Supporting Information for

An Easily Prepared Palladium-Hydrogel Nanocomposite Catalyst for C-C Coupling Reactions

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Contents

General considerations

All starting materials and solvents were obtained from commercial sources and were used without further purification. Distilled water was used for Suzuki and Sonogashira cross coupling reactions. Melting points of the product were determined on a Digimelt melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker NMR spectrometer at 400 MHz and 100 MHz, respectively. Scanning election micrographs were recorded on a SERION instrument. Prior to the measurements the dried gels were coated with a thin gold layer. AFM imaging was carried out on a JPK NANO WIZARD II in non-contact mode. The X-ray powder diffraction (XRD) of samples XG-Pd and XG were carried out on a Bruker D8 Discover using CuK_{α} as radiation. Transmission electron microscopy (TEM) was done on a JEM 2100F instrument. Samples were placed on a carbon-coated copper grid with subsequent drying and staining with uranyl acetate, followed by air and then vacuum drying. Palladium content was measured on a Thermo Scientific X-Series-2 ICP-MS. For the recovered xerogel catalyst (XG-Pd 1), the SEM sample was prepared by the dispersion of the recovered catalyst (1 mg) in water (100 µl), and drop-casting 20 µl of the dispersion on a carbon tape. The TEM sample was prepared in a similar way by drop-casting of the dispersion on a carbon coated Cu grid.

Metal-cholate gel preparation

A) Calcium-cholate (Ca-Ch) gel

Ca-Ch gel was prepared by heating equal volumes of sodium cholate (60 mM) and $Ca(NO_3)_2$ (120 mM) separately at 60°C for 5 min followed by mixing. A translucent gel was formed. This was freeze dried to have a sample of "**XG**".

B) PdNPs-containing calcium-cholate (PdNP/Ca-Ch) gel

Aqueous K_2PdCl_4 (20 µl of 120 mM, 2.4 µmol) mixed with aqueous sodium cholate (280 µl of 60 mM, 16.8 µmol) and $Ca(NO_3)_2$ (300 µl of 120 mM, 36 µmol) were heated separately at 60°C for 5 min and then mixed in a 4 ml test tube (1 cm diameter) and sonicated for 1 min to get a translucent yellow gel, with the final concentration of K_2PdCl_4 of 4 mM. On the top of the gel aqueous sodium cyanoborohydride (1 ml of 10 mM, 10 µmol) was added. The entire gel become deep brown color after 10 h. Excess $NaBH_3CN$ solution was decanted from the top of the gel, and the resulting gel was freeze-dried to give a sample of "**XG-Pd**".

ICP-MS analysis

Sample preparation of ICP-MS analysis: a known weight of XG-Pd, XG-Pd 1 (1-2 mg), or the biphenyl product after the Suzuki reaction were digested with concentrated HNO_3 and 30% H_2O_2 (2 mL and 0.2 mL, respectively) at 130°C for 2 h. The solution was cooled to room temperature and diluted to 50 mL with double-distilled water to prepare the unknown sample solution. The concentration of Pd was found out from a standard calibration curve.

No	Experiment	Pd content (ppb)	Wt%
1	PdNP/Ca-Ch xerogel (XG-Pd) (1.48 mg)	120	0.40
2	Recovered palladium catalyst (XG-Pd 1) (1.11 mg)	406	1.83
3	Biphenyl product (Table 1, entry 6)	1.74	-
4	Biphenyl (Table 5, entry 1)	1.41	-
5	Biphenyl (Table 5, entry 2)	1.19	-
6	Biphenyl product extracted from the top of reaction mixture (Catalytic activity test of the mother liquor)	0.01	-
7	Water layer after reaction and removing all product and catalyst (Catalytic activity test of the mother liquor)	0.89	-

General procedure for the Suzuki reactions of aryl halides with boronic acids catalysed by XG-Pd

A typical procedure is given here for the reaction shown in entry 4 of Table 1. Iodobenzene (55 µl, 0.49 mmol), phenylboronic acid (91 mg, 0.74 mmol), K_2CO_3 (136 mg, 0.98 mmol), H_2O (1 mL) and XG-Pd (10 mg, 0.077 mol% of Pd with respect to iodobenzene) were introduced to a 10 mL r.b. flask. The mixture was stirred at 90°C, and the reaction was monitored by TLC using petroleum ether as the eluent. After the reaction was complete it was filtered (to remove the catalyst) and reaction mixture was washed several times with diethyl ether (total volume 20 mL). Combined organic layer was washed with water (5 mL). The ether extract was dried, and the crude product was purified by column chromatography using petroleum ether (ethyl acetate-petroleum ether for more polar products). The same procedure was followed for other iodo and bromo derivatives.

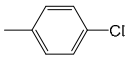
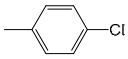
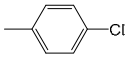
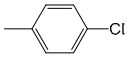
For biphenyl carboxylic acid derivatives (**2e**, **2p**)

After the reaction was complete, the mixture was filtered, and the aqueous layer was acidified with HCl (1 M) dropwise, when a white precipitate was formed. This was extracted with diethyl ether (20 mL) and purified as previously described (20% ethyl acetate-petroleum ether).

General procedure for the Suzuki reactions of chloro arene with phenylboronic acids catalysed by XG-Pd

Same reaction procedure was followed for Suzuki coupling reaction of chlorobenzene/4-clhlorotoluene (0.49 mmol), phenylboronic acid (91 mg, 0.74 mmol), K_2CO_3 (136 mg, 0.98 mmol) in H_2O (1 mL) and XG-Pd (10 mg, 0.077 mol% of Pd with respect to iodobenzene) and stirred at 90°C. The yield was <10%. To improve the yield tetrabutylamonium bromide [(TBAB) (0.49 mmol)] was added as an additive but no significant increase in yield was observed. Changing the base to KOH and Cs_2CO_3 also showed no difference (Table S-1).

Table S-1 Suzuki coupling reaction of chloro derivatives and phenyl boronic acid XG-Pd at 90°C in water.[a]

No	Substrate	Base	Additive	Time	% Yield[b]
1.		K_2CO_3	None	4 h	9
2.		K_2CO_3	TBAB	12 h	5
3.		K_2CO_3	TBAB	12 h	8
4.		KOH	TBAB	24 h	10[c]
5.		K_2CO_3	TBAB	24 h	6[c]
6.		Cs_2CO_3	TBAB	24 h	5[c]

[a] Reaction condition : Chloro arene (0.49 mmol), phenylboronic acid (0.74 mmol), K_2CO_3 (0.98 mmol), H_2O (1.0 mL), XG-Pd (10 mg, 0.077 mol% Pd), TBAB (0.49 mmol); [b] Isolated yield; [c] With XG-Pd (20 mg, 0.15 mol % of Pd).

General procedure for the Sonogashira reactions of aryl iodide with phenyl acetylene catalyzed by XG-Pd

In a typical experiment, XG-Pd (10 mg, 0.077 mol% Pd with respect to iodobenzene) was dispersed in water (600 µL). To this, iodobenzene (0.49 mmol), phenylacetylene (0.6 mmol) and pyrrolidine (2.45 mmol) were added. The reaction was carried out at 90°C with stirring, and the extent of reaction was monitored by TLC. After cooling to room temperature, the reaction mixture was extracted with diethyl ether. Purification by column chromatography (silica gel, ethyl acetate/petroleum ether) gave the desired products. We are unable to recover the catalyst, possible because of its degradation in presence of pyrrolidine.

Catalyst recyclability studies

(i) "One-pot" reuse of XG-Pd catalyst

The Suzuki reaction of iodobenzene with phenylboronic acid was carried out as described in the general procedure of Suzuki reactions [iodobenzene (0.49 mmol), phenylboronic acid (0.74 mmol), K_2CO_3 (0.98 mmol), H_2O (1.0 mL), XG-Pd (0.11 mol %) at 90°C]. After the reaction was complete (TLC), the mixture was cooled to room temperature. Diethyl ether (5 mL) was added and the mixture was stirred for 1 min. The organic layer was separated to remove the product. The extraction was repeated 5 times (5 mL each) until the organic layer contained no product (TLC). Product was purified by column chromatography. The water layer was put in vacuum to remove the residual diethyl ether. The water layer now comprised of supported catalyst and K_2CO_3. Fresh iodobenzene (0.49 mmol) and phenylboronic acid (0.74 mmol) were added and stirred at 90°C for a subsequent cycle. After the reaction was completed, the same procedure was repeated for reusing of the catalyst for the 3rd time, and so on.

(ii) Reuse of recovered XG-Pd (XG-Pd 1)

The coupling reaction of iodobenzene with phenylboronic acid was carried out as described in the general procedure of Suzuki coupling reactions. For recovering the catalyst the reaction mixture was centrifuged (the product was removed by extraction with diethyl ether) and the residue was washed with H_2O and Et_2O. Then the recovered solid catalyst was dried under high vacuum. It was used directly for second coupling experiment. The process was then repeated. After every cycle the catalyst quantity decreased.

SEM images of XG after different reaction conditions

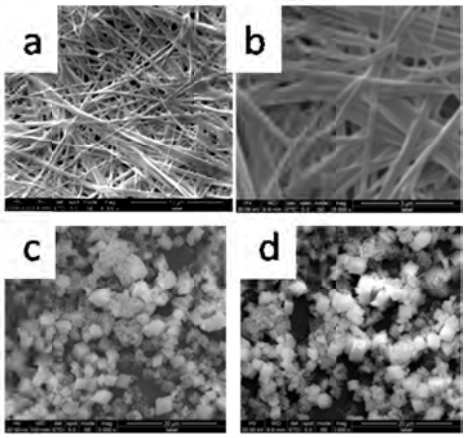


Figure S-1 (a, b) XG after only heating at 90°C only in water, (c, d) XG after Suzuki reaction conditions

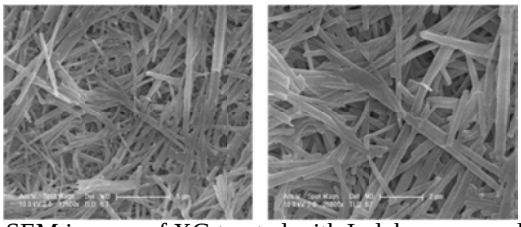


Figure S-2 SEM images of XG treated with Iodobenzene and H2O in 90°C for 4 h

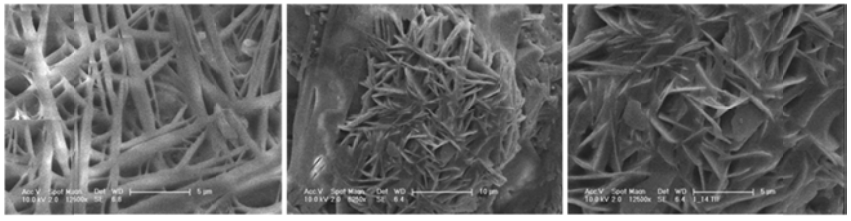


Figure S-3 SEM images of XG (Ca-Ch) treated with only K2CO3 and H2O in 90°C for 4 h

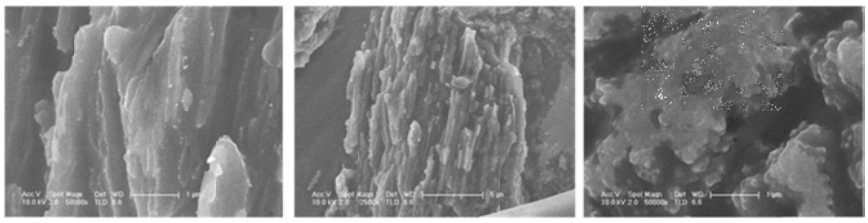


Figure S-4 SEM images of XG (Ca-Ch) treated with Phenylboronic acid and H_2O in 90°C for 4 h

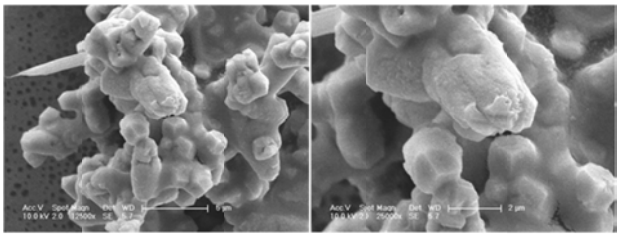


Figure S-5 SEM images of XG-Pd after treating with only pyrrolidine and water at 90°C for 4 h.

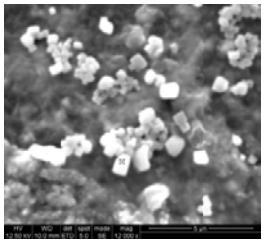


Figure S-6 Sample 5-SEM images of XG-Pd after treating with only triethylamine and water at 90°C for 4 h

The SEM images showed that no morphological changed was observed on heating only in water but the gel fibers changed to a cubic structure under the reaction condition. It was noticed that in addition to K_2CO_3, phenylboronic acid (which has coordination sites) could also change the morphology. XRD of recovered XG-Pd (XG-Pd 1) peaks matched with calcite structure of $CaCO_3$ (Reference code: 01-086-2339),[1] suggesting the conversion of Ca-Ch to $CaCO_3$. Organic bases such as pyrrolidine and triethylamine also destroyed the morphology of the xerogel.

pXRD data of recovered XG-Pd (XG-Pd 1) after 1st cycle of Suzuki reaction

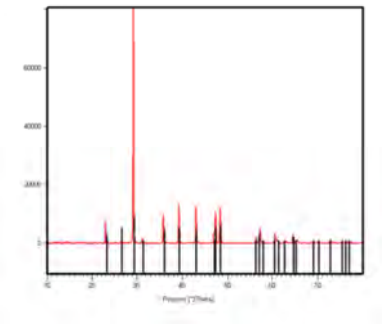


Figure S-2 pXRD of XG-Pd 1

TEM images of XG-Pd and elemental mapping

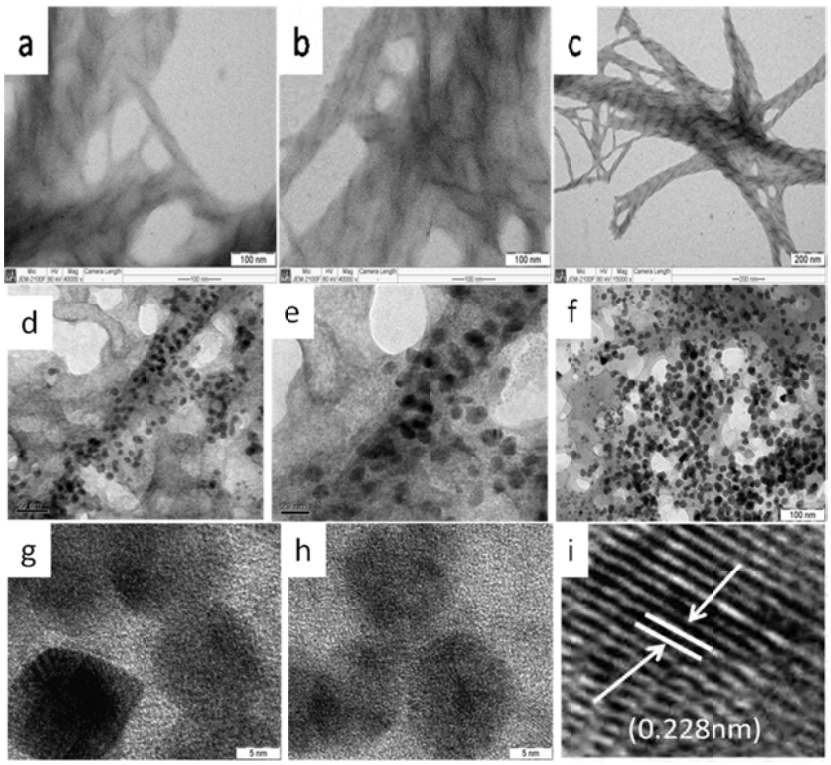


Figure S-3 (a-d) XG-Pd, (e, f) HRTEM images of XG-Pd

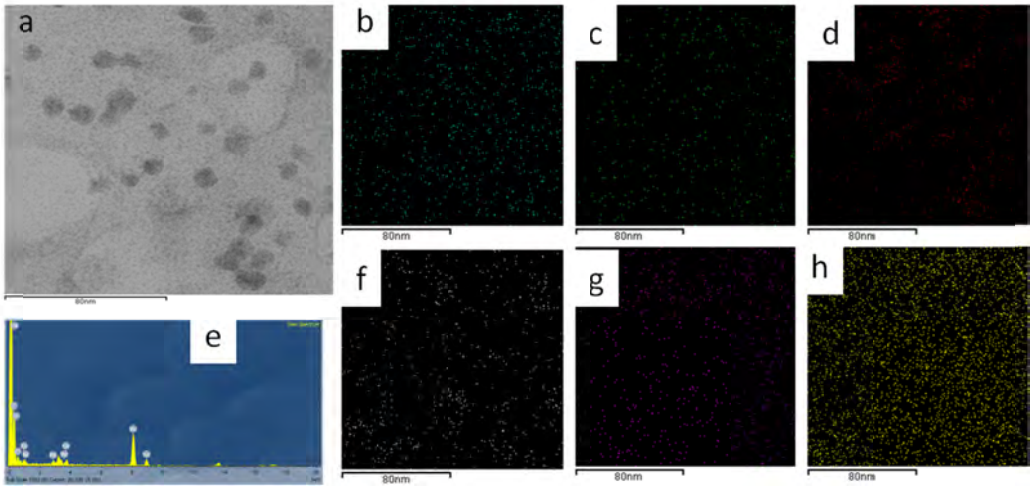


Fig S-4- a) TEM image, Elemental Mapping b) N, c) Na, d) Pd, f) Ca, g) O, h) C

Additional TEM images of XG-Pd were included here.

SEM images of XG-Pd and recovered XG-Pd and their elemental mapping

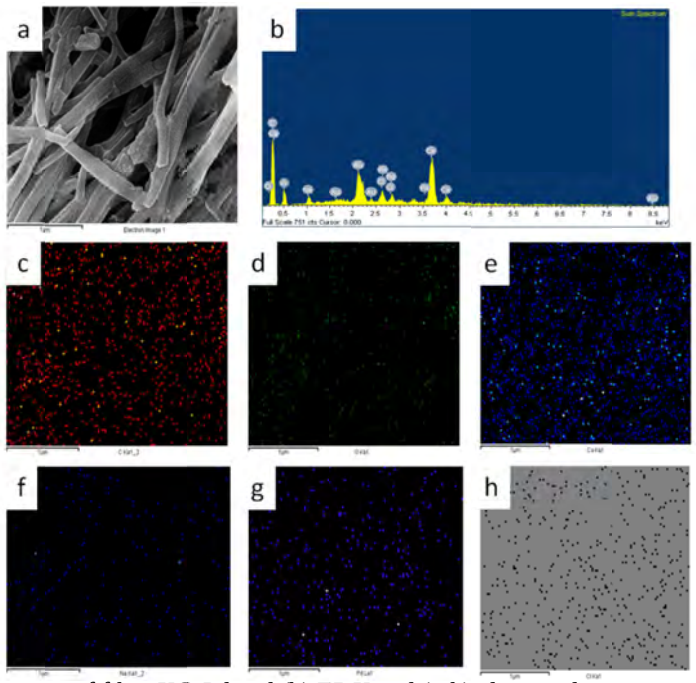


Fig S-5- (a) SEM images of fiber XG-Pd and (b) EDX and (c-h) elemental mapping

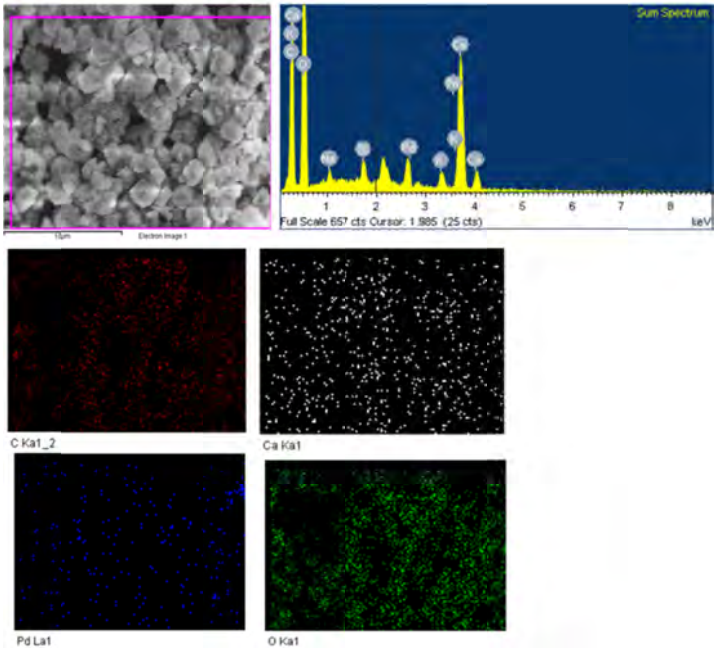


Fig S-6- (a) SEM images of recovered XG-Pd, EDX and elemental mapping

X-ray photoelectron Spectroscopy

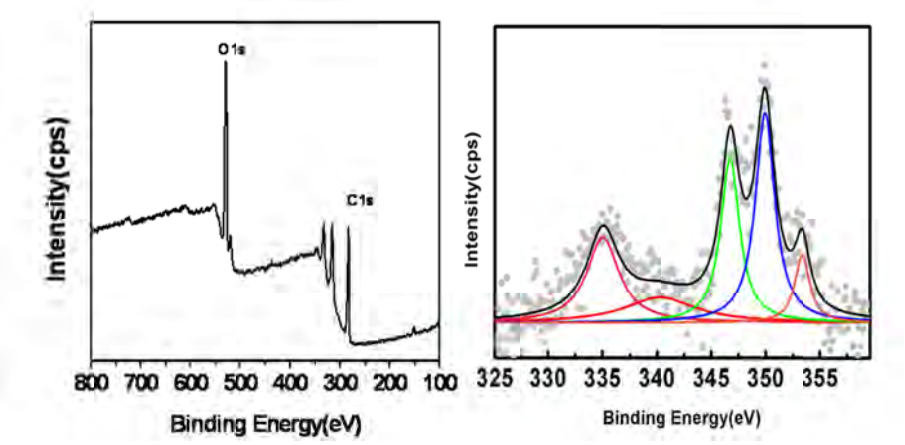


Fig S-7- (a) XPS survey spectrum and (b) high resolution spectrum of Pd 3d for XG-Pd

X-ray photoelectron spectroscopy (XPS) was employed to examine the surface chemical composition and electronic structure of the nanoparticles. The survey spectrum presented in Fig 10 confirms the existence of Ca, O, C and very weak peak for palladium. Because of interference of calcium, palladium peak did not observed properly. In the high resolution Pd 3d spectrum (b) characteristic peaks were observed with binding energies (BE) of 335.00 eV (Pd $3d_{5/2}$) and 340.30 eV (Pd $3d_{3/2}$), conventional to Pd (0) and no obvious peak of Pd^{2+} was observed, which indicates that most of the palladium was in the reduced form. Additional peaks with binding energies of 346.6 (Ca $2p_{3/2}$), 349.8 (Ca $2p_{1/2}$) and 353.1 eV were reported for Ca(II).

