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Dioxazolones as Masked Ester Surrogates in the Pd(II)-Catalyzed Direct C-H Arylation of 6,5-Fused Heterocycles.

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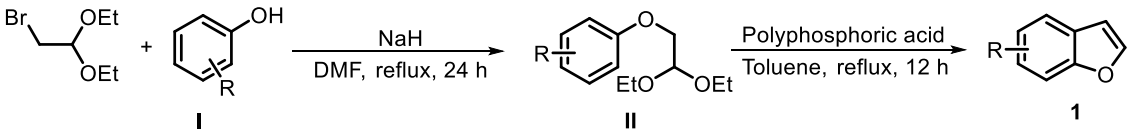
1. Experimental Section:

(i) General Methods:

All commercially available compounds were used without purification. Unless otherwise noted, all reactions were performed in oven-dried glassware. All reactions were run under nitrogen or oxygen atmosphere. All solvents used in the reactions were purified before use. Tetrahydrofuran was distilled from sodium and benzophenone, whereas dry dichloromethane, dimethylformamide, dioxane, toluene and dichloroethane were distilled from CaH_2. Petroleum ether with a boiling range of 40–60 °C was used. Melting points are uncorrected. ^{1}H, and ^{13}C NMR: Recorded on 400 and 500 MHz NMR Spectrometers; spectra were recorded at 295 K in $CDCl_3$; chemical shifts are calibrated to the residual proton and carbon resonance of the solvent: $CDCl_3$ (^{1}H δ 7.25; ^{13}C δ 77.0). LC-HRMS: Recorded on a Q-ToF with electron spray ionization (ESI) or Atmospheric pressure chemical ionization (APCI). GC-HRMS: Performed GC-QToF (with Electron Impact (EI), 70eV) using DB-5 column. GC-LRMS: Performed GC-MS (EI 70 eV) using DB-5 column. IR were recorded as thin films between KBr plates.

(ii) General Procedures:



Scheme S1: Synthesis of 2, 3-unsubstituted benzo[*b*]furan 1.[1a]

To a stirring solution of the phenol **I** (5.32 mmol) in *N*,*N*-dimethylformamide (4 mL), was added NaH (319 mg, 7.97 mmol, 60% dispersion in mineral oil) and the resulting mixture was stirred gently at room temperature. This was followed by the addition of 2-bromo-1,1-diethoxyethane (1.24 mL, 7.97 mmol), and the reaction mixture was then stirred at reflux for 24 h. Upon completion of the reaction and subsequent cooling to room temperature, the mixture was poured over crushed ice and stirred vigorously. This mixture was then extracted with ethyl acetate (3×10 mL), and the combined organic extract was washed with NaOH solution (1N) and brine. The extract was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to give the desired product **II** that was used as such for the next step, without any purification.

The product **II** (5.30 mmol) was dissolved in toluene (15.0 mL) and to this was added polyphosphoric acid (3.58 g, 10.64 mmol) and the mixture was stirred at reflux for 12 h during which the reaction was found to be complete. Upon cooling to room temperature, the mixture was filtered through a plug of silica gel and eluted with petroleum ether. The organic filtrate was concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography (petroleum ether) to afford the desired benzofuran product **1**.

4-methylbenzofuran (1b): Prepared according to the general procedure and the title compound was isolated as a colorless liquid (51% yield). Spectral data obtained were in good agreement with those reported in the literature.[1a]

4-methoxybenzofuran (1d): Prepared according to the general procedure and the title compound was isolated as a colorless liquid (10% yield). Spectral data obtained were in good agreement with those reported in the literature.[1a]

7-methylbenzofuran (1e): Prepared according to the general procedure and the title compound was isolated as a colorless liquid (42% yield). Spectral data obtained were in good agreement with those reported in the literature.[1b]

4,7-dimethylbenzofuran (1f): Prepared according to the general procedure and the title compound was isolated as a colorless liquid (47% yield). Spectral data obtained were in good agreement with those reported in the literature.[1a]

4,6-dimethylbenzofuran(1g): Prepared according to the general procedure and the title compound was isolated as a colorless liquid (44% yield). Spectral data obtained were in good agreement with those reported in the literature.[1a]

5-methylbenzofuran (1h): Prepared according to the general procedure and the title compound was isolated as a colorless liquid (41% yield). Spectral data obtained were in good agreement with those reported in the literature.[1b]

4-(*tert*-butyl)benzofuran (1i): Prepared according to the general procedure and the title compound was isolated as a colorless liquid (37% yield). Spectral data obtained were in good agreement with those reported in the literature.[1a]

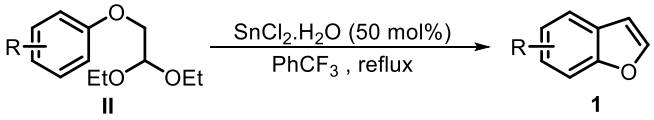
5-phenylbenzofuran (1j): Prepared according to the general procedure and the title compound was isolated as a white solid (35% yield). Spectral data obtained were in good agreement with those reported in the literature.[1a]

5-chlorobenzofuran (1l): Prepared according to the general procedure and the title compound was isolated as a colorless oil (31% yield). Spectral data obtained were in good agreement with those reported in the literature.[1a]

5-iodobenzofuran (1m): Prepared according to the general procedure and the title compound was isolated as a colorless oil (8% yield). Spectral data obtained were in good agreement with those reported in the literature.[1b]

5-methoxybenzofuran (1n): Prepared according to the general procedure and the title compound was isolated as a colorless oil (42% yield). Spectral data obtained were in good agreement with those reported in the literature.[1b]

Scheme S2: Synthesis of 2,3-unsubstituted benzo[*b*]furan (1):[2]

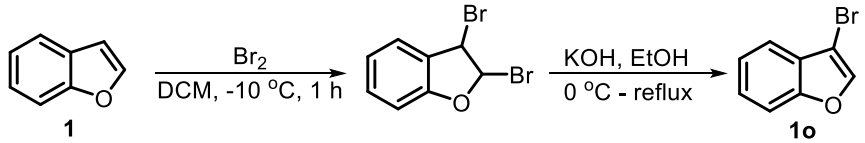


To a stirring solution of 2-aryloxyacetaldehyde diethyl acetal (1 mmol) in trifluorotoluene (10 mL) was added $SnCl_2.H_2O$ (0.5 mmol). The resulting mixture was refluxed, and the progress of the reaction was followed by TLC. Upon completion of the reaction and subsequent cooling to room temperature, the reaction mixture was quenched with water and extracted with Et_2O (3×5 mL). The solution was washed with water, brine and dried over anhydrous Na_2SO_4. The organic extract was filtered and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography (petroleum ether: EtOAc) to afford the desired 2,3-unsubstituted benzo[*b*]furans **1**.

4-bromobenzofuran (1d): Prepared according to the general procedure and the title compound was isolated as a colorless oil (40% yield). Spectral data obtained were in good agreement with those reported in the literature.[2]

5-bromobenzofuran (1l): Prepared according to the general procedure and the title compound was isolated as a colorless oil (44% yield). Spectral data obtained were in good agreement with those reported in the literature.[2]

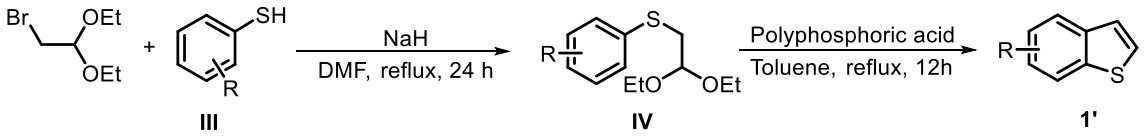
Scheme S3: Synthesis of 3-bromobenzo[*b*]furan (1o):[3]



In a round bottom flask, benzofuran (500 mg, 4.23 mmol, 1.0 equiv.) was dissolved in 10 mL of DCM and this stirring solution was cooled to -10 °C. A solution of bromine (0.3 mL, 4.66 mmol, 1.1 equiv.) in DCM (1.5 mL) was slowly added at this temperature. The reaction mixture was stirred for 1 h at that temperature. Subsequently aq. NaOH solution (0.5 mL, 1 M) was added. The resulting mixture was diluted with water (20 mL) and then $Na_2S_2O_3$ solution was added (10 mL). This was extracted with DCM and the combined organic extract was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was dissolved in ethanol (10 mL) and was added dropwise to a saturated solution of KOH in ethanol (10mL) at 0 °C. After refluxing for 2 h, water was added (5 mL) and the EtOH was removed under reduced pressure. The aqueous residue was extracted with ethyl acetate and the organic extract was washed successively with water, brine and dried over anhydrous Na_2SO_4. Upon filtration, this organic extract was concentrated under reduced pressure and the residue was purified by silica gel flash column chromatography (petroleum ether: EtOAc, 20:1) and the product was obtained as a dark yellow oil (482 mg, 56%).

Spectral data obtained were in good agreement with those reported in the literature.[3] **^{1}H NMR** (400 MHz,$CDCl_3$): δ 7.63 (s, 1H), 7.52 (d, *J* = 7.3 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.26 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.41, 142.62, 127.12, 125.44, 123.44, 119.80, 111.75, 97.94; **GC-MS**: 196.0$[M]^+$.

Scheme S4: Synthesis of 2,3-unsubstituted benzo[*b*]thiophene (1'):[1a]

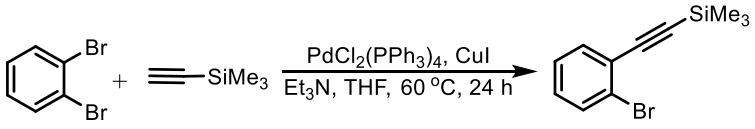


III IV 1'

Thiophenol **III** (4.54 mmol) was dissolved in *N*,*N*-dimethylformamide (4 mL) and to this stirring solution was added NaH (273 mg, 6.82 mmol) in portions at room temperature. This was followed by the addition of 2-bromo-1,1-diethoxyethane (1.24 mL, 6.82mmol) and the reaction mixture was refluxed for about 24 h. Upon completion of the reaction and subsequent cooling to room temperature, the reaction mixture was poured over crushed ice and stirred vigorously. This was extracted with ethyl acetate (3×10 mL) and the combined organic extract was washed with NaOH solution (1N) and brine, dried over anhydrous Na_2SO_4. Filtration and concentration under reduced pressure resulted in the desired product **IV** that was used as such without further purification for the next step.

To a stirring solution of the crude product **IV** (4.0 mmol) in toluene (12 mL) was added polyphosphoric acid (2.41g, 8.0 mmol) and the mixture was refluxed for 12 h. Thereafter, the mixture was allowed to cool to room temperature and then filtered through a plug of silica gel, eluting with petroleum ether. The filtrate was concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography (eluting with petroleum ether) to afford the desired benzothiophene product **1'**.

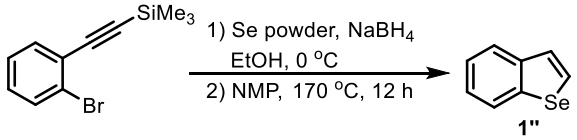
Scheme S5: Synthesis of ((2-bromophenyl)ethynyl)trimethylsilane:[4]



In a round bottom flask, 1, 2-dibromobenzene (480 mg, 2.04 mmol) was dissolved in THF (2 mL) and triethylamine (2 mL). To the deaerated solution, trimethylsilylacetylene (0.3 mL, 2.04 mmol), $PdCl_2(PPh_3)_2$ (49.9 mg, 40.7 µmol) and copper(I) iodide (38.8 mg, 204 µmol) were added. The reaction mixture was refluxed for about 24 h at 60 °C. Upon completion of

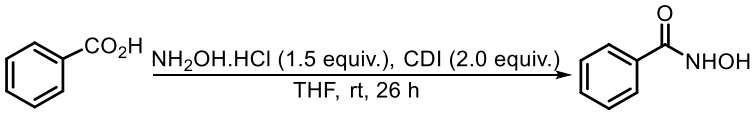
the reaction and subsequent cooling to room temperature, the mixture was diluted with water (10 mL) and extracted with chloroform (10 mL × 2). The extract was washed with brine, dried over anhydrous Na_2SO_4 and concentration under reduced pressure. The oily residue was purified by silica gel flash column chromatography (eluting with petroleum ether) and the product was obtained as a dark yellow oil. Spectral data obtained were in good agreement with those reported in the literature.[4]

Scheme S6: Synthesis of benzo[*b*]selenophene (1''):[4]



In a round bottom flask, sodium borohydride (40 mg, 1.0 mmol) was added to a suspension of selenium powder (84 mg, 1.0 mmol) in ethanol (4 mL) at 0 °C. After stirring the reaction mixture for 40 min, NMP (8 mL) and 1-bromo-2-(trimethylsilylethynyl)benzene (150 mg, 0.6 mmol) was added and stirred at 170 °C. The progress of the transformation was monitored by TLC. Upon completion of the reaction, the mixture was cooled and diluted with saturated aqueous ammonium chloride solution (20 mL) and extracted with pentane (10 mL × 2). The extract was washed with brine and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (petroleum ether) to afford the desired benzo[*b*]selenophene (**1''**). Spectral data obtained were in good agreement with those reported in the literature.[4]

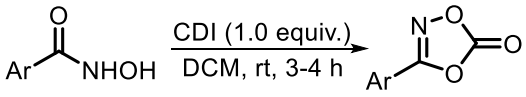
Scheme S7: Preparation of the hydroxamic acids:[5]



In a round-bottom flask, CDI (16.39 mmol, 2.0 equiv.) was added portion-wise to a stirring solution of aromatic acid (8.19 mmol, 1.0 equiv.) in THF (45 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for another 1.5 h. This mixture was then cooled to 0 °C and $NH_2OH.HCl$ (12.29 mmol, 1.5 equiv.) was added to it in portions and the resulting mixture was allowed to warm up to room temperature. The progress of the transformation was monitored by TLC. Upon completion of the reaction, the solvent was removed under reduced pressure, and the reaction mixture was diluted with saturated $KHSO_4$ (20 mL) and extracted twice with EtOAc. The organic layer was washed with brine and dried

over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (2:1, petroleum ether: EtOAc). Spectral data obtained were in good agreement with those reported in the literature.[4]

Scheme S8: Preparation of 3-aryl-1,4,2-dioxazol-5-ones (2):[6]



CDI was added (810 mg, 5.0 mmol, 1.0 equiv.) to a stirred solution of the hydroxamic acid (5.0 mmol, 1.0 equiv.) in dichloromethane (50 mL) at room temperature. After 3 h, the reaction mixture was quenched with 1N HCl, extracted with dichloromethane and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by silica gel flash column chromatography (9:1, petroleum ether: EtOAc) to afford the 3-aryl-1, 4, 2-dioxazol-5-ones.

3-(*p*-tolyl)-1,4,2-dioxazol-5-one (2a): Prepared according to the general procedure and the title compound was isolated as a white solid (90% yield). Spectral data obtained were in good agreement with those reported in the literature.[6a]

3-(4-methoxyphenyl)-1,4,2-dioxazol-5-one (2f): Prepared according to the general procedure and the title compound was isolated as a white solid (85% yield). Spectral data obtained were in good agreement with those reported in the literature.[6a]

3-(4-bromophenyl)-1,4,2-dioxazol-5-one (2g): Prepared according to the general procedure and the title compound was isolated as a white solid (61% yield). Spectral data obtained were in good agreement with those reported in the literature.[6a]

3-(4-chlorophenyl)-1,4,2-dioxazol-5-one (2h): Prepared according to the general procedure and the title compound was isolated as a white solid (82% yield). Spectral data obtained were in good agreement with those reported in the literature.[6a]

3-(4-fluorophenyl)-1,4,2-dioxazol-5-one (2i): Prepared according to the general procedure and the title compound was isolated as a white solid (75% yield). Spectral data obtained were in good agreement with those reported in the literature.[6a]

3-(*m*-tolyl)-1,4,2-dioxazol-5-one (2j): Prepared according to the general procedure and the title compound was isolated as awhite solid (92% yield). Spectral data obtained were in good agreement with those reported in the literature.[6b]

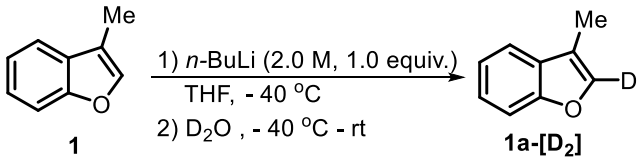
3-(*m*-methoxy)-1,4,2-dioxazol-5-one (2k): Prepared according to the general procedure and the title compound was isolated as a white solid (83% yield). Spectral data obtained were in good agreement with those reported in the literature.[6c]

3-(*o*-tolyl)-1,4,2-dioxazol-5-one (2l): Prepared according to the general procedure and the title compound was isolated as a white solid (90% yield). Spectral data obtained were in good agreement with those reported in the literature.[6a]

3-(naphthalen-2-yl)-1,4,2-dioxazol-5-one (2m): Prepared according to the general procedure and the title compound was isolated as a white solid (54% yield). Spectral data obtained were in good agreement with those reported in the literature.[6a,c]

3-(*m*-bromo)-1,4,2-dioxazol-5-one (2n): Prepared according to the general procedure and the title compound was isolated as a white solid (61% yield). Spectral data obtained were in good agreement with those reported in the literature.[6a]

Scheme S9: Preparation of 3-methylbenzofuran-2-*d* (1a-[D_2]):[7]



To the solution of 3-methyl benzofuran (200 mg, 1.51 mmol) in dry THF (8 mL) cooled to –40 °C, *n*-butyllithium (1.50 mL, 2.27 mmol, 2.0 M solution in cyclohexane) was added dropwise. The resulting mixture was stirred for 4 h at –40 °C and D_2O (0.5 mL) was added. The resulting mixture was stirred for 2 h at room temperature before H_2O was added (1.0 mL). The contents were transferred to a separatory funnel and Et_2O was added and the layers were separated. The aqueous phase was re-extracted with Et_2O. The combined organic extract was washed with water, brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (eluting with hexane) to afford 3-methylbenzofuran-2-*d* as a colourless oil (180 mg, 91%). Spectral data obtained were in good agreement with those reported in the literature.[7]

iii) General procedure for the Pd-catalyzed C-2 arylation with dioxazolones.

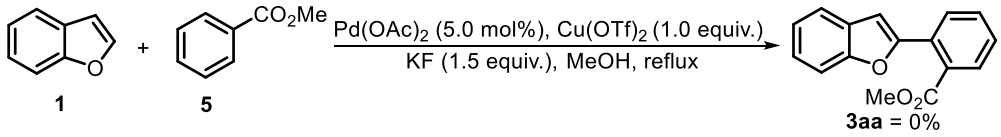
In a Schlenk tube equipped with a stir bar, the 6,5-fused heterocycle (0.17 mmol) was dissolved in MeOH (1.0 mL). The reaction mixture was degassed with nitrogen for ~10 min followed by the addition of $Pd(OAc)_2$ (5 mol%), $Cu(OTf)_2$ (1.0 equiv.), KF (1.5 equiv.) and

3-aryl-1,4,2-dioxazol-5-ones (2.0 equiv.). The tube was fitted with a reflux condenser under a nitrogen flow. The reaction mixture was allowed to stir at reflux temperature under a nitrogen atmosphere for 12-24 h until completion of the reaction (confirmed by TLC). The reaction was cooled to room temperature, filtered through a pad of celite, eluting with EtOAc. The filtrate was transferred to a separatory funnel and washed with $NaHCO_3$ solution. The organic extract was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by a silica gel flash column chromatography to yield the desired C-2 arylated product.

2. Experimental Procedures for the Mechanistic Studies:

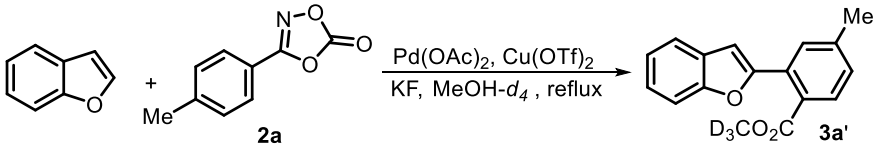
Scheme S10: Control Experiments:

(a) Reaction with methyl benzoate:



In a Schlenk tube equipped with a stir bar, the benzofuran (0.25 mmol) was dissolved in MeOH (2 mL). The reaction mixture was degassed with nitrogen for 10 min followed by the addition of $Pd(OAc)_2$ (2.5 mg, 5 mol%), $Cu(OTf)_2$ (90 mg, 1.0 equiv.), KF (22 mg, 1.5 equiv.) and methyl benzoate (34 mg, 2.0 equiv.). The tube was fitted with a reflux condenser under a nitrogen flow. The reaction mixture was allowed to stir at reflux temperature for 24h. The reaction progress was monitored *via* TLC, no C-2 arylation product was formed and the starting material remained unreacted.

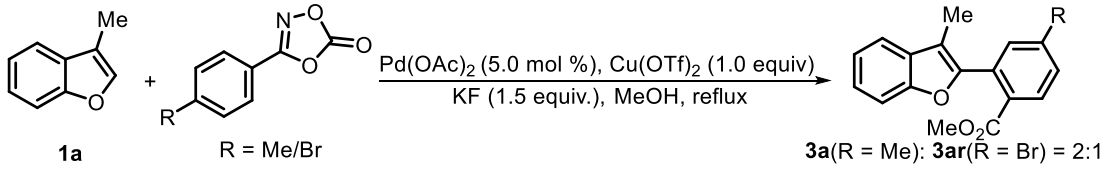
(b) Arylation with deuterated protic solvent.



In a Schlenk tube equipped with a stir bar, the substrate benzofuran (30 mg, 0.25 mmol) was dissolved in MeOH-d_4 (2 mL, 0.38 mmol). The reaction mixture was degassed with nitrogen for 10 min followed by the addition of $Pd(OAc)_2$ (2.5 mg, 5 mol%), $Cu(OTf)_2$ (90 mg,1.0 equiv.), KF (22 mg, 1.5 equiv.) and 3-(*p*-tolyl)-1,4,2-dioxazol-5-ones (88.5 mg, 2.0 equiv.). The tube was fitted with a reflux condenser under a nitrogen flow. The reaction mixture was allowed to stir at reflux temperature under a nitrogen atmosphere for 12 h until completion of the reaction (as indicated by TLC). The reaction was cooled to room temperature, filtered through a pad of celite, eluting with EtOAc. The filtrate was transferred to a separatory funnel and washed with $NaHCO_3$ solution. The organic extract was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by a silica gel flash column chromatography (eluting with 9:1 petroleum ether: EtOAc) and the compound was analyzed by ^1H NMR which shows complete deuterium incorporation in the

ester functionality of the C-2 aryl ring. Yield: 60%; Physical appearance: pale yellow liquid; **^{1}H NMR** (400 MHz,$CDCl_3$): δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.57 (s, 1H), 7.49 (d, *J*= 8.0 Hz, 1H), 7.33 – 7.22 (m, 3H), 6.92 (s, 1H), 2.46 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 169.21, 155.05, 154.96,141.56, 129.87, 129.71, 129.40, 128.93, 128.16, 124.41, 122.87, 121.15, 111.07, 104.34, 21.45; **ESI-HRMS**: Calculated for $C_{17}H_{11}D_3NaO_3^+$ $[M+Na]^+$ 292.1023, found 292.1016.

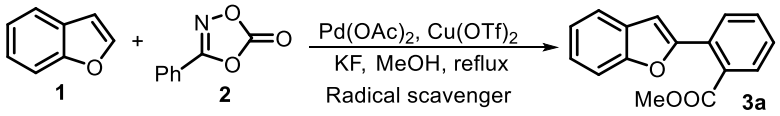
(c) Intermolecular Competition Experiment:



An oven dried Schlenk tube was charged with 3-methyl benzo[*b*]furan (30 mg, 0.25 mmol, 1.0 equiv.), 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (88.5 mg, 0.37 mmol, 1.5 equiv.) and 3-(*p*-bromo)-1,4,2-dioxazol-5-one (91 mg, 0.37 mmol, 1.5 equiv.) along with $Pd(OAc)_2$ (2.5 mg,5.0 mol %), $Cu(OTf)_2$ (90 mg, 1.0 equiv.), KF (22 mg, 1.5 equiv.) were stirred in MeOH (2 mL) under N_2 at reflux temperature for 6 h. The reaction progress was monitored by TLC until completion of the reaction. The reaction was cooled to room temperature, filtered through a pad of celite and eluting with EtOAc. The filtrate was transferred to a separatory funnel and washed with $NaHCO_3$ solution. The organic extract was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The composition of the products was found to be ((R=Me): (R=Br) = 2:1) as determined by ^{1}H NMR.

Scheme S11: Mechanistic Studies:

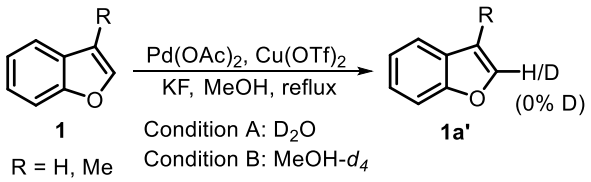
(a) Radical Trap Experiments:



Radical Scavenger	**3a** Yield (%)
TEMPO (1.0 equiv.)	47
TEMPO (3.0 equiv.)	51
BHT (1.0 equiv.)	52
$Ph_2CH{=}CH_2$ (1.0 equiv.)	55

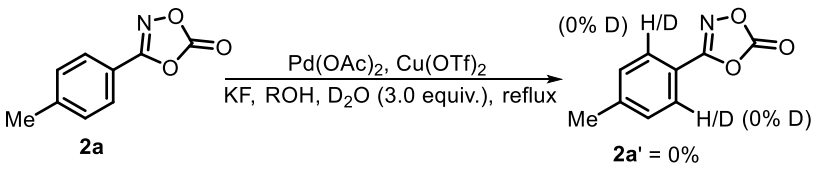
In a Schlenk tube equipped with a stir bar, benzo[*b*]furan (30 mg, 0.25 mmol) was dissolved in MeOH (2 mL). The reaction mixture was degassed with nitrogen for 10 min followed by the addition of $Pd(OAc)_2$ (2.5 mg, 5 mol%), $Cu(OTf)_2$ (90 mg, 1.0 equiv.), KF (22 mg, 1.5 equiv.), 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (88.5 mg, 2.0 equiv.) and radical scavengers (1.0 equiv.). The reaction mixture was stirred at reflux temperature for 6 h. Upon cooling to room temperature, the reaction mixture was diluted with EtOAc and filtered through a pad of celite. The filtrate was transferred to a separatory funnel and washed with $NaHCO_3$. The organic extract was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by a silica gel flash column chromatography (eluting with Petroleum ether: EtOAc (19:1)) to yield the product. Similarly, reactions were performed with increased equivalents (upto 3.0 equivalents) of the radical scavengers and no significant reduction in the yield of the product was observed.

(b) (i) Reversibility of metalation at benzo[*b*]furan:



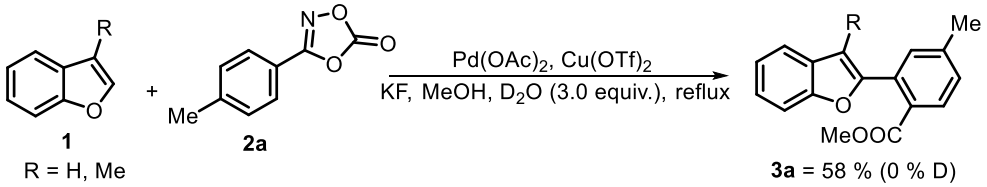
To a Schlenk tube, benzo[*b*]furan **1** (20 mg, 0.17 mmol) was dissolved in MeOH (1 mL) and reaction mixture was degassed with nitrogen for 10 min. Subsequently $Pd(OAc)_2$ (2.0 mg, 5 mol%), $Cu(OTf)_2$ (58.0 mg, 0.17 mmol, 1.0 equiv.), and KF (14.5 mg, 0.25 mmol, 1.5 equiv.) along with D_2O (30 μL, 1.70 mmol) was stirred at reflux temperature for 30 minutes. Upon cooling to room temperature, the reaction mixture was diluted with EtOAc and filtered through a pad of celite. The filtrate was transferred to a separatory funnel and washed with $NaHCO_3$. The organic extract was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was analysed by ^{1}HNMR for the extent of deuteration at the recovered starting material and it showed no deuterium incorporation in the compound **1a'**. This indicated that the C(2)-H activation step at the benzofuran may be irreversible (yield of recovered starting material: 88%).

(b) (ii) Reversibility of metalation at dioxazolone:



In a Schlenk tube, dioxazolone (20 mg, 0.11 mmol) was dissolved in MeOH (1mL). $Pd(OAc)_2$ (1.5 mg, 5 mol%), $Cu(OTf)_2$ (37.7 mg, 0.11 mmol, 1.0 equiv.), and KF (10 mg, 0.17 mmol, 1.5 equiv.) along with D_2O (30 µL, 1.10 mmol) was charged. The reaction mixture was stirred at reflux temperature for 30 min. The resulting mixture was diluted with EtOAc (4 mL) and filtered through a plug of celite. The filtrate was evaporated to dryness under reduced pressure. No starting material **2a** was observed after 30 minutes of refluxing hence no deuterated **2a** was isolated.

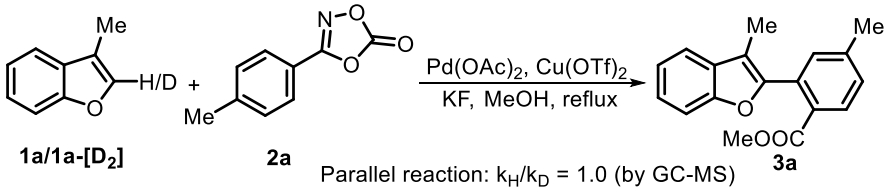
(b) (ii) Reversibility study in C-2 arylation:



To a Schlenk tube, benzo[*b*]furan **1** (20 mg, 0.17 mmol) was dissolved in MeOH (1.0 mL) and reaction mixture was degassed with nitrogen for 10 min. Subsequently $Pd(OAc)_2$ (2.0 mg, 5 mol%), $Cu(OTf)_2$ (58.0 mg, 0.17 mmol, 1.0 equiv.), KF (14.5 mg, 0.25 mmol, 1.5 equiv.) and 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (60 mg, 2.0 equiv.) along with D_2O (30 μL, 1.70 mmol) was stirred at reflux temperature for 30 minutes. Upon cooling to room temperature, the reaction mixture was diluted with EtOAc and filtered through a pad of celite. The filtrate was transferred to a separatory funnel and washed with $NaHCO_3$. The organic extract was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was analysed by ^{1}H-NMR for the extent of deuteration at the recovered starting material and it showed no deuterium incorporation in the compound **3a**.

(c) Kinetic Isotope Effect Studies:

(i) Determination of the kinetic isotope effect (k_H/k_D): (Parallel experiment)



Two parallel reactions were set in two different Schlenk tubes, one having 3-methylbenzo[*b*]furan (0.17 mmol) and other having D_2-3-methylbenzo[*b*]furan (0.17 mmol)

each dissolved in 1.0 mL of MeOH. The reaction mixture was degassed with nitrogen for 10 min. Subsequently $Pd(OAc)_2$ (2.0 mg, 5 mol%), $Cu(OTf)_2$ (58.0 mg, 0.17 mmol, 1.0 equiv.), and KF (14.5 mg, 0.25 mmol, 1.5 equiv.) was added along with dodecane (8.0 μL) as the internal standard. The reaction was stirred at reflux temperature and aliquots of 50 μL were drawn at every 4-minute intervals and the conversions were analysed by GC-MS. The consumption of starting material was plotted with time and k_H/k_D was found to be 1.0 (average of 3 runs). A representative plot is shown below:

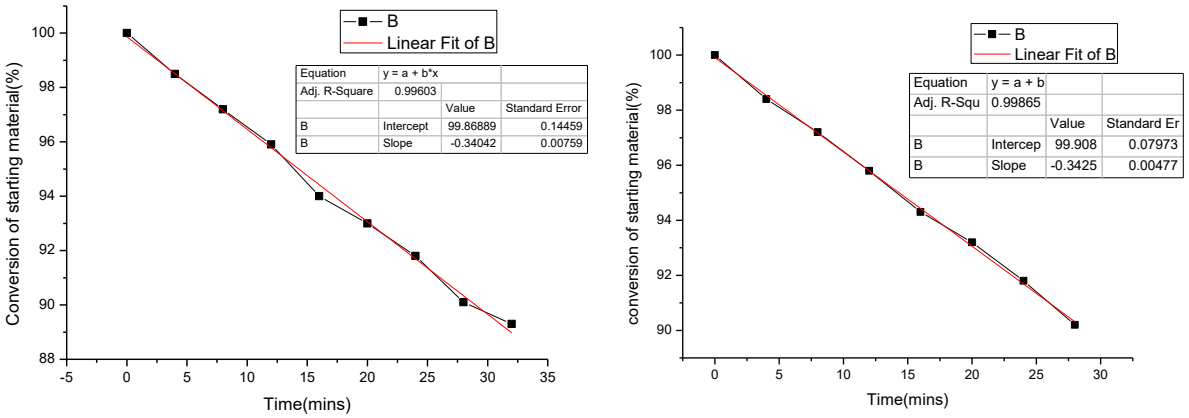


Figure S1: Initial rate measurement w.r.t non-deuterated substrate for the determination of KIE.

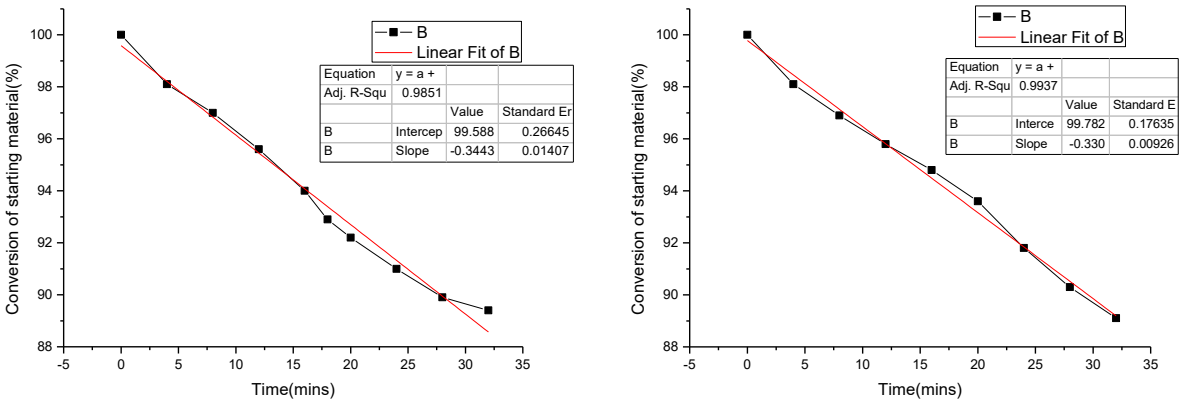
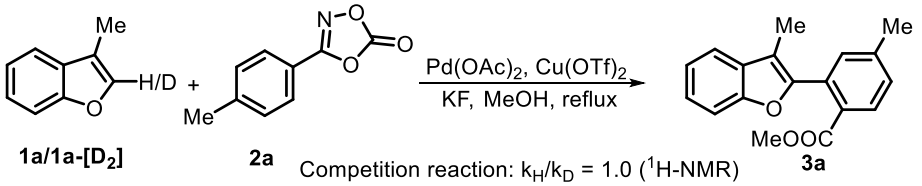


Figure S2: Initial rate measurement w.r.t deuterated substrate for the determination of KIE. Kinetic isotope effect k_H/k_D = 1.0 (Average value of 3 runs)

(ii) Determination of the kinetic isotope effect (k_H/k_D): (Competition experiment)



In a Schlenk tube equipped with a stir bar, C-H and C-D substrates in equimolar amount (0.25 mmol) were taken in same reaction flask and dissolved in MeOH (2.0 mL). The reaction mixture was degassed with nitrogen for 5 min followed by the addition of $Pd(OAc)_2$ (5 mol%), $Cu(OTf)_2$ (1.0 equiv.), KF (1.5 equiv.) and 3-substituted-1,4,2-dioxazol-5-ones (2.0 equiv.). The tube was fitted with a reflux condenser under nitrogen flow. The reaction mixture was allowed to stir at reflux temperature for 15 minutes, followed by dilution with EtOAc and filtered through a short pad of celite. The filtrate was transferred to a separatory funnel and washed with brine. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure and the crude mixture was purified by silica gel flash column chromatography (Petroleum ether: EtOAc (19:1)). The recovered starting materials (C-H and C-D substrates) were analyzed by ^1H NMR and relative integration of the characteristic peaks of the recovered starting materials yielded a value of k_H/k_D= 1.0 (average of 3 experiments).

Scheme S12: Application to Other Heterocycles:

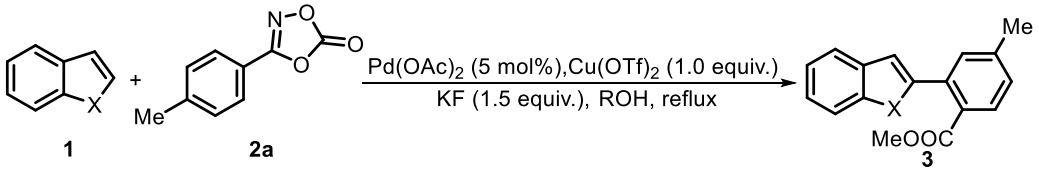
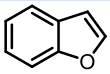
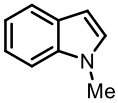
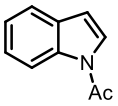
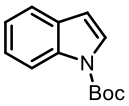
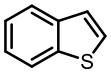
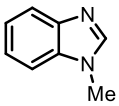
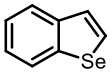
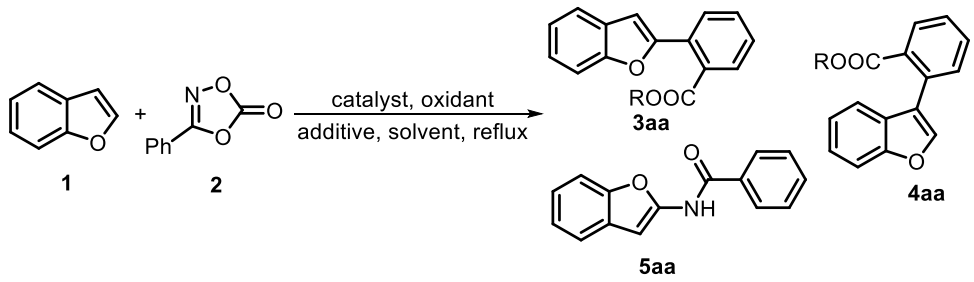


Table S1: Screening of heterocycles:

Entry	Heterocycle	Yield (%) of **3**
1		60
2		-
3		-
4		-
5		58
6		-
7		58

Optimization Studies:

Table S2: Optimization of reaction conditions:[a]



Entry	Conditions	Yield of 3aa (%)[b]
1	$Pd(OAc)_2$ / $Cu(OTf)_2$/ KF/ DCE/ 80 ^oC/ 12 h	NR
2	$Pd(OAc)_2$ / $Cu(OTf)_2$/ KF/ MeOH/ reflux/ 6 h	55
3	$Pd(OAc)_2$ / $Cu(OTf)_2$/ MeOH/ reflux/ 12 h	<10
4	$Cu(OTf)_2$/ KF/ MeOH/ reflux/ 12 h	NR
5	$Pd(OAc)_2$/ MeOH/ reflux/ 12 h	NR
6	**$Pd(OAc)_2$ (5 mol%)/ $Cu(OTf)_2$/ KF/ MeOH/ reflux/ 6 h**	**60**
7	$Pd(OAc)_2$ / AgOTf/ KF/ MeOH/ reflux/ 12 h	41
8	$Pd(OAc)_2$ / AgOTf/ MeOH/ reflux/ 12 h	27
9	$Pd(OAc)_2$ / AgOTf/ KF/ DCE/ reflux/ 12 h	NR
10	$Pd(TFA)_2$ /AgOTf/ KF/ MeOH/ reflux/ 12 h	20
11	$Pd(OAc)_2$ / $Cu(OTf)_2$/ KOAc/ MeOH/ reflux/ 24 h	NR
12	$Pd(OAc)_2$ / $Cu(OTf)_2$/ KF/ DCM/ 50 ^oC/ 12 h	NR
13	$Pd(OAc)_2$ / $Cu(OTf)_2$/ KF/ Toluene/ 100 ^oC/ 12 h	Complex mixture
14	$Pd(OAc)_2$ / $Cu(OTf)_2$/ KF/ Dioxane/ 100 ^oC/ 24 h	NR
15	$Pd(OAc)_2$ / $Cu(OTf)_2$/ KF/ IPA/ 80 ^oC / 12 h	51
16	$Pd(OAc)_2$ / $Cu(OTf)_2$ (2.0 equiv.)/ KF/ MeOH/ reflux/ 12 h	42
17	$Pd(OAc)_2$ / $Cu(OAc)_2$/ KF/ MeOH/ reflux/ 24 h	NR
18	$Pd(OAc)_2$ /AgOAc/ KF/ MeOH/ reflux/ 24 h	NR
19	$Pd(TFA)_2$/ $Cu(OTf)_2$/ KF/ MeOH/ reflux/ 6 h	35
20[c]	$Pd(OAc)_2$ / $Cu(OTf)_2$/ KF/ MeOH/ reflux/ 12 h	NR
21	$Pd(OAc)_2$ / $Cu(OTf)_2$/ KF/ MeOH/ rt/ 12 h	20
22	KF/ MeOH/ reflux/ 12 h	NR
23	$[RhCp^*Cl_2]_2$ (3 mol%)/ $AgSbF_6$ (10 mol%)/ KOAc (1 equiv.)/ DCE/ 80 ^oC/ 12 h	NR
24	$[RhCp^*Cl_2]_2$ (3 mol%)/ $AgSbF_6$ (10 mol%)/ KOAc (1 equiv.)/ MeOH/ reflux/ 12 h	NR

25	$[RhCp^*Cl_2]_2$ (3 mol%)/ $AgSbF_6$ (10 mol%)/ MeOH/ reflux/ 12 h	NR
26	$[Ru(p\text{-cym})Cl_2]_2$ (3 mol%)/ $AgSbF_6$ (10 mol%)/ KOAc (1 equiv.)/ DCE/ 80 ^oC/ 12 h	NR
27	$[Ru(p\text{-cym})Cl_2]_2$ (3 mol%)/ $AgSbF_6$ (10 mol%)/ KOAc (1 equiv.)/ MeOH/ reflux/ 12 h	NR
28	$[Ru(p\text{-cym})Cl_2]_2$ (3 mol%)/ $AgSbF_6$ (10 mol%)/ KF (1 equiv.)/ MeOH/ reflux/ 12 h	Complex mixture
29	$Co(OAc)_2$ (3 mol%)/ $AgSbF_6$ (10 mol%)/ $Cu(OTf)_2$ (1 equiv)/ DCE/ 80 ^oC/ 12 h	NR
30	$Co(acac)_2$ (3 mol%)/ $AgSbF_6$ (10 mol%)/ AgOAc (1 equiv)/ MeOH/ reflux/ 12 h	NR
31	$Cp^*Co(CO)I_2$ (3 mol%)/ $AgSbF_6$ (10 mol%)/ NaOAc (1 equiv)/ DCE/ 80 ^oC/ 12 h	NR
32	$Cp^*Co(CO)I_2$ (3 mol%)/ $AgSbF_6$ (10 mol%)/ NaOAc (1 equiv)/ MeOH/ reflux/ 12 h	NR

[a]Unless otherwise noted, all reactions were carried out using **1** (0.15 mmol), **2a** (0.22 mmol), catalyst (10 mol %), oxidant (1.0 equiv.) in the presence of additive (1.5 equiv.) in a solvent (1.0 mL) at reflux temperature for 12 h under N_2. [b]Isolated yields after column chromatography. [c]Reaction under oxygen atmosphere. NR = No reaction.

