Electronic Supplementary Material (ESI) for ChemComm.

Gold-Catalysed Cross-Coupling between Aryldiazonium Salts and Arylboronic Acids: Probing the Usefulness of Photoredox Conditions.

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Supplementary Information

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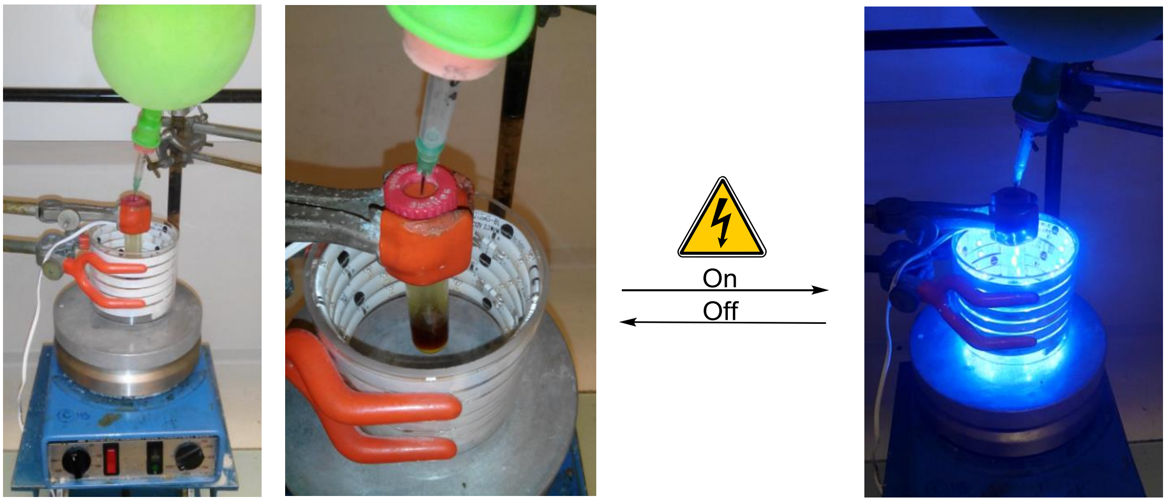
A) General methods

All commercial materials were used without further purification, unless indicated. ^1H NMR and ^{13}C NMR were recorded on Bruker DPX-200 FT (^1H: 200MHz, ^{13}C: 50.2MHz), Bruker Avance 300 FT (^1H: 300MHz, ^{13}C: 75.3MHz) spectrometers. The chemical shifts for the NMR spectra are reported in ppm relative to the solvent residual peak[1]. Coupling constants J are reported in hertz (Hz). The following abbreviations are used for the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; st, sextet; m, multiplet; br, broad; dd, doublet of doublet. Yields refer to isolated material determined to be pure by NMR spectroscopy and thin-layer chromatography (TLC), unless specified in the text. Analytical TLC was performed on Fluka Silica Gel 60 F254. High resolution mass spectra were performed by the CESAMO (Talence, France) and were recorded on Qq-TOF tadem mass spectrometer (API Q-STAR Pulsari, Applied Biosystems). Positive ion mode ESI-MS was used for the analysis. Blue light irradiations were performed with a Flexled INSPIRE LED lamp (1.5m, 45LED, 25 LUMEN, 3.45 W; λ = 465 nm) coiled inside a glass tube. Absorption spectra were recorded on a Varian Cary 5000 spectrophotometer in 1 cm pathlength quartz cells. All the reactions were performed in a sealed tube. When the irradiation was turned on, the internal temperature of the photochemical system slightly increased and stabilized at 30°C. The two-chamber system (S) was bought at SyTracks (http://www.sytracks.com).



Blue light irradiation

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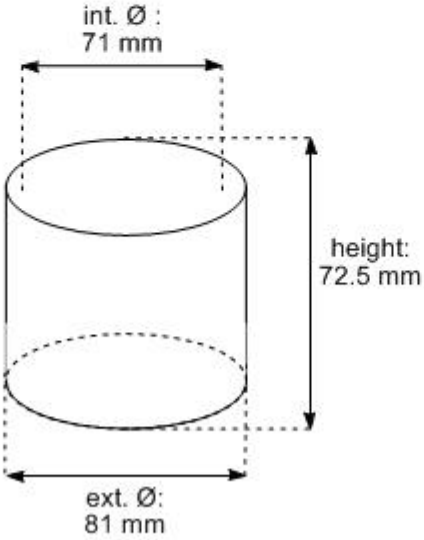
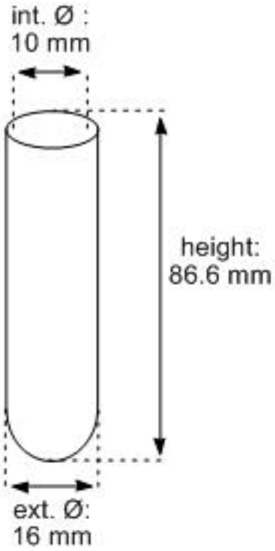
[1] Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw,J. E.; Goldberg, K. I. *Organometallics* **2010**, 29, 2176

Photochemical system



Reaction tube

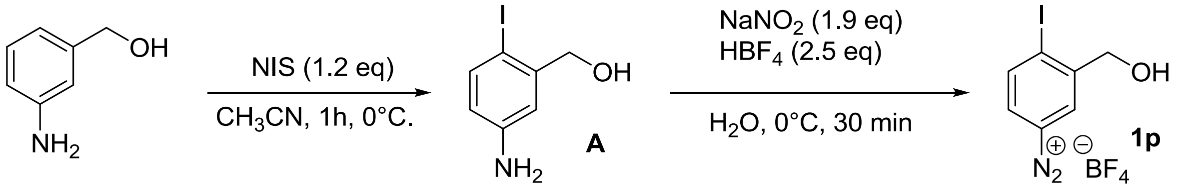


B) General procedures

1) Preparation of the aryldiazonium salts

Aryl diazonium salts were synthesized according to previous literature reports.[2] The aniline (10 mmol, 1eq) was added to 6 mL of a 1:1 mixture of a solution of fluoroboric acid (50% w/w in H_2O) and distilled water at 0°C. Then, an ice-cold solution of sodium nitrite (704 mg, 10.2 mmol, 1.02 eq) in distilled water (3mL) was added. After stirring for 30 min at 0°C., the precipitate was collected on a Hirch funnel and washed three times with 1-2 mL of ice-cold distilled water. The solid was dissolved in acetone and precipitated by slow addition of diethyl ether to the solution. The mixture was triturated, the supernatant was removed and this procedure was repeated two times. Aryldiazonium salts were obtained as white crystalline solids with yields ranging from 65% to 92%.

2) Preparation of 3-(hydroxymethyl)-4-iodobenzenediazonium tetrafluoroborate 1p



3-Aminobenzylalcohol (1.23g, 10 mmol, 1eq) was dissolved in 30 mL of CH_3CN and stirred at 0°C. A solution of N-iodosuccinimide (2.7g, 12 mmol, 1.2eq), in 30 mL of CH_3CN was added dropwise. The reaction mixture was stirred at 0°C for 30 min. Then, the reaction was quenched with a saturated aqueous solution of $Na_2S_2O_3$ (60 mL). The mixture was extracted three times with ethyl acetate (3 x 30 mL). The combined organic phases were washed four times (4 x 20 mL) with an aqueous solution of HCl (2.5M). The acid aqueous layer was collected and solid NaOH was added until reaching pH 11. The aqueous layer was extracted three times with ethyl acetate (3 x 30 ml). The combined organic layers were dried with $MgSO_4$ and the solvent was removed under reduced pressure to give 2.5 g of **A** as a white power (10 mmol, 100%).

Compound **A** (1.0 g, 4 mmol, 1eq) was added to a 1:1 mixture of aqueous tetrafluoroboric acid (1.25 mL, 10 mmol, 2.5eq, 50% w/w) and water (1.25 mL) at room temperature. The mixture was cooled to 0 °C and a solution of sodium nitrite (524 mg, 7.6 mmol, 1.9eq) in H_2O (1.1 mL) was added dropwise. The reaction mixture was stirred at 0 °C for 30 minutes, and the resulting solid was filtered off using a sintered-glass filter. The solid was recrystallized from acetone and ice-cold diethyl ether to give 791 mg of **1p** (2.27mmol, 57%) as a brown solid.

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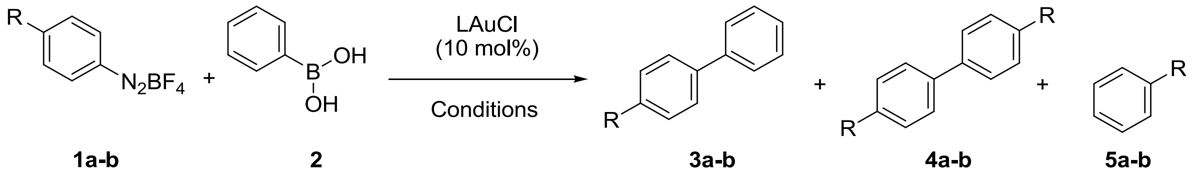
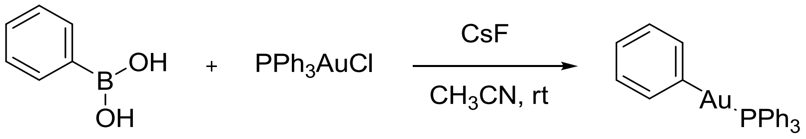
[2] Broxton, T. J.; Bunnett, J. F.; Paik, C. H. *J. Org. Chem.* **1977**, 42, 643

3) Optimization of the conditions



In a tube were added 30.5 mg of phenylboronic acid **2** (250 µmol, 1 eq), the diazonium salt **1a** or **1b**, the gold complex (25 µmol, 10 mol%), the base (0.5 to 2.0 eq) and the photosensitizer if needed. The tube was sealed, purged three times with argon, and placed inside the turned-off photochemical reactor. CH_3CN (2 mL) was added and the blue light irradiation was turned on. The reaction mixture was stirred at 30°C (controlled by a thermometer) under blue light irradiation for 16h. The **1**/**3**/**4**/**5** ratios were determined by analysis of the ^1H NMR of the crude mixture.

4) Preparation of PPh_3AuPh



In a vial was added PPh_3AuCl (49.5 mg, 0.1 mmol, 1 eq), dried CsF (30.4 mg, 0.2 mmol, 2 eq) and phenylboronic acid (12.2 mg, 0.1 mmol, 1 eq). The vial was purged three times with argon and CH_3CN (1 mL) was added. The reaction mixture was stirred at room temperature for 45 min. The solvent was removed under reduced pressure. Benzene (2 mL) was added to the residue and the mixture was filtered through a Celite pad. The filtrate was evaporated under reduced pressure and triturated with pentane to precipitate the product. The resulting white suspension was evaporated under reduced pressure to give 53 mg of PPh_3AuPh (0.1 mmol, 100%) as a white solid. ^1H-NMR spectrum was in accordance to the data previously reported.[3]

5) Gold-catalysed cross coupling of arylboronic acids and aryldiazonium salts

Conditions with the acridinium as photosensitizer (A):

In a tube were added the boronic acid **2** (250 µmol, 1 eq), the diazonium salt **1** (375 µmol, 1.5 eq), 12.4 mg of PPh_3AuCl (25 µmol, 10 mol%), 4.0 mg of 9-mesityl-10-acridinium tetrafluoroborate (10 µmol, 4 mol%) and 40.0 mg of dried CsF (263 µmol, 1.05 eq). The tube was sealed, purged three times with argon, and placed inside the turned-off photochemical reactor. CH_3CN (2 mL) was added and the blue light irradiation was turned on. The reaction mixture was stirred at 30°C (controlled by a

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[3] Hashmi, A. S. K.; Ramamurthi, T. D.; Rominger, F. *J. Organomet. Chem.*, **2009**, *694*, 592.

thermometer) under blue light irradiation for 16h. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel.

Conditions with of $Ru(bpy)_3^{2+}$ as photosensitizer (R):

In a tube were added the boronic acid **2** (250 µmol, 1 eq), the diazonium salt **1** (375 µmol, 1.5 eq), 12.4 mg of PPh_3AuCl (25 µmol, 10 mol%), 4.3 mg of $Ru(bpy)_3(PF_6)_2$ (5 µmol, 2 mol%) and 40.0 mg of dried CsF (263 µmol, 1.05 eq). The tube was sealed, purged three times with argon, and placed inside the turned-off photochemical reactor. CH_3CN (2 mL) was added and the blue light irradiation was turned on. The reaction mixture was stirred at 30°C (controlled by a thermometer) under blue light irradiation for 16h. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel.

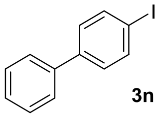
Conditions in the dark (D):

In a tube were added the boronic acid **2** (250 µmol, 1 eq), the diazonium salt **1** (375 µmol, 1.5 eq), 12.4 mg of PPh_3AuCl (25 µmol, 10 mol%) and 40.0 mg of dried CsF (263 µmol, 1.05 eq). The tube was sealed, purged three times with argon, fully covered by an aluminum foil and placed inside the turned-off photochemical reactor. CH_3CN (2 mL) was added and the blue light irradiation was turned on. The reaction mixture was stirred at 30°C (controlled by a thermometer) under blue light irradiation for 16h. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel.

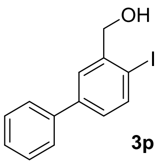
6) Carbonylation of **3p** with the two-chamber system (S)

In the chamber 1 of the two-chamber system were added Ph_2MeSi-$^{13}COOH$ **8*** (28.5 mg, 0.117 mmol, 1 eq). The chamber 1 was sealed with a screwcap fitted with a silicone/PTFE seal. In the chamber 2 of the two-chamber system were added successively the aryl iodide **3p** (40 mg, 0.129 mmol, 1.1 eq), $Pd(dba)_2$ (6.7 mg, 11.7 µmol, 10 mol%), xantphos (6.8 mg, 11.7 µmol, 10 mol%), DABCO (28.9 mg, 0.257mmol, 2 eq). The chamber 2 was sealed with a screwcap fitted with a silicone/PTFE seal. The atmosphere of the two-chamber system was purged three times with argon. Then, 1 mL of dry THF was added by syringe in each chamber through the silicone/PTFE seal. The loaded two-chamber system was stirred at 70°C, then 12 µl of a solution of TBAF (1M in THF, 12 *µ*mol, 10 mol%) were added through a silicone/PTFE seal in the chamber 1. The system was stirred at 70°C for 1 hour. After a careful opening, the crude reaction mixture from chamber 2 was concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (60/40:cyclohexane/diethyl ether) affording 22 mg of **7** (0.104 mmol, 90%) as a white solid.

7) Coupling of **1n** and **1p** under Shi’s conditions:

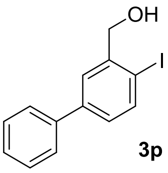

3n

Ph$_3$PAu(TA)OTf (prepared according to a previously described procedure)[i] (14.8 mg, 0.04 mmol, 10 mol%), 2,2′-bipyridyl (12.4 mg, 0.08 mmol, 20 mol%), sodium carbonate (84.8 mg, 0.8 mmol, 2 eq) and phenyl boronic acid **2** (48.8 mg, 0.4 mmol, 1 eq) were added to 0.8 mL of freshly distilled acetonitrile in a 1 mL-dram vial. To this solution was added the diazonium salt **1n** (0.48 mmol, 1.2 eq). The mixture was stirred under room temp for 10 hrs. Upon reaction completion, the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (cyclohexane) affording 16 mg of **3n** (0.057 mmol, 14%) as a white solid.

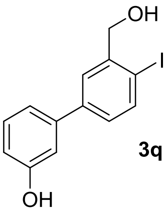

3p

Ph$_3$PAu(TA)OTf (14.8 mg, 0.04mmol, 10 mol%), 2,2′-bipyridyl (12.4 mg, 0.08 mmol, 20 mol%), sodium carbonate (84.8 mg, 0.8 mmol, 2 eq) and phenyl boronic acid **2** (48.8 mg, 0.4 mmol, 1 eq) were added to 0.8 mL of freshly distilled acetonitrile in a 1 mL-dram vial. To this solution was added the diazonium salt **1p** (167 mg, 0.48 mmol, 1.2 eq). The mixture was stirred under room temp for 10 hrs. Upon reaction completion, the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (80/20:cyclohexane/diethyl ether) affording 12 mg of **3p** (0.039 mmol, 10%) as a white solid.

8) Coupling under Felpin’s conditions:


3p

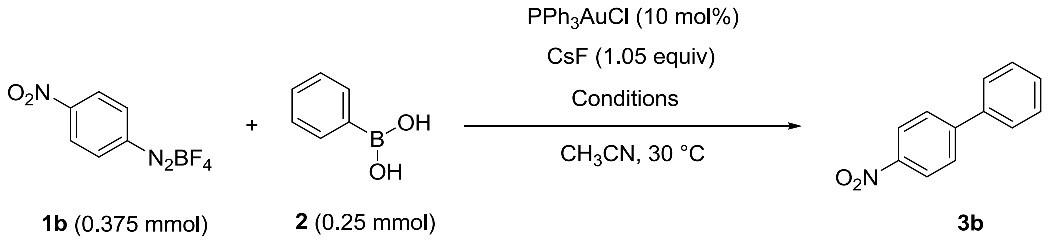
To a solution of the diazonium salt **1p** (125 mg, 0.36 mmol, 1.2 eq) in MeOH (4.8 mL) were added phenyl boronic acid **2** (36 mg, 0.3 mmol, 1eq) and 5% w/w Pd(0)/BaCO$_3$ (3.2 mg, 0.5 mol%). The resulting mixture was stirred for 12 hours at room temperature and then concentrated under reduced pressure. The crude was purified by flash chromatography (cyclohexane) affording 5.5 mg of **3p** (0.018 mmol, 6 %) as a white solid.


3q

To a solution of the diazonium salt **1q** (125 mg, 0.36 mmol, 1.2 eq) in MeOH (4.8 mL) were added 3-hydroxyphenyl boronic acid (41 mg, 0.3 mmol, 1eq) and 5% w/w Pd(0)/BaCO$_3$ (3.2 mg, 0.5 mol%). The resulting mixture was stirred for 12 hours at room temperature and then concentrated under reduced pressure. The crude was purified by flash chromatography (cyclohexane) affording 15 mg of **3q** (0.046 mmol, 15 %) as a white solid.

9) Course of the PPh$_3$AuCl-catalysed synthesis of 4-nitro-1,1'-biphenyl (3b)

In a tube were added 30.5 mg of phenyl boronic acid **2** (250 µmol, 1 eq), 88.8 mg of 4-nitrobenzenediazonium tetrafluoroborate **1b** (375 µmol, 1.5 eq), 12.4 mg of PPh$_3$AuCl (25 µmol, 10 mol%), 40.0 mg of dried CsF (263 µmol, 1.05 eq) and 14 mg of 1,3,5-trimethoxybenzene (83 µmol, 0.33 eq) as internal standard. 4.3 mg of Ru(bpy)$_3$(PF$_6$)$_2$ (5 µmol, 2 mol%) were also added for the reaction performed under blue light irradiation. The tube was sealed and purged three times with nitrogen, and placed inside the turned-off photochemical reactor. CH$_3$CN (2 mL) was added and the blue light irradiation was turned on. The reaction mixture was stirred at 30°C (controlled by a thermometer) under blue light irradiation (blue line) or under the dark (covered by an aluminium foil, orange line). The yields of 4-nitro-1,1'-biphenyl (**3b**) were determined by analysis of the ^{1}H-NMR spectra of aliquots of the reaction mixture (protected from light, diluted in CDCl$_3$, 1,3,5-trimethoxybenzene as internal standard,).



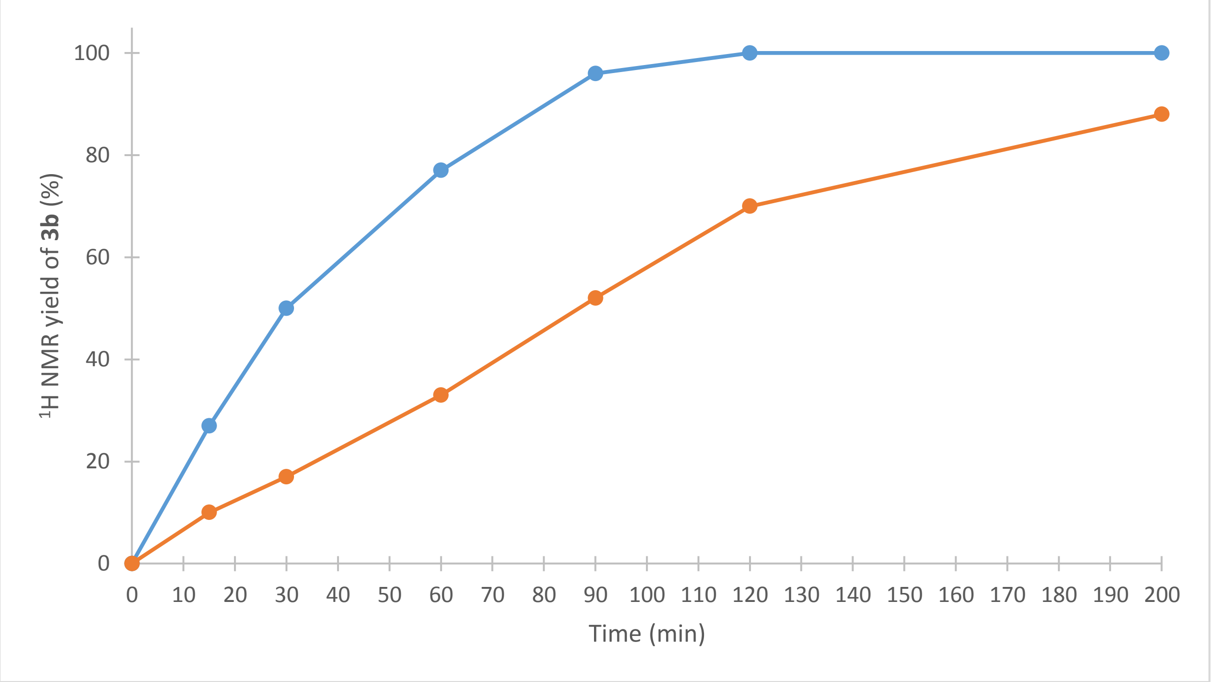


Figure 1: Evolution in time of the ^{1}H NMR yield of ***3b*** *in the dark (orange line) or under blue LEDs irradiation in combination with Ru(bpy)$_3$(PF$_6$)$_2$ (blue line).*

10) Determination of the quantum yields (ϕ)

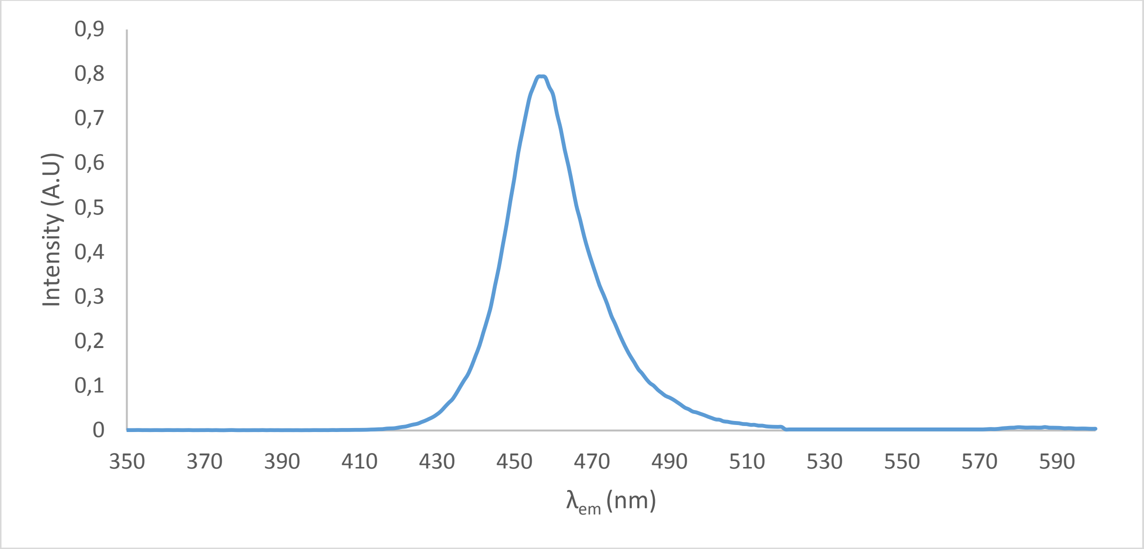
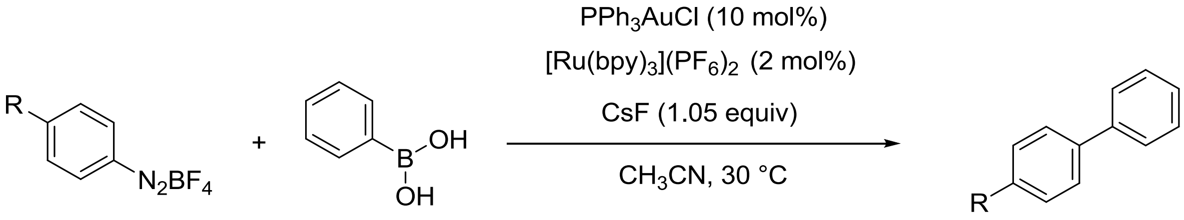


Figure 2 : Emission spectrum of the blue LEDs of the photochemical system (λ_{max} = 458 nm)

Following a modified procedure reported previously,[ii] an aqueous ferrioxalate actinometer solution was prepared and stored in the dark. This actinometer solution measures the photodecomposition of ferric oxalate anions to ferrous oxalate anions, which are then reacted with 1, 10-phenanthroline to form $Fe(Phen)_3^{2+}$. Its concentration is then estimated by UV/Vis absorbance at 510 nm. The number of moles of $Fe(Phen)_3^{2+}$ complex formed is related to the number of photons absorbed by the actinometer solution.

