Iron-mediated oxidative C-H coupling of arenes and alkenes directed by sulfur: a novel route to dihydrobenzofurans

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General Information

Glassware for inert atmosphere reactions was oven-dried and cooled under a flow of nitrogen. THF was distilled over sodium wire and benzophenone; CH_2Cl_2 was distilled over calcium hydride. All other solvents and reagents were purchased from commercial sources and used as supplied. ^{1}H-NMR spectra were obtained at room temperature on a 400 or 500 MHz Bruker spectrometer. ^{13}C-NMR spectra were obtained at 100 or 125 MHz. All NMR spectra were processed using *ACDLabs*© NMR software. All chemical shift values are reported in parts per million (ppm) relative to the solvent signal and were determined in $CDCl_3$, with coupling constant (*J*) values reported in Hz. The notation of signals is: Proton: δ chemical shift in ppm (number of protons, multiplicity, *J* value(s), proton assignment). Carbon: δ chemical shift in ppm (carbon assignment). If assignment is ambiguous, for example in the case of overlapping signals, a range of shifts is reported. Routine TLC analysis was carried out on aluminium sheets coated with silica gel. Plates were viewed with a 254 nm ultraviolet lamp and dipped in aqueous potassium permanganate/*p*-anisaldehyde, or phosphomolybdic acid solution. Low resolution and high-resolution mass spectra were obtained using either positive and/or negative electrospray ionisation (ES), or atmospheric-pressure chemical ionisation (APCI) techniques. IR spectra were recorded on an ATR FTIR spectrometer using neat samples.

For the synthesis of compounds not included below, please see our preliminary report:

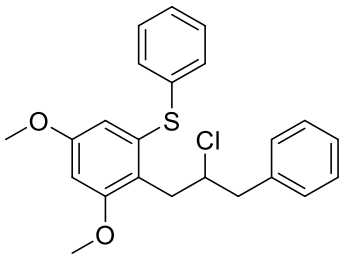
C. W. Cavanagh, M. H. Aukland, A. Hennessy, D. J. Procter, *Chem. Commun.* **2015**, *51*, 9272-9275

Fe(III)-Mediated C-H Coupling of Arylsulfides and Terminal Alkenes

General Procedure A

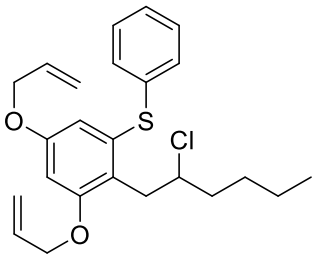
A solution of $FeCl_3$ (1.4 mmol) in $MeNO_2$ (2 mL) was added dropwise over 1 h to a stirred solution of the corresponding sulfide (0.34 mmol) and alkene (1.7 mmol) in CH_2Cl_2 (2 mL) at room temperature. The mixture was then left to stir for 1 h. The reaction mixture was then quenched with H_2O (4 ml), diluted with CH_2Cl_2 (2 mL) and 2,2'-bipyridine (127 mg, 1.4 mmol) was added. The organic layer was then washed with H_2O (2 × 4 ml) and the combined aqueous was extracted with CH_2Cl_2 (3 × 4 mL). The combined organic extracts were dried with Na_2SO_4, filtered and solvent removed *in vacuo*. The crude mixture was then passed through a silica plug with $CHCl_3$ eluent.

(2-(2-Chloro-3-phenylpropyl)-3,5-dimethoxyphenyl)(phenyl)sulfide ***2h***



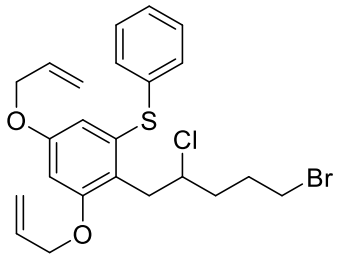
As described in general procedure A, **1a** (50 mg, 0.2 mmol), allylbenzene (135 μL, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **XX** (30.1 mg, 0.09 mmol, 46%) as a colourless oil; δ_H (500 MHz, $CDCl_3$) 3.02 (1 H, dd, J 14.8, 8.8 Hz, ArC*H*$_2$CHCl), 3.08 (1 H, dd, J 14.5, 4.7 Hz, ArC*H*$_2$CHCl), 3.29 (1 H, dd, J 13.6, 6.6 Hz, ArC*H*$_2$CHCl), 3.39 (1 H, dd, J 13.9, 7.6 Hz, ArC*H*$_2$CHCl), 3.69 (3 H, s, OC*H*$_3$), 3.81 (3 H, s, OC*H*$_3$), 4.45 - 4.52 (1 H, m, C*H*Cl), 6.41 (1 H, d, J 2.5 Hz, aryl H), 6.45 (1 H, d, J 2.5 Hz, aryl H), 7.15 - 7.31 (10 H, m); δ_C (125 MHz, $CDCl_3$) 36.1 (Ar*C*H$_2$CHCl), 44.3 (Ar*C*H$_2$CHCl), 55.3 (O*C*H$_3$), 55.6 (O*C*H$_3$), 63.1 (*C*HCl), 98.4 (aryl *C*-H), 109.0 (aryl *C*-H), 121.0 (aryl *C*), 126.5 (aryl *C*-H), 126.6 (aryl *C*-H), 128.2 (aryl *C*-H), 129.1 (aryl *C*-H), 129.2 (aryl *C*-H), 130.0 (aryl *C*-H), 136.3 (aryl *C*), 136.6 (aryl *C*), 138.7 (aryl *C*), 159.1 (aryl *C*), 159.4 (aryl *C*); ν_{max} (thin film/cm^{-1}) 1046 (vs), 1154 (s), 1198 (s), 1296 (m), 1437 (m), 1454 (s), 1477 (s), 1571 (vs), 1596 (vs), 2835 (w), 2935 (w), 2957 (w), 3000 (w), 3025 (w); MS (APCI) *m/z* 399 (M+H); HRMS $C_{23}H_{24}O_2ClS$ (M+H) Expected 399.1180, Found 399.1169.

(3,5-bis(Allyloxy)-2-(2-chlorohexyl)phenyl)(phenyl)sulfide ***2s***



As described in general procedure A, **1j** (1.00 g, 3.35 mmol), 1-hexene (2.1 mL, 16.8 mmol) and $FeCl_3$ (2.16 g, 13.4 mmol), after purification by column chromatography (30% $CHCl_3$ in hexanes) gave **2s** (700 mg, 0.10 mmol, 50%) as a colourless oil; δ_H (400 MHz, $CDCl_3$) 0.88 (3 H, t, *J* 7.2 Hz, C*H*$_3$), 1.20 - 1.42 (3 H, m, C*H*$_2$), 1.51 - 1.64 (1 H, m, C*H*$_2$), 1.70 - 1.78 (2 H, m, C*H*$_2$), 3.26 (1 H, dd, *J* 13.7, 7.0 Hz, ArC*H*$_2$CHCl), 3.36 (1 H, dd, *J* 13.7, 7.6 Hz, ArC*H*$_2$CHCl), 4.24 - 4.34 (1 H, m, C*H*Cl), 4.37 (2 H, dt, *J* 5.4, 1.3 Hz, OC*H*$_2$), 4.53 (2 H, dt, *J* 4.9, 1.6 Hz, OC*H*$_2$), 5.23 (1 H, dq, *J* 10.4, 1.3 Hz, CH=C*H*$_2$), 5.27-5.34 (2 H, m, CH=C*H*$_2$), 5.45 (1 H, dq, *J* 17.2, 1.6 Hz, CH=C*H*$_2$), 5.95 (1 H, ddt, *J* 17.3, 10.6, 5.4, 5.4 Hz, C*H*=CH$_2$), 6.06 (1 H, ddt, *J* 17.2, 10.4, 5.1, 5.1 Hz, C*H*=CH$_2$), 6.39 - 6.44 (2 H, m, aryl H), 7.19 - 7.32 (5 H, m, aryl H); δ_C (100 MHz, $CDCl_3$) 14.0 (*C*H$_3$), 22.2 (*C*H$_2$), 28.9 (*C*H$_2$), 36.4 (Ar*C*H$_2$CHCl), 37.5 (*C*H$_2$), 63.3 (*C*HCl), 68.8 (O*C*H$_2$), 68.9 (O*C*H$_2$), 99.8 (aryl *C*-H), 109.6 (aryl *C*-H), 117.3 (CH=*C*H$_2$), 118.1 (CH=*C*H$_2$), 121.4 (aryl *C*), 126.7 (aryl *C*-H), 129.1 (aryl *C*-H), 130.3 (aryl *C*-H), 132.8 (*C*H=CH$_2$ x 2), 136.2 (aryl *C*), 136.8 (aryl *C*), 157.9 (aryl *C*), 158.1 (aryl *C*); ν_{max} (thin film/cm^{-1}) 928 (m), 1024 (s), 1045 (s), 1142 (s), 1176 (s), 1276 (w), 1412 (m), 1456 (m), 1477 (m), 1570 (s), 1595 (s), 2860 (w), 2929 (w), 2956 (w), 3080 (w); MS (ES$^+$) *m/z* 417 (M+H$^+$); HRMS $C_{24}H_{30}ClO_2S$ (M+H$^+$) Expected 417.1650, Found 417.1649.

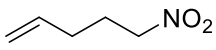
(3,5-bis(Allyloxy)-2-(5-bromo-2-chloropentyl)phenyl)(phenyl)sulfide ***2t***



As described in general procedure A, **1j** (95 mg, 0.32 mmol), 5-bromo-1-pentene (250 mg, 1.7 mmol) and $FeCl_3$ (217 mg, 1.4 mmol), after purification by column chromatography (30% $CHCl_3$ in hexanes) gave **2t** (59.6 mg, 0.08 mmol, 39%) as a colourless oil; δ_H (400 MHz, $CDCl_3$) 1.70 - 1.93 (3 H, m, C*H*$_2$), 2.03 - 2.17 (1 H, m, C*H*$_2$), 3.20 (1 H, dd, *J* 13.9, 7.6 Hz, ArC*H*$_2$CHCl), 3.25 - 3.36 (3 H, m, ArC*H*$_2$CHCl + C*H*$_2$Br), 4.17 - 4.26 (1 H, m, C*H*Cl), 4.29 (2 H, dt, *J* 5.4, 1.3 Hz, OC*H*$_2$), 4.46 (2 H, dt, *J* 5.0, 1.5 Hz, OC*H*$_2$), 5.15 (1 H, dq, *J* 10.6, 1.3 Hz, CH=C*H*$_2$), 5.18 - 5.27 (2 H, m, CH=C*H*$_2$), 5.36 (1

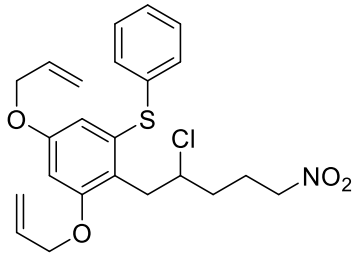
H, dq, *J* 17.2, 1.5 Hz, CH=CH_2), 5.81 - 5.92 (1 H, m, C*H*=CH_2) 5.93 - 6.04 (1 H, m, C*H*=CH_2), 6.32 - 6.35 (2 H, m, aryl H), 7.12 - 7.25 (5 H, m, aryl H); δ_C (100 MHz, $CDCl_3$) 29.8 (*C*H_2), 33.2 (*C*H_2Br), 35.9 (*C*H_2), 36.2 (Ar*C*H_2CHCl), 61.8 (*C*HCl), 68.9 (O*C*H_2), 69.0 (O*C*H_2), 99.9 (aryl *C*-H), 109.8 (aryl *C*-H), 117.8 (CH=*C*H_2), 118.0 (CH=*C*H_2), 120.8 (aryl *C*), 126.8 (aryl *C*-H), 129.2 (aryl *C*-H), 130.3 (aryl *C*-H), 132.7 (*C*H=CH_2), 132.8 (*C*H=CH_2), 135.9 (aryl *C*), 136.8 (aryl *C*), 157.9 (aryl *C*), 158.2 (aryl *C*); ν_{max} (thin film/cm^{-1}) 927.0 (m), 1023 (s), 1044 (s), 1275 (m), 1417 (m), 1439 (m), 1455 (m), 1476 (m), 1569 (s), 1595 9s), 2863 (w), 2916 (w), 2959 (w), 3075 (w); MS (APCI) *m/z* 481 ($M+H^+$); HRMS $C_{23}H_{27}ClBrO_2S$ ($M+H^+$) Expected 481.0598, Found 481.0612.

5-Nitro-1-pentene[1]



5-Bromo-1-pentene (2.5 g, 17.0 mmol) was added to a solution of sodium nitrite (1.29 g, 18.7 mmol) in DMF (34 mL) and stirred at rt for 2 h. The reaction was quenched with H_2O (30 mL) and extracted with Et_2O (3 × 30 mL). The combined organic extracts were washed with LiCl (10% in H_2O, 2 × 30 mL), dried with $MgSO_4$, filtered and solvent removed *in vacuo*. The crude product was purified by column chromatography on silica gel with 10% $CHCl_3$ in hexanes eluent to give 5-nitro-1-pentene (0.50 g, 4.9 mmol, 26%) as a yellow oil; δ_H (400 MHz, $CDCl_3$) 2.07 - 2.22 (4 H, m, CH_2), 4.40 (2 H, t, *J* 6.7 Hz, CH_2NO_2), 5.04 - 5.13 (2 H, m, CH_2=CH), 5.77 (1 H, ddt, *J* 17.0, 10.4, 6.5 Hz, CH_2=C*H*CH_2); δ_C (125 MHz, $CDCl_3$) 26.3 (*C*H_2), 30.1 (CH_2*C*H_2CH=CH_2), 74.7 (*C*H_2NO_2), 116.8 (CH=*C*H_2), 135.7 (*C*H=CH_2).

(3,5-bis(Allyloxy)-2-(2-chloro-5-nitropentyl)phenyl)(phenyl)sulfide ***2u***

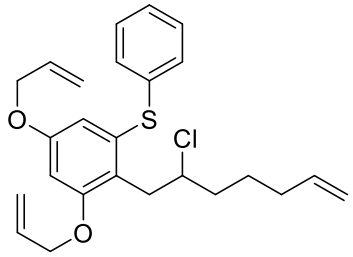


As described in general procedure A, **1j** (95 mg, 0.32 mmol), 5-nitro-1-pentene (193 mg, 1.7 mmol) and $FeCl_3$ (217 mg, 1.4 mmol), after purification by column chromatography (50% $CHCl_3$ in hexanes) gave **2u** (42.3 mg, 0.10 mmol, 30%) as a yellow oil; δ_H (400 MHz, $CDCl_3$) 1.72 - 1.87 (2 H, m, CH_2), 2.01 - 2.15 (1 H, m, CH_2), 2.27 - 2.41 (1 H, m, CH_2), 3.28 (1 H, dd, *J* 13.6, 7.8 Hz, ArCH_2CHCl), 3.38 (1 H, dd, *J* 13.6, 6.6 Hz, ArCH_2CHCl), 4.25 - 4.40 (5 H, m, CH_2NO_2 + C*H*Cl + OCH_2), 4.54 (2 H, dt, *J* 5.0, 1.4 Hz, OCH_2), 5.24 (1 H, dq, *J* 10.5, 1.3 Hz, CH=CH_2), 5.27 - 5.36 (2 H, m, CH=CH_2), 5.44 (1

[1] J. A. Burkhard, B. H. Tchitchanov, E. M. Carreira, *Angew. Chem. Int. Ed.* **2011**, 50, 5379 - 5382

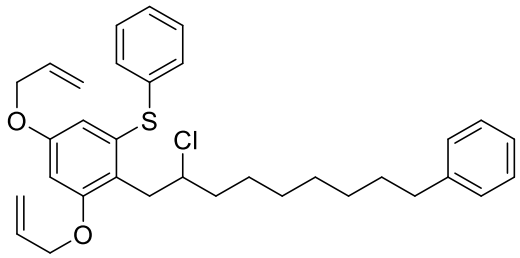
H, dq, *J* 17.2, 1.6 Hz, CH=C*H*$_2$), 5.95 (1 H, ddt, *J* 17.2, 10.5, 5.4 Hz, C*H*=CH$_2$), 6.06 (1 H, ddt, *J* 17.2, 10.5, 5.1 Hz, C*H*=CH$_2$), 6.42 (2 H, s, aryl H), 7.21 - 7.34 (5 H, m, aryl H); δ_C (100 MHz, $CDCl_3$) 24.6 (*C*H$_2$), 33.7 (*C*H$_2$), 36.2 (Ar*C*H$_2$CHCl), 61.3 (*C*HCl), 68.9 (O*C*H$_2$), 69.0 (O*C*H$_2$), 75.0 (*C*H$_2$NO$_2$), 99.9 (aryl *C*-H), 109.8 (aryl *C*-H), 117.6 (CH=*C*H$_2$), 118.1 (CH=*C*H$_2$), 120.3 (aryl *C*), 126.9 (aryl *C*-H), 129.2 (aryl *C*-H), 130.3 (aryl *C*-H), 132.7 (*C*H=CH$_2$), 132.8 (*C*H=CH$_2$), 135.7 (aryl *C*), 136.8 (aryl *C*), 157.9 (aryl *C*), 158.4 (aryl *C*); ν_{max} (thin film/cm^{-1}) 1138 (s), 1169 (s), 1417 (m), 1551 (vs), 1569 (s), 1595 (s), 2864 (w), 2920 (w), 3075 (w); MS (APCI) *m/z* 448 (M+H$^+$); HRMS $C_{23}H_{27}NO_4ClS$ (M+H$^+$) Expected 448.1344, Found 448.1339.

(3,5-bis(allyloxy)-2-(2-chlorohept-6-en-1-yl)phenyl)(phenyl)sulfide ***2v***



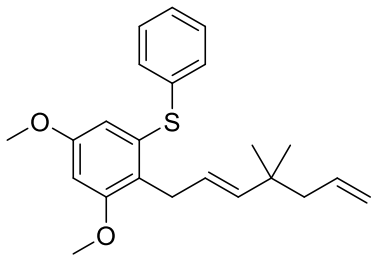
As described in general procedure A, **1j** (95 mg, 0.32 mmol), 1,6-heptadiene (162 mg, 1.7 mmol) and $FeCl_3$ (217 mg, 1.4 mmol), after purification by column chromatography (20% $CHCl_3$ in hexanes) gave **2v** (70.5 mg, 0.17 mmol, 52%) as a colourless oil; δ_H (400 MHz, $CDCl_3$) 1.31 - 1.44 (1 H, m, C*H*$_2$), 1.56 - 1.72 (3 H, m, C*H*$_2$), 1.88 - 2.01 (2 H, m, C*H*$_2$CH=CH$_2$), 3.18 (1 H, dd, *J* 13.9, 7.3 Hz, ArC*H*$_2$CHCl), 3.27 (1 H, dd, *J* 13.9, 7.3 Hz, ArC*H*$_2$CHCl), 4.17 – 4.25 (1 H, m, C*H*Cl), 4.28 (2 H, dt, *J* 5.3, 1.3 Hz, OC*H*$_2$), 4.44 (2 H, dt, *J* 4.8, 1.5 Hz, OC*H*$_2$), 4.82 - 4.93 (2 H, m, CH=C*H*$_2$), 5.14 (1 H, dq, *J* 10.6, 1.3 Hz, OCH$_2$CH=C*H*$_2$), 5.17 - 5.25 (2 H, m, OCH$_2$CH=C*H*$_2$), 5.35 (1 H, dq, *J* 17.2, 1.5 Hz, OCH$_2$CH=C*H*$_2$), 5.68 (1 H, ddt, *J* 17.0, 10.2, 6.7 Hz, C*H*=CH$_2$), 5.86 (1 H, ddt, *J* 17.2, 10.3, 5.5 Hz, OCH$_2$C*H*=CH$_2$), 5.96 (1 H, ddt, *J* 17.3, 10.5, 5.0 Hz, OCH$_2$C*H*=CH$_2$), 6.31 - 6.34 (2 H, m, aryl H), 7.10 - 7.23 (5 H, m, aryl H); δ_C (100 MHz, $CDCl_3$) 25.9 (*C*H$_2$), 33.1 (*C*H$_2$CH=CH$_2$), 36.4 (Ar*C*H$_2$CHCl), 37.1 (*C*H$_2$), 62.9 (*C*HCl), 68.8 (O*C*H$_2$), 69.0 (O*C*H$_2$), 99.8 (aryl *C*-H), 109.7 (aryl *C*-H), 114.6 (CH=*C*H$_2$), 117.3 (OCH$_2$CH=*C*H$_2$), 118.0 (OCH$_2$CH=*C*H$_2$), 121.2 (aryl *C*), 126.7 (aryl *C*-H), 129.1 (aryl *C*-H), 130.3 (aryl *C*-H), 132.8 (OCH$_2$*C*H=CH$_2$), 132.9 (OCH$_2$*C*H=CH$_2$), 136.1 (aryl *C*), 136.9 (aryl *C*), 138.4 (*C*H=CH$_2$), 157.9 (aryl *C*), 158.2 (aryl *C*); ν_{max} (thin film/cm^{-1}) 919 (m), 1024 (m), 1045 (m), 1141 (s), 1172 (s), 1275 (m), 1417 9m), 1439 (m), 1477 (m), 1569 (s), 1595 (s), 2859 (w), 2927 (w), 3075 (w); MS (APCI) *m/z* 429 (M+H$^+$); HRMS $C_{25}H_{30}ClO_2S$ (M+H$^+$) Expected 429.1650, Found 429.1657.

(3,5-bis(Allyloxy)-2-(2-chloro-9-phenylnonyl)phenyl)(phenyl)sulfide ***2w***



As described in general procedure A, **1j** (103 mg, 0.34 mmol), 9-phenyl-1-nonene (346 mg, 1.7 mmol) and $FeCl_3$ (218 mg, 1.4 mmol), after purification by column chromatography (30% $CHCl_3$ in hexanes) gave **2w** (78 mg, 0.14 mmol, 42%) as a colourless oil; δ_H (500 MHz, $CDCl_3$) 1.23 - 1.41 (7 H, m, C*H*$_2$), 1.57 - 1.65 (3 H, m, C*H*$_2$), 1.71 - 1.78 (2 H, m, C*H*$_2$), 2.59 - 2.64 (2 H, m, ArC*H*$_2$CH$_2$), 3.28 (1 H, dd, *J* 13.7, 6.9 Hz, ArC*H*$_2$CHCl), 3.37 (1 H, dd, *J* 13.7, 7.6 Hz, ArC*H*$_2$CHCl), 4.26 - 4.34 (1 H, m, C*H*Cl), 4.39 (2 H, dt, *J* 5.4, 1.4 Hz, OC*H*$_2$), 4.54 (2 H, dt, *J* 5.1, 1.5 Hz, OC*H*$_2$), 5.24 (1 H, dq, *J* 10.4, 1.5 Hz, CH=C*H*$_2$), 5.26 – 5.33 (2 H, m, CH=C*H*$_2$), 5.45 (1 H, dq, *J* 17.3, 1.4 Hz, CH=C*H*$_2$), 5.96 (1 H, ddt, *J* 17.3, 10.6, 5.4 Hz, C*H*=CH$_2$), 6.06 (1 H, ddt, *J* 17.2, 10.4, 5.1 Hz, C*H*=CH$_2$), 6.42 - 6.45 (2 H, m, aryl H), 7.16 - 7.27 (5 H, m, aryl H), 7.27 - 7.32 (5 H, m, aryl H); δ_C (125 MHz, $CDCl_3$) 26.7 (*C*H$_2$), 29.0 (*C*H$_2$), 29.2 (*C*H$_2$), 29.3 (*C*H$_2$), 31.5 (*C*H$_2$), 36.0 (*C*H$_2$), 36.4 (*C*H$_2$), 37.8 (*C*H$_2$), 63.2 (*C*HCl), 68.9 (O*C*H$_2$), 69.0 (O*C*H$_2$), 100.0 (aryl *C*-H), 109.8 (aryl *C*-H), 117.3 (CH=*C*H$_2$), 118.0 (CH=*C*H$_2$), 121.4 (aryl *C*), 125.6 (aryl *C*-H), 126.7 (aryl *C*-H), 128.2 (aryl *C*-H), 128.4 (aryl *C*-H), 129.1 (aryl *C*-H), 130.3 (aryl *C*-H), 132.9 (*C*H=CH$_2$), 132.9 (*C*H=CH$_2$), 136.2 (aryl *C*), 136.9 (aryl *C*), 142.9 (aryl *C*), 158.0 (aryl *C*), 158.2 (aryl *C*); ν_{max} (thin film/cm^{-1}) 925 (m), 1024 (s), 1045 (s), 1106 (w), 1145 (s), 1175 (s), 1215 (s), 1275 (w), 1380 (vw), 1416 (m), 1476 (s), 1495 (m), 1569 (vs), 1648 (vw), 2854 (m), 2926 (m), 3024 (w), 3082 (w); MS (APCI) *m/z* 535 (M+H$^+$); HRMS $C_{33}H_{40}ClO_2S$ (M+H$^+$) Expected 535.2432, Found 535.2423.

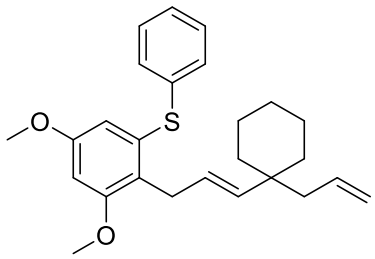
(E)-(2-(4,4-Dimethylhepta-2,6-dien-1-yl)-3,5-dimethoxyphenyl)(phenyl)sulfide ***2y***



As described in general procedure A, **1a** (50 mg, 0.2 mmol), 4,4-dimethylhepta-1,6-diene (127 mg, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **2y** (15.3 mg, 0.04 mmol, 21%) as a colourless oil; δ_H (400 MHz, $CDCl_3$) 0.89 (6 H, s,

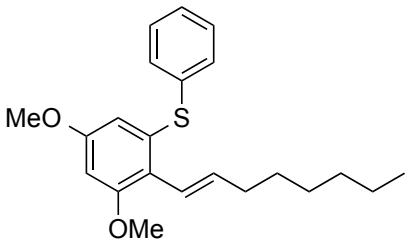
$C(CH_3)_2$), 1.95 (2 H, d, *J* 7.3 Hz, $CH_2CH=CH_2$), 3.50 (2 H, dd, *J* 6.1, 1.0 Hz, $ArCH_2CH=CH$), 3.69 (3 H, s, OCH_3), 3.81 (3 H, s, OCH_3), 4.90 - 4.97 (2 H, m, $CH=CH_2$), 5.29 (1 H, dt, *J* 15.6, 6.1 Hz, $ArCH_2CH=CH$), 5.40 (1 H, dt, *J* 15.6, 1.0 Hz, $ArCH_2CH=CH$), 5.72 (1 H, ddt, *J* 16.6, 10.6, 7.3 Hz, $CH=CH_2$), 6.41 (1 H, d, *J* 2.3 Hz, aryl H), 6.43 (1 H, d, *J* 2.5 Hz, aryl H), 7.16 - 7.30 (5 H, m, aryl H); δ_C (100 MHz, $CDCl_3$) 26.9 ($C(CH_3)_2$), 30.5 ($ArCH_2CH=CH$), 35.6 (alkyl C_q), 47.5 ($CH_2CH=CH_2$), 55.3 (OCH_3), 55.7 (OCH_3), 98.5 (aryl *C*-H), 108.7 (aryl *C*-H), 116.2 ($CH=CH_2$), 123.4 ($ArCH_2CH=CH$), 124.1 (aryl *C*), 126.4 (aryl *C*-H), 129.0 (aryl *C*-H), 130.0 (aryl *C*-H), 135.5 (aryl *C*), 136.1 ($CH=CH_2$), 136.8 (aryl *C*), 140.4 ($ArCH_2CH=CH$), 158.7 (aryl *C*), 158.8 (aryl *C*); ν_{max} (thin film/cm^{-1}) 1050 (s), 1150 (m), 1274 (w), 1295 (w), 1409 (m), 1436 (m), 1477 (m), 1571 (s), 1596 (s), 2834 (w), 2935 (m), 2957 (m), 3000 (w), 3072 (w); MS (ES^+) *m/z* 369 (M+H); HRMS $C_{23}H_{29}O_2S$ (M+H) Expected 369.1883, Found 369.1881.

(E)-(2-(3-(1-Allylcyclohexyl)allyl)-3,5-dimethoxyphenyl)(phenyl)sulfide ***2z***



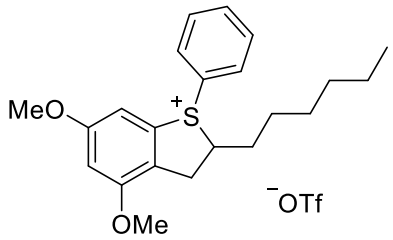
As described in general procedure A, **1a** (50 mg, 0.2 mmol), 1,1-diallylcyclohexane (168 mg, 1 mmol) and $FeCl_3$ (131 mg, 0.8 mmol), after purification by column chromatography (30 % $CHCl_3$ in hexanes) gave **2z** (19.1 mg, 0.04 mmol, 23%) as a colourless oil; δ_H (400 MHz, $CDCl_3$) 1.15 - 1.31 (4 H, m, CH_2), 1.33 - 1.48 (6 H, m, CH_2), 1.97 (2 H, d, *J* 7.3 Hz, $CH_2CH=CH_2$), 3.53 (2 H, d, *J* 5.3 Hz, $ArCH_2CH=CH$), 3.69 (3 H, s, OCH_3), 3.81 (3 H, s, OCH_3), 4.89 - 4.96 (2 H, m, $CH=CH_2$), 5.22 (1 H, d, *J* 15.9 Hz, $ArCH_2CH=CH$), 5.29 (1 H, dt, *J* 15.9, 5.3 Hz, $ArCH_2CH=CH$), 5.63 – 5.76 (1 H, m, $CH=CH_2$), 6.41 (1 H, d, *J* 2.5 Hz, aryl H), 6.42 (1 H, d, *J* 2.5 Hz, aryl H), 7.16 - 7.22 (1 H, m, aryl H), 7.24 - 7.29 (4 H, m); δ_C (100 MHz, $CDCl_3$) 22.1 (CH_2), 26.5 (CH_2), 30.7 ($ArCH_2CH=CH$), 35.8 (CH_2), 38.7 (alkyl C_q), 46.5 ($CH_2CH=CH_2$), 55.3 (OCH_3), 55.6 (OCH_3), 98.4 (aryl *C*-H), 108.5 (aryl *C*-H), 116.0 ($CH=CH_2$), 123.9 (aryl *C*), 125.7 ($ArCH_2CH=CH$), 126.4 (aryl *C*-H), 129.0 (aryl *C*-H), 130.1 (aryl *C*-H), 135.5 (aryl *C*), 135.8 ($CH=CH_2$), 136.7 (aryl *C*), 138.4 ($ArCH_2CH=CH$), 158.7 (aryl *C*), 158.8 (aryl *C*); ν_{max} (thin film/cm^{-1}) 1050 (s), 1144 (m), 1204 (s), 1275 (w), 1295 (w), 1460 (m), 1572 (s), 1597 (s), 2852 (m), 2925 (vs), 3000 (w), 3071 (w); MS (ES^+) *m/z* 409 (M+H); HRMS $C_{26}H_{33}O_2S$ (M+H) Expected 409.2196, Found 409.2196.

(E)-(3,5-Dimethoxy-2-(oct-1-en-1-yl)phenyl)(phenyl)sulfide ***3f***



$NaNH_2$ (8.3 mg, 0.21 mmol) was added in one portion to a solution of **2a** (35.3 mg, 0.09 mmol) in THF (1.0 mL). The solution was stirred under reflux for 18 h, then cooled to room temperature and quenched with H_2O (2 mL) and diluted with EtOAc (5 mL). The organic phase was washed with H_2O (3 × 2 mL), dried over $MgSO_4$, filtered and solvent removed *in vacuo*. The crude mixture was purified by column chromatography (30% $CHCl_3$ in hexanes) to give **3f** (27.2 mg, 0.08 mmol, 85%) as a colourless oil; δ_H (500 MHz, $CDCl_3$) 0.89 (3 H, t, *J* 6.6 Hz, C*H*3), 1.23 - 1.37 (6 H, m, C*H*2), 1.37 - 1.45 (2 H, m, C*H*2), 2.19 (2 H, qd, *J* 6.9, 1.3 Hz, CH=CHC*H*2CH2), 3.66 (3 H, s, OC*H*3), 3.83 (3 H, s, OC*H*3), 6.27 (1 H, dt, *J* 16.1, 6.9 Hz, ArCH=C*H*CH2), 6.35 (1 H, d, *J* 2.5 Hz, aryl H), 6.39 (1 H, d, *J* 2.5 Hz, aryl H), 6.53 (1 H, dt, *J* 16.1, 1.3 Hz, ArC*H*=CHCH2), 7.21 - 7.33 (5 H, m, aryl H); δ_C (125 MHz, $CDCl_3$) 14.2 (*C*H3), 22.7 (*C*H2), 28.9 (*C*H2), 29.4 (*C*H2), 31.8 (*C*H2), 34.1 (CH=CH*C*H2CH2), 55.3 (O*C*H3), 55.6 (O*C*H3), 98.0 (aryl *C*-H), 107.8 (aryl *C*-H), 121.0 (aryl C), 122.7 (ArCH=*C*HCH2), 126.9 (aryl *C*-H), 129.1 (aryl *C*-H), 131.1 (aryl *C*-H), 135.7 (aryl C), 136.1 (aryl C), 136.6 (Ar*C*H=CHCH2), 158.6 (aryl C), 158.7 (aryl C); ν_{max} (thin film/cm^{-1}) 1046 (s), 1153 (s), 1200 (m), 1210 (m), 1298 (m), 1407 (w), 1434 (w), 1459 (m), 1563 (s), 1593 (s), 2854 (w), 2925 (m), 2954 (w), 3000 (w); MS (ES^+) m/z 357.3 (M+H); HRMS $C_{22}H_{29}O_2S$ (M+H) Expected 357.1883, Found 357.1887.

