Palladium Photocatalysis: A Strategic Approach for Visible-Light-Mediated C(sp)^2–H Arylation

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Supporting Information

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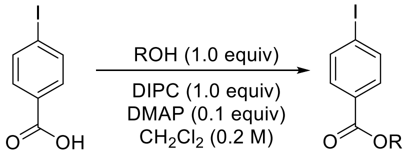
1. General information

Main Reactions were performed in oven-dried vial under open atmosphere with magnetic stirrer and 456 nm Kessil light as the source of light. Solvents and liquid chemicals were transferred by using syringes and micropipette. Commercially available technical grade solvents were dried as per standard procedure for reaction solvent and simply distilled for extraction or chromatography (ethyl acetate, hexane and dichloromethane) prior to use. Chemicals and catalysts were purchased from Sigma-Aldrich, Alfa-Aesar, TCI, GLR Innovations, BLDpharm and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) performed on silica gel 60 F254 plates from Merck. Flash column chromatography was performed on silica gel 60 (40–63 µm, 230–400 mesh, ASTM) from Merck using the indicated solvents. ^{1}H, ^{13}C, and ^{19}F NMR spectra recorded in $CDCl_3$ unless otherwise stated on JEOL JNM ECS–400 instrument. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CDCl_3$: δ = 7.26 ppm for ^{1}H NMR and $CDCl_3$: δ = 77.16 ppm for ^{13}C NMR. Data are reported as follows: chemical shift, multiplicity (br = broad singlet, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. All the HRMS data were recorded on XEVO G2–XS QTOF.

2. Preparation of starting materials

Starting methyl 4-iodobenzoate were synthesized from corresponding Benzoic acids following GP-1. Iodobenzene derivatives were purchased directly from TCI, GLR Innovations, Sigma-Aldrich and BLDpharm. For others esterification the following procedure was used.

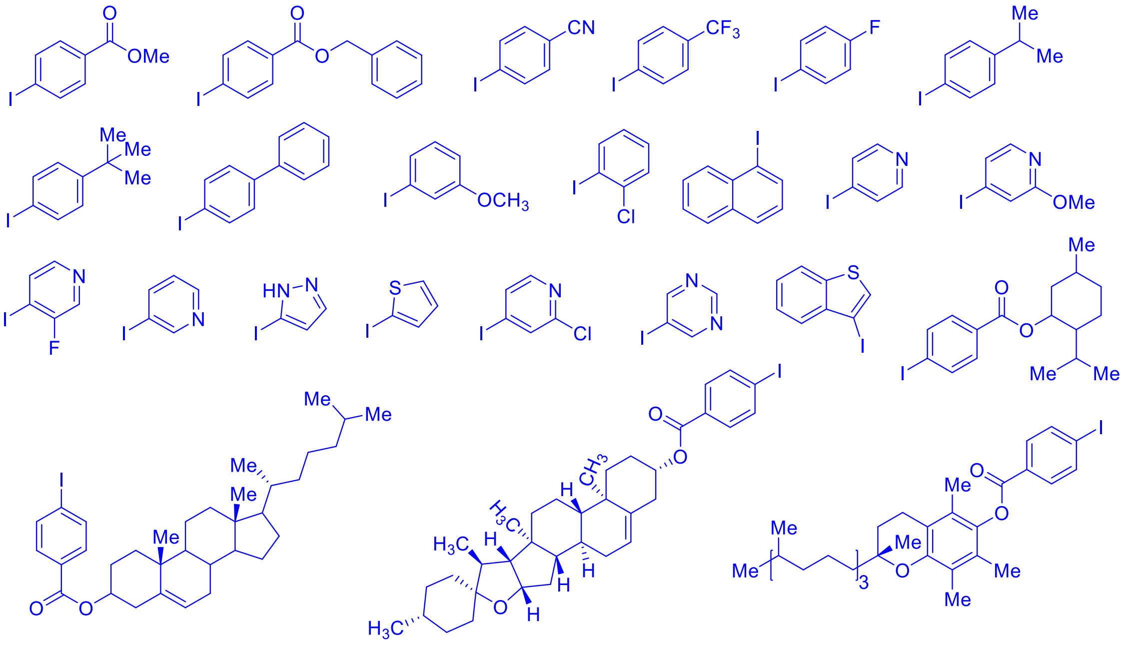


2.1 General procedure 1 (GP-1)

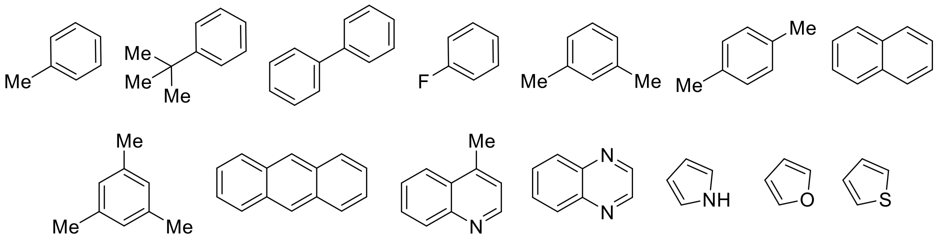
A round-bottom flask was charged with (if solid) carboxylic acid (1.0 equiv), (if solid) Alcohol (1.0 equiv) and DMAP (0.1 equiv). Dichloromethane was added (0.2 M), and the mixture was stirred vigorously. Alcohol (1.0 equiv) was added via syringe (if liquid) and the mixture was allowed to stir until the acid was consumed (determined by TLC). Typical reaction times were between 10 h to 16 h. The mixture was filtered and rinsed with additional CH_2Cl_2. The solvent was removed under reduced pressure, and purification by column chromatography afforded corresponding esters.

3. List of starting materials

3.1 List of successful iodobenzene derivatives for C-H functionalization

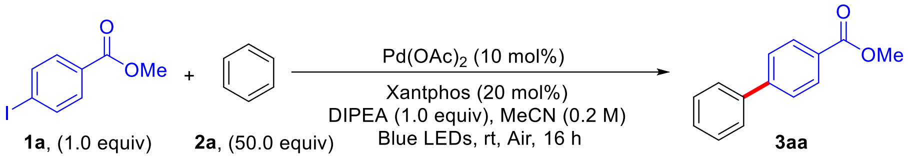


3.2 List of successful derivatives for C-H functionalization



4. Optimization of reaction conditions

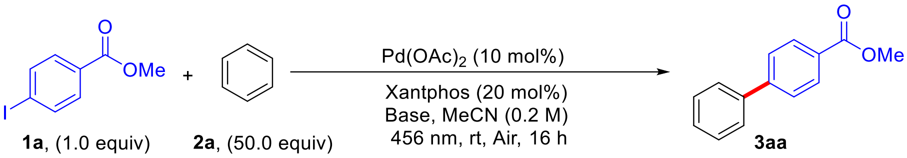
Table S1. Optimization of light



Entry	Light source	% Yield[a]
1	456 nm (Kessil)	52
2	450 nm (Hepatochem)	52
3	455 nm (Yarev)	34
4	427 nm (Kessil)	37

[a] Reaction scale 0.1 mmol, yields reported are the isolated yield.

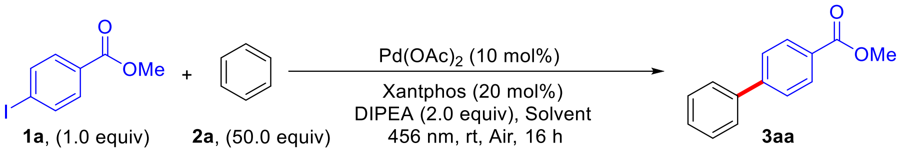
Table S2. Screening of bases



Entry	**Base (equiv)**	**% Yield**[a]
1	DIPEA (2.0)	64
2	DIPEA (3.0)	50
3	DIPEA (1.0)	52
4	DIPA (0.2)	28
5	TMP (0.2)	22
6	TMEDA (0.2)	17
7	Collidine (0.2)	0
9	^{t}BuOK (0.2)	14
10	Cs_2CO_3 (0.2)	21
11	K_2CO_3 (0.2)	9
12	K_3PO_4 (0.2)	7
13	KOH (0.2)	11
14	Et_2NH (0.2)	Trace
15	Ph_2NH (0.2)	0
16	Diisobutylamine (0.2)	7
17	Tert-Butylamine (0.2)	0
18	Tribenzylamine (0.2)	0
19	Morpholine (0.2)	20

[a] Reaction scale 0.1 mmol, yields reported are the isolated yield.

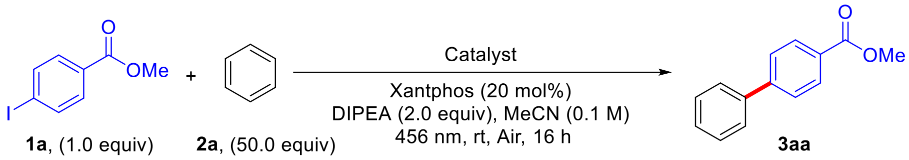
Table S3. Optimization of solvents



Entry	Solvent (M)	% Yield[a]
1	CH_3CN (0.1)	68
2	CH_3CN (0.2)	64
3	CH_3CN (0.07)	57
4	CH_3CN (0.05)	47
5	DMSO (0.1)	43
6	DME (0.1)	10
7	DMA (0.1)	0
8	DMF (0.1)	0
9	THF (0.1)	25
10	DCM (0.1)	28
11	DCE (0.1)	33
12	Acetone (0.1)	18
13	1,4-Dioxane (0.1)	Trace
14	EtOAc (0.1)	10
15	EtOH (0.1)	11
16	1,2-DFB (0.1)	28
17	1,2-DCB (0.1)	Trace

[a] Reaction scale 0.1 mmol, yields reported are the isolated yield.

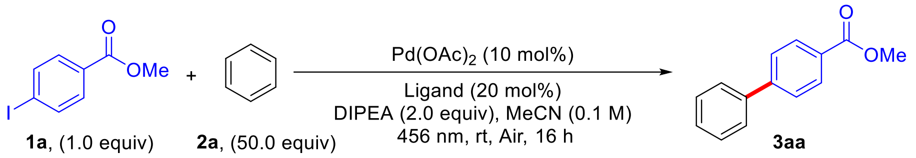
Table S4. Screening of catalyst and catalyst loading

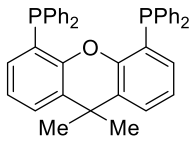


Entry	Catalyst (mol %)	% Yield[a]
1	$Pd(OAc)_2$ (10)	68
2	$Pd(OAc)_2$ (15)	68
3	$Pd(OAc)_2$ (7.5)	62
4	$Pd(OAc)_2$ (5)	56
5	Palladium pivalate (10)	38
6	$PdCl_2[P(cy)_3]_2$ (10)	Trace
7	$Pd(PPh_3)_4$ (10)	57
8	$PdCl_2(PPh_3)_2$ (10)	28
9	$Pd_2(dba)_3$ (10)	52
10	$Pd(dppf)Cl_2.CH_2Cl_2$ (10)	Trace
11	X-Phos-PdG2 (10)	25
12	$Pd(dba)_2$ (10)	50
13	$Pd_2(dba)_3.CHCl_3$ (10)	54
14	$Pd(C_5H_7O_2)_2$ (10)	Trace

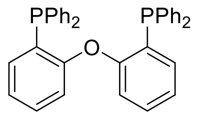
[a] Reaction scale 0.1 mmol, yields reported are the isolated yield.

Table S5. Screening of ligand

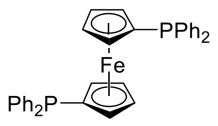




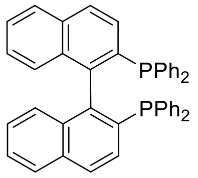
L1, 68%



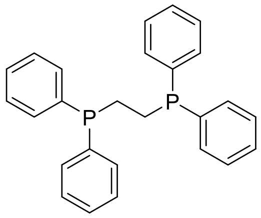
L2, 38%



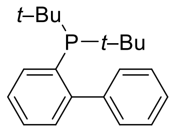
L3, 0



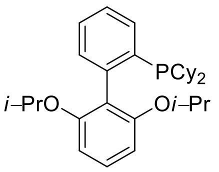
L4, 0



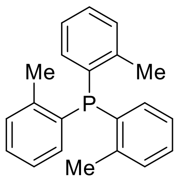
L5, Trace



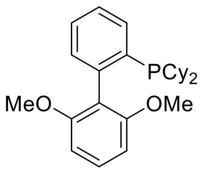
L6, 0



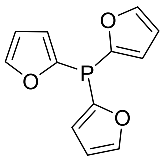
L7, 0



L8, 0



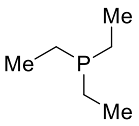
L9, 42%



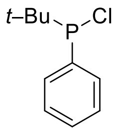
L10, 35%

PPh$_3$

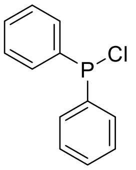
L11, 0



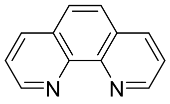
L12, 0



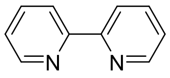
L13, 0



L14,0



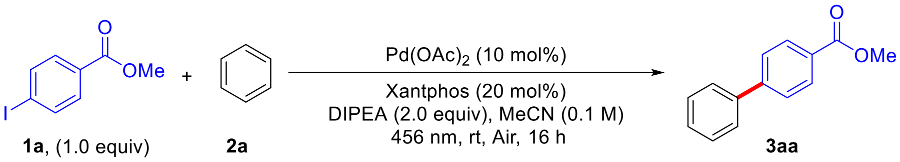
L15, 0



L16, 0

[a] Reaction scale 0.1 mmol, yields reported are the isolated yield.

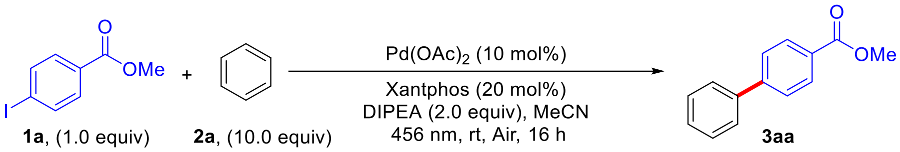
Table S6. Optimization of equivalency of benzene



Entry	Benzene (equiv)	% Yield[a]
1	50	68
2	30	65
3	20	60
4	10	57

[a] Reaction scale 0.1 mmol, yields reported are the isolated yield.

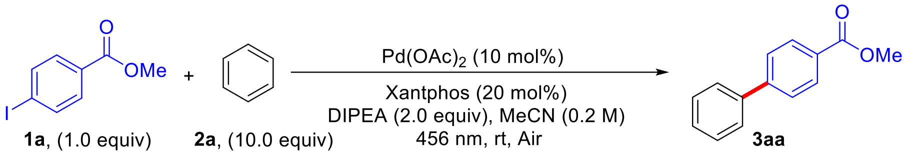
Table S7. Optimization of solvent concentration



Entry	Solvent (M)	% Yield[a]
1	0.1	55
2	0.13	55
3	0.2	60
4	0.4	60

[a] Reaction scale 0.1 mmol, yields reported are the isolated yield.

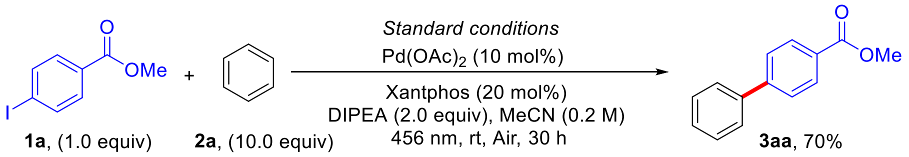
Table S8. Screening of time



Entry	Time (hour)	% Yield[a]
1	16	50
2	24	60
3	30	70
4	48	70

[a] Reaction scale 0.1 mmol, yields reported are the isolated yield.

Table S9. Control experiment



Entry	Deviation from standard conditions	% Yield[a]
1	No catalyst	0
2	No ligand	0
3	No light	0
4	No base	Trace
5	Under argon atmosphere	65
6	Benzene as a solvent	55

[a] Reaction scale 0.1 mmol, yields reported are the isolated yield.

5. Mechanistic studies

5.1 Determination of Quantum yield

(A) Determination of light intensity of Blue LED

The determination of photon flux was performed by the use of standard ferrioxalate actinometry.[1,2] A 0.15 M solution of ferrioxalate was prepared by the addition of 737 mg of potassium ferrioxalate hydrate in 10 ml of 0.05 M H_2SO_4. Thereafter, a solution of phenanthroline was made by adding 25 mg of phenanthroline and 5.63 g of sodium acetate in 25 mL of 0.5 M H_2SO_4. Both solutions were kept in a dark environment. Next, for the determination of photon flux, 1.0 mL of the ferrioxalate solution Both a cuvette and irradiated for 60.0 seconds at λ = 456 nm placing 8 cm away from 36 W Kessil blue LED lamp. After irradiation, 0.175 mL of the phenanthroline solution was added to the cuvette. The solution was left for 1 h to permit the ferrous ions to completely coordinate to the phenanthroline. The solution gave an absorbance at 510 nm which was recorded. The same was prepared but this time without irradiation and its absorbance was determined at 510 nm. Conversion was calculated using eq. **1**

$$\text{mol of Fe}^{2+} = \frac{\text{v}.\Delta A}{\varepsilon.l} \quad \ldots\ldots\ldots\ldots\mathbf{1}$$

Where v stands for total volume (0.001175 L) of the solution after addition of the phenanthroline. ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}).

$$\text{mol of Fe}^{2+} = \frac{0.001175L.\ (0.968-0.850)}{11100\ \text{L}.cm^{-1}\cdot mol^{-1}.\ 1\ cm}$$

$$= 1.2490 \times 10^{-8}$$

The photon flux can be calculated using eq **2**.

$$\text{Photon Flux} = \frac{mol\ Fe^{2+}}{\Phi.\ t.f} \ldots\ldots\ldots\ldots\ldots\ \mathbf{2}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.01 for a 0.15 M solution at λ = 456 nm), t is the time (60 s), and f is the fraction of light absorbed at λ = 456 nm, f = 1.000 -10^{-A}.

Calculated f = $1.000 - 10^{-A} = 1.000 - 10^{-0.968} = 0.8923$

$$\text{Photon Flux} = \frac{1.2490 \times 10^{-8}}{1.01 \times 60 \times 0.8923}$$

$$= 2.31 \times 10^{-8} \text{ Einstein.S}^{-1}$$

(B) Quantum yield calculation 1:

An oven-dried glass vial was charged with a magnetic stir bar, methyl 4-iodobenzoate **(1a)** (26 mg, 0.1 mmol, 1.0 equiv), Benzene **(2a)** (89.06 µl, 1.0 mmol, 10.0 equiv), Pd(OAc)$_2$ (2.2 mg, 0.01 mmol, 0.1 equiv), Xantphos (11.6 mg, 0.02 mmol, 0.2 equiv), DIPEA (34.8 µl , 0.2 mmol, 2 equiv) and MeCN (0.2 M). were added to the mixture under open atmosphere. The vial was maintained for 30 h at room temperature under 456 nm blue LED with constant stirring. The reaction mixtures were then filtered through a short pad of celite to remove insolubles and washed with EtOAc. The product of high analytical purity was achieved through column chromatography on silica gel, employing a (2–5%) solution of petroleum ether and ethyl acetate as the elution solvents. The product (**3aa**) was confirmed by NMR. The product recorded a yield of 70% (9.944×10^{-5} mol).

The Quantum yield was calculated as follows:

$$\phi = \frac{mol\ product}{flux.\ t.f}$$

Where, flux is the photon flux determined by ferrioxalate actinometry (2.31×10^{-8} Einstein.S^{-1}), t is the time (86400 s), and f (> 0.999) is the fraction of light absorbed by Pd(OAc)$_2$ at 456 nm under the reaction condition mentioned above.

$$\Phi = \frac{6.944 \times 10^{-5}}{2.31 \times 10^{-8} \times 86400 \times 1}$$

$$= 0.034$$

(C) Quantum yield calculation 2:

An oven-dried glass vial was charged with a magnetic stir bar, 1-(tert-butyl)-4-iodobenzene **(1g)** (26.0 mg, 0.1 mmol, 1.0 equiv), Benzene **(2a)** (89.06 µl, 1.0 mmol, 10.0 equiv), Pd(OAc)$_2$ (2.2 mg, 0.01 mmol, 0.1 equiv), Xantphos (11.6 mg, 0.02 mmol, 0.2 equiv.), DIPEA (34.8 µl , 0.2 mmol, 2 equiv.) and MeCN (0.2 M). were added to the mixture under open atmosphere. The vial was maintained for 30 h at room temperature under 456 nm blue

LED with constant stirring. The reaction mixtures were then filtered through a short pad of celite to remove insolubles and washed with EtOAc. The product of high analytical purity was achieved through column chromatography on silica gel, employing a (2–5%) solution of petroleum ether and ethyl acetate as the elution solvents. The product (**3ga**) was confirmed by NMR. The product recorded a yield of 43% (4.3×10^{-5} mol).

The Quantum yield was calculated as follows:

$$\phi = \frac{mol\ product}{flux.\ t.f}$$

Where, flux is the photon flux determined by ferrioxalate actinometry (2.31×10^{-8} Einstein.S^{-1}), t is the time (86400 s), and f (> 0.999) is the fraction of light absorbed by $Pd(OAc)_2$ at 456 nm under the reaction condition mentioned above.

$$\phi = \frac{4.3 \times 10^{-5}}{2.31 \times 10^{-8} \times 86400 \times 1}$$

$$= 0.021$$

(D) Quantum yield calculation 3:

An oven-dried glass vial was charged with a magnetic stir bar, benzyl 4-iodobenzoate **(1b)** (26.0 mg, 0.1 mmol, 1.0 equiv), Benzene **(2a)** (89.06 µl, 1.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.1 equiv), Xantphos (11.6 mg, 0.02 mmol, 0.2 equiv), DIPEA (34.8 µl , 0.2 mmol, 2.0 equiv) and MeCN (0.2 M). were added to the mixture under open atmosphere. The vial was maintained for 30 h at room temperature under 456 nm blue LED with constant stirring. The reaction mixtures were then filtered through a short pad of celite to remove insolubles and washed with EtOAc. The product of high analytical purity was achieved through column chromatography on silica gel, employing a (2–5%) solution of petroleum ether and ethyl acetate as the elution solvents. The product **(3ba)** was confirmed by NMR. The product recorded a yield of 89% (8.895×10^{-5} mol).

The Quantum yield was calculated as follows:

$$\phi = \frac{mol\ product}{flux.\ t.f}$$

Where, flux is the photon flux determined by ferrioxalate actinometry (2.31×10^{-8} Einstein.S^{-1}), t is the time (86400 s), and f (> 0.999) is the fraction of light absorbed by $Pd(OAc)_2$ at 456 nm under the reaction condition mentioned above.

$$\Phi = \frac{8.895 \times 10^{-5}}{2.31 \times 10^{-8} \times 86400 \times 1}$$

$$= 0.0445$$

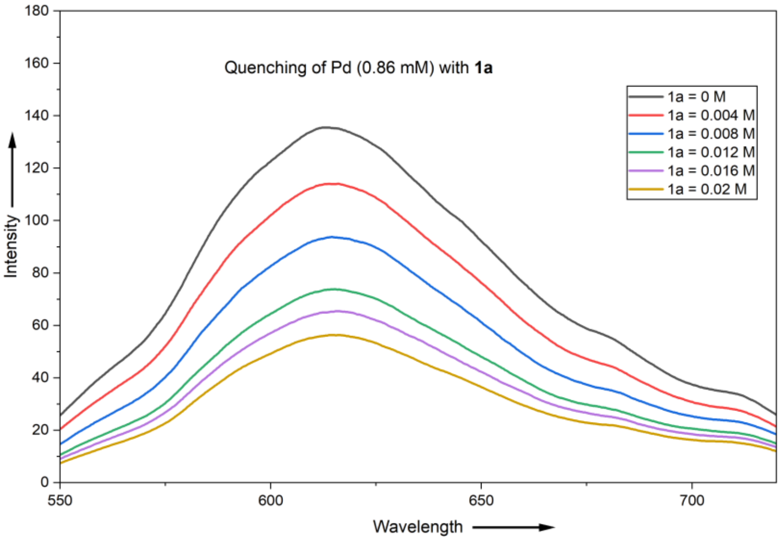
5.2 Luminescence Quenching experiments:

(A) Preparation of the stock solution:

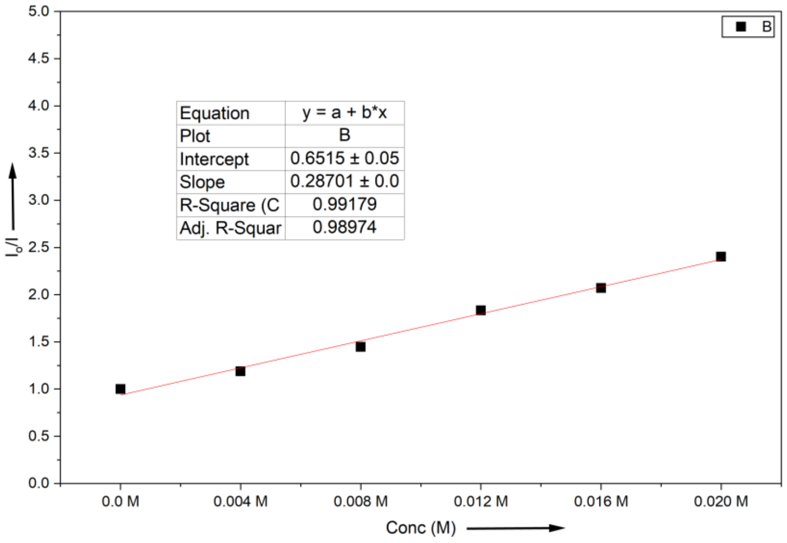
To verify the role of the Pd(0) catalyst as the photoabsorbing species, emission quenching studies were undertaken. Although the $Pd(Xantphos)_2$ complex was synthesized following the reported method,[3] it exhibited poor solubility in commonly used organic solvents such as CH_3CN and benzene. As a result, $Pd(PPh_3)_4$ was employed for the quenching experiments, as it was demonstrated to be an effective catalyst for the visible-light-mediated $C(sp)^2$–H Arylation. (see optimization Table **S4**). So, Emission quenching studies were performed using a 0.86 mM of $Pd(PPh_3)_4$ in CH_3CN, with methyl 4-iodobenzoate **(1a)** in CH_3CN at varying concentrations (4, 8, 12, 16, and 20 mM). The samples were excited at 380 nm, and the emission intensity at 615 nm was recorded.[4-6] The extent of quenching was quantified by the ratio I_0/I, where I_0 denotes the emission intensity of the Pd catalyst at 615 nm in the absence of any quencher, and I represents the measured intensity at a given quencher concentration. The fluorescence emission spectra along with the corresponding Stern–Volmer plot are shown in the figures below.

(C) Luminescence spectra:

Luminescence spectra of Pd(PPh3)4 (0.86 mM in CH3CN) as a function of concentration of methyl 4-iodobenzoate (1a).



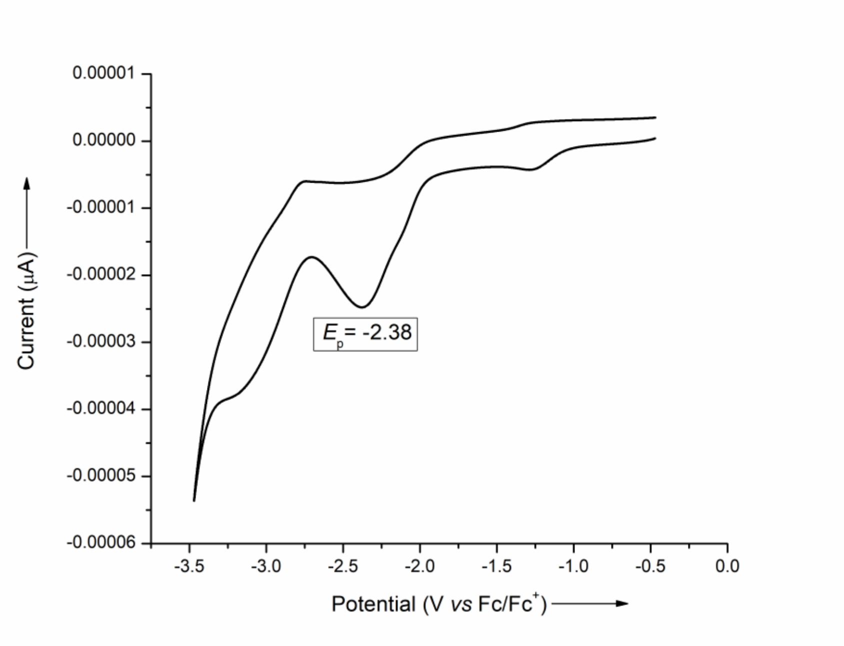
Stern-Volmer plot for the emission quenching of Pd(PPh3)4 by various concentrations of methyl 4-iodobenzoate (1a) in CH3CN.



5.3 Cyclic Voltammetry experiments:

Cyclic voltammograms were recorded for methyl 4-iodobenzoate **(1a)**. This electrochemical cell contains a glassy carbon (disc shaped with 3-mm diameter) as working electrode, Pt wire as counter electrode, and Ag wire as pseudo-reference electrode. The glassy carbon working electrode was polished with 1.0 micron α-alumina polishing powder using a figure eight motion. Electrolyte solution (0.1 M) was prepared from CH_3CN and tetra-nbutylammonium hexafluorophosphate (Bu_4NPF_6). The CH_3CN was degassed by nitrogen gas sparging for 10 minutes prior to measurements. The potential was externally calibrated against the ferrocene/ferrocenium couple (0.47 V) for **1a**. When the cyclic voltammetry (CV) value of the methyl 4-iodobenzoate **(1a)** is referenced to the saturated calomel electrode, it is approximately E_p = - 2.0 V vs SCE. in CH_3CN (using Pavlishchuk and Addison conversion constant for SCE).[7]

(a) Cyclic Voltammogram of methyl 4-iodobenzoate (1a)

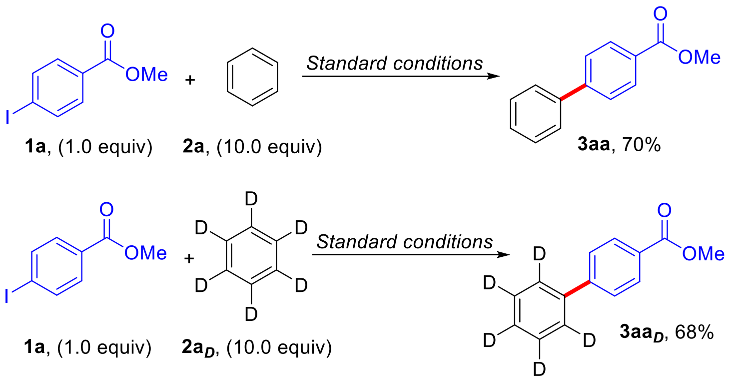


5.4 Independent kinetic isotope exchange (KIE) study

Following **GP–2**, Six set of reactions were performed independently with non–deuterated and deuterated analogue of **2a** and quenched at 5 h, 10 h, 15 h, 20 h and 25 h, 30 h. The isolated yields were calculated at a particular time and repeated three times to minimize the error. Then the graph of % yield vs. Reaction time was plotted for both analogues and from the slopes of the graphs, the k_H/k_D was calculated.

Procedure: According to **GP–2**, using **1a** (52 mg, 0.2 mmol, 1.0 equiv), **2a** (178 µl, 2.0 mmol, 10.0 equiv) and Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl , 0.4 mmol, 2.0 equiv), The mixture was dissolved in MeCN (0.2 M) under open atmosphere followed by the vial was sealed with a Teflon cap and rapped with parafilm. six sets of reactions were performed separately. After the mentioned time, the reaction mixtures were purified separately by column chromatography on silica gel using 2.5% ethyl acetate in hexane as eluent.

The same procedure was followed for the deuterated analogue using **1a** (52 mg, 0.2 mmol, 1.0 equiv), **2a*D*** (178 µl, 2.0 mmol, 10.0 equiv) and Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl , 0.4 mmol, 2.0 equiv), The mixture was dissolved in MeCN (0.2 M) under open atmosphere followed by the vial was sealed with a Teflon cap and rapped with parafilm. Six sets of reactions were performed separately. After the mentioned time, the reaction mixtures were purified separately by column chromatography on silica gel using 2.5% ethyl acetate in hexane as eluent.

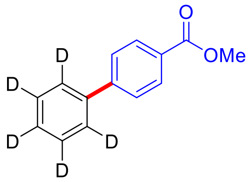


Reaction time (h)	% yield of 3aa	% yield of 3aa$_D$
5	10	12
10	25	23
15	45	40
20	55	50
25	65	60
30	70	68

methyl [1,1'-biphenyl]-4-carboxylate-2',3',4',5',6'-*d*$_5$ (3aa$_D$) (536)

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.11 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.6 Hz, 2H), 3.94 (s, 3H).

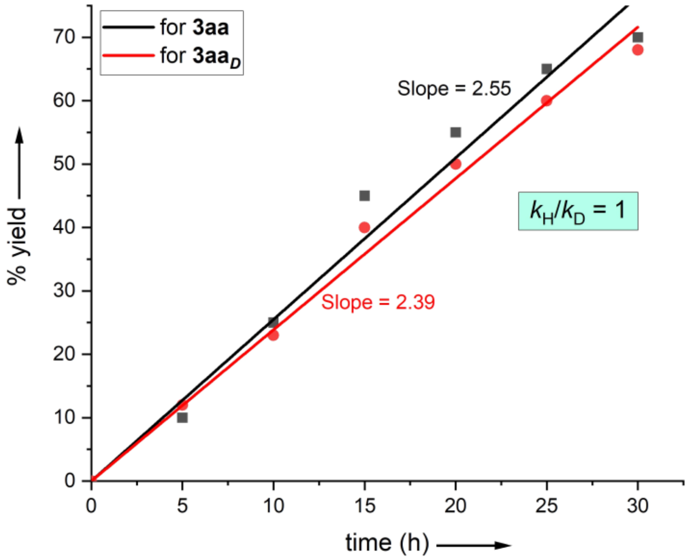
^{13}C NMR (101 MHz, CDCl$_3$) δ 167.2, 145.7, 139.9, 130.2, 128.9, 127.1, 52.3.

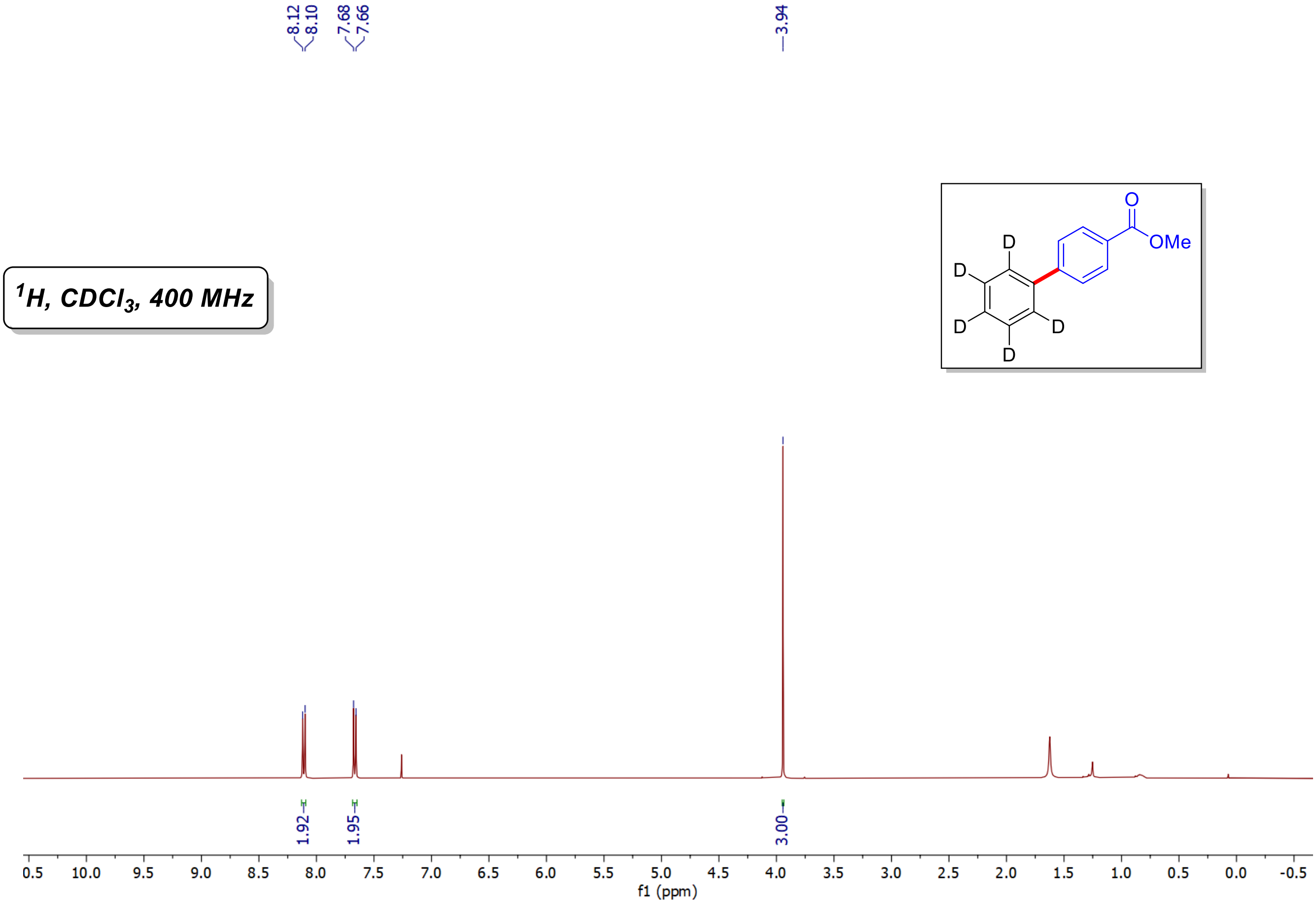


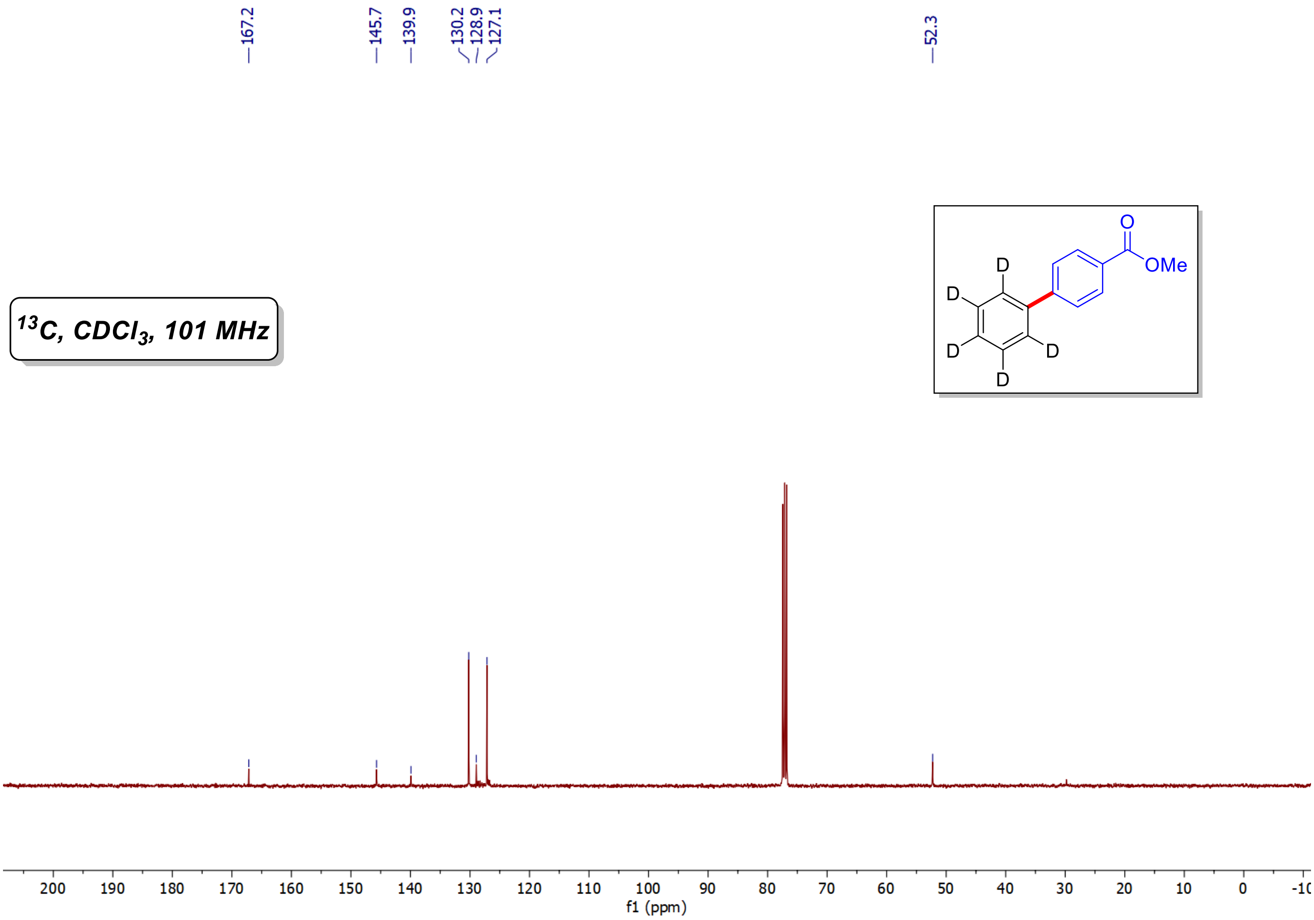
$C_{14}H_7D_5O_2$
M. W.: 217.2785

Yield vs. time plot for determining k_H/k_D.

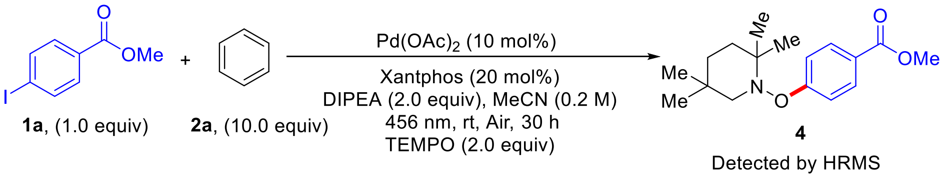
Linear fitting of the experimental points has been done by keeping intercept = 0. Ratio of the slopes of the straight lines for **3aa** and **3aa*D*** indicates the value of k_H/k_D which is nearly 1 in this case.







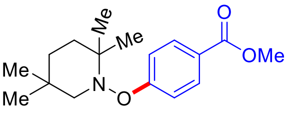
5.5 Radical trap experiment:



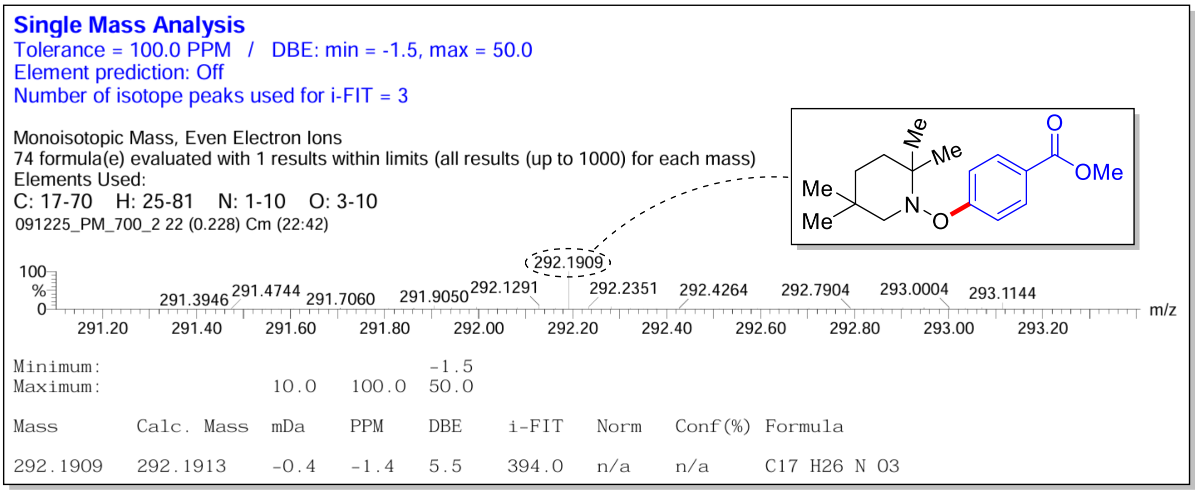
Following standard procedure, methyl 4-iodobenzoate **(1a)** (52 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl , 0.4 mmol, 2.0 equiv), TEMPO (63.5 mg, 0.4 mmol, 2.0 equiv). The mixture was dissolved in MeCN (0.2 M) under open atmosphere followed by the vial was sealed with a teflon cap and rapped with parafilm. The reaction mixture was then stirred under the irradiation of 456 nm light for about 30 h at room temperature. The reaction mixtures were then filtered through a short pad of celite to remove insolubles and washed with EtOAc. The product was confirmed by HRMS.

