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# Benzofuran Synthesis via Copper-Mediated Oxidative Annulation of Phenols and Unactivated Internal Alkynes

## (Supporting Information)

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# Contents

# General Considerations

**Methods:** The reactions were carried out in oven-dried glassware sealed with rubber plug using vacuum line technique. Reactions were stirred using Teflon-coated magnetic stir bars. Room temperature in the laboratory was 20 ± 2 °C. Elevated temperatures were maintained using the parallel synthesizer. Organic solutions were concentrated using a Büchi rotary evaporator (water bath temperature 35-40 °C) with a desktop vacuum pump. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator visualized by ultraviolet light. Purification of products was accomplished by flash chromatography on silica gel 300 mesh.
GC analyses were conducted with an Agilent 6820 GC equipped with an HP-5 column (25 m × 0.20 mm ID × 0.33 μm film) and an FID detector. The temperature for each run was held at 80 °C for 2 min, ramped from 80 °C to 260 °C at 30 °C/min, and held at 260 °C for 2 min.
$^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) was registered on Bruker spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts are referenced to residual solvent peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for $^1$H, 77.00 ppm for $^{13}$C). Data for $^1$H-NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (Hz), and integration. Infrared spectra were recorded on an AVATAR 330 Fourier transform spectrometer (FT-IR) with an OMNI sampler and are reported in wavenumbers ($cm^{-1}$). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI) in the State-authorized Analytical Center in Peking University.

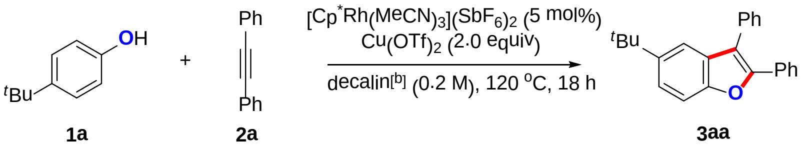
**Materials:** Decalin (mixtures of *cis* and *trans*) was purchased from Alfa Aesar and was degassed before use. $[Cp^*RhCl_2]_2$ was purchased from Sinocompound, stored in a dessicator and weighed out to air. Silver hexafluorophosphate was purchased from Alfa Aesar, stored and weighed in a glove-box. $[Cp^*Rh(MeCN)_3](SbF_6)_2$ was prepared via literature procedure[1], stored in a dessicator and weighed out to air. All the substituted phenols are commercially available. Diphenylacetylene was purchased from Alfa Aesar. Diarylacetylene **2b-2i** were prepared through literature method[2], Unsymmetric Diarylacetylene **2j-2m** were prepared through literature method[3].

# General Procedure for the Copper-Mediated Annulation

4-*tert*-butylphenol **1a** (0.30 mmol, 45.0 mg), diphenylacetylene **2a** (0.10 mmol, 17.8 mg), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5 mol%, 0.005 mmol, 4.2 mg), acetanilide (0.20 equiv, 0.02 mmol, 2.7 mg), DTAC (dodecyl trimethyl ammonium chloride) (0.5 equiv, 0.05 mmol, 13.2 mg) were weighed in the air and $Cu(OTf)_2$ (1.0 equiv, 0.10 mmol, 36.2 mg), $AgPF_6$ (2.5 equiv, 0.25 mmol, 63.2 mg) were weighed in the glovebox and charged into an oven-dried 50 mL Schlenk tube. The tube was evacuated and refilled with $N_2$, which was repeated for 3 times. After addition of 0.5 mL of decalin under a positive pressure of $N_2$ *via* syringe, the sealed tube was placed in a 120 $^o$C parallel synthesizer and stirred for 3 h. After completion, the reaction mixture was cooled down to room temperature and directly purified by flash column chromatography eluting with petroleum ether.

# Optimization of the Reaction Condition

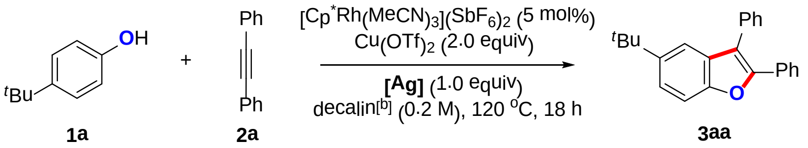
***Table S1.*** Optimization of the Ratio of **1a** to **2a**[a]



| entry | the ritio of **1a** to **2a** | GC ratio[c] |
|---|---|---|
| 1 | 4 : 1 | 0.91 |
| 2 | 3 : 1 | 0.94 |
| 3 | 2 : 1 | 0.79 |
| 4 | 1 : 1 | 0.48 |
| 5 | 1 : 2 | 0.53 |
| 6 | 1 : 3 | 0.63 |

[a] Reaction conditions: 0.30 mmol of **1a**, 0.10 mmol of **2a**, 0.005 mmol of $[Cp^*Rh(MeCN)_3](SbF_6)_2$, 0.20 mmol of $Cu(OTf)_2$, 0.50 mL of solvent, 120 °C, 18 h. [b] decalin: decahydronaphthalene. [c] 20 μL *n*-dodecane was used as an internal standard, the ratio was the area of product to the area of *n*-dodecane.

***Table S2.*** Optimization of Different Silver Salts[a]

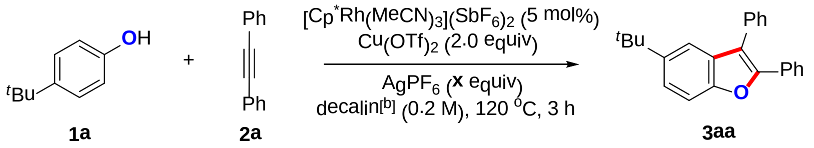


| entry | **[Ag]** | GC ratio[c] |
|---|---|---|
| 1 | no [Ag] | 0.71 |
| 2 | $Ag_2CO_3$ | 0.59 |
| 3 | AgOAc | 1.06 |
| 4 | AgOTFA | 0.82 |
| 5 | $Ag_2O$ | 0.69 |
| 6 | $AgSbF_6$ | 1.01 |
| 7 | $AgPF_6$ | 1.14 |
| 8 | $AgBF_4$ | 1.10 |
| 9 | AgOTf | 1.10 |

[a] Reaction conditions: 0.30 mmol of **1a**, 0.10 mmol of **2a**, 0.005 mmol of $[Cp^*Rh(MeCN)_3](SbF_6)_2$, 0.20 mmol of $Cu(OTf)_2$, 0.10 mmol [Ag], 0.50 mL of solvent, 120 °C,

18 h. [b] decalin: decahydronaphthalene. [c] 20 µL *n*-dodecane was used as an internal standard, the ratio was the area of product to the area of *n*-dodecane.

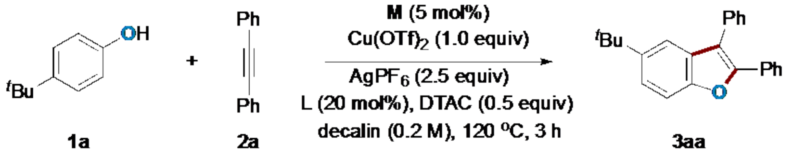
***Table S3.*** Optimization of the Ratio of $AgPF_6$[a]



| entry | x | GC ratio[c] |
|---|---|---|
| 1 | 1.0 | 0.58 |
| 2 | 1.5 | 0.80 |
| 3 | 2.0 | 0.88 |
| 4 | 2.5 | 0.99 |
| 5 | 3.0 | 0.95 |

[a] Reaction conditions: 0.30 mmol of **1a**, 0.10 mmol of **2a**, 0.005 mmol of $[Cp^*Rh(MeCN)_3](SbF_6)_2$, 0.20 mmol of $Cu(OTf)_2$, 0.50 mL of solvent, 120 °C, 3 h. [b] decalin: decahydronaphthalene. [c] 20 µL *n*-dodecane was used as an internal standard, the ratio was the area of product to the area of *n*-dodecane.

***Table S4.*** Optimization of Different Metals[a]

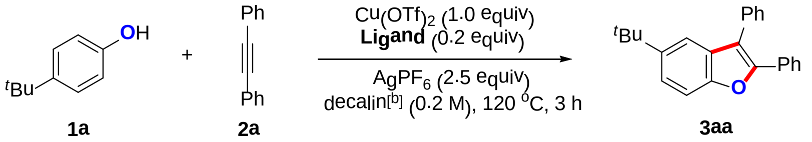


| Entry | M | GC[b] | Entry | M | GC[b] |
|---|---|---|---|---|---|
| 1 | none | 1.28 | 8 | $PtCl_2$ | 1.16 |
| 2 | $[Cp^*Rh(MeCN)_3](SbF_6)_2$ | 1.55 | 9 | $AlCl_3$ | 1.37 |
| 3 | $Pd(OAc)_2$ | 0.99 | 10 | $Mn(OAc)_2$ | 1.28 |
| 4 | $[Ru(p\text{-}cymene)Cl_2]_2$ | 1.34 | 11 | Au(IPr)Cl | 1.20 |
| 5 | $Fe(acac)_3$ | 1.22 | 12 | $Ce(SO_4)_2$ | 1.40 |
| 6 | $Ni(acac)_2$ | 1.25 | 13 | $Zn(OAc)_2$ | 1.40 |
| 7 | $Co(acac)_3$ | 1.31 | | | |

[a] Reaction conditions: 0.30 mmol of **1a**, 0.10 mmol of **2a**, 0.005 mmol of **M**, 0.10 mmol of $Cu(OTf)_2$, 0.25 mmol of $AgPF_6$, 0.02 mmol of L, 0.05 mmol of DTAC, 0.50 mL of solvent, 120 °C, 3 h. [b] 20 µL *n*-dodecane was used as an internal standard, the ratio was the area of product to the area of

*n*-dodecane.

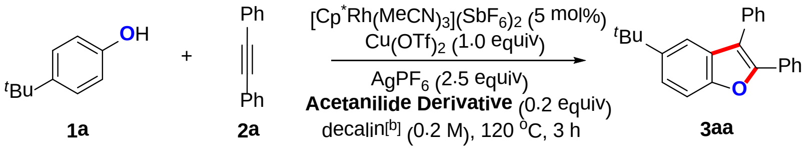
***Table S5.*** Optimization of Different Ligands[a]



| entry | **Ligand** | GC ratio[c] |
|---|---|---|
| 1 | no ligand | 0.96 |
| 2 | phenanthroline | 0.89 |
| 3 | neocuproine | 0.92 |
| 4 | acetanilide | 1.08 |
| 5 | IMes·HCl | 0.84 |

[a] Reaction conditions: 0.30 mmol of **1a**, 0.10 mmol of **2a**, 0.10 mmol of $Cu(OTf)_2$, 0.02 mmol ligand, 0.25 mmol $AgPF_6$, 0.50 mL of solvent, 120 °C, 3 h. [b] decalin: decahydronaphthalene. [c] 20 μL *n*-dodecane was used as an internal standard, the ratio was the area of product to the area of *n*-dodecane.

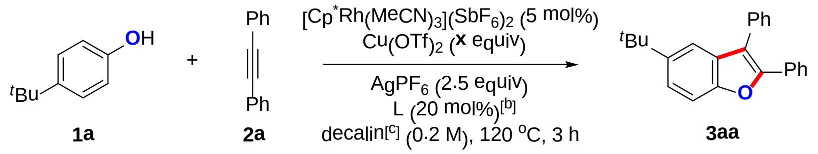
***Table S6.*** Optimization of Different Acetanilide Derivatives[a]



| entry | **Acetanilide Derivative** | GC ratio[c] |
|---|---|---|
| 1 | **Acetanilide** | 1.15 |
| 2 | 4-MeO-**Acetanilide** | 1.02 |
| 3 | 4-F-**Acetanilide** | 1.04 |
| 4 | 4-AcO-**Acetanilide** | 0.82 |
| 5 | 2-Me-**Acetanilide** | 1.16 |
| 6 | 4-$N_2O$-**Acetanilide** | 0.95 |
| 7 | *N*-Me-**Acetanilide** | 1.08 |

[a] Reaction conditions: 0.30 mmol of **1a**, 0.10 mmol of **2a**, 0.005 mmol of $[Cp^*Rh(MeCN)_3](SbF_6)_2$, 0.10 mmol of $Cu(OTf)_2$, 0.25 mmol $AgPF_6$, 0.02 mmol acetanilide derivative, 0.50 mL of solvent, 120 °C, 3 h. [b] decalin: decahydronaphthalene. [c] 20 μL *n*-dodecane was used as an internal standard, the ratio was the area of product to the area of *n*-dodecane.

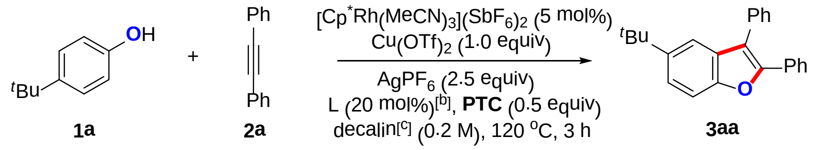
***Table S7.*** Optimization of the Ratio of $Cu(OTf)_2$[a]



| entry | x | GC ratio[d] |
|---|---|---|
| 1 | 1.0 | 1.22 |
| 2 | 1.5 | 1.18 |
| 3 | 2.0 | 1.08 |
| 4 | 2.5 | 1.11 |
| 5 | 3.0 | 0.98 |

[a] Reaction conditions: 0.30 mmol of **1a**, 0.10 mmol of **2a**, 0.005 mmol of $[Cp^*Rh(MeCN)_3](SbF_6)_2$, 0.25 mmol $AgPF_6$, 0.02 mmol acetanilide derivative, 0.50 mL of solvent, 120 °C, 3 h. [b] L: acetanilide. [c] decalin: decahydronaphthalene. [d] 20 μL *n*-dodecane was used as an internal standard, the ratio was the area of product to the area of *n*-dodecane.

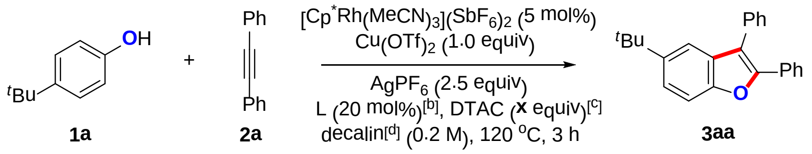
***Table S8.*** Optimization of PTCs[a]



| entry | PTC | GC ratio[d] |
|---|---|---|
| 1 | no PTC | 1.04 |
| 2 | $\overset{\oplus}{N}BnMe_3\overset{\ominus}{Cl}$ | 1.12 |
| 3 | TBAB | 1.17 |
| 4 | TBAI | 1.19 |
| 5 | $\overset{\oplus}{N}{}^nBu_4\overset{\ominus}{PF_6}$ | 1.15 |
| 6 | DTAC[e] | 1.30 |
| 7 | HTAC[f] | 1.09 |

[a] Reaction conditions: 0.30 mmol of **1a**, 0.10 mmol of **2a**, 0.005 mmol of $[Cp^*Rh(MeCN)_3](SbF_6)_2$, 0.10 mmol of $Cu(OTf)_2$, 0.25 mmol $AgPF_6$, 0.02 mmol acetanilide derivative, 0.50 mL of solvent, 120 °C, 3 h. [b] L: acetanilide. [c] decalin: decahydronaphthalene. [d] 20 μL *n*-dodecane was used as an internal standard, the ratio was the area of product to the area of *n*-dodecane. [e] DTAC: Dodecyl trimethyl ammonium chloride. [f] HTAC: *N*-Hexadecyltrimethylammonium chloride.

***Table S9.*** Optimization of the Ratio of DTAC[a]

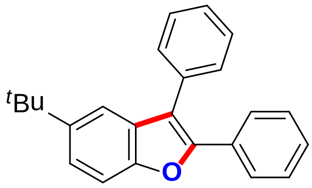


| entry | x | GC ratio[e] |
|---|---|---|
| 1 | 0.25 | little |
| 2 | 0.5 | 1.16 |
| 3 | 0.75 | 1.28 |
| 4 | 1.0 | 1.17 |
| 5 | 1.25 | 0.68 |
| 6 | 1.5 | little |
| 7 | 2.0 | trace |

[a] Reaction conditions: 0.30 mmol of **1a**, 0.10 mmol of **2a**, 0.005 mmol of $[Cp^*Rh(MeCN)_3](SbF_6)_2$, 0.10 mmol of $Cu(OTf)_2$, 0.25 mmol $AgPF_6$, 0.02 mmol acetanilide derivative, 0.50 mL of solvent, 120 °C, 3 h. [b] L: acetanilide. [c] DTAC: Dodecyl trimethyl ammonium chloride. [d] decalin: decahydronaphthalene. [e] 20 μL *n*-dodecane was used as an internal standard, the ratio was the area of product to the area of *n*-dodecane.

# Characterization of Products

### 5-*t*-butyl-2, 3-diphenylbenzofuran 3aa



Prepared according to General Procedure using **1a** (45.0 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (21.5 mg, 66% yield) as a white solid.

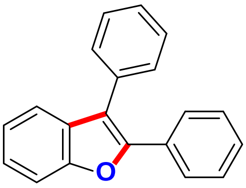
**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.63-7.62 (d, *J* = 6.8 Hz, 2H), 7.52-7.40 (m, 8H), 7.30-7.28 (m, 3H), 1.35 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 152.2, 150.8, 146.1, 133.1, 130.8, 129.8, 129.0, 128.4, 128.2, 127.5, 127.0, 122.7, 118.0, 115.9, 110.4, 34.8, 31.8.

**HRMS (ESI):** calculated for $C_{24}H_{22}OH$ ($M+H^+$) 327.1749, found 327.1752.

**FTIR (cm$^{-1}$):** *v* 2960, 2368, 2345, 1476, 763.

### 2, 3-diphenylbenzofuran 3ba



Prepared according to General Procedure using **1b** (28.2 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (7.8 mg, 29% yield) as a white solid.

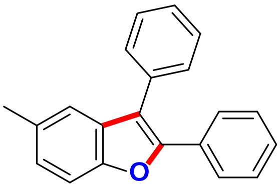
**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.67-7.65 (m, 2H), 7.56-7.38 (m, 7H), 7.35-7.22 (m, 5H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 154.0, 150.5, 132.9, 130.7, 130.3, 129.8, 129.0, 128.4, 128.3, 127.6, 127.0, 124.7, 122.9, 120.0, 117.5, 111.1.

**HRMS (ESI):** calculated for $C_{20}H_{14}OH$ ($M+H^+$) 271.1123, found 271.1116.

**FTIR (cm$^{-1}$):** *v* 2925, 2360, 1455, 831, 749.

### 5-methyl-2, 3-diphenylbenzofuran 3ca

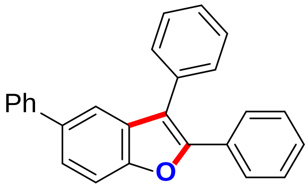


Prepared according to General Procedure using **1c** (32.4 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (19.4 mg, 68% yield) as a white solid.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.65-7.63 (m, 2H), 7.51-7.38 (m, 6H), 7.32-7.27 (m, 4H), 7.15-7.13 (d, *J* = 8.4 Hz, 1H), 2.42 (s, 3H).

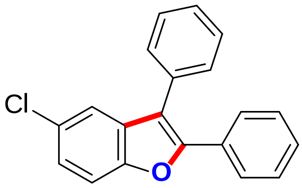
**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 152.4, 150.6, 133.0, 132.4, 130.8, 130.3, 129.8, 128.9, 128.4, 128.2, 127.5, 126.9, 125.9, 119.8, 117.3, 110.6, 21.4.
**HRMS (ESI):** calculated for $C_{21}H_{16}OH$ (M+H$^+$) 285.1279, found 285.1269.
**FTIR (cm$^{-1}$):** *v* 2921, 1602, 1473, 1064, 759.

### 2, 3, 5-Triphenylbenzofuran 3da



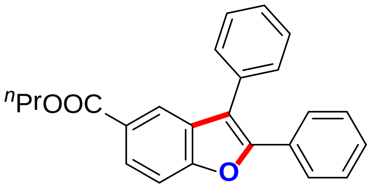
Prepared according to General Procedure using **1d** (51.0 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (18.2 mg, 53% yield) as a yellow solid.
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.68-7.66 (m, 3H), 7.62-7.52 (m, 6H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 3H), 7.33-7.30 (m, 4H).
**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 153.6, 151.2, 141.7, 136.7, 132.8, 130.8, 130.6, 129.8, 129.0, 128.7, 128.4, 127.7, 127.5, 127.0, 126.9, 124.4, 118.5, 117.7, 111.2.
**HRMS (ESI):** calculated for $C_{26}H_{18}OH$ (M+H$^+$) 347.1436, found 347.1426.
**FTIR (cm$^{-1}$):** *v* 2989, 1463, 1063, 763, 745.

### 5-chloro-2, 3-diphenylbenzofuran 3ea



Prepared according to General Procedure using **1e** (38.7 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (15.4 mg, 50% yield) as a white solid.
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.65-7.63 (m, 2H), 7.50-7.40 (m, 7H), 7.32-7.26 (m, 4H).
**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 152.3, 151.9, 132.1, 131.7, 130.2, 129.6, 129.1, 128.7, 128.6, 128.5, 127.9, 127.0, 124.8, 119.6, 117.1, 112.1.
**HRMS (ESI):** calculated for $C_{20}H_{13}ClOH$ (M+H$^+$) 305.0733, found 305.0735.
**FTIR (cm$^{-1}$):** *v* 2372, 1451, 1440, 762, 744.

### propyl 2,3-diphenylbenzofuran-5-carboxylate 3fa



Prepared according to General Procedure using **1f** (54.0 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether: ethyl acetate = 50:1) provided the title compound (21.9 mg, 62% yield) as a white solid.

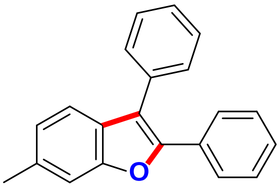
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 8.22 (d, *J* = 1.2 Hz, 1H), 8.08-8.06 (dd, *J* = 1.6 Hz, *J* = 8.8 Hz, 1H), 7.67-7.65 (m, 2H), 7.59-7.57 (d, *J* = 8.4 Hz, 1H), 7.51-7.44 (m, 5H), 7.34-7.32 (m, 3H), 4.29 (t, *J* = 6.8 Hz, 2H), 1.84-1.75 (m, 2H), 1.02 (t, *J* = 7.2 Hz, 3H).

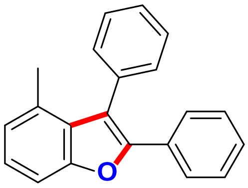
**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 166.9, 156.5, 151.8, 132.1, 130.3, 130.1, 129.7, 129.1, 128.7, 128.5, 127.9, 127.0, 126.4, 125.7, 122.5, 117.8, 110.9, 66.5, 22.1, 10.5.

**HRMS (ESI):** calculated for $C_{24}H_{20}O_3H$ (M+H$^+$) 357.1491, found 357.1490.

**FTIR (cm$^{-1}$):** *v* 2966, 2363, 1714, 1235, 760.

**6-methyl-2, 3-diphenylbenzofuran 3ga and 4-methyl-2, 3-diphenylbenzofuran 3ga'**





Prepared according to General Procedure using **1g** (32.4 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (12.3 mg, 43% yield) as a 3.2:1 mixture of regioisomers as a white solid.

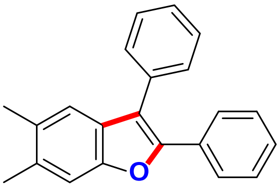
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.65-7.63 (dd, *J* = 1.6 Hz, *J* = 8.0 Hz, 2H), 7.52-7.36 (m, 9.77H), 7.33-7.18 (m, 5.03H), 7.08-7.06 (d, *J* = 8.0 Hz, 1H), 6.95-6.93 (d, *J* = 7.2 Hz, 0.30H), 2.50 (s, 3H), 2.04 (s, 0.93H).

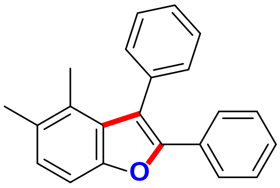
**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 154.4, 153.7, 150.1, 149.9, 135.0, 134.7, 133.0, 132.2, 130.9, 130.8, 130.7, 129.7, 128.9, 128.6, 128.4, 128.3, 128.1, 127.9, 127.8, 127.5, 126.9, 126.4, 124.4, 124.4, 124.3, 119.5, 117.4, 111.3, 108.8, 21.7, 19.2.

**HRMS (ESI):** calculated for $C_{21}H_{16}OH$ (M+H$^+$) 285.1279, found 285.1275.

**FTIR (cm$^{-1}$):** *v* 3054, 1602, 1443, 1063, 761.

**5, 6-dimethyl-2, 3-diphenylbenzofuran 3ha and 4, 5-dimethyl-2, 3-diphenylbenzofuran 3ha'**





Prepared according to General Procedure using **1h** (36.6 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (19.1 mg, 64% yield) as a 3.4:1 mixture of regioisomers as a white solid.

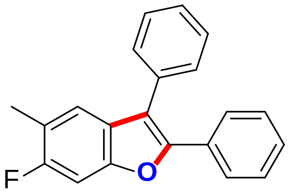
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.64 (s, 1H), 7.62 (s, 1H), 7.50-7.38 (m, 7.26H), 7.33-7.21 (m, 6.63H), 7.12-7.10 (d, *J* = 8.0 Hz, 0.30H), 2.39 (s, 3H), 2.31 (s, 3H), 2.30 (s, 0.89H), 1.93 (s, 0.89H).

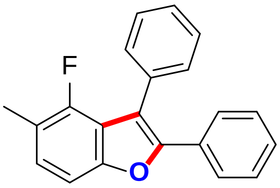
**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 152.9, 152.4, 150.2, 149.7, 135.1, 133.9, 133.2, 131.5, 131.0, 130.8, 130.7, 130.0, 129.8, 128.9, 128.7, 128.3, 128.2, 128.1, 128.0, 127.8, 127.5, 126.8, 126.7, 126.4, 120.0, 117.2, 111.6, 108.1, 20.5, 20.0, 19.6, 15.1.

**HRMS (ESI):** calculated for $C_{22}H_{18}OH$ (M+H$^+$) 299.1436, found 299.1430.

**FTIR (cm$^{-1}$):** *v* 3056, 1462, 1442, 762, 745.

### 6-fluoro-5-methyl-2, 3-diphenylbenzofuran 3ia and 4-fluoro-5-methyl-2, 3-diphenylbenzofuran 3ia’





Prepared according to General Procedure using **1i** (37.8 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (18.3 mg, 61% yield) as a 3.0:1 mixture of regioisomers as a white solid.

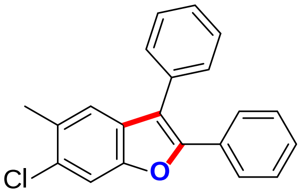
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.62-7.60 (m, 2.12H), 7.57-7.40 (m, 7.93H), 7.35-7.21 (m, 7.30H), 7.10 (t, *J* = 7.6 Hz, 0.34H), 2.32 (d, *J* = 1.6 Hz, 3H), 2.30 (d, *J* = 2.0 Hz, 1.01H).

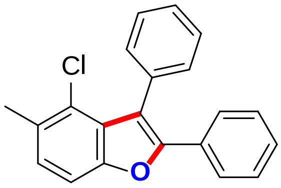
**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 160.8, 158.4, 152.4, 152.3, 150.9, 150.8, 132.8, 132.7, 131.6, 130.5, 130.3, 129.7, 129.0, 128.5, 128.4, 128.4, 128.3, 128.2, 127.7, 127.1, 127.1, 127.0, 126.7, 126.2, 121.0, 120.9, 120.6, 120.4, 117.0, 106.7, 106.7, 106.7, 98.4, 98.2, 14.9 (*J* = 4.3 Hz), 14.0 (*J* = 4.1 Hz).

**HRMS (ESI):** calculated for $C_{21}H_{15}FOH$ (M+H$^+$) 303.1185, found 303.1187.

**FTIR (cm$^{-1}$):** *ν* 2924, 1602, 1463, 1061, 763.

### 6-chloro-5-methyl-2, 3-diphenylbenzofuran 3ja and 4-chloro-5-methyl-2, 3-diphenylbenzofuran 3ja’





Prepared according to General Procedure using **1j** (42.9 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (24.9 mg, 78% yield) as a 1.9:1 mixture of regioisomers as a white solid.

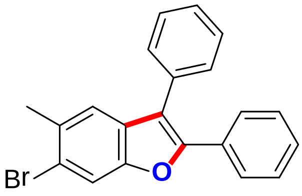
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.63-7.61 (m, 2H), 7.56 (s, 1H), 7.50-7.39 (m, 9.04H), 7.38-7.35 (d, *J* = 8.4 Hz, 0.59H), 7.30-7.23 (m, 6.23H), 7.18-7.16 (d, *J* = 8.0 Hz, 0.52H), 2.41 (s, 3H), 2.39 (s, 1.56H).

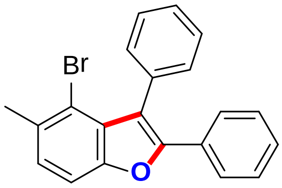
**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 152.8, 152.5, 151.5, 151.0, 133.1, 132.5, 131.2, 130.8, 130.8, 130.7, 130.4, 129.7, 129.2, 129.0, 128.4, 128.3, 128.3, 127.8, 126.9, 126.8, 126.7, 126.0, 120.9, 117.6, 117.0, 111.6, 109.2, 20.3, 19.6.

**HRMS (ESI):** calculated for $C_{21}H_{15}ClOH$ (M+H$^+$) 319.0890, found 319.0888.

**FTIR (cm$^{-1}$):** *ν* 3053, 1455, 1441, 1002, 760.

### 6-bromo-5-methyl-2, 3-diphenylbenzofuran 3ka and 4-bromo-5-methyl-2, 3-diphenylbenzofuran 3ka'





Prepared according to General Procedure using **1k** (56.1 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (24.6 mg, 68% yield) as a 1.7:1 mixture of regioisomers as a white solid.

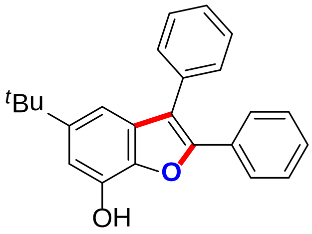
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.75 (s, 1H), 7.63-7.61 (m, 2.07H), 7.50-7.40 (m, 10.04H), 7.31-7.29 (m, 4.26H), 7.24-7.23 (m, 2.15H), 7.20-7.17 (d, $J$ = 8.4 Hz, 0.67H), 2.44 (s, 3H), 2.43 (s, 1.75H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 152.6, 152.4, 151.7, 151.0, 133.0, 132.8, 132.4, 132.2, 131.6, 130.4, 130.3, 129.8, 129.7, 129.0, 128.9, 128.5, 128.4, 128.3, 127.9, 127.8, 126.9, 126.7, 126.6, 120.7, 120.6, 118.4, 117.0, 115.8, 114.8, 109.8, 23.0, 22.6.

**HRMS (ESI):** calculated for $C_{21}H_{15}BrOH$ (M+H$^+$) 363.0385, found 363.0389.

**FTIR (cm$^{-1}$):** *ν* 2917, 1453, 1440, 984, 759.

### 5-*tert*-butyl-2, 3-diphenylbenzofuran-7-ol 3la



Prepared according to General Procedure using **1l** (49.8 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) provided the title compound (14.4 mg, 43% yield) as a yellow oil.

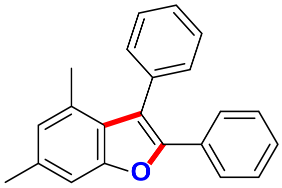
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.55-7.52 (m, 2H), 7.44-7.34 (m, 5H), 7.24-7.22 (m, 3H) 6.97 (s, 1H), 6.91 (s, 1H), 5.21 (s, 0.84H), 1.26 (s, 9H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 150.9, 147.9, 140.4, 139.9, 132.8, 131.2, 130.6, 129.8, 129.0, 128.4, 128.4, 127.6, 127.0, 118.4, 109.4, 108.3, 34.9, 31.8.

**HRMS (ESI):** calculated for $C_{24}H_{22}O_2H$ (M+H$^+$) 343.1698, found 343.1700.

**FTIR (cm$^{-1}$):** *ν* 2964, 1603, 1479, 1219, 952.

### 4, 6-dimethyl-2, 3-diphenylbenzofuran 3ma



Prepared according to General Procedure using **1m** (36.6 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (15.2

mg, 51% yield) as a white solid.

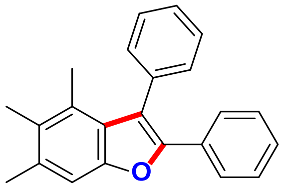
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.49-7.44 (m, 7H), 7.24-7.20 (m, 4H), 6.78 (s, 1H) 2.44 (s, 3H), 2.00 (s, 3H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 154.2, 149.5, 134.8, 134.7, 131.6, 131.0, 130.7, 128.6, 128.3, 127.7, 127.6, 126.2, 125.9, 118.3, 109.0, 21.5, 19.1.

**HRMS (ESI):** calculated for $C_{22}H_{18}OH$ (M+H$^+$) 299.1436, found 299.1427.

**FTIR (cm$^{-1}$):** *v* 2920, 2363, 1443, 1070, 761.

**4, 5, 6-trimethyl-2, 3-diphenylbenzofuran 3na**



Prepared according to General Procedure using **1n** (40.8 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (18.9 mg, 61% yield) as a white solid.

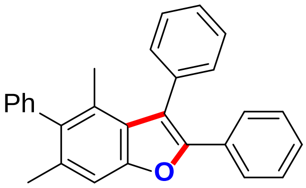
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.44 (m, 7H), 7.22-7.20 (m, 4H), 2.42 (s, 3H), 2.19 (s, 3H), 1.96 (s, 3H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 152.1, 149.4, 135.3, 133.9, 131.1, 130.8, 129.8, 129.7, 128.8, 128.2, 127.7, 127.5, 126.8, 126.2, 118.3, 109.5, 21.7, 15.5, 15.0.

**HRMS (ESI):** calculated for $C_{23}H_{20}OH$ (M+H$^+$) 313.1592, found 313.1583.

**FTIR (cm$^{-1}$):** *v* 2921, 1601, 1443, 1070, 761.

**4, 6-dimethyl-2, 3, 5-triphenylbenzofuran 3oa**



Prepared according to General Procedure using **1o** (59.4 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (23.4 mg, 63% yield) as a yellow solid.

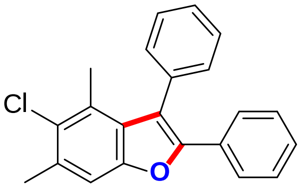
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.50-7.48 (m, 2H), 7.44-7.37 (m, 7H), 7.34-7.29 (m, 2H), 7.26-7.20 (m, 2H), 7.13-7.11 (m, 2H), 2.12 (s, 3H), 1.69 (s, 3H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 152.9, 149.9, 141.2, 137.4, 134.9, 133.6, 131.0, 130.8, 129.8, 129.7, 128.6, 128.3, 128.3, 127.7, 127.7, 126.5, 126.5, 126.3, 118.6, 109.4, 21.9, 16.9.

**HRMS (ESI):** calculated for $C_{28}H_{22}OH$ (M$^+$) 374.1671, found 374.1668.

**FTIR (cm$^{-1}$):** *v* 3055, 1442, 1071, 761, 748.

### 5-chloro-4, 6-dimethyl-2, 3-diphenylbenzofuran 3pa



Prepared according to General Procedure using **1p** (46.8 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (27.2 mg, 82% yield) as a white solid.

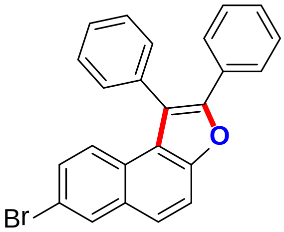
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.46-7.39 (m, 7H), 7.30 (s, 1H), 7.24-7.22 (m, 3H), 2.50 (s, 3H), 2.06 (s, 3H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 151.9, 150.5, 134.3, 132.9, 130.7, 130.6, 129.6, 129.5, 128.9, 128.3, 128.0, 127.7, 126.3, 118.2, 110.3, 21.8, 16.1.

**HRMS (ESI):** calculated for $C_{22}H_{17}ClOH$ (M+H$^+$) 333.1046, found 333.1038.

**FTIR (cm$^{-1}$):** *v* 3054, 1443, 1010, 771, 763.

### 7-bromo-1, 2-diphenylnaphtho[2, 1-*b*]furan 3qa



Prepared according to General Procedure using **1q** (66.9 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (24.0 mg, 60% yield) as a colorless oil.

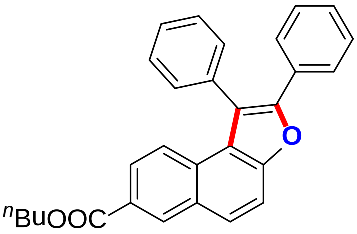
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 8.05 (s, 1H), 7.74-7.72 (d, *J* = 8.8 Hz, 1H), 7.64-7.62 (d, *J* = 8.8 Hz, 1H), 7.55-7.53 (m, 7H), 7.39-7.24 (m, 5H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 151.3, 150.5, 134.3, 132.2, 130.8, 130.6, 130.4, 129.5, 129.1, 128.4, 128.4, 128.0, 126.7, 126.2, 124.8, 124.7, 123.8, 119.2, 118.0, 113.2.

**HRMS (ESI):** calculated for $C_{24}H_{15}BrOH$ (M+H$^+$) 399.0385, found 399.0369.

**FTIR (cm$^{-1}$):** *v* 2924, 1736, 1395, 818, 764.

### butyl 1, 2-diphenylnaphtho[2, 1-*b*]furan-7-carboxylate 3ra



Prepared according to General Procedure using **1r** (73.2 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether, then petroleum ether: ethyl acetate = 50:1) provided the title compound (25.2 mg, 60% yield) as a colorless oil.

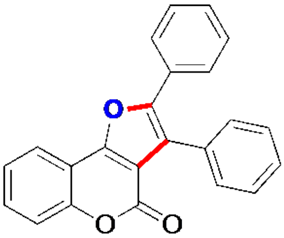
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 8.66 (s, 1H), 7.87-7.76 (m, 3H), 7.56-7.54 (m, 8H), 7.28-7.25 (m, 3H), 4.35 (t, *J* = 6.8 Hz, 3H), 1.80-1.73 (m, 2H), 1.54-1.45 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 166.8, 152.5, 150.6, 134.2, 131.7, 130.7, 130.5, 130.4, 130.0, 129.4, 128.4, 128.4, 128.0, 127.1, 126.2, 126.1, 125.6, 123.7, 123.1, 119.4, 113.0, 64.8, 30.8, 19.3, 13.8.

**HRMS (ESI):** calculated for $C_{29}H_{24}O_3H$ (M+H$^+$) 421.1804, found 421.1791.

**FTIR (cm$^{-1}$):** *v* 2959, 2358, 1714, 1252, 1189.

**2, 3-diphenyl-4*H*-furo[3, 2-*c*]chromen-4-one 3sa**



Prepared according to General Procedure using **1s** (48.6 mg, 0.30 mmol), **2a** (17.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether: ethyl acetate = 20:1) provided the title compound (23.0 mg, 68% yield) as a white solid.

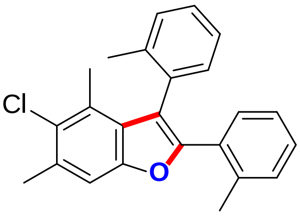
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.99-7.97 (dd, *J* = 1.2 Hz, *J* = 7.6 Hz, 1H), 7.55-7.49 (m, 5H), 7.45-7.43 (m, 4H), 7.39-7.30 (m, 4H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 157.4, 156.4, 152.7, 151.3, 130.7, 130.2, 130.1, 129.3, 128.8, 128.6, 128.5, 128.4, 126.7, 124.4, 120.9, 117.2, 112.7, 111.3.

**HRMS (EI)$^4$:** calculated for $C_{23}H_{14}O_3$ (M$^+$) 338.0943, found 338.0943.

**FTIR (cm$^{-1}$)$^4$:** *v* 3060, 2923, 1744, 1626, 1500.

**5-chloro-4, 6-dimethyl-2, 3-di-*o*-tolylbenzofuran 3pb**



Prepared according to General Procedure using **1p** (46.8 mg, 0.30 mmol), **2b** (20.6 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (24.7 mg, 69% yield) as a white solid.

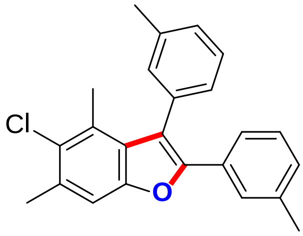
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.31 (s, 1H), 7.25-7.12 (m, 6H), 7.08-7.06 (m, 1H), 7.02-6.98 (m, 1H), 2.51 (s, 3H), 2.34 (s, 3H), 2.10 (s, 6H), 2.07 (s, 3H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 152.6, 152.4, 137.9, 137.8, 132.9, 132.5, 131.4, 130.5, 130.3, 129.9, 129.8, 129.5, 129.4, 128.8, 127.9, 126.8, 125.7, 125.3, 118.4, 110.5, 21.7, 20.6, 20.1, 15.3.

**HRMS (ESI):** calculated for $C_{24}H_{21}ClOH$ (M+H$^+$) 361.1359, found 361.1357.

**FTIR (cm$^{-1}$):** *v* 2925, 1451, 1066, 1010, 762.

### 5-chloro-4, 6-dimethyl-2, 3-di-*m*-tolylbenzofuran 3pc



Prepared according to General Procedure using **1p** (46.8 mg, 0.30 mmol), **2c** (20.6 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (29.7 mg, 83% yield) as a white solid.