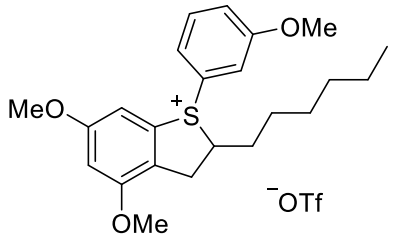
2-Hexyl-4,6-dimethoxy-1-phenyl-2,3-dihydro-1H-benzo[b]thiophen-1-ium trifluoromethanesulfonate ***3h***



AgOTf (62.5 mg, 0.24 mmol) was added to a solution of **2a** (104 mg, 0.24 mmol) in DCE (2.40 mL) under N_2 and the resulting suspension stirred at 80 °C for 18 h. H_2O (2.50 mL) was then added and the organic layer washed with H_2O (2 × 2.50 ml). The combined aqueous layers were then extracted with CH_2Cl_2 (3 × 2.50 mL), the combined organic extracts dried with Na_2SO_4, filtered and the solvent removed *in vacuo*. The crude product was purified by column chromatography on silica gel (20% MeOH in CH_2Cl_2) to give **3h** (117 mg, 0.21 mmol, 87%), as a colourless oil; δ_H (400 MHz, $CDCl_3$)

0.81 - 0.93 (6 H, m, 1 × CH_2CH_3 from isomer A and 1 × CH_2CH_3 from isomer B), 1.15 - 1.38 (13 H, m, 3 × CH_2 from isomer A and 2 × CH_2 from isomer B), 1.43 - 1.55 (3 H, m, 1 × CH_2 from isomer A and 1 × CH_2 from isomer B), 1.56 - 1.64 (1 H, m, 1 × CH_2 from isomer B), 1.73 - 1.84 (1 H, m, 1 × $ArCH_2CHCH_2$ from isomer A), 1.93 - 2.04 (1 H, m, 1 × $ArCH_2CHCH_2$ from isomer B), 2.21 - 2.32 (1 H, m, 1 × $ArCH_2CHCH_2$ from isomer B), 3.01 (1 H, dd, *J* 16.7, 10.2 Hz, $ArCH_2CHCH_2$ from isomer A), 3.27 - 3.35 (1 H, m, $ArCH_2CHCH_2$ from isomer B), 3.66 - 3.76 (2 H, m, 1 × $ArCH_2CHCH_2$ from isomer A and 1 × $ArCH_2CHCH_2$ from isomer B), 3.84 (3 H, s, OCH_3), 3.84 (3 H, s, OCH_3), 3.92 - 3.95 (6 H, m, OCH_3), 4.51 - 4.59 (1 H, m, $ArCH_2CHCH_2$ from isomer B), 4.88 - 4.99 (1 H, m, $ArCH_2CHCH_2$ from isomer A), 6.70 - 6.76 (2 H, m, 1 × aryl *H* from isomer A and 1 × aryl *H* from isomer B), 6.97 (1 H, d, *J* 2.0 Hz, aryl *H* from isomer B), 7.01 (1 H, d, *J* 2.0 Hz, aryl *H* from isomer A), 7.39 - 7.44 (2 H, m, aryl *H*), 7.59 - 7.65 (6 H, m, aryl *H*), 7.67 - 7.70 (1 H, m, aryl *H* from isomer B), 7.70 - 7.76 (1 H, m, aryl *H* from isomer A); δ_C (100 MHz, $CDCl_3$) 13.9 (CH_2CH_3 from isomer A), 14.0 (CH_2CH_3 from isomer B), 22.4 (CH_2), 22.4 (CH_2), 27.6 (CH_2), 27.7 (CH_2), 28.7 (CH_2), 28.7 (CH_2), 29.5 (CH_2), 31.3 (CH_2), 31.4 (CH_2), 33.2 (CH_2), 34.4 ($ArCH_2CHCH_2$ from isomer A), 34.9 ($ArCH_2CHCH_2$ from isomer B), 56.1 (OCH_3), 56.4 (OCH_3), 56.4 (OCH_3), 65.1 ($ArCH_2CHCH_2$ from isomer A), 71.0 ($ArCH_2CHCH_2$ from isomer B), 102.6 (aryl *C*–H), 102.8 (aryl *C*–H), 104.3 (aryl *C*–H), 104.5 (aryl *C*–H), 120.8 (aryl *C*), 126.1 (aryl *C*), 126.2 (aryl *C*), 126.5 (aryl *C*), 126.8 (aryl *C*), 127.0 (aryl *C*), 130.0 (aryl *C*–H), 131.1 (aryl *C*–H), 131.2 (aryl *C*–H), 131.3 (aryl *C*–H), 134.4 (aryl *C*–H), 134.6 (aryl *C*–H), 157.1 (aryl *C*), 157.6 (aryl *C*), 163.1 (aryl *C*), 163.3 (aryl *C*); ν_{max} (thin film/cm^{-1}): 1029 (s), 1140 (m), 1204 (w), 1223 (s), 1259 (s), 1437 (w), 1447 (w), 1495 (w), 1577 (w), 1607 (w), 2857 (w), 2929 (w), 2953 (w), 3091 (w); MS (ES^+) *m/z* 357 (M); HRMS $C_{22}H_{29}O_2S$ (M) Expected 357.1883, Found 357.1884.

2–Hexyl–4,6–dimethoxy–1–(3–methoxyphenyl)–2,3–dihydro–1H–benzo[b]thiophen–1–ium trifluoromethanesulfonate ***3i***

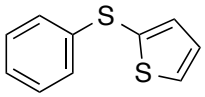


AgOTf (63.8 mg, 0.24 mmol) was added to a solution of **2r** (102 mg, 0.24 mmol) in DCE (2.40 mL) under N_2 and the resulting suspension stirred at 80 °C for 18 h. H_2O (2.50 mL) was then added and the organic layer washed with H_2O (2 × 2.50 ml). The combined aqueous layers were then extracted with CH_2Cl_2 (3 × 2.50 mL) and the combined organic extracts dried with Na_2SO_4, filtered and the solvent removed *in vacuo*. The crude product was purified by column chromatography on silica gel (20% MeOH in CH_2Cl_2) to give **3i** (102 mg, 0.21 mmol, 89%), as a colourless oil; δ_H (500 MHz,

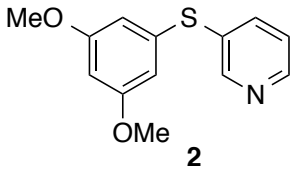
$CDCl_3$) 0.80 - 0.91 (6 H, m, 1 × CH_2CH_3 from isomer A and 1 × CH_2CH_3 from isomer B), 1.17 - 1.63 (16 H, m, 4 × CH_2 from isomer A and 4 × CH_2 from isomer B), 1.76 - 1.87 (2 H, m, $ArCH_2CHCH_2$ from isomer A), 1.92 - 2.02 (1 H, m, $ArCH_2CHCH_2$ from isomer B), 2.22 - 2.34 (1 H, m, $ArCH_2CHCH_2$ from isomer B), 3.02 (1 H, m, $ArCH_2CHCH_2$ from isomer A), 3.28 (1 H, m, $ArCH_2CHCH_2$ from isomer B), 3.65 - 3.72 (2 H, m, 1 × $ArCH_2CHCH_2$ from isomer A and 1 × $ArCH_2CHCH_2$ from isomer B), 3.83 (3 H, s, OCH_3), 3.84 (3 H, s, OCH_3), 3.87 (3 H, s, OCH_3), 3.91 (3 H, s, OCH_3), 3.92 (3 H, s, OCH_3), 3.93 (3 H, s, OCH_3), 4.56 (1 H, dd, *J* 7.5, 3.1 Hz, $ArCH_2CHCH_2$ from isomer B), 4.89 (1 H, t, *J* 8.9 Hz, $ArCH_2CHCH_2$ from isomer A), 6.72 (2 H, s, aryl *H*), 6.85 (1 H, d, *J* 7.8 Hz, aryl *H*), 6.93 - 6.96 (1 H, m, aryl *H*), 6.98 (1 H, d, *J* 1.8 Hz, aryl *H*), 7.06 (1 H, s, aryl *H*), 7.18 (1 H, dd, *J* 8.3, 2.2 Hz, aryl *H*), 7.22 (2 H, dd, *J* 8.3, 2.2 Hz, aryl *H*), 7.37 (1 H, t, *J* 2.0 Hz, aryl *H*), 7.48 (2 H, dt, *J* 16.6, 8.2 Hz, aryl *H*); δ_C (125 MHz, $CDCl_3$) 13.9 (CH_2CH_3 from isomer A), 13.9 (CH_2CH_3 from isomer B), 22.3 (CH_2), 22.4 (CH_2), 27.6 (CH_2), 27.7 (CH_2), 28.7 (CH_2), 28.7 (CH_2), 29.4 (CH_2), 31.3 (CH_2), 31.4 (CH_2), 33.1 (CH_2), 34.5 ($ArCH_2CHCH_2$ from isomer A), 34.7 ($ArCH_2CHCH_2$ from isomer B), 56.1 (OCH_3), 56.2 (OCH_3), 56.3 (OCH_3), 56.4 (OCH_3), 65.1 ($ArCH_2CHCH_2$ from isomer A), 70.9 ($ArCH_2CHCH_2$ from isomer B), 102.6 (aryl *C*–H), 102.7 (aryl *C*–H), 104.2 (aryl *C*–H), 104.4 (aryl *C*–H), 115.2 (aryl *C*–H), 116.7 (aryl *C*–H), 119.5 (aryl *C*–H), 120.4 (aryl *C*–H), 120.9 (aryl *C*–H), 121.6 (aryl *C*–H), 122.1 (aryl *C*), 122.5 (aryl *C*–H), 126.1 (aryl *C*), 126.4 (aryl *C*), 126.7 (aryl *C*), 126.9 (aryl *C*), 127.0 (aryl *C*), 131.9 (aryl *C*–H), 157.1 (aryl *C*), 157.6 (aryl *C*), 161.1 (aryl *C*), 161.3 (aryl *C*), 163.0 (aryl *C*), 163.2 (aryl *C*); ν_{max} (thin film/cm^{-1}): 990 (w), 1028 (s), 1095 (w), 1140 (s), 1204 (w), 1223 (s), 1255 (s), 1317 (w), 1436 (w), 1465 (w), 1483 (w), 1575 (w), 1595 (w), 2856 (w), 2929 (w), 3092 (w); MS (ES^+) *m/z* 387 (M); HRMS $C_{23}H_{32}O_3S$ (M) Expected 387.1976, Found 387.1994.

Additional Substrates That Failed to Undergo C-H Coupling with 1-octene

A) Heterocyclic sulfide substrate

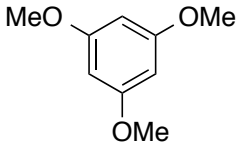


1



2

B) Substrates designed to probe the dependence of sulfur



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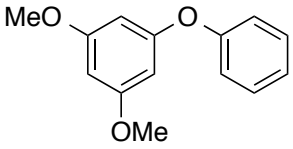

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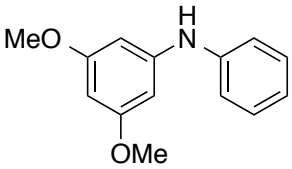

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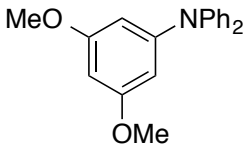


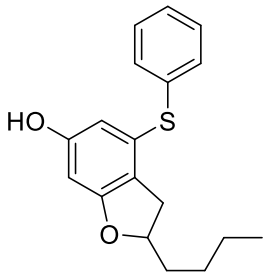
4

Pd-Catalysed Deallylation/Cyclisation

General Procedure B

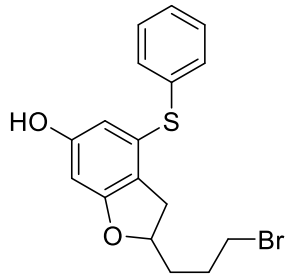
Morpholine (2.2 equiv.) was added to a stirred mixture of the corresponding allyloxy-sulfide (1 equiv.), $Pd(PPh_3)_4$ (0.1 equiv.) and $NaBH_4$ (2.4 equiv.) in THF (0.1 M) at room temperature and stirred for 16 h. The reaction was then cooled to 0 °C and 1 N HCl (10 mL) was added slowly. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic extracts were then washed with brine (10 mL), dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude product was purified by column chromatography on silica gel to give the corresponding dihydrobenzofuran product.

2-Butyl-4-(phenylsulfanyl)-2,3-dihydrobenzofuran-6-ol ***4a***



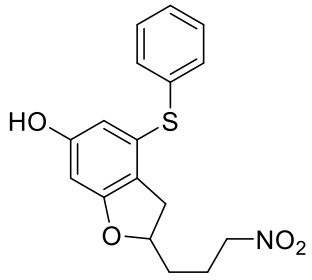
As described in general procedure B, **2s** (50 mg, 0.12 mmol), morpholine (23 µL, 0.26 mmol), $Pd(PPh_3)_4$ (13.9 mg, 0.01 mmol) and $NaBH_4$ (10.9 mg, 0.29 mmol), after purification by column chromatography (10% EtOAc in hexanes), gave **4a** (30.1 mg, 0.10 mmol, 84%) as a pale yellow oil; δ_H (400 MHz, $CDCl_3$) 0.90 (3 H, t, *J* 6.8 Hz, C*H*$_3$), 1.29 - 1.49 (4 H, m, C*H*$_2$), 1.58 - 1.71 (1 H, m, CH(O)C*H*$_2$CH$_2$), 1.72 - 1.86 (1 H, m, CH(O)C*H*$_2$CH$_2$), 2.65 (1 H, dd, *J* 15.4, 7.7 Hz, ArC*H*$_2$CH(O)), 3.08 (1 H, dd, *J* 15.4, 8.9 Hz, ArC*H*$_2$CH(O)), 4.73 - 4.89 (2 H, m, C*H*(O) + ArO*H*), 6.14 (1 H, d, *J* 2.3 Hz, aryl H), 6.19 (1 H, d, *J* 2.3 Hz, aryl H), 7.24 - 7.37 (5 H, m, aryl H); δ_C (100 MHz, $CDCl_3$) 14.0 (*C*H$_3$), 22.6 (*C*H$_2$), 27.3 (*C*H$_2$), 34.2 (Ar*C*H$_2$CH(O)), 35.8 (CH(O)*C*H$_2$CH$_2$), 84.5 (*C*H(O)), 96.4 (aryl *C*-H), 108.6 (aryl *C*-H), 120.2 (aryl *C*), 127.2 (aryl *C*-H), 129.2 (aryl *C*-H), 131.2 (aryl *C*-H), 132.3 (aryl *C*), 134.0 (aryl *C*), 156.3 (aryl *C*), 160.9 (aryl *C*); ν_{max} (thin film/cm^{-1}) 994 (s), 1111 (s), 1216 (m), 1354 (w), 1439 (s), 1477 (s), 1591 (s), 1609 (s), 2848 (m), 2916 (m), 2955 (m), 3404 (s, br, O-H stretch); MS (ES$^+$) *m/z* 301 (M+H$^+$); HRMS $C_{18}H_{21}O_2S$ (M+H$^+$) Expected 301.1257, Found 301.1255.

2-(3-Bromopropyl)-4-(phenylsulfanyl)-2,3-dihydrobenzofuran-6-ol ***4b***



As described in general procedure B, **2t** (60.7 mg, 0.12 mmol), morpholine (24 μL, 0.26 mmol), $Pd(PPh_3)_4$ (14.9 mg, 0.012 mmol) and $NaBH_4$ (11.8 mg, 0.29 mmol), after purification by column chromatography (10% EtOAc in hexanes), gave **4b** (36.3 mg, 0.09 mmol, 79%) as a colourless oil; δ_H (400 MHz, $CDCl_3$) 1.78 - 2.14 (4 H, m, CH_2), 2.66 (1 H, dd, *J* 15.6, 7.3 Hz, ArCH_2CH(O)), 3.11 (1 H, dd, *J* 15.6, 9.1 Hz, ArCH_2CH(O)), 3.40 - 3.52 (2 H, m, CH_2Br), 4.76 (1 H, s, ArO*H*), 4.82 (1 H, dtd, *J* 9.1, 7.3, 7.3, 5.3 Hz, C*H*(O)), 6.16 (1 H, d, *J* 2.0 Hz, aryl H), 6.19 (1 H, d, *J* 2.0 Hz, aryl H), 7.25 - 7.37 (5 H, m, aryl H); δ_C (100 MHz, $CDCl_3$) 28.6 (*C*H_2), 33.4 (*C*H_2Br), 34.3 (Ar*C*H_2CH(O)), 34.6 (*C*H_2), 83.3 (*C*H(O)), 96.5 (aryl *C*-H), 108.9 (aryl *C*-H), 119.8 (aryl *C*), 127.4 (aryl *C*-H), 129.3 (aryl *C*-H), 131.3 (aryl *C*-H), 132.5 (aryl *C*), 133.9 (aryl *C*), 156.4 (aryl *C*), 160.7 (aryl *C*); ν_{max} (thin film/cm^{-1}) 992 (s), 1113 (s), 1253 (w), 1437 (s), 1476 (m), 1591 (m), 1607 (m), 2849 (w), 2939 (w), 3396 (m, br, O-H stretch); MS (APCI) *m/z* 365 ($M+H^+$); HRMS $C_{17}H_{18}O_2BrS$ ($M+H^+$) Expected 365.0205, Found 365.0188.

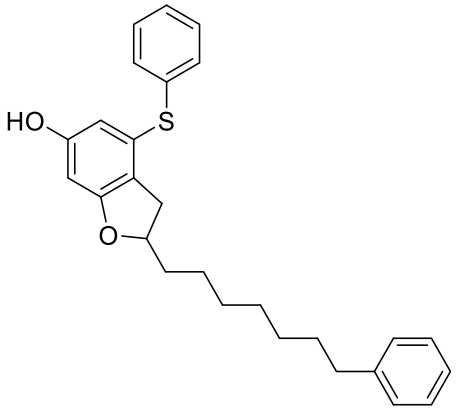
2-(3-Nitropropyl)-4-(phenylsulfanyl)-2,3-dihydrobenzofuran-6-ol ***4c***



As described in general procedure B, **2u** (41.8 mg, 0.09 mmol), morpholine (20 μL, 0.20 mmol), $Pd(PPh_3)_4$ (10.3 mg, 0.009 mmol) and $NaBH_4$ (8.6 mg, 0.22 mmol), after purification by column chromatography (20% EtOAc in hexanes), gave **4c** (25.2 mg, 0.07 mmol, 82%) as a yellow oil; δ_H (400 MHz, $CDCl_3$) 1.71 - 1.87 (2 H, m, CH_2), 2.09 - 2.29 (2 H, m, CH_2), 2.64 (1 H, dd, *J* 15.6, 7.3 Hz, ArCH_2CH(O)), 3.12 (1 H, dd, *J* 15.6, 9.0 Hz, ArCH_2CH(O)), 4.39 - 4.53 (2 H, m, C*H*(O) + ArO*H*), 4.69 - 4.79 (2 H, m, CH_2NO_2), 6.17 (1 H, d, *J* 2.3 Hz, aryl H), 6.19 (1 H, d, *J* 2.3 Hz, aryl H), 7.28 - 7.37 (5 H, m, aryl H); δ_C (100 MHz, $CDCl_3$) 23.5 (*C*H_2), 32.6 (*C*H_2), 34.3 (Ar*C*H_2CH(O)), 75.2 (*C*H_2NO_2), 83.0 (*C*H(O)), 96.6 (aryl *C*-H), 109.0 (aryl *C*-H), 119.4 (aryl *C*), 127.4 (aryl *C*-H), 129.3

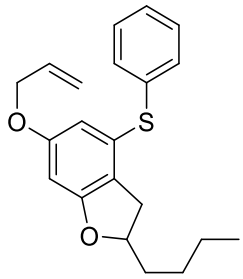
(aryl *C*-H), 131.4 (aryl *C*-H), 132.7 (aryl *C*), 133.8 (aryl *C*), 156.6 (aryl *C*), 160.5 (aryl *C*); ν_{max} (thin film/cm^{-1}) 993 (s), 1117 (s), 1221 (m), 1377 (m), 1437 (s), 1477 (s), 1549 (s), 1609 (s), 2852 (m), 2934 (m), 3060 (m), 3419 (s, br, O-H stretch); MS (APCI) *m/z* 332 ($M+H^+$); HRMS $C_{17}H_{18}O_4NS$ ($M+H^+$) Expected 332.0951, Found 332.0936.

2-(7-Phenylheptyl)-4-(phenylthio)-2,3-dihydrobenzofuran-6-ol ***4d***



As described in General Procedure B, **2w** (52.0 mg, 0.10 mmol), morpholine (18 μL, 0.21 mmol), $Pd(PPh_3)_4$ (12.1 mg, 0.011 mmol) and $NaBH_4$ (9.0 mg, 0.24 mmol), after purification by column chromatography (10% EtOAc in hexanes), gave **4d** (33.1 mg, 0.08 mmol, 81%) as a colourless oil; δ_H (400 MHz, $CDCl_3$) 1.22 – 1.44 (8 H, m, CH_2), 1.48 – 1.62 (3 H, m, CH_2), 1.65 – 1.78 (1 H, m, CH(O)C$H_2$$CH_2$), 2.50 – 2.62 (3 H, m, ArCH_2CH(O) & Ar$CH_2$$CH_2$), 3.01 (1 H, dd, *J* 15.4, 8.9 Hz, ArCH_2CH(O)), 4.62 – 4.77 (2 H, m, ArCH_2C*H*(O) & O*H*), 6.06 (1 H, d, *J* 2.3 Hz, aryl H), 6.10 (1 H, d, *J* 2.3 Hz, aryl H), 7.09 – 7.15 (3 H, m, aryl H), 7.17 – 7.30 (7 H, m, aryl H); δ_C (100 MHz, $CDCl_3$) 25.2 (*C*H_2), 29.2 (*C*H_2), 29.3 (*C*H_2), 29.4 (*C*H_2), 31.5 (*C*H_2), 34.3 (Ar*C*H_2CH(O)), 36.0 (Ar*C*$H_2$$CH_2$), 36.1 (Ar$CH_2$CH(O)*C*$H_2$), 84.6 (*C*H(O)), 96.6 (aryl *C*-H), 108.8 (aryl *C*-H), 120.4 (aryl *C*), 125.6 (aryl *C*-H), 127.3 (aryl *C*-H), 128.3 (aryl *C*-H), 128.4 (aryl *C*-H), 129.3 (aryl *C*-H), 131.2 (aryl *C*-H), 132.3 (aryl *C*), 134.1 (aryl *C*), 142.9 (aryl *C*), 156.4 (aryl *C*), 161.0 (aryl *C*); ν_{max} (thin film/cm^{-1}) 993 (s), 1114 (vs), 1174 (w), 1220 (w), 1266 (w), 1353 (w), 1438 (s), 1477 (s), 1591 (s), 1607 (s), 2853 (m), 2927 (s), 3924 (w), 3402 (br); MS (APCI) *m/z* 419 ($M+H^+$); HRMS $C_{27}H_{31}O_2S$ ($M+H^+$) Expected 419.2027, Found 419.2039.

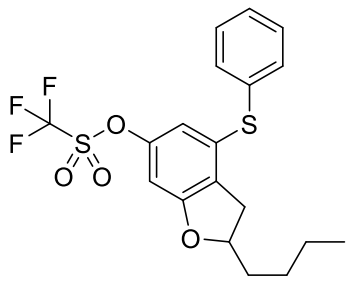
6-(Allyloxy)-2-butyl-4-(phenylsulfanyl)-2,3-dihydrobenzofuran ***4e***



As described in general procedure B, **2s** (50 mg, 0.12 mmol), morpholine (23 μL, 0.26 mmol), $Pd(PPh_3)_4$ (13.9 mg, 0.01 mmol) and NaH (11.7 mg, 0.29 mmol, 60% dispersion in mineral oil), after purification by column chromatography (10% EtOAc in hexanes), gave **4e** (40 mg, 0.11 mmol, 92%) as a colourless oil; δ_H (400 MHz, $CDCl_3$) 0.92 (3 H, t, *J* 7.0 Hz, CH_3), 1.30 - 1.48 (4 H, m, CH_2), 1.59 - 1.69 (1 H, m, CH(O)CH_2CH$_2$), 1.73 - 1.84 (1 H, m, CH(O)CH_2CH$_2$), 2.65 (1 H, dd, *J* 15.4, 7.7 Hz, ArCH_2CH(O)), 3.08 (1 H, dd, *J* 15.4, 8.9 Hz, ArCH_2CH(O)), 4.42 (2 H, dt, *J* 5.3, 1.5 Hz, OCH_2), 4.73 - 4.83 (1 H, m, C*H*(O)), 5.25 (1 H, dq, *J* 10.5, 1.5 Hz, CH=CH_2), 5.34 (1 H, dq, *J* 17.3, 1.5 Hz, CH=CH_2) 5.99 (1 H, ddt, *J* 17.3, 10.6, 5.3 Hz, C*H*=CH$_2$), 6.30 (2 H, s, aryl H), 7.22 - 7.35 (5 H, m, aryl H); δ_C (100 MHz, $CDCl_3$) 14.0 (*C*H$_3$), 22.6 (*C*H$_2$), 27.4 (*C*H$_2$), 34.4 (Ar*C*H$_2$CH(O)), 35.8 (CH(O)*C*H$_2$CH$_2$), 69.1 (O*C*H$_2$), 84.4 (*C*H(O)), 96.1 (aryl *C*-H), 109.0 (aryl *C*-H), 117.8 (CH=*C*H$_2$), 120.8 (aryl *C*), 126.9 (aryl *C*-H), 129.2 (aryl *C*-H), 130.4 (aryl *C*-H), 131.6 (aryl *C*), 133.1 (*C*H=CH$_2$), 134.6 (aryl *C*), 159.6 (aryl *C*), 160.9 (aryl *C*); ν_{max} (thin film/cm^{-1}) 925 (m), 980 (s), 1024 (s), 1114 (s), 1181 (m), 1423 (m), 1477 (s), 1578 (s), 1606 (s), 2859 (w), 2929 (m), 2954 (m); MS (APCI) *m/z* 341 ($M+H^+$); HRMS $C_{21}H_{25}O_2S$ ($M+H^+$) Expected 341.1570, Found 341.1567.

Pd-catalysed Cross-Coupling

2-Butyl-4-(phenylsulfanyl)-2,3-dihydrobenzofuran-6-yl trifluoromethanesulfonate ***5***



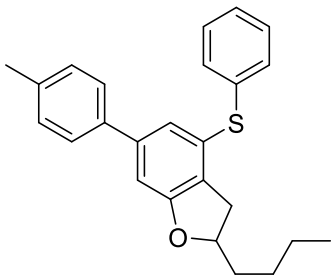
Sodium *tert*-butoxide (187 mg, 1.95 mmol) was added to a stirred solution of *N*-phenyl-bis(trifluoromethanesulfonimide) (696 mg, 1.95 mmol) and **4a** (532 mg, 1.77 mmol) in THF (18 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C, then warmed to room temperature and stirred for a further 1 h. The mixture was then quenched with H_2O (20 mL) and the aqueous layer extracted with EtOAc (3 × 30 mL). The combined organic extracts were washed with brine (30 mL), dried with

$MgSO_4$, filtered and the solvent removed *in vacuo*. The crude product was purified by column chromatography on silica gel (10% Et_2O in hexanes) to give **5** (666 mg, 1.54 mmol, 87%) as a colourless oil; δ_H (400 MHz, $CDCl_3$) 0.94 (3 H, t, *J* 7.1 Hz, CH_3), 1.31 - 1.51 (4 H, m, CH_2), 1.62 - 1.74 (1 H, m, (CH(O)CH_2CH$_2$)), 1.76 - 1.89 (1 H, m, (CH(O)CH_2CH$_2$)), 2.73 (1 H, dd, *J* 16.1, 7.5 Hz, ArCH_2CH(O)), 3.17 (1 H, dd, *J* 16.1, 9.2 Hz, ArCH_2CH(O)), 4.83 - 4.93 (1 H, m, C*H*(O)), 6.39 (1 H, d, *J* 2.2 Hz, aryl H), 6.51 (1 H, d, *J* 2.2 Hz, aryl H), 7.35 - 7.43 (5 H, m, aryl H); δ_C (100 MHz, $CDCl_3$) 14.0 (*C*H$_3$), 22.5 (*C*H$_2$), 27.3 (*C*H$_2$), 34.3 (Ar*C*H$_2$CH(O)), 35.8 (CH(O)*C*H$_2$CH$_2$), 85.2 (*C*H(O)), 101.3 (aryl *C*-H), 112.9 (aryl *C*-H), 127.1 (aryl *C*), 128.5 (aryl *C*-H), 129.6 (aryl *C*-H), 131.8 (aryl *C*), 132.5 (aryl *C*-H), 135.0 (aryl C), 149.6 (aryl *C*), 160.6 (aryl C); ν_{max} (thin film/cm^{-1}) 983 (s), 1092 (m), 1140 (s), 1209 (vs, C-F stretch?),[1] 1420 (s), 1592 (m), 2861 (w), 2933 (w), 2957 (w); MS (ES$^+$) *m/z* 433 (M+H$^+$); HRMS $C_{19}H_{20}F_3O_4S_2$ (M+H$^+$) Expected 433.0750, Found 433.0749.

General Procedure C – Pd-catalysed Suzuki coupling

$Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) and boronic acid (0.2 mmol) were added to a microwave vial with Teflon-lined septum pre-flushed with N_2. K_2CO_3 (2 M in H_2O, 1 mL) and **5** (43 mg, 0.1 mmol) in 1,4-dioxane (1 mL) were then added and the resulting mixture was heated to 135 °C and stirred for 5 h. The mixture was then cooled, diluted with H_2O (15 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were dried with $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude product was purified by column chromatography on silica gel.

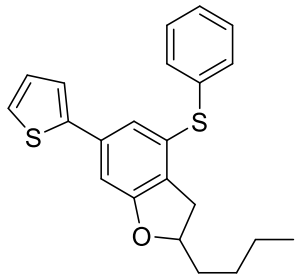
2-Butyl-4-(phenylsulfanyl)-6-(p-tolyl)-2,3-dihydrobenzofuran ***6a***



As described in general procedure C, triflate **5** (44.1 mg, 0.1 mmol) and 4-methylphenylboronic acid (27 mg, 0.2 mmol), after purification by column chromatography (2% Et_2O in hexanes), gave **6a** (34.6 mg, 0.09 mmol, 90%) as a white solid; m.p 59.9-61.2 °C; δ_H (400 MHz, $CDCl_3$) 0.95 (3 H, t, *J* 6.8 Hz, CH_3), 1.33 - 1.52 (4 H, m, CH_2), 1.61 - 1.72 (1 H, m, (CH(O)CH_2CH$_2$)), 1.78 - 1.89 (1 H, m, (CH(O)CH_2CH$_2$)), 2.39 (3 H, s, ArCH_3), 2.75 (1 H, dd, *J* 16.1, 7.5 Hz, ArCH_2CH(O)), 3.18 (1 H, dd, *J* 16.1, 9.0 Hz, ArCH_2CH(O)), 4.77 - 4.87 (1 H, m, C*H*(O)), 6.93 (1 H, d, *J* 1.5 Hz, aryl H), 7.03 (1 H, d, *J* 1.5 Hz, aryl H), 7.19 - 7.34 (7 H, m, aryl H), 7.38 - 7.43 (2 H, m, aryl H); δ_C (100 MHz, $CDCl_3$) 14.0 (*C*H$_3$), 21.1 (Ar*C*H$_3$), 22.6 (*C*H$_2$), 27.4 (*C*H$_2$), 34.9 (Ar*C*H$_2$CH(O)), 35.8 (CH(O)*C*H$_2$CH$_2$), 83.9 (*C*H(O)), 107.2 (aryl *C*-H), 122.3 (aryl *C*-H), 126.7 (aryl *C*-H), 126.8 (aryl *C*-H), 127.9 (aryl *C*),

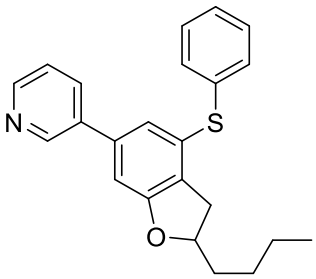
129.2 (aryl *C*-H), 129.4 (aryl *C*-H), 130.0 (aryl *C*-H), 131.2 (aryl *C*), 135.0 (aryl *C*), 137.2 (aryl *C*), 137.7 (aryl *C*), 142.4 (aryl *C*), 160.5 (aryl *C*); ν_{max} (thin film/cm^{-1}) 814 (vs, oop para-subst. arene), 950 (m), 1206 (m), 1468 (s), 1561 (s), 1578 (s), 2858 (m), 2929 (s), 2954 (s); MS (APCI) *m/z* 375 ($M+H^+$); HRMS $C_{25}H_{27}OS$ ($M+H^+$) Expected 375.1777, Found 375.1775.