5.5.1 Experimental details for the TEMPO adduct:

methyl 4-((2,2,5,5-tetramethylpiperidin-1-yl)oxy)benzoate



HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{17}H_{26}NO_3]^+$: 292.1913; Found 292.1909.



Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

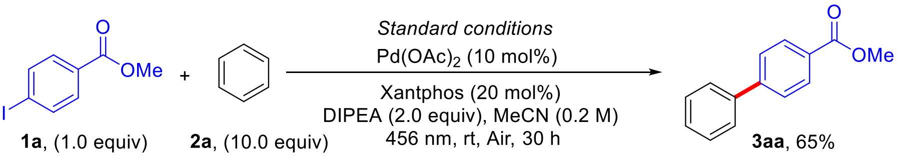
Monoisotopic Mass, Even Electron Ions
74 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 17-70 H: 25-81 N: 1-10 O: 3-10
091225_PM_700_2 22 (0.228) Cm (22:42)

```
Minimum:                         -1.5
Maximum:              10.0  100.0 50.0

Mass      Calc. Mass  mDa   PPM   DBE    i-FIT   Norm   Conf(%)  Formula

292.1909  292.1913    -0.4  -1.4  5.5    394.0   n/a    n/a      C17 H26 N O3
```

6. 1 mmol scale synthesis



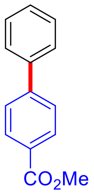
An 15 ml oven-dried glass vial was charged with a magnetic stir bar, methyl 4-iodobenzoate **(1a)** (260 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (890 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (22 mg, 0.02 mmol, 0.1 equiv), Xantphos (116 mg, 0.04 mmol, 0.2 equiv), DIPEA (348 µl, 0.4 mmol, 2.0 equiv). The mixture was dissolved in MeCN (0.2 M) under open atmosphere followed by the vial was sealed with a Teflon cap and rapped with parafilm. The reaction mixture was then stirred under the irradiation of 456 nm light for about 30 h at room temperature. The reaction mixtures were then filtered through a short pad of celite to remove insolubles and washed with EtOAc. The product of high analytical purity was achieved through column chromatography on silica gel, employing a (2–5%) solution of petroleum ether and ethyl acetate as the elution solvents. The product (**3aa**) was obtained as colorless solid, recording a yield of 65% (140 mg). The product was confirmed by NMR and Mass spectroscopy.

7. General procedure for the visible-light-mediated C(sp)^2–H Arylation (GP-2)

An oven-dried glass vial was charged with a magnetic stir bar, Aryl iodide **(1)** (0.2 mmol, 1.0 equiv), Arenes **(2)** (**a.** 2.0 mmol, 10.0 equiv for volatile and less than 100ºC boiling point. **b.** 0.6 mmol, 3.0 equiv for non-volatile and more than 100ºC boiling point), Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv). The mixture was dissolved in MeCN (0.2 M) under open atmosphere followed by the vial was sealed with a Teflon cap and rapped with parafilm. The reaction mixture was then stirred under the irradiation of 456 nm light for about 30 h at room temperature. The reaction mixtures were then filtered through a short pad of celite to remove insolubles and washed with EtOAc. The product of high analytical purity was achieved through column chromatography on silica gel, employing a (2–5%) solution of petroleum ether and ethyl acetate as the elution solvents. The product was confirmed by NMR and Mass spectroscopy.

8. Experimental details for the synthesized compounds obtained from GP–2

methyl [1,1'-biphenyl]-4-carboxylate (3aa)



$C_{14}H_{12}O_2$
M. W.: 212.2480 g/mol

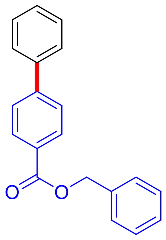
Prepared according to the **GP-2**, using methyl 4-iodobenzoate **(1a)** (52 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3aa**) was obtained as colorless solid, recording a yield of 70% (30 mg).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{14}H_{13}O_2]^+$: 213.0916; Found 213.0933.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12–8.10 (m, 2H), 7.68–7.65 (m, 2H), 7.64–7.61 (m, 2H), 7.49–7.45 (m, 2H), 7.42–7.38 (m, 1H), 3.94 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 145.8, 140.1, 130.2, 129.1, 129.0, 128.3, 127.4, 127.2, 52.3.

benzyl [1,1'-biphenyl]-4-carboxylate (3ba)



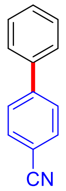
$C_{20}H_{16}O_2$
M. W.: 288.3460 g/mol

Prepared according to the **GP-2**, using methyl benzyl 4-iodobenzoate **(1b)** (67.6 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl , 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ba**) was obtained as colorless solid, recording a yield of 90% (52 mg). Analytical data matched those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.6 Hz, 2H), 7.68–7.65 (m, 2H), 7.63 (dd, *J* = 7.3, 1.9 Hz, 2H), 7.49–7.46 (m, 4H), 7.43–7.34 (m, 4H), 5.40 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 145.9, 140.1, 136.2, 130.4, 129.1, 128.9, 128.8, 128.4, 128.3, 128.3, 127.4, 127.2, 66.8.

[1,1'-biphenyl]-4-carbonitrile (3ca)



$C_{13}H_9N$
M. W.: 179.2220 g/mol

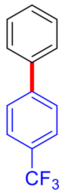
Prepared according to the **GP-2**, using 4-iodobenzonitrile **(1c)** (45.6 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ca**) was obtained as colorless solid, recording a yield of 60% (22 mg).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{13}H_{10}N]^+$: 180.0833; Found 180.0843.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.72 (m, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.61 – 7.58 (m, 2H), 7.51 – 7.47 (m, 2H), 7.45 – 7.41 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.9, 132.3, 131.7, 130.2, 129.2, 127.0, 122.6, 119.0, 112.6.

4-(trifluoromethyl)-1,1'-biphenyl (3da)



$C_{13}H_9F_3$
M. W.: 222.2102 g/mol

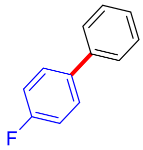
Prepared according to the **GP-2**, using methyl 1-iodo-4-(trifluoromethyl)benzene **(1d)** (54.4 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl , 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3da**) was obtained as colorless solid, recording a yield of 70% (31 mg). Analytical data matched those reported in the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 4H), 7.62–7.59 (m, 2H), 7.50–7.46 (m, 2H), 7.43–7.39 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 130.4 (q, J = 32.6 Hz), 129.1, 128.3, 127.8, 127.6, 127.4, 126.1 (q, *J* = 3.8 Hz), 124.3 (q, J = 272.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.55 (3F).

4-fluoro-1,1'-biphenyl (3ea)



$C_{12}H_9F$
M. W.: 172.2024 g/mol

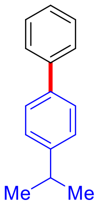
Prepared according to the **GP-2**, using methyl 1-fluoro-4-iodobenzene **(1e)** (44.4 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl , 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ea**) was obtained as colorless solid, recording a yield of 50% (17 mg). Analytical data matched those reported in the literature.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.61 (m, 2H), 7.52–7.49 (m, 2H), 7.32–7.28 (m, 1H), 7.26–7.22 (m, 2H), 6.87–6.81 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 246.2 Hz), 140.4, 137.4, 129.0, 128.8 (d, *J* = 7.9 Hz), 127.4, 127.2, 115.8 (d, *J* = 21.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.77 (1F).

4-isopropyl-1,1'-biphenyl (3fa)



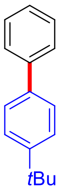
$C_{15}H_{16}$
M. W.: 196.2930 g/mol

Prepared according to the **GP-2**, using methyl 1-iodo-4-isopropylbenzene **(1f)** (49.2 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3fa**) was obtained as colorless solid, recording a yield of 65% (25 mg). Analytical data matched those reported in the literature.[11]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 (d, J = 7.6 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.45–7.42 (m, 2H), 7.35–7.30 (m, 3H), 3.02–2.91 (m, 1H), 1.30 (d, J = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 148.1, 141.3, 138.9, 128.8, 128.0, 127.2, 127.0, 123.7, 33.9, 24.2.

4-(tert-butyl)-1,1'-biphenyl (3ga)



$C_{16}H_{18}$
M. W.: 210.3200 g/mol

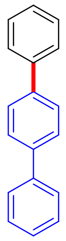
Prepared according to the **GP-2**, using methyl 1-(tert-butyl)-4-iodobenzene **(1g)** (52 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ga**) was obtained as colorless solid, recording a yield of 43% (18 mg).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{16}H_{19}]^+$: 211.1487; Found 211.1466.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.59 (m, 2H), 7.56–7.53 (m, 2H), 7.49–7.42 (m, 4H), 7.36–7.31 (m, 1H), 1.37 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 141.2, 138.4, 128.8, 127.2, 127.1, 126.9, 125.9, 34.7, 31.5.

1,1':4',1''-terphenyl (3ha)



$C_{18}H_{14}$
M. W.: 230.3100 g/mol

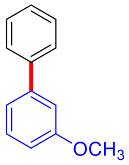
Prepared according to the **GP-2**, using methyl 4-iodo-1,1'-biphenyl **(1h)** (56 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl , 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ha**) was obtained as colorless solid, recording a yield of 70% (32 mg).

HRMS (ESI): m/z $[M+Na]^+$ Calculated for $[C_{18}H_{14}Na]^+$: 253.0993; Found 253.0995.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 4H), 7.67–7.64 (m, 4H), 7.48 (t, *J* = 7.6 Hz, 4H), 7.40–7.36 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 140.2, 129.0, 127.6, 127.5, 127.2.

3-methoxy-1,1'-biphenyl (3ia)



$C_{13}H_{12}O$
M. W.: 184.2380 g/mol

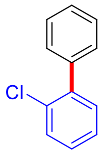
Prepared according to the **GP-2**, using methyl 1-iodo-3-methoxybenzene **(1i)** (46.8 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0

equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ia**) was obtained as colorless solid, recording a yield of 55% (20 mg). Analytical data matched those reported in the literature.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.59 (m, 2H), 7.47–7.42 (m, 2H), 7.39–7.34 (m, 2H), 7.20–7.18 (m, 1H), 7.14 (t, *J* = 2.3 Hz, 1H), 6.91 (dd, *J* = 8.3, 2.6 Hz, 1H), 3.87 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 142.9, 141.2, 129.9, 128.9, 127.6, 127.3, 119.8, 113.0, 112.8, 55.4.

2-chloro-1,1'-biphenyl (3ja)



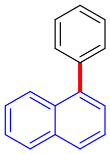
$C_{12}H_9Cl$
M. W.: 188.6540 g/mol

Prepared according to the **GP-2**, using methyl 1-chloro-2-iodobenzene **(1j)** (47.6 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ja**) was obtained as colorless solid, recording a yield of 85% (32 mg). Analytical data matched those reported in the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.2, 1.9 Hz, 1H), 7.46–7.45 (m, 4H), 7.44–7.37 (m, 1H), 7.36–7.34 (m, 1H), 7.32 (dd, *J* = 6.8, 2.2 Hz, 1H), 7.30–7.27 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 139.5, 132.6, 131.5, 130.1, 129.6, 128.7, 128.2, 127.7, 127.0.

1-phenylnaphthalene (3ka)



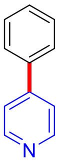
$C_{16}H_{12}$
M. W.: 204.2720 g/mol

Prepared according to the **GP-2**, using methyl 1-iodonaphthalene **(1k)** (50.8 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ka**) was obtained as colorless solid, recording a yield of 75% (31 mg). Analytical data matched those reported in the literature.[14]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.52–7.48 (m, 5H), 7.46–7.42 (m, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 140.9, 140.4, 133.9, 131.7, 130.2, 128.9, 128.4, 128.0, 127.8, 127.4, 127.1, 126.2, 125.9, 125.5.

4-phenylpyridine (3la)



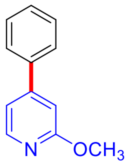
$C_{11}H_9N$
M. W.: 155.2000 g/mol

Prepared according to the **GP-2**, using methyl 4-iodopyridine **(1l)** (40.8 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3la**) was obtained as colorless liquid, recording a yield of 45% (16 mg). Analytical data matched those reported in the literature.[15]

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.67 (s, 2H), 7.66–7.63 (m, 2H), 7.52–7.44 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 129.3, 129.2 (2C), 127.2, 121.8 (2C).

2-methoxy-4-phenylpyridine (3ma)



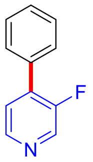
$C_{12}H_{11}NO$
M. W.: 185.2260 g/mol

Prepared according to the **GP-2**, using methyl 4-iodo-2-methoxypyridine **(1m)** (47 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ma**) was obtained as colorless liquid, recording a yield of 55% (20 mg). Analytical data matched those reported in the literature.[16]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 5.5 Hz, 1H), 7.63–7.60 (m, 2H), 7.49–7.41 (m, 3H), 7.11 (dd, *J* = 5.4, 1.7 Hz, 1H), 6.96 (s, 1H), 3.99 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 151.3, 147.3, 138.4, 129.1, 129.1, 127.1, 115.5, 108.6, 53.7.

3-fluoro-4-phenylpyridine (3na)



$C_{11}H_8FN$
M. W.: 173.1904 g/mol

Prepared according to the **GP-2**, using methyl 3-fluoro-4-iodopyridine **(1n)** (44.4 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3na**) was obtained as colorless liquid, recording a yield of 70% (24 mg).

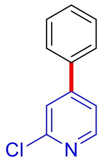
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{11}H_9FN]^+$: 174.0719; Found 174.0725.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 2.6 Hz, 1H), 8.47 (d, *J* = 5.1 Hz, 1H), 7.63–7.60 (m, 2H), 7.52–7.46 (m, 3H), 7.42–7.39 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8 (d, *J* = 257.0 Hz), 146.1 (d, *J* = 5.5 Hz), 139.2 (d, *J* = 25.9 Hz), 136.2 (d, *J* = 10.6 Hz), 133.1, 129.4, 129.0, 124.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -132.85 (1F).

2-chloro-4-phenylpyridine (3oa)



$C_{11}H_8ClN$
M. W.: 189.6420 g/mol

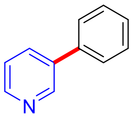
Prepared according to the **GP-2**, using methyl 2-chloro-4-iodopyridine **(1o)** (47.8 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3oa**) was obtained as colorless liquid, recording a yield of 75% (28 mg).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{11}H_9ClN]^+$: 190.0424; Found 190.0435.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 5.1 Hz, 1H), 7.62–7.59 (m, 2H), 7.54 (s, 1H), 7.52–7.46 (m, 3H), 7.43 (dd, *J* = 5.4, 1.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 151.7, 150.1, 136.9, 129.8, 129.4, 127.2, 122.2, 120.6.

3-phenylpyridine (3pa)



$C_{11}H_9N$
M. W.: 155.2000 g/mol

Prepared according to the **GP-2**, using methyl 3-iodopyridine **(1p)** (40.8 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and

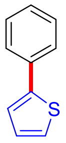
MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3pa**) was obtained as colorless liquid, recording a yield of 65% (20 mg).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{11}H_{10}N]^+$: 156.0808; Found 156.0813.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 2.3 Hz, 1H), 8.59 (dd, *J* = 4.9, 1.6 Hz, 1H), 7.88 (dt, *J* = 8.2, 2.2 Hz, 1H), 7.60–7.57 (m, 2H), 7.51–7.46 (m, 2H), 7.43–7.36 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 148.5, 138.0, 136.8, 134.5, 129.2, 128.3, 127.3, 123.7.

2-phenylthiophene (3qa)



$C_{10}H_8S$
M. W.: 160.2340 g/mol

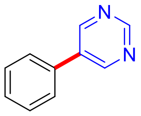
Prepared according to the **GP-2**, using methyl 2-iodothiophene **(1q)** (42 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3qa**) was obtained as colorless liquid, recording a yield of 75% (24 mg).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{10}H_9S]^+$: 161.0425; Found 161.0435.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.62 (m, 2H), 7.42–7.37 (m, 2H), 7.34–7.28 (m, 3H), 7.11–7.09 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 134.5, 129.0, 128.1, 127.6, 126.1, 124.9, 123.2.

5-phenylpyrimidine (3ra)



$C_{10}H_8N_2$
M. W.: 156.1880 g/mol

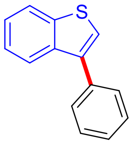
Prepared according to the **GP-2**, using methyl 5-iodopyrimidine **(1r)** (41 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1

equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ra**) was obtained as colorless liquid, recording a yield of 70% (22 mg). Analytical data matched those reported in the literature.[17]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.95 (s, 2H), 7.60–7.56 (m, 2H), 7.54–7.50 (m, 2H), 7.49–7.44 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 155.0, 134.5, 134.4, 129.6, 129.1, 127.1.

3-phenylbenzo[b]thiophene (3sa)



$C_{14}H_{10}S$
M. W.: 210.2940 g/mol

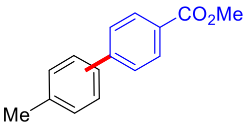
Prepared according to the **GP-2**, using methyl 3-iodobenzo[*b*]thiophene **(1s)** (52 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3sa**) was obtained as colorless liquid, recording a yield of 80% (34 mg). Analytical data matched those reported in the literature.[18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.91 (m, 2H), 7.62–7.59 (m, 2H), 7.52–7.48 (m, 2H), 7.44–7.39 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 138.2, 138.0, 136.1, 129.1, 128.9, 127.7, 126.6, 124.6, 124.5, 123.6, 123.1.

Arene variation

Toluene as arene (3ab): The product was obtained as a colorless solid, mixture of three isomers in a ratio of o:m:p = 3:1.7:1. Spectral data for all products matched the reported literature values. *ortho*[19], *meta*[19], *para.*[20]



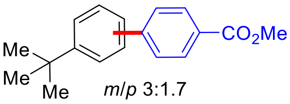
o/*m*/*p* 3:1.7:1.1

Prepared according to the **GP-2**, using methyl 4-iodobenzoate **(1a)** (52 mg, 0.2 mmol, 1.0 equiv), Toluene **(2b)** (106 µl, 0.6 mmol, 3.0 equiv), Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ab**) was obtained as colorless solid, recording a yield of 60% (27 mg). Analytical data matched those reported in the literature *ortho*, *meta*, *para.*[19, 20]

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.11–8.07 (m, 3.8H), 7.65 (dd, *J* = 8.2, 3.1 Hz, 1.9H), 7.55–7.52 (m, 0.75H), 7.46–7.44 (m, 1.12H), 7.42–7.39 (m, 2.03H), 7.36 (t, *J* = 7.5 Hz, 0.69H), 7.30–7.25 (m, 4.15H), 7.24–7.20 (m, 1.84H), 3.95 (s, 3H$_{ortho}$), 3.94 (s, 2H$_{meta}$), 3.94 (s, 1H$_{para}$), 2.44 (s, 2H$_{meta}$), 2.41 (s, 1H$_{para}$), 2.27 (s, 3H$_{ortho}$).

^{13}C NMR (101 MHz, CDCl$_3$) δ 167.2, 146.9, 145.9, 141.0, 140.1, 138.7, 138.3, 137.2, 135.3, 130.6, 130.2, 130.2, 129.8, 129.7, 129.6, 129.4, 129.0, 129.0, 128.9, 128.7, 128.5, 128.2, 128.0, 127.2, 127.2, 126.9, 126.0, 124.5, 52.3, 21.7, 21.3, 20.5.

***tert*-butylbenzene as arene (3ac)**: The product was obtained as a colorless solid, mixture of two isomers in a ratio of m:p = 3:1.7. Spectral data for para product matched the reported literature values. *Para.*[21]



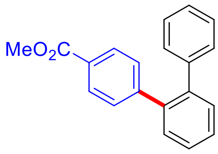
m/*p* 3:1.7

Prepared according to the **GP-2**, using methyl 4-iodobenzoate **(1a)** (52 mg, 0.2 mmol, 1.0 equiv), *tert*-butylbenzene **(2c)** (92 µl, 0.6 mmol, 3.0 equiv), Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ac**) was obtained as colorless solid, recording a yield of 55% (30 mg). Analytical data matched those reported in the literature, *para.*[21]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12–8.08 (m, 3.1H), 7.68–7.65 (m, 3.32H), 7.63–7.62 (m, 1.05H), 7.59–7.56 (m, 1.17H), 7.51–7.48 (m, 1.16H), 7.46–7.43 (m, 2.01H), 7.42–7.38 (m, 1.17H), 3.94 (s, $3H_{meta}$), 3.94 (s, $1.7H_{para}$), 1.38 (s, $9.0H_{meta}$), 1.37 (s, $5.3H_{para}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 152.0, 146.4, 139.9, 130.2, 128.8, 127.3, 127.1, 127.0, 126.1, 125.4, 124.7, 124.5, 52.3, 35.0, 31.5, 31.4.

methyl [1,1':2',1''-terphenyl]-4-carboxylate (3ad)



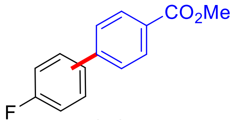
$C_{20}H_{16}O_2$
M. W.: 288.3460 g/mol

Prepared according to the **GP-2**, using methyl 4-iodobenzoate **(1a)** (52 mg, 0.2 mmol, 1.0 equiv), 1,1'-biphenyl **(2d)** (92.4 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ad**) was obtained as colorless solid, recording a yield of 60% (35 mg). Analytical data matched those reported in the literature.[22]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.46–7.42 (m, 4H), 7.23–7.19 (m, 5H), 7.14–7.09 (m, 2H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 146.5, 141.1, 140.8, 139.6, 130.9, 130.5, 130.0, 130.0, 129.3 (2C), 128.3, 128.2, 127.7, 126.9, 52.2.

Fluorobenzene as arene (3ae): The product was obtained as a colorless solid, mixture of three isomers in a ratio of *o*:*m*:*p* = 3:2.3:0.5. Spectral data for all products matched the reported literature values. *ortho*, *meta*, *para.*[23]



o/m/p 3:2.3:0.5

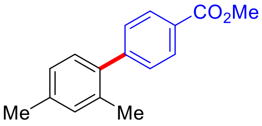
Prepared according to the **GP-2**, using methyl 4-iodobenzoate **(1a)** (52 mg, 0.2 mmol, 1.0 equiv), Fluorobenzene **(2e)** (193 µl, 2.0 mmol, 10 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ae**) was obtained as colorless solid, recording a yield of 65% (29 mg). Analytical data matched those reported in the literature *ortho*, *meta*, *para*.[23]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13–8.09 (m, 1.88H), 7.68–7.61 (m, 1.98H), 7.61–7.57 (m, 0.28H), 7.48–7.40 (m, 1.28H), 7.39–7.30 (m, 0.94H), 7.24–7.20 (m, 0.50H), 7.18–7.15 (m, 0.47H), 7.13–7.06 (m, 0.37H) 3.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 167.0, 163.3 (d, J = 247.45 Hz), 159.8 (d, J = 250.48 Hz), 144.4 (d, J = 2.02 Hz), 142.4 (d, J = 8.08 Hz), 140.5, 130.8(d, J = 3.03 Hz), 130.6 (d, J = 8.08 Hz), 130.3, 129.9 (d, J = 8.08 Hz), 129.8, 129.5, 129.3, 129.2 (d, J = 8.08 Hz), 128.2, 128.0, 127.4, 127.2, 127.0, 124.7 (d, J = 4.04 Hz), 123.1, 116.4 (d, J = 22.2 Hz), 116.0 (d, J = 22.2 Hz), 115.1(d, J = 21.21 Hz), 114.3 (d, J = 22.2 Hz), 52.4 (t, J = 3.03 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.54 (F_{meta}), -114.11 (F_{para}), -117.43 (F_{ortho}).

methyl 2',4'-dimethyl-[1,1'-biphenyl]-4-carboxylate (3af)



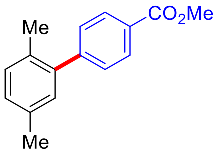
$C_{16}H_{16}O_2$
M. W.: 240.3020 g/mol

Prepared according to the **GP-2**, using methyl 4-iodobenzoate **(1a)** (52 mg, 0.2 mmol, 1.0 equiv), *m*-xylene **(2f)** (63.6 µl, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3af**) was obtained as colorless solid, recording a yield of 56% (27 mg). Analytical data matched those reported in the literature.[24]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10–8.06 (m, 2H), 7.41–7.37 (m, 2H), 7.14–7.07 (m, 3H), 3.94 (s, 3H), 2.37 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 146.9, 138.1, 137.7, 135.1, 131.4, 129.6, 129.5, 129.5, 128.5, 126.8, 52.2, 21.2, 20.5.

methyl 2',5'-dimethyl-[1,1'-biphenyl]-4-carboxylate (3ag)



$C_{16}H_{16}O_2$
M. W.: 240.3020 g/mol

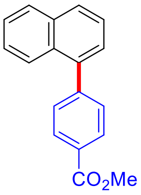
Prepared according to the **GP-2**, using methyl 4-iodobenzoate **(1a)** (52 mg, 0.2 mmol, 1.0 equiv), *p*-xylene **(2g)** (63.6 µl, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ag**) was obtained as colorless solid, recording a yield of 50% (24 mg). Analytical data matched those reported in the literature.[25]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–8.06 (m, 2H), 7.41–7.38 (m, 2H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.05 (s, 1H), 3.95 (s, 3H), 2.36 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 147.1, 140.8, 135.5, 132.1, 130.6, 130.4, 129.5, 129.4, 128.7, 128.6, 52.3, 21.0, 20.0.

Naphthalene as arene (3ah): Two products were obtained as a colorless solid. We are isolated separately. The reaction produces a mixture of two structural isomers. The ratio of the two products C_1:C_2 = 5:4.

methyl 4-(naphthalen-1-yl)benzoate (3ah) (C_1)



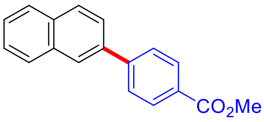
$C_{18}H_{14}O_2$
M. W.: 262.3080 g/mol

Prepared according to the **GP-2**, using methyl 4-iodobenzoate **(1a)** (52 mg, 0.2 mmol, 1.0 equiv), naphthalene **(2h)** (76.8 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ah**) **(C_1)** was obtained as colorless solid, recording a yield of 40% (21 mg). Analytical data matched those reported in the literature.[26]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.2 Hz, 2H), 7.94–7.84 (m, 3H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.56–7.49 (m, 2H), 7.47–7.42 (m, 2H), 3.98 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 145.7, 139.2, 133.9, 131.3, 130.3, 129.7, 129.1, 128.5, 128.4, 127.1, 126.5, 126.1, 125.7, 125.5, 52.4.

methyl 4-(naphthalen-2-yl)benzoate (3ah) (C_2)



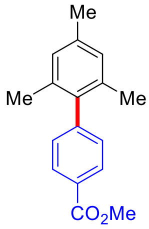
$C_{18}H_{14}O_2$
M. W.: 262.3080 g/mol

Prepared according to the **GP-2**, using methyl 4-iodobenzoate **(1a)** (52 mg, 0.2 mmol, 1.0 equiv), naphthalene **(2h)** (76.8 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product **(3ah)** **(C_2)** was obtained as colorless solid, recording a yield of 30% (16 mg). Analytical data matched those reported in the literature.[27]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.3 Hz, 2H), 8.09 (s, 1H), 7.96–7.87 (m, 3H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.77 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.56–7.49 (m, 2H), 3.96 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 145.7, 137.4, 133.7, 133.1, 130.3, 129.0, 128.8, 128.5, 127.8, 127.4, 126.7, 126.6, 126.5, 125.4, 52.4.

methyl 2',4',6'-trimethyl-[1,1'-biphenyl]-4-carboxylate (3ai)



$C_{17}H_{18}O_2$
M W.: 254.3290 g/mol

Prepared according to the **GP-2**, using methyl 4-iodobenzoate **(1a)** (52 mg, 0.2 mmol, 1.0 equiv), mesitylene **(2i)** (72 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ai**) was obtained as colorless solid, recording a yield of 65% (33 mg).

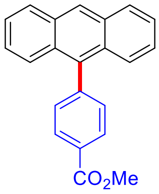
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{17}H_{19}O_2]^+$: 255.1385; Found 255.1392.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.95 (s, 2H), 3.94 (s, 3H), 2.33 (s, 3H), 1.98 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 146.4, 138.1, 137.2, 135.7, 129.9, 129.6, 128.3, 52.3, 21.2, 20.8.

Anthracene as arene (3aj): The products were obtained as a colorless solid. The reaction produces a mixture of three structural isomers. The major product Methyl 4-(anthracen-9-yl)benzoate **(3aj)** (constituting ~35% of the total yield 65%) is the stable isomer, while the other two positional isomers in a ratio = 3:1.

methyl 4-(anthracen-9-yl)benzoate (3aj) (C^{10})



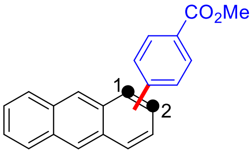
$C_{22}H_{16}O_2$
M. W.: 312.3680 g/mol

Prepared according to the **GP-2**, using methyl 4-iodobenzoate **(1a)** (52 mg, 0.2 mmol, 1.0 equiv), anthracene **(2j)** (108 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3aj**) was obtained as colorless solid, recording a yield of 35% (22 mg). Analytical data matched those reported in the literature.[27]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.26 (d, *J* = 8.2 Hz, 2H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.54–7.52 (m, 2H), 7.49–7.45 (m, 2H), 7.38–7.34 (m, 2H), 4.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 144.1, 135.8, 131.6, 131.4, 123.0, 129.8, 129.5, 128.6, 127.3, 126.5, 125.8, 125.3, 52.4.

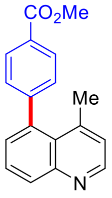
methyl 4-(anthracen-9-yl)benzoate (3aj) (C_1 and C_2)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.39 (s, 1H), 8.23 (d, *J* = 8.0 Hz, 2.04H), 8.11–8.01 (m, 2.96H), 7.87 (d, *J* = 8.2 Hz, 0.99H), 7.74 (d, *J* = 7.9 Hz, 0.4H) 7.68 (d, *J* = 8.2 Hz, 2.13H), 7.63–7.60 (m, 0.81H), 7.55–7.48 (m, 2.74H), 7.47–7.39 (m, 3.05H), 7.37–7.33 (m, 0.94H), 4.00 (s, 3H), 3.96 (s, 0.96H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 145.9, 139.3, 133.0, 132.0, 131.9, 131.6, 130.3, 129.9, 129.9, 129.3, 129.0, 128.8, 128.7, 128.1, 128.0, 127.0, 126.9, 126.5, 126.1, 125.9, 125.8, 125.7, 125.5, 124.9, 124.7, 124.2, 52.4.

methyl 4-(4-methylquinolin-5-yl)benzoate (3ak)



$C_{18}H_{15}NO_2$
M. W.: 277.3230

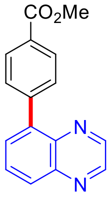
Prepared according to the **GP-2**, using methyl 4-iodobenzoate **(1a)** (52 mg, 0.2 mmol, 1.0 equiv), 4-methylquinoline **(2k)** (85.9 µl, 0.6 mmol, 3.0 equiv), Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ak**) was obtained as colorless liquid, recording a yield of 43% (24 mg).

MS (ESI) m/z: [M + H]+ Calcd for $[C_{18}H_{16}NO_2]^+$: 278.12; Found 278.20.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.77 (d, *J* = 4.3 Hz, 1H), 8.16 (dd, *J* = 8.6, 1.3 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 2H), 7.68 (dd, *J* = 8.4, 7.0 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.35 (dd, *J* = 7.0, 1.6 Hz, 1H), 7.15 (d, *J* = 4.4 Hz, 1H), 3.97 (s, 3H), 2.01 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 167.1, 150.1, 149.2, 148.8, 145.4, 139.4, 130.7, 129.7, 129.6, 129.3 (2C), 127.9, 126.7, 124.6, 52.4, 24.7.

methyl 4-(quinoxalin-5-yl)benzoate (3al)



$C_{16}H_{12}N_2O_2$
M. W.: 264.2840 g/mol

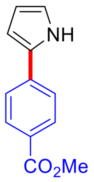
Prepared according to the **GP-2**, using methyl 4-iodobenzoate **(1a)** (52 mg, 0.2 mmol, 1.0 equiv), quinoxaline **(2l)** (78 mg, 0.6 mmol, 3.0 equiv), Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3al**) was obtained as colorless solid, recording a yield of 57% (30 mg).

MS (ESI) m/z: [M + H]+ Calcd for [$C_{16}H_{13}N_2O_2$]$^+$: 265.10; Found 265.23.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 1.5 Hz, 2H), 8.19–8.16 (m, 3H), 7.89–7.82 (m, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 3.96 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 145.0, 145.0, 143.0, 141.0, 140.2, 130.8 (2C), 130.0, 129.8, 129.5 (2C), 129.5, 52.4.

methyl 4-(1H-pyrrol-2-yl)benzoate (3am)



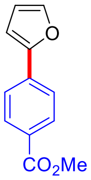
$C_{12}H_{11}NO_2$
M. W.: 201.2250 g/mol

Prepared according to the **GP-2**, using methyl 4-iodobenzoate **(1a)** (52 mg, 0.2 mmol, 1.0 equiv), 1*H*-pyrrole **(2m)** (134 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3am**) was obtained as colorless liquid, recording a yield of 55% (22 mg). Analytical data matched those reported in the literature.[28]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (br, 1H), 8.03 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 6.94–6.92 (m, 1H), 6.67–6.65 (m, 1H), 6.34–6.32 (m, 1H), 3.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 136.9, 131.1, 130.5, 127.4, 123.3, 120.4, 110.8, 108.1, 52.2.

methyl 4-(furan-2-yl)benzoate (3an)



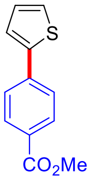
$C_{12}H_{10}O_3$
M. W.: 202.2090 g/mol

Prepared according to the **GP-2**, using methyl 4-iodobenzoate **(1a)** (52 mg, 0.2 mmol, 1.0 equiv), Furan **(2n)** (136 µl, 2 mmol, 10.0 equiv), Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3an**) was obtained as colorless liquid, recording a yield of 60% (24 mg). Analytical data matched those reported in the literature.[29]

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 1.6 Hz, 1H), 6.79 (d, *J* = 3.6 Hz, 1H), 6.51 (dd, *J* = 3.2, 1.8 Hz, 1H), 3.92 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 167.0, 153.1, 143.3, 134.9, 130.3, 128.6, 123.5, 112.2, 107.4, 52.3.

methyl 4-(thiophen-2-yl)benzoate (3ao)



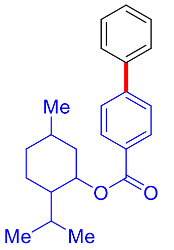
$C_{12}H_{10}O_2S$
M. W.: 218.2700 g/mol

Prepared according to the **GP-2**, using methyl 4-iodobenzoate **(1a)** (52 mg, 0.2 mmol, 1.0 equiv), Thiophene **(2o)** (168 µl, 2 mmol, 10.0 equiv), Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ao**) was obtained as colorless liquid, recording a yield of 60% (26 mg). Analytical data matched those reported in the literature.[30]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.44–7.42 (m, 1H), 7.37 (d, *J* = 4.9 Hz, 1H), 7.13–7.11 (m, 1H), 3.93 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 143.2, 138.8, 130.4, 128.9, 128.5, 126.4, 125.7, 124.6, 52.3.

2-isopropyl-5-methylcyclohexyl [1,1'-biphenyl]-4-carboxylate (3ta)



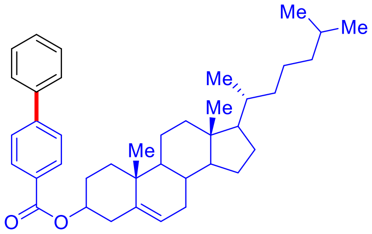
$C_{23}H_{28}O_2$
M. W.: 336.4750 g/mol

Prepared according to the **GP-2**, using 2-isopropyl-5-methylcyclohexyl 4-iodobenzoate **(1t)** (77.2 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ta**) was obtained as colorless solid, recording a yield of 82% (55 mg). Analytical data matched those reported in the literature.[31]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.11 (m, 2H), 7.68–7.61 (m, 4H), 7.50–7.44 (m, 2H), 7.42–7.38 (m, 1H), 4.97 (td, *J* = 10.9, 4.4 Hz, 1H), 2.18–2.12 (m, 1H), 2.04–1.95 (m, 1H), 1.78–1.72 (m, 2H), 1.62–1.53 (m, 3H), 1.17–1.09 (m, 2H), 0.94 (dd, *J* = 6.7, 3.0 Hz, 6H), 0.82 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 145.6, 140.3, 132.8, 130.2, 129.7, 129.1, 128.4, 128.2, 127.4, 127.2, 75.0, 47.4, 41.1, 34.5, 31.6, 26.6, 23.8, 22.2, 20.9, 16.7.

(10R,13R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl [1,1'-biphenyl]-4-carboxylate (Cholesterol) (3ua)



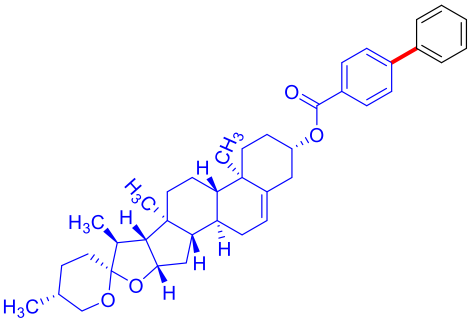
$C_{40}H_{54}O_2$
M. W.: 566.8700 g/mol

Prepared according to the **GP-2**, using Cholesterol tag iodoester **(1u)** (123.3 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ua**) was obtained as colorless solid, recording a yield of 45% (51 mg). Analytical data matched those reported in the literature.[32]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.2 Hz, 2H), 7.67–7.62 (m, 4H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.42–7.37 (m, 1H), 5.44 (d, *J* = 3.9 Hz, 1H), 4.93–4.85 (m, 1H), 2.49 (d, *J* = 8.0 Hz, 2H), 2.05–1.90 (m, 4H), 1.88–1.80 (m, 1H), 1.78–1.69 (m, 1H), 1.63–1.56 (m, 2H), 1.54–1.44 (m, 4H), 1.39–1.33 (m, 3H), 1.29–1.21 (m, 3H), 1.19–1.12 (m, 4H), 1.08 (s, 3H), 1.06–0.97 (m, 4H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 1.8 Hz, 3H), 0.87 (d, *J* = 1.9 Hz, 3H), 0.70 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 145.6, 140.2, 139.8, 130.2, 129.7, 129.0, 128.2, 127.4, 127.1, 122.9, 74.7, 56.8, 56.2, 50.1, 42.4, 39.8, 39.6, 38.4, 37.2, 36.8, 36.3, 35.9, 32.1, 32.0, 28.4, 28.2, 28.0, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0.

(1s,4R,4'S,6a'R,6b'S,8a'S,8b'R,9'S,11a'S,12a'S,12b'S)-4,6a',8a',9'-tetramethyl-1',3',4',5',6',6a',6b',7',8',8a',8b',9',11a',12',12a',12b'-hexadecahydrospiro[cyclohexane-1,10'-naphtho[2',1':4,5]indeno[2,1-b]furan]-4'-yl [1,1'-biphenyl]-4-carboxylate (Nitogenin) (3va)



$C_{40}H_{50}O_4$
M. W.: 594.8360

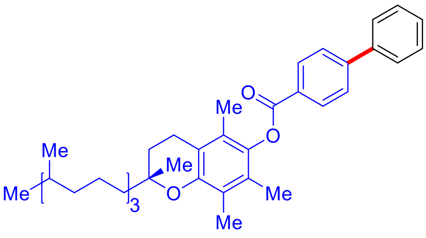
Prepared according to the **GP-2**, using Nitogenin tag iodoester **(1v)** (128.8 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3va**) was obtained as colorless solid, recording a yield of 80% (95 mg).

MS (ESI) m/z: [M + H]+ Calcd for $[C_{40}H_{51}O_4]^+$: 595.38; Found 595.47.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.67–7.61 (m, 4H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.41–7.37 (m, 1H), 5.43 (d, *J* = 4.9 Hz, 1H), 4.92–4.84 (m, 1H), 4.45–4.39 (m, 1H), 3.50–3.46 (m, 1H), 3.38 (t, *J* = 10.8 Hz, 1H), 2.49 (d, *J* = 8.1 Hz, 2H), 2.06–1.97 (m, 3H), 1.95–1.85 (m, 2H), 1.81–1.72 (m, 3H), 1.71–1.64 (m, 3H), 1.61–1.39 (m, 6H), 1.34–1.13 (m, 4H), 1.10 (s, 3H), 1.06–1.02 (m, 1H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.79 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 145.6, 140.2, 139.8, 130.2, 129.6, 129.1, 128.2, 127.4, 127.1, 122.6, 109.4, 81.0, 74.6, 67.0, 62.2, 56.6, 50.0, 41.7, 40.4, 39.9, 38.3, 37.1, 36.9, 32.2, 32.0, 31.5, 31.5, 30.4, 28.9, 28.0, 21.0, 19.6, 17.3, 16.4, 14.7.

(2R)-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl [1,1'-biphenyl]-4-carboxylate (Vitamin E) (3wa)



$C_{42}H_{58}O_3$
M. W.: 610.9230

Prepared according to the **GP-2**, using Vitamin E tag iodoester **(1w)** (86 mg, 0.2 mmol, 1.0 equiv), Benzene **(2a)** (178 µl, 2.0 mmol, 10.0 equiv), Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), Xantphos (23.2 mg, 0.04 mmol, 0.2 equiv), DIPEA (69.6 µl, 0.4 mmol, 2.0 equiv) and MeCN (0.2 M). A (2–5%) solution of petroleum ether and ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3wa**) was obtained as colorless liquid, recording a yield of 75% (31 mg).