References:

1) (a) V. Ramella, Z. He, C.–G. Daniliuc and A. Studer, *Eur. J. Org. Chem*., 2016, 2268; (b) S. Lips, B.–A. Frontana-Uribe, M. Dörr, D. Schollmeyer, R. Franke and S. –R. Waldvogel, *Chem. -Eur. J.*, 2018, **24**, 6057.

2) N. Sun, P. Huang, Y. Wang, W. Mo, B. Hu, Z. Shen and X. Hu, *Tetrahedron*, 2013, **69**, 4429.

3) S. Fredrich, A. Bonasera, V. Valderrey and S. Hecht, *J. Am. Chem. Soc.*, 2018, **140**, 6432.

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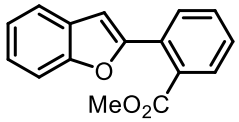
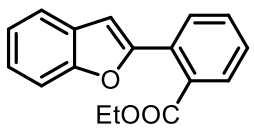
7) M. V. Pham and N. Cramer, *Angew. Chem., Int. Ed.*, 2014, **53**, 14575.

Analytical data for new compounds

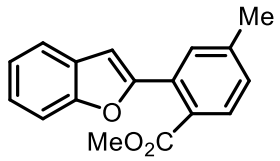
Methyl 2-(benzofuran-2-yl)benzoate (3aa): Yield: 61% (25 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 7.8Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.29 (t, *J* = 7.3 Hz,1H), 7.22 (d, *J* = 7.4 Hz, 1H), 6.93 (s, 1H), 3.81 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 168.40, 153.05, 131.47, 130.96, 128.94, 128.64, 128.58, 125.02, 123.14, 121.44, 111.18, 105.49, 52.63; **IR** (KBr, cm^{-1}): 3404, 2408, 2362, 1733, 1598, 1289,1094, 844, 750; **ESI-HRMS**: Calculated for $C_{16}H_{12}NaO_3^+$ $[M+Na]^+$ 275.0679, found 275.0667.



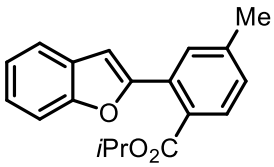
Ethyl 2-(benzofuran-2-yl)benzoate(3ab): Yield: 52% (22 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (t, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 2H), 7.33 – 7.22 (m, 3H), 6.93 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.13 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 163.24, 155.05, 131.46, 130.94, 129.46, 129.18, 128.71, 124.46, 122.91, 121.15, 111.13, 104.34, 61.47, 13.99; **IR** (KBr, cm^{-1}): 3394, 2935, 2382, 1707, 1658, 1196, 1075, 823, 749; **ESI-HRMS**: Calculated for $C_{17}H_{14}NaO_3^+$ $[M+Na]^+$ 289.0835, found 289.0839.



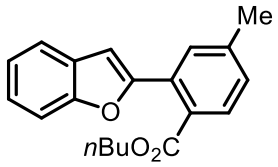
Methyl 2-(benzofuran-2-yl)-4-methylbenzoate (3ac): Yield: 58% (26 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.54 (s, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.26 – 7.20 (m, 2H), 6.90 (s, 1H), 3.78 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 169.20, 154.96, 141.56, 129.86, 129.72, 129.40, 128.93, 128.14, 124.42, 122.87, 121.15, 111.08, 104.35, 52.36, 21.45; **IR** (KBr, cm^{-1}): 3405, 2775, 2362, 1733, 1598, 1289, 1094, 844, 750; **ESI-HRMS**: Calculated for $C_{17}H_{14}NaO_3^+$ $[M+Na]^+$ 289.0835, found 289.0834.



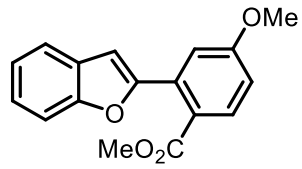
Isopropyl 2-(benzofuran-2-yl)-4-methylbenzoate (3ad): Yield: 55% (27 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 1.6 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.22 (m, 3H), 6.91 (s, 1H), 5.17 (m, 1H), 2.43 (s, 3H), 1.12 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 168.23, 155.33, 154.96, 141.28, 130.10, 129.78, 129.73, 129.45, 129.19, 128.94, 124.25, 122.80, 121.03, 111.17, 104.18, 68.78, 21.61; **IR** (KBr, cm^{-1}): 3397, 2980, 2934, 2369, 1719, 1601, 1281, 1255, 1096, 805, 748; **ESI-HRMS**: Calculated for $C_{19}H_{18}NaO_3^+$ $[M+Na]^+$ 317.1148, found 317.1145.



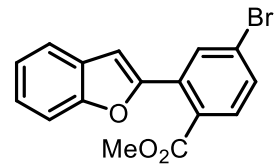
Butyl 2-(benzofuran-2-yl)-4-methylbenzoate (3ae): Yield: 51% (26 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.55 (s, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 6.92 (s, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 2.47 (s, 3H), 1.49 – 1.41 (m, 2H), 1.23 – 1.12 (m, 2H), 0.77 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 168.81, 155.22, 155.03, 141.44, 130.07, 129.94, 129.79, 129.45, 128.95, 128.72, 124.31, 122.83, 121.06, 111.13, 104.26, 65.22, 30.47, 21.43, 19.00, 13.56; **IR** (KBr, cm^{-1}): 3405, 2963, 2369, 1719, 1456, 1286, 1096, 936, 776, 748; **ESI-HRMS**: Calculated for $C_{20}H_{20}NaO_3^+$ $[M+Na]^+$ 331.1305, found 331.1300.



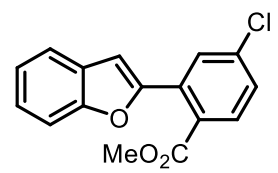
Methyl 2-(benzofuran-2-yl)-4-methoxybenzoate (3af): Yield: 60% (29 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.6 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 2.5 Hz, 2H), 6.93 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.90 (s, 1H), 3.87 (s, 3H), 3.74 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 168.46, 161.67, 154.75, 132.30, 132.05, 128.85, 124.51, 122.89, 121.21, 114.95, 114.05, 111.12, 104.80, 99.98, 55.59, 52.24; **IR** (KBr, cm^{-1}): 3390, 2936, 2369, 1708, 1596, 1239, 1112, 1029, 934, 752; **ESI-HRMS**: Calculated for $C_{17}H_{14}NaO_4^+$ $[M+Na]^+$ 305.0784, found 305.0774.



Methyl 2-(benzofuran-2-yl)-4-bromobenzoate (3ag): Yield: 48% (27 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.63 – 7.55 (m, 3H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.27 – 7.21 (m, 1H), 6.96 (s, 1H), 3.81 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 168.40, 153.05, 131.47, 128.94, 128.58, 125.02, 123.14, 121.44, 111.18, 105.49, 52.63; **IR** (KBr, cm^{-1}): 3405, 2958, 2367, 1711, 1632, 1456, 1280, 1109, 952, 734; **ESI-HRMS**: Calculated for $C_{16}H_{11}BrNaO_3^+$ $[M+Na]^+$ 352.9784 and 354.9763, found 352.9781 and 354.9760.



Methyl 2-(benzofuran-2-yl)-4-chlorobenzoate (3ah): Yield: 45% (22 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 2.1 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.40 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.31 (t, *J*= 7.3 Hz, 1H), 7.25 (m, 1H), 6.97 (s, 1H), 3.81 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 168.40, 155.13, 153.05, 137.22, 131.47, 130.96, 129.10, 128.94, 128.64, 128.58, 125.02, 123.14, 121.44, 111.18, 105.49, 52.63; **IR** (KBr, cm^{-1}): 3401, 2920, 2454, 2334, 1778, 1610,



1426, 1257, 1092, 1052, 752; **ESI-HRMS**: Calculated for $C_{16}H_{11}ClNaO_3^+$ $[M+Na]^+$ 309.0289, found 309.0286.

Methyl 2-(benzofuran-2-yl)-4-fluorobenzoate (3ai): Yield: 45% (20 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.79 (dd, *J* = 8.6, 5.7 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.38 – 7.32 (m, 1H), 7.29 – 7.26 (m, 1H), 7.16 (td, *J* = 8.2, 2.6 Hz, 1H), 7.01 (d, *J* = 1.0 Hz, 1H), 3.85 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 168.31, 155.06(d, *J* = 227. 8 Hz), 153.14, 132.00(d, *J* = 9.2 Hz), 128.64, 124.99, 123.11, 121.42, 119.14, 116.11(d, *J* = 23.9 Hz), 115.87(d, *J* = 21.6 Hz), 111.16, 105.47, 77.31, 52.55; **^{19}F NMR** (376 MHz, $CDCl_3$): δ –108.01; **IR** (KBr, cm^{-1}): 3391, 2775, 2361, 1731, 1601, 1335, 1205, 1084, 823, 776; **ESI-HRMS**: Calculated for $C_{16}H_{11}FNaO_3^+$ $[M+Na]^+$ 293.0584, found 293.0581.

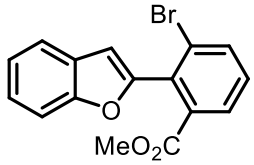
Methyl 2-(benzofuran-2-yl)-5-methylbenzoate (3aj): Yield: 64% (28 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 7.3 Hz, 1H), 7.51 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.28 – 7.17 (m, 3H), 6.85 (s, 1H), 3.78 (s, 3H), 2.40 (s, 3H); **(For peak clarity ^{1}H NMR in MeOH-*d*$_4$) ^{1}H NMR** (400 MHz, Methanol-*d*$_4$): δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.53 (s, 1H), 7.50 – 7.44 (m, 2H), 7.31 (dt, *J* = 7.3, 1.3 Hz, 1H), 7.25 (dt, *J* = 7.5, 1.1 Hz, 1H), 6.99 (s, 1H), 3.82 (s, 3H), 2.45 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 169.50, 154.99, 138.91, 131.71, 130.79, 129.88, 128.96, 126.85, 124.30, 122.84, 121.05, 111.02, 103.83, 52.44, 21.14; **IR** (KBr, cm^{-1}): 3411, 2923, 2860, 1752, 1694, 1450, 1278, 1159, 893, 750; **ESI-HRMS**: Calculated for $C_{17}H_{14}NaO_3^+$ $[M+Na]^+$ 289.0835, found 289.0834.

Methyl 2-(benzofuran-2-yl)-5-methoxybenzoate (3ak): Yield: 61% (30 mg), Physical appearance: pale-yellow gel, TLC R_f 0.30 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.6 Hz, 1H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.30 – 7.17 (m, 3H), 7.07 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.81 (s, 1H), 3.88 (s, 3H), 3.80 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 169.08, 159.75, 154.82, 132.22, 130.65, 129.08, 124.13, 122.83, 122.31, 120.95, 117.14, 114.27, 110.96, 103.27, 55.63, 52.56, **IR** (KBr, cm^{-1}): 3381, 2927, 2365, 2334, 1721, 1654, 1267, 1053, 803, 763; **ESI-HRMS**: Calculated for $C_{17}H_{14}NaO_4^+$ $[M+Na]^+$ 305.0784, found 305.0781.

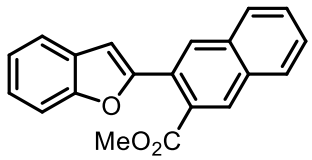
Methyl 2-(benzofuran-2-yl)-6-methylbenzoate (3al): Yield: 57% (25 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.8

Hz, 1H), 7.28 (ddd, *J* = 8.2, 7.3, 1.5 Hz, 1H), 7.25 – 7.19 (m, 2H), 6.91 (s, 1H), 3.87 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 169.50, 154.99, 138.91, 131.71, 130.79, 129.88, 128.96, 126.85, 124.30, 122.84, 121.05, 111.02, 103.83, 52.44, 21.14; **IR** (KBr, cm^{-1}): 3410, 2928, 2860, 1740, 1690, 1450, 1159, 893, 704; **ESI-HRMS**: Calculated for $C_{17}H_{14}NaO_3^+$ $[M+Na]^+$ 289.0835, found 289.0834.

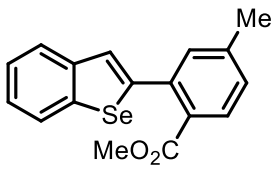
Methyl 2-(benzofuran-2-yl)-3-bromobenzoate (3an): Yield: 61% (35 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 2.7 Hz, 1H), 7.73 – 7.63 (m, 2H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 6.96 (s, 1H), 3.85 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 167.87, 153.42, 134.03, 132.31, 130.30, 128.72, 124.86, 123.10, 121.31, 111.12, 104.98, 52.75; **IR** (KBr, cm^{-1}): 3399, 2923, 2851, 2347, 1721, 1601, 1329, 1158, 890, 725; **ESI-HRMS**: Calculated for $C_{16}H_{11}BrNaO_3^+$ $[M+Na]^+$ 352.9784 and 354.9763, found 352.9772 and 354.9752.



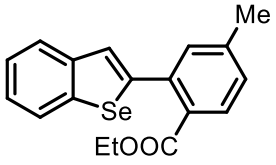
Methyl 3-(benzofuran-2-yl)-2-naphthoate (3am): Yield: 48% (25 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 8.24 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.67 – 7.56 (m, 3H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.27 (m, 1H), 7.01 (s, 1H), 3.87 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 167.27, 135.52, 132.50, 131.07, 129.36, 128.23, 128.15, 127.76, 127.41, 126.64, 125.23, 52.24; **IR** (KBr, cm^{-1}): 3410, 2950, 2373, 1828,1721, 1529, 1450, 1267, 1128, 868, 751; **ESI-HRMS**: Calculated for $C_{20}H_{14}NaO_3^+$ $[M+Na]^+$ 325.0835, found 325.0833.



Methyl 2-(benzoselenophen-2-yl)-4-methylbenzoate (3ao): Yield: 58% (21 mg), Physical appearance: colorless oil, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99 – 7.95 (m, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.79 (s, 1H), 7.39 – 7.35 (m, 1H), 7.34 – 7.29 (m, 3H), 7.28 – 7.25 (m, 1H), 3.46 (s, 3H), 2.46 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 167.92, 142.47, 141.56, 140.92, 140.74, 137.97, 132.28, 130.46, 128.60, 125.82, 124.81, 124.43, 124.36, 51.86, 21.45; **IR** (KBr, cm^{-1}): 3394, 2923, 1718, 1607, 1436, 1256, 1022, 761, 728; **ESI-HRMS**: Calculated for $C_{17}H_{14}NaO_2Se^+$ $[M+Na]^+$ 353.0057, found 353.0052.



Ethyl 2-(benzo[b]selenophen-2-yl)-4-methylbenzoate (3ap): Yield: 41% (18 mg), Physical appearance: colorless oil, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.9 Hz,2H), 7.77 (s, 1H), 7.38 – 7.30 (m, 3H), 7.26 (s, 2H), 3.98-3.72 (m, 2H), 2.46 (s, 3H), 0.68 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 168.71, 155.21, 154.98, 141.46, 130.01, 129.91, 129.79, 129.45, 128.93, 128.64, 124.33, 122.83, 121.08, 111.10, 104.26, 61.27, 21.43, 13.99; **IR** (KBr, cm^{-1}): 3407, 2927, 2361, 1708, 1630,



1421, 1278, 1020, 757, 620; **ESI-HRMS**: Calculated for $C_{18}H_{16}NaO_2Se^+$ $[M+Na]^+$ 367.0208, found 367.0204.

Methyl 2-(benzoselenophen-2-yl)-4-chlorobenzoate (3aq): Yield: 41% (16 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99 – 7.94 (m, 2H), 7.84 (s, 1H), 7.50 (dd, J = 8.4, 2.2 Hz, 1H), 7.47 (d, J = 2.1 Hz, 1H), 7.38 – 7.31 (m, 3H), 3.47 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 167.12, 141.02, 140.81, 139.66, 139.25, 137.99, 131.72, 131.51, 129.80, 128.06, 125.90, 124.64, 124.59, 124.08, 52.15; **IR** (KBr, cm^{-1}): 3393, 2924, 2369, 1708, 1638, 1421, 1285, 1020, 759, 647; **ESI-HRMS**: Calculated for $C_{16}H_{11}ClNaO_2Se^+$ $[M+Na]^+$ 372.9514, found 372.9503.

Methyl 4-methyl-2-(3-methylbenzofuran-2-yl)benzoate (3a): Yield: 60% (26 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82 (d, J = 7.9 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.45 – 7.40 (m, 1H), 7.36 (d, J= 1.8 Hz, 1H), 7.31 – 7.21 (m, 3H), 3.68 (s, 3H), 2.44 (s, 3H), 2.25 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 169.33, 155.51, 154.33, 141.46, 134.74, 129.65, 129.63, 129.17, 128.03, 126.41, 124.31, 120.60, 111.28, 104.18, 52.35, 21.76, 21.44; **IR** (KBr, cm^{-1}): 3400, 2927, 2852, 2373, 1720, 1639, 1259, 1033, 805, 773; **ESI-HRMS**: Calculated for $C_{18}H_{16}NaO_3^+$ $[M+Na]^+$ 303.0992, found 303.0987.

Methyl 4-methyl-2-(4-methylbenzofuran-2-yl)benzoate (3b): Yield: 60% (26 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67 (d, J= 7.9 Hz, 1H), 7.56 (s, 1H), 7.49 (d, J = 7.9 Hz, 1H), 7.33 – 7.30 (m, 1H), 7.26 (d, J = 7.9 Hz, 1H), 7.09 (d, J = 7.9 Hz, 1H), 6.89 (d, J = 0.9 Hz, 1H), 3.82 (s, 3H), 2.50 (s, 3H), 2.47 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 169.33, 155.51, 154.33, 141.46, 134.74, 129.65, 129.63, 129.17, 128.03, 126.41, 124.31, 120.60, 111.28, 104.18, 52.35, 21.76, 21.44; **IR** (KBr, cm^{-1}): 3405, 2863, 1712, 1684, 1354, 1296, 1209, 1101, 840, 784, 767; **ESI-HRMS**: Calculated for $C_{18}H_{16}NaO_3^+$ $[M+Na]^+$ 303.0992, found 303.0990.

Methyl 2-(4-bromobenzofuran-2-yl)-4-methylbenzoate (3c): Yield: 52% (20 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72 (d, J = 7.9 Hz, 1H), 7.68 (s, 1H), 7.55 (d, J = 1.5 Hz, 1H), 7.48 (d, J = 8.3 Hz, 1H), 7.39 (dd, J = 8.3, 1.7 Hz, 1H), 7.31 (d, J = 1.3 Hz, 1H), 6.90 (d, J = 1.0 Hz, 1H), 3.82 (s, 3H), 2.48 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 170.88, 154.36, 142.21, 135.68, 130.49, 129.50, 127.87, 125.09, 124.57, 123.01, 121.17, 111.11, 103.82, 52.46, 19.46; **IR** (KBr, cm^{-1}): 2926, 2862, 2378, 1726, 1609, 1438, 1289, 1096, 1051, 833, 779; **ESI-HRMS**: Calculated for $C_{17}H_{13}BrNaO_3^+$ $[M+Na]^+$ 366.9940 and 368.9920, found 366.9938 and 368.9919.

Methyl 2-(4-methoxybenzofuran-2-yl)-4-methylbenzoate (3d): Yield: 55% (22 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.56 (s, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.04 (s, 1H), 6.91 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.88 (s, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 2.47 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 169.24, 156.01, 155.71, 150.13, 141.52, 129.89, 129.73, 129.68, 129.46, 129.35, 128.07, 113.28, 111.53, 104.50, 103.44, 55.93, 52.37, 21.46; **IR** (KBr, cm^{-1}): 3410, 2922, 2854, 1723, 1609, 1449, 1278, 1103, 825, 724; **ESI-HRMS**: Calculated for $C_{18}H_{16}NaO_4^+$ $[M+Na]^+$ 319.0941, found 319.0938.

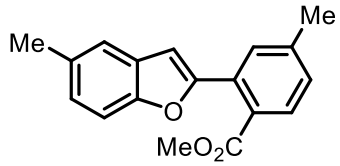
Methyl 4-methyl-2-(7-methylbenzofuran-2-yl)benzoate (3e): Yield: 42% (18 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.9 Hz, 1H), 7.55 (s, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.23 (s, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.10 – 7.05 (m, 1H), 6.90 (s, 1H), 3.78 (s, 3H), 2.52 (s, 3H), 2.44 (s, 3H); **(For peak clarity ^{1}H NMR in MeOH-*d*$_4$) ^{1}H NMR** (400 MHz, Methanol-*d*$_4$): δ 7.64 (s, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.10 – 7.07 (m, 1H), 7.01 (s, 1H), 3.80 (s, 3H), 2.52 (s, 3H), 2.47 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 169.43, 154.64, 154.15, 141.41, 129.88, 129.65, 129.57, 129.29, 128.38, 128.24, 125.31, 122.92, 121.29, 118.60, 104.44, 52.27, 21.45, 15.03; **IR** (KBr, cm^{-1}): 3406, 2925, 2837, 2352, 1721, 1601, 1423, 1289, 763, 733; **ESI-HRMS**: Calculated for $C_{18}H_{16}NaO_3^+$ $[M+Na]^+$ 303.0992, found 303.0991.

Methyl 2-(4,7-dimethylbenzofuran-2-yl)-4-methylbenzoate (3f): Yield: 55% (22 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.54 (s, 1H), 7.27 – 7.21 (m, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.93 (m, 2H), 3.78 (s, 3H), 2.50 (s, 3H), 2.47 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 169.54, 154.22, 153.90, 141.36, 129.58, 129.54, 129.19, 128.22, 128.17, 125.20, 123.10, 118.47, 103.08, 76.76, 52.25, 21.45, 18.37, 14.79; **IR** (KBr, cm^{-1}): 3403, 2924, 2360, 1609, 1443, 1263, 1099, 776, 744; **ESI-HRMS**: Calculated for $C_{19}H_{18}NaO_3^+$ $[M+Na]^+$ 317.1148, found 317.1145.

Methyl 2-(4,6-dimethylbenzofuran-2-yl)-4-methylbenzoate (3g): Yield: 64% (26 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.55 (s, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.12 (s, 1H), 6.88 (d, *J* = 3.5 Hz, 2H), 3.80 (s, 3H), 2.51 (s, 3H), 2.45 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 169.45, 155.38, 153.84, 141.41, 134.71, 130.52, 130.07, 129.59, 129.07, 128.00, 126.28, 124.73, 108.69, 102.85,

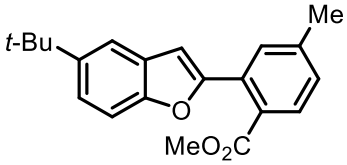
52.34, 21.70, 21.44, 18.58; **IR** (KBr, cm^{-1}): 3390, 2927, 2378, 1781, 1609, 1438, 1289, 1096, 833, 779; **ESI-HRMS**: Calculated for $C_{19}H_{18}NaO_3^+$ $[M+Na]^+$ 317.1148, found 317.1147.

Methyl 2-(5-(methyl)benzofuran-2-yl)-4-methylbenzoate (3h): Yield: 65% (28 mg),



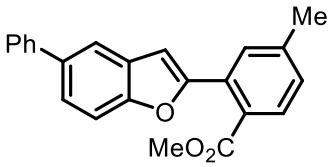
Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.41 (s, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.12 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.87 (s, 1H), 3.81 (s, 3H), 2.47 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 169.33, 155.00, 153.52, 141.47, 132.29, 129.93, 129.70, 129.63, 129.28, 129.03, 128.12, 125.70, 120.94, 110.56, 104.09, 52.34, 21.44, 21.35; **IR** (KBr, cm^{-1}): 3391, 2775, 2361, 1701, 1610, 1336, 1284, 1091, 823, 776; **ESI-HRMS**: Calculated for $C_{18}H_{16}NaO_3^+$ $[M+Na]^+$ 303.0992, found 303.0989.

Methyl 2-(5-(tert-butyl)benzofuran-2-yl)-4-methylbenzoate (3i): Yield: 58% (23 mg),



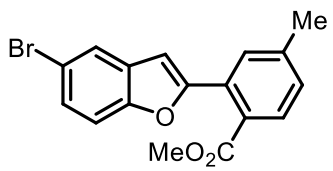
Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 8.3, 2.6 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.56 (s, 1H), 7.46 – 7.35 (m, 2H), 7.28 – 7.23 (m, 1H), 6.90 (d, *J* = 0.9 Hz, 1H), 3.83 (s, 3H), 2.47 (s, 3H), 1.40 (d, *J* = 6.1 Hz, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 169.30, 154.98, 153.31, 145.91, 141.47, 130.02, 129.71, 129.62, 129.24, 128.09, 122.44, 117.32, 110.35, 104.54, 52.37, 34.73, 31.86, 21.46; **IR** (KBr, cm^{-1}): 3394, 2923, 2364, 1717, 1605, 1469, 1261, 1116, 873, 750, 669; **ESI-HRMS**: Calculated for $C_{21}H_{22}NaO_3^+$ $[M+Na]^+$ 345.1461, found 345.1455.

Methyl 4-methyl-2-(5-phenylbenzofuran-2-yl)benzoate (3j): Yield: 51% (18 mg), Physical



appearance: white solid, M.P 100-102 ^oC; TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.60 (s, 1H), 7.58 – 7.53 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.41 – 7.34 (m, 1H), 7.32 – 7.29 (m, 1H), 6.98 (s, 1H), 3.84 (s, 3H), 2.49 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 169.12, 155.69, 154.69, 141.68, 141.63, 136.63, 129.92, 129.78, 129.51, 127.45, 126.88, 124.18, 119.66, 111.17, 104.53, 52.39, 21.46; **IR** (KBr, cm^{-1}): 3405, 2958, 2369, 1719, 1621, 1468, 1285, 936, 767; **ESI-HRMS**: Calculated for $C_{23}H_{18}NaO_3^+$ $[M+Na]^+$ 365.1148, found 365.1142.

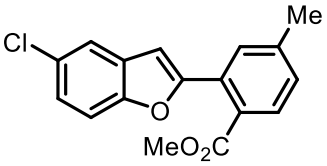
Methyl 2-(5-bromobenzofuran-2-yl)-4-methylbenzoate (3l): Yield: 60% (22 mg), Physical



appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 2.0 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.24 (s, 1H), 3.56 (s, 3H), 2.47 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 168.77, 156.43, 153.76, 141.79, 130.90, 130.12, 129.92, 129.82, 129.51, 128.15, 127.27, 123.73, 115.92, 112.52, 103.75, 52.37, 21.43; **IR** (KBr, cm^{-1}): 3399, 2923, 2356, 1721, 1601, 1328, 1273, 1054, 890, 752; **ESI-HRMS**:

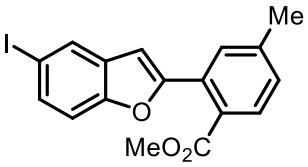
Calculated for $C_{17}H_{13}BrNaO_3^+$ $[M+Na]^+$ 366.9940 and 368.9920, found 366.9938 and 368.9919.

Methyl 2-(5-chlorobenzofuran-2-yl)-4-methylbenzoate (3k): Yield: 60% (24 mg), Physical



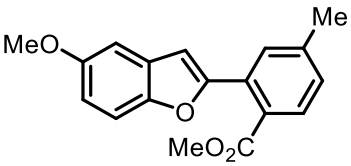
appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 2.1 Hz, 1H), 7.55 (s, 1H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.28 – 7.24 (m, 1H), 6.87 (s, 1H), 3.81 (s, 3H), 2.48 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 168.78, 156.57, 141.78, 130.10, 129.91, 129.80, 128.14, 124.58, 120.67, 112.03, 103.91, 52.37, 21.43; **IR** (KBr, cm^{-1}): 3414, 3030, 2854, 2352, 1623, 1459, 1055,908, 750; **ESI-HRMS**: Calculated for $C_{17}H_{13}ClNaO_3^+$ $[M+Na]^+$ 323.0445, found 323.0442.

Methyl 2-(5-iodobenzofuran-2-yl)-4-methylbenzoate (3m): Yield: 45% (17 mg), Physical



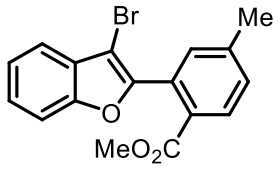
appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz,$CDCl_3$): δ 7.96 (d, *J* = 1.8 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.58 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.55 (s, 1H), 7.32 – 7.30 (m, 1H), 7.28 – 7.27 (m, 2H), 6.85 (s, 1H), 3.81 (s, 3H), 2.48 (s, 3H); **(For peak clarity ^{1}H NMR in MeOH-*d*$_4$) ^{1}H NMR** (400 MHz, Methanol-*d*$_4$): δ 7.80 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.62 (s, 1H), 7.43 (s, 2H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.00 (s, 1H), 3.79 (s, 3H), 2.48 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 169.50, 154.99, 154.85, 138.91, 131.71, 130.79, 129.88, 128.96, 126.85, 124.30, 122.84, 121.05, 111.02, 103.83, 52.44, 21.14; **IR** (KBr, cm^{-1}): 3393, 2925, 1734, 1445,1261, 1097, 1040, 803, 776; **ESI-HR**MS: Calculated for $C_{17}H_{13}INaO_3^+$ $[M+Na]^+$ 414.9802, found 414.9798.

Methyl 2-(5-methoxybenzofuran-2-yl)-4-methylbenzoate (3n): Yield: 60% (26 mg),



Physical appearance: pale-yellow gel, TLC R_f 0.30 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz,$CDCl_3$): δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.56 (s, 1H), 7.39 (d, *J* = 8.9 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.08 (d, *J* = 2.6 Hz, 1H), 6.92 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.87 (s, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 2.47 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 169.24, 156.01, 155.71, 150.13, 141.52, 129.89, 129.73, 129.68, 129.46, 129.35, 128.07, 113.28, 111.53, 104.50, 103.44, 55.93, 52.37, 21.46; **IR** (KBr, cm^{-1}): 3402, 2894, 2798, 1718, 1610, 1436, 1267, 1100, 851, 714; **ESI-HRMS**: Calculated for $C_{18}H_{16}NaO_4^+$ $[M+Na]^+$ 319.0941, found 319.0938.

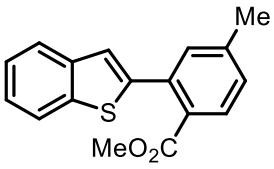
Methyl 2-(3-bromobenzofuran-2-yl)-4-methylbenzoate(3o): Yield: 61% (24 mg), Physical



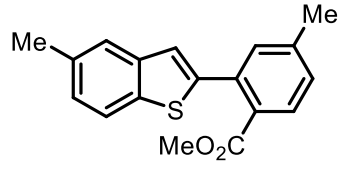
appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.57 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.33

– 7.28 (m, 1H), 7.26 – 7.22 (m, 1H), 6.92 (s, 1H), 3.80 (s, 3H), 2.46 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 169.19, 155.05, 154.96, 141.56, 129.86, 129.71, 129.40, 128.93, 128.15, 124.42, 122.87, 121.15, 111.08, 104.35, 52.35, 21.44; **IR** (KBr, cm^{-1}):3400, 2927, 2352, 1723, 1628, 1441, 1292, 1053, 805, 746; **ESI-HRMS**: Calculated for $C_{17}H_{13}BrNaO_3^+$ $[M+Na]^+$ 366.9940 and 368.9920, found 366.9938 and 368.9919.

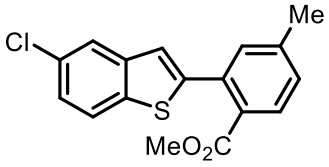
Methyl 2-(benzo[*b*]thiophen-2-yl)-4-methylbenzoate (3q): Yield: 58% (29 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 – 7.87 (m, 2H), 7.47 – 7.41 (m, 1H), 7.38 – 7.29 (m, 4H), 7.27 (s, 1H), 3.45 (s, 3H), 2.45 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 169.50, 154.99, 138.91, 131.71, 130.79, 129.88, 128.96, 126.85, 124.30, 122.84, 121.05, 111.02, 103.83, 52.44, 21.14; **IR** (KBr, cm^{-1}): 3405, 2923, 2352, 1721, 1601, 1423, 1289, 1088, 763, 733; **ESI-HRMS**: Calculated for $C_{17}H_{15}O_2S^+$ $[M+H]^+$ 283.0787 found 283.0782.



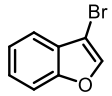
Methyl 4-methyl-2-(5-methylbenzo[*b*]thiophen-2-yl)benzoate (3r): Yield: 62% (23 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.76 (s, 1H), 7.34 – 7.14 (m, 7H), 3.51 (s, 3H), 2.50 (s, 3H), 2.48 (s, 3H); **(For peak clarity ^{1}H NMR in DMSO-d_6) ^{1}H NMR** (500 MHz, DMSO-d_6): δ 7.91 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.58 (s, 1H), 7.39 (d, J = 7.9 Hz, 1H), 7.30 (s, 1H), 7.22 (d, J = 8.0, 1H), 7.13 (s, 1H), 3.43 (s, 3H), 2.43 (s, 3H), 2.35 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 168.15, 142.34, 139.34, 137.06, 136.76, 136.48, 133.95, 132.31, 130.39, 128.60, 128.54, 126.00, 123.07, 122.32, 122.20, 51.85, 21.44; **IR** (KBr, cm^{-1}): 3410, 2927, 2386, 1717, 1608, 1425, 1292, 1121, 1086, 779; **ESI-HRMS**: Calculated for $C_{18}H_{17}O_2S^+$ $[M+H]^+$ 297.0944, found 297. 0941.



Methyl 4-methyl-2-(5-chlorobenzo[*b*]thiophen-2-yl)benzoate (3s): Yield: 57% (21 mg), Physical appearance: pale-yellow gel, TLC R_f 0.40 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.93 (d, J= 7.8 Hz, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.38 (s, 1H), 7.36 – 7.28 (m, 3H), 7.22 (s, 1H), 3.54(s, 3H), 2.46 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 166.82, 143.22, 142.24, 136.54, 135.25, 131.17, 129.90, 127.93, 125.71, 124.35, 52.11, 21.63; **IR** (KBr, cm^{-1}): 3397, 2977, 2842, 1721, 1601, 1268, 1035, 804, 743; **ESI-HRMS**: Calculated for $C_{17}H_{13}ClNaO_2S^+$ $[M+Na]^+$ 339.0217, found 339.0202.

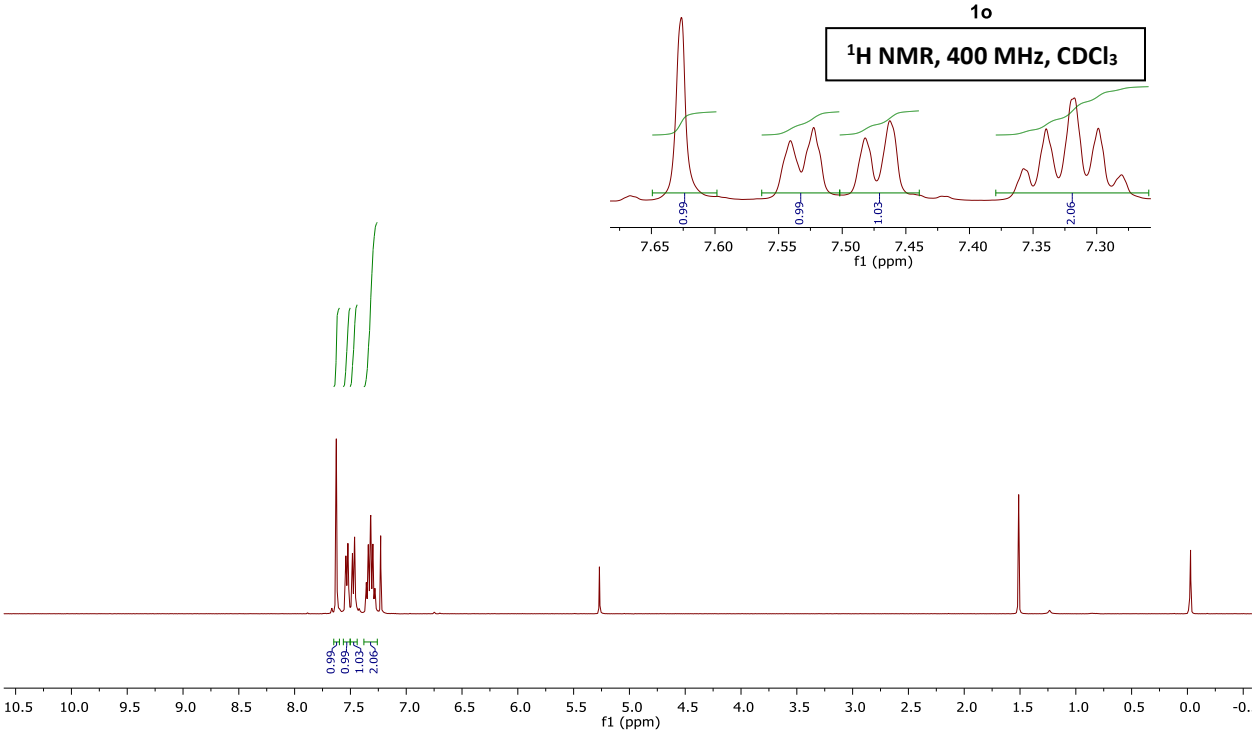


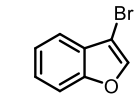
^{1}H and ^{13}C-NMR Spectra of new compounds:



