Electronic Supplementary Material (ESI) for ChemComm.

Acid-Mediated Intermolecular C–F/C–H Cross-Coupling of 2-Fluorobenzofurans with Arenes: Synthesis of 2-Arylbenzofurans

Takeshi Fujita,* Ryutaro Morioka, Takuya Fukuda, Naoto Suzuki, and Junji Ichikawa*

Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba
Tsukuba, Ibaraki 305-8571, Japan
fujita@chem.tsukuba.ac.jp
junji@chem.tsukuba.ac.jp

Supporting Information

Table of Contents

1. General Statement S2
2. Synthesis of 2-Arylbenzofurans **3** S2
3. Orthogonal Synthesis of Eupomatenoid 6 (**4**) S15
4. Mechanistic Studies S18
5. Reaction Mechanisms S20
6. References S20
7. ^{1}H, ^{13}C, and ^{19}F NMR Charts S22

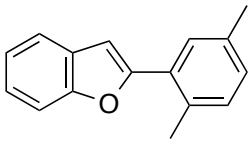
1. General Statement

^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker Avance 500. Chemical shift values are given in ppm relative to internal Me_4Si (for ^{1}H NMR: δ = 0.00 ppm), $CDCl_3$ (for ^{13}C NMR: δ = 77.0 ppm), and C_6F_6 (for ^{19}F NMR: δ = 0.00 ppm). IR spectra were recorded on a Horiba FT-300S spectrometer by the attenuated total reflectance (ATR) method. Mass spectra were measured on a JEOL JMS-T100GCV and a JEOL JMS-T100CS spectrometer. Gel permeation chromatography (GPC) was performed on a Japan Analytical Industry LC-908 apparatus equipped with a JAIGEL-1H and -2H assembly. Elemental analyses were carried out at the Elemental Analysis Laboratory, Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba. X-ray diffraction studies were performed on a Bruker APEXII ULTRA instrument equipped with a CCD diffractometer using MoKα (graphite monochromated, λ = 0.71069 Å) radiation. The structure refinement was performed using the Yadokari-XG software.[1] The structure was solved by direct methods (SIR97).[2] The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F2 by the full-matrix least-squares method using SHELX-97.[3] Hydrogen atoms were placed at calculated positions and refined with the riding mode on their corresponding carbon atoms. The CCDC deposition number of compound **4** is 2075144.

Column chromatography and preparative thin-layer chromatography were conducted on silica gel (Silica Gel 60 N, Kanto Chemical Co., Inc. for column chromatography and Wakogel B-5F, Wako Pure Chemical Industries for preparative thin-layer chromatography). Dichloromethane was purified by a solvent-purification system (GlassContour) equipped with columns of activated alumina and supported-copper catalyst (Q-5) before use. 1,1,1,3,3,3-Hexafluoropropan-2-ol (HFIP) was distilled from molecular sieves 4A and stored over activated molecular sieves 4A. 1,2-Dichloroethane (DCE) was distilled from P_2O_5 and stored over activated molecular sieves 4A. *p*-Xylene (**2a**) and *m*-xylene (**2b**) were distilled from CaH_2 and stored over activated molecular sieves 4A. 2-Fluorobenzofurans **1a**–**1l** and **1n**,[4,5] 2-fluorobenzothiophene (**1m**),[6] 5-bromo-3-methylbenzofuran-2-carboxylic acid,[7,8] 2-chlorobenzofuran (**1a-Cl**),[9,10] 2-bromobenzofuran (**1a-Br**),[11,12] and 2-iodobenzofuran (**1a-I**)[13,14] were prepared according to the literature procedures, and their spectral data showed good agreement with the literature data. Unless otherwise noted, materials were obtained from commercial sources and used directly without further purifications.

2. Synthesis of 2-Arylbenzofurans 3

2-(2,5-Dimethylphenyl)benzofuran (3aa)



Method A:

To a dichloromethane (2.0 mL) suspension of $AlCl_3$ (41 mg, 0.31 mmol) and *p*-xylene (**2a**, 0.12

mL, 1.0 mmol) was added 2-fluorobenzofuran (**1a**, 27 mg, 0.20 mmol) at –20 °C. After stirring at the same temperature for 1 h, aqueous NaOH (2 M, 1 mL) was added and allowed to warm to room temperature. To the mixture was added aqueous HCl (2 M, 1 mL), and organic materials were extracted with dichloromethane (2 mL) three times. The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) to give **3aa** (28 mg, 63%) as a colorless crystal.

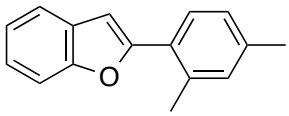
Method B:

To a mixture of $AlCl_3$ (41 mg, 0.31 mmol) and *p*-xylene (**2a**, 0.50 mL, 4.1 mmol) was added 2-fluorobenzofuran (**1a**, 28 mg, 0.20 mmol) at room temperature. After stirring at room temperature for 1 h, aqueous NaOH (2 M, 1 mL) was added. To the mixture was added aqueous HCl (2 M, 1 mL), and organic materials were extracted with dichloromethane (2 mL) three times. The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) to give **3aa** (41 mg, 91%) as a colorless crystal.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.39 (s, 3H), 2.53 (s, 3H), 6.88 (d, J = 0.9 Hz, 1H), 7.10 (d, J = 7.8 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.22–7.30 (m, 2H), 7.52 (dd, J = 8.2, 0.8 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.68 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.9, 21.4, 104.9, 111.0, 120.8, 122.7, 124.1, 128.5, 129.16, 129.23, 129.6, 131.2, 132.7, 135.5, 154.3, 155.7.

Spectral data for this compound showed good agreement with literature data.[14]

2-(2,4-Dimethylphenyl)benzofuran (3ab)

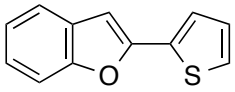


2-Arylbenzofuran **3ab** was synthesized by Method A using 2-fluorobenzofuran (**1a**, 27 mg, 0.20 mmol), *m*-xylene (**2b**, 0.12 mL, 1.0 mmol), $AlCl_3$ (40 mg, 0.30 mmol), and dichloromethane (2.0 mL) at –20 °C for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3ab** (29 mg, 67%) as a colorless crystal.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.38 (s, 3H), 2.56 (s, 3H), 6.86 (s, 1H), 7.13–7.14 (m, 2H), 7.23–7.31 (m, 2H), 7.53 (d, J = 8.2 Hz, 1H), 7.61 (dd, J = 7.6, 0.7 Hz, 1H), 7.76 (d, J = 8.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.2, 21.9, 104.5, 111.1, 120.8, 122.7, 124.0, 126.9, 127.2, 128.1, 129.3, 132.1, 135.7, 138.5, 154.3, 155.9.

Spectral data for this compound showed good agreement with literature data.[15]

2-(Thiophen-2-yl)benzofuran (3ac)

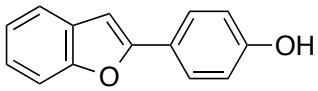


2-Arylbenzofuran **3ac** was synthesized by Method A using 2-fluorobenzofuran (**1a**, 27 mg, 0.20 mmol), thiophene (**2c**, 80 μL, 1.0 mmol), $AlCl_3$ (40 mg, 0.30 mmol), and dichloromethane (2.0 mL) at –20 °C for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3ac** (33 mg, 84%) as a colorless crystal.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.87 (d, J = 0.9 Hz, 1H), 7.11 (dd, J = 5.1, 3.7 Hz, 1H), 7.20–7.29 (m, 2H), 7.34 (dd, J = 5.1, 1.1 Hz, 1H), 7.48–7.50 (m, 2H), 7.54 (ddd, J = 7.6, 1.4, 0.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 101.1, 111.1, 120.7, 123.1, 124.3, 124.6, 125.8, 127.9, 129.1, 133.3, 151.3, 154.5.

Spectral data for this compound showed good agreement with literature data.[16]

4-(Benzofuran-2-yl)phenol (3ad)

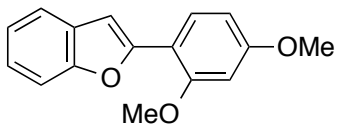


2-Arylbenzofuran **3ad** was synthesized by Method A using 2-fluorobenzofuran (**1a**, 27 mg, 0.20 mmol), phenol (**2d**, 94 mg, 1.0 mmol), $AlCl_3$ (40 mg, 0.30 mmol), and dichloromethane (2.0 mL) at room temperature for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 3/1) gave **3ad** (14 mg, 34%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.99 (s, 1H), 6.88 (d, J = 0.8 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 7.19–7.27 (m, 2H), 7.49 (d, J = 8.2 Hz, 1H), 7.55 (d, J = 6.5 Hz, 1H), 7.76 (d, J = 8.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 99.7, 111.0, 115.7, 120.6, 122.8, 123.6, 123.8, 126.7, 129.4, 154.7, 155.9, 156.0.

Spectral data for this compound showed good agreement with literature data.[17]

2-(2,4-Dimethoxyphenyl)benzofuran (3ae)

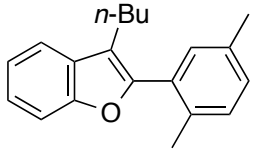


2-Arylbenzofuran **3ae** was synthesized by Method A using 2-fluorobenzofuran (**1a**, 56 mg, 0.41 mmol), 1,3-dimethoxybenzene (**2e**, 0.26 mL, 2.0 mmol), $AlCl_3$ (82 mg, 0.61 mmol), and dichloromethane (4.0 mL) at 40 °C for 24 h. Purification by GPC (chloroform) gave **3ae** (67 mg, 64%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.85 (s, 3H), 3.96 (s, 3H), 6.56 (d, J = 2.3 Hz, 1H), 6.61 (dd, J = 8.6, 2.3 Hz, 1H), 7.17–7.24 (m, 3H), 7.47 (d, J = 8.0 Hz, 1H), 7.55 (dd, J = 7.5, 1.4 Hz, 1H), 7.97 (d,

J = 8.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 55.45, 55.48, 98.8, 104.2, 104.8, 110.6, 112.8, 120.7, 122.5, 123.5, 128.0, 130.0, 152.4, 153.7, 157.8, 160.9. IR (neat): ν 2960, 2939, 2837, 1612, 1504, 1452, 1290, 1254, 1211, 1159, 1049, 1032, 798, 750 cm^{-1}. HRMS (EI): m/z Calcd. for $C_{16}H_{14}O_3$ $[M]^+$: 254.0943; Found: 254.0947.

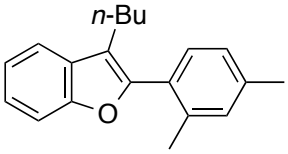
3-Butyl-2-(2,5-dimethylphenyl)benzofuran (3ba)



2-Arylbenzofuran **3ba** was synthesized by Method A using 3-butyl-2-fluorobenzofuran (**1b**, 39 mg, 0.20 mmol), *p*-xylene (**2a**, 0.12 mL, 1.0 mmol), $AlCl_3$ (40 mg, 0.30 mmol), and dichloromethane (1.0 mL) at –20 °C for 3 h. Purification by silica gel column chromatography (hexane/ethyl acetate = 25/1) gave **3ba** (40 mg, 70%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.86 (t, J = 7.3 Hz, 3H), 1.29–1.36 (m, 2H), 1.62–1.68 (m, 2H), 2.27 (s, 3H), 2.36 (s, 3H), 2.65 (t, J = 7.7 Hz, 2H), 7.16 (d, J = 8.0 Hz, 1H), 7.19–7.21 (m, 2H), 7.23–7.30 (m, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 13.8, 19.7, 20.9, 22.5, 23.7, 31.7, 111.1, 116.8, 119.7, 122.1, 123.7, 129.6, 129.8, 130.2, 130.4, 131.1, 134.9, 135.2, 152.3, 154.3. IR (neat): ν 2954, 2927, 2858, 1452, 1257, 1101, 872, 812, 743 cm^{-1}. HRMS (EI): m/z Calcd. for $C_{20}H_{22}O$ $[M]^+$: 278.1671; Found: 278.1670.

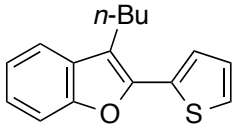
3-Butyl-2-(2,4-dimethylphenyl)benzofuran (3bb)



2-Arylbenzofuran **3bb** was synthesized by Method A using 3-butyl-2-fluorobenzofuran (**1b**, 48 mg, 0.25 mmol), *m*-xylene (**2b**, 133 mg, 1.3 mmol), $AlCl_3$ (52 mg, 0.39 mmol), and dichloromethane (2.5 mL) at room temperature for 2 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3bb** (39 mg, 57%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, J = 7.5 Hz, 3H), 1.33 (qt, J = 7.5, 7.5 Hz, 2H), 1.65 (tt, J = 7.5, 7.5 Hz, 2H), 2.30 (s, 3H), 2.40 (s, 3H), 2.66 (t, J = 7.5 Hz, 2H), 7.09 (d, J = 7.8 Hz, 1H), 7.15 (s, 1H), 7.24–7.30 (m, 3H), 7.47 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 7.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 13.8, 20.1, 21.3, 22.6, 23.7, 31.8, 111.1, 116.8, 119.7, 122.0, 123.6, 126.2, 127.5, 129.7, 130.5, 131.3, 138.2, 138.9, 152.3, 154.3. IR (neat): ν 2956, 2927, 2858, 1614, 1454, 1259, 744, 592 cm^{-1}. HRMS (EI): m/z Calcd. for $C_{20}H_{22}O$ $[M]^+$: 278.1671; Found: 278.1680.

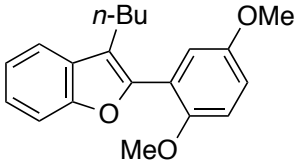
3-Butyl-2-(thiophen-2-yl)benzofuran (3bc)



2-Arylbenzofuran **3bc** was synthesized by Method A using 3-butyl-2-fluorobenzofuran (**1b**, 39 mg, 0.20 mmol), thiophene (**2c**, 84 mg, 1.0 mmol), $AlCl_3$ (42 mg, 0.31 mmol), and dichloromethane (2.0 mL) at room temperature for 1 h. Purification by silica gel column chromatography (hexane) gave **3bb** (20 mg, 38%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.97 (t, J = 7.3 Hz, 3H), 1.46–1.54 (m, 2H), 1.69–1.74 (m, 2H), 2.92 (t, J = 8.0 Hz, 2H), 7.14–7.15 (m, 1H), 7.21–7.29 (m, 2H), 7.37 (ddd, J = 5.1, 1.2, 1.2 Hz, 1H), 7.45–7.48 (m, 2H), 7.53 (dd, J = 7.7, 0.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.0, 22.9, 24.0, 31.5, 110.9, 116.0, 119.4, 122.5, 124.3, 124.8, 125.5, 127.5, 130.4, 133.2, 146.5, 153.8. IR (neat): ν 2954, 2927, 2858, 1454, 1259, 1214, 1103, 1013, 851, 743, 694 cm^{-1}. HRMS (EI): m/z Calcd. for $C_{16}H_{16}OS$ $[M]^+$: 256.0922; Found: 256.0925.

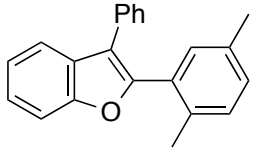
3-Butyl-2-(2,4-dimethoxyphenyl)benzofuran (3bf)



2-Arylbenzofuran **3bf** was synthesized by Method A using 3-butyl-2-fluorobenzofuran (**1b**, 39 mg, 0.20 mmol), 1,4-dimethoxybenzene (**2f**, 57 mg, 0.41 mmol), $AlCl_3$ (41 mg, 0.31 mmol), and dichloromethane (2.0 mL) at room temperature for 2 h. Purification by silica gel column chromatography (toluene/dichloromethane = 10/1) gave **3bf** (47 mg, 75%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, J = 7.4 Hz, 3H), 1.35 (qt, J = 7.5, 7.4 Hz, 2H), 1.63–1.69 (m, 2H), 2.69 (t, J = 7.8 Hz, 2H), 3.79 (s, 3H), 3.82 (s, 3H), 6.93–6.97 (m, 2H), 7.05 (dd, J = 1.1, 1.1 Hz, 1H), 7.22–7.29 (m, 2H), 7.48 (dd, J = 7.8, 0.7 Hz, 1H), 7.59 (dd, J = 7.6, 0.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 13.9, 22.8, 24.1, 31.6, 55.8, 56.3, 111.1, 112.8, 115.6, 116.6, 118.1, 119.8, 121.0, 122.0, 123.8, 129.9, 148.6, 151.8, 153.4, 154.5. IR (neat): ν 2954, 2858, 2832, 2360, 1498, 1454, 1473, 1223, 1174, 1039, 804, 733 cm^{-1}. HRMS (EI): m/z Calcd. for $C_{20}H_{22}O_3$ $[M]^+$: 310.1569; Found: 310.1564.

2-(2,5-Dimethylphenyl)-3-phenylbenzofuran (3ca)

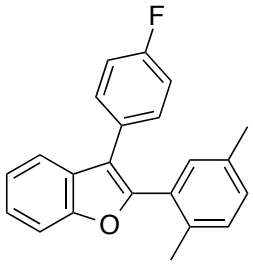


2-Arylbenzofuran **3ca** was synthesized by Method A using 2-fluoro-3-phenylbenzofuran (**1c**, 42 mg, 0.20 mmol), *p*-xylene (**2a**, 0.12 mL, 1.0 mmol), $AlCl_3$ (40 mg, 0.30 mmol), and dichloromethane (2.0 mL) at –20 °C for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 20/1) gave **3ca** (12 mg, 21%) as a white solid.

2-Arylbenzofuran **3ca** was also synthesized by Method B using 2-fluoro-3-phenylbenzofuran (**1c**, 25 mg, 0.12 mmol), *p*-xylene (**2a**, 0.38 mL, 3.1 mmol), and $AlCl_3$ (31 mg, 0.23 mmol) at room temperature for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3ca** (9.0 mg, 26%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.03 (s, 3H), 2.29 (s, 3H), 7.10 (d, J = 1.7 Hz, 1H), 7.24–7.39 (m, 9H), 7.55 (d, J = 8.2 Hz, 1H), 7.74–7.76 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.6, 20.8, 111.2, 118.3, 120.0, 122.8, 124.3, 126.9, 127.1, 128.6, 128.67, 128.72, 130.0, 130.5, 131.2, 132.8, 134.5, 135.1, 152.1, 154.5. IR (neat): ν 3033, 2924, 1653, 1606, 1452, 814, 742, 698 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{22}H_{18}O$ $[M]^+$: 298.1358; Found: 298.1350.

2-(2,5-Dimethylphenyl)-3-(4-fluorophenyl)benzofuran (3da)



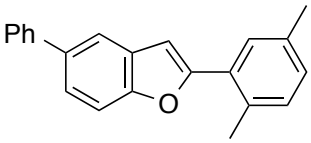
2-Arylbenzofuran **3da** was synthesized by Method A using 2-fluoro-3-(4-fluorophenyl)benzofuran (**1d**, 46 mg, 0.20 mmol), *p*-xylene (**2a**, 0.12 mL, 1.0 mmol), $AlCl_3$ (40 mg, 0.30 mmol), and dichloromethane (2.0 mL) at –20 °C for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 20/1) gave **3da** (16 mg, 25%) as a white solid.

2-Arylbenzofuran **3da** was also synthesized by Method B using 2-fluoro-3-(4-fluorophenyl)benzofuran (**1d**, 31 mg, 0.14 mmol), *p*-xylene (**2a**, 0.38 mL, 3.1 mmol), and $AlCl_3$ (30 mg, 0.22 mmol) at room temperature for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3da** (14 mg, 33%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.03 (s, 3H), 2.28 (s, 3H), 7.03 (dd, J_{HF} = 8.6 Hz, J = 8.6 Hz, 2H), 7.10 (s, 1H), 7.21 (br s, 1H), 7.27–7.35 (m, 4H), 7.53 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 8.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.6, 20.8, 111.4, 115.7 (d, J_{CF} = 21 Hz, 1H), 117.4, 119.8, 122.9, 124.4, 128.4, 128.9 (d, J_{CF} = 3 Hz, 1H), 129.9 (d, J_{CF} = 5 Hz, 1H), 130.1, 130.4 (d, J_{CF} = 8 Hz, 1H), 130.6, 131.2, 134.5, 135.2, 152.2, 154.5, 161.9 (d, J_{CF} = 247 Hz, 1H). ^{19}F NMR (500 MHz, $CDCl_3$):

δ 47.8 (tt, J_{FH} = 9, 5 Hz). IR (neat): ν 2962, 2922, 1512, 1450, 1221, 837, 812, 744, 525 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{22}H_{17}FO$ $[M]^+$: 316.1263; Found: 316.1265.

2-(2,5-Dimethylphenyl)-5-phenylbenzofuran (3ea)

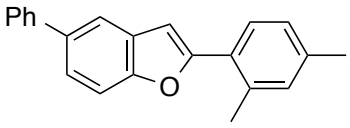


2-Arylbenzofuran **3ea** was synthesized by Method A using 2-fluoro-5-phenylbenzofuran (**1e**, 42 mg, 0.20 mmol), *p*-xylene (**2a**, 0.12 mL, 1.0 mmol), $AlCl_3$ (40 mg, 0.30 mmol), and dichloromethane (2.0 mL) at –20 °C for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3ea** (42 mg, 70%) as a white solid.

2-Arylbenzofuran **3ea** was also synthesized by Method B using 2-fluoro-5-phenylbenzofuran (**1e**, 43 mg, 0.20 mmol), *p*-xylene (**2a**, 0.50 mL, 4.1 mmol), and $AlCl_3$ (39 mg, 0.29 mmol) at room temperature for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3ea** (59 mg, 96%) as a white solid.

^1H NMR (500 MHz, $CDCl_3$): δ 2.40 (s, 3H), 2.55 (s, 3H), 6.91 (s, 1H), 7.10–7.19 (m, 2H), 7.33–7.36 (m, 1H), 7.43–7.78 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.0, 21.4, 105.1, 111.1, 119.3, 123.9, 126.8, 127.4, 128.6, 128.7, 129.3, 129.5, 129.7, 131.2, 132.7, 135.5, 136.4, 141.7, 153.9, 156.5. IR (neat): ν 3030, 2922, 2862, 1458, 1036, 804, 760, 698 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{22}H_{18}O$ $[M]^+$: 298.1358; Found: 298.1361. Elem. Anal. Calcd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.52; H, 6.12.

2-(2,4-Dimethylphenyl)-5-phenylbenzofuran (3eb)



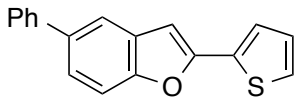
2-Arylbenzofuran **3eb** was synthesized by Method A using 2-fluoro-5-phenylbenzofuran (**1e**, 44 mg, 0.21 mmol), *m*-xylene (**2b**, 0.12 mL, 1.0 mmol), $AlCl_3$ (40 mg, 0.30 mmol), and dichloromethane (2.0 mL) at –20 °C for 1 h. Purification by preparative thin-layer chromatography (hexane) gave **3eb** (31 mg, 51%) as a colorless crystal.

2-Arylbenzofuran **3eb** was also synthesized by Method B using 2-fluoro-5-phenylbenzofuran (**1e**, 43 mg, 0.20 mmol), *m*-xylene (**2b**, 0.50 mL, 4.1 mmol), and $AlCl_3$ (40 mg, 0.30 mmol) at room temperature for 1 h. Purification by preparative thin-layer chromatography (hexane) gave **3eb** (61 mg, 99%) as a colorless crystal.

^1H NMR (500 MHz, $CDCl_3$): δ 2.35 (s, 3H), 2.54 (s, 3H), 6.86 (s, 1H), 7.10–7.11 (m, 2H), 7.31–

7.34 (m, 1H), 7.43 (dd, J = 8.0, 7.9 Hz, 2H), 7.49 (dd, J = 8.5, 1.9 Hz, 1H), 7.54 (d, J = 8.5 Hz, 1H), 7.61 (dd, J = 8.0, 0.9 Hz, 2H), 7.74–7.76 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.2, 21.8, 104.6, 111.1, 119.2, 123.7, 126.79, 126.84, 127.0, 127.4, 128.1, 128.7, 129.8, 132.0, 135.6, 136.4, 138.5, 141.7, 153.9, 156.6. IR (neat): ν 3030, 2922, 1462, 1036, 800, 760, 696 cm^{-1}. HRMS (EI): m/z Calcd. for $C_{22}H_{18}O$ $[M]^+$: 298.1358, Found: 298.1359.

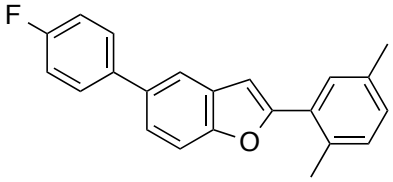
5-Phenyl-2-(thiophen-2-yl)benzofuran (3ec)



2-Arylbenzofuran **3ec** was synthesized by Method A using 2-fluoro-5-phenylbenzofuran (**1e**, 42 mg, 0.20 mmol), thiophene (**2c**, 80 μL, 1.0 mmol), $AlCl_3$ (41 mg, 0.31 mmol), and dichloromethane (2.0 mL) at –20 °C for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3ec** (17 mg, 30%) as a colorless crystal.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.91 (s, 1H), 7.11–7.13 (m, 1H), 7.34–7.37 (m, 2H), 7.44–7.56 (m, 5H), 7.62–7.64 (m, 2H), 7.73 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 101.2, 111.1, 119.2, 124.0, 124.7, 125.9, 126.9, 127.4, 127.9, 128.7, 129.6, 133.2, 136.8, 141.6, 151.9, 154.2. IR (neat): ν 1464, 1265, 1201, 1147, 999, 879, 827, 800, 762, 696 cm^{-1}. HRMS (EI): m/z Calcd for $C_{18}H_{12}OS$ $[M]^+$: 276.0609; Found: 276.0617.

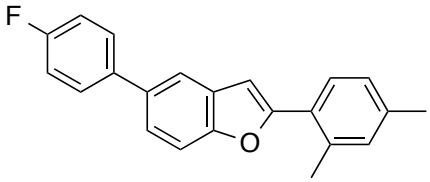
2-(2,5-Dimethylphenyl)-5-(4-fluorophenyl)benzofuran (3fa)



2-Arylbenzofuran **3fa** was synthesized by Method A using 2-fluoro-5-(4-fluorophenyl)benzofuran (**1f**, 46 mg, 0.20 mmol), *p*-xylene (**2a**, 0.12 mL, 1.0 mmol), $AlCl_3$ (40 mg, 0.30 mmol), and dichloromethane (2.0 mL) at –20 °C for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 20/1) gave **3fa** (47 mg, 74%) as a colorless crystal.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.38 (s, 3H), 2.53 (s, 3H), 6.88 (s, 1H), 7.09–7.13 (m, 3H), 7.17 (d, J = 7.7 Hz, 1H), 7.43 (dd, J = 8.5, 1.9 Hz, 1H), 7.53–7.56 (m, 3H), 7.68 (br s, 1H), 7.70 (d, J = 1.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.0, 21.5, 105.0, 111.2, 115.5 (d, J_{CF} = 21 Hz), 119.2, 123.7, 128.6, 128.9 (d, J_{CF} = 8 Hz), 129.4, 129.5, 129.8, 131.3, 132.7, 135.5, 135.6, 137.8 (d, J_{CF} = 3 Hz), 153.9, 156.6, 162.2 (d, J_{CF} = 260 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 46.3 (tt, J_{FH} = 9, 5 Hz). IR (neat): ν 3039, 2927, 2864, 1514, 1460, 1219, 1157, 837, 802, 526 cm^{-1}. HRMS (EI): m/z Calcd. for $C_{22}H_{17}FO$ $[M]^+$: 316.1263; Found: 316.1262.

2-(2,4-Dimethylphenyl)-5-(4-fluorophenyl)benzofuran (3fb)

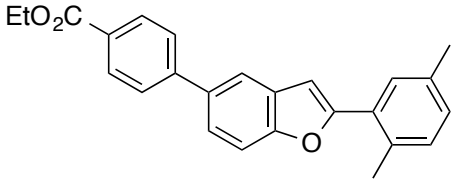


2-Arylbenzofuran **3fb** was synthesized by Method A using 2-fluoro-5-(4-fluorophenyl)benzofuran (**1f**, 47 mg, 0.21 mmol), *m*-xylene (**2b**, 0.12 mL, 1.0 mmol), $AlCl_3$ (40 mg, 0.30 mmol), and dichloromethane (2.0 mL) at –20 °C for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3fb** (37 mg, 56%) as a colorless crystal.

2-Arylbenzofuran **3fb** was also synthesized by Method B using 2-fluoro-5-(4-fluorophenyl)benzofuran (**1f**, 51 mg, 0.22 mmol), *m*-xylene (**2b**, 0.50 mL, 4.1 mmol), and $AlCl_3$ (41 mg, 0.31 mmol) at room temperature for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3fb** (46 mg, 65%) as a colorless crystal.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.36 (s, 3H), 2.55 (s, 3H), 6.85 (s, 1H), 7.10–7.14 (m, 4H), 7.42 (dd, J = 8.5, 1.9 Hz, 1H), 7.53–7.57 (m, 3H), 7.70 (d, J = 1.9 Hz, 1H), 7.74 (d, J = 8.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.2, 21.8, 104.5, 111.1, 115.5 (d, J_{CF} = 21 Hz), 119.1, 123.6, 126.9, 127.0, 128.1, 128.9 (d, J_{CF} = 8 Hz), 129.9, 132.1, 135.5, 135.7, 137.9 (d, J_{CF} = 3 Hz), 138.6, 153.8, 156.7, 162.2 (d, J_{CF} = 246 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 46.2 (tt, J_{FH} = 9, 5 Hz). IR (neat): ν 2983, 2918, 1514, 1464, 1225, 1161, 1018, 798 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{22}H_{17}FO$ $[M]^+$: 316.1263; Found: 316.1260.

Ethyl 4-[2-(2,5-Dimethylphenyl)benzofuran-5-yl]benzoate (3ga)

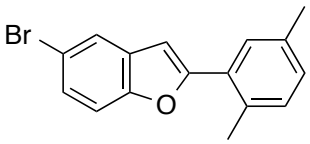


2-Arylbenzofuran **3ga** was synthesized by Method A using ethyl 4-(2-fluorobenzofuran-5-yl)benzoate (**1g**, 57 mg, 0.20 mmol), *p*-xylene (**2a**, 0.12 mL, 1.0 mmol), $AlCl_3$ (40 mg, 0.30 mmol), and dichloromethane (2.0 mL) at –20 °C for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 10/1) gave **3ga** (38 mg, 52%) as a colorless crystal.

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.43 (t, J = 7.2 Hz, 3H), 2.41 (s, 3H), 2.56 (s, 3H), 4.41 (q, J = 7.2 Hz, 2H), 6.94 (d, J = 0.8 Hz, 1H), 7.13 (d, J = 7.7 Hz, 1H), 7.20 (d, J = 7.7 Hz, 1H), 7.55 (dd, J = 8.5, 1.9 Hz, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.70–7.71 (m, 3H), 7.83–7.84 (m, 1H), 8.13 (d, J = 8.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.4, 21.0, 21.5, 60.9, 105.1, 111.3, 119.6, 123.9, 127.2,

128.6, 128.8, 129.4, 129.5, 129.9, 130.1, 131.3, 132.8, 135.3, 135.6, 146.1, 154.3, 156.8, 166.6. IR (neat): ν 2976, 2927, 1714, 1608, 1275, 1103, 810, 771 cm^{-1}. HRMS (ESI+): *m*/*z* Calcd. for $C_{25}H_{23}O_3$ $[M + H]^+$: 371.1647; Found: 371.1644.

5-Bromo-2-(2,5-dimethylphenyl)benzofuran (3ha)

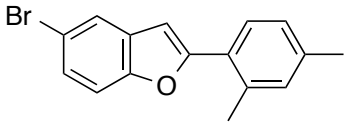


2-Arylbenzofuran **3ha** was synthesized by Method A using 5-bromo-2-fluorobenzofuran (**1h**, 43 mg, 0.20 mmol), *p*-xylene (**2a**, 0.12 mL, 1.0 mmol), $AlCl_3$ (41 mg, 0.31 mmol), and dichloromethane (2.0 mL) at –20 °C for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3ha** (45 mg, 74%) as a colorless crystal.

2-Arylbenzofuran **3ha** was also synthesized by Method B using 5-bromo-2-fluorobenzofuran (**1h**, 46 mg, 0.21 mmol), *p*-xylene (**2a**, 0.50 mL, 4.1 mmol), and $AlCl_3$ (41 mg, 0.30 mmol) at room temperature for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3ha** (55 mg, 86%) as a colorless crystal.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.38 (s, 3H), 2.51 (s, 3H), 6.80 (s, 1H), 7.10–7.19 (m, 2H), 7.37–7.38 (m, 2H), 7.67 (s, 1H), 7.71 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.9, 21.4, 104.2, 112.4, 115.7, 123.4, 126.9, 128.6, 129.0, 129.6, 131.2, 131.3, 132.8, 135.6, 153.0, 157.1. IR (neat): ν 2922, 2862, 1504, 1442, 1263, 1178, 904, 795, 771, 669 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{16}H_{13}{}^{79}BrO$ $[M]^+$: 300.0150; Found: 300.0155.