2-Butyl-4-(phenylsulfanyl)-6-(thien-2-yl)-2,3-dihydrobenzofuran ***6b***



As described in general procedure C, triflate **5** (42.8 mg, 0.1 mmol) and 2-thienylboronic acid (25.6 mg, 0.2 mmol), after purification by column chromatography (2% Et_2O in hexanes), gave **6b** (31.2 mg, 0.09 mmol, 87%) as a colourless oil; δ_H (400 MHz, $CDCl_3$) 0.93 (3 H, t, *J* 7.0 Hz, CH_3), 1.32 - 1.50 (4 H, m, CH_2), 1.60 - 1.70 (1 H, m, (CH(O)CH_2CH$_2$), 1.75 - 1.87 (1 H, m, (CH(O)CH_2CH$_2$), 2.71 (1 H, dd, *J* 16.3, 7.5 Hz, ArCH_2CH(O)), 3.14 (1 H, dd, *J* 16.3, 9.0 Hz, ArCH_2CH(O)), 4.81 (1 H, dtd, *J* 8.9, 7.3, 5.9 Hz, C*H*(O)), 6.96 (1 H, d, *J* 1.5 Hz, aryl H), 7.04 (1 H, dd, *J* 5.1, 3.6 Hz, aryl H), 7.06 (1 H, d, *J* 1.5 Hz, aryl H), 7.20 (1 H, dd, *J* 3.6, 1.1 Hz, aryl H), 7.22 - 7.34 (6 H, m, aryl H); δ_C (100 MHz, $CDCl_3$) 14.0 (*C*H$_3$), 22.6 (*C*H$_2$), 27.3 (*C*H$_2$), 34.9 (Ar*C*H$_2$CH(O)), 35.8 (CH(O)*C*H$_2$CH$_2$), 84.0 (*C*H(O)), 106.1 (aryl *C*-H), 121.1 (aryl *C*-H), 123.2 (aryl *C*-H), 124.8 (aryl *C*-H), 126.8 (aryl *C*-H), 127.8 (aryl *C*-H), 128.4 (aryl *C*), 129.2 (aryl *C*-H), 130.1 (aryl *C*-H), 131.6 (aryl *C*), 134.7 (aryl *C*), 135.3 (aryl *C*), 143.8 (aryl *C*), 160.5 (aryl *C*); ν_{max} (thin film/cm^{-1}) 932 (m), 1023 (m), 1224 (s), 1413 (m), 1476 (m), 1569 (s), 1603 (m), 2858 (w), 2930 (m), 2953 (m); MS (APCI) *m/z* 367 ($M+H^+$); HRMS $C_{22}H_{23}OS_2$ ($M+H^+$) Expected 367.1185, Found 367.1186.

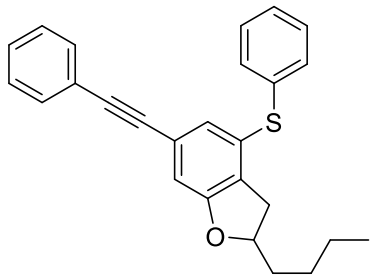
3-(2-Butyl-4-(phenylsulfanyl)-2,3-dihydrobenzofuran-6-yl)pyridine ***6c***



As described in general procedure C, **5** (43 mg, 0.1 mmol) and 3-pyridylboronic acid (24.5 mg, 0.2 mmol), after purification by column chromatography (50% Et_2O in hexanes), gave **6c** (25.7 mg, 0.07 mmol, 71%) as a colourless oil; δ_H (400 MHz, $CDCl_3$) 0.93 (3 H, t, *J* 7.0 Hz, CH_3), 1.33 - 1.52 (4 H,

m, CH_2), 1.61 - 1.73 (1 H, m, (CH(O)CH_2CH$_2$), 1.77 - 1.90 (1 H, m, (CH(O)CH_2CH$_2$), 2.76 (1 H, dd, *J* 16.3, 7.5 Hz, ArCH_2CH(O)), 3.19 (1 H, dd, *J* 16.3, 9.0 Hz, ArCH_2CH(O)), 4.79 - 4.90 (1 H, m, C*H*(O)), 6.88 (1 H, d, *J* 1.5 Hz, aryl H), 6.94 (1 H, d, *J* 1.5 Hz, aryl H), 7.21 - 7.40 (6 H, m, aryl H), 7.76 (1 H, dt, *J* 8.0, 2.0 Hz, aryl H), 8.56 (1 H, d, *J* 3.0 Hz, aryl H), 8.73 (1 H, br. s., aryl H); δ_C (100 MHz, $CDCl_3$) 14.0 (*C*H$_3$), 22.5 (*C*H$_2$), 27.3 (*C*H$_2$), 34.8 (Ar*C*H$_2$CH(O)), 35.8 (CH(O)*C*H$_2$CH$_2$), 84.1 (*C*H(O)), 106.9 (aryl *C*-H), 121.6 (aryl *C*-H), 123.5 (aryl *C*-H), 121.2 (aryl *C*-H), 128.6 (aryl *C*), 129.3 (aryl *C*-H), 130.7 (aryl *C*-H), 132.4 (aryl *C*), 134.2 (aryl *C*-H), 136.1 (aryl *C*), 138.9 (aryl *C*), 148.1 (aryl *C*-H), 148.5 (aryl *C*-H), 160.6 (aryl *C*); ν_{max} (thin film/cm^{-1}) 946 (s), 1023 (m), 1218 (s), 1293 (w), 1399 (m), 1426 (s), 1463 (m), 1577 (s), 2858 (w), 2929 (m), 2954 (m); MS (ES$^+$) *m/z* 362 (M+H$^+$); HRMS $C_{23}H_{24}ONS$ (M+H$^+$) Expected 362.1573, Found 362.1566.

2-Butyl-6-(phenylethynyl)-4-(phenylsulfanyl)-2,3-dihydrobenzofuran ***6d***



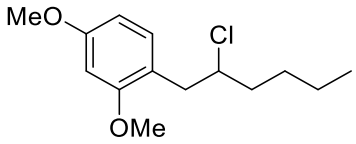
Et_3N (014 mL, 1.0 mmol) was added to a microwave vial with Teflon-lined septum pre-flushed with N_2 and containing a stirred mixture of $PdCl_2(PPh_3)_2$ (7.0 mg, 0.01 mmol), phenylacetylene (20 mg, 0.2 mmol) and triflate **5** (43.8 mg, 0.1 mmol) in DMF (0.5 mL). The mixture was heated to 90 °C and stirred for 18 h. The mixture was then cooled to room temperature and diluted with H_2O. The aqueous layer was extracted with Et_2O (3 × 10 mL) and the combined organic extracts were washed with LiCl (10% in H_2O, 15 mL), dried with $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude product was purified by column chromatography on silica gel (10% $CHCl_3$ in hexanes) to give **6d** (36.2 mg, 0.09 mmol, 94%) as a pale yellow oil; δ_H (400 MHz, $CDCl_3$) 0.93 (3 H, t, *J* 6.9 Hz, C*H*$_3$), 1.32 - 1.47 (4 H, m, C*H*$_2$), 1.61 - 1.69 (1 H, m, CH(O)C*H*$_2$CH$_2$), 1.76 - 1.83 (1 H, m, CH(O)C*H*$_2$CH$_2$), 2.73 (1 H, dd, *J* 16.5, 7.5 Hz, ArC*H*$_2$CH(O)), 3.16 (1 H, dd, *J* 16.4, 9.1 Hz, ArC*H*$_2$CH(O)), 4.76 - 4.84 (1 H, m, C*H*(O)), 6.83 (1 H, d, *J* 0.9 Hz, aryl H), 6.96 (1 H, d, *J* 0.9 Hz, aryl H), 7.24 - 7.39 (8 H, m, aryl H), 7.47 - 7.52 (2 H, m, aryl H); δ_C (125 MHz, $CDCl_3$) 14.0 (*C*H$_3$), 22.5 (*C*H$_2$), 27.3 (*C*H$_2$), 35.0 (Ar*C*H$_2$CH(O)), 35.7 (CH(O)*C*H$_2$CH$_2$), 83.9 (*C*H(O)), 89.0 (Ar*C*≡CAr), 89.1 (Ar*C*≡CAr), 111.2 (aryl *C*-H), 123.1 (aryl *C*), 123.6 (aryl C), 126.5 (aryl *C*-H), 127.1 (aryl *C*-H), 128.2 (aryl *C*-H), 128.3 (aryl *C*-H), 129.3 (aryl *C*-H), 129.7 (aryl *C*), 130.6 (aryl *C*-H), 131.6 (aryl *C*-H), 131.7 (aryl *C*), 134.3 (aryl *C*), 159.8 (aryl *C*); ν_{max} (thin film/cm^{-1}) 755 (vs), 987 (m), 1220 (s), 1410 (m), 1562 (s), 1600 (m), 2858 (w), 2929 (m), 2955 (m); MS (ES$^+$) *m/z* 385 (M+H$^+$); HRMS $C_{26}H_{25}OS$ (M+H$^+$) Expected 385.1621, Found 385.1621.

Raney Ni Desulfurisation

General Procedure D

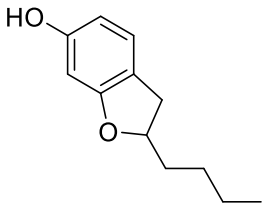
A solution of the corresponding sulfide (0.1 mmol) in EtOH (1 mL) was added dropwise to a suspension of Raney Nickel in EtOH (1 mL). The reaction was stirred at room temperature for 1 h and then filtered through Celite (Et_2O eluent). The solvent was then removed *in vacuo*, and the crude product was purified by column chromatography.

*1-(2-Chlorohexyl)-2,4-dimethoxybenzene **7a***



As described in General Procedure D, **2a** (40.1 mg, 0.11 mmol), Raney Nickel (700 mg of slurry), after column chromatography on silica gel (10% $CHCl_3$ in hexanes), gave **7a** (22.8 mg, 0.09 mmol, 81%) as a colourless oil; δ_H (500 MHz, $CDCl_3$) 0.91 (3 H, t, *J* 7.2 Hz, CH_3), 1.19 – 1.46 (3 H, m, CH_2), 1.52 – 1.62 (1 H, m, CH_2), 1.63 – 1.72 (1 H, m, ArCH$_2$CH(Cl)CH_2), 1.73 – 1.82 (1 H, m, ArCH$_2$CH(Cl)CH_2), 2.93 (1 H, dd, *J* 13.7, 7.6 Hz, ArCH_2), 3.04 (1 H, dd, 13.7, 6.3 Hz, ArCH_2), 3.81 (3 H, s, OCH_3), 3.82 (3 H, s, OCH_3), 4.15 – 4.22 (1 H, m, C*H*Cl), 6.42 – 6.47 (2 H, m, aryl H), 7.08 (1 H, d, *J* 7.8 Hz, aryl H); δ_C (125 MHz, $CDCl_3$) 14.0 (*C*H$_3$), 22.2 (*C*H$_2$), 28.6 (*C*H$_2$), 37.5 (ArCH$_2$CH(Cl)*C*H$_2$), 39.4 (Ar*C*H$_2$), 55.2 (O*C*H$_3$), 55.3 (O*C*H$_3$), 63.4 (*C*HCl), 98.4 (aryl *C*-H), 103.7 (aryl *C*-H), 119.0 (aryl *C*), 131.6 (aryl *C*-H), 158.4 (aryl *C*), 159.8 (aryl *C*); ν_{max} (thin film/cm^{-1}) 935 (w), 1036 (s), 1131 (m), 1155 (s), 1207 (s), 1287 (m), 1437 (w), 1464 (m), 1506 (s), 1587 (m), 1613 (m), 2836 (w), 2858 (w), 2928 (w), 2955 (w); MS (APCI) *m/z* 257 (M+H$^+$); HRMS $C_{14}H_{22}O_2Cl$ (M+H$^+$) Expected 257.1303, Found 257.1299

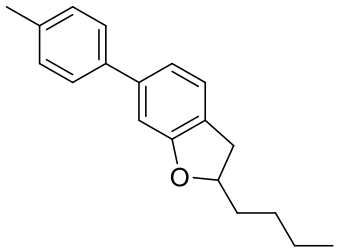
*2-Butyl-2,3-dihydrobenzofuran-6-ol **7b***



As described by general procedure D, **4a** (53.8 mg, 0.18 mmol), Raney Nickel (700 mg of slurry), after column chromatography on silica gel (10% EtOAc in hexanes), gave **7b** (33.3 mg, 0.18 mmol, 97%) as a colourless oil; δ_H (400 MHz, $CDCl_3$) 0.94 (3 H, t, *J* 7.2 Hz, CH_3), 1.33 – 1.54 (4 H, m, CH_2), 1.61 – 1.73 (1 H, m, ArCH$_2$CH(O)CH_2), 1.76 – 1.91 (1 H, m, ArCH$_2$CH(O)CH_2), 2.78 (1 H, dd, *J* 15.1, 7.8 Hz, ArCH_2), 3.19 (1 H, dd, *J* 15.1, 8.8 Hz, ArCH_2), 4.74 – 4.84 (1 H, m, C*H*(O)), 4.91 (1

H, s, O*H*), 6.27 – 6.33 (2 H, m, aryl H), 6.94 – 7.00 (1 H, m, aryl H); δ_C (100 MHz, $CDCl_3$) 14.0 (*C*H_3), 22.6 (*C*H_2), 27.5 (*C*H_2), 34.7 (Ar*C*H_2CH(O)), 35.7 (CH(O)*C*H_2CH$_2$), 84.6 (*C*H(O)), 97.5 (aryl *C*-H), 106.8 (aryl *C*-H) 119.1 (aryl *C*), 125.0 (aryl *C*-H), 155.9 (aryl *C*), 160.8 (aryl *C*); ν_{max} (thin film/cm^{-1}) 964 (s), 1096 (s), 1136 (s), 1186 (m), 1214 (m), 1269 (w), 1352 (w), 1458 (s), 1497 (s), 1606 (m), 1622 (m), 2859 (w), 2930 (w), 2956 (w), 3388 (br, w, O-H stretch); MS (APCI) *m/z* 193 (M+H$^+$); HRMS $C_{12}H_{17}O_2$ (M+H$^+$) Expected 193.1223, Found 193.1215.

2-Butyl-6-(p-tolyl)-2,3-dihydrobenzofuran ***7c***



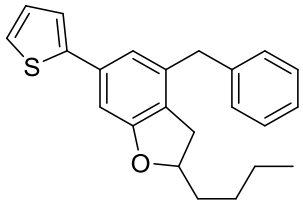
As described by general procedure D, **6a** (37.0 mg, 0.10 mmol), Raney Nickel (700 mg of slurry), after column chromatography on silica gel (10% $CHCl_3$ in hexanes), gave **7c** (23.5 mg, 0.09 mmol, 89%) as a colourless oil; δ_H (500 MHz, $CDCl_3$) 0.97 (3 H, t, *J* 7.0 Hz, CH$_2$C*H*$_3$), 1.37 – 1.59 (4 H, m, C*H*$_2$), 1.66 – 1.78 (1 H, m, ArCH$_2$CH(O)C*H*$_2$), 1.83 – 1.95 (1 H, m, ArCH$_2$CH(O)C*H*$_2$), 2.41 (3 H, s, ArC*H*$_3$), 2.91 (1 H, dd, *J* 15.4, 7.8 Hz, ArC*H*$_2$), 3.31 (1 H, dd, *J* 15.4, 8.9 Hz, ArC*H*$_2$), 4.78 – 4.88 (1 H, m, C*H*(O)), 7.00 (1 H, s, aryl H), 7.06 (1 H, d, *J* 7.6 Hz, aryl H), 7.20 (1 H, d, *J* 7.6 Hz, aryl H), 7.24 (2 H, d, *J* 8.1 Hz, aryl H), 7.48 (2 H, d, *J* 8.1 Hz, aryl H); δ_C (125 MHz, $CDCl_3$) 13.8 (CH$_2$*C*H$_3$), 20.8 (Ar*C*H$_3$), 22.4 (*C*H$_2$), 27.4 (*C*H$_2$), 35.0 (Ar*C*H$_2$), 35.6 (ArCH$_2$CH(O)*C*H$_2$), 83.6 (*C*H(O)), 107.6 (aryl *C*-H), 118.8 (aryl *C*-H), 124.7 (aryl *C*-H), 125.6 (aryl C), 126.7 (aryl *C*-H), 129.1 (aryl *C*-H), 136.6 (aryl *C*), 138.2 (aryl *C*), 141.3 (aryl *C*), 160.0 (aryl *C*); ν_{max} (thin film/cm^{-1}) 971 (s), 1110 (w), 1166 (w), 1204 (m), 1295 (m), 1378 (w), 1431 (m), 1483 (s), 1568 (w), 1588 (w), 1618 (w), 2858 (w), 2928 (w), 2954 (w); MS (APCI) *m/z* 267 (M+H$^+$); HRMS $C_{19}H_{23}O$ (M+H$^+$) Expected 267.1743, Found 267.1740.

Ni-catalysed Kumada-Corriu coupling

General Procedure E

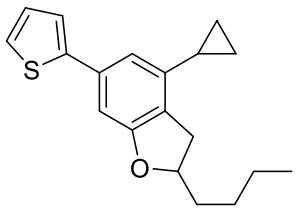
Ni(PPh$_3$)Cl$_2$ (6.5 mg, 0.01 mmol) was added to a microwave vial with Teflon-lined septum before evacuating and backfilling with Ar (3 cycles). Sulfide (0.1 mmol), benzene (1.5 mL) and Grignard reagent solution (0.3 mmol) were then added at room temperature and the mixture was heated to 80 °C and stirred for 24 h. The reaction mixture was then cooled to room temperature and quenched with aqueous saturated NH_4Cl (10 mL). The aqueous layer was then extracted with EtOAc (3 × 10 mL) and the combined organic extracts were dried with $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude product was purified by column chromatography on silica gel.

4-Benzyl-2-butyl-6-(thien-2-yl)-2,3-dihydrobenzofuran ***8a***



As described in general procedure E, **6b** (33.0 mg, 0.09 mmol), benzylmagnesium chloride (1.82 M in THF, 0.15 mL, 0.3 mmol) and $Ni(PPh_3)_2Cl_2$ (6.5 mg, 0.01 mmol), after column chromatography on silica gel (15% toluene in hexanes), gave **8a** (27.4 mg, 0.08 mmol, 88%) as a white solid; m.p. 35.3-36.8 °C; δ_H (400 MHz, $CDCl_3$) 0.93 (3 H, t, *J* 7.3 Hz, CH_3), 1.32 - 1.52 (4 H, m, CH_2), 1.59 - 1.72 (1 H, m, CH(O)CH_2CH$_2$), 1.75 - 1.88 (1 H, m, CH(O)CH_2CH$_2$), 2.66 (1 H, dd, *J* 15.7, 7.7 Hz, ArCH_2CH(O)), 3.10 (1 H, dd, *J* 15.7, 8.9 Hz, ArCH_2CH(O)), 3.94 (2 H, s, ArCH_2Ar), 4.78 (1 H, dtd, *J* 8.9, 7.7, 6.0 Hz, C*H*(O)), 6.93 (1 H, d, *J* 1.5 Hz, aryl H), 6.97 (1 H, d, *J* 1.5 Hz, aryl H), 7.05 (1 H, dd, *J* 5.1, 3.6 Hz, aryl H), 7.17 - 7.26 (5 H, m, aryl H), 7.28 - 7.33 (2 H, m, aryl H); δ_C (100 MHz, $CDCl_3$) 14.0 (*C*H$_3$), 22.6 (*C*H$_2$), 27.5 (*C*H$_2$), 34.2 (ArCH$_2$CH(O)), 35.9 (CH(O)*C*H$_2$CH$_2$), 39.7 (ArCH$_2$Ar), 83.8 (*C*H(O)), 105.0 (aryl *C*-H), 119.3 (aryl *C*-H), 122.9 (aryl *C*-H), 124.3 (aryl *C*-H), 125.7 (aryl *C*), 126.2 (aryl *C*-H), 127.8 (aryl *C*-H), 128.5 (aryl *C*-H), 128.7 (aryl *C*-H), 134.6 (aryl *C*), 137.7 (aryl *C*), 139.6 (aryl *C*), 144.7 (aryl *C*), 160.3 (aryl *C*); ν_{max} (thin film/cm^{-1}) 841 (m), 971 (w), 1030 (w), 1222 (s), 1434 (s), 1590 (s), 1614 (w), 2858 (w), 2929 (m), 2954 (m), 3026 (w), 3061 (w); MS (APCI) *m/z* 349 (M+H$^+$); HRMS $C_{23}H_{25}OS$ (M+H$^+$) Expected 349.1621, Found 349.1605.

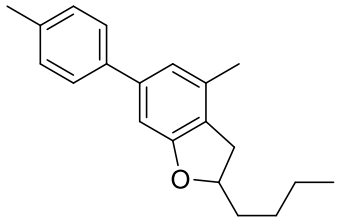
2-Butyl-4-cyclopropyl-6-(thiophen-2-yl)-2,3-dihydrobenzofuran ***8b***



As described in general procedure E, **6b** (33.0 mg, 0.09 mmol), cyclopropylmagnesium bromide (0.5 M in THF, 0.6 mL, 0.3 mmol) and $Ni(PPh_3)_2Cl_2$ (6.5 mg, 0.01 mmol), after column chromatography on silica gel (10% toluene in hexanes) gave **8b** (19.2 mg, 0.07 mmol, 72%) as a colourless oil; δ_H (400 MHz, $CDCl_3$) 0.73 - 0.79 (2 H, m, CH(CH_2)$_2$), 0.92 - 1.00 (5 H, m, CH_3 + CH(CH_2)$_2$), 1.36 - 1.55 (4 H, m, CH_2), 1.66 - 1.96 (3 H, m, CH(O)CH_2CH$_2$ + C*H*(CH$_2$)$_2$), 2.90 (1 H, dd, *J* 15.6, 7.5 Hz, ArCH_2CH(O)), 3.35 (1 H, dd, *J* 15.6, 8.8 Hz, ArCH_2CH(O)), 4.84 (1 H, dtd, *J* 8.8, 7.5, 6.1 Hz, C*H*(O)), 6.63 (1 H, d, *J* 1.5 Hz, aryl H), 6.85 (1 H, d, *J* 1.5 Hz, aryl H), 7.02 - 7.07 (1 H, m, aryl H), 7.20 - 7.24 (2 H, m, aryl H); δ_C (100 MHz, $CDCl_3$) 7.80 (CH(*C*H$_2$)$_2$), 13.1 (*C*H(CH$_2$)$_2$), 14.0 (*C*H$_3$), 22.6 (*C*H$_2$), 27.6 (*C*H$_2$), 34.2 ((ArCH$_2$CH(O)), 36.0 (CH(O)*C*H$_2$CH$_2$), 83.8 (*C*H(O)), 104.3 (aryl *C*-

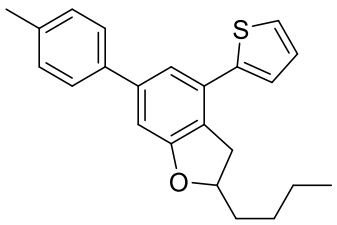
H), 113.9 (aryl *C*-H), 122.8 (aryl *C*-H), 124.2 (aryl *C*-H), 125.9 (aryl *C*), 127.8 (aryl *C*-H), 134.6 (aryl *C*), 140.6 (aryl *C*), 145.0 (aryl *C*), 159.7 (aryl *C*); ν_{max} (thin film/cm^{-1}) 823 (s), 905 (m), 992 (m), 1023 (s), 1223 (s), 1425 (s), 1432 (s), 1483 (w), 1589 (s), 1613 (m), 2858 (m), 2930 (s), 2953 (s), 3003 (w), 3081 (w); MS (APCI) *m/z* 299 (M+H$^+$); HRMS $C_{19}H_{23}OS$ (M+H$^+$) Expected 299.1464, Found 299.1451.

2-Butyl-4-methyl-6-(p-tolyl)-2,3-dihydrobenzofuran ***8c***



As described in general procedure E, **6b** (37.5 mg, 0.1 mmol), methylmagnesium chloride (3 M in THF, 0.1 mL, 0.3 mmol) and $Ni(PPh_3)_2Cl_2$ (6.5 mg, 0.01 mmol), after column chromatography on silica gel (10% toluene in hexanes), gave **8c** (20.9 mg, 0.08 mmol, 75%) as a white solid; m.p. 44.1-45.2 °C; δ_H (400 MHz, $CDCl_3$) 0.96 (3 H, t, *J* 7.0 Hz, CH_3), 1.36 - 1.59 (4 H, m, CH_2), 1.66 - 1.77 (1 H, m, CH(O)CH_2CH$_2$), 1.83 - 1.95 (1 H, m, CH(O)CH_2CH$_2$), 2.29 (3 H, s, ArCH_3), 2.40 (3 H, s, ArCH_3), 2.80 (1 H, dd, *J* 15.4, 7.9 Hz, ArCH_2CH(O)), 3.23 (1 H, dd, *J* 15.4, 8.9 Hz, ArCH_2CH(O)), 4.79 – 4.89 (1 H, m, C*H*(O)), 6.83 (1 H, s, aryl H), 6.89 (1 H, s, aryl H), 7.20 – 7.25 (2 H, m, aryl H), 7.44 - 7.48 (2 H, m, aryl H); δ_C (100 MHz, $CDCl_3$) 14.0 (*C*H$_3$), 19.1 (Ar*C*H$_3$), 21.1 (Ar*C*H$_3$), 22.6 (*C*H$_2$), 27.6 (*C*H$_2$), 34.3 (Ar*C*H$_2$CH(O)), 36.0 (CH(O)*C*H$_2$CH$_2$), 83.6 (*C*H(O)), 105.2 (aryl *C*-H), 120.2 (aryl *C*-H), 124.9 (aryl *C*), 126.9 (aryl *C*-H), 129.3 (aryl *C*-H), 134.7 (aryl *C*), 136.8 (aryl *C*), 138.6 (aryl *C*), 141.5 (aryl *C*), 159.9 (aryl *C*); ν_{max} (thin film/cm^{-1}) 814 (vs), 975 (s), 1204 (m), 1479 (s), 1598 (s), 2858 (m), 2929 (s), 2954 (s), 3024 (w); MS (APCI) *m/z* 281 (M+H$^+$); HRMS $C_{20}H_{25}O$ (M+H$^+$) Expected 281.1900, Found 281.1893.

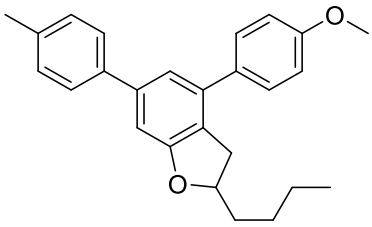
2-Butyl-4-(thien-2-yl)-6-(p-tolyl)-2,3-dihydrobenzofuran ***8d***



As described in general procedure E, **6a** (37.2 mg, 0.1 mmol), 2-thienylmagnesium bromide (1 M in THF, 0.3 mL, 0.3 mmol) and $Ni(PPh_3)_2Cl_2$ (6.5 mg, 0.01 mmol), after column chromatography on silica gel (20% $CHCl_3$ in hexanes), gave **8d** (24.3 mg, 0.07 mmol, 74%) as a colourless oil; δ_H (500 MHz, $CDCl_3$) 0.97 (3 H, t, *J* 6.9 Hz, CH_3), 1.37 - 1.59 (4 H, m, CH_2), 1.70 - 1.80 (1 H, m,

CH(O)CH_2CH$_2$), 1.84 - 1.96 (1 H, m, CH(O)CH_2CH$_2$), 2.41 (3 H, s, ArCH_3), 3.09 (1 H, dd, *J* 15.6, 7.6 Hz, ArCH_2CH(O)), 3.53 (1 H, dd, *J* 15.6, 9.0 Hz, ArCH_2CH(O)), 4.84 - 4.92 (1 H, m, C*H*(O)), 6.95 (1 H, d, *J* 1.3 Hz, aryl H), 7.13 (1 H, dd, *J* 5.0, 3.5 Hz, aryl H), 7.24 - 7.28 (2 H, m, aryl H), 7.30 - 7.34 (2 H, m, aryl H), 7.36 (1 H, dd, *J* 5.2, 1.1 Hz, aryl H), 7.51 (2 H, d, *J* 7.9 Hz, aryl H); δ_C (125 MHz, $CDCl_3$) 14.0 (*C*H$_3$), 21.1 (Ar*C*H$_3$), 22.6 (*C*H$_2$), 27.6 (*C*H$_2$), 36.0 (CH(O)*C*H$_2$CH$_2$), 36.2 (Ar*C*H$_2$CH(O)), 83.7 (*C*H(O)), 107.0 (aryl *C*-H), 118.3 (aryl *C*-H), 122.7 (aryl *C*), 124.9 (aryl *C*-H), 125.1 (aryl *C*-H), 127.0 (aryl *C*-H), 127.6 (aryl *C*-H), 129.4 (aryl *C*-H), 131.5 (aryl *C*), 137.2 (aryl *C*), 138.2 (aryl *C*), 142.1 (aryl *C*), 143.0 (aryl *C*), 160.9 (aryl *C*); ν_{max} (thin film/cm^{-1}) 977 (s), 1045 (w), 1102 (w), 1171 (w), 1201 (s), 1218 (w), 1254 (m), 1297 (m), 1363 (w), 1400 (m), 1420 (s), 1436 (m), 1473 (m), 1516 (w), 1584 (s), 1611 (m), 2858 (w), 2928 (m), 2953 (m), 3023 (w); MS (APCI) *m/z* 349 (M+H$^+$); HRMS $C_{23}H_{25}OS$ (M+H$^+$) Expected 349.1621, Found 349.1606.

2-Butyl-4-(4-methoxyphenyl)-6-(p-tolyl)-2,3-dihydrobenzofuran ***8e***



As described in general procedure E, **6a** (35.5 mg, 0.1 mmol), 4-methoxyphenylmagnesium bromide (0.5 M in THF, 0.6 mL, 0.3 mmol) and Ni(PPh$_3$)$_2$Cl$_2$ (6.5 mg, 0.01 mmol), after column chromatography on silica gel (5% Et$_2$O in hexanes), gave **8e** (22.6 mg, 0.06 mmol, 64%) as a white solid; m.p. 69.8-70.7 °C; δ_H (400 MHz, $CDCl_3$) 0.95 (3 H, t, *J* 7.2 Hz, C*H*$_3$), 1.34 - 1.57 (4 H, m, C*H*$_2$), 1.66 - 1.77 (1 H, m, CH(O)C*H*$_2$CH$_2$), 1.85 - 1.96 (1 H, m, CH(O)C*H*$_2$CH$_2$), 2.41 (3 H, s, ArC*H*$_3$), 2.98 (1 H, dd, *J* 15.7, 8.0 Hz, ArC*H*$_2$CH(O)), 3.38 (1 H, dd, *J* 15.7, 8.7 Hz, ArC*H*$_2$CH(O)), 3.88 (3 H, s, OC*H*$_3$), 4.78 - 4.88 (1 H, m, C*H*(O)), 6.95 - 7.03 (3 H, m, aryl H), 7.12 (1 H, d, *J* 1.5 Hz, aryl H), 7.25 (2 H, d, *J* 8.0 Hz, aryl H), 7.43 - 7.49 (2 H, m, aryl H), 7.52 (2 H, d, *J* 8.0 Hz, aryl H); δ_C (100 MHz, $CDCl_3$) 14.0 (*C*H$_3$), 21.1 (Ar*C*H$_3$), 22.6 (*C*H$_2$), 27.6 (*C*H$_2$), 35.4 (Ar*C*H$_2$CH(O)), 35.8 (CH(O)*C*H$_2$CH$_2$), 55.3 (O*C*H$_3$), 83.8 (*C*H(O)), 106.5 (aryl *C*-H), 113.8 (aryl *C*-H), 119.4 (aryl *C*-H), 123.5 (aryl *C*), 127.0 (aryl *C*-H), 129.2 (aryl *C*-H), 129.4 (aryl *C*-H), 133.0 (aryl *C*), 137.0 (aryl *C*), 138.4 (aryl *C*), 138.5 (aryl *C*), 141.9 (aryl *C*), 158.8 (aryl *C*), 160.5 (aryl *C*); ν_{max} (thin film/cm^{-1}) 814 (vs), 938 (m), 1034 (m), 1108 (m), 1176 (m), 1246 (s), 1290 (m), 1466 (m), 1513 (s), 1609 (m), 2835 (w), 2858 (w), 2929 (w), 2935 (w), 2996 (w), 3029 (w); MS (APCI) *m/z* 373 (M+H$^+$); HRMS $C_{26}H_{29}O_2$ (M+H$^+$) Expected 373.2162, Found 373.2144.

