RSC Advances

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Very efficient and broad-in-scope palladium-catalyzed Hiyama cross-coupling. The role of water and copper(I) salts.

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

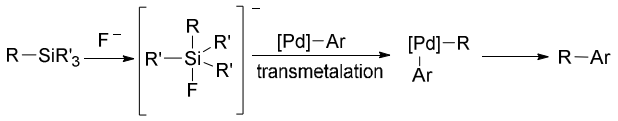
DOI: 10.1039/b000000x

A very high-yielding Pd-catalyzed cross-coupling between aryl halides and aryl(trialkoxy)silanes is achieved in the presence of Cu(I) and a measured amount of water. This novel methodology is useful for the generation of a wide range of biaryls, particularly non-*para* substituted derivatives, which are usually less reported.

Metal-catalyzed carbon-carbon bond forming reactions have become crucial synthetic tools for preparing complex molecules from simple precursors.[1] Among them, Hiyama reaction is drawing increasing attention as a very attractive methodology for obtaining biaryl and alkyl and vinyl aromatic derivatives. Hiyama coupling is achieved by treating aryl or alkenyl halides or pseudo halides with organosilicon compounds under palladium catalysis and activation by a fluoride ion or a base.[2]

Particularly, the synthesis of unsymmetrical biaryl moieties have wide applications as polymers, agrochemicals, and pharmaceutical intermediates.[3] While Stille[4] and Suzuki[5] reactions have been widely recognized for generating aryl-aryl coupling products, the value of Hiyama reaction lays on the use of organosilanes as coupling partners, due to their ease of preparation and handling, stability toward air/moisture, and low toxicity compared to tin and boron reagents. Besides, Hiyama coupling is interesting from the environmental point of view since silicon waste is easily converted to innocuous silicon dioxide by incineration.[6]

The importance of this methodology was established by Hiyama and Hatanaka when they demonstrated that the high affinity between silicon and fluoride ions can accelerate the rate-determining transmetalation step (Scheme 1).[7]



Scheme 1 Cross-coupling Hiyama reaction.

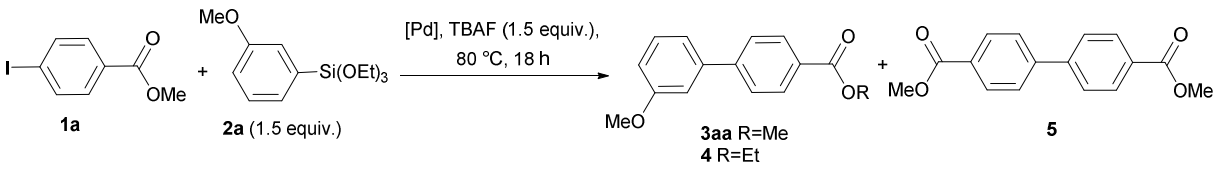
Better results were later obtained when fluorophilicity of the silanes was increased by introducing F-Si bounds.[2a] However, Hiyama coupling did not achieve great success in its early days. The reason was probably the intrinsic resistance of the organosilicon compounds to undergo cross-coupling reactions in the absence of a significant polarity at the C-Si bond. After the introduction by Tamao et al[8] of silicon species containing oxygen atoms, Hiyama coupling has expanded its use to a wide range of substrates by improving reactivity and selectivity since oxygen facilitate coordination to palladium atom, apart from increasing polarity at the C−Si bond. Since then, an extensive research has been carried out within this field, establishing different and very useful variants, such as those introduced by DeShong,[9] and Denmark.[10]

As part of our research dealing with the generation of libraries of biologically promising compounds,[11] we were particularly interested in carboxy-substituted biaryl derivatives, which have demonstrated attractive antimitotic properties as modulators of tubulin dynamics.[12] We notice that, despite of the success of Hiyama coupling, most of the examples involving synthetically accessible aryl(trialkoxy)silanes[9b] are referring to the preparation of 4'-substituted 1,1'-biphenyl derivatives. Reaction of *ortho* and *meta*-substituted aryl iodide with (3-substituted-phenyl)triethoxysilanes is less described and, in many cases, achieved in low to moderate yields.[6,9a,13]

Hence, we decided to study the synthesis of methyl 3'-methoxybiphenyl-4-carboxylate (**3aa**) as model compound, starting from methyl 4-iodobenzoate (**1a**) and the corresponding aryl(triethoxy)silane (**2a**) in the presence of palladium catalyst and TBAF (Table 1). Using standard conditions, 1.5 equivalents of **2a** and TBAF, catalytic tetrakis(triphenylphosphine)-palladium(0) (0.025 equiv.), at 80 °C in dry THF, for 18 h, the expected biaryl **3aa** was obtained in only 19% isolated yield (Entry 1). Interestingly, the ethyl ester analogue **4** was the major product (33%). Formation of **4** could be explained by a Pd-catalyzed transesterification with an ethoxy group which can be generated by a nucleophilic cleavage of one Si-O bond by the fluoride coming from the TBAF.[14] Yield of **3aa** increased from 19 to 45% without evidence of ethyl ester formation, under the same conditions but using non-anhydrous THF (Entry 2). Later, by adding 2 equivalents of CuI, isolated yield of **3aa** was improved to 85% (Entry 3). The addition of stoichiometric copper(I) salts has been suggested to improve efficiency in Pd-catalized cross-coupling reactions,[15] including Hiyama coupling.[16] CuI has also proven to have a beneficial effect by preventing homocoupling of the aryl halide.[17]

Recently, the role of water in Hiyama reaction has began to be considered. Denmark noticed that hydration level of TBAF was crucial for the success of this cross-coupling during the synthesis of natural product Isodomoic Acid H,[18] while Sajiki found that the addition of a measured amount of water significantly increase the yield of Hiyama cross-coupling between aryl halides and

Table 1 Optimization of the cross-coupling reactions using methyl 4-iodobenzoate (**1a**) and the aryl(triethoxy)silane **2a**.