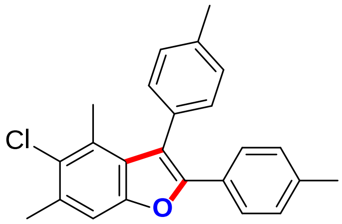
**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.38-7.32 (m, 2H), 7.29 (s, 1H), 7.24-7.17 (m, 4H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.04-7.02 (m, 1H), 2.49 (s, 3H), 2.38 (s, 3H), 2.26 (s, 3H), 2.07 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 151.8, 150.6, 138.4, 137.9, 134.2, 132.7, 131.3, 130.6, 129.6, 129.5, 128.7, 128.6, 128.1, 127.8, 127.0, 123.5, 118.3, 110.3, 21.8, 21.5, 21.4, 16.1.

**HRMS (ESI):** calculated for $C_{24}H_{21}ClOH$ ($M+H^+$) 361.1359, found 361.1349.

**FTIR ($cm^{-1}$):** *v* 2923, 1448, 1076, 836, 785.

### 5-chloro-4, 6-dimethyl-2, 3-di-*p*-tolylbenzofuran 3pd



Prepared according to General Procedure using **1p** (46.8 mg, 0.30 mmol), **2d** (20.6 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (23.9 mg, 66% yield) as a white solid.

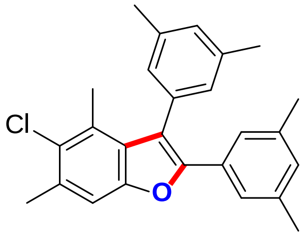
**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.37-7.35 (d, *J* = 8.0 Hz, 2H), 7.27-7.26 (m, 5H), 7.05-7.03 (d, *J* = 8.0 Hz, 2H), 2.49 (s, 3H), 2.45 (s, 3H), 2.29 (s, 6H), 2.07 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 151.8, 150.8, 137.9, 137.6, 132.5, 131.2, 130.6, 129.6, 129.5, 129.4, 129.0, 127.9, 127.9, 126.3, 117.5, 110.3, 21.8, 21.4, 21.2, 16.0.

**HRMS (ESI):** calculated for $C_{24}H_{21}ClOH$ ($M+H^+$) 361.1359, found 361.1344.

**FTIR ($cm^{-1}$):** *v* 2920, 1520, 1078, 1009, 820.

### 5-chloro-2, 3-bis(3, 5-dimethylphenyl)-4, 6-dimethylbenzofuran 3pe



Prepared according to General Procedure using **1p** (46.8 mg, 0.30 mmol), **2e** (23.4 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (31.4

mg, 81% yield) as a white solid.

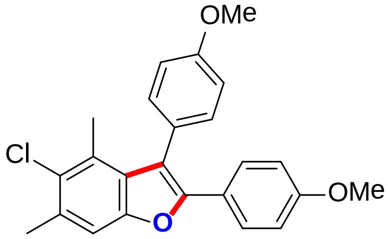
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.28 (s, 1H), 7.12 (s, 2H), 7.07 (s, 1H), 7.01 (s, 2H), 6.86 (s, 1H), 2.49 (s, 3H), 2.34 (s, 6H), 2.20 (s, 6H), 2.09 (s, 3H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 151.8, 150.6, 138.1, 137.7, 134.1, 132.5, 130.5, 129.6, 129.5, 129.5, 129.4, 128.4, 127.8, 124.2, 118.3, 110.3, 21.8, 21.4, 21.3, 16.1.

**HRMS (ESI):** calculated for $C_{26}H_{25}ClOH$ (M+H$^+$) 389.1672, found 389.1677.

**FTIR (cm$^{-1}$):** *v* 2919, 1602, 1448, 1009, 849.

**5-chloro-2, 3-bis(4-methoxyphenyl)-4, 6-dimethylbenzofuran 3pf**



Prepared according to General Procedure using **1p** (46.8 mg, 0.30 mmol), **2f** (23.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether: ethyl acetate = 50:1) provided the title compound (28.6 mg, 73% yield) as a colorless oil.

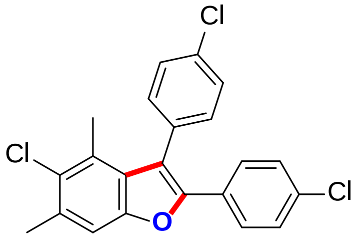
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.42-7.40 (d, *J* = 9.2 Hz, 2H), 7.30-7.28 (m, 3H), 7.00-6.98 (d, *J* = 8.8 Hz, 2H), 6.79-6.77 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 3.77 (s, 3H), 2.48 (s, 3H), 2.08 (s, 3H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 159.3, 159.3, 151.7, 150.9, 132.2, 131.9, 129.5, 129.2, 128.0, 127.7, 126.4, 123.5, 116.2, 114.3, 113.8, 110.2, 55.2, 55.2, 21.7, 16.0.

**HRMS (ESI):** calculated for $C_{24}H_{21}ClO_3H$ (M+H$^+$) 393.1257, found 393.1261.

**FTIR (cm$^{-1}$):** *v* 2930, 1517, 1250, 1177, 831.

**5-chloro-2, 3-bis(4-chlorophenyl)-4, 6-dimethylbenzofuran 3pg**



Prepared according to General Procedure using **1p** (46.8 mg, 0.30 mmol), **2g** (24.7 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (25.7 mg, 64% yield) as a white solid.

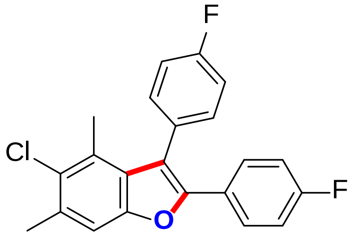
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.47-7.45 (m, 2H), 7.36-7.29 (m, 5H), 7.24-7.22 (m, 2H), 2.50 (s, 3H), 2.07 (s, 3H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 151.9, 149.7, 134.4, 134.1, 133.5, 132.5, 132.0, 129.9, 129.4, 129.3, 128.8, 128.7, 127.6, 127.3, 117.4, 110.5, 21.8, 16.3.

**HRMS (ESI):** calculated for $C_{22}H_{15}Cl_3OH$ (M+H$^+$) 401.0267, found 401.0265.

**FTIR (cm$^{-1}$):** *v* 2923, 1497, 1092, 1012, 829.

### 5-chloro-2, 3-bis(4-fluorophenyl)-4, 6-dimethylbenzofuran 3ph



Prepared according to General Procedure using **1p** (46.8 mg, 0.30 mmol), **2h** (21.4 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (29.4 mg, 80% yield) as a white solid.

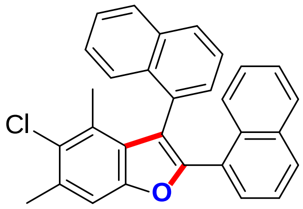
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.43-7.39 (dd, *J* = 5.2 Hz, *J* = 8.8 Hz, 2H), 7.37-7.34 (dd, *J* = 5.2 Hz, *J* = 8.8 Hz, 2H), 7.28 (s, 1H), 7.18 (t, *J* = 8.4 Hz, 3H), 2.50 (s, 3H), 2.07 (s, 3H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 163.9-163.7 (d, *J* = 25.1 Hz), 161.4-161.2 (d, *J* = 26.4 Hz), 151.8, 150.0, 133.1, 132.4-128.2 (dd, *J* = 8.0 Hz, *J* = 415.9 Hz), 130.0-126.6 (dd, *J* = 3.5 Hz, *J* = 331.0 Hz), 129.8, 129.3, 127.4, 116.8, 116.2, 116.0, 115.6, 115.4, 110.4, 21.8, 16.1.

**HRMS (ESI):** calculated for $C_{22}H_{15}ClF_2OH$ (M+H$^+$) 369.0858, found 369.0857.

**FTIR (cm$^{-1}$):** *ν* 2974, 1515, 1498, 1235, 834.

### 5-chloro-4, 6-dimethyl-2, 3-di(naphthalen-1-yl)benzofuran 3pi



Prepared according to General Procedure using **1p** (46.8 mg, 0.30 mmol), **2i** (27.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (26.7 mg, 62% yield) as a colorless oil.

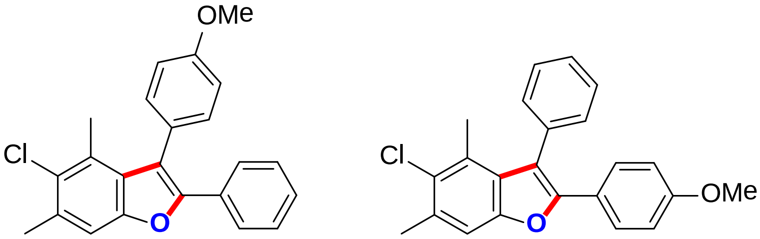
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 8.11-8.10 (m, 1H), 7.87-7.78 (m, 4H), 7.72-7.70 (d, *J* = 8.4 Hz, 1H), 7.49-7.38 (m, 5H), 7.32-7.27 (m, 2H), 7.19-7.17 (m, 1H), 7.13-7.09 (m, 1H), 2.55 (s, 3H), 1.82 (s, 3H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 153.2, 152.7, 133.8, 133.6, 133.4, 133.0, 132.2, 131.0, 129.8, 129.5, 128.8, 128.3, 128.3, 127.8, 127.6, 126.5, 126.0, 125.9, 125.9, 125.4, 124.9, 118.6, 110.7, 21.8, 15.6.

**HRMS (ESI):** calculated for $C_{30}H_{21}ClOH$ (M+H$^+$) 433.1359, found 433.1362.

**FTIR (cm$^{-1}$):** *ν* 3046, 1738, 1386, 795, 775.

### 5-chloro-3-(4-methoxyphenyl)-4, 6-dimethyl-2-phenylbenzofuran 3pj and 5-chloro-2-(4-methoxyphenyl)-4, 6-dimethyl-3-phenylbenzofuran 3pj’



Prepared according to General Procedure using **1p** (46.8 mg, 0.30 mmol), **3j** (20.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (30.3 mg, 84% yield) as a 3.8:1 mixture of regioisomers (inseparable mixture) as a colorless oil.

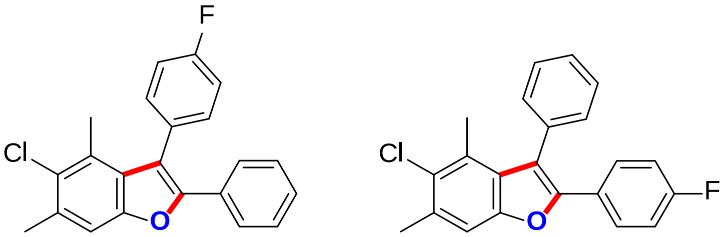
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.49-7.37 (m, 3H), 7.30-7.23 (m, 5H), 7.01-6.99 (d, *J* = 8.4 Hz, 1.59H), 6.77-6.75 (d, *J* = 8.8 Hz, 0.36H), 3.89 (s, 2.44H), 3.76 (s, 0.64H), 2.49 (s, 3H), 2.09, 2.05 (s, 3H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 159.3, 151.8, 151.7, 150.7, 150.6, 132.8, 131.8, 130.9, 130.7, 129.6, 128.8, 128.3, 127.9, 127.8, 126.3, 126.1, 117.9, 114.3, 113.8, 110.4, 110.2, 55.2, 55.2, 21.8, 21.8, 16.1, 16.0.

**HRMS (ESI):** calculated for $C_{23}H_{19}ClO_2H$ (M+H$^+$) 363.1152, found 363.1153.

**FTIR (cm$^{-1}$):** *ν* 2928, 1513, 1247, 1174, 756.

### 5-chloro-3-(4-fluorophenyl)-4, 6-dimethyl-2-phenylbenzofuran 3pk and 5-chloro-2-(4-fluorophenyl)-4, 6-dimethyl-3-phenylbenzofuran 3pk’



Prepared according to General Procedure using **1p** (46.8 mg, 0.30 mmol), **2k** (19.6 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (22.1 mg, 63% yield) as a 1.1:1 mixture of regioisomers as a white solid.

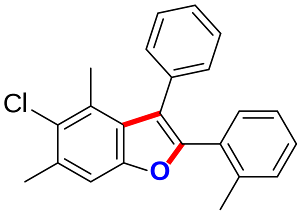
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.47-7.36 (m, 5.62H), 7.30-7.25 (m, 3.04H), 7.17 (t, *J* = 8.8 Hz, 1.17H), 6.92 (t, *J* = 8.8 Hz, 0.93H), 2.50 (s, 3H), 2.07 (s, 1.53H), 2.06 (s, 1.45H).

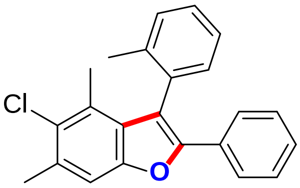
**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 163.9-163.6 (d, *J* = 29.7 Hz), 161.4-161.1 (d, *J* = 31.1 Hz), 151.9, 151.8, 150.8, 149.8, 134.1, 133.1, 132.9, 132.5, 132.4, 130.7, 130.4, 130.2, 130.1, 129.7, 129.5, 129.3, 129.0, 128.4, 128.3, 128.2, 128.1, 127.6, 127.6, 126.9, 126.8, 126.4, 117.9, 117.1, 116.1, 115.9, 115.5, 115.3, 110.5, 110.4, 21.8, 16.1, 16.1.

**HRMS (ESI):** calculated for $C_{22}H_{16}ClFOH$ (M+H$^+$) 351.0952, found 351.0951.

**FTIR (cm$^{-1}$):** *ν* 2926, 2358, 1510, 1233, 837.

### 5-chloro-4, 6-dimethyl-3-phenyl-2-*o*-tolylbenzofuran 3pl and 5-chloro-4, 6-dimethyl-2-phenyl-3-*o*-tolylbenzofuran 3pl'





Prepared according to General Procedure using **1p** (46.8 mg, 0.30 mmol), **2l** (19.2 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (24.6 mg, 71% yield) as a 1.6:1 mixture of regioisomers as a white solid.

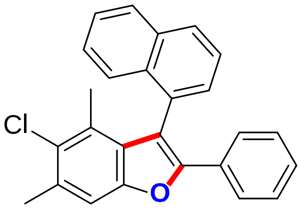
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.45-7.14 (m, 10.14H), 7.05 (t, *J* = 6.8 Hz, 0.39H), 2.51, 2.50 (s, 3H), 2.23, 2.21 (s, 2.28H), 2.11 (s, 1.89H), 2.00 (s, 1.82H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 152.9, 152.4, 152.1, 149.9, 138.1, 137.9, 133.7, 133.4, 132.9, 132.5, 131.0, 130.9, 130.8, 130.3, 130.3, 129.9, 129.7, 129.5, 129.4, 128.9, 128.4, 128.1, 127.9, 127.4, 127.3, 126.5, 126.5, 125.7, 125.3, 120.0, 117.1, 110.5, 110.5, 21.8, 21.7, 20.4, 20.0, 16.8, 15.0.

**HRMS (ESI):** calculated for $C_{23}H_{19}ClOH$ (M+H$^+$) 347.1203, found 347.1199.

**FTIR (cm$^{-1}$):** *ν* 2921, 1451, 1389, 1010, 762.

### 5-chloro-4, 6-dimethyl-3-(naphthalen-1-yl)-2-phenylbenzofuran 3pm



Prepared according to General Procedure using **1p** (46.8 mg, 0.30 mmol), **2m** (22.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (22.5 mg, 59% yield) as a colorless oil.

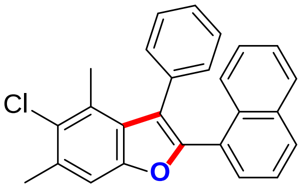
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.97 (t, *J* = 8.4 Hz, 2H), 7.69-7.67 (d, *J* = 8.4 Hz, 1H), 7.56-7.49 (m, 3H), 7.39-7.34 (m, 4H), 7.14-7.12 (m, 3H), 2.52 (s, 3H), 1.73 (s, 3H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 152.1, 151.2, 133.7, 133.3, 133.1, 131.8, 130.4, 129.7, 129.6, 128.7, 128.6, 128.4, 128.4, 128.3, 128.0, 126.7, 126.3, 126.1, 125.9, 125.8, 115.9, 110.5, 21.9, 15.2.

**HRMS (ESI):** calculated for $C_{26}H_{19}ClOH$ (M+H$^+$) 383.1203, found 383.1208.

**FTIR (cm$^{-1}$):** *ν* 3056, 1444, 1072, 934, 778.

### 5-chloro-4, 6-dimethyl-2-(naphthalen-1-yl)-3-phenylbenzofuran 3pm'



Prepared according to General Procedure using **1p** (46.8 mg, 0.30 mmol), **2m** (22.8 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (6.7 mg, 18% yield) as a colorless oil.

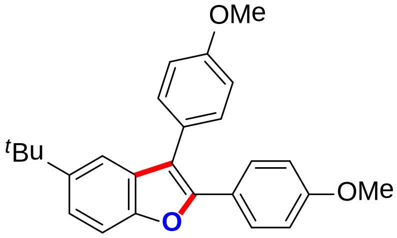
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.99-7.97 (m, 1H), 7.86-7.81 (m, 2H), 7.51-7.45 (m, 2H), 7.37 (s, 1H), 7.34-7.25 (m, 8H), 2.54 (s, 3H), 2.24 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 152.6, 152.3, 133.6, 133.3, 132.8, 132.3, 130.8, 129.8, 129.6, 129.5, 128.3, 128.1, 127.7, 127.4, 126.7, 126.5, 126.0, 126.0, 124.9, 120.9, 110.6, 21.8, 16.7.

**HRMS (ESI):** calculated for $C_{26}H_{19}ClOH$ (M+H$^+$) 383.1203, found 383.1208.

**FTIR (cm$^{-1}$):** *v* 2918, 1387, 1066, 1011, 775.

### 5-*t*-butyl-2, 3-bis(4-methoxyphenyl)benzofuran 3af



Prepared according to General Procedure using **1a** (45.0 mg, 0.30 mmol), **2f** (20.7 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether: ethyl acetate = 50:1) provided the title compound (16.8 mg, 44% yield) as a white solid.

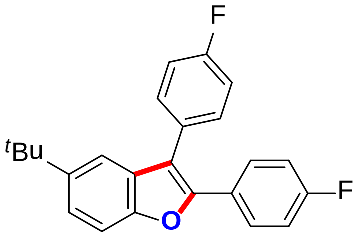
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.58-7.56 (d, *J* = 8.8 Hz, 2H), 7.46-7.35 (m, 5H), 7.03-7.01 (d, *J* = 8.8, 2H), 6.85-6.83 (d, *J* = 8.8, 2H), 3.89 (s, 3H), 3.81 (s, 3H), 1.35 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 159.5, 158.9, 152.0, 150.7, 145.9, 130.9, 130.1, 128.3, 125.3, 123.7, 122.1, 115.8, 115.7, 114.4, 113.8, 110.2, 55.3, 55.2, 34.8, 31.9.

**HRMS (ESI):** calculated for $C_{26}H_{26}O_3H$ (M+H$^+$) 387.1960, found 387.1966.

**FTIR (cm$^{-1}$):** *v* 2960, 1518, 1251, 1174, 1033.

### 5-*t*-butyl-2, 3-bis(4-fluorophenyl)benzofuran 3ah



Prepared according to General Procedure using **1a** (45.0 mg, 0.30 mmol), **2h** (21.4 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (26.3 mg, 73% yield) as a white solid.

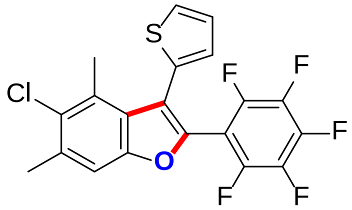
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.59-7.55 (dd, *J* = 6.4, 8.8 Hz, 2H), 7.48-7.40 (m, 5H), 7.18 (t, *J* = 8.8, 2H), 7.00 (t, *J* = 8.8, 2H), 1.35 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 163.8-163.6 (d, *J* = 24.8 Hz), 161.4-161.1 (d, *J* = 22.9 Hz), 152.1, 150.0, 146.4, 131.5-131.4 (d, *J* = 7.9 Hz), 129.6, 128.8-128.7 (d, *J* = 8.1 Hz), 126.9 (d, *J* = 3.2 Hz), 122.9, 116.4, 116.3, 116.1, 115.7, 115.5, 110.5, 34.8, 31.8.

**HRMS (ESI):** calculated for $C_{24}H_{20}F_2O$ (M$^+$) 362.1482, found 362.1487.

**FTIR (cm$^{-1}$):** *v* 2963, 1515, 1223, 1157, 831.

### 5-chloro-4, 6-dimethyl-2-(perfluorophenyl)-3-(thiophen-2-yl)benzofuran 3pn



Prepared according to General Procedure using **1p** (46.8 mg, 0.30 mmol), **2n** (27.4 mg, 0.10 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (24.7 mg, 58% yield) as a white solid.

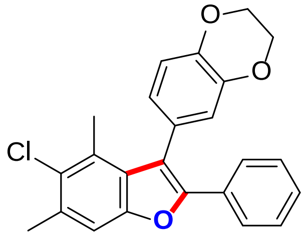
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.39 (t, *J* = 3.2 Hz, 1H), 7.32 (s, 1H), 7.07-7.06 (m, 2H), 2.52 (s, 3H), 2.28 (s, 3H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 153.4, 134.6, 131.1, 130.5, 130.2, 129.5, 127.3, 127.2, 125.9, 118.0, 110.8, 21.8, 16.0.

**HRMS (ESI):** calculated for $C_{20}H_{10}ClF_5OSH$ (M+H$^+$) 429.0139, found 429.0143.

**FTIR (cm$^{-1}$):** *ν* 2922, 1514, 1497, 1008, 988.

### 6-(5-chloro-4, 6-dimethyl-2-phenylbenzofuran-3-yl)-2, 3-dihydrobenzo[b][1, 4]dioxine 3po



Prepared according to General Procedure using **1p** (46.8 mg, 0.30 mmol), **2o** (29.6 mg, 0.12 mmol); flash chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) provided the title compound (38.3 mg, 82% yield) as a yellow oil.

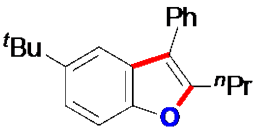
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.53-7.51 (m, 2H), 7.28-7.23 (m, 4H), 6.96-6.94 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 1.6 Hz, 1H), 6.87-6.84 (dd, *J* = 8.4 Hz, *J* = 2.0, 1H), 4.36-4.32 (m, 4H), 2.49 (s, 3H), 2.13 (s, 3H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 151.8, 150.6, 143.8, 143.5, 132.8, 130.8, 130.7, 129.6, 128.9, 128.3, 127.9, 127.8, 127.1, 126.3, 123.9, 119.4, 117.7, 110.3, 64.4, 64.3, 21.8, 16.0.

**HRMS (ESI):** calculated for $C_{24}H_{19}ClO_3H$ (M+H$^+$) 391.1101, found 391.1106.

**FTIR (cm$^{-1}$):** *ν* 2924, 1508, 1282, 1251, 1068.

### 5-(*tert*-butyl)-3-phenyl-2-propylbenzofuran 3pq



Prepared according to General Procedure using **1a** (180.0 mg, 1.20 mmol), **2q** (57.6 mg, 0.40 mmol); flash chromatography on silica gel (petroleum ether) provided the title compound (10.7 mg, 10% yield) as a colorless oil.

**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.53-7.52 (m, 1H), 7.49-7.47 (m, 4H), 7.40-7.36 (m, 2H), 7.34-7.32 (m, 1H), 2.81 (t, *J* = 7.2 Hz, 2H), 1.83-1.74 (m, 2H), 1.35 (s, 9H), 0.96 (t, *J* = 7.6 Hz, 3H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 155.4, 152.2, 145.7, 133.1, 129.2, 128.7, 128.5, 126.9, 121.4, 117.1, 115.5, 110.1, 34.8, 31.9, 28.7, 21.8, 13.9.

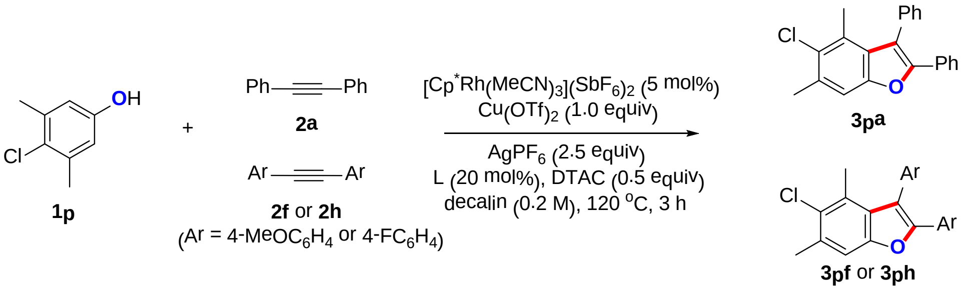
**HRMS (ESI):** calculated for $C_{24}H_{24}OH$ (M+H$^+$) 293.1905, found 293.1900.

**FTIR (cm$^{-1}$):** *v* 2968, 2900, 1393, 1066, 1027.

# Mechanistic Experiments

## Competition Experiments: with electronically different alkynes

## General Procedure for the Competition Experiments



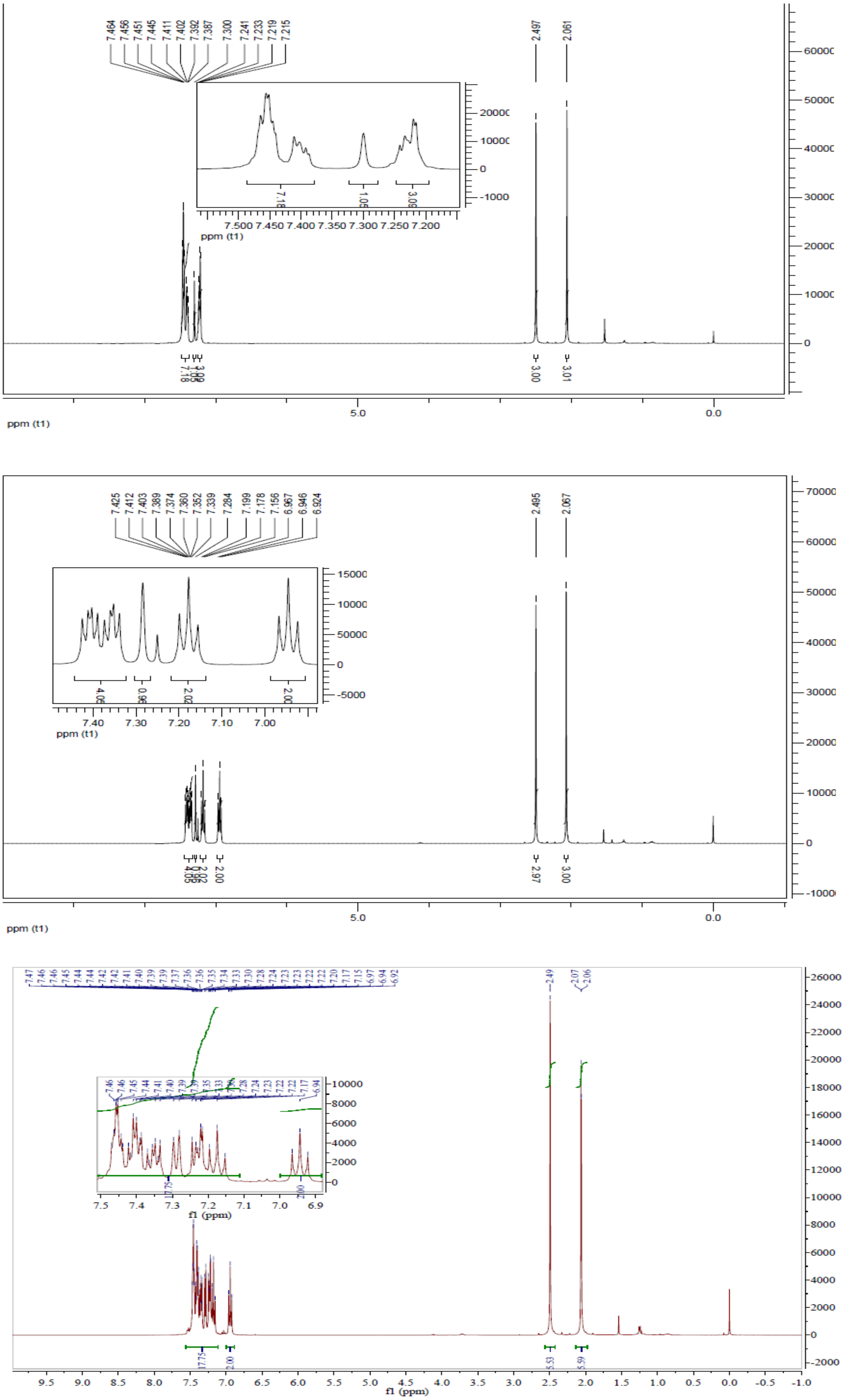
**1p** (0.30 mmol, 45.0 mg), diphenylacetylene **2a** (0.10 mmol, 17.8 mg), **2f** (0.10 mmol, 23.8 mg) or **2h** (0.10 mmol, 21.4 mg), [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (5 mol%, 0.005 mmol, 4.2 mg), acetanilide (0.20 equiv, 0.02 mmol, 2.7 mg), DTAC (dodecyl trimethyl ammonium chloride) (0.5 equiv, 0.05 mmol, 13.2 mg) were weighed in the air and Cu(OTf)$_2$ (1.0 equiv, 0.10 mmol, 36.2 mg), AgPF$_6$ (2.5 equiv, 0.25 mmol, 63.2 mg) were weighed in the glovebox and charged into an oven-dried 50 mL Schlenk tube. The tube was evacuated and refilled with N$_2$, which was repeated for 3 times. After addition of 0.5 mL of decalin under a positive pressure of N$_2$ *via* syringe, the sealed tube was placed in a 120 $^o$C parallel synthesizer and stirred for 3 h. After completion, the reaction mixture was cooled down to room temperature and directly purified by flash column chromatography. After purification, the mixture was analyzed by $^1$H NMR.

### I) Using 2f as another alkyne:

The two products were purified by flash column chromatography to get product **3pa** (eluent: petroleum ether a) with 24% yield and product **3pf** (eluent: petroleum ether : ethyl acetate = 50:1) with 81% yield. The ratio of product **3pa** to product **3pf** was 1.0:3.4.

### II) Using 2h as another alkyne:

The two products were inseparable mixtures which were analyzed by $^1$H NMR (Figure 1). The result showed that the ratio of product **3pa** to product **3ph** was 1.0:1.2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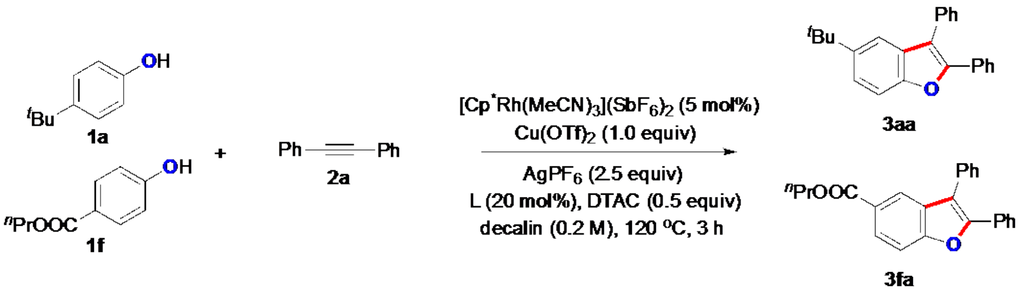
7.445
7.411
7.402
7.392
7.387
7.300
7.241
7.233
7.219
7.215
2.497
2.061
7.18
1.05
3.09
3.00
3.01
ppm (t1)
5.0
0.0
7.425
7.412
7.403
7.389
7.374
7.360
7.352
7.339
7.284
7.199
7.178
7.156
6.967
6.946
6.924
2.495
2.067
4.05
0.96
2.02
2.00
2.97
3.00
2.49
2.07
2.06
17.75
5.53
5.59
f1 (ppm)

**Figure 1**

## Competition Experiments: with electronically different phenols

## General Procedure for the Competition Experiments



**1a** (0.15 mmol, 22.5 mg), **1g** (0.15 mmol, 27.0 mg), diphenylacetylene **2a** (0.10 mmol, 17.8 mg), [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (5 mol%, 0.005 mmol, 4.2 mg), acetanilide (0.20 equiv, 0.02 mmol, 2.7 mg), DTAC (dodecyl trimethyl ammonium chloride) (0.5 equiv, 0.05 mmol, 13.2 mg) were weighed in the air and Cu(OTf)$_2$ (1.0 equiv, 0.10 mmol, 36.2 mg), AgPF$_6$ (2.5 equiv, 0.25 mmol, 63.2 mg) were weighed in the glovebox and charged into an oven-dried 50 mL Schlenk tube. The tube was evacuated and refilled with N$_2$, which was repeated for 3 times. After addition of 0.5 mL of decalin under a positive pressure of N$_2$ *via* syringe, the sealed tube was placed in a 120 °C parallel synthesizer and stirred for 3 h. After completion, the reaction mixture was cooled down to room temperature and directly purified by flash column chromatography. After purification, the mixture was analyzed by $^1$H NMR. The result showed that the ratio of **3aa** to **3fa** was 1.5:1.

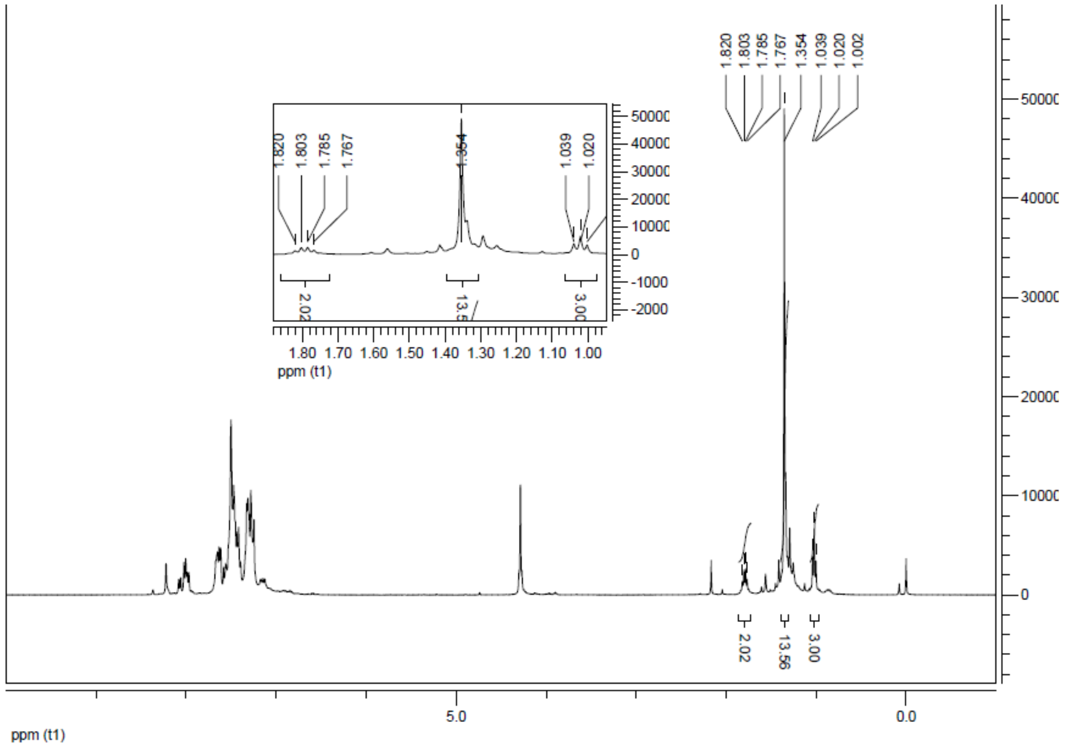
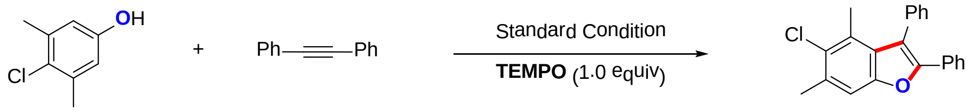


Figure 2

## Radical Trapping Experiment

## General Procedures for the Radical Trapping Experiment



**1p** **2a** **3pa**, 29% (NMR)

**1p** (0.30 mmol, 46.8 mg), diphenylacetylene **2a** (0.10 mmol, 17.8 mg), [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (5 mol%, 0.005 mmol, 4.2 mg), acetanilide (0.20 equiv, 0.02 mmol, 2.7 mg), DTAC (dodecyl trimethyl ammonium chloride) (0.5 equiv, 0.05 mmol, 13.2 mg), **TEMPO** (1.0 equiv, 0.10 mmol, 15.6 mg) were weighed in the air and Cu(OTf)$_2$ (1.0 equiv, 0.10 mmol, 36.2 mg), AgPF$_6$ (2.5 equiv, 0.25 mmol, 63.2 mg) were weighed in the glovebox and charged into an oven-dried 50 mL Schlenk tube. The tube was evacuated and refilled with N$_2$, which was repeated for 3 times. After addition of 0.5 mL of decalin under a positive pressure of N$_2$ *via* syringe, the sealed tube was placed in a 120 $^{o}$C parallel synthesizer and stirred for 3 h. After completion, the reaction mixture was cooled down to room temperature and directly purified by flash column chromatography. After purification, 0.086 mmol (6.0 μL) CH$_2$Br$_2$ was added as an internal standard, the mixture was analyzed by $^1$H NMR. The result showed that **3pa** was obtained with 29% yield (NMR).