1o

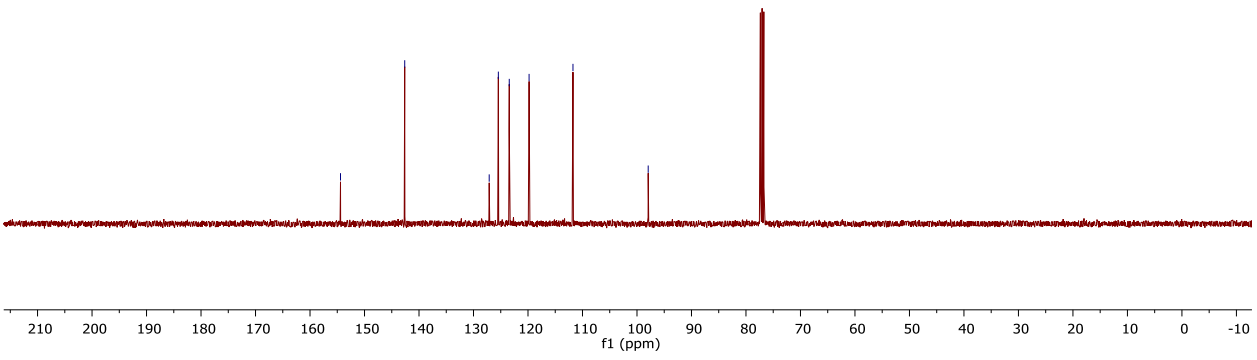
^{1}H NMR, 400 MHz, $CDCl_3$

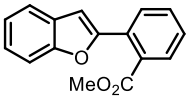




1o

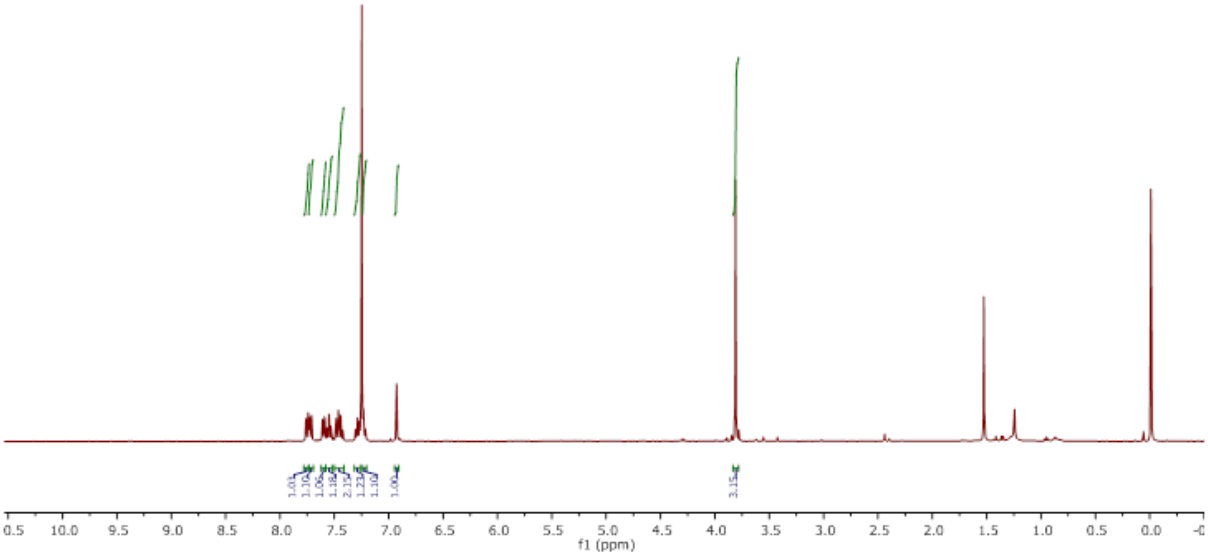
^{13}C NMR, 101 MHz, $CDCl_3$

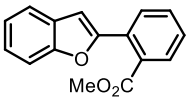




3aa

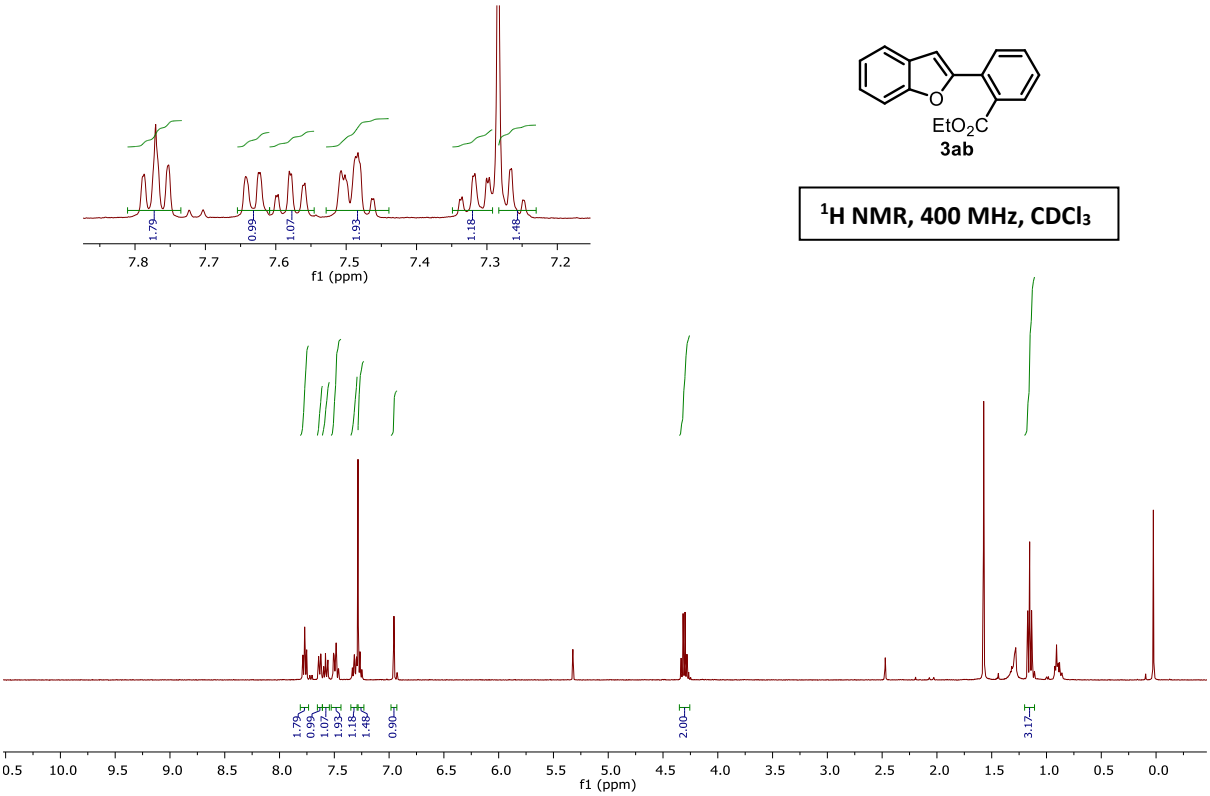
^{1}H NMR, 400 MHz, $CDCl_3$

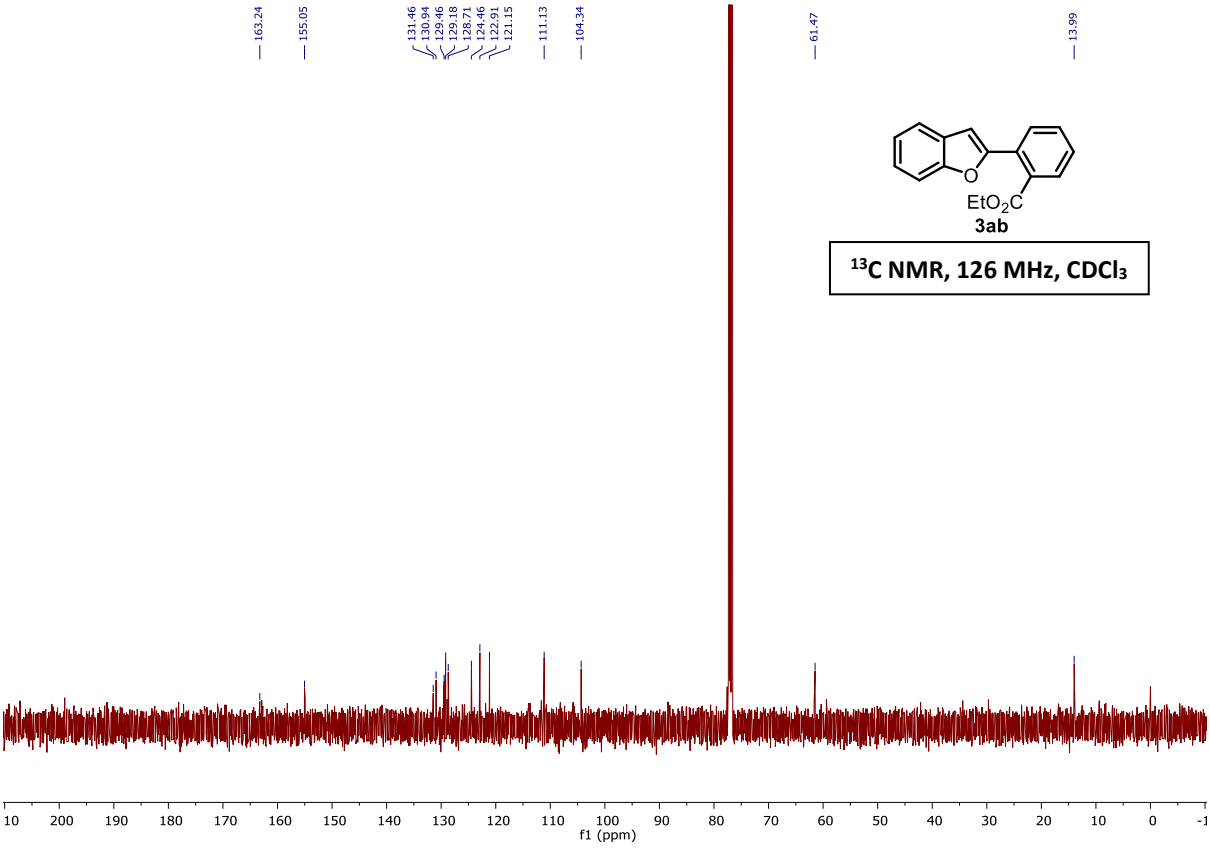


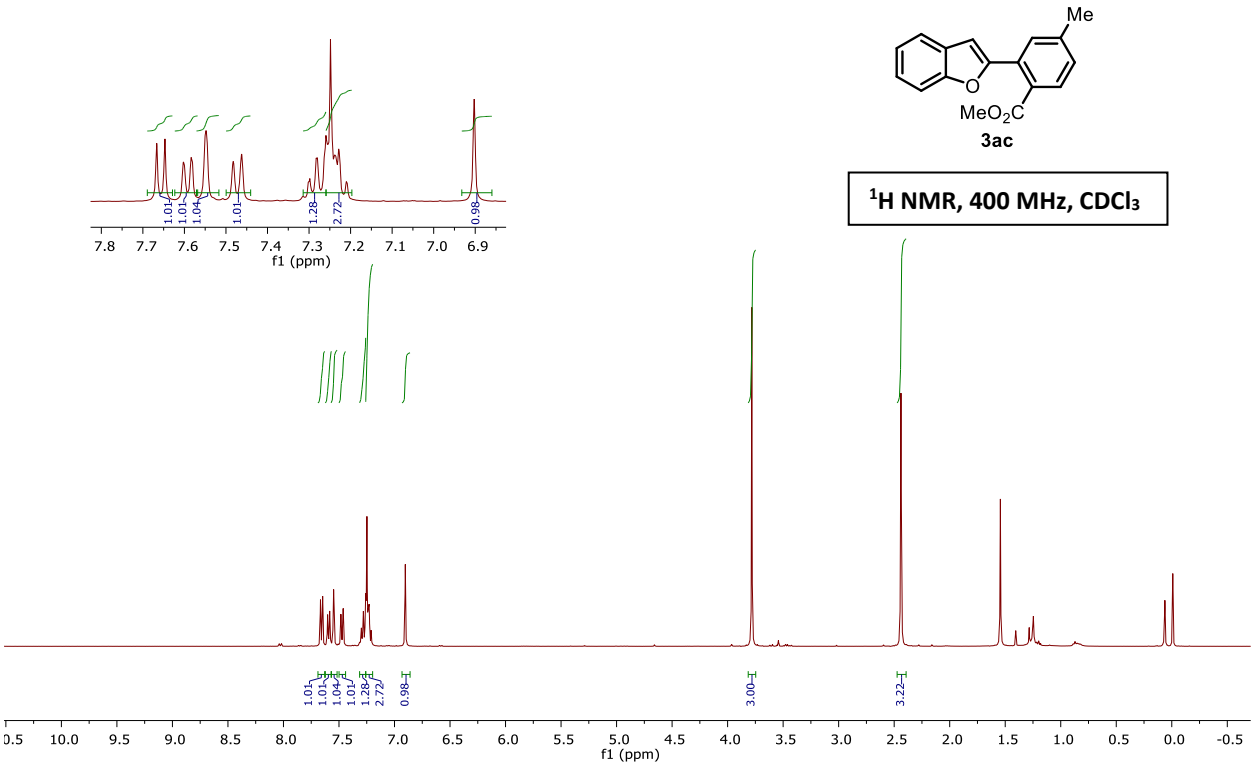


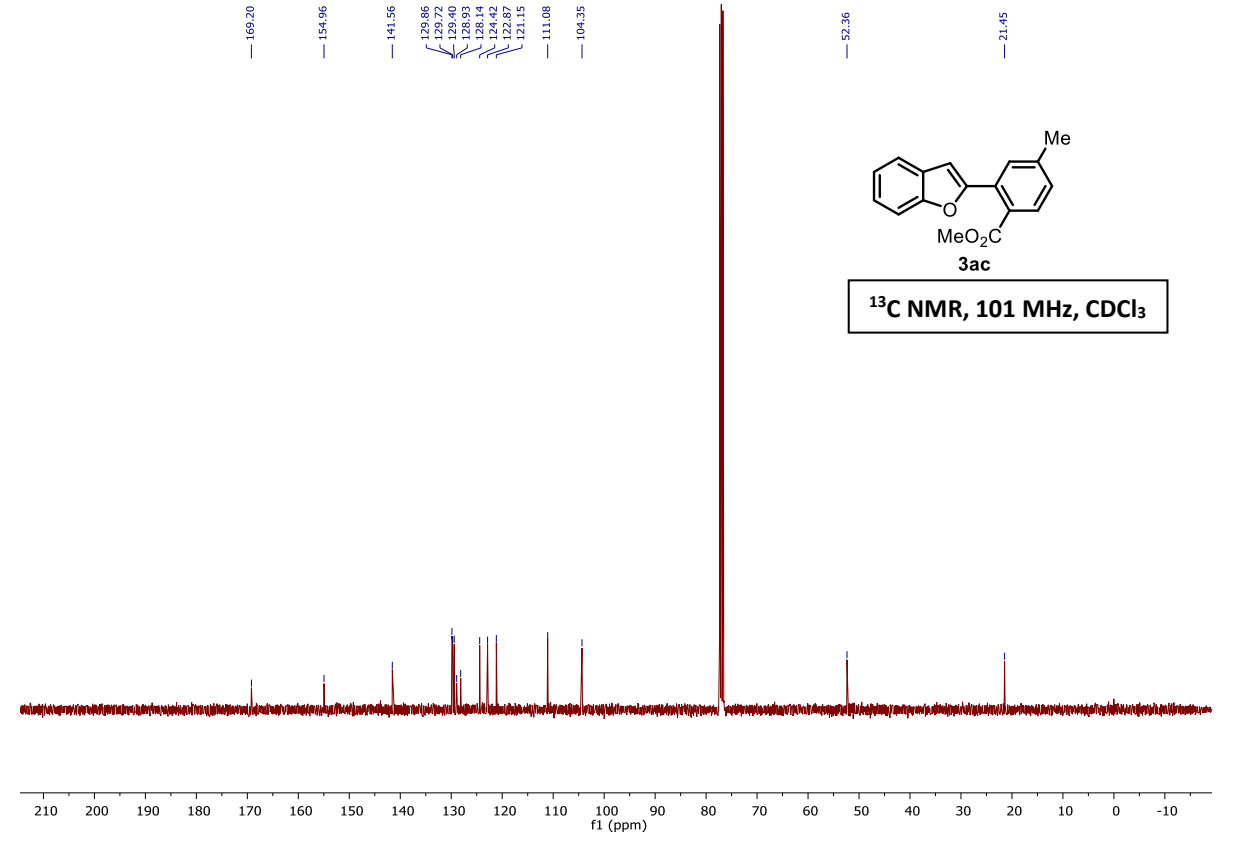
3aa

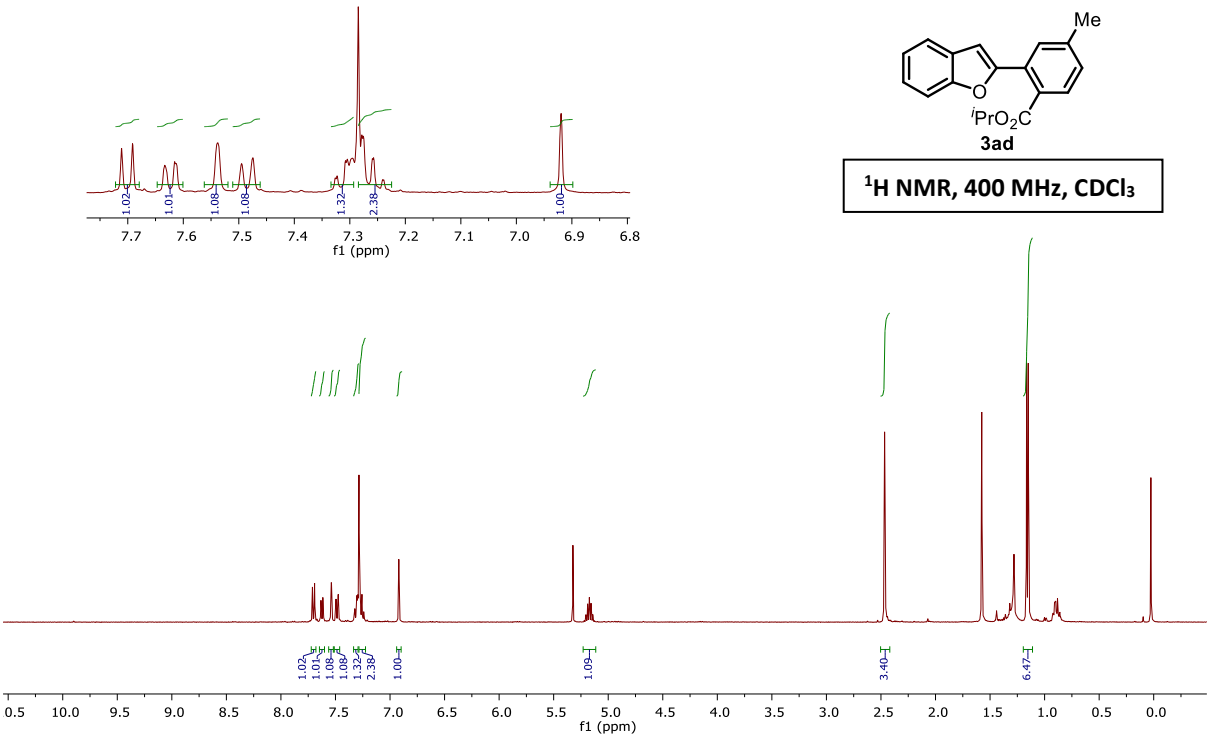
^{13}C NMR, 101 MHz, $CDCl_3$

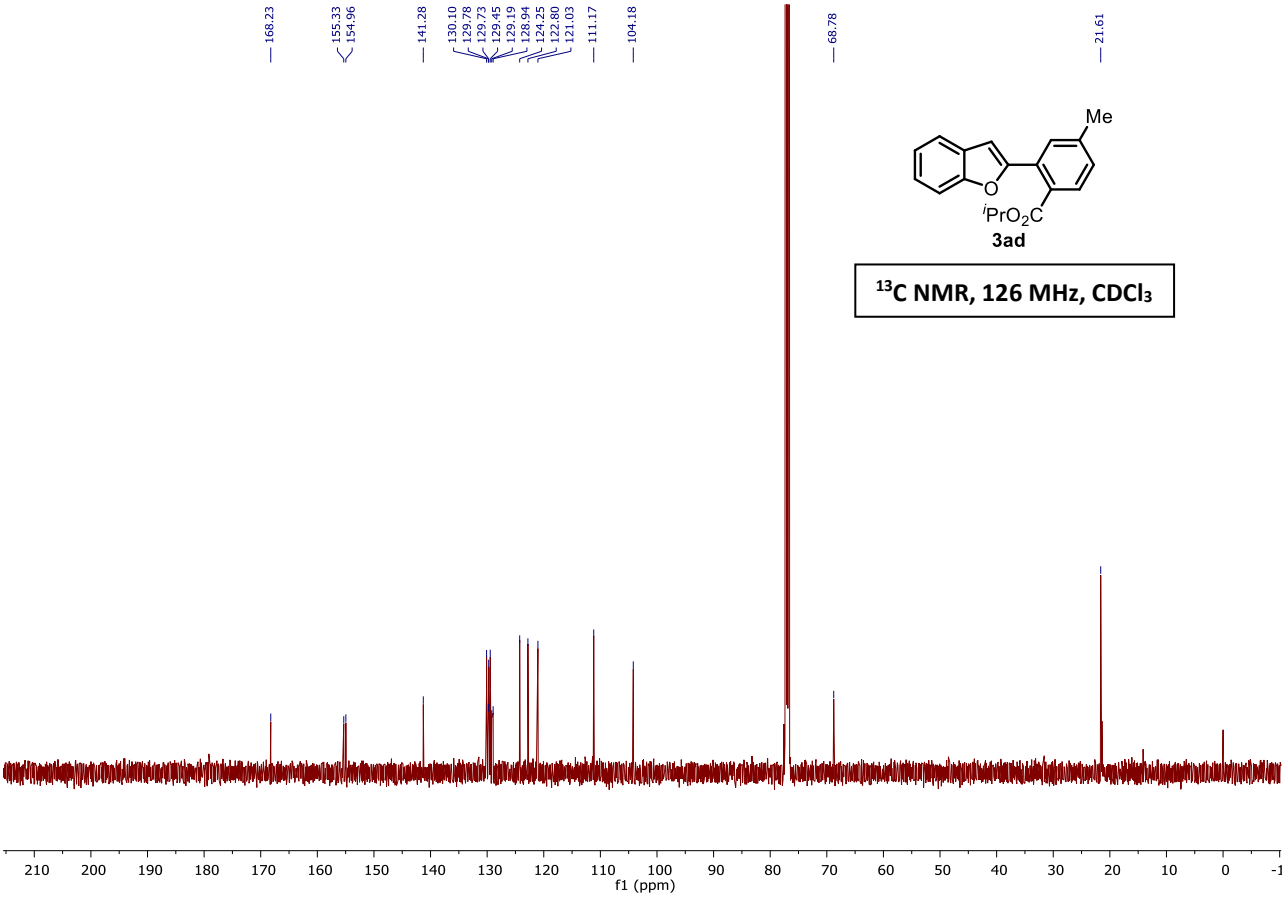

EtO2C
3ab
1H NMR, 400 MHz, CDCl3
f1 (ppm)

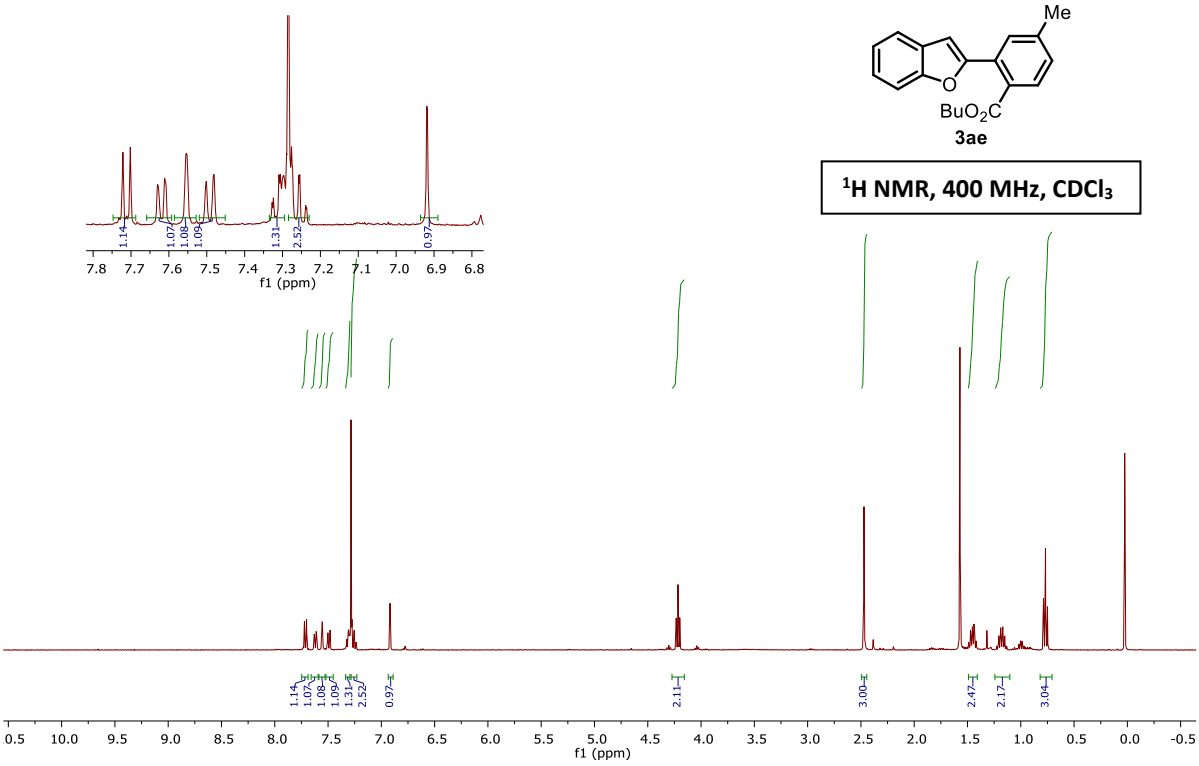

163.24
155.05
131.46
130.94
129.46
129.18
128.71
124.46
122.91
121.15
111.13
104.34
61.47
13.99
EtO2C
3ab
13C NMR, 126 MHz, CDCl3
f1 (ppm)

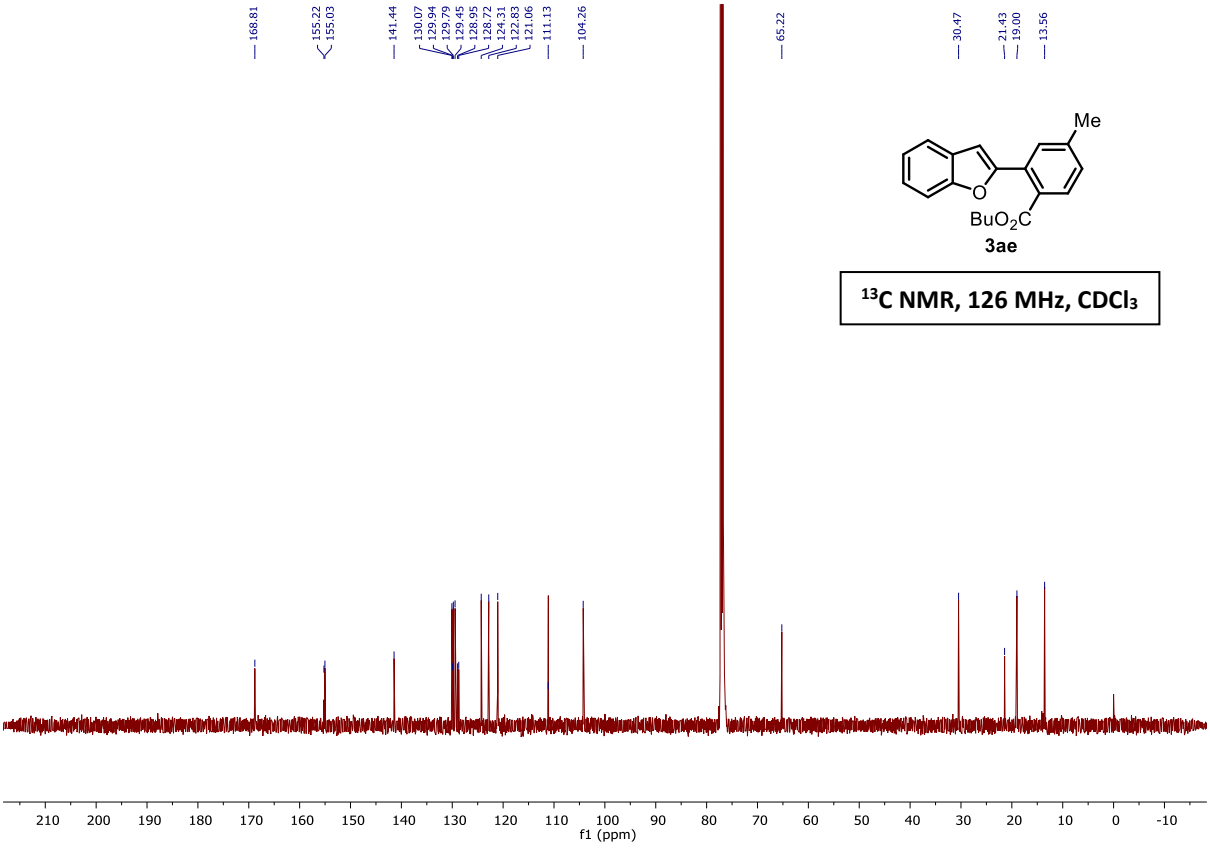

Me
O
MeO2C
3ac
1H NMR, 400 MHz, CDCl3
f1 (ppm)

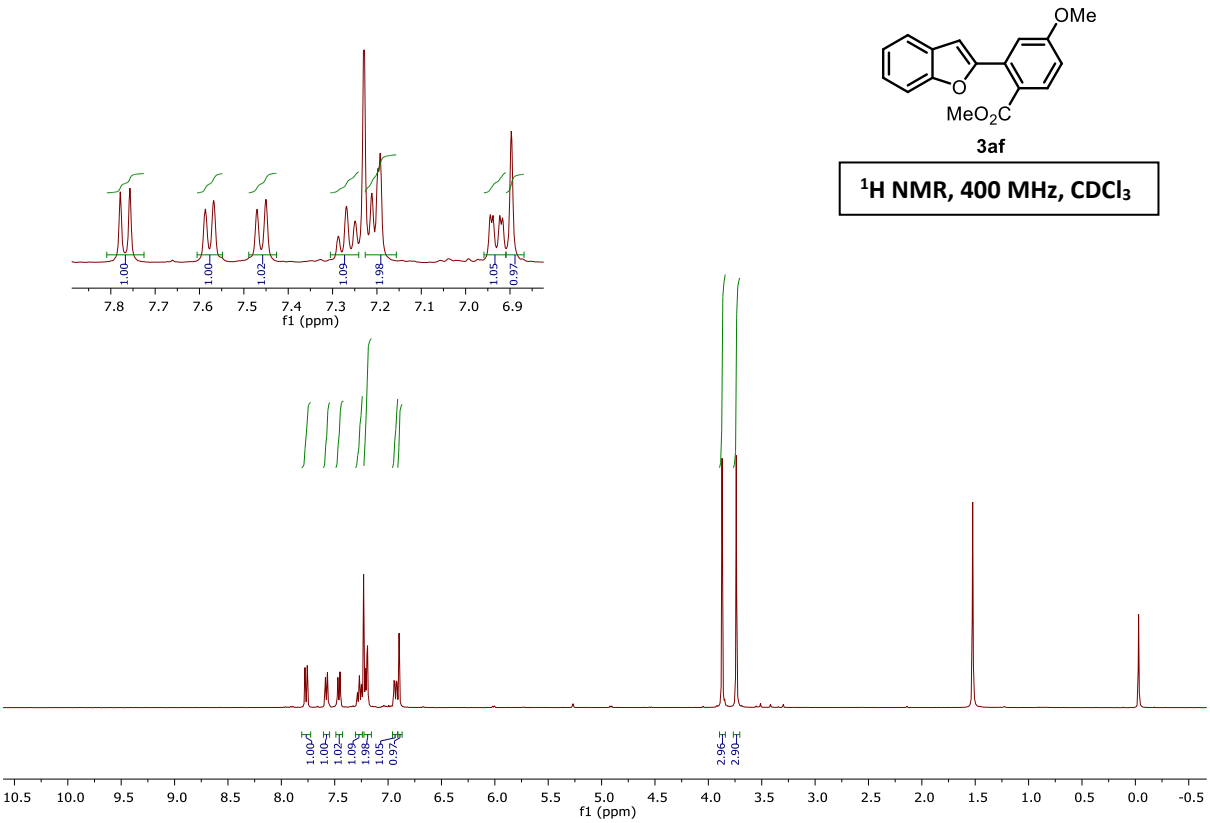

169.20
154.96
141.56
129.86
129.72
129.40
128.93
128.14
124.42
122.87
121.15
111.08
104.35
52.36
21.45
Me
O
MeO2C
3ac
13C NMR, 101 MHz, CDCl3
f1 (ppm)

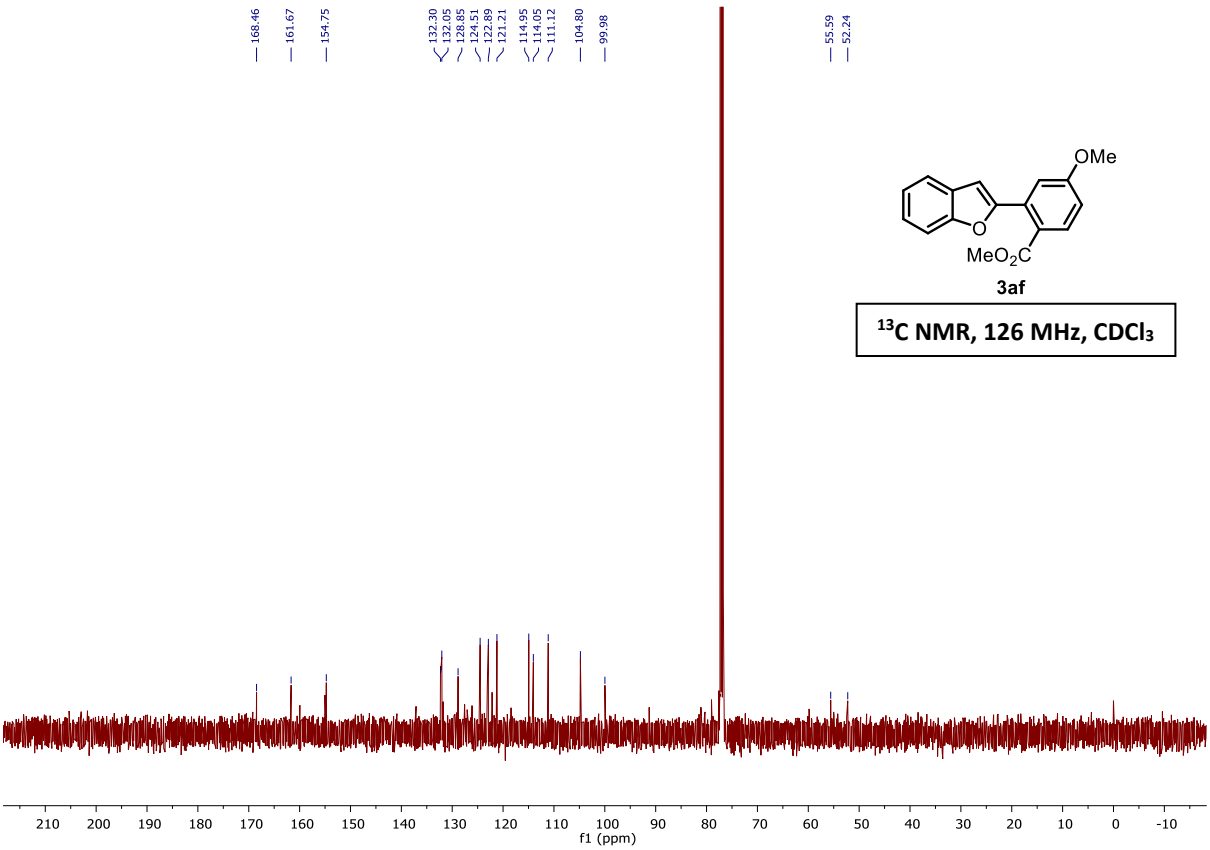

Me
O
iPrO2C
3ad
1H NMR, 400 MHz, CDCl3
f1 (ppm)

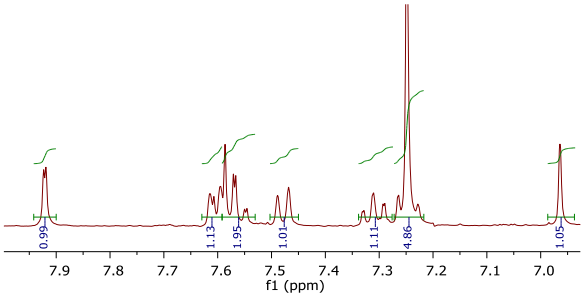

168.23
155.33
154.96
141.28
130.10
129.78
129.73
129.45
129.19
128.94
124.25
122.80
121.03
111.17
104.18
68.78
21.61
Me
O
iPrO2C
3ad
13C NMR, 126 MHz, CDCl3
f1 (ppm)

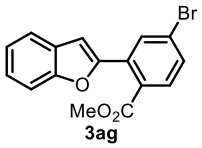

Me
BuO2C
3ae
1H NMR, 400 MHz, CDCl3
f1 (ppm)


Me
BuO2C
3ae
13C NMR, 126 MHz, CDCl3
f1 (ppm)


OMe
MeO2C
3af
1H NMR, 400 MHz, CDCl3
f1 (ppm)

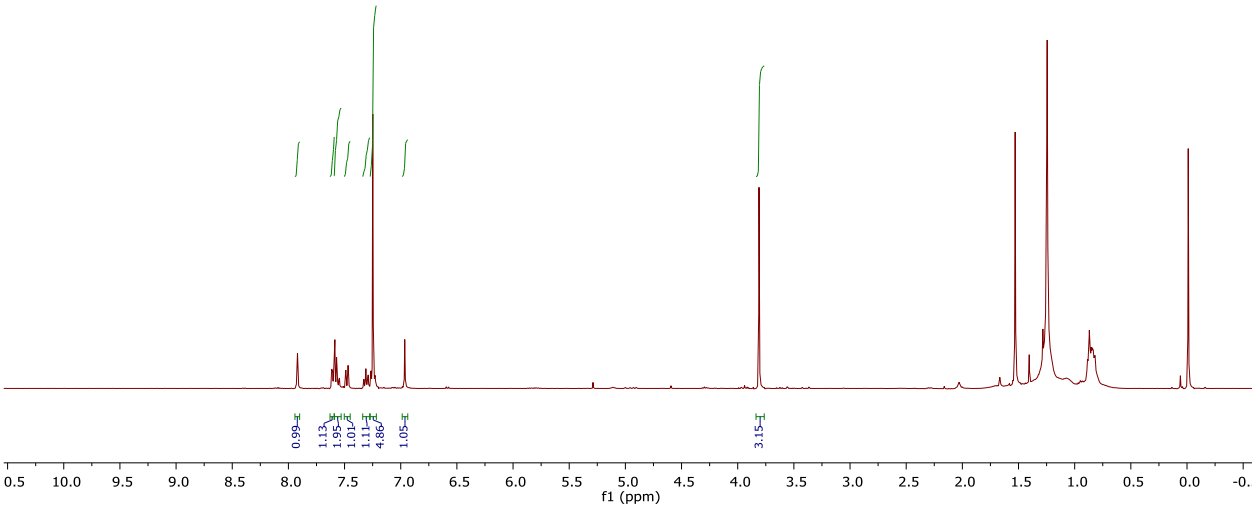

168.46
161.67
154.75
132.30
132.05
128.85
124.51
122.89
121.21
114.95
114.05
111.12
104.80
99.98
55.59
52.24
OMe
MeO2C
3af
13C NMR, 126 MHz, CDCl3
f1 (ppm)