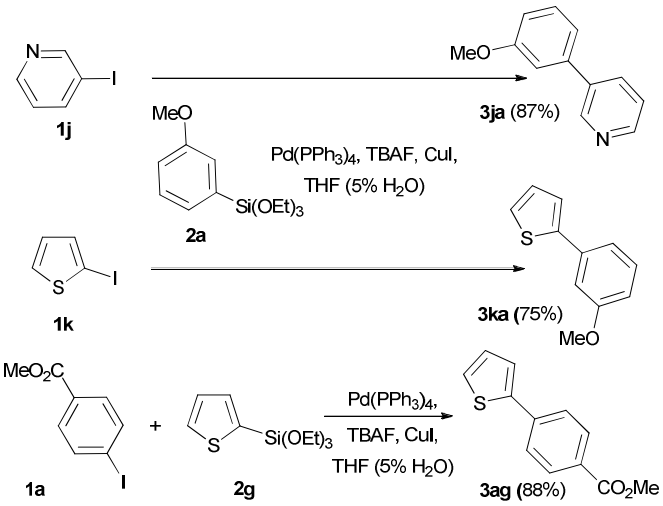
Entry	Catalyst (equiv.)	Co-catalyst (equiv.)	Solvent	Product (%)[a]
1	$Pd(PPh_3)_4$ (0.025)	-	THF (anhydrous)	**3aa** (19) / **4** (33)
2	$Pd(PPh_3)_4$ (0.025)	-	THF (no anhydrous)	**3aa** (44)
3	$Pd(PPh_3)_4$ (0.025)	CuI (2)	THF (no anhydrous)	**3aa** (85)
4	$Pd(PPh_3)_4$ (0.025)	CuI (2)	THF (5% H_2O)	**3aa** (93)
5	-	CuI (2)	THF (5% H_2O)	NR
6	$Pd(PPh_3)_4$ (0.025)	CuI (2)	THF (5% H_2O)	NR[b]
7	$Pd(PPh_3)_4$ (0.025)	CuI (2)	THF (5% H_2O)	**3aa** (88)[c]
8	$Pd(PPh_3)_4$ (0.025)	CuI (2)	THF (50% H_2O)	**1a**/**3aa**/**5**[d]
9	$Pd(OAc)_2$ (0.025)	CuI (2)	THF (5% H_2O)	**3aa**/**5**[d]

[a]Yield calculated after purification by column chromatography. NR= No reaction. [b]No TBAF was added. [c]CsF was added instead of TBAF. [d]Determined from the ^1H NMR spectrum of the crude reaction mixture.

aryltriethoxysilanes.[19] For this reason we decided to add 5% of water to the best conditions obtained until that moment. To our delight, methyl 3'-methoxybiphenyl-4-carboxylate (**3aa**) was isolated by column chromatography in 93% yield (Entry 4). Based on Entry 5, we could assume that CuI is only a co-catalyst, since no reaction was observed in the absence of Pd. Furthermore, TBAF is absolutely necessary since no reaction occurred in its absence (Entry 6). Nevertheless, TBAF is not the only fluoride source that can be used, CsF was equally efficient, giving similar yield of the coupling product **3aa** (Entry 7). The addition increasing amount of water (Entry 8), produced a mixture of **3aa**, the starting material and homocoupling product **5**. Such result was in agreement with a report by Sajiki and co-workers,[20] where they assumed that the addition of a large excess of water might speed up the formation of an inactive silanol polymer which decreases the reactivity of the silane. Regarding palladium source, $Pd(OAc)_2$ was not as efficient as $Pd(PPh_3)_4$ giving a mixture of **3aa** and the homocoupling product **5** (Entry 9).

To evaluate the scope and efficiency of the optimized methodology, we have synthesized a range of biaryl derivatives, achieving the same excellent results (Table 2). Complete conversion was obtained, in all cases with very high isolated yields. Both *para* and *meta*-substituted methyl iodobenzoates (**1a-b**) reacted smoothly with various *para* and *meta*-substituted aryltriethoxysilanes carrying an electron-donating or an electron-withdrawing group (Entries 1-13). Moreover, in the case of the *ortho*-substituted methyl iodobenzoate (**1c**), coupling with triethoxy(3-methoxyphenyl)silane (**2a**) and triethoxy(*p*-tolyl)silane (**2c**) gave also the corresponding 3' and 4'-substituted biphenyl-2-carboxylates (**3ca** and **3cc**) in very high isolated yield (82 and 88%), albeit longer reaction times were required (Entries 14 and 16). Apart from carboxy-substituted iodides, other aryl iodides were tested (Entries 17-30). They have proven to be very effective substrates for our Hiyama coupling conditions, including those bearing strong electron-donating groups (Entries 27-30). Following our aim to apply the Hiyama reaction to compounds of greater complexity and interest, we decided to use the optimized conditions on β-lactam derivatives. Thus, biaryl-contained β-lactams (**3id** and **3ie**) where obtained in very high isolated yield (Entries 31 and 32, Table 2).

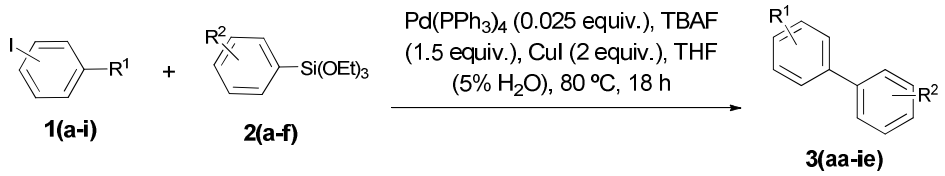
Since biaryl derivatives substituted with heteroatoms are present in biologically active structures,[21] we have extended the scope to the reaction with heteroaryl iodides and silanes. The 3-iodopyridine (**1j**), 2-iodothiophene (**1k**) and triethoxy(thiophen-2-yl)silane (**2g**) successfully underwent the coupling reaction to give the desired products in very high yields (Scheme 2).