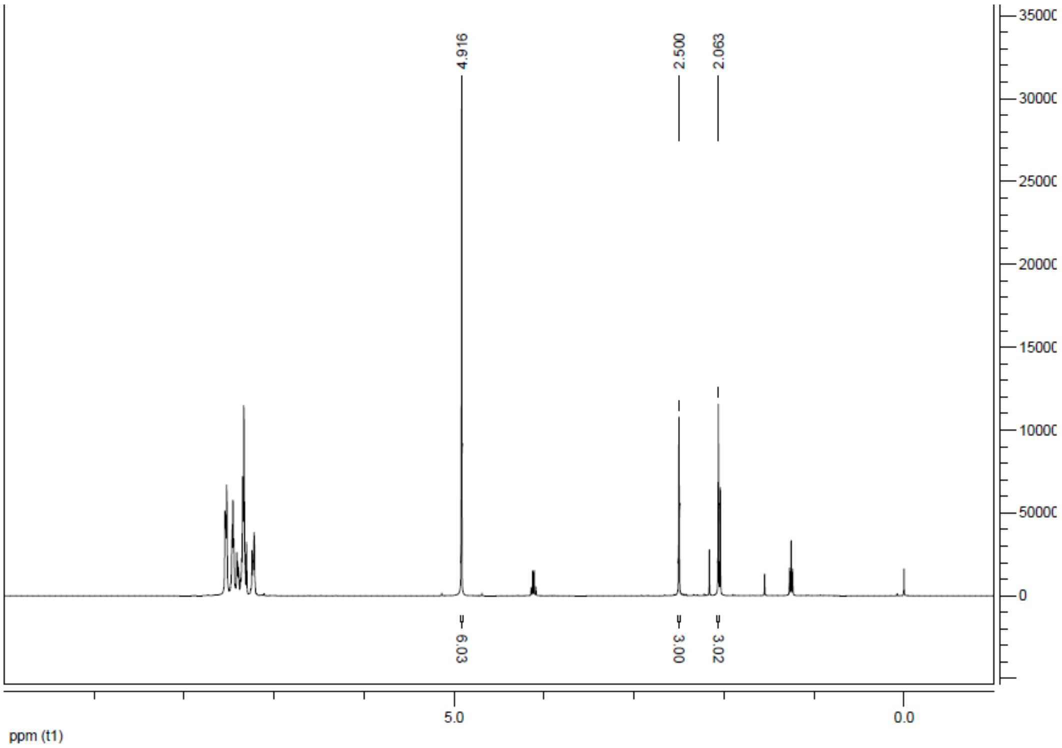


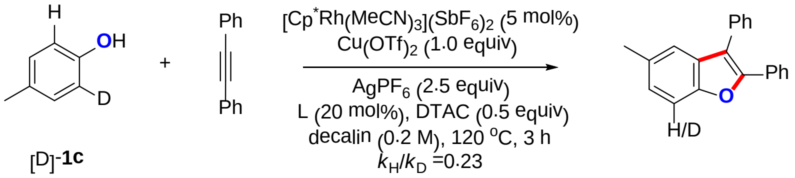
Figure 3

## Deuterium-Labeling Experiments

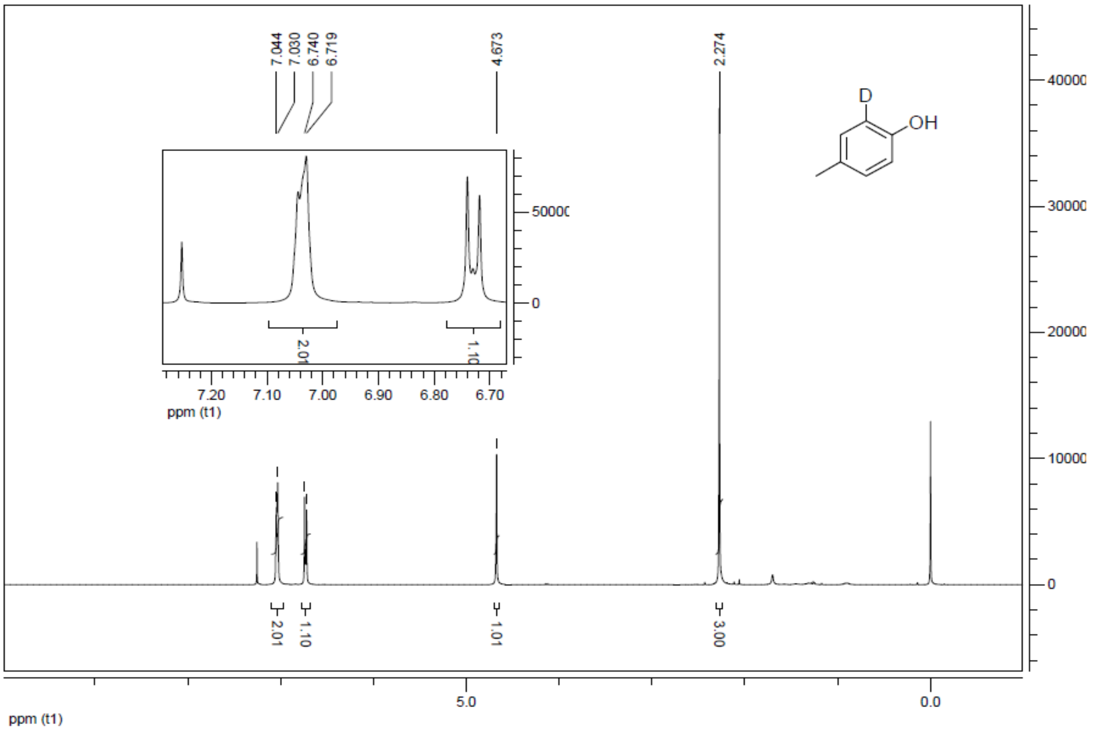
### General Procedures for the Synthesis of [D]-1c

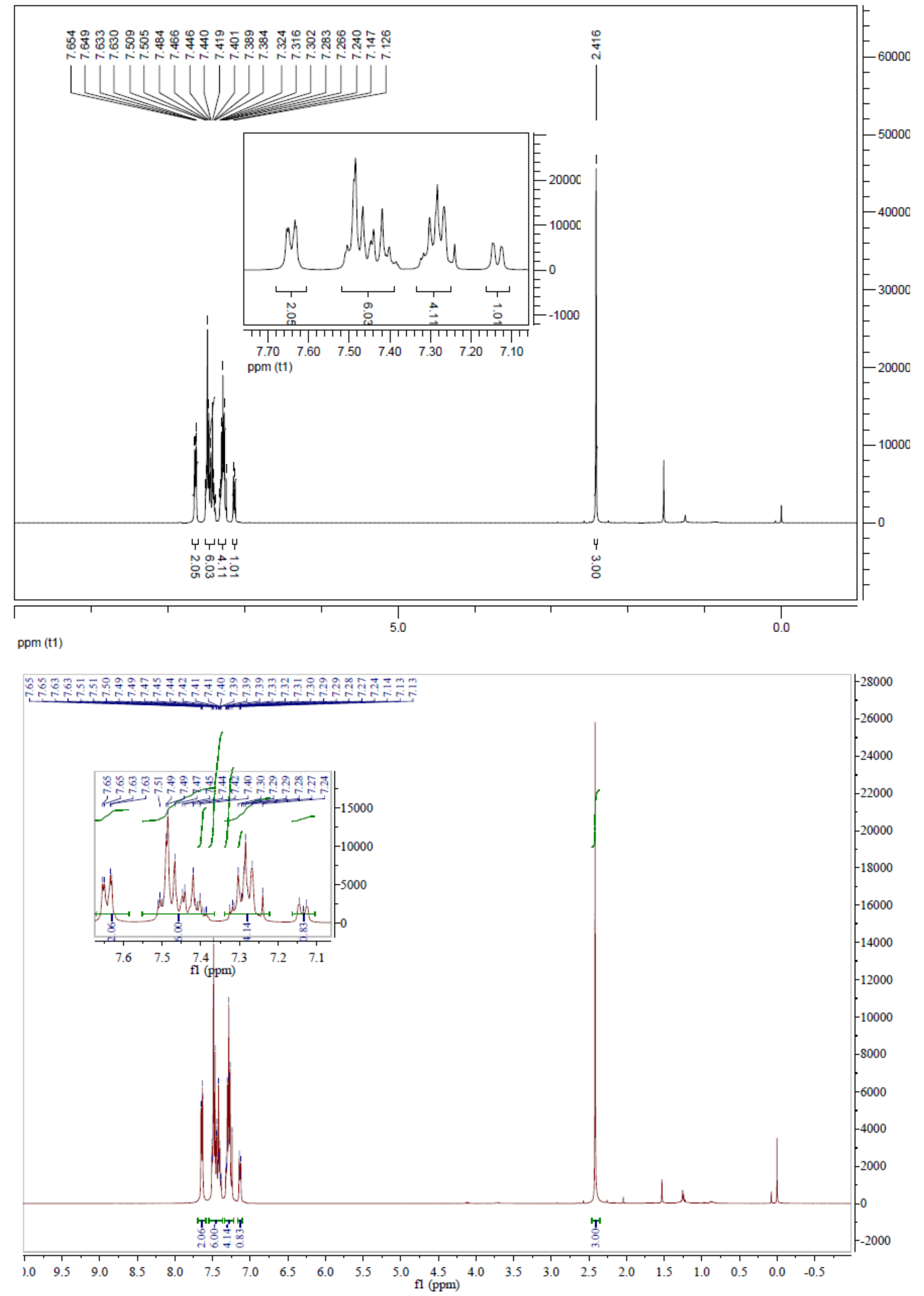
To a solution of 2-bromo-4-methylphenol (561 mg, 3.0 mmol, 0.36 mL) in 2.0 mL freshly distilled THF, *n*BuLi (7.5 mmol, 4.7 mL, 1.6 M in hexane) was added dropwise to the solution at -78 °C, the solution was stirred for 12 h, then 3 mL $D_2O$ was added dropwise to the solution at 0 °C, after that the solution was stirred for 2 h. The mixture was extracted with $Et_2O$, organic layer was dried with $Na_2SO_4$, concentrated and the mixture was purified by flash chromatography (petroleum ether : ethyl acetate = 10 : 1) to give [D]-**1c** with 71% yield and 90%(D%).

### General Procedures for the Intramolecular Kinetic Isotopic Effect



**[D]-1c** (90% D-substituted) (0.30 mmol, 32.7 mg, 31.6 μL), diphenylacetylene **2a** (0.10 mmol, 17.8 mg), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5 mol%, 0.005 mmol, 4.2 mg), acetanilide (0.20 equiv, 0.02 mmol, 2.7 mg), DTAC (dodecyl trimethyl ammonium chloride) (0.5 equiv, 0.05 mmol, 13.2 mg) were weighed in the air and $Cu(OTf)_2$ (1.0 equiv, 0.10 mmol, 36.2 mg), $AgPF_6$ (2.5 equiv, 0.25 mmol, 63.2 mg) were weighed in the glovebox and charged into an oven-dried 50 mL Schlenk tube. The tube was evacuated and refilled with $N_2$, which was repeated for 3 times. After addition of 0.5 mL of decalin under a positive pressure of $N_2$ *via* syringe, the sealed tube was placed in a 120 °C parallel synthesizer and stirred for 3 h. After completion, the reaction mixture was cooled down to room temperature and directly purified by flash column chromatography with petroleum ether as eluent to get product with 59% yield. The result was analyzed by $^1H$ NMR (Figure 4). The result showed that $k_H/k_D$ = 0.23. Then the reaction was stirred for 10 min, however, no detectable deuterium incorporation was observed. Both results indicated the existence of H/D exchange.

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7.649
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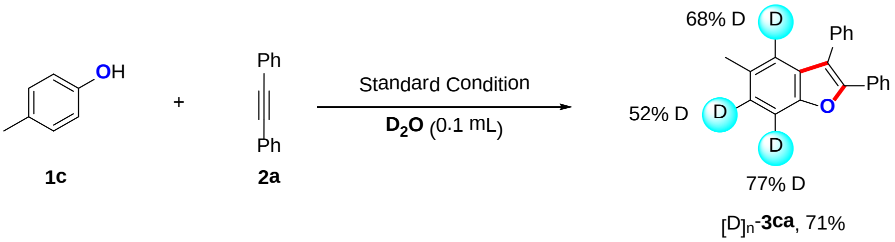
7.630
7.509
7.505
7.484
7.466
7.446
7.440
7.419
7.401
7.389
7.384
7.324
7.316
7.302
7.283
7.266
7.240
7.147
7.126
2.416
2.05
6.03
4.11
1.01
3.00
7.70
7.60
7.50
7.40
7.30
7.20
7.10
ppm (t1)
20000
10000
0
-1000
60000
50000
40000
30000
20000
10000
0
5.0
0.0
ppm (t1)
7.65
7.65
7.63
7.63
7.51
7.51
7.50
7.49
7.49
7.47
7.45
7.45
7.44
7.42
7.41
7.41
7.40
7.39
7.39
7.39
7.33
7.32
7.31
7.30
7.29
7.29
7.28
7.27
7.24
7.14
7.13
7.13
2.06
6.00
4.14
0.83
3.00
15000
10000
5000
0
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
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)

**Figure 4**

## General Procedures for the Deuterium-Labeling Experiment



**1c** (0.30 mmol, 32.4 mg), diphenylacetylene **2a** (0.10 mmol, 17.8 mg), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5 mol%, 0.005 mmol, 4.2 mg), acetanilide (0.20 equiv, 0.02 mmol, 2.7 mg), DTAC (dodecyl trimethyl ammonium chloride) (0.5 equiv, 0.05 mmol, 13.2 mg) were weighed in the air and $Cu(OTf)_2$ (1.0 equiv, 0.10 mmol, 36.2 mg), $AgPF_6$ (2.5 equiv, 0.25 mmol, 63.2 mg) were weighed in the glovebox and charged into an oven-dried 50 mL Schlenk tube. The tube was evacuated and refilled with $N_2$, which was repeated for 3 times. After addition of 0.5 mL of decalin and 0.1 mL **$D_2O$** under a positive pressure of $N_2$ *via* syringe, the sealed tube was placed in a 120 °C parallel synthesizer and stirred for 3 h. After completion, the reaction mixture was cooled down to room temperature and directly purified by flash column chromatography eluting with petroleum ether. 20.1 mg product was obtained with 71% yield. The result showed that the existence of H/D exchange (Figure 5).

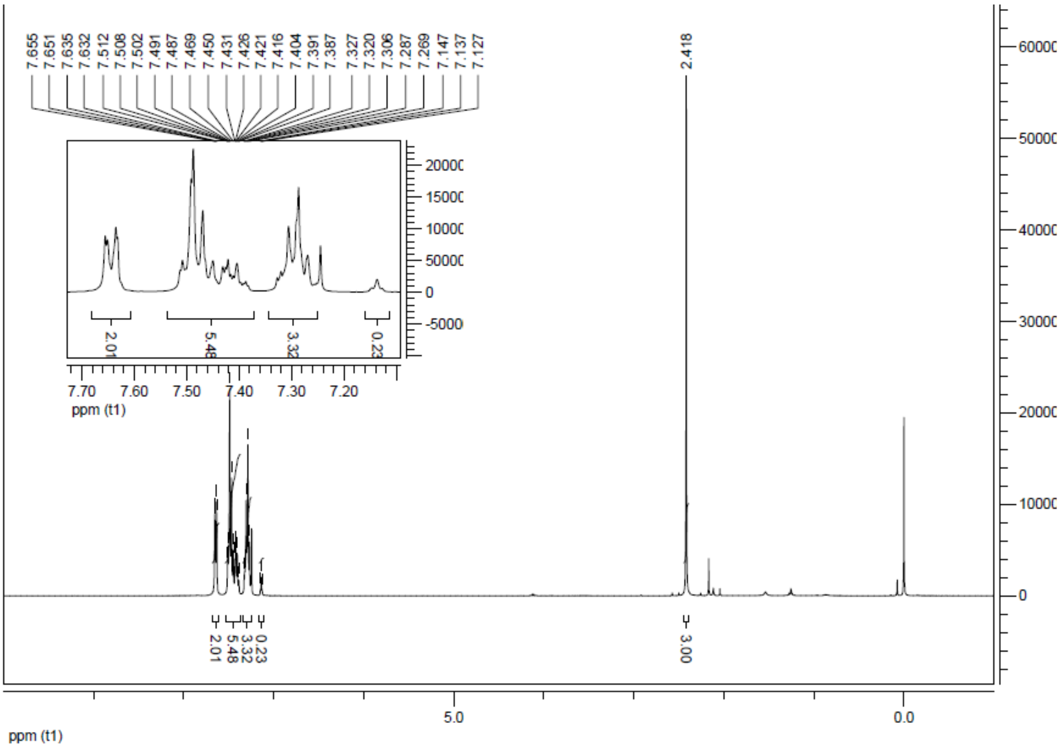


Figure 5

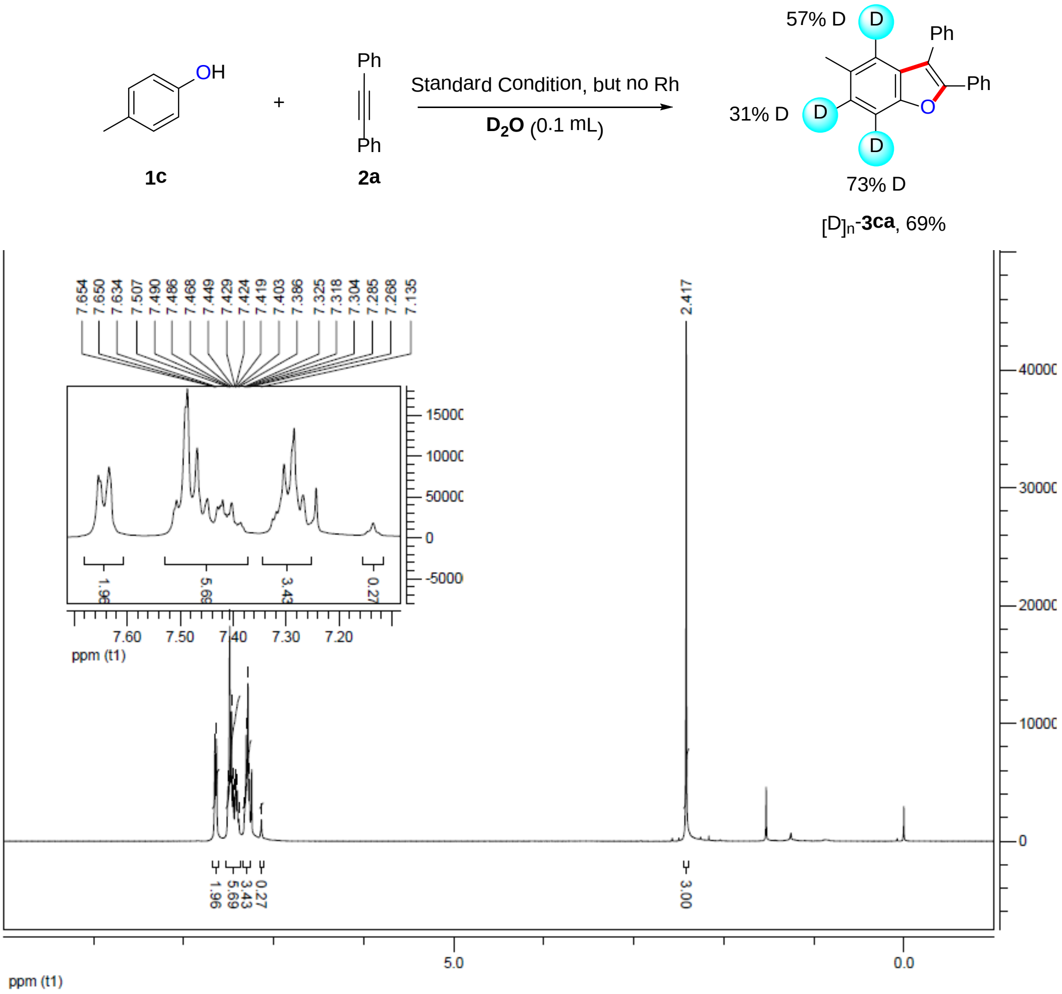

OH
+
Ph
Ph
Standard Condition, but no Rh
D2O (0.1 mL)
1c
2a
57% D
D
Ph
Ph
O
31% D
D
D
73% D
[D]n-3ca, 69%
7.654
7.650
7.634
7.507
7.490
7.486
7.468
7.449
7.429
7.424
7.419
7.403
7.386
7.325
7.318
7.304
7.285
7.268
7.135
2.417
15000
10000
50000
0
-5000
1.96
5.69
3.43
0.27
7.60
7.50
7.40
7.30
7.20
ppm (t1)
40000
30000
20000
10000
0
1.96
5.69
3.43
0.27
3.00
5.0
0.0
ppm (t1)

Figure 6

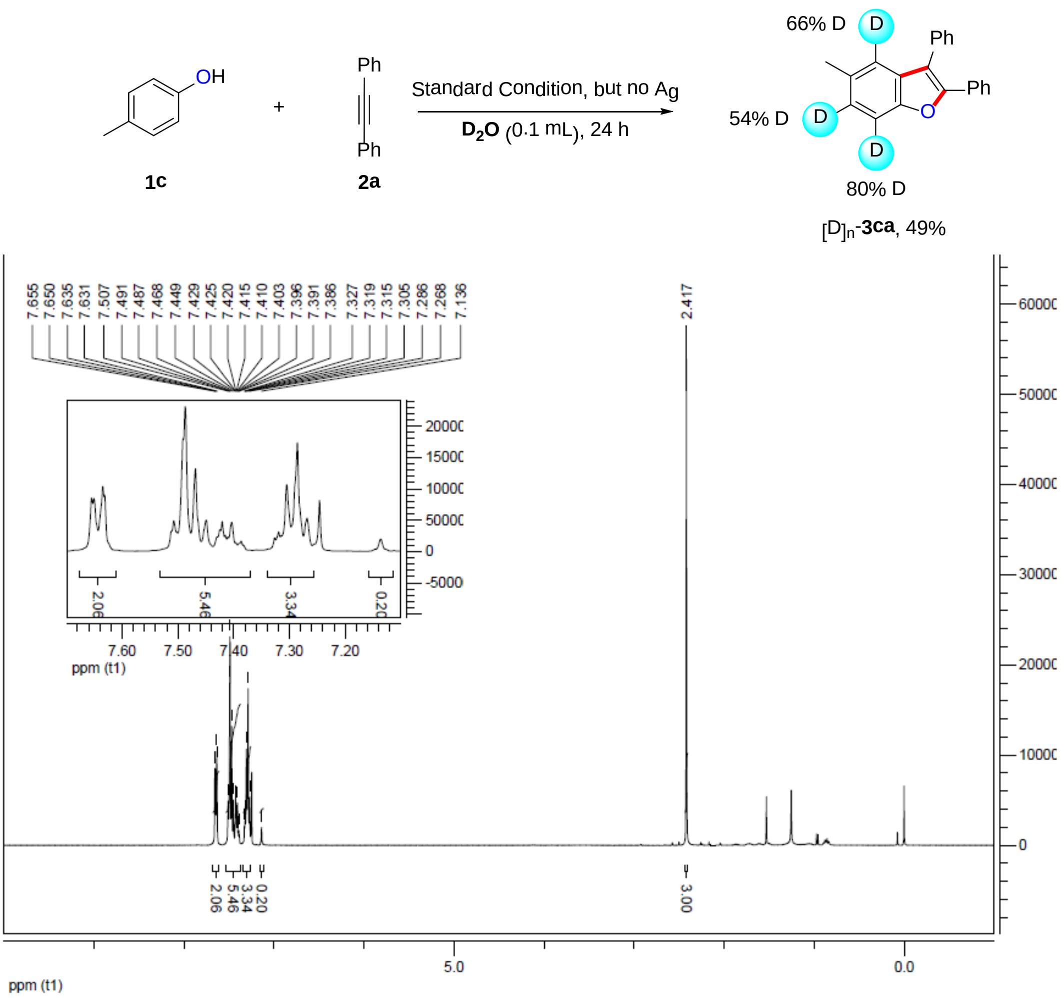
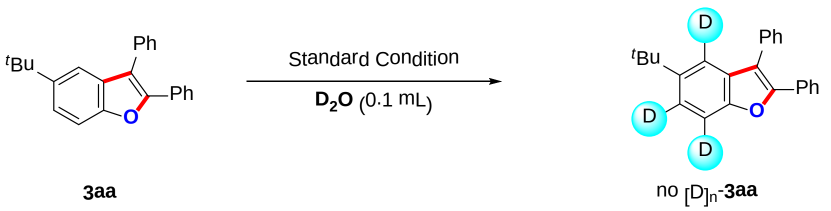


Figure 7

## General Procedures for the Deuterium-Labeling Experiment



**3aa** (0.10 mmol, 32.6 mg), [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (5 mol%, 0.005 mmol, 4.2 mg), acetanilide (0.20 equiv, 0.02 mmol, 2.7 mg), DTAC (dodecyl trimethyl ammonium chloride) (0.5 equiv, 0.05 mmol, 13.2 mg) were weighed in the air and Cu(OTf)$_2$ (1.0 equiv, 0.10 mmol, 36.2 mg), AgPF$_6$ (2.5 equiv, 0.25 mmol, 63.2 mg) were weighed in the glovebox and charged into an oven-dried 50 mL Schlenk tube. The tube was evacuated and refilled with N$_2$, which was repeated for 3 times. After addition of 0.5 mL of decalin and 0.1 mL **D$_2$O** under a positive pressure of N$_2$ *via* syringe, the sealed tube was placed in a 120 °C parallel synthesizer and stirred for 3 h. After completion, the reaction mixture was cooled down to room temperature and directly purified by flash column chromatography eluting with petroleum ether. The result showed that no detectable deuterium incorporation was observed (Figure 8).

Electronic Supplementary Material (ESI) for Chemical Science
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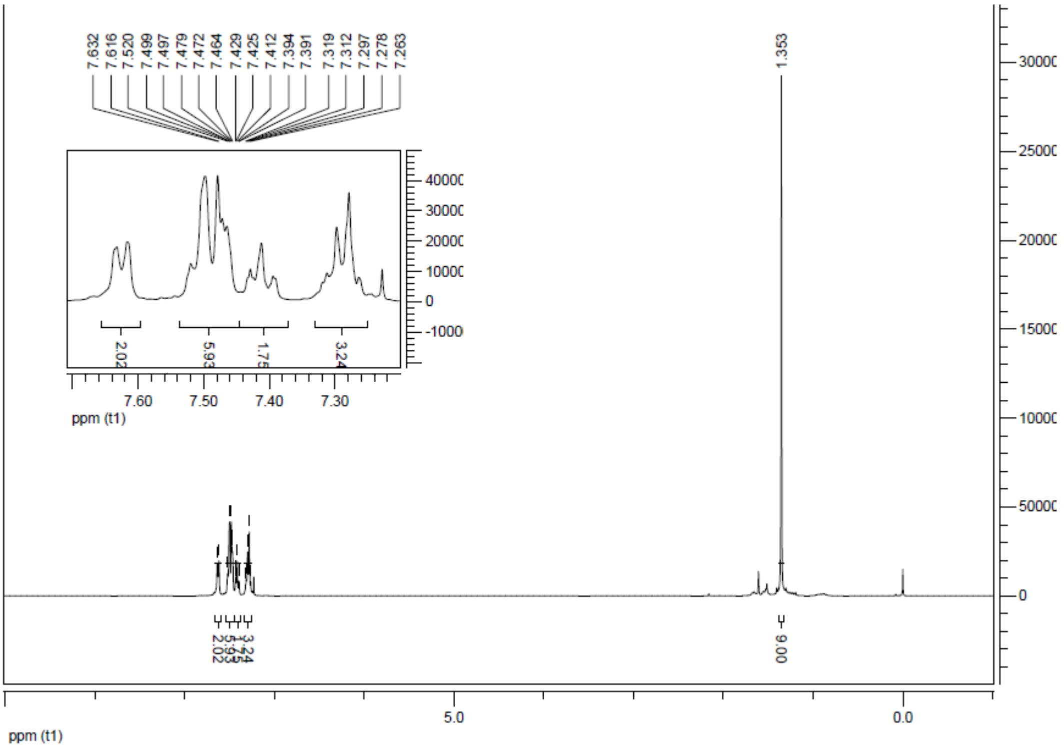
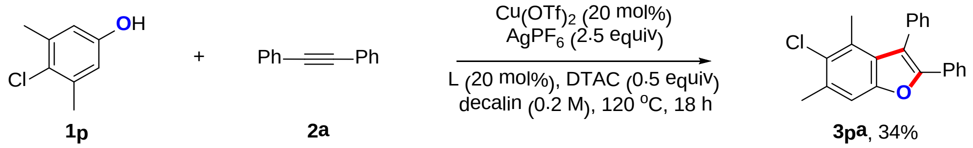


Figure 8

## Catalytic Reaction

## Gerneral Procedures for Catalytic Reaction



**1p** (0.30 mmol, 46.8 mg), diphenylacetylene **2a** (0.10 mmol, 17.8 mg), acetanilide (0.20 equiv, 0.02 mmol, 2.7 mg), DTAC (dodecyl trimethyl ammonium chloride) (0.5 equiv, 0.05 mmol, 13.2 mg) were weighed in the air and $Cu(OTf)_2$ (0.2 equiv, 0.02 mmol, 7.6 mg), $AgPF_6$ (2.5 equiv, 0.25 mmol, 63.2 mg) were weighed in the glovebox and charged into an oven-dried 50 mL Schlenk tube. The tube was evacuated and refilled with $N_2$, which was repeated for 3 times. After addition of 0.5 mL of decalin under a positive pressure of $N_2$ *via* syringe, the sealed tube was placed in a 120 $^{o}$C parallel synthesizer and stirred for 18 h. After completion, the reaction mixture was cooled down to room temperature and directly purified by flash column chromatography. 11.4 mg of **3pa** was obtained, the isolated yield was 34%.

## Control Experiment

| | |
|---|---|
| standard condition: | 82% |
| standard condition, but no Rh: | 48% |
| standard condition, but no Cu: | *n.d.* |
| standard condition, but no Ag: | 45% |

# References

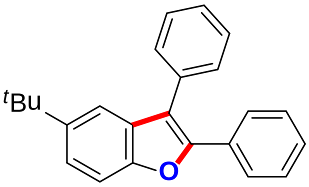
[1] Y. Li, B.-J. Li, W.-H. Wang, W.-P. Huang, X.-S. Zhang, K. Chen, Z.-J. Shi, *Angew. Chem. Int. Ed.* **2011**, *50*, 2115.

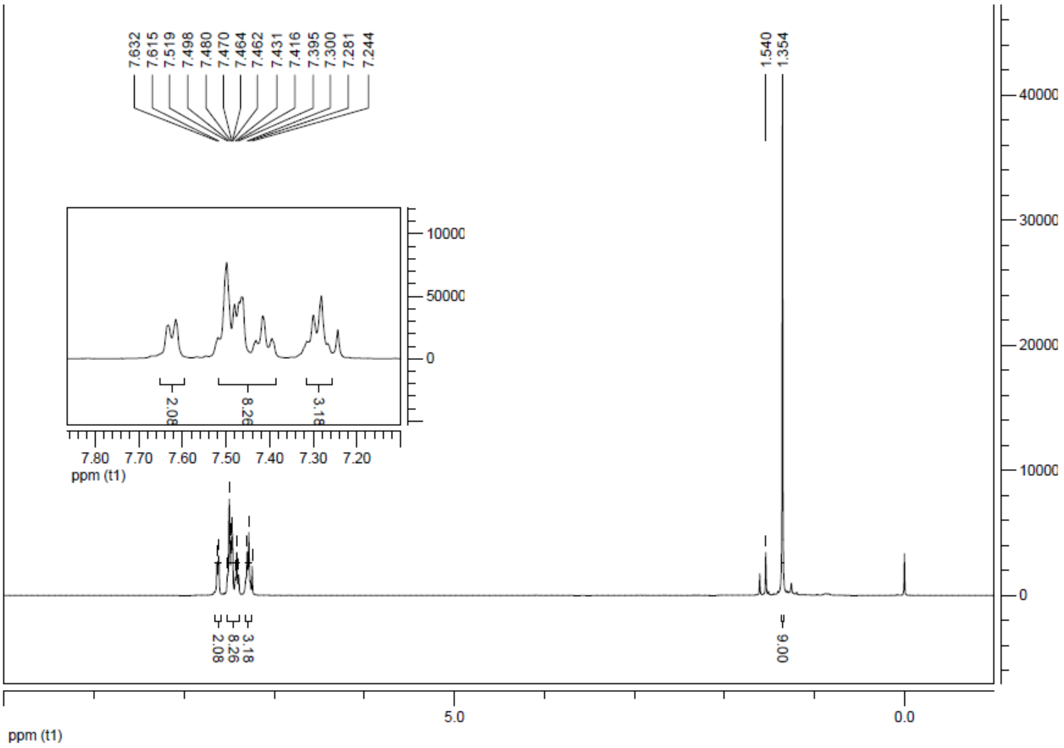
[2] M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth, P. A. Grieco, *Org. Lett.* **2002**, *4*, 3199.

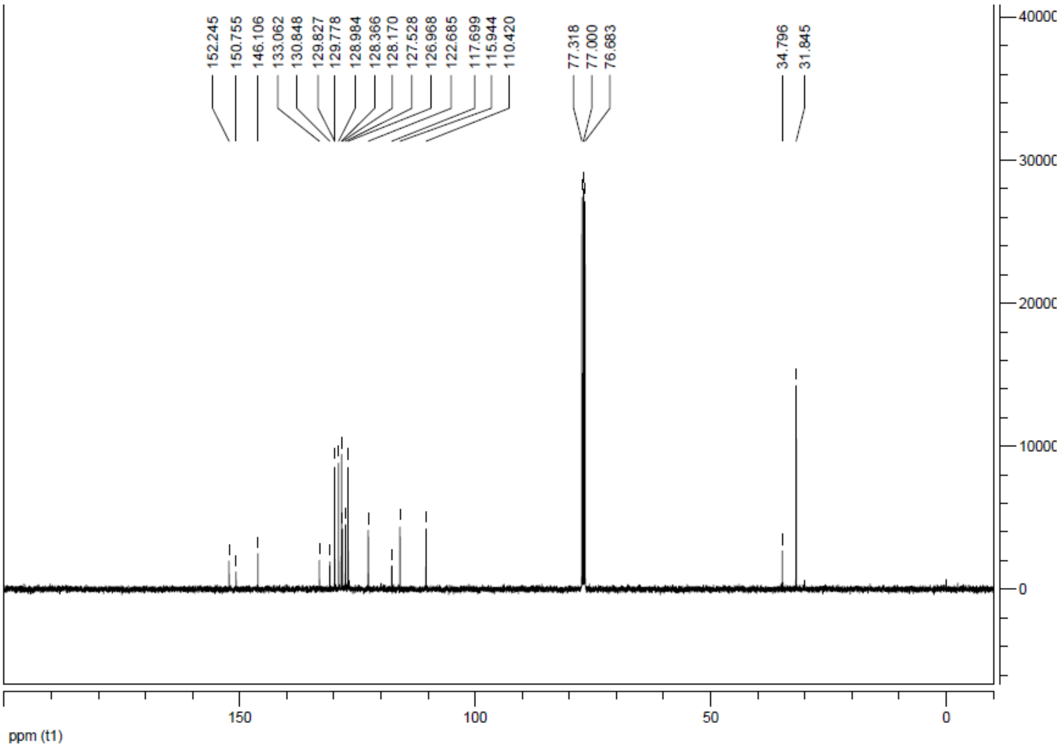
[3] S.-Y. Shi, Y.-H. Zhang, *Synlett*. **2007**, *12*, 1843.

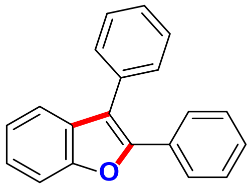
[4] G. Raffa, M. Rusch, G. Balme, N. Monteiro, *Org. Lett.* **2009**, *11*, 5254.

# $^1$H NMR and $^{13}$C NMR Spectra of Products





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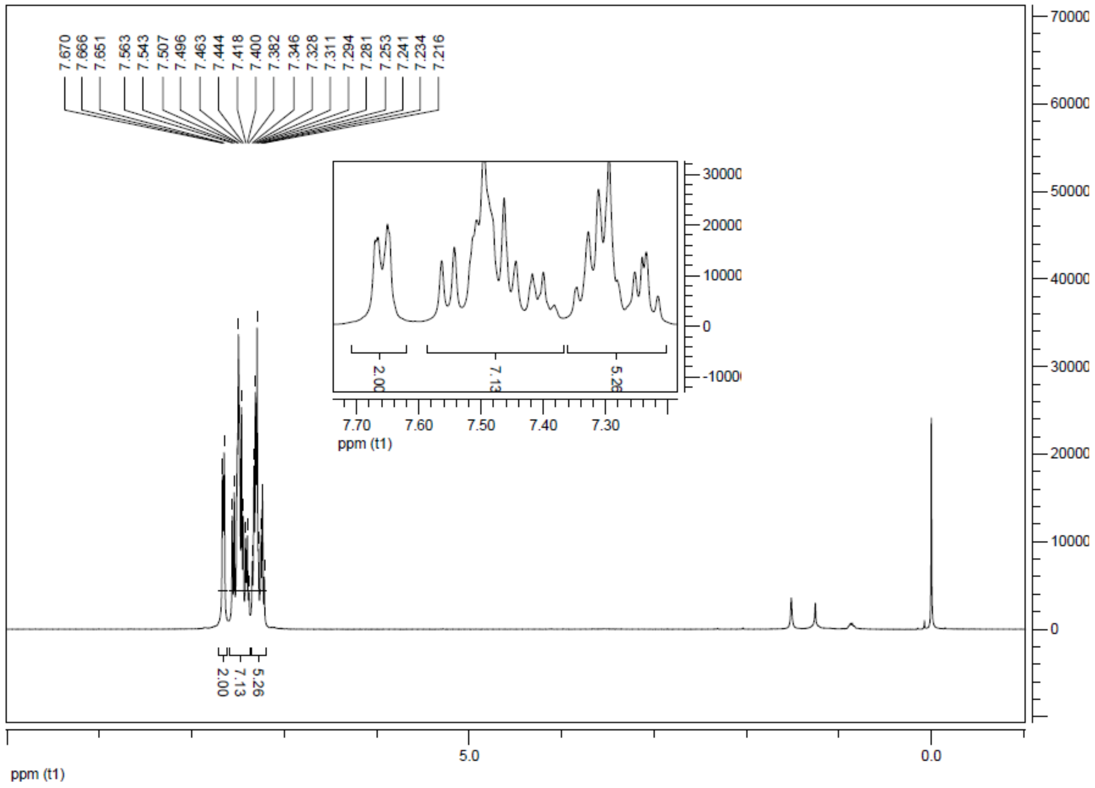
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7.328
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7.294
7.281
7.253
7.241
7.234
7.216
2.00
7.13
5.26
7.70
7.60
7.50
7.40
7.30
ppm (t1)
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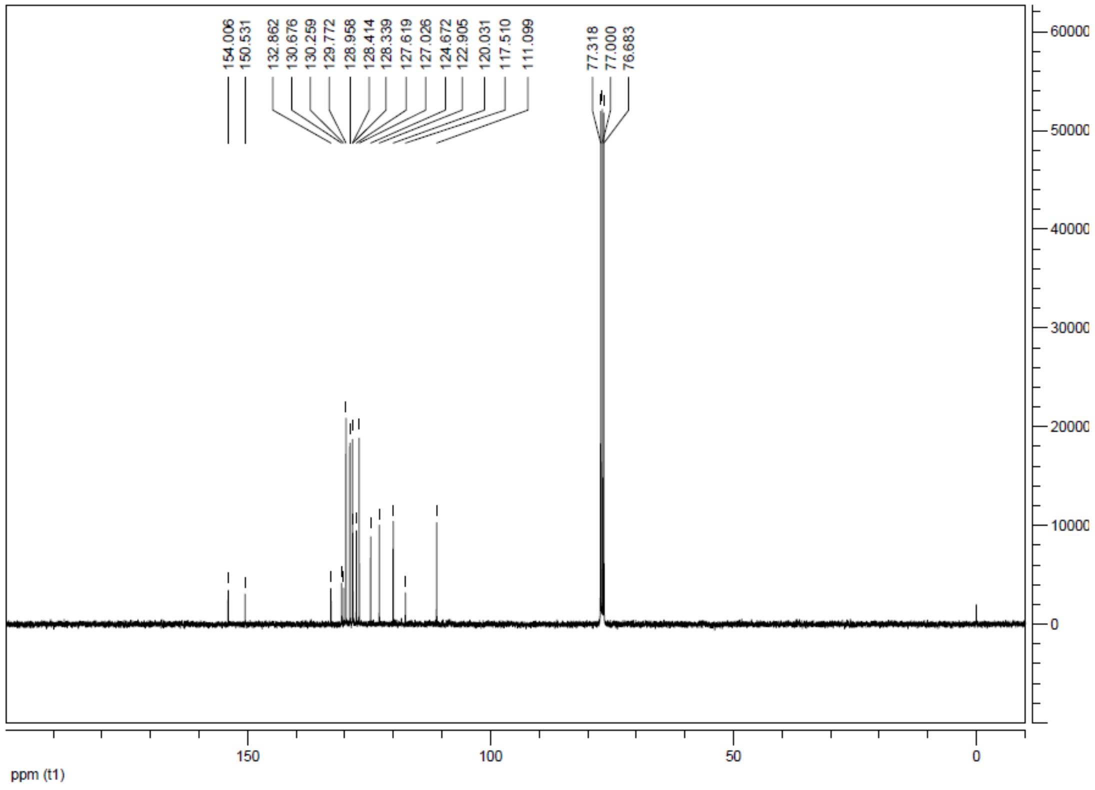
ppm (t1)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122.905
120.031
117.510
111.099
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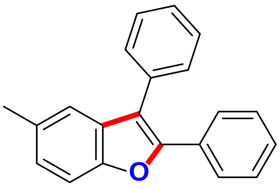
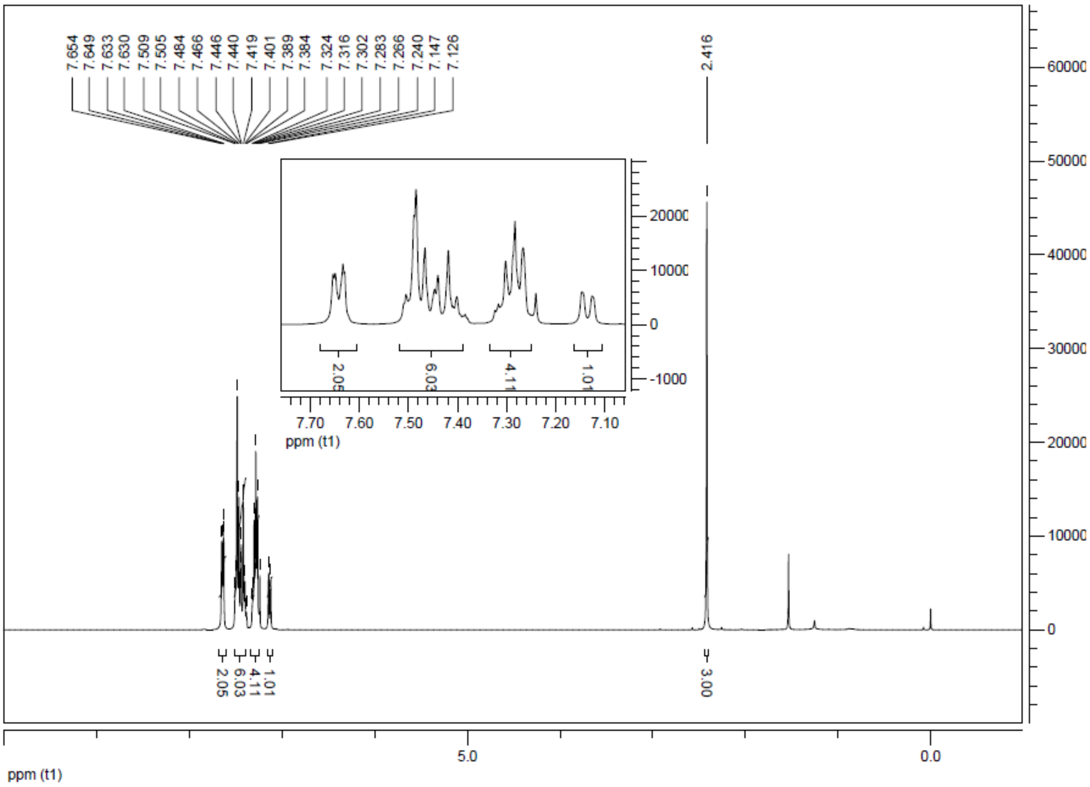
ppm (t1)