FTIR (the type of functional group of support)

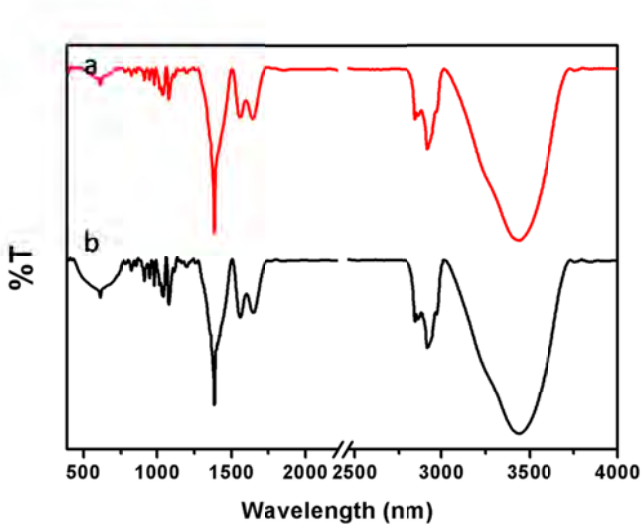
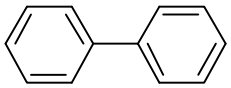


Fig S-7- FTIR of (a) XG-Pd and (b) XG

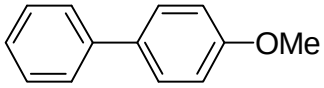
FTIR of XG and XG-Pd did not show much difference, which indicate that functional groups ($-COO^-$) did not support palladium nanoparticles directly, rather hydrophobic gel fibers was stabilizing nanoparticles.

Characterization data of the products



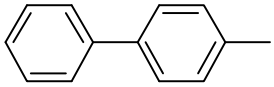
Biphenyl (2a)

White solid, mp 69.2°C (lit.[2] 70-71°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (4H, d, J = 8 Hz), 7.41 (4H, t, J = 8 Hz), 7.32 (2H, t, J = 7.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.31, 128.83, 127.33, 127.24.



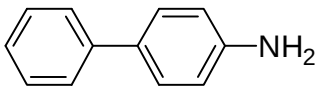
4-Methoxybiphenyl (2b)

White solid, mp: 87-89°C (lit.[2] 88-89°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (t, 3H, J= 8 Hz), 7.40 (t, 2H, J= 8 Hz), 7.29 (t, 1H, J= 8 Hz), 6.97 (d, 2H, J= 8 Hz), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.20, 140.88, 133.83, 128.79, 128.22, 126.80, 126.72, 114.26, 55.39.



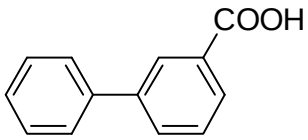
4-Methylbiphenyl (2c)

White solid, mp: 42-43°C (lit.[2] 43-44°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.56 (m, 2H), 7.48 (d, 2H, J= 8 Hz), 7.44-7.39 (m, 2H), 7.35-7.28 (m, 1H), 7.24-7.18 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.25, 138.45, 137.09, 129.56, 128.79, 127.25, 127.07, 127.05, 21.17.



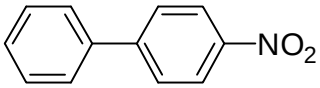
4-Aminobiphenyl (2d)

Brown solid, mp: 53°C (lit.[3] 51-52°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, 2H, J=8 Hz), 7.40-7.35 (m, 4H), 7.24 (t, 1H, J= 8 Hz), 6.69 (d, 2H, J= 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.94, 141.21, 131.54, 128.76, 128.05, 126.46, 126.33, 115.47.



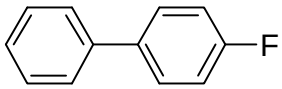
3-Phenylbenzoic acid (2e)

White solid, mp: 168-170°C (lit.[4] 163-166°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 8.11 (d, 1H, J= 8 Hz), 7.85 (d, 1H J= 8 Hz), 7.64 (d, 2H J= 8 Hz), 7.56 (t, 1H, J= 8 Hz), 7.48 (t, 2H, J= 8Hz), 7.39 (t, 1H, J= 8Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.35, 141.77, 140.06, 132.60, 129.97, 129.15, 129.12, 129.09, 129.01, 127.99, 127.32.



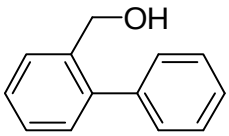
4-Nitrobiphenyl (2f)

Yellowish white solid, mp: 112-113°C (lit.[2] 113-114°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, 2H, J= 8 Hz), 7.72 (d, 2H, J= 8 Hz), 7.61 (d, 2H, J= 8 Hz), 7.51-7.42 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.65, 147.09, 138.77, 129.2, 128.97, 127.82, 127.41, 124.13.



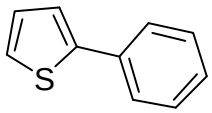
4-Fluorobiphenyl (2g)

White solid, mp: 72-74°C (lit.[5] 72-73°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.54 (m, 4H), 7.46-7.43 (m, 2H), 7.37-7.34 (m, 1H), 7.16-7.11 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.61 (d, J= 245 Hz), 140.41, 137.49 (d, J= 4 Hz), 128.96, 128.83 (d, J= 8 Hz), 127.40, 127.16, 115.74 (d, J= 21 Hz).



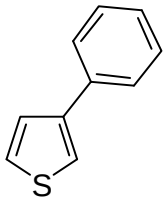
Biphenyl-2-yl-methanol (2h)

White solid, mp: 45-47°C (lit.[6] 50-52°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.48 (d, 1H, J= 4 Hz), 7.39-7.30 (m, 7H), 7.24 (d, 1H J= 8 Hz), 4.45 (s, 2H), 2.15 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.21, 140.63, 138.01, 130.01, 129.13, 128.33, 128.24, 127.68, 127.57, 127.22, 62.92.



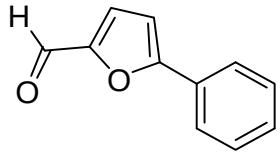
2-Phenylthiophene (2i)

Greenish Solid, mp: 35-36°C (lit.[7] 34-35°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, 2H, J= 8 Hz), 7.32 (t, 2H, J= 8 Hz), 7.26-7.19 (m, 3H), 7.03-7.01 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.42, 134.41, 128.91, 128.03, 127.47, 125.95, 124.81, 123.1.



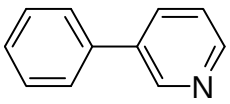
3-Phenylthiophene (2j)

Yellowish white solid, mp: 90°C (lit.[8] 90.5-91°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, J= 8 Hz), 7.40-7.31 (m, 5H), 7.25 (t, 1H, J= 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.42, 135.92, 128.90, 127.22, 126.53, 126.41, 126.29, 120.36.



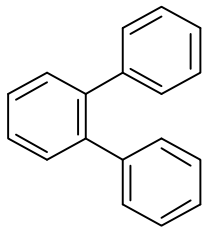
5-Phenylfurfural (2k)

Liquid, (lit.[9] mp: 33-35°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.62 (1H, s), 7.81-7.79 (m, 2H), 7.44-7.35 (m, 3H), 7.30-7.29 (d, 1H, J= 4H), 6.82 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.17, 159.35, 151.95, 129.64, 128.90, 125.23, 123.62, 107.68.



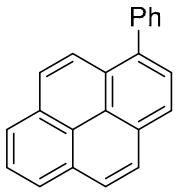
3-Phenyl-pyridine (2l)

Yellow liquid,[2] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85-8.84 (d, 1H, J= 4 Hz), 8.58-8.57 (d,1H, J= 4 Hz),7.84 (d,1H, J= 8 Hz), 7.56 (d, 2H, J= 8 Hz), 7.46 (t, 2H, J= 8 Hz), 7.38 (t, 1H, J= 8 Hz), 7.34-7.31 (dd, 1H, J= 8 Hz, 4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.41, 148.26, 137.74, 136.54, 134.26, 129.01, 128.03, 127.07, 123.47.



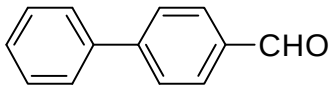
1, 2-Diphenylbenzene (2m)

Liquid,[10] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.38 (m, 4H), 7.21-7.17 (m, 6H), 7.14-7.12 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.60, 140.66, 130.67, 129.97, 127.93 127.55, 126.51.



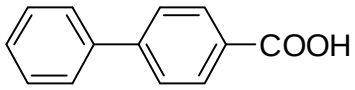
1-phenylpyrene (2n)

Solid, mp: 79-81°C (lit.[11] 82-83°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29-8.20 (m, 4H), 8.13 (s, 2H), 8.06 (t, 3H, J= 8Hz), 7.71 (d, 2H, J= 4 Hz), 7.65 (t, 2H, J= 8 Hz), 7.57 (t, 1H, J= 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.31, 137.79, 131.55, 131.04, 130.70, 130.65, 128.56, 128.46, 127.68, 127.55, 127.48, 127.32, 126.05, 125.34, 125.17, 125.04, 124.99, 124.89, 124.72.



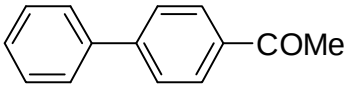
Biphenyl-4-carbaldehyde (2o)

White solid, mp: 59-60°C (lit.[3] 60-61°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 1H), 7.92 (d, 2H, J= 8 Hz), 7.72 (d, 2H, J= 8Hz), 7.61 (m, 2H), 7.48-7.38 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.90, 147.14, 139.68, 135.20, 130.26, 129.02, 128.48, 127.65, 127.36.



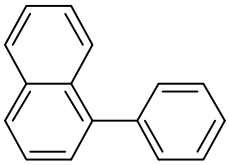
4-Phenylbenzoic acid (2p)

White solid, mp: 226-227°C (lit.[2] 228-230°C), ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.03 (d, 2H, J= 8Hz), 7.79 (d, 2H, J= 8Hz), 7.73-7.72 (d, 2H, J= 4 Hz), 7.51-7.48 (m, 2H), 7.43-7.30 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.24, 144.38, 139.09, 130.04, 129.67, 129.16, 128.36, 127.03, 126.88.



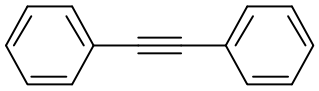
4-acetylbiphenyl (2q)

White solid, mp: 118-120°C (lit.[8] 122-123°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, 2H, J= 8 Hz), 7.67 (d, 2H, J= 8 Hz), 7.62 (d, 2H, J= 8 Hz), 7.46 (t, 2H, J= 8 Hz), 7.39 (t, 1H, J= 8 Hz), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.82, 145.81, 139.89, 135.88, 129.0, 128.96, 128.28, 127.31, 127.26, 26.71.



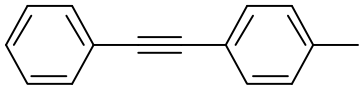
1-phenylnaphthalene (2r)

Liquid,[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.88 (m, 2H), 7.84 (d, 1H, J= 8Hz), 7.52-7.40 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.90, 140.40, 133.93, 131.76, 130.21, 128.39, 127.77, 127.37, 127.06, 126.16, 125.90, 125.51.



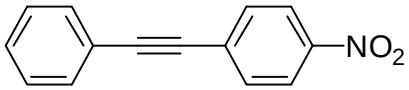
Diphenylacetylene (3a)

Yellow solid, mp: 60°C (lit.[12] 60°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, 4H, J= 8Hz), 7.31-7.29 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.65, 128.39, 128.30, 123.32, 89.47.



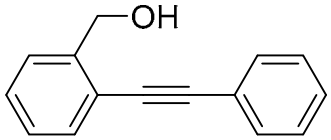
1-Methyl-4-(phenylethynyl)benzene (3b)

White solid, mp: 66-68°C (lit.[13] 68-70°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, 2H, J= 8 Hz), 7.43 (d, 2H, J= 8Hz), 7.33 (d, 3H, J= 8 Hz), 7.15 (d, 2H, J= 8 Hz), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.46, 131.62, 131.57, 129.19, 128.39, 128.15, 123.54, 120.25, 89.63, 88.79, 21.59.



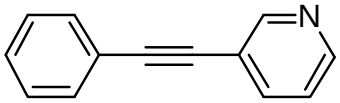
1-Nitro-4-(phenylethynyl)benzene (3c)

Light yellow solid, mp: 116-118°C (lit.[12] 117-118°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, 2H, J= 8 Hz), 7.66 (d, 2H, J= 8 Hz), 7.56 (t, 2H, J= 4 Hz), 7.39-7.38 (d, 3H, J= 4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.04, 132.34, 131.92, 130.33, 129.36, 128.61, 123.71, 122.17, 94.78, 87.62.



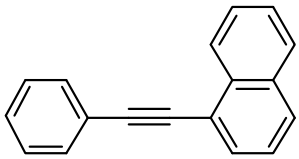
(2-(Phenylethynyl)phenyl)methanol (3d)

Solid, mp: 71-72°C (lit.[14] 71-72°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.51 (m, 3H), 7.47-7.46 (d, 1H, J= 4 Hz), 7.35-7.32 (m, 4H), 7.29-7.24 (m, 1H), 4.90 (s, 2H), 2.28 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.60, 132.21, 131.60, 128.80, 128.61, 128.49, 127.51, 127.27, 122.97, 121.31, 94.25, 86.79, 64.01.



3-(Phenylethynyl)pyridine (3e)

Brown solid, mp: 49-50°C (lit.[12] 49-50°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77-8.76 (m, 1H), 8.54-8.53 (dd, 1H, J= 4 Hz), 7.81-7.78 (dt, 1H, J= 8 Hz, 4 Hz), 7.56- 7.52 (m, 2H), 7.38-7.34 (m, 3H), 7.28-7.24 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.25, 148.56, 138.43, 131.70, 128.82, 128.46, 123.04, 122.52, 120.47, 92.66, 85.96.



1-(Phenylethynyl)naphthalene (3f)

Liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, 1H, J= 8 Hz), 7.81 (t, 2H, J= 8 Hz), 7.75 (d, 1H, J= 8 Hz), 7.65-7.63 (m, 2H), 7.59- 7.56 (m, 1H), 7.50 (t, 1H, J= 8 Hz), 7.43-7.31 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.34, 133.28, 131.73, 130.43, 128.83, 128.49, 128.45, 128.38, 126.84, 126.49, 126.28, 125.34, 123.47, 120.96, 94.41, 87.63.

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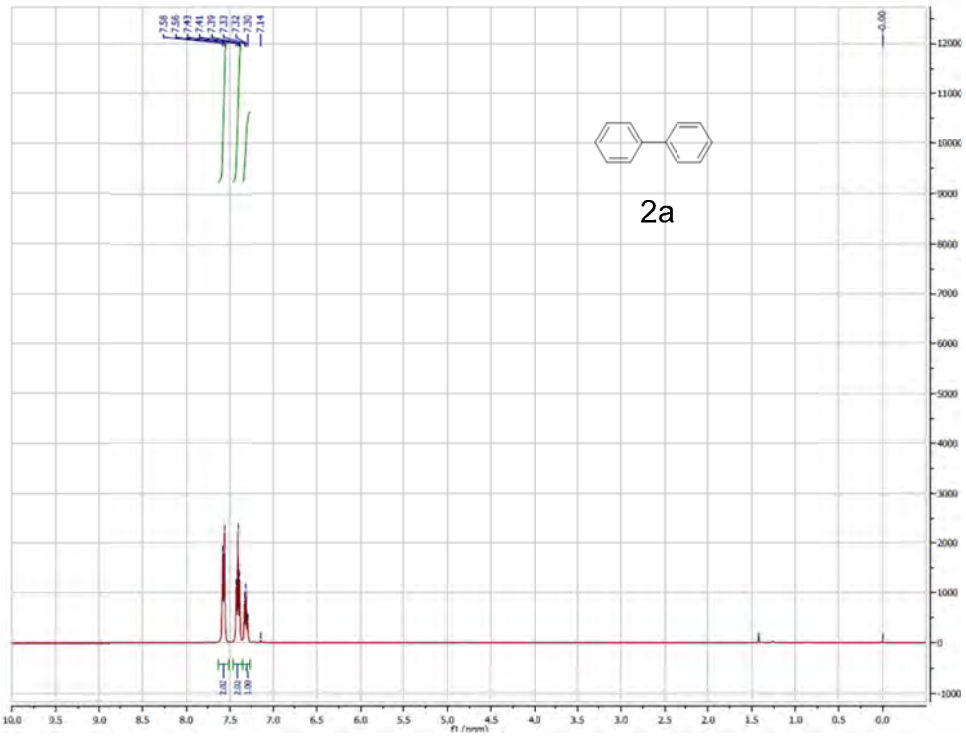
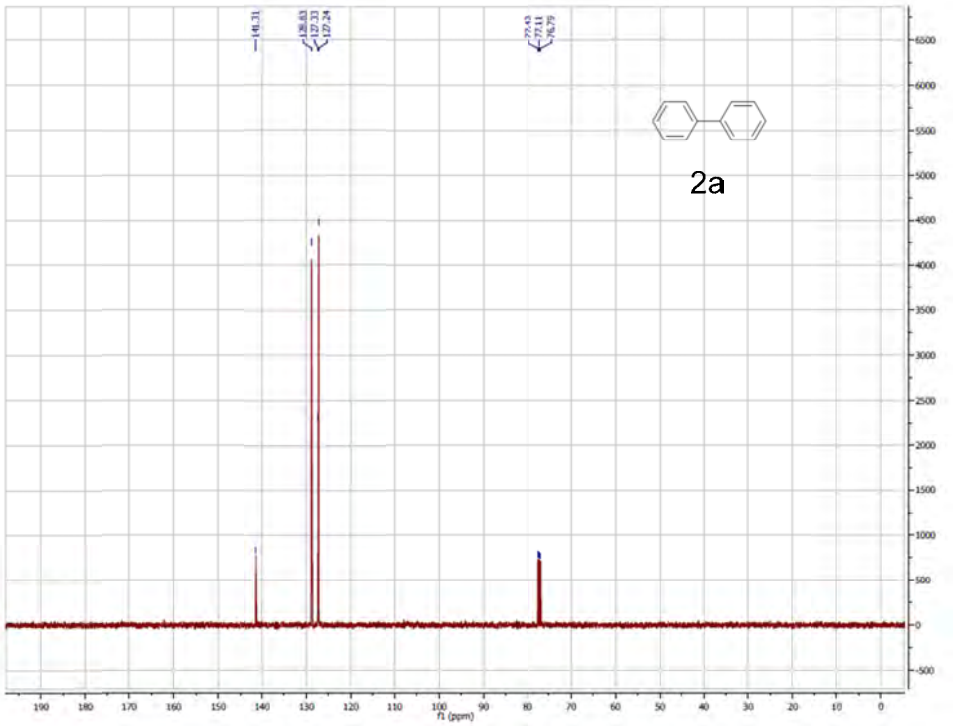
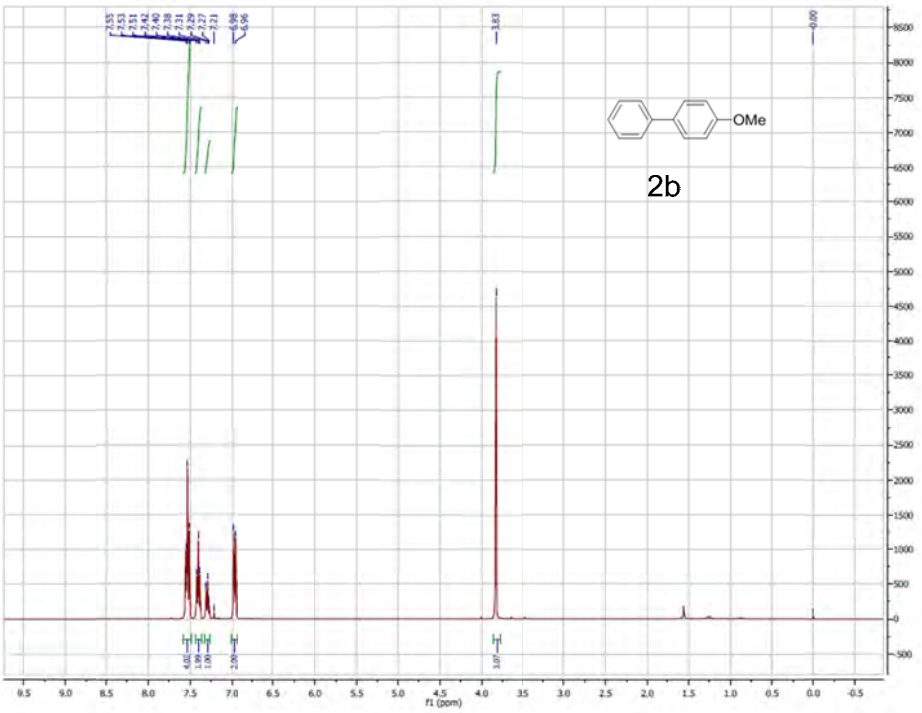
Copies of ^{1}H, ^{13}C NMR spectra