5-Bromo-2-(2,4-dimethylphenyl)benzofuran (3hb)

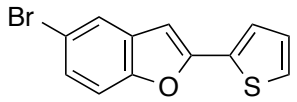


2-Arylbenzofuran **3hb** was synthesized by Method A using 5-bromo-2-fluorobenzofuran (**1h**, 43 mg, 0.20 mmol), *m*-xylene (**2b**, 0.12 mL, 1.0 mmol), $AlCl_3$ (41 mg, 0.31 mmol), and dichloromethane (2.0 mL) at –20 °C for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3hb** (47 mg, 79%) as a colorless crystal.

2-Arylbenzofuran **3hb** was also synthesized by Method B using 5-bromo-2-fluorobenzofuran (**1h**, 44 mg, 0.20 mmol), *m*-xylene (**2b**, 0.50 mL, 4.1 mmol), and $AlCl_3$ (41 mg, 0.31 mmol) at room temperature for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3hb** (53 mg, 86%) as a colorless crystal.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.36 (s, 3H), 2.51 (s, 3H), 6.75 (s, 1H), 7.09–7.10 (m, 2H), 7.33–7.37 (m, 2H), 7.68–7.71 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.2, 21.8, 103.7, 112.4, 115.7, 123.3, 126.5, 126.8, 126.9, 128.1, 131.3, 132.1, 135.7, 138.9, 153.0, 157.2. IR (neat): *n* 3016, 2922, 2862, 1610, 1454, 1441, 1259, 1049, 1020, 793, 671 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{16}H_{13}{}^{79}BrO$ $[M]^+$: 300.0150; Found: 300.0155.

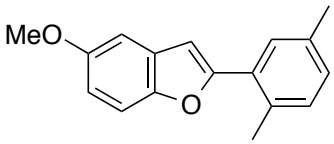
5-Bromo-2-(thiophen-2-yl)benzofuran (3hc)



2-Arylbenzofuran **3hc** was synthesized by Method A using 5-bromo-2-fluorobenzofuran (**1h**, 43 mg, 0.20 mmol), thiophene (**2c**, 80 μL, 1.0 mmol), $AlCl_3$ (40 mg, 0.30 mmol), and dichloromethane (2.0 mL) at –20 °C for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3hc** (23 mg, 40%) as a colorless crystal.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.80 (s, 1H), 7.11 (dd, *J* = 5.0, 3.6 Hz, 1H), 7.35–7.37 (m, 3H), 7.49 (d, *J* = 3.6, 1.0 Hz, 1H), 7.66 (dd, *J* = 1.2, 1.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 100.3, 112.4, 116.1, 123.2, 125.1, 126.3, 127.0, 127.9, 131.1, 132.6, 152.5, 153.2. IR (neat): *n* 1442, 1263, 1200, 1051, 997, 876, 850, 795, 706 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{12}H_7{}^{79}BrOS$ $[M]^+$: 277.9401; Found: 277.9394.

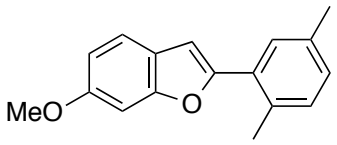
2-(2,5-Dimethylphenyl)-5-methoxybenzofuran (3ia)



2-Arylbenzofuran **3ia** was synthesized by Method A using 2-fluoro-5-methoxybenzofuran (**1i**, 28 mg, 0.17 mmol), *p*-xylene (**2a**, 0.10 mL, 0.84 mmol), $AlCl_3$ (33 mg, 0.25 mmol), and dichloromethane (2.0 mL) at room temperature for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3ia** (18 mg, 43%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.37 (s, 3H), 2.51 (s, 3H), 3.84 (s, 3H), 6.80 (d, *J* = 0.8 Hz, 1H), 6.88 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.05 (d, *J* = 2.6 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.9 Hz, 1H), 7.64 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.9, 21.4, 55.9, 103.2, 105.1, 111.4, 112.8, 128.5, 129.2, 129.65, 129.68, 131.2, 132.6, 135.5, 149.3, 155.9, 156.5. IR (neat): *n* 2954, 2831, 1616, 1477, 1205, 1032, 808 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{17}H_{16}O_2$ $[M]^+$: 252.1150; Found: 252.1145.

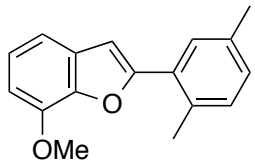
2-(2,5-Dimethylphenyl)-6-methoxybenzofuran (3ja)



2-Arylbenzofuran **3ja** was synthesized by Method A using 2-fluoro-6-methoxybenzofuran (**1j**, 28 mg, 0.17 mmol), *p*-xylene (**2a**, 0.10 mL, 0.84 mmol), $AlCl_3$ (33 mg, 0.25 mmol), and dichloromethane (2.0 mL) at room temperature for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3ja** (18 mg, 43%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.40 (s, 3H), 2.53 (s, 3H), 3.88 (s, 3H), 6.82 (s, 1H), 6.89 (dd, J = 8.5, 2.3 Hz, 1H), 7.08–7.09 (m, 2H), 7.18 (d, J = 7.7 Hz, 1H), 7.47 (d, J = 8.5 Hz, 1H), 7.67 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.0, 21.5, 55.7, 95.7, 104.8, 111.8, 120.9, 122.6, 128.2, 128.8, 129.8, 131.2, 132.2, 135.5, 154.9, 155.3, 158.0. IR (neat): ν 2952, 2833, 1620, 1491, 1306, 1275, 1151, 1111, 812 cm^{-1}. HRMS (EI): *m*/*z* Calcd for $C_{17}H_{16}O_2$ [M]$^+$: 252.1150; Found: 252.1157. Elem. Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.80; H, 6.66.

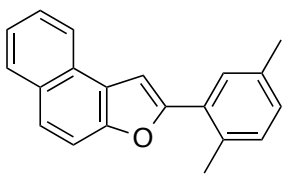
2-(2,5-Dimethylphenyl)-7-methoxybenzofuran (3ka)



2-Arylbenzofuran **3ka** was synthesized by Method A using 2-fluoro-7-methoxybenzofuran (**1k**, 33 mg, 0.20 mmol), *p*-xylene (**2a**, 0.12 mL, 1.0 mmol), $AlCl_3$ (40 mg, 0.30 mmol), and dichloromethane (2.0 mL) at room temperature for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3ka** (23 mg, 46%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.38 (s, 3H), 2.53 (s, 3H), 4.05 (s, 3H), 6.82 (d, J = 7.8 Hz, 1H), 6.87 (s, 1H), 7.09 (d, J = 7.9 Hz, 1H), 7.14–7.21 (m, 3H), 7.71 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.9, 21.4, 56.2, 105.3, 106.6, 113.3, 123.4, 128.7, 129.3, 129.5, 130.9, 131.1, 132.6, 135.5, 143.6, 145.3, 155.8. IR (neat): ν 2966, 2839, 1493, 1321, 1271, 1198, 1101, 983, 808, 731 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{17}H_{16}O_2$ [M]$^+$: 252.1150; Found: 252.1159.

2-(2,5-Dimethylphenyl)naphtho[2,1-*b*]furan (3la)



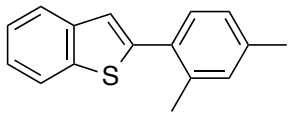
2-Arylnaphthofuran **3la** was synthesized by Method A using fluoronaptho[2,1-*b*]furan (**1l**, 37 mg, 0.20 mmol), *p*-xylene (**2a**, 0.12 mL, 1.0 mmol), $AlCl_3$ (40 mg, 0.30 mmol), and dichloromethane

(2.0 mL) at room temperature for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3la** (20 mg, 37%) as a yellow solid.

2-Arylnaphthofuran **3la** was also synthesized by Method B using fluoronaptho[2,1-*b*]furan (**1l**, 37 mg, 0.20 mmol), *p*-xylene (**2a**, 0.50 mL, 4.1 mmol), and $AlCl_3$ (41.2 mg, 0.30 mmol) at room temperature for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) gave **3la** (23 mg, 43%) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.39 (s, 3H), 2.59 (s, 3H), 7.08 (d, J = 6.9 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H), 7.34 (s, 1H), 7.46 (dd, J = 7.0, 6.9 Hz, 1H), 7.57 (dd, J = 7.0, 7.0 Hz, 1H), 7.67–7.73 (m, 3H), 7.93 (d, J = 8.1 Hz, 1H), 8.16 (d, J = 8.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.0, 21.6, 104.0, 112.2, 123.4, 124.38, 124.44, 125.0, 126.2, 127.6, 128.4, 128.8, 129.1, 129.7, 130.3, 131.3, 132.4, 135.6, 151.8, 155.2. IR (neat): ν 3051, 2922, 2862, 1504, 1385, 1169, 993, 798, 771, 774 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_{20}H_{16}O$ $[M]^+$: 272.1201, Found 272.1191.

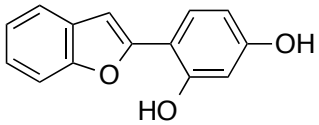
2-(2,4-Dimethylphenyl)benzo[*b*]thiophene (3mb)



2-Arylbenzothiophene **3mb** was synthesized by Method A using 2-fluorobenzo[*b*]thiophene (**1m**, 30 mg, 0.20 mmol), *m*-xylene (**2b**, 0.12 mL, 1.0 mmol), $AlCl_3$ (41 mg, 0.31 mmol), and dichloromethane (2.0 mL) at –20 °C for 1 h. Purification by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) and GPC (chloroform) gave **3mb** (16 mg, 33%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.36 (s, 3H), 2.43 (s, 3H), 7.06 (d, J = 7.8 Hz, 1H), 7.11 (s, 1H), 7.21 (s, 1H), 7.29–7.37 (m, 3H), 7.76 (d, J = 7.7 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.0, 21.1, 122.0, 122.7, 123.3, 123.9, 124.3, 126.7, 130.5, 131.2, 131.6, 136.2, 138.2, 140.0, 140.2, 143.6. IR (neat): ν 3060, 3012, 2952, 2918, 1493, 1456, 1435, 814, 744, 725 cm^{-1}. HRMS (EI): *m*/*z* Calcd for $C_{16}H_{14}S$ $[M]^+$: 238.0816; Found: 238.0812.

4-(Benzofuran-2-yl)benzene-1,2-diol (3ag, DHBF)

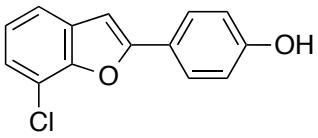


To a HFIP (12.0 mL) and dichloromethane (1.2 mL) solution of $AlCl_3$ (40 mg, 0.30 mmol) and resorcinol (**2g**, 110 mg, 1.0 mmol) was added 2-fluorobenzofuran (**1a**, 27 mg, 0.20 mmol) at room temperature. After stirring at room temperature for 2 h, aqueous NaOH (2 M, 3 mL) was added. To the mixture was added aqueous HCl (2 M, 3 mL), and organic materials were extracted with dichloromethane (3 mL) three times. The combined extracts were dried over Na_2SO_4. After removal

of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 4/1 to 2/1) to give **3ag** (22 mg, 49%) as a colorless crystal.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.97 (br s, 1H), 6.48–6.50 (m, 2H), 6.90 (d, J = 0.9 Hz, 1H), 7.22–7.28 (m, 2H), 7.35 (br s, 1H), 7.48–7.50 (m, 1H), 7.53–7.57 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 101.4, 104.0, 107.9, 108.7, 109.4, 110.9, 120.7, 123.4, 124.0, 128.6, 153.7, 154.6, 154.9, 157.5. IR (neat): ν 3494, 3379, 1624, 1599, 1506, 1446, 1304, 1242, 1151, 976, 916, 796, 735 cm^{-1}. HRMS (ESI–): m/z Calcd for $C_{14}H_9O_3$ $[M - H]^-$: 225.0552; Found: 225.0550.

4-(7-Chlorobenzofuran-2-yl)phenol (3nd)

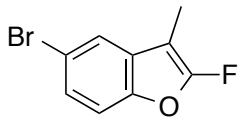


To a dichloromethane (2.0 mL) suspension of $AlCl_3$ (39 mg, 0.29 mmol) and phenol (**2d**, 96 mg, 1.0 mmol) was added 7-chloro-2-fluorobenzofuran (**1n**, 34 mg, 0.20 mmol) at room temperature. After stirring at room temperature for 1 h, aqueous NaOH (2 M, 1 mL) was added. To the mixture was added aqueous HCl (2 M, 1 mL), and organic materials were extracted with dichloromethane (1 mL) three times. The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 4/1) to give **3nd** (27 mg, 54%) as a colorless crystal.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.87 (s, 1H), 6.91 (d, J = 8.8 Hz, 2H), 7.12 (dd, J = 7.8, 7.8 Hz, 1H), 7.22 (dd, J = 7.8, 1.0 Hz, 1H), 7.42 (dd, J = 7.8, 1.0 Hz, 1H), 7.77 (d, J = 8.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 100.1, 115.8, 116.4, 119.1, 122.9, 123.7, 123.9, 126.9, 131.1, 150.4, 156.4, 156.8. IR (neat): ν 3336, 1502, 1473, 1423, 1290, 1244, 1236, 906, 835, 808, 735 cm^{-1}. HRMS (ESI–): m/z Calcd for $C_{14}H_8ClO_2$ $[M - H]^-$: 243.0213; Found: 243.0210.

3. Orthogonal Synthesis of Eupomatenoid 6 (4)

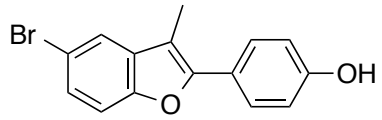
5-Bromo-2-fluoro-3-methylbenzofuran (1o)[18]



To a 1,2-dichloroethane (20 mL) and H_2O (10 mL) suspension of Selectfluor (4.25 g, 12.0 mmol) and KF (1.39 g, 23.9 mmol) was added 5-bromo-3-methylbenzofuran-2-carboxylic acid (1.47 g, 5.76 mmol) at room temperature. After stirring at 70 °C for 12 h, H_2O (20 mL) was added, and organic materials were extracted with dichloromethane (20 mL) three times. The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane) to give **1o** (1.07 g, 81%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.06 (d, J_{HF} = 1.7 Hz, 3H) 7.20 (d, J = 8.6 Hz, 1H), 7.32 (dd, J = 8.6, 2.1 Hz, 1H), 7.51 (d, J = 2.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 5.4, 86.1 (d, J_{CF} = 13 Hz), 112.2, 116.4, 121.8 (d, J_{CF} = 6 Hz), 126.1 (d, J_{CF} = 4 Hz), 131.6, 145.6, 157.4 (d, J_{CF} = 280 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 44.7 (s). IR (neat): ν 2931, 1676, 1454, 1442, 1354, 1194, 796, 744, 623, 519 cm^{-1}. HRMS (EI): *m*/*z* Calcd. for $C_9H_6{}^{79}BrFO$ $[M]^+$: 227.9586; Found: 227.9581.

4-(5-Bromo-3-methylbenzofuran-2-yl)phenol (3od)

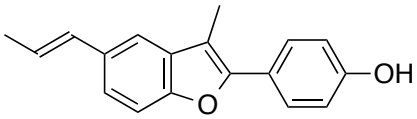


To a 1,2-dichloroethane (4.0 mL) suspension of $AlCl_3$ (70 mg, 0.52 mmol) and phenol (**2d**, 189 mg, 2.0 mmol) was added 5-bromo-3-methyl-2-fluorobenzofuran (**1o**, 93 mg, 0.40 mmol) at room temperature. After stirring at 80 °C for 4 h, aqueous NaOH (2 M, 3 mL) was added. To the mixture was added aqueous HCl (2 M, 3 mL), and organic materials were extracted with dichloromethane (3 mL) three times. The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane/diethyl ether = 5/1) to give **3od** (87 mg, 71%) as a colorless crystal.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.37 (s, 3H), 5.00 (s, 1H), 6.93 (d, J = 8.8 Hz, 2H) 7.30 (d, J = 8.6 Hz, 1H), 7.33 (dd, J = 8.6, 1.9 Hz, 1H), 7.60 (d, J = 1.9 Hz, 1H), 7.66 (d, J = 8.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 9.3, 109.2, 112.2, 115.4, 115.7, 121.8, 123.8, 126.6, 128.5, 133.3, 152.0, 152.3, 155.6.

Spectral data for this compound showed good agreement with literature data.[17]

Eupomatenoid 6 (4)



A *t*-BuOH (0.5 mL) and H_2O (0.1 mL) suspension of 4-(5-bromo-3-methylbenzofuran-2-yl)phenol (**3od**, 16 mg, 0.051 mmol), potassium (*E*)-propenyltetrafluoroborate (9.9 mg, 0.067 mmol), $Pd(PPh_3)_4$ (2.9 mg, 2.5 μmol), and Cs_2CO_3 (52 mg, 0.16 mmol) was degassed by using freeze-pump-thaw method three times. After stirring at 80 °C for 16 h, H_2O (2 mL) was added, and organic materials were extracted with dichloromethane (2 mL) three times. The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by preparative thin-layer chromatography (hexane/ether = 5/1) to give **4** (13 mg, 99%) as a colorless crystal.

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.91 (dd, J = 6.6, 1.7 Hz, 3H), 2.42 (s, 3H), 4.92 (s, 1H), 6.23 (dq, J = 15.5, 6.6 Hz, 1H), 6.51 (dd, J = 15.5, 1.7 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 7.27 (dd, J = 8.4, 1.7 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.43 (d, J = 1.7 Hz, 1H), 7.68 (d, J = 8.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 9.4, 18.5, 109.8, 110.6, 115.6, 116.1, 122.2, 124.2, 124.4, 128.3, 131.3, 131.5,

132.6, 151.1, 152.9, 155.3.

Spectral data for this compound showed good agreement with literature data.[19] The structure of **4** was also confirmed by X-ray diffraction analysis (Figure S1 and Table S1).

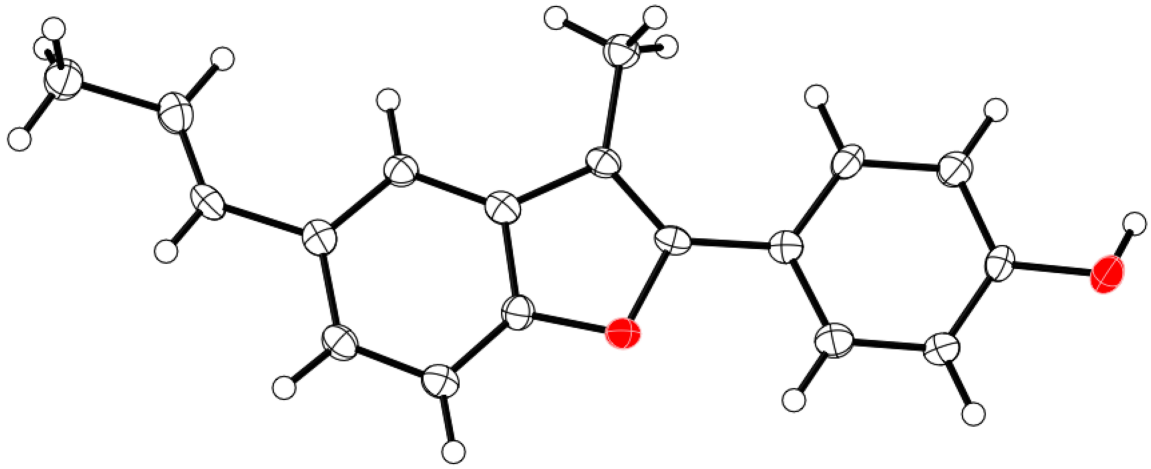


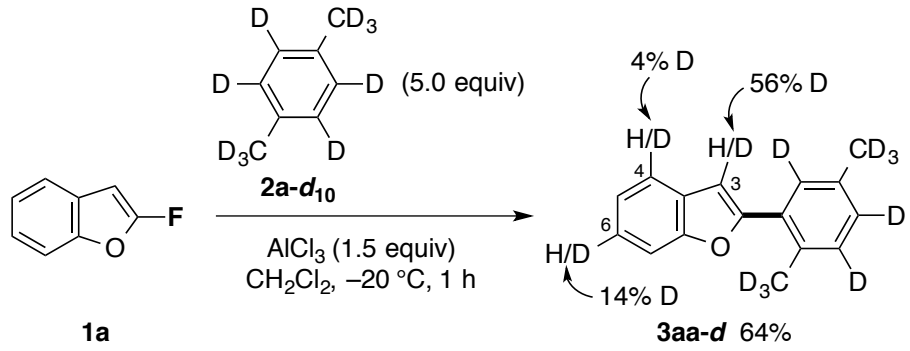
Figure S1. ORTEP Drawing of **4** with 50% Ellipsoid Probability

Table S1. Crystal Data Collection Parameters for **4**

compound	**4**
formula	$C_{18}H_{16}O_2$
crystal system	Orthorhombic
space group	*Pbca*
R, R_w ($I > 2\sigma(I)$)	0.0884, 0.1791
$R1$, $wR2$ (all data)	0.1546, 0.2040
GOF on F^2	1.079
a (Å)	4.768(2)
b (Å)	18.775(9)
c (Å)	31.234(15)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	2796(2)
Z	8
T (K)	120(2)
crystal size (mm)	0.47, 0.35, 0.01
D_{calcd} (g/cm^3)	1.256
$2\theta_{min}$, $2\theta_{max}$ (deg)	2.60, 50.00

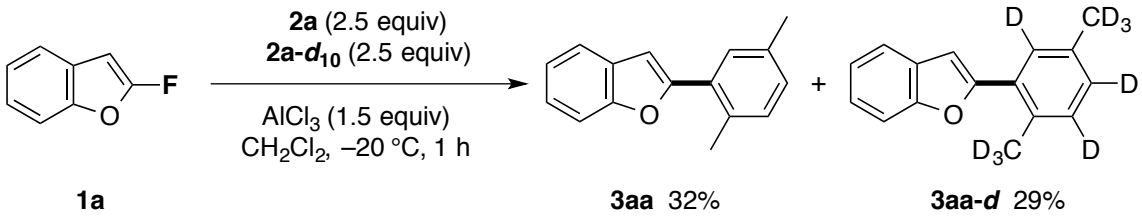
4. Mechanistic Studies

Control Experiments Using 1a and 2a-d_{10}



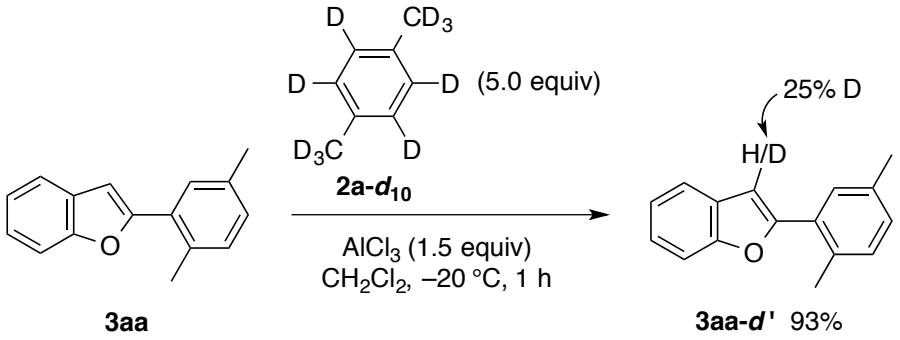
To a dichloromethane (2.0 mL) suspension of $AlCl_3$ (41 mg, 0.31 mmol) and *p*-xylene-d_{10} (**2a-*d*$_{10}$**, 0.12 mL, 1.0 mmol) was added 2-fluorobenzofuran (**1a**, 28 mg, 0.20 mmol) at –20 °C. After stirring at the same temperature for 1 h, aqueous NaOH (2 M, 1 mL) was added and allowed to warm to room temperature. To the mixture was added aqueous HCl (2 M, 1 mL), and organic materials were extracted with dichloromethane (2 mL) three times. The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 30/1) to give **3aa** (30 mg, 64%) as a colorless oil. The ratio of deuterium incorporation of each position was determined by ^{1}H NMR spectroscopy.

Control Experiments Using 1a, 2a, and 2a-d_{10}



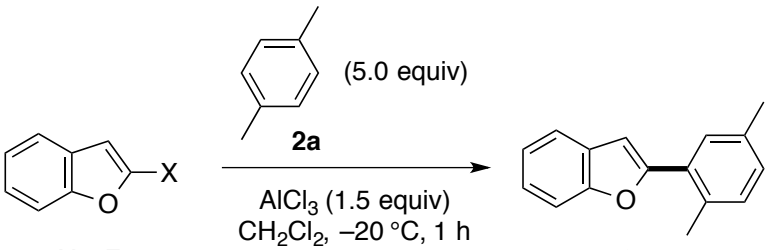
To a dichloromethane (2.0 mL) suspension of $AlCl_3$ (40 mg, 0.30 mmol), *p*-xylene (**2a**, 62 μL, 0.50 mmol), and *p*-xylene-d_{10} (**2a-*d*$_{10}$**, 61 μL, 0.50 mmol) was added 2-fluorobenzofuran (**1a**, 27 mg, 0.20 mmol) at –20 °C. After stirring at the same temperature for 1 h, aqueous NaOH (2 M, 1 mL) was added and allowed to warm to room temperature. To the mixture was added aqueous HCl (2 M, 1 mL), and organic materials were extracted with dichloromethane (2 mL) three times. The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the yields of **3aa** and **3aa-*d*** were determined by ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard.

Control Experiments Using 3aa and 2a-d_{10}



To a dichloromethane (1.0 mL) suspension of $AlCl_3$ (20 mg, 0.15 mmol) and *p*-xylene-d_{10} (**2a-*d*$_{10}$**, 61 μL, 0.50 mmol) was added 2-arylbenzofuran **3aa** (22 mg, 0.10 mmol) at –20 °C. After stirring at the same temperature for 1 h, aqueous NaOH (2 M, 1 mL) was added and allowed to warm to room temperature. To the mixture was added aqueous HCl (2 M, 1 mL), and organic materials were extracted with dichloromethane (2 mL) three times. The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the yield of **3aa-*d*'** and the ratio of deuterium incorporation of each position was determined by ^{1}H NMR spectroscopy.

Effect of Halogens on the 2-Positions in Benzofurans



To a dichloromethane (2.0 mL) suspension of $AlCl_3$ (1.5 equiv) and *p*-xylene (**2a**, 5.0 equiv) was added 2-halobenzofuran (**1a**: X = F; **1a-Cl**: X = Cl; **1a-Br**: X = Br; **1a-I**: X = I) at –20 °C. After stirring at the same temperature for 1 h, aqueous NaOH (2 M, 1 mL) was added and allowed to warm to room temperature. To the mixture was added aqueous HCl (2 M, 1 mL), and organic materials were extracted with dichloromethane (2 mL) three times. The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the yield of **3aa** was determined by ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard.

5. Reaction Mechanisms

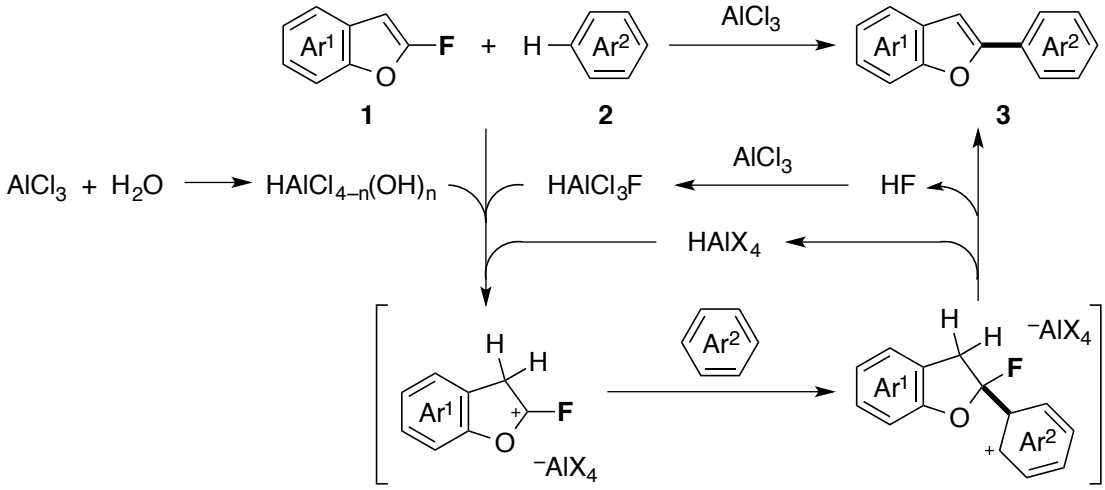


Figure S2. Plausible Mechanism

6. References

(1) C. Kabuto, S. Akine, S. Nemoto and E. Kwon, *J. Cryst. Soc. Jpn.*, 2009, **51**, 218–224.

(2) A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115–119.

(3) G. M. Sheldrick, *Programs for Crystal Structure Analysis (Release 972)*; Institut für Anorganische Chemie der Universität: Göttingen, Germany, 1998.

(4) R. Morioka, T. Fujita and J. Ichikawa, *Helv. Chim. Acta*, 2020, **103**, e2000159.

(5) J. Ichikawa, Y. Wada, T. Okauchi and T. Minami, *Chem. Commun.*, 1997, 1537–1538.

(6) R. Hofsäß, D. Rombach and H.-A. Wagenknecht, *Synlett*, 2017, **28**, 1422–1426.

(7) J. Li, T. S. Rush III, W. Li, D. DeVincentis, X. Du, Y. Hu, J. R. Thomason, J. S. Xiang, J. S. Skotnicki, S. Tam, K. M. Cunningham, P. S. Chockalingam, E. A. Morris and J. I. Levin, *Bioorg. Med. Chem. Lett.*, 2005, **15**, 4961–4966.

(8) N. D. Adams, C. J. Aquino, J. M. Ghergurovich, D. L. Musso, C. A. Parrish and A. J. Reif, WO2012037299, 2012.

(9) J. Yang, S. Liu, J.-F. Zheng and J. S. Zhou, *Eur. J. Org. Chem.*, 2012, 6248–6249.

(10) L. Lu, H. Yan, P. Sun, Y. Zhu, H. Yang, D. Liu, G. Rong and J. Mao, *Eur. J. Org. Chem.*, 2013, 1644–1648.

(11) M.-L. Yao, M. S. Reddy, L. Yong, I. Walfish, D. W. Blevins and G. W. Kabalka, *Org. Lett.*, 2010, **12**, 700–703.

(12) T. T. B. Nguyen, T. Lomberget, N. C. Tran, E. Colomb, L. Nachtegaele, S. Thoret, J. Dubois, J. Guillaume, R. Abdayem, M. Haftek and R. Barret, *Bioorg. Med. Chem. Lett.*, 2012, **22**, 7227–7231.

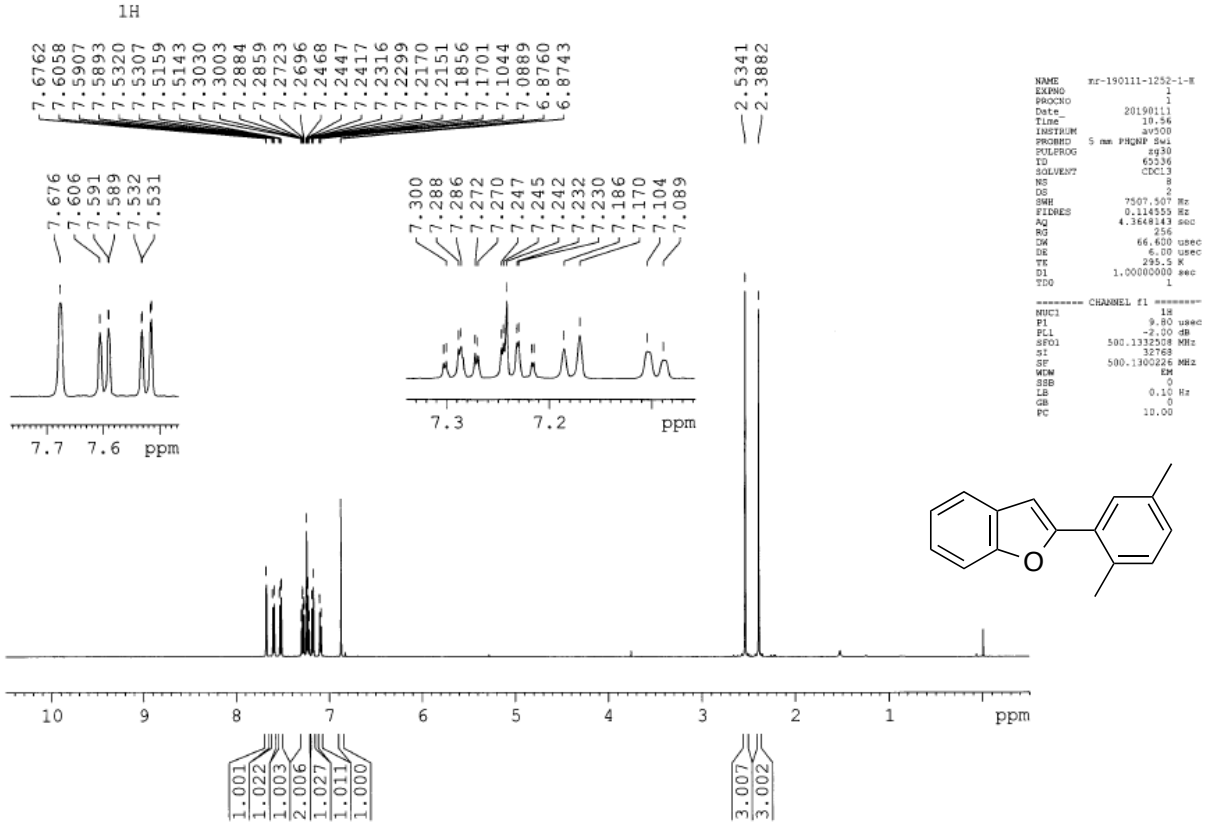
(13) H. Naka, M. Uchiyama, Y. Matsumoto, A. E. H. Wheatley, M. McPartlin, J. V. Morey and Y. Kondo, *J. Am. Chem. Soc.*, 2007, **129**, 1921–1930.