O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7.401
7.389
7.384
7.324
7.316
7.302
7.283
7.266
7.240
7.147
7.126
2.416
2.05
6.03
4.11
1.01
3.00
20000
10000
0
-1000
7.70
7.60
7.50
7.40
7.30
7.20
7.10
ppm (t1)
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40000
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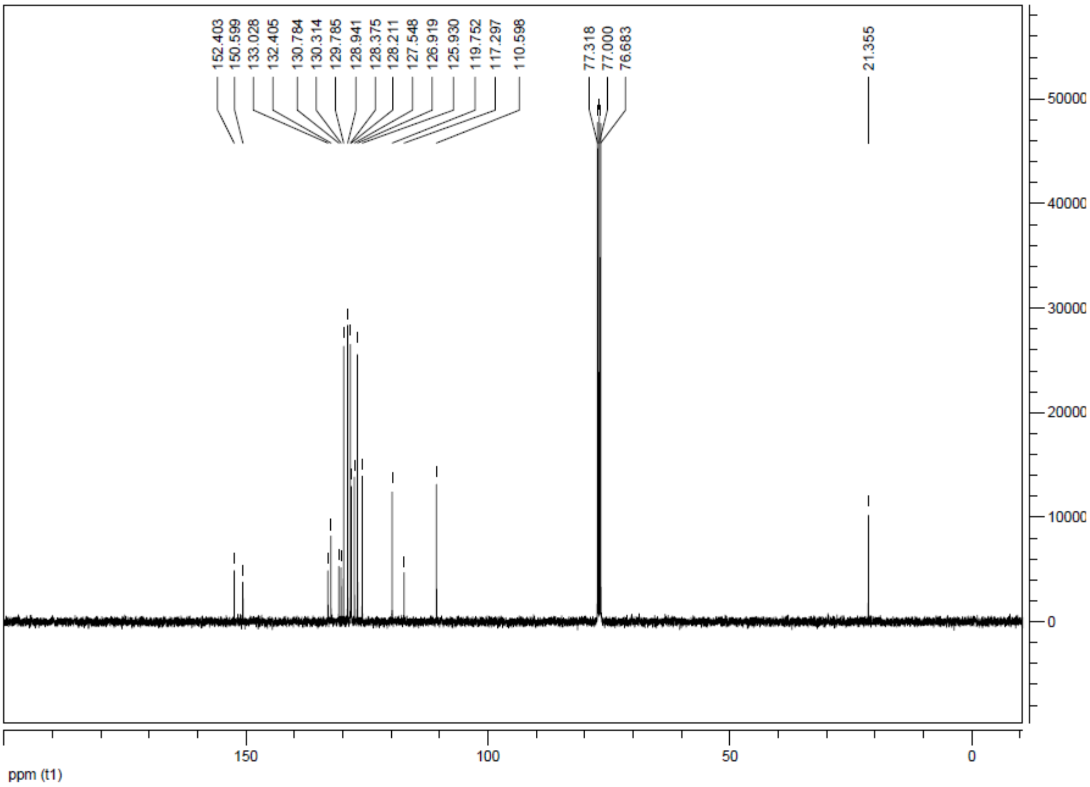
0.0
ppm (t1)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125.930
119.752
117.297
110.598
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50000
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30000
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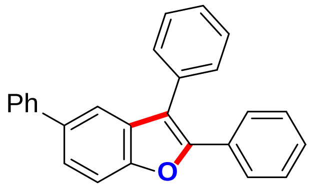
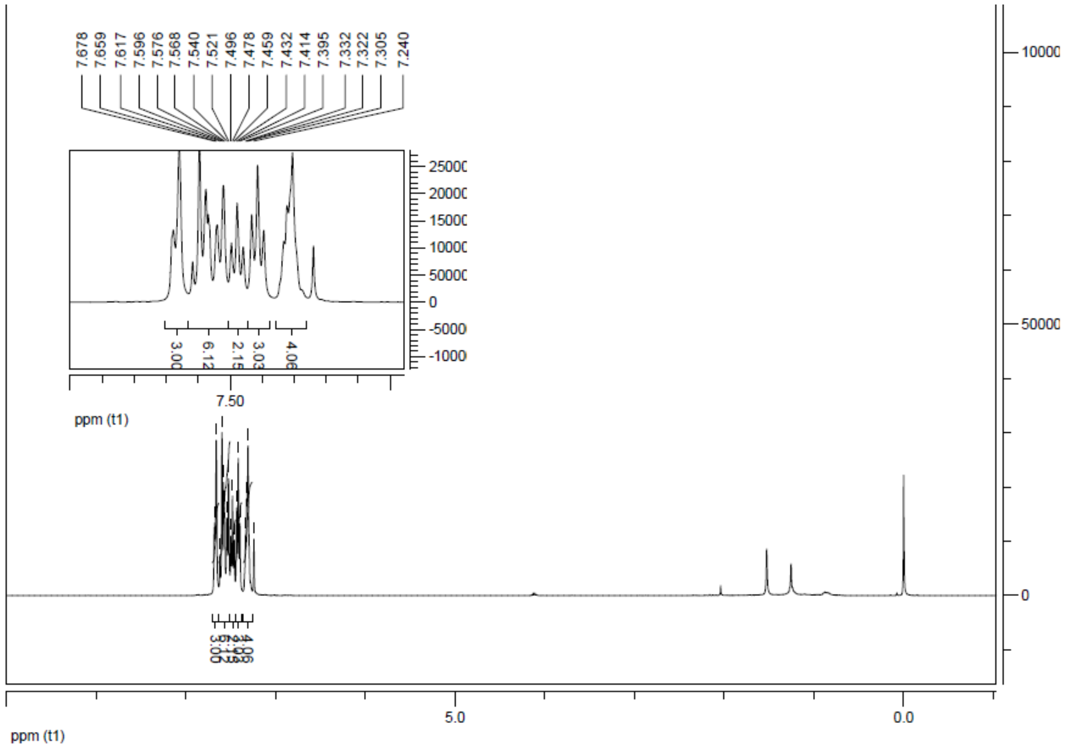
10000
0
150
100
50
0
ppm (t1)


Ph
O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7.521
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7.478
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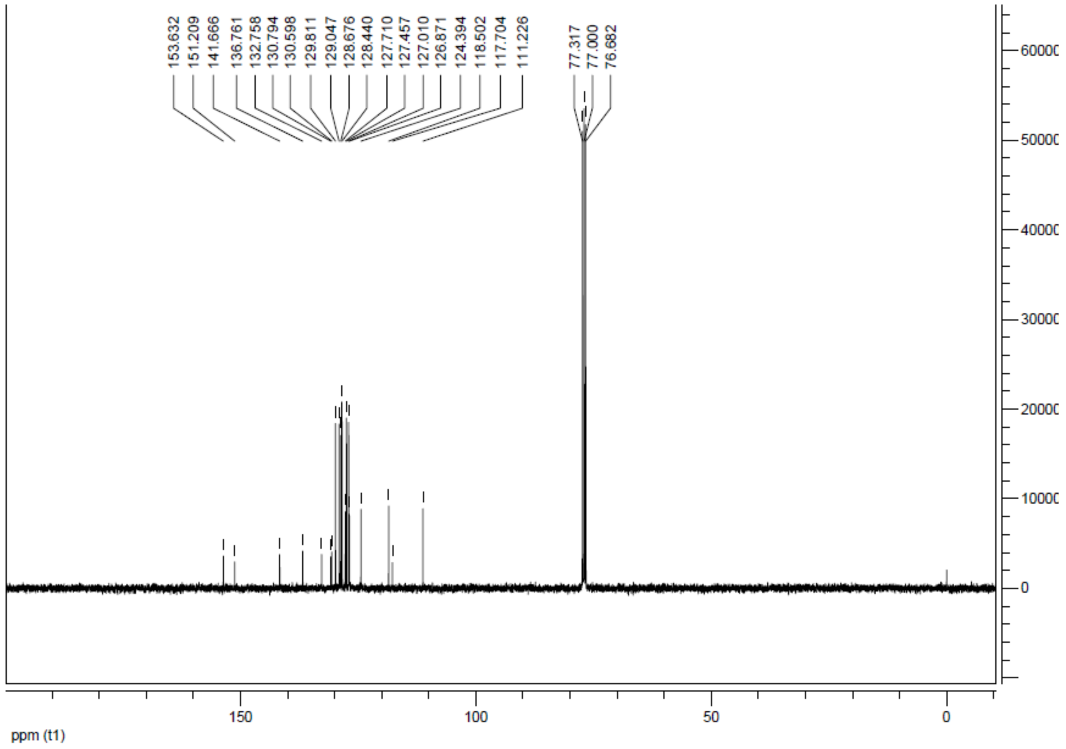
7.395
7.332
7.322
7.305
7.240
25000
20000
15000
10000
50000
0
-5000
-1000
3.00
6.12
2.15
3.03
4.06
7.50
ppm (t1)
10000
50000
0
5.0
0.0
ppm (t1)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130.598
129.811
129.047
128.676
128.440
127.710
127.457
127.010
126.871
124.394
118.502
117.704
111.226
77.317
77.000
76.682
60000
50000
40000
30000
20000
10000
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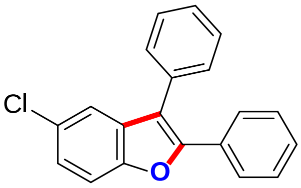
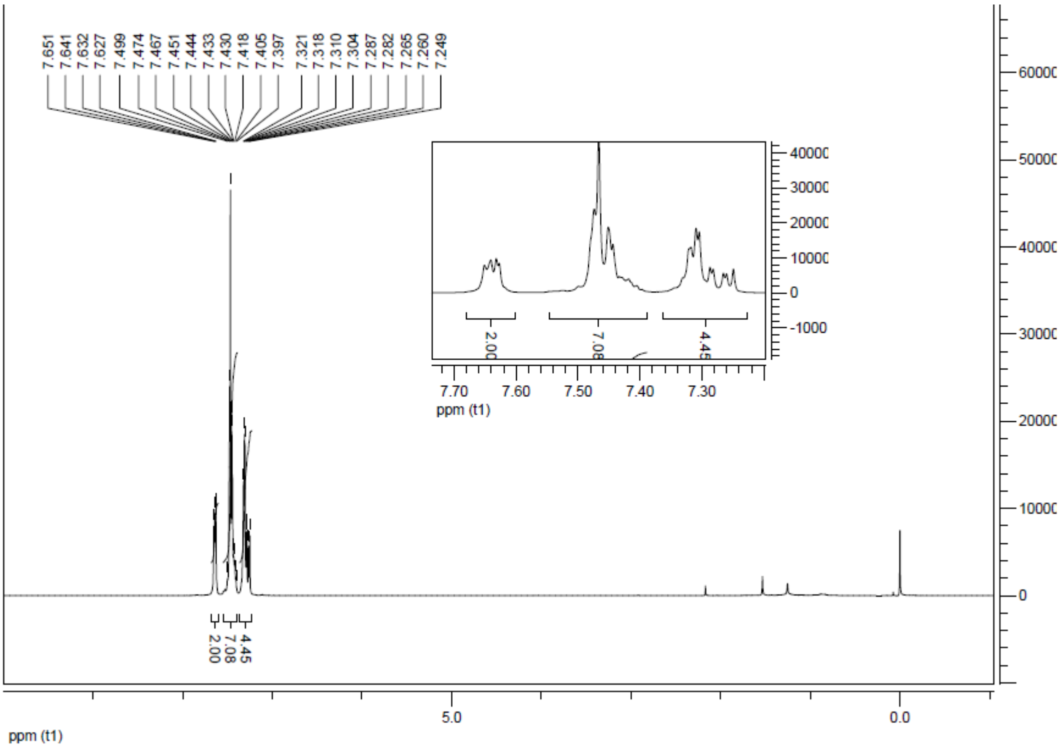
100
50
0
ppm (t1)


Cl
O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7.632
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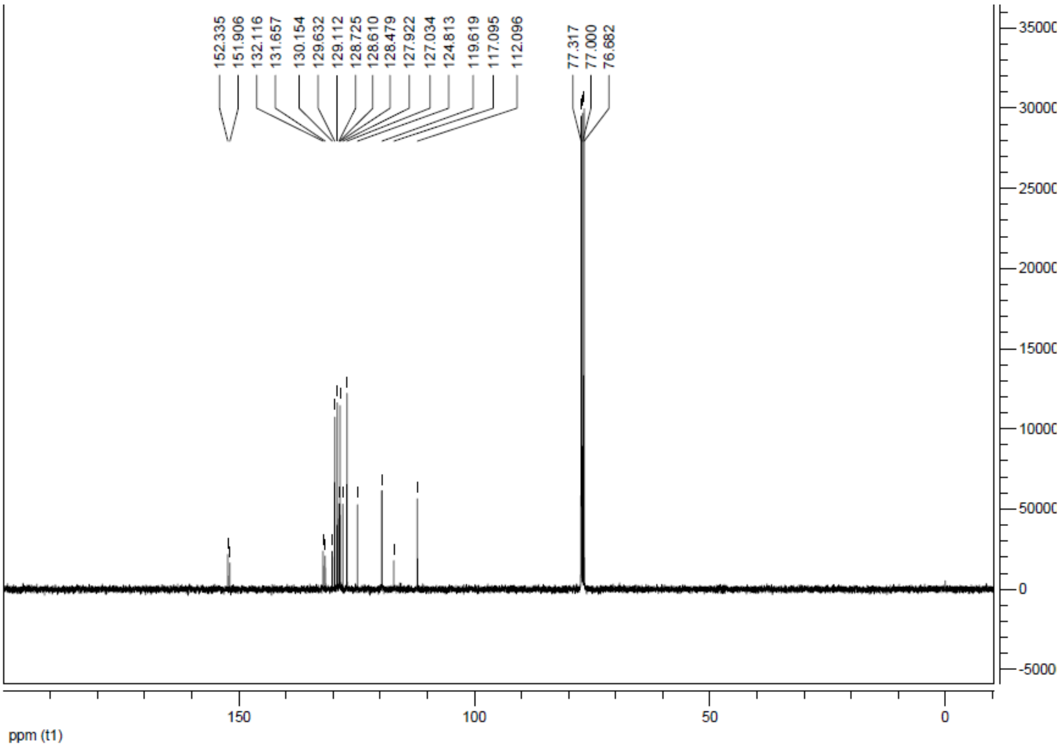
7.467
7.451
7.444
7.433
7.430
7.418
7.405
7.397
7.321
7.318
7.310
7.304
7.287
7.282
7.265
7.260
7.249
2.00
7.08
4.45
7.70
7.60
7.50
7.40
7.30
ppm (t1)
40000
30000
20000
10000
0
-1000
60000
50000
40000
30000
20000
10000
0
5.0
0.0
ppm (t1)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130.154
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129.112
128.725
128.610
128.479
127.922
127.034
124.813
119.619
117.095
112.096
77.317
77.000
76.682
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30000
25000
20000
15000
10000
50000
0
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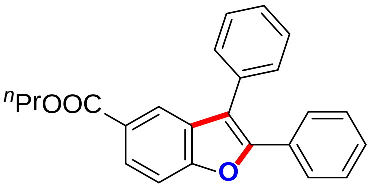
150
100
50
0
ppm (t1)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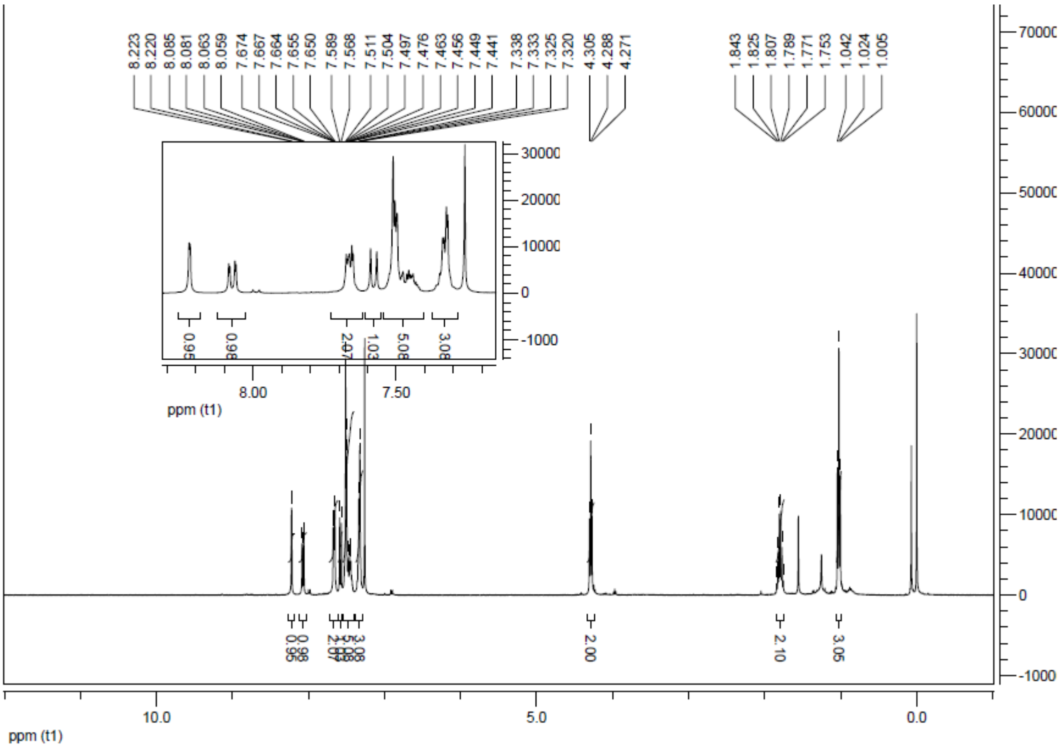
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7.667
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7.655
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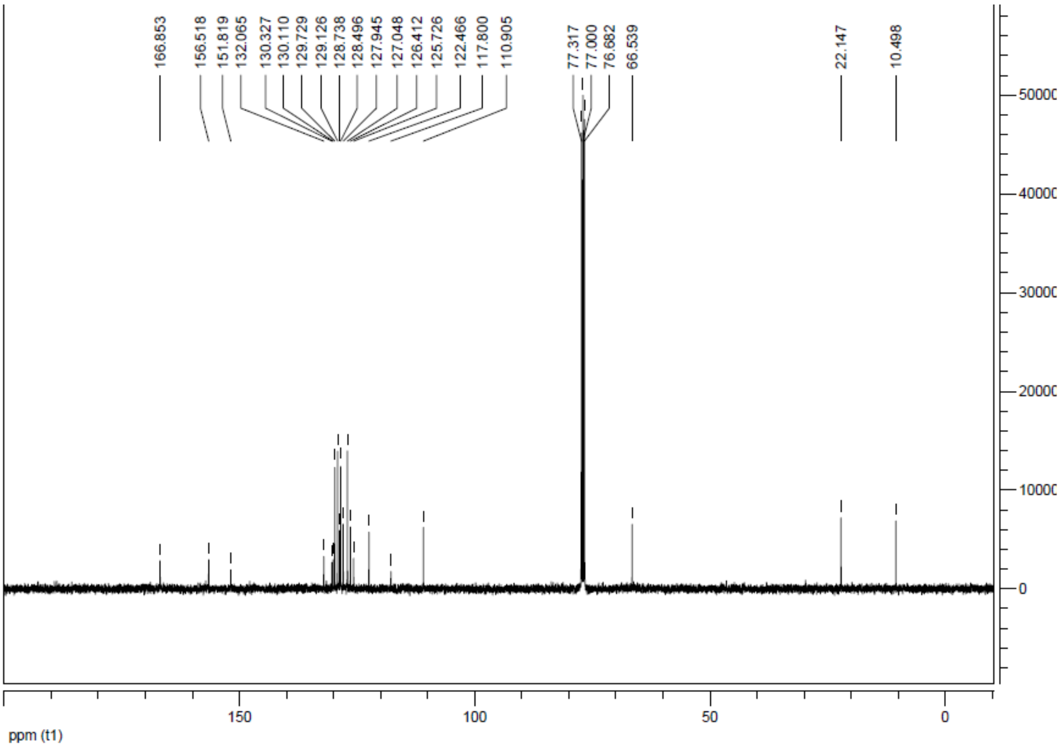
7.589
7.568
7.511
7.504
7.497
7.476
7.463
7.456
7.449
7.441
7.338
7.333
7.325
7.320
4.305
4.288
4.271
1.843
1.825
1.807
1.789
1.771
1.753
1.042
1.024
1.005
30000
20000
10000
0
-1000
0.95
0.98
2.07
1.03
5.08
3.08
8.00
7.50
ppm (t1)
70000
60000
50000
40000
30000
20000
10000
0
-1000
0.95
0.98
2.07
1.03
5.08
3.08
2.00
2.10
3.05
10.0
5.0
0.0
ppm (t1)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156.518
151.819
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129.126
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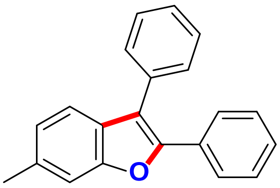
128.496
127.945
127.048
126.412
125.726
122.466
117.800
110.905
77.317
77.000
76.682
66.539
22.147
10.498
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)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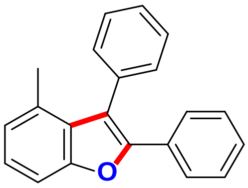
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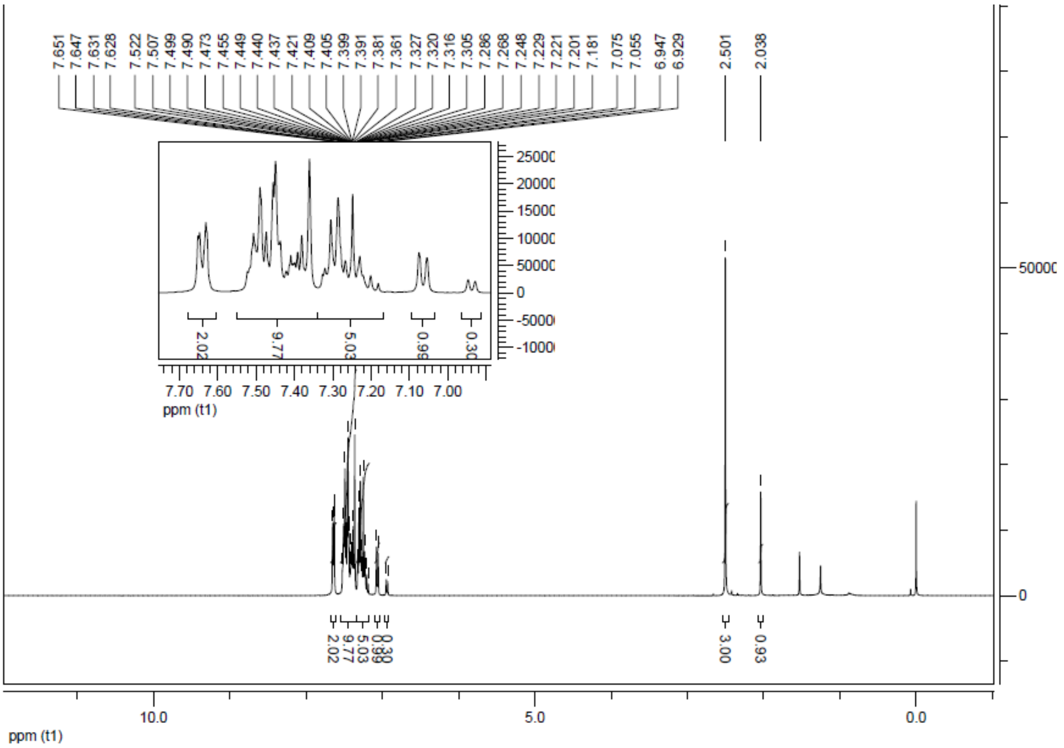
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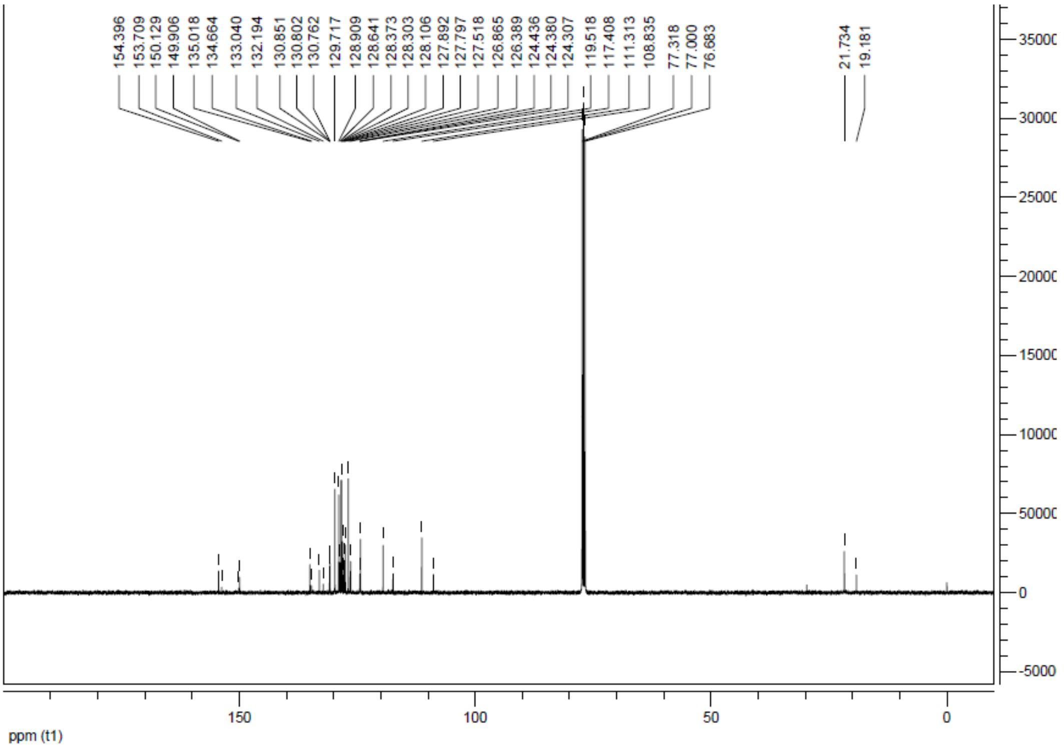
7.631
7.628
7.522
7.507
7.499
7.490
7.473
7.455
7.449
7.440
7.437
7.421
7.409
7.405
7.399
7.391
7.381
7.361
7.327
7.320
7.316
7.305
7.286
7.268
7.248
7.229
7.221
7.201
7.181
7.075
7.055
6.947
6.929
2.501
2.038
25000
20000
15000
10000
50000
0
-5000
-1000
2.02
9.77
5.03
0.99
0.30
7.70 7.60 7.50 7.40 7.30 7.20 7.10 7.00
ppm (t1)
50000
0
3.00
0.93
10.0
5.0
0.0
ppm (t1)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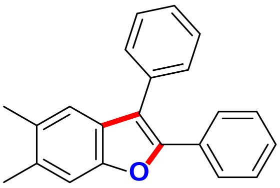
153.709
150.129
149.906
135.018
134.664
133.040
132.194
130.851
130.802
130.762
129.717
128.909
128.641
128.373
128.303
128.106
127.892
127.797
127.518
126.865
126.389
124.436
124.380
124.307
119.518
117.408
111.313
108.835
77.318
77.000
76.683
21.734
19.181
35000
30000
25000
20000
15000
10000
50000
0
-5000
150
100
50
0
ppm (t1)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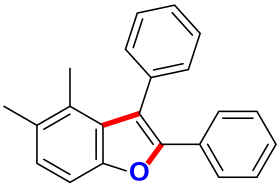
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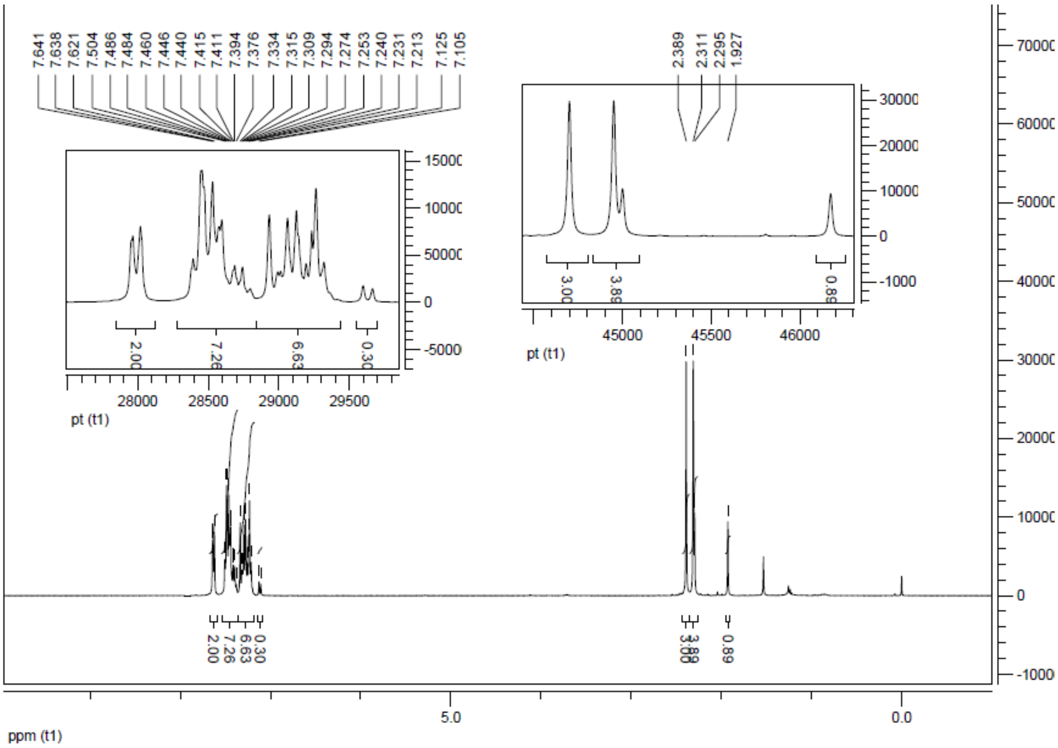
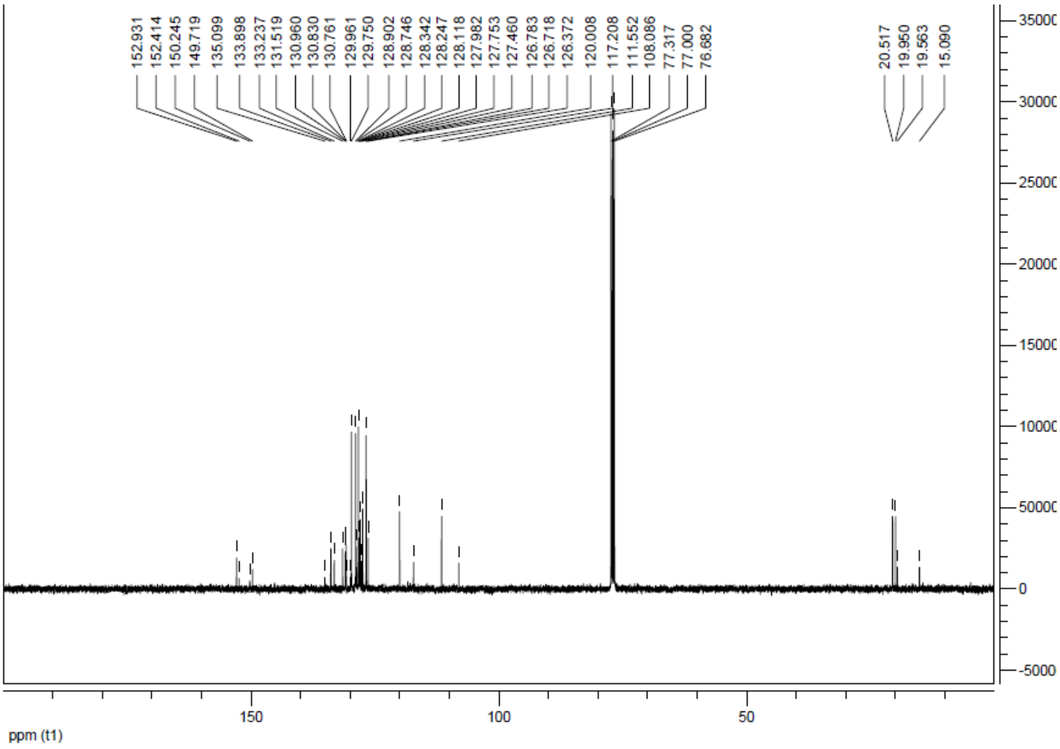

7.641
7.638
7.621
7.504
7.486
7.484
7.460
7.446
7.440
7.415
7.411
7.394
7.376
7.334
7.315
7.309
7.294
7.274
7.253
7.240
7.231
7.213
7.125
7.105
2.389
2.311
2.295
1.927
2.00
7.26
6.63
0.30
3.00
3.89
0.89
28000
28500
29000
29500
pt (t1)
45000
45500
46000
pt (t1)
5.0
0.0
ppm (t1)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152.414
150.245
149.719
135.099
133.898
133.237
131.519
130.960
130.830
130.761
129.961
129.750
128.902
128.746
128.342
128.247
128.118
127.982
127.753
127.460
126.783
126.718
126.372
120.008
117.208
111.552
108.086
77.317
77.000
76.682
20.517
19.950
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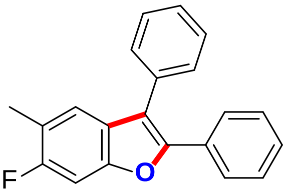
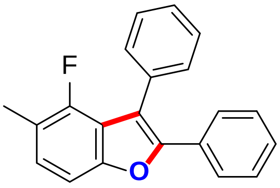
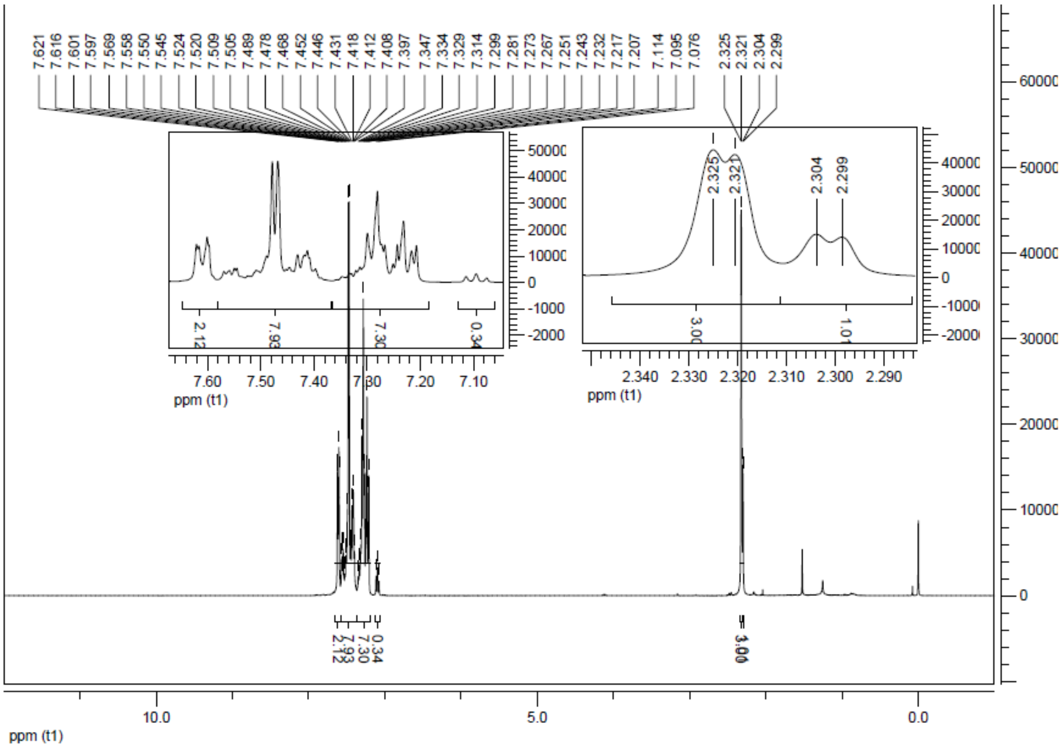
15.090
150
100
50
ppm (t1)


F
O


F
O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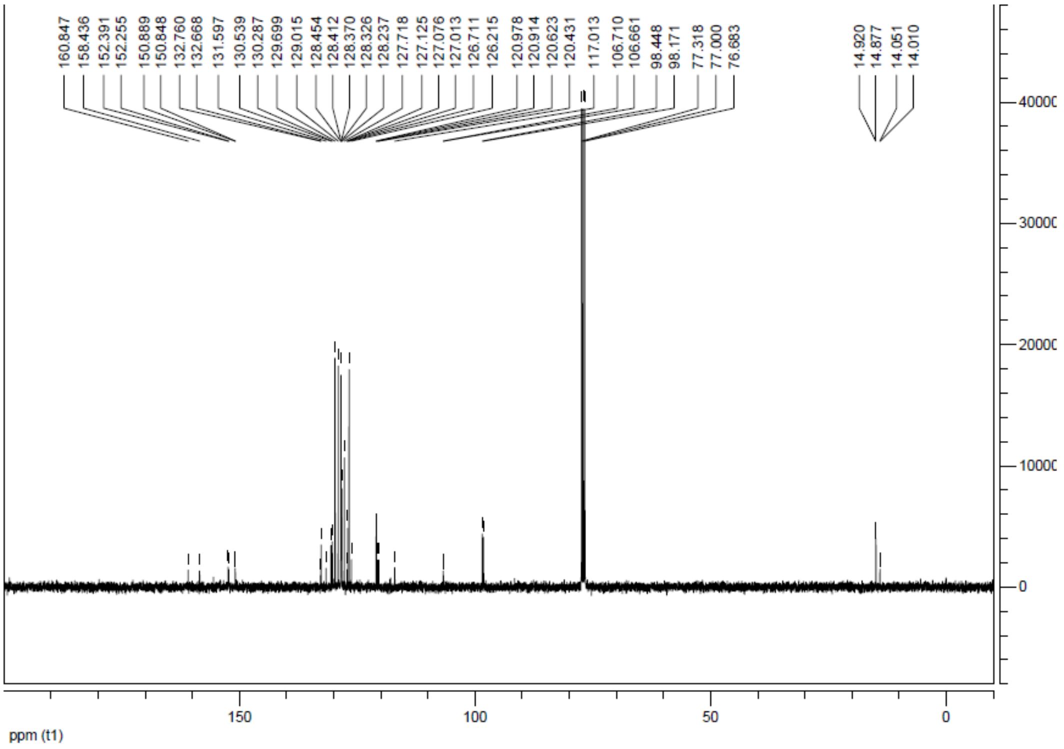
7.616
7.601
7.597
7.569
7.558
7.550
7.545
7.524
7.520
7.509
7.505
7.489
7.478
7.468
7.452
7.446
7.431
7.418
7.412
7.408
7.397
7.347
7.334
7.329
7.314
7.299
7.281
7.273
7.267
7.251
7.243
7.232
7.217
7.207
7.114
7.095
7.076
2.325
2.321
2.304
2.299
2.12
7.93
7.30
0.34
3.00
1.01
ppm (t1)
10.0
5.0
0.0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150.889
150.848
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130.539
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129.699
129.015
128.454
128.412
128.370
128.326
128.237
127.718
127.125
127.076
127.013
126.711
126.215
120.978
120.914
120.623
120.431
117.013
106.710
106.661
98.448
98.171
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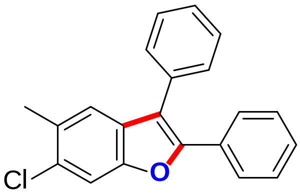
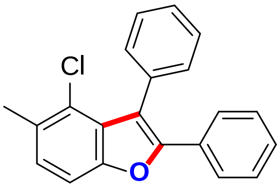
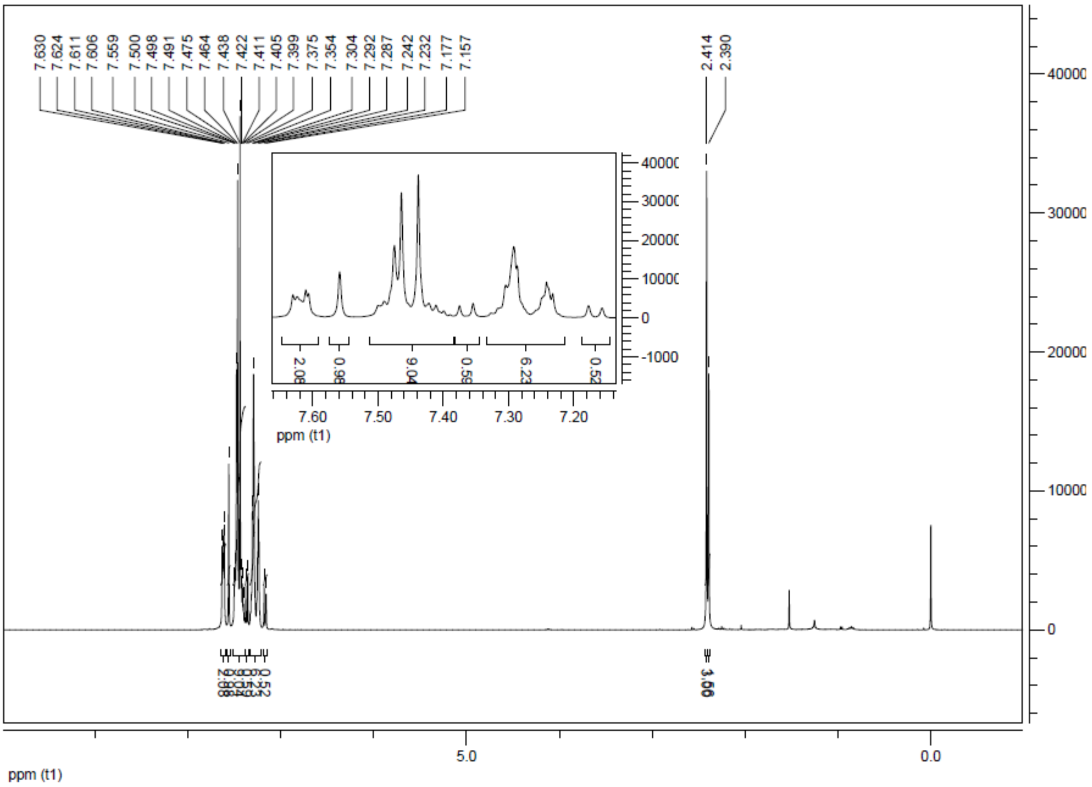
77.000
76.683
14.920
14.877
14.051
14.010
ppm (t1)
150
100
50
0