Preparation of the solutions used for the studies:

1) Potassium ferrioxalate solution: Potassium ferrioxalate trihydrate (295 mg) and 95-98% H_2SO_4 (140 µL) were added to a 50 mL volumetric flask and filled to the mark with distilled water. The solution was stored in the dark.
2) Buffered solution of phenantroline : 1,10-phenantroline (25 mg), sodium acetate (5.63 g) in H_2SO_4 (25 mL of 0.5 M). The solution was stored in the dark.
3) The reaction solution: the phenylboronic acid **2** (250 µmol, 1 eq), the diazonium salt **1a** or **1b** (375 µmol, 1.5 eq), 12.4 mg of PPh_3AuCl (25 µmol, 10 mol%), 4.3 mg of $Ru(bpy)_3(PF_6)_2$ (5 µmol, 2 mol%) and 40.0 mg of dried CsF (263 µmol, 1.05 eq) were added to a sealable quartz cuvette (l = 1 cm) containing a stirring bar. In the absence of light, CH_3CN (2.0 mL) was added under argon.



1a-b (0.375 mmol) **2** (0.25 mmol) **3a-b**

Actinometry measurements:

a) Two quartz cuvettes (l = 1 cm) were filled with 2 mL of the potassium ferrioxalate solution. One of the cuvettes was placed in the photochemical system (λ_{max}= 458 nm) and irradiated for 90 s, the second cuvette was stored in the dark.

b) After irradiation, 0.35 mL of phenantroline solution was added to both cuvettes. The mixtures were stirred in the dark for 1 h to allow complete coordination of the phenantroline to ferrous ions.

c) The absorbance of both solutions were measured by UV/Vis spectrophotometry at λ = 510 nm.

d) The number of moles of Fe^{2+} formed was determined by the following equation:

$$mol\ Fe^{2+} = \frac{V.\Delta A(510\ nm)}{l \times \varepsilon}$$

Where:

V = Irradiated volume (0.00235 L).

ΔA (510 nm) = Difference in absorbance between the irradiated solution and the solution stored in dark.

ε = Molar extinction coefficient of $[Fe(Phen)_3]^{2+}$ complex (11100 $L.mol^{-1}.cm^{-1}$).

l = Optical path-length of the cuvette (1 cm).

e) The photon flux can be calculated using :

$$Photon\ flux = \frac{mol\ Fe^{2+}}{\Phi \times t \times f}$$

Where:

Φ = Quantum yield for the ferrioxalate actinometer (0.85 at λ_{ex}=458 nm).[iii]

t = Irradiation time (90 s)

f = Fraction of light absorbed at λ_{ex}= 458 nm by the actinometer. This value is calculated using $f = 1\text{-}10^{-A(458\ nm)}$, A(458 nm) is the absorbance of the ferrioxalate solution at 458 nm.

f) The photon flux was determined to be 5.03×10^{-9} $einsteins.s^{-1}$ (average of three experiments).

g) After 1h of irradiation, the number of moles of the biaryl product (**3a** or **3b**) was determined by ^1H NMR analysis of the crude using 1,3,5-trimethoxybenzene as internal standard. The measured absorbance of the reaction solution at 458 nm by UV/Vis spectrophotometer was greater than 3. Thus, the number of moles of photons absorbed by the reaction mixture is roughly equal to the number of moles of incident photon per unit time (Photon flux). The calculated apparent quantum yield (Φ) was determined using :

$$\Phi = \frac{mol\ of\ product\ formed}{Photon\ flux \times t \times f}$$

Where:

Photon flux = 5.03×10^{-9} einsteins.s^{-1}.

t = Reaction time (3600 s).

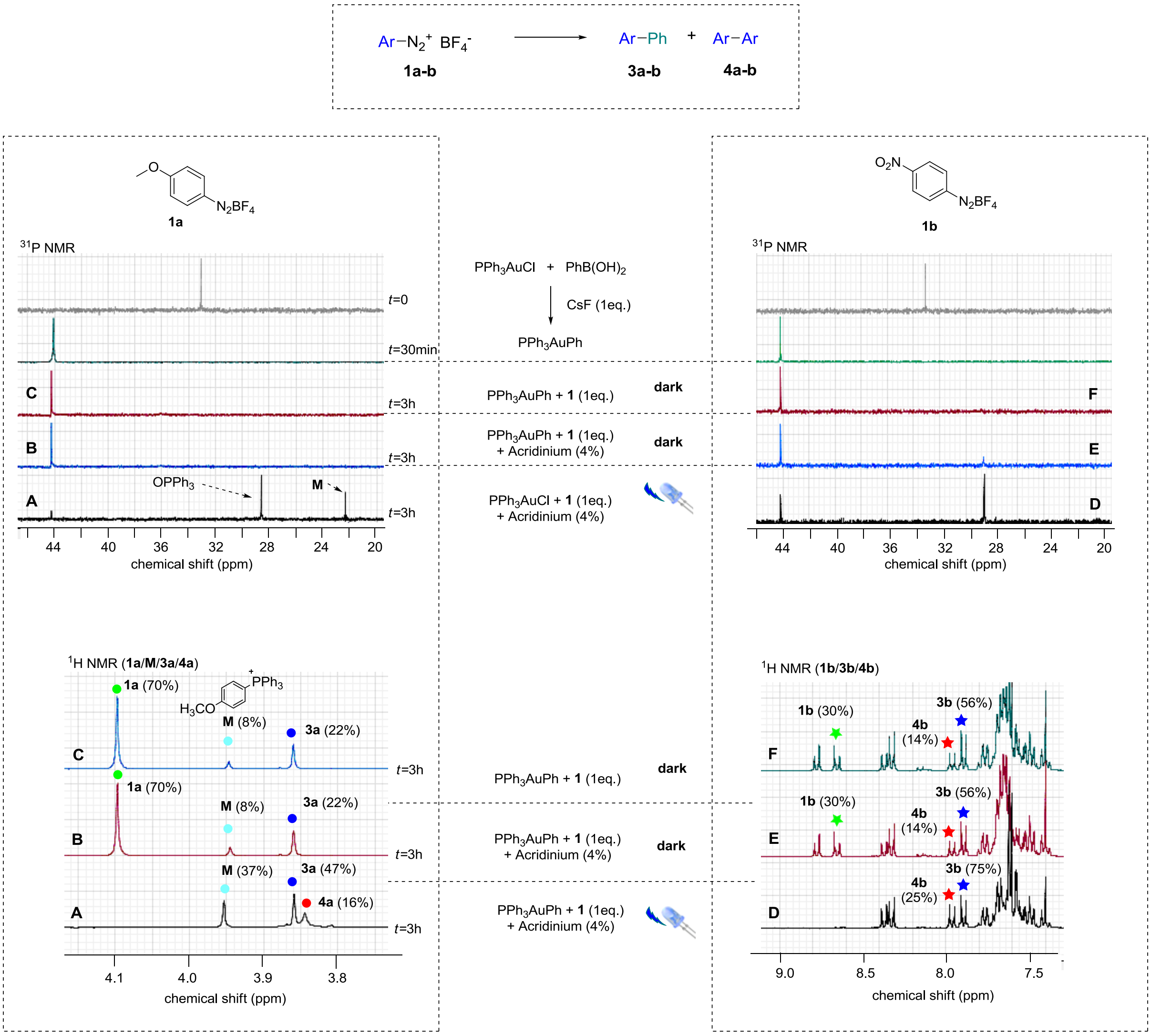
f = Fraction of light absorbed at λ_{ex}= 458 nm by the reaction mixture. This value is calculated using f = 1-10$^{-A(458\ nm)}$, A(458 nm) is the absorbance of the reaction mixture at 458 nm.

h) The reaction quantum yield (Φ) was thus determined to be 1.4 with **1a** and 9.6 with **1b**

11) Stoichiometric reactions between PPh_3AuPh and **1a** / **1b**

Six NMR tubes were labelled as **A, B, C, D, E** and **F**. PPh_3AuPh (5.4 mg, 10 µmol), 4-methoxybenzenediazonium tetrafluoroborate **1a** (2.2 mg, 10 µmol) and 9-mesityl-10-acridinium tetrafluoroborate (0.2mg, 0.5 µmol) were added in tube **A** and **B** and dissolved in 0.4 ml of CD_3CN. PPh_3AuPh (5.4 mg, 10 µmol) and diazonium salt **1a** (2.2 mg, 10 µmol) were added in tube **C** and dissolved in 0.4 ml of CD_3CN. PPh_3AuPh (5.4 mg, 10 µmol), 4-nitrobenzenediazonium tetrafluoroborate **1b** (2.4 mg, 10 µmol) and 9-mesityl-10-acridinium tetrafluoroborate (0.2mg, 0.5 µmol) were added in tube **D** and **E** and dissolved in 0.4 ml of CD_3CN. PPh_3AuPh (5.4 mg, 10 µmol) and diazonium salt **1b** (2.4 mg, 10 µmol) were added in tube **F** and dissolved in 0.4 ml of CD_3CN.

Tubes **B, C, E** and **F** were each fully covered by an aluminum foil and all tubes **A, B, C, D, E** and **F** were placed in the photochemical reactor. The reactions were monitored by ^1H NMR and ^{31}P NMR after 3h.



After 3h, ^{1}H NMR analysis of the reactions performed in the dark indicated 30% of conversion for the methoxy-substituted diazonium salt **1a** (tube **B** and **C**) and 70% of conversion of the nitro-substituted diazonium salt **1b** (tube **E** and **F**). However, both diazonium **1a** and **1b** fully disappeared within 3h when the reactions were performed under blue light irradiation in presence of the acridinium **6**. In tube **A**, **M** may originate from the Au^{III} intermediates.[4]

It should be noted that in ^{31}P NMR, only monitoring of the remaining PPh_3AuPh was possible. Indeed, formation of the free PPh_3 couldn't be precisely seen on this scale, probably due to the concomitant formation of gold nanoparticules or gold mirrors in these stoichiometric experiments.

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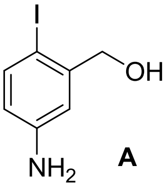
[4] Shu, X.; Zhang, M.; He, Y.; Frei, H.; Toste, F. D. *J. Am. Chem. Soc.* **2014**, *136*, 5844.

C) Compounds characterization



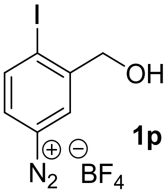
5-Amino-2-iodobenzylalcohol A

White solid.

^{1}H NMR (200MHz, MeOD): 7.38 (d, *J*=8.4 Hz, 1H), 6.94 (d, *J*=2.9 Hz, 1H), 6.42 (dd, *J*=8.48 Hz, 2.9 Hz, 1H), 4.54 (s, 2H).

^{13}C NMR (75MHz, MeOD): 149.9, 144.8, 140.5, 117.4, 116.4, 81.6, 69.6.

HRMS (ESI) C_7H_8INO, calculated for [M+H]: 249.9723, found 249.9713.

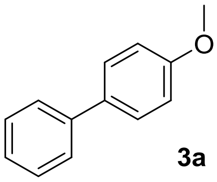


3-(Hydroxymethyl)-4-iodobenzenediazonium tetrafluoroborate 1p

Light brown solid.

^{1}H NMR (300MHz, CD_3CN): 8.51 (d, *J*=2.7 Hz, 1H), 8.38 (d, *J*=8.7 Hz, 1H), 8.12 (dd, *J*=8.7 Hz, 2.7 Hz, 1H), 4.59 (s, 2H).

^{13}C NMR (75MHz, CD_3CN): 150.8, 143.4, 131.2, 129.4, 115.5, 115.4, 68.2.



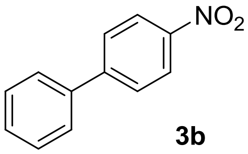
3a

4-Methoxy-1,1'-biphenyl[iv] 3a

The residue was purified by silica gel flash chromatography (90/10:cyclohexane/diethyl ether) affording **3a** as a white solid (*conditions R:* 29.0 mg, 63% yield; *conditions A:* 25.3 mg, 55% yield; *conditions D:* 9.2 mg, 20% yield).

^{1}H NMR (300MHz, $CDCl_3$): 7.56-7.50 (m, 4H), 7.4 (t, *J*=7.7 Hz, 2H), 7.33-7.26 (m, 1H), 6.97 (d, *J*=8.2 Hz, 2H), 3.84 (s, 3H).

^{13}C NMR (75MHz, $CDCl_3$): 159.0, 140.7, 133.6, 128.6, 128.0, 126.6, 126.5, 114.0, 55.2.



3b

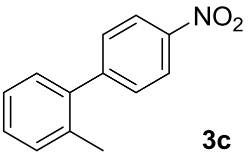
4-Nitro-1,1'-biphenyl[v] 3b

The residue was purified by silica gel flash chromatography (90/20:cyclohexane/diethyl ether) affording **3b** as a pale yellow solid (*conditions R:* 37.4 mg, 75% yield; *conditions A:* 37.8 mg, 76% yield; *conditions D:* 40.3 mg, 81% yield).

^{1}H NMR (300MHz, $CDCl_3$): 8.28 (d, *J*=8.7 Hz, 2H), 7.72 (d, *J*=8.7 Hz, 2H), 7.64-7.58 (m, 2H), 7.58-7.53 (m, 3H).

^{13}C NMR (75MHz, $CDCl_3$): 147.9, 147.4, 139.1, 129.5, 129.2, 128.1, 127.7, 124.4.

2-Methyl-4'-nitro-1,1'-biphenyl[vi] 3c



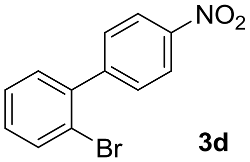
3c

The residue was purified by silica gel flash chromatography (80/20:cyclohexane/diethyl ether) affording **3c** as a colourless oil (*conditions R:* 48.0 mg, 90% yield; *conditions A:* 49.0 mg, 92% yield).

^{1}H NMR (300MHz, $CDCl_3$): 8.27 (d, *J*=8.7 Hz, 2H), 7.48 (d, *J*=8.7 Hz, 2H), 7.33-7.25 (m, 3H), 7.22-7.17 (m, 1H), 2.25 (s, 3H).

^{13}C NMR (75MHz, $CDCl_3$): 149.1, 147.1, 139.9, 135.3, 131.0, 130.4, 129.7, 128.7, 126.4, 123.7, 20.6.

2-Bromo-4'-nitro-1,1'-biphenyl[vii] 3d



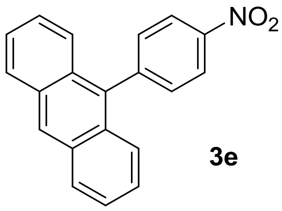
3d

The residue was purified by silica gel flash chromatography (80/20:cyclohexane/diethyl ether) affording **3d** as a colorless oil (*conditions R:* 50.7 mg, 73% yield; *conditions A:* 55.6 mg, 80% yield).

^{1}H NMR (300MHz, $CDCl_3$): 8.27 (d, *J*=8.7 Hz, 2H), 7.69 (dd, *J*=7.3 Hz, 1.5 Hz, 1H), 7.57 (d, *J*=8.7 Hz, 2H), 7.40 (dt, *J*=7.3 Hz, 1.5 Hz, 1H), 7.32-7.25 (m, 2H).

^{13}C NMR (75MHz, $CDCl_3$): 147.7, 145.5, 140.6, 133.7, 131.1, 130.7, 130.1, 127.9, 123.5, 122.2.

9-(4-Nitrophenyl)anthracene[viii] 3e



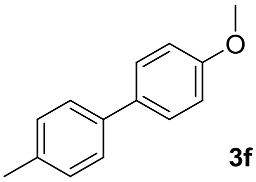
3e

The residue was purified by silica gel flash chromatography (80/20:cyclohexane/diethyl ether) affording **3e** as a yellow solid (*conditions R:* 29.9 mg, 40% yield; *conditions A:* 41.2 mg, 55% yield).

^{1}H NMR (300MHz, $CDCl_3$): 8.55 (s, 1H), 8.45 (d, *J*=8.6 Hz, 2H), 8.06 (d, *J*=8.5 Hz, 2H), 7.62 (d, *J*=8.6 Hz, 2H), 7.53-7.44 (m, 4H), 7.41-7.34 (m, 2H).

^{13}C NMR (150MHz, $CDCl_3$): 147.7, 146.5, 134.2, 132.6, 131.4, 129.9, 128.8, 128.0, 126.3, 126.0, 125.5, 123.9.

4-Methoxy-4'-methyl-1,1'-biphenyl[ix] 3f



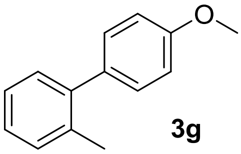
3f

The residue was purified by silica gel flash chromatography (90/10:cyclohexane/diethyl ether) affording **3f** as a white solid (*conditions R:* 27.3 mg, 55% yield; *conditions A:* 19.8 mg, 40% yield).

^{1}H NMR (300MHz, $CDCl_3$): 7.5 (d, *J*=8.6 Hz, 2H), 7.44 (d, *J*=7.7 Hz, 2H), 7.22 (d, *J*=7.7 Hz, 2H), 6.96 (d, *J*=8.6 Hz, 2H), 3.83 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (75MHz, $CDCl_3$): 159.6, 138.0, 136.4, 129.5, 128.0, 126.6, 114.2, 55.4, 21.1.

4'-Methoxy-2-methyl-1,1'-biphenyl[x] 3g



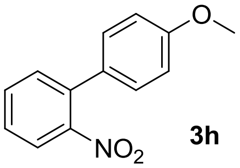
3g

The residue was purified by silica gel flash chromatography (90/10:cyclohexane/diethyl ether) affording **3g** as a colourless oil (*conditions R:* 44.6 mg, 90% yield).

^{1}H NMR (300MHz, $CDCl_3$): 7.34-7.27 (m, 6H), 7.02 (d, *J* = 8.6 Hz, 2H), 3.92 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (75MHz, $CDCl_3$): 158.6, 141.6, 135.5, 134.4, 130.4, 130.3, 130.0, 127.0, 125.8, 113.5, 55.3, 20.6.

4'-Methoxy-2-nitro-1,1'-biphenyl[xi] 3h



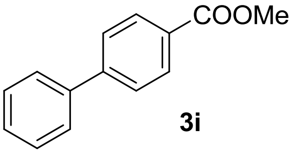
3h

The residue was purified by silica gel flash chromatography (90/10:cyclohexane/diethyl ether) affording **3h** as a yellow oil (*conditions R:* 52.7 mg, 92% yield).

^{1}H NMR (300MHz, $CDCl_3$): 7.85 (dd, *J*=8.5 Hz, 1.4 Hz, 1H), 7.66-7.60 (m, 1H), 7.48 (t, *J*=7.6 Hz, 2H), 7.30 (d, *J*=8.7 Hz, 2H) 7.00 (d, *J*=8.7 Hz, 2H), 3.89 (s, 3H).

^{13}C NMR (75MHz, $CDCl_3$): 159.8, 149.6, 136.0, 132.3, 132.1, 129.6, 128.7, 127.9, 127.2, 124.2, 114.4, 55.5.

Methyl (1,1'-biphenyl)-4-carboxylate[xii] 3i



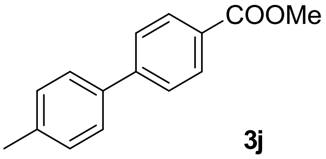
3i

The residue was purified by silica gel flash chromatography (90/10:cyclohexane/diethyl ether) affording **3i** as a white solid (*conditions R:* 34.5 mg, 65% yield; *conditions A:* 34.5 mg, 65% yield).

^{1}H NMR (300MHz, $CDCl_3$): 8.09 (d, *J*=8.4 Hz, 2H), 7.68-7.57 (m, 4H), 7.49-7.33 (m, 3H), 3.93 (s, 3H).

^{13}C NMR (75MHz, $CDCl_3$): 166.8, 145.4, 139.8, 129.9, 128.7, 127.9, 127.1, 126.9, 52.0.

Methyl 4'-methyl-(1,1'-biphenyl)-4-carboxylate[xiii] **3j**



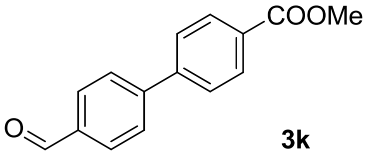
3j

The residue was purified by silica gel flash chromatography (90/10:cyclohexane/diethyl ether) affording **3j** as a white solid (*conditions R:* 28.3 mg, 50% yield; *conditions A:* 28.2 mg, 50% yield).

^{1}H NMR (300MHz, $CDCl_3$): 7.99 (d, *J*=8.4 Hz, 2H), 7.54 (d, *J*=8.4 Hz, 2H), 7.43 (d, *J*=7.9 Hz, 2H), 7.17 (d, *J*=7.9 Hz, 2H), 3.83 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (75MHz, $CDCl_3$): 167.1, 145.6, 138.2, 137.1, 130.1, 129.7, 128.6, 127.1, 126.8, 52.2, 21.2

Methyl 4'-formyl-(1,1'-biphenyl)-4-carboxylate[xiv] **3k**



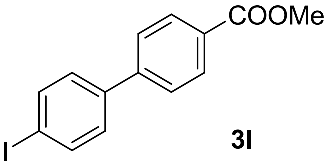
3k

The residue was purified by silica gel flash chromatography (80/20:cyclohexane/diethyl ether) affording **3k** as a white solid (*conditions R:* 30.0 mg, 50% yield; *conditions A:* 30.1 mg, 50% yield).

