Electronic Supplementary Information

# Cu(II)-Catalyzed Aerobic Oxidative Coupling of Furans with Indoles Enables Expeditious Synthesis of Indolyl-Furans with Blue Fluorescence

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## 1. General Method:

### Instrumentation:

The reactions were carried out under compressed air unless otherwise noted. Analytical thin-layer chromatography was performed on *Merck TLC Silica gel 60* with F-254 indicator, visualized by UV light or stained with vanillin, iodine, potassium permanganate, ninhydrin, or phosphomolybdic acid as deemed appropriate for different reactions. Column chromatography was performed using 100-200 mesh silica gel. Solvent mixtures are calculated as volume/volume.

$^1$H-NMR and $^{13}$C-NMR have been recorded on Bruker Avance III 400 and Avance III HD 500 spectrometers in the deuterated solvents as mentioned. NMR data are reported in the following order: chemical shift (δ) values are reported in ppm with the solvent resonance as internal standard (CDCl3: $\delta = 7.26$ ppm for $^1$H, $\delta = 77.16$ ppm for $^{13}$C). The multiplicities are presented as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (*J*) are given in hertz (Hz).

High-resolution mass spectra were recorded on Agilent LCMS-QTOF (6200 series TOF/6500 series Q-TOF). The ionization method used was electron-spray ionization. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded with a Shimadzu IRAffinity-1S spectrometer (ATR, neat) and are reported as wavenumber (cm$^{-1}$) of absorption. All yields reported are after the isolation of the pure substance by column chromatography.

### Chemicals:

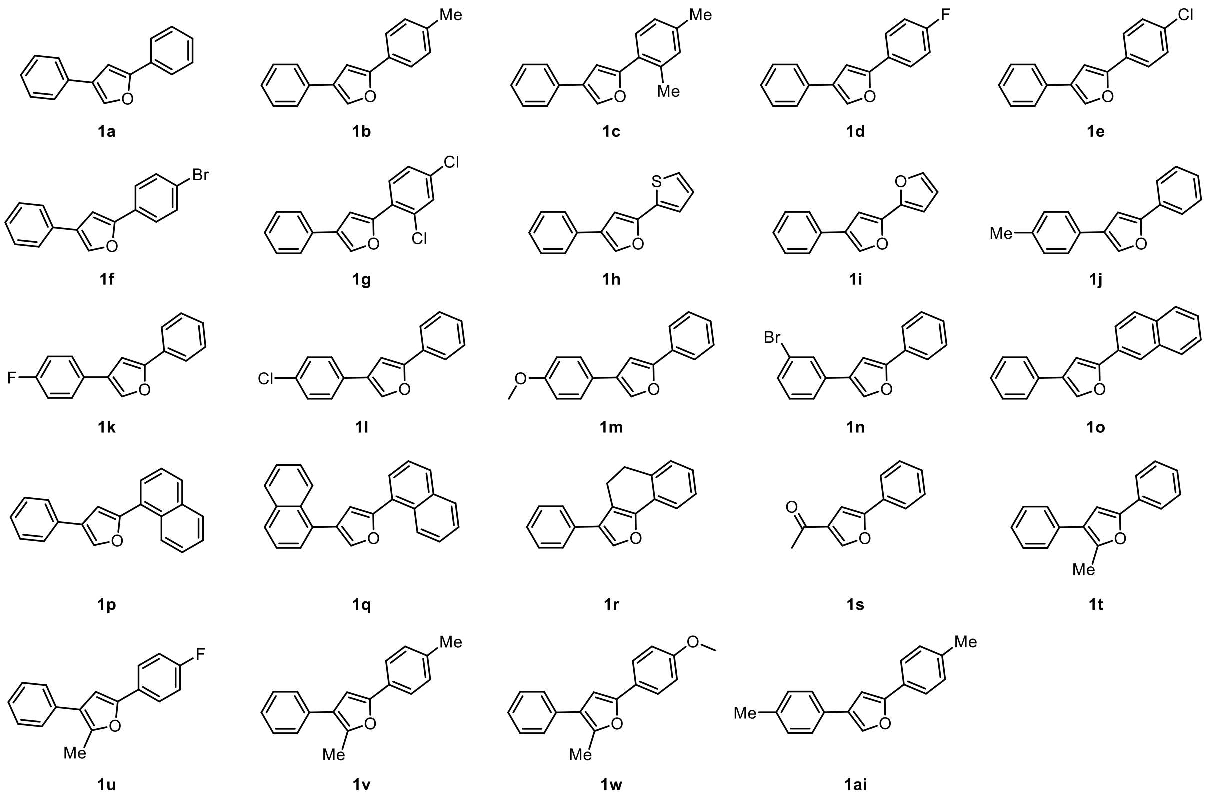
Unless otherwise noted, all commercially available compounds were used without further purification. Solvents such as toluene, ethanol, acetonitrile etc. were purchased from Merck and used as such for oxidative cross-coupling reactions. Solvents for chromatography were technical grade and distilled before use. The chemicals and solvents were purchased from these companies: Sigma-Aldrich, TCI, Acros Organics, Spectrochem, SRL chemicals, Qualigens, and Avra.

## 2. Preparation of Starting materials:

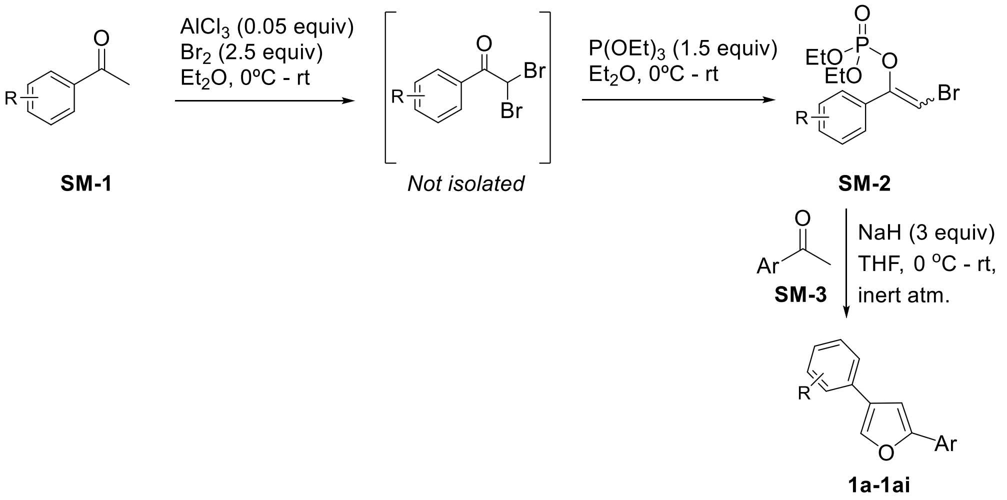
Both indoles and furans were synthesized using literature-known procedures. Their identity and purity were confirmed by comparison with reported characterization data. The characterization data for the new furans are reported below.

### 2.1 General procedure for the synthesis of furans 1a-1ai (GP-1):

All the furans were synthesized through a three-step protocol as described in scheme S1 by a known literature method by Fernandes et al.[1]

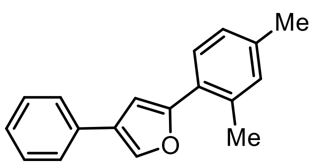


**Scheme S1:** Synthesized furans **1a-1ai**



**Scheme S2**: General synthesis of furans **1a-1ai**

## 2.2 Characterization details of the new Furans:



**2-(2,4-dimethylphenyl)-4-phenylfuran, 1c:** Furan **1c** was synthesized using appropriate starting materials according to the **GP-1**. The product was obtained in 40% yield as a light yellow solid.

**R*f* -value:** 0.75 (5% $Et_2O$/Hexane)

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 7.74 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 5.3 Hz, 2H), 6.77 (s, 1H), 2.50 (s, 3H), 2.33 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)**: δ 154.8, 137.6, 137.3, 134.6, 132.7, 132.0, 128.9, 128.0, 127.2, 127.1, 126.8, 125.9, 123.9, 107.0, 21.8, 21.2.

**IR** (KBr, $cm^{-1}$): = 2922, 2326, 1610, 1490, 1448, 1145, 929, 908, 808, 748, 692.

**HRMS** (ESI) m/z**:** $[M]^+$ Calcd for $C_{18}H_{16}O$: 248.1201, found: 248.1196

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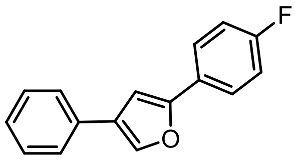

**2-(4-fluorophenyl)-4-phenylfuran, 1d:** Furan **1d** was synthesized using starting materials according to the **GP-1**. The product was obtained in 55% yield as a white solid.

**R*f* -value:** 0.75 (5% $Et_2O$/Hexane)

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 7.72 (s, 1H), 7.68 – 7.66 (m, 2H), 7.53 – 7.51 (m, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.30-7.23 (m, 1H), 7.09 (t, *J* = 8.7 Hz, 2H), 6.88 (s, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)**: δ 162.3 (d, *J* = 247.4 Hz), 161.1, 154.0, 137.9, 132.3, 128.9, 128.5, 127.1 (d, *J* = 3.4 Hz), 125.7 (d, *J* = 8.1 Hz), 115.9, 115.7, 103.7 (d, *J* = 1.0 Hz).

**$^{19}$F NMR (377 MHz, $CDCl_3$):** δ -113.89.

**IR** (KBr, $cm^{-1}$): = 1759, 1598, 1496, 1450, 1411, 1226, 1157, 1099, 912, 837, 804, 746, 690.

**HRMS** (ESI) m/z: $[M]^+$ Calcd for $C_{16}H_{11}FO$: 238.0794, found: 238.0786

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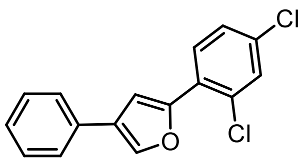

**2-(2,4-dichlorophenyl)-4-phenylfuran, 1g:** Furan **1g** was synthesized using appropriate starting materials according to the **GP-1**. The product was obtained in 55% yield as a white solid.

**R*f* -value:** 0.76 (5% $Et_2O$/Hexane)

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 7.83 (d, *J* = 8.6 Hz, 1H), 7.79 (s, 1H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.48 (d, *J* = 2.0 Hz, 1H), 7.44-7.39 (m, 3H), 7.33-7.31 (m, 2H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)**: δ 150.1, 138.1, 133.3, 132.0, 130.6, 130.5, 128.9, 128.6, 128.5, 127.6, 127.3, 125.9, 123.9, 110.2.

**IR** (KBr, cm$^{-1}$): = 1757, 1467, 1377, 1199, 1147, 1105, 1010, 912, 867, 815, 744, 690.

**LCMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{11}Cl_2O$: 289, found: 289.

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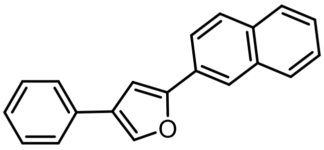

**2-(naphthalen-2-yl)-4-phenylfuran, 1o:** Furan **1o** was synthesized using appropriate starting materials according to the **GP-1**. The product was obtained in 48% yield as a white solid.

**R*f* -value:** 0.75 (5% $Et_2O$/Hexane)

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.20 (s, 1H), 7.90-7.87 (m, 2H), 7.84-7.82 (m, 3H), 7.58 (d, *J* = 7.1 Hz, 2H), 7.49 (dd, *J* = 7.9, 6.1 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.10 (s, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)**: δ 154.9, 138.2, 133.5, 132.8, 132.3, 128.9, 128.6, 128.5, 128.2, 128.0, 127.8, 127.2, 126.6, 126.1, 125.9, 122.3, 122.3, 104.6.

**IR** (KBr, cm$^{-1}$): = 1753, 1450, 1141, 966, 921, 902, 864, 808, 744, 692.

**HRMS** (ESI) m/z: $[M]^+$ Calcd for $C_{20}H_{14}O$: 270.1045, found: 270.1037.

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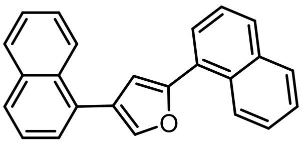


**2,4-di(naphthalen-1-yl)furan, 1q:** Furan **1q** was synthesized using appropriate starting materials according to the **GP-1**. The product was obtained in 45% yield as a white solid.

**R*f* -value:** 0.75 (5% $Et_2O$/Hexane)

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.52 (d, *J* = 8.3 Hz, 1H), 8.28 (dd, *J* = 6.2, 3.4 Hz, 1H), 7.90-7.82 (m, 6H), 7.57-7.48 (m, 7H), 7.04 (s, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)**: δ 153.8, 140.3, 134.1, 134.0, 131.8, 130.8, 130.4, 128.9, 128.7, 128.6, 128.4, 128.0, 127.0, 126.8, 126.6, 126.4, 126.3, 126.1, 126.0, 125.7, 125.62, 125.5, 125.4, 112.0.

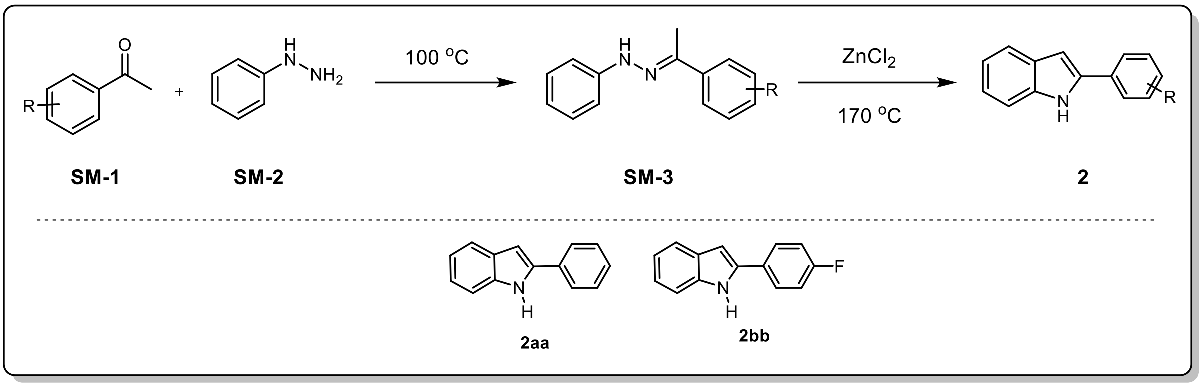
**IR** (KBr, cm$^{-1}$): = 1766, 1508, 1394, 1163, 1010, 906, 800, 771, 727, 646.

**LCMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{17}O$: 321, found: 321.

### 2.3 General procedures for the synthesis of Indoles 2 (GP):

Indoles were synthesized by the literature known method as mentioned below. The identity of the indoles were confirmed by comparison with reported NMR data.

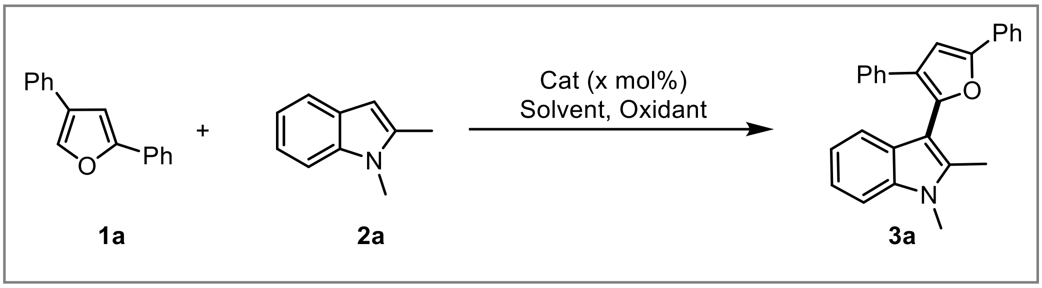
### General procedure 2 (GP2): Fischer Indole synthesis



The procedure is based on a modified literature method.[2] The Acetophenone derivatives (**SM-1**) (1.00 equiv.), and phenylhydrazine (**SM-2**) (1.00 equiv.) were combined in a clean and dry round bottom flask and heated in an oil bath at 100 °C. The reaction mixture was maintained at this temperature for 30 min to 1 h. On completion of the reaction (as indicated by TLC analysis), the mixture was cooled to room temperature as a solid was formed then diluted with EtOH and kept for crystallization. The crystallized product hydrazone (**SM-3**) (1.00 equiv.), and $ZnCl_2$ (7.00 equiv.) were combined in a clean and dry round bottom flask and heated in an oil bath at 170 °C. The reaction mixture was maintained at this temperature for 30 min. On completion of the reaction (as indicated by TLC analysis), Silica (4 times) was added to the flask and stirred solid mass with a glass rod to remove the mixture's stickiness then water and a small amount of conc. HCl was added to the flask to dissolve $ZnCl_2$. Filter out this mixture and solid boiled with EtOH then silica was separated through filtration, combined filtrates collected and purification was done by crystallization to afford pure **2**.

## 3. Optimization Reactions:

**Table S1:** Optimization of the reaction conditions for the oxidative coupling of 2,4-diphenyl furan **1a** and 1,2-dimethylindole **2a**



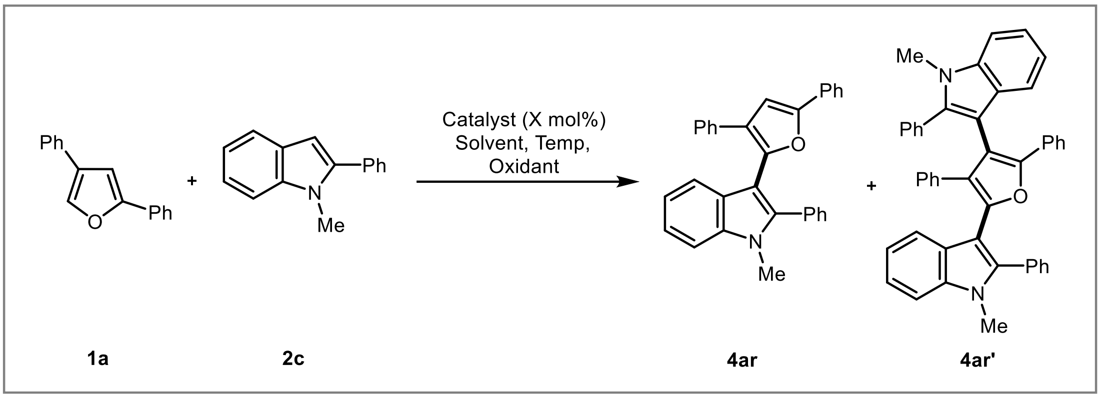
| Entry | Catalyst | (x mol%) | Solvent | Oxidant | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | CuBr | 20 | MeOH | Air | <5 |
| 2 | $Cu(CH_3CN)_4PF_6$ | 20 | MeOH | Air | 24 |
| 3[c] | $CuCl_2{\cdot}2H_2O$ | 30 | MeOH | Air | 22 |
| 4[c] | $CuCl_2{\cdot}2H_2O$ | 30 | EtOH | Air | 36 |
| 5 | $CuCl_2{\cdot}2H_2O$ | 30 | EtOH | Air | 47 |
| 6 | $CuCl_2{\cdot}2H_2O$ | 30 | $MeNO_2$ | Air | 39 |
| 7 | $CuCl_2{\cdot}2H_2O$ | 30 | EtOAc | Air | <5 |
| 8 | $CuCl_2{\cdot}2H_2O$ | 30 | DMF | Air | <5 |
| 9 | $CuCl_2{\cdot}2H_2O$ | 30 | DMSO | Air | <5 |
| 10 | $CuCl_2{\cdot}2H_2O$ | 10*3 | EtOH | Air | 63 |
| 11 | $CuCl_2{\cdot}2H_2O$ | 120 | EtOH | Air | 73 |
| 12 | $CuCl_2{\cdot}2H_2O$ | 50 | EtOH | Air | 67 |
| 13[d] | $CuCl_2{\cdot}2H_2O$ | 20 | EtOH | $H_2O_2$ | 38 |
| 14 | $CuCl_2{\cdot}2H_2O$ | 20 | EtOH | TBHP | ND |
| 15[e] | $CuCl_2{\cdot}2H_2O$ | 20 | EtOH | Oxone | 30 |
| 16 | $CuCl_2{\cdot}2H_2O$ | 30 | EtOH | CA | 71 |
| **17** | **$CuCl_2{\cdot}2H_2O$** | **30** | **EtOH/MeCN (10:1)** | **CA** | **81** |
| 18 | $CuCl_2{\cdot}2H_2O$ | 30 | EtOH/MeCN (5:1) | CA | 61 |
| 19 | $CuCl_2{\cdot}2H_2O$ | 20 | EtOH/MeCN (10:1) | CA | 60 |
| 20 | $CuCl_2{\cdot}2H_2O$ | 30 | MeOH | CA | 80 |
| 21[f] | $CuCl_2{\cdot}2H_2O$ | 30 | EtOH/MeCN (10:1) | CA | 61 |
| 22 | CuCl | 20 | EtOH | CA | 78 |
| 23 | Anhyd. $CuCl_2$ | 30 | EtOH/MeCN (10:1) | CA | 54 |
| 24 | $FeCl_3.6H_2O$ | 20 | Toluene | $O_2$ | 55[g] |
| 25 | $CuCl_2{\cdot}2H_2O$ | 30 | EtOH | $N_2$ | <10[h] |
| 26 | none | - | EtOH/MeCN | CA | ND |

[a]Conditions: Furan (1 equiv.), Indole (2 equiv.), catalyst, rt or temperature as mentioned, solvent (as mentioned). [b]Yields were determined after column chromatography. [c]reaction was carried out at 60 C [d]4 equiv of $H_2O_2$ was used. [e]2 equiv of oxone was used. [f]1.2 equiv of indole was used. [g]The reaction

required 5 equiv of indole for completion. [h]Complex reactivity (CA: Compressed air balloon; $O_2$ means oxygen balloon; ND: Not detected)

**Cu(II)-mediated oxidative coupling of *N*-Me-2-Aryl indoles with furans 1:**

**Table S2.** Optimization of reaction conditions for the oxidative coupling of N-Me-2-phenylindole **2c** with furan **1a**[a]

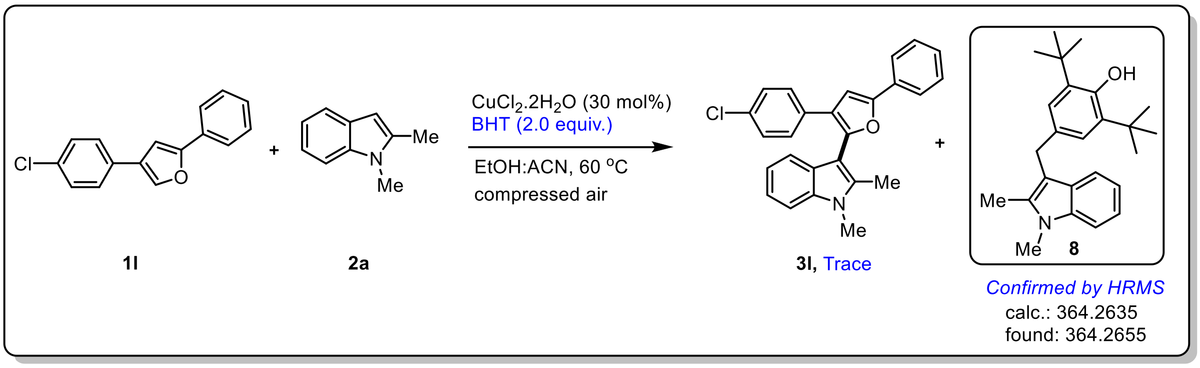


| Entry | Indole (equiv.) | Catalyst (x mol%) | Solvent | Oxidant | Yield (%)[b] |
|---|---|---|---|---|---|
| 1[c] | 2 | $CuCl_2.2H_2O$ (30) | EtOH:ACN (10:1) | CA | Incomplete |
| 2[d] | 4 | $CuCl_2.2H_2O$ (30) | MeOH | - | Incomplete |
| 3 | 4 | $CuCl_2.2H_2O$ (50) | MeOH | $O_2$ | 34 |
| 4[e] | 4 | $CuCl_2.2H_2O$ (30) | MeOH | Oxone | 19 (25) |
| 5[f] | 4 | $CuCl_2.2H_2O$ (30) | MeOH | Oxone | 28 |
| 6 | 4 | $CuCl_2.2H_2O$ (100) | MeOH | - | 54 (18) |
| 7[g] | 4 | $CuCl_2.2H_2O$ (100) | MeOH | - | Incomplete |
| 8 | 4 | $CuCl_2.2H_2O$ (200) | MeOH | - | 68 (25) |
| 9 | 4 | $CuCl_2.2H_2O$ (300) | MeOH | - | 82 |
| 10[h] | 4 | $CuCl_2.2H_2O$ (400) | MeOH | - | 90 |
| 11 | 4 | $CuCl_2.2H_2O$ (500 ) | MeOH | - | 90 |
| 12 | **4** | **$CuCl_2.2H_2O$ (400)** | **EtOH** | **-** | **82** |
| 13 | 2 | CuCl (20) | ACN | Oxone | Incomplete |
| 14[i] | 2 | $CuCl_2.2H_2O$ (50) | Toluene | $O_2$ | Trace |
| 15 | 2 | $FeCl_3$ (anhyd.) (30) | Toluene | $O_2$ | Trace |
| 16[i] | 2 | $FeCl_3$ (anhyd.) (10) | Toluene | $O_2$ | 38 |
| 17[i,j] | 2 | $FeCl_3$ (anhyd.) (30) | Toluene | $O_2$ | 40 |
| 18[i,j] | 2 | $FeCl_3$ (anhyd.) (50) | Toluene | $O_2$ | 36 |
| 19[i,j] | 4 | $FeCl_3$ (anhyd.) (50) | Toluene | $O_2$ | 25 |
| 20 | 2 | $FeCl_3$ (anhyd.) (10) | HFIP | $O_2$ | Trace |
| 21 | 2 | $FeCl_3$ (anhyd.) (30) | ACN | $O_2$ | Incomplete |
| 22[i] | 2 | $Fe(NO_3)_3.9H_2O$ (30) | Toluene | $O_2$ | ND |

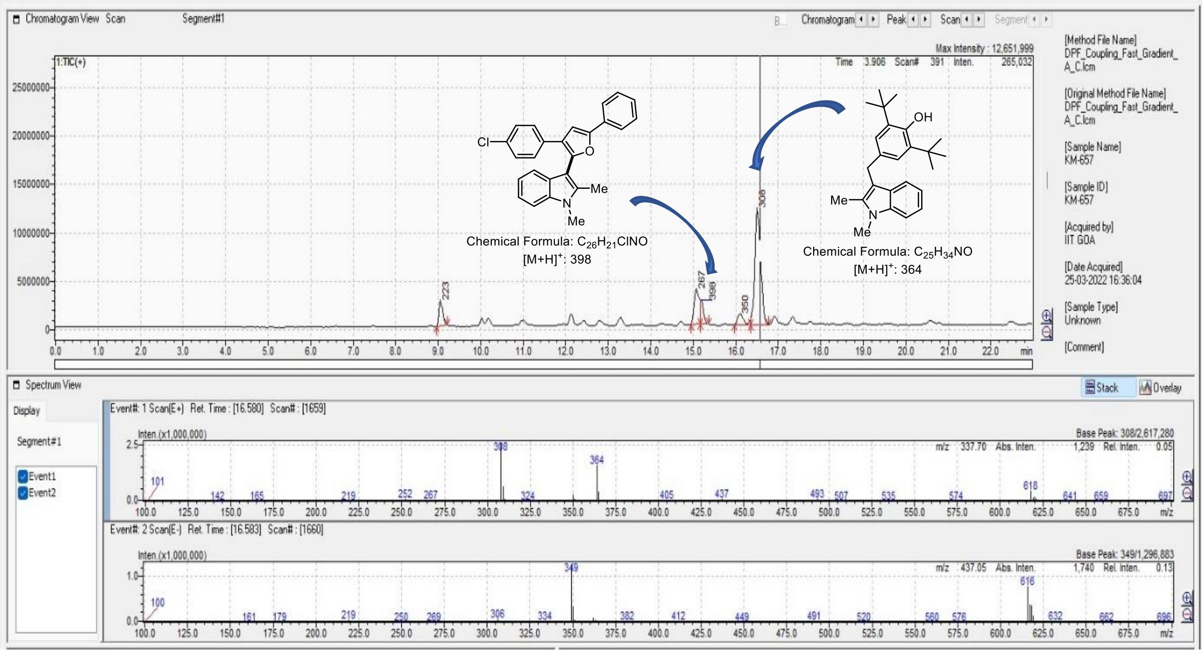
[a]Conditions: Furan (0.09 mmol, 1 equiv.)**,** Indole (equiv. as mentioned)**,** catalyst, rt or temperature as mentioned, solvent (as mentioned). [b]Isolated yields determined by column chromatography and BRSM yield in parenthesis. [c]Approximately 20% conversion was observed. [d]Halted after 7 days. [e]0.25 equiv. of oxone was added in 6 batches over 24 hour interval [f]0.5 equiv. of oxone was added in 6 batches over 24 hour interval. [g]Reaction mixture was heated at 50º C [h]In Methanol, slower reactions tend to form some unidentified impurity which complicates the purification procedure, to overcome this issue Ethanol can be used as a solvent. [i] Reaction mixture was heated at 90º C. [j]Product **4ar** showed a tendency to get converted into product **4ar'** in significant amounts**.** (CA: Compressed air balloon; $O_2$ means oxygen balloon; ND: Not detected)

## 4. Mechanistic Experiments:

(i) Radical trap experiment in the presence of *t*-Butylated Hydroxytoluene (BHT):



Furan **1l** (15 mg, 0.06 mmol, 1 equiv) and 1,2-dimethylindole (17 mg, 0.12 mmol, 2 equiv) was transferred to a clean and dried round bottom flask and dissolved in EtOH:ACN (10:1) (2 mL). To the resulting mixture, $CuCl_2.2H_2O$ (3 mg, 0.3 equiv) was added followed by the addition of BHT (26 mg, 2 equiv) and the reaction was stirred at 60 °C under compressed air condition. Progress of the reaction was monitored using TLC. However, only a trace amount of product **3l** could be detected and all the indole and BHT was consumed in 6 hrs. LC-MS analysis of the reaction mixture showed remaining furan **1l** ($[M+H]^+$ = 255) whereas most of the indole was consumed in the reaction. A clear peak corresponding to 1,2-dimethylindole-BHT adduct **8** ($[M+H]^+$ = 364) was observed in the reaction. The same was also confirmed through HRMS after isolation: calc. for $[M+H]^+$ $C_{25}H_{34}NO$: 364.2635, found: 364.2655.


Max Intensity : 12,651,999
Time 3.906 Scan# 391 Inten. 265,032

[Method File Name]
DPF_Coupling_Fast_Gradient_A_C.lcm

[Original Method File Name]
DPF_Coupling_Fast_Gradient_A_C.lcm

[Sample Name]
KM-657

[Sample ID]
KM-657

[Acquired by]
IIT GOA

[Date Acquired]
25-03-2022 16:36:04

[Sample Type]
Unknown

[Comment]

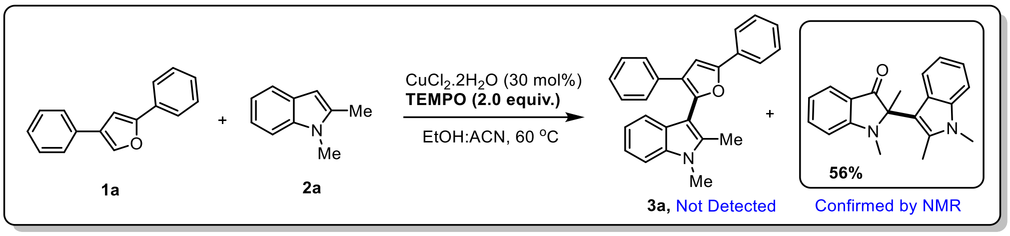
Chemical Formula: $C_{26}H_{21}ClNO$
$[M+H]^+$: 398

Chemical Formula: $C_{25}H_{34}NO$
$[M+H]^+$: 364

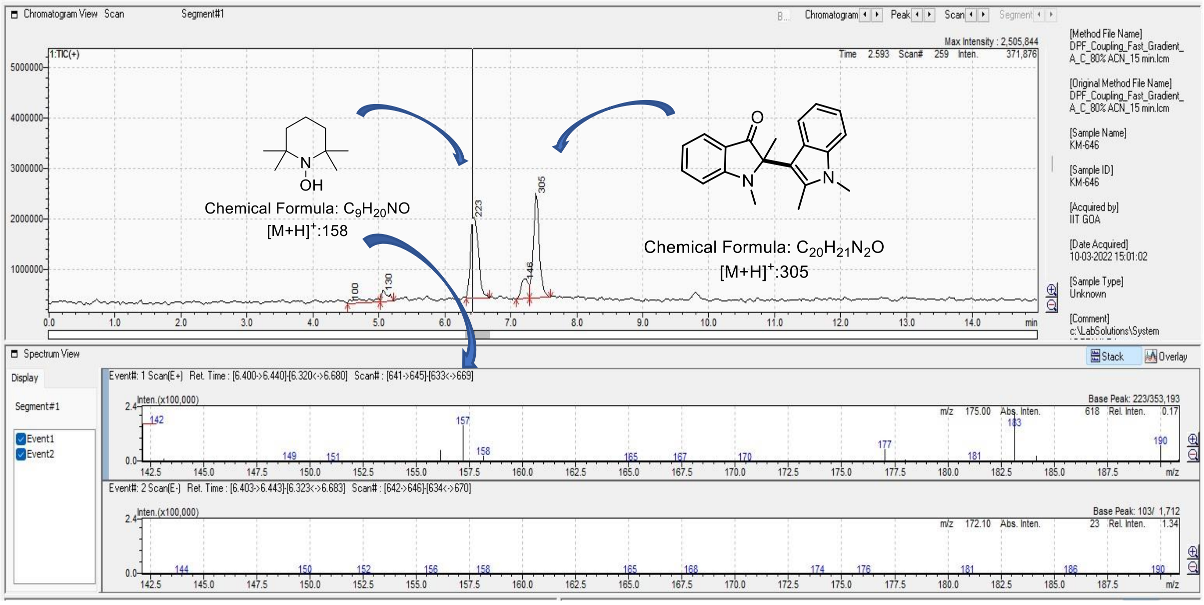
Event#: 1 Scan(E+) Ret. Time : [16.580] Scan# : [1659]
Base Peak: 308/2,617,280
m/z 337.70 Abs. Inten. 1,239 Rel. Inten. 0.05

Event#: 2 Scan(E-) Ret. Time : [16.583] Scan# : [1660]
Base Peak: 349/1,296,883
m/z 437.05 Abs. Inten. 1,740 Rel. Inten. 0.13

(ii) Radical trap experiment in the presence of 2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO):



Furan **1a** (30 mg, 0.13 mmol, 1 equiv) and 1,2-dimethylindole **2a** (39 mg, 0.27 mmol, 2.0 equiv) was transferred to a clean and dried round bottom flask and dissolved in EtOH:ACN (10:1) (2 mL). To the resulting mixture, $CuCl_2.2H_2O$ (7 mg, 0.3 equiv) was added followed by the addition of TEMPO (43 mg, 2.0 equiv), and the reaction was stirred at 60 °C. Progress of the reaction was monitored using TLC. However, product **3a** was not detected via TLC despite a prolonged reaction time. ESI-MS analysis of the reaction mixture only showed the remaining furan whereas all the indoles were consumed in the reaction.



Chemical Formula: $C_9H_{20}NO$
$[M+H]^+$:158

Chemical Formula: $C_{20}H_{21}N_2O$
$[M+H]^+$:305

[Method File Name]
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[Original Method File Name]
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[Sample Name]
KM-646

[Sample ID]
KM-646

[Acquired by]
IIT GOA

[Date Acquired]
10-03-2022 15:01:02

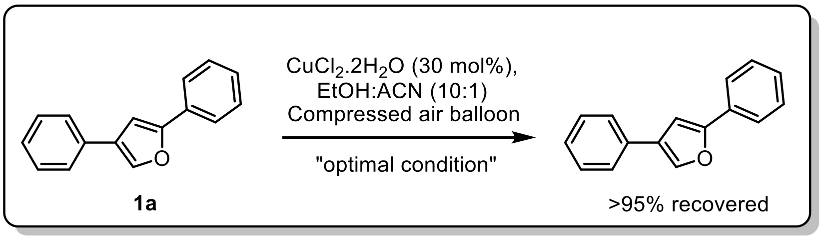
[Sample Type]
Unknown

[Comment]
c:\LabSolutions\System

Event#: 1 Scan(E+) Ret. Time : [6.400->6.440]-[6.320<->6.680] Scan# : [641->645]-[633<->669]
Base Peak: 223/353,193
m/z 175.00 Abs. Inten. 618 Rel. Inten. 0.17

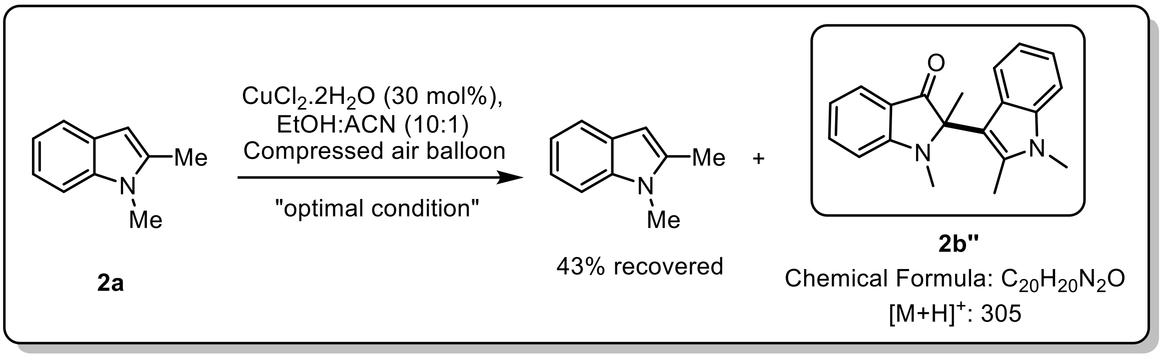
Event#: 2 Scan(E-) Ret. Time : [6.403->6.443]-[6.323<->6.683] Scan# : [642->646]-[634<->670]
Base Peak: 103/ 1,712
m/z 172.10 Abs. Inten. 23 Rel. Inten. 1.34

(iii) Control reaction without indole under standard optimal condition:

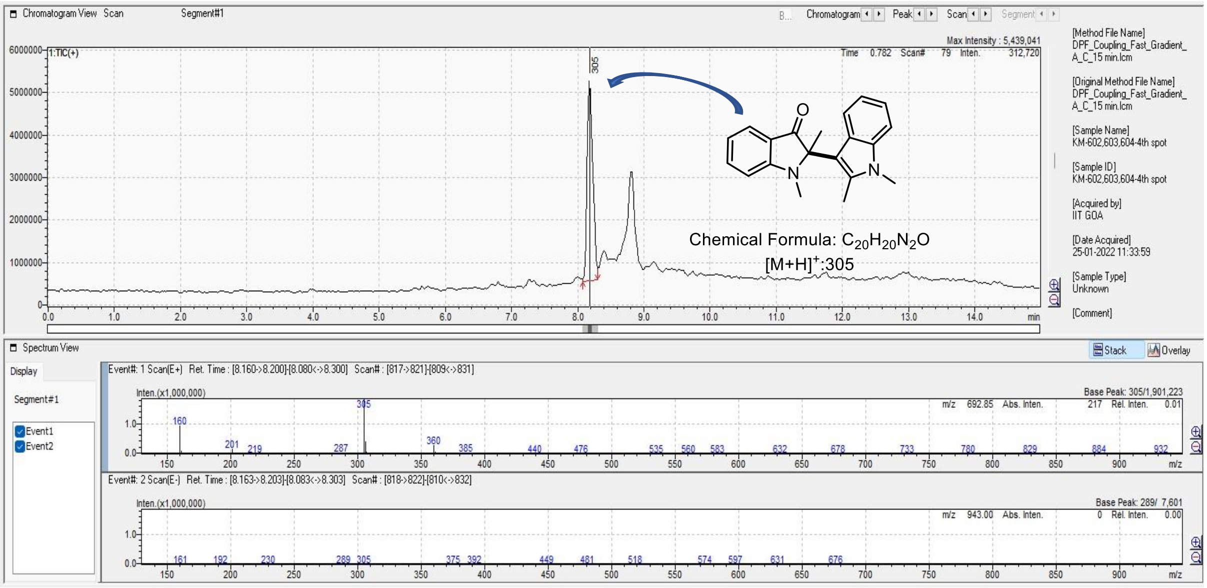


Furan **1a** (30 mg, 1 equiv.) was added to a clean and dried round bottom flask and dissolved in EtOH:ACN (10:1) (1 mL). To this solution, $CuCl_2.2H_2O$ (0.3 equiv.) was added and the resulting mixture was stirred at 60˚ C for 2 days under compressed air. The progress of the reaction was monitored using TLC. After 2 days, the reaction mixture was worked up using standard procedure and purified via column chromatography to recover 29.5 mg (98%) of furan **1a**.

### (iv) Control reaction without furan under standard optimal condition:



1,2-dimethylindole **2a** (30 mg, 1 equiv.) was transferred to a clean and dried round bottom flask and dissolved in EtOH:CAN (10:1) (1 mL). To this solution, $CuCl_2.2H_2O$ (0.3 equiv.) was added and the resulting mixture was stirred at 60˚ C for 2 days under compressed air. The progress of the reaction was monitored using TLC. After 2 days, the reaction mixture was worked up using standard procedure and purified via column chromatography to recover 13 mg (43%) of 1,2-dimethylindole **2a**. ESI-MS analysis of the reaction mixture indicated the formation of indole homocoupled oxidized product **2b''** ($[M+H]^+$ = 305). **2b''** is known to form from 1,2-dimethylindole under oxidative conditions.[3]



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DPF_Coupling_Fast_Gradient_A_C_15 min.lcm

[Original Method File Name]
DPF_Coupling_Fast_Gradient_A_C_15 min.lcm

[Sample Name]
KM-602,603,604-4th spot

[Sample ID]
KM-602,603,604-4th spot

[Acquired by]
IIT GOA

[Date Acquired]
25-01-2022 11:33:59

[Sample Type]
Unknown

[Comment]

Event#: 1 Scan(E+) Ret. Time : [8.160->8.200]-[8.080<->8.300] Scan# : [817->821]-[809<->831]

Base Peak: 305/1,901,223

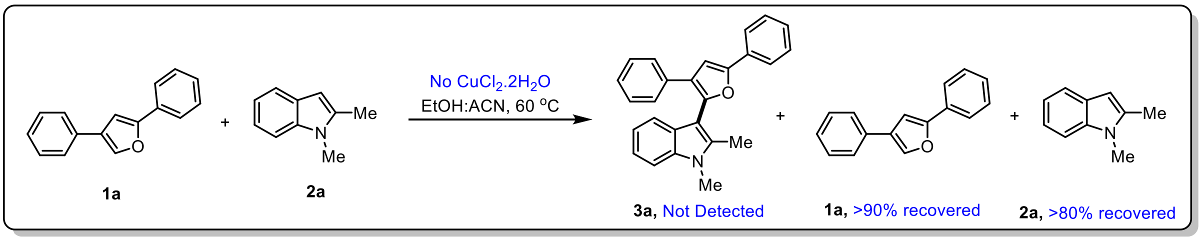
m/z 692.85 Abs. Inten. 217 Rel. Inten. 0.01

Event#: 2 Scan(E-) Ret. Time : [8.163->8.203]-[8.083<->8.303] Scan# : [818->822]-[810<->832]

Base Peak: 289/ 7,601

m/z 943.00 Abs. Inten. 0 Rel. Inten. 0.00

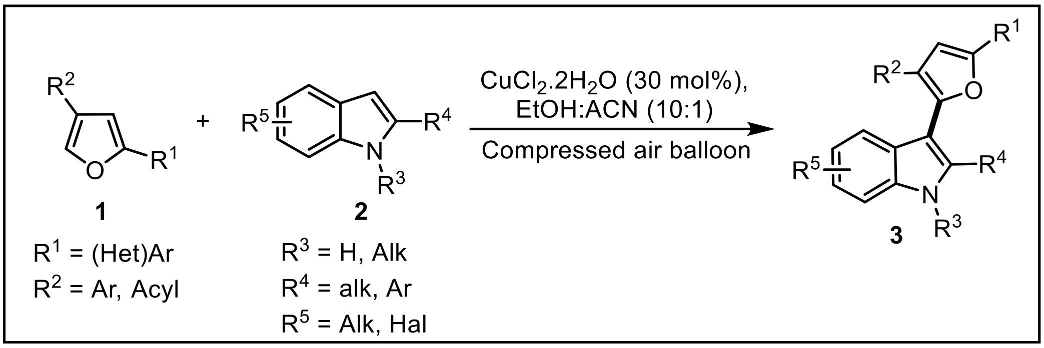
### (v) Control experiment without catalyst:



The reaction was performed using furan **1a** (15 mg, 0.068 mmol, 1.0 equiv.) and indole **2a** (20 mg, 0.137 mmol, 2.0 equiv.) under standard conditions without adding any catalyst. The cross-coupled product **3a** couldn’t be detected in the reaction mixture. Instead, > 90% furan and > 80% indole was recovered.

## 5. Characterization Details of the cross-coupled products:

### 5.1 General Procedure for the synthesis of compounds 3a-3r (GP-3):



To a clean and dried round bottom flask was added the furan **1** (0.13 mmol, 1.0 equiv.) and indole **2** (0.27 mmol, 2.0 equiv.) followed by the addition of $CuCl_2.2H_2O$ (0.04 mmol, 0.3 equiv.). The mixture was dissolved in 2 mL of EtOH:ACN (10:1). Reaction mixture was stirred at room temperature under the compressed air balloon till completion. The progress of the reaction was monitored using TLC ($Et_2O$/hexane 1:19) under UV exposure. Upon completion (usually 72 -96 h) as evidenced by complete consumption of furan on TLC, the reaction mixture was diluted with saturated aq. $NaHCO_3$ (5 mL) and the layers were separated. The aqueous layer was washed with DCM (3 x 10 ml) and the combined organic layer was dried over anhydrous $Na_2SO_4$. The solvent was removed *in vacuo* to obtain the mixture of crude products. Column chromatography (0-5% diethyl ether in PE) provided the pure product **3** as indicated below.

**Characterization Details of the Cross-Coupled Products 3a-3r:**

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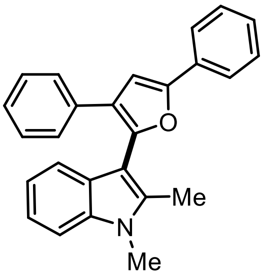

**3-(3,5-diphenylfuran-2-yl)-1,2-dimethyl-1H-indole, 3a:** The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.13 mmol, 1 equiv) and indole (39.5 mg, 0.27 mmol, 2 equiv) in 2 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3a** in 81% yield (40 mg, 0.11 mmol) as a white solid.

**$R_f$ -value:** 0.40 (5% $Et_2O$/Hexane)

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, $J$ = 7.8 Hz, 2H), 7.55 (d, $J$ = 7.9 Hz, 1H), 7.43 – 7.35 (m, 4H), 7.31 (d, $J$ = 8.2 Hz, 1H), 7.25 – 7.20 (m, 4H), 7.19 – 7.15 (m, 1H), 7.08 (t, $J$ = 7.5 Hz, 1H), 7.02 (s, 1H), 3.67 (s, 3H), 2.13 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)**: δ 153.1, 145.7, 137.1, 136.4, 133.5, 131.7, 131.0, 128.9, 128.9, 127.4, 126.7, 123.7, 122.8, 121.6, 120.3, 120.1, 120.0, 109.0, 106.7, 104.0, 29.9, 11.8.

**IR** (KBr, $cm^{-1}$): = 1625, 1598, 1494, 1415, 1130, 918, 767.

**HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{22}NO$: 364.1696, found: 364.1681.

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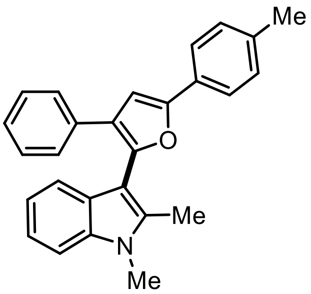

**1,2-dimethyl-3-(3-phenyl-5-(p-tolyl)furan-2-yl)-1H-indole, 3b:** The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.128 mmol, 1 equiv) and Indole (37 mg, 0.256 mmol, 2 equiv) in 2 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3b** in 91% yield (44 mg, 0.116 mmol) as a white solid.

**$R_f$ -value:** 0.47 (5% $Et_2O$/hexane)

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.40 (m, 2H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.27 (s, 1H), 7.25-7.17 (m, 5H), 7.09 –7.12 (m, 1H), 6.98 (s, 1H), 3.71 (s, 3H), 2.39 (s, 3H), 2.16 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 153.1, 145.0, 137.0, 136.2, 134.7, 129.5, 128.5, 128.5, 127.4, 127.0, 126.3, 124.3, 123.8, 123.7, 121.5, 120.1, 120.1, 108.9, 106.4, 104.4, 29.9, 21.4, 11.8.