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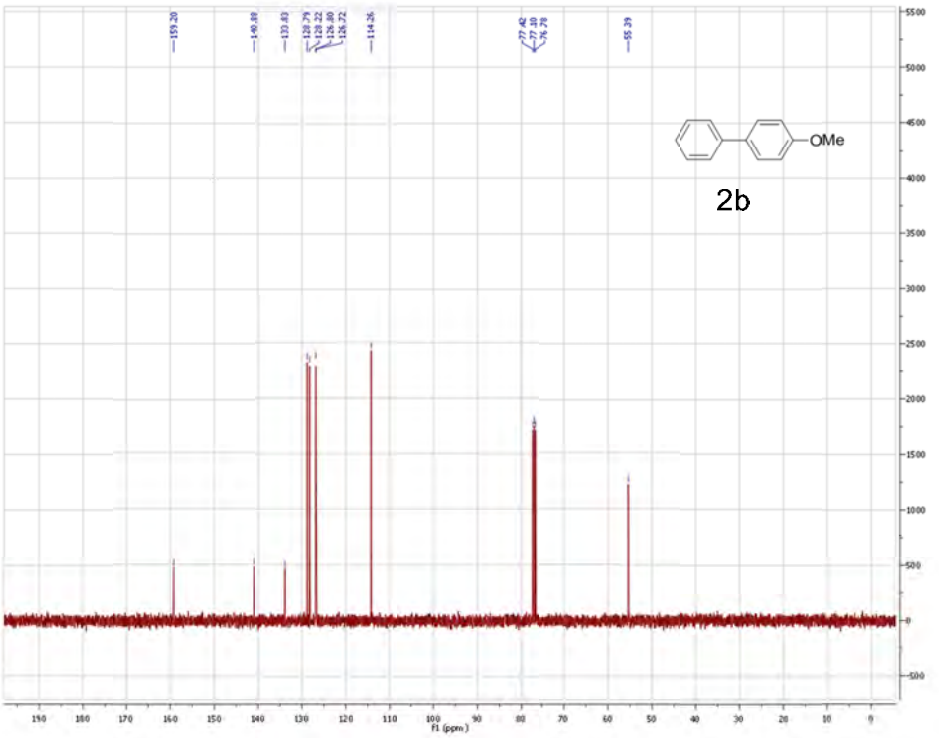
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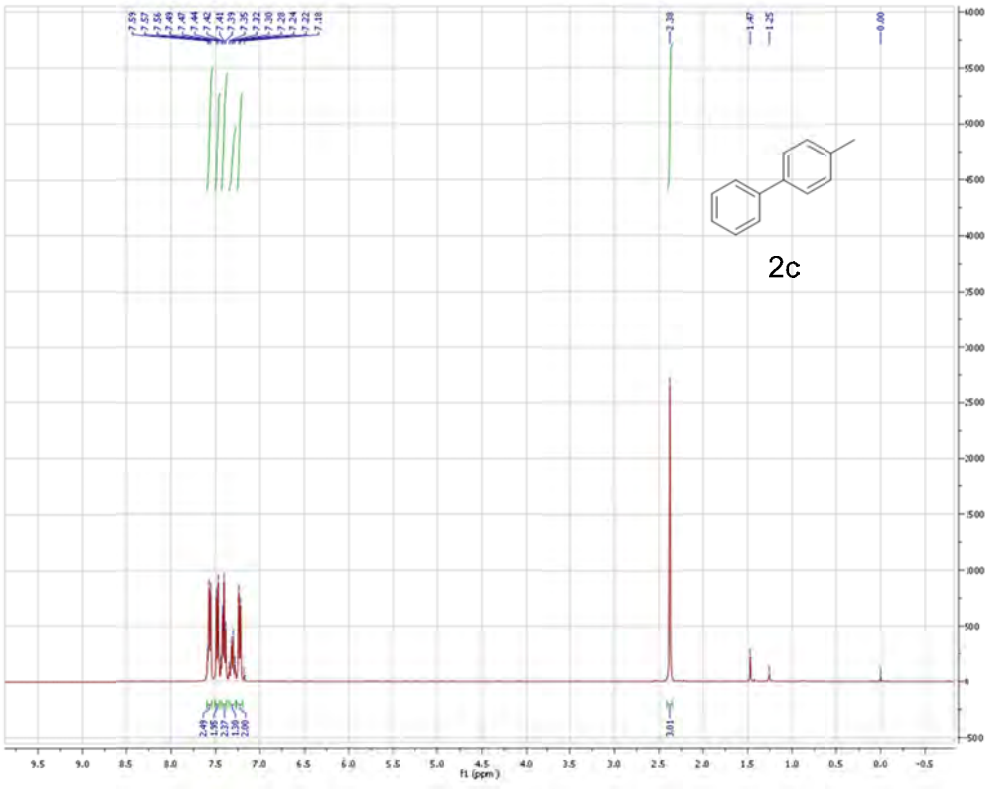
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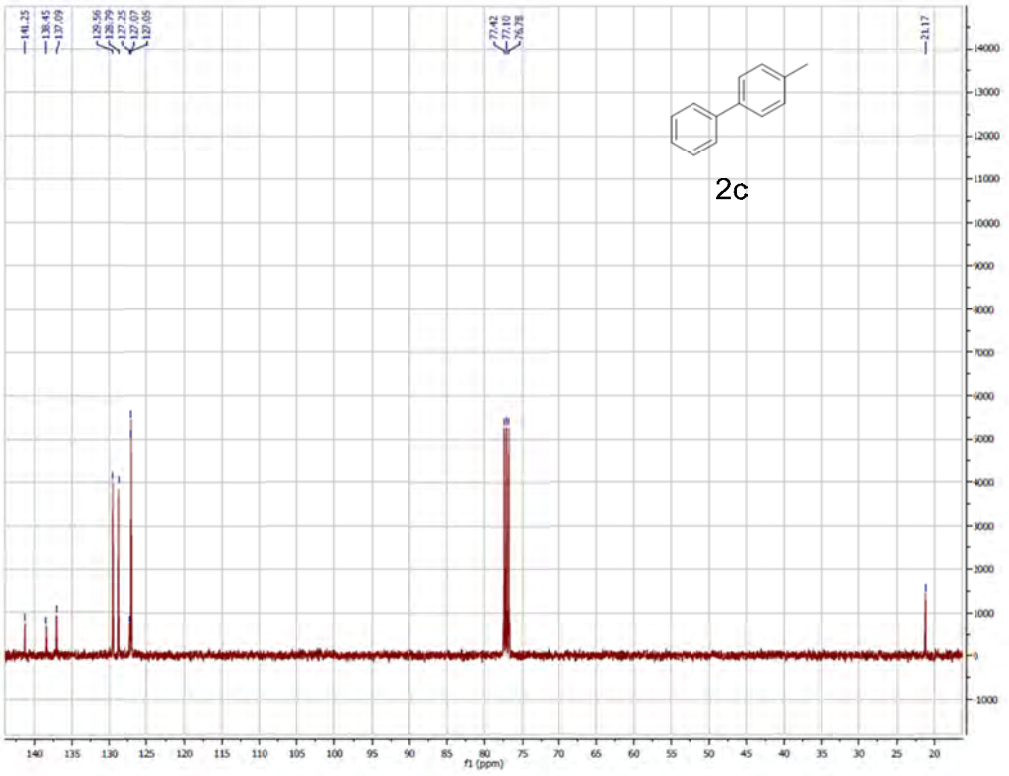
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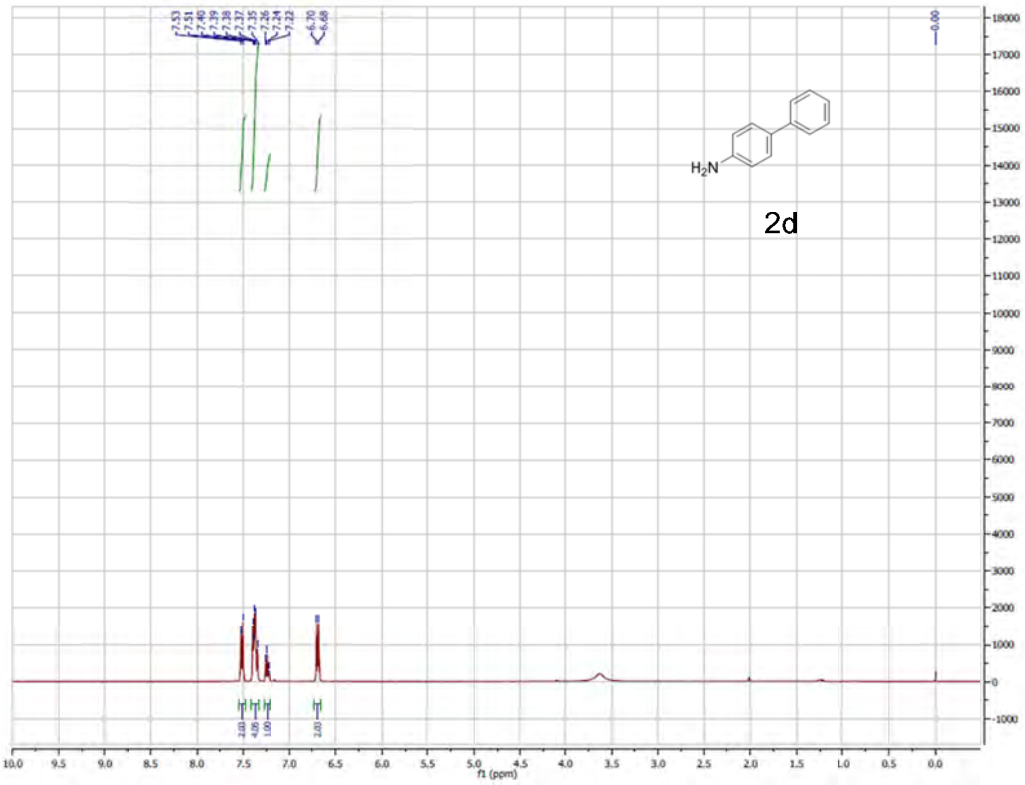
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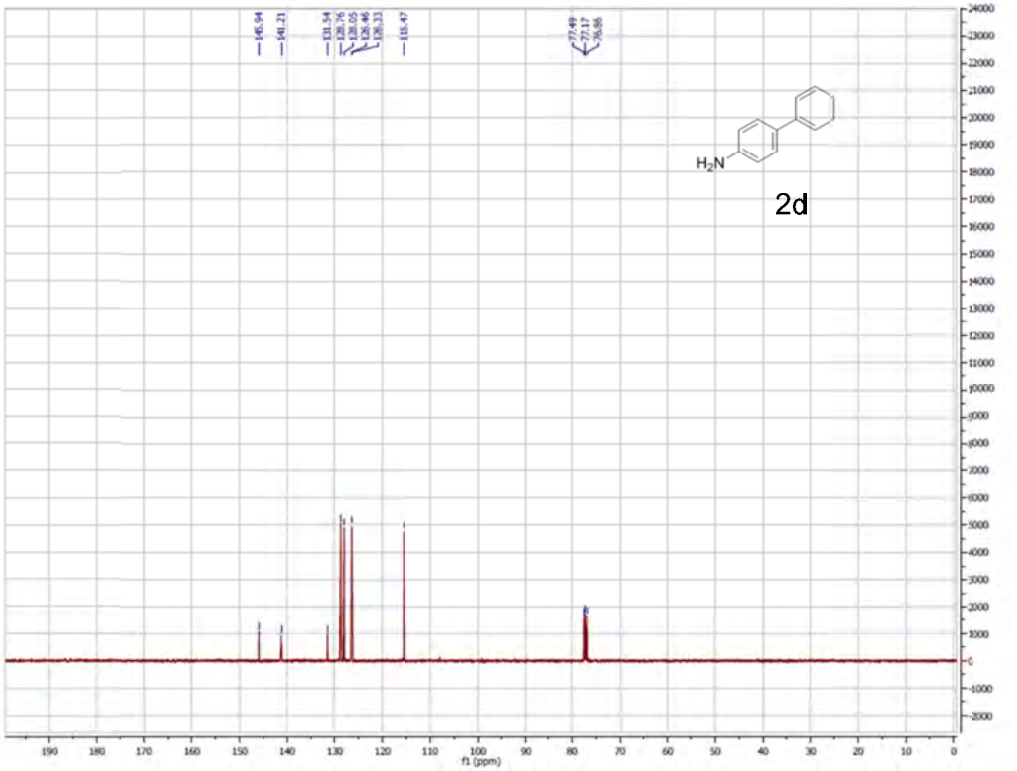
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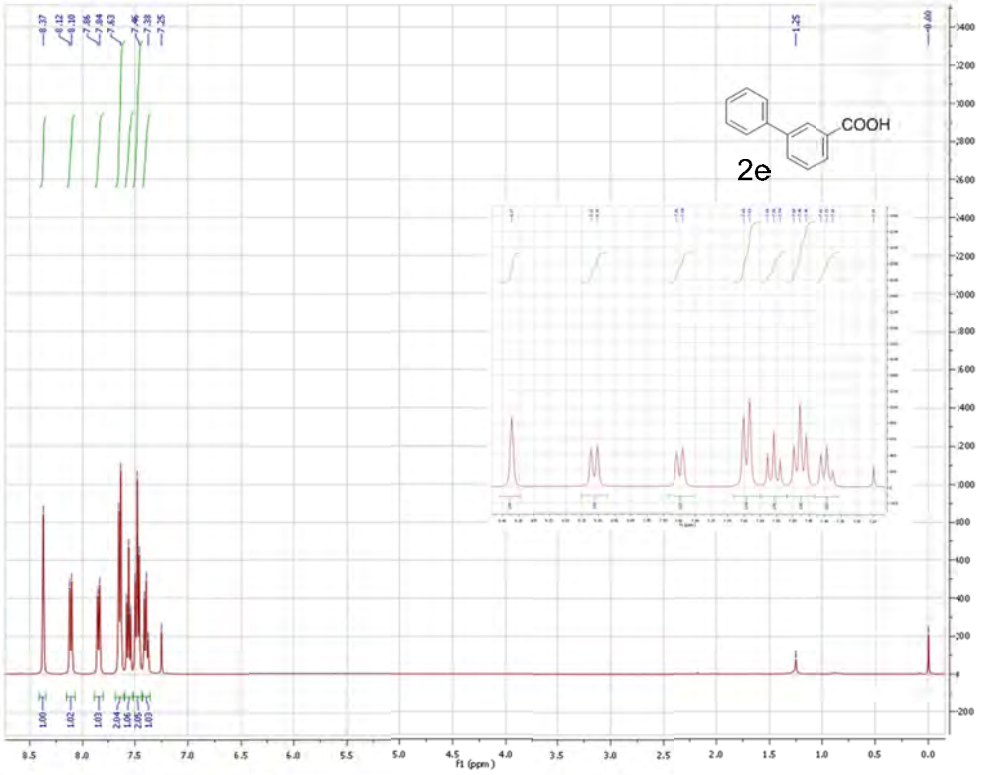
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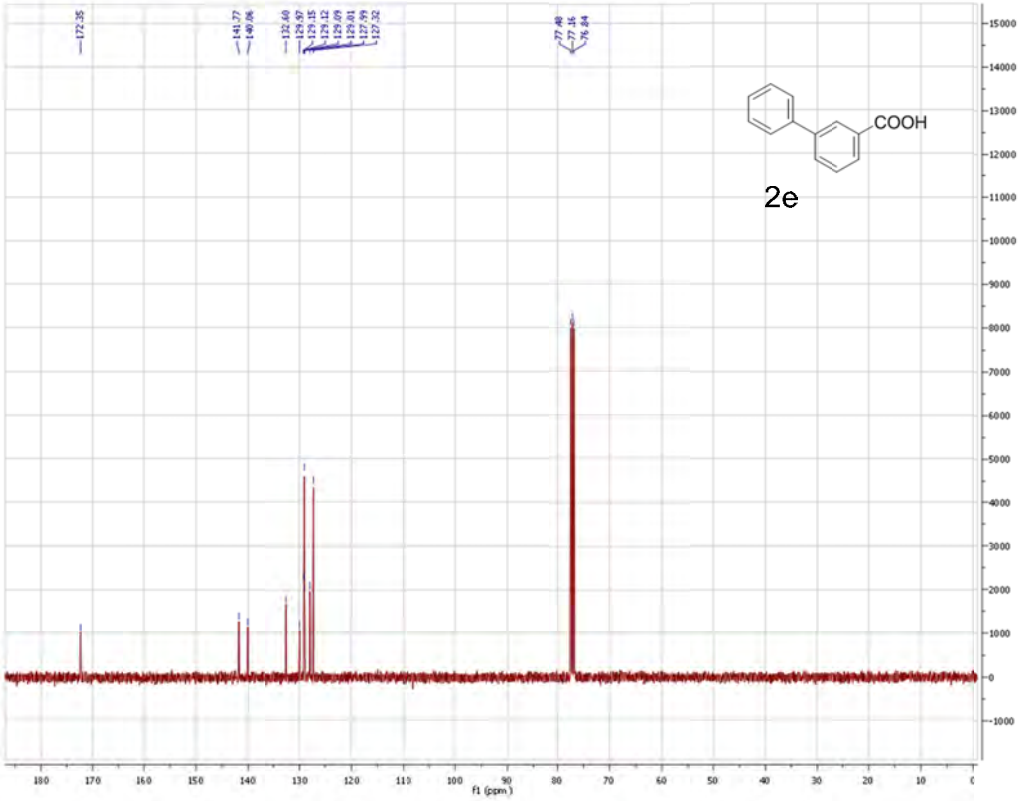
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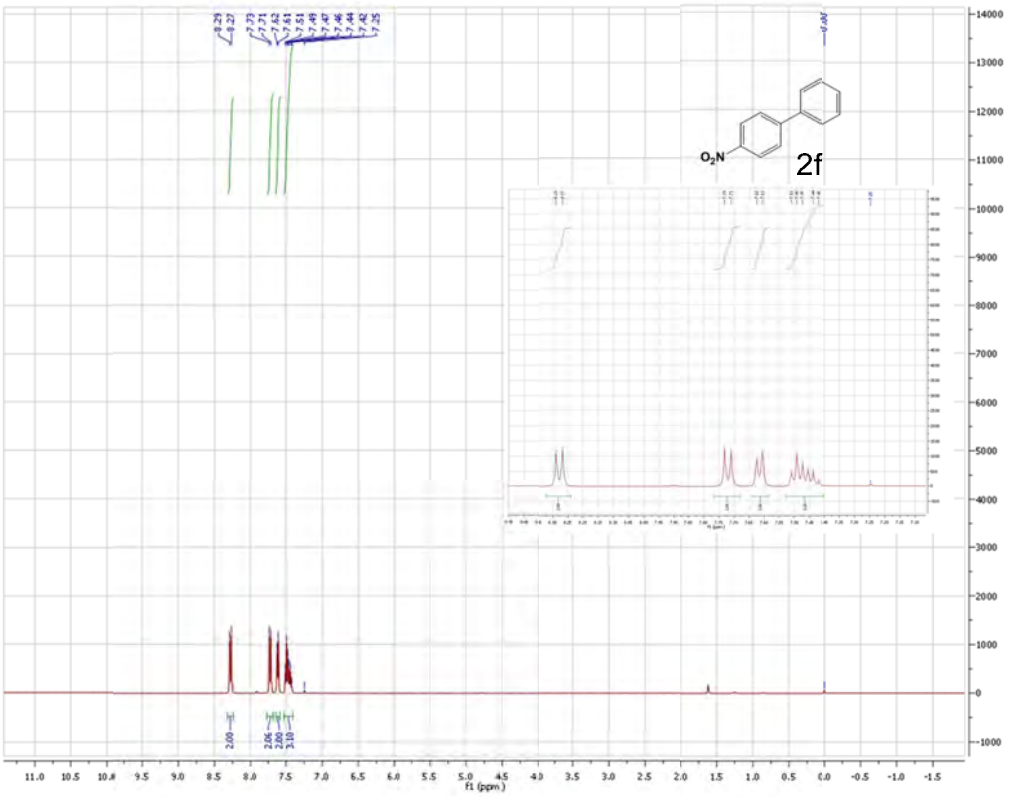