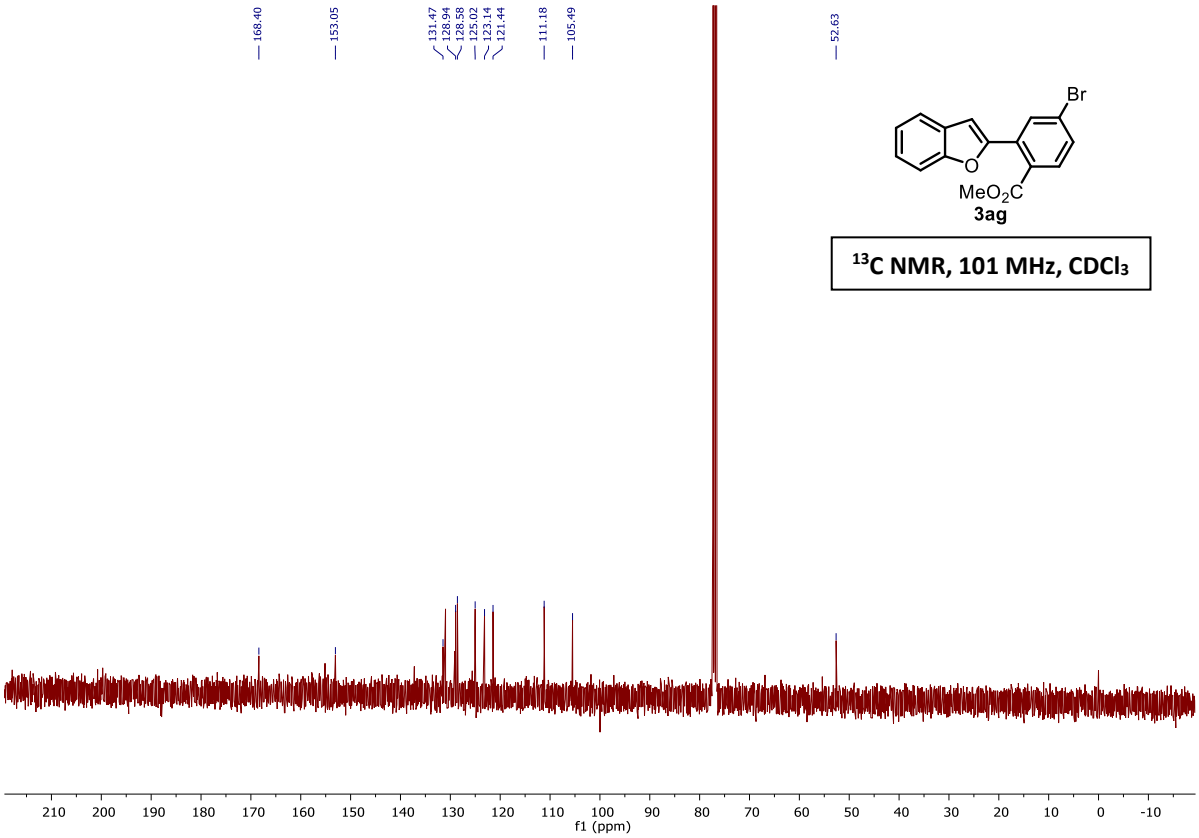




3ag

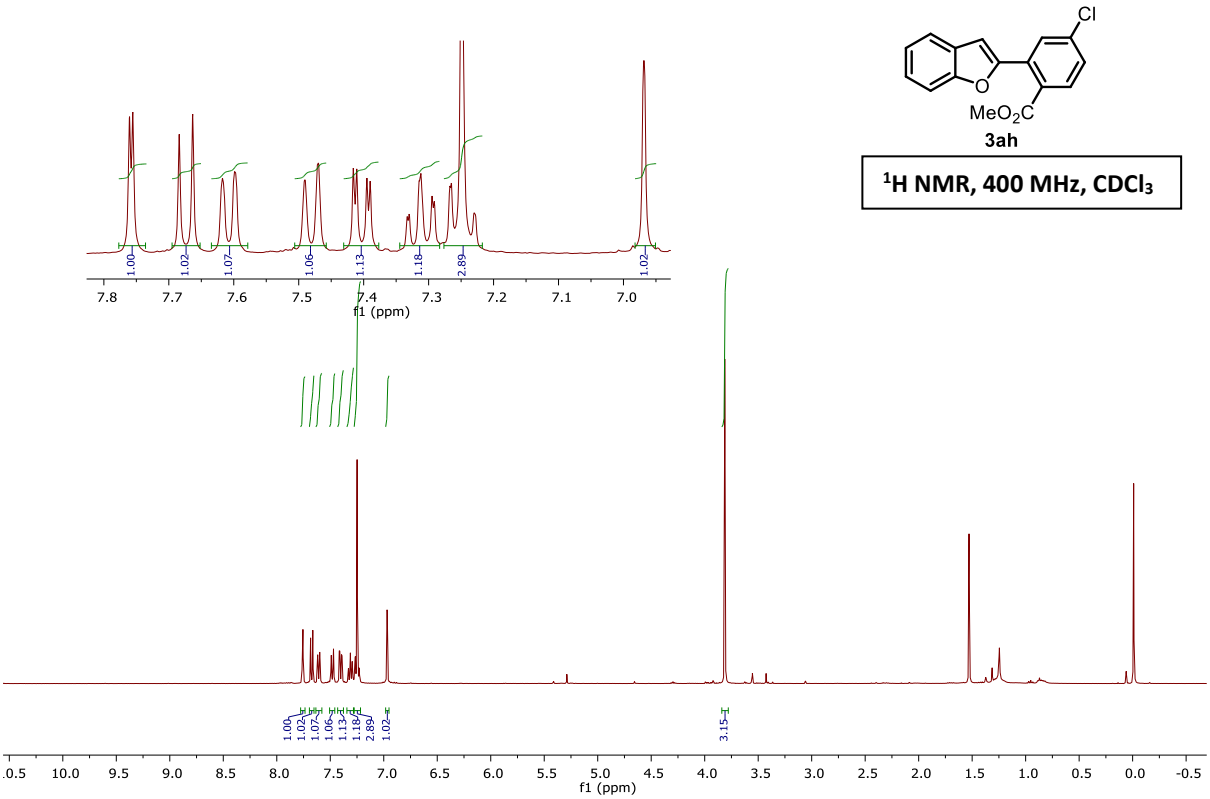
^{1}H NMR, 400 MHz, $CDCl_3$

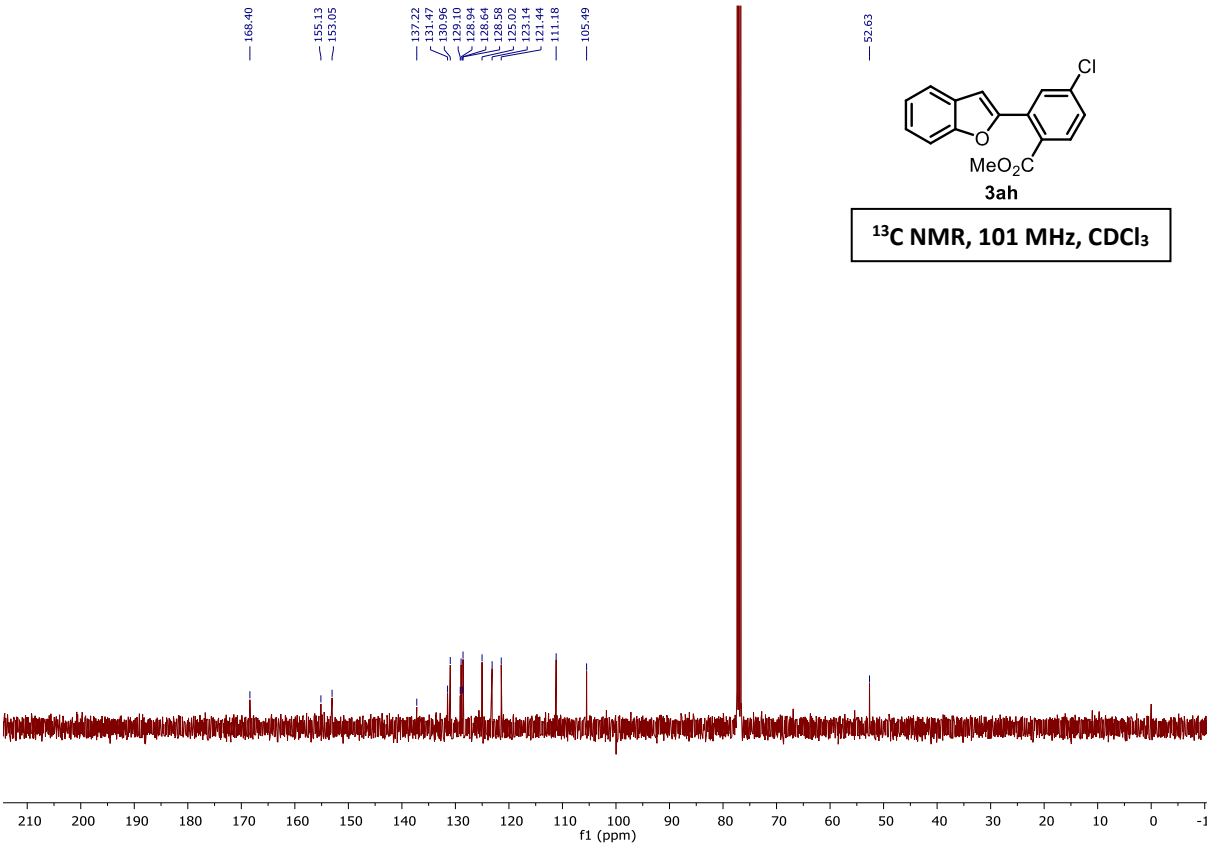


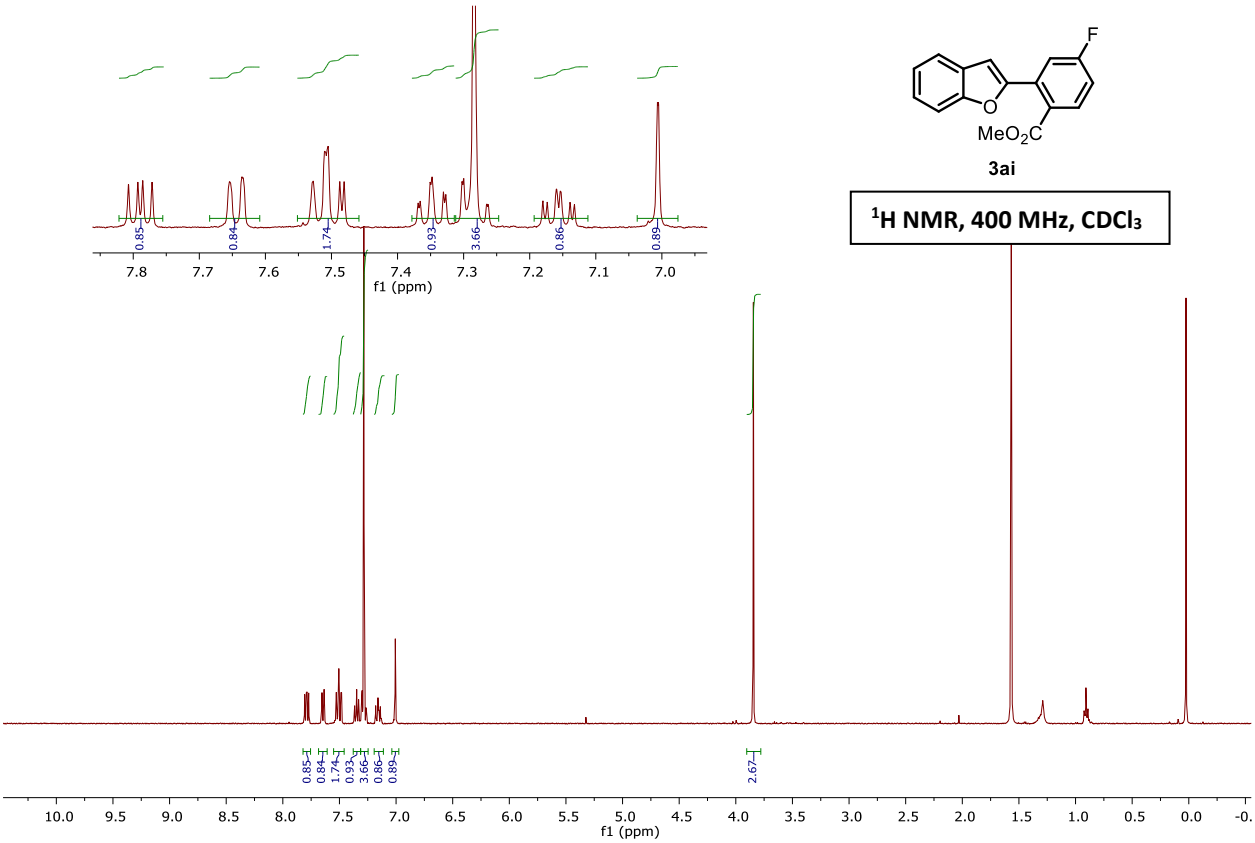


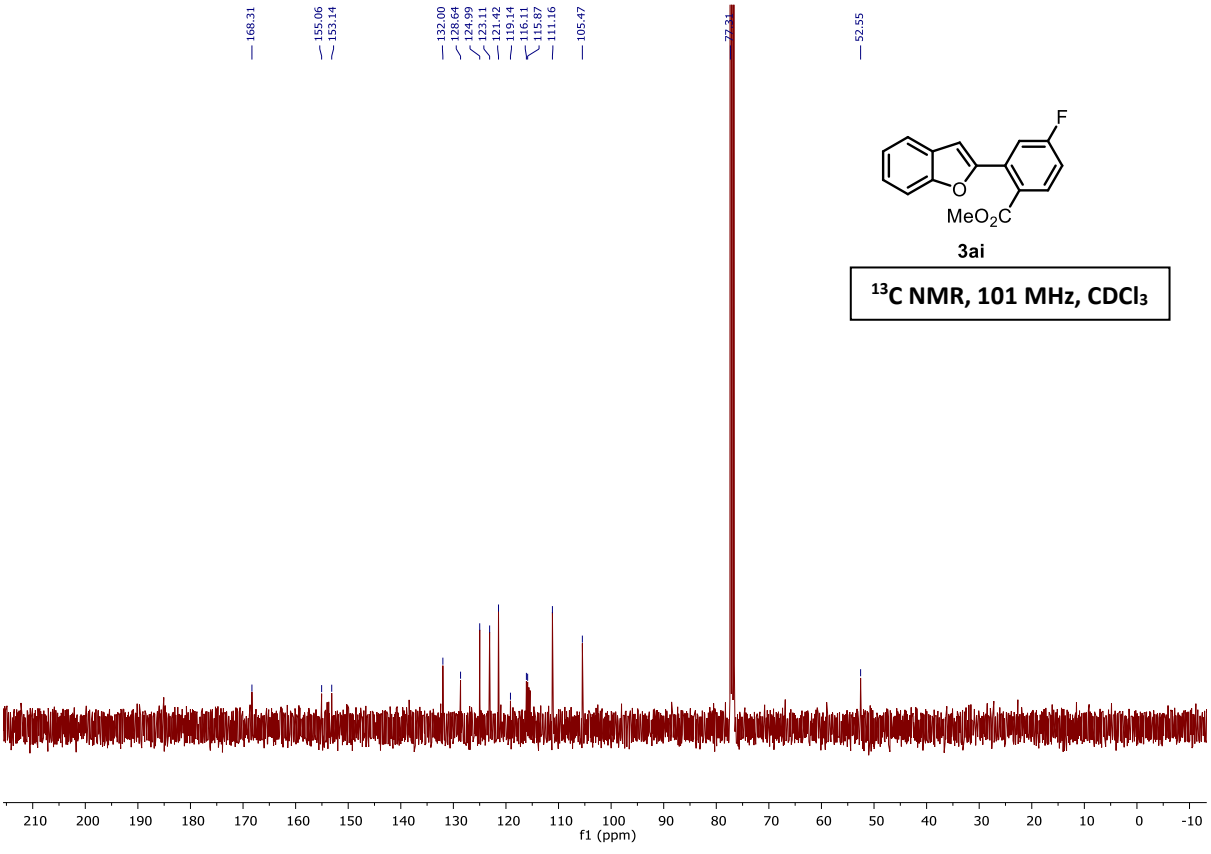
3ag

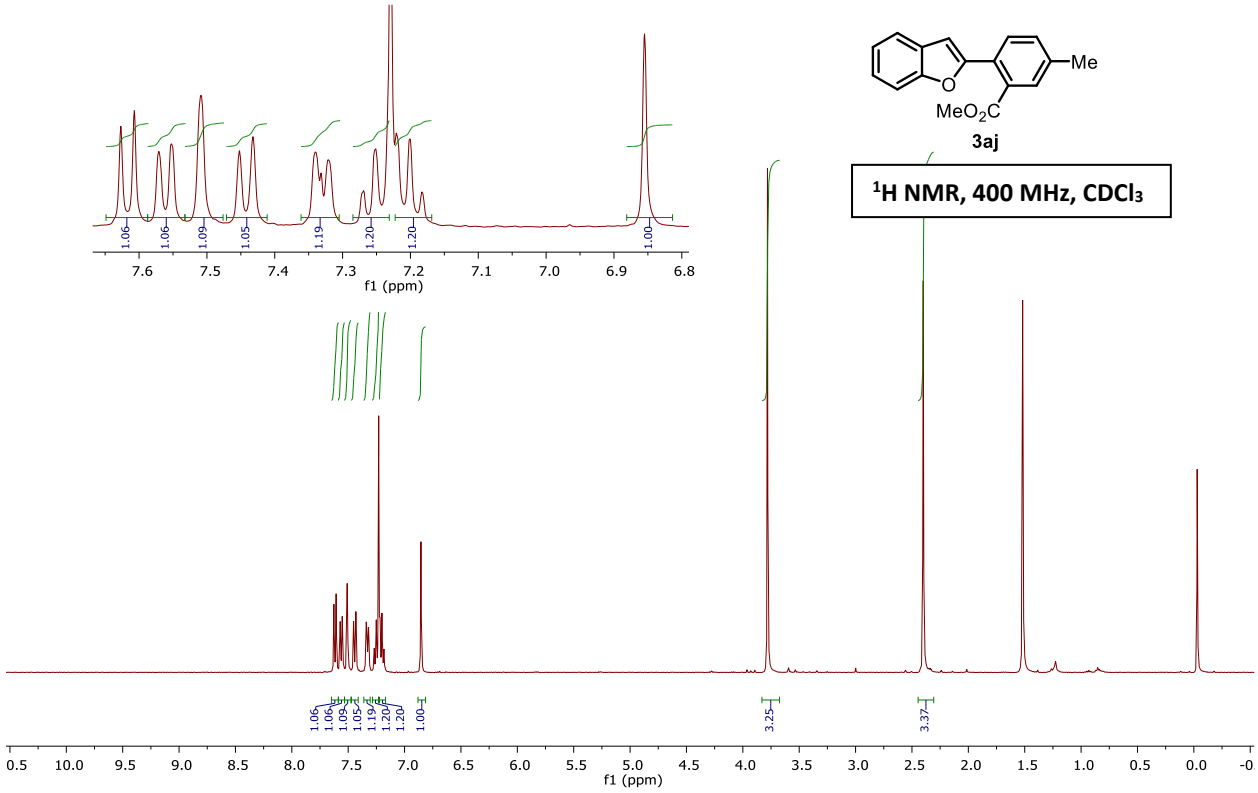
^{13}C NMR, 101 MHz, $CDCl_3$

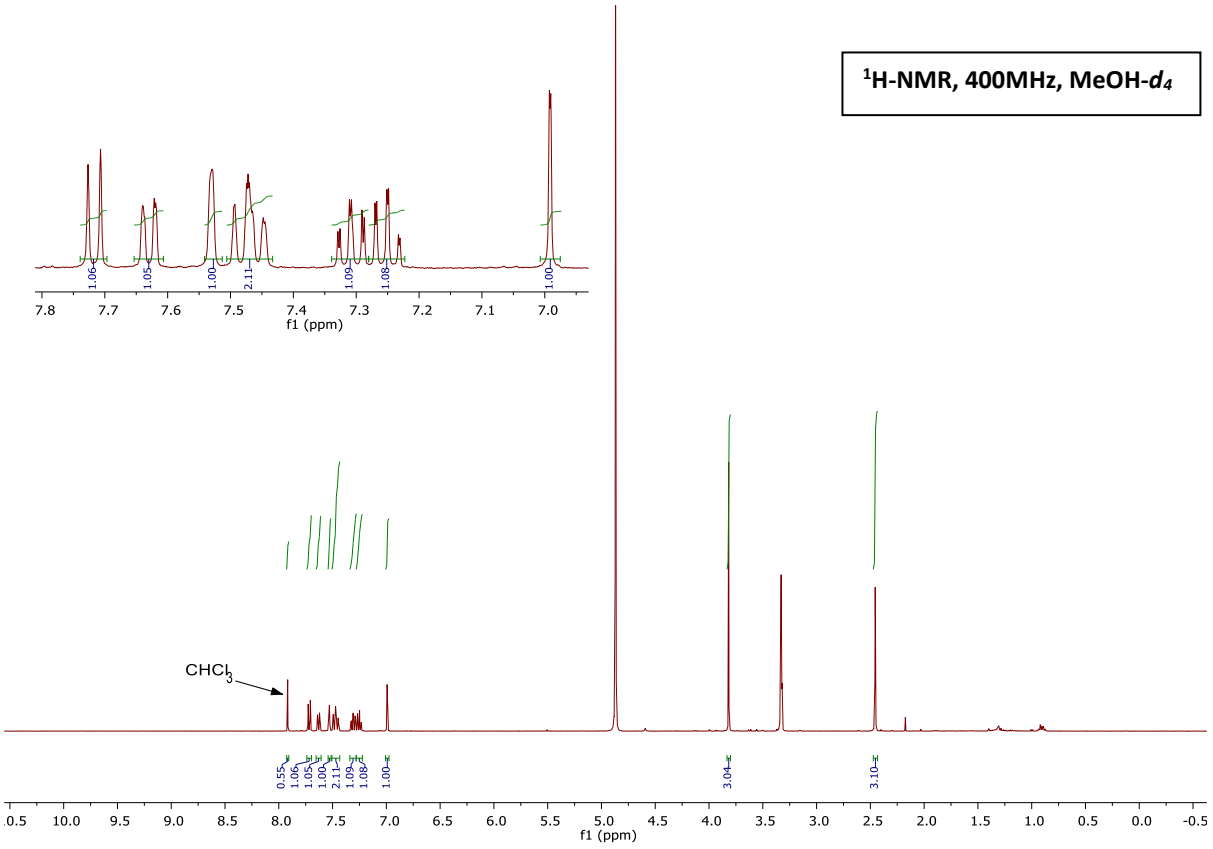

Cl
O
MeO2C
3ah
1H NMR, 400 MHz, CDCl3
1.00
1.02
1.07
1.06
1.13
1.18
2.89
1.02
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
f1 (ppm)
3.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

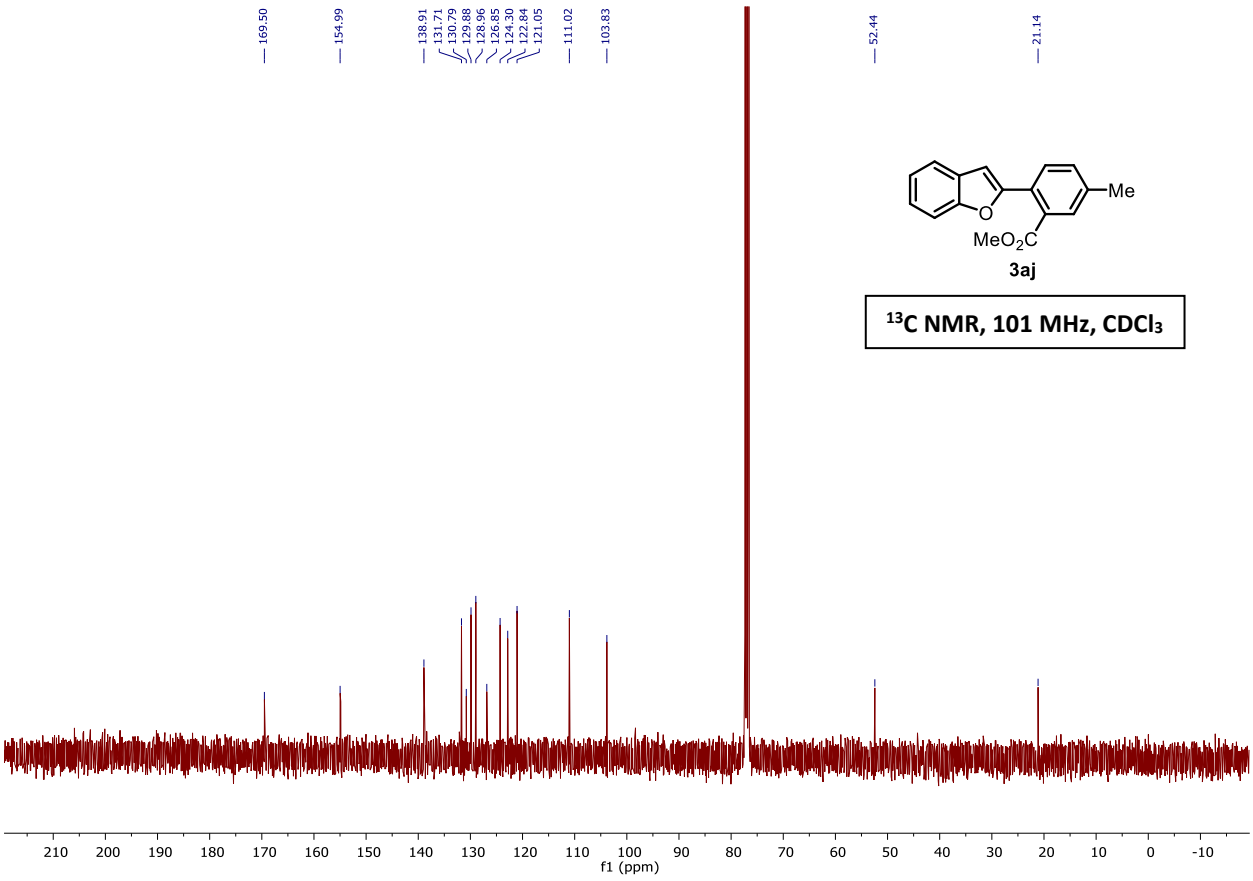

168.40
155.13
153.05
137.22
131.47
130.96
129.10
128.94
128.64
128.58
125.02
123.14
121.44
111.18
105.49
52.63
Cl
O
MeO2C
3ah
13C NMR, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

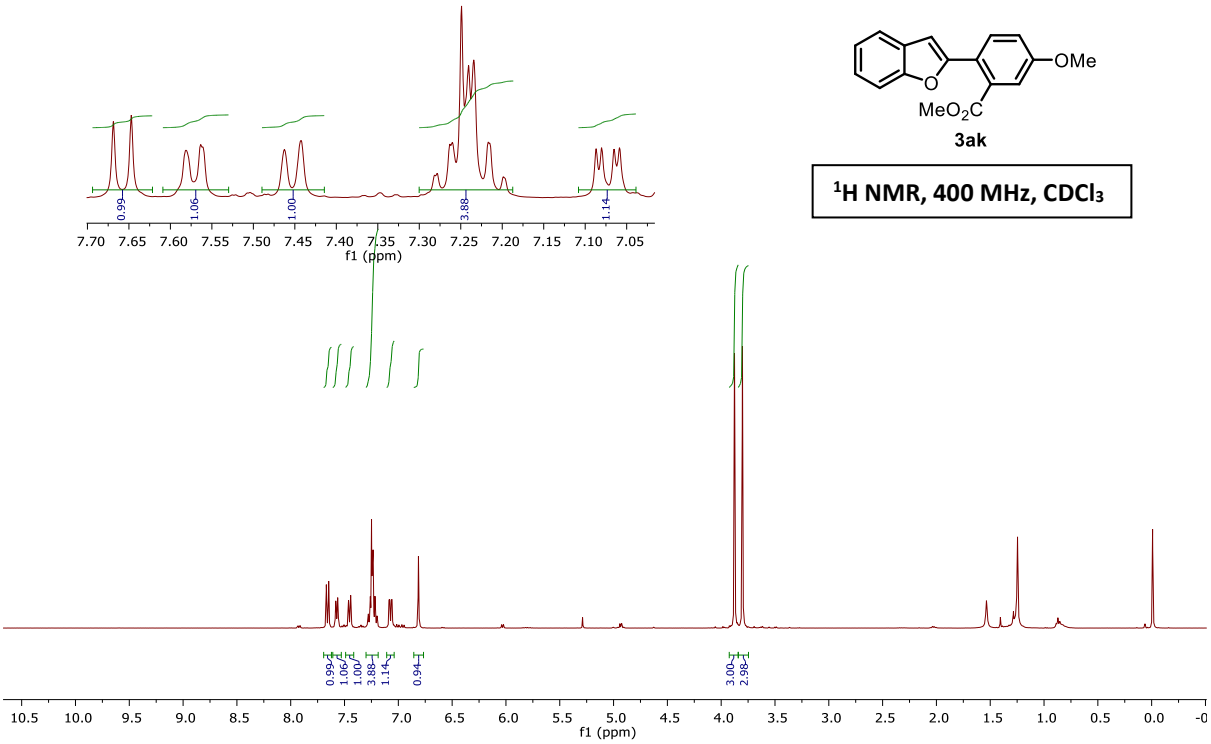

F
O
MeO2C
3ai
1H NMR, 400 MHz, CDCl3
0.85
0.84
1.74
0.93
3.66
0.86
0.89
2.67
f1 (ppm)

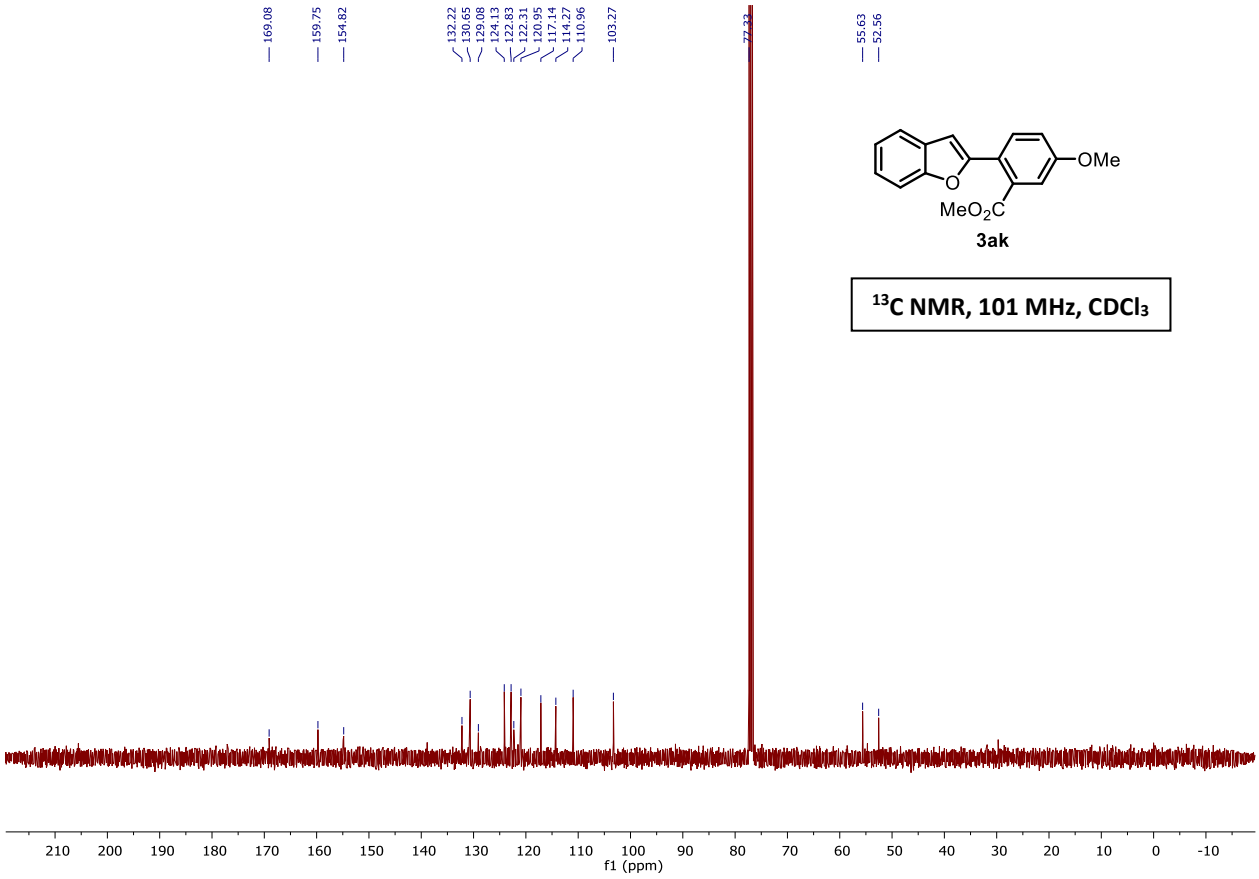

168.31
155.06
153.14
132.00
128.64
124.99
123.11
121.42
119.14
116.11
115.87
111.16
105.47
77.31
52.55
F
O
MeO2C
3ai
13C NMR, 101 MHz, CDCl3
f1 (ppm)

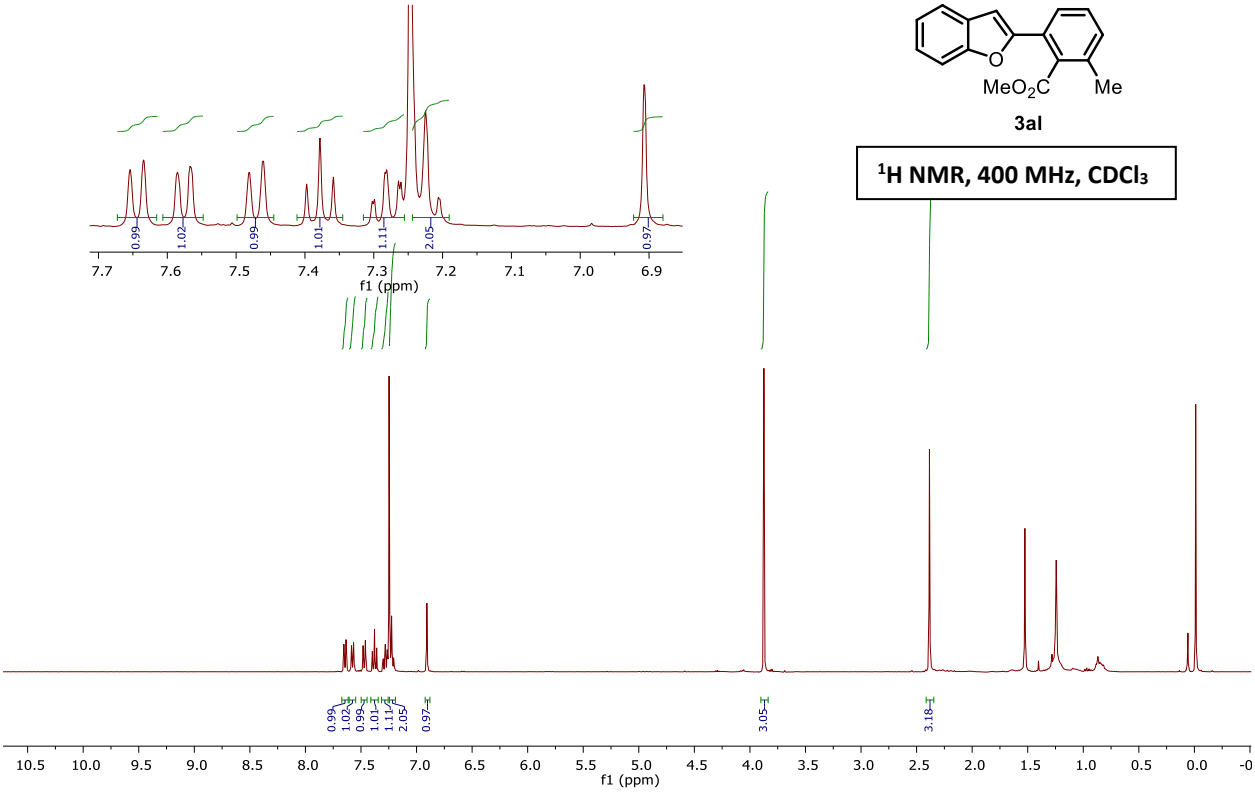

Me
MeO2C
3aj
1H NMR, 400 MHz, CDCl3
f1 (ppm)

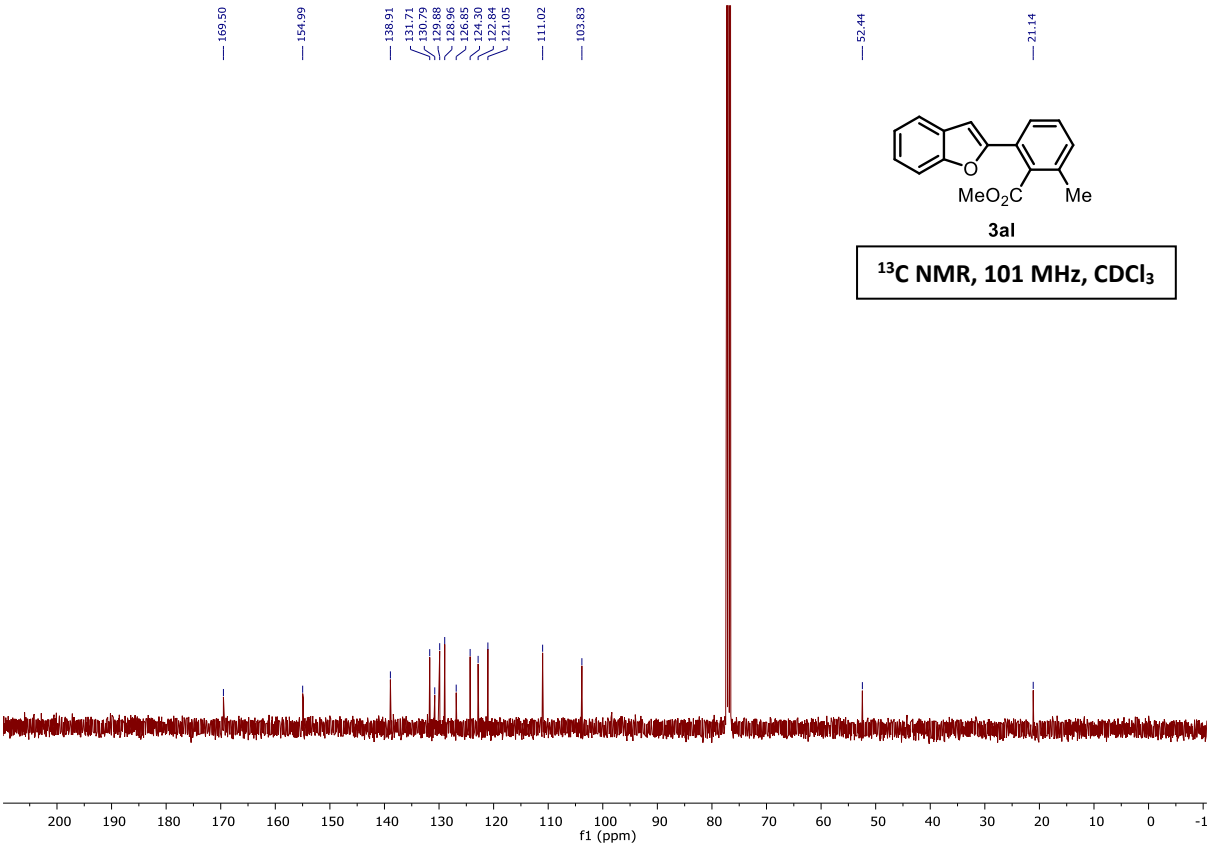

1H-NMR, 400MHz, MeOH-d4
CHCl3
f1 (ppm)

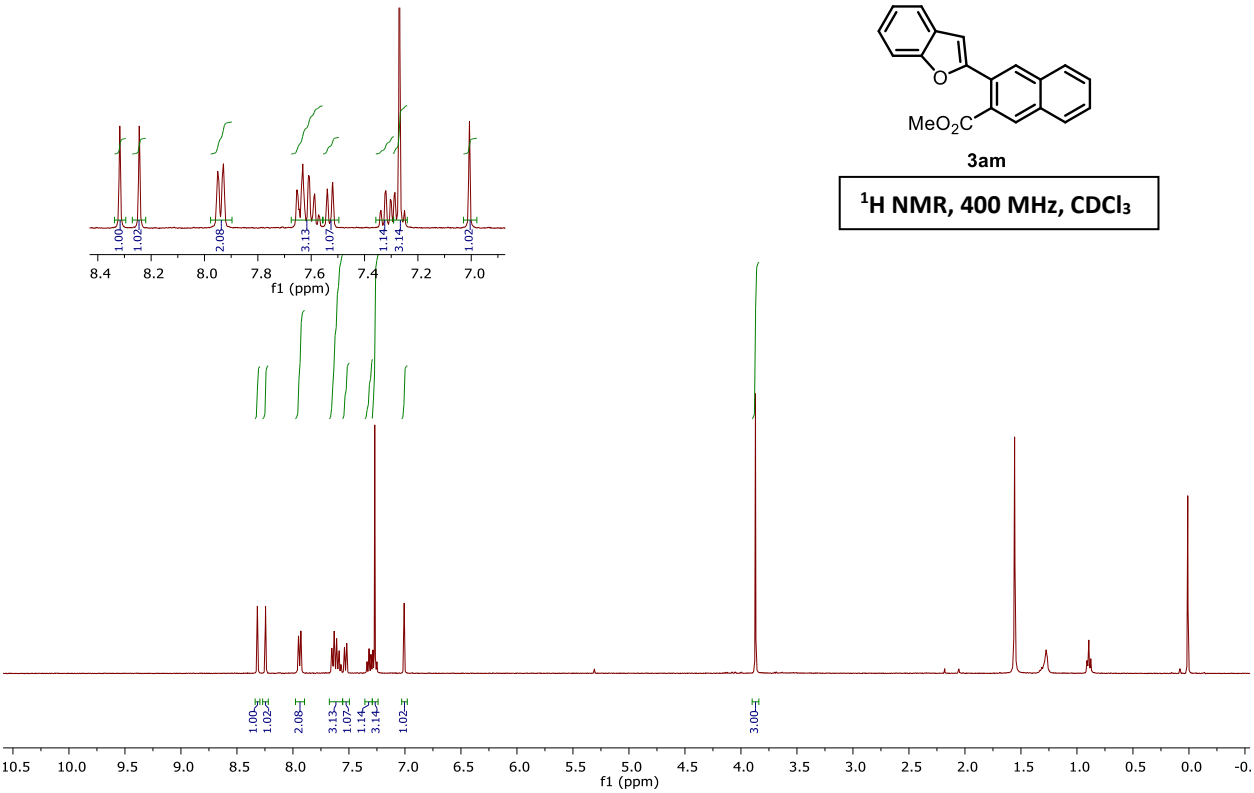

169.50
154.99
138.91
131.71
130.79
129.88
128.96
126.85
124.30
122.84
121.05
111.02
103.83
52.44
21.14
Me
O
MeO2C
3aj
13C NMR, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

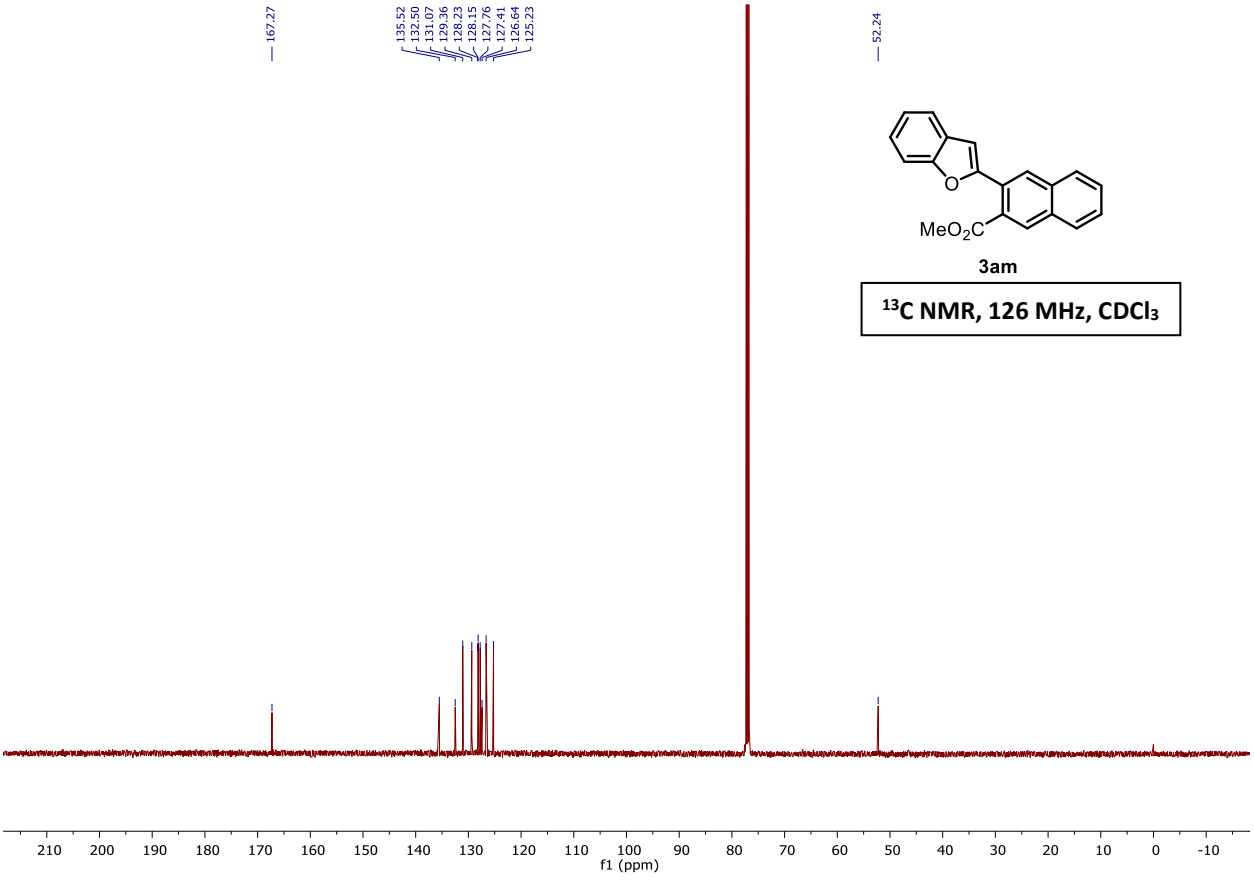

OMe
MeO2C
3ak
1H NMR, 400 MHz, CDCl3
f1 (ppm)

