**Supporting Information**

# Multicomponent Formation to A New Class of Oxygen-Based 1,3-Dipolar Cycloaddition Reagent and the Modular Synthesis of Furans

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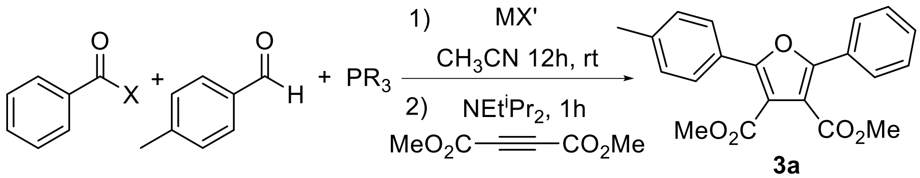
## I. General Procedures

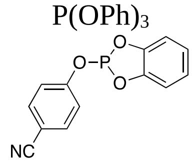
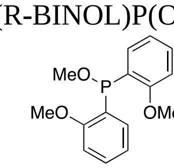
All manipulations were conducted in a glovebox under a nitrogen atmosphere. Unless otherwise noted, all reagents were purchased from commercial sources and used without purification. Solvents were dried by filtration over activated alumina under nitrogen using an MBraun solvent purifier system. Solvents were stored over activated 3Å molecular sieves inside the glovebox. Deuterated acetonitrile was stirred over calcium hydride, vacuum transferred, degassed, and stored over 4Å molecular sieves. 2-Phenyl-benzo[1,3,2]dioxaphosphole ((catechyl)PPh),[1] the alkyne-tethered aldehyde,[2] and aldehyde **7**,[3] were prepared using literature procedures. Acyl bromides and iodides were prepared by halide exchange from the acid chloride, as previously reported.[4] Nuclear magnetic resonance (NMR) characterization was performed on 500 MHz spectrometers for proton, 126 MHz for carbon, 377 MHz for fluorine and 162 MHz for phosphorus. $^{1}$H, and $^{13}$C NMR chemical shifts were referenced to residual solvent. Mass spectra were recorded on a high-resolution electrospray ionization quadrupole mass spectrometer.

## II. Supplementary Tables

### Table S1. Supplementary Optimization Data with Activating Salts and $PR_3$ Variation[a]



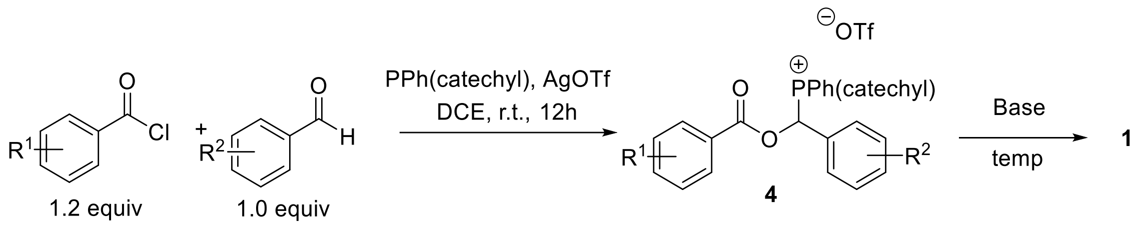

**3a**

| X | MX' | Solvent | $PR_3$ | Base | % **3a**[b] |
|---|---|---|---|---|---|
| Cl | - | $CD_3CN$ | PPh(catechyl) | $NEt^iPr_2$ | - |
| Cl | $AlCl_3$ | $CD_3CN$ | PPh(catechyl) | $NEt^iPr_2$ | - |
| Br or I | - | $CD_3CN$ | PPh(catechyl) | $NEt^iPr_2$ | - |
| Cl | TMSBr | $CD_3CN$ | PPh(catechyl) | $NEt^iPr_2$ | - |
| Cl | TMSI | $CD_3CN$ | PPh(catechyl) | $NEt^iPr_2$ | - |
| Cl | NaI | $CD_3CN$ | PPh(catechyl) | $NEt^iPr_2$ | - |
| Cl | NaI[e] | $CD_3CN$ | PPh(catechyl) | $NEt^iPr_2$ | - |
| Cl | NaI[c] | $CD_3CN$ | PPh(catechyl) | $NEt^iPr_2$ | 32 |
| Cl | TMSI[c] | $CD_3CN$ | PPh(catechyl) | $NEt^iPr_2$ | 25 |
| Br[c] | - | $CD_3CN$ | PPh(catechyl) | $NEt^iPr_2$ | 45 |
| I[c] | - | $CD_3CN$ | PPh(catechyl) | $NEt^iPr_2$ | 70 |
| Cl | AgOTf | DCE | PPh(catechyl) | $NEt^iPr_2$ | 80 |
| Cl | AgOTf[e] | DCE | PPh(catechyl) | $NEt^iPr_2$ | 64 |
| Cl | AgOTf[d] | DCE | PPh(catechyl) | $NEt^iPr_2$ | 87 |
| Cl | $Mg(OTf)_2$ | DCE | PPh(catechyl) | $NEt^iPr_2$ | <10 |
| Cl | $Cu(OTf)_2$ | DCE | PPh(catechyl) | $NEt^iPr_2$ | 54 |
| Cl | KOTf | DCE | PPh(catechyl) | $NEt^iPr_2$ | - |
| Cl | NaOTf | DCE | PPh(catechyl) | $NEt^iPr_2$ | - |
| Cl | AgOTf | $CDCl_3$ | PPh(catechyl) | $NEt^iPr_2$ | 41 |
| Cl | AgOTf | $CH_2Cl_2$ | PPh(catechyl) | $NEt^iPr_2$ | 47 |
| Cl | AgOTf | Chlorobenzene | PPh(catechyl) | $NEt^iPr_2$ | 27 |
| Cl | AgOTf | DCE | PPh(catechyl) | DBU | 89 |
| Cl | AgOTf | DCE | PPh(catechyl) | 2,4,6-collidine | 45 |
| Cl | AgOTf | DCE | $PPh_3$ | $NEt^iPr_2$ | - |
| Cl | AgOTf | DCE | $PCy_3$ | $NEt^iPr_2$ | - |
| Cl | AgOTf | DCE | $P(OCH_2CF_3)_3$ | $NEt^iPr_2$ | - |
| Cl | AgOTf | DCE | (PhO)P(catechyl) | $NEt^iPr_2$ | 8 |
| Cl | AgOTf | DCE | $P(OPh)_3$ | $NEt^iPr_2$ | 48[f] |
| Cl | AgOTf | DCE | $P(OPh)_3$ | $NEt^iPr_2$ | 55 |
| Cl | AgOTf | DCE |   | $NEt^iPr_2$ | 25 |
| Cl | AgOTf | DCE | (R-BINOL)P(OPh) | $NEt^iPr_2$ | - |
| Cl | AgOTf | DCE |   | $NEt^iPr_2$ | - |

[a]0.12 mmol acyl chloride, 0.1 mmol aldehyde, 0.12 mmol $PR_3$, 1 ml Solvent, then 0.15 mmol MX' for 12 h, followed by the addition of alkyne (0.15 mmol) and then base (0.15 mmol). DCE = 1,2-dichloromethane.

[b]NMR yields vs an internal standard. [c]benzoyl chlorides, TMSI, and benzaldehyde first mixed in 1 ml $CD_3CN$ for 12 h, followed by addition of PPh(catechyl). [d]use 0.10 mmol AgOTf instead. [e]only 1h for first step. [f]cycloaddition performed for 2h.

**Table S2. Substrates Variation for in situ Observation of 1[a]**

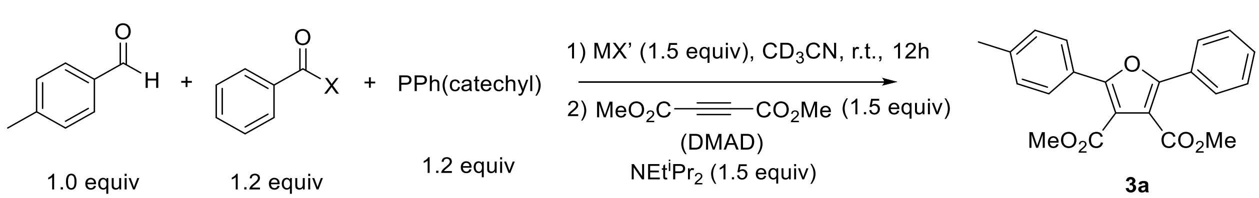



| Entry | $R^1$ | $R^2$ | % **4** | Temp. (°C) | Base | % **1** |
| --- | --- | --- | --- | --- | --- | --- |
| 1 | - | 4-methyl | 90 | -32 | $NEt^iPr_2$ | - |
| 2 | 4-methoxy | 4-$CF_3$ | - | -32 | - | - |
| 3 | 4-methoxy | 4-Me | - | -32 | - | - |
| 4 | 2-methyl | 4-fluoro | 92 | -32 | $NEt^iPr_2$ | - |
| 5 | 2-methyl | 4-$CF_3$ | - | -32 | - | - |
| 6 | 2,4,6-trimethyl | 4-$CF_3$ | - | -32 | - | - |
| 7 | 2,4,6-trimethyl | 4-fluoro | 93 | -32 | $NEt^iPr_2$ | - |
| 8 | 2,4,6-trimethyl | 4-fluoro | 93 | -32 | DBU | 73 |
| 9 | 2,4,6-trimethyl | 4-fluoro | 93 | r.t. | LiHMDS | 93 |

[a]Step 1: 0.12 mmol acyl chloride, and AgOTf (26 mg, 0.10 mmol) in 0.7 ml of 1,2-dichloroethane, stir for 1 h, then add 0.1 mmol aldehyde and PhP(catechyl) (27 mg, 0.12 mmol) stir for 30 min then *in situ* NMR analysis. Step 2: addition of base (0.15 mmol) at temperature noted, the *in situ* NMR analysis.

Preliminary analysis: The use of a methoxy substituent on the acid chloride led to side reactions in step 1 believed to arise from intramolecular Friedel-Crafts cyclization of the oxonium salt on the electron rich arene (entries 2, 3). The use of an electron poor para-trifluoromethyl substituted aldehyde did not appear to allow efficient O-acylation (entry 2, 5, 6). Interesting, the addition of $NEt^iPr_2$ to **4** with the optimized substrate (entry 7) did not lead to complete deprotonation, despite the use of this base in furan synthesis, suggesting **1** is generated in equilibrium under the reaction conditions. The strong inorganic base LiHMDS would fully deprotonate **4** to form **1** in high yield (entry 9).

## III. Conditions for Reaction Development (Table 1, Table S1)



Entries 1-5: In a glovebox, p-tolualdehyde (12 mg, 0.10 mmol), benzoyl halide (0.12 mmol), PPh(catechyl) (26 mg, 0.12 mmol) and $(CH_3)_2SO_2$ internal standard (5 mg, 0.05 mmol) were dissolved in 1 ml of acetonitrile, followed by additive MX' (0.12 mmol). This mixture was allowed to stir for 12 hours at room temperature, and dimethylacetylene dicarboxylate (21 mg, 0.15 mmol) and diisopropylethylamine (19 mg, 0.15 mmol) were added. This mixture was stirred for 1 h at room temperature. The yield of furan **3a** was determined by $^1H$ NMR analysis relative to the $(CH_3)_2SO_2$ internal standard.

Entries 6-8: In a glovebox, p-tolualdehyde (12 mg, 0.10 mmol), benzoyl halide (0.12 mmol) and $(CH_3)_2SO_2$ internal standard (5 mg, 0.05 mmol) were dissolved in 1 ml of $CD_3CN$, followed by additive MX' (0.12 mmol). This mixture was allowed to stir for 12 hours at room temperature. PPh(catechyl) (26 mg, 0.12 mmol) was added and the mixture was stirred for another 6 hours. Finally, dimethylacetylene dicarboxylate (21 mg, 0.15 mmol) and diisopropylethylamine (19 mg, 0.15 mmol) were added. This mixture was stirred for 1 h at room temperature.

Entries 9-15: In a glovebox, p-tolualdehyde (12 mg, 0.10 mmol), benzoyl chloride (17 mg, 0.12 mmol), $PR_3$ (0.12 mmol) and $(CH_3)_2SO_2$ internal standard (5 mg, 0.05 mmol) were dissolved in 1 ml of 1,2-dichloroethane (DCE), followed by the addition of AgOTf (39 mg, 0.15 mmol). This mixture was stirred for 12 hours at room temperature, then dimethylacetylene dicarboxylate (21 mg, 0.15 mmol) and diisopropylethylamine (19 mg, 0.15 mmol) were added. This mixture was stirred for 1 h at room temperature.

## IV. Furan and Oxazole Synthetic Procedures

### Synthesis of Furans (Table 2)

In a glovebox, aldehyde (0.20 mmol), acyl chloride (34 mg, 0.24 mmol) and (catechyl)PPh (54 mg, 0.24 mmol) were dissolved in 1 ml of 1,2-dichloroethane in a 20 ml vial, followed by addition of silver triflate (54 mg, 0.20 mmol). This mixture was allowed to stir for 12 hours at room temperature, and alkyne (0.30 mmol) and diisopropylethylamine (39 mg, 0.30 mmol) were added in order. This mixture was stirred for 30 min at room temperature. The solvent was removed in vacuo, and the furan product **3** was isolated by column chromatography using gradient 0-20% ethyl acetate in hexanes.

In the case of **3g, m, o-s, v, y**, **aa, bb** acid chloride and AgOTf were first mixed in 1 ml 1,2-dichloroethane for 2 h, before addition of the other reagents as noted above. For **3f** and **3g**, the mixture was heated for 12 h at 80 ºC or 100 ºC, respectively, after adding the alkene and base.

**Synthesis of Oligomeric Furan 6**

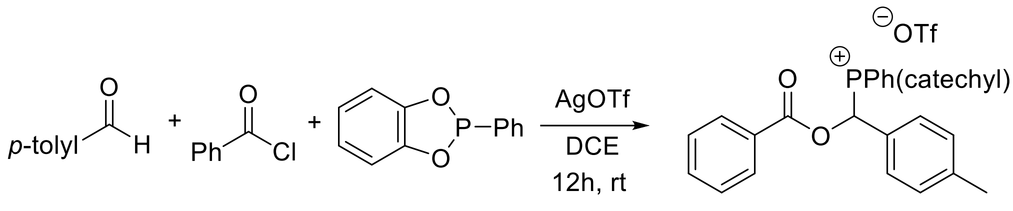
In a glovebox, 1,4-benzenedicarbonyl chloride (49 mg, 0.24 mmol), p-methoxybenzaldehyde (54 mg, 0.40 mmol) and (catechyl)PPh (104 mg, 0.48 mmol) were dissolved in 1 ml of dichloroethane, followed by addition of silver triflate (124 mg, 0.24 mmol). The mixture was allowed to stir for 12 hours at room temperature, and the DMAD (82, 0.6 mmol) and diisopropylethylamine (78 mg, 0.60 mmol) was added, and stirred for 30 minutes at room temperature. The solvent and removed in vacuo, and the product **6** was isolated by column chromatography using ethyl acetate-hexanes as a white solid. (39%, 51 mg, 0.078 mmol).

**Synthesis of Oxazole 8**

In a glovebox, 2-(2-formylphenoxy)acetonitrile (32 mg, 0.20 mmol), benzoyl chloride (34 mg, 0.24 mmol) and (catechyl)PPh (52 mg, 0.24 mmol) were dissolved in 1 ml of dichloroethane, followed by addition of silver triflate (62 mg, 0.24 mmol). This mixture was allowed to stir for 12 hours at room temperature, and diisopropylethylamine (39 mg, 0.30 mmol) was added. This mixture was stirred for 30 min at room temperature. The solvent was removed in vacuo, and the product **8** was isolated by column chromatography using ethyl acetate-hexanes as a white solid. (82%, 41 mg, 0.164 mmol).

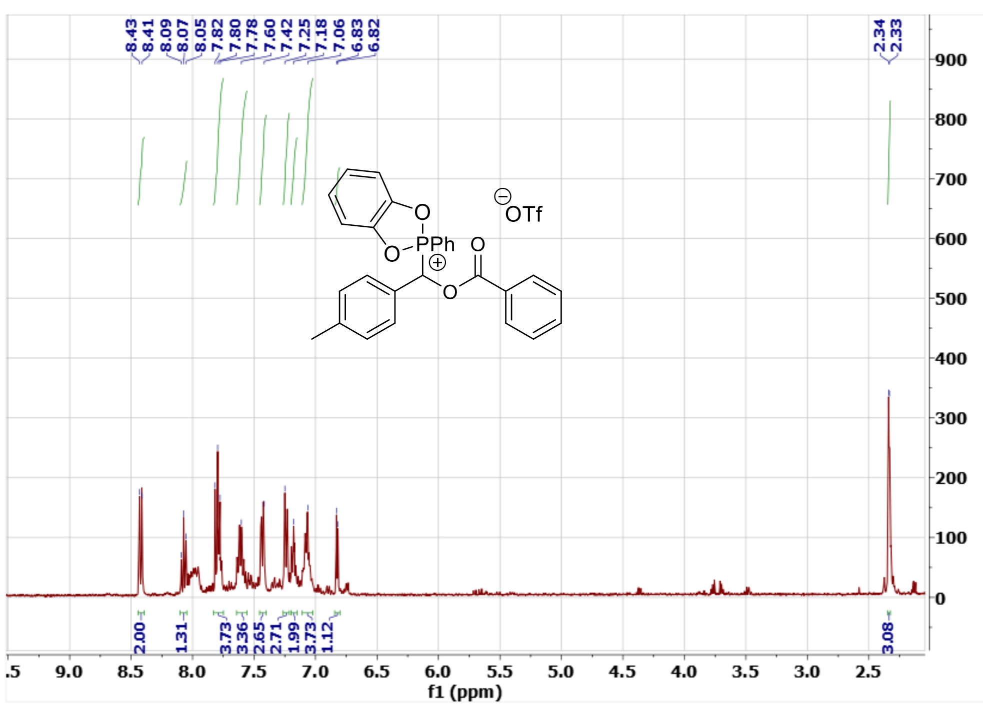
## V. Generation of Reaction Intermediates

### In situ formation of phosphonium salt of 4a

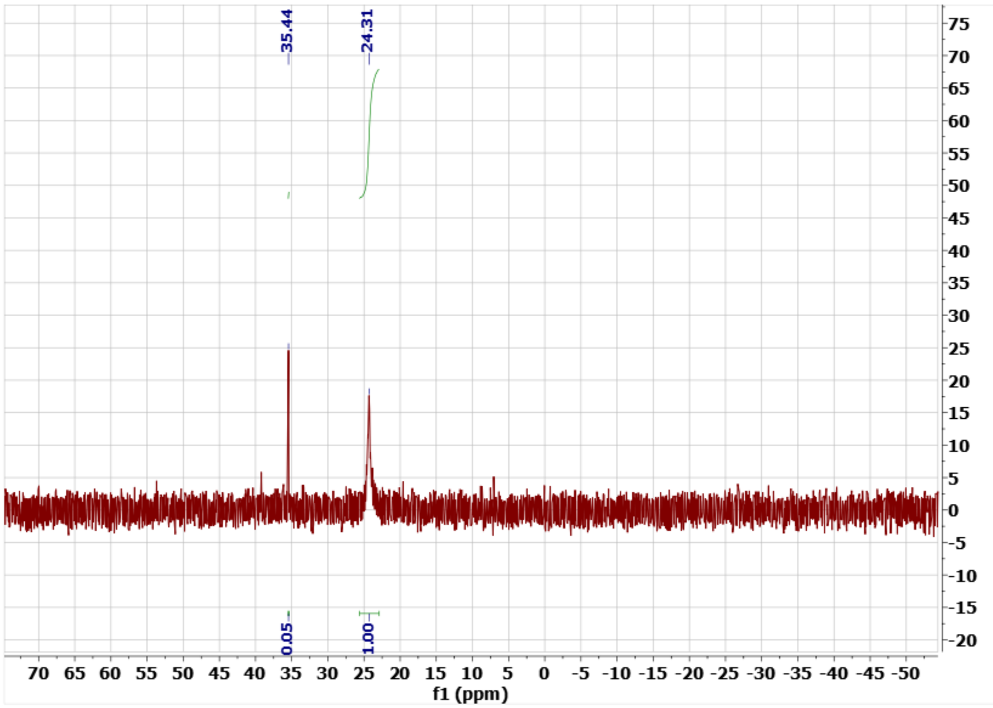



In a glovebox, benzoyl chloride (34 mg, 0.24 mmol) was dissolved in 1 ml of 1,2-dichloroethane in a 20 ml vial, followed by the addition of AgOTf (54 mg, 0.20 mmol). The mixture was stirred for 2 h. To this solution was added p-tolualdehyde (24 mg, 0.20 mmol) and then (catechyl)PPh (52 mg, 0.24 mmol) using 0.5 ml 1,2-dichloroethane. This mixture was stirred for 30 minutes at room temperature. The solvent was removed in vacuo, and the resulting oil washed with 2 ml of pentane, leaving **4a** as a brown-green precipitate together with trace impurites: **$^1$H NMR** (400 MHz, $CD_3CN$) δ 8.42 (d, *J* = 7.3 Hz, 2H), 8.07 (t, *J* = 7.6 Hz, 1H), 7.86 – 7.74 (m, 3H), 7.61 (m, 3H), 7.43 (dd, *J* = 8.4, 2.5 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.14 (m, 2H), 7.11 – 7.03 (m, 3H), 6.82 (d, *J* = 4.5 Hz, 1H), 2.34 (d, *J* = 2.6 Hz, 3H). **$^{31}$P NMR** (162 MHz, $CD_3CN$) δ 24.3 ppm. **HRMS** ($ESI^+$) for $C_{27}H_{22}O_4P$[NaOH]; calculated 481.1175, found 481.1184 (error m/z = -1.9 ppm).

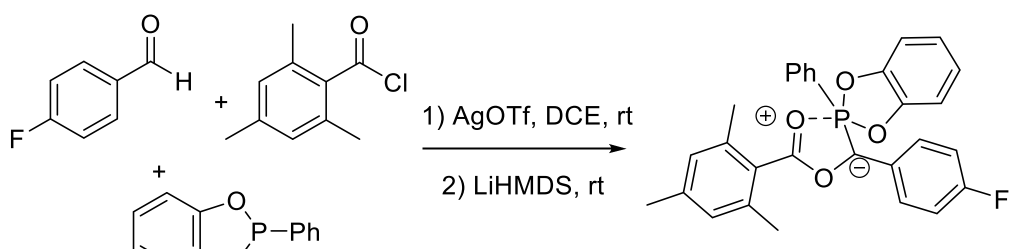
***in situ* $^1$H NMR Spectra of 4a ($CD_3CN$)**



***in situ* ³¹P NMR Spectra of 4a ($CD_3CN$)**

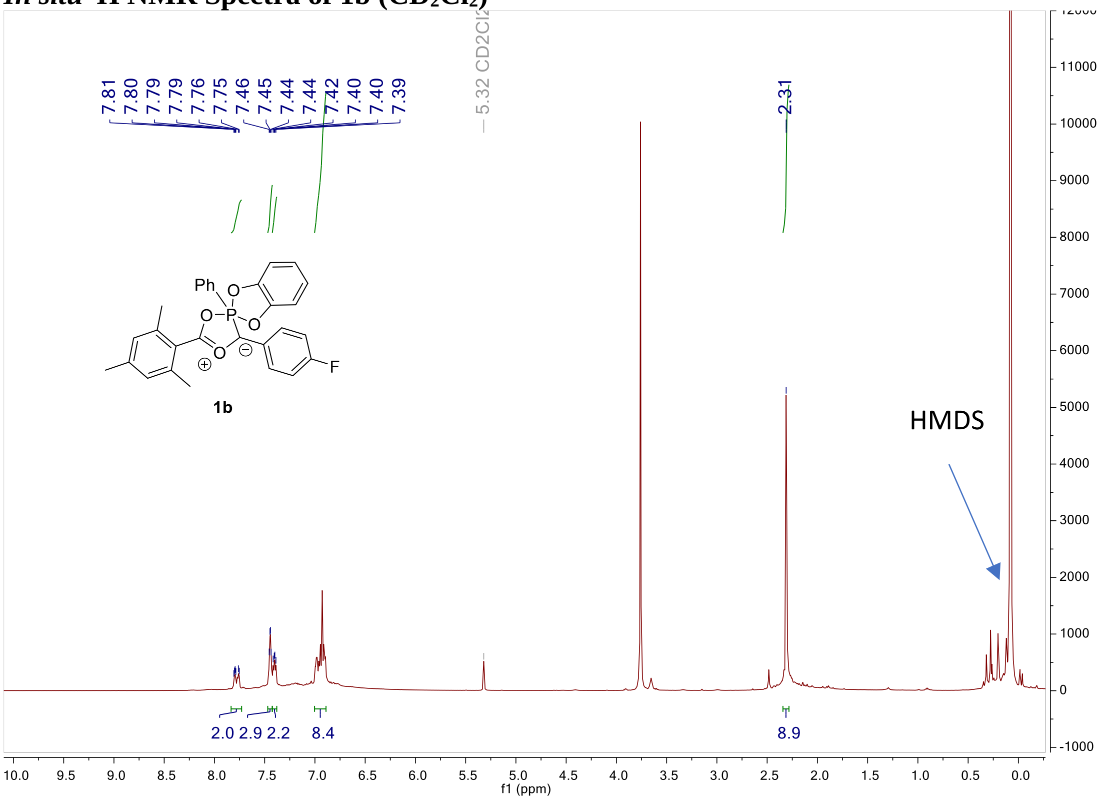



***In situ* Generation of 1b**

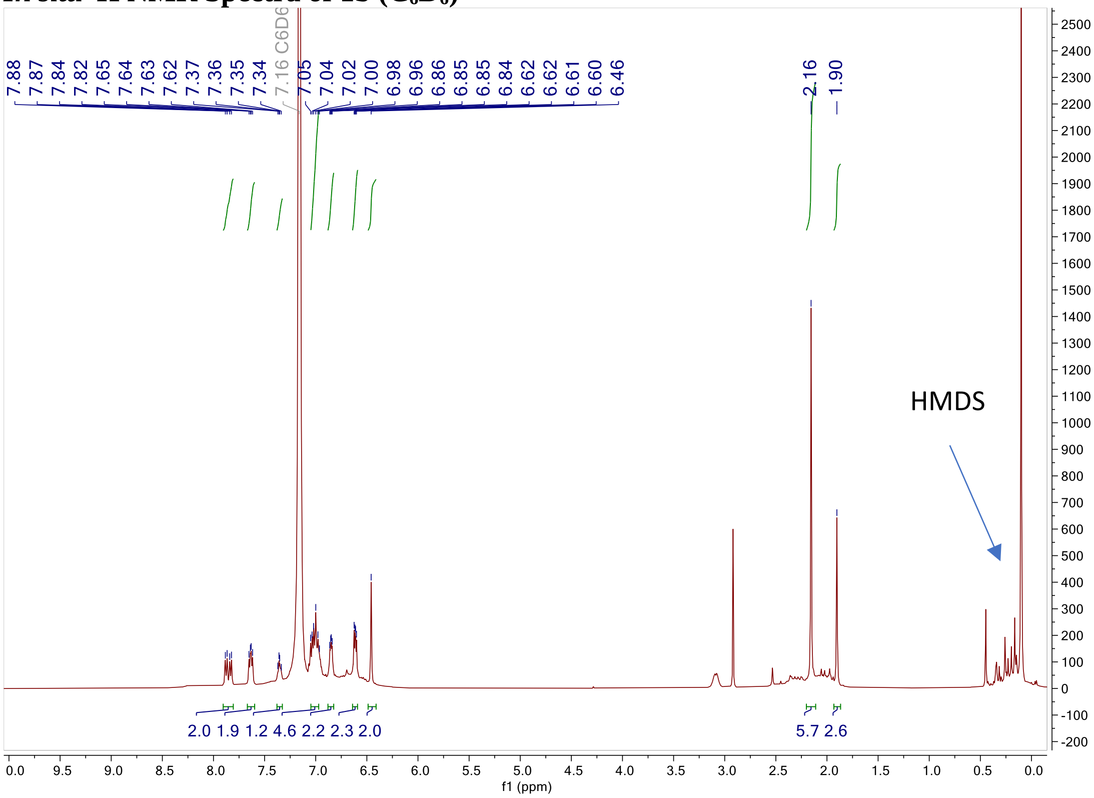



In a glovebox, 2,4,6-trimethylbenzoyl chloride (45 mg, 0.24 mmol) was dissolved in 1 ml of 1,2-dichloroethane in a 20 ml vial. AgOTf (54 mg, 0.20 mmol) was added and the mixture stirred for 2 h. To this was added 4-fluorobenzaldehyde (25 mg, 0.20 mmol) and (catechyl)PPh (52 mg, 0.24 mmol) in 0.5 ml of 1,2-dichloroethane. This mixture was stirred for 30 minutes at room temperature. LiHMDS (50 mg, 0.30 mmol) was then added to the mixture at room temperature, and it produced a bright red solution. After 10 min, the 1,2-dichloroethane solvent was removed in vacuo, and the product dissolved in either $CD_2Cl_2$ or $C_6D_6$ for in situ NMR experiments. **$^1$H NMR** (500 MHz, $CD_2Cl_2$) δ 7.80 – 7.75 (m, 2H), 7.45 (dd, *J* = 3.5, 3.1 Hz, 3H), 7.40 (dd, *J* = 8.4, 5.4 Hz, 2H), 6.99 – 6.89 (br, 8H), 2.31 (s, 9H) ppm. **$^1$H NMR** (500 MHz, $C_6D_6$) δ 7.85 (dd, *J* = 7.2, 6.8 Hz, 2H), 7.64 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.37 – 7.33 (m, 1H), 7.04 – 6.96 (m, 4H), 6.85 (dd, *J* = 5.8, 3.4 Hz, 2H), 6.61 (dd, *J* = 5.8. 3.4 Hz, 2H), 6.46 (s, 2H), 2.16 (s, 6H), 1.90 (s, 3H) ppm. $^{13}$**C NMR** (126 MHz, $CD_2Cl_2$) δ 170.3 (d, *J* = 4.8 Hz), 159.2 (d, *J* = 238.9 Hz), 146.4, 142.8, 139.1, 133.8 (d, *J* = 2.6 Hz), 133.6 (d, *J* = 2.6 Hz), 131.2 (d, *J* = 3.6 Hz), 130.2, 129.4 (d, *J* = 11.5 Hz) ,129.1, 129.0, 126.2, 126.1, 126.0, 114.9 (d, *J* = 21.1 Hz), 112.1 (d, *J* = 9.6 Hz), 93.1 (d, *J* = 252.7 Hz), 21.5, 21.4 ppm. $^{31}$**P NMR** (162 MHz, $CD_2Cl_2$) δ 9.8 (br) ppm. $^{31}$**P NMR** (162 MHz, 1,2-dichloroethane) δ 8.3 (br) ppm.