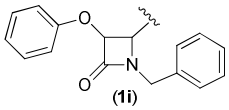
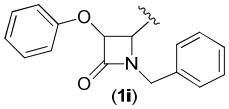
Scheme 2 Hiyama reaction using 3-iodopyridine (**1j**), 2-iodothiophene (**1k**) and triethoxy(thiophen-2-yl)silane (**2g**) as substrates.

A tentative mechanism for this undescribed version of the

Table 2 Synthesis of a variety of biaryl compounds by optimized reaction conditions.



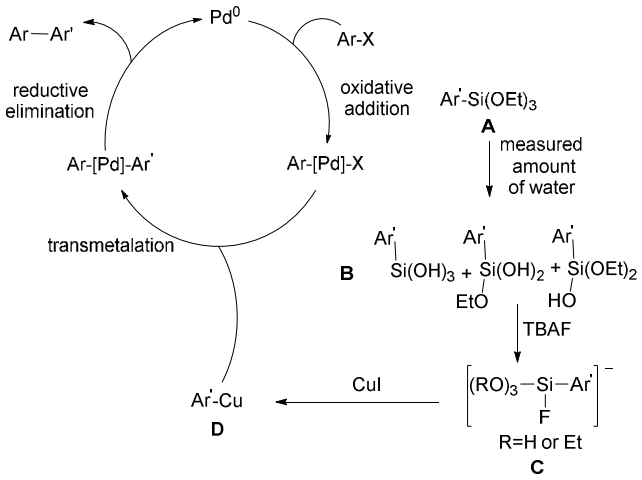
1(a-i) **2(a-f)** **3(aa-ie)**

Entry	Aryl iodide	Silane	Product	Yield (%)[a]
1	4-I, R^1=COOMe (**1a**)	R^2=3-OMe (**2a**)	**3aa**	93
2	4-I, R^1=COOMe (**1a**)	R^2=-H (**2b**)	**3ab**	84
3	4-I, R^1=COOMe (**1a**)	R^2=4-Me (**2c**)	**3ac**	98
4	4-I, R^1=COOMe (**1a**)	R^2=4-OMe (**2d**)	**3ad**	86
5	4-I, R^1=COOMe (**1a**)	R^2=4-Cl (**2e**)	**3ae**	93
6	4-I, R^1=COOMe (**1a**)	R^2=4-CF_3 (**2f**)	**3af**	77
7	4-I, R^1=COOMe (**1a**)	R^2=3-OMe (**2a**)	**3aa**	90[b]
8	3-I, R^1=COOMe (**1b**)	R^2=3-OMe (**2a**)	**3ba**	93
9	3-I, R^1=COOMe (**1b**)	R^2=-H (**2b**)	**3bb**	78
10	3-I, R^1=COOMe (**1b**)	R^2=-H (**2b**)	**3bb**	78[b]
11	3-I, R^1=COOMe (**1b**)	R^2=4-Me (**2c**)	**3bc**	76
12	3-I, R^1=COOMe (**1b**)	R^2=4-OMe (**2d**)	**3bd**	92
13	3-I, R^1=COOMe (**1b**)	R^2=4-Cl (**2e**)	**3be**	85
14	2-I, R^1=COOMe (**1c**)	R^2=3-OMe (**2a**)	**3ca**	82[c]
15	2-I, R^1=COOMe (**1c**)	R^2=-H (**2b**)	**3cb**	90[c]
16	2-I, R^1=COOMe (**1c**)	R^2=4-Me (**2c**)	**3cc**	88[c]
17	4-I, R^1=COMe (**1d**)	R^2=3-OMe (**2a**)	**3da**	91
18	4-I, R^1=COMe (**1d**)	R^2=-H (**2b**)	**3db**	88
19	4-I, R^1=COMe (**1d**)	R^2=4-Me (**2c**)	**3dc**	93
20	4-I, R^1=COMe (**1d**)	R^2=4-OMe (**2d**)	**3dd**	85
21	4-I, R^1=COMe (**1d**)	R^2=4-Cl (**2e**)	**3de**	91
22	4-I, R^1=Me (**1e**)	R^2=3-OMe (**2a**)	**3ea**	76
23	4-I, R^1=Me (**1e**)	R^2=4-OMe (**2d**)	**3ed**	93
24	4-I, R^1=Me (**1e**)	R^2=4-Cl (**2e**)	**3ee**	62[d]
25	I, R^1=H (**1f**)	R^2=3-OMe (**2a**)	**3fa**	88
26	I, R^1=H (**1f**)	R^2=4-OMe (**2d**)	**3fd**	93
27	4-I, R^1=NEt_2 (**1g**)	R^2=-H (**2b**)	**3gb**	65
28	4-I, R^1=NEt_2 (**1g**)	R^2=4-OMe (**2d**)	**3gd**	71
29	4-I, R^1=OMe (**1h**)	R^2=-H (**2b**)	**3fd**	95
30	4-I, R^1=OMe (**1h**)	R^2=4-Me (**2c**)	**3ed**	92
31	4-I, R^1=  (**1i**)	R^2=4-OMe (**2d**)	**3id**	68
32	4-I, R^1=  (**1i**)	R^2=4-Cl (**2e**)	**3ie**	90

[a]Yield calculated after purification by column chromatography. [b]Reaction carried out using 0.5 equiv. of CuI. [c]Reaction time: 40 h. [d]Yield calculated by ^{1}H NMR from an inseparable mixture of cross-coupling product **3ee** and homocoupling product from the silane **2e**.