Cl
O


Cl
O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7.624
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7.606
7.559
7.500
7.498
7.491
7.475
7.464
7.438
7.422
7.411
7.405
7.399
7.375
7.354
7.304
7.292
7.287
7.242
7.232
7.177
7.157
2.414
2.390
2.08
0.98
9.04
0.59
6.23
0.52
3.66
7.60
7.50
7.40
7.30
7.20
ppm (t1)
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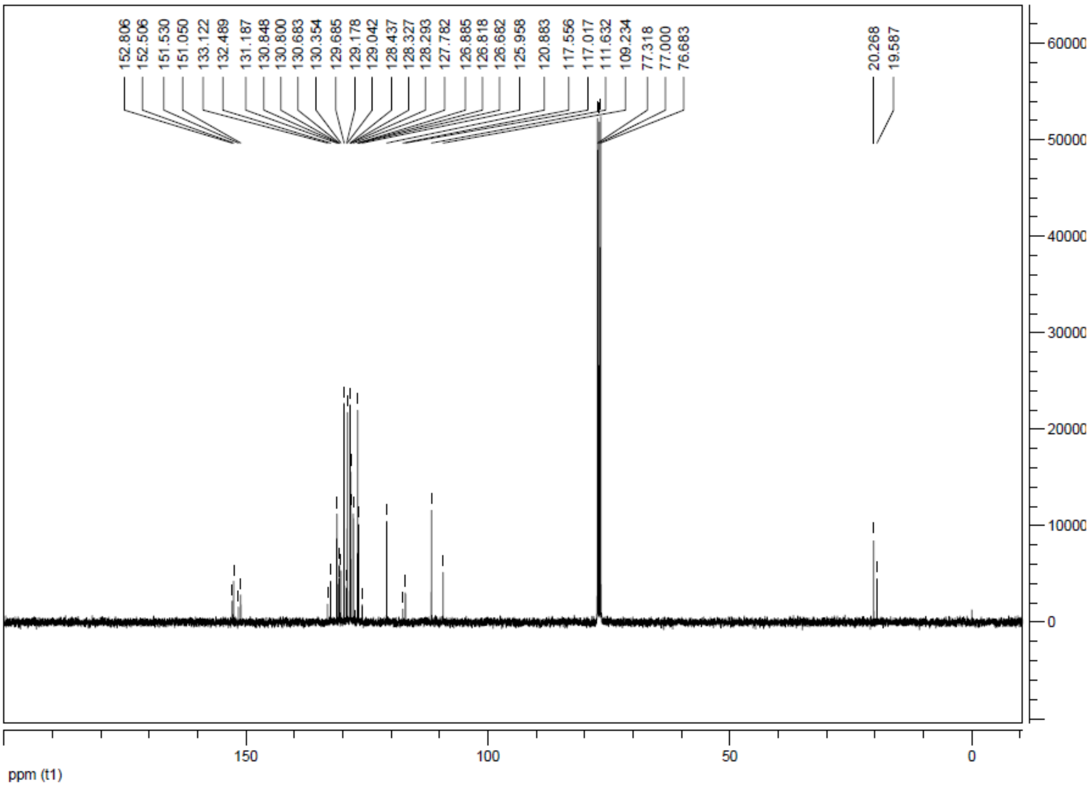
30000
20000
10000
0
-1000
5.0
0.0
ppm (t1)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151.530
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131.187
130.848
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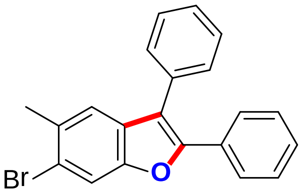
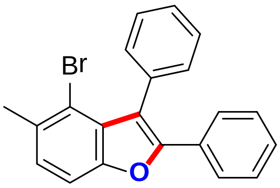
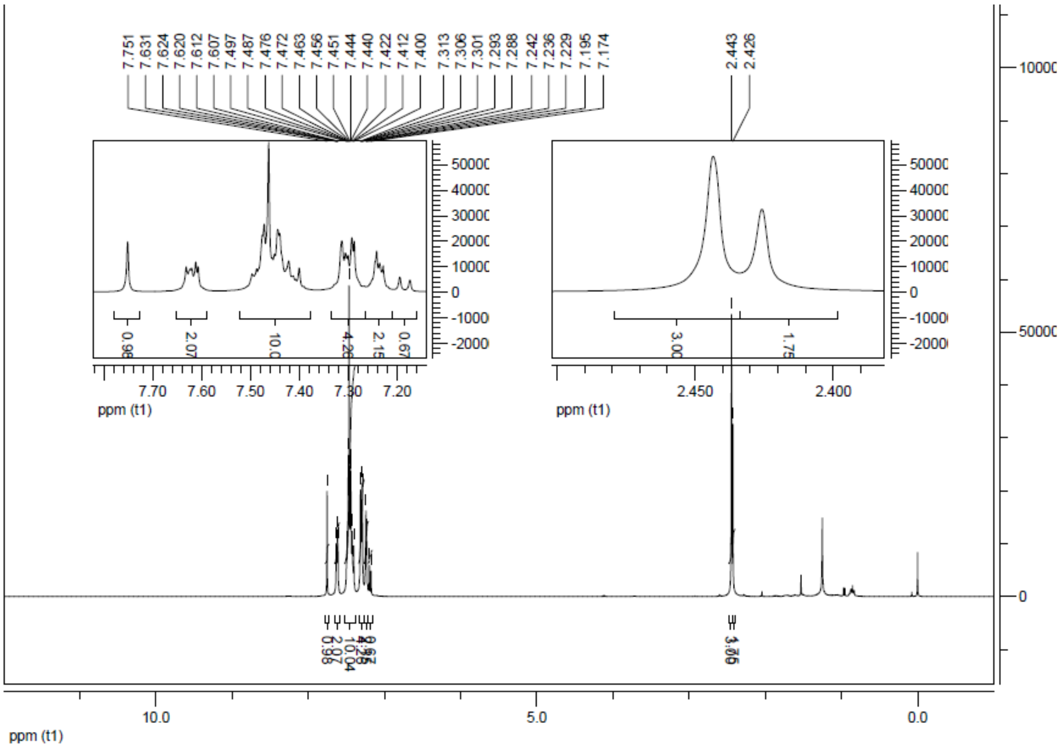
130.683
130.354
129.685
129.178
129.042
128.437
128.327
128.293
127.782
126.885
126.818
126.682
125.958
120.883
117.556
117.017
111.632
109.234
77.318
77.000
76.683
20.268
19.587
60000
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)


Br
O


Br
O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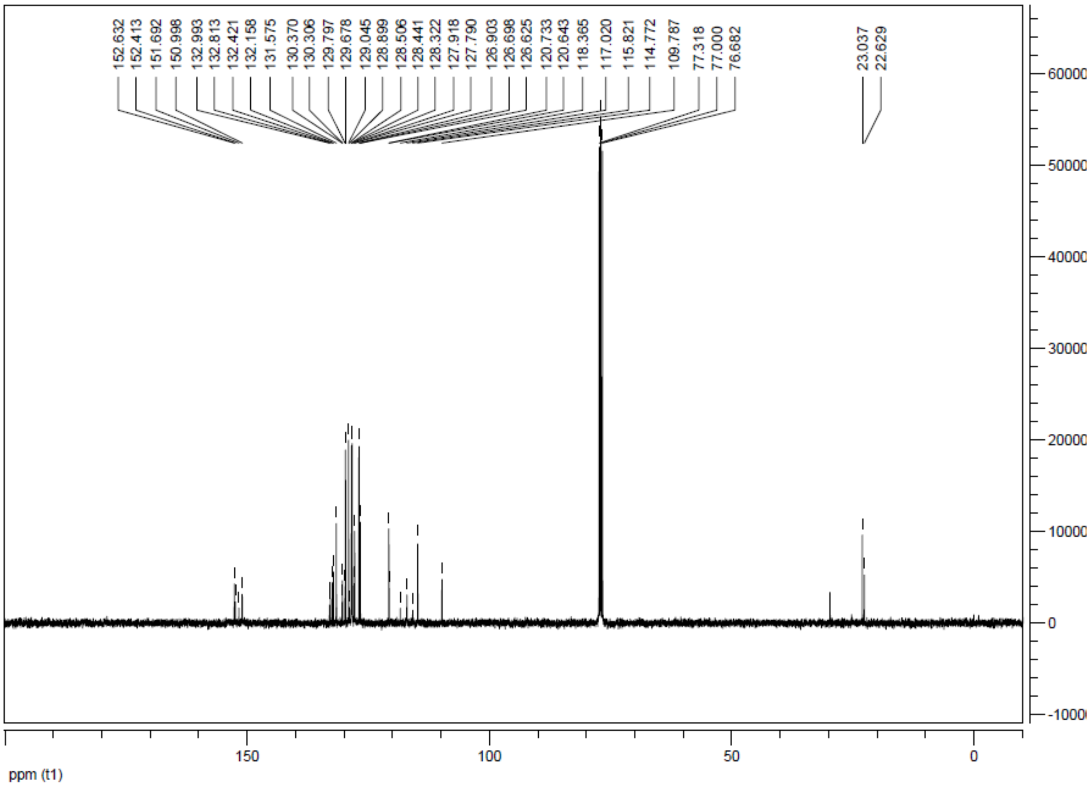
7.472
7.463
7.456
7.451
7.444
7.440
7.422
7.412
7.400
7.313
7.306
7.301
7.293
7.288
7.242
7.236
7.229
7.195
7.174
2.443
2.426
0.98
2.07
10.0
4.26
2.15
0.67
3.00
1.75
7.70
7.60
7.50
7.40
7.30
7.20
2.450
2.400
ppm (t1)
10.0
5.0
0.0
ppm (t1)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152.413
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150.998
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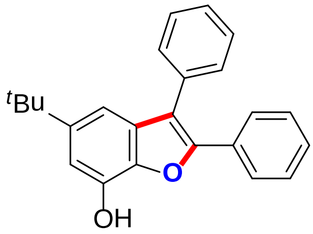
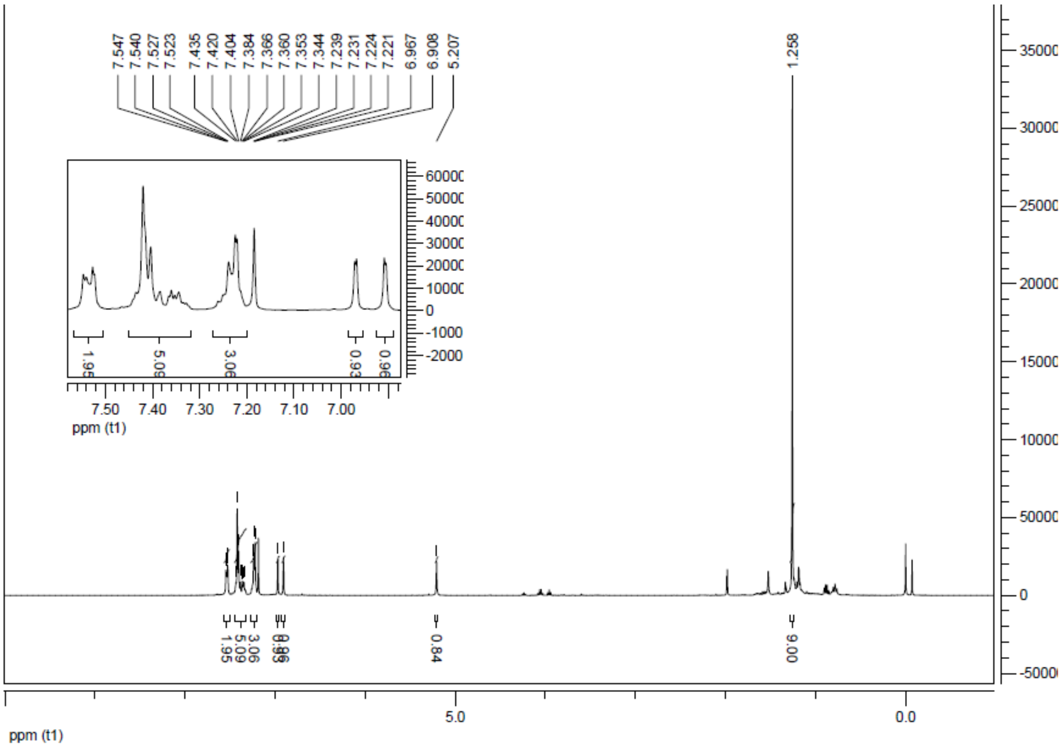
132.813
132.421
132.158
131.575
130.370
130.306
129.797
129.678
129.045
128.899
128.506
128.441
128.322
127.918
127.790
126.903
126.698
126.625
120.733
120.643
118.365
117.020
115.821
114.772
109.787
77.318
77.000
76.682
23.037
22.629
150
100
50
0
ppm (t1)


$^t$Bu
O
OH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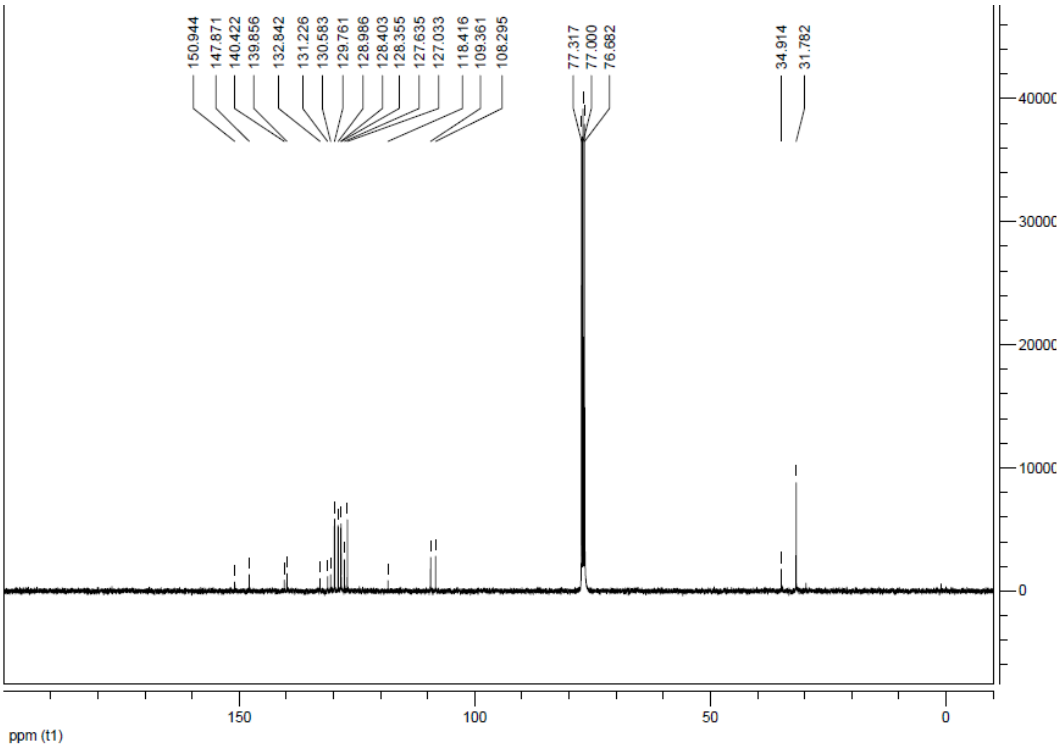
7.527
7.523
7.435
7.420
7.404
7.384
7.366
7.360
7.353
7.344
7.239
7.231
7.224
7.221
6.967
6.908
5.207
1.258
1.95
5.09
3.06
0.93
0.96
0.84
9.00
7.50
7.40
7.30
7.20
7.10
7.00
ppm (t1)
5.0
0.0
ppm (t1)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129.761
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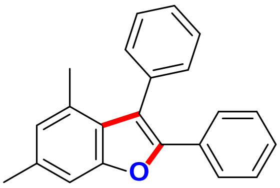
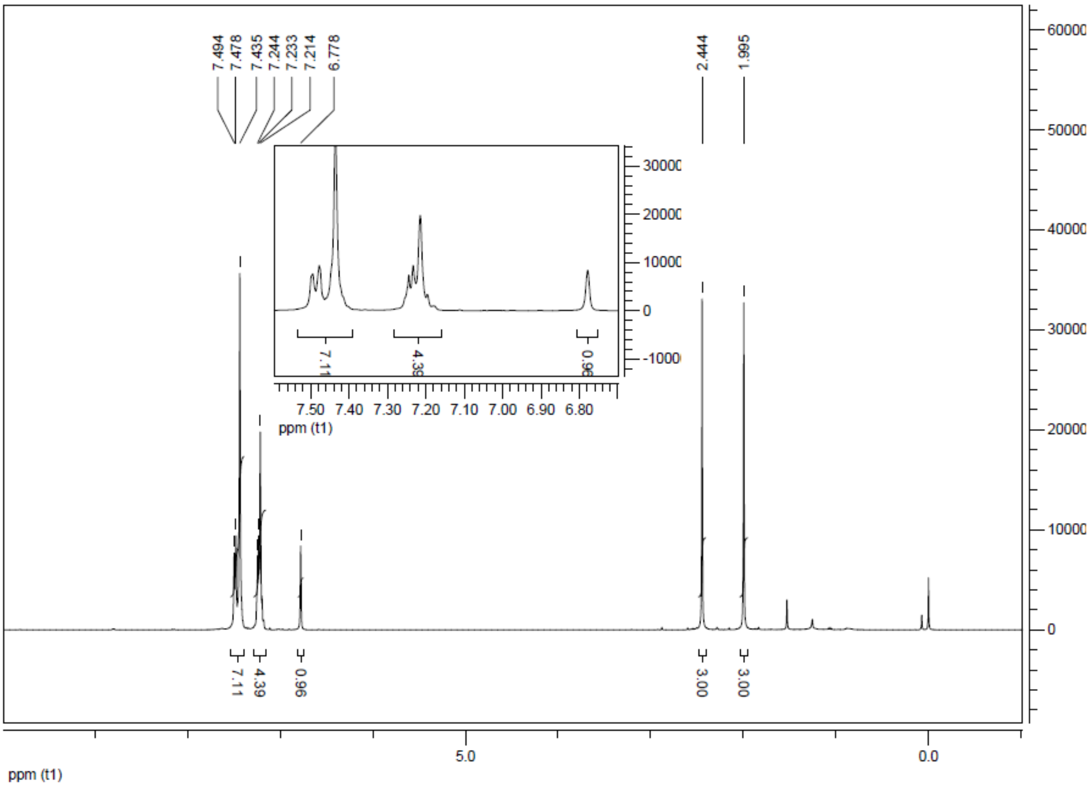
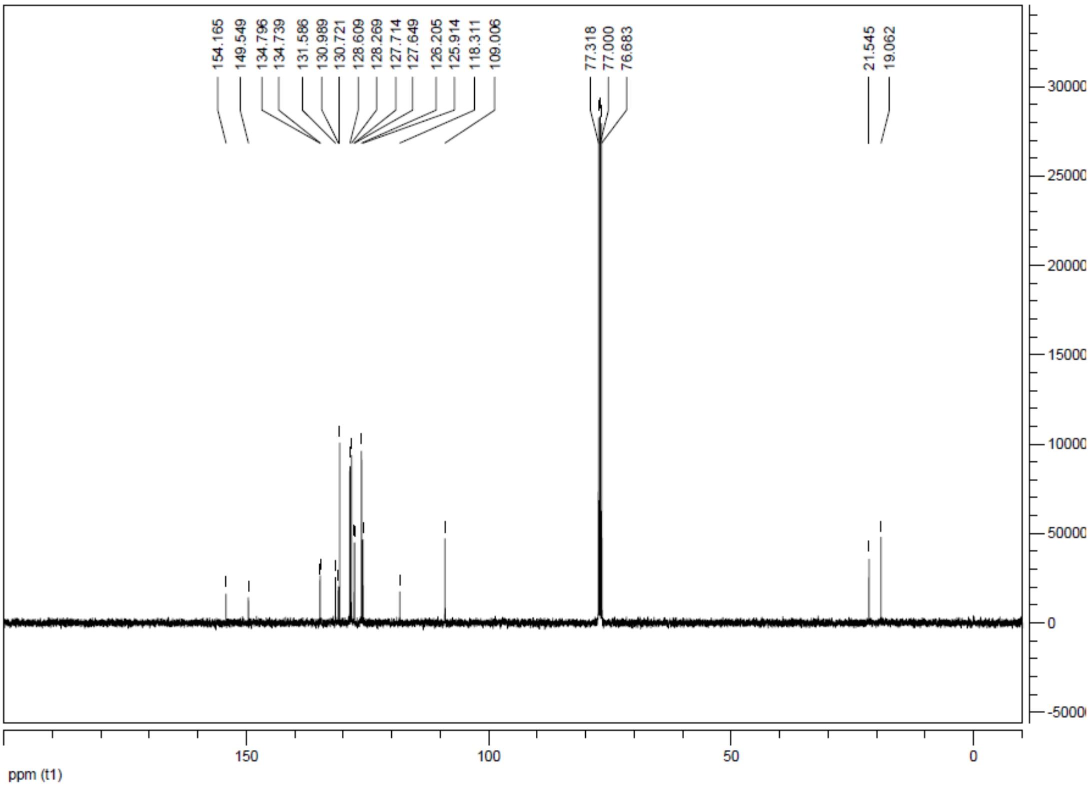
128.403
128.355
127.635
127.033
118.416
109.361
108.295
77.317
77.000
76.682
34.914
31.782
150
100
50
0
ppm (t1)


O


7.494
7.478
7.435
7.244
7.233
7.214
6.778
2.444
1.995
7.11
4.39
0.96
3.00
3.00
7.50 7.40 7.30 7.20 7.10 7.00 6.90 6.80
ppm (t1)
30000
20000
10000
0
-1000
60000
50000
40000
30000
20000
10000
0
5.0
0.0
ppm (t1)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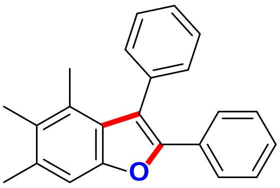
130.721
128.609
128.269
127.714
127.649
126.205
125.914
118.311
109.006
77.318
77.000
76.683
21.545
19.062
30000
25000
20000
15000
10000
50000
0
-5000
150
100
50
0
ppm (t1)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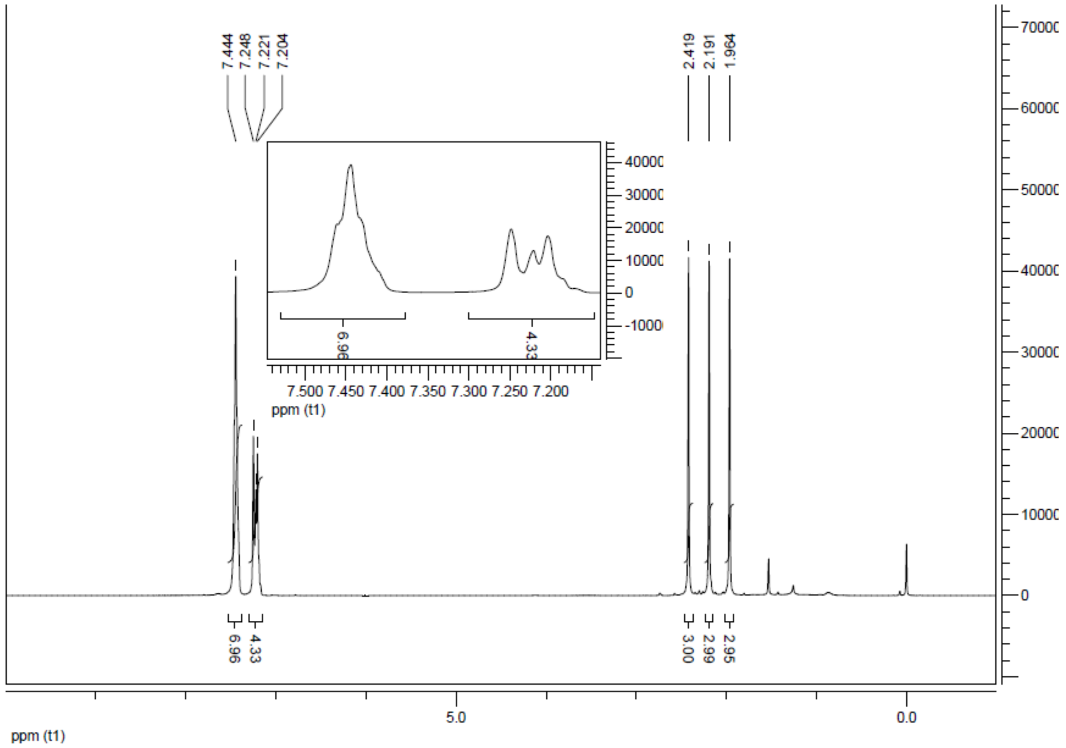
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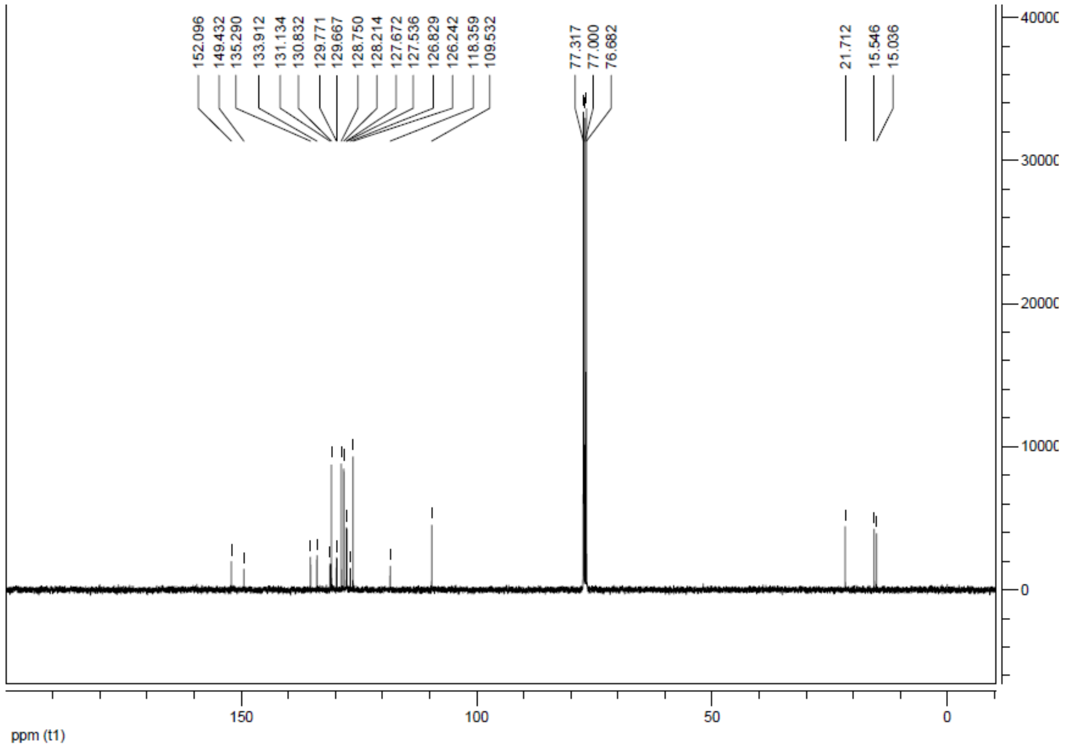
7.248
7.221
7.204
2.419
2.191
1.964
6.96
4.33
3.00
2.99
2.95
7.500 7.450 7.400 7.350 7.300 7.250 7.200
ppm (t1)
40000
30000
20000
10000
0
-1000
70000
60000
50000
40000
30000
20000
10000
0
5.0
0.0
ppm (t1)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131.134
130.832
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129.667
128.750
128.214
127.672
127.536
126.829
126.242
118.359
109.532
77.317
77.000
76.682
21.712
15.546
15.036
40000
30000
20000
10000
0
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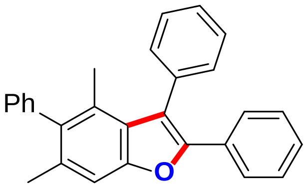
100
50
0
ppm (t1)


Ph
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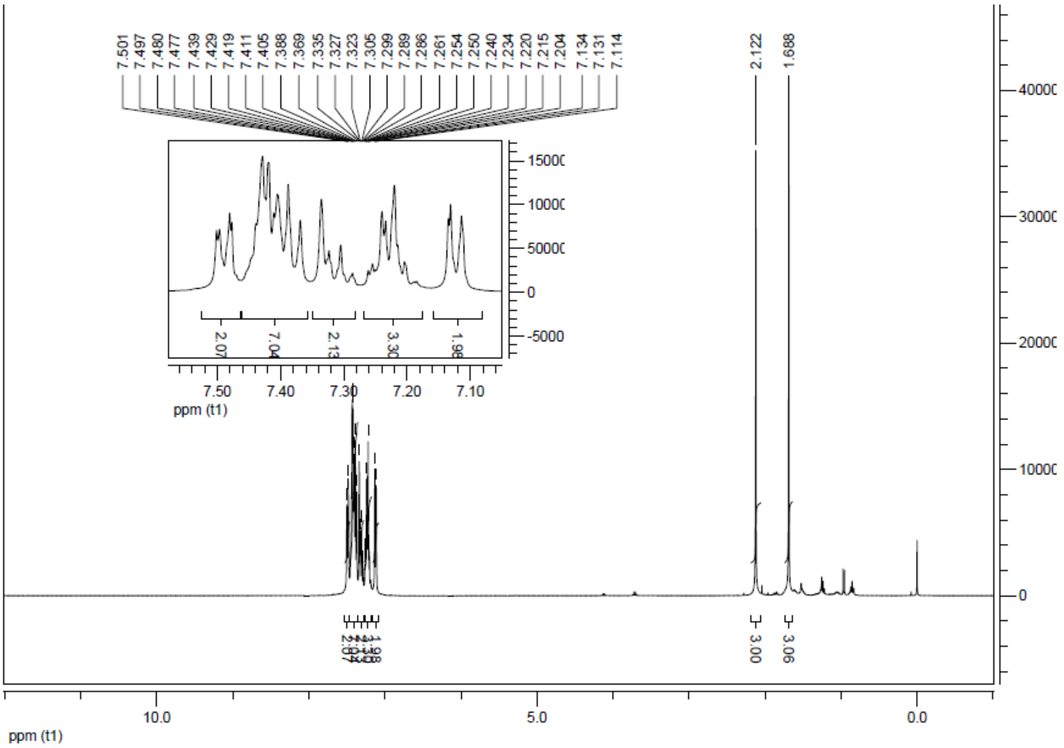
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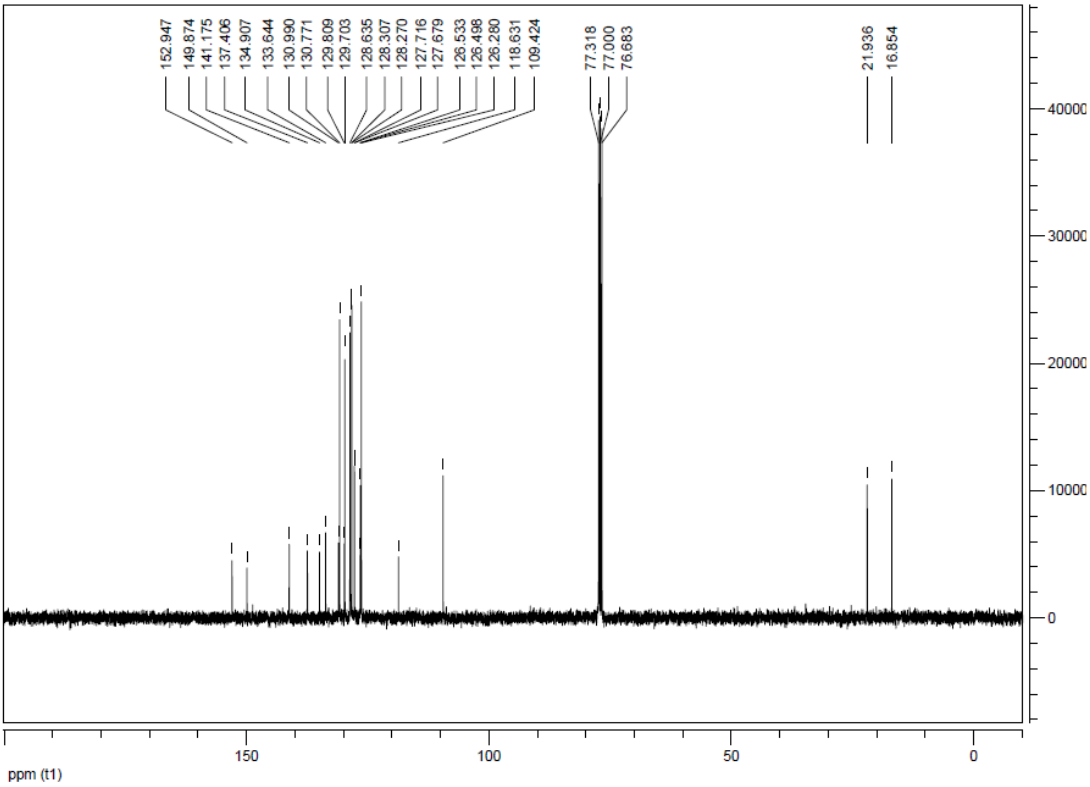
7.497
7.480
7.477
7.439
7.429
7.419
7.411
7.405
7.388
7.369
7.335
7.327
7.323
7.305
7.299
7.289
7.286
7.261
7.254
7.250
7.240
7.234
7.220
7.215
7.204
7.134
7.131
7.114
2.122
1.688
2.07
7.04
2.13
3.30
1.98
3.00
3.06
7.50
7.40
7.30
7.20
7.10
ppm (t1)
15000
10000
5000
0
-5000
40000
30000
20000
10000
0
10.0
5.0
0.0
ppm (t1)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141.175
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134.907
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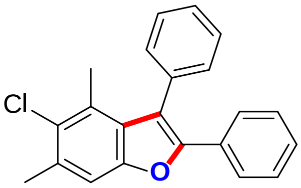
130.990
130.771
129.809
129.703
128.635
128.307
128.270
127.716
127.679
126.533
126.498
126.280
118.631
109.424
77.318
77.000
76.683
21.936
16.854
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)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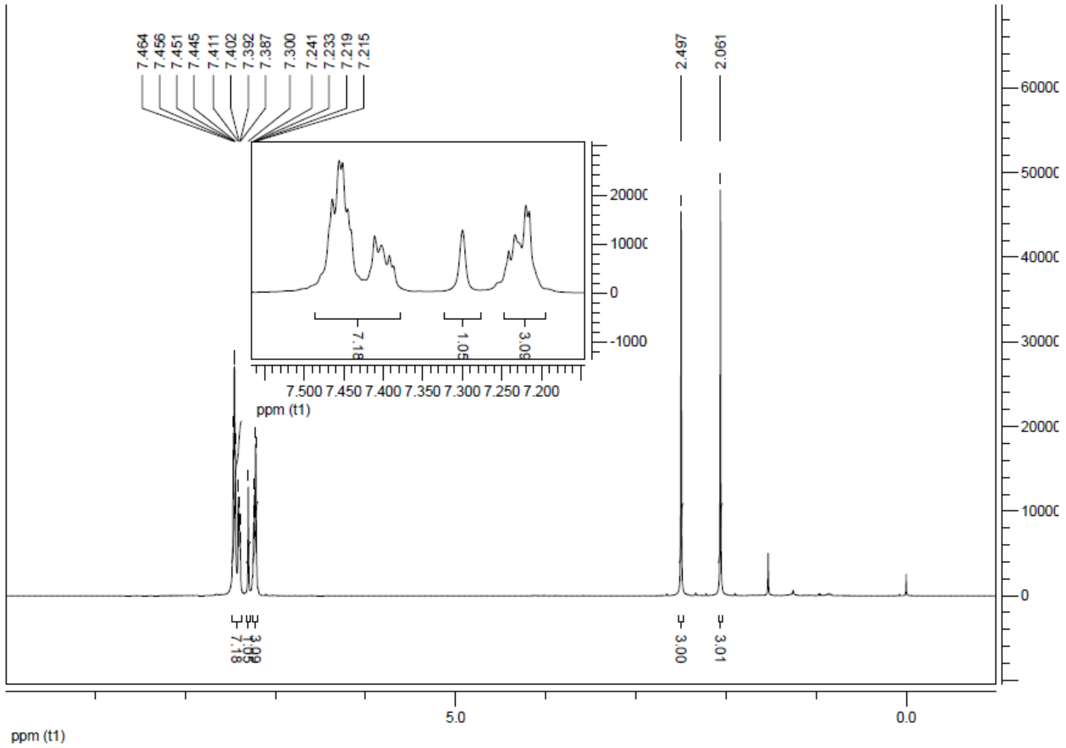
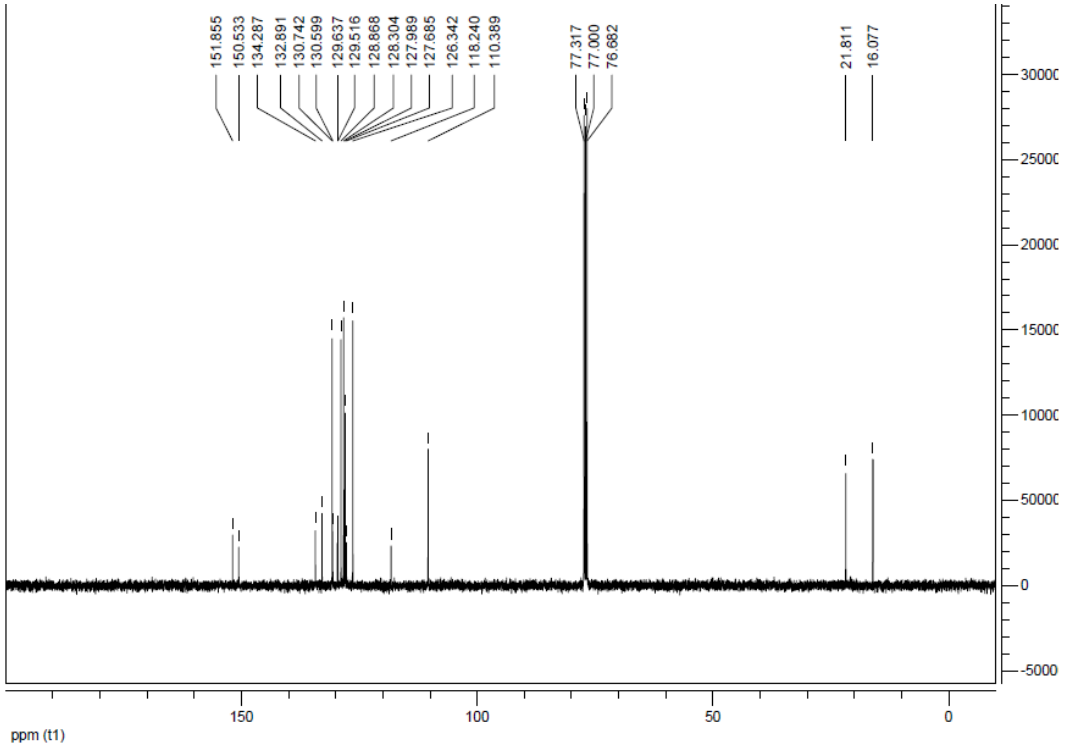

7.464
7.456
7.451
7.445
7.411
7.402
7.392
7.387
7.300
7.241
7.233
7.219
7.215
2.497
2.061
7.18
1.05
3.09
7.500 7.450 7.400 7.350 7.300 7.250 7.200
ppm (t1)
20000
10000
0
-1000
60000
50000
40000
30000
20000
10000
0
7.18
1.05
3.09
3.00
3.01
5.0
0.0
ppm (t1)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150.533
134.287
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130.742
130.599
129.637
129.516
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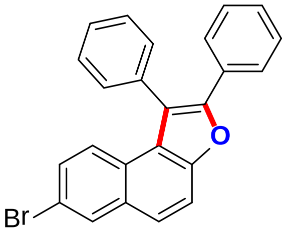
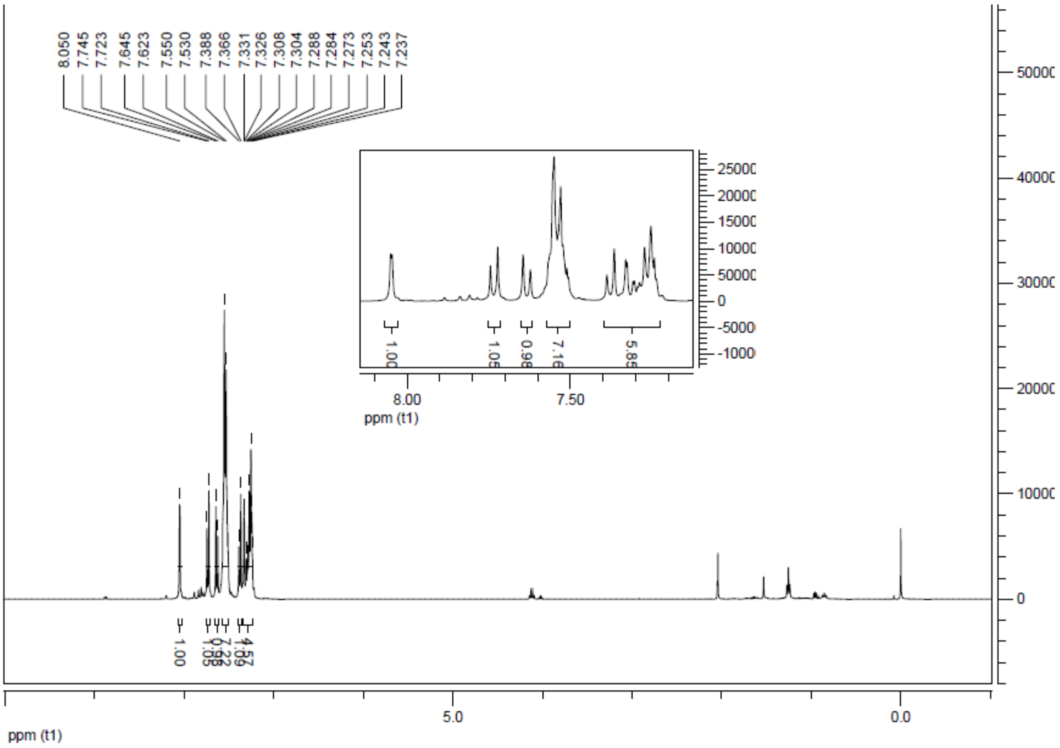
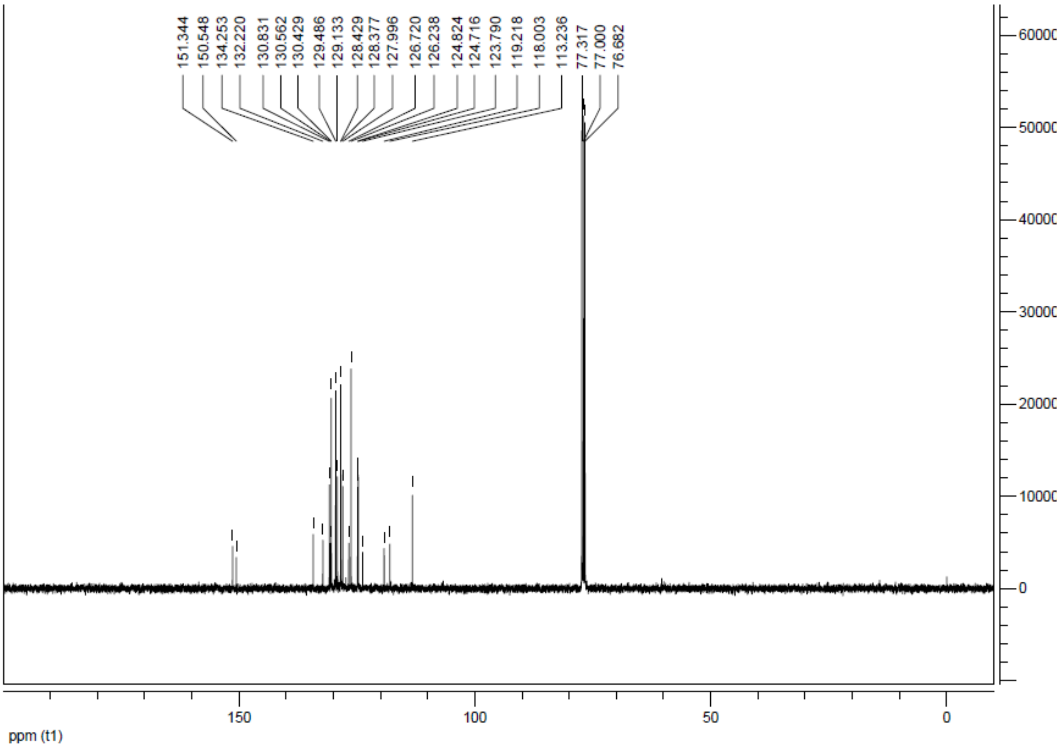
128.304
127.989
127.685
126.342
118.240
110.389
77.317
77.000
76.682
21.811
16.077
30000
25000
20000
15000
10000
5000
0
-5000
150
100
50
0
ppm (t1)