(14) T. A. Dwight, N. R. Rue, D. Charyk, R. Josselyn and B. DeBoef, *Org. Lett.*, 2007, **9**, 3137–3139.
(15) Y. Li, L. Cheng, X.Liu, B. Li and N. Sun, *Beilstein J. Org. Chem.*, 2014, **10**, 2886–2891.
(16) X.-F. Duan, J. Zeng, Z.-B. Zhang and G.-F. Zi, *J. Org. Chem.*, 2007, **72**, 10283–10286.
(17) N. Takeda, O. Miyata and T. Naito, *Eur. J. Org. Chem.*, 2007, 1491–1509.
(18) X. Yuan, J.-F. Yao and Z.-Y. Tang, *Org. Lett.*, 2017, **19**, 1410–1413.
(19) O. Miyata, N. Takeda and T. Naito, *Org. Lett.*, 2004, **6**, 1761–1763.

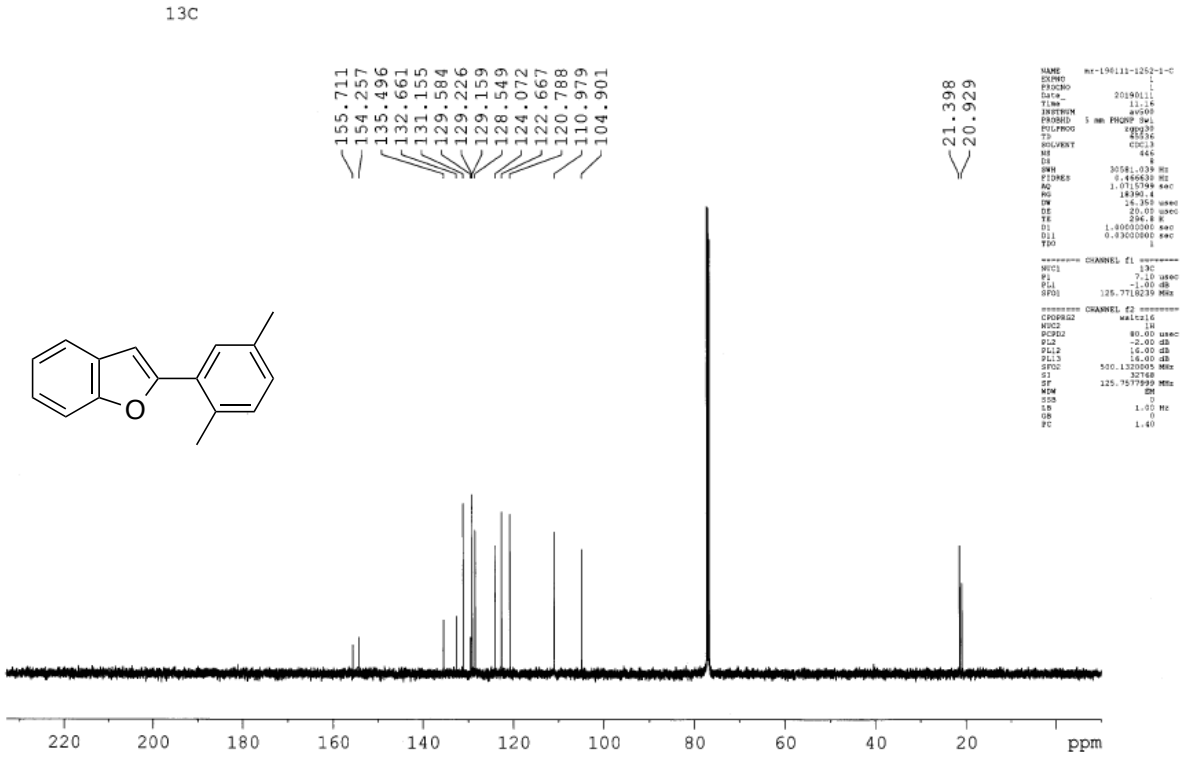
7. ^{1}H, ^{13}C, and ^{19}F NMR Charts

2-(2,5-Dimethylphenyl)benzofuran (3aa)

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

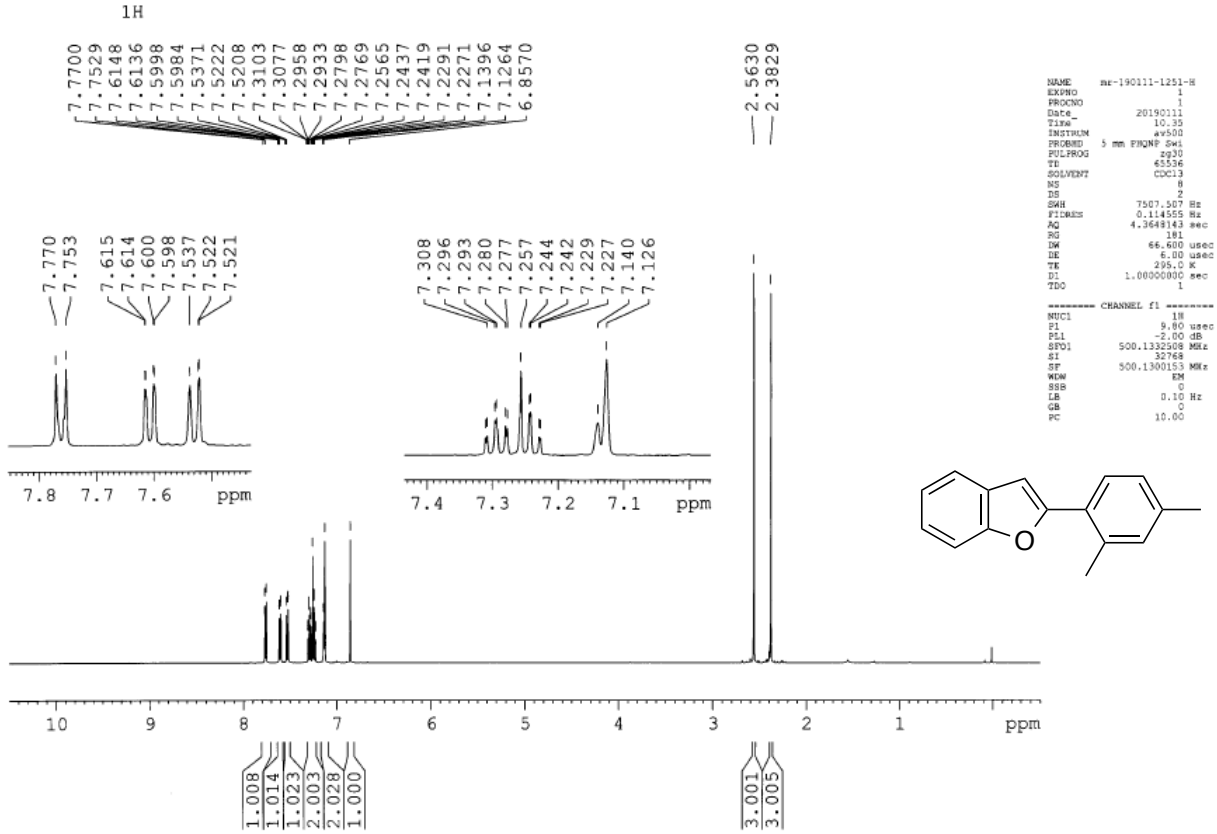


^{13}C NMR (126 MHz, $CDCl_3$)

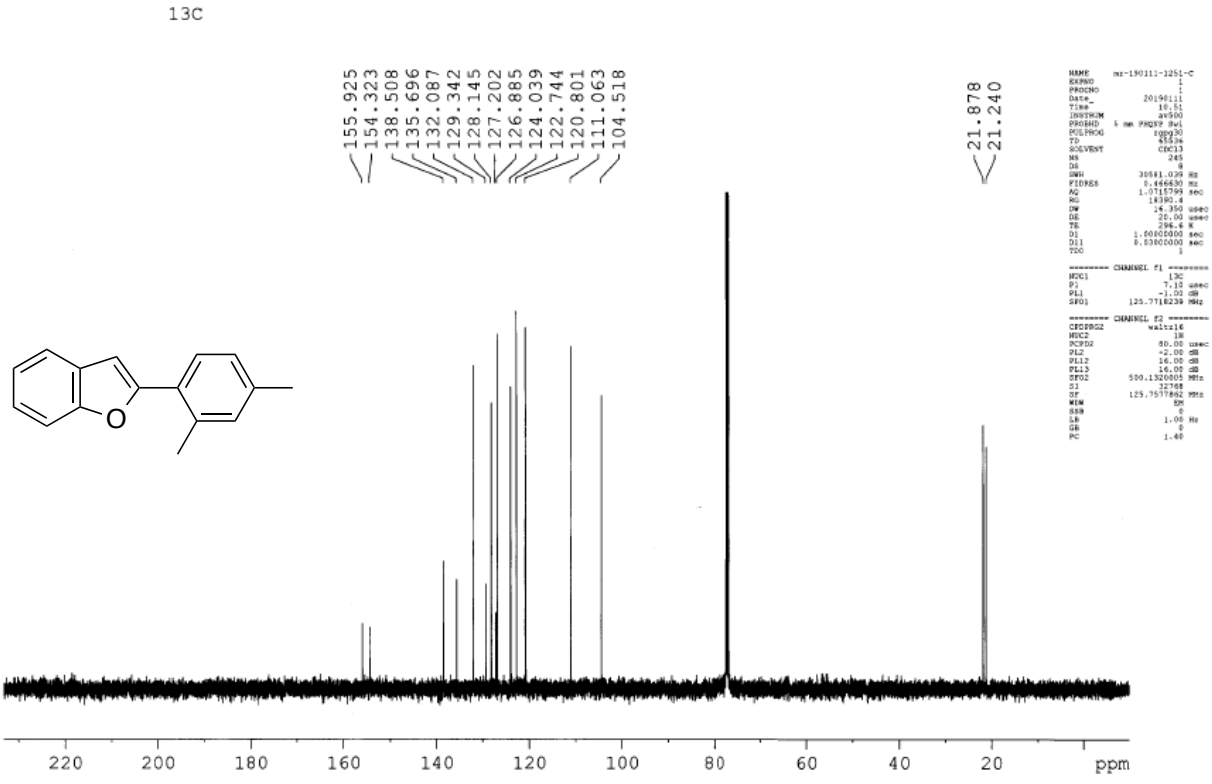


2-(2,4-Dimethylphenyl)benzofuran (3ab)

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

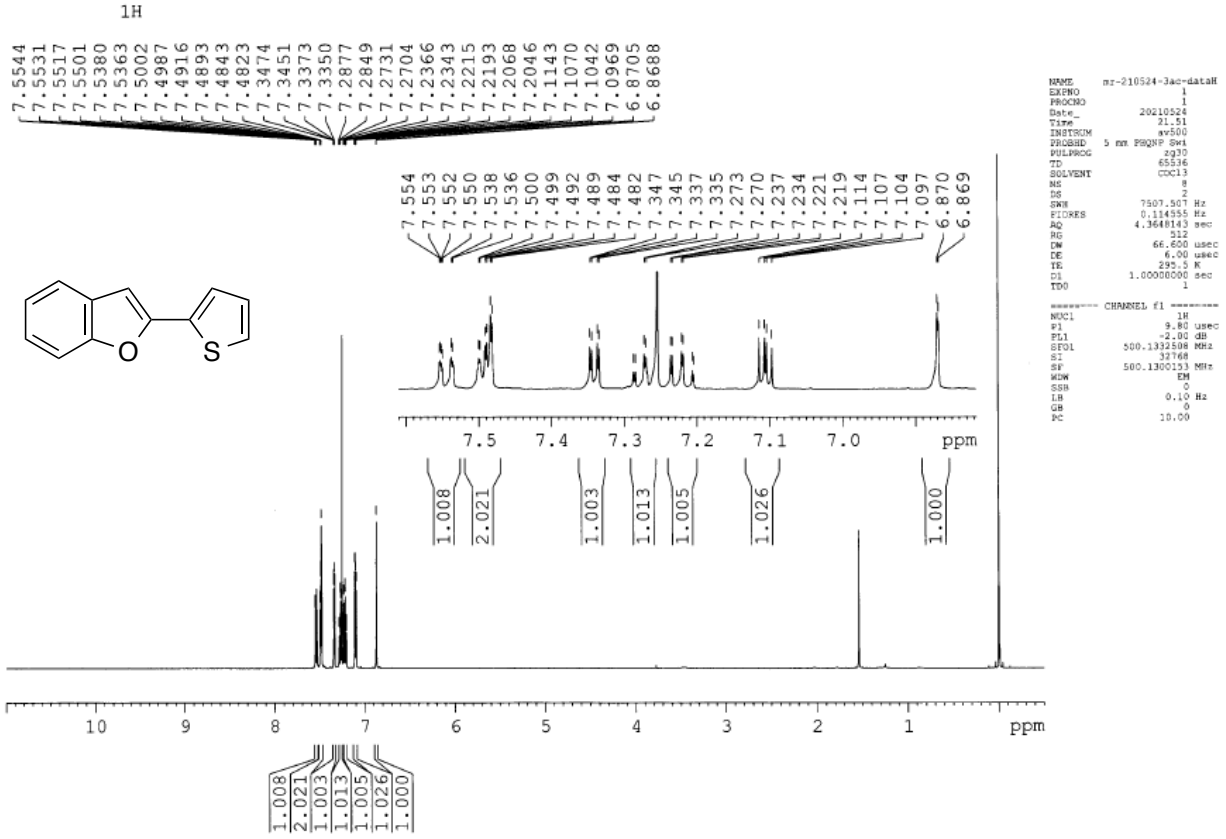


^{13}C NMR (126 MHz, $CDCl_3$)

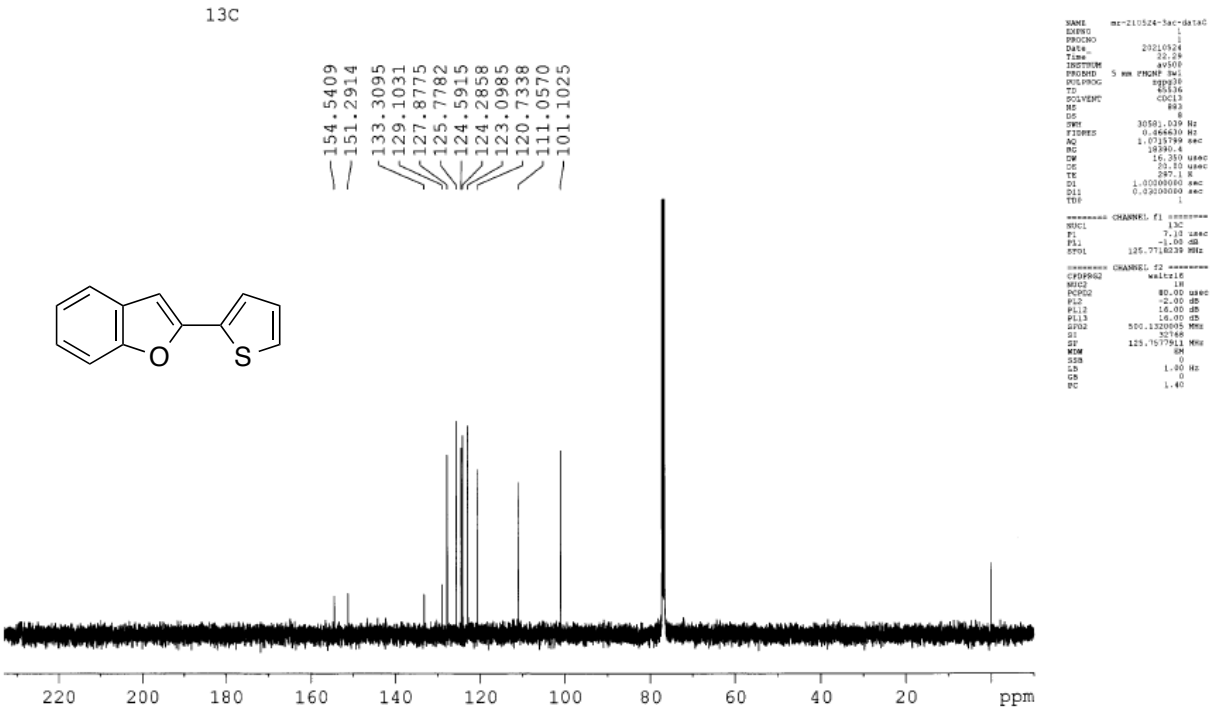


2-(Thiophen-2-yl)benzofuran (3ac)

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

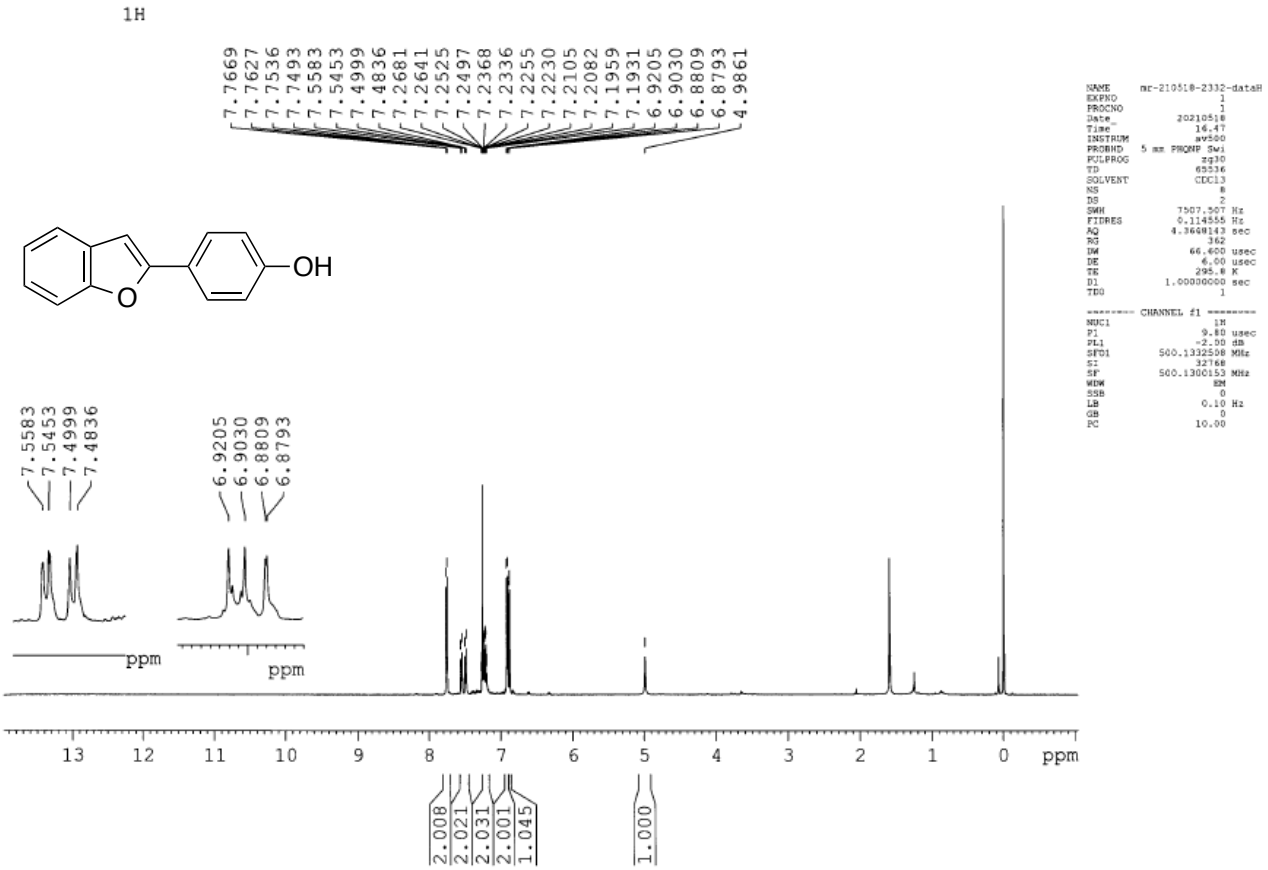


^{13}C NMR (126 MHz, $CDCl_3$)

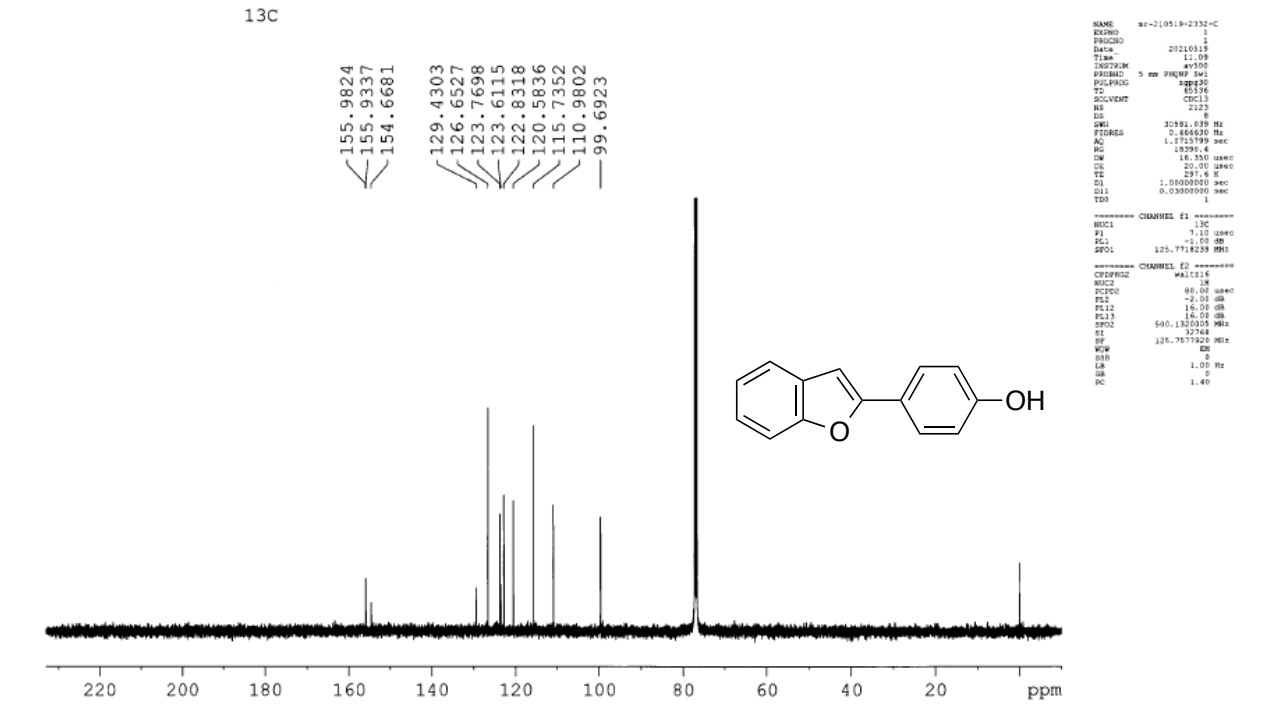


4-(Benzofuran-2-yl)phenol (3ad)

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

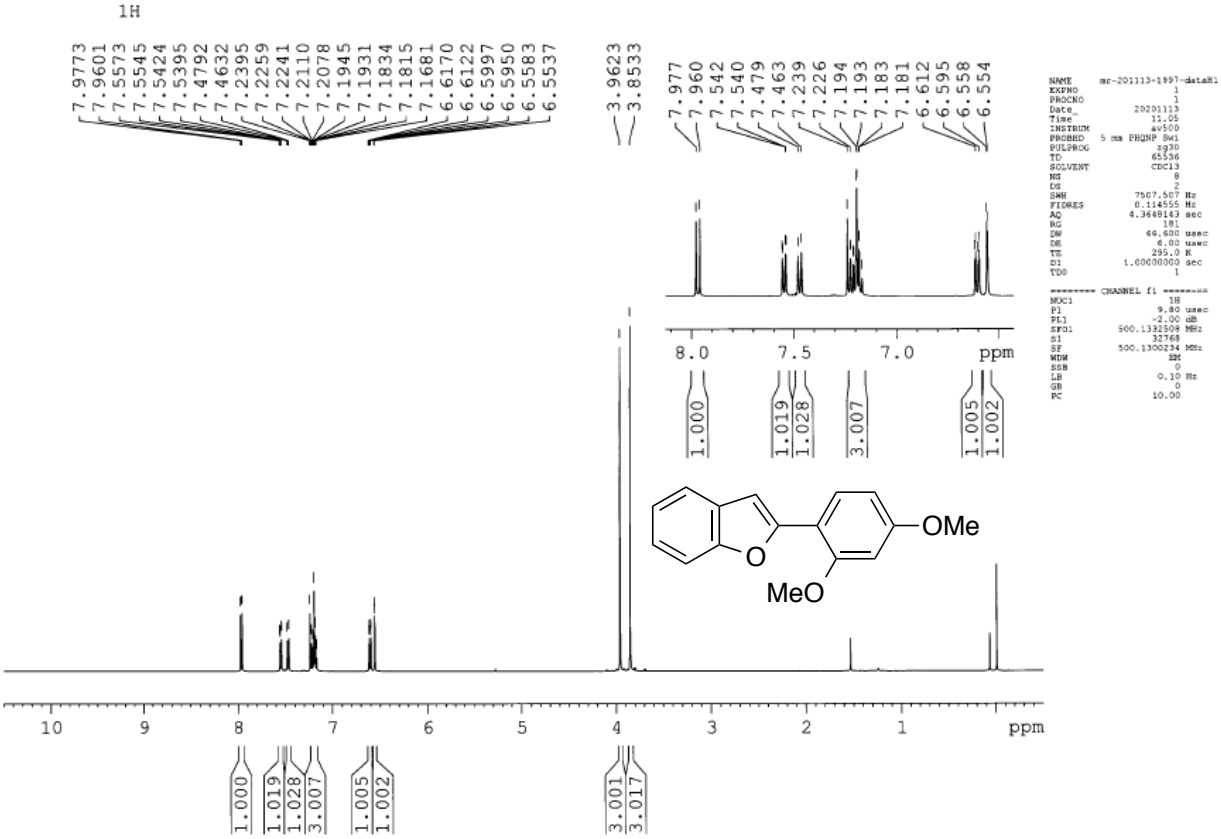


^{13}C NMR (126 MHz, $CDCl_3$)

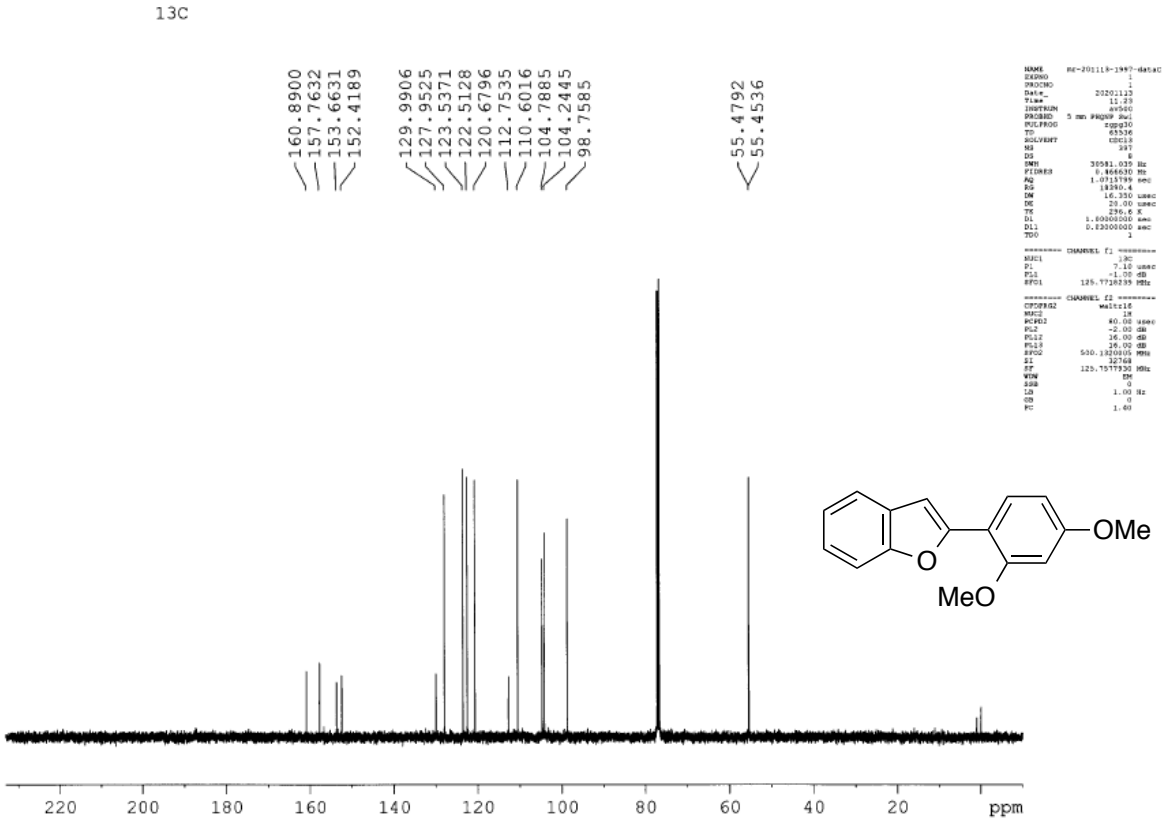


2-(2,4-Dimethoxyphenyl)benzofuran (3ae)

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

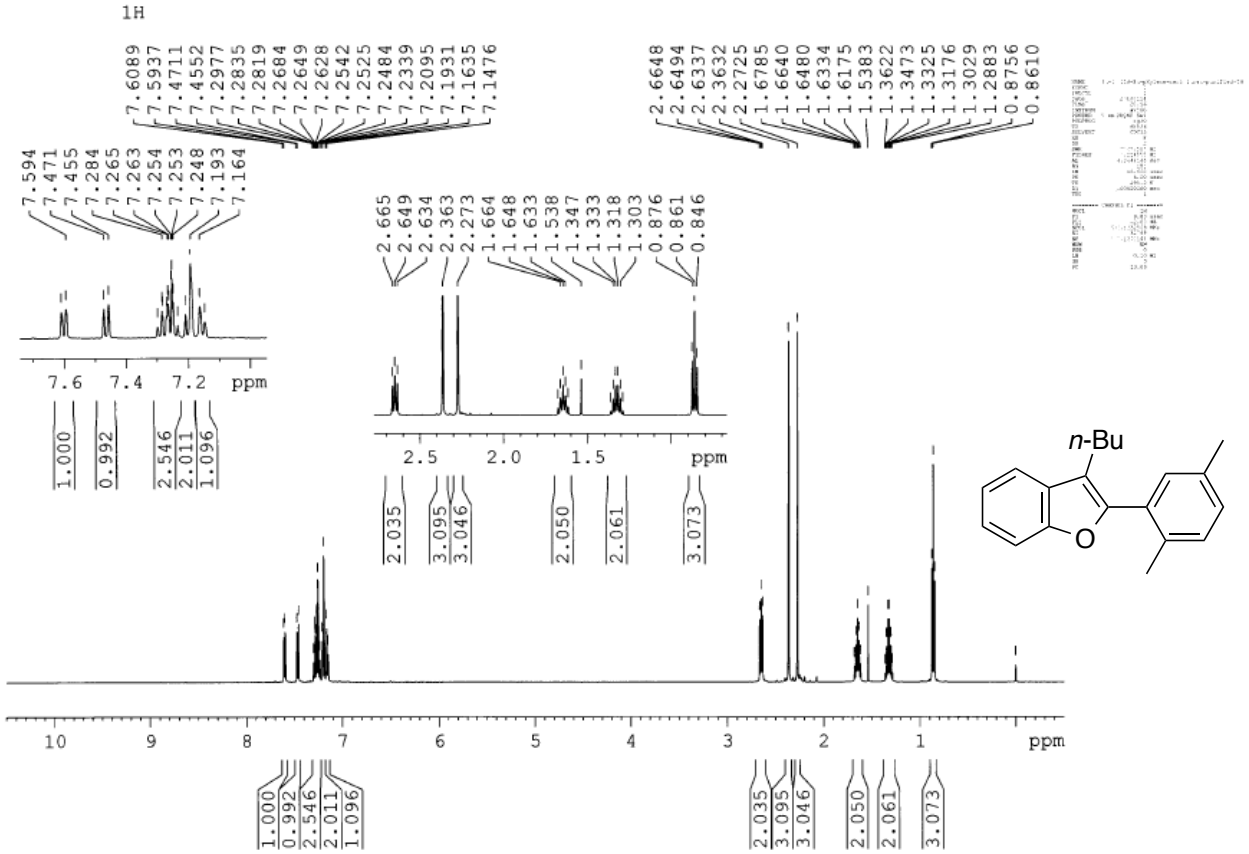


^{13}C NMR (126 MHz, $CDCl_3$)