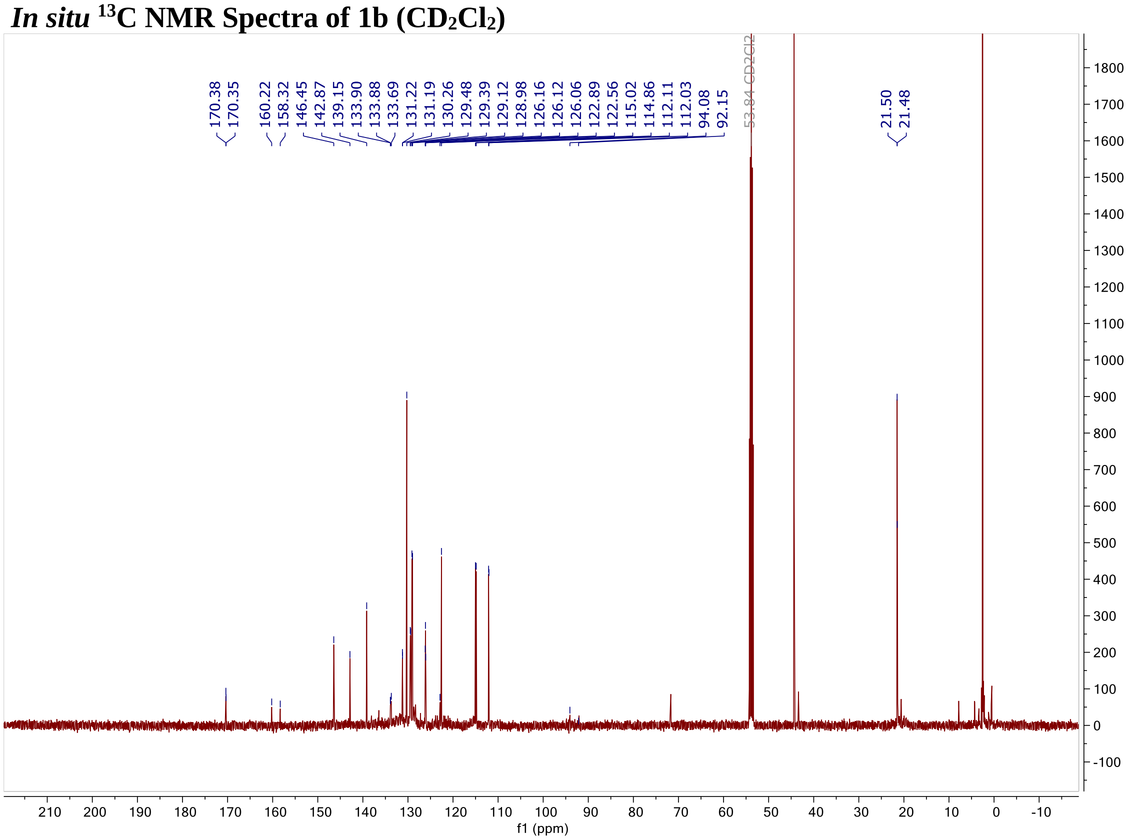
***In situ*** **$^{1}$H NMR Spectra of 1b ($CD_2Cl_2$)**



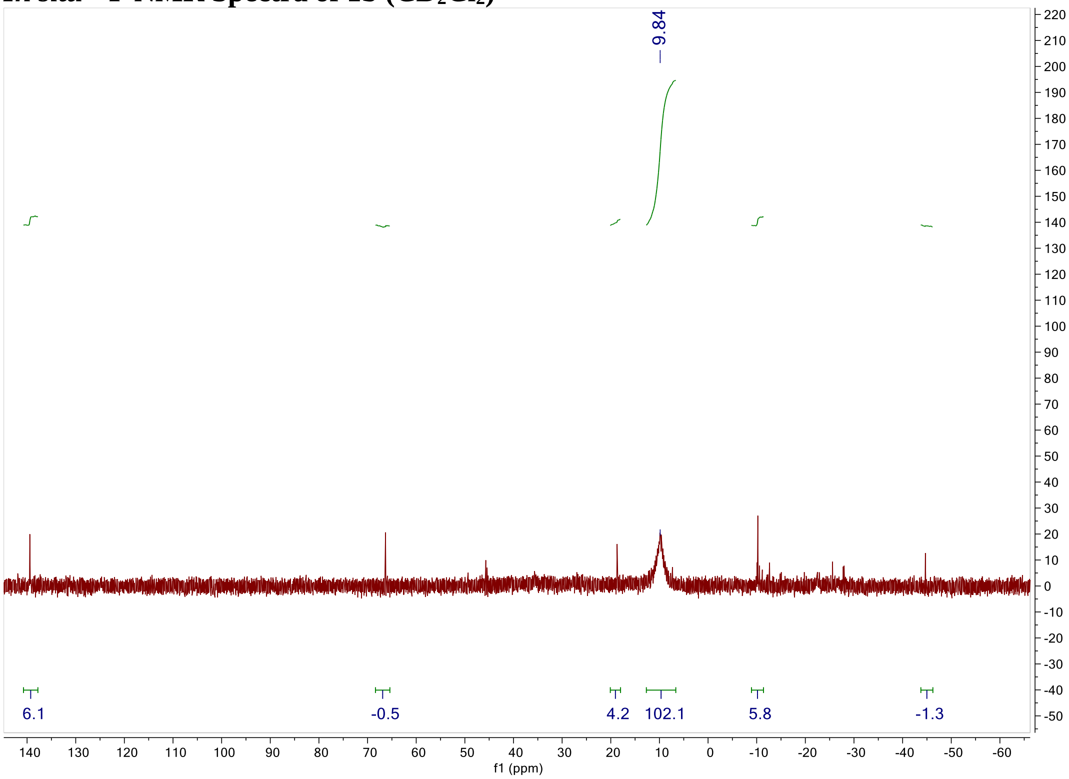
*In situ* $^{1}$H NMR Spectra of 1b ($C_6D_6$)



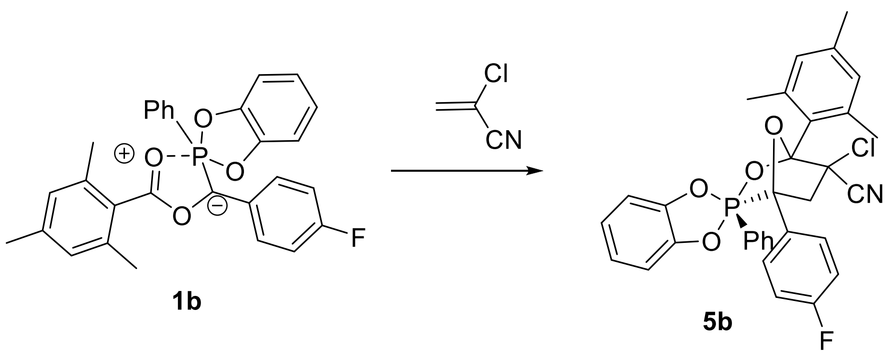

*In situ* $^{13}$C NMR Spectra of 1b ($CD_2Cl_2$)



***In situ* $^{31}$P NMR Spectra of 1b ($CD_2Cl_2$)**



**Synthesis of 5b**

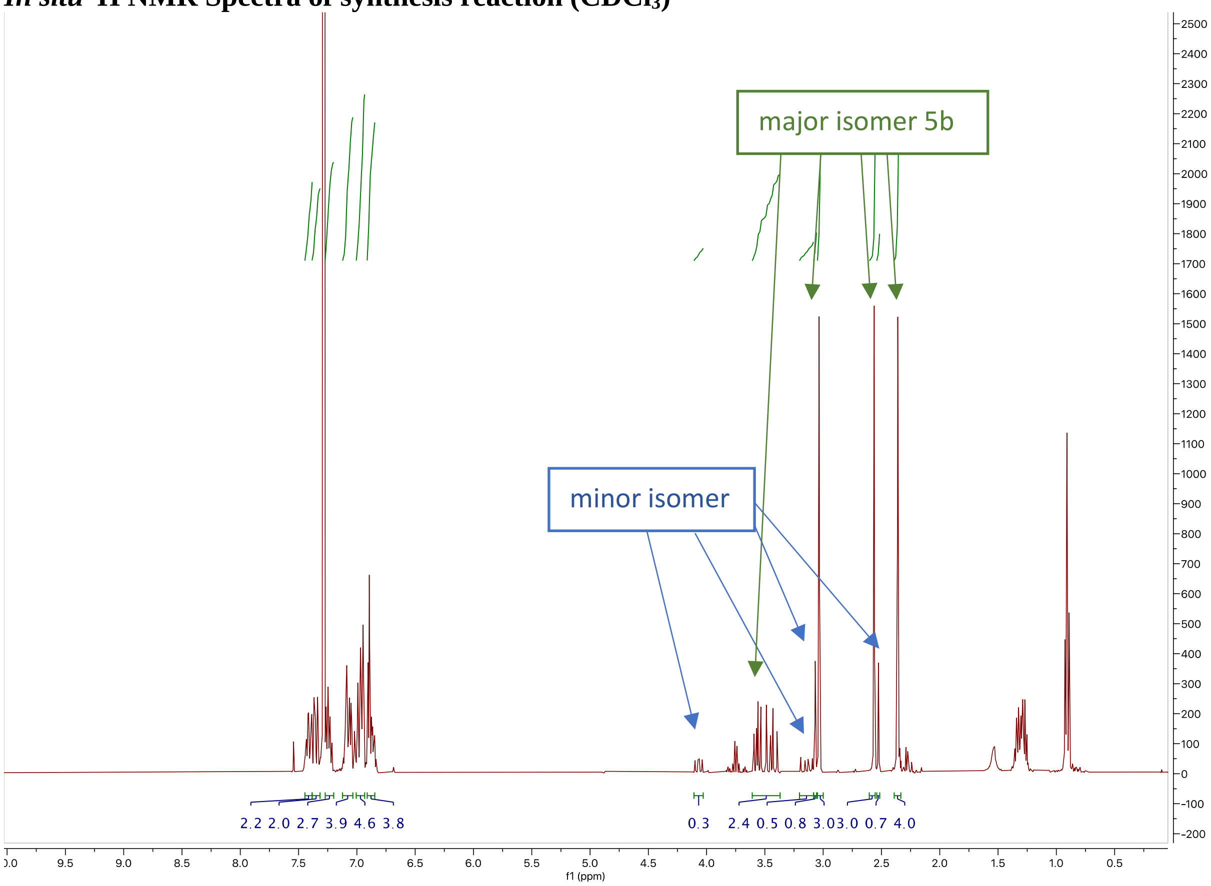


To the freshly made bright red solution of **1b** (0.20 mmol scale) in 1,2-dichloromethane in a glovebox was added 1,1-chlorocyanoethylene (22 mg, 0.25 mmol). The solution immediately turned yellow. In situ $^{1}$H, $^{19}$F and $^{31}$P NMR show what appears to be two isomers in a 4.4:1 ratio (see spectra below). The mixture was then brought outside the glovebox and purified by flash column chromatography using 0-6% ethyl acetate in hexanes. The partially purified isomer **5b** was fully isolated by silica prepTLC using 5% ethyl acetate in pentane ($R_f$ = 0.5). 20 mg (17 %) of white oily solid product **5b** was collected.

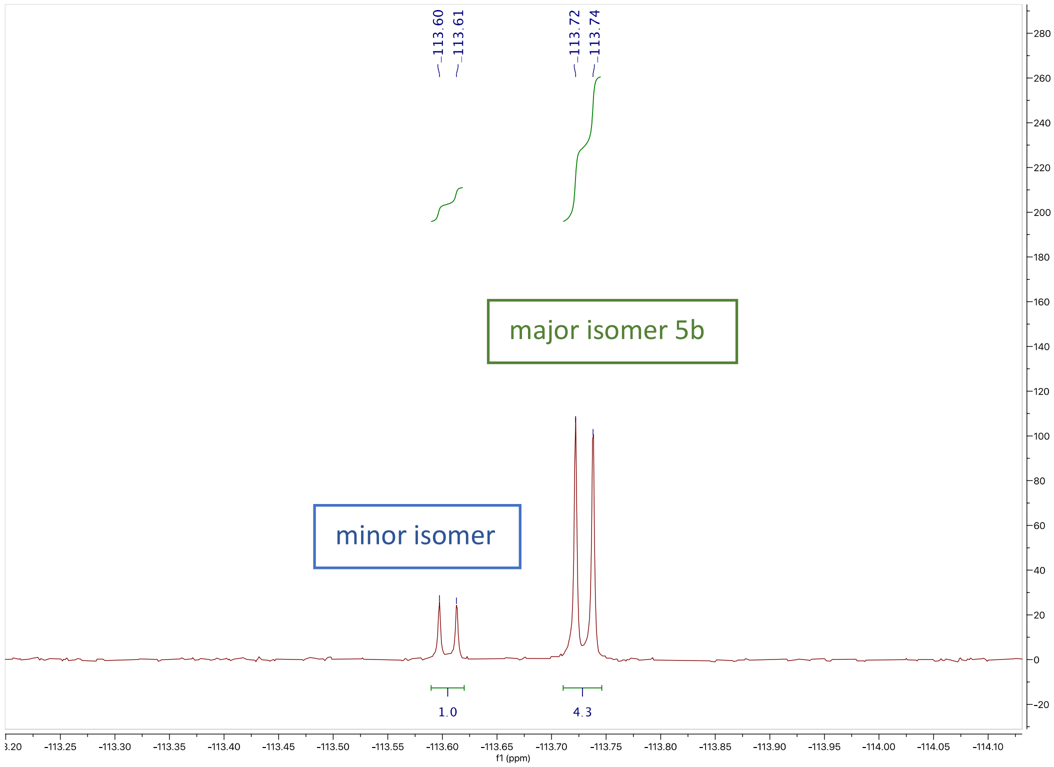
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.42 (tt, *J* = 7.2, 1.3 Hz, 1H), 7.27 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.24 (dd, *J* = 8.3, 7.4 Hz, 2H), 7.09 (s, 1H), 7.07 (dd, *J* = 8.9, 5.3 Hz, 2H), 6.99 – 6.96 (m, 2H), 6.96 (s, 1H), 6.95 – 6.94

(m, 1H), 6.91 – 6.89 (m, 2H), 6.88 – 6.84 (m, 1H), 3.57 (dd, $J^{H\text{-}P}$ = 67.3 Hz, $J$ = 14.3 Hz, 1H), 3.45 (dd, $J^{H\text{-}P}$ = 54.3 Hz, $J$ = 14.3 Hz, 1H), 3.04 (s, 3H), 2.57 (s, 3H), 2.36 (s, 3H) ppm. $^{13}$**C NMR** (126 MHz, $CDCl_3$) δ 162.4 (dd, $J^{C\text{-}F}$ = 247.4 Hz, $J^{C\text{-}P}$ = 3.7 Hz), 144.9 (d, $J$ = 1.7 Hz), 143.2 (d, $J$ = 4.7 Hz), 139.4 (d, $J^{C\text{-}P}$ = 25.1 Hz), 138.5 (d, $J^{C\text{-}P}$ = 1.3 Hz), 132.9 (d, $J^{C\text{-}P}$ = 10.6 Hz), 132.8 (d, $J^{C\text{-}P}$ = 3.7 Hz), 132.3, 132.2, 131.9, 128.5 (dd, $J^{C\text{-}F}$ = 8.4 Hz, $J^{C\text{-}P}$ = 4.4 Hz), 128.4 (d, $J^{C\text{-}P}$ = 14.7 Hz), 127.3, 124.7, 124.6, 121.9, 121.7, 118.0, 114.7 (dd, $J^{C\text{-}F}$ = 21.6 Hz, $J^{C\text{-}P}$ = 2.7 Hz), 111.4 (d, $J^{C\text{-}P}$ = 16.0 Hz), 110.3 (d, $J^{C\text{-}P}$ = 8.2 Hz), 83.8 (d, $J^{C\text{-}P}$ = 134.1 Hz), 63.8 (d, $J^{C\text{-}P}$ = 4.7 Hz), 49.1, 24.8, 24.6, 20.8 ppm. $^{31}$**P NMR** (167 MHz, $CDCl_3$) δ -11.35 (d, $J^{F\text{-}P}$ = 5.9 Hz, 1P) ppm. $^{19}$**F NMR** (377 MHz, $CDCl_3$) δ -113.72 (d, $J^{F\text{-}P}$ = 5.9 Hz, 1F) ppm. **HRMS** (ESI$^+$) for $C_{32}H_{26}ClFNNaO_4P$; calculated 596.1164, found 596.1172 (error m/z = 1.3 ppm).

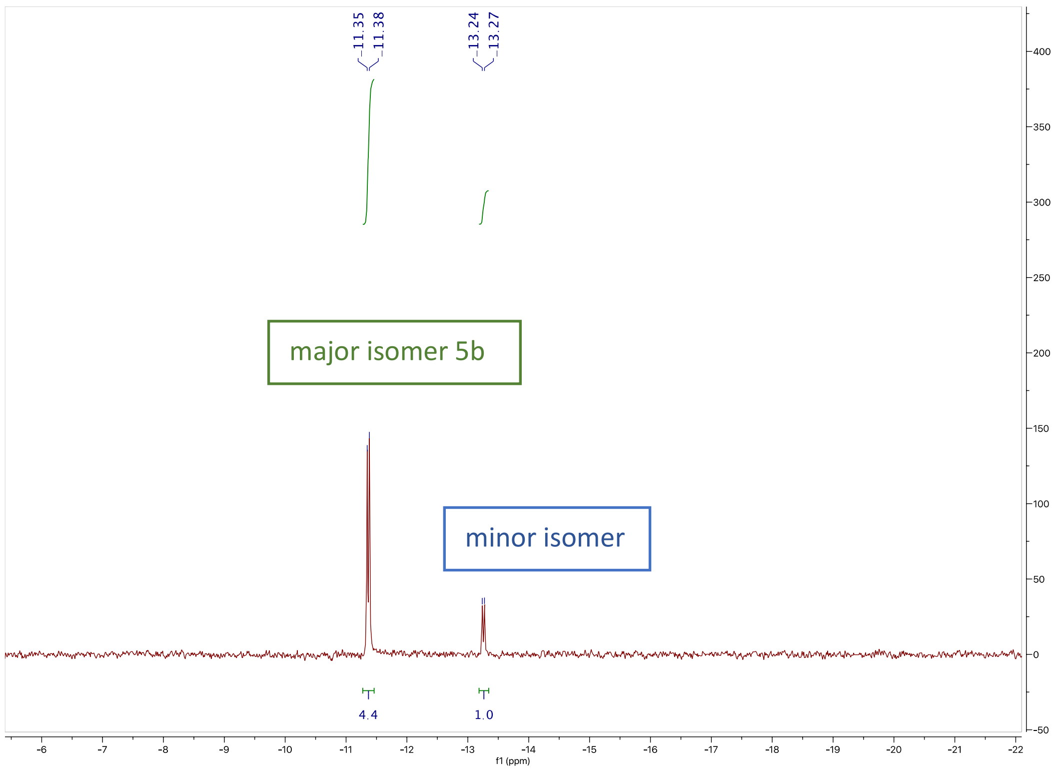
***In situ* $^{1}$H NMR Spectra of synthesis reaction ($CDCl_3$)**



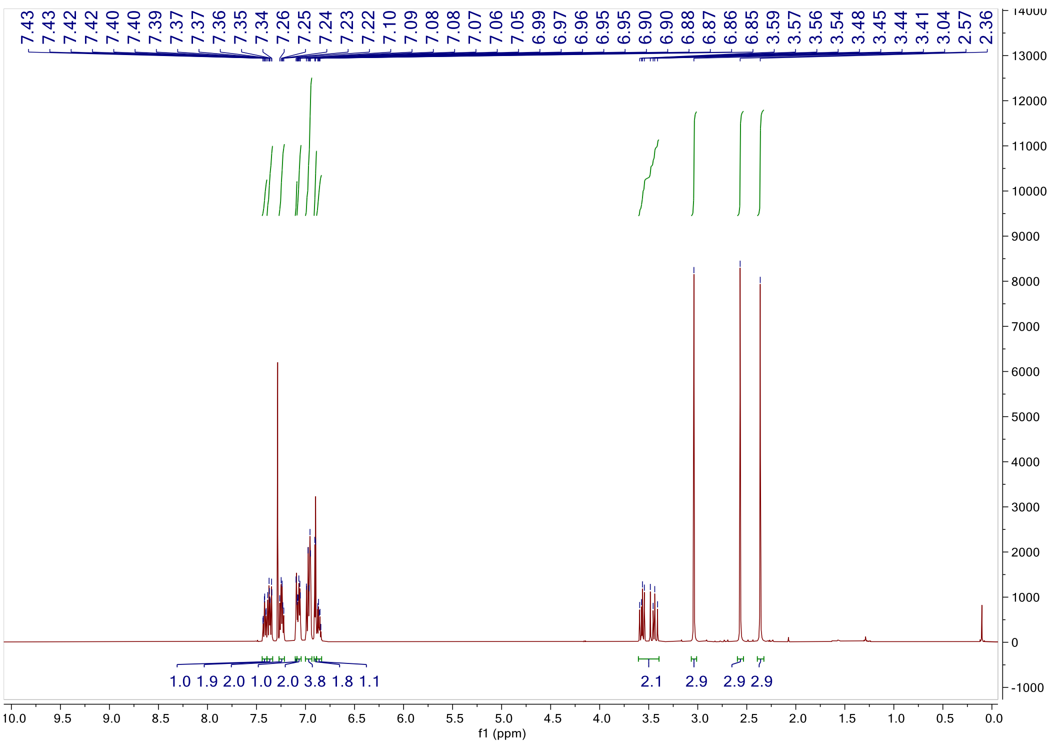

***In situ* $^{19}$F NMR Spectra of synthesis reaction ($CDCl_3$)**



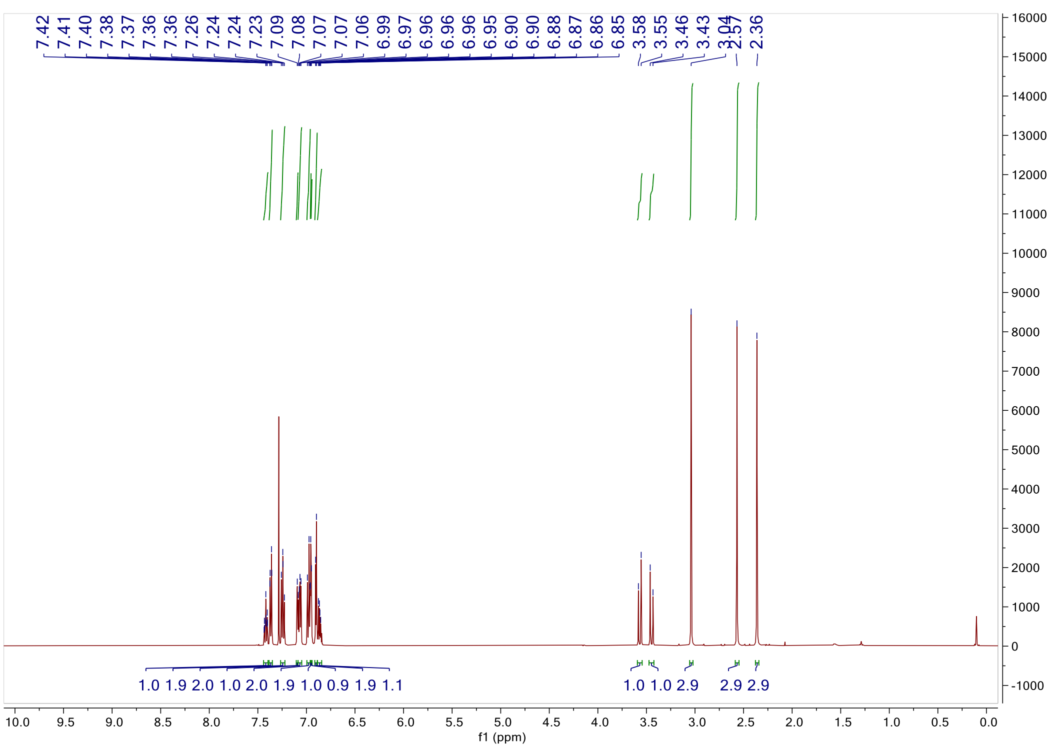

*In situ* $^{31}$P NMR Spectra of synthesis reaction ($CDCl_3$)



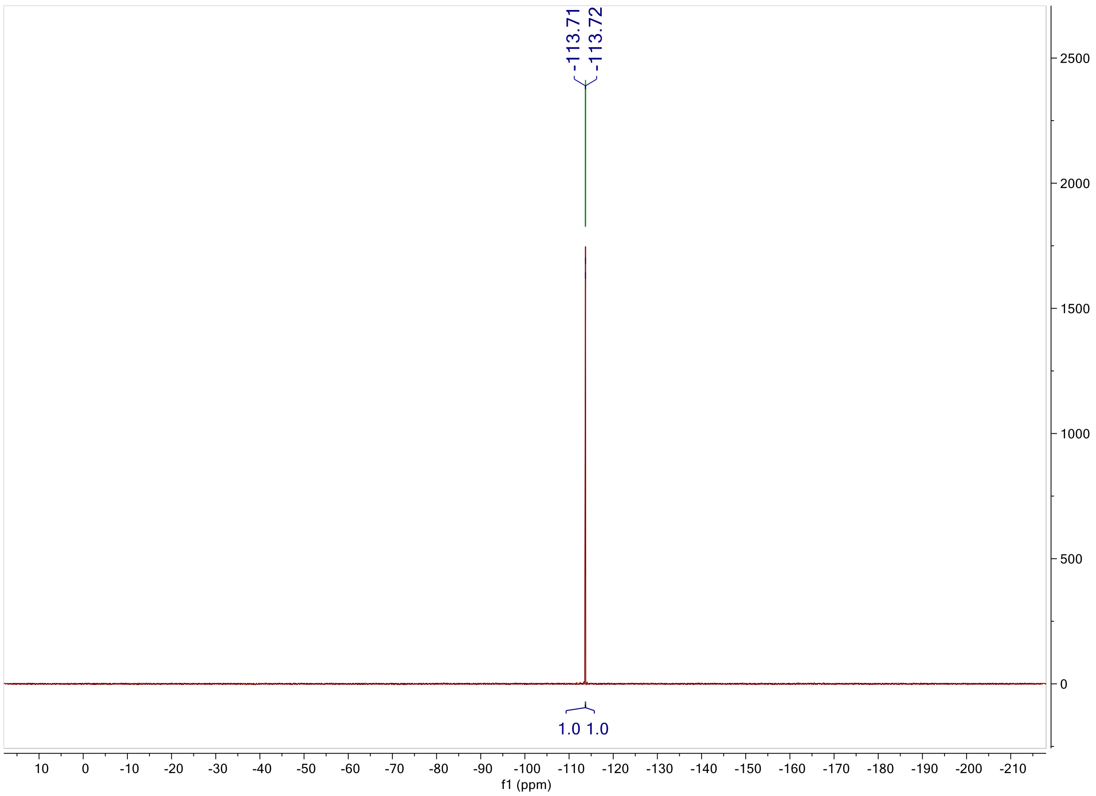
$^1$H NMR Spectra of 5b ($CDCl_3$)



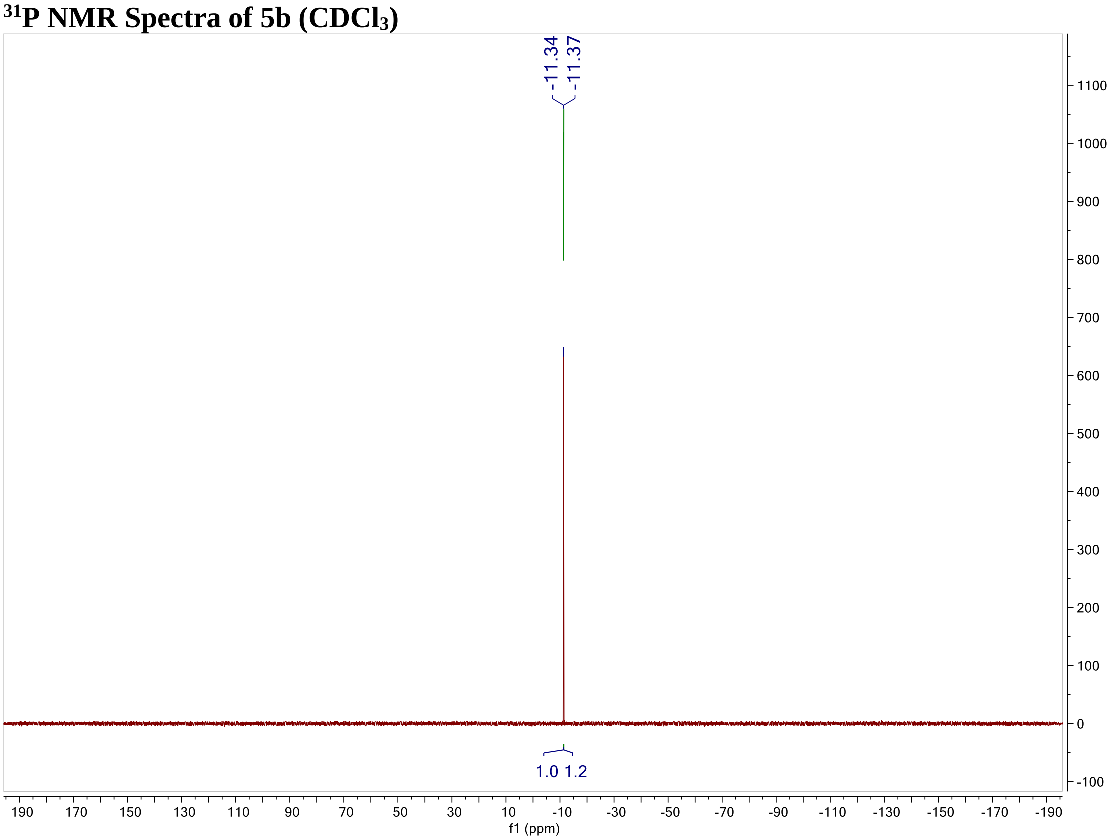

Phosphorus Decoupled $^1$H NMR Spectra of 5b ($CDCl_3$)



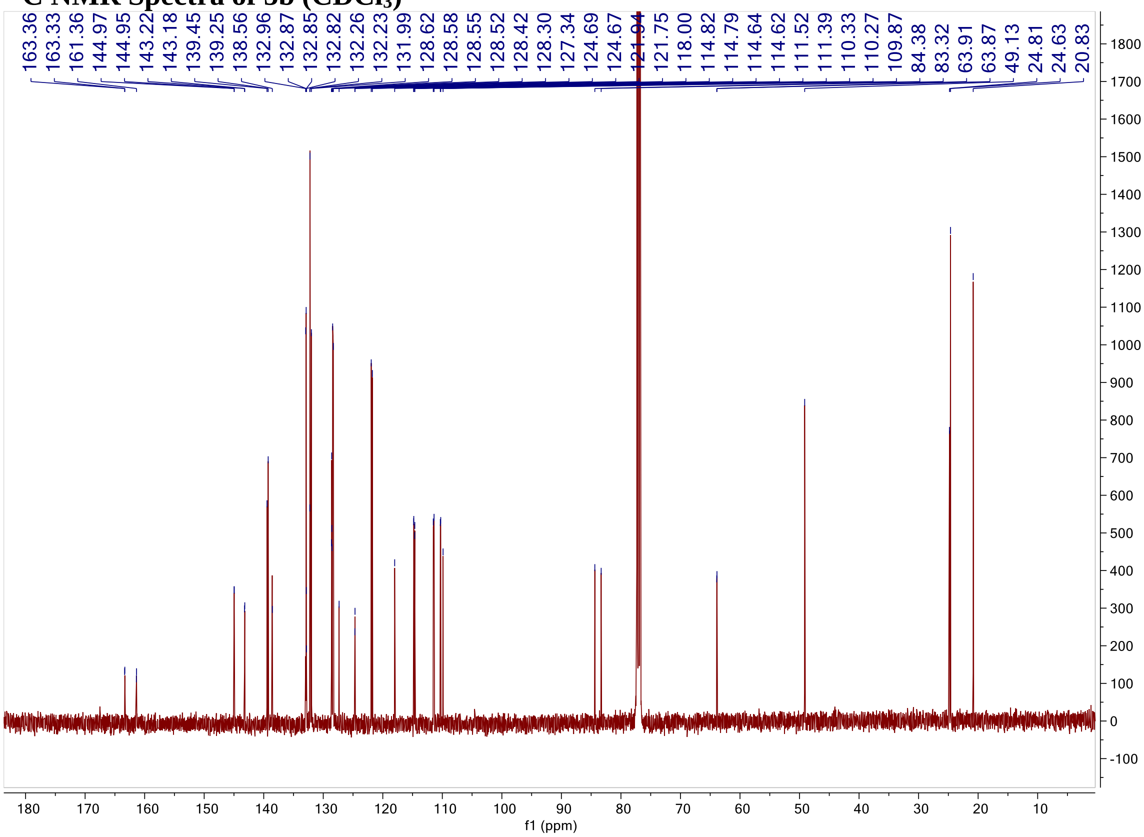
**$^{19}$F NMR Spectra of 5b ($CDCl_3$)**



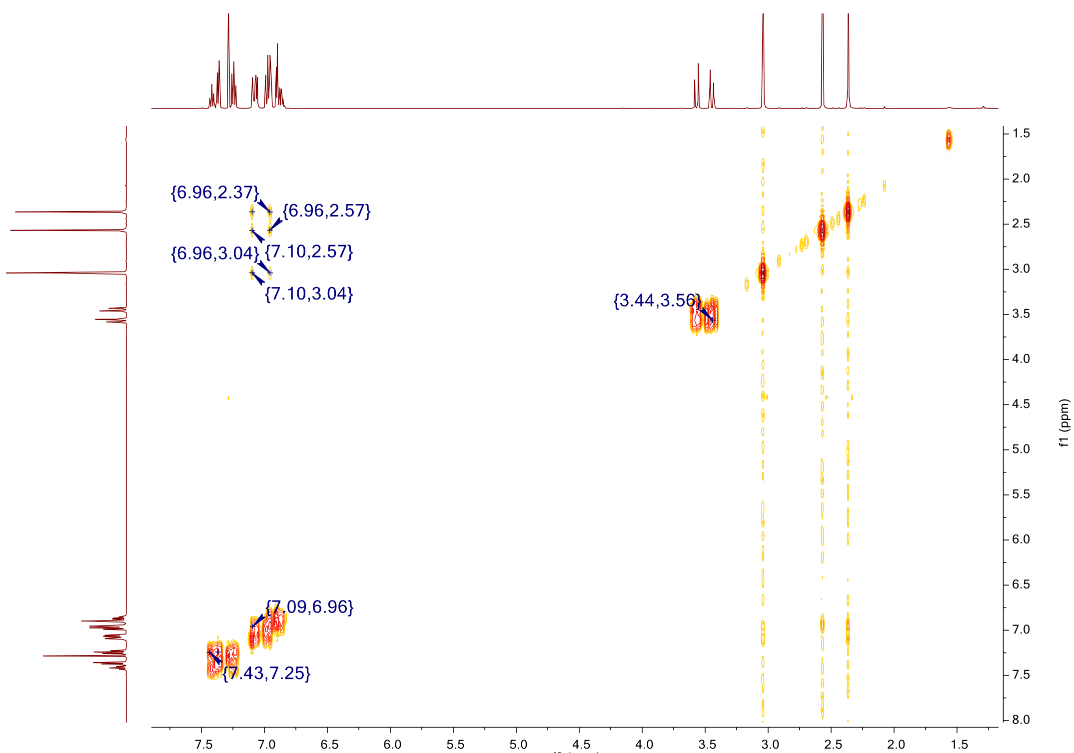

**$^{31}$P NMR Spectra of 5b ($CDCl_3$)**



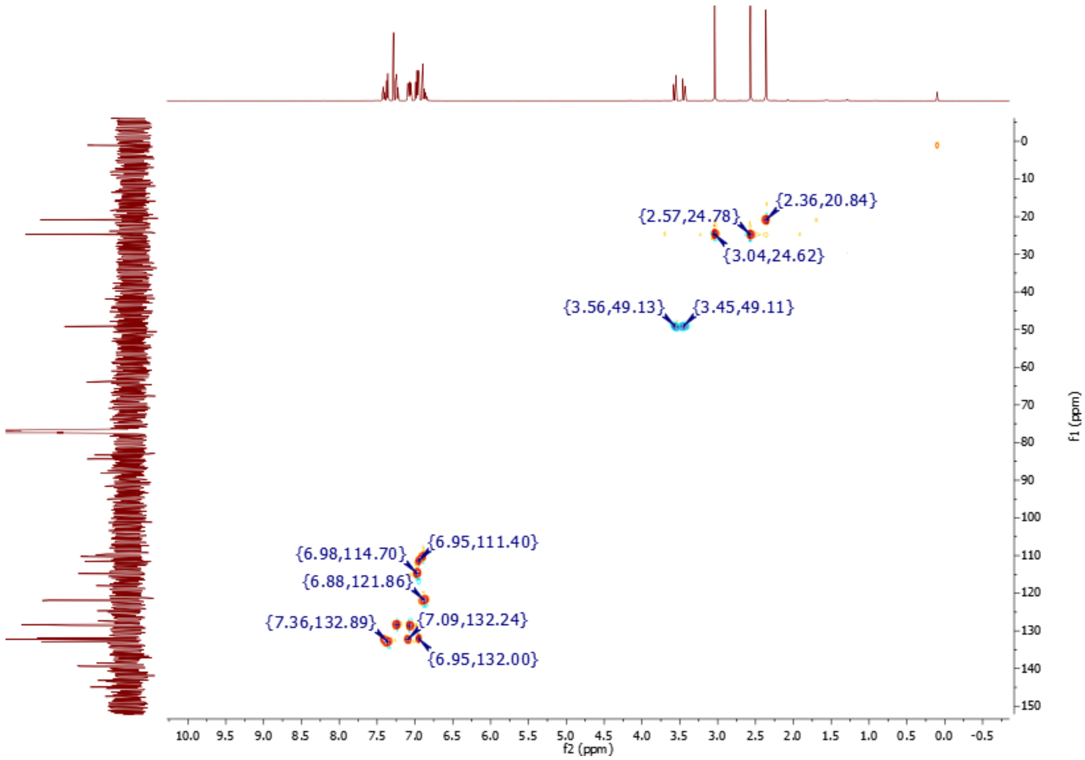
## $^{13}C$ NMR Spectra of 5b ($CDCl_3$)



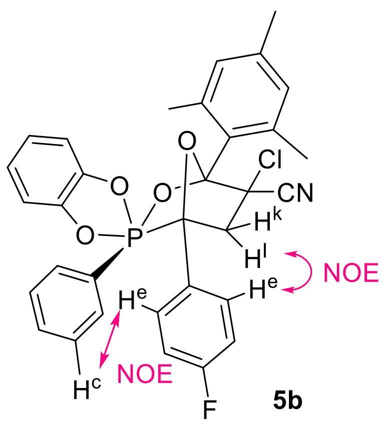

## COSY NMR Spectra of 5b ($CDCl_3$)



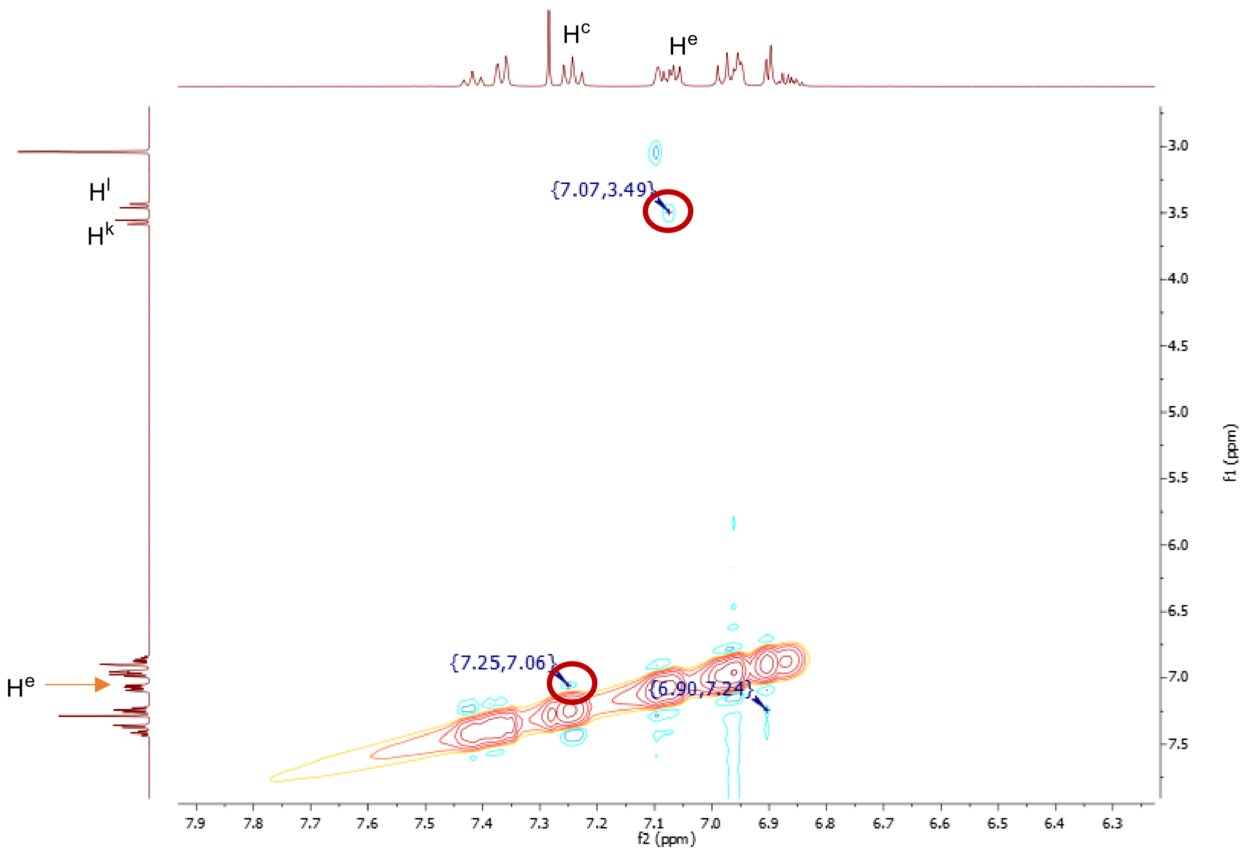
**HSQC NMR Spectra of 5b ($CDCl_3$)**




**NOESY NMR Spectra of 5b ($CDCl_3$)**

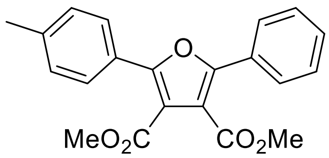



**5b**

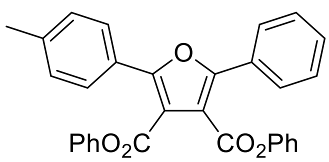


H^c
H^e
H^l
H^k
H^e
{7.07,3.49}
{7.25,7.06}
{6.90,7.24}
f2 (ppm)
f1 (ppm)

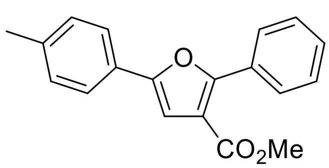
**VI. Characterization Data for 3, 6, and 8**



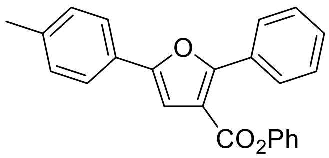

Dimethyl 2-phenyl-5-(p-tolyl)furan-3,4-dicarboxylate (**3a**) Colorless liquid, 56 mg, 80%. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.0 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.46 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 3H), 3.90 (s, 3H), 2.43 (s, 3H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 164.4, 164.2, 154.0, 153.1, 139.9, 129.5, 129.2, 128.9, 128.5, 127.4, 127.3, 126.0, 115.2, 114.6, 52.4, 52.3, 21.5 ppm. **HRMS** ($ESI^+$) for $C_{21}H_{18}NaO_5$; calculated 373.1046, found 373.1049 (error m/z = 0.7 ppm).