Spectra

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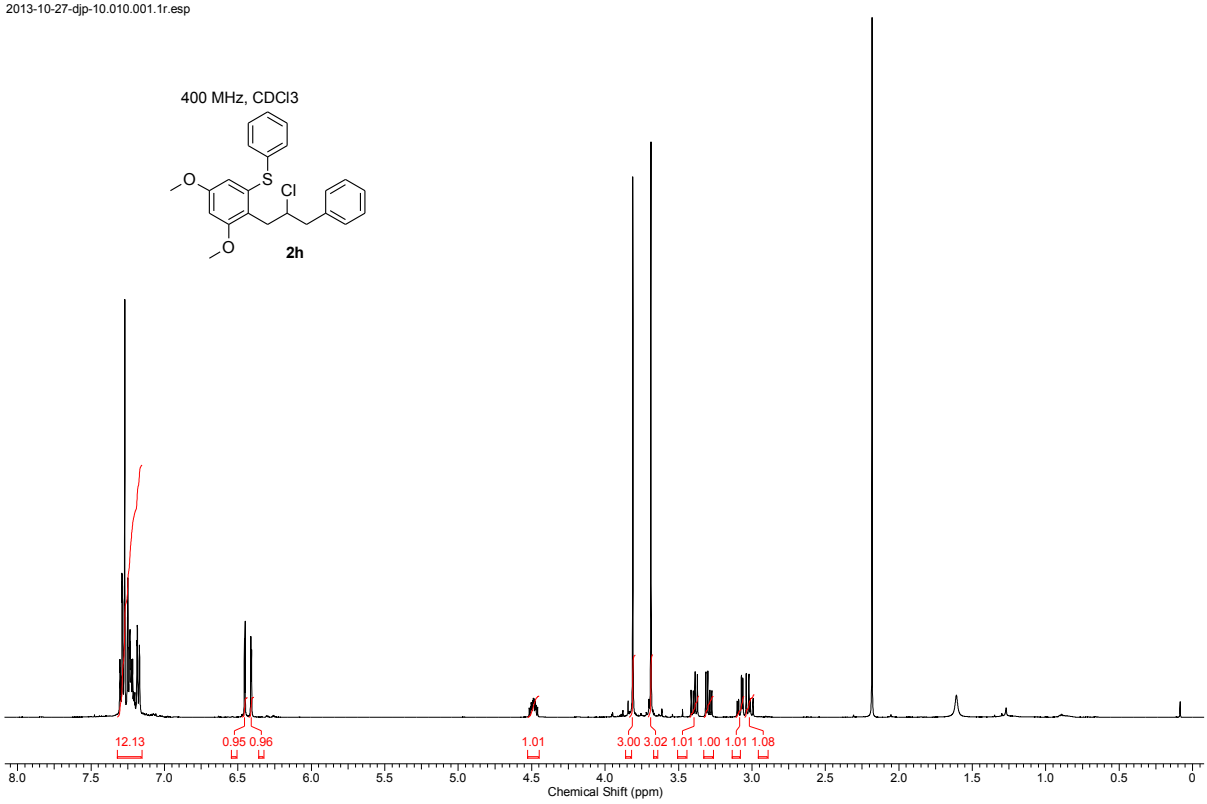

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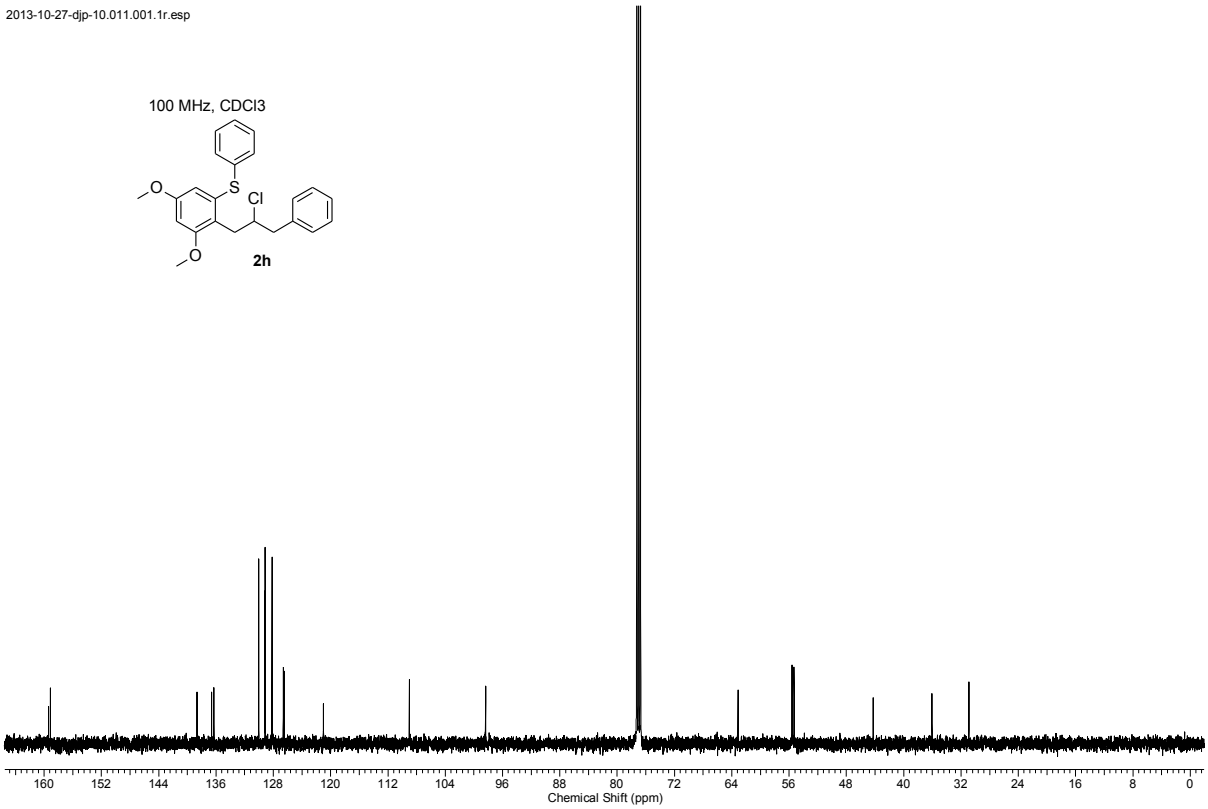

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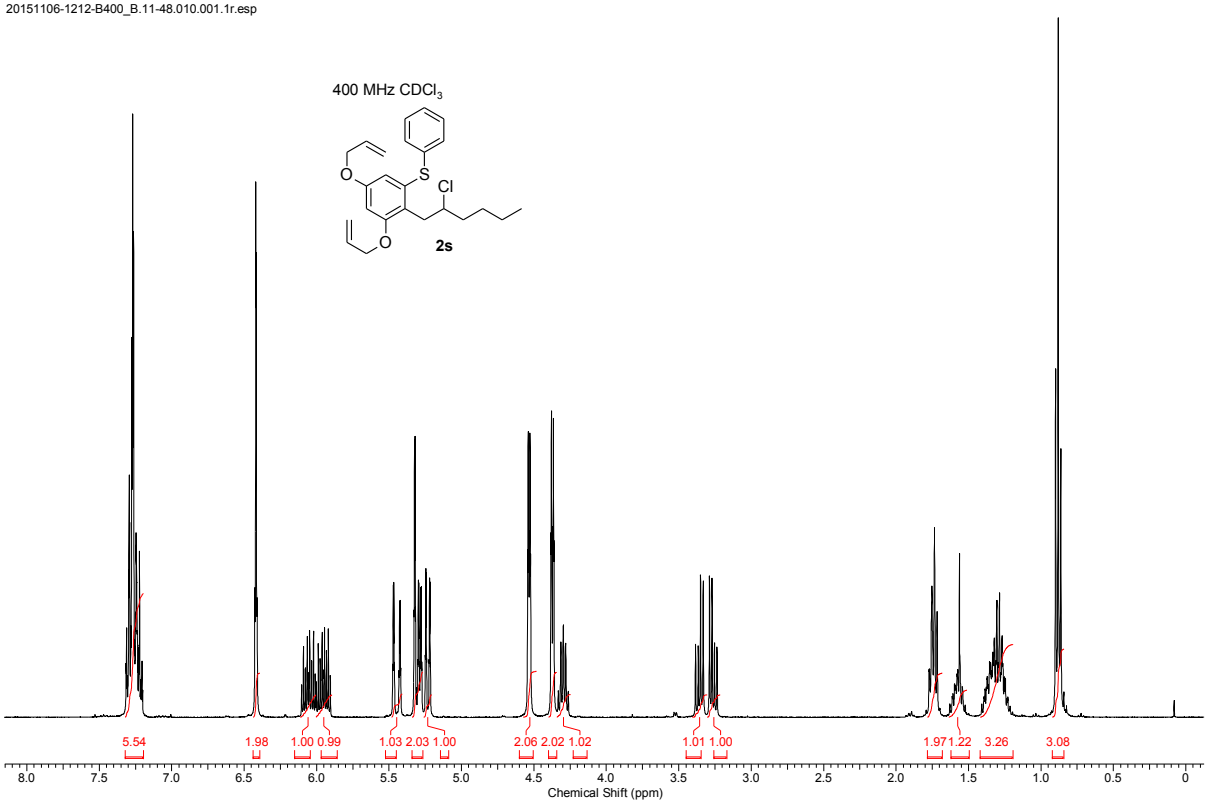

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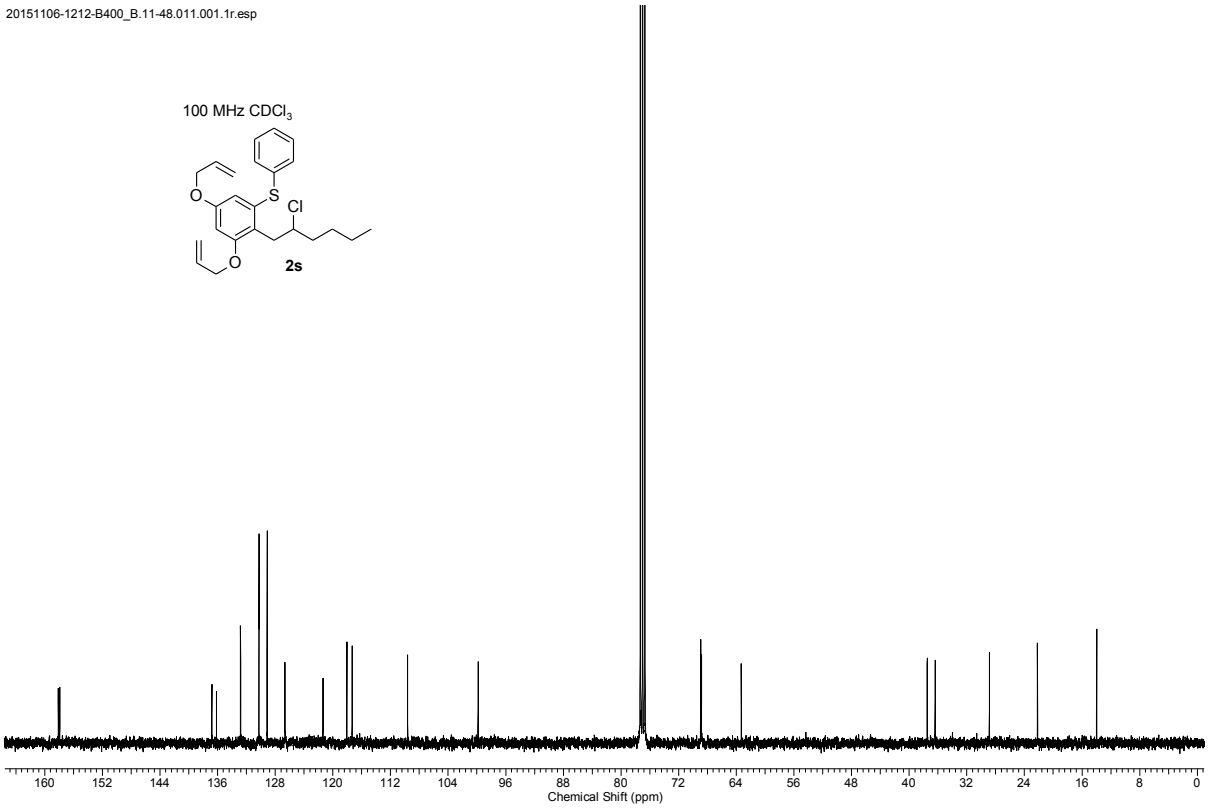

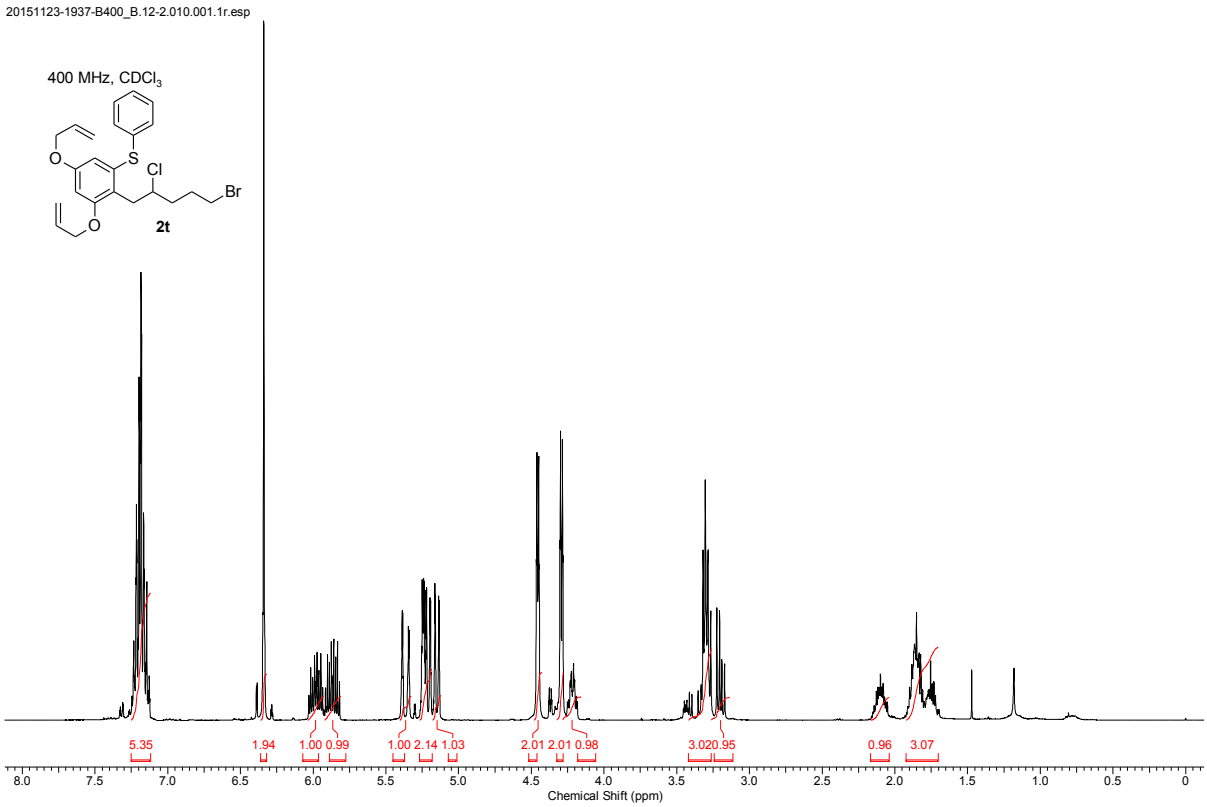
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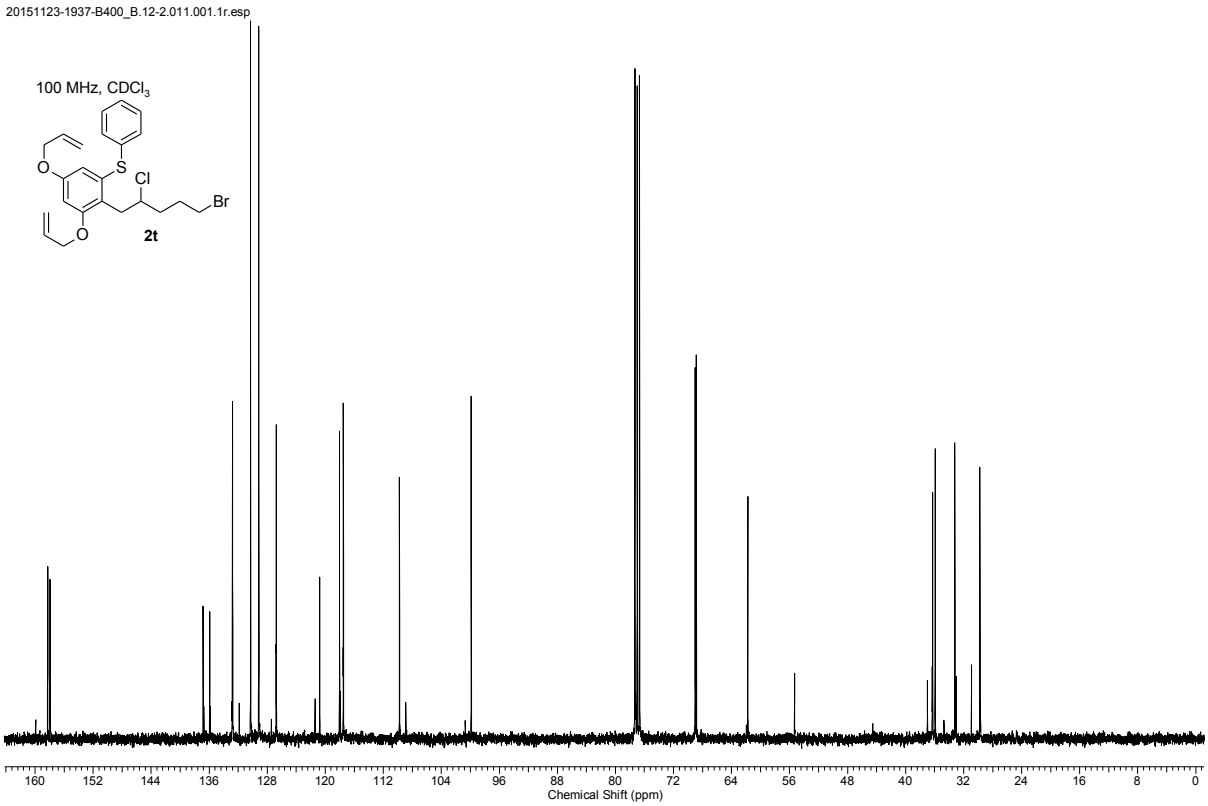
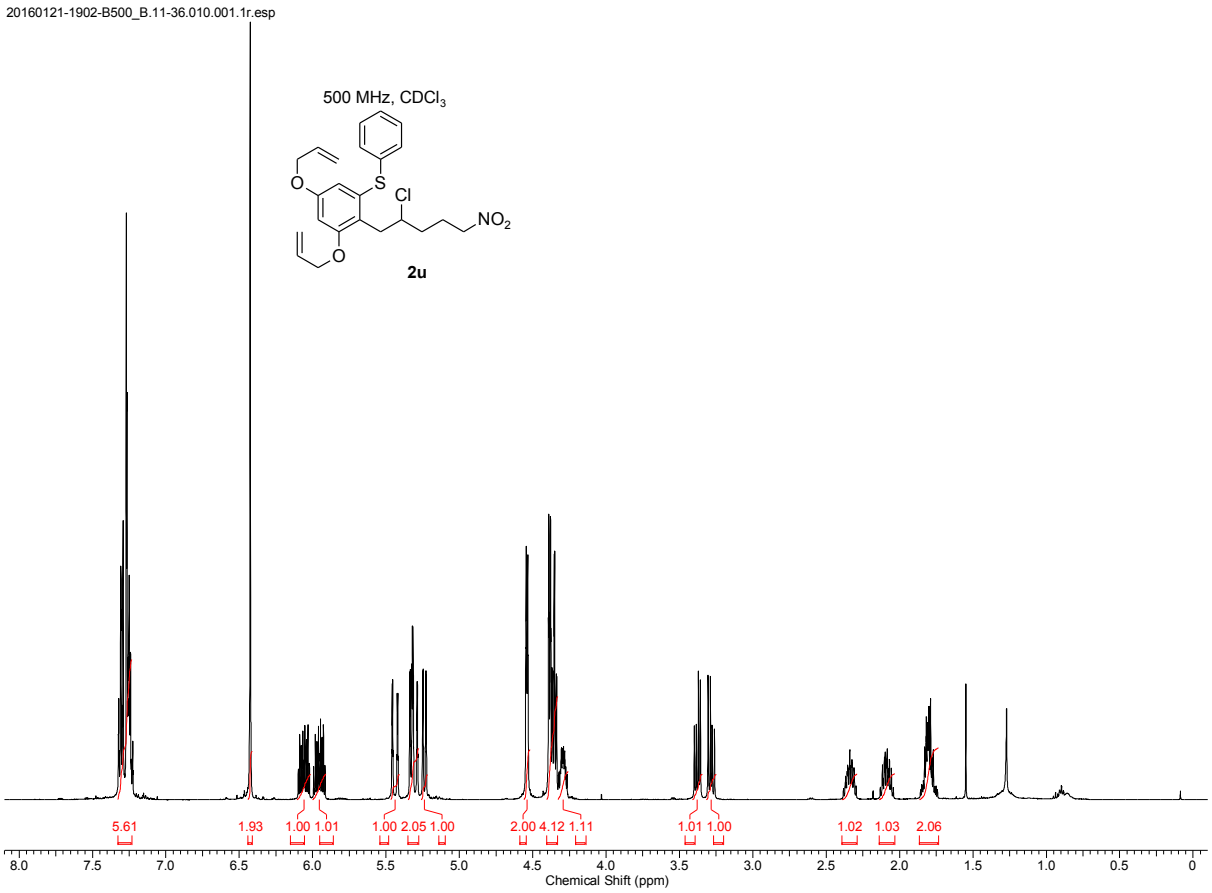
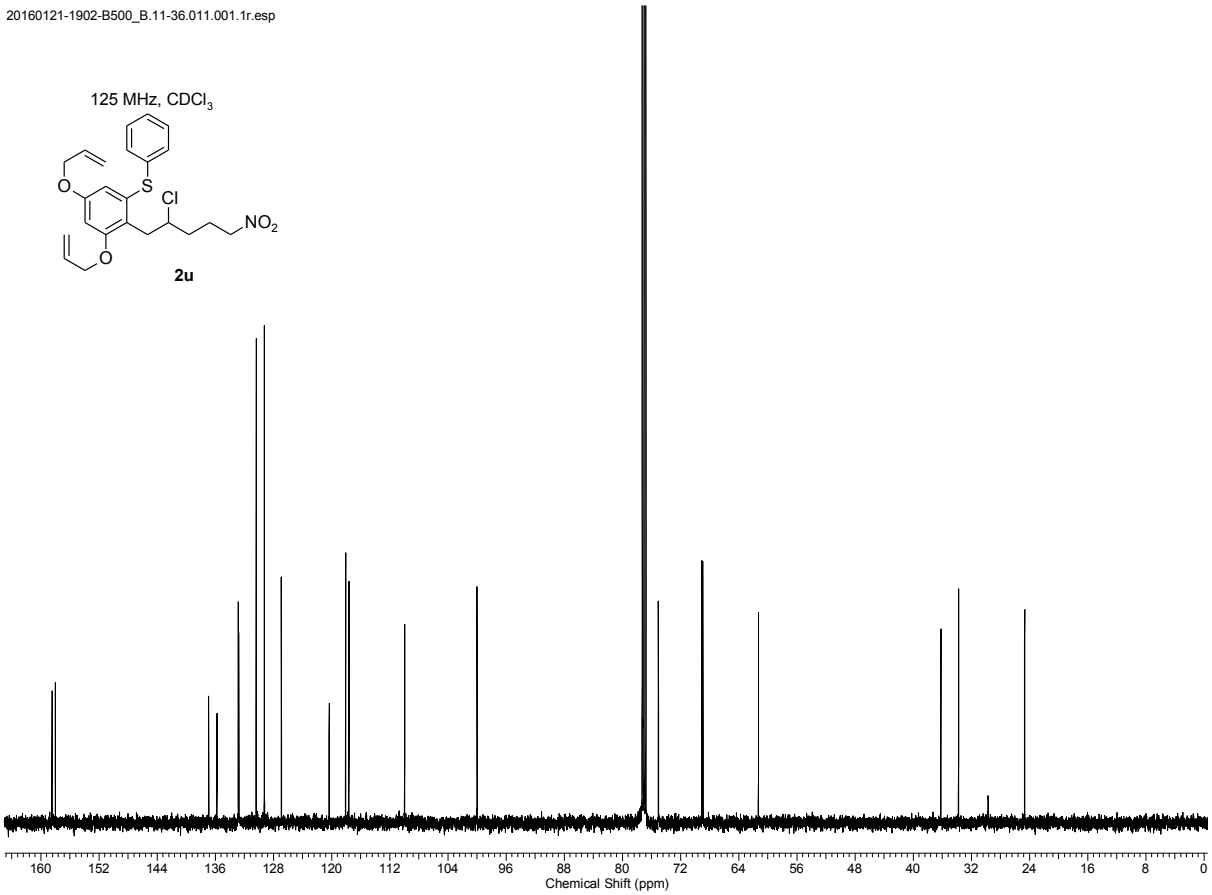
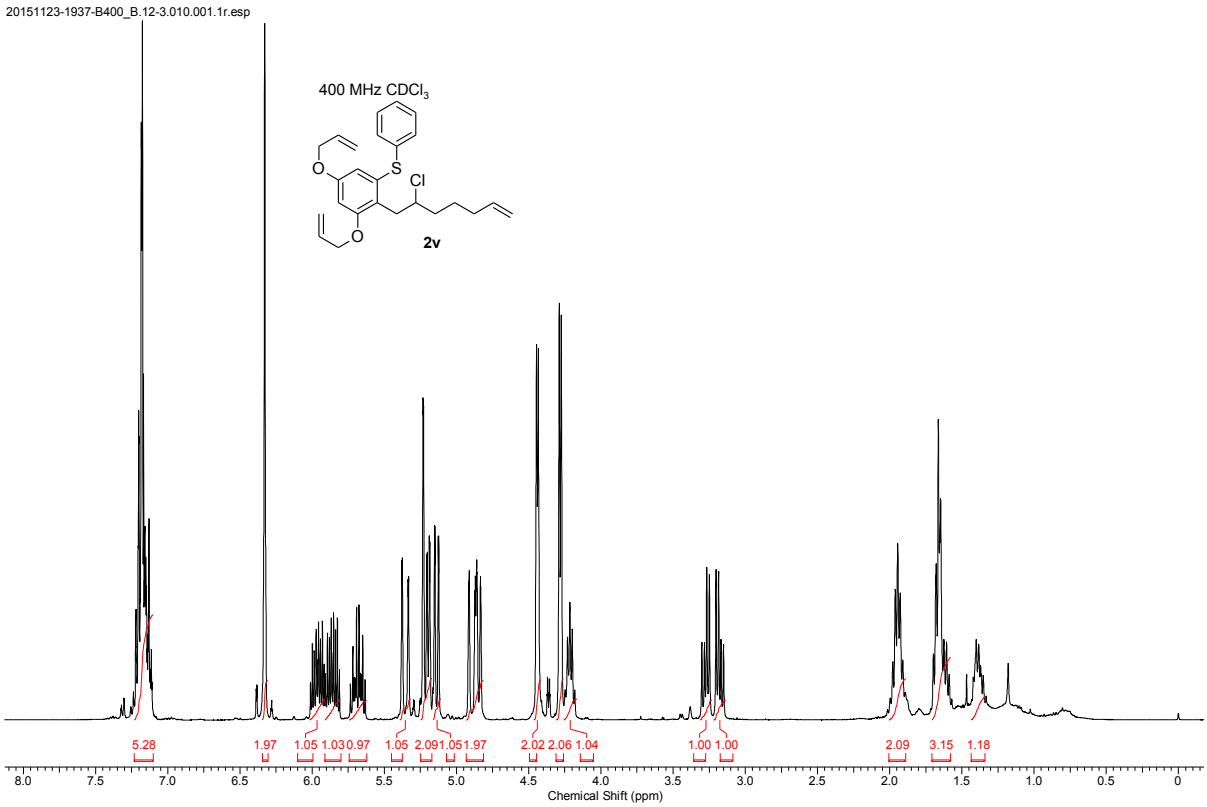
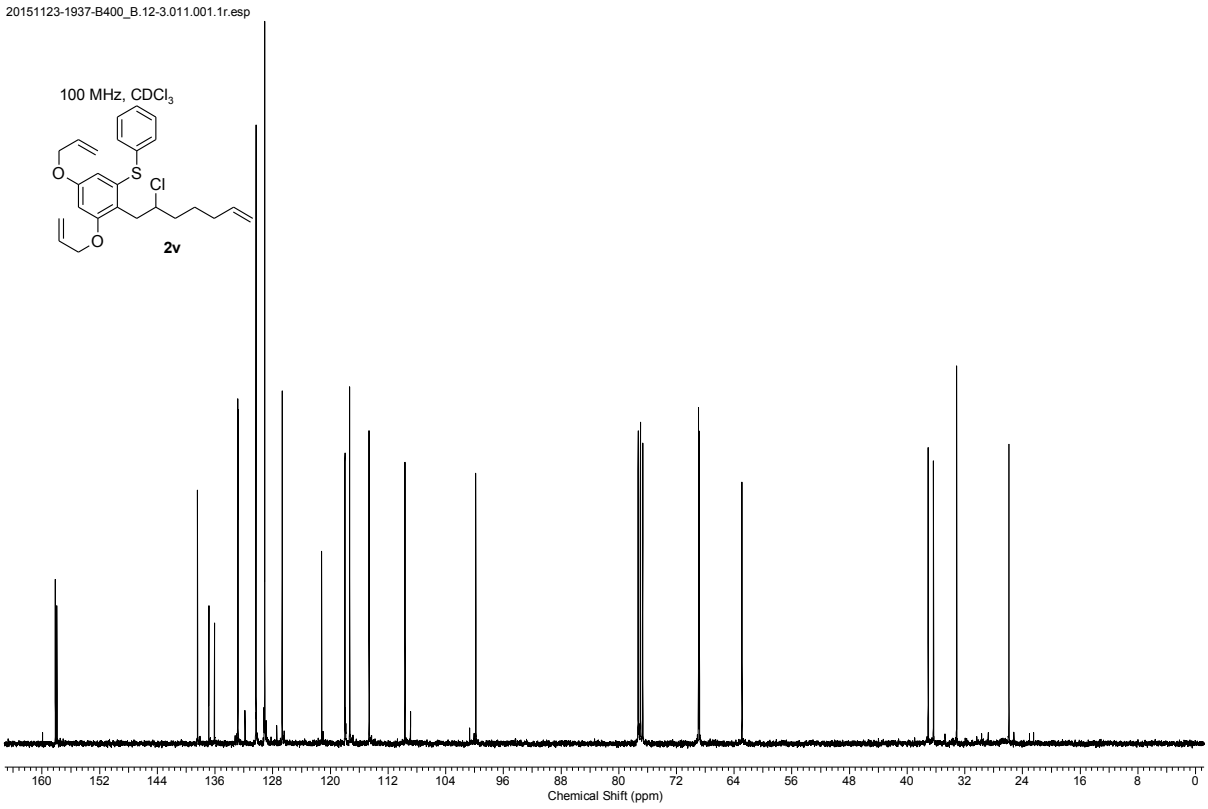
2.01
2.01
0.98
3.02
0.95
0.96
3.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