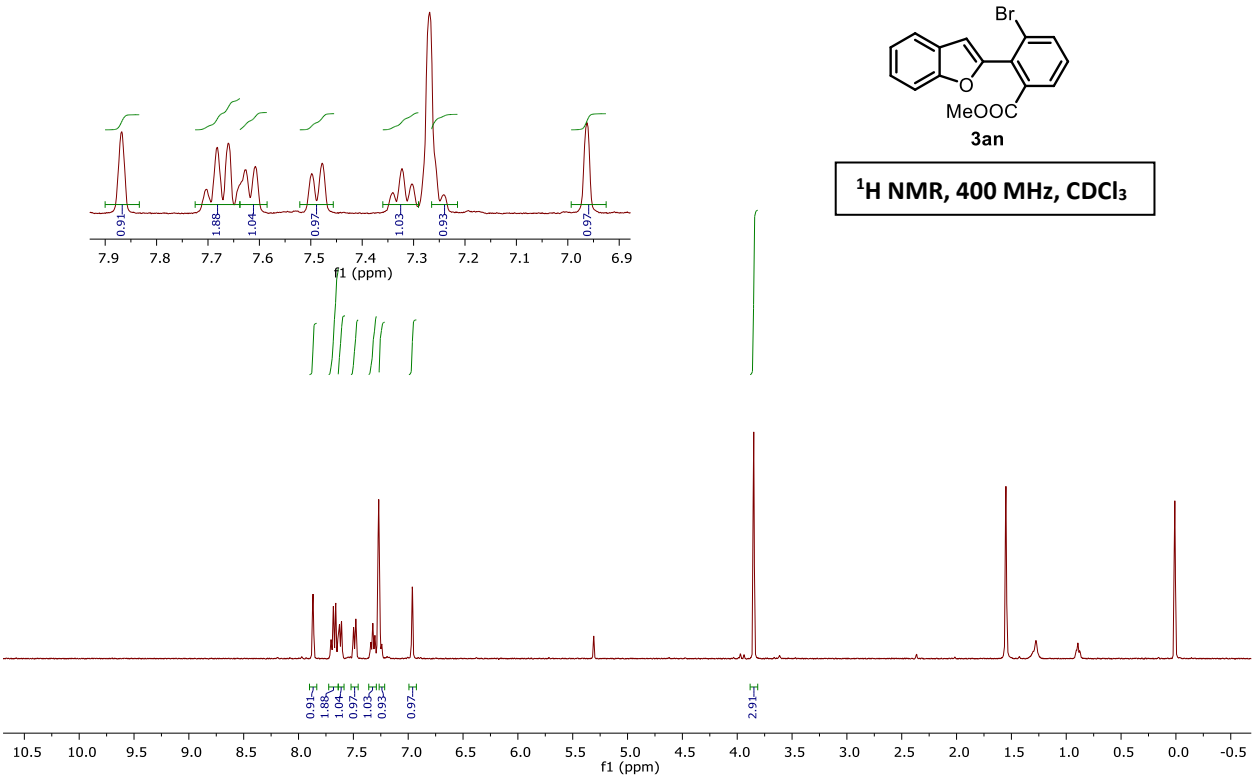

169.08
159.75
154.82
132.22
130.65
129.08
124.13
122.83
122.31
120.95
117.14
114.27
110.96
103.27
77.32
55.63
52.56
OMe
MeO2C
3ak
13C NMR, 101 MHz, CDCl3
f1 (ppm)

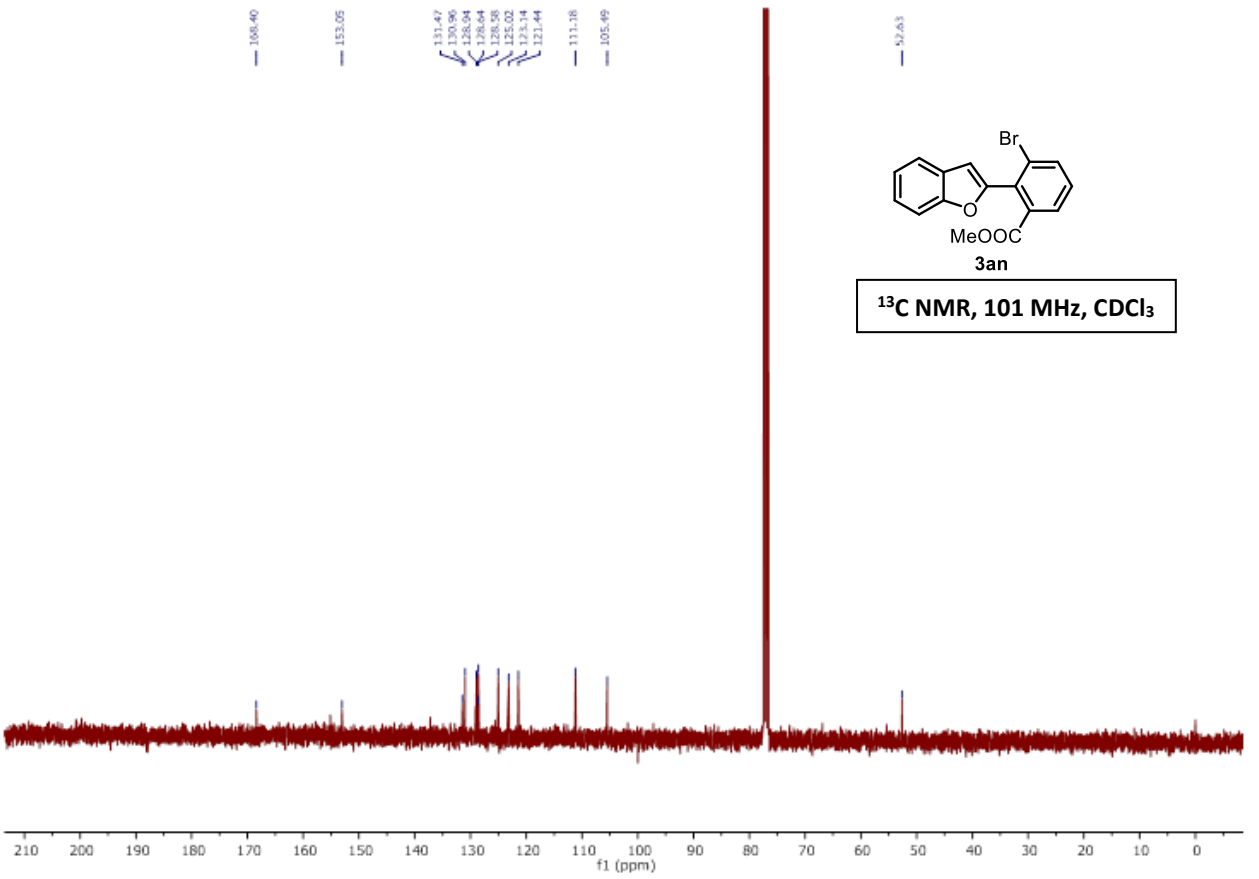

MeO2C
Me
3al
1H NMR, 400 MHz, CDCl3
f1 (ppm)

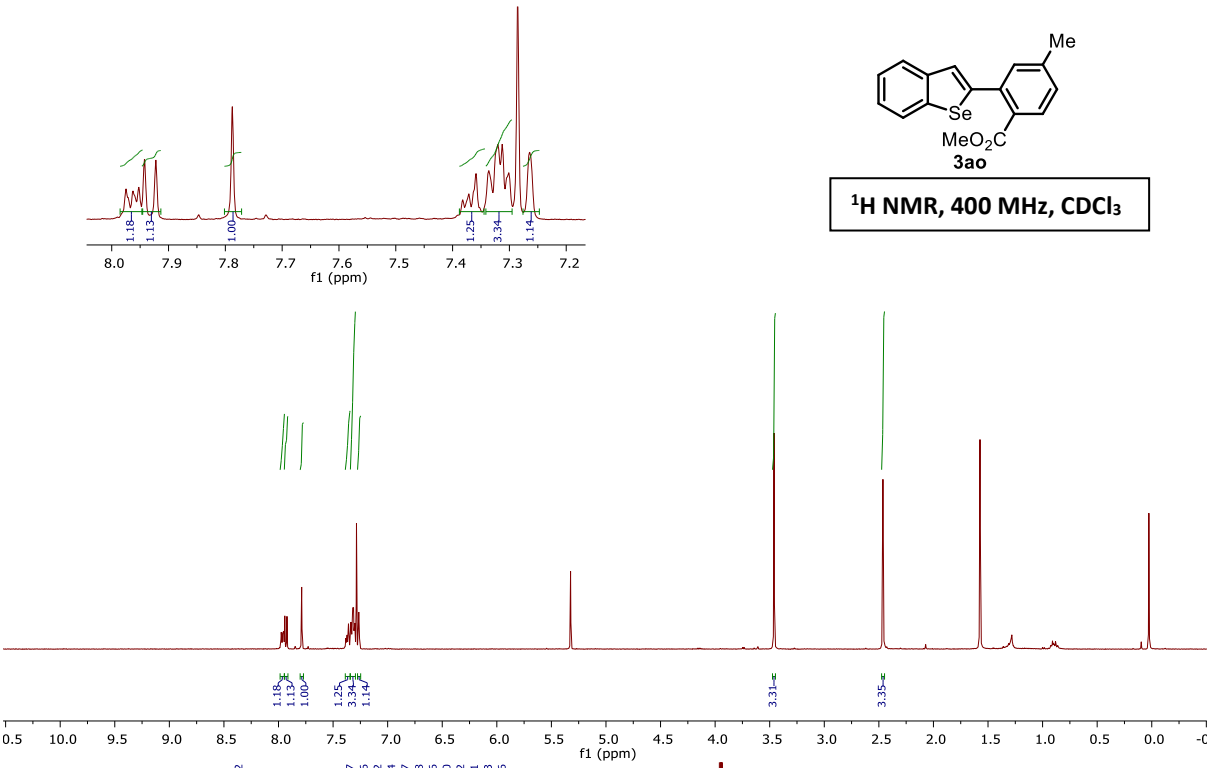

MeO2C
Me
3al
13C NMR, 101 MHz, CDCl3
f1 (ppm)

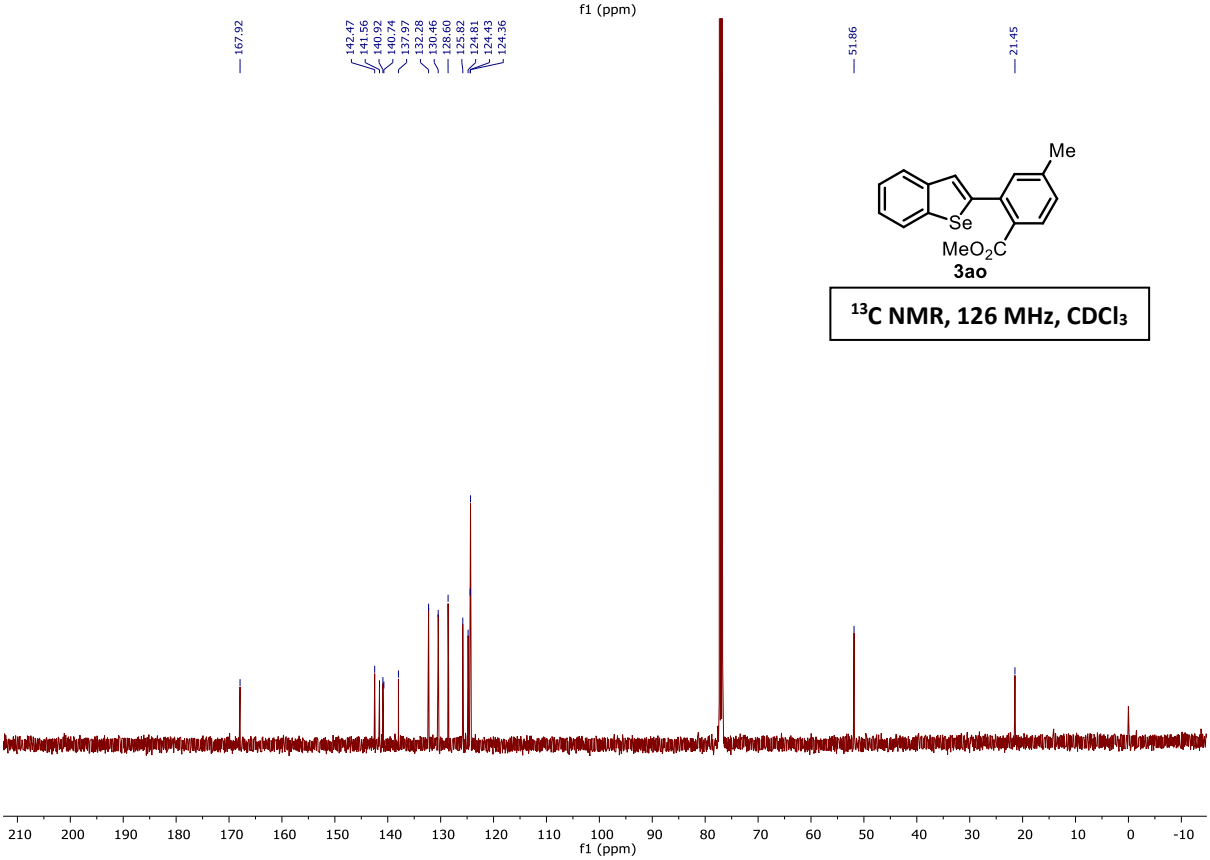

MeO2C
3am
1H NMR, 400 MHz, CDCl3
f1 (ppm)

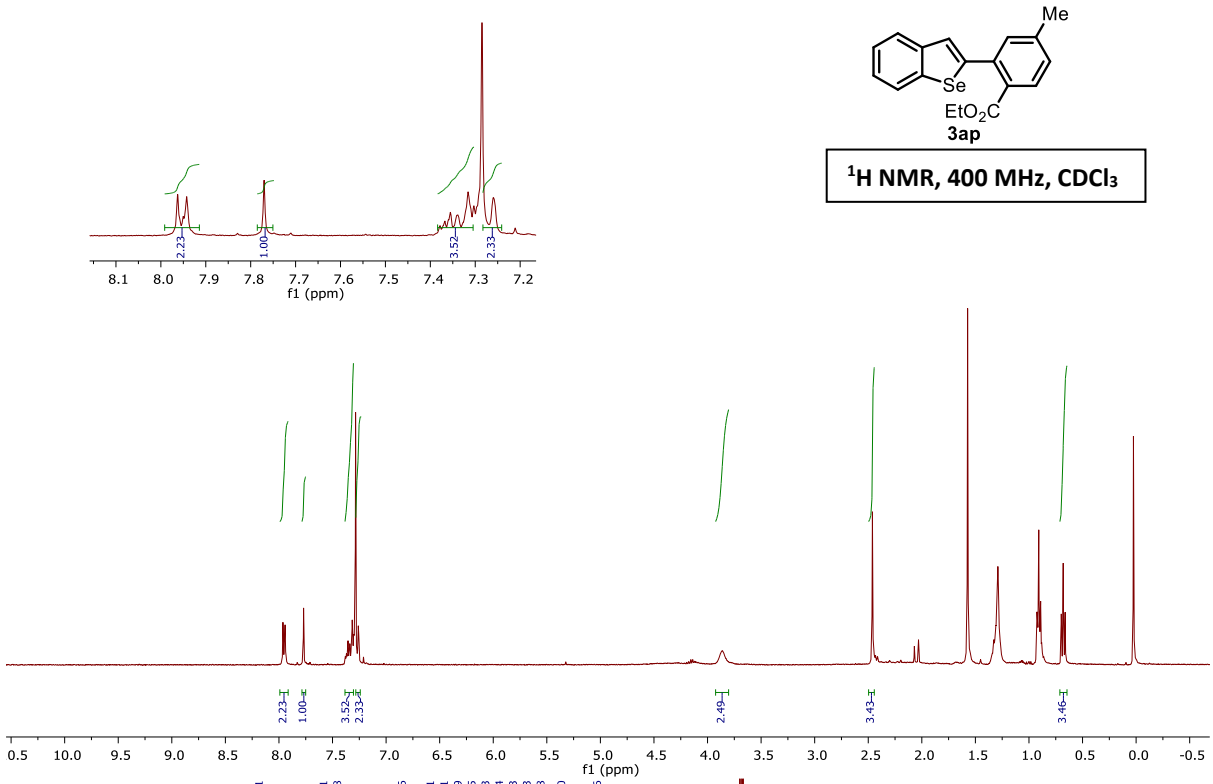

MeO2C
3am
13C NMR, 126 MHz, CDCl3
167.27
135.52
132.50
131.07
129.36
128.23
128.15
127.76
127.41
126.64
125.23
52.24
f1 (ppm)

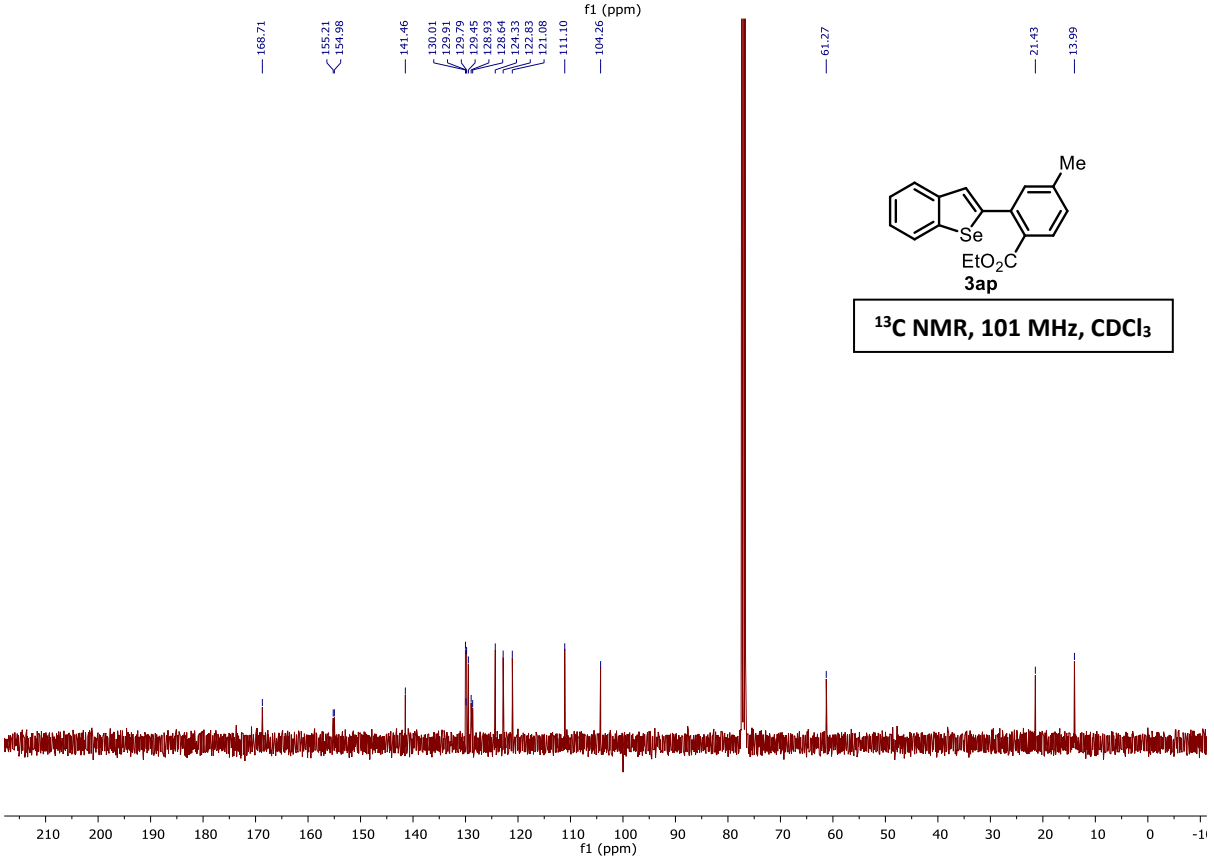

Br
O
MeOOC
3an
^{1}H NMR, 400 MHz, CDCl$_3$
f1 (ppm)

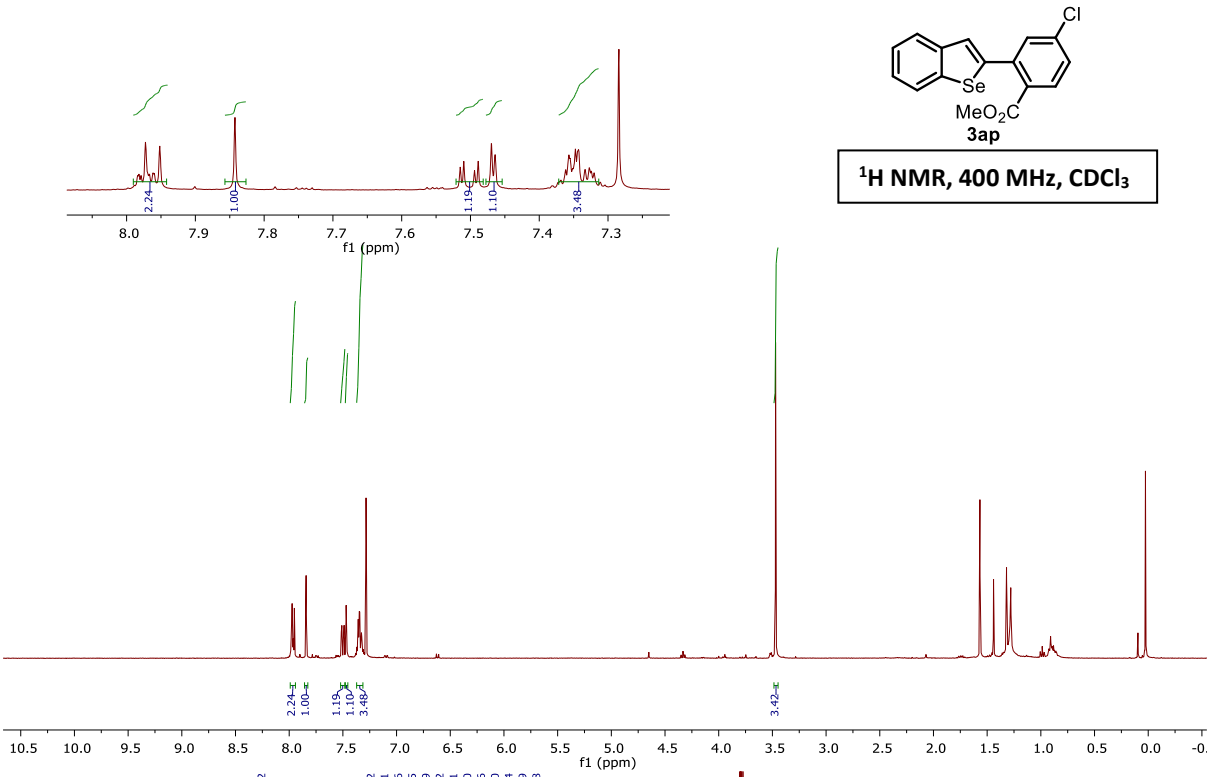

Br
O
MeOOC
3an
^{13}C NMR, 101 MHz, CDCl$_3$
f1 (ppm)

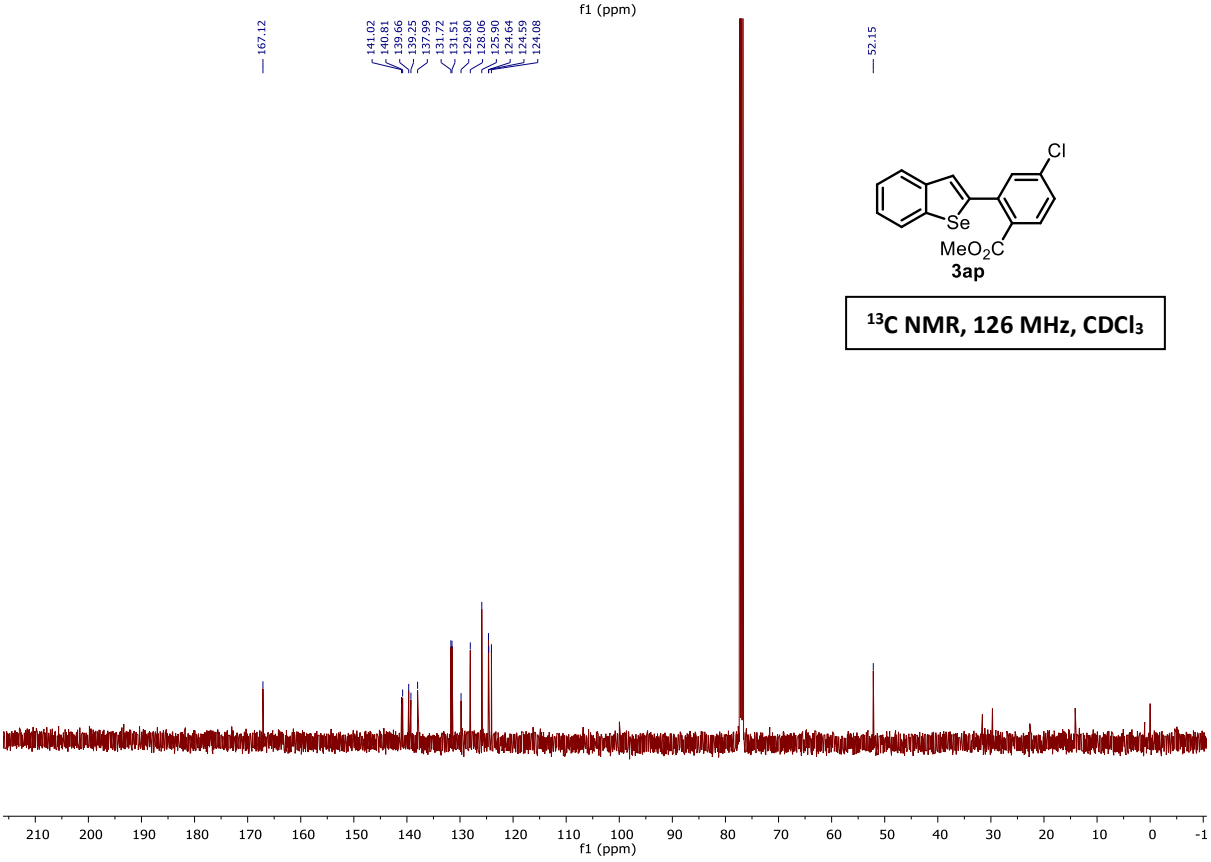

Me
Se
MeO2C
3ao
1H NMR, 400 MHz, CDCl3
f1 (ppm)

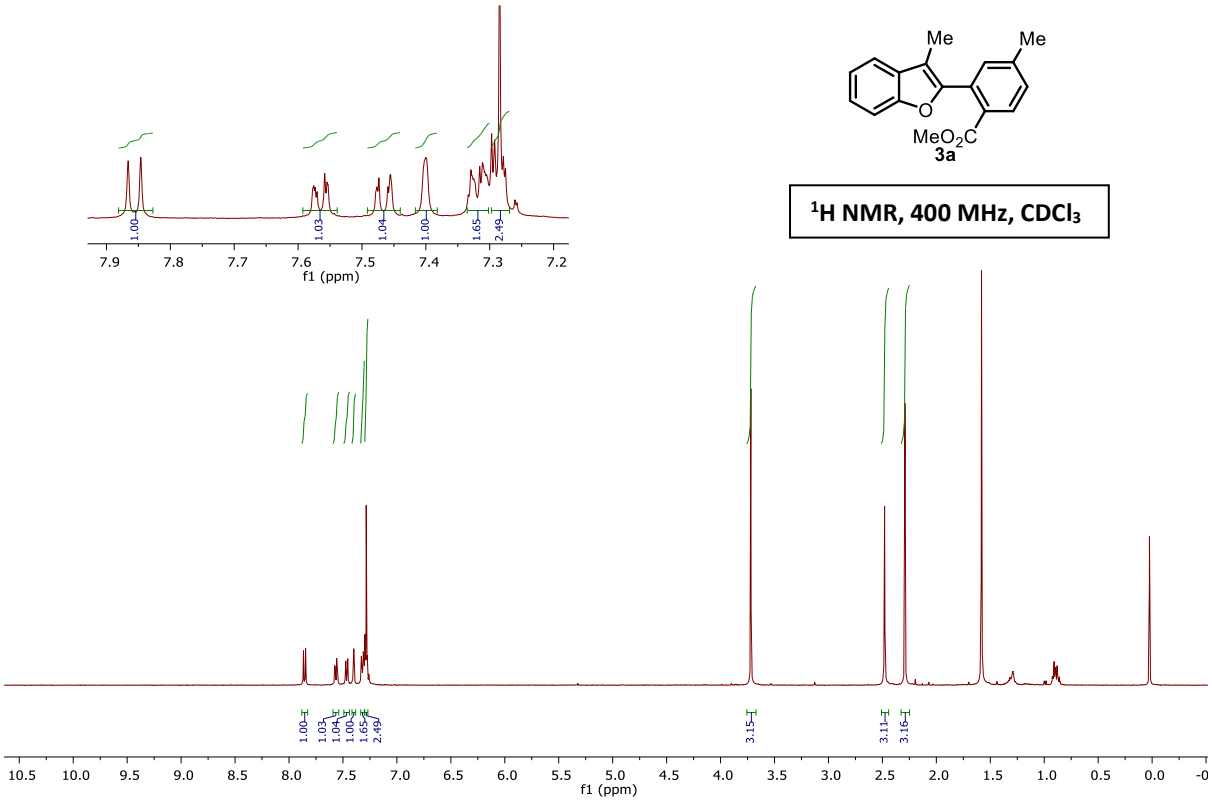

Me
Se
MeO2C
3ao
13C NMR, 126 MHz, CDCl3
f1 (ppm)

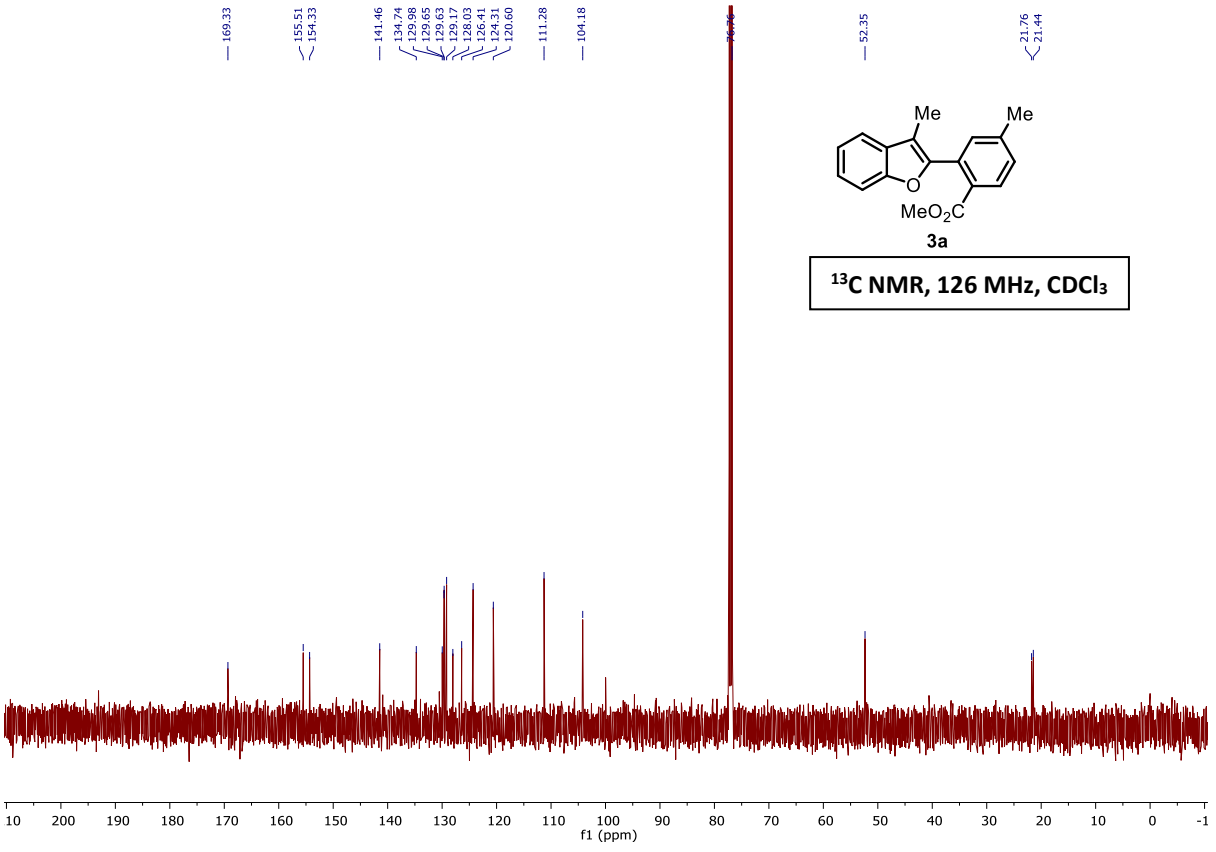

Me
Se
EtO2C
3ap
1H NMR, 400 MHz, CDCl3
f1 (ppm)

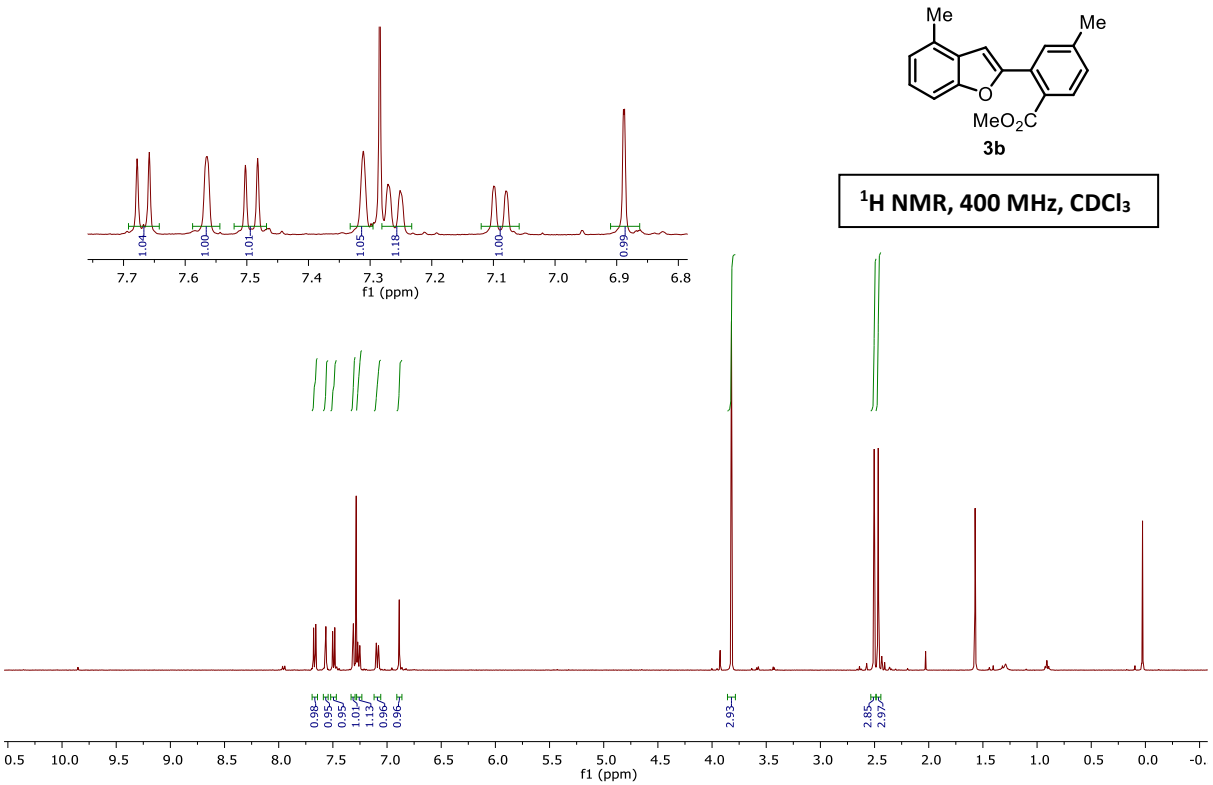

Me
Se
EtO2C
3ap
13C NMR, 101 MHz, CDCl3
f1 (ppm)

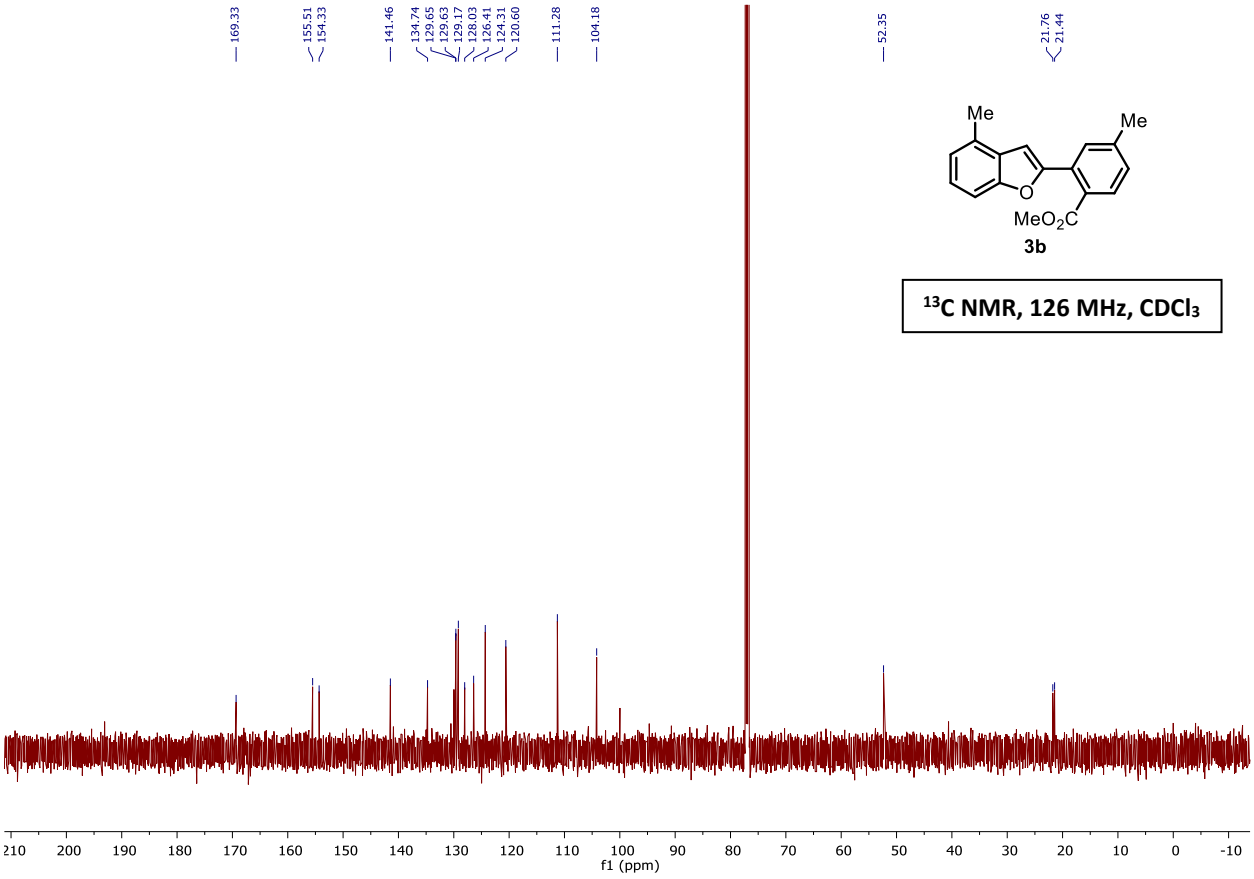

Cl
Se
MeO2C
3ap
1H NMR, 400 MHz, CDCl3
f1 (ppm)

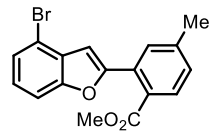

167.12
141.02
140.81
139.66
139.25
137.99
131.72
131.51
129.80
128.06
125.90
124.64
124.59
124.08
52.15
Cl
Se
MeO2C
3ap
13C NMR, 126 MHz, CDCl3
f1 (ppm)


Me
Me
O
MeO2C
3a
1H NMR, 400 MHz, CDCl3
f1 (ppm)


169.33
155.51
154.33
141.46
134.74
129.98
129.65
129.63
129.17
128.03
126.41
124.31
120.60
111.28
104.18
77.36
52.35
21.76
21.44
Me
Me
O
MeO2C
3a
13C NMR, 126 MHz, CDCl3
f1 (ppm)

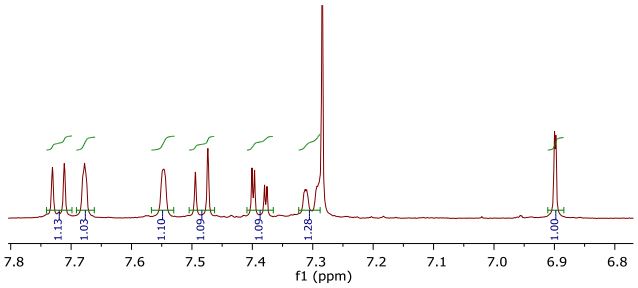

Me
Me
MeO2C
3b
1H NMR, 400 MHz, CDCl3
f1 (ppm)

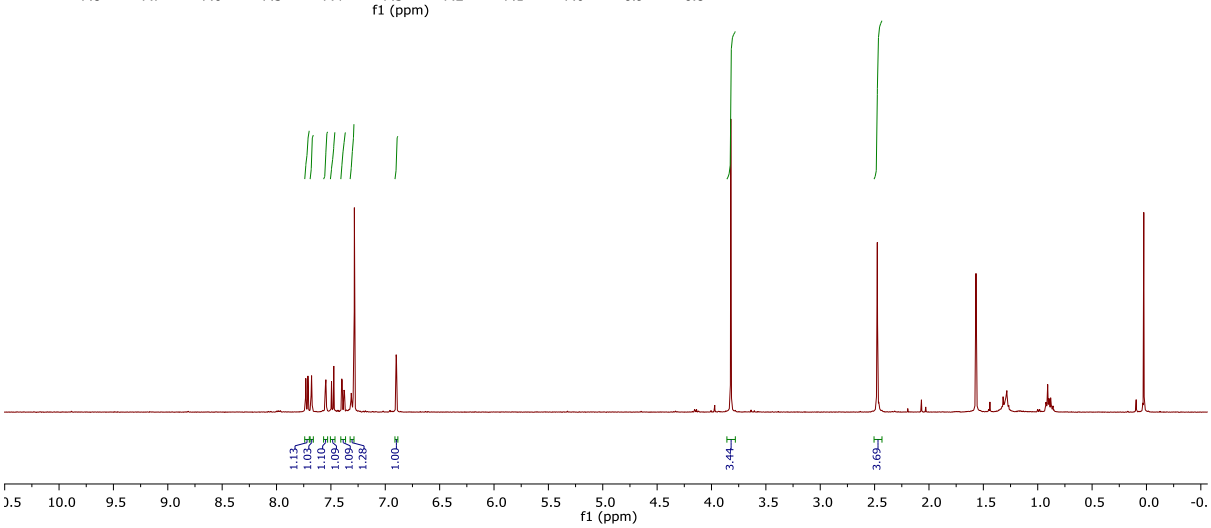

169.33
155.51
154.33
141.46
134.74
129.65
129.63
129.17
128.03
126.41
124.31
120.60
111.28
104.18
52.35
21.76
21.44
Me
Me
MeO2C
3b
13C NMR, 126 MHz, CDCl3
f1 (ppm)

