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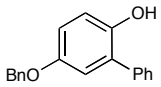
I. General Information

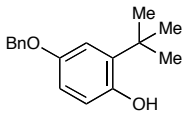
MeCN, THF and CH_2Cl_2 were purified by elution through alumina as described by Grubbs.[1] A 23 W (1200 lumens) SLI Lighting Mini-Lynx compact fluorescent light bulb (CFL) was used for all photochemical reactions. Flash-column chromatography was performed with Silicycle 40–63Å silica (230–40 mesh). Styrene, α-methylstyrene, *trans*-methylisoeugenol (**4**), *trans*-anethole, 4-methoxyphenol (**3**), 4-(benzyloxy)phenol, 2-methoxy-4-methylphenol, 2-chloro-4-methoxyphenol, and 4-methoxynaphthalen-1-ol were purchased from Sigma Aldrich, then purified by either distillation or recrystallization prior to use. (*E*)-*N*-(3-(4-Methoxyphenyl)allyl)-4-methylbenzenesulfonamide, (*E*)-*tert*-butyldimethyl(4-(prop-1-en-1-yl)phenoxy)silane (**32**), and 4'-methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl were synthesized according to previously reported methods.[2] All other styrene substrates were synthesized according to methods adapted from Lin *et al*.[3] 4-Methoxy-3-methylphenol,[4] 4-(allyloxy)phenol,[5] and 4-(2-hydroxyethoxy)phenol[6] were synthesized according to previously reported methods. The synthesis of *cis*-anethole was carried out according to procedures for hydroboration-protodeboration adapted from Nakamura *et al*.[7] (*E*)-Prop-1-en-1-ylboronic acid was synthesized according to methods adapted from Althaus *et al*.[8] 2,2'-Bipyrazine and $Ru(bpz)_3(PF_6)_2$ were synthesized according to previously reported methods.[3] Unless otherwise noted, all other compounds were purchased from Sigma Aldrich or Strem and used without further purification.

Diastereomer ratios for all compounds were determined by ^1H NMR analysis of unpurified reaction mixtures and assigned based on analogy to literature precedent. Relative stereochemistry for compound **30** was assigned by 1D NOESY (see below). ^1H and ^{13}C NMR data for all previously uncharacterized compounds were obtained using a Bruker AVANCE-400 spectrometer and are referenced to TMS (0.0 ppm) and $CDCl_3$ (77.0 ppm), respectively. IR spectral data were obtained using a Bruker Vector 22 spectrometer (thin film on NaCl). Melting points were obtained using a Mel-Temp II (Laboratory Devices, Inc., USA) melting point apparatus. Mass spectrometry was performed with a Waters (Micromass) AutoSpec®. These facilities are funded by the NSF (CHE-9974839, CHE-9304546) and the University of Wisconsin.

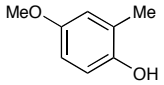
II. Substrate synthesis:



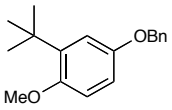
5-(Benzyloxy)-[1,1'-biphenyl]-2-ol: A suspension of [1,1'-biphenyl]-2,5-diol[9] (1.98 g, 10.6 mmol) and K_2CO_3 (1.59 g, 11.5 mmol) in MeCN (27 mL) was placed in a flame-dried 100 mL flask containing a magnetic stirbar. The flask was capped with a septum and flushed with N_2. Benzyl bromide (1.3 mL, 10.9 mmol) was then added to the stirring mixture *via* syringe. The flask was equipped with a reflux condenser and heated to reflux for 21 h. After cooling to room temperature, the flask contents were transferred to a separatory funnel with EtOAc and 1 M HCl. After separating, the aqueous layer was extracted once with EtOAc. The combined organic extracts were then washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was purified by flash-column chromatography (15–50% EtOAc/Hexanes) to afford the desired product as a white solid (559 mg, 19% yield). All spectral data were in agreement with previously reported values.[10]



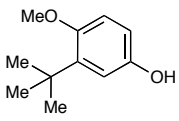
4-(Benzyloxy)-2-(*tert*-butyl)phenol: Into a flame-dried 100 mL round-bottom flask were weighed K_2CO_3 (838 mg, 6.07 mmol) and *tert*-butylhydroquinone (2.00 g, 12.05 mmol). A magnetic stirbar was then added, and the flask was capped with a septum and flushed with N_2. MeCN (30 mL) was then added *via* syringe. Upon stirring, a yellow suspension formed, to which benzyl bromide (1.45 mL, 12.19 mmol) was added *via* syringe. The flask was equipped with a reflux condenser (under N_2) and heated to reflux for 18 h. After cooling, the resulting reddish suspension was transferred into a separatory funnel with H_2O, and Et_2O. The layers were separated, and the aqueous layer was extracted twice more with Et_2O. The combined organic extracts were then washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by flash-column chromatography (7-10% EtOAc/Hexanes) to afford the desired product as a white solid. Mass: 1.44 g, (46% yield). IR (thin film) 3422 (br), 2957, 1506, 1422, 1239, 1079 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.28 (m, 5H), 6.94 (d, J = 2.9 Hz, 1H), 6.67 (dd, J = 8.5, 2.9 Hz, 1H), 6.58 (d, J = 8.5 Hz, 1H), 4.99 (s, 2H), 4.44 (s, 1H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.72, 148.47, 137.64, 137.42, 128.60, 127.95, 127.69, 116.84, 115.28, 111.78, 70.83, 34.76, 29.55. HRMS (ESI) calculated for $[C_{17}H_{20}O_2]^+$ requires *m/z* 256.1457, found *m/z* 256.1466. Melting point: 90–92 °C.



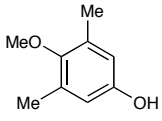
4-Methoxy-2-methylphenol: 4-Methoxyl-2-methylbenzaldehyde (900 μL, 6.63 mmol) was dissolved in dry dichloromethane (10 mL) in a 100 mL round-bottomed flask. After capping with a septum, the flask was flushed with N_2 and cooled to 0 ºC in an ice bath. Solid *m*-CPBA (70-77% from Sigma Aldrich, 2.48 g, 10.06 mmol) was added in a single portion. The resulting suspension was stirred for 5 min at 0 ºC and then allowed to warm to room temperature, where it was stirred for 3.5 h. The resulting suspension was transferred to a separatory funnel using dichloromethane, and the organic layers were washed twice with 10% aqueous Na_2SO_3. The organic layer was then washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was dissolved in 10:1 MeOH:6M HCl (11 mL), and stirred for 12 h under N_2 atmosphere. The orange solution was then concentrated *in vacuo*, and the crude oil was taken up in EtOAc and transferred to a separatory funnel. The organic layer was washed with sat. aq. $NaHCO_3$ (8x) to remove benzoic acid, then washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by flash-column chromatography (20% EtOAc/Hexanes) to afford the desired product as an off-white solid (725 mg, 79% yield). All spectral data were in agreement with previously reported values.[11]



4-(Benzyloxy)-2-(tert-butyl)-1-methoxybenzene (S1): Into a flame-dried round-bottom flask equipped with a magnetic stirbar were weighed 4-(benzyloxy)-2-(*tert*-butyl)phenol (753 mg, 2.94 mmol) and K_2CO_3 (492 mg, 3.56 mmol). A magnetic stirbar and acetone (8.5 mL) were added to the flask, which was then capped with septum and flushed with N_2. To the stirring suspension was added methyl iodide (500 μL, 8.03 mmol) *via* syringe, and the mixture was heated to reflux. The reaction progress was monitored by TLC. Upon reacting full conversion (approx 144 h), the flask was cooled to room temperature, and the reaction was quenched with methanol, then H_2O. The flask contents were concentrated *in vacuo* in a fume hood, and the residue was washed into a separatory funnel with H_2O, and Et_2O. After separating, the organic layer was washed with 1 M NaOH (aq.) and brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by flash-column chromatography (10% EtOAc/Hexanes) to afford the desired product as a white solid (757 mg, 95% yield). IR (thin film) 2912, 1587, 1500, 1458, 1283, 1209 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.25 (m, 5H), 6.94 (d, J = 3.0 Hz, 1H), 6.65 (dd, J = 8.5, 3.0 Hz, 1H), 6.54 (d, J = 8.5 Hz, 1H), 4.98 (s, 2H), 4.54 (s, 1H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, CDCl3) δ 153.11, 152.56, 139.90, 137.52, 128.59, 127.91, 127.65, 115.27, 112.26, 111.04, 70.65, 55.64, 34.99, 29.72. HRMS (EI) calculated for $[C_{18}H_{22}O_2]^+$ requires *m/z* 270.1615, found *m/z* 270.1614. Melting point: 39–40 °C

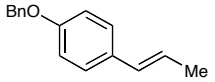


3-(*tert*-Butyl)-4-methoxyphenol: 4-(Benzyloxy)-2-(tert-butyl)-1-methoxybenzene (**S1**, 757 mg, 2.80 mmol) was weighed into a 25 mL round-bottomed flask containing a magnetic stirbar. Dichloromethane (15 mL) was added, and the mixture was stirred until all solids were dissolved. The flask was then capped with a septum and purged with N_2 for 5 min. Solid Pd/C (10 wt%, 239 mg, 0.225 mmol) was then added, and H_2 (introduced with balloon and syringe) was bubbled through the black suspension. After 15 min, the needle was removed from the suspension, and the hydrogen atmosphere was maintained with rapid stirring for 18 h. The black suspension was filtered over Celite, and the filter cake was washed thoroughly with DCM. The eluent was concentrated in vacuo to afford clean product as a white solid (499 mg, 99% yield). IR (thin film) 3319 (br), 2870, 1500, 1286, 1086 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.88 – 6.68 (m, 2H), 6.63 (dd, J = 8.6, 3.1 Hz, 1H), 4.31 (s, 1H), 3.79 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.87, 148.87, 139.96, 114.40, 112.79, 112.47, 55.73, 34.83, 29.64. HRMS (EI) calculated for $[C_{11}H_{16}O_2]^+$ requires *m/z* 180.1145, found *m/z* 180.1149. Melting point: 63–65 °C

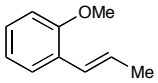


4-Methoxy-3,5-dimethylphenol: 4-Hydroxy-3,5-dimethylbenzaldehyde (996 mg, 6.63 mmol), and K_2CO_3 (1.10 g, 7.97 mg) were weighed into a flame-dried round-bottomed flask. A magnetic stirbar and acetone (8.5 mL) were added to the flask, which was then capped with septum and flushed with N_2. To this stirring suspension was added methyl iodide (600 μL, 9.64 mmol) dropwise *via* needle and syringe. The flask was then equipped with a reflux condenser under N_2, and heated to reflux for 96 h. After cooling to room temperature, methanol and H_2O were added to quench remaining methyl iodide, and the contents of the flask were concentrated *in vacuo* in a fume hood. The resulting residue was transferred to a separatory funnel using H_2O and Et_2O. After separating, the organic layer was washed with 1 M NaOH (aq.) and brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by flash-column chromatography (15% EtOAc/Hexanes) to afford 4-methoxy-3,5-dimethylbenzaldehyde as a white solid (507 mg, 47% yield) with spectral properties identical to those previously reported.[12] The isolated benzaldehyde (507 mg, 3.09 mmol) was subsequently dissolved in dichloromethane (4.6 mL) in a 25 mL round-bottomed flask, which was then capped with a septum, and flushed with N_2. After cooling to 0 ºC in an ice bath, solid *m*-CPBA (70-77%, 1.06 g, 4.3 mmol) was added in a single portion. The resulting suspension was stirred for 5 min at 0 ºC and then allowed to warm to room temperature, where it

was stirred for 2 h. The resulting suspension was transferred to a separatory funnel using dichloromethane and washed twice with 10% aqueous Na_2SO_3. The organic layer was then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was dissolved in 10:1 MeOH:6M HCl (11 mL), and stirred for 24 h under N_2. The orange solution that resulted was concentrated *in vacuo*, and the resulting residue was transferred to a separatory funnel with EtOAc. The organic layer was washed with sat. aq. $NaHCO_3$ (8x) to remove benzoic acid, then washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by flash-column chromatography (20% EtOAc/Hexanes) to afford the desired product as an off-white solid (378 mg, 82% yield). IR (thin film) 3390 (br), 2947, 1603, 1470, 1322, 1215 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.47 (s, 2H), 5.08 – 4.53 (s br, 1H), 3.67 (s, 3H), 2.23 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.25, 150.69, 131.95, 115.03, 60.00, 16.16. HRMS (ESI) calculated for $[C_9H_{12}O_2]^+$ requires *m/z* 152.0832, found *m/z* 152.0833. Melting point: 87–89 °C

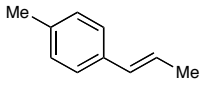


(*E*)-1-(Benzyloxy)-4-(prop-1-en-1-yl)benzene: Ethyltriphenylphosphonium iodide (9.67 g, 23.1 mmol) was weighed into a flame-dried flask containing a magnetic stirbar. The flask was capped with a rubber septum and placed under nitrogen. THF (100 mL) was added, and the flask was cooled to 0 °C. *n*-BuLi (15 mL of a 1.6M solution in hexanes, 24.0 mmol) was then added dropwise over 5 min by syringe, resulting in a red solution. After stirring for 30 minutes at 0 °C, 4-(benzyloxy)benzaldehyde (2.45 g, 11.5 mmol) in THF (10 mL) was added dropwise over 3 min. The flask was allowed to warm slowly to room temperature and stirred until TLC showed complete consumption of starting material. After quenching with dropwise addition of sat. aq. NH_4Cl, the resulting mixture was rinsed into a separatory funnel with water and Et_2O. The aqueous layer was extracted with Et_2O (2 x 30 mL). The combined organic layers were then washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude solid was purified by silica gel chromatography (5% EtOAc/Hexanes) to afford the title compound as a white solid. 2.55 g (98% yield, E:Z = 8:1). To improve the isomer ratio, the purified E/Z mixture was dissolved in benzene (110 mL) in a 250 mL round-bottomed flask, which was then purged with N_2. AIBN (135 mg, 0.82 mmol) and PhSH (200 μL, 1.95 mmol) were then added, and the reaction was heated under N_2 at reflux for 15 h. After cooling to room temperature, the solution was diluted with Et_2O (30 mL) and washed with sat. aq. $NaHCO_3$ (3 x 40 mL). The organic layer was then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash-column chromatography (hexanes) to afford the desired product as a single isomer (2.22 g, 87% yield). All spectral data were in agreement with previously reported values.[3]

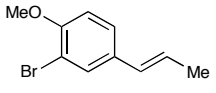


(*E*)-1-Methoxy-2-(prop-1-en-1-yl)benzene: Ethyltriphenylphosphonium bromide (12.46 g, 22.6 mmol) was weighed into a flame-dried flask containing a magnetic stirbar. The flask was capped with a rubber septum and placed under N_2. THF (40 mL) was then added, and the flask contents were stirred vigorously. Potassium *tert*-butoxide (3.55 g, 31.6 mmol) was added in three portions over 5 min, forming a red suspension. After stirring 30 minutes at room temperature, the flask was cooled to –78 °C (dry ice/acetone bath), and 2-methoxybenzaldehyde (2.04 g) in THF (10 mL) was added dropwise over 10 min. The flask was allowed to warm to room temperature, and the reaction was monitored by TLC. After stirring 40 h, the orange mixture was quenched *via* dropwise addition of sat. aq. NH_4Cl. The resulting suspension was diluted with water (10 mL) and transferred to a separatory funnel. The aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude oil was purified by silica gel chromatography (15% EtOAc/Hexanes) to afford the title compound as a colorless oil. 2.08 g (94% yield, E:Z = 1:2.5). To improve the isomer ratio, 2.08 g of the *E*/*Z* mixture was dissolved in

benzene (110 mL) in a 250 mL round-bottomed flask, which was purged with N_2. AIBN (236.4 mg, 1.44 mmol) and PhSH (145 μL, 1.32 mmol) were added to the solution, and the flask was equipped with a reflux condenser. The flask was then heated to reflux for 16 h under N_2. After cooling to room temperature, Et_2O (100 mL) was added, and the flask contents were transferred to a separatory funnel containing sat. aq. $NaHCO_3$. After separating, the organic layer was washed twice more with sat. aq. $NaHCO_3$ (2 x 20 mL). The organic layer was then dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by flash-column chromatography (hexanes) to afford the desired product as a single isomer (1.80 g, 86% yield). All spectral data were in agreement with previously reported values.[13]

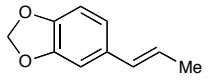


(*E*)-1-Methyl-4-(prop-1-en-1-yl)benzene: Ethyltriphenylphosphonium iodide (8.21 g, 20.0 mmol) was weighed into a flame-dried flask containing a magnetic stirbar. The flask was capped with a rubber septum and placed under nitrogen. THF (100 mL) was added, and the flask was cooled to 0 °C. *n*-BuLi (12.5 mL of a 1.6M solution in hexanes, 20.0 mmol) was then added dropwise over 5 min by syringe, resulting in a red solution. After stirring for 30 minutes at 0 °C, *p*-tolualdehyde (2.45 g, 10.2 mmol) in THF (10 mL) was added dropwise over 3 min. The flask was allowed to warm slowly to room temperature and stirred until TLC showed complete consumption of starting material (45 min). After quenching with dropwise addition of sat. aq. NH_4Cl, the resulting mixture was rinsed into a separatory funnel with water and Et_2O. The aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic layers were then washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude solid was purified by silica gel chromatography (100% Hexanes) to afford the title compound as a colorless oil. 870 mg (65% yield, E:Z = 3:1). To improve the isomer ratio, the purified E/Z mixture was dissolved in benzene (50 mL) in a 100 mL round-bottomed flask, which was then purged with N_2. AIBN (107 mg, 0.65 mmol) and PhSH (70 μL, .64 mmol) were then added, and the reaction was heated under N_2 at reflux for 15 h. After cooling to room temperature, the solution was diluted with Et_2O (30 mL) and washed with sat. aq. $NaHCO_3$ (3 x 40 mL). The organic layer was then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash-column chromatography (hexanes) to afford the desired product as a single isomer (520 mg, 60% yield). All spectral data were in agreement with previously reported values.[14]

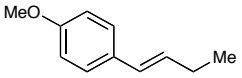


(*E*)-2-Bromo-1-methoxy-4-(prop-1-en-1-yl)benzene: Ethyltriphenylphosphonium bromide (5.94 g, 16.0 mmol) was weighed into a flame-dried flask containing a magnetic stirbar. The flask was capped with a rubber septum and placed under N_2. THF (25 mL) was then added, and the flask contents were stirred vigorously. Potassium *tert*-butoxide (1.79 g, 15 mmol) was added in three portions over 5 min, forming a red suspension. After stirring 30 minutes at room temperature, the flask was cooled to –78 °C (dry ice/acetone bath), and 3-bromo-4-methoxybenzaldehyde (2.15 g) in THF (5 mL) was added dropwise over 10 min. The flask was allowed to warm to room temperature, and the reaction was monitored by TLC. After stirring 14 h, the orange mixture was quenched *via* dropwise addition of sat. aq. NH_4Cl. The resulting suspension was diluted with water (10 mL) and transferred to a separatory funnel. The aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude oil was purified by silica gel chromatography (5% EtOAc/Hexanes) to afford the title compound as a colorless oil. 1.78 g (78% yield, E:Z = 1:1.5). To improve the isomer ratio, 1.40 g of the *E*/*Z* mixture was dissolved in benzene (20 mL) in a 100 mL round-bottomed flask, which was purged with N_2. AIBN (102 mg, 0.62 mmol) and PhSH (70 μL, 0.62 mmol) were added to the solution, and the flask was equipped with a reflux condenser. The flask was then heated to reflux for 16 h under N_2. After cooling to room temperature, Et_2O (20 mL) was added, and the

flask contents were transferred to a separatory funnel containing sat. aq. $NaHCO_3$. After separating, the organic layer was washed twice more with sat. aq. $NaHCO_3$ (2 x 20 mL). The organic layer was then dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by flash-column chromatography (hexanes) to afford the desired product as a single isomer (0.919 g, 65% yield). IR (thin film) 2850, 2362, 1277, 1021 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 2.1 Hz, 1H), 7.20 (dd, J = 8.5, 2.2 Hz, 1H), 6.82 (d, J = 8.5 Hz, 1H), 6.27 (dd, J = 15.7, 1.7 Hz, 1H), 6.10 (dd, J = 15.7, 6.6 Hz, 1H), 3.88 (s, 3H), 1.86 (dd, J = 6.6, 1.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.69, 132.31, 130.47, 129.12, 125.95, 125.08, 111.87, 111.84, 56.31, 18.39. HRMS (ESI) calculated for $[C_{10}H_{11}BrO]^+$ requires *m/z* 225.9987, found *m/z* 225.9983.

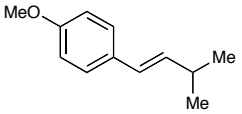


(*E*)-5-(Prop-1-en-1-yl)benzo[*d*][1,3]dioxole: Ethyltriphenylphosphonium iodide (4.10 g, 10.0 mmol) was weighed into a flame-dried flask containing a magnetic stirbar. The flask was capped with a rubber septum and placed under nitrogen. THF (50 mL) was added, and the flask was cooled to 0 °C. *n*-BuLi (7.0 mL of a 1.6M solution in hexanes, 9.8 mmol) was then added dropwise over 5 min by syringe, resulting in a red solution. After stirring for 30 minutes at 0 °C, piperonal (765 mg, 5.03 mmol) in THF (5 mL) was added dropwise over 3 min. The flask was allowed to warm slowly to room temperature and stirred until TLC showed complete consumption of starting material (30 min). After quenching with dropwise addition of sat. aq. NH_4Cl, the resulting mixture was rinsed into a separatory funnel with water and EtOAc. The aqueous layer was extracted with EtOAc (2 x 30 mL). The combined organic layers were then washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude solid was purified by silica gel chromatography (20% EtOAc/Hexanes) to afford the title compound as a white solid. 740 mg (90% yield, E:Z = 4:1). To improve the isomer ratio, the purified E/Z mixture was dissolved in benzene (50 mL) in a 100 mL round-bottomed flask, which was then purged with N_2. AIBN (83 mg, 0.51 mmol) and PhSH (55 μL, 0.50 mmol) were then added, and the reaction was heated under N_2 at reflux for 18 h. After cooling to room temperature, the solution was diluted with Et_2O (30 mL) and washed with sat. aq. $NaHCO_3$ (3 x 40 mL). The organic layer was then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash-column chromatography (5% EtOAc/Hexanes) to afford the desired product as a single isomer (516 mg, 75% yield). All spectral data were in agreement with previously reported values.[15]

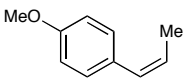


(*E*)-1-(But-1-en-1-yl)-4-methoxybenzene: (4-Methoxybenzyl)triphenylphosphonium bromide[16] (4.63 g, 10.0 mmol) was weighed into a flame-dried flask containing a magnetic stirbar. The flask was capped with a rubber septum and purged with N_2. THF (50 mL) was added, and the flask was cooled to 0 °C in an ice bath. *n*-BuLi (7.2 mL of a 1.6M solution in hexanes, 10.1 mmol) was added dropwise over 4 minutes, forming a red solution. After stirring for 30 minutes at 0 °C, propanal (350 μL, 4.85 mmol) was added dropwise over 3 minutes. The flask was allowed to warm slowly to room temperature, and the reaction was monitored by TLC. Upon complete consumption of starting material (1.5 h), the mixture was the quenched by dropwise addition of sat. aq. NH_4Cl. The resulting suspension was rinsed into a separatory funnel with water and EtOAc. The aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic layers were then washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude solid was purified by silica gel chromatography (15–20% EtOAc/Hexanes) to afford the title compound as a white solid. Mass: 0.740 g (90% yield, E:Z = 1.8:1). To improve the isomer ratio, the purified *E*/*Z* mixture was dissolved in benzene (40 mL) in a 100 mL round-bottomed flask containing a magnetic stirbar. The flask was capped with a septum and purged with nitrogen. AIBN (72 mg, 0.44 mmol) and PhSH (45 μL, 0.44 mmol) were then added, and the

flask was equipped with a reflux condenser under N_2. The flask was then heated at reflux for 12 h. After cooling to room temperature, the solution was diluted with Et_2O (20 mL), and then transferred into a separatory funnel. A solution of sat. aq. $NaHCO_3$ was added, and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 20 mL), and then the combined organics were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude residue was purified by flash-column chromatography (1–10% EtOAc/Hexanes) to afford the desired product as a single isomer. Mass: 0.449 g, (63% yield). IR (thin film) 1834, 1603, 1490, 1244, 1202, 1031 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 2H), 6.91 – 6.73 (m, 2H), 6.32 (dt, *J* = 16.0, 1.5 Hz, 1H), 6.21 – 5.97 (m, 1H), 3.78 (d, *J* = 0.8 Hz, 3H), 2.20 (dtd, *J* = 9.0, 7.5, 6.1 Hz, 2H), 1.07 (td, *J* = 7.5, 1.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.62, 130.81, 130.54, 128.14, 126.99, 113.92, 55.30, 26.07, 13.84. HRMS (ESI) calculated for $[C_{11}H_{14}O]^+$ requires *m/z* 162.1040, found *m/z* 162.1033.



(*E*)-1-Methoxy-4-(3-methylbut-1-en-1-yl)benzene: (4-Methoxybenzyl)triphenylphosphonium bromide[16] (2.07 g, 4.5 mmol) was weighed into a flame-dried flask containing a magnetic stirbar. The flask was capped with a rubber septum and purged with N_2. THF (50 mL) was added, and the flask was cooled to 0 °C in an ice bath. *n*-BuLi (3.70 mL of a 1.6M solution in hexanes, 5.2 mmol) was added dropwise over 4 minutes, forming a red solution. After stirring for 30 minutes at 0 °C, isobutyraldehyde (350 μL, 3.83 mmol) was added dropwise over 3 minutes. The flask was allowed to warm slowly to room temperature, and the reaction was monitored by TLC. Upon complete consumption of starting material (12 h), the mixture was the quenched by dropwise addition of sat. aq. NH_4Cl. The resulting suspension was rinsed into a separatory funnel with water and EtOAc. The aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic layers were then washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude solid was purified by silica gel chromatography (15% EtOAc/Hexanes) to afford the title compound as a colorless oil. Mass: 643 mg (95% yield, E:Z = 2:1). To improve the isomer ratio, the purified *E*/*Z* mixture was dissolved in benzene (30 mL) in a 100 mL round-bottomed flask containing a magnetic stirbar. The flask was capped with a septum and purged with nitrogen. AIBN (66 mg, 0.40 mmol) and PhSH (40 μL, 0.39 mmol) were then added, and the flask was equipped with a reflux condenser under N_2. The flask was then heated at reflux for 14 h. After cooling to room temperature, the solution was diluted with Et_2O (20 mL), and then transferred into a separatory funnel. A solution of sat. aq. $NaHCO_3$ was added, and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 20 mL), and then the combined organics were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude residue was purified by flash-column chromatography (3% EtOAc/Hexanes) to afford the desired product as a single isomer (568 mg, 88% yield. IR (thin film) 2964, 2362, 1606, 1509, 1247, 1176 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.16 (m, 2H), 6.98 – 6.70 (m, 2H), 6.42 – 6.16 (m, 1H), 6.05 (dd, *J* = 15.9, 6.8 Hz, 1H), 3.80 (s, 3H), 2.60 – 2.28 (m, 1H), 1.08 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.61, 135.97, 130.79, 127.02, 126.14, 113.91, 55.31, 31.50, 22.59. HRMS (EI) calculated for $[C_{12}H_{16}O]^+$ requires *m/z* 176.1196, found *m/z* 176.1191.

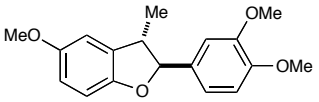


(*Z*)-1-Methoxy-4-(prop-1-en-1-yl)benzene: A solution of cyclohexene (1.42 mL, 14.0 mmol) in THF (6.5 mL) was placed in a flame-dried 100 mL three-necked flask under N_2 atmosphere. The flask was cooled to 0 ºC, and a 2.0 M solution of $BH_3 \cdot SMe_2$ in toluene (3.50 mL, 7.00 mmol) was added dropwise over 5 min *via* syringe. The resulting solution was stirred vigorously, and a white precipitate was observed after ~10 min. The suspension was stirred for 1 h at 0 ºC. A solution of 1-methoxy-4-(prop-1-yn-1-yl)benzene[17] (930 mg, 6.37 mmol) in THF (8.5 mL) was added dropwise over 5 min at 0 ºC. The resulting white suspension was stirred for 1 h at 0 ºC, then for 2 h at room temperature. The flask was then cooled to 0 ºC, and glacial acetic acid (1.3 mL) was added *via* syringe. The solution

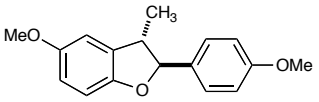
was stirred for 1 h at 0 ºC, then an additional 2 h at room temperature. The resulting pale yellow solution was transferred to a separatory funnel with H_2O, sat. aq. $NaHCO_3$, and Et_2O. The layers were separated, and aqueous phase was extracted with Et_2O. The combined organics were then washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by flash-column chromatography (3% EtOAc/Hexanes) to afford the desired product as a single isomer. Mass: 800.8 mg, (85% yield). All spectral data were in agreement with previously reported values.[18]

III. Photocyclization Reactions:

General Procedure: In an oven-dried Schlenk flask were placed the appropriate phenol (1.0 equiv.) and styrene (1.3–2 equiv.) coupling partners, along with $Ru(bpz)_3(PF_6)_2$ (**2**, 5 mol %), and ammonium peroxydisulfate (2.1 equiv.). A magnetic stirbar was added, and MeCN (1–4 mL) was introduced *via* syringe. The flask was sealed with a glass stopper and degassed by three freeze-pump-thaw cycles in a dry-ice/acetone bath. After the final thaw, the flask was backfilled with nitrogen, and stirred evenly under irradiation with a 23 W (1200 lumens) SLI Mini-Lynx compact fluorescent light bulb (placed 3–4 inches from the reaction flask) for the duration of the reaction. During irradiation, the reaction was sonicated periodically (once in the first 2–6 hours, and once every 6–12 hours afterwards), to maintain an even suspension. After completion, the reaction was diluted with EtOAc (5–10 mL), and eluted through a plug of silica using EtOAc. After concentrating *in vacuo*, the crude product was purified by flash-column chromatography.

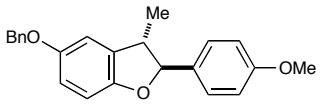


Compound 5. *Experiment 1*: Prepared according to the general procedure using 49 mg (0.39 mmol) of 4-methoxyphenol, 92 mg (0.51 mmol) of *trans*-methylisoeugenol (**4**), 186 mg (0.82 mmol) of ammonium persulfate and 17.1 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 27 h. The crude residue was purified by flash-column chromatography using 10% EtOAc/Hexanes to afford 92 mg (0.31 mmol, 78% yield) of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 49 mg (0.40 mmol) of 4-methoxyphenol, 92 mg (0.52 mmol) of *trans*-methylisoeugenol (**4**), 184 mg (0.92 mmol) of ammonium persulfate and 16.6 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 27 h. The crude residue was purified by flash-column chromatography using 10% EtOAc/Hexanes to afford 92 mg (0.31 mmol, 77% yield) of the desired cycloadduct as a colorless oil. All spectral data were in agreement with previously reported values.[19]

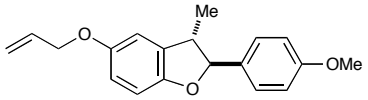


Compound 6. *Experiment 1*: Prepared according to the general procedure using 49 mg (0.39 mmol) of 4-methoxyphenol, 75 mg (0.51 mmol) of *trans*-anethole, 209 mg (0.92 mmol) of ammonium persulfate and 15.4 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 27 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 87 mg (0.32 mmol, 82% yield) of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 50 mg (0.40 mmol) of 4-methoxyphenol, 77 mg (0.52 mmol) of *trans*-anethole, 209 mg (0.92 mmol) of ammonium persulfate and 17.1 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 27 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 95 mg (0.35 mmol, 88% yield) of the desired cycloadduct as a colorless oil. *Experiment 3*: Prepared according to the general procedure using 51 mg (0.41 mmol) of 4-methoxyphenol, 88 mg (0.51 mmol) of *cis*-anethole, 191 mg (0.84 mmol) of ammonium persulfate and 17.6 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 76 mg (0.28 mmol, 69% yield) of the desired cycloadduct as a colorless oil. *Experiment 4*: Prepared according to the general

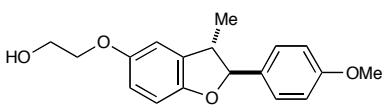
procedure using 50 mg (0.41 mmol) of 4-methoxyphenol, 86 mg (0.58 mmol) of *cis*-anethole, 189 mg (0.83 mmol) of ammonium persulfate and 17.9 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 71 mg (0.26 mmol, 64% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2965, 2837, 1519, 1266 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.25 (m, 2H), 6.95 – 6.84 (m, 2H), 6.80 – 6.55 (m, 3H), 5.06 (d, *J* = 9.1 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.47 – 3.24 (m, 1H), 1.36 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.68, 154.46, 153.32, 133.18, 132.74, 127.71, 114.04, 112.90, 110.13, 109.39, 92.64, 56.06, 55.34, 45.74, 17.62. HRMS (EI) calculated for $[C_{17}H_{18}O_3+NH_4]^+$ requires *m/z* 288.1595, found *m/z* 288.1597.



Compound 7. *Experiment 1*: Prepared according to the general procedure using 82 mg (0.41 mmol) of 4-benzyloxyphenol, 79 mg (0.53 mmol) of *trans*-anethole, 196 mg (0.86 mmol) of ammonium persulfate and 17.5 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 108 mg (0.31 mmol, 76% yield) of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 82 mg (0.41 mmol) of 4-benzyloxyphenol, 80 mg (0.54 mmol) of *trans*-anethole, 197 mg (0.85 mmol) of ammonium persulfate and 17.3 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 109 mg (0.32 mmol, 77% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2964, 1613, 1516, 1273, 1199, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.25 (m, 7H), 6.96 – 6.83 (m, 2H), 6.83 – 6.66 (m, 3H), 5.06 (d, *J* = 9.1 Hz, 1H), 5.00 (s, 2H), 3.78 (s, 3H), 3.40 (p, 6.8 Hz, 1H), 1.35 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.70, 153.68, 153.57, 137.45, 133.23, 132.71, 128.61, 127.95, 127.73, 127.60, 114.09, 114.06, 111.37, 109.41, 92.69, 71.12, 55.37, 45.73, 17.63. HRMS (ESI) calculated for $[C_{23}H_{22}O_3H]^+$ requires *m/z* 347.1642, found *m/z* 347.1627. Melting point: 87–88 °C

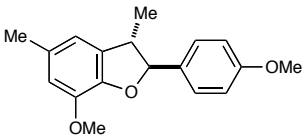


Compound 8: *Experiment 1*: Prepared according to the general procedure using 61 mg (0.41 mmol) of 4-allyloxyphenol, 80 mg (0.54 mmol) of *trans*-anethole, 190 mg (0.83 mmol) of ammonium persulfate and 17.8 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 94 mg (0.32 mmol, 77% yield) of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 60 mg (0.40 mmol) of 4-allyloxyphenol, 82 mg (0.55 mmol) of *trans*-anethole, 186 mg (0.82 mmol) of ammonium persulfate and 17.5 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 91 mg (0.31 mmol, 76% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2960, 1613, 1247, 1199, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 2H), 7.00 – 6.86 (m, 2H), 6.81 – 6.67 (m, 3H), 6.06 (ddt, *J* = 17.3, 10.6, 5.3 Hz,1H), 5.41 (dt, *J* = 17.3, 1.7 Hz, 1H), 5.27 (dq, *J* = 10.5, 1.4 Hz, 1H), 5.07 (d, *J* = 9.0 Hz, 1H), 4.49 (dt, *J* = 5.3, 1.6 Hz, 2H), 3.81 (s, 4H), 3.48 – 3.31 (m, 1H), 1.37 (d, *J* = 6.8, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.65, 153.44, 153.40, 133.73, 133.12, 132.68, 127.67, 117.46, 114.01, 113.99, 111.19, 109.32, 92.63, 69.93, 55.34, 45.67, 17.57. HRMS (EI) calculated for $[C_{19}H_{20}O_3]^+$ requires *m/z* 296.1407, found *m/z* 196.1402.

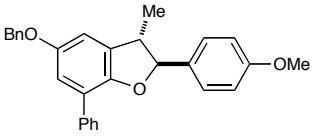


Compound 9. *Experiment 1*: Prepared according to the general procedure using 62 mg (0.40 mmol) of 4-(2-hydroxyethoxy)phenol, 80 mg (0.54 mmol) of

trans-anethole, 191 mg (0.84 mmol) of ammonium persulfate and 17.7 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 50% EtOAc/Hexanes to afford 84 mg (0.28 mmol, 70% yield) of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 62 mg (0.40 mmol) of 4-methoxy-2-methylphenol, 80 mg (0.54 mmol) of *trans*-anethole, 190 mg (0.83 mmol) of ammonium persulfate and 17.2 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 50% EtOAc/Hexanes to afford 83 mg (0.28 mmol, 69% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 3419 (br), 2068, 1512, 1459, 1180 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.29 (m, 2H), 6.97 – 6.81 (m, 2H), 6.81 – 6.63 (m, 3H), 5.07 (d, *J* = 9.1 Hz, 1H), 4.09 – 3.97 (m, 2H), 3.92 (t, *J* = 4.9 Hz, 2H), 3.79 (s, 3H), 3.49 – 3.30 (m, 1H), 2.39 (s, 1H), 1.36 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.67, 153.64, 153.41, 133.25, 132.63, 127.68, 114.05, 113.99, 111.11, 109.44, 92.66, 70.37, 61.60, 55.35, 45.66, 17.61. HRMS (EI) calculated for $[C_{18}H_{20}O_4]^+$ requires *m/z* 300.1357, found *m/z* 300.1353.

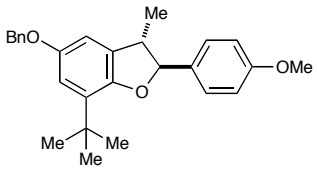


Compound 10. *Experiment 1*: Prepared according to the general procedure using 55 mg (0.40 mmol) of 2-methoxy-4-methylphenol, 78 mg (0.53 mmol) of *trans*-anethole, 194 mg (0.85 mmol) of ammonium persulfate and 17.2 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 34 h. The crude residue was purified by flash-column chromatography using 7–10% EtOAc/Hexanes to afford 59 mg (0.21 mmol, 52% yield) of the desired cycloadduct as a colorless oil. *Experiment 2:* Prepared according to the general procedure using 56 mg (0.41 mmol) of 2-methoxy-4-methylphenol, 80 mg (0.54 mmol) of *trans*-anethole, 196 mg (0.86 mmol) of ammonium persulfate and 17.3 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 34 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 66 mg (0.23 mmol, 58% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2362, 1496, 1458, 1328, 1251, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 2H), 6.98 – 6.68 (m, 2H), 6.61 (s, 1H), 6.58 (s, 1H), 5.11 (d, *J* = 9.2 Hz, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 3.50 – 3.34 (m, 1H), 2.32 (s, 3H), 1.36 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.61, 145.24, 143.87, 133.06, 132.62, 131.03, 127.91, 116.13, 113.87, 112.32, 93.16, 55.98, 55.31, 45.83, 21.35, 17.79. HRMS (ESI) calculated for $[C_{18}H_{20}O_3H]^+$ requires *m/z* 285.1486, found *m/z* 285.1482.

