**Supporting Information for:**

# Palladium-Catalyzed Cross-Coupling of 2-Aryl-1,3-Dithianes

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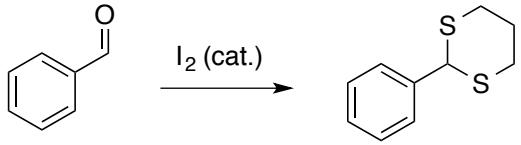
## General Experimental Details

**General:** All aryl bromides, palladium acetate, and bases were purchased from commercial sources and used as received without further purification. Solvent was purchased from Sigma-Aldrich (anhydrous, sure-seal) and used as received. NiXantphos was purchased from Strem Chemical, Inc., catalogue no. 15-0437.

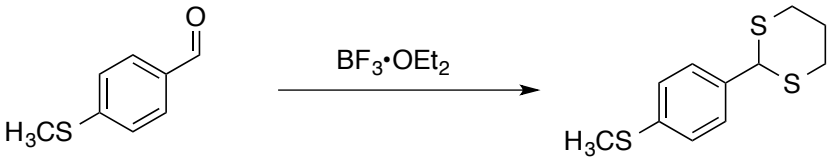
Thin layer chromatography was carried out on silica gel plates and eluted plates were visualized with UV light (254 nm). Flash chromatography was carried out on silica gel (230-400 mesh). All yields refer to isolated yields of analytically pure product. Melting points are uncorrected. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker 400 MHz instrument. Spectra were recorded in ppm and referenced to residual solvent C**H**$Cl_3$ (7.28 ppm). $^{1}H$ NMR data are presented as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, dd=doublet of doublets, etc.), integration, and coupling constant(s) in Hertz (Hz). $^{13}C$ NMR data are reported in ppm relative to the solvent signal, $CDCl_3$ (77.0 ppm). Low resolution, electron impact (EI) mass spectral data is presented as follows: mass ion peak (relative intensity). For high-resolution mass spectral data, the sample mass was recorded on a Waters GCT Premier is a high-resolution time-of-flight mass spectrometer using liquid injection field desorption ionization (LIFDI). The analyte was applied to the filament in ethyl acetate and/or dichloromethane. The solvent was allowed to evaporate before ramping to a 12K voltage field and ramping the filament current from zero to 85 mA. All samples ionized at 0-40 mA with peak ion counts ~0-25 mA. Chloropentafluorobenzene was used as an internal standard locking the peak at 201.9605 Da. Data is reported as follows: expected mass, actual mass, error (in mDa).

### Representative Syntheses of Aryl Dithianes




**Representative synthesis using catalytic iodine (2-phenyl-1,3-dithiane).** A modified procedure of Firouzabadi et al was used.[1] To a 1000 mL round bottom flask with a Teflon-coated magnetic stir bar charged with 300 mL of chloroform was added benzaldehyde (10.17 mL, 100.0 mmol) via syringe. Next, propane-1,3-dithiol (12.03 mL, 120 mmol, 1.2 equiv.) was added via syringe. Catalytic $I_2$ (2.60 g, 10 mmol, 0.1 equiv.) dissolved in 100 mL $CHCl_3$ was added in a single portion. The reaction stirred for 3h at room temperature, or until complete consumption of the aldehyde as monitored via (TLC, HPLC). Within 5 minutes a color change from pale yellow to dark red-brown was observed. Upon completion, the iodine was quenched with an aqueous sodium metabisulfite solution (50 mL, 0.4 M) and allowed to stir until the dark red coloration disappeared. The contents were transferred to a 1000 mL separatory funnel and the organic layer was washed sequentially with 2.0 M aqueous NaOH (3 x 75 mL) and brine (1 x 70 mL), and dried over $MgSO_4$. The drying agent was filtered

and the solvent was removed under reduced pressure. A pale yellow solid was recrystallized from isopropanol. A white crystalline solid was isolated and dried under vacuum overnight. 10.64 grams of 2-phenyl-1,3-dithiane (54%) was isolated. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.49 (dd, *J*=8.4, 6.4 Hz, 2H), 7.34 (m, 3H), 5.19 (s, 1 H), 3.09 (t, 2H, *J*=6 Hz), 2.95 (d, 2H, *J*=13.6), 2.20 (m, 1H), 1.97 (m, 1H) $^{13}$C NMR (100 MHz, $CDCl_3$): 139.1, 128.7, 128.4, 127.8, 51.5, 32.1, 25.1.




**Representative synthesis using boron trifluoride etherate (2-(4-thiomethyl)-1,3-dithiane).**[2] An oven-dried 100 mL round bottom flask with a Teflon-coated magnetic stir bar was capped with a septa, flushed with nitrogen and charged with 50 mL of dichloromethane and 1.33 mL 4-methylthiobenzaldehyde (1.52 g, 10 mmol). Next, propane-1,3-dithiol (1.10 mL, 11 mmol, 1.1 equiv.) was added via syringe. The reaction was cooled to 0-5 °C using an ice bath and $BF_3$•$OEt_2$ (0.62 mL, 1.1 equiv.) was added over 15 minutes via syringe. The reaction was removed from the ice bath and stirred for 2-18 h at room temperature, or until complete consumption of starting material as monitored either via TLC or HPLC. The contents were transferred to a 250 mL separatory funnel. The organic layer was washed sequentially with 2.0 M aqueous NaOH (3 x 50 mL) and with brine (1 x 25 mL), transferred to Erlenmeyer flask and dried over $MgSO_4$. The filtrate was transferred to a round bottom flask and solvent was removed under vacuum. A white solid was isolated and this crude product was recrystallized from ethanol or *iso*-propanol. 1.361g of 2-(4-thiomethylphenyl)-1,3-dithiane (56%) was isolated. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, 2H, *J*=8.4 Hz), 7.23 (d, 2H, *J*=8.4 Hz), 5.15 (s, 1 H), 3.09 (t, 2H, *J*=12.2 Hz), 2.93 (d, 2H, *J*=13.6 Hz), 2.49 (s, 3H), 2.19 (m, 1H), 1.99 (m, 1H).

## Title Compounds Synthesis & Characterization

**General procedure for the synthesis of title 2,2-diaryl-1,3-dithianes:** All reactions were prepared at the 1.0 mmol scale in a glovebox using 8-mL screw cap vials with a and fit with a Teflon-coated stir bar. The vial was charged with 1 mmol of the appropriate 2-aryl-1,3-dithiane and 1.0 mmol of the desired aryl bromide. Next, 2.5 mol % $Pd(OAc)_2$ (0.0056g, 0.025 mmol) and 2.5 mol % NiXantphos (0.0136 g, 0.025 mmol) was added to 2.0 mL CPME. Once complete dissolution of the palladium salt and ligand was achieved, the solution was transferred to the reaction vial. Finally 3.0 mL of a 1.0 M solution of KO*t*Bu in CPME was added to the reaction vial. The reaction was capped, removed from the glovebox and allowed to stir on an aluminum block preheated to 80 °C for 24–48 hours as indicated in Table 2.

Upon completion, the reaction was allowed to cool and quenched with $H_2O$ (5 mL). The contents were transferred to a separatory funnel and extracted using $Et_2O$ (3 x 15 mL). The organic layers were combined and washed with brine (1 x 10 mL), and dried over $MgSO_4$. The solvent was removed under vacuum and the resulting crude oil or solid was subjected to flash chromatography.

