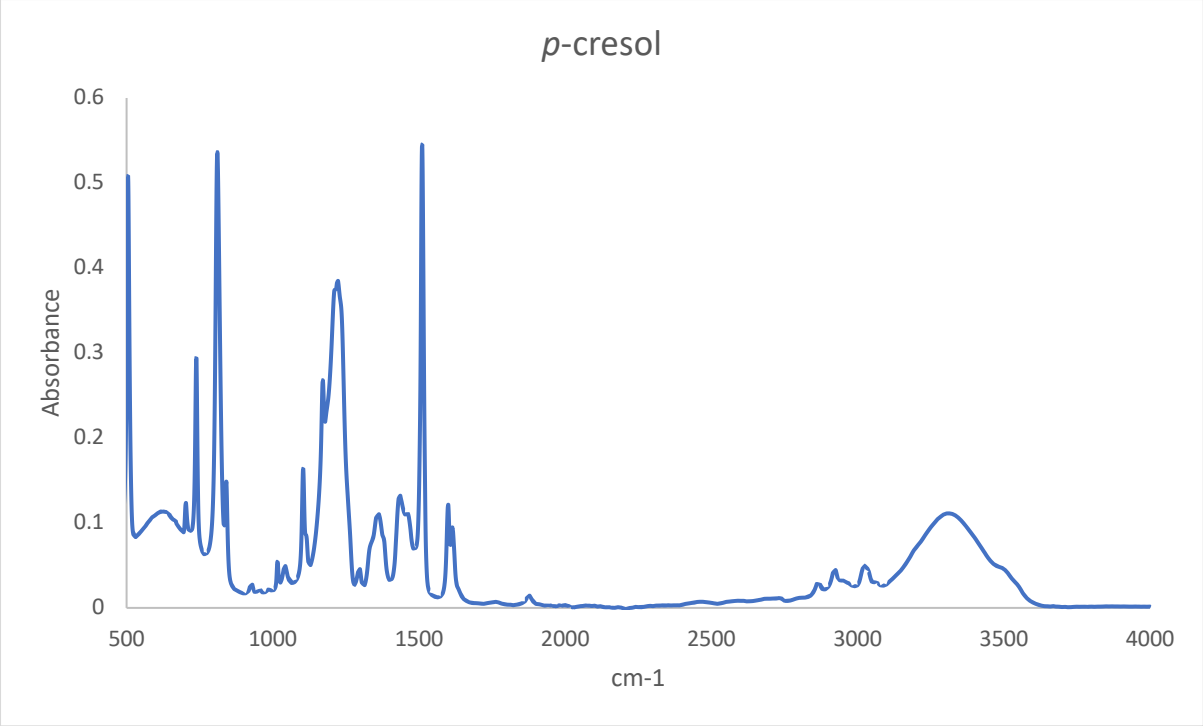


Figure S22. FT-IR spectrum of *p*-cresol.

Detection of reaction intermediates using UPLCMS(ESI)

Aliquots (10 µL) were withdrawn from the reaction flask at x h intervals. The aliquots were diluted to 0.001 M in MeOH (990 µL). The sample was passed through a PTFE 0.45 µm syringe filter to remove titanium dioxide. This solution (2 µL) was injected into the UPLCMS for analysis.

UPLC: C18 column (2.1 mm x 5 cm). Flow rate = 0.5 mL/min. Mobile phase gradient: 50% MeCN/H_2O with 0.1% formic acid for 0.5 min, changed to 95% MeCN/H_2O with 0.1% formic over 2 min and held for 0.5 min, reduced to 5% MeCN/H_2O with 0.1% formic acid over 5 s and held for an additional 25 s. Detection = UV-Vis (TWC).

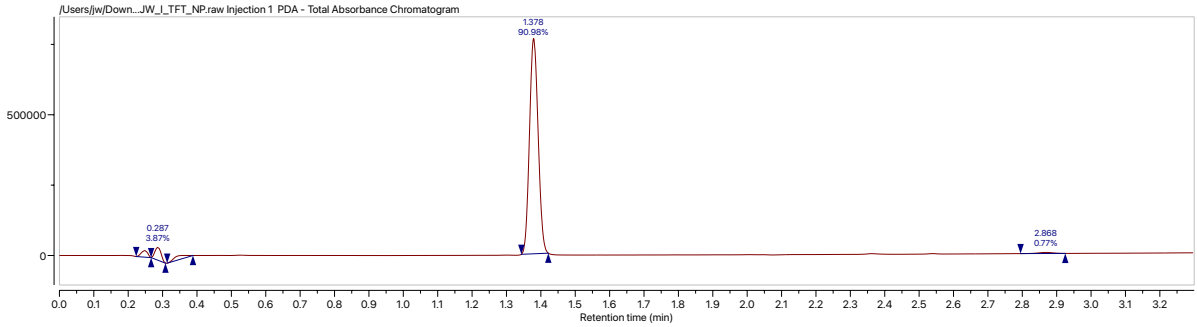


Figure S23: UPLC traces for TFT used in reaction. t_R (TFT) =1.37 min

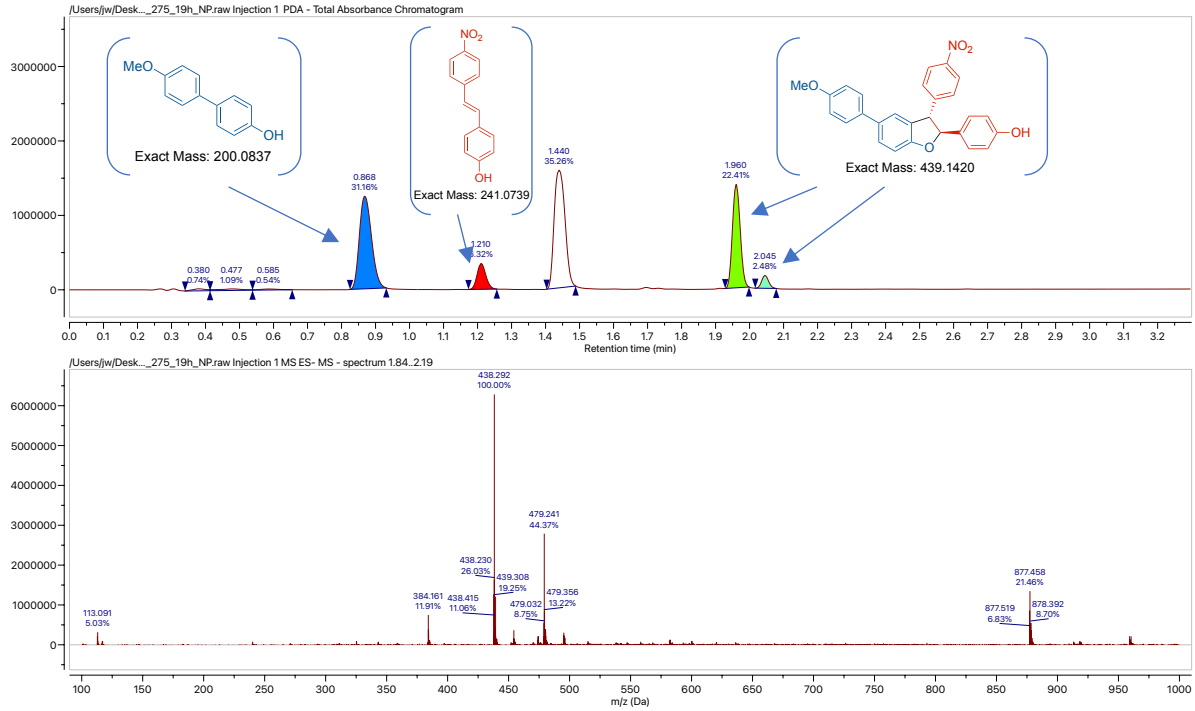


Figure S24: UPLCMS-ESI spectrum for the reaction of **3ig** without titanium dioxide after 19 hours. t_R (**1i**) =0.88 min, t_R (**2g**) =1.21 min, t_R (TFT) =1.43 min, t_R (**3ig**) =1.97 min. ESI-MS: t_R (**3ig**) =1.84-2.19 min, m/z=438.292.

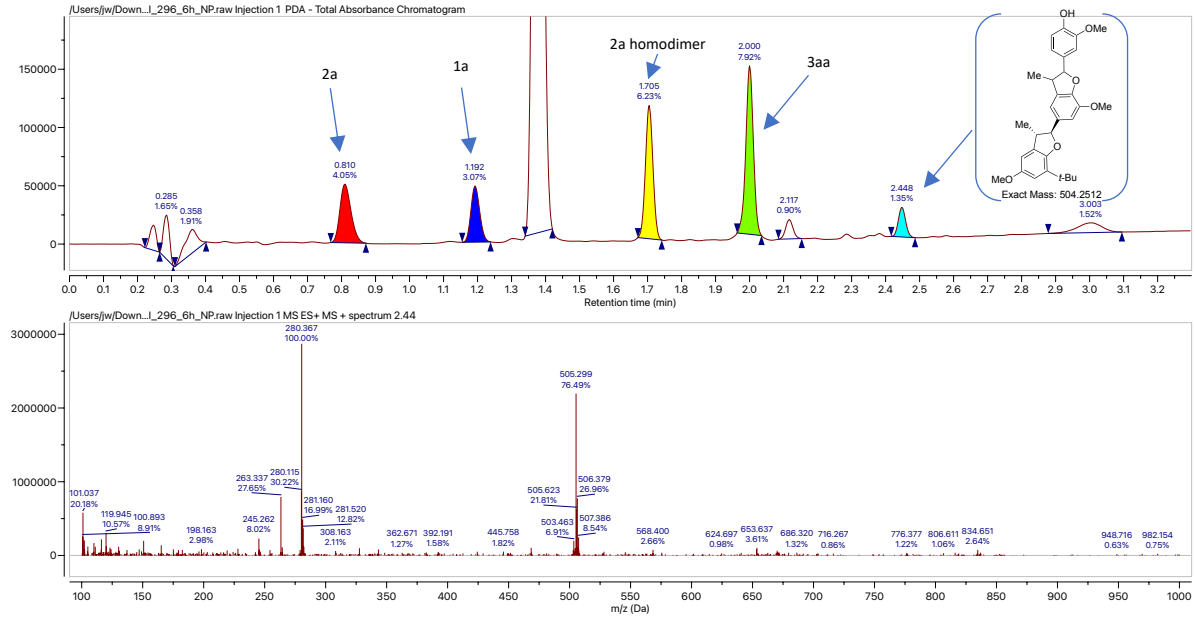


Figure S25: UPLCMS-ESI spectrum for the reaction of **3aa** without titanium dioxide after 6 hours. t_R (**2a**) =0.83 min, t_R (**1a**) =1.20 min, t_R (TFT) =1.37 min, t_R (**2a homodimer**) =1.70 min, t_R (**3aa**) =2.00 min, t_R (**over oxidized adduct**) =2.45 min. ESI$^+$MS: t_R (**over oxidized adduct**) =2.44 min, m/z=505.299.

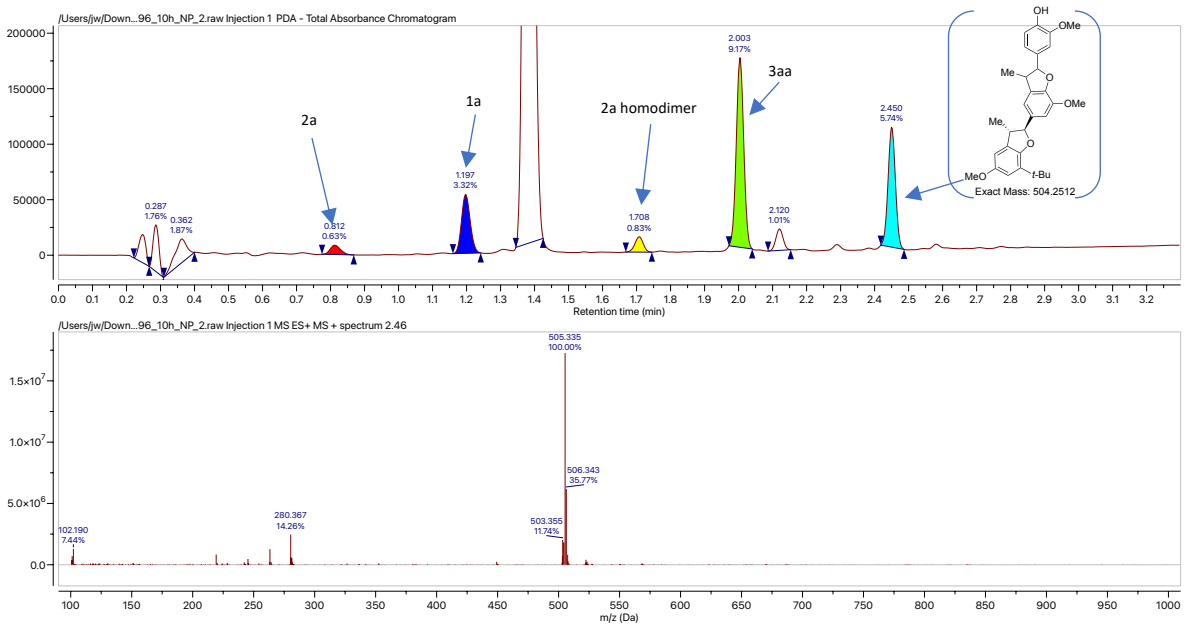


Figure S26: UPLCMS-ESI spectrum for the reaction of **3aa** without titanium dioxide after 10 hours. t_R (**2a**) =0.83 min, t_R (**1a**) =1.20 min, t_R (TFT) =1.38 min, t_R (**2a homodimer**) =1.70 min, t_R (**3aa**) =2.00 min, t_R (**over oxidized adduct**) =2.45 min. ESI^+MS: t_R (**over oxidized adduct**) =2.46 min, m/z=505.335.

Substrate Limitations:

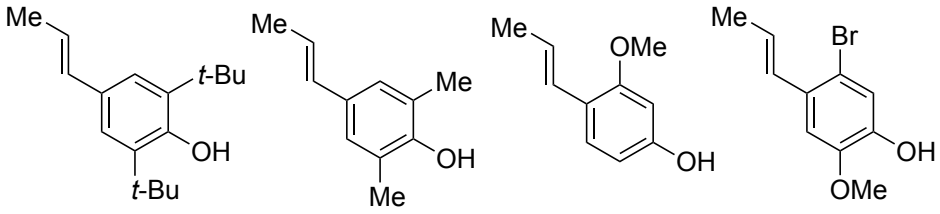
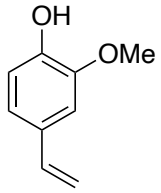


Figure S27: Alkenyl-phenol substrates that degraded rapidly under standard reaction conditions.

Characterization of Alkenyl Phenol Substrates



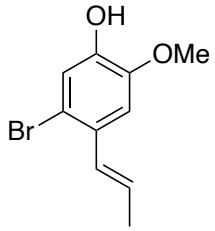
2-Methoxy-4-vinylphenol (2c)

General procedure A was followed using 4-hydroxy-3-methoxybenzaldehyde (1.0 g, 6.6 mmol, 1.0 equiv), KO*t*Bu (1.5 g, 13 mmol, 2.0 equiv), methyltriphenylphosphonium bromide (4.7 g, 13 mmol, 2.0 equiv), and dry THF (24 mL) for 12 h. Flash column chromatography (*n*-hexanes/EtOAc 95:5) afforded the product as a yellow oil (0.6 g, 3.9 mmol) in 60% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 – 6.84 (m, 3H), 6.64 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.66 (s, 1H), 5.60(dd, *J* = 17.5, 0.9 Hz, 1H), 5.13 (dd, *J* = 10.8, 0.9 Hz, 1H), 3.91 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ146.7, 145.8, 136.8, 130.4, 120.2, 114.5, 111.6, 108.2, 56.0.

Spectral data in agreement with those reported in *Chem. Eur. J.* **2013**, *19*, 9807–9810.[5]



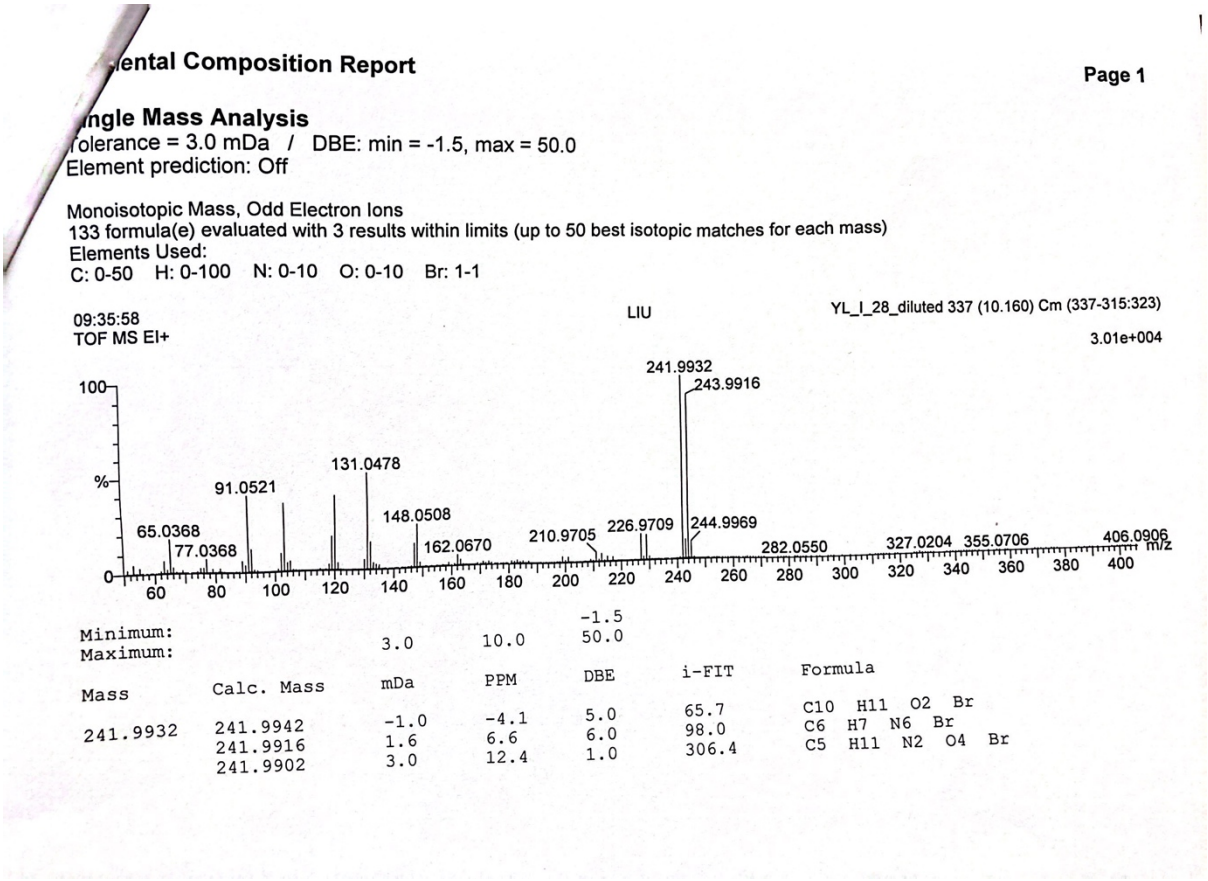
5-Bromo-2-methoxy-4-(prop-1-en-1-yl)phenol

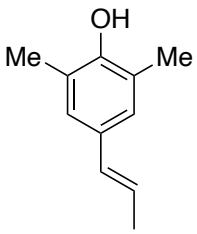
General procedure A was followed using 2-bromo-4-hydroxy-5-methoxybenzaldehyde (1.0 g, 4.3 mmol, 1.0 equiv), KO*t*Bu (1.0 g, 8.6 mmol, 2.0 equiv), ethyltriphenylphosphonium bromide (3.2 g, 8.6 mmol, 2.0 equiv), and dry THF (24 mL) for 12 h. Flash column chromatography (*n*-hexanes/EtOAc 85:15) afforded the product as a yellow oil (2:1 *E:Z*, 0.8 g, 3.1 mmol) in 72% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) *E*-isomer δ 7.15 (s, 1H), 6.79 (s, 1H), 6.41 (dd, *J* = 11.4, 1.8 Hz, 1H), 5.81 (dq, *J* = 11.4, 7.1 Hz, 1H), 5.63 (s, 1H), 3.87 (s, 3H), 1.79 (dd, *J* = 7.1, 1.8 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *E*-isomer δ 145.5, 145.2, 129.9, 129.5, 127.1, 118.5, 112.7, 108.5, 56.2, 14.5.

HRMS (EI-TOF) *m/z* 241.9942 calcd for $C_{10}H_{11}BrO_2$ $[M]^+$; found 241.9932.





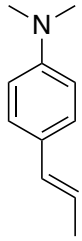
2,6-Dimethyl-4-(prop-1-en-1-yl)phenol

General procedure A was followed using 4-hydroxy-3,5-dimethylbenzaldehyde (3.0 g, 20 mmol, 1.0 equiv), KO*t*Bu (4.5 g, 40 mmol, 2.0 equiv), ethyltriphenylphosphonium bromide (14.8 g, 39.8 mmol, 2.00 equiv), and dry THF (48 mL) for 12 h. Flash column chromatography (*n*-hexanes/EtOAc 95:5) afforded the product as a yellow oil (6:1 *E:Z*, 2.7 g, 16.8 mmol) in 84% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) *E*-isomer δ 6.98 (s, 2H), 6.35 (dd, *J* = 11.9, 1.9 Hz, 1H), 5.70 (dq, *J* = 11.9, 7.2 Hz, 1H), 3.51 (s, 1H), 2.28 (s, 6H), 1.93 (dt, *J* = 7.2, 1.9 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *E*-isomer δ 151.0, 130.6, 129.3, 126.2, 124.8, 122.9, 16.1, 14.7.

Spectral data in agreement with those reported in *Chem. Commun*. **2020**, *56*, 7941-7944.[6]



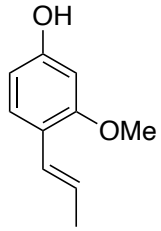
***N*,*N*-Dimethyl-4-(prop-1-en-1-yl)aniline (2f)**

General procedure A was followed using 4-(dimethylamino)benzaldehyde (2.00 g, 13.4 mmol, 1.00 equiv), KO*t*Bu (3.0 g, 27 mmol, 2.0 equiv), ethyltriphenylphosphonium bromide (9.9 g, 27 mmol, 2.0 equiv), and dry THF (48 mL) for 12 h. Flash column chromatography (*n*-hexanes/EtOAc 85:15) afforded the product as a yellow oil (3:1 *E:Z*, 1.3 g, 8.1 mmol) in 60% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) *E*-isomer δ 7.28 – 7.25 (m, 2H), 6.77 – 6.73 (m, 2H), 6.35 (dd, *J* = 11.6, 1.9 Hz, 1H), 5.65 (dq, *J* = 11.6, 7.2 Hz, 1H), 2.99 (s, 6H), 1.95 (dd, *J* = 7.2, 1.8 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *E*-isomer δ 149.3, 130.9, 129.9, 126.8, 123.5, 112.3, 40.7, 14.9.

Spectral data in agreement with those reported in *Org. Lett.* **2020**, *22*, 1193−1198.[7]



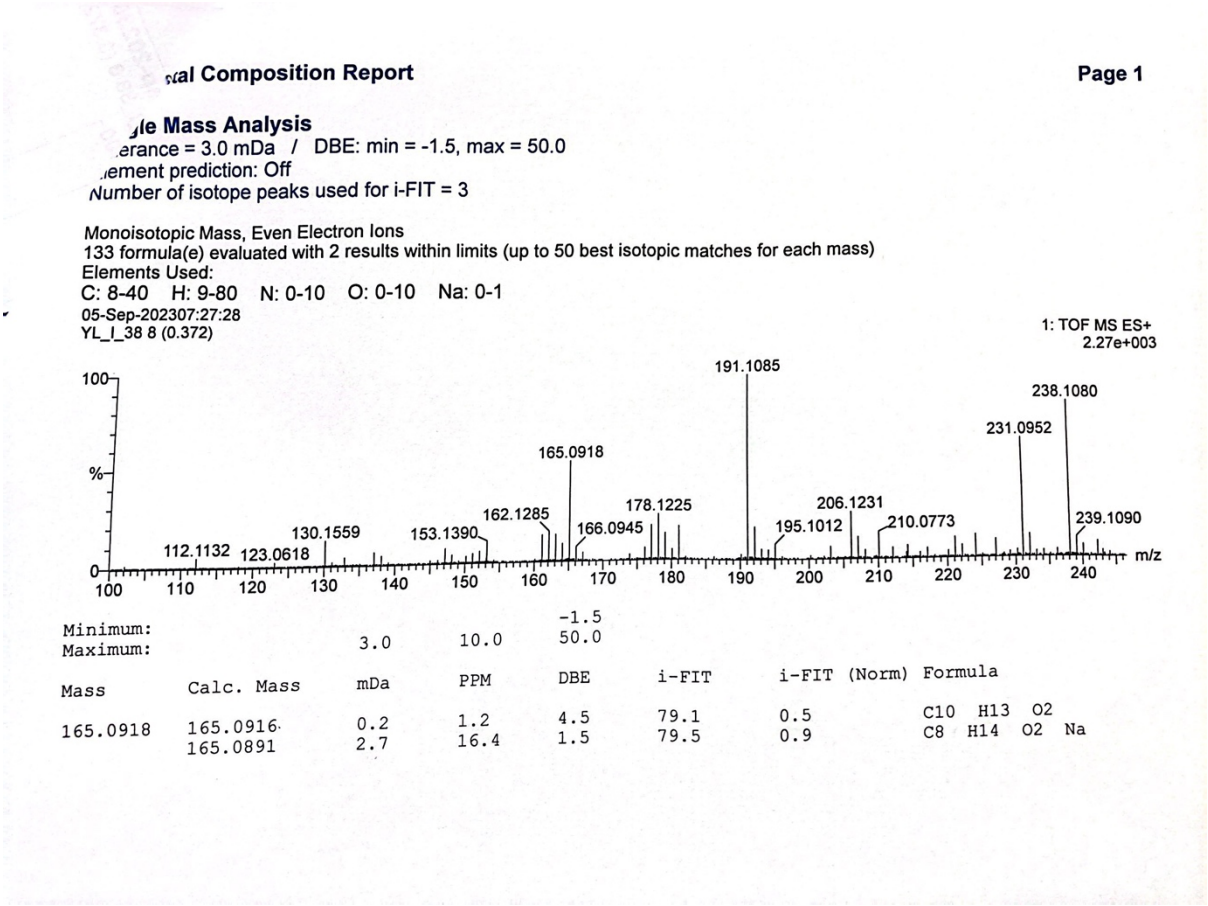
3-Methoxy-4-(prop-1-en-1-yl)phenol

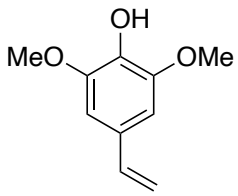
General procedure A was followed using 4-hydroxy-2-methoxybenzaldehyde (1.0 g, 6.6 mmol, 1.0 equiv), KO*t*Bu (1.5 g, 13 mmol, 2.0 equiv), ethyltriphenylphosphonium bromide (4.9 g, 13 mmol, 2.0 equiv), and dry THF (48 mL) for 12 h. Flash column chromatography (*n*-hexanes/EtOAc 90:10) afforded the product as a yellow oil (8:1 *E:Z*, 0.9 g, 5.5 mmol) in 84% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) *E*-isomer δ 7.12 (d, *J* = 8.1, 1H), 6.49 – 6.36 (m, 3H), 5.77 (dq, *J* = 11.5, 8.1, 7.0 Hz, 1H), 5.06 (s, 1H), 3.80 (s, 3H), 1.81 (dd, *J* = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *E*-isomer δ 158.3, 155.8, 130.8, 125.9, 124.8, 119.2, 106.5, 99.0, 55.6, 14.7.

HRMS (ESI-TOF) *m/z* 165.0916 calcd for $C_{10}H_{13}O_2$ $[M + H]^+$; found 165.0918.





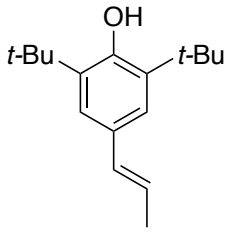
2,6-Dimethoxy-4-vinylphenol (2d)

General procedure A was followed using 2,6-dimethoxy-4-vinylphenol (2.0 g, 11 mmol, 1.0 equiv), KO*t*Bu (2.5 g, 22 mmol, 2.0 equiv), methyltriphenylphosphonium bromide (7.9 g, 11 mmol, 2.0 equiv), and dry THF (24 mL) for 12 h. Flash column chromatography (*n*-hexanes/EtOAc 80:20) afforded the product as a clear oil (1.0 g, 5.8 mmol) in 53% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 (s, 2H), 6.56 (dd, *J* = 17.5, 10.9, 1H), 5.67 (s, 1H), 5.58 (d, *J* = 17.5, 1H), 5.10 (d, *J* = 10.9 Hz, 1H), 3.82 (s, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.0, 136.7, 134.8, 129.0, 111.5, 103.0, 56.0.

Spectral data in agreement with those reported in *Eur. Polym. J.* **2020**, *125*, 109534.[8]



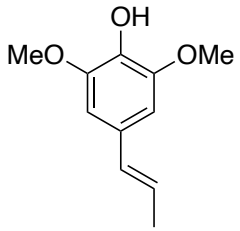
2,6-Di-*tert*-butyl-4-(prop-1-en-1-yl)phenol

General procedure A was followed using 3,5-di-tert-butyl-4-hydroxybenzaldehyde (2.0 g, 8.5 mmol, 1.0 equiv), KO*t*Bu (1.9 g, 17 mmol, 2.0 equiv), ethyltriphenylphosphonium bromide (6.3 g, 17 mmol, 2.0 equiv), and dry THF (24 mL) for 12 h. Flash column chromatography (*n*-hexanes/EtOAc 100:0) afforded the product as a yellow oil (4:1 *E:Z*, 1.4 g, 5.7 mmol) in 67% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) *E*-isomer δ 7.18 (s, 2H), 6.40 (dq, *J* = 11.6, 1.9 Hz, 1H), 5.69 (dd, *J* = 11.6, 7.1 Hz, 1H), 5.20 (s, 1H), 1.95 (dd, *J* = 7.2, 1.9 Hz, 3H), 1.48 (s, 18H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *E*-isomer δ 152.6, 135.6, 130.5, 129.0, 125.8, 124.3, 34.5, 30.5, 14.9.

Spectral data in agreement with those reported in *Chem. Commun*. **2020**, *56*, 7941-7944.[2]



2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol (2b)

General procedure A was followed using 4-hydroxy-3,5-dimethoxybenzaldehyde (1.0 g, 5.5 mmol, 1.0 equiv), KO*t*Bu (1.2 g, 11 mmol, 2.0 equiv), ethyltriphenylphosphonium bromide (4.0 g, 11 mmol, 2.0 equiv), and dry THF (24 mL) for 12 h. Flash column chromatography (*n*-hexanes/EtOAc 85:15) afforded product as a yellow oil (>20:1 *E:Z*, 0.6 g, 2.9 mmol)in 53% isolated yield.

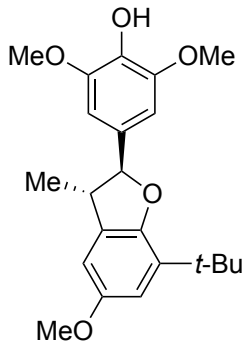
^{1}H NMR (400 MHz, $CDCl_3$) *E*-isomer δ 6.52 (s, 2H), 6.33 (dq, *J* = 11.6, 1.9 Hz, 1H), 5.68 (dq, *J* = 11.5, 7.2 Hz, 1H), 5.58 (s, 1H), 3.85 (s, 6H), 1.89 (dd, *J* = 7.2, 1.9 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *E*-isomer δ 146.7, 133.6, 129.9, 128.9, 125.3, 105.8, 56.2, 14.6.

Spectral data in agreement with those reported in *Angew. Chem. Int. Ed*. **2020**, *59*, 21930–21934.[9]

Characterization of products:

Unless stated in the substrate preparation section, all starting materials were obtained from commercially available sources.



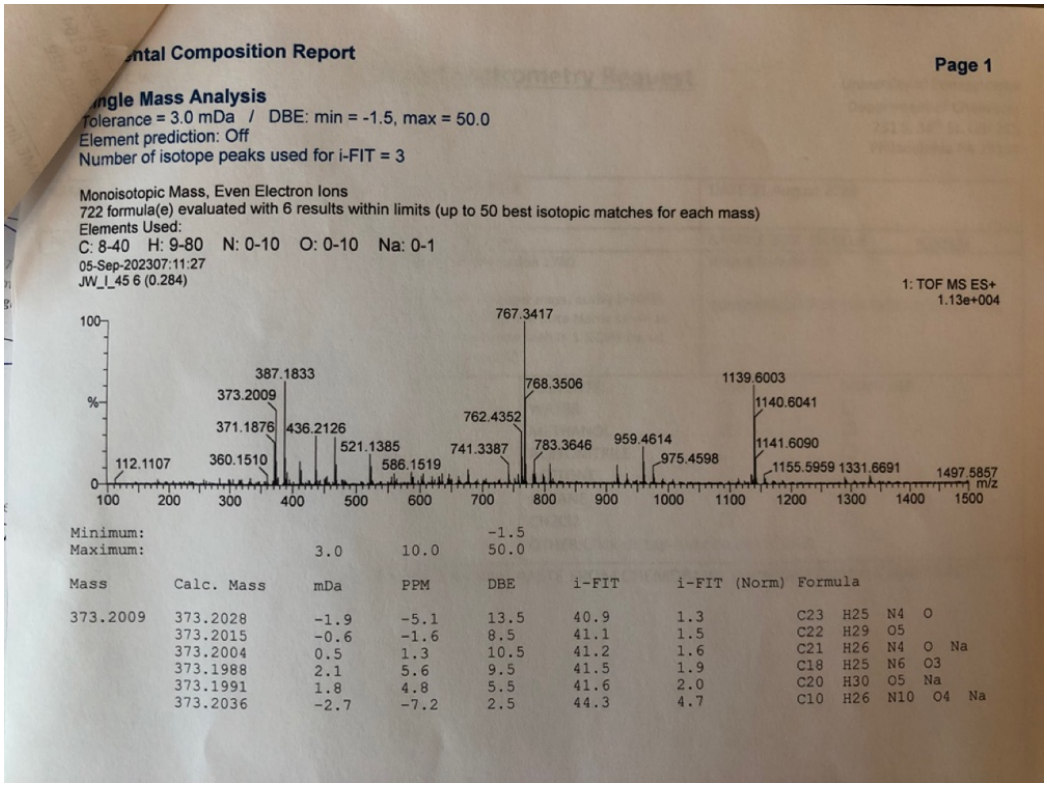
(±)-4-((2*S*,3*S*)-7-(*tert*-Butyl)-5-methoxy-3-methyl-2,3-dihydrobenzofuran-2-yl)-2,6-dimethoxyphenol (3ab)

General procedure C was followed using 2,6-dimethoxy-4-(prop-1-en-1-yl)phenol (**2b**) (0.56 mmol, 1.00 equiv), 2-*tert*-butyl-4-methoxyphenol (1.12 mmol, 2.00 equiv), TiO_2 (5.60 mmol, 10.0 equiv) and HFIP/TFT 1:1 mixture (4.00 mL, 0.14 M) for 7 h. General procedure D was used followed by flash column chromatography (*n*-hexane/EtOAc 85:15) to afford an orange oil (>20:1 dr, 0.15 g, 0.40 mmol)in 71% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (dd, *J* = 2.7, 0.8 Hz, 1H), 6.68 (s, 2H), 6.58 (dd, *J* = 2.7, 1.0 Hz, 1H), 5.58 (s, 1H), 5.07 (d, *J* = 9.0 Hz, 1H), 3.89 (s, 6H), 3.80 (s, 3H), 3.35 – 3.30 (quintet, *J* = 7.4 Hz, 1H), 1.42 (d, *J* = 6.8 Hz, 3H), 1.41 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.2, 151.1, 147.2, 134.5, 133.7, 133.0, 132.7, 111.7, 106.3, 102.7, 92.2, 56.4, 56.0, 46.2, 34.4, 29.3, 18.1.

HRMS (ESI-TOF) *m/z* 373.2005 calcd for $C_{22}H_{29}O_5$ $[M + H]^+$; found 373.2015.



ntal Composition Report

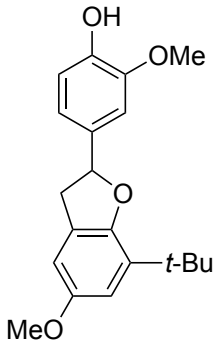
Page 1

ngle Mass Analysis
Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
722 formula(e) evaluated with 6 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 8-40 H: 9-80 N: 0-10 O: 0-10 Na: 0-1
05-Sep-202307:11:27
JW_I_45 6 (0.284)

1: TOF MS ES+
1.13e+004

Minimum:				-1.5			
Maximum:		3.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
373.2009	373.2028	-1.9	-5.1	13.5	40.9	1.3	C23 H25 N4 O
	373.2015	-0.6	-1.6	8.5	41.1	1.5	C22 H29 O5
	373.2004	0.5	1.3	10.5	41.2	1.6	C21 H26 N4 O Na
	373.1988	2.1	5.6	9.5	41.5	1.9	C18 H25 N6 O3
	373.1991	1.8	4.8	5.5	41.6	2.0	C20 H30 O5 Na
	373.2036	-2.7	-7.2	2.5	44.3	4.7	C10 H26 N10 O4 Na



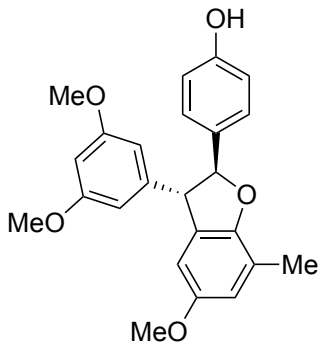
4-(7-(*tert*-Butyl)-5-methoxy-2,3-dihydrobenzofuran-2-yl)-2-methoxyphenol (3ac)

General procedure C was followed using 2-methoxy-4-vinylphenol (**2g**) (0.56 mmol, 1.00 equiv), 2-*tert*-butyl-4-methoxyphenol (1.12 mmol, 2.00 equiv), TiO_2 (5.60 mmol, 10.0 equiv) and HFIP/TFT mixture (4.00 mL, 0.14 M) for 6 h. General procedure D was used followed by flash column chromatography (*n*-hexane/EtOAc 8.5:1.5) to afford a yellow oil (>20:1 dr 0.03 g, 0.10 mmol)in 17% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 – 6.87 (m, 3H), 6.72 (d, *J* = 2.6 Hz, 1H), 6.64 (d, *J* = 2.6 Hz, 1H), 5.69 (dd, *J* = 9.4, 8.4 Hz, 1H), 5.62 (s, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 3.55 (ddt, *J* = 15.6, 9.5, 0.9 Hz, 1H), 3.12 (ddt, *J* = 15.5, 8.4, 1.0 Hz, 1H), 1.40 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.0, 151.7, 146.7, 145.3, 135.1, 133.6, 127.5, 118.8, 114.4, 111.8, 108.3, 107.4, 83.6, 56.1, 56.0, 39.3, 34.4, 29.4.

HRMS



(±)-4-(3-(3,5-Dimethoxyphenyl)-5-methoxy-7-methyl-2,3-dihydrobenzofuran-2-yl)phenol (3ce)

General procedure C was followed using pterostilbene (**2i**) (0.56 mmol, 1.00 equiv), 4-methoxy-2-methylphenol (1.12 mmol, 2.00 equiv), TiO_2 (5.60 mmol, 10.0 equiv) and HFIP/TFT 1:1 mixture (4.00 mL, 0.14 M) for 24 h. General procedure D was used followed by flash column chromatography (*n*-hexane/EtOAc 85:15) to afford a beige oil (>20:1 dr, 0.13 g, 0.33 mmol) in 59% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 6.64 (d, *J* = 2.5 Hz, 1H), 6.43 (d, *J* = 2.4 Hz, 1H), 6.40 (t, *J* = 2.3 Hz, 1H), 6.34 (d, *J* = 2.3 Hz, 2H), 5.44 (d, *J* = 8.6 Hz, 1H), 4.45 (d, *J* = 8.7 Hz, 1H), 3.75 (s, 6H), 3.72 (s, 3H), 2.30 (s, 3H).

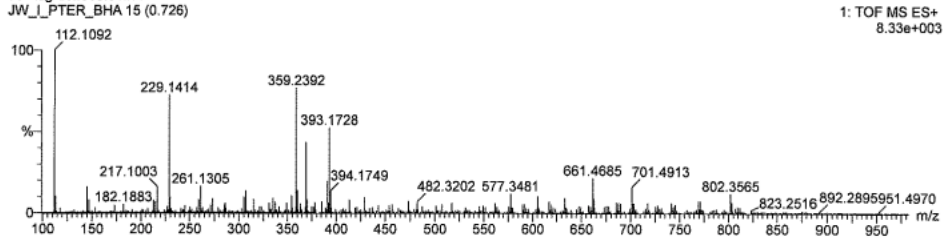
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.1, 155.8, 154.5, 152.6, 144.1, 133.0, 129.8, 127.8, 120.3, 116.0, 115.5, 108.1, 106.6, 99.1, 92.4, 58.9, 56.2, 55.5, 15.7.

HRMS (ESI-TOF) *m/z* 393.1702 calcd for $C_{24}H_{25}O_5$ $[M + H]^+$; found 393.1728.

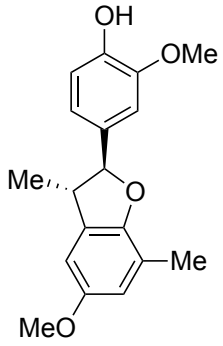
Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
253 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 8-40 H: 9-80 N: 0-5 O: 3-8 Na: 0-1
30-Aug-202308:31:22
JW_I_PTER_BHA 15 (0.726)



Minimum:				-1.5							
Maximum:		3.0	10.0	50.0							
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula				
393.1728	393.1702	2.6	6.6	12.5	38.8	0.0	C24	H25	O5		
	393.1750	-2.2	-5.6	5.5	42.5	3.8	C16	H26	N4	O6	Na



(±)-2-Methoxy-4-(5-methoxy-3,7-dimethyl-2,3-dihydrobenzofuran-2-yl)phenol (3ca)

General procedure C was followed using *iso*-eugenol (**2a**) (0.56 mmol, 1.00 equiv), 4-methoxy-2-methylphenol (1.12 mmol, 2.00 equiv), TiO_2 (5.60 mmol, 10.0 equiv) and HFIP/TFT 1:1 mixture (4.00 mL, 0.14 M) for 6 h. General procedure D was used followed by flash column chromatography (*n*-hexane/EtOAc 85:15) to afford a beige oil (>20:1 dr, 0.10 g, 0.32 mmol) in 57% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (t, *J* = 1.1 Hz, 1H), 6.92 (m, 2H), 6.57 (m, 2H), 5.03 (d, *J* = 9.4 Hz, 1H), 3.90 (s, 3H), 3.78 (s, 3H), 3.41 (m, 1H), 2.24 (s, 3H), 1.37 (d, *J* = 6.8 Hz, 3H).