**IR** (KBr, $cm^{-1}$)**:** 2918, 1500, 1471, 1446, 1406, 1386, 1251, 1130, 1012, 916, 806.

**HRMS**: (ESI) m/z: $[M]^+$ Calcd for $C_{27}H_{23}NO$ 377.1780; Found 377.1793.

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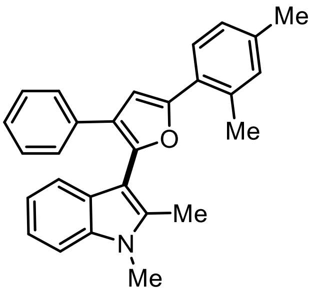

**3-(5-(2,4-dimethylphenyl)-3-phenylfuran-2-yl)-1,2-dimethyl-1H-indole), 3c:** The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.12 mmol, 1 equiv) and Indole (35.0 mg, 0.24 mmol, 2 equiv) in 3 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3c** in 53% yield (25 mg, 0.06 mmol) as a white solid.

**$R_f$ -value:** 0.38 (5% $Et_2O$/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 2H), 7.36 – 7.30 (m, 1H), 7.29 – 7.25 (m, 2H), 7.23 – 7.15 (m, 2H), 7.14 – 7.02 (m, 3H), 6.87 (s, 1H), 3.71 (s, 3H), 2.59 (s, 3H), 2.36 (s, 3H), 2.17 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ 152.8, 144.7, 137.1, 136.2, 134.8, 134.3, 133.6, 132.1, 128.6, 127.7, 127.4, 126.9, 126.8, 126.3, 125.2, 124.8, 123.5, 121.4, 120.2, 120.1, 110.1, 108.9, 29.9, 22.3, 21.2, 11.8.

**IR** (KBr, $cm^{-1}$): 3024, 2349, 2912, 1622, 1537, 1496, 1381, 1207, 1012, 910, 819, 746, 694.

**HRMS** (ESI, m/z): $[M]^+$ calcd for $C_{28}H_{25}NO$: 391.1936, found: 391.1922.

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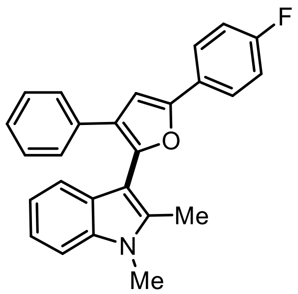

**3-(5-(4-fluorophenyl)-3-phenylfuran-2-yl)-1,2-dimethyl-1H-indole, 3d:** The product was obtained by following the **GP-3** using appropriate furan (50 mg, 0.209 mmol) and Indole (61 mg, 0.419 mmol) in 3 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3d** in 78% yield (63 mg, 0.165 mmol) as a white solid.

**R*f* -value:** 0.44 (5% $Et_2O$/hexane)

**$^1$H NMR (500 MHz, CDCl$_3$)**: δ 7.82 (dd, *J* = 8.3, 5.5 Hz, 2H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.37 – 7.27 (m, 4H), 7.21 –7.17 (m, 3H), 7.05 (s, 1H), 3.76 (s, 3H), 2.23 (s, 3H).

**$^{13}$C NMR (126 MHz, CDCl$_3$):** δ 162.1 (d, *J* = 246.8 Hz), 152.0, 145.5, 137.0, 136.3, 134.4, 128.6, 127.5 (d, *J* = 3.2 Hz), 127.3, 126.9, 126.4, 125.3 (d, *J* = 8.0 Hz), 123.9, 121.5, 120.2, 119.9, 115.8 (d, *J* = 22.0 Hz), 109.0, 106.8, 104.2, 29.8, 11.7.

**$^{19}$F NMR (377 MHz, CDCl$_3$):** δ -114.58.

**IR** (KBr, cm$^{-1}$)**:** 1627, 1595, 1496, 1475, 1226, 1128, 1097, 981, 918, 713.

**HRMS** (ESI) m/z: [M]$^+$ Calcd for $C_{26}H_{20}FNO$ 381.1529; Found 381.1543.

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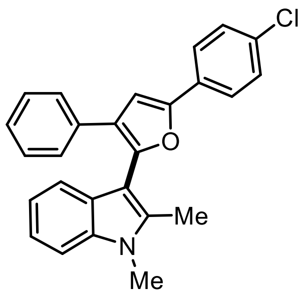

**3-(5-(4-chlorophenyl)-3-phenylfuran-2-yl)-1,2-dimethyl-1H-indole, 3e:** The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.117 mmol, 1 equiv), Indole (34.20 mg, 0.235 mmol, 2 equiv) and additional $CuCl_2.2H_2O$ (6 mg, 30 mol%) in 5 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3e** in 78% yield (36 mg, 0.09 mmol) as a white solid.

**R*f* -value:** 0.40 (5% $Et_2O$/hexane)

**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.72 (d, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.44 – 7.35 (m, 5H), 7.29 (dd, *J* = 8.7, 6.1 Hz, 3H), 7.24 –7.20 (m, 1H), 7.16 – 7.11 (m, 1H), 7.05 (s, 1H), 3.73 (s, 3H), 2.17 (s, 3H).

**$^{13}$C NMR (101 MHz, CDCl$_3$)**: δ 151.8, 145.9, 137.0, 136.4, 134.4, 132.8, 129.7, 129.0, 128.6, 127.4, 126.9, 126.5, 124.9, 124.0, 121.6, 120.3, 120.0, 108.9, 107.7, 104.1, 29.9, 11.8.

**IR** (KBr, cm$^{-1}$)**:** 3057, 2908, 1624, 1575, 1556, 1537, 1479, 1446, 1402, 1220, 1010, 916, 759.

**HRMS** (ESI, m/z): [M]$^+$ calcd for $C_{26}H_{20}ClNO$: 397.1233, found: 397.1220.

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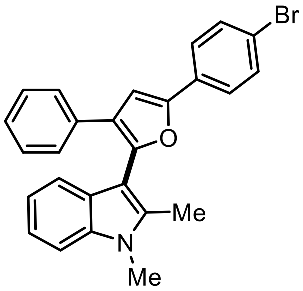

**3-(5-(4-bromophenyl)-3-phenylfuran-2-yl)-1,2-dimethyl-1H-indole, 3f:** The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.100 mmol, 1 equiv) and Indole (29 mg, 0.200 mmol, 2 equiv) in 4 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3f** in 74% yield (33 mg, 0.074 mmol) as a white solid.

**$R_f$ -value:** 0.42 (5% $Et_2O$/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$)**: δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.56 – 7.47 (m, 3H), 7.37 (d, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.27 – 7.21 (m, 3H), 7.20 – 7.14 (m, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.01 (s, 1H), 3.68 (s, 3H), 2.12 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)**: δ 151.8, 145.9, 137.0, 136.4, 134.3, 132.0, 130.1, 128.6, 127.4, 126.8, 126.5, 125.1, 124.0, 121.6, 120.8, 120.3, 120.0, 109.0, 107.8, 104.1, 29.9, 11.8.

**IR** (KBr, $cm^{-1}$)**:** 2910, 1624, 1589, 1573, 1477, 1398, 1251, 1128, 1070, 914, 800.

**HRMS** (ESI) m/z: $[M]^+$ Calcd for $C_{26}H_{20}BrNO$ 441.0728; Found 441.0718.

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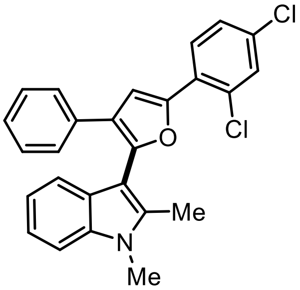

**3-(5-(2,4-dichlorophenyl)-3-phenylfuran-2-yl)-1,2-dimethyl-1H-indole, 3g:** The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.103 mmol, 1 equiv), Indole (30.1 mg, 0.206 mmol, 2 equiv) in the presence of catalyst ( 10 mg, 60 mol%) in 7 days at 60 °C. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3g** in 34% (54% BRSM) yield (15.3 mg, 0.035 mmol) as a white solid.

**$R_f$ -value:** 0.34 (5% $Et_2O$/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.95 (d, *J* = 8.5 Hz, 1H), 7.61–7.57 (m, 2H), 7.53 (s, 1H), 7.46 (d, *J* = 6.9 Hz, 3H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.35 – 7.28 (m, 4H), 7.15 (t, *J* = 6.9 Hz, 1H), 3.75 (s, 3H), 2.18 (s, 3H)

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ 148.2, 146.0, 137.1, 136.5, 134.3, 132.6, 130.5, 130.2, 128.6, 128.2, 128.0, 127.9, 127.5, 126.8, 126.6, 124.0, 121.6, 120.3, 119.9, 113.6, 109.0, 103.8, 29.9, 11.8.

**IR** (KBr, $cm^{-1}$): 3057, 2924, 1672, 1583, 1562, 1467, 1394, 1377, 1249, 1205, 1134, 1080, 916, 815, 543.

**HRMS**: (ESI) m/z: $[M]^+$ Calcd for $C_{26}H_{19}Cl_2NO$: 431.0844, found: 431.0834.

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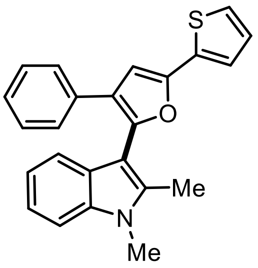

**3-(5-(furan-2-yl)-3-phenylthiophen-2-yl)-1,2-dimethyl-1H-indole, 3h:** The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.132 mmol, 1 equiv) and Indole (38.5 mg, 0.265 mmol, 2 equiv) in 2 days. The crude reaction mixture was purified using 1% Et$_2$O/Hexane to give **3h** in 69% yield (34 mg, 0.091 mmol) as a white solid.

**R$_f$ -value:** 0.78 (10% EtOAc/hexane)

**$^1$H NMR (500 MHz, CDCl$_3$):** δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 7.3 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.31 – 7.26 (m, 4H), 7.22 (s, 1H), 7.16 – 7.09 (m, 2H), 6.92 (s, 1H), 3.72 (s, 3H), 2.19 (s, 3H).

**$^{13}$C NMR (126 MHz, CDCl$_3$):** δ 148.5, 145.0, 137.0, 136.4, 134.3, 134.2, 128.5, 127.8, 127.4, 126.8, 126.5, 123.9, 123.8, 122.3, 121.5, 120.2, 120.1, 108.9, 107.1, 104.0, 29.9, 11.7.

**IR** (KBr, cm$^{-1}$): 1621, 1573, 1508, 1471, 1388, 1361, 1120, 918, 765, 692.

**HRMS** (ESI) m/z: [M]$^+$ Calcd for C$_{24}$H$_{19}$NOS: 369.1187, found: 369.1187.

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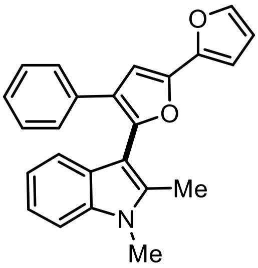

**1,2-dimethyl-3-(4-phenyl-[2,2'-bifuran]-5-yl)-1H-indole, 3i:** The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.136 mmol, 1 equiv) and Indole (41.5 mg, 0.285 mmol, 2 equiv) in 2 days. The crude reaction mixture was purified using 1% Et$_2$O/Hexane to give **3i** in 28% yield (14 mg, 0.039 mmol) as a white solid.

**R$_f$ -value:** 0.71 (10% EtOAc/hexane)

**$^1$H NMR (400 MHz, CDCl$_3$)**: δ 7.55 (d, *J* = 7.9 Hz, 1H), 7.48 (s, 1H), 7.46 – 7.40 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.24 (m, 3H), 7.24 – 7.20 (m, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.97 (s, 1H), 6.64 (d, *J* = 3.0 Hz, 1H), 6.56 – 6.47 (m, 1H), 3.73 (s, 3H), 2.17 (s, 3H).

**$^{13}$C NMR:** (126 MHz, CDCl$_3$) δ 151.5, 147.0, 141.8, 137.1, 136.5, 134.2, 128.6, 127.4, 127.4, 127.0, 126.7, 126.5, 123.6, 121.5, 120.2, 120.0, 111.6, 108.9, 107.0, 105.0, 29.9, 11.7.

**IR** (KBr, cm$^{-1}$)**:** 2922, 1494, 1446, 1325, 1251, 1155, 918, 763.

**HRMS** (ESI) m/z: [M]$^+$ Calcd for C$_{24}$H$_{19}$NO$_2$: 353.1416, found: 353.1404.

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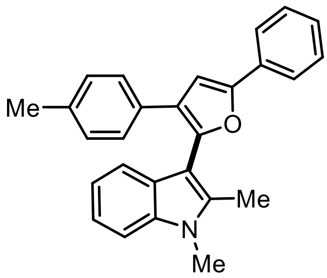

**1,2-dimethyl-3-(5-phenyl-3-(p-tolyl)furan-2-yl)-1H-indole, 3j:** The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.128 mmol, 1 equiv) and Indole (37.18 mg, 0.256 mmol, 2 equiv) in 3 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3j** in 90% yield (43.5 mg, 0.115 mmol) as a white solid.

**$R_f$ -value:** 0.52 (5% $Et_2O$/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$)**: δ 7.82 (d, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 2H), 7.40 – 7.28 (m, 5H), 7.15 (m, 3H), 7.07 (s, 1H), 3.74 (s, 3H), 2.37 (s, 3H), 2.21 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ 152.7, 145.2, 137.0, 136.3, 136.0, 131.6, 131.2, 129.3, 128.8, 127.2, 127.1, 127.0, 123.8, 123.6, 121.4, 120.1, 120.0, 108.9, 107.2, 104.4, 29.9, 21.3, 11.8.

**IR** (KBr, $cm^{-1}$): 3032, 2912, 1625, 1600, 1510, 1471, 1409, 1130, 914, 800**.**

**HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{24}NO$: 378.1852, found: 378.1841.

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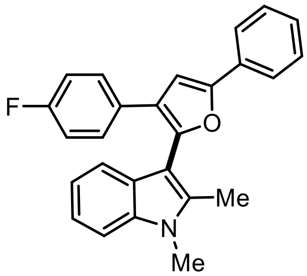
**3-(3-(4-fluorophenyl)-5-phenylfuran-2-yl)-1,2-dimethyl-1H-indole, 3k:** The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.125 mmol, 1 equiv) and Indole (36 mg, 0.251 mmol, 2 equiv) in 5 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3k** in 71% yield (34 mg, 0.089 mmol) as a white solid.



**$R_f$ -value:** 0.45 (5% $Et_2O$/hexane)

**$^1$H NMR (500 MHz, $CDCl_3$)**: δ 7.76 (d, *J* = 7.4 Hz, 2H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.99 (s, 1H), 6.95 (t, *J* = 8.7 Hz, 2H), 3.72 (s, 3H), 2.19 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)**: δ 161.5 (d, *J* = 245.5 Hz), 152.9, 145.2, 136.9, 136.2, 130.9, 130.5 (d, *J* = 3.1 Hz), 128.8 (d, *J* = 7.8 Hz), 128.7, 127.2, 126.7, 123.5, 122.8, 121.5, 120.1, 119.9, 115.3 (d, *J* = 21.3 Hz), 108.9, 106.9, 104.0, 29.8, 11.6.

**$^{19}$F NMR (377 MHz, $CDCl_3$):** δ -116.05.

**IR** (KBr, $cm^{-1}$)**:** 3049, 1604, 1564, 1539, 1506, 1445, 1409, 1325, 1056, 916, 839.

**HRMS** (ESI) m/z: $[M]^+$ Calcd for $C_{26}H_{20}FNO$: 381.1529, found: 381.1526.

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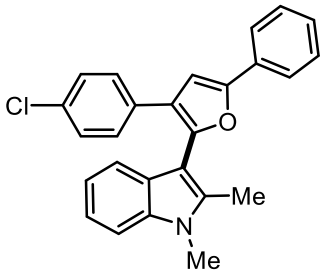

**3-(3-(4-chlorophenyl)-5-phenylfuran-2-yl)-1,2-dimethyl-1H-indole, 3l:** The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.117 mmol, 1 equiv), Indole (34 mg, 0.235 mmol, 2 equiv) and additional catalyst (30 mol%, 5 mg) in 7 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3l** in 78% yield (37 mg, 0.092 mmol) as a white solid.

***R<sub>f</sub>*** = 0.48 (5% $Et_2O$/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$)**: δ 7.80 (d, *J* = 7.2, 2H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.72 Hz, 2H), 7.39 – 7.34 (m, 3H), 7.26 (s, 3H), 7.25 – 7.23 (m, 1H), 7.17 – 7.11 (m, 1H), 7.02 (s, 1H), 3.74 (s, 3H), 2.22 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 153.1, 145.7, 137.1, 136.4, 133.1, 132.0, 131.0, 128.9, 128.7, 128.6, 127.4, 126.7, 123.7, 122.8, 121.6, 120.3, 120.0, 109.0, 106.8, 104.0, 29.9, 11.8.

**IR** (KBr, $cm^{-1}$)**:** 3047, 2912, 2349, 1622, 1602, 1583, 1487, 1409, 1132, 916, 756.

**HRMS** (ESI) m/z: $[M]^+$ Calcd for $C_{26}H_{20}ClNO$: 397.1233, found: 397.1217.

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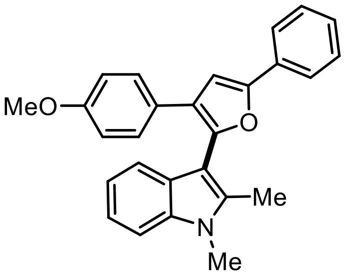

**3-(3-(4-methoxyphenyl)-5-phenylfuran-2-yl)-1,2-dimethyl-1H-indole, 3m:** The product was obtained by following the **GP-3** using appropriate furan (20 mg, 0.079 mmol, 1 equiv), Indole (23.2 mg, 0.16 mmol, 2 equiv) and $CuCl_2.2H_2O$ (1.34 mg, 0.0079 mmol, 10 mol%) in 2 days. The crude reaction mixture was purified using 1-2% $Et_2O$/Hexane to give **3m** in 64% yield (20 mg, 0.05 mmol) as a white solid.

**$R_f$ -value:** 0.42 (5% $Et_2O$/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$)**: δ 7.82 – 7.78 (m, 2H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.39 – 7.35 (m, 3H), 7.32 – 7.28 (m, 2H), 7.16 – 7.12 (m, 1H), 7.03 (s, 1H), 6.84 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H), 3.74 (s, 3H), 2.21 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)**: δ 158.2, 152.7, 144.8, 137.1, 136.3, 131.2, 128.8, 128.5, 127.1, 127.1, 127.0, 123.6, 123.5, 121.4, 120.2, 120.1, 114.0, 108.9, 107.2, 104.4, 55.4, 29.9, 11.8.

**IR** (KBr, $cm^{-1}$): 2910, 1608, 1571, 1541, 1390, 1411, 1247, 1033, 916, 746.

**HRMS** (ESI, m/z): $[M]^+$ calcd for $C_{27}H_{23}NO_2$: 393.1729, found: 393.1720.

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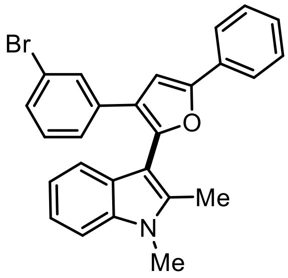

**3-(3-(3-bromophenyl)-5-phenylfuran-2-yl)-1,2-dimethyl-1H-indole, 3n:** The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.1 mmol, 1 equiv) and Indole (29 mg, 0.2 mmol, 2 equiv) in 6 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3n** in 59% (70% BRSM) yield (26 mg, 0.058 mmol) as a white solid.

**$R_f$ -value:** 0.40 (5% $Et_2O$/hexane)

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 7.82 – 7.78 (m, 2H), 7.64 (t, $J$ = 1.7 Hz, 1H), 7.58 (d, $J$ = 7.9 Hz, 1H), 7.45 (t, $J$ = 7.7 Hz, 2H), 7.39 – 7.27 (m, 5H), 7.20 –7.10 (m, 2H), 7.04 (s, 1H), 3.76 (s, 3H), 2.23 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 153.1, 146.0, 137.1, 136.8, 136.4, 130.9, 130.1, 130.0, 129.3, 128.9, 127.4, 126.7, 125.9, 123.7, 122.7, 122.3, 121.6, 120.3, 120.0, 109.1, 106.8, 103.9, 29.9, 11.9.

**IR** (KBr, $cm^{-1}$): 3055, 2918, 1593, 1556, 1471, 1446, 1132, 921, 783, 758, 688.

**HRMS** (ESI) m/z: $[M]^+$ Calcd for $C_{26}H_{20}BrNO$: 441.0728, found: 441.0723.

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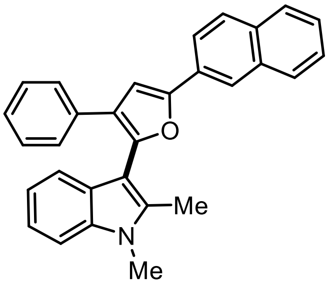

**1,2-dimethyl-3-(5-(naphthalen-2-yl)-3-phenylfuran-2-yl)-1H-indole, 3o:** The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.11 mmol, 1 equiv) and Indole (32.23mg, 0.22 mmol, 2 equiv) in 5 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3o** in 55% yield (25 mg, 0.04 mmol) as a yellowish solid.

**$R_f$ -value:** 0.30 (5% $Et_2O$/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.26 (s, 1H), 7.91 – 7.84 (m, 4H), 7.66 (d, $J$ = 7.8 Hz, 1H), 7.53 – 7.46 (m, 4H), 7.38 (d, $J$ = 8.2 Hz, 1H), 7.33 – 7.28 (m, 3H), 7.24 (dt, $J$ = 4.4, 1.8 Hz, 1H), 7.19 (s, 1H), 7.16 (ddd, $J$ = 8.0, 7.1, 1.0 Hz, 1H), 3.75 (s, 3H), 2.21 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ 153.0, 145.8, 137.1, 136.4, 134.5, 133.8, 132.8, 128.6, 128.5, 128.4, 128.3, 127.9, 127.4, 127.0, 126.6, 126.5, 125.9, 124.1, 122.4, 121.8, 121.6, 120.3, 120.1, 108.9, 107.8, 104.3, 29.9, 11.8.

**IR** (KBr, $cm^{-1}$): = 3047, 2908, 2349, 1622, 1595, 1508, 1473, 1446, 1253, 918, 813, 744, 696.

**HRMS** (ESI, m/z): $[M]^+$ calcd for $C_{30}H_{23}NO$: 413.1780, found: 413.1776.

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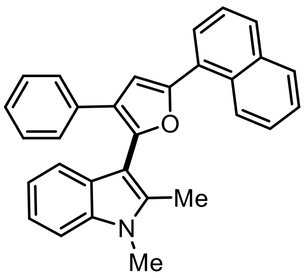

**1,2-dimethyl-3-(5-(naphthalen-1-yl)-3-phenylfuran-2-yl)-1H-indole, 3p:** The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.11 mmol, 1 equiv) and Indole (32.23 mg, 0.22 mmol, 2 equiv) in 6 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3p** in 61% yield (28 mg, 0.06 mmol) as a white solid.

**$R_f$ -value:** 0.47 (5% $Et_2O$/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$)**: δ 8.70 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.94 (ddd, *J* = 4.4, 3.2, 1.7 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.63 – 7.55 (m, 4H), 7.53 – 7.49 (m, 2H), 7.39 – 7.28 (m, 4H), 7.23 (dt, *J* = 6.4, 1.3 Hz, 1H), 7.18 (s, 1H), 7.13 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 3.75 (s, 3H), 2.25 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)**: δ 152.4, 145.8, 137.1, 136.4, 134.6, 134.2, 130.3, 128.8, 128.7, 128.6, 128.3, 128.3, 127.5, 126.9, 126.6, 126.4, 126.0, 125.9, 125.8, 125.6, 123.7, 121.5, 120.2, 111.5, 108.9, 104.3, 29.9, 11.9.

**IR** (KBr, $cm^{-1}$):3047, 2922, 2349, 1618, 1591, 1533, 1471, 1392, 1070, 916, 792, 651.

**HRMS** (ESI, m/z): $[M]^+$ calcd. for $C_{30}H_{23}NO$: 413.1780, found: 413.1774.

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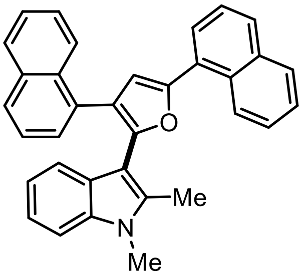

**3-(3,5-di(naphthalen-1-yl)furan-2-yl)-1,2-dimethyl-1H-indole, 3q:** The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.09 mmol, 1 equiv), Indole (27.19 mg, 0.18 mmol, 2 equiv) and additional $CuCl_2.2H_2O$ ( 5 mg, 30 mol%) in 7 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3q** in 26% yield (11 mg, 0.02 mmol) as a white solid.

**$R_f$ -value:** 0.40 (5% $Et_2O$/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$)**: δ 8.72 (dd, *J* = 8.4, 1.3 Hz, 1H), 8.31 – 8.27 (m, 1H), 7.98 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.93 – 7.88 (m, 2H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.56 – 7.52 (m, 2H), 7.51 (dd, *J* = 6.8, 1.3 Hz, 1H), 7.47 (dd, *J* = 5.8, 1.5 Hz, 1H), 7.45-7.41 (m, 1H), 7.41 – 7.33 (m, 2H), 7.21 – 7.17 (m, 2H), 7.06 (dd, *J* = 4.4, 3.5 Hz, 1H), 3.57 (s, 3H), 1.84 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 151.9, 147.7, 136.9, 136.1, 136.1, 134.3, 134.1, 132.8, 132.1, 130.3, 128.8, 128.5, 128.3, 127.8, 127.4, 127.0, 126.7, 126.1, 126.1, 126.0, 125.9, 125.9, 125.8, 125.8, 125.6, 121.8, 121.4, 120.2, 120.1, 114.3, 108.8, 104.0, 29.7, 11.6.

**IR** (KBr, $cm^{-1}$): = 3045, 2920, 2349, 1618, 1589, 1573, 1554, 1473, 1392, 1253, 1103, 912, 790.

**HRMS** (ESI, m/z): $[M]^+$ calcd. for $C_{34}H_{25}NO$: 463.1936, found: 463.1925.

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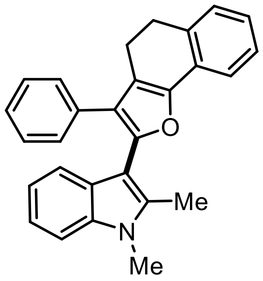

**1,2-dimethyl-3-(3-phenyl-4,5-dihydronaphtho[1,2-b]furan-2-yl) 1H-indole, 3r:** The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.12 mmol, 1 equiv) and Indole (35.37 mg, 0.24 mmol, 2 equiv) in 3 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3r** in 74% yield (35 mg, 0.09 mmol) as white solid.

**R*f* -value:** 0.50 (5% $Et_2O$/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$)**: δ 7.62 (dd, *J* = 10.8, 7.8 Hz, 2H), 7.35 – 7.30 (m, 5H), 7.30 – 7.26 (m, 2H), 7.25-7.22 (m, 2H), 7.18 – 7.09 (m, 2H), 3.68 (s, 3H), 3.09 (t, *J* = 7.8 Hz, 2H), 2.98 – 2.90 (m, 2H), 2.07 (s, 3H)

**$^{13}$C NMR (101 MHz, $CDCl_3$)**: δ 149.2, 146.3, 137.0, 136.04, 134.6, 134.4, 128.8, 128.6, 128.5, 127.9, 127.4, 127.0, 126.9, 126.3, 126.2, 122.3, 121.4, 120.2, 120.1, 119.2, 108.8, 104.2, 29.8, 29.4, 20.9, 11.6.

**IR** (KBr, cm$^{-1}$): 3055, 2939, 1614, 1598, 1562, 1496, 1471, 1375, 1259, 923, 756, 740.

**HRMS** (ESI) m/z: $[M]^+$ Calcd for $C_{28}H_{23}NO$: 389.1780, found: 389.1774.

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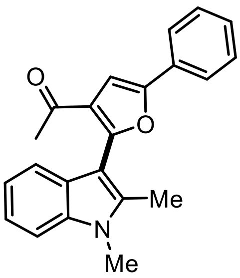


**1-(2-(1,2-dimethyl-1H-indol-3-yl)-5-phenylfuran-3-yl)ethan-1-one, 3s:** The product was obtained with using 1-(5-phenylfuran-3-yl)ethan-1-one (30 mg, 0.16 mmol, 1.0 equiv.) and 1,2-dimethyl-1H-indole (116 mg, 0.80 mmol, 5.0 equiv.) in the presence of $FeCl_3.6H_2O$ (65 mg, 1.2 equiv.) in 4d 20hrs. The crude reaction mixture was purified using 10% EtOAc/hexane to give **3s** (13 mg, 0.039 mmol) in 24% yield as a light yellowish solid.

**R*f* -value:** 0.31 (10% EtOAc/hexane)

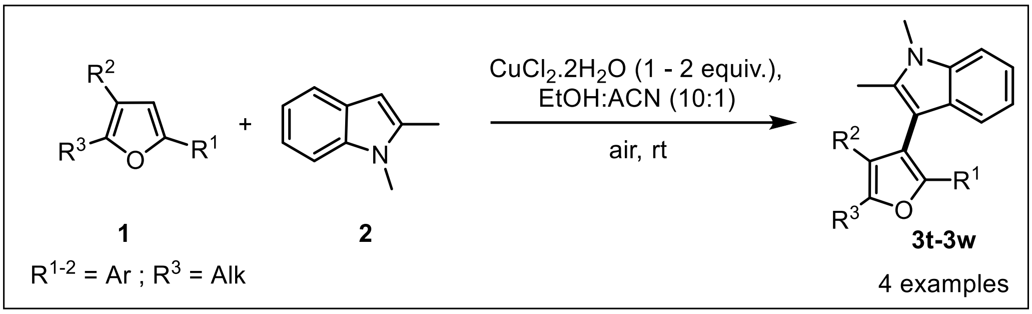
**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.34-7.26 (m, 2H), 7.23-7.19 (m, 1H), 7.18 (s, 1H), 3.78 (s, 3H), 2.48 (s, 3H), 2.32 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ 193.9, 153.4, 152.7, 138.6, 136.7, 130.2, 128.8, 127.9, 127.0, 125.5, 123.9, 121.9, 120.8, 119.3, 109.3, 105.9, 103.6, 29.9, 28.6, 12.2.

**IR** (KBr, cm$^{-1}$): 1676, 1558, 1531, 1473, 1379, 1224, 1095, 1010, 958, 918, 748, 692, 671, 559.

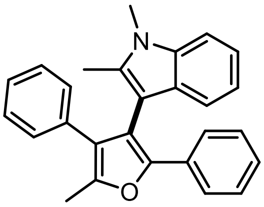
**HRMS** (ESI) m/z: $[M]^+$ Calcd for $C_{22}H_{19}NO_2$ 329.1416; Found 329.1420.

### 5.2 General Procedure for the synthesis of compounds 3t-3w (GP-4):



To a clean and dried round bottom flask was added the furan **1** (0.1 mmol, 1.0 equiv.) and indole **2a** (0.2 mmol, 2.0 equiv.) followed by the addition of $CuCl_2.2H_2O$ (1-2 equiv.) depending on substrates. The mixture was dissolved in 2 mL of EtOH:ACN (10:1). Reaction mixture was stirred at room temperature till completion. The progress of the reaction was monitored using TLC ($Et_2O$/hexane 1:19) under UV exposure. Upon completion (usually 72 - 96 h), the reaction mixture was diluted with saturated aq. $NaHCO_3$ (5 mL) and the layers were separated. The aqueous layer was washed with EtOAc (3 x 10 ml) and the combined organic layer was dried over anhydrous $Na_2SO_4$. The solvent was removed *in vacuo* to obtain the mixture of crude products. Column chromatography (0-5% diethyl ether in PE) provided the pure product as indicated below.

### Characterization Details of the Cross-Coupled Products (3t-3w):



**1,2-dimethyl-3-(5-methyl-2,4-diphenylfuran-3-yl)-1H-indole, 3t:** The product was obtained according to the **GP-4** using 2-methyl-3,5-diphenylfuran (25 mg, 0.11 mmol, 1.0 equiv.), 1,2-dimethyl-1H-indole (46 mg, 0.32 mmol, 3.0 equiv.) and $CuCl_2.2H_2O$ (36 mg, 0.21 mmol, 2.0 equiv.). The crude reaction mixture was purified using 2% EtOAc/hexane to give **3t** (16 mg for 0.042 mmol) in 40% yield as a light yellow solid.

**$R_f$ -value:** 0.60 (5% EtOAc/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.39 (dd, *J* = 6.9, 1.3 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.10-6.99 (m, 8H), 6.93-6.91 (m, 2H), 6.87-6.83 (m, 1H), 3.52 (s, 3H), 2.42 (s, 3H), 1.81 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ 146.6, 146.4, 136.0, 133.9, 132.8, 130.7, 128.0, 127.1, 126.8, 126.5, 125.2, 125.0, 124.1, 123.5, 119.5, 118.6, 118.1, 114.2, 107.4, 103.5, 28.6, 11.8, 9.8.

**IR** (KBr, $cm^{-1}$): 2922, 1598, 1469, 1444, 1375, 1327, 1232, 1091, 1012, 916, 758, 736, 700.

**HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{23}NNaO$ 400.1672; Found 400.1649.

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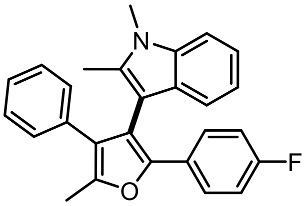

**3-(2-(4-fluorophenyl)-5-methyl-4-phenylfuran-3-yl)-1,2-dimethyl-1H-indole, 3u:** The product was obtained according to the **GP-4** using 5-(4-fluorophenyl)-2-methyl-3-phenylfuran (50 mg, 0.198 mmol, 1.0 equiv.), 1,2-dimethyl-1H-indole (86 mg, 0.594 mmol, 3.0 equiv.) and $CuCl_2.2H_2O$ (50 mg, 0.297 mmol, 1.5 equiv.). The crude reaction mixture was purified using 2% EtOAc/hexane to give **3u** (35 mg for 0.088 mmol) in 45% yield as a light orange solid.

**R*f* -value:** 0.61 (5% EtOAc/hexane)

**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.49 – 7.41 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.18-7.11 (m, 5H), 7.05 – 7.00 (m, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.85 (t, *J* = 8.7 Hz, 2H), 3.64 (s, 3H), 2.52 (s, 3H), 1.91 (s, 3H).

**$^{13}$C NMR (101 MHz, CDCl$_3$):** δ 162.6, 160.2, 147.1 (d, *J* = 51.4 Hz), 137.1, 135.0, 133.8, 129.0, 128.0 (d, *J* = 3.2 Hz), 127.9, 127.4, 126.3 (d, *J* = 7.8 Hz), 126.1, 125.2, 120.7, 119.5, 119.3, 115.1 (d, *J* = 21.5 Hz), 114.9, 108.5, 104.3, 29.7, 12.8, 10.8.

**$^{19}$F NMR (377 MHz, CDCl$_3$):** δ -115.63.

**IR** (KBr, cm$^{-1}$): 1498, 1469, 1226, 1157, 1091, 918, 833, 738, 696, 596, 582.

**HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{23}FNO$ 396.1764; Found 396.1736.

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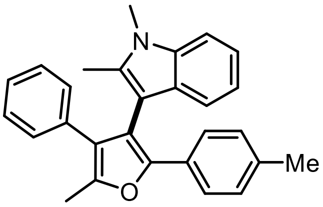

**1,2-dimethyl-3-(5-methyl-4-phenyl-2-(p-tolyl)furan-3-yl)-1H-indole, 3v:** The product was obtained according to the **GP-4** using 2-methyl-3-phenyl-5-(*p*-tolyl)furan (50 mg, 0.201 mmol, 1.0 equiv.), 1,2-dimethyl-1H-indole (87 mg, 0.604 mmol, 3.0 equiv.) and $CuCl_2.2H_2O$ (51 mg, 0.301 mmol, 1.5 equiv.). The crude reaction mixture was purified using 2% EtOAc/hexane to give **3v** (32 mg for 0.082 mmol) in 41% yield as a light orange solid.

**R*f* -value: 0.62** (5% EtOAc/hexane)

**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.33 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 5.2 Hz, 1H), 7.17-7.07 (m, 5H), 6.98 (dd, *J* = 7.6, 1.5 Hz, 2H), 6.94-6.89 (m, 3H), 3.60 (s, 3H), 2.48 (s, 3H), 2.22 (s, 3H), 1.87 (s, 3H).

**$^{13}$C NMR (101 MHz, CDCl$_3$):** δ 146.8, 146.0, 136.0, 134.9, 133.9, 133.0, 132.9, 128.0, 127.8, 126.8, 126.6, 124.9, 124.0, 123.4, 119.4, 118.6, 118.1, 113.4, 107.3, 103.7, 28.6, 20.1, 11.8, 9.8.

**IR** (KBr, cm$^{-1}$): 2922, 1500, 1471, 1375, 1328, 1259, 1232, 1089, 1018, 916, 812, 736, 700.

**HRMS** (ESI) m/z: $[M]^+$ Calcd for $C_{28}H_{25}NO$: 391.1936; Found: 391.1929

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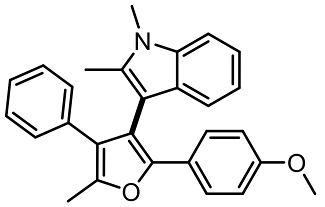

**3-(2-(4-methoxyphenyl)-5-methyl-4-phenylfuran-3-yl)-1,2-dimethyl-1H-indole, 3w:** The product was obtained according to the **GP-4** using 5-(4-methoxyphenyl)-2-methyl-3-phenylfuran (50 mg, 0.19 mmol, 1.0 equiv.), 1,2-dimethyl-1H-indole (110 mg, 0.76 mmol, 4.0 equiv.) and $CuCl_2.2H_2O$ (32 mg, 0.19 mmol, 1.0 equiv.). The crude reaction mixture was purified using 3% EtOAc/hexane to give **3w** (43 mg for 0.11 mmol) 56% yield as a light yellow solid.

**R*f* -value:** 0.55 (5% EtOAc/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.42 (d, *J* = 8.9 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.18 – 7.10 (m, 4H), 7.05 – 6.99 (m, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 8.9 Hz, 2H), 3.74 (s, 3H), 3.63 (s, 3H), 2.51 (s, 3H), 1.91 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ 158.1, 147.7, 146.7, 137.1, 135.0, 134.0, 129.0, 127.9, 127.7, 126.0, 125.9, 125.0, 124.8, 120.5, 119.7, 119.1, 113.6, 113.5, 108.4, 104.7, 55.1, 29.7, 12.8, 10.8.

**IR** (KBr, cm-1): 2922, 1608, 1504, 1471, 1377, 1246, 1172, 1089, 1026, 916, 827, 742, 700.

**HRMS** (ESI) m/z: [M+H]+ Calcd for $C_{28}H_{26}NO_2$ 408.1958; Found 408.1949.

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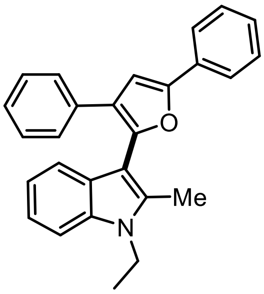
**Scope for Indoles:**

**3-(3,5-diphenylfuran-2-yl)-1-ethyl-2-methyl-1H-indole, 3x:**



The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.13 mmol, 1 equiv) and Indole (43 mg, 0.27 mmol, 2 equiv) in 2 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3x** in 72% yield (37 mg, 0.09 mmol) as a pale yellow solid.

**R*f* -value:** 0.43 (5% $Et_2O$/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 7.7 Hz, 2H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.44 – 7.36 (m, 4H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.14 (m, 5H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.02 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.11 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ 152.9, 145.6, 135.9, 135.5, 134.6, 131.2, 128.8, 128.5, 127.4, 127.2, 127.2, 126.4, 123.9, 123.6, 121.4, 120.1, 120.1, 109.0, 107.1, 104.4, 38.2, 15.3, 11.5.

**IR** (KBr, $cm^{-1}$): 2926, 1597, 1487, 1462, 1346, 758, 692.

**HRMS** (ESI) m/z: $[M]^+$ Calcd for $C_{27}H_{23}NO$ 377.1780; Found 377.1785.

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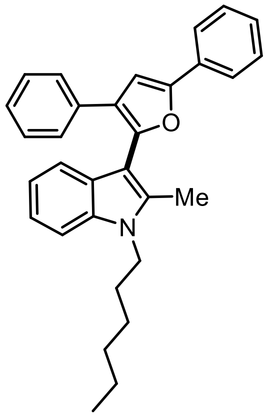
**3-(3,5-diphenylfuran-2-yl)-1-hexyl-2-methyl-1H-indole, 3y:**



The product was obtained by following the **GP-3** using appropriate furan (37 mg, 0.13 mmol, 1 equiv) and Indole (72 mg, 0.33 mmol, 2 equiv) in 3 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3y** in 67% yield (49 mg, 0.11 mmol) as white solid.

**R*f* -value:** 0.58 (5% $Et_2O$/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.43 – 7.36 (m, 4H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.27 – 7.14 (m, 5H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.02 (s, 1H), 4.06 (t, *J* = 7.3 Hz, 2H), 2.09 (s, 3H), 1.84 – 1.68 (m, 2H), 1.35 – 1.26 (m, 6H), 0.92 – 0.85 (m, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ 152.9, 145.6, 136.3, 135.8, 134.6, 131.1, 128.8, 128.5, 127.4, 127.3, 127.2, 127.1, 126.4, 123.9, 123.7, 121.4, 120.1, 109.3, 107.1, 104.3, 43.6, 31.7, 30.1, 26.8, 22.7, 14.2, 11.8.

**IR** (KBr, cm$^{-1}$): 2927, 1598, 1564, 1487, 1463, 1348, 1128, 758.

**HRMS** (ESI) m/z: $[M]^+$ Calcd for $C_{31}H_{31}NO$ 433.2406; Found 433.2409.

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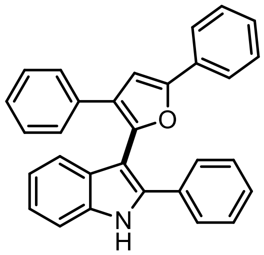

**3-(3,5-diphenylfuran-2-yl)-2-phenyl-1H-indole (4a):** The product was obtained according to the **GP-3** using 2,4-diphenylfuran (30 mg, 0.136 mmol, 1 equiv.) and N-*H* 2-Ph indole (52 mg, 0.27 mmol, 2.0 equiv.) and in 72 hrs. The crude reaction mixture was purified using 5% EtOAc/hexane to give **4a** (17 mg, 0.041 mmol) in 30% yield as a yellow solid.

**R*f* -value:** 0.52 (20% EtOAc/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.25 (s, 1H), 7.56 (d, *J* = 7.3 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.31-7.24 (m, 5H), 7.18 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.14-7.09 (m, 5H), 7.01-6.95 (m, 4H), 6.92 (s, 1H).
**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ 153.2, 144.1, 137.1, 135.9, 133.7, 132.2, 130.9, 128.7, 128.6, 128.5, 128.2, 128.0, 127.4, 127.3, 127.2, 126.3, 125.3, 123.7, 123.0, 120.8, 120.7, 111.0, 107.0, 104.7.

**IR** (KBr, cm$^{-1}$): 3392, 3061, 1595, 1485, 1446, 1325, 1143, 1051, 1010, 933, 813, 758, 746, 692, 530.

**HRMS** (ESI) m/z: $[M]^+$ Calcd for $C_{30}H_{21}NO$ 411.1623; Found 411.1616.

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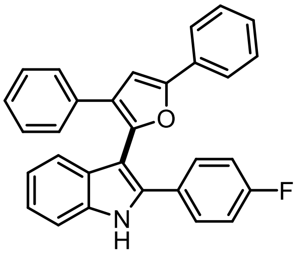

**3-(3,5-diphenylfuran-2-yl)-2-(4-fluorophenyl)-1H-indole, (4b):** The product was obtained to the **GP-3** using 2,4-diphenylfuran (30 mg, 0.136 mmol, 1 equiv.) and 2-(4-fluorophenyl)-1H-indole (57 mg, 0.27 mmol, 2.0 equiv in 96 hrs. The crude reaction mixture was purified using 5% EtOAc/hexane to give **4b** (13 mg, 0.031 mmol) in 23% yield as light yellow solid.

**R$_f$ -value:** 0.53 (20% EtOAc/hexane)

**$^1$H NMR (400 MHz, CDCl$_3$):** δ 8.31 (s, 1H), 7.68 (d, *J* = 7.4 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.43-7.31 (m, 5H), 7.24-7.20 (m, 4H), 7.12-7.06 (m, 4H), 6.99 (s, 1H), 6.90 (t, *J* = 8.6 Hz, 2H).

**$^{13}$C NMR (101 MHz, CDCl$_3$):** δ 163.7, 162.5 (d, *J* = 248.1 Hz), 153.2, 144.0, 135.9 (d, *J* = 18.0 Hz), 133.6, 130.8, 129.2 (d, *J* = 8.4 Hz), 128.7, 128.4 (d, *J* = 3.9 Hz), 128.2, 127.3, 127.2, 126.4, 125.2, 123.6, 123.1, 120.9, 120.7, 115.7, 115.5, 110.9, 107.0, 104.7.

**$^{19}$F NMR (377 MHz, CDCl$_3$):** δ -113.32.

**IR** (KBr, cm$^{-1}$): 3392, 3055, 1600, 1506, 1489, 1456, 1224, 1157, 1008, 931, 835, 758, 690.

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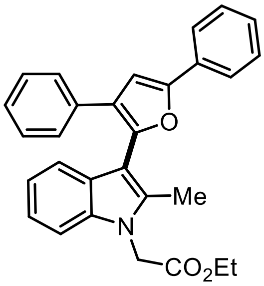

**Ethyl 2-(3-(3,5-diphenylfuran-2-yl)-2-methyl-1H-indol-1-yl) acetate, 3aa:** The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.136 mmol, 1 equiv) and Indole (59 mg, 0.272 mmol, 2 equiv) in 8 days. The crude reaction mixture was purified using 1% Et$_2$O/Hexane to give **3aa** in 64% (71% BRSM) yield (38 mg, 0.085 mmol) as a white solid.

**R$_f$ -value:** 0.28 (5% Et$_2$O/hexane)

**$^1$H NMR (400 MHz, CDCl$_3$)**: δ 7.77 (d, *J* = 7.7 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.43 – 7.36 (m, 4H), 7.29 – 7.21 (m, 5H), 7.20 – 7.15 (m, 1H), 7.11 (t, *J* = 7.1 Hz, 1H), 7.03 (s, 1H), 4.79 (s, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.09 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (126 MHz, CDCl$_3$)**: δ 168.4, 153.1, 145.0, 136.9, 136.0, 134.4, 131.1, 128.8, 128.6, 127.4, 127.3, 127.3, 126.4, 124.3, 123.7, 122.0, 120.7, 120.3, 108.6, 107.1, 105.6, 61.9, 45.2, 14.3, 11.6.

**IR** (KBr, cm$^{-1}$): 2927, 1747, 1598, 1568, 1498, 1469, 1193, 1018, 916, 698.

**HRMS** (ESI) m/z: [M]$^+$ Calcd for $C_{29}H_{25}NO_3$: 435.1834, found: 435.1809.

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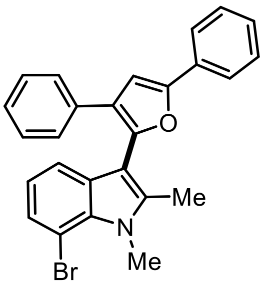

**7-bromo-3-(3,5-diphenylfuran-2-yl)-1,2-dimethyl-1H-indole, 3ab:** The product was obtained by following the **GP-3** using appropriate furan (30 mg, 0.136 mmol, 1 equiv) and Indole (61 mg, 0.272 mmol, 2 equiv) in 8 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3ab** in 50% (75% BRSM) yield (30 mg, 0.068 mmol) as a white solid.

**R*f* -value:** 0.40 (5% $Et_2O$/hexane)

**$^1$H NMR (500 MHz, $CDCl_3$)**: δ 7.79 – 7.74 (m, 2H), 7.49 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.39 – 7.34 (m, 3H), 7.31 – 7.27 (m, 3H), 7.24 –7.21 (m, 1H), 7.05 (s, 1H), 6.90 (t, *J* = 7.7 Hz, 1H), 4.10 (s, 3H), 2.15 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)**: δ 153.2, 144.3, 138.4, 134.1, 133.4, 131.0, 130.1, 128.9, 128.6, 127.4, 127.3, 127.1, 126.6, 124.7, 123.7, 121.2, 119.3, 107.0, 105.0, 103.5, 32.9, 12.2.

**IR** (KBr, cm$^{-1}$): 1629, 1604, 1568, 1527, 1450, 1371, 1130, 1087, 1053, 779, 688.

**HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{21}BrNO$: 442.0801, found: 442.0791

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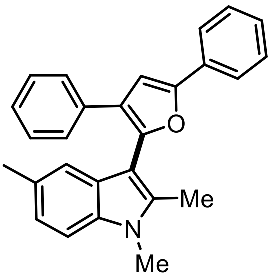

**3-(3,5-diphenylfuran-2-yl)-1,2,5-trimethyl-1H-indole, 3ac:**

The product was obtained by following the **GP-3** using appropriate furan (35 mg, 0.15 mmol, 1 equiv) and Indole (50 mg, 0.31 mmol, 2 equiv) in 2 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3ac** in 38% yield (23 mg, 0.06 mmol) as white solid.