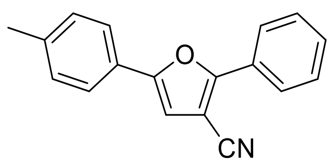

(2-phenyl-5-(p-tolyl)furan-3,4-diyl)bis(phenylmethanone) (**3b**): light yellow solid, 60 mg, 66%. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.83 – 7.67 (m, 6H), 7.62 (d, J = 8.2 Hz, 2H), 7.45 (m, 2H), 7.34 (m, 3H), 7.27 (m, 4H), 7.16 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H) ppm.**$^{13}$C NMR** (126 MHz, CDCl3) δ 191.5, 153.3, 152.6, 139.6, 137.6, 137.5, 133.2, 133.2, 129.4, 129.3, 129.2, 128.9, 128.6, 128.4, 127.2, 127.2, 126.1, 123.2, 122.7, 21.4 ppm. **HRMS** ($ESI^+$) for $C_{31}H_{22}NaO_5$; calculated 497.1359, found 497.1355 (error m/z = 0.9 ppm).



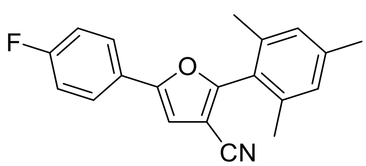

Methyl 2-phenyl-5-(p-tolyl)furan-3-carboxylate (**3c**) Pale yellow liquid, 45 mg, 78%. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.09 – 8.07 (m, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.04 (s, 1H), 3.88 (s, 3H), 2.40 (s, 3H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 164.1, 156.3, 152.7, 138.1, 129.8, 129.5, 129.3, 128.3, 128.2, 127.1, 124.0, 115.3, 107.1, 51.7, 21.4 ppm. **HRMS** ($ESI^+$) for $C_{19}H_{17}O_3$; calculated 293.1172, found 293.1173 (error m/z = 0.2 ppm).



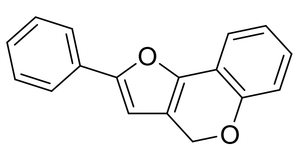

Phenyl 2-phenyl-5-(p-tolyl)furan-3-carboxylate (**3e**) white solid, 40 mg, 55%. $^{1}$**H NMR** (500 MHz, $CDCl_3$) δ 8.20 – 8.17 (m, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.43 (m, 5H), 7.35 – 7.29 (m, 3H), 7.27 – 7.24 (m, 3H), 2.45 (s, 3H). $^{13}$**C NMR** (126 MHz, $CDCl_3$) δ 162.2, 157.7, 153.0, 150.7, 138.4, 129.7, 129.7, 129.6, 129.6, 128.5, 128.3, 127.0, 126.0, 124.2, 121.9, 114.8, 107.2, 21.5 ppm. **HRMS** ($ESI^+$) for $C_{24}H_{18}NaO_3$; calculated 377.1148, found 377.1136 (error m/z = 3.3 ppm).



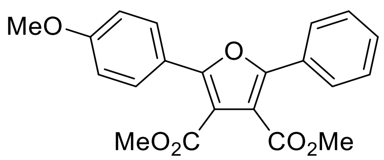

2-Phenyl-5-(p-tolyl)furan-3-carbonitrile (**3f**) Pale yellow liquid, 35 mg, 67%. $^{1}$**H NMR** (500 MHz, $CDCl_3$) δ 8.07 – 8.05 (m, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.53 (t, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 2H), 6.83 (s, 1H), 2.42 (s, 3H) ppm. $^{13}$**C NMR** (126 MHz, $CDCl_3$) δ 158.4, 153.9, 139.1, 130.0, 129.7, 129.1, 128.2, 126.1, 125.3, 124.2, 115.1, 107.0, 93.4, 21.4 ppm. **HRMS** ($ESI^+$) for $C_{18}H_{14}ON$; calculated 260.1070, found 260.1080 (error m/z = 4.1 ppm).



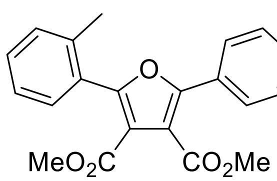

5-(4-fluorophenyl)-2-mesitylfuran-3-carbonitrile (**3g**) yellow solid, 38 mg, 62 %. $^{1}$**H NMR** (500 MHz, $CDCl_3$) δ 7.66 – 7.63 (m, 2H), 7.14 – 7.10 (m, 2H), 6.98 (s, 2H), 6.83 (s, 1H), 2.35 (s, 3H), 2.24 (s, 6H) ppm. $^{13}$**C NMR** (126 MHz, CDCl3) δ 163.9, 161.d (d, *J* = 162.5 Hz), 153.5, 140.7, 138.6, 128.7, 126.0 (d, *J* = 8.3 Hz), 125.4 (d, *J* = 3.4 Hz), 124.3, 116.1 (d, *J* = 22.1 Hz), 113.9, 105.6, 105.6, 98.5, 21.3, 20.0 ppm. **HRMS** ($ESI^+$) for $C_{20}H_{17}FNO$; calculated 306.1289, found 306.1292 (error m/z = **-**1.2 ppm)



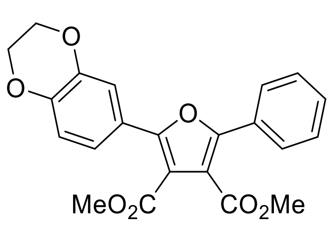
2-phenyl-4*H*-furo[3,2-*c*]chromene (**3h**): light yellow solid, 11 mg, 29%. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.2 Hz, 2H), 7.49 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.14 (td, *J* = 8.0, 1.6 Hz, 1H), 6.99 (td, *J* = 7.5, 1.0 Hz, 1H), 6.90 (dd, *J* = 8.1, 0.8 Hz, 1H), 6.57 (s, 1H), 5.44 (s, 2H). **$^{13}$C NMR** (126 MHz, CDCl3) δ 154.4, 153.0, 145.4, 130.4, 128.8, 128.4, 127.6, 123.7, 121.5, 119.4, 116.8, 116.2, 115.7, 103.3, 65.9 ppm. **HRMS** (ESI$^+$) for $C_{18}H_{14}NaO_2$; calculated 285.0886, found 287.0668 (error m/z = 3.9 ppm).



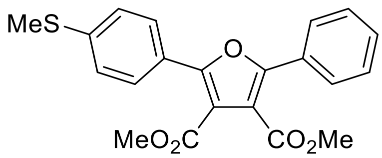

Dimethyl 2-(4-methoxyphenyl)-5-phenylfuran-3,4-dicarboxylate (**3i)** White solid, 63 mg, 86%. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 4H), 7.52 – 7.38 (m, 3H), 7.00 (d, *J* = 9.0 Hz, 2H), 3.91 (s, 3H), 3.89 (s, 3H), 3.89 (s, 3H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 164.6, 164.2, 160.7, 154.4, 152.4, 129.4, 129.3, 128.9, 128.6, 127.1, 121.5, 115.3, 113.9, 113.8, 55.4, 52.4, 52.3 ppm. **HRMS** (ESI$^+$) for $C_{21}H_{19}O_6$; calculated 367.1176, found 367.1188 (error m/z = 3.1 ppm).



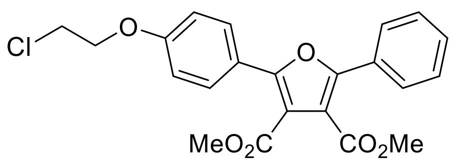

Dimethyl 2-phenyl-5-(o-tolyl)furan-3,4-dicarboxylate (**3j**) White solid, 36 mg, 59%. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.79 – 7.76 (m, 2H), 7.49 – 7.36 (m, 5H), 7.32 – 7.26 (m, 2H), 3.93 (s, 3H), 3.74 (s, 3H), 2.37 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 165.3, 163.5, 156.5, 152.9, 138.3, 131.2, 130.8, 130.4, 129.7, 129.2, 129.1, 129.0, 127.0, 125.8, 116.7, 114.9, 53.0, 52.4, 20.6 ppm. **HRMS** (ESI$^+$) for $C_{21}H_{18}NaO_5$; calculated 373.1046, found 373.1042 (error m/z = 1.1 ppm)



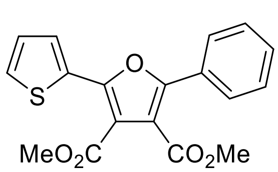
Dimethyl 2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-5-phenylfuran-3,4-dicarboxylate (**3k**) White solid, 55 mg, 70%. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 2H), 7.46 – 7.37 (m, 5H), 6.93 (d, *J* = 8.5 Hz, 2H), 3.93 (s, 3H), 4.29 (s, 4H), 3.88 (s, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 164.5, 164.2, 153.6, 152.7, 145.1, 143.5, 129.5, 128.9, 128.6, 127.3, 122.3, 121.2, 117.5, 116.7, 115.3, 114.2, 64.6, 64.4, 52.5, 52.4 ppm. **HRMS** ($ESI^+$) for $C_{22}H_{18}NaO_7$; calculated 417.0945, found 417.0926 (error m/z = 4.5 ppm).



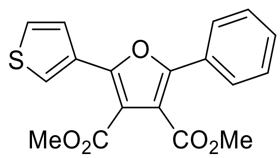

Dimethyl 2-(4-(methylthio)phenyl)-5-phenylfuran-3,4-dicarboxylate (**3l)** White solid, 54 mg, 71%. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.52 – 7.41 (m, 3H), 7.32 (d, *J* = 8.6 Hz, 2H), 3.91 (s, 3H), 3.90 (s, 3H), 2.54 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 164.4, 164.1, 153.6, 153.0, 141.1, 129.6, 128.8, 128.6, 127.8, 127.2, 125.8, 125.2, 115.4, 114.7, 52.4, 52.4, 15.2. **HRMS** ($ESI^+$) for $C_{21}H_{18}NaO_5S$; calculated 405.0767, found 405.0767 (error m/z = 0.0 ppm).



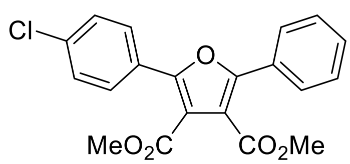

Dimethyl 2-(4-(2-chloroethoxy)phenyl)-5-phenylfuran-3,4-dicarboxylate (**3m**) 55 mg, 65%. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 9.0 Hz, 2H), 7.83 – 7.81 (m, 2H), 7.46 – 7.39 (m, 3H), 6.99 (d, *J* = 9.0 Hz, 2H), 4.28 (t, *J* = 5.9 Hz, 2H), 3.89 (s, 3H), 3.87 (s, 3H), 3.84 (t, *J* = 5.9 Hz, 2H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 164.6, 164.2, 159.3, 154.1, 152.6, 129.5, 129.4, 128.9, 128.6, 127.2, 122.2, 115.4, 114.7, 114.1, 68.1, 52.5, 52.4, 41.8 ppm. **HRMS** ($ESI^+$) for $C_{22}H_{19}ClO_6$; calculated 414.0870, found 415.0942 (error m/z = 0.2 ppm).



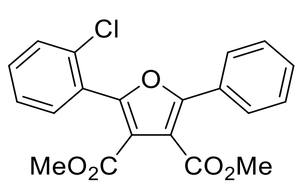

Dimethyl 2-phenyl-5-(thiophen-2-yl)furan-3,4-dicarboxylate (**3n**) Pale yellow liquid, 51 mg, 74%. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.82 (d, *J* = 7.0 Hz, 2H), 7.52 – 7.40 (m, 4H), 7.16 (dd, *J* = 5.0, 3.8 Hz, 1H), 3.93 (s, 3H), 3.93 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 164.7, 163.2, 151.4, 150.6, 130.4, 129.5, 129.0, 129.0, 128.7, 128.5, 127.6, 126.7, 115.6, 113.1, 52.6, 52.2 ppm. **HRMS** (ESI$^+$) for $C_{18}H_{14}NaO_5S$; calculated 365.0454, found 365.0462 (error m/z = 2.3 ppm).



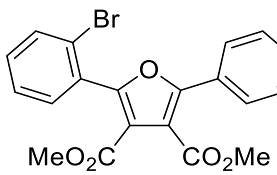

Dimethyl 2-phenyl-5-(thiophen-3-yl)furan-3,4-dicarboxylate (**3o**) Pale yellow solid, 41 mg, 60%. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 3.0, 1.1 Hz, 1H), 7.82 – 7.80 (m, 2H), 7.67 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.38 (dd, *J* = 5.1, 3.0 Hz, 1H), 3.89 (s, 3H), 3.89 (s, 3H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 164.9, 163.8, 151.8, 151.4, 129.8, 129.6, 128.9, 128.8, 127.0, 126.9, 126.5, 125.9, 115.5, 113.8, 52.6, 52.4 ppm. **HRMS** (ESI$^+$) for $C_{18}H_{14}NaO_5S$; calculated 365.0454, found 365.0462 (error m/z = 2.2 ppm).



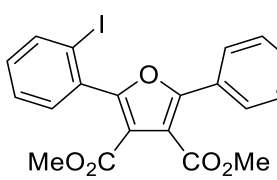

Dimethyl 2-(4-chlorophenyl)-5-phenylfuran-3,4-dicarboxylate (**3p**) white solid, 35 mg, 45%. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.86 – 7.83 (m, 4H), 7.49 – 7.43 (m, 5H), 3.89 (s, 3H), 3.88 (s, 3H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 164.2, 164.0, 153.6, 152.6, 135.8, 129.8 (2 signals overlapped), 128.9, 128.8, 128.7, 127.4, 127.3, 115.6, 115.5, 52.6 (2 signals overlapped) ppm. **HRMS** (ESI$^+$) for $C_{20}H_{15}ClNaO_5$; calculated 393.0500, found 393.0490 (error m/z = 2.6 ppm).



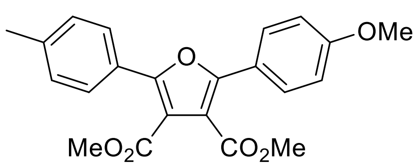

Dimethyl 2-(2-chlorophenyl)-5-phenylfuran-3,4-dicarboxylate (**3q**) white solid 60 mg, 78%. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.80 – 7.78 (m, 2H), 7.57 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.51 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.45 – 7.39 (m, 4H), 7.37 (td, *J* = 7.5, 1.4 Hz, 1H), 3.93 (s, 3H), 3.76 (s, 3H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 164.8, 162.9, 153.3, 152.9, 134.2, 132.2, 131.2, 130.1, 129.6, 128.7 (2 signals overlapped), 128.5, 126.9, 126.6, 117.6, 114.7, 52.7, 52.2. **HRMS** (ESI$^+$) for $C_{20}H_{15}ClNaO_5$; calculated 393.0500, found 393.0493 (error m/z = 1.9 ppm).



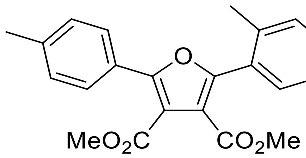

<u>Dimethyl 2-(2-bromophenyl)-5-phenylfuran-3,4-dicarboxylate (**3r**)</u> white solid, 71mg, 83%. **$^1$H NMR** (500 MHz, CDCl$_3$) δ 7.81 – 7.78 (m, 2H), 7.70 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.54, (dd, *J* = 7.7, 1.8 Hz, 1H), 7.45 – 7.38 (m, 4H), 7.34 (td, *J* = 7.8, 1.8 Hz, 1H), 3.93 (s, 1H), 3.74 (s, 3H) ppm. **$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 164.8, 162.7, 154.3, 153.1, 133.2, 132.5, 131.4, 130.6, 129.6, 128.7 (2 signals overlapped), 127.1, 126.8, 123.8, 117.3, 114.6, 52.7, 52.2 ppm. **HRMS** (ESI$^+$) for $C_{20}H_{15}BrNaO_5$; calculated 436.9995, found 436.9985 (error m/z = 2.4 ppm).



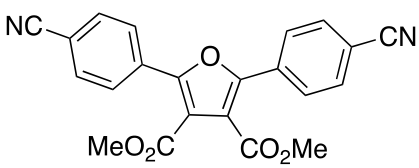

<u>Dimethyl 2-(2-iodophenyl)-5-phenylfuran-3,4-dicarboxylate (**3s**)</u> Colorless oil, 78 mg, 81%. **$^1$H NMR** (500 MHz, CDCl$_3$) δ 7.97 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.83 – 7.81 (m, 2H), 7.49 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.45 – 7.38 (m, 4H), 7.16 (ddd, *J* = 8.0, 7.3, 1.8 Hz, 1H), 3.94 (s, 3H), 3.73 (s, 3H) ppm. **$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 164.8, 162.6, 156.6, 152.8, 139.5, 134.8, 132.1, 131.3, 129.5, 128.7, 128.7, 127.7, 126.8, 116.8, 114.6, 98.1, 52.7, 52.1 ppm. **HRMS** (ESI$^+$) for $C_{20}H_{15}INaO_5$; calculated 484.9856, found 484.9873 (error m/z = 3.5 ppm).



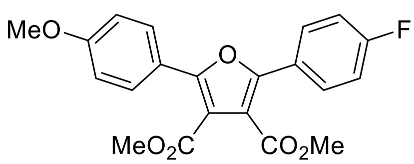

<u>Dimethyl 2-(4-methoxyphenyl)-5-(p-tolyl)furan-3,4-dicarboxylate (**3t)**</u> Pale yellow liquid, 62 mg, 82%. **$^1$H NMR** (500 MHz, CDCl$_3$) δ 7.86 (d, *J* = 9.0 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 3.88 (s, 3H), 2.42 (s, 3H). **$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 164.6, 164.3, 160.7, 153.9, 153.0, 139.7, 129.3, 129.2, 127.1, 126.1, 121.6, 114.7, 113.9, 113.8, 55.4, 52.4, 52.3, 21.5 ppm. **HRMS** (ESI$^+$) for $C_{22}H_{21}O_6$; calculated 381.1333, found 381.1342 (error m/z = 2.5 ppm).



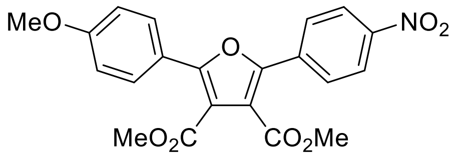

Dimethyl 2-(o-tolyl)-5-(p-tolyl)furan-3,4-dicarboxylate (**3u**) White solid, 56 mg, 77%. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.49 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.39 (td, *J* = 7.5, 1.4 Hz, 1H), 7.34 – 7.23 (m, 4H), 3.94 (s, 3H), 3.76 (s, 3H), 2.41 (s, 3H), 2.39 (s, 3H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 165.0, 163.3, 155.8, 153.1, 139.6, 137.9, 130.8, 130.5, 130.0, 129.4, 128.7, 126.7, 126.1, 125.4, 116.3, 113.9, 52.6, 52.0, 21.4, 20.3 ppm. **HRMS** ($ESI^+$) for $C_{22}H_{20}NaO_5$; calculated 387.1203, found 387.1218 (error m/z = 3.9 ppm).



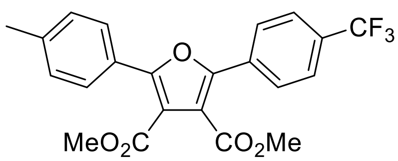

Dimethyl 2,5-bis(4-cyanophenyl)furan-3,4-dicarboxylate (**3v**) Yellow solids, 45 mg, 56%. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.6 Hz, 4H), 7.78 (d, *J* = 8.7 Hz, 4H), 3.94 (d, 6H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 163.3, 152.0, 132.5, 132.3, 127.8, 118.3, 117.9, 113.4, 53.0 ppm. **HRMS** (ESI+) for $C_{22}H_{15}N_2O_5$; calculated 398.0975, found 387.0970 (error m/z = 1.3 ppm).



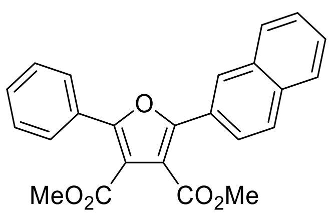

Dimethyl 2-(4-fluorophenyl)-5-(4-methoxyphenyl)furan-3,4-dicarboxylate (**3w**) Brown liquid, 58 mg, 76%. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 9.0, 5.3 Hz, 2H), 7.84 (d, *J* = 9.0 Hz, 2H), 7.16 (t, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 3.88 (s, 3H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 164.3, 164.2, 163.4 (d, *J* = 249.5 Hz), 160.9, 154.0, 152.1, 129.5 (d, *J* = 8.4 Hz), 129.1, 125.2 (d, *J* = 3.5 Hz), 121.3, 115.6 (d, J = 22.0 Hz), 115.0, 114.0, 113.9, 55.4, 52.4, 52.3 ppm. **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -110.6 ppm. **HRMS** ($ESI^+$) for $C_{21}H_{18}O_6F$; calculated 385.1082, found 385.1089 (error m/z = 1.8 ppm).



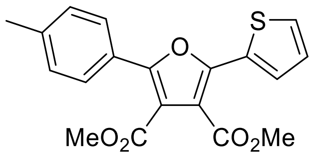

Dimethyl 2-(4-methoxyphenyl)-5-(4-nitrophenyl)furan-3,4-dicarboxylate (**3x)** Yellow solid, 45 mg, 55%. **$^{1}$H NMR** (500 MHz, CDCl$_3$) δ 8.31 (d, *J* = 9.0 Hz, 2H), 8.04 (d, *J* = 9.0 Hz, 2H), 7.87 (d, *J* = 8.9 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 2H), 3.95 (s, 3H), 3.90 (s, 6H) ppm. **$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 164.1, 163.6, 161.2, 155.9, 149.3, 147.6, 134.6, 129.5, 127.4, 124.0, 120.8, 118.3, 114.3, 114.1, 55.4, 52.8, 52.4 ppm. **HRMS** (ESI$^+$) for $C_{21}H_{17}NaO_8N$; calculated 434.0846, found 434.0858 (error m/z = 2.6 ppm).



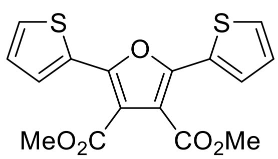

Dimethyl 2-(p-tolyl)-5-(4-(trifluoromethyl)phenyl)furan-3,4-dicarboxylate (**3y**) pale yellow solid, 55 mg, 63%. **$^{1}$H NMR** (500 MHz, CDCl$_3$) δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 7.9 HZ, 2H), 3.90 (s, 3H), 3.88 (s, 3H), 2.41 (s, 3H) ppm. **$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 164.1, 164.0, 154.9, 151.2, 140.4, 132.23, 131.15 (q, *J* = 32.7 Hz), 129.4, 127.6, 127.5, 125.81, 125.6 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.3 Hz), 116.9, 114.9, 52.7, 52.5, 21.6 ppm. **$^{19}$F NMR** (471 MHz, CDCl$_3$) δ **-** 62.8 ppm. **HRMS** (ESI$^+$) for $C_{22}H_{17}F_3NaO_5$; calculated 441.0920, found 441.0919 (error m/z = 0.3 ppm).



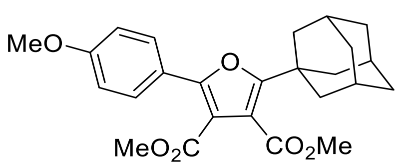

Dimethyl 2-(naphthalen-2-yl)-5-phenylfuran-3,4-dicarboxylate (**3z**) White solid, 57 mg, 74%. **$^{1}$H NMR** (500 MHz, CDCl$_3$) δ 8.42 (s, 1H), 7.98 – 7.91 (m, 5H), 7.90 – 7.87 (m, 1H), 7.59 – 7.54 (m, 2H), 7.53 – 7.45 (m, 3H), 3.95 (s, 3H), 3.94 (s, 3H). **$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 164.3, 164.2, 153.7, 153.6, 133.6, 133.0, 129.7, 128.9, 128.8, 128.6, 128.2, 127.8, 127.5, 127.3, 127.2, 126.7, 126.1, 124.3, 115.6, 115.4, 52.5, 52.5 ppm. **HRMS** (ESI$^+$) for $C_{21}H_{18}NaO_5$; calculated 409.1046, found 409.1056 (error m/z = 2.2 ppm).



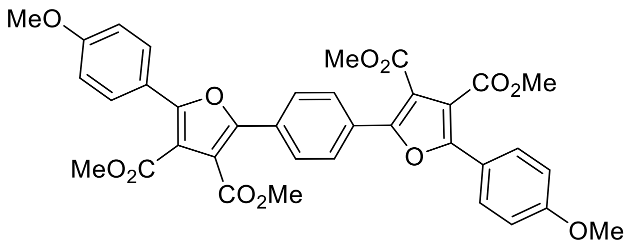
Dimethyl 2-(thiophen-2-yl)-5-(p-tolyl)furan-3,4-dicarboxylate (**3aa**) Yellow oil, 40 mg, 55%. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.46 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.25 – 7.23 (m, 2H), 7.13 (dd, *J* = 5.0, 3.8 Hz, 1H),3.90 (s, 3H), 3.89 (s, 3H), 2.30 (s, 3H). **$^{13}$C NMR**(126 MHz, $CDCl_3$) δ 164.8, 163.4, 152.1, 150.3, 139.9, 136.1, 135.4, 130.6, 129.5, 128.9, 128.4, 127.7, 126.9, 125.9, 115.0, 113.2, 52.6, 52.2, 21.6 ppm. **HRMS** ($ESI^+$) for $C_{19}H_{17}O_5S$; calculated 357.0791, found 357.0789 (error m/z = 1.4 ppm).



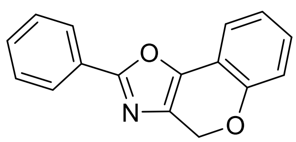
Dimethyl 2,5-di(thiophen-2-yl)furan-3,4-dicarboxylate (**3bb**) White oil, 25 mg, 37%. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 3.8, 1.2 Hz, 2H), 7.45 (d, *J* = 5.0, 1.2 Hz, 2H), 7.12 (d, *J* = 5.0, 3.8 Hz, 2H), 3.91 (s, 6H) ppm. $^{13}$C NMR(126 MHz, $CDCl_3$) δ 163.6, 149.2, 130.2, 128.5, 128.4, 127.8, 113.6, 52.4 ppm. **HRMS** ($ESI^+$) for $C_{16}H_{12}O_5S_2Na$; calculated 371.0018, found 371.0031 (error m/z = 3.5 ppm).



Dimethyl 2-((3r,5r,7r)-adamantan-1-yl)-5-(4-methoxyphenyl)furan-3,4-dicarboxylate (**3cc)** White solid, 48 mg, 57%. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.90 (s, 3H), 3.87 (s, 3H), 3.81 (s, 3H), 2.08 (s, 9H), 1.79 (s, 6H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 166.0, 163.8, 160.5, 160.3, 153.9, 129.6, 122.0, 113.9, 113.7, 112.0, 55.4, 52.4, 51.9, 40.0, 36.5, 36.3, 28.2 ppm. **HRMS** ($ESI^+$) for $C_{25}H_{28}NaO_6$; calculated 447.1778, found 447.1781 (error m/z = 0.7 ppm).




Tetramethyl 5,5'-(1,4-phenylene)bis(2-(4-methoxyphenyl)furan-3,4-dicarboxylate) (**6**) White solid, 51 mg, 39%. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.94 (s, 4H), 7.88 (d, *J* = 8.9 Hz, 4H), 7.01 (d, *J* = 8.9 Hz, 4H), 3.94 (s, 6H), 3.90 (s, 12H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 164.5, 164.0, 160.9, 154.7, 151.4, 129.4, 129.3, 129.1, 127.0, 121.3, 116.1, 114.0, 55.4, 52.6, 52.3 ppm. **HRMS** ($ESI^+$) for $C_{36}H_{30}NaO_{12}$; calculated 677.1654, found 677.1645 (error m/z = -1.3 ppm).



2-phenyl-4H-chromeno[3,4-d]oxazole (**8**) White solid, 41 mg, 82%. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 9.7 Hz, 2H), 7.60 – 7.48 (m, 3H), 7.43 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.23 – 7.14 (m, 1H), 7.01 (td, *J* = 7.5, 1.0 Hz, 1H), 6.94 (dd, *J* = 8.2, 0.8 Hz, 1H), 5.55 (s, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 161.8, 153.0, 142.5, 130.9, 130.6, 129.3, 128.9, 127.2, 126.3, 121.7, 119.9, 116.5, 115.1, 66.4. **HRMS** ($ESI^+$) for $C_{16}H_{12}NO_2$; calculated 250.0863, found 250.0865 (error m/z = 1.1 ppm).

## VII. References

(1) St. Cyr, D. J.; Arndtsen, B. A., *J. Am. Chem. Soc.* **2007**, *129*, 12366-12367.

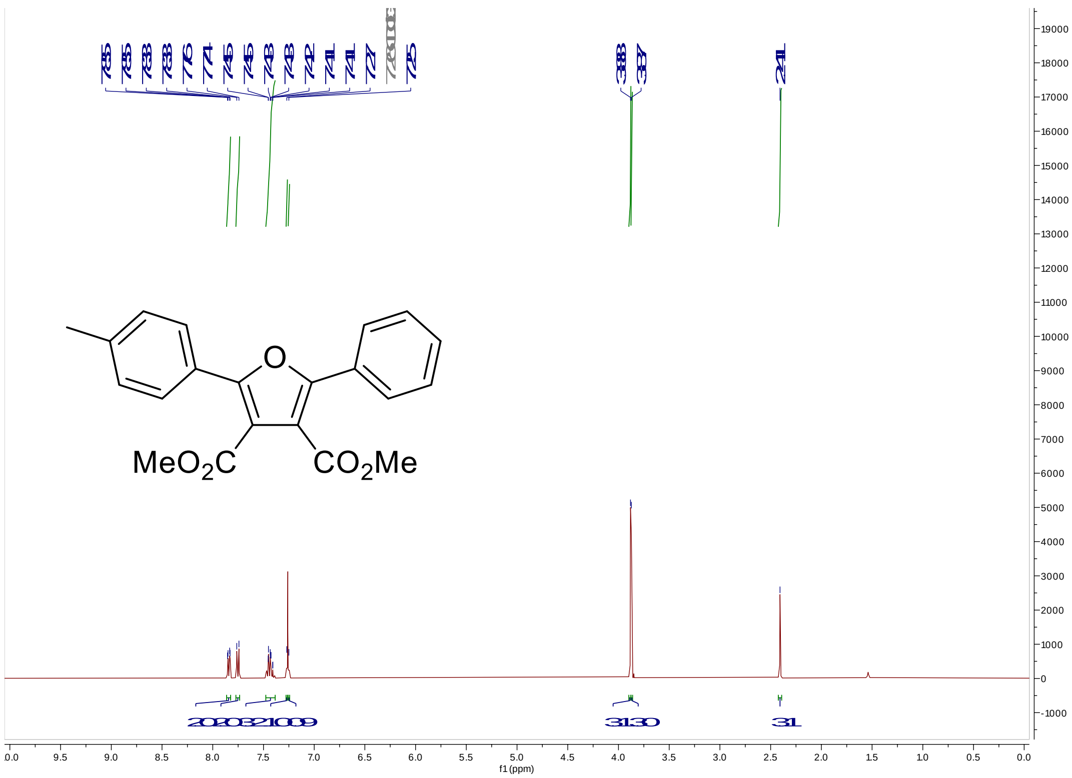
(2) Naouri, A.; Djemoui, A.; Ouahrani, M. R.; Lahrech, M. B.; Lemouari, N.; Rocha, D. H. A.; Albuquerque, H.; Mendes, R. F.; Almeida Paz, F. A.; Helguero, L. A.; Bachari, K.; Talhi, O.; Silva, A. M. S. *J. Mol. Struct*. **2020**, *1217*, 128325.

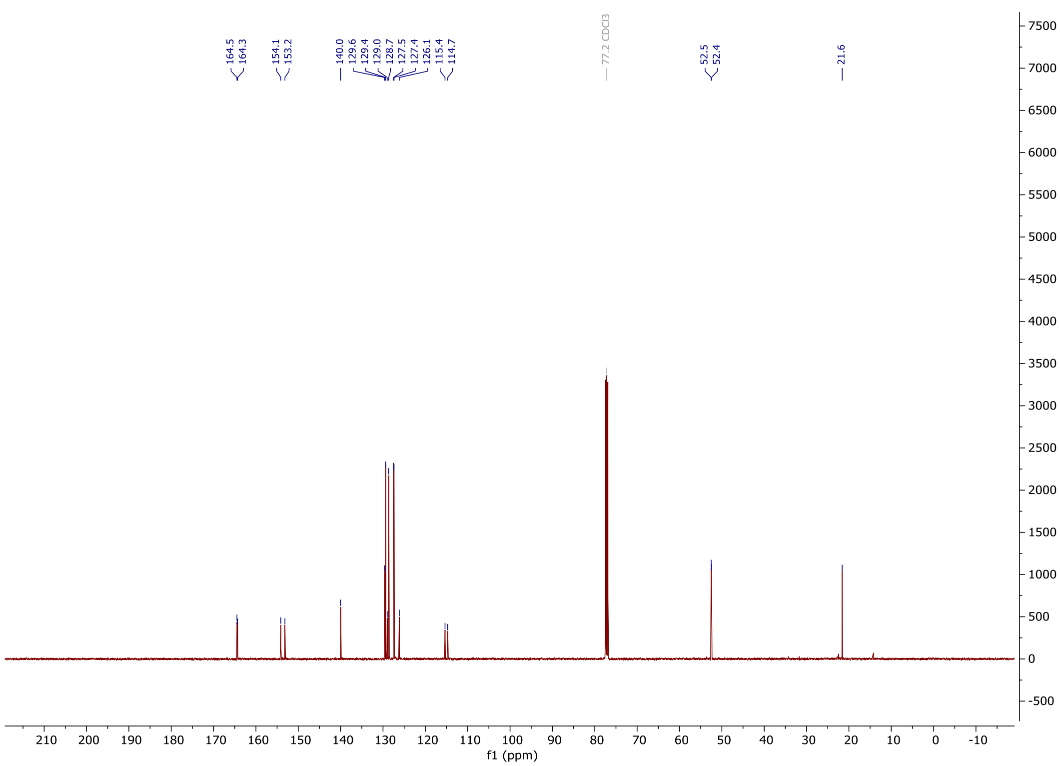
(3) Vedachalam, S.; Zeng, J.; Gorityala, B. K.; Antonio, M.; Liu, X.-W., *Org. Lett.* **2010**, *12*, 352-355.