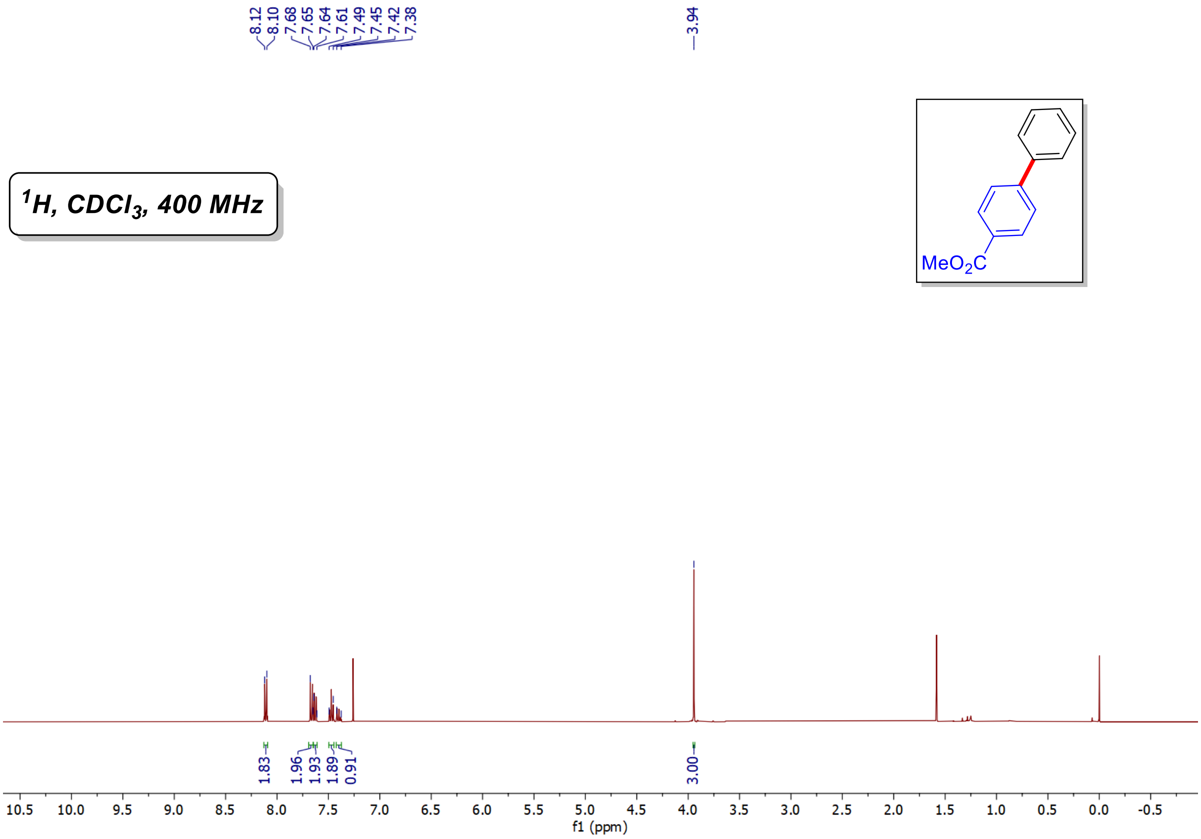
MS (ESI) m/z: [M + Na]+ Calcd for $[C_{42}H_{58}O_3Na]^+$: 633.42; Found 633.40.

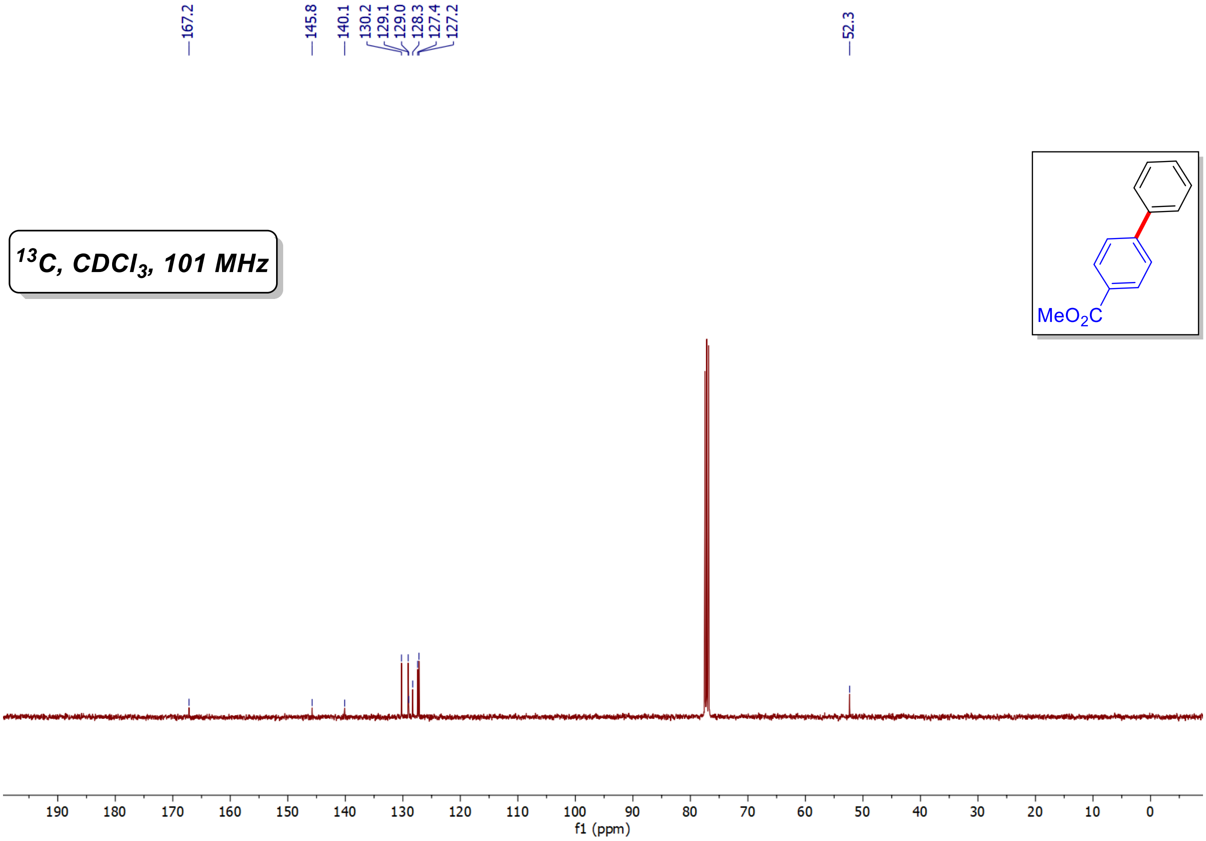
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.68–7.66 (m, 2H), 7.52–7.48 (m, 2H), 7.45–7.41 (m, 1H), 2.64 (t, *J* = 6.8 Hz, 2H), 2.14 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 1.87–1.77 (m, 2H), 1.57–1.48 (m, 2H), 1.46–1.37 (m, 4H), 1.31–1.24 (m, 10H), 1.19–1.01 (m, 8H), 0.88 (s, 3H), 0.87 (s, 3H), 0.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 149.6, 146.3, 140.8, 140.1, 130.8, 129.1, 128.5, 128.4, 127.5, 127.4, 127.1, 125.3, 123.3, 117.6, 75.2, 40.6, 39.5, 37.5, 37.4, 32.9, 31.2, 29.8, 28.1, 25.0, 24.6, 24.3, 23.8, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 13.2, 12.4, 12.0.

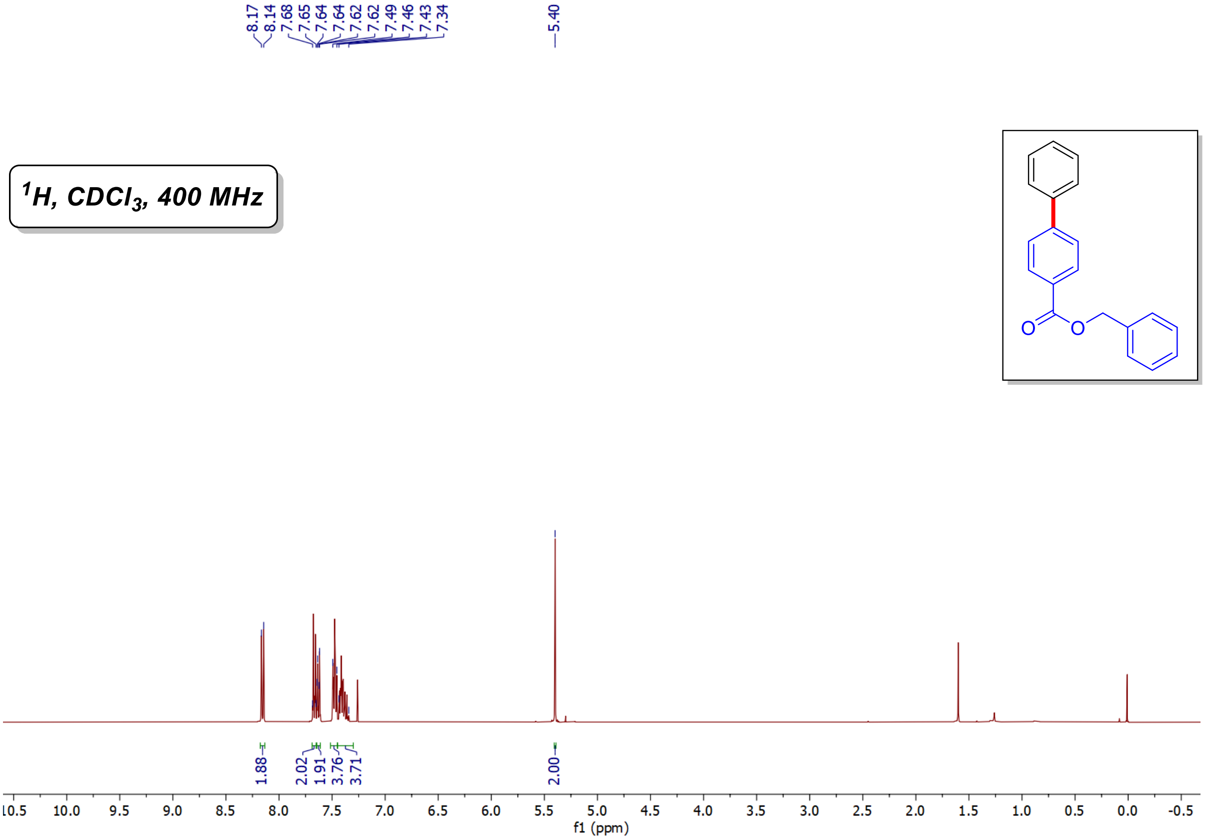
9. Experimental NMR data

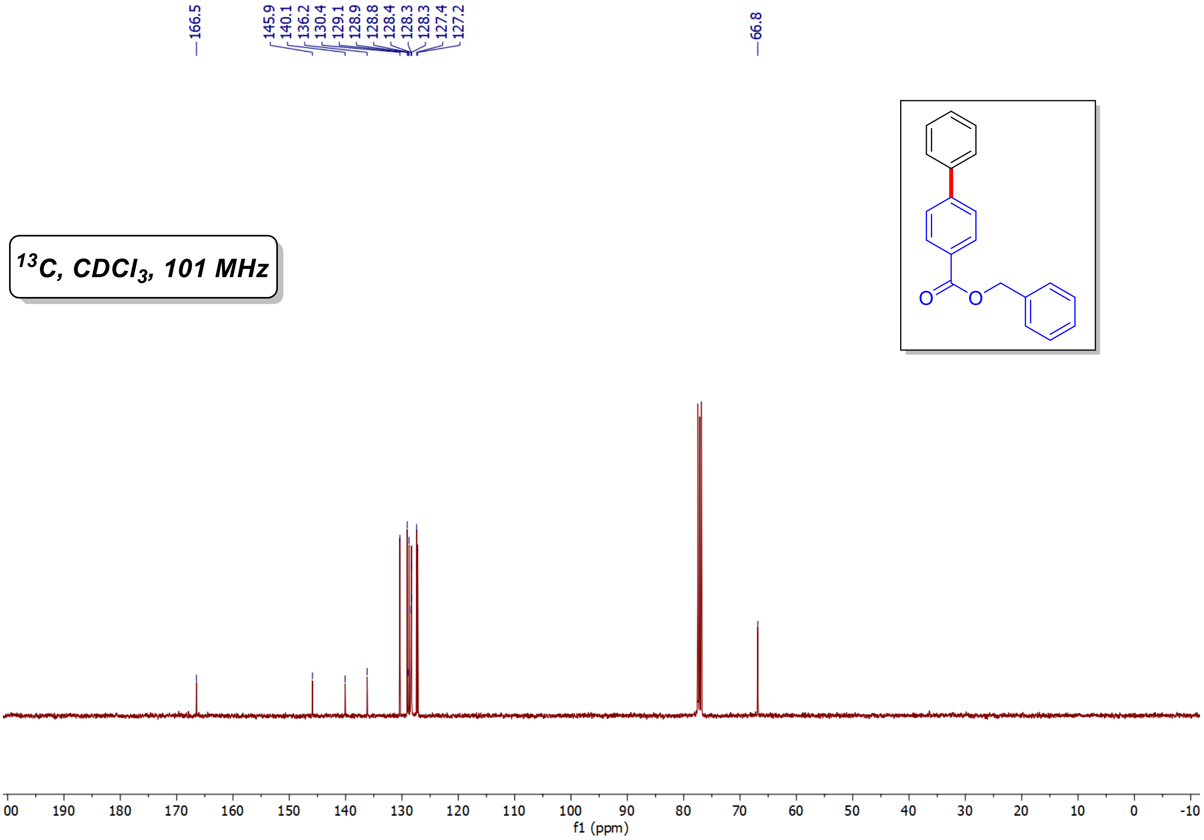
methyl [1,1'-biphenyl]-4-carboxylate (3aa)





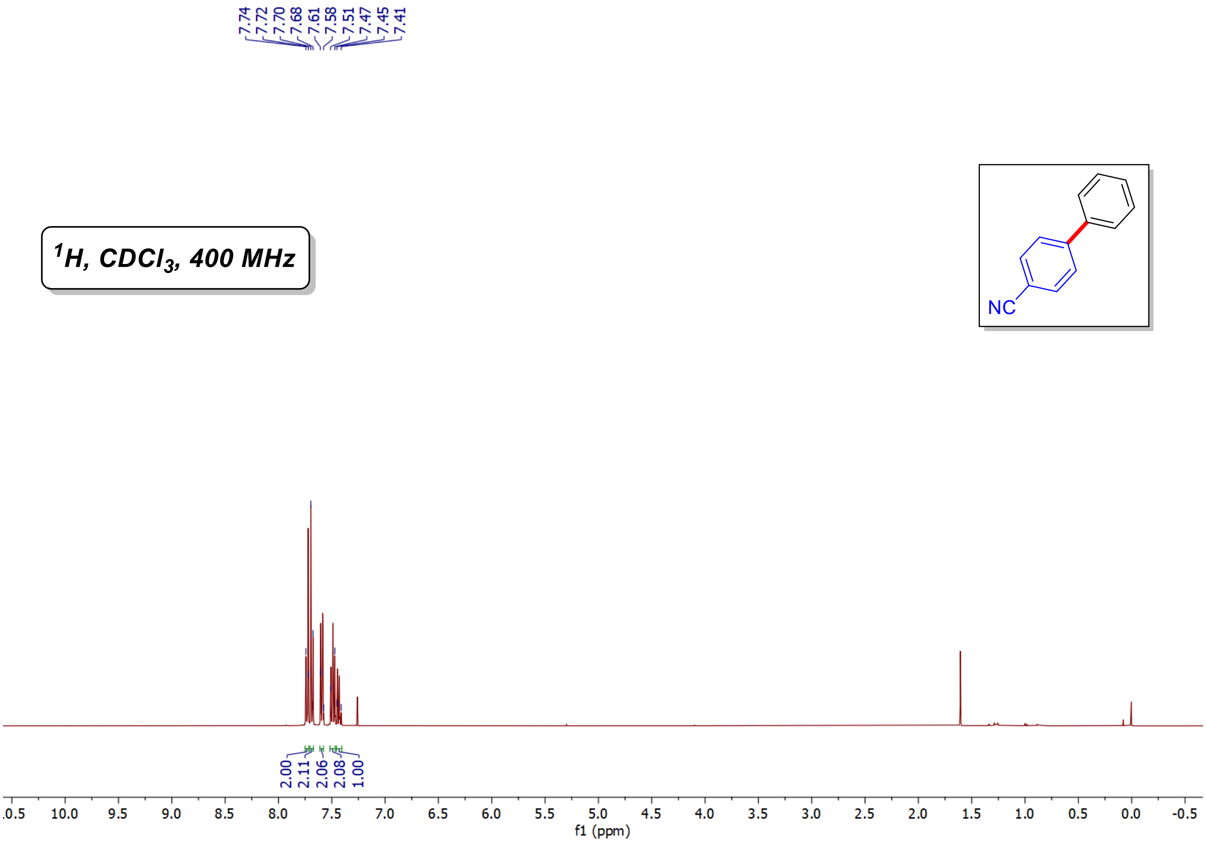
benzyl [1,1'-biphenyl]-4-carboxylate (3ba)



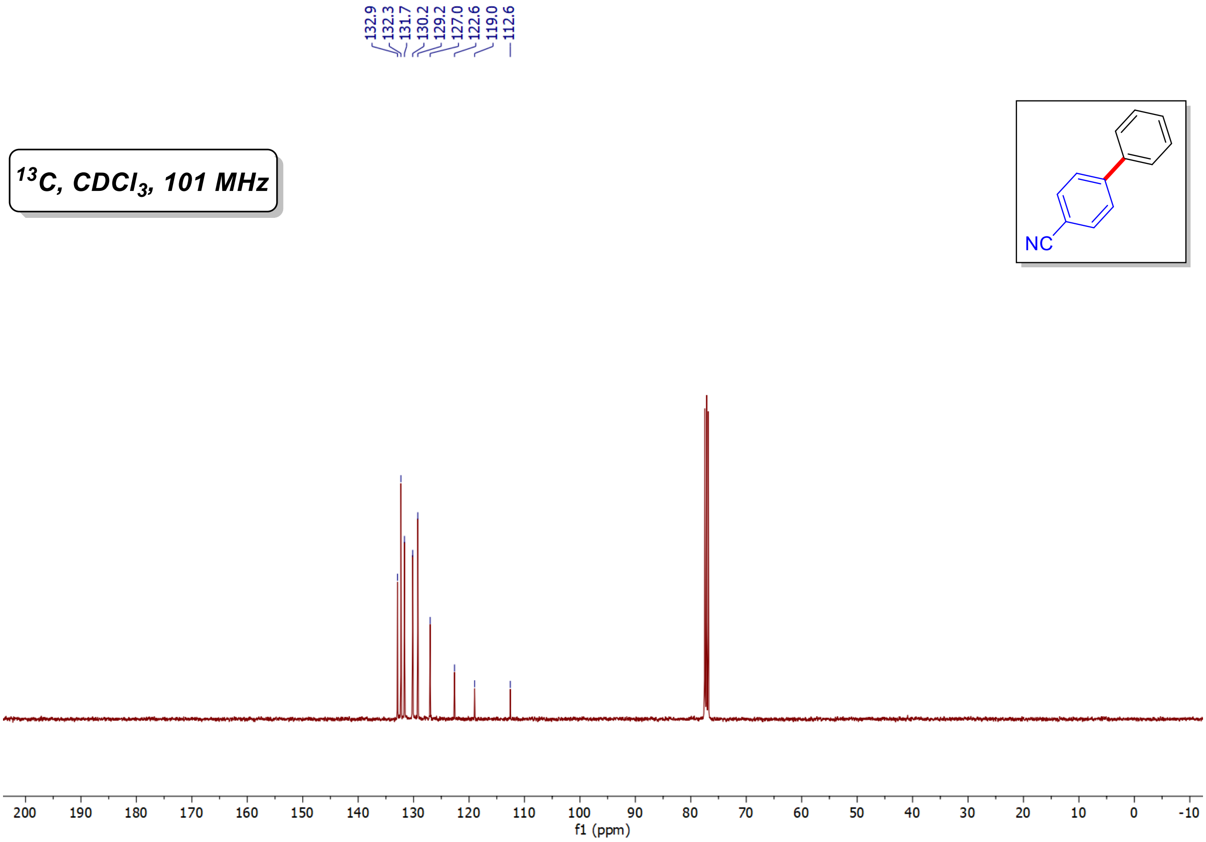


[1,1'-biphenyl]-4-carbonitrile (3ca)

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

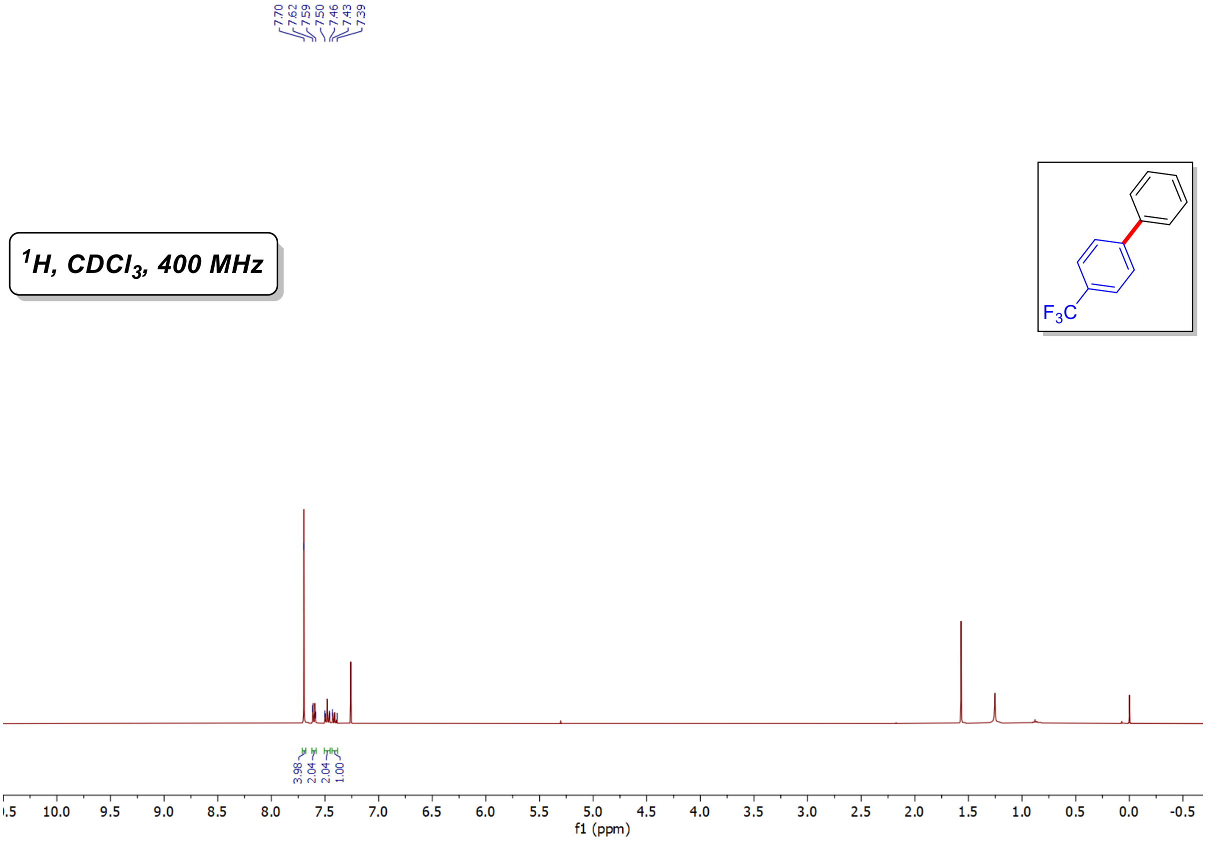


^{13}C, $CDCl_3$, 101 MHz

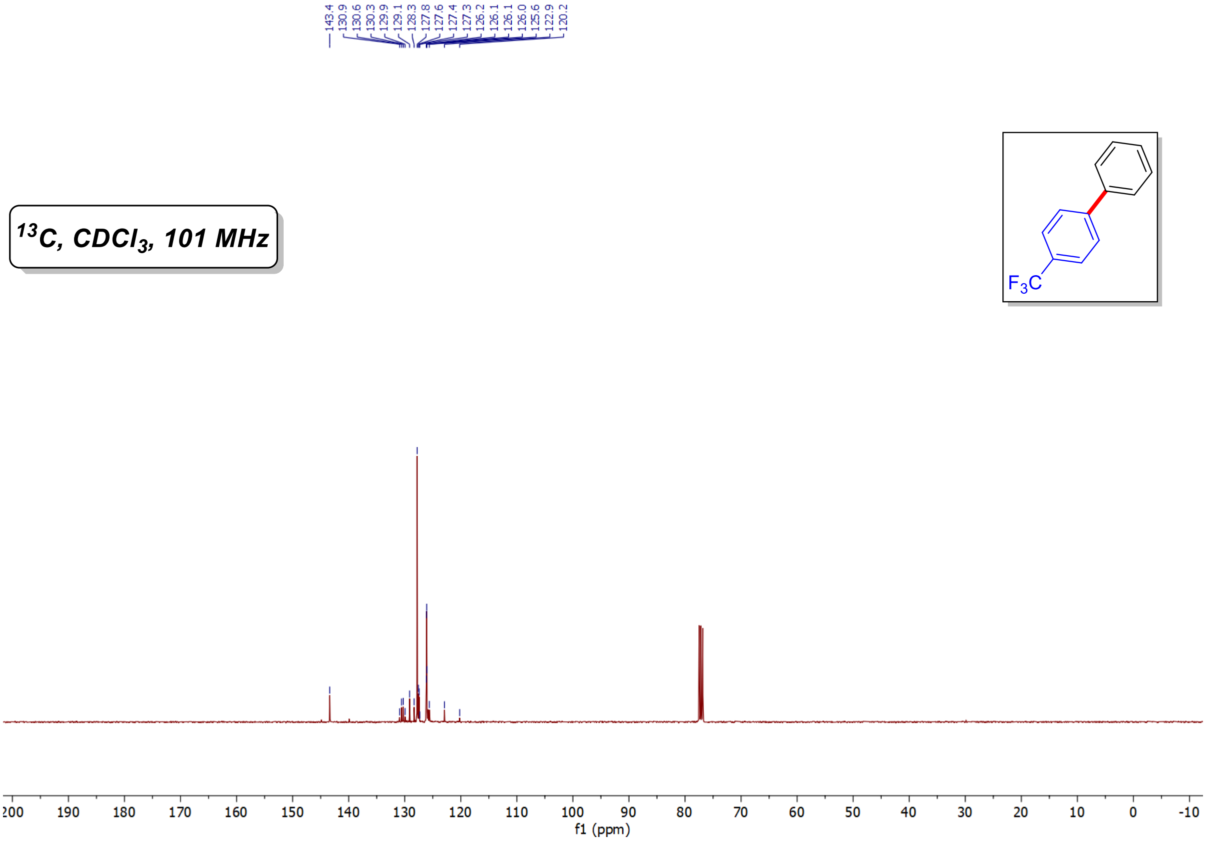


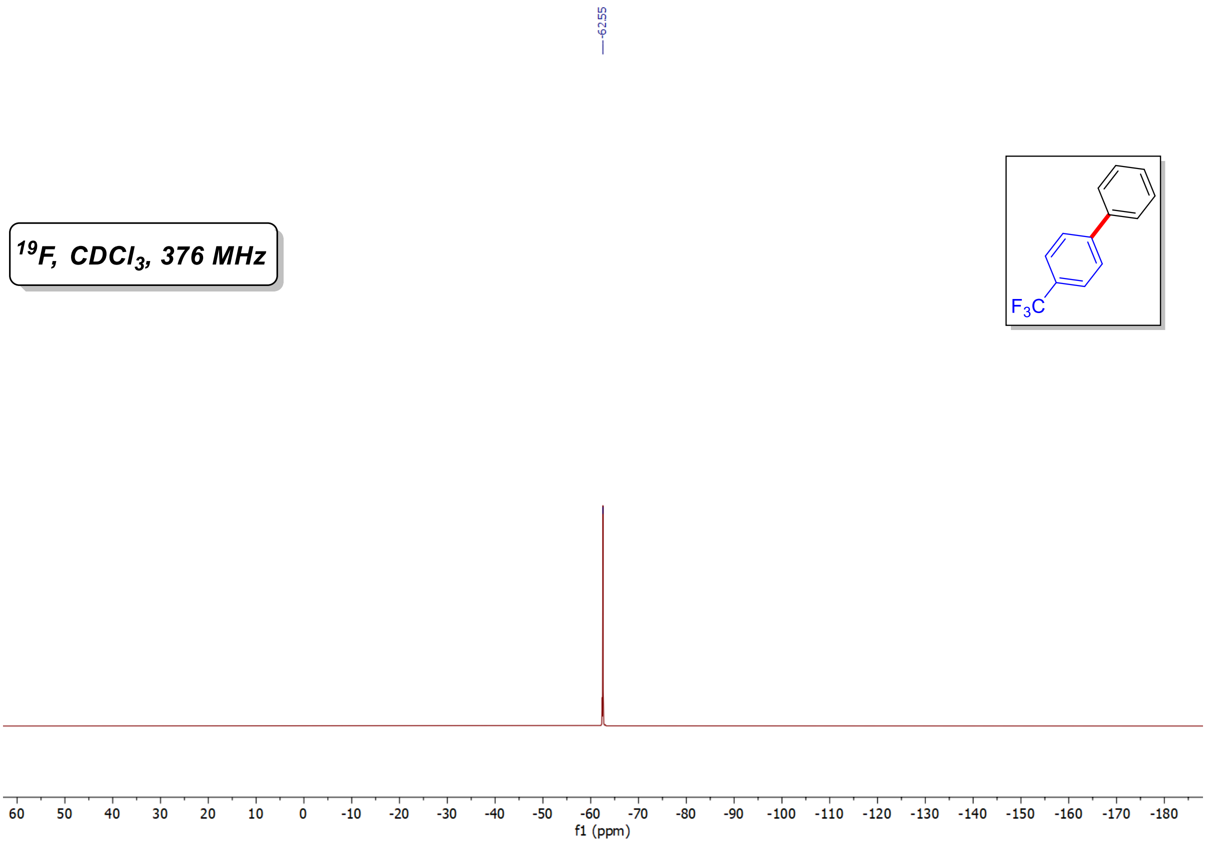
4-(trifluoromethyl)-1,1'-biphenyl (3da)

^{1}H, CDCl$_3$, 400 MHz

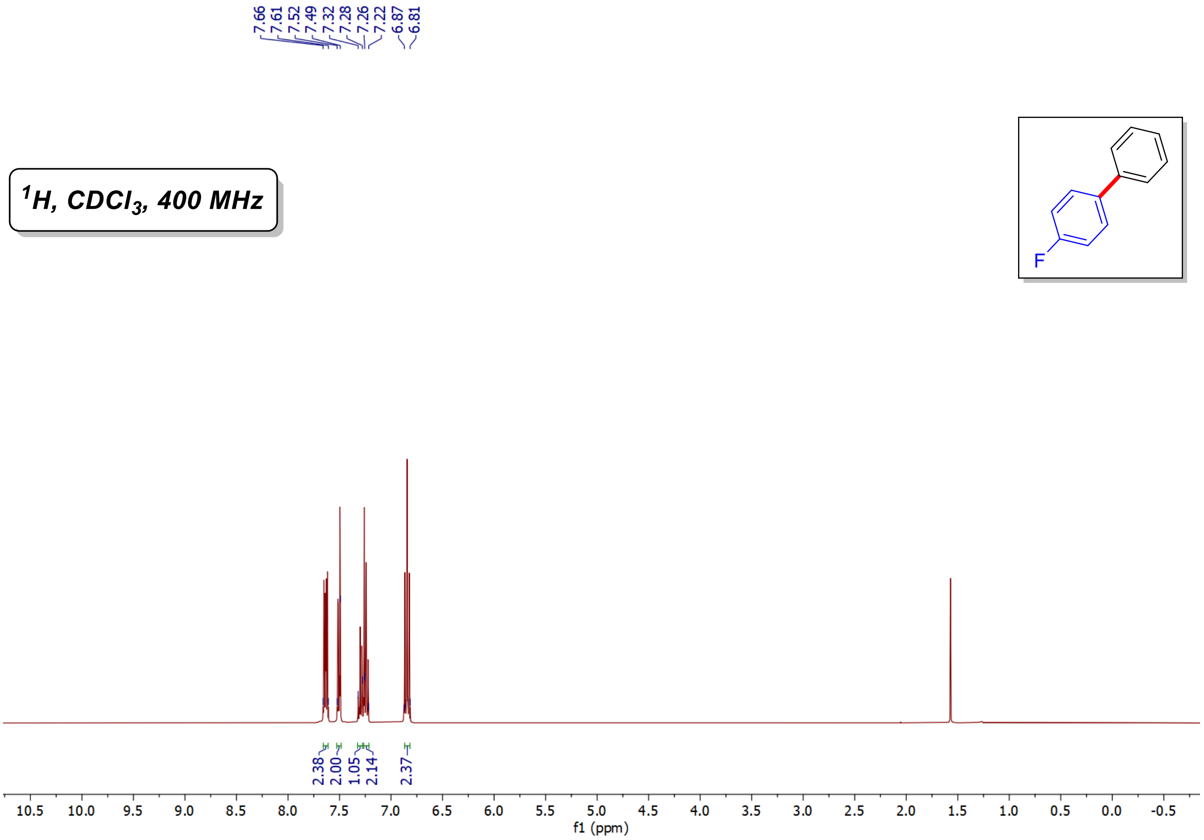


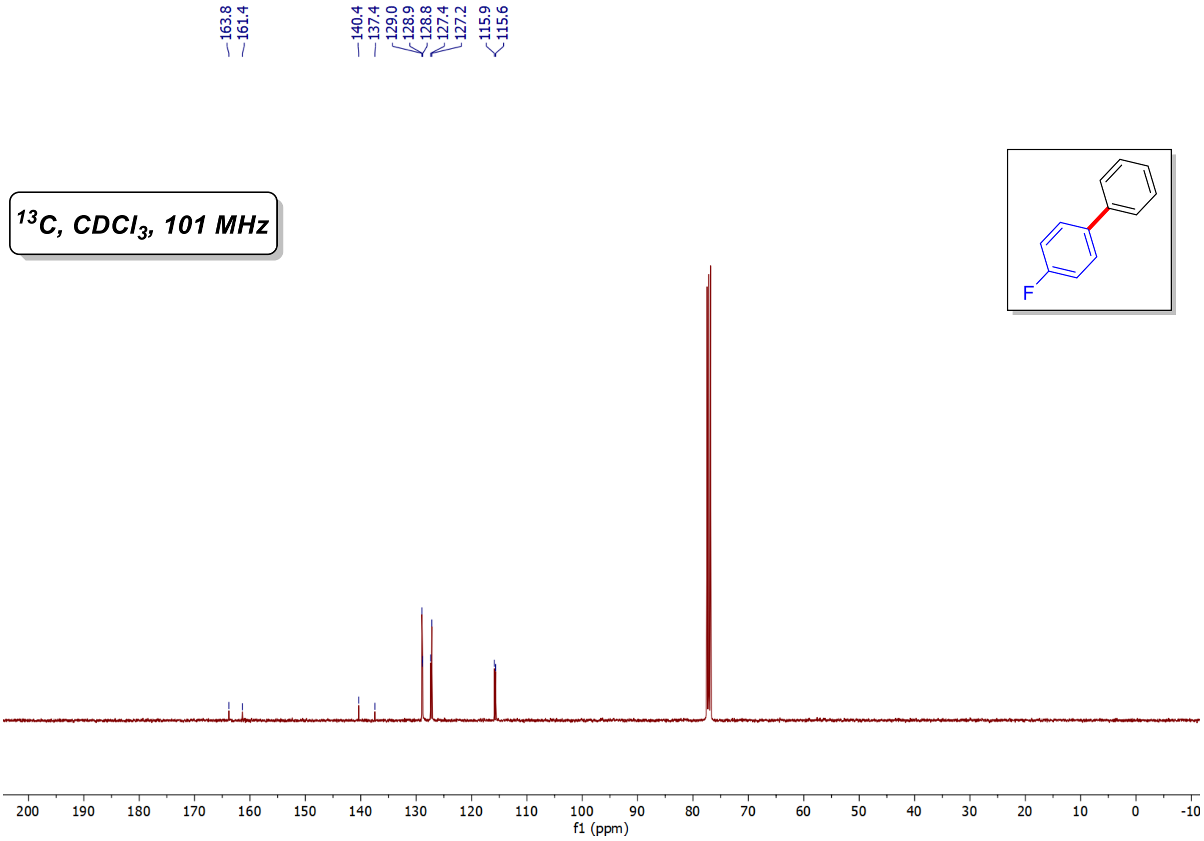
^{13}C, CDCl$_3$, 101 MHz

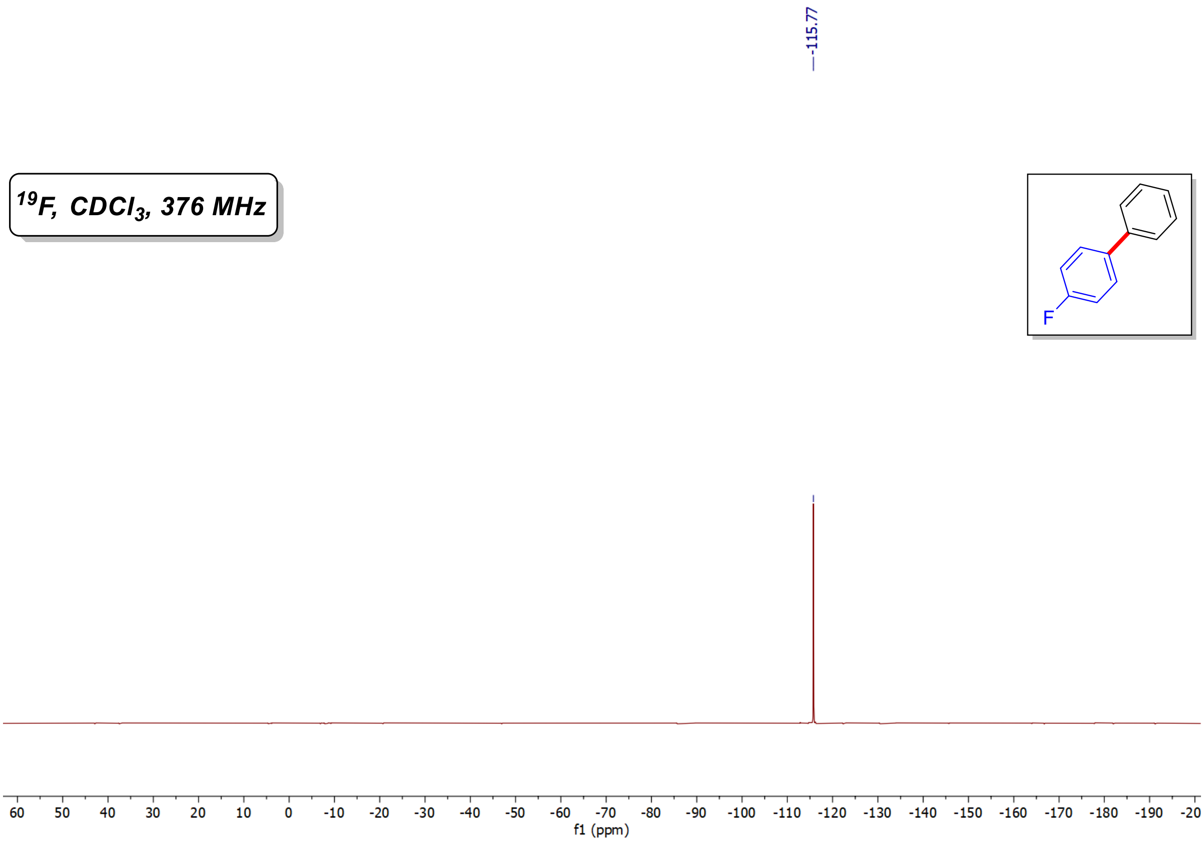



-62.55
^{19}F, CDCl$_3$, 376 MHz
F$_3$C
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

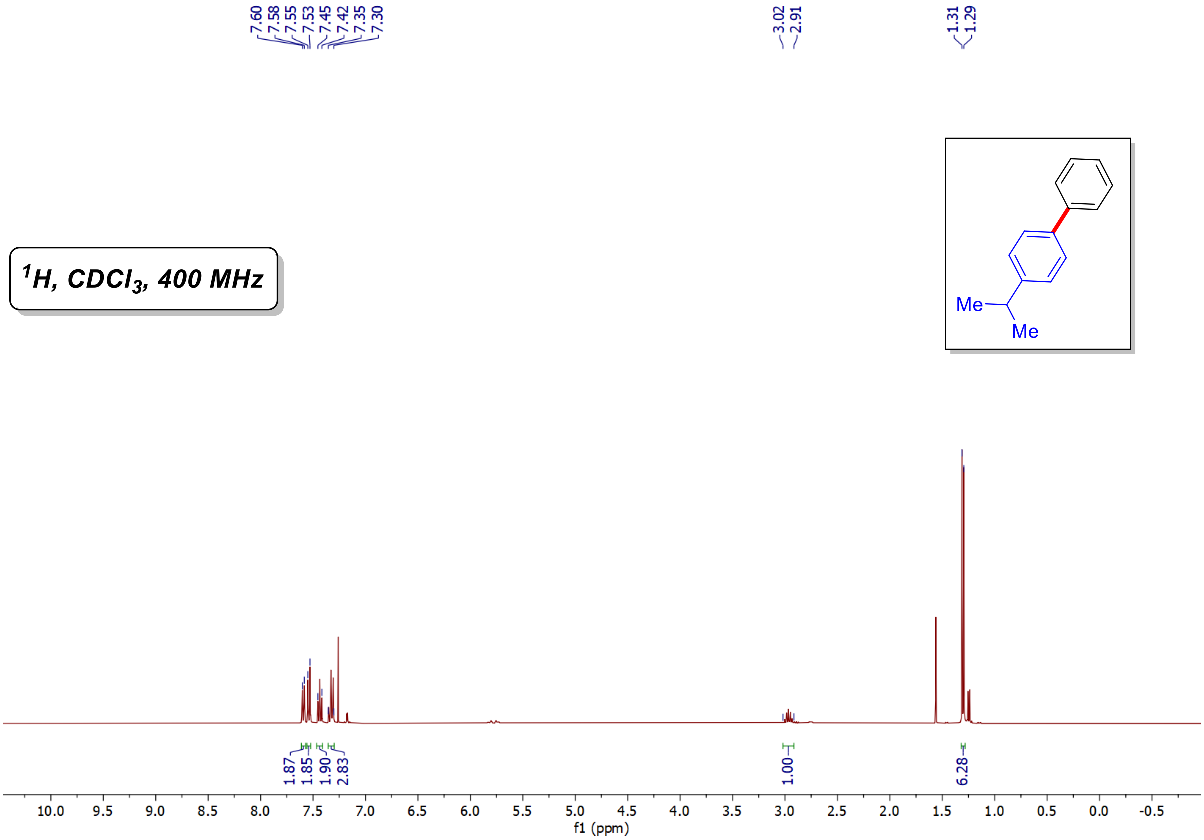
4-fluoro-1,1'-biphenyl (3ea)