^{13}C{^{1}H} NMR 101 MHz, $CDCl_3$) δ 154.3, 151.7, 146.7, 145.7, 132.7, 132.2, 120.0, 119.8, 114.6, 114.2, 108.7, 107.1, 92.7, 56.1, 56.0, 46.1, 17.4, 15.5.

HRMS (ESI-TOF) *m/z* 301.1416 calcd for $C_{18}H_{21}O_4$ $[M + H]^+$; found 301.1445.

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
172 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
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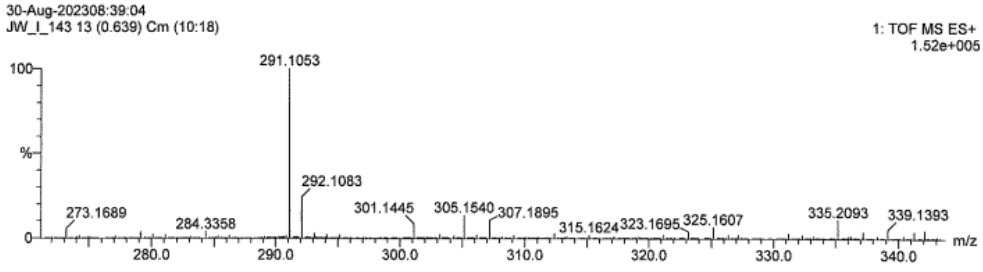
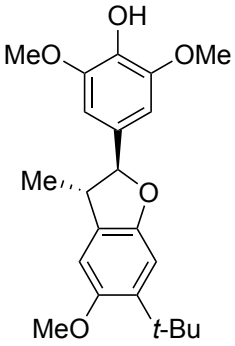
30-Aug-202308:39:04
JW_I_143 13 (0.639) Cm (10:18)



Minimum:				-1.5			
Maximum:		3.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
301.1445	301.1416	2.9	9.6	5.5	228.1	0.6	C16 H22 O4 Na
	301.1440	0.5	1.7	8.5	228.2	0.8	C18 H21 O4



(±)-4-(-6-(*tert*-Butyl)-5-methoxy-3-methyl-2,3-dihydrobenzofuran-2-yl)-2,6-dimethoxyphenol (3bb)

General procedure C was followed using 2,6-dimethoxy-4-(prop-1-en-1-yl)phenol (**2b**) (0.56 mmol, 1.00 equiv), 3-(*tert*-butyl)4-methoxyphenol (1.10 mmol, 2.00 equiv), TiO_2 (5.60 mmol, 10.0 equiv) and HFIP/TFT 1:1 mixture (4.00 mL, 0.14 M) for 12 h. General procedure D was used followed by flash column chromatography (*n*-hexane/EtOAc 85:15) to afford a beige yellow oil (>20:1 dr, 0.09 g, 0.24 mmol) in 43% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 1H), 6.72 (s, 1H), 6.69 (s, 2H), 5.02 (d, J = 9.6 Hz, 1H), 3.90 (s, 6H), 3.84 (s, 3H), 3.43 (quintet, J = 8.3 Hz, 1H), 1.41 (d, J = 6.8 Hz, 3H), 1.38 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.6, 152.8, 147.2, 138.7, 134.8, 131.8, 129.2, 108.1, 108.0, 103.2, 93.4, 56.5, 56.1, 46.1, 35.1, 29.9, 17.4.

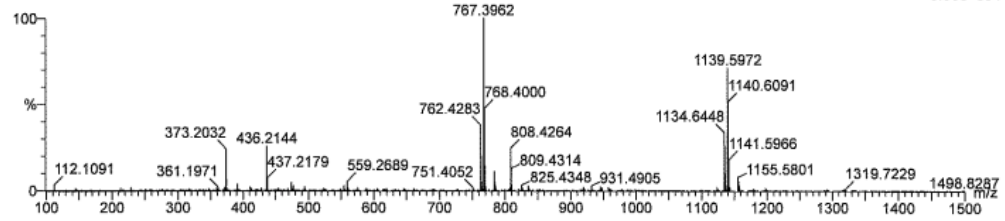
HRMS (ESI-TOF) *m/z* 373.2015 calcd for $C_{22}H_{29}O_5$ $[M + H]^+$; found 373.2032.

Elemental Composition Report **Page 1**

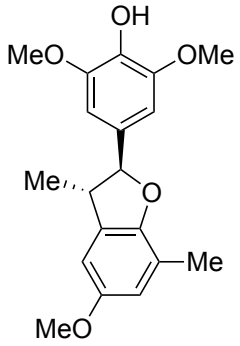
Single Mass Analysis
Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
241 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 8-40 H: 9-80 N: 0-5 O: 3-8 Na: 0-1
30-Aug-202308:35:24
JW_I_155 12 (0.596)

1: TOF MS ES+
5.36e+004



Minimum:				-1.5			
Maximum:		3.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
373.2032	373.2015	1.7	4.6	8.5	62.5	0.0	C22 H29 O5



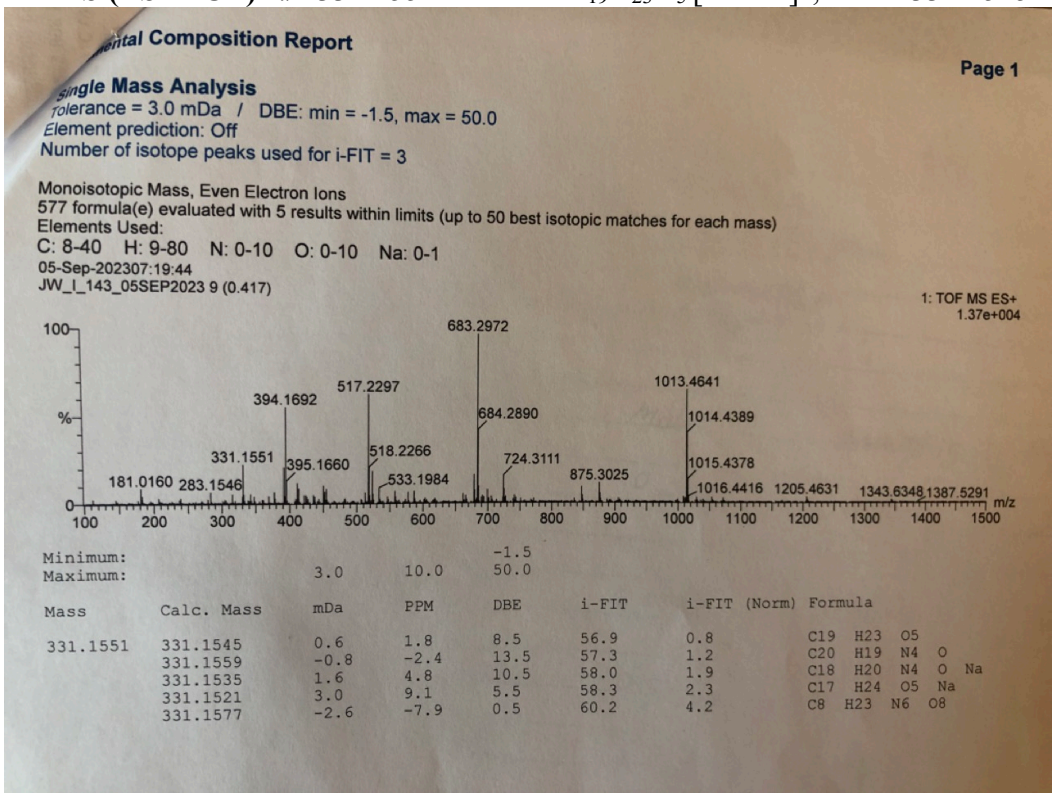
(±)-2,6-Dimethoxy-4-(5-methoxy-3,7-dimethyl-2,3-dihydrobenzofuran-2-yl)phenol (3cb)

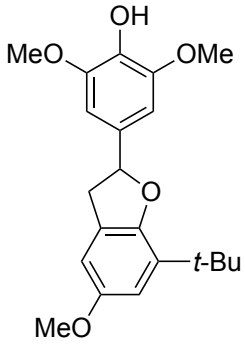
General procedure C was followed using 2,6-dimethoxy-4-(prop-1-en-1-yl)phenol (**2b**) (0.56 mmol, 1.00 equiv), 2-methyl-4-methoxyphenol (1.12 mmol, 2.00 equiv), TiO_2 (5.60 mmol, 10.0 equiv) and HFIP/TFT 1:1 mixture (4.00 mL, 0.14 M) for 12 h. General procedure D was used followed by flash column chromatography (*n*-hexane/EtOAc 85:15) to afford a beige yellow oil (>20:1 dr, 0.11 g, 0.34 mmol) in 60% isolated yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.68 (s, 2H), 6.57 (s, 1H), 6.56 (s, 1H), 5.54 (s, 1H), 5.00 (d, *J* = 9.5 Hz, 1H), 3.90 (s, 6H), 3.77 (s, 3H), 3.41 (quintet, *J* = 8.2 Hz, 1H), 1.37 (d, *J* = 6.8 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 154.5, 151.7, 147.2, 134.9, 132.2, 131.9, 120.1, 114.8, 107.1, 103.4, 93.1, 56.5, 56.2, 46.3, 17.6, 15.7.

HRMS (ESI-TOF) *m/z* 331.1551 calcd for $C_{19}H_{23}O_5$ [M + H]$^+$; found 331.1545.





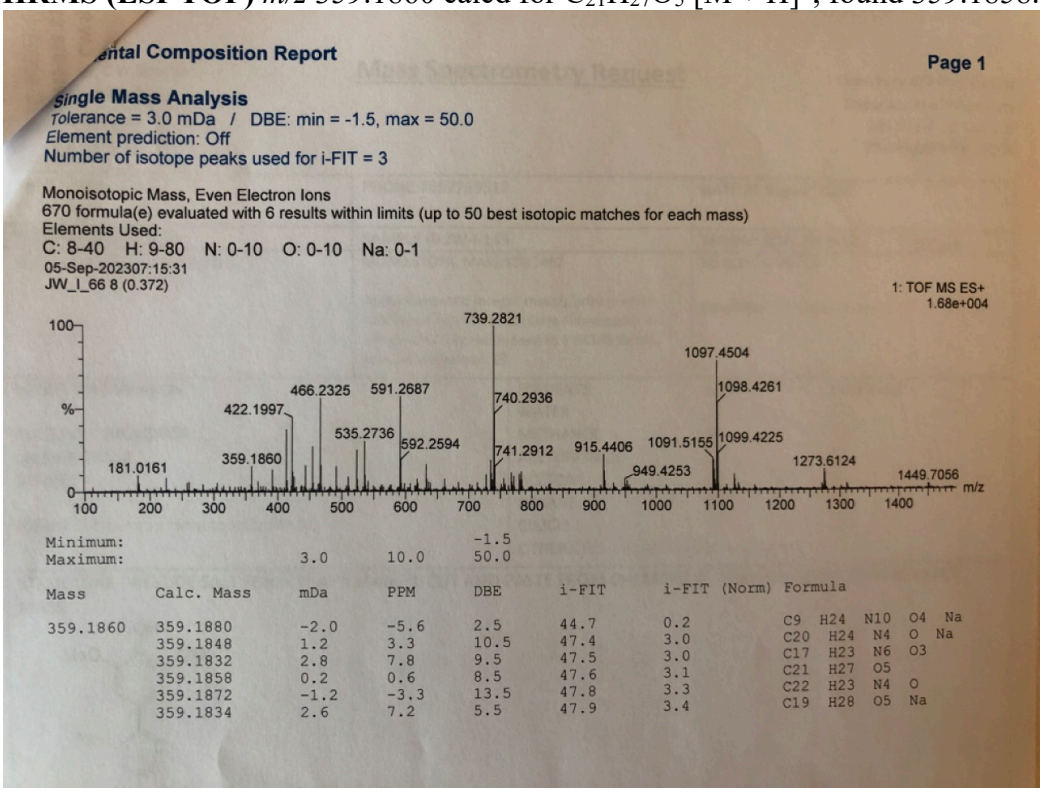
(±)-4-(7-(*tert*-Butyl)-5-methoxy-2,3-dihydrobenzofuran-2-yl)-2,6-dimethoxyphenol (3ad)

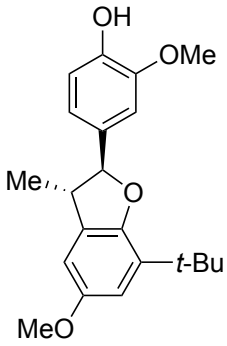
General procedure C was followed using 2,6-dimethoxy-4-vinylphenol (**2f**) (0.56 mmol, 1.00 equiv), 2-*tert*-butyl-4-methoxyphenol (1.12 mmol, 2.00 equiv), TiO_2 (5.60 mmol, 10.0 equiv) and HFIP/TFT 1:1 mixture (4.00 mL, 0.14 M) for 7 h. General procedure B was used followed by flash column chromatography (*n*-hexane/EtOAc 85:15) to afford a beige yellow oil (0.08 g, 0.21 mmol) in 37% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (d, *J* = 2.6 Hz, 1H), 6.63 (d, *J* = 2.6 Hz, 1H), 6.62 (s, 2H), 5.68 (dd, *J* = 9.5, 8.1 Hz, 1H), 5.47 (s, 1H), 3.86 (s, 6H), 3.77 (s, 3H), 3.56 (ddt, *J* = 15.5, 9.5, 0.9 Hz, 1H), 3.10 (ddt, *J* = 15.5, 8.1, 1.0 Hz, 1H), 1.40 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.1, 151.7, 147.2, 134.4, 134.3, 133.6, 127.3, 111.8, 107.5, 102.4, 83.8, 56.4, 56.1, 39.5, 34.4, 29.4.

HRMS (ESI-TOF) *m/z* 359.1860 calcd for $C_{21}H_{27}O_5$ $[M + H]^+$; found 359.1858.





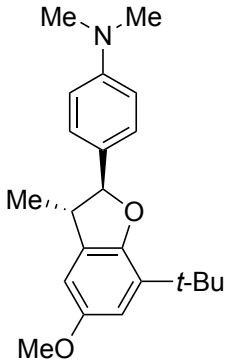
(±)-4-(7-(*tert*-Butyl)-5-methoxy-3-methyl-2,3-dihydrobenzofuran-2-yl)-2-methoxyphenol (3aa)

General procedure C was followed using *iso*-eugenol (**2a**) (0.56 mmol, 1.00 equiv), 2-*tert*-butyl-4-methoxyphenol (1.12 mmol, 2.00 equiv), TiO_2 (5.60 mmol, 10.0 equiv) and HFIP/TFT 1:1 mixture (4.00 mL, 0.14 M) for 6 h. General procedure B was used followed by flash column chromatography (*n*-hexane/EtOAc 85:15) to afford a beige yellow oil (>20:1 dr, 0.13 g, 0.37 mmol) in 66% isolated yield.

For 1g scale reaction: general procedure C was followed using *iso*-eugenol (**2a**) (5.60 mmol, 1.00 equiv), 2-*tert*-butyl-4-methoxyphenol (11.2 mmol, 2.00 equiv), TiO_2 (56.0 mmol, 10.0 equiv) and HFIP/TFT 1:1 mixture (43 mL, 0.14 M) for 16 h. General procedure B was used followed by flash column chromatography (*n*-hexane/EtOAc 85:15) to afford a beige yellow oil (>20:1 dr, 0.773 g, 2.18 mmol) in 39% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 1.3 Hz, 1H), 6.92 (m, 2H), 6.73 (dd, *J* = 2.7, 1.0 Hz, 1H), 6.57 (dd, *J* = 2.7, 1.1 Hz, 1H), 5.60 (s, 1H), 5.06 (d, *J* = 9.2 Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H), 3.34 – 3.26 (m, 1H), 1.40 (d, *J* = 7.0 Hz, 3H), 1.39 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.2, 151.3, 146.8, 145.6, 133.9, 133.8, 132.9, 119.2, 114.3, 111.7, 108.4, 106.3, 92.1, 56.1, 56.0, 46.1, 34.4, 29.4, 17.9.



(±)-4-(7-(*tert*-Butyl)-5-methoxy-3-methyl-2,3-dihydrobenzofuran-2-yl)-*N*,*N*-dimethylaniline (3af)

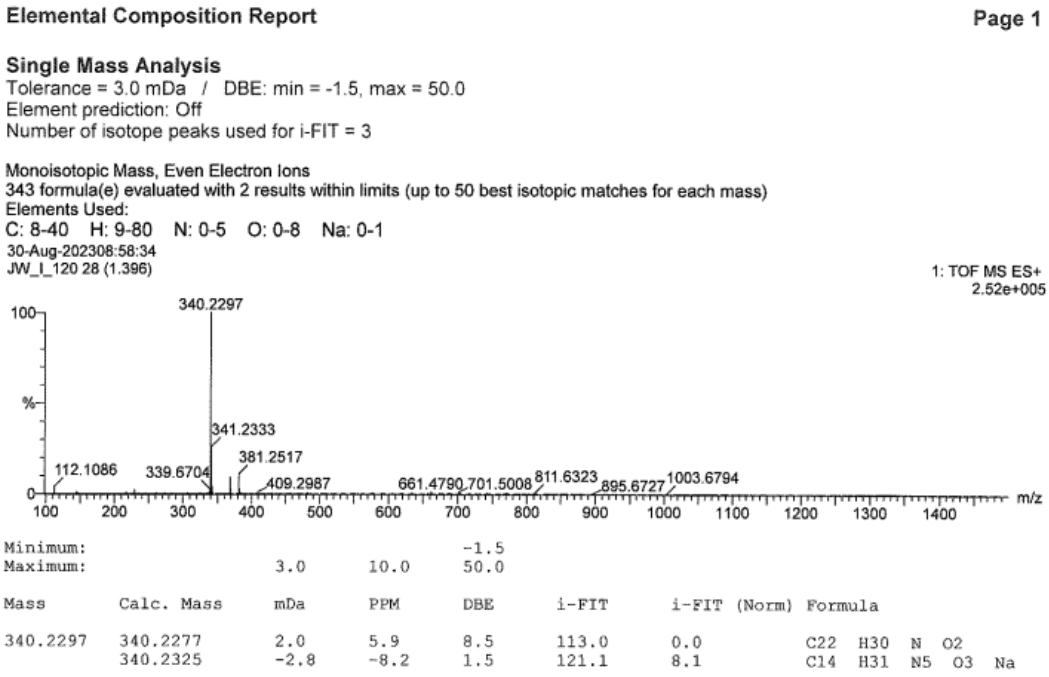
General procedure C was followed using *N*,*N*-dimethyl-4-(prop-1-en-1-yl)aniline (**2h**) (0.56 mmol, 1.00 equiv), 2-*tert*-butyl-4-methoxyphenol (1.12 mmol, 2.00 equiv), TiO_2 (5.60 mmol, 10.0 equiv) and HFIP/TFT 1:1 mixture (4.00 mL, 0.14 M) for 8 h. General procedure B was

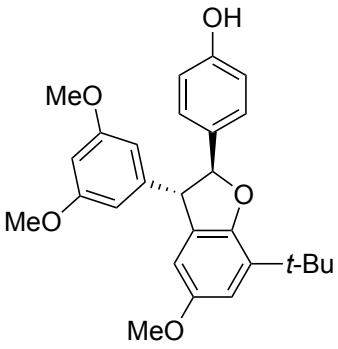
used followed by flash column chromatography (*n*-hexane/EtOAc 95:5) to afford a beige amorphous solid (7:3 dr, 0.12 g, 0.34 mmol) in 61% isolated yield.

^{1}H NMR (600 MHz, $CDCl_3$) major diastereomer δ 7.33 (t, *J* = 8.7 Hz, 2H), 6.81 – 6.77 (m, 2H), 6.72 – 6.71 (m, 1H), 6.57 (dd, *J* = 2.7, 1.1 Hz, 1H), 5.05 (d, *J* = 9.5 Hz, 1H), 3.80 (s, 3H), 3.38 – 3.27 (m, 1H), 2.98 (s, 6H), 1.40 (d, *J* = 8.1 Hz, 3H), 1.38 (s, 9H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 154.0, 151.5, 133.6, 133.2, 127.5, 127.3, 111.4, 107.0, 106.2, 92.3, 87.5, 56.1, 45.8, 41.3, 34.4, 29.4, 17.6.

HRMS (ESI-TOF) *m/z* 340.2297 calcd for $C_{22}H_{30}NO_5$ $[M + H]^+$; found 340.2277.





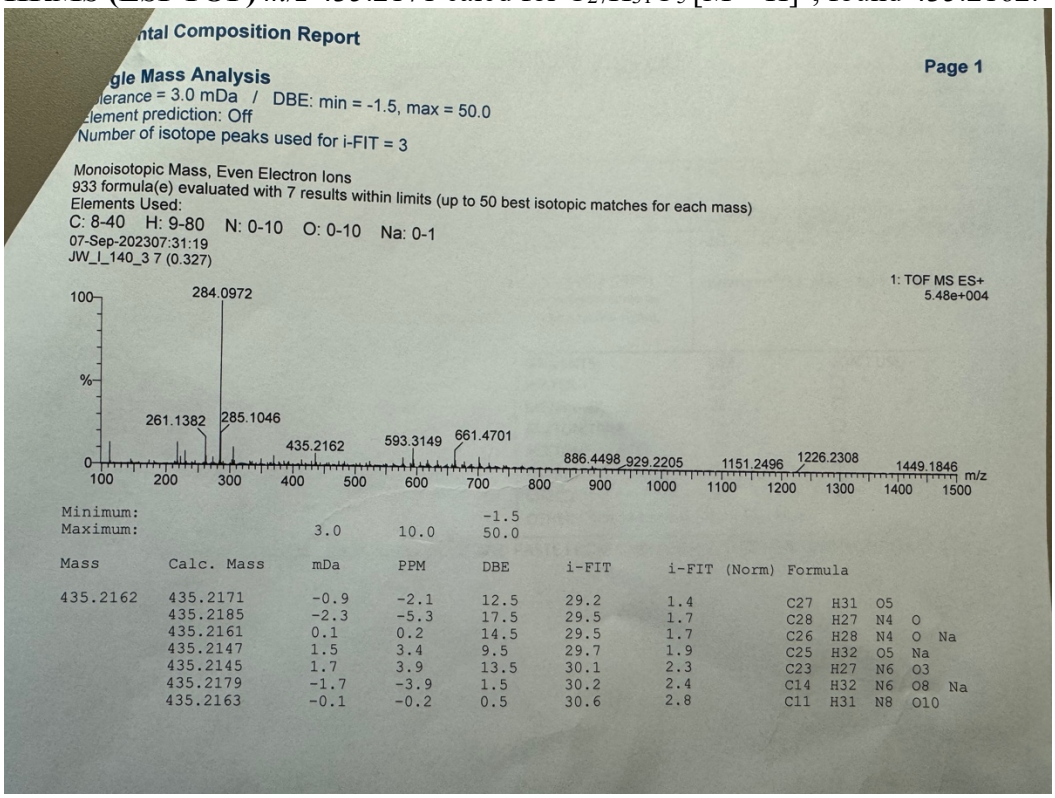
(±)-4-(7-(*tert*-Butyl)-3-(3,5-dimethoxyphenyl)-5-methoxy-2,3-dihydrobenzofuran-2-yl)phenol (3ae)

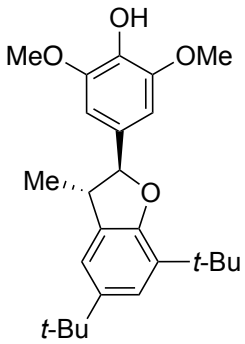
General procedure C was followed using pterostilbene (**2e**) (0.56 mmol, 1.00 equiv), 2-*tert*-butyl-4-methoxyphenol (1.12 mmol, 2.00 equiv), TiO_2 (5.60 mmol, 10.0 equiv) and HFIP/TFT 1:1 mixture (4.00 mL, 0.14 M) for 24 h. General procedure B was used followed by flash column chromatography (*n*-hexane/EtOAc 85:15) to afford a beige oil (>20:1 dr, 0.19 g, 0.44 mmol) in 79% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 6.76 (dd, *J* = 2.7, 0.9 Hz, 1H), 6.42 – 6.36 (m, 2H), 6.32 (d, *J* = 2.3 Hz, 2H), 5.45 (d, *J* = 8.5 Hz, 1H), 4.33 (d, *J* = 8.5 Hz, 1H), 3.75 (s, 6H), 3.70 (s, 3H), 1.42 (s, 9H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 161.2, 155.4, 154.4, 152.0, 144.5, 134.1, 130.7, 127.4, 115.4, 112.8, 107.2, 106.6, 99.1, 92.0, 58.8, 56.1, 55.5, 34.5, 29.7, 29.4.

HRMS (ESI-TOF) *m/z* 435.2171 calcd for $C_{27}H_{31}O_5$ $[M + H]^+$; found 435.2162.





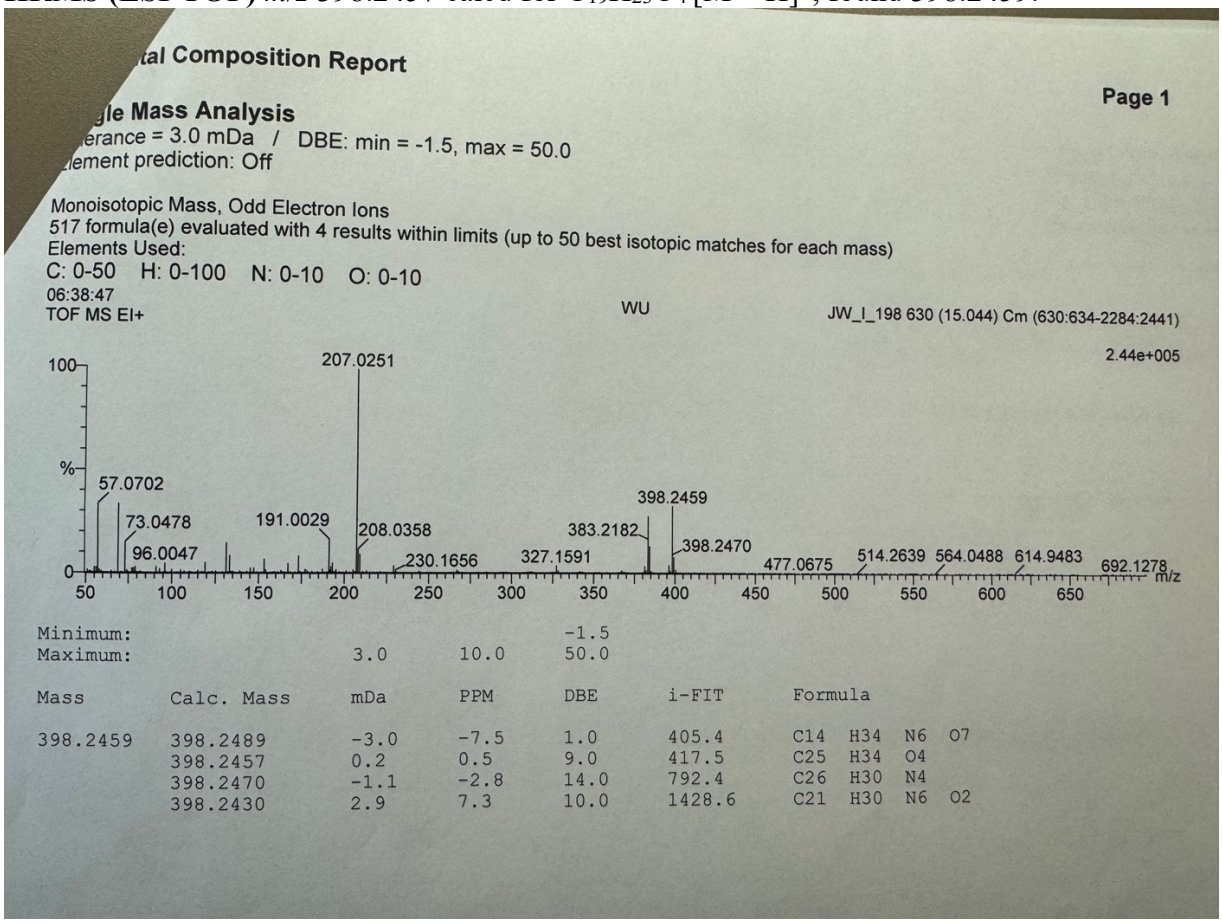
(±)-4-(5,7-Di-*tert*-butyl-3-methyl-2,3-dihydrobenzofuran-2-yl)-2,6-dimethoxyphenol (3db)

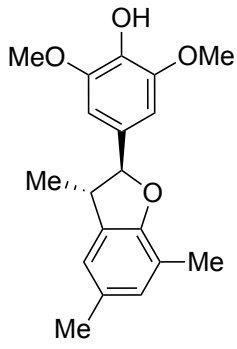
General procedure C was followed using 2,6-dimethoxy-4-(prop-1-en-1-yl)phenol (**2b**), 2,4-di-*tert*-butylphenol (0.56 mmol, 1.00 equiv), (1.12 mmol, 2.00 equiv), TiO_2 (5.60 mmol, 10.0 equiv) and HFIP/TFT 1:1 mixture (4.00 mL, 0.14 M) for 12 h. General procedure B was used followed by flash column chromatography (*n*-hexane/EtOAc 80:20) to afford a beige amorphous solid (>20:1 dr, 0.05 g, 0.13 mmol) in 24% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 2.1, 0.8 Hz, 1H), 7.02 (dd, *J* = 2.1, 1.1 Hz, 1H), 6.69 (s, 2H), 5.06 (d, *J* = 9.5 Hz, 1H), 3.89 (s, 6H), 3.33 (ddt, *J* = 9.5, 7.7, 6.2 Hz, 1H), 1.44 (d, *J* = 6.8 Hz, 3H), 1.42 (s, 9H),1.34 (s, 9H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 154.9, 147.2, 143.5, 134.5, 133.0, 132.0, 131.7, 122.2, 118.1, 102.8, 92.4, 56.4, 46.0, 34.7, 34.5, 32.0, 29.6, 17.8.

HRMS (ESI-TOF) *m/z* 398.2457 calcd for $C_{19}H_{23}O_4$ $[M + H]^+$; found 398.2459.





(±)-2,6-Dimethoxy-4-(3,5,7-trimethyl-2,3-dihydrobenzofuran-2-yl)phenol (3eb)

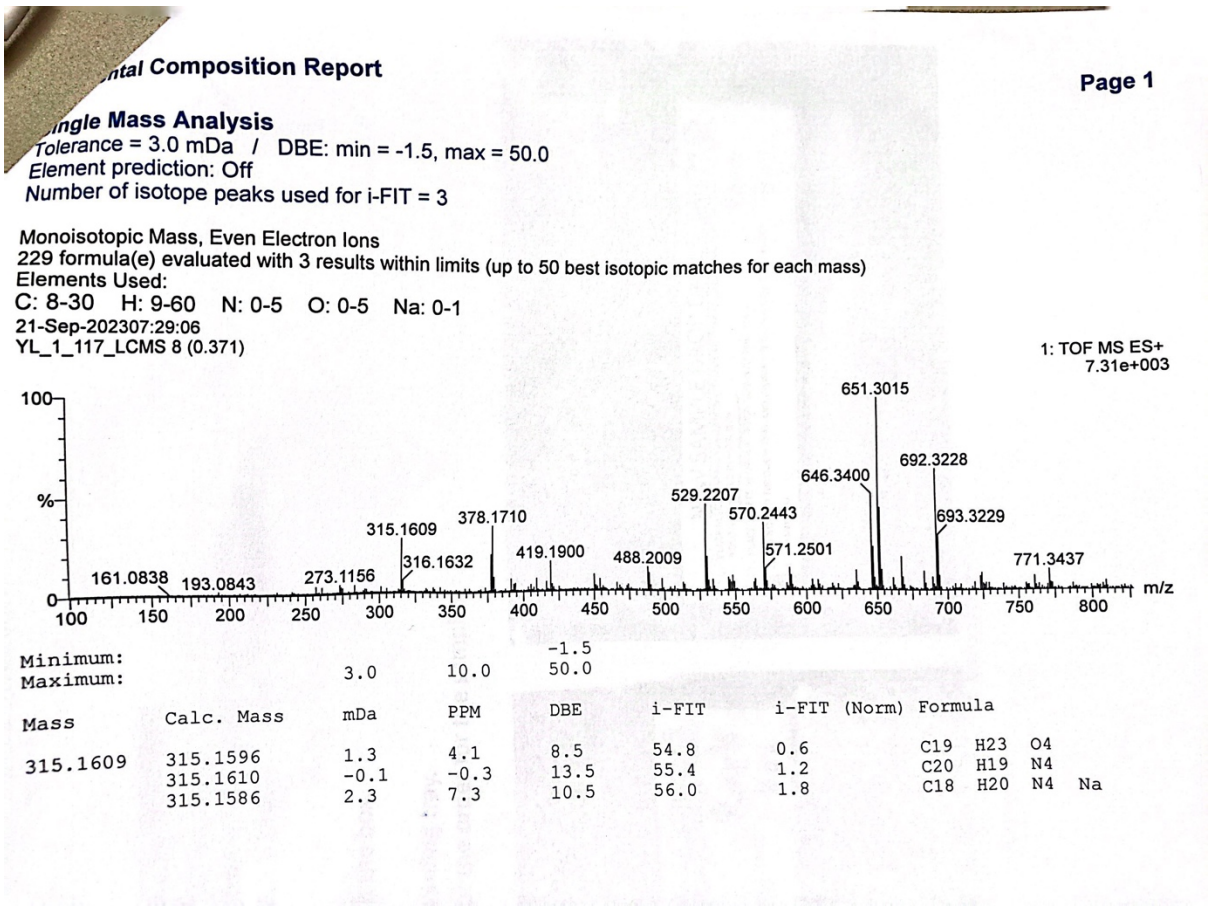
General procedure C was followed using 2,6-dimethoxy-4-(prop-1-en-1-yl)phenol (**2b**) (0.56 mmol, 1.00 equiv), 2,4-dimethyphenol (1.12 mmol, 2.00 equiv), TiO_2 (5.60 mmol, 10.0 equiv) and HFIP/TFT 1:1 mixture (4.00 mL, 0.14 M) for 12 h. General procedure B was used followed

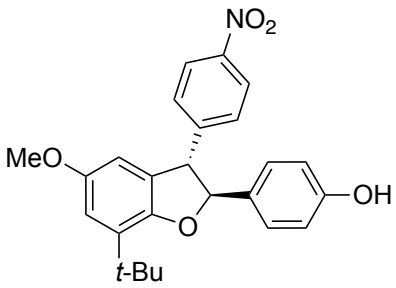
by flash column chromatography (*n*-hexane/EtOAc 80:20) to afford a beige amorphous solid (>20:1 dr, 0.05 g, 0.18 mmol) in 32% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 1H), 6.79 (s, 1H), 6.67 (s, 2H), 5.52 (s, 1H), 5.01 (d, J = 9.5 Hz, 1H), 3.89 (s, 6H), 3.41 (dq, J = 9.5, 6.6 Hz, 1H), 2.29 (s, 3H), 2.23 (s, 3H), 1.38 (d, J = 6.8 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 155.5, 147.2, 134.8, 132.0, 131.4, 130.2 (2), 121.5, 119.4, 103.4, 93.0, 56.5, 46.0, 20.9, 17.7, 15.4.

HRMS (ESI-TOF) *m/z* 314.1596 calcd for $C_{19}H_{23}O_4$ $[M + H]^+$; found 314.1609.





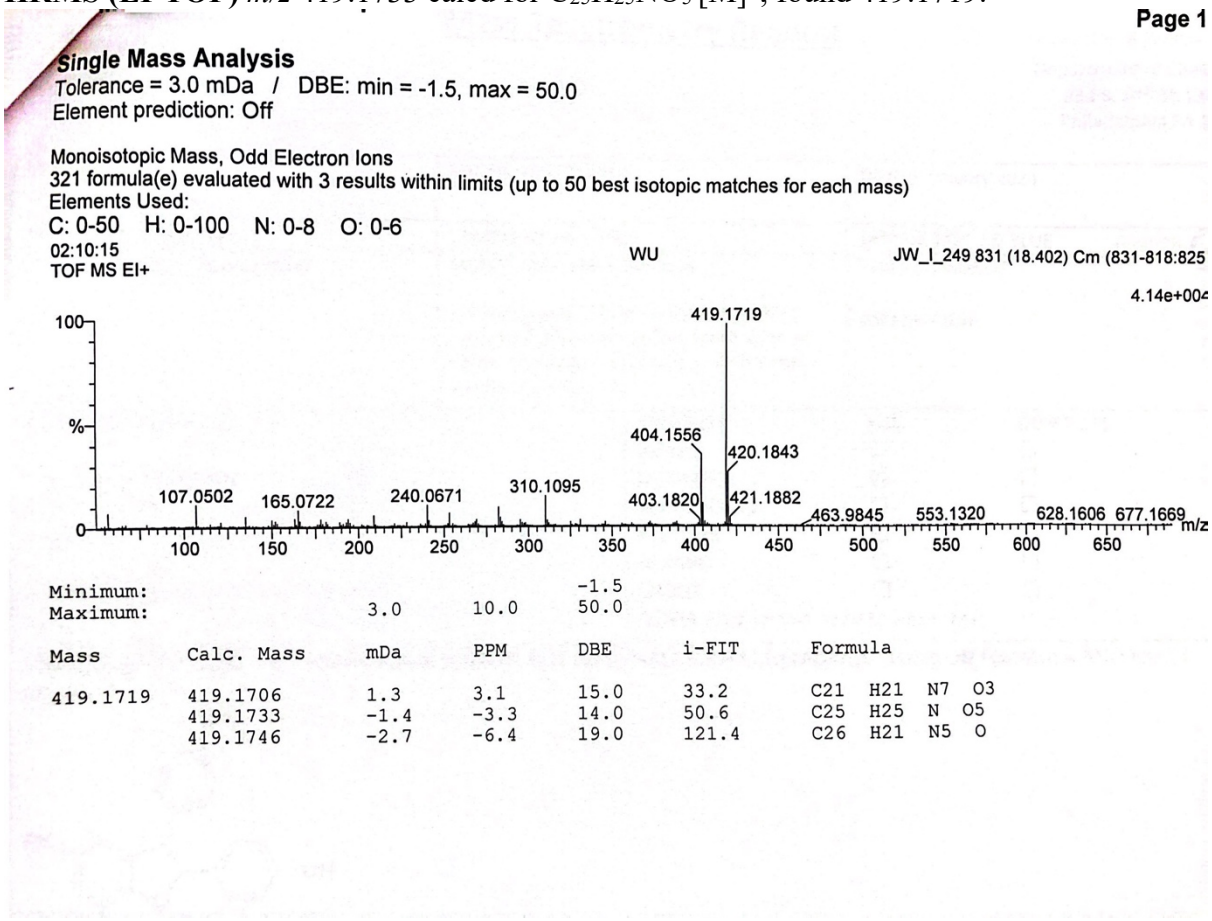
(±)-4-(-7-(*tert*-Butyl)-5-methoxy-3-(4-nitrophenyl)-2,3-dihydrobenzofuran-2-yl)phenol (3ag)

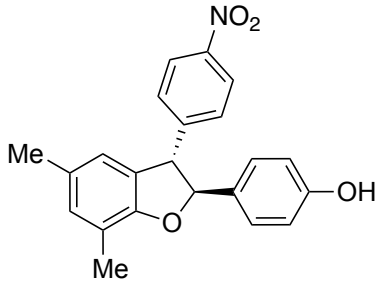
General procedure C was followed using 4-hydroxy-4'-nitrostilbene (**2g**) (0.60 mmol, 1.00 equiv), 2-*tert*-butyl-4-methoxyphenol (0.60 mmol, 1.00 equiv), TiO_2 (6.00 mmol, 10.0 equiv) and HFIP/TFT 5:1 mixture (6.00 mL, 0.1 M) for 24 h. General procedure B was used followed by flash column chromatography (*n*-hexane/EtOAc 80:20) to afford a yellow oil (>20:1 dr, 0.17 g, 0.41 mmol) in 69% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.85 – 6.79 (m, 3H), 6.30 (dd, *J* = 2.7, 1.0 Hz, 1H), 5.41 (d, *J* = 8.6 Hz, 1H), 4.54 (d, *J* = 8.6 Hz, 1H), 3.70 (s, 3H), 1.42 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 154.6, 152.1, 149.5, 147.4, 134.6, 132.9, 129.7, 129.5, 127.4, 124.3, 115.7, 113.3, 106.9, 92.1, 58.6, 56.0, 34.6, 29.4.

HRMS (EI-TOF) *m/z* 419.1733 calcd for $C_{25}H_{25}NO_5$ $[M]^+$; found 419.1719.