O
Br


8.050
7.745
7.723
7.645
7.623
7.550
7.530
7.388
7.366
7.331
7.326
7.308
7.304
7.288
7.284
7.273
7.253
7.243
7.237
1.00
1.05
0.98
7.16
5.85
8.00
7.50
ppm (t1)
25000
20000
15000
10000
50000
0
-5000
-1000
1.00
5.0
0.0
ppm (t1)
50000
40000
30000
20000
10000
0


151.344
150.548
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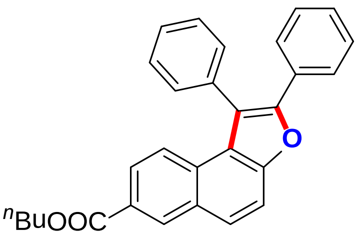
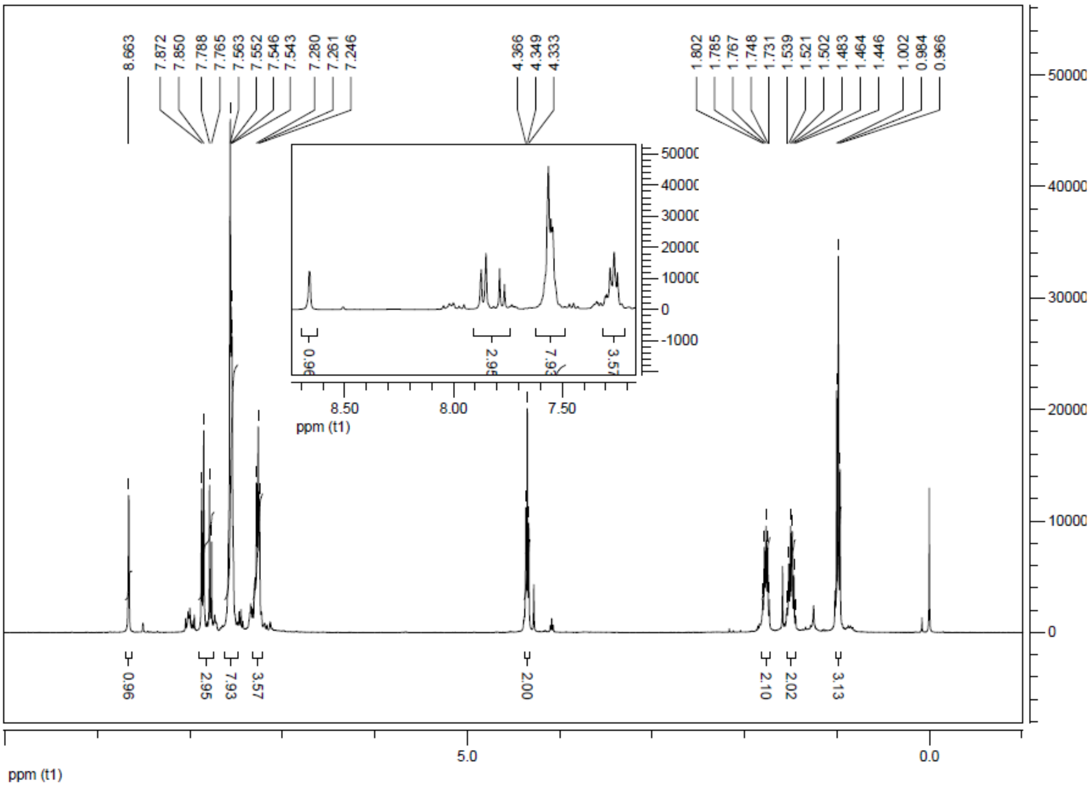
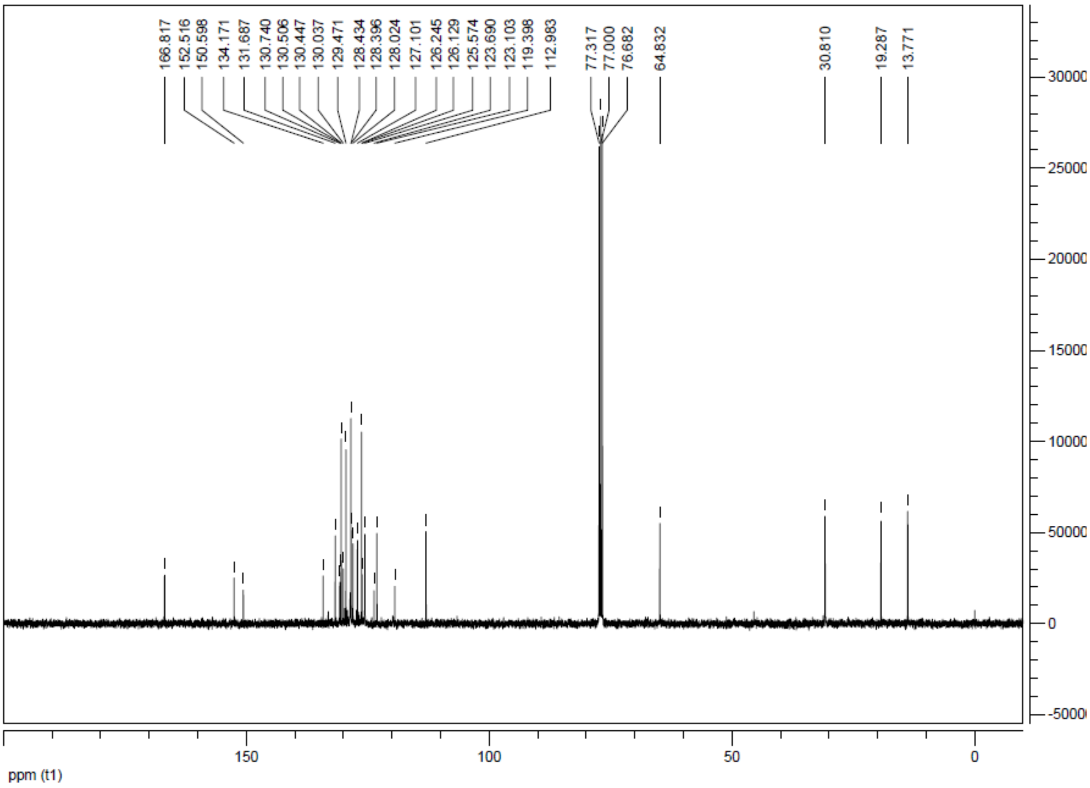
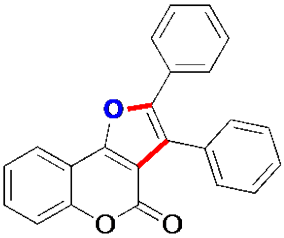
132.220
130.831
130.562
130.429
129.486
129.133
128.429
128.377
127.996
126.720
126.238
124.824
124.716
123.790
119.218
118.003
113.236
77.317
77.000
76.682
150
100
50
0
ppm (t1)
60000
50000
40000
30000
20000
10000
0


O
$^n$BuOOC


8.663
7.872
7.850
7.788
7.765
7.563
7.552
7.546
7.543
7.280
7.261
7.246
4.366
4.349
4.333
1.802
1.785
1.767
1.748
1.731
1.539
1.521
1.502
1.483
1.464
1.446
1.002
0.984
0.966
0.96
2.95
7.93
3.57
2.00
2.10
2.02
3.13
50000
40000
30000
20000
10000
0
-1000
8.50
8.00
7.50
ppm (t1)
5.0
0.0
ppm (t1)


166.817
152.516
150.598
134.171
131.687
130.740
130.506
130.447
130.037
129.471
128.434
128.396
128.024
127.101
126.245
126.129
125.574
123.690
123.103
119.398
112.983
77.317
77.000
76.682
64.832
30.810
19.287
13.771
30000
25000
20000
15000
10000
50000
0
-5000
150
100
50
0
ppm (t1)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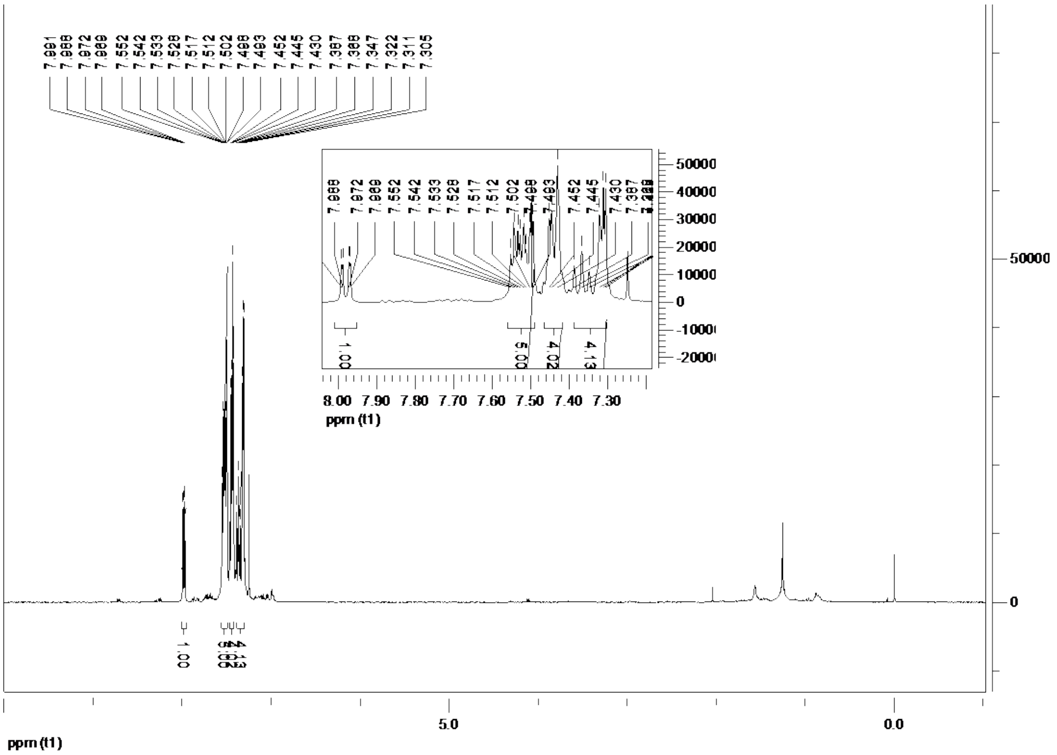
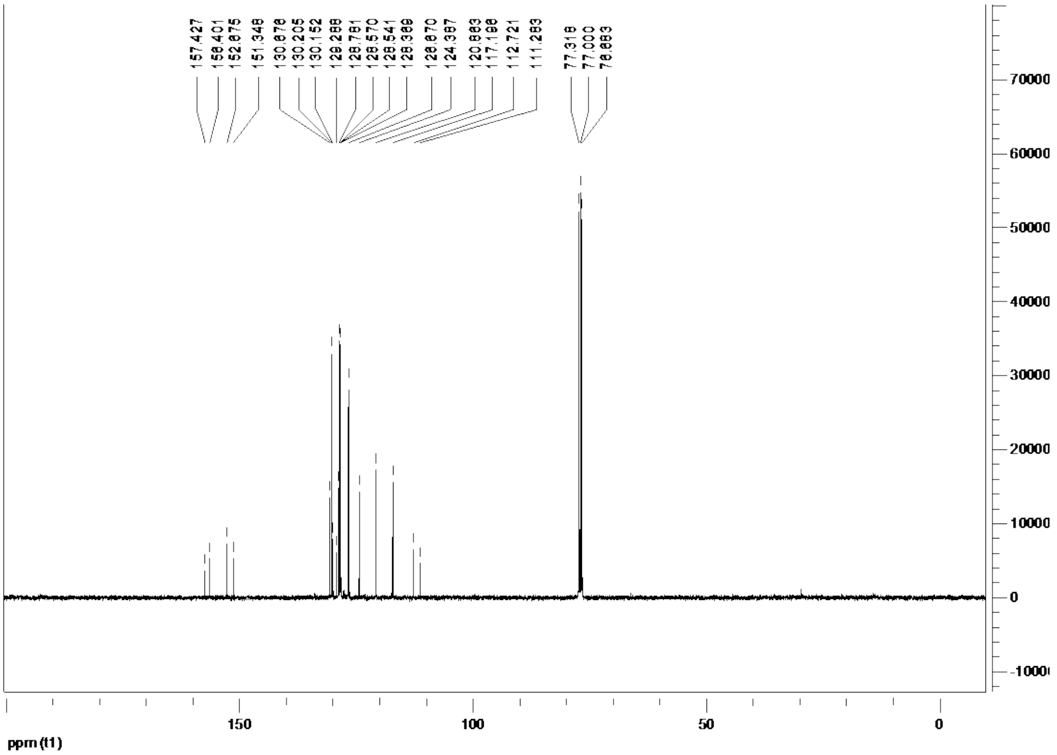
O
O


7.991
7.988
7.972
7.969
7.552
7.542
7.533
7.528
7.517
7.512
7.502
7.498
7.493
7.452
7.445
7.430
7.387
7.366
7.347
7.322
7.311
7.305
1.00
5.00
4.02
4.13
50000
40000
30000
20000
10000
0
8.00
7.90
7.80
7.70
7.60
7.50
7.40
7.30
ppm (t1)
5.0
0.0
ppm (t1)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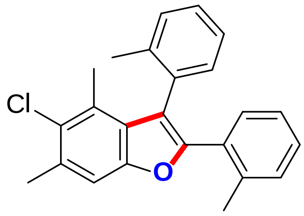
152.875
151.348
130.876
130.205
130.152
129.289
128.781
128.570
128.541
128.389
126.870
124.387
120.883
117.198
112.721
111.283
77.318
77.000
76.683
70000
60000
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)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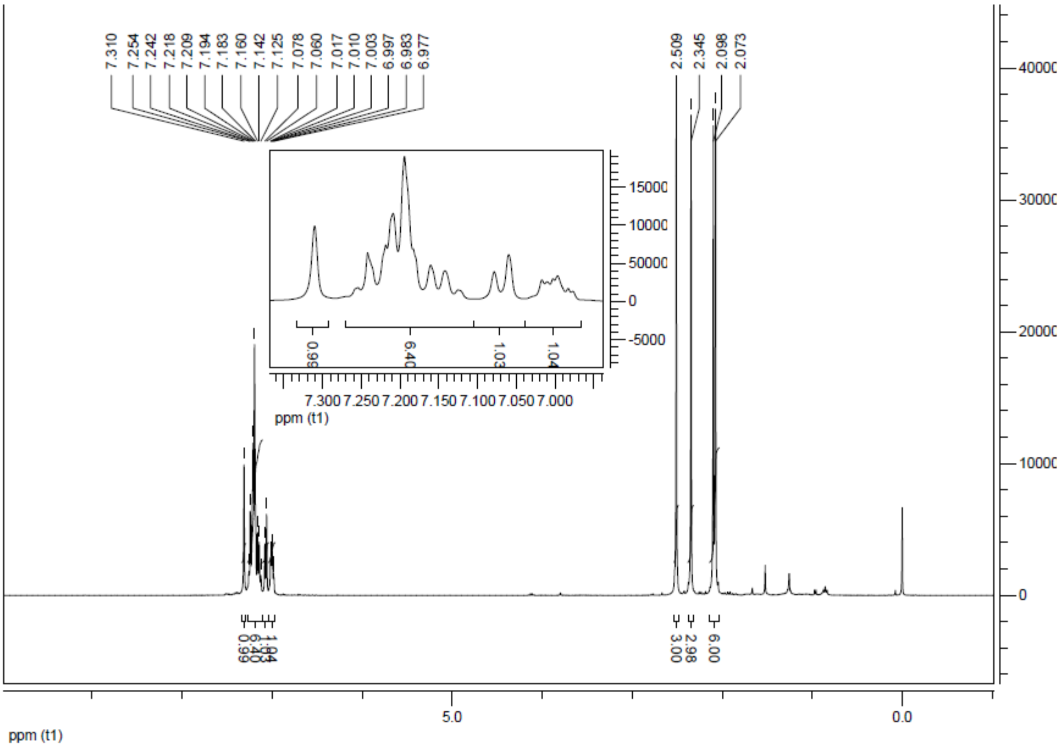
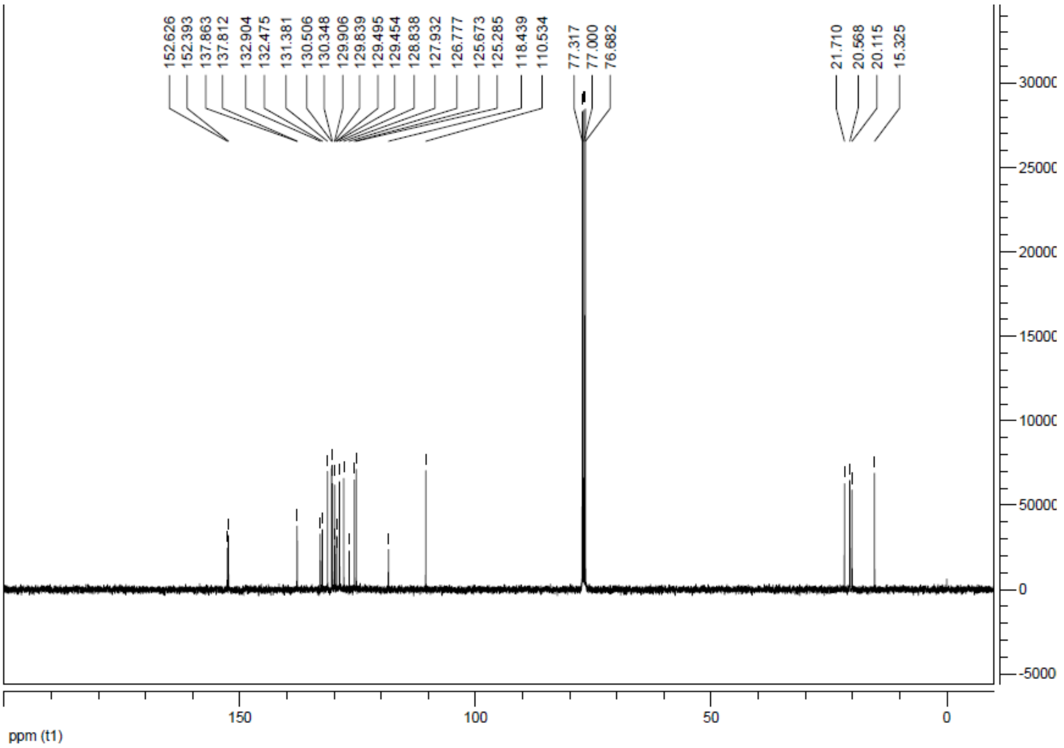
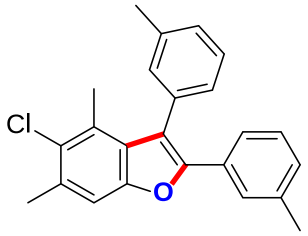

7.310
7.254
7.242
7.218
7.209
7.194
7.183
7.160
7.142
7.125
7.078
7.060
7.017
7.010
7.003
6.997
6.983
6.977
2.509
2.345
2.098
2.073
0.99
6.40
1.03
1.04
3.00
2.98
6.00
7.300
7.250
7.200
7.150
7.100
7.050
7.000
ppm (t1)
15000
10000
50000
0
-5000
40000
30000
20000
10000
0
5.0
0.0
ppm (t1)


152.626
152.393
137.863
137.812
132.904
132.475
131.381
130.506
130.348
129.906
129.839
129.495
129.454
128.838
127.932
126.777
125.673
125.285
118.439
110.534
77.317
77.000
76.682
21.710
20.568
20.115
15.325
30000
25000
20000
15000
10000
50000
0
-5000
150
100
50
0
ppm (t1)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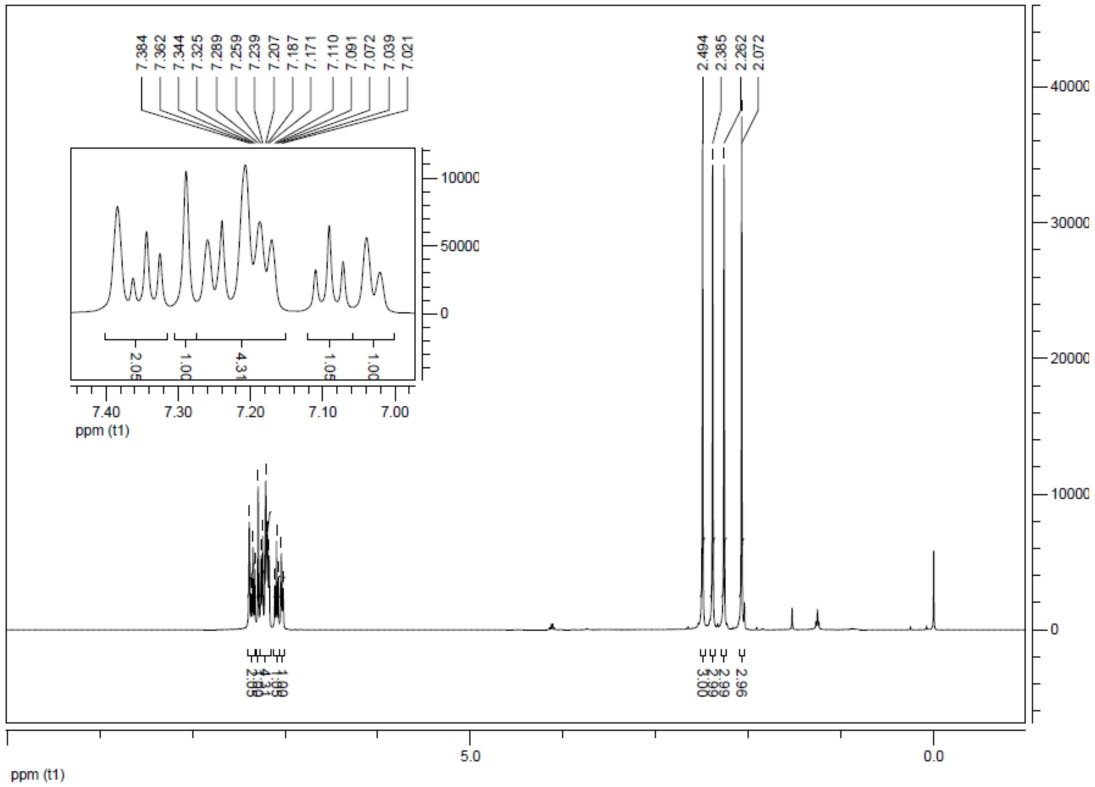
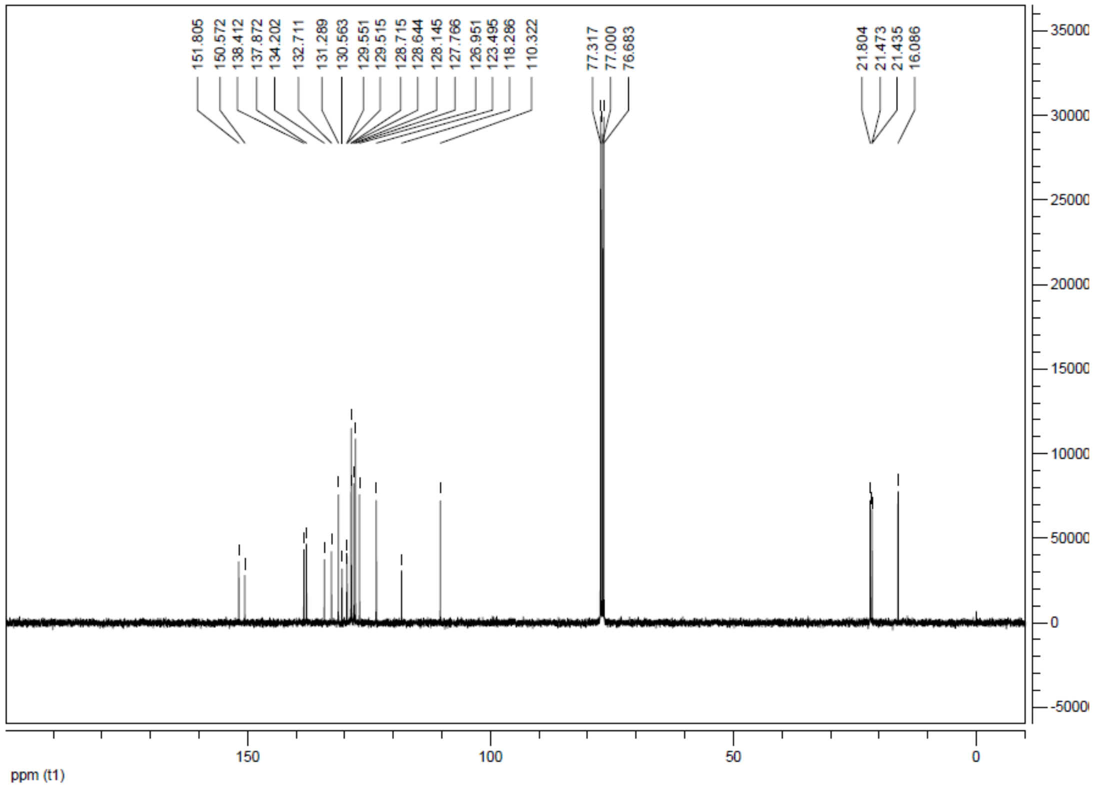

7.384
7.362
7.344
7.325
7.289
7.259
7.239
7.207
7.187
7.171
7.110
7.091
7.072
7.039
7.021
2.494
2.385
2.262
2.072
10000
50000
0
2.05
1.00
4.31
1.05
1.00
7.40
7.30
7.20
7.10
7.00
ppm (t1)
40000
30000
20000
10000
0
3.00
2.99
2.99
2.96
5.0
0.0
ppm (t1)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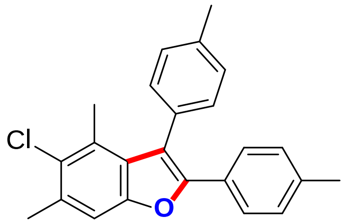
137.872
134.202
132.711
131.289
130.563
129.551
129.515
128.715
128.644
128.145
127.766
126.951
123.495
118.286
110.322
77.317
77.000
76.683
21.804
21.473
21.435
16.086
35000
30000
25000
20000
15000
10000
50000
0
-5000
150
100
50
0
ppm (t1)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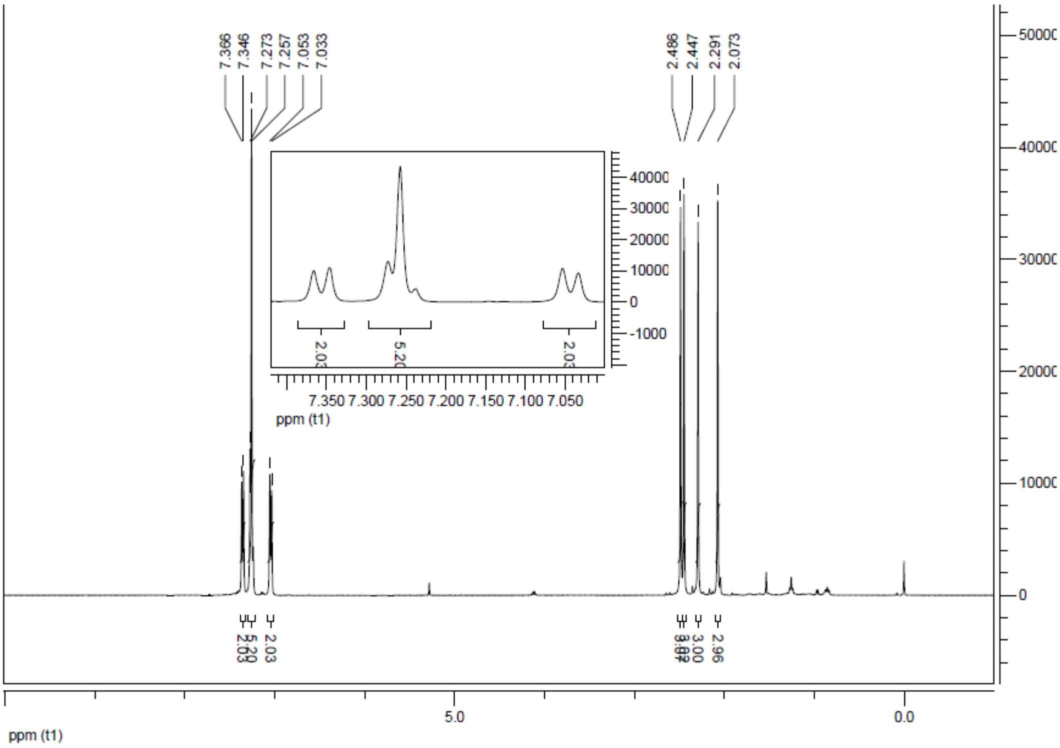
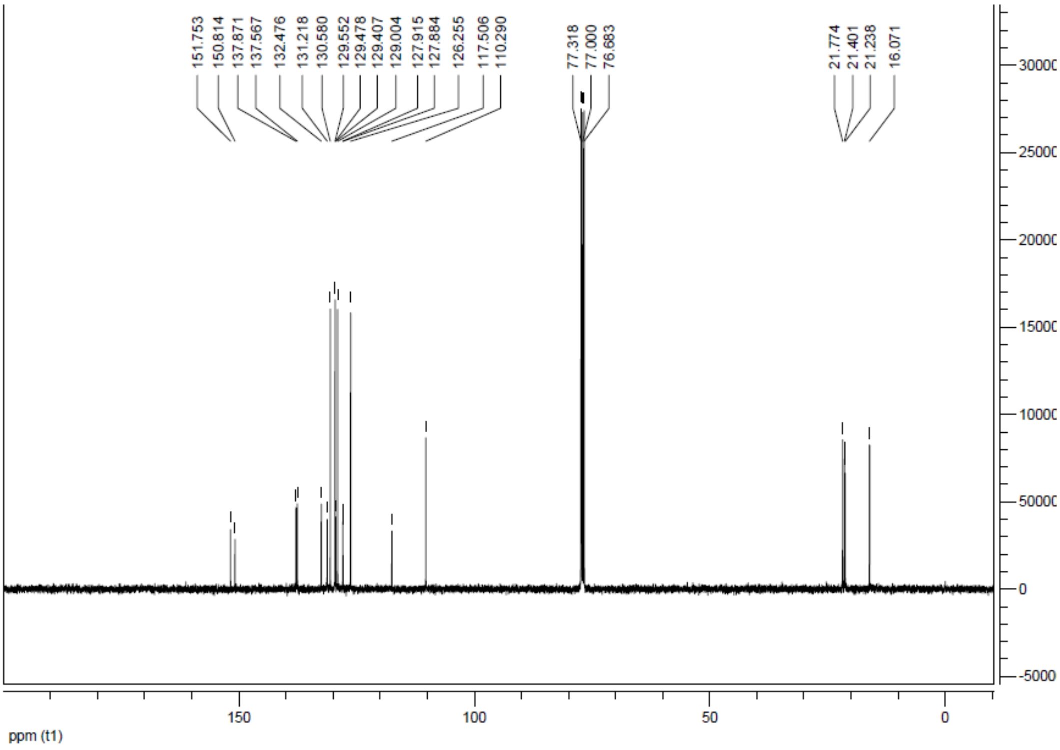

7.366
7.346
7.273
7.257
7.053
7.033
2.486
2.447
2.291
2.073
2.03
5.20
2.03
3.00
2.96
7.350 7.300 7.250 7.200 7.150 7.100 7.050
ppm (t1)
40000
30000
20000
10000
0
-1000
50000
40000
30000
20000
10000
0
5.0
0.0
ppm (t1)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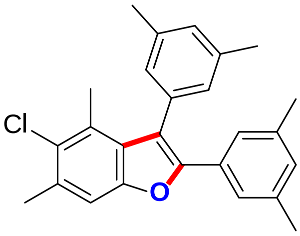
137.567
132.476
131.218
130.580
129.552
129.478
129.407
129.004
127.915
127.884
126.255
117.506
110.290
77.318
77.000
76.683
21.774
21.401
21.238
16.071
30000
25000
20000
15000
10000
50000
0
-5000
150
100
50
0
ppm (t1)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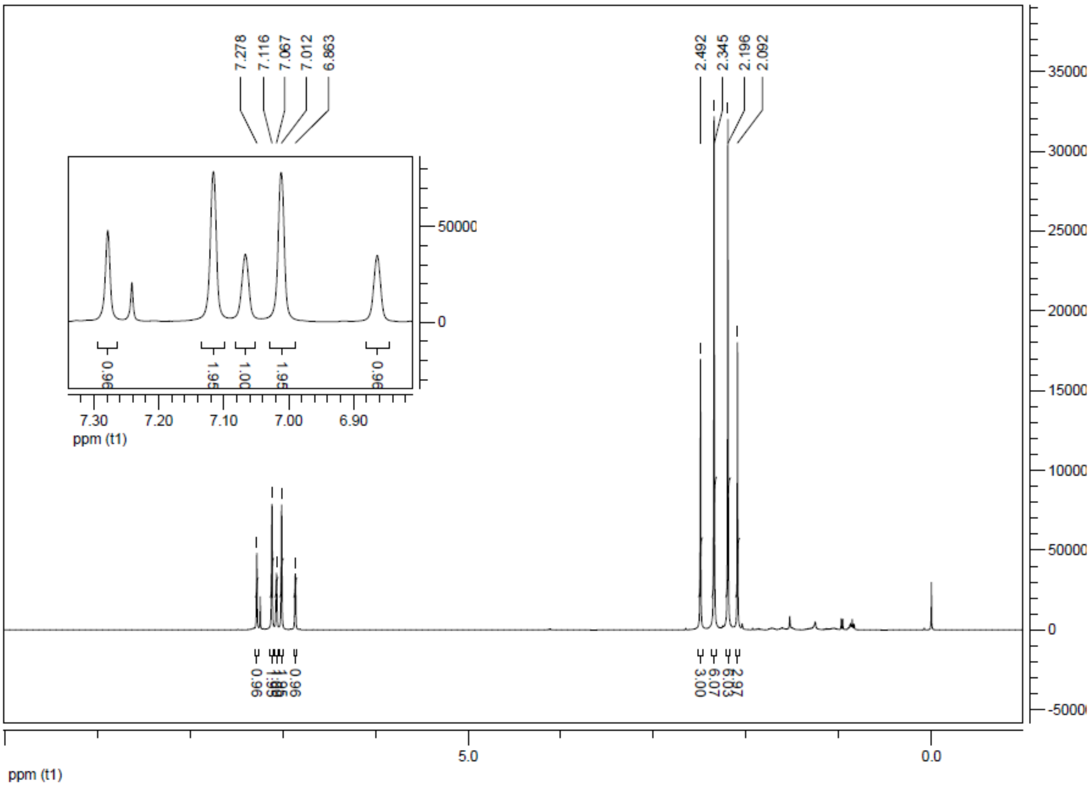
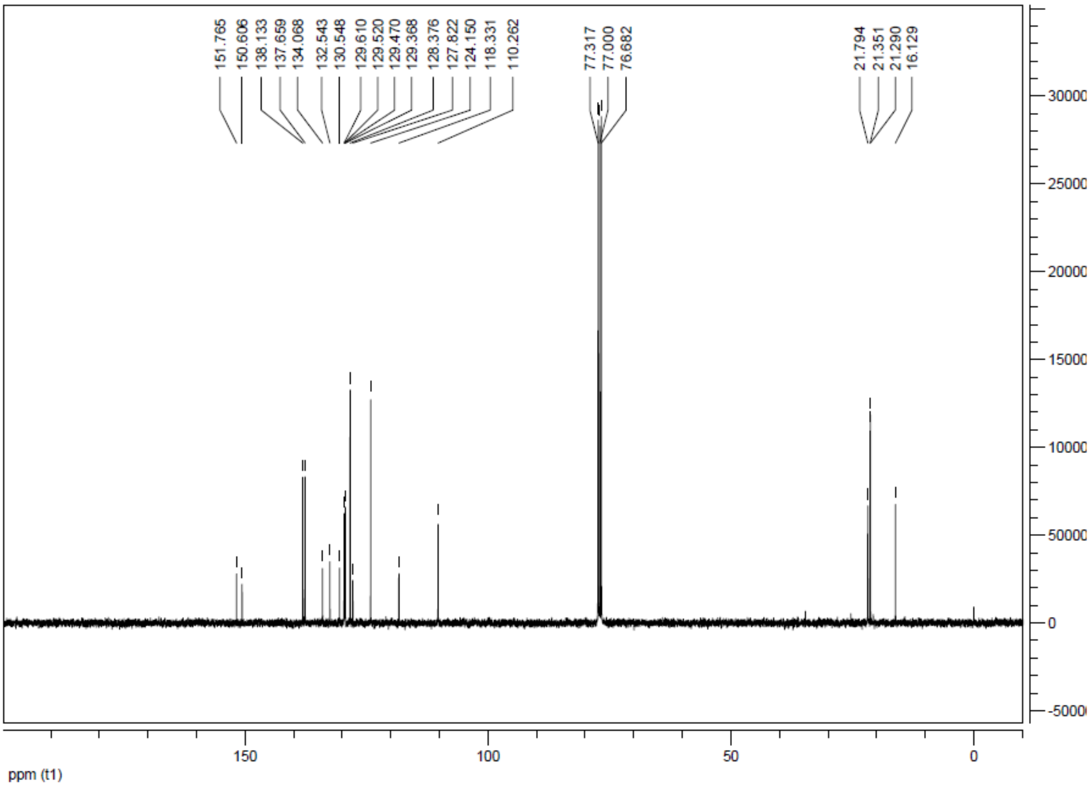

7.278
7.116
7.067
7.012
6.863
2.492
2.345
2.196
2.092
0.96
1.95
1.00
1.95
0.96
7.30
7.20
7.10
7.00
6.90
ppm (t1)
50000
0
3.00
6.07
6.05
2.97
35000
30000
25000
20000
15000
10000
50000
0
-5000
5.0
0.0
ppm (t1)