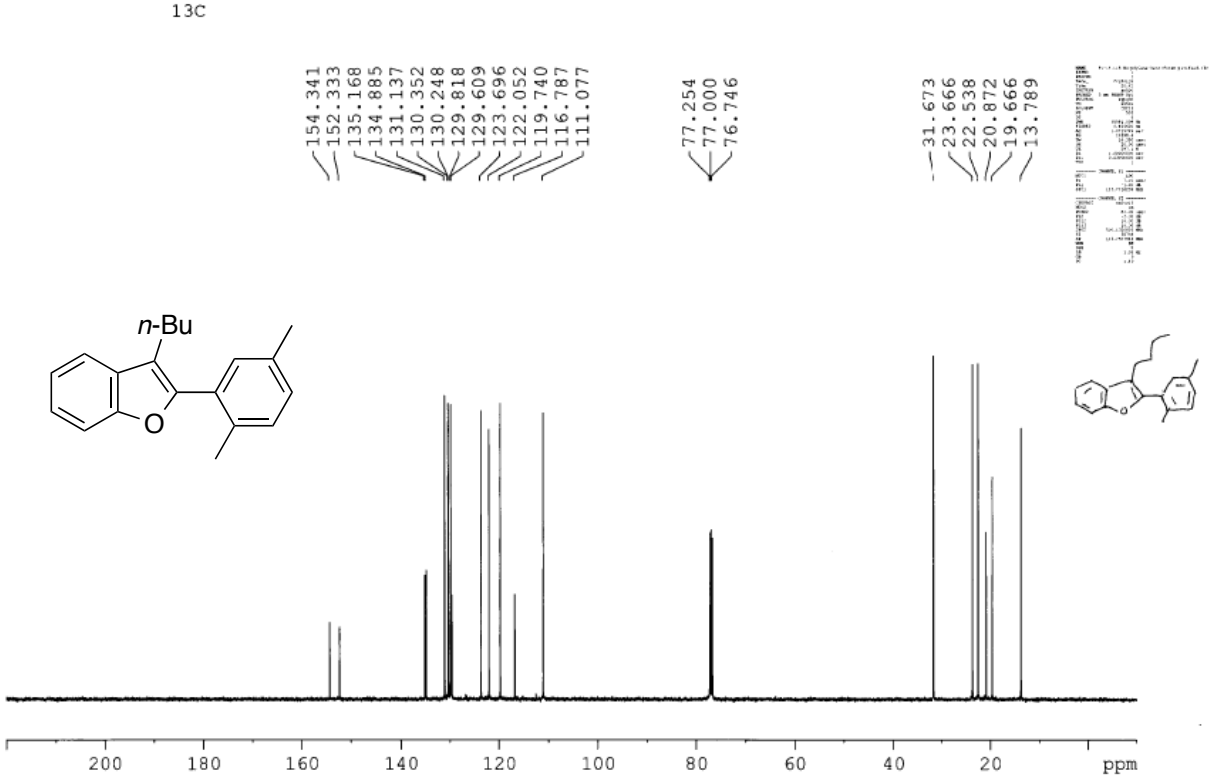


3-Butyl-2-(2,5-dimethylphenyl)benzofuran (3ba)

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

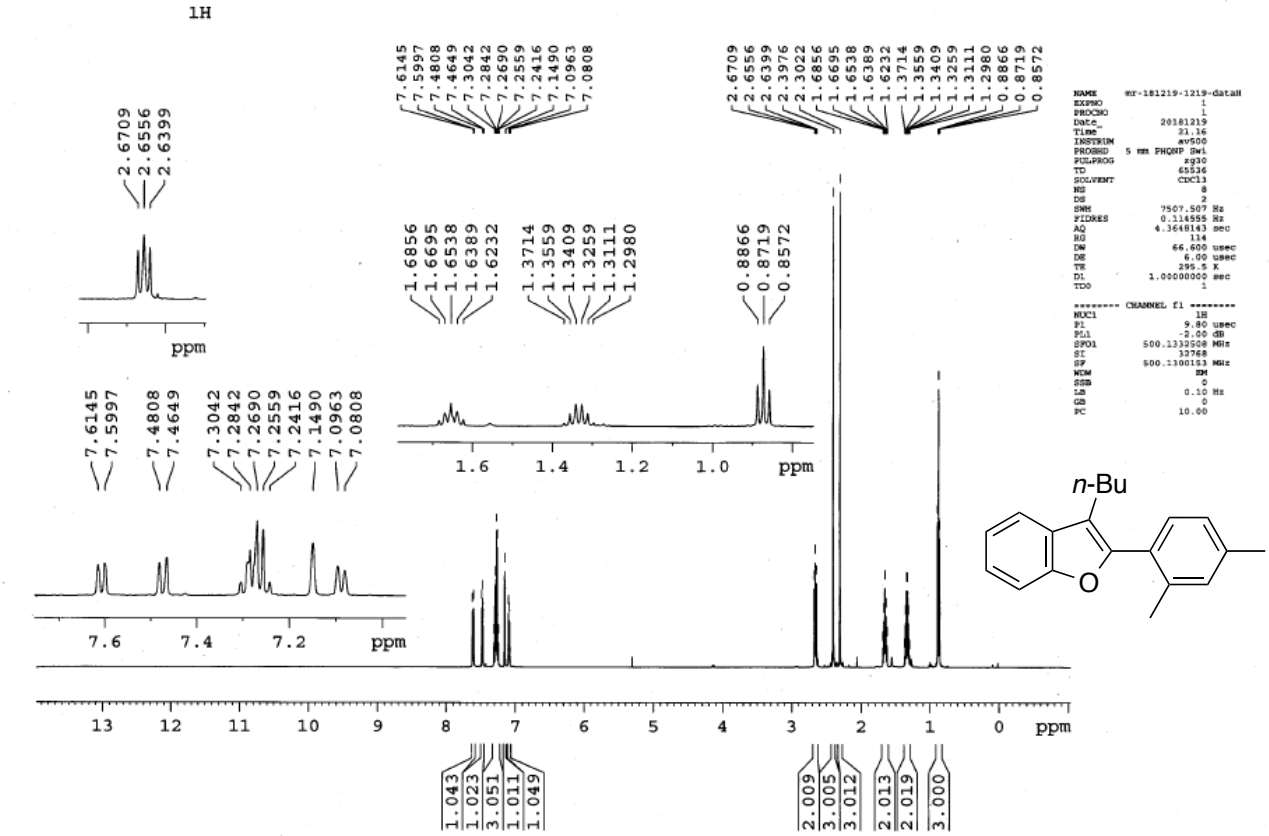


^{13}C NMR (126 MHz, $CDCl_3$)

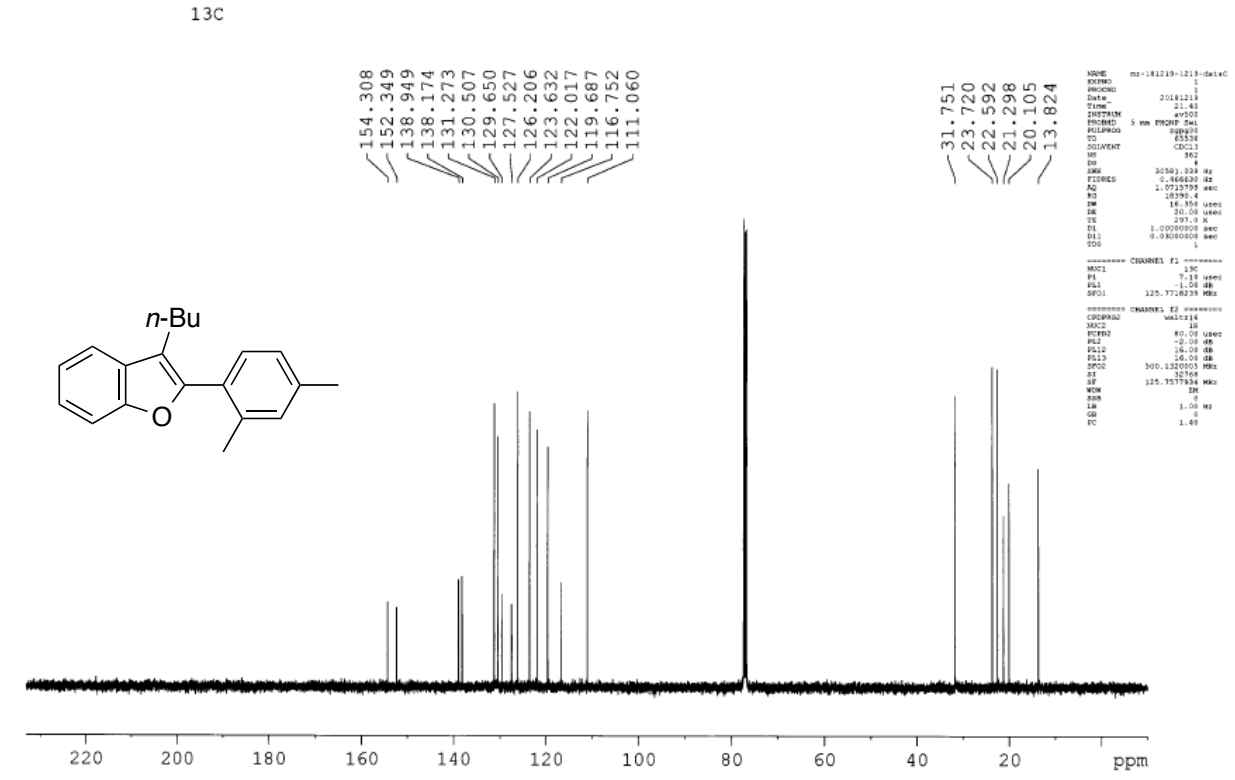


3-Butyl-2-(2,4-dimethylphenyl)benzofuran (3bb)

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

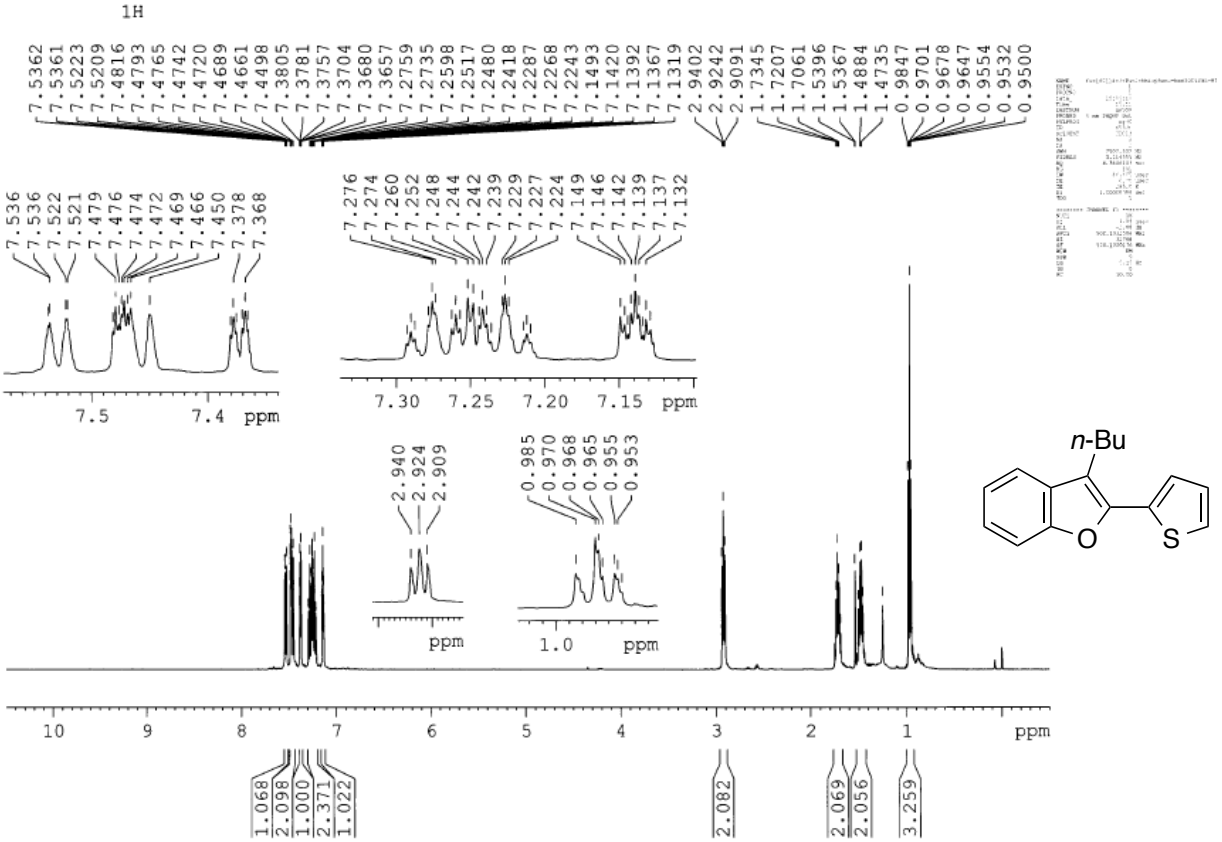


^{13}C NMR (126 MHz, $CDCl_3$)

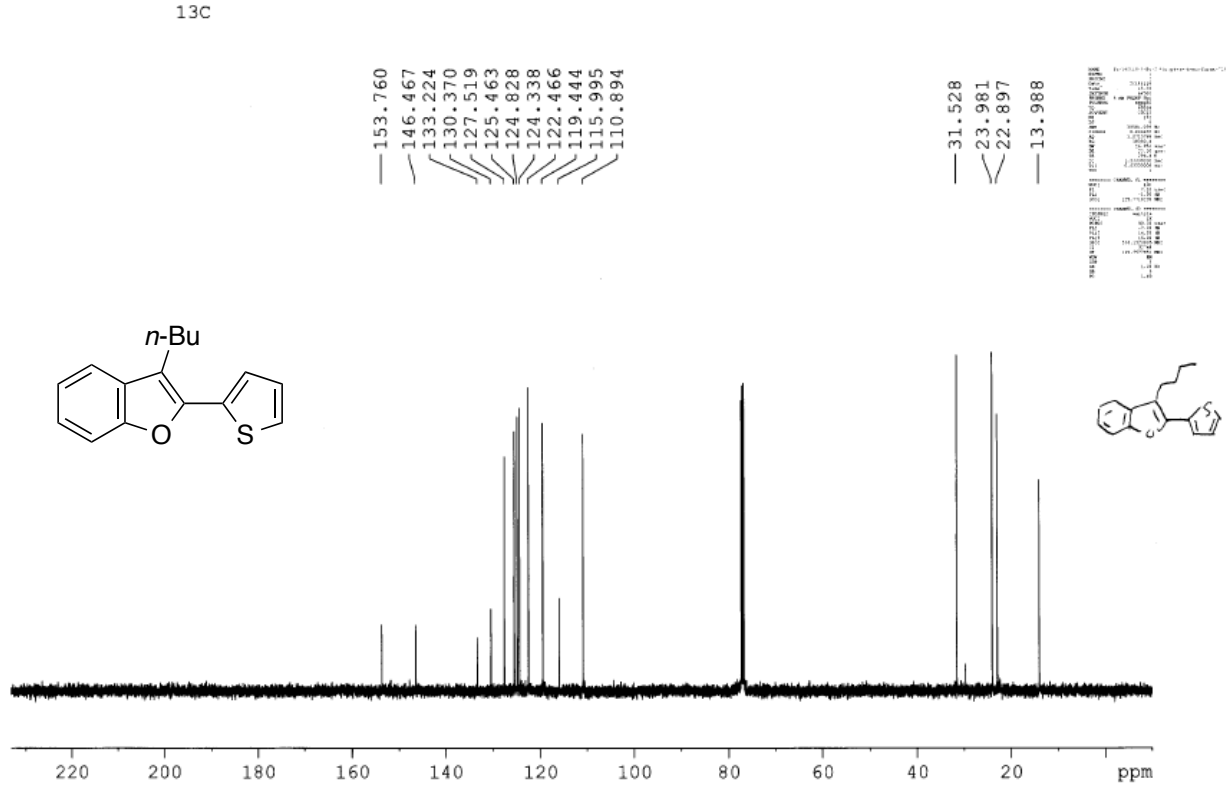


3-Butyl-2-(thiophen-2-yl)benzofuran (3bc)

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

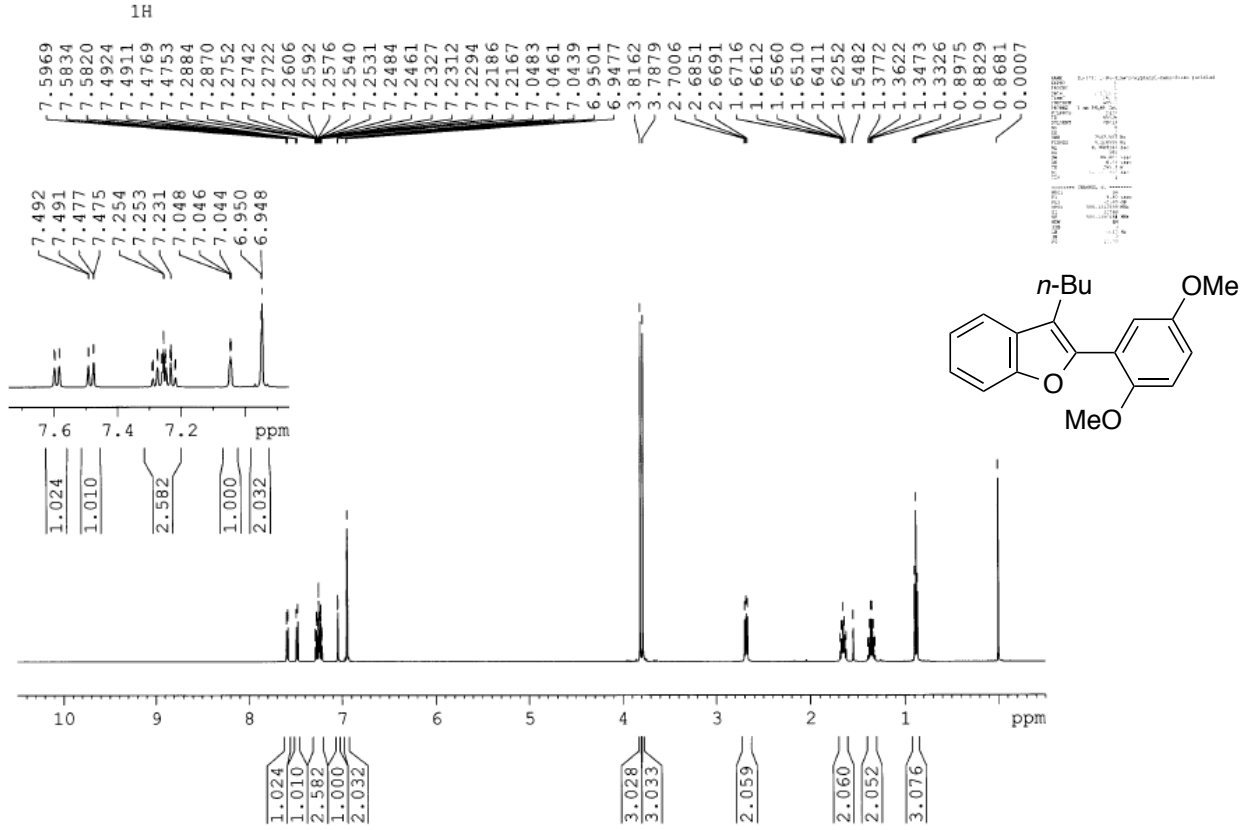


^{13}C NMR (126 MHz, $CDCl_3$)

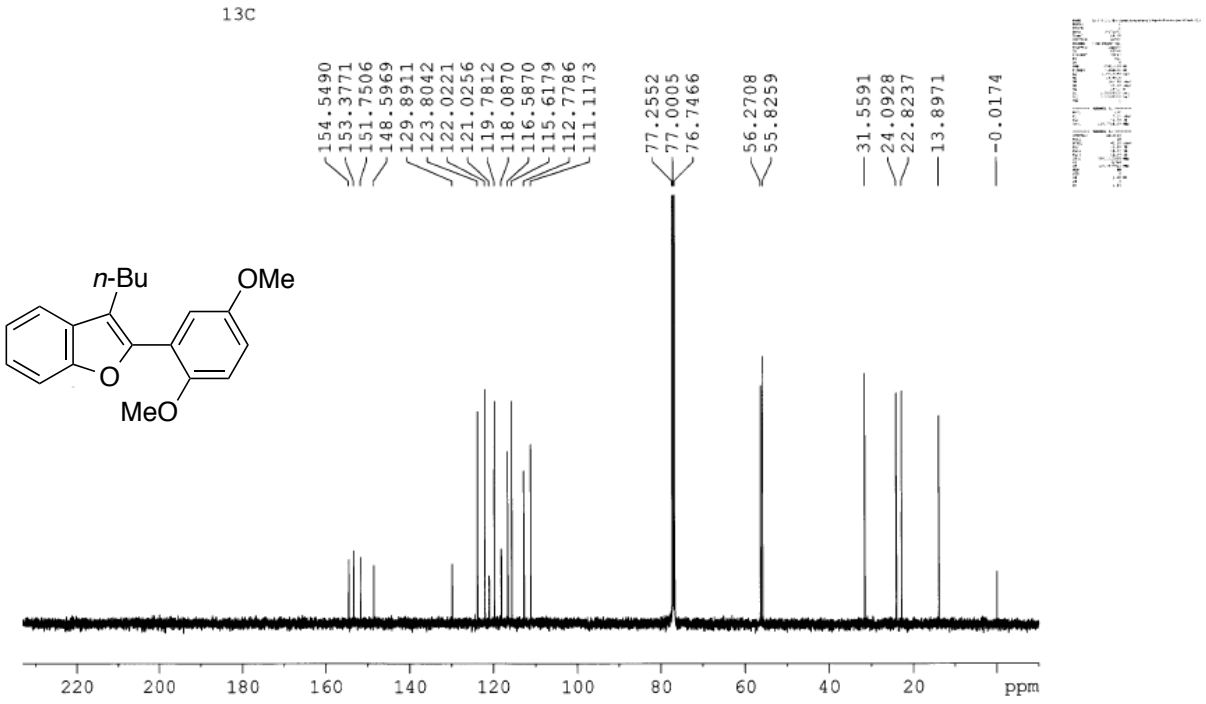


3-Butyl-2-(2,4-dimethoxyphenyl)benzofuran (3bf)

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

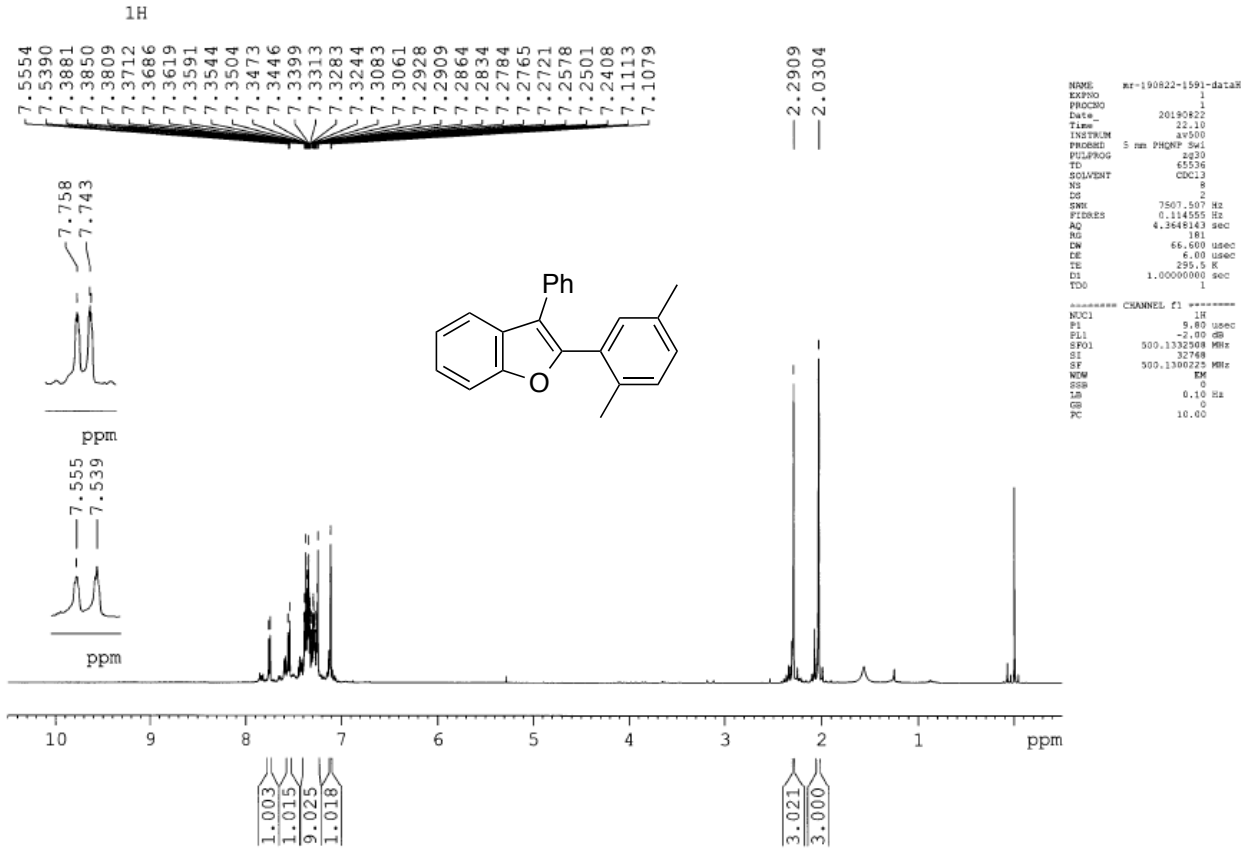


^{13}C NMR (126 MHz, $CDCl_3$)

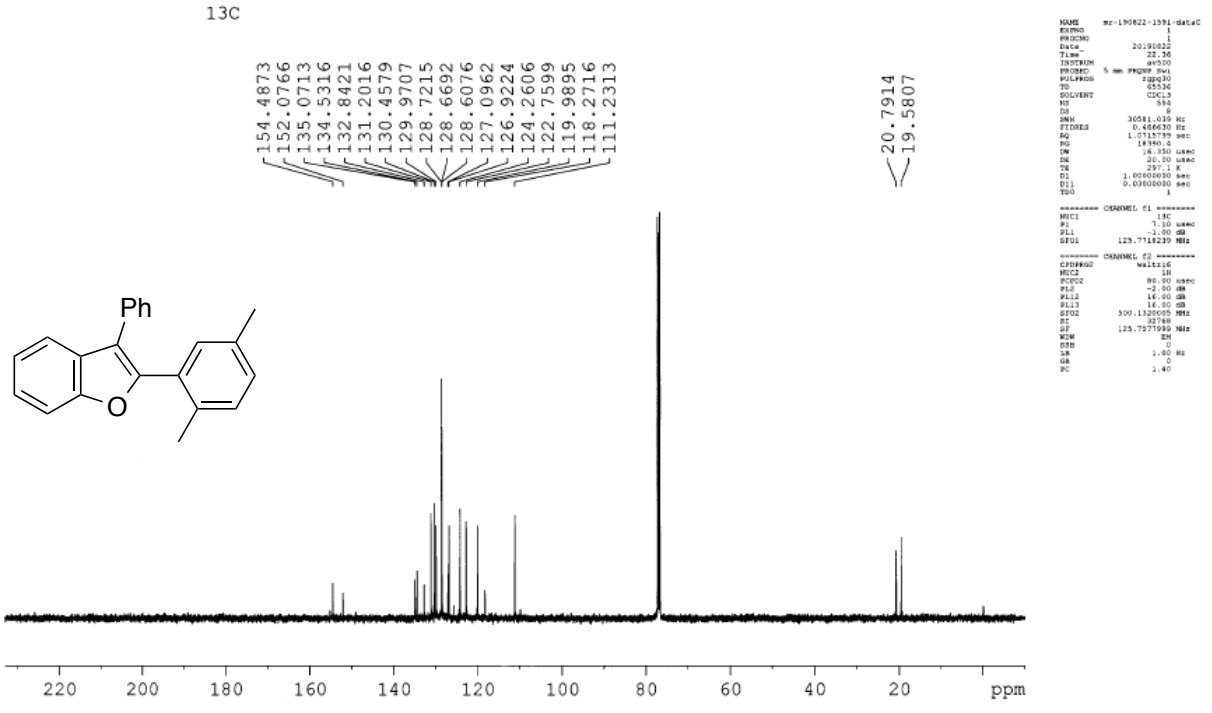


2-(2,5-Dimethylphenyl)-3-phenylbenzofuran (3ca)

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

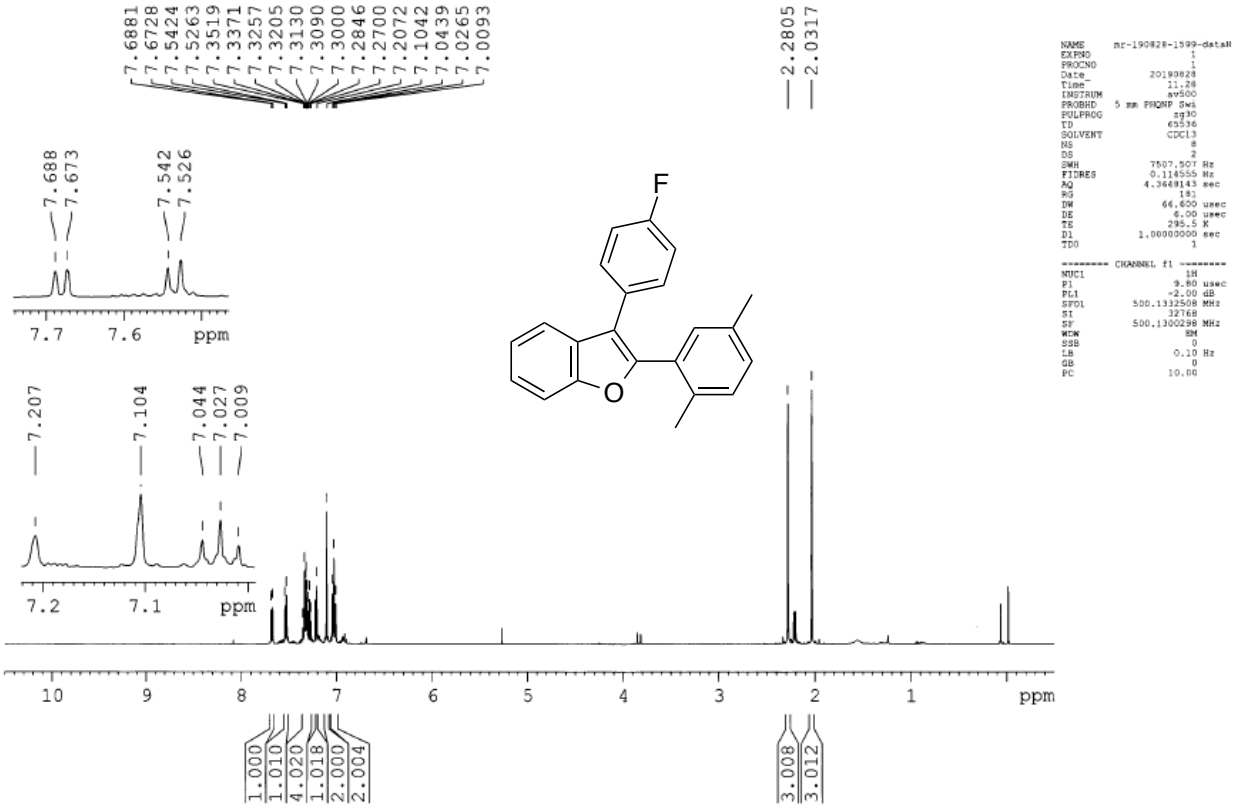


^{13}C NMR (126 MHz, $CDCl_3$)

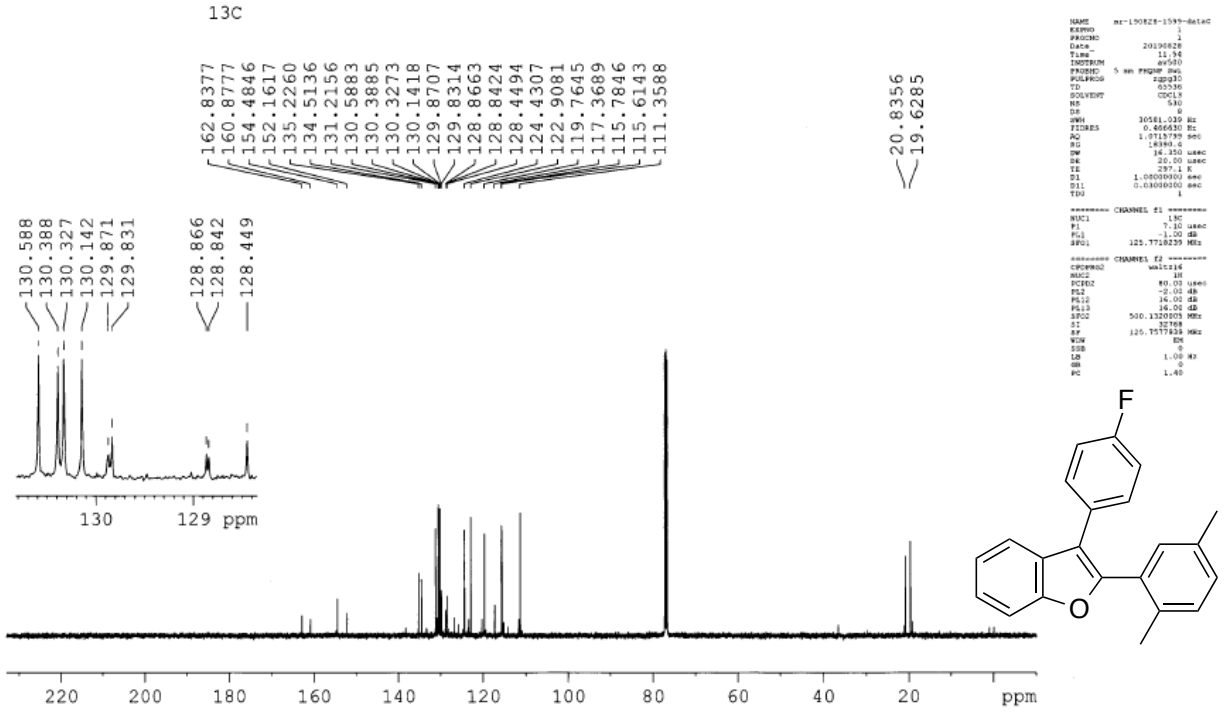


2-(2,5-Dimethylphenyl)-3-(4-fluorophenyl)benzofuran (3da)