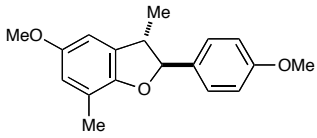


Compound 11 *Experiment 1*: Prepared according to the general procedure using 110 mg (0.40 mmol) of 5-(benzyloxy)-[1,1'-biphenyl]-2-ol, 78 mg (0.52 mmol) of *trans*-anethole, 188 mg (0.82 mmol) of ammonium persulfate and 17.1 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 159.8 mg (0.378 mmol, 95% yield) of the desired cycloadduct as a white crystalline solid. *Experiment 2*: Prepared according to the general procedure using 111 mg (0.40 mmol) of 5-(benzyloxy)-[1,1'-biphenyl]-2-ol, 83 mg (0.56 mmol) of *trans*-anethole, 194 mg (0.85 mmol) of ammonium persulfate and 17.6 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 164.0 mg (0.388 mmol, 97% yield) of the desired cycloadduct as a white crystalline solid. IR (thin film) 2362, 1516, 1254, 1176 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.64 (m, 2H), 7.48 – 7.40 (m, 2H), 7.40 – 7.17 (m, 8H), 7.00 (dd, *J* = 2.7, 0.9 Hz, 1H), 6.95 – 6.83 (m, 2H), 6.77 (dd, *J* = 2.6, 1.2 Hz, 1H), 5.10 (d, *J* = 9.1 Hz, 1H), 5.04 (s, 2H), 3.76 (s, 3H), 3.47 – 3.32 (m, 1H), 1.37 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.66, 154.02, 150.90, 137.44, 137.17, 134.14, 133.08, 128.68, 128.50, 128.47, 128.04, 127.70, 127.27, 123.36, 114.05, 113.90, 110.48, 92.50, 71.20, 55.38, 45.92, 17.79 (One peak missing due to

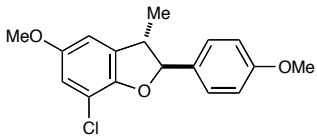
accidental equivalence). HRMS (EI) calculated for $[C_{29}H_{26}O_3]^+$ requires *m/z* 422.1877, found *m/z* 422.1886. Melting point: 113–114 °C



Compound 12 *Experiment 1*: Prepared according to the general procedure using 104 mg (0.41 mmol) of 4-(benzyloxy)-2-(tert-butyl)-1-methoxybenzene, 82 mg (0.55 mmol) of *trans*-anethole, 186 mg (0.81 mmol) of ammonium persulfate and 17.6 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 5% EtOAc/Hexanes to afford 155 mg (0.38 mmol, 94% yield) of the desired cycloadduct as an off-white solid. *Experiment 2*: Prepared according to the general procedure using 103 mg (0.39 mmol) of 4-(benzyloxy)-2-(tert-butyl)-1-methoxybenzene, 83 mg (0.59 mmol) of *trans*-anethole, 194 mg (0.85 mmol) of ammonium persulfate and 17.4 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 152 mg (0.38 mmol, 97% yield) of the desired cycloadduct as an off-white solid. IR (thin film) 2973, 1613, 1254, 1189, 1173 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.1 Hz, 2H), 7.42 – 7.25 (m, 5H), 6.90 (d, *J* = 8.3 Hz, 2H), 6.80 (d, *J* = 2.5 Hz, 1H), 6.72 – 6.58 (m, 1H), 5.07 (d, *J* = 9.3 Hz, 1H), 5.04 – 4.96 (m, 2H), 3.79 (s, 3H), 3.37 – 3.21 (m, 1H), 1.42 – 1.32 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.47, 153.41, 151.47, 137.60, 133.78, 133.73, 132.92, 128.62, 127.95, 127.74, 127.34, 114.00, 112.64, 107.37, 91.84, 71.08, 55.37, 45.95, 34.41, 29.36, 17.72. HRMS (ESI) calculated for $[C_{27}H_{30}O_3H]^+$ requires *m/z* 403.2268, found *m/z* 403.2251. Melting point: 90–92 °C.

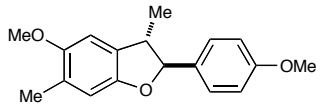


Compound 13 *Experiment 1*: Prepared according to the general procedure using 56 mg (0.41 mmol) of 4-methoxy-2-methylphenol, 82 mg (0.56 mmol) of *trans*-anethole, 187 mg (0.82 mmol) of ammonium persulfate and 17.8 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 109 mg (0.38 mmol, 94% yield) of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 56 mg (0.40 mmol) of 4-methoxy-2-methylphenol, 80 mg (0.54 mmol) of *trans*-anethole, 190 mg (0.83 mmol) of ammonium persulfate and 17.2 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 108 mg (0.38 mmol, 94% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2931, 1616, 1302, 1251, 1144 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.55 (apparent s, 2H), 5.03 (d, *J* = 9.2 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.47 – 3.30 (m, 1H), 2.22 (s, 3H), 1.34 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.67, 154.36, 151.80, 133.07, 132.20, 127.76, 119.91, 114.65, 114.05, 107.10, 92.25, 56.03, 55.34, 46.16, 17.72, 15.61. HRMS (ESI) calculated for $[C_{18}H_{20}O_3H]^+$ requires *m/z* 285.1486, found *m/z* 285.1483.

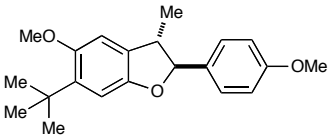


Compound 14. *Experiment 1:* Prepared according to the general procedure using 63 mg (0.40 mmol) of 2-chloro-4-methoxyphenol, 78 mg (0.53 mmol) of *trans*-anethole, 193 mg (0.84 mmol) of ammonium persulfate and 17.3 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 34 h. The crude residue was purified by flash-column chromatography using 10–15% EtOAc/Hexanes to afford 48 mg (0.14 mmol, 36% yield) of the desired cycloadduct as a colorless oil. *Experiment 2:* Prepared according to the general procedure using 64 mg (0.40 mmol) of 2-chloro-4-methoxyphenol, 83 mg (0.56 mmol) of *trans*-anethole, 199 mg (0.87 mmol) of ammonium persulfate and 17.6 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 34 h. The crude residue was purified by flash-

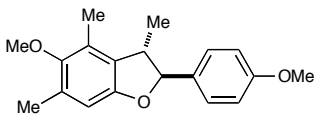
column chromatography 10–15% EtOAc/Hexanes to afford 46 mg (0.14 mmol, 34% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2838, 1596, 1480, 1441, 1209 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 2H), 6.95 – 6.86 (m, 2H), 6.72 (dd, *J* = 2.5, 0.9 Hz, 1H), 6.62 (dd, *J* = 2.5, 1.2 Hz, 1H), 5.15 (d, *J* = 9.0 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.46 (d, *J* = 6.8 Hz, 1H), 1.37 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.80, 154.68, 149.33, 134.41, 131.93, 127.80, 114.44, 114.04, 113.06, 109.12, 93.07, 56.19, 55.35, 46.42, 17.64. HRMS (EI) calculated for $[C_{17}H_{17}ClO_3]^+$ requires *m/z* 304.0861, found *m/z* 304.8074. Melting point: 88–89 °C.



Compound 15. *Experiment 1*: Prepared according to the general procedure using 56 mg (0.40 mmol) of 4-methoxy-2-methylphenol, 84 mg (0.55 mmol) of *trans*-anethole, 186 mg (0.81 mmol) of ammonium persulfate and 17.1 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 7–10% EtOAc/Hexanes to afford 85 mg (0.30 mmol, 74% yield) of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 56 mg (0.40 mmol) of 4-methoxy-2-methylphenol, 82 mg (0.56 mmol) of *trans*-anethole, 170 mg (0.74 mmol) of ammonium persulfate and 17.4 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 7–10% EtOAc/Hexanes to afford 87 mg (0.31 mmol, 75% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2928, 1516, 1467, 1415, 1364 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.63–6.67 (m, 2H), 5.05 (d, *J* = 8.8 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.49 – 3.27 (m, 1H), 2.20 (s, 3H), 1.38 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.59, 152.78, 152.42, 132.99, 129.38, 127.63, 126.55, 113.99, 111.54, 106.65, 92.51, 56.35, 55.34, 45.90, 18.00, 16.58. HRMS (EI) calculated for $[C_{18}H_{20}O_3H]^+$ requires *m/z* 285.1486, found *m/z* 285.1485. Melting point: 82–83 °C.

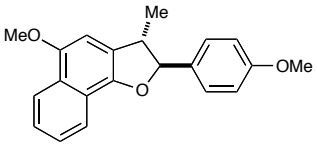


Compound 16. *Experiment 1*: Prepared according to the general procedure using 72 mg (0.40 mmol) of 3-(tert-butyl)-4-methoxyphenol, 82 mg (0.55 mmol) of *trans*-anethole, 184 mg (0.80 mmol) of ammonium persulfate and 17.3 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 5% EtOAc/Hexanes to afford 118 mg (0.36 mmol, 91% yield) of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 73 mg (0.41 mmol) of 3-(tert-butyl)-4-methoxyphenol, 78 mg (0.52 mmol) of *trans*-anethole, 183 mg (0.80 mmol) of ammonium persulfate and 17.2 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 5% EtOAc/Hexanes to afford 122 mg (0.37 mmol, 92% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2960, 1516, 1493, 1412, 1196, 1176 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.29 (m, 2H), 7.00 – 6.88 (m, 2H), 6.70 (s, 1H), 5.05 (d, *J* = 9.3 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.53 – 3.22 (m, 1H), 1.4 – 1.3 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.61, 153.42, 152.90, 138.58, 132.95, 129.23, 127.70, 114.00, 107.96, 107.94, 92.62, 56.04, 55.33, 45.91, 35.05, 29.90, 17.63. HRMS (ESI) calculated for $[C_{21}H_{26}O_3]^+$ requires *m/z* 327.1955, found *m/z* 327.1960.

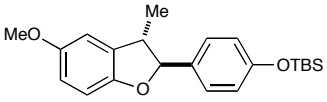


Compound 17. *Experiment 1*: Prepared according to the general procedure using 55 mg (0.36 mmol) of 4-methoxy-3,5-dimethylphenol, 124 mg (0.84 mmol) of *trans*-anethole, 182 mg (0.80 mmol) of ammonium persulfate and 17.4 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 5-10% EtOAc/Hexanes to afford 84 mg (0.28 mmol, 77% yield)

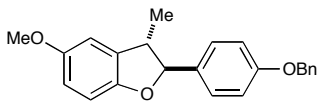
of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 62 mg (0.41 mmol) of 4-methoxy-3,5-dimethylphenol, 121 mg (0.82 mmol) of *trans*-anethole, 196 mg (0.86 mmol) of ammonium persulfate and 17.6 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 5% EtOAc/Hexanes to afford 93 mg (0.31 mmol, 76% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2934, 2362, 1512, 1251, 1176, 1050 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.18 (m, 2H), 6.90 – 6.79 (m, 2H), 6.52 (s, 1H), 5.14 (d, J = 5.4 Hz, 1H), 3.79 (s, 3H), 3.67 (s, 3H), 3.47 – 3.25 (m, 1H), 2.26 (s, 3H), 2.20 (s, 3H), 1.42 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.40, 154.84, 150.96, 134.16, 130.49, 128.45, 127.50, 126.95, 113.96, 108.63, 91.58, 60.14, 55.31, 45.54, 19.67, 16.54, 12.48. HRMS (ESI) calculated for $[C_{19}H_{22}O_3H]^+$ requires *m/z* 299.1642, found *m/z* 299.1638.



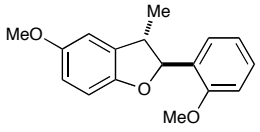
Compound 18. *Experiment 1*: Prepared according to the general procedure using 70 mg (0.40 mmol) of 4-methoxynaphthalen-1-ol, 79 mg (0.53 mmol) of *trans*-anethole, 181 mg (0.79 mmol) of ammonium persulfate and 17.1 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 12 h. The crude residue was purified by flash-column chromatography using 10-15% EtOAc/Hexanes to afford 109 mg (0.34 mmol, 85% yield) of the desired cycloadduct as an off-white solid. *Experiment 2*: Prepared according to the general procedure using 70 mg (0.40 mmol) of 4-methoxynaphthalen-1-ol, 80 mg (0.54 mmol) of *trans*-anethole, 180 mg (0.79 mmol) of ammonium persulfate and 17.9 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 12 h. The crude residue was purified by flash-column chromatography using 10–15% EtOAc/Hexanes to afford 119 mg (0.37 mmol, 92% yield) of the desired cycloadduct as an off-white solid. IR (thin film) 3067, 2838, 1596, 1377, 1247, 1118, 1047 cm^{-1}; ^1H NMR (400 MHz, CDCl3) δ 8.29 – 8.15 (m, 1H), 8.03 – 7.88 (m, 1H), 7.53 – 7.32 (m, 4H), 7.00 – 6.81 (m, 2H), 6.66 (s, 1H), 5.26 (d, J = 8.4 Hz, 1H), 3.96 (s, 3H), 3.78 (s, 3H), 3.58 (p, J = 6.4 Hz, 1H), 1.46 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.62, 150.41, 147.94, 133.52, 127.63, 126.10, 125.55, 125.08, 123.56, 122.56, 121.43, 121.00, 114.07, 100.44, 92.57, 56.12, 55.37, 47.13, 18.84. HRMS (ESI) calculated for $[C_{21}H_{20}O_3H]^+$ requires *m/z* 321.1486, found *m/z* 321.1479. Melting point: 83–84 °C



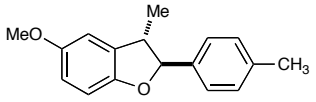
Compound 19. *Experiment 1*: Prepared according to the general procedure using 50 mg (0.40 mmol) of 4-methoxyphenol, 132 mg (0.55 mmol) of (*E*)-*tert*-butyldimethyl(4-(prop-1-en-1-yl)phenoxy)silane, 193 mg (0.85 mmol) of ammonium persulfate and 17.5 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 34 h. The crude residue was purified by flash-column chromatography using 3% EtOAc/Hexanes to afford 113 mg (0.31 mmol, 76% yield) of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 50 mg (0.40 mmol) of 4-methoxyphenol, 137 mg (0.55 mmol) of (*E*)-*tert*-butyldimethyl(4-(prop-1-en-1-yl)phenoxy)silane, 193 mg (0.84 mmol) of ammonium persulfate and 17.2 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 34 h. The crude residue was purified by flash-column chromatography using 3% EtOAc/Hexanes to afford 108 mg (0.29 mmol, 72% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2931, 2362, 1609, 1512, 1202 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.24 (m, 2H), 6.97 – 6.85 (m, 2H), 6.85 – 6.68 (m, 3H), 5.12 (d, J = 9.1 Hz, 1H), 3.83 (s, 3H), 3.46 (p, J = 6.6 Hz, 1H), 1.43 (d, J = 6.8 Hz, 3H), 1.04 (s, 9H), 0.25 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.77, 154.43, 153.29, 133.30, 133.18, 127.61, 120.20, 112.85, 110.11, 109.36, 92.70, 56.06, 45.68, 25.73, 18.25, 17.64, -4.36, -4.37. HRMS (ESI) calculated for $[C_{22}H_{30}O_3SiH]^+$ requires *m/z* 371.2037, found *m/z* 371.2044.



Compound 20. *Experiment 1*: Prepared according to the general procedure using 49 mg (0.40 mmol) of 4-methoxyphenol, 117 mg (0.52 mmol) of (*E*)-1-(benzyloxy)-4-(prop-1-en-1-yl)benzene, 197 mg (0.86 mmol) of ammonium persulfate and 17.2 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 34 h. The crude residue was purified by flash-column chromatography using 10% EtOAc/Hexanes to afford 119 mg (0.342 mmol, 86% yield) of the desired cycloadduct as a colorless glass. *Experiment 2*: Prepared according to the general procedure using 49 mg (0.40 mmol) of 4-methoxyphenol, 120 mg (0.54 mmol) of (*E*)-1-(benzyloxy)-4-(prop-1-en-1-yl)benzene, 193 mg (0.84 mmol) of ammonium persulfate and 17.1 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 34 h. The crude residue was purified by flash-column chromatography using 10% EtOAc/Hexanes to afford 111 mg (0.32 mmol, 80% yield) of the desired cycloadduct as a colorless glass. IR (thin film) 2362, 1613, 1512, 1244, 1202 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.27 (m, 7H), 6.96 (m, 2H), 6.78 – 6.65 (m, 3H), 5.06 (m, 3H), 3.75 (s, 3H), 3.39 (p, J = 6.9 Hz, 1H), 1.36 (d, J = 6.9, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.88, 154.47, 153.32, 136.98, 133.17, 133.05, 128.66, 128.05, 127.73, 127.53, 115.01, 112.92, 110.15, 109.41, 92.61, 70.09, 56.09, 45.74, 17.69. HRMS (ESI) calculated for $[C_{23}H_{22}O_3H]^+$ requires *m/z* 347.1642, found *m/z* 347.1649.

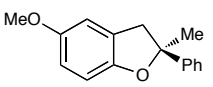


Compound 21. *Experiment 1*: Prepared according to the general procedure using 48 mg (0.38 mmol) of 4-methoxyphenol, 78 mg (0.53 mmol) of (*E*)-1-methoxy-2-(prop-1-en-1-yl)benzene, 190 mg (0.83 mmol) of ammonium persulfate and 16.8 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 50 h. The crude residue was purified by flash-column chromatography using 10% EtOAc/Hexanes to afford 89 mg (0.33 mmol, 86% yield) of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 49 mg (0.40 mmol) of 4-methoxyphenol, 83 mg (0.56 mmol) of (*E*)-1-methoxy-2-(prop-1-en-1-yl)benzene, 191 mg (0.84 mmol) of ammonium persulfate and 17.4 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 50 h. The crude residue was purified by flash-column chromatography using 10% EtOAc/Hexanes to afford 95 mg (0.36 mmol, 90% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2960, 1487, 1264, 1205 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.32 (m, 1H), 7.32 – 7.19 (m, 1H), 6.99 – 6.85 (m, 2H), 6.85 – 6.74 (m, 1H), 6.74 – 6.62 (m, 2H), 5.59 (d, J = 6.5 Hz, 1H), 3.85 (s, 3H), 3.75 (s, 3H), 3.43 – 3.27 (m, 1H), 1.44 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.56, 154.32, 153.44, 133.29, 130.03, 128.67, 126.25, 120.64, 112.82, 110.43, 110.41, 109.21, 87.00, 56.04, 55.38, 45.50, 19.83. HRMS (ESI) calculated for $[C_{17}H_{18}O_3H]^+$ requires *m/z* 271.1329, found *m/z* 271.1327.

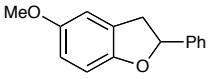


Compound 22. *Experiment 1*: Prepared according to the general procedure using 50 mg (0.40 mmol) of 4-methoxyphenol, 110 mg (0.83 mmol) of (*E*)-1-methyl-4-(prop-1-en-1-yl)benzene, 192 mg (0.84 mmol) of ammonium persulfate and 17.1 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 50 h.The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 90 mg (0.36 mmol, 89% yield) of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 50 mg (0.40 mmol) of 4-methoxyphenol, 113 mg (0.85 mmol) of (*E*)-1-methyl-4-(prop-1-en-1-yl)benzene, 194 mg (0.85 mmol) of ammonium persulfate and 17.2 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 50 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 83 mg (0.33 mmol, 82% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2938, 1487, 1180, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 7.7 Hz, 2H), 7.18 (d, J = 7.7 Hz, 2H), 6.85 – 6.61 (m, 3H), 5.09 (d, J = 9.0 Hz, 1H), 3.76 (s, 3H), 3.39 (p, J = 6.8 Hz, 1H), 2.35 (s, 3H), 1.38 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.46, 153.38, 138.01, 137.83, 133.12, 129.33, 126.20, 112.91, 110.14, 109.39, 92.73, 56.08,

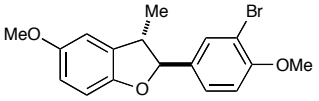
45.91, 21.25, 17.79. HRMS (ESI) calculated for $[C_{17}H_{18}O_2H]^+$ requires *m/z* 255.1380, found *m/z* 255.1388.



Compound 23. *Experiment 1*: Prepared according to the general procedure using 50 mg (0.41 mmol) of 4-methoxyphenol, 111 mg (0.94 mmol) of α-methylstyrene, 194 mg (0.85 mmol) of ammonium persulfate and 17.1 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 50 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 64 mg (0.27 mmol, 65% yield) of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 49 mg (0.40 mmol) of 4-methoxyphenol, 98 mg (0.83 mmol) of α-methylstyrene, 192 mg (0.84 mmol) of ammonium persulfate and 17.1 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 50 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 69 mg (0.29 mmol, 72% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2973, 1487, 1448, 1225, 1150, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.40 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 6.75 – 6.57 (m, 2H), 3.73 (s, 3H), 3.52 – 3.20 (m, 2H), 1.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.16, 153.06, 146.90, 128.37, 127.49, 127.04, 124.56, 113.01, 111.38, 109.42, 89.22, 56.03, 45.19, 29.27. HRMS (EI) calculated for $[C_{16}H_{16}O_2]^+$ requires *m/z* 240.1145, found *m/z* 240.1143.

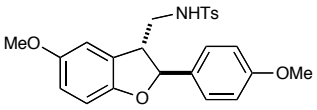


Compound 24. *Experiment 1*: Prepared according to the general procedure using 50 mg (0.40 mmol) of 4-methoxyphenol, 100 μL (0.87 mmol) of styrene, 190 mg (0.84 mmol) of ammonium persulfate and 17.3 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 50 h. The crude residue was purified by flash-column chromatography using 5-6% EtOAc/Hexanes to afford 40 mg (0.18 mmol, 44% yield) of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 50 mg (0.41 mmol) of 4-methoxyphenol, 100 μL (0.87 mmol) of styrene, 195 mg (0.85 mmol) of ammonium persulfate and 17.5 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 50 h. The crude residue was purified by flash-column chromatography using 5–6% EtOAc/Hexanes to afford 42 mg (0.18 mmol, 45% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2938, 1487, 1205, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.21 (m, 5H), 6.88 – 6.52 (m, 3H), 5.72 (t, *J* = 8.7 Hz, 1H), 3.75 (s, 3H), 3.58 (dd, *J* = 15.7, 9.3 Hz, 1H), 3.18 (dd, *J* = 15.7, 8.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.35, 153.83, 142.06, 128.65, 128.00, 127.53, 125.79, 113.07, 111.25, 109.23, 84.26, 56.07, 38.91. HRMS (EI) calculated for $[C_{15}H_{14}O_2]^+$ requires *m/z* 226.0989, found *m/z* 226.0988.

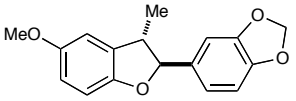


Compound 25. *Experiment 1*: Prepared according to the general procedure using 50 mg (0.40 mmol) of 4-methoxyphenol, 119 mg (0.52 mmol) of (*E*)-2-bromo-1-methoxy-4-(prop-1-en-1-yl)benzene, 193 mg (0.85 mmol) of ammonium persulfate and 16.4 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 28 h. The crude residue was purified by flash-column chromatography using 5% EtOAc/Hexanes to afford 95 mg (0.27 mmol, 68% yield) of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 49 mg (0.40 mmol) of 4-methoxyphenol, 117 mg (0.52 mmol) of (*E*)-2-bromo-1-methoxy-4-(prop-1-en-1-yl)benzene, 194 mg (0.85 mmol) of ammonium persulfate and 17.0 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 28 h. The crude residue was purified by flash-column chromatography using 5% EtOAc/Hexanes to afford 103 mg (0.30 mmol, 75% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2960, 1614, 1519, 1372 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 2.1 Hz, 1H), 7.31 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 6.80 – 6.63 (m, 3H), 5.03 (d, *J* = 8.9 Hz, 1H), 3.88 (s, 3H), 3.76 (s, 3H), 3.50 – 3.22 (m, 1H),

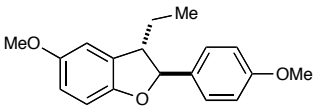
1.38 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.82, 154.58, 153.06, 134.41, 132.76, 131.24, 126.54, 113.03, 111.88, 111.87, 110.12, 109.45, 91.63, 56.35, 56.07, 45.90, 17.76. HRMS (ESI) calculated for $[C_{17}H_{17}O_3BrH]^+$ requires *m/z* 349.0434, found *m/z* 349.0427.



Compound 26. *Experiment 1*: Prepared according to the general procedure using 50 mg (0.40 mmol) of 4-methoxyphenol, 166 mg (0.52 mmol) of (*E*)-*N*-(3-(4-methoxyphenyl)allyl)-4-methylbenzenesulfonamide, 197 mg (0.86 mmol) of ammonium persulfate and 17.4 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 40 h. The crude residue was purified by flash-column chromatography using 20–40% EtOAc/Hexanes to afford 121 mg (0.27 mmol, 68% yield) of the desired cycloadduct as a white solid. *Experiment 2*: Prepared according to the general procedure using 50 mg (0.40 mmol) of 4-methoxyphenol, 169 mg (0.53 mmol) of (*E*)-*N*-(3-(4-methoxyphenyl)allyl)-4-methylbenzenesulfonamide, 196 mg (0.86 mmol) of ammonium persulfate and 17.1 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 40 h. The crude residue was purified by flash-column chromatography using 25% EtOAc/Hexanes + 2% Acetone to afford 133 mg (0.31 mmol, 75% yield) of the desired cycloadduct as a white solid. IR (thin film) 3277 (br), 2838, 1490, 1160 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.9 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.24 – 7.14 (m, 2H), 6.91 – 6.77 (m, 2H), 6.77 – 6.56 (m, 3H), 5.40 (d, J = 6.4 Hz, 1H), 4.89 (t, J = 6.5 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 3.46 (q, J = 6.0 Hz, 1H), 3.24 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.59, 154.38, 153.93, 143.72, 136.58, 133.01, 129.88, 127.34, 127.11, 127.05, 114.32, 114.09, 110.39, 109.93, 87.12, 56.05, 55.32, 50.89, 45.35, 21.57. HRMS (ESI) calculated for $[C_{24}H_{25}NO_5S+NH_4]^+$ requires *m/z* 457.1792, found *m/z* 457.1798. Melting point: 88–89 °C

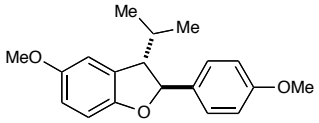


Compound 27. *Experiment 1*: Prepared according to the general procedure using 50 mg (0.41 mmol) of 4-methoxyphenol, 90 mg (0.55 mmol) of (*E*)-isosafrole, 196 mg (0.86 mmol) of ammonium persulfate and 17.3 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 15% EtOAc/Hexanes to afford 92 mg (0.32 mmol, 79% yield) of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 50 mg (0.41 mmol) of 4-methoxyphenol, 83 mg (0.54 mmol) of (*E*)-isosafrole, 199 mg (0.87 mmol) of ammonium persulfate and 17.2 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 30 h. The crude residue was purified by flash-column chromatography using 15% EtOAc/Hexanes to afford 98 mg (0.34 mmol, 85% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2964, 1613, 1487, 1251, 1147, 1034 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 – 6.66 (m, 6H), 5.95 (s, 2H), 5.03 (d, J = 8.9 Hz, 1H), 3.77 (s, 3H), 3.37 (m, 1H), 1.38 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.48, 153.16, 148.00, 147.61, 134.64, 132.94, 119.96, 112.93, 110.11, 109.38, 108.19, 106.60, 101.15, 92.69, 56.07, 45.85, 17.73. HRMS (ESI) calculated for $[C_{17}H_{16}O_4+NH_4]^+$ requires *m/z* 302.1387, found *m/z* 302.1386.

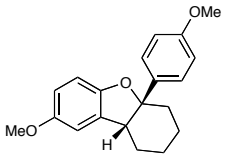


Compound 28. *Experiment 1*: Prepared according to the general procedure using 51 mg (0.41 mmol) of 4-methoxyphenol, 89 mg (0.55 mmol) of (*E*)-1-(but-1-en-1-yl)-4-methoxybenzene, 194 mg (0.85 mmol) of ammonium persulfate and 17.3 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 50 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 104 mg (0.36 mmol, 89% yield) of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 51 mg (0.41 mmol) of 4-methoxyphenol, 87 mg (0.54 mmol) of (*E*)-1-(but-1-en-1-yl)-4-methoxybenzene, 192 mg (0.84 mmol) of ammonium persulfate and 17.2 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 50 h. The crude residue was purified by flash-

column chromatography using 7% EtOAc/Hexanes to afford 109 mg (0.38 mmol, 93% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2964, 1516, 1487, 1247, 1144, 1037 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.24 (m, 2H), 7.01 – 6.81 (m, 2H), 6.81 – 6.64 (m, 3H), 5.25 (d, *J* = 6.7 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.32 (q, *J* = 6.6 Hz, 1H), 2.06 – 1.62 (m, 2H), 1.00 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.49, 154.24, 153.60, 134.15, 131.55, 127.48, 114.02, 112.96, 110.86, 109.20, 89.78, 56.05, 55.32, 52.24, 27.27, 11.30. HRMS (ESI) calculated for $[C_{19}H_{20}O_3]^+$ requires *m/z* 284.1407, found *m/z* 284.1411.

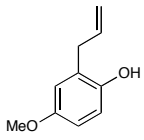


Compound 29. *Experiment 1*: Prepared according to the general procedure using 50 mg (0.40 mmol) of 4-methoxyphenol, 92 mg (0.52 mmol) of (*E*)-1-methoxy-4-(3-methylbut-1-en-1-yl)benzene, 197 mg (0.86 mmol) of ammonium persulfate and 17.5 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 50 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 95 mg (0.32 mmol, 79% yield) of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 50 mg (0.40 mmol) of 4-methoxyphenol, 100 mg (0.57 mmol) of (*E*)-1-methoxy-4-(3-methylbut-1-en-1-yl)benzene, 195 mg (0.86 mmol) of ammonium persulfate and 17.2 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 50 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 96 mg (0.32 mmol, 79% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2834, 2367, 1516, 1247, 1176, 1037 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.12 (m, 2H), 6.98 – 6.81 (m, 2H), 6.81 – 6.62 (m, 3H), 5.38 (d, *J* = 4.7 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.27 (t, *J* = 4.7 Hz, 1H), 2.10 – 2.00 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.29, 154.14, 154.03, 135.25, 129.77, 126.94, 114.02, 113.07, 111.64, 109.00, 86.41, 57.38, 56.02, 55.30, 32.06, 19.61, 18.94. HRMS (ESI) calculated for $[C_{19}H_{22}O_3+NH_4]^+$ requires *m/z* 316.1908, found *m/z* 316.1917.

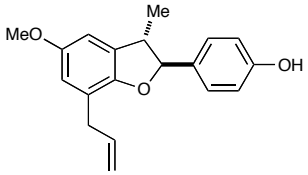


Compound 30. *Experiment 1*: Prepared according to the general procedure using 50 mg (0.40 mmol) of 4-methoxyphenol, 154 mg (0.82 mmol) of 4'-methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl, 197 mg (0.86 mmol) of ammonium persulfate and 16.8 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 52 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 82 mg (0.27 mmol, 66% yield) of the desired cycloadduct as a colorless oil. *Experiment 2*: Prepared according to the general procedure using 51 mg (0.41 mmol) of 4-methoxyphenol, 153 mg (0.81 mmol) of 4'-methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl, 194 mg (0.85 mmol) of ammonium persulfate and 17.4 mg (0.02 mmol) of $Ru(bpz)_3(PF_6)_2$. The reaction was irradiated for 52 h. The crude residue was purified by flash-column chromatography using 7% EtOAc/Hexanes to afford 86 mg (0.28 mmol, 68% yield) of the desired cycloadduct as a colorless oil. IR (thin film) 2938, 1613, 1516, 1180, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.40 (m, 2H), 6.90 – 6.80 (m, 2H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.70 – 6.58 (m, 2H), 3.78 (s, 3H), 3.74 (s, 3H), 3.54 (t, *J* = 5.9 Hz, 1H), 2.12 – 1.92 (m, 3H), 1.92 – 1.76 (m, 1H), 1.70 – 1.56 (m, 1H), 1.55 – 1.43 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.62, 154.19, 152.53, 137.95, 133.59, 126.75, 113.50, 112.27, 110.25, 109.84, 90.72, 55.93, 55.26, 47.31, 35.36, 27.79, 21.28, 20.91. HRMS (EI) calculated for $[C_{20}H_{22}O_3]^+$ requires *m/z* 310.1564, found *m/z* 310.1572.

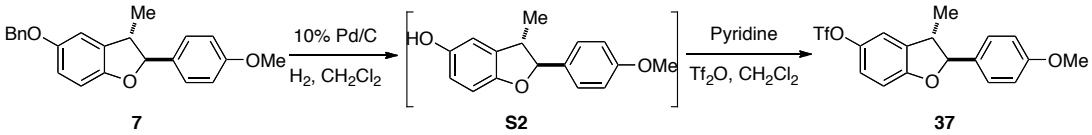
IV. Natural Product Syntheses



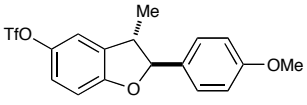
2-Allyl-4-methoxyphenol (33): 4-Methoxyphenol (1.80 g, 14.6 mmol) and potassium carbonate (2.13 g, 15.4 mmol) were combined in a 25 mL flame-dried round-bottomed flask containing a magnetic stirbar. Acetone (5 mL) was added, and flask was capped with a septum and flushed with N_2. Allyl bromide (1.90 mL, 22.0 mmol) was then added dropwise *via* syringe to the stirring suspension, and the flask was fitted with a reflux condenser under N_2. The stirring mixture was heated to reflux for 3.5 h. After cooling to room temperature, the mixture was rinsed into a separatory funnel with dichloromethane and 2 M NaOH. The layers were separated, and the organic layer was washed once more with 2 M NaOH. The organic extract was then dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford 1-(allyloxy)-4-methoxybenzene (2.22 g, 93% yield) as a viscous oil. All spectral data were in agreement with previously reported values.[20] This material was carried on without further purification. The unpurified product (2.22 g, 13.5 mmol) was transferred into a round-bottomed flask containing a magnetic stirbar. The flask was equipped with a reflux condenser and heated (neat) to 195 ºC for 5 h. The crude reaction mixture was then cooled to room temperature, and purified directly by flash-column chromatography (20% EtOAc/hexanes) to afford the title compound as a pale yellow oil (2.01 g, 91% yield). All spectral data were in agreement with previously reported values.[20]



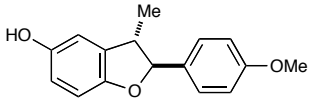
Compound 35: Phenol **33** (66 mg, 0.40 mmol), (*E*)-*tert*-butyldimethyl(4-(prop-1-en-1-yl)phenoxy)silane (196 mg, 0.79 mmol), $Ru(bpz)_3(PF_6)_2$ (17.4 mg, 0.02 mmol), and ammonium peroxydisulfate (191 mg, 0.84 mmol) were combined in an oven-dried Schlenk flask. A magnetic stirbar was added, and MeCN (4 mL) was introduced by syringe. The flask was sealed with a glass stopper, and the solution was degassed by three freeze-pump-thaw cycles in dry-ice/acetone. The flask was then backfilled with N_2, and the reaction was stirred evenly under irradiation with a 23 W (1200 lumens) SLI Mini-Lynx compact fluorescent light bulb (placed 3-4 inches from the reaction flask) for 40 h. During irradiation, the reaction was sonicated as needed to maintain catalyst suspension (see general procedure above). At 40 h, the reaction was diluted with EtOAc (7 mL), and eluted through a plug of silica using EtOAc. After concentrating *in vacuo*, the eluent was transferred to a 10 mL round-bottomed flask containing a magnetic stirbar, and dissolved in 2 mL THF under N_2. The flask was cooled to 0 °C in an ice bath, and solid tetrabutylammonium fluoride trihydrate ($TBAF{\cdot}H_2O$, 186 mg, 0.59 mmol) was added in one portion. The resulting solution was stirred for 15 min at room temperature, and TLC analysis showed reaction completion. The solution was transferred to a separatory funnel, and the reaction was quenched by the addition of saturated aqueous ammonium chloride. The resulting aqueous layer was extracted with EtOAc (3x). The combined organic extracts were then washed with sat. aq. $NaHCO_3$, then brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by flash-column chromatography to afford pure **35** (96 mg, 81% yield) as a yellow oil. IR (thin film) 3422 (br), 2964, 1454, 1199, 1041 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 2H), 6.88 – 6.65 (m, 2H), 6.58 (apparent s, 2H), 5.99 (ddt, J = 16.8, 10.1, 6.6 Hz 1H), 5.28 (br s, 1H), 5.20 – 4.93 (m, 3H), 3.77 (s, 3H), 3.52 – 3.26 (m, 3H), 1.36 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.59, 154.37, 151.31, 136.20, 133.19, 132.52, 127.79, 122.11, 115.94, 115.45, 113.66, 107.76, 92.20, 56.17, 46.13, 34.03, 17.80. HRMS (EI) calculated for $[C_{19}H_{20}O_3]^+$ requires *m/z* 296.1407, found *m/z* 296.1415.



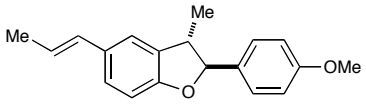
7 S2 37



Compound 36: Compound **7** (231 mg, 0.67 mmol) was weighed into a 100 mL round-bottom flask containing a magnetic stirbar. THF (40 mL) was added, and the mixture was stirred until all solids were dissolved. The flask was then capped with a septum and purged with N_2 for 5 min. Solid Pd/C (10 wt%, 72 mg, 0.067 mmol) was then added, and hydrogen gas (balloon equipped with a syringe needle) was bubbled through the black suspension for 15 min. After 15 min, the needle was removed from the suspension, and the hydrogen atmosphere was maintained with rapid stirring for 4.5 h. The black mixture was then filtered over Celite, and the filter cake was washed thoroughly with CH_2Cl_2. The eluent was concentrated *in vacuo* to afford phenol (**S2**) cleanly as a colorless glass (177 mg, quantitative yield). The crude product was carried on without further purification. **S2** was weighed into a flame-dried 12 mL vial, then dissolved in toluene and concentrated *in vacuo* to azeotropically remove water. A magnetic stirbar was added, and the vial was capped with a septum and flushed with N_2. Dichloromethane (2.5 mL) was added by syringe, and after the mixture became homogenous, the vial was cooled to 0 °C in an ice bath. Pyridine (250 μL, 3.1 mmol) was added in one portion *via* syringe, and then triflic anhydride (200 μL, 1.2 mmol) was added dropwise over 5 min. After stirring the yellow-green solution for 5 min at 0 °C, the vial was allowed to warm to room temperature. The reaction was stirred for an additional 3 h under N_2 and subsequently quenched by addition of 5 mL of 1 M HCl. The resulting mixture was transferred to a separatory funnel using dichloromethane and H_2O. The layers were separated, and the aqueous layer was extracted once with dichloromethane. The combined organic extracts were washed once with sat. aq. $NaHCO_3$, then washed with brine, the dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by flash-column chromatography (10% EtOAC/hex) to afford **36** (241 mg, 93% yield) as a white crystalline solid. IR (thin film) 2359, 1422, 1251, 1144 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.29 (m, 2H), 7.15 – 6.98 (m, 2H), 6.98 – 6.54 (m, 3H), 5.18 (d, J = 9.2 Hz, 1H), 3.82 (s, 3H), 3.56 – 3.36 (m, 1H), 1.40 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 159.95, 158.67, 143.35, 134.29, 131.61, 127.69, 121.25, 118.8 (q, J_{CF} = 322 Hz) 117.16, 114.17, 110.12, 93.54, 55.36, 45.23, 17.47. HRMS (EI) calculated for $[C_{17}H_{15}F_3O_5S]^+$ requires *m/z* 388.0587, found *m/z* 388.0588. Melting point: 32–33 °C



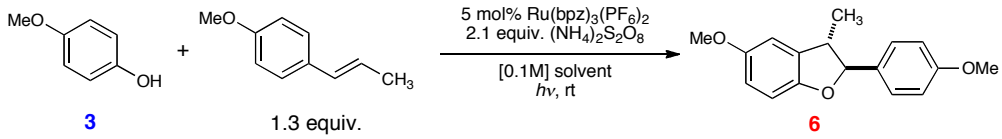
An analytically pure sample of **S2** could be isolated as intermediate in synthesis of **37**. It was purified by flash-column chromatography (30% EtOAc/Hexanes) to afford desired product as a white glass. IR (thin film) 3403 (br), 2964, 1616, 1454, 1251 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.28 (m, 2H), 7.00 – 6.81 (m, 2H), 6.77 – 6.50 (m, 3H), 5.20 – 4.88 (m, 2H), 3.80 (s, 3H), 3.48 – 3.25 (m, 1H), 1.33 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.63, 153.07, 149.97, 133.31, 132.61, 127.75, 114.47, 114.07, 111.19, 109.53, 92.66, 55.38, 45.58, 17.53. HRMS (EI) calculated for $[C_{16}H_{16}O_3]^+$ requires *m/z* 256.1094, found *m/z* 256.1097.