**R*f* -value:** 0.44 (5% $Et_2O$/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.45 – 7.37 (m, 4H), 7.34 (s, 1H), 7.27 – 7.14 (m, 5H), 7.06 – 7.01 (m, *J* = 8.8 Hz, 2H), 3.65 (s, 3H), 2.38 (s, 3H), 2.10 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ 152.8, 145.7, 136.3, 135.4, 134.6, 131.2, 129.4, 128.8, 128.5, 127.4, 127.2, 127.1, 126.3, 123.8, 123.7, 122.9, 119.8, 108.6, 107.1, 103.7, 29.9, 21.6, 11.7.

**IR** (KBr, cm$^{-1}$): 3055, 2939, 1614, 1598, 1562, 1496, 1471, 1375, 1259, 923, 756, 740.

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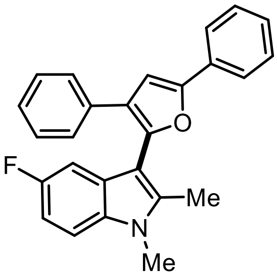


**3-(3,5-diphenylfuran-2-yl)-5-fluoro-1,2-dimethyl-1H-indole, 3ad:**

The product was obtained by following the **GP-3** using appropriate furan (50 mg, 0.22 mmol, 1 equiv) and Indole (74 mg, 0.45 mmol, 2 equiv) in 2 days. The crude reaction mixture was purified using 1% $Et_2O$/Hexane to give **3ad** in 45% yield (38 mg, 0.09 mmol) as white solid.

**R*f* -value:** 0.31 (5% $Et_2O$/hexane)

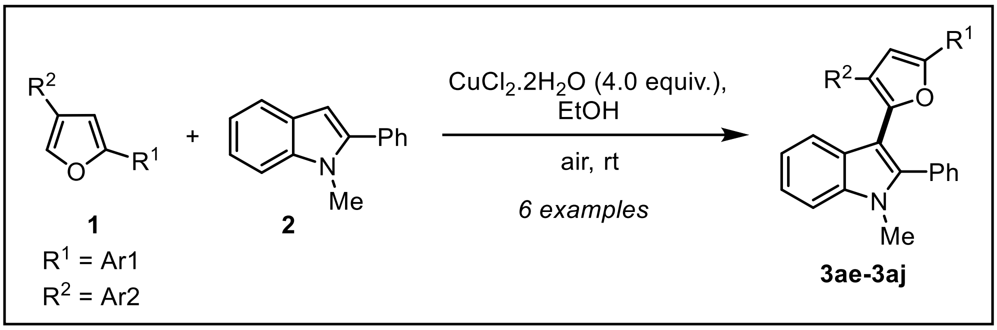
**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.45 – 7.35 (m, 4H), 7.29 – 7.23 (m, 3H), 7.22 – 7.14 (m, 3H), 7.01 (s, 1H), 6.93 (t, *J* = 8.9 Hz, 1H), 3.66 (s, 3H), 2.14 (s, 3H).

**$^{13}$C NMR (101 MHz, CDCl$_3$):** δ 158.4 (d, *J* = 234.7 Hz), 153.0, 144.8, 138.0, 134.4, 133.6, 131.0, 128.9, 128.6, 127.4 (d, *J* = 4.4 Hz), 127.2, 126.6, 124.0, 123.7, 109.6 (d, *J* = 19.4 Hz), 109.4 (d, *J* = 2.6 Hz), 107.2, 105.2, 105.0, 104.5 (d, *J* = 4.4 Hz), 30.1, 11.9.

**$^{19}$F NMR (377 MHz, CDCl$_3$):** δ -124.20.

**IR** (KBr, cm$^{-1}$): 3055, 2926, 1624, 1598, 1583, 1361, 1141, 950, 756, 740.

5.3 **General Procedure for the synthesis of compounds 3ae-3aj (GP-5):**



To a clean and dried screw cap vial was added the furan **1** (1 equiv) and indole **2c** (4 equiv) followed by the addition of $CuCl_2{\cdot}2H_2O$ (4 equiv). The mixture was dissolved in 2 mL of the suitable solvent (methanol or ethanol). The reaction mixture was stirred at room temperature till completion (usually 2-3 days). The progress of the reaction was monitored using TLC ($Et_2O$/hexane 1:19) under UV exposure. The reaction mixture was diluted with saturated aq. $NaHCO_3$ (5 mL) and the layers were separated, as evidenced by the complete consumption of furan on TLC. The aqueous layer was washed with EtOAc (3 x 10 ml) and the combined organic layer was dried over anhydrous $Na_2SO_4$. The solvent was removed *in vacuo* to obtain the mixture of crude products. Column chromatography (0-5% diethyl ether in PE) provided the pure product as indicated below.

**Characterization details of the cross-coupled products, 3ae-3aj:**

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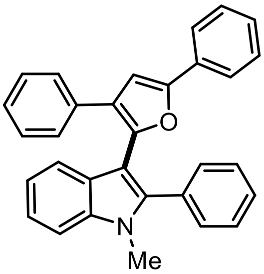

**3-(3,5-diphenylfuran-2-yl)-1-methyl-2-phenyl-1H-indole, 3ae:** The product was obtained according to the **GP-5** using 2,4-diphenylfuran (25 mg, 0.113 mmol, 1.0 equiv.), 1-methyl-2-phenyl-1H-indole (94 mg, 0.45 mmol, 4.0 equiv.) and $CuCl_2.2H_2O$ (78 mg, 0.45 mmol, 4.0 equiv.) in 48 h. The crude reaction mixture was purified using 1% EtOAC/hexane to give **3ae** (40 mg for 0.094 mmol) in 82% yield as a white solid.

***R$_f$*** = 0.53 (5 % EtOAC/ Hexane)

**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.63 (dt, *J*=8.1, 1.5, 2H), 7.59 – 7.56 (m, 1H), 7.46 (d, *J*=8.2, 1H), 7.42 – 7.32 (m, 3H), 7.30 – 7.26 (m, 4H), 7.26 – 7.22 (m, 2H), 7.22 – 7.18 (m, 3H), 7.13 (d, *J* = 2.0 Hz, 3H), 6.90 (s, 1H), 3.74 (s, 3H)

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ 152.7, 144.9, 140.7, 137.6, 134.2, 131.5, 131.1, 130.6, 128.7, 128.2, 128.1, 128.0, 127.6, 127.1, 127.0, 126.2, 124.8, 123.6, 122.4, 120.7, 120.6, 109.7, 107.3, 105.3, 31.2

**IR** (KBr, cm$^{-1}$)**:** 3052, 2920, 1562, 1463, 1375, 1250, 1134, 1089, 994, 916, 812.

**HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{23}NO$ 426.1852; Found 426.1838.

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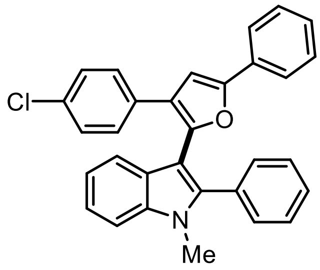

**3-(3-(4-chlorophenyl)-5-phenylfuran-2-yl)-1-methyl-2-phenyl-1H-indole, 3af:** The product was obtained according to the **GP-5** using 4-(4-chlorophenyl)-2-phenylfuran (30 mg, 0.12 mmol, 1.0 equiv.), 1-methyl-2-phenyl-1H-indole (97 mg, 0.47 mmol, 4.0 equiv.) and $CuCl_2.2H_2O$ (80 mg, 0.47 mmol, 4.0 equiv.) in 3d. The crude reaction mixture was purified using 3% $Et_2O$/hexane to give **3af** (50 mg for 0.11 mmol) in 93% yield as a yellowish solid.

**$R_f$ -value:** 0.30 (5% $Et_2O$/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.61 (dd, *J* = 7.9, 2.4 Hz, 3H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.38-7.31 (m, 3H), 7.24-7.23 (m, 4H), 7.20-7.13 (m, 3H), 7.05-7.01 (m, 4H), 6.79 (s, 1H), 3.68 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ 152.9, 145.2, 140.5, 137.5, 132.7, 131.7, 131.2, 130.9, 130.5, 128.8, 128.7, 128.2, 128.1, 128.1, 127.2, 126.8, 123.5, 123.5, 122.5, 120.7, 120.5, 109.8, 106.9, 104.8, 31.2.

**IR** (KBr, cm-1): 2922, 1600, 1564, 1469, 1249, 1132, 1089, 999, 908, 833, 810, 765, 740, 694.

**HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{23}ClNO$ 460.1463; Found 460.1456.

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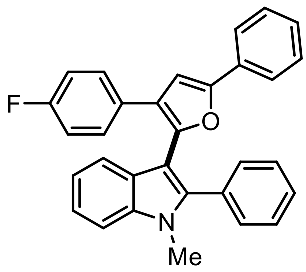

**3-(3-(4-fluorophenyl)-5-phenylfuran-2-yl)-1-methyl-2-phenyl-1H-indole, 3ag:** The product was obtained according to the **GP-5** using 4-(4-fluorophenyl)-2-phenylfuran (30 mg, 0.13 mmol, 1.0 equiv.), 1-methyl-2-phenyl-1H-indole (104 mg, 0.50 mmol, 4.0 equiv.) and $CuCl_2.2H_2O$ (85 mg, 4.0 equiv.) in 45 h. The crude reaction mixture was purified using 3% $Et_2O$/hexane to give **3ag** (51 mg, 0.12 mmol) in 91% yield as a white solid.

**$R_f$ -value:** 0.29 (5% $Et_2O$/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.57 (d, *J* = 7.0 Hz, 3H), 7.39-7.26 (m, 4H), 7.23-7.16 (m, 4H), 7.15-7.12 (m, 3H), 7.06 – 6.97 (m, 2H), 6.78 – 6.68 (m, 3H), 3.63 (s, 3H).

**$^{13}$C NMR (101 MHz, CDCl$_3$):** δ 161.5 (d, *J* = 244.8 Hz), 152.8, 144.9, 140.5, 137.5, 131.3, 131.0, 130.5, 130.3 (d, *J* = 3.3 Hz), 129.1 (d, *J* = 7.9 Hz), 128.7, 128.1, 128.0, 127.1, 126.9, 123.7, 123.5, 122.5, 120.6 (d, *J* = 9.7 Hz), 115.1, 114.8, 109.8, 107.2, 104.9, 31.1.

**$^{19}$F NMR (377 MHz, CDCl$_3$):** δ -116.63.

**IR** (KBr, cm$^{-1}$): 3059, 2927, 1604, 1508, 1465, 1379, 1220, 1155, 1130, 916, 837, 740, 692.

**HRMS** (ESI) m/z: $[M]^+$ Calcd for $C_{31}H_{22}FNO$ 443.1685; Found 443.1681.

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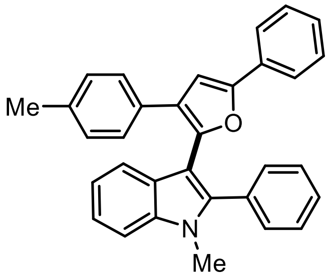

**1-methyl-2-phenyl-3-(5-phenyl-3-(p-tolyl)furan-2-yl)-1H-indole, 3ah:** The product was obtained according to the **GP-5** using 2-phenyl-4-(*p*-tolyl)furan (25 mg, 0.106 mmol, 1.0 equiv.), 1-methyl-2-phenyl-1H-indole (88 mg, 0.424 mmol, 4.0 equiv.) and $CuCl_2.2H_2O$ (80 mg, 0.40 mmol, 4.0 equiv.) in 45 h. The crude reaction mixture was purified using 1% EtOAC/hexane to give **3ah** (28 mg, 0.063 mmol) in 60% yield as a white solid.

***Rf*** = 0.25 (5% $Et_2O$/hexane)

**$^1$H NMR (500 MHz, CDCl$_3$)**: δ 7.59 (d, *J* = 7.4 Hz, 2H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.30 (m, 3H), 7.27 (m, 6H), 7.15 – 7.13 (m, 1H), 7.09 (d, *J* = 7.3 Hz, 2H), 6.95 (d, *J* = 7.4 Hz, 2H), 6.87 (s, 1H), 3.73 (s, 3H), 2.31 (s, 3H).

**$^{13}$C NMR (126 MHz, CDCl$_3$)**: δ 152.6, 144.5, 140.6, 137.5, 135.7, 131.2, 131.2, 131.1, 130.6, 128.9, 128.7, 128.1, 128.0, 127.4, 127.0, 126.9, 124.7,123.6, 122.4, 120.8,120.5, 109.7, 107.2, 105.5, 31.2, 21.2.

**IR** (KBr, cm$^{-1}$)**:** 3061, 2920, 1604, 1562, 1463, 1375, 1249, 1134, 1089, 993, 916, 810.

**HRMS** (ESI, m/z): Calc. for $[M]^+$ $C_{32}H_{25}NO$: 439.1936, found: 439.1936.

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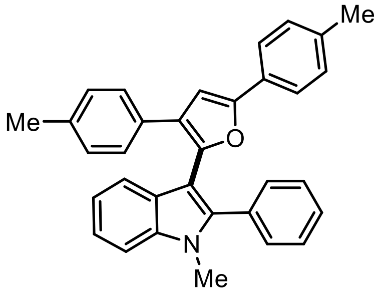

**3-(3,5-di-p-tolylfuran-2-yl)-1-methyl-2-phenyl-1H-indole, 3ai:** The product was obtained according to the **GP-5** using 2,4-di-*p*-tolylfuran (25 mg, 0.100 mmol, 1.0 equiv.), 1-methyl-2-phenyl-1H-indole (83 mg, 0.40 mmol, 4.0 equiv.) and $CuCl_2.2H_2O$ (80 mg, 0.40 mmol, 4.0 equiv.) in 40 h. The crude reaction mixture was purified using 1% EtOAC/hexane to give **3ai** (26 mg, 0.057 mmol) in 87% yield as a white solid.

**R*f*** = 0.31 (5% $Et_2O$/hexane)

**$^1$H-NMR (500 MHz, CDCl$_3$):** δ 7.55 – 7.42 (m, 4H), 7.36 – 7.24 (m, 6H), 7.20 – 7.07 (m, 5H), 6.94 (d, *J* = 7.1 Hz, 2H), 6.81 (s, 1H), 3.73 (s, 3H), 2.38 (s, 3H), 2.30 (s, 3H).

**$^{13}$C NMR (126 MHz, CDCl$_3$):** δ 152.8, 144.1, 140.5, 137.5, 136.8, 135.6, 131.6, 131.3, 130.6, 129.4, 128.9, 128.5, 128.1, 128.0, 127.4, 127.0, 124.6, 123.6, 122.3, 120.8, 120.5,109.7, 106.5, 105.6, 31.2, 21.4, 21.2.

**IR** (KBr, cm$^{-1}$)**:** 3022, 2920, 2852, 1606, 1570, 1500, 1469, 1440, 1408, 1379, 1308, 796, 704.

**HRMS** (ESI) m/z: [M]$^+$ Calcd for $C_{33}H_{27}NO$: 453.2093, found: 453.2090.

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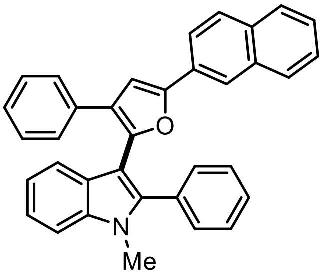

**1-methyl-3-(5-(naphthalen-2-yl)-3-phenylfuran-2-yl)-2-phenyl-1H-indole, 3aj:** The product was obtained according to the **GP-5** using 2-(naphthalen-2-yl)-4-phenylfuran (30 mg, 0.11 mmol, 1.0 equiv.), 1-methyl-2-phenyl-1H-indole (92 mg, 0.44 mmol, 4.0 equiv.) and $CuCl_2.2H_2O$ (75 mg, 4.0 equiv.) in 3d. The crude reaction mixture was purified using 3% $Et_2O$/hexane to give **3af** (33 mg, 0.07 mmol) in 59% yield as a white solid.

**R*f* -value:** 0.30 (5% $Et_2O$/hexane)

**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.88 (s, 1H), 7.77 – 7.70 (m, 3H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.33 (m, 3H), 7.25 – 7.21 (m, 1H), 7.21 – 7.16 (m, 5H), 7.15 – 7.11 (m, 2H), 7.09 – 7.03 (m, 4H), 6.89 (s, 1H), 3.64 (s, 3H).

**$^{13}$C NMR (101 MHz, CDCl$_3$)**: δ 152.8, 145.3, 140.8, 137.6, 134.2, 133.8, 132.7, 131.6, 130.6, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 127.9, 127.7, 126.9, 126.5, 126.3, 125.8, 124.9, 122.5, 122.3, 121.8, 120.9, 120.7, 109.8, 108.0, 105.4, 31.3.

**IR** (KBr, cm$^{-1}$): 3055, 2924, 1597, 1465, 1381, 1128, 918, 856, 812, 740, 694.

**HRMS** (ESI) m/z: [M]$^+$ Calcd for $C_{35}H_{25}NO$ 475.1936; Found 475.1893.

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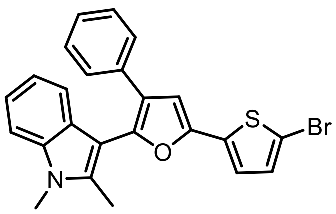
## 5.5 Functionalization of the cross-coupled products:



### 3-(5-(5-bromothiophen-2-yl)-3-phenylfuran-2-yl)-1,2-dimethyl-1H-indole, 5:

Under nitrogen atmosphere, N-Bromosuccinimide (NBS; 25 mg, 0.14 mmol, 1.05 eq) was added into a solution of **3h** (50 mg, 0.135 mmol, 1.0 eq.) in THF (5 mL) at 0° C and the reaction mixture was stirred for 10 minutes. Reaction was monitored by TLC. Upon completion, Triethylamine (2 mL) was added, and the solvent evaporated. The crude reaction mixture was purified using petroleum ether to give **5** (37 mg, 0.08 mmol) in 61% yield as a yellow solid.

**R*f* -value:** 0.43 (5% $Et_2O$/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.15 (m, 4H), 7.11 – 7.03 (m, 2H), 6.99 (d, *J* = 3.9 Hz, 1H), 6.82 (s, 1H), 3.68 (s, 3H), 2.13 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 147.4, 145.5, 137.0, 136.5, 135.7, 134.1, 130.7, 128.6, 127.4, 126.7, 126.6, 123.8, 122.1, 121.6, 120.3, 120.0, 110.8, 109.0, 107.5, 103.8, 29.9, 11.8.

**IR** (KBr, $cm^{-1}$): 2915, 1600, 1589, 1573, 1477, 1398, 1251, 1128, 1070, 913, 800.

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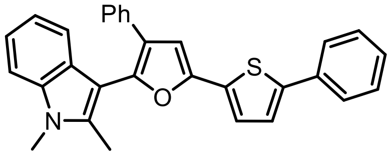
### 1,2-dimethyl-3-(3-phenyl-5-(5-phenylthiophen-2-yl)furan-2-yl)-1H-indole, 3ak:



To a solution of phenylboronic acid (0.058 mmol, 7 mg) in 1.5 mL of THF were added **5** (0.044 mmol, 20 mg), tetrakis(triphenylphosphine)palladium (0.0011 mmol, 1 mg), 2 mL of a solution of $Na_2CO_3$ (0.45 M in water) and 1.5 mL of EtOH. The reaction mixture was stirred for 2h at 85 °C. The crude mixture was extracted with EtOAc, washed with water and brine, dried over $Na_2SO_4$ and concentrated in vacuo. The crude residue was purified by chromatography on silica gel using 0% to 5% (EtOAc/hexane) to afford the desired compound **3ak** (16 mg, 80%) as a yellow solid.

**R*f* -value:** 0.40 (5% EA/hexane)

**$^1$H NMR (400 MHz, CDCl3):** δ 7.61 (d, *J* = 7.4 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.34(m, 4H), 7.32 – 7.26 (m, 3H), 7.24 – 7.14 (m, 5H), 7.11 – 7.05 (m, 1H), 6.88 (s, 1H), 3.68 (s, 3H), 2.14 (s, 3H).

**$^{13}$C NMR (101 MHz, CDCl3):** δ 148.4, 145.2, 142.7, 137.1, 136.5, 134.4, 134.3, 133.4, 129.1, 128.6, 127.6, 127.4, 126.8, 126.5, 125.7, 123.9, 123.9, 123.1, 121.5, 120.2, 120.1, 108.9, 107.3, 104.0, 29.9, 11.8.

**IR** (KBr, $cm^{-1}$): 3047, 2922, 1492, 1475, 1446, 1390, 1253, 1147, 1068, 792.

**HRMS** (ESI) m/z: $[M]^+$ Calcd for $C_{30}H_{23}NOS$ 445.1500; Found 445.1495.

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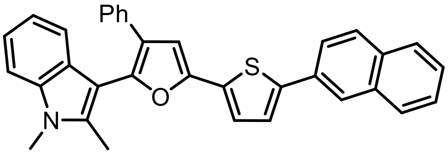
**1,2-dimethyl-3-(5-(5-(naphthalen-2-yl)thiophen-2-yl)-3-phenylfuran-2-yl)-1H-indole, 3al:**



To a solution of 2-Naphthylboronic acid (0.058 mmol, 10 mg) in 1.5 mL of THF were added **5** (0.044 mmol, 20 mg), tetrakis(triphenylphosphine)palladium (0.0011 mmol, 1 mg), 2 mL of a solution of $Na_2CO_3$ (0.45 M in water) and 1.5 mL of EtOH. The reaction mixture was stirred for 2h at 85 °C. The crude mixture was extracted with EtOAc, washed with water and brine, dried over $Na_2SO_4$ and concentrated in vacuo. The crude residue was purified by chromatography on silica gel using 0% to 5% (EtOAc/hexane) to afford the desired compound **3al** (16 mg, 71%) as a yellow solid.

**$R_f$ -value:** 0.33 (5% EA/hexane)

**$^1$H NMR (400 MHz, CDCl3):** $^1$H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.90 – 7.80 (m, 4H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.43 (m, 1H), 7.42 – 7.39 (m, 1H), 7.36 – 7.32 (m, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.93 (s, 1H), 3.71 (s, 3H), 2.17 (s, 3H).

**$^{13}$C NMR (101 MHz, CDCl3):** δ 148.4, 145.3, 142.7, 137.1, 136.5, 134.3, 133.8, 133.6, 132.8, 131.9, 129.1, 128.7, 128.6, 128.2, 127.9, 127.4, 126.8, 126.7, 126.6, 126.1, 124.3, 124.1, 124.0, 123.2, 121.6, 120.2, 120.1, 108.9, 107.4, 104.0, 29.9, 11.8.

**IR** (KBr, $cm^{-1}$): 3047, 2912, 1600, 1568, 1475, 1446, 792, 742.

**HRMS** (ESI) m/z: $[M]^+$ Calcd for $C_{34}H_{25}NOS$ 495.1657; Found 495.1654.

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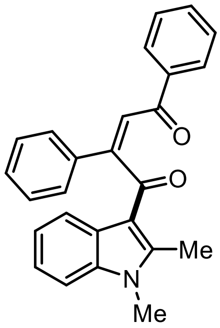

**1-(1,2-dimethyl-1H-indol-3-yl)-2,4-diphenylbut-2-ene-1,4-dione, 6:** To a stirred solution of Cross coupled product **3a** (30 mg, 0.082 mmol) and KBr (5–10 mol%) in MeCN/$H_2O$ (10:1, 0.1 M) at 0 °C was added oxone (40 mg, 0.131 mmol, MW= 307) in one batch. The resulting solution was warmed to rt, and stirred for 3 hours. After the reaction was completed, as determined by TLC analysis, it was quenched by the addition of aqueous saturated $NaHCO_3$, and was then diluted with EtOAc (5 mL). The organic fractions were collected, and the aqueous phase was extracted with EtOAc (3 x 5 mL). The crude reaction mixture was purified by column chromatography using 20% EtOAc/Hexane to give **6** in 89% yield (28 mg, 0.073 mmol) as a white solid.

**$R_f$** = 0.12 (20% EtOAc/Hexane)

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.01 – 7.96 (m, 3H), 7.73 – 7.69 (m, 2H), 7.55 – 7.51 (m, 2H), 7.43 (ddd, *J* = 8.2, 6.7, 1.2 Hz, 2H), 7.40 – 7.35 (m, 3H), 7.26 – 7.23 (m, 1H), 7.17 (ddd, *J* = 8.1, 7.1, 1.3 Hz, 1H), 7.14 – 7.09 (m, 1 H), 3.67 (s, 3H), 2.80 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ 192.1, 189.0, 158.3, 146.0, 144.6, 138.1, 137.0, 135.2, 133.0, 130.5, 129.4, 129.2, 128.7, 127.7, 126.3, 122.3, 120.9, 119.8, 113.4, 109.4, 29.7, 12.7.

**IR** (KBr, cm$^{-1}$)**:** 3327, 2997, 2358, 1670, 1625, 1577, 1465, 1431, 1361, 1066, 869, 754.

**HRMS** (ESI) m/z: calc. for $[M+Na]^+$ $C_{26}H_{21}NaNO_2$: 402.1465, found: 402.1460.

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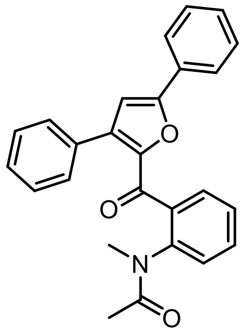


**N-(2-(3,5-diphenylfuran-2-carbonyl)phenyl)-N-methylacetamide, 7:** To a solution of cross-coupled product **3a** (50 mg, 0.14 mmol, 1.0 equiv.) in DCM at 0 °C was added m-CPBA (65%, 73 mg, 0.28 mmol, 2.0 equiv.). The resulting solution was allowed to warm to room temperature and stirred till completion. The progress of the reaction was monitored by TLC. After completion, aqueous saturated $NaHCO_3$ was added to the reaction mixture and then diluted with DCM (10 mL). The organic fractions were collected, and the aqueous phase was extracted with DCM (5 mL) three times. The combined organic fractions were washed with brine, dried over $Na_2SO_4$ filtered, and concentrated under reduced pressure. The crude reaction mixture was purified using 20% EtOAc/hexane to give **7** (38 mg, 0.10 mmol) in 77% yield as a light orange solid.

**$R_f$ -value:** 0.28 (30% EtOAc/hexane)

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 6.7 Hz, 2H), 7.61-7.56 (m, 4H), 7.45 – 7.37 (m, 7H), 7.28 (s, 1H), 7.00 (s, 1H), 3.16 (s, 3H), 1.83 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ 183.1, 170.9, 156.5, 145.6, 142.3, 138.2, 137.9, 131.6, 131.4, 129.6, 129.6, 129.2, 129.1, 129.0, 128.9, 128.7, 128.3, 127.7, 125.0, 110.3, 37.5, 22.3.

**IR** (KBr, cm$^{-1}$): 3093, 1641, 1595, 1525, 1471, 1382, 1298, 1143, 1076, 894, 879, 767, 690.

**HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{22}NO_3$ 396.1594; Found 396.1632.

## 6. Photophysical studies of cross-coupled products:

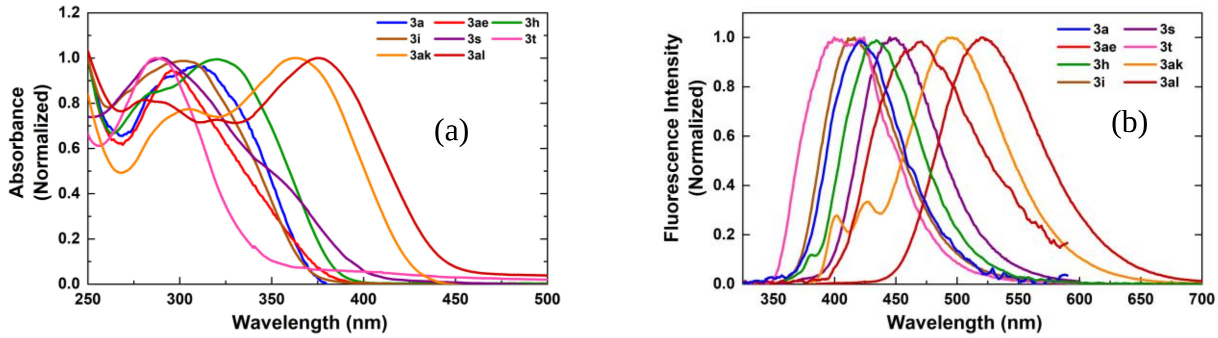


**Figure S1.** Normalized (a) absorption and (b) emission spectra of compounds in ACN. Emission spectra are collected by exciting the samples at individual $\lambda_{abs}^{max}$.

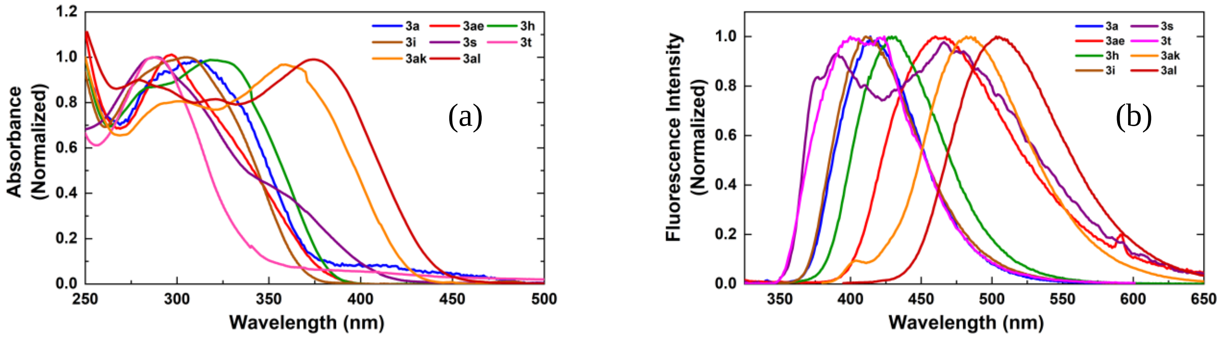
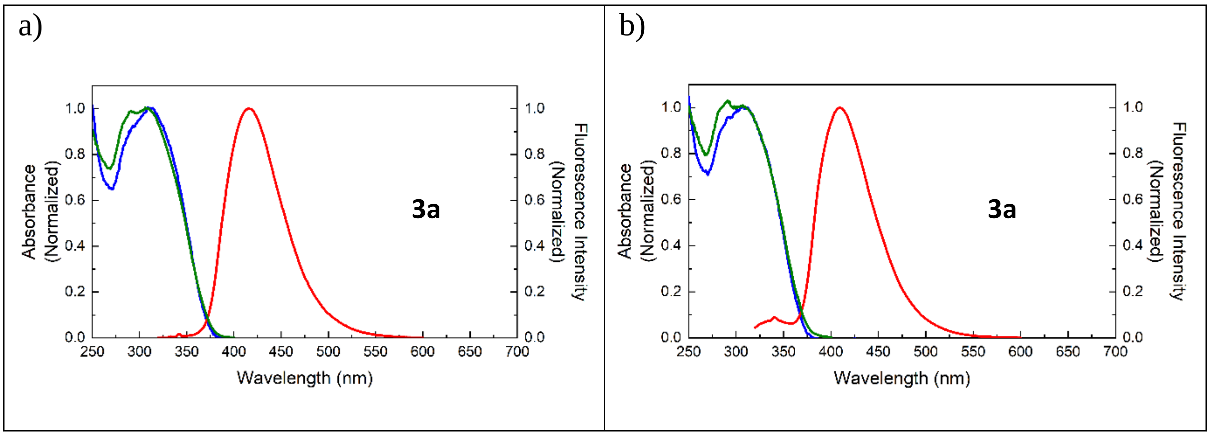
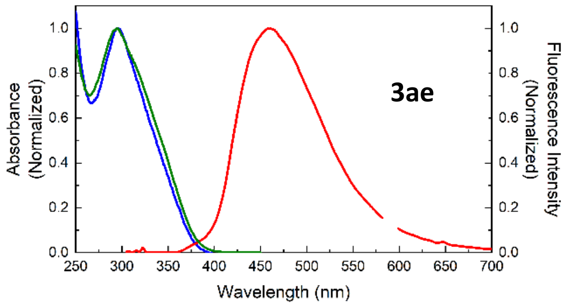


**Figure S2.** Normalized (a) absorption and (b) emission spectra of compounds in MeOH. Emission spectra are collected by exciting the samples at individual $\lambda_{abs}^{max}$.

## Electronic Spectra of the compounds (ESI):



c)


3ae
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Fluorescence Intensity (Normalized)
Wavelength (nm)
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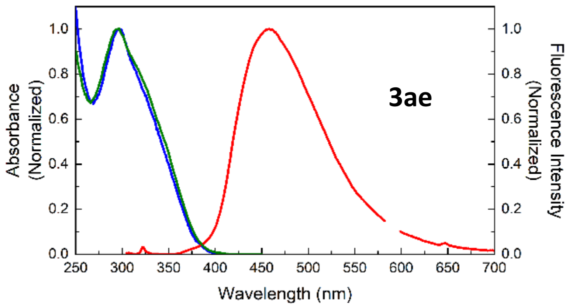
0.4
0.6
0.8
1.0
250
300
350
400
450
500
550
600
650
700

d)


3ae
Absorbance (Normalized)
Fluorescence Intensity (Normalized)
Wavelength (nm)
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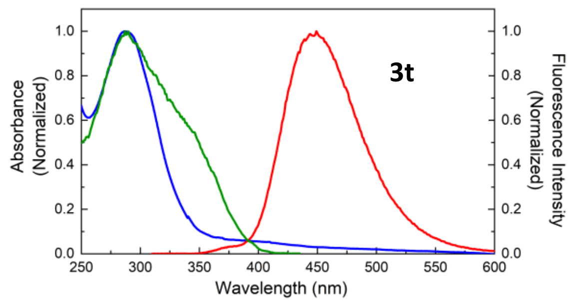
0.6
0.8
1.0
250
300
350
400
450
500
550
600
650
700

e)


3t
Absorbance (Normalized)
Fluorescence Intensity (Normalized)
Wavelength (nm)
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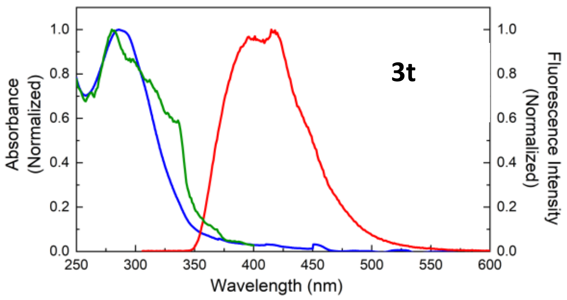
0.2
0.4
0.6
0.8
1.0
250
300
350
400
450
500
550
600

f)


3t
Absorbance (Normalized)
Fluorescence Intensity (Normalized)
Wavelength (nm)
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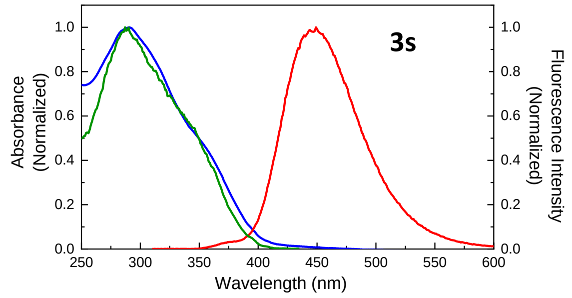
300
350
400
450
500
550
600

g)


3s
Absorbance (Normalized)
Fluorescence Intensity (Normalized)
Wavelength (nm)
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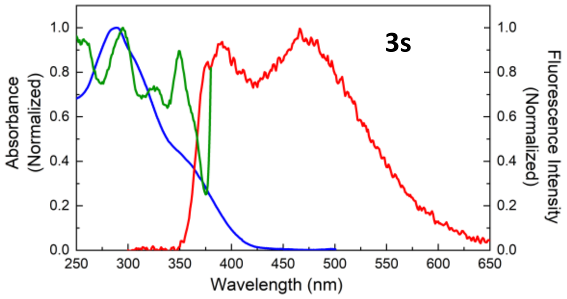
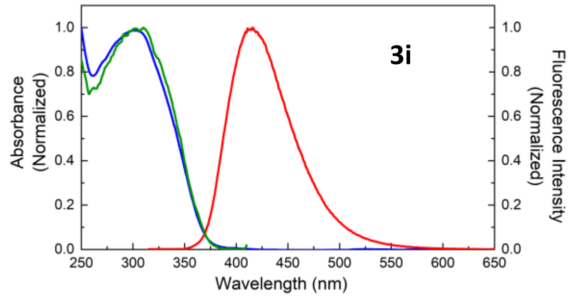
0.4
0.6
0.8
1.0
250
300
350
400
450
500
550
600

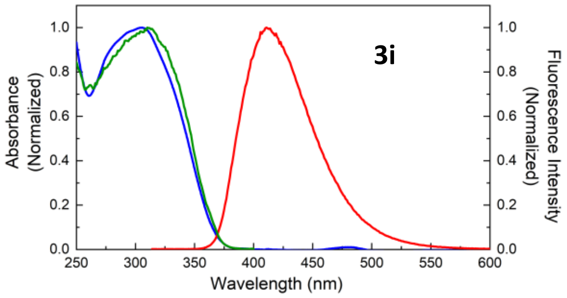
h)


3s
Absorbance (Normalized)
Fluorescence Intensity (Normalized)
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
250
300
350
400
450
500
550
600
650

i)


3i
Absorbance (Normalized)
Fluorescence Intensity (Normalized)
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
250
300
350
400
450
500
550
600
650

j)


3i
Absorbance (Normalized)
Fluorescence Intensity (Normalized)
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
250
300
350
400
450
500
550
600

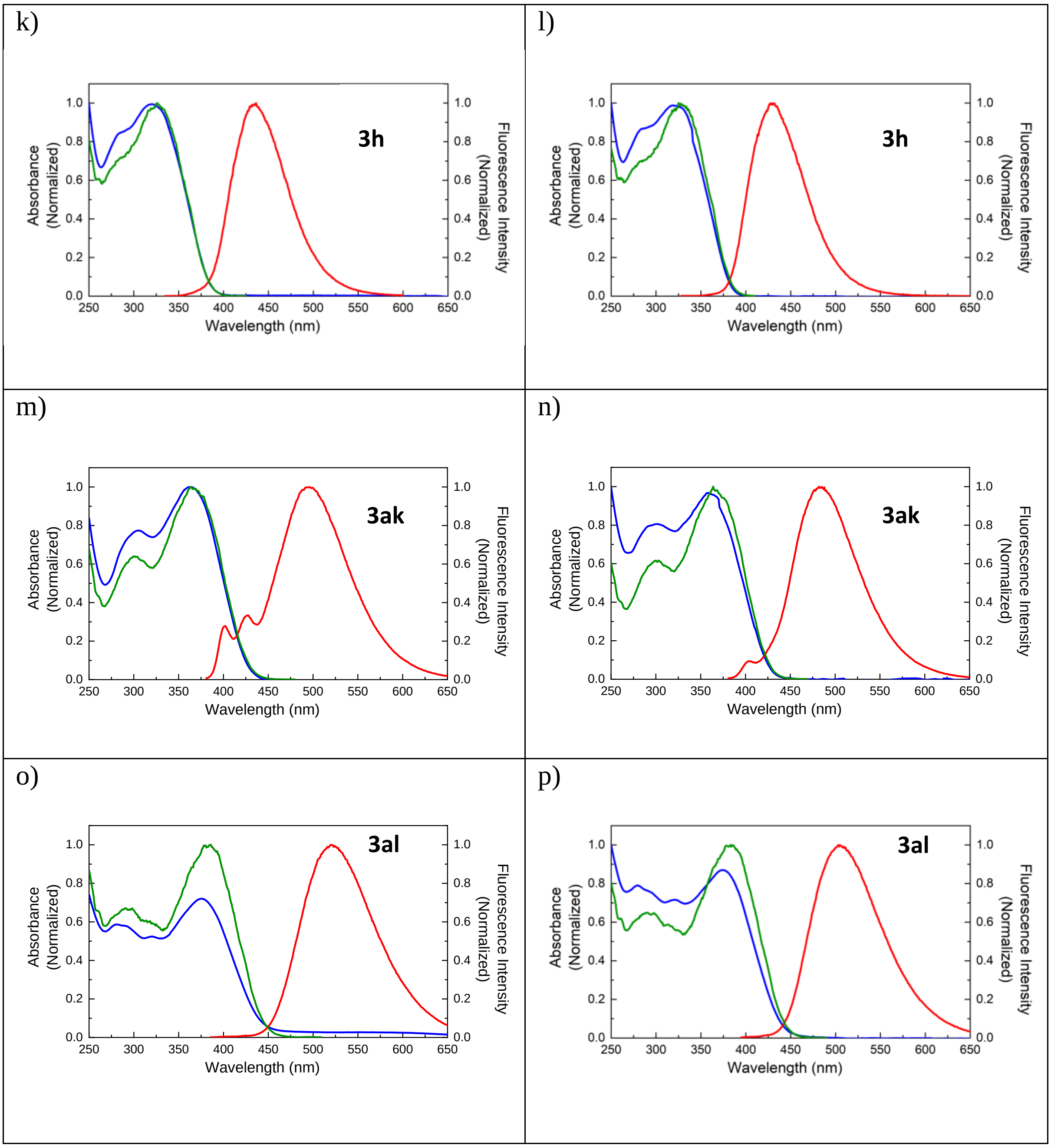
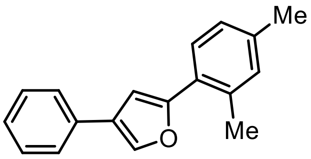
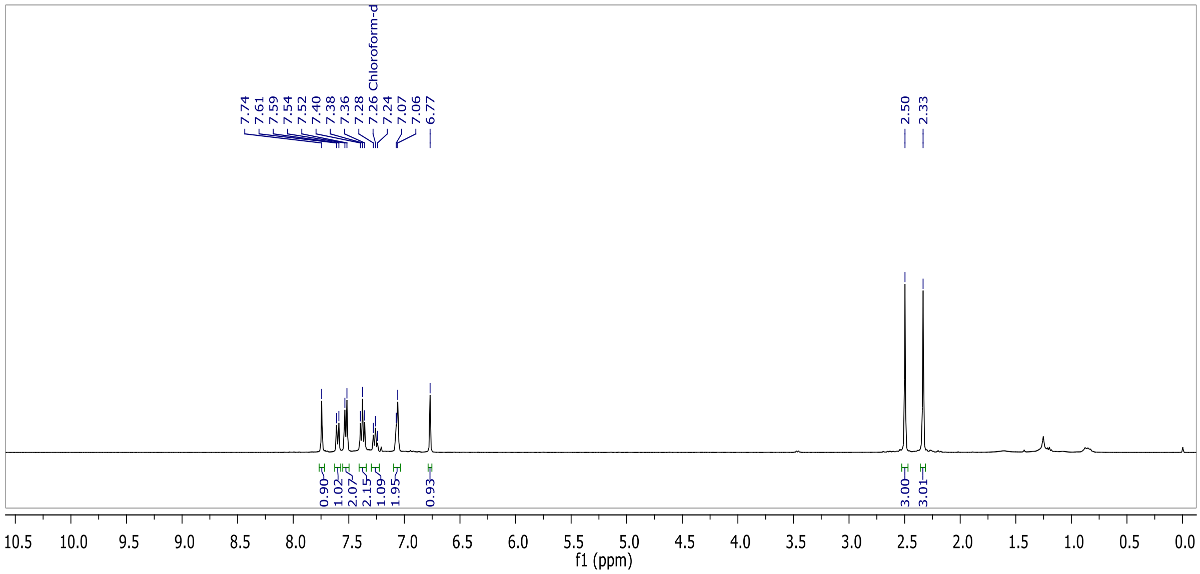


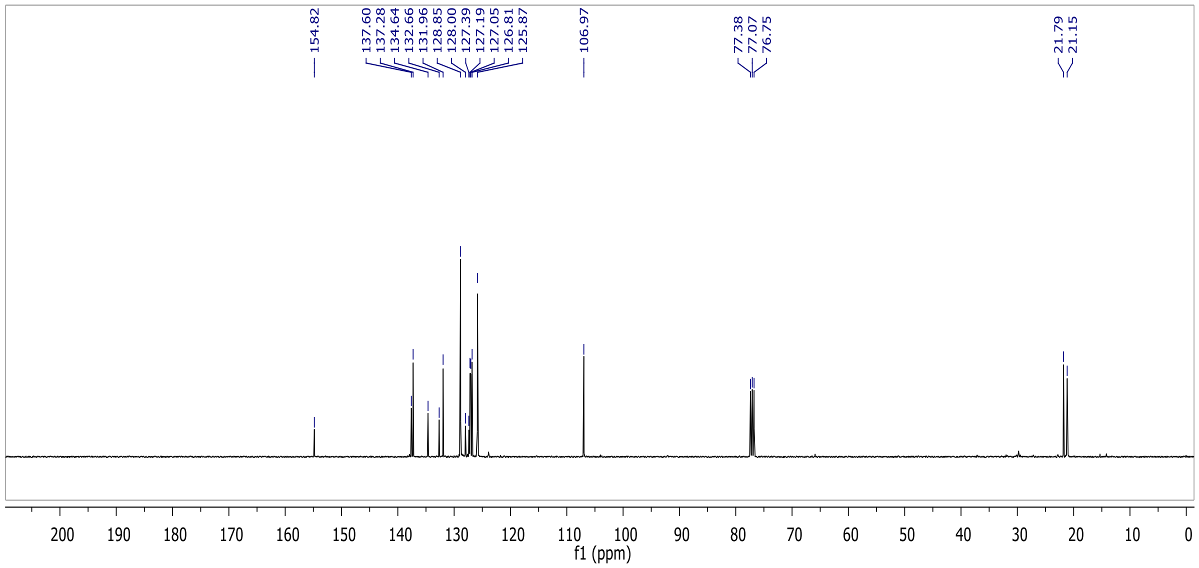
**Figure S3.** Normalized absorption (blue), emission (red) and excitation (green) spectra of compounds in (a, c, e, g, i, k, m, o) in acetonitrile and (b, d, f, h, j, l, n, p) in methanol. Emission spectra are recorded by exciting at individual $\lambda_{abs}^{max}$and excitation spectra are recorded by parking emission at individual $\lambda_{em}^{max}$.