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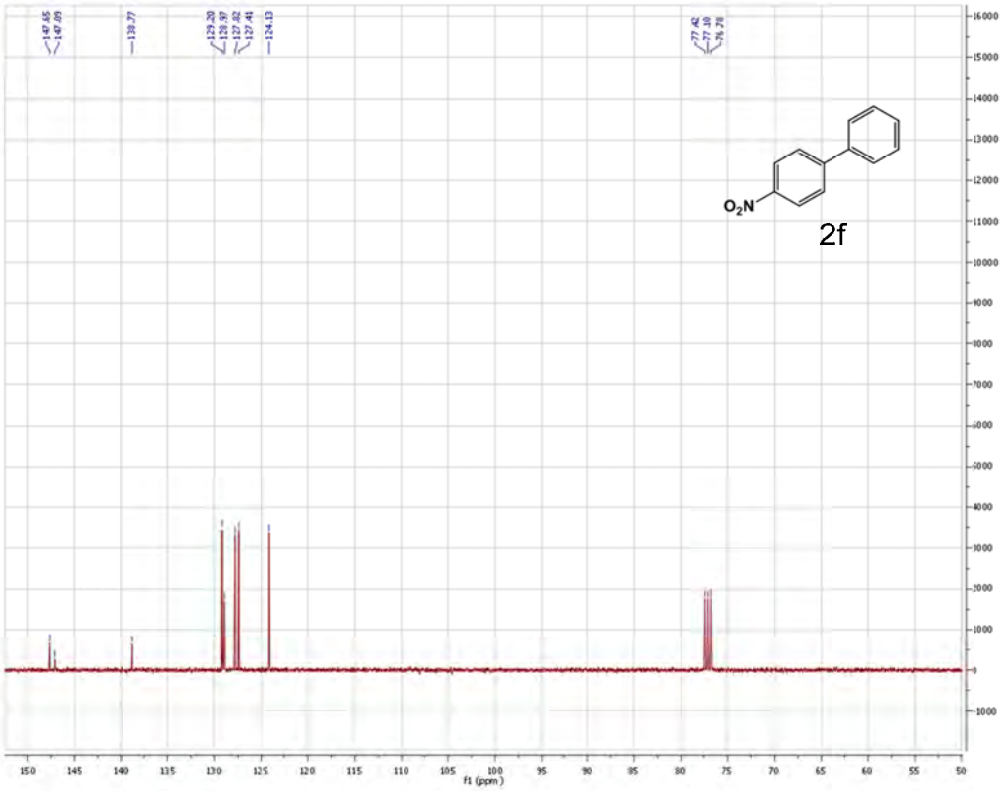
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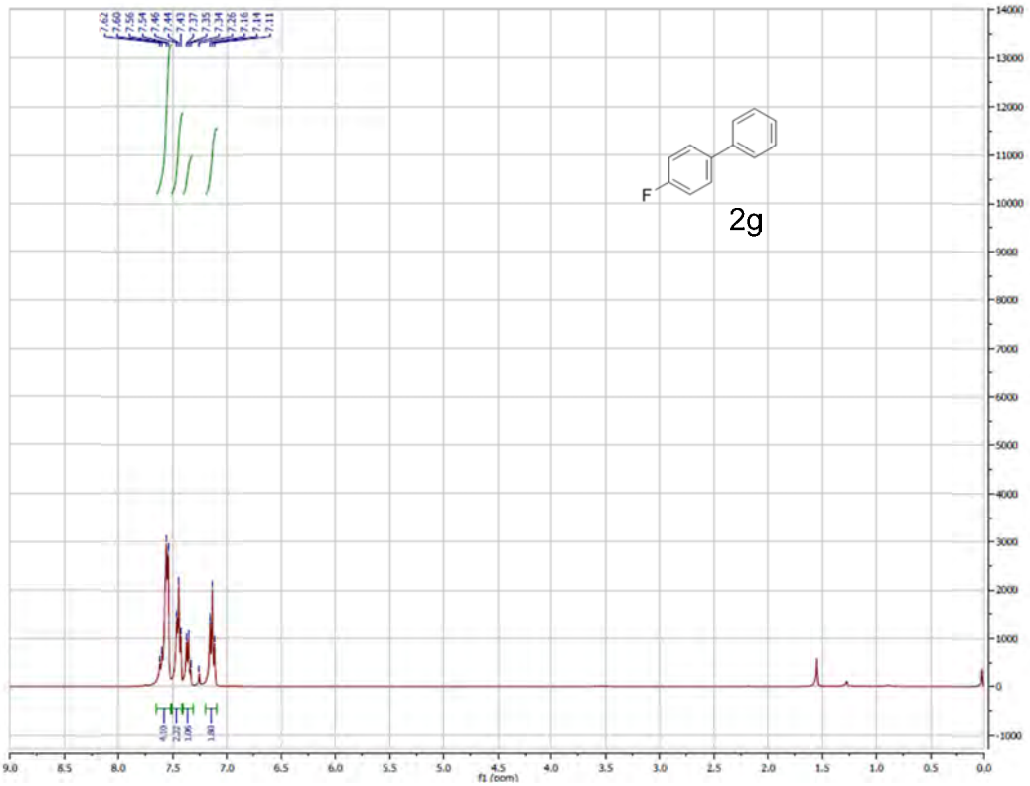
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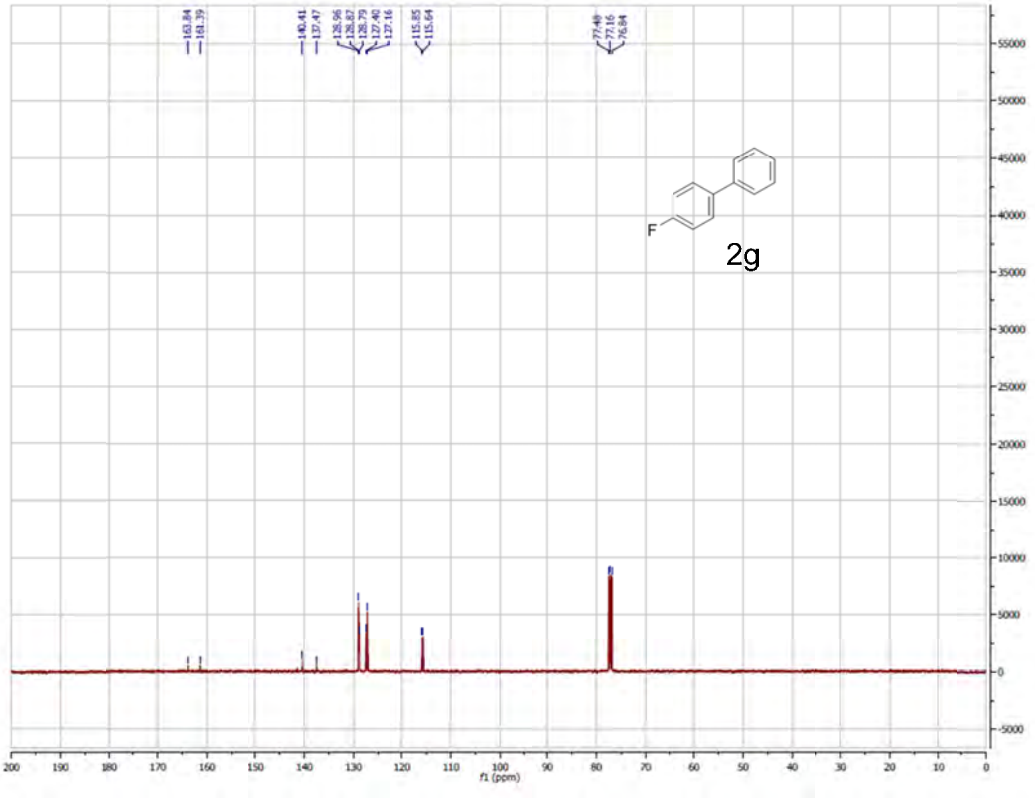
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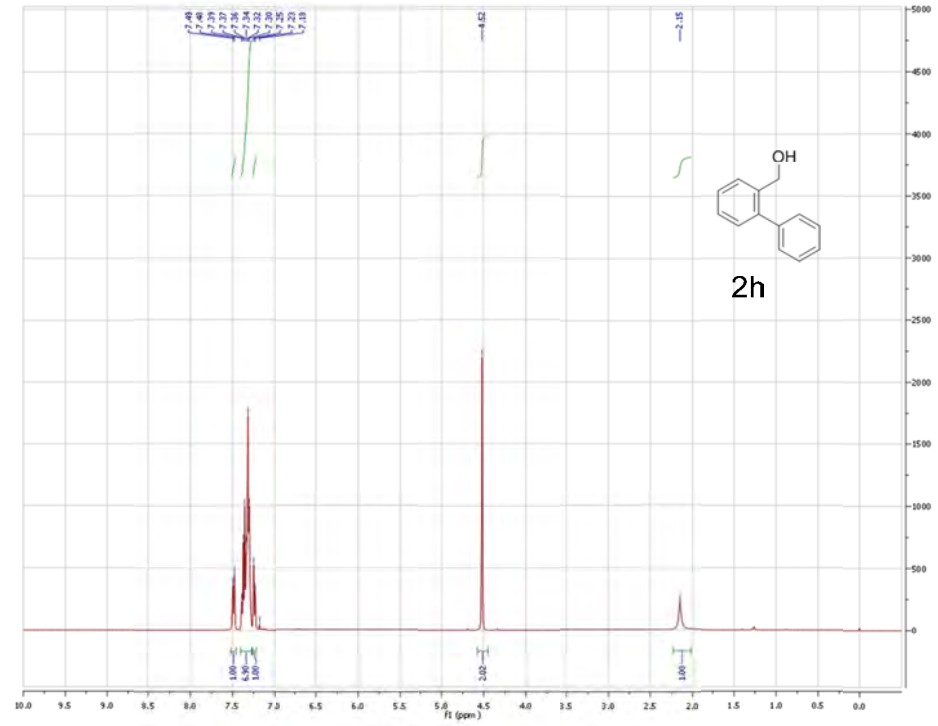
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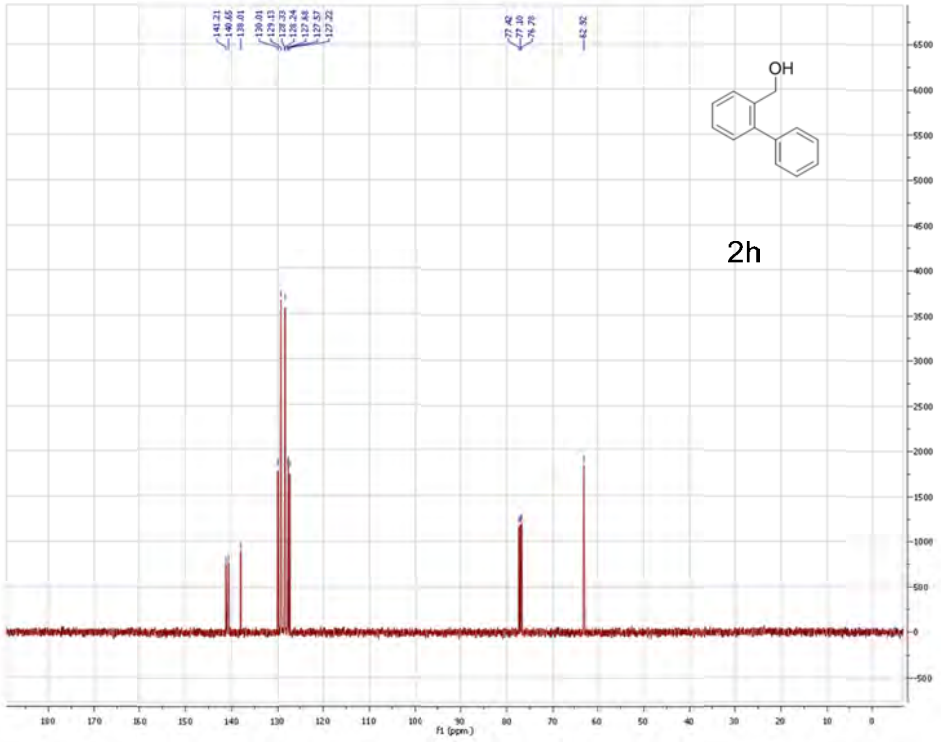
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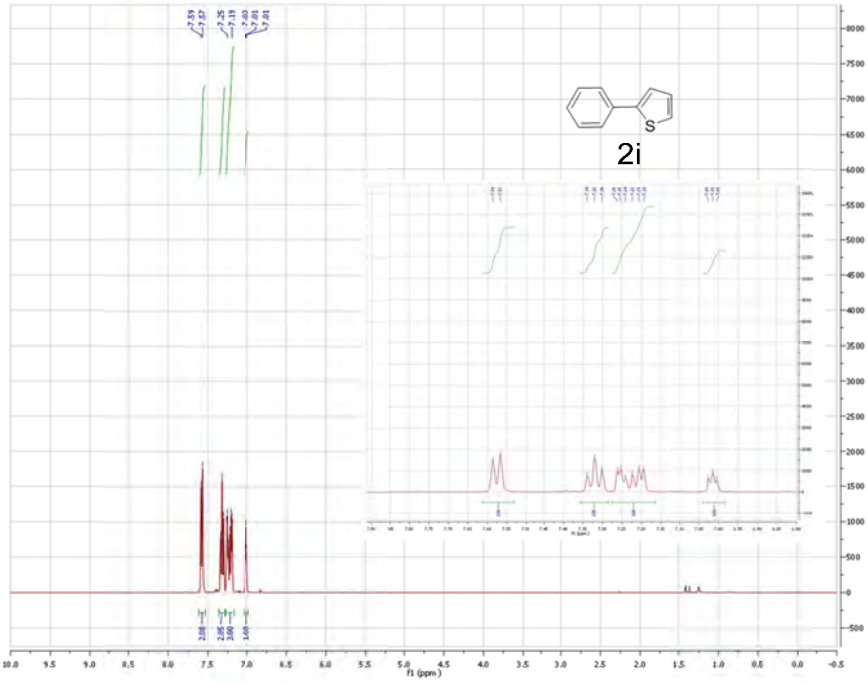
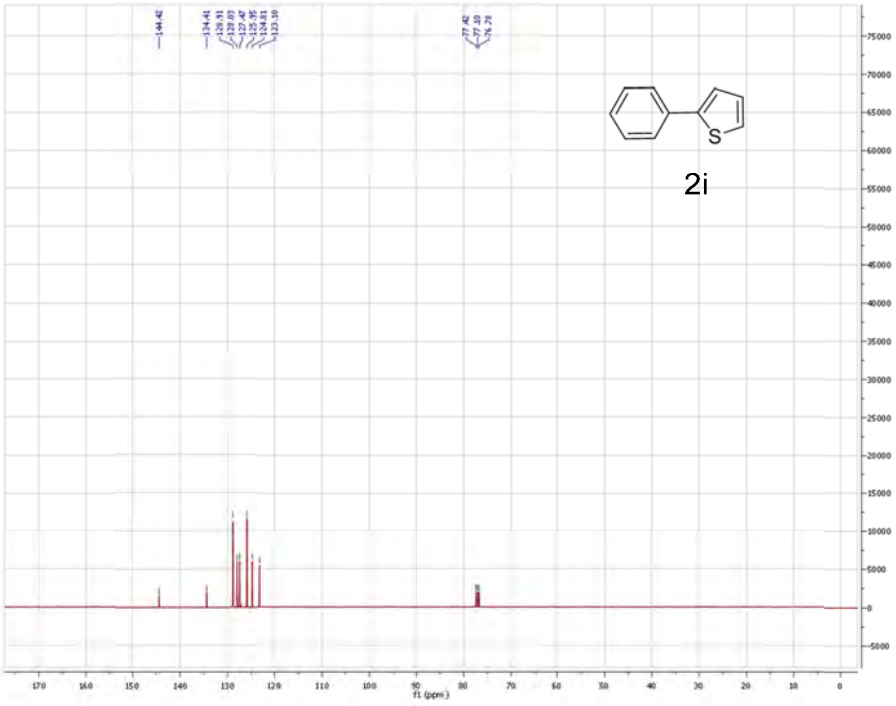
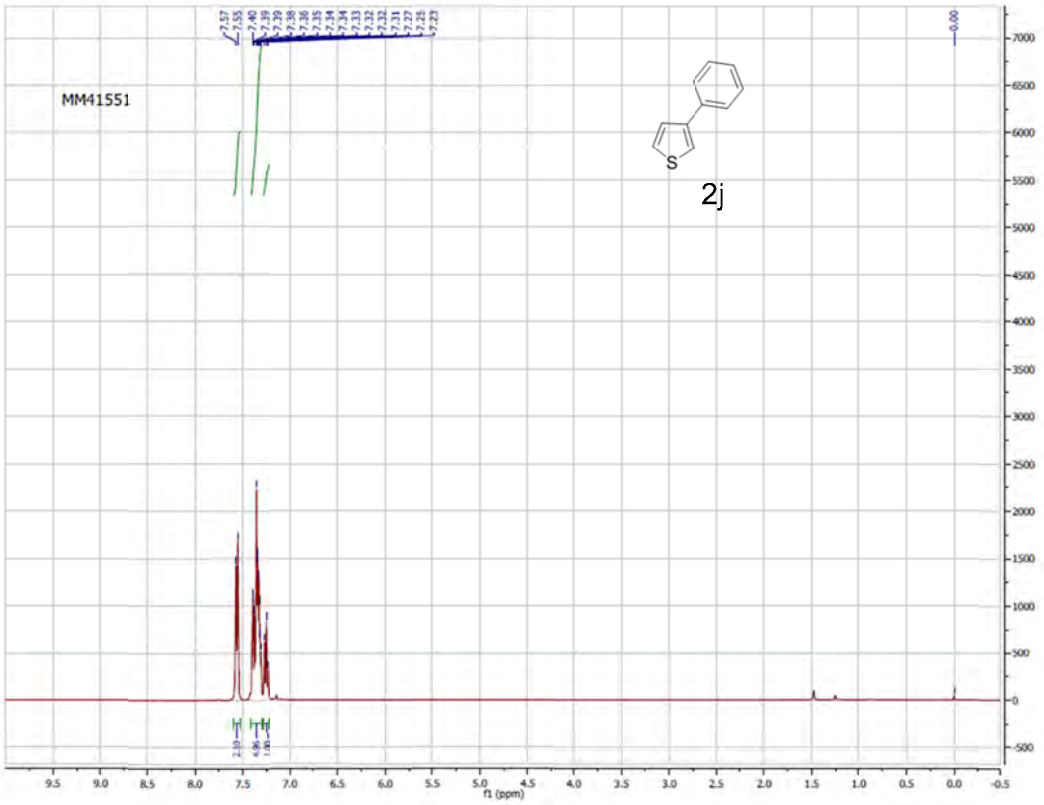
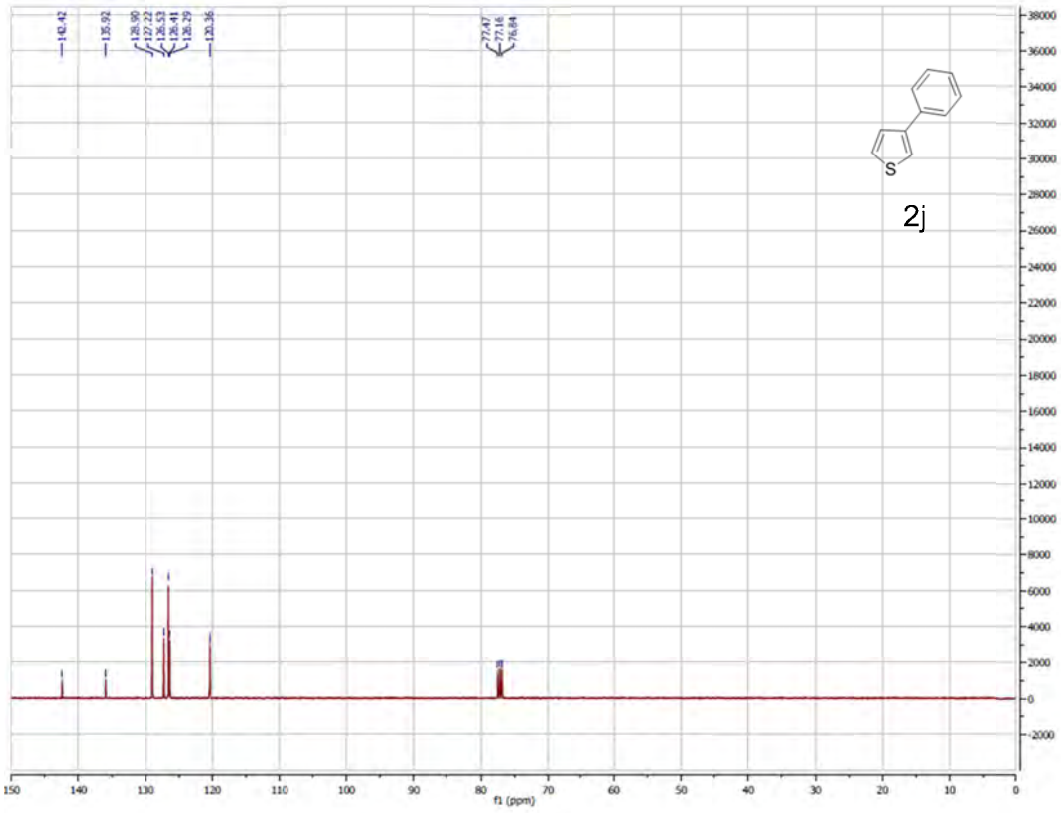
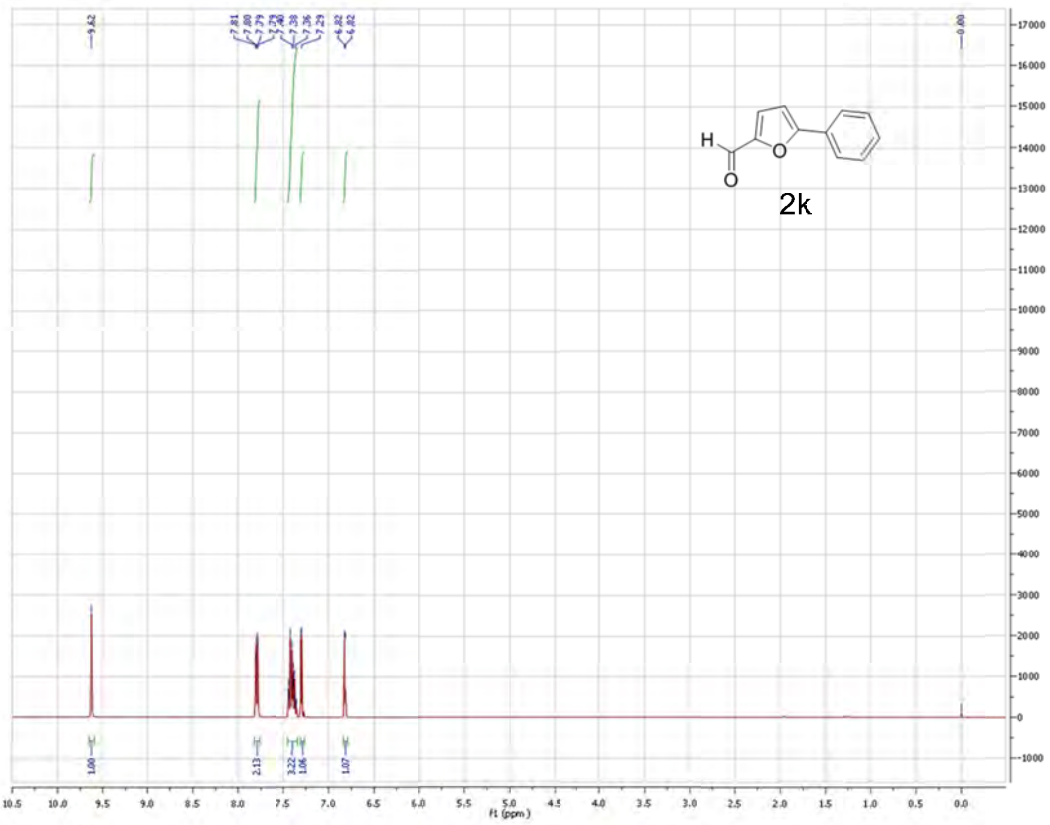
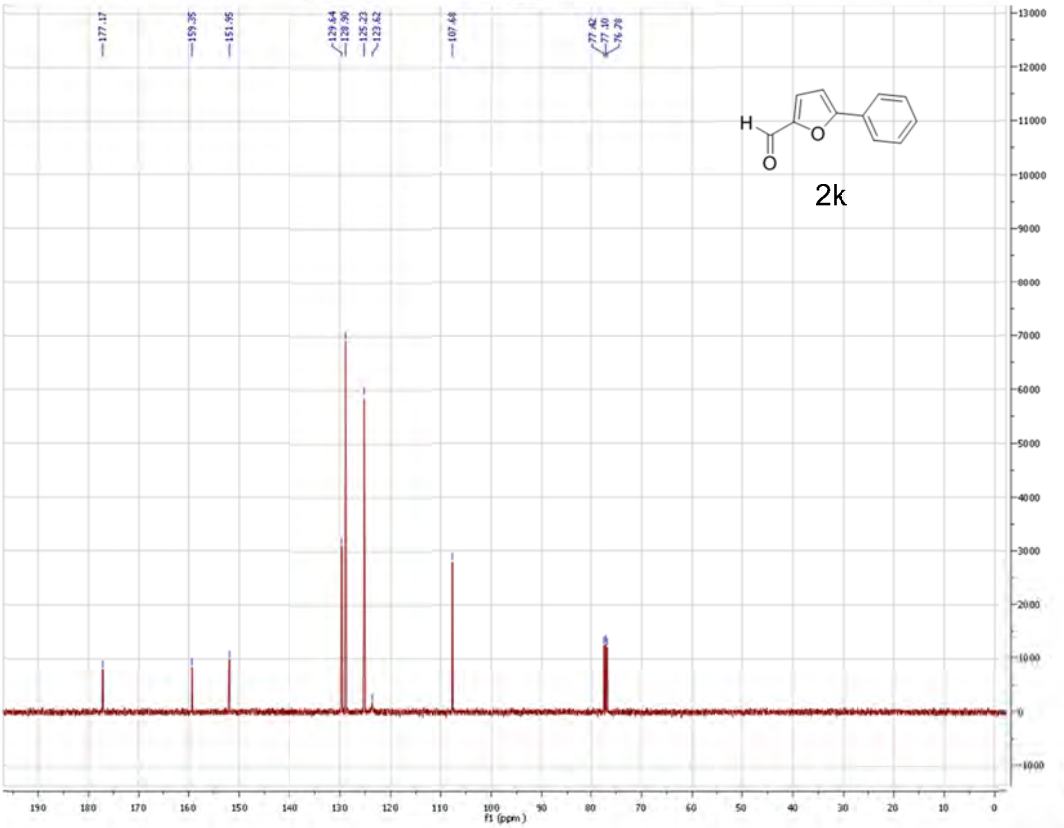