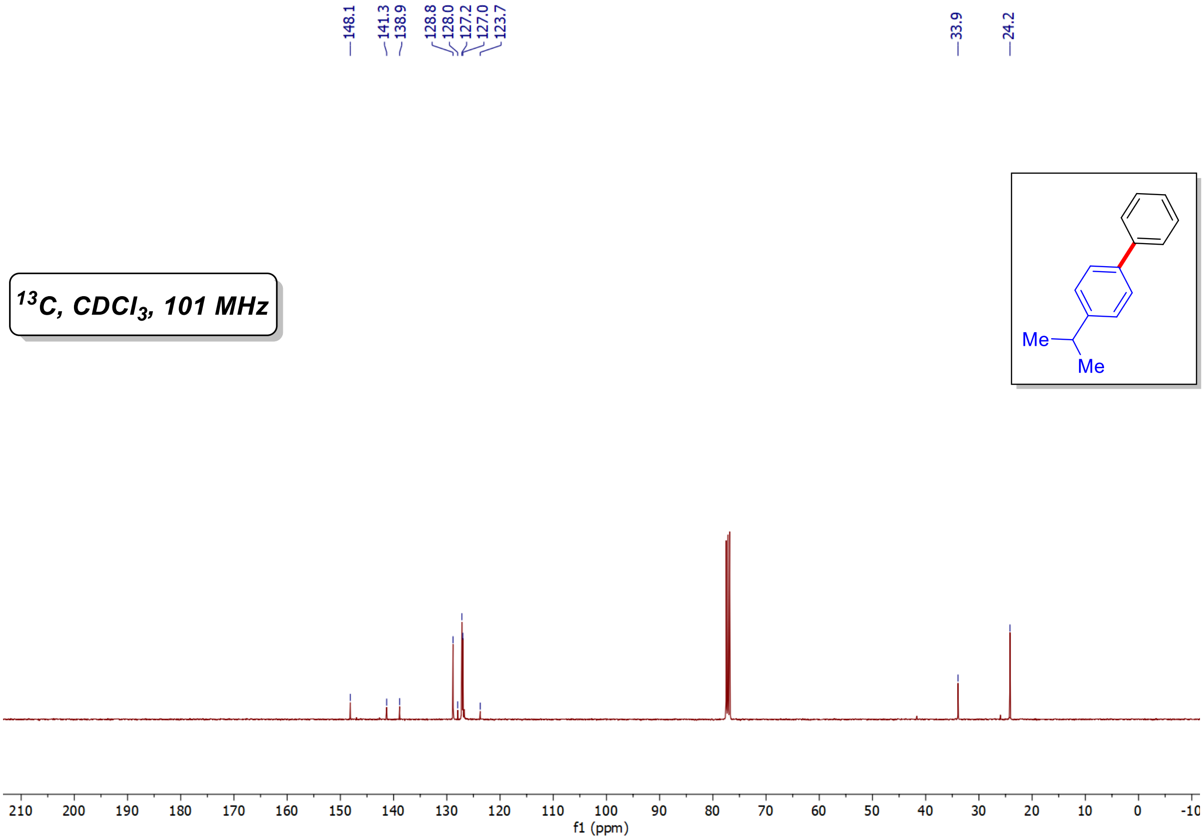




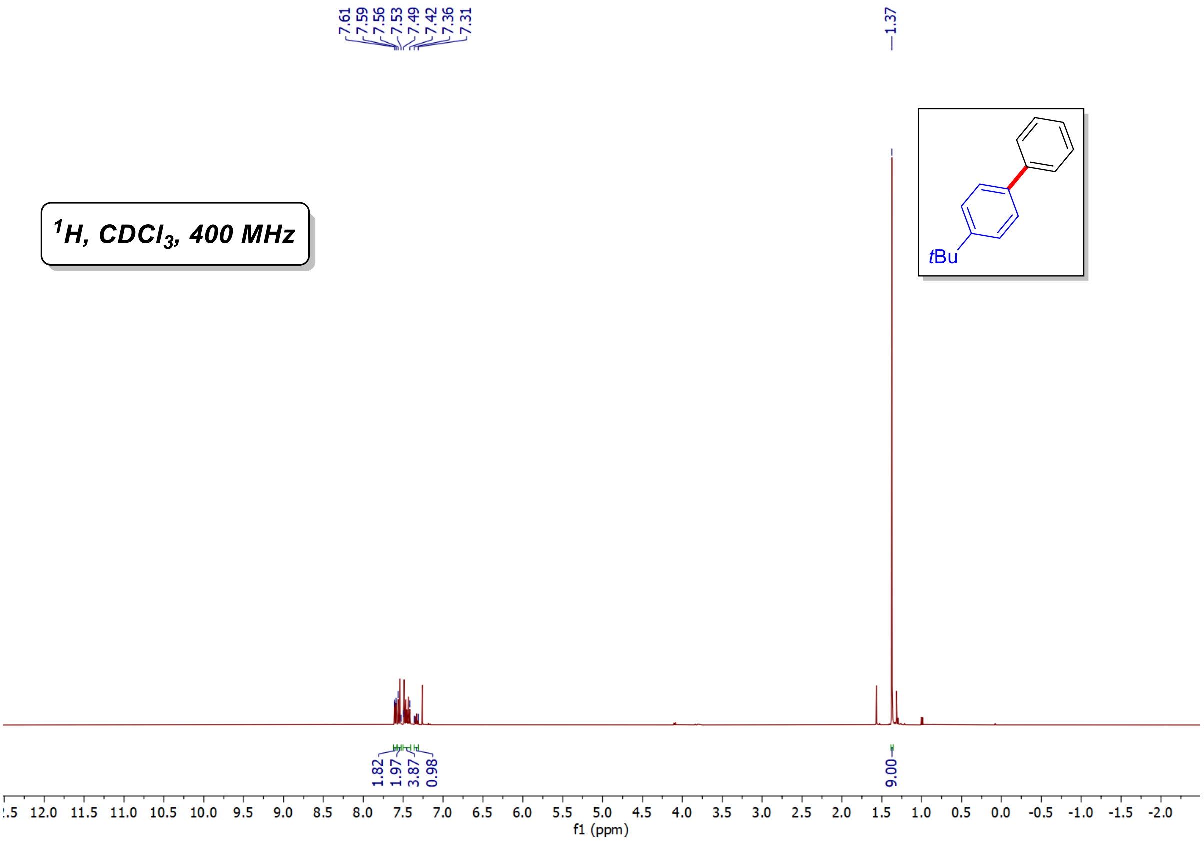

-115.77
19F, CDCl3, 376 MHz
F
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
f1 (ppm)

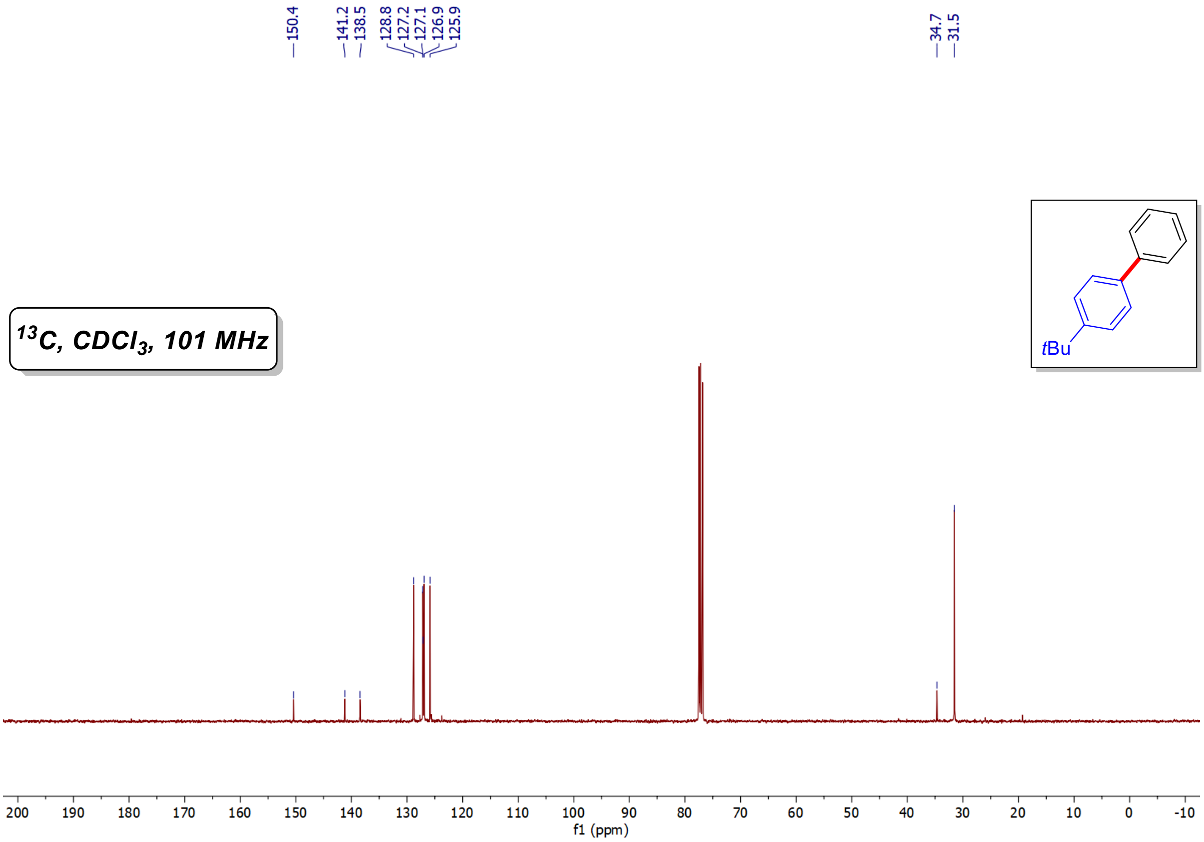
4-isopropyl-1,1'-biphenyl (3aj)



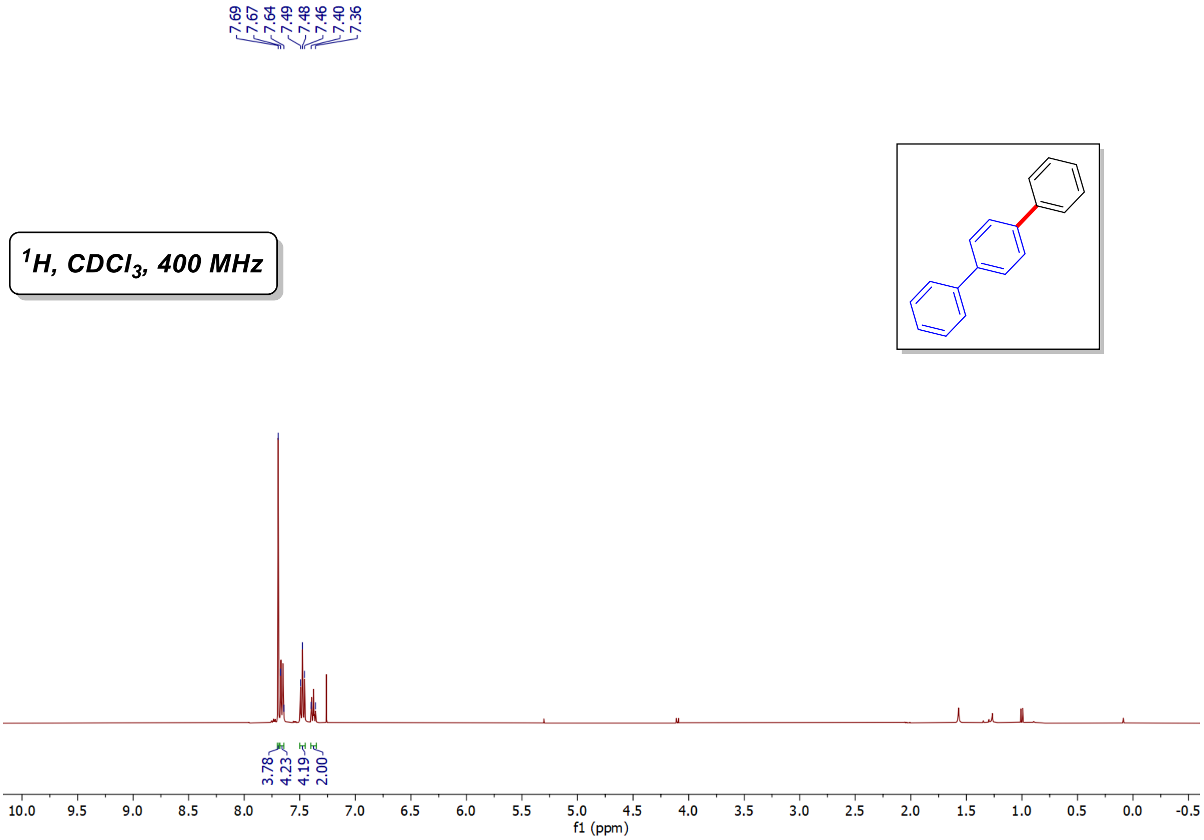


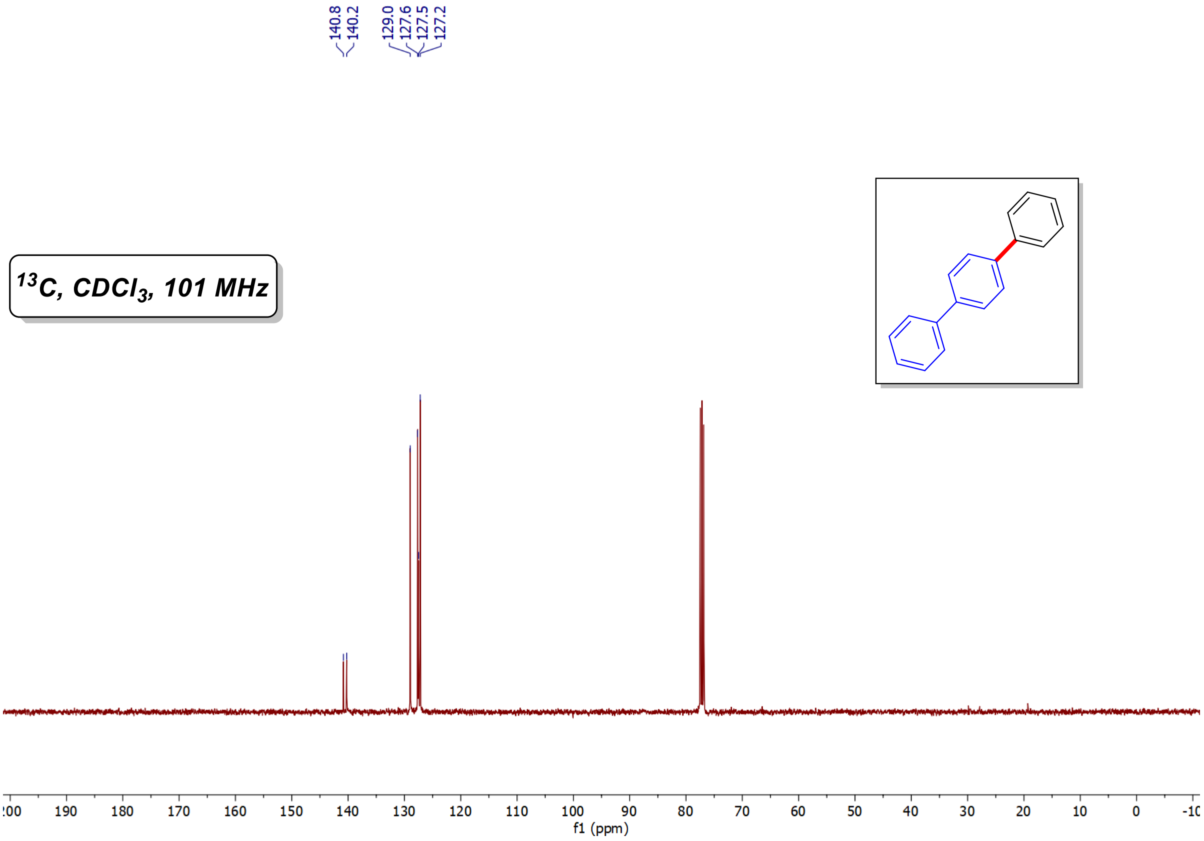
4-(tert-butyl)-1,1'-biphenyl (3ga)


7.61
7.59
7.56
7.53
7.49
7.42
7.36
7.31
1.37
1H, CDCl3, 400 MHz
tBu
1.82
1.97
3.87
0.98
9.00
12.0 11.5 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 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

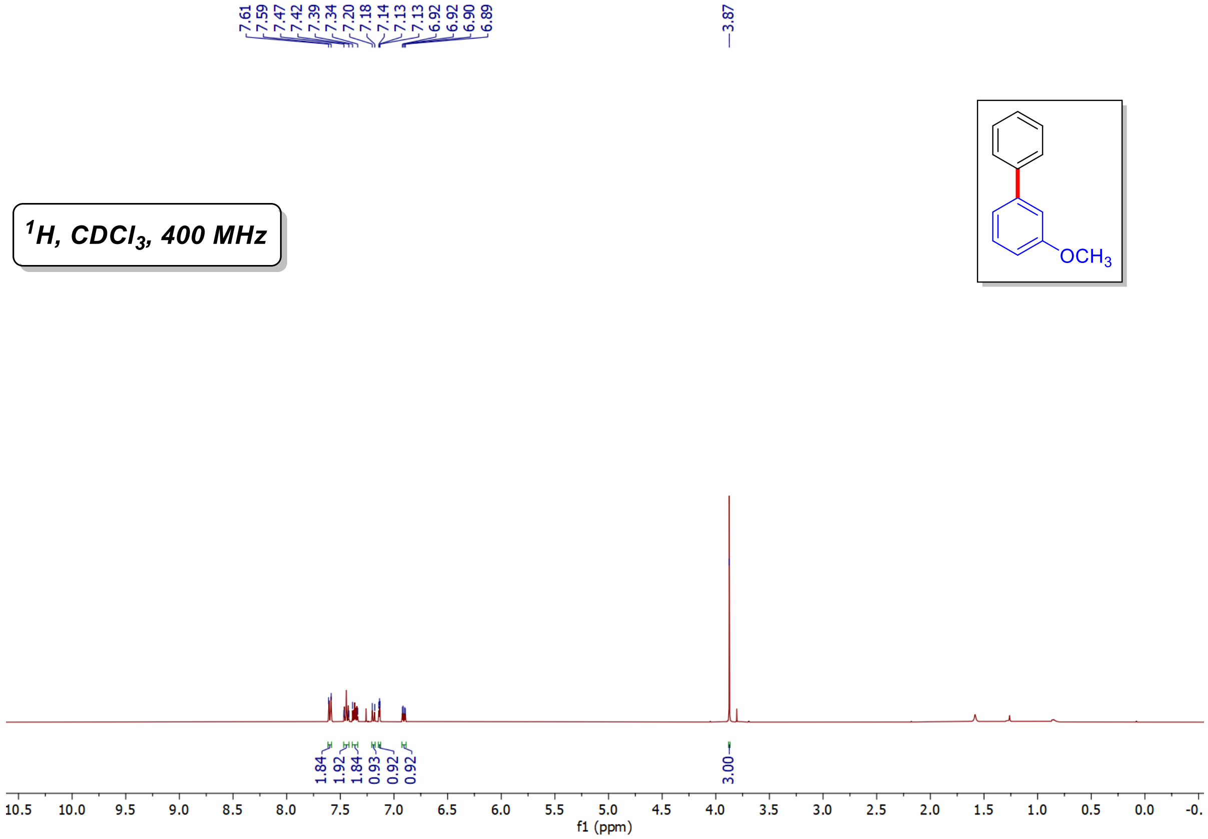

150.4
141.2
138.5
128.8
127.2
127.1
126.9
125.9
34.7
31.5
13C, CDCl3, 101 MHz
tBu
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

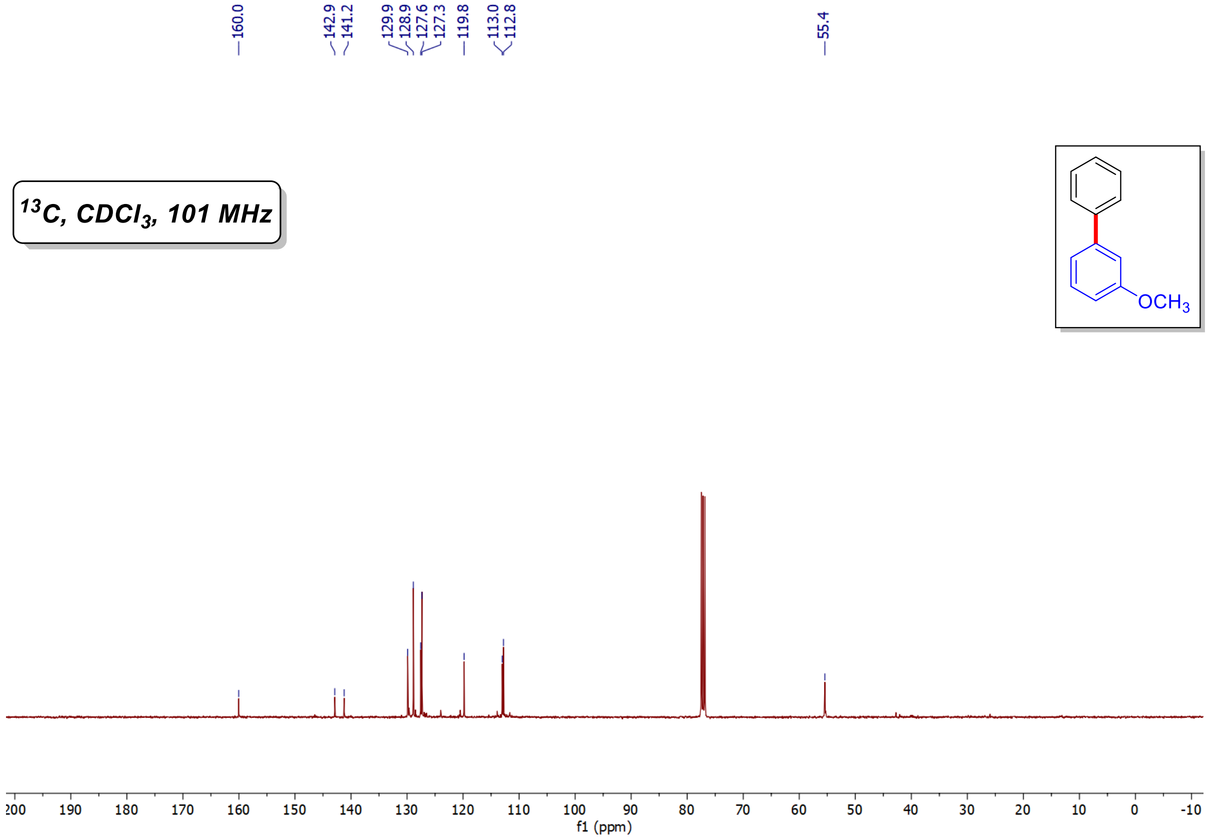
1,1':4',1''-terphenyl (3ha)



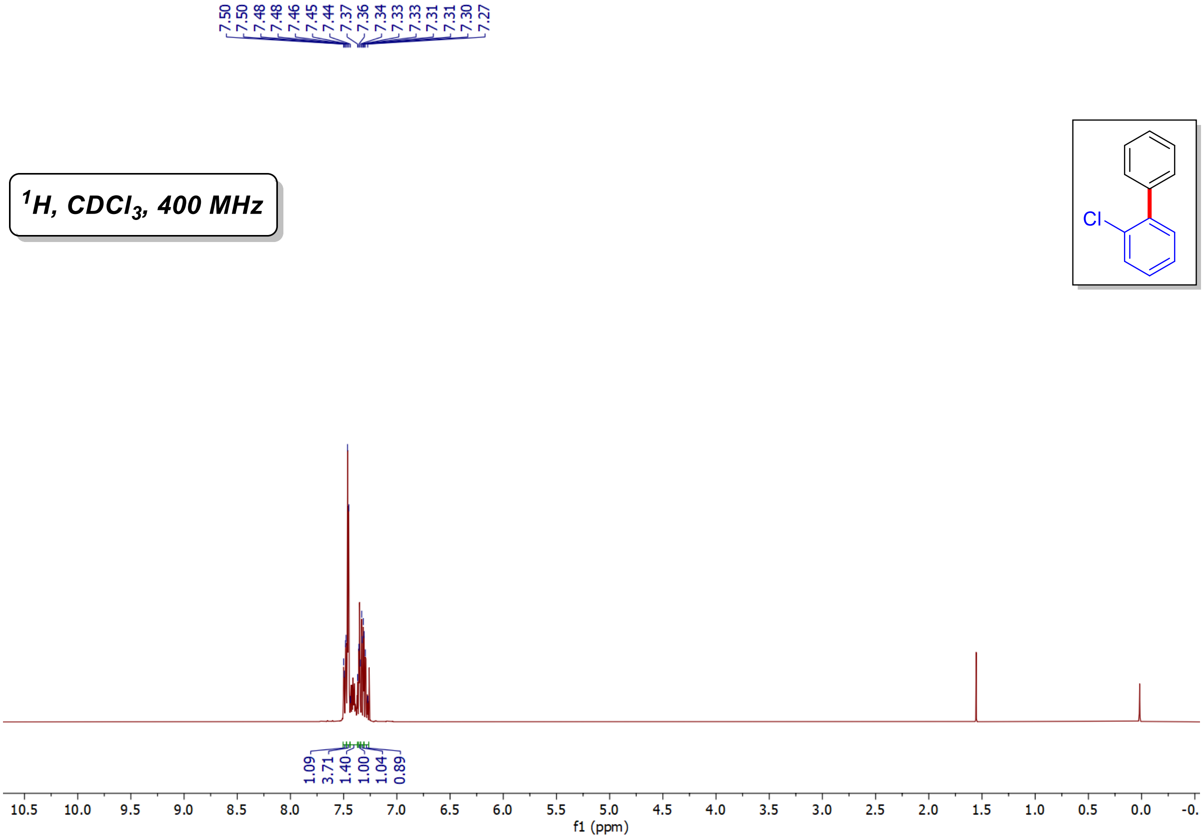


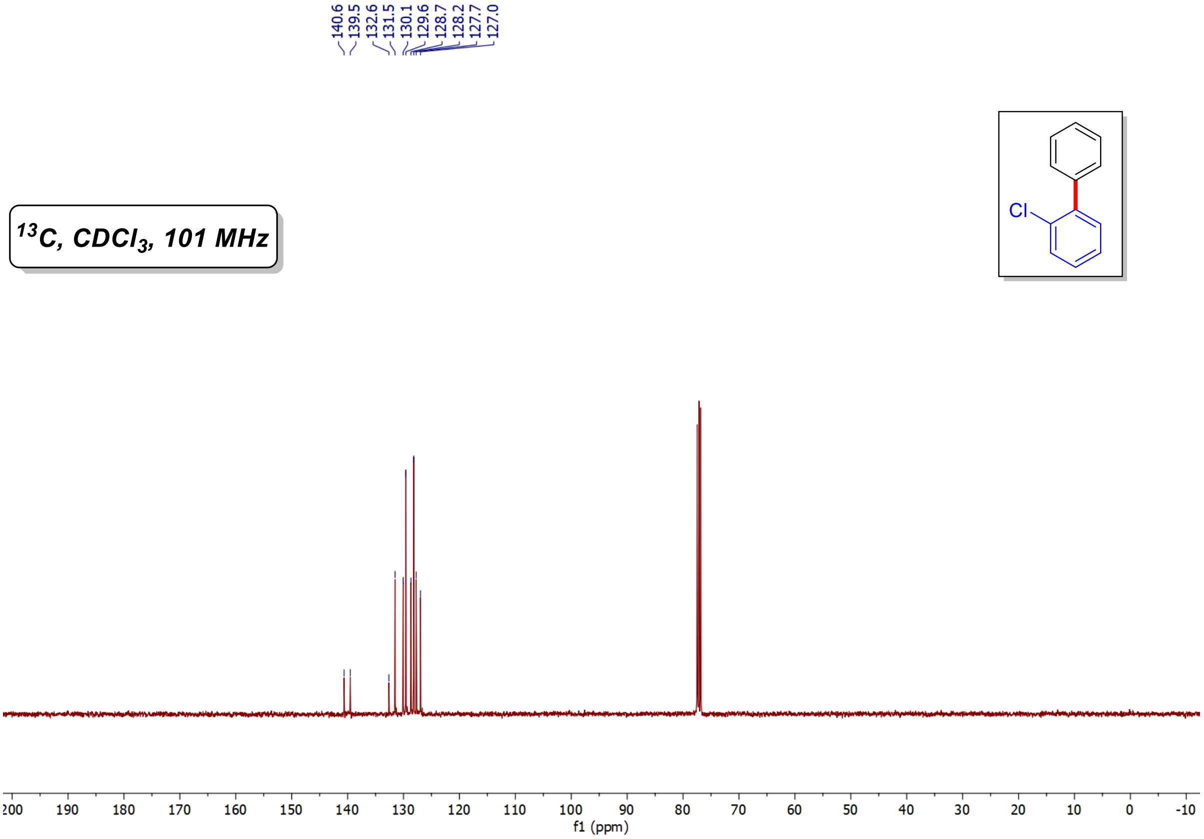
3-methoxy-1,1'-biphenyl (3ia)



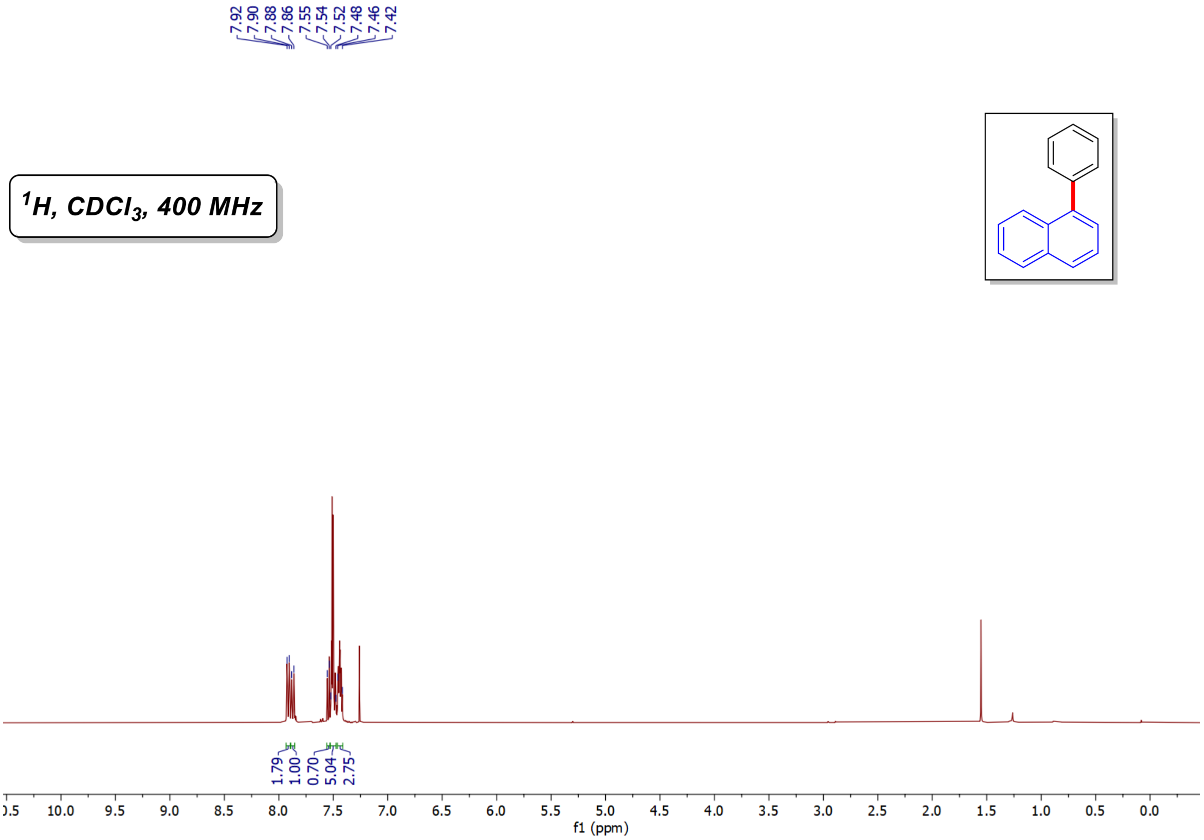


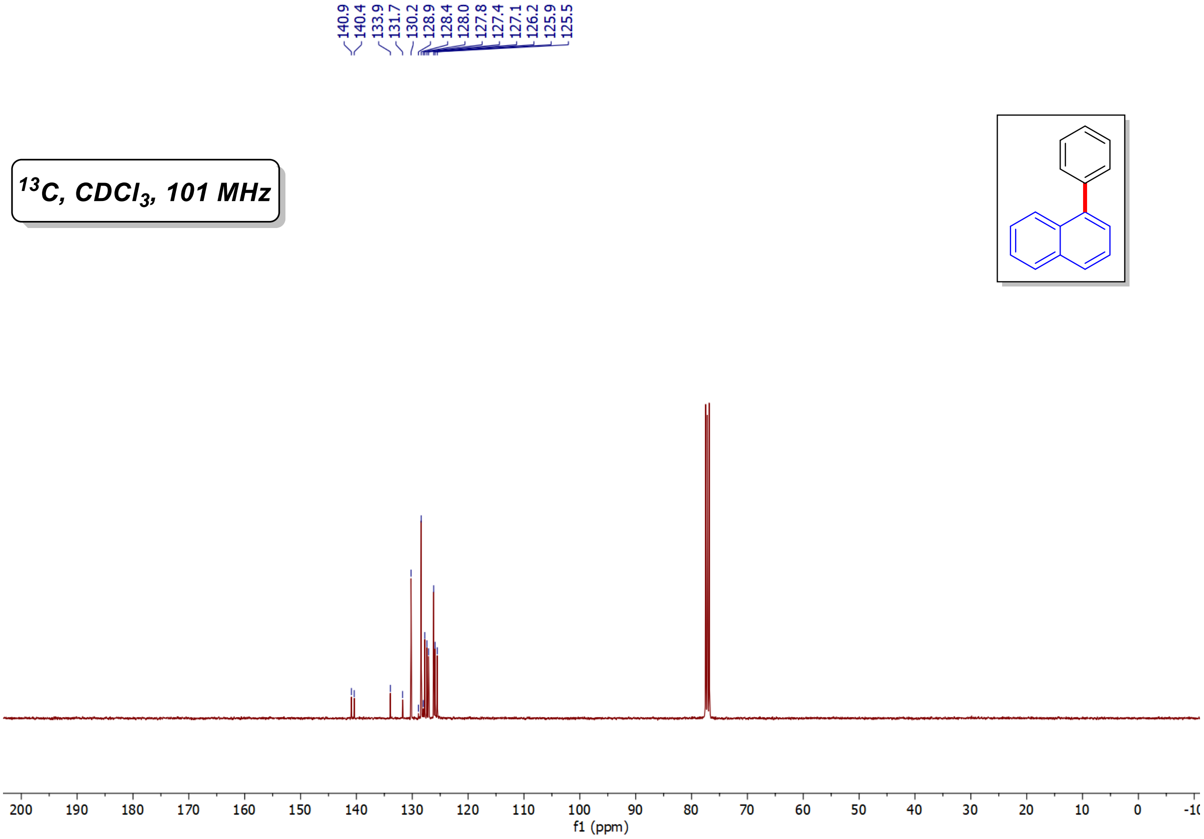
2-chloro-1,1'-biphenyl (3ja)



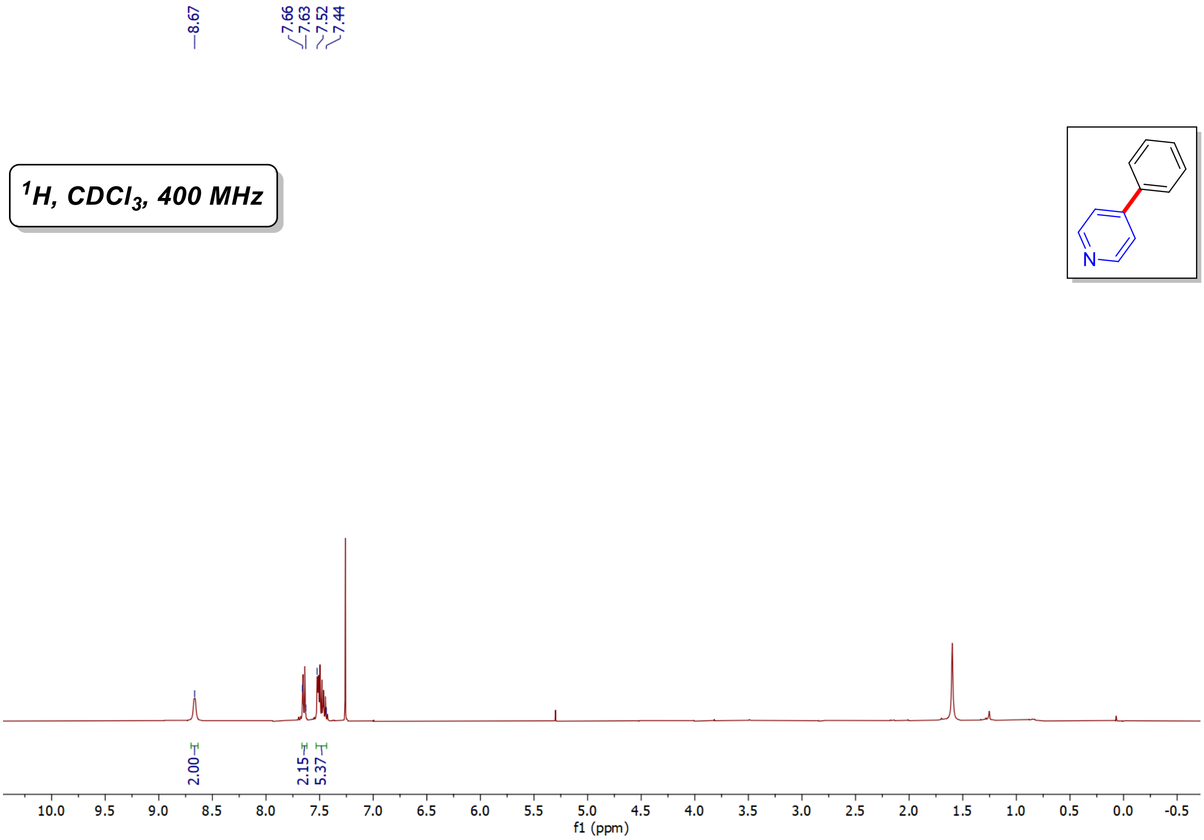


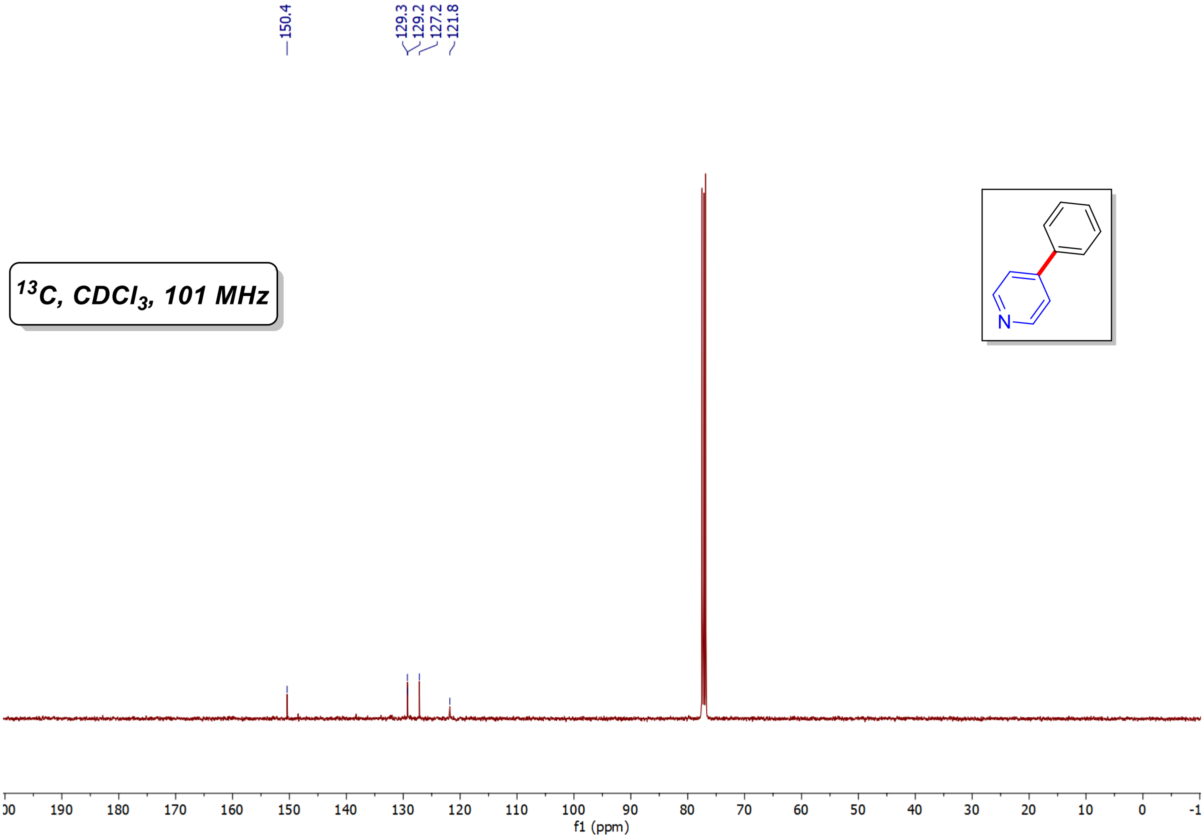
1-phenylnaphthalene (3ka)



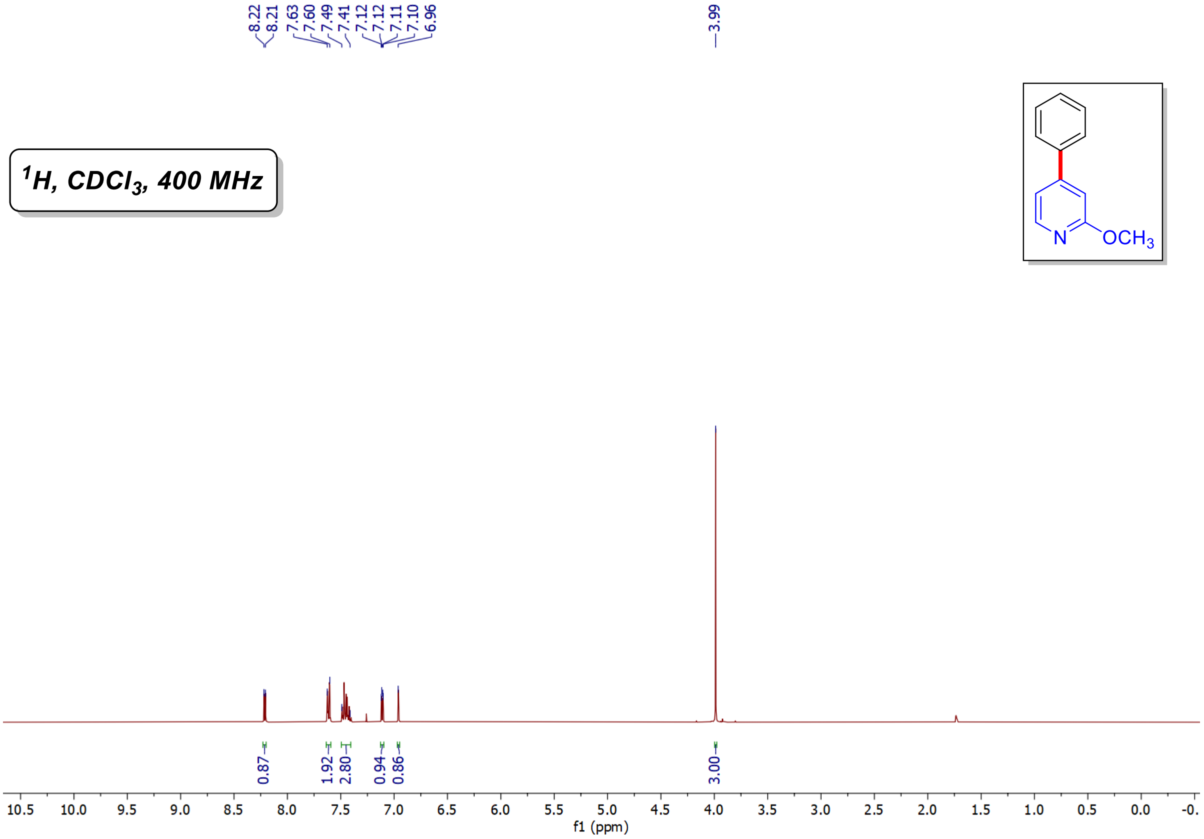


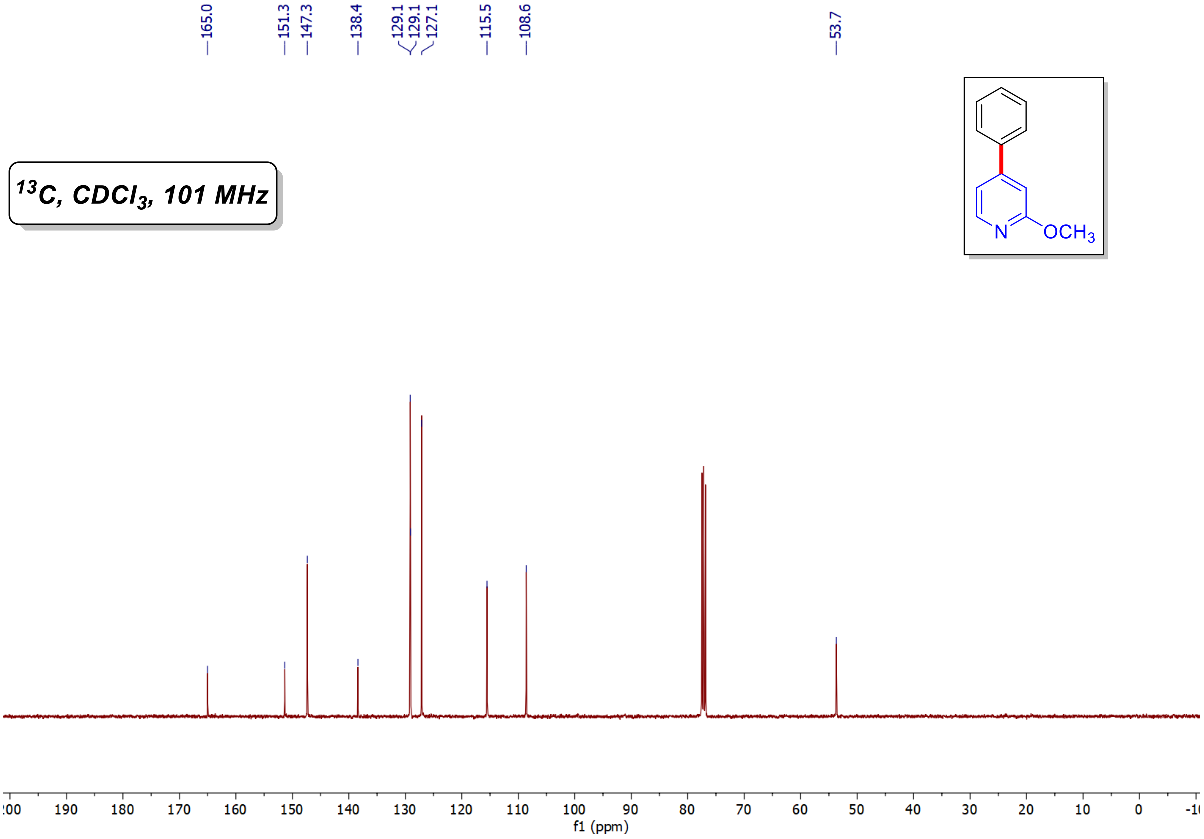
4-phenylpyridine (3la)