(4) Hoffmann, H. M. R.; Haase, K. *Synthesis* **1981**, *9*, 715-719.

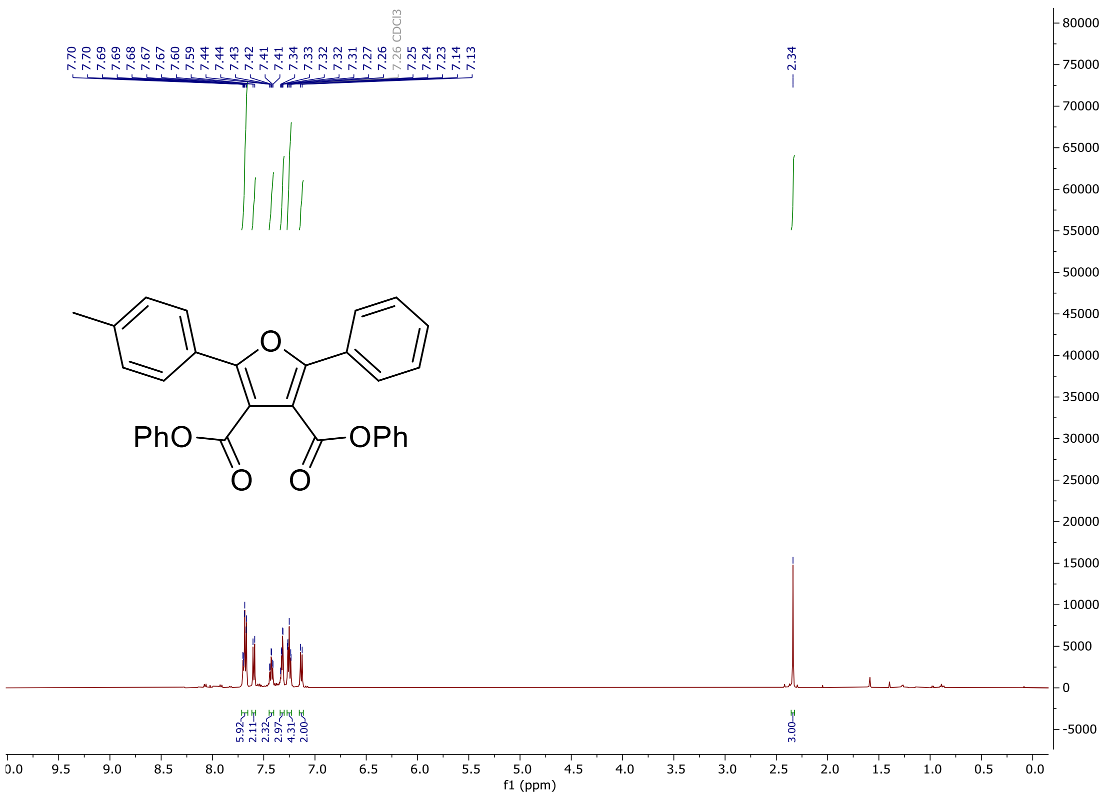
## VIII. NMR spectra for 3, 6 and 8.

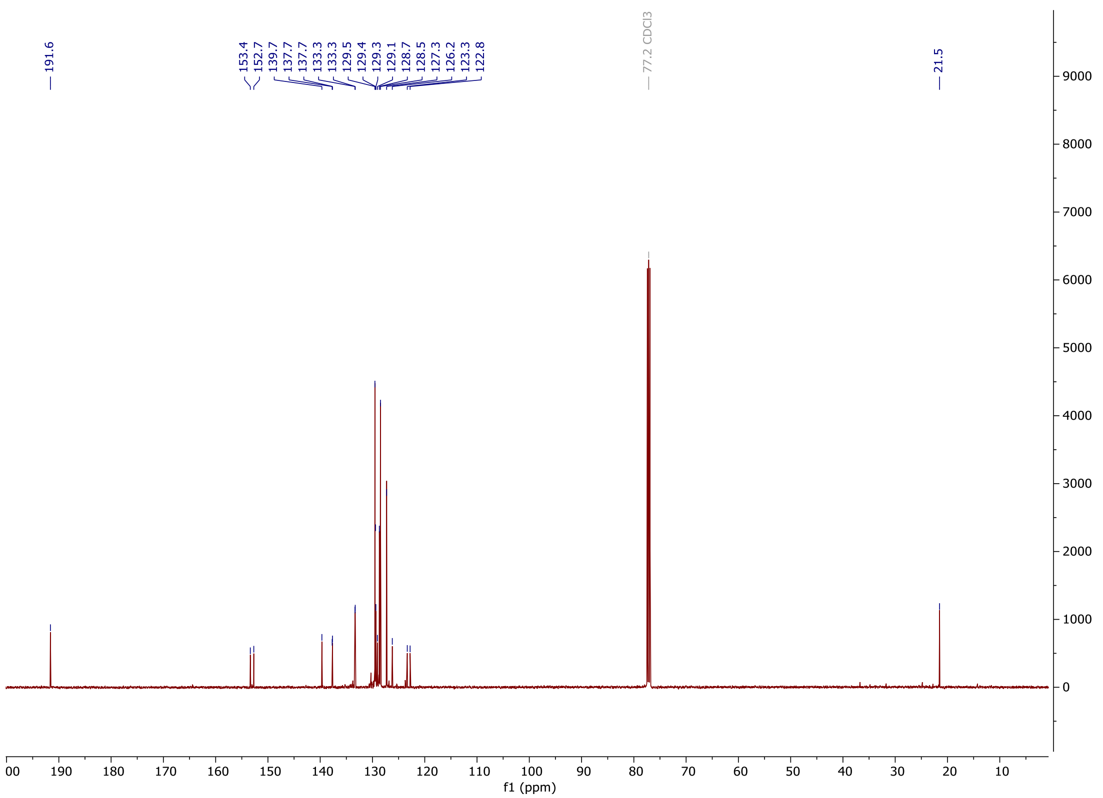
### $^1$H and $^{13}$C NMR Spectra of 3a ($CDCl_3$)



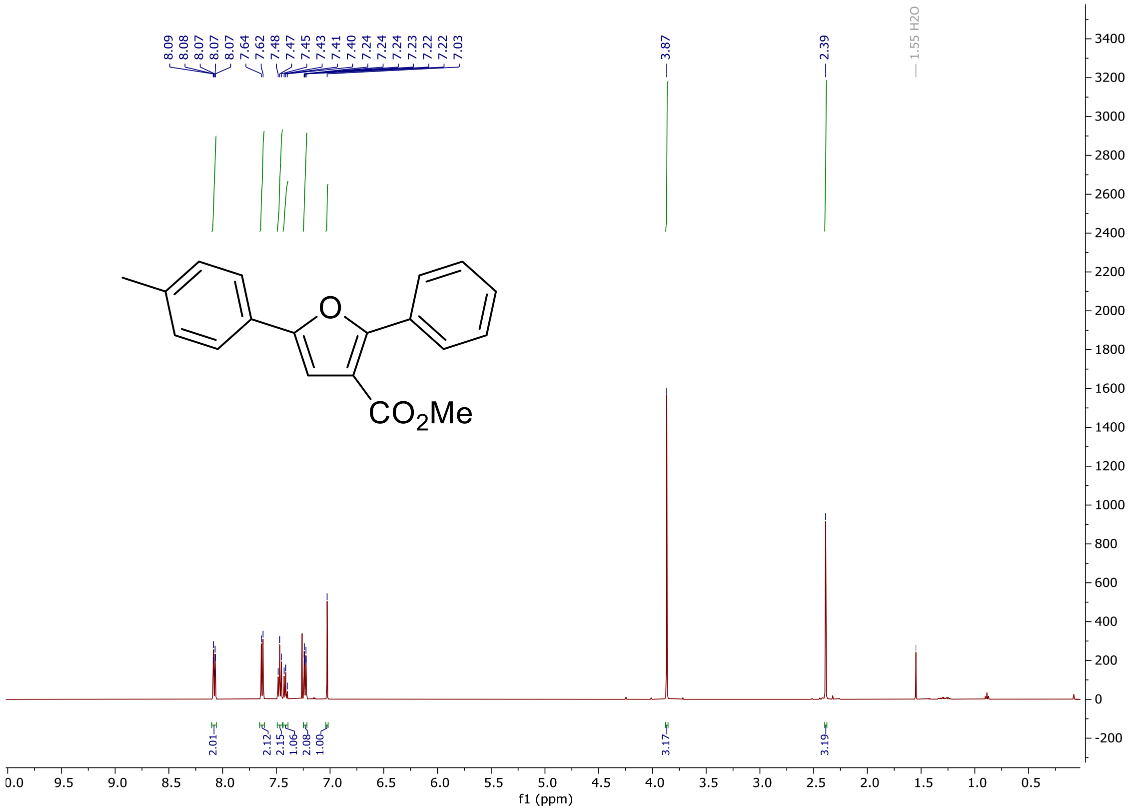



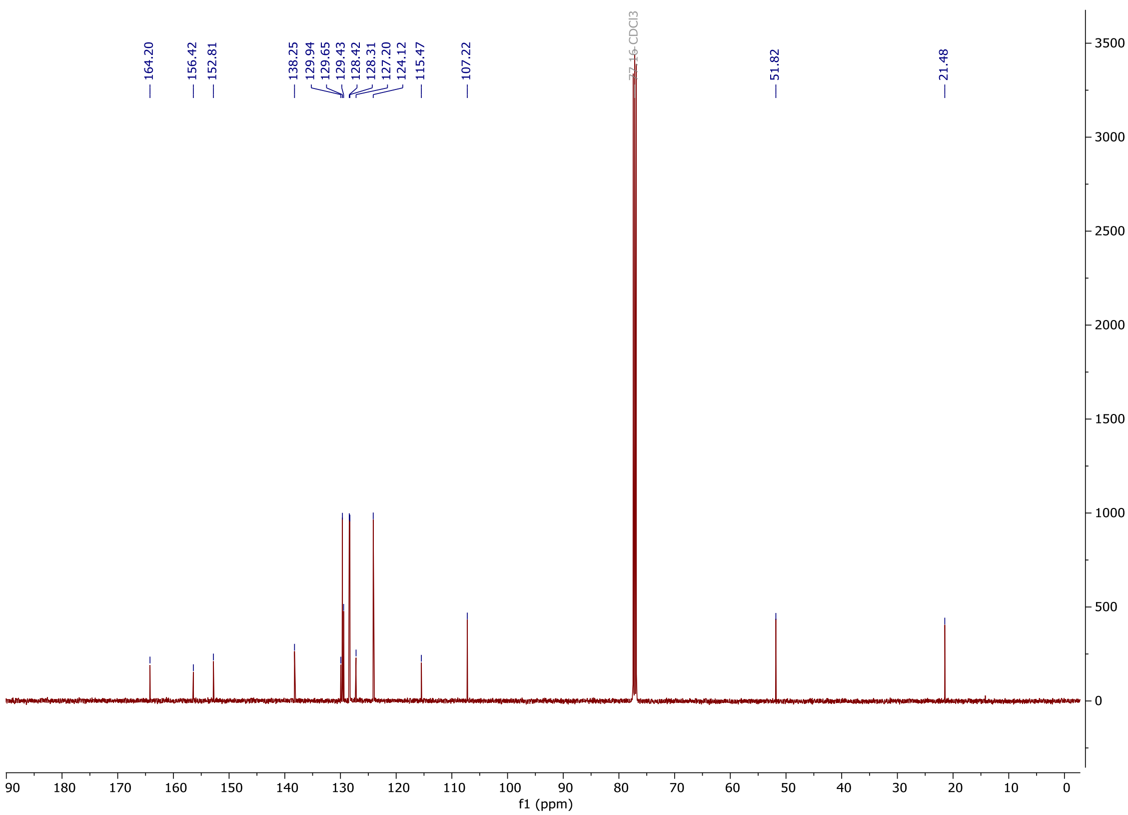
## $^{1}H$ and $^{13}C$ NMR Spectra of 3b ($CDCl_3$)



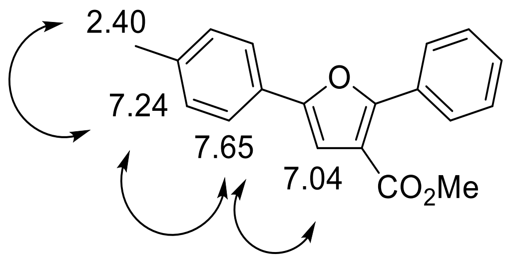



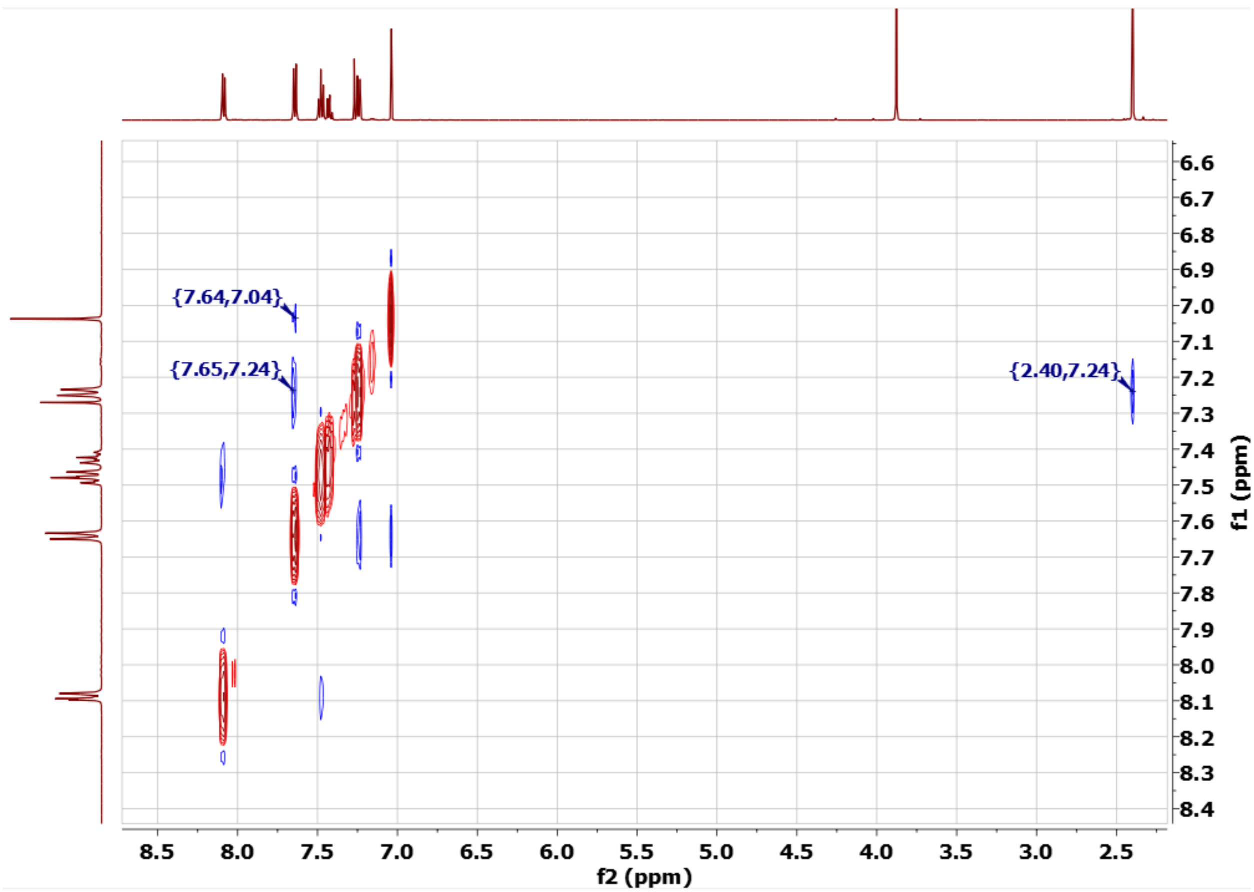
## $^{1}H$ and $^{13}C$ NMR Spectra of 3c ($CDCl_3$)



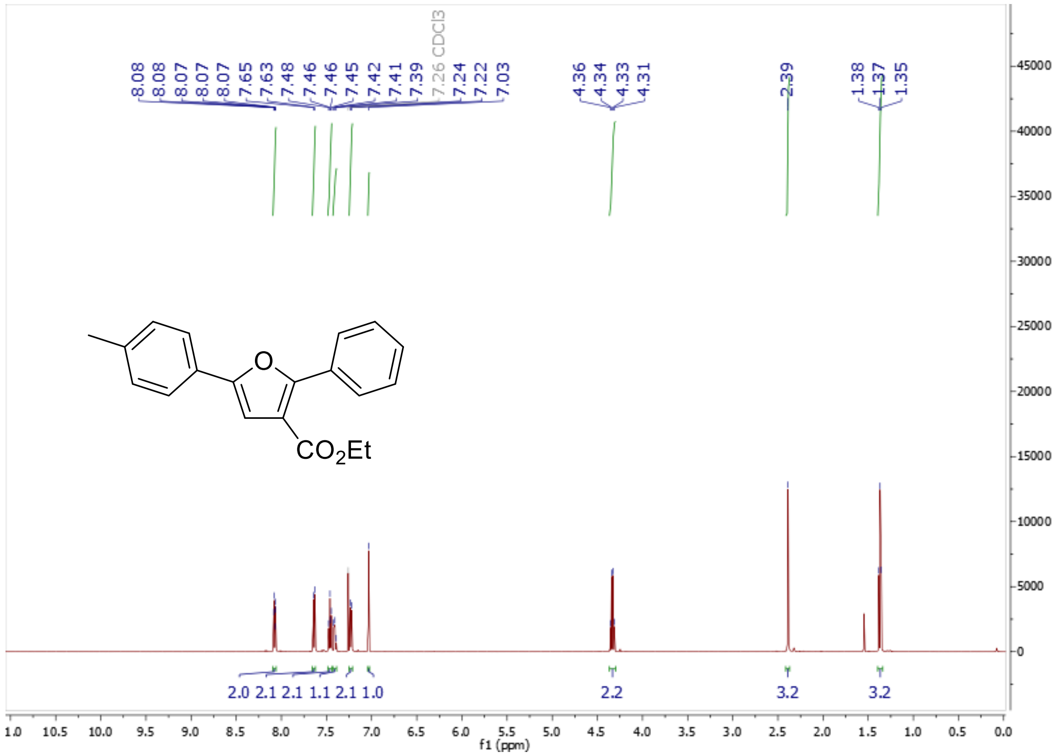



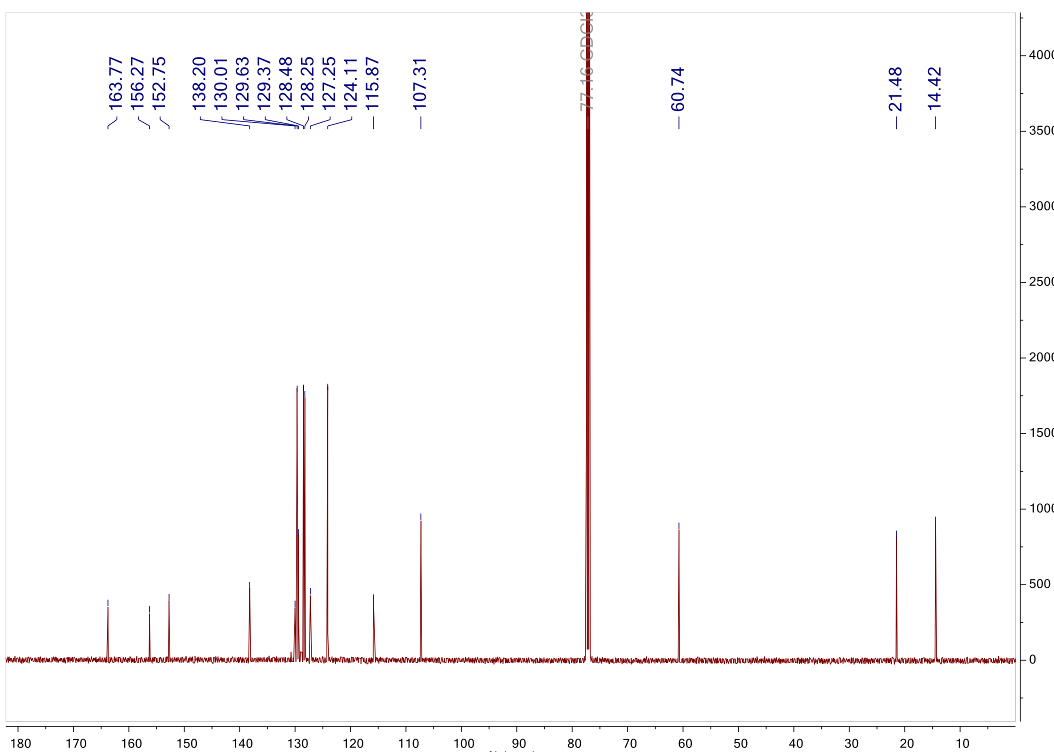
**2D-NOE Spectra of 3c ($CDCl_3$)**



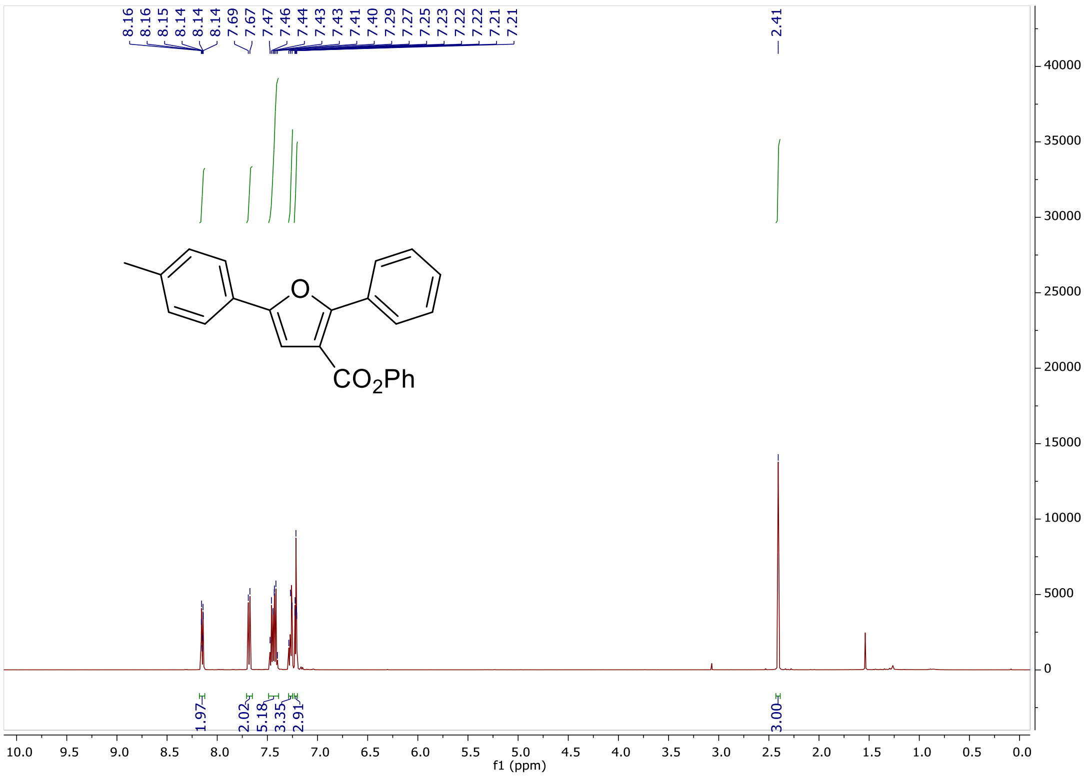



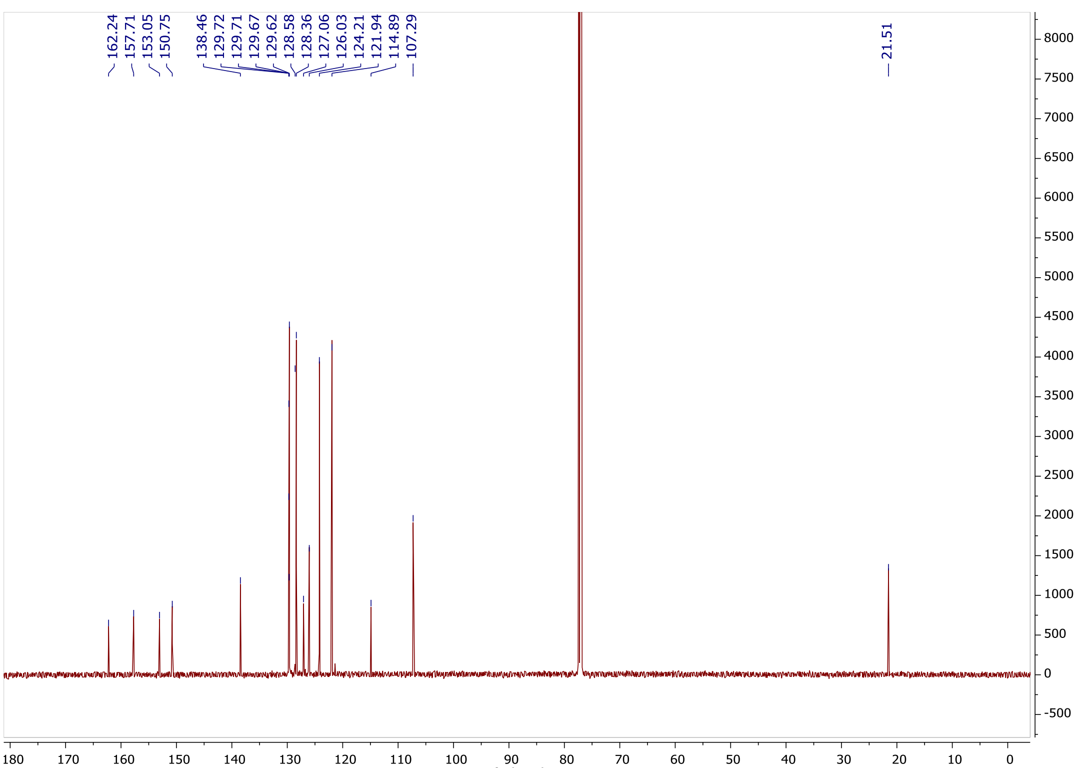
**$^{1}H$ and $^{13}C$ NMR Spectra of 3d ($CDCl_3$)**



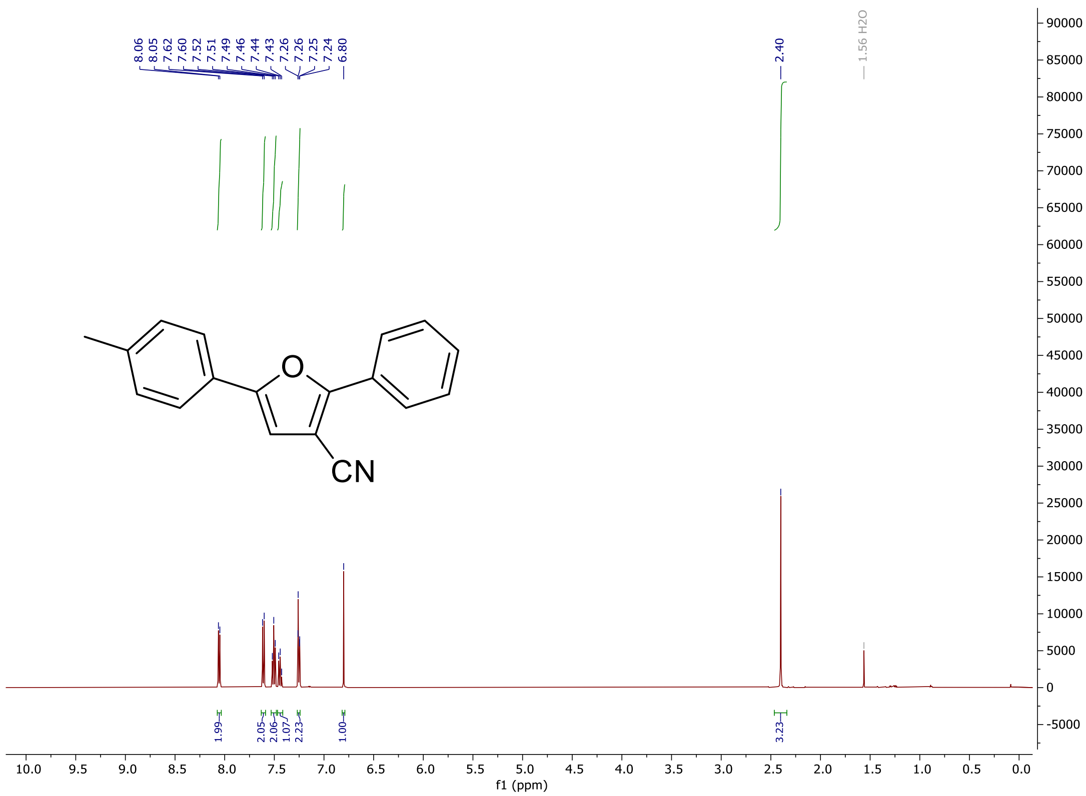



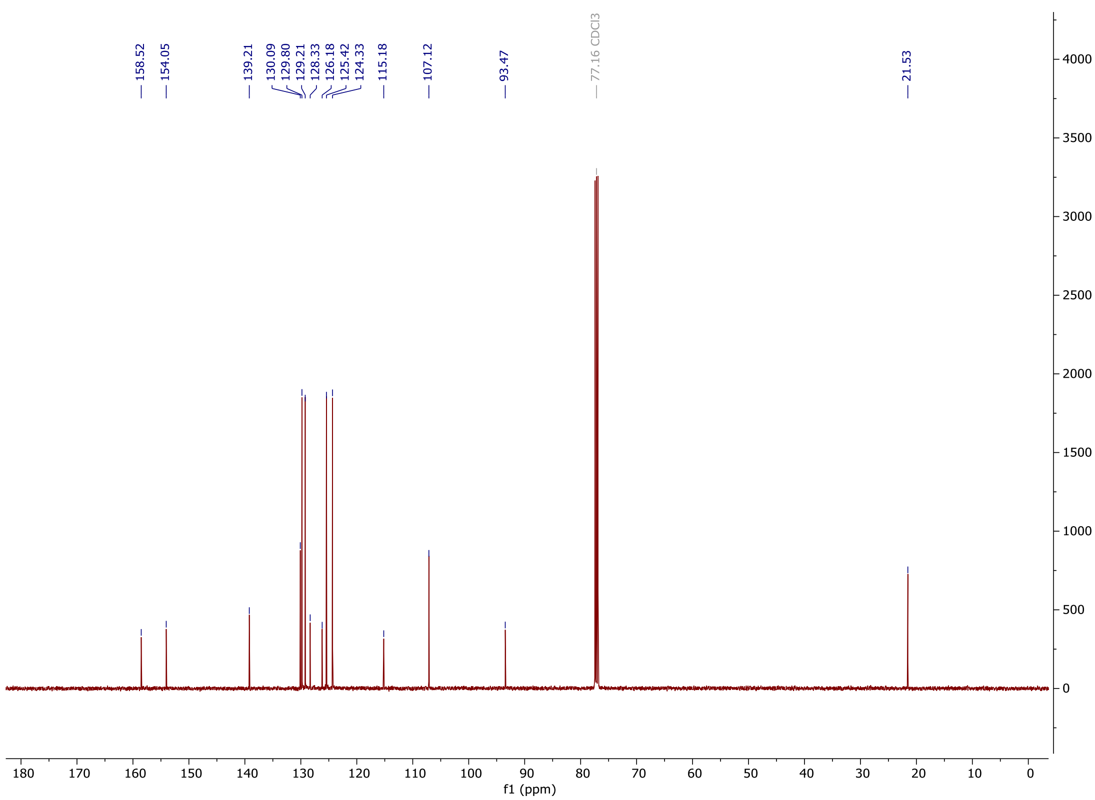
[1]H and [13]C NMR Spectra of 3e ($CDCl_3$)



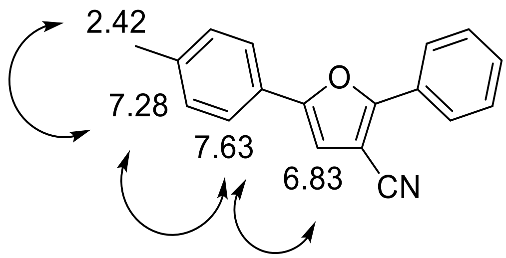



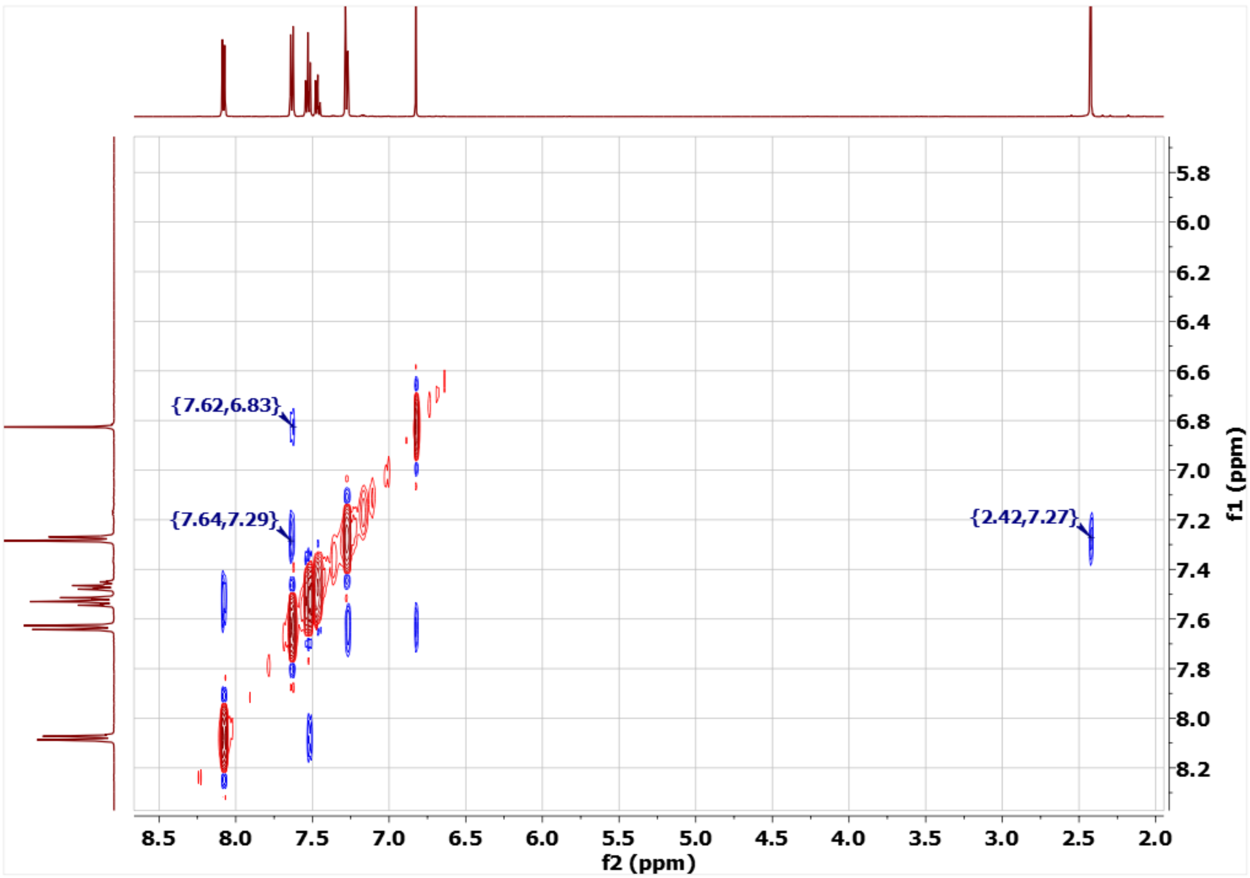
**$^{1}$H and $^{13}$C NMR Spectra of 3f ($CDCl_3$)**