2i

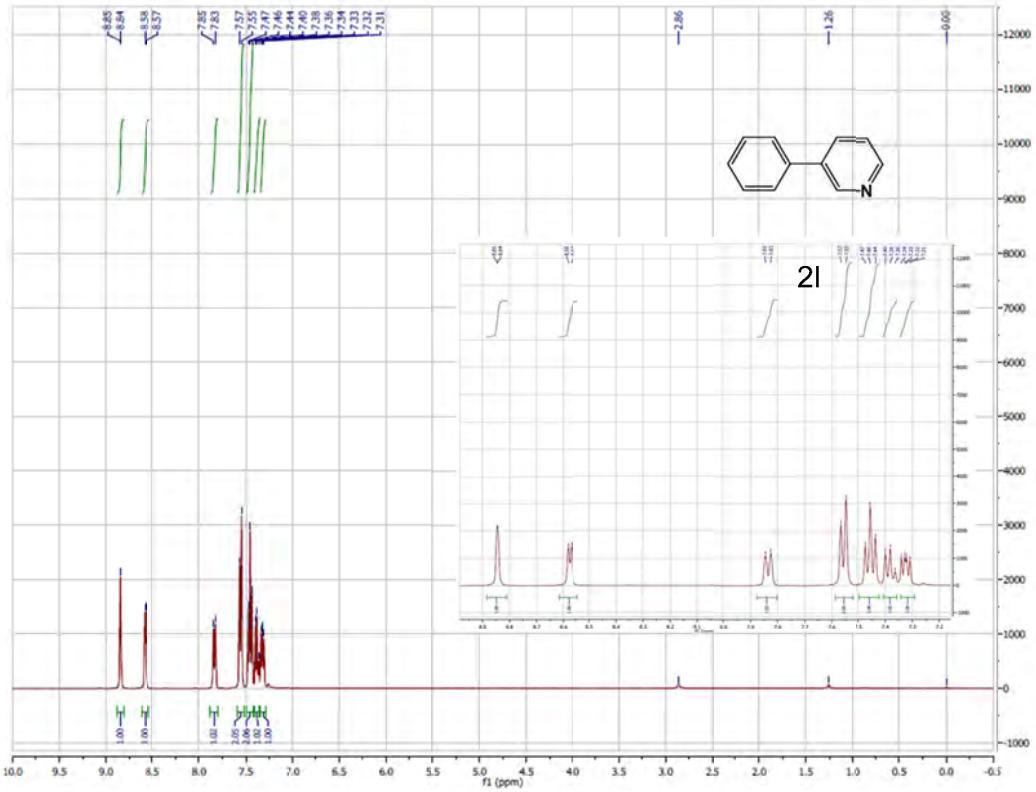

2i

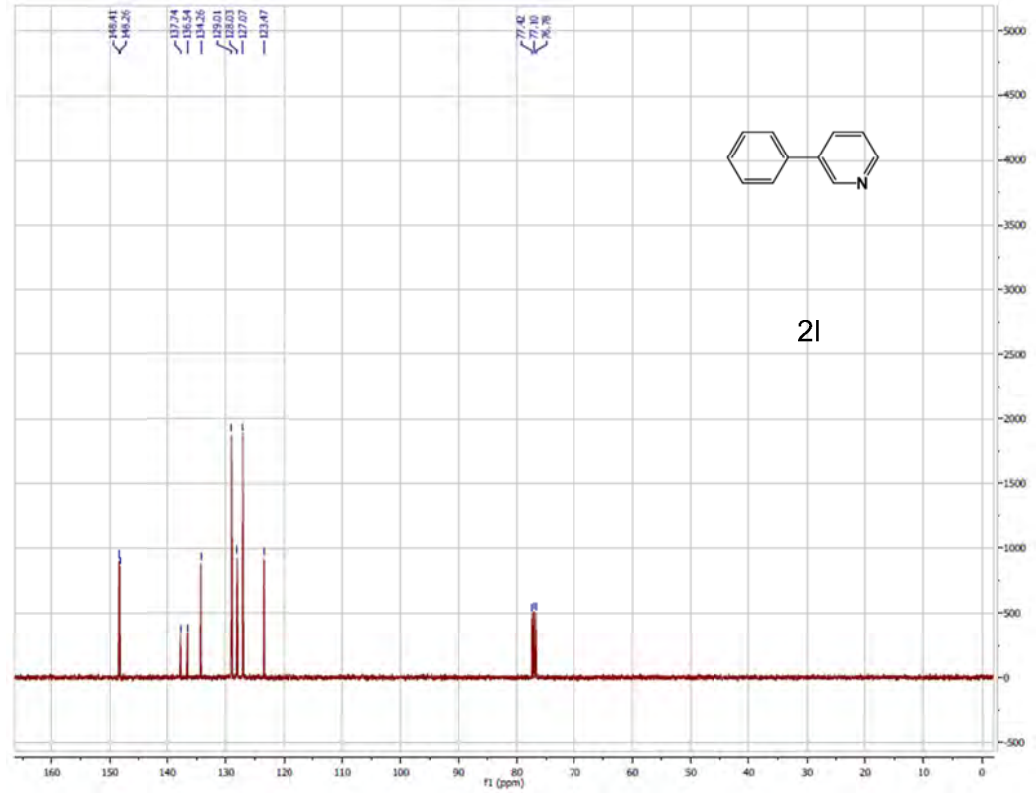

MM41551
S
2j
f1 (ppm)

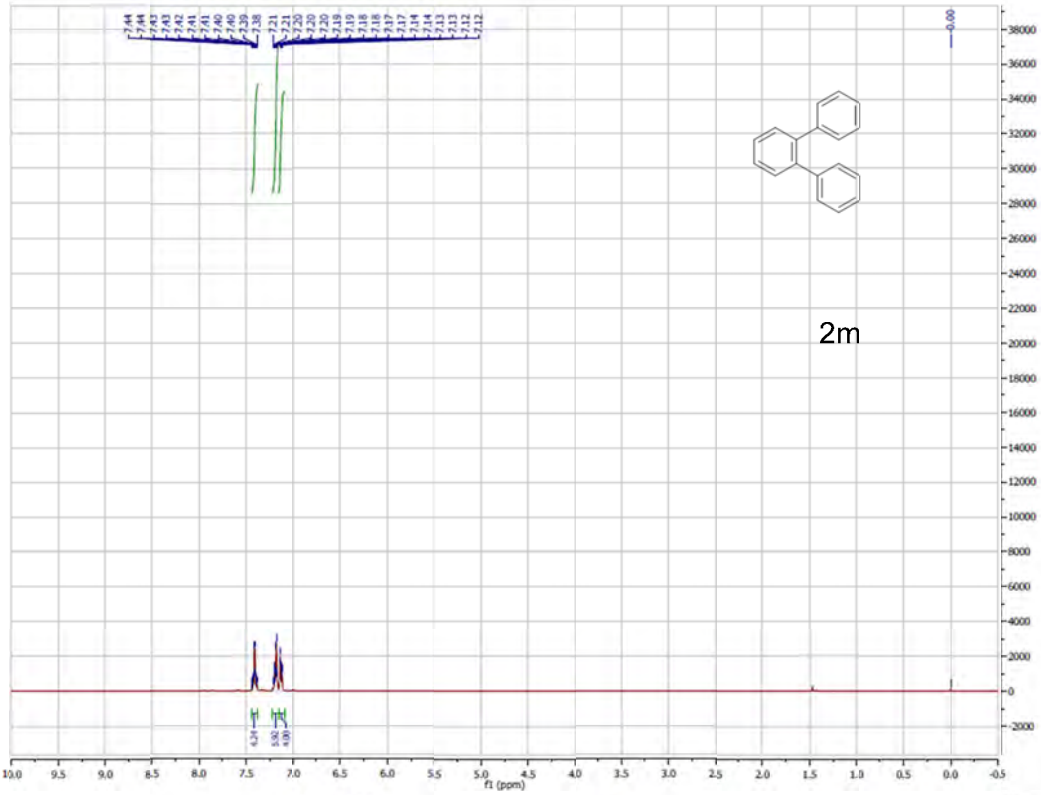

S
2j
f1 (ppm)

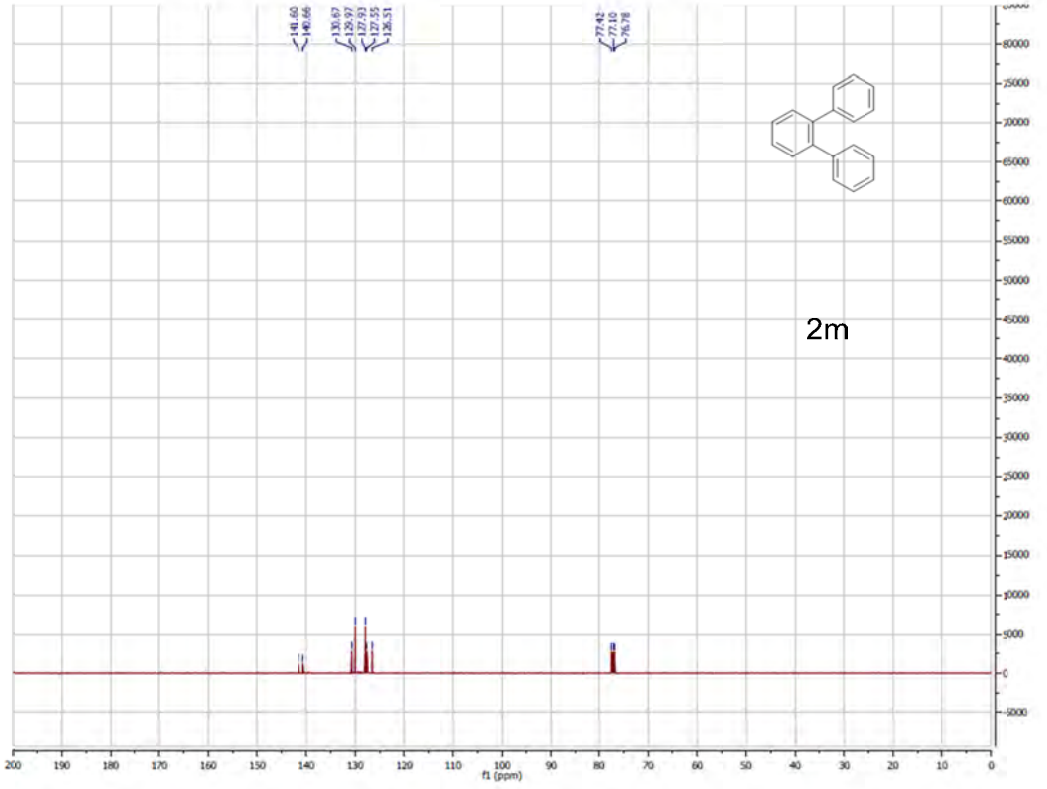

9.62
7.81
7.80
7.79
7.38
7.36
7.29
6.82
6.82
0.00
H
O
O
2k
1.00
2.13
3.22
1.06
1.07
f1 (ppm)