Compound 37: Compound **36** (148 mg, 0.44 mmol) and *trans*-1-propen-1-ylboronic acid (75 mg, 0.88 mmol) were combined in a 50 mL round bottomed flask containing a magnetic stirbar. Toluene (12 mL), ethanol (3.5 mL) and H_2O (5.2 mL) were added to the flask, which was then capped with a septum and flushed with N_2. The mixture was stirred, and solid $Pd[PPh_3]_4$ (50.6 mg, 0.44 mmol) and potassium carbonate (172 mg,

1.25 mmol) were added to the flask. The flask was then equipped with a reflux condenser attached to a vacuum manifold and carefully evacuated until gentle bubbling of solvent was observed, whereupon the atmosphere was immediately backfilled with N_2. The system was evacuated and refilled in the same way three more times, then heated to reflux (110–120 °C) for 7.5 h with vigorous stirring. The flask was then cooled to room temperature, and the reaction was quenched by addition of 1 M HCl. The resulting mixture was transferred to a separatory funnel with EtOAc and H_2O. The layers were separated, and the organic phase was washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by flash-column chromatography (5–10% EtOAc/Hexanes) to afford **35** (117 mg, 95% yield) as a colorless oil. Spectral data matched those previously reported.[21] IR (thin film) 3022, 2952, 1422, 1212, 1144 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.26 (m, 2H), 7.11 (d, *J* = 10.3 Hz, 2H), 6.97 – 6.83 (m, 2H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.35 (dq, *J* = 15.7, 1.7 Hz, 1H), 6.07 (dq, *J* = 15.7, 6.6 Hz, 1H), 5.07 (d, *J* = 8.9 Hz, 1H), 3.78 (s, 3H), 3.38 (p, *J* = 6.8 Hz, 1H), 1.85 (dd, *J* = 6.6, 1.7 Hz, 3H), 1.37 (d, *J* = 6.8 Hz, 3H). ^1H NMR (400 MHz, Acetone-d_6) δ 7.48 – 7.31 (m, 2H), 7.24 (s, 1H), 7.18 – 7.07 (m, 1H), 7.05 – 6.89 (m, 2H), 6.71 (d, *J* = 8.2 Hz, 1H), 6.38 (d, *J* = 15.7 Hz, 1H), 6.12 (dq, *J* = 15.7, 6.6 Hz, 1H), 5.12 (d, *J* = 8.7 Hz, 1H), 3.80 (s, 3H), 3.46 – 3.25 (m, 1H), 1.82 (dd, *J* = 6.6, 1.6 Hz, 3H), 1.38 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.71, 158.42, 132.73, 132.47, 131.28, 130.87, 127.71, 126.37, 123.01, 120.80, 114.07, 109.34, 92.72, 55.35, 45.29, 18.51, 17.86. ^{13}C NMR (101 MHz, Acetone-d_6) δ 159.79, 158.54, 132.93, 132.61, 131.17, 131.01, 127.59, 126.28, 122.20, 120.90, 113.86, 108.85, 92.33, 54.69, 45.21, 17.66, 17.26. HRMS (EI) calculated for $[C_{19}H_{20}O_2]^+$ requires *m/z* 280.1458, found *m/z* 280.1457.

V. Timecourse Studies:



Representative Reaction Timecourse:
The reaction was set up according to the general procedure (see page S-8) with 4-methoxyphenol (**3**, 1 equiv.), *trans*-anethole (1.3 equiv.), ammonium persulfate (2.1 equiv.), $Ru(bpz)_3(PF_6)_2$ (0.05 equiv), and trimethyl(phenyl)silane as an internal standard in MeCN (0.1 M). After degassing by three freeze-pump-thaw cycles, the reaction flask was irradiated with a 23 W CFL light source and reaction progress was monitored by ^1H NMR using reaction aliquots taken under N_2 purge to maintain an oxygen-free environment. The resulting data (Figure S1) revealed an induction period of several hours corresponding to the formation of a red precipitate in the reaction.

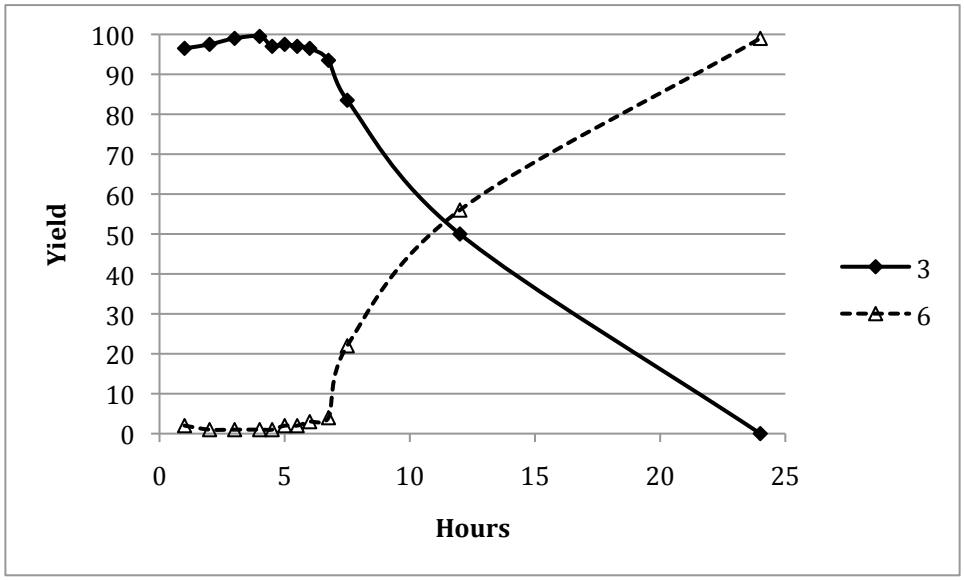


Figure S1: Representative reaction timecourse

Precipitate removal experiments
Reactions were set up according to the general procedure (see page S-8) with 4-methoxyphenol (**3**, 1 equiv.), *trans*-anethole (1.3 equiv.), ammonium persulfate (2.1 equiv.), $Ru(bpz)_3(PF_6)_2$ (0.05 equiv), and trimethyl(phenyl)silane as an internal standard in MeCN (0.1M). After degassing by three freeze-pump-thaw cycles, the reaction flasks were irradiated with a 23 W CFL light source, and stirred for 4.5 h. The reaction media were then filtered separately through medium frits into clean, dry Schlenk flasks containing magnetic stirbars. The resulting solutions were then either immediately degassed again by three freeze-pump-thaw cycles (Figure S2-A), or degassed by 3x freeze-pump-thaw cycles following the addition of ammonium persulfate (2.1 equiv.) (Figure S2-B). The resulting reactions were then monitored by ^1H NMR using reaction aliquots taken under N_2 purge to maintain an oxygen-free environment. Both experiments resulted in negligible further consumption of **3**, indicating that the majority of the active catalyst was likely removed by filtration.

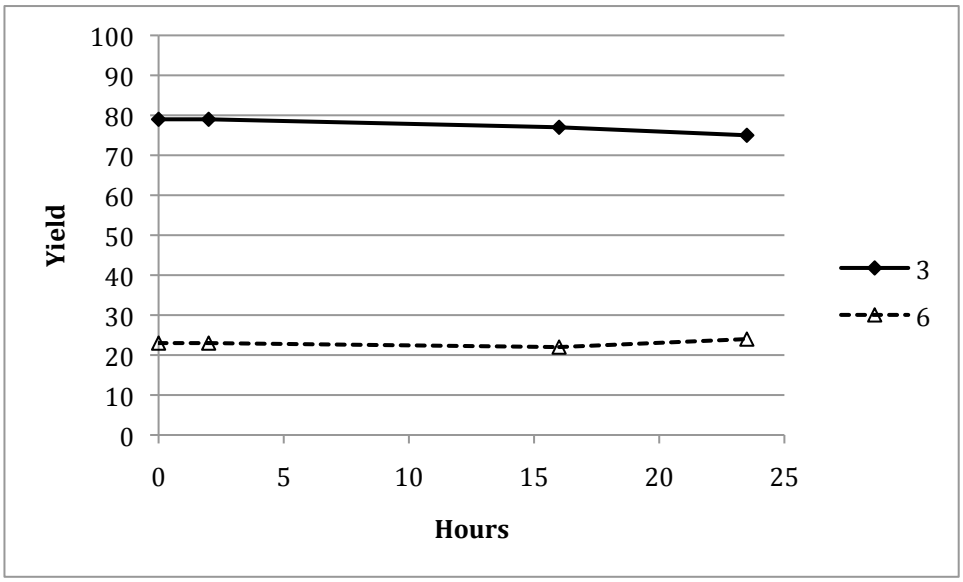


Figure S2-A: Precipitate removal experiment with no added ammonium persulfate

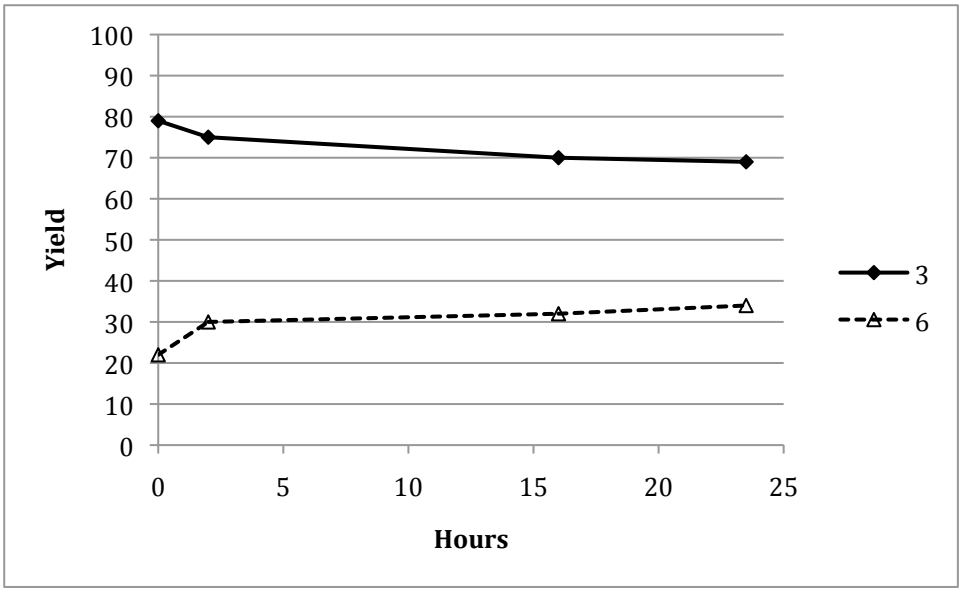


Figure S2-B: Precipitate removal experiment with 2.1 equiv of added ammonium persulfate.

Catalyst filtration experiment

The reaction was set up according to the general procedure (see page S-8) with 4-methoxyphenol (**3**, 1 equiv.), *trans*-anethole (1.3 equiv.), ammonium persulfate (2.1 equiv.), $Ru(bpz)_3(PF_6)_2$ (0.05 equiv) in MeCN (0.1 M). After degassing by three freeze-pump-thaw cycles, the reaction flask was irradiated with a 23 W CFL light source and stirred for 7 h. The reaction medium was then filtered through a medium frit, and the collected orange-brown solid was washed thoroughly with MeCN. The solid was then dried thoroughly on the frit, and care was taken to exclude light wherever possible. The dry solid was then added to a new Schlenk flask containing 4-methoxyphenol (**5**, 1 equiv.), *trans*-anethole (1.3 equiv.), ammonium persulfate (2.1 equiv.), and trimethyl(phenyl)silane in MeCN (0.1 M). The resulting mixture was then degassed by three freeze-pump-thaw cycles. The reaction was then monitored by ^{1}H NMR using reaction aliquots

taken under N_2 purge to maintain an oxygen-free environment. The resulting data (Figure S3) suggest that the solid precipitate contains the active catalyst.

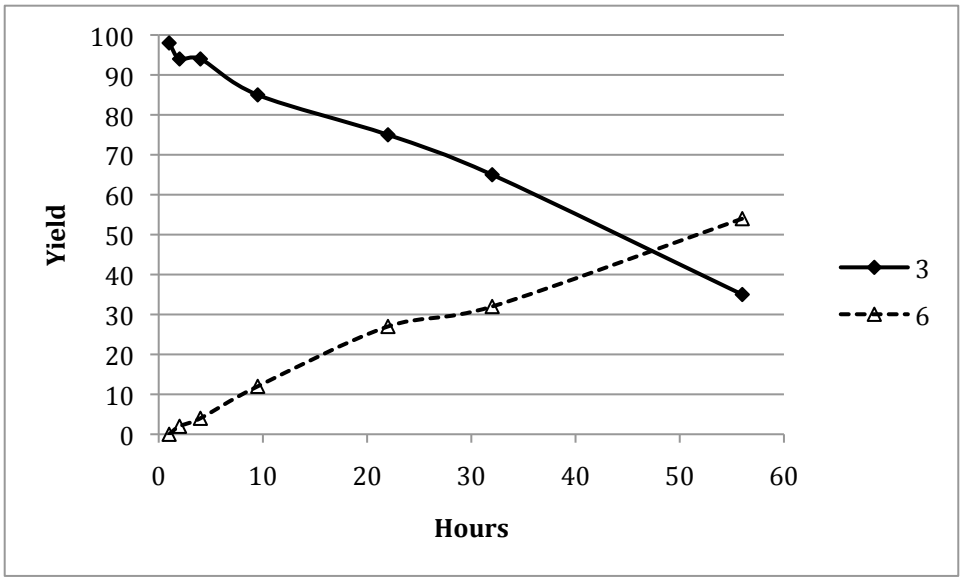


Figure S3: Catalyst filtration timecourse

Synthesis and Reactivity of $Ru(bpz)_3(S_2O_8)$

*Note: All manipulations were undertaken in a manner that would minimize light exposure due to the potential photosensitivity of the $Ru(bpz)_3(S_2O_8)$ salt. The synthesis of this salt was thus performed in a darkened lab, inside a fume hood made opaque with aluminum foil to exclude light scattered from external sources.

$Ru(bpz)_3(PF_6)_2$ (1 equiv.) and $(NBu_4)_2(S_2O_8)$[22] (1 equiv.) were combined in a 15 mL flame-dried vial containing a magnetic stirbar. MeCN (0.1 M) was added to the vial, which was then sealed, and the contents were stirred for 20 h in the dark forming a dark precipitate as observed by red light. The resulting suspension was filtered through a medium frit, and the solid was washed generously with MeCN, then with Et_2O, and finally dried under vacuum. The isolated solid was then used as a catalyst without further purification. The photochemical reaction was set up according to the general procedure (see page S-8) in a dark lab with 4-methoxyphenol (**3**, 1 equiv.), *trans*-anethole (1.3 equiv.), ammonium persulfate (2.1 equiv.), $Ru(bpz)_3(S_2O_8)$ (0.05 equiv), ammonium hexafluorophosphate (0.5 equiv) and trimethyl(phenyl)silane as an internal standard in MeCN (0.1 M). After degassing by three freeze-pump-thaw cycles, the reaction flask were irradiated with a 23 W CFL light source, and reaction progress was monitored by ^1H NMR using reaction aliquots taken under N_2 purge to maintain an oxygen-free environment. The resulting data can be seen in figures S4.

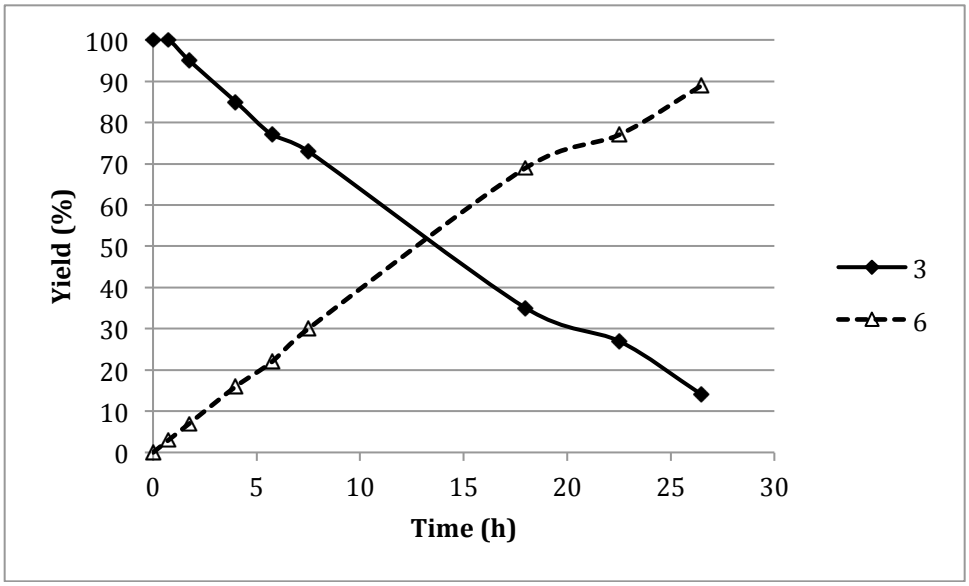


Figure S4: Reactivity profile for $Ru(bpz)_3(S_2O_8)$ with added ammonium persulfate