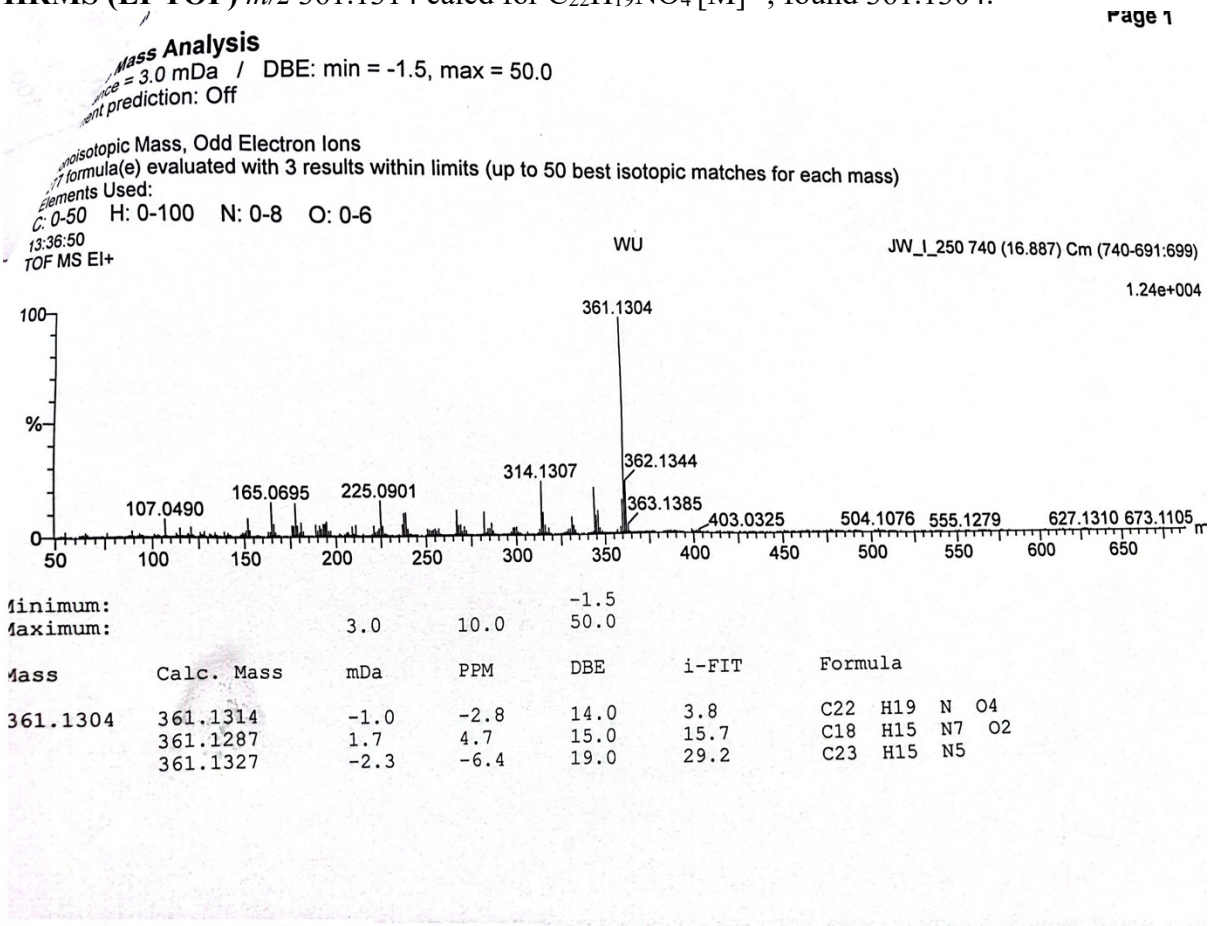
(±)-4-(-5,7-Dimethyl-3-(4-nitrophenyl)-2,3-dihydrobenzofuran-2-yl)phenol (3eg)

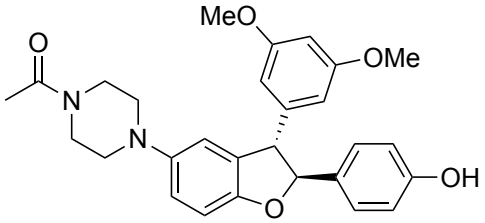
General procedure C was followed using 4-hydroxy-4'-nitrostilbene (**2g**) (0.60 mmol, 1.00 equiv), 2,4-dimethyphenol (0.60 mmol, 1.00 equiv), TiO_2 (6.00 mmol, 10.0 equiv) and HFIP/TFT 5:1 mixture (6.00 mL, 0.1 M) for 24 h. General procedure B was used followed by flash column chromatography (*n*-hexane/EtOAc 80:20) to afford a yellow oil (>20:1 dr, 0.14 g, 0.39 mmol) in 65% isolated yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.90 (s, 1H), 6.82 (d, *J* = 8.5 Hz, 2H), 6.57 (s, 1H), 5.39 (d, *J* = 8.5 Hz, 1H), 5.00 (s, 1H), 4.62 (d, *J* = 8.5 Hz, 1H), 2.29 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 155.9, 149.7, 147.3, 132.5, 131.4, 130.9, 129.4, 128.3, 127.8, 124.2, 122.8, 119.9, 115.8, 92.3, 58.5, 20.9, 15.5.

HRMS (EI-TOF) *m/z* 361.1314 calcd for $C_{22}H_{19}NO_4$ $[M]^+$; found 361.1304.





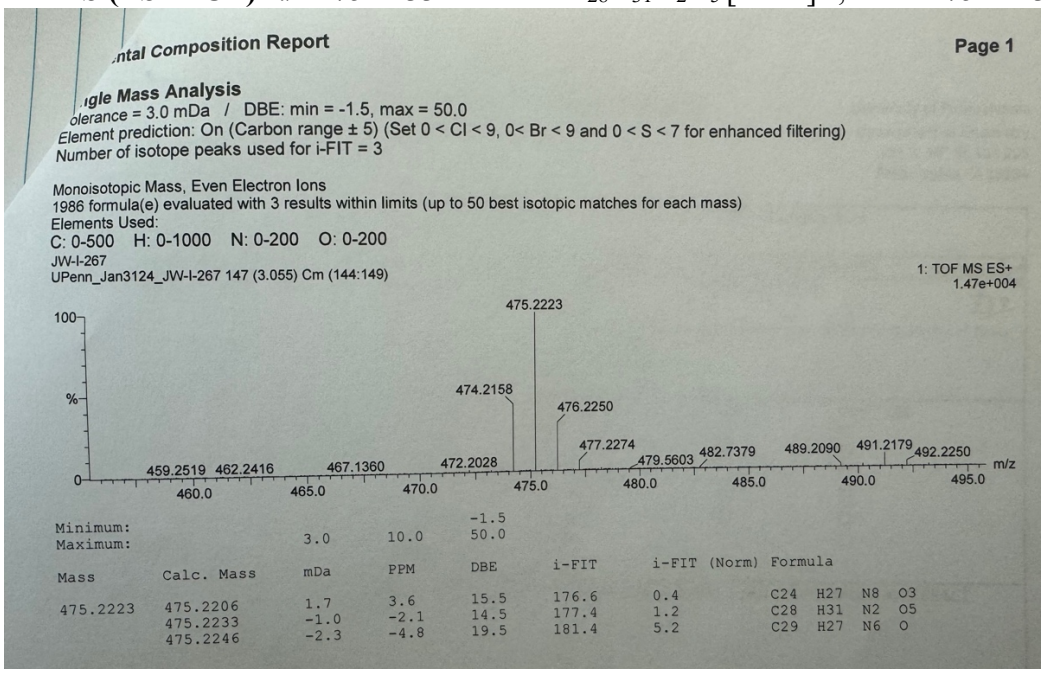
(±)-1-(4-(-3-(3,5-Dimethoxyphenyl)-2-(4-hydroxyphenyl)-2,3-dihydrobenzofuran-5-yl)piperazin-1-yl)ethan-1-one (3ge)

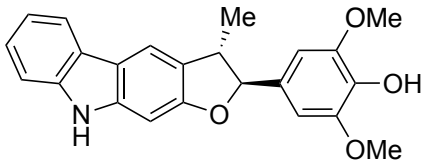
General procedure C was followed using pterostilbene (**2e**) (0.60 mmol, 1.00 equiv), 1-(4-(4-hydroxyphenyl)piperazin-1-yl)ethan-1-one (**1g**) (0.60 mmol, 1.00 equiv), TiO_2 (6.00 mmol, 10.0 equiv) and HFIP/TFT 1:1 mixture (6.00 mL, 0.1 M) for 24 h. General procedure B was used followed by flash column chromatography (EtOAc) to afford a white amorphous solid (>20:1 dr, 0.173 g, 0.365 mmol) in 65% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.13 (m, 2H), 6.87 – 6.77 (m, 4H), 6.64 (d, *J* = 2.2 Hz, 1H), 6.38 (t, *J* = 2.3 Hz, 1H), 6.30 (d, *J* = 2.3 Hz, 2H), 5.44 (d, *J* = 8.5 Hz, 1H), 4.43 (d, *J* = 8.5 Hz, 1H), 3.73 (s, 6H), 3.74-3.75 (m, 2H), 3.57 (dd, *J* = 6.4, 3.9 Hz, 2H), 3.04 – 2.91 (m, 4H), 2.13 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 161.1, 156.5, 154.9, 146.1, 144.0, 132.1, 130.9, 127.5, 118.5, 115.7, 115.5, 109.6, 106.5, 98.9, 92.9, 58.3, 55.4, 51.6, 51.4, 46.5, 41.8, 21.3.

HRMS (ESI-TOF) *m/z* 475.2233 calcd for $C_{28}H_{31}N_2O_5$ $[M+H]^+$; found475.2223.





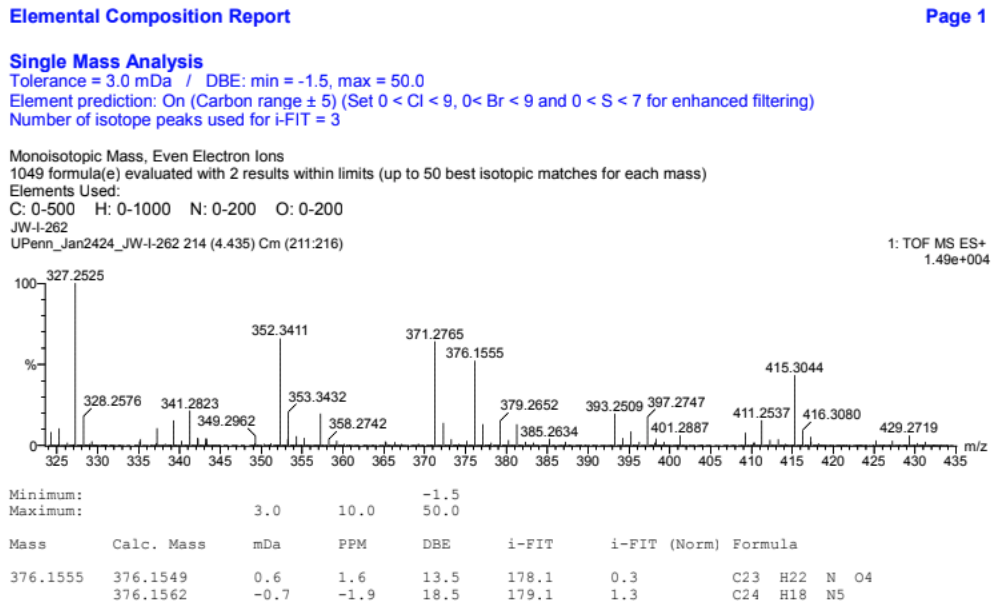
(±)-2,6-dimethoxy-4-(-3-methyl-3,5-dihydro-2*H*-furo[3,2-*b*]carbazol-2-yl)phenol (3fb)

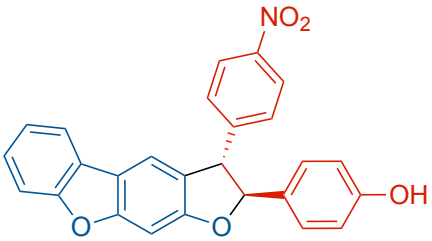
General procedure C was followed using 2,6-dimethoxy-4-(prop-1-en-1-yl)phenol (**2b**) (0.60 mmol, 1.00 equiv), 2-hydroxycarbazole (**1f**) (0.60 mmol, 1.00 equiv), TiO_2 (6.00 mmol, 10.0 equiv) and HFIP/TFT 5:1 mixture (6.00 mL, 0.1 M) for 8 h. General procedure B was used followed by flash column chromatography (*n*-hexane/EtOAc 80:20) to afford a colorless oil (2:1 dr, 0.057 g, 0.15 mmol) in 27% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.96 (m, 1H), 7,80 (s, 1H), 7.46 – 7.31 (m, 2H), 7.26-7.19 (m, 1H), 6.91 (s, 1H), 6.73 (s, 2H), 5.56 (s, 1H), 5.16 (d, *J* = 9.0 Hz, 1H), 3.93 (s, 6H), 3.66 – 3.54 (m, 1H), 1.54 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.7, 147.2, 140.3, 139.5, 134.8, 131.6, 125.4, 124.3, 123.6, 119.5, 119.1, 117.6, 114.9, 110.3, 103.2, 94.0, 91.6, 56.4, 45.1, 18.0.

HRMS (ESI-TOF) *m/z* 376.1549 calcd for $C_{23}H_{22}NO_4$ $[M+H]^+$; found 376.1555.



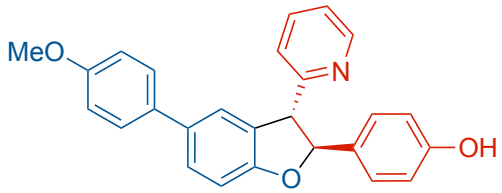


(±)4-(-3-(4-Nitrophenyl)-3,9-dihydro-2*H*-furo[2,3-*b*]dibenzofuran-2-yl)phenol (3hg)

General procedure C was followed using 4-(4-nitrostyryl)phenol (**2g**) (0.56 mmol, 1.00 equiv), dibenzo[b,d]furan-3-ol (**1h**) (0.56 mmol, 1.00 equiv), TiO_2 (5.60 mmol, 10.0 equiv) and HFIP/TFT 5:1 mixture (6.0 mL, 0.1 M) for 28 h. General procedure B was used followed by flash column chromatography (*n*-hexane/EtOAc 70:30) to afford a white amorphous solid (>20:1 dr, 0.089 g, 0.21 mmol) in 38% isolated yield.

^{1}H NMR (400 MHz, Acetone) δ 8.52 (s, 1H), 8.28 – 8.21 (m, 2H), 7.62 – 7.57 (m, 3H), 7.54 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.38 (ddd, *J* = 8.4, 7.0, 1.7 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.16 (d, *J* = 8.8 Hz, 1H), 7.06 – 6.95 (m, 2H), 6.92 – 6.84 (m, 2H), 5.62 (d, *J* = 7.4 Hz, 1H), 5.34 (d, *J* = 7.5 Hz, 1H).

^{13}C NMR (101 MHz, Acetone) δ 157.8, 157.0, 156.7, 151.8, 149.3, 147.4, 131.1, 129.4, 127.7, 124.2, 122.7, 122.6, 122.5, 121.1, 121.0, 115.5, 115.4, 111.6, 111.4, 108.8, 93.5, 56.8.

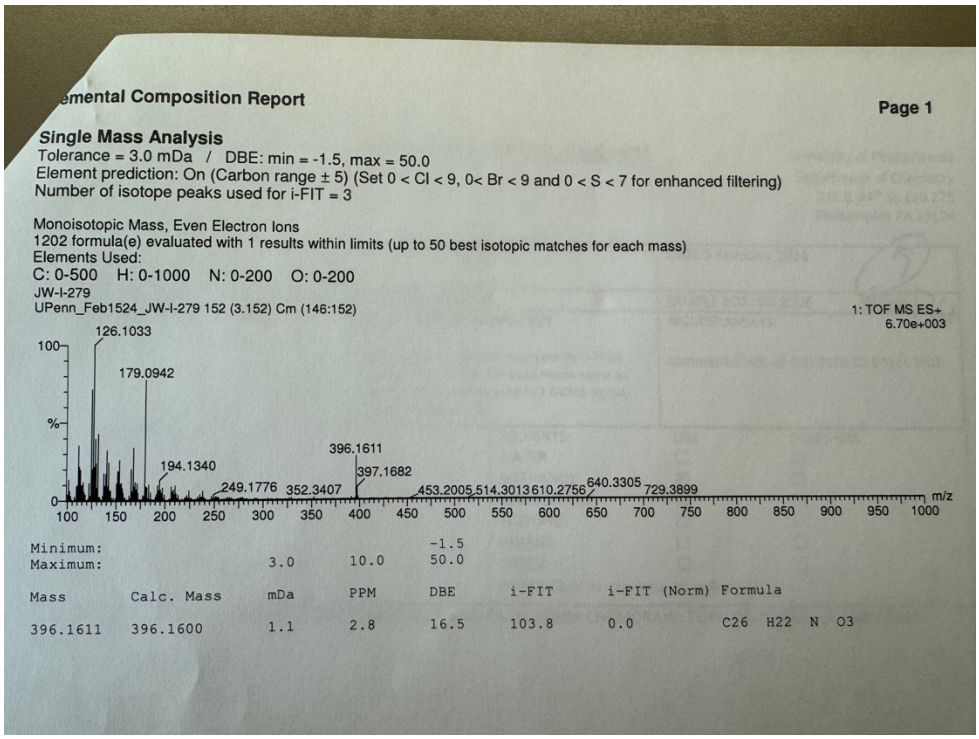


(±)-4-(-5-(4-Methoxyphenyl)-3-(pyridin-2-yl)-2,3-dihydrobenzofuran-2-yl)phenol (3ih)

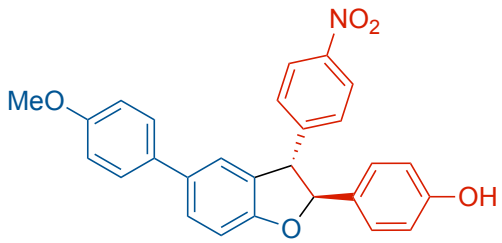
General procedure C was followed using 4-(2-(pyridin-2-yl)vinyl)phenol (**2h**) (0.56 mmol, 1.00 equiv), 4-methoxy-[1,1-biphenyl]-4-ol (**1i**) (0.84 mmol, 1.50 equiv), TiO_2 (5.60 mmol, 10.0 equiv) and HFIP/TFT 1:1 mixture (10.0 mL, 0.056 M) for 24 h. General procedure B was used followed by flash column chromatography (*n*-hexane/EtOAc 70:30) to afford a yellow amorphous solid (>20:1 dr, 0.090 g, 0.23 mmol) in 41% isolated yield.

^{1}H NMR (600 MHz, DMSO) δ 9.59 (s, 1H), 8.22 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 7.48 (m, 3H), 7.45 (d, J = 8.7 Hz, 1H), 7.22 (d, J = 8.6 Hz, 1H), 7.16 (t, J = 1.5 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 6.77 (d, J = 8.6 Hz, 2H), 5.60 (d, J = 8.2 Hz, 1H), 4.92 (d, J = 8.2 Hz, 1H), 3.75 (s, 3H).

^{13}C NMR (151 MHz, DMSO) δ 158.8, 158.7, 158.2, 149.7, 147.2, 133.9, 132.9, 131.1, 130.0, 129.9, 128.4, 127.8, 127.7, 124.5, 123.3, 115.8, 114.7, 110.3, 92.3, 56.1, 55.6. One carbon signal is overlapping.



HRMS (ESI-TOF) *m/z* 396.1600 calcd for $C_{26}H_{22}NO_3$ $[M+H]^+$; found 396.1611.

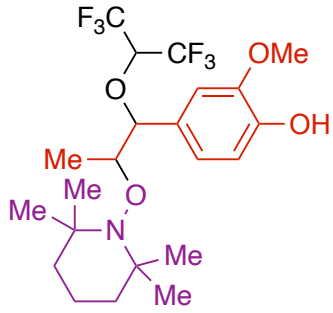


(±)-4-(-5-(4-Methoxyphenyl)-3-(4-nitrophenyl)-2,3-dihydrobenzofuran-2-yl)phenol (3ig)

General procedure C was followed using 4-(4-nitrostyryl)phenol (**2g**) (0.56 mmol, 1.00 equiv), 4-methoxy-[1,1-biphenyl]-4-ol (**1i**) (1.12 mmol, 2.00 equiv), TiO_2 (5.60 mmol, 10.0 equiv) and HFIP/TFT 7:5 mixture (12.0 mL, 0.047 M) for 28 h. General procedure B was used followed by flash column chromatography (*n*-hexane/EtOAc 70:30) to afford a yellow amorphous solid (>20:1 dr, 0.090 g, 0.23 mmol) in 88% isolated yield.

^{1}H NMR (400 MHz, DMSO) δ 9.58 (s, 1H), 8.22 (d, *J* = 8.7 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.50 – 7.40 (m, 3H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.16 (s, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 5.60 (d, *J* = 8.2 Hz, 1H), 4.92 (d, *J* = 8.2 Hz, 1H), 3.75 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 158.8, 158.7, 158.2, 149.7, 147.2, 133.9, 132.9, 131.1, 130.0, 129.9, 128.4, 127.8, 127.7, 124.5, 123.3, 115.8, 114.7, 110.3, 92.3, 56.1, 55.6.



4-(1-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propyl)-2-methoxyphenol (2a-TEMPO)

2a-TEMPO was prepared as described in the radical trapping experiment section.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.91 – 6.87 (m, 2H), 6.79 (dd, *J* = 8.0, 1.9 Hz, 1H), 5.67 (s, 1H), 4.60 (d, *J* = 6.1 Hz, 1H), 4.29 (quintet, *J* = 6.4 Hz, 1H), 4.07 (quintet, *J* = 5.9 Hz, 1H), 3.88 (s, 3H), 1.61 – 1.24 (m, 5H), 1.23 – 1.00 (m, 16H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 146.2, 127.6, 121.9 (q, $J_{C\text{-}F}$ = 107.4 Hz), 122.3, 114.0, 110.5, 87.3, 80.2, 72.6 (t, $J_{C\text{-}F}$= 32.4 Hz), 61.0, 59.0, 55.9, 40.6, 40.3, 34.3, 34.0, 20.5, 20.3, 17.3, 16.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ –72.04 (q, *J* = 9.5 Hz), –73.30 (q, *J* = 9.4 Hz).

Computation Details

General Remarks

All optimizations of intermediates and transition states were calculated using unrestricted B3LYP[10]-D3[11] with Stuttgart/Dresden ECP (SDD)[12] basis set for Ti and the 6-31G(d,p)[13] basis set for other atoms using an ultrafine (99,590) grid with the "opt=noeigen" keyword as implemented in Gaussian16. Frequency calculations, using the same method, were used to obtain thermal corrections (at 298.15K; enthalpy and free energy) and to characterize the obtained stationary points as transition states (only one single imaginary frequency) or intermediate (zero imaginary frequencies). Conformational searches were performed manually for all intermediates and transition states, and only the lowest energy species were shown and discussed. Intrinsic reaction coordinate (IRC)[14] calculations were undertaken to ensure that the transition states connect to the correct associated local minima. Single point energy calculations using UM06[15]/6-311++G(d,p)[16] with implicit solvent (1,1,1,3,3,3-hexafluoro-2-propanol, ε=16.7) using CPCM[17] were also performed on all structures. Vibrational frequencies were corrected using Truhlar's quasiharmonic oscillator approximation, setting all vibrational frequencies below 100 cm^{-1} to 100 cm^{-1}.[18] The quasiharmonic oscillator corrections were obtained using the GoodVibes.py program by Prof. Robert Paton.[19] UV-Vis spectra were simulated with TD-DFT using the same geometry optimization method with the additional keyword IOP(9/40=2). Obtained outputs were opened in GaussSum 3.0[20] and the corresponding electronic transitions were generated (see instructions on GaussSum webpage). All 3-D structures were generated using CYLview.[21] Spin density values were obtained using Natural Bond Order (NBO) analysis. Noncovalent interaction (NCI) analysis, also known as reduce density gradient (RDG) method, was performed on Multiwfn to study the possible effect of noncovalent interaction in different conformations.[22] Extension distance of 0 Bohr, medium quality grid (totally about 512000 points) were set by default. Further visualization of the color-filled RDG isosurface was realized by VMD, where RDG isosurface and color range were set as 0.5, and -0.035 to 0.2, respectively.[23]

Full Reference of Gaussian 16 Software

Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

Supporting Figures

Table S3. Excitation energies, oscillator strength, and main transitions calculated at TD-UB3LYP-D3/6-31G(d,p)-SDD(Ti) level for TiO_2-**2a** adduct. Wavefunctions and contributions to the electronic transitions are presented in the last column.

Wavelength (nm)	Oscillator Strength (f)	Wavefunction (|coefficient|^2)
524.11	0.0004	HOMO→LUMO (37%)

490.75	0.0001	HOMO→LUMO+2 (27%)
471.76	0.0003	HOMO→LUMO+1 (40%)
433.51	0.0205	HOMO→LUMO+3 (43%)
407.37	0.1079	HOMO→LUMO+4 (13%)

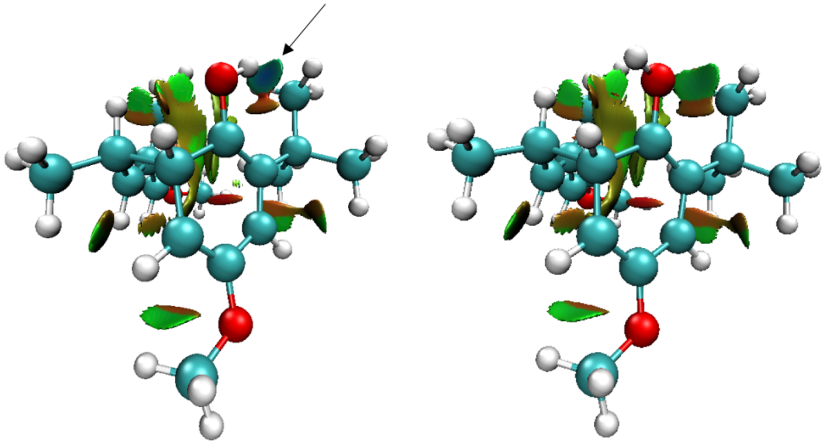


Figure S28. NCI plots of two conformations for **int-7**, showing that the hydroxyl is not pointing away from the *tert*-butyl after the coupling as it is in **1a**.

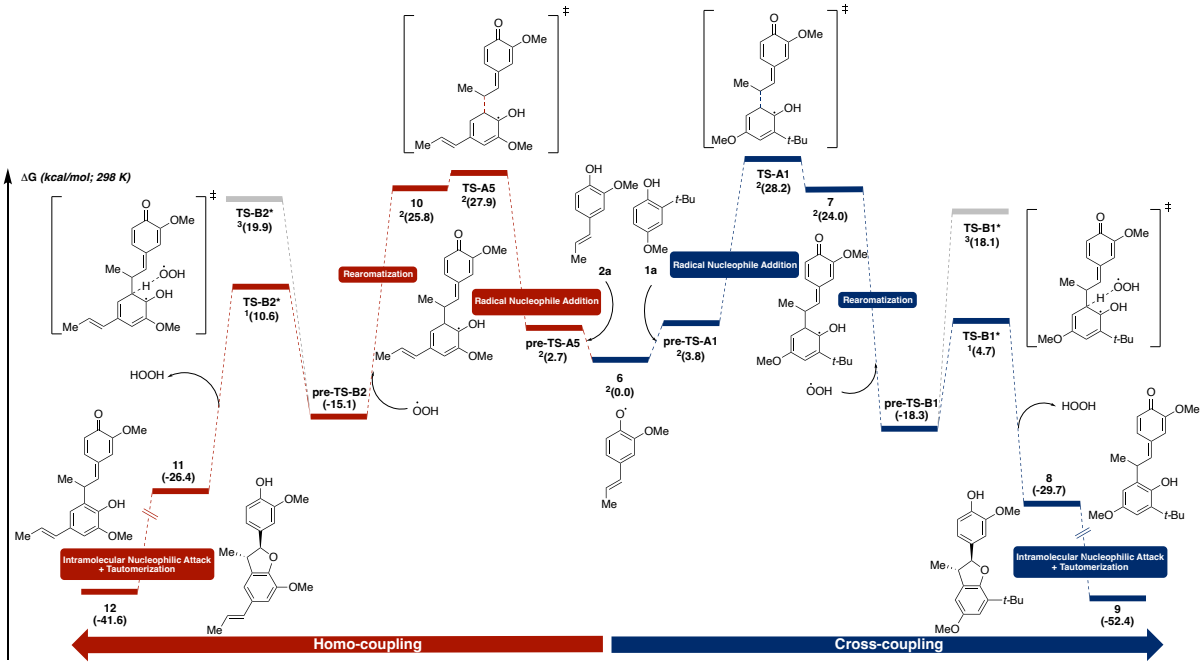


Figure S29. More complete energy profile with grey pathways representing triplet spin states. Free energies were computed using UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p).

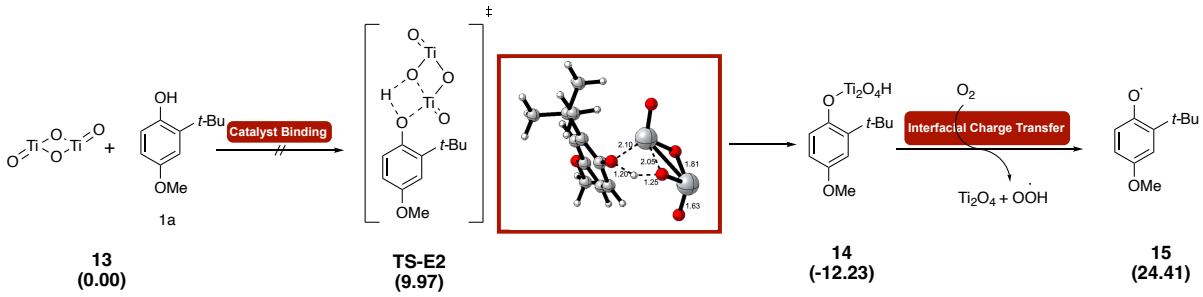


Figure S30. Less favored alternative pathway to generate common intermediate, phenoxyl radical **15**. Free energies were computed using UM06/6-311++G(d,p)-SDD(Ti) CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)-SDD(Ti).

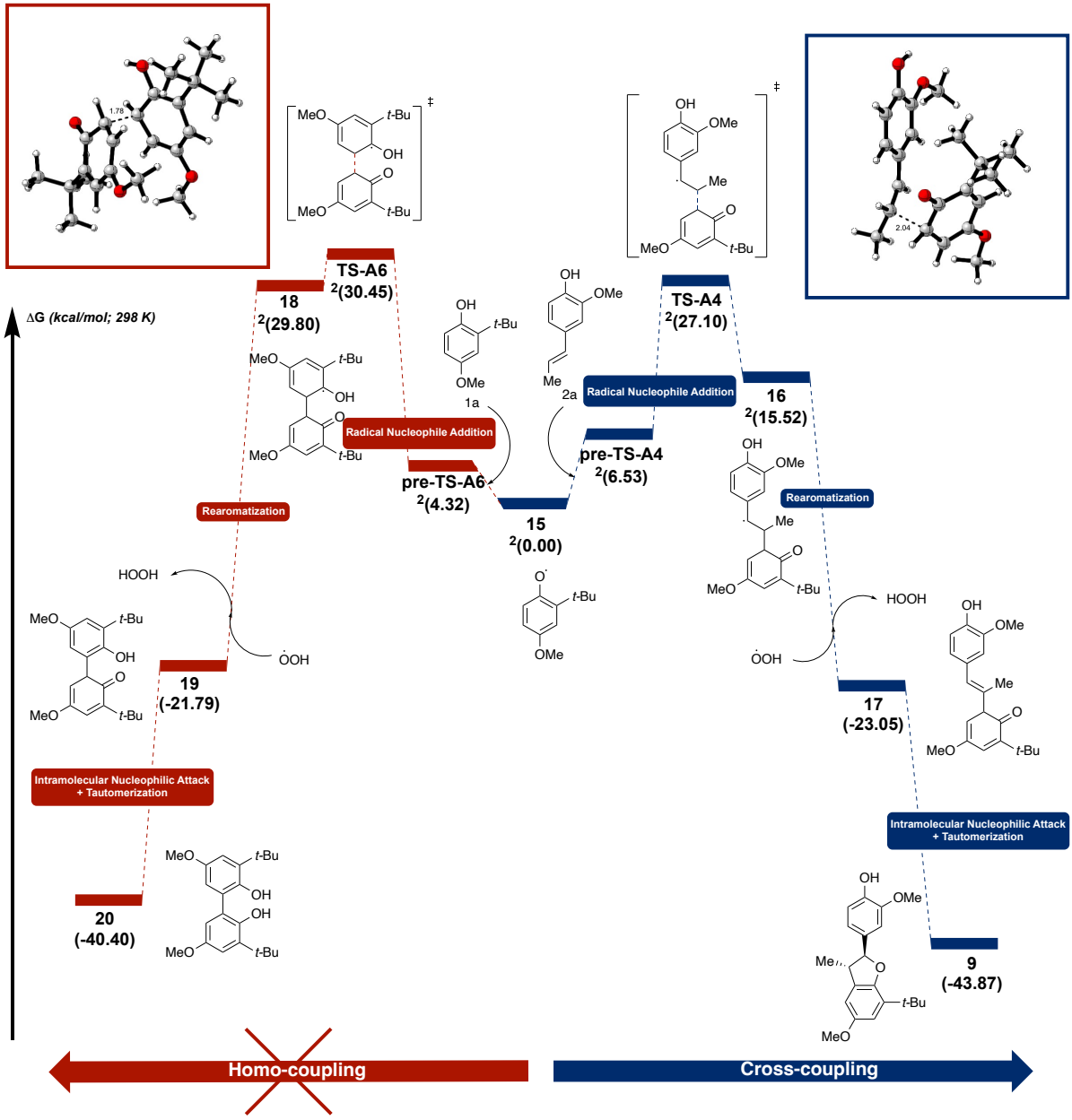


Figure S31. Alternative PES showing **1a** homocoupling is energetically unfavorable, thus using excess **1a** will not lead to large amount of undesired byproducts. Free energies were computed using UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p).

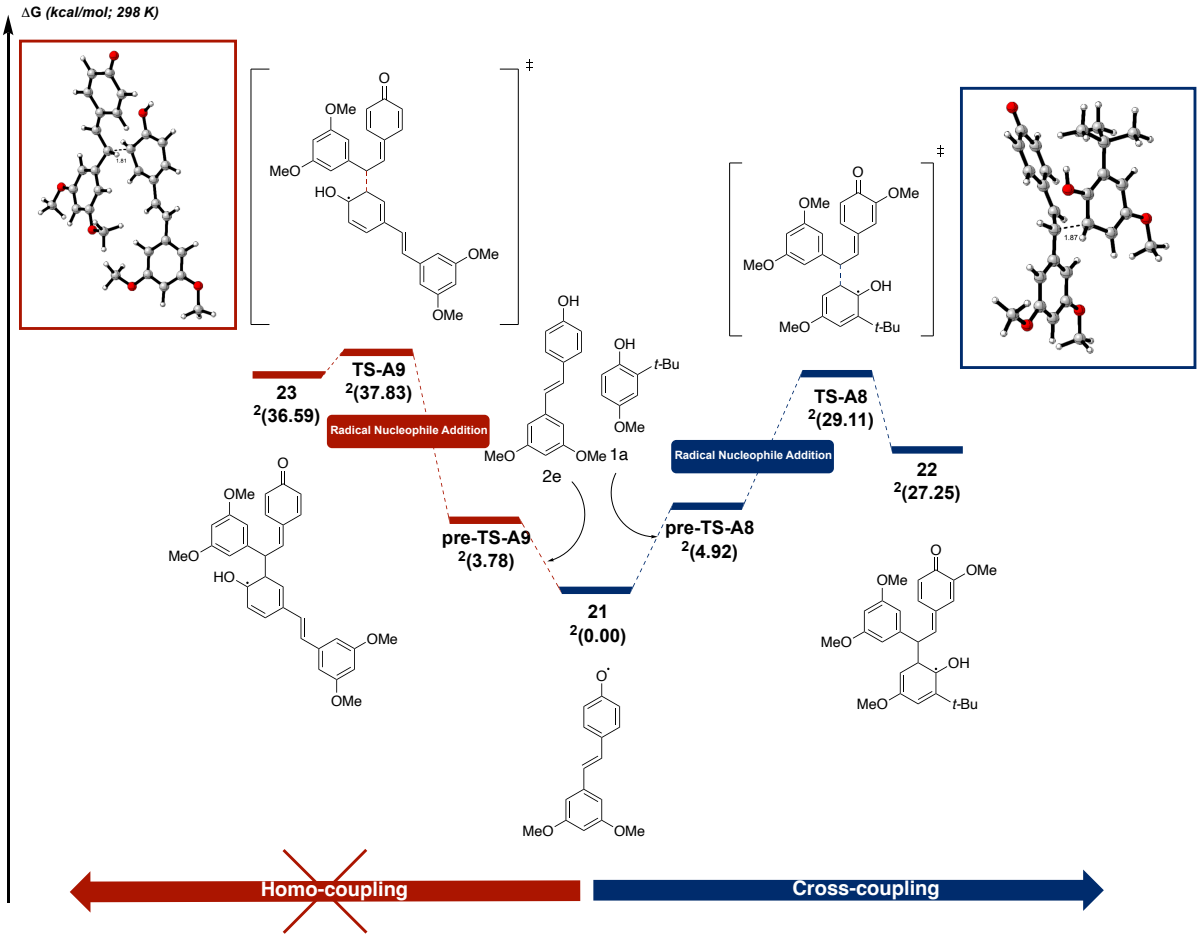
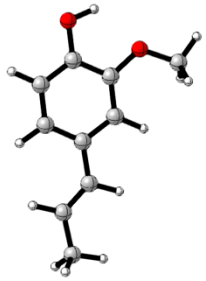


Figure S32. Partial PES on key coupling step and rationalizing the absence of **2e** homocoupling. Free energies were computed using UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p).