**Title Compounds:**

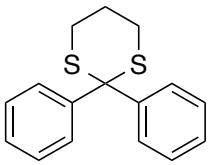


**Table 2, Entry 1: 2,2-diphenyl-1,3-dithiane.** Using the general procedure outlined above, the crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 2% $Et_2O$ in hexanes ($R_f$ = 0.31) and 0.221 g (81%) of an oil that solidified upon standing was isolated. M.p. 110-111 °C (lit: 111-112 °C).[3] IR (neat): 3060, 2927, 2911, 2891, 1480, 1443, 735, 694 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.75 (d, 4H, *J*=7.6 Hz), 7.38 (m, 4H), 7.30 (m, 2H), 2.82 (m, 4H), 2.04 (m, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 142.6, 129.4, 128.4, 127.6, 62.8, 29.4, 24.5 ppm. EI MS, *m/z*: 272 (25), 198 (80), 182 (20), 165 (100), 121 (40), 105 (40), 77 (40), 51 (10). HRMS (LIFDI): calculated, 272.0693; found, 272.0694; error, 0.1 mDa. $^1H$ and $^{13}C$ NMR spectral data was in agreement with literature.[4]

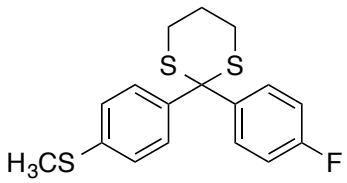


**Table 2, Entry 2: 2-(4'-fluorophenyl)-2-(4''methylphenyl)-1,3-dithiane.** Using the general procedure outlined above, the crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 2% $Et_2O$ in hexanes ($R_f$ = 0.35) and 0.220 g (72%) of an oil that solidified upon standing was isolated. M.p. 81-82 °C. IR (neat): 3060, 2927, 2911, 2892, 1480, 1443, 1280, 1033, 736, 694 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.7-7.5 (overlapping m, 4H), 7.25 (d, 2H, *J*=8.8 Hz), 7.04 (apparent t, 2H, *J*=8.8 Hz), 2.77 (m, 4H), 2.49 (s, 3H), 2.00 (m, 2H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 162.0 (d, $J_{C\text{-}F}$=246 Hz), 139.0, 138.5, 138.3, 131.2 (d, $J_{C\text{-}C\text{-}C\text{-}F}$=8 Hz), 129.8, 126.1, 115.2 (d, $J_{C\text{-}C\text{-}F}$=21 Hz), 61.8, 29.5, 24.4, 15.4 ppm. EI MS, *m/z*: 336 (18), 262 (100), 246 (15), 229 (35), 195 (20), 152 (35), 135 (60), 106 (23), 77 (10). HRMS (LIFDI): calculated, 336.0476; found, 336.0476; error, 1.1 mDa.

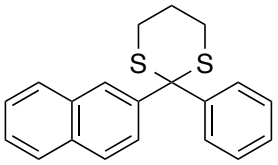


**Table 2, Entry 3: 2-(2'-naphthyl)-2-phenyl -1,3-dithiane.** Using the general procedure outlined above, the crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 3% EtOAc in hexanes ($R_f$ = 0.35) and 0.210 g (65%) of an oil that solidified upon standing was isolated. M.p. 118-120 °C. IR (neat): 3050, 2906, 1612, 1578, 1412, 1116, 740, 696, 477 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.85 (overlapping m, 4H), 7.70 (d, 2H, *J*=8.4 Hz), 7.51 (t, 2H, *J*=4.8 Hz), 7.32 (overlapping m, 3H), 2.85 (m, 4H), 2.06 (m, 2H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): 142.8, 139.7, 133.1, 132.6, 129.2, 129.0, 128.5, 128.4, 128.3, 128.2, 127.8, 127.4, 127.3, 126.5, 126.2, 62.8, 29.8, 29.4, 24.5 ppm. EI MS, *m/z*: 322 (25) 248 (90), 215 (100), 171 (18), 121 (12), 77 (10). HRMS (LIFDI): calculated, 322.0850; found, 322.0841; error, 0.9 mDa.

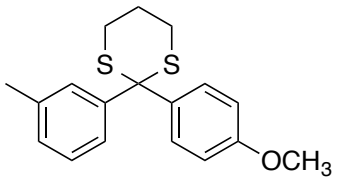


**Table 2, Entry 4: 2-(3'methylphenyl)-2-(4''-methoxyphenyl)-1,3-dithiane.** Using the general procedure outlined above, though allowing the reaction to age for 48 h, the crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 2% $Et_2O$ in hexanes ($R_f$ = 0.29) and 0.221 g (81%) of an oil that solidified upon standing was isolated. M.p. 75-76 °C. IR (neat): 3011, 2946, 2896, 2835, 1599, 1506, 1459, 1244, 1172, 1029, 768, 677 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.75 (d, 4H, *J*=7.6 Hz), 7.38 (m, 4H), 7.30 (m, 2H), 2.82 (m, 4H), 2.04 (m, 2H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 142.6, 129.4, 128.4, 127.6, 62.8, 29.4, 24.5 ppm. EI MS, *m/z*: 316 (20), 242 (100), 226 (33), 209 (50), 195 (33), 165 (15), 152 (15), 135 (90), 119 (15), 106 (15), 91 (10), 77 (10). HRMS (LIFDI): calculated, 316.0956; found, 316.0969; error, 1.3 mDa.

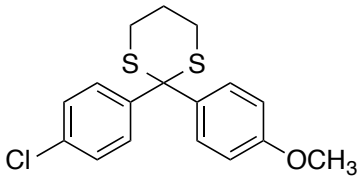


**Table 2, Entry 5: 2-(4'chlorophenyl)-2-(4''-methoxyphenyl)-1,3-dithiane.** Using the general procedure outlined above, the crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 15% $Et_2O$ in hexanes ($R_f$ = 0.36) and 0.290 g (86%) of an oil that solidified upon standing was isolated. M.p. 92-94 °C. IR (neat): 3010, 2926, 2897, 2835, 1904, 1604, 1505, 1252, 1175, 1029, 813, 579 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.58 (d, 2H, *J*=8.8 Hz), 7.34 (d, 2H, *J*=8.8 Hz), 7.34 (d, 2H, *J*=8.8 Hz), 6.89 (d, 2H, *J*=9.2 Hz), 3.83 (s, 3H), 2.78 (m, 3H), 2.01 (m, 2H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 159.0, 141.5, 134.3,

133.4, 131.0, 130.5, 128.5, 113.8, 61.8, 55.3, 29.5, 42.4 ppm. EI MS, *m/z*: 336 (25), 262 (100), 246 (25), 229 (25), 215 (33), 183 (60), 151 (33), 123 (25), 95 (25). HRMS (LIFDI): calculated, 336.0409; found, 336.0434; error, 2.5 mDa.

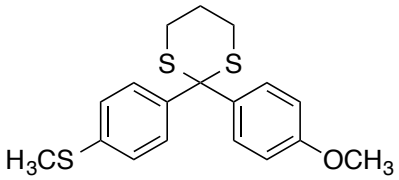



**Table 2, Entry 6: 2-(4'methylthiophenyl)-2-(4''-methoxyphenyl)-1,3-dithiane.** Using the general procedure outlined above, the crude reaction mixture was filtered through celite and 0.342 g (98%) of a white solid was isolated. M.p. 104-106 °C. IR (neat): 3011, 2992, 2947, 2901, 2829, 1601, 1504, 1255, 1241, 1176, 1028, 813, 579 $cm^{-1}$. $^{1}H$ NMR (400 MHz, $CDCl_3$): δ 7.68 (d, 2H, *J*=8.0 Hz), 7.60 (d, 2H, *J*=8.8 Hz), 7.24 (d, 2H, *J*=8.8 Hz), 6.88 (d, 2H, *J*=8.8), 3.81 (s, 3H), 2.78 (m, 4H), 2.50 (s, 3H) 2.00 (m, 2H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 158.9, 139.5, 138.0, 134.6, 130.5, 130.0, 126.1, 113.7, 62.1, 55.3, 29.5, 24.5, 15.5 ppm. EI MS, *m/z*: 348 (20), 274 (100), 242 (50), 227 (55), 195 (15), 152 (30), 108 (10). HRMS (LIFDI): calculated, 348.0676; found, 348.0691; error, 1.5 mDa.