VI. References

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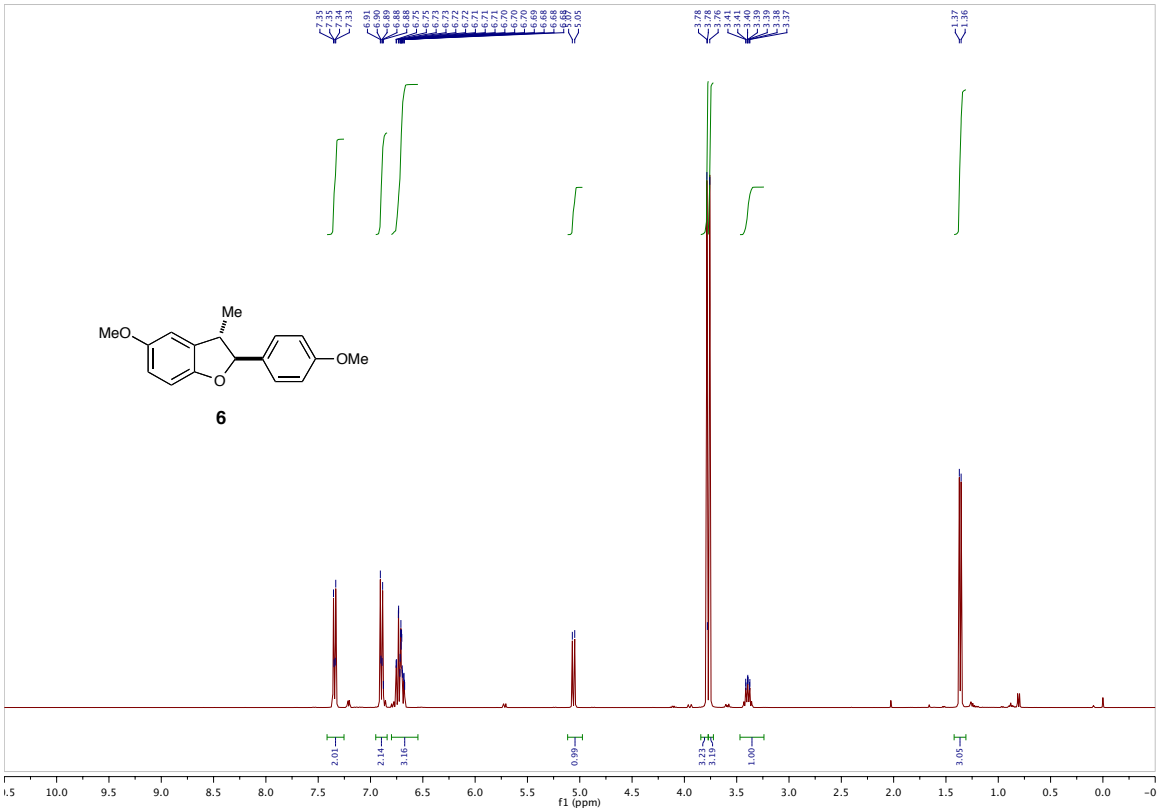
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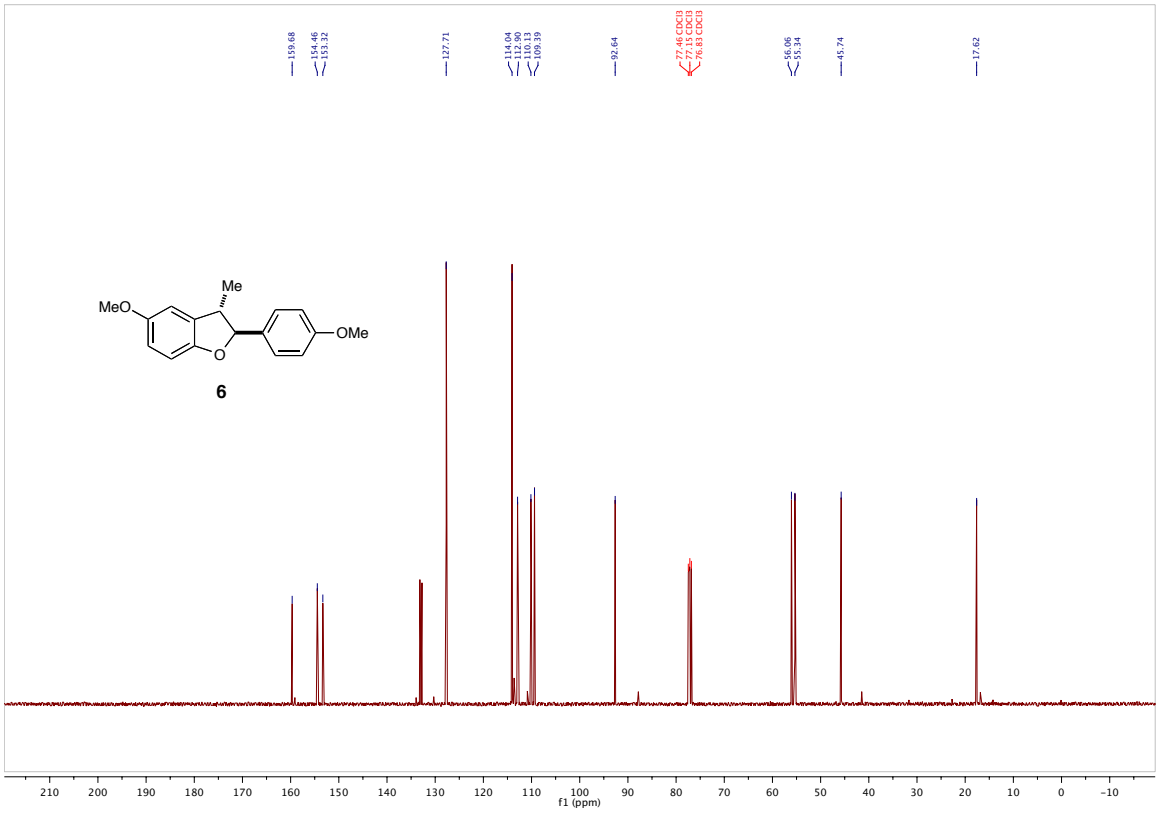
f1 (ppm)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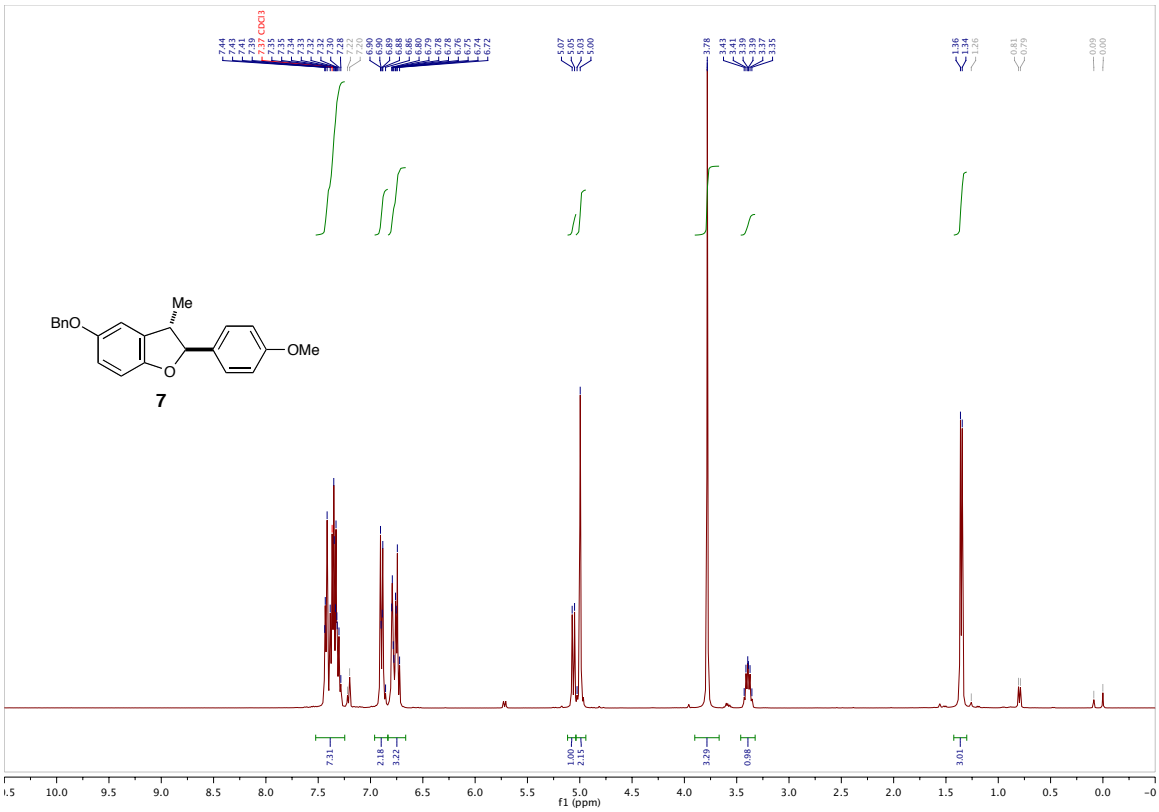
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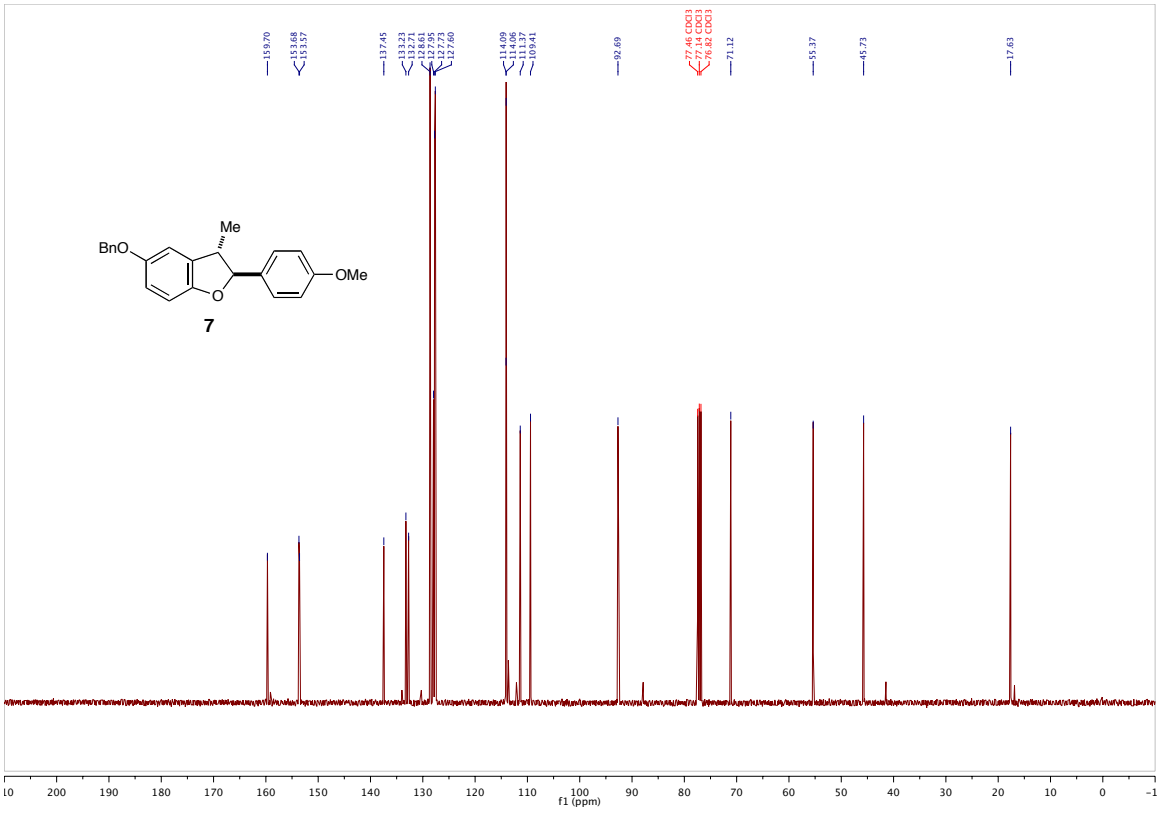
f1 (ppm)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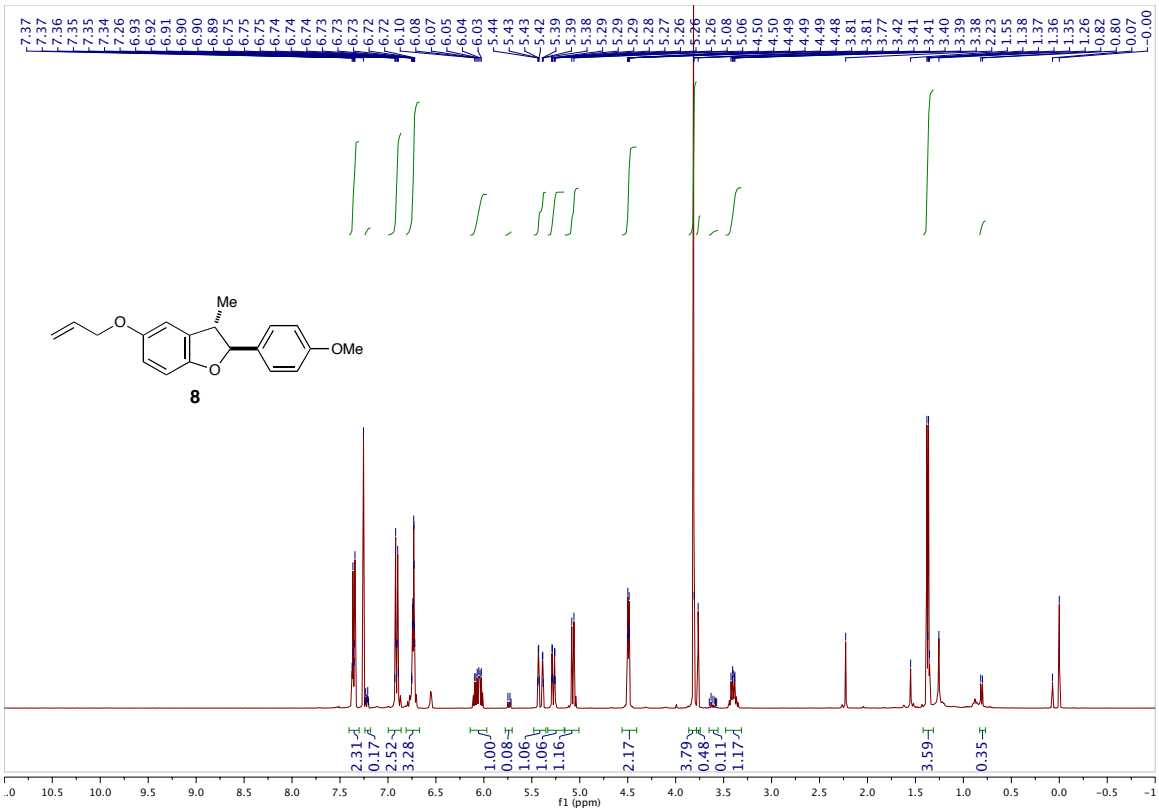
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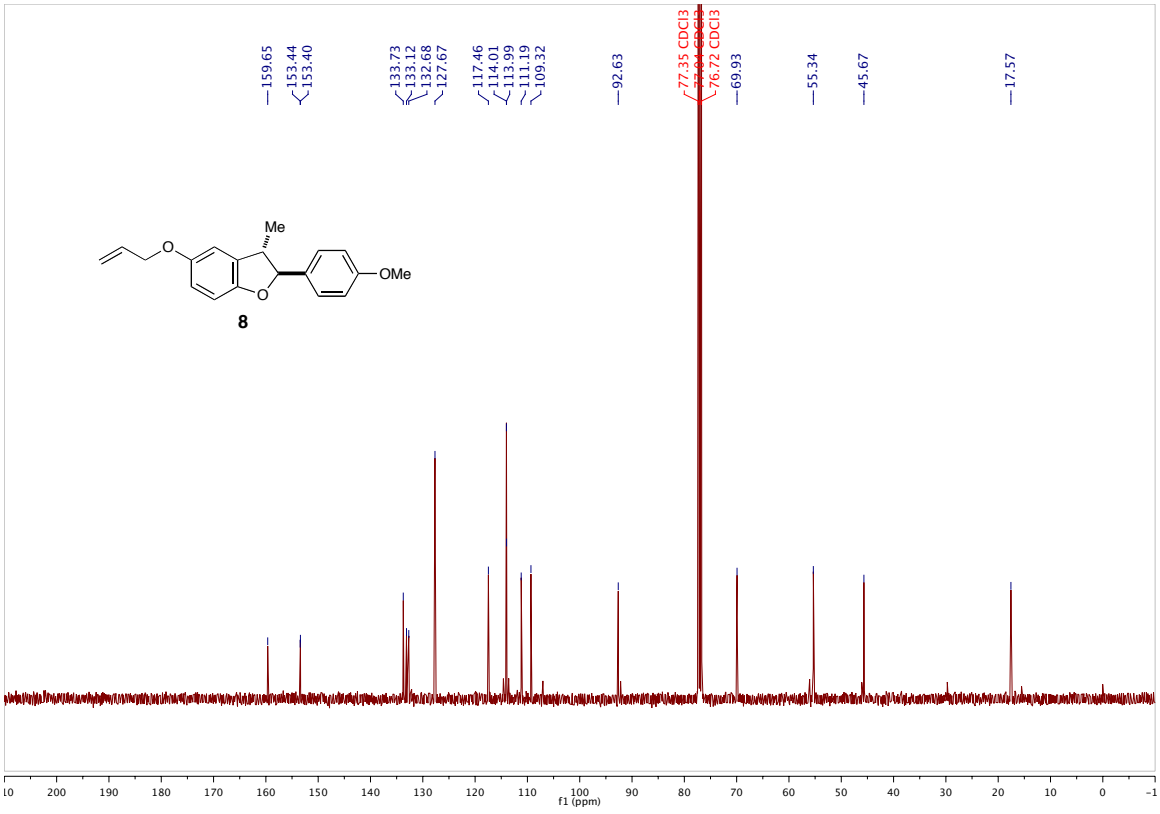
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92.63
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O
OMe
O
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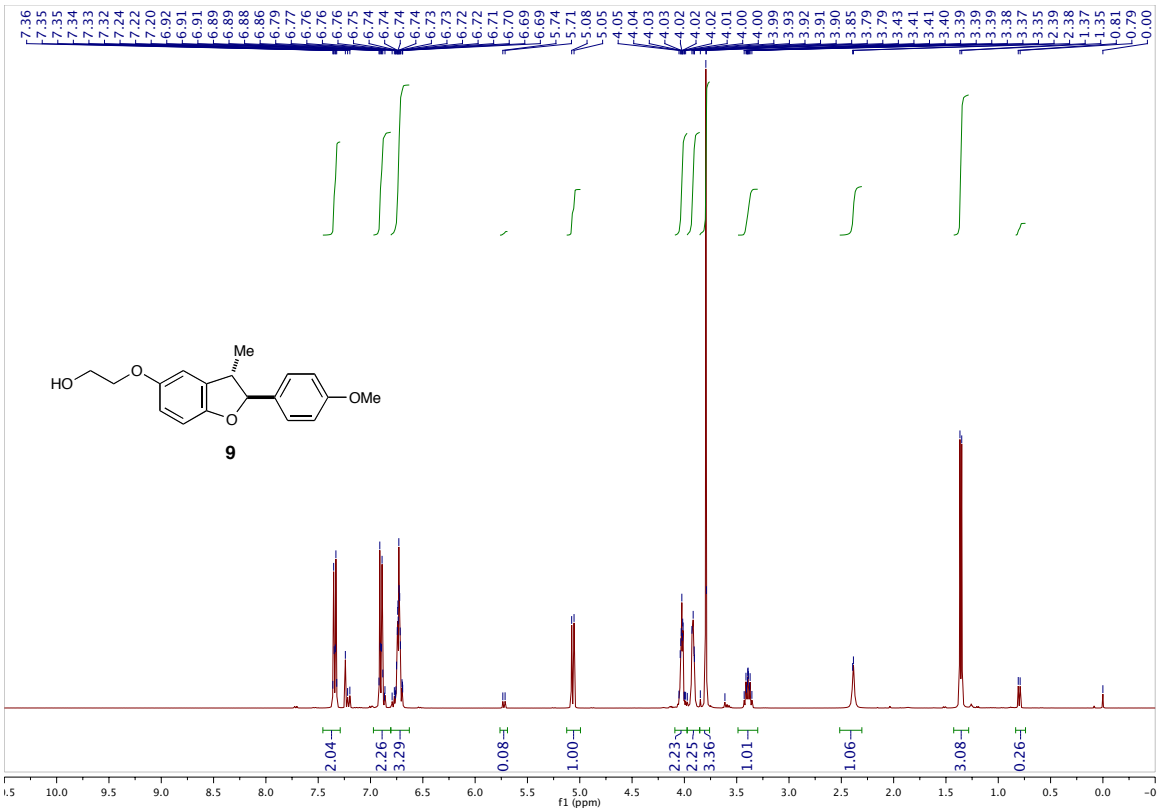
f1 (ppm)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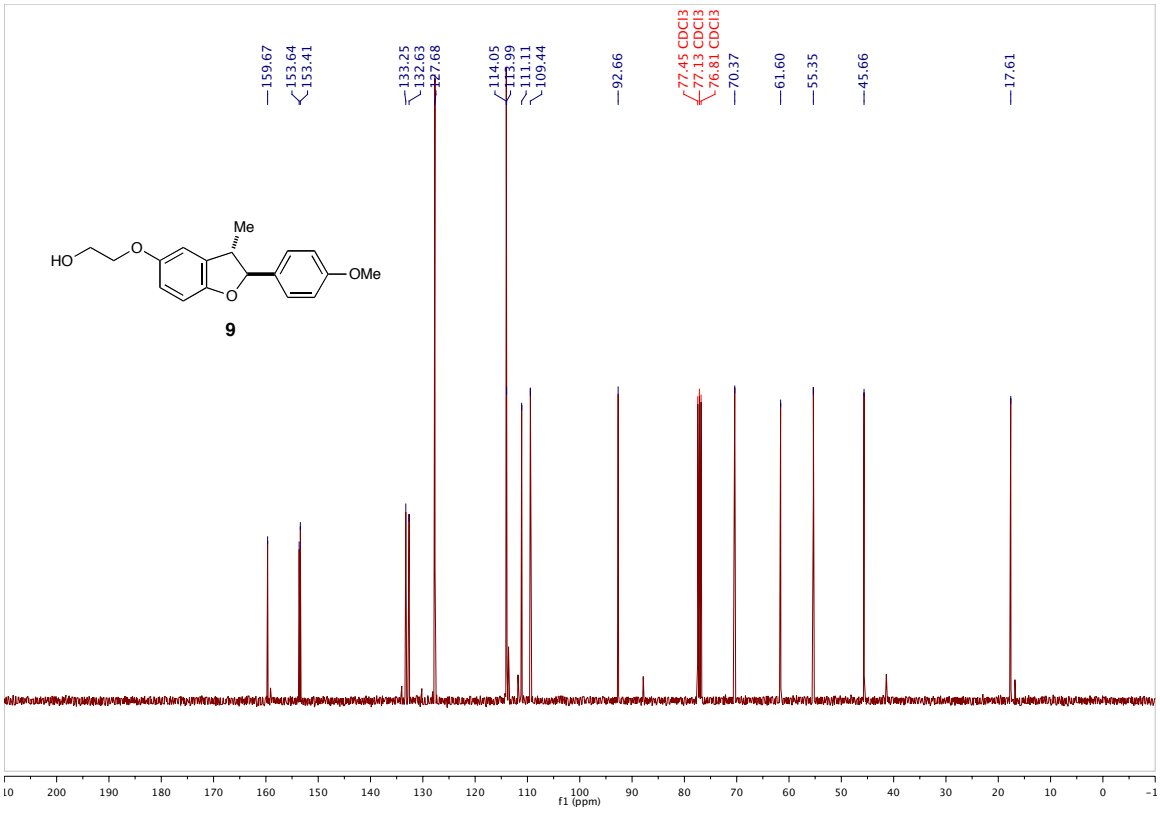
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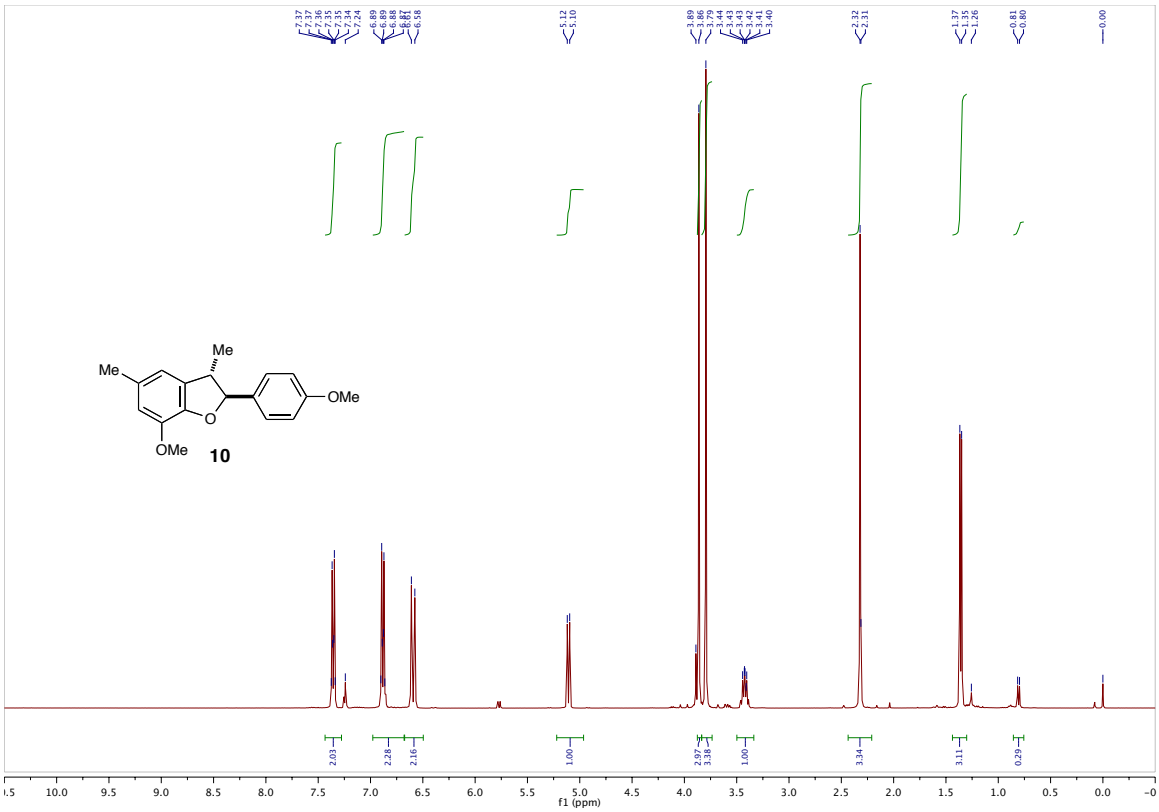
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OMe
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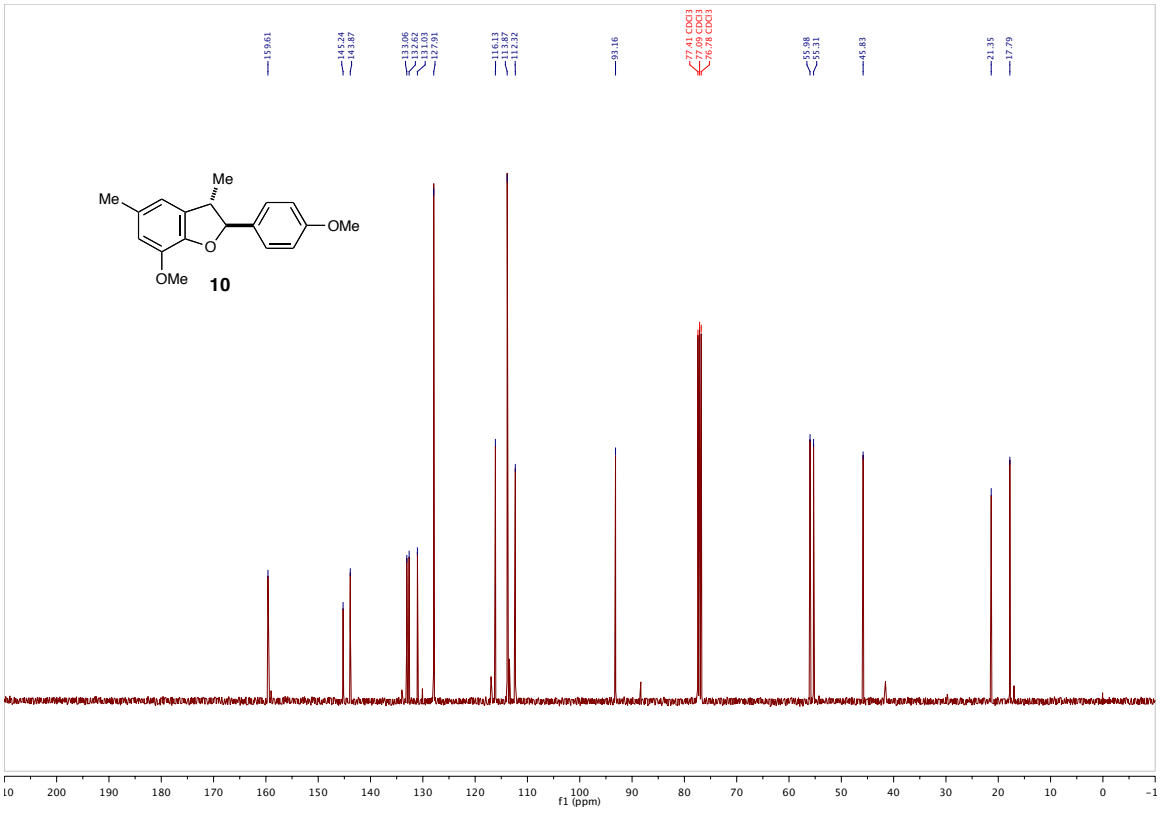
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OMe
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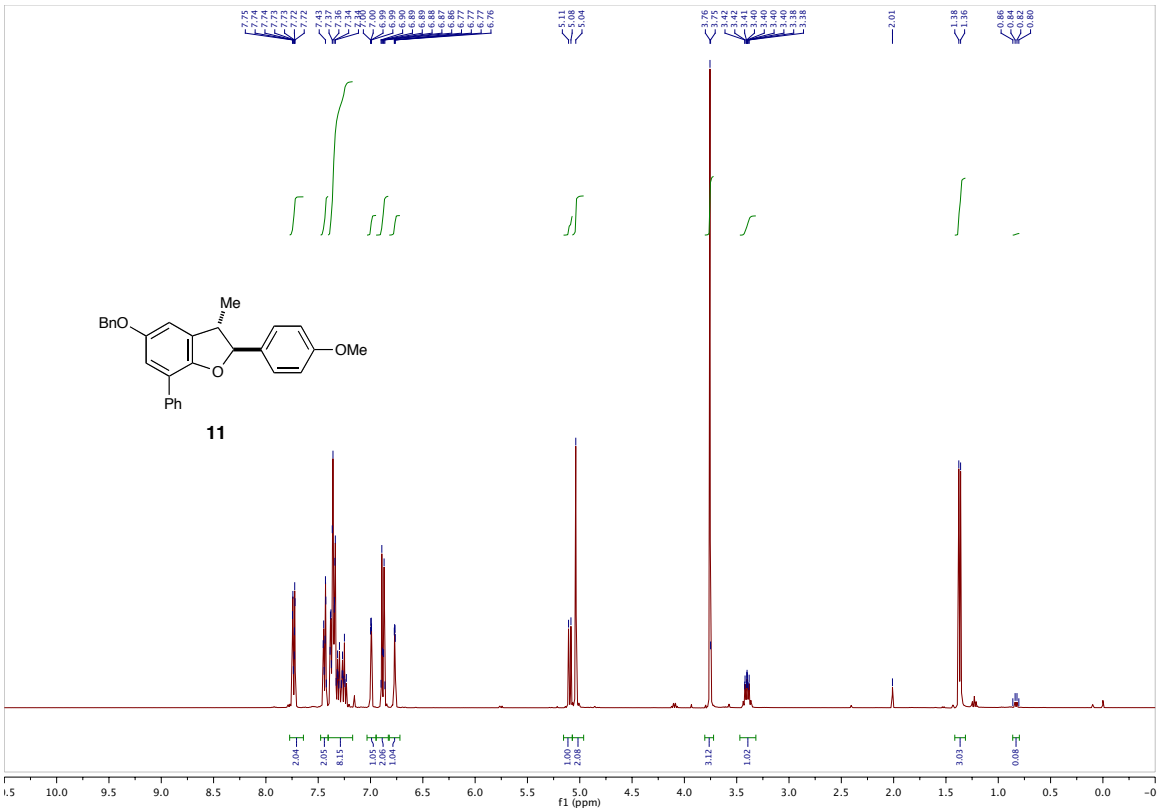
f1 (ppm)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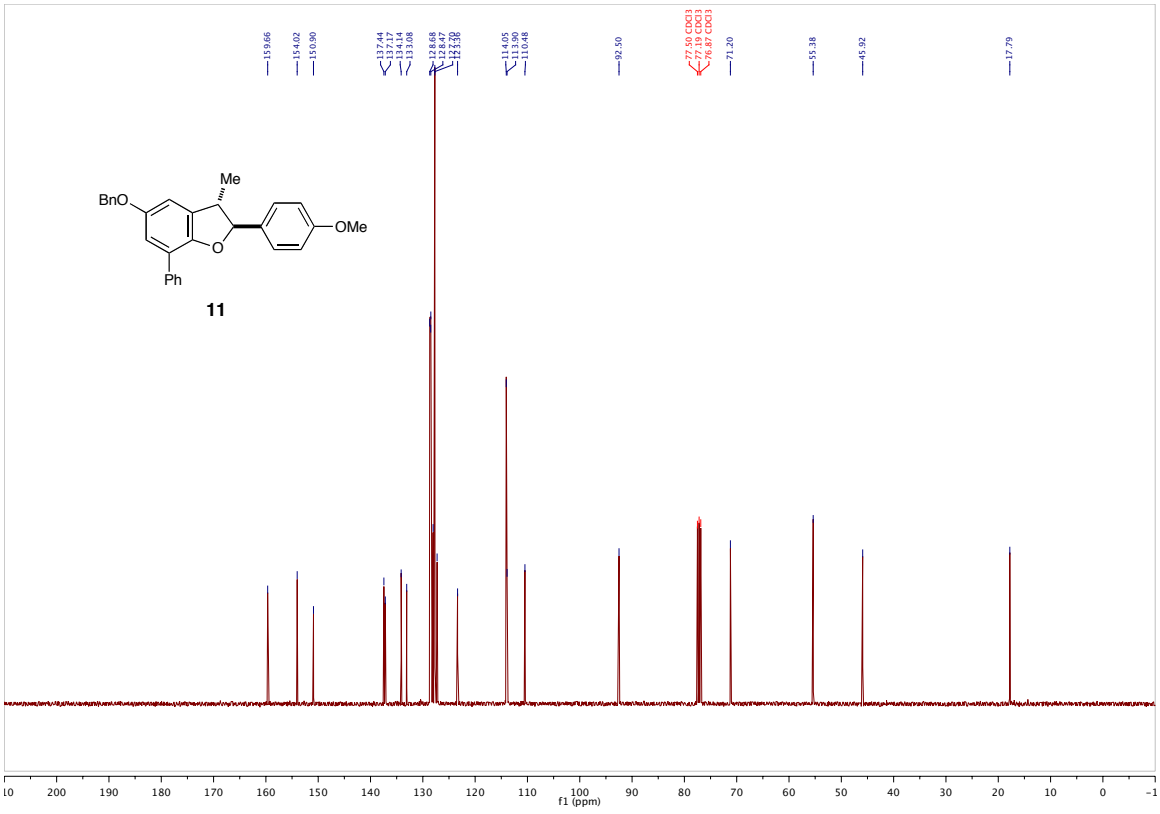
Me
OMe
O
Ph
11
f1 (ppm)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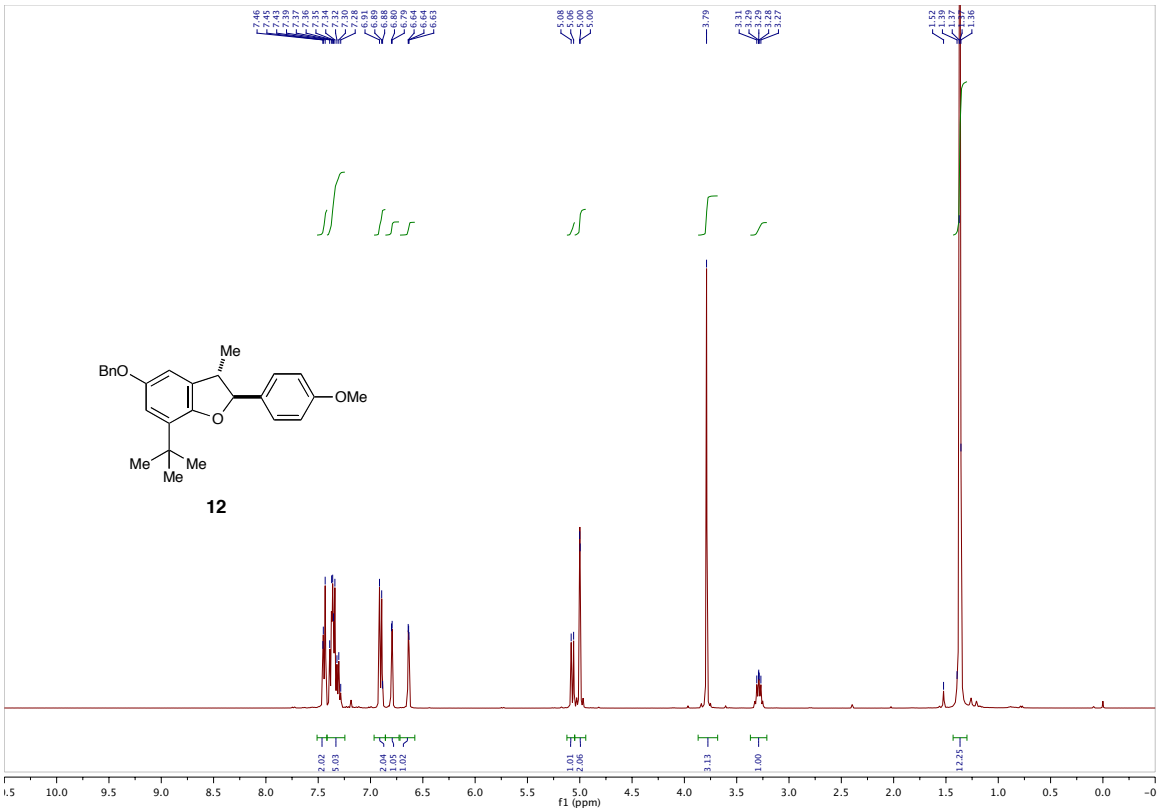
f1 (ppm)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OMe
O
Me
Me
Me
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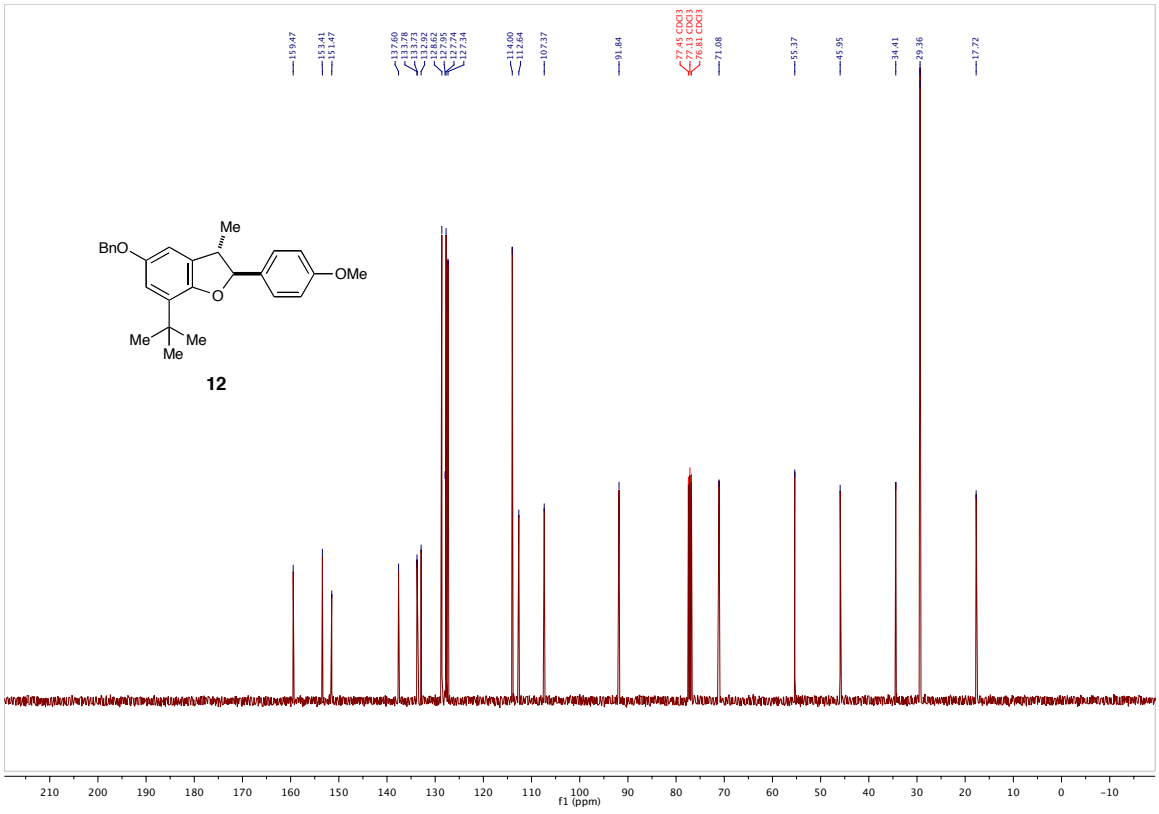
f1 (ppm)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OMe
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Me
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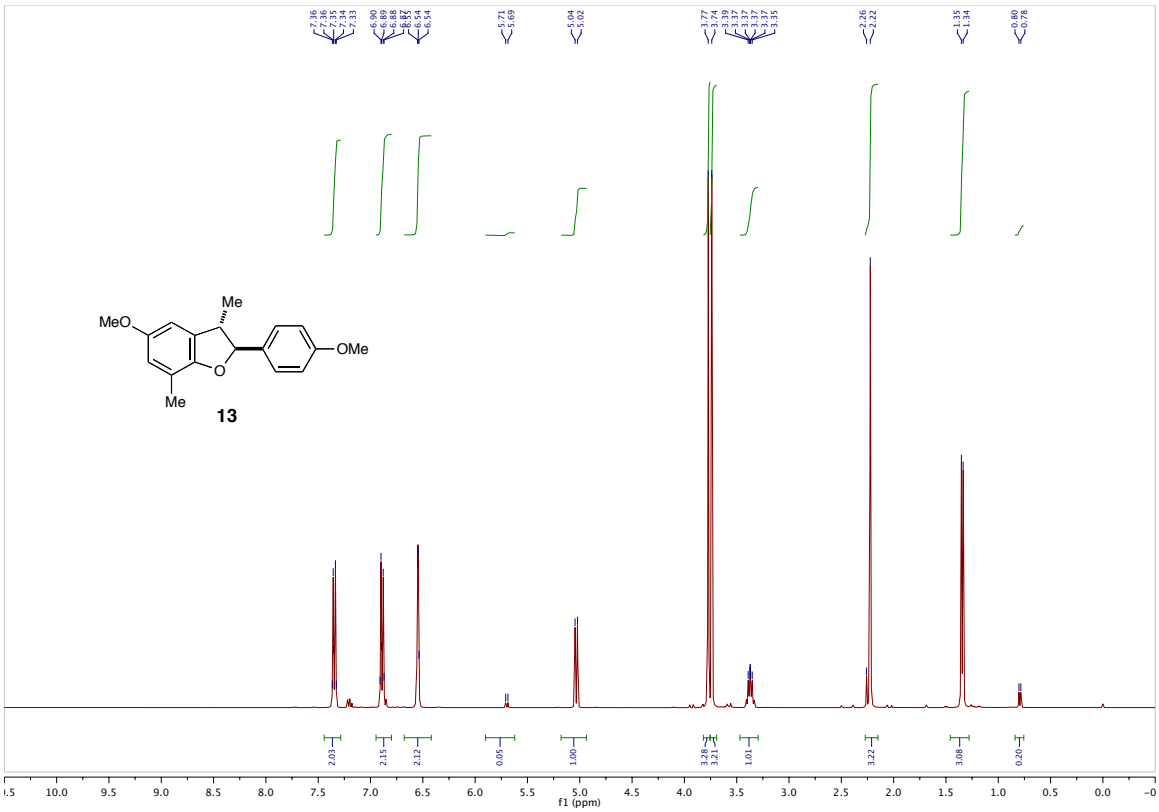
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OMe