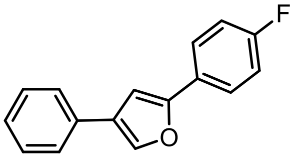
# NMR spectra for the precursor furans 1:



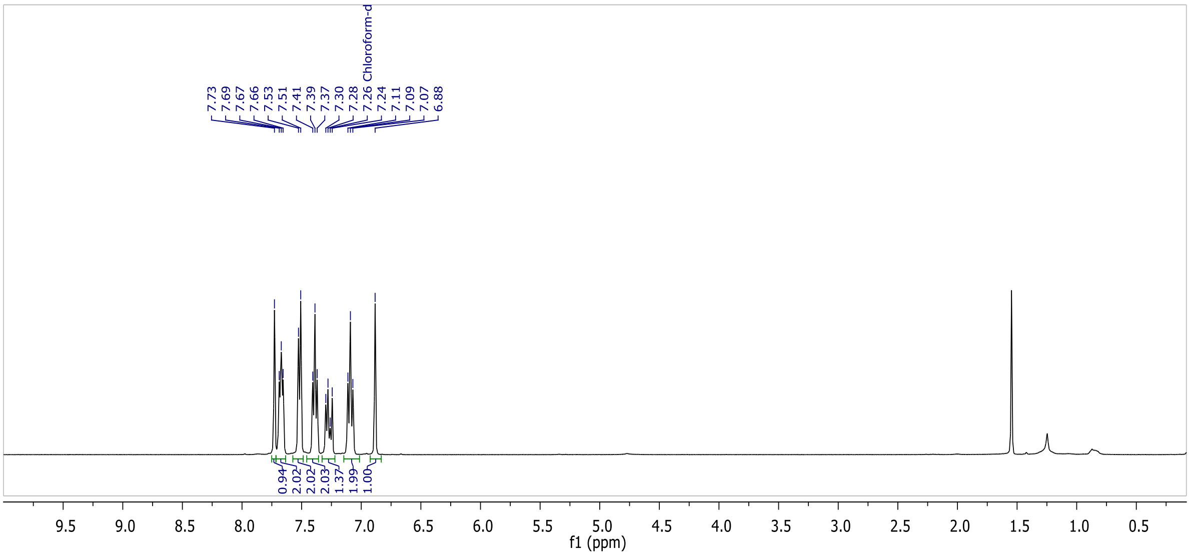
**1c**

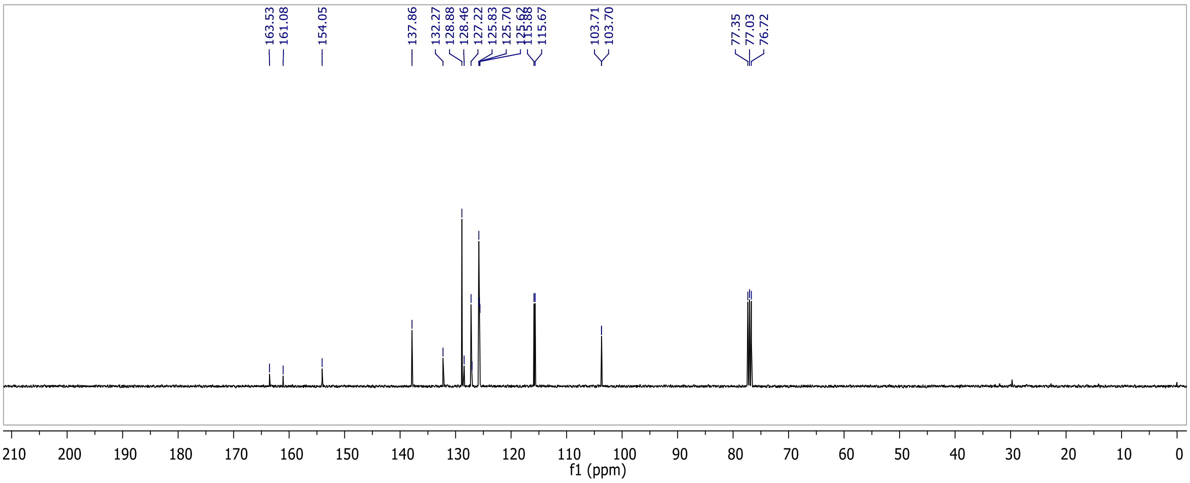


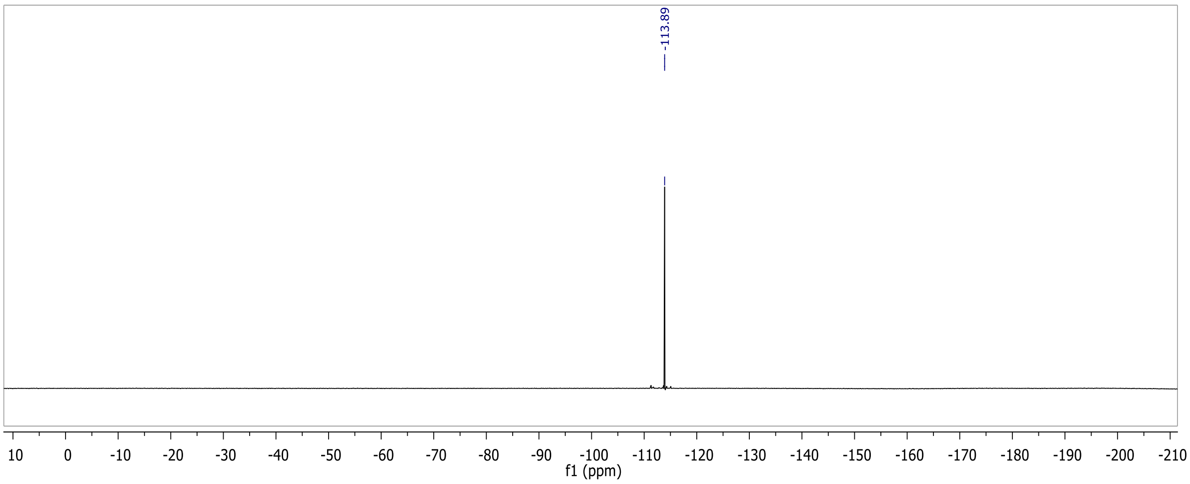


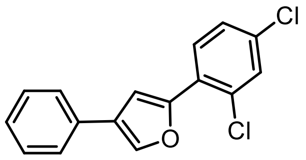


**1d**

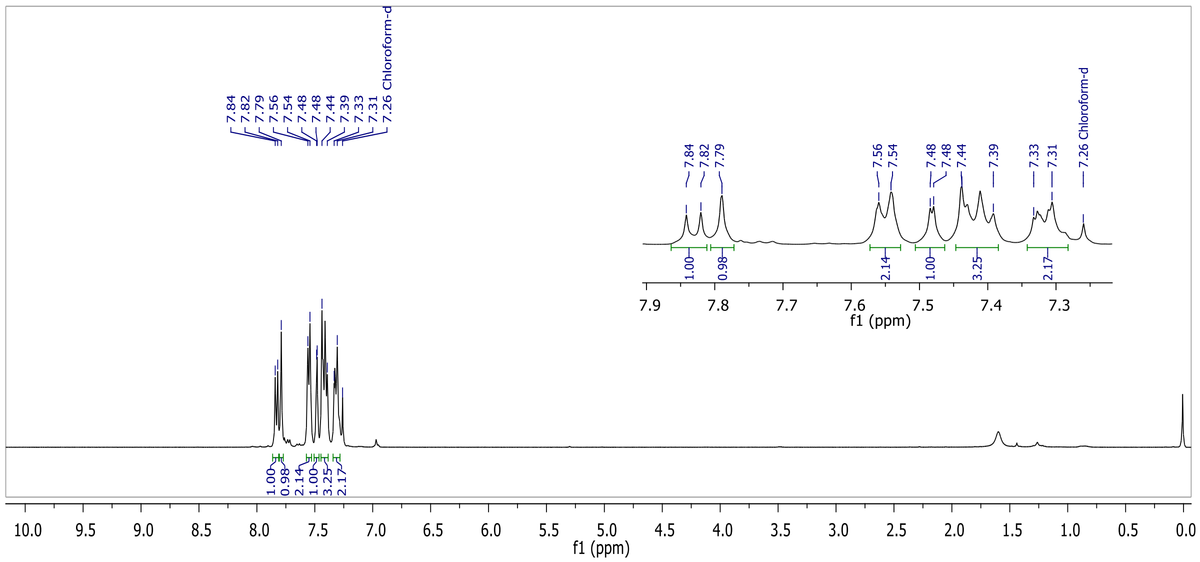

7.73
7.69
7.67
7.66
7.53
7.51
7.41
7.39
7.37
7.30
7.28
7.26 Chloroform-d
7.24
7.11
7.09
7.07
6.88
0.94
2.02
2.02
2.03
1.37
1.99
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

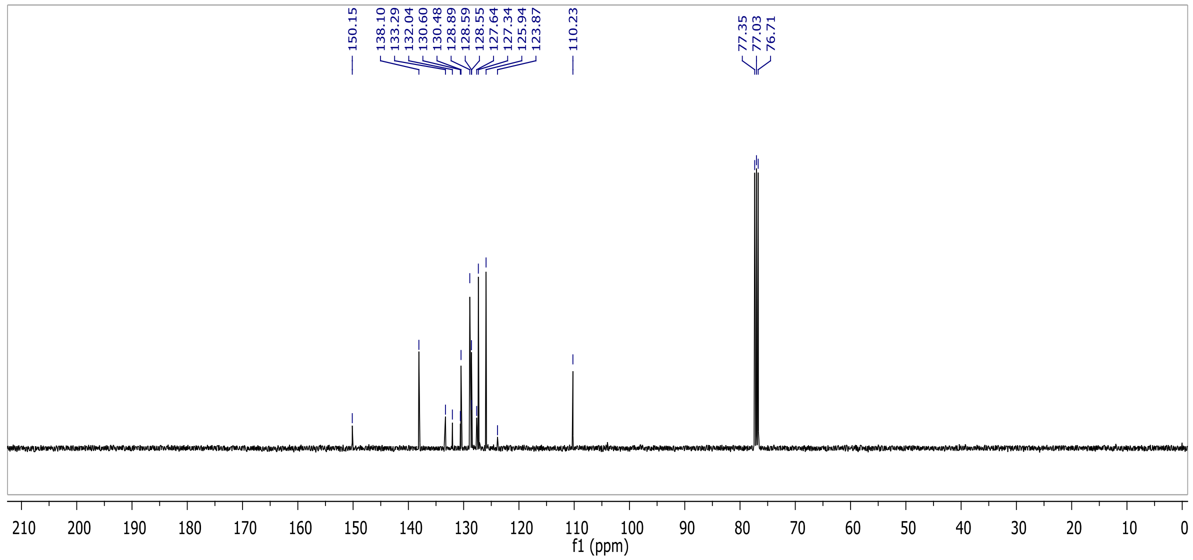

163.53
161.08
154.05
137.86
132.27
128.88
128.46
127.22
125.83
125.70
125.62
115.88
115.67
103.71
103.70
77.35
77.03
76.72
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

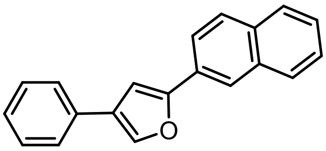

-113.89
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


Cl
Cl
O

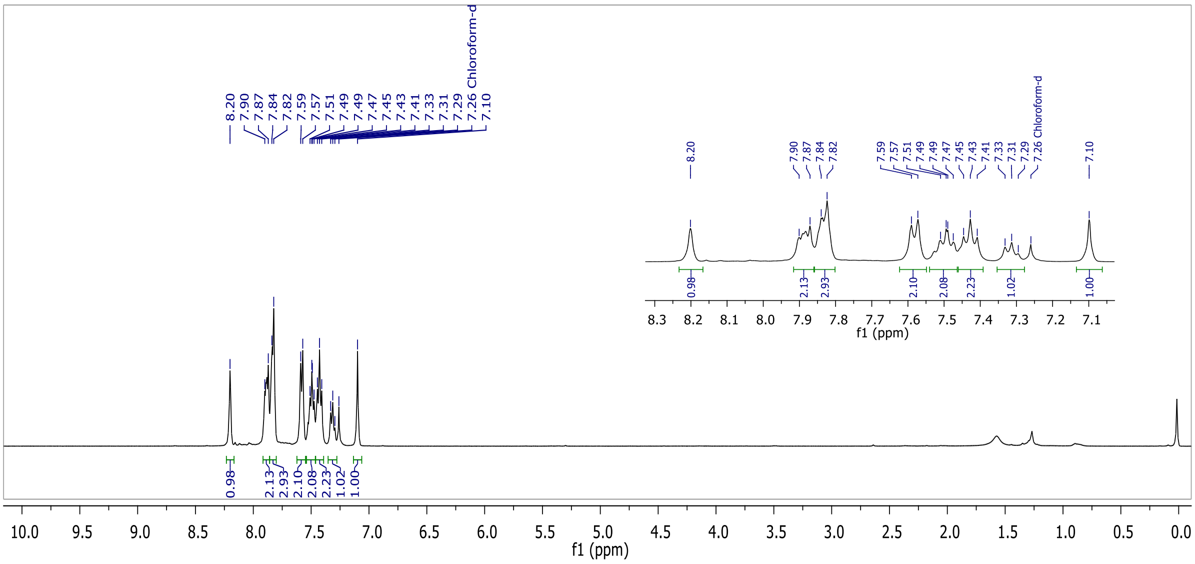
**1g**

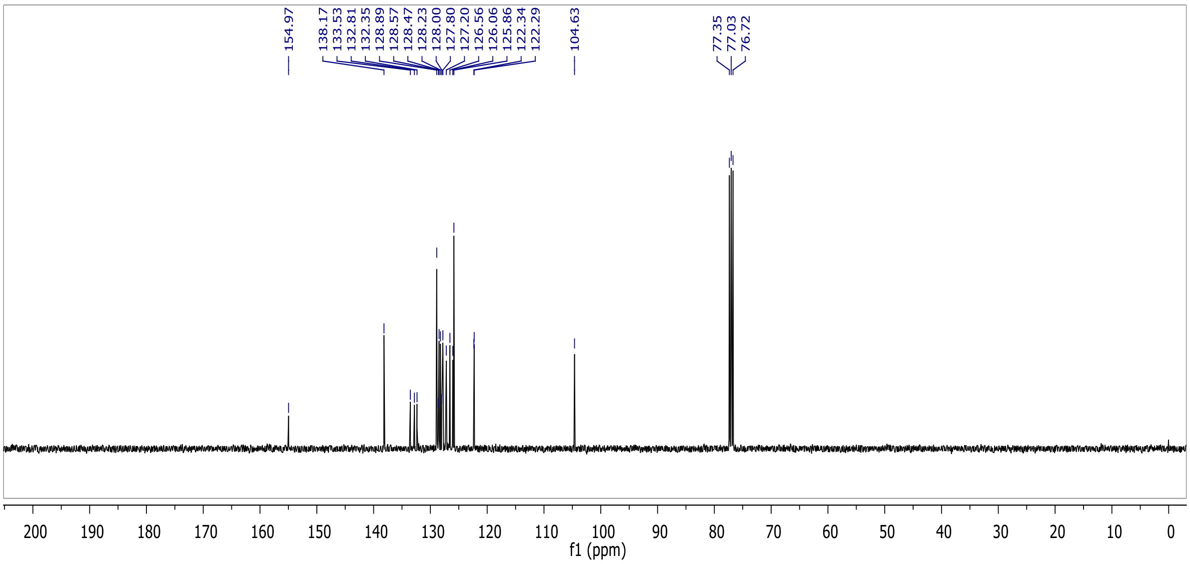

7.84
7.82
7.79
7.56
7.54
7.48
7.48
7.44
7.39
7.33
7.31
7.26 Chloroform-d
1.00
0.98
2.14
1.00
3.25
2.17
7.9
7.8
7.7
7.6
7.5
7.4
7.3
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

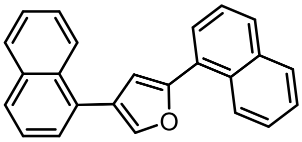

150.15
138.10
133.29
132.04
130.60
130.48
128.89
128.59
128.55
127.64
127.34
125.94
123.87
110.23
77.35
77.03
76.71
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



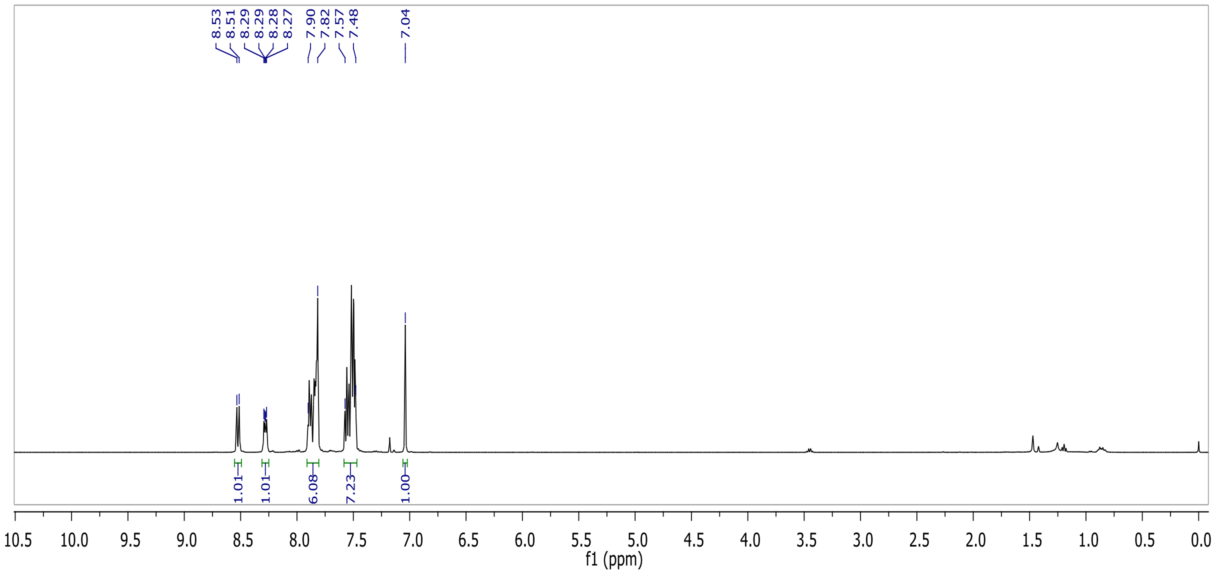
**1o**

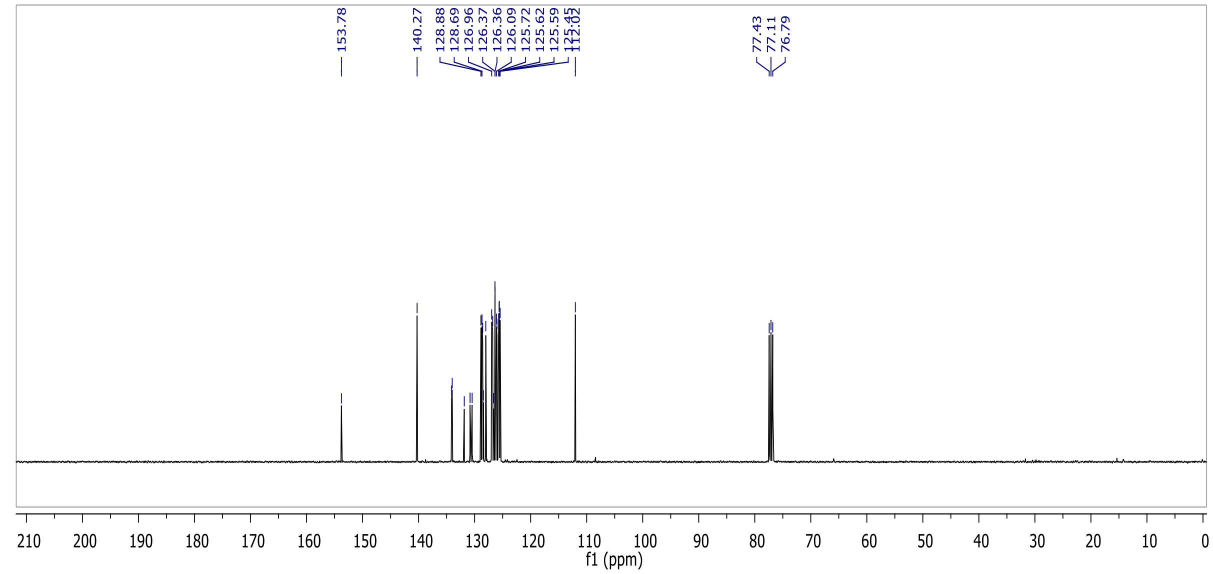

8.20
7.90
7.87
7.84
7.82
7.59
7.57
7.51
7.49
7.47
7.45
7.43
7.41
7.33
7.31
7.29
7.26 Chloroform-d
7.10
0.98
2.13
2.93
2.10
2.08
2.23
1.02
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)

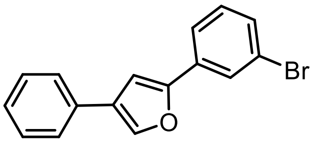

154.97
138.17
133.53
132.81
132.35
128.89
128.57
128.47
128.23
128.00
127.80
127.20
126.56
126.06
125.86
122.34
122.29
104.63
77.35
77.03
76.72
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



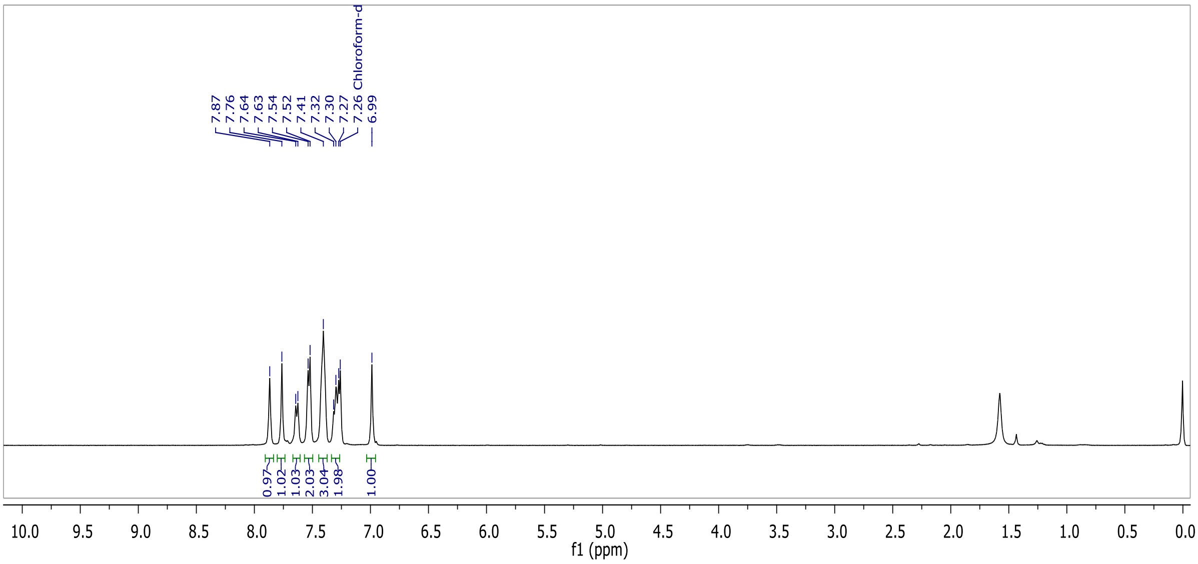
**1q**

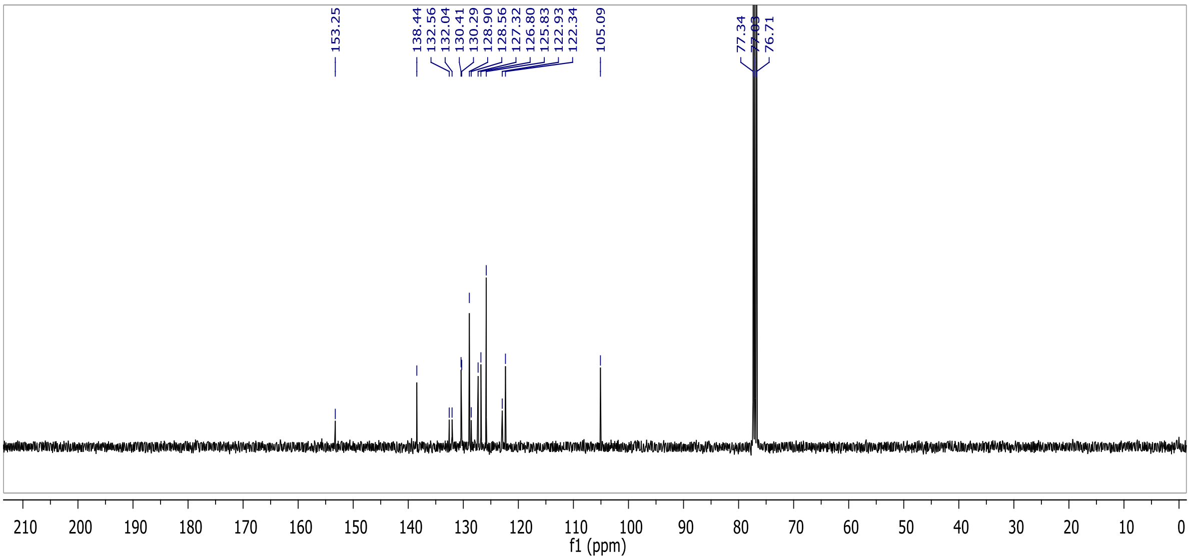

8.53
8.51
8.29
8.29
8.28
8.27
7.90
7.82
7.57
7.48
7.04
1.01
1.01
6.08
7.23
1.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


153.78
140.27
128.88
128.69
126.96
126.37
126.36
126.09
125.72
125.62
125.59
125.45
112.02
77.43
77.11
76.79
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

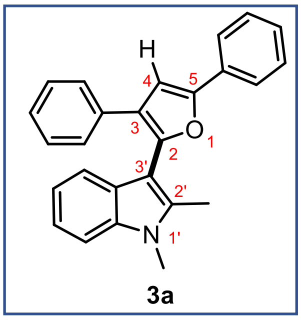

Br
O

**1u**

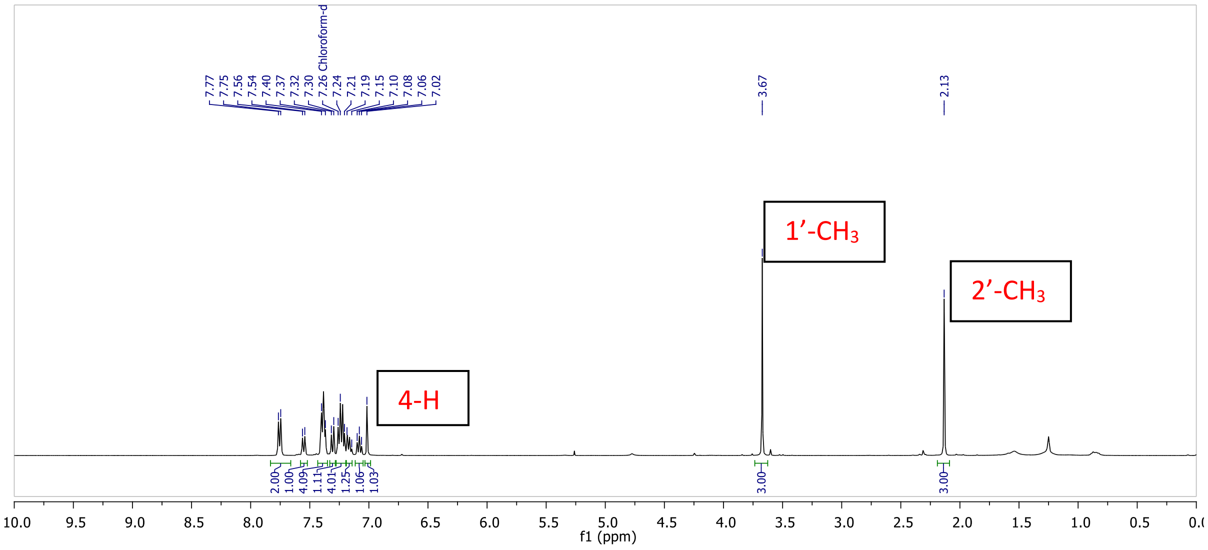

7.87
7.76
7.64
7.63
7.54
7.52
7.41
7.32
7.30
7.27
7.26 Chloroform-d
6.99
0.97
1.02
1.03
2.03
3.04
1.98
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

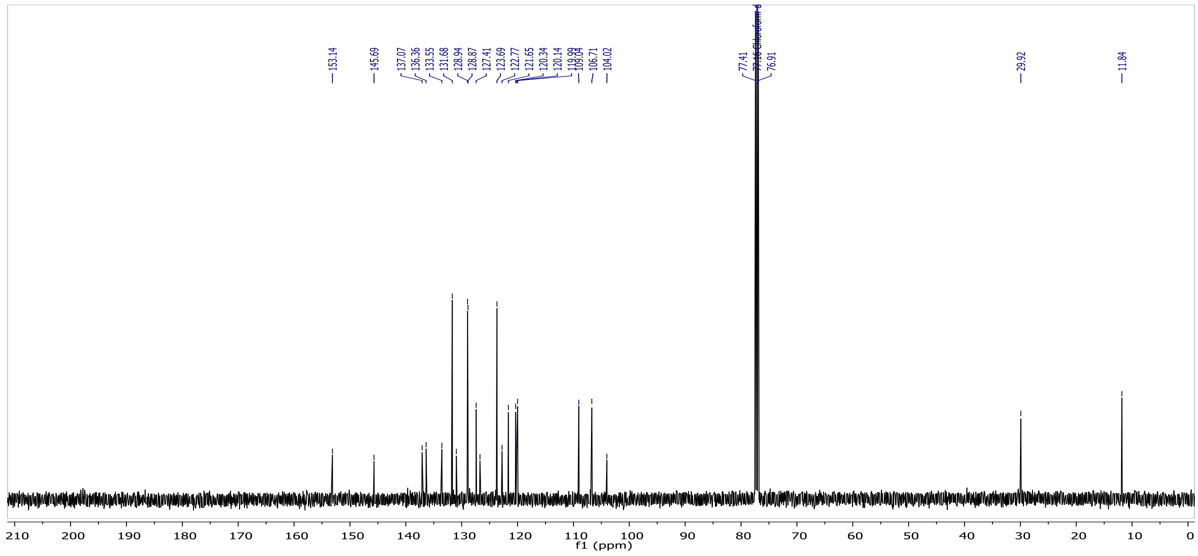

153.25
138.44
132.56
132.04
130.41
130.29
128.90
128.56
127.32
126.80
125.83
122.93
122.34
105.09
77.34
77.03
76.71
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

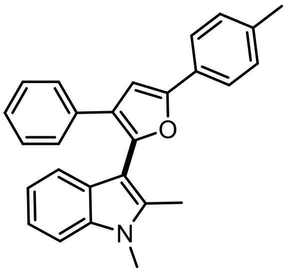
## NMR spectra for the cross-coupling products 3:



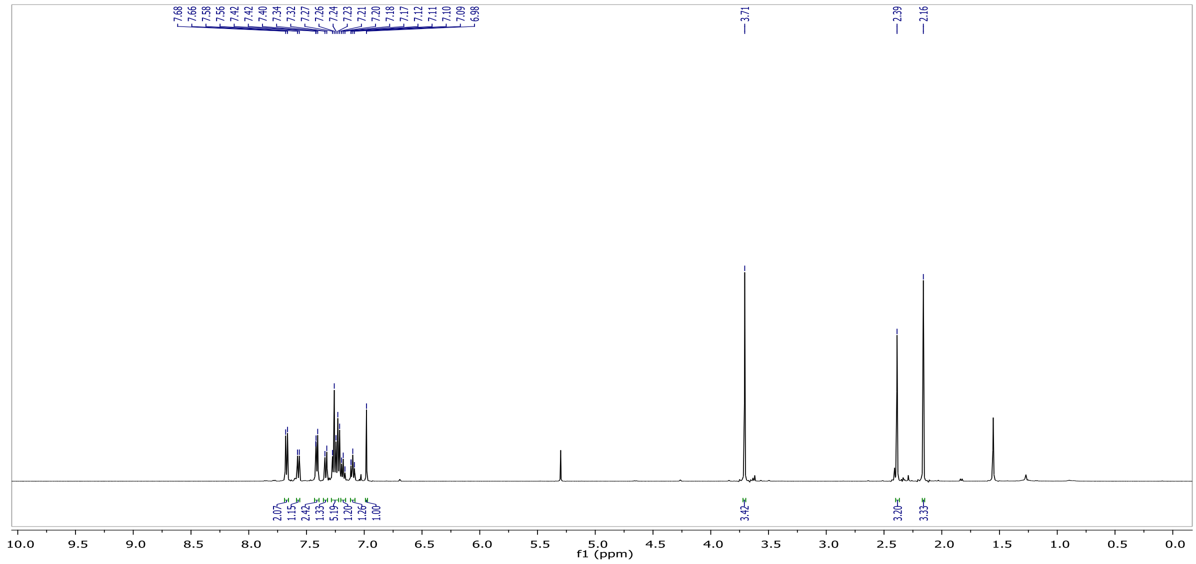
3a

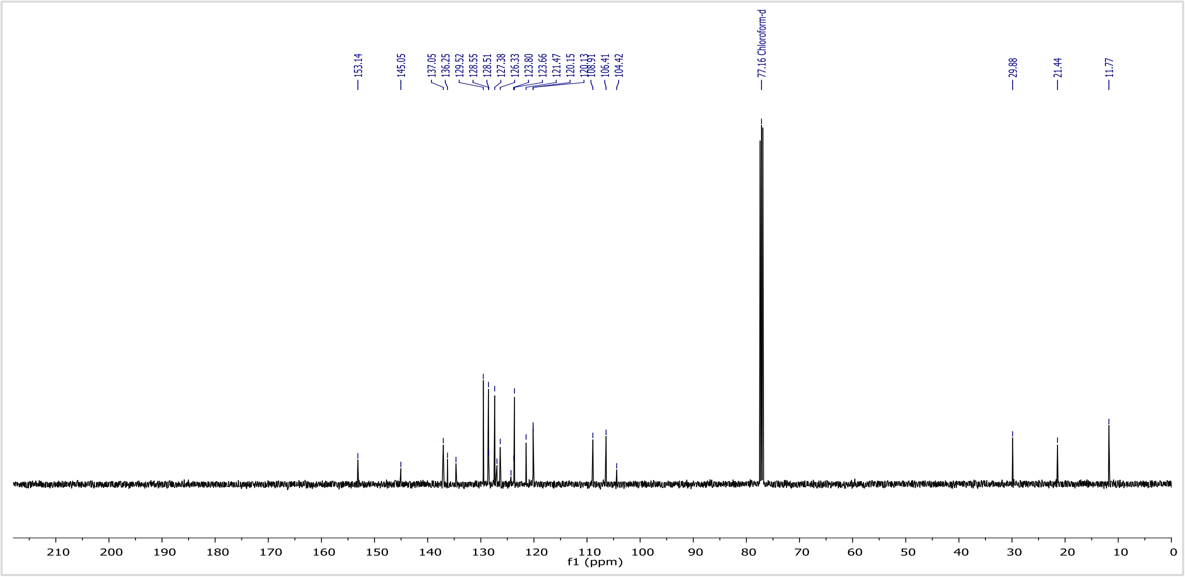


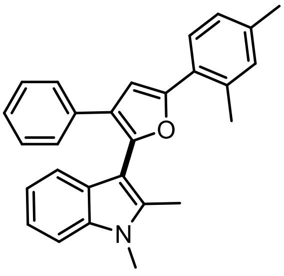



O
N

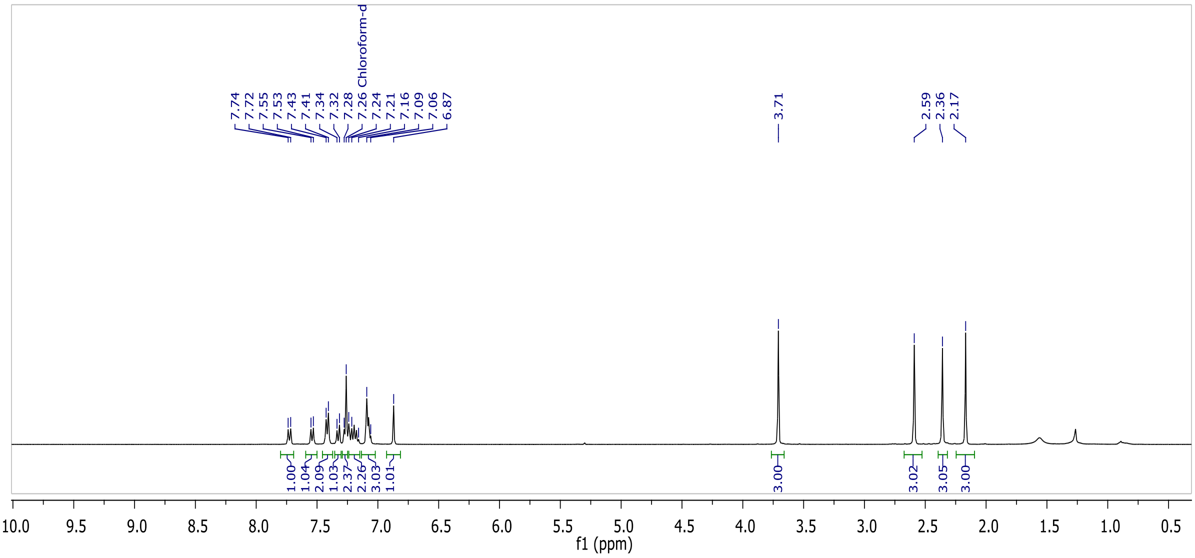
**3b**

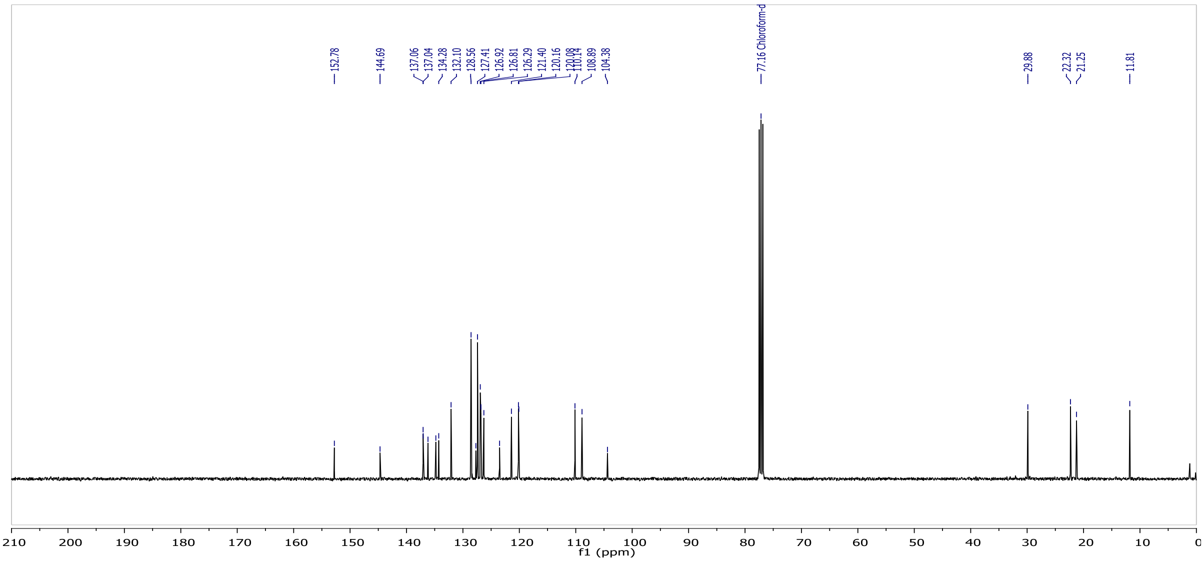

7.68
7.66
7.58
7.56
7.42
7.42
7.40
7.34
7.32
7.27
7.26
7.24
7.23
7.21
7.20
7.18
7.17
7.12
7.11
7.10
7.09
6.98
3.71
2.39
2.16
2.07
1.15
2.42
1.33
5.19
1.20
1.26
1.00
3.42
3.20
3.33
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

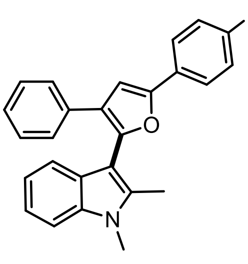

153.14
145.05
137.05
136.25
129.52
128.55
128.51
127.38
126.33
123.80
123.66
121.47
120.15
120.13
108.91
106.41
104.42
77.16 Chloroform-d
29.88
21.44
11.77
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



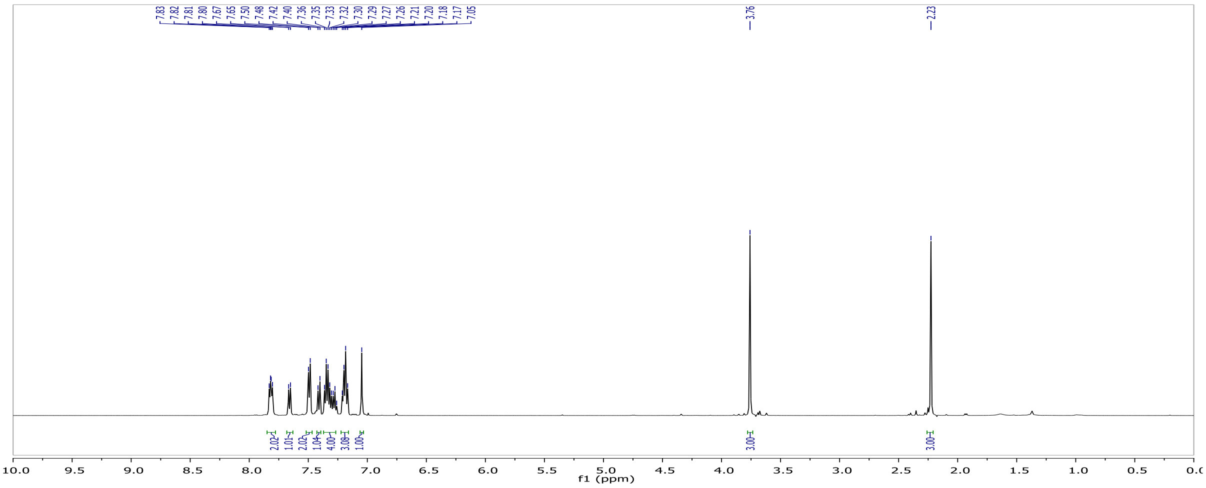
**3c**

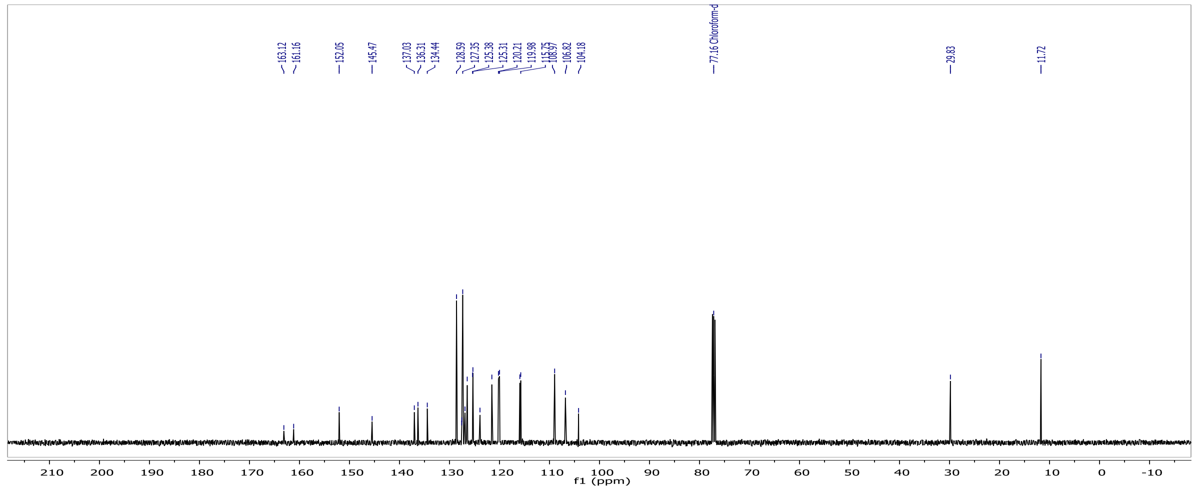

7.74
7.72
7.55
7.53
7.43
7.41
7.34
7.32
7.28
7.26 Chloroform-d
7.24
7.21
7.16
7.09
7.06
6.87
3.71
2.59
2.36
2.17
1.00
1.04
2.09
1.03
2.37
2.26
3.03
1.01
3.00
3.02
3.05
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

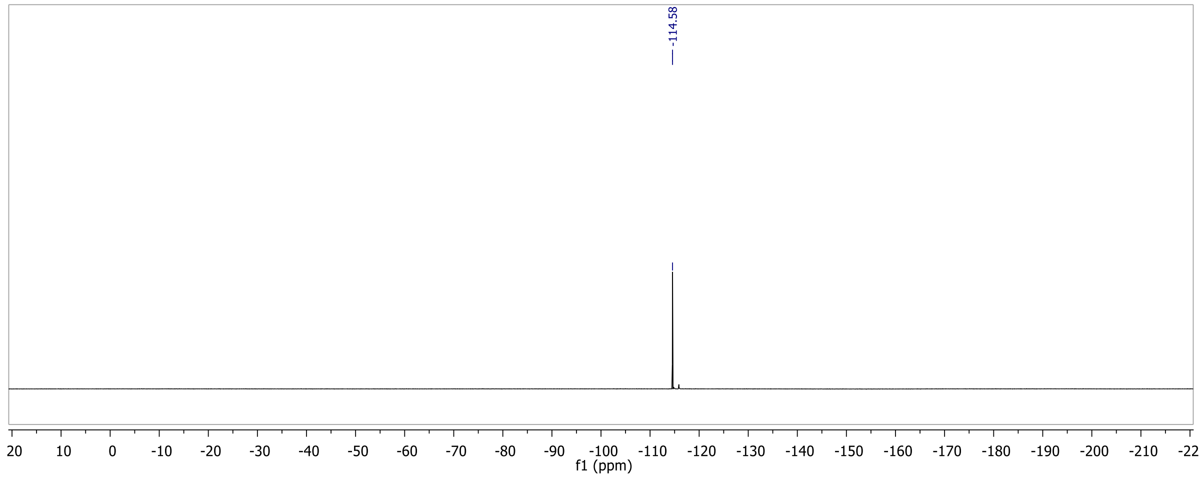

152.78
144.69
137.06
137.04
134.28
132.10
128.56
127.41
126.92
126.81
126.29
121.40
120.16
120.08
110.14
108.89
104.38
77.16 Chloroform-d
29.88
22.32
21.25
11.81
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

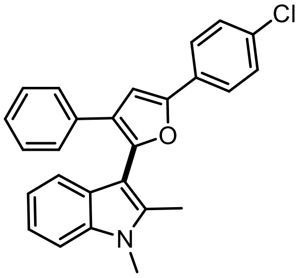

F
O
N

**3d**

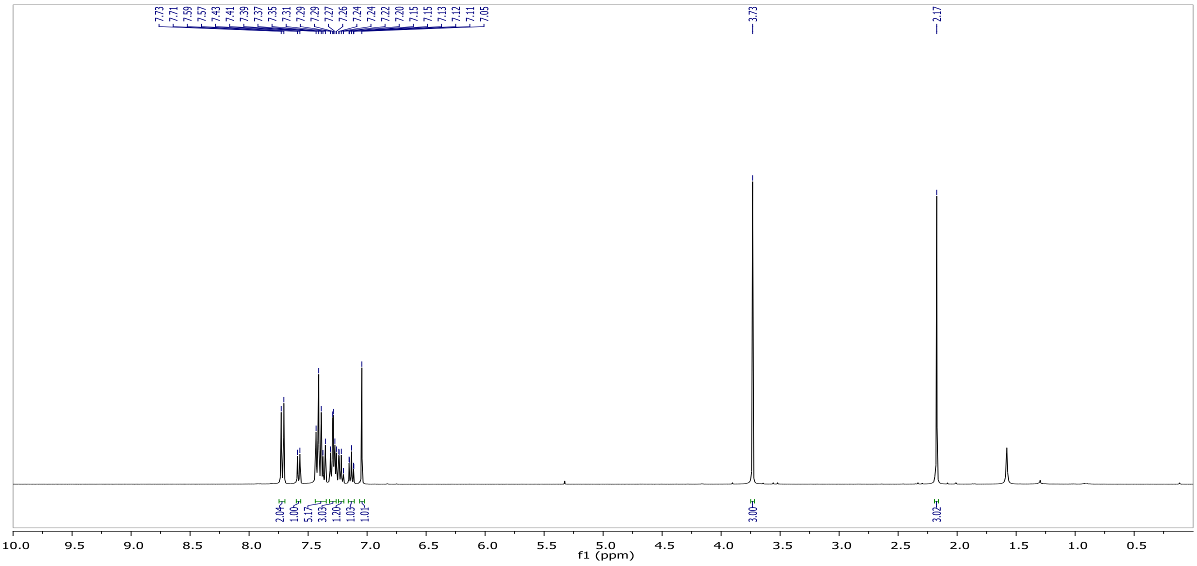

7.83
7.82
7.81
7.80
7.67
7.65
7.50
7.48
7.42
7.40
7.36
7.35
7.33
7.32
7.30
7.29
7.27
7.26
7.21
7.20
7.18
7.17
7.05
3.76
2.23
2.02
1.01
2.02
1.04
4.00
3.08
1.00
3.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

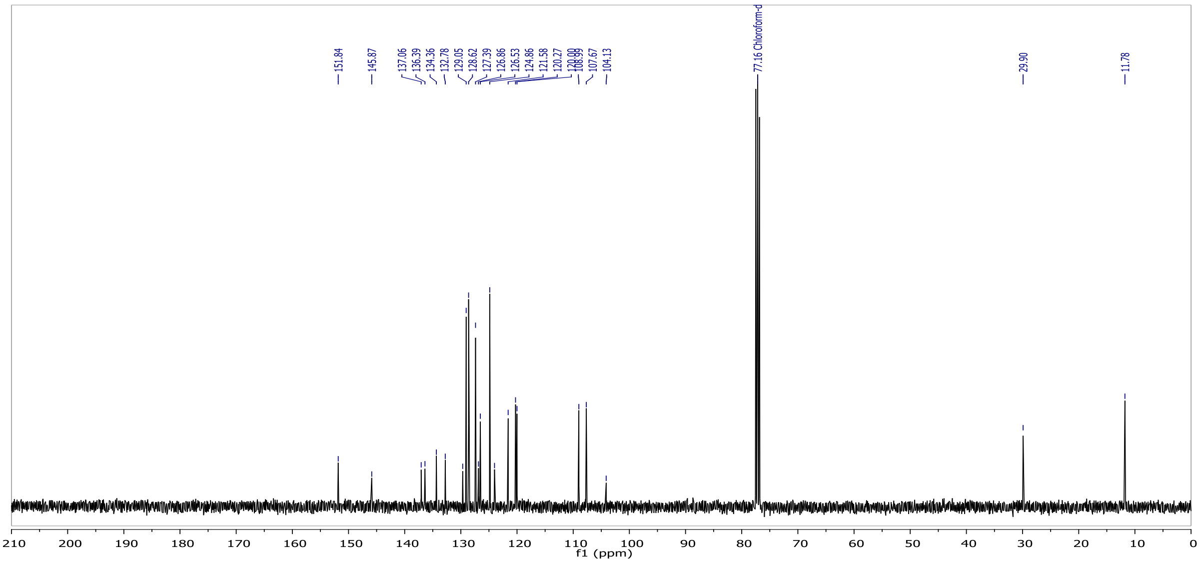

163.12
161.16
152.05
145.47
137.03
136.31
134.44
128.59
127.35
125.38
125.31
120.21
119.98
115.75
108.97
106.82
104.18
77.16 Chloroform-d
29.83
11.72
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-114.58
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-22
f1 (ppm)


Cl
O
N

**3e**


7.73
7.71
7.59
7.57
7.43
7.41
7.39
7.37
7.35
7.31
7.29
7.29
7.27
7.26
7.24
7.24
7.22
7.20
7.15
7.15
7.13
7.12
7.11
7.05
3.73
2.17
2.04
1.00
5.17
3.03
1.20
1.03
1.01
3.00
3.02
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
f1 (ppm)