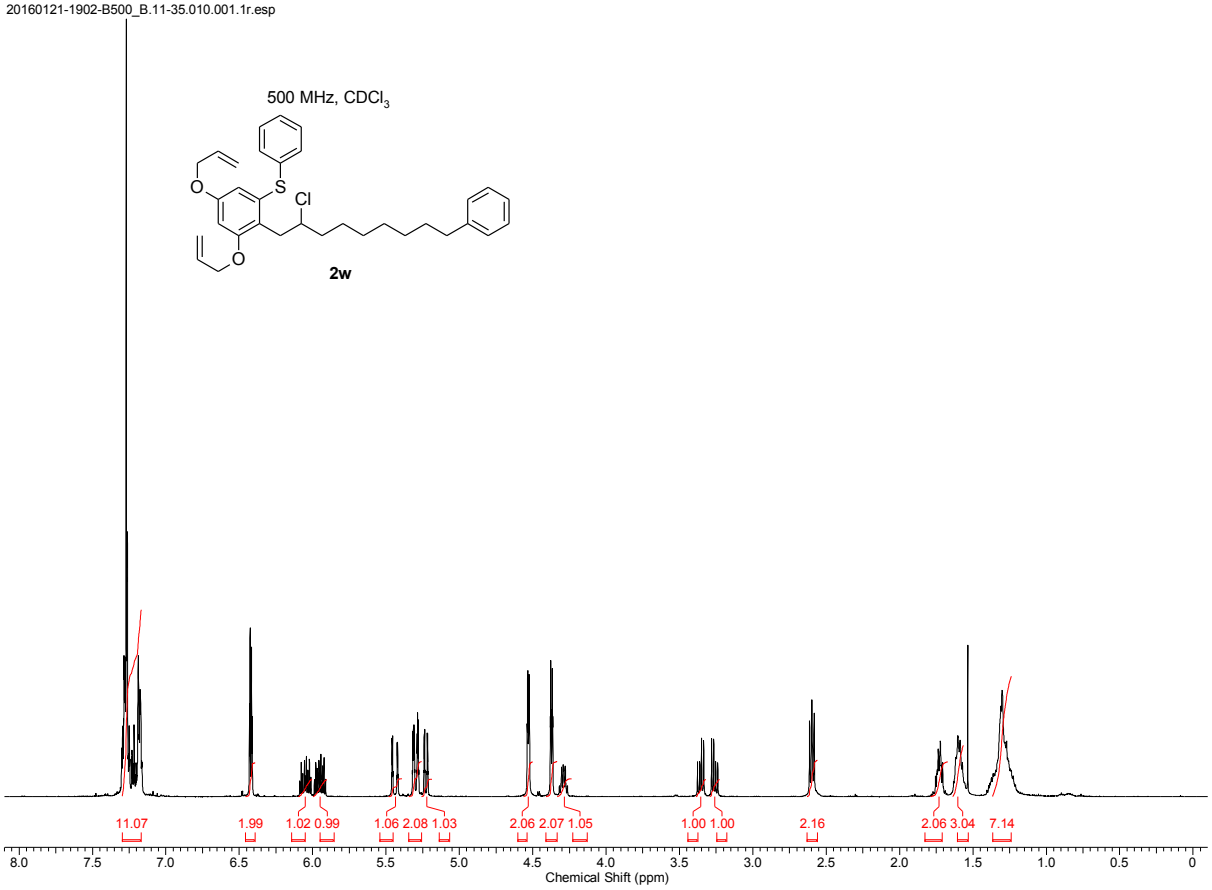

20151123-1937-B400_B.12-2.011.001.1r.esp
100 MHz, CDCl3
O
S
Cl
Br
O
2t
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

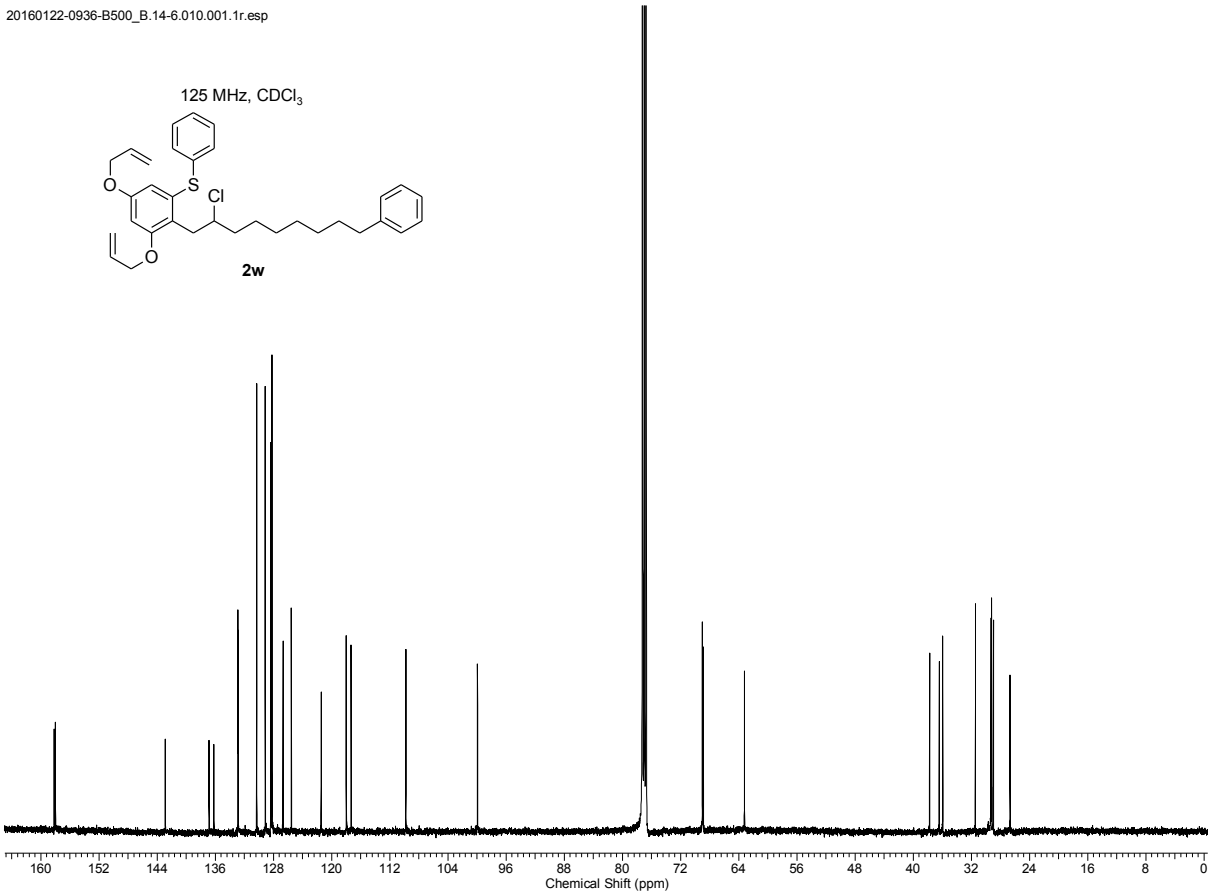

20160121-1902-B500_B.11-36.010.001.1r.esp
500 MHz, CDCl3
O
S
Cl
NO2
O
2u
5.61
1.93
1.00
1.01
1.00
2.05
1.00
2.00
4.12
1.11
1.01
1.00
1.02
1.03
2.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


20160121-1902-B500_B.11-36.011.001.1r.esp
125 MHz, CDCl3
O
S
Cl
NO2
O
2u
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


20151123-1937-B400_B.12-3.010.001.1r.esp
400 MHz CDCl3
S
Cl
O
O
2v
5.28
1.97
1.05
1.03
0.97
1.05
2.09
1.05
1.97
2.02
2.06
1.04
1.00
1.00
2.09
3.15
1.18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

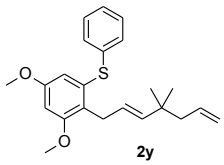

20151123-1937-B400_B.12-3.011.001.1r.esp
100 MHz, CDCl3
S
Cl
O
O
2v
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


20160121-1902-B500_B.11-35.010.001.1r.esp
500 MHz, CDCl3
O
S
Cl
O
2w
11.07
1.99
1.02 0.99
1.06 2.08 1.03
2.06 2.07 1.05
1.00 1.00
2.16
2.06 3.04
7.14
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


20160122-0936-B500_B.14-6.010.001.1r.esp
125 MHz, CDCl3
O
S
Cl
O
2w
160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

20160219-1426-B400_B.11-47.010.001.1r.esp

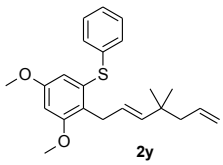
400 MHz, $CDCl_3$



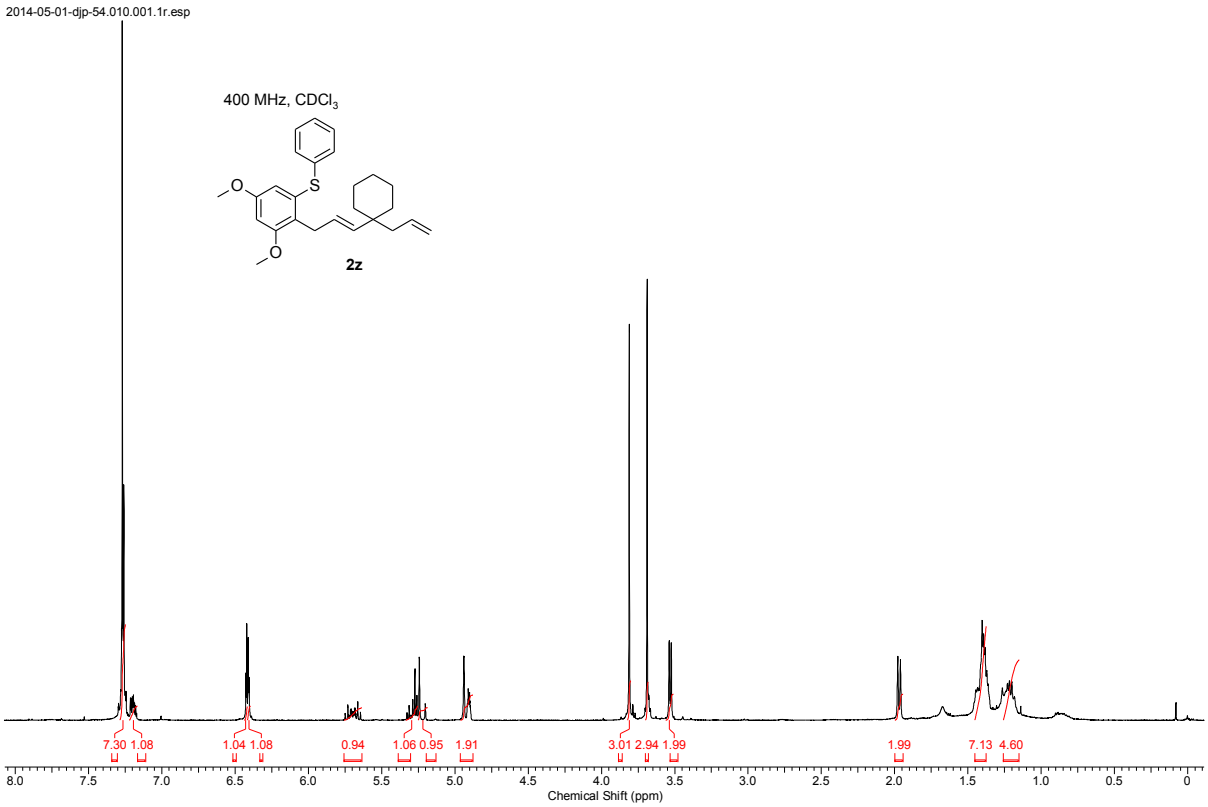
2y

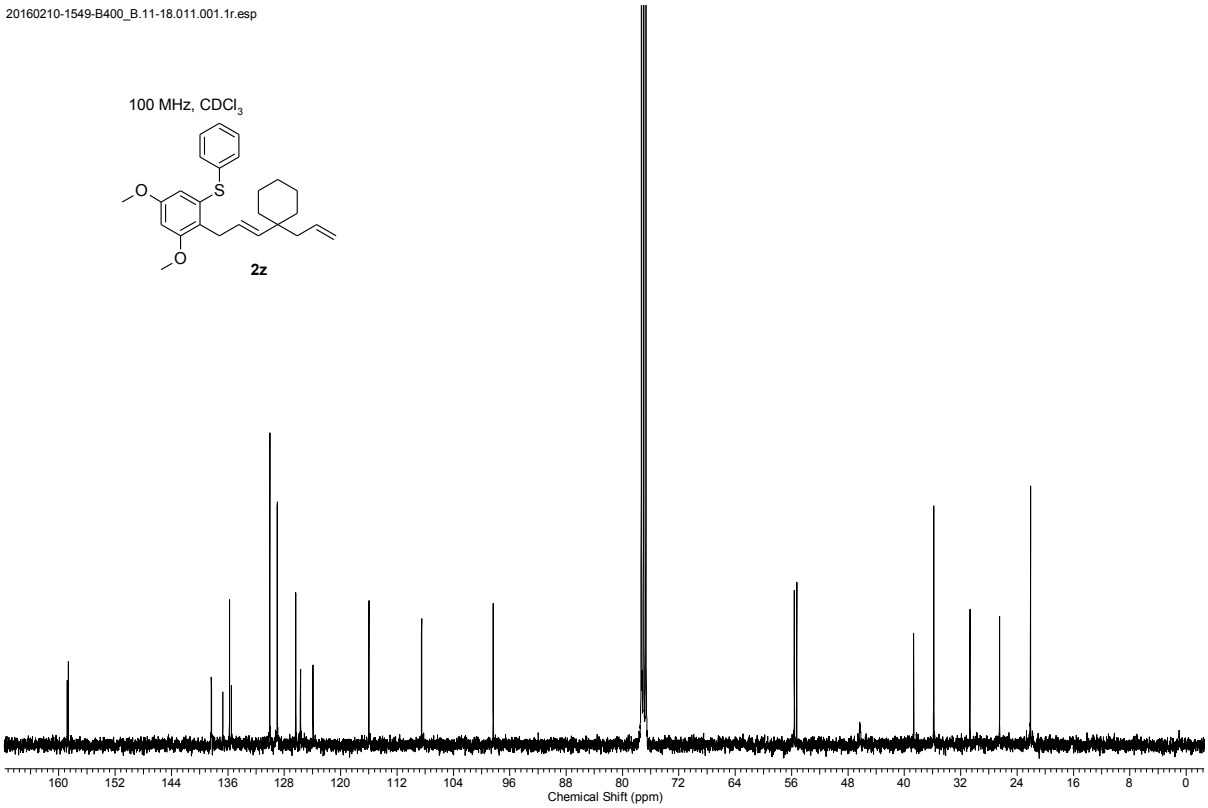
20160219-1426-B400_B.11-47.011.001.1r.esp

100 MHz, $CDCl_3$

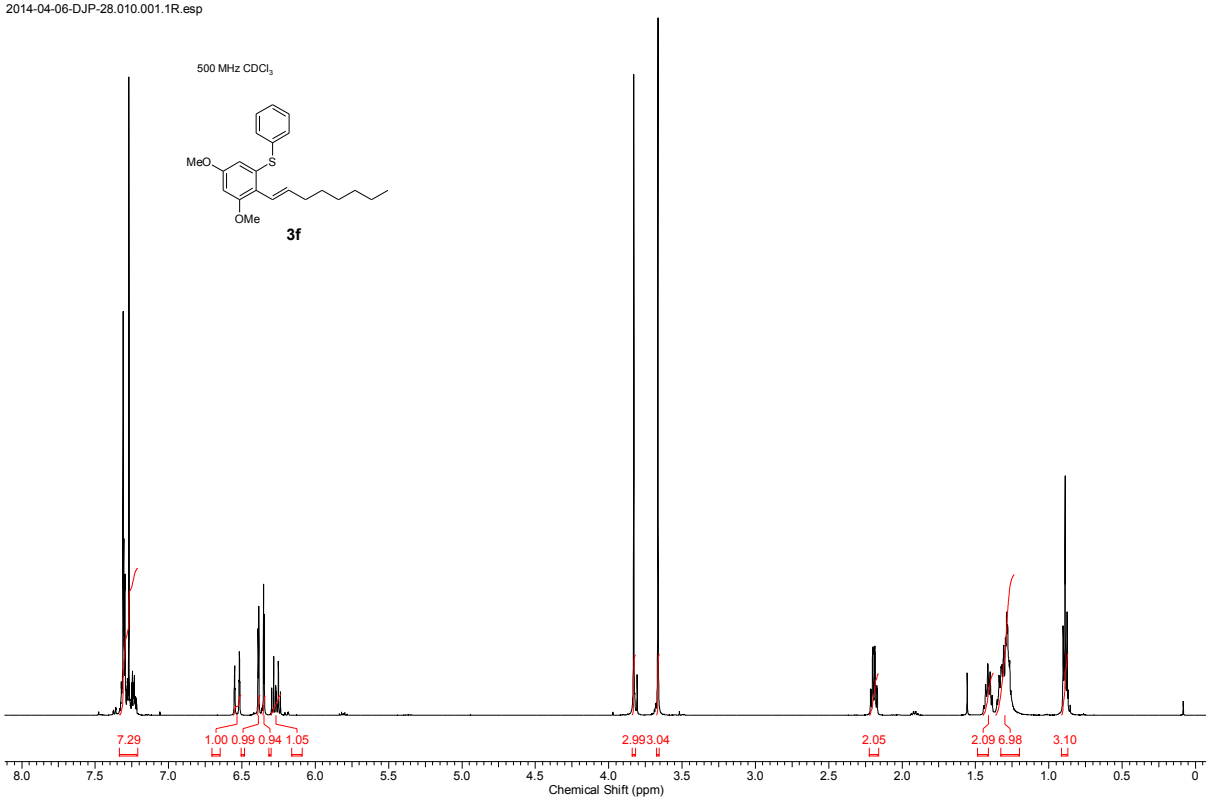


2y

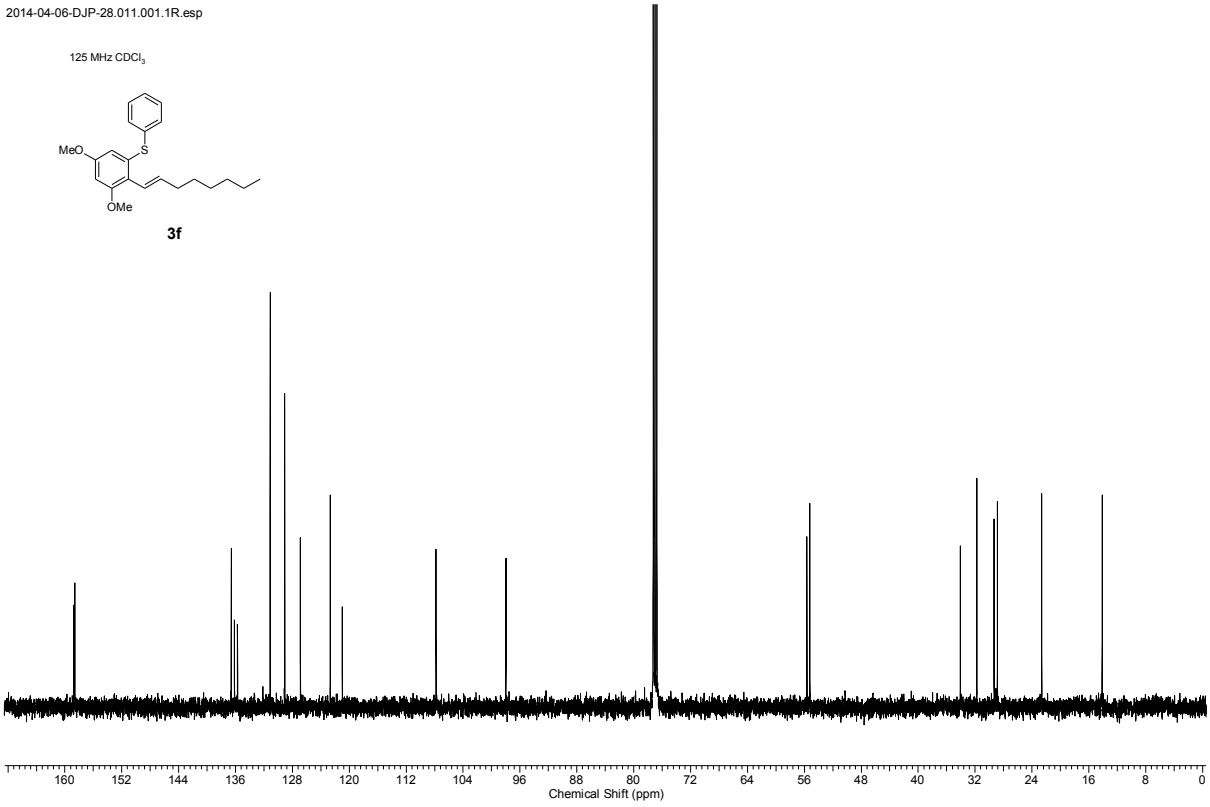

2014-05-01-djp-54.010.001.1r.esp
400 MHz, CDCl3
2z
7.30 1.08 1.04 1.08 0.94 1.06 0.95 1.91 3.01 2.94 1.99 1.99 7.13 4.60
Chemical Shift (ppm)

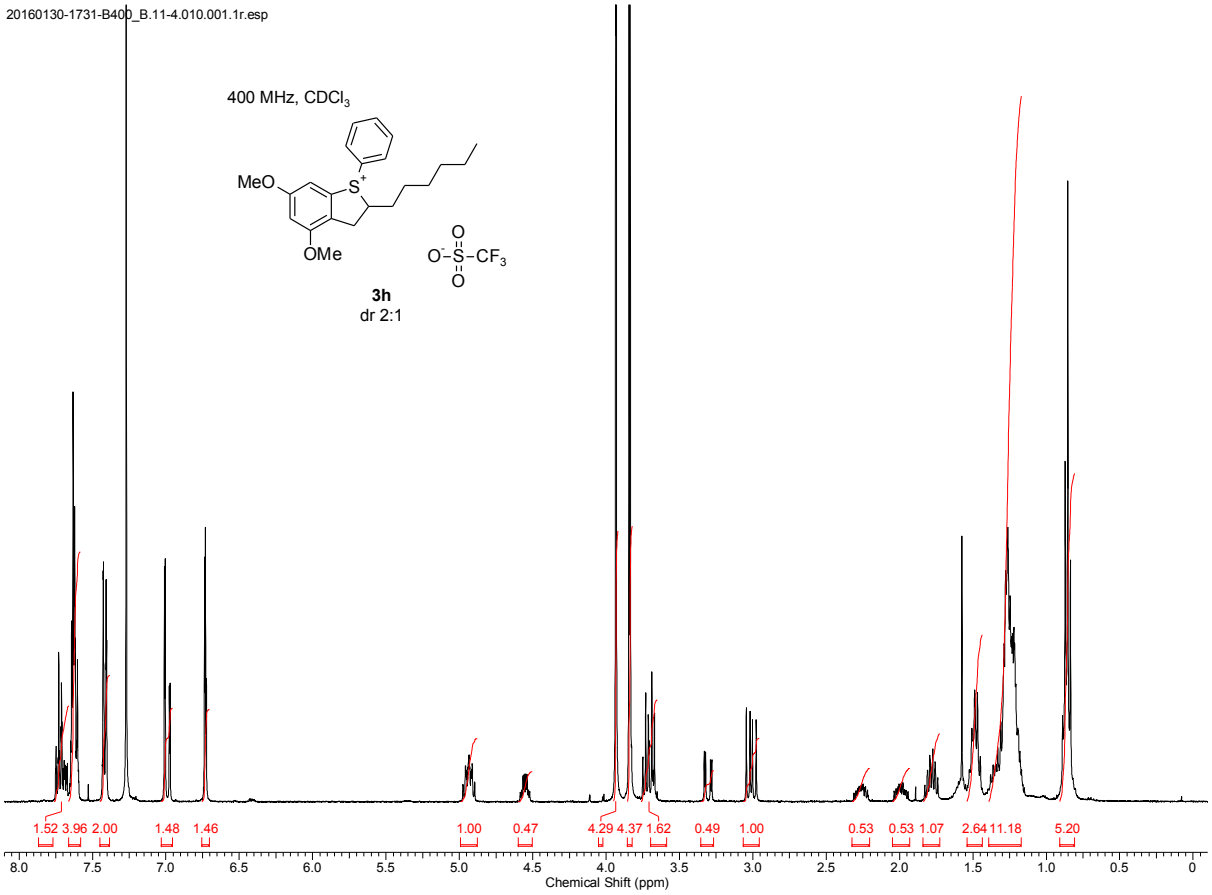

20160210-1549-B400_B.11-18.011.001.1r.esp
100 MHz, CDCl3
2z
Chemical Shift (ppm)

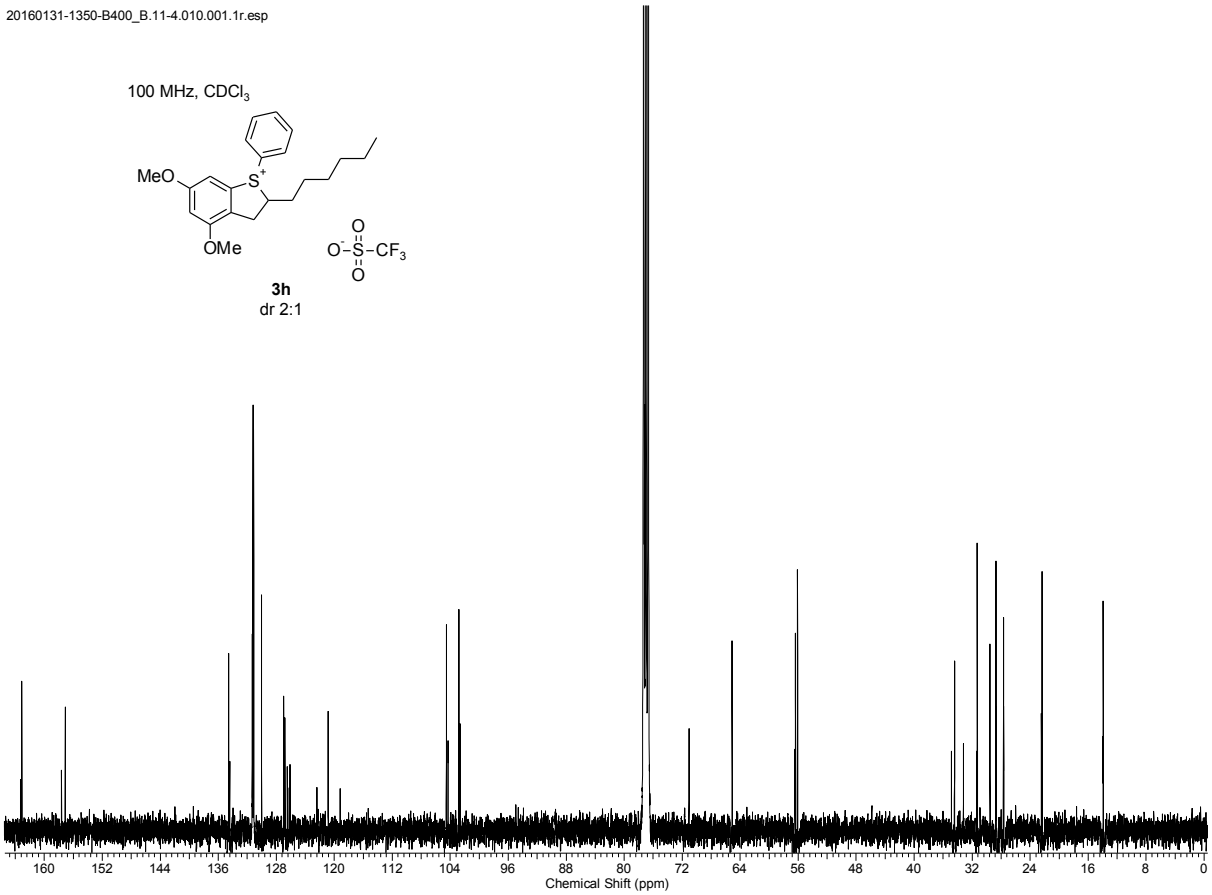
2014-04-06-DJP-28.010.001.1R.esp

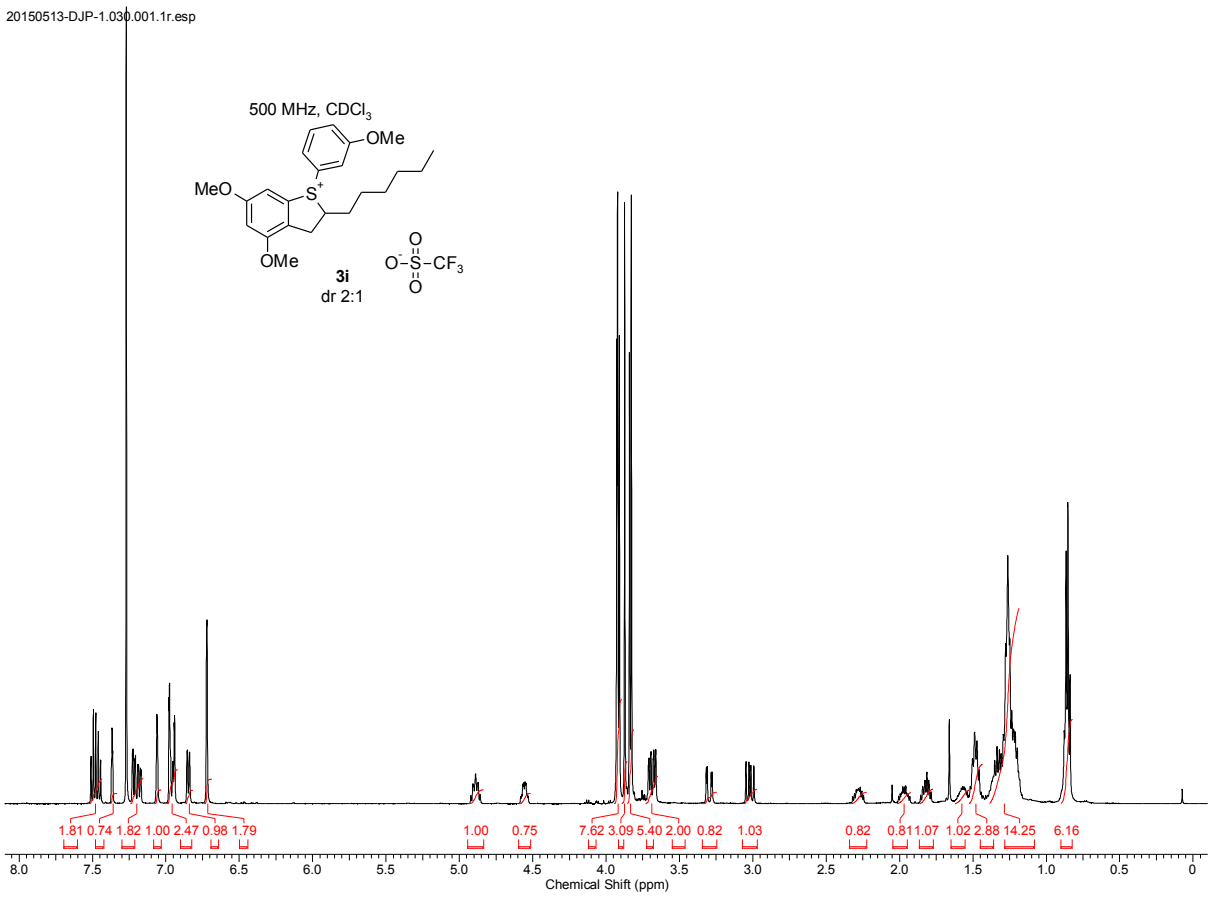


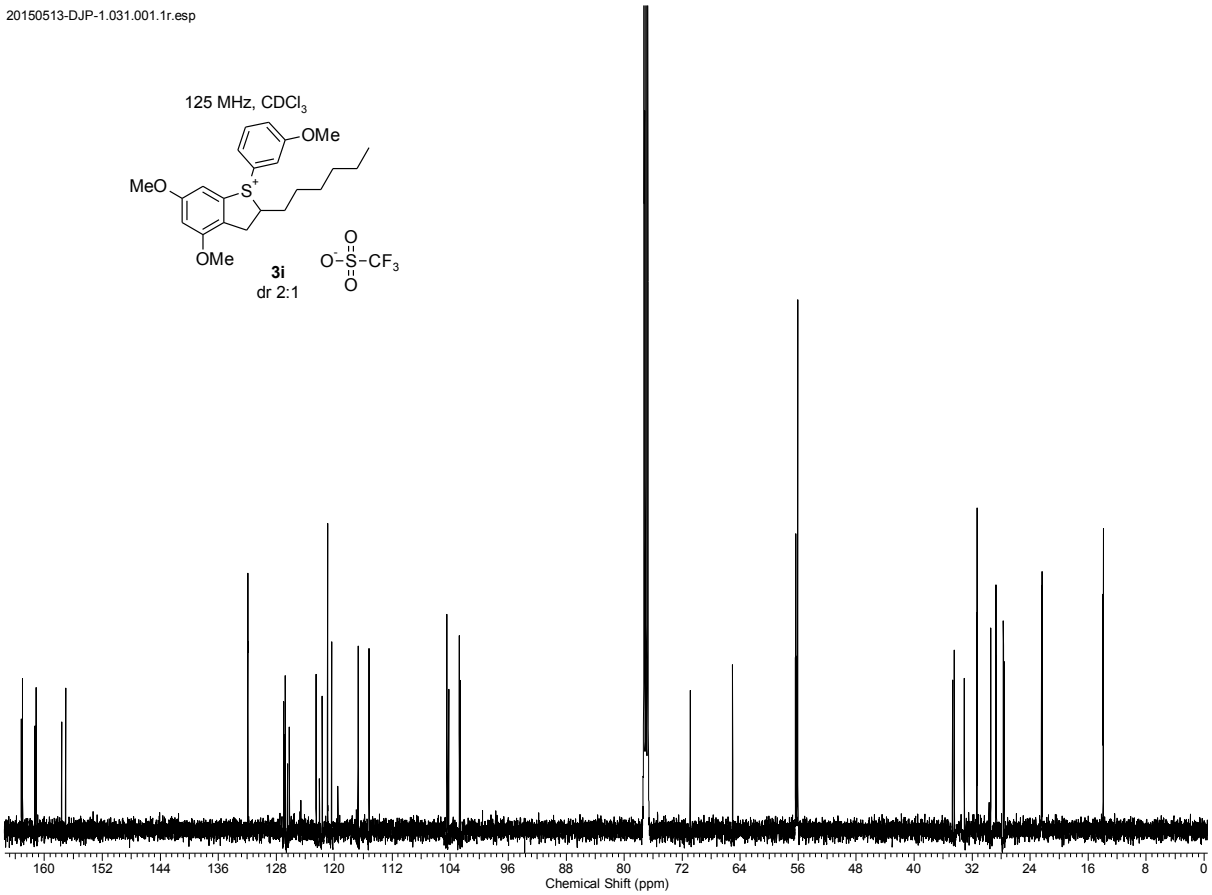
2014-04-06-DJP-28.011.001.1R.esp



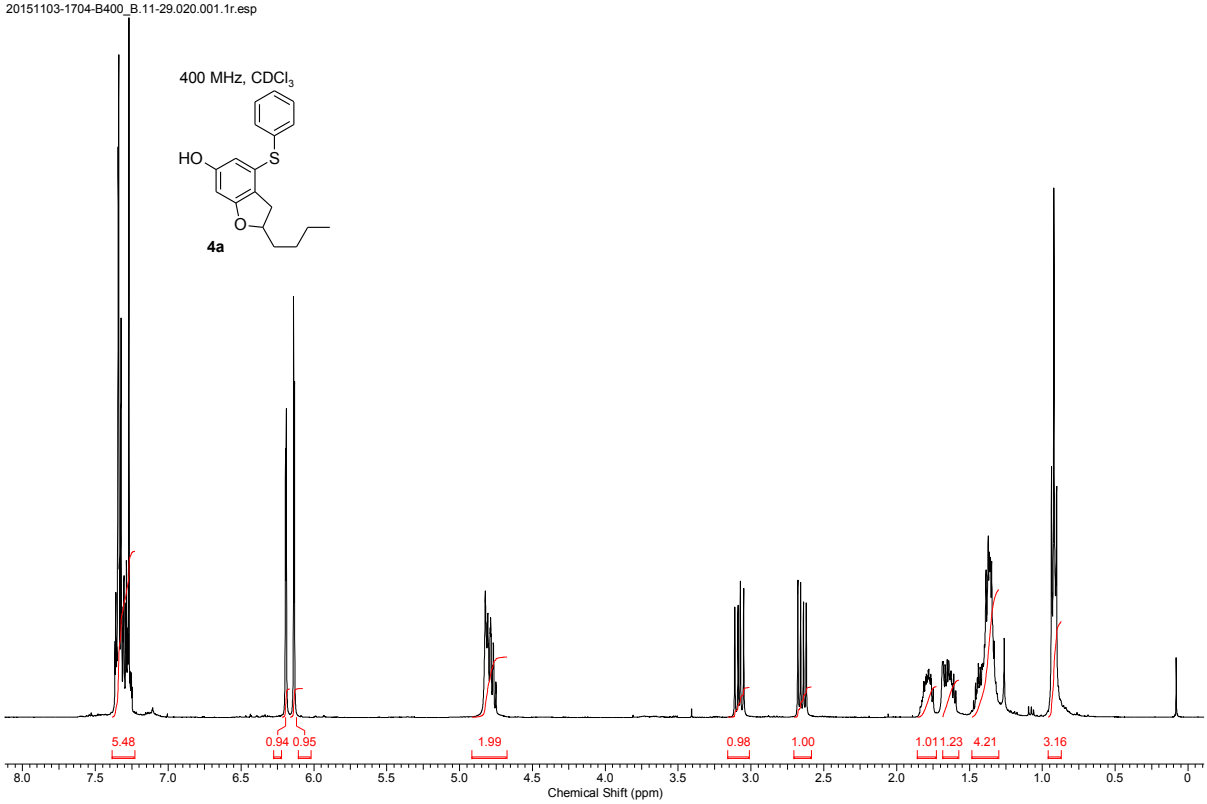

20160130-1731-B400_B.11-4.010.001.1r.esp
400 MHz, CDCl3
MeO
OMe
S+
O
O-S-CF3
O
3h
dr 2:1
1.52 3.96 2.00 1.48 1.46 1.00 0.47 4.29 4.37 1.62 0.49 1.00 0.53 0.53 1.07 2.64 11.18 5.20
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