Calculated Structures and Energies

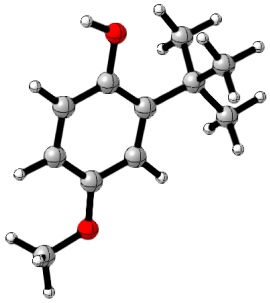
2a



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.198662 (Hartree/Particle)
Thermal correction to Energy= 0.210759
Thermal correction to Enthalpy= 0.211703
Thermal correction to Gibbs Free Energy= 0.159473
Sum of electronic and zero-point Energies= -538.548293
Sum of electronic and thermal Energies= -538.536196
Sum of electronic and thermal Enthalpies= -538.535252
Sum of electronic and thermal Free Energies= -538.587482

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -538.484241

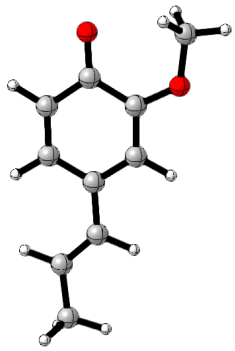
1a



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.250165 (Hartree/Particle)
Thermal correction to Energy= 0.263676
Thermal correction to Enthalpy= 0.264620
Thermal correction to Gibbs Free Energy= 0.212834
Sum of electronic and zero-point Energies= -579.015139
Sum of electronic and thermal Energies= -579.001627
Sum of electronic and thermal Enthalpies= -579.000683
Sum of electronic and thermal Free Energies= -579.053812

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -578.996099

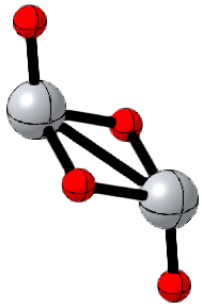
int-6



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.185826 (Hartree/Particle)
Thermal correction to Energy= 0.197644
Thermal correction to Enthalpy= 0.198588
Thermal correction to Gibbs Free Energy= 0.148040
Sum of electronic and zero-point Energies= -537.926917
Sum of electronic and thermal Energies= -537.915099
Sum of electronic and thermal Enthalpies= -537.914154
Sum of electronic and thermal Free Energies= -537.965819

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -537.847590

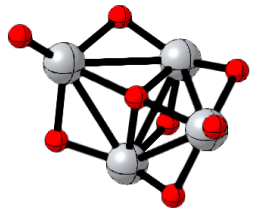
Ti_2O_4



UB3LYP-D3/6-31G(d,p)-SDD(Ti)
Zero-point correction= 0.014540 (Hartree/Particle)
Thermal correction to Energy= 0.020897
Thermal correction to Enthalpy= 0.021841
Thermal correction to Gibbs Free Energy= -0.017076
Sum of electronic and zero-point Energies= -417.818363
Sum of electronic and thermal Energies= -417.812006
Sum of electronic and thermal Enthalpies= -417.811062
Sum of electronic and thermal Free Energies= -417.849979

UM06/6-311++G(d,p)-SDD(Ti)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)-SDD(Ti)
HF = -417.814017

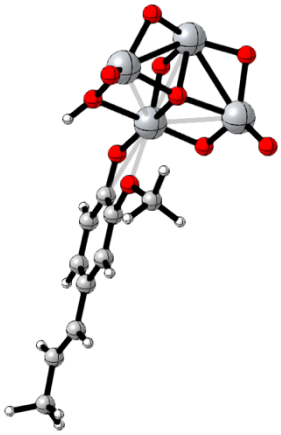
Ti_4O_8



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.031730 (Hartree/Particle)
Thermal correction to Energy= 0.044460
Thermal correction to Enthalpy= 0.045404
Thermal correction to Gibbs Free Energy= -0.007563
Sum of electronic and zero-point Energies= -835.840254
Sum of electronic and thermal Energies= -835.827523
Sum of electronic and thermal Enthalpies= -835.826579
Sum of electronic and thermal Free Energies= -835.879546

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -835.4874204

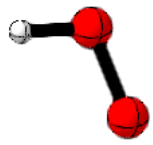
Ti_4O_8-2a



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.231054 (Hartree/Particle)
Thermal correction to Energy= 0.257479
Thermal correction to Enthalpy= 0.258423
Thermal correction to Gibbs Free Energy= 0.173603
Sum of electronic and zero-point Energies= -1374.491384
Sum of electronic and thermal Energies= -1374.464959
Sum of electronic and thermal Enthalpies= -1374.464015
Sum of electronic and thermal Free Energies= -1374.548834

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1374.1931237

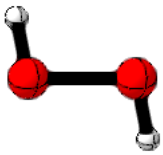
•OOH



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.014091 (Hartree/Particle)
Thermal correction to Energy= 0.016948
Thermal correction to Enthalpy= 0.017892
Thermal correction to Gibbs Free Energy= -0.008097
Sum of electronic and zero-point Energies= -150.890004
Sum of electronic and thermal Energies= -150.887146
Sum of electronic and thermal Enthalpies= -150.886202
Sum of electronic and thermal Free Energies= -150.912192

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -150.882956

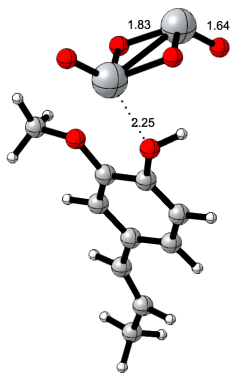
H_2O_2



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.026370 (Hartree/Particle)
Thermal correction to Energy= 0.029631
Thermal correction to Enthalpy= 0.030575
Thermal correction to Gibbs Free Energy= 0.004029
Sum of electronic and zero-point Energies= -151.517176
Sum of electronic and thermal Energies= -151.513916
Sum of electronic and thermal Enthalpies= -151.512971
Sum of electronic and thermal Free Energies= -151.539518

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -151.529984

int-4

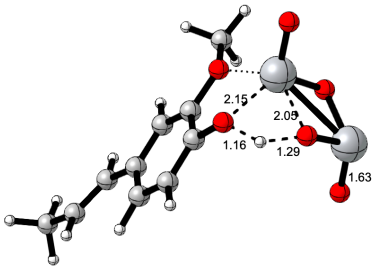


UB3LYP-D3/6-31G(d,p)-SDD(Ti)
Zero-point correction= 0.214958 (Hartree/Particle)

Thermal correction to Energy= 0.234728
Thermal correction to Enthalpy= 0.235672
Thermal correction to Gibbs Free Energy= 0.163787
Sum of electronic and zero-point Energies= -956.435360
Sum of electronic and thermal Energies= -956.415590
Sum of electronic and thermal Enthalpies= -956.414646
Sum of electronic and thermal Free Energies= -956.486531

UM06/6-311++G(d,p)-SDD(Ti)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)-SDD(Ti)
HF = -956.321007

TS-E1

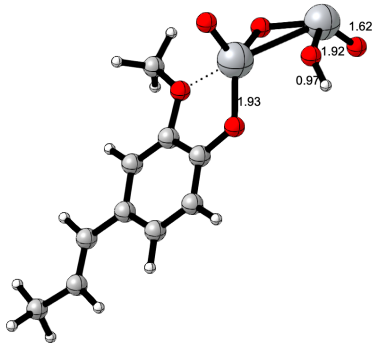


Imaginary frequency = -934.38 cm^{-1}

UB3LYP-D3/6-31G(d,p)-SDD(Ti)
Zero-point correction= 0.210597 (Hartree/Particle)
Thermal correction to Energy= 0.229658
Thermal correction to Enthalpy= 0.230602
Thermal correction to Gibbs Free Energy= 0.160895
Sum of electronic and zero-point Energies= -956.435169
Sum of electronic and thermal Energies= -956.416108
Sum of electronic and thermal Enthalpies= -956.415164
Sum of electronic and thermal Free Energies= -956.484871

UM06/6-311++G(d,p)-SDD(Ti)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)-SDD(Ti)
HF = -956.311439

int-5

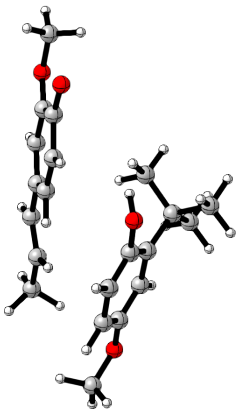


UB3LYP-D3/6-31G(d,p)-SDD(Ti)
Zero-point correction= 0.213583 (Hartree/Particle)
Thermal correction to Energy= 0.233736
Thermal correction to Enthalpy= 0.234680
Thermal correction to Gibbs Free Energy= 0.161687

Sum of electronic and zero-point Energies= -956.457805
Sum of electronic and thermal Energies= -956.437652
Sum of electronic and thermal Enthalpies= -956.436708
Sum of electronic and thermal Free Energies= -956.509701

UM06/6-311++G(d,p)-SDD(Ti)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)-SDD(Ti)
HF = -956.346402

pre-TS-A1



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.438105 (Hartree/Particle)
Thermal correction to Energy= 0.465072
Thermal correction to Enthalpy= 0.466016
Thermal correction to Gibbs Free Energy= 0.386025
Sum of electronic and zero-point Energies= -1116.983573
Sum of electronic and thermal Energies= -1116.956606
Sum of electronic and thermal Enthalpies= -1116.955662
Sum of electronic and thermal Free Energies= -1117.041709

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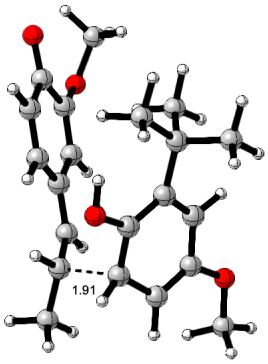
HF = -1116.850396

TS-A1



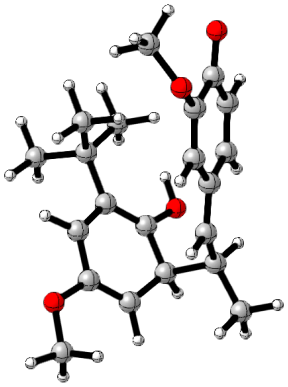
Imaginary frequency = -587.65 cm^{-1}

UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.438281 (Hartree/Particle)
Thermal correction to Energy= 0.463862
Thermal correction to Enthalpy= 0.464806

Thermal correction to Gibbs Free Energy= 0.387501
Sum of electronic and zero-point Energies= -1116.935986
Sum of electronic and thermal Energies= -1116.910406
Sum of electronic and thermal Enthalpies= -1116.909462
Sum of electronic and thermal Free Energies= -1116.990990

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1116.812857

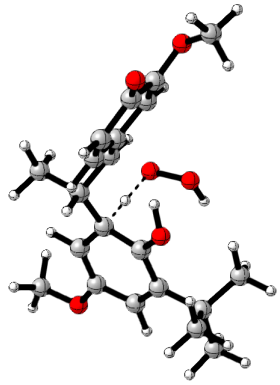
int-7



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.439923 (Hartree/Particle)
Thermal correction to Energy= 0.465708
Thermal correction to Enthalpy= 0.466652
Thermal correction to Gibbs Free Energy= 0.38909
Sum of electronic and zero-point Energies= -1116.940648
Sum of electronic and thermal Energies= -1116.914864
Sum of electronic and thermal Enthalpies= -1116.913920
Sum of electronic and thermal Free Energies= -1116.996210

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1116.821314

TS-B1-s



Imaginary frequency = -595.02cm^{-1}

UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.453841 (Hartree/Particle)
Thermal correction to Energy= 0.482469

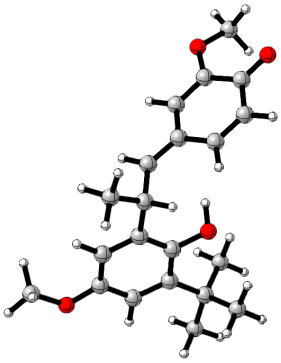
Thermal correction to Enthalpy= 0.483413
Thermal correction to Gibbs Free Energy= 0.394187
Sum of electronic and zero-point Energies= -1267.880090
Sum of electronic and thermal Energies= -1267.851462
Sum of electronic and thermal Enthalpies= -1267.850517
Sum of electronic and thermal Free Energies= -1267.939743

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1267.7483206

TS-B1-t
UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.451444 (Hartree/Particle)
Thermal correction to Energy= 0.479021
Thermal correction to Enthalpy= 0.479965
Thermal correction to Gibbs Free Energy= 0.393262
Sum of electronic and zero-point Energies= -1267.827176
Sum of electronic and thermal Energies= -1267.799600
Sum of electronic and thermal Enthalpies= -1267.798656
Sum of electronic and thermal Free Energies= -1267.885359

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1267.6877021

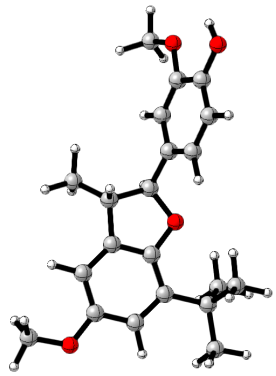
int-8



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.430055 (Hartree/Particle)
Thermal correction to Energy= 0.455570
Thermal correction to Enthalpy= 0.456514
Thermal correction to Gibbs Free Energy= 0.374225
Sum of electronic and zero-point Energies= -1116.395998
Sum of electronic and thermal Energies= -1116.370484
Sum of electronic and thermal Enthalpies= -1116.369540
Sum of electronic and thermal Free Energies= -1116.451828

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1116.263723

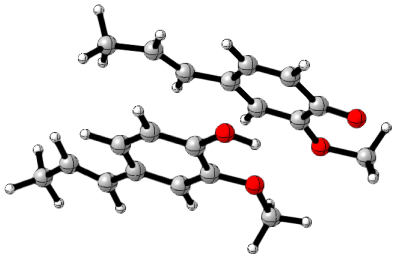
int-9



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.432395 (Hartree/Particle)
Thermal correction to Energy= 0.456890
Thermal correction to Enthalpy= 0.457834
Thermal correction to Gibbs Free Energy= 0.378106
Sum of electronic and zero-point Energies= -1116.432513
Sum of electronic and thermal Energies= -1116.408018
Sum of electronic and thermal Enthalpies= -1116.407074
Sum of electronic and thermal Free Energies= -1116.486801

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1116.303689

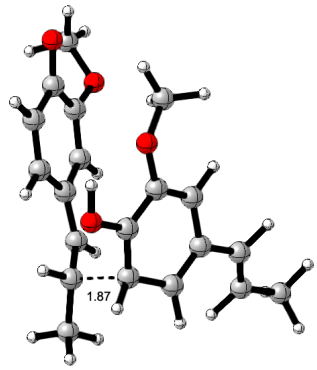
pre-TS-A5



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.385594 (Hartree/Particle)
Thermal correction to Energy= 0.411391
Thermal correction to Enthalpy= 0.412336
Thermal correction to Gibbs Free Energy= 0.333919
Sum of electronic and zero-point Energies= -1076.495114
Sum of electronic and thermal Energies= -1076.469316
Sum of electronic and thermal Enthalpies= -1076.468372
Sum of electronic and thermal Free Energies= -1076.554290

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1076.346385

TS-A5

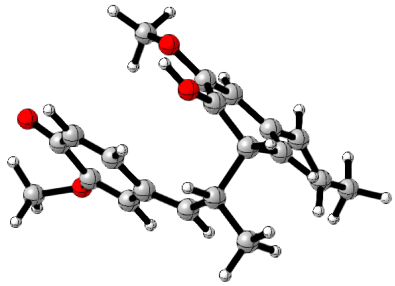


Imaginary frequency = -539.06 cm^{-1}

UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.385865 (Hartree/Particle)
Thermal correction to Energy= 0.410290
Thermal correction to Enthalpy= 0.411235
Thermal correction to Gibbs Free Energy= 0.328808
Sum of electronic and zero-point Energies= -1076.443474
Sum of electronic and thermal Energies= -1076.419049
Sum of electronic and thermal Enthalpies= -1076.418105
Sum of electronic and thermal Free Energies= -1076.499532

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1076.301171

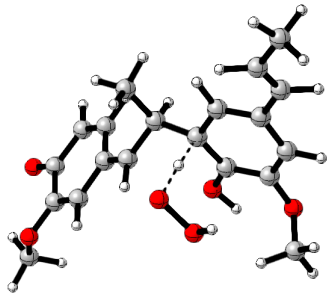
int-10



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.387257 (Hartree/Particle)
Thermal correction to Energy= 0.411896
Thermal correction to Enthalpy= 0.412840
Thermal correction to Gibbs Free Energy= 0.330815
Sum of electronic and zero-point Energies= -1076.445492
Sum of electronic and thermal Energies= -1076.420853
Sum of electronic and thermal Enthalpies= -1076.419908
Sum of electronic and thermal Free Energies= -1076.501934

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1076.306435

TS-B2-s
Imaginary frequency = -560.12 cm^{-1}



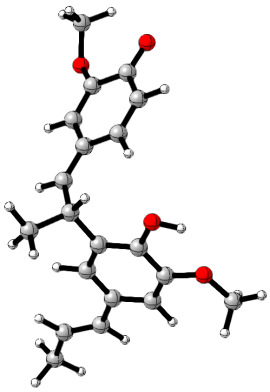
UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.401163 (Hartree/Particle)
Thermal correction to Energy= 0.428831
Thermal correction to Enthalpy= 0.429776
Thermal correction to Gibbs Free Energy= 0.340375
Sum of electronic and zero-point Energies= -1227.376378
Sum of electronic and thermal Energies= -1227.348709
Sum of electronic and thermal Enthalpies= -1227.347765
Sum of electronic and thermal Free Energies= -1227.437165

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1227.2325628

TS-B2-t
UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.398508 (Hartree/Particle)
Thermal correction to Energy= 0.425397
Thermal correction to Enthalpy= 0.426341
Thermal correction to Gibbs Free Energy= 0.338627
Sum of electronic and zero-point Energies= -1227.325122
Sum of electronic and thermal Energies= -1227.298233
Sum of electronic and thermal Enthalpies= -1227.297289
Sum of electronic and thermal Free Energies= -1227.385004

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1227.173523

int-11

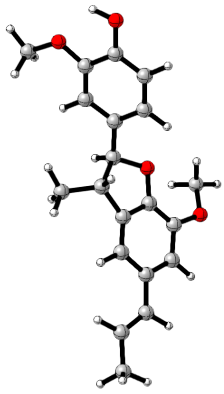


UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.377937 (Hartree/Particle)

Thermal correction to Energy= 0.402381
Thermal correction to Enthalpy= 0.403325
Thermal correction to Gibbs Free Energy= 0.320551
Sum of electronic and zero-point Energies= -1075.902672
Sum of electronic and thermal Energies= -1075.878228
Sum of electronic and thermal Enthalpies= -1075.877283
Sum of electronic and thermal Free Energies= -1075.960058

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1075.756110

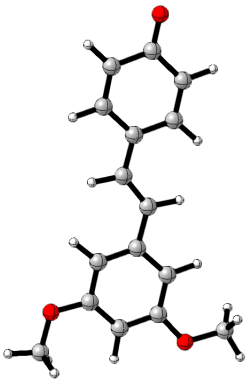
int-12



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.379720 (Hartree/Particle)
Thermal correction to Energy= 0.403182
Thermal correction to Enthalpy= 0.404126
Thermal correction to Gibbs Free Energy= 0.324601
Sum of electronic and zero-point Energies= -1075.929012
Sum of electronic and thermal Energies= -1075.905550
Sum of electronic and thermal Enthalpies= -1075.904606
Sum of electronic and thermal Free Energies= -1075.984131

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1075.785349

int-21

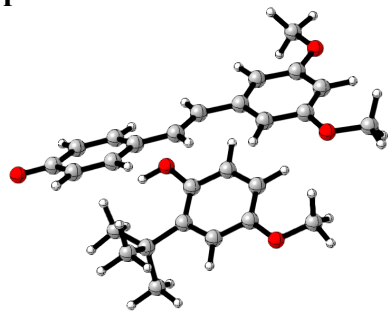


UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.271472 (Hartree/Particle)

Thermal correction to Energy= 0.288835
Thermal correction to Enthalpy= 0.289779
Thermal correction to Gibbs Free Energy= 0.223681
Sum of electronic and zero-point Energies= -844.121640
Sum of electronic and thermal Energies= -844.104277
Sum of electronic and thermal Enthalpies= -844.103333
Sum of electronic and thermal Free Energies= -844.169431

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -843.983940

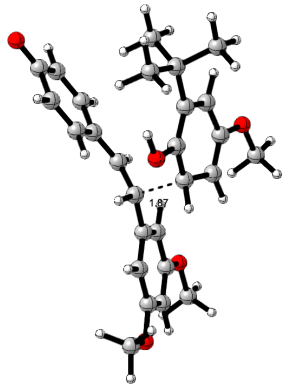
pre-TS-A8



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.523690 (Hartree/Particle)
Thermal correction to Energy= 0.556318
Thermal correction to Enthalpy= 0.557262
Thermal correction to Gibbs Free Energy= 0.453194
Sum of electronic and zero-point Energies= -1423.179031
Sum of electronic and thermal Energies= -1423.146404
Sum of electronic and thermal Enthalpies= -1423.145459
Sum of electronic and thermal Free Energies= -1423.245018

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1422.988881

TS-A8



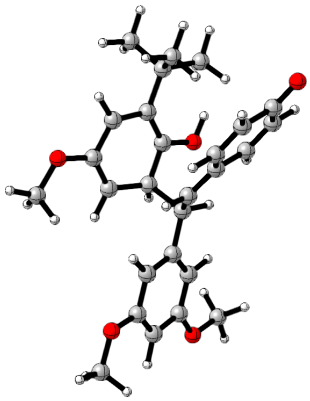
Imaginary frequency = -482.89 cm^{-1}

UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.524294 (Hartree/Particle)
Thermal correction to Energy= 0.555497

Thermal correction to Enthalpy= 0.556441
Thermal correction to Gibbs Free Energy= 0.453085
Sum of electronic and zero-point Energies= -1423.133919
Sum of electronic and thermal Energies= -1423.102717
Sum of electronic and thermal Enthalpies= -1423.101772
Sum of electronic and thermal Free Energies= -1423.196762

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1422.950211

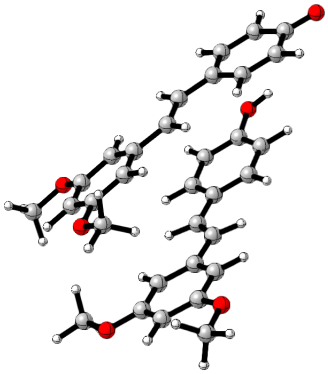
int-22



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.525516 (Hartree/Particle)
Thermal correction to Energy= 0.557000
Thermal correction to Enthalpy= 0.557944
Thermal correction to Gibbs Free Energy= 0.454195
Sum of electronic and zero-point Energies= -1423.135216
Sum of electronic and thermal Energies= -1423.103732
Sum of electronic and thermal Enthalpies= -1423.102788
Sum of electronic and thermal Free Energies= -1423.198602

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1422.954294

pre-TS-A9

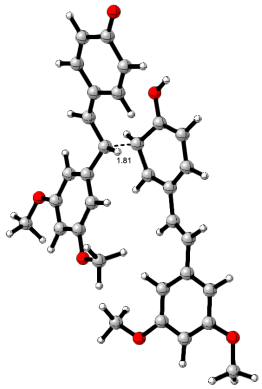


UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.557806 (Hartree/Particle)
Thermal correction to Energy= 0.594395
Thermal correction to Enthalpy= 0.595339

Thermal correction to Gibbs Free Energy= 0.486274
Sum of electronic and zero-point Energies= -1688.896351
Sum of electronic and thermal Energies= -1688.859761
Sum of electronic and thermal Enthalpies= -1688.858817
Sum of electronic and thermal Free Energies= -1688.967882

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1688.621164

TS-A9

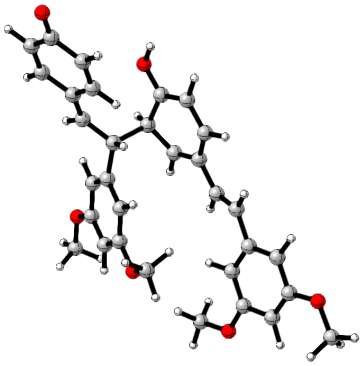


Imaginary frequency = -395.97 cm^{-1}

UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.558290 (Hartree/Particle)
Thermal correction to Energy= 0.593577
Thermal correction to Enthalpy= 0.594521
Thermal correction to Gibbs Free Energy= 0.488955
Sum of electronic and zero-point Energies= -1688.837269
Sum of electronic and thermal Energies= -1688.801983
Sum of electronic and thermal Enthalpies= -1688.801038
Sum of electronic and thermal Free Energies= -1688.906605

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1688.568011

int-23

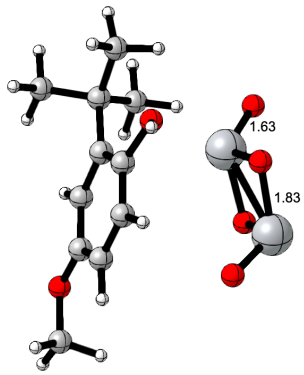


UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.557806 (Hartree/Particle)
Thermal correction to Energy= 0.594395

Thermal correction to Enthalpy= 0.595339
Thermal correction to Gibbs Free Energy= 0.486274
Sum of electronic and zero-point Energies= -1688.896351
Sum of electronic and thermal Energies= -1688.859761
Sum of electronic and thermal Enthalpies= -1688.858817
Sum of electronic and thermal Free Energies= -1688.967882

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1688.570017

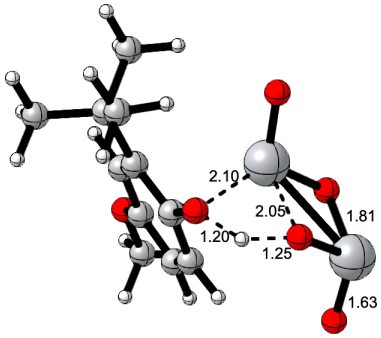
int-13



UB3LYP-D3/6-31G(d,p)-SDD(Ti)
Zero-point correction= 0.267205 (Hartree/Particle)
Thermal correction to Energy= 0.288313
Thermal correction to Enthalpy= 0.289258
Thermal correction to Gibbs Free Energy= 0.215413
Sum of electronic and zero-point Energies= -996.911051
Sum of electronic and thermal Energies= -996.889943
Sum of electronic and thermal Enthalpies= -996.888998
Sum of electronic and thermal Free Energies= -996.962843

UM06/6-311++G(d,p)-SDD(Ti)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)-SDD(Ti)
HF = -996.815497

TS-E2



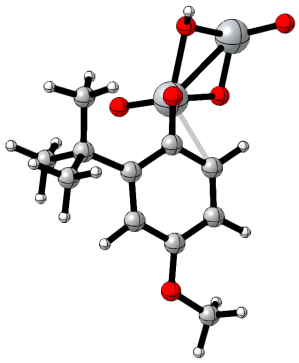
Imaginary frequency = -1134.89 cm^{-1}

UB3LYP-D3/6-31G(d,p)-SDD(Ti)
Zero-point correction= 0.262902 (Hartree/Particle)
Thermal correction to Energy= 0.283215

Thermal correction to Enthalpy= 0.284159
Thermal correction to Gibbs Free Energy= 0.213848
Sum of electronic and zero-point Energies= -996.902460
Sum of electronic and thermal Energies= -996.882148
Sum of electronic and thermal Enthalpies= -996.881203
Sum of electronic and thermal Free Energies= -996.951514

UM06/6-311++G(d,p)-SDD(Ti)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)-SDD(Ti)
HF = -996.798051

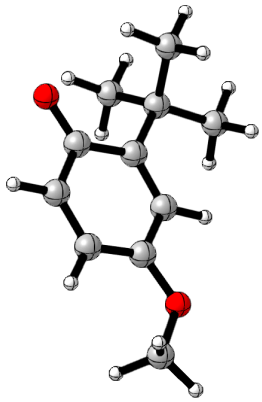
int-14



UB3LYP-D3/6-31G(d,p)-SDD(Ti)
Zero-point correction= 0.265696 (Hartree/Particle)
Thermal correction to Energy= 0.287094
Thermal correction to Enthalpy= 0.288038
Thermal correction to Gibbs Free Energy= 0.213668
Sum of electronic and zero-point Energies= -996.925652
Sum of electronic and thermal Energies= -996.904254
Sum of electronic and thermal Enthalpies= -996.903310
Sum of electronic and thermal Free Energies= -996.977680

UM06/6-311++G(d,p)-SDD(Ti)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)-SDD(Ti)
HF = -996.833382

int-15

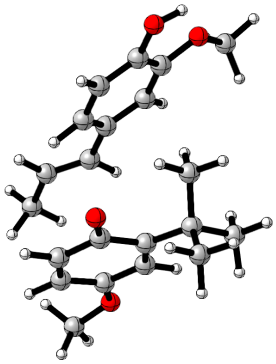


UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.238359 (Hartree/Particle)
Thermal correction to Energy= 0.251338
Thermal correction to Enthalpy= 0.252282

Thermal correction to Gibbs Free Energy= 0.199406
Sum of electronic and zero-point Energies= -578.424040
Sum of electronic and thermal Energies= -578.411061
Sum of electronic and thermal Enthalpies= -578.410117
Sum of electronic and thermal Free Energies= -578.462993

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -578.365271

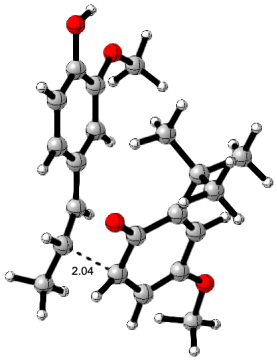
pre-TS-A4



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.438228 (Hartree/Particle)
Thermal correction to Energy= 0.465217
Thermal correction to Enthalpy= 0.466161
Thermal correction to Gibbs Free Energy= 0.378839
Sum of electronic and zero-point Energies= -1116.984895
Sum of electronic and thermal Energies= -1116.957906
Sum of electronic and thermal Enthalpies= -1116.956962
Sum of electronic and thermal Free Energies= -1117.044284

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1116.859008

TS-A4



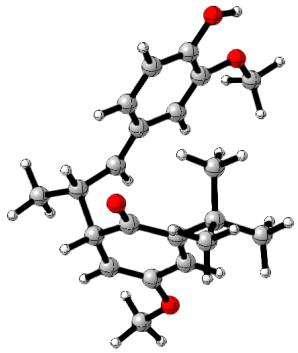
Imaginary frequency = -568.47 cm^{-1}

UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.438694 (Hartree/Particle)
Thermal correction to Energy= 0.464093
Thermal correction to Enthalpy= 0.465037

Thermal correction to Gibbs Free Energy= 0.383451
Sum of electronic and zero-point Energies= -1116.955458
Sum of electronic and thermal Energies= -1116.930059
Sum of electronic and thermal Enthalpies= -1116.929115
Sum of electronic and thermal Free Energies= -1117.010701

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1116.830831

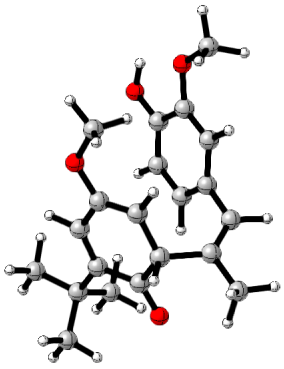
int-16



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.440608 (Hartree/Particle)
Thermal correction to Energy= 0.466135
Thermal correction to Enthalpy= 0.467079
Thermal correction to Gibbs Free Energy= 0.385143
Sum of electronic and zero-point Energies= -1116.970289
Sum of electronic and thermal Energies= -1116.944762
Sum of electronic and thermal Enthalpies= -1116.943818
Sum of electronic and thermal Free Energies= -1117.025754

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1116.850975

int-17

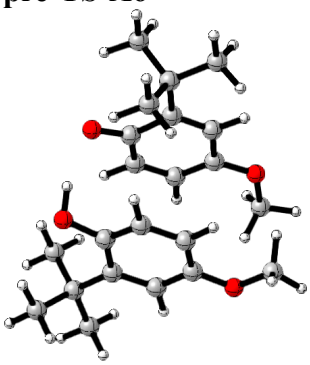


UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.429698 (Hartree/Particle)
Thermal correction to Energy= 0.454970
Thermal correction to Enthalpy= 0.455914
Thermal correction to Gibbs Free Energy= 0.375102
Sum of electronic and zero-point Energies= -1116.395334

Sum of electronic and thermal Energies= -1116.370062
Sum of electronic and thermal Enthalpies= -1116.369118
Sum of electronic and thermal Free Energies= -1116.449930

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1116.267493

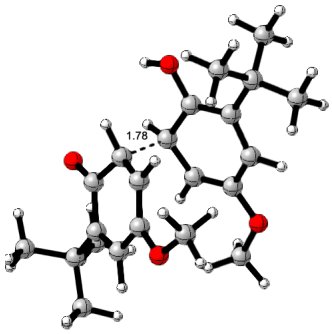
pre-TS-A6



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.491753 (Hartree/Particle)
Thermal correction to Energy= 0.519047
Thermal correction to Enthalpy= 0.519991
Thermal correction to Gibbs Free Energy= 0.436412
Sum of electronic and zero-point Energies= -1157.494038
Sum of electronic and thermal Energies= -1157.466745
Sum of electronic and thermal Enthalpies= -1157.465801
Sum of electronic and thermal Free Energies= -1157.549379

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1157.378652

TS-A6



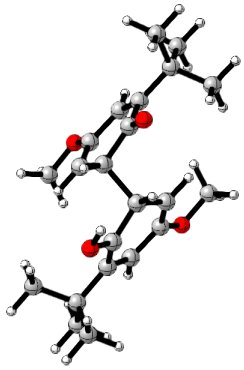
Imaginary frequency = -289.14 cm^{-1}

UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.490282 (Hartree/Particle)
Thermal correction to Energy= 0.517373
Thermal correction to Enthalpy= 0.518317
Thermal correction to Gibbs Free Energy= 0.434242
Sum of electronic and zero-point Energies= -1157.439528
Sum of electronic and thermal Energies= -1157.412437
Sum of electronic and thermal Enthalpies= -1157.411493

Sum of electronic and thermal Free Energies= -1157.495568

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1157.334841

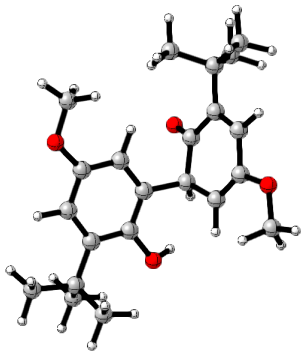
int-18



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.490999 (Hartree/Particle)
Thermal correction to Energy= 0.518509
Thermal correction to Enthalpy= 0.519453
Thermal correction to Gibbs Free Energy= 0.434211
Sum of electronic and zero-point Energies= -1157.439053
Sum of electronic and thermal Energies= -1157.411544
Sum of electronic and thermal Enthalpies= -1157.410599
Sum of electronic and thermal Free Energies= -1157.495842

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1157.335855

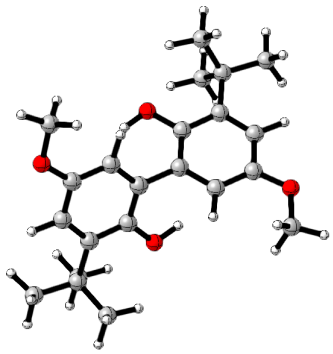
int-19



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.481355 (Hartree/Particle)
Thermal correction to Energy= 0.508507
Thermal correction to Enthalpy= 0.509451
Thermal correction to Gibbs Free Energy= 0.425581
Sum of electronic and zero-point Energies= -1156.886819
Sum of electronic and thermal Energies= -1156.859668
Sum of electronic and thermal Enthalpies= -1156.858724
Sum of electronic and thermal Free Energies= -1156.942593

UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1156.774528

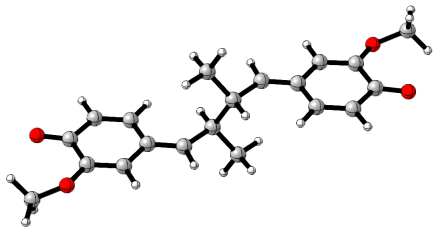
int-20



UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.482265 (Hartree/Particle)
Thermal correction to Energy= 0.509268
Thermal correction to Enthalpy= 0.510213
Thermal correction to Gibbs Free Energy= 0.426757
Sum of electronic and zero-point Energies= -1156.921528
Sum of electronic and thermal Energies= -1156.894524
Sum of electronic and thermal Enthalpies= -1156.893580
Sum of electronic and thermal Free Energies= -1156.977035

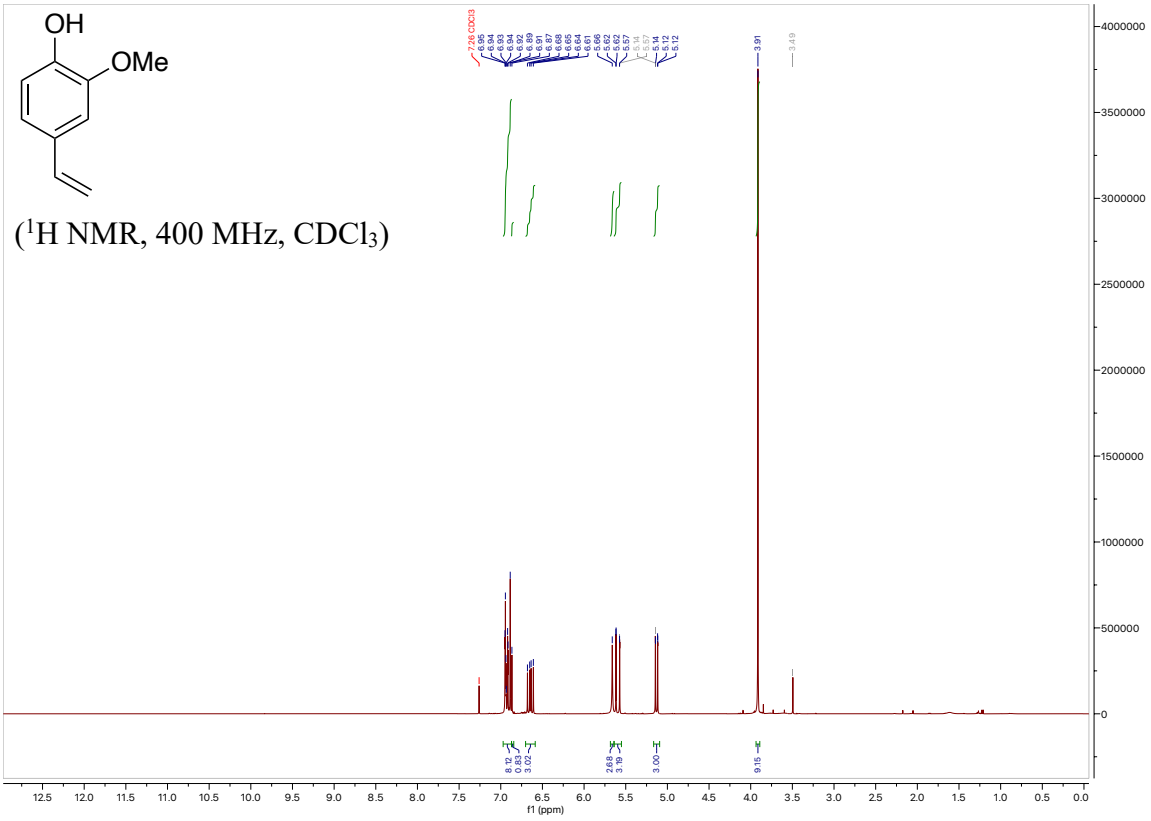
UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1156.805372

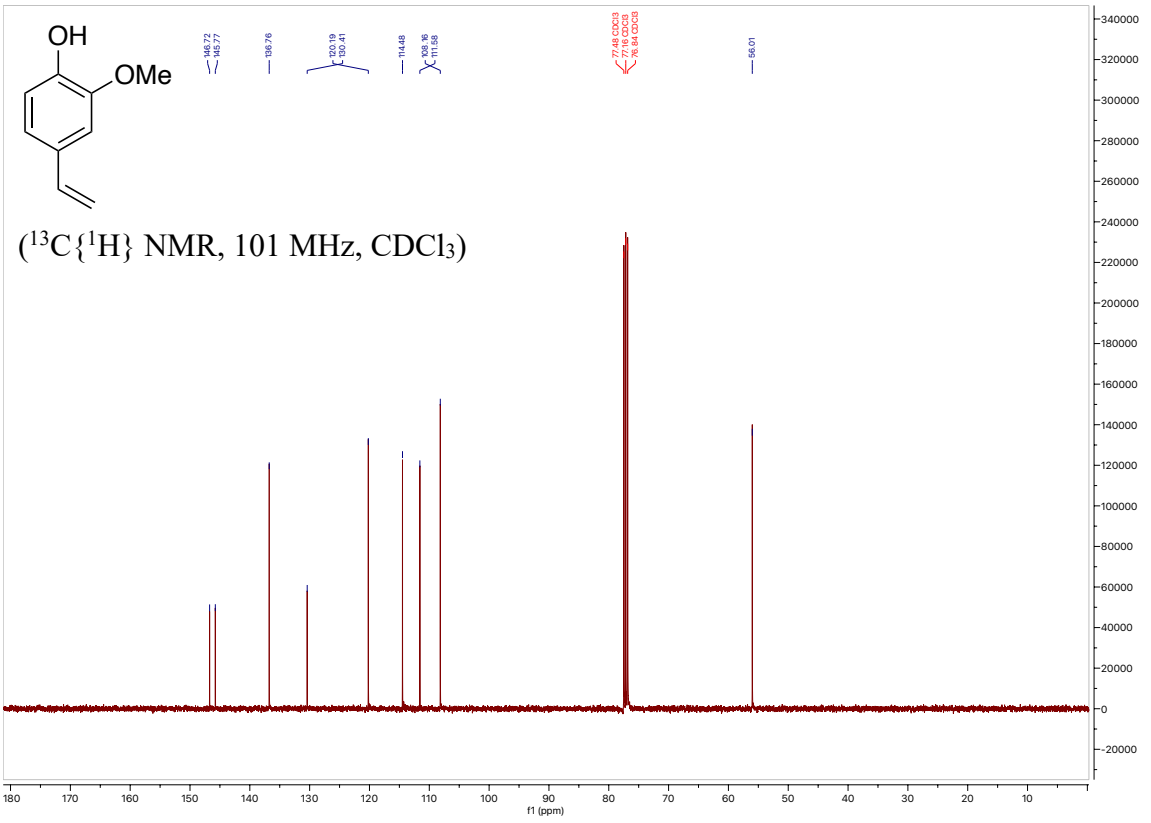
β-β adduct

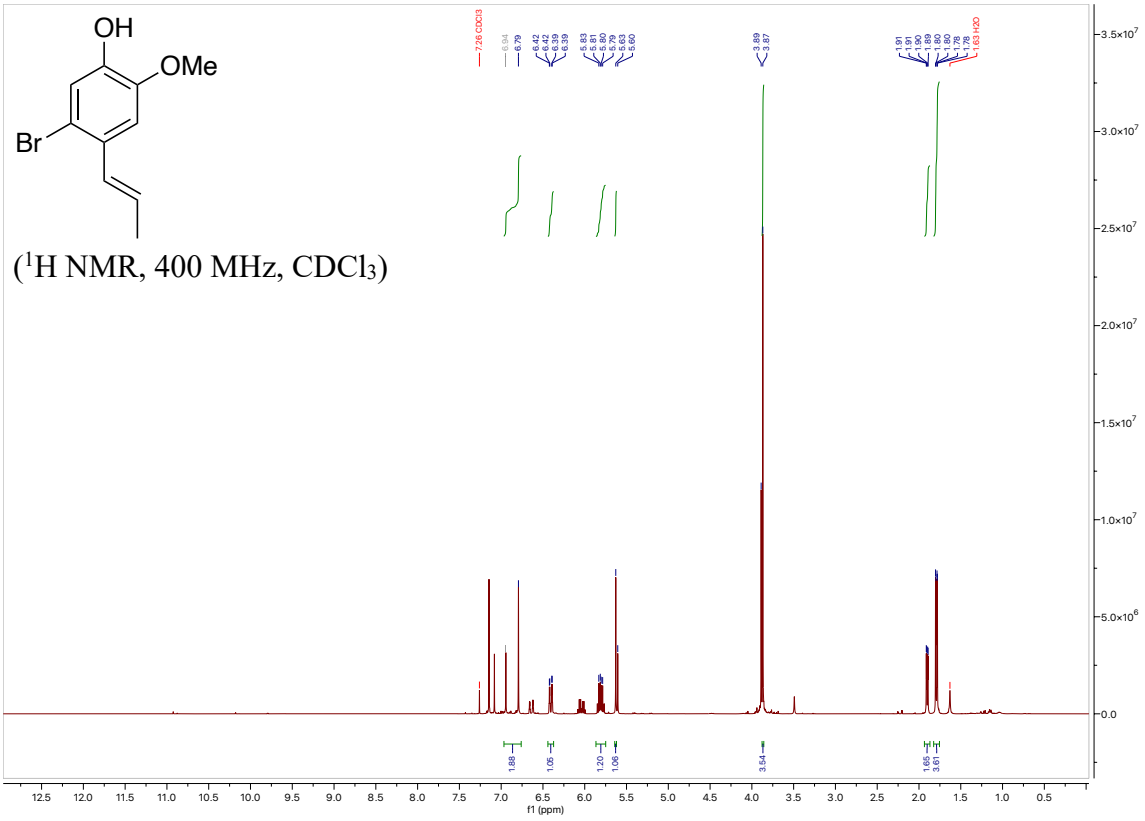


UB3LYP-D3/6-31G(d,p)
Zero-point correction= 0.377721 (Hartree/Particle)
Thermal correction to Energy= 0.401949
Thermal correction to Enthalpy= 0.402893
Thermal correction to Gibbs Free Energy= 0.320068
Sum of electronic and zero-point Energies= -1075.879468
Sum of electronic and thermal Energies= -1075.855240
Sum of electronic and thermal Enthalpies= -1075.854296
Sum of electronic and thermal Free Energies= -1075.937121

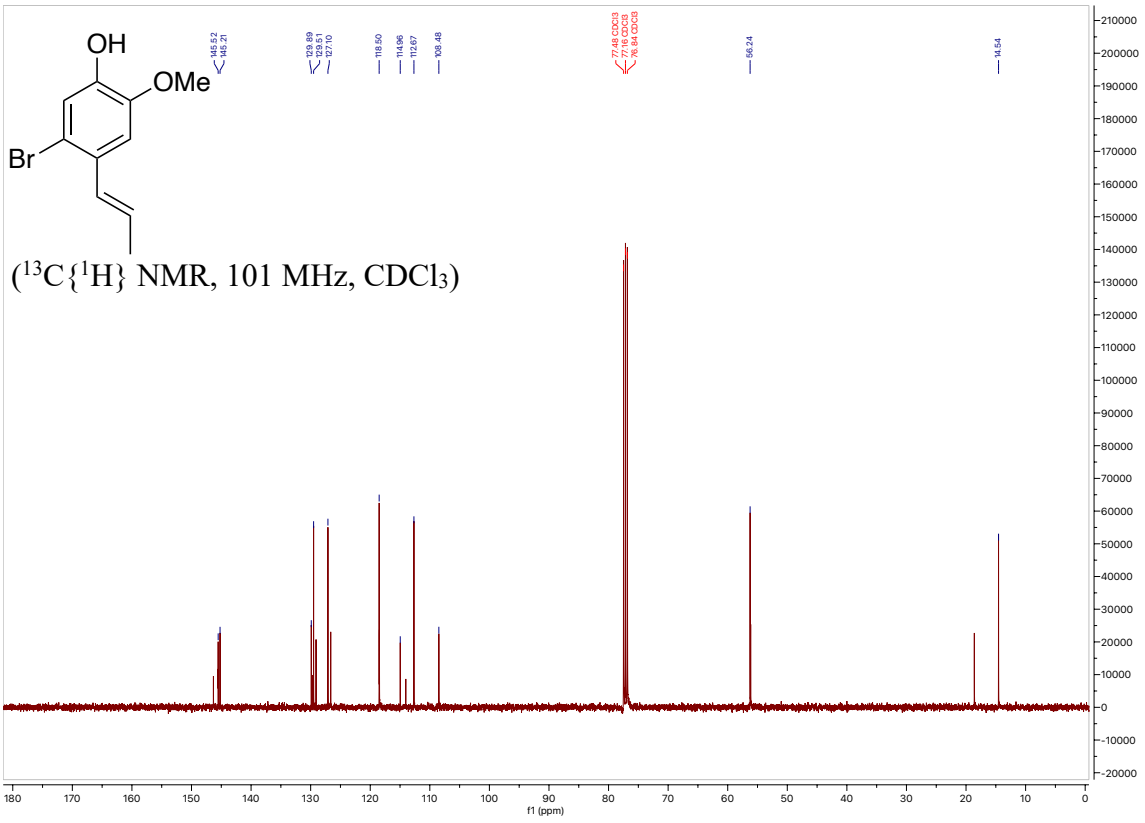
UM06/6-311++G(d,p)-CPCM(HFIP)//UB3LYP-D3/6-31G(d,p)
HF = -1075.734484