^{1}H NMR (300MHz, $CDCl_3$): 10.06 (s, 1H), 8.12 (d, *J*=8.6 Hz, 2H), 7.96 (d, *J*=8.3 Hz, 2H), 7.77 (d, *J*=8.3 Hz, 2H), 7.69 (d, *J*=8.6 Hz, 2H), 3.94 (s, 3H).

^{13}C NMR (75MHz, $CDCl_3$): 191.9, 130.5, 130.4, 128.1, 127.5, 127.3, 52.4.

Methyl 4'-iodo-(1,1'-biphenyl)-4-carboxylate[xv] **3l**



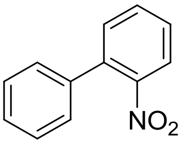
3l

The residue was purified by silica gel flash chromatography (80/20:cyclohexane/diethyl ether) affording **3l** as a white solid (*conditions R:* 46.5 mg, 55% yield; *conditions A:* 31.3 mg, 37% yield).

^{1}H NMR (300MHz, $CDCl_3$): 8.08 (d, *J*=8.2 Hz, 2H), 7.77 (d, *J*=8.12 Hz, 2H), 7.59 (d, *J*=8.1 Hz, 2H), 7.33 (d, *J*=8.2 Hz, 2H), 3.92 (s, 3H).

^{13}C NMR (75MHz, $CDCl_3$): 166.7, 144.3, 137.9, 130.0, 129.1, 128.9, 127.1, 126.9, 126.6, 94.0, 52.0.

2-Nitro-1,1'-biphenyl[xvi] 3m

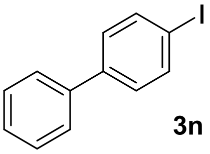

3m

The residue was purified by silica gel flash chromatography (80/20:cyclohexane/diethyl ether) affording **3m** as a yellow oil (*conditions R:* 20.4 mg, 41% yield; *conditions A:* 37.3 mg, 75% yield).

^{1}H NMR (300MHz, CDCl$_3$): 7.88-7.80 (m, 1H), 7.65-7.56 (m, 1H), 7.51-7.37 (m, 5H), 7.35-7.27 (m, 2H).

^{13}C NMR (75MHz, CDCl$_3$): 137.6, 136.5, 132.5, 132.5, 128.9, 128.4, 128.1, 124.3.

4-Iodo-1,1'-biphenyl[xvii] 3n

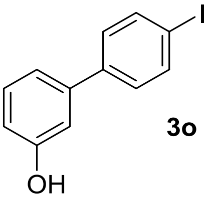

3n

The residue was purified by silica gel flash chromatography (cyclohexane) affording **3n** as a white solid (*conditions R:* 23.1 mg, 33% yield; *conditions A:* 32.9 mg, 47% yield).

^{1}H NMR (300MHz, CDCl$_3$): 7.75 (d, *J*=8.4 Hz, 2H), 7.57-7.50 (m, 2H), 7.47-7.29 (m, 5H).

^{13}C NMR (75MHz, CDCl$_3$): 141.0, 140.3, 138.3, 138.2, 138.1, 129.3, 129.2, 128.0, 127.2, 93.3.

4'-iodo-1,1'-biphenyl-3-ol[xviii] 3o

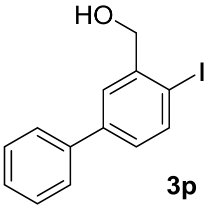

3o

The residue was purified by silica gel flash chromatography (60/40:cyclohexane/diethyl ether) affording **3o** as a white solid (*conditions R:* 35 mg, 47% yield; *conditions A:* 22 mg, 30% yield).

^{1}H NMR (300MHz, CDCl$_3$): 7.73 (d, *J*=8.4 Hz, 2H), 7.32-7.25 (m, 3H), 7.12-7.07 (m, 1H), 7.01-6.99 (m, 1H), 6.81 (dd, *J* = 2.6, 8.1 Hz, 1H).

^{13}C NMR (75MHz, CDCl$_3$): 156.1, 141.9, 140.3, 138.0, 132.7, 130.3, 129.1, 124.7, 120.6, 114.8, 114.0, 93.4.

2-Iodo-5-phenylbenzylalcohol 3p



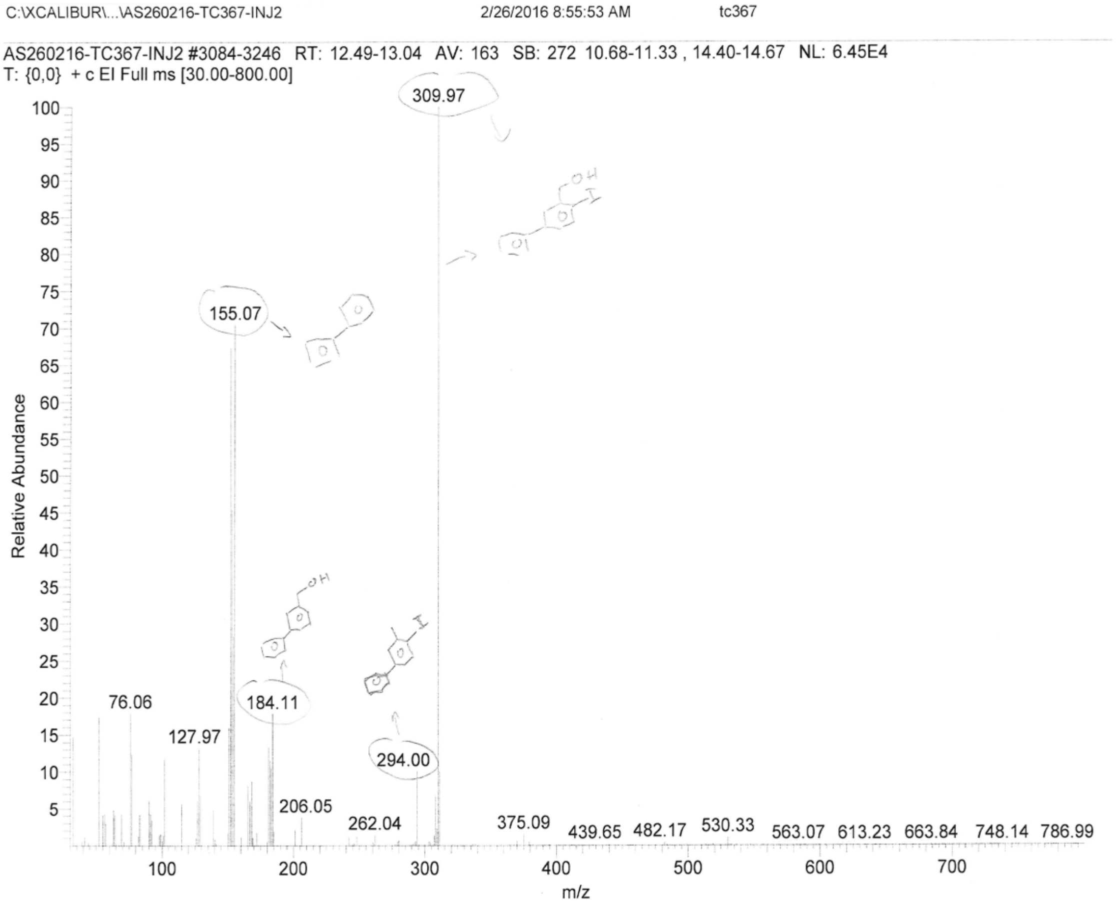
3p

The residue was purified by silica gel flash chromatography (80/20:cyclohexane/diethyl ether) affording **3p** as a white solid (*conditions R:* 38.7 mg, 50% yield; *conditions A:* 38.8 mg, 50% yield, *Felpin's conditions (Pd):* 5.5 mg, 6 % yield).

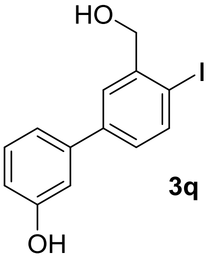
^{1}H NMR (300MHz, CDCl$_3$): 7.90 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 2.5 Hz, 1H), 7.63-7.57 (m, 2H), 7.52-7.40 (m, 3H), 7.27-7.21 (m, 1H), 7.71 (d, *J* = 2.5 Hz, 2H), 2.05 (t, *J* = 2.5 Hz, 1H).

^{13}C NMR (75MHz, CDCl$_3$): 143.2, 142.0, 140.2, 139.8, 129.2, 128.2, 127.5, 127.2, 96.2, 69.6.

MS (EI) $C_{13}H_{11}IO$, calculated for [M$^+$]: 309.98, found 309.97.



3'-(Hydroxymethyl)-4'-iodo-1,1'-biphenyl-3-ol 3q



3q

The residue was purified by silica gel flash chromatography (50/50:cyclohexane/diethyl ether) affording **3q** as a white solid (*conditions R:* 37 mg, 47% yield; *conditions A:* 24 mg, 29% yield; *Felpin's conditions (Pd):* 15 mg, 15% yield).

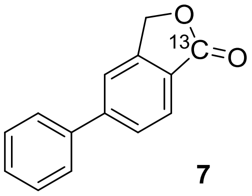
^{1}H NMR (300MHz, $CDCl_3$): 7.85 (d, *J* = 8.26 Hz, 1H); 7.65 (d, *J* = 2.33 Hz, 1H); 7.32-7.25 (m, 1H); 7.21-7.16 (m, 1H); 7.15-7.11 (m, 1H); 7.04-7.01 (m, 1H); 6.84-6.79 (m, 1H); 4.72 (s, 2H)/

^{13}C NMR (75MHz, $CDCl_3$):160.5, 155.8, 143.0, 139.3, 130.0, 127.7, 126.9, 119.3, 114.5, 113.7, 96.0, 69.5.

MS (FD+{eiFi}) $C_{13}H_{11}IO_2$, calculated for [M^+]: 325.9804, found 325.9809.

1-^{13}C-5-Phenylisobenzofuran-1(3H)-one 7

White solid.



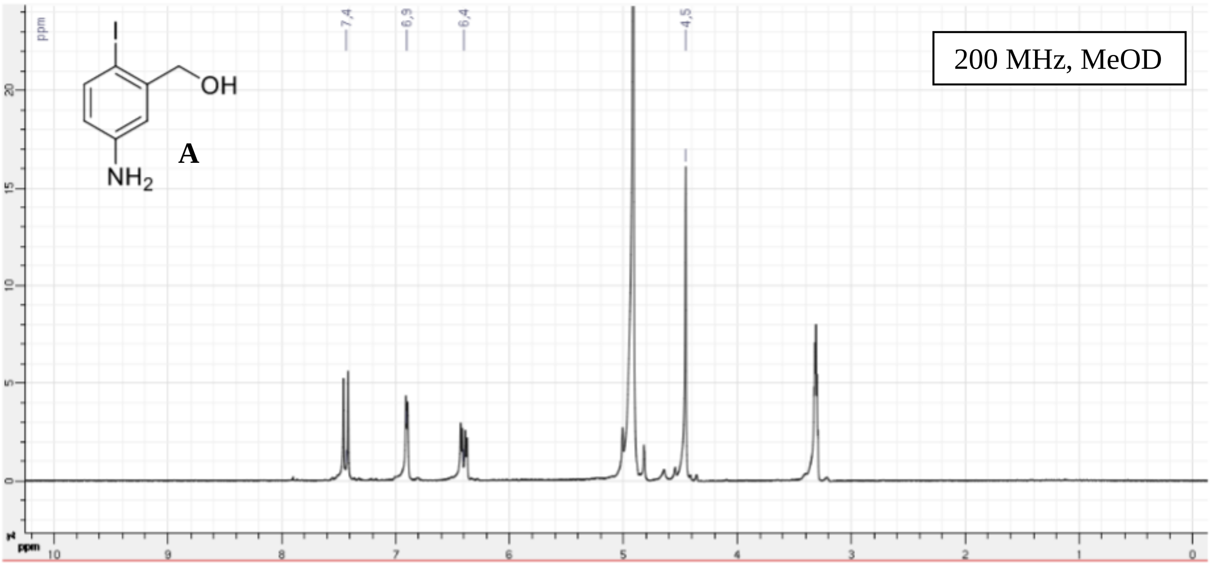
7

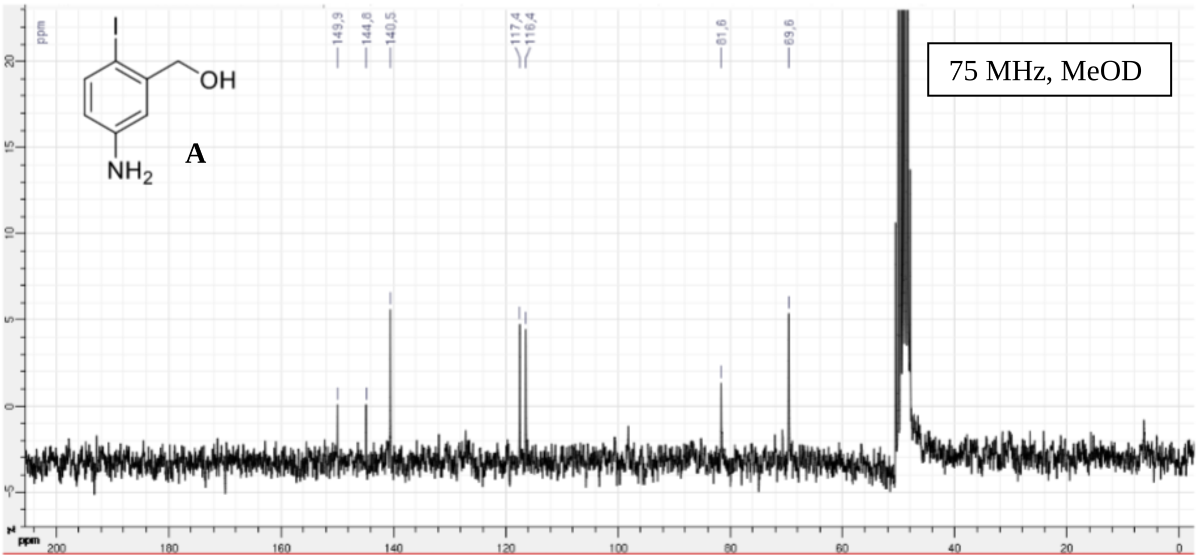
^{1}H NMR (300MHz, $CDCl_3$): 7.96 (dd, *J*=8.0 Hz, 2.7 Hz, 1H), 7.72 (d, *J*=8.0 Hz, 1H), 7.65 (s, 1H), 7.62-7.58 (m, 2H), 7.51-7.41 (m, 3H), 5.35 (d, *J*=2.1 Hz, 2H).

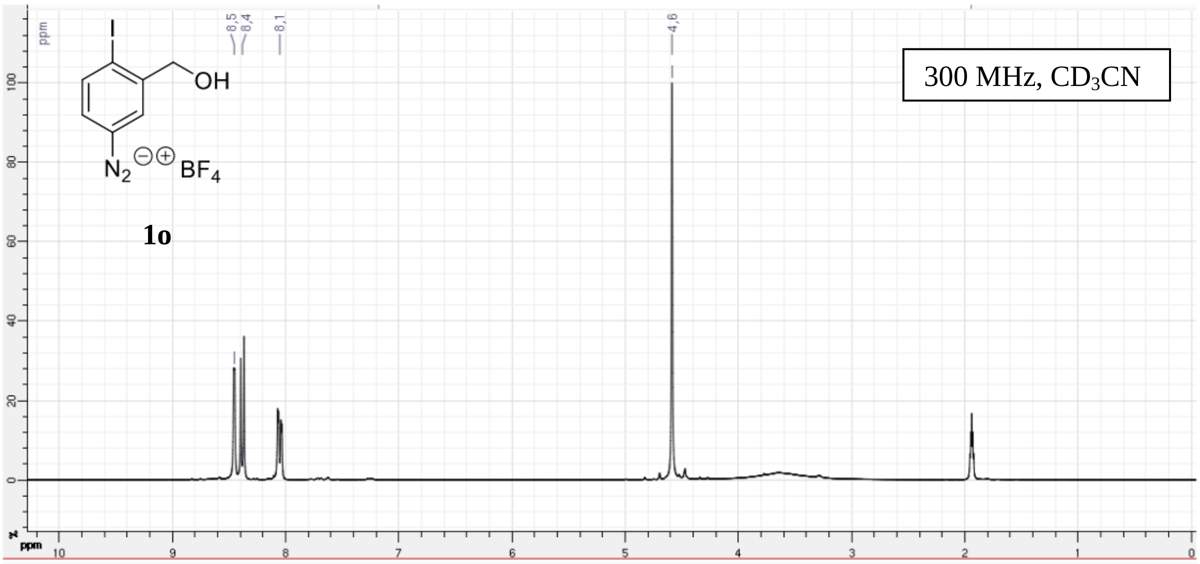
^{13}C NMR (75MHz, $CDCl_3$): 171.2 (^{13}C-enriched), 147.6, 129.3, 128.8, 128.7, 128.6, 127.7, 126.3, 126.2, 120.8, 120.8, 69.8.

HRMS (IC) $C_{13}{}^{13}CH_{10}O_2$, calculated for [M^+]: 211.0714, found: 211.0719.