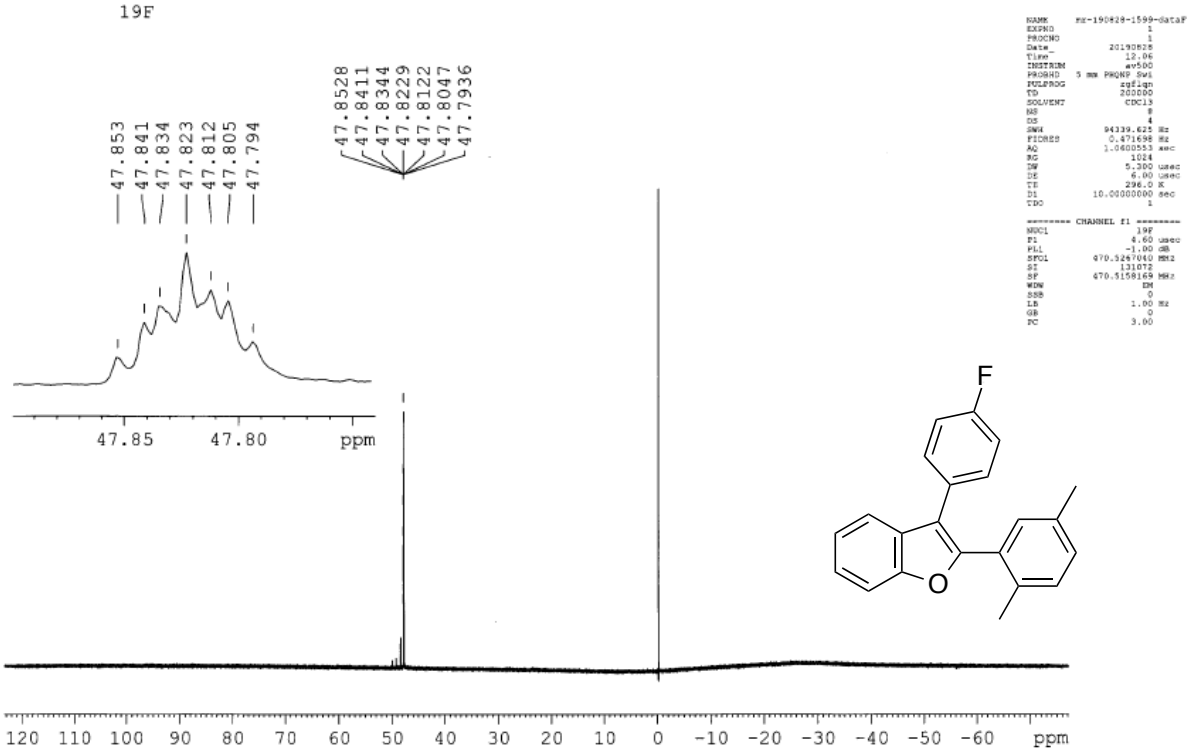
^{1}H NMR (500 MHz, $CDCl_3$)



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

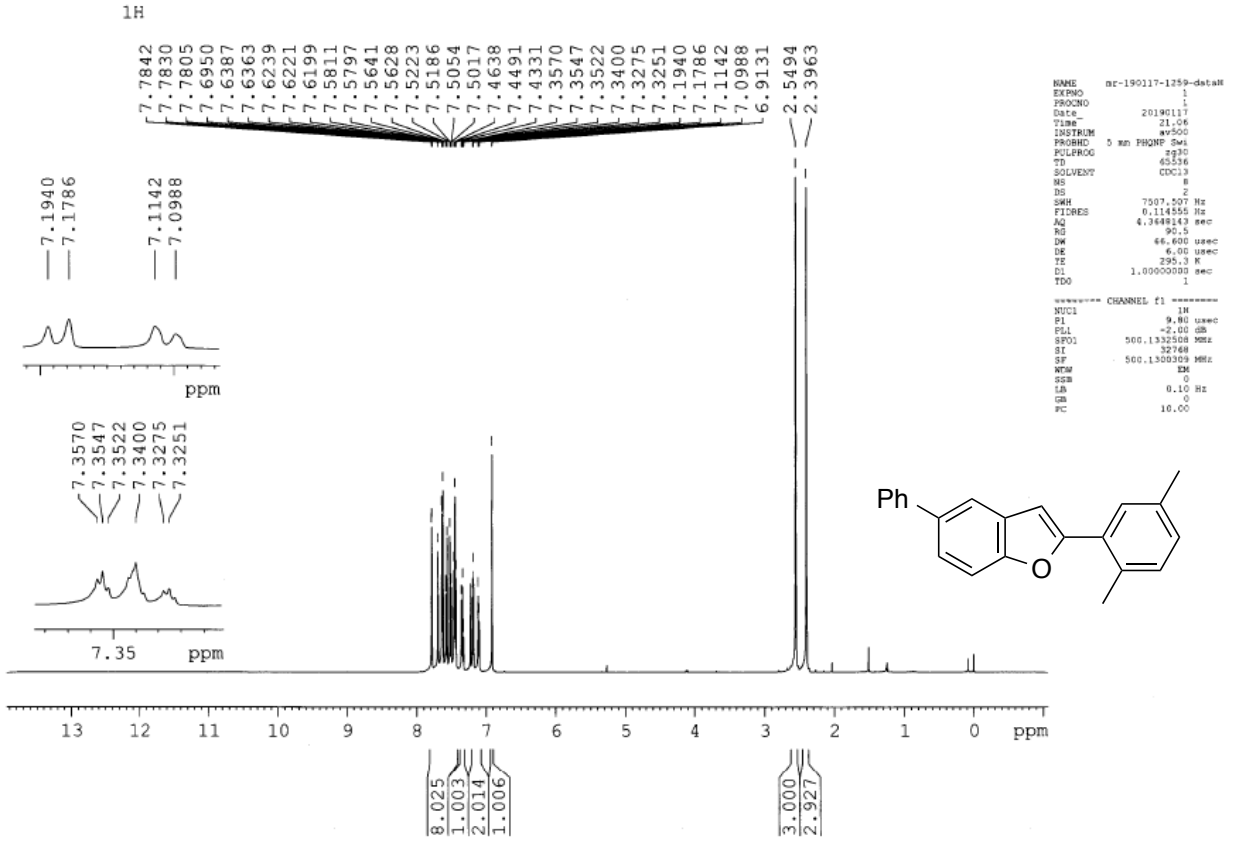


^{19}F NMR (470 MHz, $CDCl_3$)

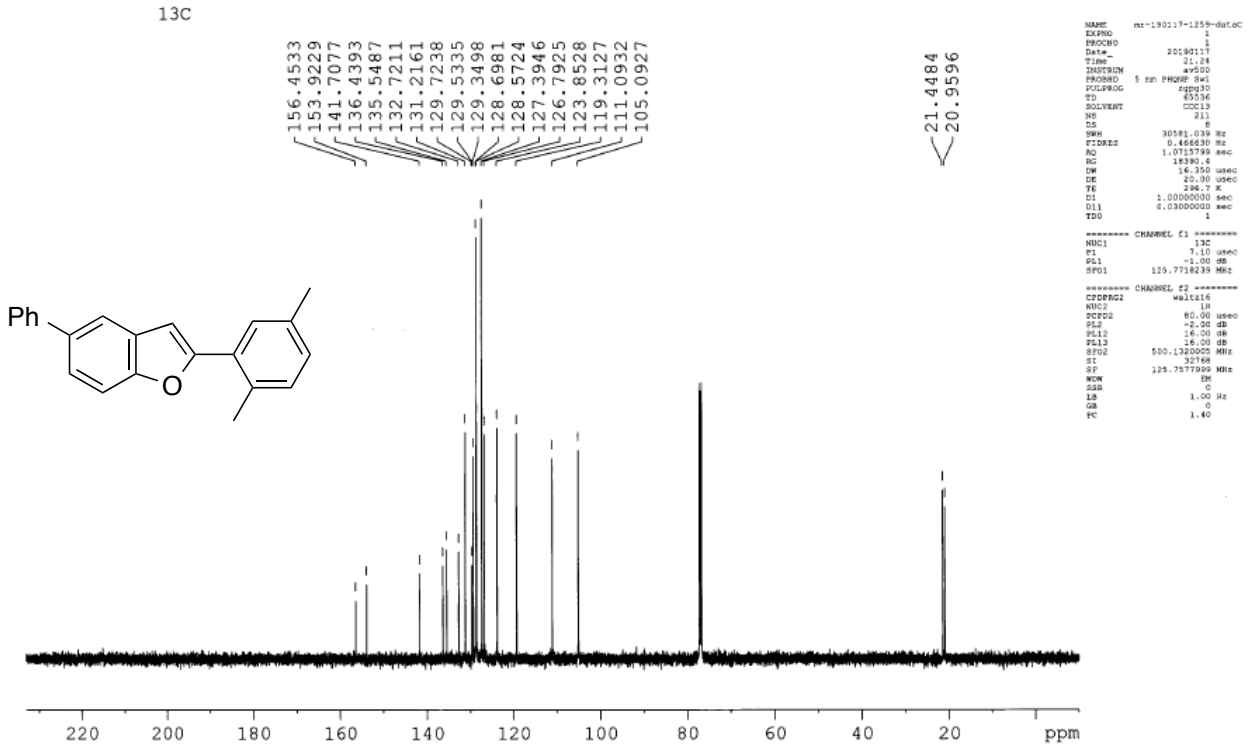


2-(2,5-Dimethylphenyl)-5-phenylbenzofuran (3ea)

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

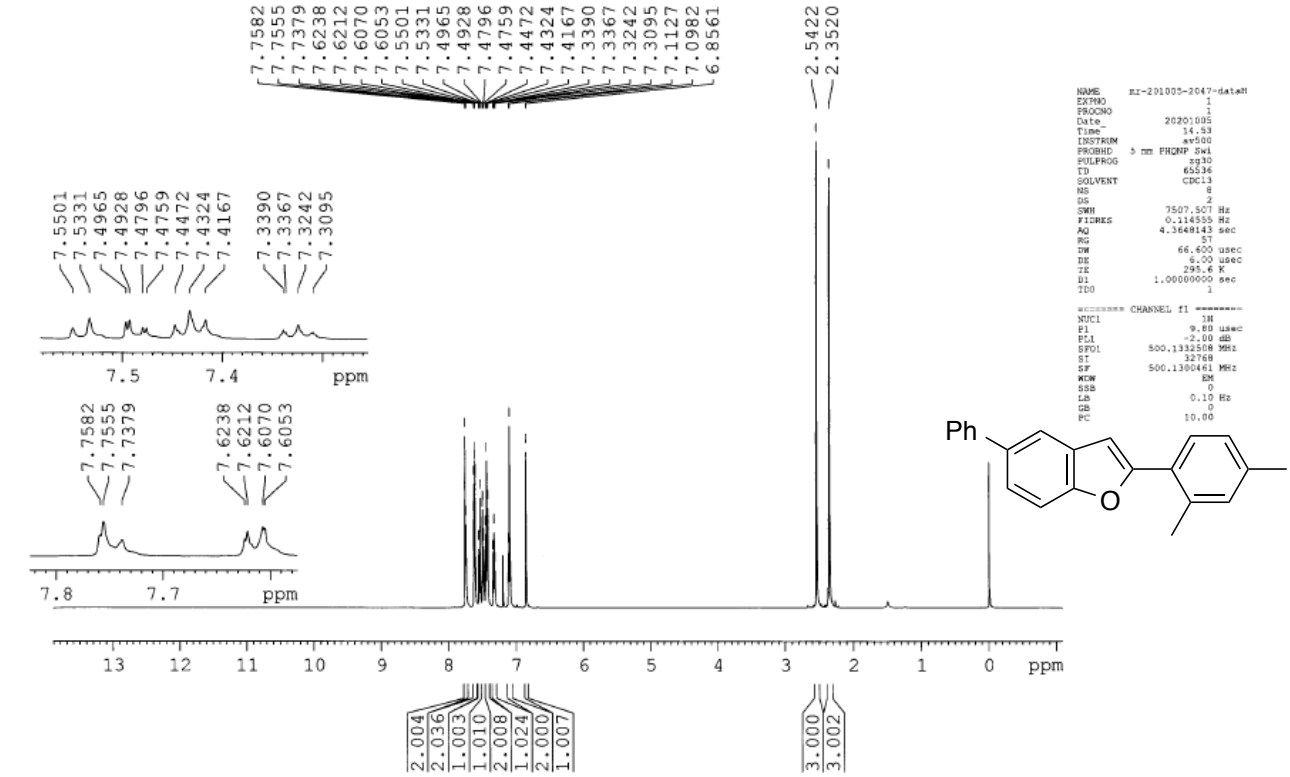


^{13}C NMR (126 MHz, $CDCl_3$)

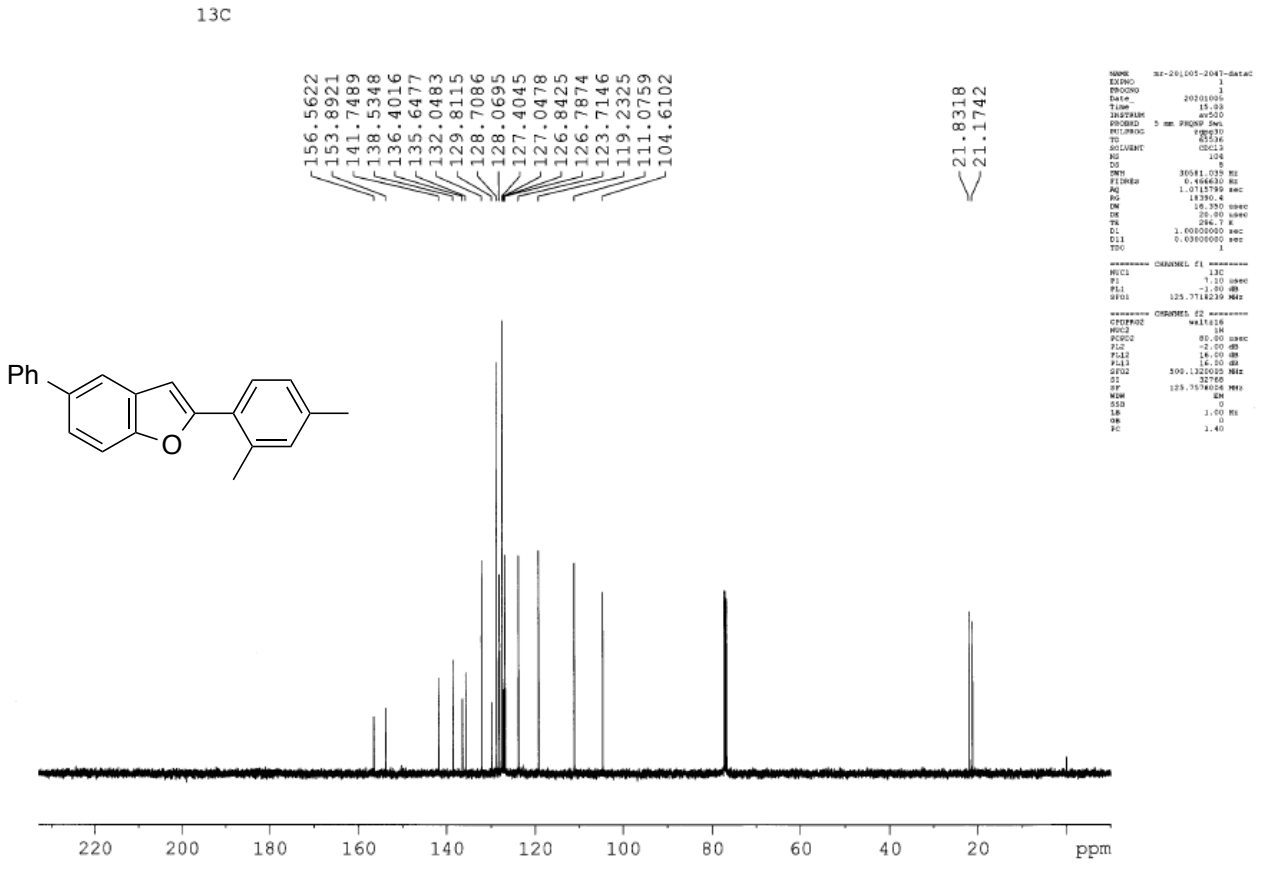


2-(2,4-Dimethylphenyl)-5-phenylbenzofuran (3eb)

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

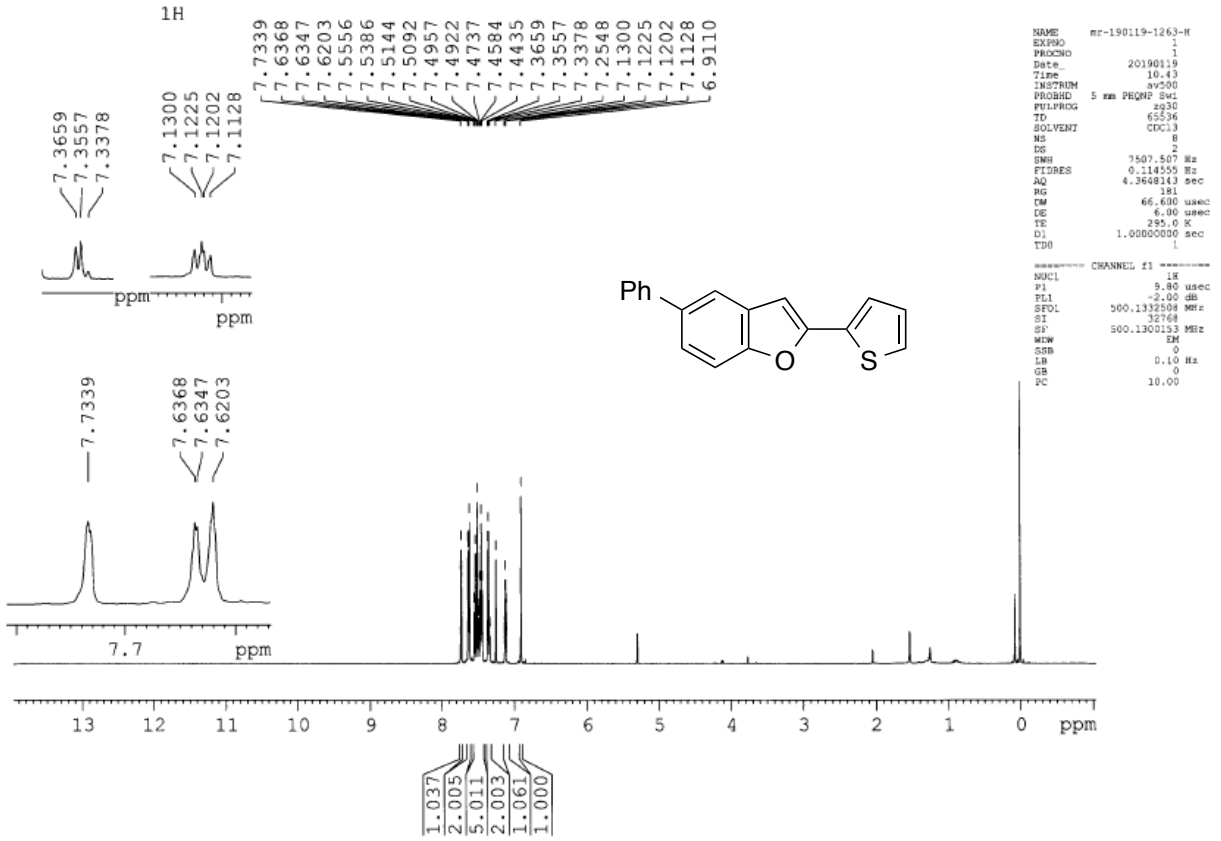


^{13}C NMR (126 MHz, $CDCl_3$)

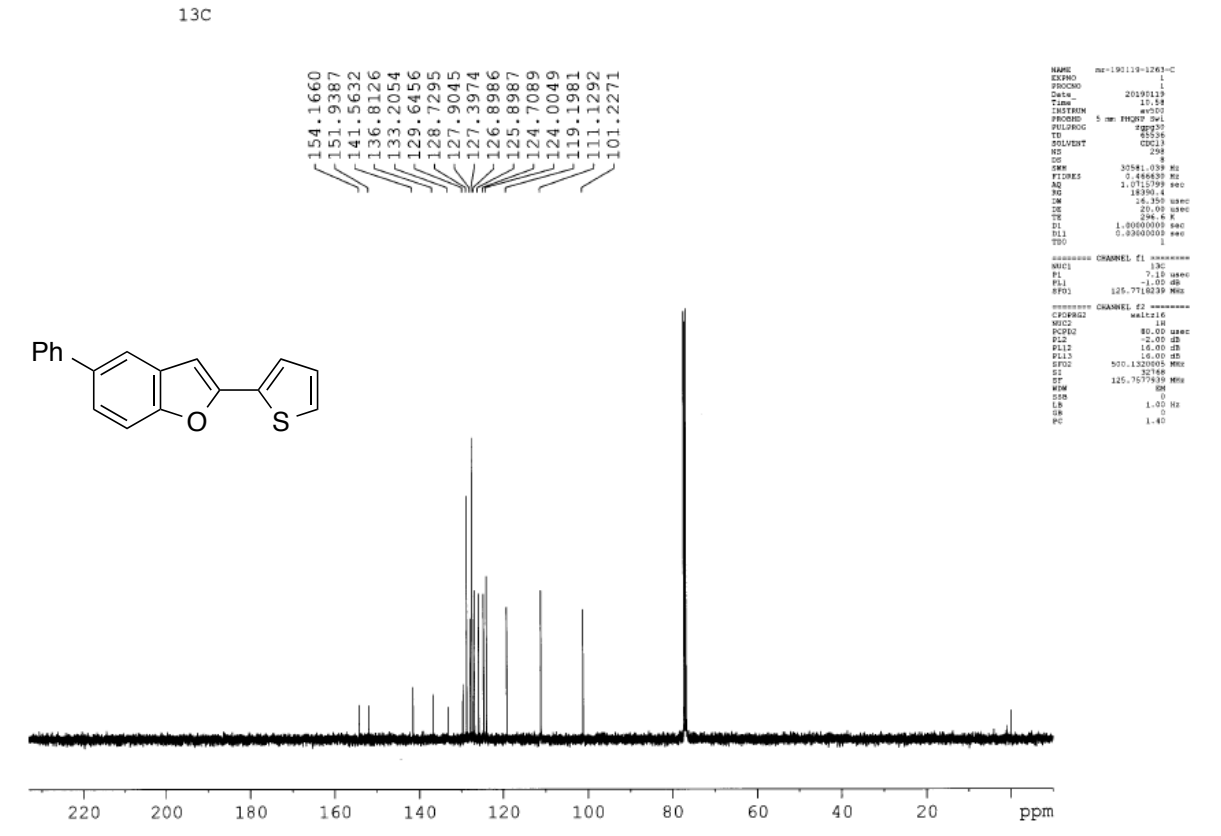


5-Phenyl-2-(thiophen-2-yl)benzofuran (3ec)

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

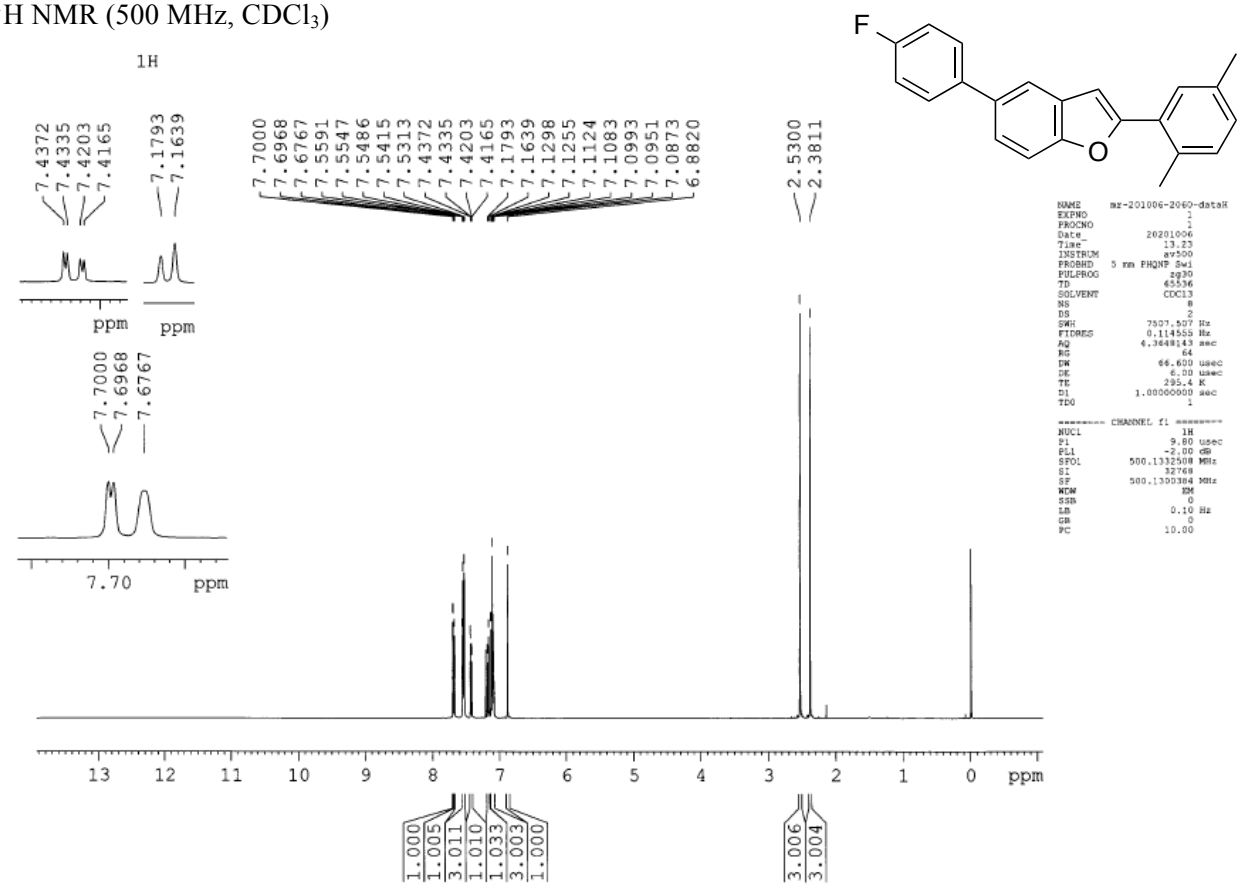


^{13}C NMR (126 MHz, $CDCl_3$)

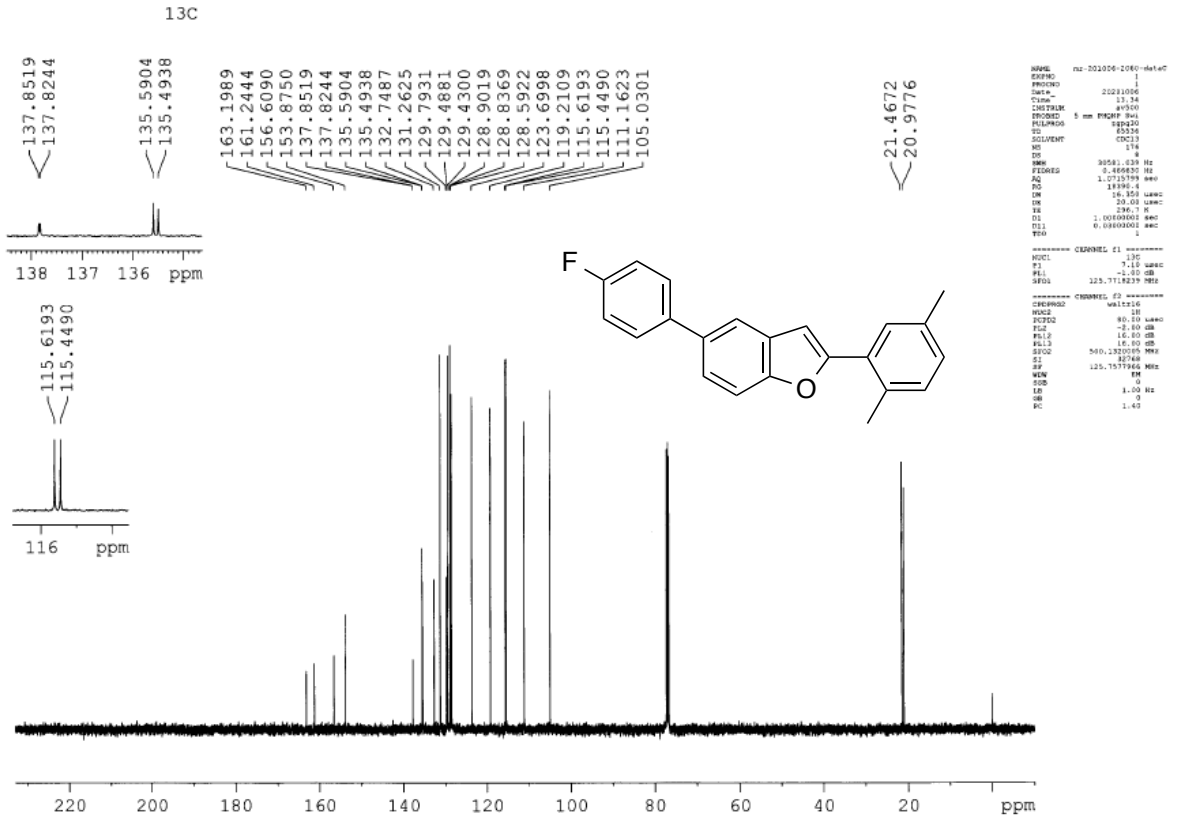


2-(2,5-Dimethylphenyl)-5-(4-fluorophenyl)benzofuran (3fa)

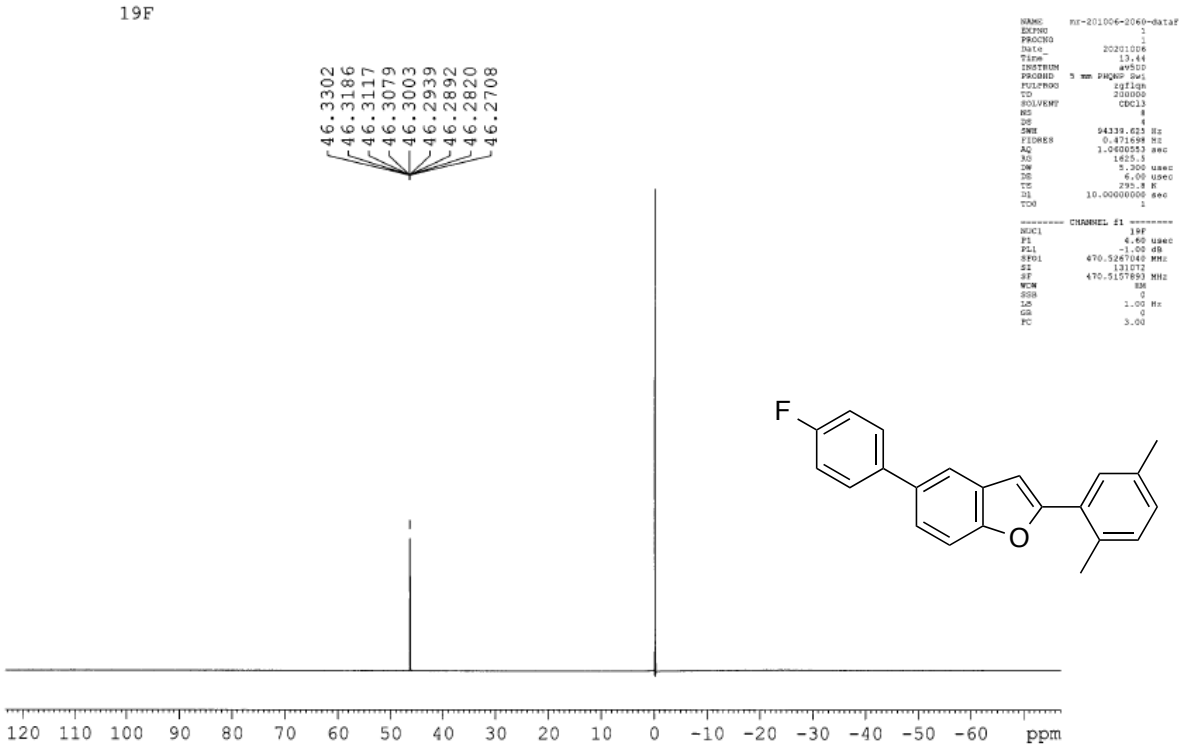
^{1}H NMR (500 MHz, $CDCl_3$)