OH
OMe
(^{1}H NMR, 400 MHz, CDCl$_3$)
f1 (ppm)

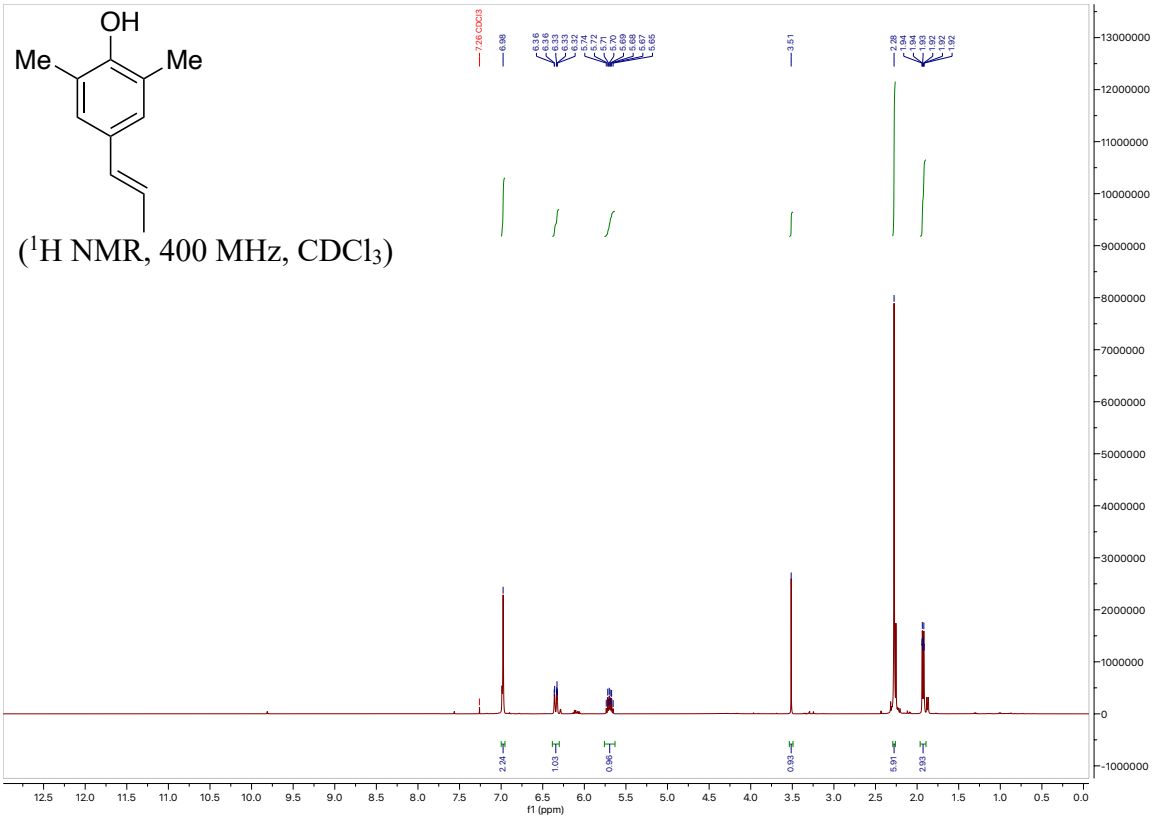

OH
OMe
(^{13}C{^{1}H} NMR, 101 MHz, CDCl$_3$)
f1 (ppm)

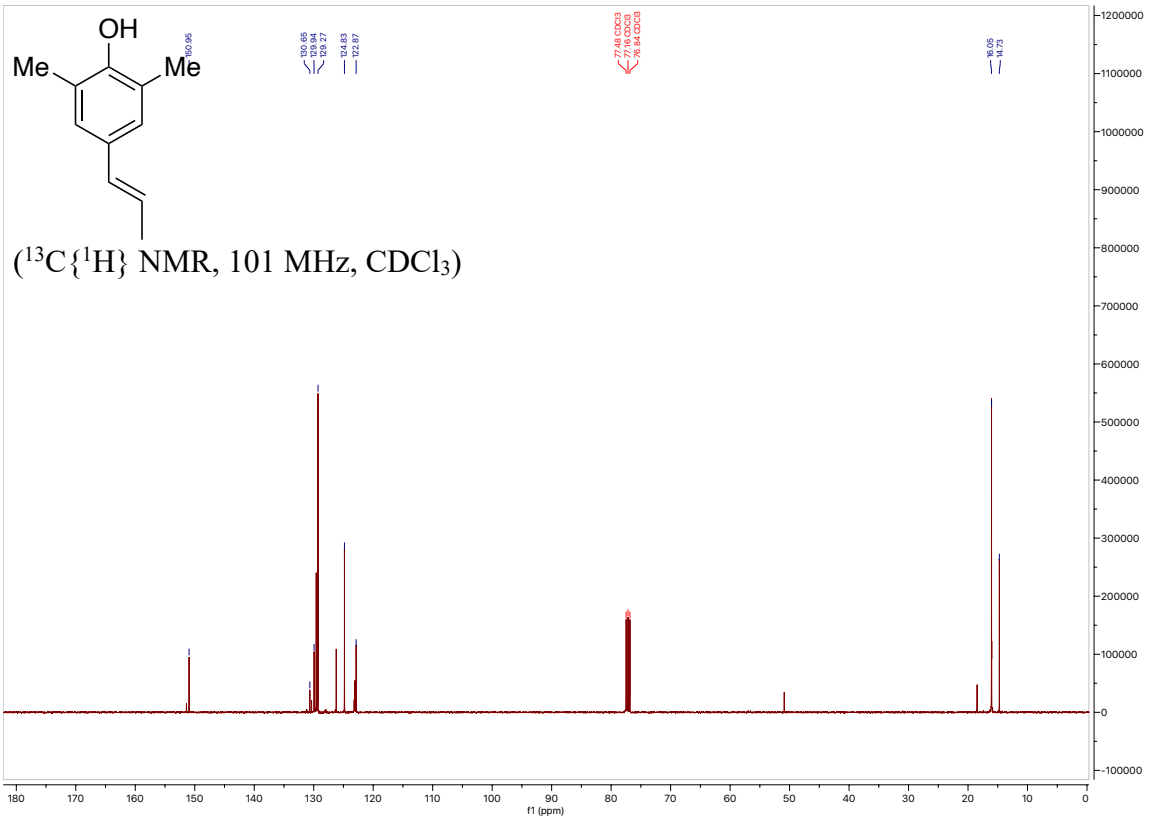


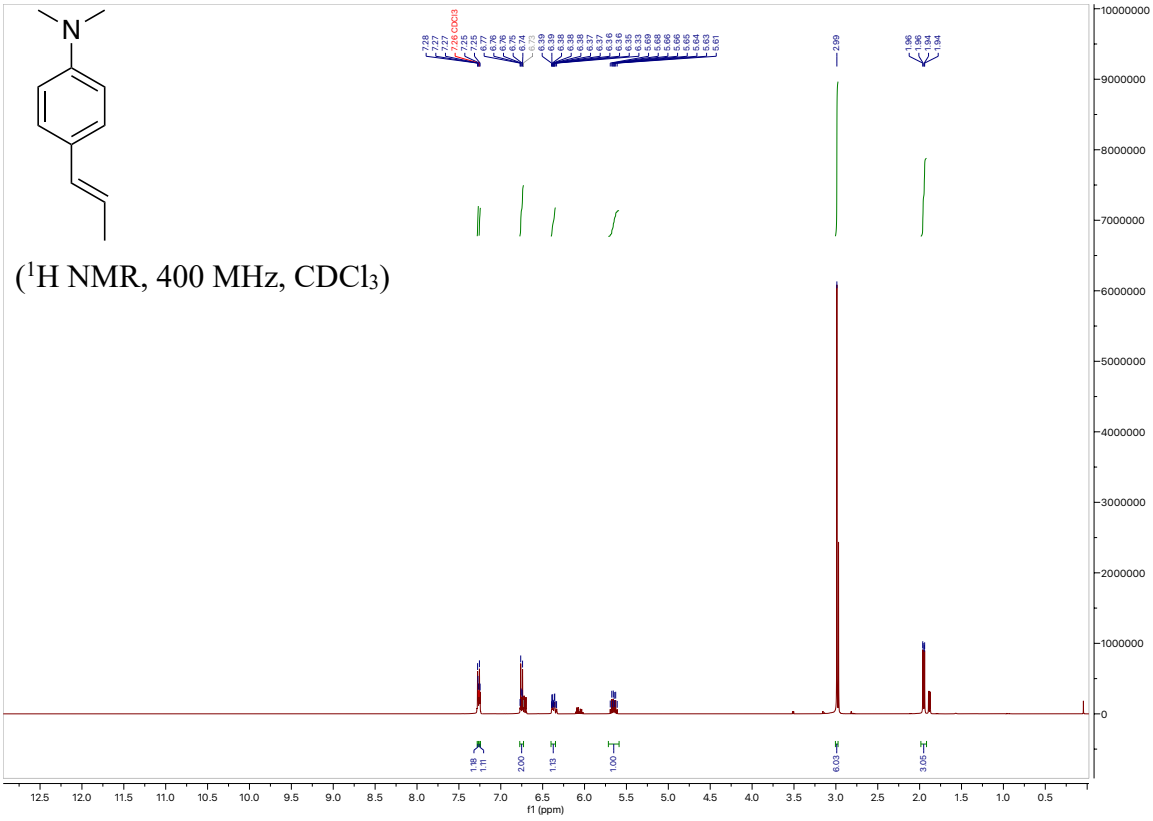
(^{1}H NMR, 400 MHz, $CDCl_3$)



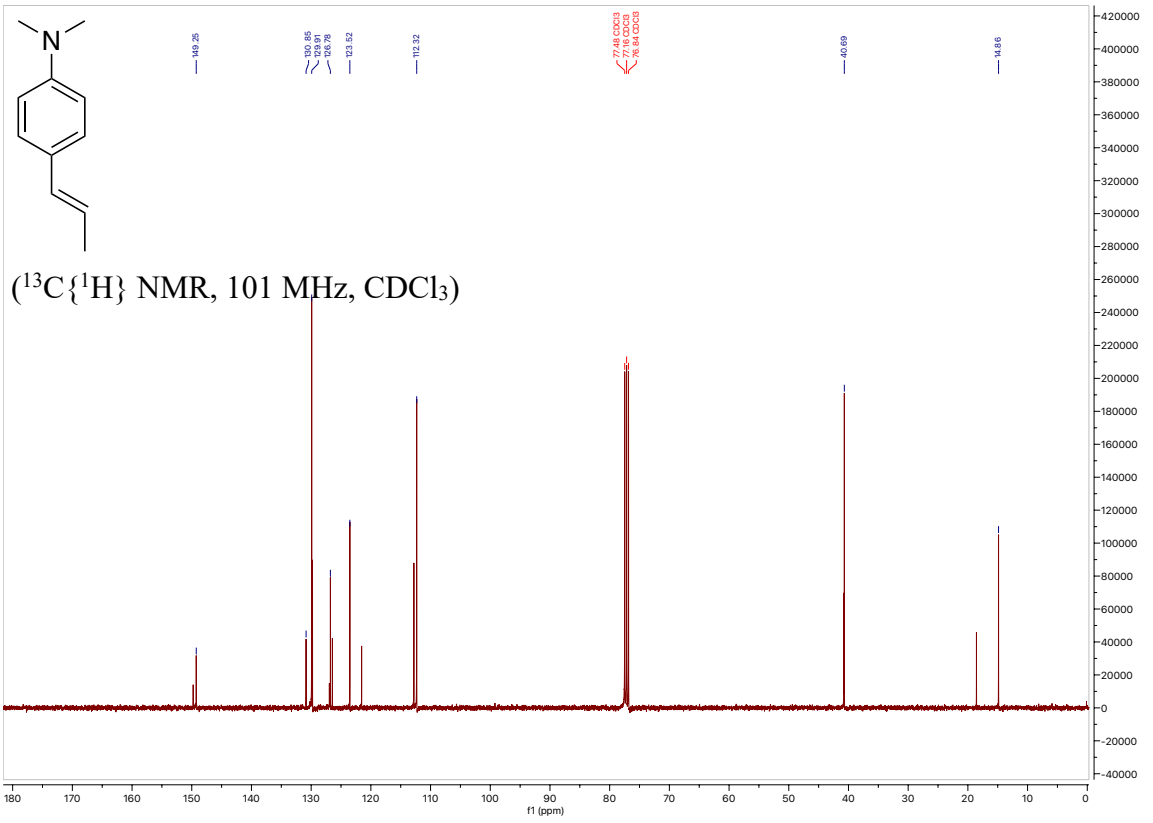
(^{13}C{^{1}H} NMR, 101 MHz, $CDCl_3$)


OH
Me
Me
(1H NMR, 400 MHz, CDCl3)
7.26 CDCl3
6.98
6.36
6.35
6.33
6.32
5.74
5.72
5.71
5.70
5.69
5.68
5.67
5.65
3.51
2.28
1.94
1.94
1.93
1.92
1.92
2.24
1.03
0.96
0.93
5.91
2.93
f1 (ppm)

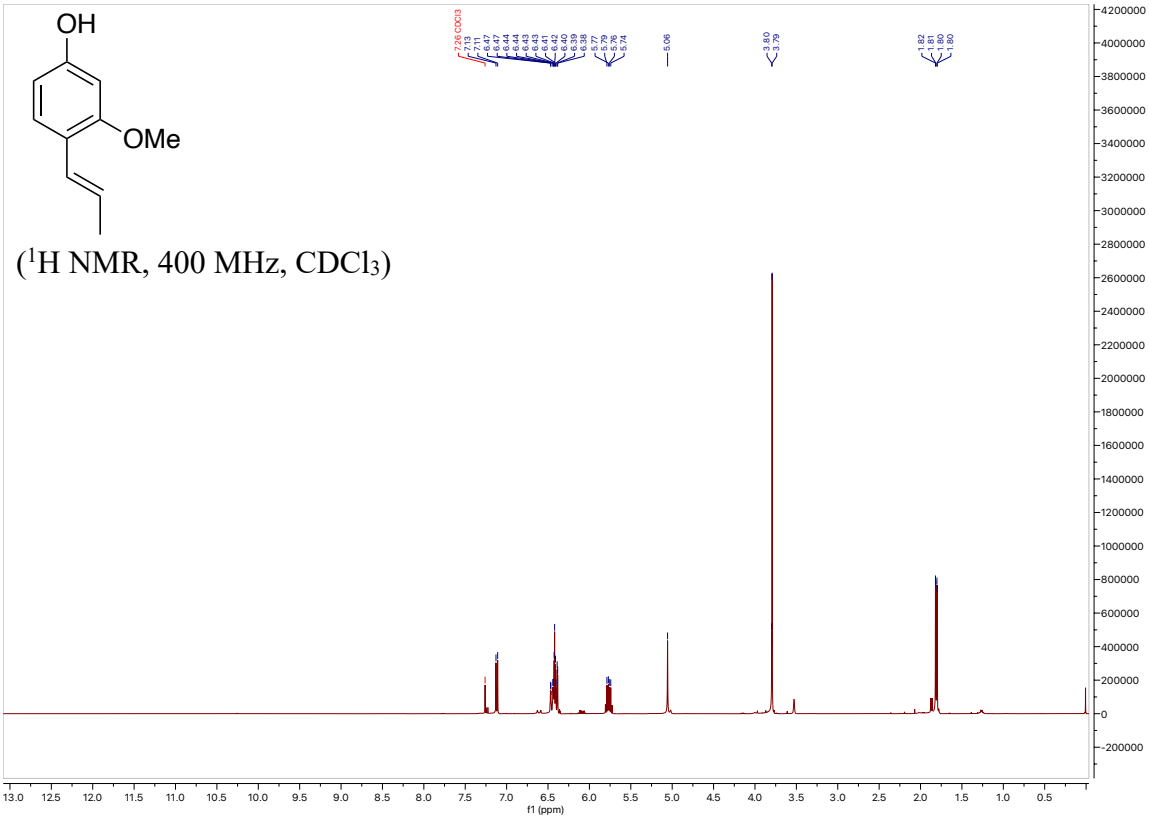

OH
Me
Me
(13C{1H} NMR, 101 MHz, CDCl3)
150.95
130.65
129.94
129.27
124.83
122.87
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
16.05
14.73
f1 (ppm)

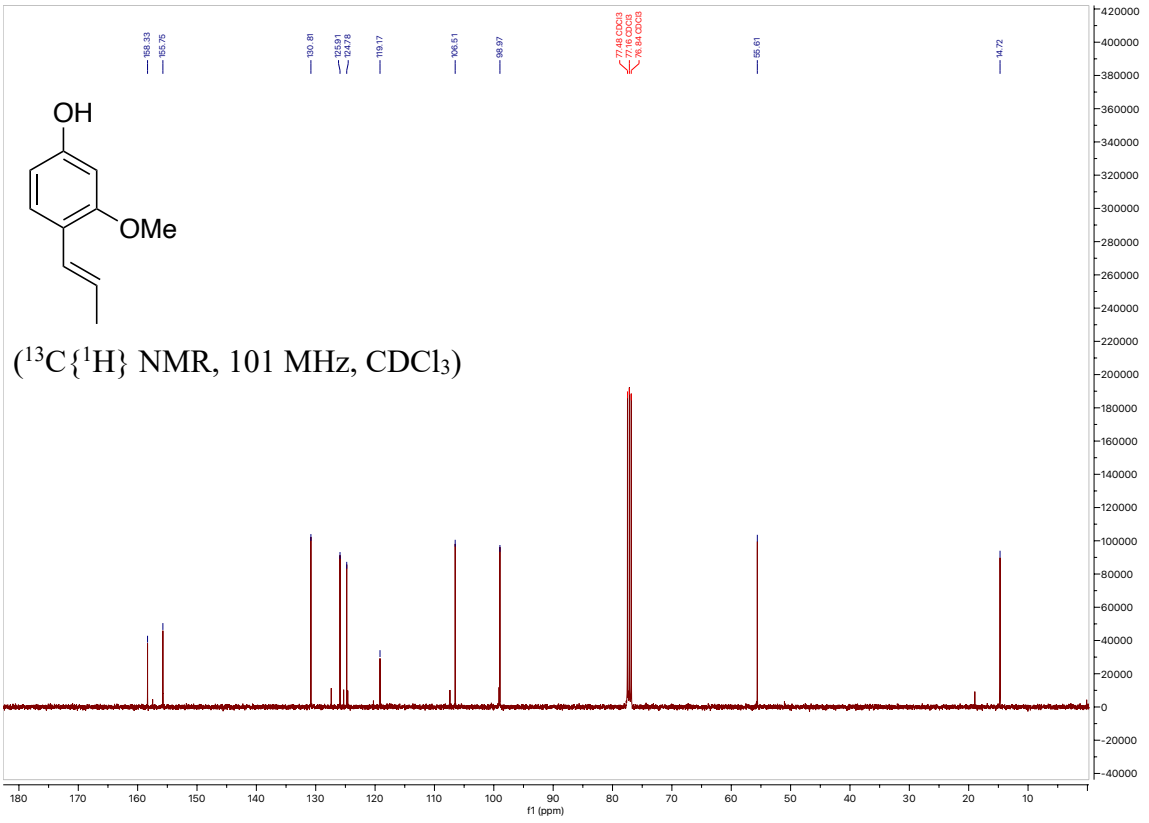


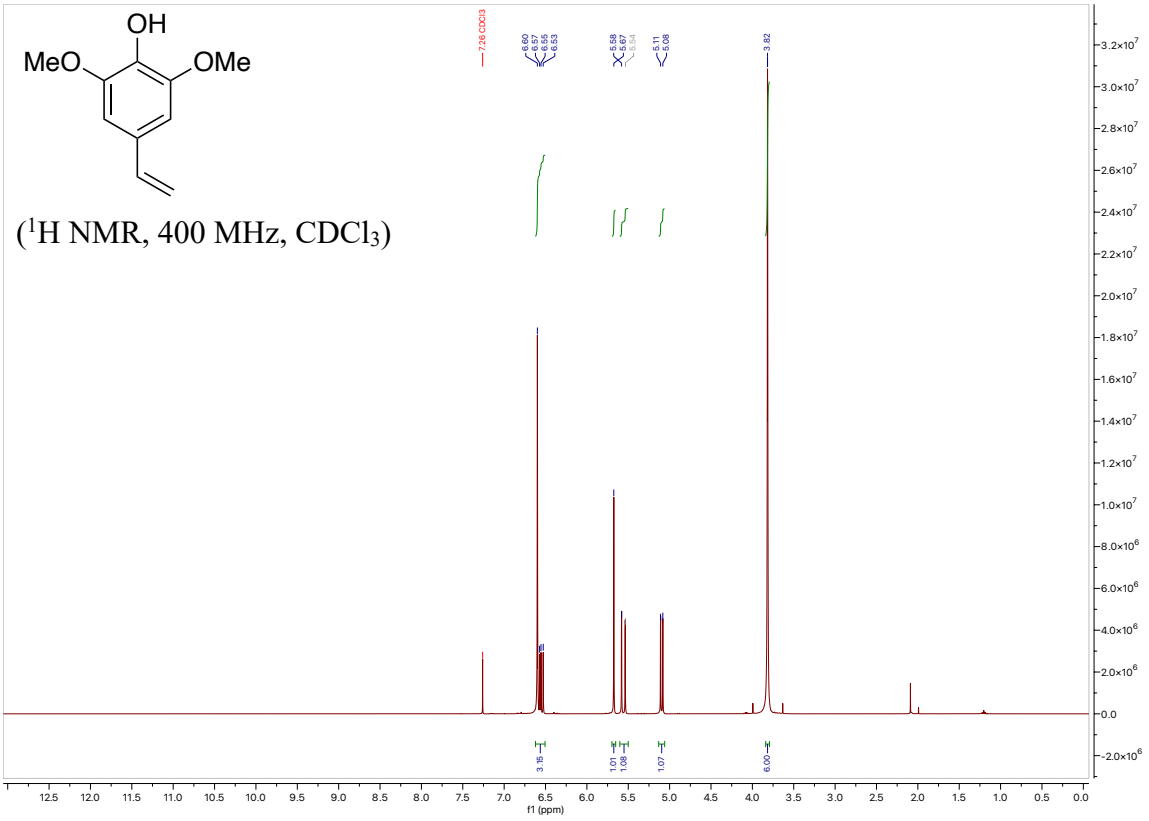
(^{1}H NMR, 400 MHz, $CDCl_3$)



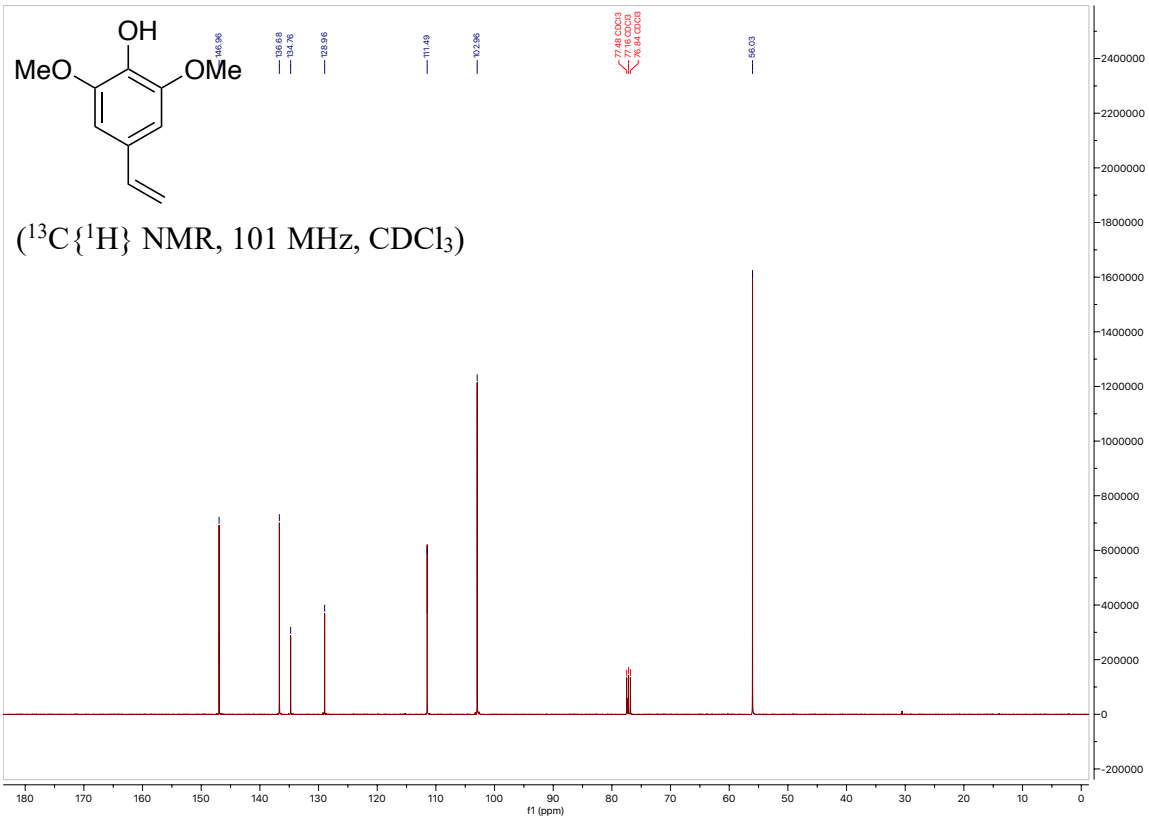
(^{13}C{^{1}H} NMR, 101 MHz, $CDCl_3$)


OH
OMe
(^{1}H NMR, 400 MHz, CDCl$_3$)
7.26 CDCl3
7.13
7.11
6.47
6.47
6.44
6.44
6.43
6.41
6.42
6.40
6.39
6.38
5.77
5.76
5.76
5.74
5.06
3.80
3.79
1.82
1.81
1.80
1.80
f1 (ppm)

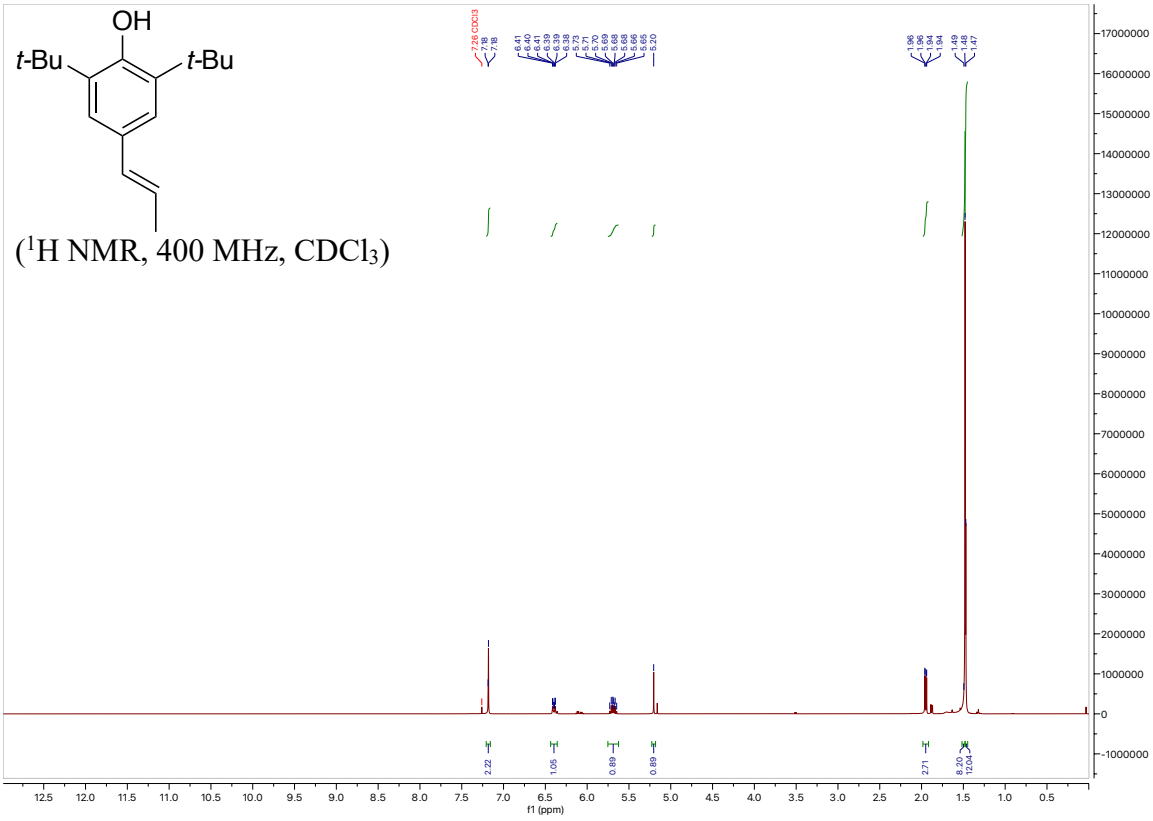

OH
OMe
(^{13}C{^{1}H} NMR, 101 MHz, CDCl$_3$)
158.33
155.75
130.81
125.91
124.78
119.17
106.51
98.97
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.61
14.72
f1 (ppm)



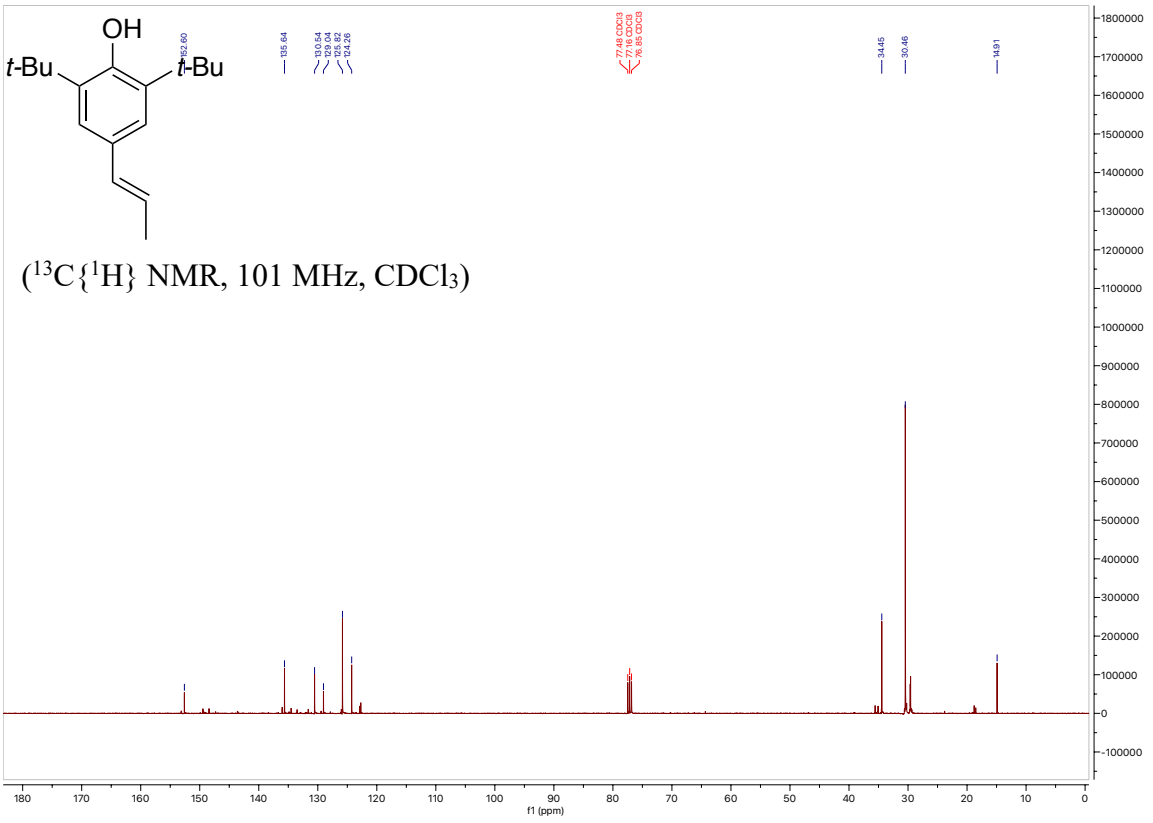
(^{1}H NMR, 400 MHz, $CDCl_3$)



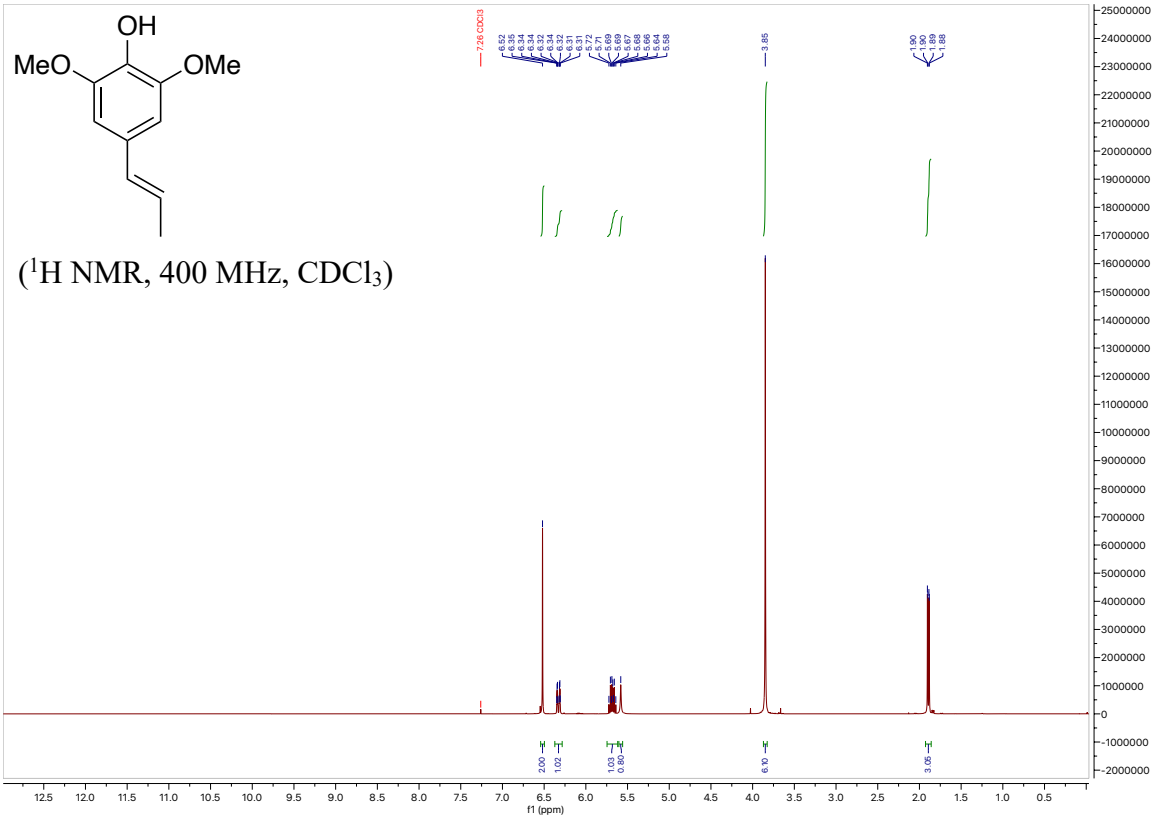
(^{13}C{^{1}H} NMR, 101 MHz, $CDCl_3$)

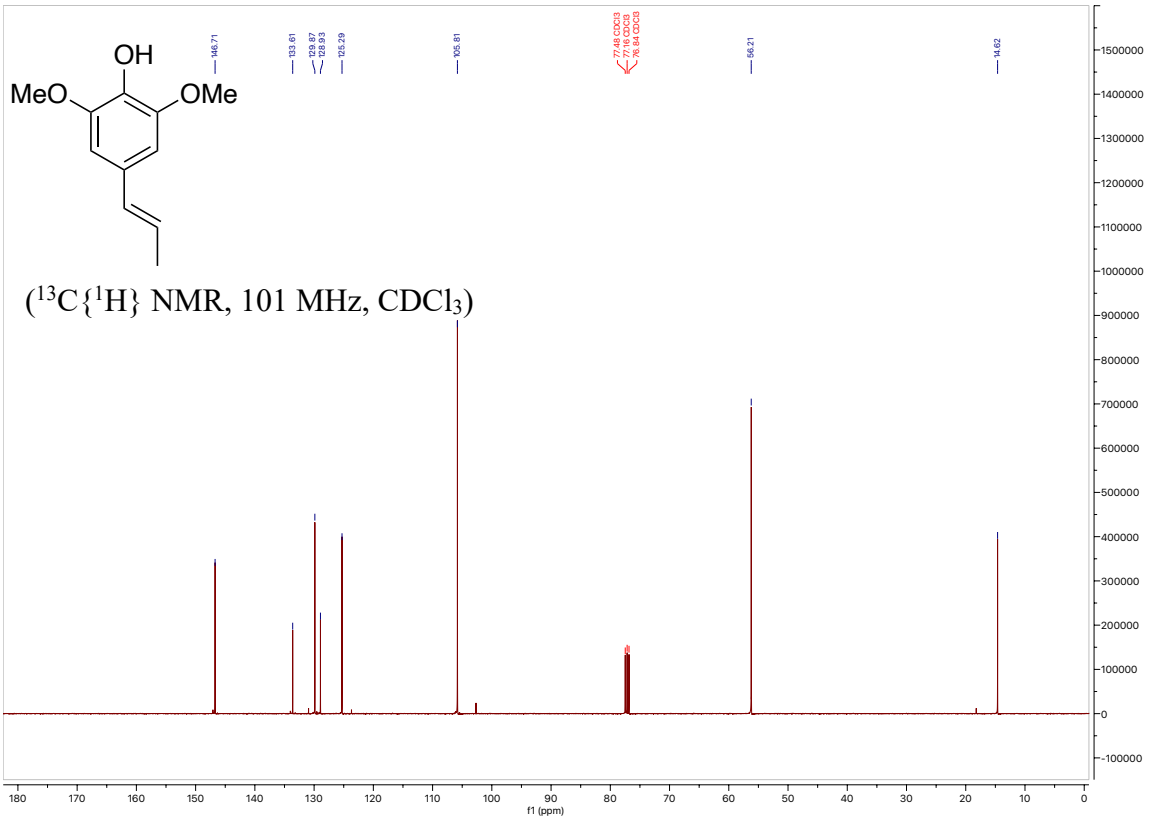


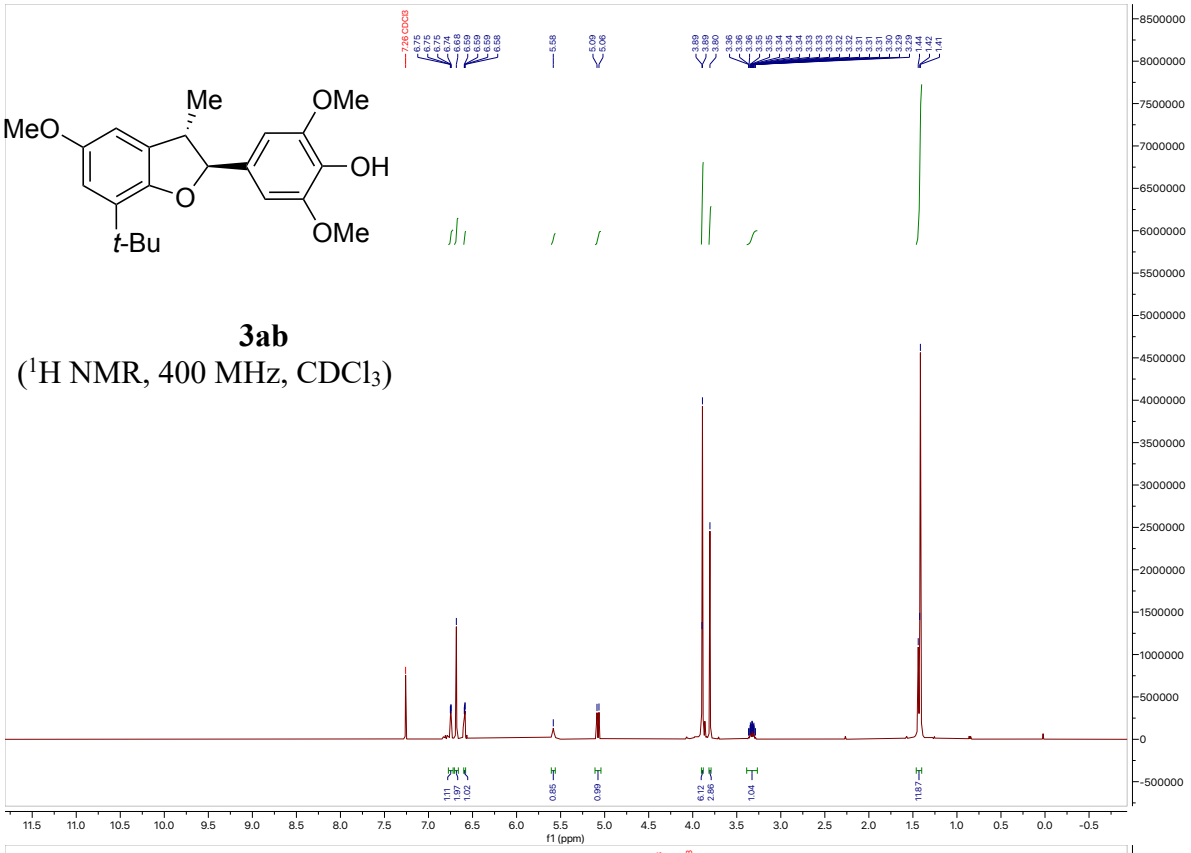
(^{1}H NMR, 400 MHz, $CDCl_3$)