151.765
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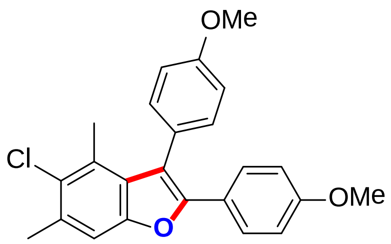
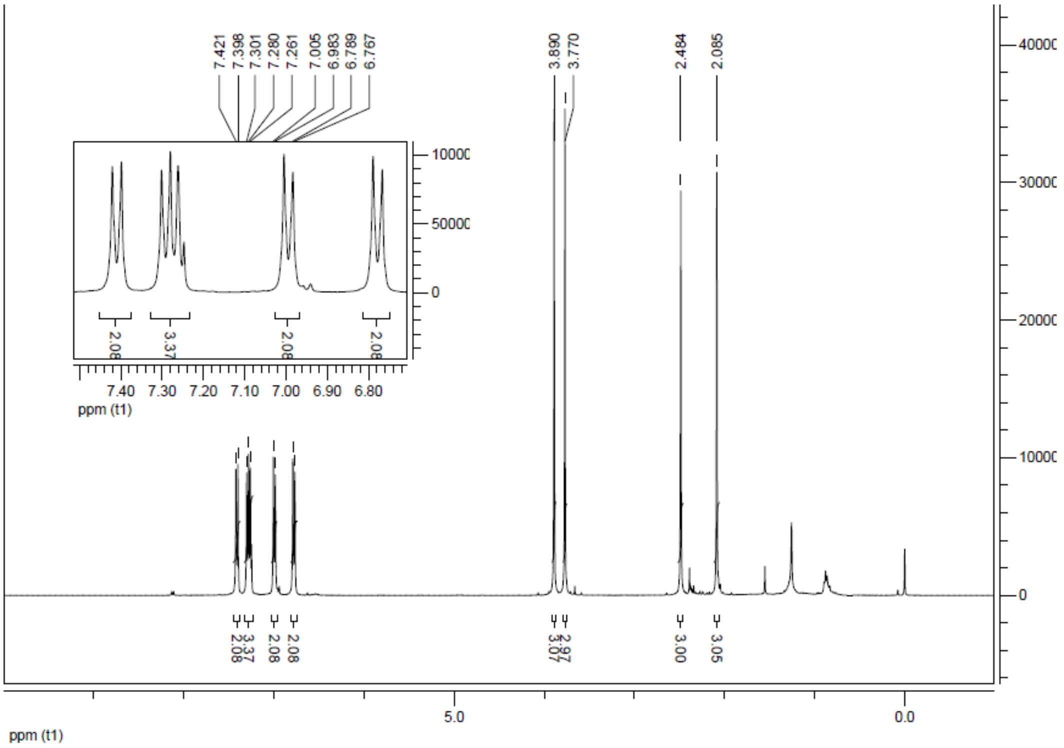
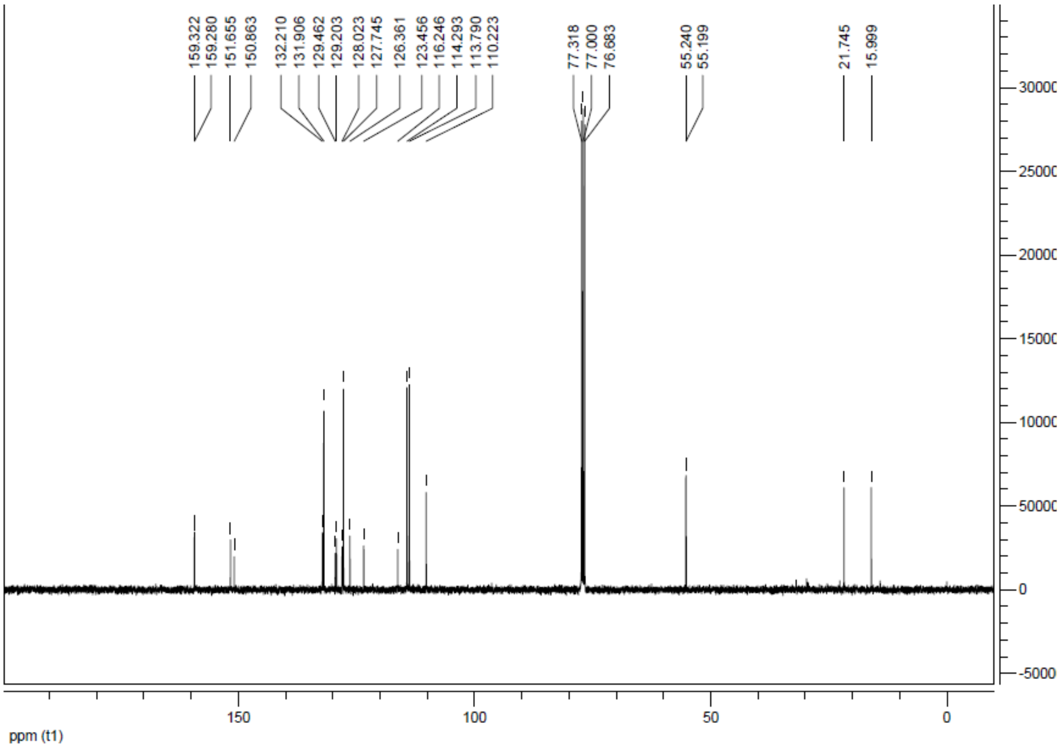
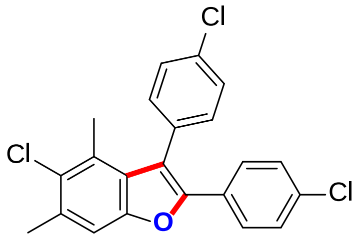
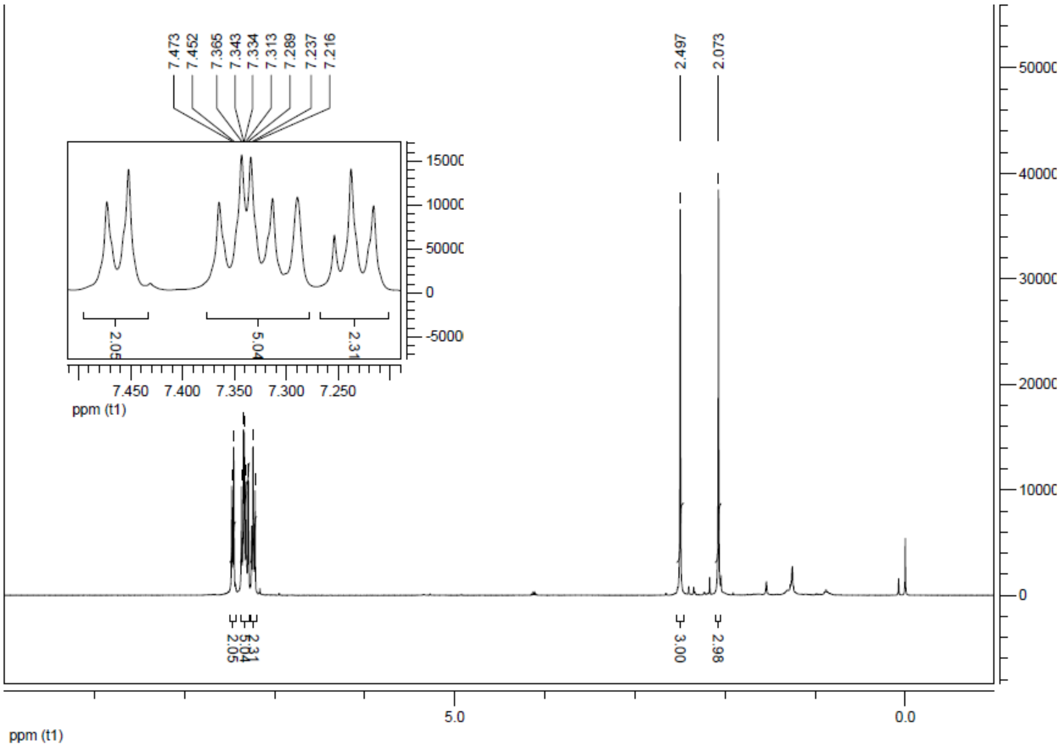
138.133
137.659
134.068
132.543
130.548
129.610
129.520
129.470
129.368
128.376
127.822
124.150
118.331
110.262
77.317
77.000
76.682
21.794
21.351
21.290
16.129
30000
25000
20000
15000
10000
50000
0
-5000
150
100
50
0
ppm (t1)

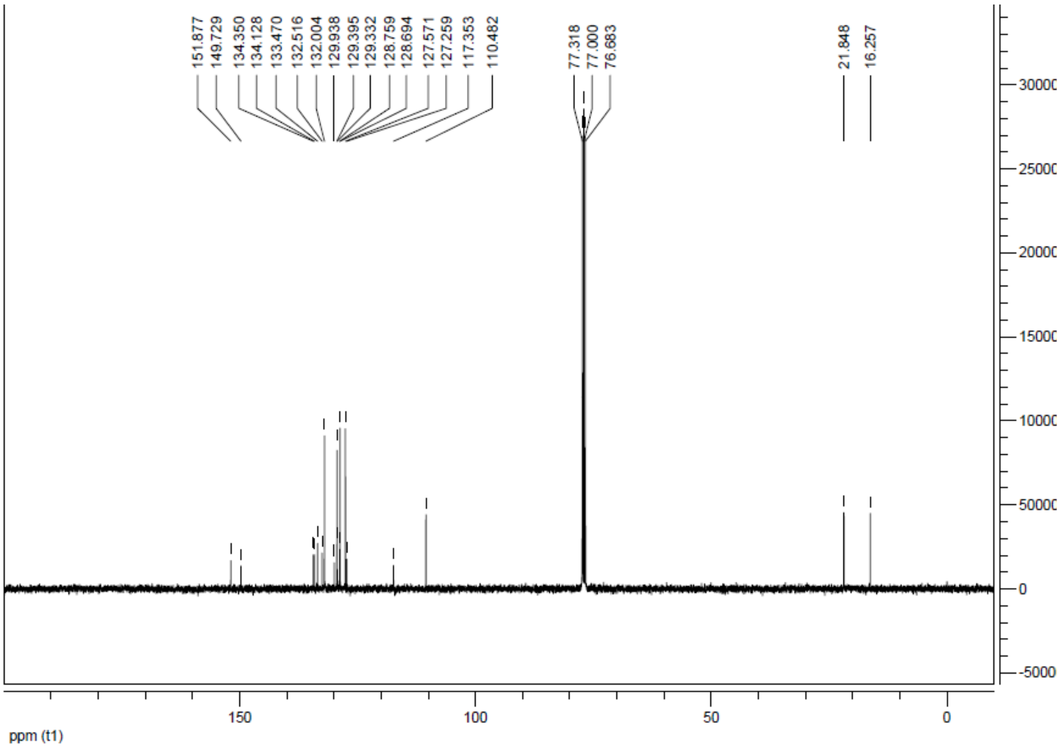

OMe
Cl
O
OMe

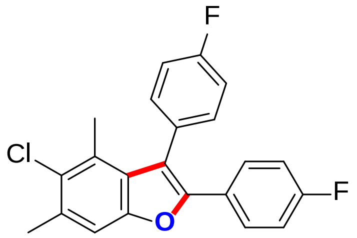

7.421
7.398
7.301
7.280
7.261
7.005
6.983
6.789
6.767
3.890
3.770
2.484
2.085
1000
5000
0
2.08
3.37
2.08
2.08
7.40
7.30
7.20
7.10
7.00
6.90
6.80
ppm (t1)
4000
3000
2000
1000
0
2.08
3.37
2.08
2.08
3.07
2.97
3.00
3.05
5.0
0.0
ppm (t1)

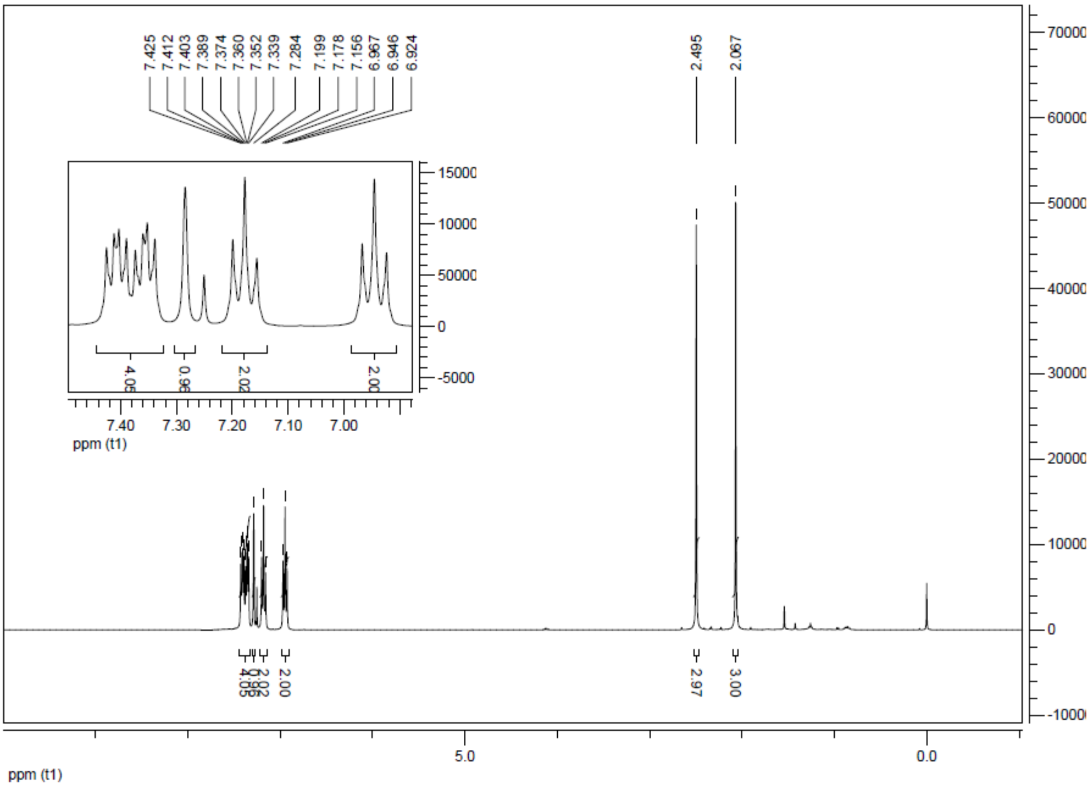

159.322
159.280
151.655
150.863
132.210
131.906
129.462
129.203
128.023
127.745
126.361
123.456
116.246
114.293
113.790
110.223
77.318
77.000
76.683
55.240
55.199
21.745
15.999
3000
2500
2000
1500
1000
5000
0
-5000
150
100
50
0
ppm (t1)

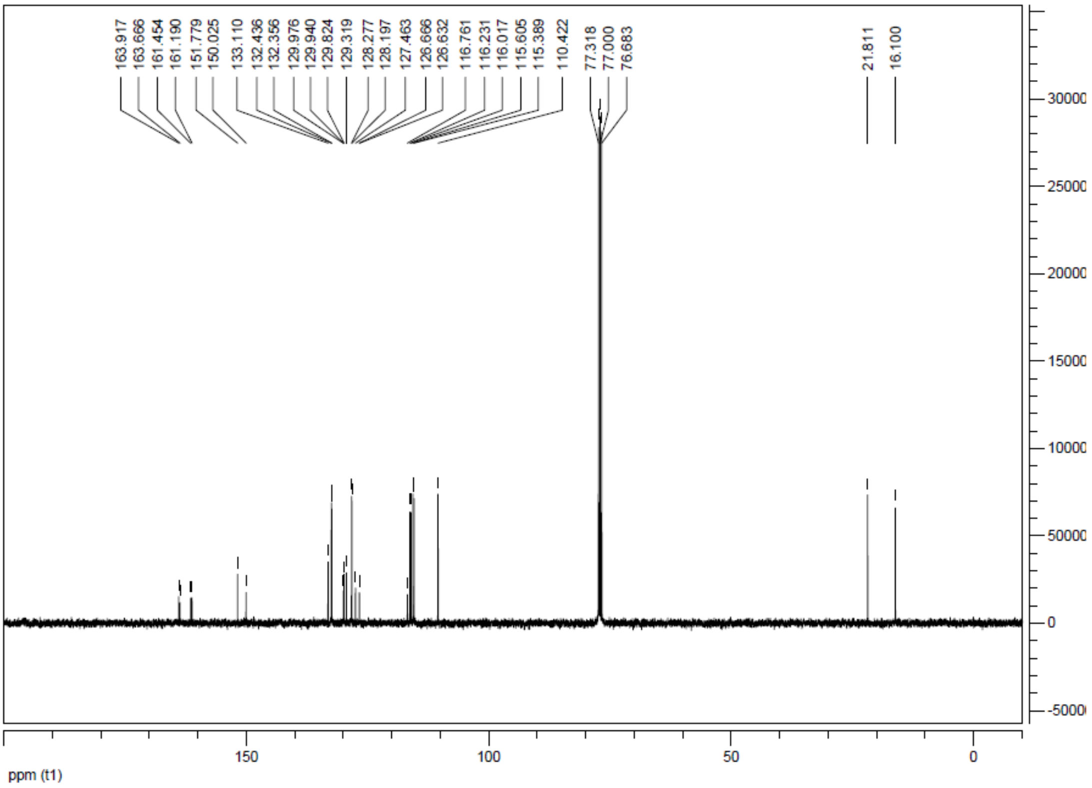

Cl
Cl
Cl
O


7.473
7.452
7.365
7.343
7.334
7.313
7.289
7.237
7.216
2.497
2.073
15000
10000
50000
0
-5000
2.05
5.04
2.31
7.450
7.400
7.350
7.300
7.250
ppm (t1)
5000C
4000C
3000C
2000C
1000C
0
2.05
5.04
2.31
3.00
2.98
5.0
0.0
ppm (t1)


151.877
149.729
134.350
134.128
133.470
132.516
132.004
129.938
129.395
129.332
128.759
128.694
127.571
127.259
117.353
110.482
77.318
77.000
76.683
21.848
16.257
3000C
2500C
2000C
1500C
1000C
5000C
0
-5000
150
100
50
0
ppm (t1)


F
Cl
O
F


7.425
7.412
7.403
7.389
7.374
7.360
7.352
7.339
7.284
7.199
7.178
7.156
6.967
6.946
6.924
2.495
2.067
4.05
0.96
2.02
2.00
2.97
3.00
7.40
7.30
7.20
7.10
7.00
ppm (t1)
15000
10000
50000
0
-5000
70000
60000
50000
40000
30000
20000
10000
0
-1000
5.0
0.0
ppm (t1)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163.666
161.454
161.190
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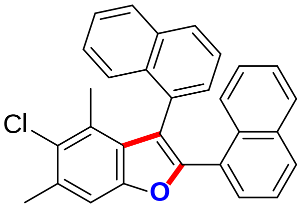
133.110
132.436
132.356
129.976
129.940
129.824
129.319
128.277
128.197
127.463
126.666
126.632
116.761
116.231
116.017
115.605
115.389
110.422
77.318
77.000
76.683
21.811
16.100
30000
25000
20000
15000
10000
50000
0
-5000
150
100
50
0
ppm (t1)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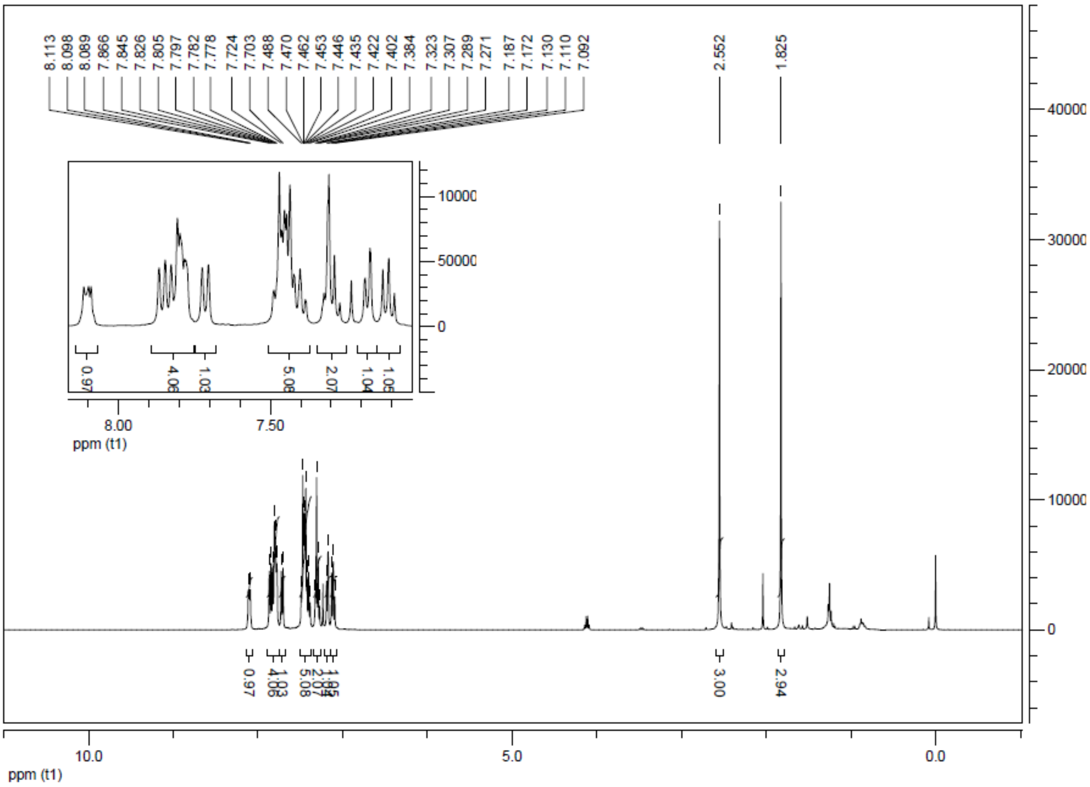
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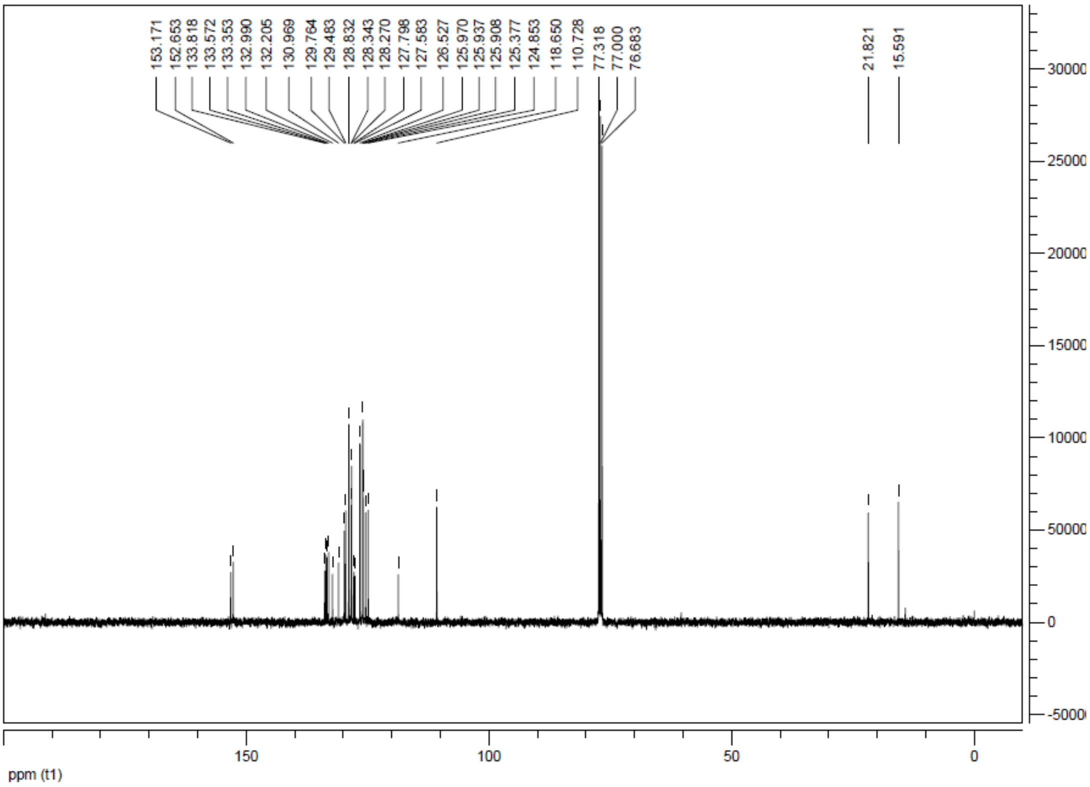
8.089
7.866
7.845
7.826
7.805
7.797
7.782
7.778
7.724
7.703
7.488
7.470
7.462
7.453
7.446
7.435
7.422
7.402
7.384
7.323
7.307
7.289
7.271
7.187
7.172
7.130
7.110
7.092
2.552
1.825
0.97
4.06
1.03
5.08
2.07
1.04
1.05
3.00
2.94
8.00
7.50
ppm (t1)
10.0
5.0
0.0
ppm (t1)
0
10000
20000
30000
40000
50000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133.572
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132.205
130.969
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129.483
128.832
128.343
128.270
127.798
127.583
126.527
125.970
125.937
125.908
125.377
124.853
118.650
110.728
77.318
77.000
76.683
21.821
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150
100
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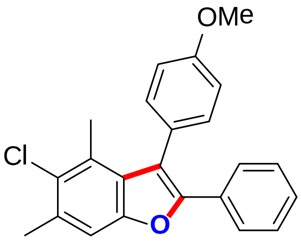
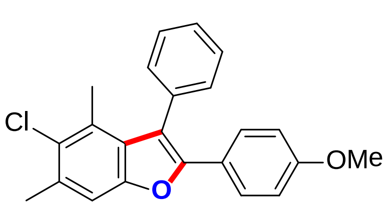
10000
15000
20000
25000
30000
-5000


OMe
Cl
O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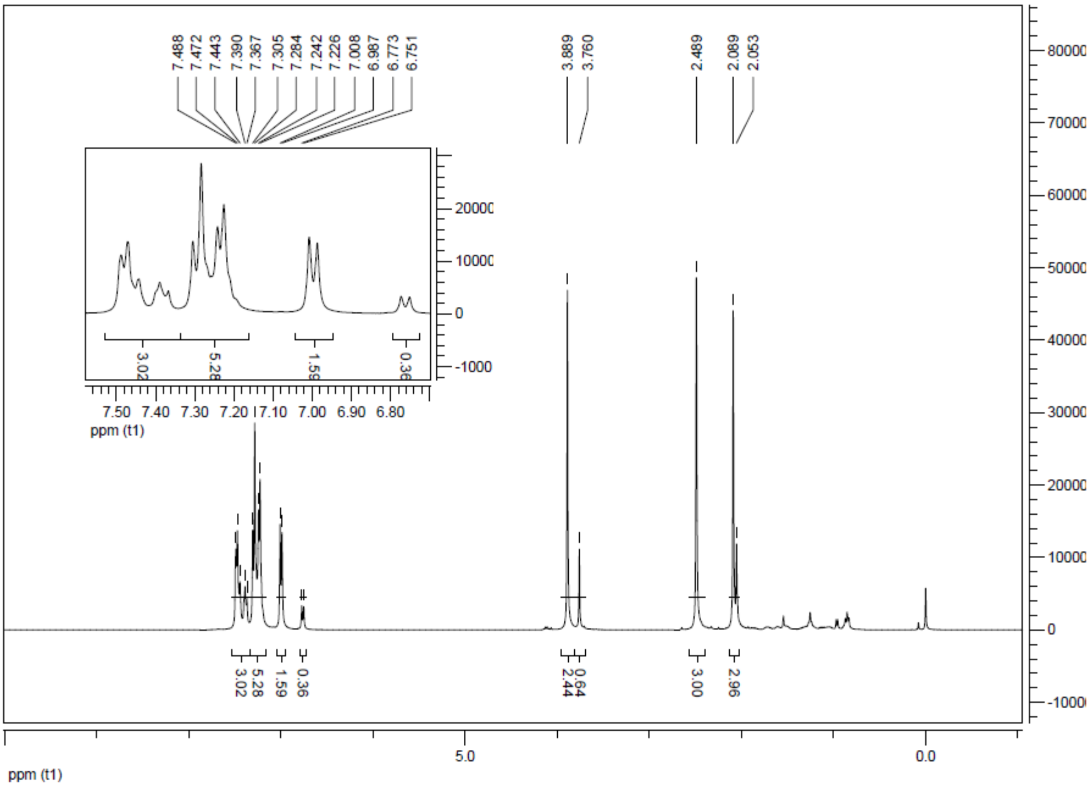
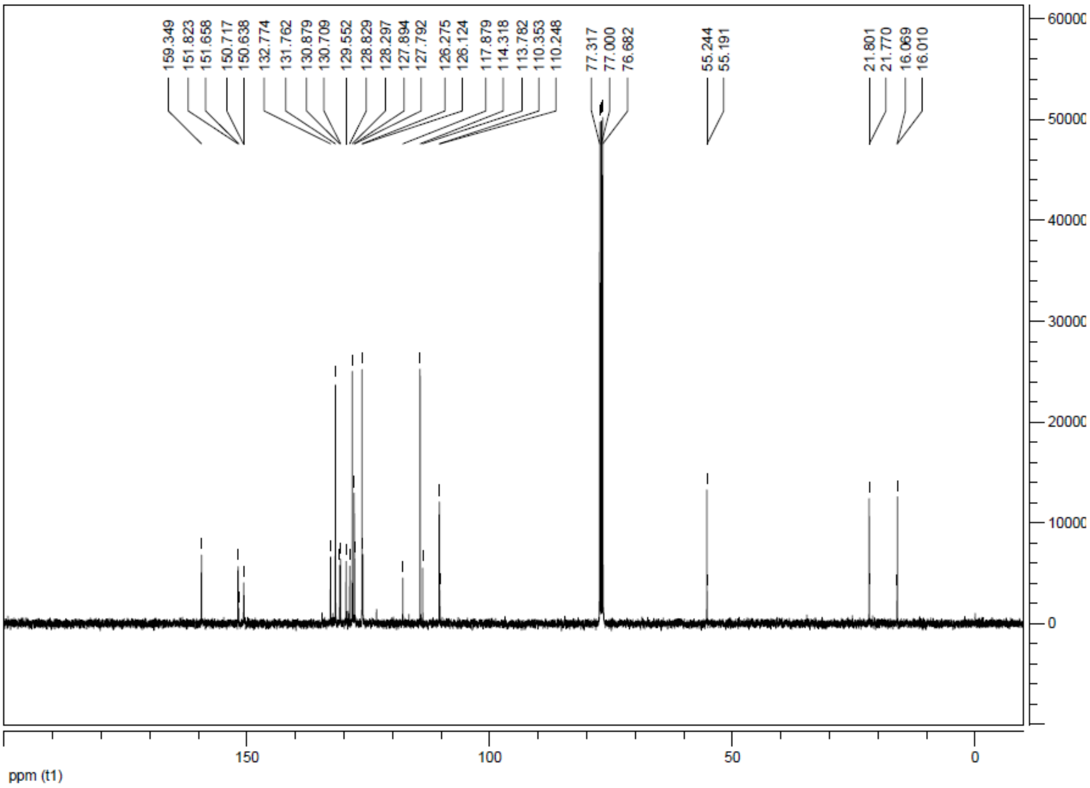
O
OMe


7.488
7.472
7.443
7.390
7.367
7.305
7.284
7.242
7.226
7.008
6.987
6.773
6.751
3.889
3.760
2.489
2.089
2.053
3.02
5.28
1.59
0.36
2.44
0.64
3.00
2.96
7.50 7.40 7.30 7.20 7.10 7.00 6.90 6.80
ppm (t1)
20000
10000
0
-1000
80000
70000
60000
50000
40000
30000
20000
10000
0
-1000
5.0
0.0
ppm (t1)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151.823
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129.552
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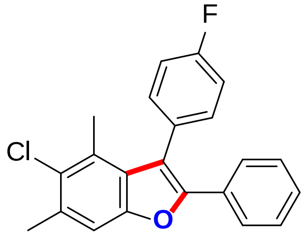
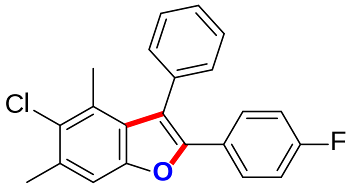
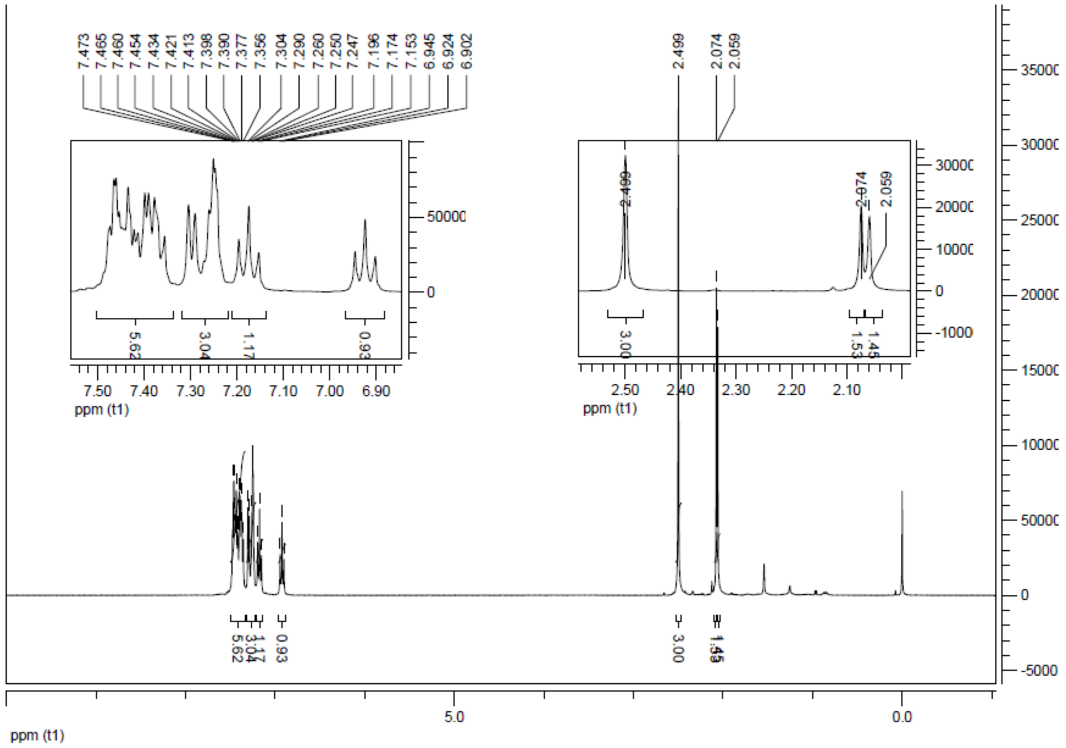
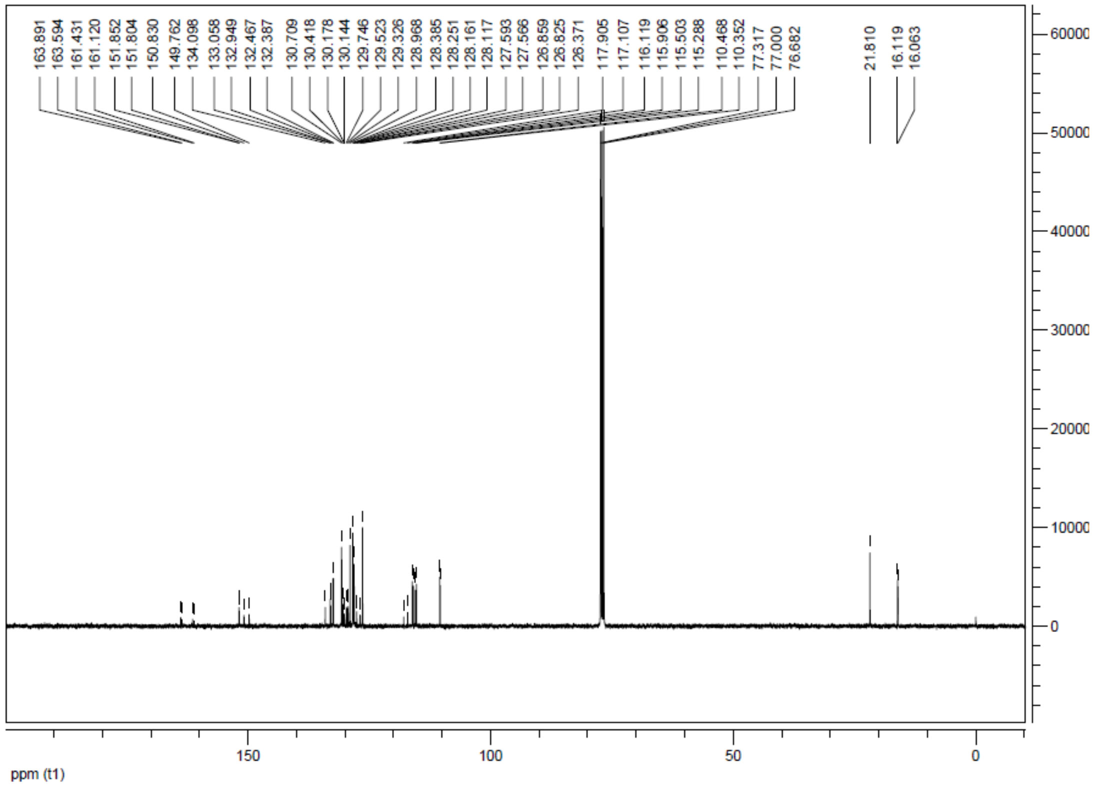
128.297
127.894
127.792
126.275
126.124
117.879
114.318
113.782
110.353
110.248
77.317
77.000
76.682
55.244
55.191
21.801
21.770
16.069
16.010
60000
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)

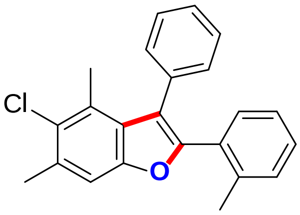
## Supporting Information







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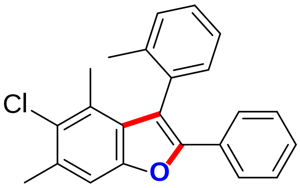
Cl
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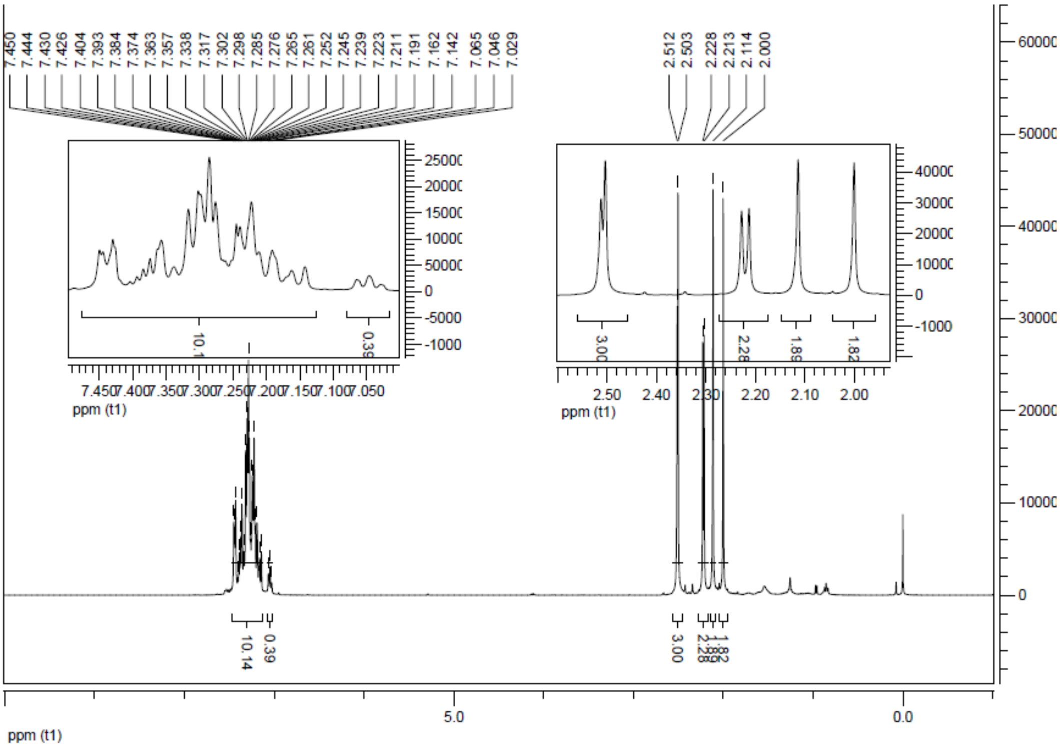
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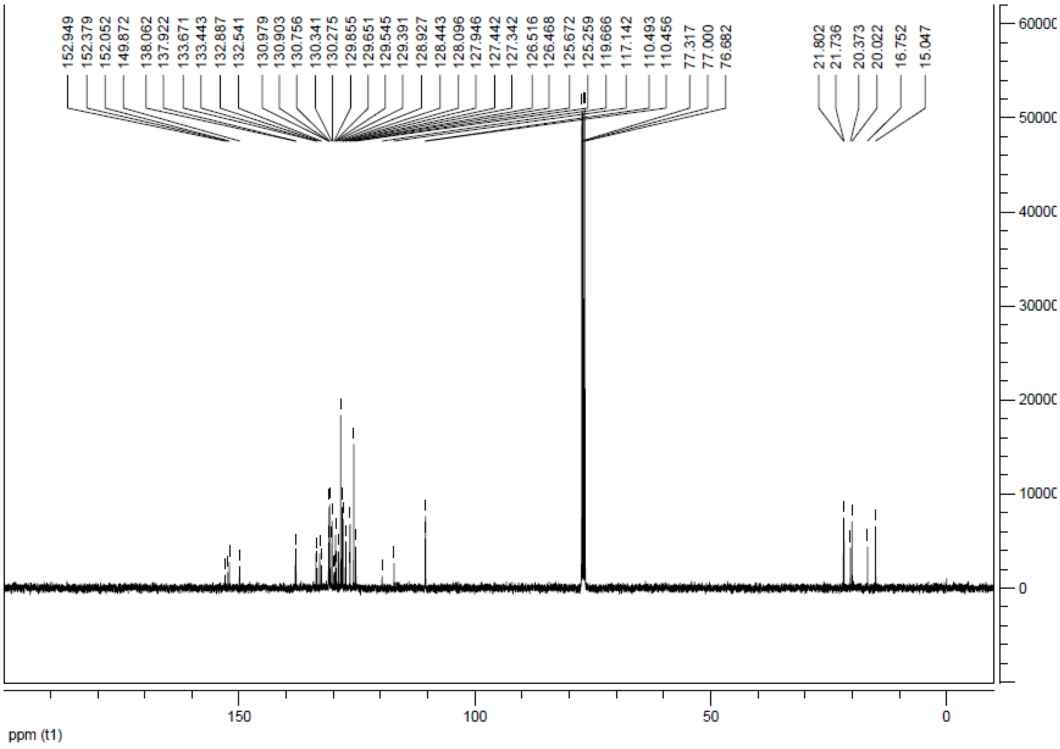
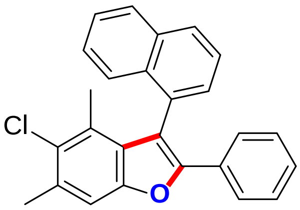
7.444
7.430
7.426
7.404
7.393
7.384
7.374
7.363
7.357
7.338
7.317
7.302
7.298
7.285
7.276
7.265
7.261
7.252
7.245
7.239
7.223
7.211
7.191
7.162
7.142
7.065
7.046
7.029
2.512
2.503
2.228
2.213
2.114
2.000
10.14
0.39
3.00
2.28
1.89
1.82
7.450 7.400 7.350 7.300 7.250 7.200 7.150 7.100 7.050
ppm (t1)
2.50 2.40 2.30 2.20 2.10 2.00
ppm (t1)
5.0
0.0
ppm (t1)