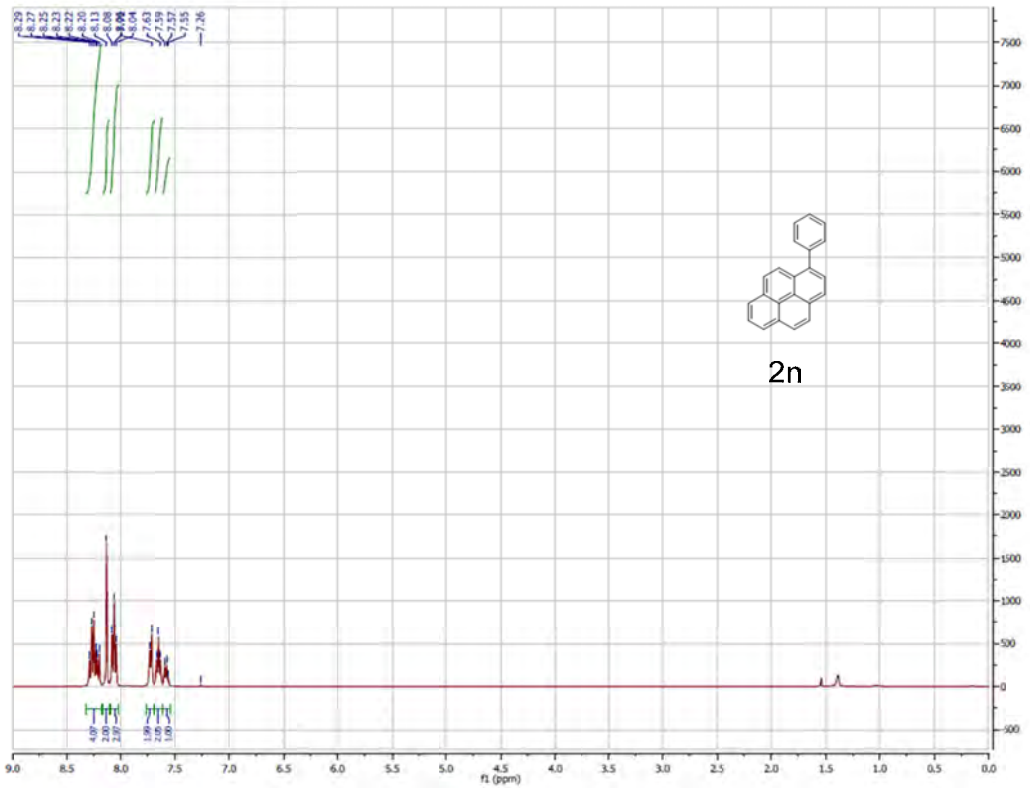

177.17
159.35
151.95
129.64
129.50
125.23
123.62
107.68
77.42
77.10
76.78
H
O
O
2k
f1 (ppm)

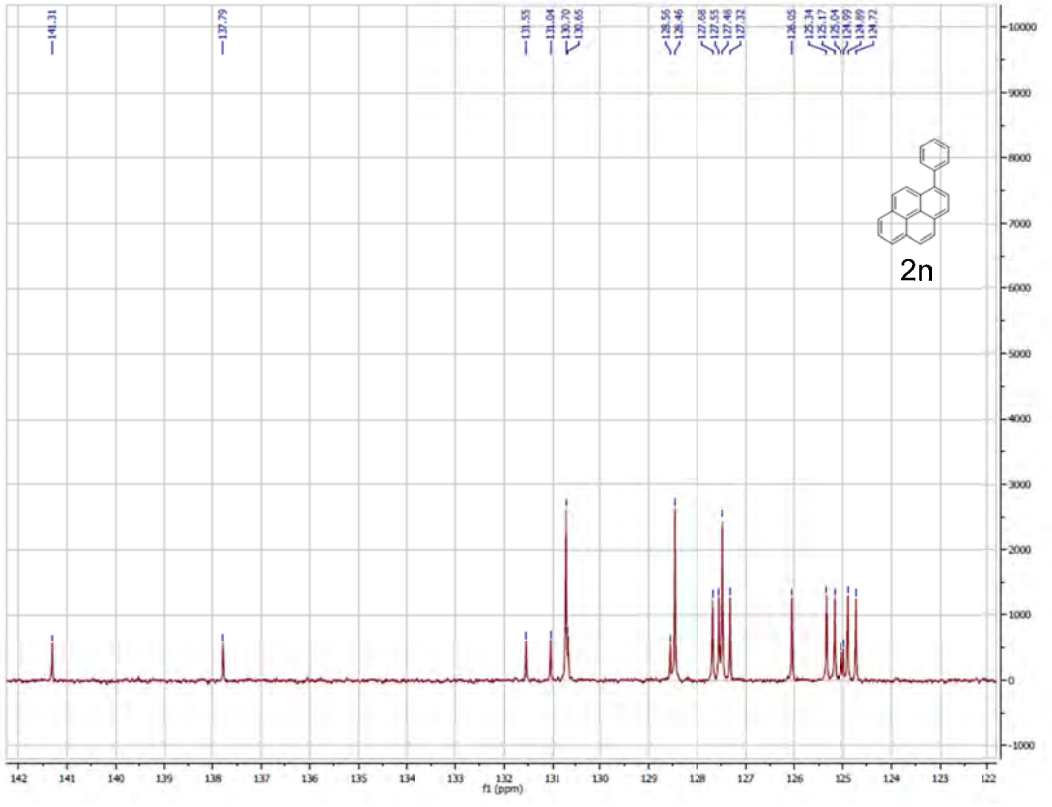

8.85
8.84
8.58
8.57
7.85
7.83
7.57
7.55
7.47
7.46
7.44
7.40
7.38
7.36
7.34
7.33
7.32
7.31
2.86
1.26
0.00
N
2l
f1 (ppm)


149.41
149.26
137.74
136.54
134.26
129.01
128.03
127.07
123.47
77.42
77.10
76.78
N
2l
f1 (ppm)


2m
f1 (ppm)


2m
f1 (ppm)


2n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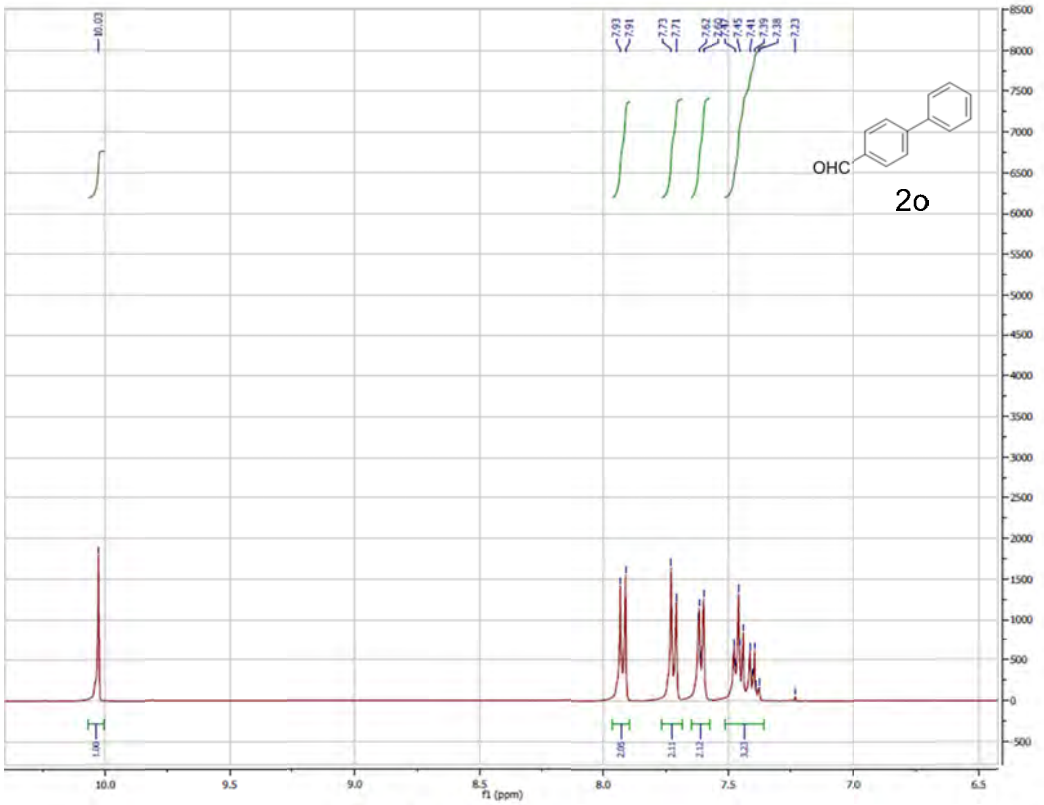
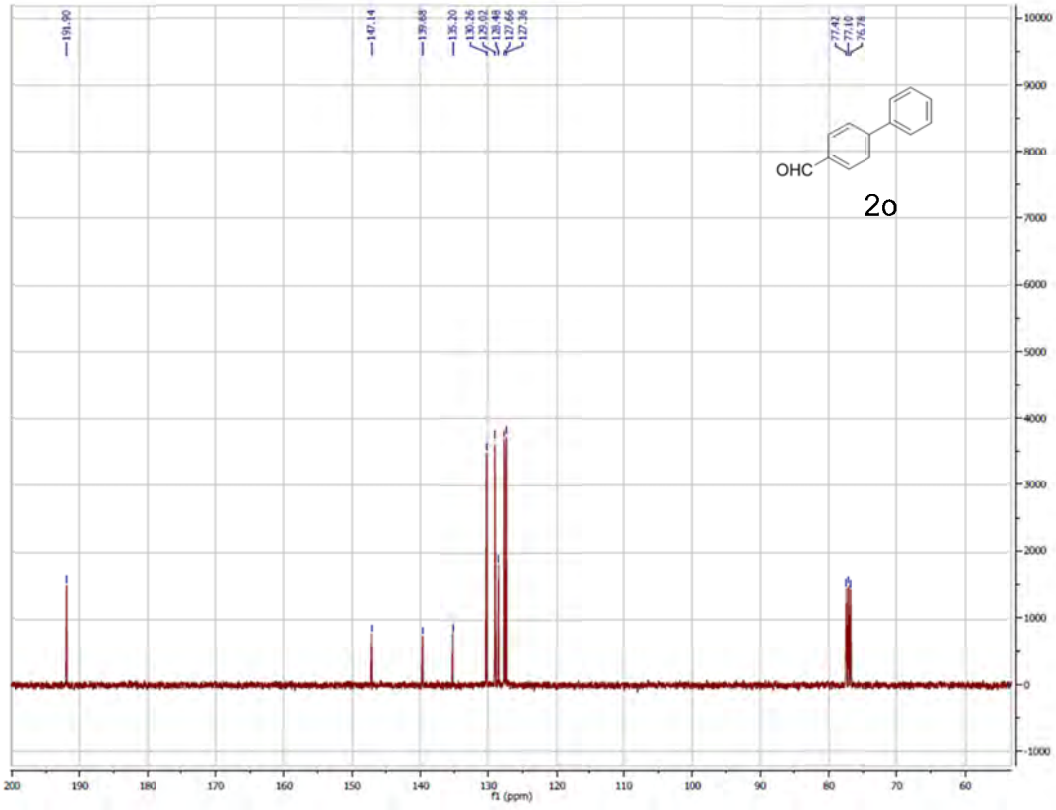
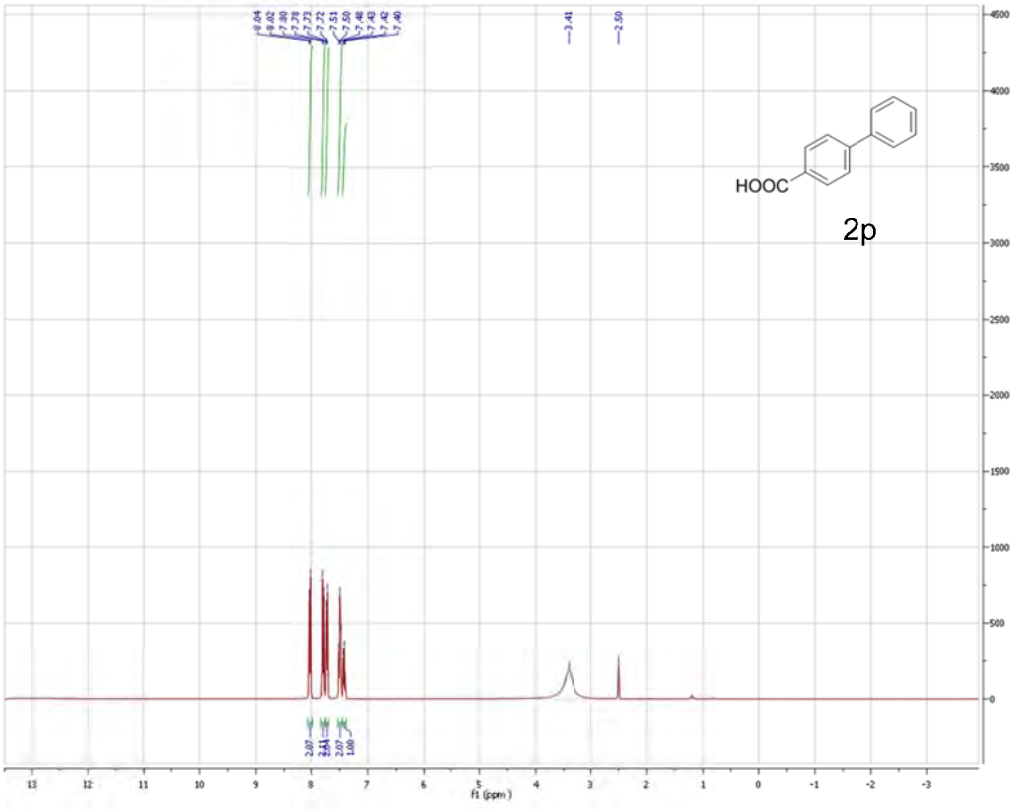
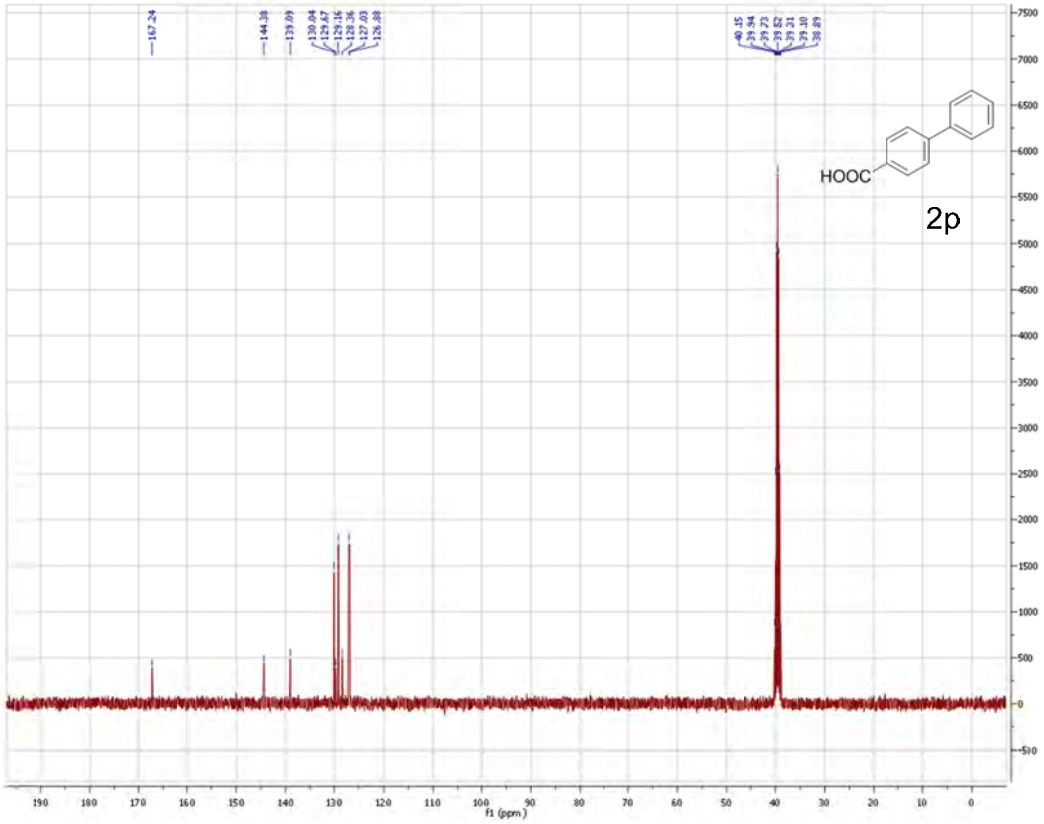
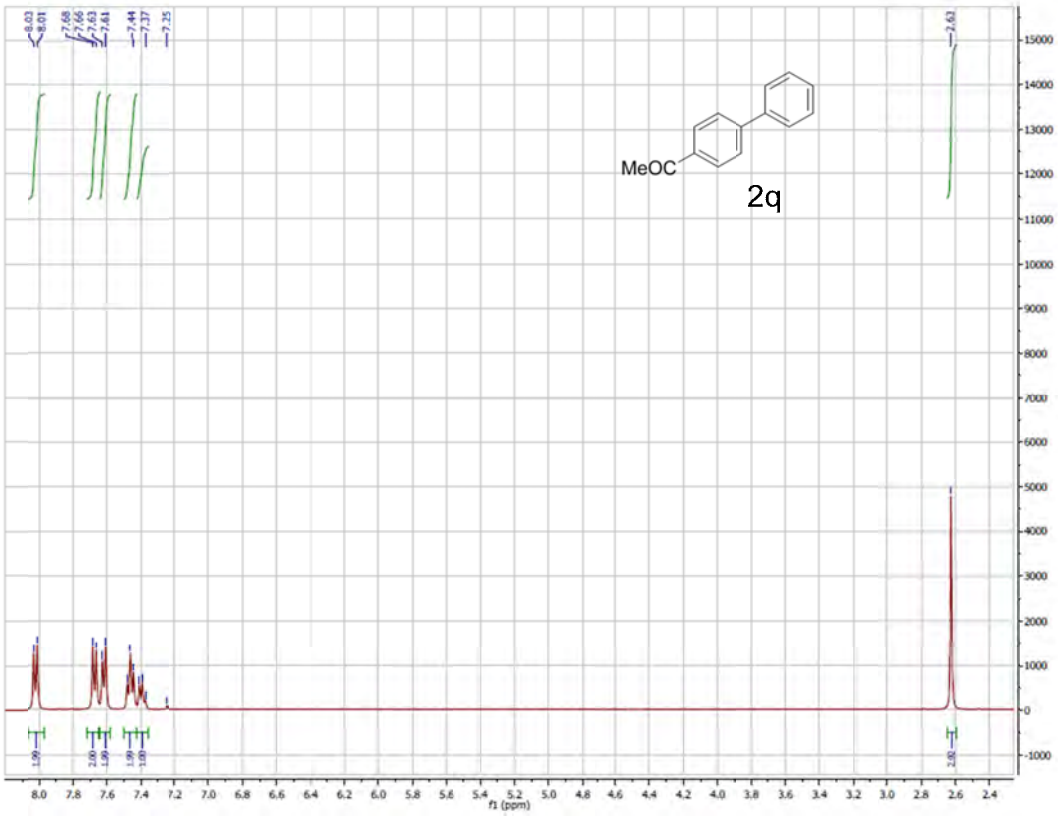
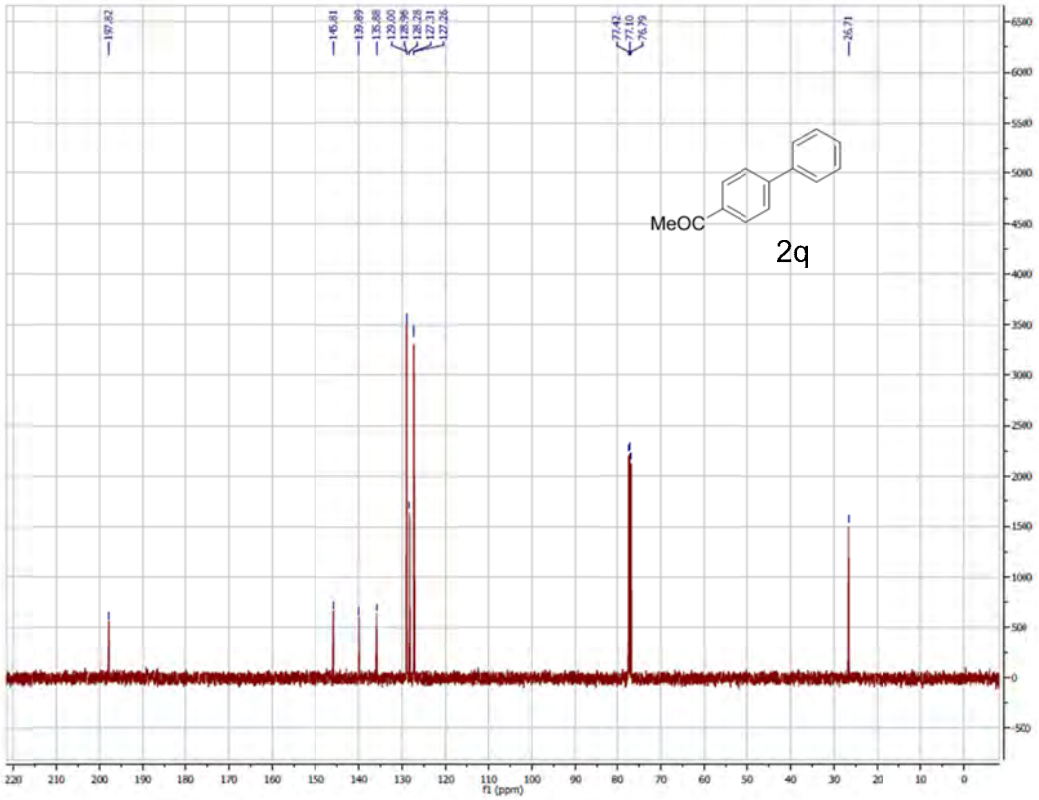