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

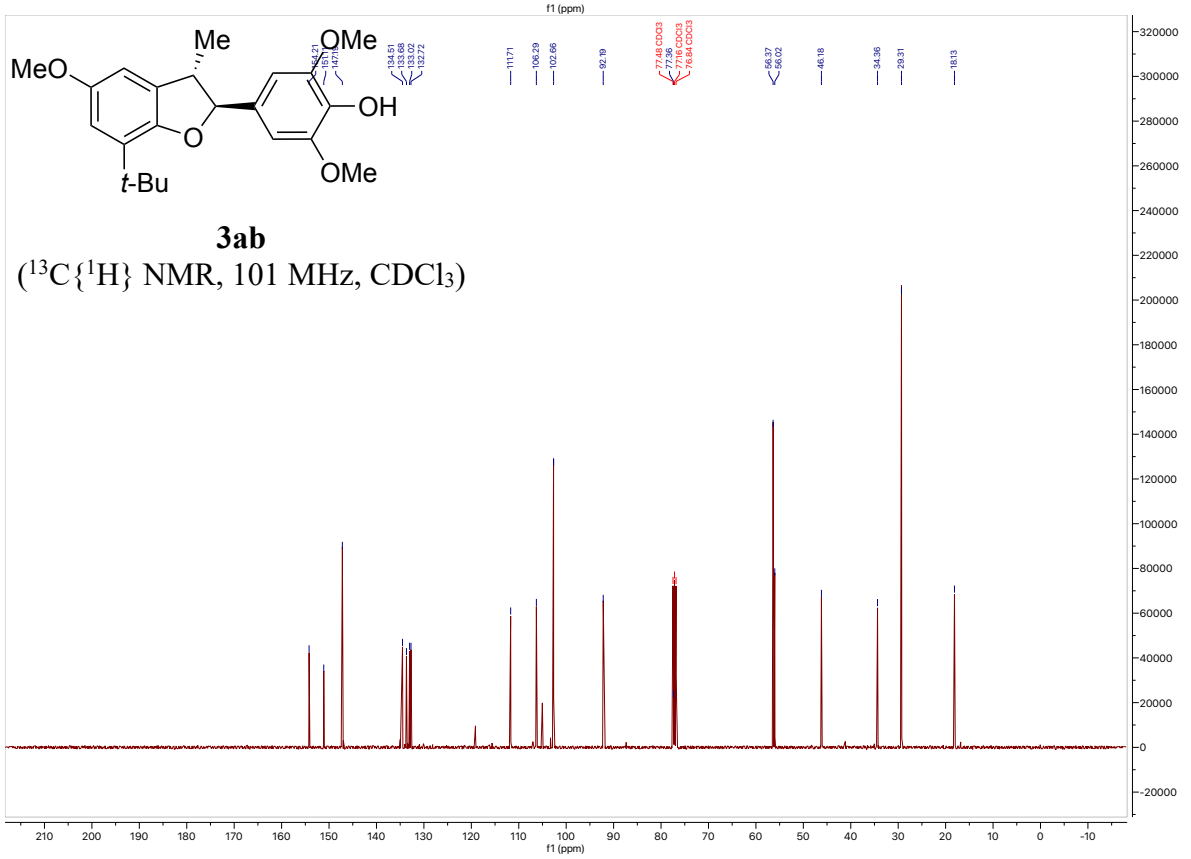

OH
MeO
OMe
(1H NMR, 400 MHz, CDCl3)
f1 (ppm)


OH
MeO
OMe
(13C{1H} NMR, 101 MHz, CDCl3)
f1 (ppm)



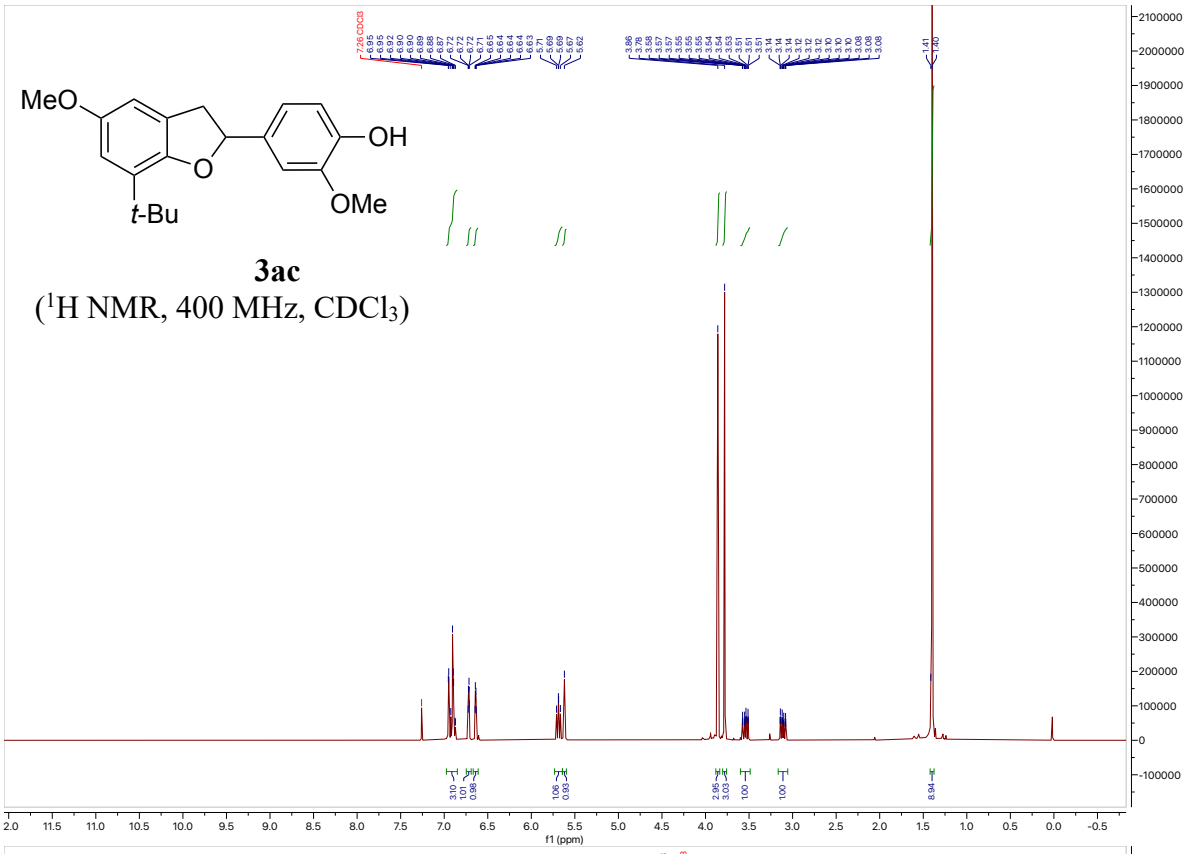
3ab

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



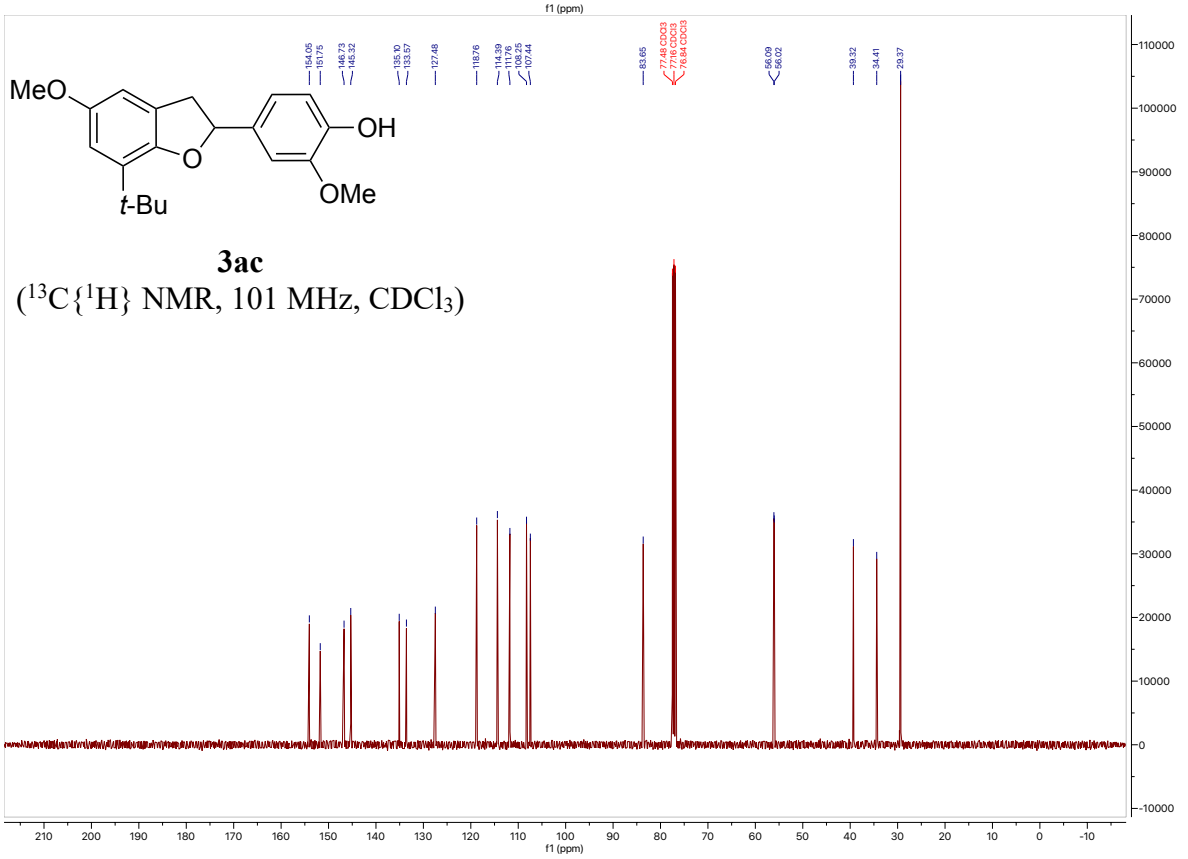
3ab

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



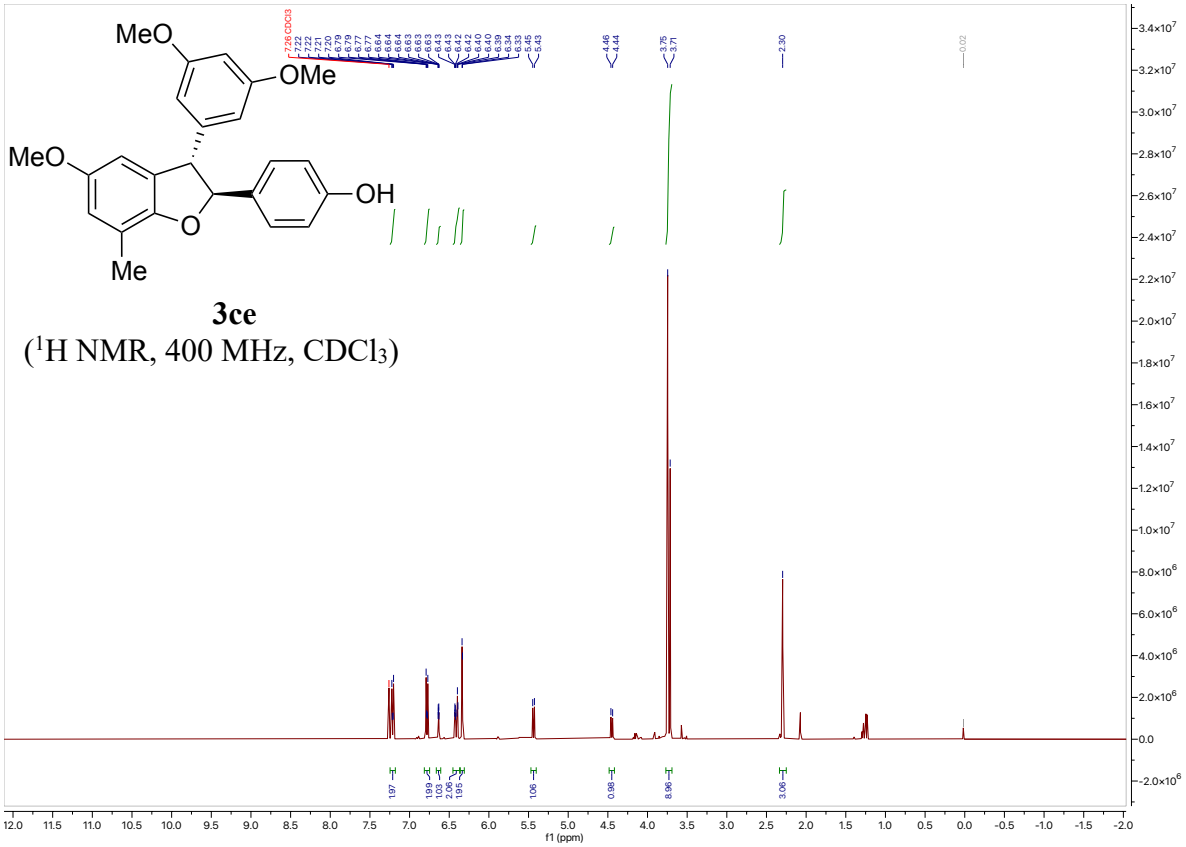
3ac

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



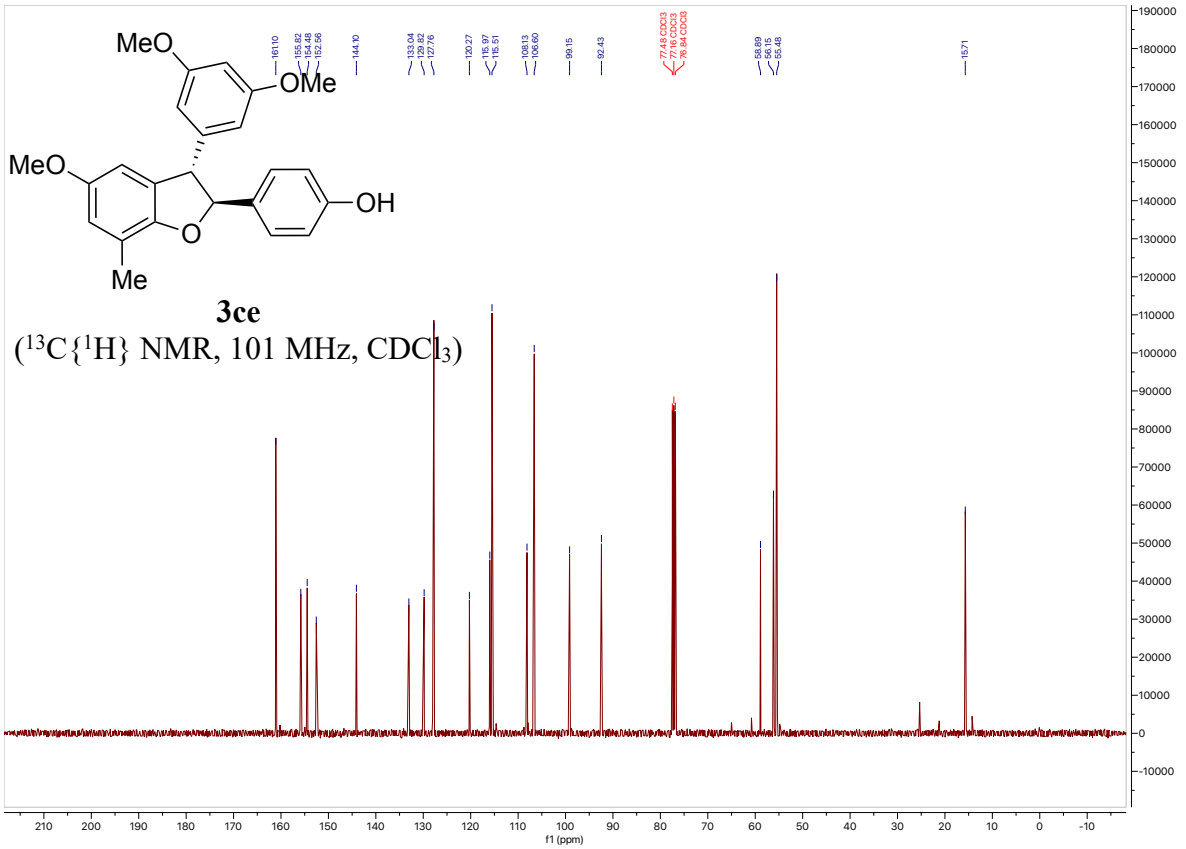
3ac

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



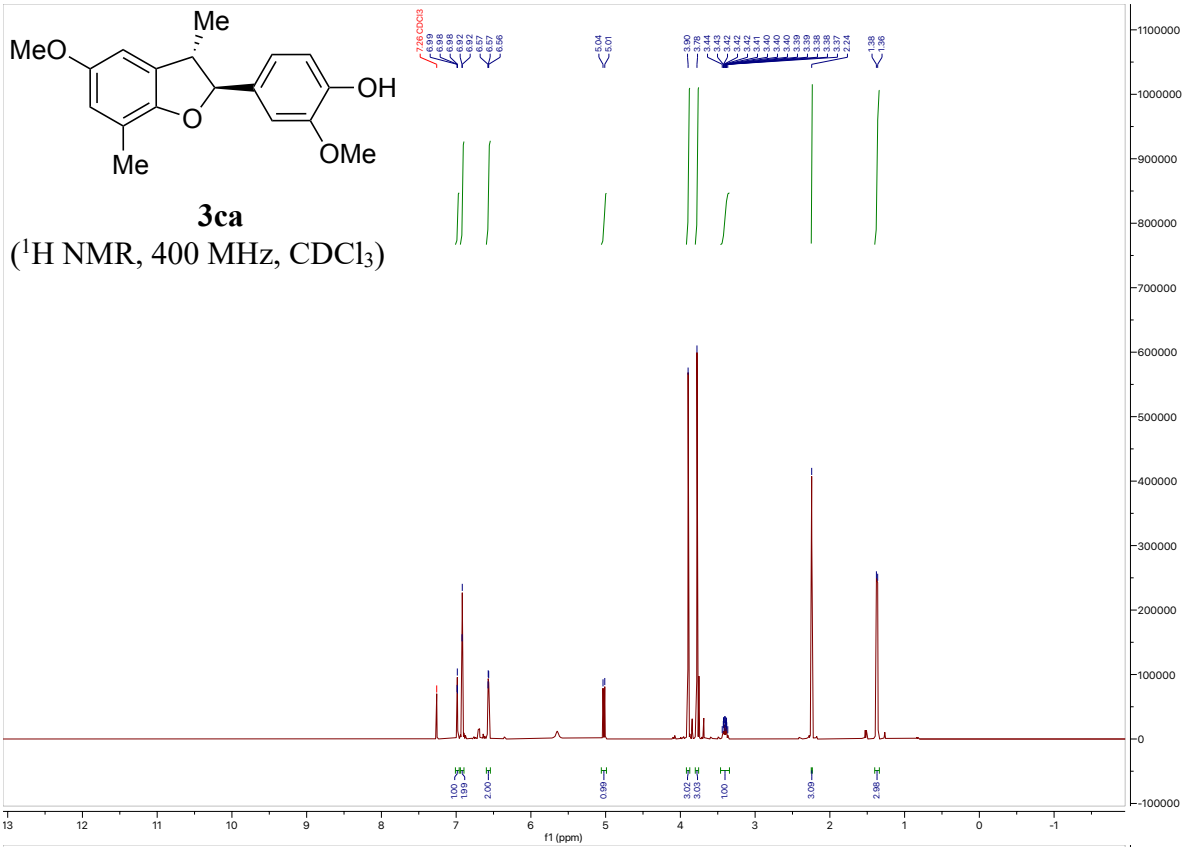
3ce

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



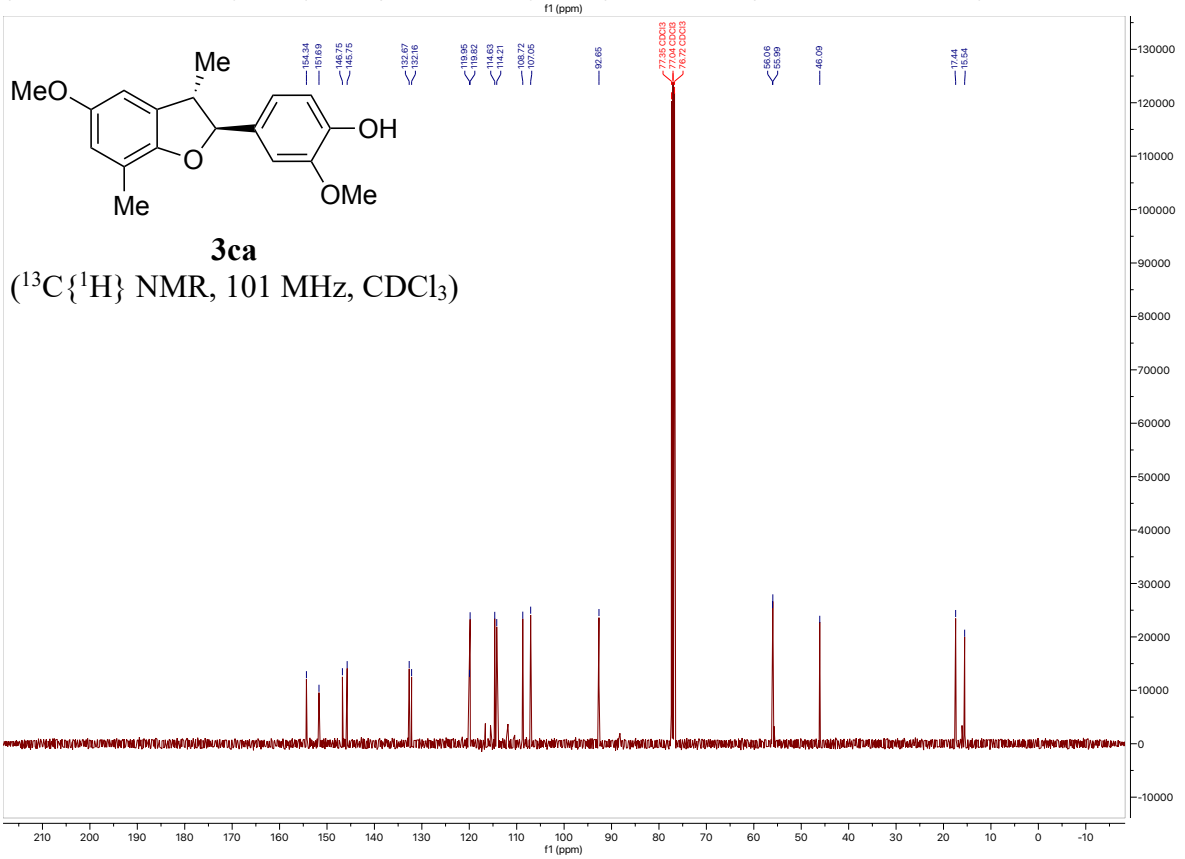
3ce

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



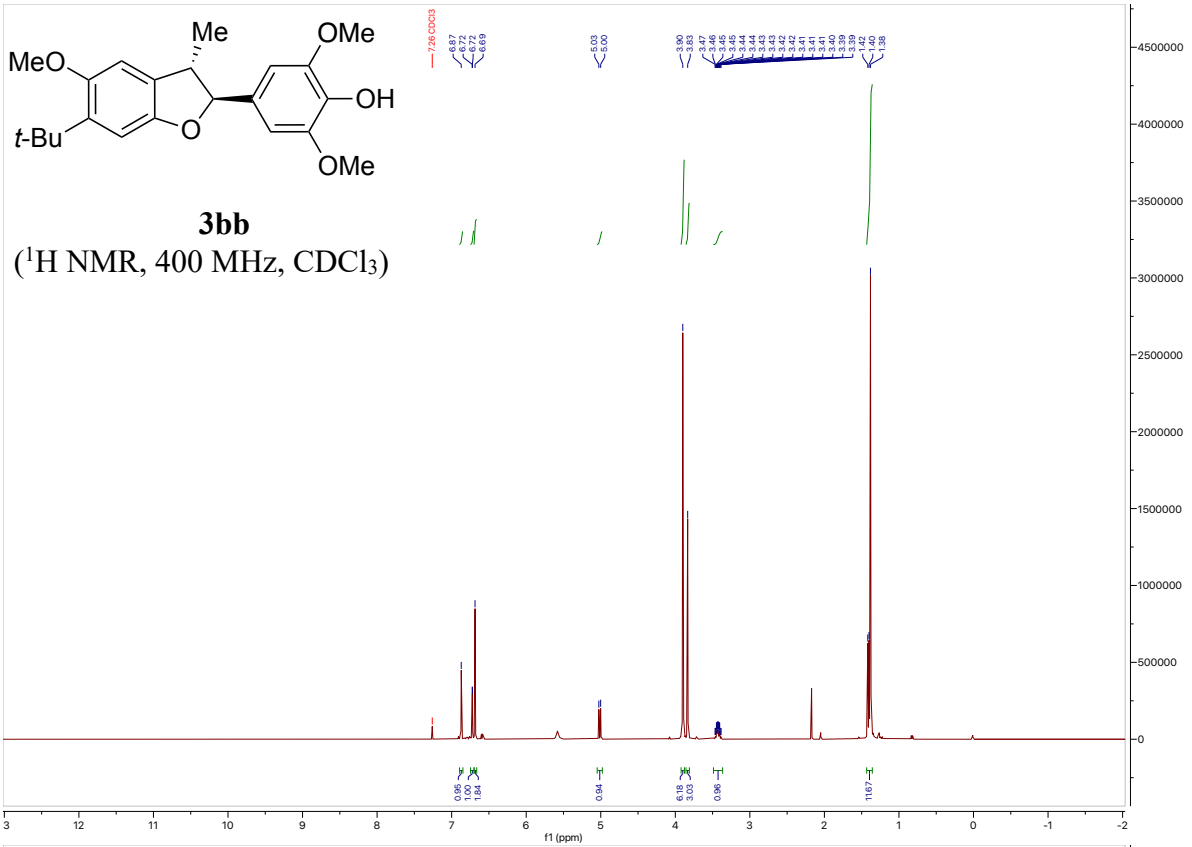
3ca

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



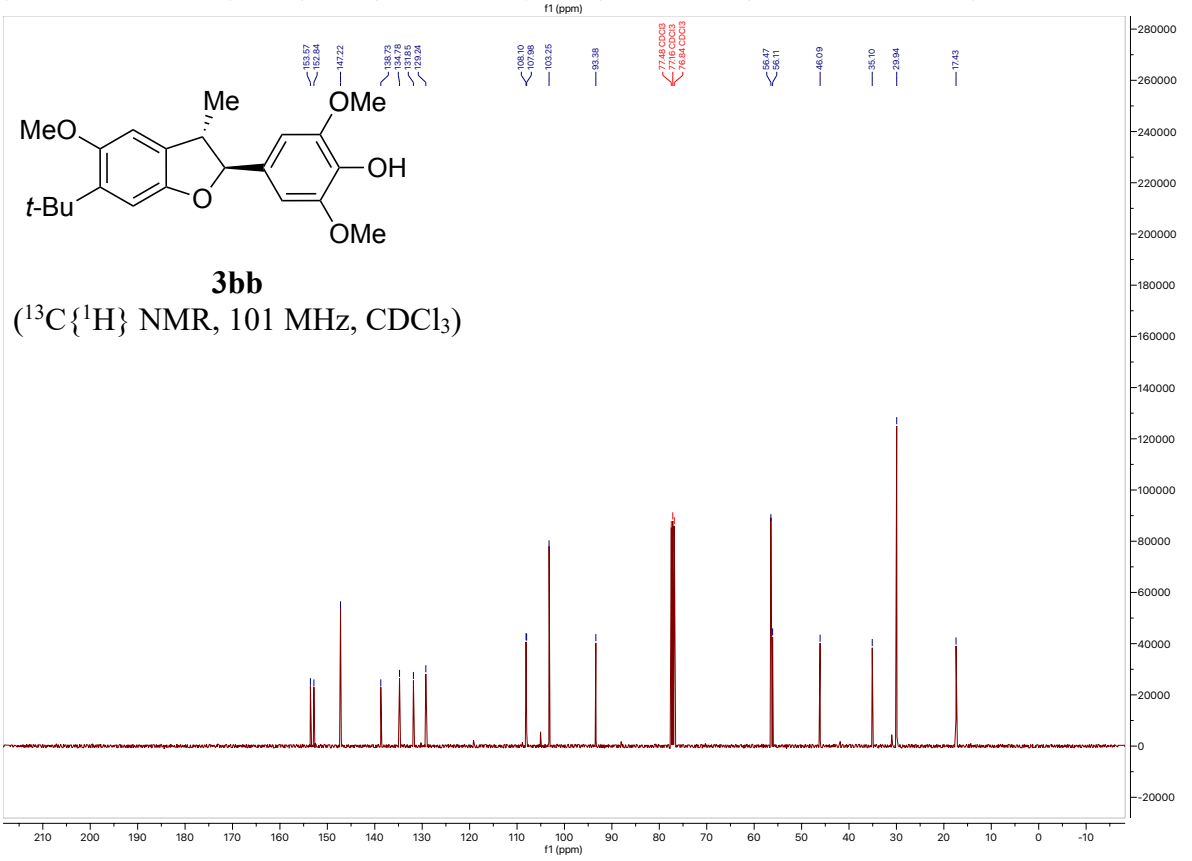
3ca

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



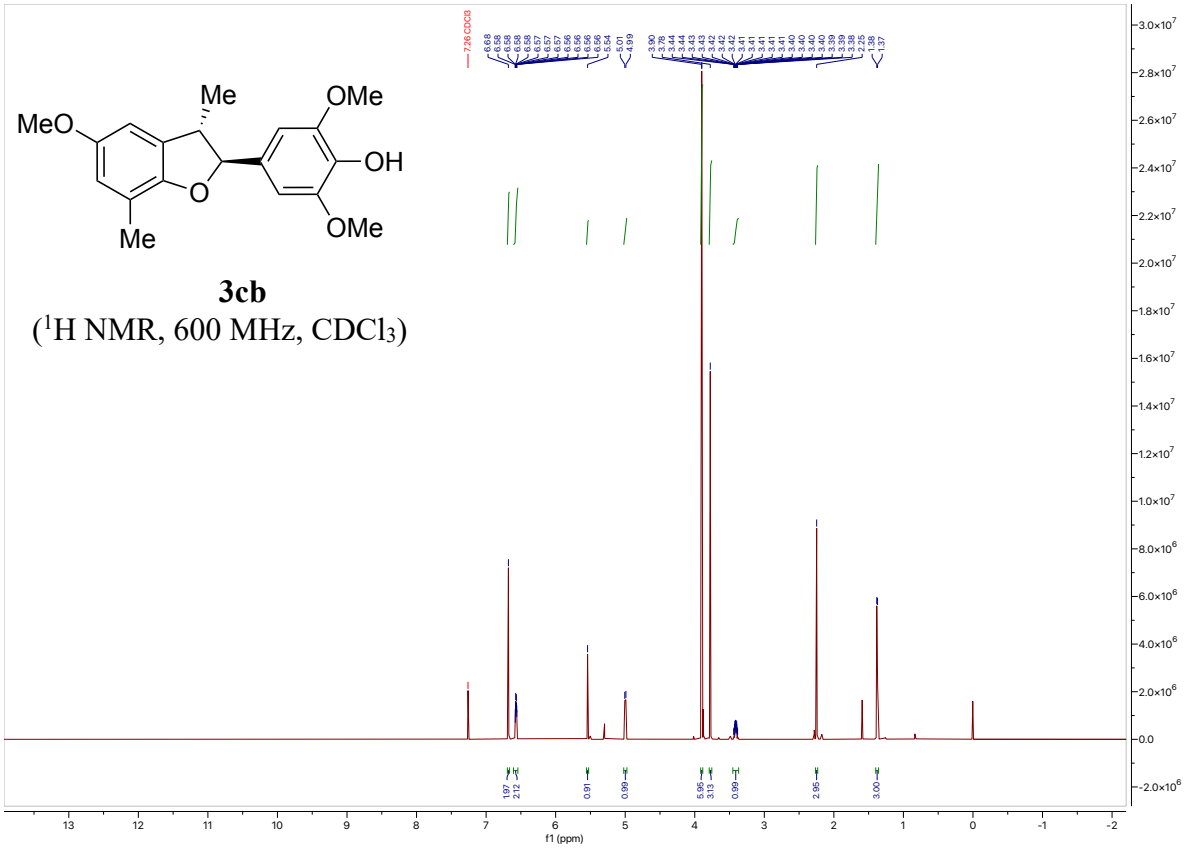
3bb

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



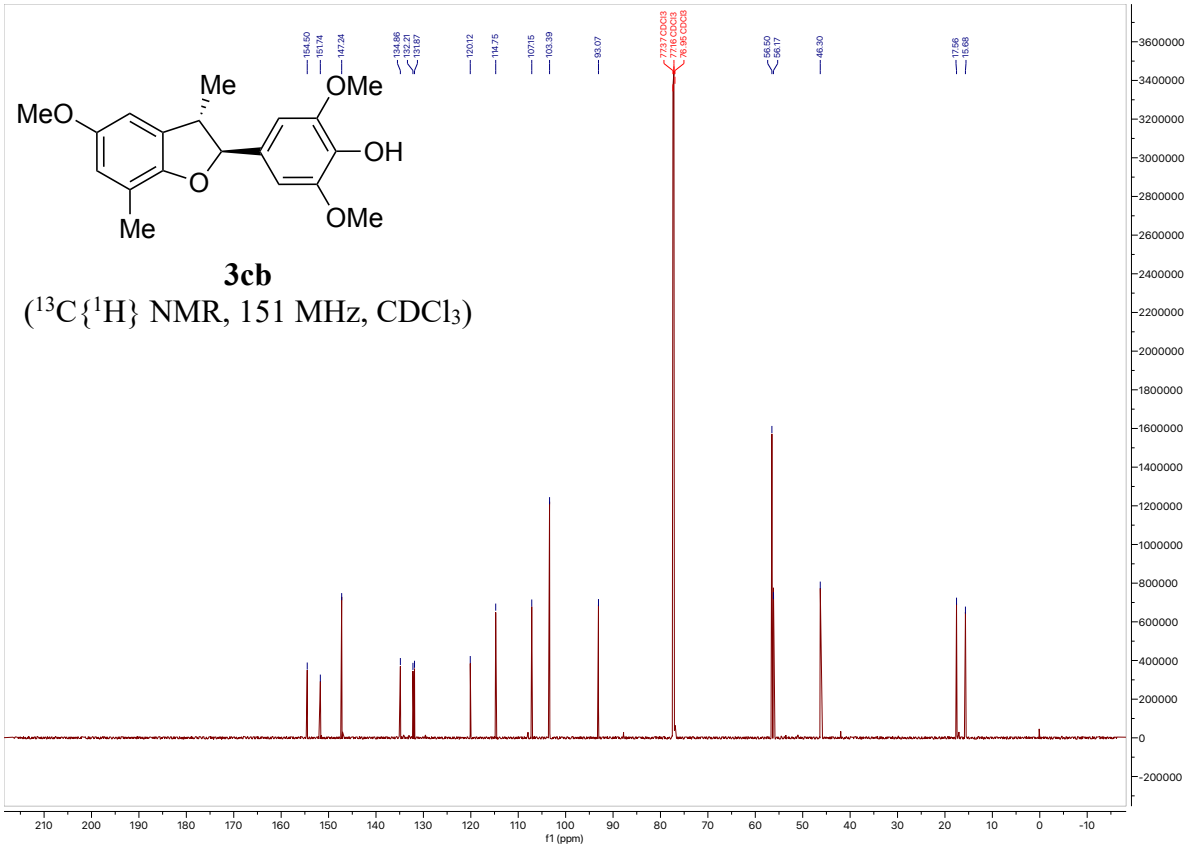
3bb

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



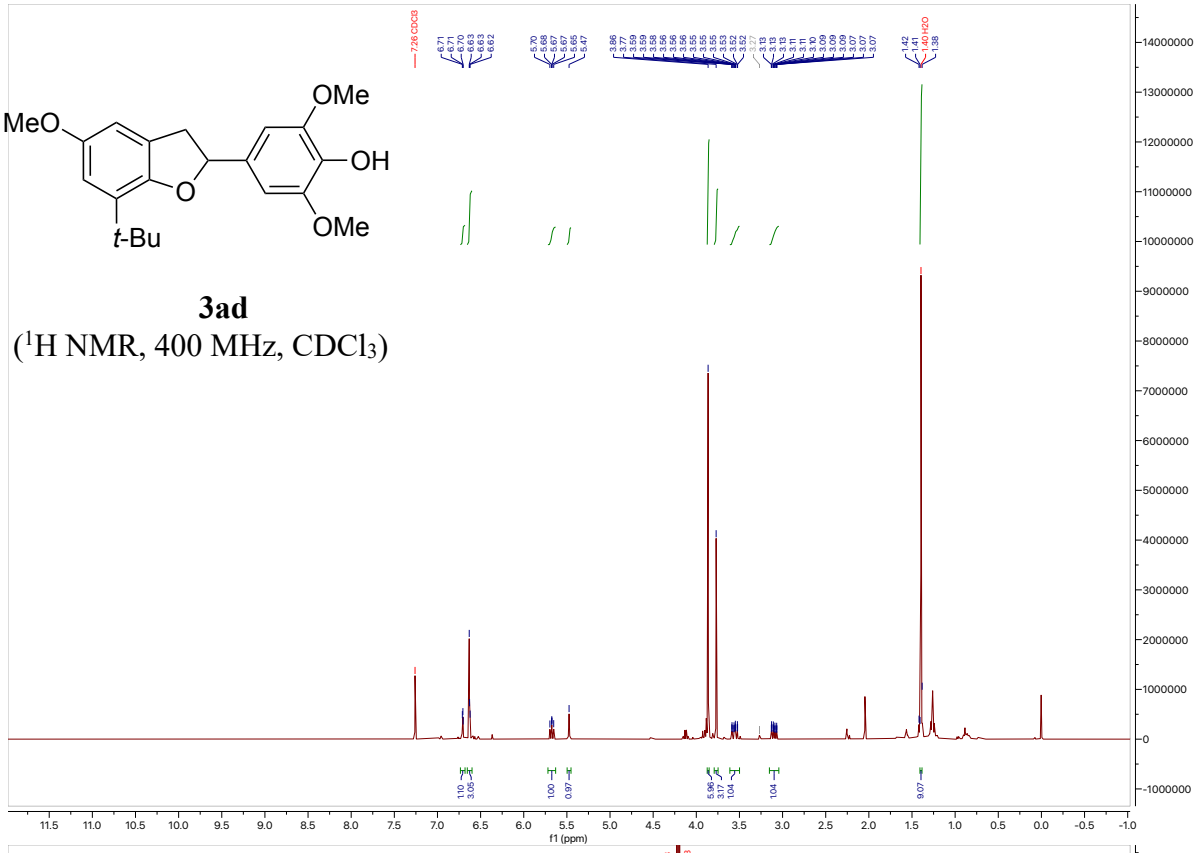
3cb

(^{1}H NMR, 600 MHz, $CDCl_3$)