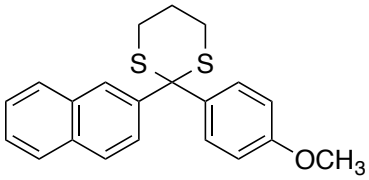



**Table 2, Entry 7: 2-(2'naphthyl)-2-(4''-methoxyphenyl)-1,3-dithiane.** Using the general procedure outlined above, the crude reaction mixture filtered through a plug of celite and 0.320 g (91%) of a colorless oil was isolated which never solidifies. IR (neat): 3053, 2902, 2832, 2056, 1602, 1503, 1248, 1174, 1031, 785, 476 $cm^{-1}$. $^{1}H$ NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.90-7.83 (overlapping signals, 4H), 7.57 (d, 2H, *J*=8.0 Hz), 7.50 (m, 2H), 6.86 (d, 2H, *J*=8.0 Hz), 3.82 (s, 3H), 2.84 (m, 4H), 2.04 (m, 2H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 159.0, 139.9, 134.9, 133.1, 132.6, 130.5, 129.0, 128.5, 128.2, 127.4, 127.3, 126.5, 126.2, 113.7, 62.4, 55.3, 29.5, 24.5 ppm. EI MS, *m/z*: 352 (30), 278 (100), 245 (50), 202 (40), 171 (10), 151 (15). HRMS (LIFDI): calculated, 352.0956; found, 352.0932; error, 2.4 mDa.

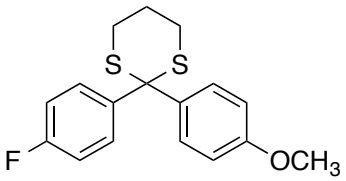



**Table 2, Entry 8: 2-(4'-fluorophenyl)-2-(4''methoxylphenyl)-1,3-dithiane.** Using the general procedure outlined above, the crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 30% $Et_2O$ in hexanes ($R_f$ = 0.36) and 0.265 g (83%) of an oil that solidified upon standing was isolated.

M.p. 103-106 °C. IR (neat): 3006, 2827, 2896, 2832, 2057, 1597, 1499, 1254, 1176, 1032, 780, 589 $cm^{-1}$. $^{1}H$ NMR (400 MHz, $CDCl_3$): δ 7.73 (m, 2H), 7.63 (d, 2H, *J*=8.8 Hz), 7.05 (m, 2H), 6.90 (d, 2H, *J*=8.8), 3.82 (s, 3H), 2.80 (m, 4H), 2.00 (m, 2H) $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 162.0 (d, $J_{C\text{-}F}$=246 Hz), 159.0, 138.8, 134.4, 121.3 (d, $J_{C\text{-}C\text{-}C\text{-}F}$=8 Hz), 130.6, 115.1 (d, $J_{C\text{-}C\text{-}F}$=21 Hz), 113.8, 61.83, 55.3, 29.5, 24.5 ppm. EI MS, *m/z*: 320 (20), 259 (5), 246 (100), 230 (40), 213 (50), 170 (30), 135 (90), 123 (10), 94 (10), 77 (8). HRMS (LIFDI): calculated, 320.0705; found, 320.0727; error, 2.2 mDa.

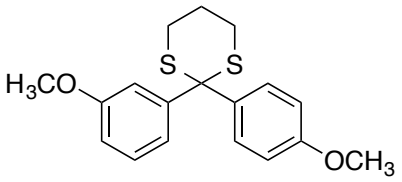



**Table 2, Entry 9: 2-(3'methoxyphenyl)-2-(4''-methoxyphenyl)-1,3-dithiane.** Using the general procedure outlined above, but allowing the reaction to heat at 80 °C for 48 hours, the crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 20% $Et_2O$ in hexanes ($R_f$ = 0.29) and 0.238 g (72%) of an oil that solidified upon standing was isolated. M.p. 96-98 °C. IR (neat): 3009, 2948, 2898, 2831, 2056, 1601, 1505, 1237, 1166, 1030, 1764, 577, 532 $cm^{-1}$. $^{1}H$ NMR (400 MHz, $CDCl_3$): δ 7.60 (d, 2H, *J*=8.4 Hz), 7.37 (d, 2H, *J*=9.2 Hz), 7.30 (t, 1H, *J*=8 Hz), 6.87 (d, 2H, *J*=7.6 Hz), 3.82 (s, 6H), 2.81 (d, 4H, 5.6 Hz), 2.01 (m, 2H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): 159.8, 158.9, 144.3, 134.7, 130.5, 129.4, 121.9, 115.4, 113.6, 112.9, 62.4, 55.3, 29.6, 24.5 ppm; 15 signals expected, 14 observed). EI MS, *m/z*: 332 (35), 258 (100), 225 (55), 151 (25). HRMS (LIFDI): calculated, 332.0905; found, 332.0913; error, 0.8 mDa.

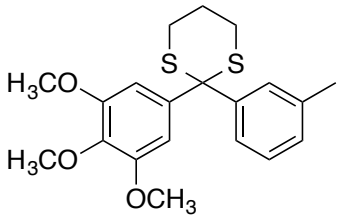



**Table 2, Entry 10: 2-(3',4',5'-trimethoxyphenyl)-2-(3''-methylphenyl)-1,3-dithiane.** Using the general procedure outlined above, the crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 35% $Et_2O$ in hexanes ($R_f$ = 0.30) and 0.305 g (81%) of an oil that solidified upon standing was isolated. M.p. 100-103 °C. IR (neat): 3004, 2995, 2946, 2895, 1580, 1499, 1404, 1230, 1124, 1003, 773, 697 $cm^{-1}$. $^{1}H$ NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.40 (d, 2H, *J*=7.6 Hz), 7.22 (t, 1H, *J*=7.6 Hz), 7.06 (m, 3H), 3.88 (s, 3H), 3.81 (s, 3H), 2.82 (m, 4H) 2.36 (s, 3H), 2.02 (m, 2H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 152.9, 142.6, 138.0, 137.8, 137.2, 129.6, 128.6, 128.2, 126.2, 107.1, 63.2, 60.8, 56.1, 29.6, 24.4, 21.6 ppm. EI MS, *m/z*: 376 (50), 302 (100), 271 (20), 255 (10), 211 (10), 135 (10), 155 (5), 91 (5). HRMS (LIFDI): calculated, 376.1167; found, 376.1155; error, 1.2 mDa.

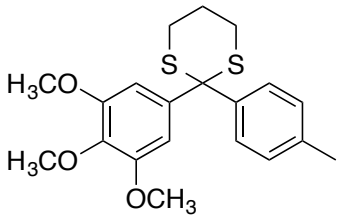



**Table 2, Entry 11: 2-(3',4',5'-trimethoxyphenyl)-2-(4''-methylphenyl)-1,3-dithiane.** Using the general procedure outlined above, the crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 35% $Et_2O$ in hexanes ($R_f$ = 0.30) and 0.279 g (74%) of a white solid was isolated. M.p. 103-104 °C. IR (neat): 3004, 2962, 2908, 2828, 1930, 1584, 1501, 1412, 1239, 1120, 1004, 781, 509 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.54 (d, 2H, *J*=8.4), 7.15 (d, 2H, *J*=8.0 Hz), 3.88 (s, 3H), 3.81 (s, 6H), 3.88 (s, 3H), 2.81 (m, 4H), 2.34 (s, 3H), 2.01 (m, 2H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 152.9, 139.7, 137.9, 137.5, 137.2, 129.1, 129.0, 107.0, 63.1, 60.8, 56.1, 29.6, 24.4, 21.0 ppm. EI MS, *m/z*: 376 (50), 302 (100), 271 (20), 255 (10), 211 (5), 135 (10), 106 (5). HRMS (LIFDI): calculated, 376.1167; found, 376.1169; error, 0.2 mDa.