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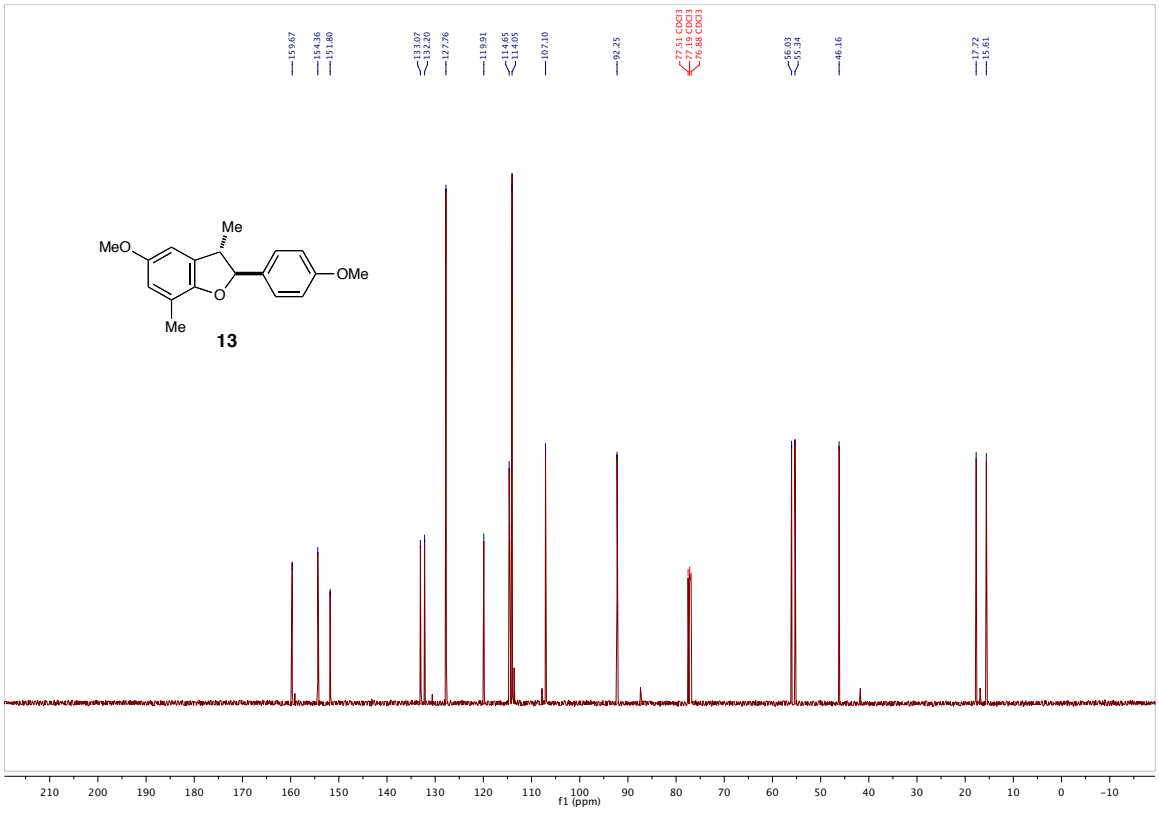
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Me
OMe
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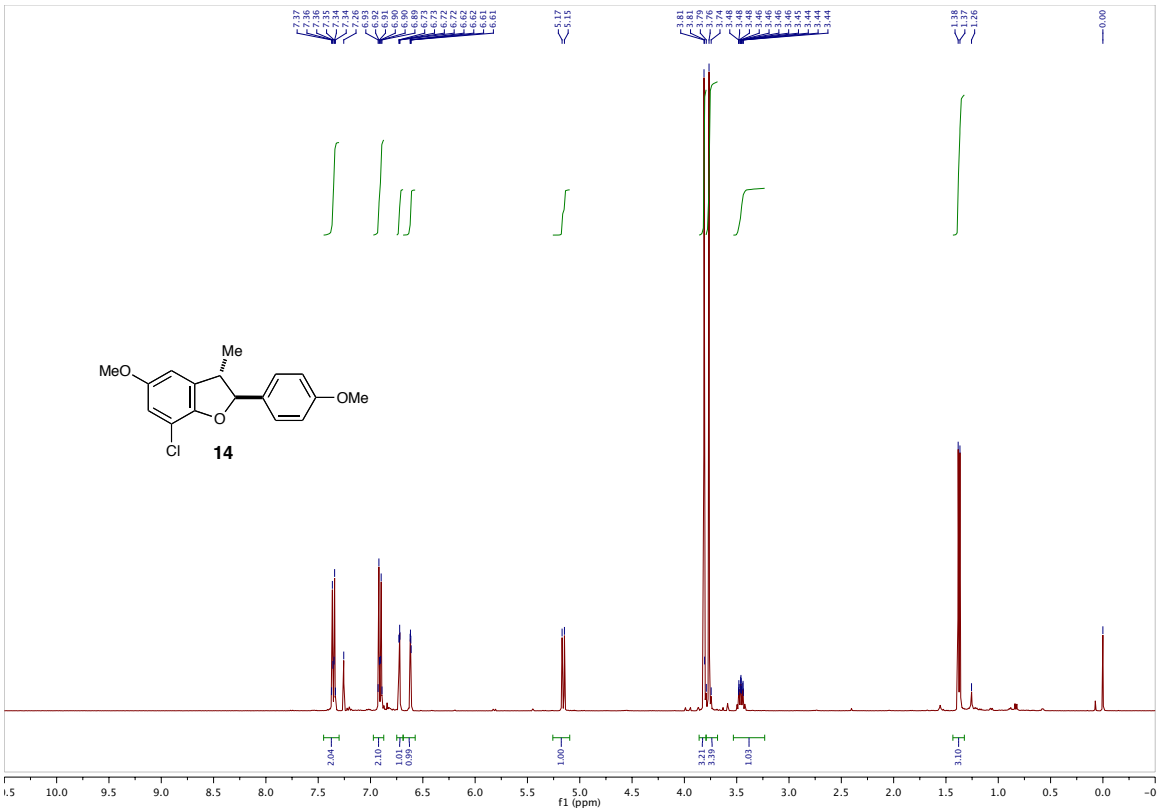
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OMe
O
Cl
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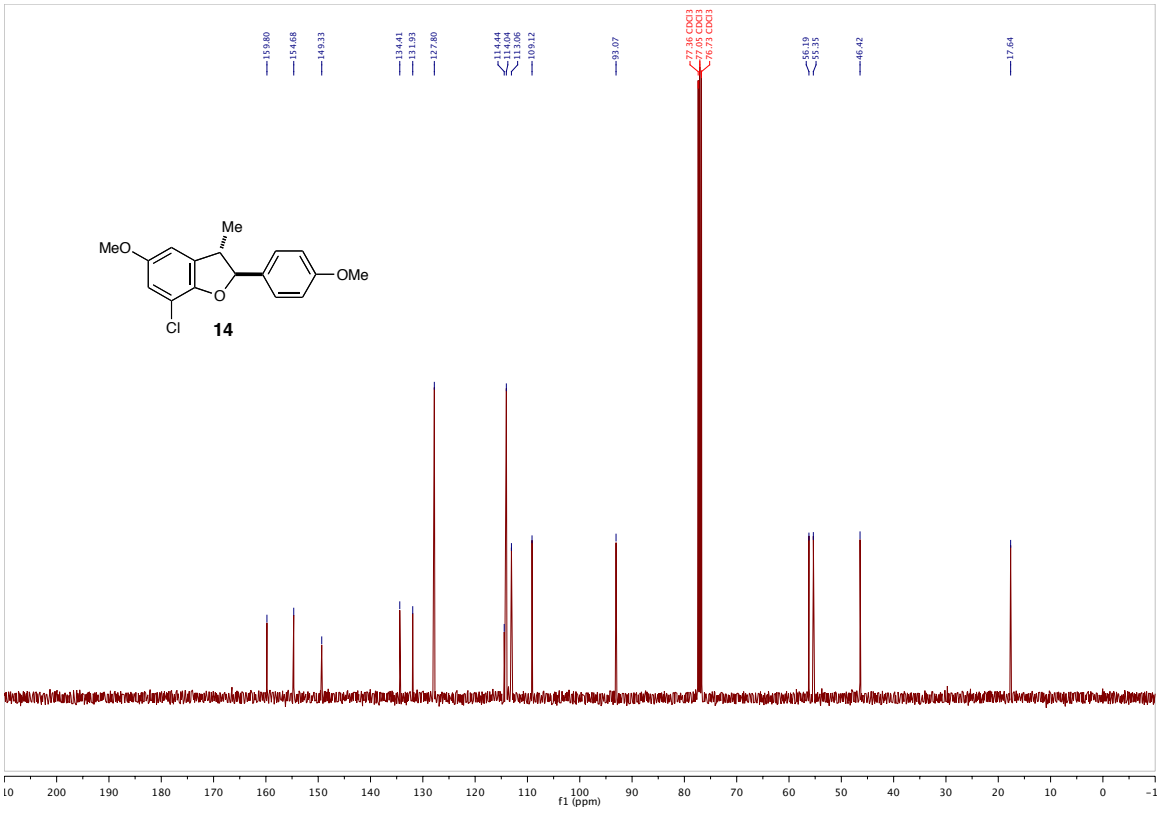
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OMe
O
Cl
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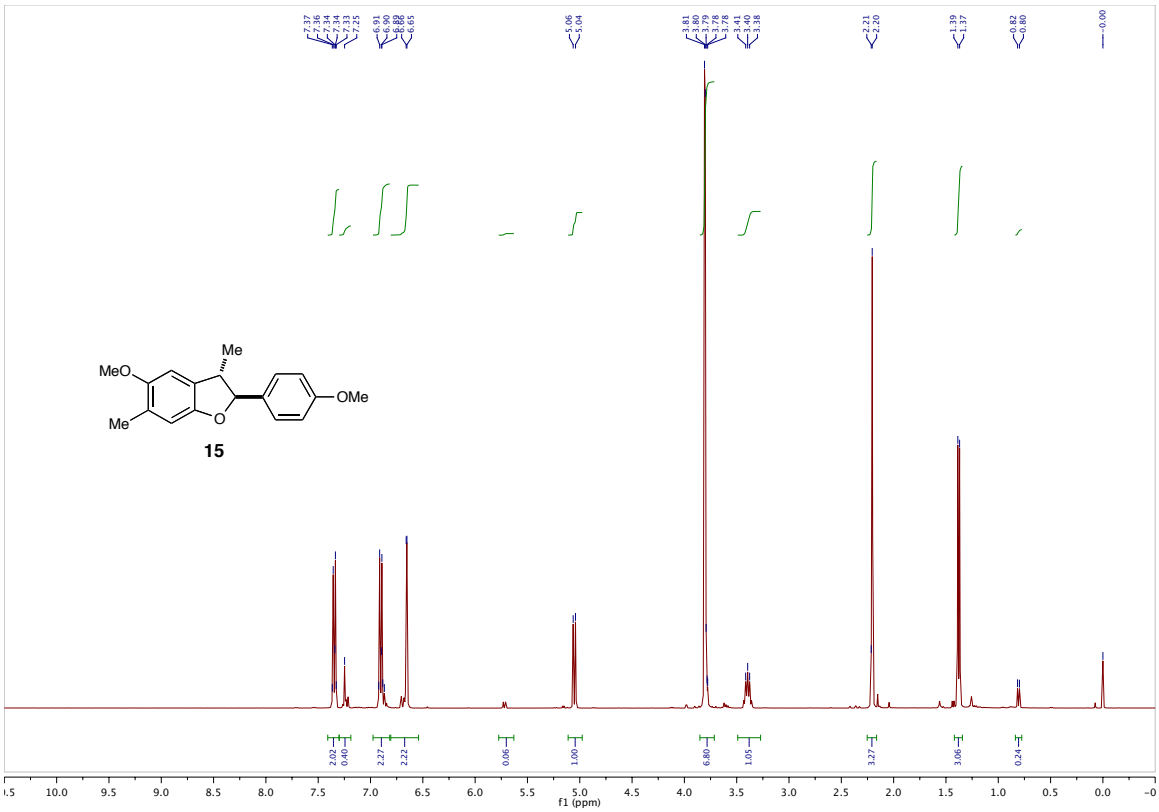
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OMe
Me
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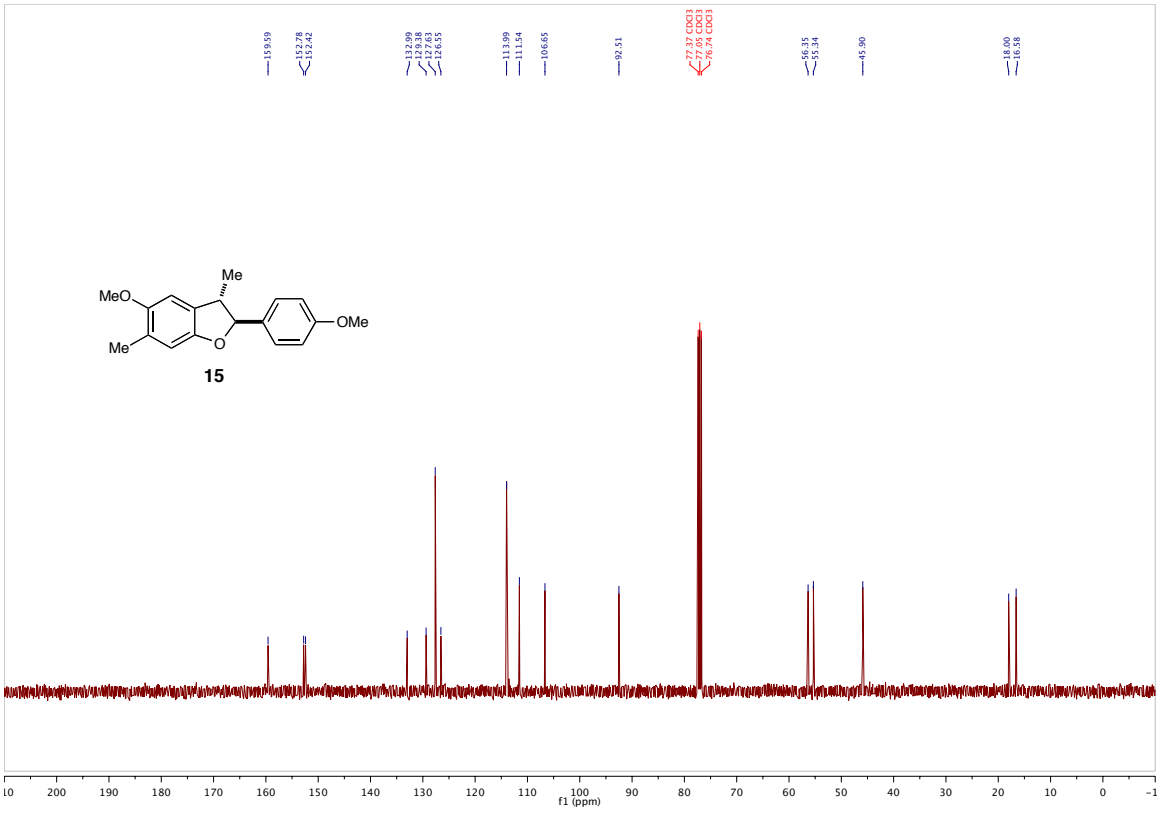
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OMe
Me
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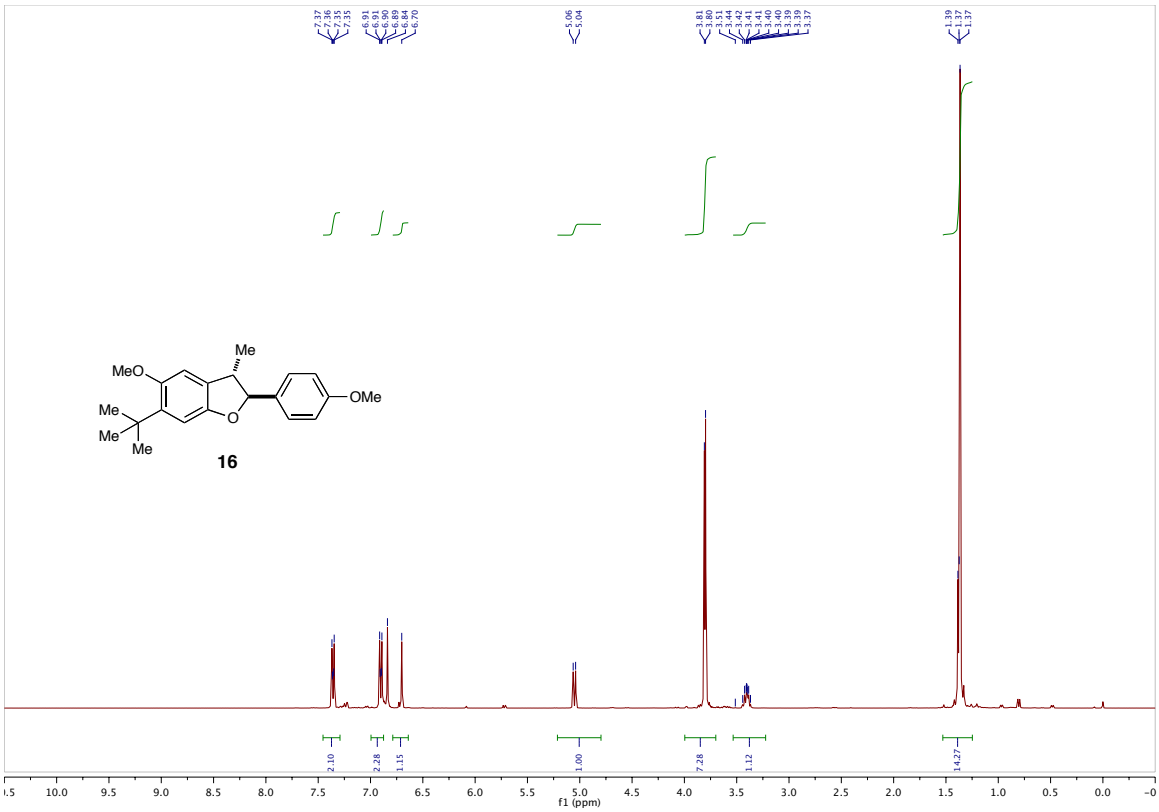
f1 (ppm)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Me
Me
OMe
O
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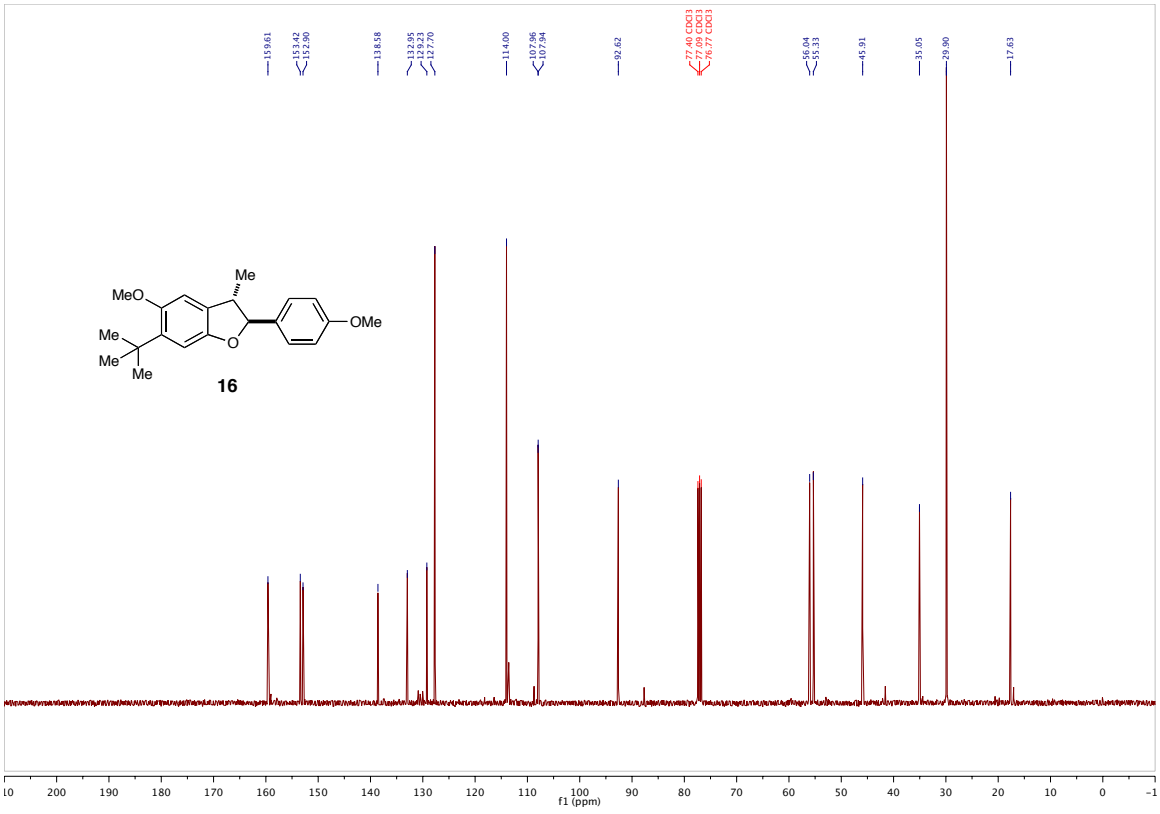
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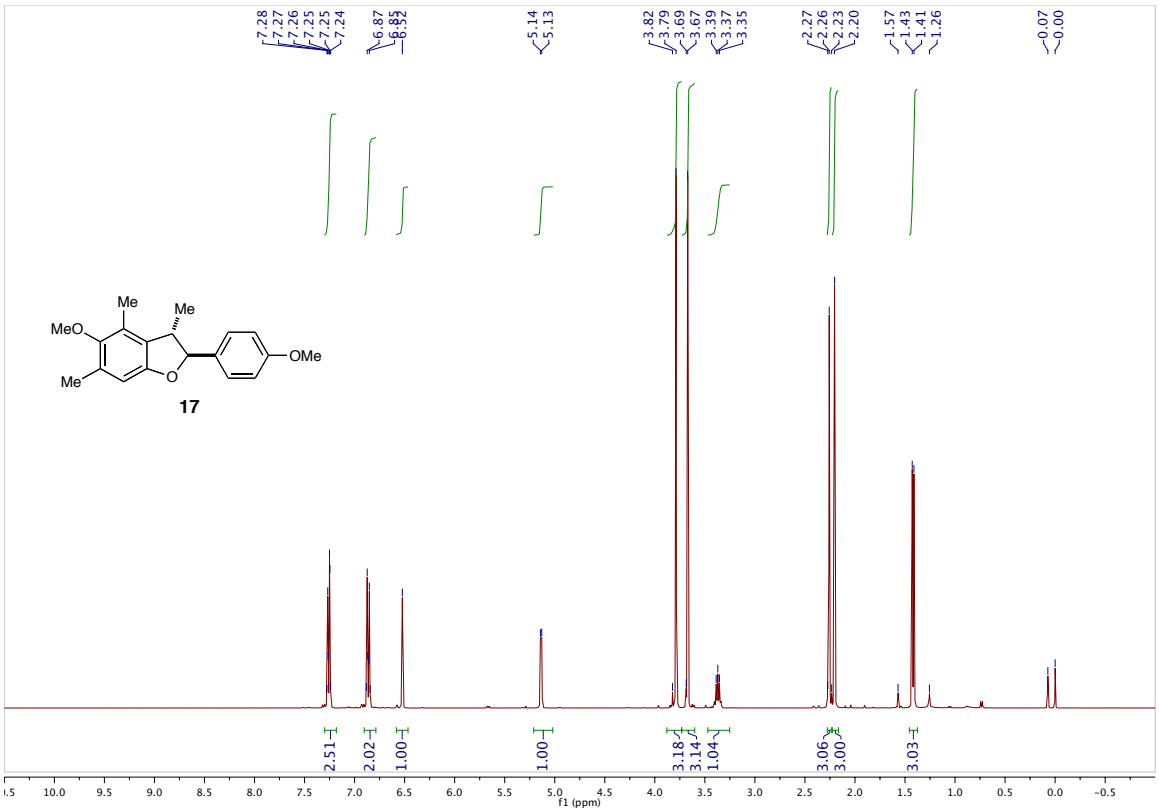
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OMe
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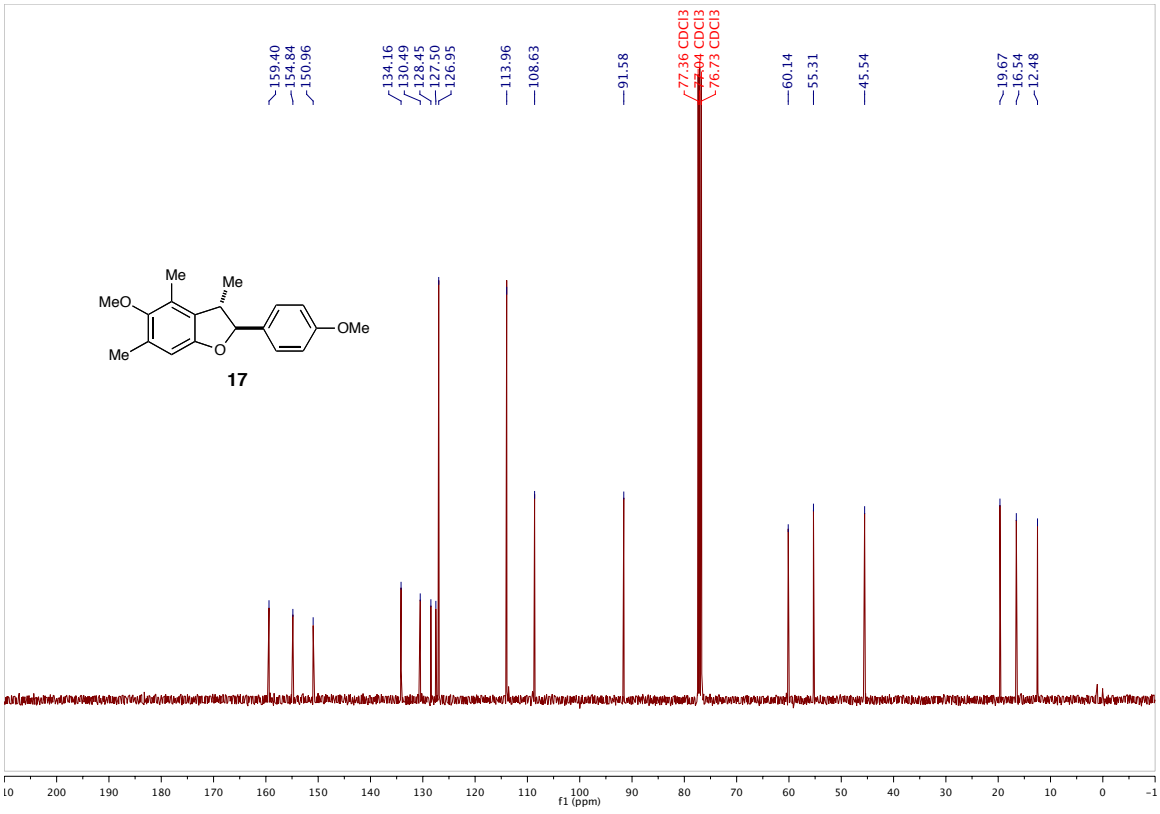
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76.73 CDCl3
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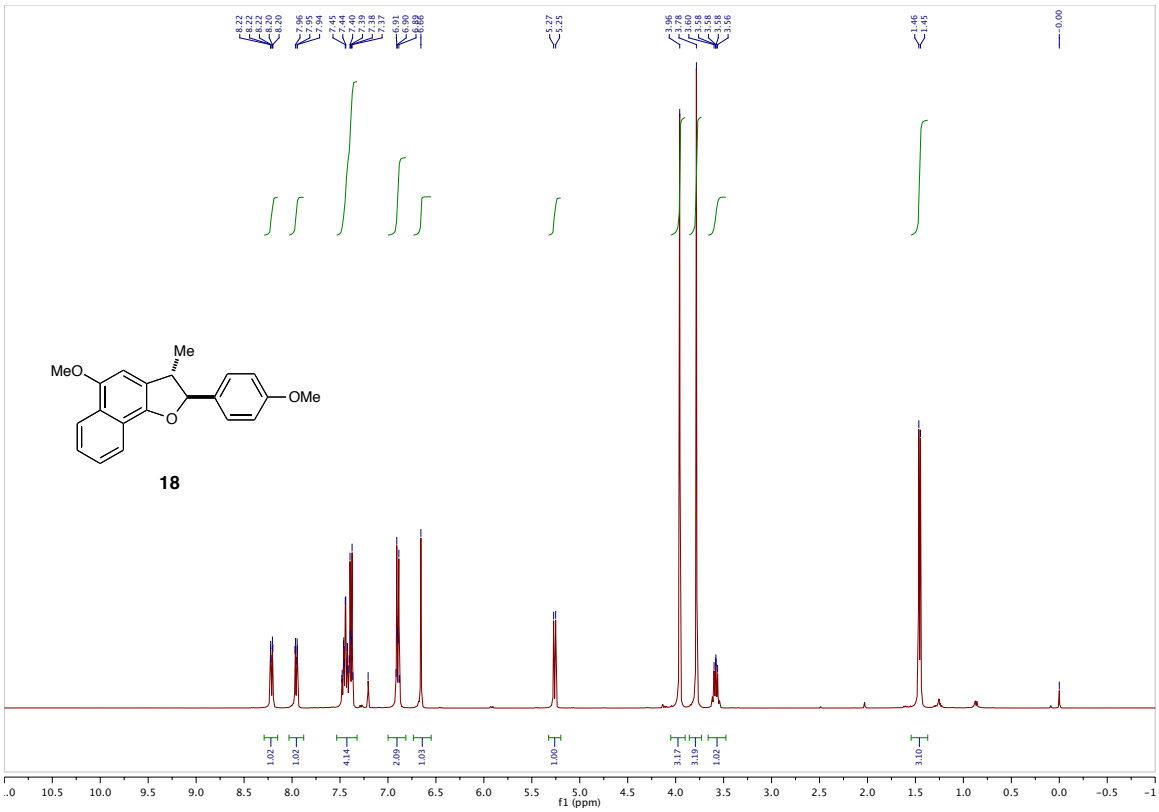
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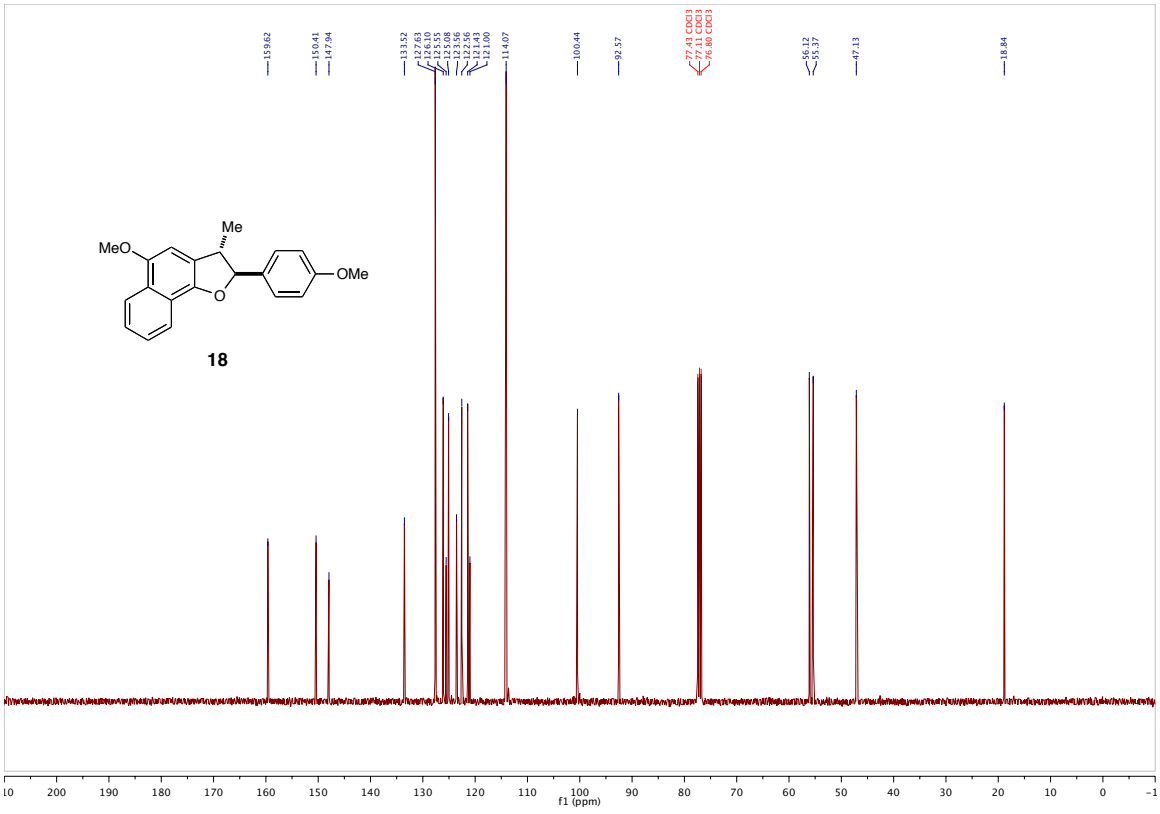
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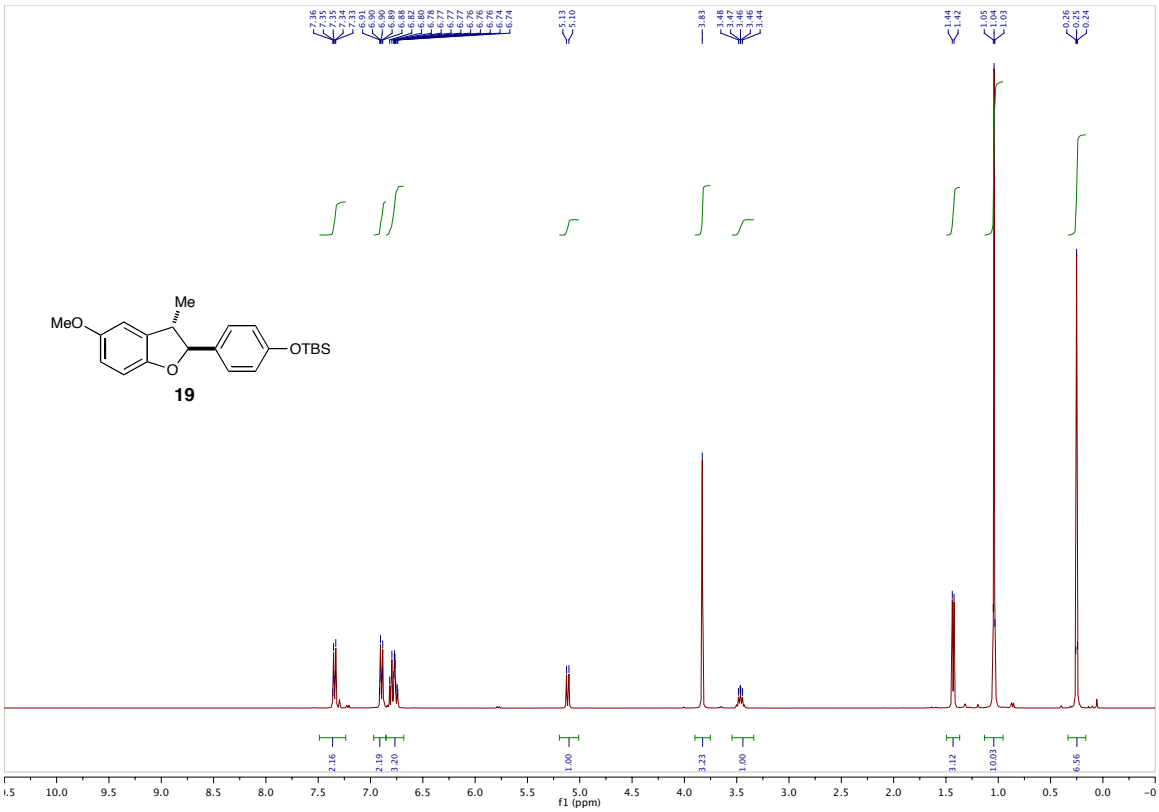
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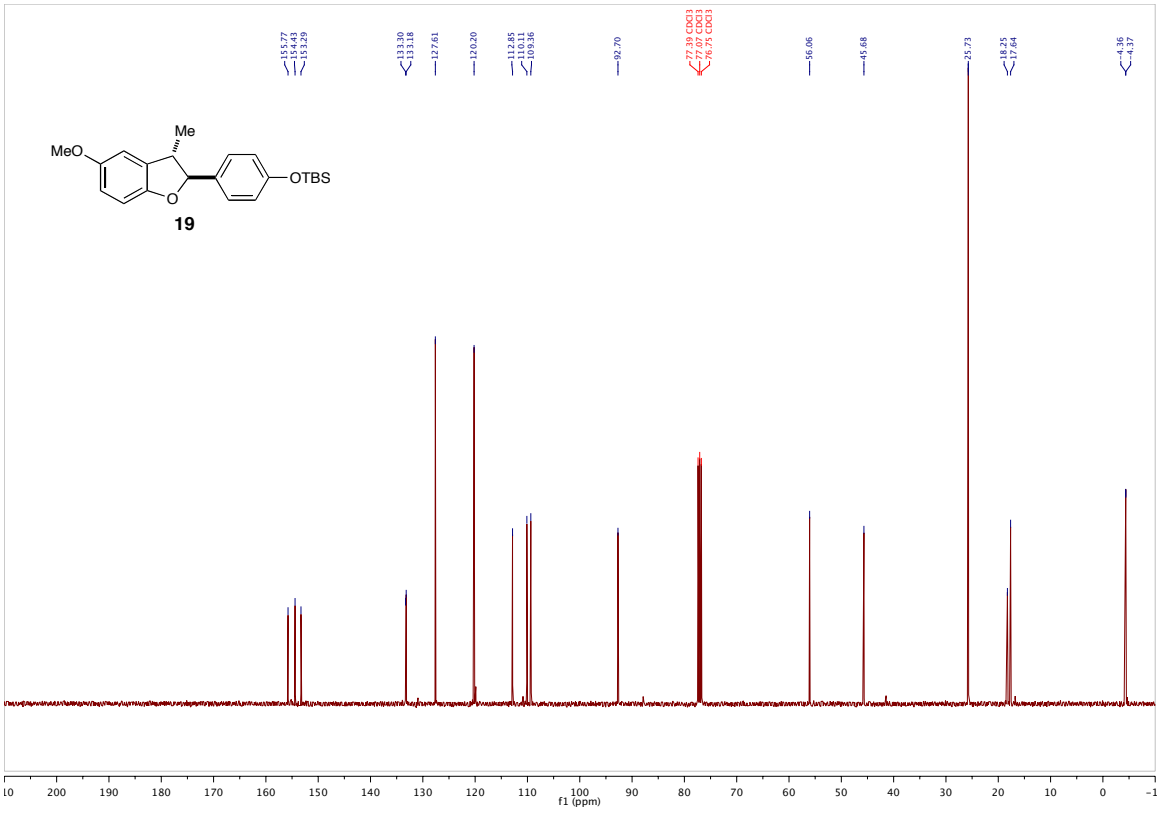
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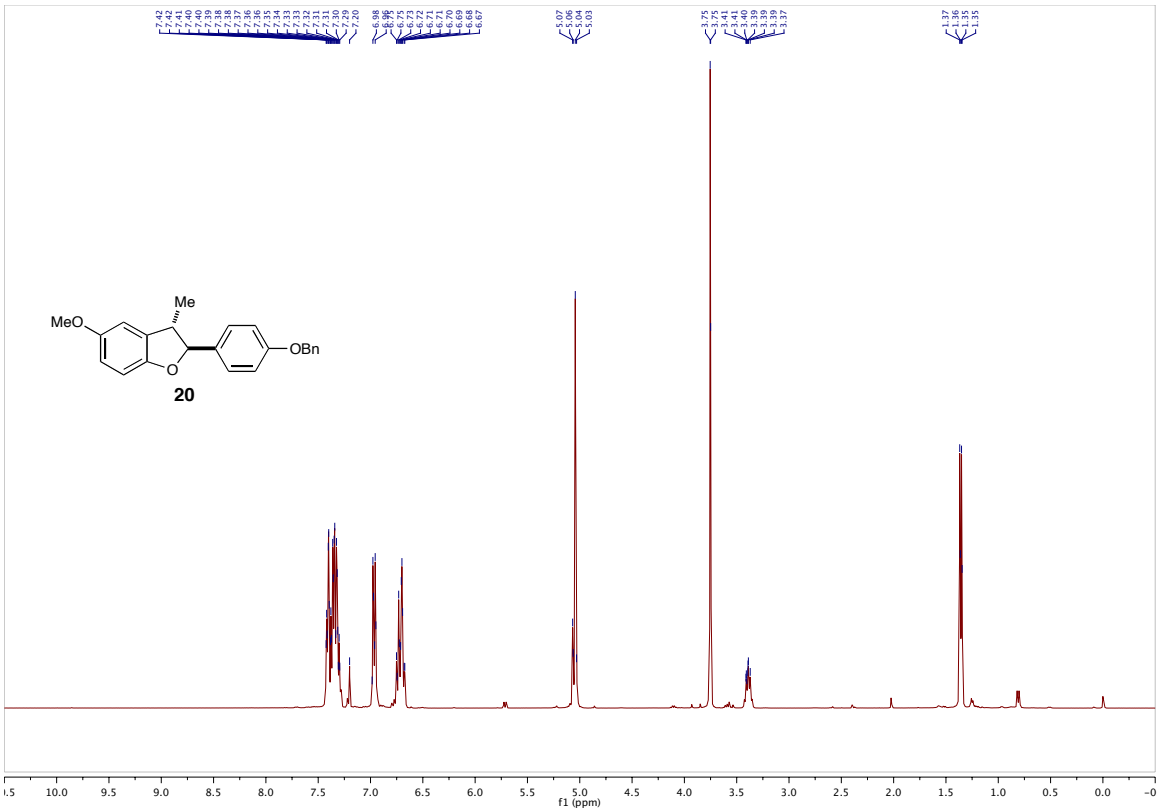
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OBn
O
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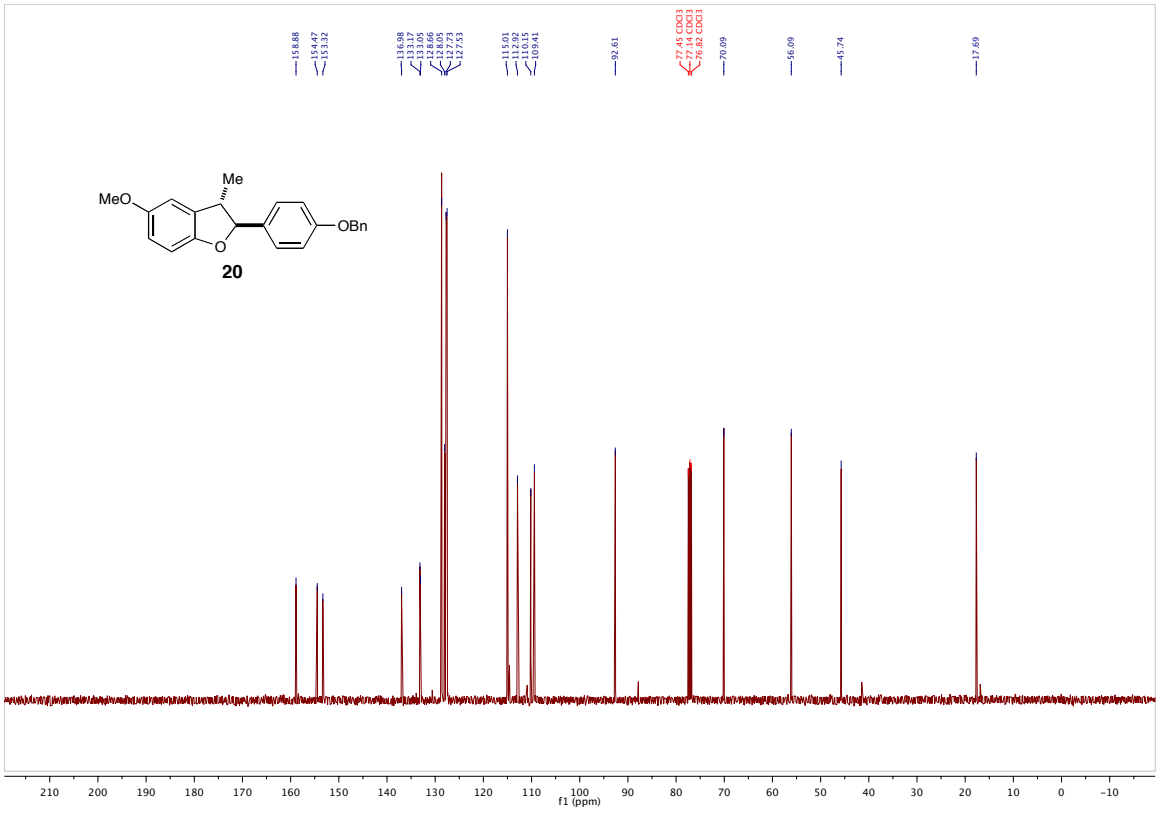