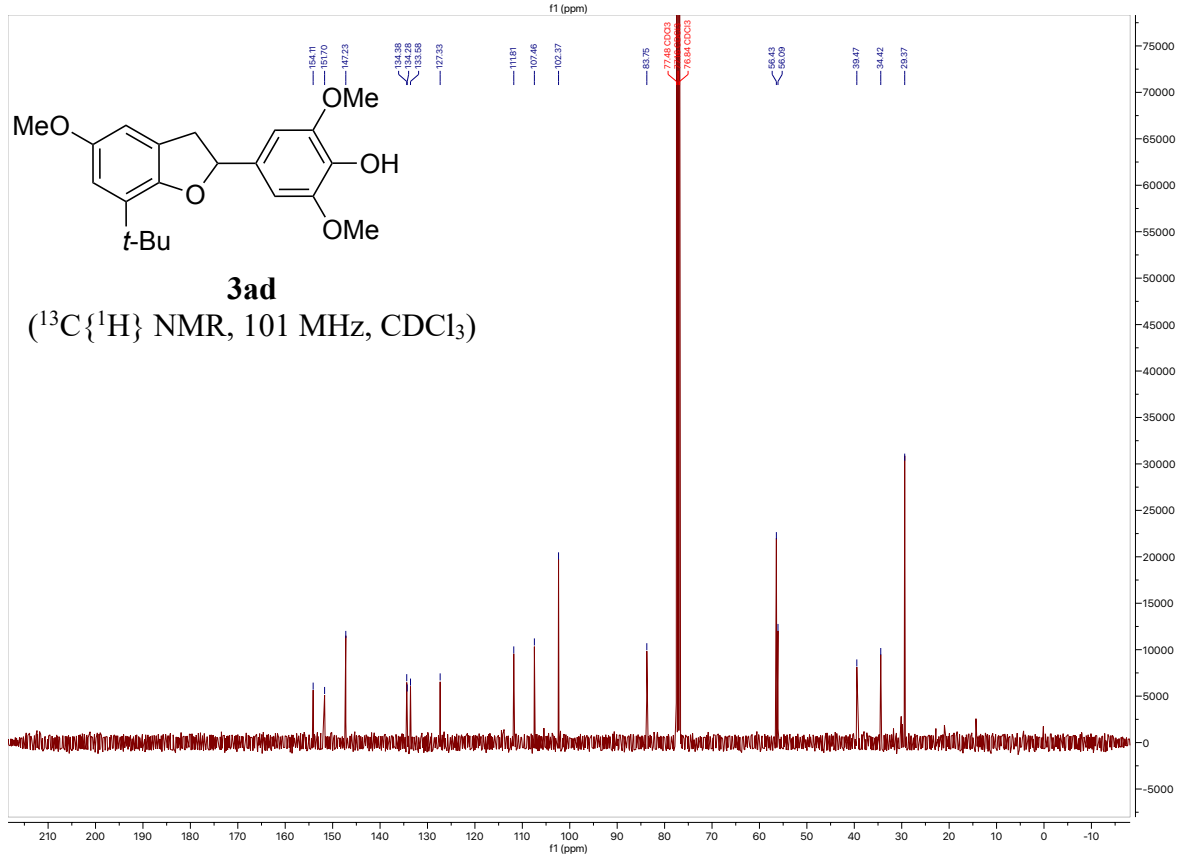
3cb

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



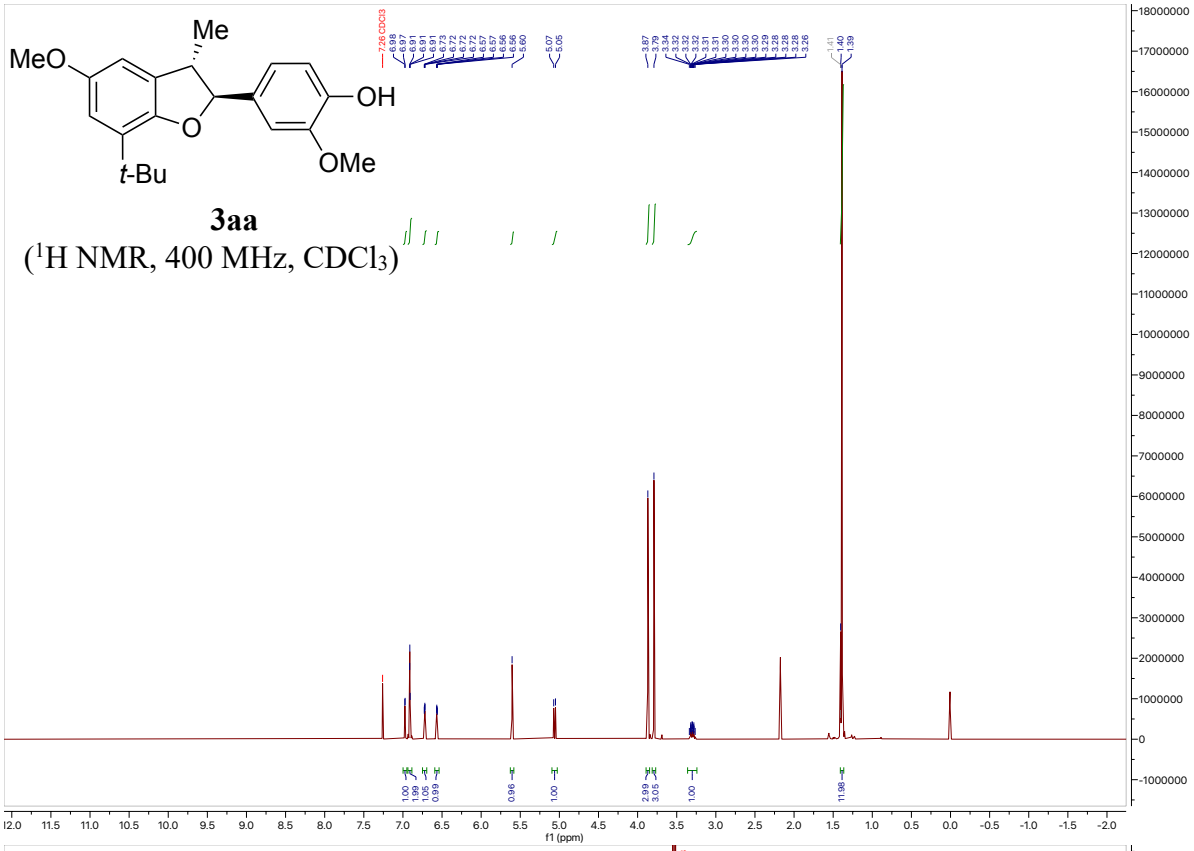
3ad

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



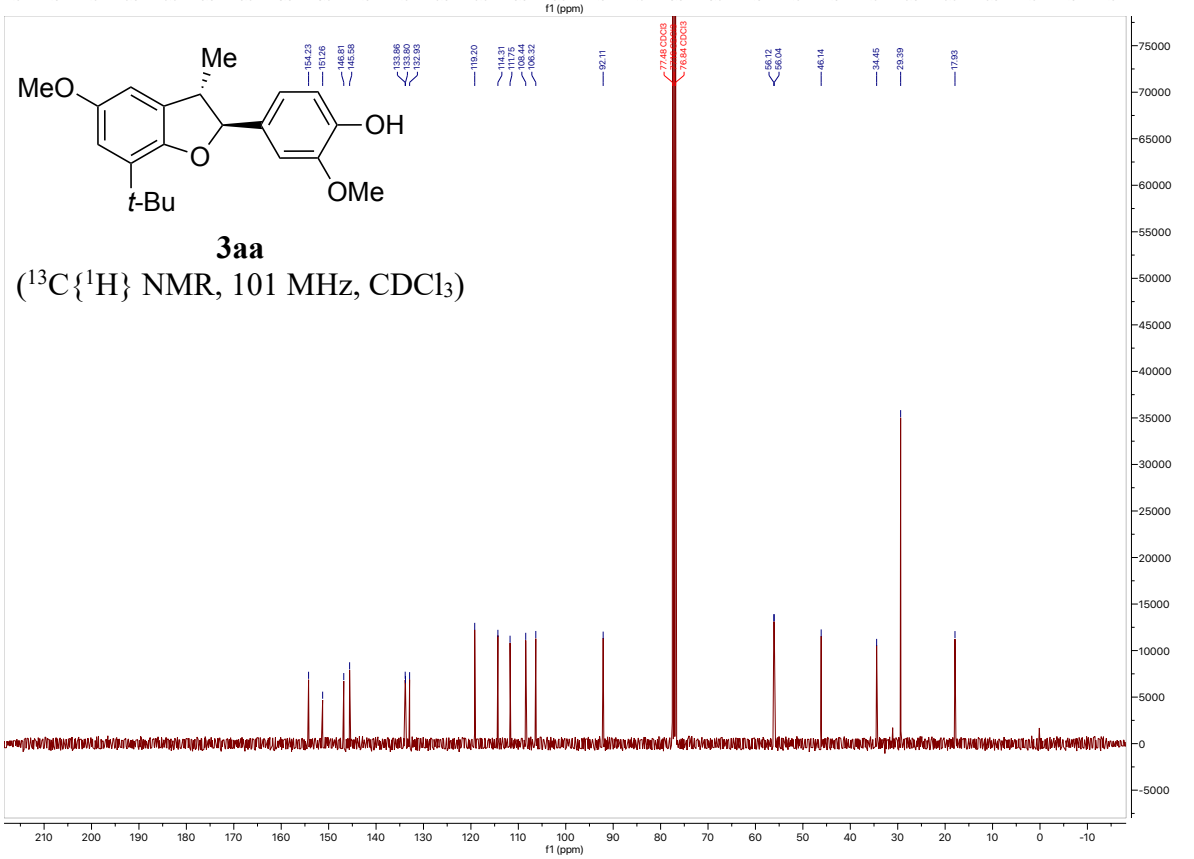
3ad

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



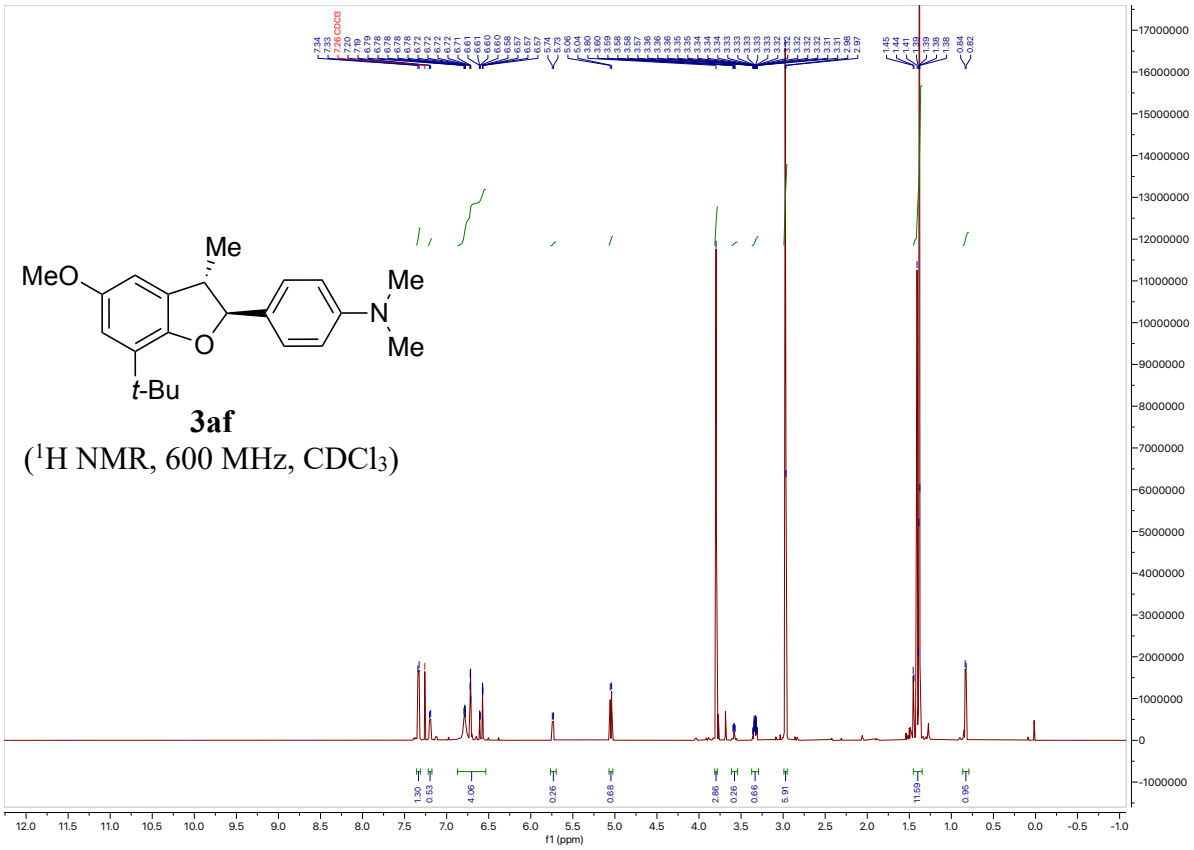
3aa

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



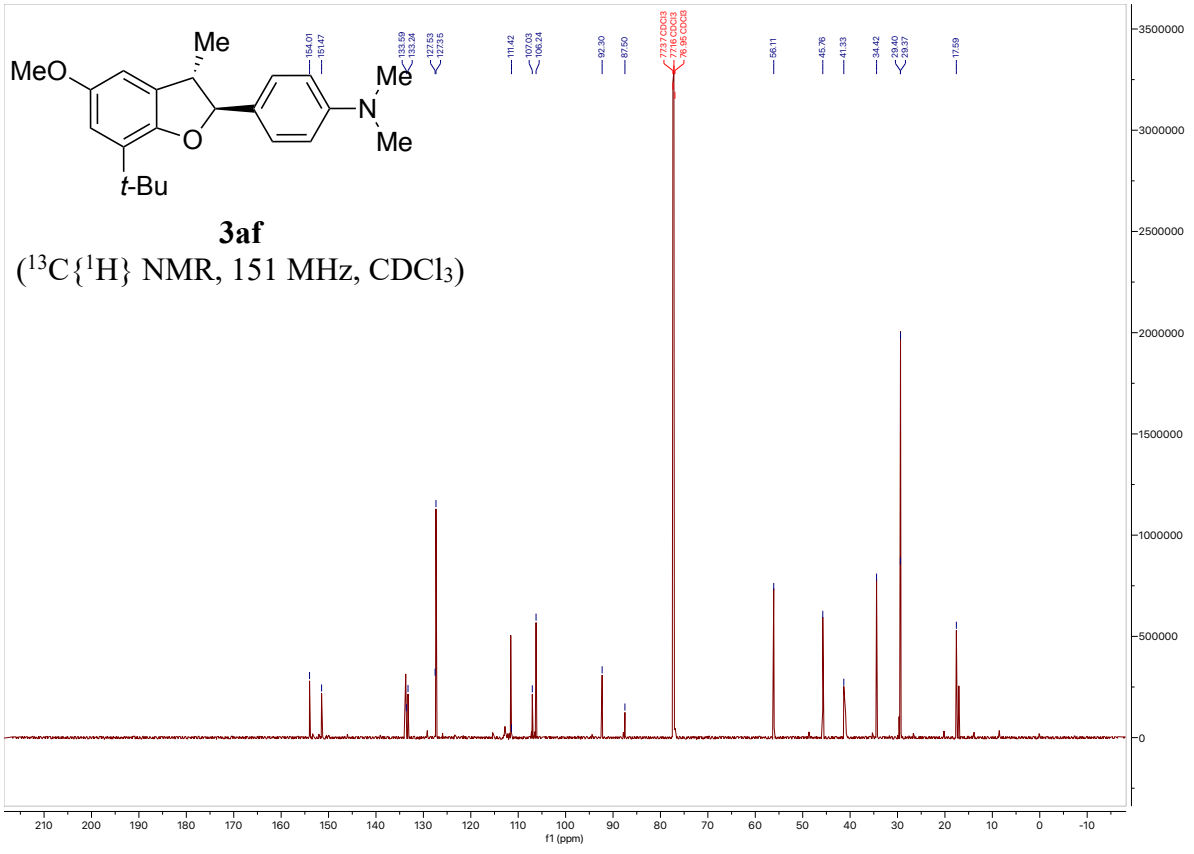
3aa

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



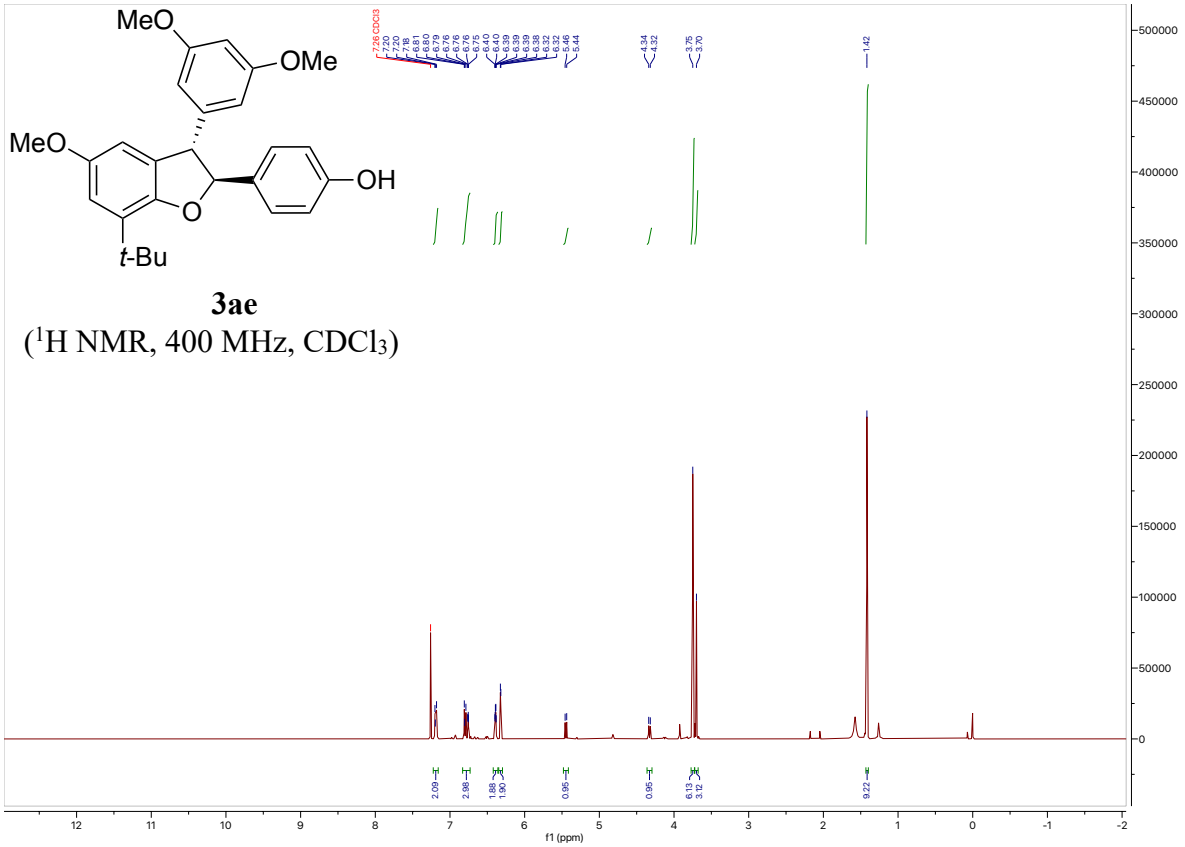
3af

(^{1}H NMR, 600 MHz, $CDCl_3$)



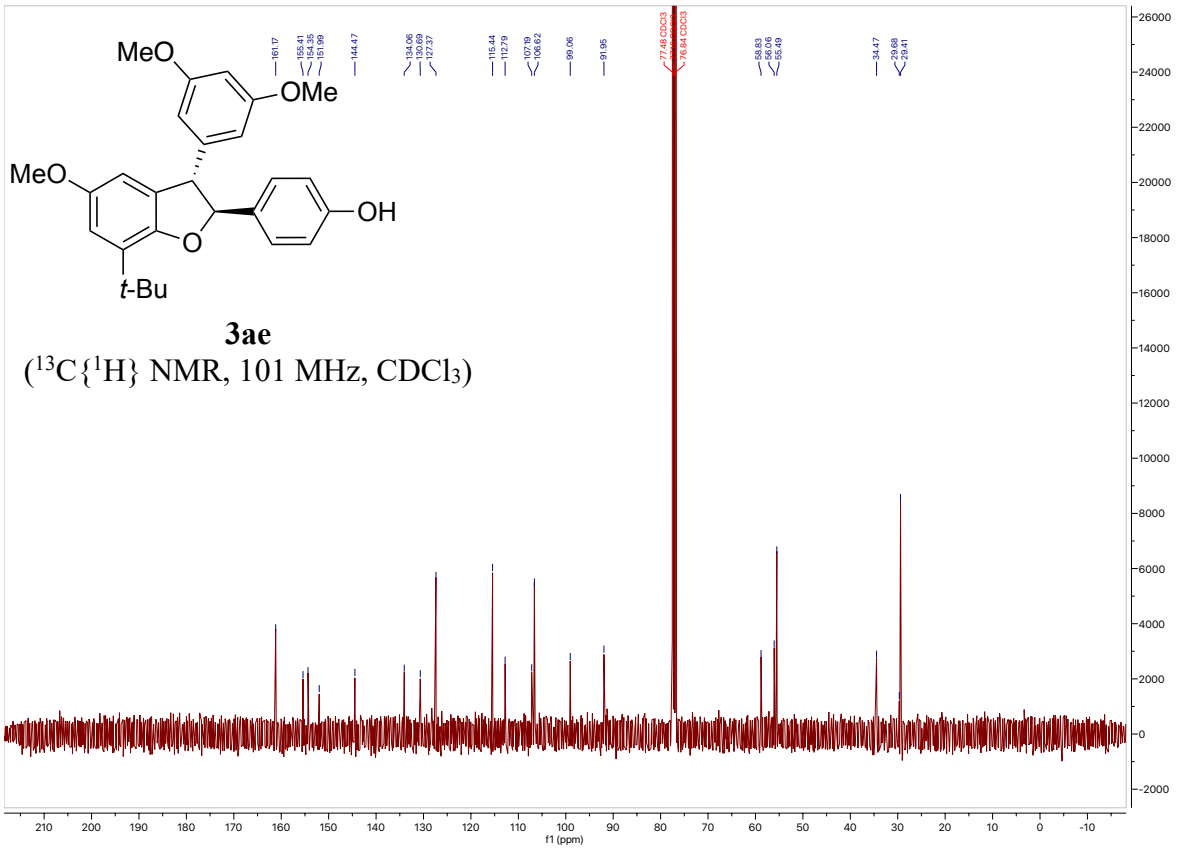
3af

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



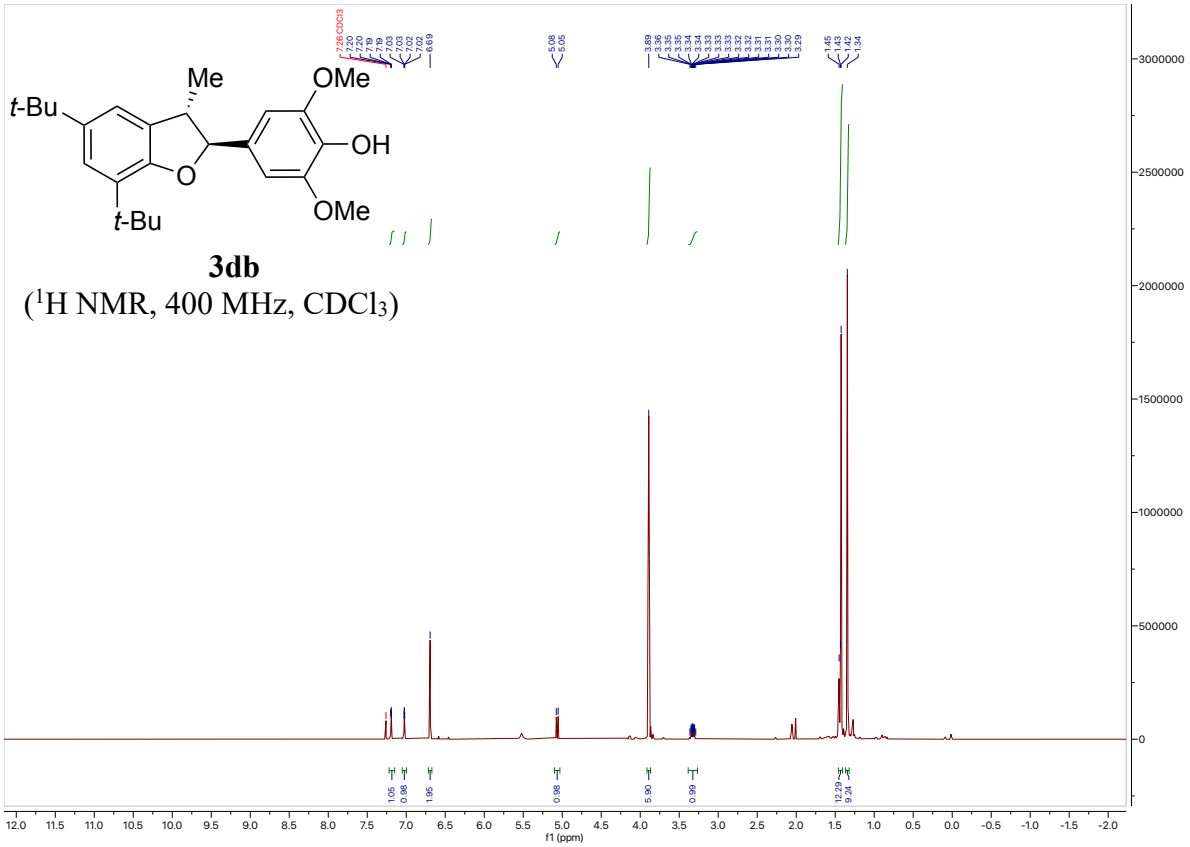
3ae

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



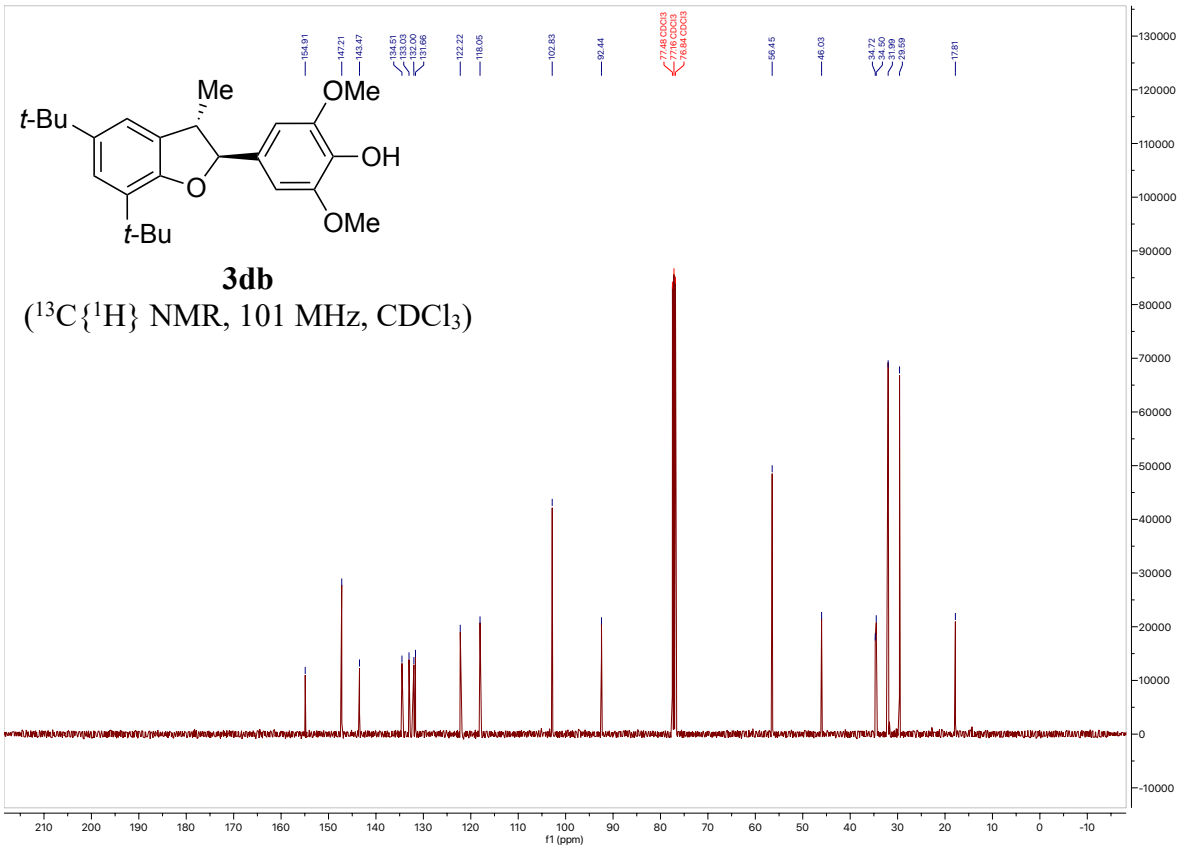
3ae

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



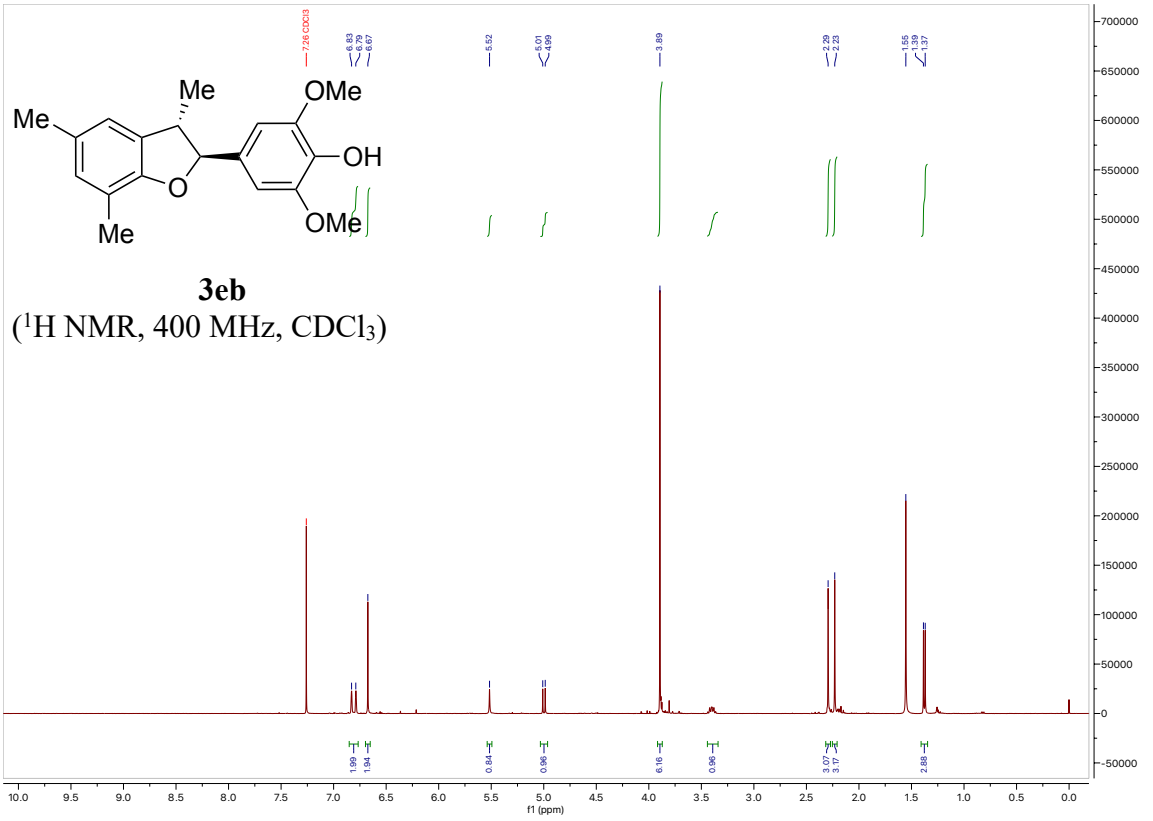
3db

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



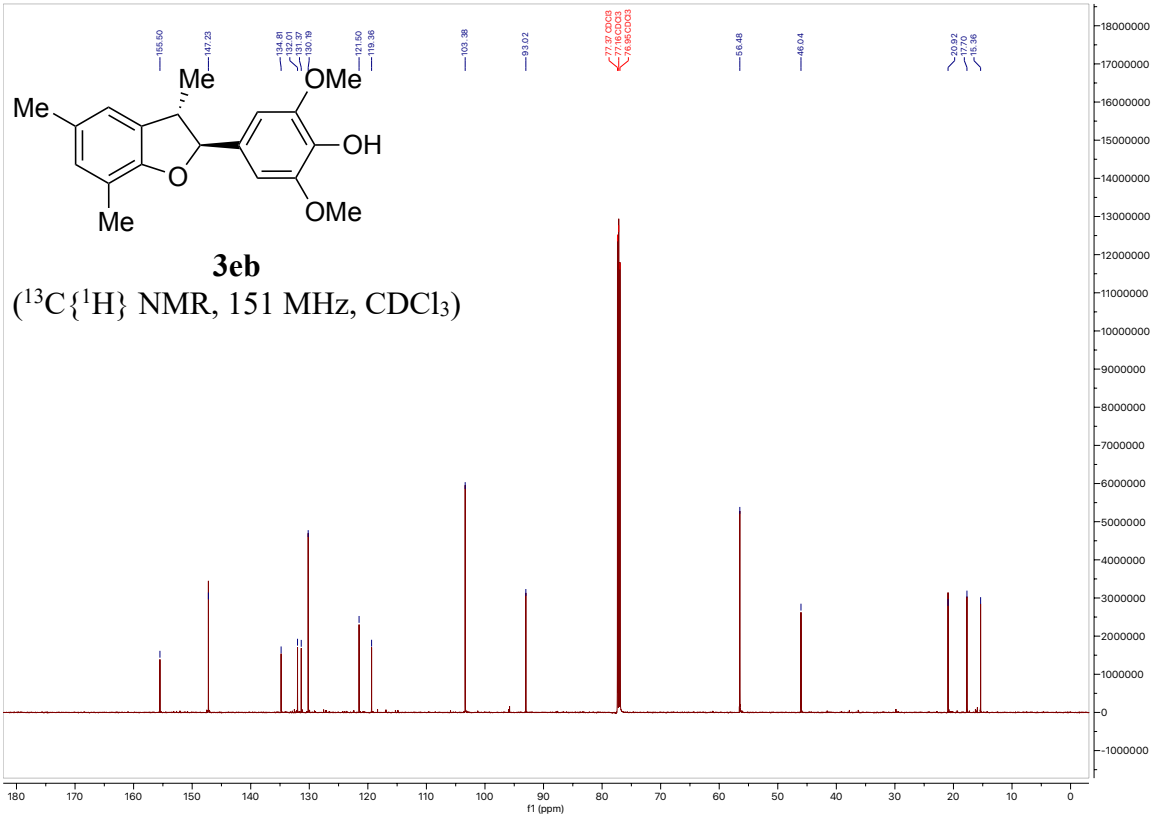
3db

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



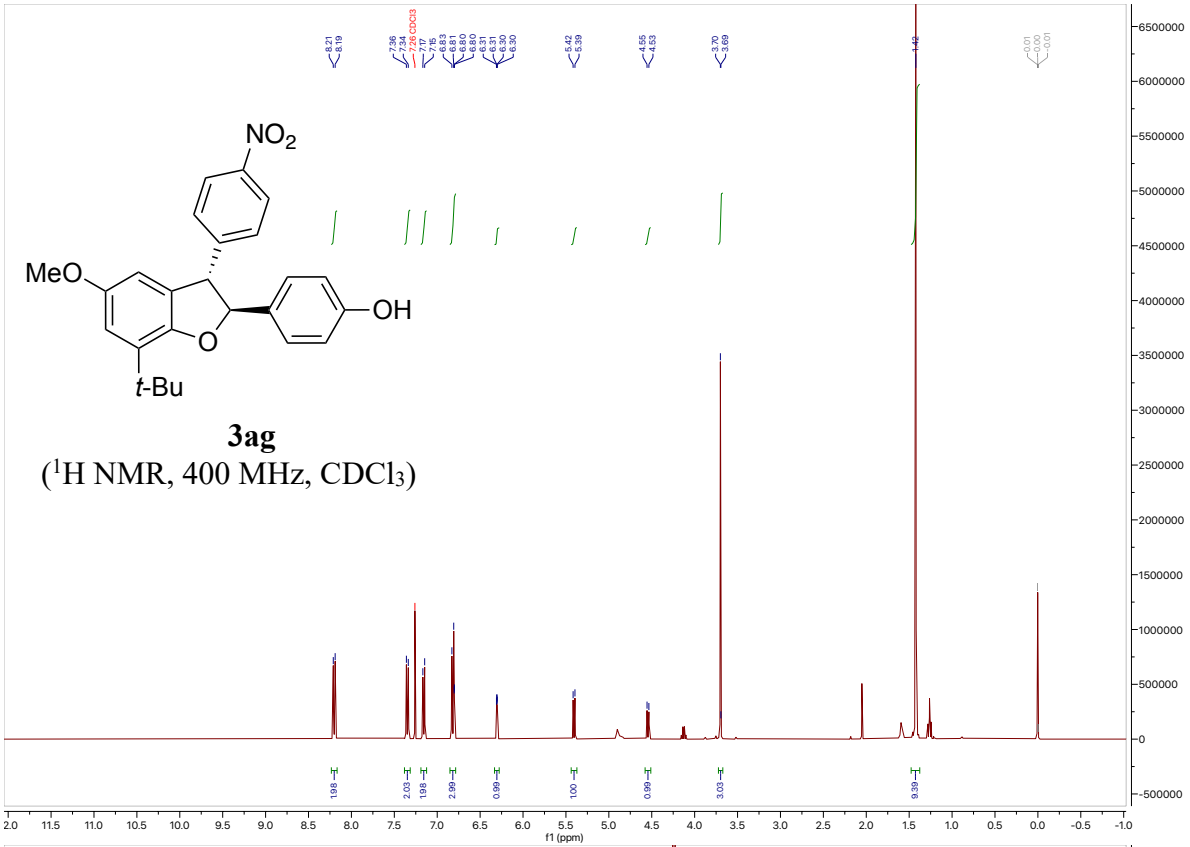
3eb

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



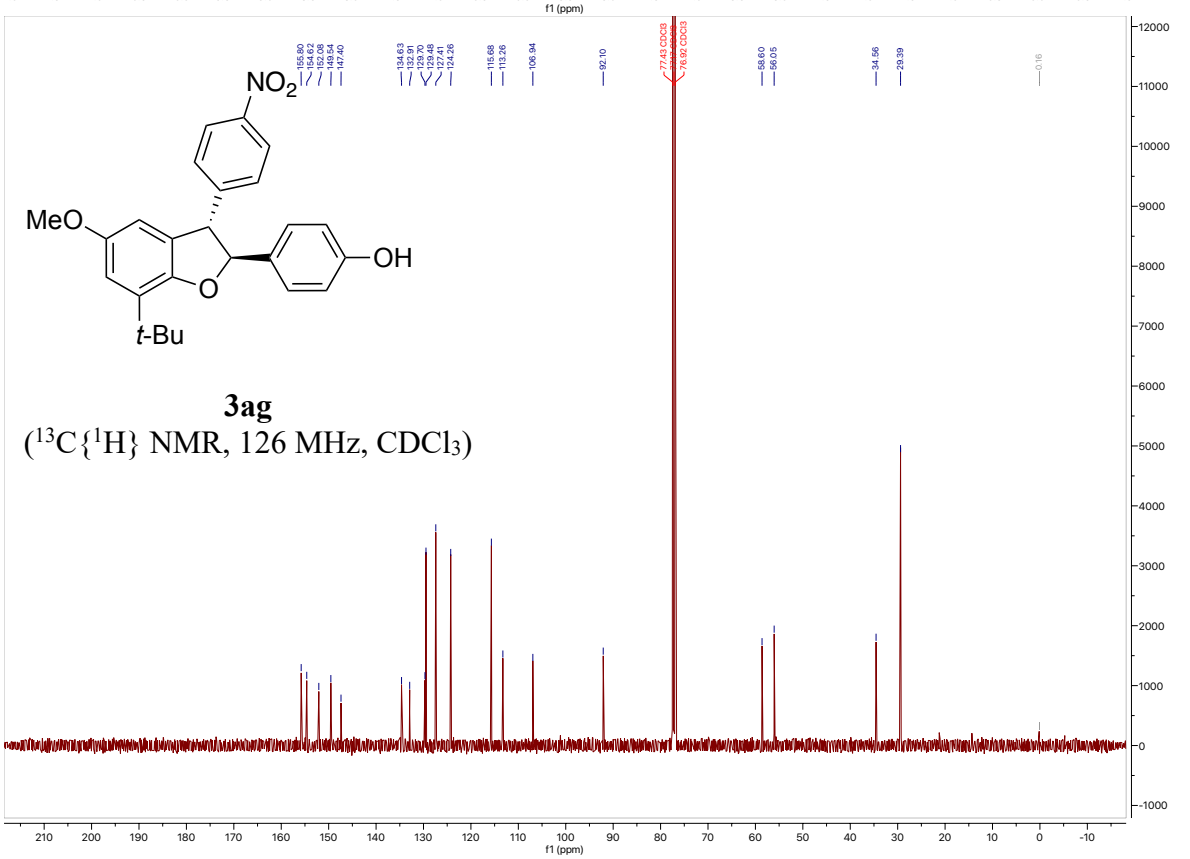
3eb

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



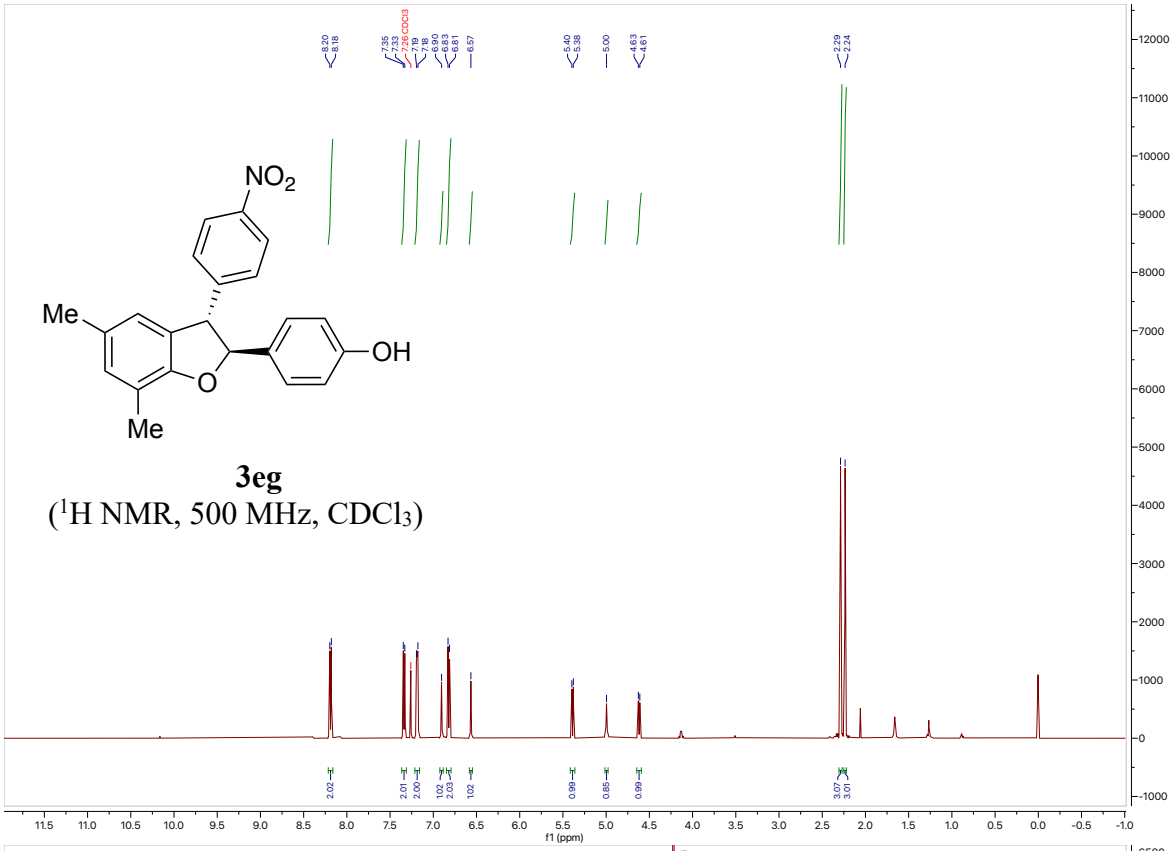
3ag

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



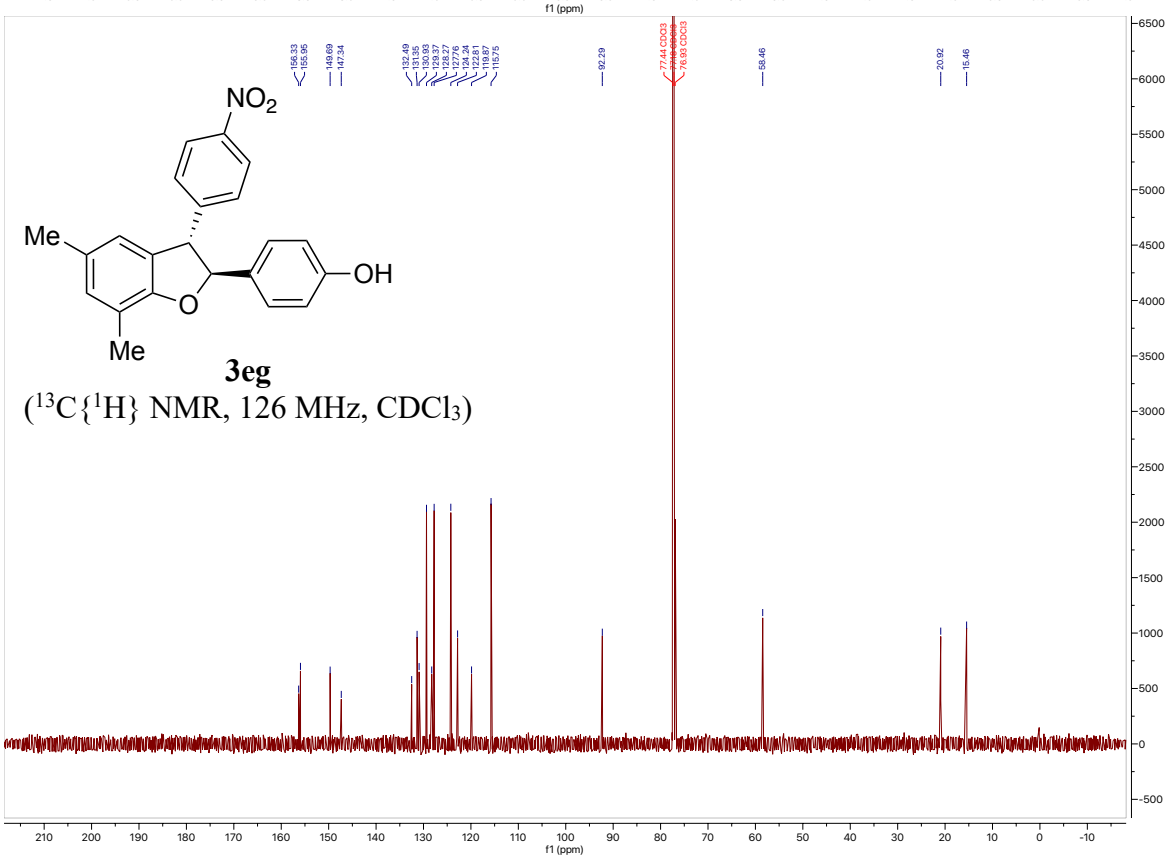
3ag

(^{13}C{^{1}H} NMR, 126 MHz, $CDCl_3$)