10.03
7.93
7.91
7.73
7.71
7.62
7.60
7.45
7.41
7.39
7.38
7.23
OHC
2o
f1 (ppm)

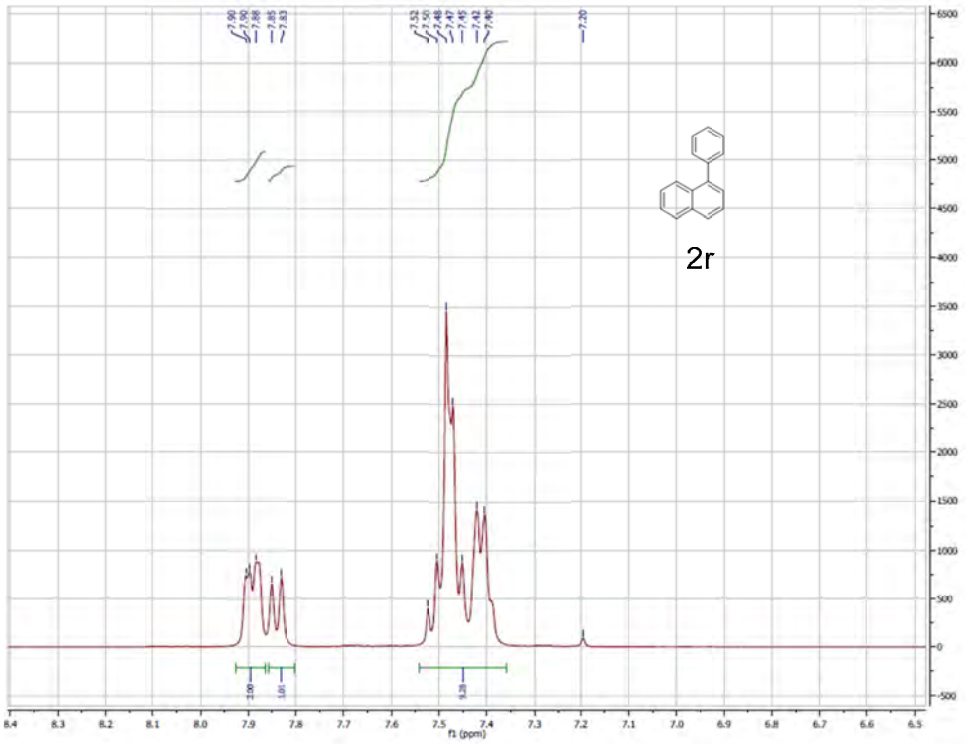

191.90
147.14
139.68
135.20
130.26
129.02
128.48
127.66
127.36
77.42
77.10
76.78
OHC
2o
f1 (ppm)

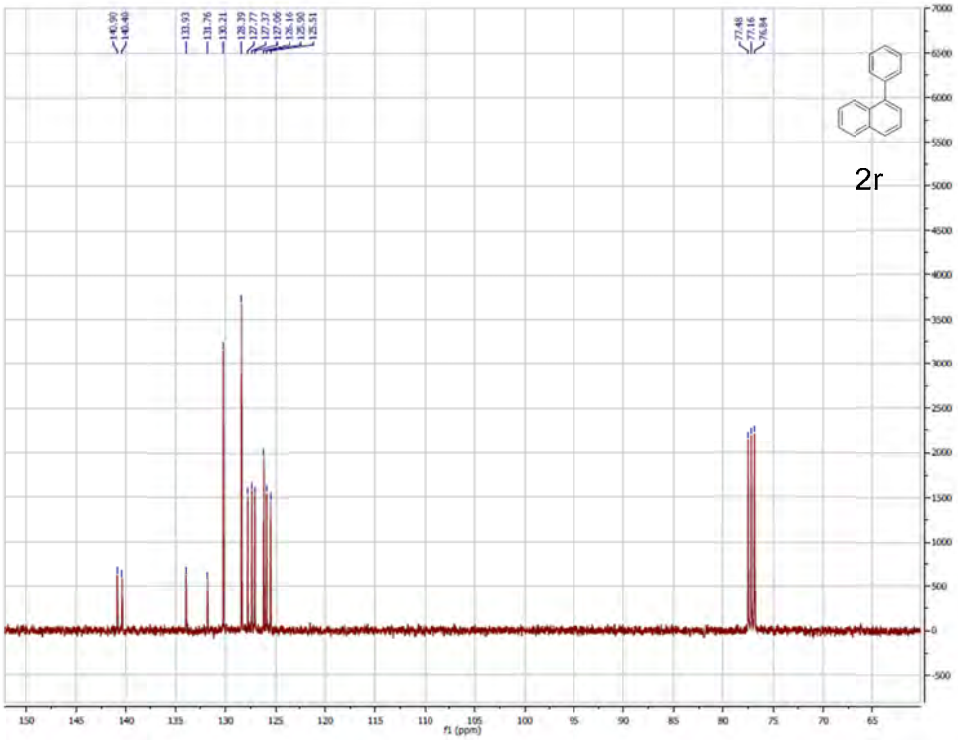

HOOC
2p
f1 (ppm)

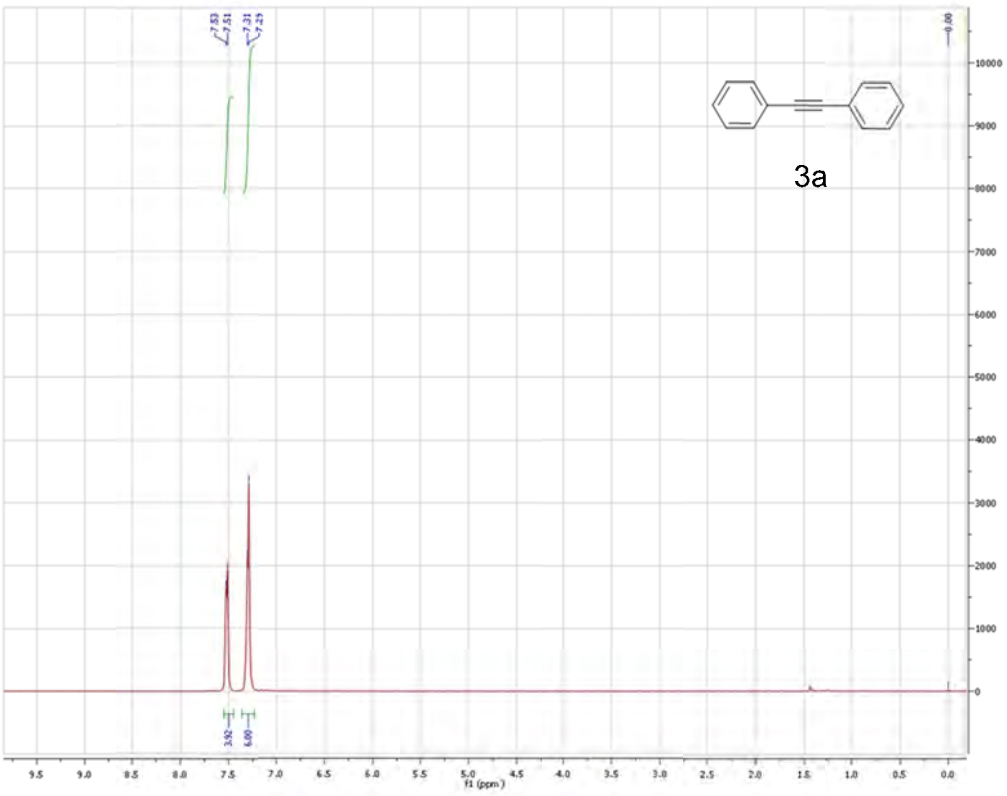

HOOC
2p
f1 (ppm)


8.03
8.01
7.68
7.66
7.63
7.61
7.44
7.37
7.35
2.63
MeOC
2q
f1 (ppm)

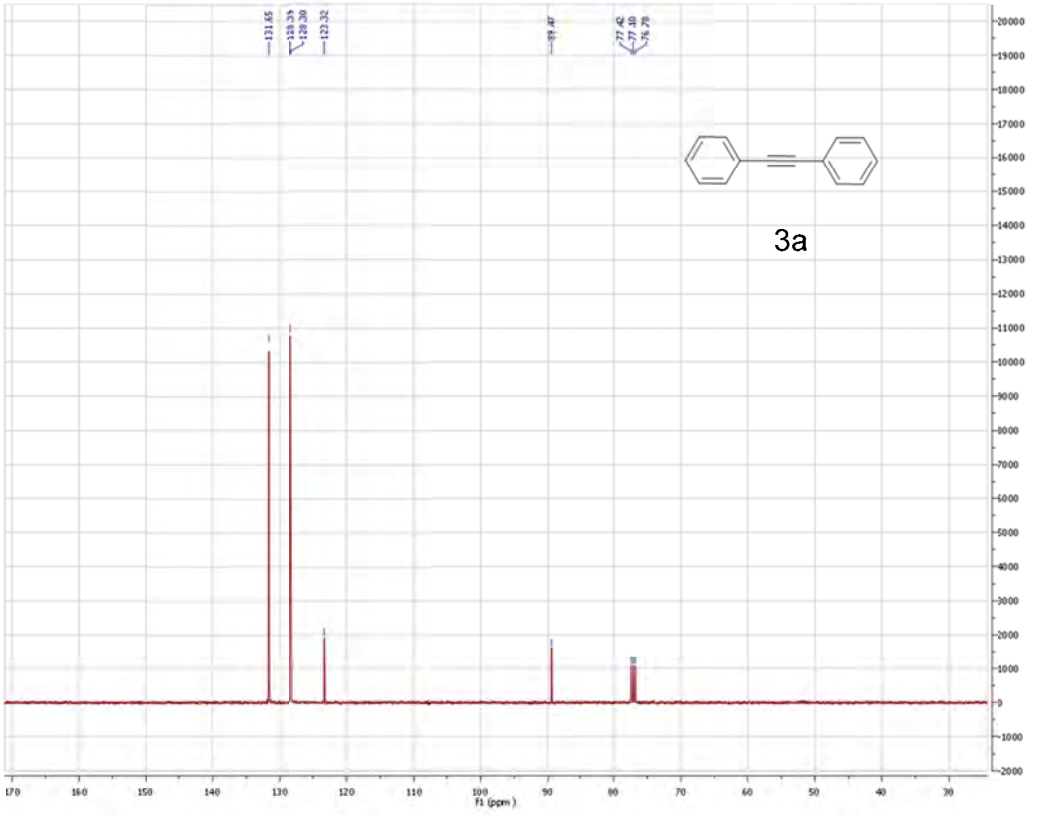

197.82
145.81
139.89
135.88
129.00
128.96
128.28
127.31
127.26
77.42
77.10
76.79
26.71
MeOC
2q
f1 (ppm)


2r
f1 (ppm)

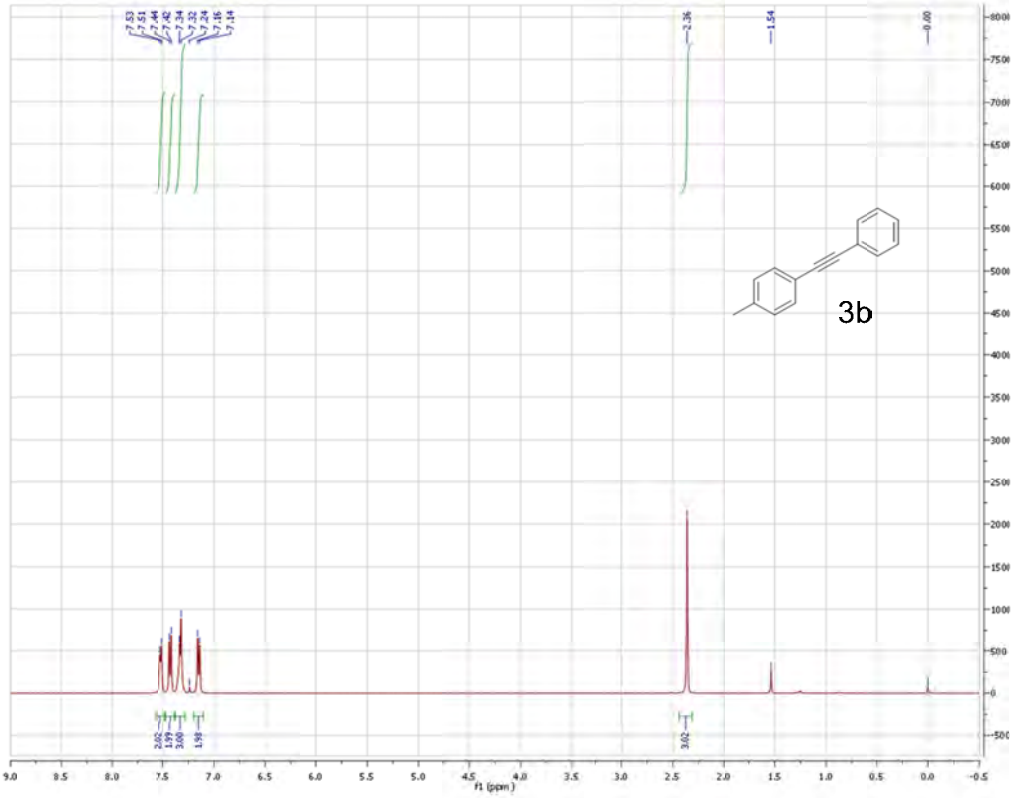

2r
f1 (ppm)

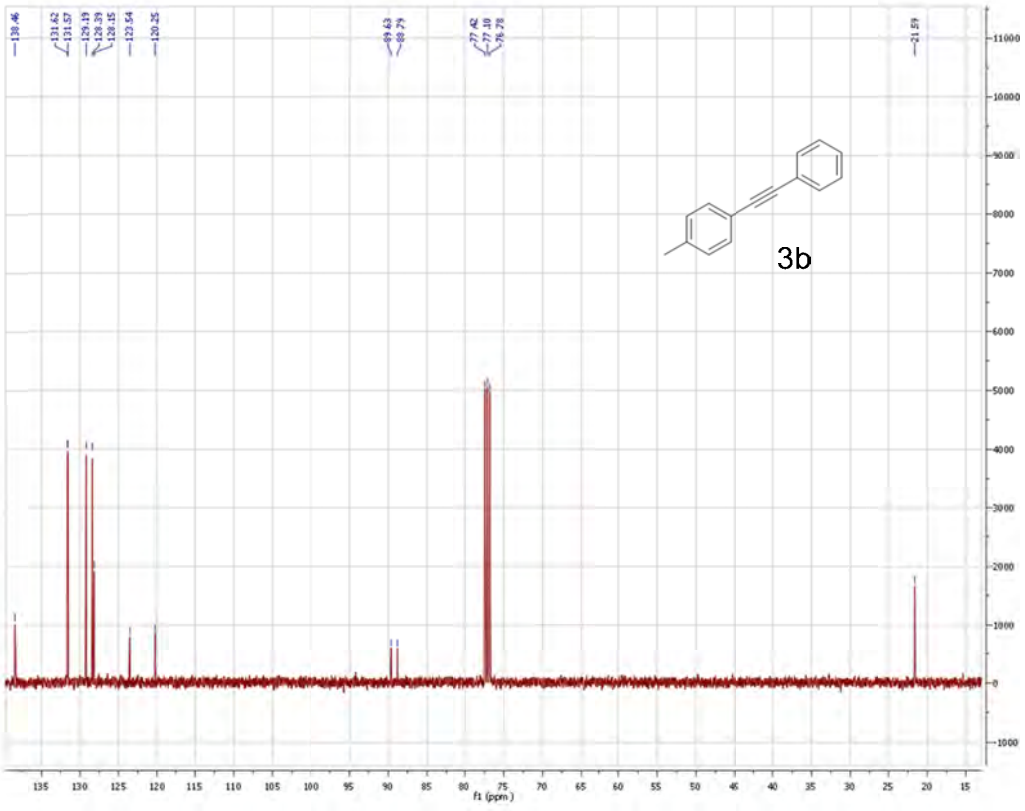

7.53
7.51
7.31
7.29
0.00
3.92
6.00
f1 (ppm)

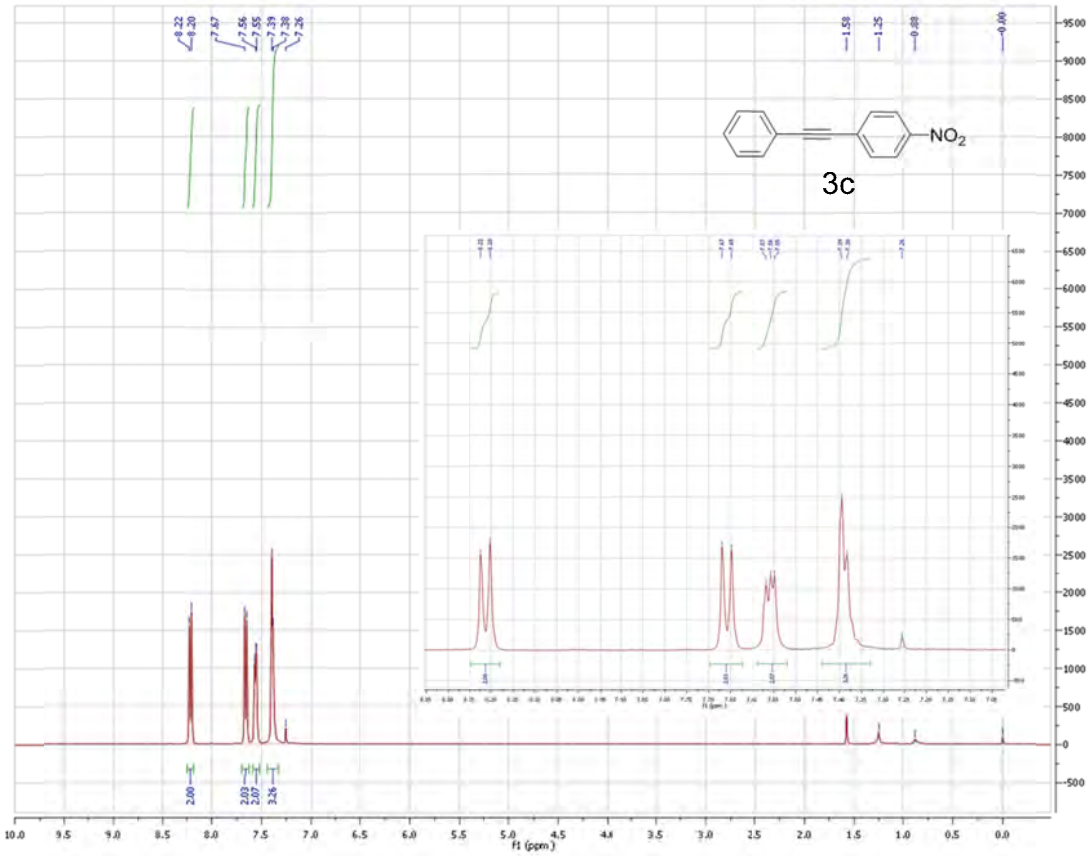
3a

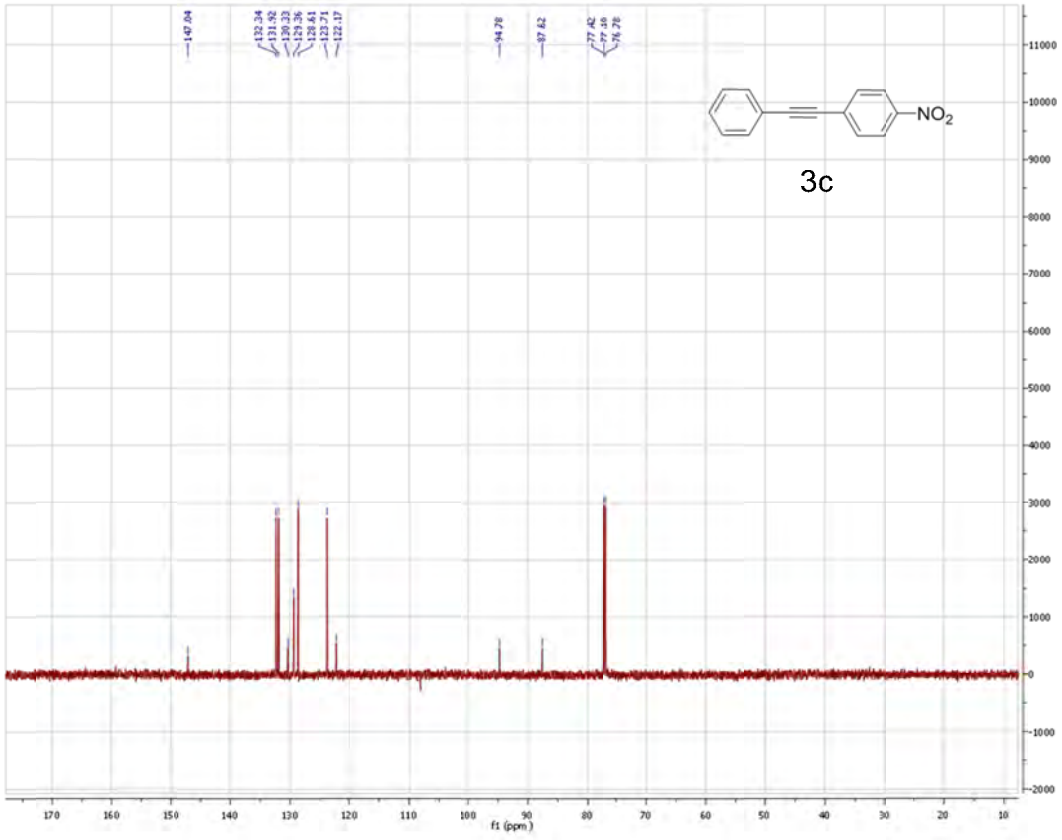

131.65
128.35
128.30
123.32
89.47
77.42
77.00
76.79
f1 (ppm)