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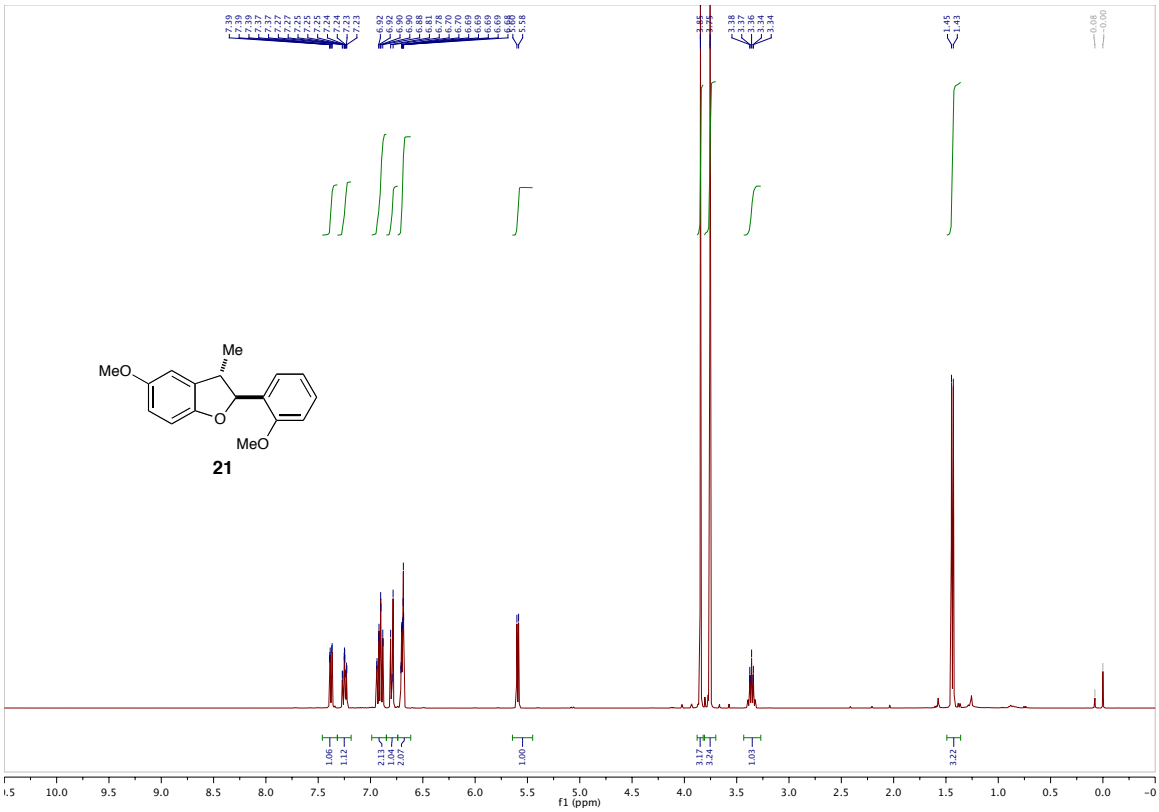
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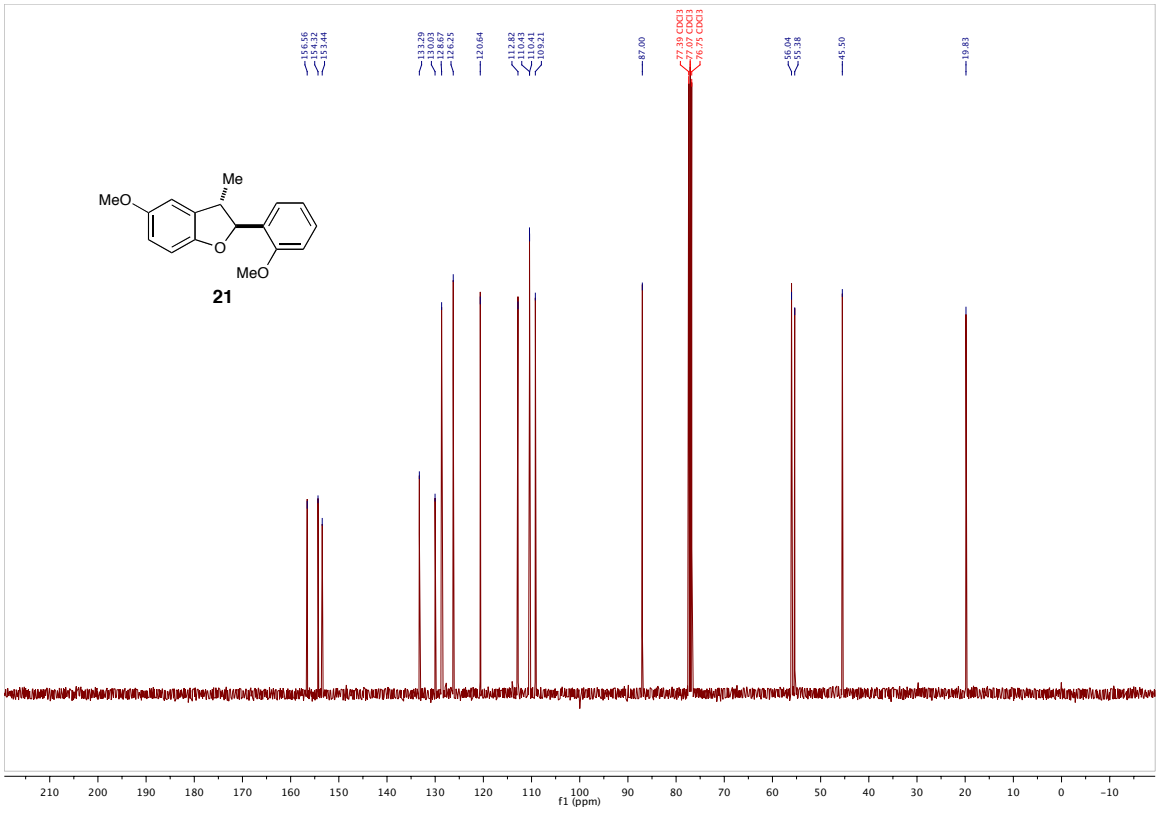
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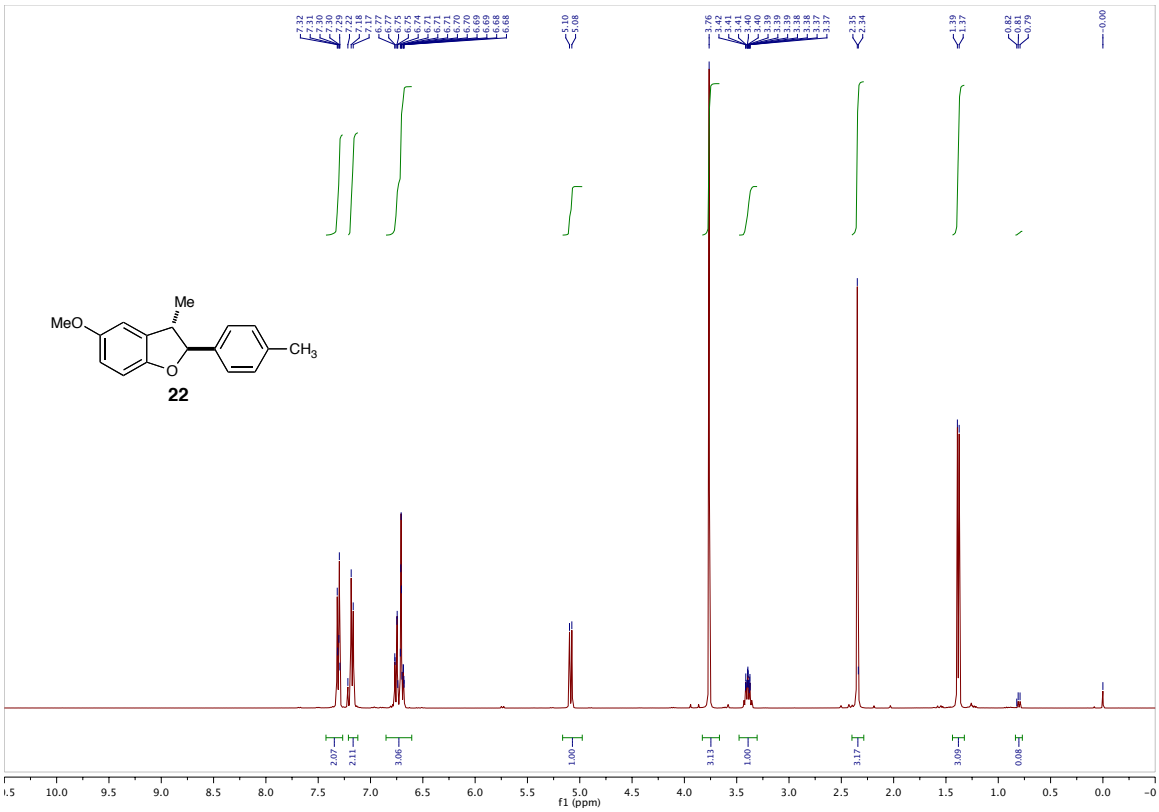
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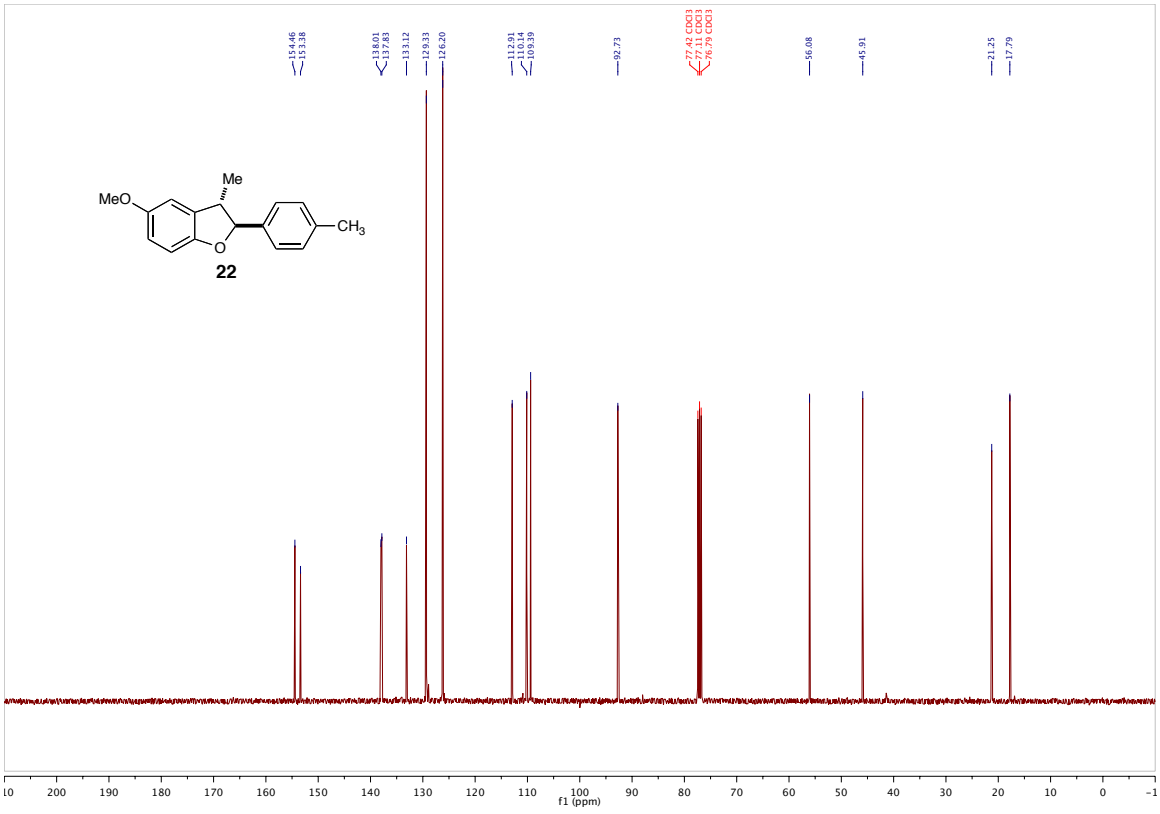
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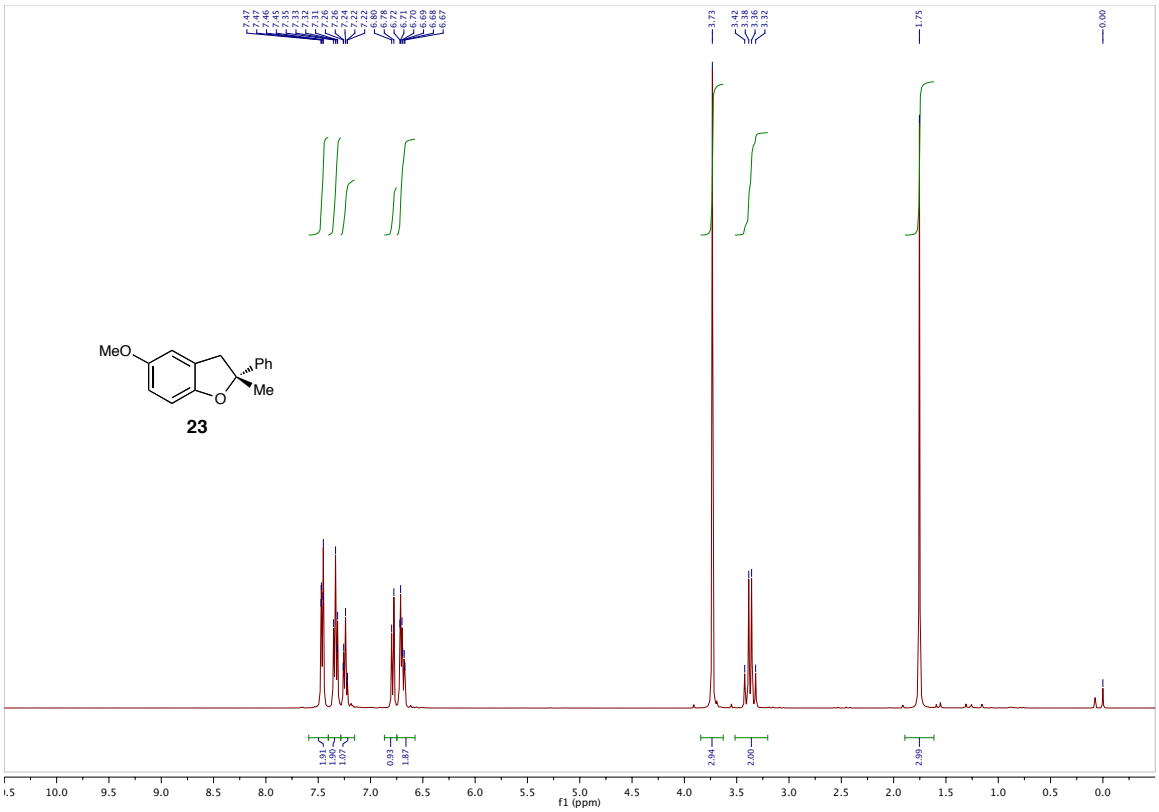
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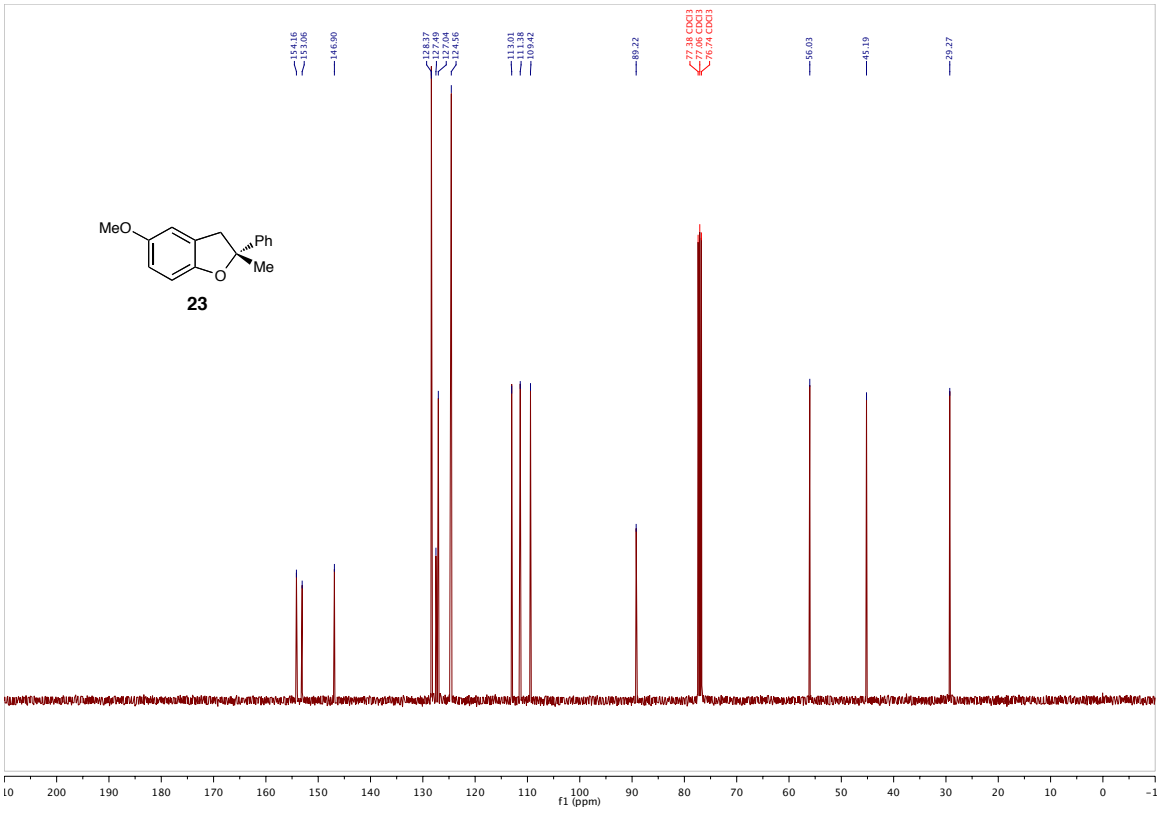
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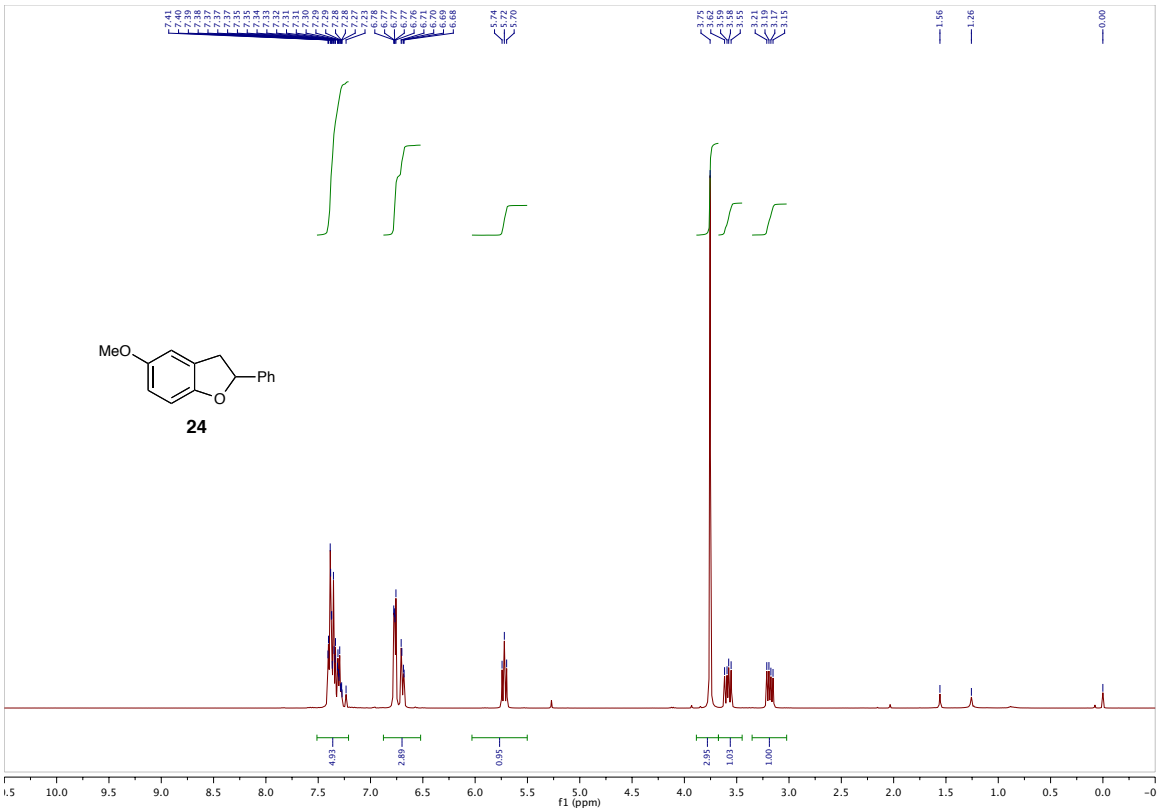
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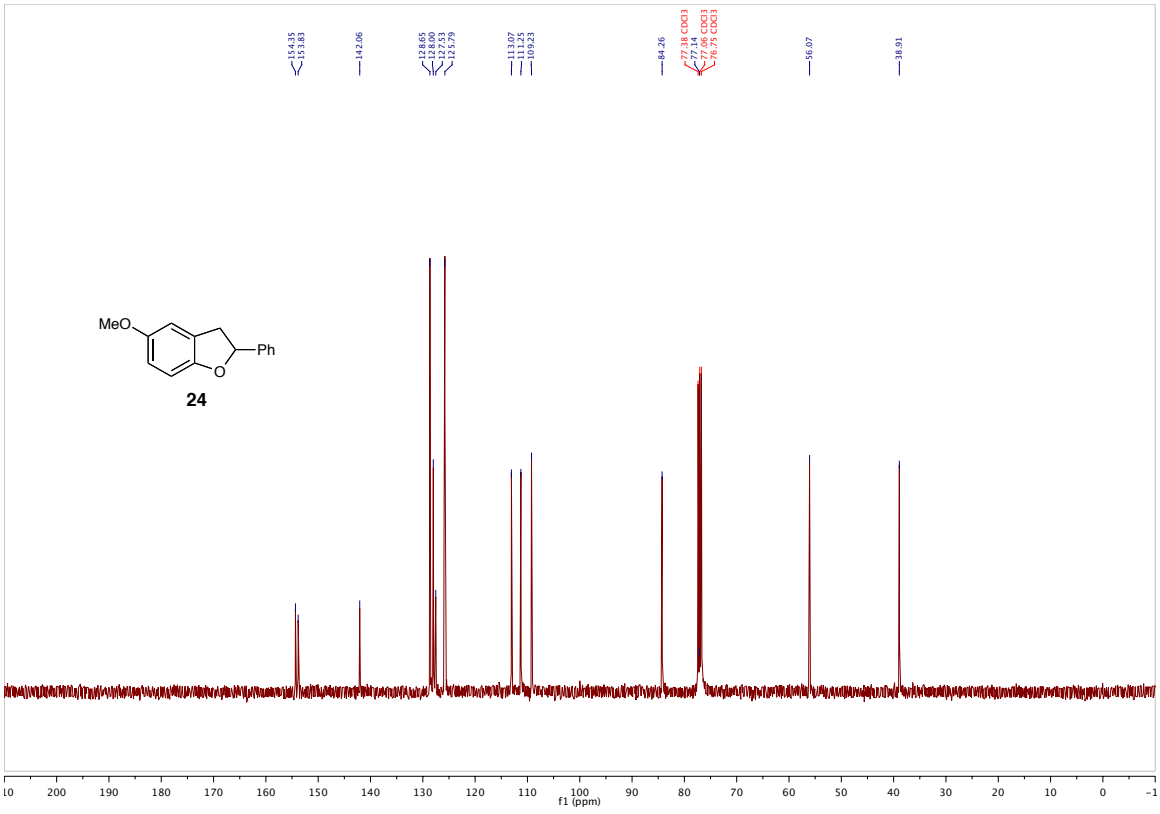
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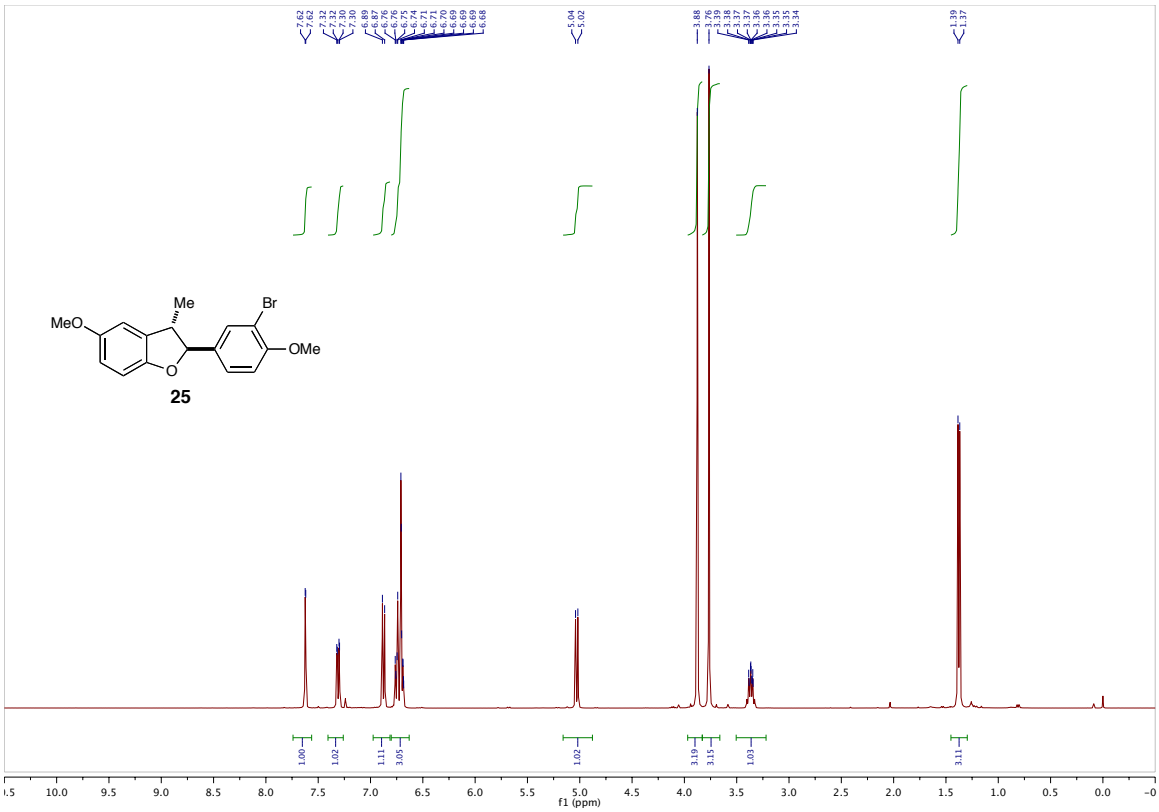
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OMe
O
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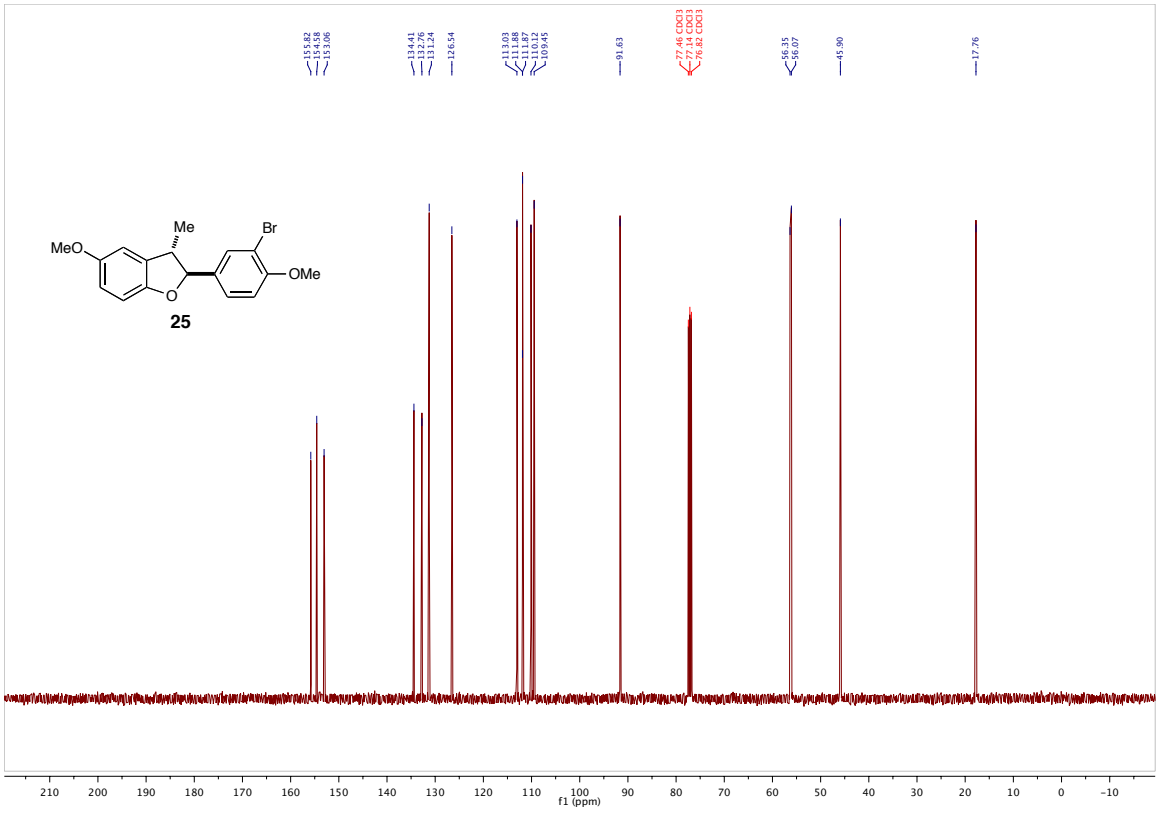
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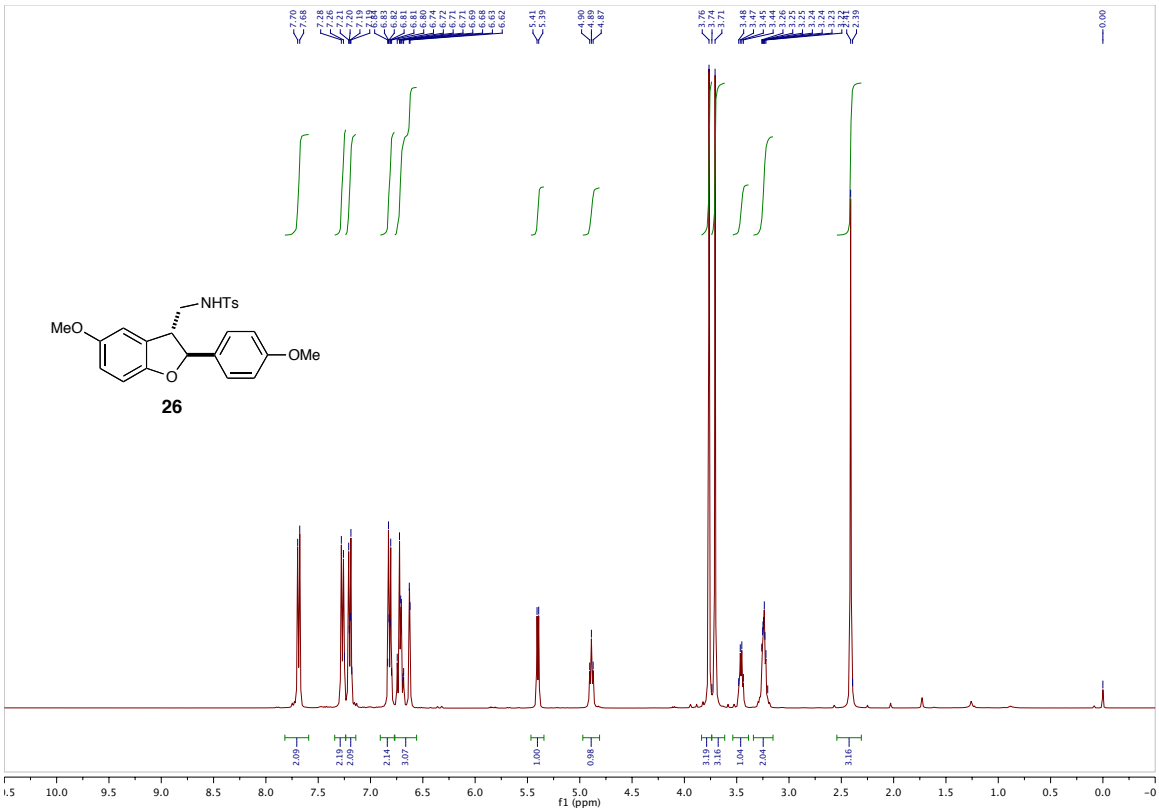
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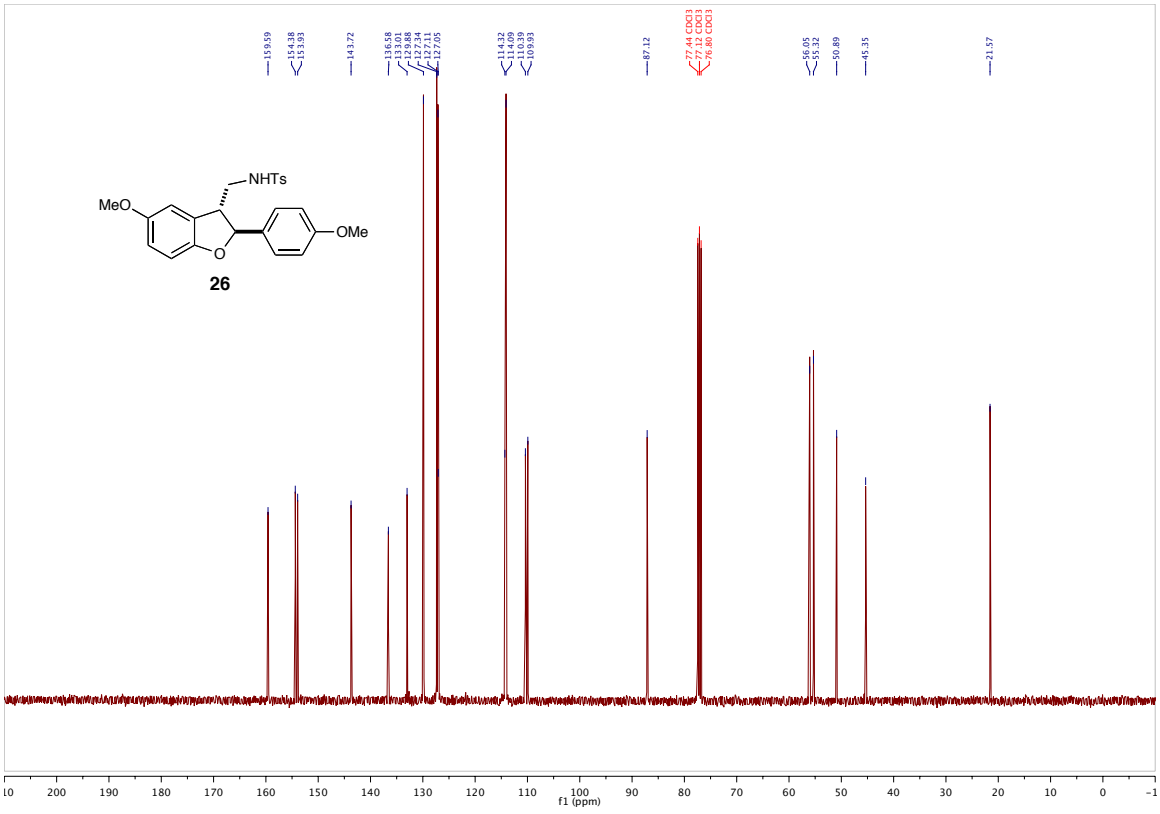
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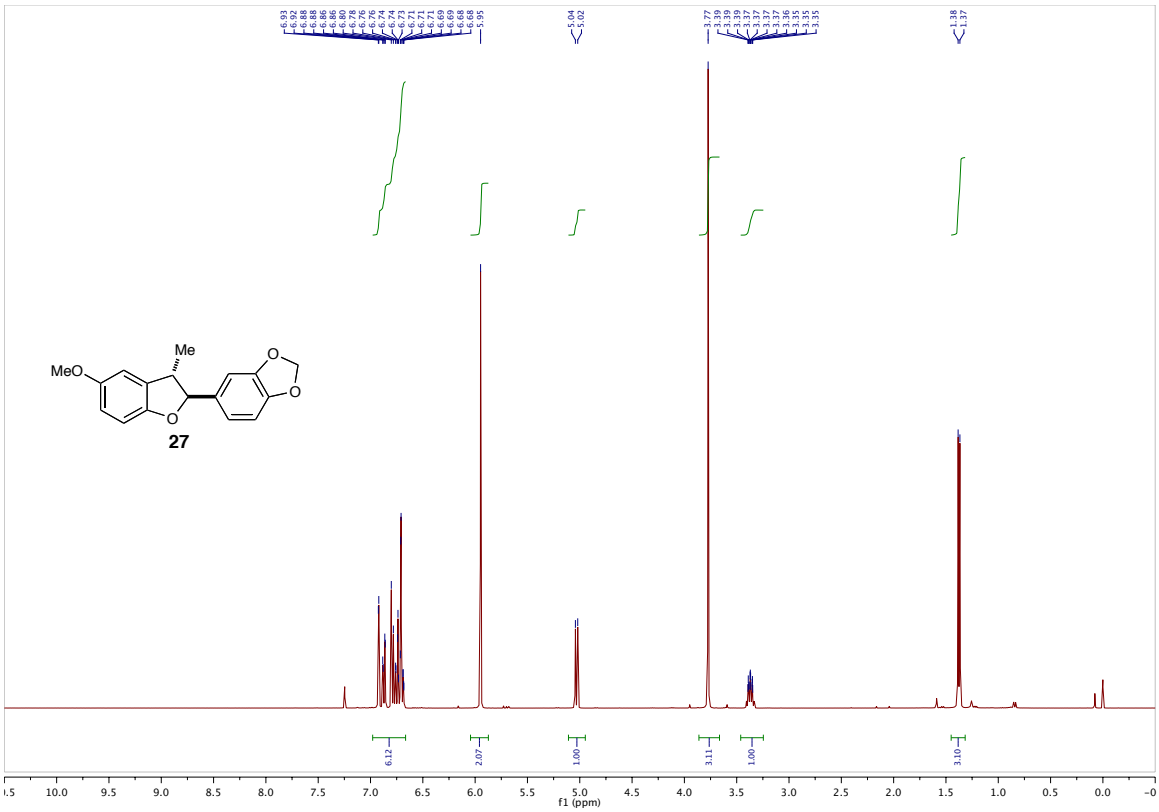
MeO
Me
O
O
O
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6.86
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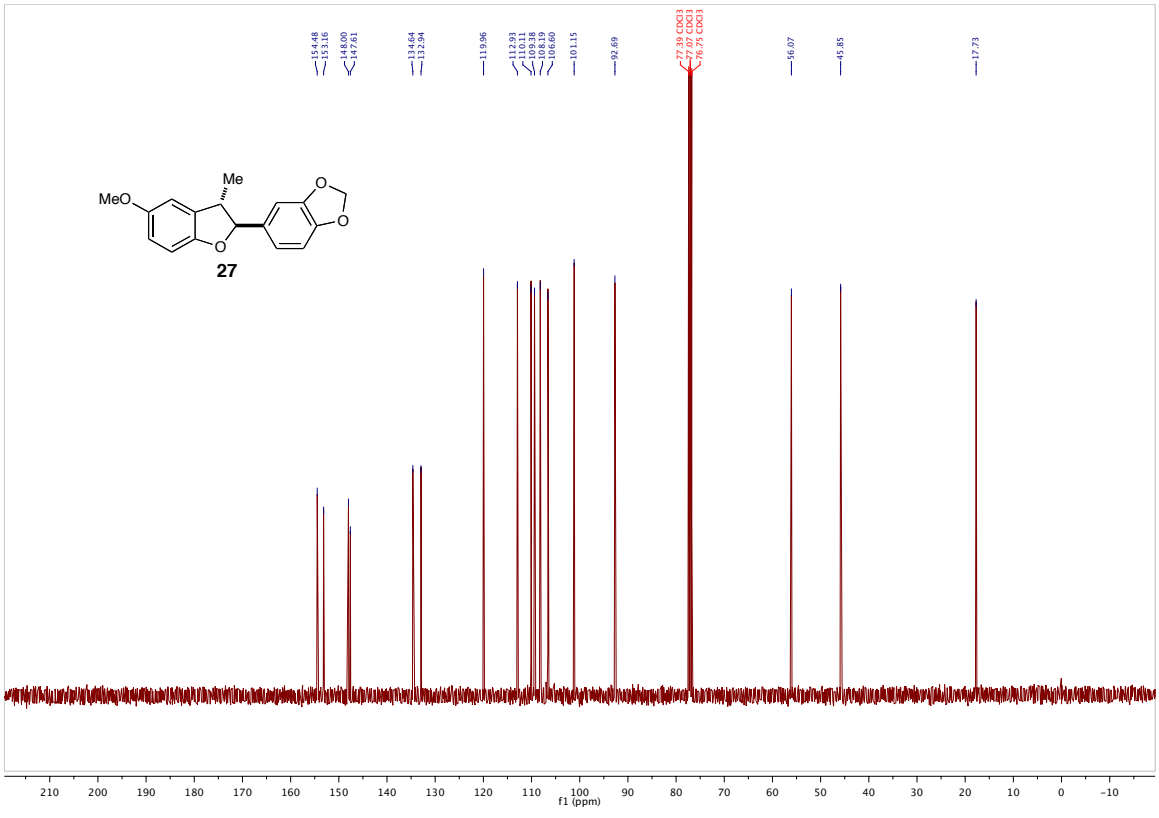
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O
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119.96
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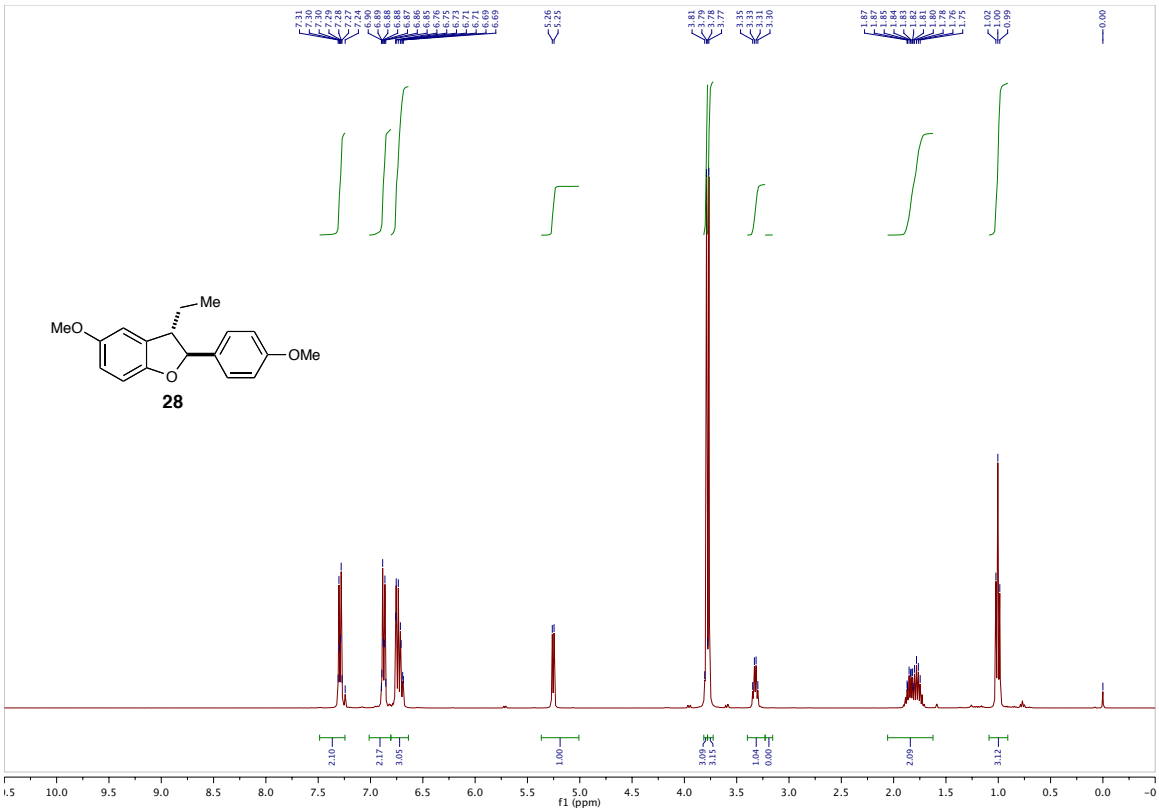
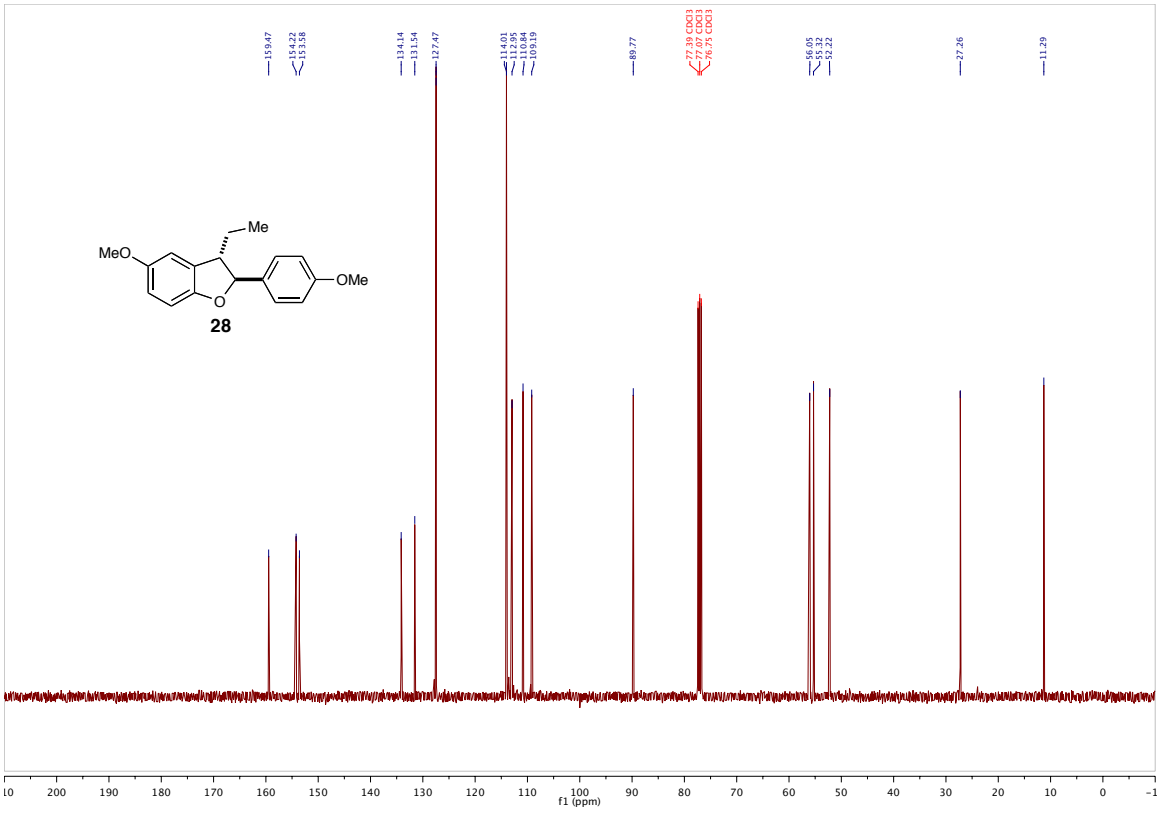
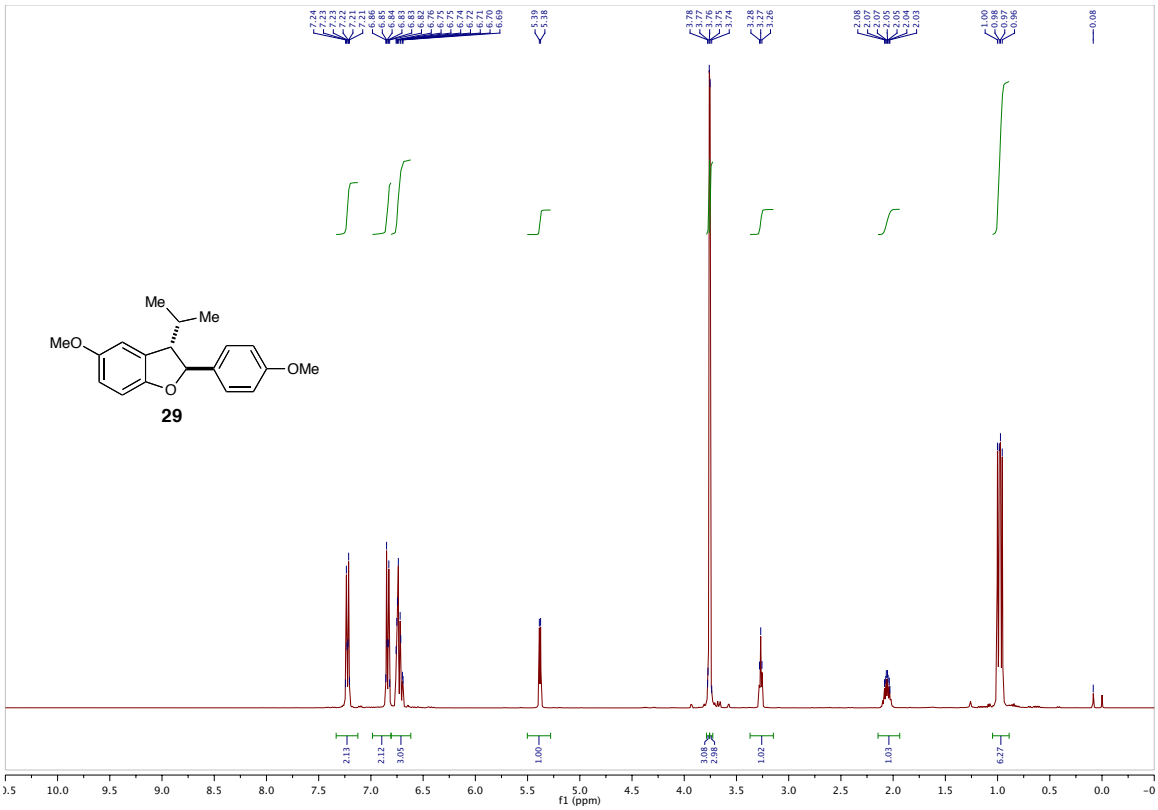
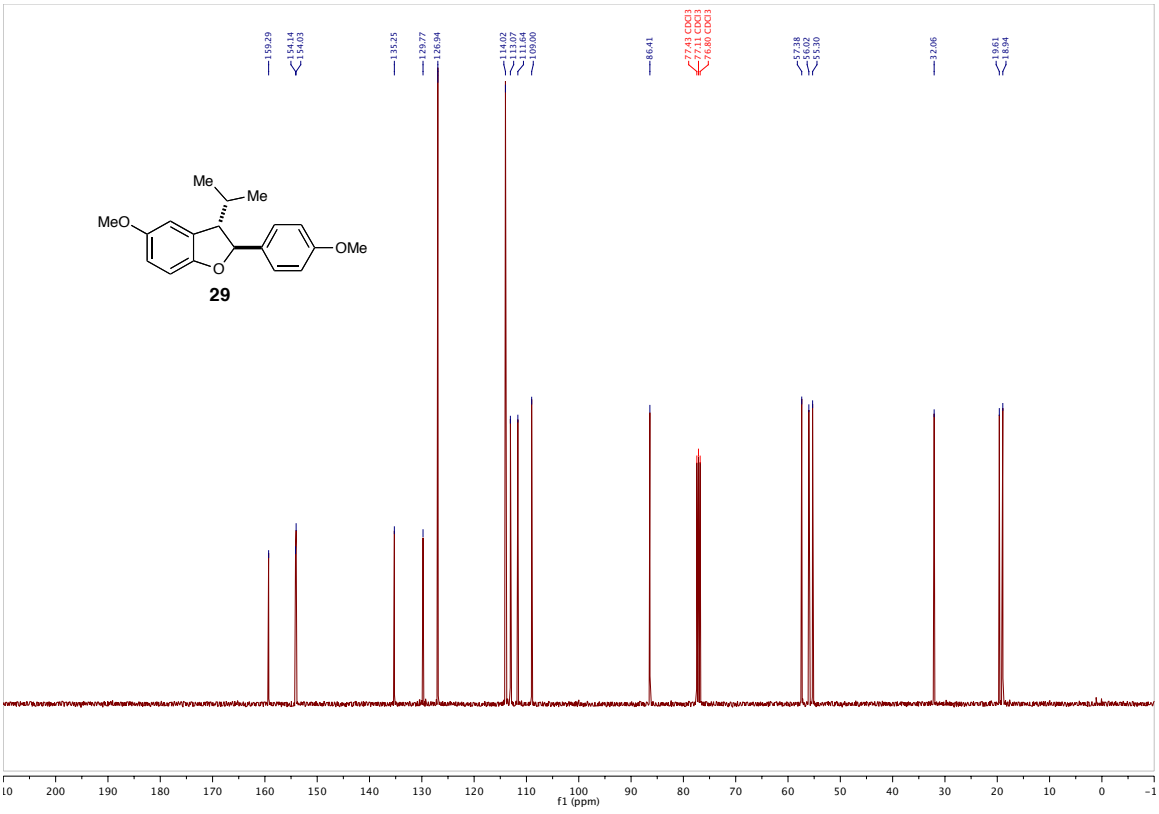
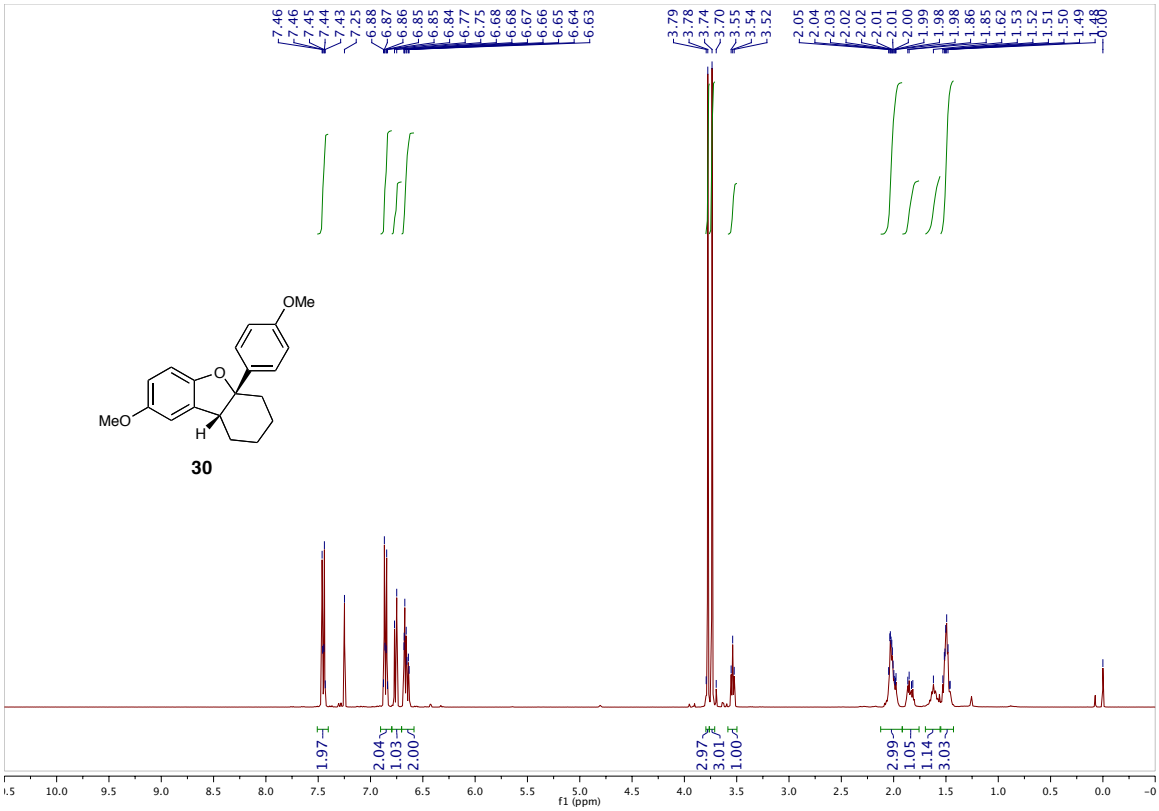
110.11
108.38
101.30
106.60
101.15
92.69
77.39 CDCl3
77.07 CDCl3
76.75 CDCl3
56.07
45.85
17.73
f1 (ppm)