151.84
145.87
137.06
136.39
134.36
132.78
129.05
128.62
127.39
126.86
126.53
124.86
121.58
120.27
120.00
108.99
107.67
104.13
77.16 Chloroform-d
29.90
11.78
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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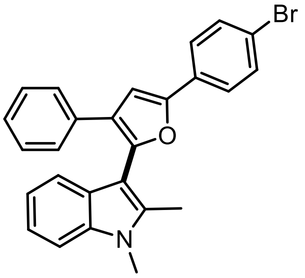
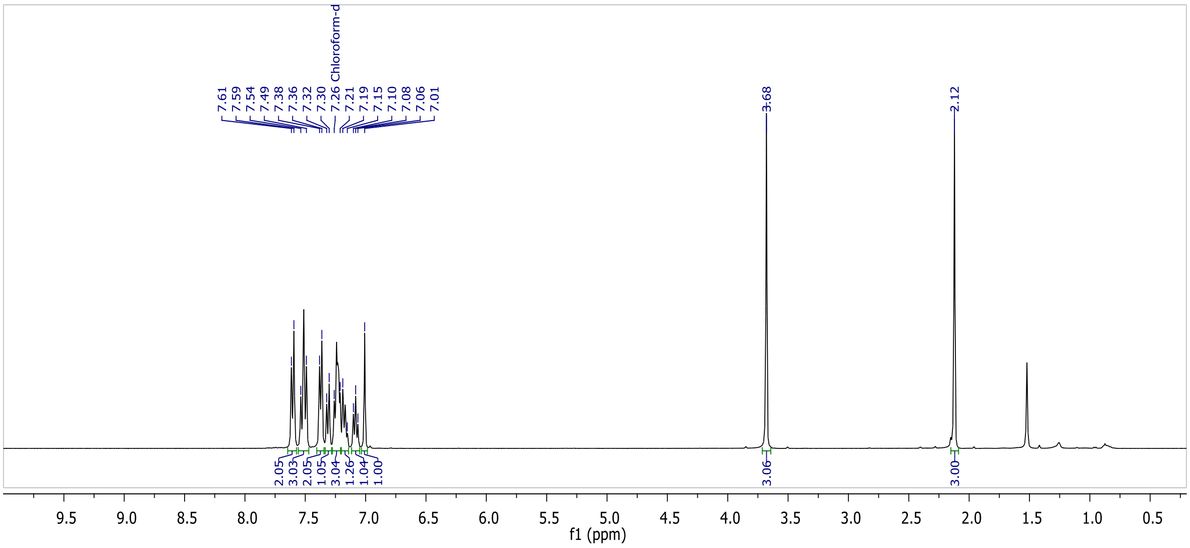
f1 (ppm)


Br
O
N

**3f**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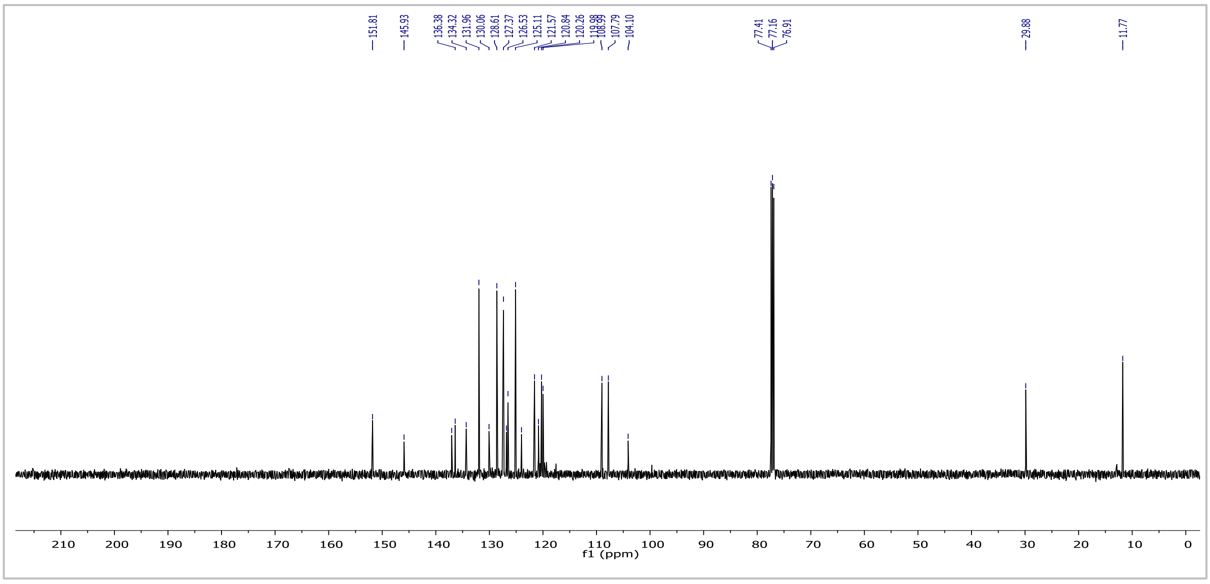
7.59
7.54
7.49
7.38
7.36
7.32
7.30
7.26 Chloroform-d
7.21
7.19
7.15
7.10
7.08
7.06
7.01
3.68
2.12
2.05
3.03
2.05
1.05
3.04
1.26
1.04
1.00
3.06
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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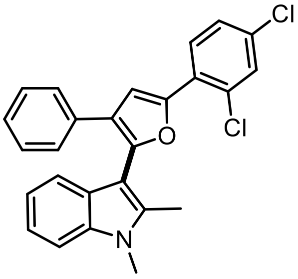
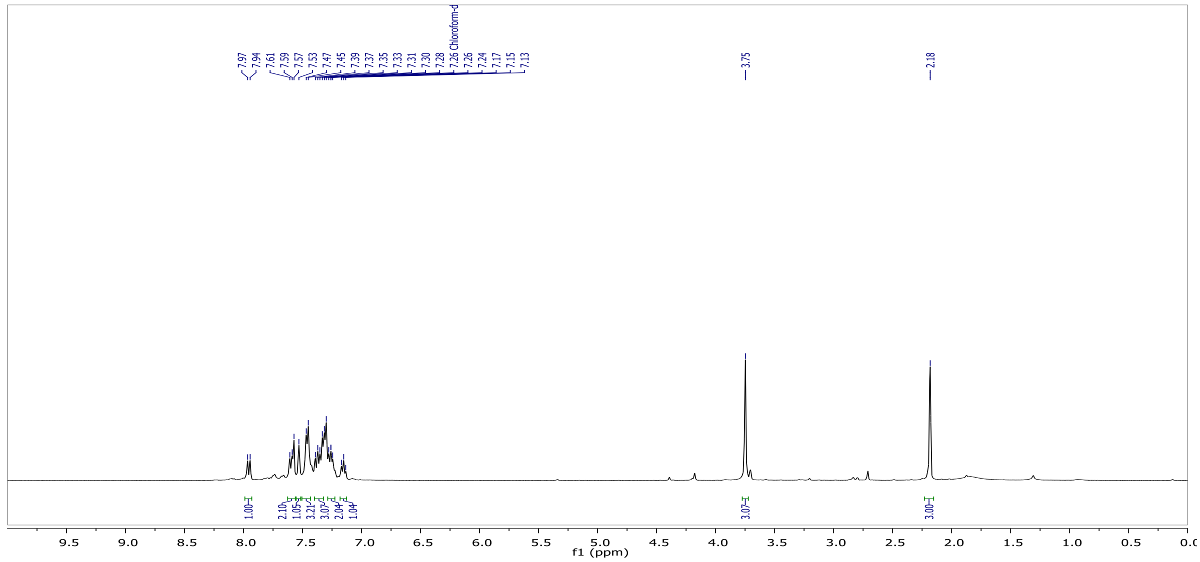
130.06
128.61
127.37
126.53
125.11
121.57
120.84
120.26
119.98
108.99
107.79
104.10
77.41
77.16
76.91
29.88
11.77
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cl
Cl
O
N

**3g**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7.53
7.47
7.45
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7.37
7.35
7.33
7.31
7.30
7.28
7.26 Chloroform-d
7.26
7.24
7.17
7.15
7.13
3.75
2.18
1.00
2.10
1.05
3.21
3.07
2.04
1.04
3.07
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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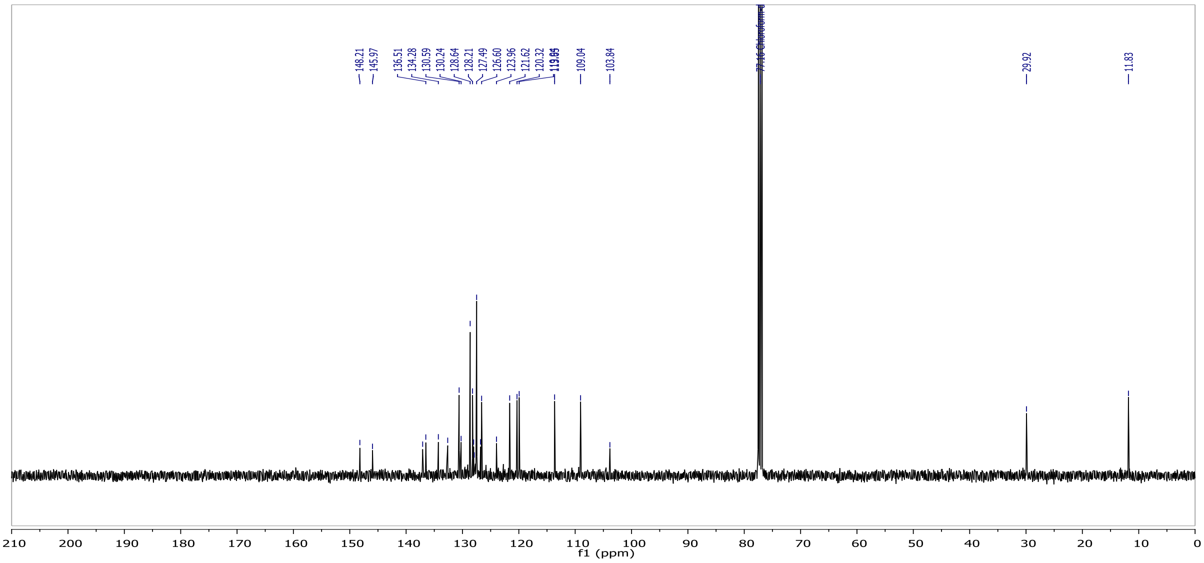
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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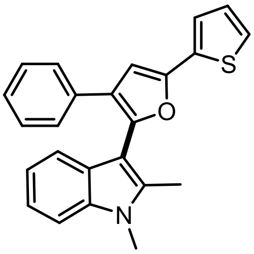
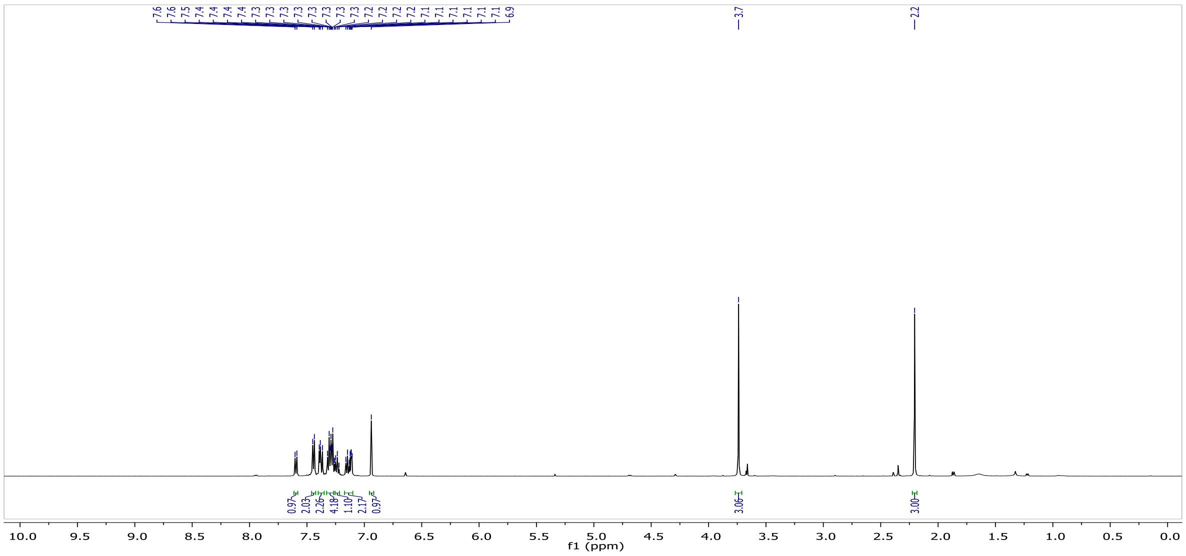
130.24
128.64
128.21
127.49
126.60
123.96
121.62
120.32
109.04
103.84
77.16 Chloroform-d
29.92
11.83
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


S
O
N

**3h**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7.6
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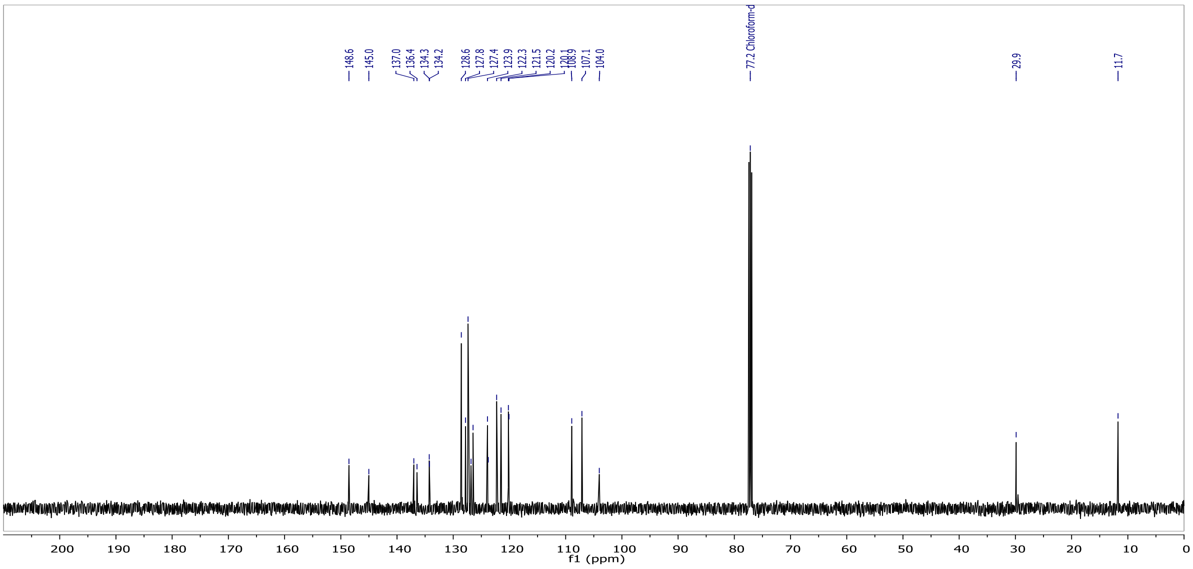
7.4
7.4
7.4
7.3
7.3
7.3
7.3
7.3
7.3
7.3
7.3
7.2
7.2
7.2
7.2
7.1
7.1
7.1
7.1
7.1
7.1
6.9
3.7
2.2
0.97
2.03
2.26
4.18
1.10
2.17
0.97
3.06
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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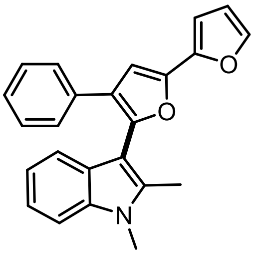
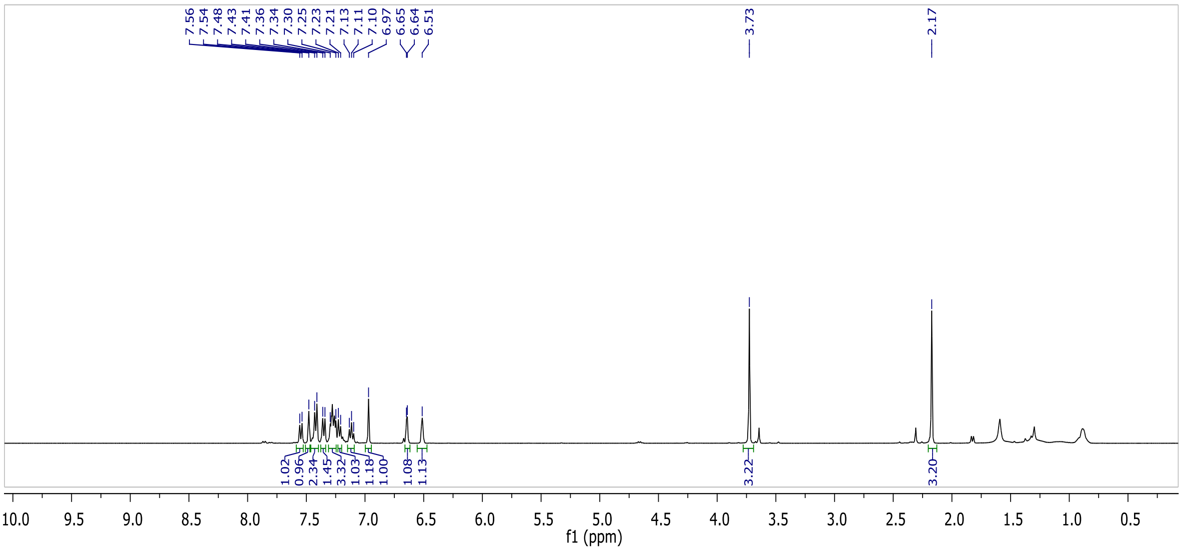
134.3
134.2
128.6
127.8
127.4
123.9
122.3
121.5
120.2
120.1
108.9
107.1
104.0
77.2 Chloroform-d
29.9
11.7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
N

**3i**


7.56
7.54
7.48
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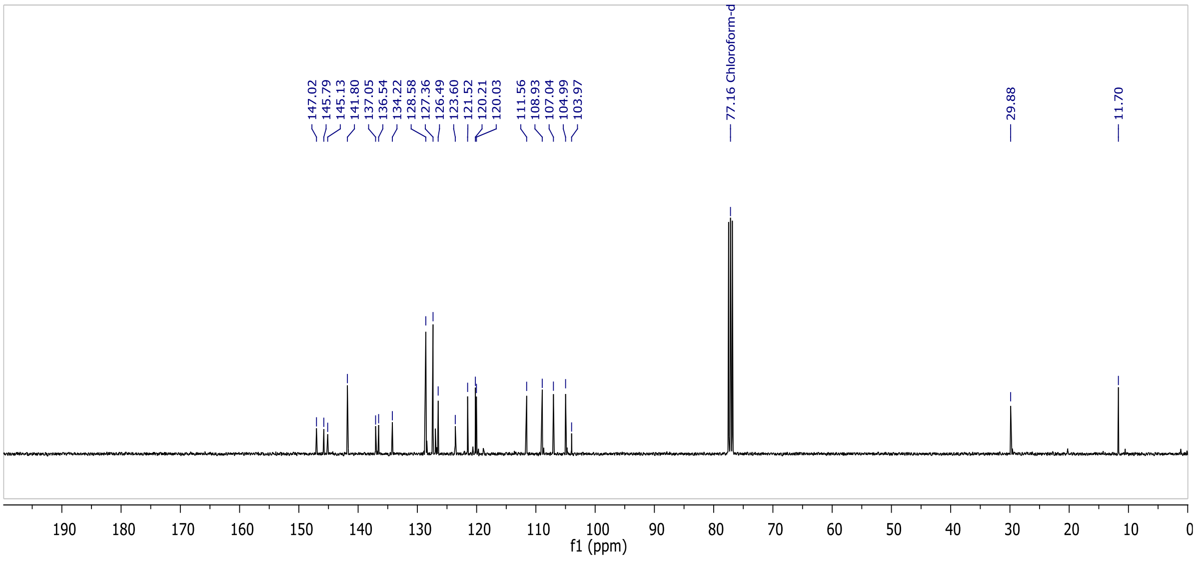
7.41
7.36
7.34
7.30
7.25
7.23
7.21
7.13
7.11
7.10
6.97
6.65
6.64
6.51
3.73
2.17
1.02
0.96
2.34
1.45
3.32
1.03
1.18
1.00
1.08
1.13
3.22
3.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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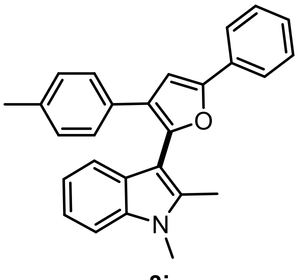
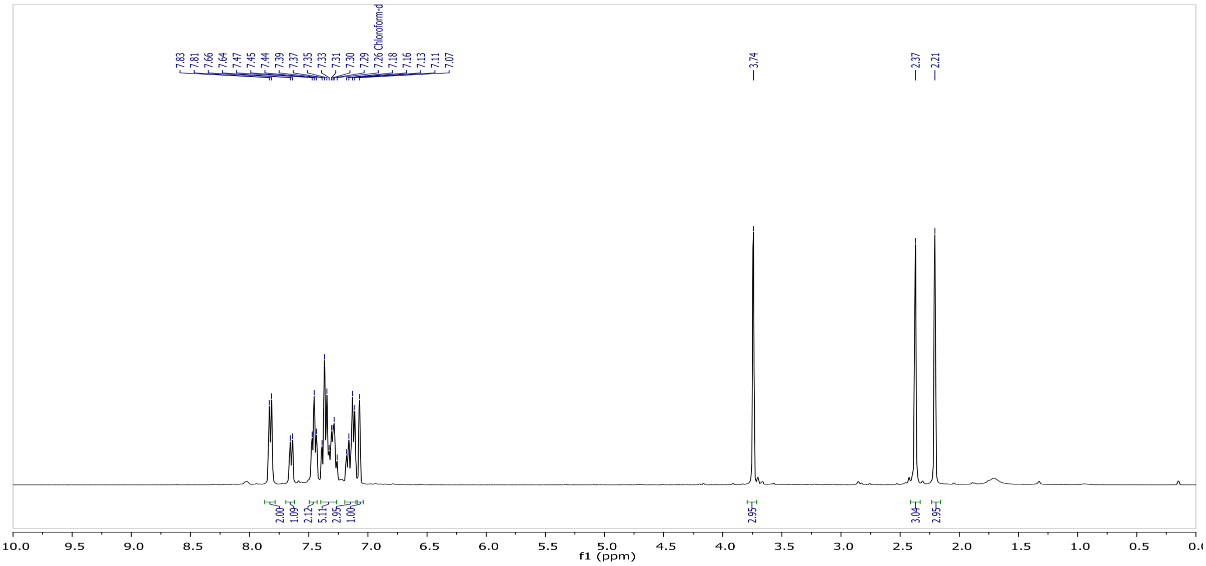
145.79
145.13
141.80
137.05
136.54
134.22
128.58
127.36
126.49
123.60
121.52
120.21
120.03
111.56
108.93
107.04
104.99
103.97
77.16 Chloroform-d
29.88
11.70
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



**3j**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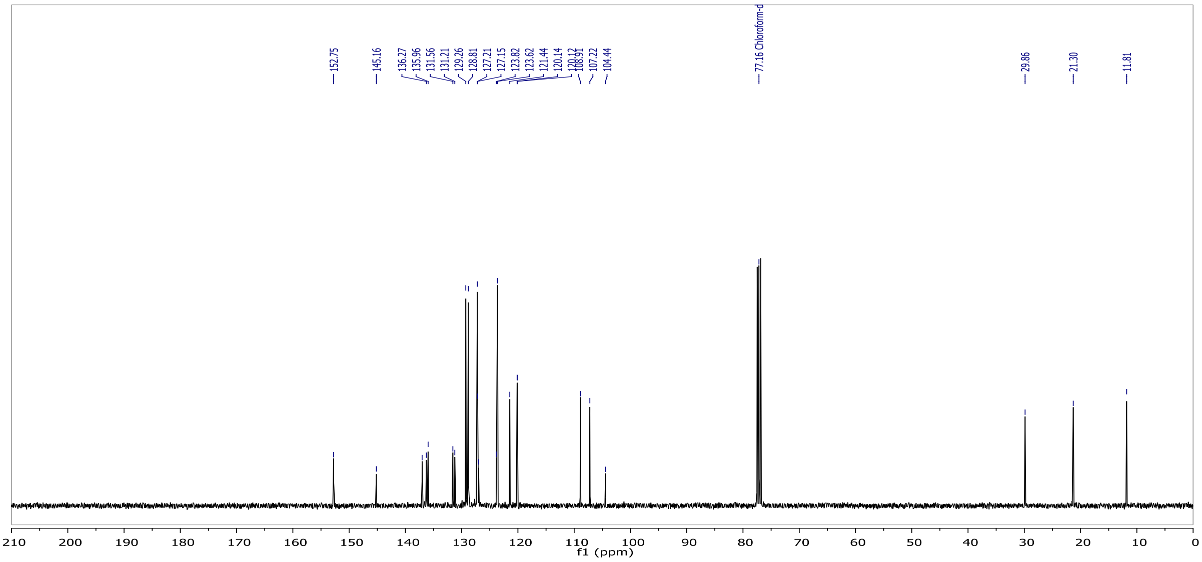
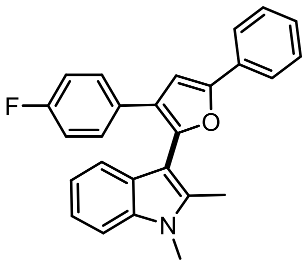
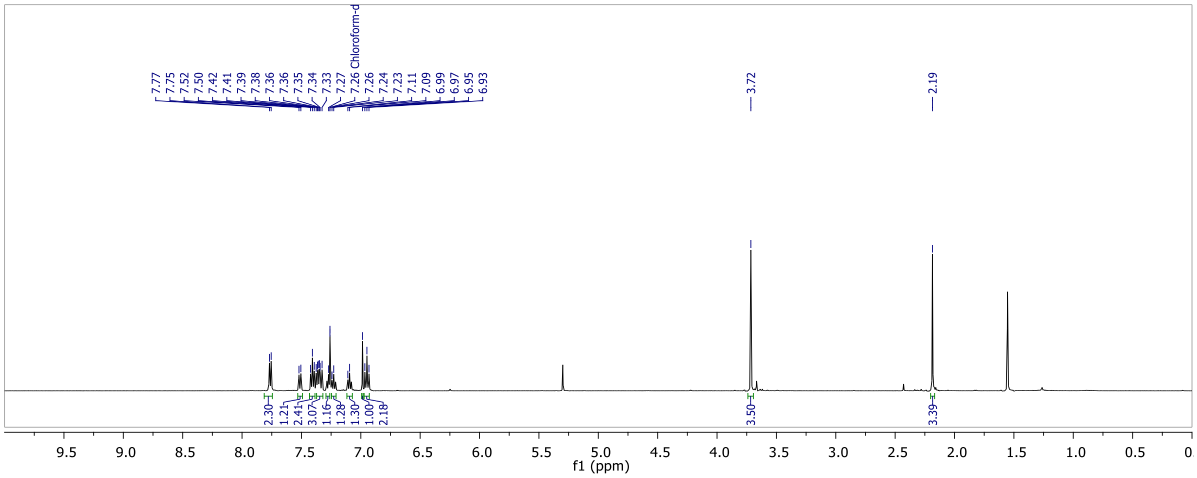
7.45
7.44
7.39
7.37
7.35
7.33
7.31
7.30
7.29
7.26 Chloroform-d
7.18
7.16
7.13
7.11
7.07
3.74
2.37
2.21
2.00
1.09
2.12
5.11
2.95
1.00
2.95
3.04
2.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


152.75
145.16
136.27
135.96
131.56
131.21
129.26
128.81
127.21
127.15
123.82
123.62
121.44
120.14
120.12
108.91
107.22
104.44
77.16 Chloroform-d
29.86
21.30
11.81
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
O
N

**3k**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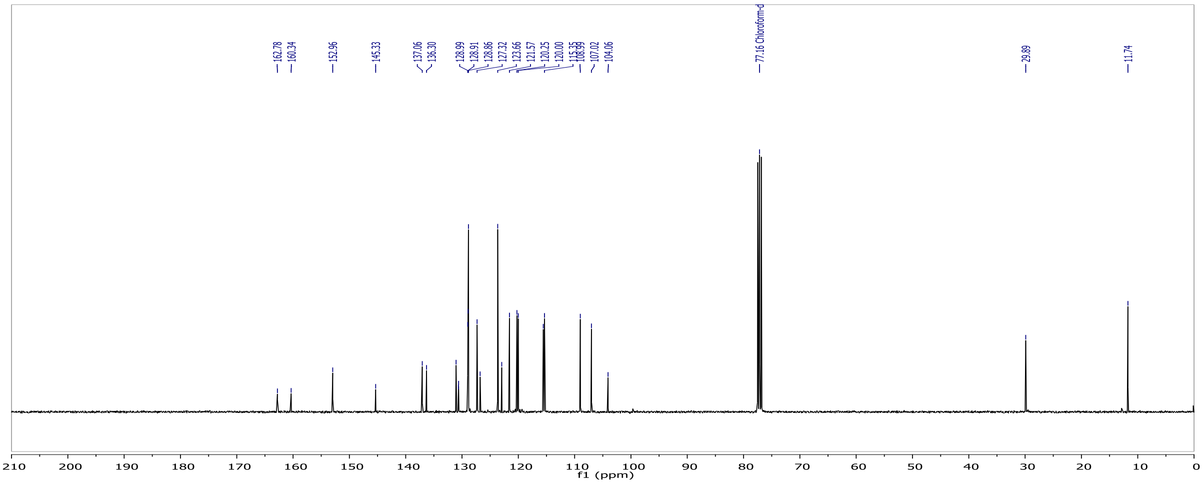
7.50
7.42
7.41
7.39
7.38
7.36
7.36
7.35
7.34
7.33
7.27
7.26 Chloroform-d
7.26
7.24
7.23
7.11
7.09
6.99
6.97
6.95
6.93
3.72
2.19
2.30
1.21
2.41
3.07
1.16
1.28
1.30
1.00
2.18
3.50
3.39
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)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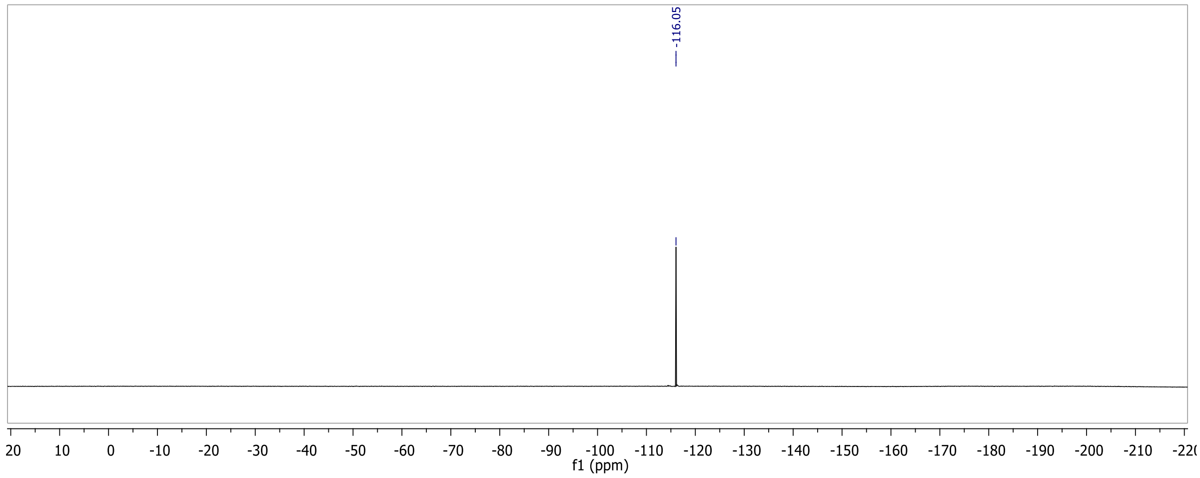
160.34
152.96
145.33
137.06
136.30
128.99
128.91
128.86
127.32
123.66
121.57
120.25
120.00
115.35
108.99
107.02
104.06
77.16 Chloroform-d
29.89
11.74
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-116.05
20
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0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
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-140
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-160
-170
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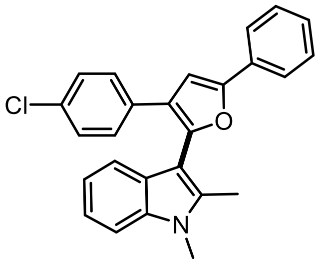
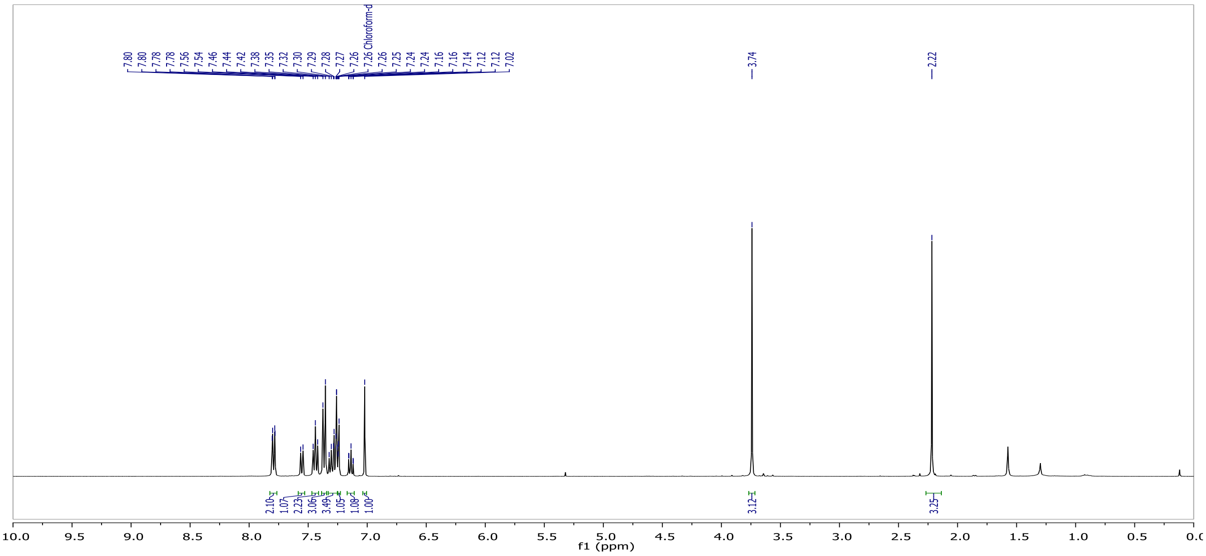
-190
-200
-210
-22(
f1 (ppm)


Cl
O
N

**3l**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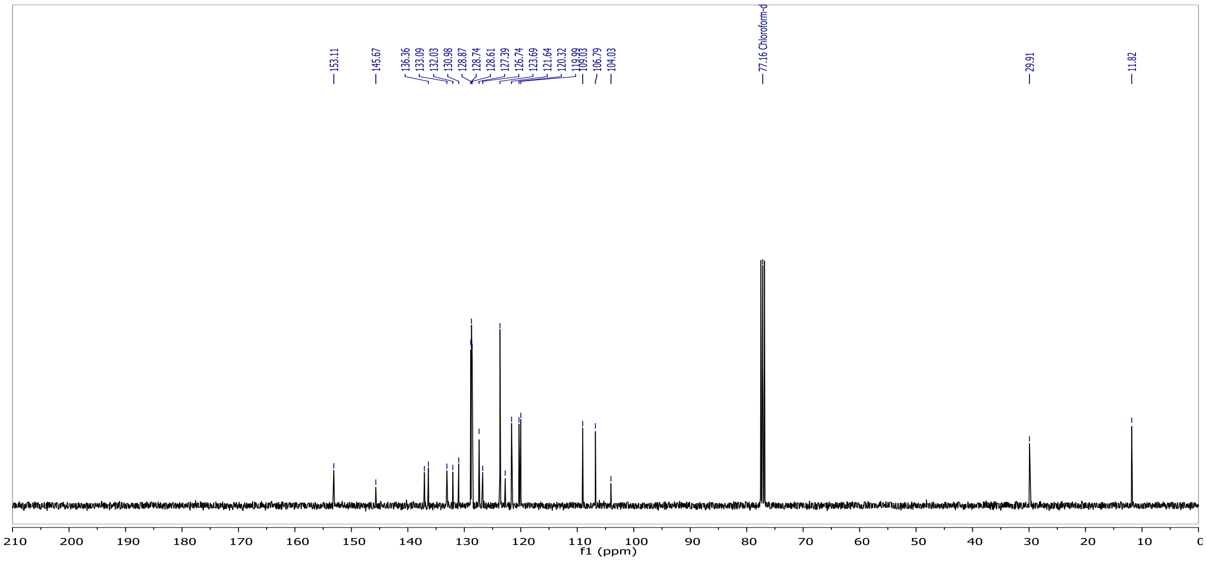
7.44
7.42
7.38
7.35
7.32
7.30
7.29
7.28
7.27
7.26 Chloroform-d
7.26
7.25
7.24
7.24
7.16
7.14
7.12
7.12
7.02
3.74
2.22
2.10
1.07
2.23
3.06
3.49
1.05
1.08
1.00
3.12
3.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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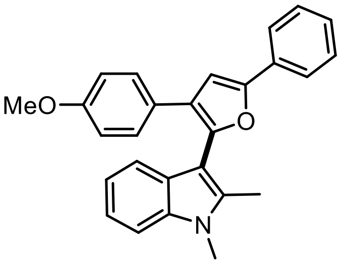
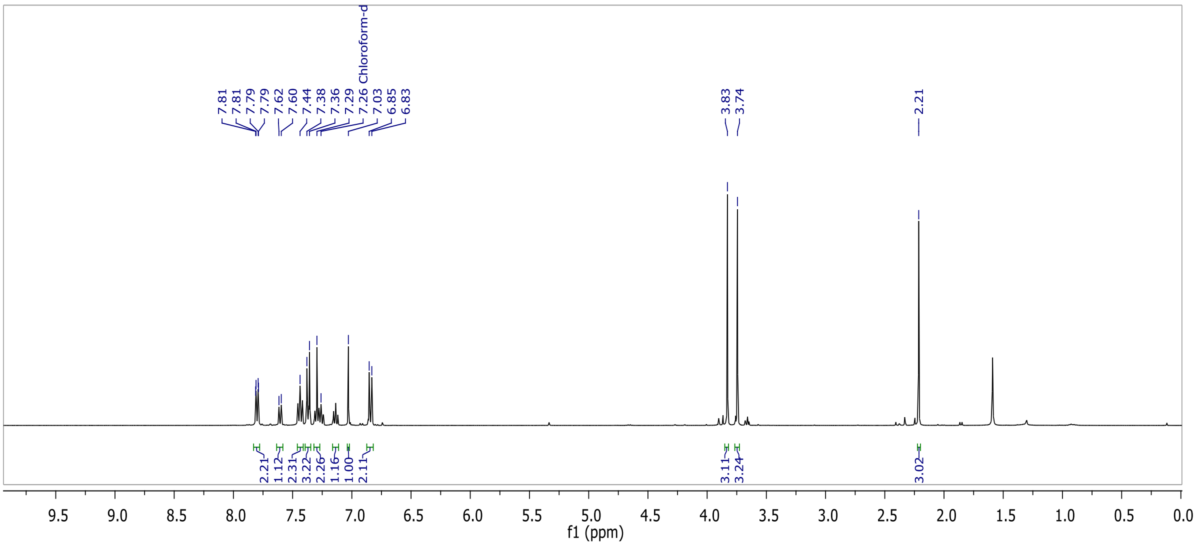
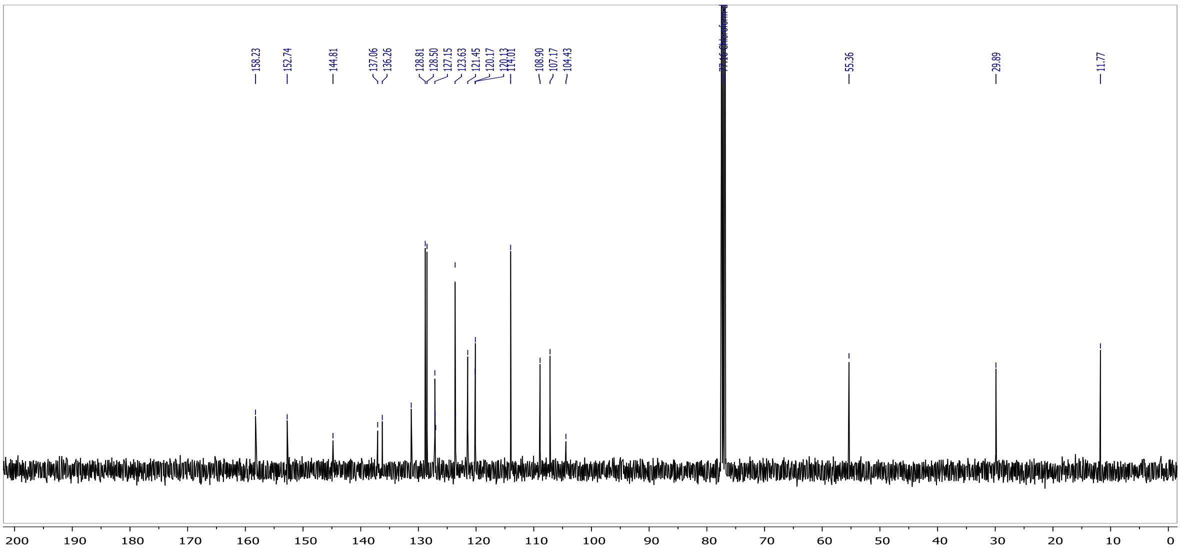
132.03
130.98
128.87
128.74
128.61
127.39
126.74
123.69
121.64
120.32
119.98
109.03
106.79
104.03
77.16 Chloroform-d
29.91
11.82
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MeO
O
N

**3m**


7.81
7.81
7.79
7.79
7.62
7.60
7.44
7.38
7.36
7.29
7.26 Chloroform-d
7.03
6.85
6.83
3.83
3.74
2.21
2.21
1.12
2.31
3.22
2.26
1.16
1.00
2.11
3.11
3.24
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.81
128.50
127.15
123.63
121.45
120.17
120.13
114.01
108.90
107.17
104.43
77.16 Chloroform-d
55.36
29.89
11.77
200
190
180
170
160
150
140
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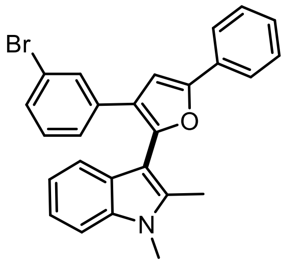
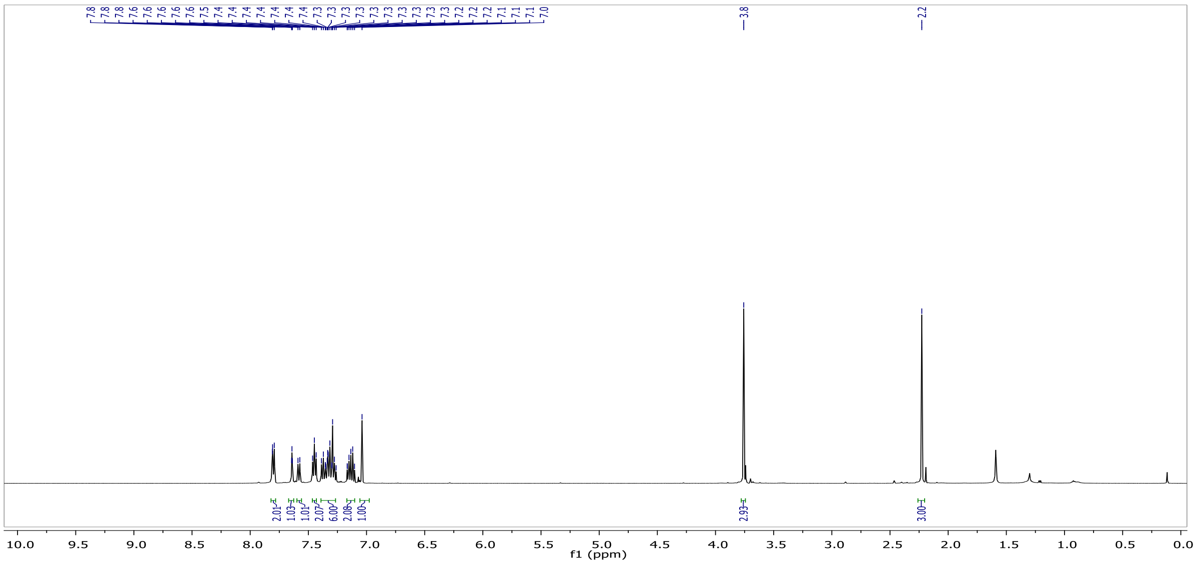
50
40
30
20
10
0


Br
O
N

**3n**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7.3
7.3
7.3
7.3
7.3
7.3
7.3
7.3
7.3
7.2
7.2
7.2
7.1
7.1
7.1
7.0
3.8
2.2
2.01
1.03
1.01
2.07
6.00
2.08
1.00
2.93
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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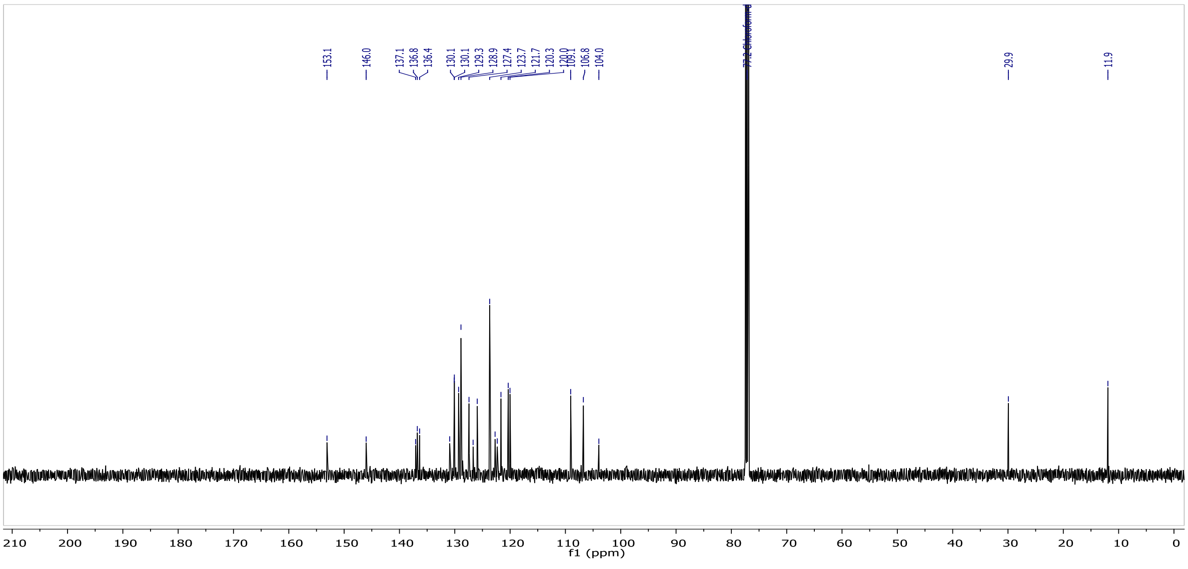
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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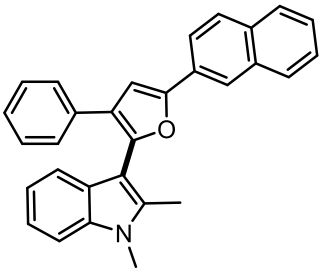
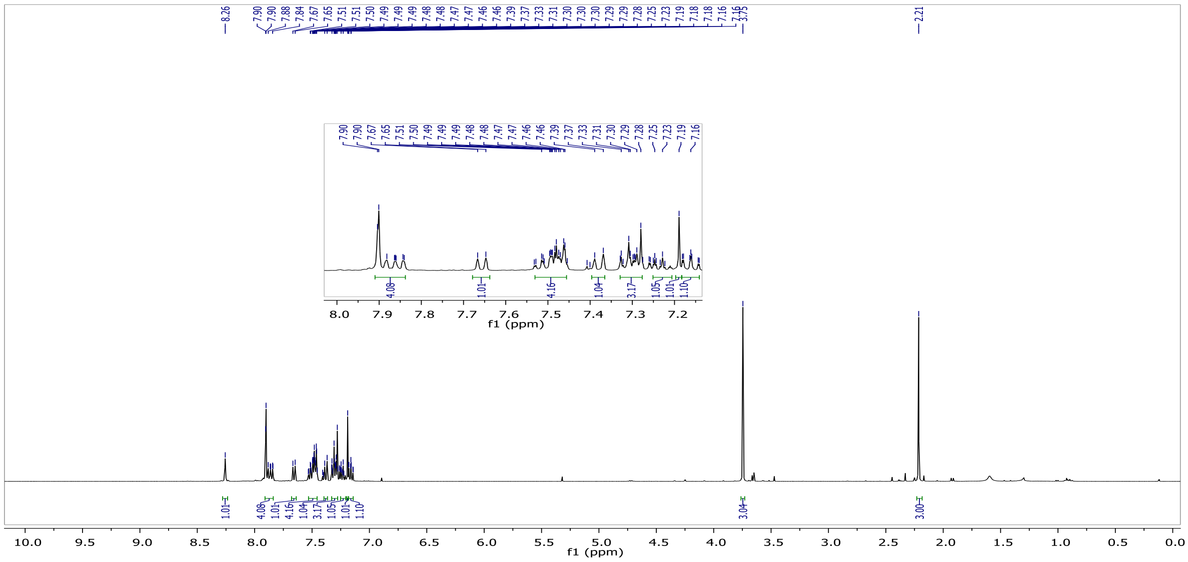
130.1
129.3
128.9
127.4
123.7
121.7
120.3
120.0
109.1
106.8
104.0
77.2 Chloroform-d
29.9
11.9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