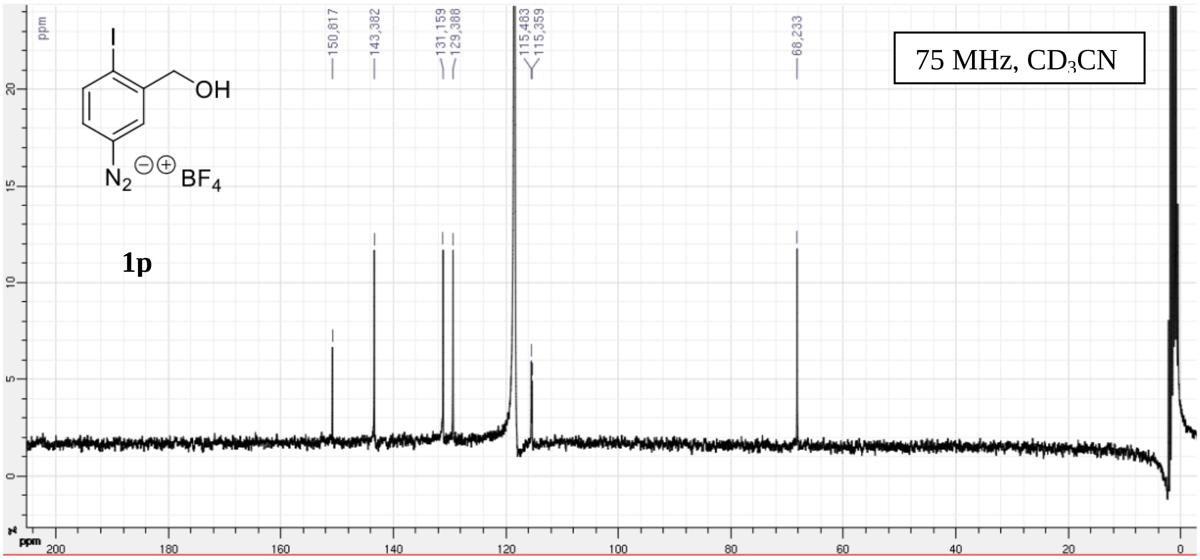
D) ^{1}H and ^{13}C NMR Spectra



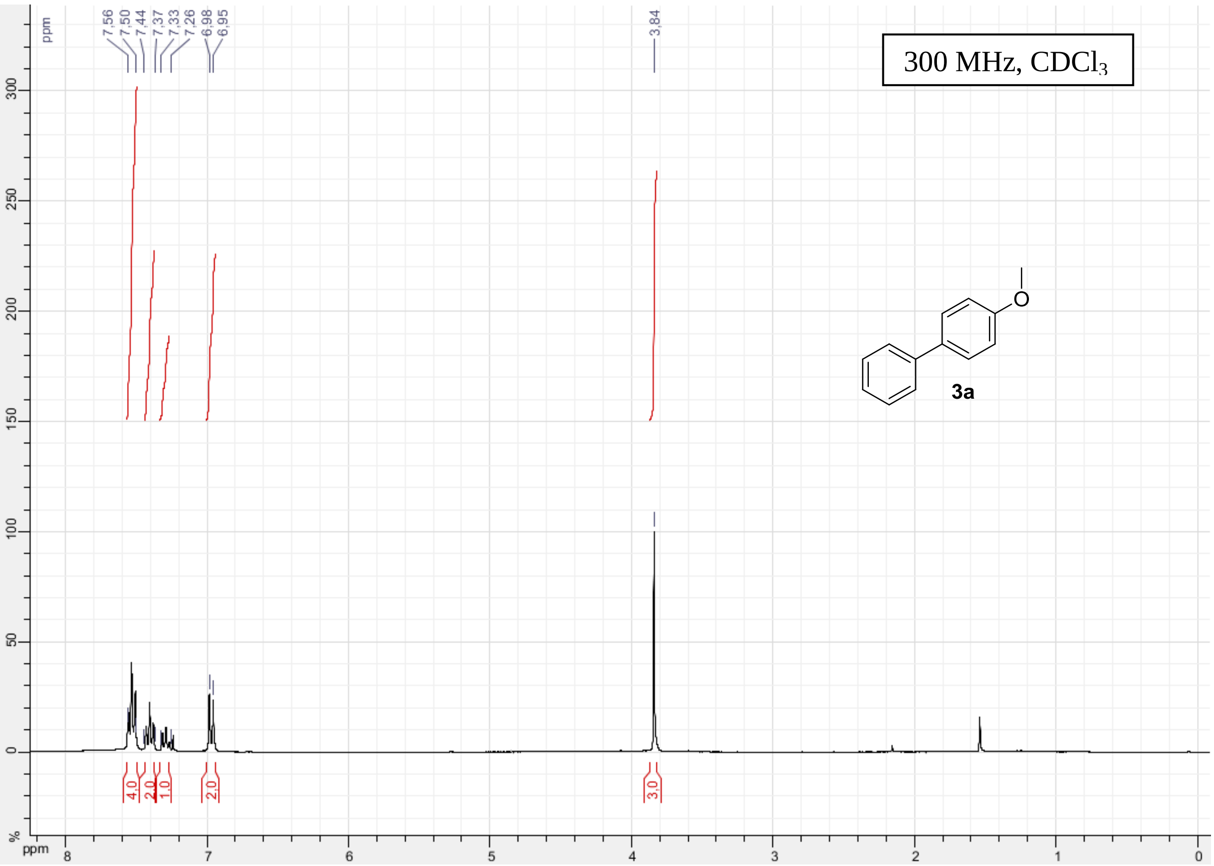


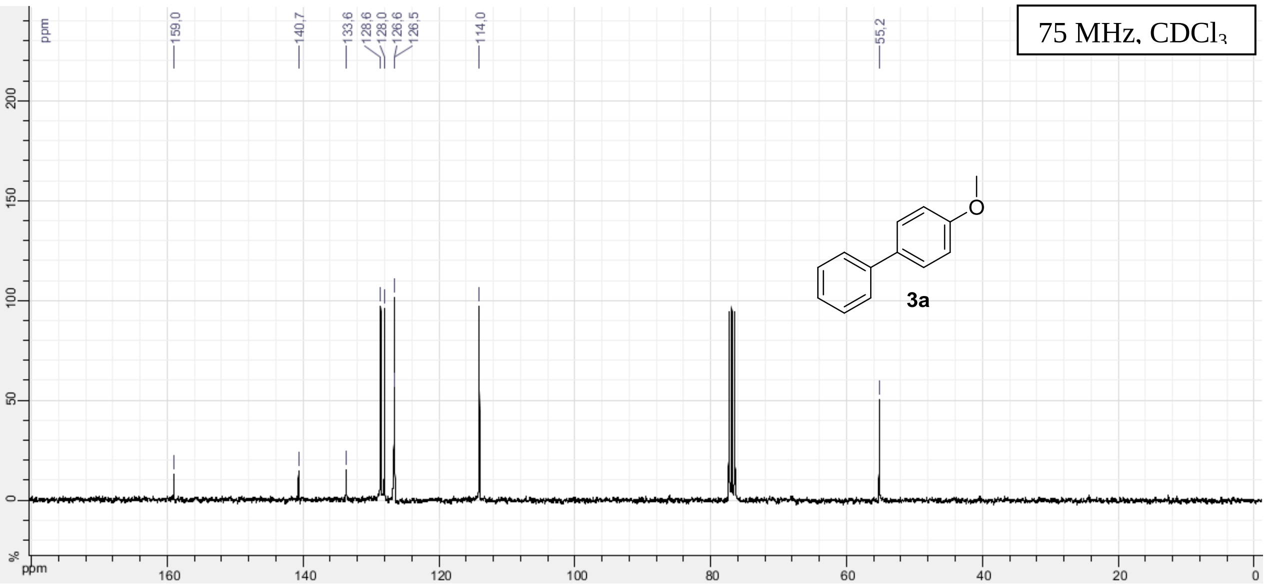

300 MHz, CD$_3$CN
I
OH
$N_2^{\ominus\oplus}BF_4$
8,5
8,4
8,1
4,6
ppm
100
80
60
40
20
0
ppm 10 9 8 7 6 5 4 3 2 1 0

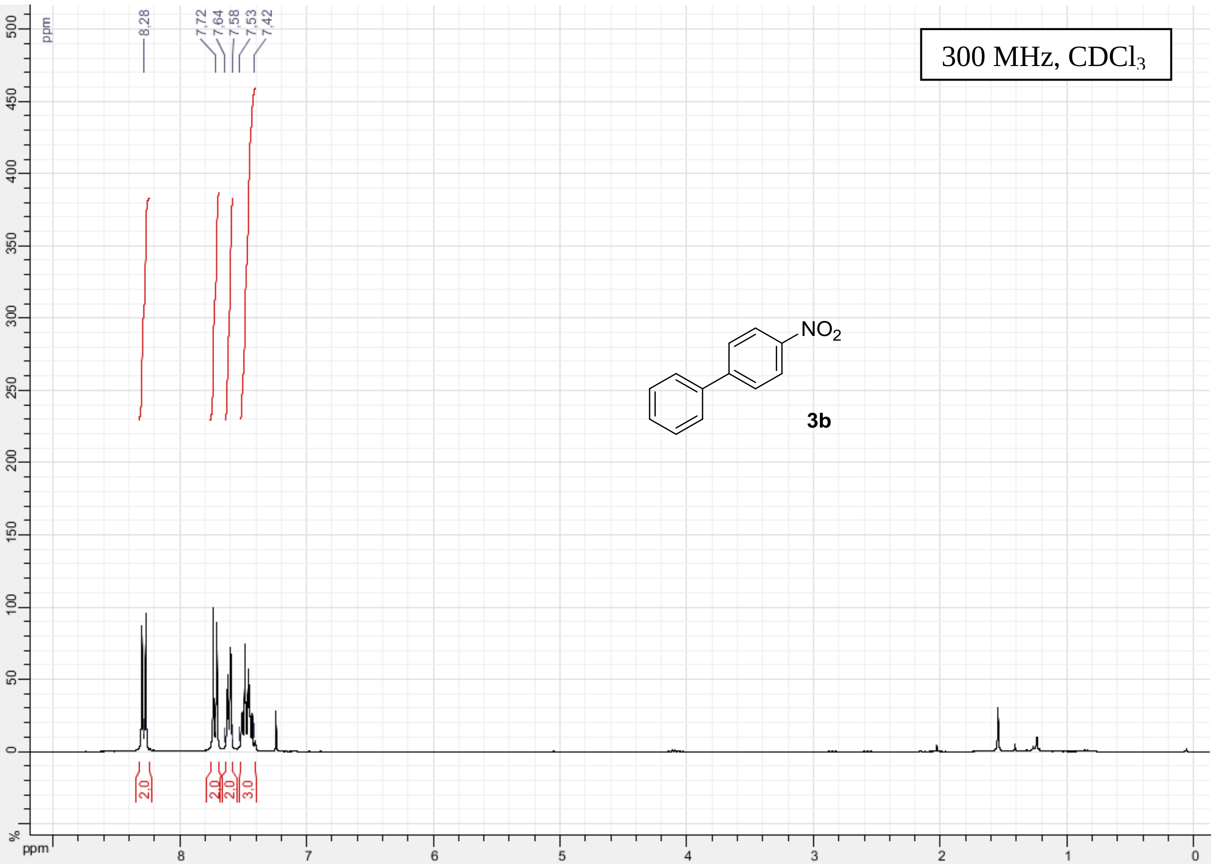
1o

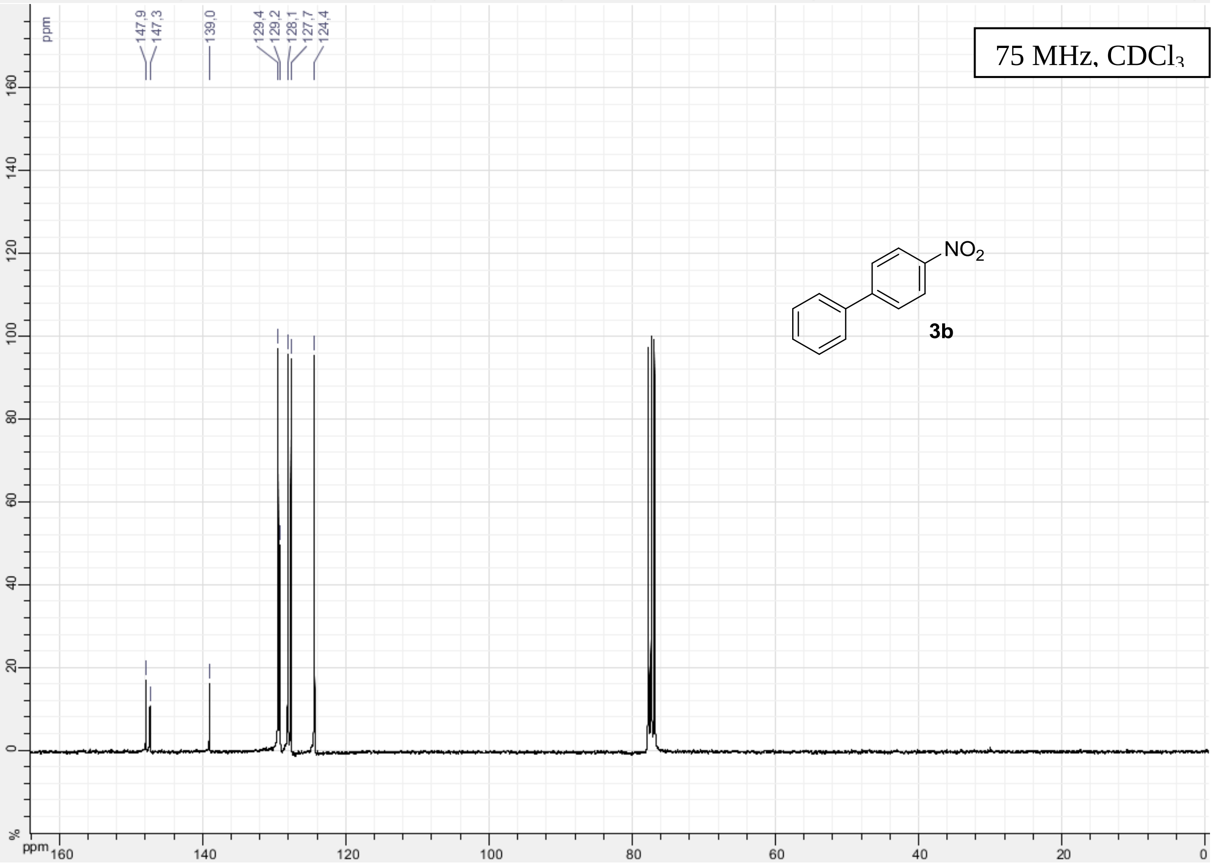

75 MHz, CD$_3$CN
I
OH
$N_2^{\ominus\oplus}BF_4$
150,817
143,382
131,159
129,388
115,483
115,359
68,233
ppm
20
15
10
5
0
ppm 200 180 160 140 120 100 80 60 40 20 0

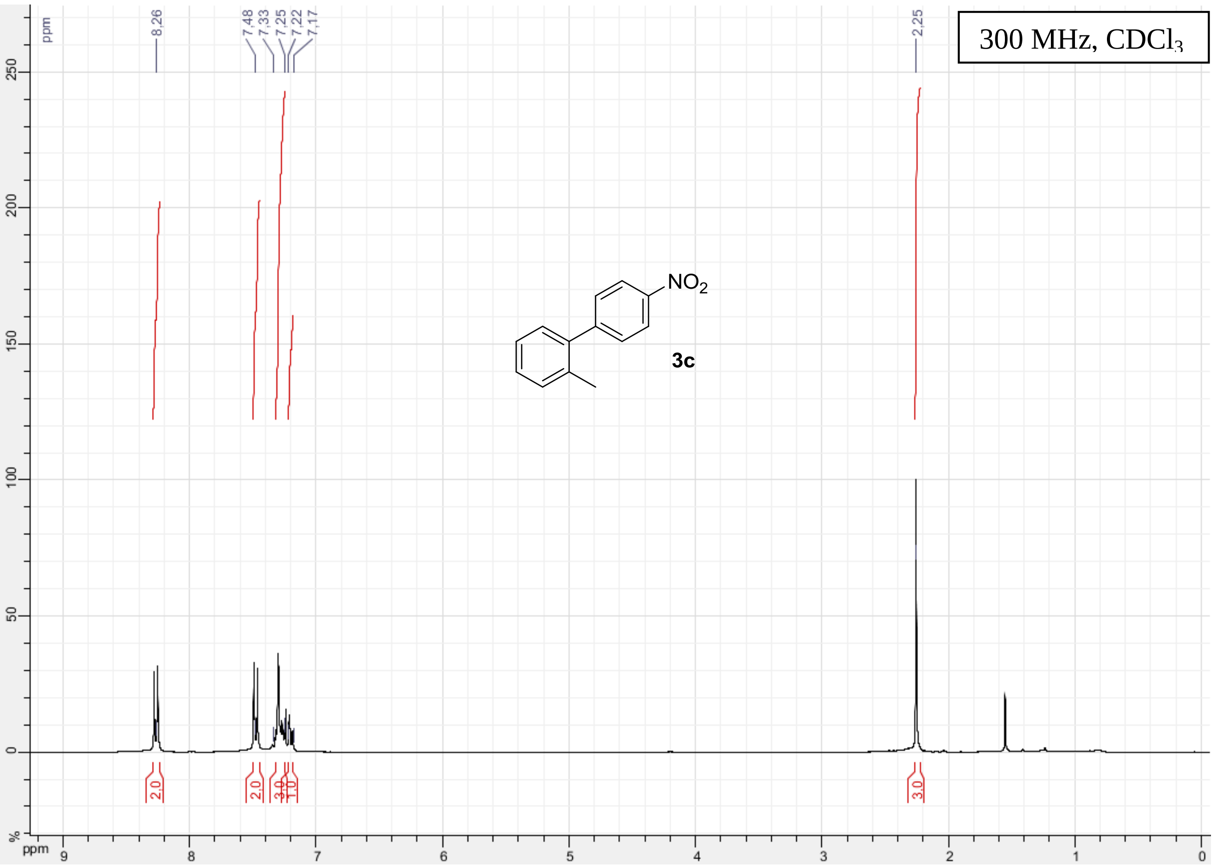
1p

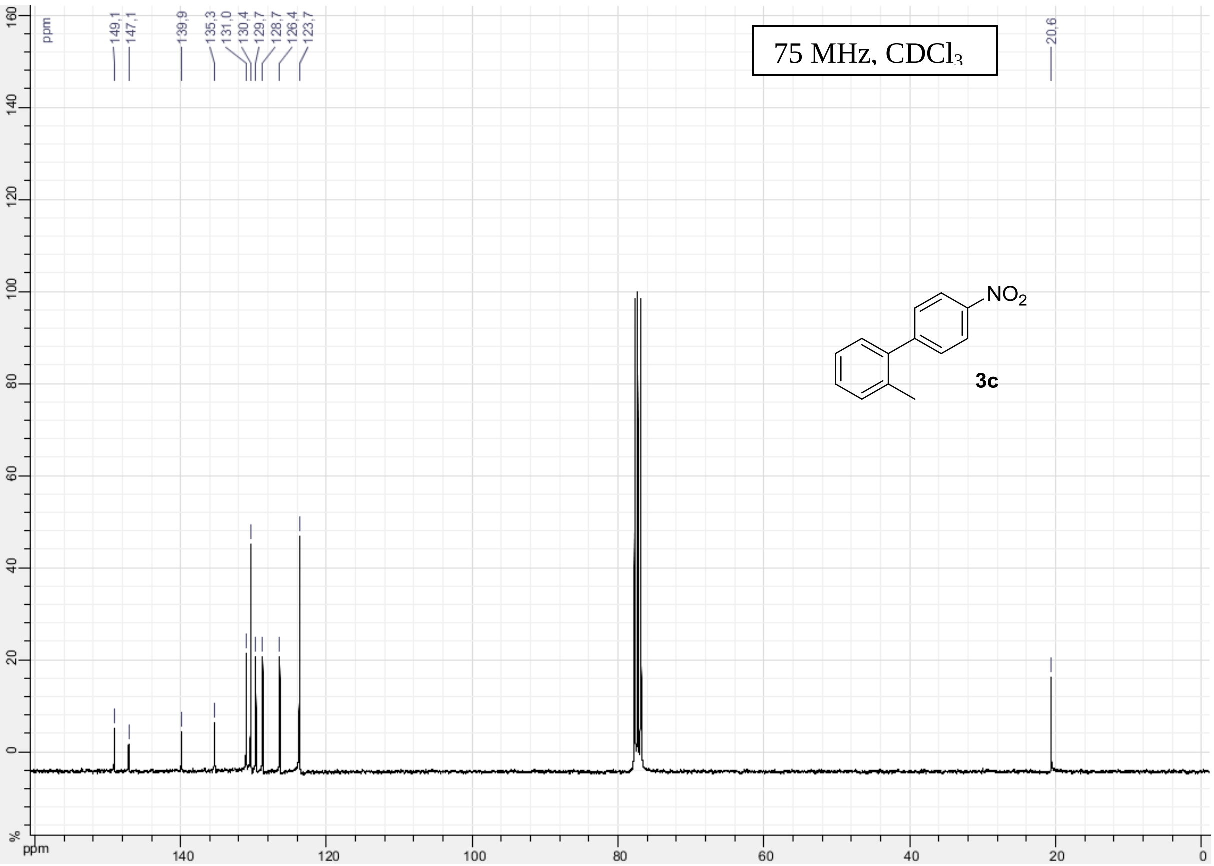

ppm
7,56
7,50
7,44
7,37
7,33
7,26
6,98
6,95
3,84
300 MHz, CDCl3
O
3a
4,0
2,0
1,0
2,0
3,0
300
250
200
150
100
50
0
%
ppm
8
7
6
5
4
3
2
1
0

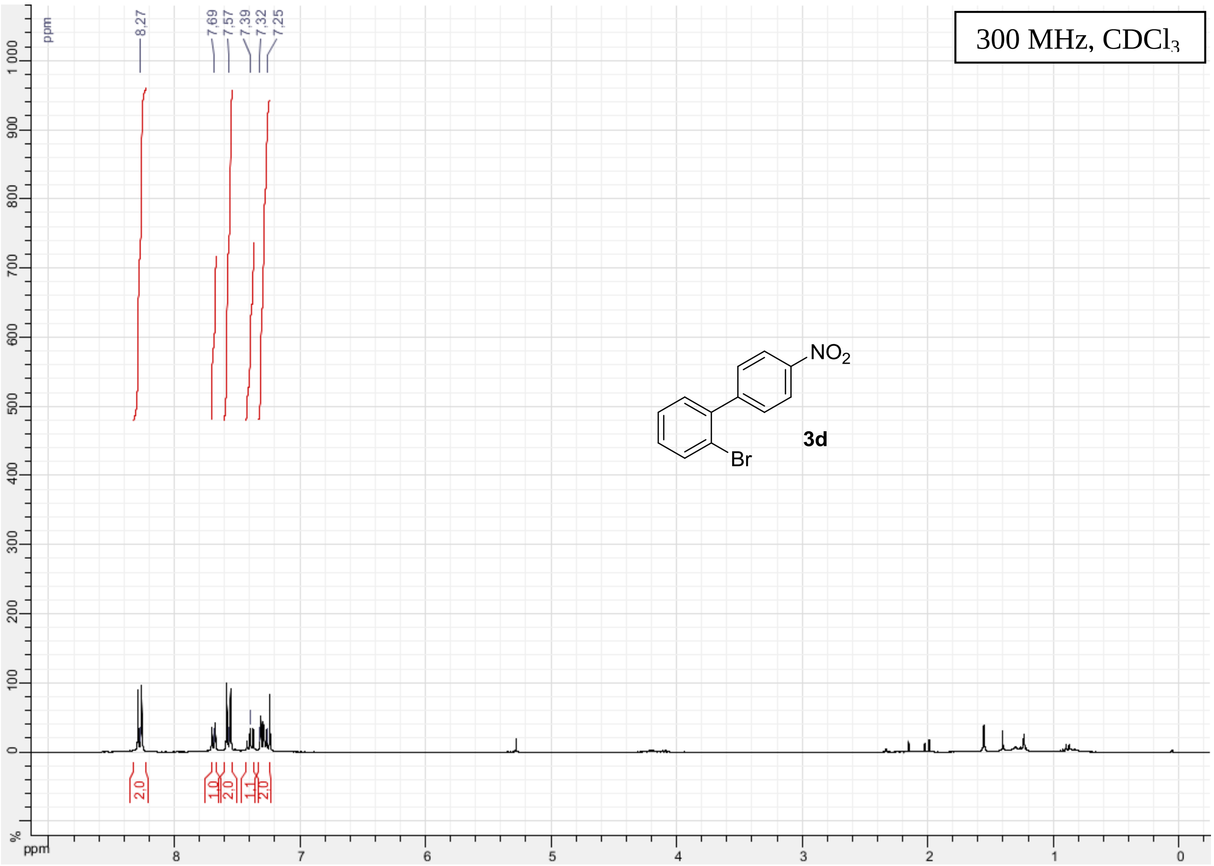

ppm
159,0
140,7
133,6
128,6
128,0
126,6
126,5
114,0
55,2
75 MHz, CDCl3
O
3a
200
150
100
50
0
%
ppm
160
140
120
100
80
60
40
20
0


300 MHz, CDCl3
8,28
7,72
7,64
7,58
7,53
7,42
2,0
2,0
2,0
3,0
NO2
3b
ppm
%
500
450
400
350
300
250
200
150
100
50
0
8
7
6
5
4
3
2
1
0

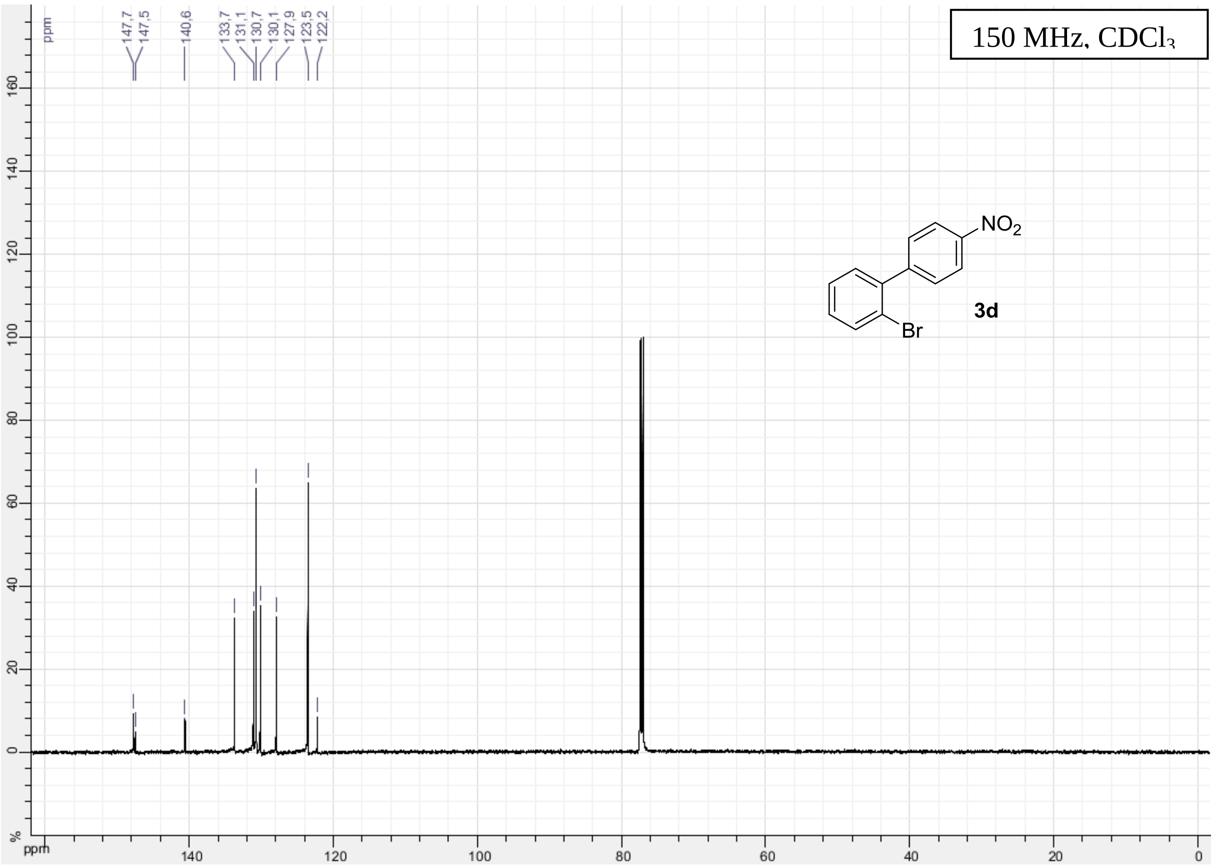

75 MHz, CDCl3
147,9
147,3
139,0
129,4
129,2
128,1
127,7
124,4
NO2
3b
ppm
%
160
140
120
100
80
60
40
20
0


300 MHz, CDCl$_3$
ppm
8,26
7,48
7,33
7,25
7,22
7,17
2,25
2,0
2,0
3,0
1,0
3,0
NO$_2$
3c
250
200
150
100
50
0
%
ppm
9
8
7
6
5
4
3
2
1
0