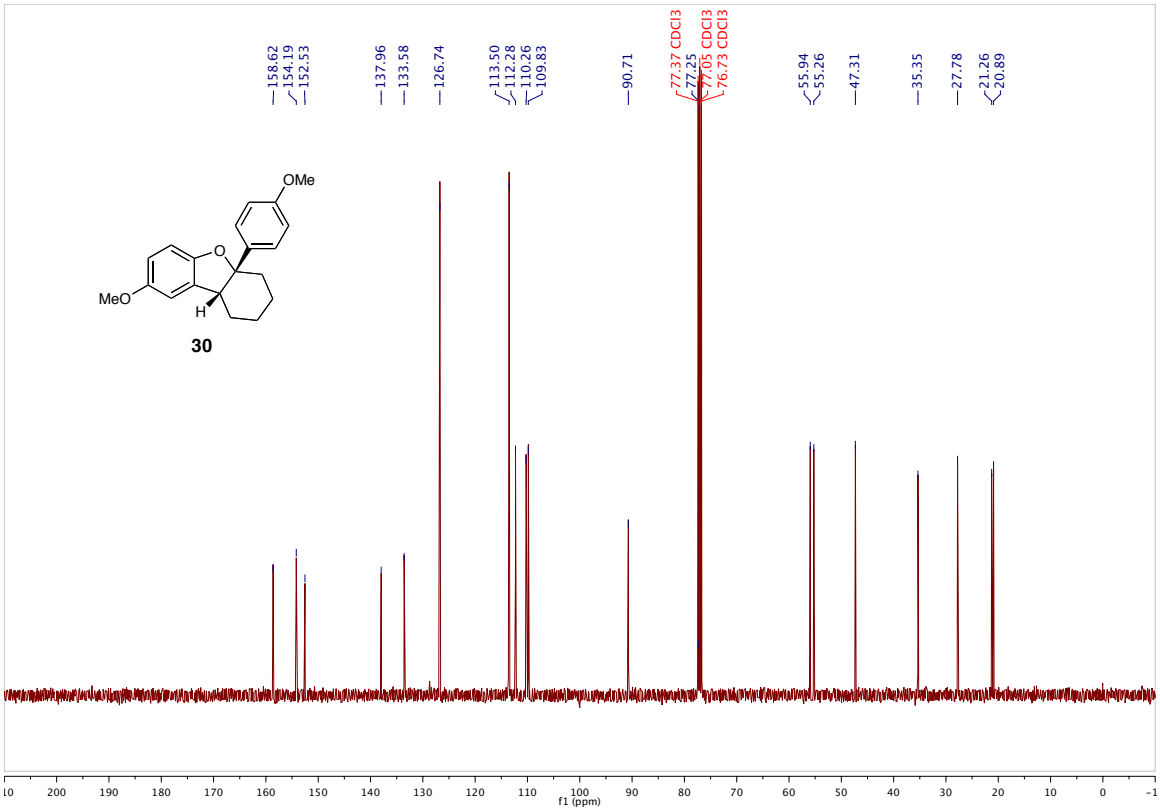

Me
MeO
OMe
O
28
f1 (ppm)

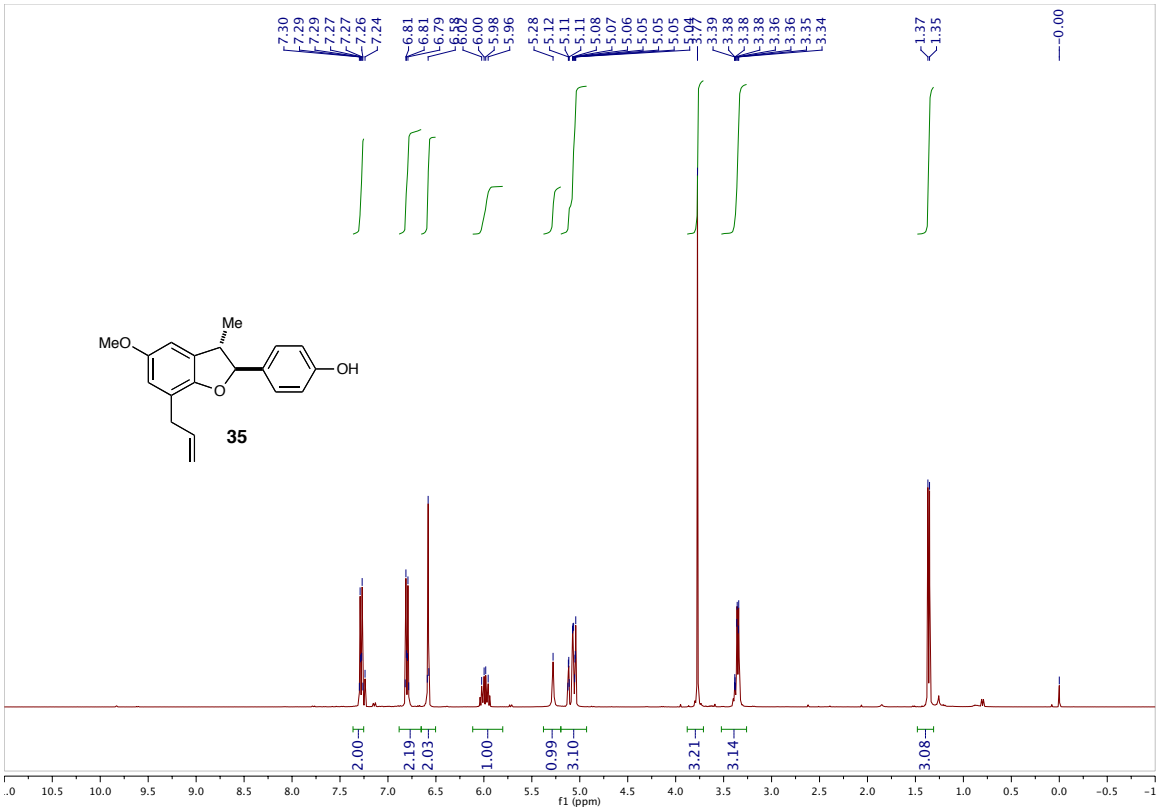

Me
MeO
OMe
O
28
f1 (ppm)

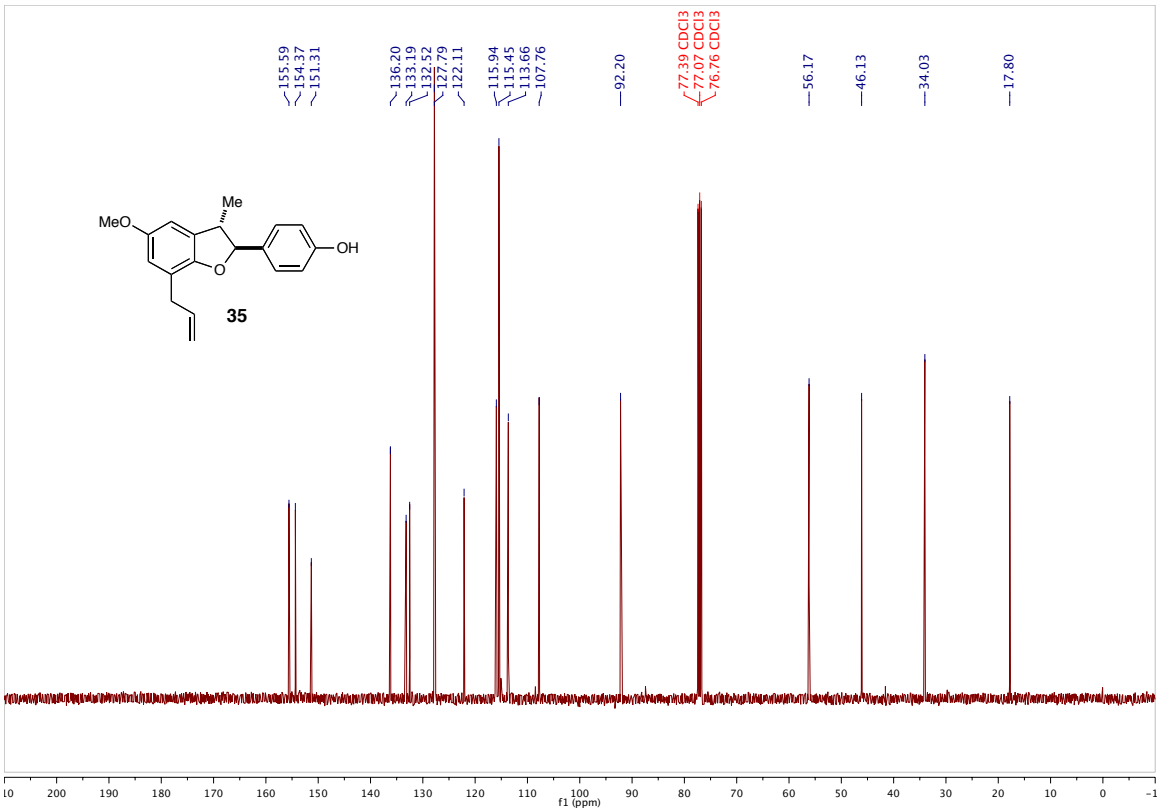

Me
Me
MeO
OMe
O
29
f1 (ppm)


Me
Me
MeO
OMe
O
29
f1 (ppm)


OMe
MeO
O
H
30
f1 (ppm)


OMe
MeO
O
H
30
f1 (ppm)


7.30
7.29
7.29
7.27
7.27
7.26
7.24
6.81
6.81
6.79
6.58
6.02
6.00
5.98
5.96
5.28
5.12
5.11
5.11
5.08
5.07
5.06
5.05
5.05
5.05
5.04
3.77
3.39
3.38
3.38
3.38
3.36
3.36
3.35
3.34
1.37
1.35
-0.00
Me
MeO
OH
O
35
2.00
2.19
2.03
1.00
0.99
3.10
3.21
3.14
3.08
f1 (ppm)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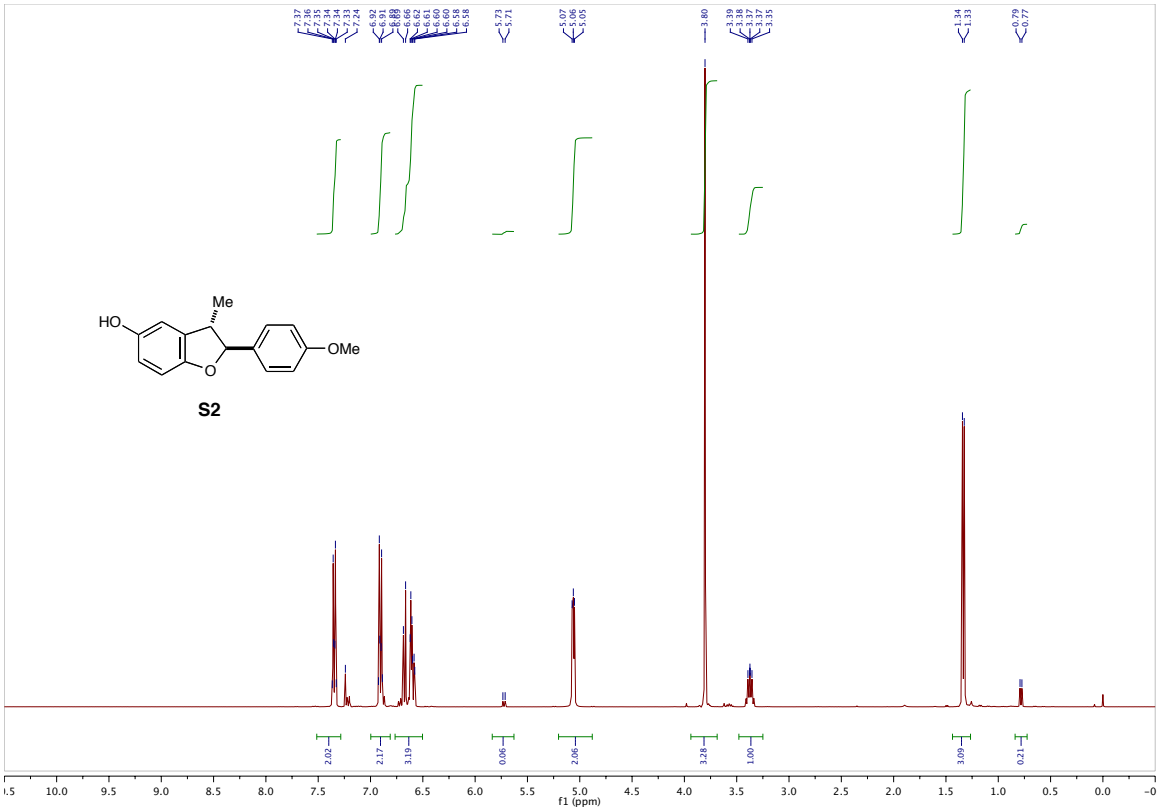
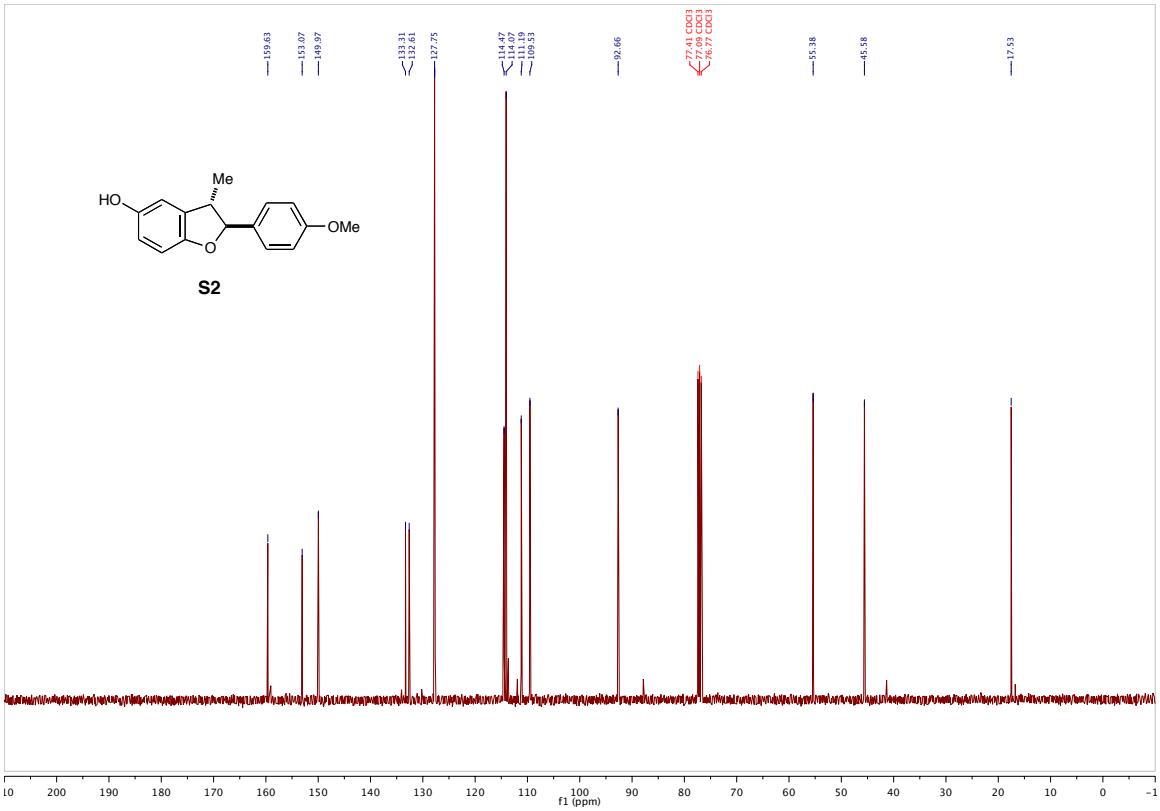
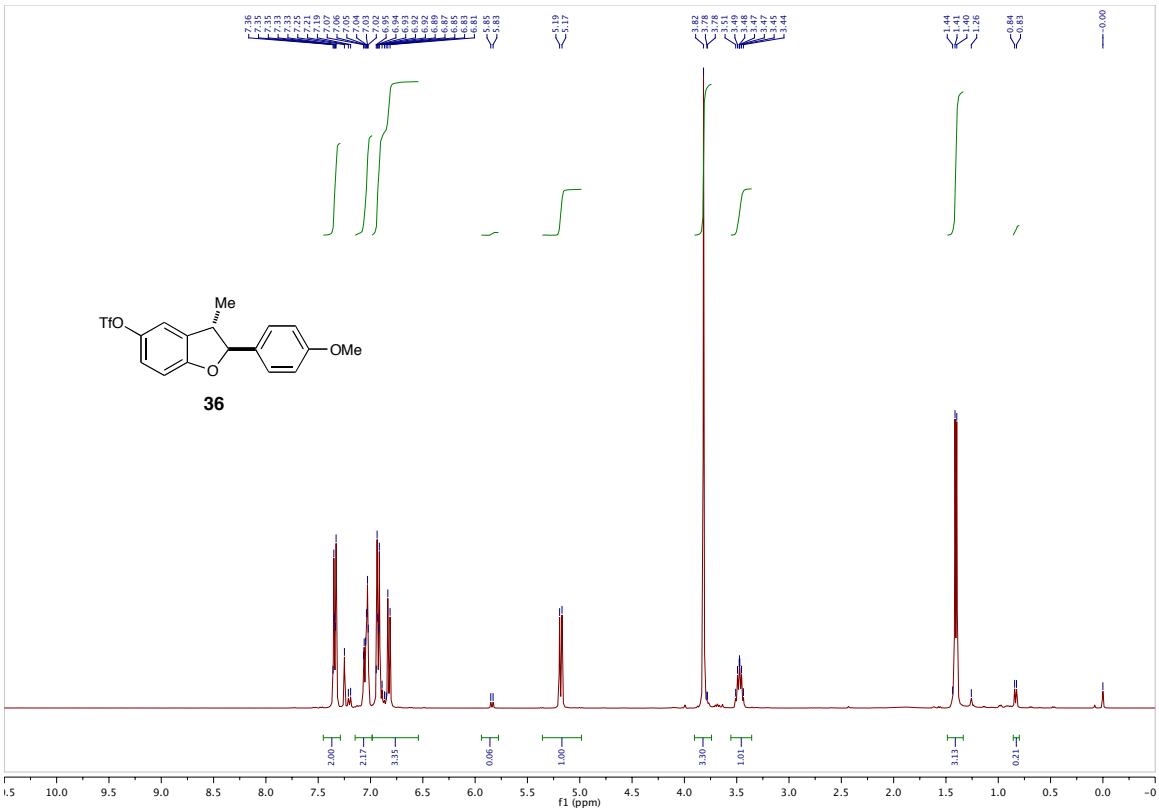
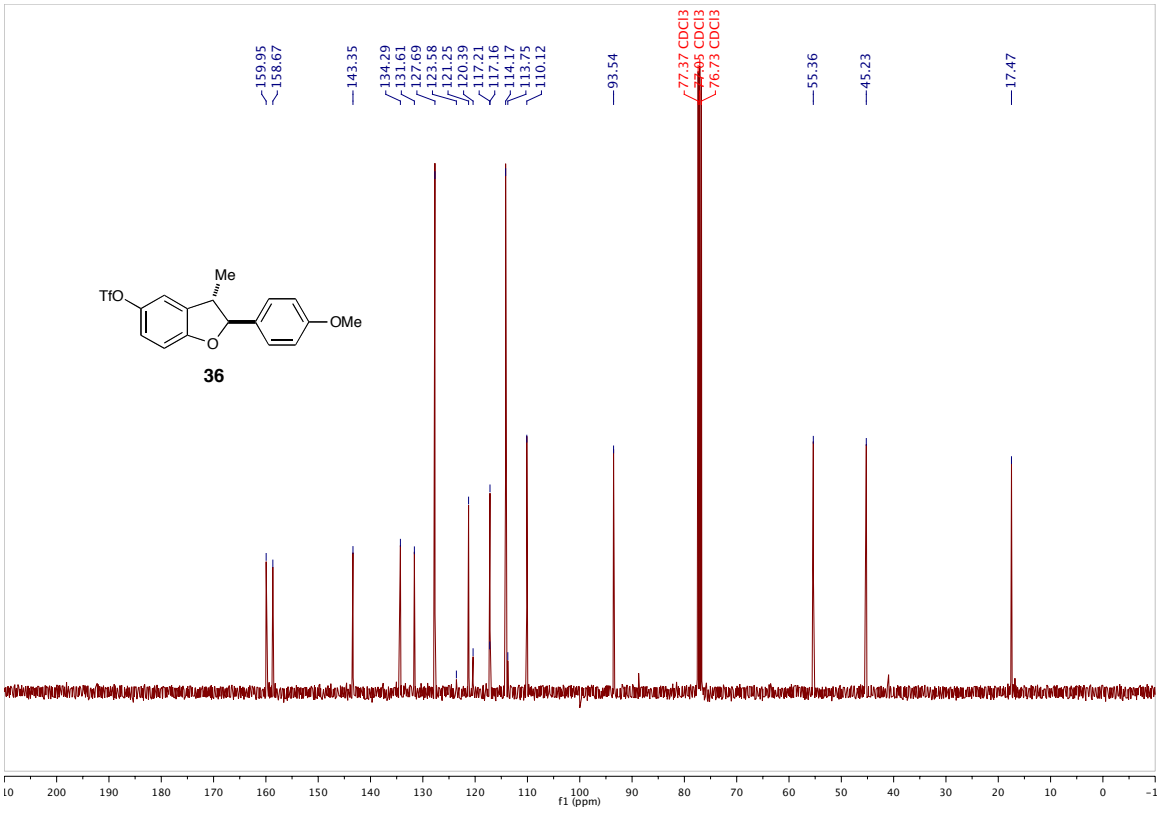
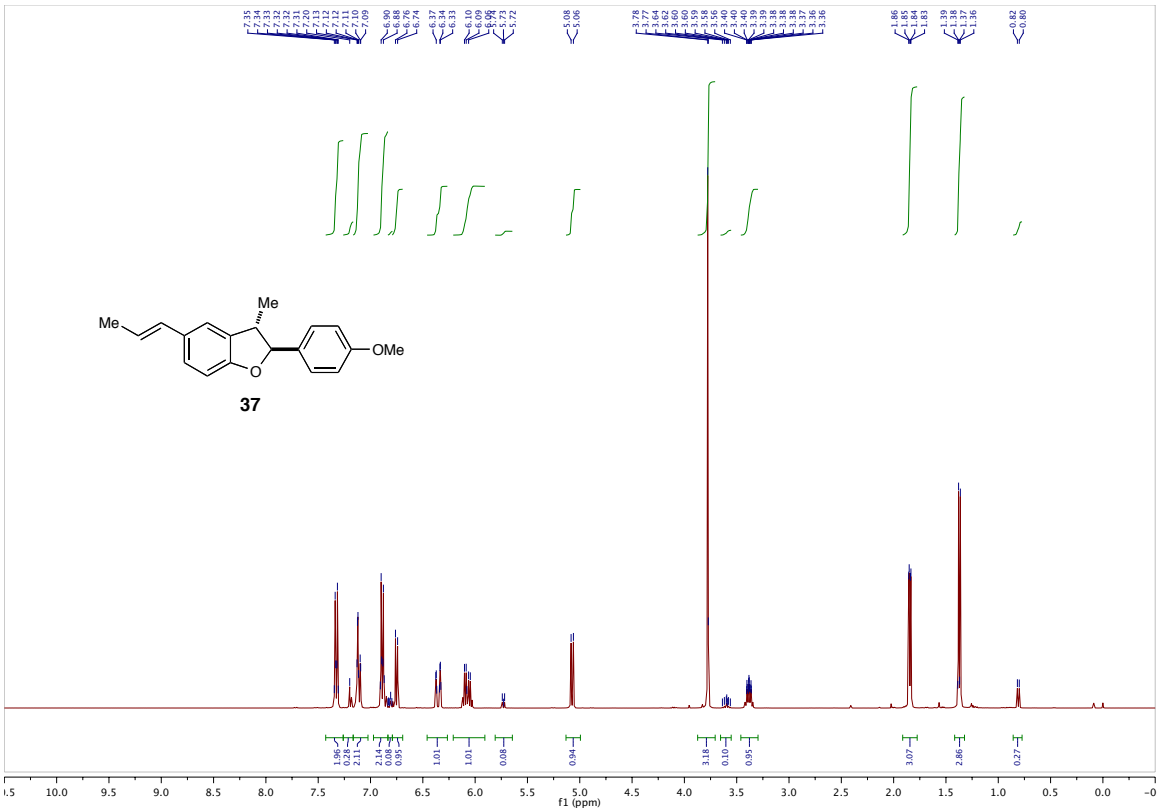
154.37
151.31
136.20
133.19
132.52
127.79
122.11
115.94
115.45
113.66
107.76
92.20
77.39 CDCl3
77.07 CDCl3
76.76 CDCl3
56.17
46.13
34.03
17.80
Me
MeO
OH
O
35
f1 (ppm)

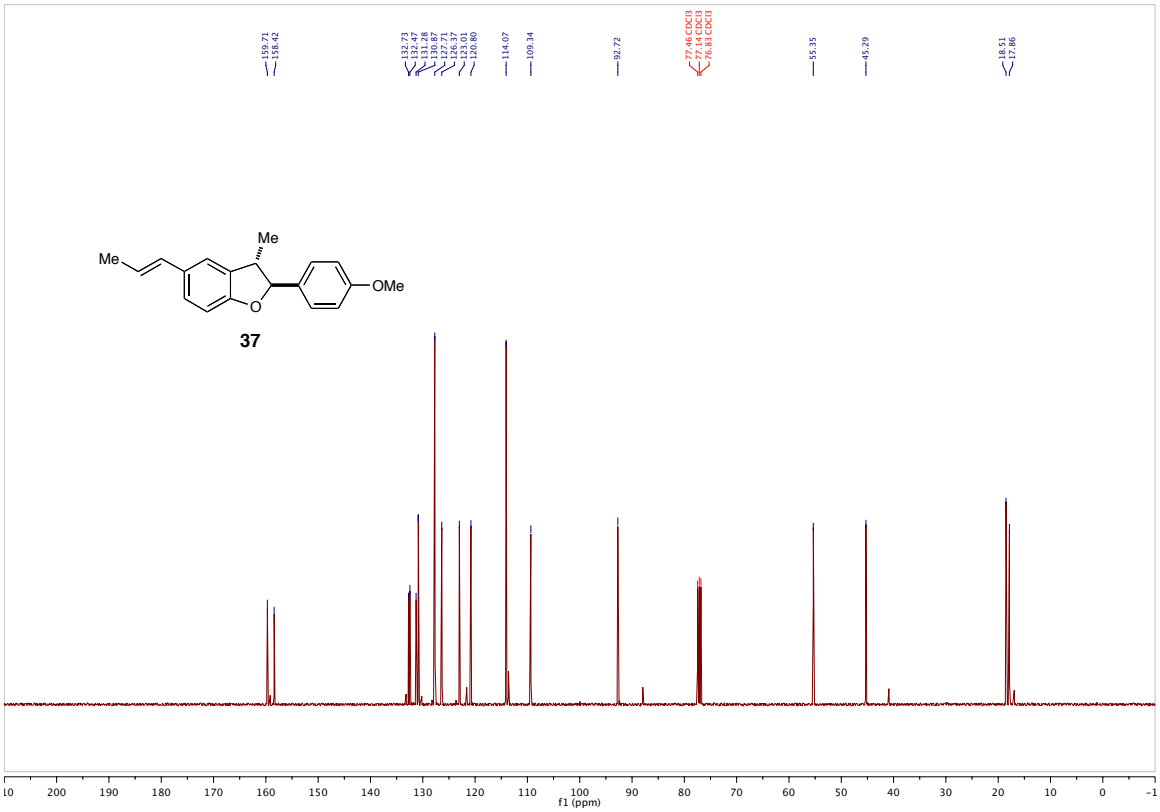

HO
Me
O
OMe
S2
f1 (ppm)

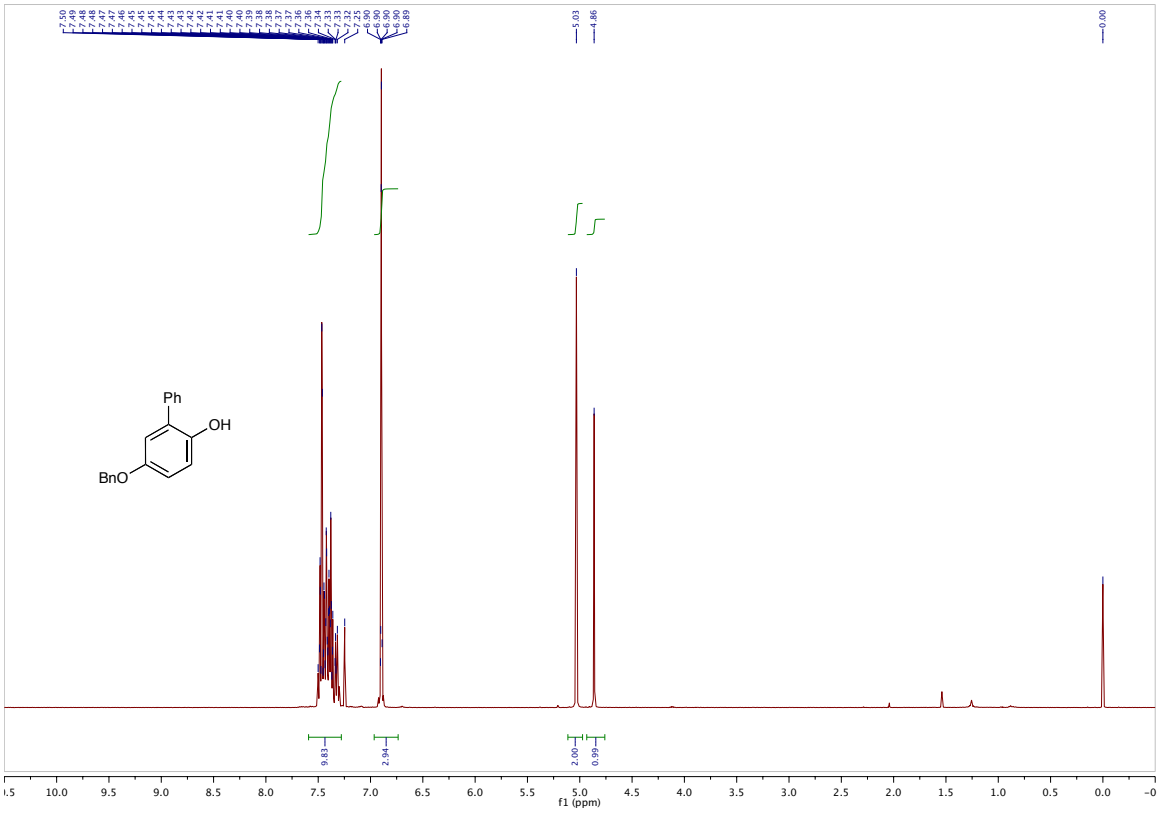

HO
Me
O
OMe
S2
f1 (ppm)