152.949
152.379
152.052
149.872
138.062
137.922
133.671
133.443
132.887
132.541
130.979
130.903
130.756
130.341
130.275
129.855
129.651
129.545
129.391
128.927
128.443
128.096
127.946
127.442
127.342
126.516
126.468
125.672
125.259
119.666
117.142
110.493
110.456
77.317
77.000
76.682
21.802
21.736
20.373
20.022
16.752
15.047
150
100
50
0
ppm (t1)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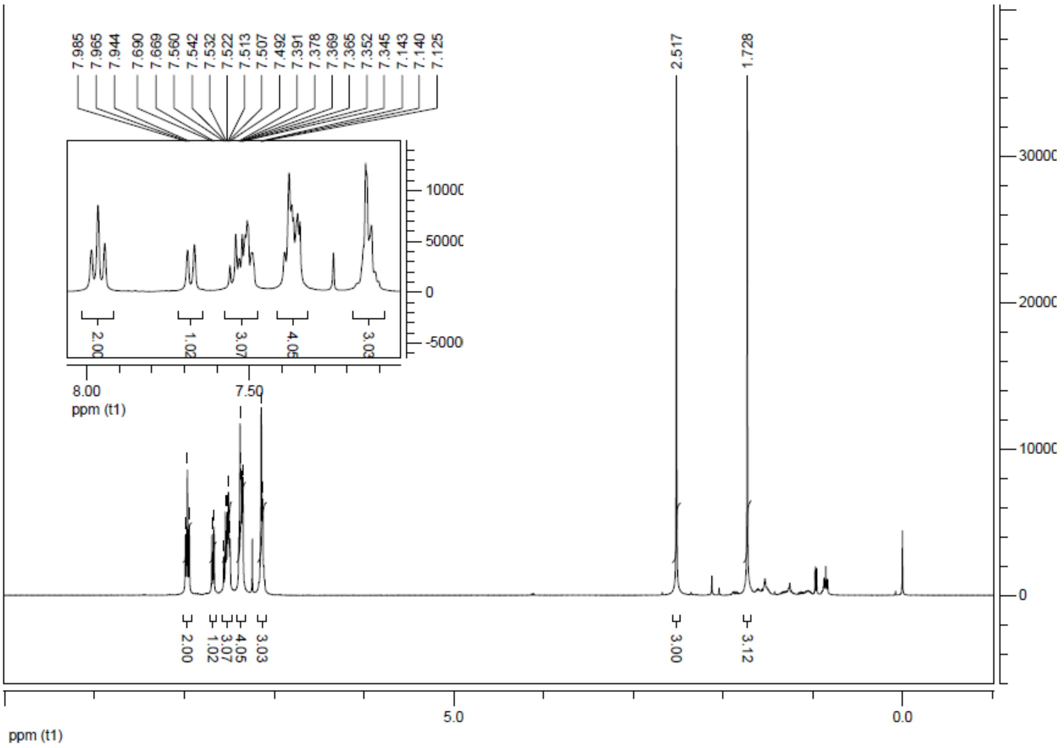
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7.690
7.669
7.560
7.542
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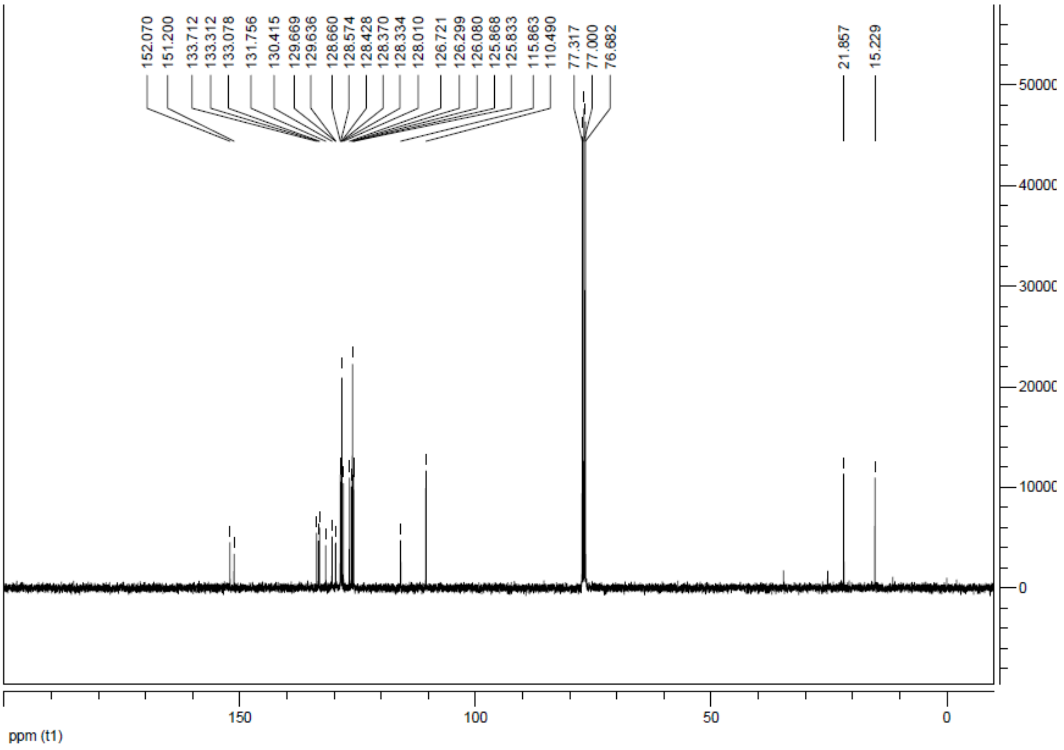
7.522
7.513
7.507
7.492
7.391
7.378
7.369
7.365
7.352
7.345
7.143
7.140
7.125
2.517
1.728
10000
50000
0
-5000
2.00
1.02
3.07
4.05
3.03
8.00
7.50
ppm (t1)
30000
20000
10000
0
2.00
1.02
3.07
4.05
3.03
3.00
3.12
5.0
0.0
ppm (t1)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151.200
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133.312
133.078
131.756
130.415
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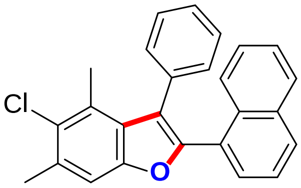
129.636
128.660
128.574
128.428
128.370
128.334
128.010
126.721
126.299
126.080
125.868
125.833
115.863
110.490
77.317
77.000
76.682
21.857
15.229
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)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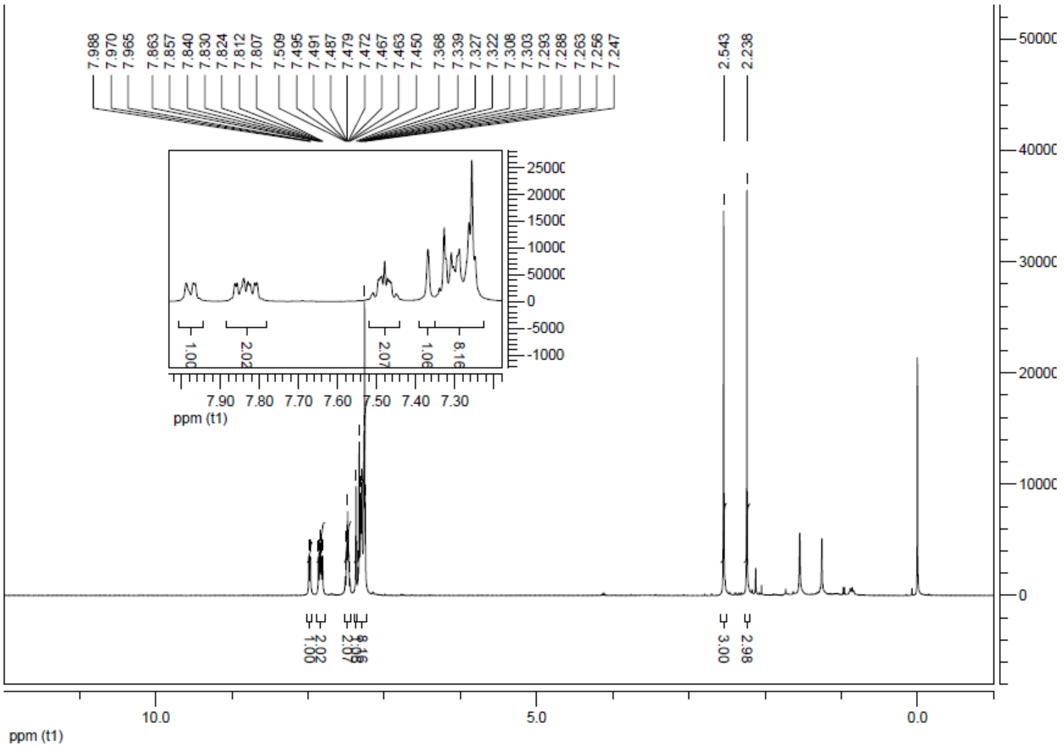
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7.830
7.824
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7.807
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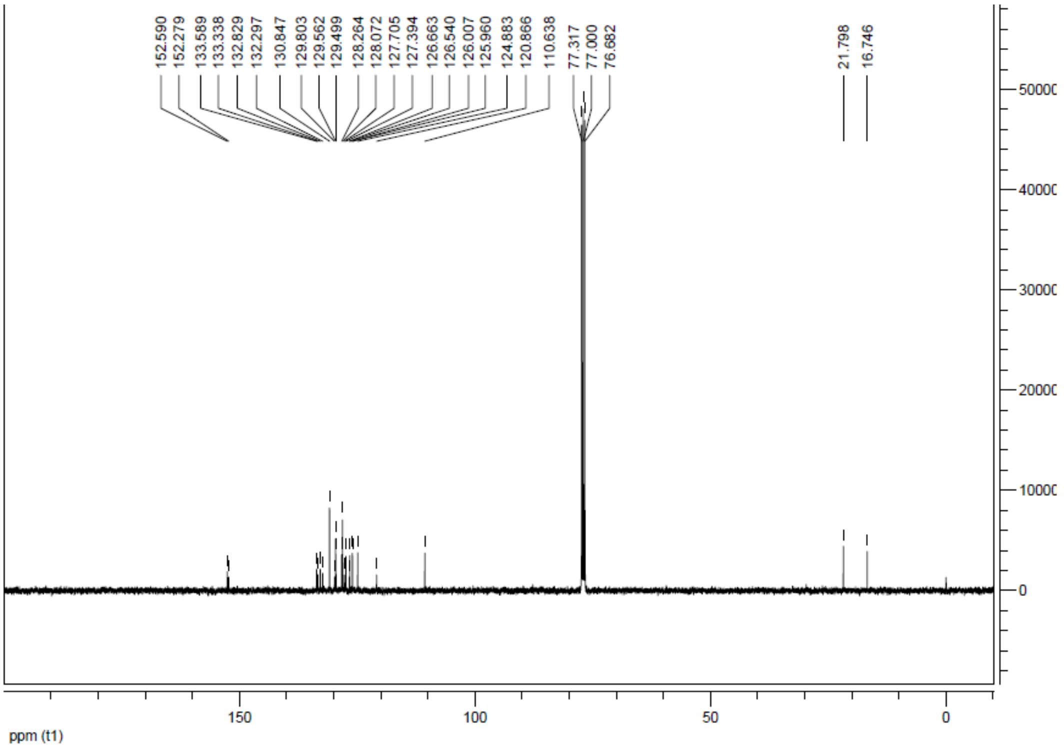
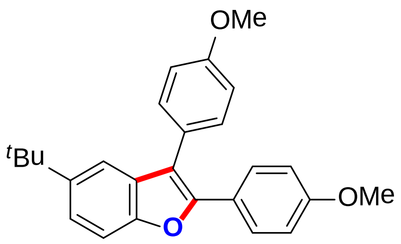
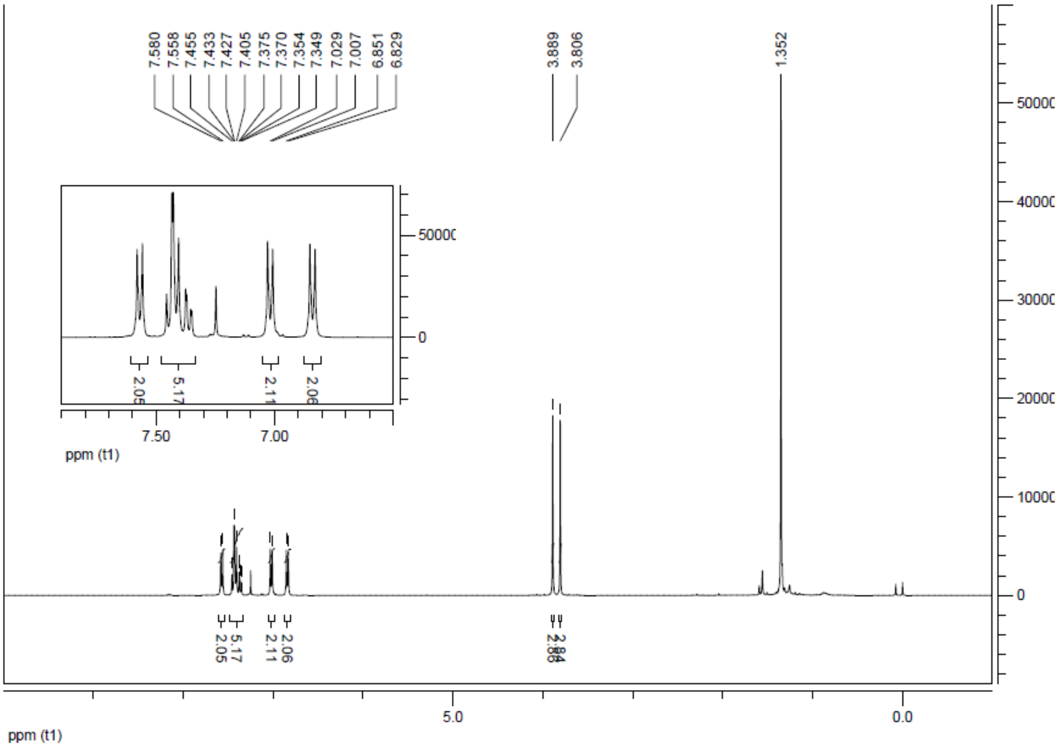
7.495
7.491
7.487
7.479
7.472
7.467
7.463
7.450
7.368
7.339
7.327
7.322
7.308
7.303
7.293
7.288
7.263
7.256
7.247
2.543
2.238
1.00
2.02
2.07
1.06
8.16
3.00
2.98
7.90 7.80 7.70 7.60 7.50 7.40 7.30
ppm (t1)
10.0
5.0
0.0
ppm (t1)


152.590
152.279
133.589
133.338
132.829
132.297
130.847
129.803
129.562
129.499
128.264
128.072
127.705
127.394
126.663
126.540
126.007
125.960
124.883
120.866
110.638
77.317
77.000
76.682
21.798
16.746
150
100
50
0
ppm (t1)


OMe
ᵗBu
O
OMe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7.455
7.433
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7.405
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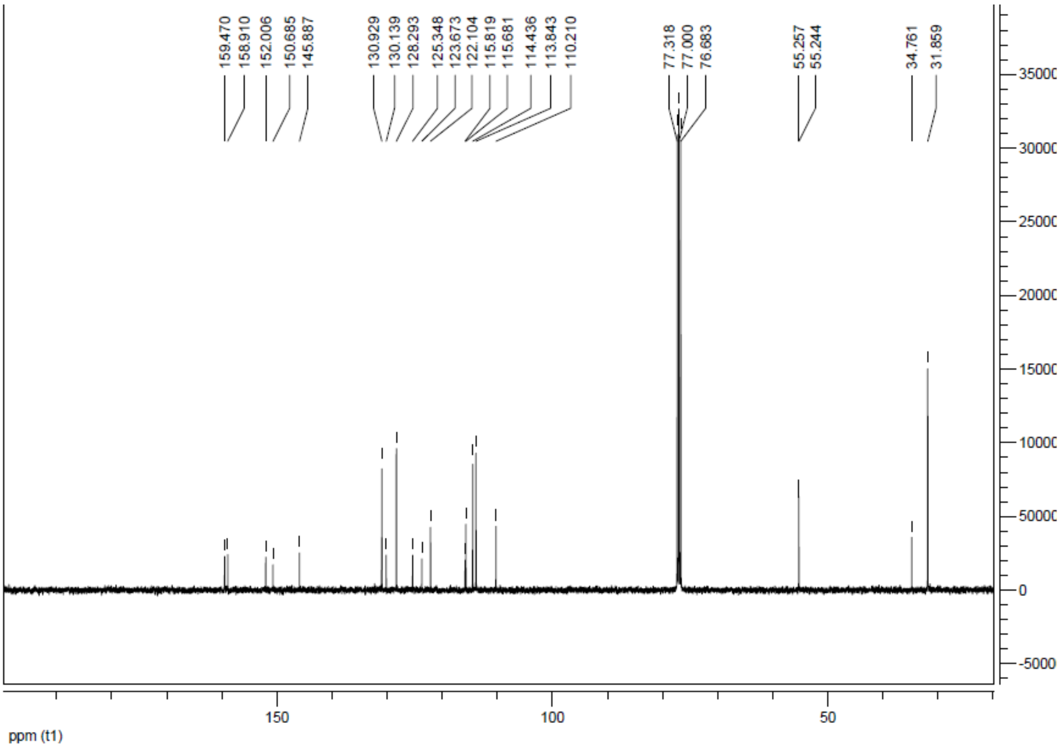
7.370
7.354
7.349
7.029
7.007
6.851
6.829
3.889
3.806
1.352
2.05
5.17
2.11
2.06
2.86
2.84
7.50
7.00
ppm (t1)
50000
0
50000
40000
30000
20000
10000
0
5.0
0.0
ppm (t1)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130.139
128.293
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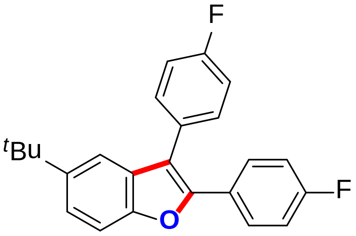
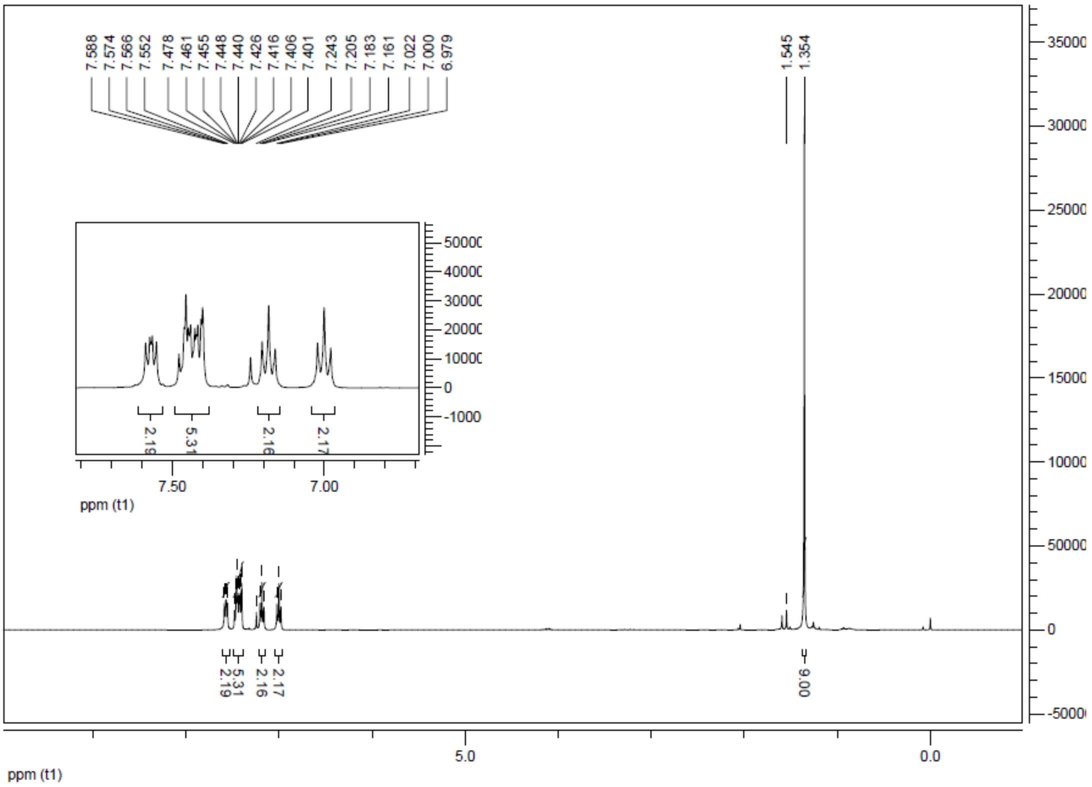
123.673
122.104
115.819
115.681
114.436
113.843
110.210
77.318
77.000
76.683
55.257
55.244
34.761
31.859
35000
30000
25000
20000
15000
10000
5000
0
-5000
150
100
50
ppm (t1)


F
tBu
O
F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7.455
7.448
7.440
7.426
7.416
7.406
7.401
7.243
7.205
7.183
7.161
7.022
7.000
6.979
1.545
1.354
2.19
5.31
2.16
2.17
9.00
7.50
7.00
ppm (t1)
5.0
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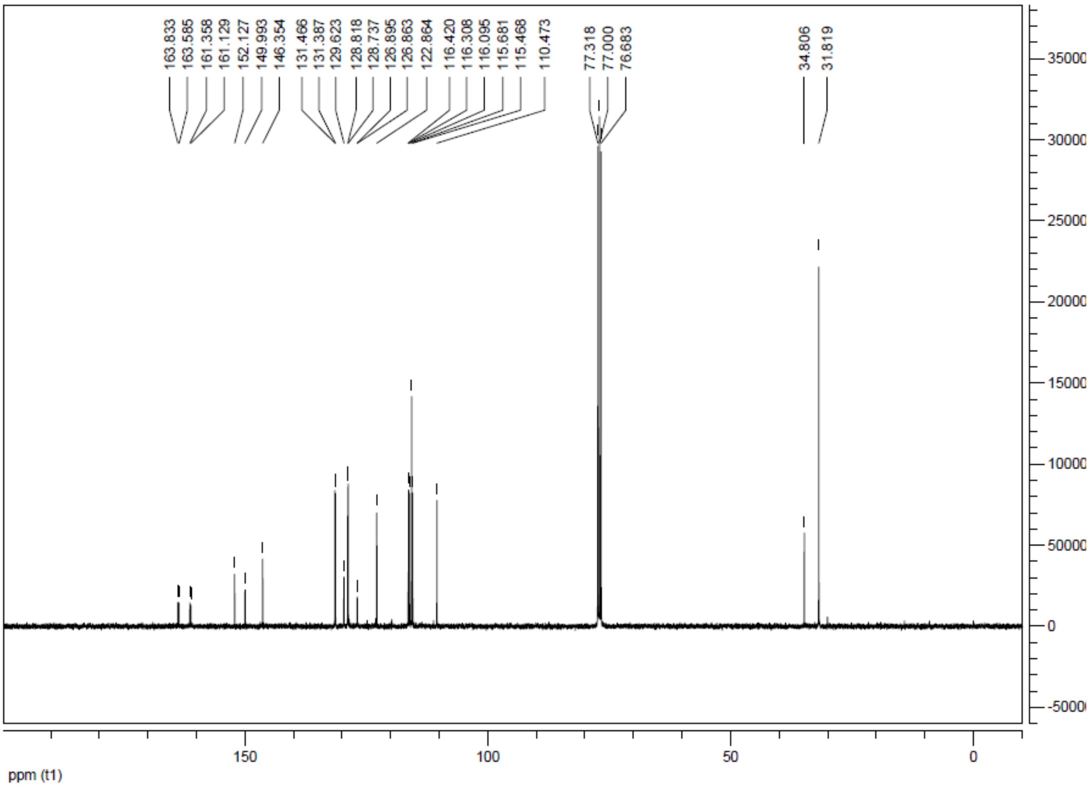
ppm (t1)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131.466
131.387
129.623
128.818
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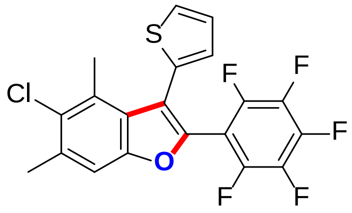
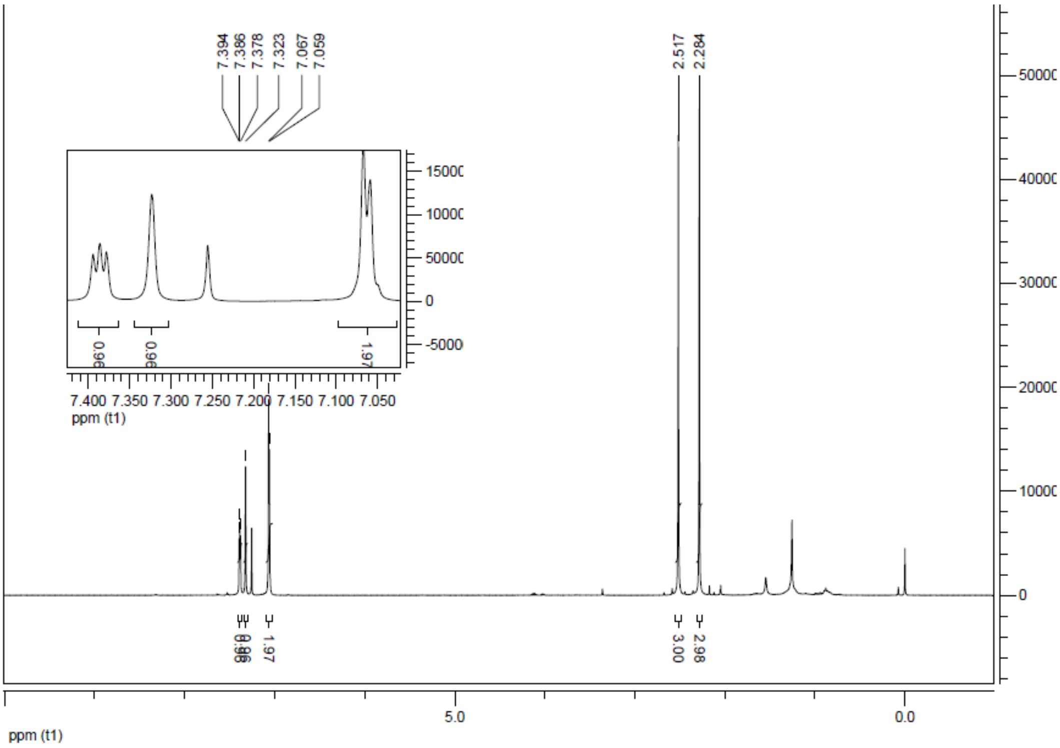
126.895
126.863
122.864
116.420
116.308
116.095
115.681
115.468
110.473
77.318
77.000
76.683
34.806
31.819
150
100
50
0
ppm (t1)


S
Cl
F
F
F
F
F
O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7.323
7.067
7.059
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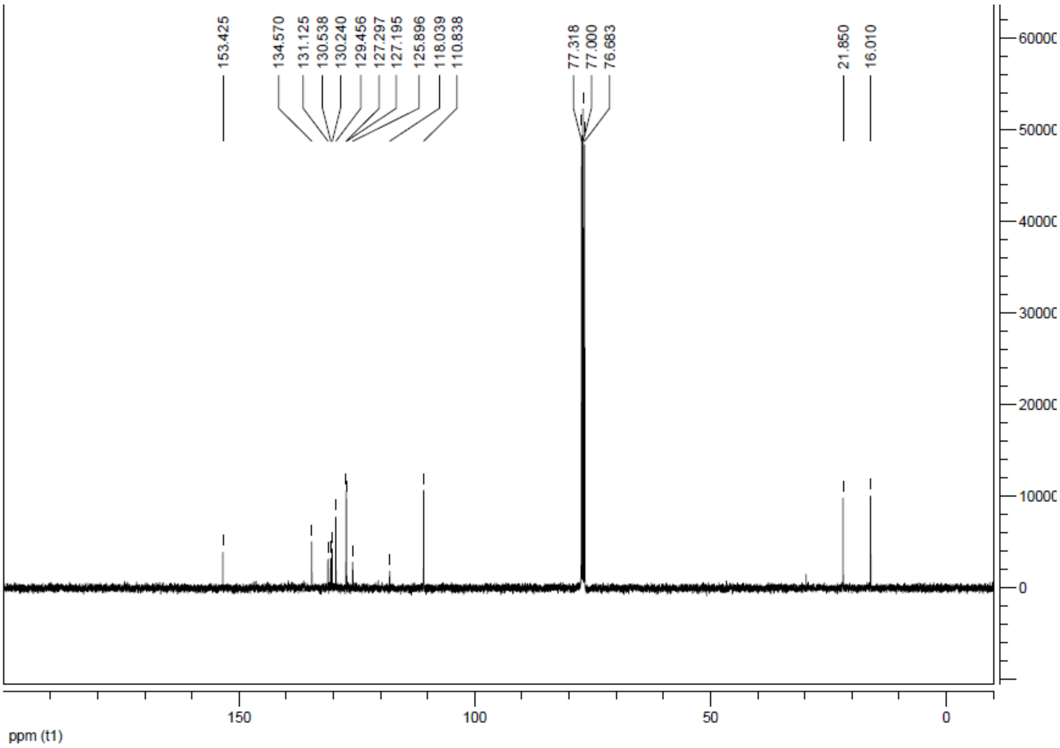
2.284
15000
10000
5000
0
-5000
0.96
0.96
1.97
7.400 7.350 7.300 7.250 7.200 7.150 7.100 7.050
ppm (t1)
0.96
0.96
1.97
3.00
2.98
50000
40000
30000
20000
10000
0
5.0
0.0
ppm (t1)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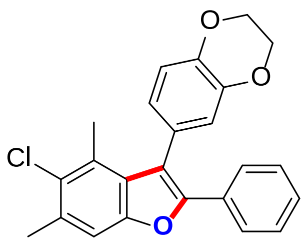
125.896
118.039
110.838
77.318
77.000
76.683
21.850
16.010
60000
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)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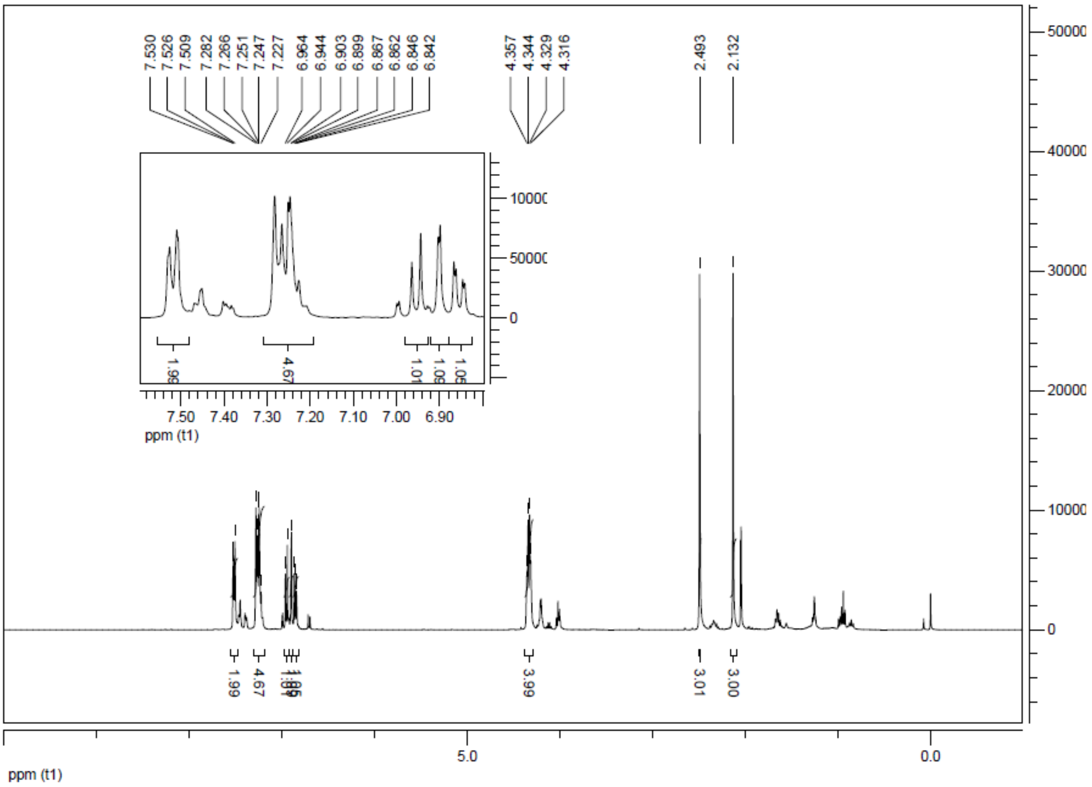
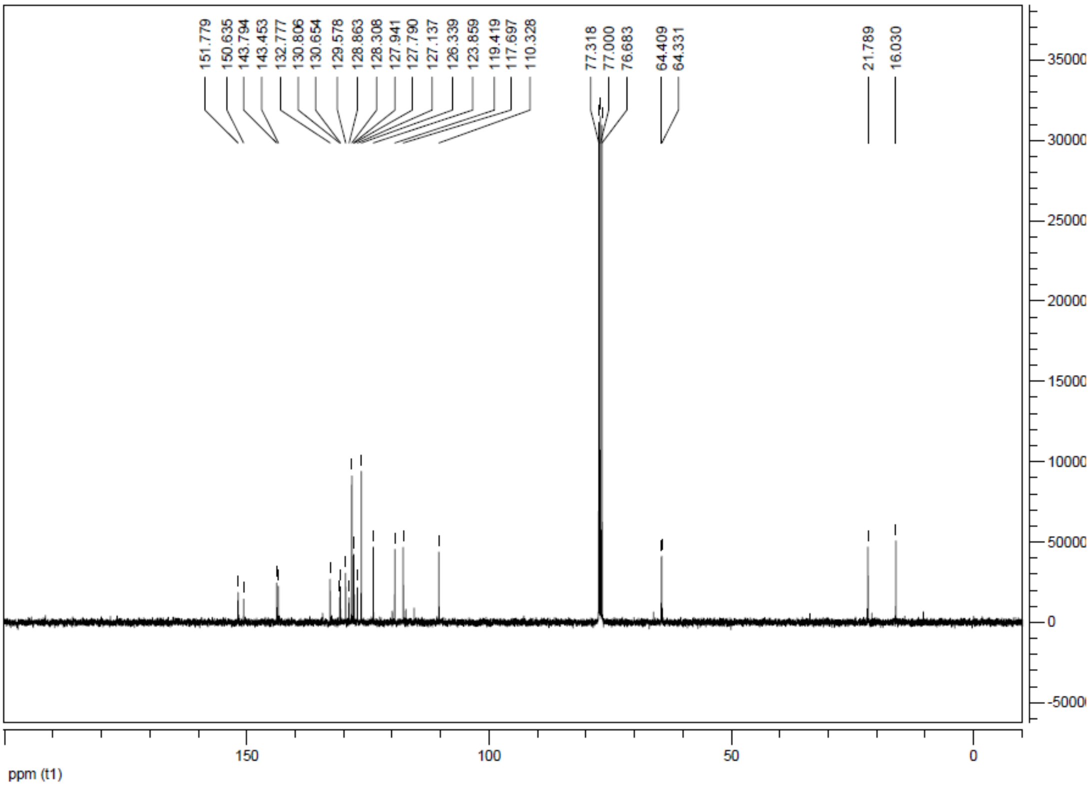
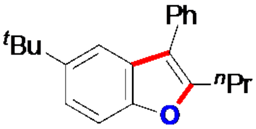
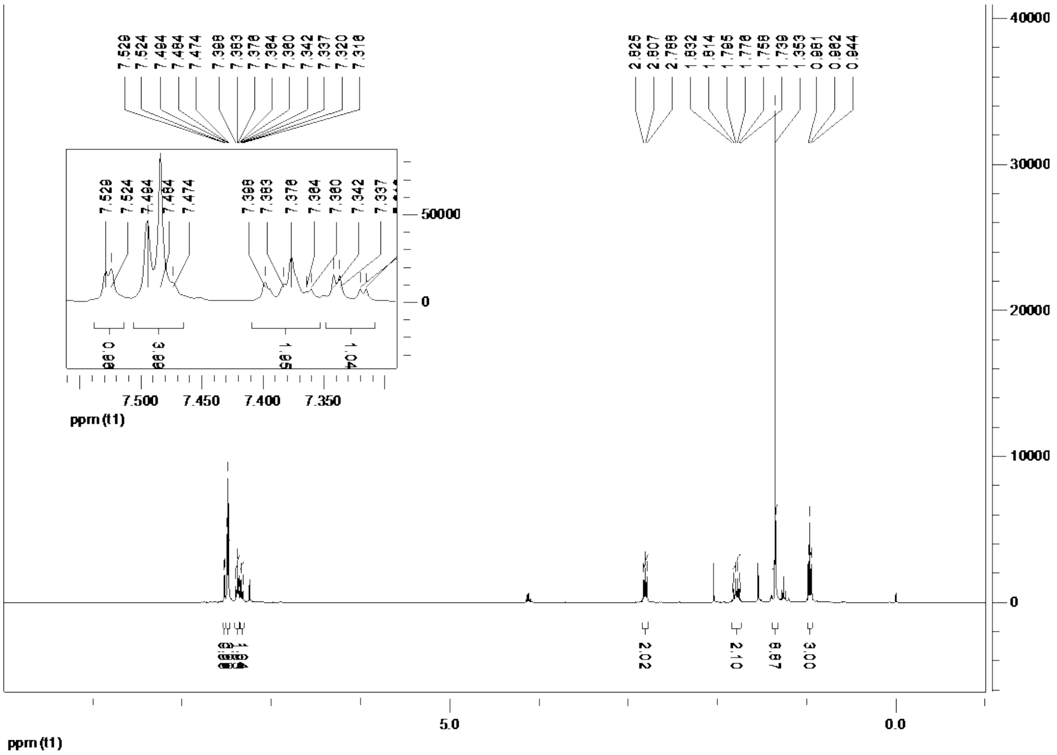
Cl
O


7.530
7.526
7.509
7.282
7.266
7.251
7.247
7.227
6.964
6.944
6.903
6.899
6.867
6.862
6.846
6.842
4.357
4.344
4.329
4.316
2.493
2.132
1.99
4.67
1.01
1.08
1.05
7.50 7.40 7.30 7.20 7.10 7.00 6.90
ppm (t1)
1.99
4.67
3.99
3.01
3.00
5.0
0.0
ppm (t1)
50000
40000
30000
20000
10000
0


151.779
150.635
143.794
143.453
132.777
130.806
130.654
129.578
128.863
128.308
127.941
127.790
127.137
126.339
123.859
119.419
117.697
110.328
77.318
77.000
76.683
64.409
64.331
21.789
16.030
150
100
50
0
ppm (t1)
35000
30000
25000
20000
15000
10000
50000
0
-5000


Ph
tBu
nPr
O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7.474
7.398
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7.378
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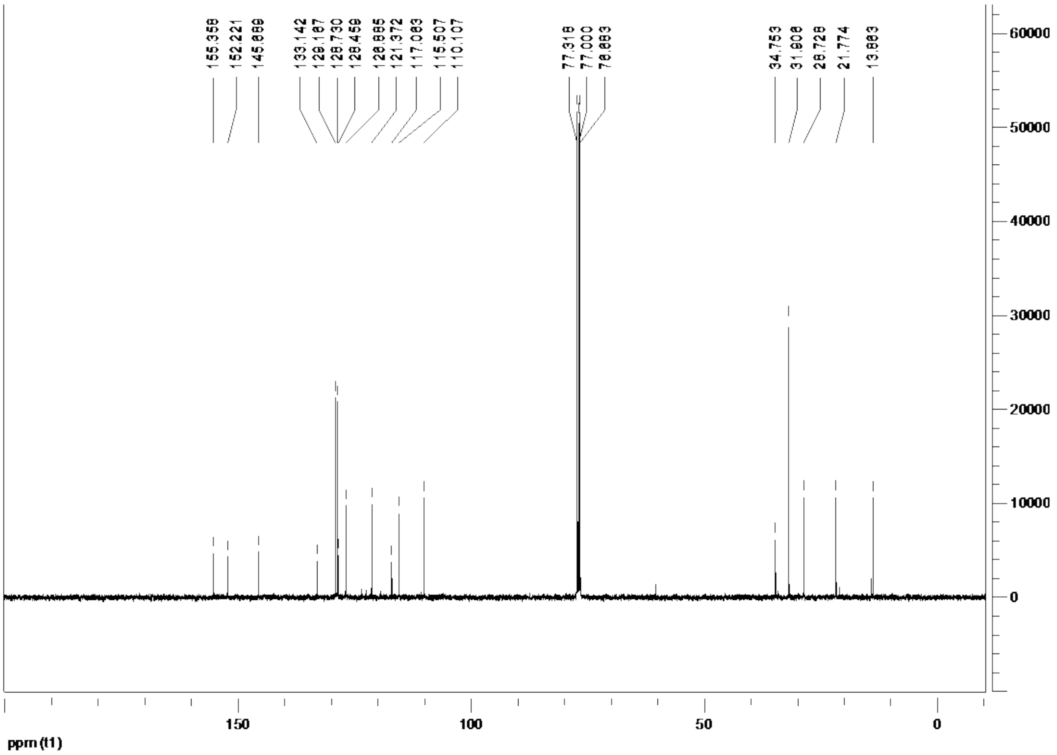
7.360
7.342
7.337
7.320
7.316
2.825
2.807
2.788
1.832
1.814
1.795
1.776
1.758
1.739
1.353
0.981
0.962
0.944
40000
30000
20000
10000
0
50000
0
0.98
3.98
1.95
1.04
7.500
7.450
7.400
7.350
ppm (t1)
2.02
2.10
8.87
3.00
5.0
0.0
ppm (t1)


155.358
152.221
145.869
133.142
129.187
128.730
128.459
126.865
121.372
117.083
115.507
110.107
77.318
77.000
76.683
34.753
31.908
28.728
21.774
13.883
60000
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)