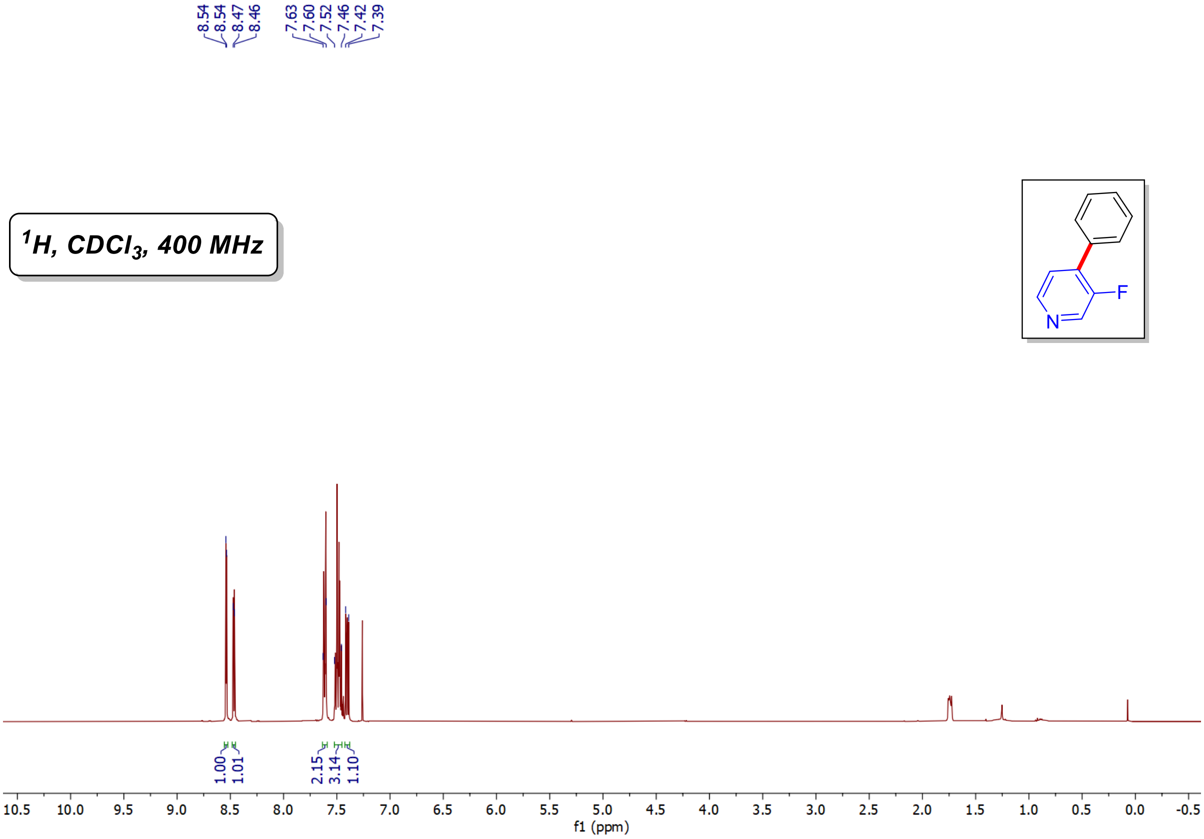


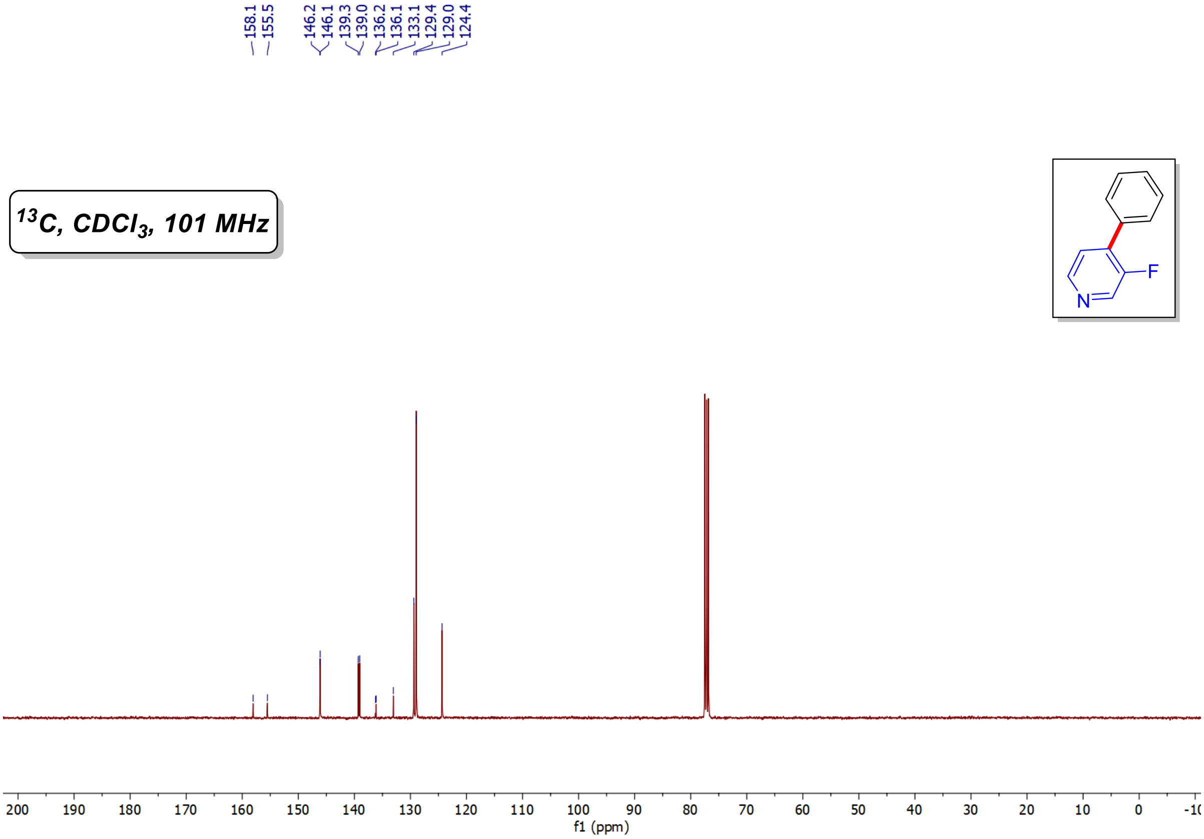
2-methoxy-4-phenylpyridine (3ma)

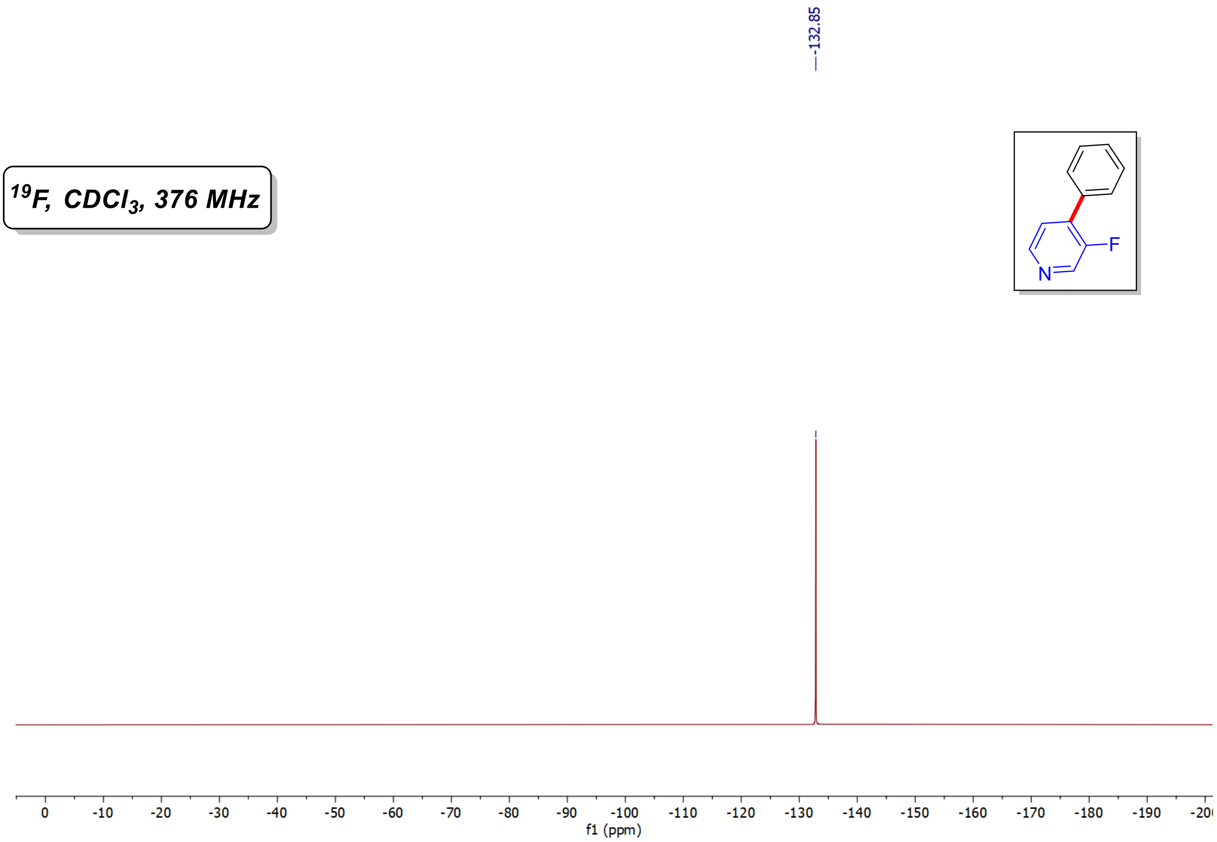




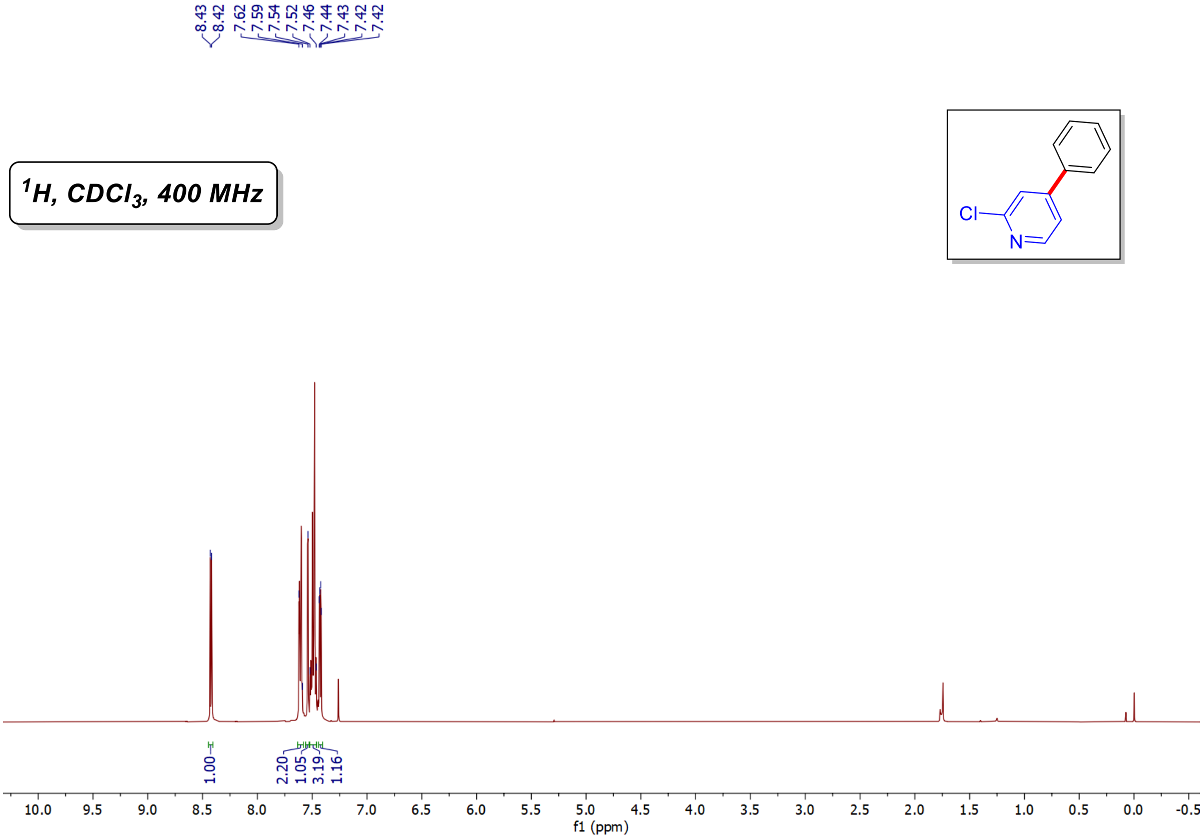
3-fluoro-4-phenylpyridine (3na)

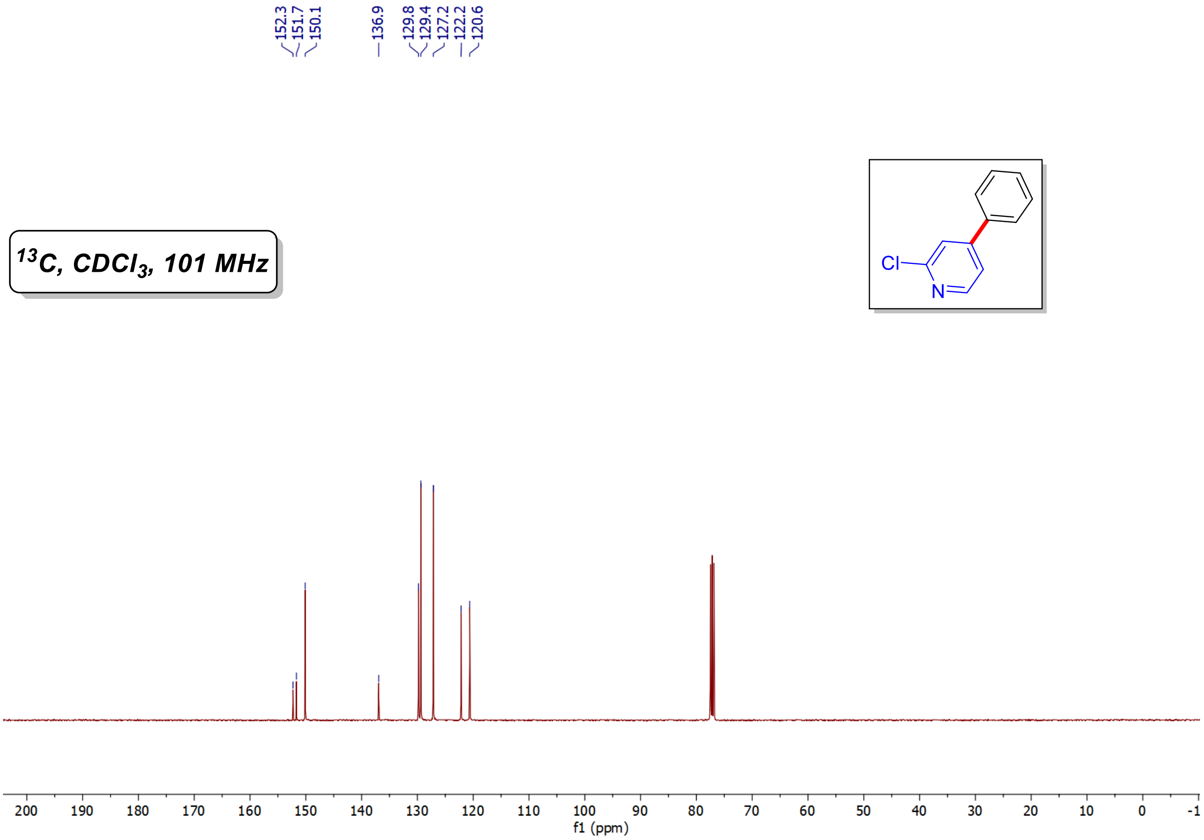




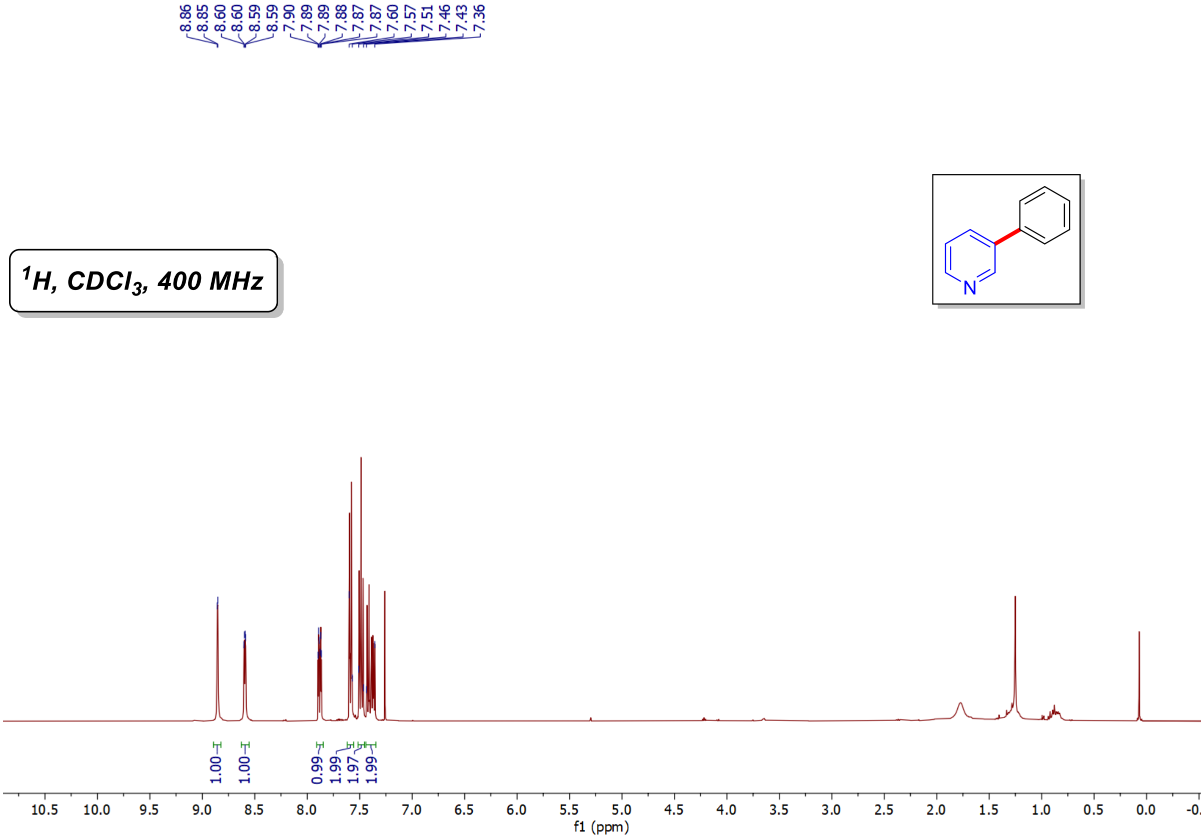

-132.85
^{19}F, $CDCl_3$, 376 MHz
F
N
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

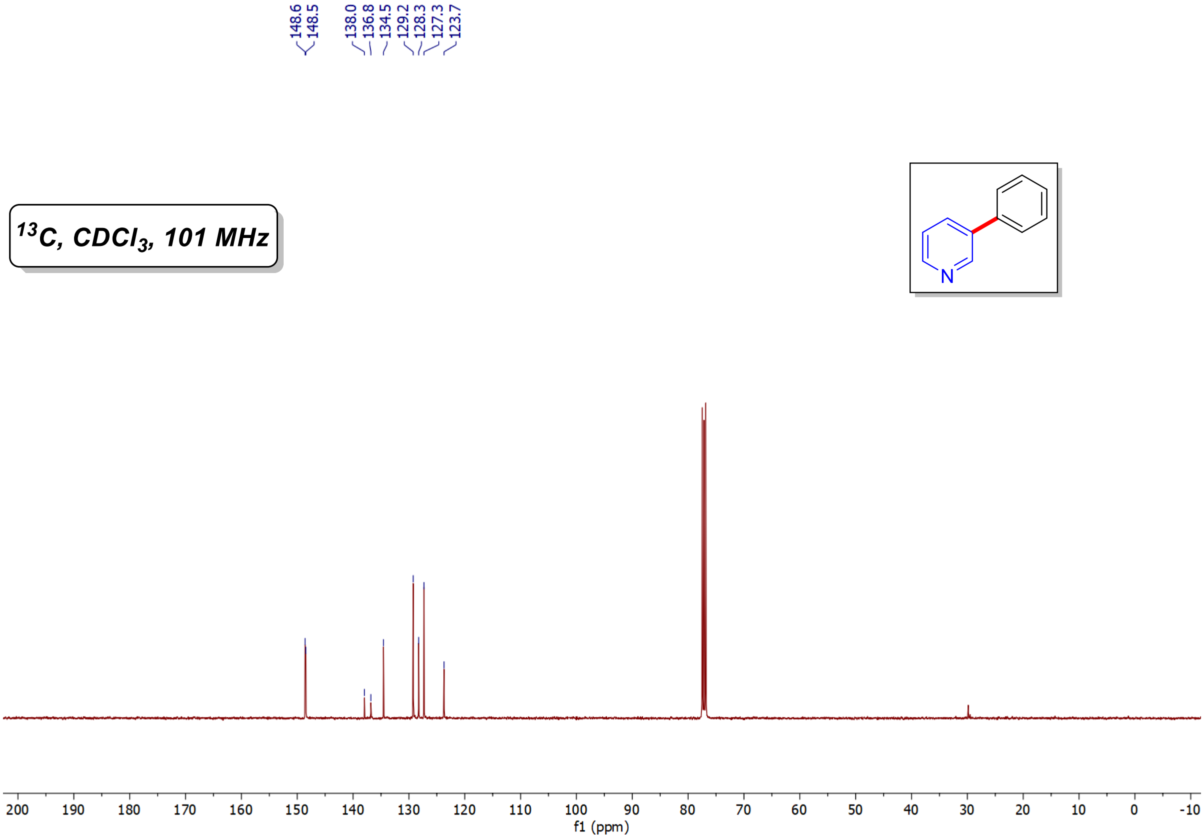
2-chloro-4-phenylpyridine (3oa)



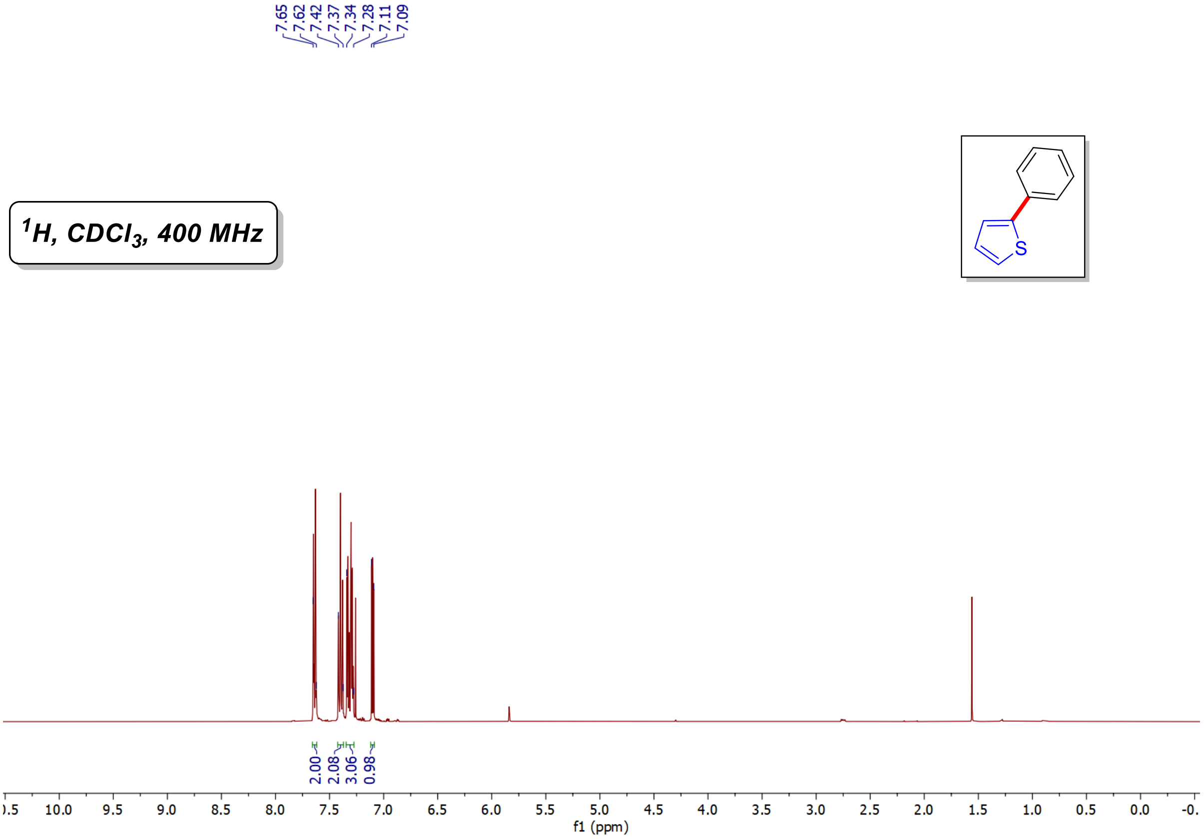


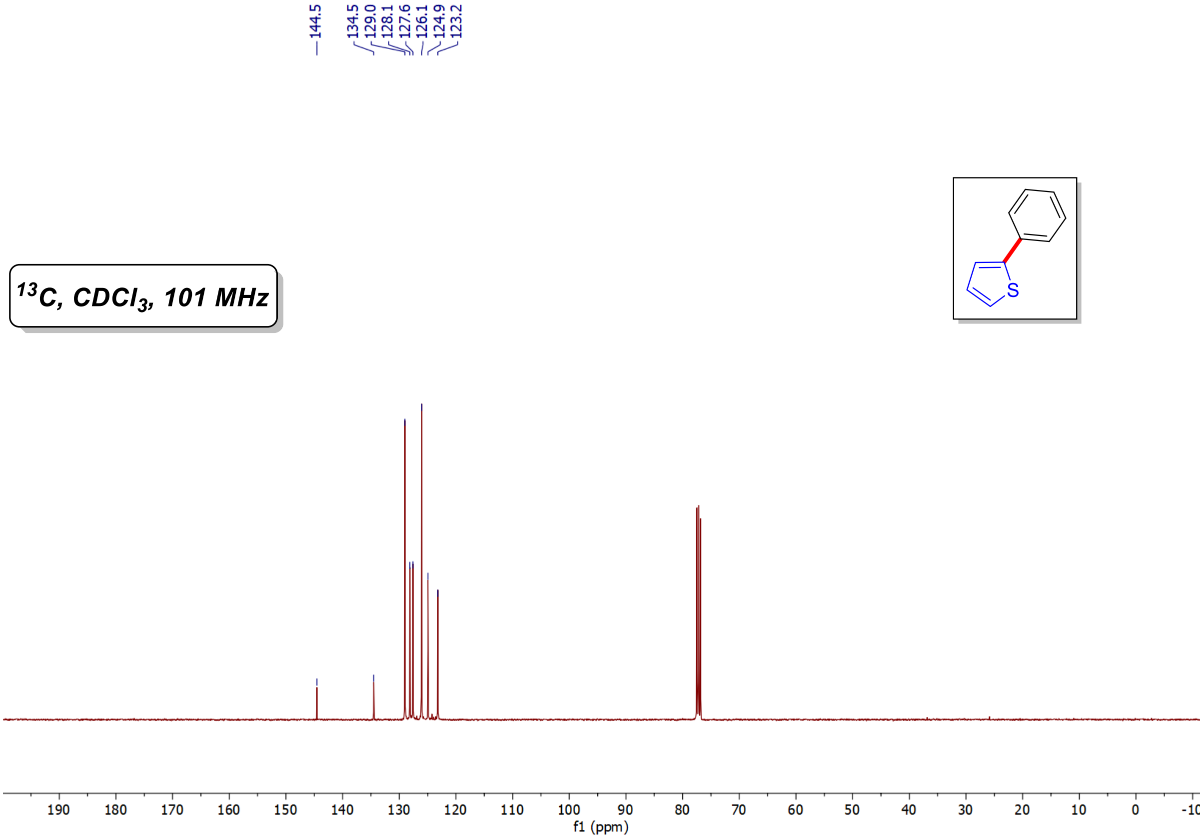
3-phenylpyridine (3pa)



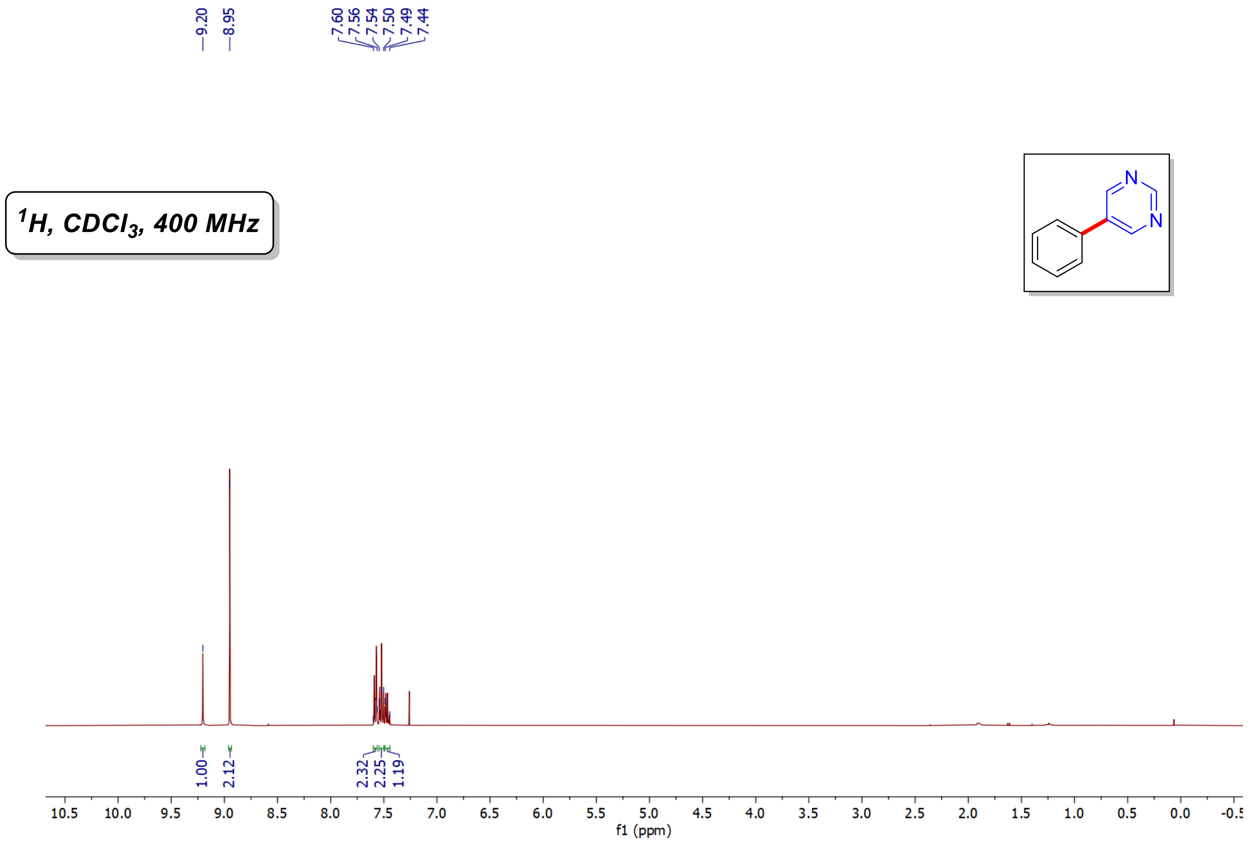


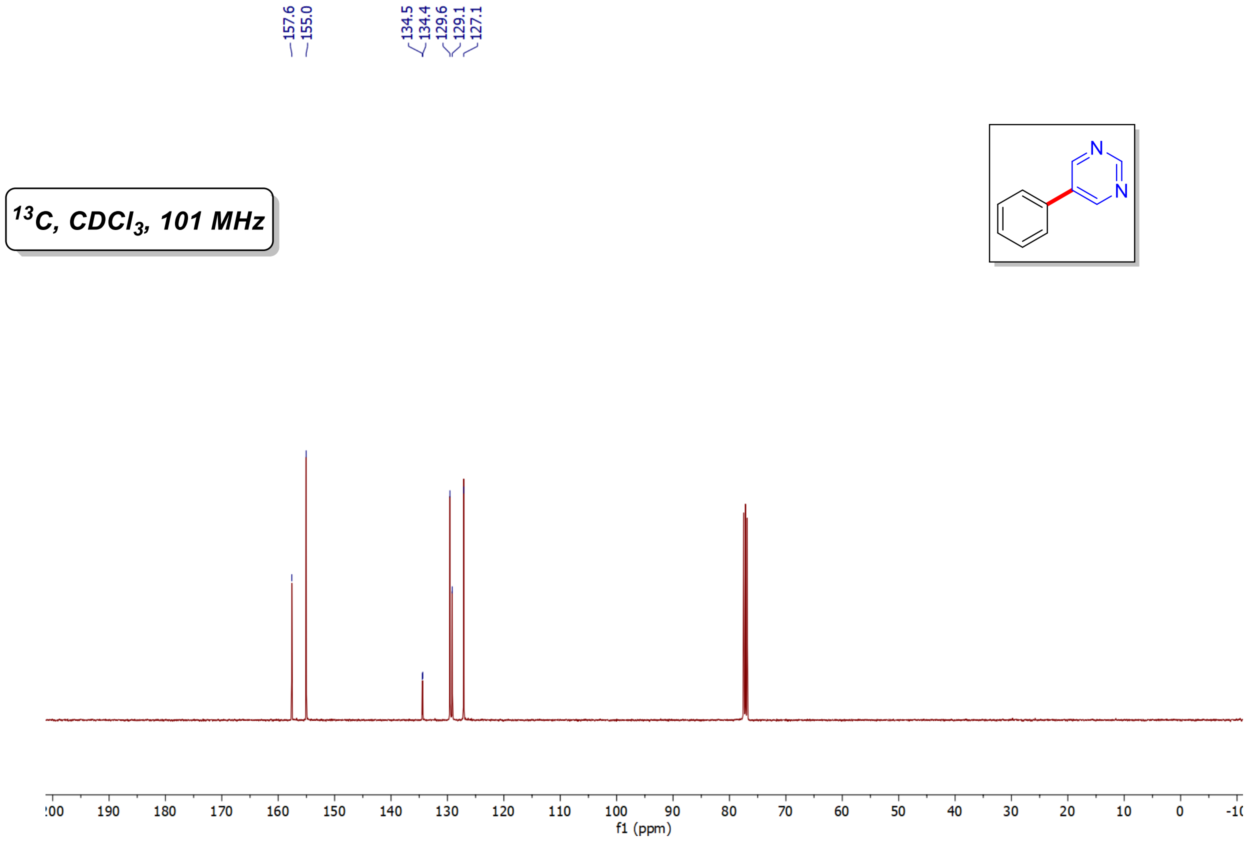
2-phenylthiophene (3qa)



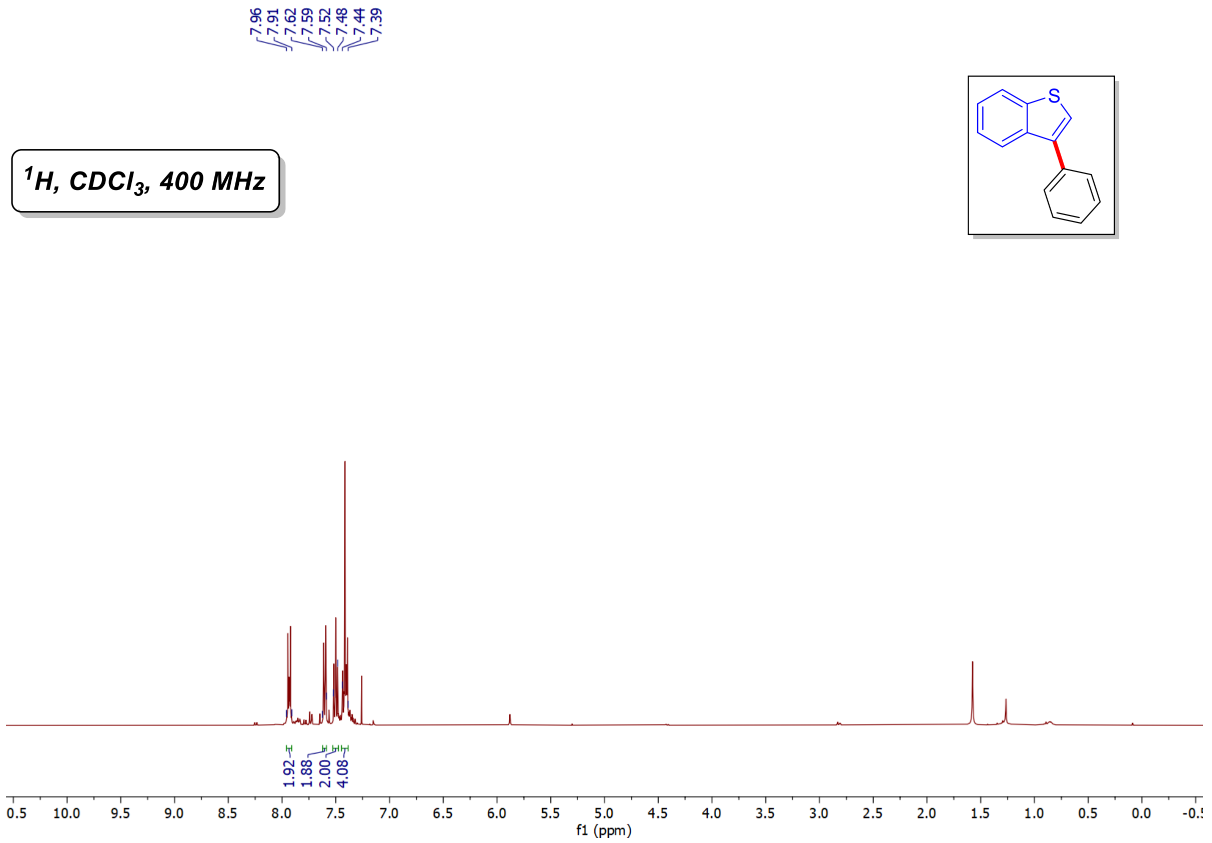


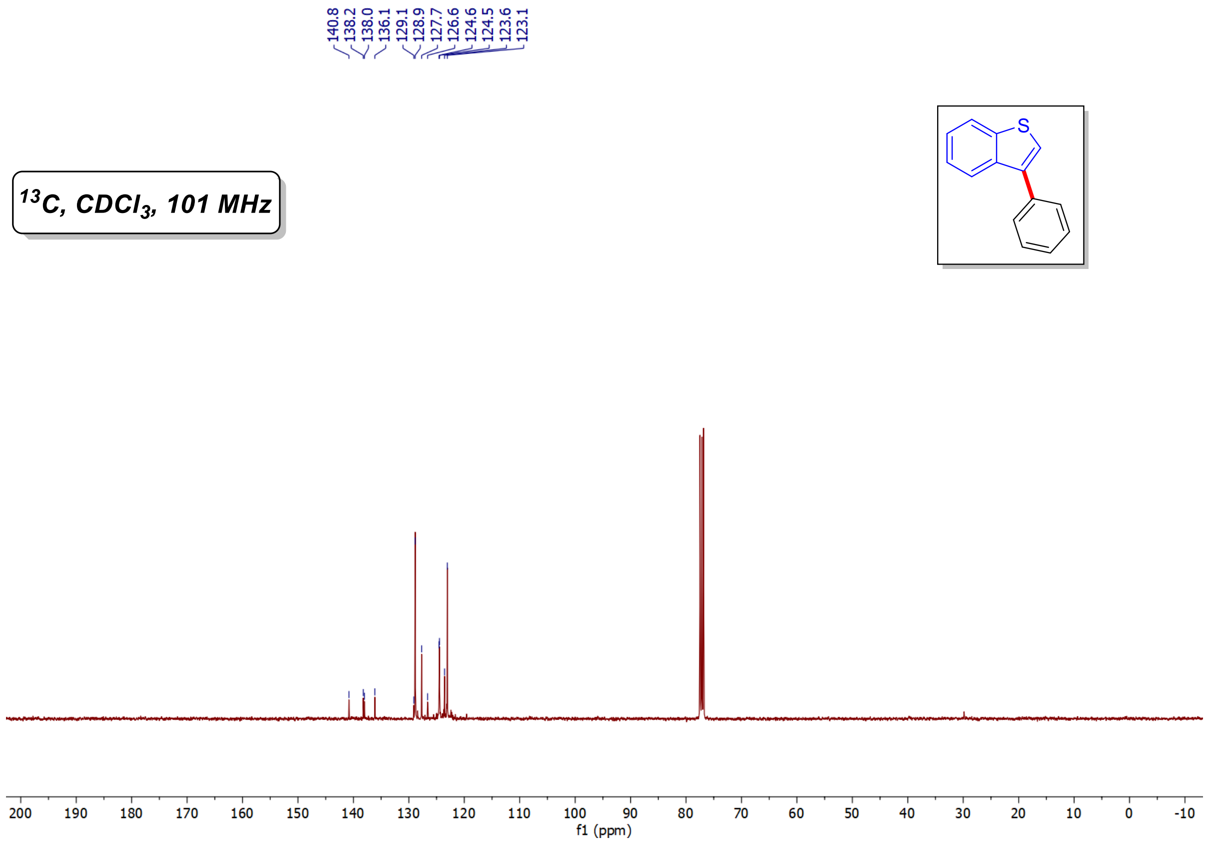
5-phenylpyrimidine (3ra)