aryl(trialkoxy)silane-type Hiyama coupling, involving the combination of adding cooper salts and a measured amount of water, is outlined in Scheme 3. It was theorized that a small amount of water could lead to a partial hydrolysis of the

arylalkoxysilanes (**A**) giving a mixture of the corresponding arilsilanol derivatives (**B**).[20] The electrophilic character of the silicon atom is strengthened by the formation of silanols **B**, facilitating the attack of the fluoride from TBAF to give the pentacoordinate arylsilicate anion **C**.[22] After the active complex **C** is formed, a transmetalation occurs in the presence of CuI to give the organocuprate intermediate **D**,[17] which, in turn, is subjected to a further transmetalation to give the organopalladium species which finally undergoes a reductive elimination to give the desired biaryl compound and regenerate the palladium (0) catalyst.[23]



Scheme 3 Plausible metal catalyzed mechanism of the Hiyama cross-coupling with copper iodide and measured amount of water.

Conclusions

In summary, we have developed a novel version of the Hiyama reaction in which the role of Cu(I) and a small amount of water is crucial for achieving very high yields, after purification by column chromatography. The reaction conditions were found to be applicable to the preparation of unsymmetrical biaryl compounds. Particularly outstanding is the generation of non-linearly substituted biphenyl derivatives, such as, for instance, 3,3', 3,4' and 4,3'-disubstituted biphenyl derivatives, which syntheses are scarcely reported and often achieved in low to moderate yields. From the best of our knowledge, the combination of adding cooper salts and a measured amount of water has not been yet applied to Hiyama coupling involving synthetically accessible aryl(trialkoxy)silanes. Further studies are in progress to extend of use of this protocol to the generation of libraries of biologically promising compounds.

Support from CONICET, ANPCyT, Fundación Prats and Universidad Nacional de Rosario from Argentina is gratefully acknowledged. C.I.T. thanks CONICET for fellowship.

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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23 Since we proposed that Cu(I) may be regenerated after the transmetalation process, a couple of test reactions were performed using 0.5 equiv. of CuI, obtaining similar yields to those using 2 equiv. of the Cu salt (Table 2, Entries 7 and 10).

Electronic Supplementary Information

Very efficient and broad-in-scope palladium-catalyzed Hiyama cross-coupling. The role of water and copper(I) salts.

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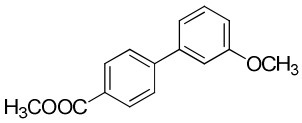
Content **Pages**

1.- Experimental Section

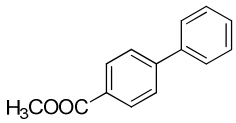
1.1.- General. ^{1}H NMR spectra were recorded in a Bruker Avance spectrometer at 300 MHz in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. ^{13}C NMR spectra were recorded on the same apparatus at 75 MHz with $CDCl_3$ as solvent and reference (76.9 ppm). The chemical shifts (δ) are reported in ppm downfield from TMS and coupling constants (*J*) are expressed in hertz. Mass spectra were recorded on a Shimadzu QP2010 Plus apparatus at an ionization voltage of 70 eV equipped with a SPB^{TM}-1 capillary column (internal diameter 0.25 mm, length 30 m). The high resolution mass spectra were obtained with a Bruker MicroTOF-Q II instrument (Bruker Daltonics, Billerica, MA). Detection of the ions was performed in electrospray ionization, positive ion mode. Solvents were dried using an MBraun solvent system (SPS-800). Analytical thin–layer chromatography (TLC) was carried out with silica gel 60 F254 pre–coated aluminum sheets. Flash column chromatography was performed using Merck silica gel 60 (230-400 mesh). Elution was carried out with hexane-EtOAc mixtures, under positive pressure and employing gradient of solvent polarity techniques. Chemical reagents were purchased from commercial sources and were used without further purification unless noted otherwise. Solvents were analytical grade or were purified by standard procedures prior to use. Triethoxysilanes were commercially available except **2f** and **2g** which were prepared following the methodology described by DeShong[1].

1.2.- General Procedure: Aryl halide **1** (0.11 mmol), $Pd(PPh_3)_4$ (0.025 equiv.) and CuI (2 equiv.) were combined in a round bottom flask and placed under argon. THF (4 mL) were added, followed by phenyltriethoxysilane **2** (1.5 equiv.), TBAF (1.5 equiv., 1.0 M in THF) and H_20 (0.2 mL). The flask was fitted with a condenser and the reaction mixture was stirred 7 h at 80 ºC. The reaction mixture was evaporated and the crude product was analyzed by ^{1}H NMR and GC/MS and then purified by column chromatography (hexane-EtOAc).



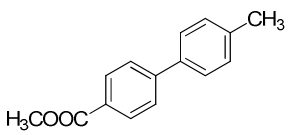
Methyl 3′-methoxy-(1,1′-biphenyl)-4-carboxylate (3aa): employing General Procedure, with methyl 4-iodobenzoate (**1a**) (30 mg, 0.11 mmol) as starting material and triethoxy(3-methoxyphenyl)silane (**2a**), desired product **3aa** was isolated in 93% yield.

Characterization of **3aa**:[2] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.87 (s, 3H), 3.94 (s, 3H), 6.94 (dd, *J* = 8.1 and 1.9 Hz, 1H), 7.15 (t, *J* = 1.9 Hz, 1H), 7.21 (da, *J* = 8.1, 1H), 7.38 (t, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 8.10 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 52.2, 55.4, 113.0, 113.5, 119.8, 127.1, 129.0, 129.9, 130.1, 141.5, 145.5, 160.0, 167.0. GC/MS: ^{t}R 21.66 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 242 (M^+), 211 (100).