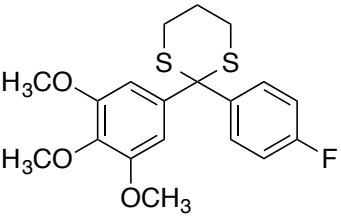



**Table 2, Entry 12: 2-(3',4',5'-trimethoxyphenyl)-2-(4''-fluorophenyl)-1,3-dithiane.** Using the general procedure outlined above, the crude reaction mixture was filtered through celite. After removal of solvent, 0.354 g (93%) of an analytically pure, white solid was isolated without further purification. M.p. 133-134 °C. IR (neat): 3008, 2930, 2904, 2828, 1583, 1499, 1407, 1219, 1120, 1006, 781, 684, 560 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.54 (m, 2H), 7.01 (m, 4H), 3.87 (s, 3H), 3.80 (s, 6H), 2.80 (m, 4H), 2.01 (m, 2H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 162.0 (d, $J_{C\text{-}F}$=246 Hz), 153.0, 138.5, 137.6, 137.3, 131.1 (d, $J_{C\text{-}C\text{-}C\text{-}F}$=8 Hz), 115.1 (d, $J_{C\text{-}C\text{-}F}$ =21 Hz), 106.9, 62.6, 60.8, 56.2, 29.6, 24.3 ppm. EI MS, *m/z*: 380 (50), 306 (100), 275 (20), 244 (10), 201 (10), 139 (15), 106 (5). HRMS (LIFDI): calculated, 380.0916; found, 390.0917; error, 0.1 mDa.

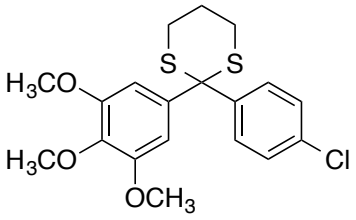



**Table 2, Entry 13: 2-(3',4',5'-trimethoxyphenyl)-2-(4''-chlorophenyl)-1,3-dithiane.** Using the general procedure outlined above, the crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 35% $Et_2O$ in hexanes ($R_f$ = 0.29) and 0.359 g (90%) of an oil that solidified upon standing was isolated. M.p. 124-127 °C. IR (neat): 3004, 2931, 2828, 1928, 1582, 1410, 1120, 1005, 736, 679, 479 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.60 (d, 2H, *J*=8.8), 7.27 (d, 2H, *J*=8.4), 6.98 (s, 2H), 3.84 (s, 3H), 3.77 (s, 6H),

2.74 (m, 4H), 1.96 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 153.0, 141.3, 137.4, 133.4, 130.8, 128.5, 106.8, 62.5, 60.8, 56.1, 29.5, 24.2 ppm; 13 signals expected, 12 observed. EI MS, *m/z*: 396 (33), 322 (100), 291 (10), 275 (5), 155 (10). HRMS (LIFDI): calculated, 396.0621; found, 396.0632; error, 1.1 mDa.

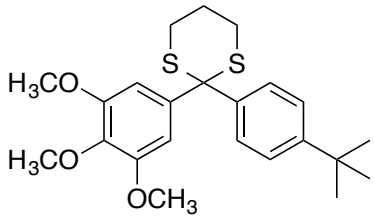



**Table 2, Entry 14: 2-(3',4',5'-trimethoxyphenyl)-2-(4''-*tert*-butylphenyl)-1,3-dithiane.** Using the general procedure outlined above, but allowing the reaction to heat at 80 °C for 48 hours, the crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 30% $Et_2O$ in hexanes ($R_f$ = 0.36) and 0.254 g (61%) of a white solid was isolated. M.p. 190-193 °C. IR (neat): 3004, 2940, 2902, 2826, 1586, 1504, 1236, 1124, 1013, 787, 689 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.53 (dd, 2H, *J*=8, 2.8 Hz), 7.35 (d, 2H, *J*=8.8 Hz), 7.11 (s, 2H), 2.82 (m, 4H), 2.04 (m, 2H) 1.31 (s, 9H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 152.9, 150.7, 139.8, 137.7, 137.1, 128.6, 125.2, 107.2, 63.0, 60.8, 56.1, 34.5, 31.3, 29.6, 24.4 ppm. EI MS, *m/z*: 418 (22), 344 (100) 313 (15). HRMS (LIFDI): calculated, 418.1636; found, 418.1635; error, 0.1 mDa.

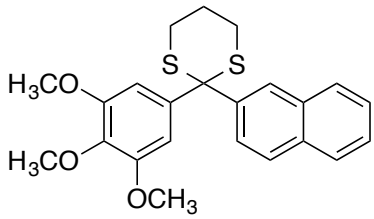



**Table 2, Entry 15: 2-(3',4',5'-trimethoxyphenyl)-2-(2''-naphthyl)-1,3-dithiane.** Using the general procedure outlined above, the crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 30% $Et_2O$ in hexanes ($R_f$ = 0.30) and 0.253 g (61%) of a glassy solid was isolated. Repeated attempts were made at removing trace hydrocarbon impurities (pentanes, hexanes, heptanes), but the title compound could never be cleanly isolated without these small impurities. IR (neat): 3004, 2930, 2906, 2830, 1958, 1382, 1408, 1320, 1233, 1122, 1004, 754, 679, 562 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.86 (m, 4H), 7.51 (t, 2H, *J*=4.4 Hz), 7.05 (s, 2H), 3.90 (s, 3H), 3.80 (s, 6H), 2.87 (m, 4H), 2.06 (m, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): 152.9, 139.7, 137.9, 137.3, 133.0, 132.6, 128.7, 128.5, 128.3, 128.1, 127.4, 127.1, 126.9, 126.5, 126.2, 107.8, 106.9, 63.2, 60.9, 56.4, 56.2, 29.6, 24.4 ppm. EI MS, *m/z*: 412 (25), 338 (100) 307 (15). HRMS (LIFDI): calculated, 412.1167; found, 412.1165; error, 0.2 mDa.

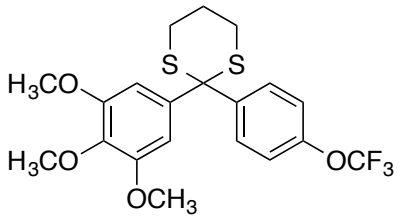



**Table 2, Entry 16: 2-(3',4',5'-trimethoxyphenyl)-2-(4''-trifluoromethoxyphenyl)-1,3-dithiane.** Using the general procedure outlined above, but allowing the reaction to age for 48h, the crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 30% $Et_2O$ in hexanes ($R_f$ = 0.25) and 0.322 g (72%) of an oil that solidified upon standing was isolated. M.p. 102-103 °C. IR (neat): 3001, 2954, 2832, 1922, 1582, 1504, 1408, 1203, 1165, 1122, 1002, 782, 691, 508 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.70 (d, 2H, *J*=9.2 Hz), 7.19 (d, 2H, *J*=9.2 Hz), 3.90 (s, 3H), 3.82 (s, 6H), 2.84 (m, 4H), 2.06 (m, 2H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 153.0, 148.5, 141.5, 137.4, 137.2, 130.8, 120.59, 120.43 (q, $J_{C-F}$=256 Hz), 106.9, 62.5, 60.8, 55.9, 29.6, 24.2 ppm. EI MS, *m/z*: 446 (25), 372 (100), 341 (10) 205 (10). HRMS (LIFDI): calculated, 446.0833; found, 446.0855; error, 2.2 mDa.