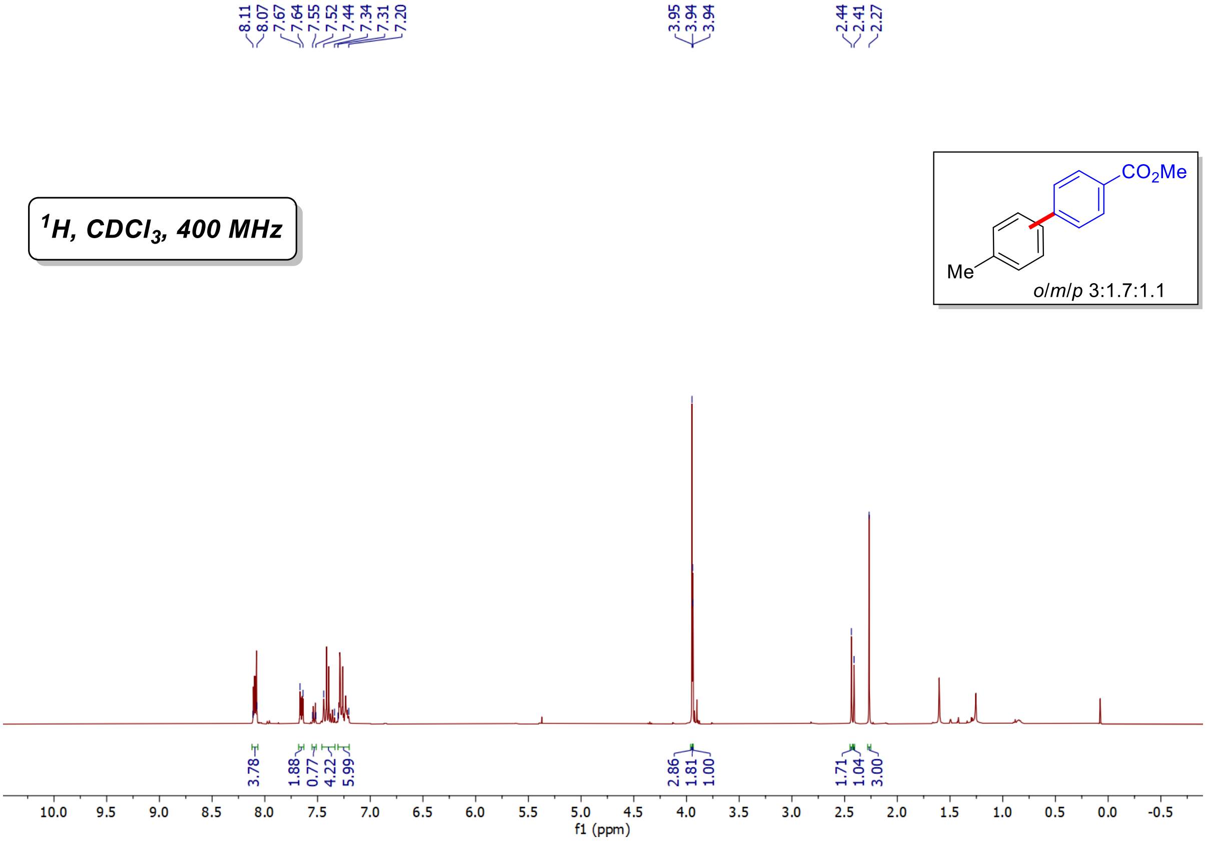
3-phenylbenzo[b]thiophene (3sa)

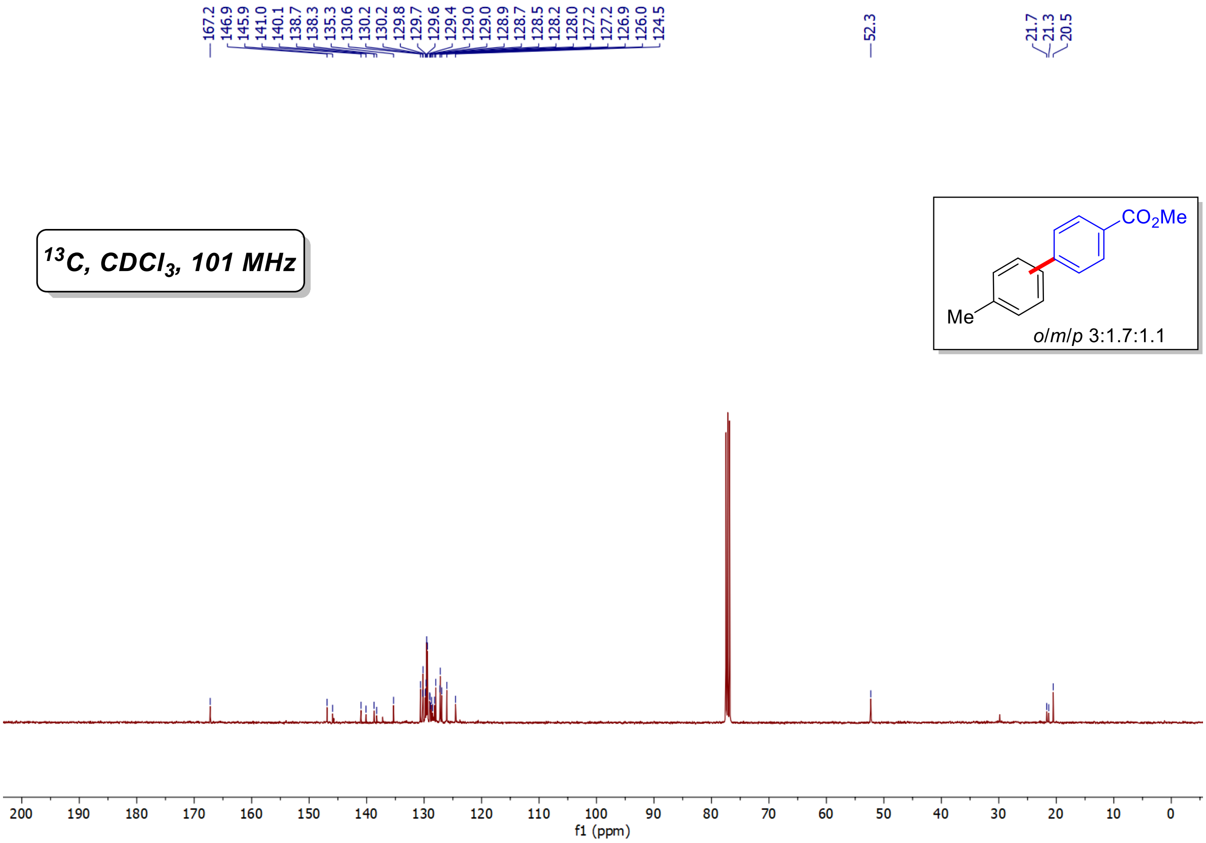




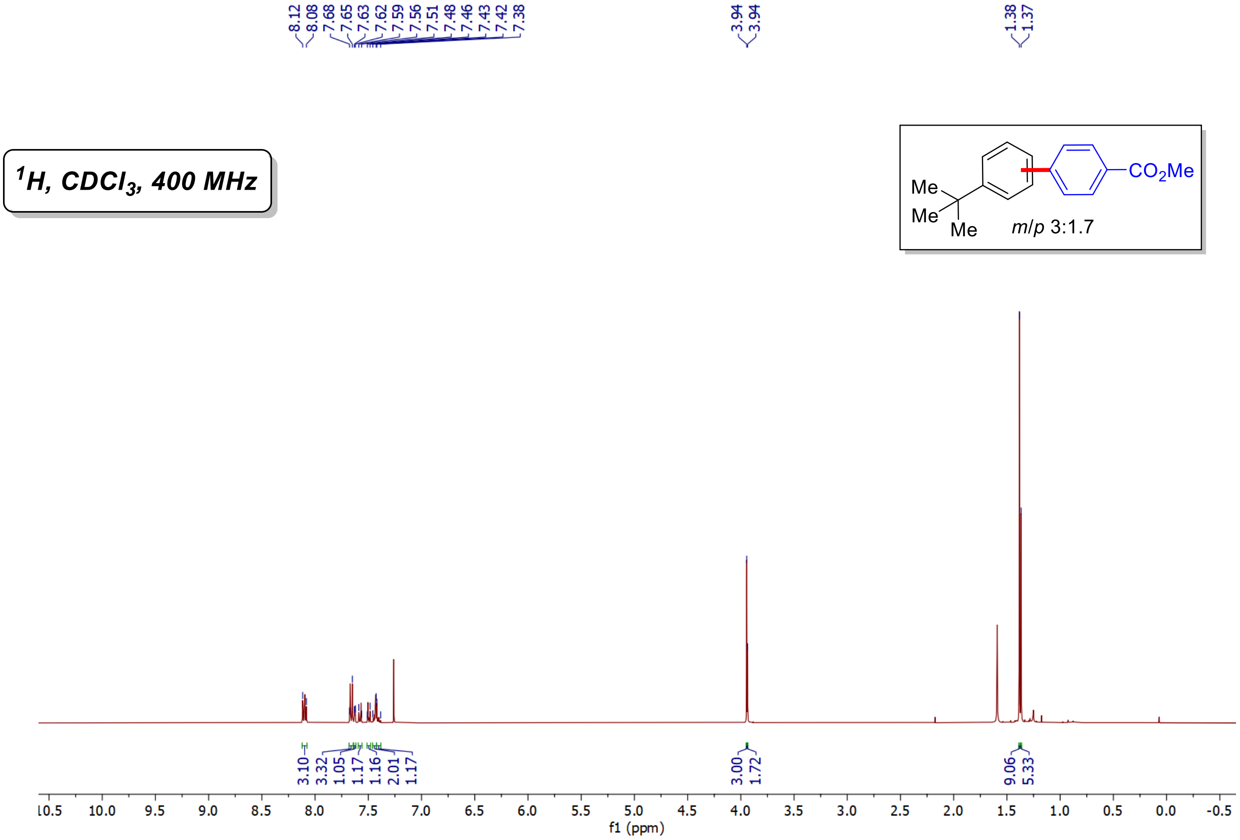
Arene variation

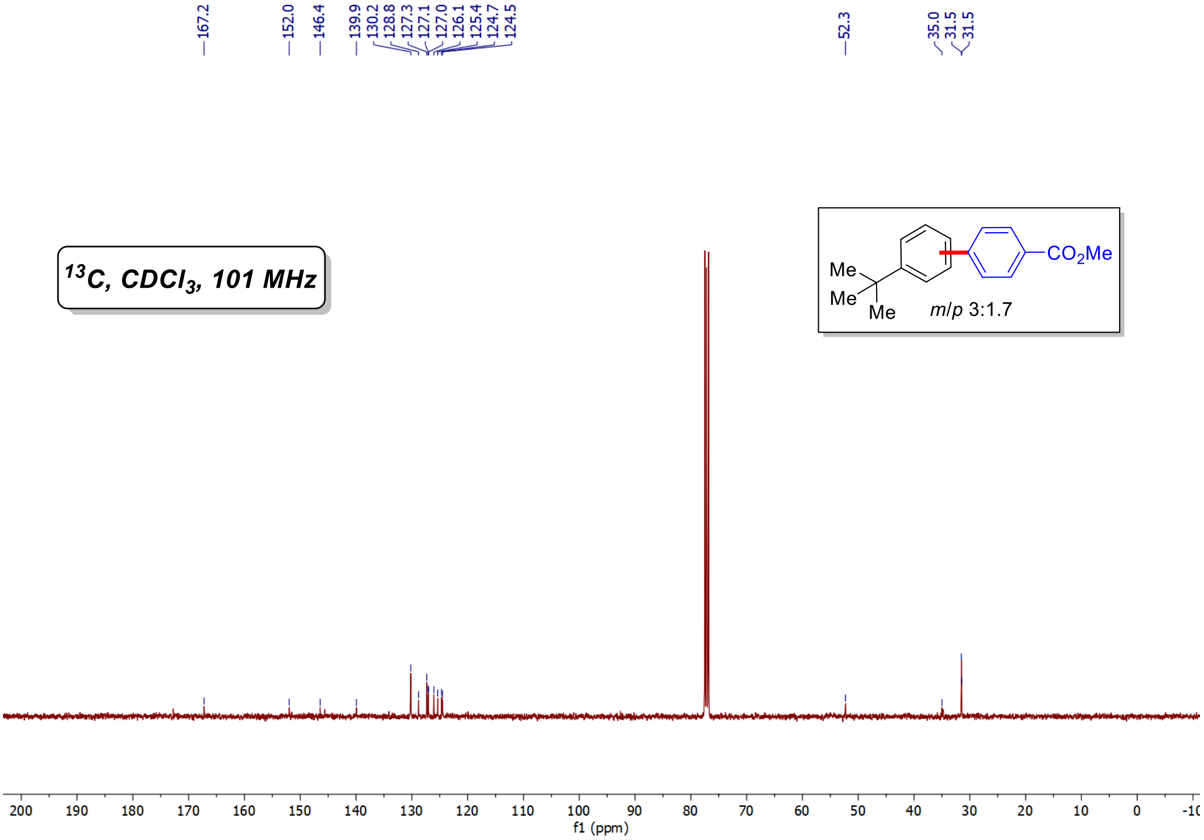
Toluene as arene (3ab)



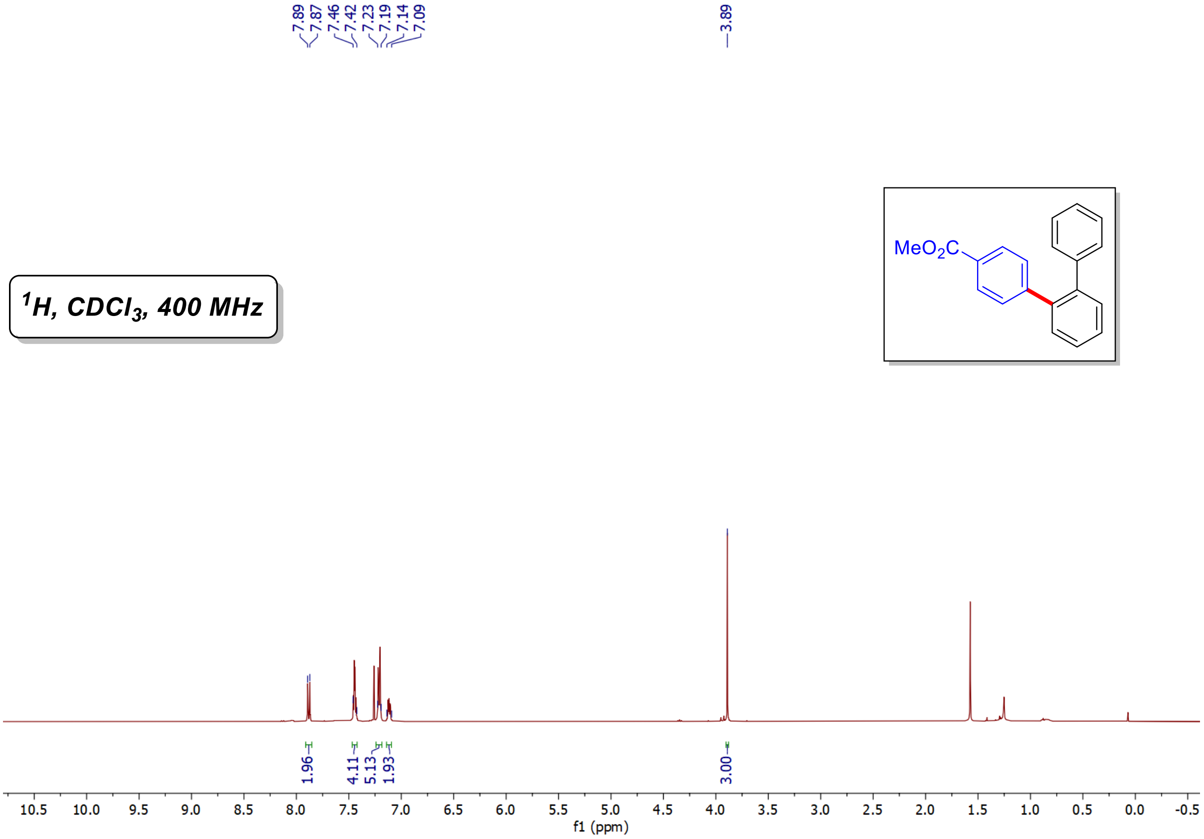


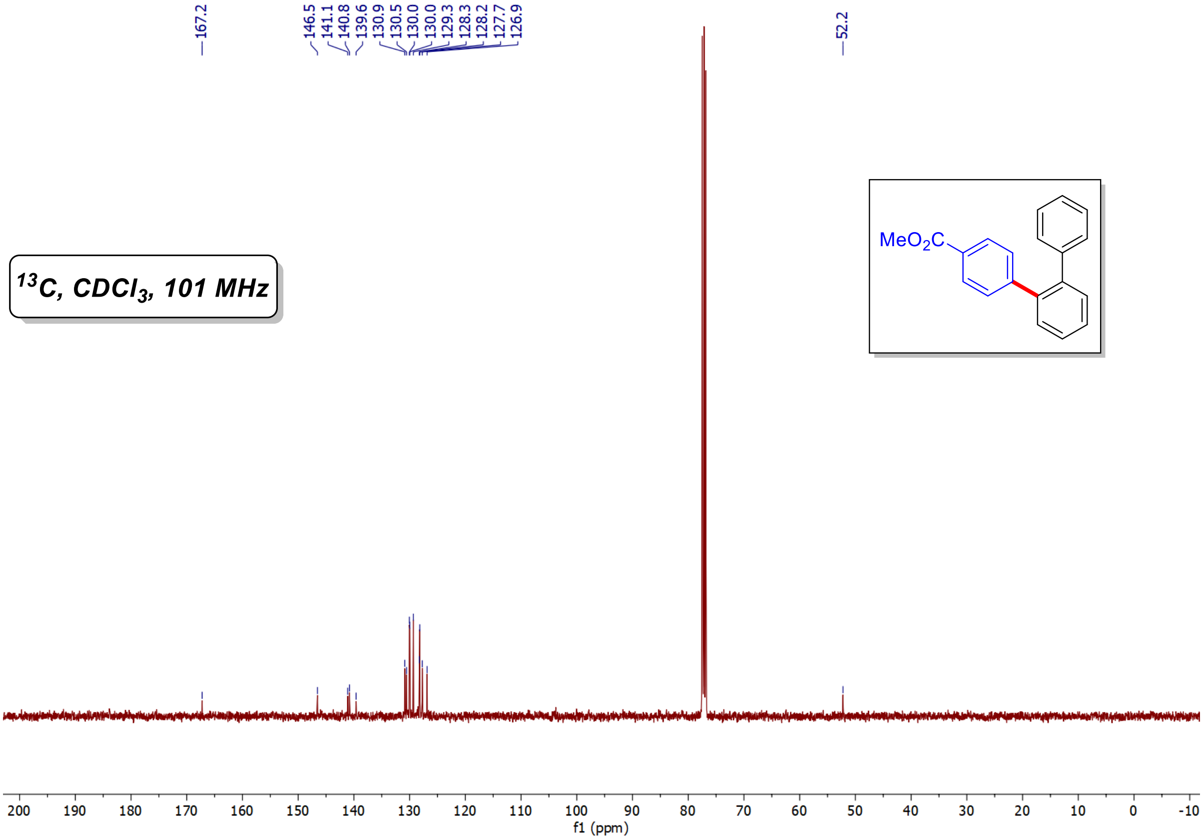
***Tert*-butylbenzene as arene (3ac)**



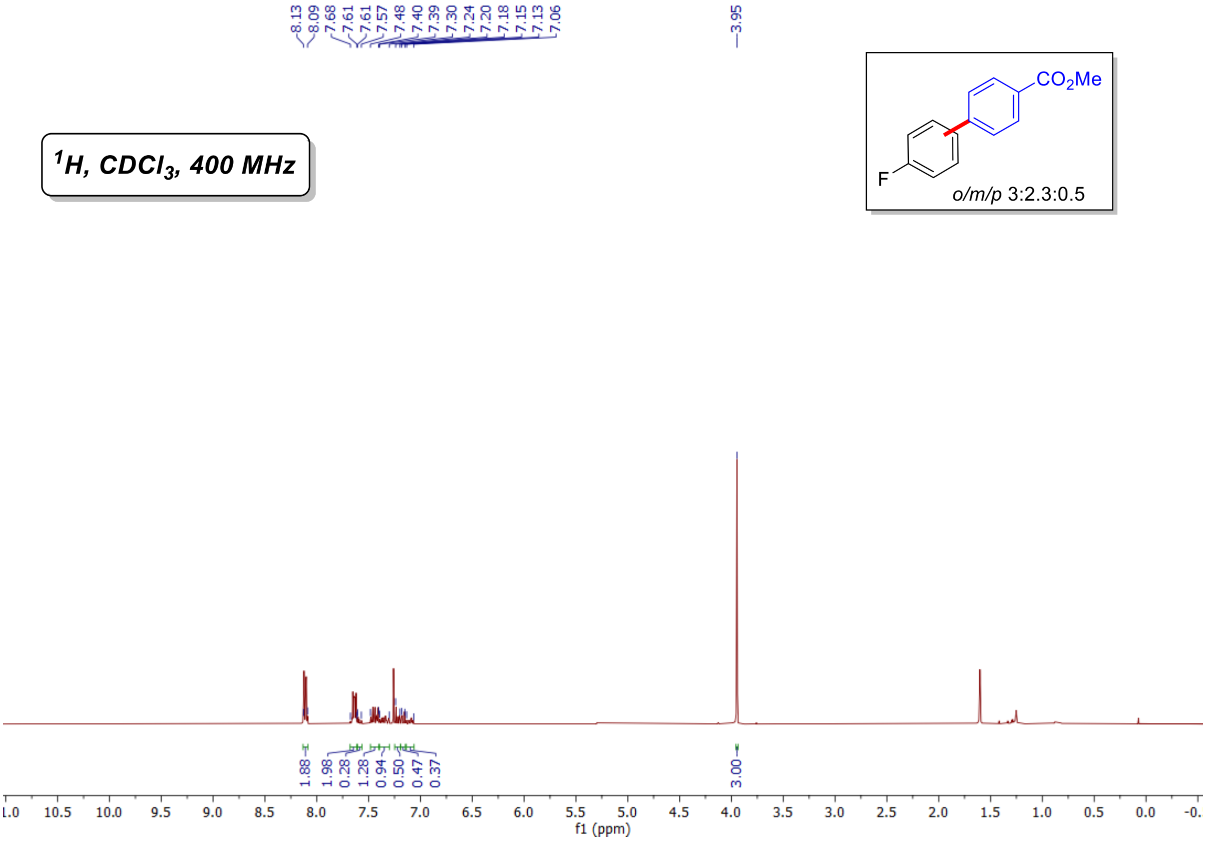


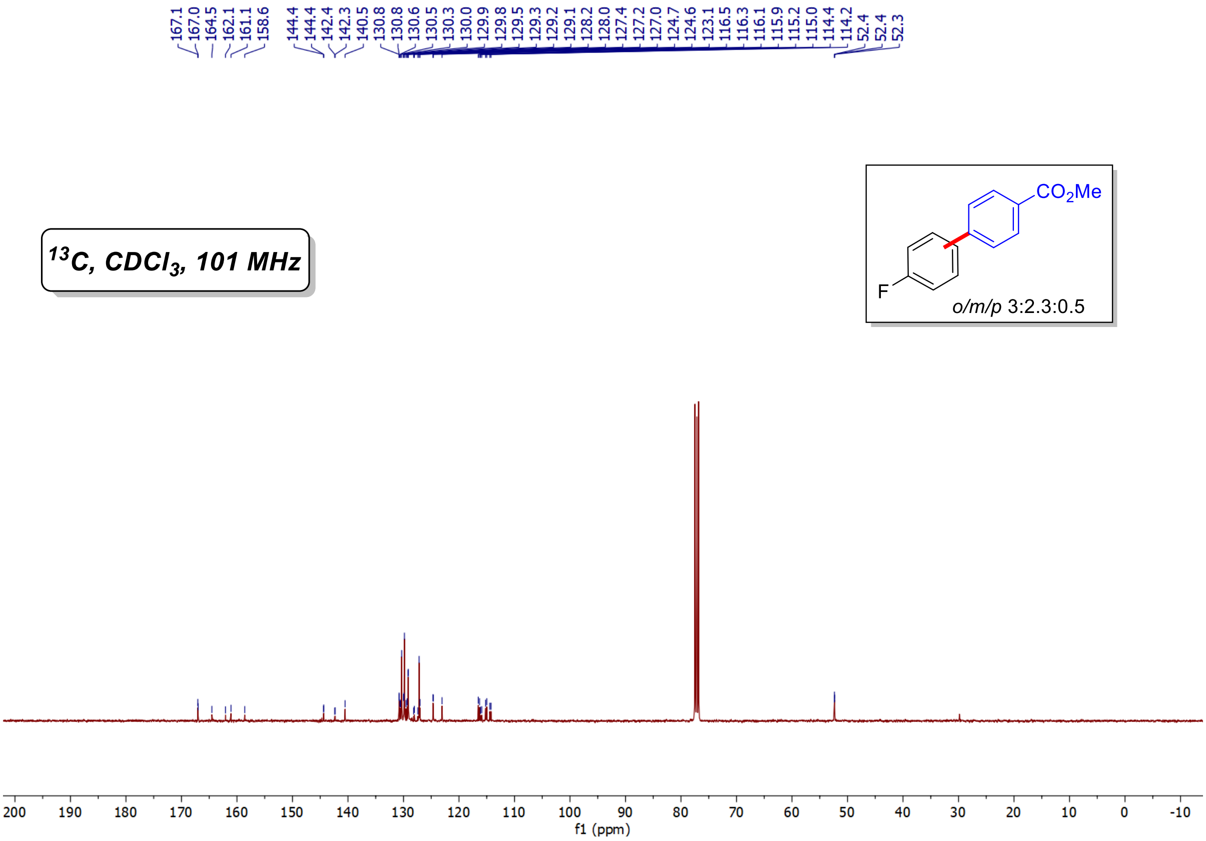
methyl [1,1':2',1''-terphenyl]-4-carboxylate (3ad)

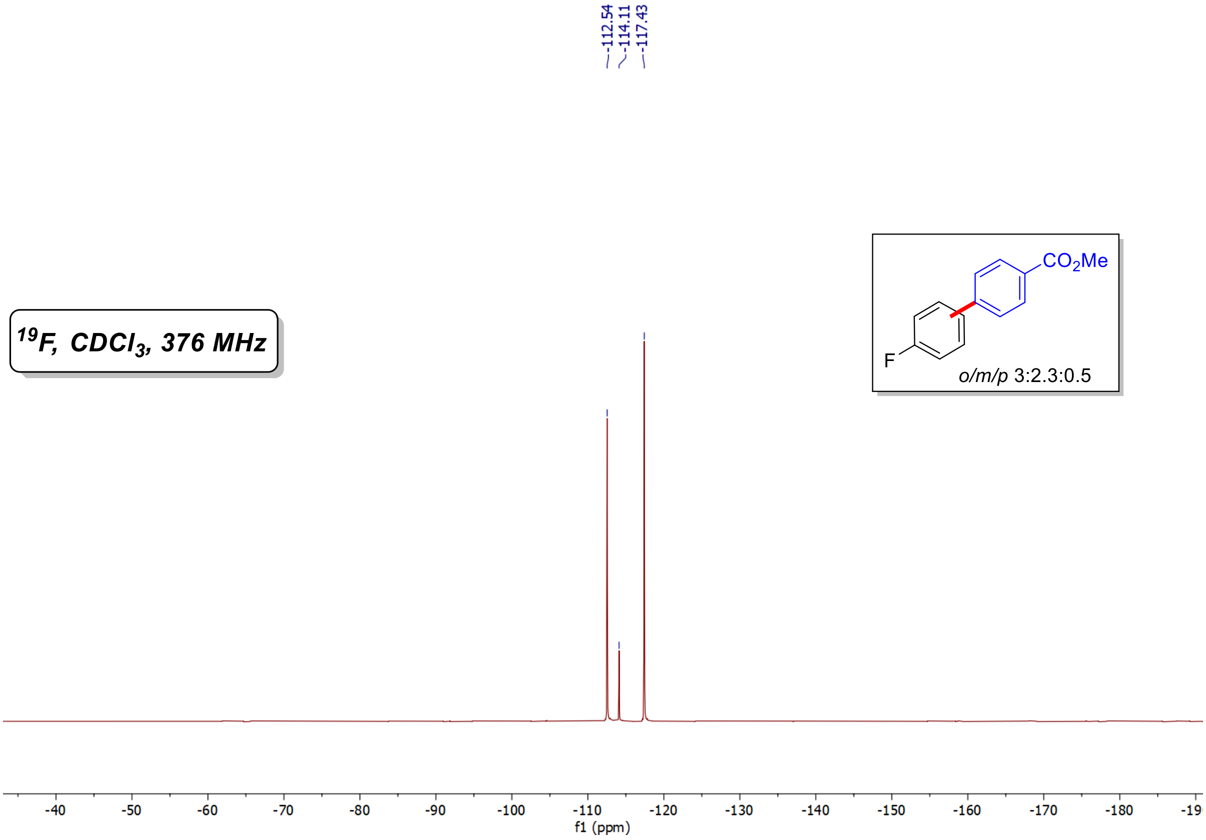




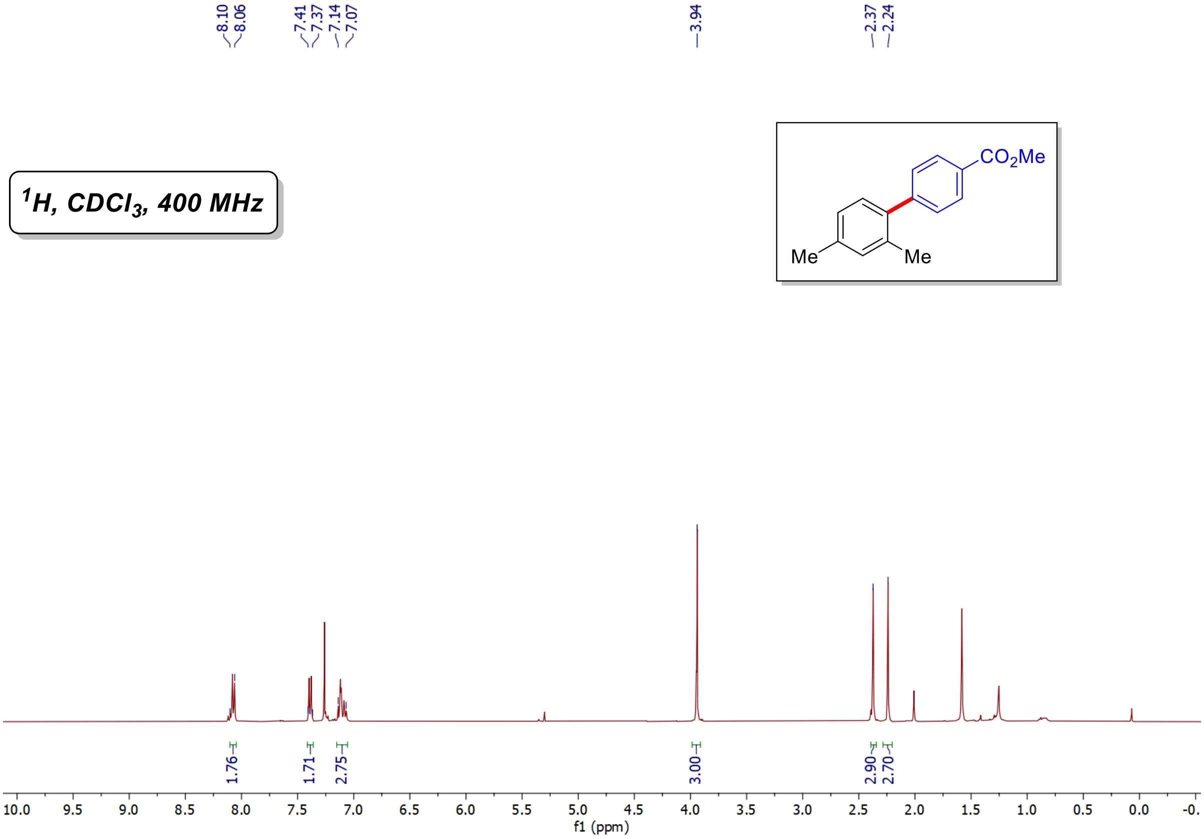
Fluorobenzene as arene (3ae)

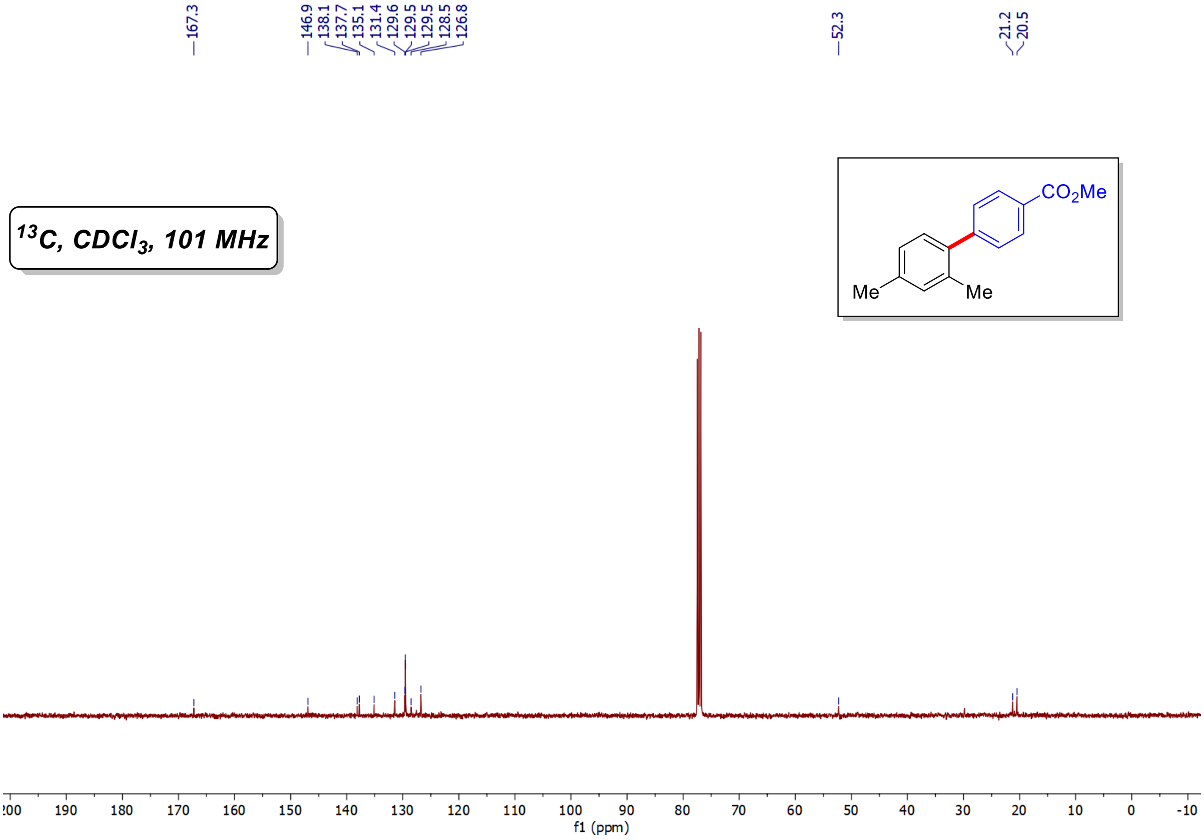



167.1
167.0
164.5
162.1
161.1
158.6
144.4
144.4
142.4
142.3
140.5
130.8
130.8
130.6
130.5
130.3
130.0
129.9
129.8
129.5
129.3
129.2
129.1
128.2
128.0
127.4
127.2
127.0
124.7
124.6
123.1
116.5
116.3
116.1
115.9
115.2
115.0
114.4
114.2
52.4
52.4
52.3
^{13}C, $CDCl_3$, 101 MHz
CO_2Me
F
o/m/p 3:2.3:0.5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

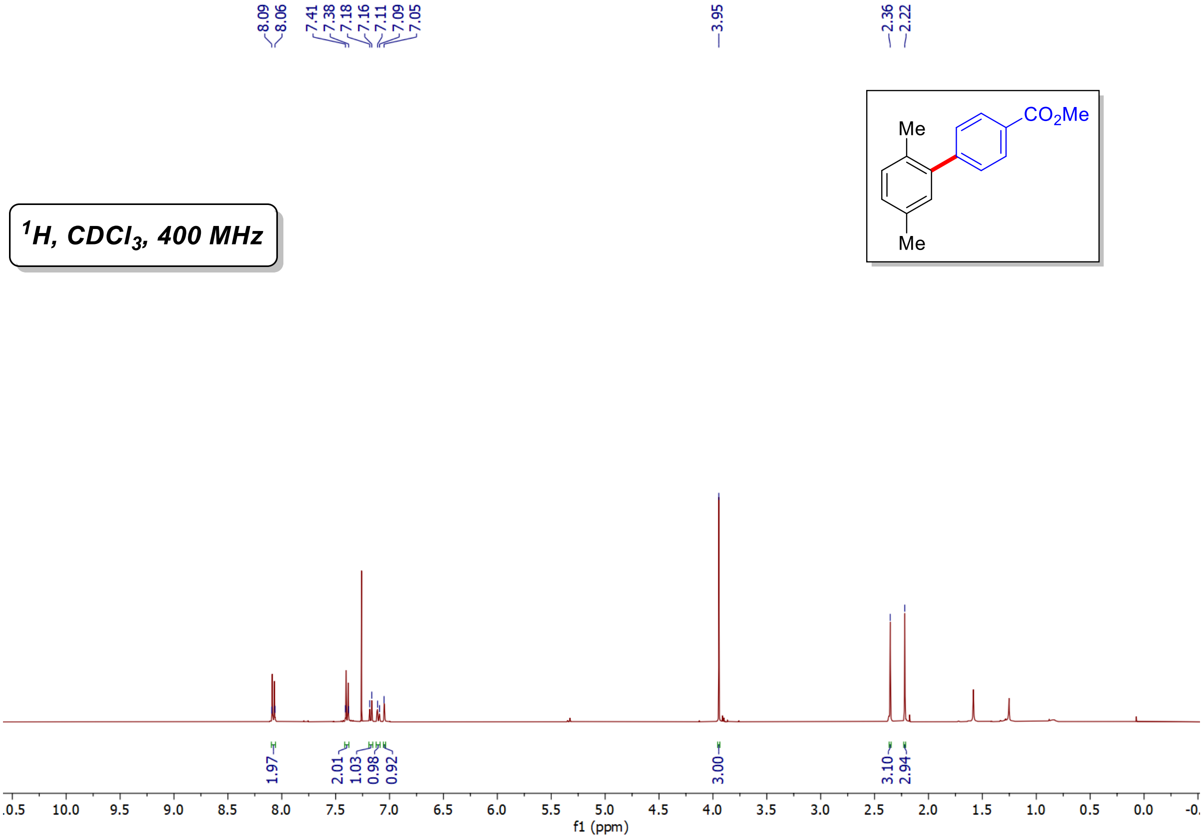

-112.54
-114.11
-117.43
^{19}F, $CDCl_3$, 376 MHz
CO_2Me
F
o/m/p 3:2.3:0.5
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-19
f1 (ppm)

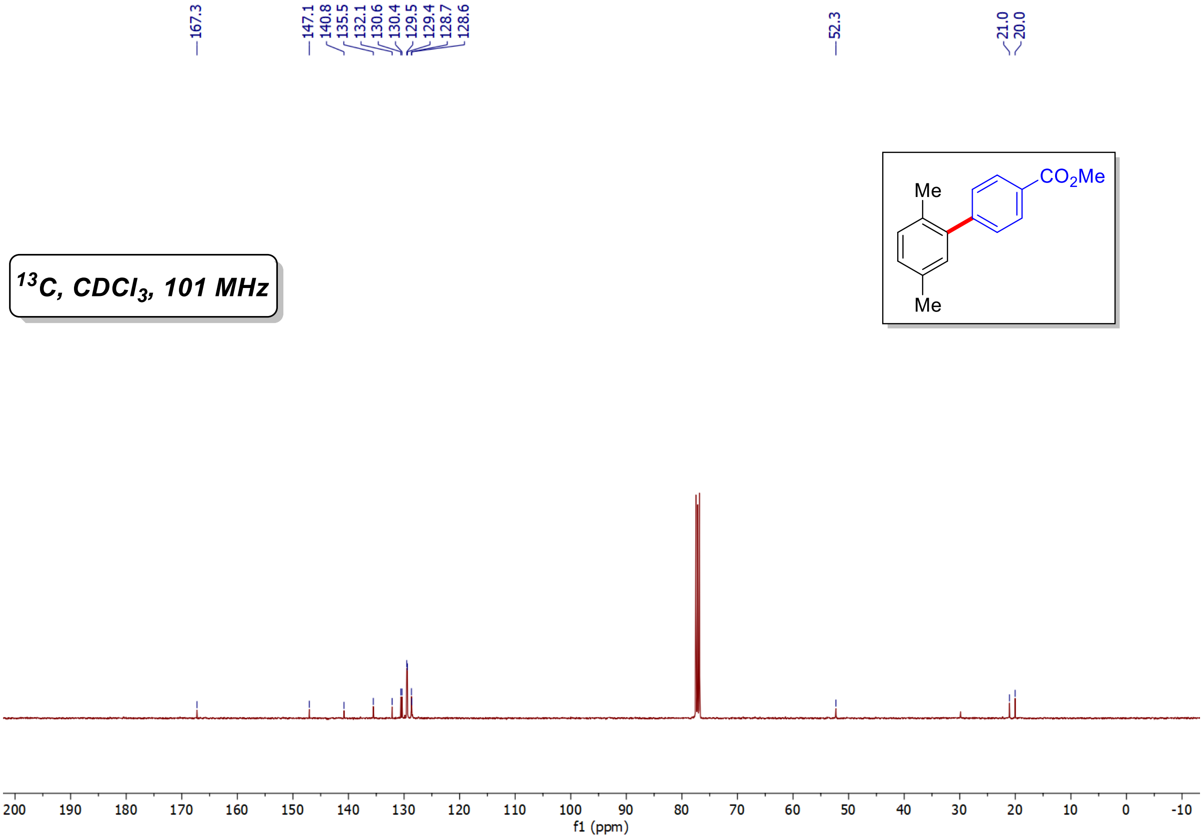
methyl 2',4'-dimethyl-[1,1'-biphenyl]-4-carboxylate (3af)