20160131-1350-B400_B.11-4.010.001.1r.esp
100 MHz, CDCl3
MeO
OMe
S+
O
O-S-CF3
O
3h
dr 2:1
160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

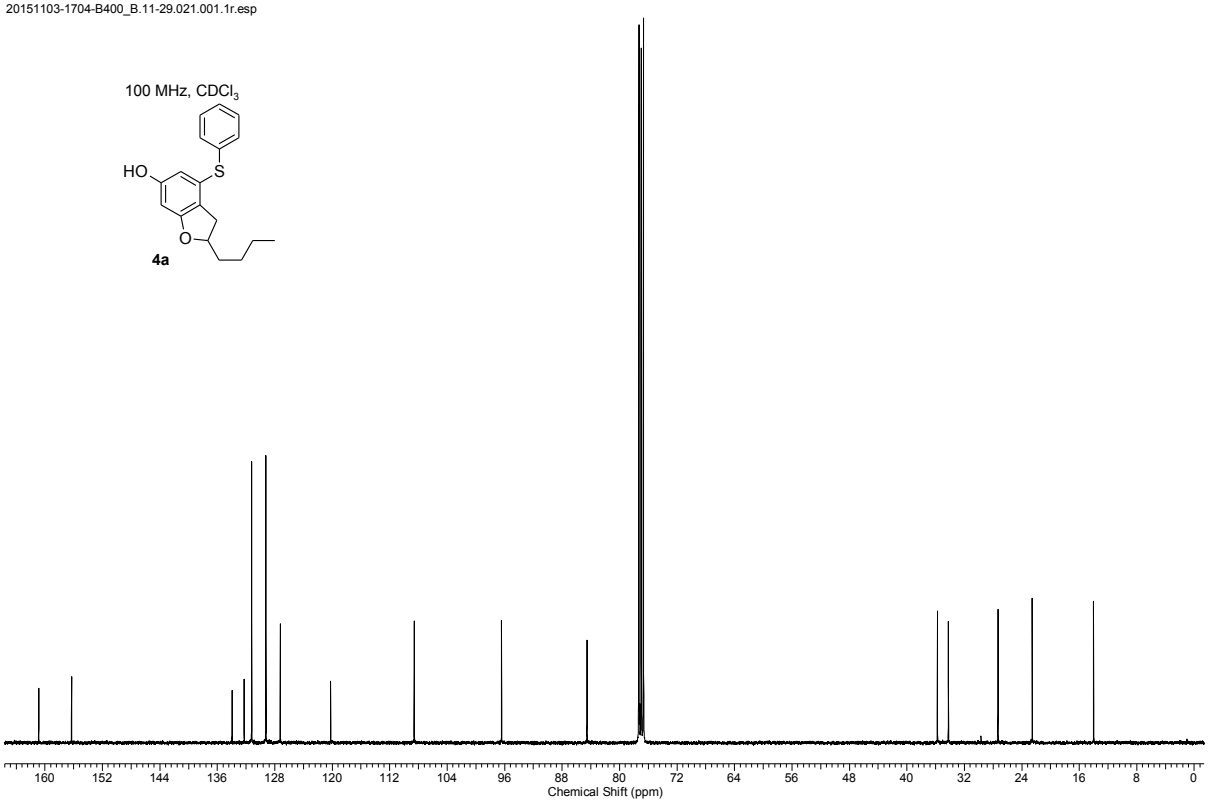

20150513-DJP-1.030.001.1r.esp
500 MHz, CDCl3
OMe
MeO
S+
OMe
O
O-S-CF3
O
3i
dr 2:1
1.81 0.74 1.82 1.00 2.47 0.98 1.79
1.00 0.75
7.62 3.09 5.40 2.00 0.82 1.03
0.82 0.81 1.07 1.02 2.88 14.25 6.16
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


20150513-DJP-1.031.001.1r.esp
125 MHz, CDCl3
OMe
MeO
S+
OMe
O
O-S-CF3
O
3i
dr 2:1
160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

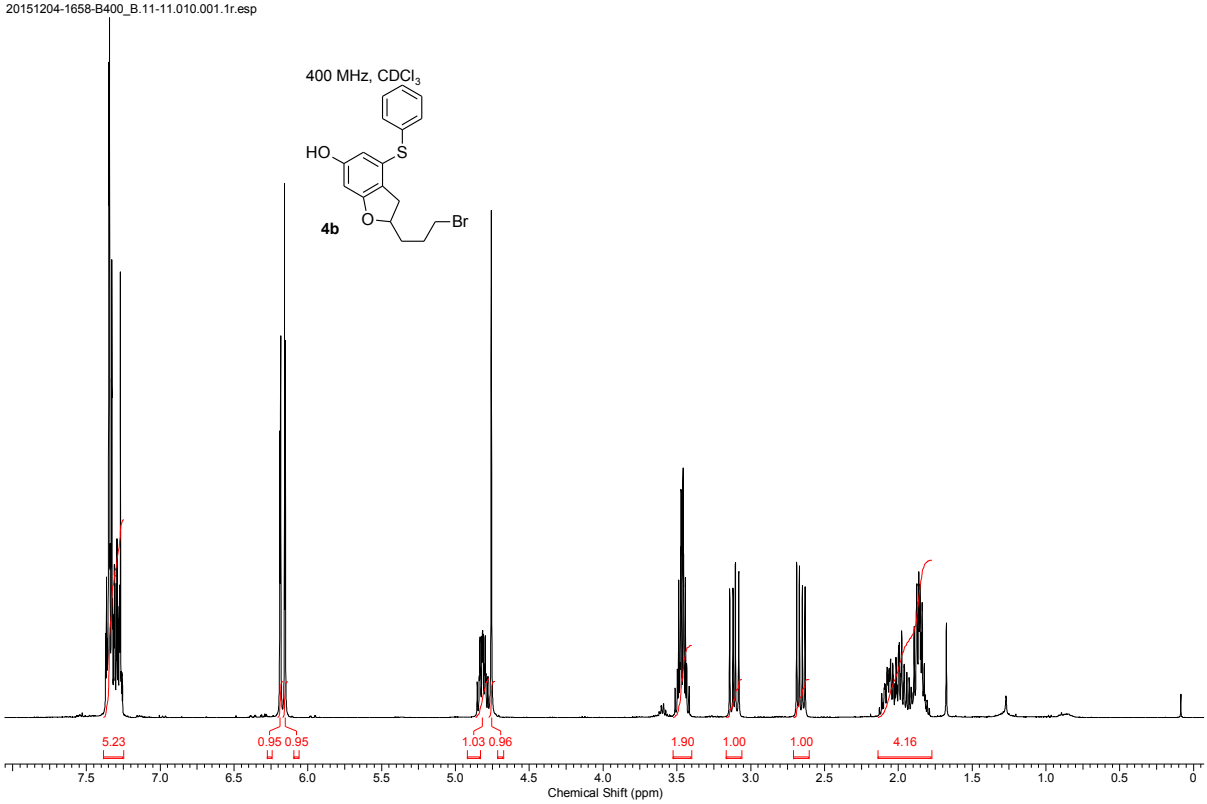
20151103-1704-B400_B.11-29.020.001.1r.esp



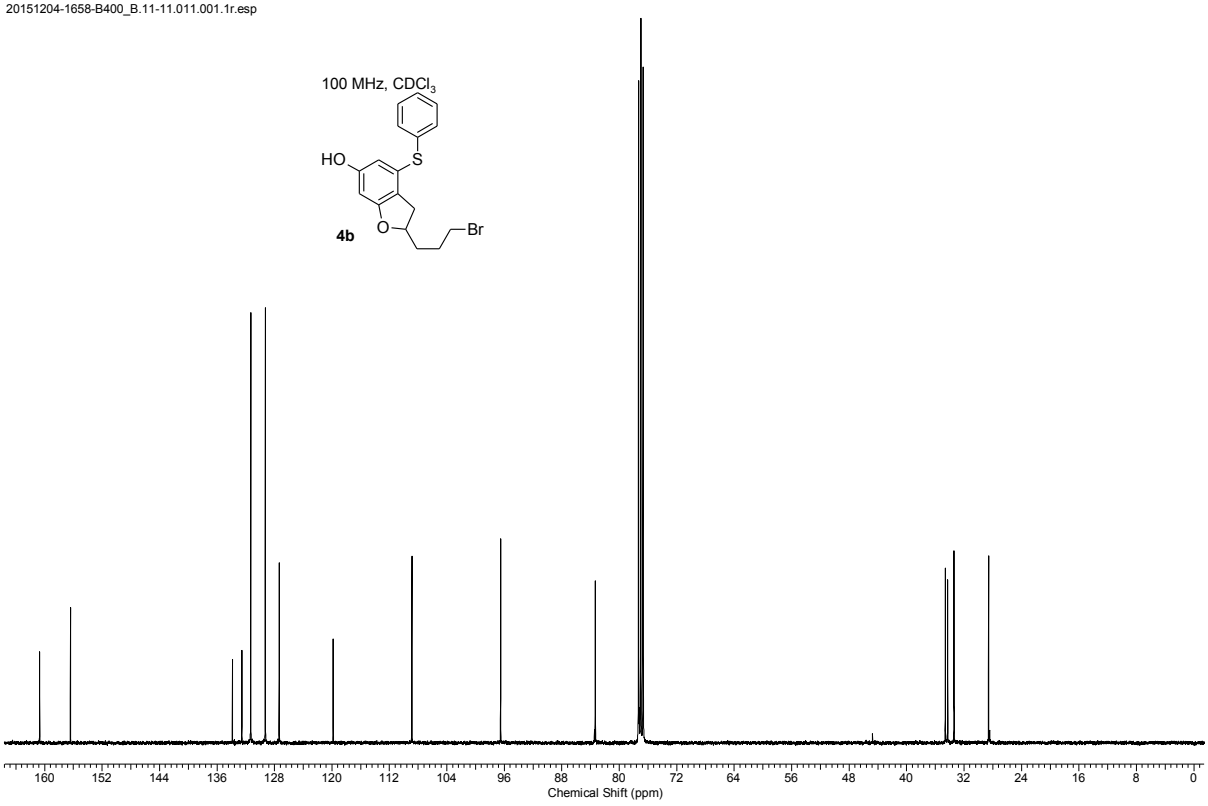
20151103-1704-B400_B.11-29.021.001.1r.esp

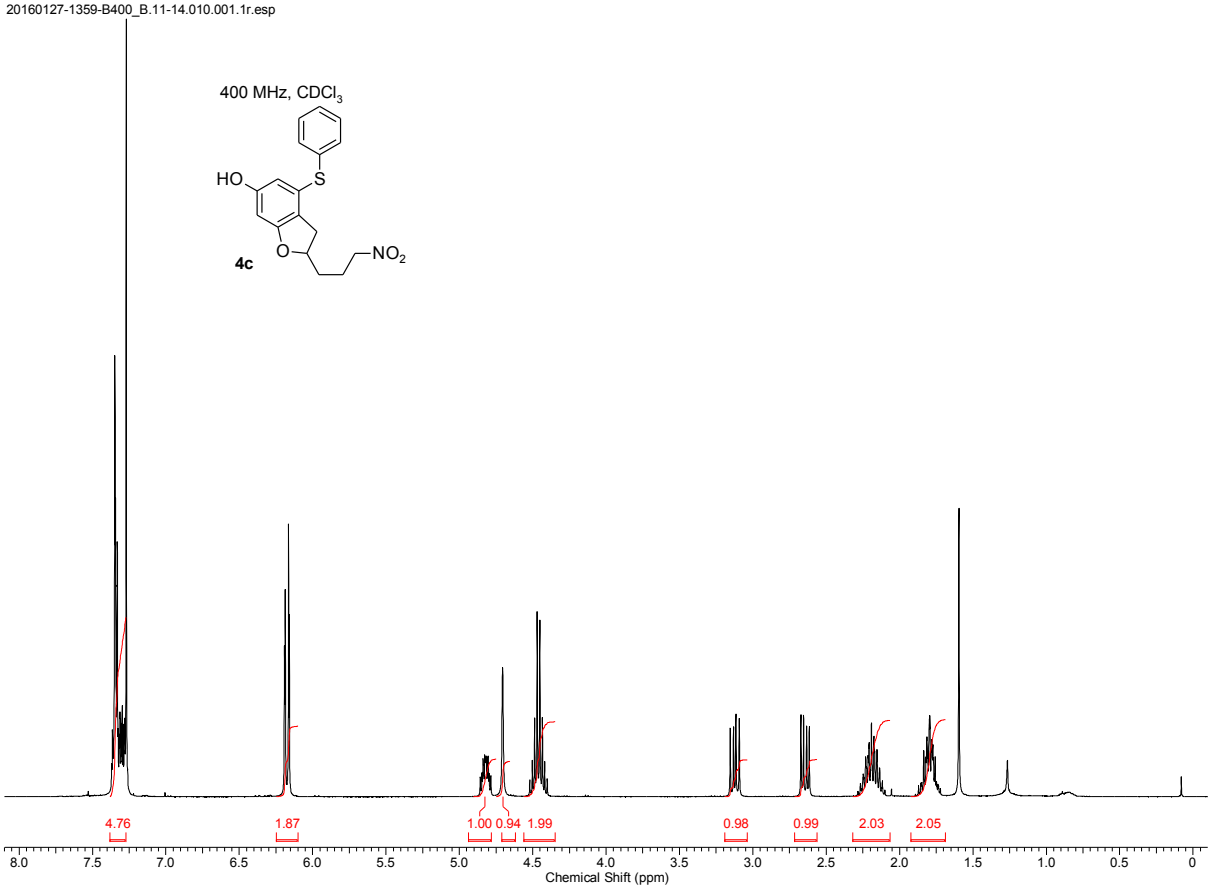


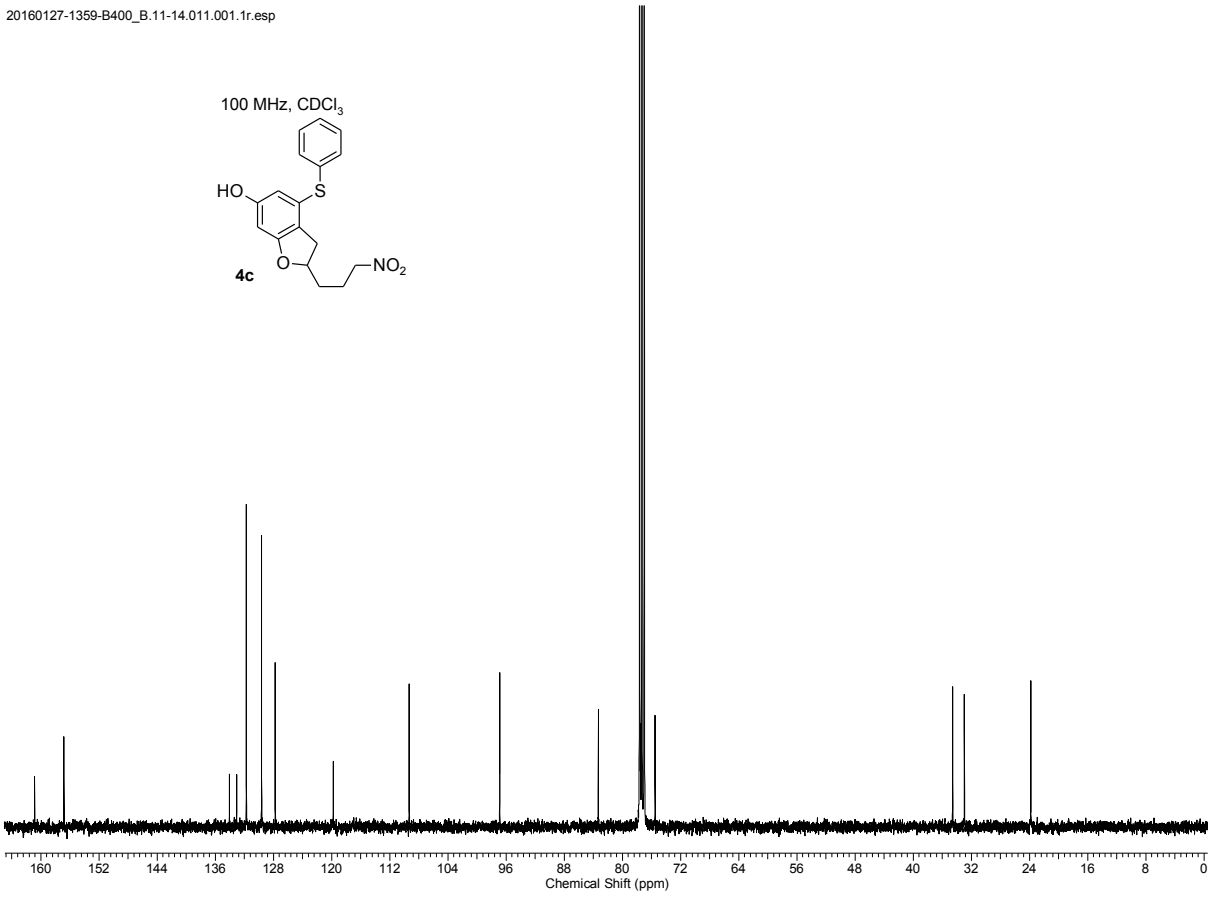
20151204-1658-B400_B.11-11.010.001.1r.esp



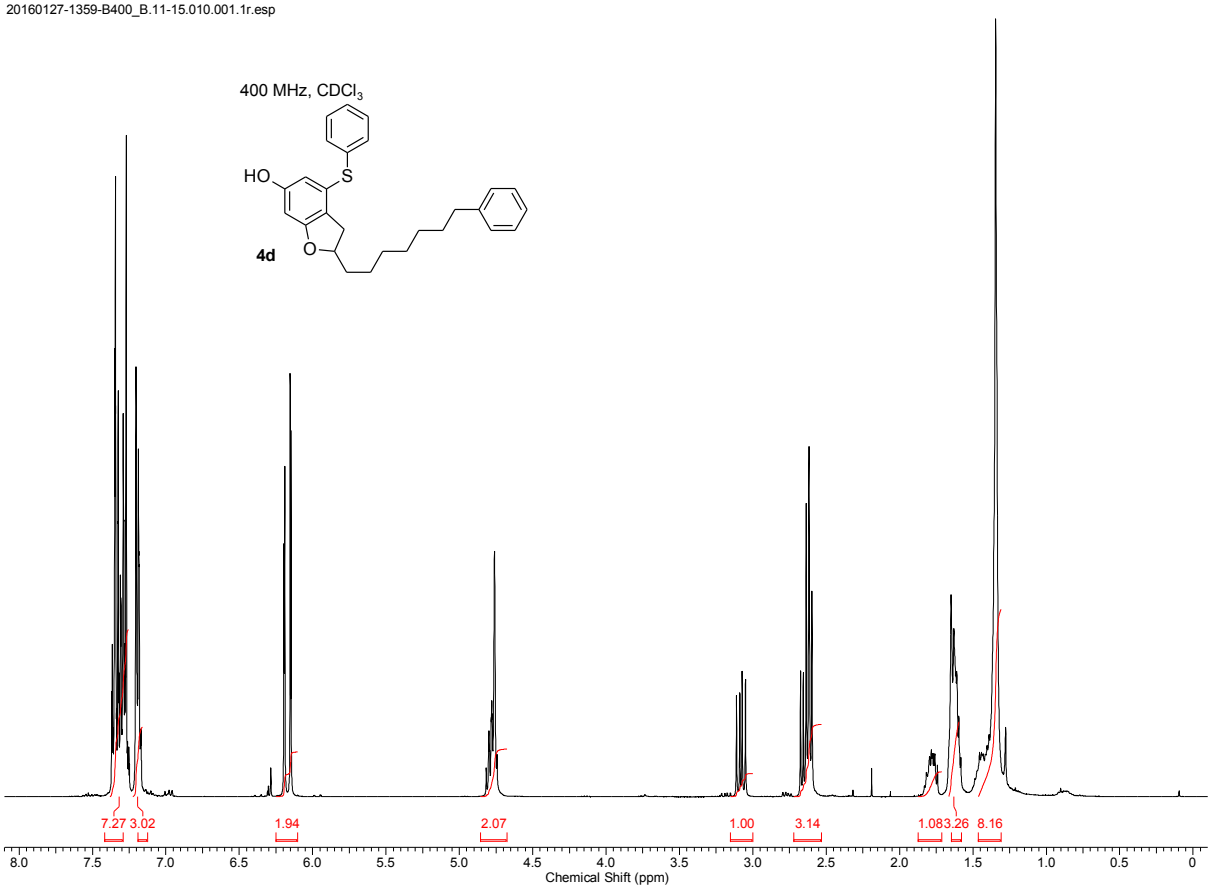
20151204-1658-B400_B.11-11.011.001.1r.esp



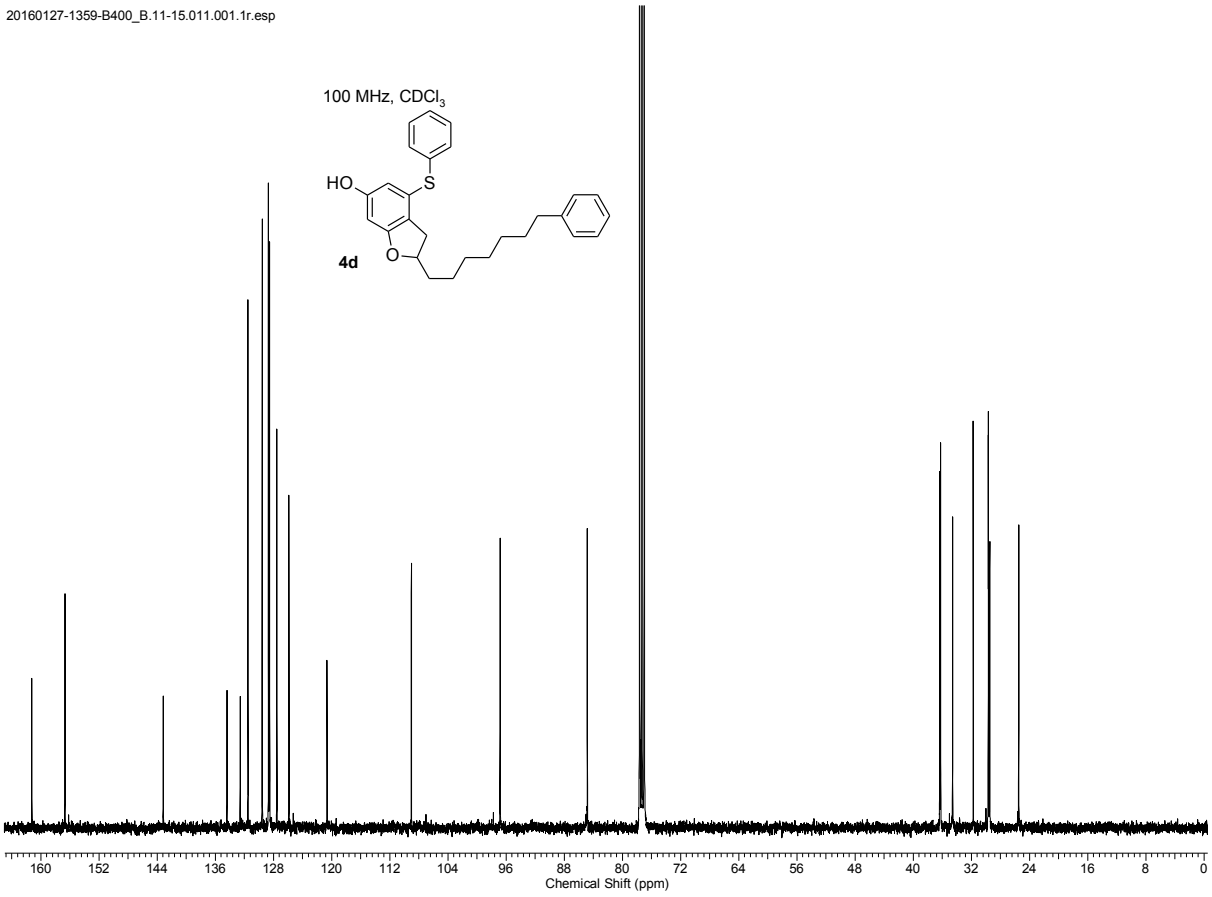

20160127-1359-B400_B.11-14.010.001.1r.esp
400 MHz, CDCl3
HO
S
O
NO2
4c
4.76
1.87
1.00
0.94
1.99
0.98
0.99
2.03
2.05
Chemical Shift (ppm)


20160127-1359-B400_B.11-14.011.001.1r.esp
100 MHz, CDCl3
HO
S
O
NO2
4c
Chemical Shift (ppm)

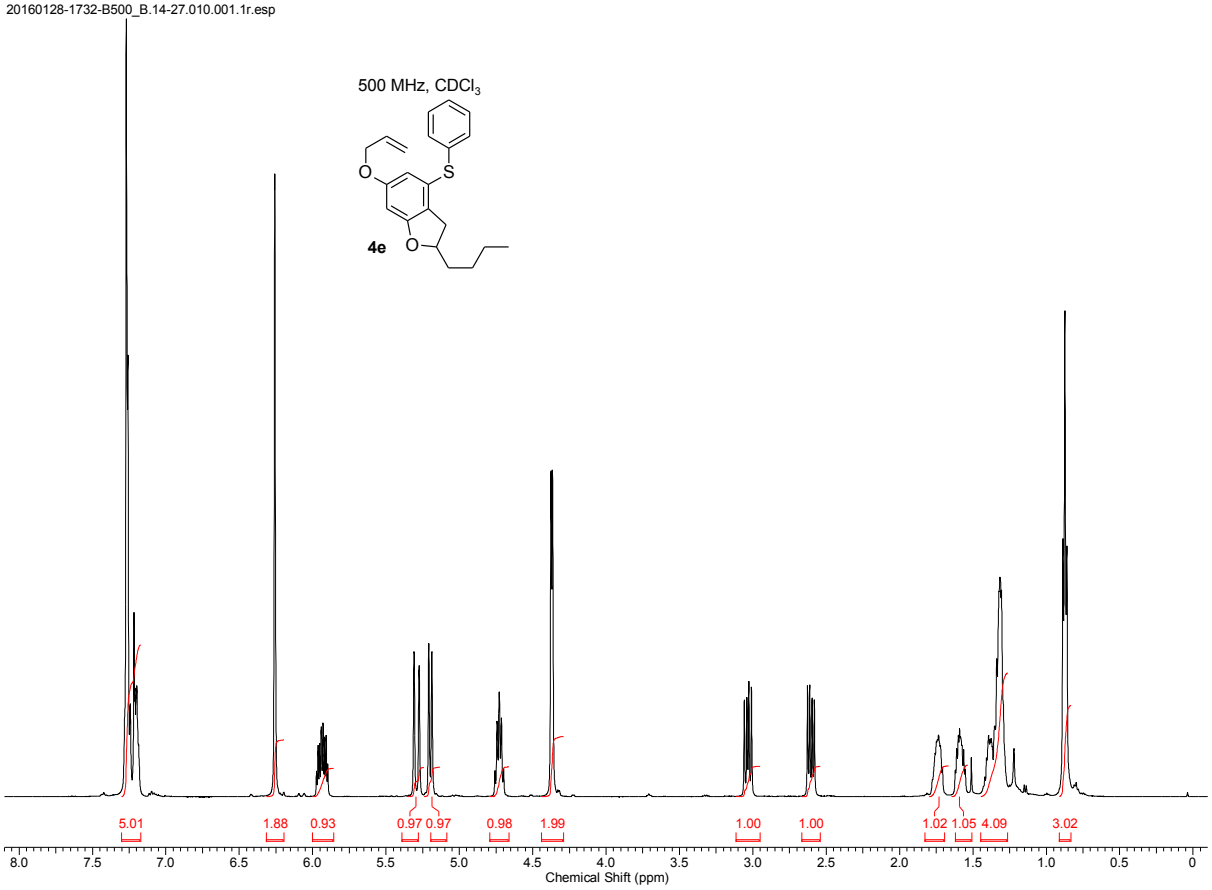
20160127-1359-B400_B.11-15.010.001.1r.esp