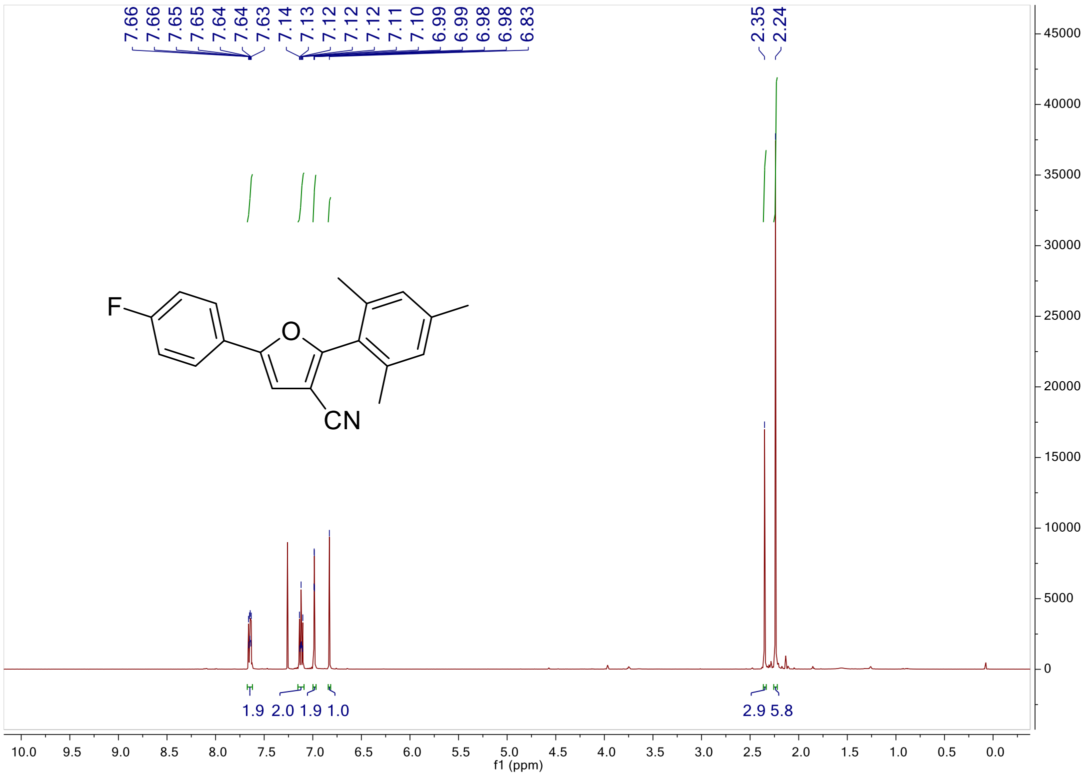



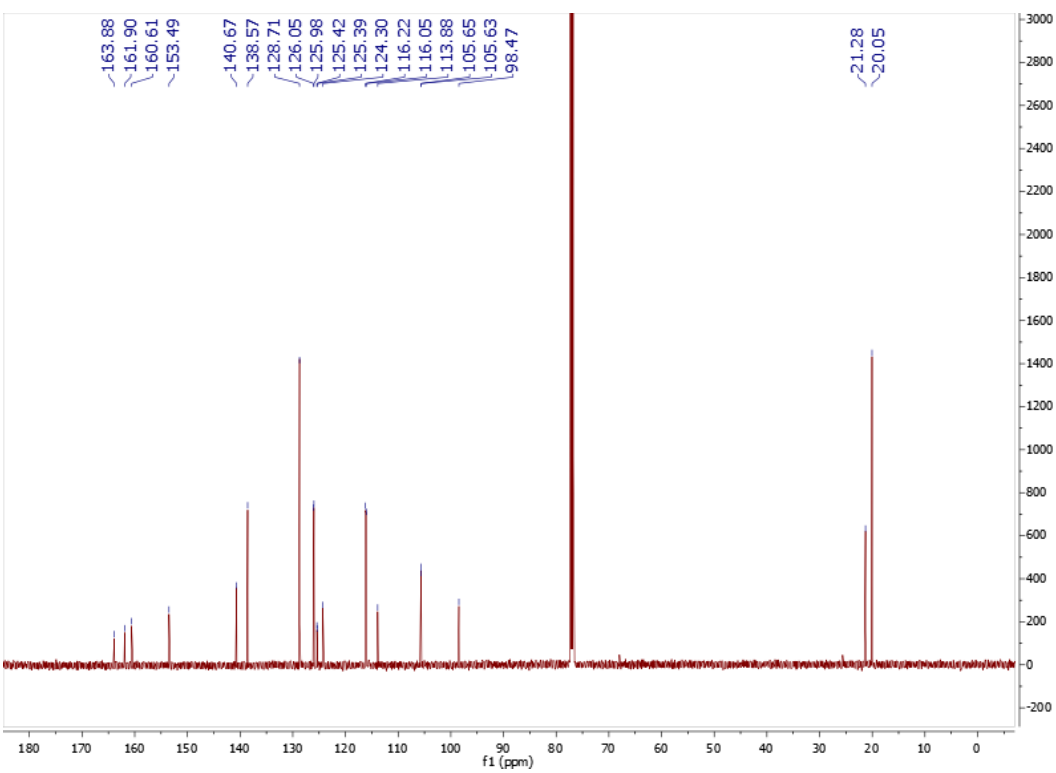
**2D-NOE Spectra of 3f ($CDCl_3$)**



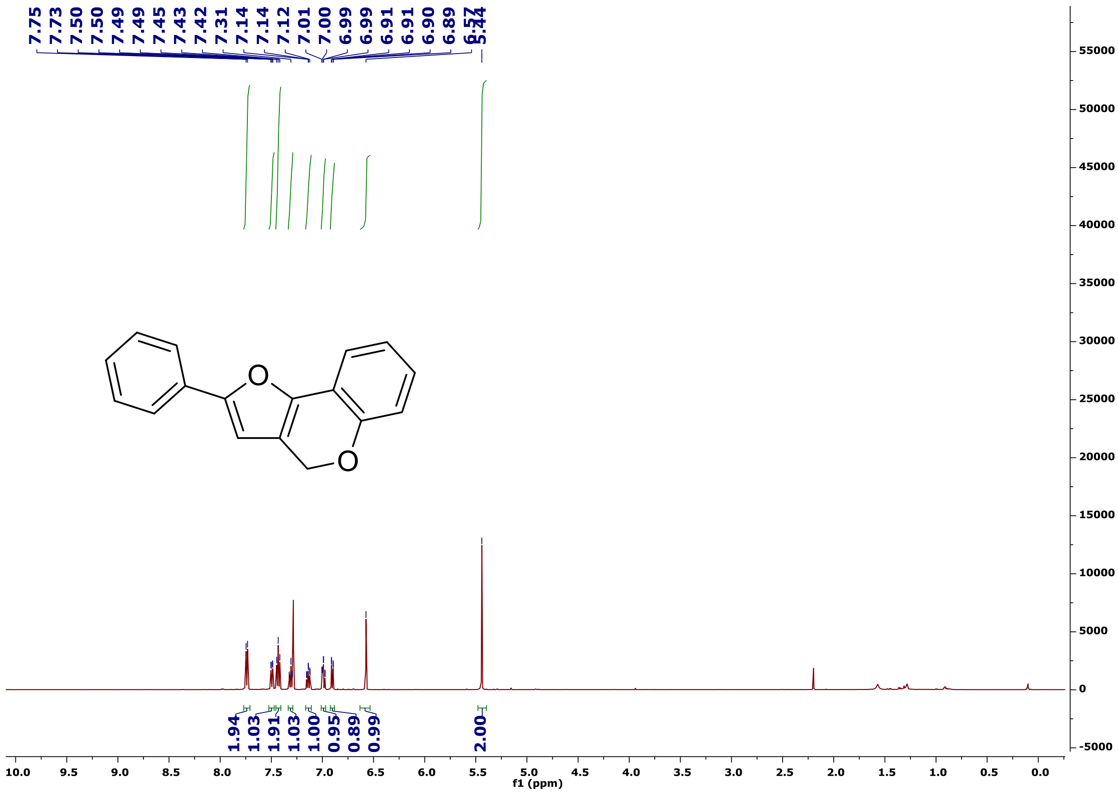



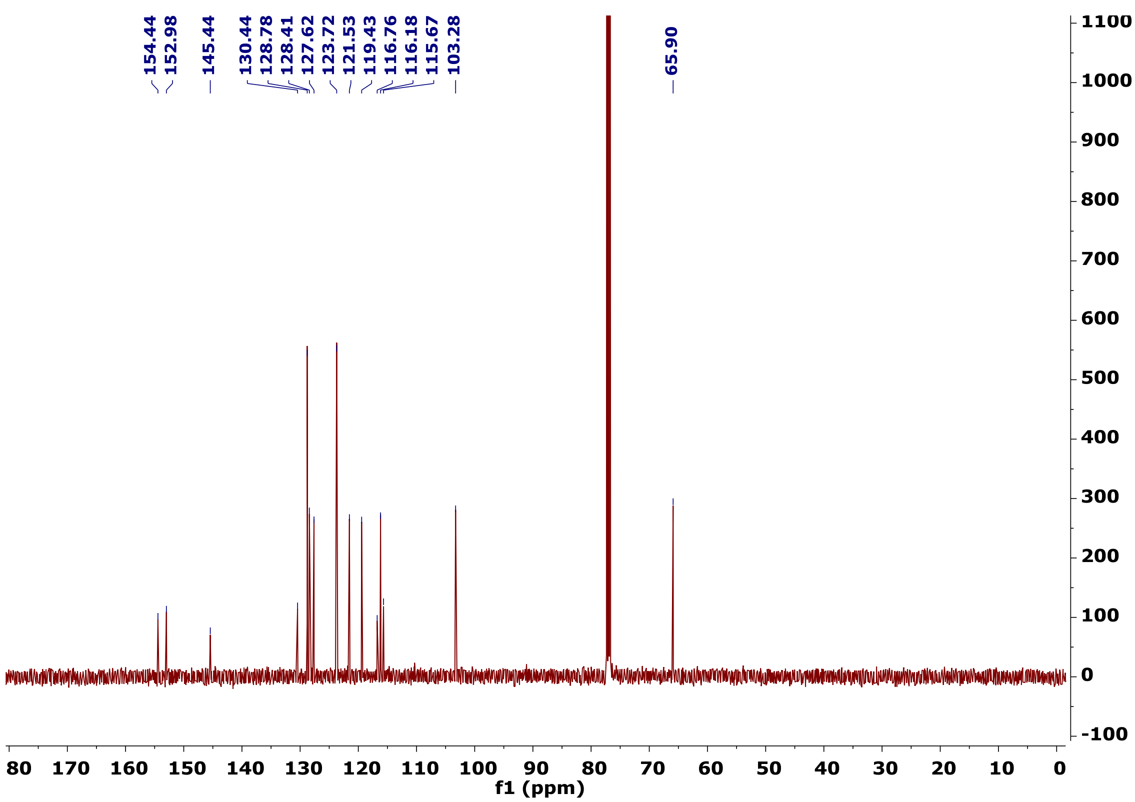
## $^{1}H$ and $^{13}C$ NMR Spectra of 3g ($CDCl_3$)



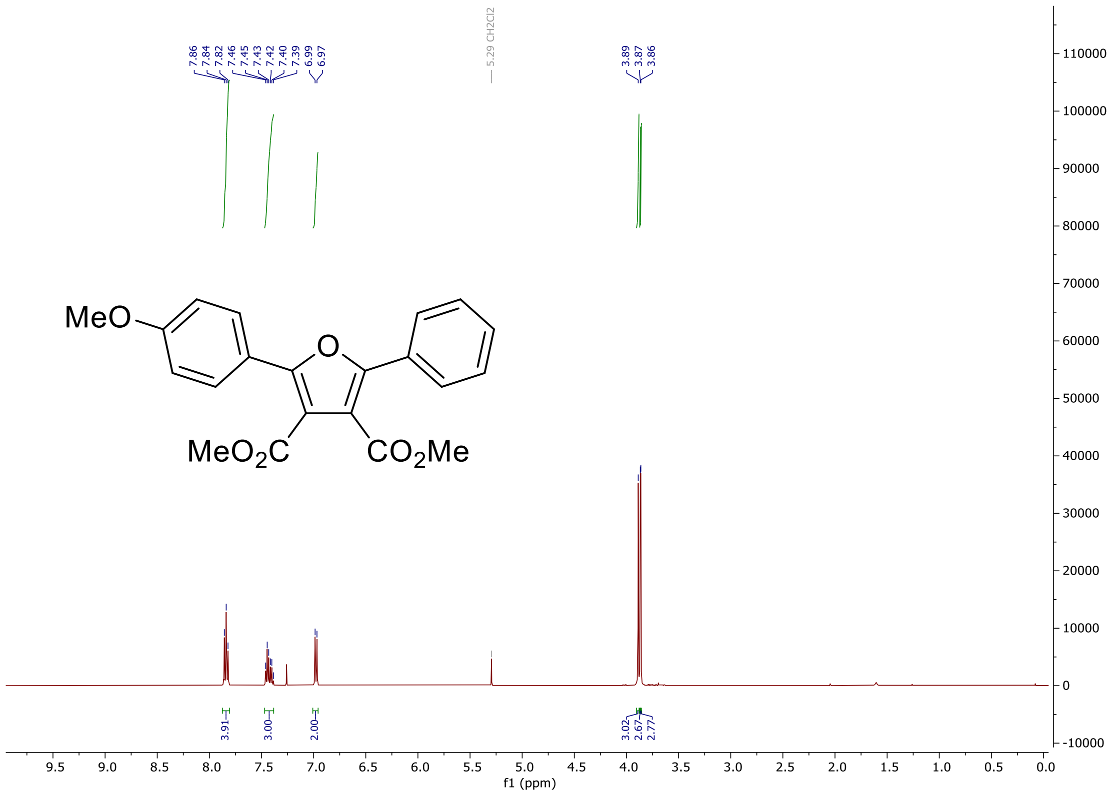



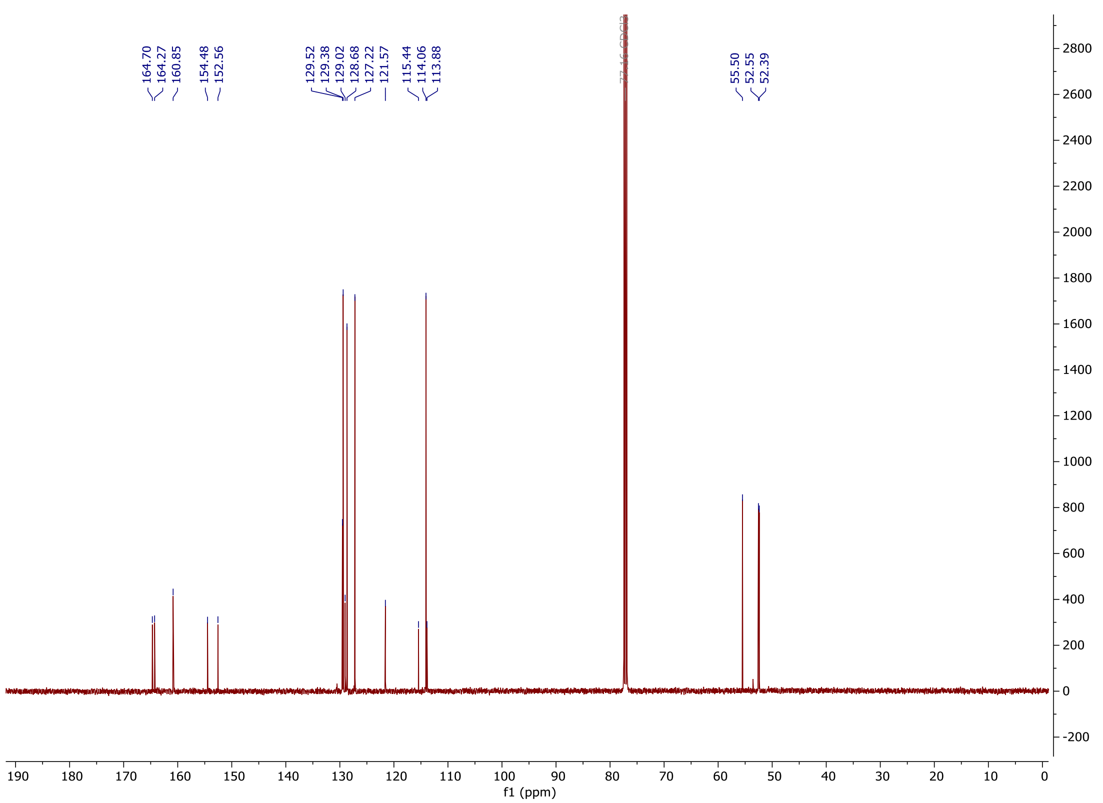
$^{1}H$ and $^{13}C$ NMR Spectra of 3h ($CDCl_3$)



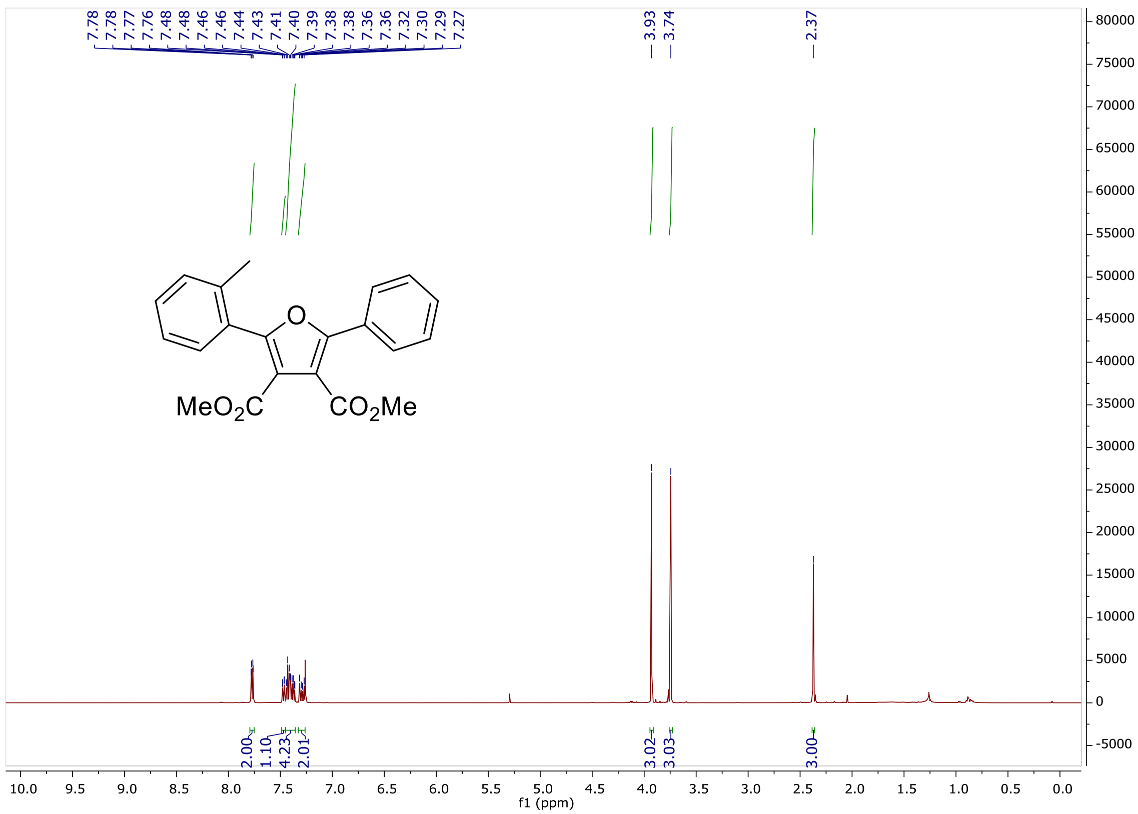


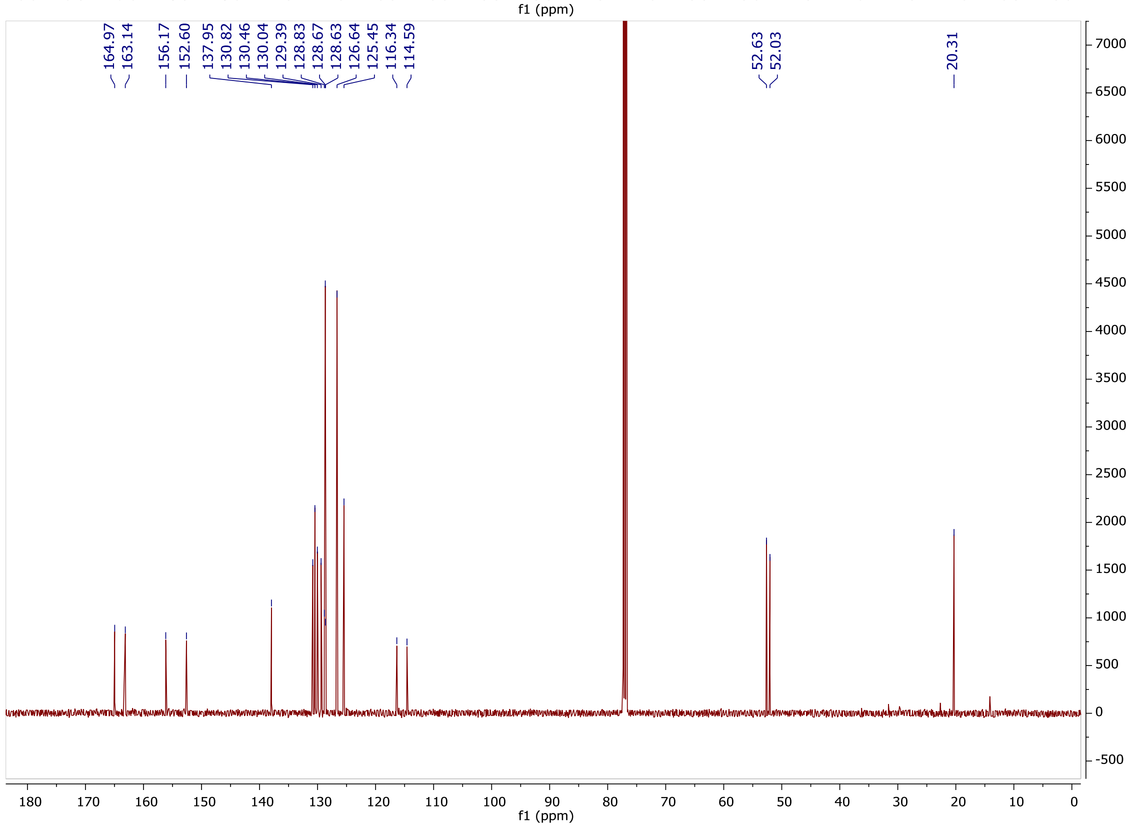
## $^1$H and $^{13}$C NMR Spectra of 3i ($CDCl_3$)



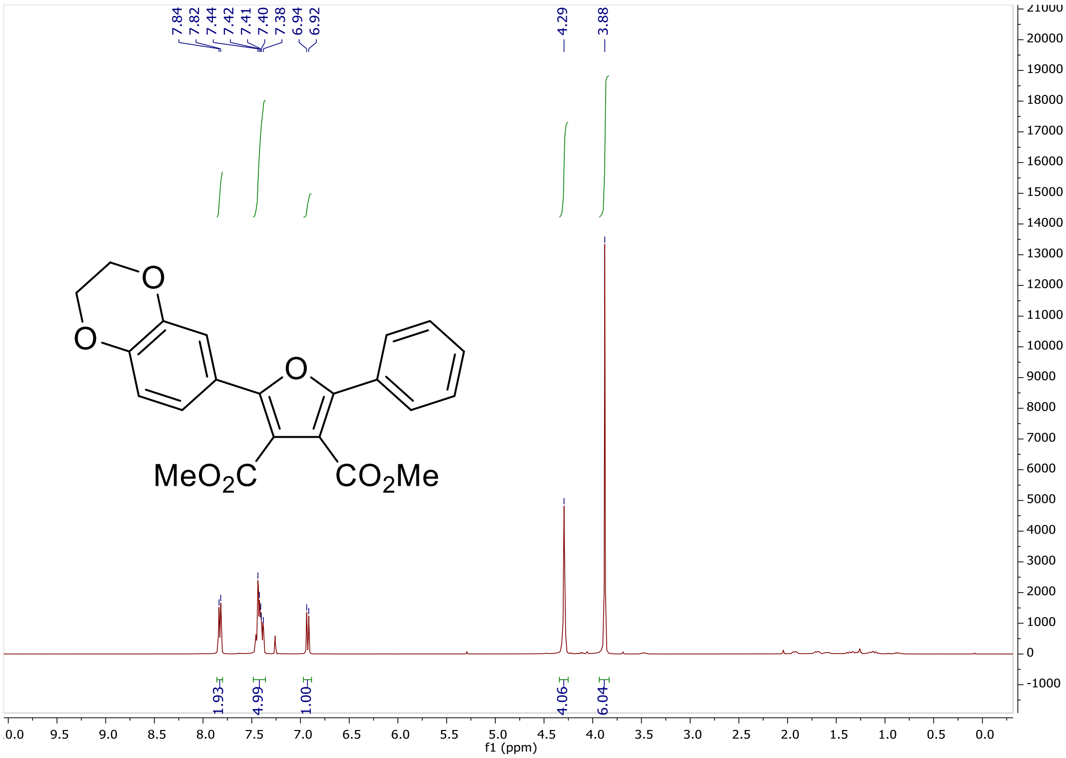



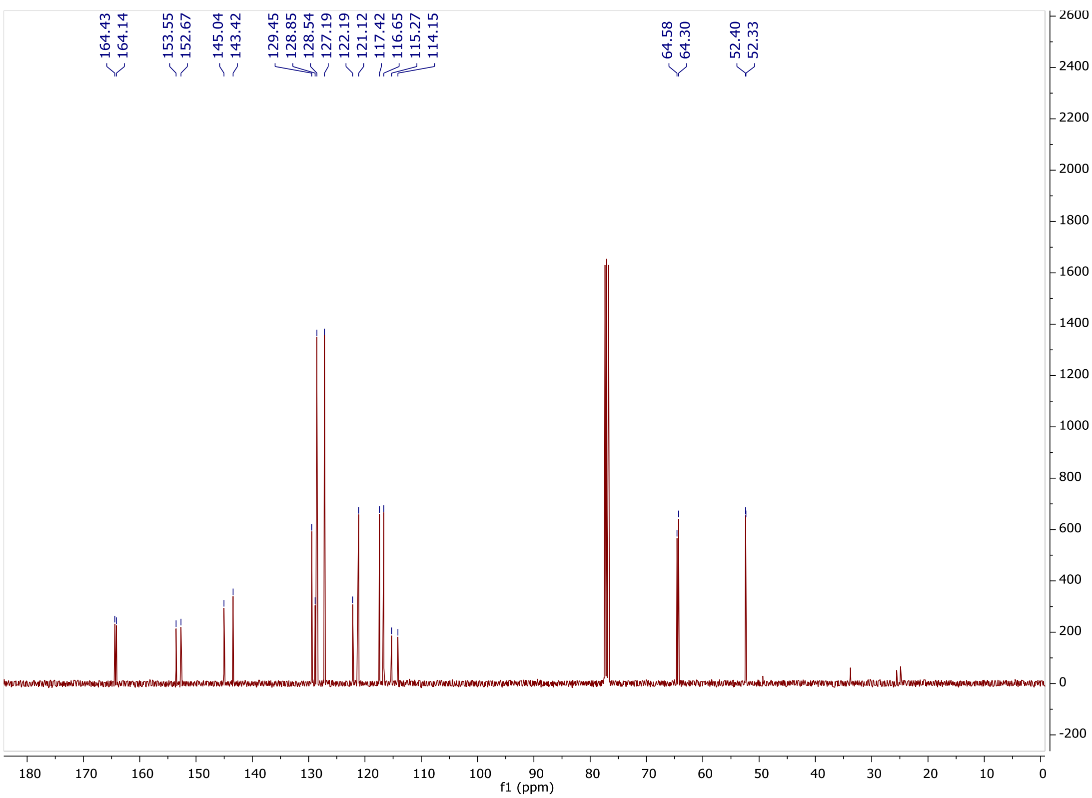
**$^{1}H$ and $^{13}C$ NMR Spectra of 3j ($CDCl_3$)**



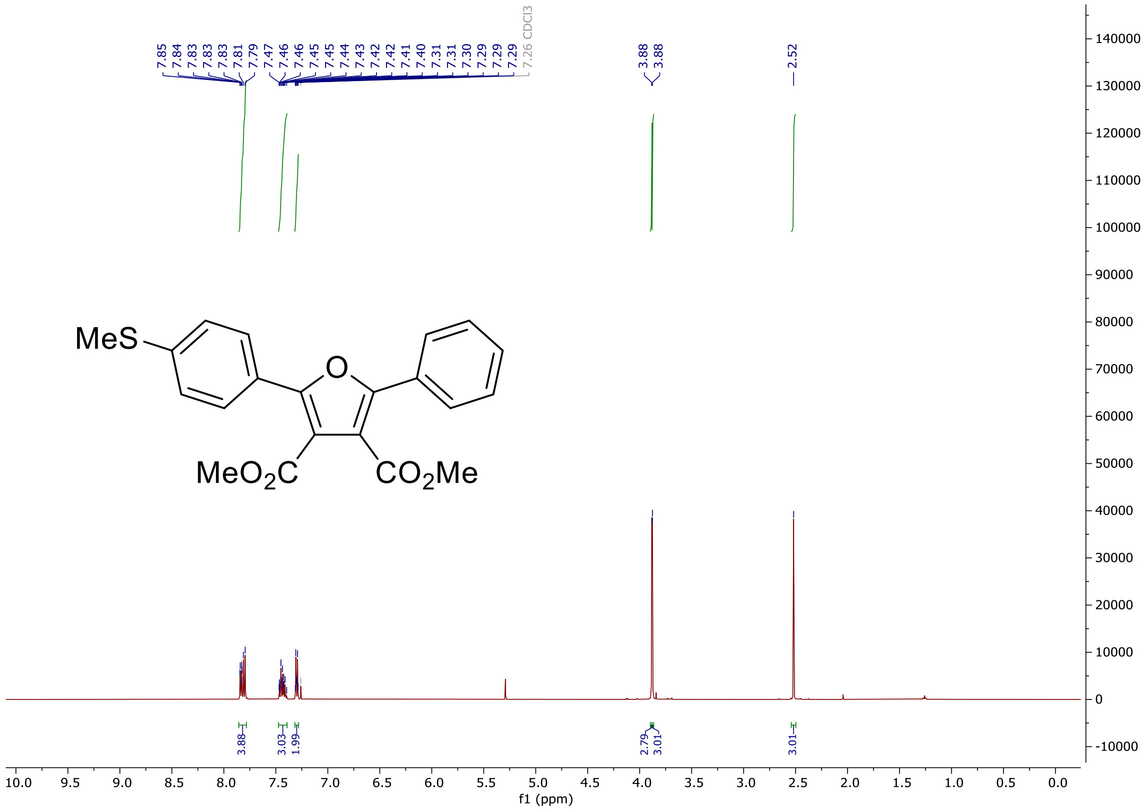



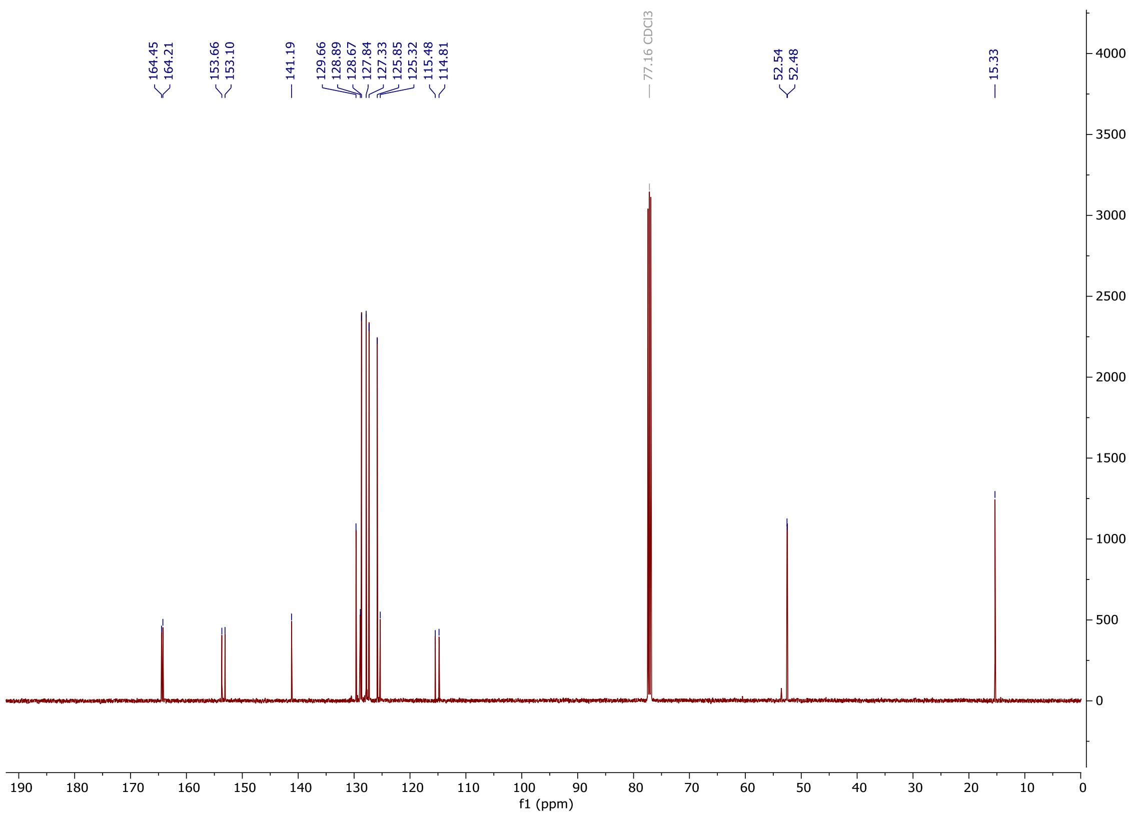
**[1]H and [13]C NMR Spectra of 3k ($CDCl_3$)**