**3o**


8.26
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7.67
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7.50
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7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.39
7.37
7.33
7.31
7.30
7.30
7.30
7.29
7.29
7.28
7.25
7.23
7.19
7.18
7.18
7.16
7.16
3.75
2.21
7.90
7.90
7.67
7.65
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7.50
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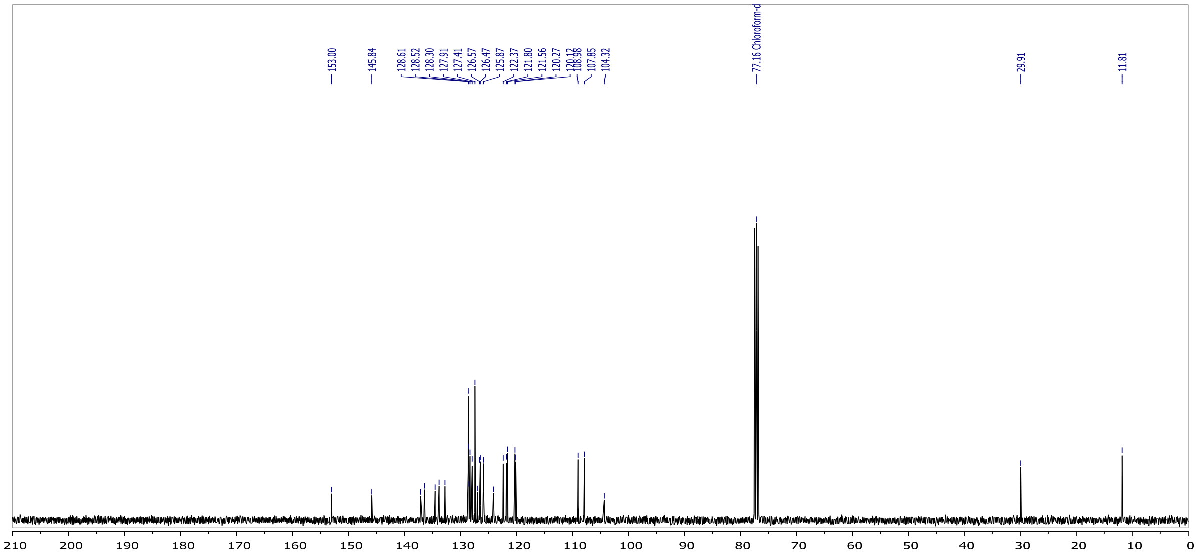
7.30
7.29
7.28
7.25
7.23
7.19
7.16
4.08
1.01
4.16
1.04
3.17
1.05
1.01
1.10
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)
1.01
4.08
1.01
4.16
1.04
3.17
1.05
1.01
1.10
3.04
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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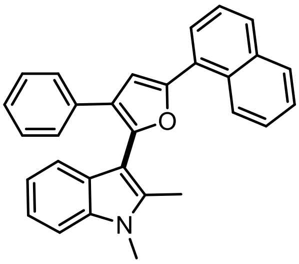
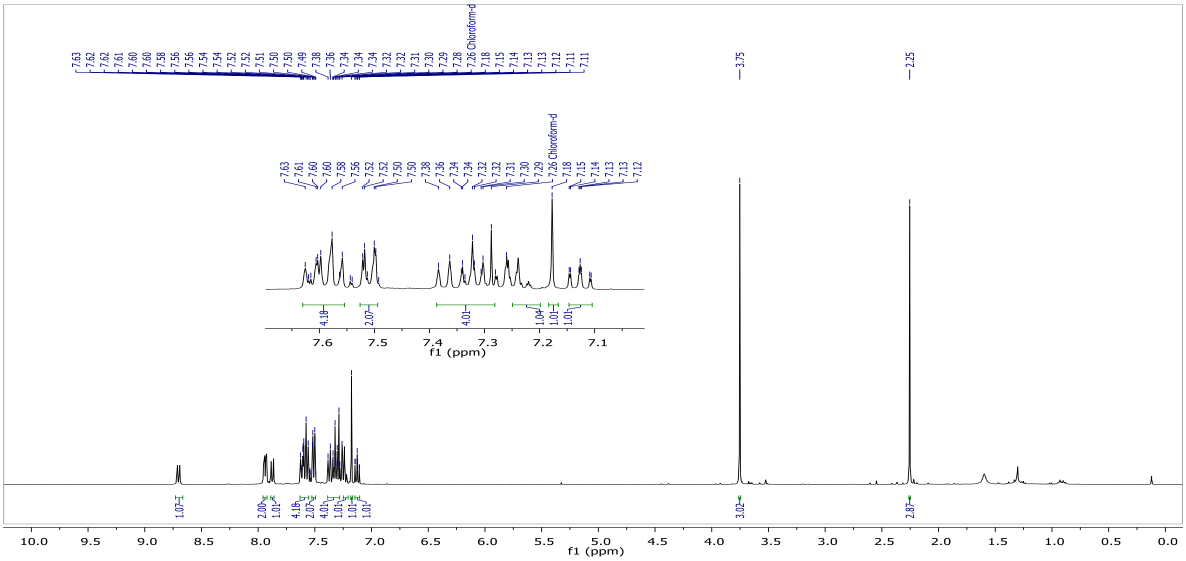
128.52
128.30
127.91
127.41
126.57
126.47
125.87
122.37
121.80
121.56
120.27
120.12
108.98
107.85
104.32
77.16 Chloroform-d
29.91
11.81
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
N

**3p**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7.62
7.62
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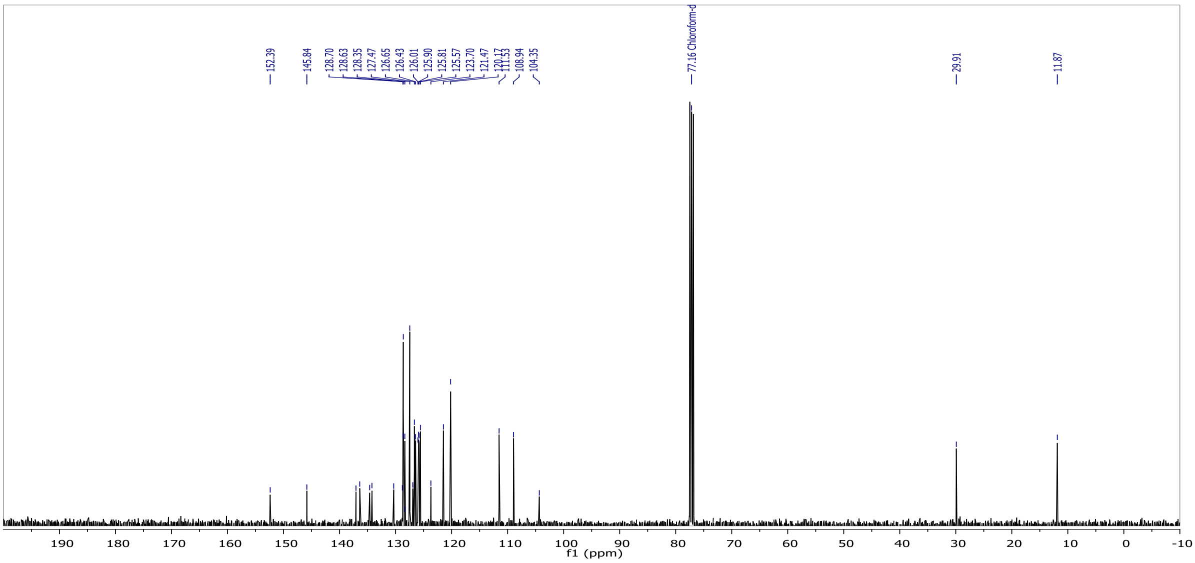
7.60
7.58
7.56
7.56
7.54
7.54
7.52
7.52
7.51
7.50
7.50
7.49
7.38
7.36
7.34
7.34
7.34
7.32
7.32
7.31
7.30
7.29
7.28
7.26 Chloroform-d
7.18
7.15
7.14
7.13
7.13
7.12
7.11
7.11
3.75
2.25
7.63
7.61
7.60
7.60
7.58
7.56
7.52
7.52
7.50
7.50
7.38
7.36
7.34
7.34
7.32
7.32
7.31
7.30
7.29
7.26 Chloroform-d
7.18
7.15
7.14
7.13
7.13
7.12
4.18
2.07
4.01
1.04
1.01
1.01
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
1.07
2.00
1.01
4.18
2.07
4.01
1.01
1.01
1.01
3.02
2.87
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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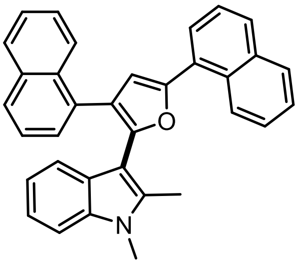
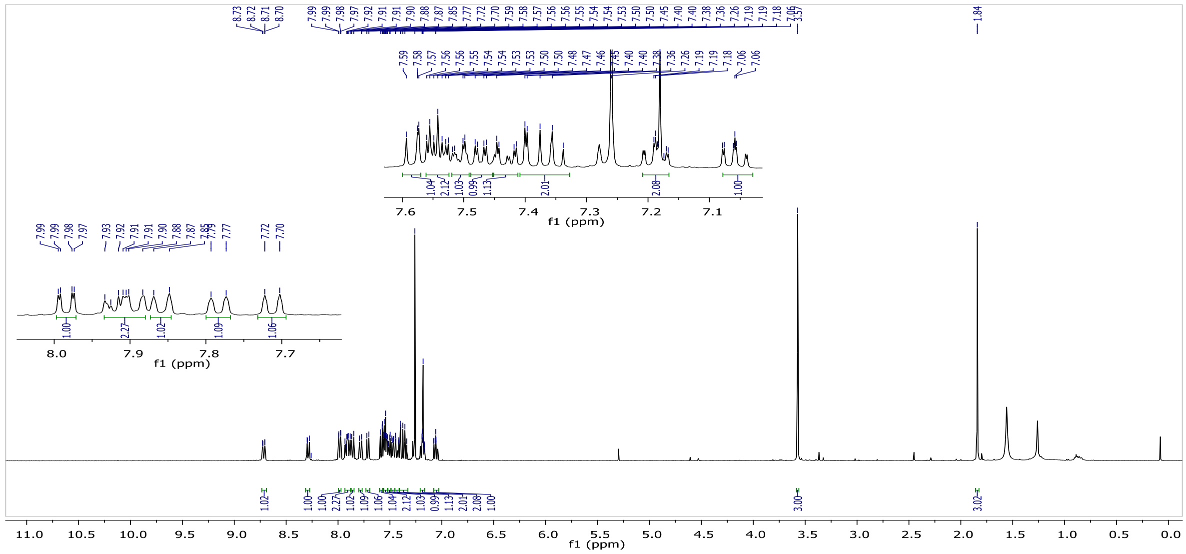
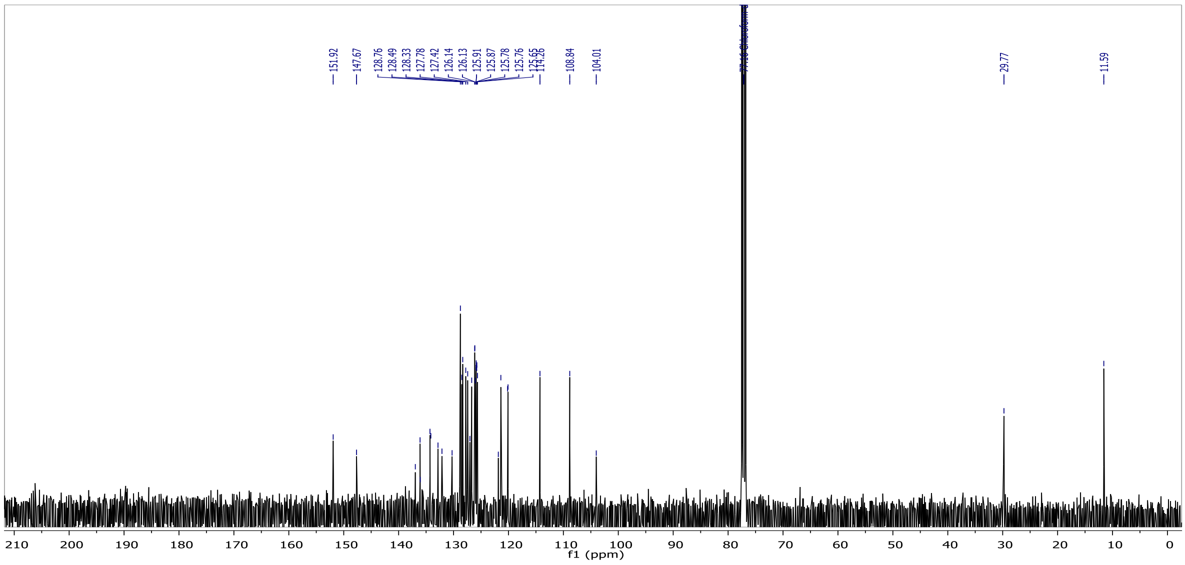
128.35
127.47
126.65
126.43
126.01
125.90
125.81
125.57
123.70
121.47
120.17
111.53
108.94
104.35
77.16 Chloroform-d
29.91
11.87
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



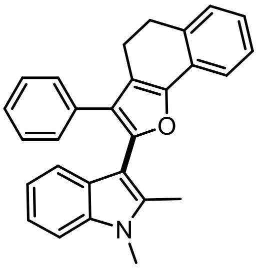
**3q**



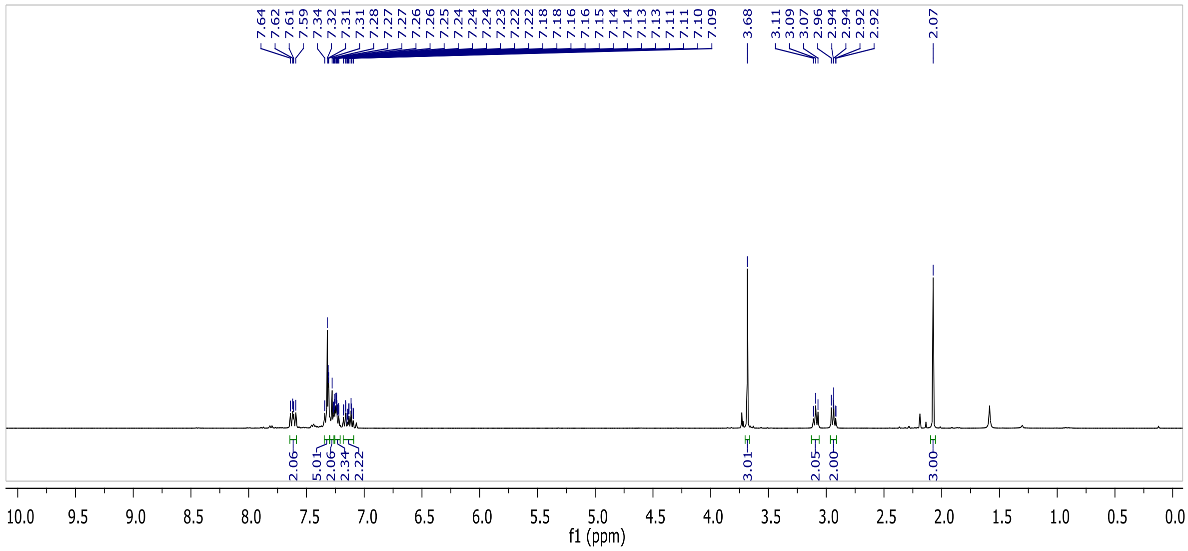
8.73 8.72 8.71 8.70
7.99 7.99 7.98 7.97 7.92 7.91 7.91 7.90 7.88 7.87 7.85 7.77 7.72 7.70 7.59 7.58 7.57 7.56 7.56 7.55 7.54 7.54 7.53 7.50 7.50 7.45 7.40 7.40 7.38 7.36 7.26 7.19 7.19 7.18 7.06 3.57
1.84
7.59 7.58 7.57 7.56 7.56 7.55 7.54 7.54 7.53 7.53 7.50 7.50 7.48 7.47 7.46 7.45 7.40 7.40 7.38 7.36 7.26 7.19 7.19 7.18 7.06 7.06
1.04 2.12 1.03 0.99 1.13 2.01 2.08 1.00
7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
7.99 7.99 7.98 7.97 7.93 7.92 7.91 7.91 7.90 7.88 7.87 7.85 7.79 7.77 7.72 7.70
1.00 2.27 1.02 1.09 1.06
8.0 7.9 7.8 7.7
f1 (ppm)
1.02 1.00 1.00 2.27 1.02 1.09 1.06 1.04 2.12 1.03 0.99 1.13 2.01 2.08 1.00 3.00 3.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

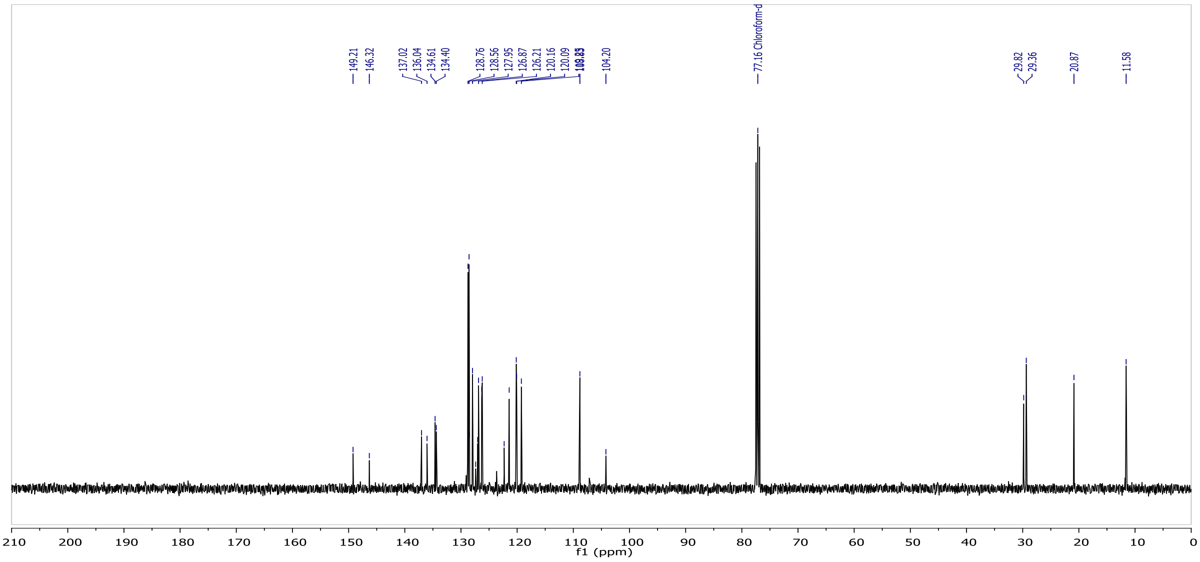


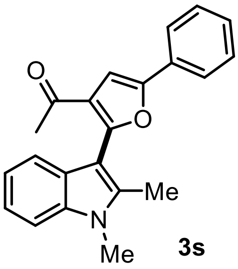
151.92
147.67
128.76 128.49 128.33 127.78 127.42 126.14 126.13 125.91 125.87 125.78 125.76 125.65 114.26
108.84
104.01
77.16 Chloroform-d
29.77
11.59
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
N

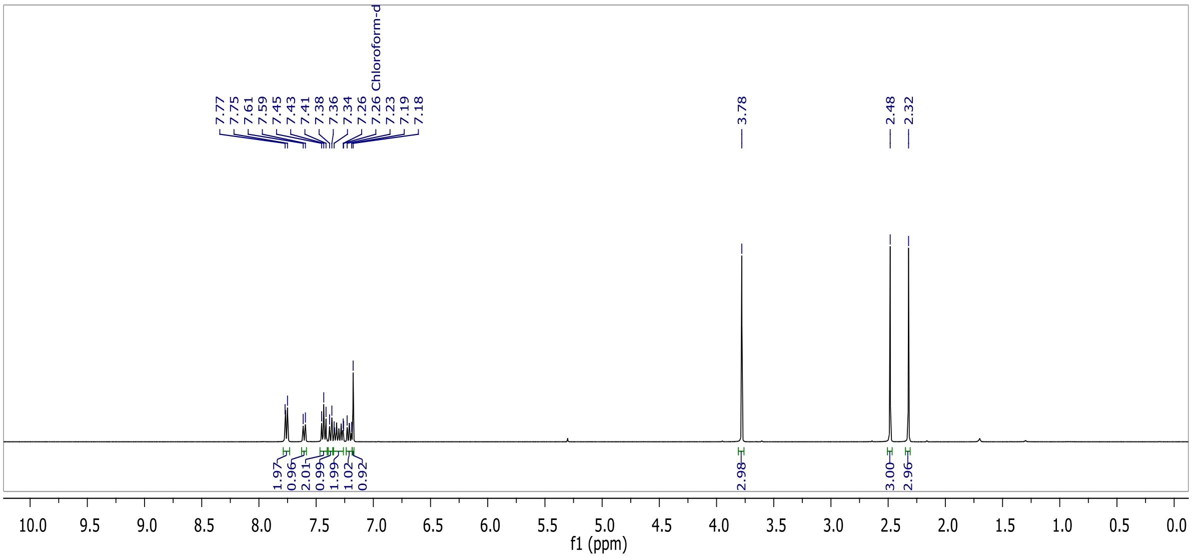
**3r**

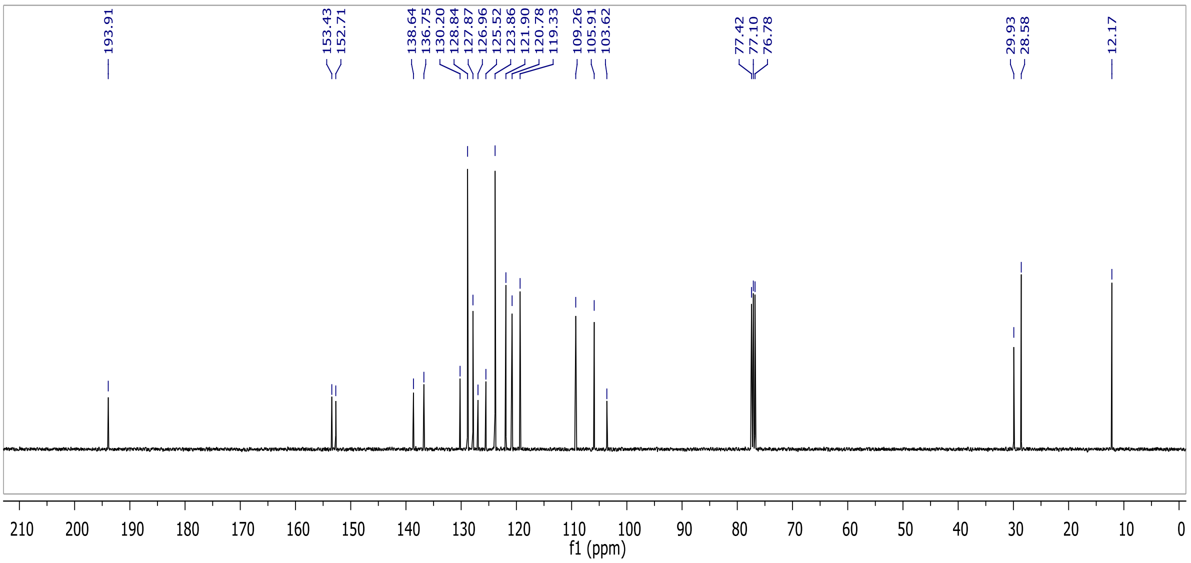

7.64
7.62
7.61
7.59
7.34
7.32
7.31
7.31
7.28
7.27
7.26
7.26
7.25
7.24
7.24
7.24
7.23
7.22
7.22
7.18
7.18
7.16
7.15
7.14
7.14
7.13
7.13
7.11
7.11
7.10
7.09
3.68
3.11
3.09
3.07
2.96
2.94
2.94
2.92
2.92
2.07
2.06
5.01
2.06
2.34
2.22
3.01
2.05
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


149.21
146.32
137.02
136.04
134.61
134.40
128.76
128.56
127.95
126.87
126.21
120.16
120.09
104.20
77.16 Chloroform-d
29.82
29.36
20.87
11.58
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

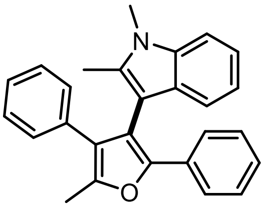

O
O
Me
N
Me

**3s**

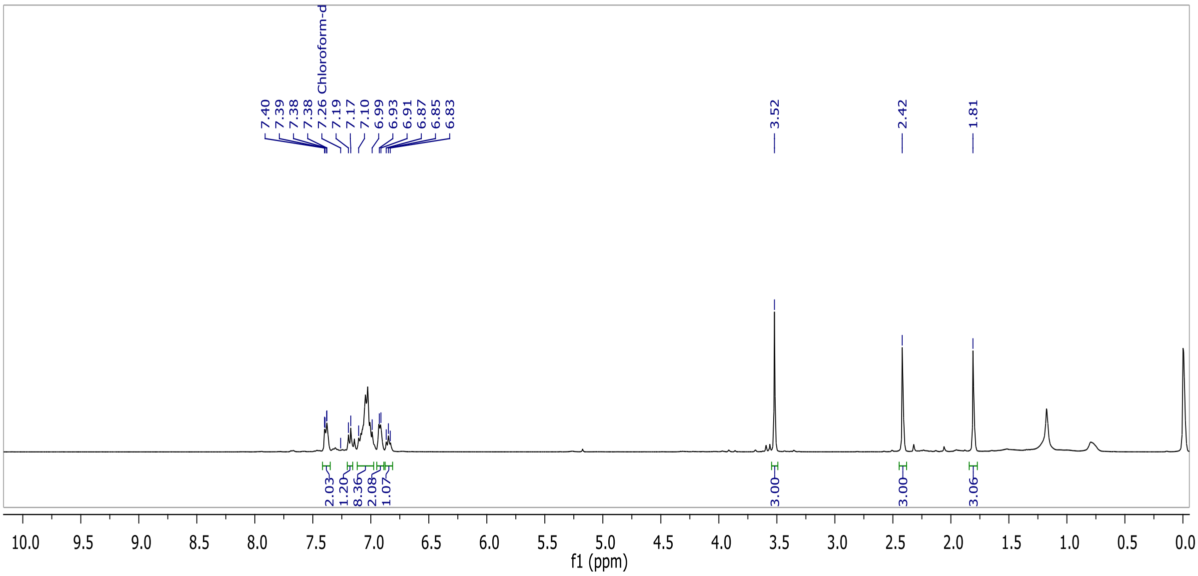

7.77
7.75
7.61
7.59
7.45
7.43
7.41
7.38
7.36
7.34
7.26 Chloroform-d
7.26
7.23
7.19
7.18
3.78
2.48
2.32
1.97
0.96
2.01
0.99
1.99
1.02
0.92
2.98
3.00
2.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

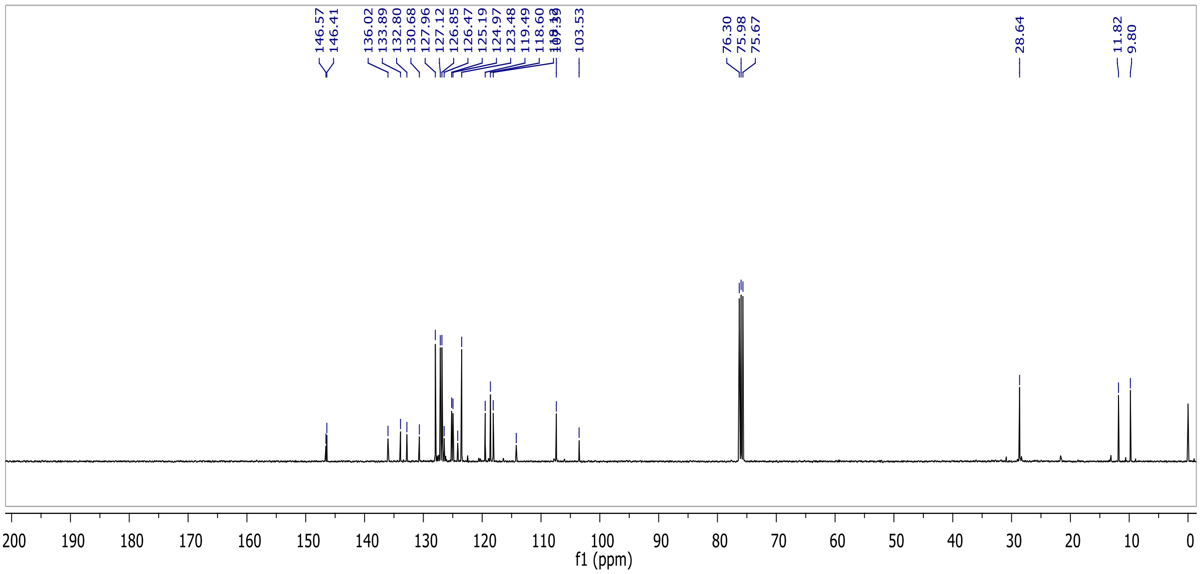

193.91
153.43
152.71
138.64
136.75
130.20
128.84
127.87
126.96
125.52
123.86
121.90
120.78
119.33
109.26
105.91
103.62
77.42
77.10
76.78
29.93
28.58
12.17
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

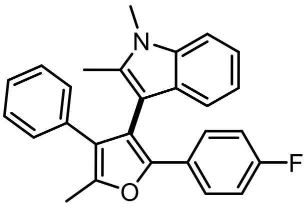
# NMR spectra for the cross-coupling products 3t-3w:



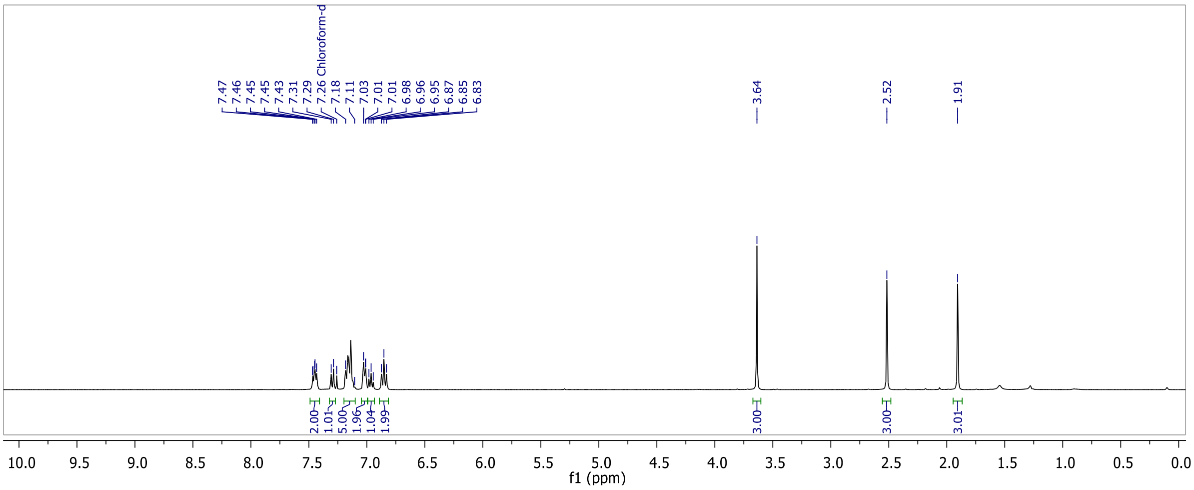
**3t**

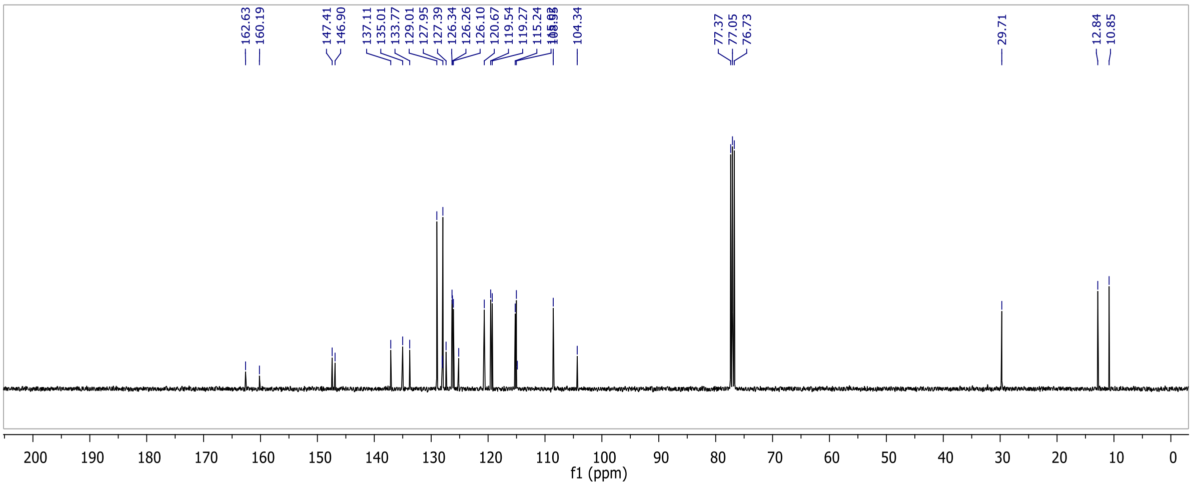


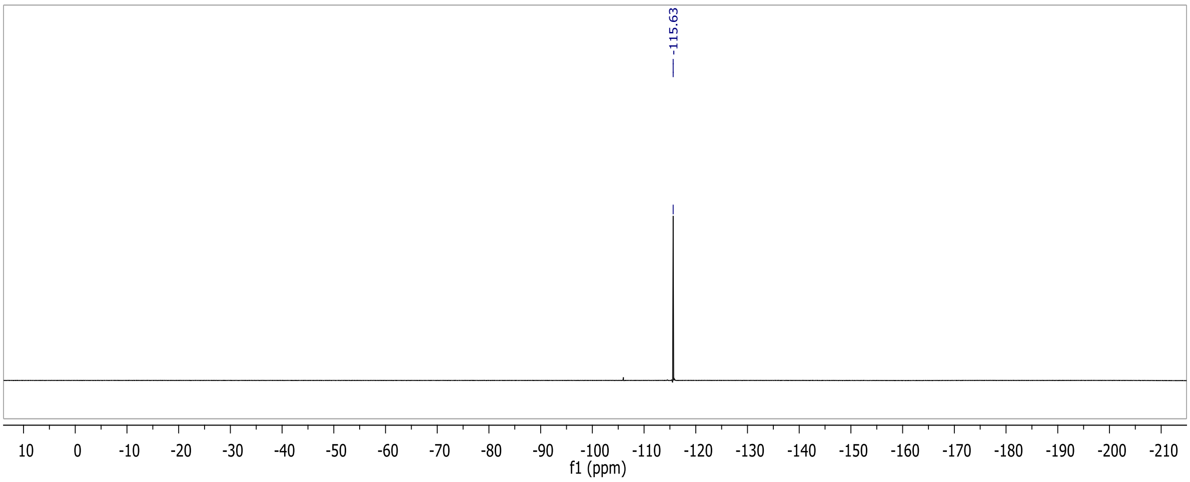


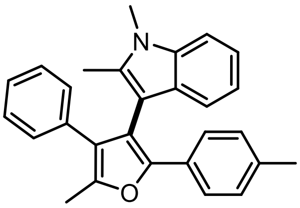

N
O
F

**3u**

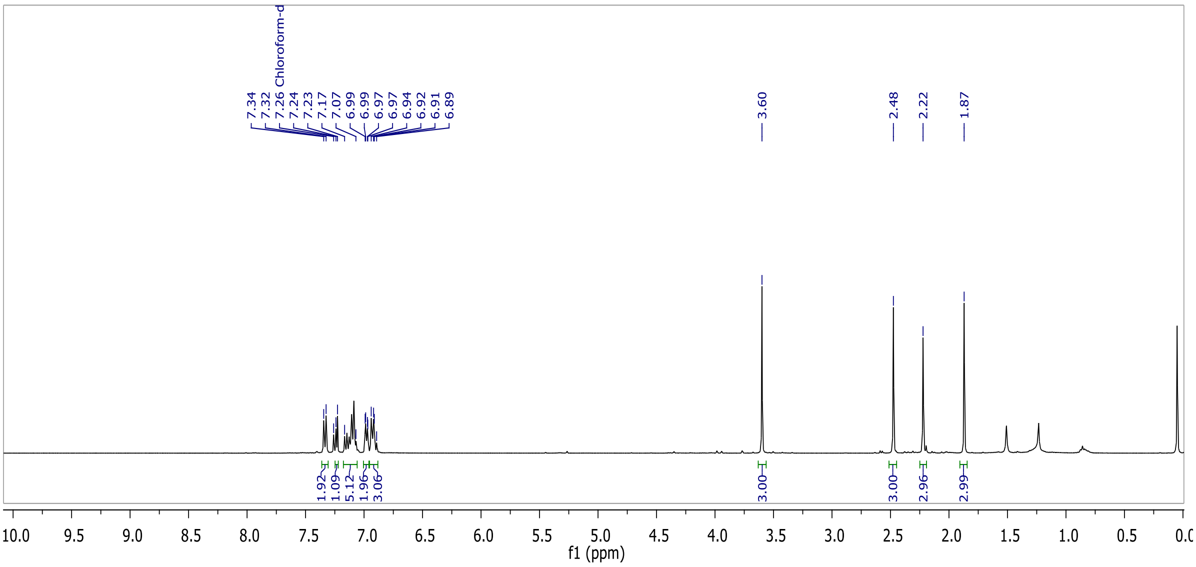

7.47
7.46
7.45
7.45
7.43
7.31
7.29
7.26 Chloroform-d
7.18
7.11
7.03
7.01
7.01
6.98
6.96
6.95
6.87
6.85
6.83
3.64
2.52
1.91
2.00
1.01
5.00
1.96
1.04
1.99
3.00
3.00
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

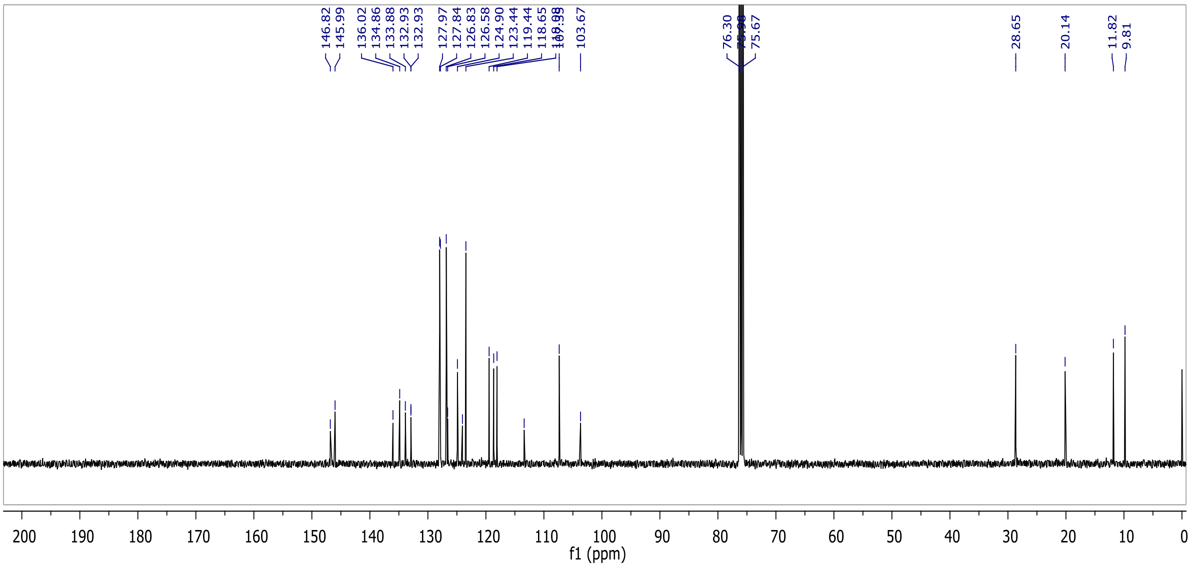

162.63
160.19
147.41
146.90
137.11
135.01
133.77
129.01
127.95
127.39
126.34
126.26
126.10
120.67
119.54
119.27
115.24
104.34
77.37
77.05
76.73
29.71
12.84
10.85
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

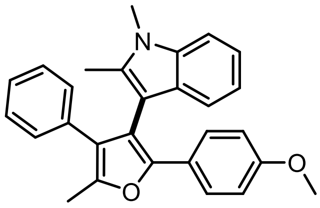

-115.63
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


N
O

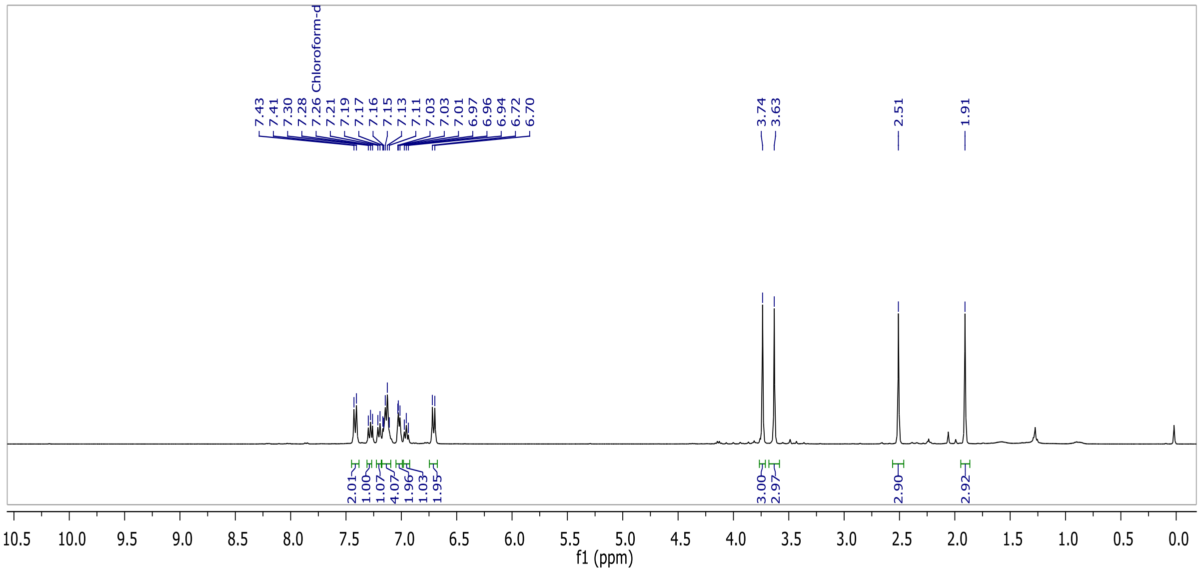
**3v**

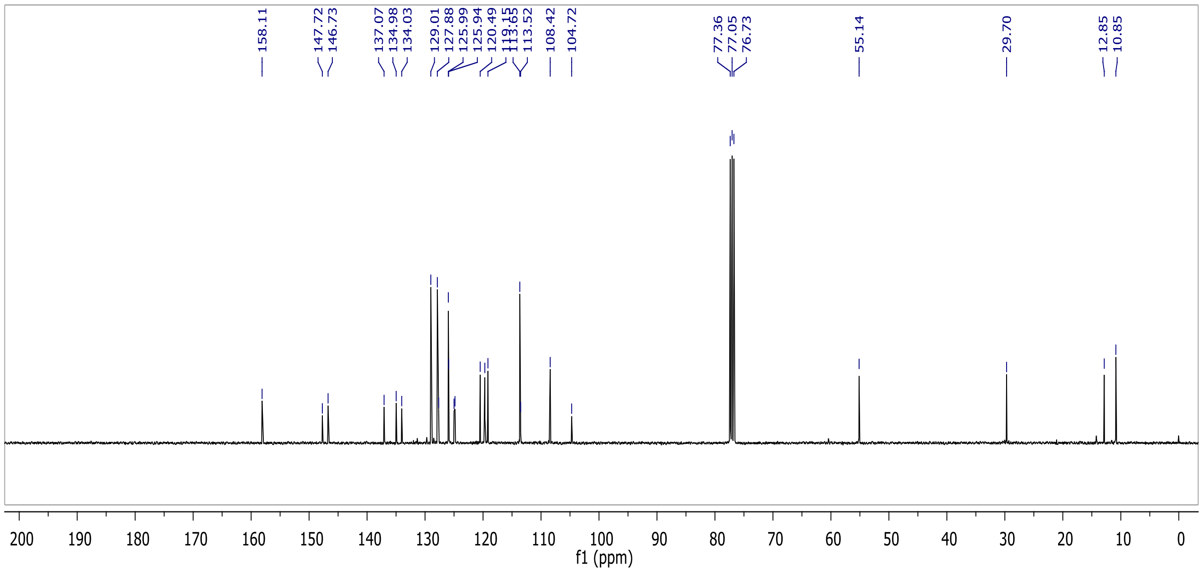

7.34
7.32
7.26 Chloroform-d
7.24
7.23
7.17
7.07
6.99
6.99
6.97
6.97
6.94
6.92
6.91
6.89
3.60
2.48
2.22
1.87
1.92
1.09
5.12
1.96
3.06
3.00
3.00
2.96
2.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


146.82
145.99
136.02
134.86
133.88
132.93
132.93
127.97
127.84
126.83
126.58
124.90
123.44
119.44
118.65
113.08
107.35
103.67
76.30
75.98
75.67
28.65
20.14
11.82
9.81
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
O
O

**3w**


7.43
7.41
7.30
7.28
7.26 Chloroform-d
7.21
7.19
7.17
7.16
7.15
7.13
7.11
7.03
7.03
7.01
6.97
6.96
6.94
6.72
6.70
3.74
3.63
2.51
1.91
2.01
1.00
1.07
4.07
1.96
1.03
1.95
3.00
2.97
2.90
2.92
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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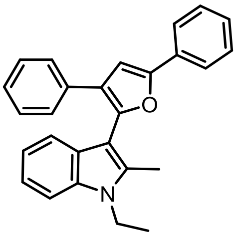
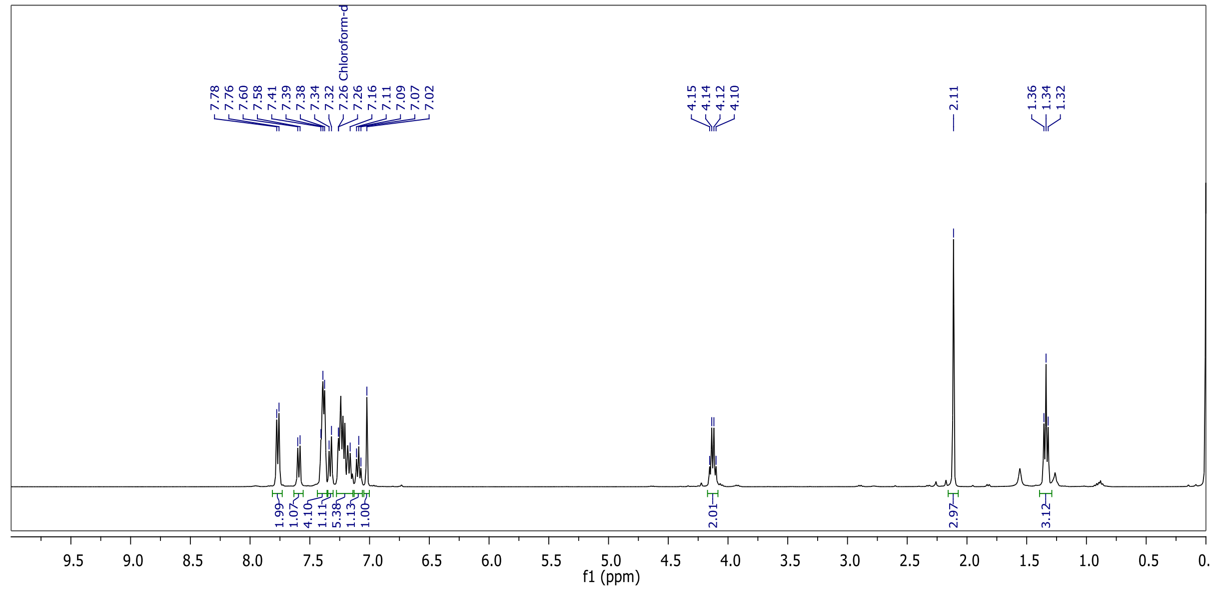
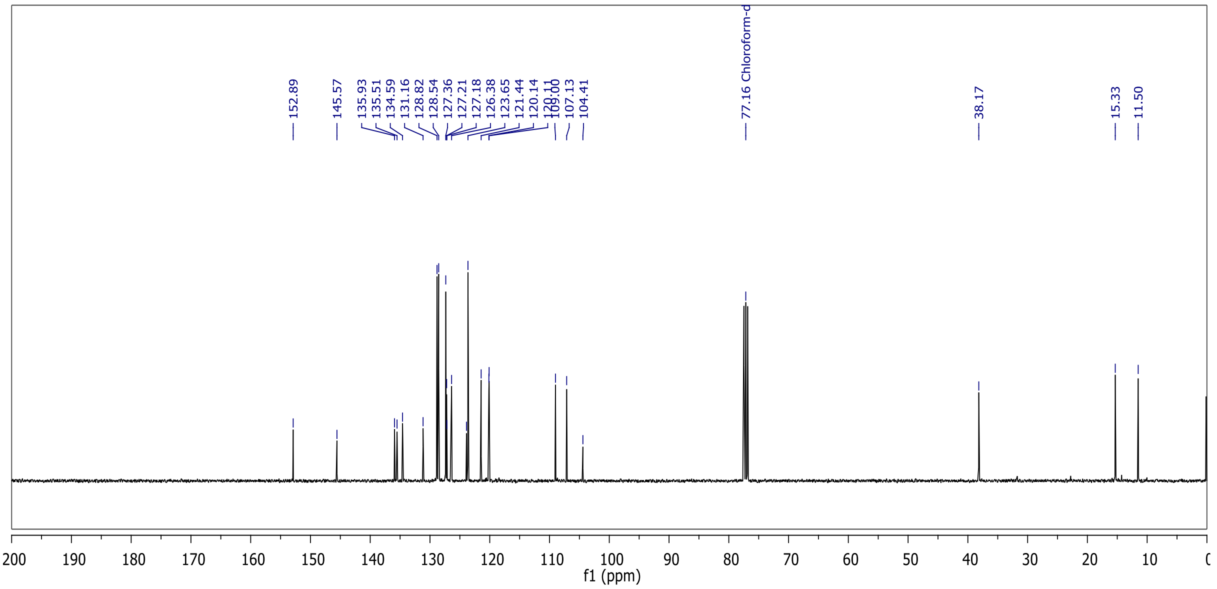
146.73
137.07
134.98
134.03
129.01
127.88
125.99
125.94
120.49
119.15
113.65
113.52
108.42
104.72
77.36
77.05
76.73
55.14
29.70
12.85
10.85
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