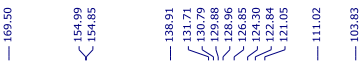


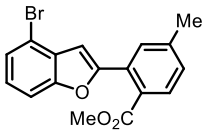
3c

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



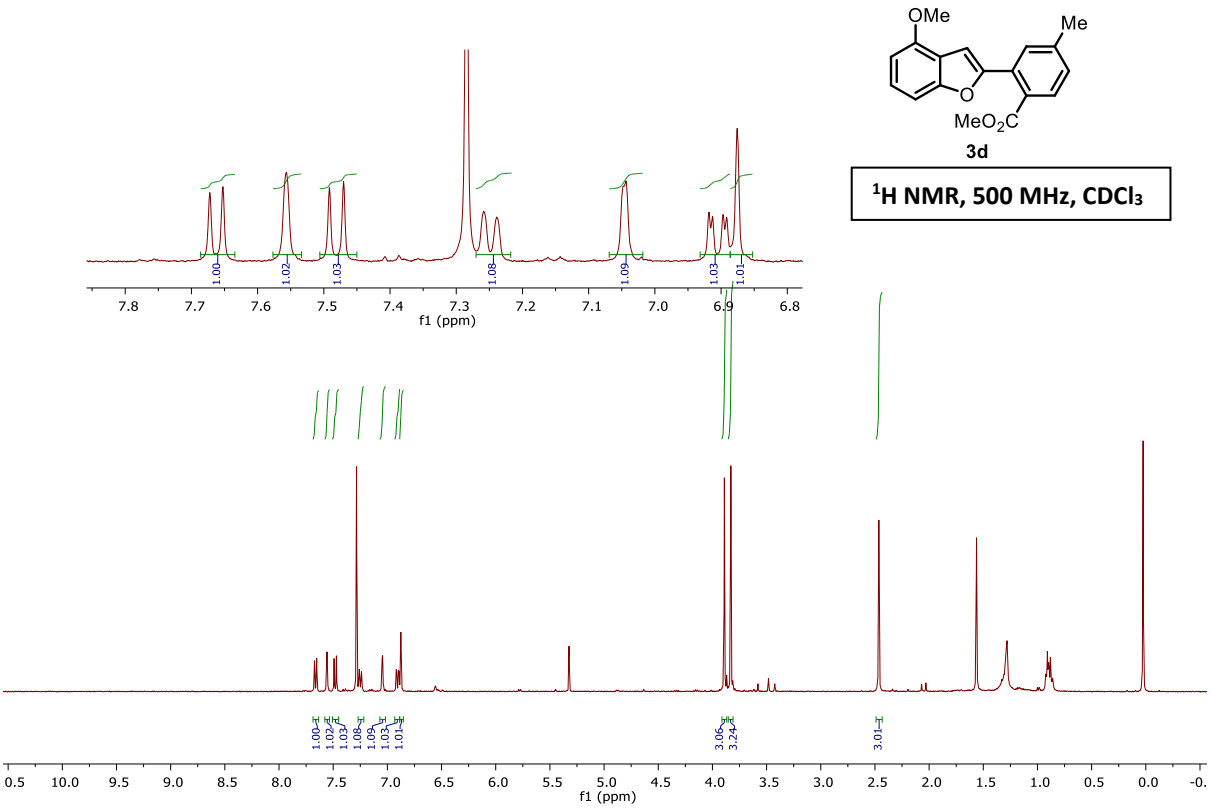


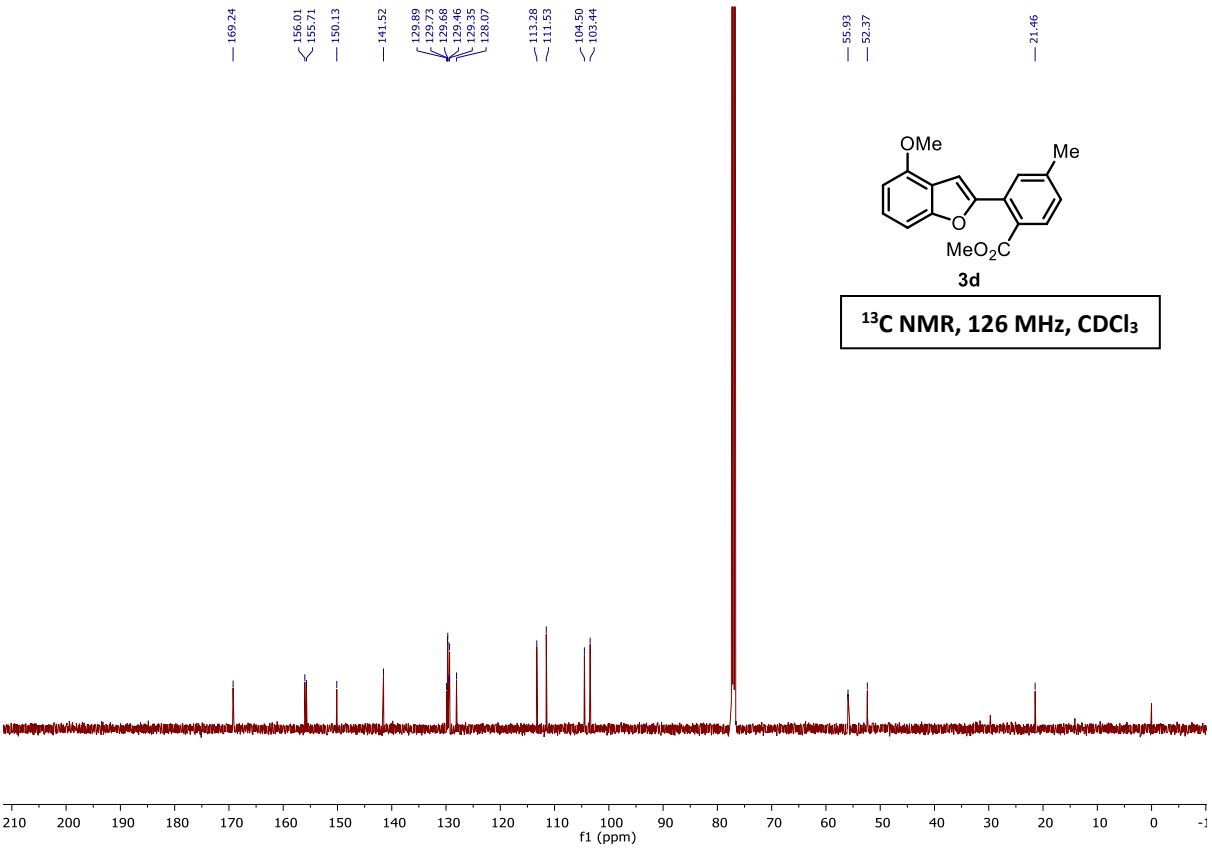




3c

^{13}C NMR, 101 MHz, $CDCl_3$


OMe
Me
O
MeO2C
3d
1H NMR, 500 MHz, CDCl3
f1 (ppm)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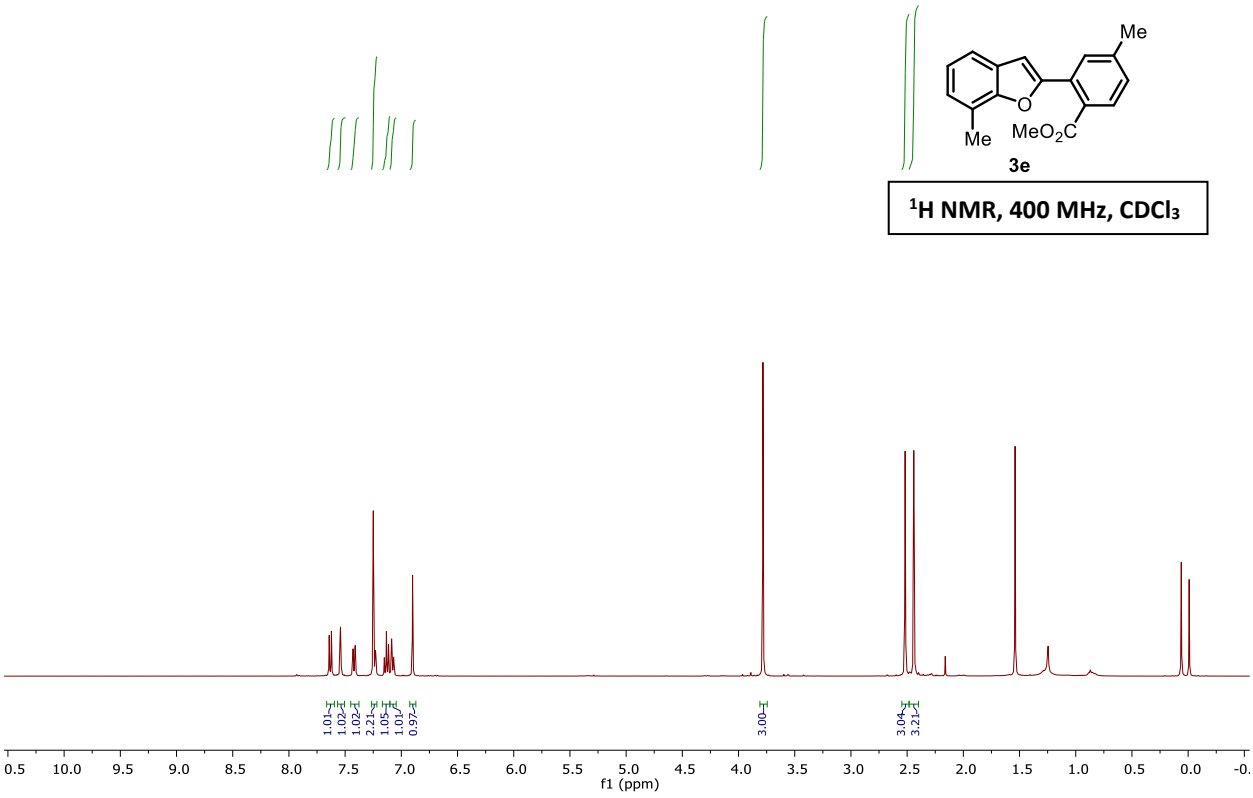
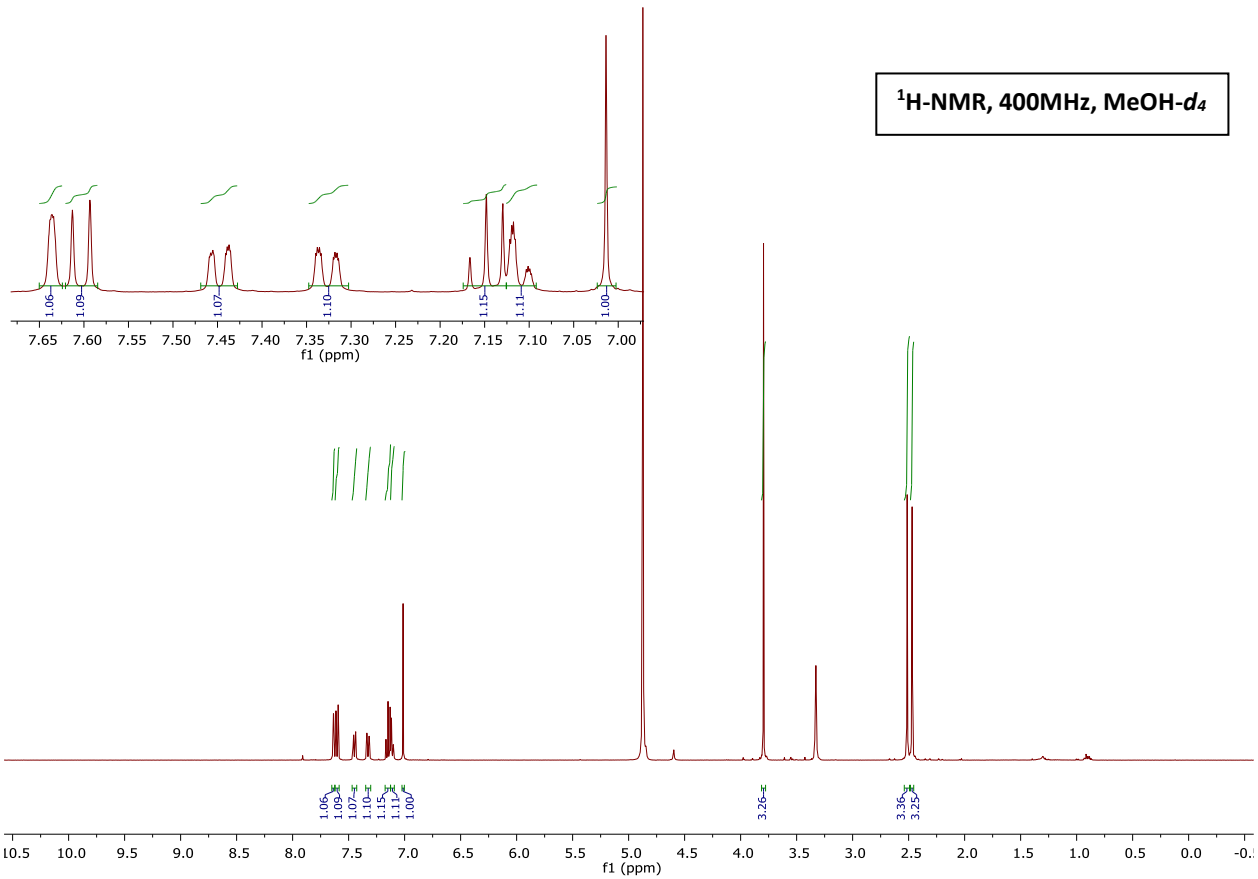
156.01
155.71
150.13
141.52
129.89
129.73
129.68
129.46
129.35
128.07
113.28
111.53
104.50
103.44
55.93
52.37
21.46
OMe
Me
O
MeO2C
3d
13C NMR, 126 MHz, CDCl3
f1 (ppm)


Me
O
Me
MeO2C
3e
1H NMR, 400 MHz, CDCl3
1.01
1.02
1.02
2.21
1.05
1.01
0.97
3.00
3.04
3.21
f1 (ppm)


1H-NMR, 400MHz, MeOH-d4
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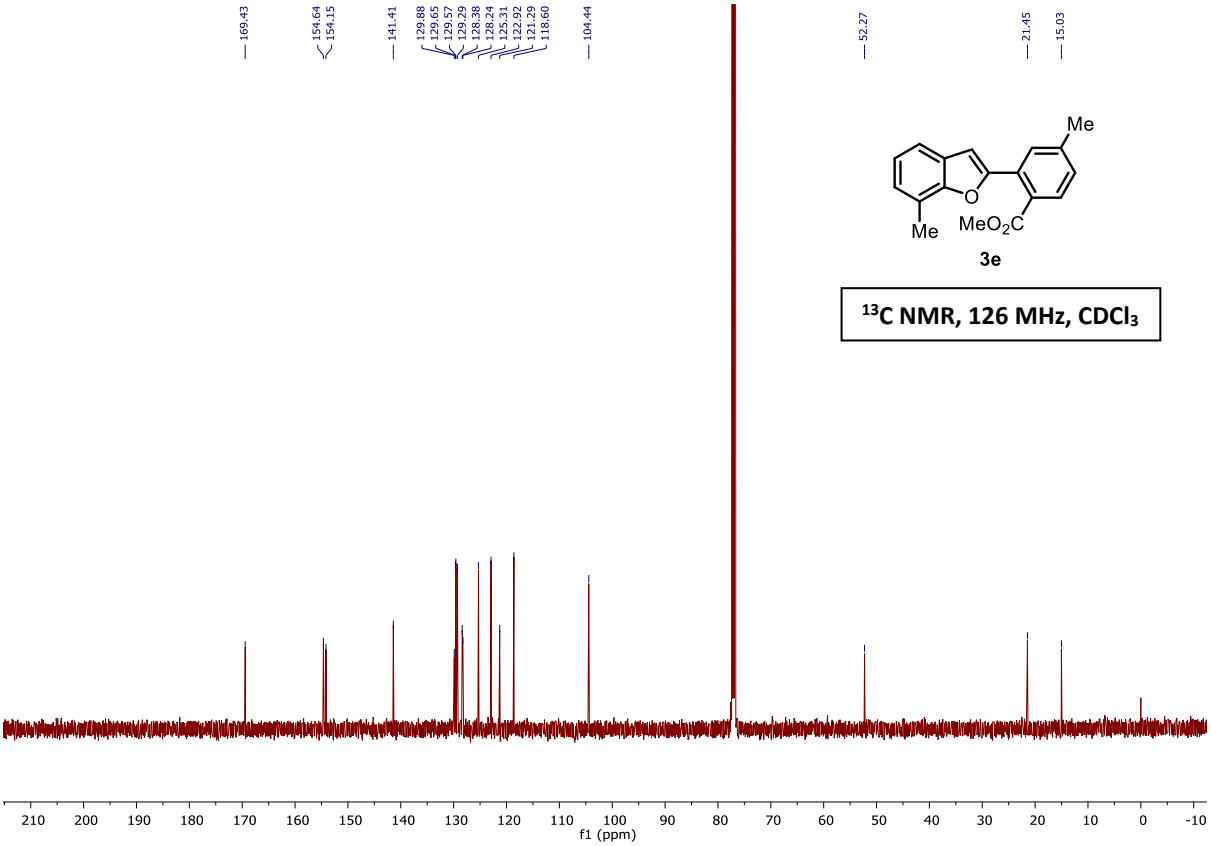
1.09
1.07
1.10
1.15
1.11
1.00
3.26
3.36
3.25
f1 (ppm)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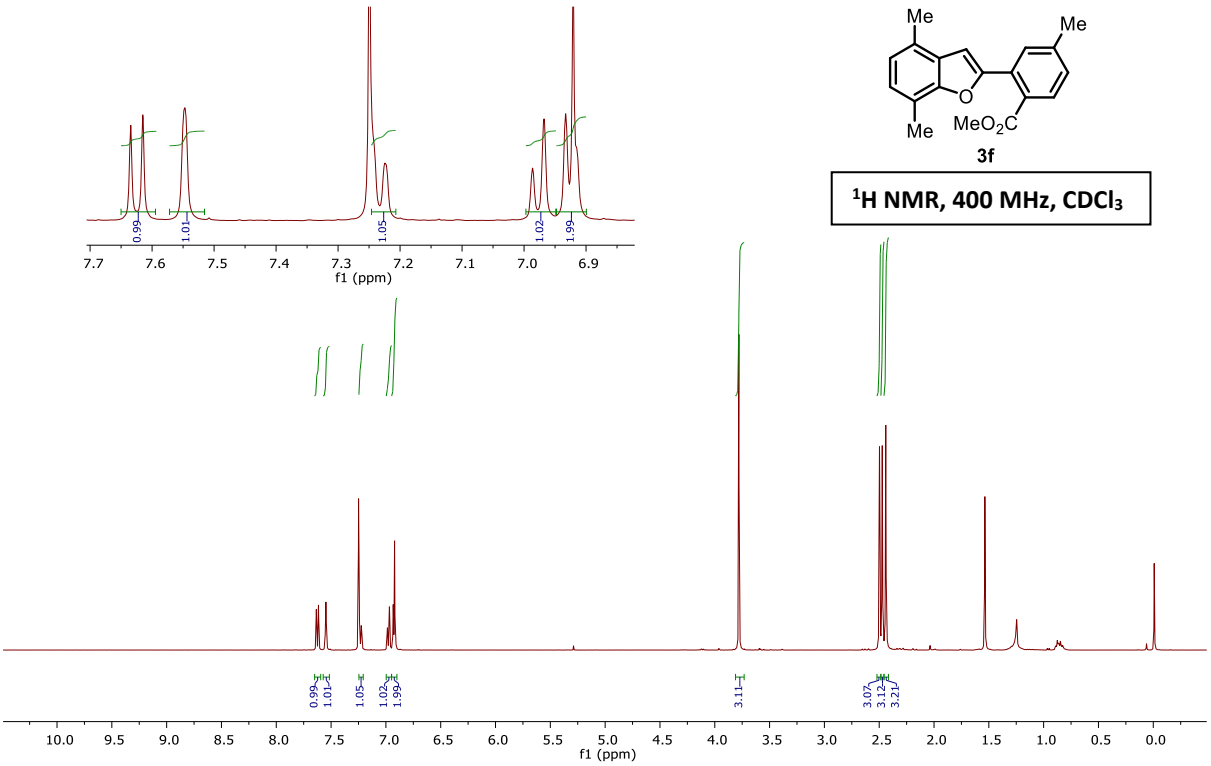
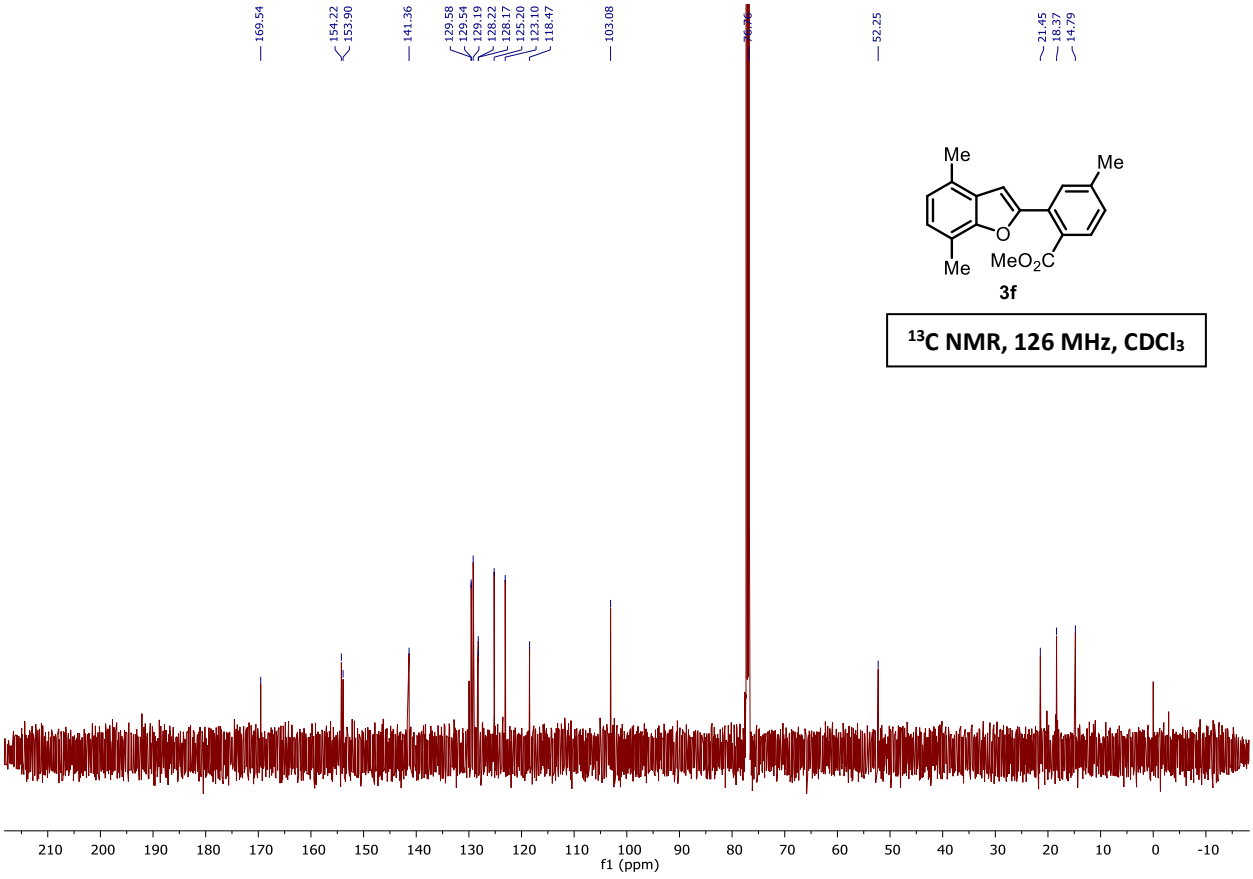
154.64
154.15
141.41
129.88
129.65
129.57
129.29
128.38
128.24
125.31
122.92
121.29
118.60
104.44
52.27
21.45
15.03
Me
O
Me
MeO2C
3e
13C NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
Me
Me
O
MeO2C
3f
1H NMR, 400 MHz, CDCl3
f1 (ppm)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154.22
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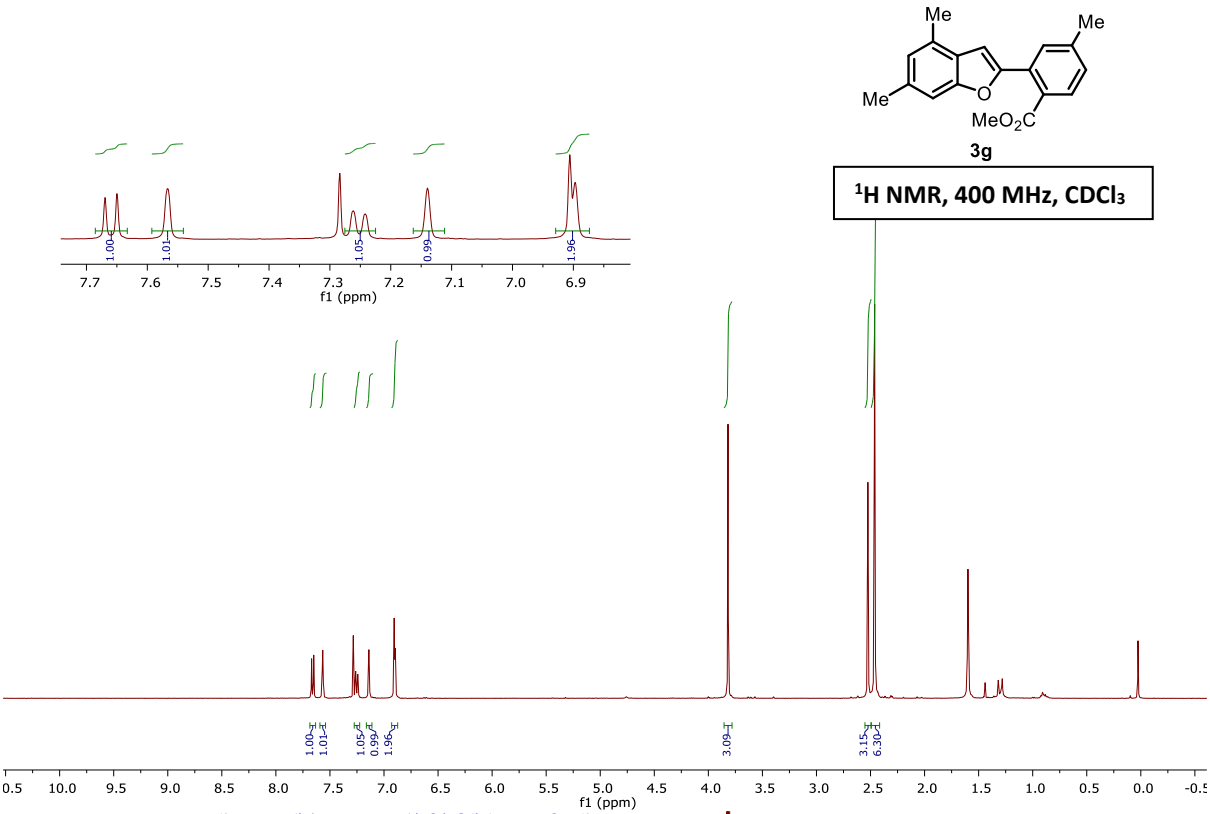
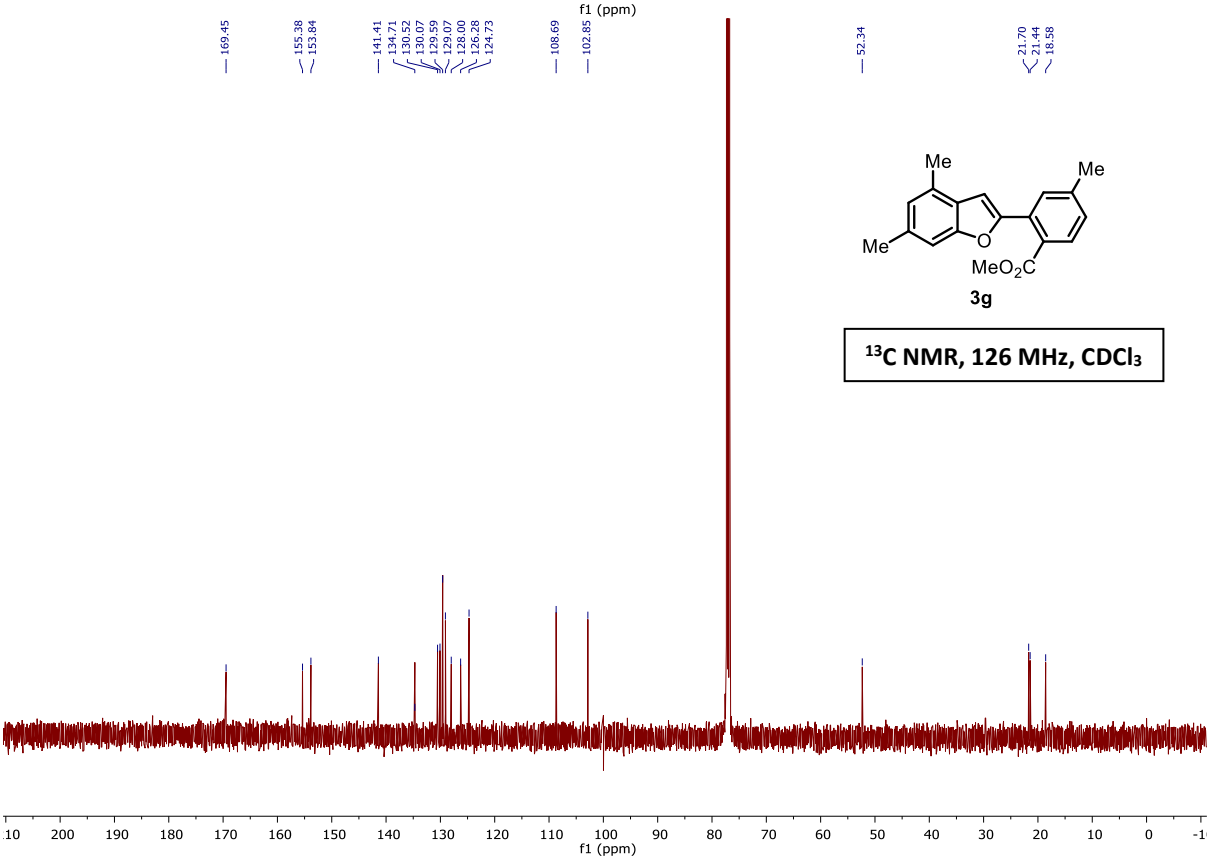
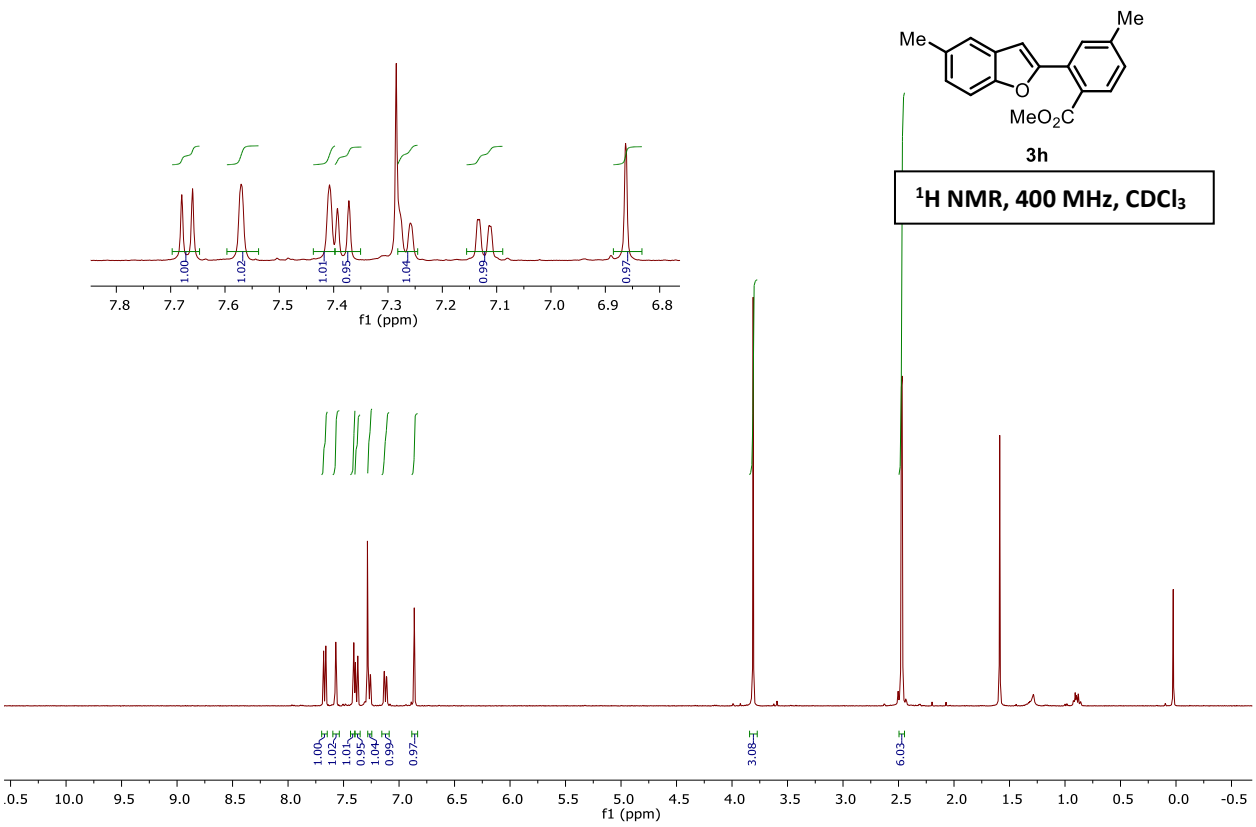
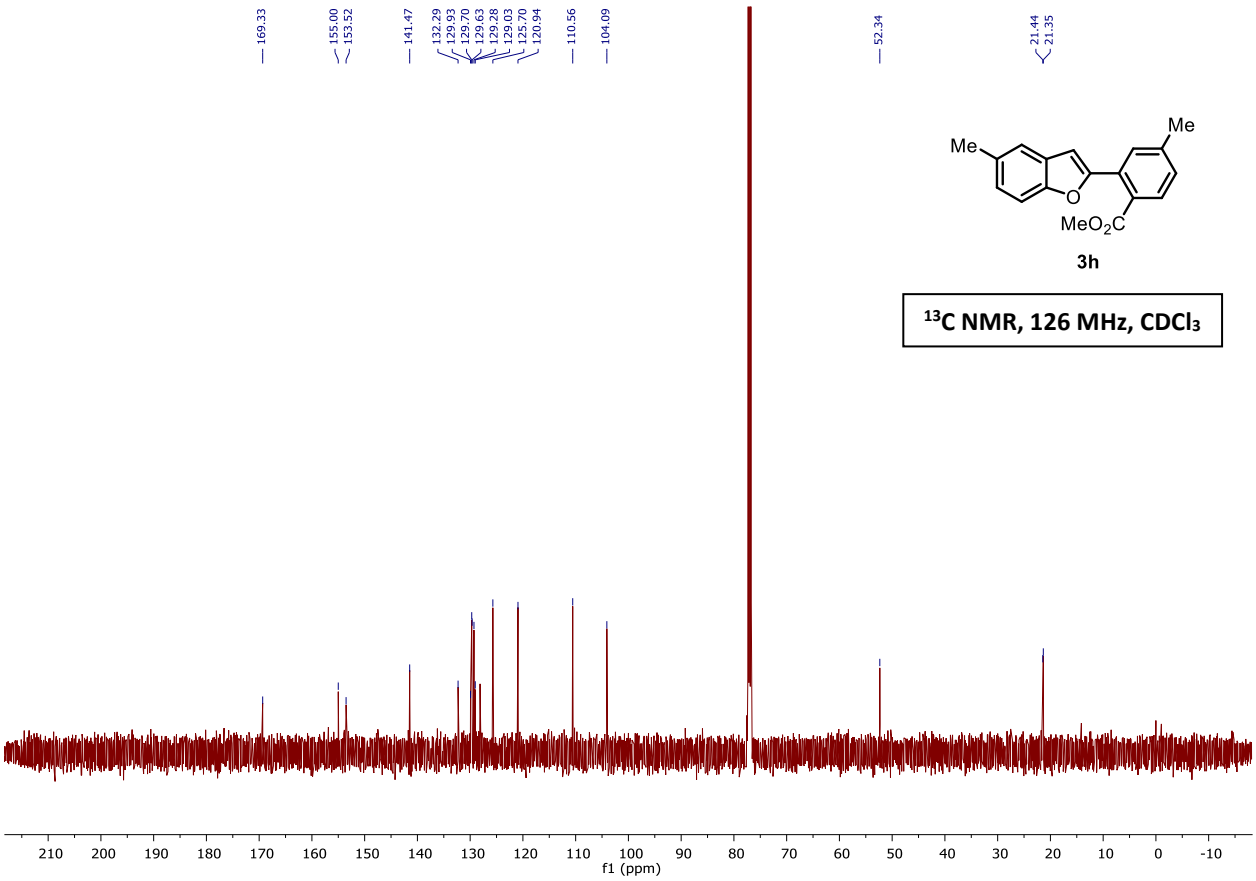
129.54
129.19
128.22
128.17
125.20
123.10
118.47
103.08
52.25
21.45
18.37
14.79
Me
Me
Me
O
MeO2C
3f
13C NMR, 126 MHz, CDCl3
f1 (ppm)


Me
Me
Me
MeO2C
3g
1H NMR, 400 MHz, CDCl3
f1 (ppm)


Me
Me
Me
MeO2C
3g
13C NMR, 126 MHz, CDCl3
f1 (ppm)