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

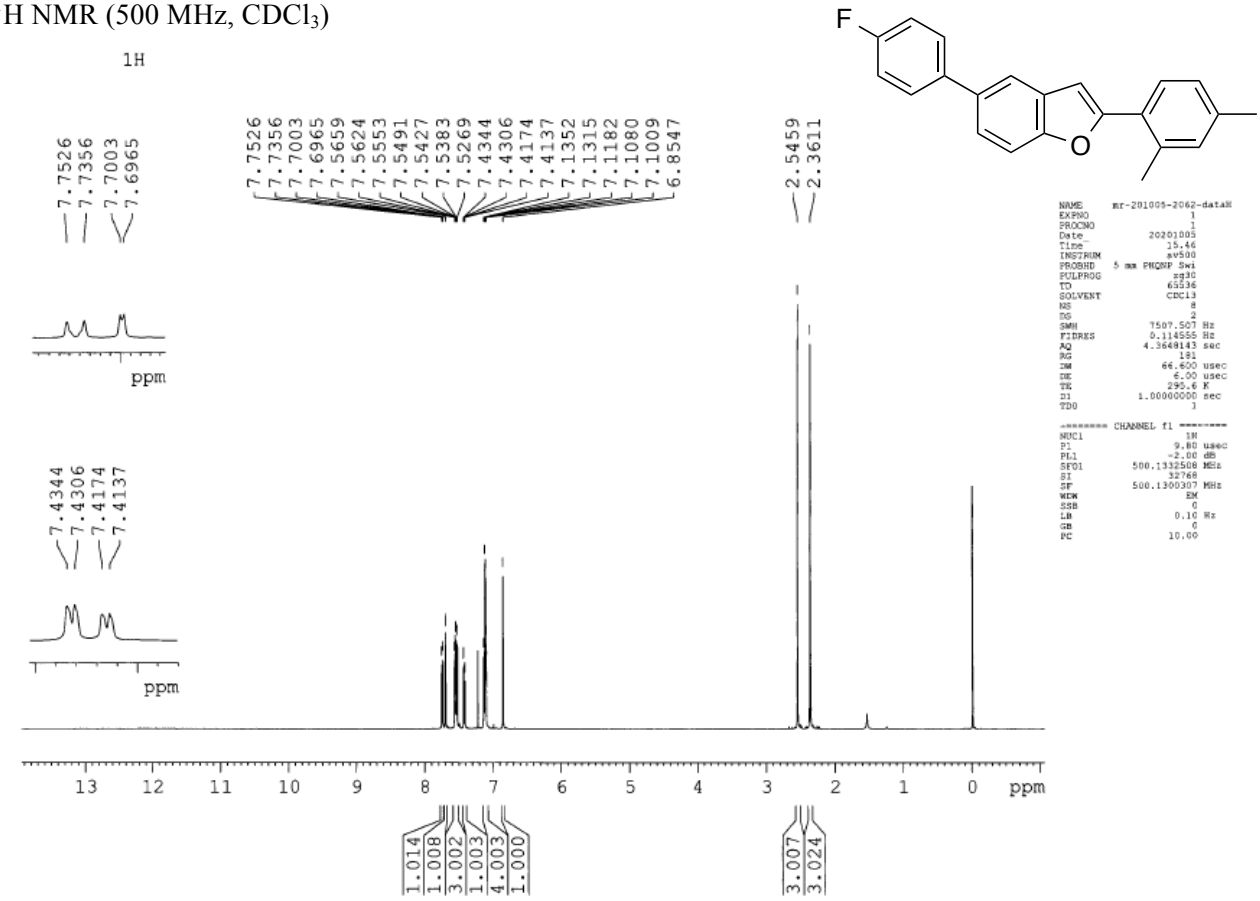


^{19}F NMR (470 MHz, $CDCl_3$)

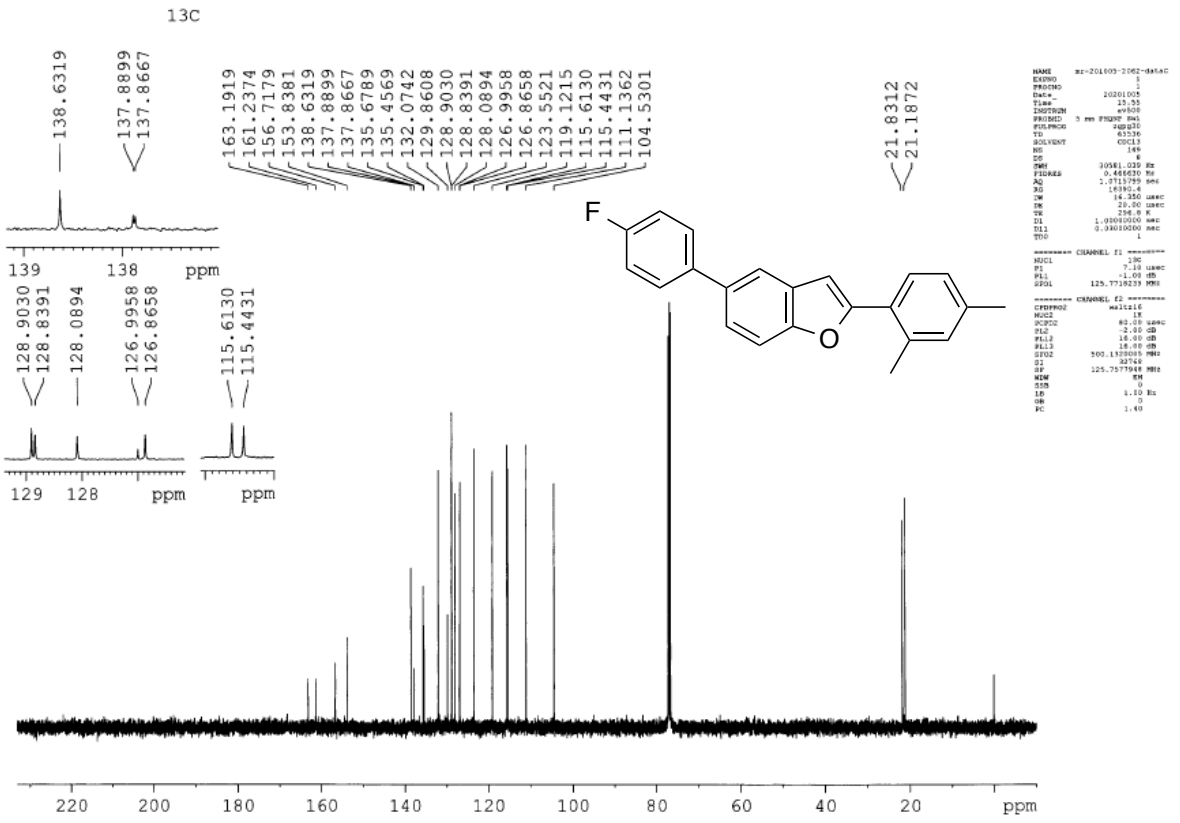


2-(2,4-Dimethylphenyl)-5-(4-fluorophenyl)benzofuran (3fb)

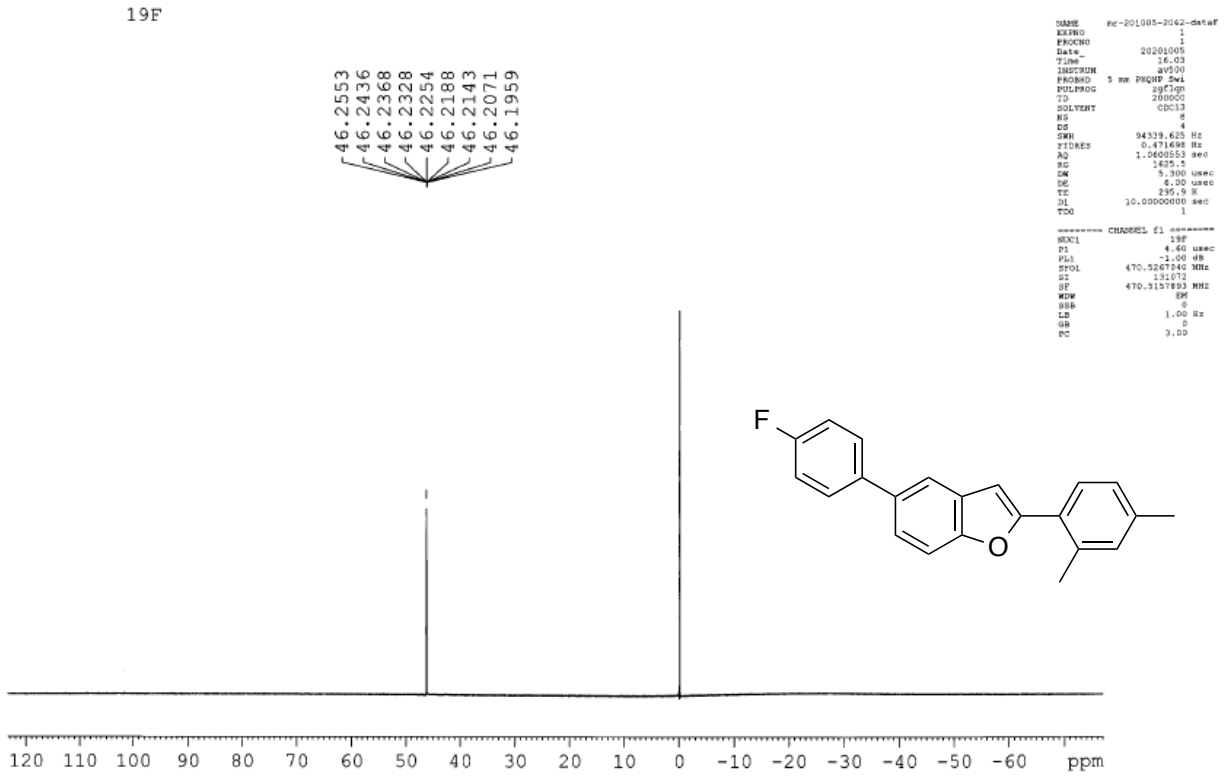
^{1}H NMR (500 MHz, $CDCl_3$)



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

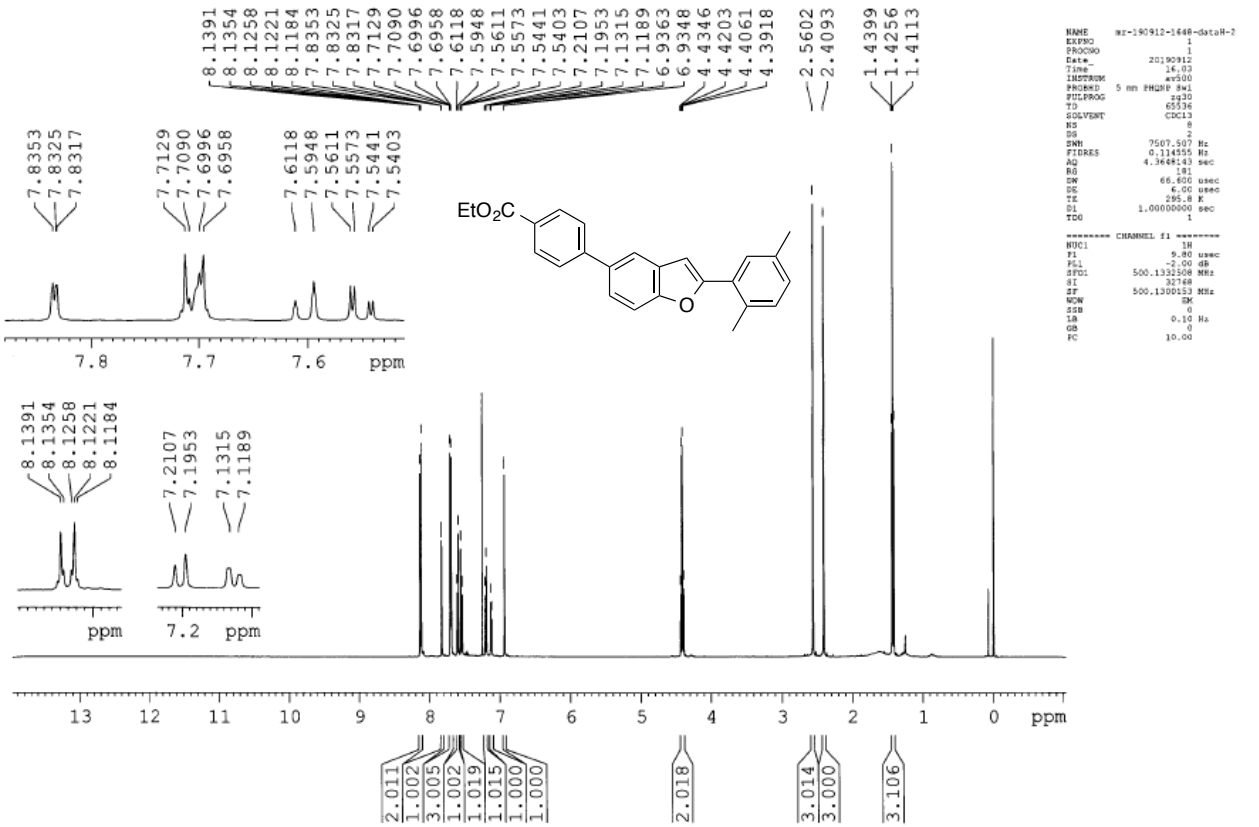


^{19}F NMR (470 MHz, $CDCl_3$)

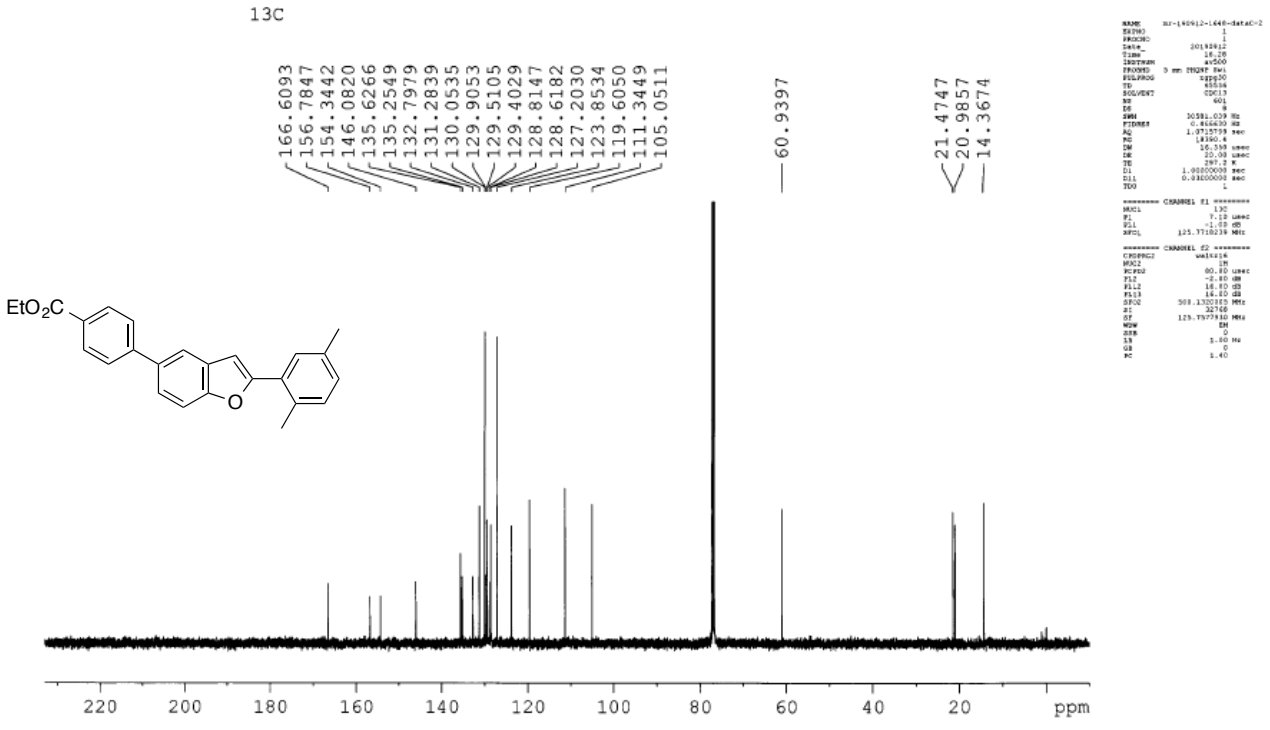


Ethyl 4-[2-(2,5-Dimethylphenyl)benzofuran-5-yl]benzoate (3ga)

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

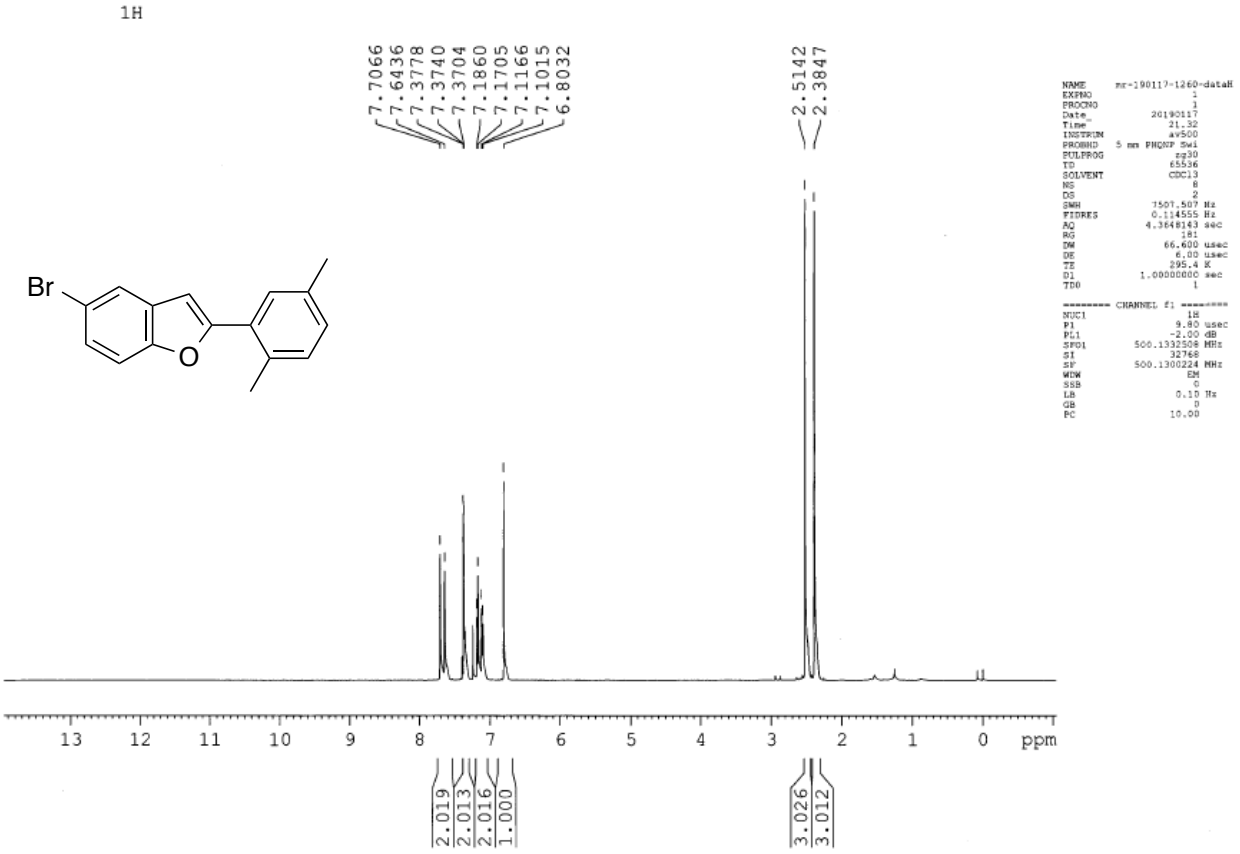


^{13}C NMR (126 MHz, $CDCl_3$)

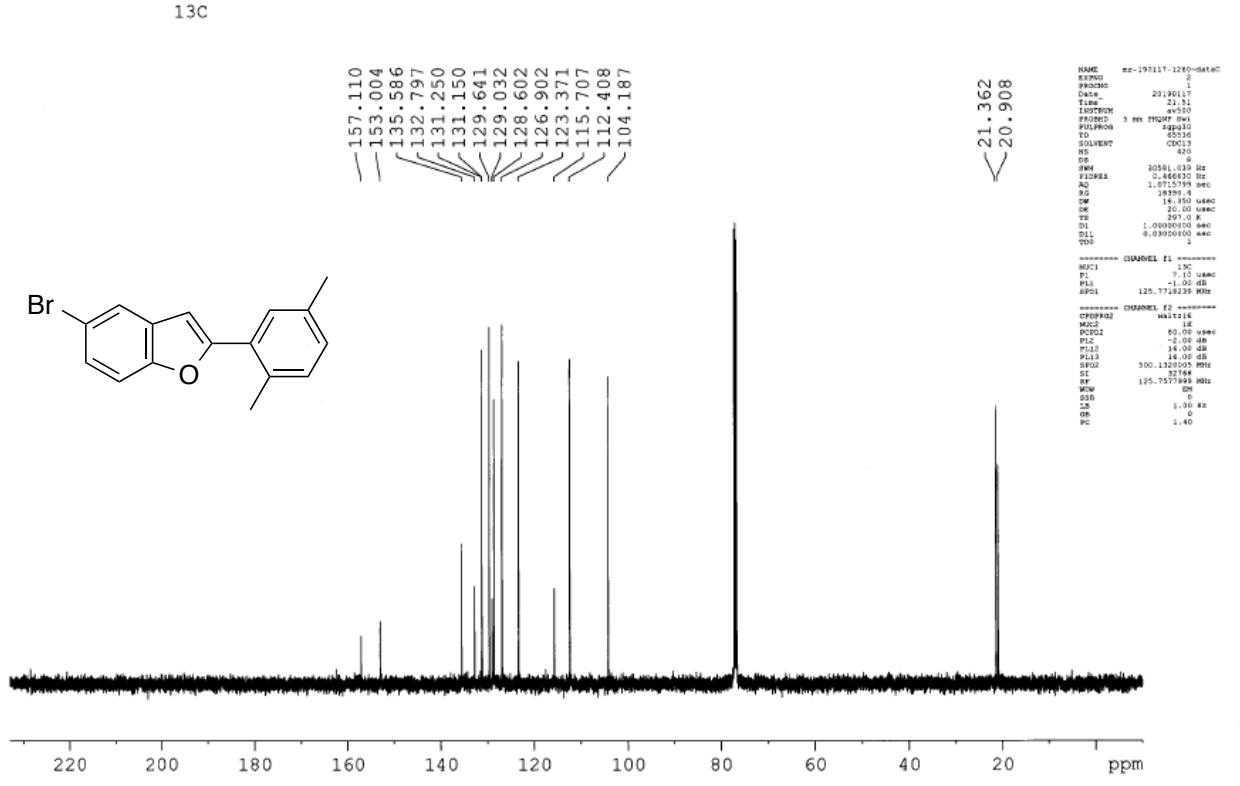


5-Bromo-2-(2,5-dimethylphenyl)benzofuran (3ha)

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

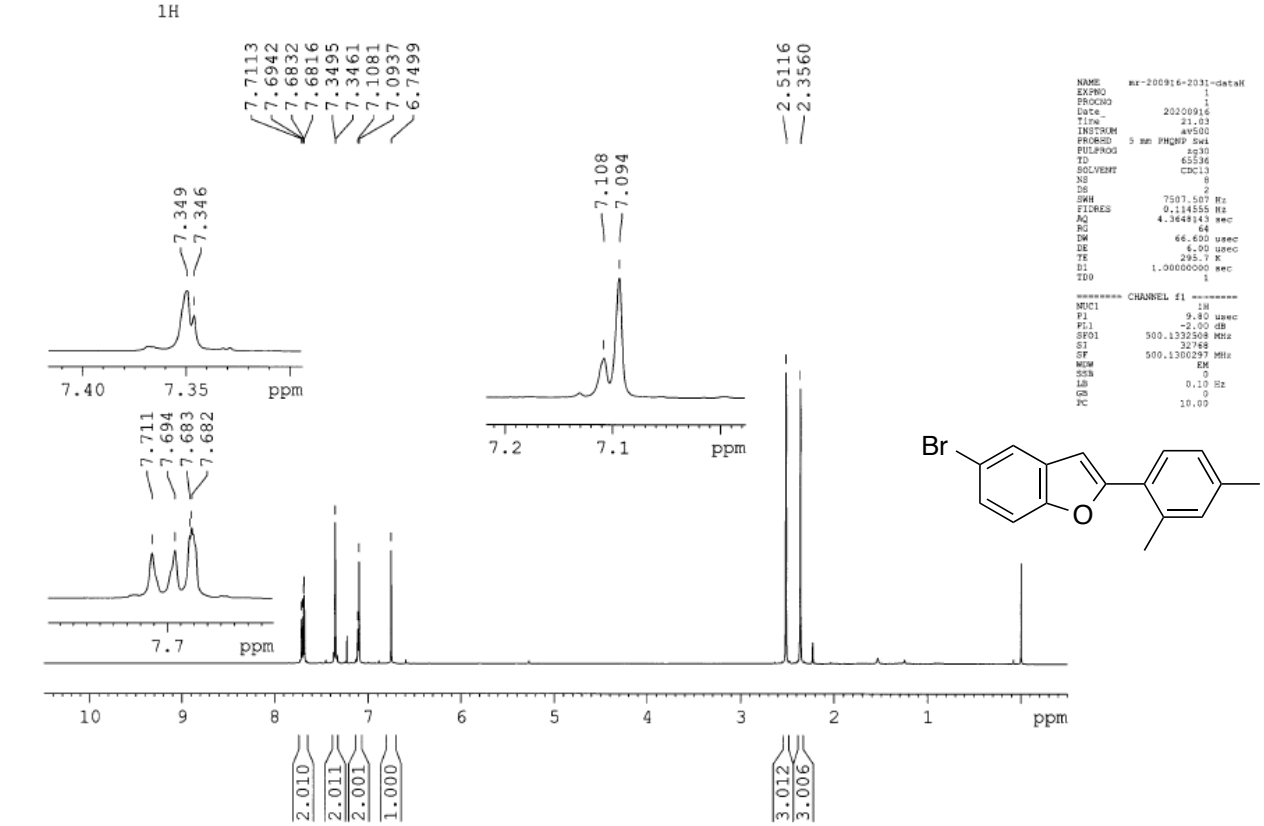


^{13}C NMR (126 MHz, $CDCl_3$)

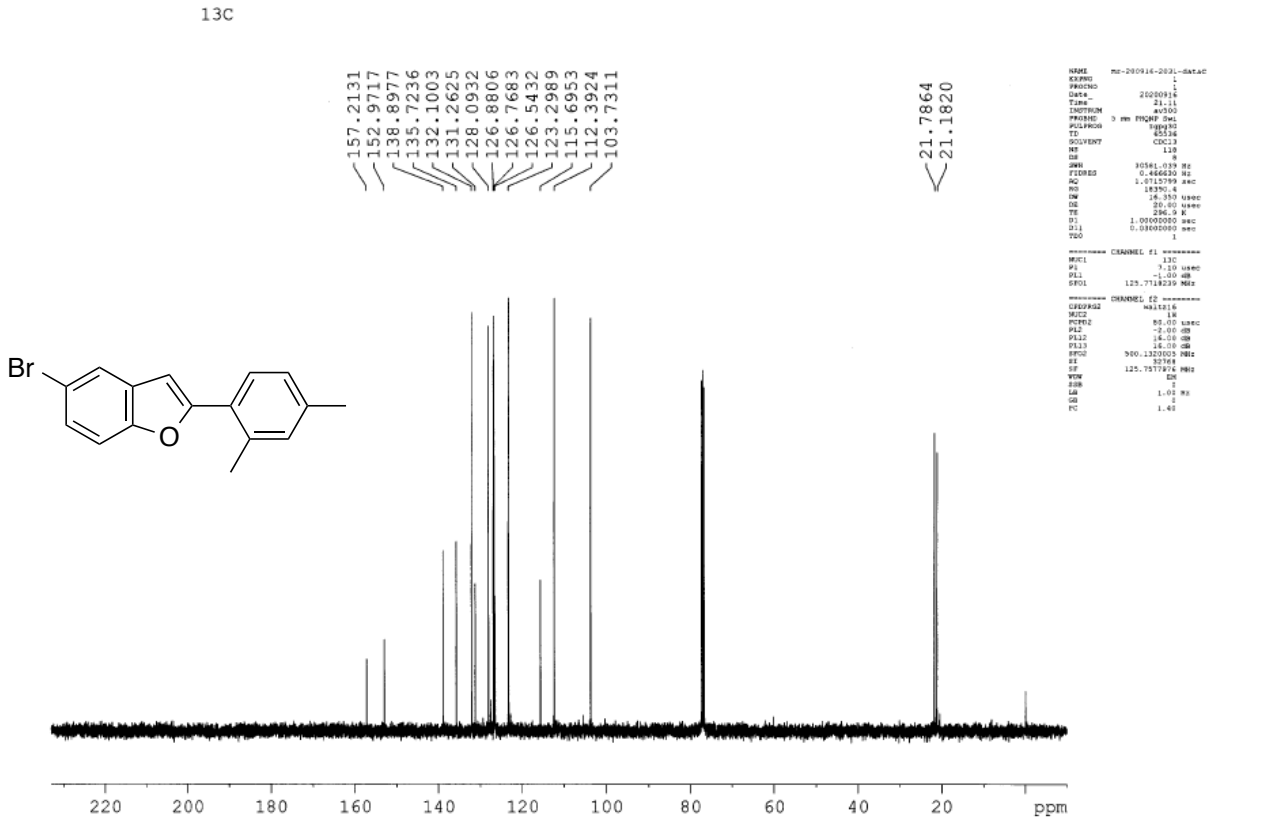


5-Bromo-2-(2,4-dimethylphenyl)benzofuran (3hb)

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

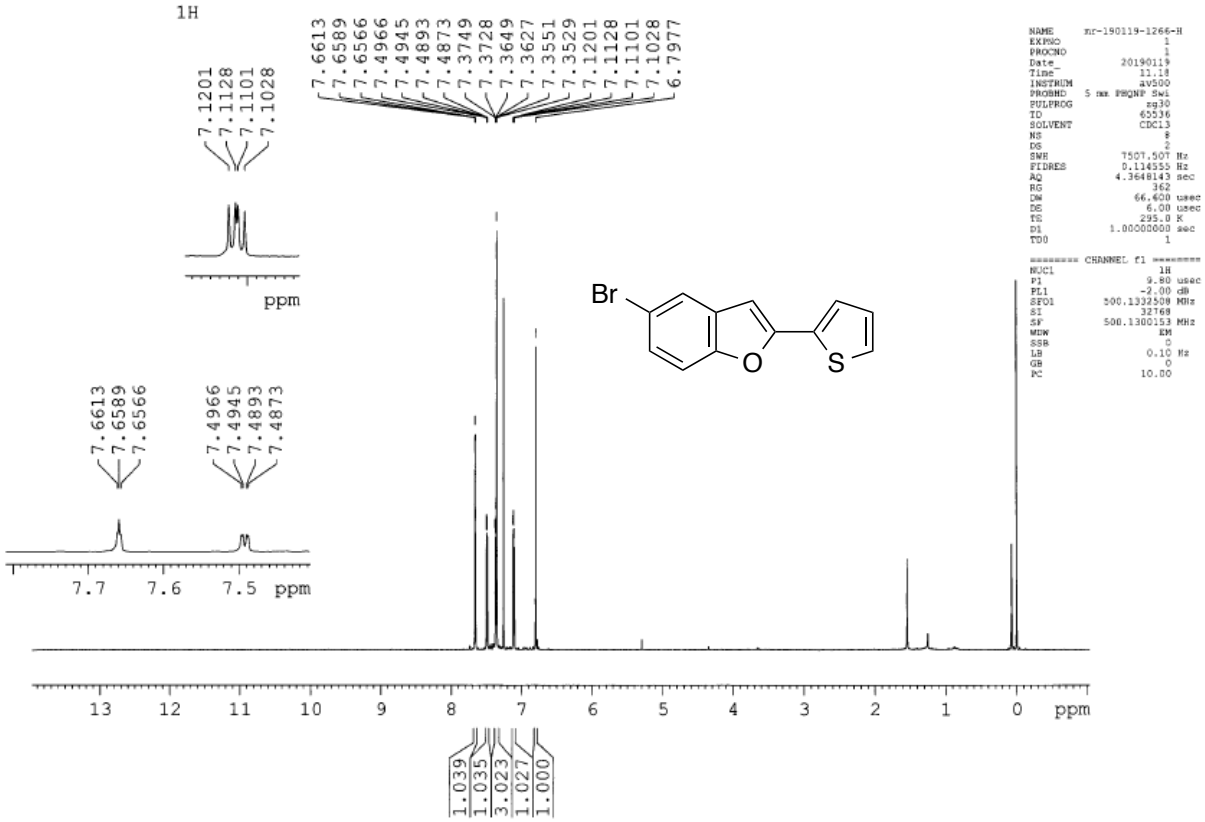


^{13}C NMR (126 MHz, $CDCl_3$)