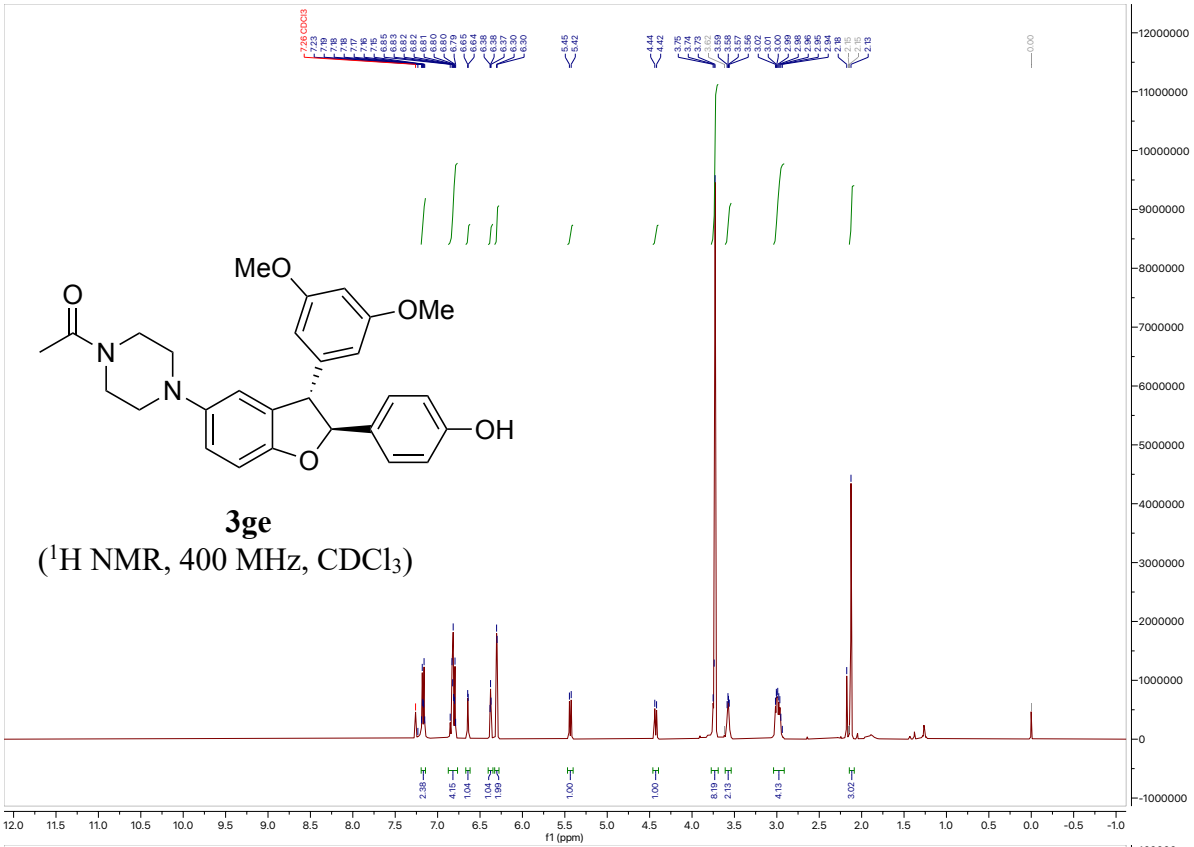
3eg

(^{1}H NMR, 500 MHz, $CDCl_3$)



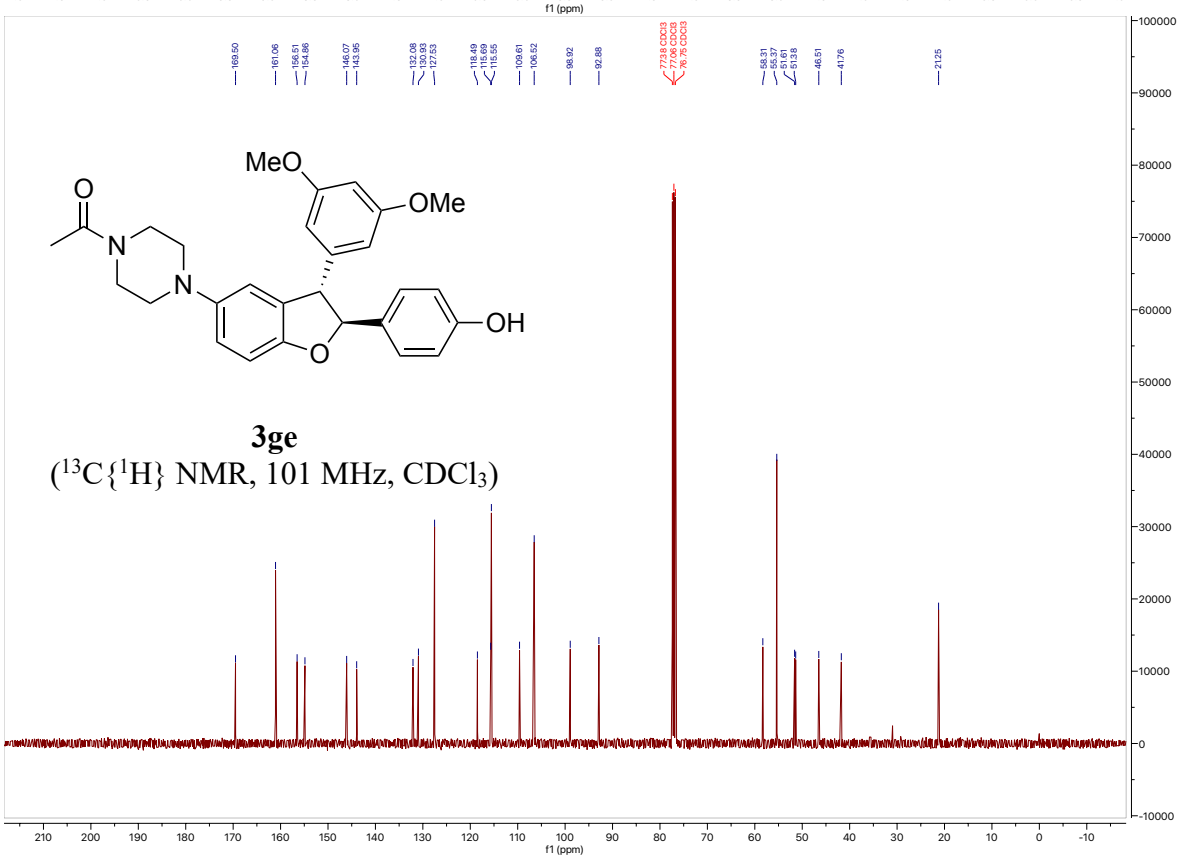
3eg

(^{13}C{^{1}H} NMR, 126 MHz, $CDCl_3$)



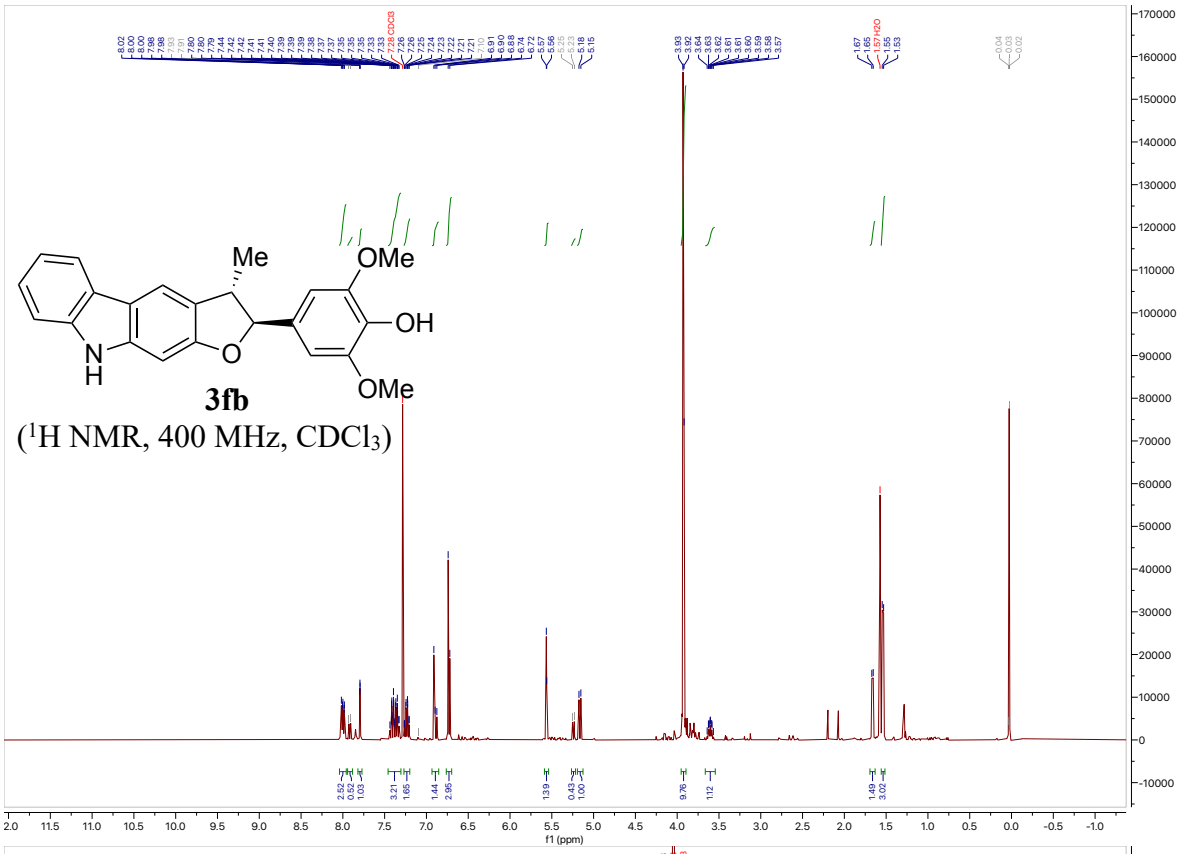
3ge

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



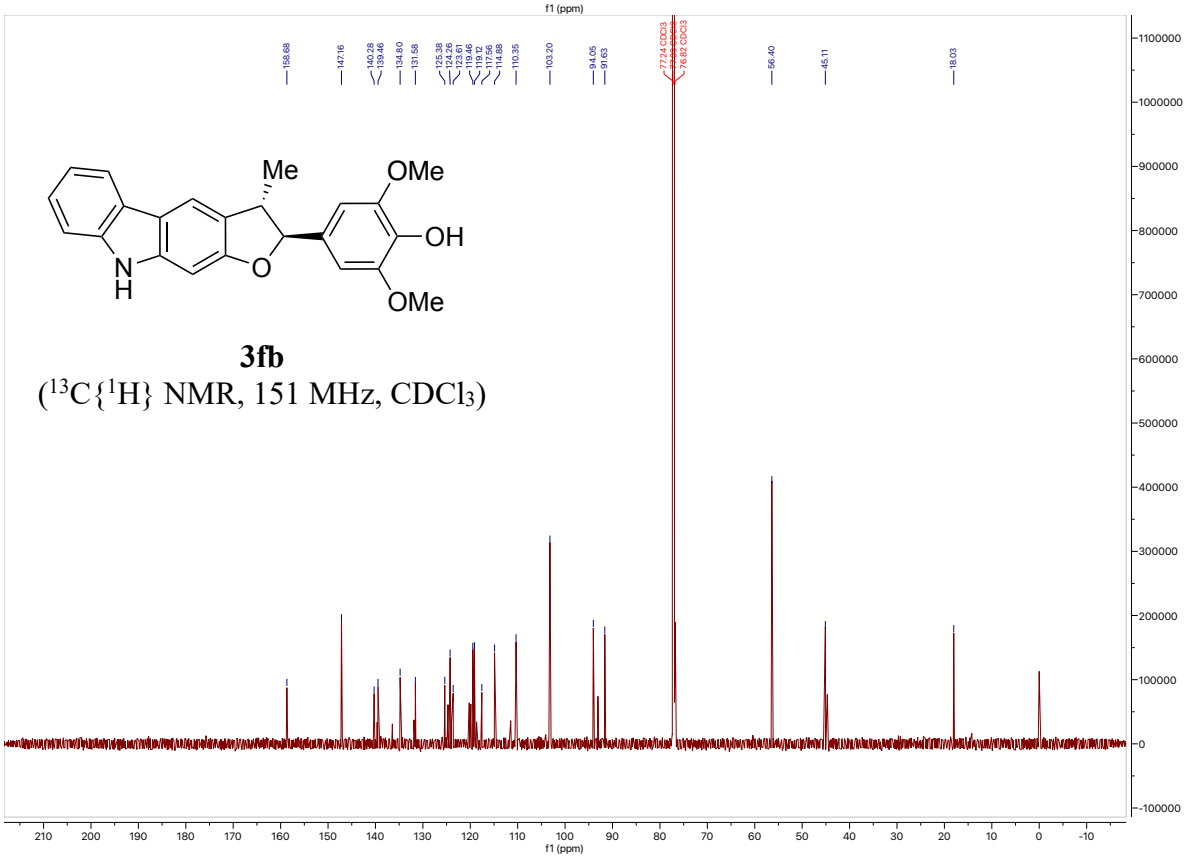
3ge

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



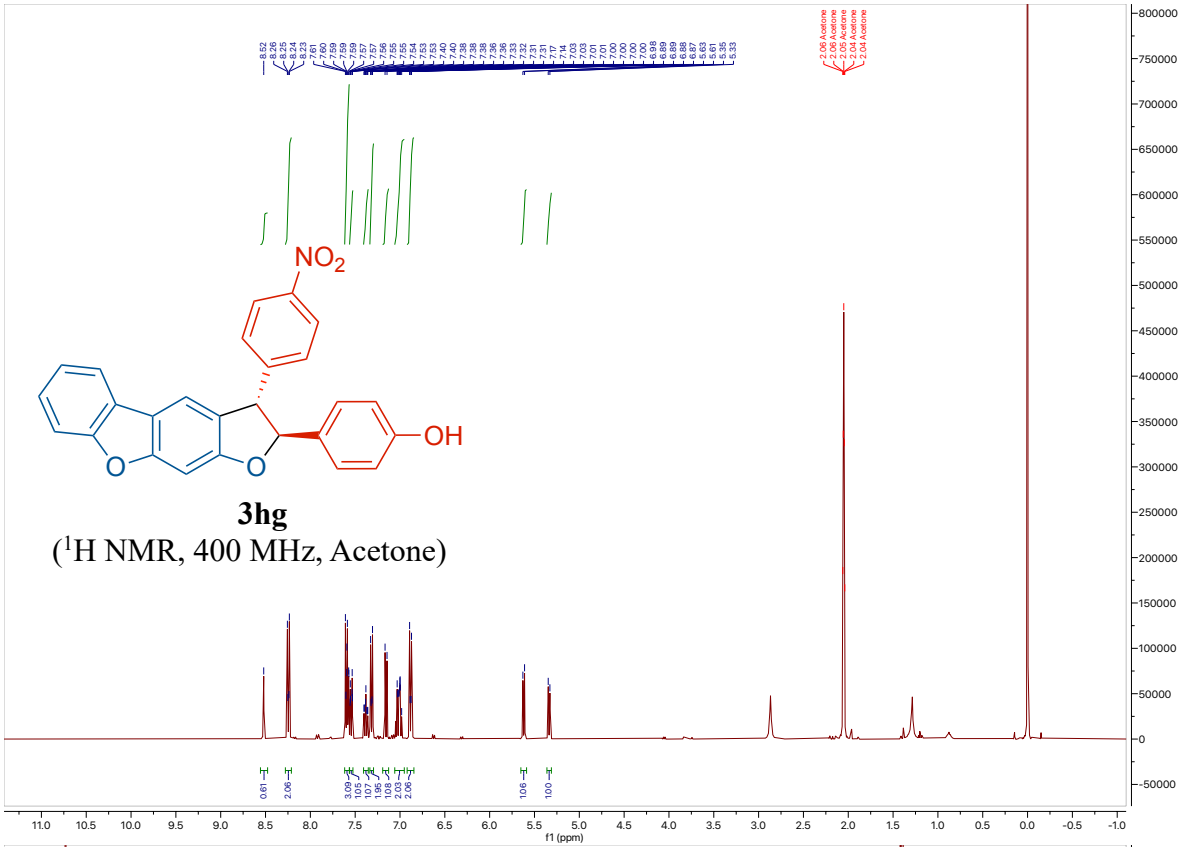
3fb

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



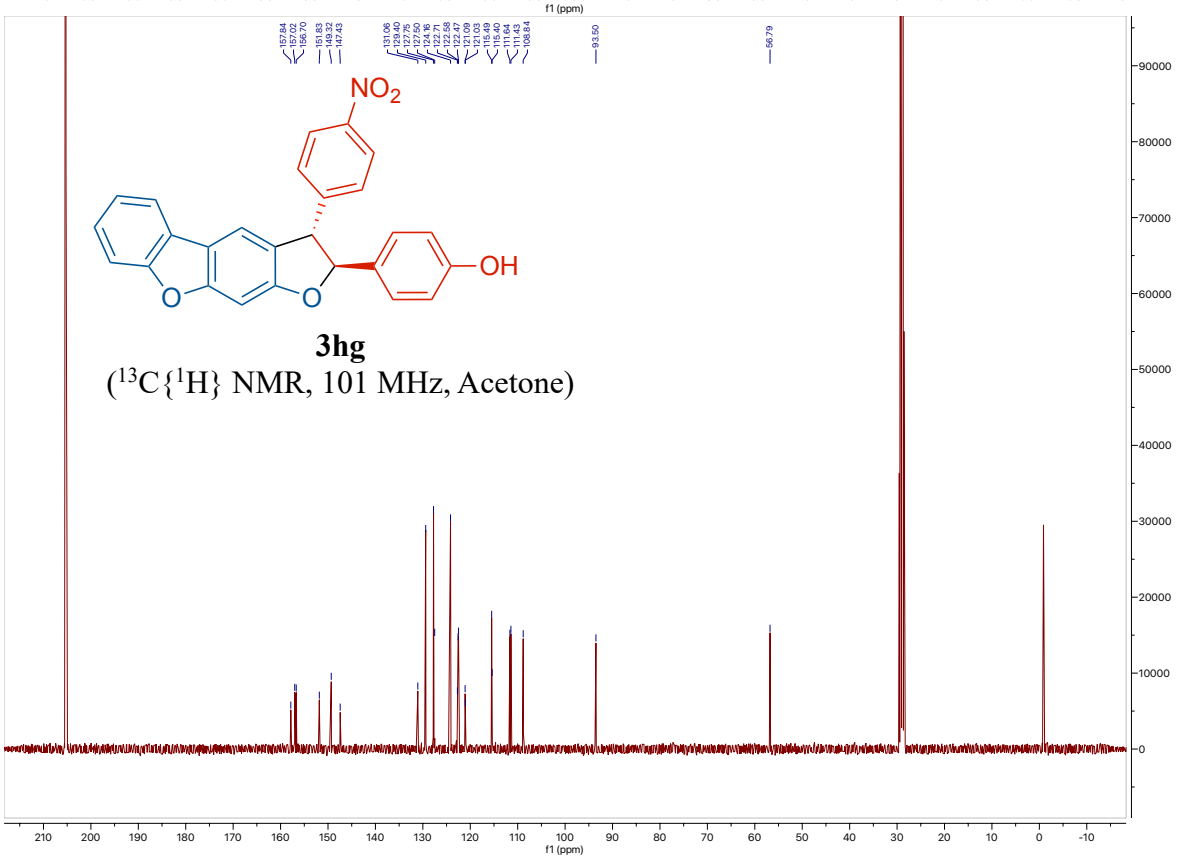
3fb

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



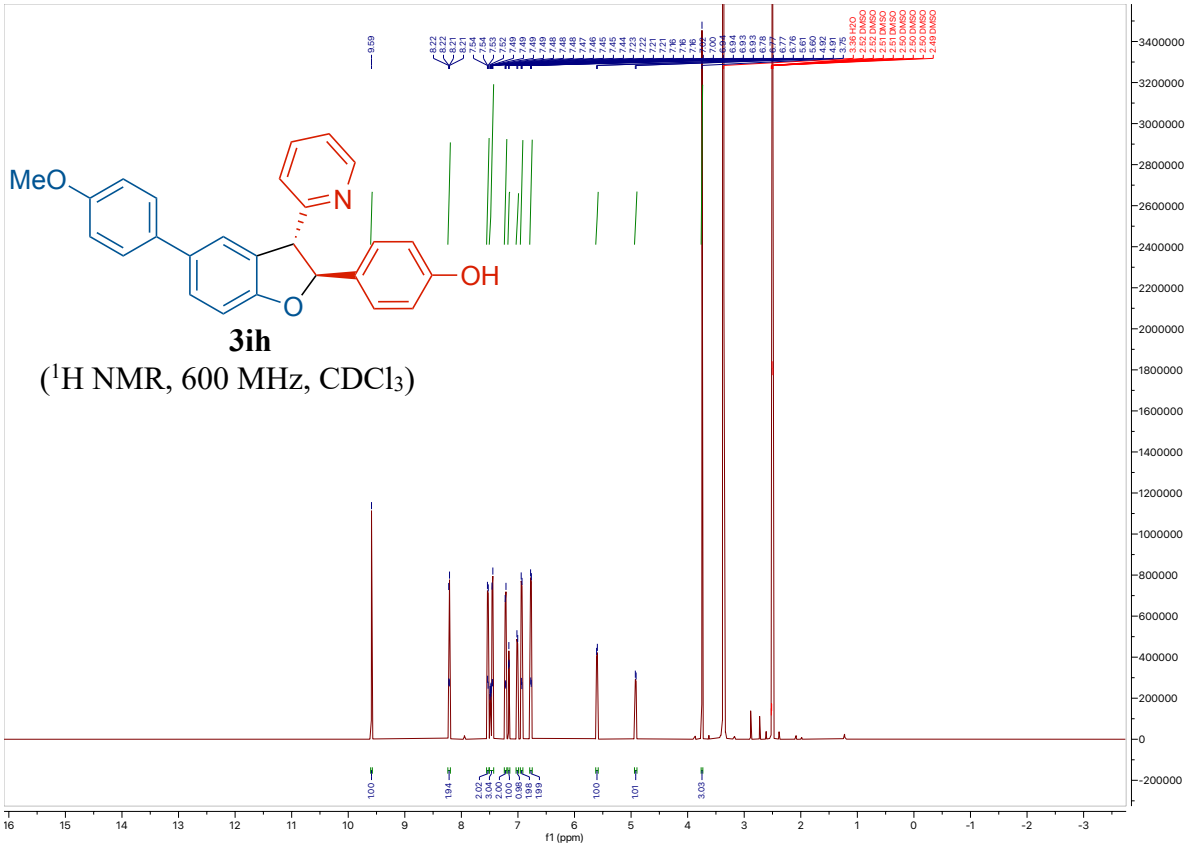
3hg

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



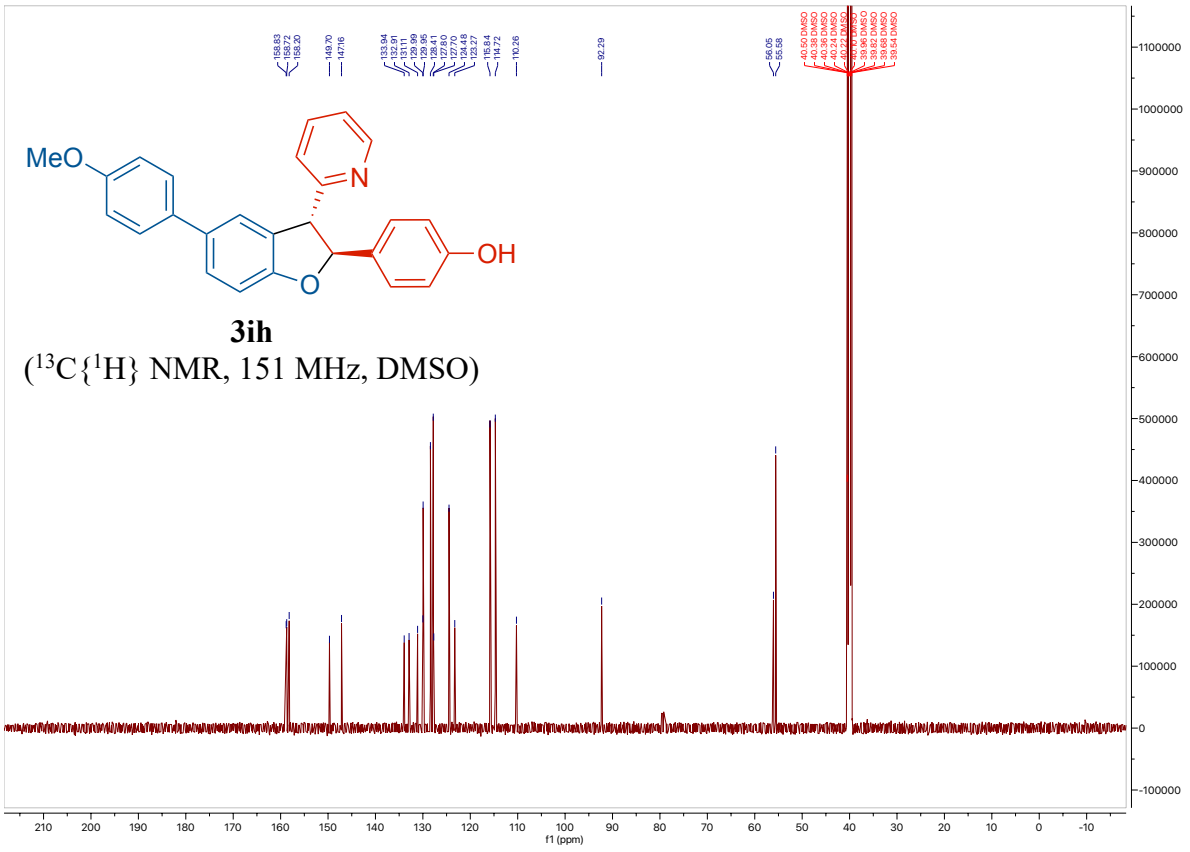
3hg

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



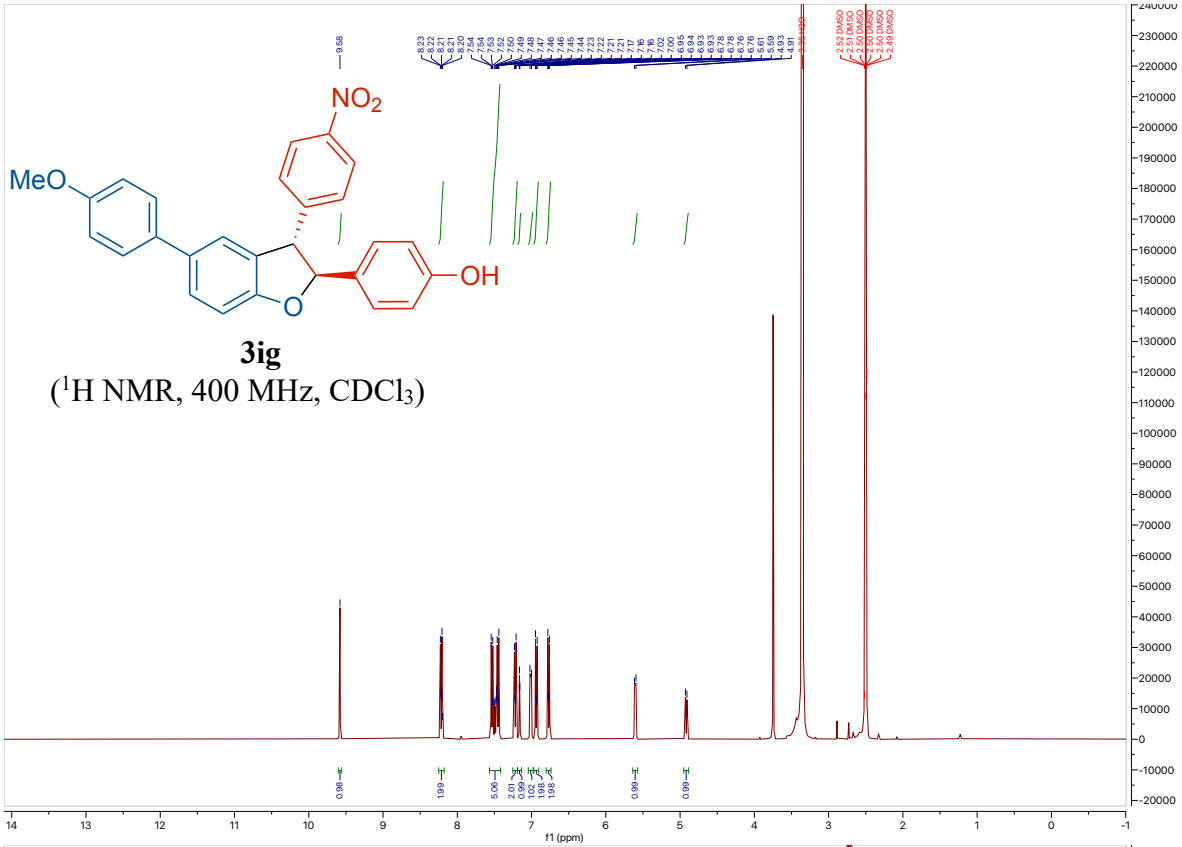
3ih

(^{1}H NMR, 600 MHz, $CDCl_3$)



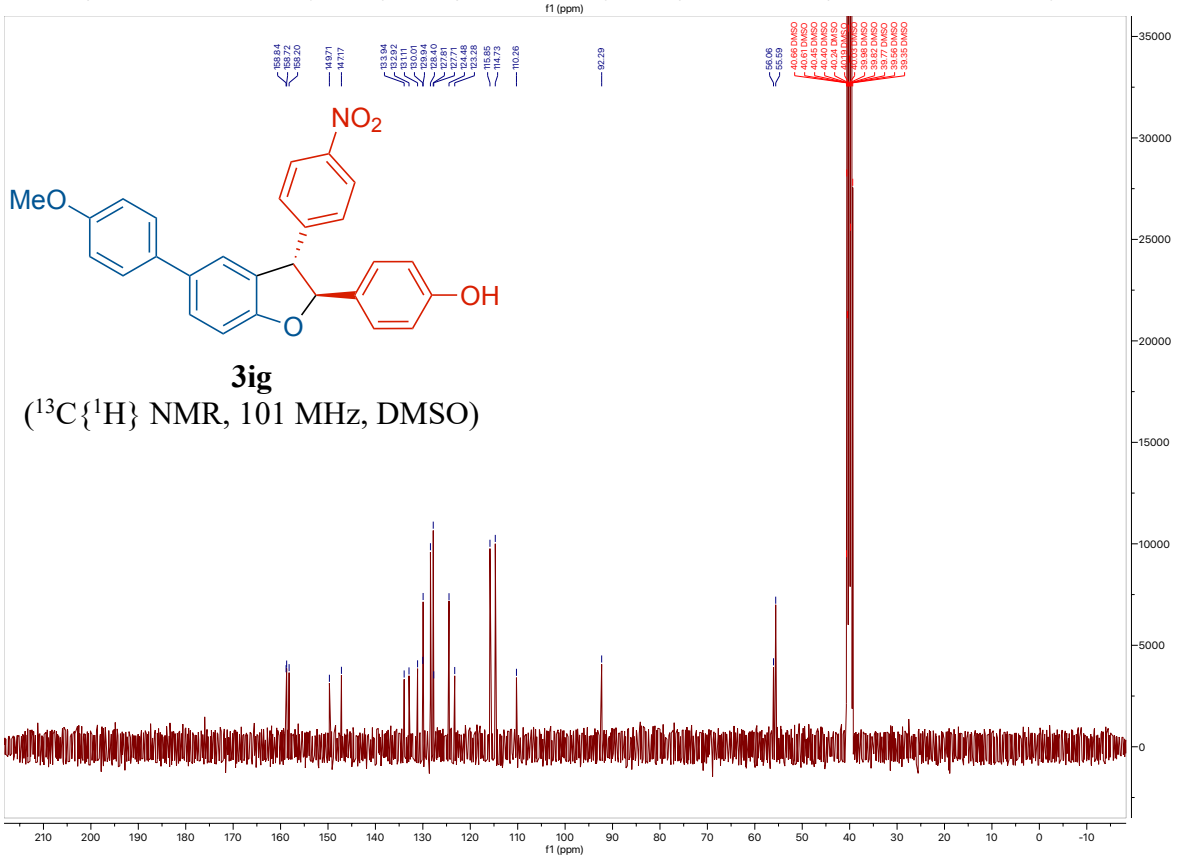
3ih

(^{13}C{^{1}H} NMR, 151 MHz, DMSO)



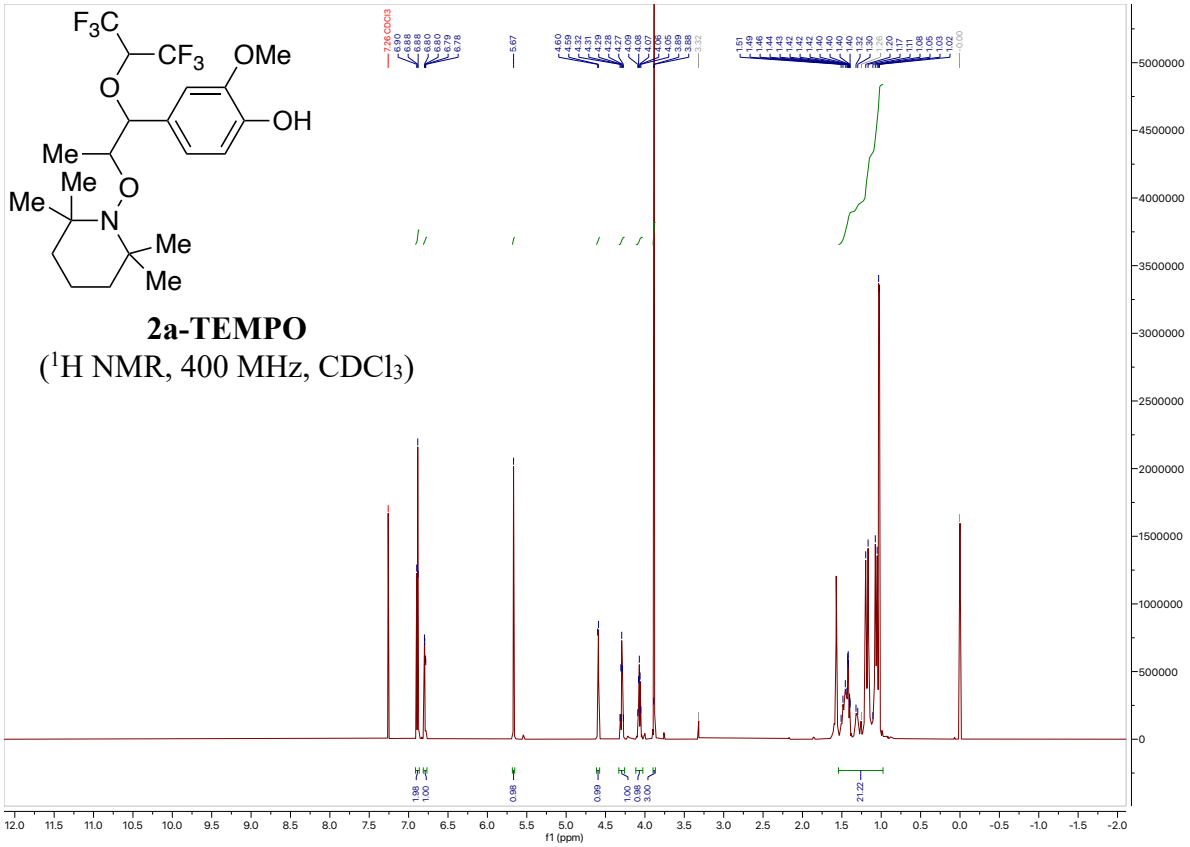
3ig

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



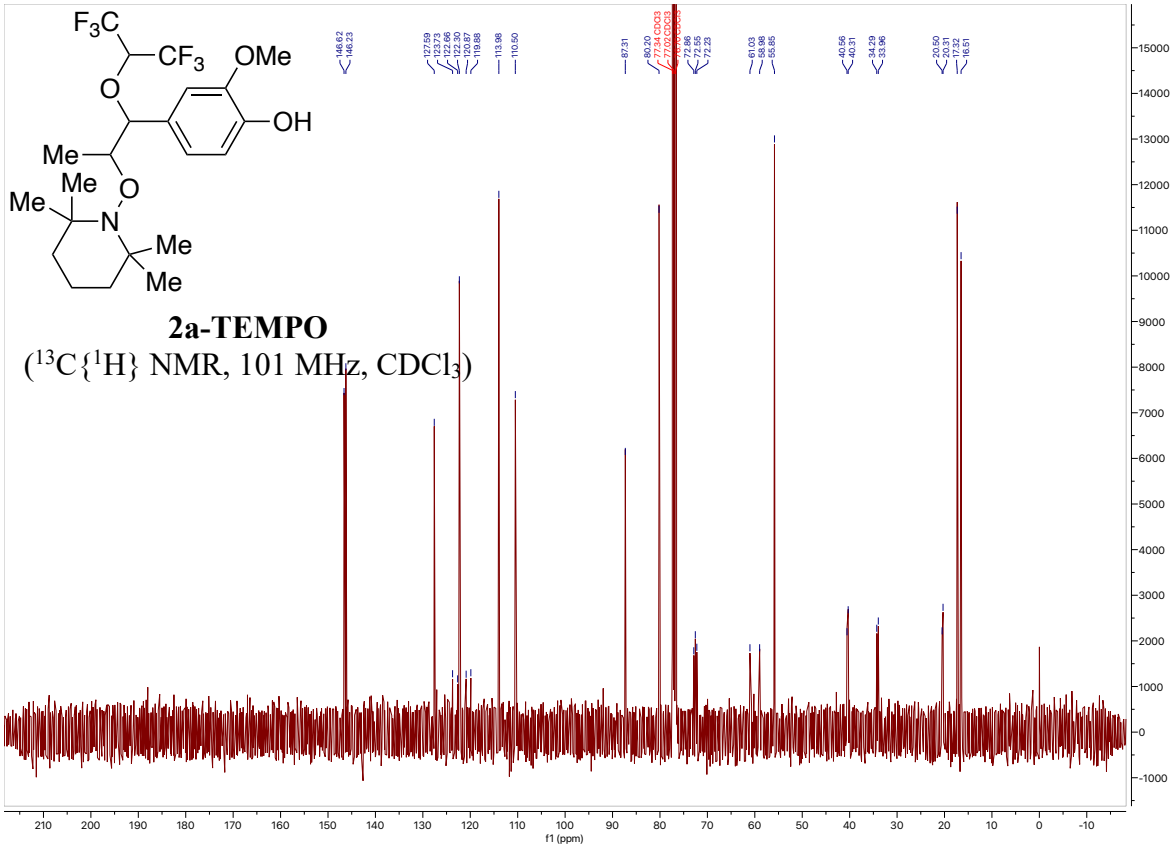
3ig

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



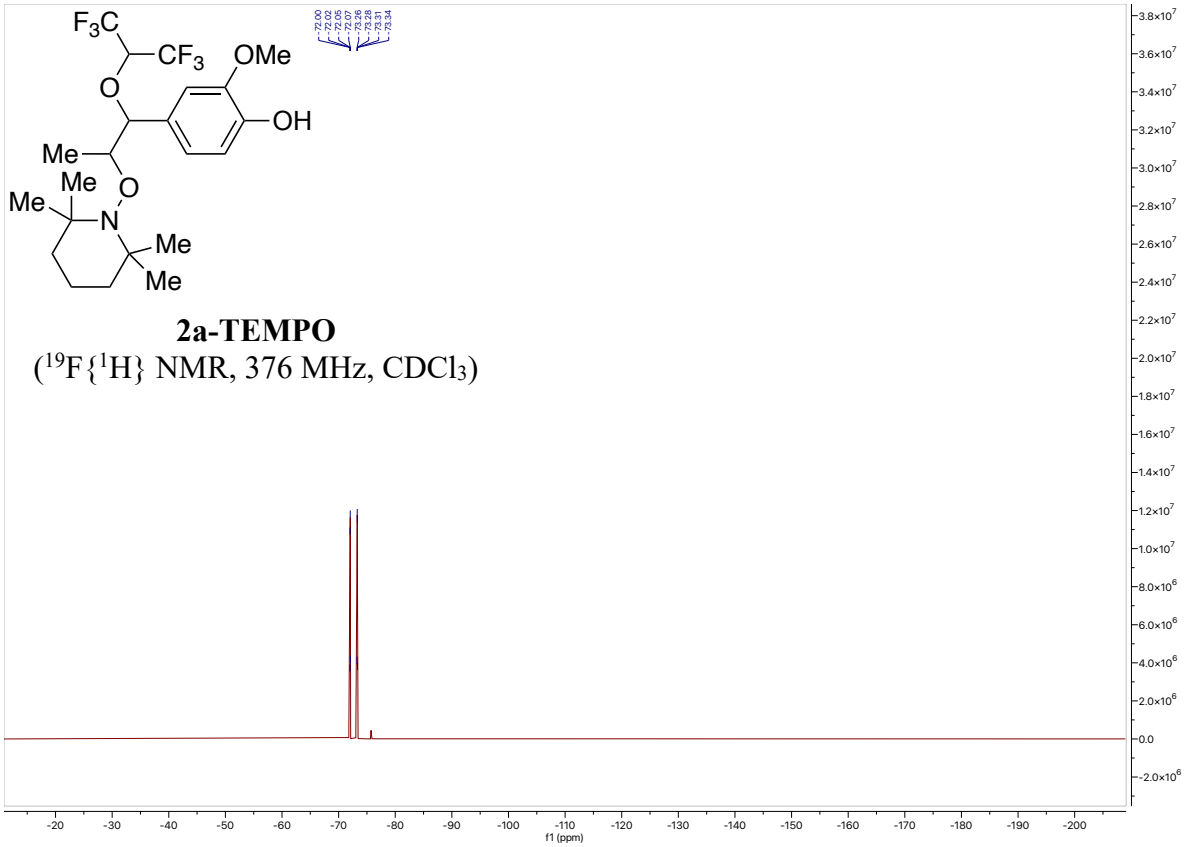
2a-TEMPO

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



2a-TEMPO

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



2a-TEMPO

($^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$)

Supplementary References

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