**3x**


7.78
7.76
7.60
7.58
7.41
7.39
7.38
7.34
7.32
7.26 Chloroform-d
7.26
7.16
7.11
7.09
7.07
7.02
4.15
4.14
4.12
4.10
2.11
1.36
1.34
1.32
1.99
1.07
4.10
1.11
5.38
1.13
1.00
2.01
2.97
3.12
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.
f1 (ppm)


152.89
145.57
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135.51
134.59
131.16
128.82
128.54
127.36
127.21
127.18
126.38
123.65
121.44
120.14
120.11
109.00
107.13
104.41
77.16 Chloroform-d
38.17
15.33
11.50
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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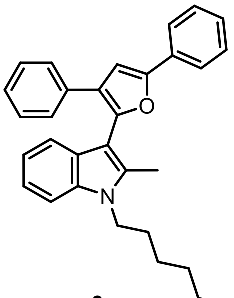
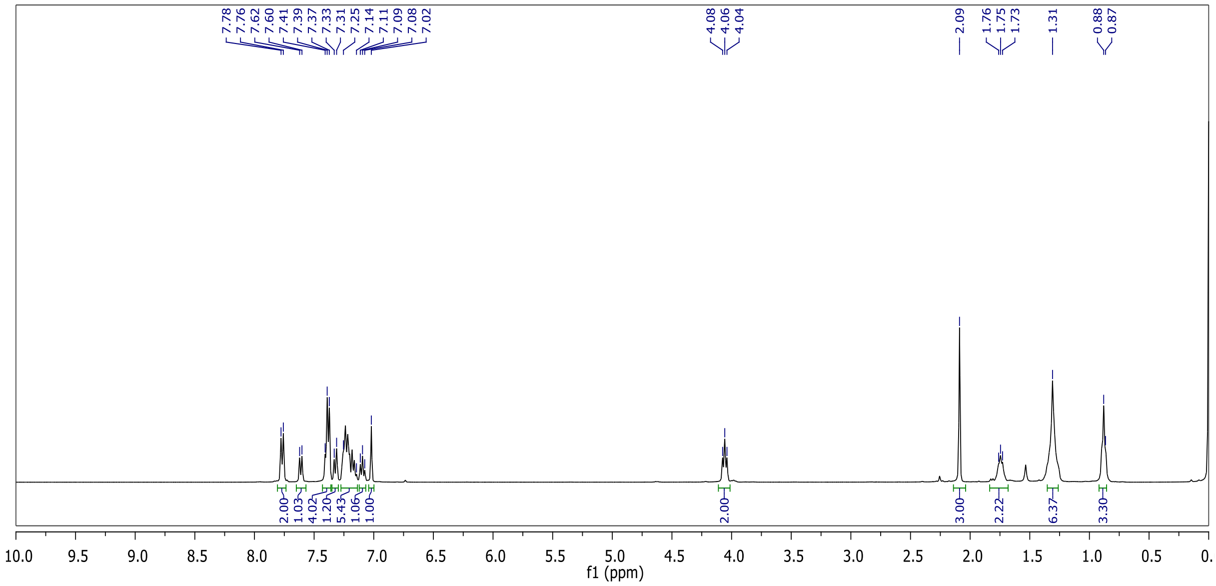
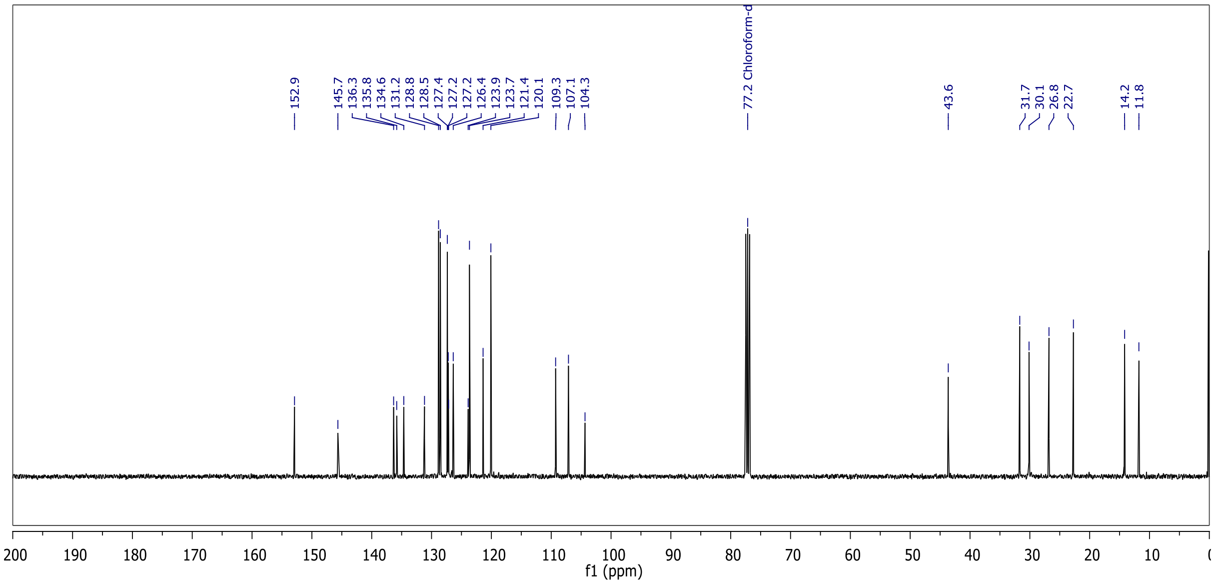
40
30
20
10
(
f1 (ppm)


O
N

**3y**


7.78
7.76
7.62
7.60
7.41
7.39
7.37
7.33
7.31
7.25
7.14
7.11
7.09
7.08
7.02
4.08
4.06
4.04
2.09
1.76
1.75
1.73
1.31
0.88
0.87
2.00
1.03
4.02
1.20
5.43
1.06
1.00
2.00
3.00
2.22
6.37
3.30
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.
f1 (ppm)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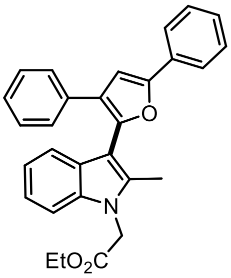
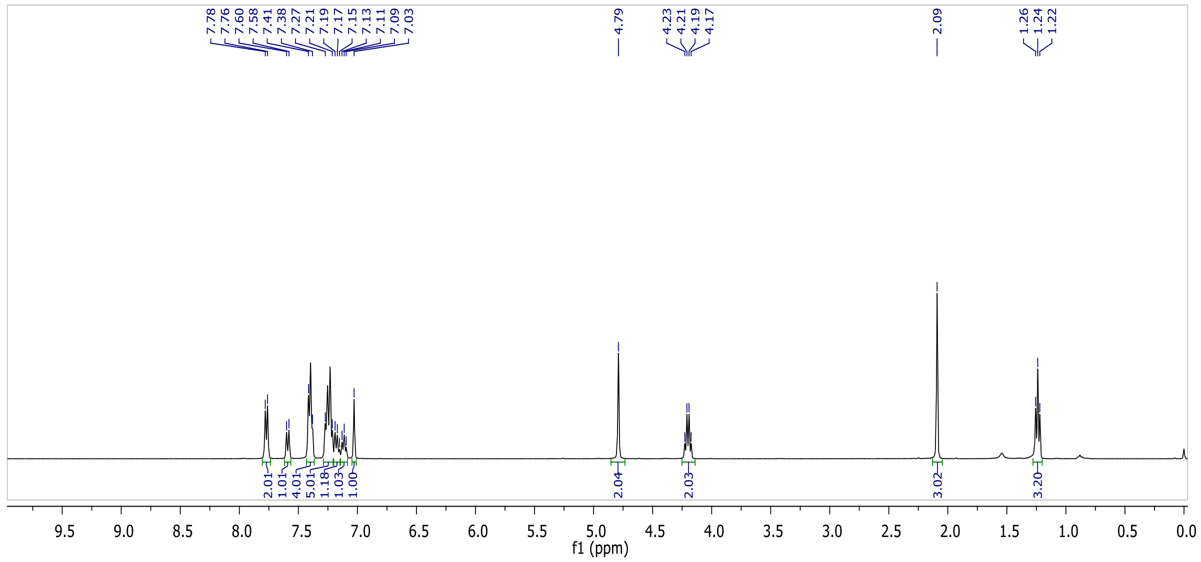
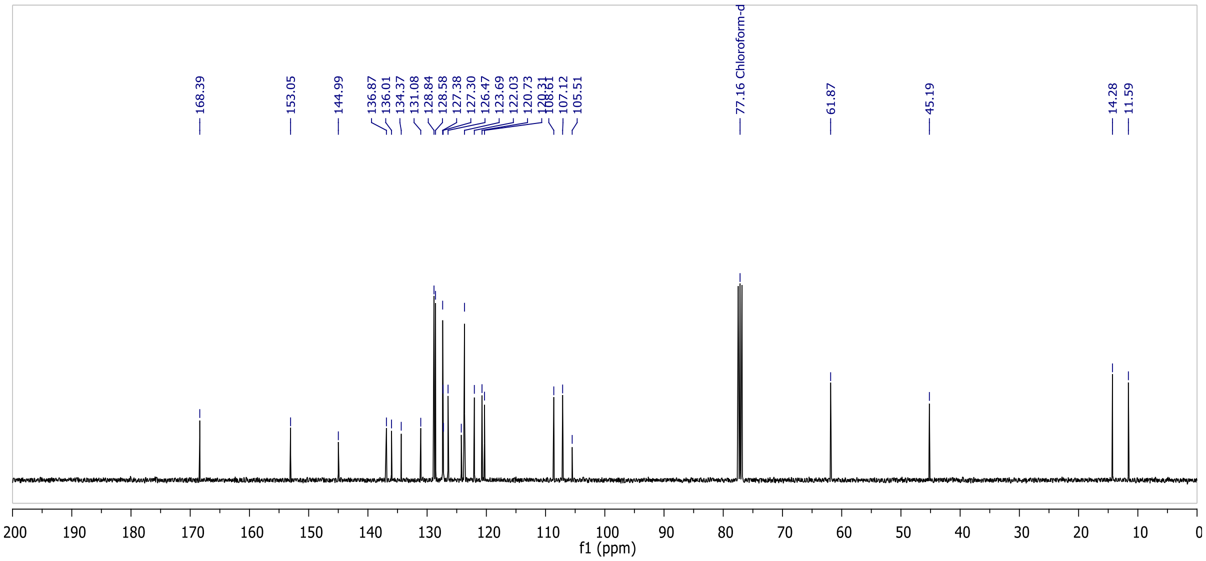
145.7
136.3
135.8
134.6
131.2
128.8
128.5
127.4
127.2
127.2
126.4
123.9
123.7
121.4
120.1
109.3
107.1
104.3
77.2 Chloroform-d
43.6
31.7
30.1
26.8
22.7
14.2
11.8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
N
EtO2C

**3aa**


7.78
7.76
7.60
7.58
7.41
7.38
7.27
7.21
7.19
7.17
7.15
7.13
7.11
7.09
7.03
4.79
4.23
4.21
4.19
4.17
2.09
1.26
1.24
1.22
2.01
1.01
4.01
5.01
1.18
1.03
1.00
2.04
2.03
3.02
3.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


168.39
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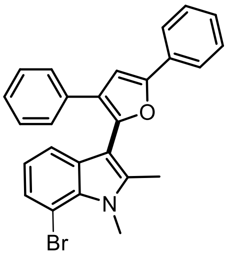
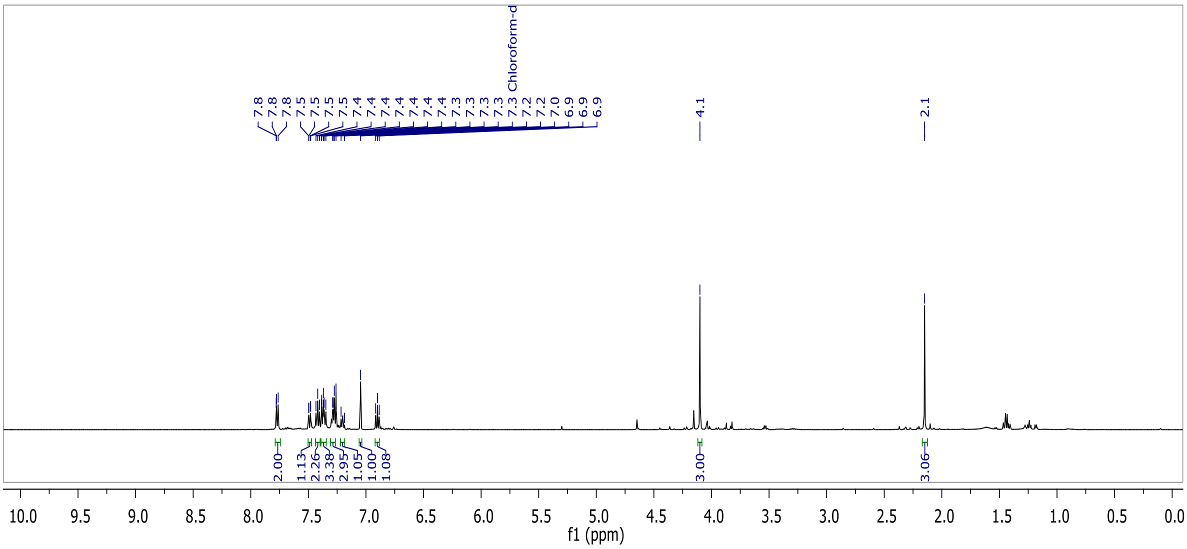
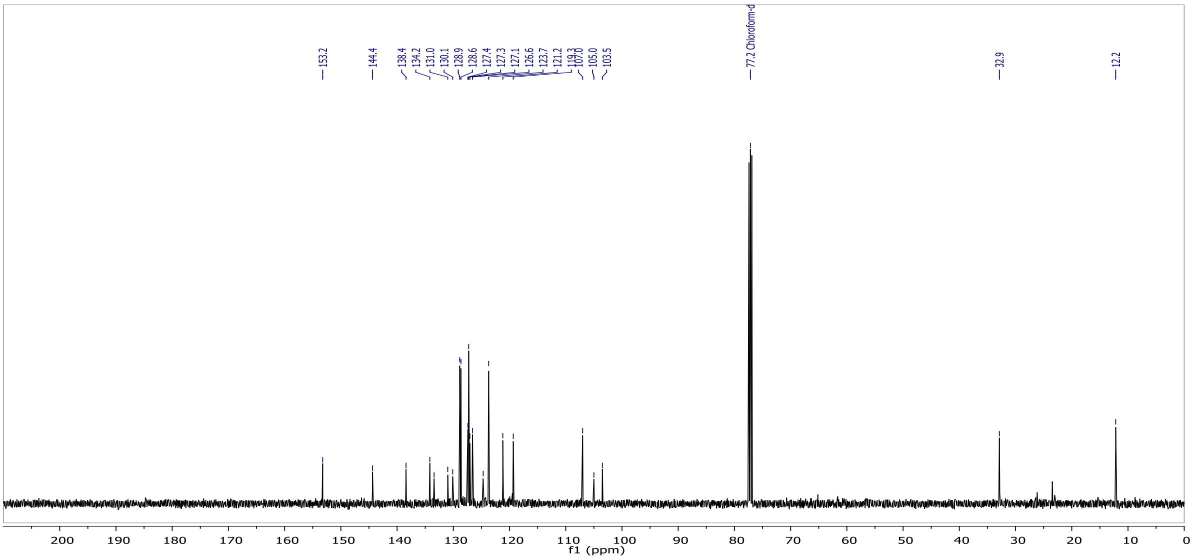
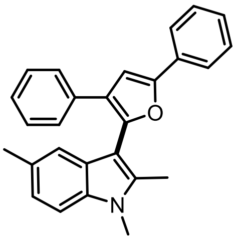
144.99
136.87
136.01
134.37
131.08
128.84
128.58
127.38
127.30
126.47
123.69
122.03
120.73
120.31
108.61
107.12
105.51
77.16 Chloroform-d
61.87
45.19
14.28
11.59
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
Br

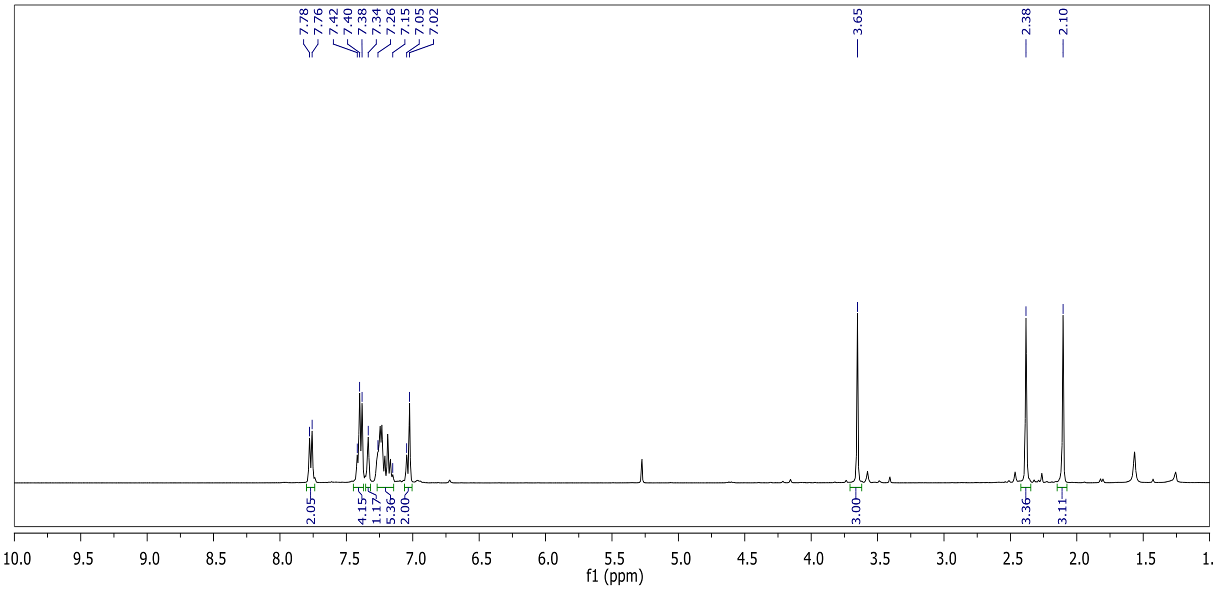
**3ab**

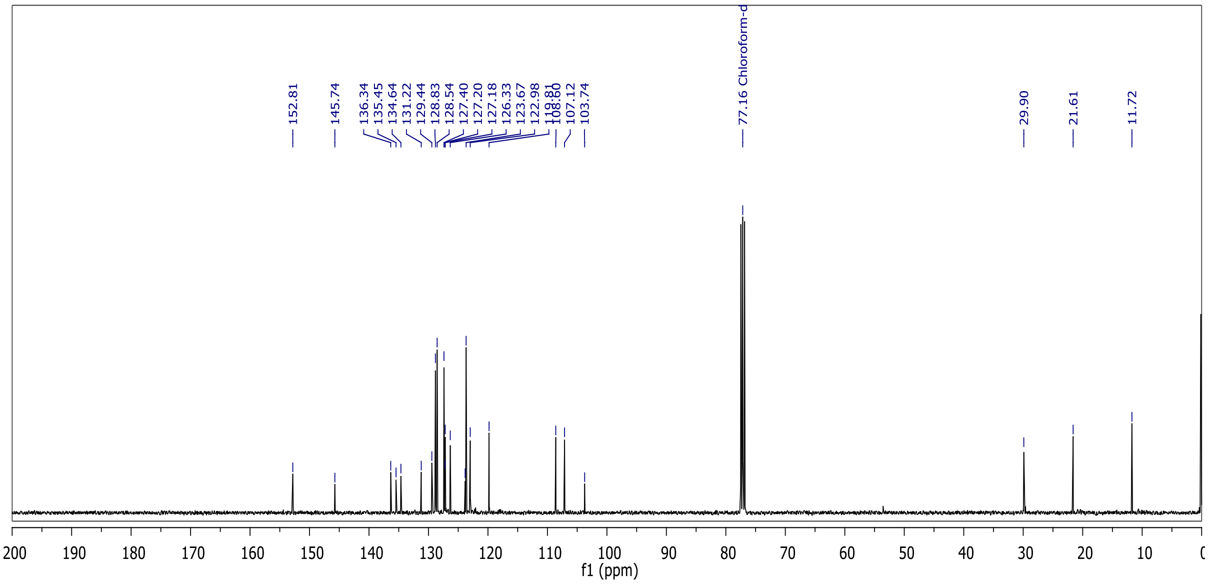

7.8
7.8
7.8
7.5
7.5
7.5
7.5
7.4
7.4
7.4
7.4
7.4
7.4
7.3
7.3
7.3
7.3
7.3 Chloroform-d
7.2
7.2
7.0
6.9
6.9
6.9
4.1
2.1
2.00
1.13
2.26
3.38
2.95
1.05
1.00
1.08
3.00
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

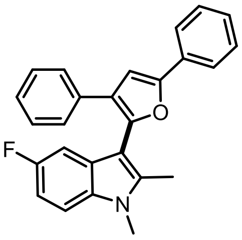

153.2
144.4
138.4
134.2
131.0
130.1
128.9
128.6
127.4
127.3
127.1
126.6
123.7
121.2
119.3
107.0
105.0
103.5
77.2 Chloroform-d
32.9
12.2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N

**3ac**

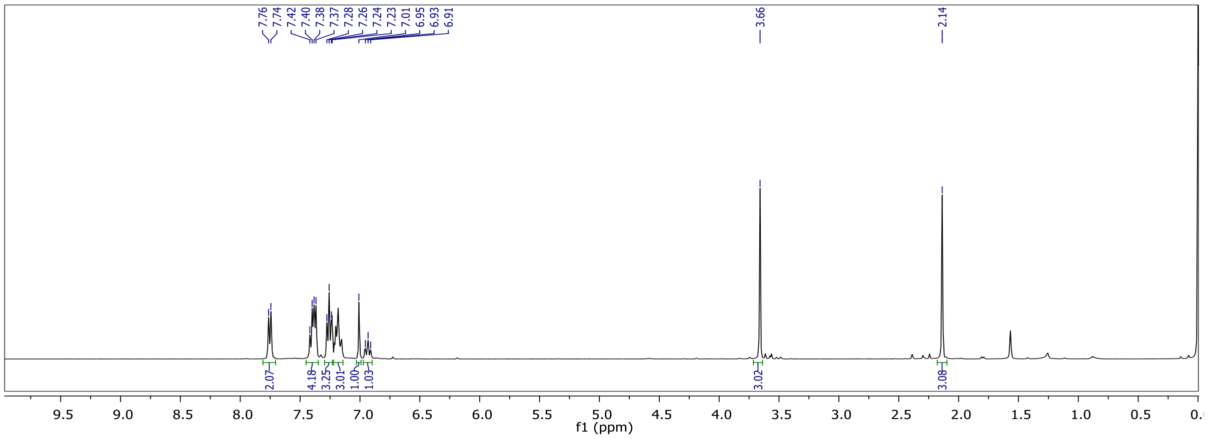

7.78
7.76
7.42
7.40
7.38
7.34
7.26
7.15
7.05
7.02
3.65
2.38
2.10
2.05
4.15
1.17
5.36
2.00
3.00
3.36
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.
f1 (ppm)


152.81
145.74
136.34
135.45
134.64
131.22
129.44
128.83
128.54
127.40
127.20
127.18
126.33
123.67
122.98
119.81
108.60
107.12
103.74
77.16 Chloroform-d
29.90
21.61
11.72
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

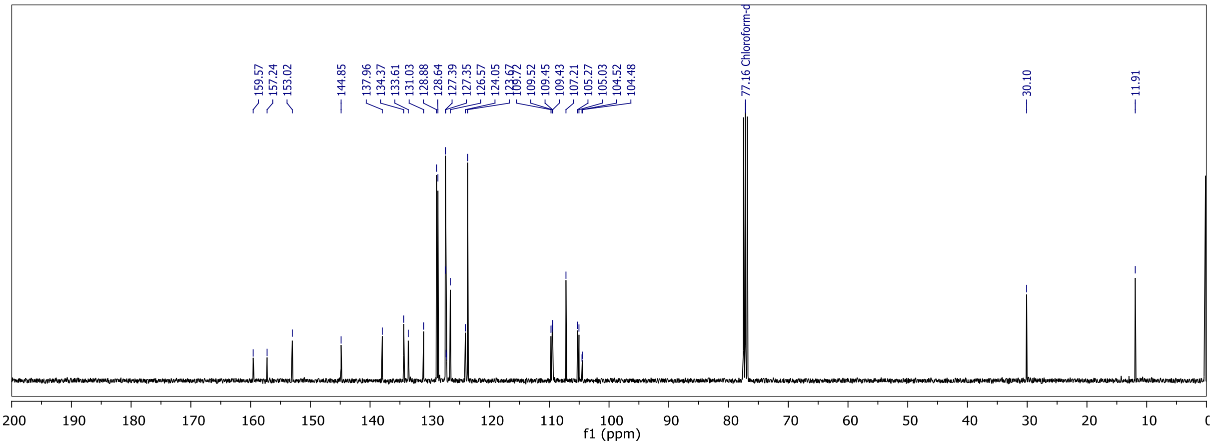


F
O
N

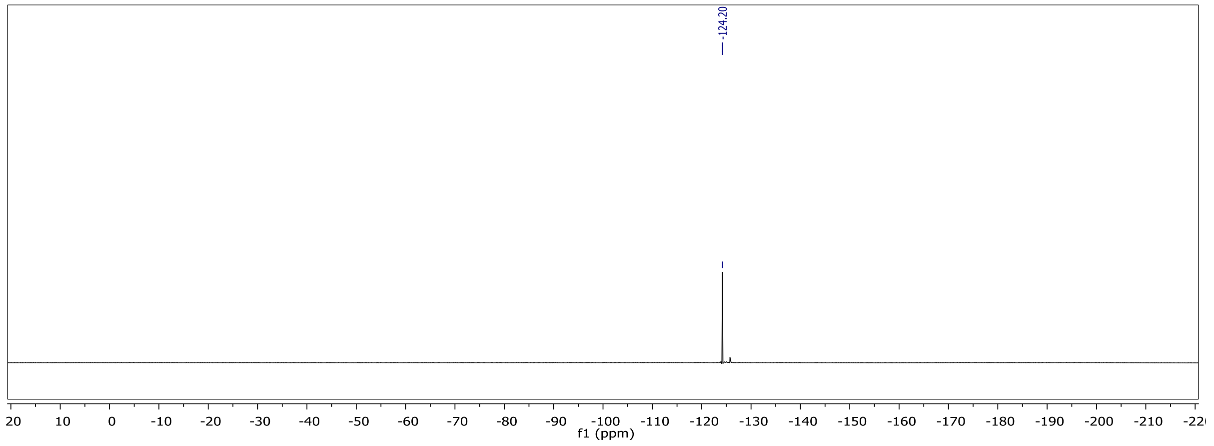
**3ad**



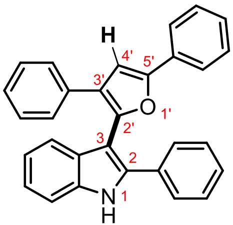
7.76
7.74
7.42
7.40
7.38
7.37
7.28
7.26
7.24
7.23
7.01
6.95
6.93
6.91
3.66
2.14
2.07
4.18
3.25
3.01
1.00
1.03
3.02
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



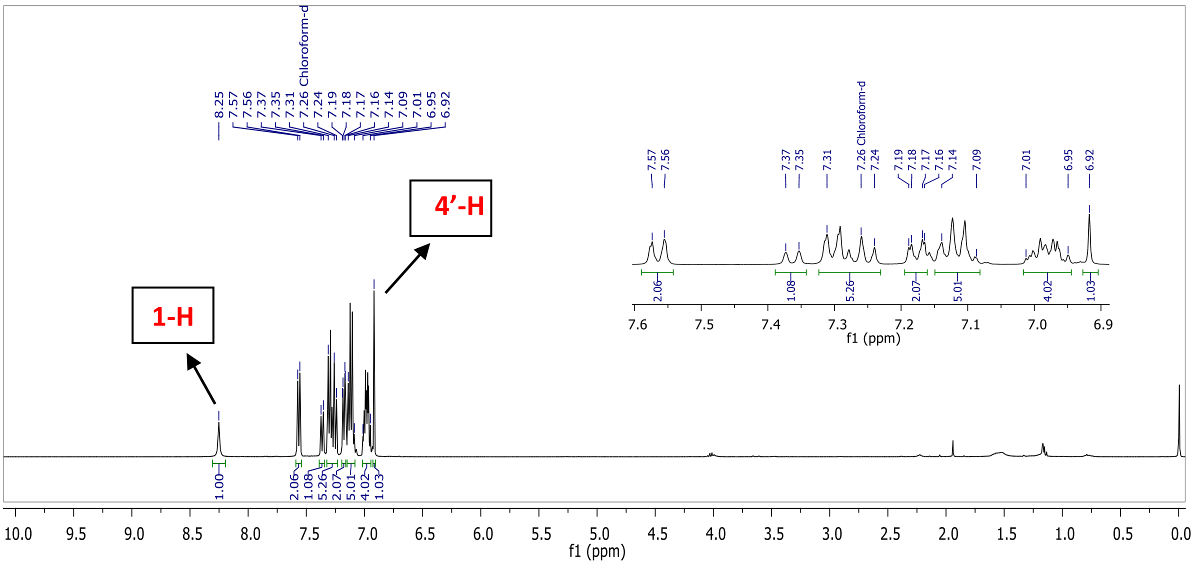
159.57
157.24
153.02
144.85
137.96
134.37
133.61
131.03
128.88
128.64
127.39
127.35
126.57
124.05
123.67
109.72
109.52
109.45
109.43
107.21
105.27
105.03
104.52
104.48
77.16 Chloroform-d
30.10
11.91
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

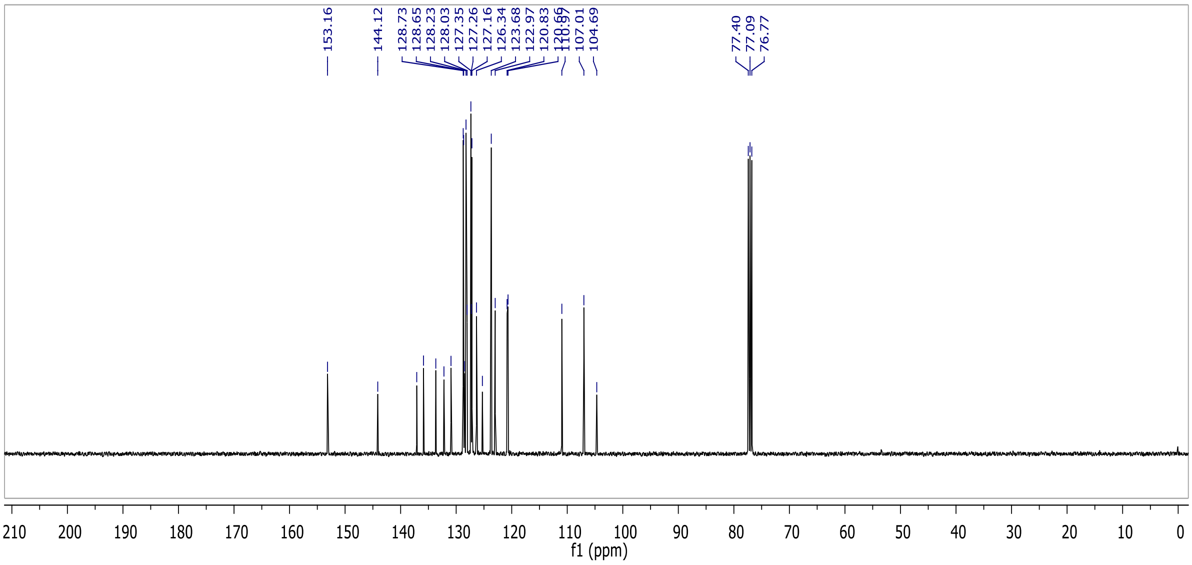


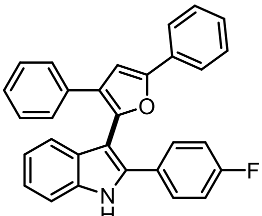
-124.20
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


H
4'
5'
3'
O
1'
2'
3
2
N
1
H

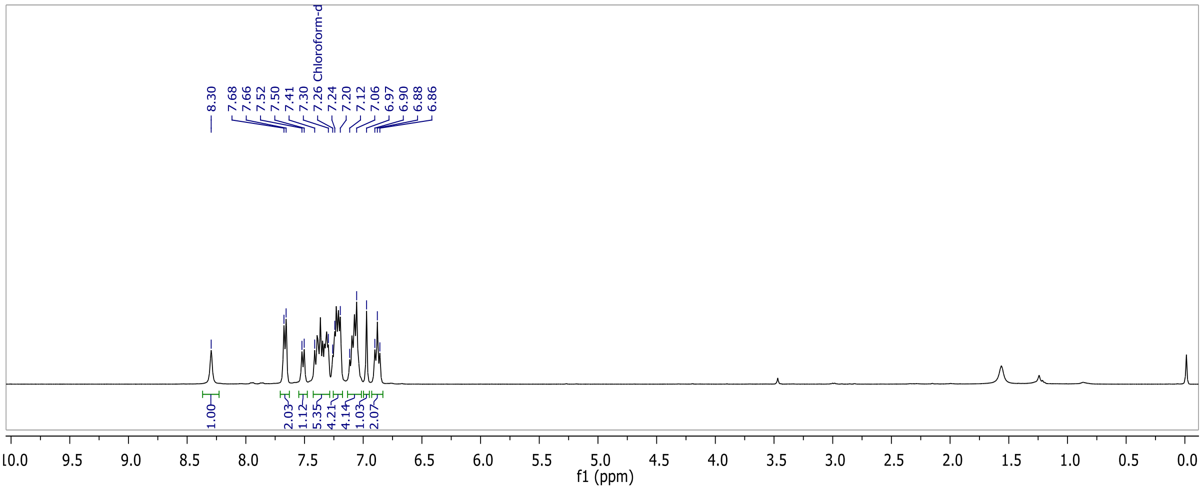
**4a**

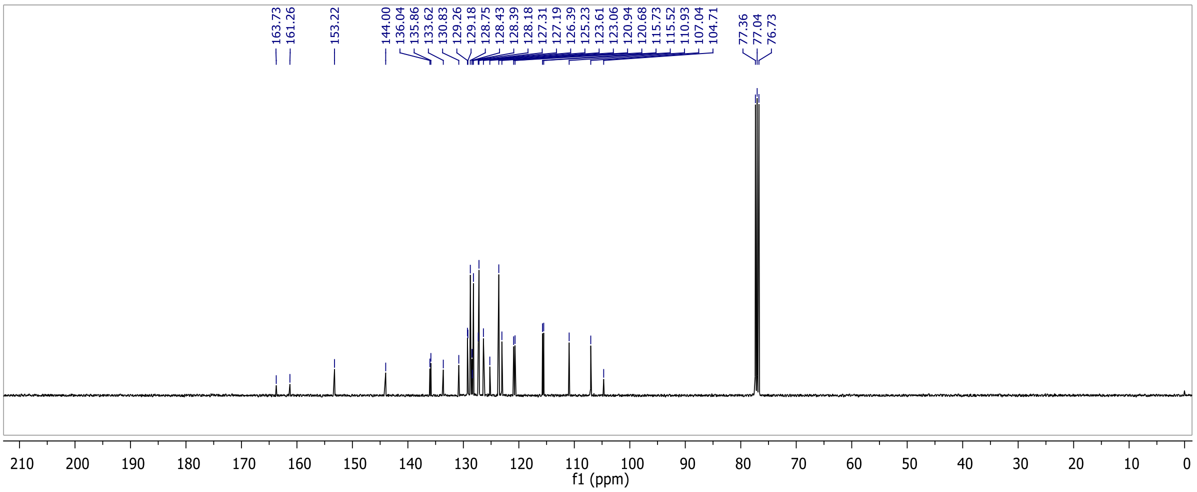

8.25
7.57
7.56
7.37
7.35
7.31
7.26 Chloroform-d
7.24
7.19
7.18
7.17
7.16
7.14
7.09
7.01
6.95
6.92
4'-H
1-H
1.00
2.06
1.08
5.26
2.07
5.01
4.02
1.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9

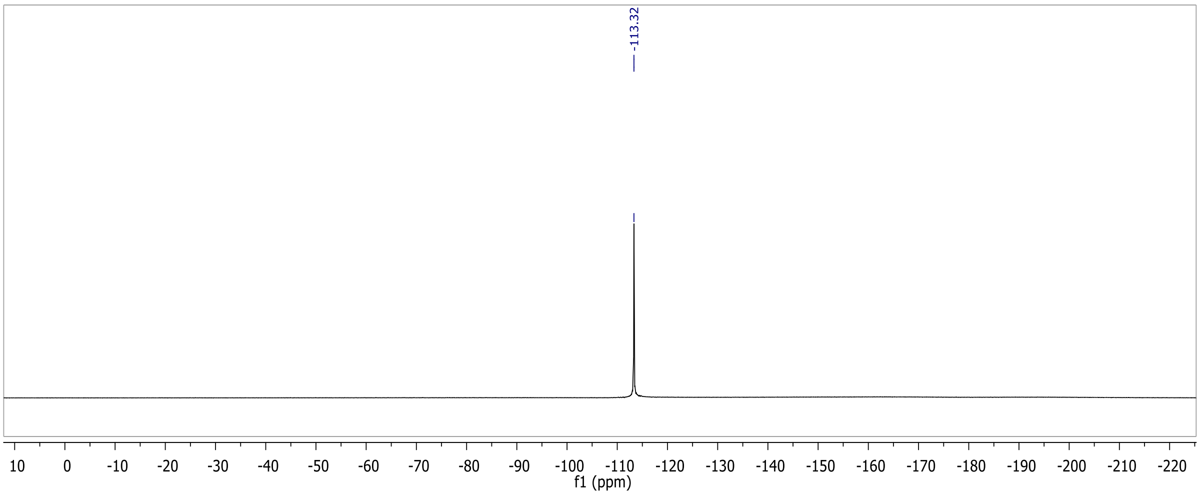

153.16
144.12
128.73
128.65
128.23
128.03
127.35
127.26
127.16
126.34
123.68
122.97
120.83
120.66
110.97
107.01
104.69
77.40
77.09
76.77
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



**4b**


8.30
7.68
7.66
7.52
7.50
7.41
7.30
7.26 Chloroform-d
7.24
7.20
7.12
7.06
6.97
6.90
6.88
6.86
1.00
2.03
1.12
5.35
4.21
4.14
1.03
2.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.73
161.26
153.22
144.00
136.04
135.86
133.62
130.83
129.26
129.18
128.75
128.43
128.39
128.18
127.31
127.19
126.39
125.23
123.61
123.06
120.94
120.68
115.73
115.52
110.93
107.04
104.71
77.36
77.04
76.73
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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-10
-20
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-40
-50
-60
-70
-80
-90
-100
-110
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-140
-150
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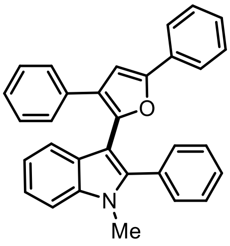
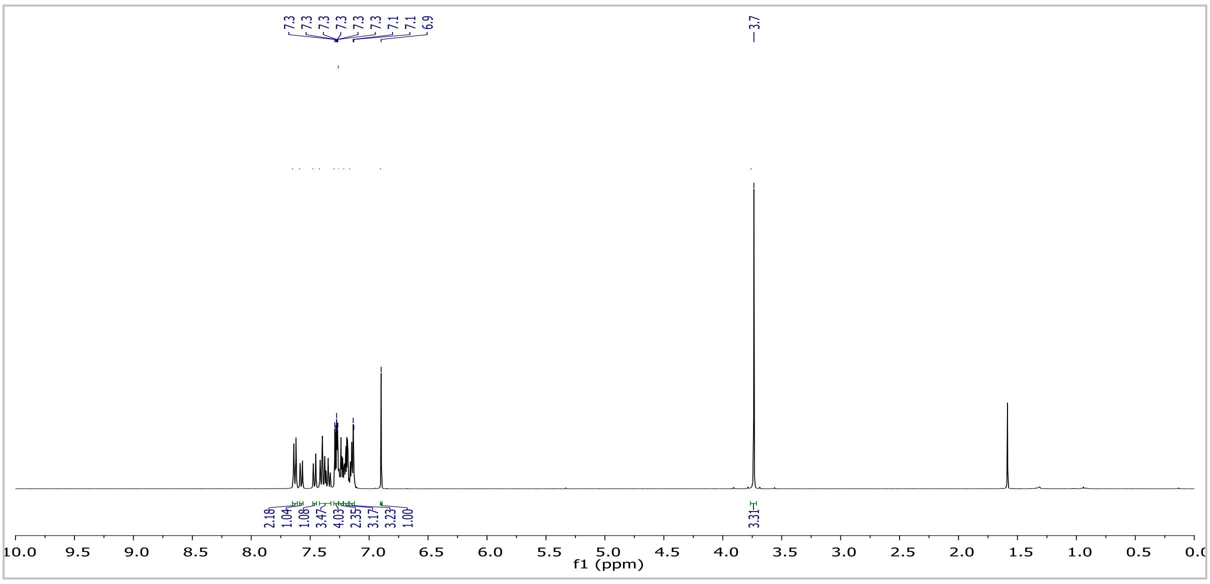
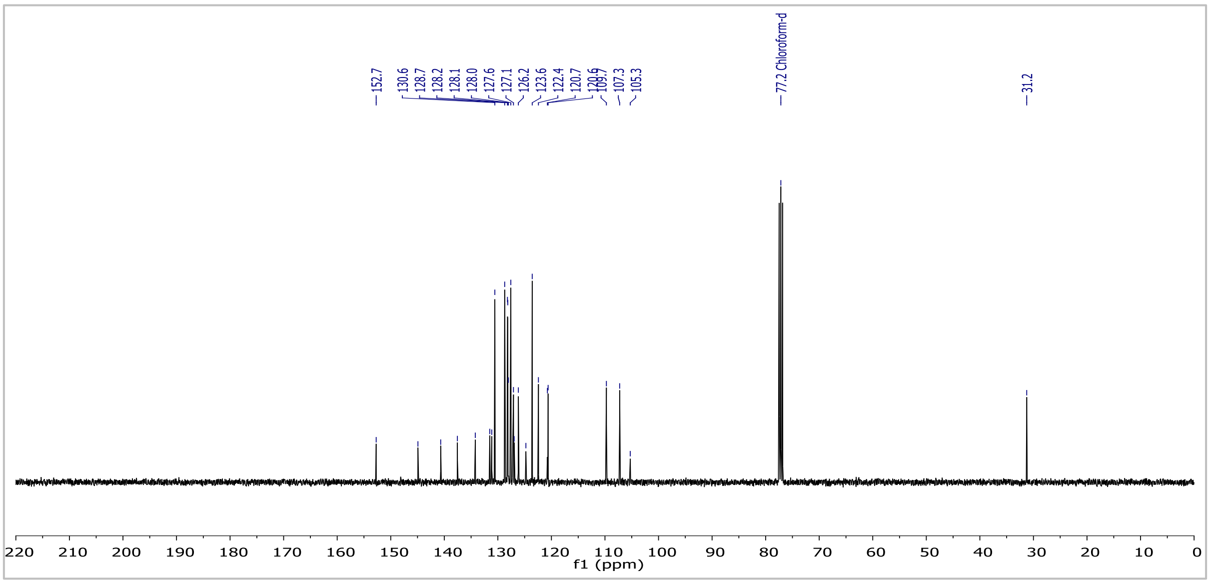
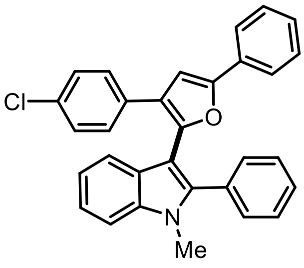
-170
-180
-190
-200
-210
-220
f1 (ppm)


O
N
Me

**3ae**

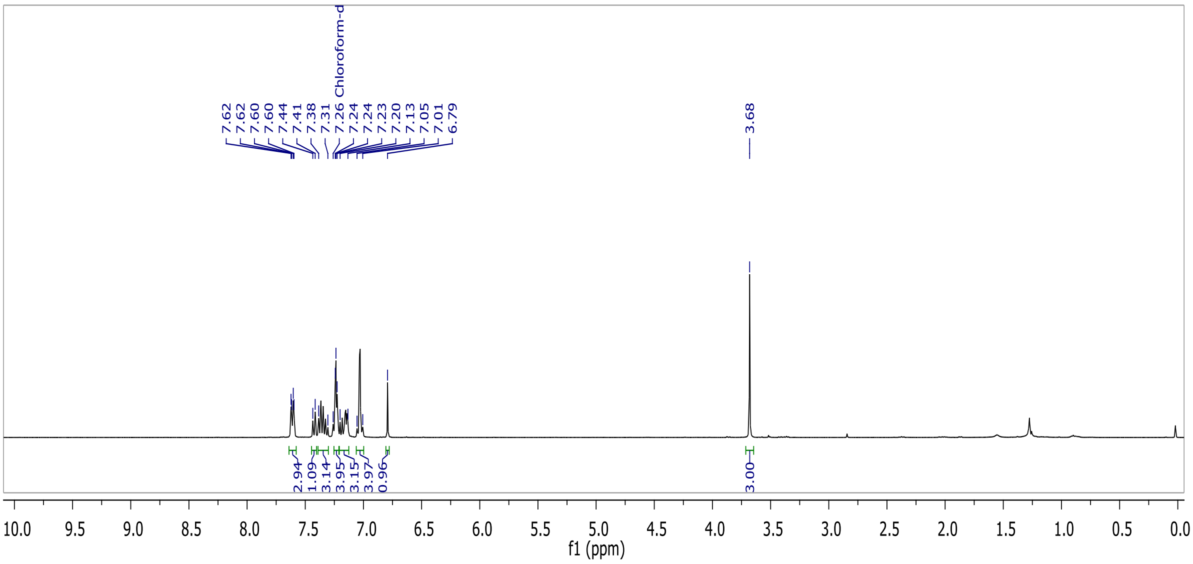

7.3
7.3
7.3
7.3
7.3
7.3
7.1
7.1
6.9
3.7
2.18
1.04
1.08
3.47
4.03
2.35
3.17
3.23
1.00
3.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


152.7
130.6
128.7
128.2
128.1
128.0
127.6
127.1
126.2
123.6
122.4
120.7
120.6
109.7
107.3
105.3
77.2 Chloroform-d
31.2
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