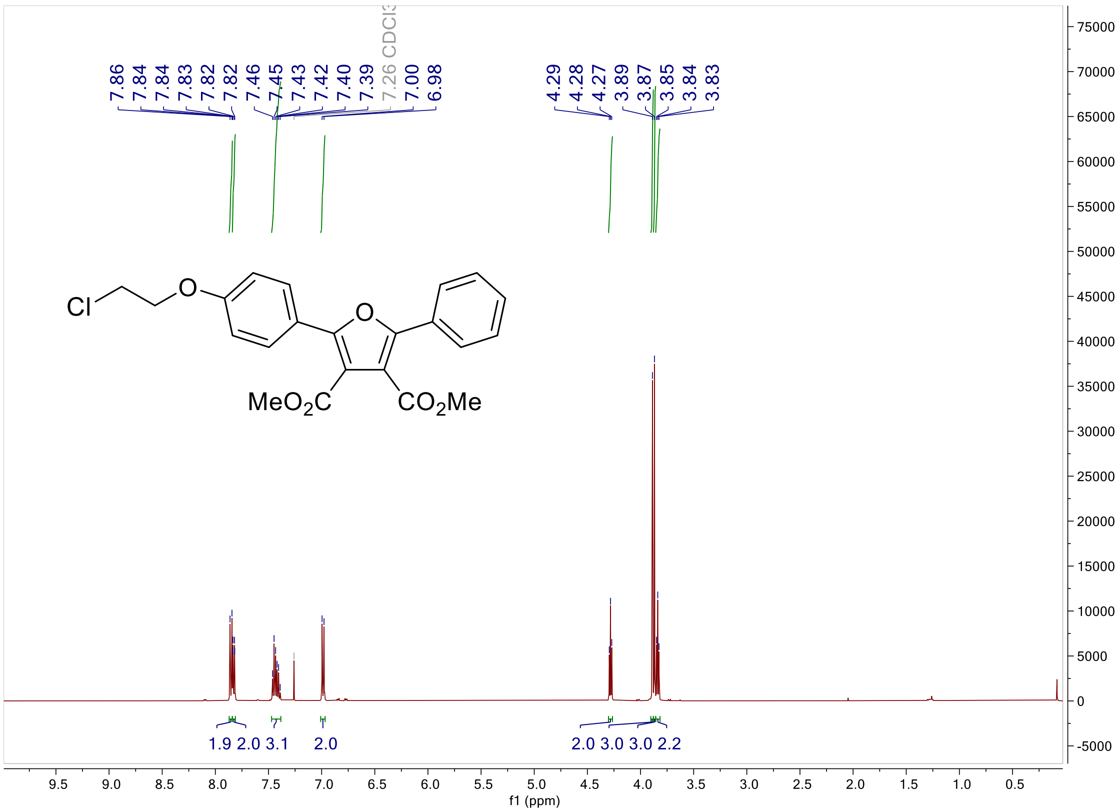



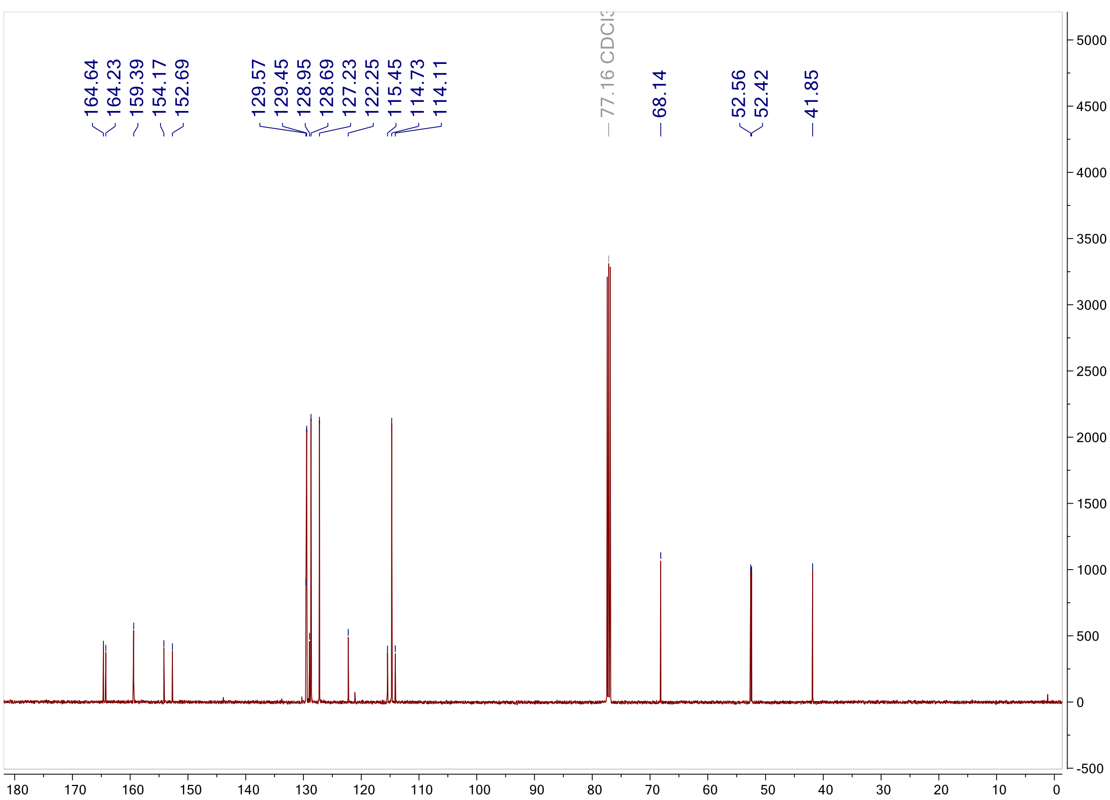
**$^{1}$H and $^{13}$C NMR Spectra of 3l ($CDCl_3$)**



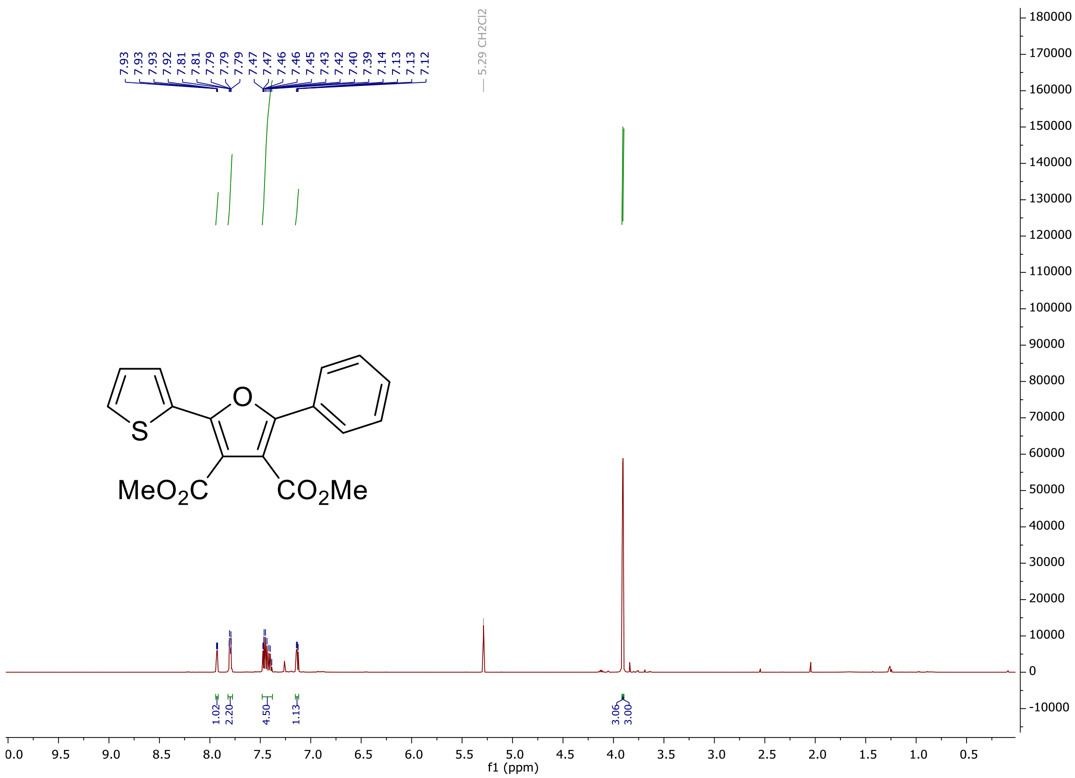


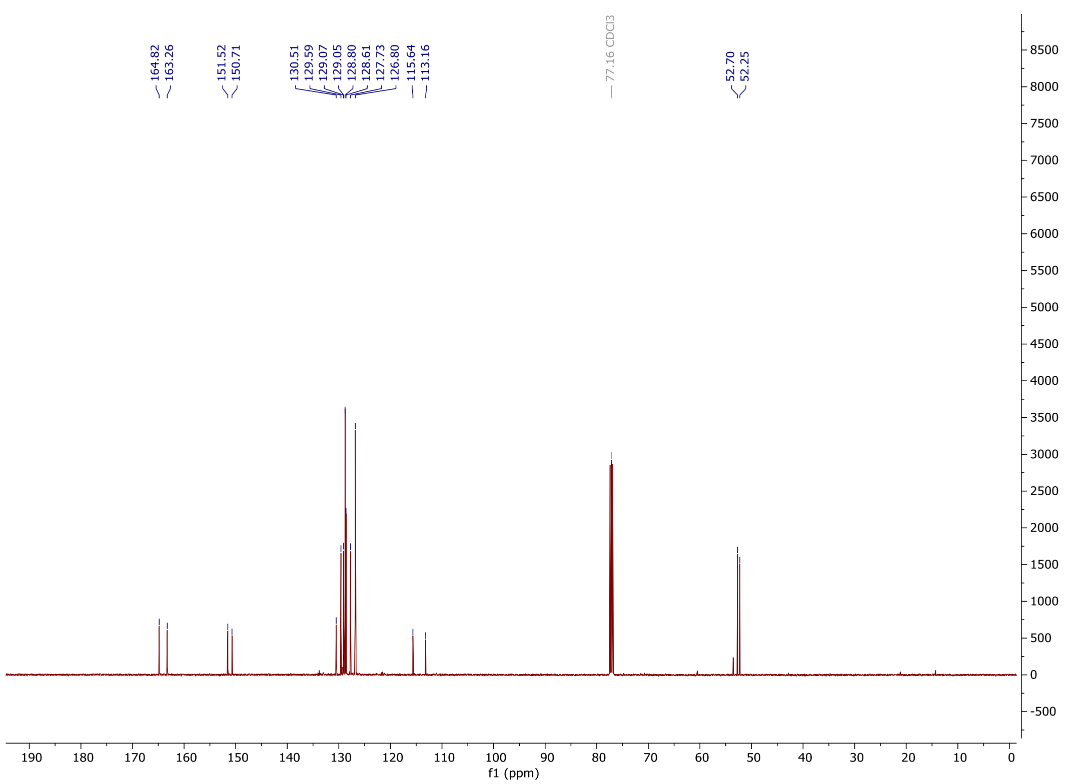
**[1]H and [13]C NMR Spectra of 3m ($CDCl_3$)**



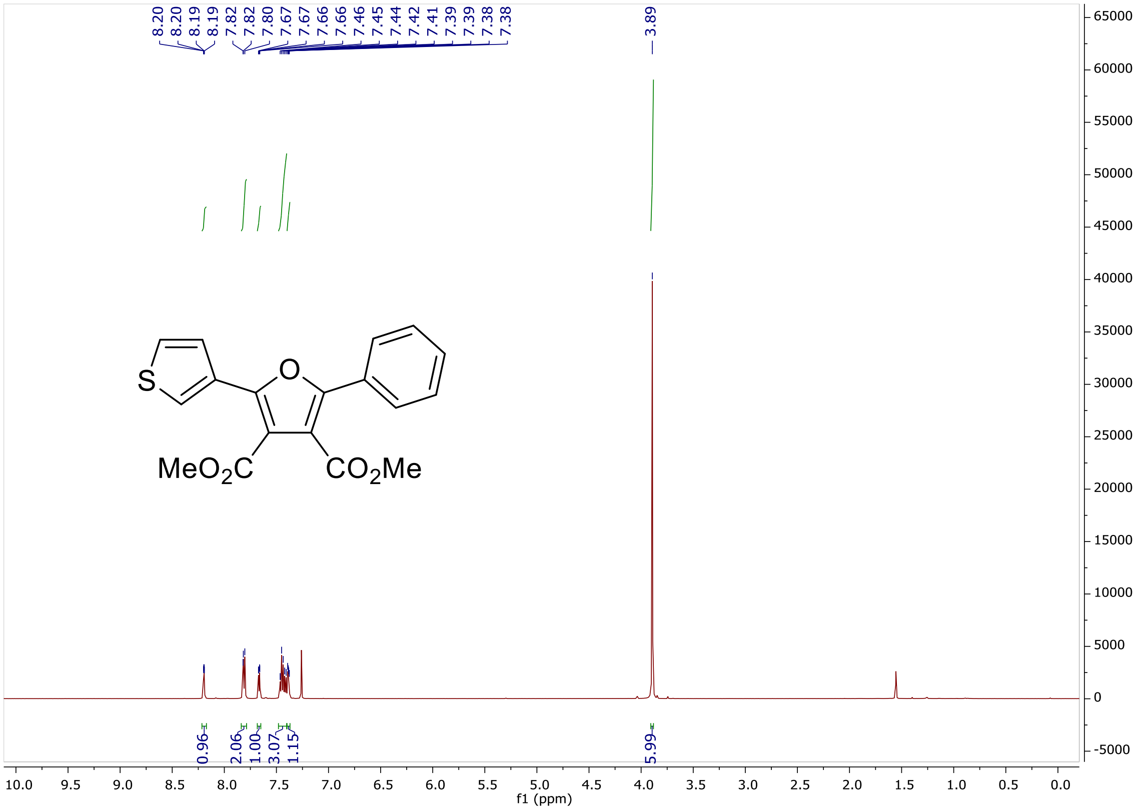



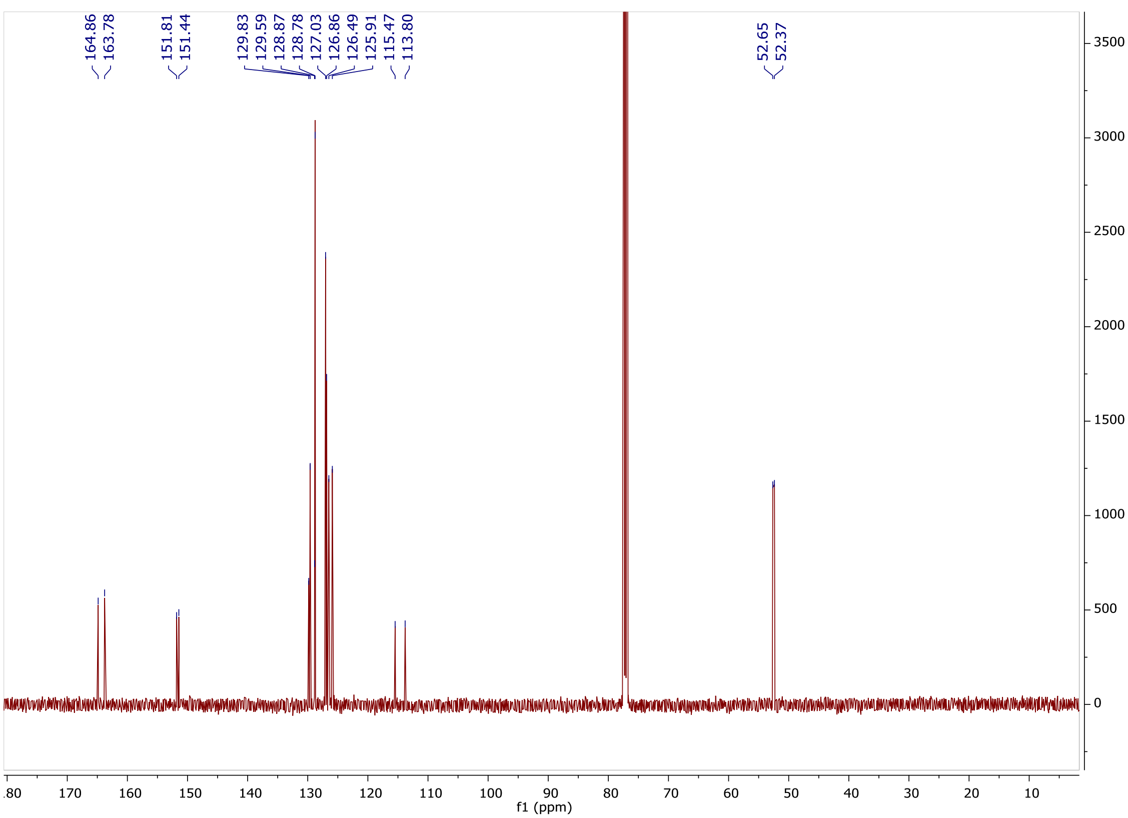
# $^{1}H$ and $^{13}C$ NMR Spectra of 3n ($CDCl_3$)



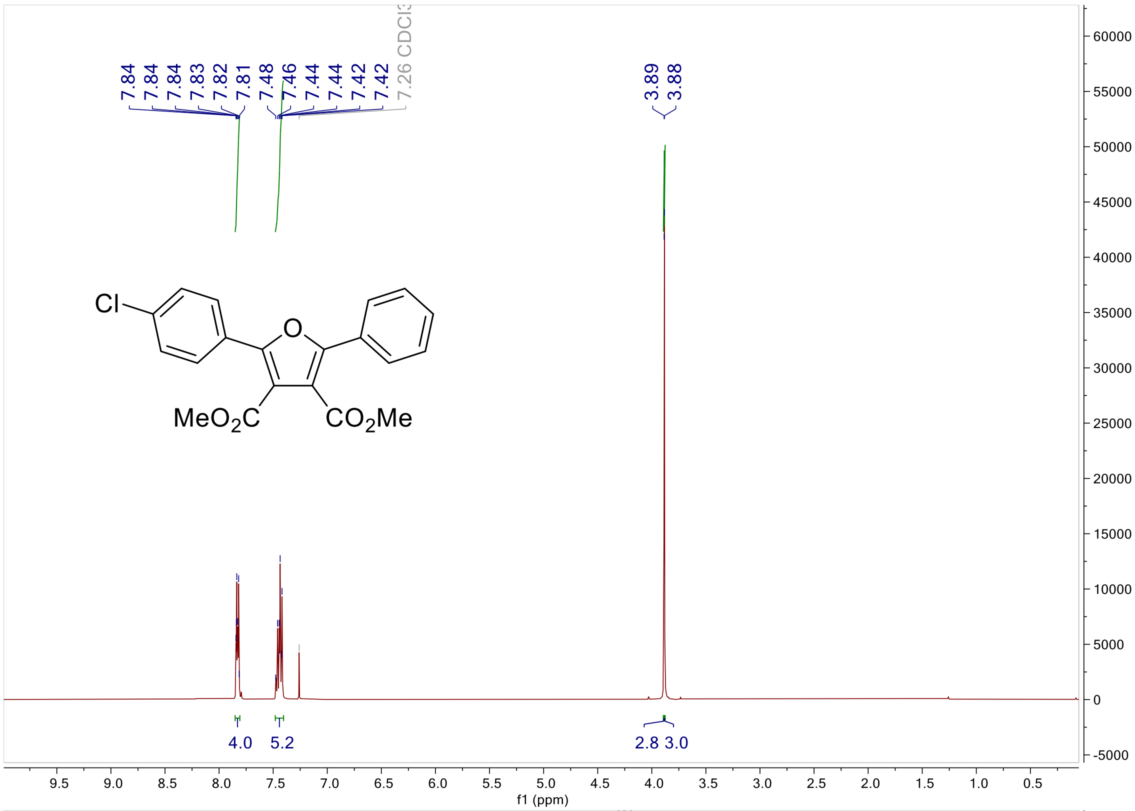



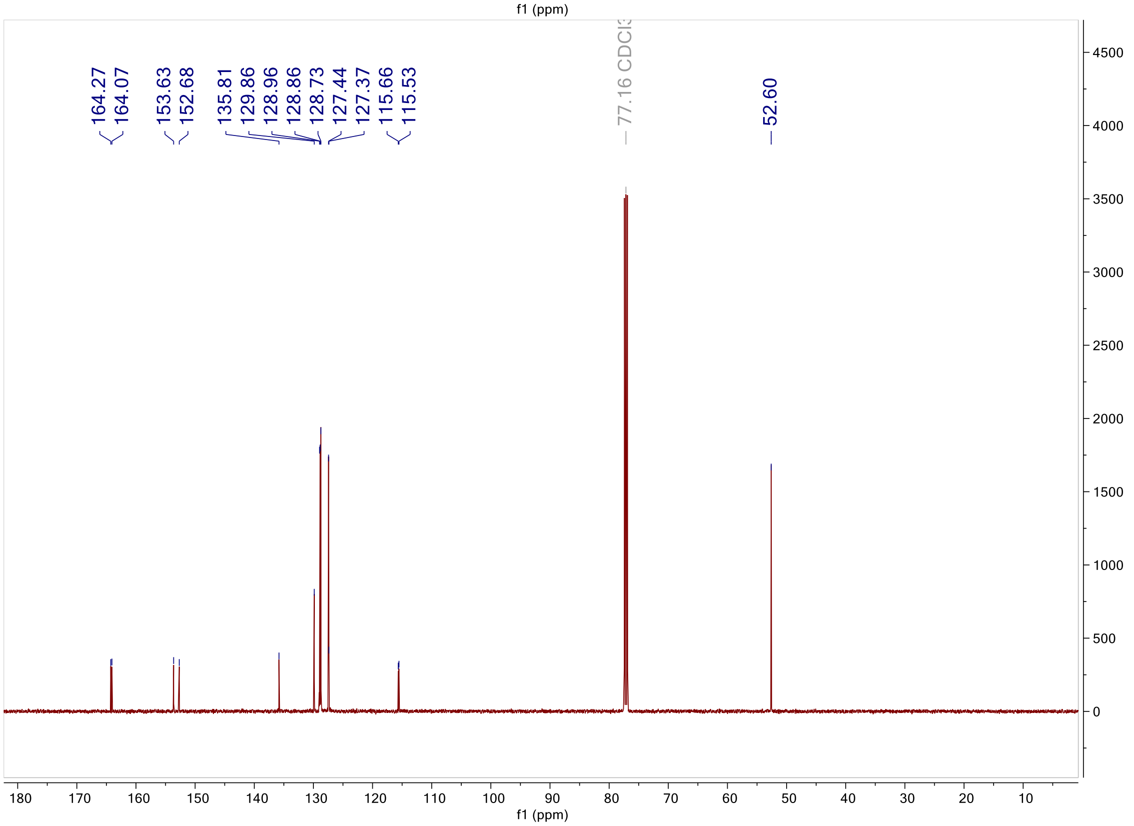
**$^{1}$H and $^{13}$C NMR Spectra of 3o ($CDCl_3$)**



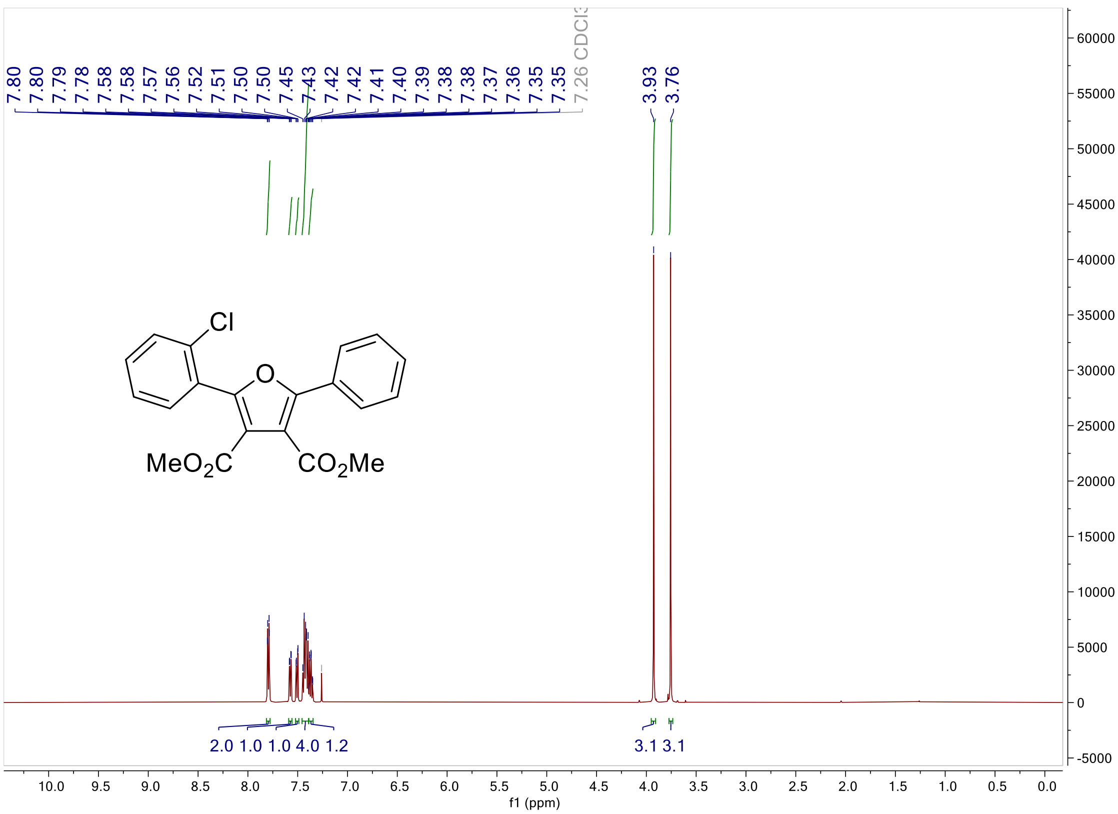


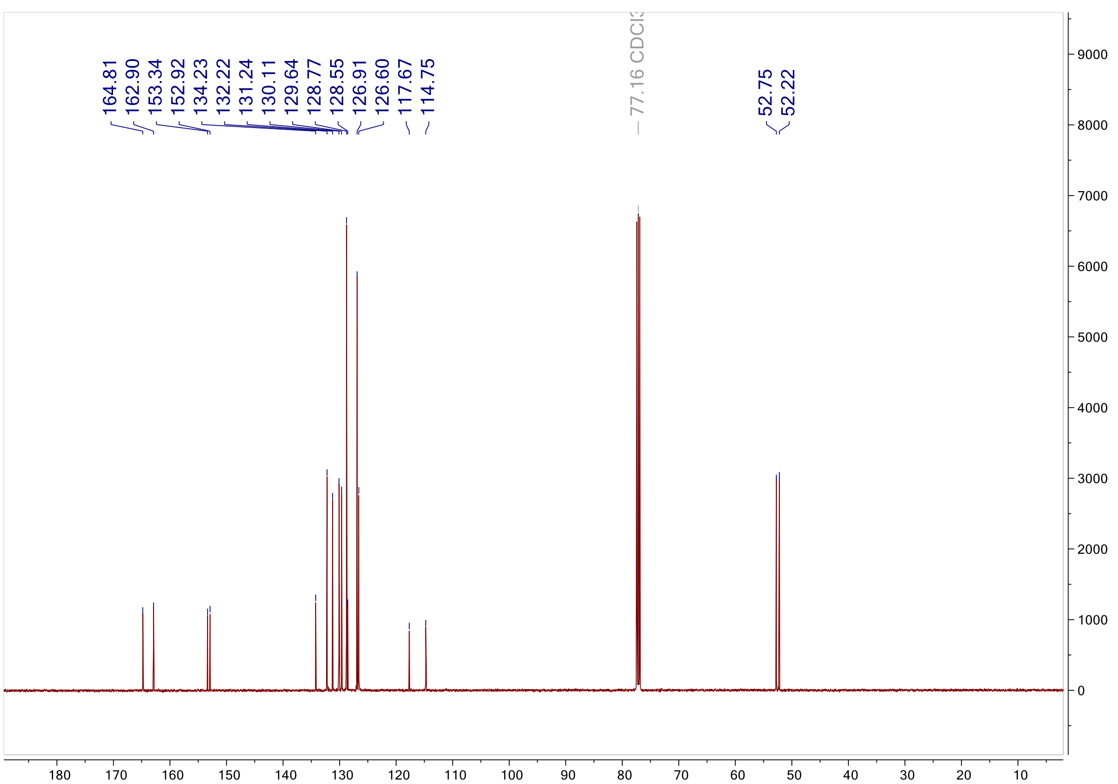
**[1]H and [13]C NMR Spectra of 3p ($CDCl_3$)**



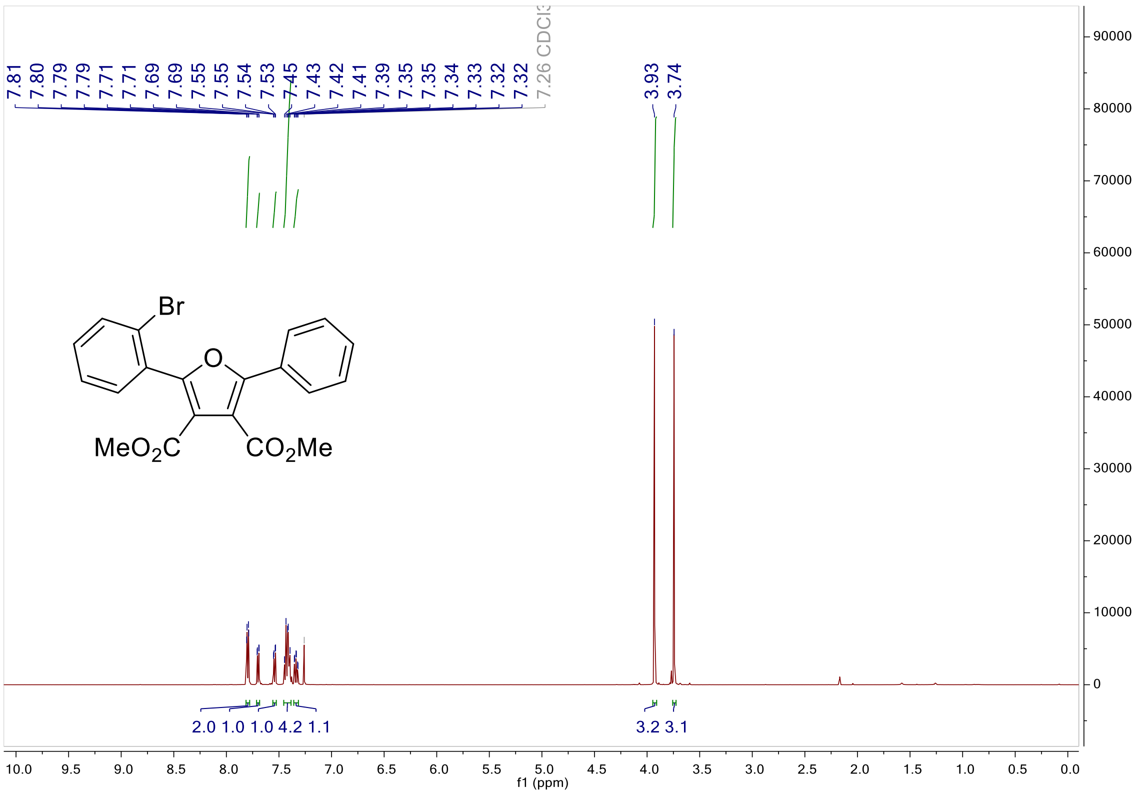



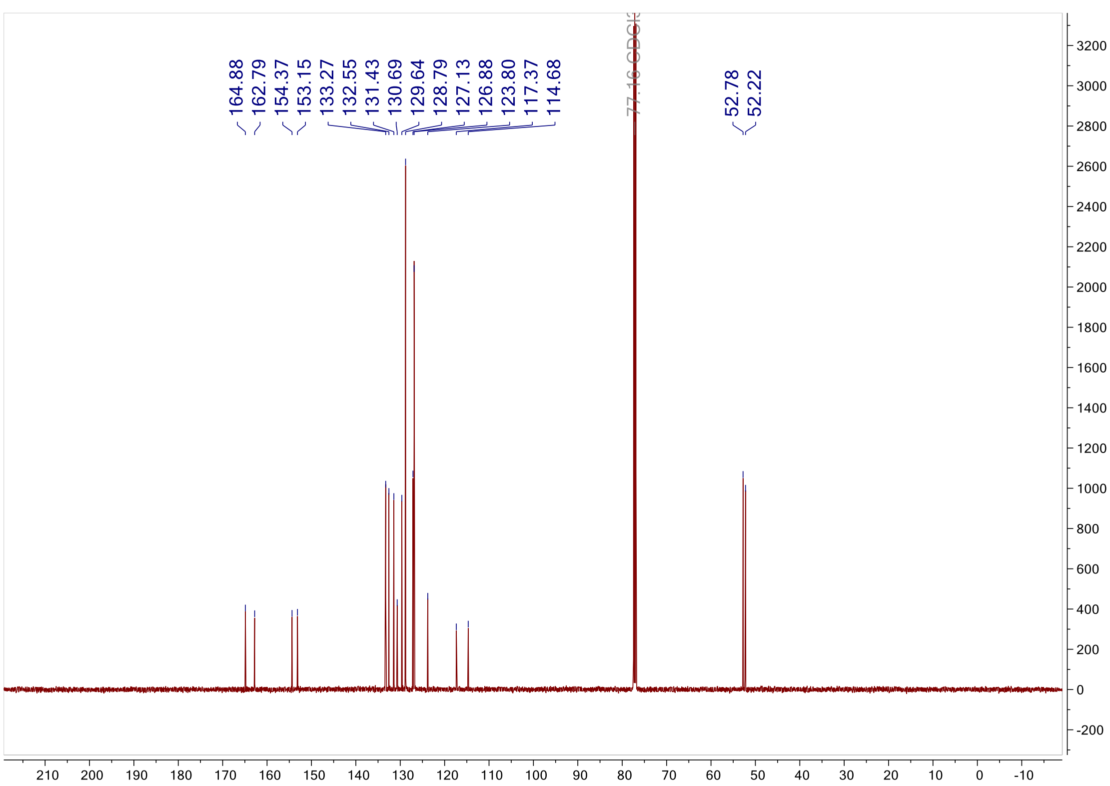
**$^{1}H$ and $^{13}C$ NMR Spectra of 3q ($CDCl_3$)**



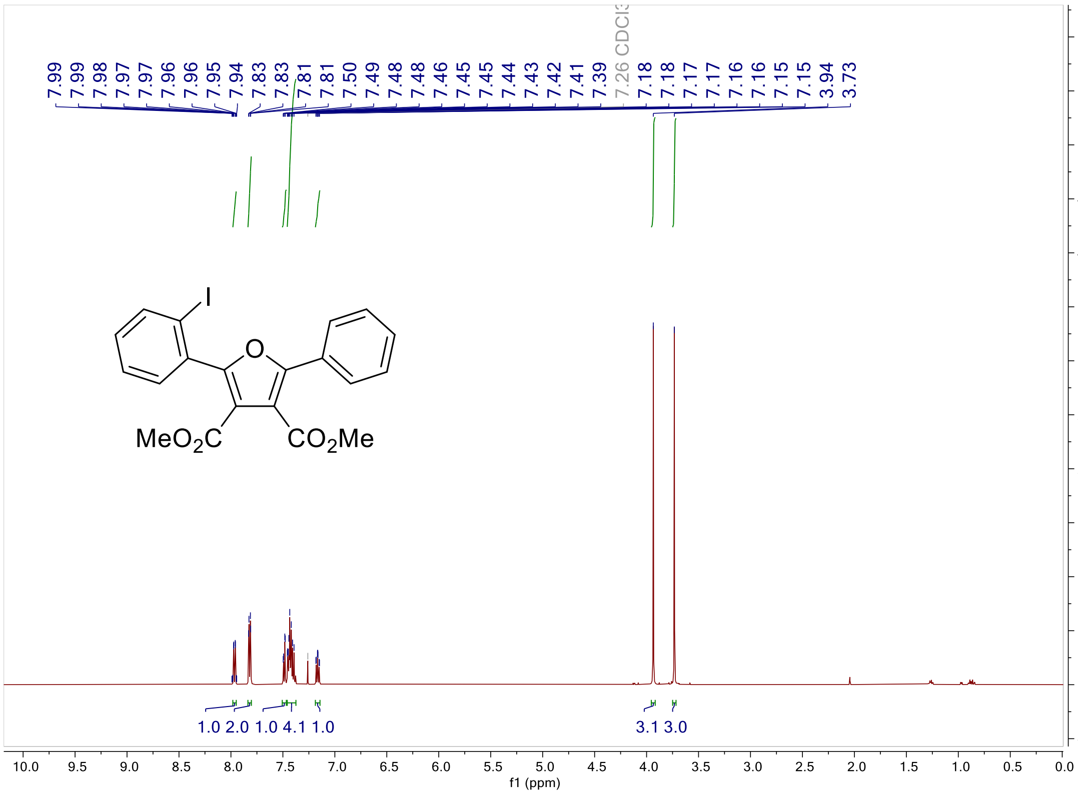



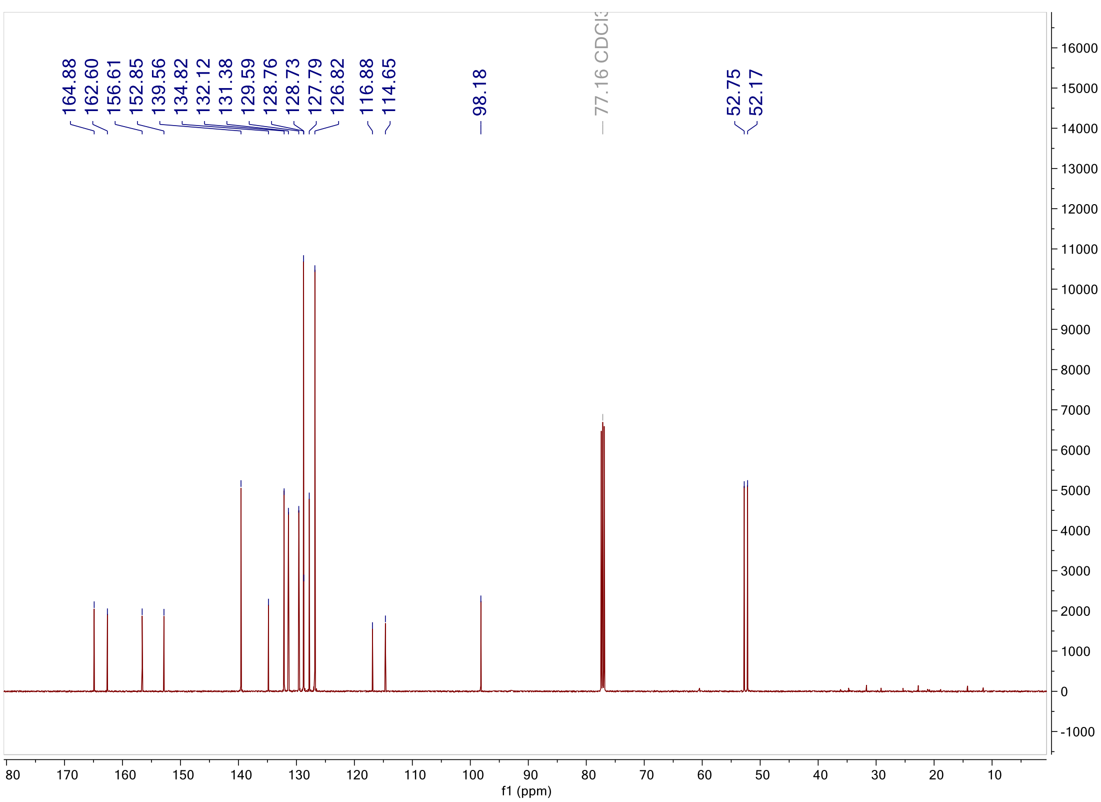
**[1]H and [13]C NMR Spectra of 3r ($CDCl_3$)**