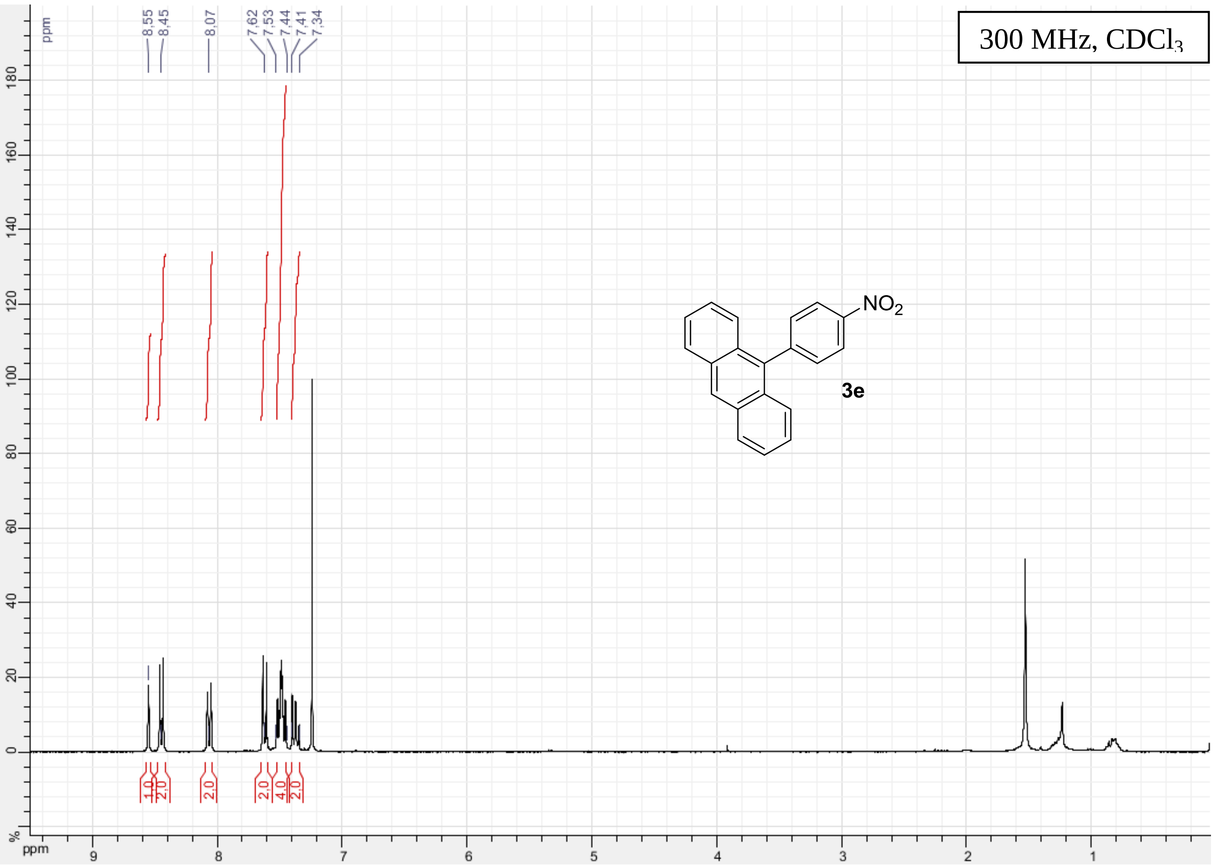

75 MHz, CDCl$_3$
ppm
149,1
147,1
139,9
135,3
131,0
130,4
129,7
128,7
126,4
123,7
20,6
NO$_2$
3c
160
140
120
100
80
60
40
20
0
%
ppm
140
120
100
80
60
40
20
0



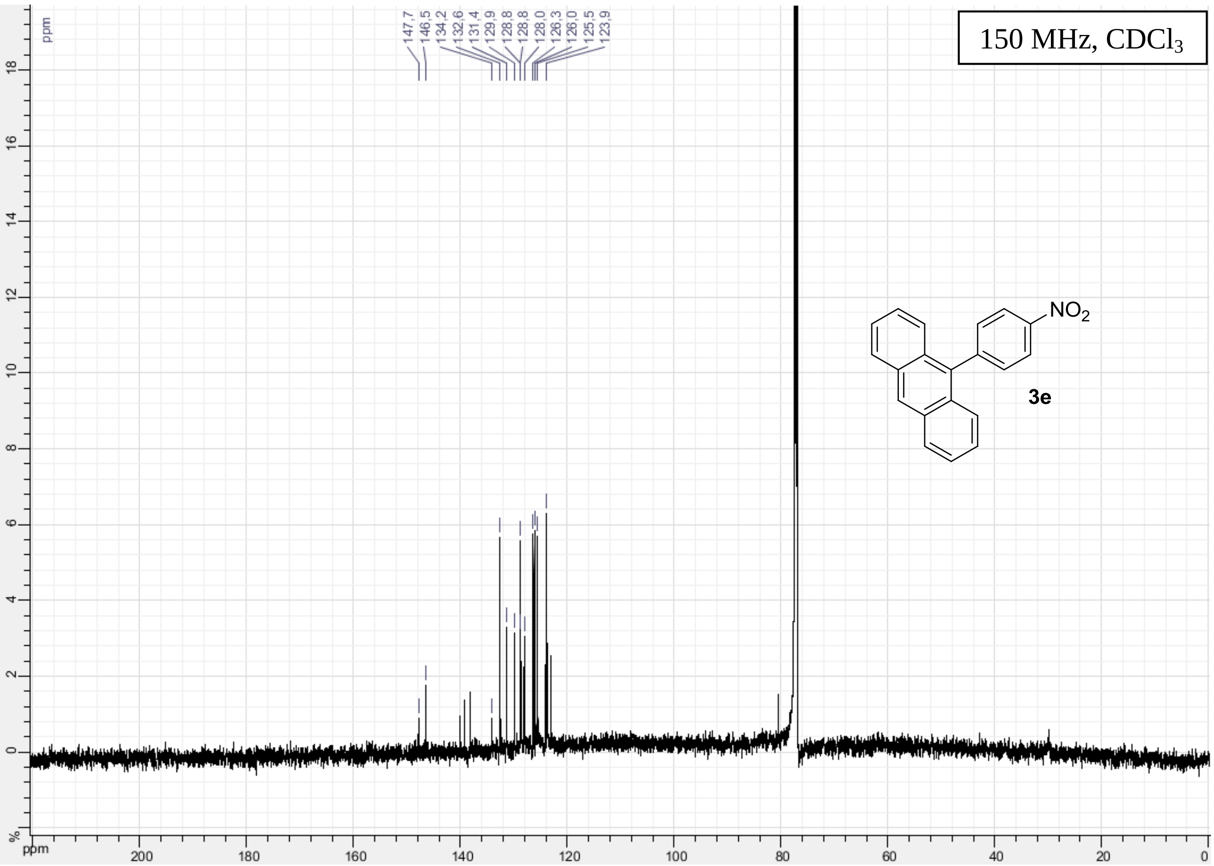
300 MHz, CDCl3
ppm
8.27
7.69
7.57
7.39
7.32
7.25
2.0
1.0
2.0
1.1
2.0
NO2
Br
3d
%
ppm
8
7
6
5
4
3
2
1
0
1 000
900
800
700
600
500
400
300
200
100
0



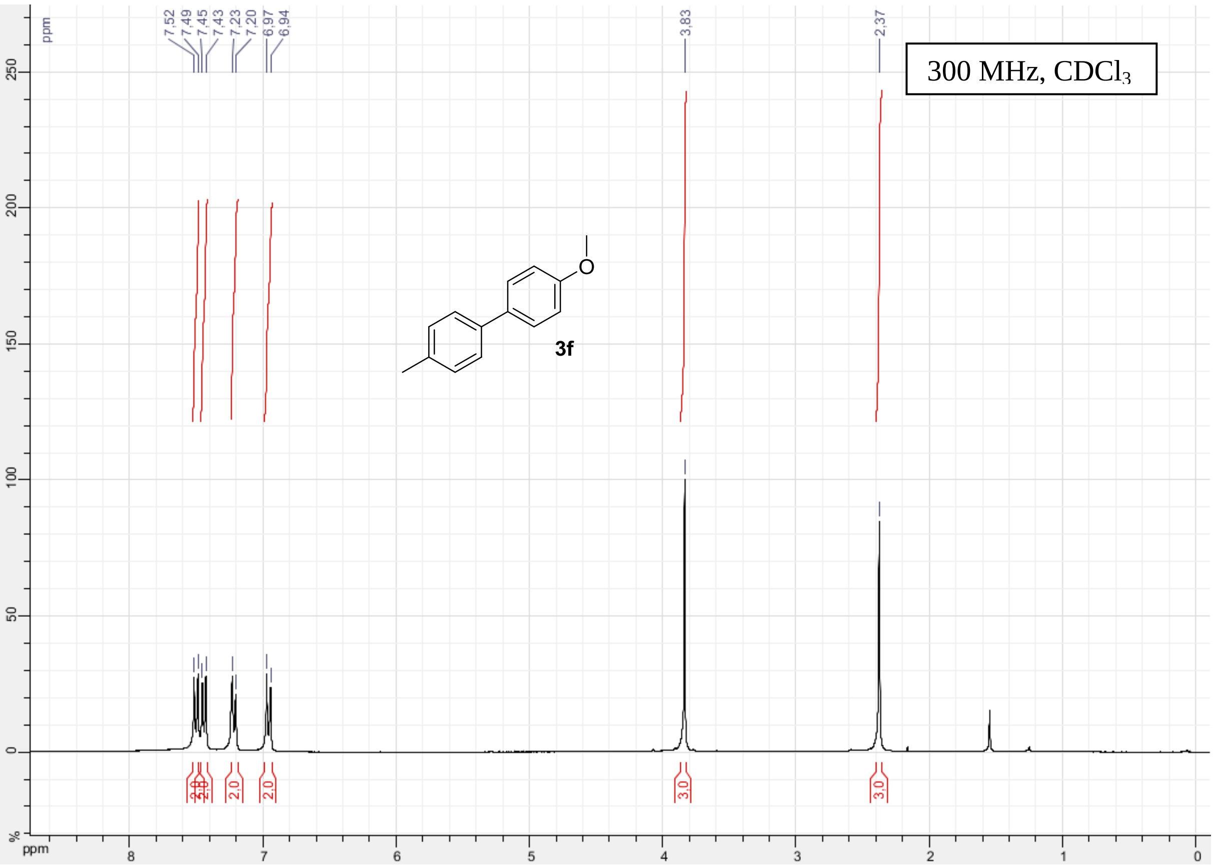
150 MHz, CDCl3
ppm
147.7
147.5
140.6
133.7
131.1
130.7
130.1
127.9
123.5
122.2
NO2
Br
3d
%
ppm
140
120
100
80
60
40
20
0
160
140
120
100
80
60
40
20
0

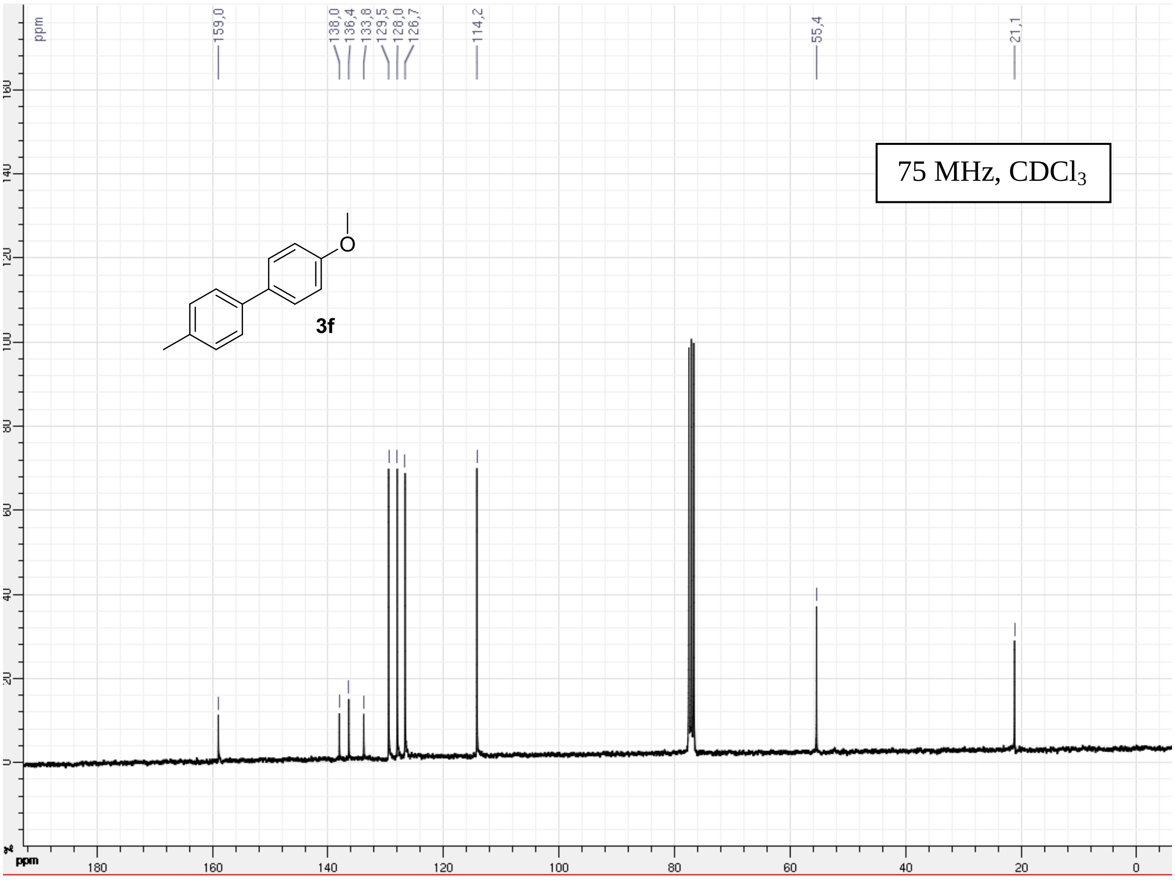


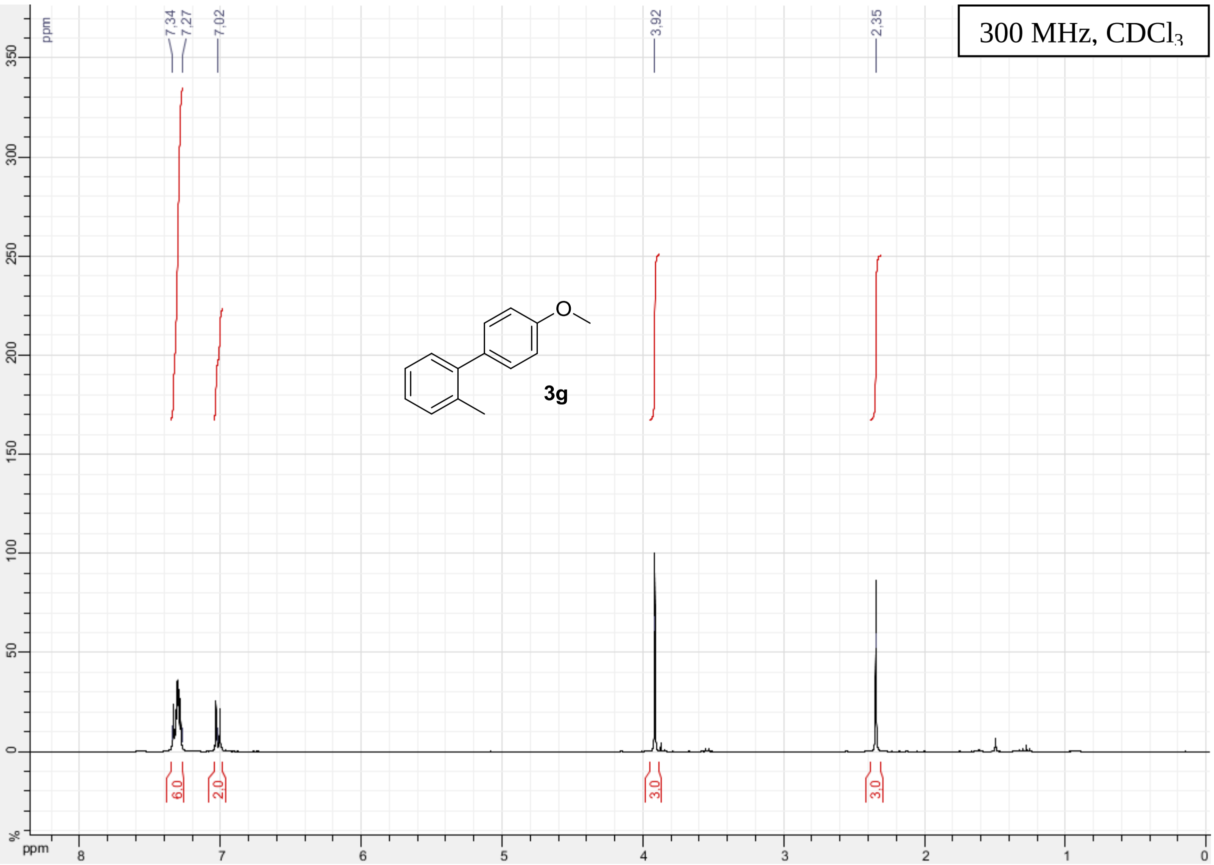
300 MHz, CDCl3
NO2
3e
8,55
8,45
8,07
7,62
7,53
7,44
7,41
7,34
1,0
2,0
2,0
2,0
4,0
2,0
ppm
%
0
20
40
60
80
100
120
140
160
180
9
8
7
6
5
4
3
2
1

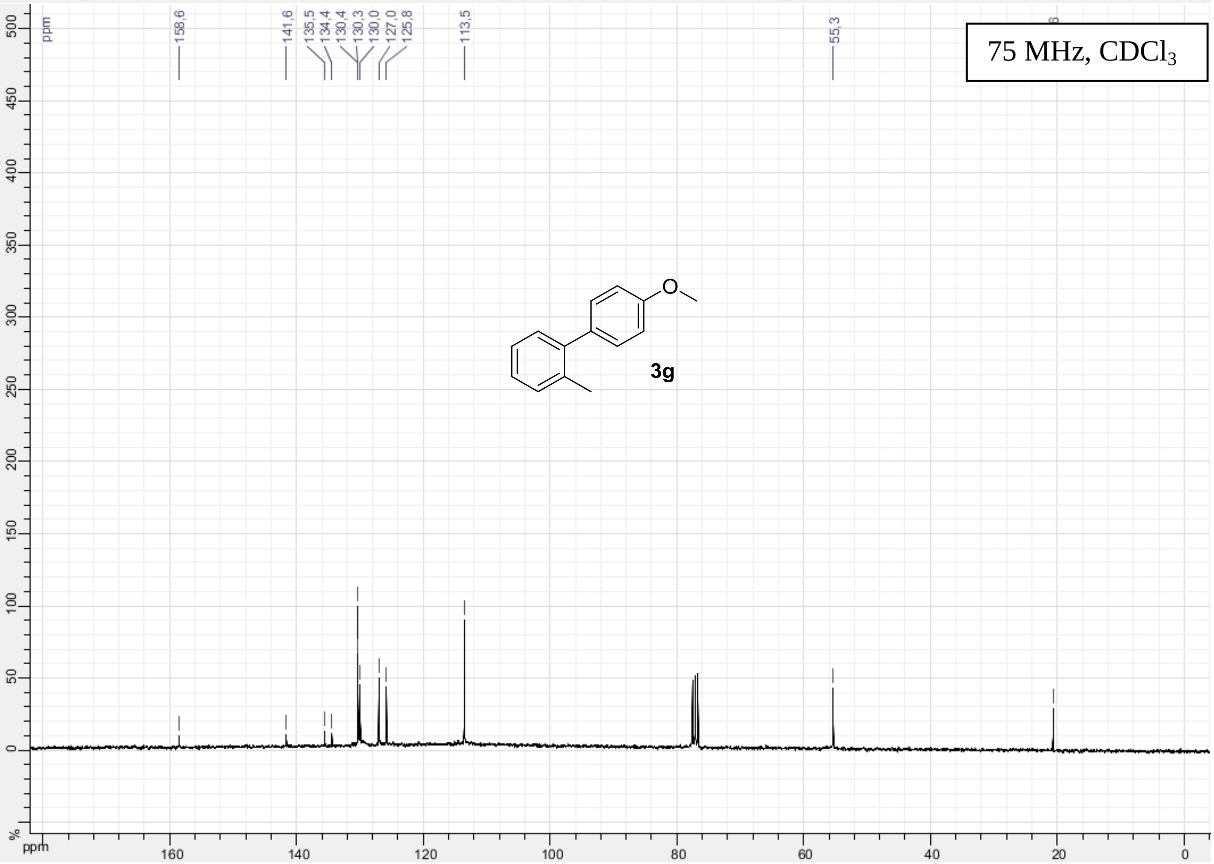


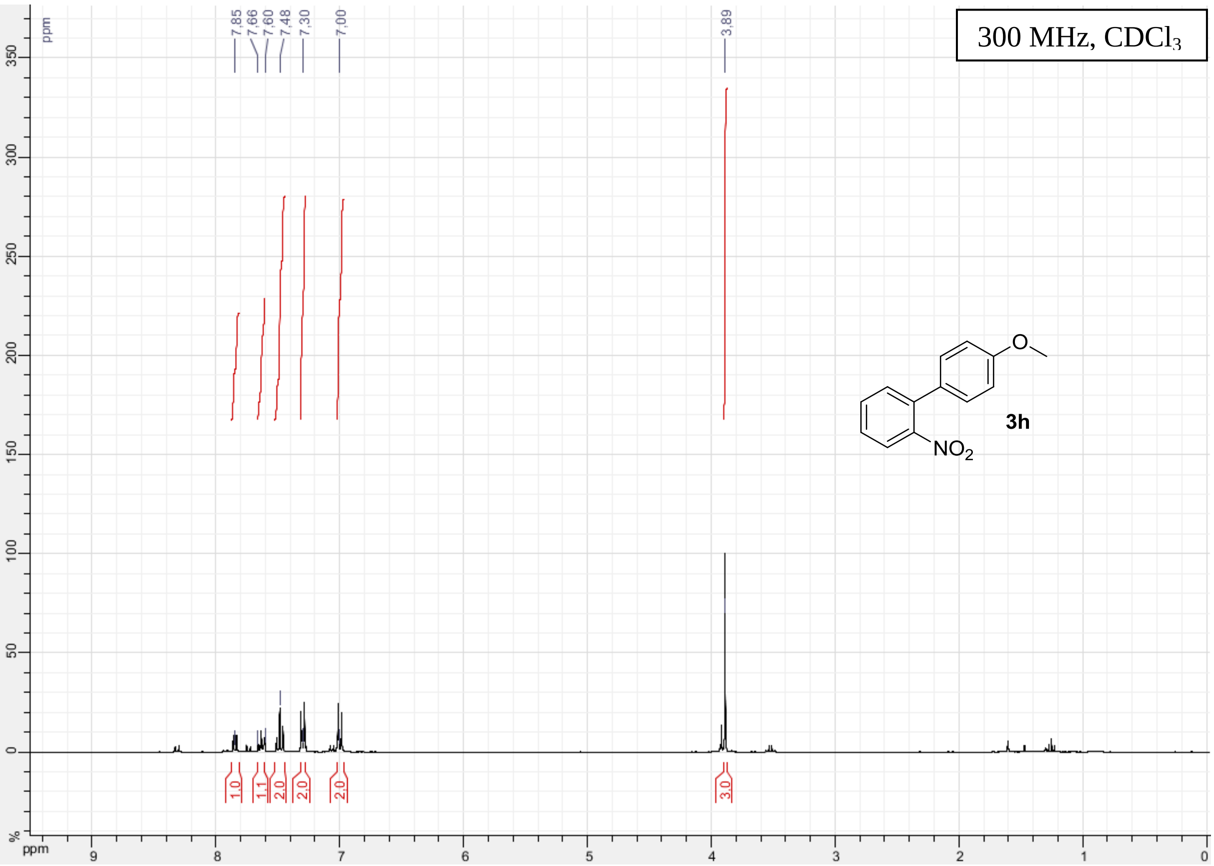
150 MHz, CDCl3
NO2
3e
147,7
146,5
134,2
132,6
131,4
129,9
128,8
128,8
128,0
126,3
126,0
125,5
123,9
ppm
%
0
2
4
6
8
10
12
14
16
18
200
180
160
140
120
100
80
60
40
20
0