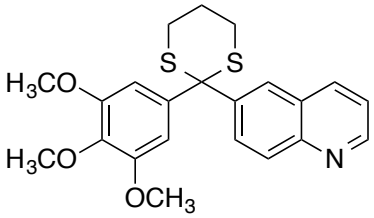



**Table 2, Entry 17: 2-(3',4',5'-trimethoxyphenyl)-2-(6''-quinolyl)-1,3-dithiane.** Using the general procedure outlined above, but allowing the reaction to age for 48h, the crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 50% $Et_2O$ in hexanes ($R_f$ = 0.35) and 0.124 g (30%) of an oil that eventually solidified to a glassy solid was isolated. IR (neat): 3005, 2929, 2904, 2832, 1582, 1409, 1232, 1123, 1003, 730, 479 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.82 (m, 1H), 8.05 (m, 4H), 7.31, (m, 1H), 6.97 (s, 2H), 3.80 (3, 3H), 3.70 (s, 6H), 2.76 (m, 4H), 1.94 (m, 2H) $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 153.0, 150.8, 147.4, 140.9, 137.4, 136.6, 130.7, 129.3, 128.5, 127.7, 121.4, 106.9, 62.8, 60.7, 56.1, 29.5, 24.2 ppm; 17 signals observed, 18 expected. EI MS, *m/z*: 413 (25), 339 (100), 308 (20), 292 (15), 207 (25), 172 (15). HRMS (LIFDI): calculated, 413.1119; found, 413.1091; error, 2.8 mDa.

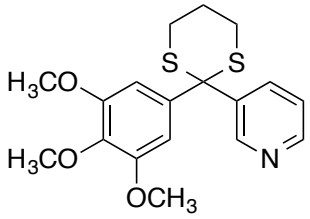



**Table 2, Entry 18: 2-(3',4',5'-trimethoxyphenyl)-2-(3''-pyridyl)-1,3-dithiane.** Using the general procedure outlined above, the crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 12% $Et_2O$ in hexanes ($R_f$ = 0.30) and 0.023 g (6%) of an amber oil was isolated. IR (neat): 3005, 2918,

2850, 1923, 1581, 1410, 1233, 1126, 752, 532 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.86 (m, 1H), 8.55 (m, 1H), 8.02, (d, 1H, *J*=8.0 Hz), 7.31 (m, 1H), 7.00 (s, 2H), 3.87 (s, 3H), 3.80 (s, 6H), 2.82 (m, 4H), 2.04 (m, 2H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 153.1, 150.4, 148.5, 137.6, 137.1, 136.6, 106.8, 60.9, 60.8, 56.2, 29.4, 24.1 ppm; 12 signals observed, 14 expected. EI MS, *m/z*: 363 (30), 289 (100), 258 (25), 242 (10), 212 (10), 167 (10), 122 (12). HRMS (LIFDI): calculated, 363.0963; found, 363.0948; error, 1.5 mDa.

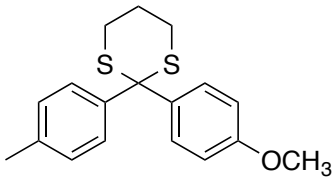



**Table 2, Entry 19: 2-(4'-methylphenyl)-2-(4''-methoxyphenyl)-1,3-dithiane.** Using the general procedure outlined above, but substituting 1.2 equivalents of 4-iodoanisole in lieu of the aryl bromide and running the reaction at 60 °C, the crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 15% $Et_2O$ in hexanes ($R_f$ = 0.30) and 0.222 g (67%) of an oil that solidified upon standing was isolated. M.p. 96-99 °C. IR (neat): 3005, 2940, 2898, 2835, 1915, 1602, 1500, 1247, 1175, 1032, 778, 587, 511 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.62 (m, 4H), 7.18 (d, 2H, *J*=8.4 Hz), 6.89 (d, 2H, *J*=8.8 Hz), 2.80 (m, 4H), 2.38 (s, 3H), 2.02 (m, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 158.8, 139.8, 137.3, 134.8, 130.6, 129.3, 129.1, 113.6, 62.2, 55.3, 29.5, 24.6, 21.0 ppm. EI MS, *m/z*: 316 (20), 242 (100), 226 (33), 209 (50), 195 (33), 165 (15), 152 (15), 135 (90), 119 (15), 106 (15), 91 (10), 77 (10). HRMS (LIFDI): calculated, 316.0956; found, 316.0960; error, 0.4 mDa.

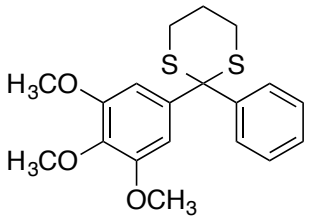



**Table 2, Entry 20: 2-(3',4',5'-trimethoxyphenyl)-2-phenyl-1,3-dithiane.** Using the general procedure outlined above, the crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 25% $Et_2O$ in hexanes ($R_f$ = 0.35) and 0.164 g (63%) of an off-white solid was isolated. M.p. 127-128 °C. IR (neat): 3063, 3007, 2922, 2824, 1582, 1505, 1444, 1408, 1234, 1122, 1014, 716, 627 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.70 (d, 2H, *J*=7.6 Hz), 7.37 (m, 2H), 7.30 (m, 1H, overlaps with $CDCl_3$), 7.03 (s, 2H), 3.89 (s, 3H), 3.81 (s, 6H), 2.83 (m, 4H), 2.04 (m, 2H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 152.9, 142.6, 137.9, 137.3, 129.2, 128.4, 127.7, 107.0, 63.2, 60.8, 56.1, 29.6, 24.4 ppm. EI MS, *m/z*: 362 (31), 288 (100), 257 (12), 241 (10), 211 (10), 183 (15), 121 (20), 77 (10). HRMS (LIFDI): calculated, 362.1010; found, 362.1039; error, 2.9 mDa.

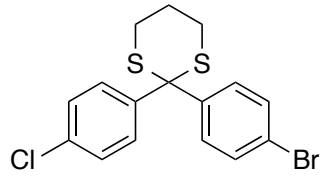



**Table 2, Entry 21: 2-(4'-chlorophenyl)-2-(4'-bromophenyl)-1,3-dithiane.** Using the general procedure outlined above (one equivalent of 1,4-dibroobenzene was used), the crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 5% $Et_2O$ in hexanes ($R_f$ = 0.31) and 0.274 g (71%) of an off-white solid was isolated. M.p. 112-114 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, 2H, *J*=8.8 Hz), 7.59 (d, 2H, *J*=8.8 Hz), 7.49 (d, 2H, *J*=8.8 Hz), 7.33 (d, 2H, *J*=8.8 Hz), 2.78 (m, 4H), 2.03 (m, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 141.4, 140.8, 133.8, 131.7, 131.2, 130.8, 128.7, 122.1, 61.7, 29.4, 24.2 ppm. EI MS, *m/z*: 388 (5) 386 (20), 384 (15), 314 (25), 312 (100), 310 (80), 277 (22), 231 (20), 199 (52), 155 (35), 120 (15). HRMS (LIFDI): calculated $^{79}$Br, 383.9409; found, 383.9392; error, 1.7 mDa; calculated $^{81}$Br, 385.9388; found, 385.9384; error, 0.4 mDa.