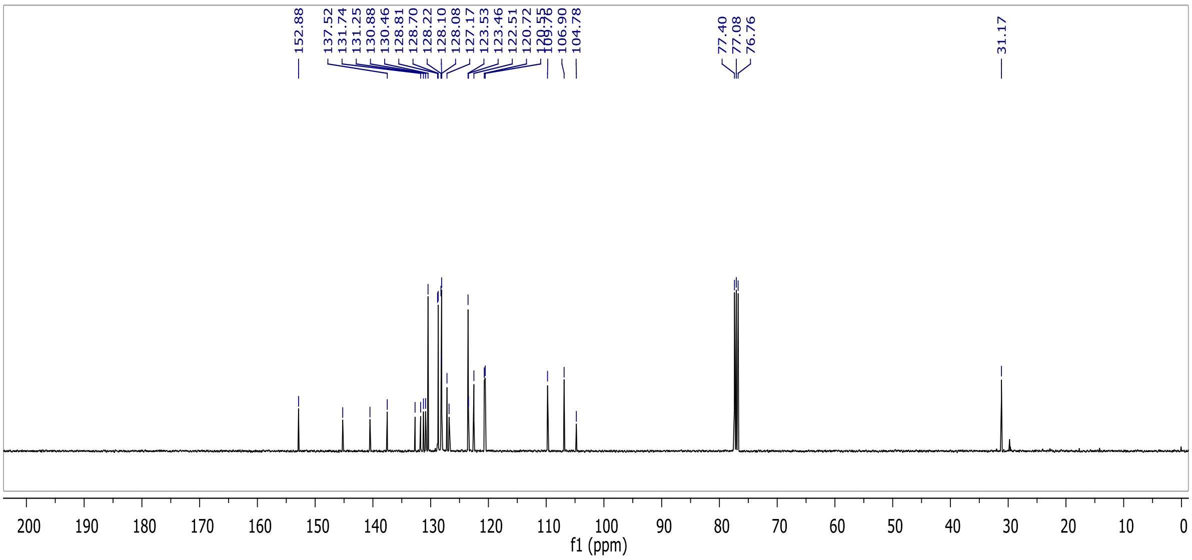


Cl
O
N
Me

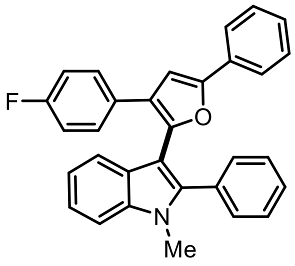
**3af**



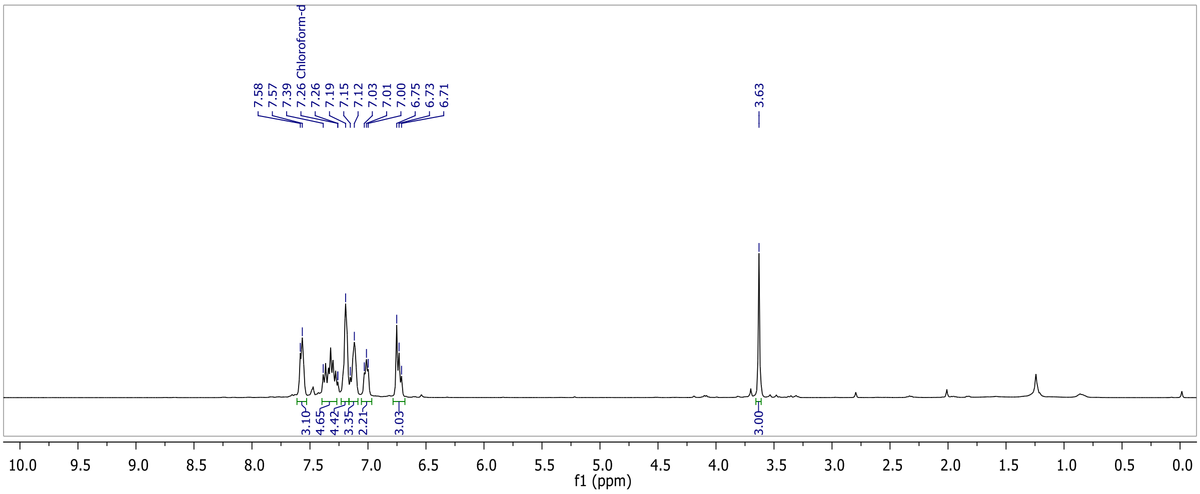
7.62
7.62
7.60
7.44
7.41
7.38
7.31
7.26 Chloroform-d
7.24
7.24
7.24
7.23
7.20
7.13
7.05
7.01
6.79
3.68
2.94
1.09
3.14
3.95
3.15
3.97
0.96
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

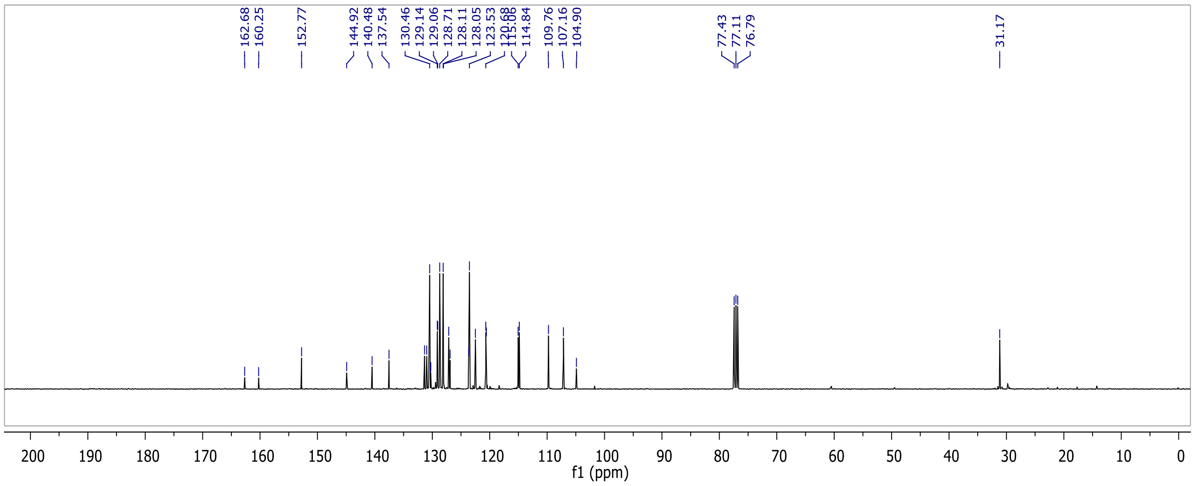


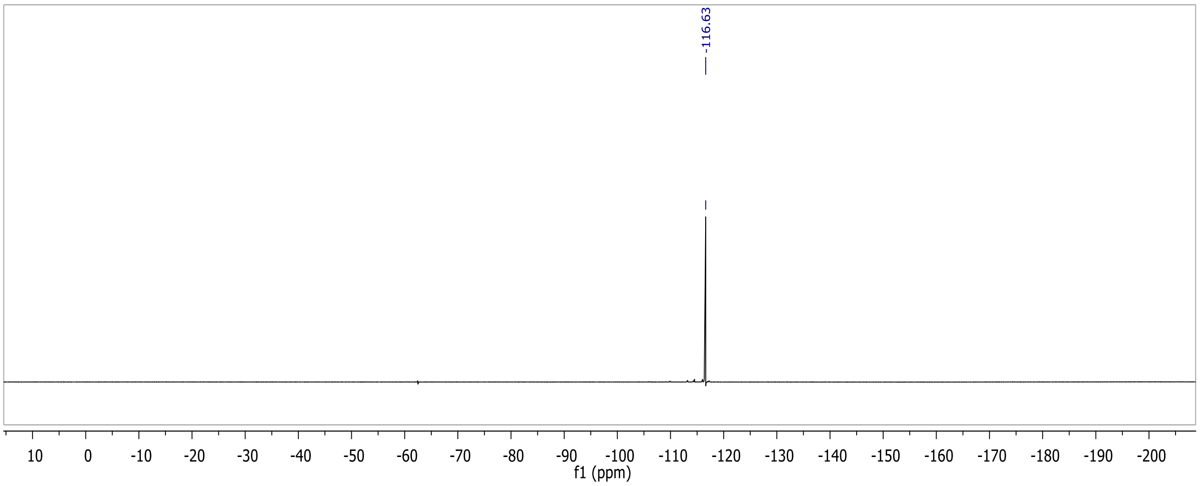
152.88
137.52
131.74
131.25
130.88
130.46
128.81
128.70
128.22
128.10
128.08
127.17
123.53
123.46
122.51
120.72
120.55
109.76
106.90
104.78
77.40
77.08
76.76
31.17
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

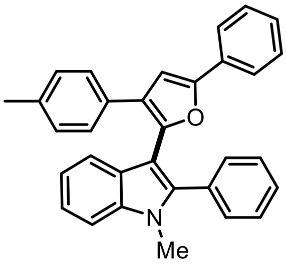

F
O
N
Me

**3ag**

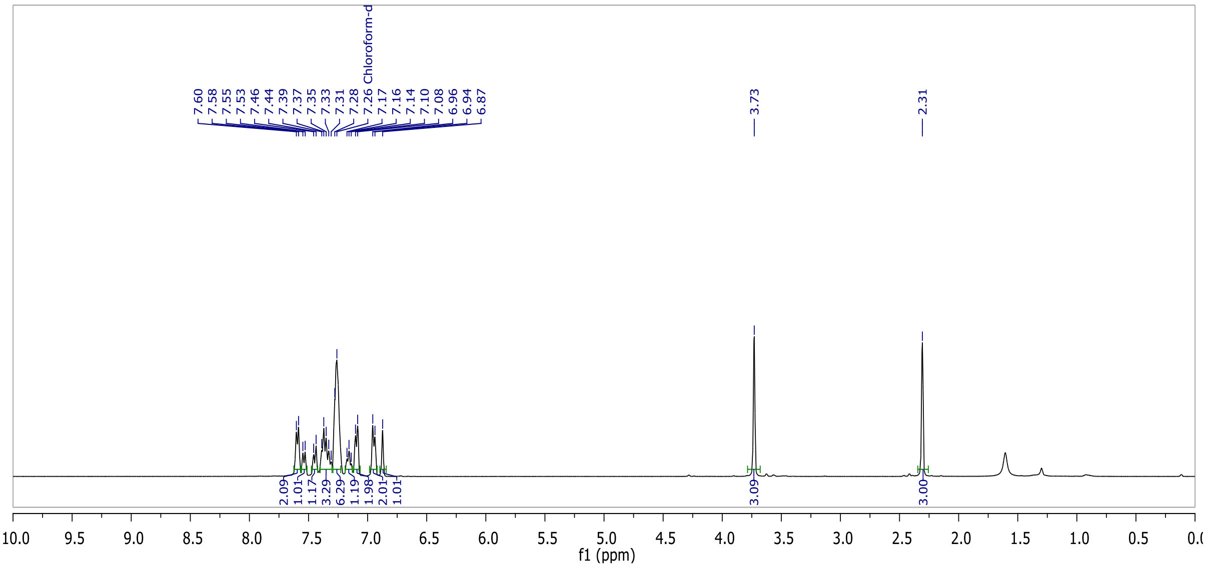

7.58
7.57
7.39
7.26 Chloroform-d
7.26
7.19
7.15
7.12
7.03
7.01
7.00
6.75
6.73
6.71
3.63
3.10
4.65
4.42
3.35
2.21
3.03
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


162.68
160.25
152.77
144.92
140.48
137.54
130.46
129.14
129.06
128.71
128.11
128.05
123.53
120.68
115.06
114.84
109.76
107.16
104.90
77.43
77.11
76.79
31.17
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-116.63
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


O
N
Me

**3ah**


7.60
7.58
7.55
7.53
7.46
7.44
7.39
7.37
7.35
7.33
7.31
7.28
7.26 Chloroform-d
7.17
7.16
7.14
7.10
7.08
6.96
6.94
6.87
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2.09
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1.17
3.29
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1.19
1.98
2.01
1.01
3.09
3.00
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7.0
6.5
6.0
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0.5
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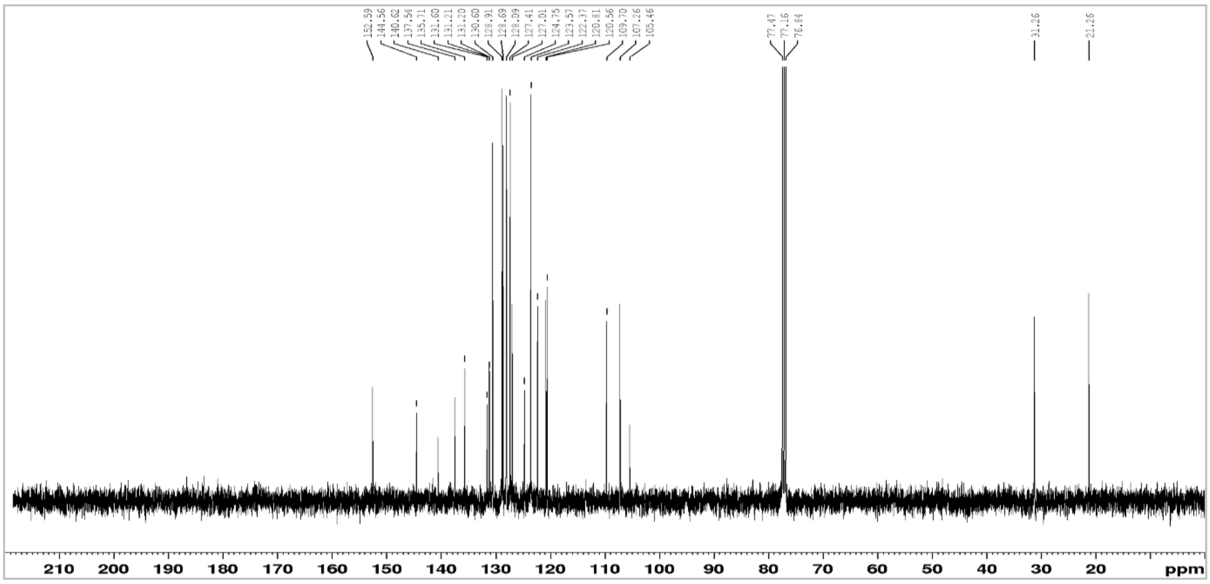
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131.21
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128.69
128.09
127.41
127.01
124.75
123.57
122.37
120.81
120.56
109.70
107.26
105.46
77.47
77.16
76.84
31.26
21.26
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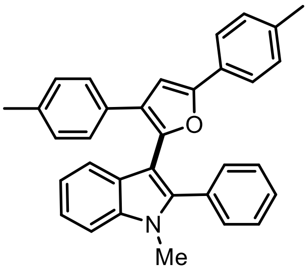
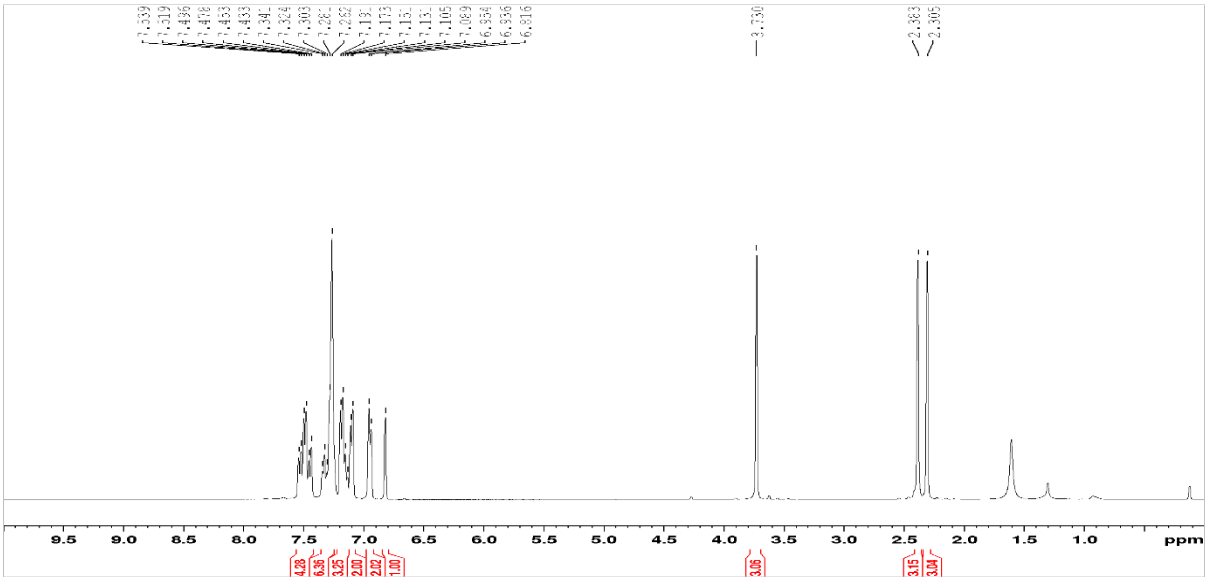
50
40
30
20
ppm


O
N
Me

**3ai**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7.262
7.191
7.173
7.151
7.131
7.105
7.089
6.954
6.936
6.816
3.730
2.383
2.305
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
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ppm
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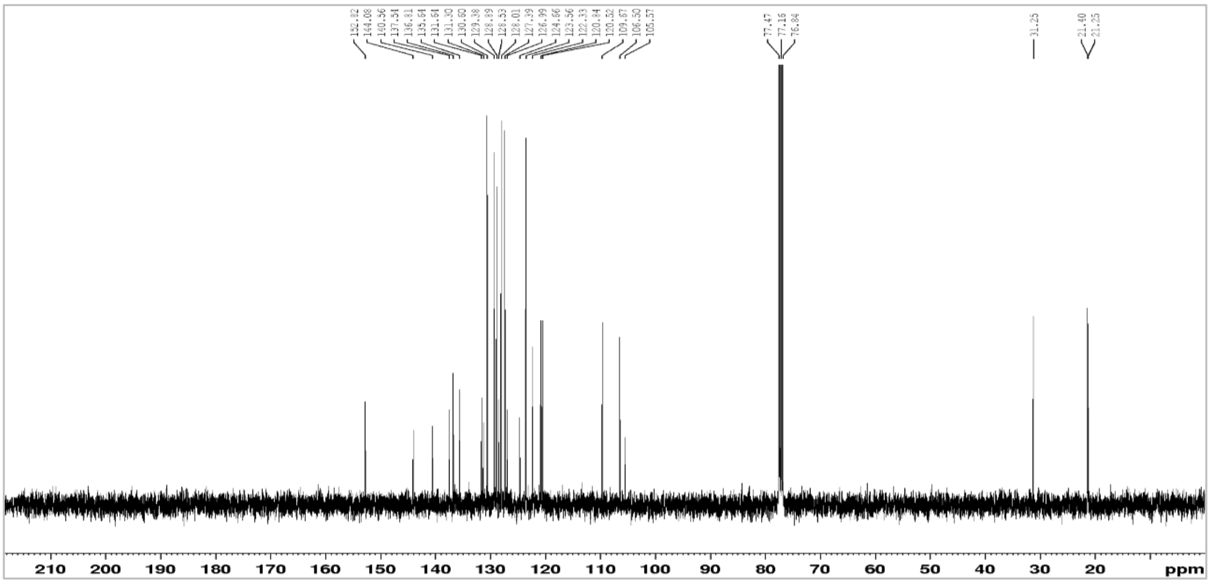
6.36
3.25
2.00
2.02
1.00
3.06
3.15
3.04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131.30
130.60
129.38
128.89
128.53
128.01
127.39
126.99
124.66
123.56
122.33
120.84
120.52
109.67
106.50
105.57
77.47
77.16
76.84
31.25
21.40
21.25
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200
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80
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40
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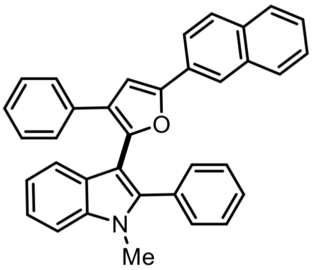
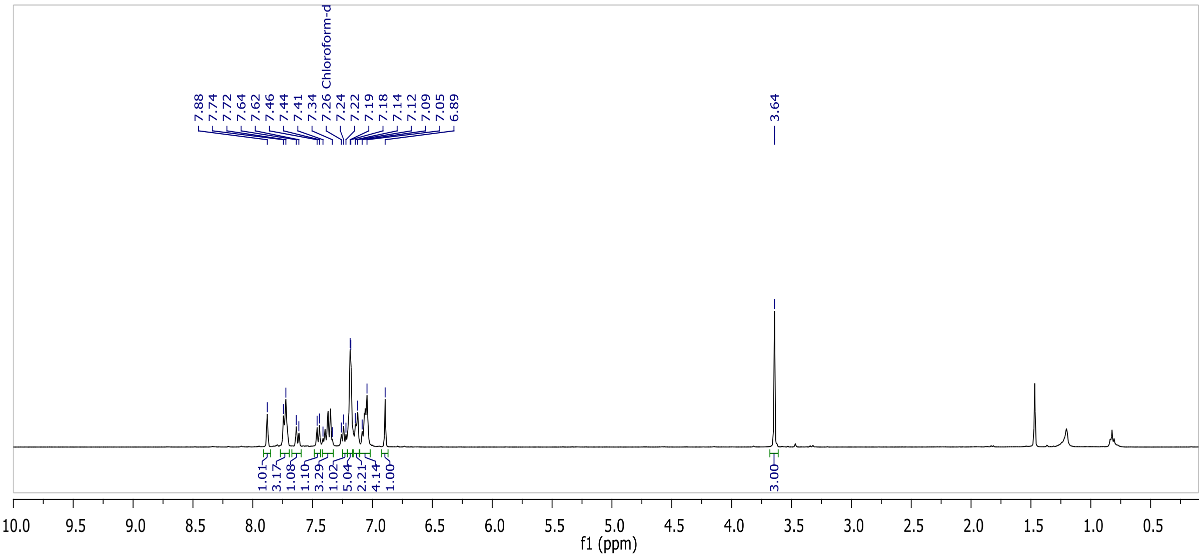
20
ppm


O
N
Me

**3aj**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7.62
7.46
7.44
7.41
7.34
7.26 Chloroform-d
7.24
7.22
7.19
7.18
7.14
7.12
7.09
7.05
6.89
3.64
1.01
3.17
1.08
1.10
3.29
1.02
5.04
2.21
4.14
1.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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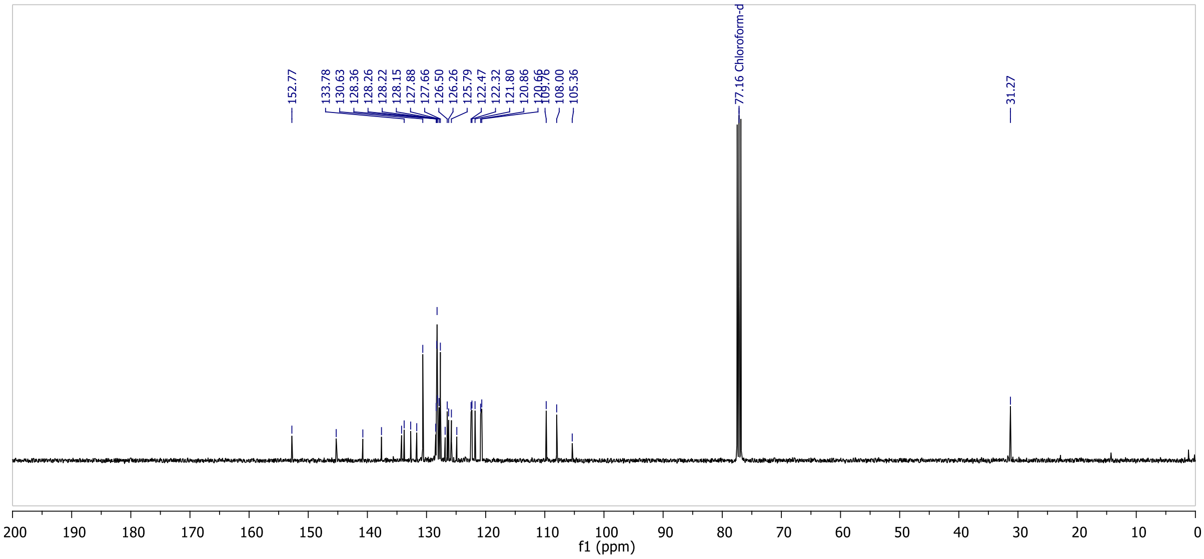
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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128.22
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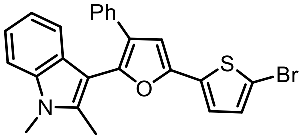
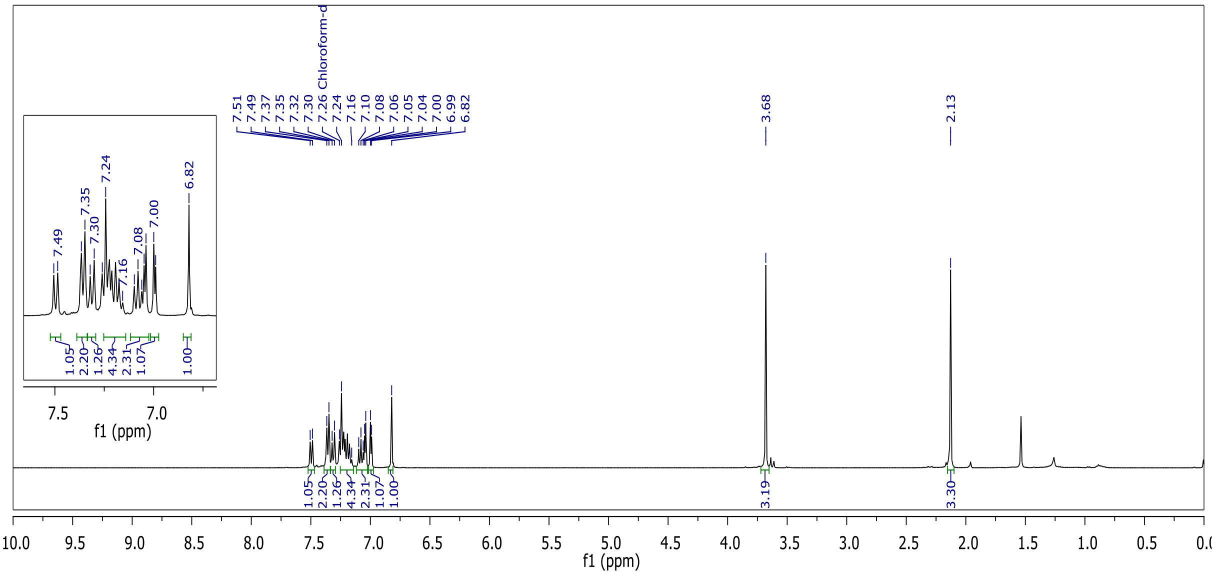
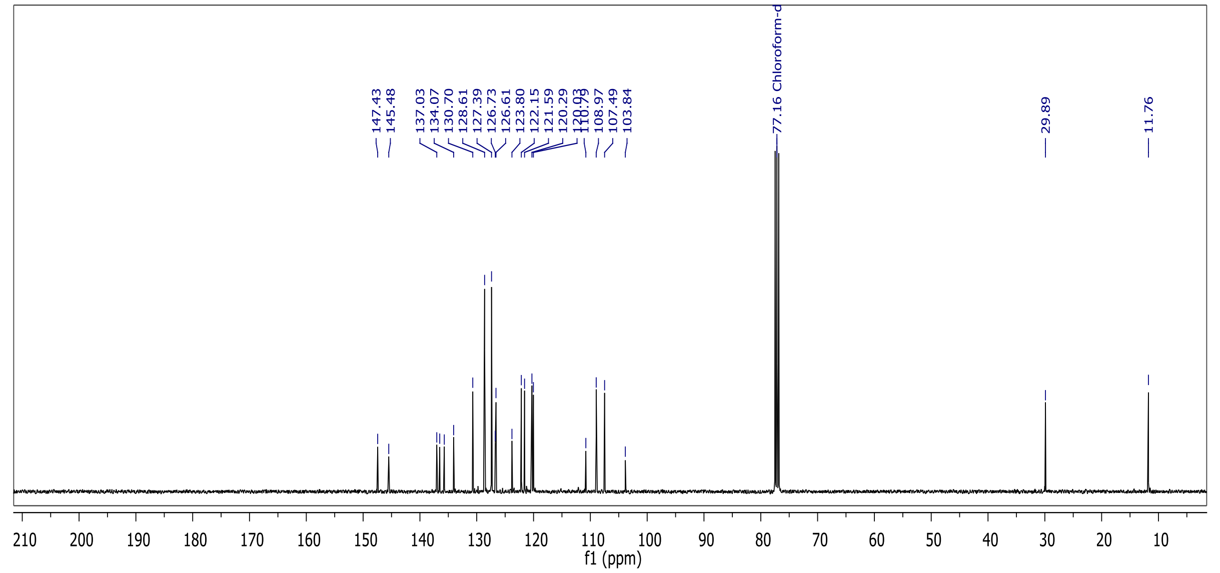
127.88
127.66
126.50
126.26
125.79
122.47
122.32
121.80
120.86
120.66
109.76
108.00
105.36
77.16 Chloroform-d
31.27
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
S
Br
O
N

**5**


7.51
7.49
7.37
7.35
7.32
7.30
7.26 Chloroform-d
7.24
7.16
7.10
7.08
7.06
7.05
7.04
7.00
6.99
6.82
3.68
2.13
1.05
2.20
1.26
4.34
2.31
1.07
1.00
3.19
3.30
7.5
7.0
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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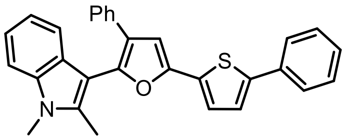
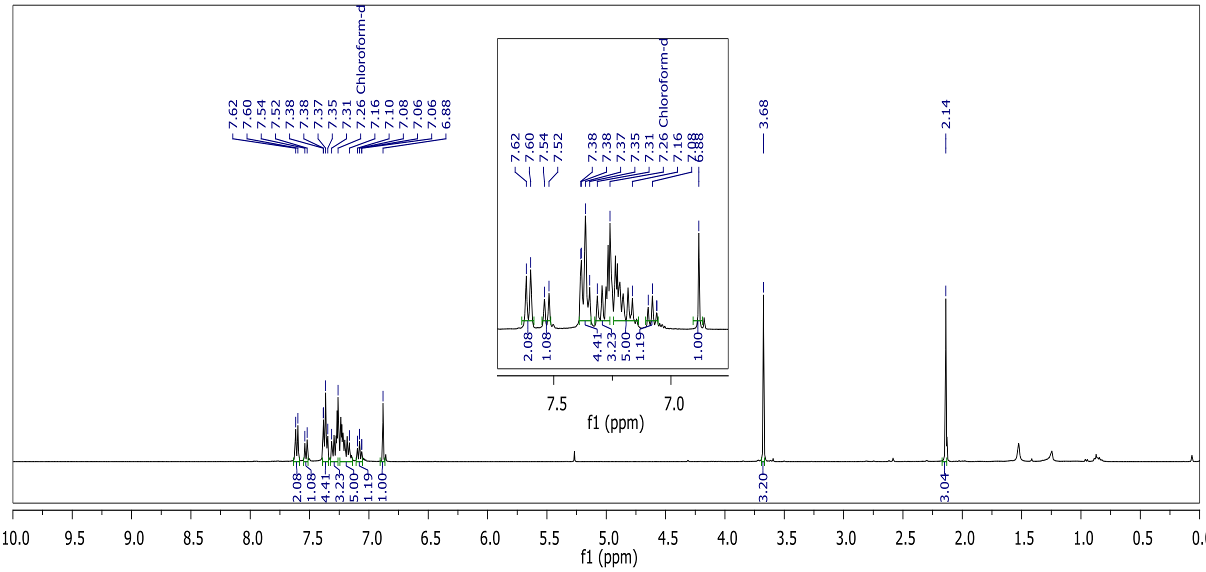
145.48
137.03
134.07
130.70
128.61
127.39
126.73
126.61
123.80
122.15
121.59
120.29
120.03
110.79
108.97
107.49
103.84
77.16 Chloroform-d
29.89
11.76
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Ph
N
O
S

**3ak**


7.62
7.60
7.54
7.52
7.38
7.38
7.37
7.35
7.31
7.26 Chloroform-d
7.16
7.10
7.08
7.06
7.06
6.88
3.68
2.14
2.08
1.08
4.41
3.23
5.00
1.19
1.00
3.20
3.04
7.62
7.60
7.54
7.52
7.38
7.38
7.37
7.35
7.31
7.26 Chloroform-d
7.16
7.08
6.88
2.08
1.08
4.41
3.23
5.00
1.19
1.00
7.5
7.0
f1 (ppm)
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
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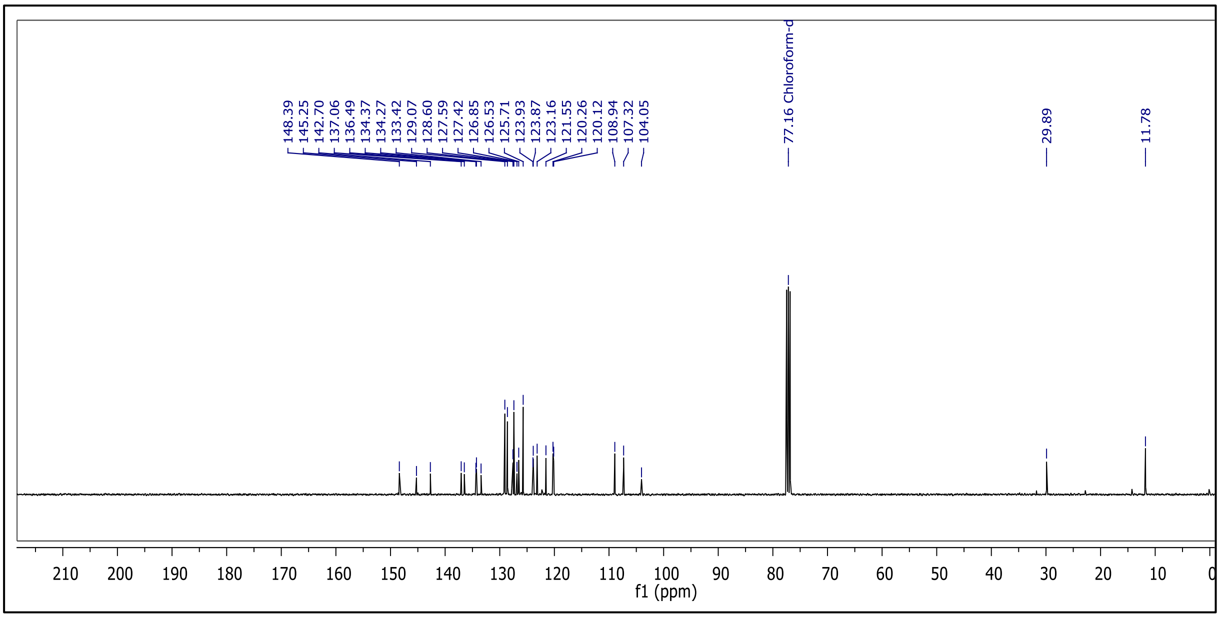
1.5
1.0
0.5
f1 (ppm)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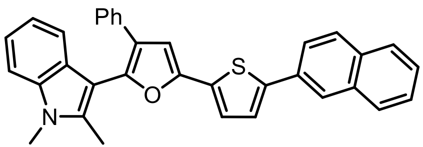
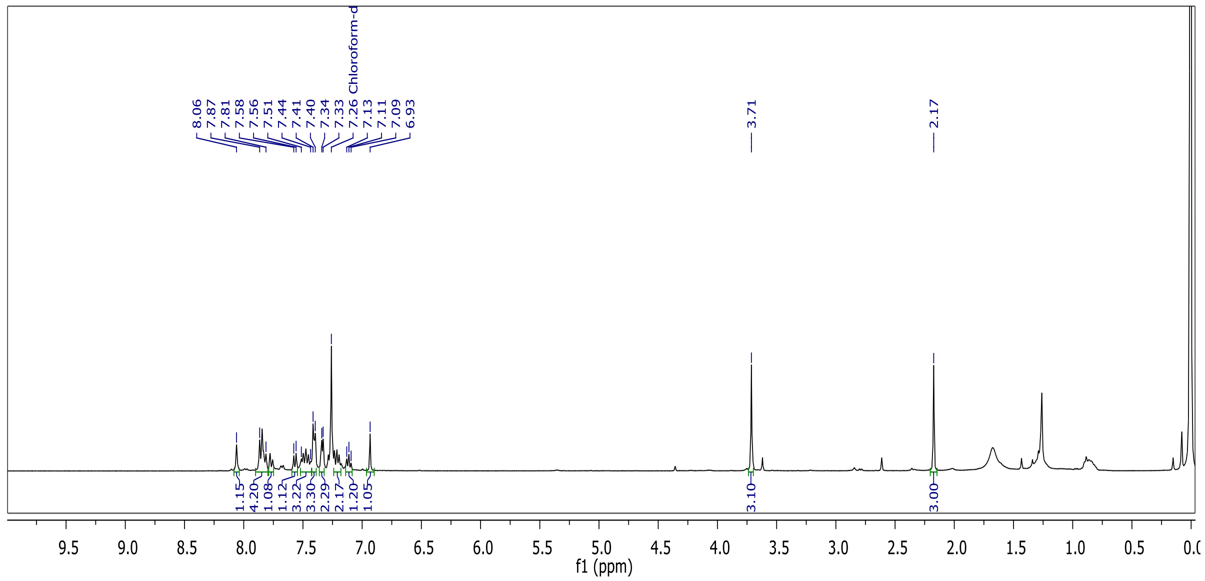
136.49
134.37
134.27
133.42
129.07
128.60
127.59
127.42
126.85
126.53
125.71
123.93
123.87
123.16
121.55
120.26
120.12
108.94
107.32
104.05
77.16 Chloroform-d
29.89
11.78
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Ph
S
O
N

**3al**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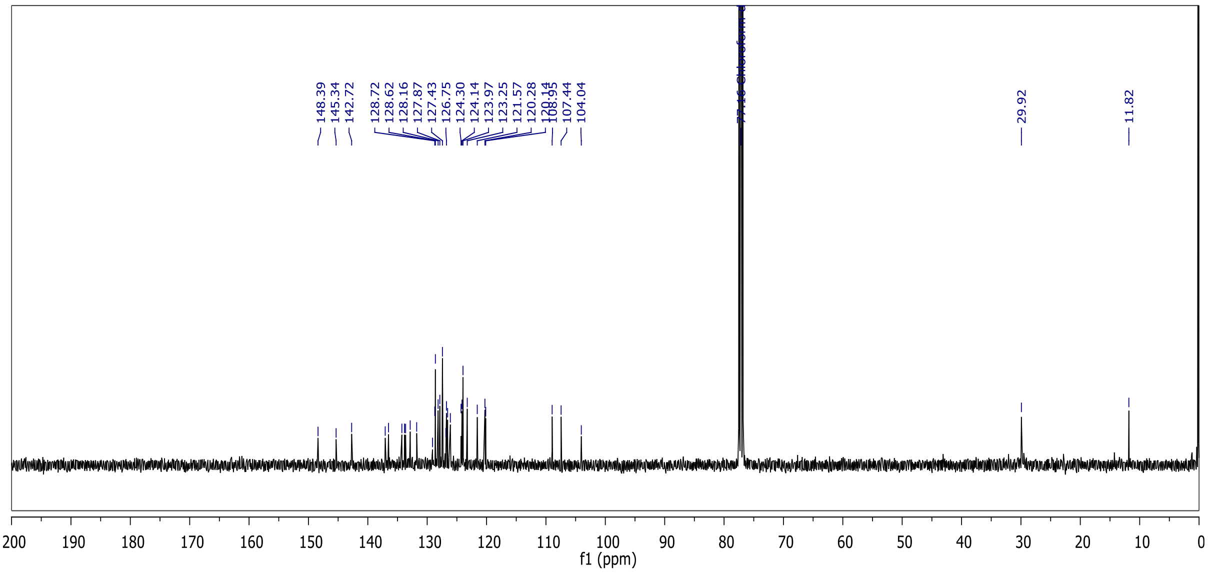
7.40
7.34
7.33
7.26 Chloroform-d
7.13
7.11
7.09
6.93
3.71
2.17
1.15
4.20
1.08
1.12
3.22
3.30
2.29
2.17
1.20
1.05
3.10
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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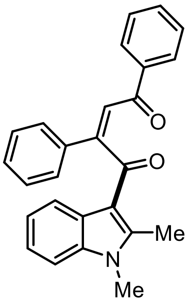
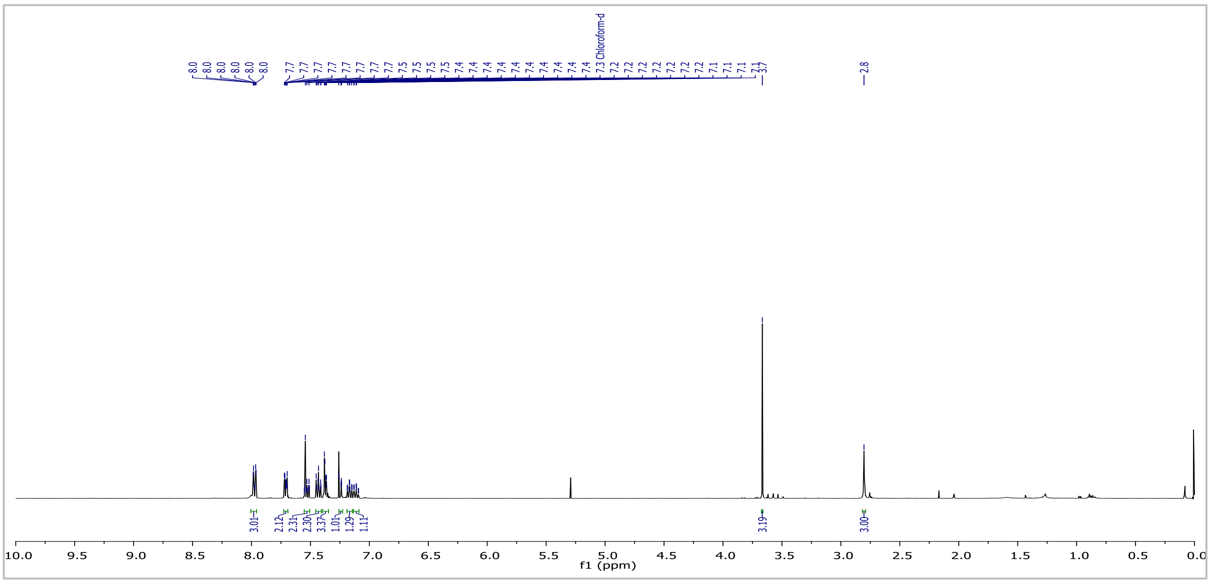
128.16
127.87
127.43
126.75
124.30
124.14
123.97
123.25
121.57
120.28
120.14
108.95
107.44
104.04
77.16 Chloroform-d
29.92
11.82
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
Me
N
Me

**6**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7.5
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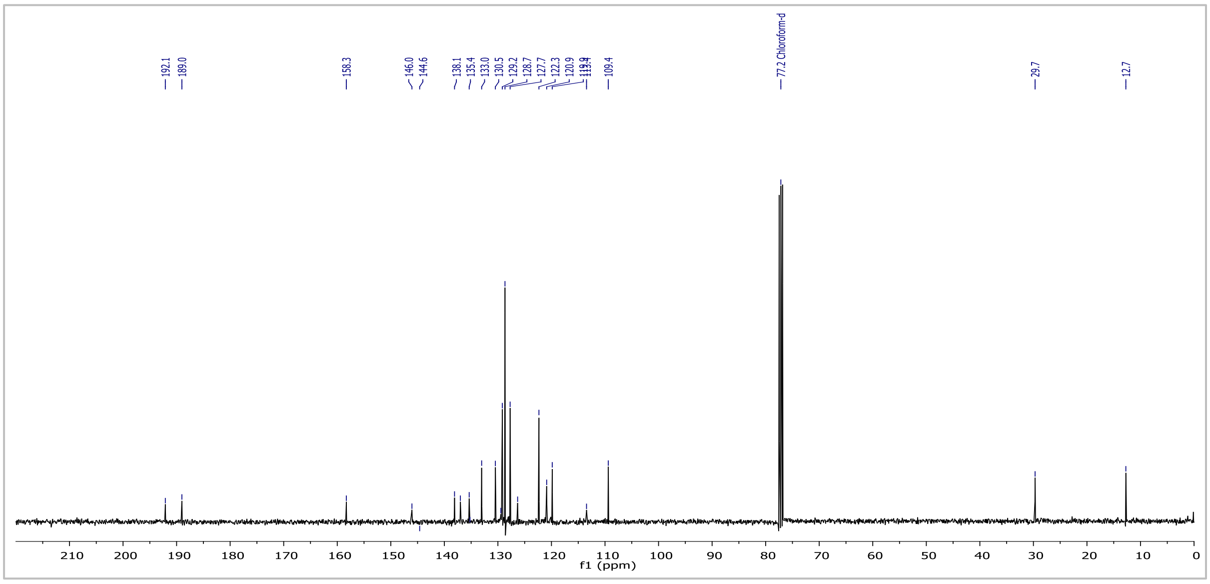
7.2
7.1
3.7
2.8
3.01
2.12
2.31
2.30
3.37
1.01
1.29
1.11
3.19
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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189.0
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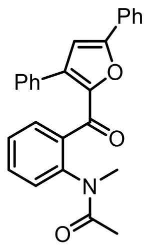
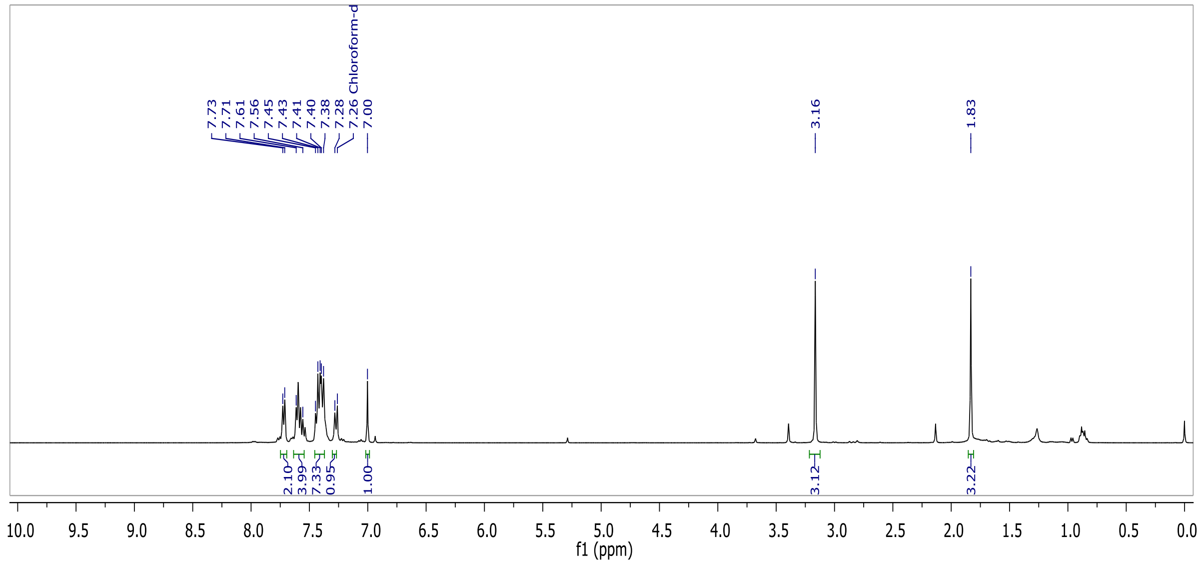
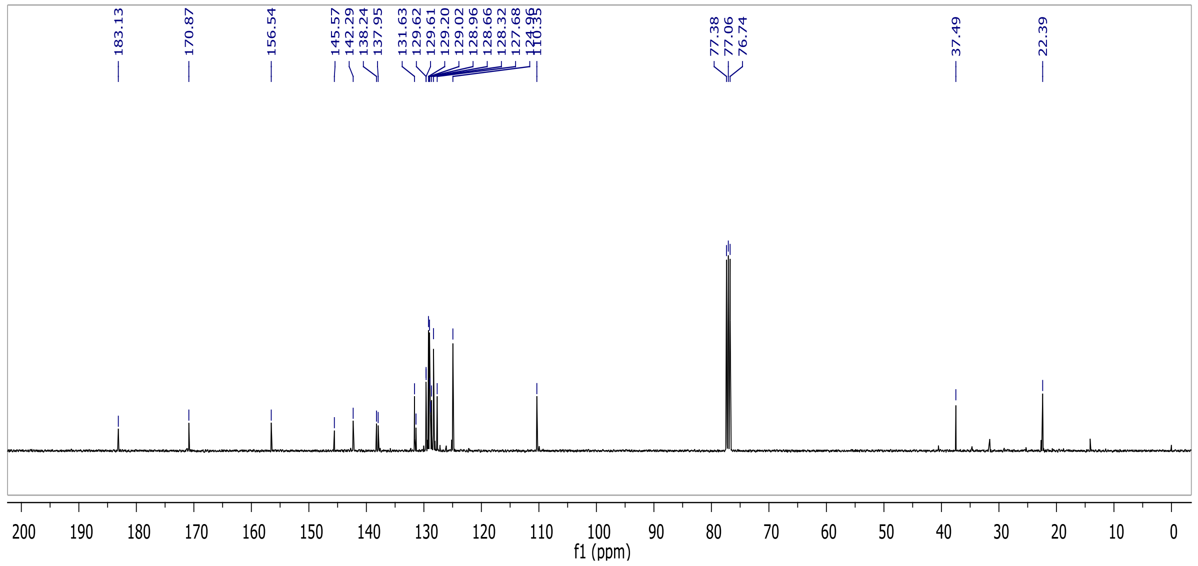
146.0
144.6
138.1
135.4
133.0
130.5
129.2
128.7
127.7
122.3
120.9
119.9
113.4
109.4
77.2 Chloroform-d
29.7
12.7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
Ph
O
O
N
O

**7**


7.73
7.71
7.61
7.56
7.45
7.43
7.41
7.40
7.38
7.28
7.26 Chloroform-d
7.00
3.16
1.83
2.10
3.99
7.33
0.95
1.00
3.12
3.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


183.13
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145.57
142.29
138.24
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131.63
129.62
129.61
129.20
129.02
128.96
128.66
128.32
127.68
124.96
110.35
77.38
77.06
76.74
37.49
22.39
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

## References

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[1] Fernandes, R.; Mhaske, K.; Narayan, R. *Tetrahedron*, **2022**, *103*, 132553.

[2] Shriner, R.L.; Ashley, W. C.; Welch, E. *Org. Synth.* **1942**, *22*, 98.

[3] Astolfi, P.; Greci, L.; Rizzolo, C.; Sgarabotto, P.; Marrosu, G. *J. Chem. Soc., Perkin Trans. 2*. **2001**, 1634–1640.