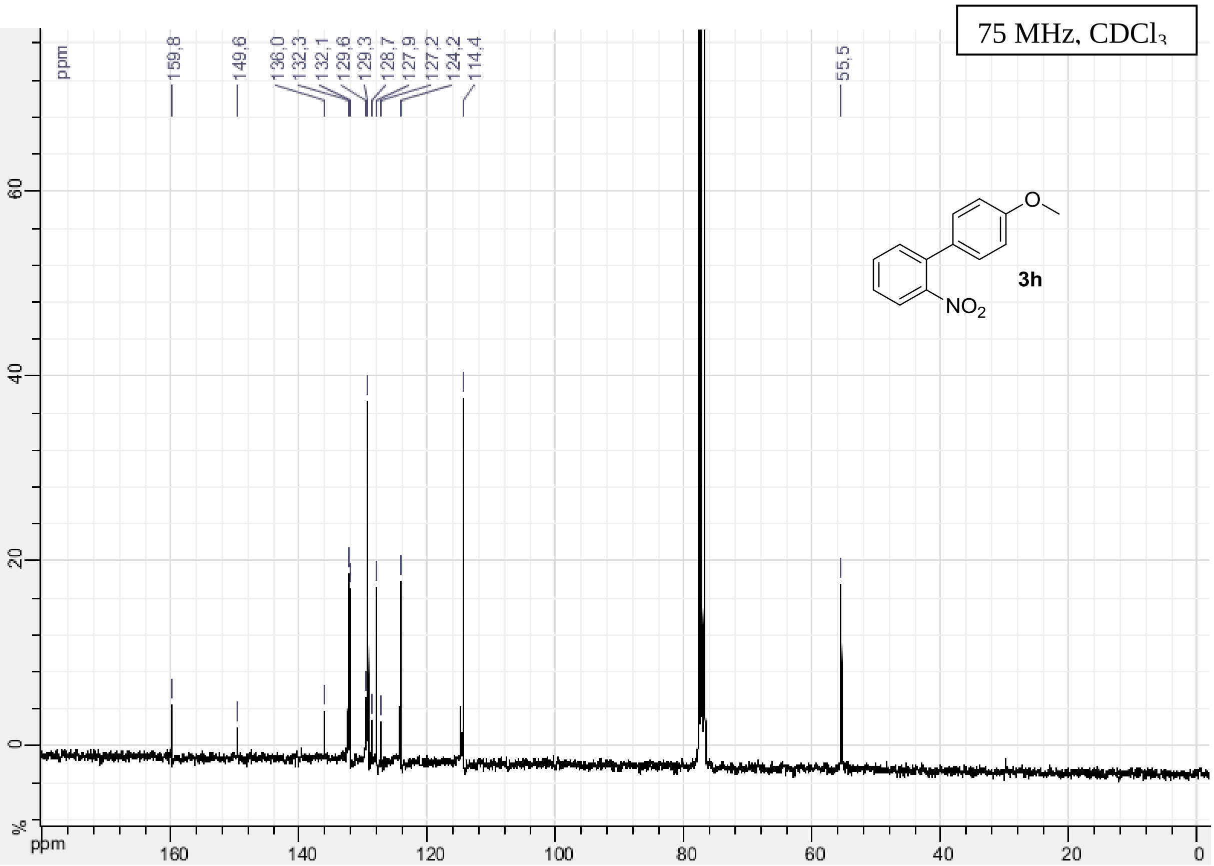

300 MHz, CDCl$_3$
3f
ppm
7,52
7,49
7,45
7,43
7,23
7,20
6,97
6,94
3,83
2,37
2,0
2,0
2,0
2,0
3,0
3,0
250
200
150
100
50
0
%
8
7
6
5
4
3
2
1
0

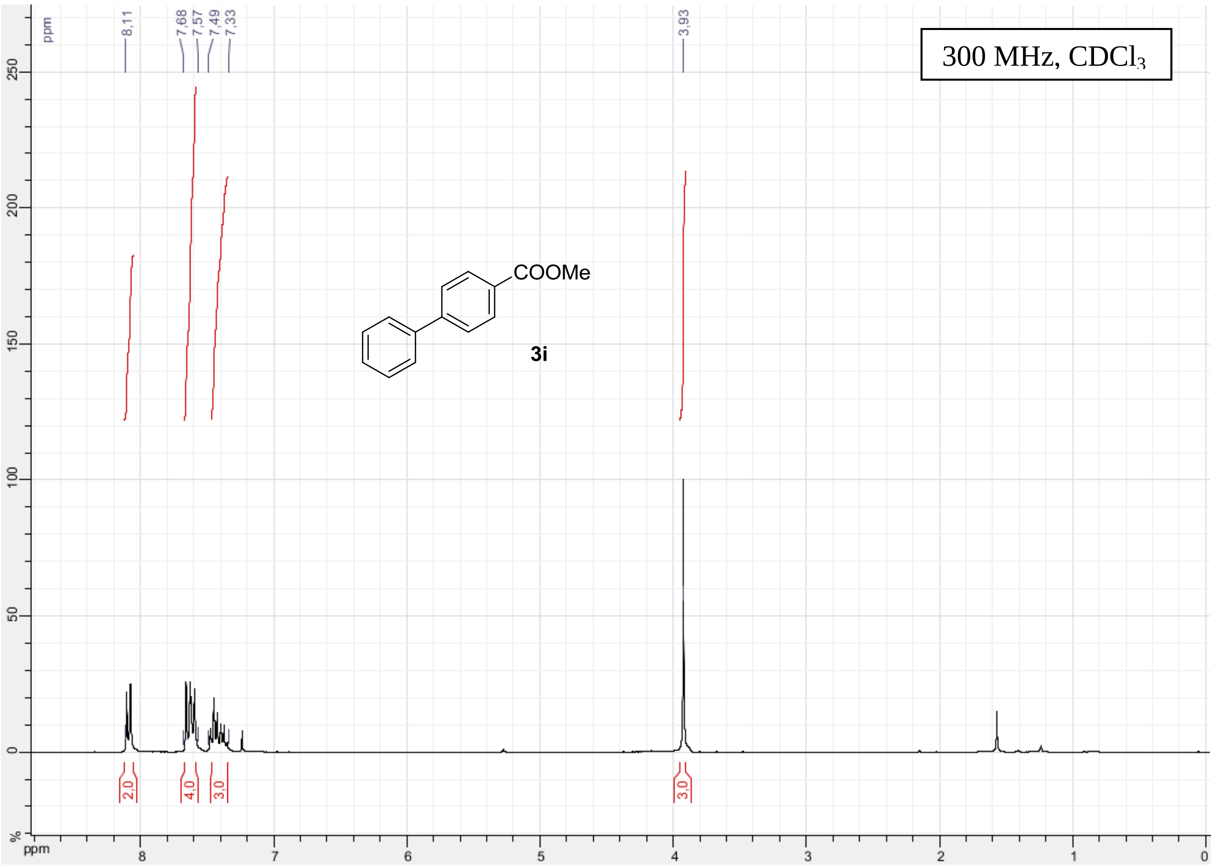

75 MHz, CDCl$_3$
3f
ppm
159,0
138,0
136,4
133,8
129,5
128,0
126,7
114,2
55,4
21,1
160
140
120
100
80
60
40
20
0
%
180
160
140
120
100
80
60
40
20
0


300 MHz, CDCl$_3$
ppm
7,34
7,27
7,02
3,92
2,35
O
3g
6,0
2,0
3,0
3,0
350
300
250
200
150
100
50
0
%
ppm
8
7
6
5
4
3
2
1
0

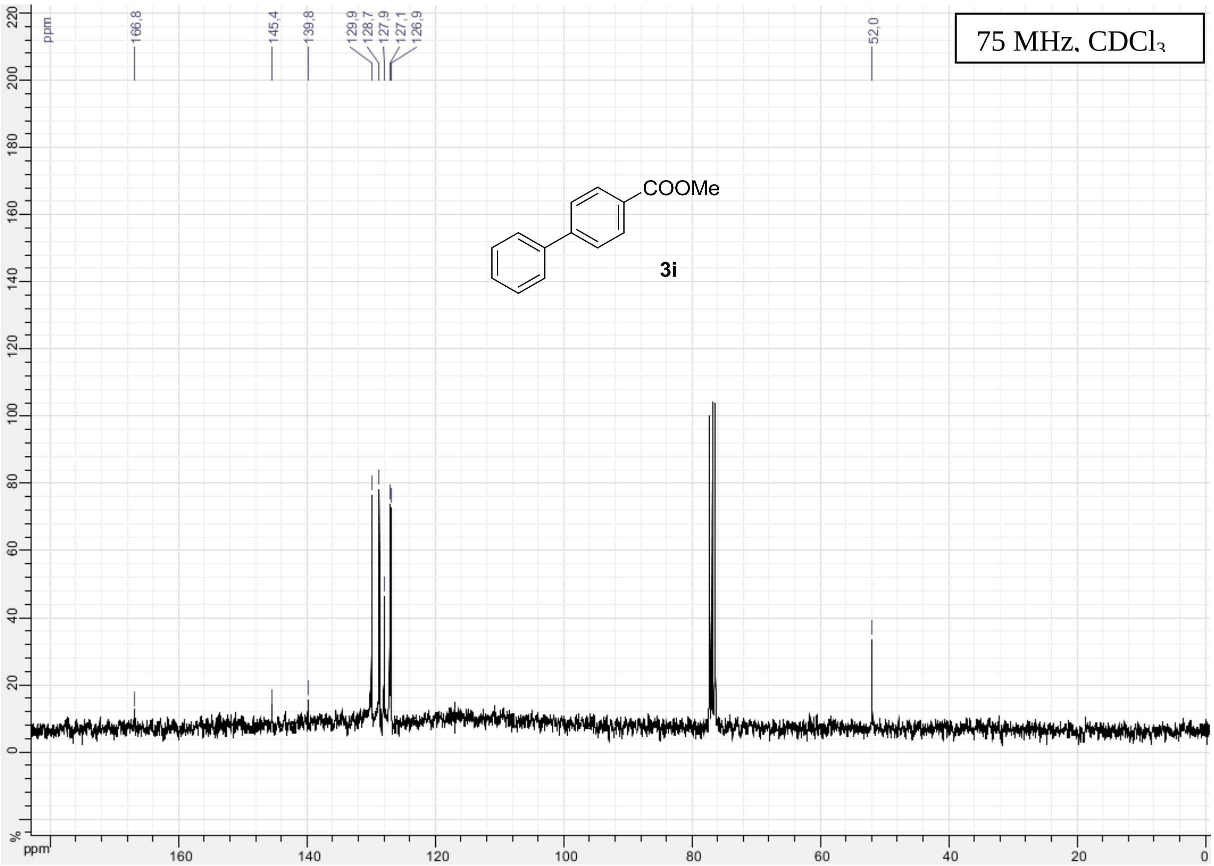

75 MHz, CDCl$_3$
ppm
158,6
141,6
135,5
134,4
130,4
130,3
130,0
127,0
125,8
113,5
55,3
O
3g
500
450
400
350
300
250
200
150
100
50
0
%
ppm
160
140
120
100
80
60
40
20
0


300 MHz, CDCl$_3$
ppm
7,85
7,66
7,60
7,48
7,30
7,00
3,89
1,0
1,1
2,0
2,0
2,0
3,0
350
300
250
200
150
100
50
0
%
ppm
9
8
7
6
5
4
3
2
1
0
O
NO$_2$
3h

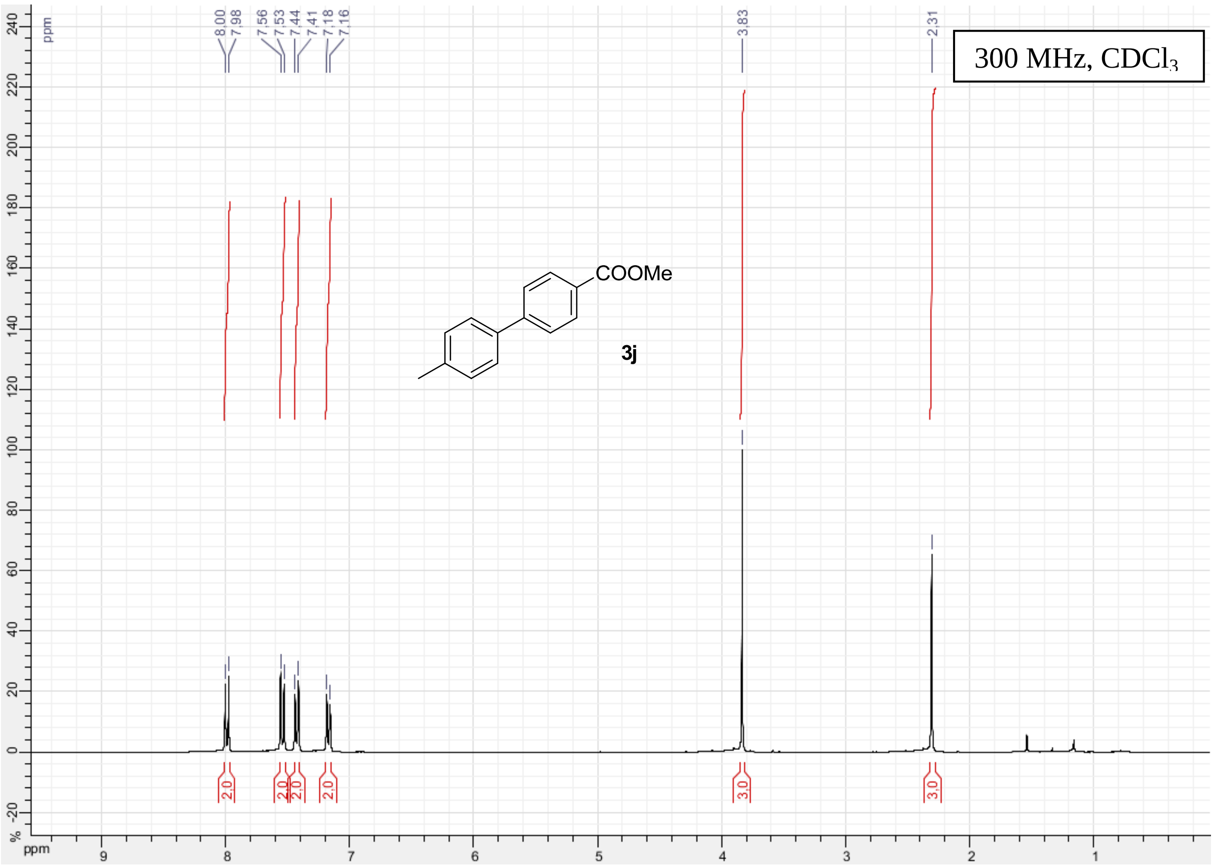

75 MHz, CDCl$_3$
ppm
159,8
149,6
136,0
132,3
132,1
129,6
129,3
128,7
127,9
127,2
124,2
114,4
55,5
60
40
20
0
%
ppm
160
140
120
100
80
60
40
20
0
O
NO$_2$
3h

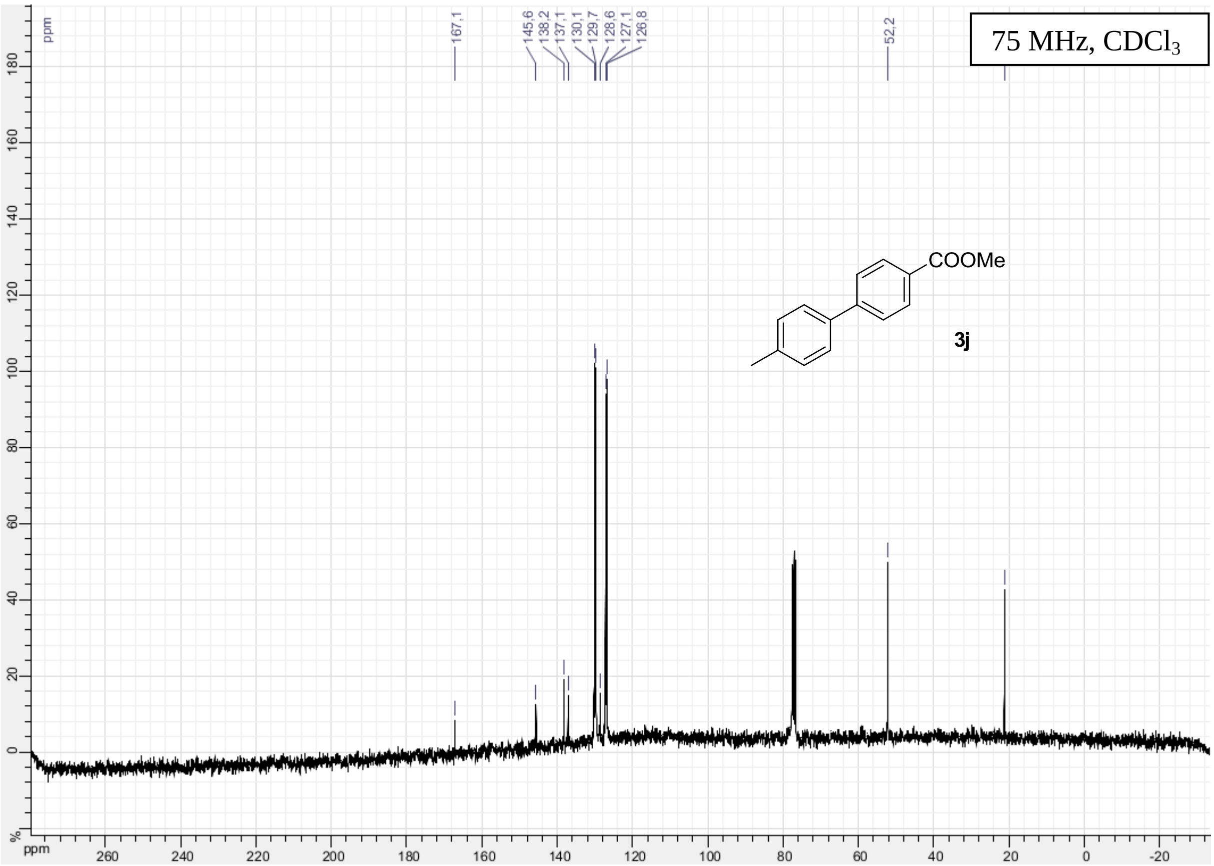


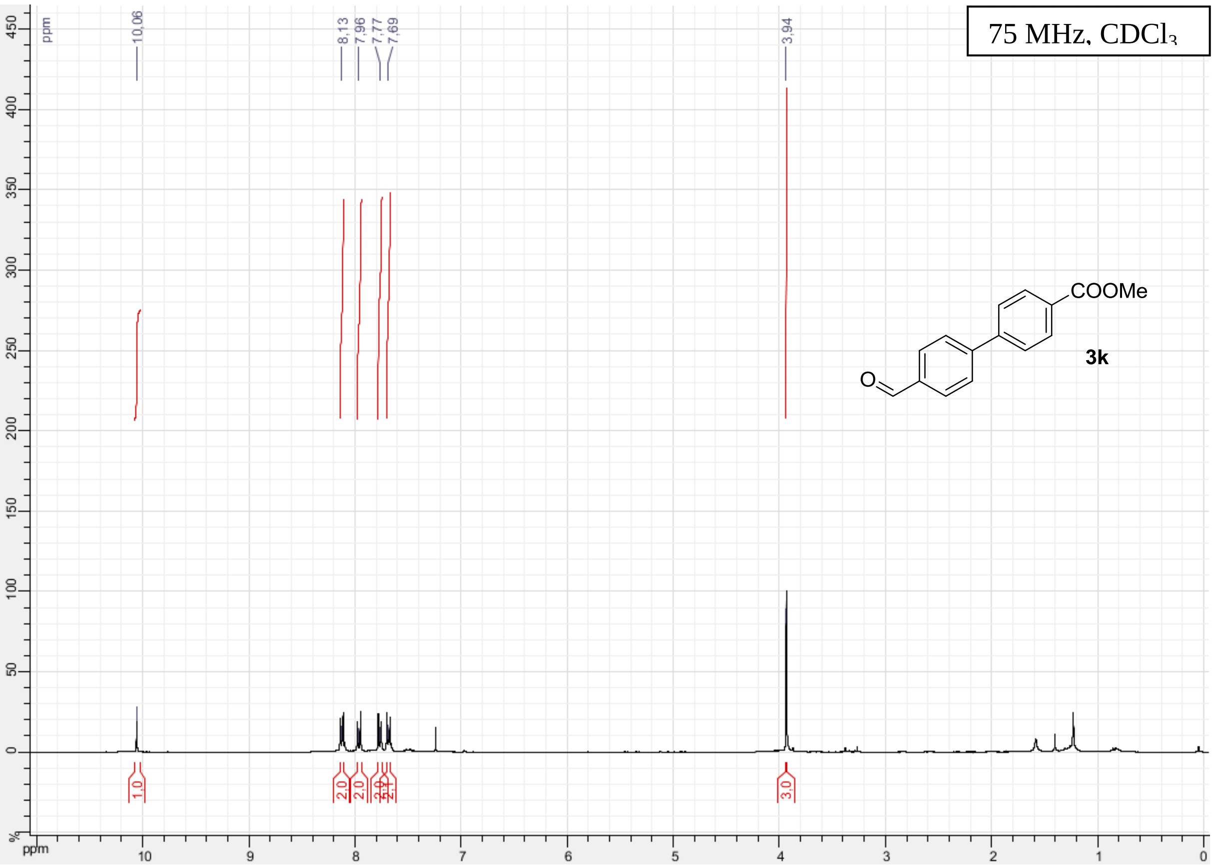
300 MHz, CDCl$_3$
8,11
7,68
7,57
7,49
7,33
3,93
2,0
4,0
3,0
3,0
COOMe
3i
ppm
%
250
200
150
100
50
0
8
7
6
5
4
3
2
1
0