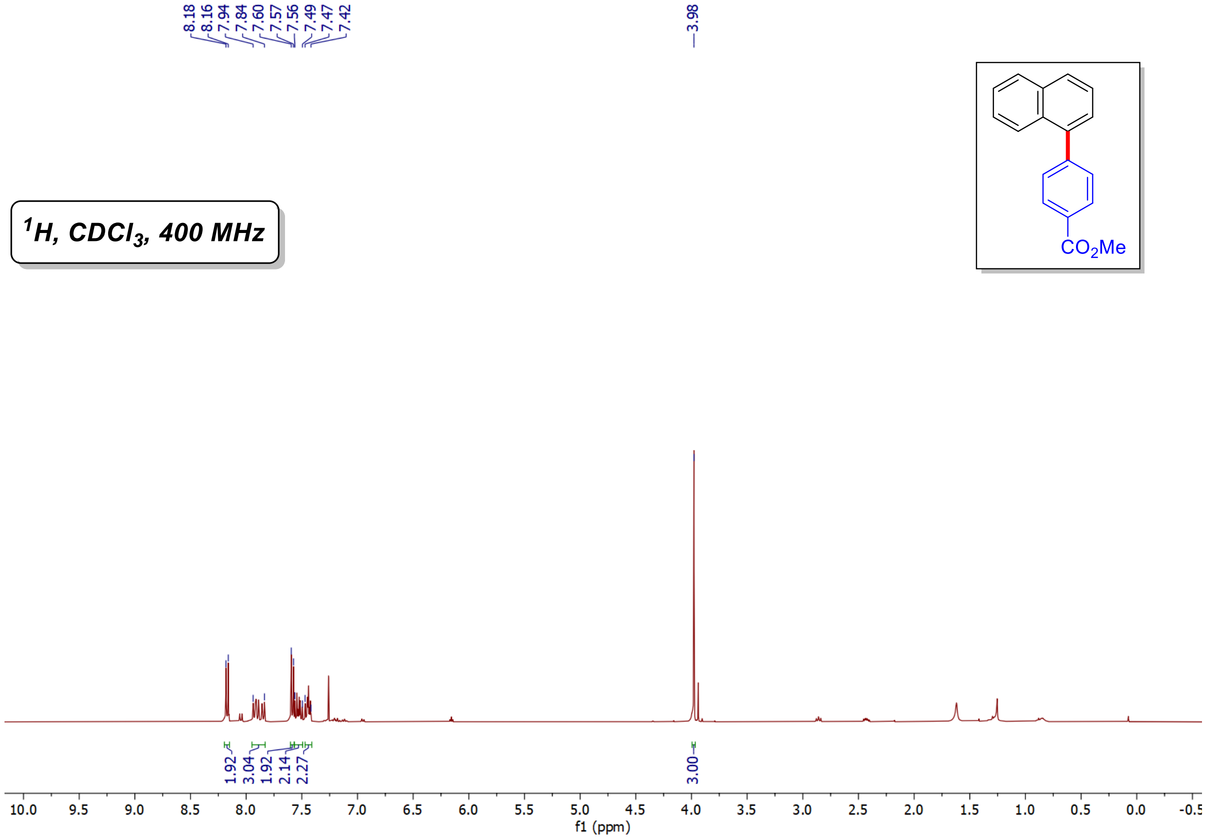


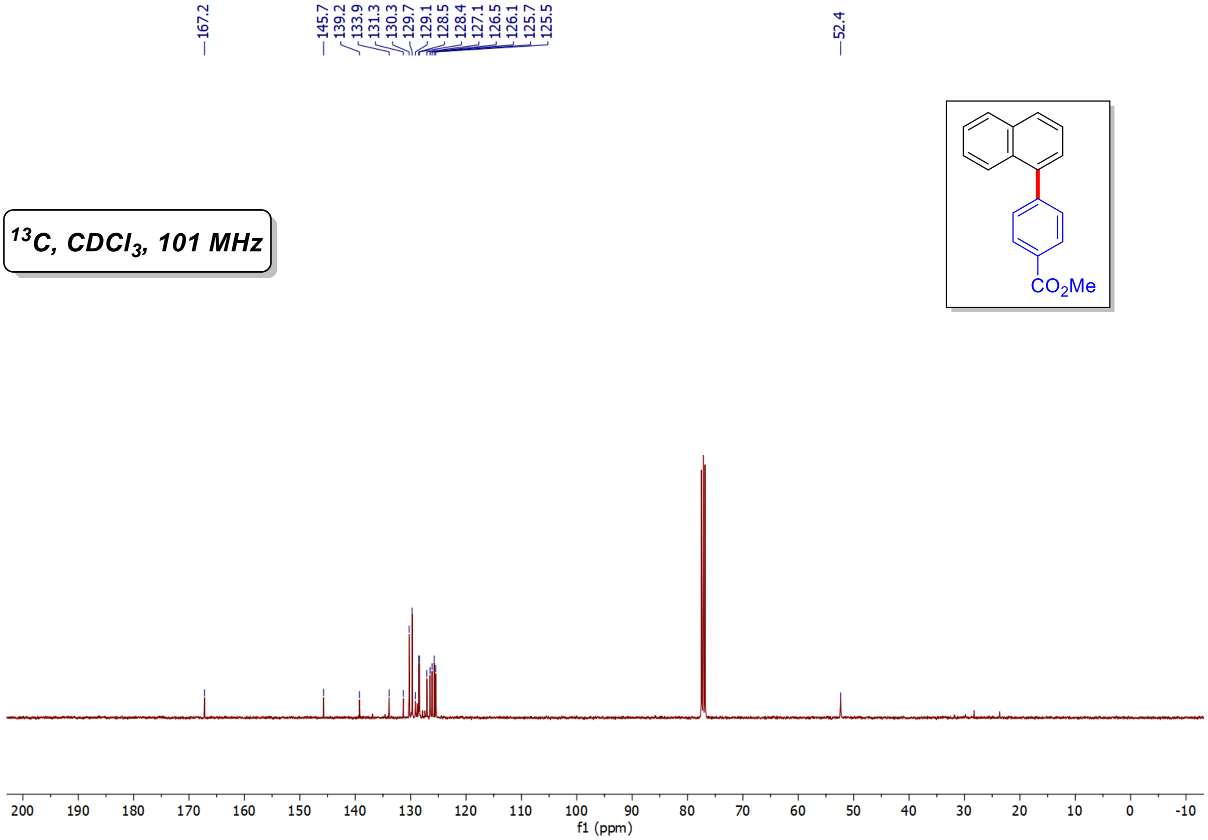
methyl 2',5'-dimethyl-[1,1'-biphenyl]-4-carboxylate (3ag)



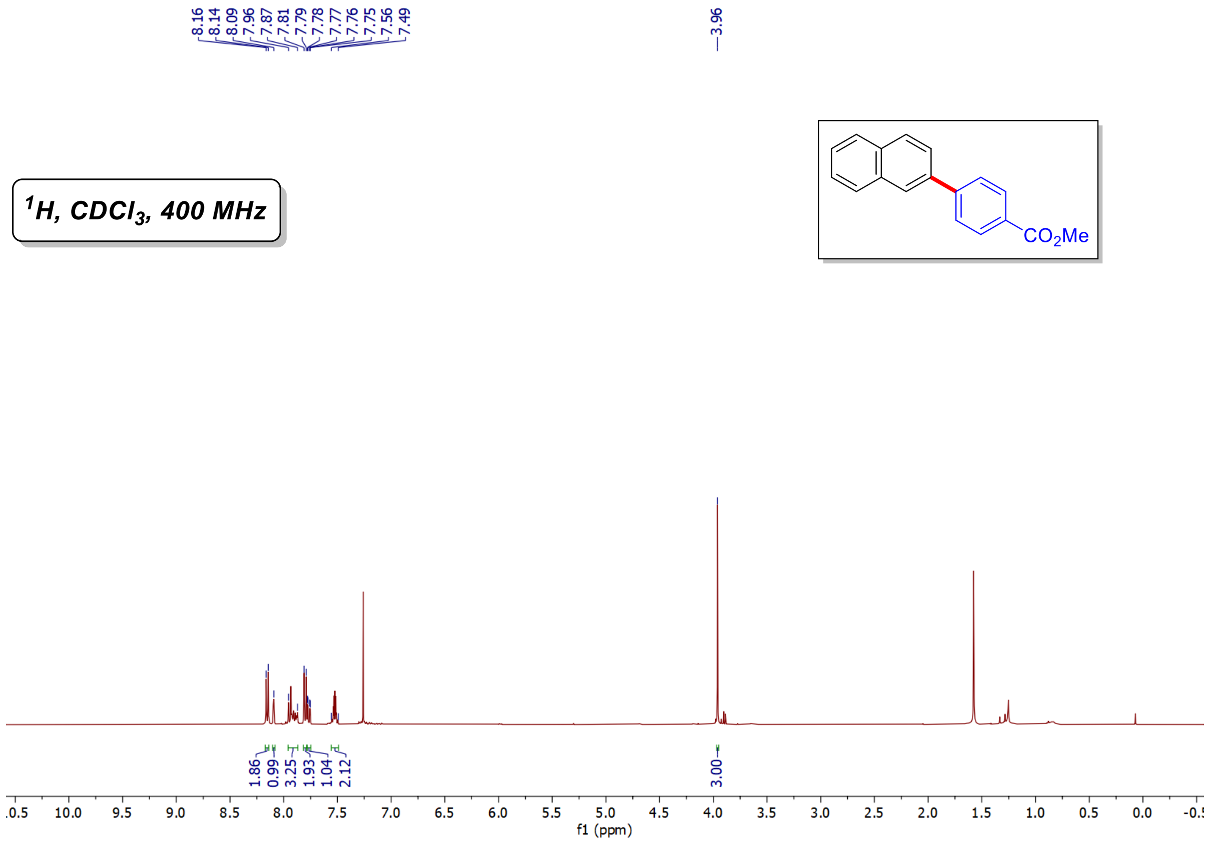


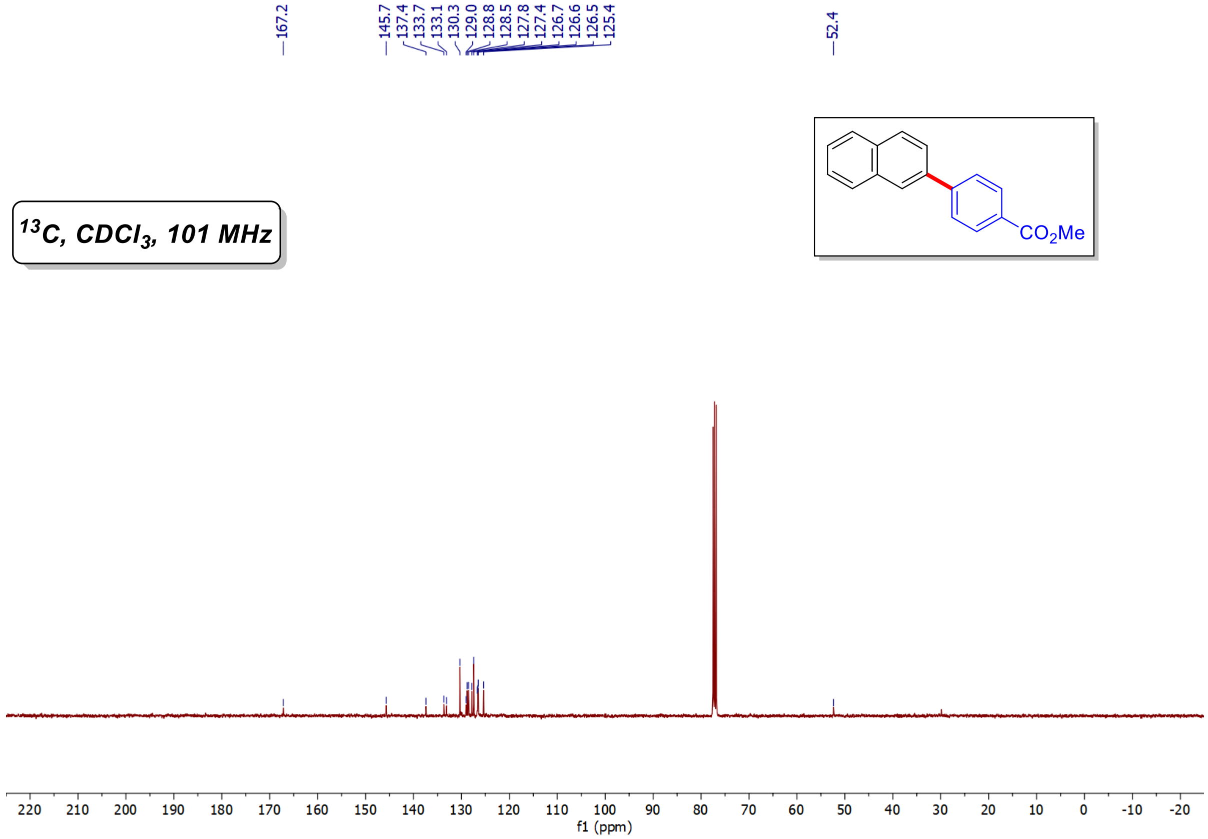
methyl 4-(naphthalen-1-yl)benzoate (3ah) (C_1)



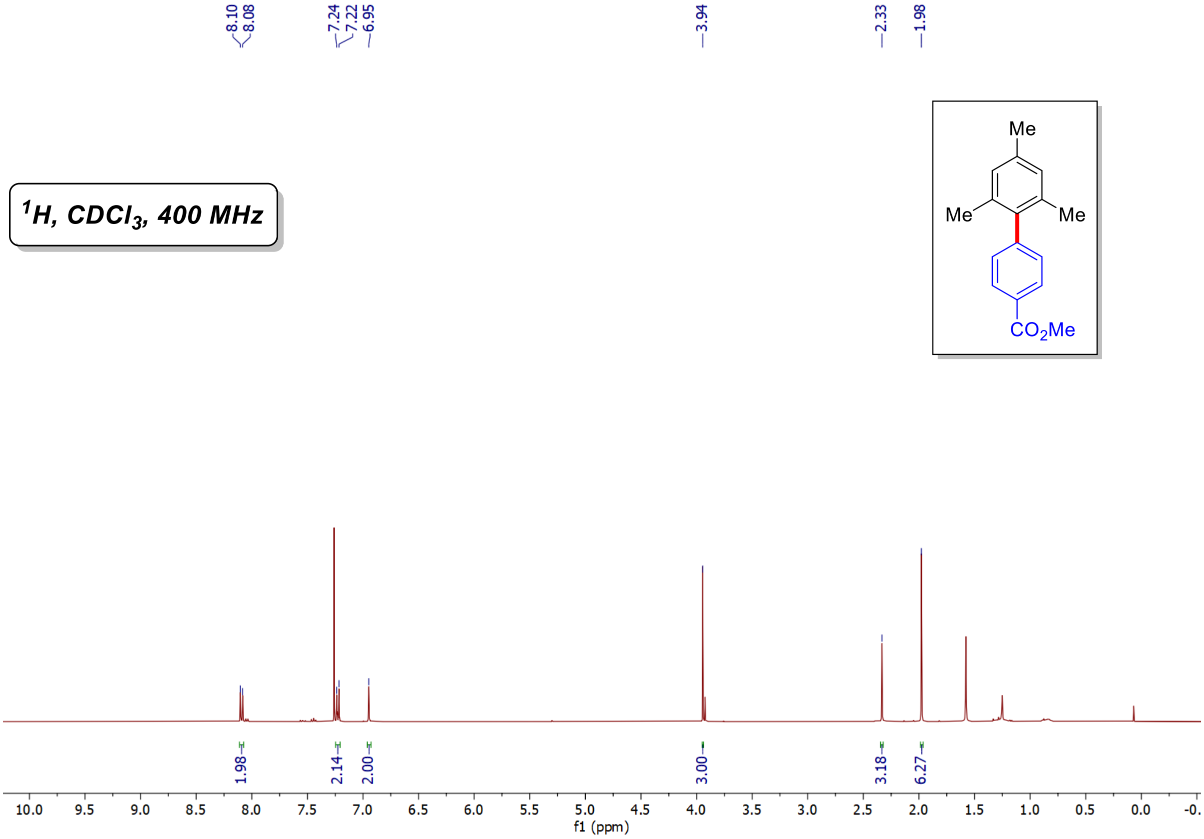


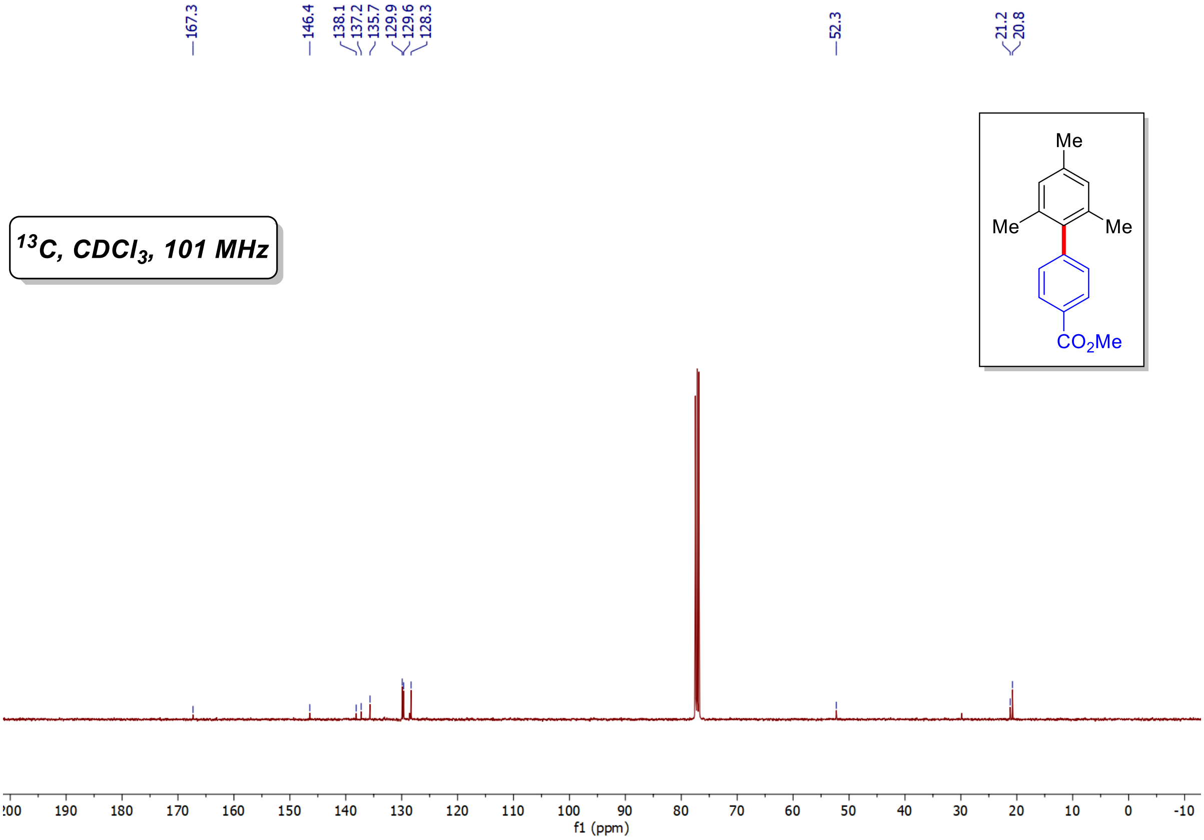
methyl 4-(naphthalen-2-yl)benzoate (3ah) (C$_2$)





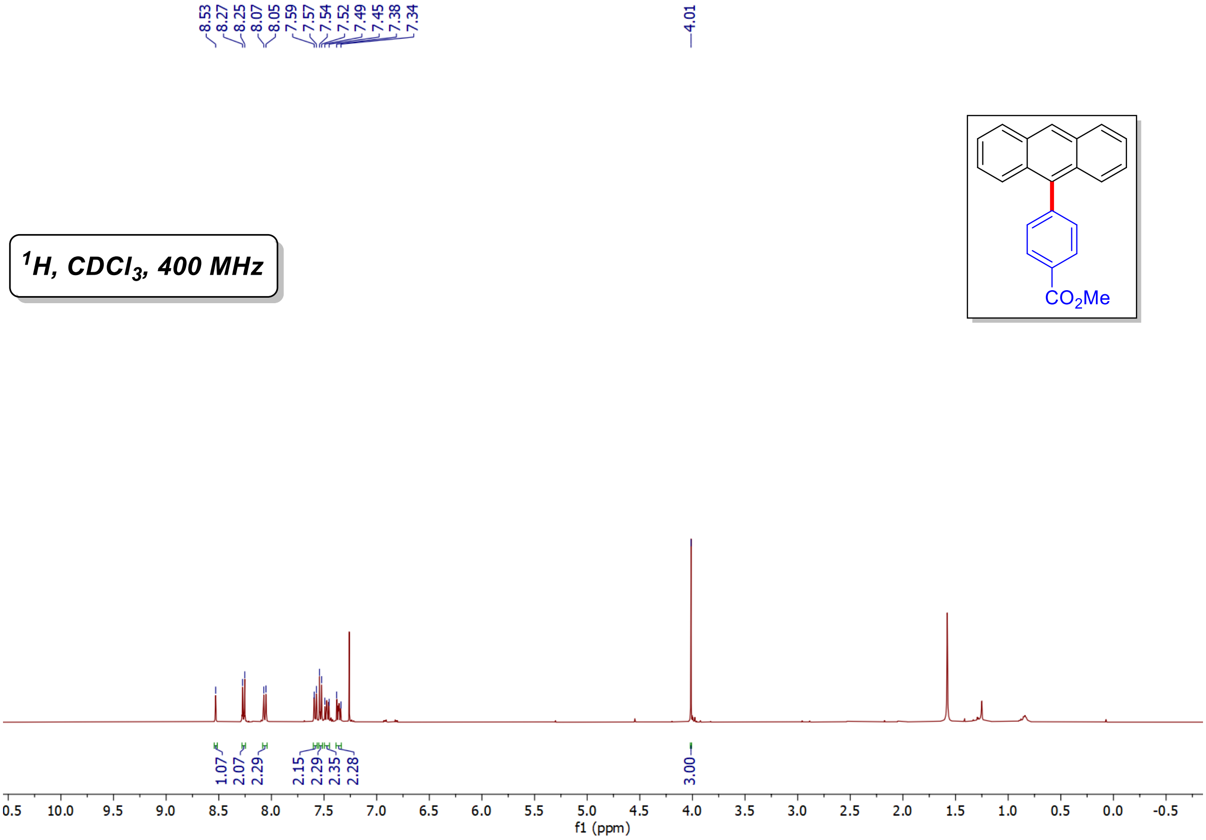
methyl 2',4',6'-trimethyl-[1,1'-biphenyl]-4-carboxylate (3ai)

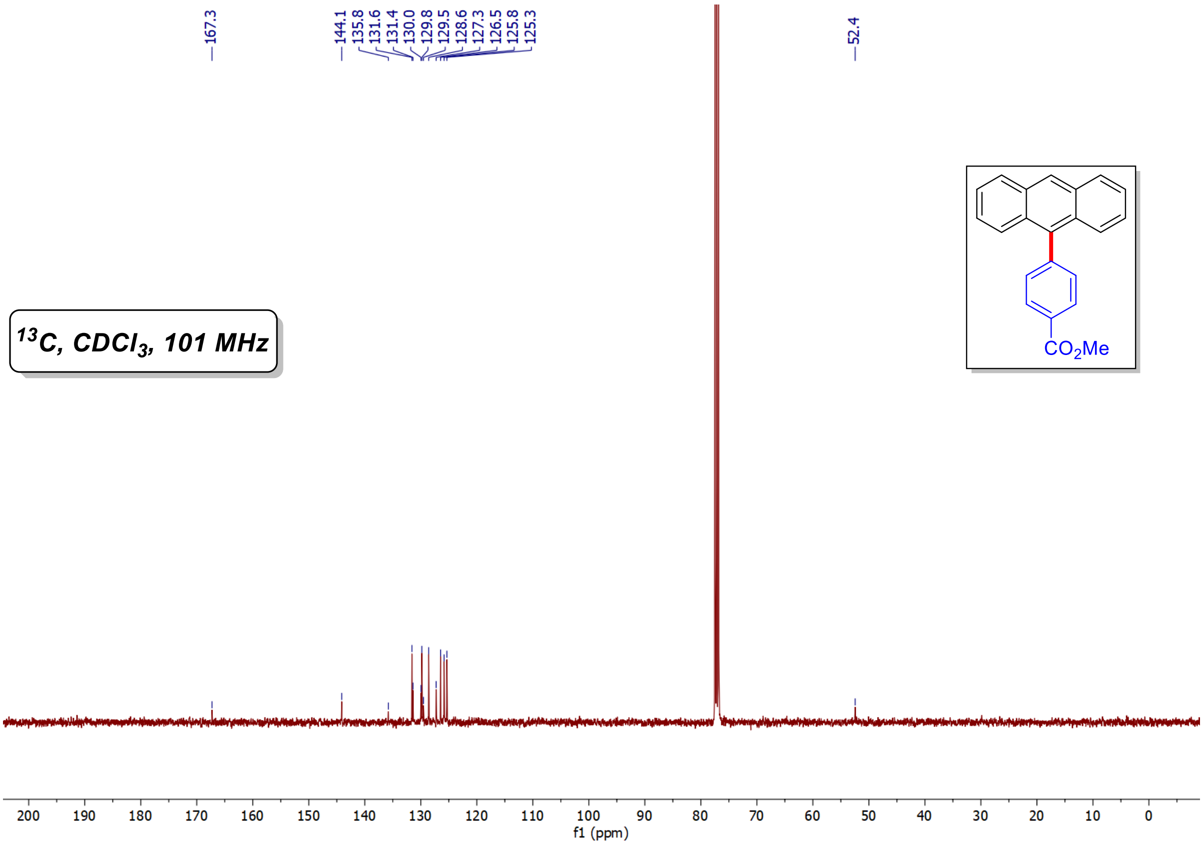




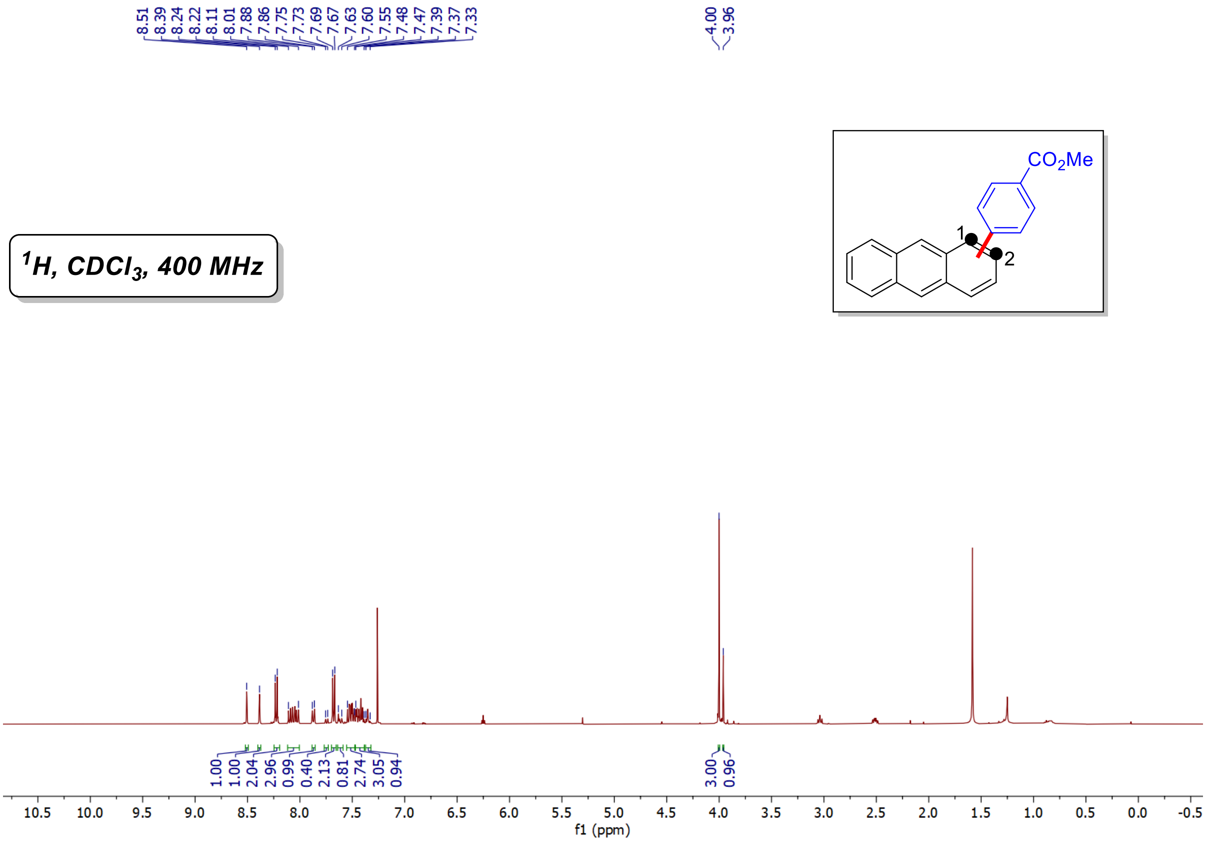
Anthracene as arene (3aj): (C^{10}/others = 5:4)

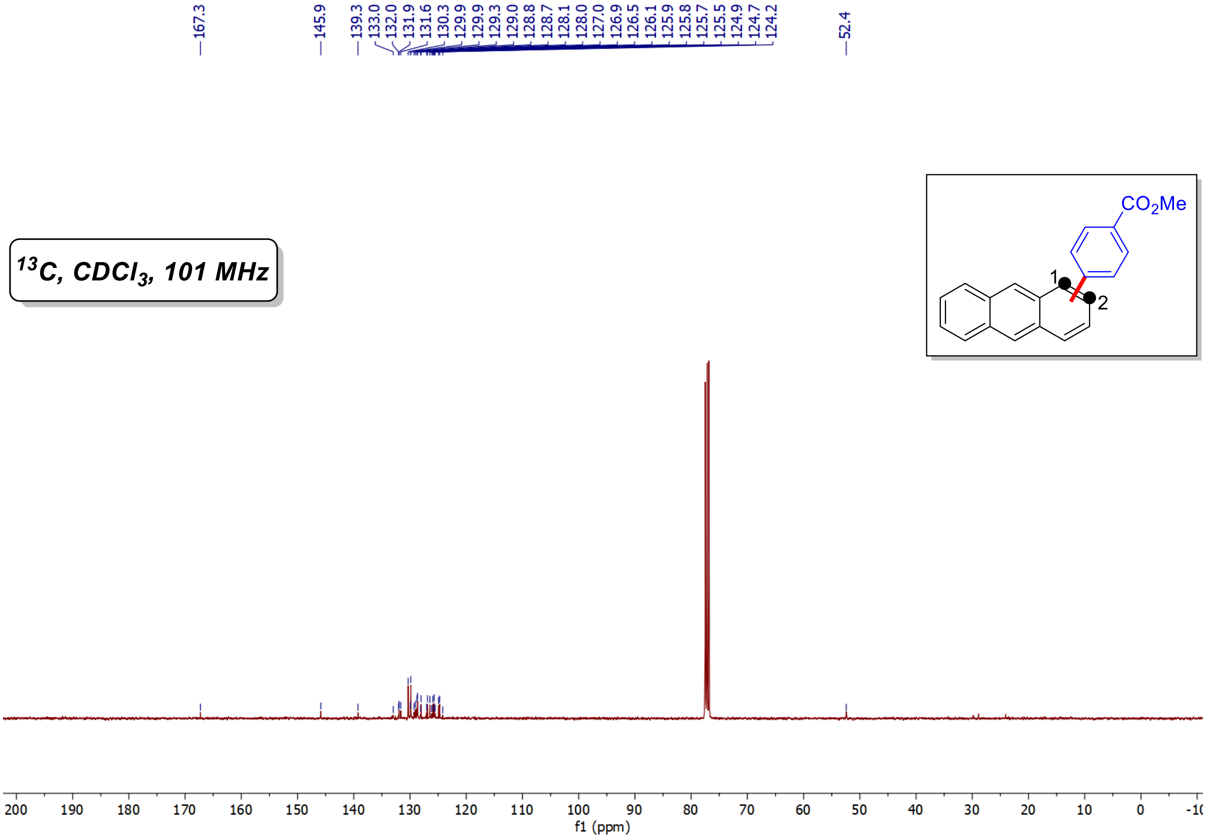
methyl 4-(anthracen-9-yl)benzoate (3aj) (C^{10})



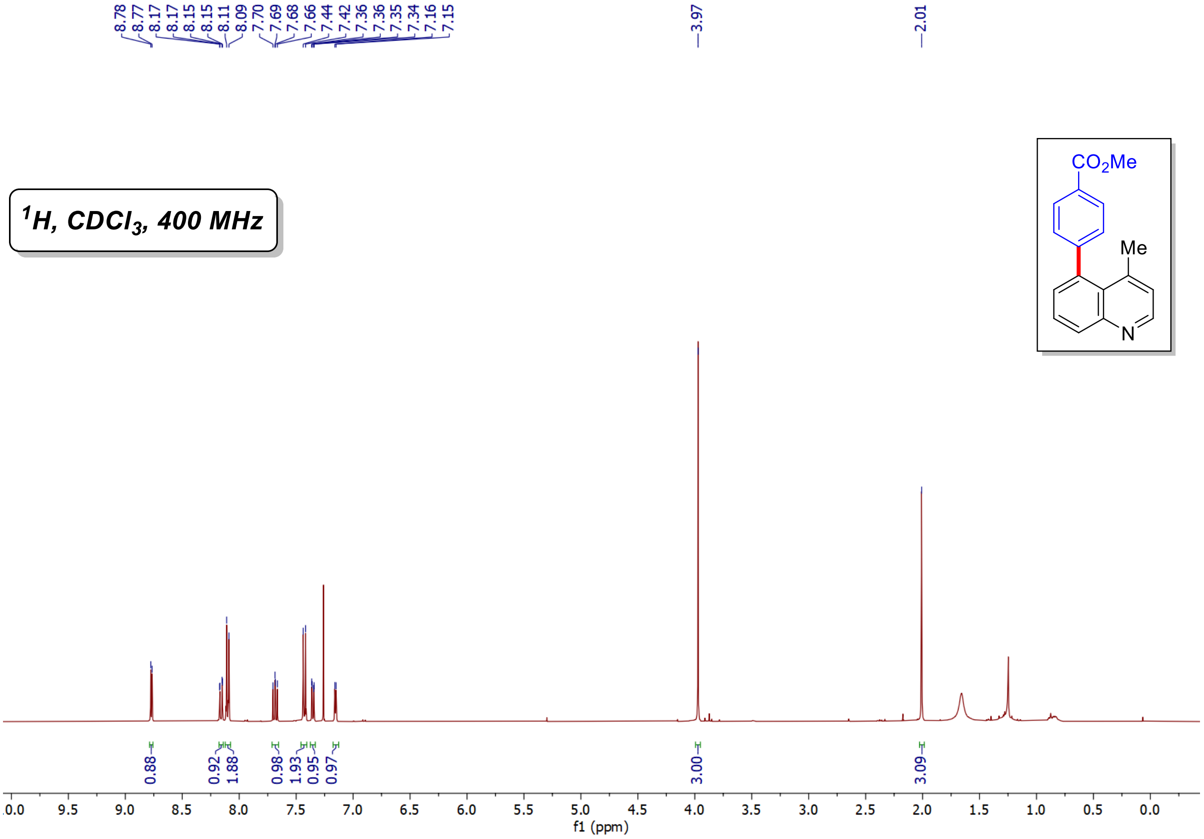


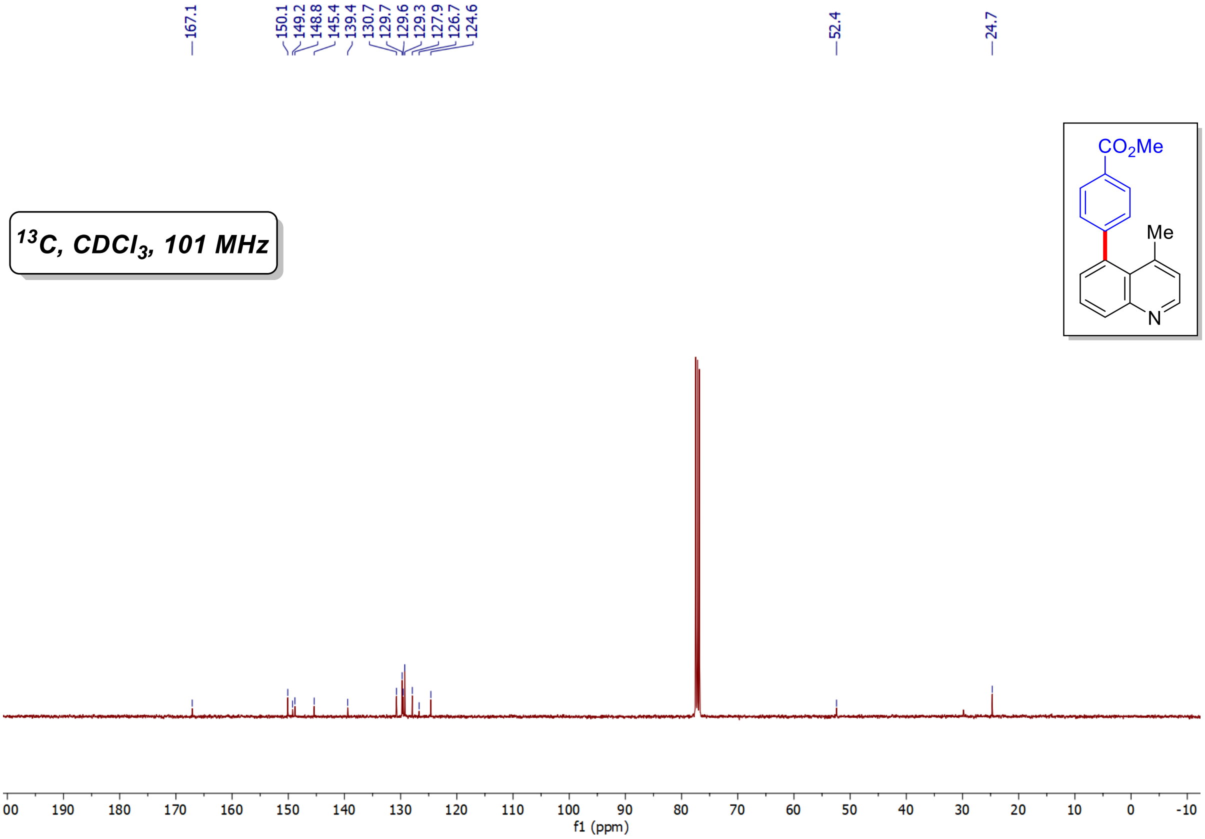
methyl 4-(anthracen-9-yl)benzoate (3aj) (C1 and C2)



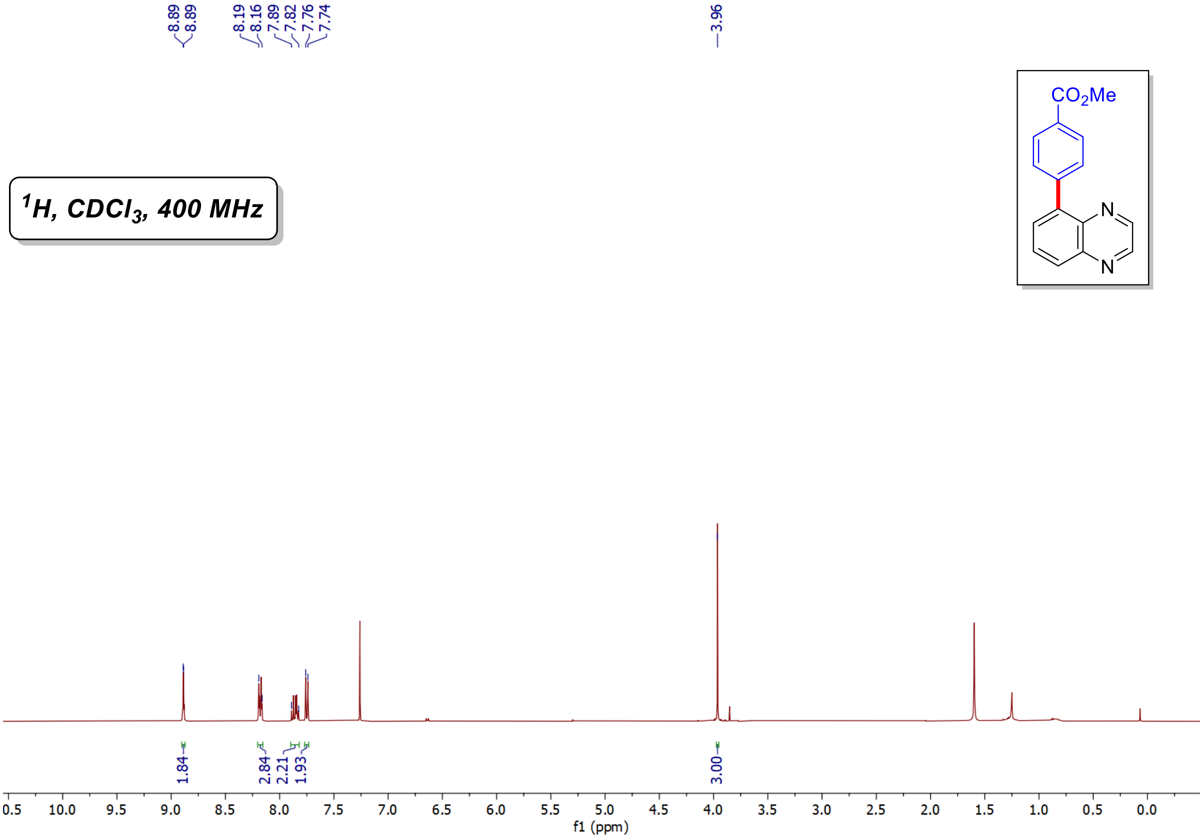


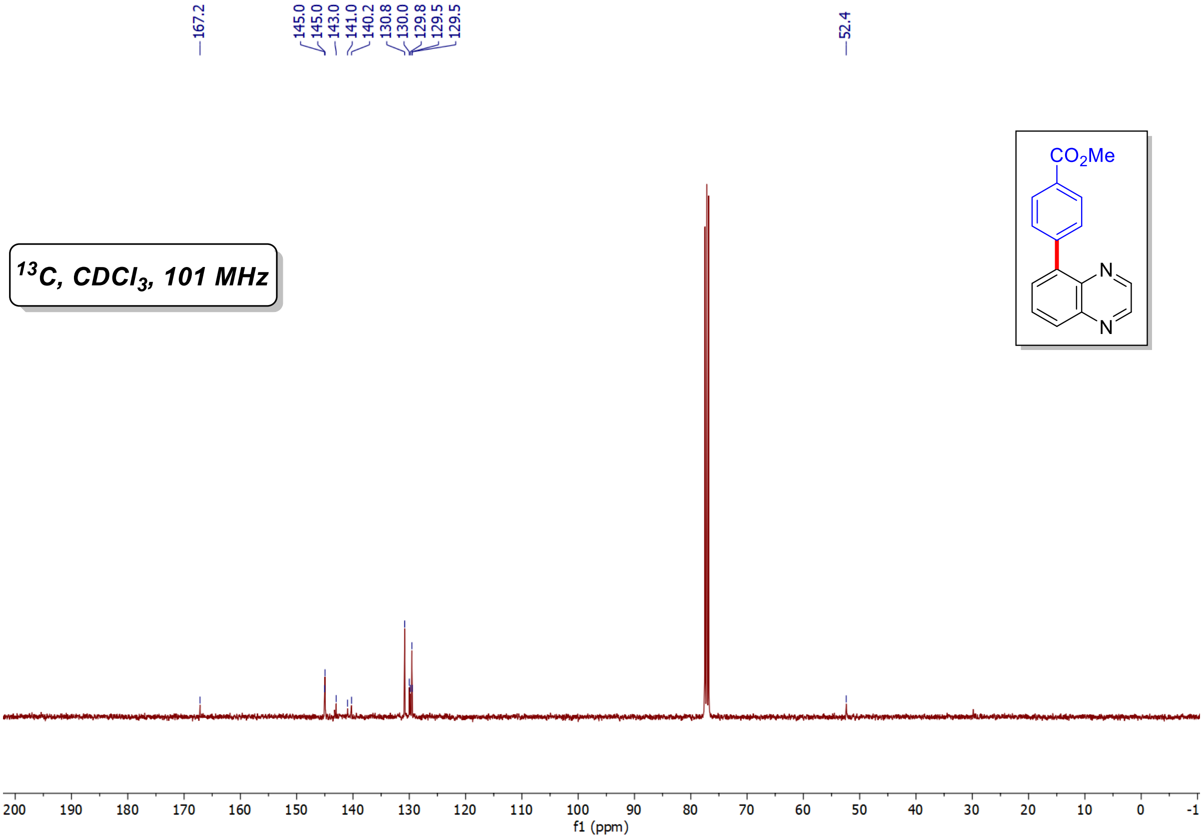
methyl 4-(4-methylquinolin-5-yl)benzoate (3ak)