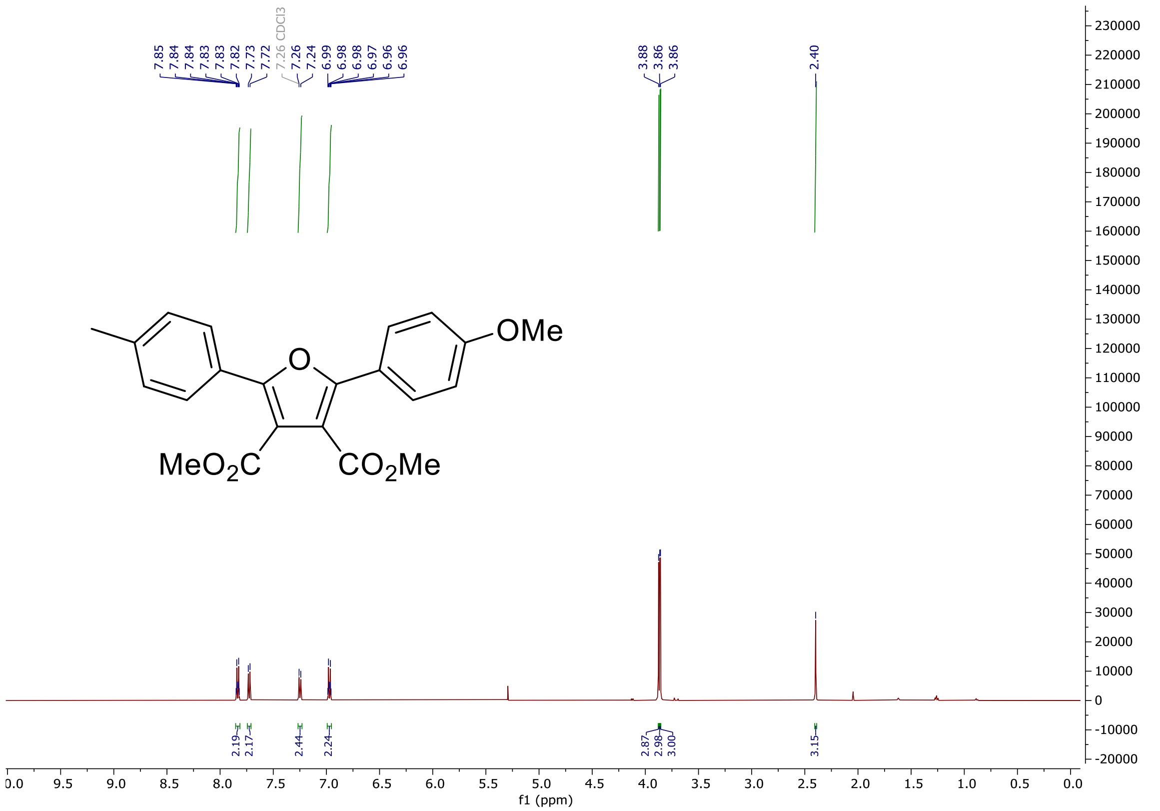



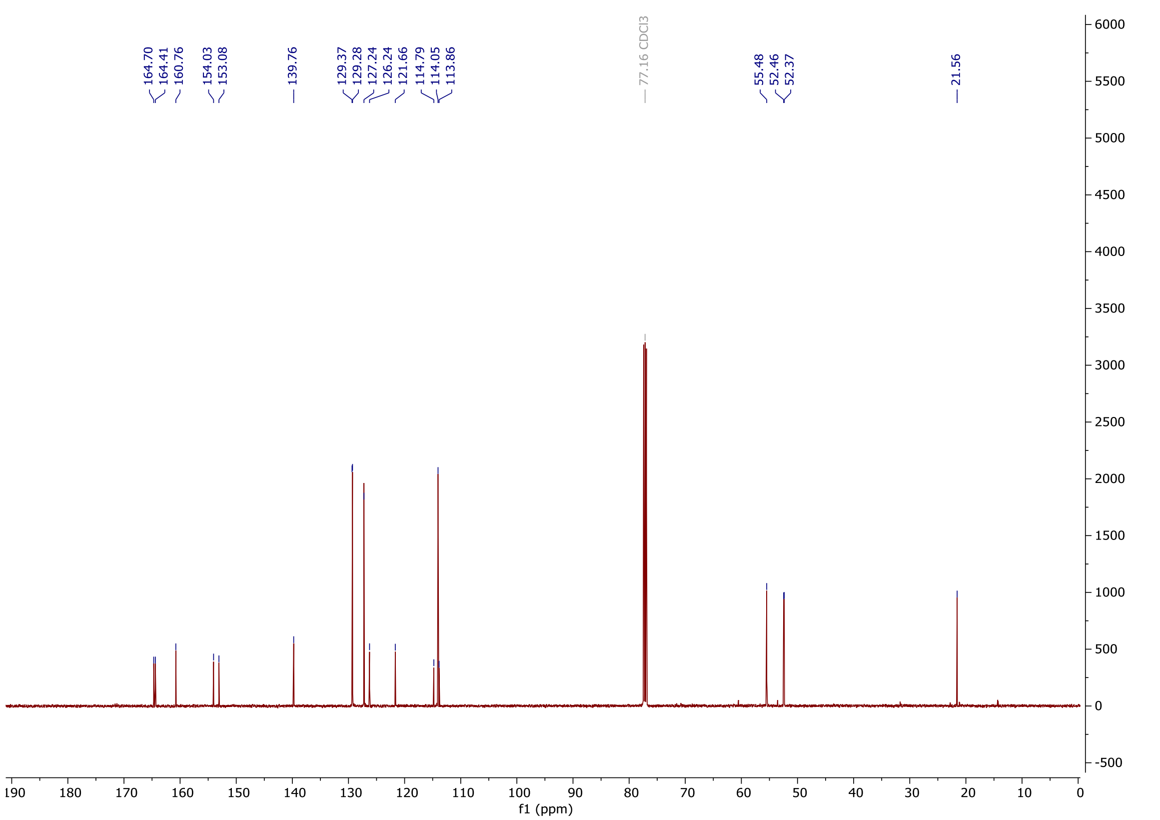
**$^{1}H$ and $^{13}C$ NMR Spectra of 3s ($CDCl_3$)**



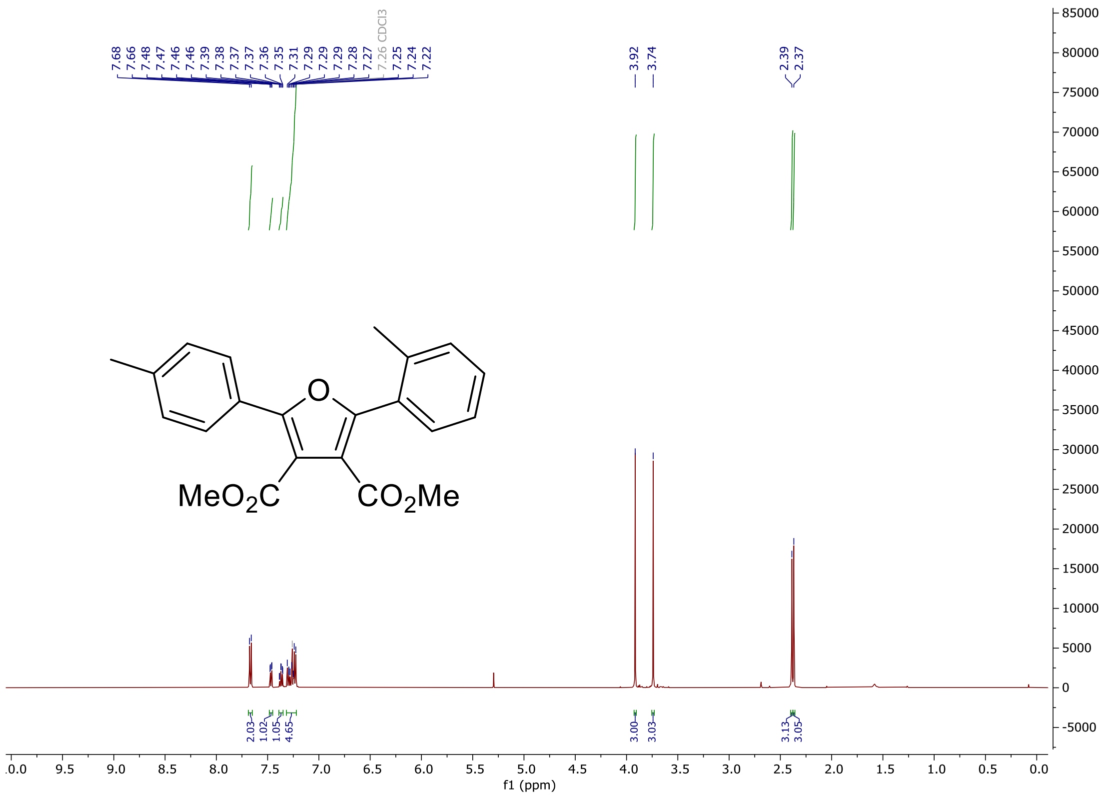



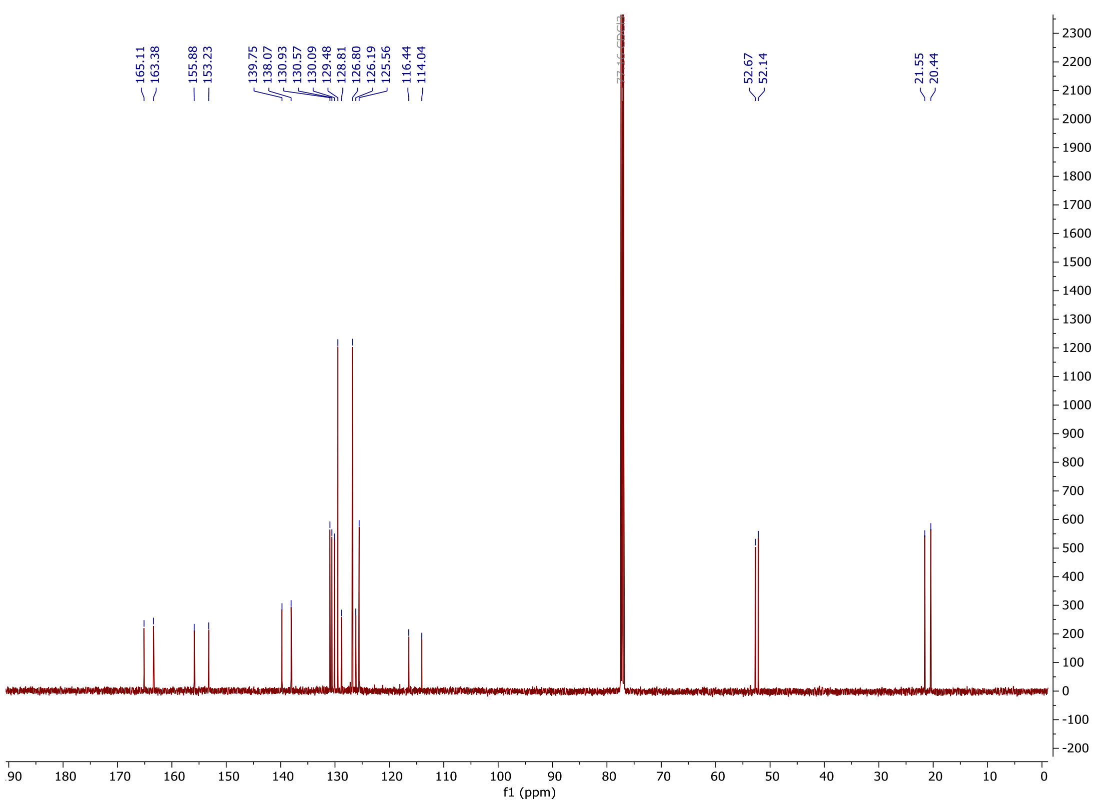
**[1]H and [13]C NMR Spectra of 3t ($CDCl_3$)**



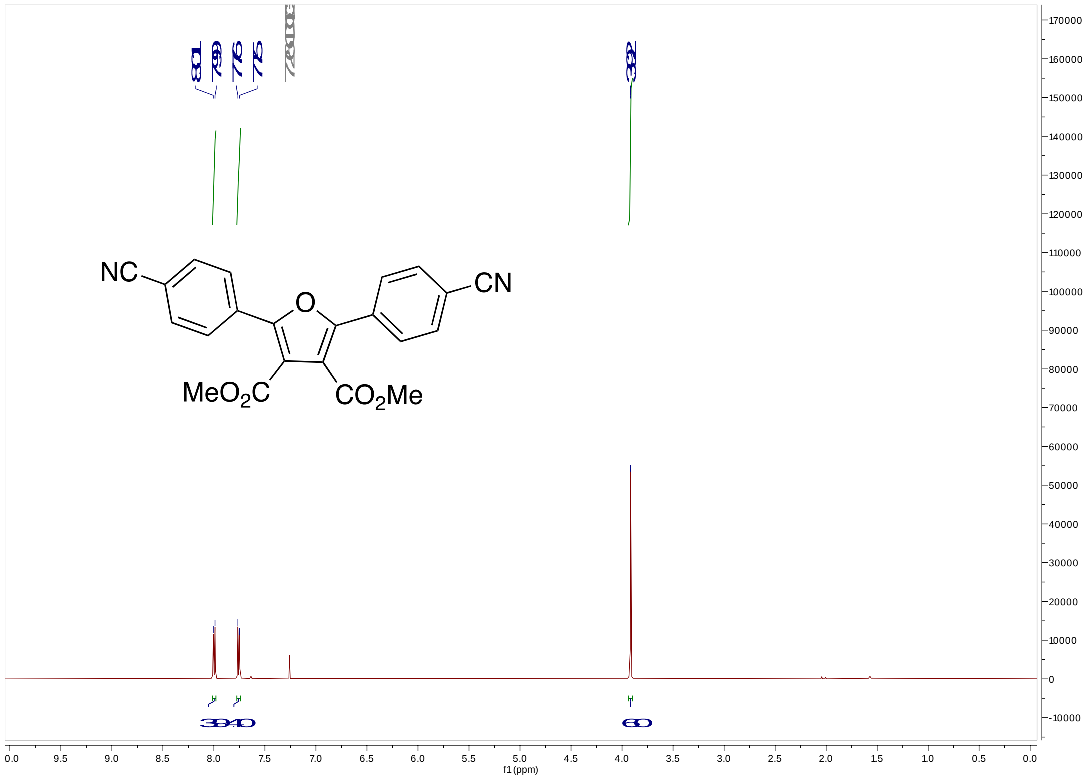



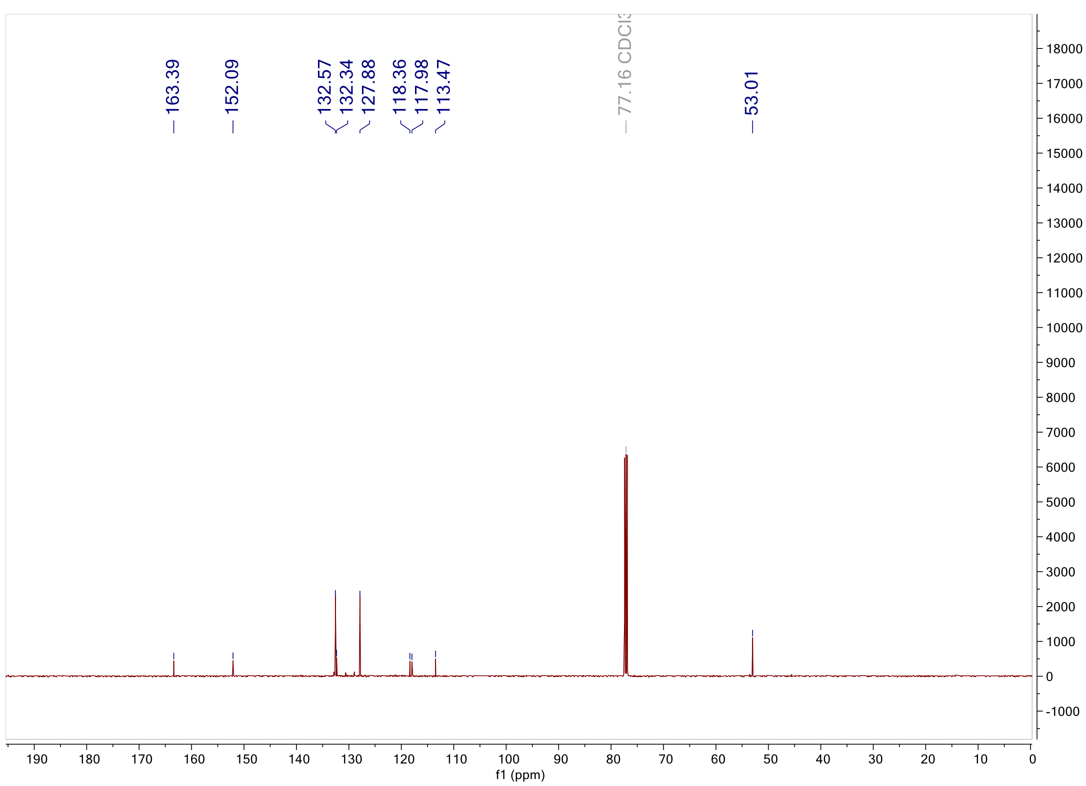
**[1]H and [13]C NMR Spectra of 3u ($CDCl_3$)**



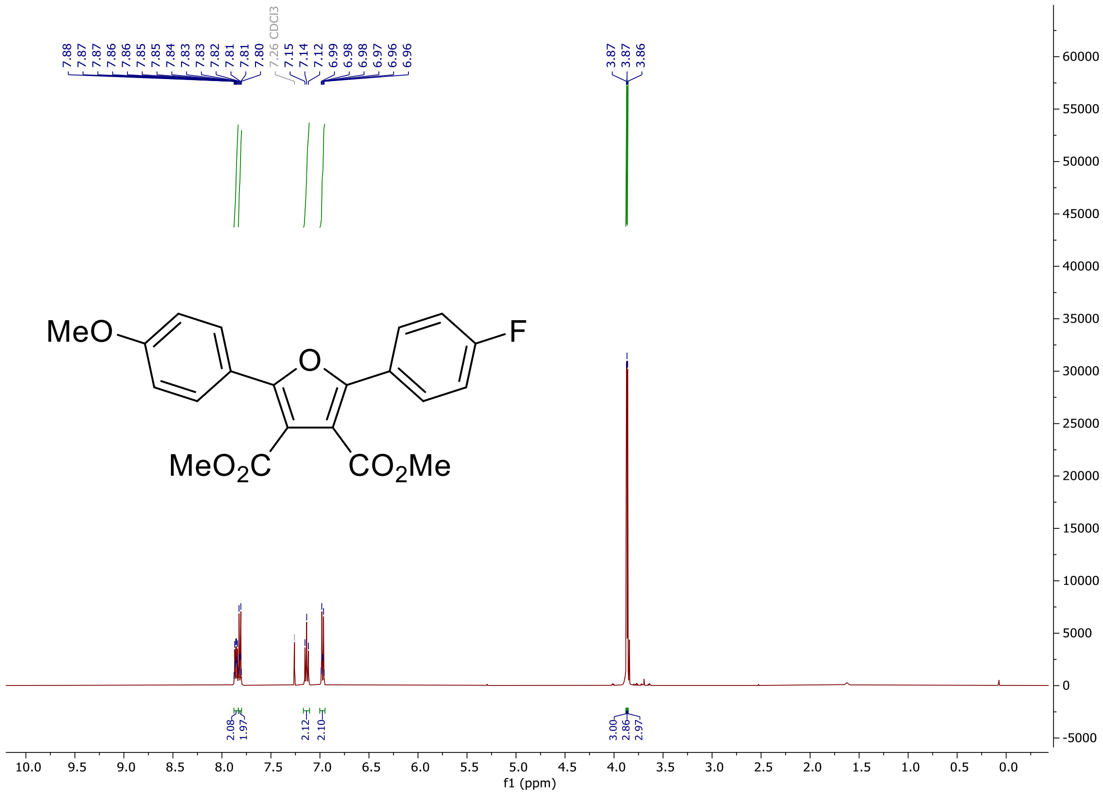



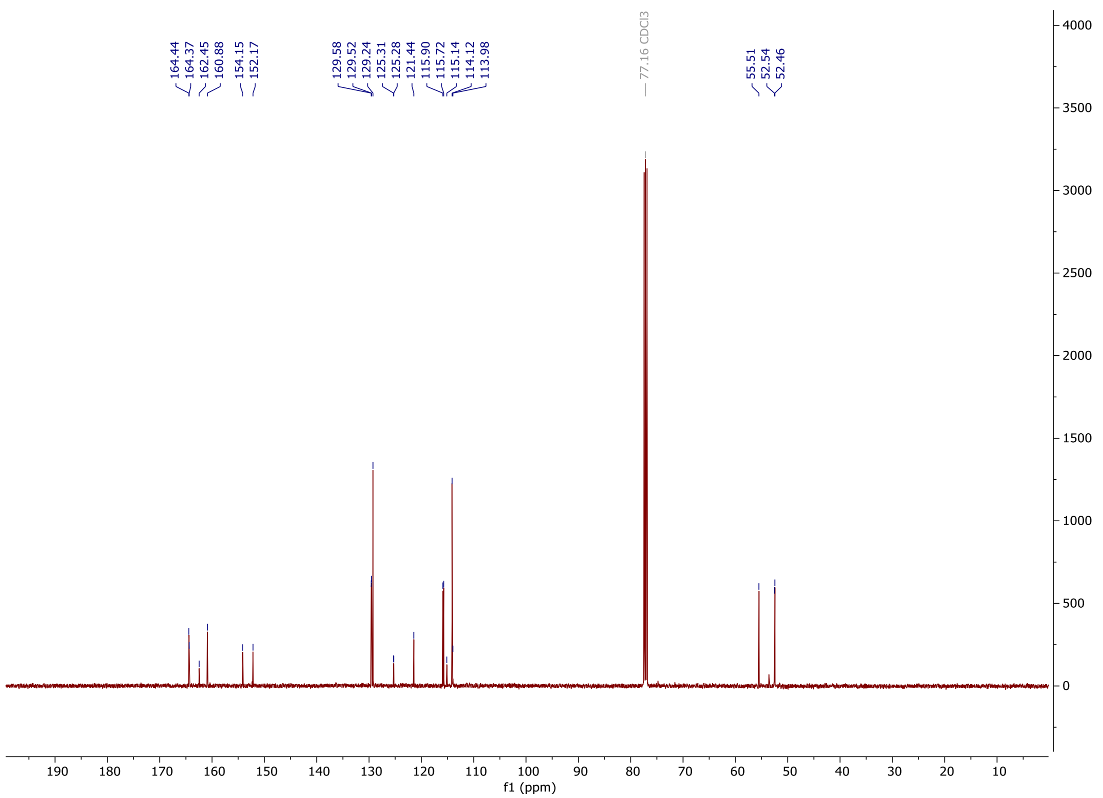
**[1]H and [13]C NMR Spectra of 3v ($CDCl_3$)**

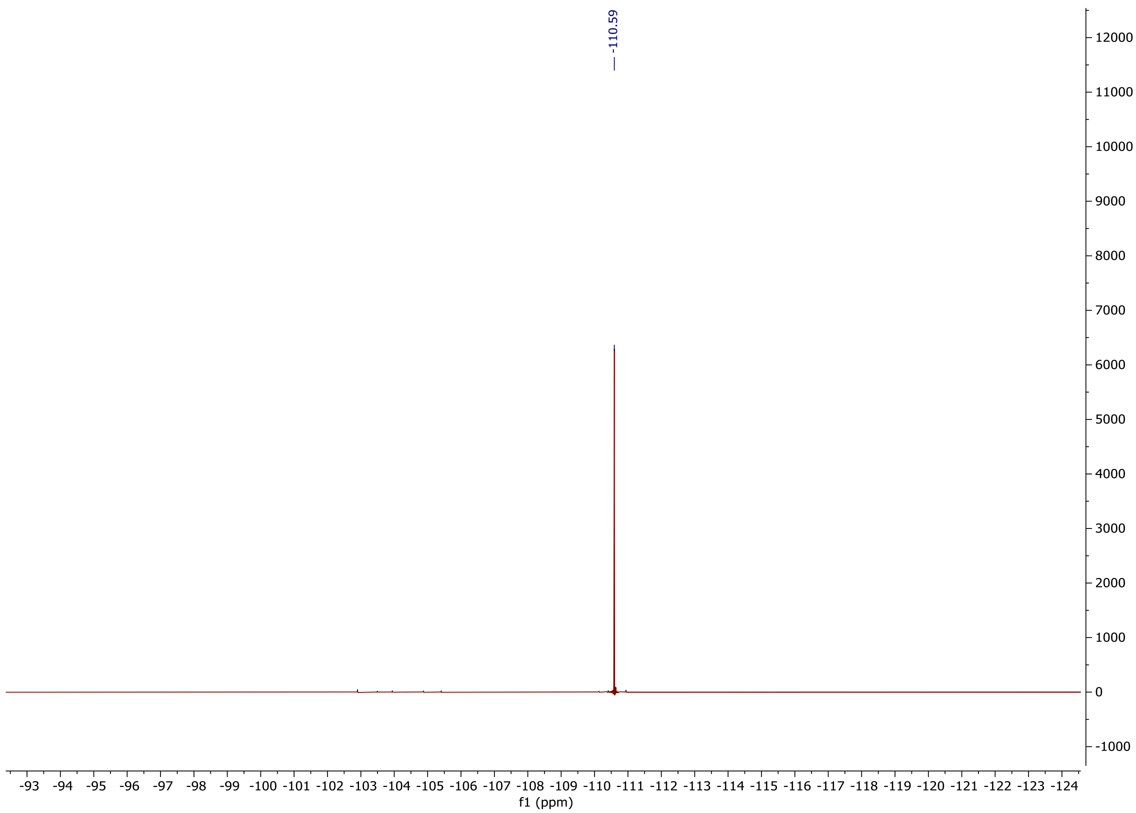




**$^{1}$H, $^{13}$C and $^{19}$F NMR Spectra of 3w ($CDCl_3$)**







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8000
7000
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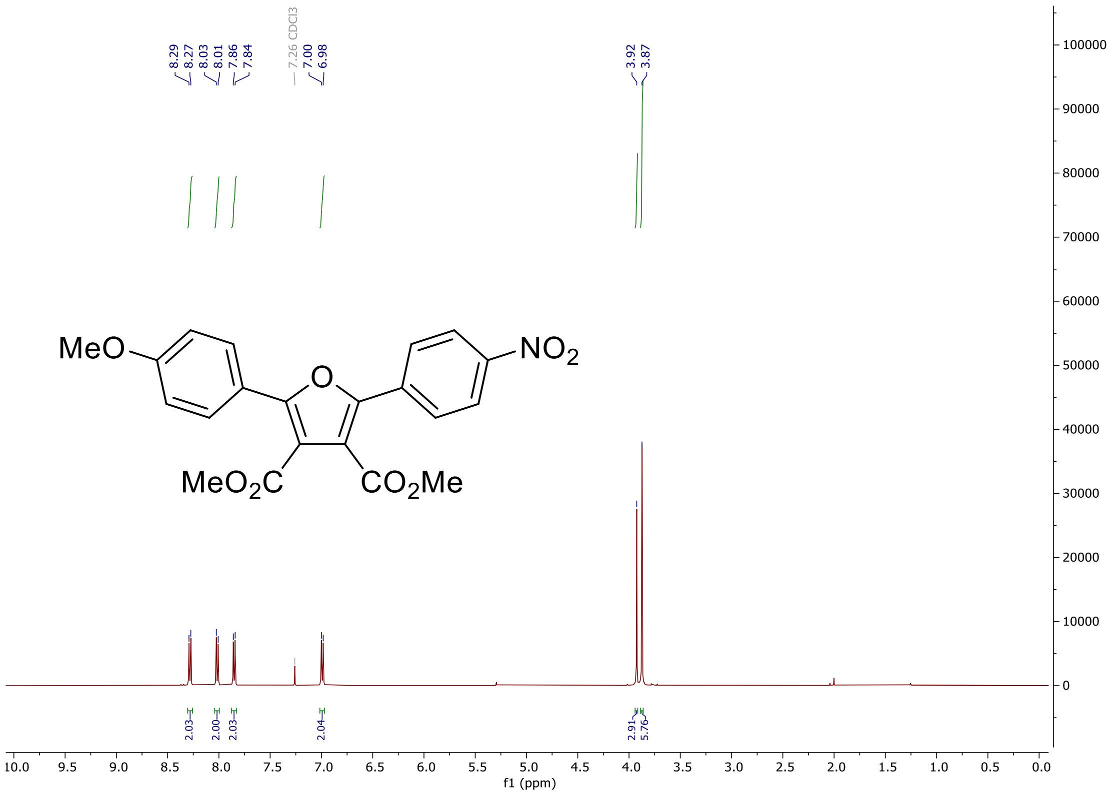
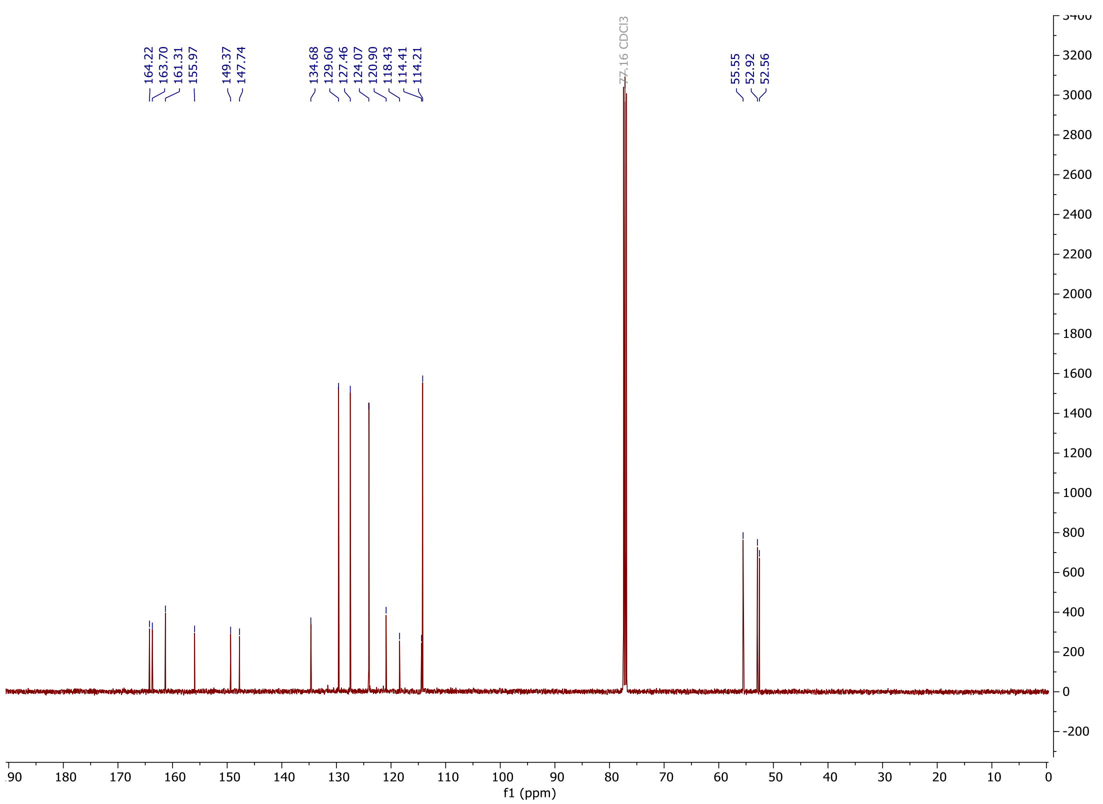
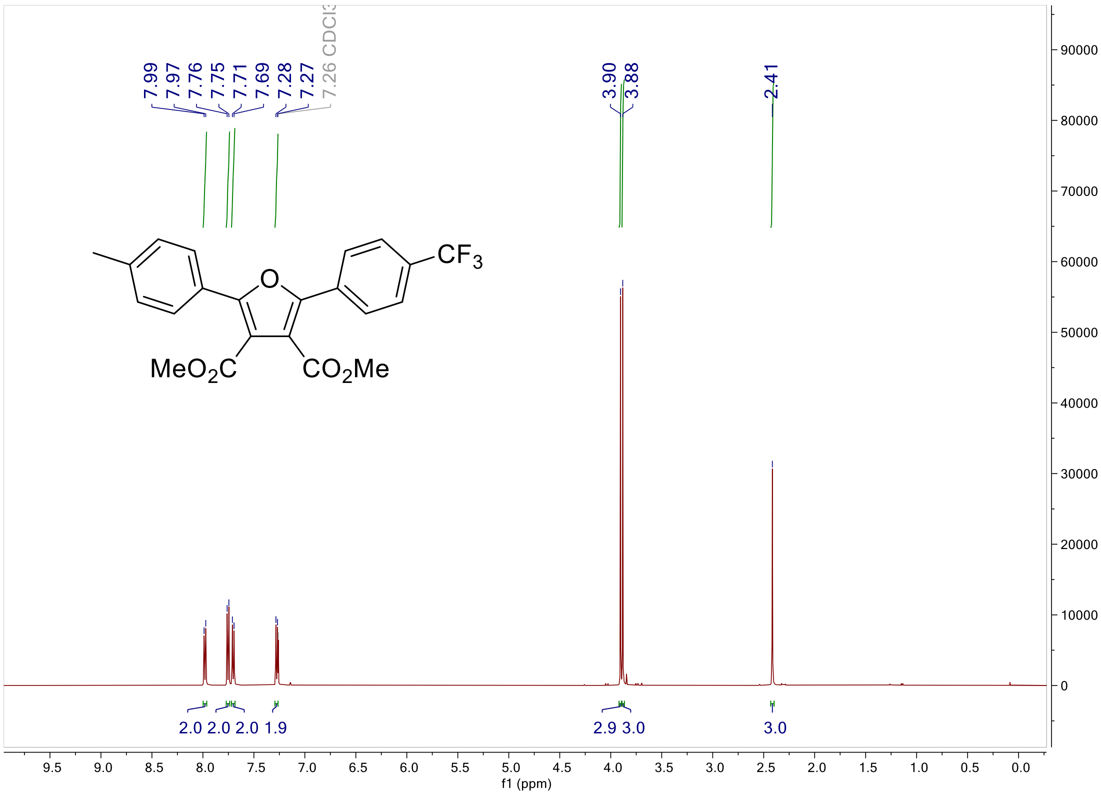
5000
4000
3000
2000
1000
0
-1000
-93 -94 -95 -96 -97 -98 -99 -100 -101 -102 -103 -104 -105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124
f1 (ppm)