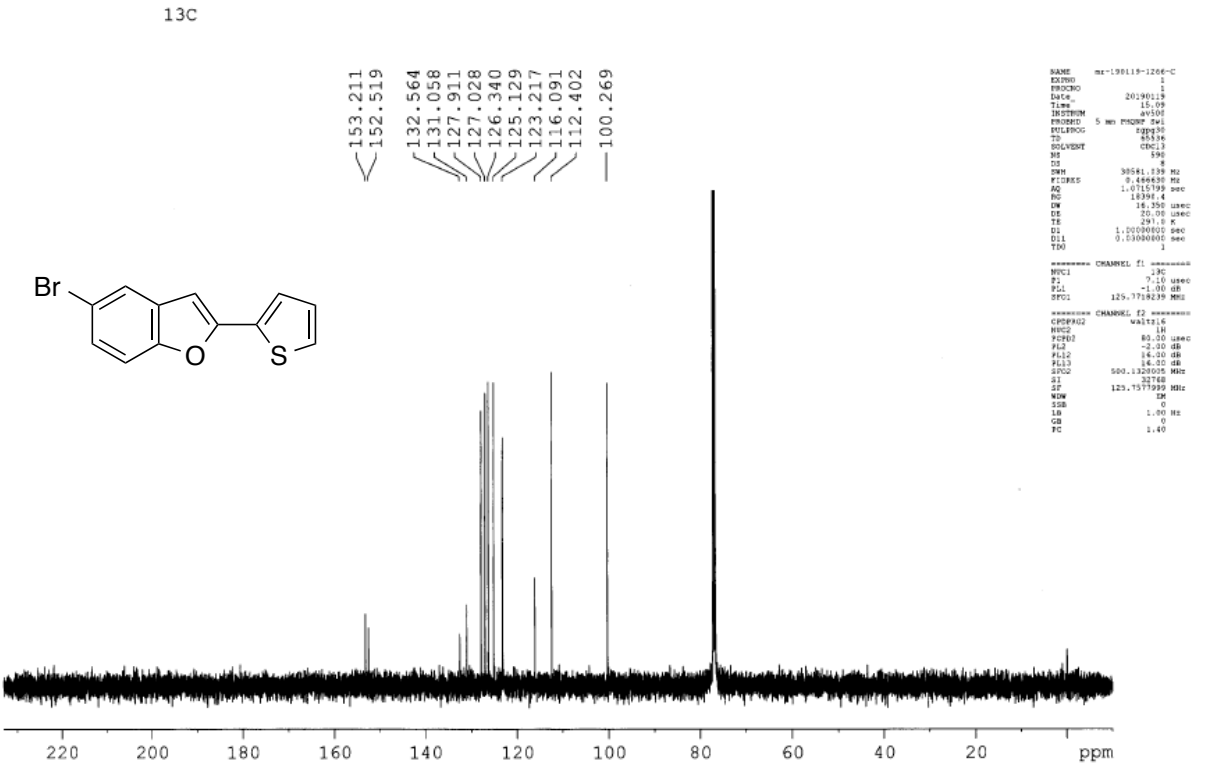


5-Bromo-2-(thiophen-2-yl)benzofuran (3hc)

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

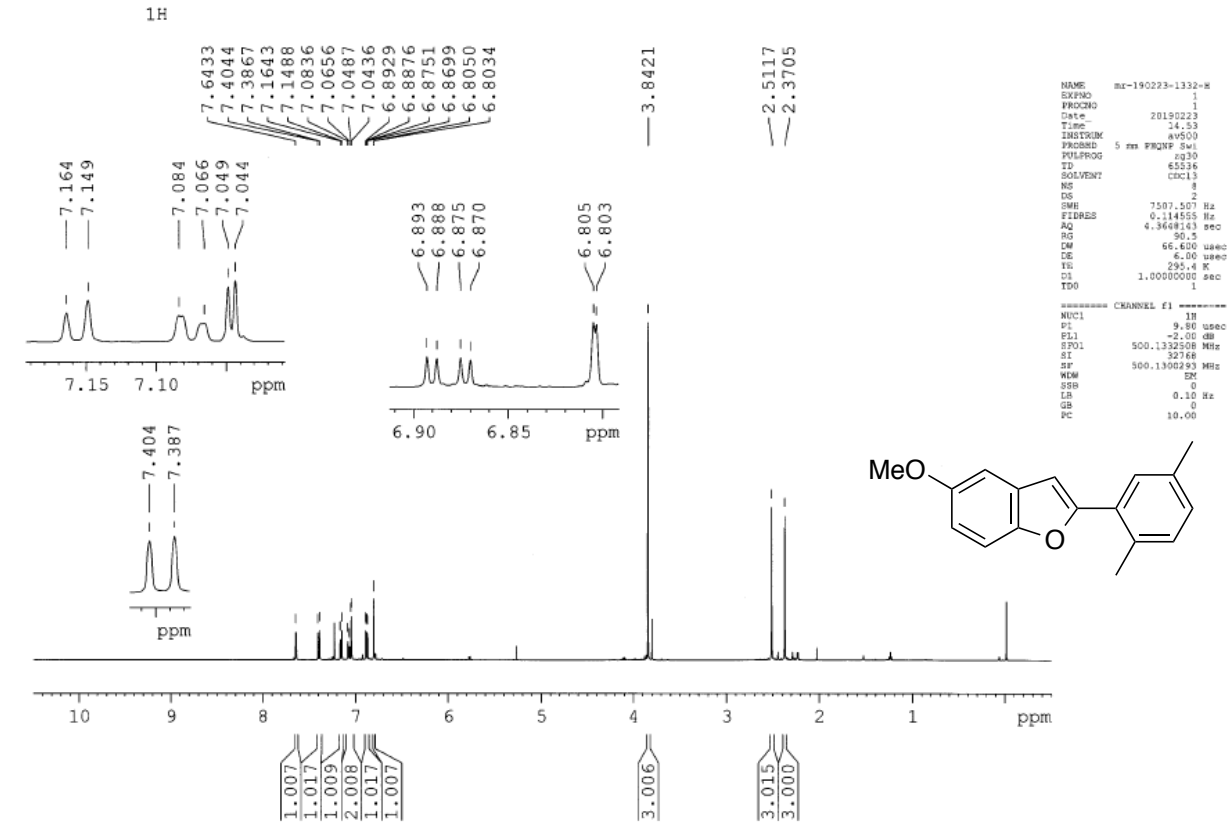


^{13}C NMR (126 MHz, $CDCl_3$)

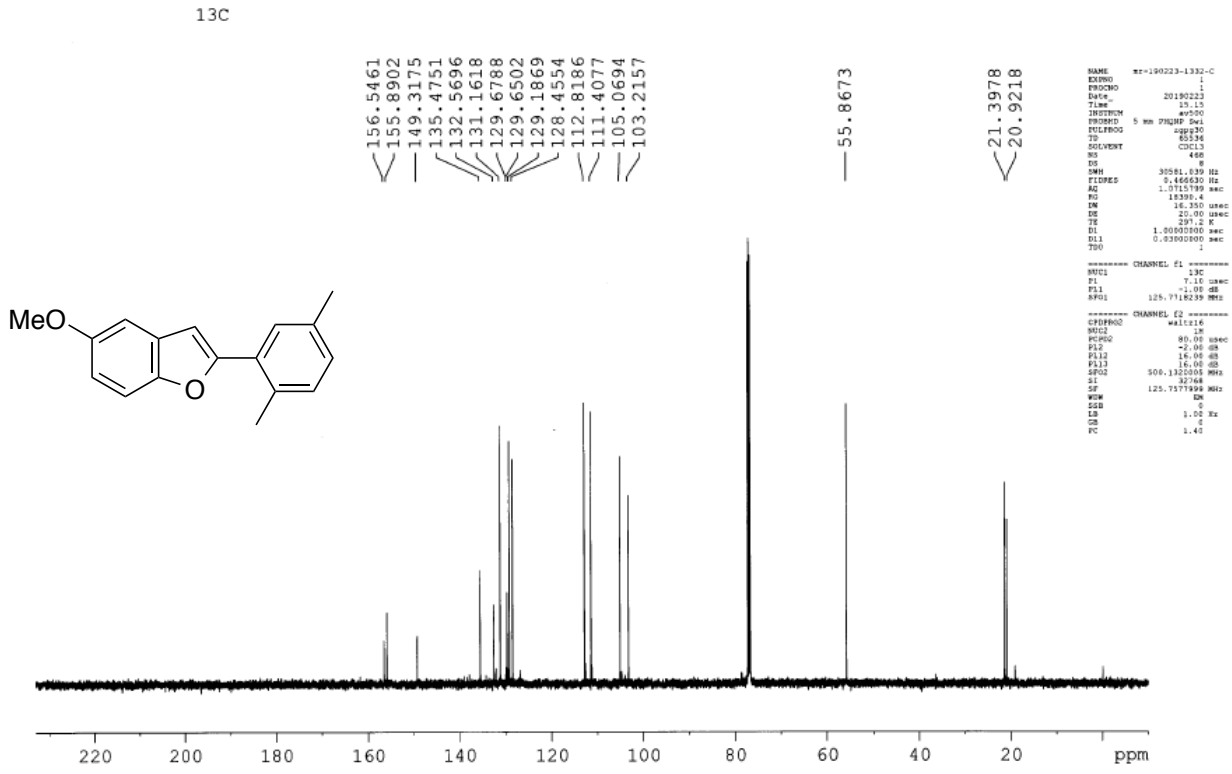


2-(2,5-Dimethylphenyl)-5-methoxybenzofuran (3ia)

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

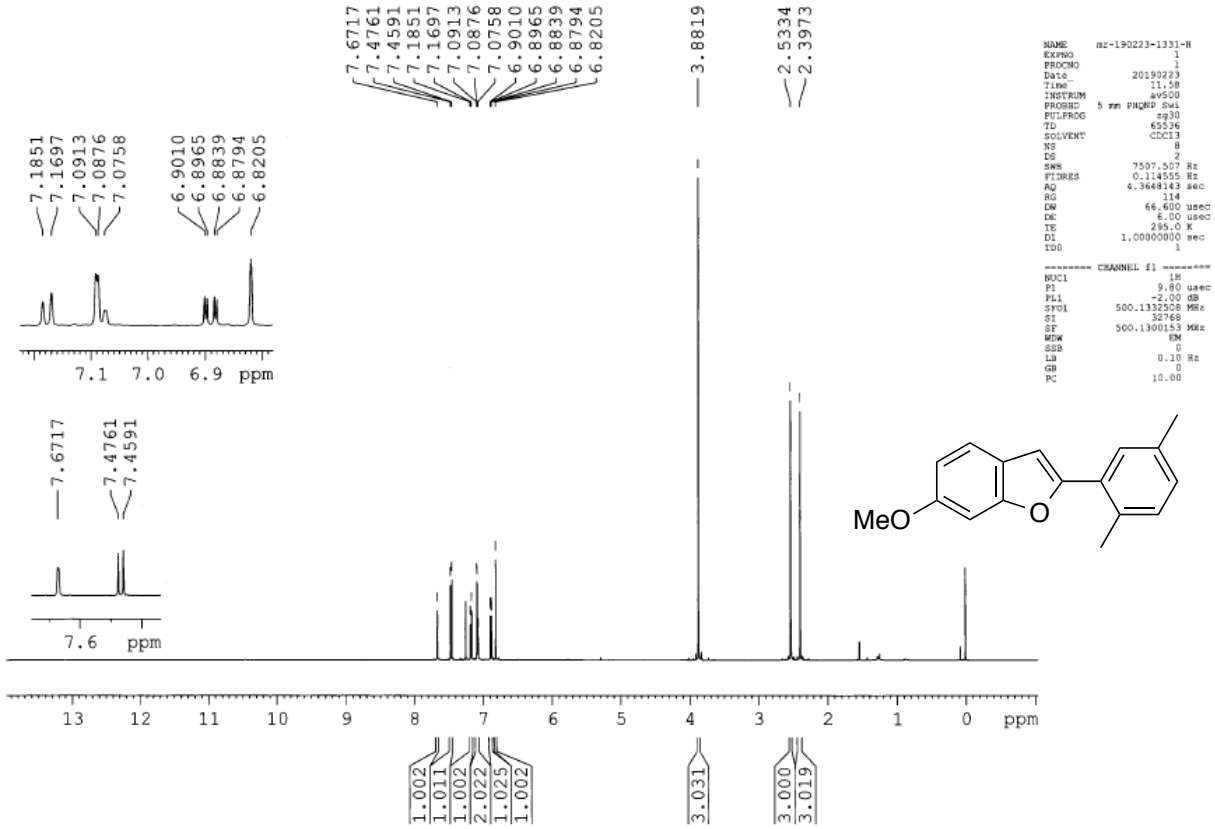


^{13}C NMR (126 MHz, $CDCl_3$)

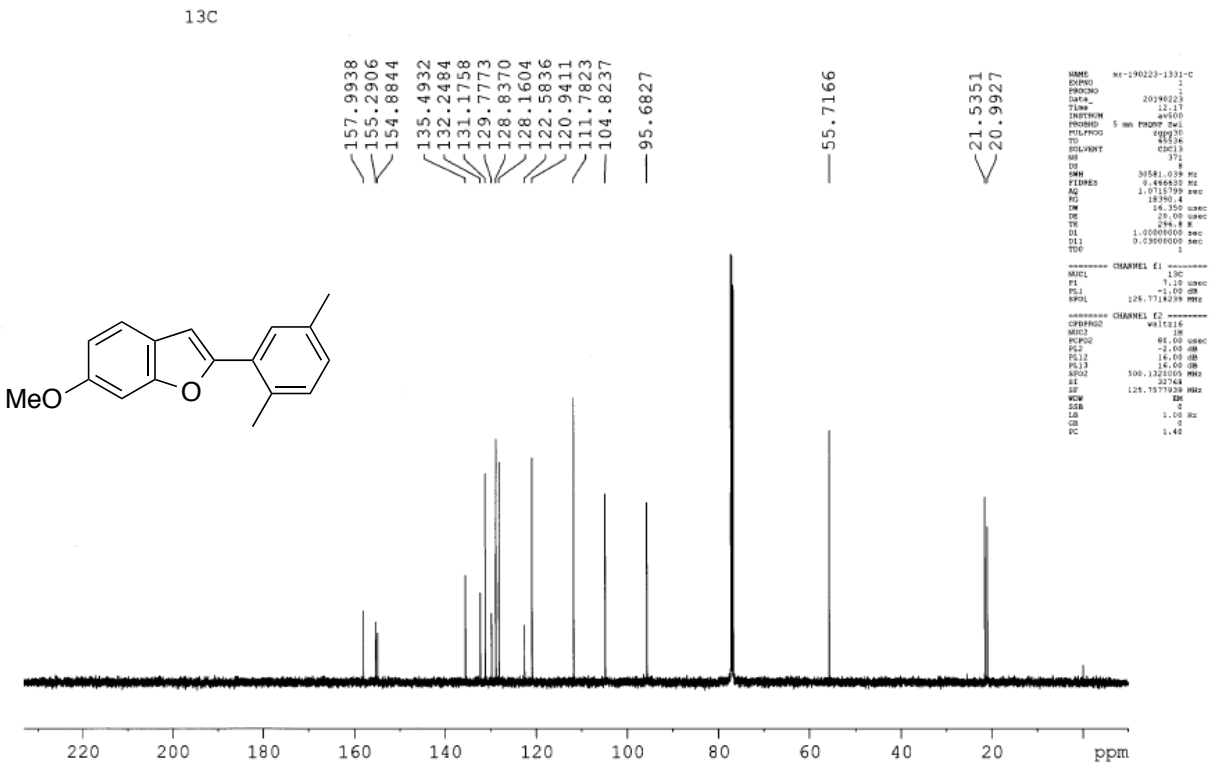


2-(2,5-Dimethylphenyl)-6-methoxybenzofuran (3ja)

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

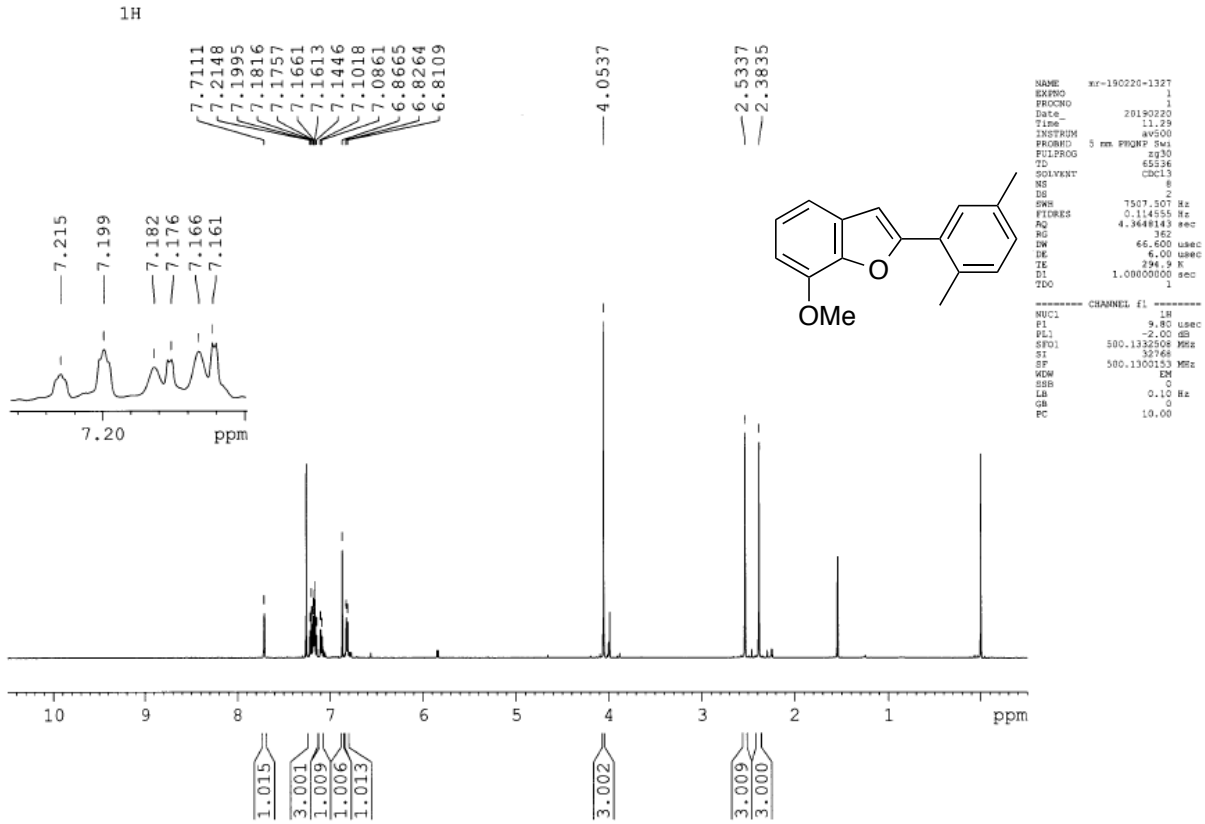


^{13}C NMR (126 MHz, $CDCl_3$)

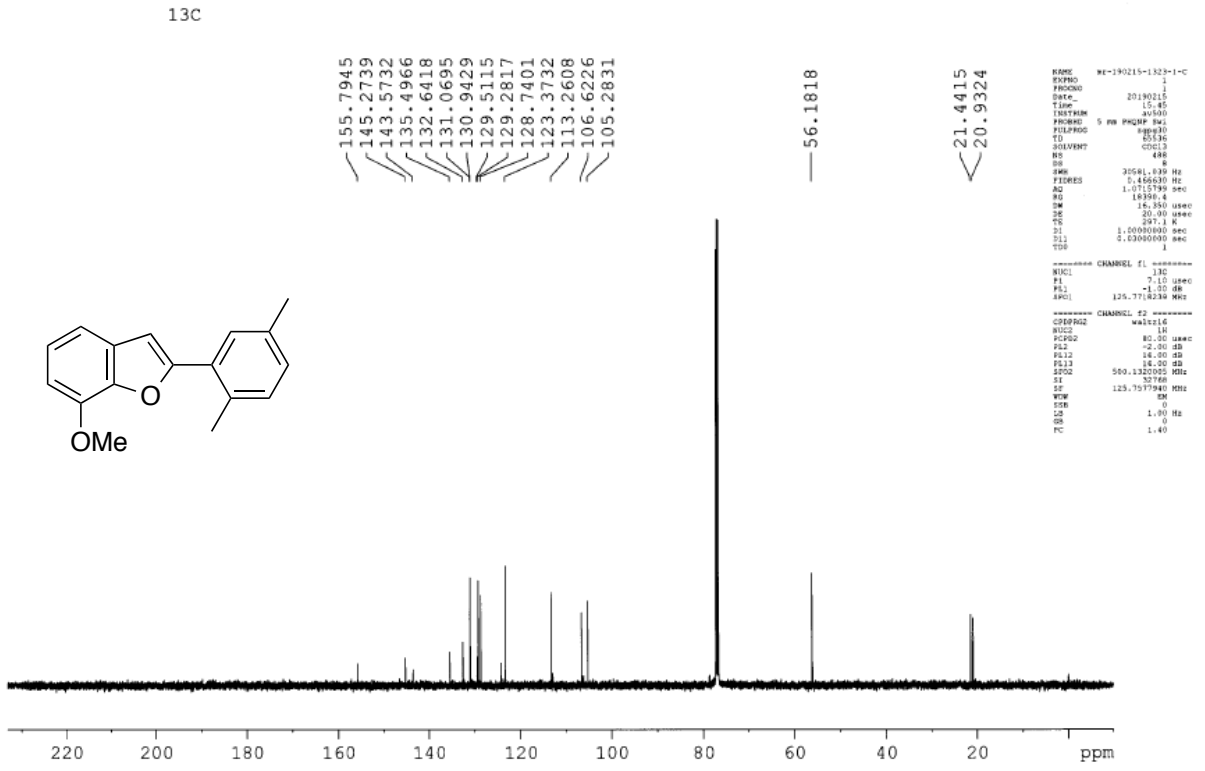


2-(2,5-Dimethylphenyl)-7-methoxybenzofuran (3ka)

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

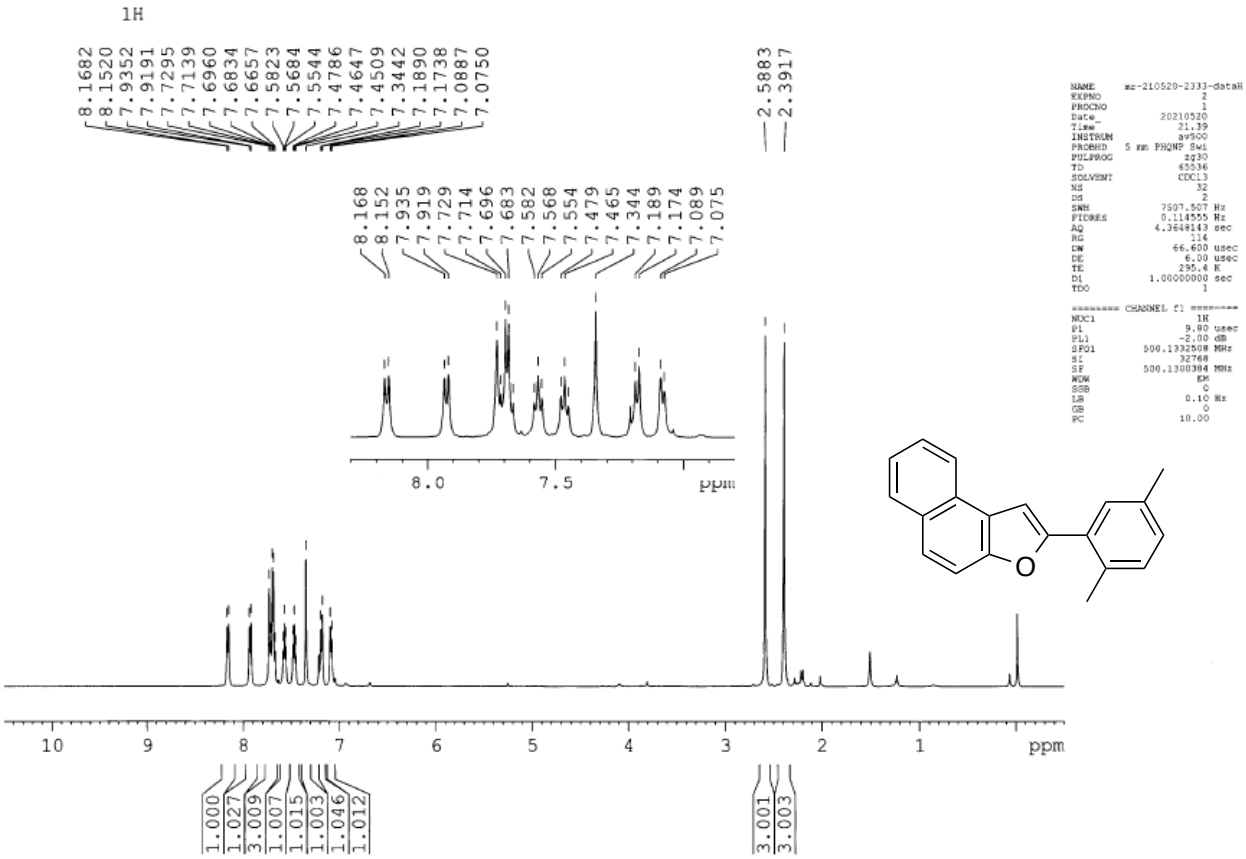


^{13}C NMR (126 MHz, $CDCl_3$)

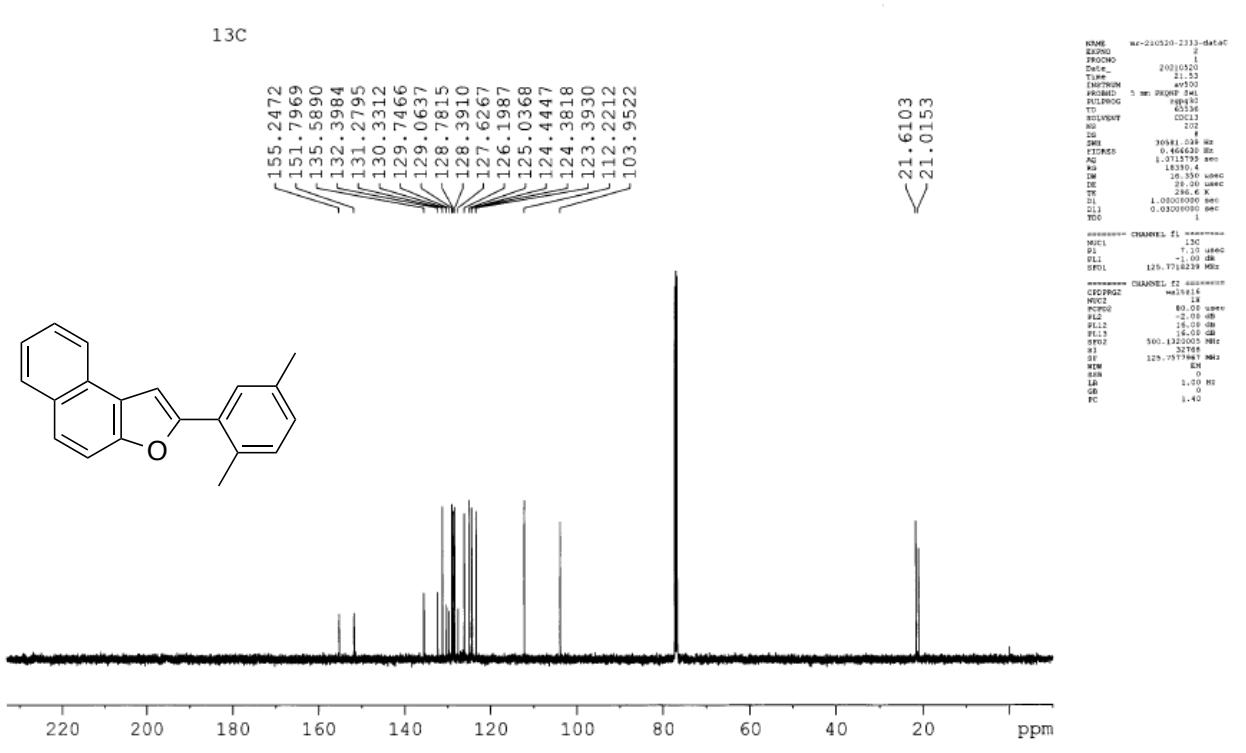


2-(2,5-Dimethylphenyl)naphtho[2,1-*b*]furan (3la)

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

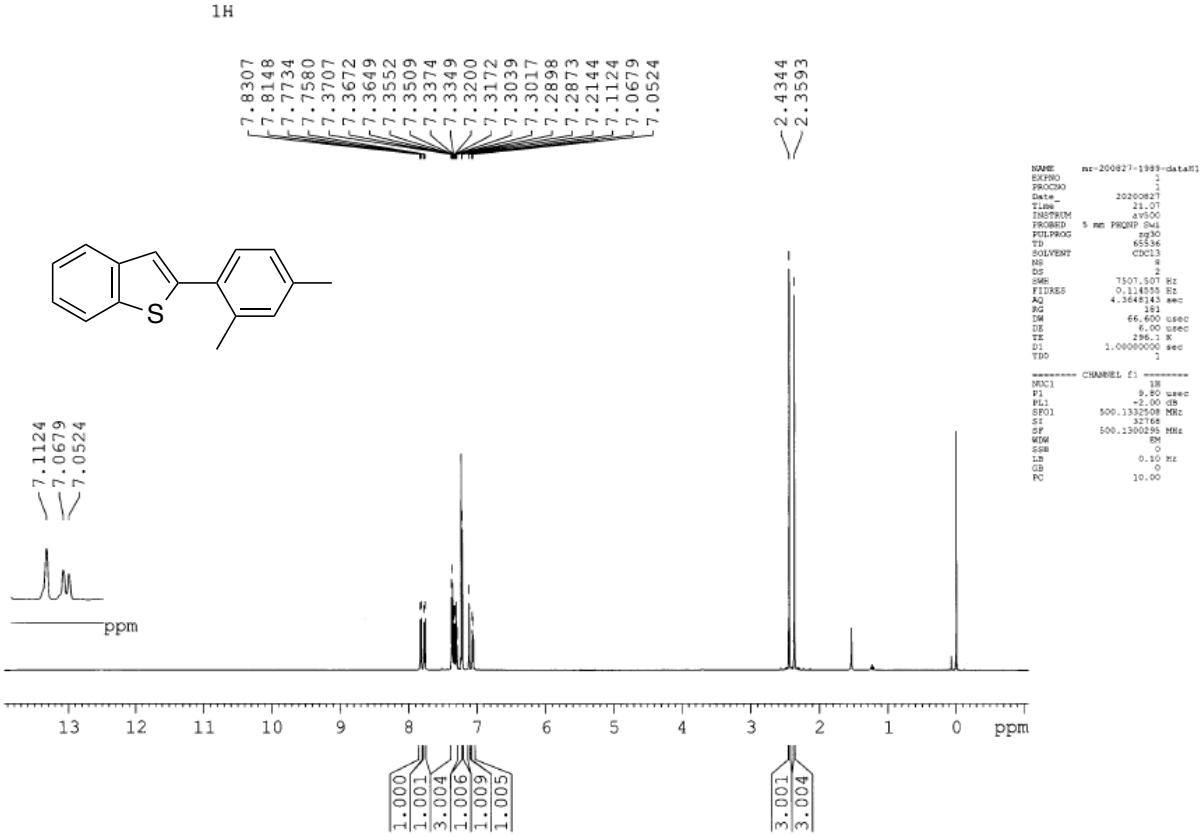


^{13}C NMR (126 MHz, $CDCl_3$)

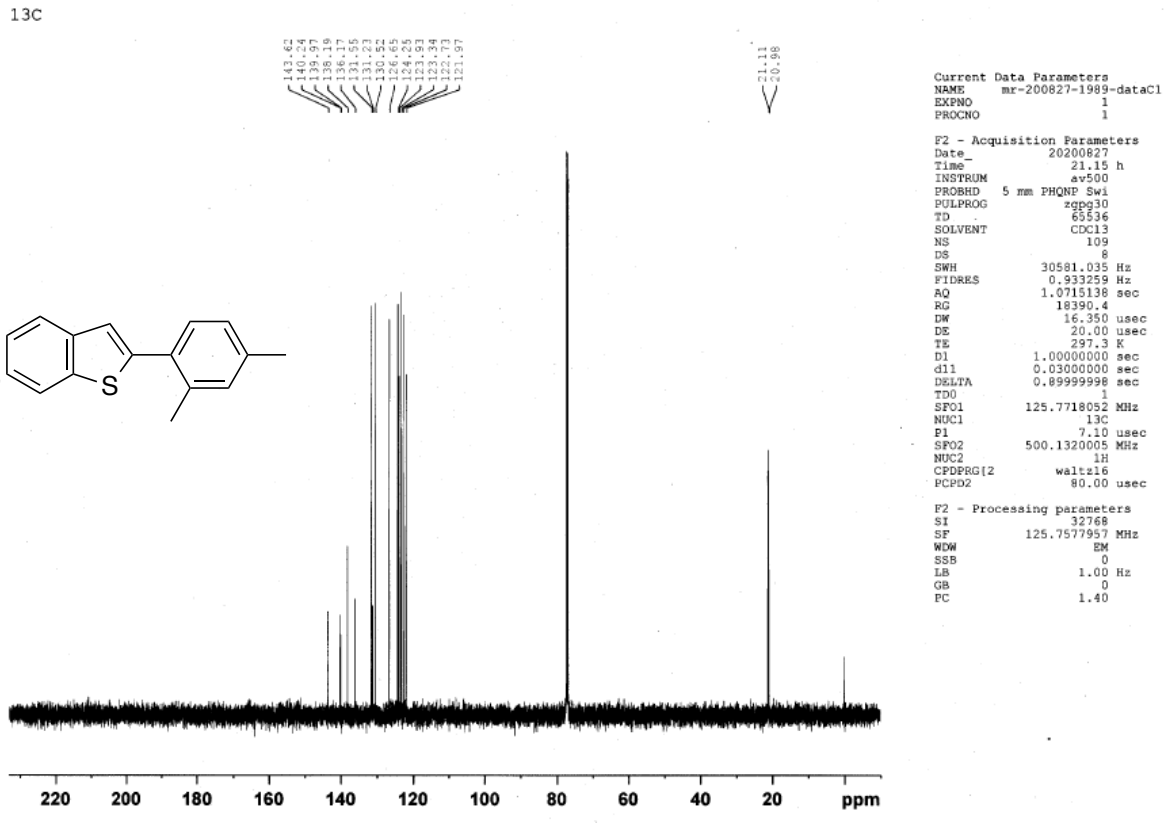


2-(2,4-Dimethylphenyl)benzo[*b*]thiophene (3mb)