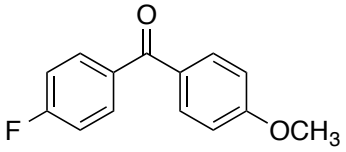



**Table 3, Entry 1: 4-fluoro-4'-methoxybenzophenone.** The first step was completed according to the general procedure whereupon the crude reaction mixture was transferred to a 20 mL glass vial with 1 g of decolorizing carbon and stirred overnight. The reaction was filtered and solvent was removed under pressure. To the 20 mL vial with the oil and Teflon-coated stirbar was added 10 mL MeCN and 5 mL $NaHCO_3$. $I_2$ (1.0152 g, 4 equiv.) was then added and the reaction was stirred at room temperature overnight. The reaction was quenched with 10 mL of $Na_2S_2O_5$:$NaHCO_3$ (1:1). The compound was extracted with EtOAc, dried over $MgSO_4$ and the solvent was removed under vacuum. The crude oil was purified using flash chromatography (silica gel, 60Å) with 5% EtOAc in heptanes ($R_f$ = 0.30). The pale yellow oil was isolated and dried under vacuum overnight to yield 0.156 g (66%) an off-white solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.81 (dt, 2H, $J_1$=8.8 Hz, $J_2$=2.8 Hz), 7.16 (t, 2H, *J*=8.8 Hz), 6.991 (d, 2H, *J*= 8.8 Hz), 3.90 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 194.1, 165.0 (d, $J_{C-F}$ 250 Hz), 163.3, 134.4 (d, $J_{C-F}$ =3 Hz), 132.3, 132.2, 130.0, 115.3 (d, $J_{C-F}$ =22 Hz) 113.6, 55.5 ppm. EI MS, *m/z*: 230 (95), 199 (15), 135 (100), 123 (42), 107 (12), 95 (38), 77 (22), 64 (10). Spectral data was in agreement with literature.[5]

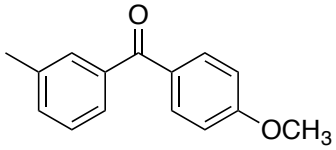



**Table 3, Entry 2: 3-methyl-4'-methoxybenzophenone.** The first step was completed according to the general procedure whereupon the crude reaction mixture was transferred to a 20 mL glass vial with 1 g of decolorizing

carbon and stirred overnight. The reaction was filtered and solvent was removed under pressure. To the 20 mL vial with the oil and Teflon-coated stirbar was added 10 mL MeCN and 5 mL $NaHCO_3$. $I_2$ (1.0152 g, 4 equiv.) was then added and the reaction was stirred at room temperature overnight. The reaction was quenched with 10 mL of $Na_2S_2O_5$:$NaHCO_3$ (1:1). The compound was extracted with EtOAc, dried over $MgSO_4$ and the solvent was removed under vacuum. The crude oil was purified using flash chromatography (silica gel, 60Å) with 5% diethyl ether in heptanes ($R_f$ = 0.29). The pale yellow oil was isolated and dried under vacuum overnight to yield 0.118 g (52%). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, 2H, *J*=8.8 Hz), 7.59 (s, 1H), 7.54 (m, 1H), 7.38 (m, 2H), 6.98 (d, 2H, *J*=8.8 Hz), 3.90 (s, 3H), 2.43 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 195.8, 163.2, 138.3, 138.0, 132.7, 130.3, 130.2, 128.0, 127.0, 113.5, 55.5, 21.4 ppm. EI MS, *m/z*: 226 (90), 211 (15), 135 (100), 119 (27), 107 (13), 91 (28), 77 (26), 65 (17). Spectral data was in agreement with literature.[6]

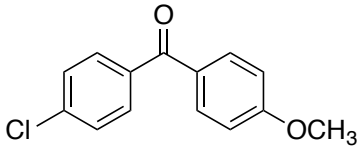



**Table 3, Entry 3: 4-chloro-4'-methoxybenzophenone.** The first step was completed according to the general procedure whereupon the crude reaction mixture was transferred to a 20 mL glass vial with 1 g of decolorizing carbon and stirred overnight. The reaction was filtered and solvent was removed under pressure. To the 20 mL vial with the oil and Teflon-coated stirbar was added 10 mL MeCN and 5 mL $NaHCO_3$. $I_2$ (1.0152 g, 4 equiv.) was then added and the reaction was stirred at room temperature overnight. The reaction was quenched with 10 mL of $Na_2S_2O_5$:$NaHCO_3$ (1:1). The compound was extracted with EtOAc, dried over $MgSO_4$ and the solvent was removed under vacuum. The crude oil was purified using flash chromatography (silica gel, 60Å) with 20% diethyl ether in heptanes ($R_f$ = 0.33). The oil was isolated and dried under vacuum overnight and 0.136 g (55%) of a white solid was isolated. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, 2H, *J*=8,8 Hz), 7.71 (d, 2H, *J*=8,8 Hz), 7.45 (d, 2H, *J*=8,8 Hz), 6.98 (d, 2H, *J*=8,8 Hz), 3.91 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 194.2, 163.4, 138.3, 136.6, 132.4, 131.2, 129.8, 128.5, 113.7, 55.5 ppm. EI MS, *m/z*: 246 (30), 248 (10), 211 (8), 175 (5), 135 (100), 111 (15), 92 (12), 77 (15), 64 (7). Spectral data was in agreement with literature.[4]

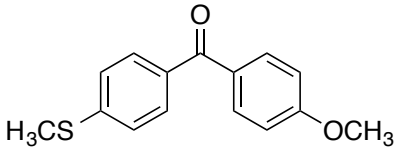



**Table 3, Entry 4: 4-methylthio-4'-methoxybenzophenone.** The first step was completed according to the general procedure whereupon the crude reaction mixture was transferred to a 20 mL glass vial with 1 g of decolorizing carbon and stirred overnight. The reaction was filtered and solvent was removed under pressure. To the 20 mL vial with the oil and Teflon-coated stirbar was added 10 mL MeCN and 5 mL $NaHCO_3$. $I_2$ (1.0152 g, 4 equiv.) was then added and the reaction was stirred at room temperature overnight. The reaction was quenched with 10 mL of $Na_2S_2O_5$:$NaHCO_3$ (1:1). The compound was extracted with EtOAc, dried over

$MgSO_4$ and the solvent was removed under vacuum. The crude oil was purified using flash chromatography (silica gel, 60Å) with 20% diethyl ether in heptanes ($R_f$ = 0.33). The oil was isolated and dried under vacuum overnight and 0.168 g (65%) of a white solid was isolated. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, 2H, *J*=8.8 Hz), 7.67 (d, 2H, *J*=8.8 Hz), 7.24 (d, 2H, *J*=8.8 Hz), 6.92 (d, 2H, *J*=8.8 Hz), 3.83 (s, 3H), 2.48 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 194.4, 163.1, 144.5, 134.3, 132.3, 130.34, 130.29, 124.8, 113.6, 55.4, 14.8 ppm. EI MS, *m/z*: 258 (95), 227 (10), 211 (33), 151 (58), 135 (100), 115 (10), 92 (15), 77 (18). Spectral data was in agreement with literature.[7]