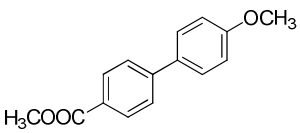
Methyl-4-biphenylcarboxylate (3ab): employing General Procedure, with methyl 4-iodobenzoate (**1a**) (30 mg, 0.11 mmol) as starting material and triethoxy(phenyl)silane (**2b**), desired product **3ab** was isolated in 84% yield.

Characterization of **3ab**:[3] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.95 (s, 3H), 7.36-7.51 (m, 3H), 7.60-7.70 (m, 4H), 8.12 (d, *J* = 8.26 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 52.1, 127.0, 127.2, 128.1, 128.9, 130.1, 140.0, 145.6, 167.0. GC/MS: ^{t}R 20.0 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 212 (M^+), 181 (100).



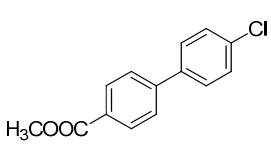
Methyl 4′-methyl-(1,1′-biphenyl)-4-carboxylate (3ac): employing General Procedure, with methyl 4-iodobenzoate (**1a**) (30 mg, 0.11 mmol) as starting material and triethoxy(p-tolyl)silane (**2c**), desired product **3ac** was isolated in 98% yield.

Characterization of **3ac**:[4] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.41 (s, 3H), 3.94 (s, 3H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 8.09 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 21.1, 52.1, 126.7, 127.1, 128.5, 129.6, 130.0, 137.1, 138.1, 145.5, 167.0. GC/MS: ^{t}R 21.16 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 226 (M^+), 195 (100).



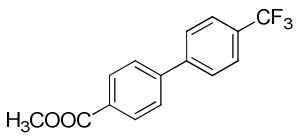
Methyl 4′-methoxy-(1,1′-biphenyl)-4-carboxylate (3ad): employing General Procedure, with methyl 4-iodobenzoate (**1a**) (30 mg, 0.11 mmol) as starting material and triethoxy(4-methoxyphenyl)silane (**2d**), desired product **3ad** was isolated in 86% yield.

Characterization of **3ad**:[2] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.86 (s, 3H), 3.93 (s, 3H), 6.99 (d, *J* = 8.6 Hz, 2H), [7.57 (d, *J* = 8.6 Hz), 7.61 (d, *J* = 8.3 Hz), 4H], 8.08 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 52.1, 55.4, 114.4, 126.6, 128.4, 128.5, 130.1, 132.4, 145.2, 159.8, 167.0. GC/MS: ^{t}R 22.95 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 242 (M^+, 100).



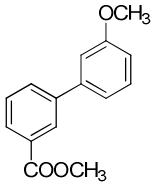
Methyl 4′-chloro-(1,1′-biphenyl)-4-carboxylate (3ae): employing General Procedure, with methyl 4-iodobenzoate (**1a**) (30 mg, 0.11 mmol) as starting material and triethoxy(4-chlorophenyl) silane (**2e**), desired product **3ae** was isolated in 93% yield.

Characterization of **3ae**:[5] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.94 (s, 3H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 8.10 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 52.2, 126.9, 128.5, 129.1, 129,2, 130.2, 134.3, 138.4, 144.3, 166.9. GC/MS: ^{t}R 22.1 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 246 (M^+), 215 (100).



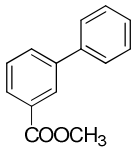
Methyl 4′-Trifluoromethyl-(1,1′-biphenyl)-4-carboxylate (3af): employing General Procedure, with methyl 4-iodobenzoate (**1a**) (30 mg, 0.11 mmol) as starting material and triethoxy(4-(trifluoromethyl)phenyl)silane (**2f**), desired product **3af** was isolated in 77% yield.

Characterization of **3af**:[6] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.96 (s, 3H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.73 (s, 4H), 8.14 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (75 MHz, CDCl3): δ 52.4, 126.0 (q, *J* = 3.8 Hz), 126.1, 127.4, 127.8, 129.9, 130.4, 143.7, 143.7, 144.2, 166.9. GC/MS: ^{t}R 19.8 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 280 (M^+), 249 (100).



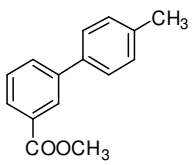
Methyl 3′-methoxy-(1,1′-biphenyl)-3-carboxylate (3ba): employing General Procedure, with methyl 3-iodobenzoate (**1b**) (30 mg, 0.11 mmol) as starting material and triethoxy(3-methoxyphenyl)silane (**2a**), desired product **3ba** was isolated in 93% yield.

Characterization of **3ba**:[7] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.88 (s, 3H), 3.95 (s, 3H), 6.93 (ddd, *J* = 8.0 and 2.6 Hz, 1H), 7.15 (t, *J* = 2.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.50 (t, *J* =7.7 Hz, 1H), 7.78 (ddd, 7.7, 1.6 and 1.2 Hz, 1H), 8.02 (dt, *J* = 7.7 and 1.6 Hz, 1H), 8.28 (t, *J* =1.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 52.1, 55.3, 112.9, 113.1, 119.6, 128.2, 128.5, 128.8, 129.9, 130.6, 131.5, 141.3, 141.6, 160.0, 167.0. GC/MS: ^{t}R 21.2 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 242 (M^+, 100).



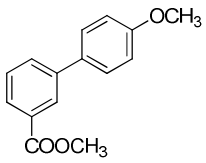
Methyl-3-biphenylcarboxylate (3bb): employing General Procedure, with methyl 3-iodobenzoate (**1b**) (30 mg, 0.11 mmol) as starting material and triethoxy(phenyl)silane (**2b**), desired product **3bb** was isolated in 78% yield.