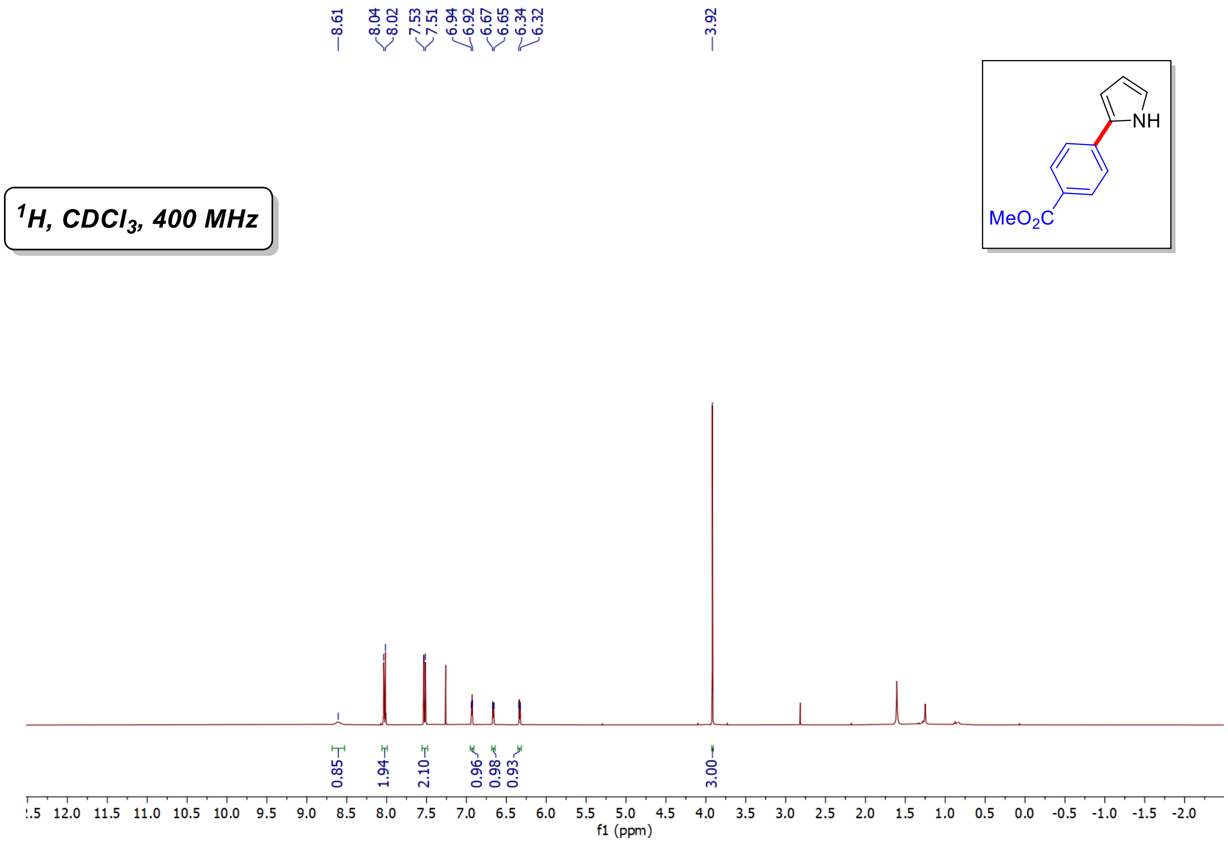


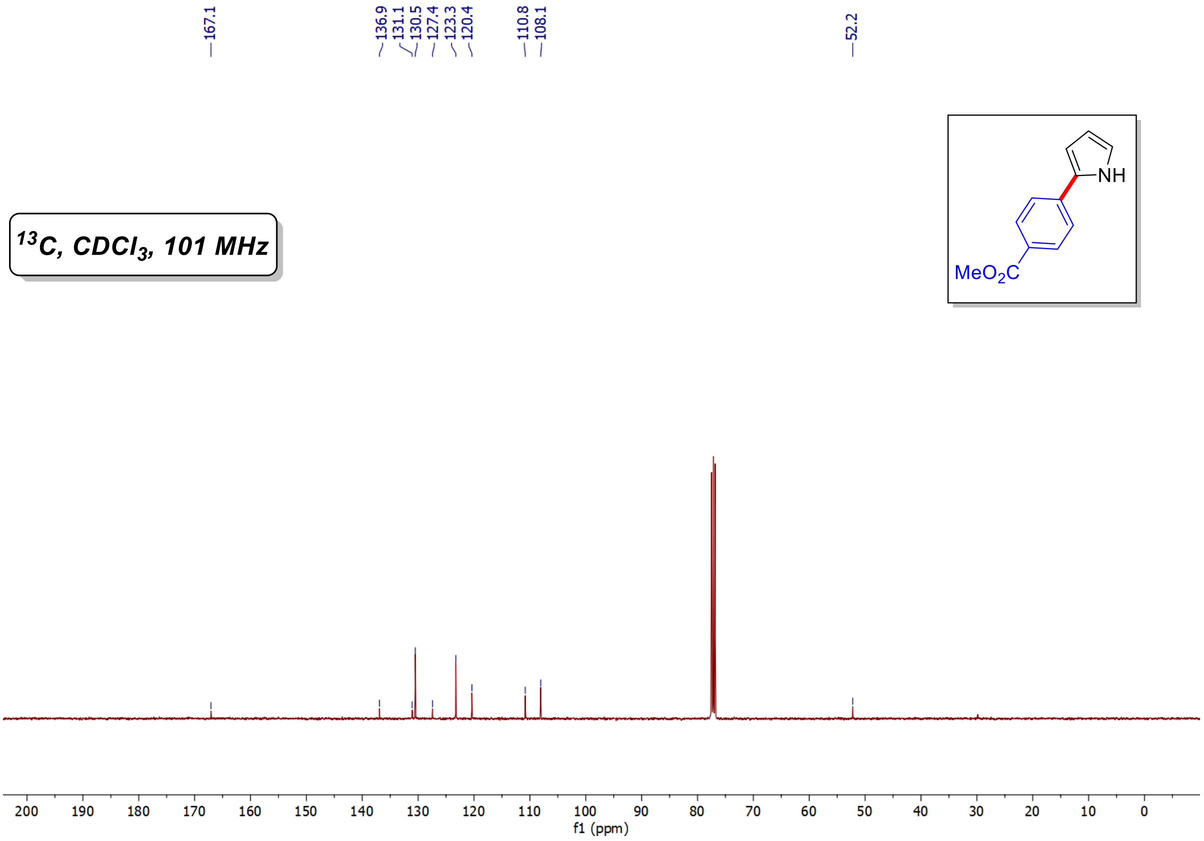
methyl 4-(quinoxalin-5-yl)benzoate (3al)



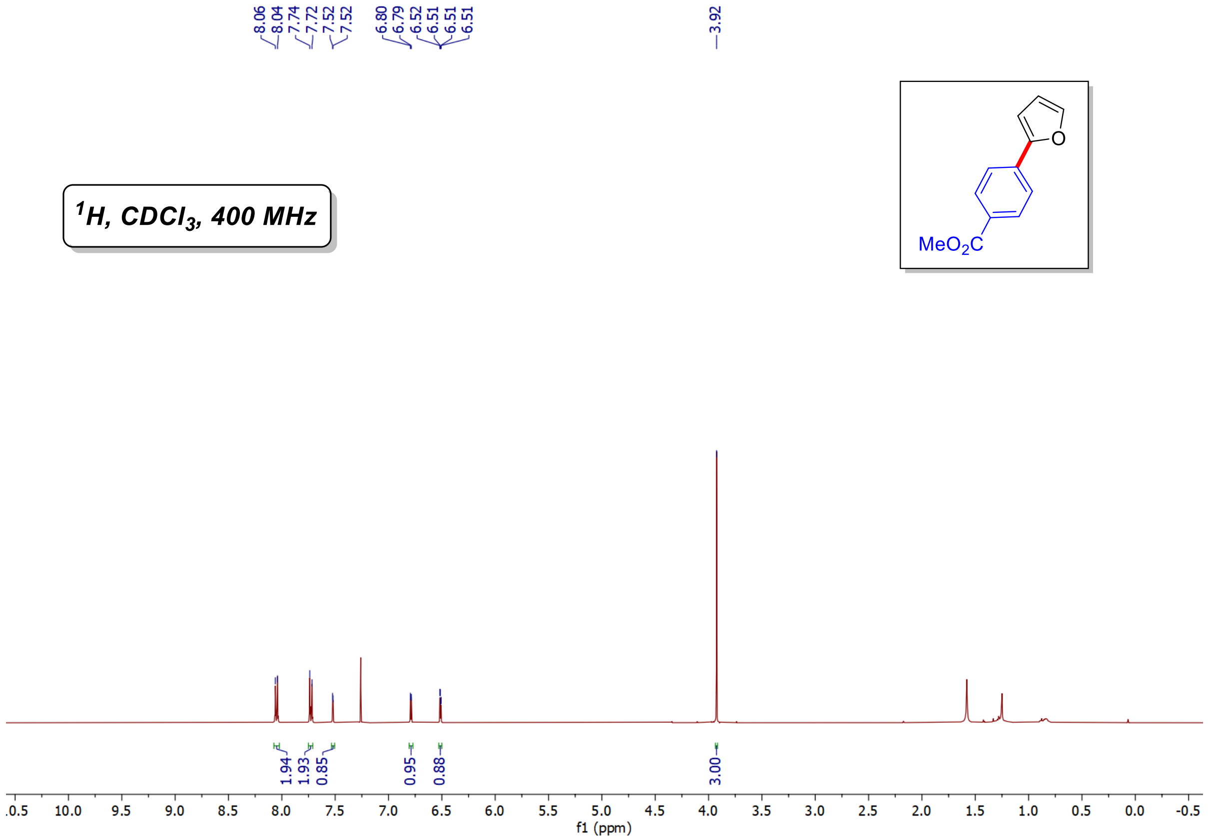


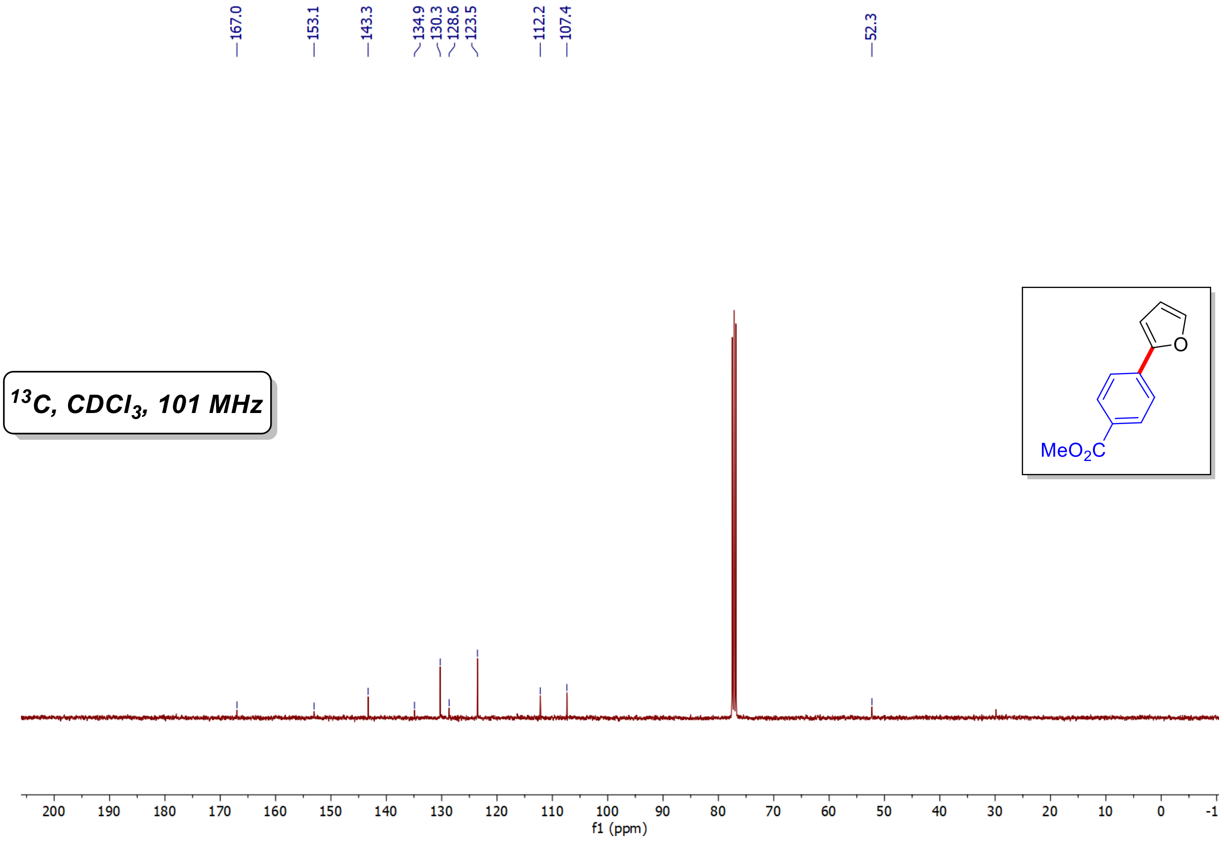
methyl 4-(1H-pyrrol-2-yl)benzoate (3am)



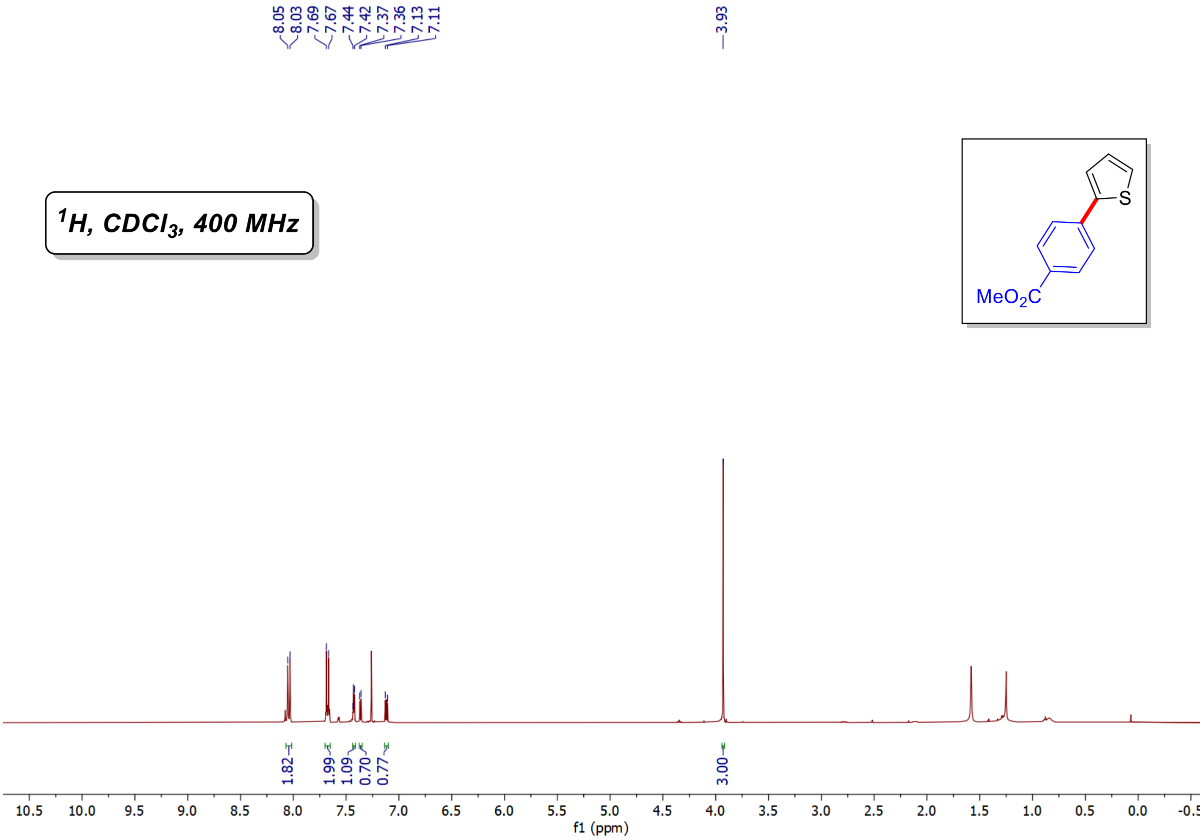


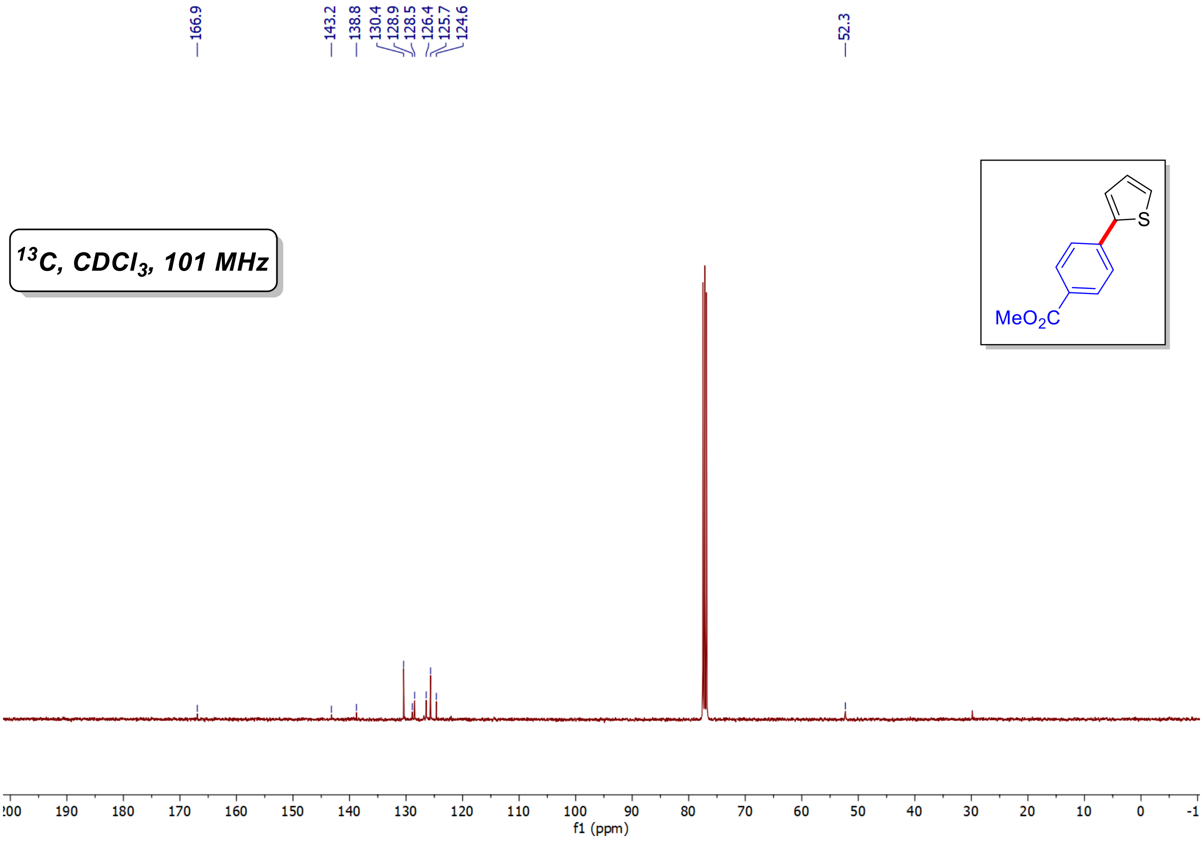
methyl 4-(furan-2-yl)benzoate (3an)



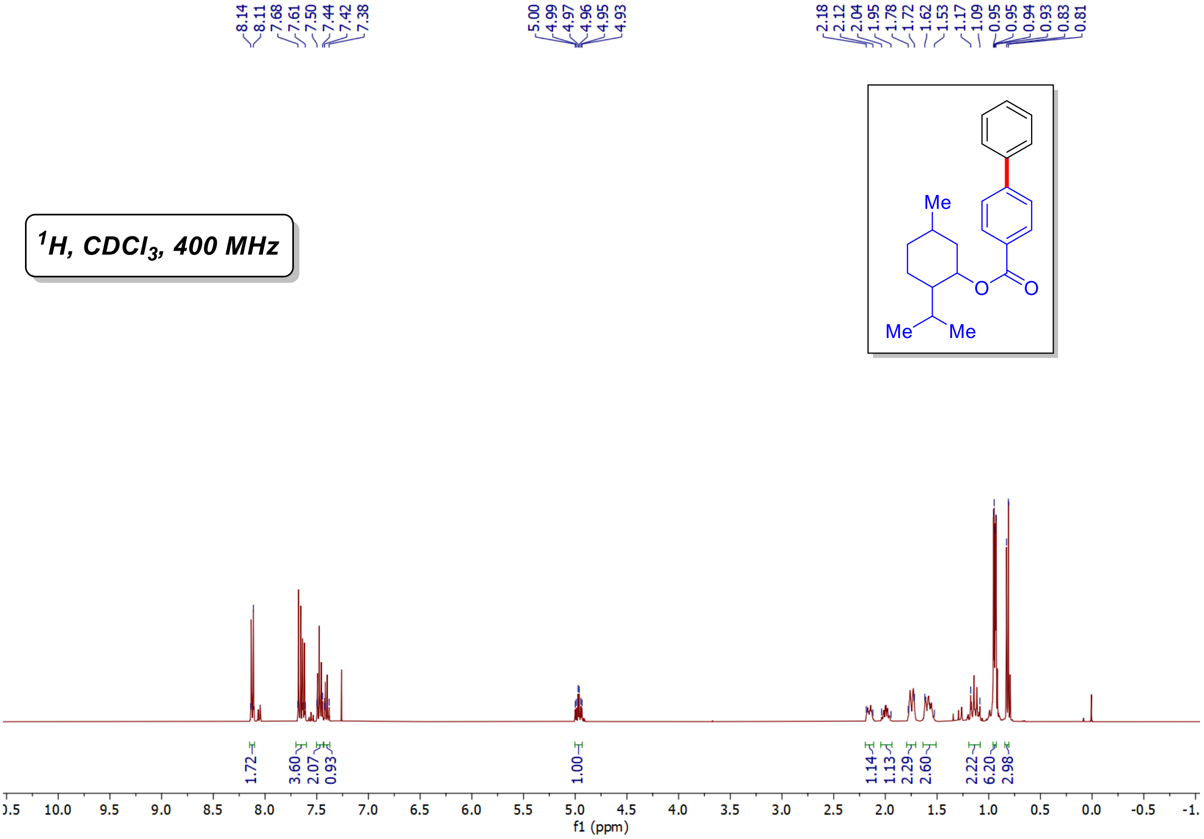


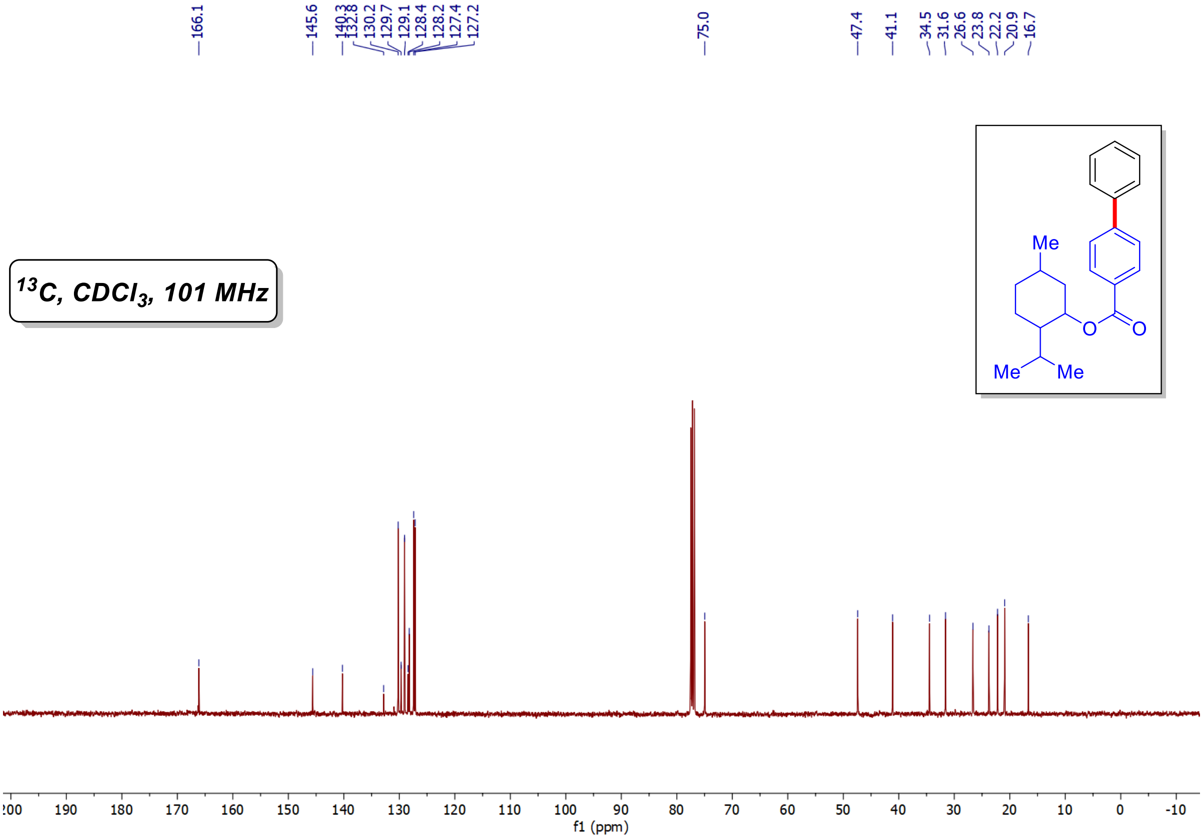
methyl 4-(thiophen-2-yl)benzoate (3ao)



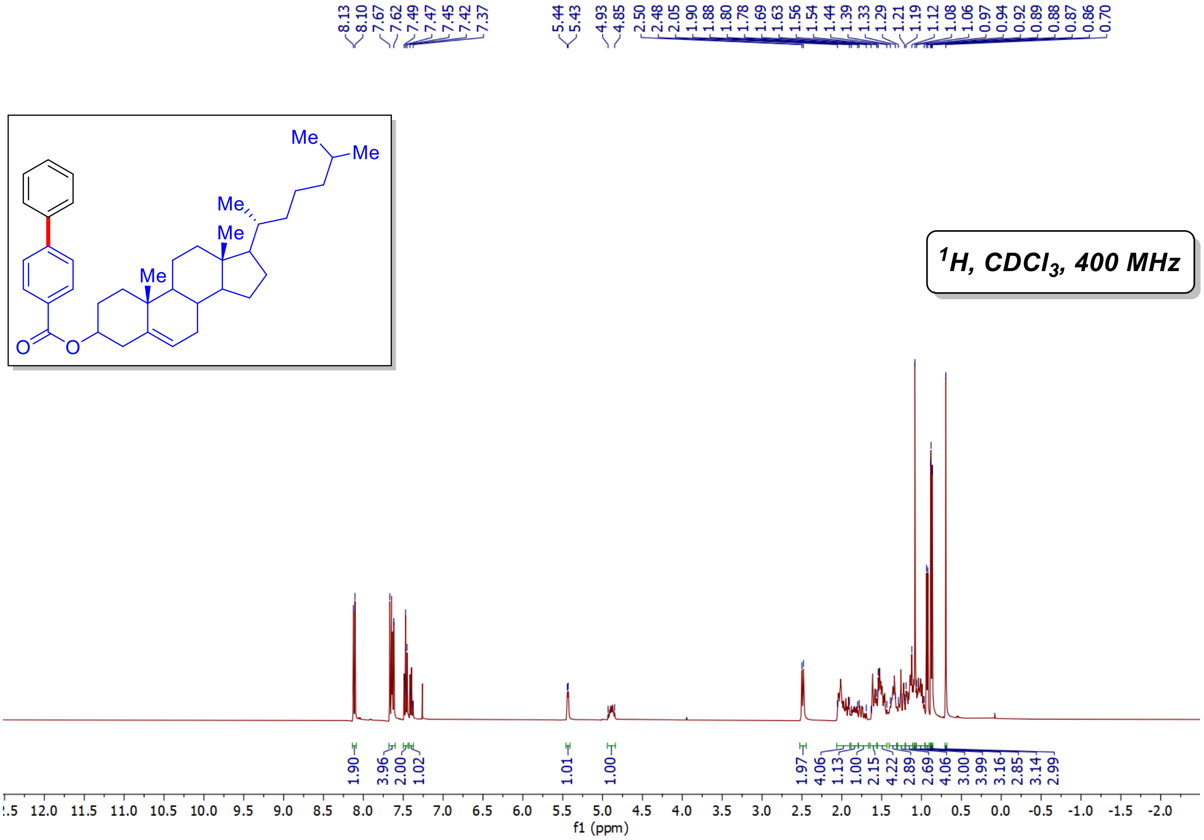


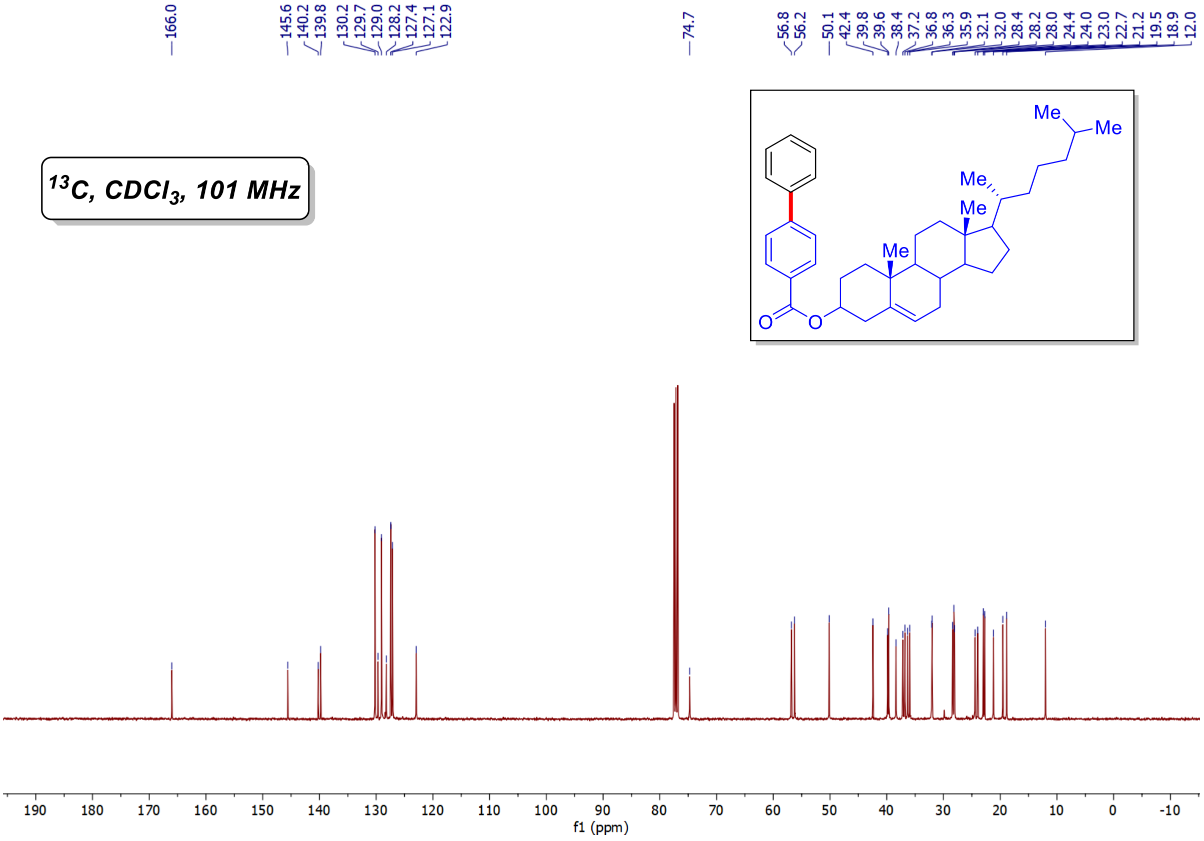
2-isopropyl-5-methylcyclohexyl [1,1'-biphenyl]-4-carboxylate (3ta)



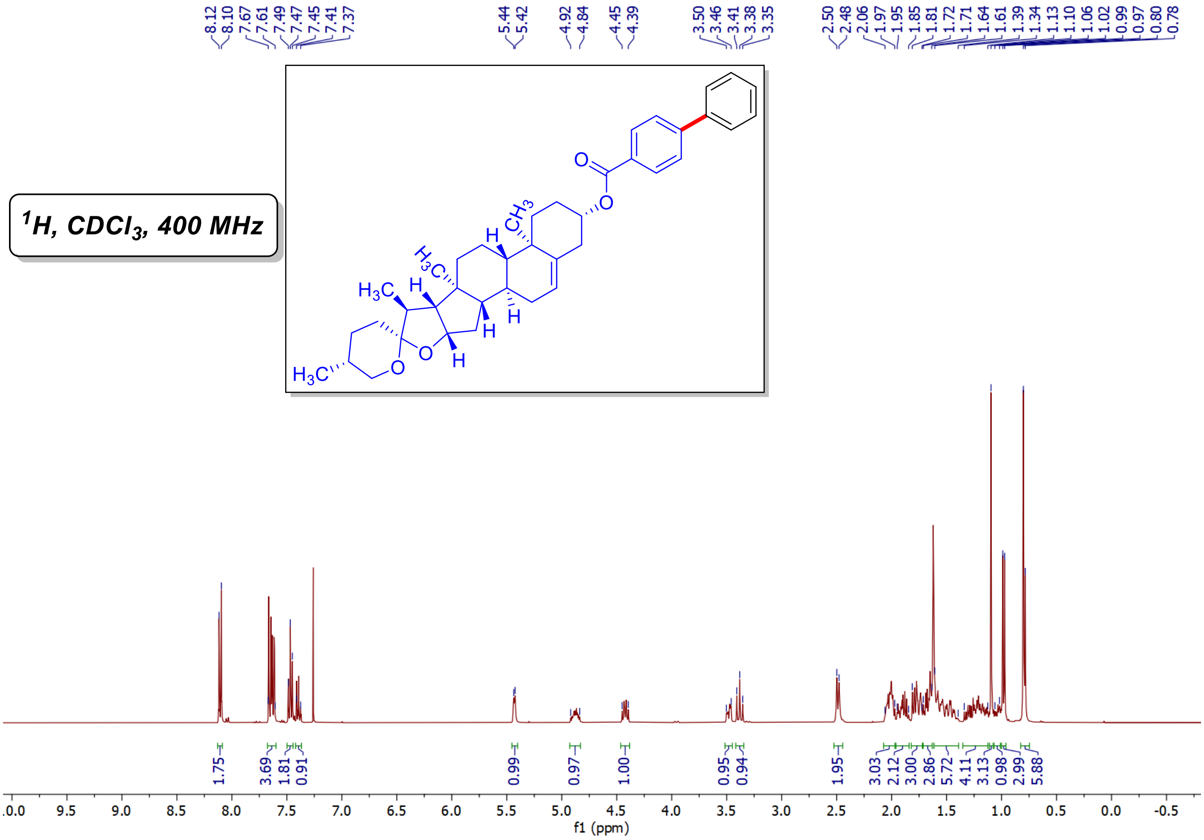


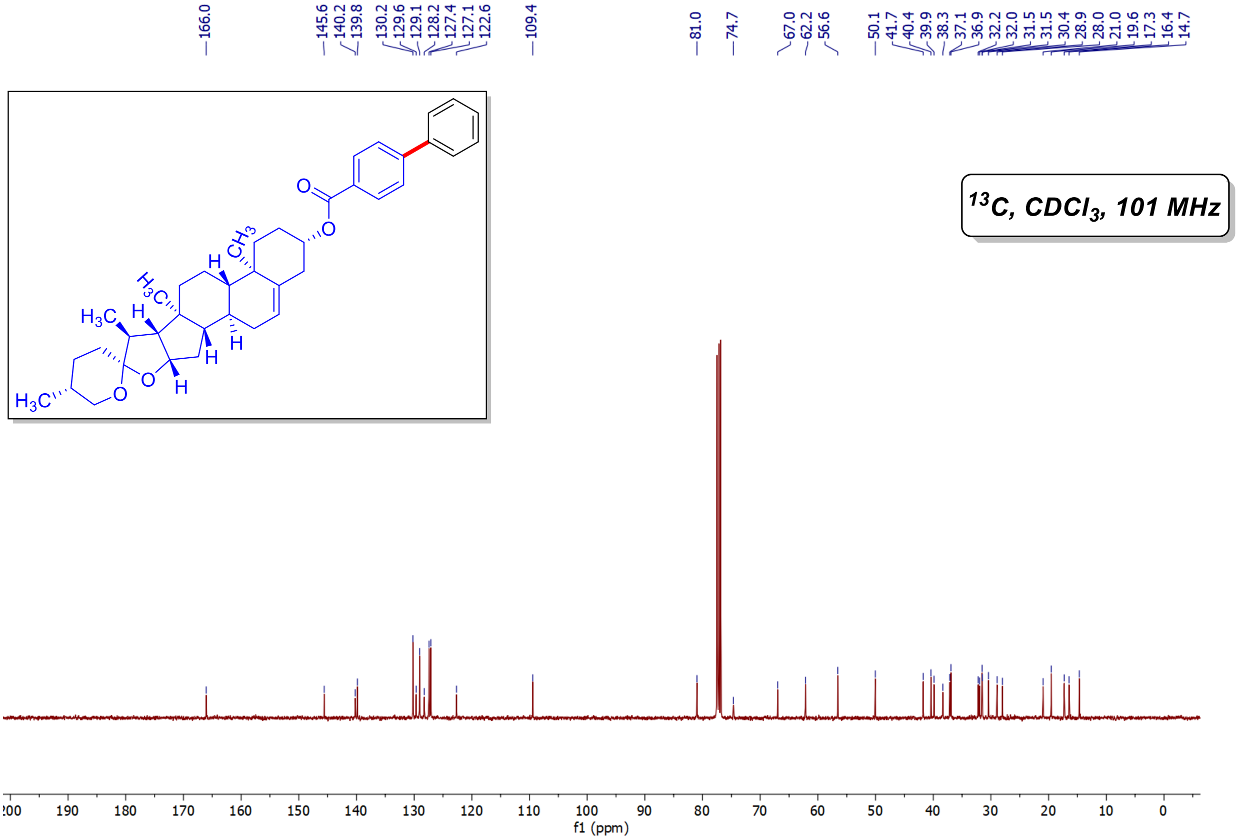
(10R,13R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl [1,1'-biphenyl]-4-carboxylate (3ua)



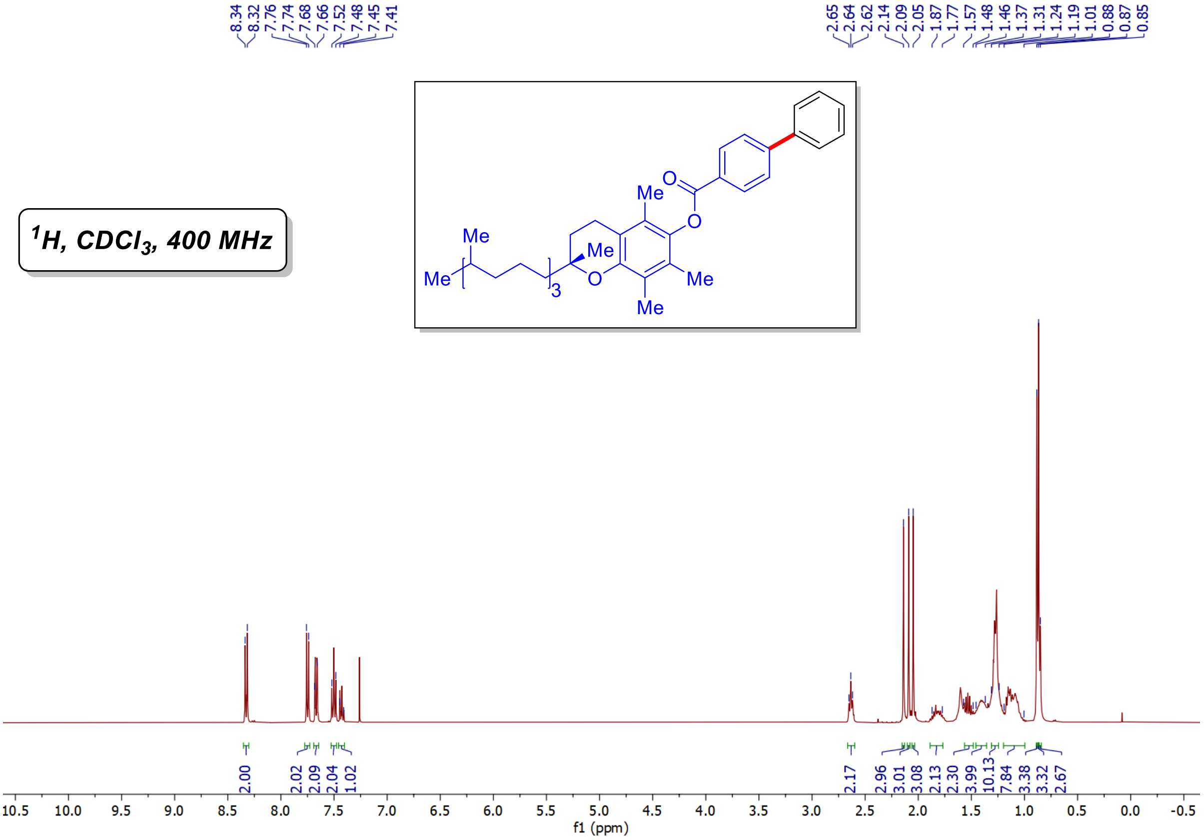


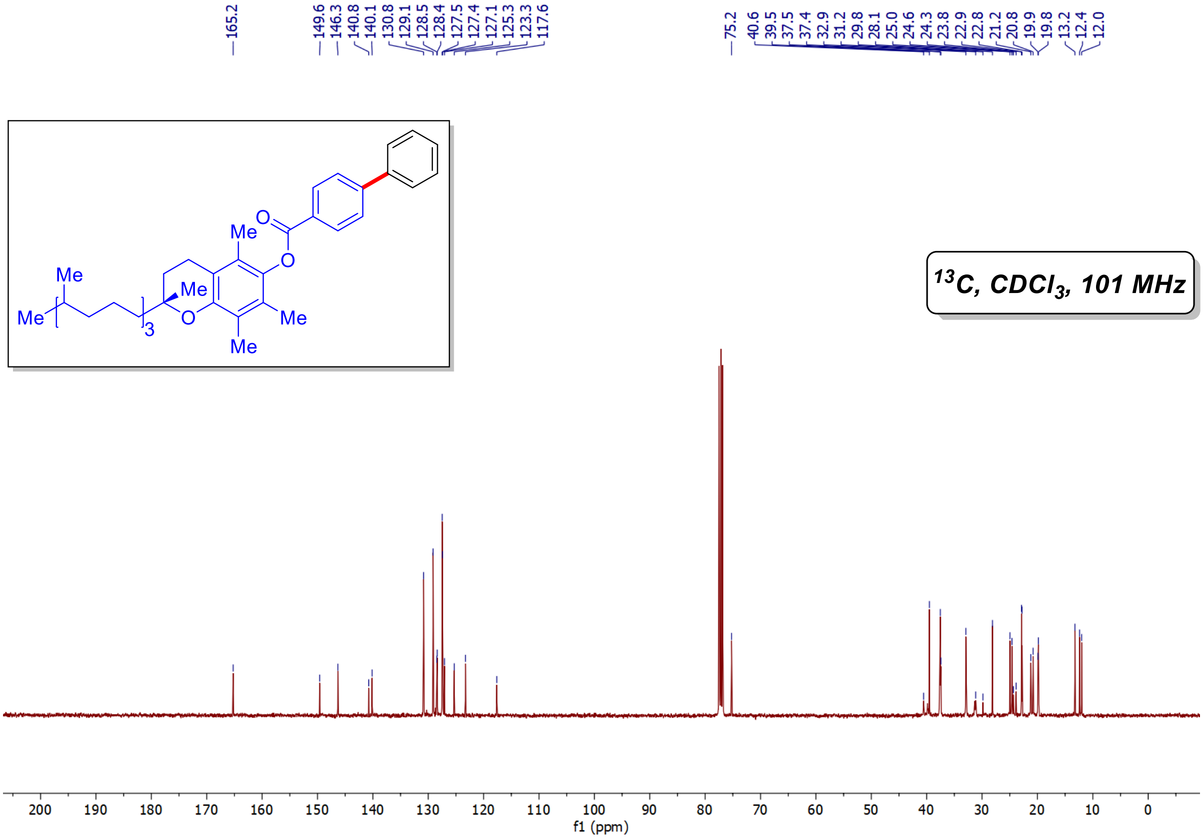
(1s,4R,4'S,6a'R,6b'S,8a'S,8b'R,9'S,11a'S,12a'S,12b'S)-4,6a',8a',9'-tetramethyl-1',3',4',5',6',6a',6b',7',8',8a',8b',9',11a',12',12a',12b'-hexadecahydrospiro[cyclohexane-1,10'-naphtho[2',1':4,5]indeno[2,1-b]furan]-4'-yl [1,1'-biphenyl]-4-carboxylate (3va)





(2R)-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl [1,1'-biphenyl]-4-carboxylate (Vitamin E) (3wa)





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