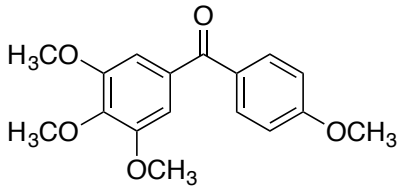



**Table 3, Entry 5: 3,4,5-trimethoxy-4'-methoxybenzophenone.** The first step was completed according to the general procedure whereupon the crude reaction mixture was transferred to a 20 mL glass vial with 1 g of decolorizing carbon and stirred overnight. The reaction was filtered and solvent was removed under pressure. To the 20 mL vial with the oil and Teflon-coated stirbar was added 10 mL MeCN and 5 mL $NaHCO_3$. $I_2$ (1.0152 g, 4 equiv.) was then added and the reaction was stirred at room temperature overnight. The reaction was quenched with 10 mL of $Na_2S_2O_5$:$NaHCO_3$ (1:1). The compound was extracted with EtOAc, dried over $MgSO_4$ and the solvent was removed under vacuum. The crude oil was purified using flash chromatography (silica gel, 60Å) with 20% diethyl ether in heptanes ($R_f$ = 0.36). The oil was isolated and dried under vacuum overnight and 0.217 g (72%) of a white solid was isolated. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, 2H, *J*=9.2 Hz), 7.04 (s, 2H), 6.98 (d, 2H, *J*=9.2 Hz), 3.95 (s, 3H), 3.91 (s, 3H), 3.89 (s, 6H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 194.6, 163.1, 152.8, 141.6, 133.3, 132.4, 130.3, 113.6, 107.5, 60.9, 56.3, 55.5 ppm. EI MS, *m/z*: 302 (100), 285 (20), 269 (22), 259 (31), 231 (12), 195 (28), 135 (80), 107 (15), 77 (21). Spectral data was in agreement with literature.[8]

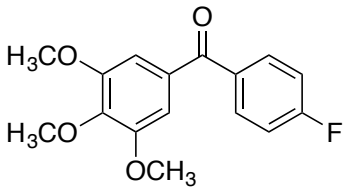



**Table 3, Entry 6: 4-fluoro-3',4',5'-trimethoxybenzophenone.** The first step was completed according to the general procedure whereupon the crude reaction mixture was transferred to a 20 mL glass vial with 1 g of decolorizing carbon and stirred overnight. The reaction was filtered and solvent was removed under pressure. To the 20 mL vial with the oil and Teflon-coated stirbar was added 10 mL MeCN and 5 mL $NaHCO_3$. $I_2$ (1.0152 g, 4 equiv.) was then added and the reaction was stirred at room temperature overnight. The reaction was quenched with 10 mL of $Na_2S_2O_5$:$NaHCO_3$ (1:1). The compound was extracted with EtOAc, dried over

$MgSO_4$ and the solvent was removed under vacuum. The crude oil was purified using flash chromatography (silica gel, 60Å) with 20% diethyl ether in heptanes ($R_f$ = 0.37). The oil was isolated and dried under vacuum overnight and 0.217 g (72%) of a white solid was isolated. M.p. 85-86 °C. IR (neat): 3061, 3013, 2947, 2835, 1651, 1579, 1408, 1329, 1123, 757, 610 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, 2H, $J_1$= 8.8 Hz, $J_2$=5.6 Hz), 7.10 (apparent t, 2H, $J$=8.4 Hz), 6.98 (s, 2H), 3.87 (s, 3H), 3.81 (s, 6H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 194.1, 165.2 (d, $J_{C-F}$=253 Hz), 152.9, 142.1, 134.0, 133.9, 132.3 (d, $J_{C-C-C-F}$=9 Hz), 115.3 (d, $J_{C-C-F}$=23 Hz), 115.2, 107.6, 60.8, 56.2 ppm. EI MS, *m/z*: 290 (100), 275 (35), 219 (15), 195 (18), 123 (40), 95 (20). HRMS (LIFDI): calculated, 290.0954; found, 290.0976; error, 2.2 mDa.

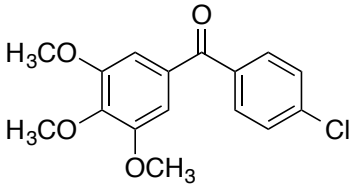



**Table 3, Entry 7: 4-chloro-3',4',5'-trimethoxybenzophenone.** The first step was completed according to the general procedure whereupon the crude reaction mixture was transferred to a 20 mL glass vial with 1 g of decolorizing carbon and stirred overnight. The reaction was filtered and solvent was removed under pressure. The filtrate was transferred to a vial, diluted with EtOAc, and stirred with 1 g of decolorizing carbon overnight. Next, the crude reaction mixture was filtered through celite and the solvent was removed under vacuum. To this crude oil was added $Fe(acac)_3$ (0.177 g, 0.50 mmol), KI (0.830 g, 5 mmol) and 15 mL EtOAc and 15 mL $H_2O$. 30 % $H_2O_2$ (20 mL) was added dropwise with stirring over 1 hour. The reaction mixture was allowed to stir overnight. The mixture was quenched with sodium thiosulfate, extracted with EtOAc (3 x 20 mL), washed with brine (1 x 15 mL), dried over $MgSO_4$ and the solvent was removed under vacuum. The crude oil was purified using column flash chromatography (silica gel, 60Å) with 30% EtOAc in heptanes ($R_f$ = 0.29) to yield 0.124 g (40 %) of a white solid. M.p. 101-102 °C. IR (neat): 3064, 3007, 2949, 2835, 1924, 1652, 1380, 1330, 1233, 1127, 990, 832, 1751 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.72 (d, 2H, $J$=6.4 Hz), 7.44 (d, 2H, $J$=8.8 Hz), 7.02 (s, 2H), 3.92 (s, 3H), 3.85 (s, 6H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 194.4, 152.9, 142.3, 138.6, 136.1, 132.2, 131.2, 128.6, 107.7, 60.9, 56.3 ppm. EI MS, *m/z*: 306 (100), 291 (30), 235 (10), 195 (25), 139 (40), 111 (10), 75 (5). HRMS (LIFDI): calculated, 306.0659; found, 306.0677; error, 1.8 mDa.

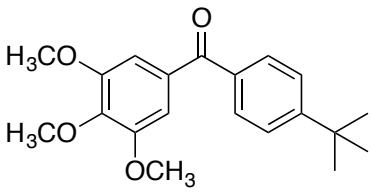



**Table 3, Entry 8: 4-*tert*-butyl-3',4',5'-trimethoxybenzophenone.** The first step was completed according to the general procedure whereupon the crude reaction mixture was transferred to a 20 mL glass vial with 1 g of decolorizing carbon and stirred overnight. The reaction was filtered and solvent was removed under pressure.

The filtrate was transferred to a vial, diluted with EtOAc, and stirred with 1 g of decolorizing carbon overnight. Next, the crude reaction mixture was filtered through celite and the solvent was removed under vacuum. To this crude oil was added $Fe(acac)_3$ (0.177 g, 0.50 mmol), KI (0.830 g, 5 mmol) and 15 mL EtOAc and 15 mL $H_2O$. 30 % $H_2O_2$ (20 mL) was added dropwise with stirring over 1 hour. The reaction mixture was allowed to stir overnight. The mixture was quenched with sodium thiosulfate, extracted with EtOAc (3 x 20 mL), washed with brine (1 x 15 mL), dried over $MgSO_4$ and the solvent was removed under vacuum. The crude oil was purified using column flash chromatography (silica gel, 60Å) with 20% EtOAc in heptanes ($R_f$ = 0.31) to yield 0.136 g (41 %) of a white solid. M.p. 90-91 °C. IR (neat): 3003, 2954, 2871, 2828, 1643, 1581, 1412, 1330, 1118, 1016, 767, 601 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.79 (d, 2H, *J*=8.4 Hz), 7.52 (d, 2H, *J*=8.8 Hz), 7.10 (s, 2H), 3.96 (s, 3H), 3.91 (s, 6H), 1.40 (s, 9H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 195.3, 156.0, 152.9, 141.9, 134.9, 132.9, 130.0, 125.2, 107.7, 60.9, 56.3, 35.1, 31.0 ppm. EI MS, *m/z*: 328 (100), 313 (55), 285 (10), 195 (25), 161 (12). HRMS (LIFDI): calculated, 328.1675; found, 328.1680; error, 0.5 mDa.