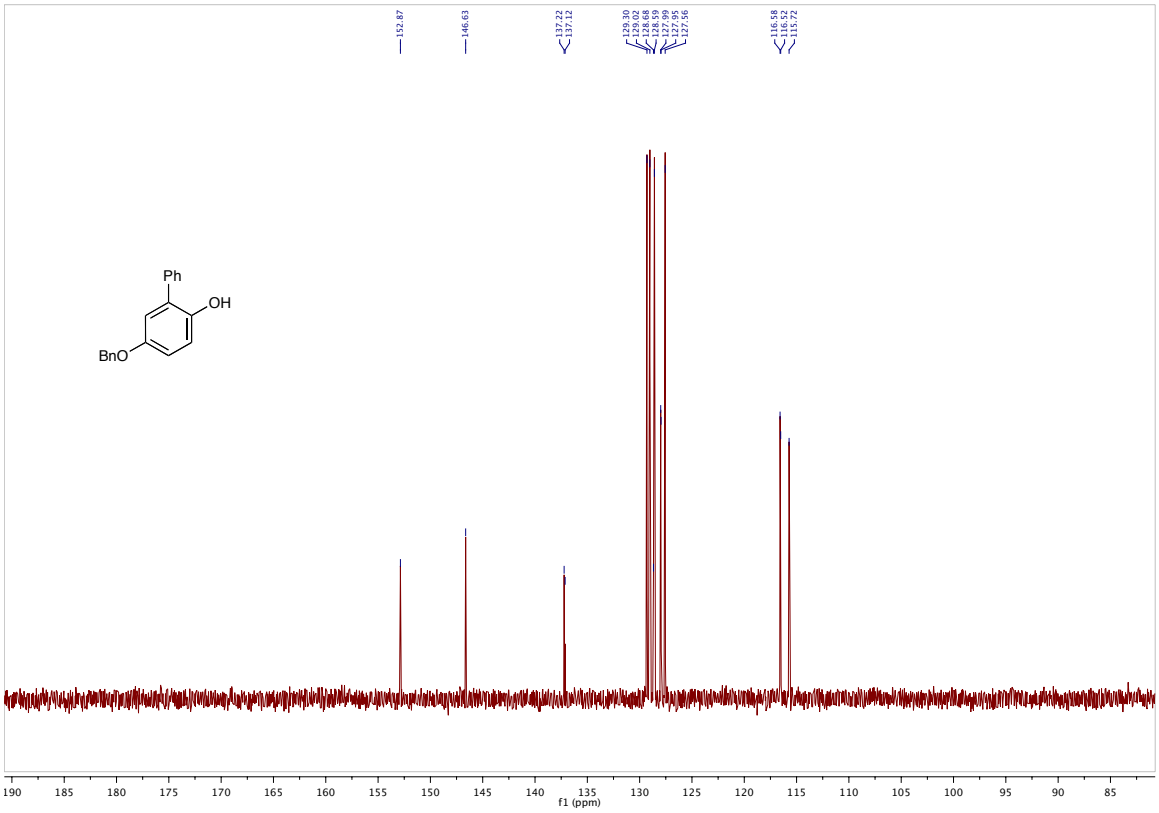

TfO
Me
OMe
O
36
f1 (ppm)

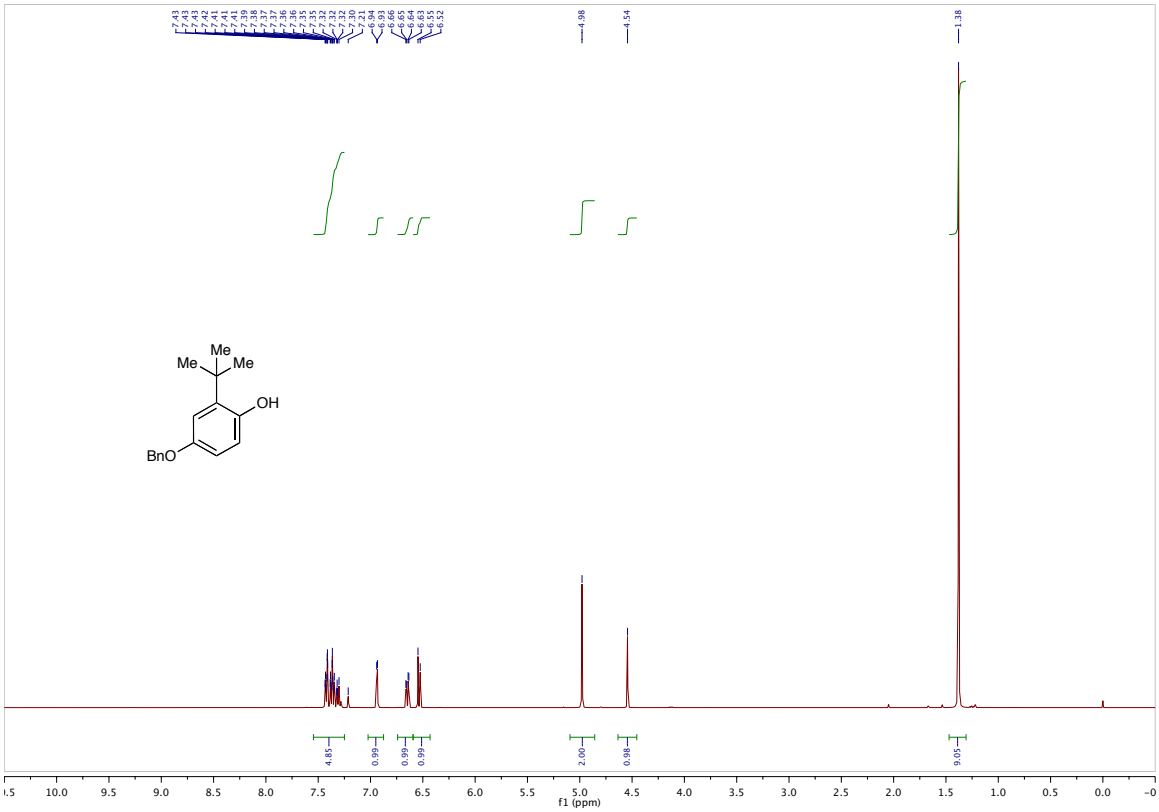

TfO
Me
OMe
O
36
f1 (ppm)

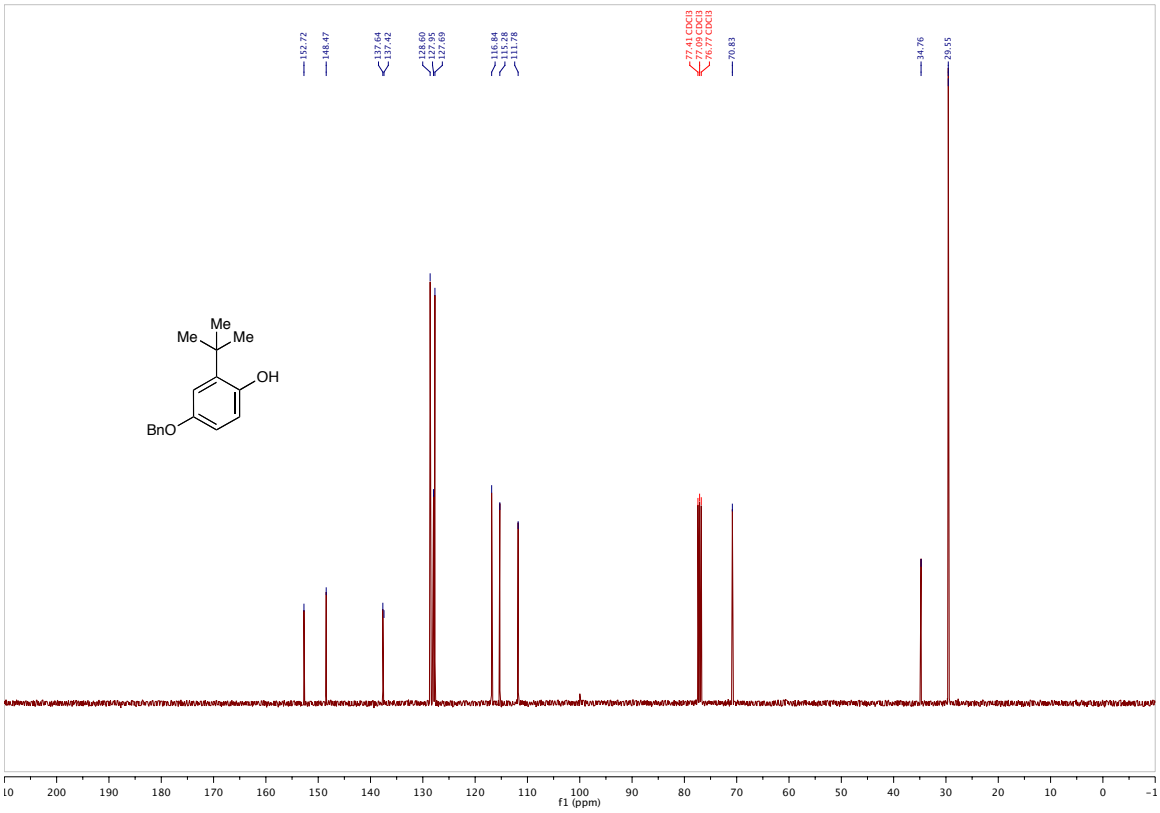

Me
Me
OMe
O
37
f1 (ppm)

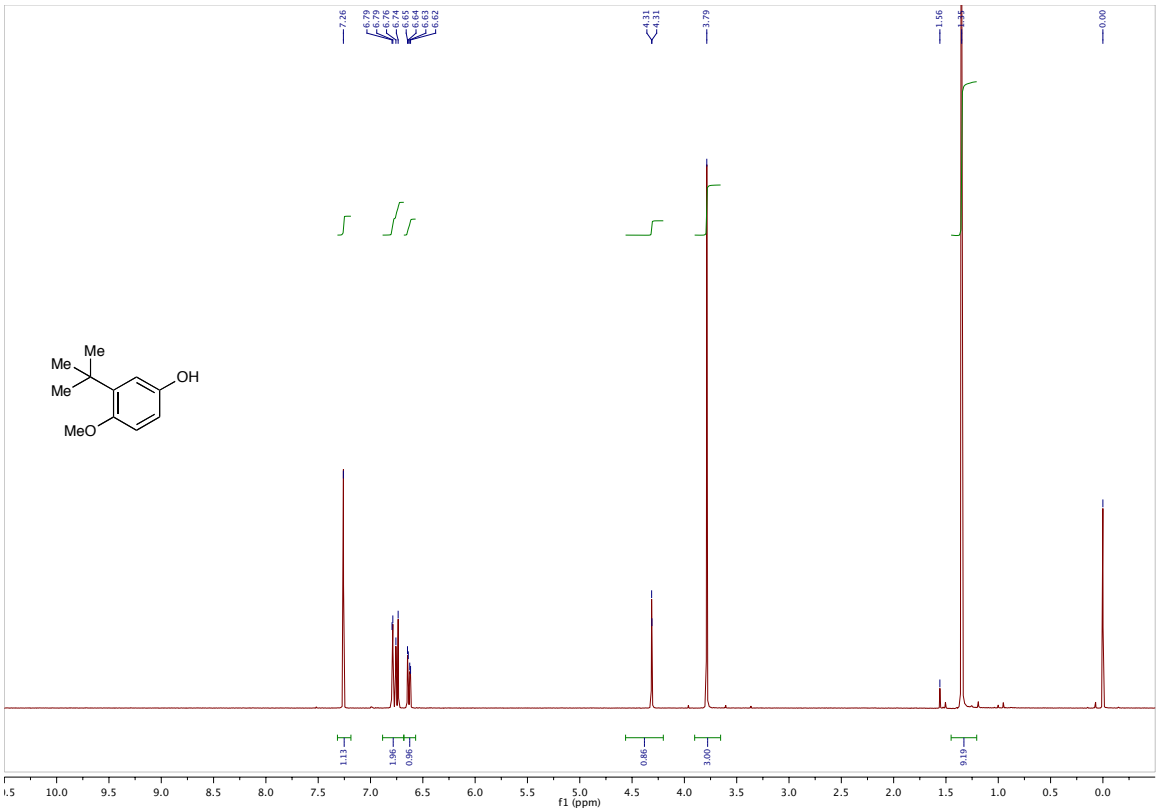

Me
Me
OMe
O
37
f1 (ppm)

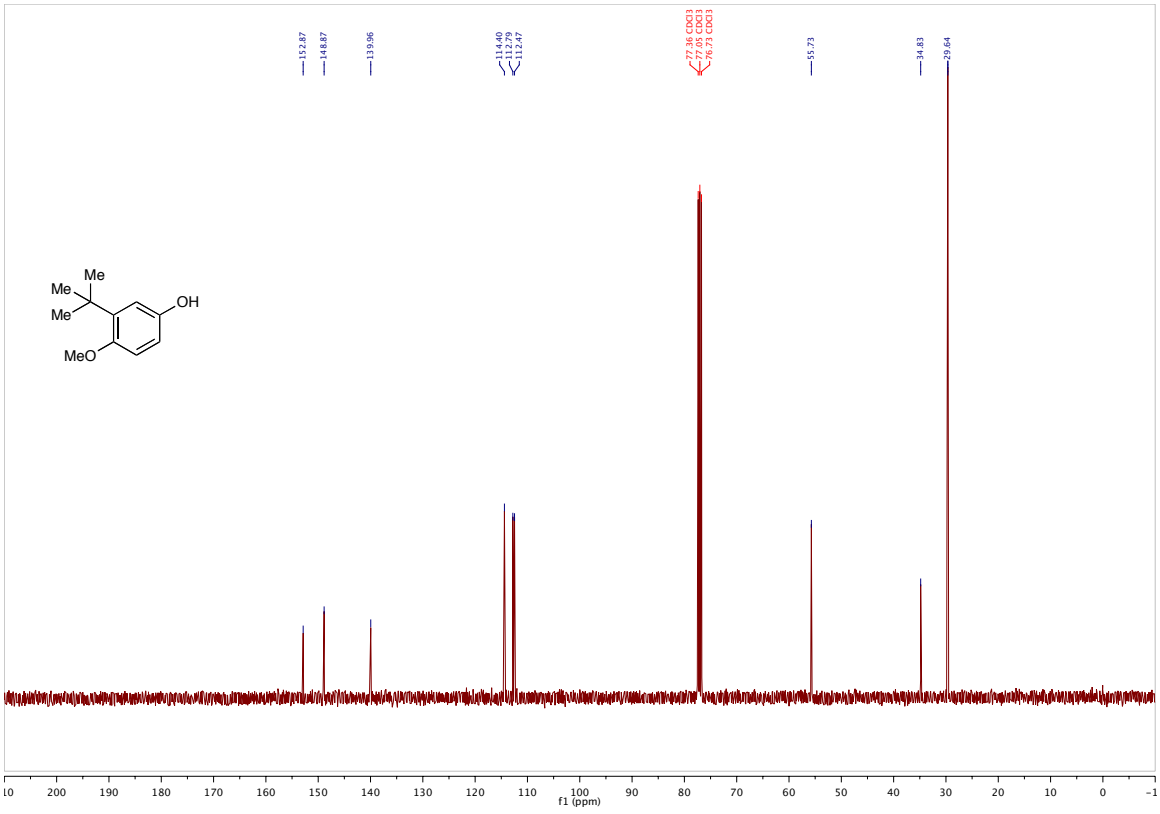

Ph
OH
BnO
f1 (ppm)

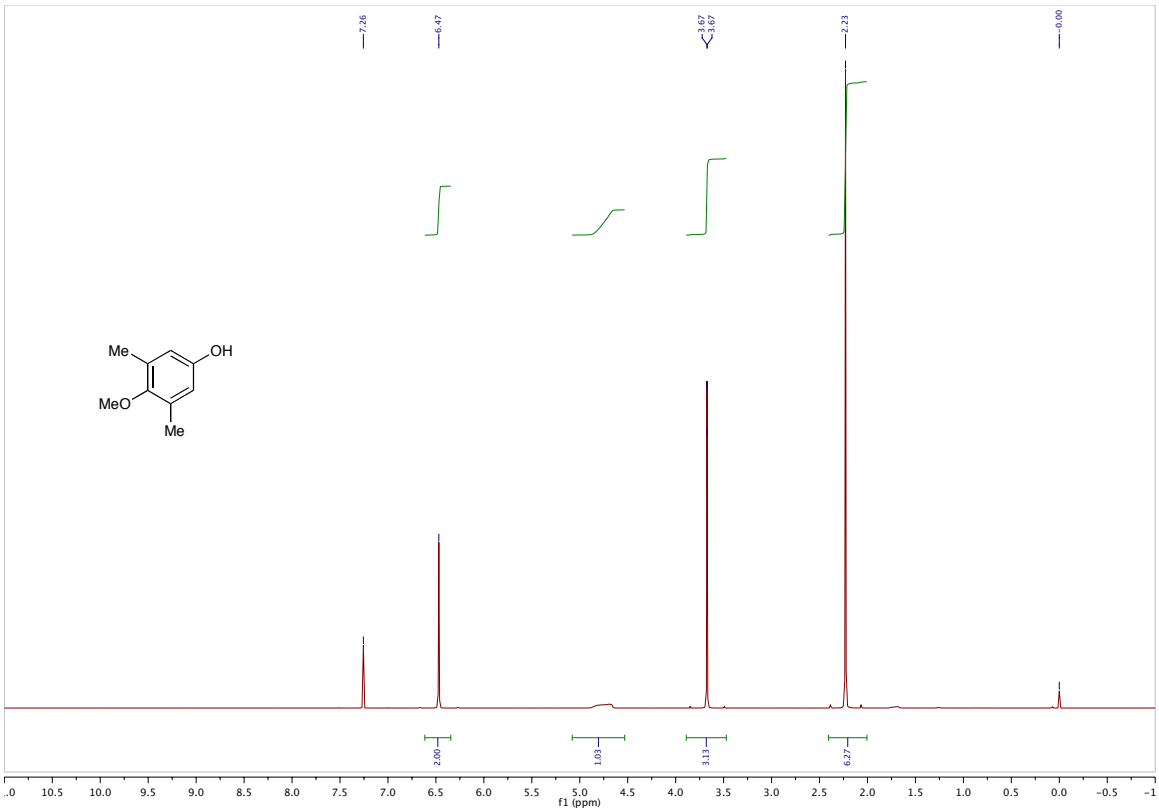

Ph
OH
BnO
f1 (ppm)

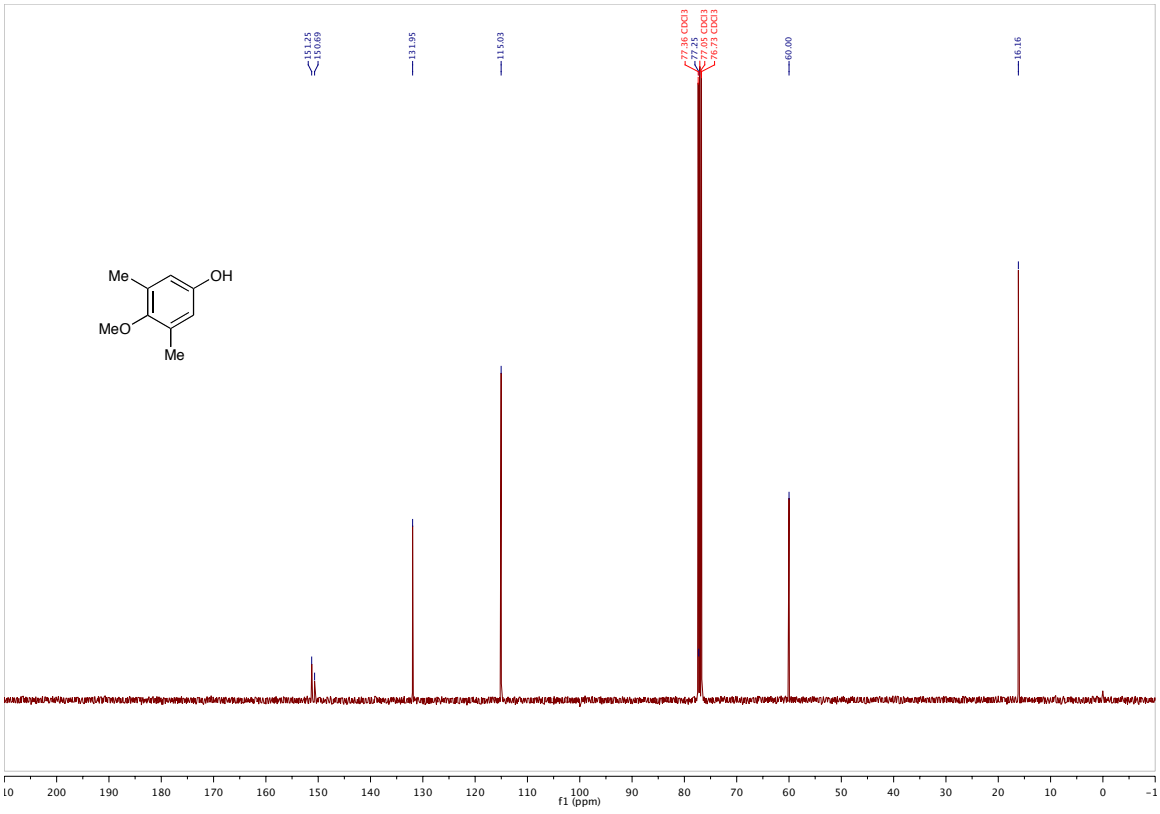

Me
Me
Me
OH
BnO
f1 (ppm)

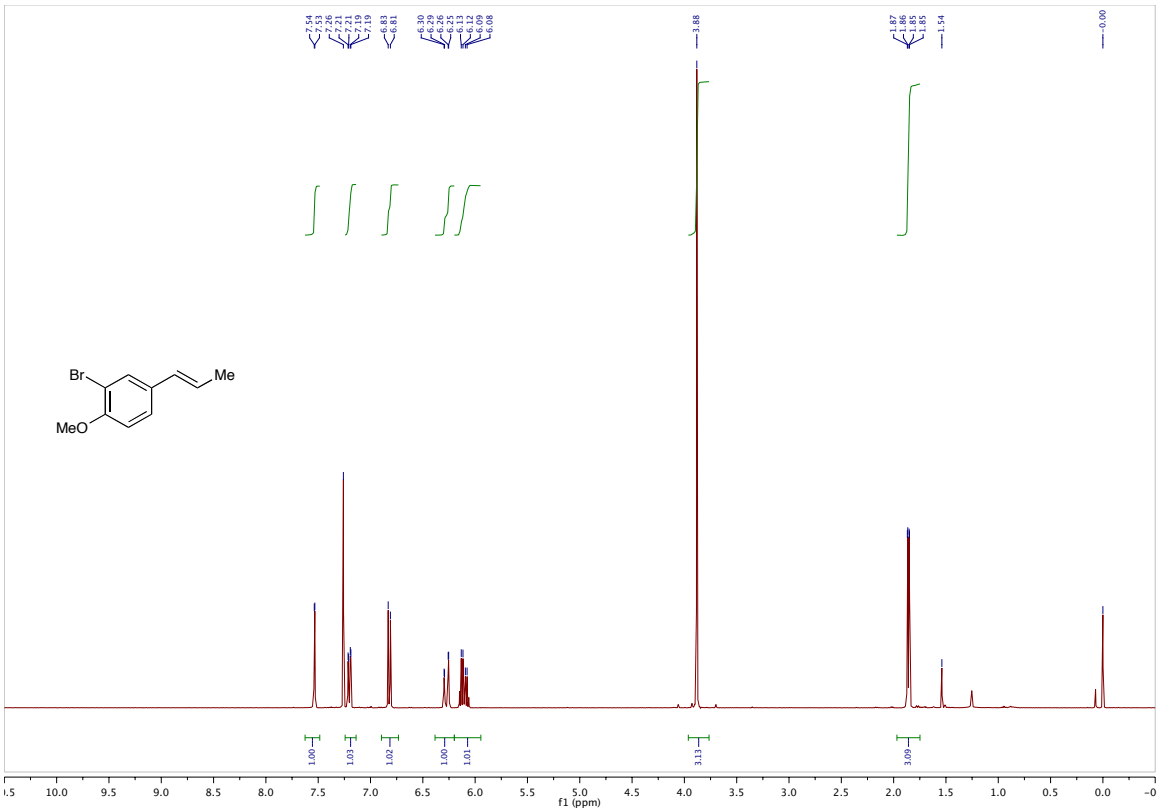

Me
Me
Me
OH
BnO
f1 (ppm)

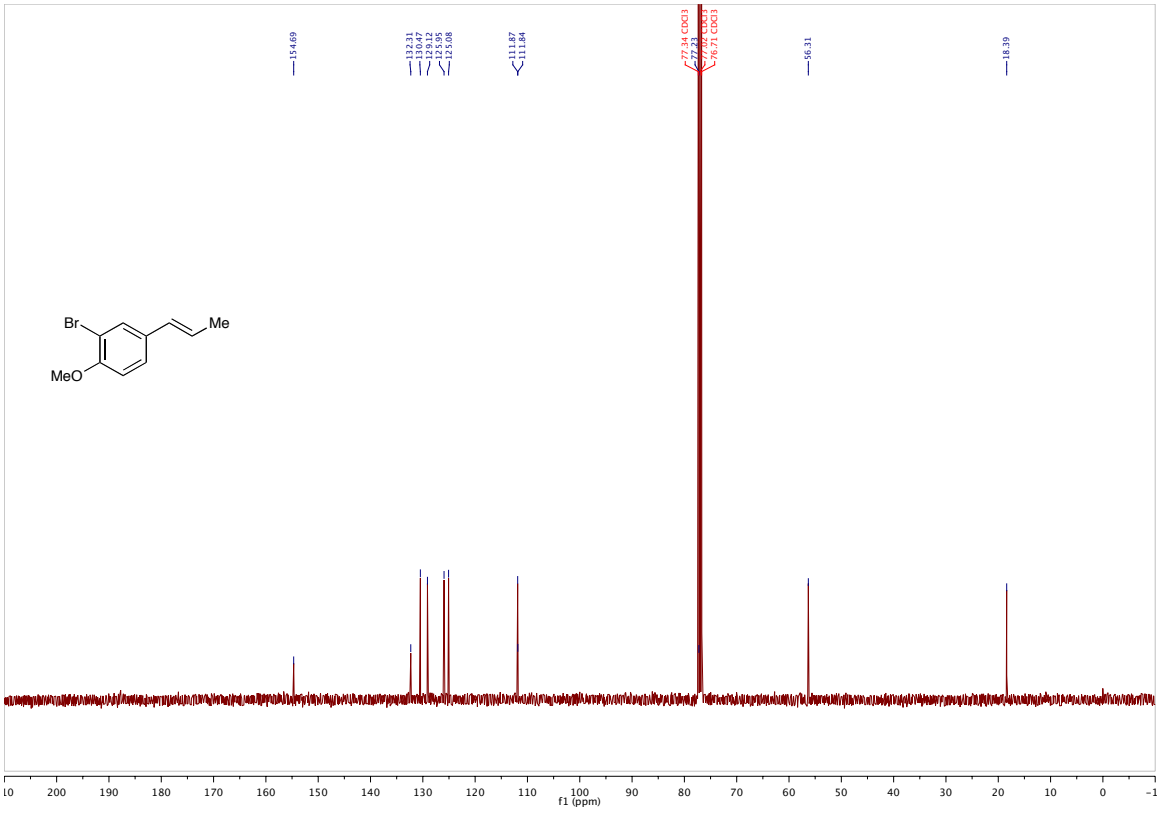

7.26
6.79
6.79
6.78
6.74
6.65
6.64
6.63
6.62
4.31
4.31
3.79
1.56
1.35
0.00
Me
Me
Me
OH
MeO
1.13
1.96
0.96
0.86
3.00
9.19
f1 (ppm)

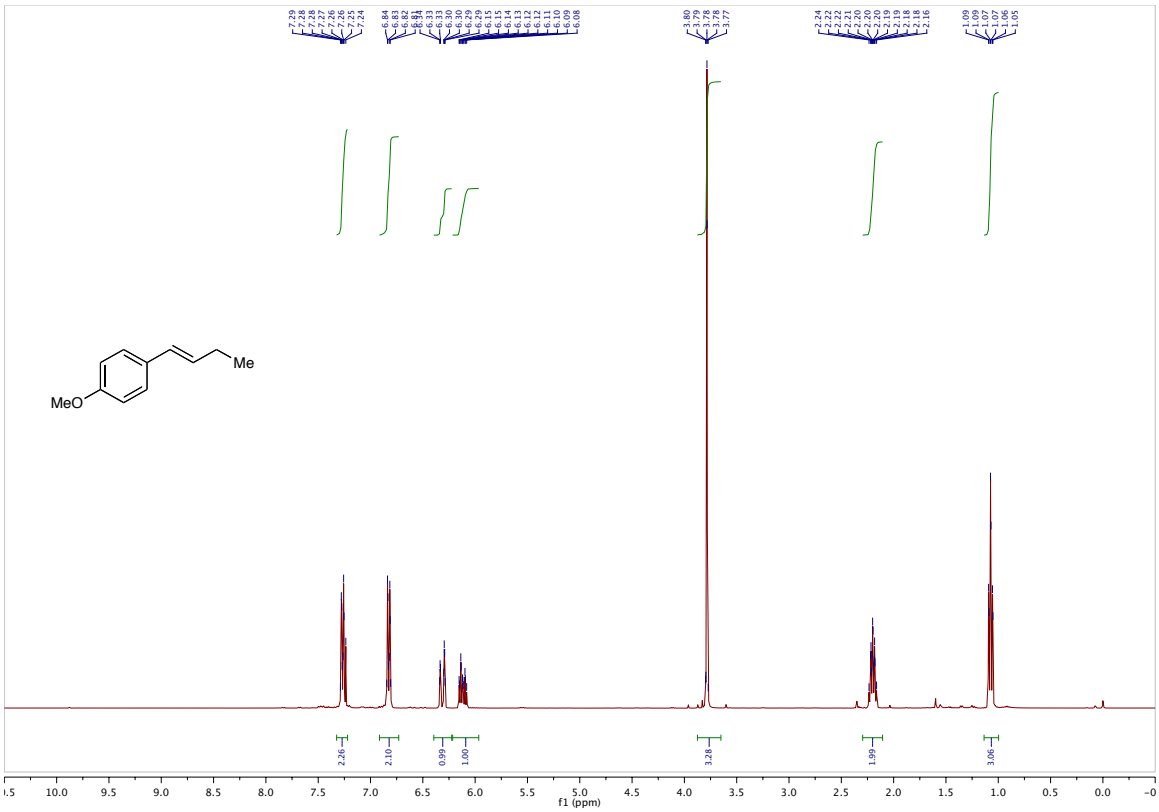

152.87
148.87
139.96
114.40
112.79
112.47
77.36 CDCl3
77.05 CDCl3
76.73 CDCl3
55.73
34.83
29.64
Me
Me
Me
OH
MeO
f1 (ppm)

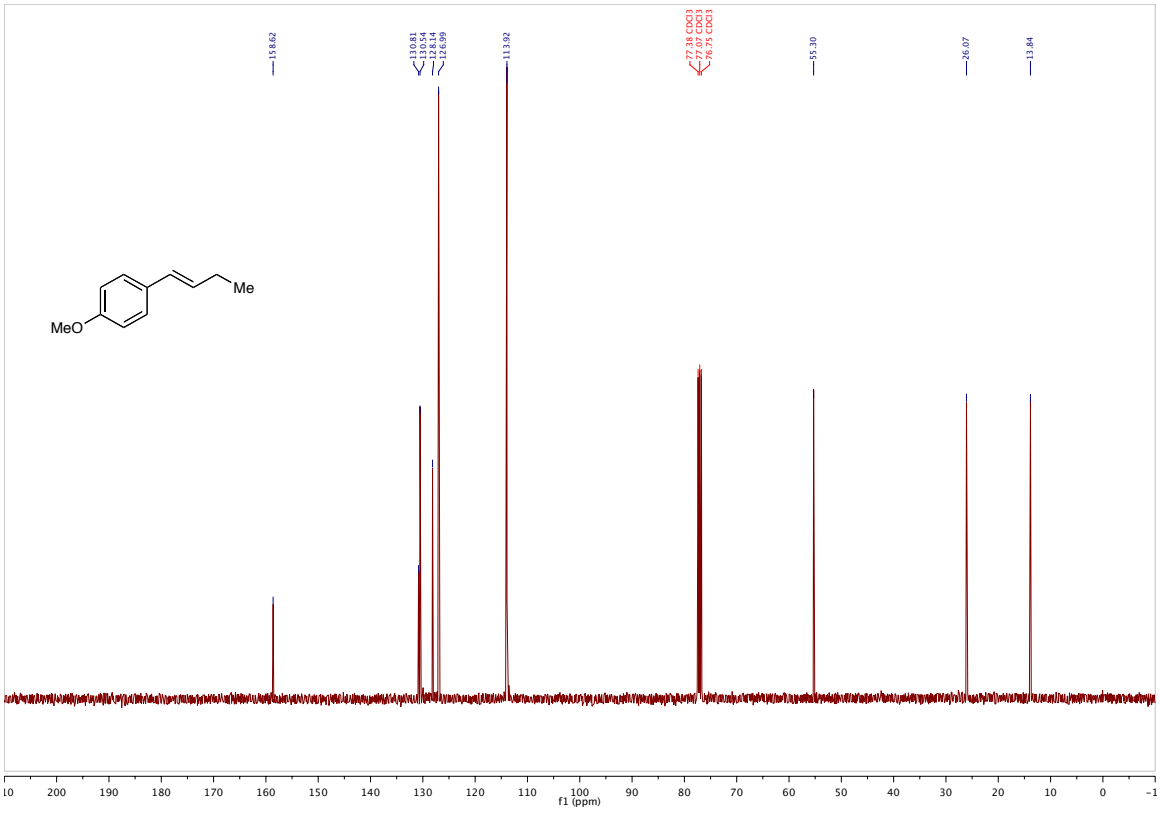

7.26
6.47
3.67
3.67
2.23
0.00
Me
OH
MeO
Me
2.00
1.03
3.13
6.27
f1 (ppm)

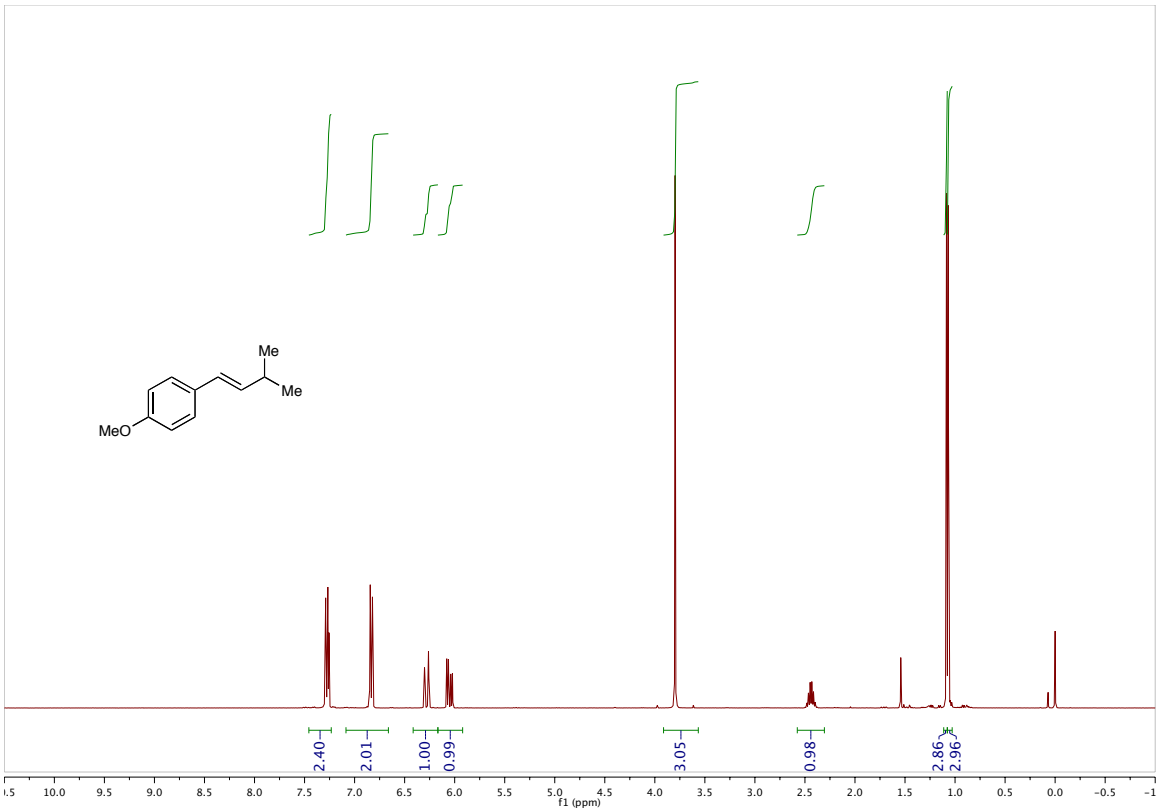

151.25
150.69
131.95
115.03
77.36 CDCl3
77.25
77.05 CDCl3
76.73 CDCl3
60.00
16.16
Me
OH
MeO
Me
f1 (ppm)

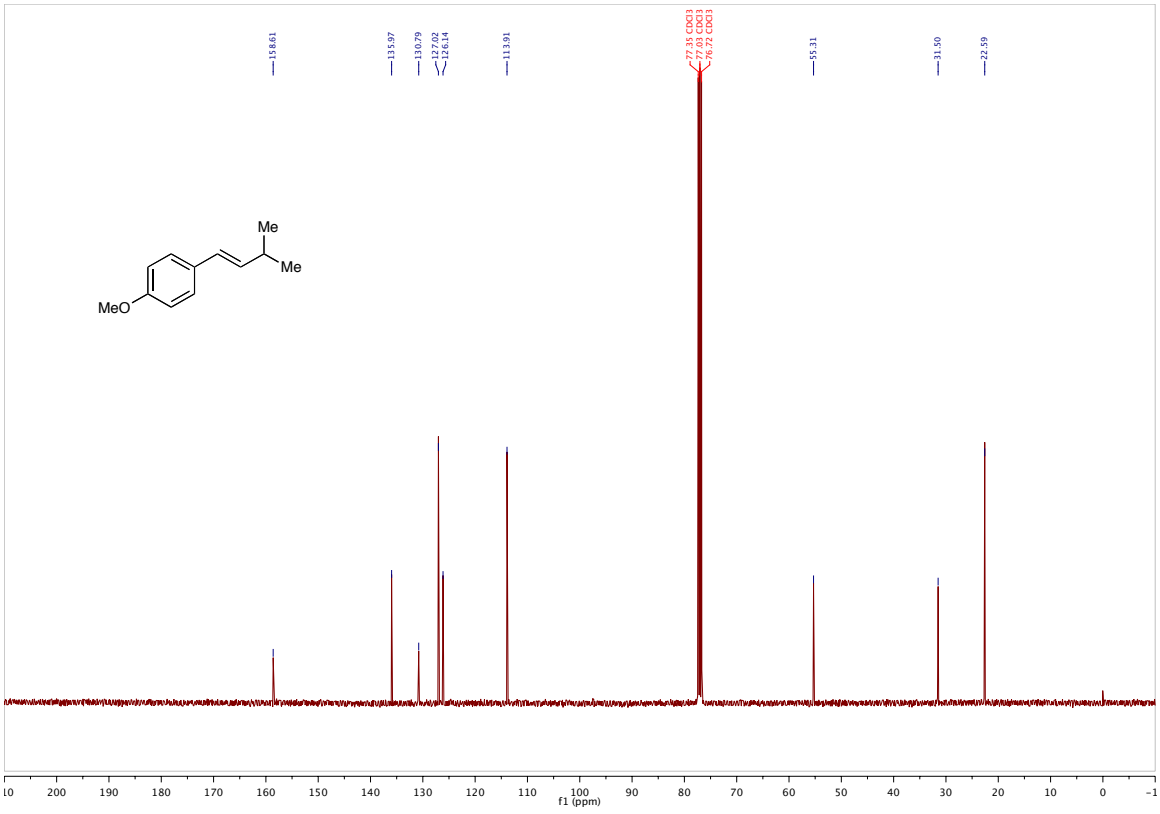

7.54
7.53
7.26
7.21
7.21
7.19
7.19
6.83
6.81
6.30
6.29
6.26
6.25
6.13
6.12
6.09
6.08
3.88
1.87
1.86
1.85
1.85
1.54
0.00
Br
Me
MeO
1.00
1.03
1.02
1.00
1.01
3.13
3.09
f1 (ppm)


154.69
132.31
130.47
129.32
125.95
125.08
111.87
111.84
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
56.31
18.39
Br
Me
MeO
f1 (ppm)


Me
MeO
f1 (ppm)


Me
MeO
f1 (ppm)


Me
Me
MeO
2.40
2.01
1.00
0.99
3.05
0.98
2.86
2.96
f1 (ppm)


158.61
135.97
130.79
127.02
126.44
113.91
77.35 CDCl3
77.03 CDCl3
76.72 CDCl3
55.31
31.50
22.59
Me
Me
MeO
f1 (ppm)