Characterization of **3bb**:[4] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.95 (s, 3H), 7.34-7.56 (m, 4H), 7.63 (d, *J* = 7.1 Hz, 2H), 7.79 (d, *J* = 7.7 Hz, 1H), 8.02 (d, *J* = 7.7 Hz, 1H), 8.28 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 52.2, 127.1, 127.7, 128.2, 128.3, 128.8, 128.8, 130.7, 131.5, 140.1, 141.4, 167.0. GC/MS: ^{t}R 18.98 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 212 (M^+), 181 (100).



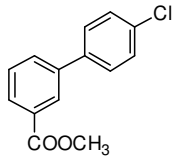
Methyl 4′-methyl-(1,1′-biphenyl)-3 –carboxylate (3bc): employing General Procedure, with methyl 3-iodobenzoate (**1b**) (30 mg, 0.11 mmol) as starting material and triethoxy(p-tolyl)silane (**2c**), desired product **3bc** was isolated in 76% yield.

Characterization of **3bc**:[8] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.41 (s, 3 H), 3.95 (s, 3H), 7.27 (d, *J* = 8.3 Hz, 2 H), 7.47-7.55 (m, 3H), 7.77 (dt, *J* = 7.5 and 1.3 Hz, 1H), 8.0 (dt, *J* = 7.5 and 1.3 Hz, 1H), 8.28 (t, *J* = 1.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 21.1, 52.1, 126.9, 128.0, 128.8, 129.6, 130.6, 131.3, 137.2, 137.6, 141.4, 167.1. GC/MS: ^{t}R 19.9 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 226 (M^+, 100).



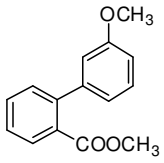
Methyl 4′-methoxy(1,1′-biphenyl)-3-carboxylate (3bd): employing General Procedure, with methyl 3-iodobenzoate (**1b**) (30 mg, 0.11 mmol) as starting material and triethoxy(4-methoxyphenyl)silane (**2d**), desired product **3bd** was isolated in 92% yield.

Characterization of **3bd**:[2] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.86 (s, 3H), 3.95 (s, 3H), 7.00 (d, *J* = 8.7 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 8.24 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 52.2, 55.2, 127.1, 127.7, 128.2, 128.3, 128.8, 128.8, 130.7, 131.5, 140.1, 141.4, 167.0. GC/MS: ^{t}R 21.9 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 242 (M^+, 100).



Methyl 4′-chloro-(1,1′-biphenyl)-3-carboxylate (3be): employing General Procedure, with methyl 3-iodobenzoate (**1b**) (30 mg, 0.11 mmol) as starting material and (4-chlorophenyl)triethoxysilane (**2e**), desired product **3be** was isolated in 85% yield.

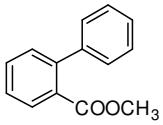
Characterization of **3be**:[9] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.95 (s, 3H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.48-7.56 (m, 3H), 7.73 (dd, *J* = 7.6 and 1.5 Hz, 1H), 8.03 (dt, *J* = 7.6 and 1.3 Hz, 1H), 8.23 (t, *J* = 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 52.2, 128.0, 128.4, 128.6, 129.0, 129.0, 130.8, 131.3, 133.9, 138.5, 140.2, 166.8. GC/MS: ^{t}R 20.8 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 246 (M^+, 100).



Methyl 3′-methoxy-(1,1′-biphenyl)-2-carboxylate (3ca): employing General Procedure, with methyl 2-iodobenzoate (**1c**) (30 mg, 0.11 mmol) as starting material and triethoxy(3-methoxyphenyl)silane (**2a**), desired product **3ca** was isolated in 82% yield.

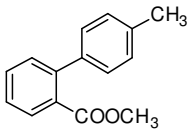
Characterization of **3ca**:[2] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.65 (s, 3H), 3.83 (s, 3H), 6.87-6.92 (m, 3H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.37-7.44 (m, 2H), 7.52 (dt, *J* = 7.5 and 1.4 Hz, 1H), 7.79-7.82 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 52.0, 55.2, 112.8, 113.8, 120.9, 127.2, 129.0, 129.6, 130.5, 131.0, 131.1, 142.2,

142.7, 159.3, 169.1. GC/MS: ^{t}R 19.19 min (50°C (3 min), 10 °C/min, 300°C, 49.6 kPa). *m/z* (%) 242 (M^+, 100).



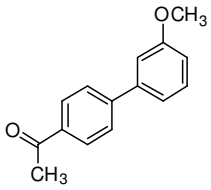
Methyl-(1,1′-biphenyl)-2-carboxylate (3cb): employing General Procedure, with methyl 2-iodobenzoate (**1c**) (30 mg, 0.11 mmol) as starting material and triethoxy(phenyl)silane (**2b**), desired product **3cb** was isolated in 90% yield.

Characterization of **3cb**:[10] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.64 (s, 3H), 7.30-7.44 (m, 7H), 7.52 (td, *J* = 7.5 and 1.4 Hz, 1H), 7.83 (dd, *J* = 7.7 and 0.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 51.9, 127.1, 127.2, 128.0, 128.3, 129.7, 169.1, 130.8, 131.2, 141.3, 142.4, 169.1. GC/MS: ^{t}R 16.5 min (50°C (3 min), 10 °C/min, 300°C, 49.6 kPa). *m/z* (%) 212 (M^+), 181 (100).



Methyl 4′-methyl-(1,1′-biphenyl)-2-carboxylate (3cc): employing General Procedure, with methyl 2-iodobenzoate (**1c**) (30 mg, 0.11 mmol) as starting material and triethoxy(p-tolyl)silane (**2c**), desired product **3cc** was isolated in 88% yield.