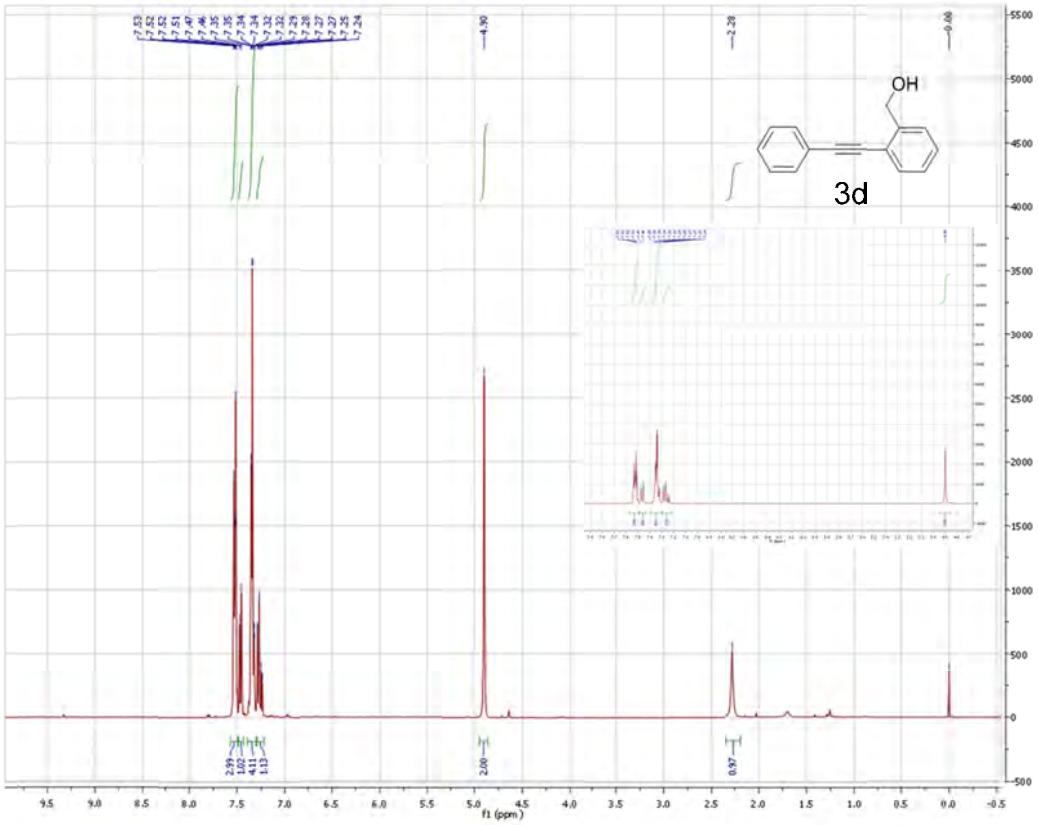
3a

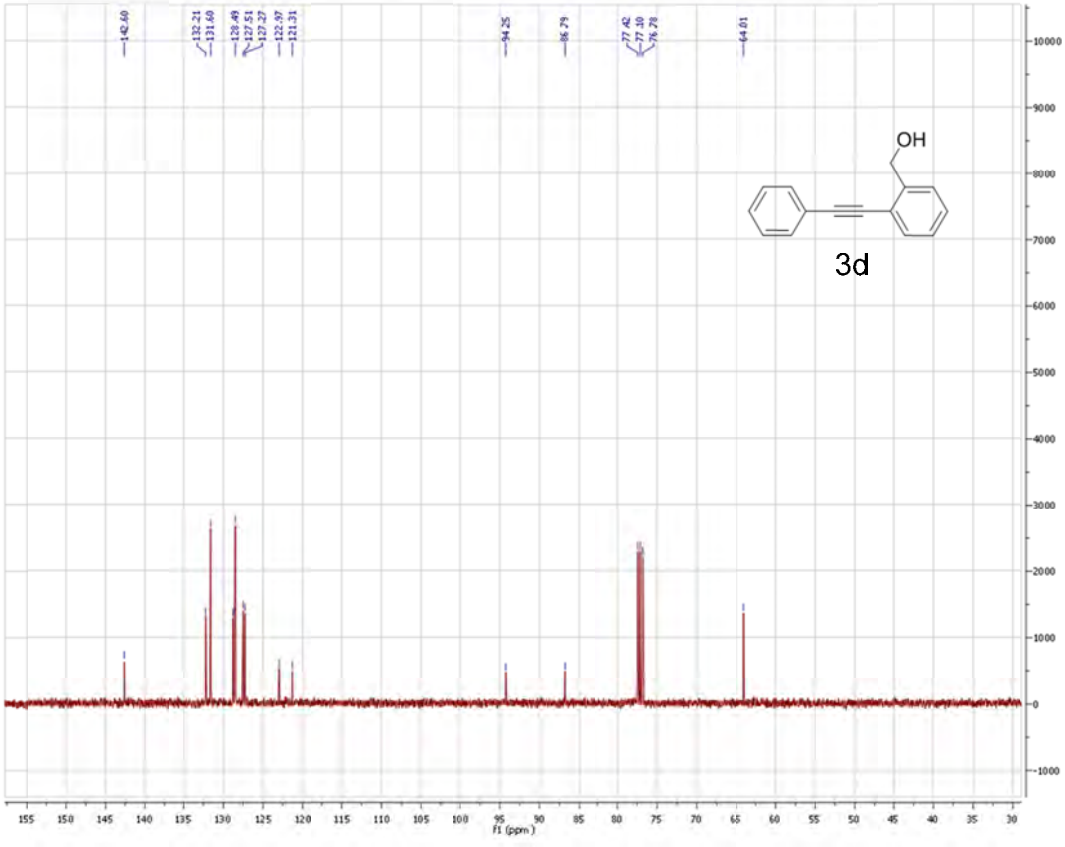

7.53
7.51
7.44
7.42
7.34
7.32
7.24
7.16
7.14
2.36
1.54
0.00
3b
f1 (ppm)

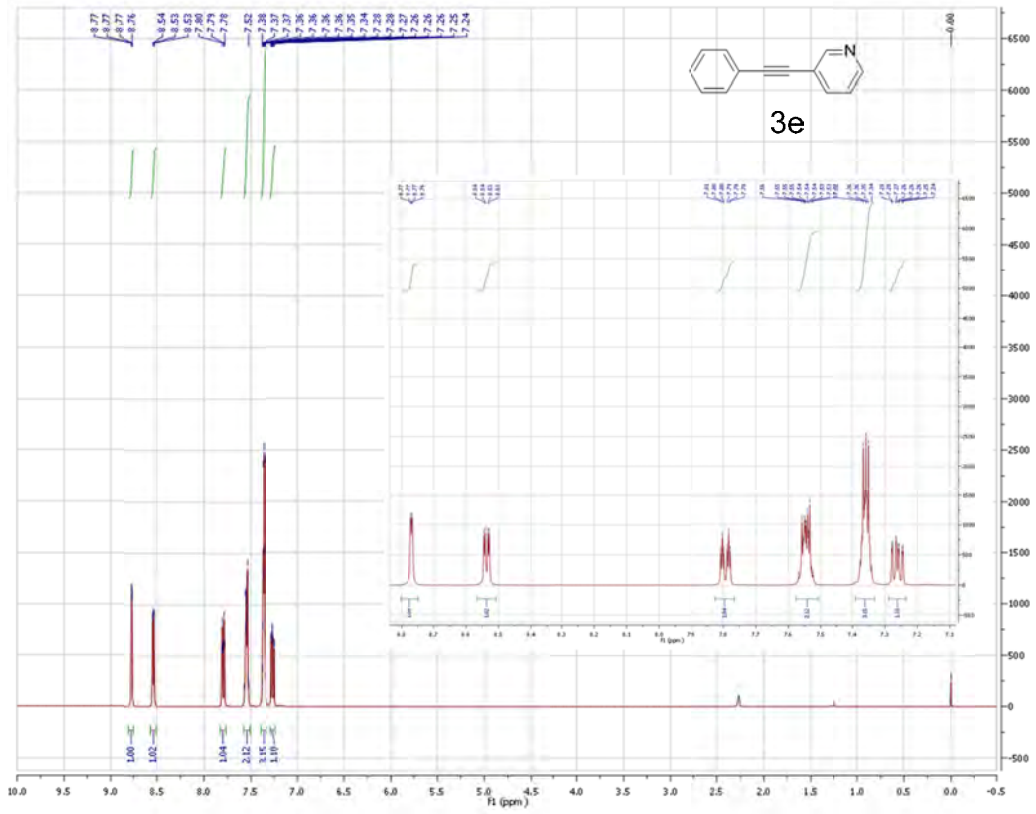

138.46
131.62
131.57
129.19
128.39
126.15
123.54
120.25
89.63
88.79
77.42
77.10
76.78
21.59
3b
f1 (ppm)

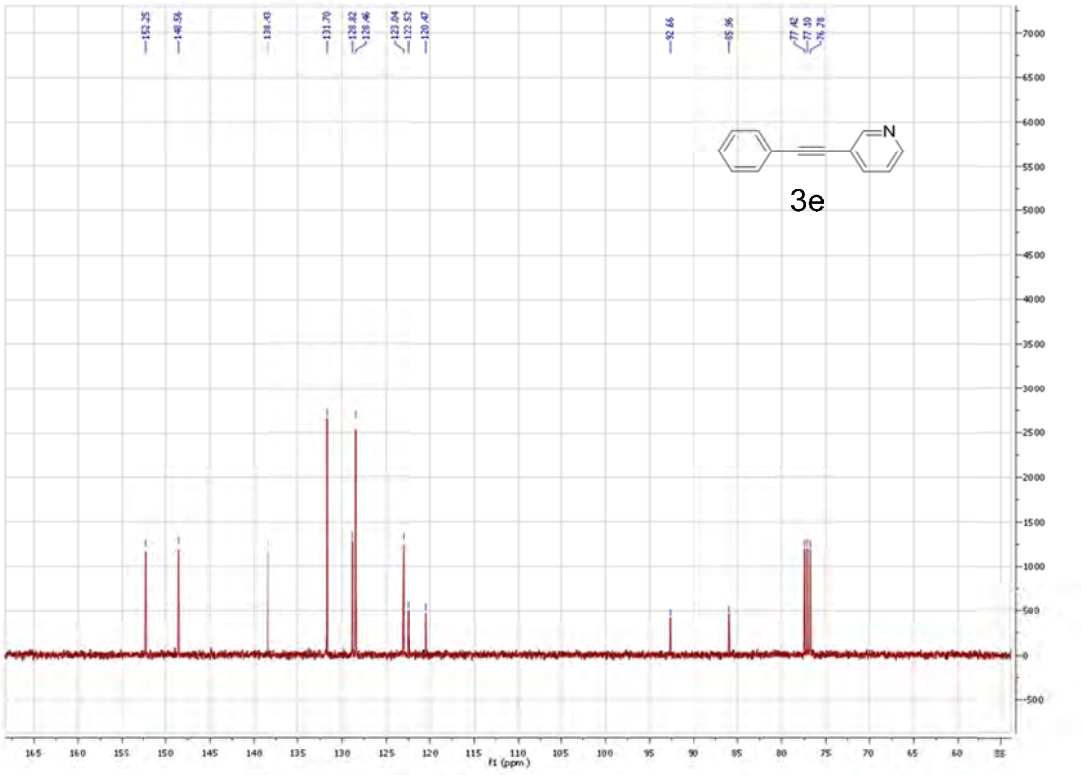

8.22
8.20
7.67
7.56
7.55
7.39
7.38
7.26
1.58
1.25
0.88
0.00
NO2
3c
2.00
2.03
2.07
3.26
f1 (ppm)

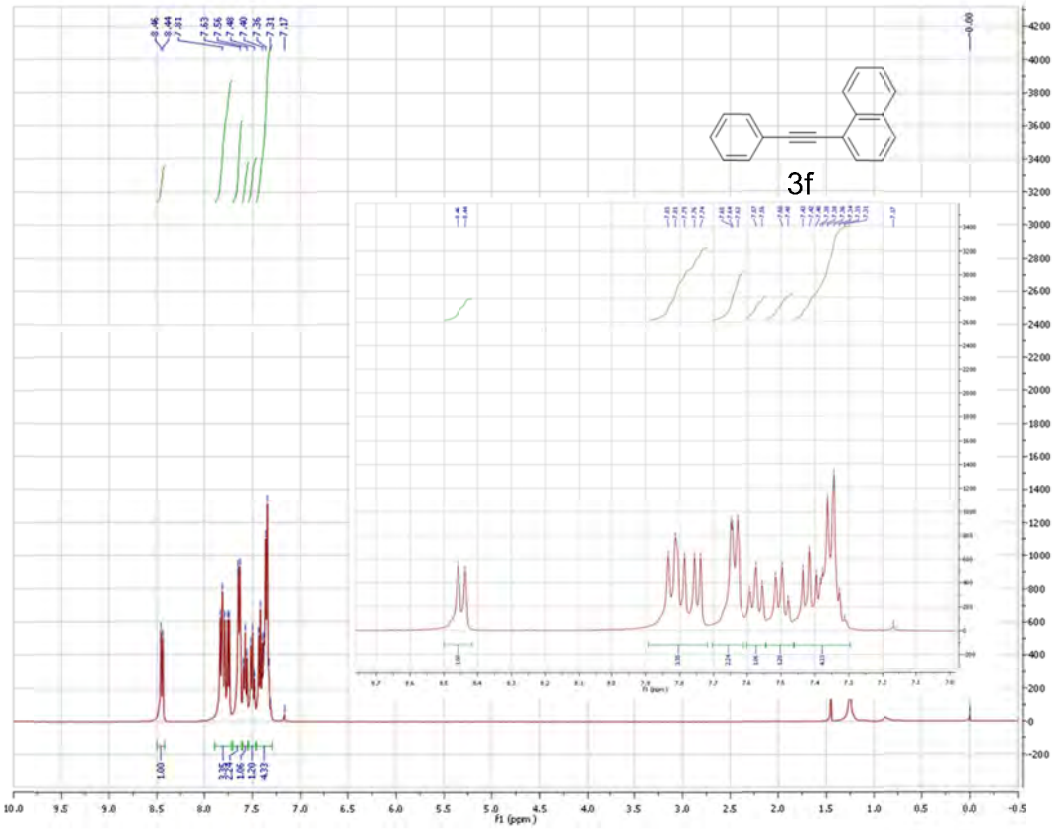

147.04
132.34
131.92
129.33
129.36
128.41
123.71
122.17
94.78
87.62
77.42
77.16
76.78
NO2
3c
f1 (ppm)

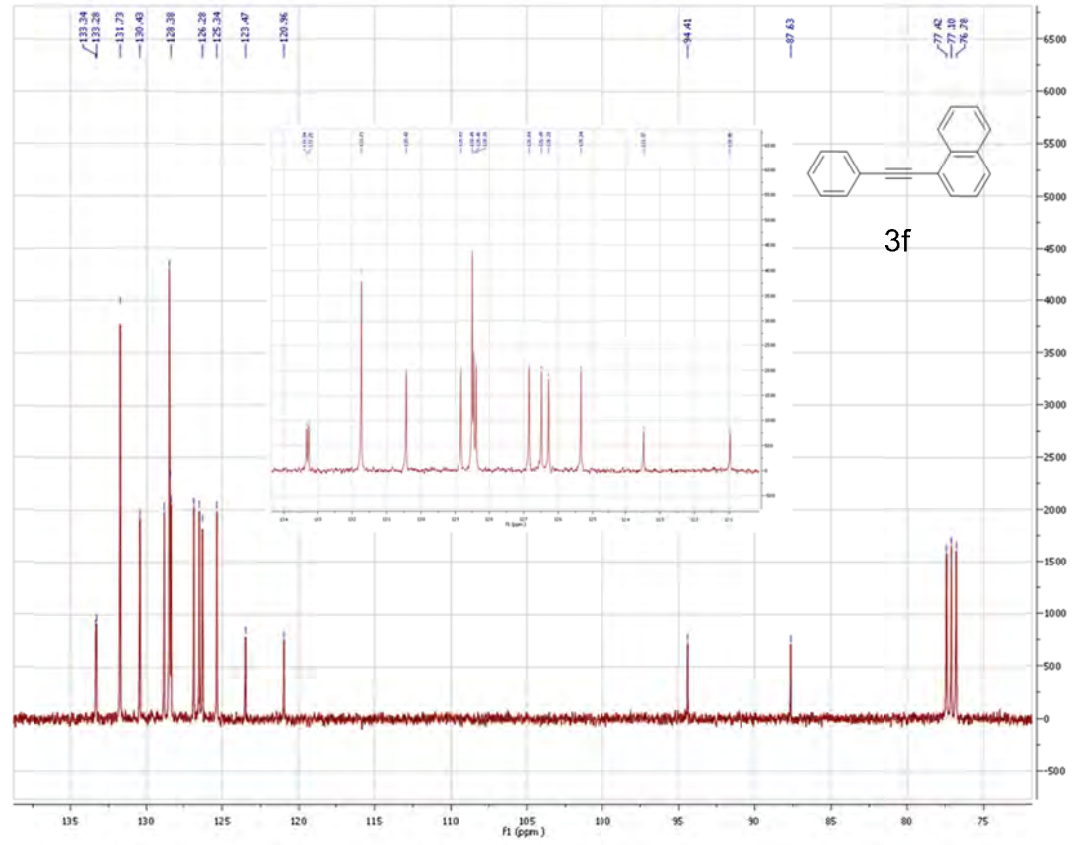

OH
3d
f1 (ppm)


OH
3d
f1 (ppm)


3e


3e


3f
F1 (ppm)


3f
F1 (ppm)