Me
Me
O
MeO2C
3h
1H NMR, 400 MHz, CDCl3
f1 (ppm)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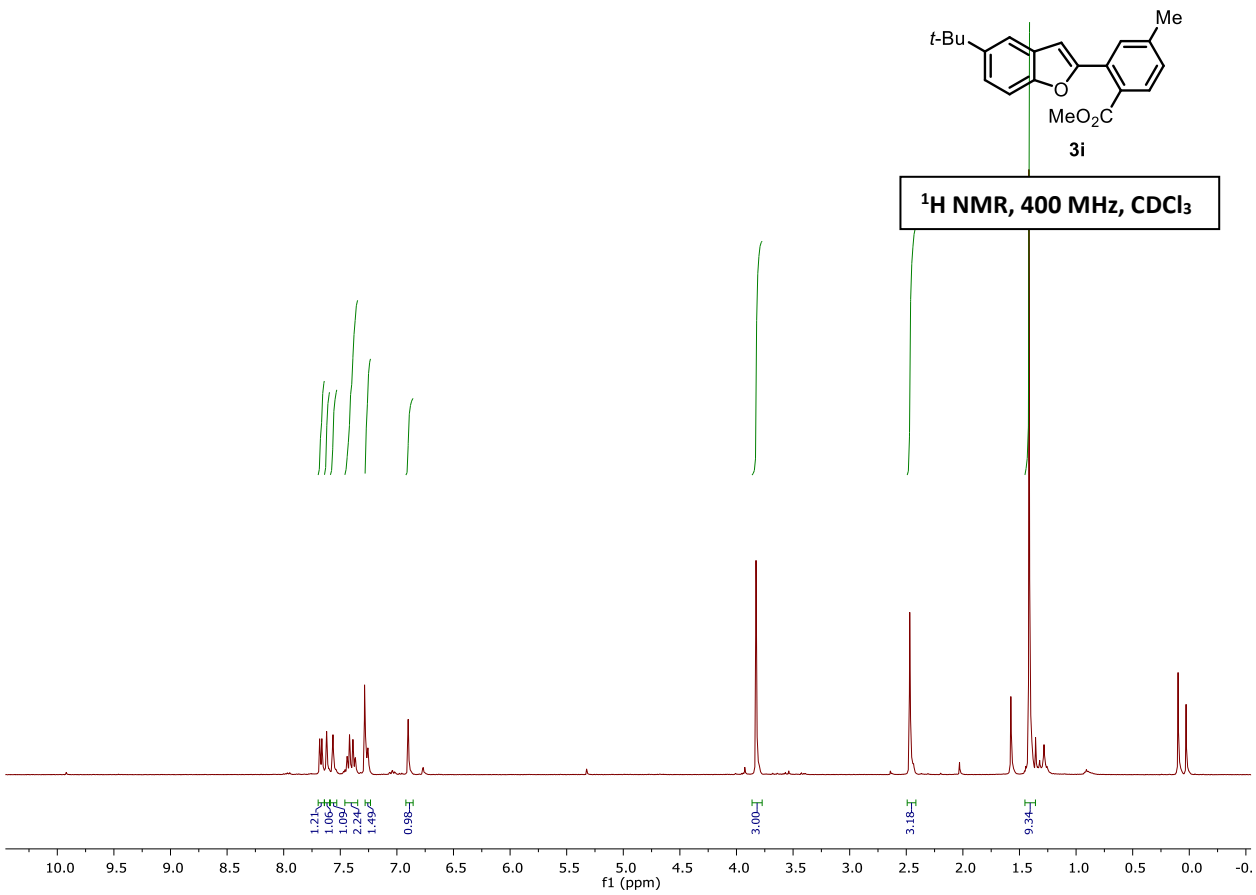
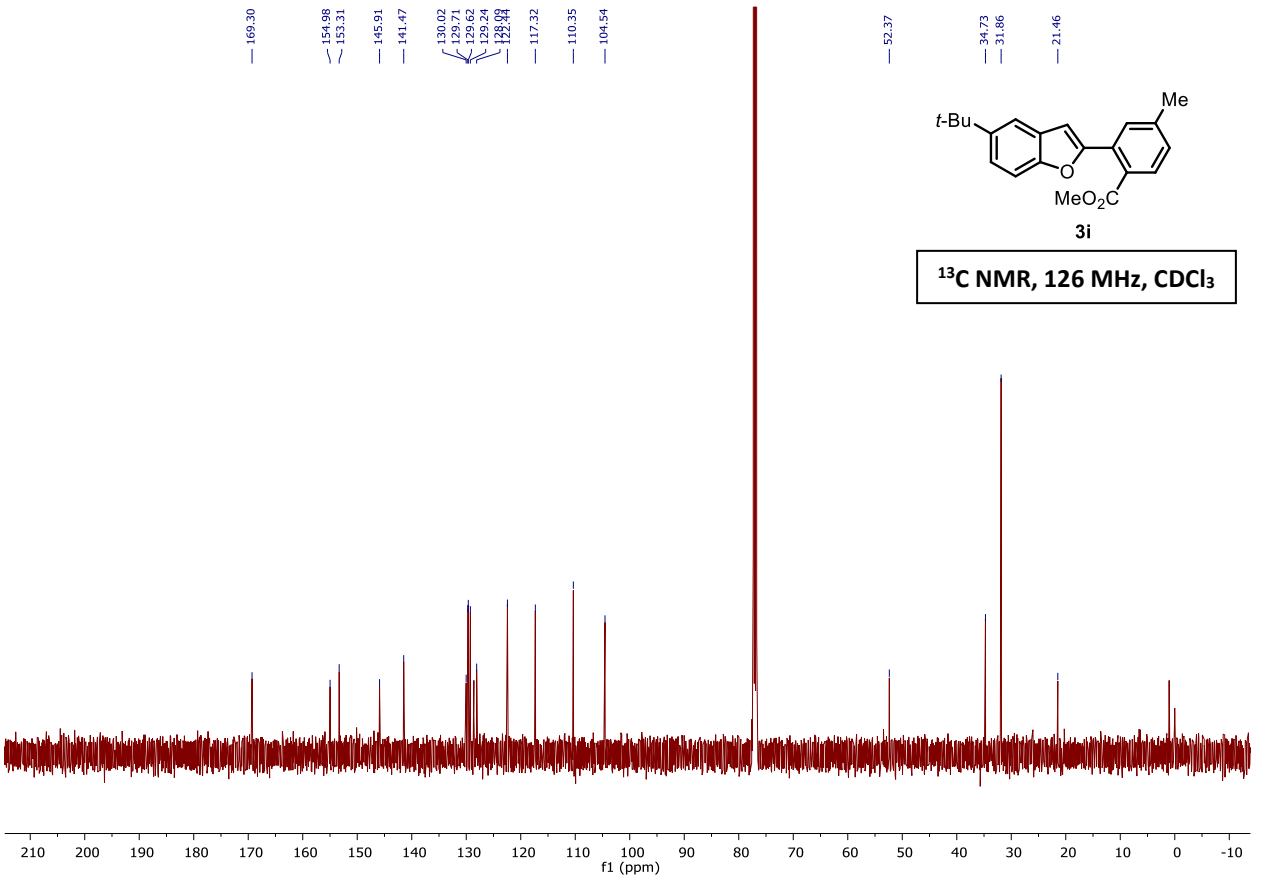
155.00
153.52
141.47
132.29
129.93
129.70
129.63
129.28
129.03
125.70
120.94
110.56
104.09
52.34
21.44
21.35
Me
Me
O
MeO2C
3h
13C NMR, 126 MHz, CDCl3
f1 (ppm)


t-Bu
Me
O
MeO2C
3i
1H NMR, 400 MHz, CDCl3
1.21
1.06
1.09
2.24
1.49
0.98
3.00
3.18
9.34
f1 (ppm)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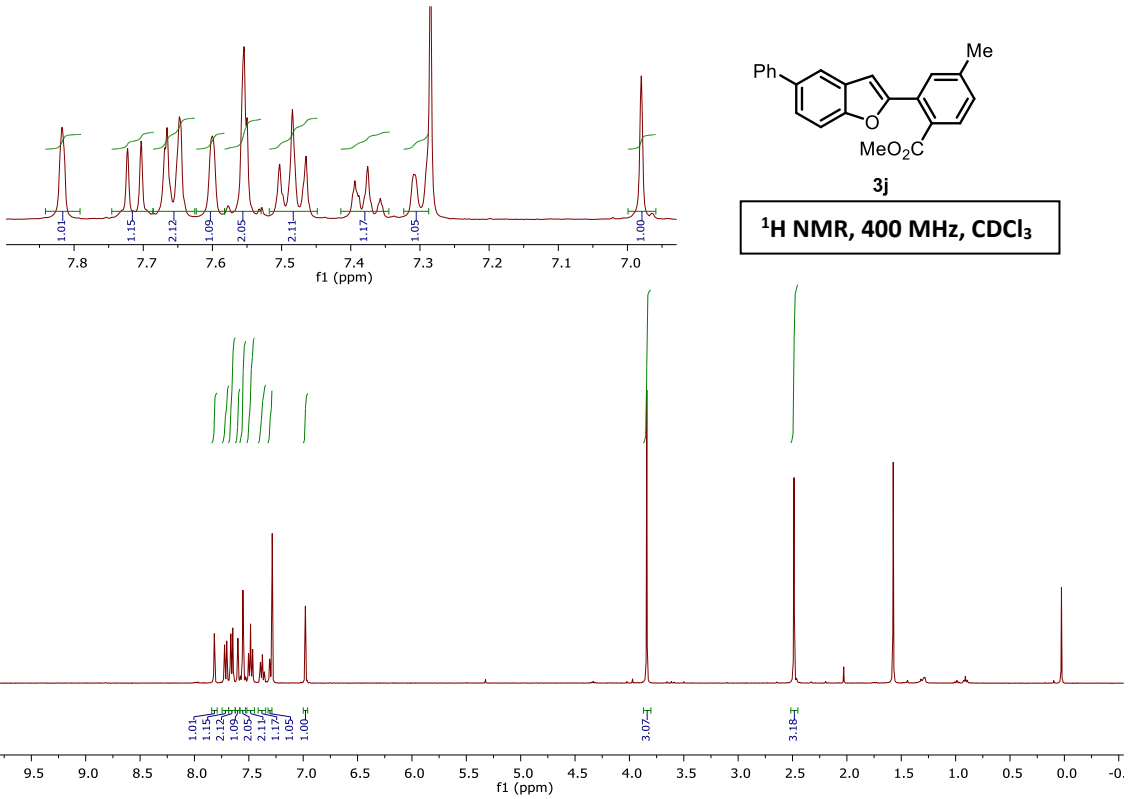
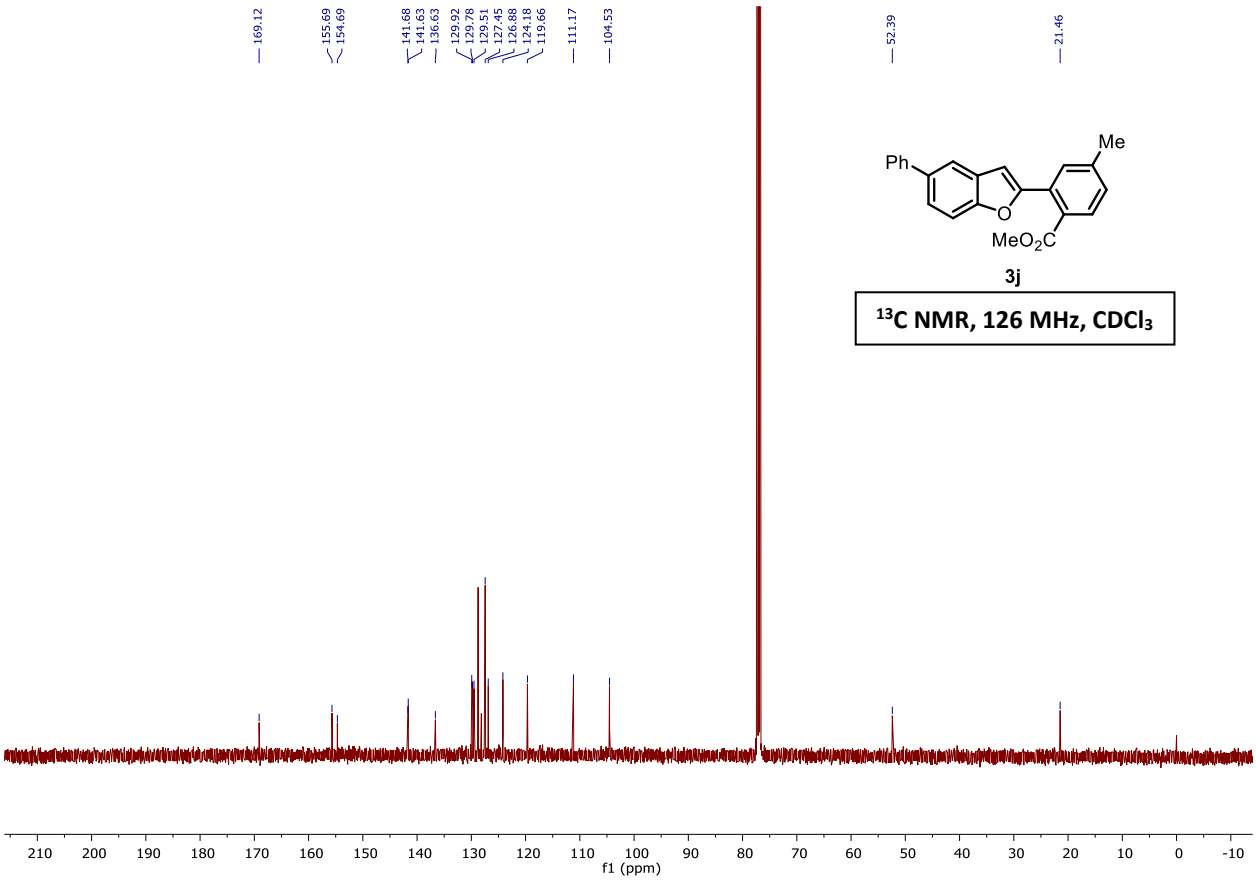
154.98
153.31
145.91
141.47
130.02
129.71
129.62
129.24
128.09
122.44
117.32
110.35
104.54
52.37
34.73
31.86
21.46
t-Bu
Me
O
MeO2C
3i
13C NMR, 126 MHz, CDCl3
f1 (ppm)


Ph
Me
O
MeO2C
3j
1H NMR, 400 MHz, CDCl3
f1 (ppm)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154.69
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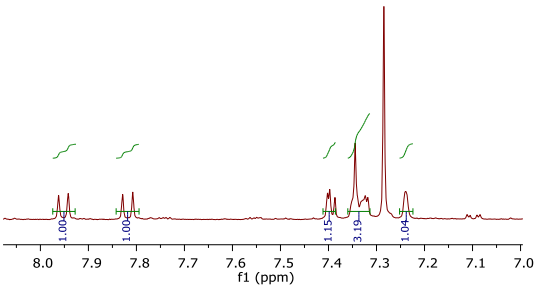
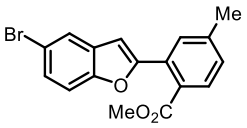
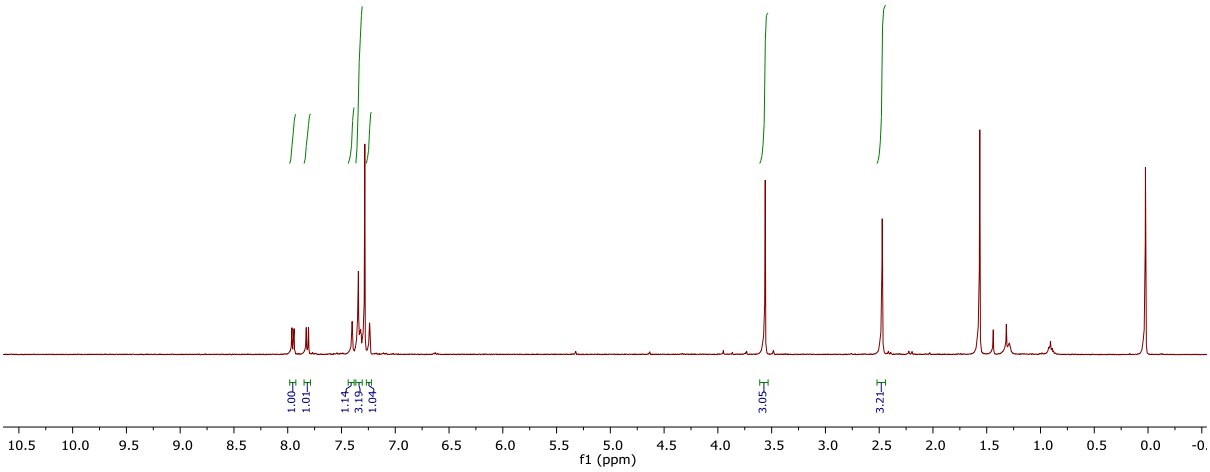
141.63
136.63
129.92
129.78
129.51
127.45
126.88
124.18
119.66
111.17
104.53
52.39
21.46
Ph
Me
O
MeO2C
3j
13C NMR, 126 MHz, CDCl3
f1 (ppm)

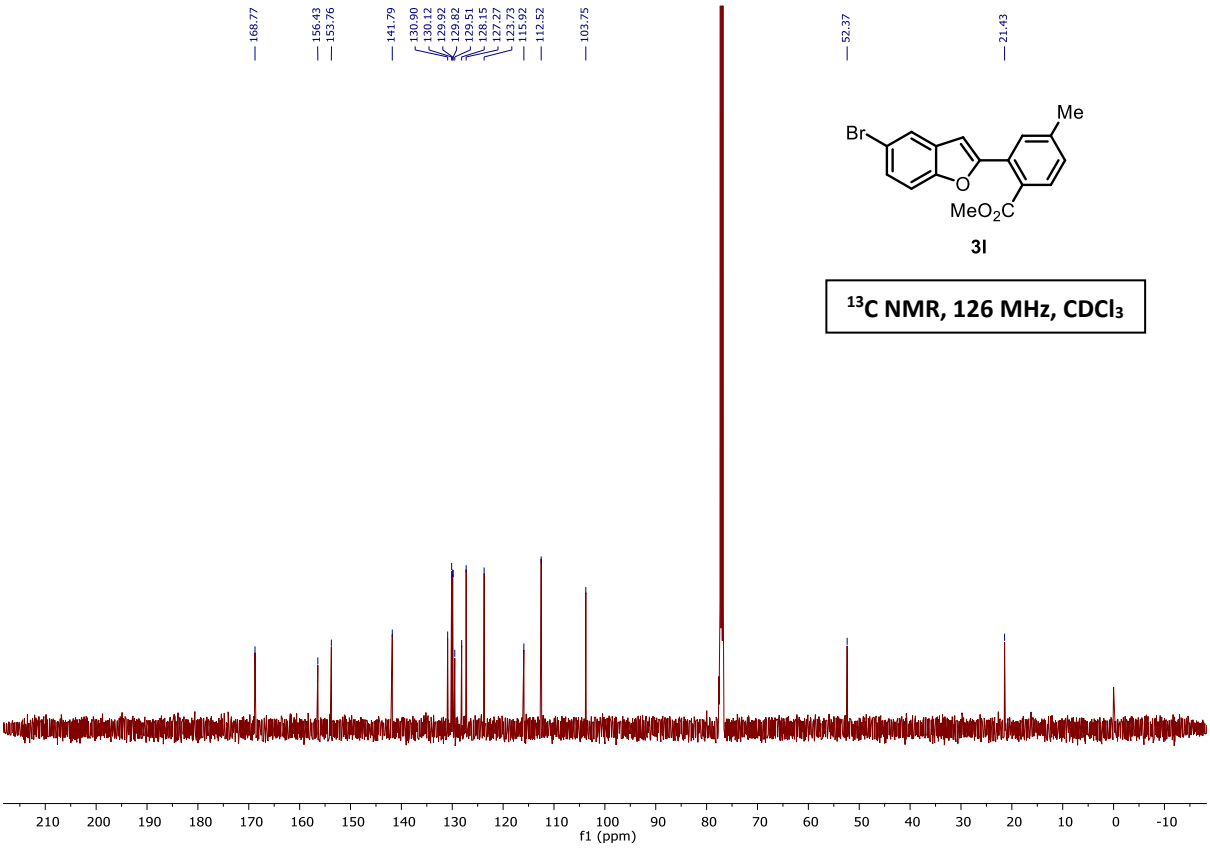




3l

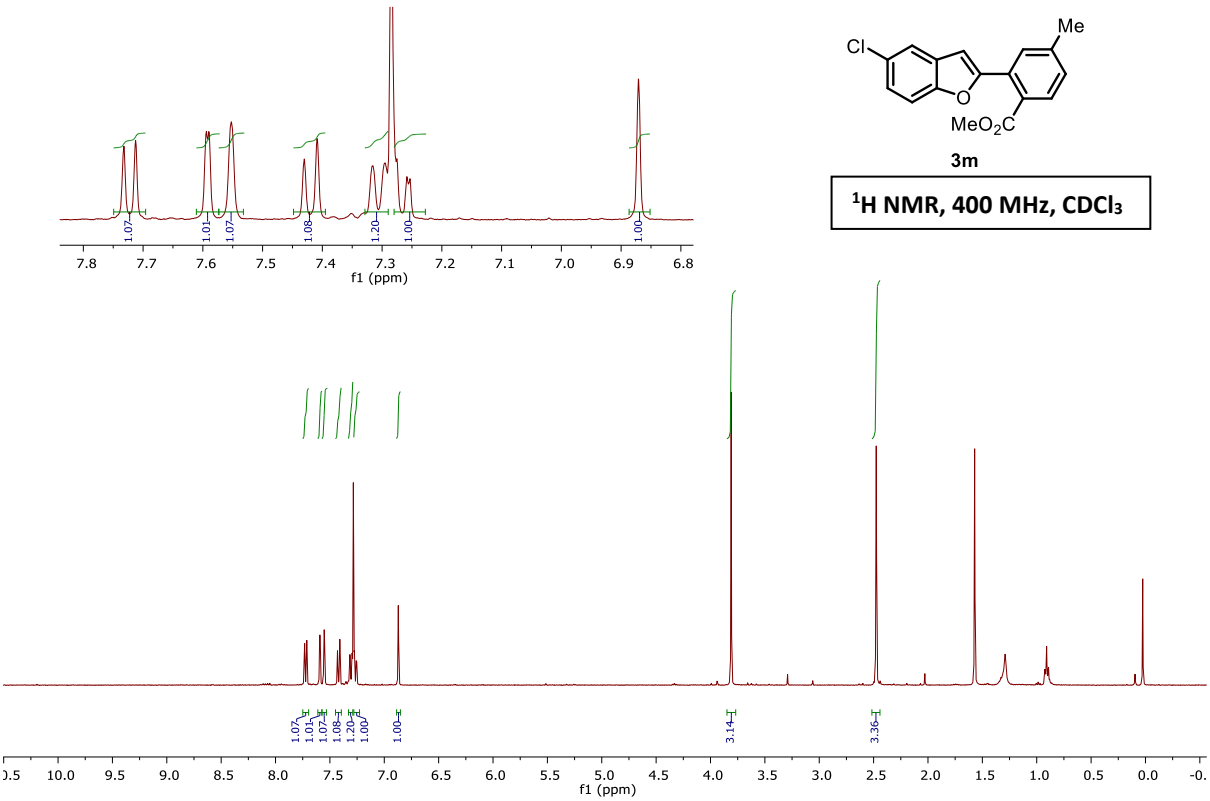
^{1}H NMR, 400 MHz, $CDCl_3$

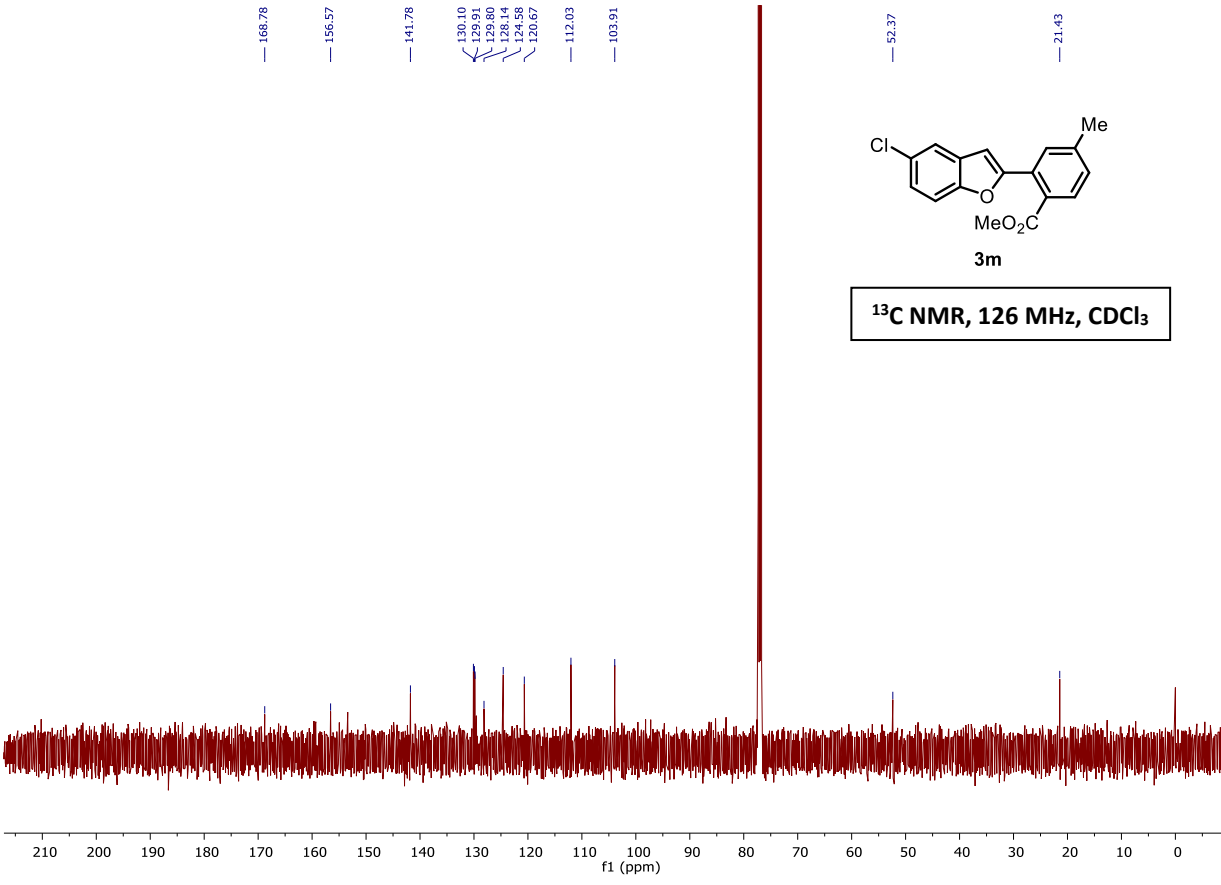




3l

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


Cl
Me
O
MeO2C
3m
1H NMR, 400 MHz, CDCl3
f1 (ppm)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130.10
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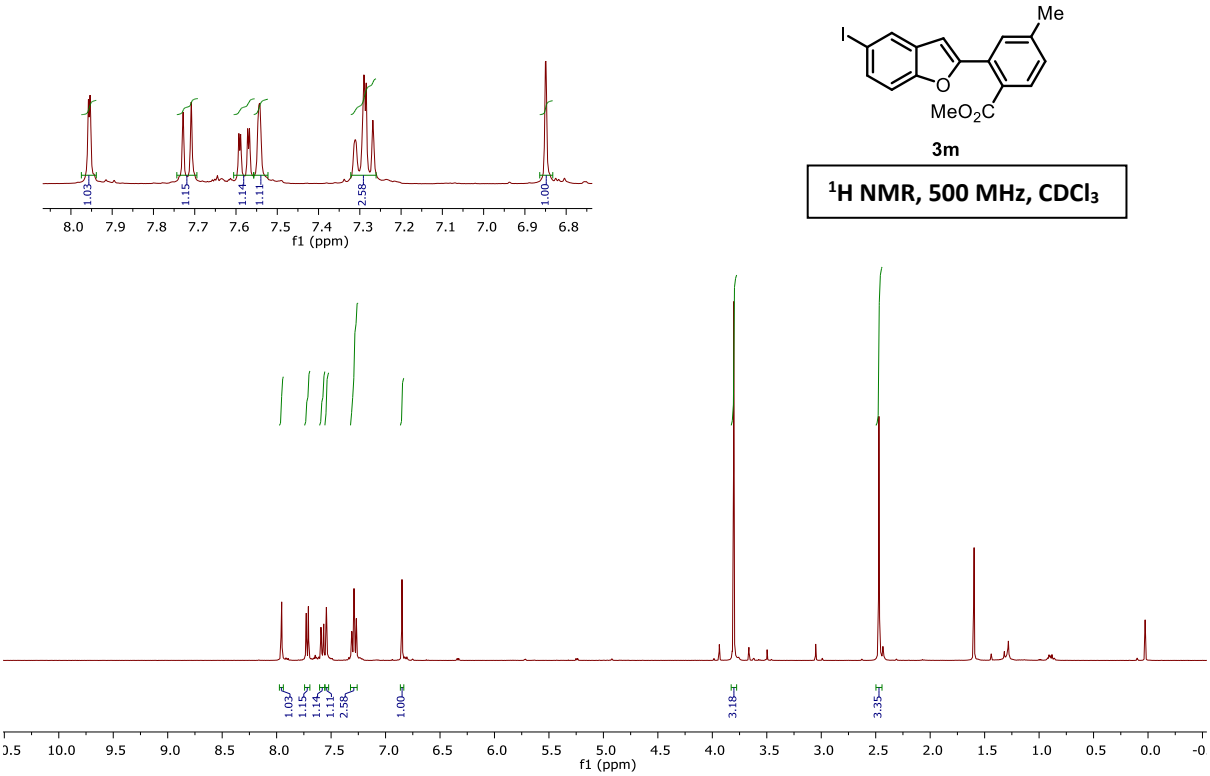
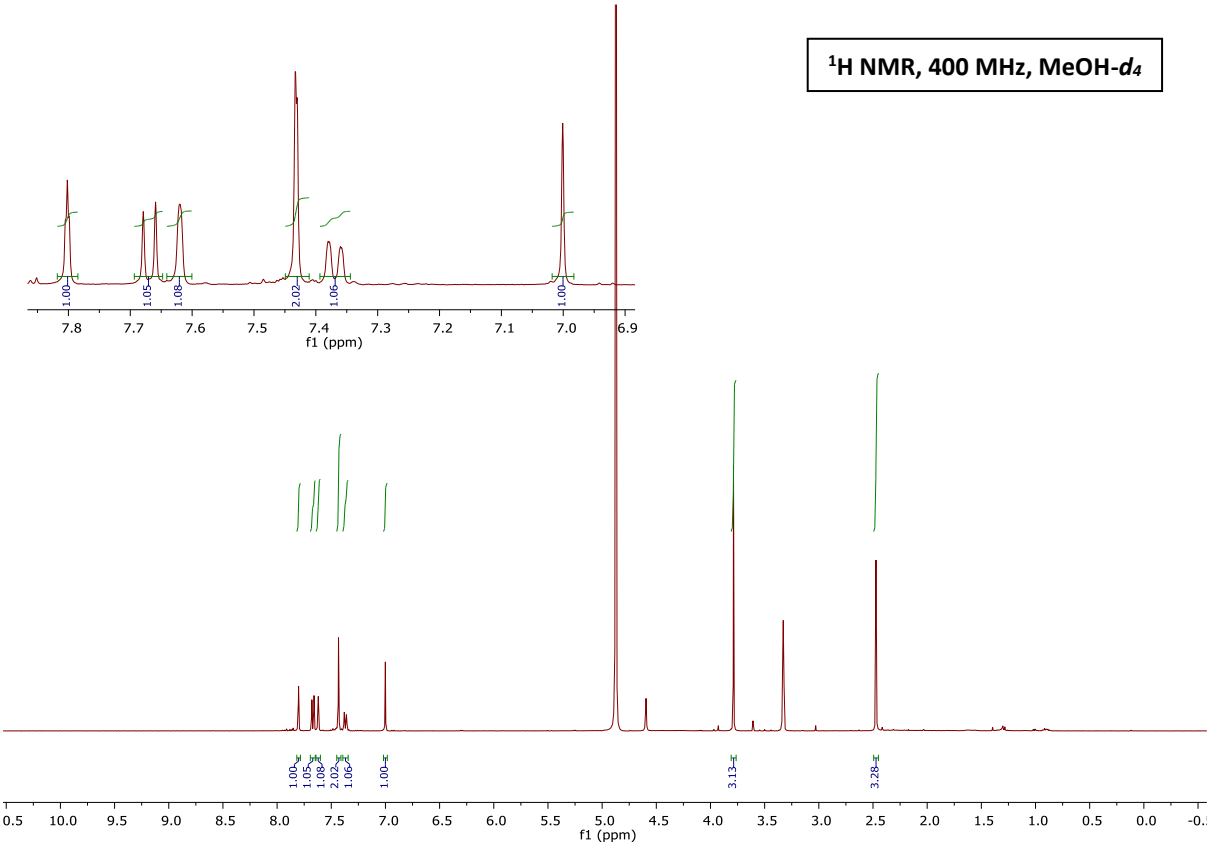
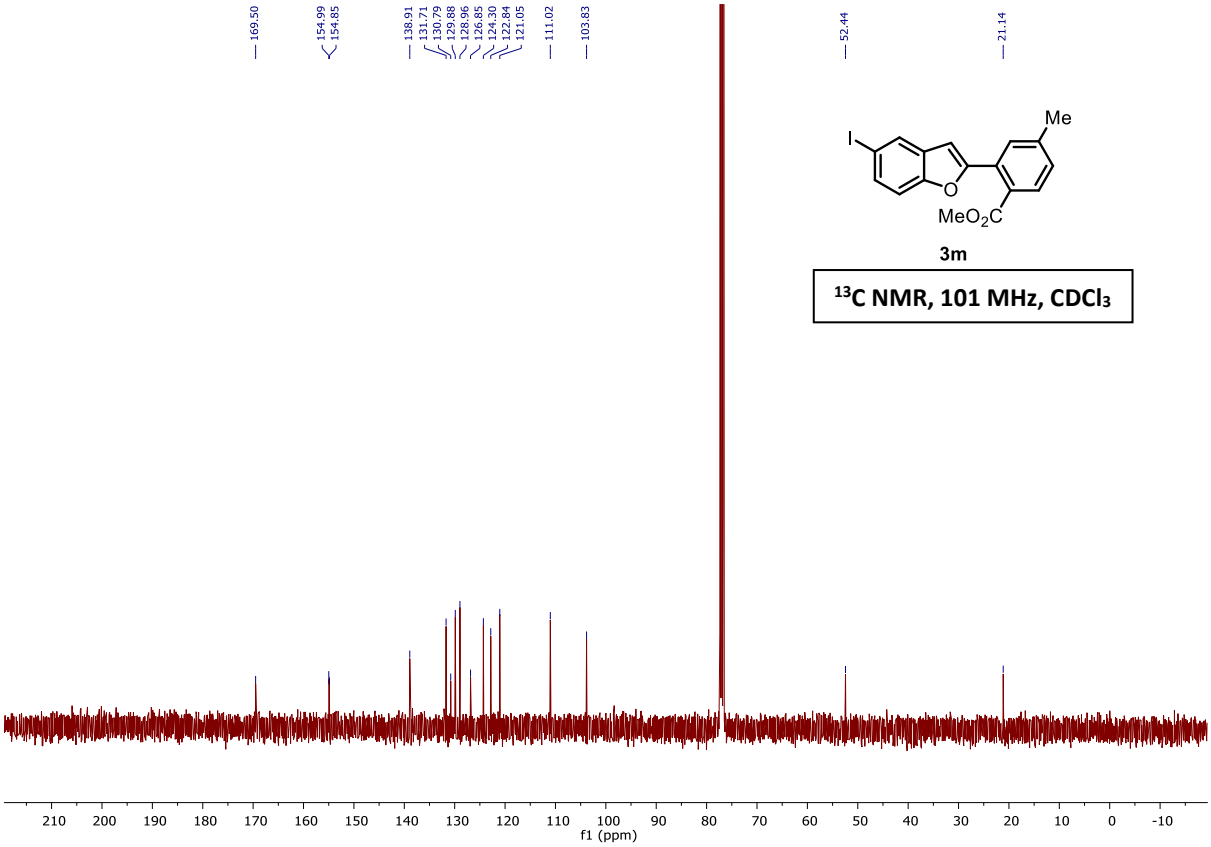
129.80
128.14
124.58
120.67
112.03
103.91
52.37
21.43
Cl
Me
O
MeO2C
3m
13C NMR, 126 MHz, CDCl3
f1 (ppm)


Me
I
O
MeO2C
3m
1H NMR, 500 MHz, CDCl3
f1 (ppm)


1H NMR, 400 MHz, MeOH-d4
f1 (ppm)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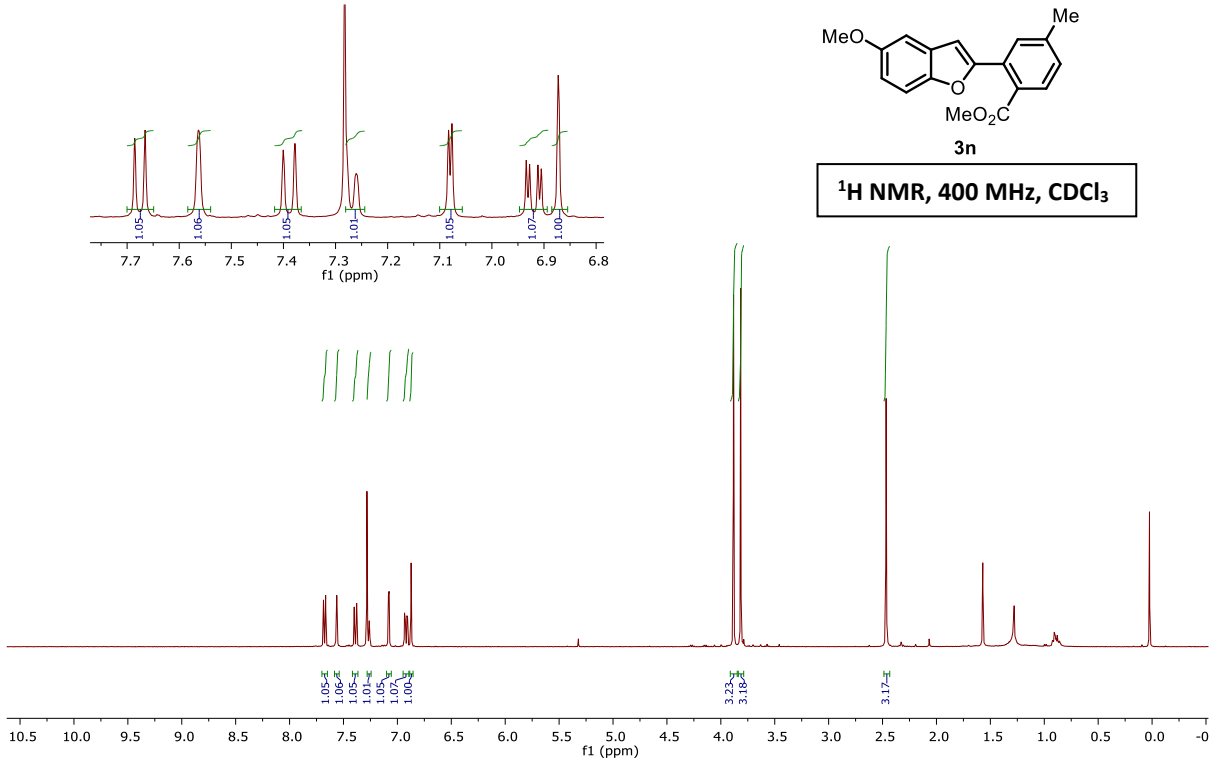
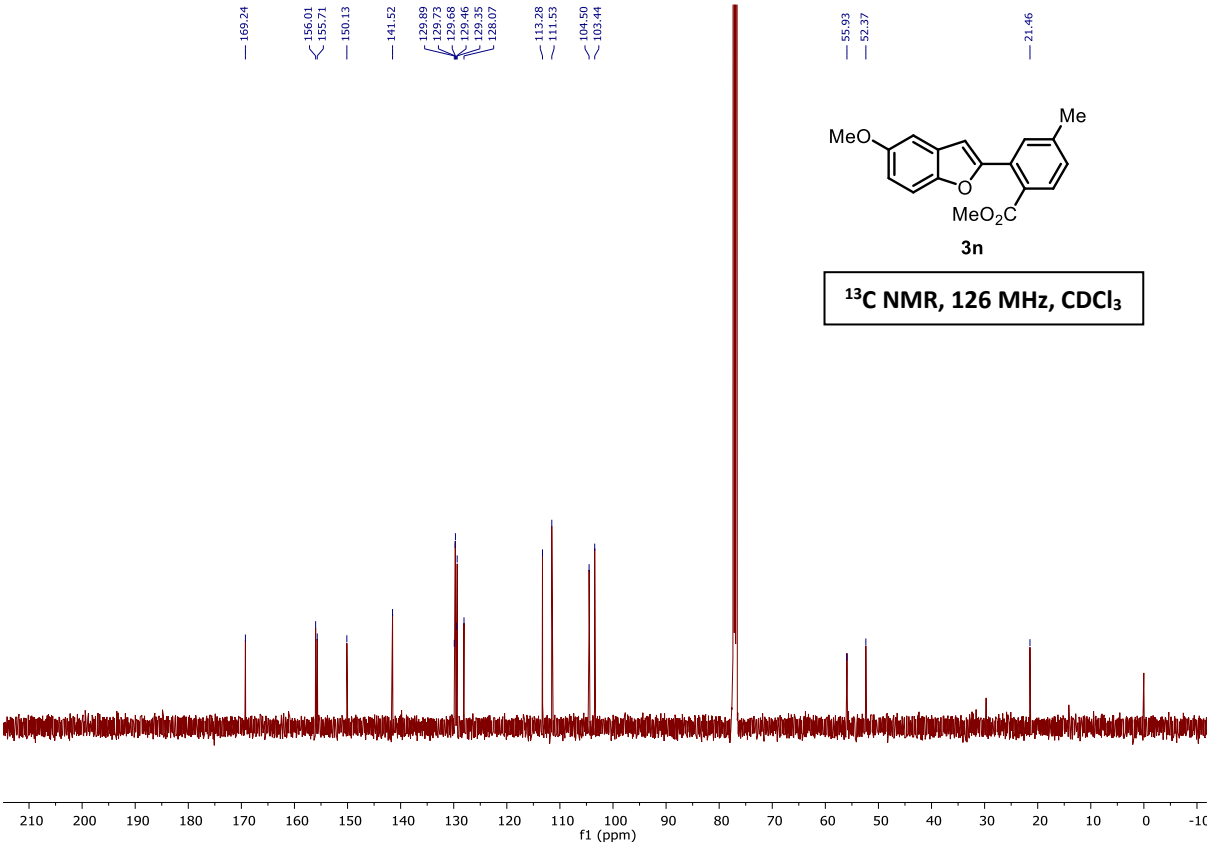
129.88
128.96
126.85
124.30
122.84
121.05
111.02
103.83
52.44
21.14
Me
I
O
MeO2C
3m
13C NMR, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
Me
O
MeO2C
3n
1H NMR, 400 MHz, CDCl3
f1 (ppm)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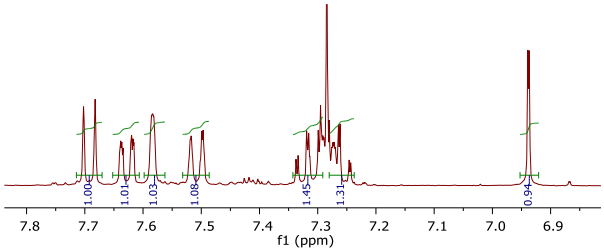
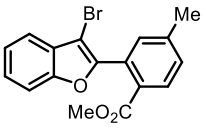
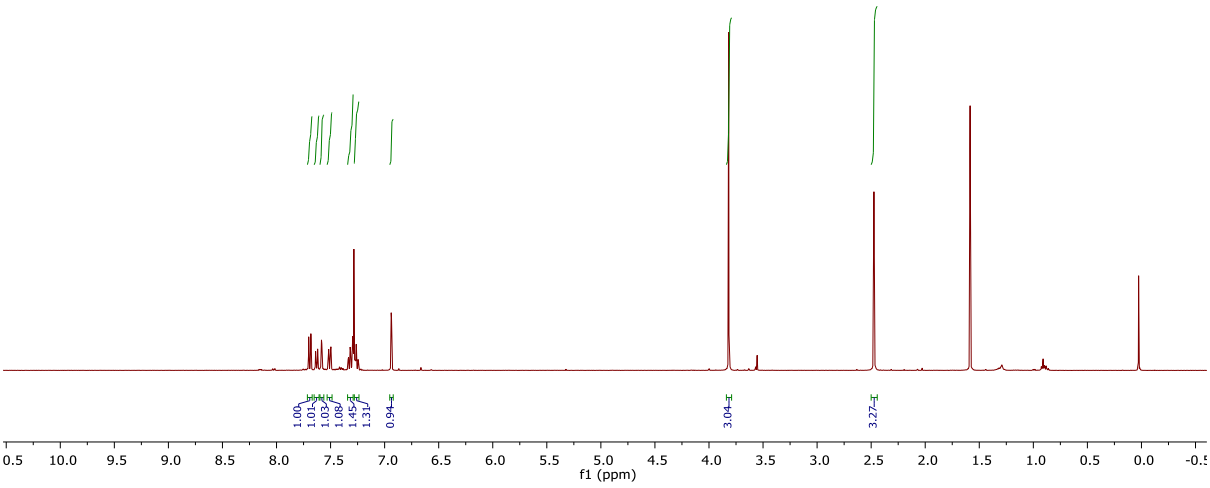
129.73
129.68
129.46
129.35
128.07
113.28
111.53
104.50
103.44
55.93
52.37
21.46
MeO
Me
O
MeO2C
3n
13C NMR, 126 MHz, CDCl3
f1 (ppm)