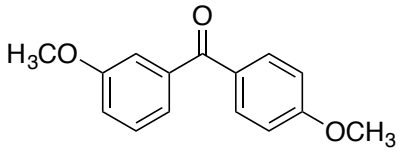



**Table 3, Entry 9: 3-methoxy-4'-methoxybenzophenone.** The first step was completed according to the general procedure whereupon the crude reaction mixture was transferred to a 20 mL glass vial with 1 g of decolorizing carbon and stirred overnight. The reaction was filtered and solvent was removed under pressure. To the 20 mL vial with the oil and Teflon-coated stirbar was added 10 mL MeCN and 5 mL $NaHCO_3$. $I_2$ (1.0152 g, 4 equiv.) was then added and the reaction was stirred at room temperature overnight. The reaction was quenched with 10 mL of $Na_2S_2O_5$:$NaHCO_3$ (1:1). The compound was extracted with EtOAc, dried over $MgSO_4$ and the solvent was removed under vacuum. The crude oil was purified using flash chromatography (silica gel, 60Å) with 30% diethyl ether in heptanes ($R_f$ = 0.30). The oil was isolated and dried under vacuum overnight and 0.193 g (66 %) of a white solid was isolated. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.77 (m, 2H), 7.10 (m, 2H), 7.25 (d, 2H, *J*=8.0), 6.98 (s, 2H), 3.87 (s, 3H), 3.81 (s, 3H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 195.0, 163.2, 159.5, 139.6, 132.4, 130.0, 129.1, 122.2, 118.0, 114.3, 113.5, 55.3, 55.2 ppm. EI MS, *m/z*: 258 (70), 211 (25), 151 (60), 135 (100), 108 (5), 92 (10), 77 (25). Spectral data was in agreement with literature.[4]

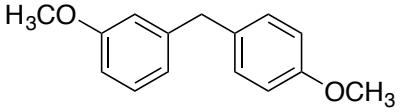



**Table 2, Entry 10: 1-methoxy-3-(4'-methoxybenzyl)benzene.** The first step was completed according to the general procedure whereupon the crude reaction mixture was transferred to a 20 mL glass vial and returned to

the glovebox The crude oil was diluted with 15 mL EtOH and stirred with Raney Nickel (1.5 tbsp, approx. 4.5 g) overnight at 80°C. The reaction was vacuum filtered through celite and solvent was removed under pressure. The crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 0.5% $Et_2O$ in heptanes ($R_f$ = 0.40) and 0.123 g (54%) of an oil was isolated. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.24 (m, 1H), 6.97 (m, 2H), 6.93 (m, 2H), 6.86 (d, 1H, *J*=8.0 Hz), 7.31 (m, 2H), 4.02 (s, 2H), 3.87 (m, 3H), 3.86 (m, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 159.9, 158.1, 143.3, 133.2, 130.0, 129.5, 121.4, 114.8, 114.0, 111.3, 55.3, 55.2, 41.2 ppm. EI MS, *m/z*: 228 (100), 213 (10), 197 (70), 165 (10), 152 (15), 141 (10), 121 (50), 91 (10), 77 (10). Spectral data was in agreement with literature.[9]

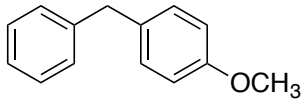



**Table 3, Entry 11: 1-methoxy-4-benzylbenzene.** The first step was completed according to the general procedure whereupon the crude reaction mixture was transferred to a 20 mL glass vial and returned to the glovebox. The crude oil was diluted with 15 mL EtOH and stirred with Raney Nickel (1.5 tbsp, approx. 4.5 g) overnight at 80 °C. The reaction was vacuum filtered through celite and solvent was removed under pressure. The crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 0.5% $Et_2O$ in heptanes ($R_f$ = 0.50) and 0.100 g (50%) of an oil was isolated. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.42 (m, 2H), 7.32 (m, 2H), 7.24 (m, 2H), 6.97 (m, 2H), 4.06 (s, 2H), 3.89 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.1, 141.7, 133.4, 130.0, 129.0, 128.6, 114.0, 55.3, 41.2 ppm. EI MS, *m/z*: 198 (100), 183 (10), 167 (40), 153 (20), 121 (30), 91 (10), 77 (10). Spectral data was in agreement with literature.[10]

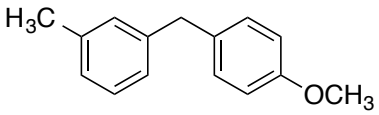



**Table 3, Entry 12: 1-methoxy-3-(4'-methylbenzyl)benzene.** The first step was completed according to the general procedure whereupon the crude reaction mixture was transferred to a 20 mL glass vial and returned to the glovebox. The crude oil was diluted with 15 mL EtOH and stirred with Raney Nickel overnight The crude oil was diluted with 15 mL EtOH and stirred with Raney Nickel (1.5 tbsp, approx. 4.5 g) overnight at 80 °C. The reaction was vacuum filtered through celite and solvent was removed under pressure. The crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 0.5% $Et_2O$ in heptanes ($R_f$ = 0.48) and 0.113 g (53%) of an oil was isolated. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.25 (m, 1H), 7.24 (d, 2H, *J*=8.4 Hz), 7.14 (m, 3H), 6.96 (d, 2H, *J*=8.4), 4.02 (s, 2H), 3.89 (s, 3H), 2.44 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.1, 141.7, 138.1, 133.5, 130.0, 129.7, 128.4, 126.9, 126.0, 114.0, 55.3, 41.1, 21.5 ppm. EI MS, [M+]: 212 (100), 197 (70), 181 (20), 165 (20), 153 (15), 121 (20), 105 (10), 91 (10), 77 (10). Spectral data was in agreement with literature.[11]

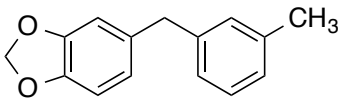


**Table 3, Entry 13: 5-(3'-methylbenzyl)benzo[d][1,3]dioxole.** The first step was completed according to the general procedure whereupon the crude reaction mixture was transferred to a 20 mL glass vial and returned to the glovebox. The crude oil was diluted with 15 mL EtOH and stirred with Raney Nickel (1.5 tbsp, approx. 4.5 g) overnight at 80 °C. The reaction was vacuum filtered through celite and solvent was removed under pressure. The crude reaction mixture was purified using column flash chromatography (silica gel, 60 Å) with 0.5% $Et_2O$ in heptanes ($R_f$ = 0.35) and 0.086 g (53%) of an oil was isolated. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.22 (m, 1H), 7.03 (m, 3H), 6.77 (m, 1H), 6.70 (m, 2H), 5.94 (s, 2H), 3.89 (s, 2H), 2.36 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 147.7, 145.8, 141.2, 138.1, 135.2, 129.6, 128.4, 126.9, 125.8, 121.7, 109.4, 121.7, 109.4, 108.2, 100.8, 41.6, 21.4 ppm. EI MS, *m/z*: 226 (100), 211 (30), 195 (15), 181 (35), 165 (15), 152 (20), 135 (18). MS (LIFDI): calculated, 226.0994; found, 226.1021; error, 2.7 mDa.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