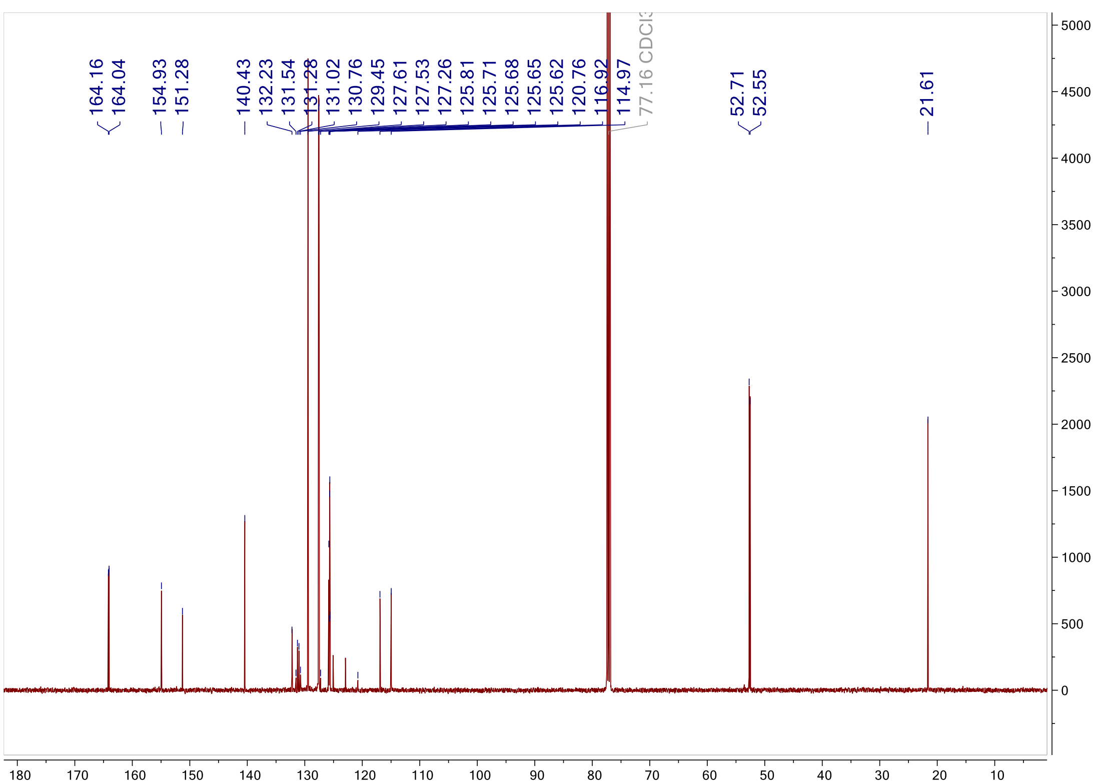
**[1]H and [13]C NMR Spectra of 3x ($CDCl_3$)**

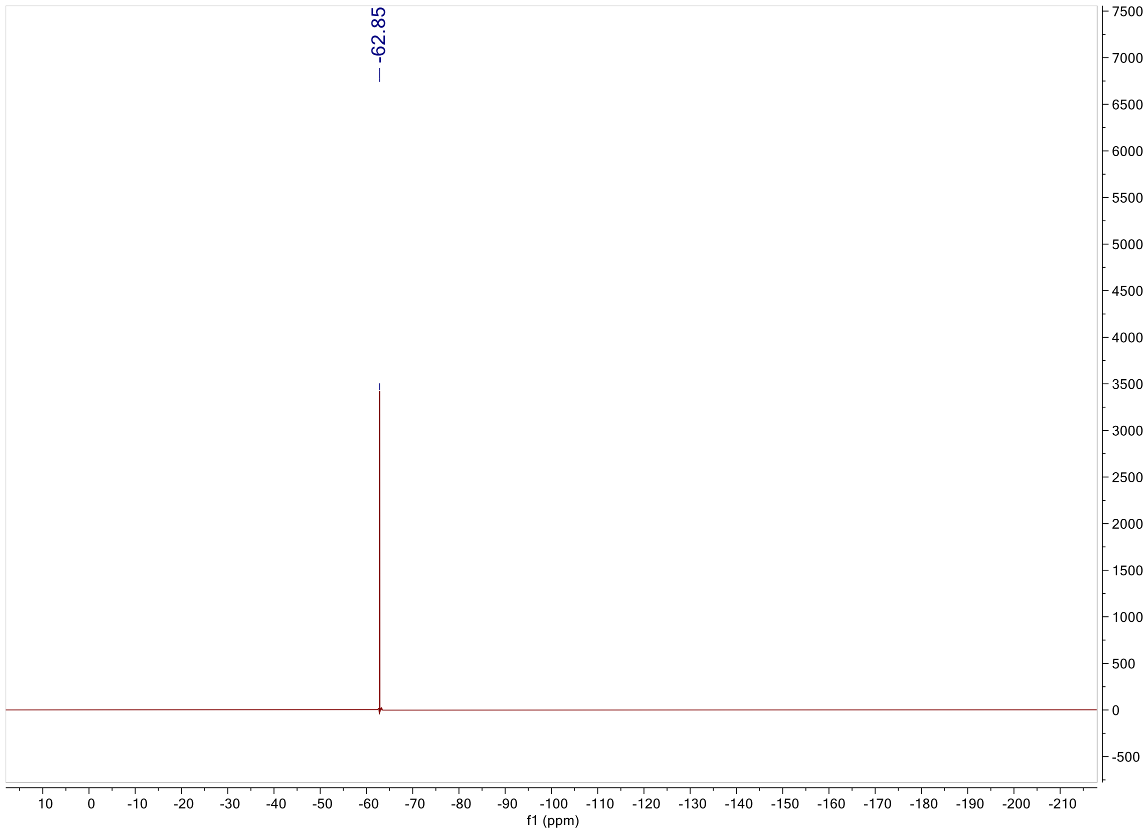




## $^{1}$H, $^{13}$C and $^{19}$F NMR Spectra of 3y ($CDCl_3$)





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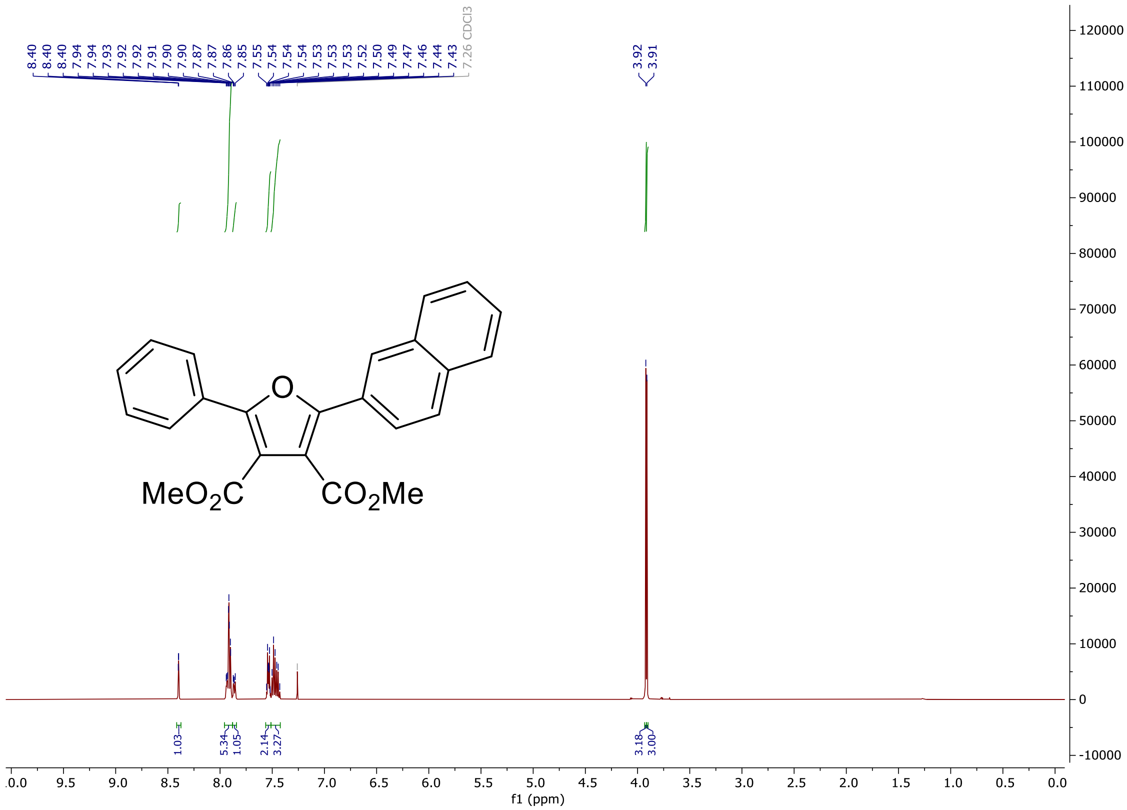
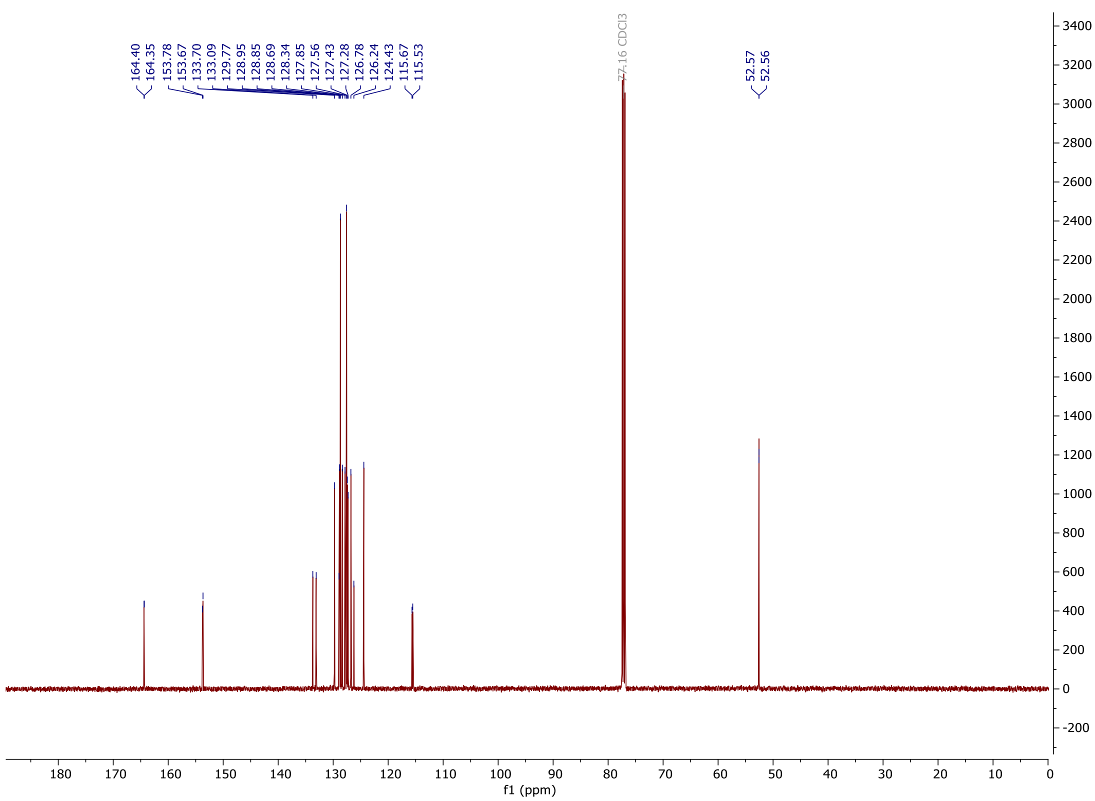
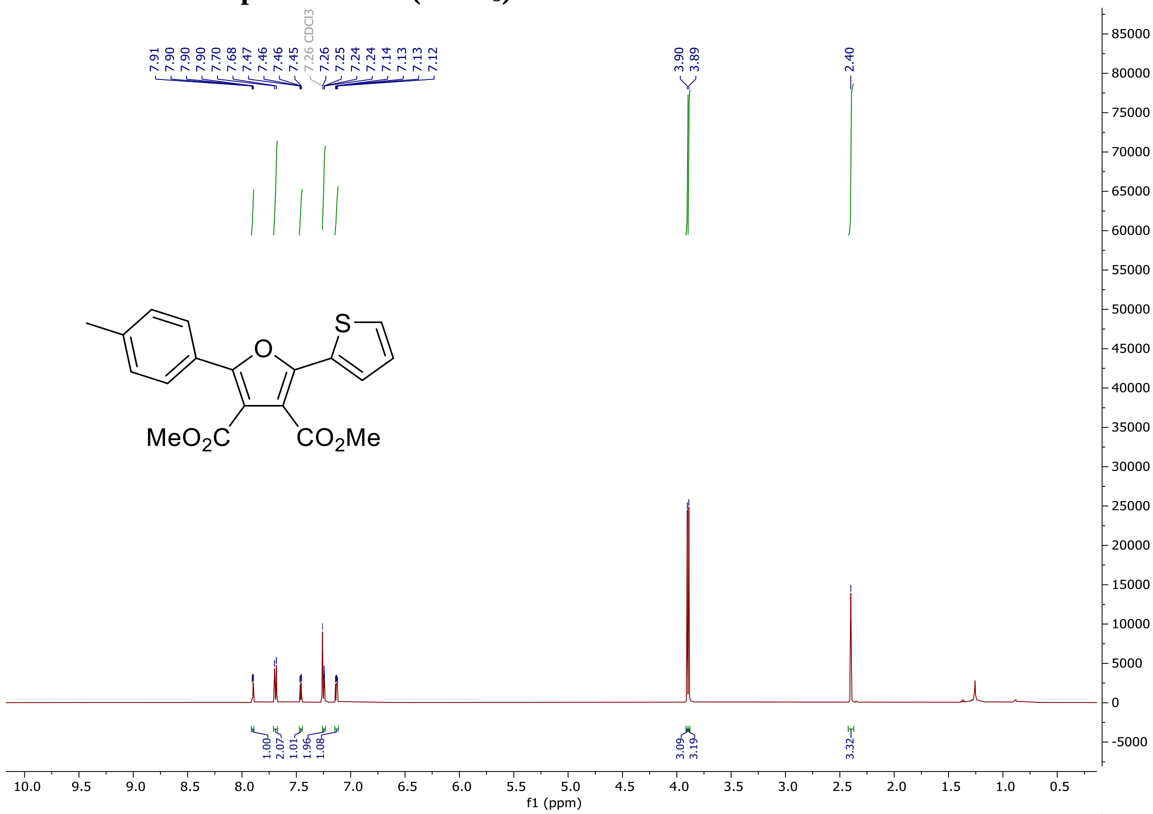
1500
1000
500
0
-500
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

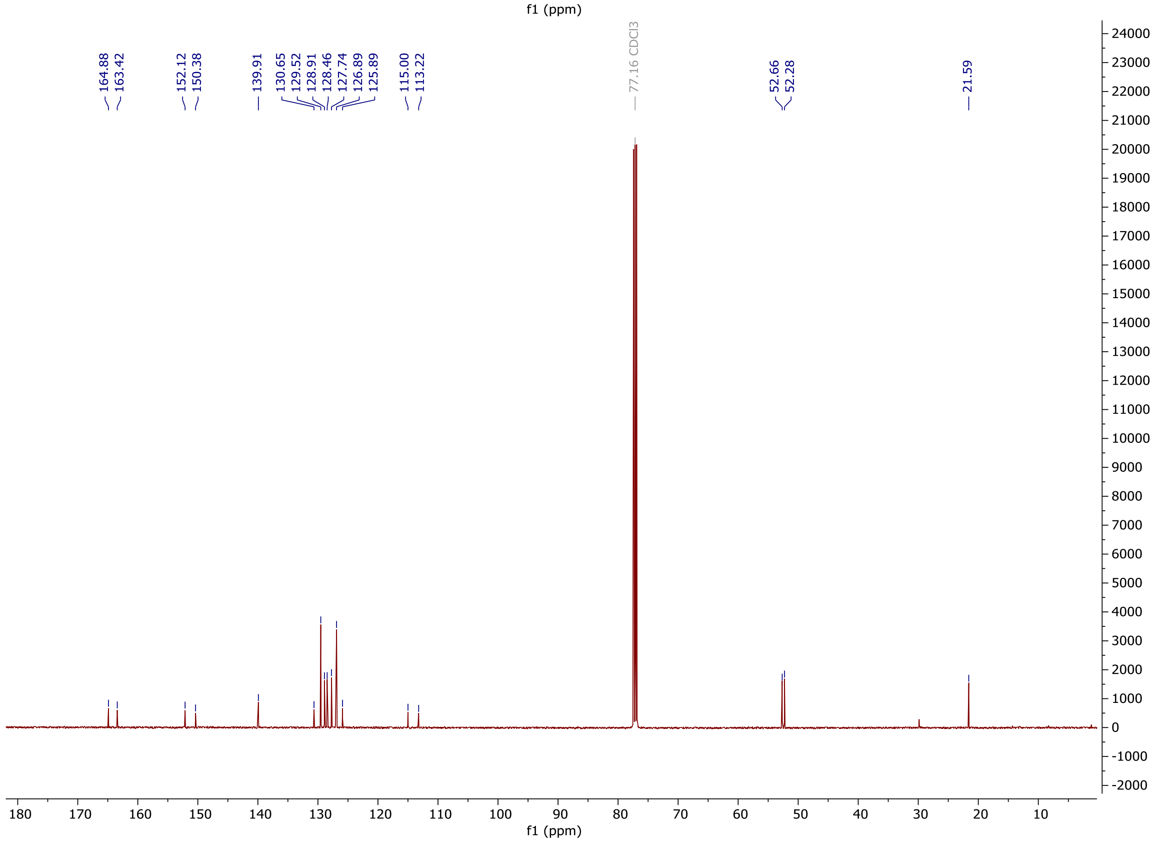
**$^{1}$H and $^{13}$C NMR Spectra of 3z ($CDCl_3$)**



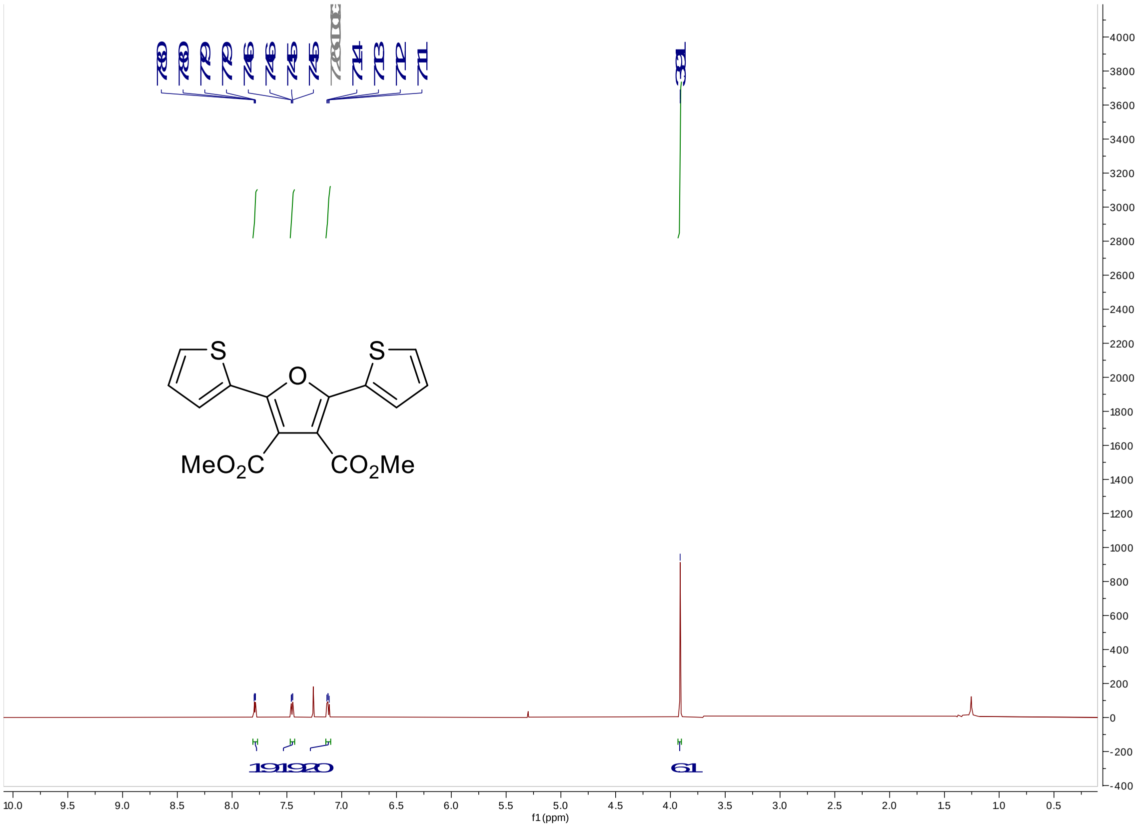



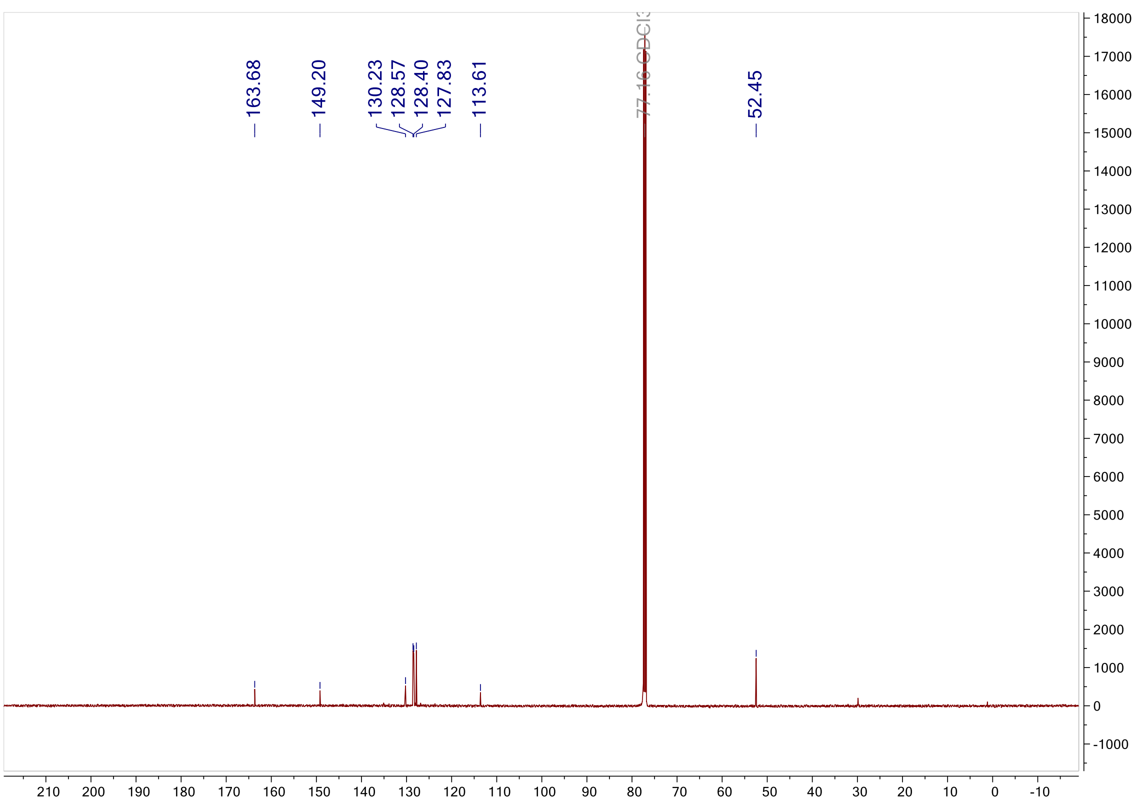
## $^{1}H$ and $^{13}C$ NMR Spectra of 3aa ($CDCl_3$)



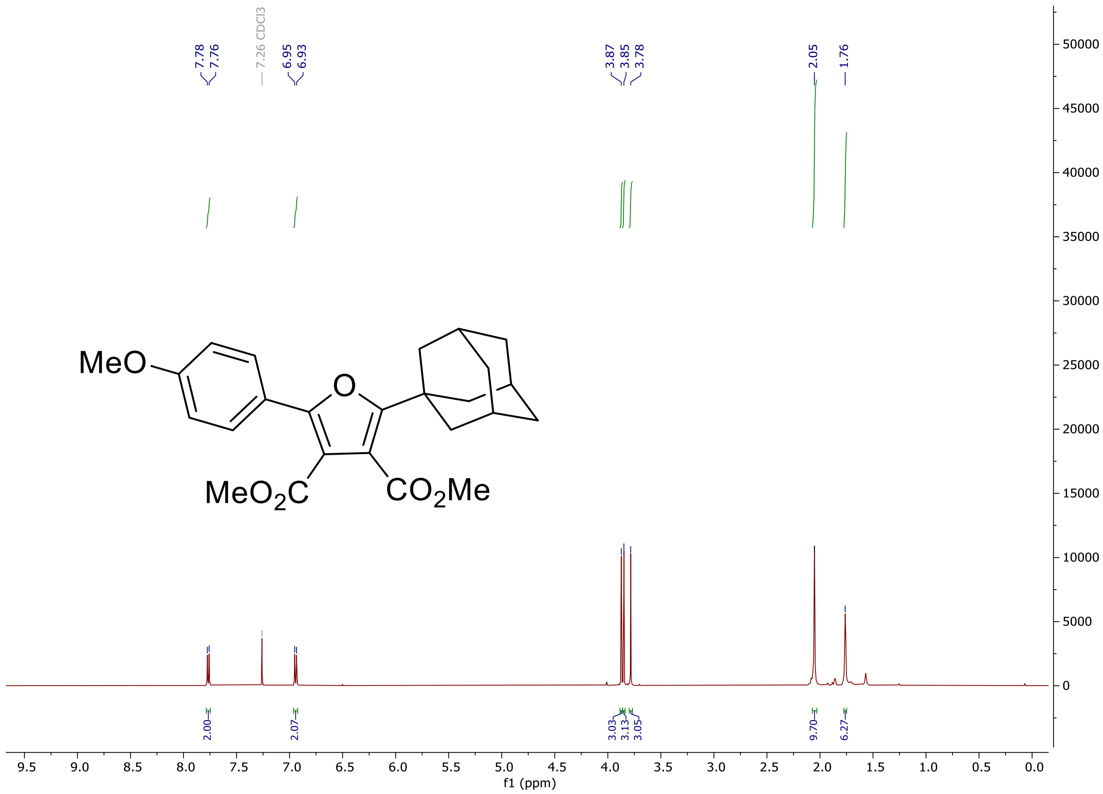



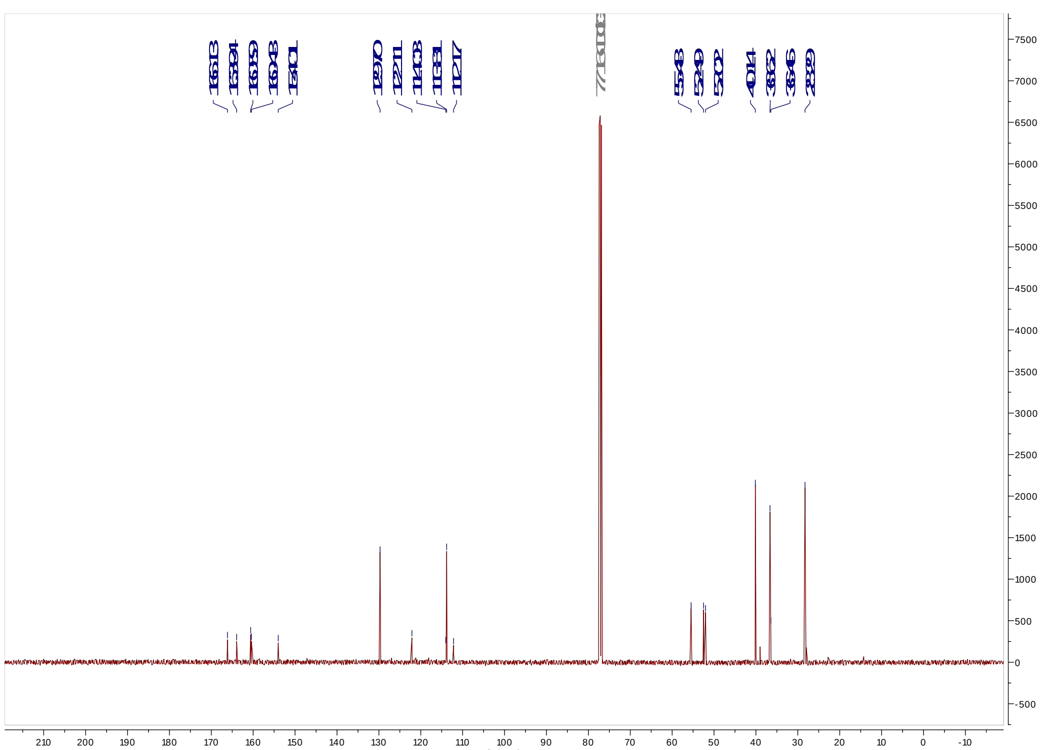
**$^{1}$H and $^{13}$C NMR Spectra of 3bb ($CDCl_3$)**



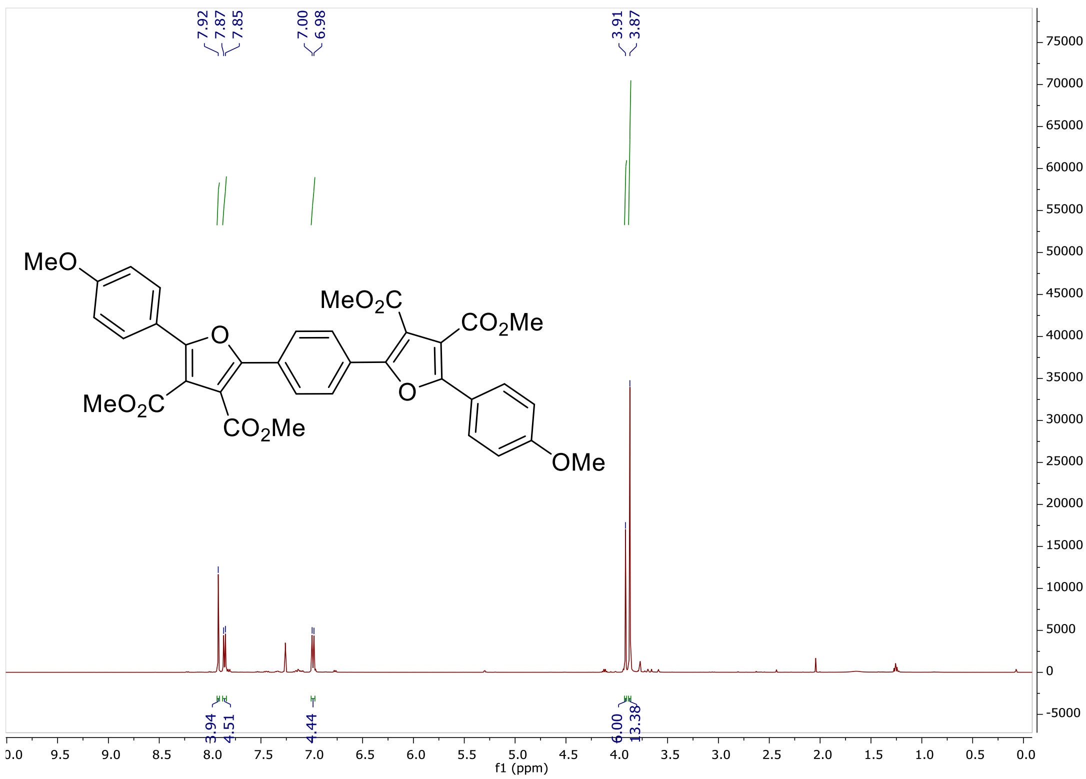



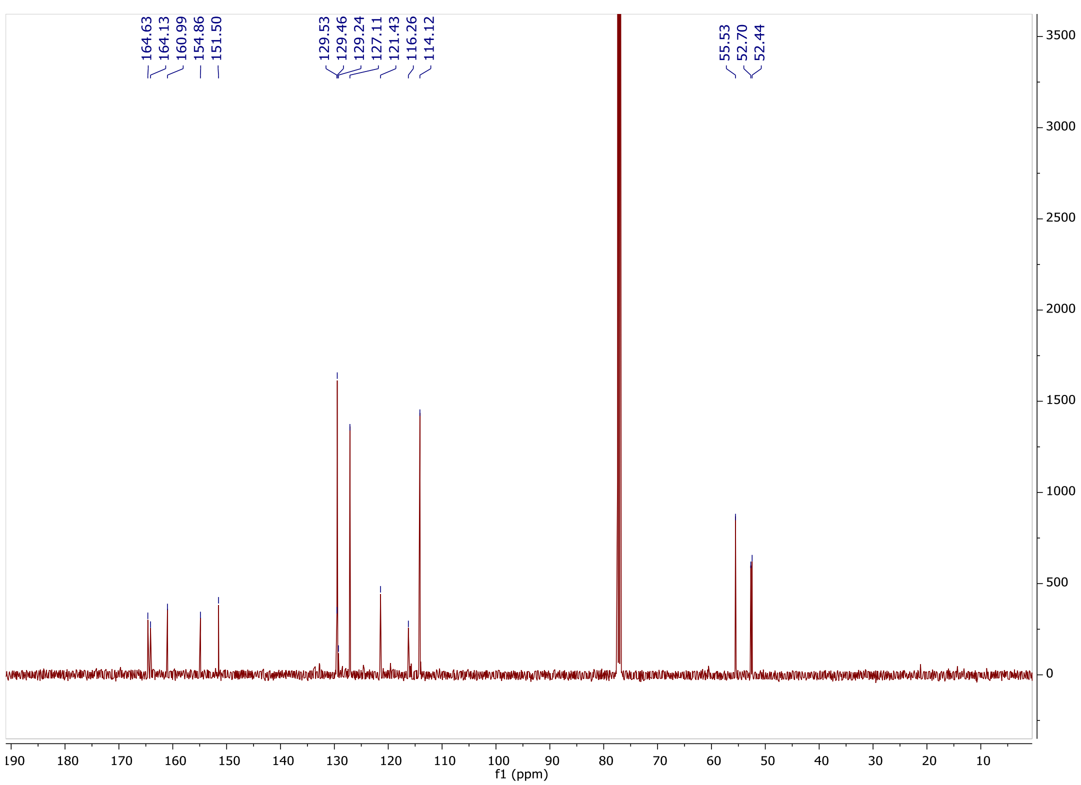
**[1]H and [13]C NMR Spectra of 3cc ($CDCl_3$)**



**$^1$H and $^{13}$C NMR Spectra of 6 ($CDCl_3$)**



**[1]H and [13]C NMR Spectra of 8 ($CDCl_3$)**