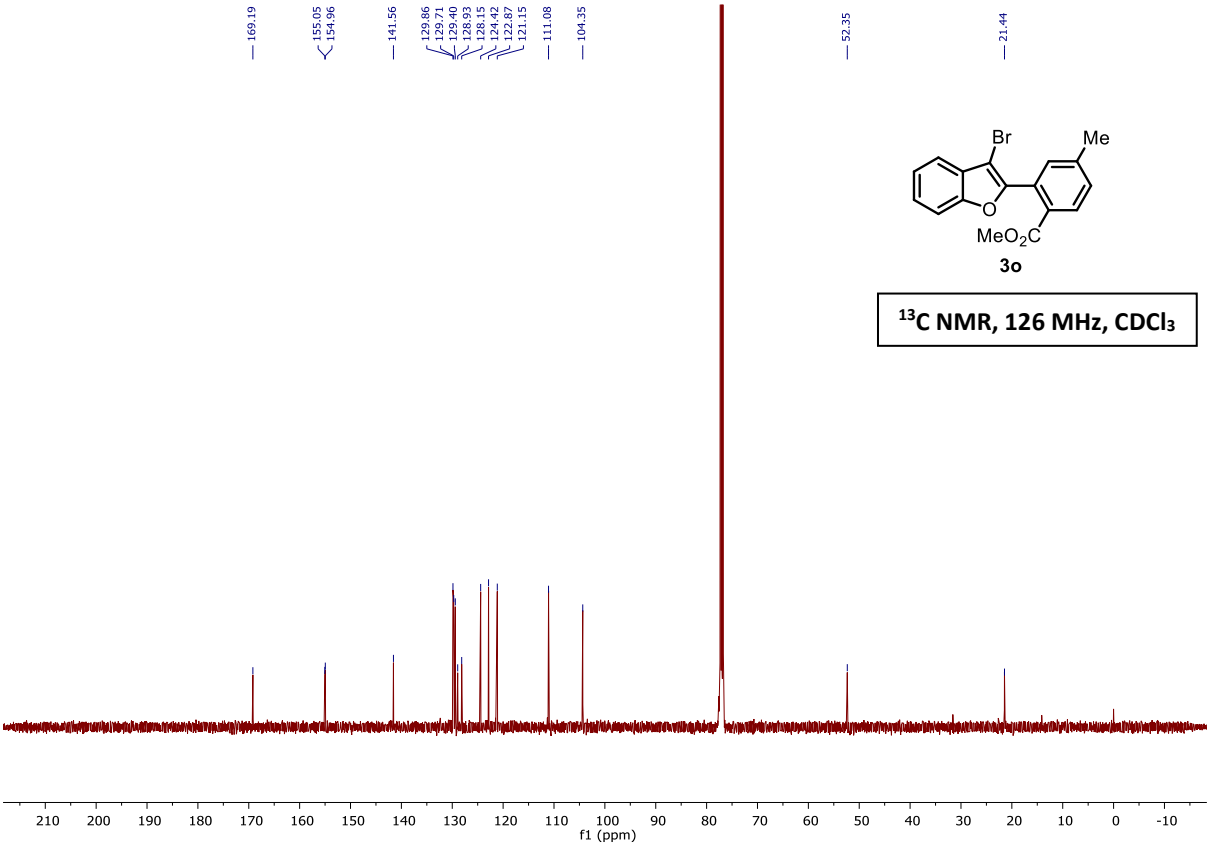




3o

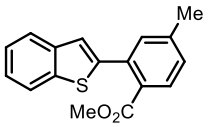
^{1}H NMR, 400 MHz, $CDCl_3$





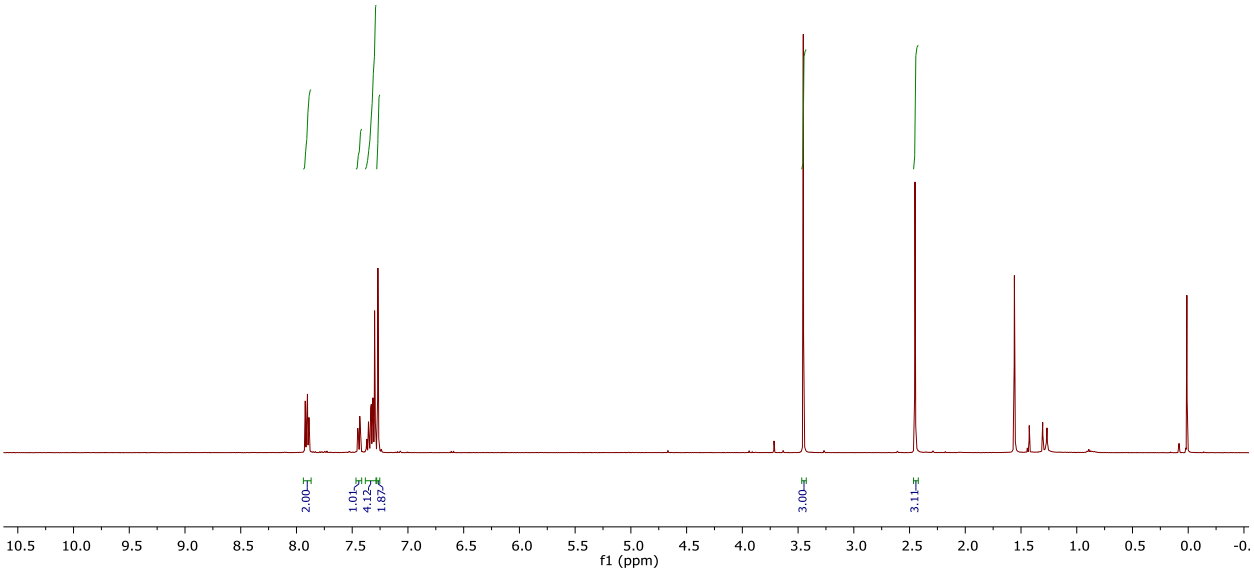
3o

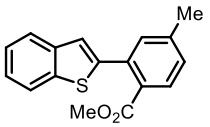
^{13}C NMR, 126 MHz, $CDCl_3$



3q

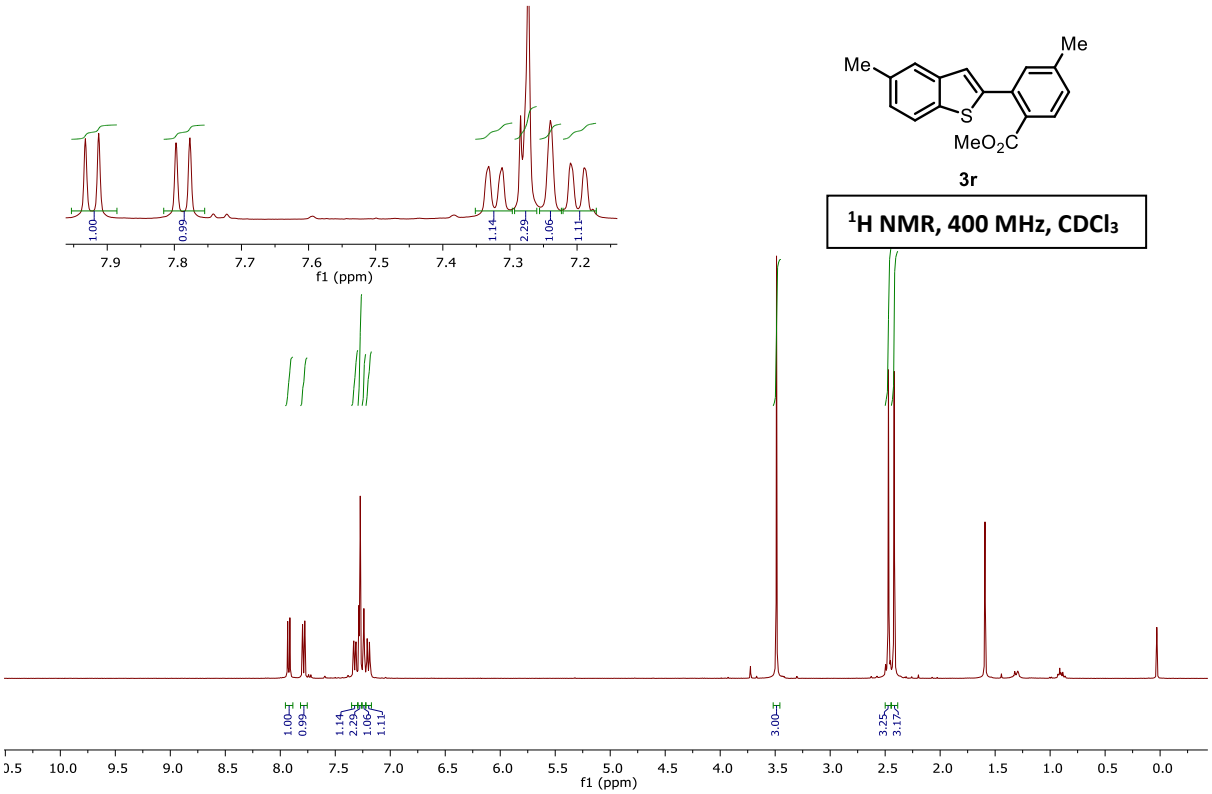
^{1}H NMR, 400 MHz, $CDCl_3$

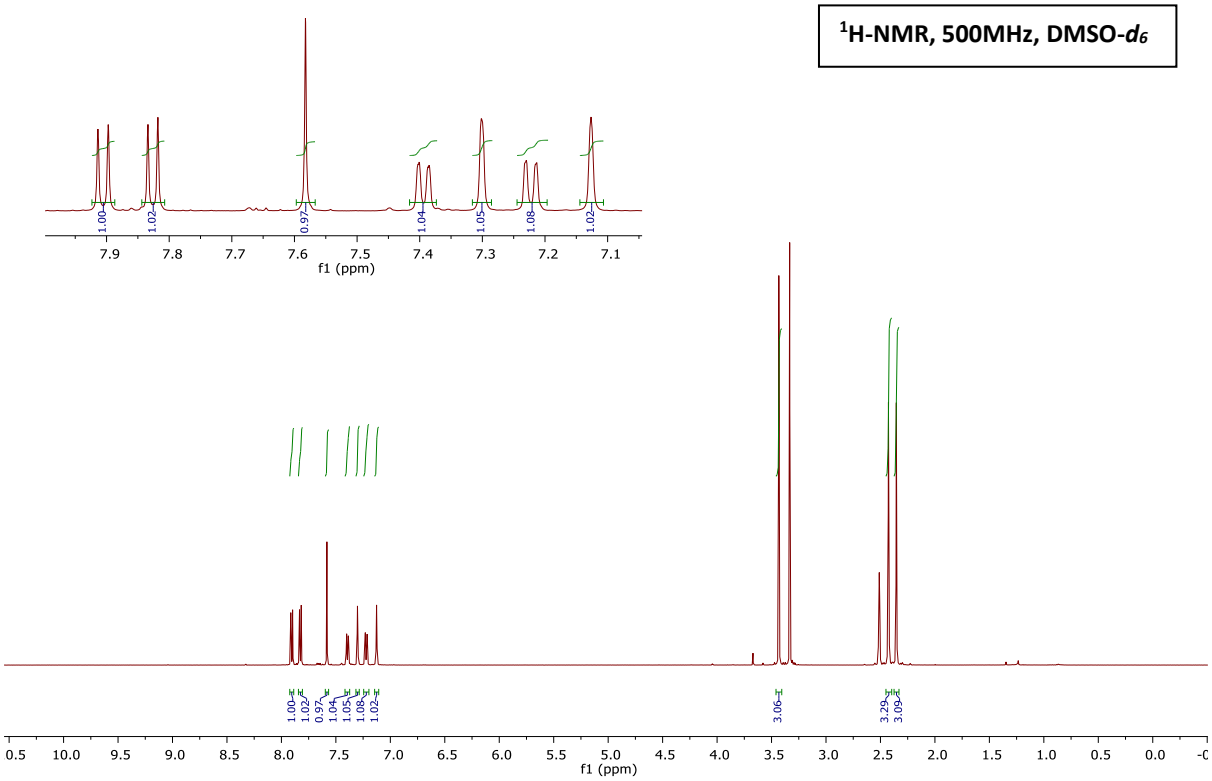


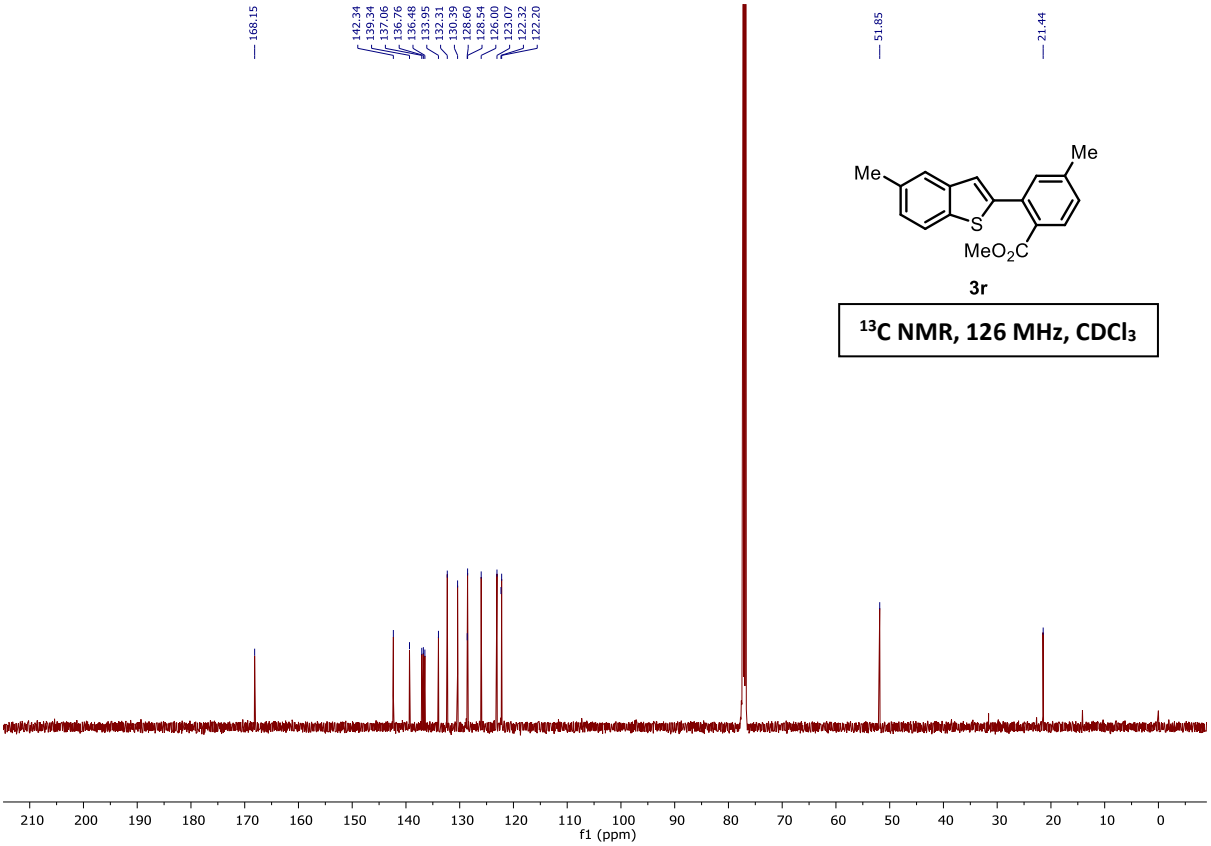


3q

^{13}C NMR, 101 MHz, $CDCl_3$


Me
Me
S
MeO2C
3r
1H NMR, 400 MHz, CDCl3
f1 (ppm)


1H-NMR, 500MHz, DMSO-d6
f1 (ppm)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137.06
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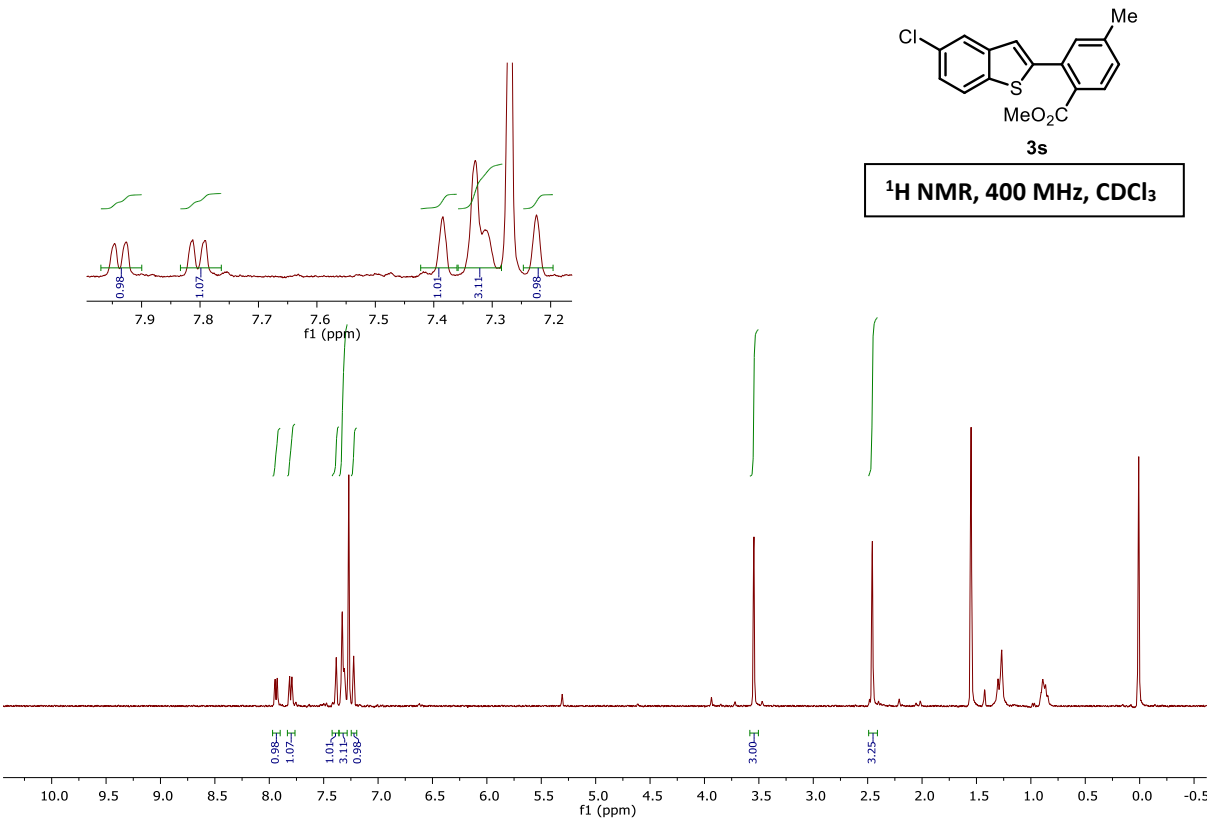
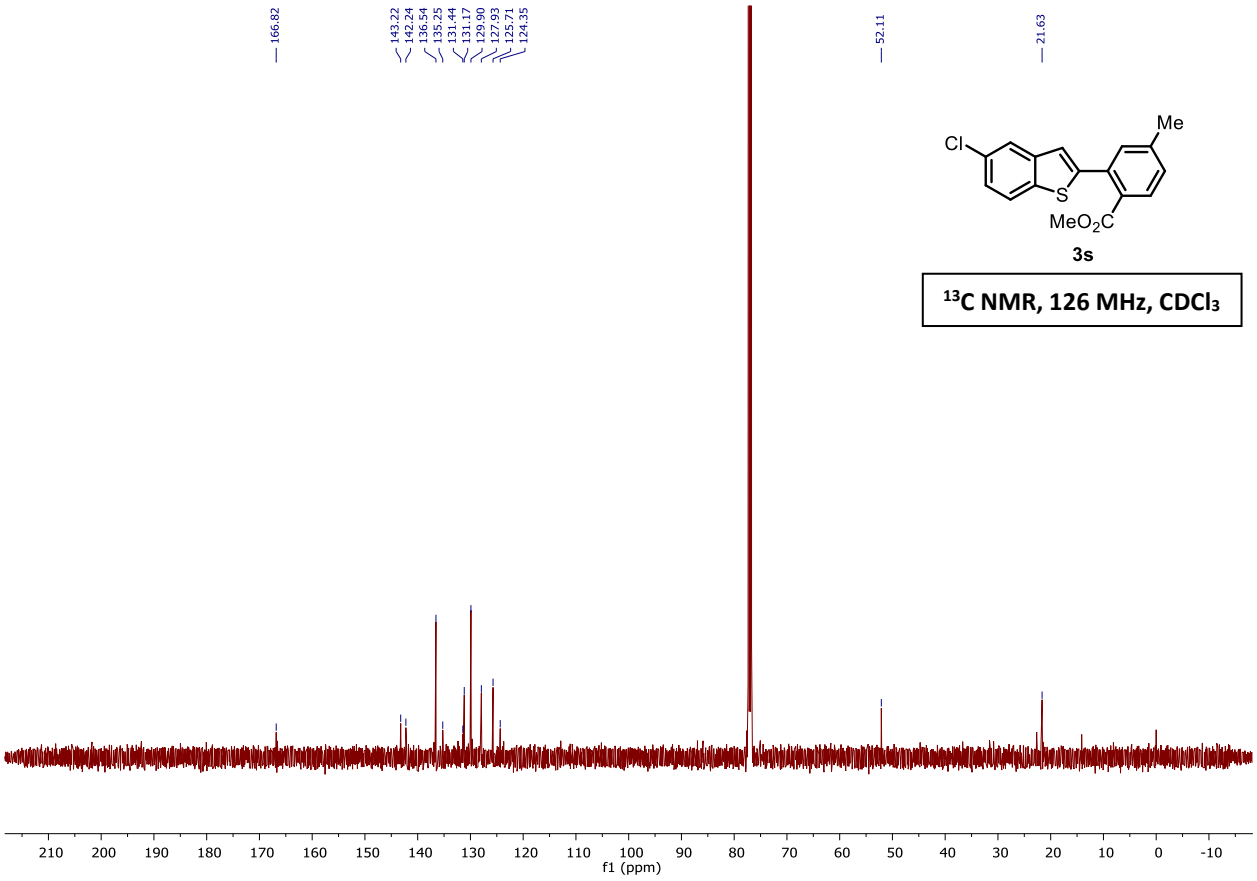
136.48
133.95
132.31
130.39
128.60
128.54
126.00
123.07
122.32
122.20
51.85
21.44
Me
Me
S
MeO2C
3r
13C NMR, 126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
Me
S
MeO2C
3s
1H NMR, 400 MHz, CDCl3
0.98
1.07
1.01
3.11
0.98
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)
0.98
1.07
1.01
3.11
0.98
3.00
3.25
10.0
9.5
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
0.0
-0.5
f1 (ppm)


166.82
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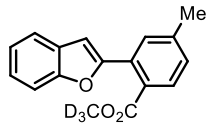
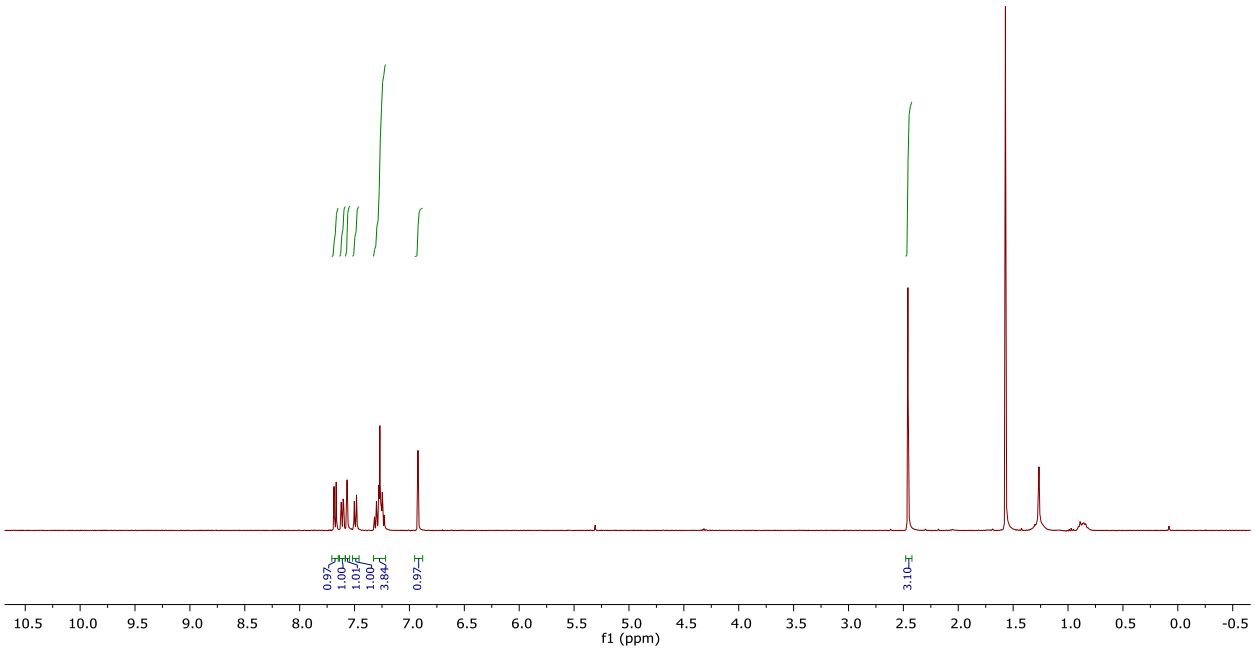
142.24
136.54
135.25
131.44
131.17
129.90
127.93
125.71
124.35
52.11
21.63
Cl
Me
S
MeO2C
3s
13C NMR, 126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

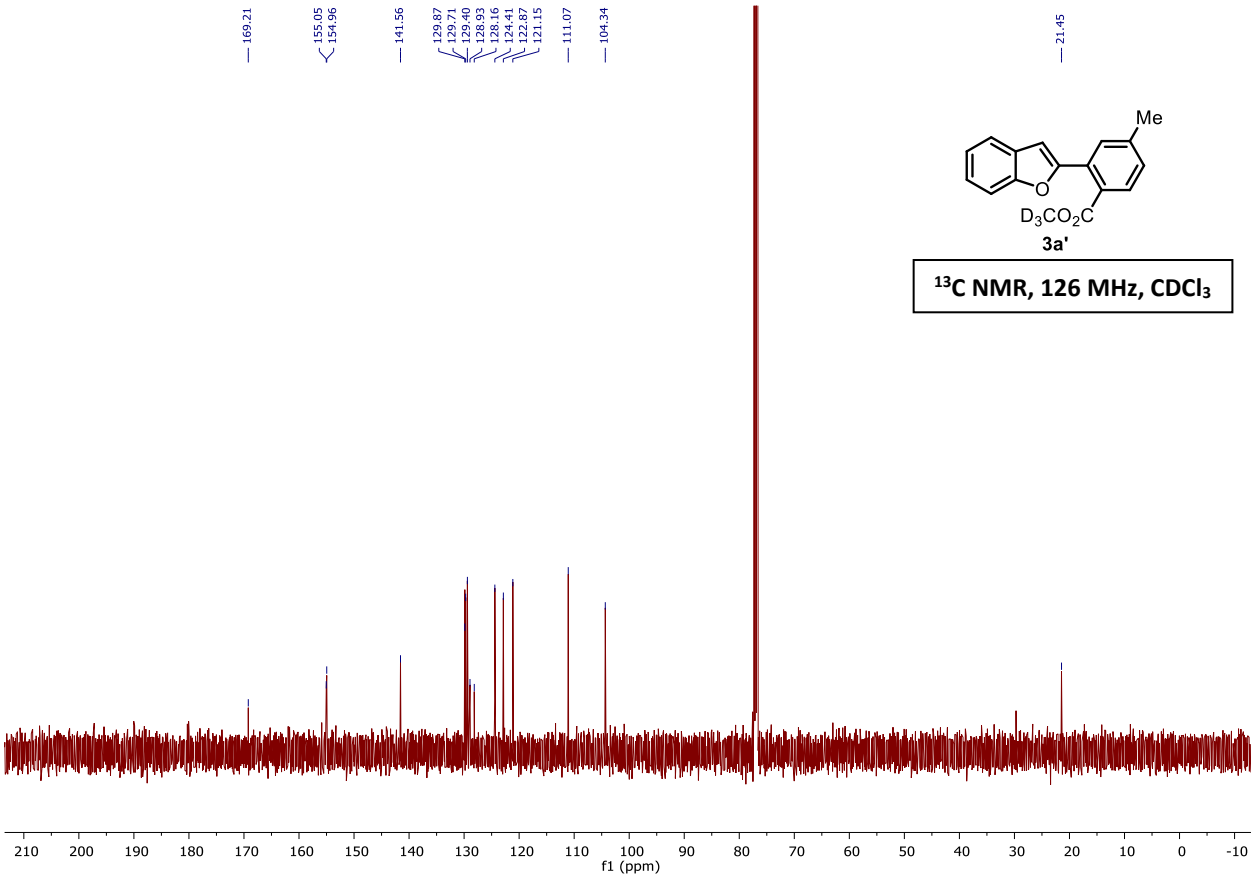
Analytical data of Mechanistic studies



3a'

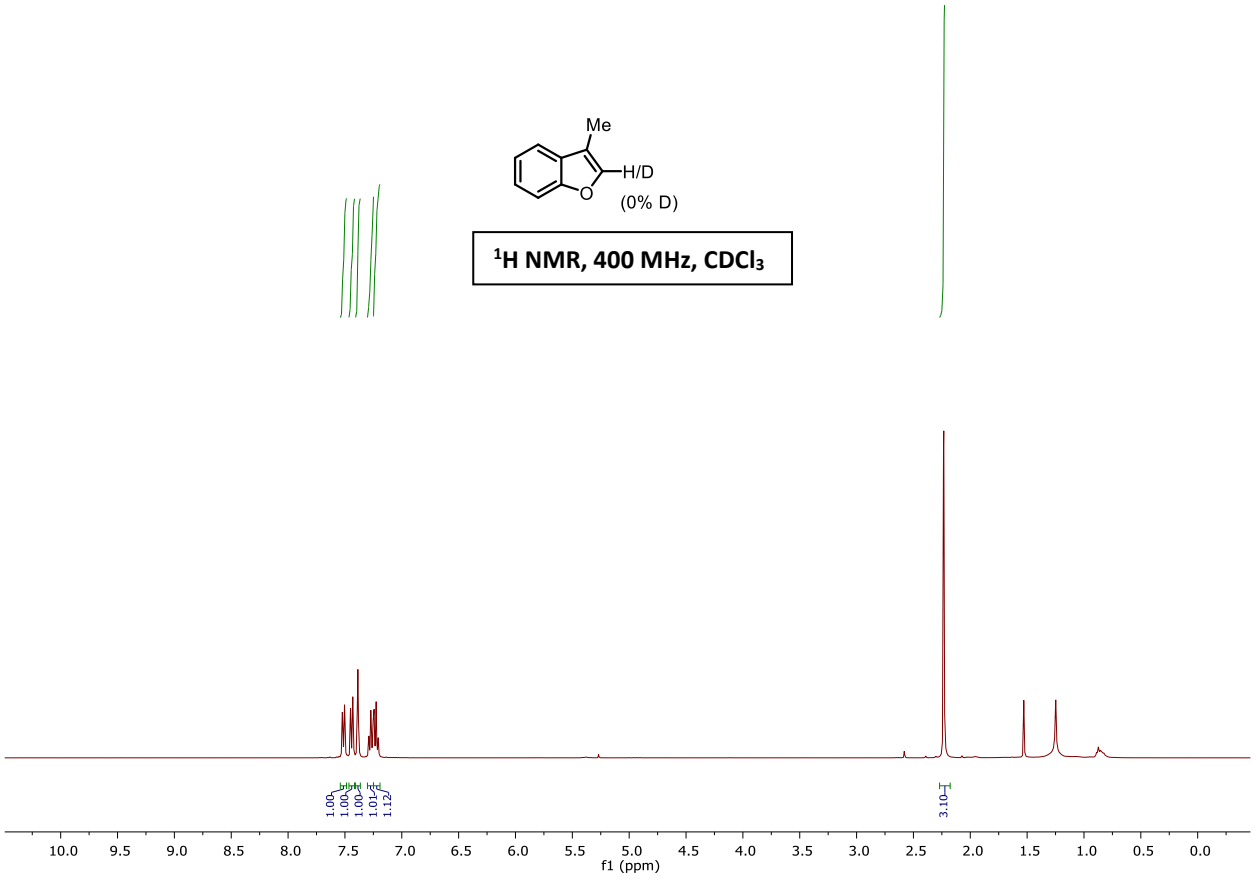
^{1}H NMR, 400 MHz, $CDCl_3$

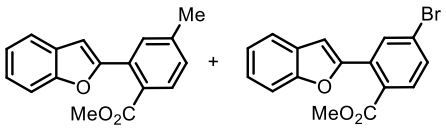




3a'

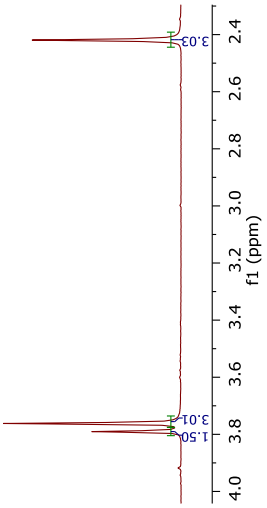
^{13}C NMR, 126 MHz, $CDCl_3$

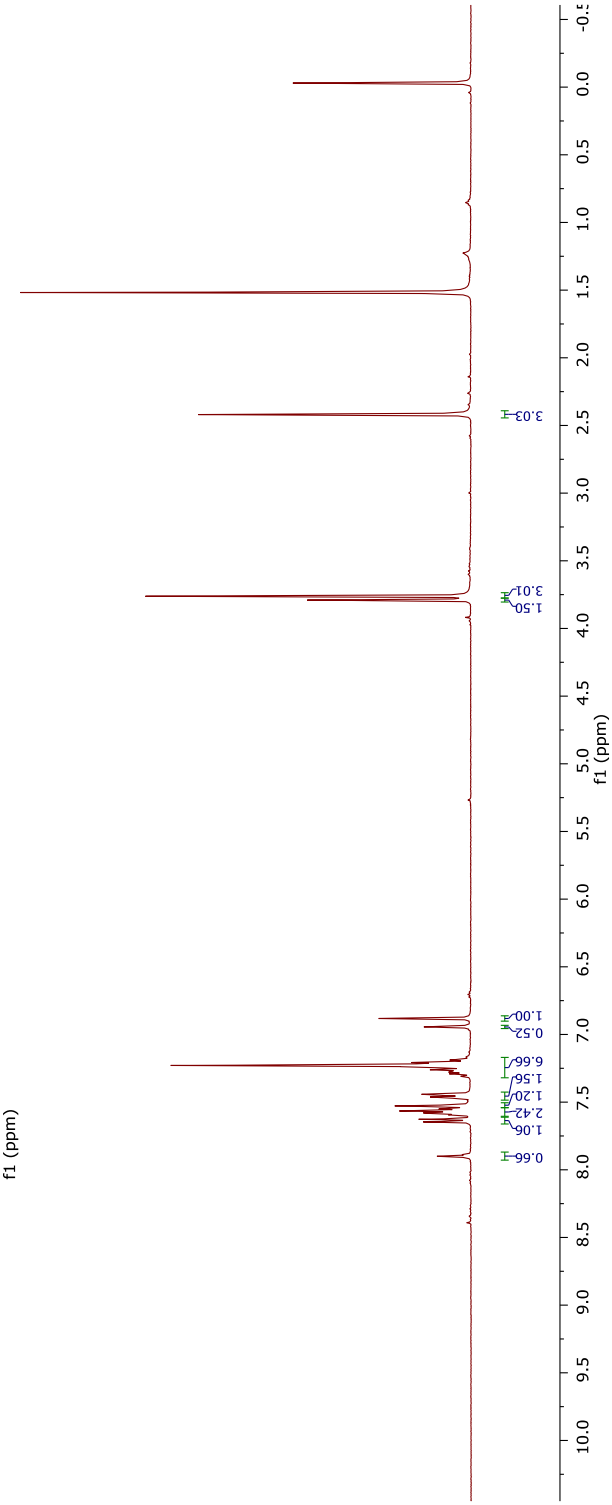

Me
H/D
(0% D)
O
1H NMR, 400 MHz, CDCl3
1.00
1.00
1.00
1.01
1.12
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



3a: 3ar (2:1)

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





X-ray crystallographic study of compound 3l:

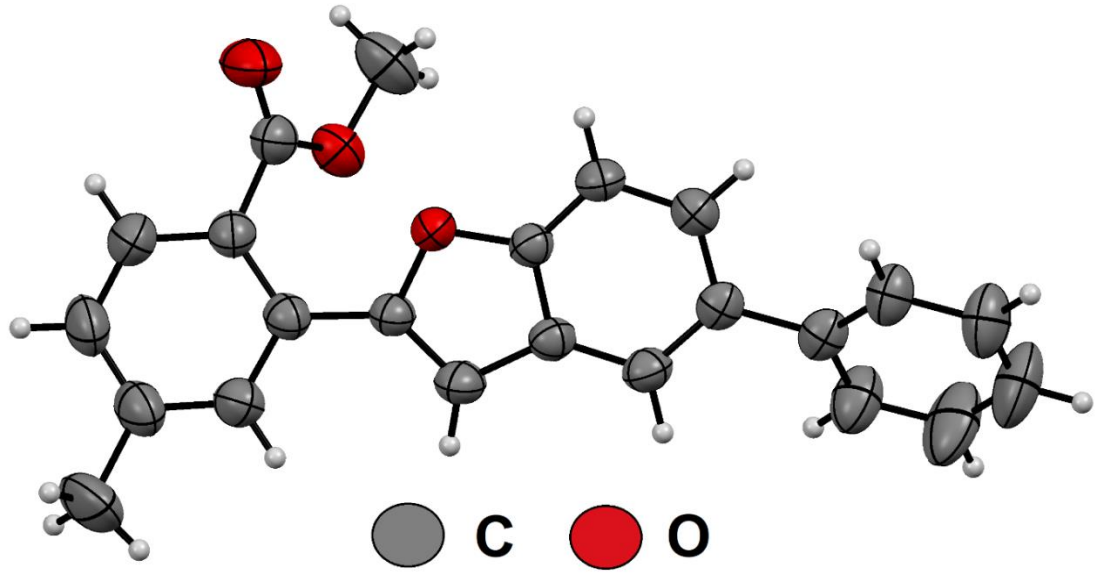


Figure 1: ORTEP of the **PS-17-11-135** drawn with 50% displacement ellipsoids.

Single crystal data of the compound **PS1711135** was collected on the Bruker D8 VENTURE diffractometer equipped with CMOS type (PHOTON 100) detector using monochromated Mo Kα radiation (λ = 0.71073 Å). Unit cell measurement, data collection, integration, scaling and absorption corrections for the crystal were done using Bruker Apex II software [1]. Data reduction was done by Bruker SAINT Suite[2]. The crystal structure was solved by direct methods using SHELXT 2014[3] and refined by the full matrix least squares method using SHELXL 2018 [4] present in the program suite WinGX (version 2014.1) [5].Absorption correction was applied using SADABS[6]. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were positioned geometrically and refined using ariding model with U_{iso}(H)=1.2U_{eq} [$C_{aromatic}$],U_{iso}(H) = 1.5Ueq (methyl groups). ORTEP was generated using Mercury 3.5.1(CCDC) program[7]. Crystallographic and refinement data of the compound was tabulated in **Table-1**.

Table 1. Crystal data and structure refinement for **PS-17-11-135**.

CCDC	1897155	
Empirical formula	C23 H18 O3	
Formula weight	342.37	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P n a 21	
Unit cell dimensions	a = 10.8534(4) Å	α= 90°.
	b = 13.6583(5) Å	β= 90°.
	c = 12.5256(4) Å	γ = 90°.
Volume	1856.78(11) $Å^3$	
Z	4	
Density (calculated)	1.225 Mg/m^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	720	
Crystal size	0.320 x 0.180 x 0.060 mm^3	
θ (min, max)range for data collection	2.397 to 30.531°.	
Index ranges	-15<=h<=15, -19<=k<=19, -17<=l<=17	
Reflections collected	33166	
Independent reflections	5665 [R(int) = 0.0893]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5665 / 1 / 238	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0590, wR2 = 0.0986	
R indices (all data)	R1 = 0.1320, wR2 = 0.1181	
Absolute structure parameter	0.2(16)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.153 and -0.179 e.$Å^{-3}$	

References:

1. Apex2, Version 2 User Manual, M86-E01078, Bruker Analytical X-ray Systems Madison, WI, 2006.

2. Siemens, SMART System, Siemens Analytical X-ray Instruments Inc. Madison, MI, 1995.

3. Sheldrick, G. M. *Acta Crystallogr*. **2015**, A71, 3-8.

4. Sheldrick, G. M. *ActaCrystallogr.***2015**, *C71*, 3-8.

5. Farrugia, L. J. *J. Appl. Crystallogr.***2012,** *45*, 849-854.

6. Sheldrick, G. M. SADABS; Bruker AXS, Inc.: Madison, WI, 2007.

7. Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock E.; Rodriguez-Monge, L.; Taylor, R.; Streek, J.; Wood, P. A. *J. Appl. Crystallogr.***2008**, *41*, 466-470.