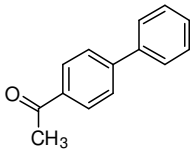
Characterization of **3cc**:[11] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.40 (s, 3H), 3.67 (s, 3H), 7.21 (s, 4H), 7.36-7.42 (m, 2H), 7.49-7.54 (m, 1H), 7.81 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 21.2, 51.9, 126.9, 128.8, 128.2, 129.7, 130.7, 130.8, 131.2, 136.9, 138.3, 142.4, 169.2. GC/MS: ^{t}R 17.7 min (50°C (3 min), 10 °C/min, 300°C, 49.6 kPa). *m/z* (%) 226 (M^+), 195 (100).



1-(3′-methoxy-[1,1′-biphenyl]-4-yl)ethanone (3da): employing General Procedure, with 4-iodoacetophenone (**1d**) (30 mg, 0.12 mmol) as starting material and triethoxy(3-methoxyphenyl)silane (**2a**), desired product **3da** was isolated in 91% yield.

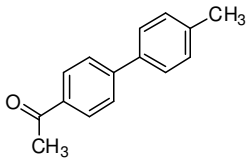
Characterization of **3da**:[16] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.63 (s, 3H), 3.87 (s, 3H), 6.95 (ddd, *J* = 7.9, 2.50 and 1.2 Hz, 1H), 7.15 (t, *J* = 1.2 Hz, 1H), 7.21 (dt, *J* = 7.9 and 1.2 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 8.02 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 26.6, 55.3, 113.0, 113.5, 119.7,

127.2, 128.8, 129.9, 135.9, 141.3, 145.6, 160.0, 197.7. GC/MS: ^{t}R 21.2 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 226 (M^+), 211 (100).



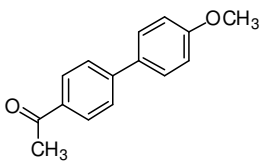
1-([1,1′-biphenyl]-4-yl)ethanone (3db): employing General Procedure, with 4-iodoacetophenone (**1d**) (30 mg, 0.12 mmol) as starting material and triethoxy(phenyl)silane (**2b**), desired product **3db** was isolated in 88% yield.

Characterization of **3db**:[4] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.64 (s, 2.64), 7.40-7.50 (m, 3H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 8.04 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 26.6**,** 127.2, 127.2, 128.2, 128.9, 128.9, 135.8, 139.8, 145.7, 197.7. GC/MS: ^{t}R 18.4 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 196 (M^+), 181(100).



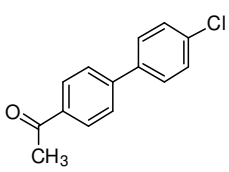
1-(4′-methyl-[1,1′-biphenyl]-4-yl)ethanone (3dc): employing General Procedure, with 4-iodoacetophenone (**1d**) (30 mg, 0.12 mmol) as starting material and triethoxy(p-tolyl)silane (**2c**), desired product **3dc** was isolated in 93% yield.

Characterization of **3dc**:[12] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.41 (s, 3H), 2.63 (s, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 21.1, 26.6, 126.9, 127.1, 128.9, 129.6, 135.6, 136.9, 138.2, 145.7, 197.74. GC/MS: ^{t}R 19.8 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 210 (M^+), 195 (100).



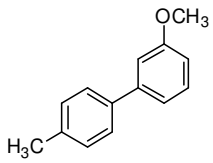
1-(4′-methoxy-[1,1′-biphenyl]-4-yl)ethanone (3dd): employing General Procedure, with 4-iodoacetophenone (**1d**) (30 mg, 0.12 mmol) as starting material and triethoxy(4-methoxyphenyl)silane (**2d**), desired product **3dd** was isolated in 85% yield.

Characterization of **3dd**:[5] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.62 (s, 3H), 3.86 (s, 3H), 7.00 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 26.6, 55.3, 114.4, 126.6, 128.3, 128.9, 132.2, 135.2, 145.3, 159.9, 197.7. GC/MS: ^{t}R 21.4 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 226 (M^+), 211 (100).



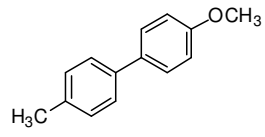
1-(4′-chloro-[1,1′-biphenyl]-4-yl)ethanone (3de): employing General Procedure, with 4-iodoacetophenone (**1d**) (30 mg, 0.12 mmol) as starting material and (4-chlorophenyl)triethoxysilane (**2e**), desired product **3de** was isolated in 91% yield.

Characterization of **3de**:[12] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.64 (s, 3H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 26.6, 127.0, 128.5, 129.0, 129.1, 134.4, 136.1, 138.2, 144.4, 197.5. GC/MS: ^{t}R 20.6 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 230 (M^+), 215 (100).



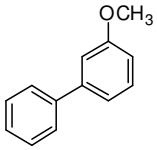
3-methoxy-4'-methyl-1,1'-biphenyl (3ea): employing General Procedure, with 4-iodotoluene (**1e**) (30 mg, 0.14 mmol) as starting material and triethoxy(3-methoxyphenyl)silane (**2a**), desired product **3ea** was isolated in 76% yield.

Characterization of **3ea**:[13] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.42 (s, 3H), 3.88 (s, 3H), 6.90 (d, *J* = 7.9 and 1.9 Hz, 1H), 7.14 (t, *J* = 1.9 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.36 (dd, *J* = 7.9 and 7.6 Hz, 1H), 7.52 (d, *J* = 8.0, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 21.1, 29.7, 55.2, 112.4, 112.7, 112.9, 119.5, 119.7, 127.0, 127.2, 127.4, 128.7, 129.4, 129.7, 137.2, 138.2, 142.7, 159.9. GC/MS: ^{t}R 18.2 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 198 (M^+, 100).