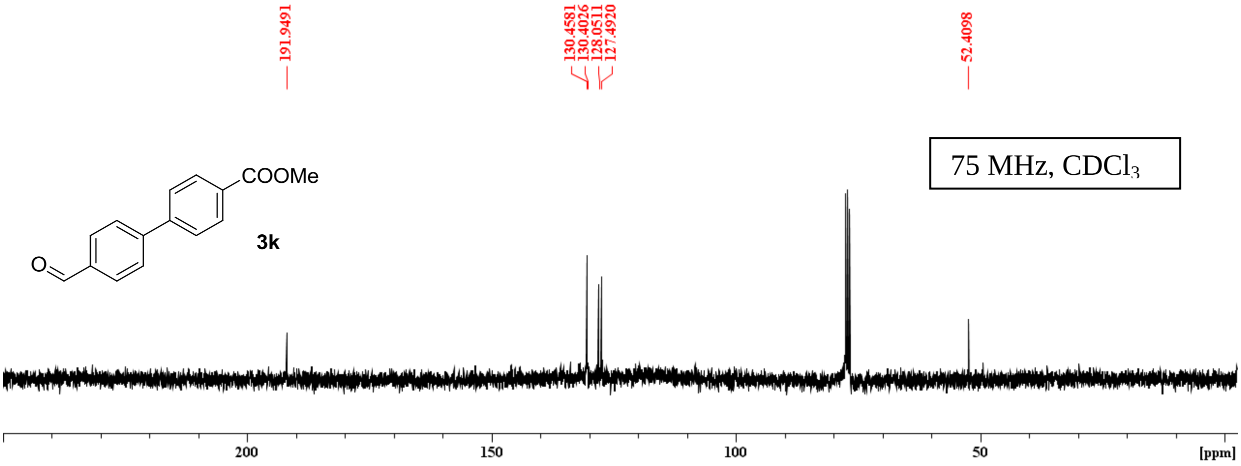


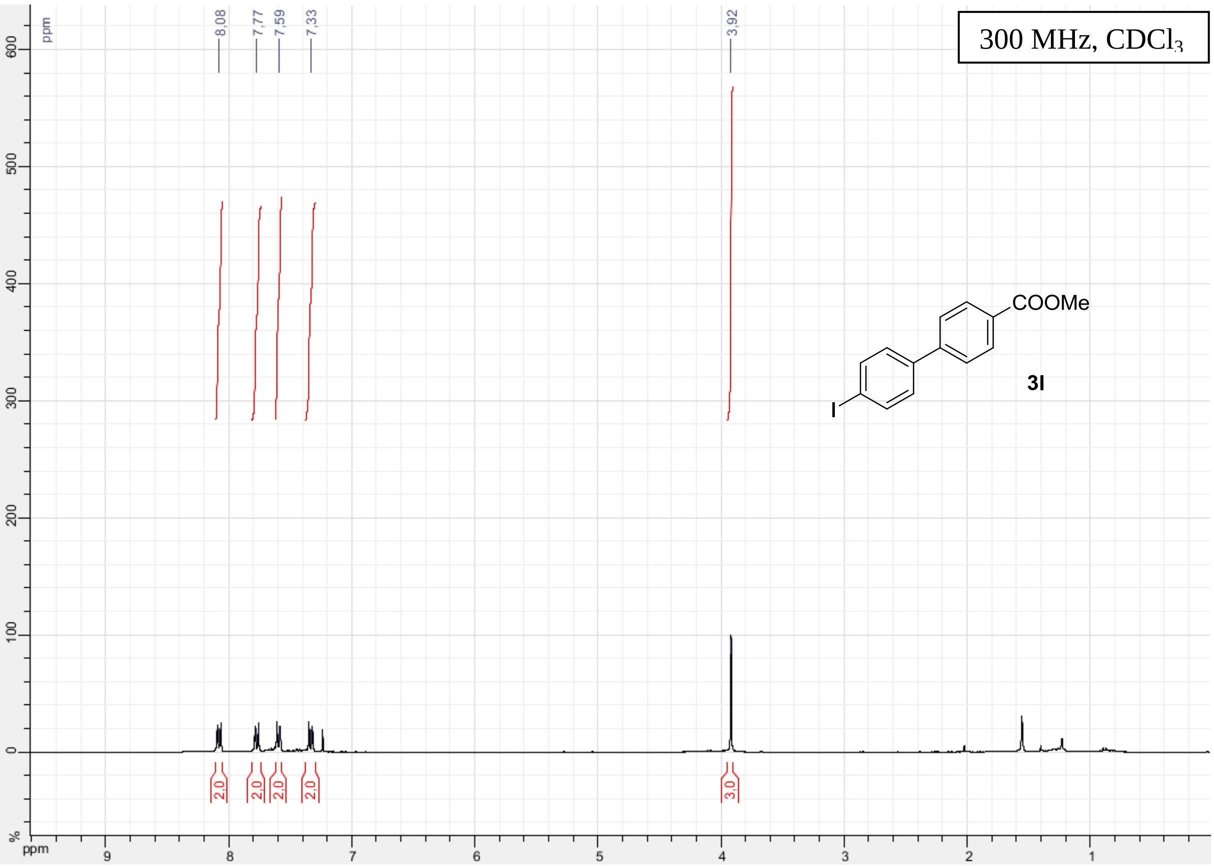
75 MHz, CDCl$_3$
166,8
145,4
139,8
129,9
128,7
127,9
127,1
126,9
52,0
COOMe
3i
ppm
%
220
200
180
160
140
120
100
80
60
40
20
0
160
140
120
100
80
60
40
20
0

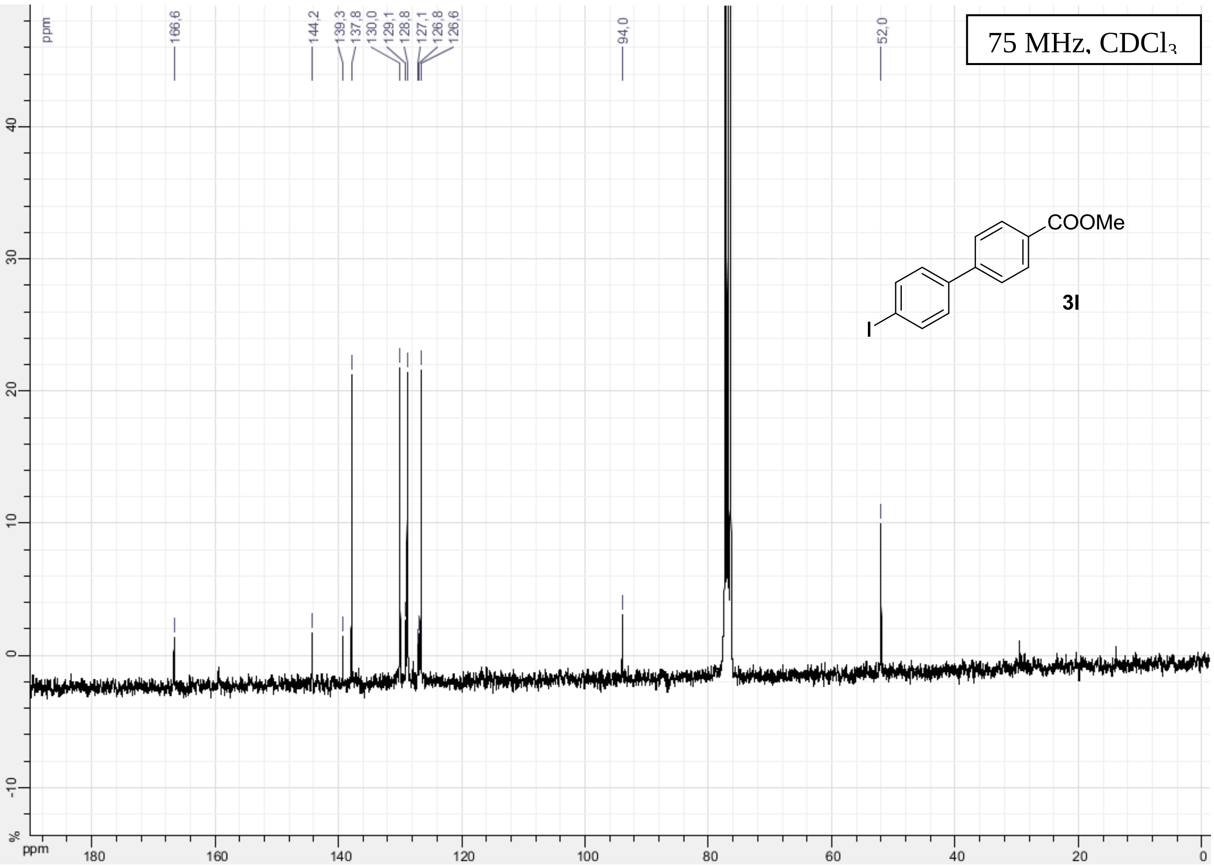

300 MHz, CDCl$_3$
COOMe
3j
8,00
7,98
7,56
7,53
7,44
7,41
7,18
7,16
3,83
2,31
2,0
2,0
2,0
2,0
3,0
3,0
ppm
%
9
8
7
6
5
4
3
2
1

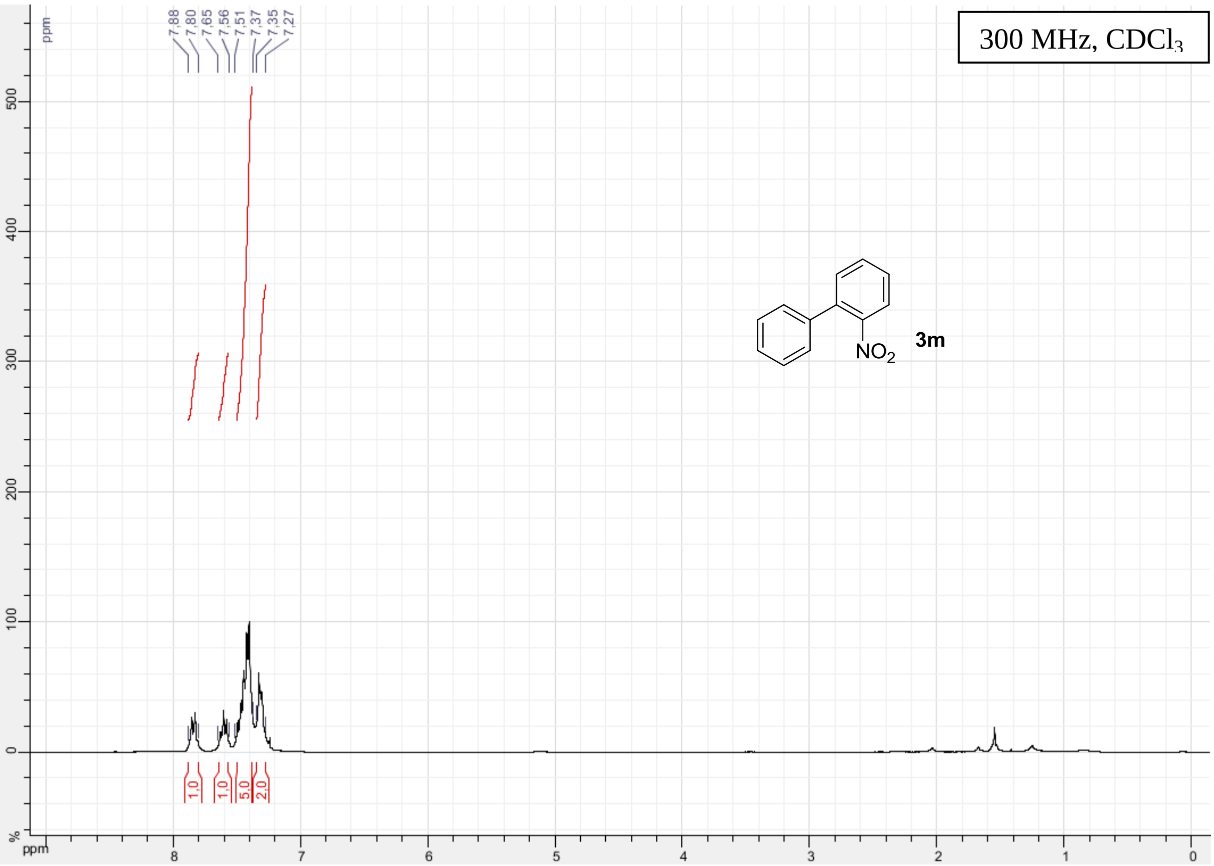

75 MHz, CDCl$_3$
COOMe
3j
167,1
145,6
138,2
137,1
130,1
129,7
128,6
127,1
126,8
52,2
ppm
%
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20

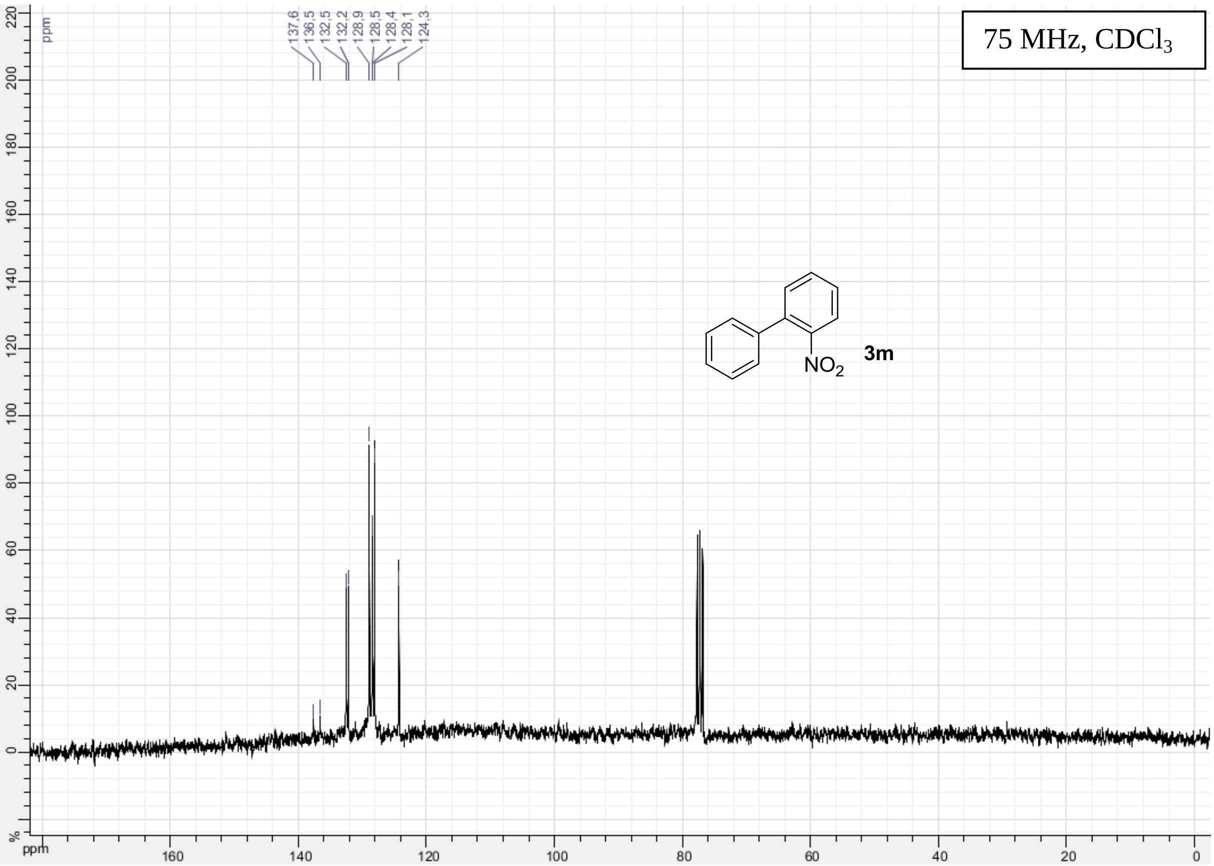

75 MHz, CDCl3
COOMe
O
3k
10.06
8.13
7.96
7.77
7.69
3.94
1.0
2.0
2.0
2.0
2.1
3.0
ppm
%
450
400
350
300
250
200
150
100
50
0
10
9
8
7
6
5
4
3
2
1
0

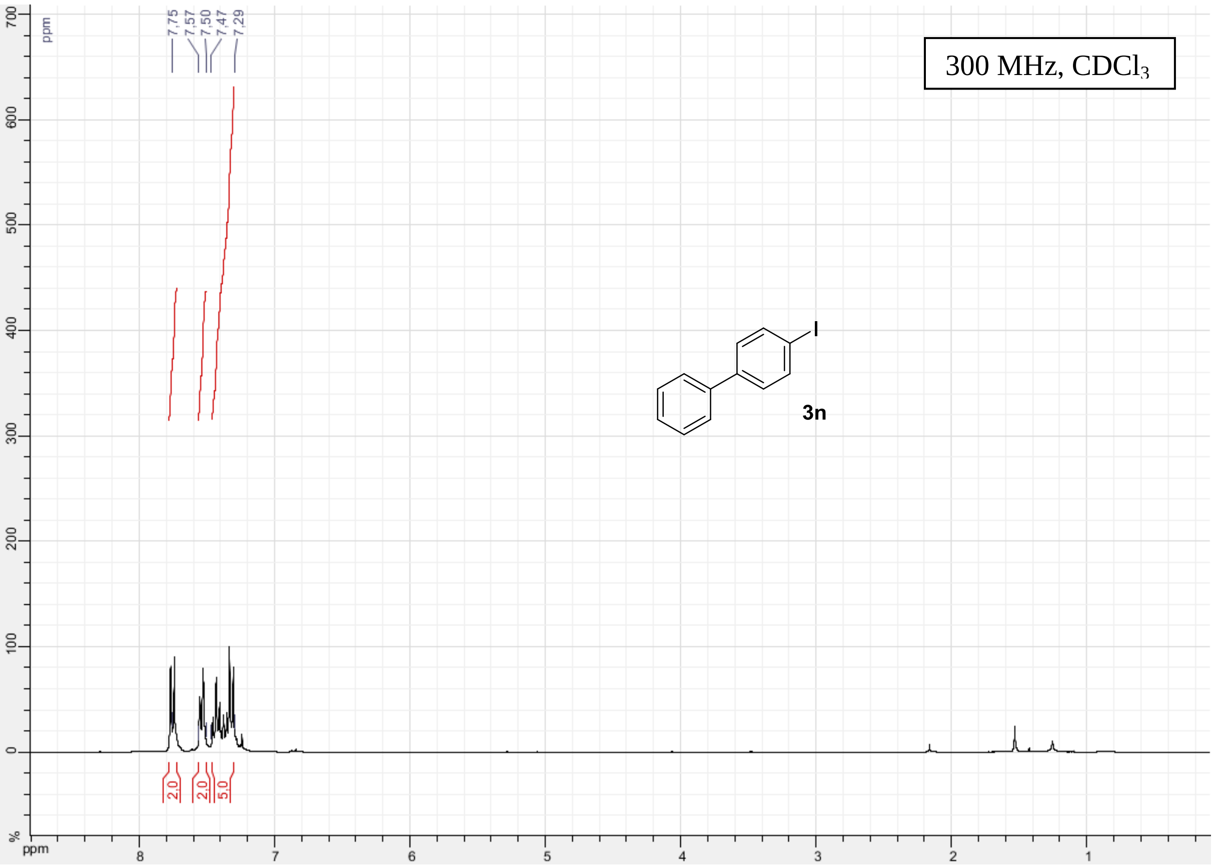

191.9491
130.4581
130.4026
128.0511
127.4920
52.4098
75 MHz, CDCl3
COOMe
O
3k
200
150
100
50
[ppm]

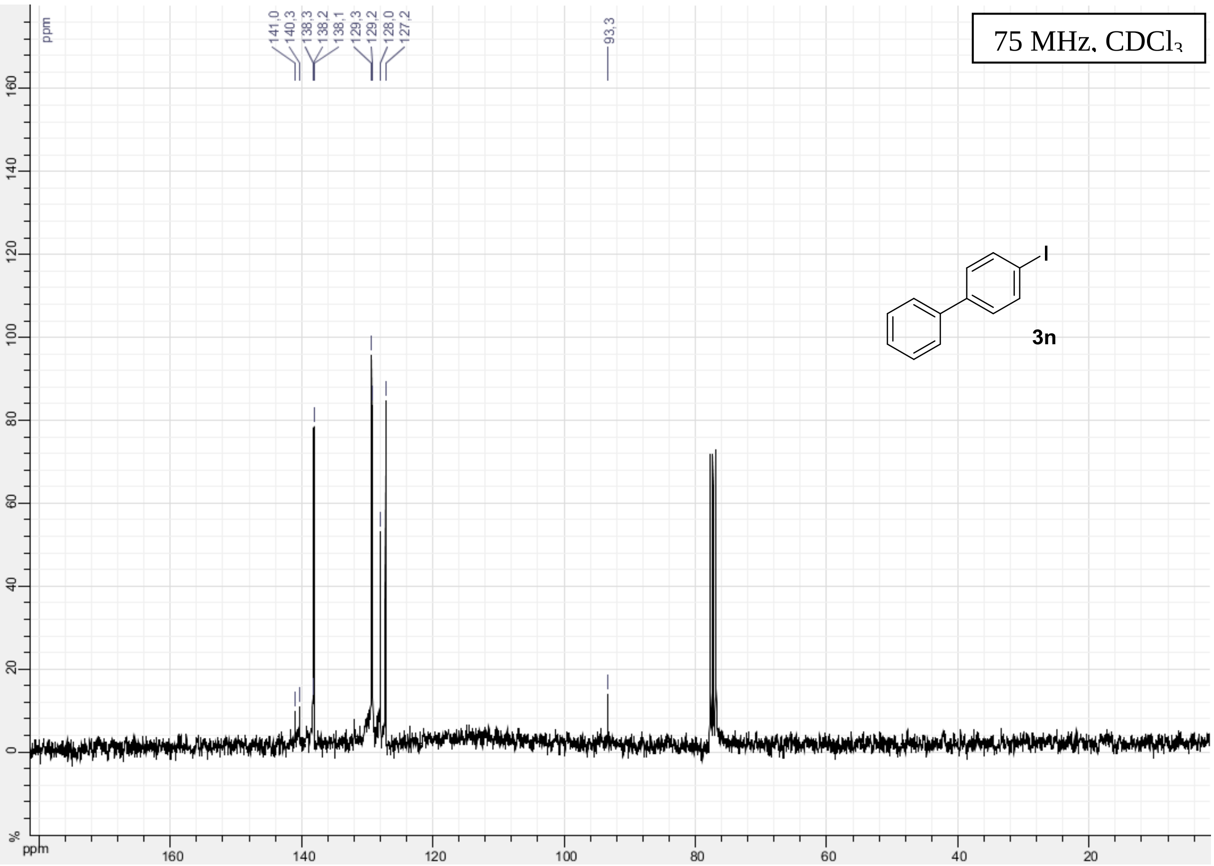

300 MHz, CDCl3
ppm
8,08
7,77
7,59
7,33
3,92
COOMe
3l
I
2,0
2,0
2,0
2,0
3,0
%
600
500
400
300
200
100
0
ppm
9
8
7
6
5
4
3
2
1

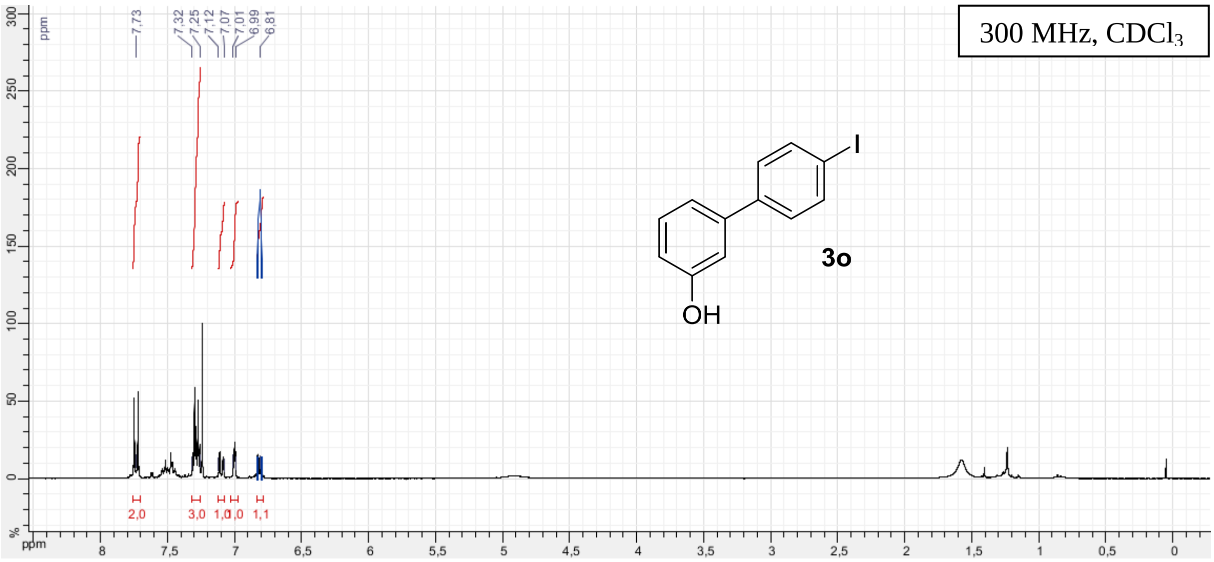

75 MHz, CDCl3
ppm
166,6
144,2
139,3
137,8
130,0
129,1
128,8
127,1
126,8
126,6
94,0
52,0
COOMe
3l
I
%
40
30
20
10
0
-10
ppm
180
160
140
120
100
80
60
40
20
0