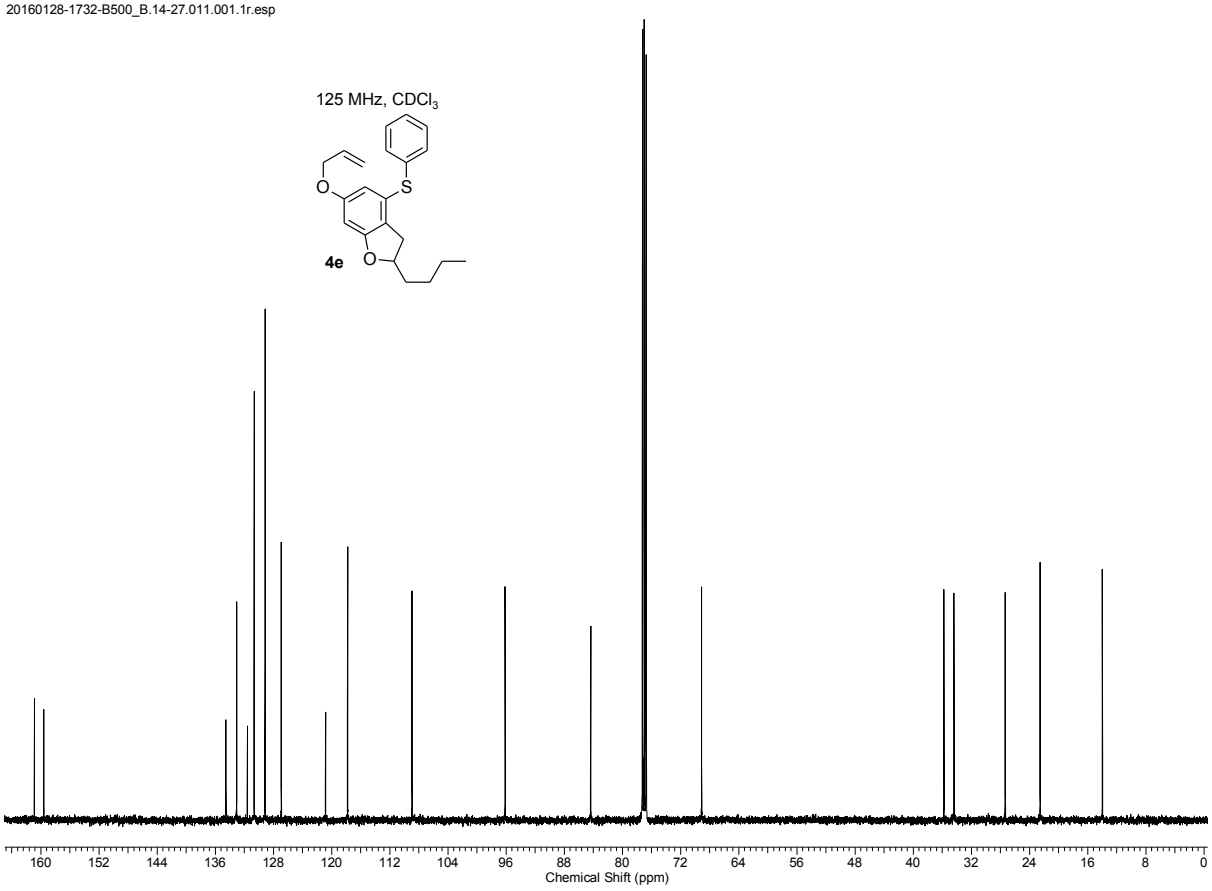
20160127-1359-B400_B.11-15.011.001.1r.esp



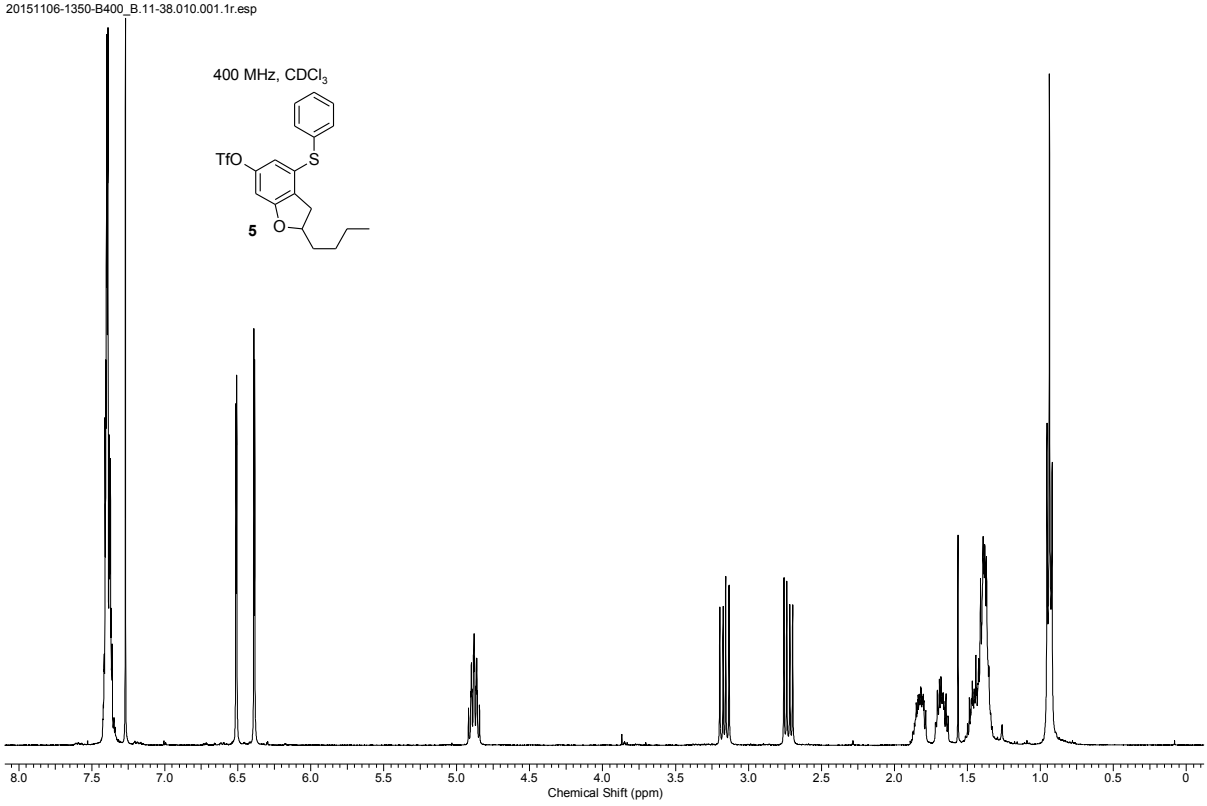
20160128-1732-B500_B.14-27.010.001.1r.esp



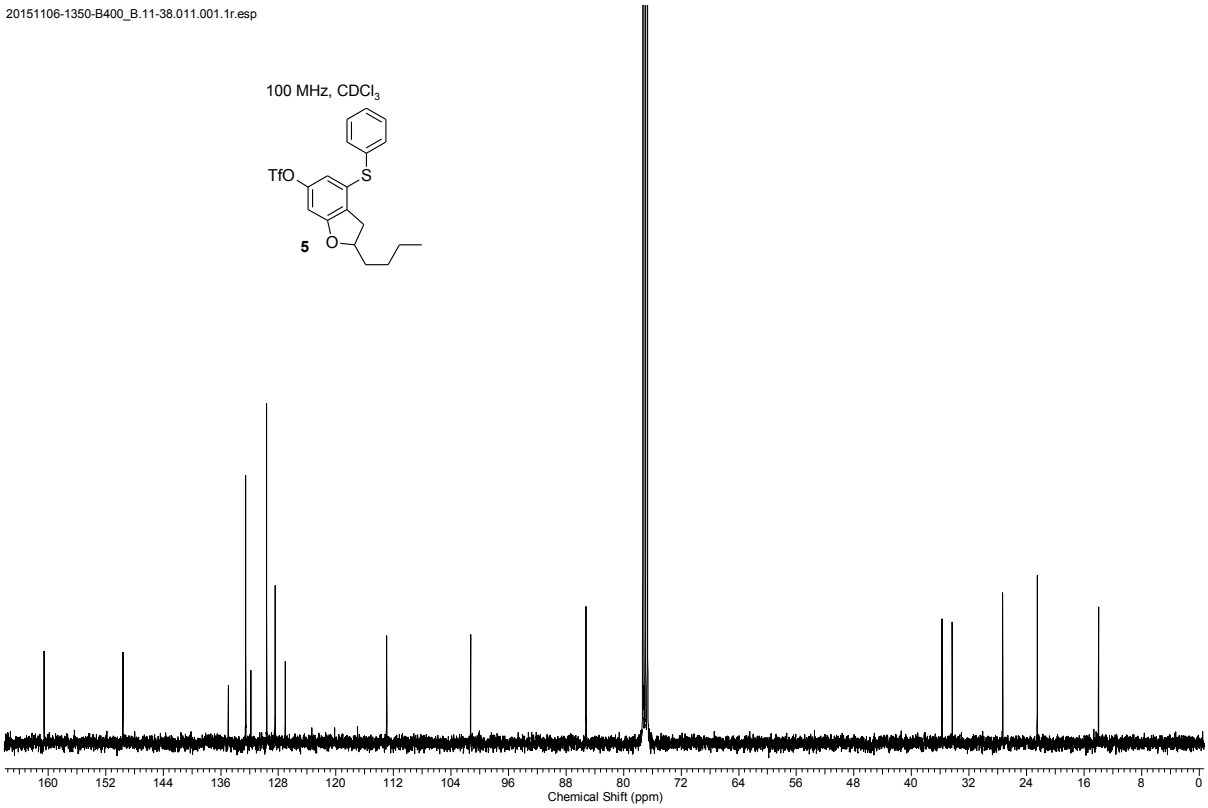
20160128-1732-B500_B.14-27.011.001.1r.esp



20151106-1350-B400_B.11-38.010.001.1r.esp

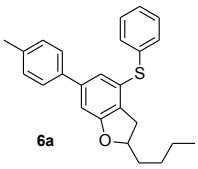


20151106-1350-B400_B.11-38.011.001.1r.esp



20151110-1126-B400_B.11-12.010.001.1r.esp

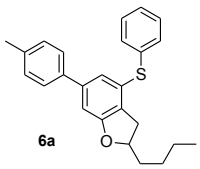
400 MHz, $CDCl_3$



6a

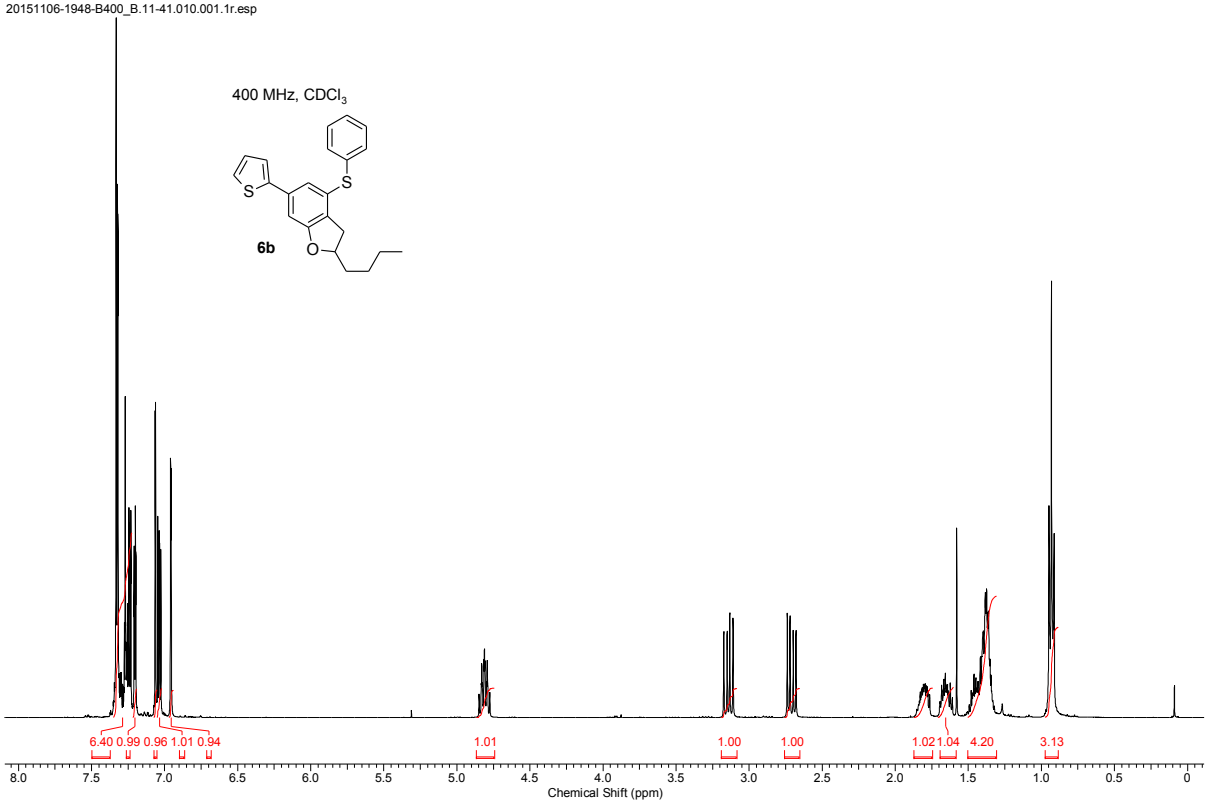
20151110-1126-B400_B.11-12.011.001.1r.esp

100 MHz, $CDCl_3$

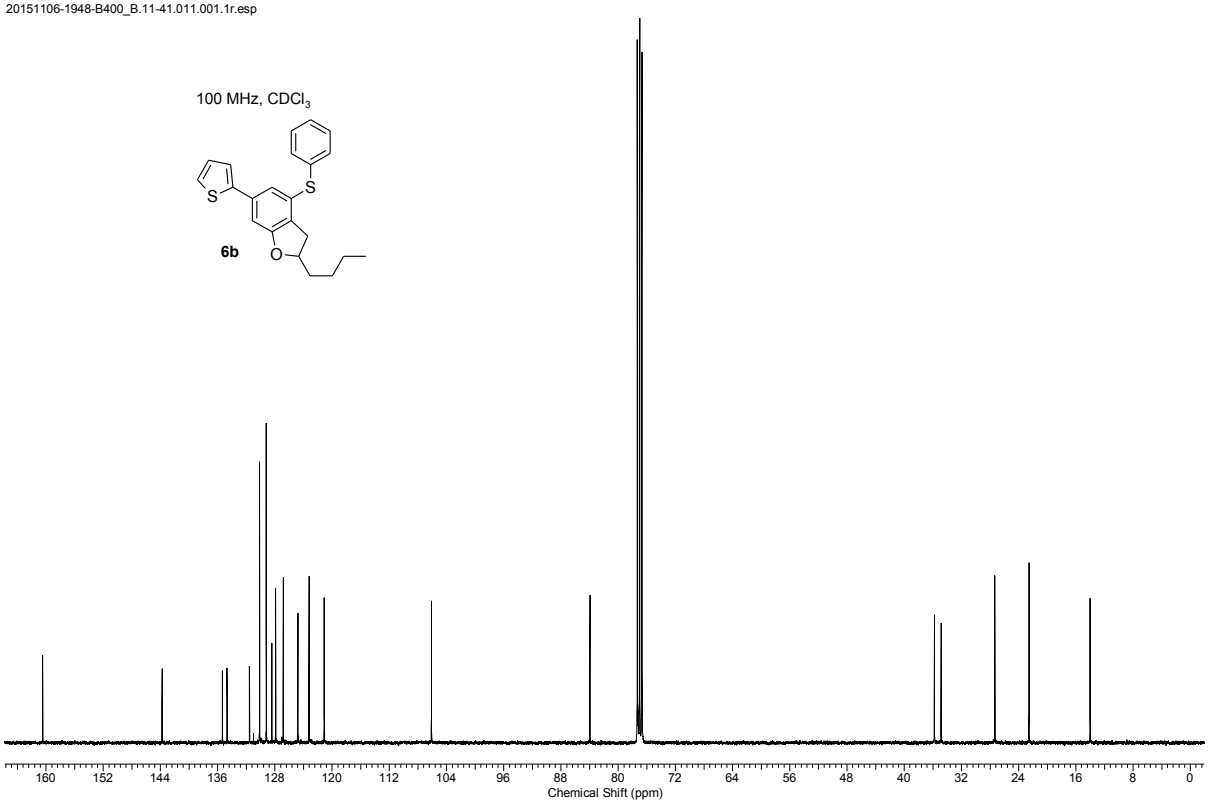


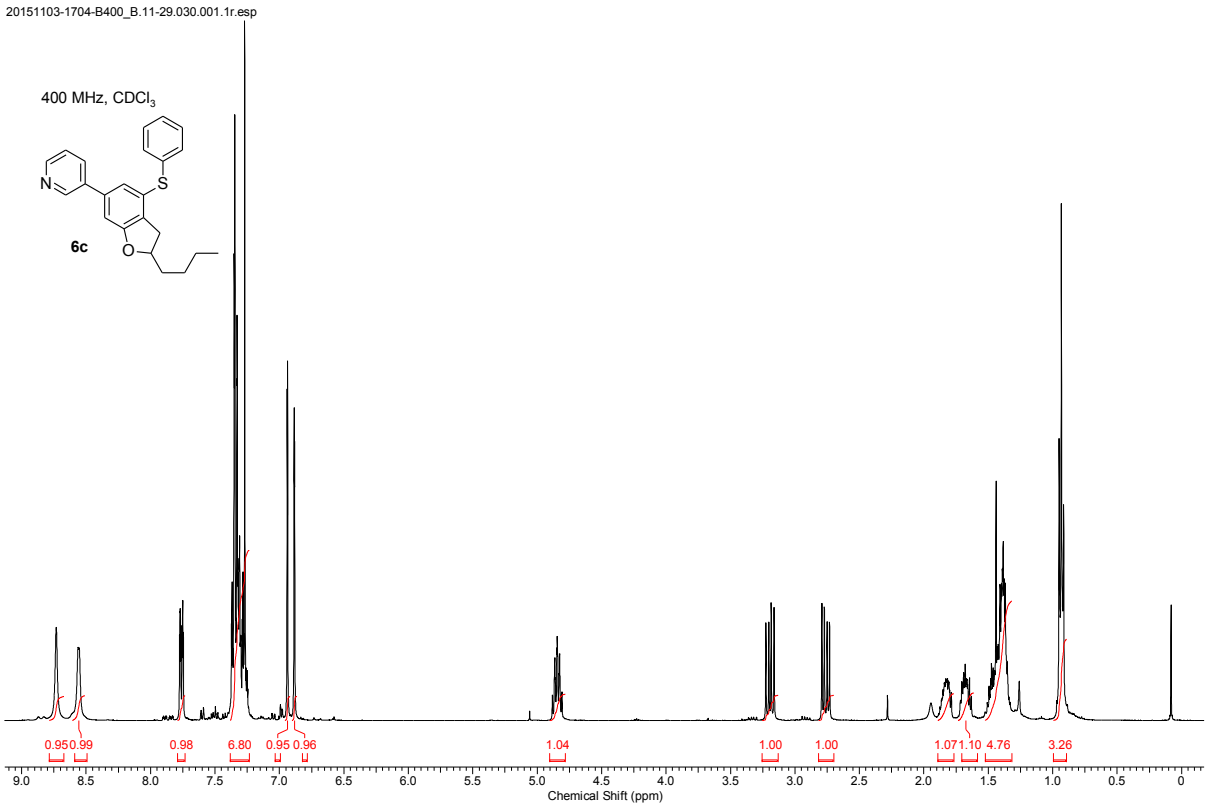
6a

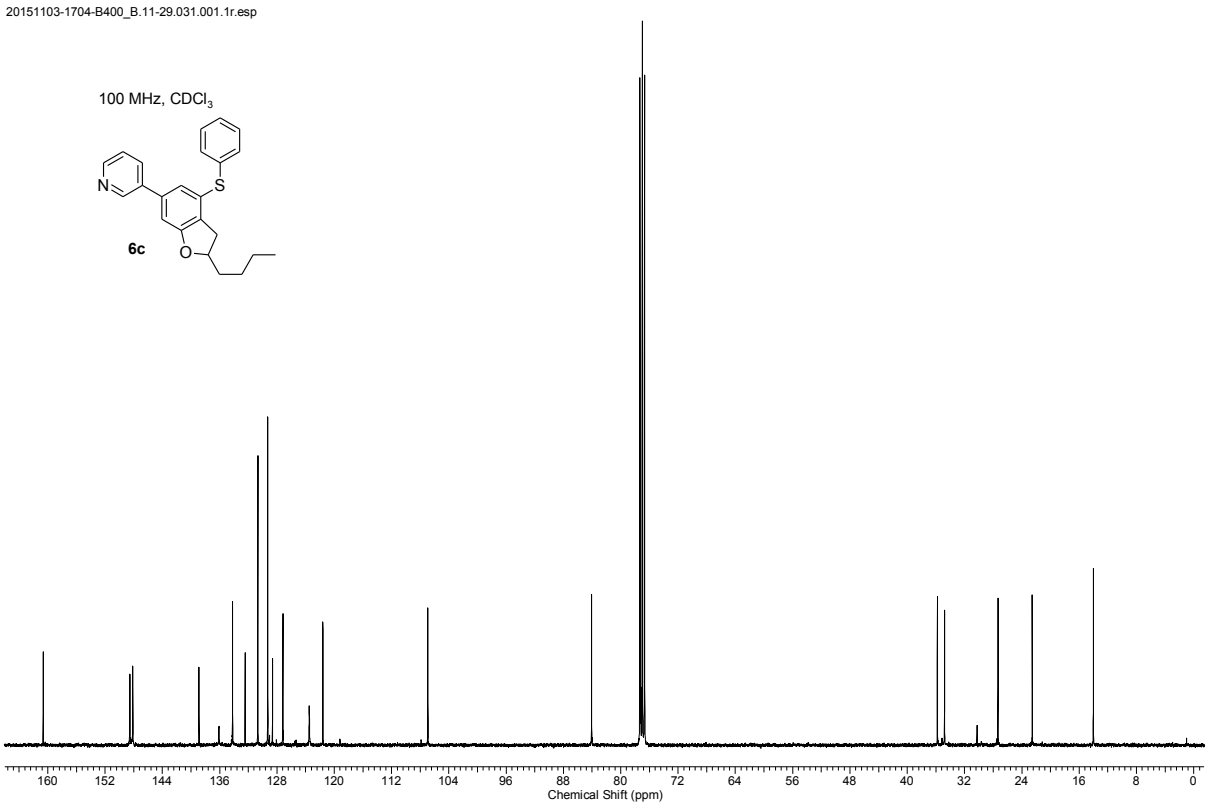
20151106-1948-B400_B.11-41.010.001.1r.esp

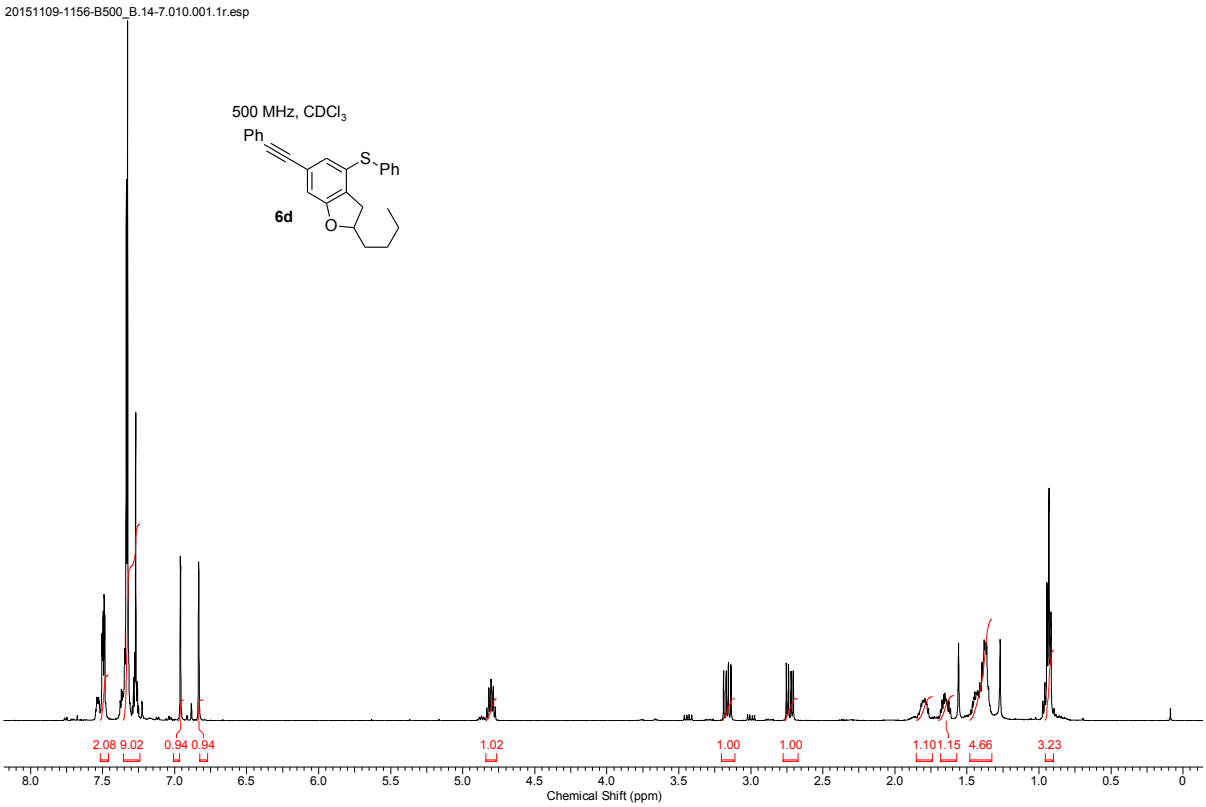


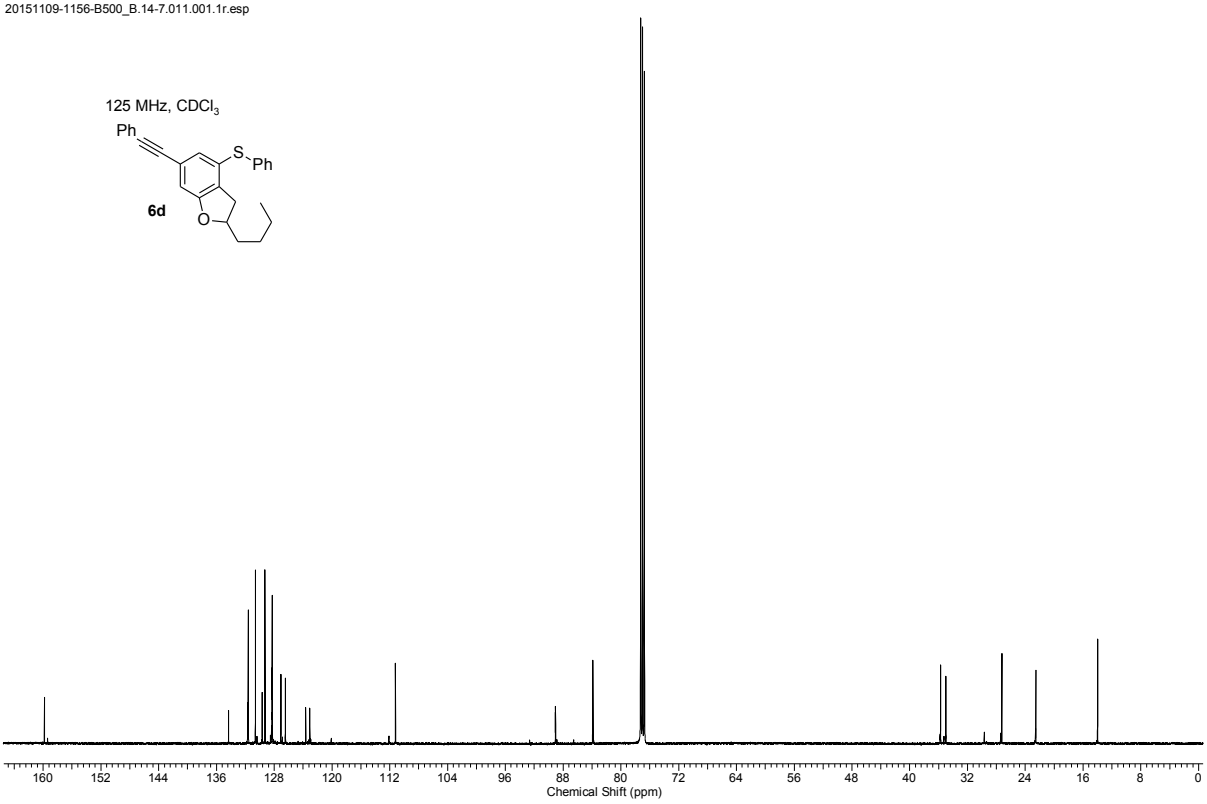
20151106-1948-B400_B.11-41.011.001.1r.esp




20151103-1704-B400_B.11-29.030.001.1r.esp
400 MHz, CDCl3
N
S
O
6c
0.95 0.99 0.98 6.80 0.95 0.96 1.04 1.00 1.00 1.07 1.10 4.76 3.26
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

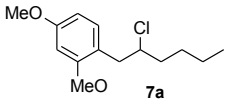

20151103-1704-B400_B.11-29.031.001.1r.esp
100 MHz, CDCl3
N
S
O
6c
160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


20151109-1156-B500_B.14-7.010.001.1r.esp
500 MHz, CDCl3
Ph
S
Ph
6d
O
2.08 9.02 0.94 0.94 1.02 1.00 1.00 1.10 1.15 4.66 3.23
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


20151109-1156-B500_B.14-7.011.001.1r.esp
125 MHz, CDCl3
Ph
S
Ph
6d
O
160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

20160111-1931-B500_B.14-4.010.001.1r.esp

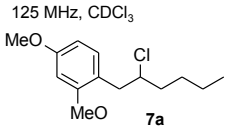
500 MHz, $CDCl_3$



7a

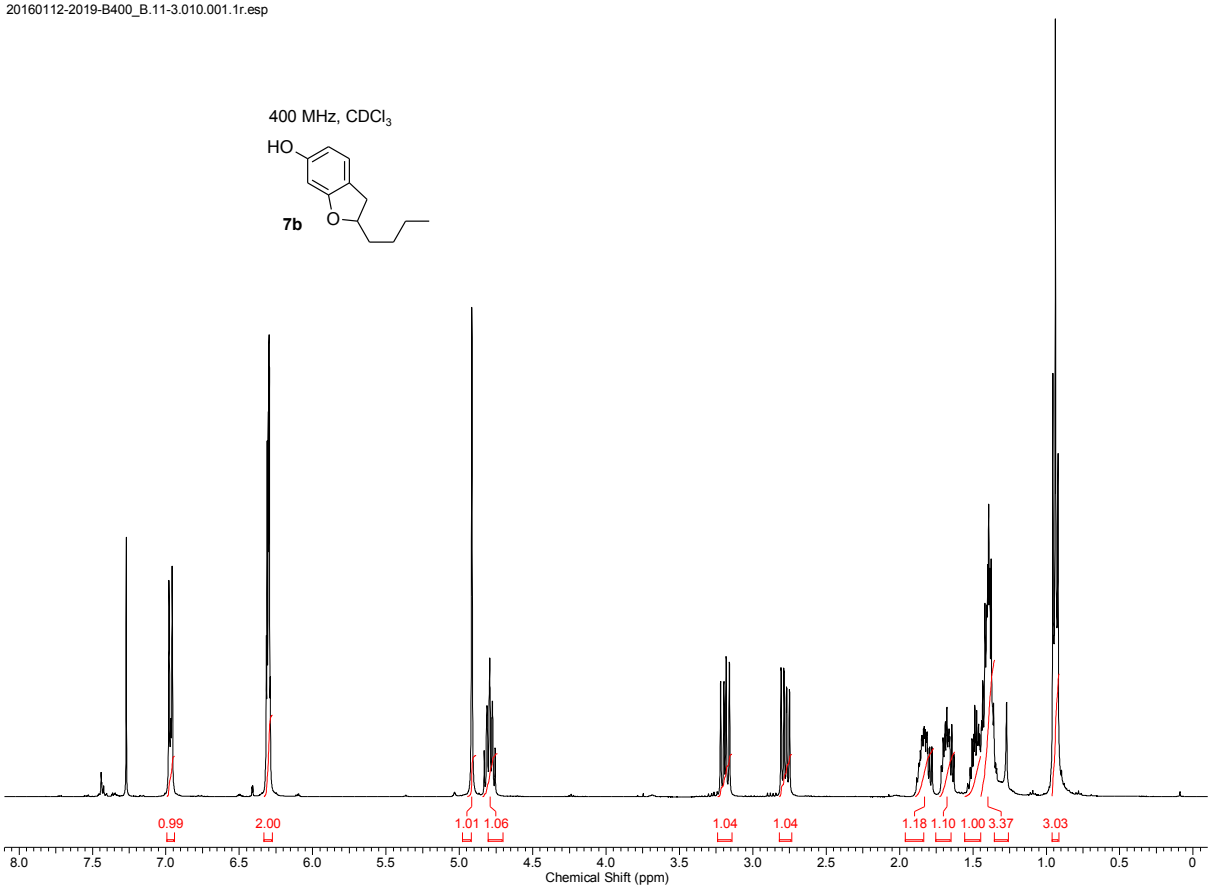
20160111-1931-B500_B.14-4.011.001.1r.esp