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

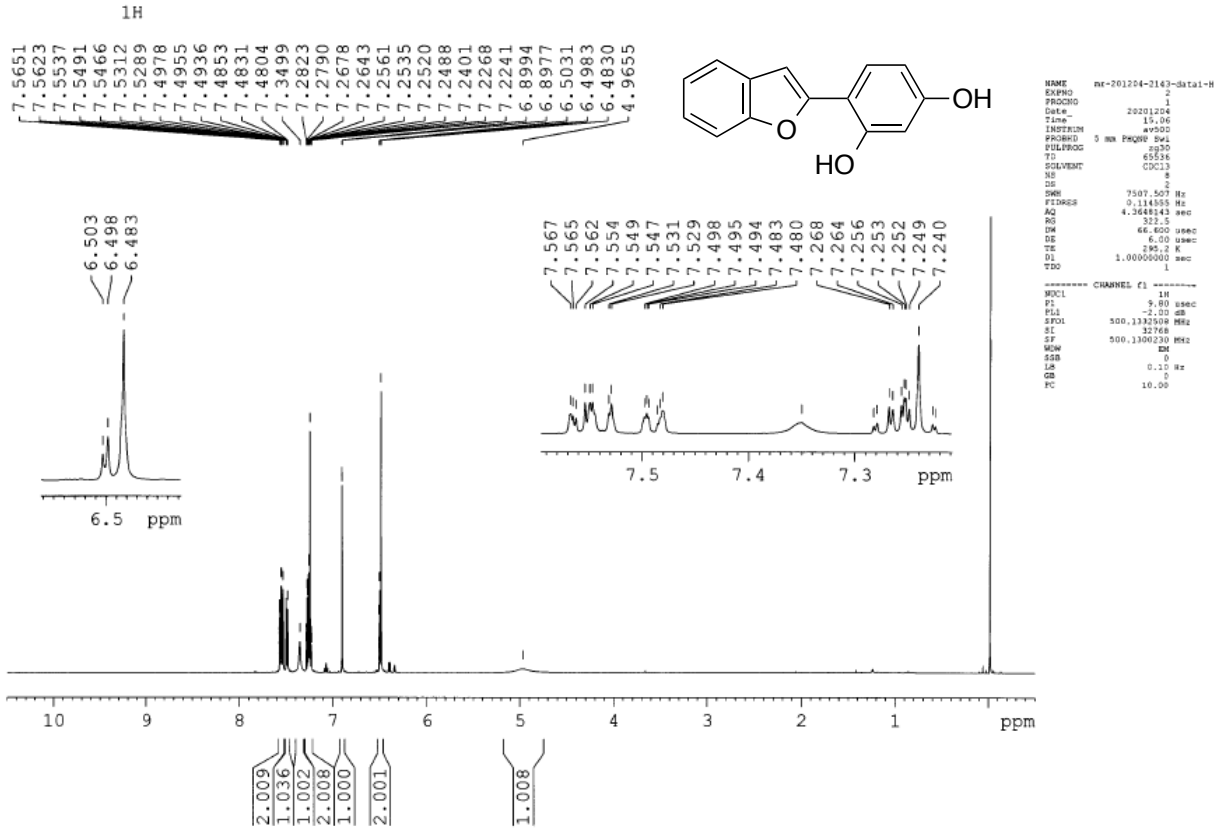


^{13}C NMR (126 MHz, $CDCl_3$)

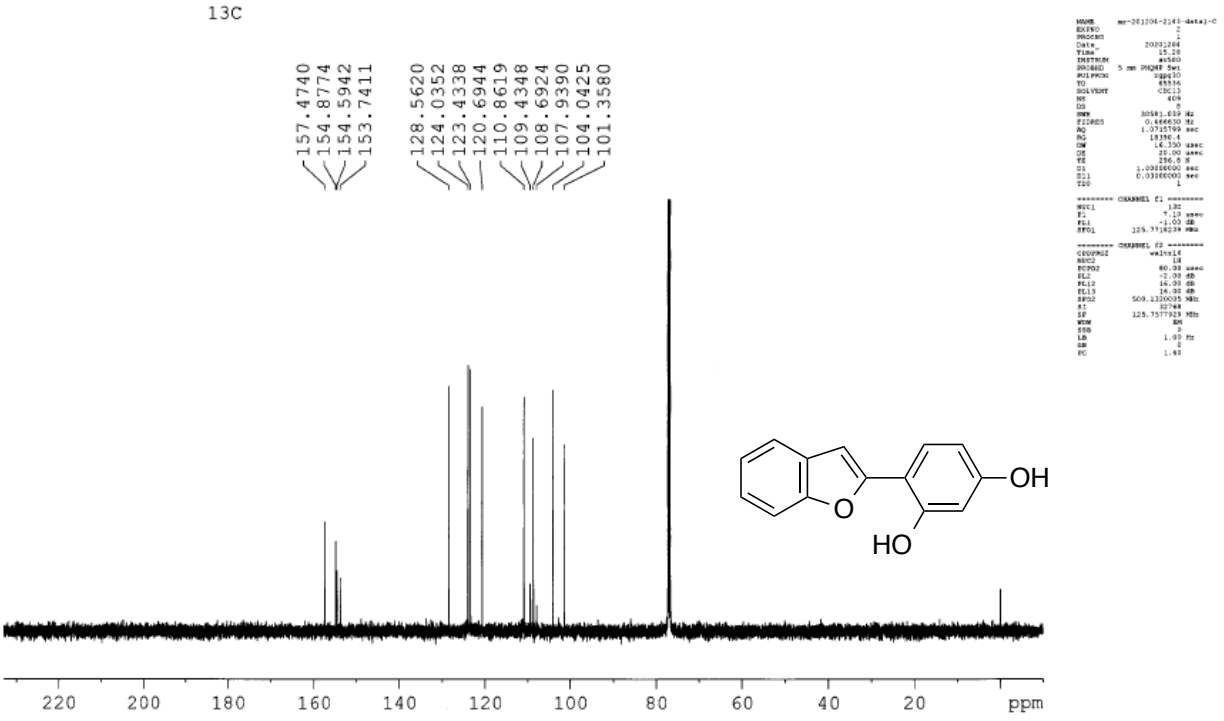


4-(Benzofuran-2-yl)benzene-1,2-diol (3ag, DHBF)

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

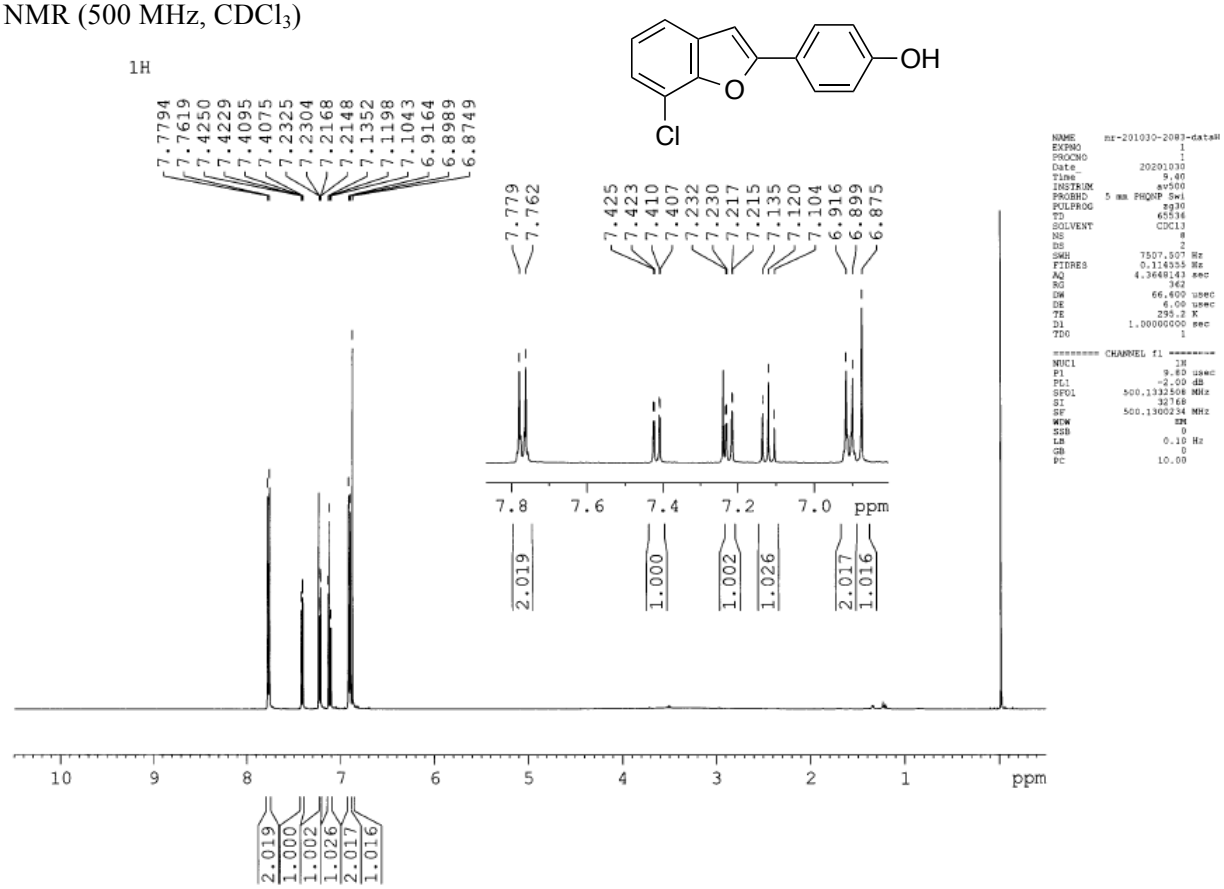


^{13}C NMR (126 MHz, $CDCl_3$)

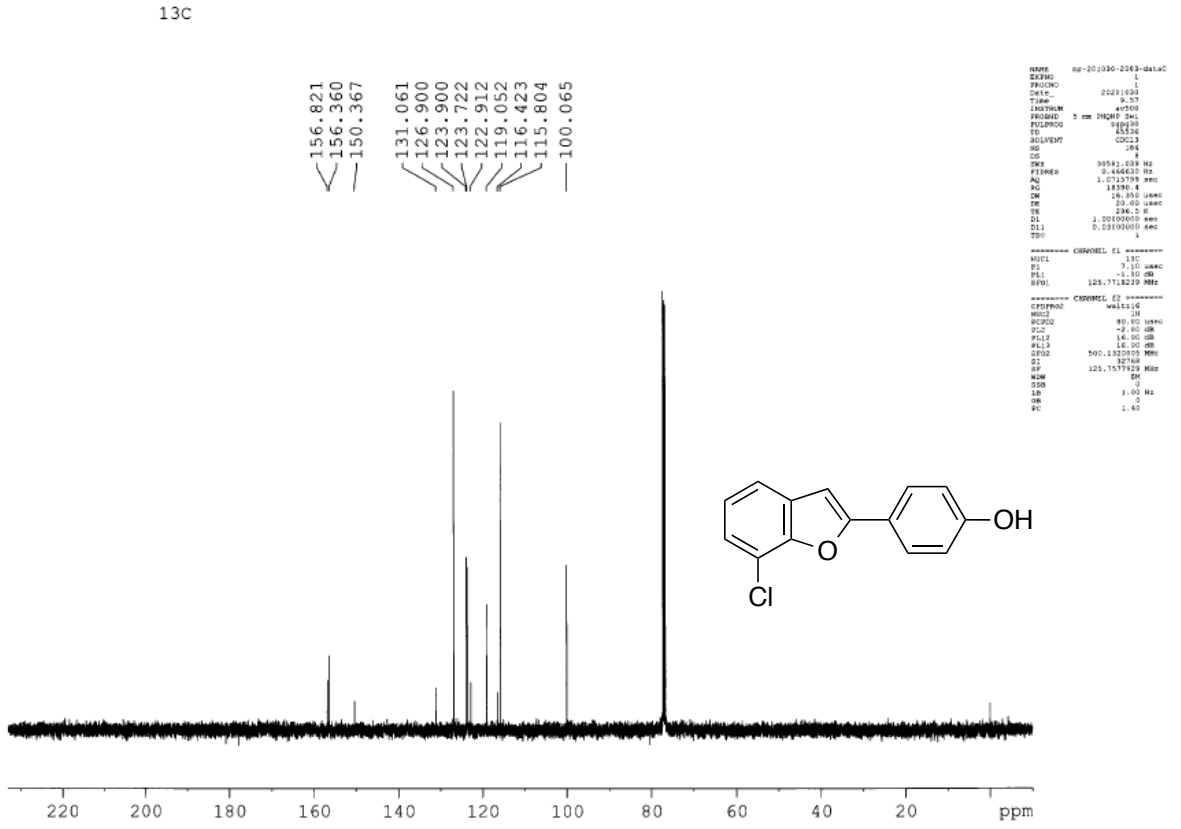


4-(7-Chlorobenzofuran-2-yl)phenol (3nd)

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

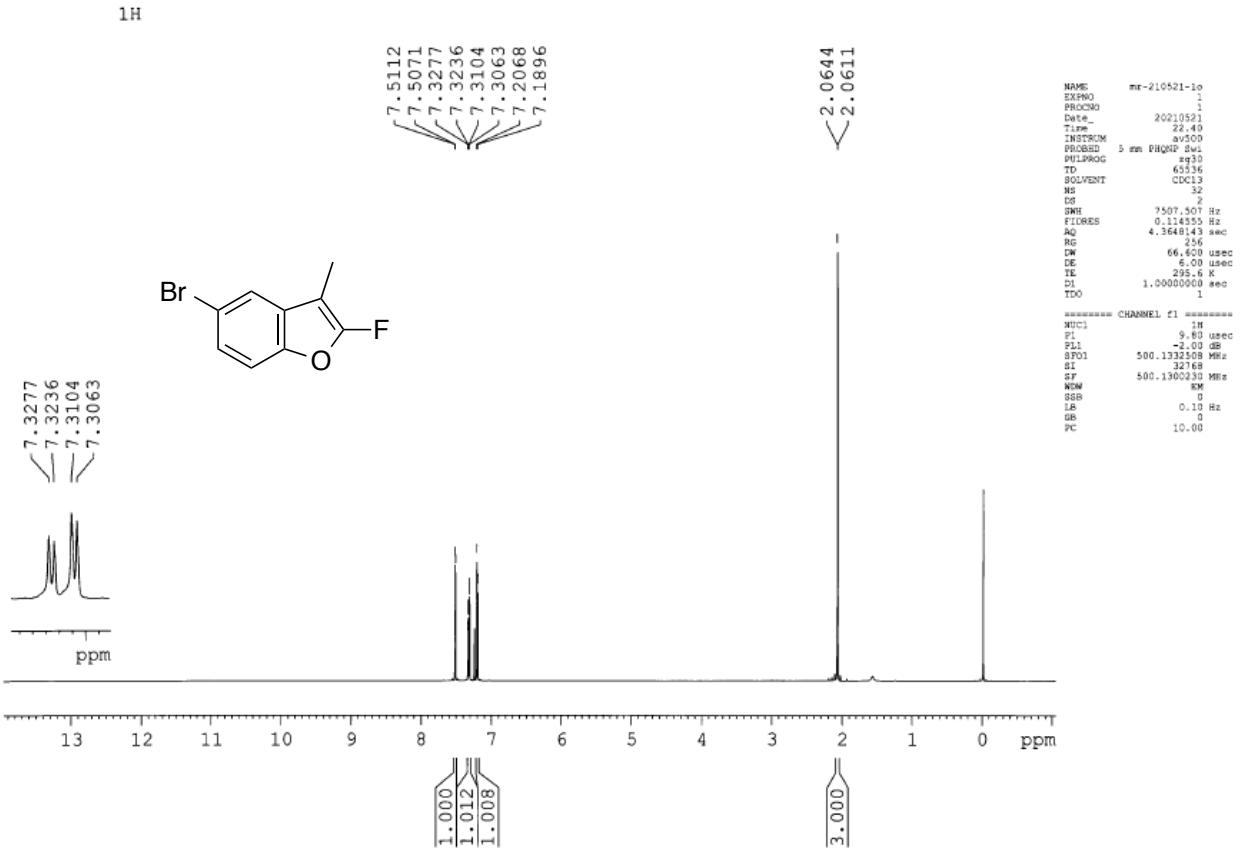


^{13}C NMR (126 MHz, $CDCl_3$)

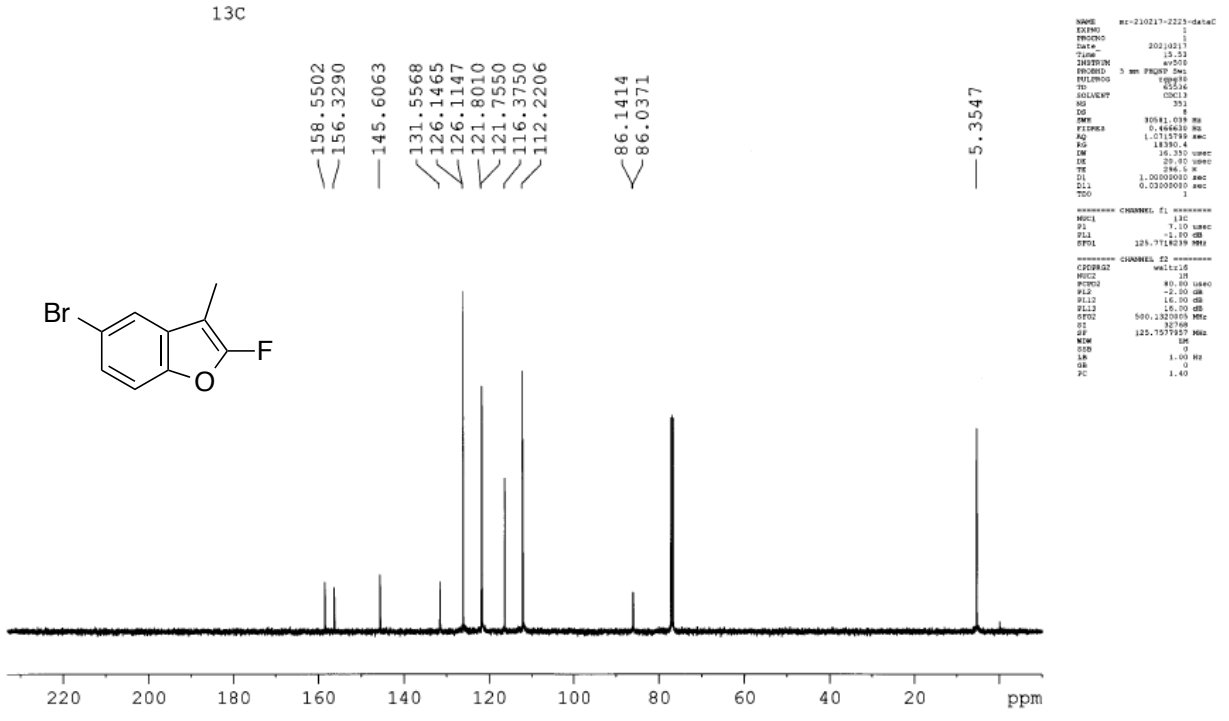


5-Bromo-2-fluoro-3-methylbenzofuran (1o)

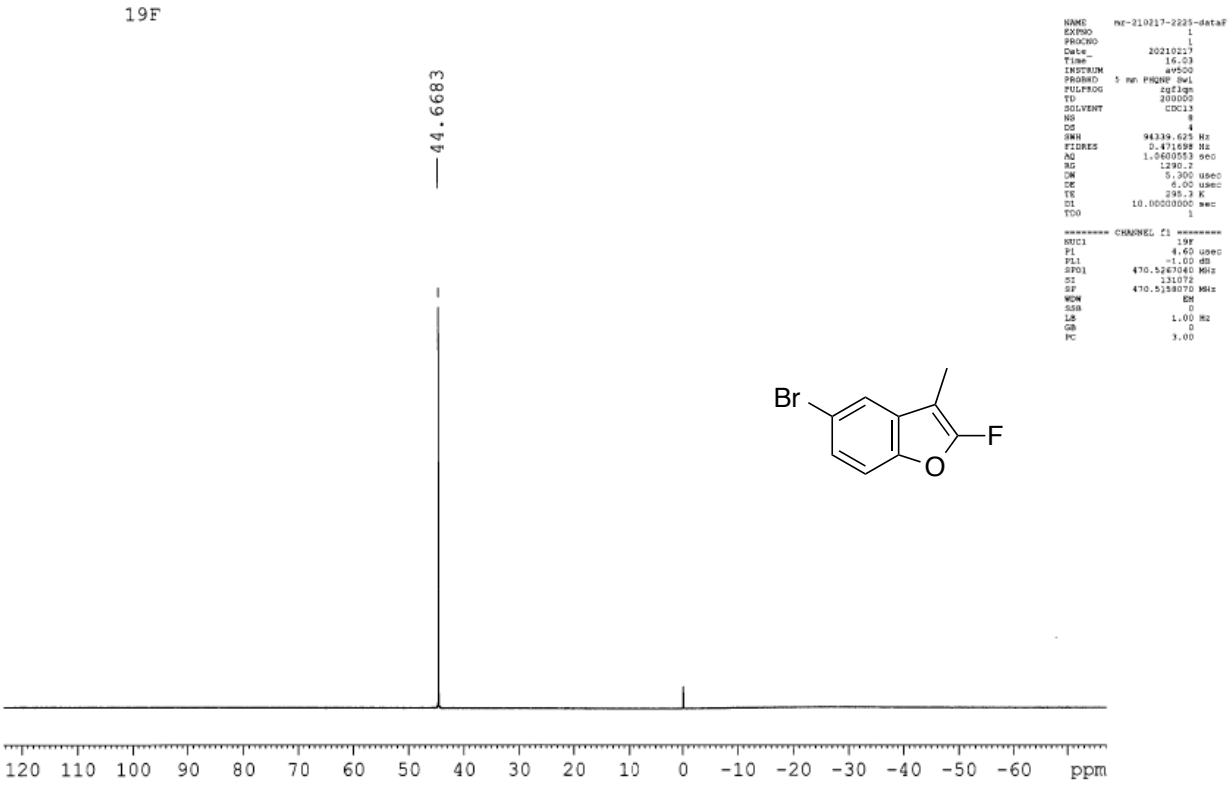
^{1}H NMR (500 MHz, $CDCl_3$)



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

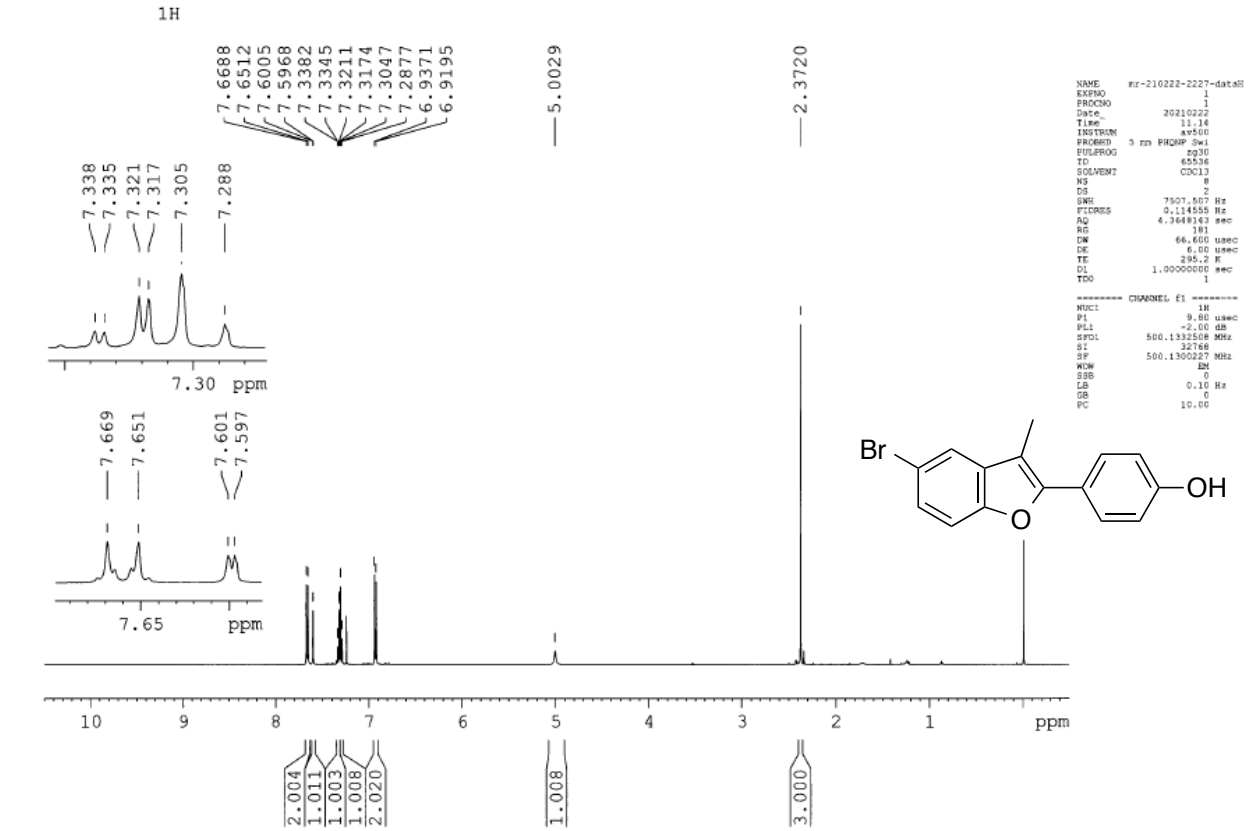


^{19}F NMR (470 MHz, $CDCl_3$)

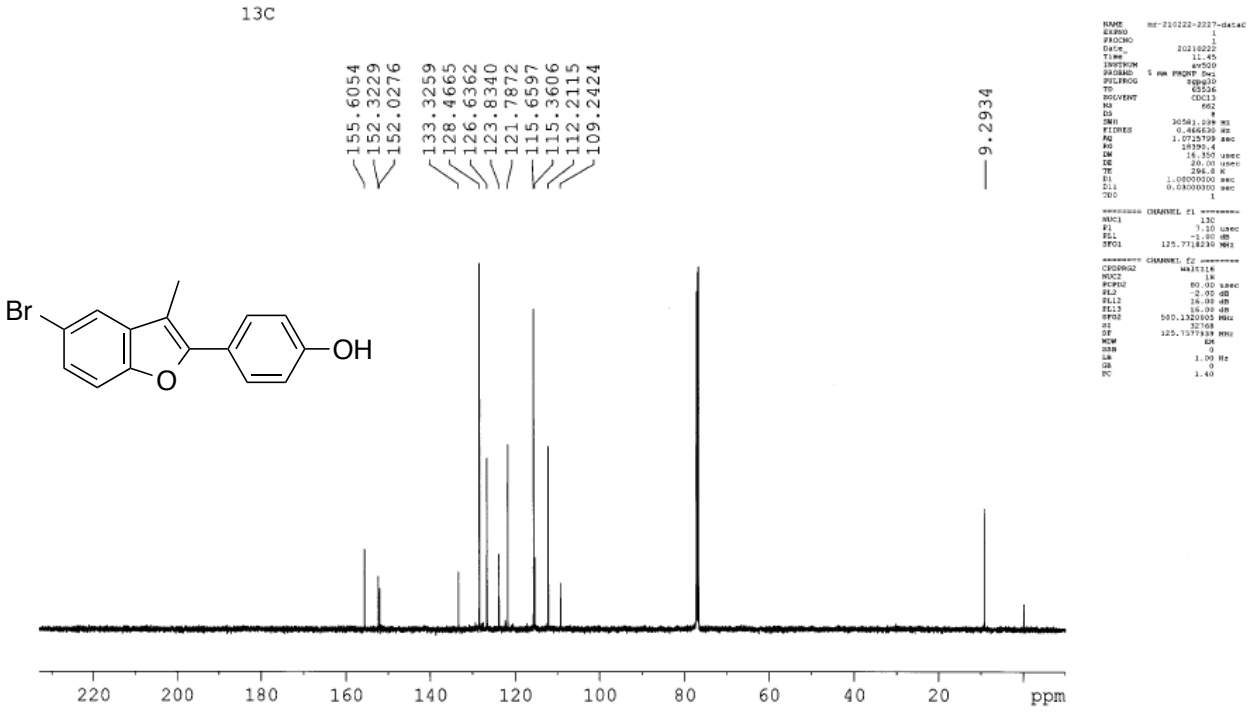


4-(5-Bromo-3-methylbenzofuran-2-yl)phenol (3od)

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

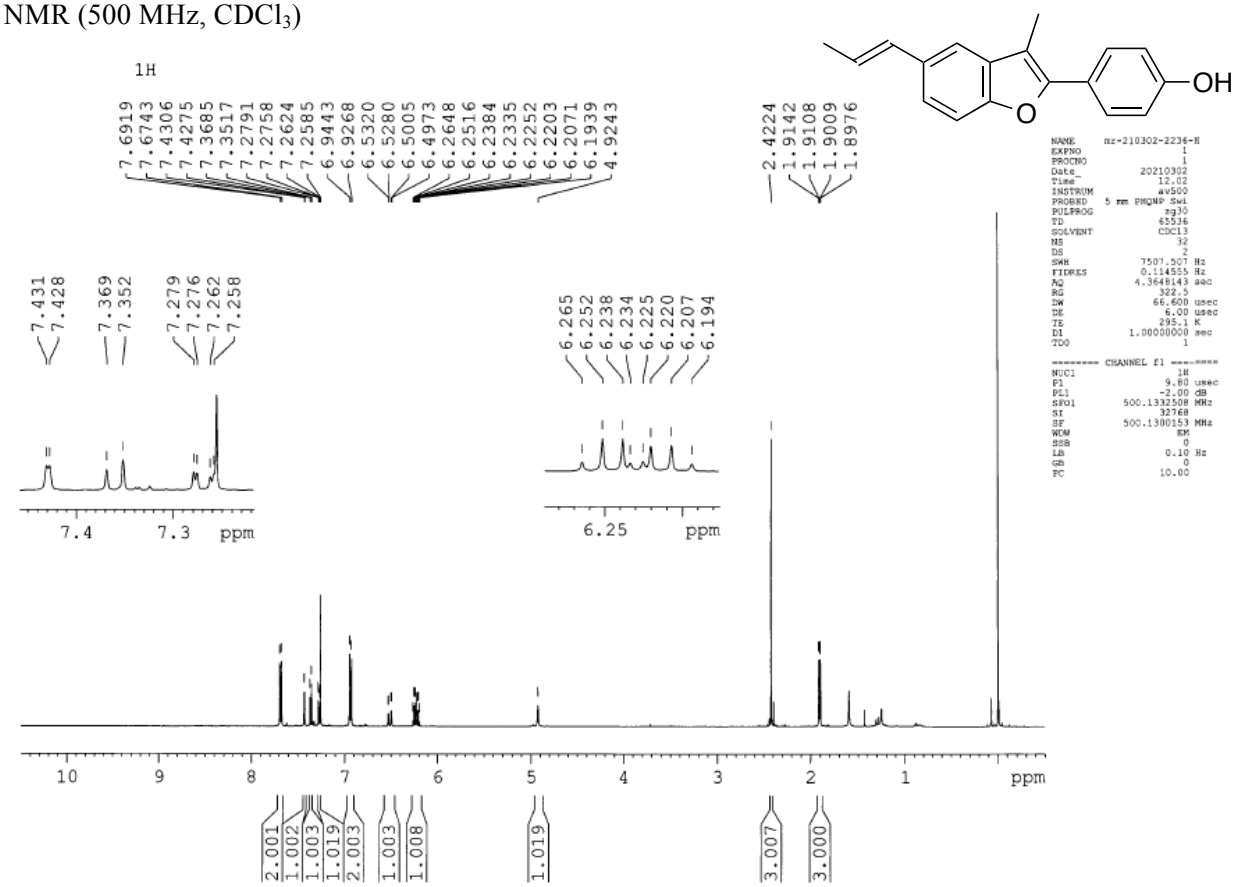


^{13}C NMR (126 MHz, $CDCl_3$)



Eupomatenoid 6 (4)

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



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