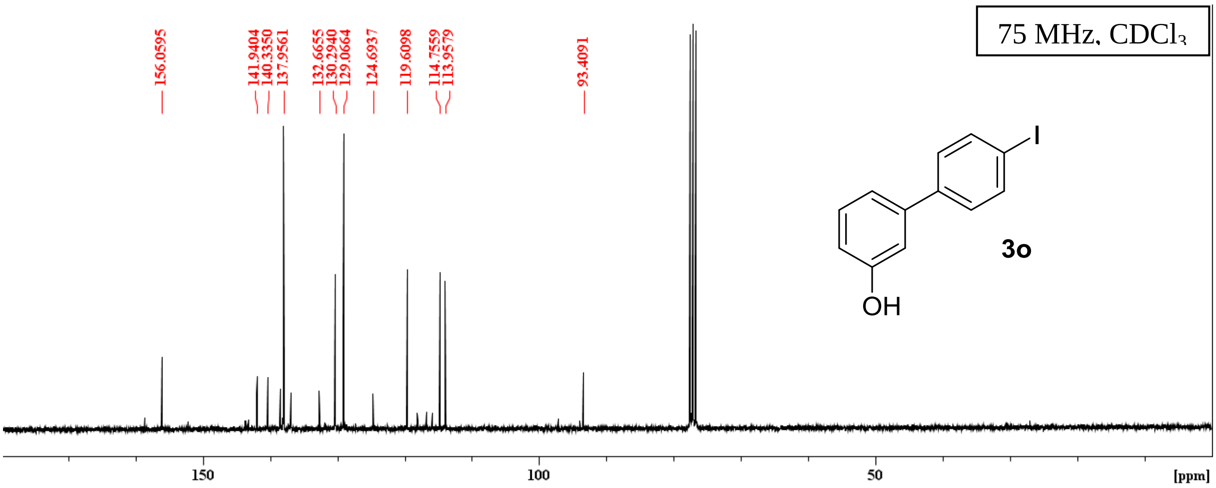

300 MHz, CDCl3
ppm
7,88
7,80
7,65
7,56
7,51
7,37
7,35
7,27
NO2
3m
1,0
1,0
5,0
2,0
500
400
300
200
100
0
%
ppm
8
7
6
5
4
3
2
1
0

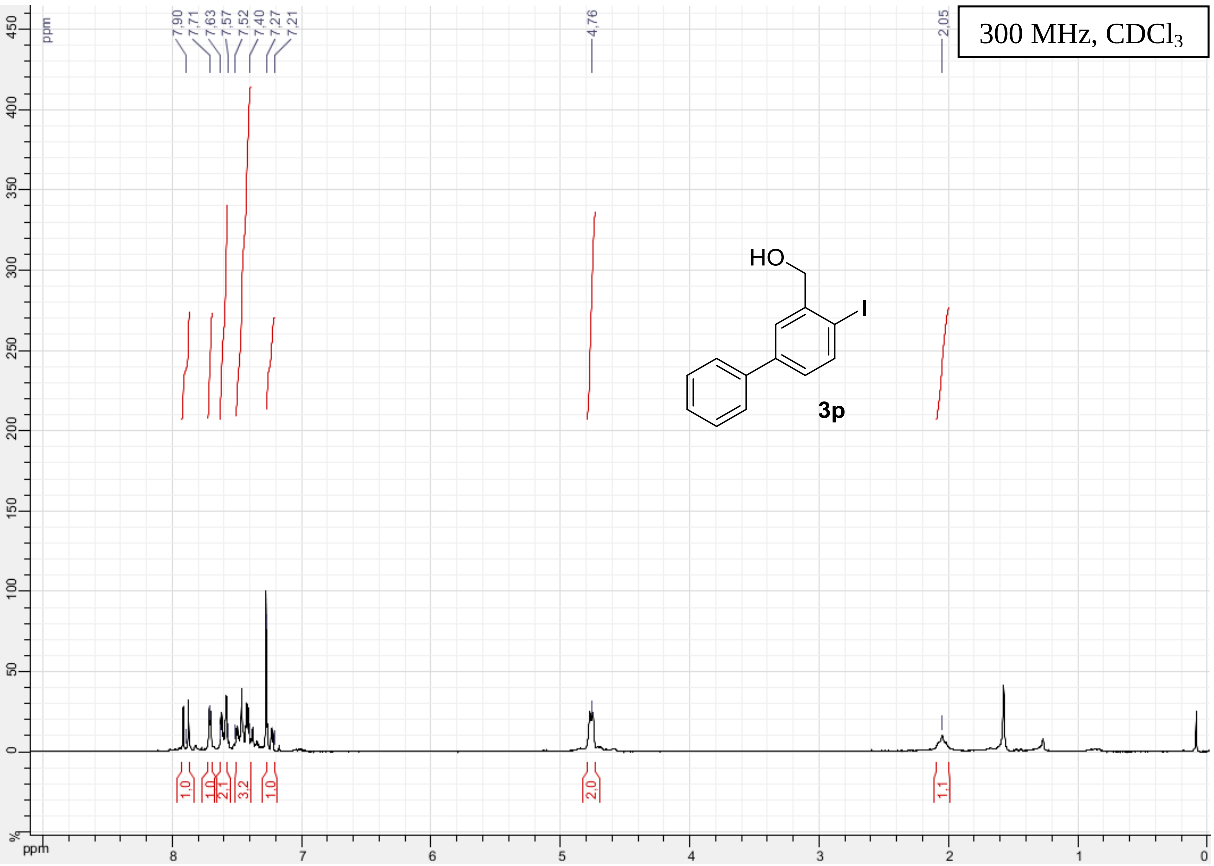

75 MHz, CDCl3
ppm
137,6
136,5
132,5
132,2
128,9
128,5
128,4
128,1
124,3
NO2
3m
220
200
180
160
140
120
100
80
60
40
20
0
%
ppm
160
140
120
100
80
60
40
20
0

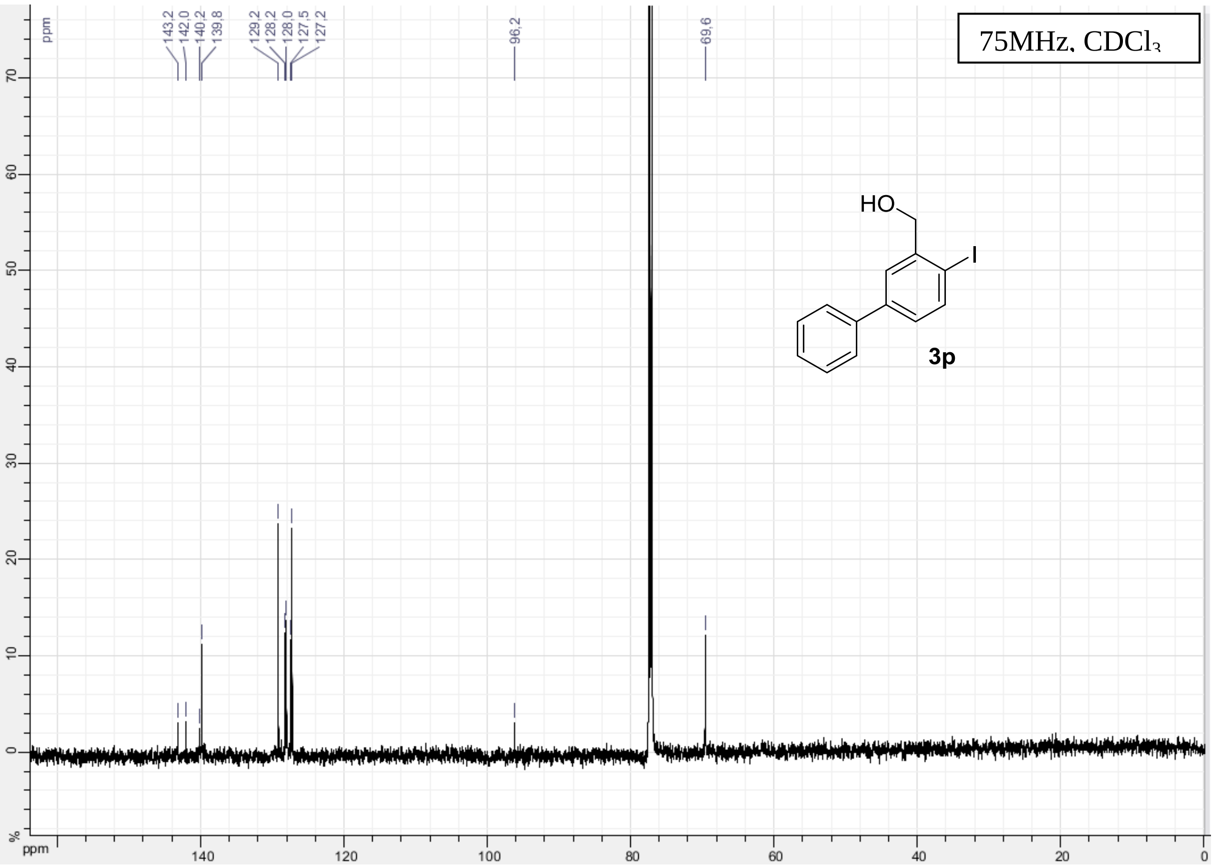

300 MHz, CDCl$_3$
7,75
7,57
7,50
7,47
7,29
2,0
2,0
5,0
I
3n
ppm
%
700
600
500
400
300
200
100
0
8
7
6
5
4
3
2
1

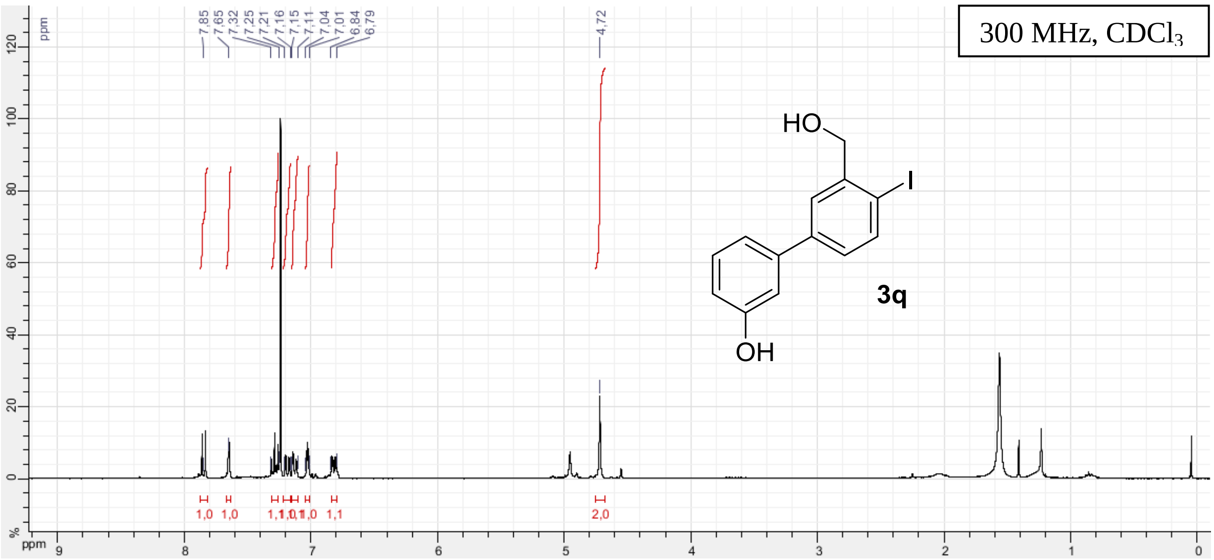

75 MHz, CDCl$_3$
141,0
140,3
138,3
138,2
138,1
129,3
129,2
128,0
127,2
93,3
I
3n
ppm
%
160
140
120
100
80
60
40
20
0

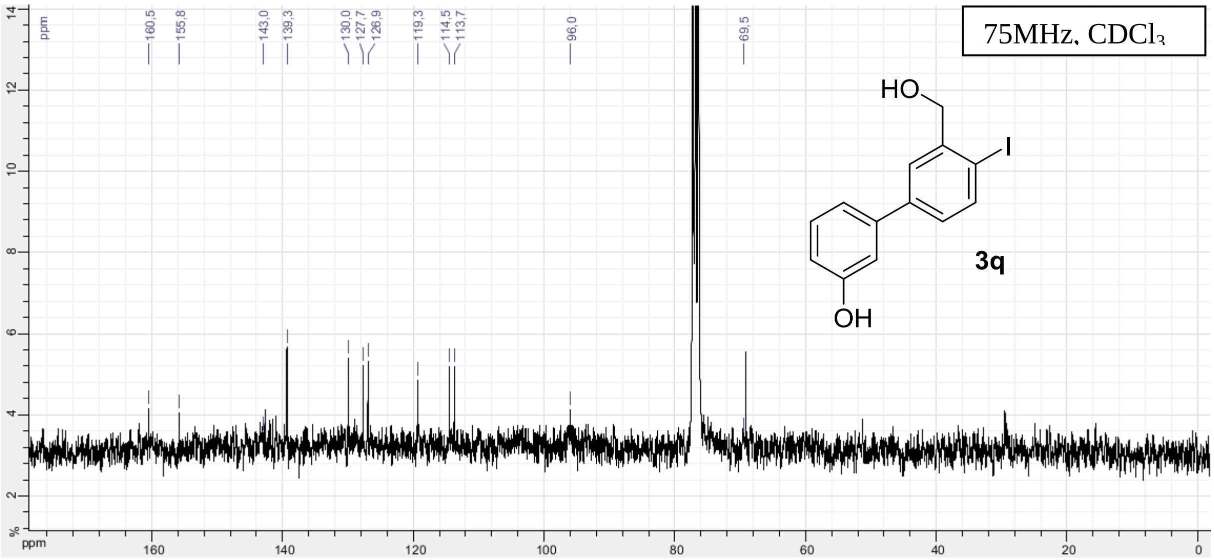

300 MHz, CDCl3
3o
OH
I
7,73
7,32
7,25
7,12
7,07
7,01
6,99
6,81
2,0
3,0
1,0
1,0
1,1
ppm
%
300
250
200
150
100
50
0
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0

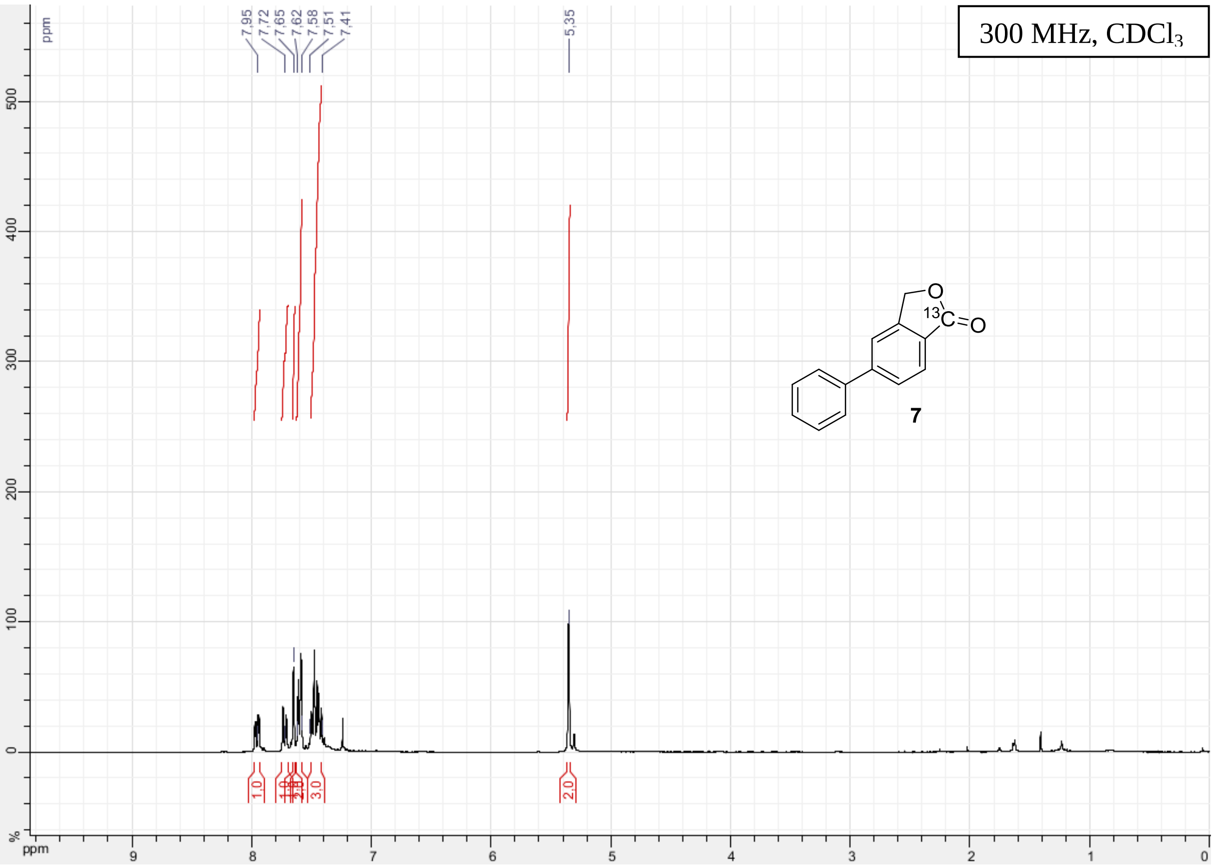

75 MHz, CDCl3
3o
OH
I
156.0595
141.9404
140.3350
137.9561
132.6655
130.2940
129.0664
124.6937
119.6098
114.7559
113.9579
93.4091
150
100
50
[ppm]

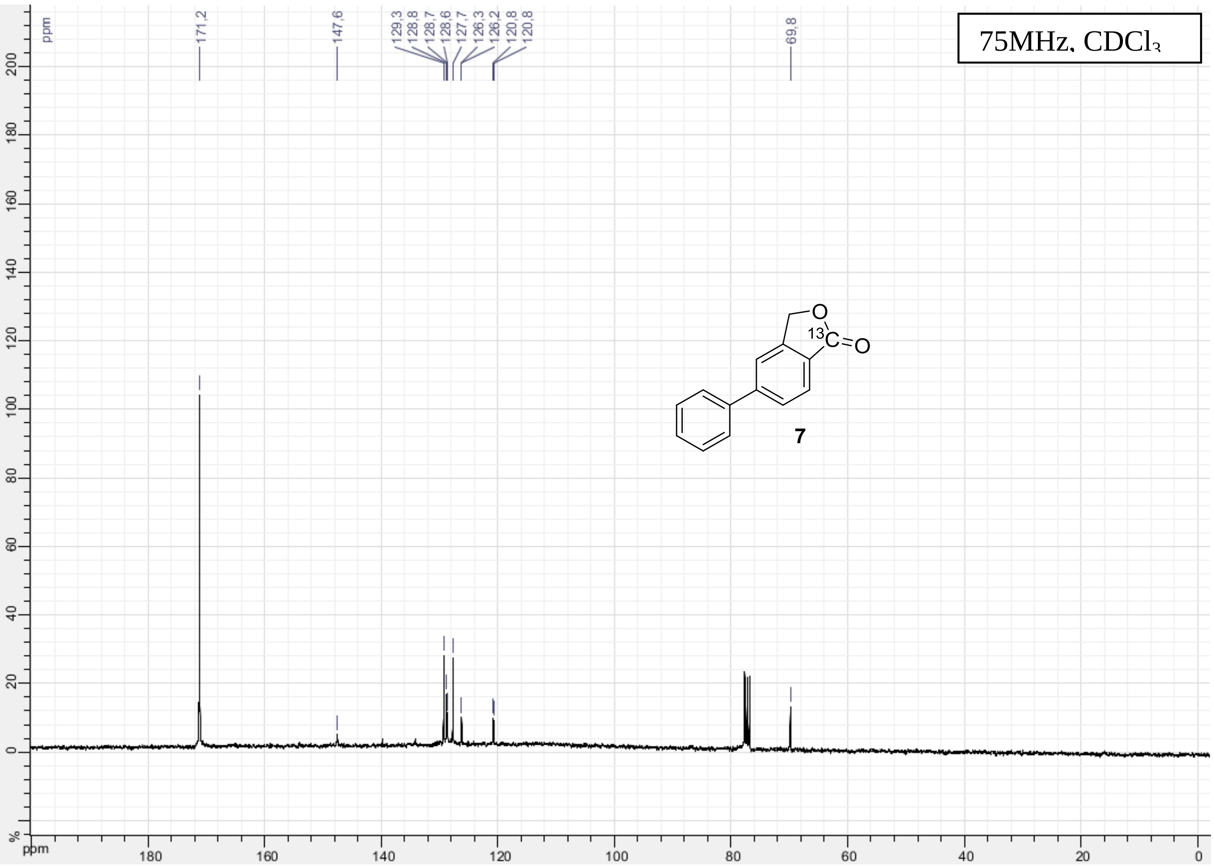

300 MHz, CDCl$_3$
7,90
7,71
7,63
7,57
7,52
7,40
7,27
7,21
4,76
2,05
1,0
1,0
2,1
3,2
1,0
2,0
1,1
HO
I
3p
ppm
%
450
400
350
300
250
200
150
100
50
0
8
7
6
5
4
3
2
1
0


75MHz, CDCl$_3$
143,2
142,0
140,2
139,8
129,2
128,2
128,0
127,5
127,2
96,2
69,6
HO
I
3p
ppm
%
70
60
50
40
30
20
10
0
140
120
100
80
60
40
20
0


300 MHz, CDCl3
HO
I
OH
3q
7,85
7,65
7,32
7,25
7,21
7,16
7,15
7,11
7,04
7,01
6,84
6,79
4,72
1,0
1,0
1,1
1,0
1,1
1,0
1,1
2,0
ppm
%
9
8
7
6
5
4
3
2
1
0


75MHz, CDCl3
HO
I
OH
3q
160,5
155,8
143,0
139,3
130,0
127,7
126,9
119,3
114,5
113,7
96,0
69,5
ppm
%
160
140
120
100
80
60
40
20
0


300 MHz, CDCl$_3$
7,95
7,72
7,65
7,62
7,58
7,51
7,41
5,35
ppm
500
400
300
200
100
0
%
1,0
1,0
2,0
3,0
2,0
7
ppm
9
8
7
6
5
4
3
2
1
0


75MHz, CDCl$_3$
171,2
147,6
129,3
128,8
128,7
128,6
127,7
126,3
126,2
120,8
120,8
69,8
ppm
200
180
160
140
120
100
80
60
40
20
0
%
7
ppm
180
160
140
120
100
80
60
40
20
0

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