125 MHz, $CDCl_3$

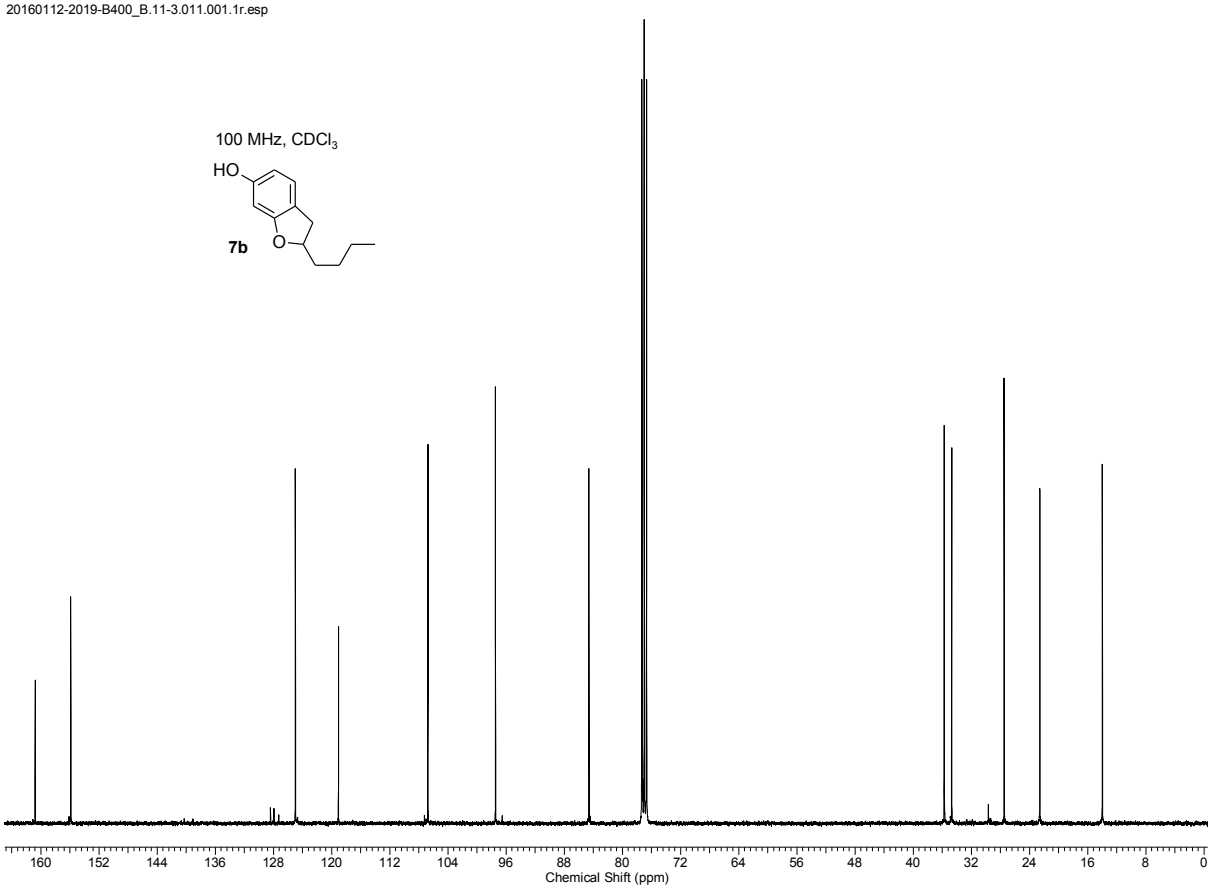


7a

20160112-2019-B400_B.11-3.010.001.1r.esp

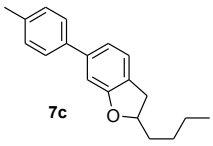


20160112-2019-B400_B.11-3.011.001.1r.esp



20160113-1602-B500_B.14-1.010.001.1r.esp

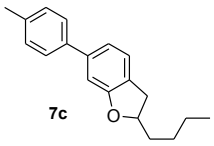
500 MHz, $CDCl_3$



7c

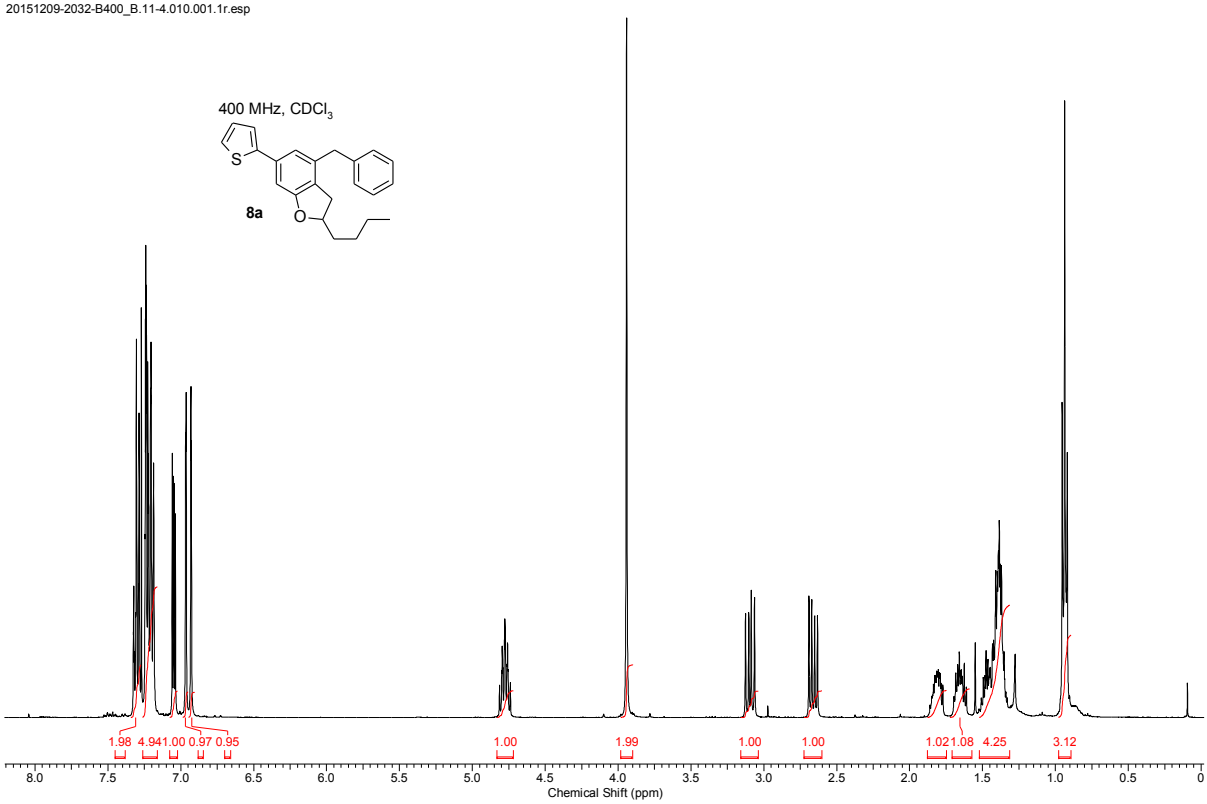
20160113-1602-B500_B.14-1.011.001.1r.esp

125 MHz, $CDCl_3$

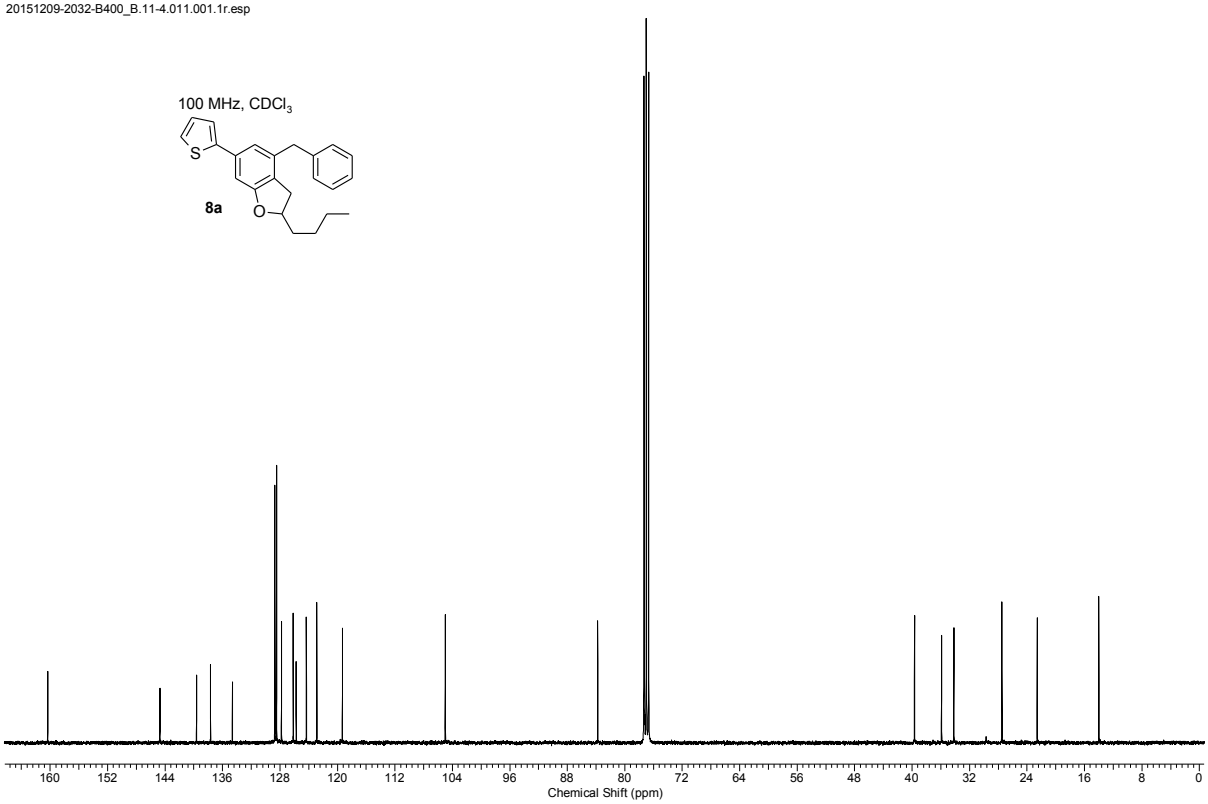


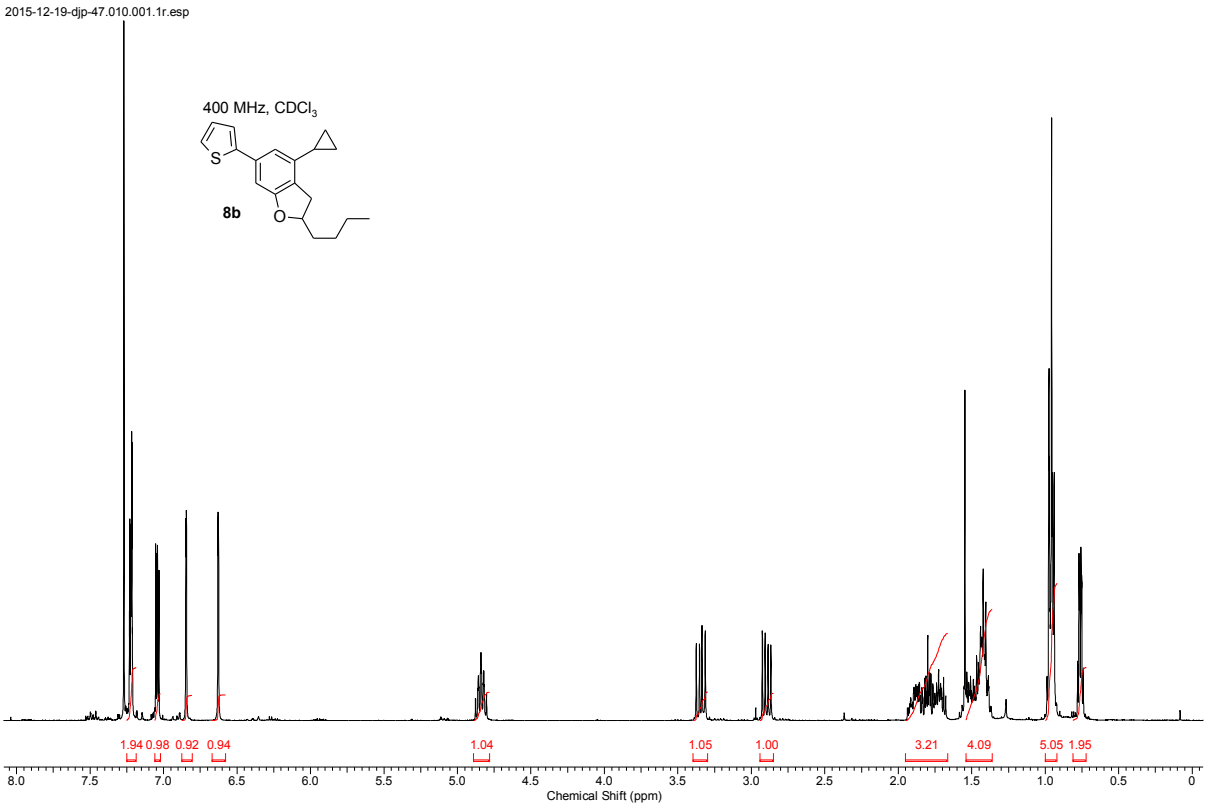
7c

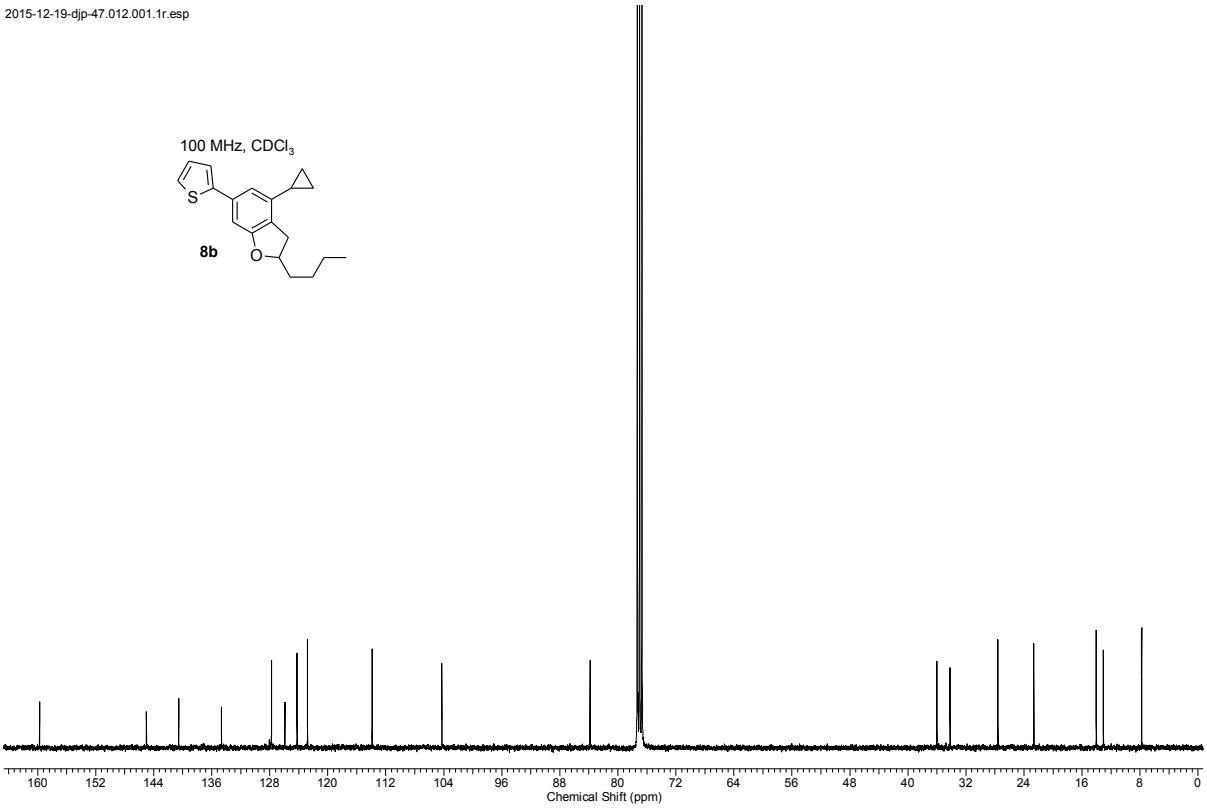
20151209-2032-B400_B.11-4.010.001.1r.esp



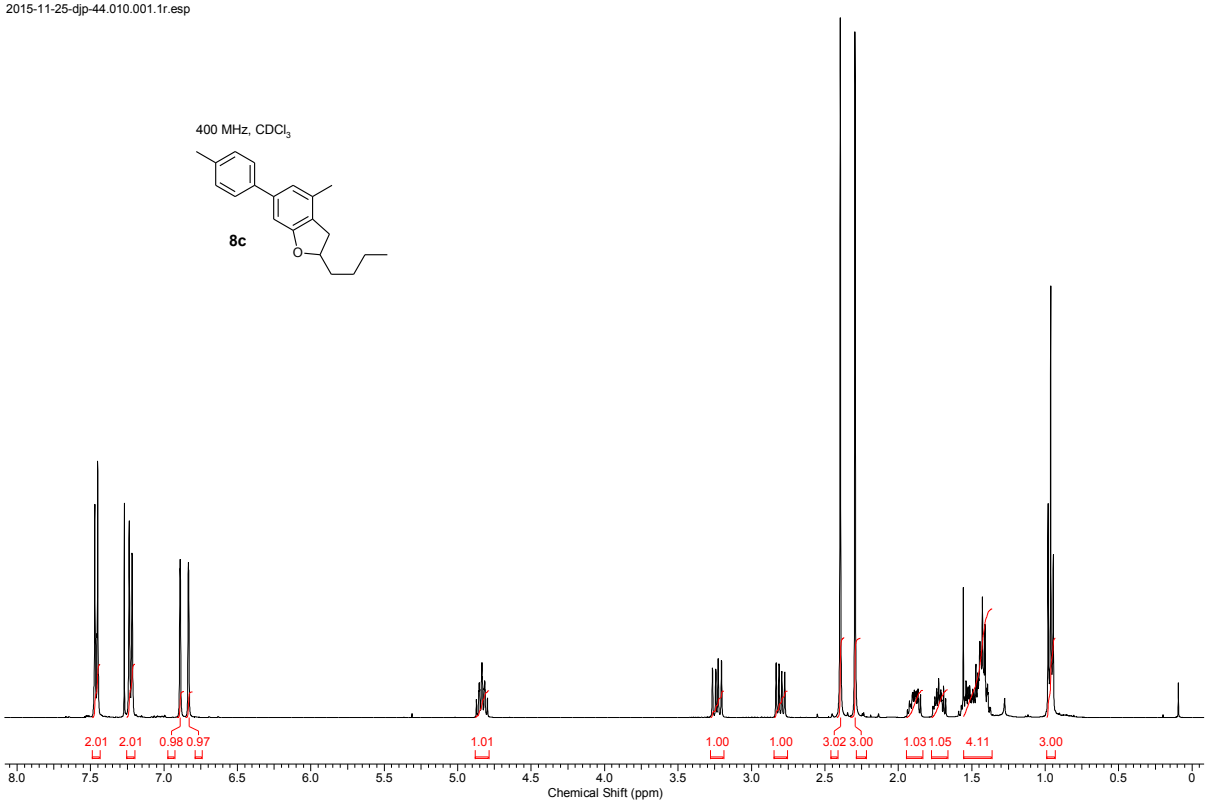
20151209-2032-B400_B.11-4.011.001.1r.esp



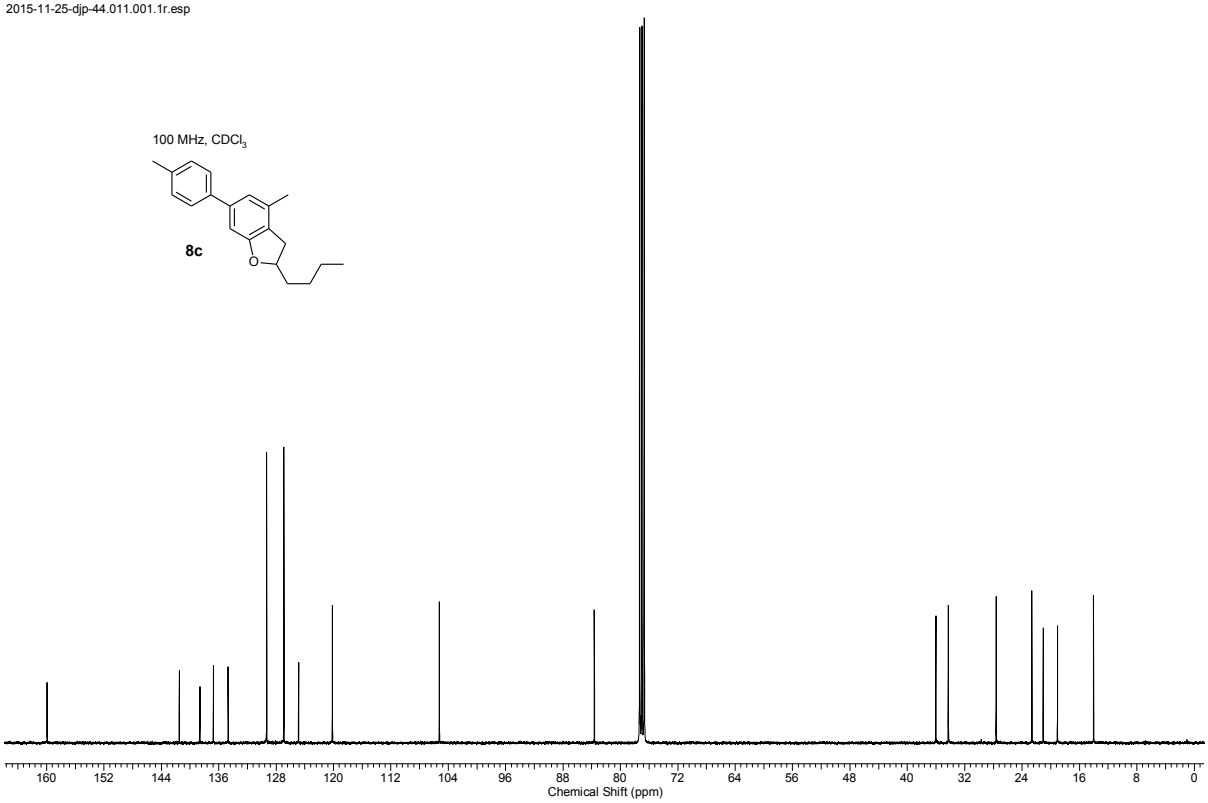

2015-12-19-djp-47.010.001.1r.esp
400 MHz, CDCl3
S
O
8b
1.94 0.98 0.92 0.94
1.04
1.05
1.00
3.21
4.09
5.05 1.95
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


2015-12-19-djp-47.012.001.1r.esp
100 MHz, CDCl3
S
O
8b
160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

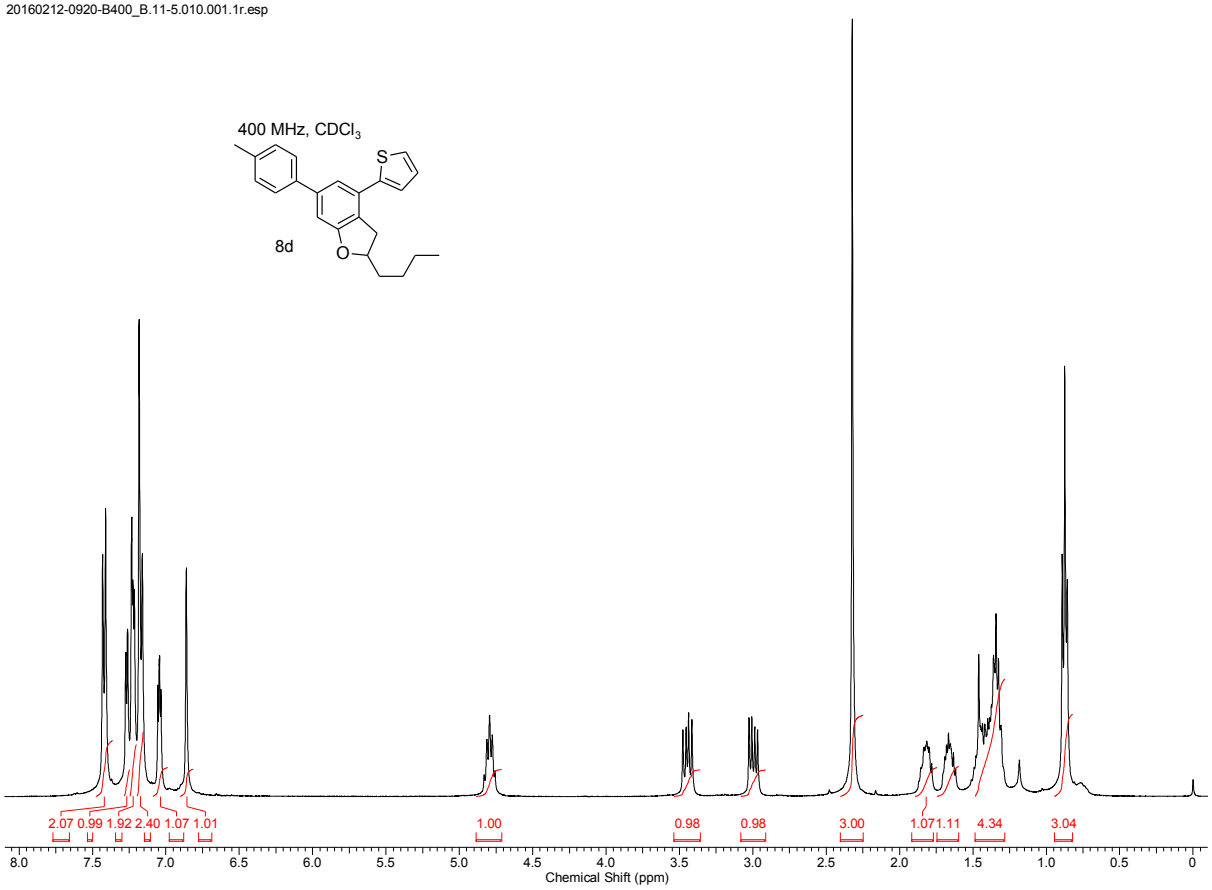
2015-11-25-djp-44.010.001.1r.esp



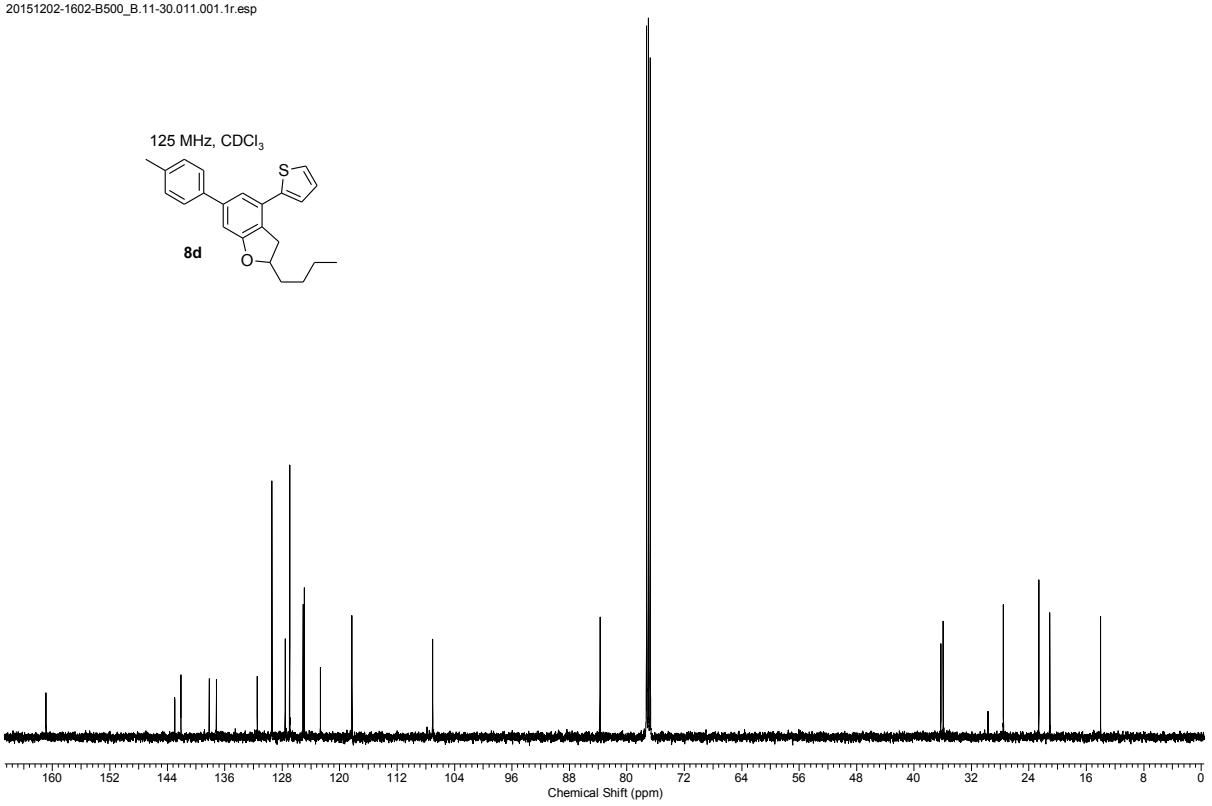
2015-11-25-djp-44.011.001.1r.esp



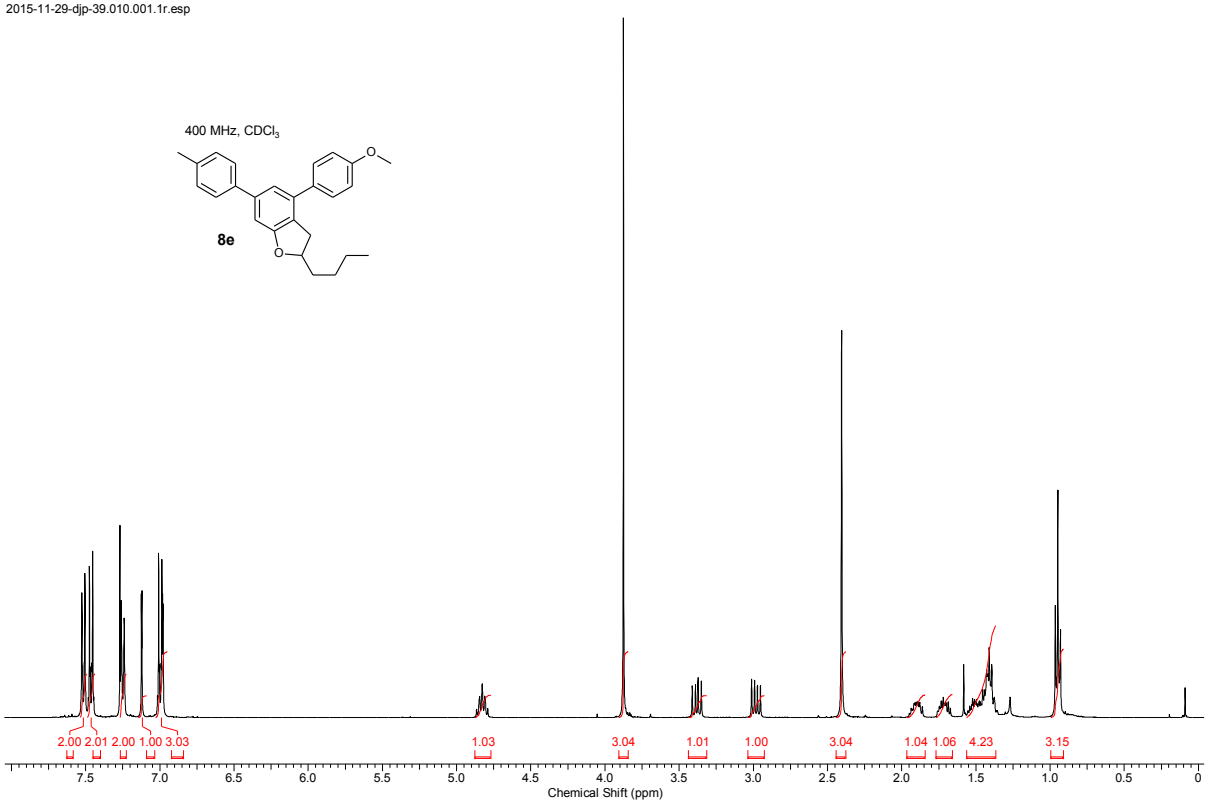
20160212-0920-B400_B.11-5.010.001.1r.esp



20151202-1602-B500_B.11-30.011.001.1r.esp



2015-11-29-djp-39.010.001.1r.esp



2015-11-29-djp-39.011.001.1r.esp