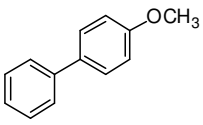
4-methoxy-4'-methyl-1,1'-biphenyl (3ed): employing General Procedure, with 4-iodotoluene (**1e**) (30 mg, 0.14 mmol) as starting material and triethoxy(4-methoxyphenyl)silane (**2d**), desired product **3ed** was isolated in 93% yield.

Characterization of **3ed**:[5] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.40 (s, 3H), 3.86 (s, 3H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 21.0**,** 55.3, 114.1, 126.6, 126.7, 127.9, 128.1, 128.7, 129.4, 133.7, 136.3, 137.9, 158.9. GC/MS: ^{t}R 18.0 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 198 (M^+, 100).



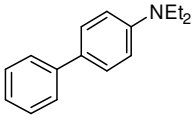
3-methoxy-1,1'-biphenyl (3fa): employing General Procedure, with 4-iodobencene (**1f**) (36.6 mg, 0.18 mmol) as starting material and triethoxy(3-methoxyphenyl)silane (**2a**), desired product **3fd** was isolated in 88% yield.

Characterization of **3fa**:[14] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.88 (s, 3H), 6.92 (dd, *J* = 5.7 and 2.3 Hz, 1H), 7.15-7.22 (m, 2H), 7.34-7.48 (m, 4H), 7.60-7.63 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 55.3, 112.7, 112.9, 119.7, 127.2, 127.4, 128.7, 129.7, 141.1, 142.8, 159.9. GC/MS: ^{t}R 16.4 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 184 (M^+, 100).



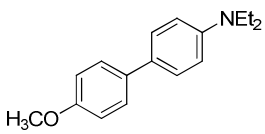
4-methoxy-1,1'-biphenyl (3fd): employing General Procedure, with 4-iodobencene (**1f**) (36.6 mg, 0.18 mmol) as starting material and triethoxy(4-methoxyphenyl)silane (**2d**), desired product **3fd** was isolated in 93% yield.

Characterization of **3fd**:[5] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.87 (s, 3H), 7.00 (d, *J* = 8.8 Hz, 2H), 7.31-7.35 (m, 1H), 7.41-7.45 (m, 2H), 7.55-7.60 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 55.3, 114.2, 126.6, 126.7, 128.1, 128.7, 133.8, 140.8, 159.1. GC/MS: ^{t}R 16.6 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 184 (M^+, 100).



N,N-diethyl-[1,1'-biphenyl]-4-amine (3gb): employing General Procedure, with N,N-diethyl-4-iodoaniline (**1g**) (45 mg, 0.16 mmol) as starting material and triethoxy(phenyl)silane (**2b**), desired product **3gb** was isolated in 65% yield.

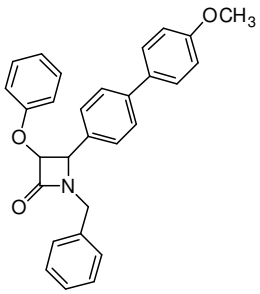
Characterization of **3gb**:[15] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.20 (t, *J* = 7.1 Hz, 6H), 3.40 (q, *J* = 7.1 Hz, 4H), 6.75 (d, *J* = 8.8 Hz, 2H), 7.21-7.26 (m, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 12.6, 44.4, 111.9, 125.7, 126.1, 127.9, 128.1, 128.6, 141.3, 147.1. GC/MS: ^{t}R 20.27 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 225 (M^+), 210 (100).



N,N-diethyl-4'-methoxy-[1,1'-biphenyl]-4-amine (3gd): employing General Procedure, with N,N-diethyl-4-iodoaniline (**1g**) (34 mg, 0.12 mmol) as starting material and triethoxy(4-methoxyphenyl)silane (**2d**), desired product **3gd** was isolated in 71% yield.

Characterization of **3gd**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.19 (t, *J* = 7.1 Hz, 6H), 3.39 (q, *J* = 7.1 Hz, 4H), 3.83 (s, 3H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 12.9, 44.9, 55.5, 112.9, 115.1, 127.6, 128.0, 134.6, 159.3. HRMS (ESI) m/z 256.16933 [(M + H^+); calcd for $C_{17}H_{22}NO$: 256.16959].

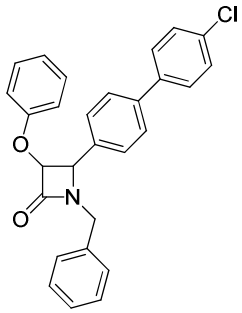
1-benzyl-4-(4'-methoxy-[1,1'-biphenyl]-4-yl)-3-phenoxyazetidin-2-one (3id):



employing General Procedure, with 1-benzyl-4-(4-iodophenyl)-3-phenoxyazetidin-2-one (**1i**) (30 mg, 0.066 mmol) as starting material and triethoxy(4-methoxyphenyl)silane (**2d**), desired product **3id** was isolated in 68% yield.

Characterization of **3id**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.85 (s, 3H), 3.91 (d, *J* = 14.7 Hz, 1H), 4.79 (d, *J* = 4.2 Hz, 1H), 4.92 (d, *J* = 14.7 Hz, 1H), 5.43 (d, *J* = 4.2 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 2H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 2H), 7.18-7.21 (m, 2H), 7.31-7.34 (m, 5H), 7.46-7.52 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 44.2, 55.3, 61.2, 82.2, 114.2, 115.6, 122.0, 126.4, 128.0, 128.0, 128.6, 128.9, 129.1, 129.2, 131.0, 132.9, 134.8, 141.0, 157.0, 159.3, 165.6. HRMS (ESI) m/z 458.1705 [(M + Na^+); calcd for $C_{29}H_{25}O_3Na$: 458.17266].

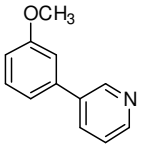
1-benzyl-4-(4'-chloro-[1,1'-biphenyl]-4-yl)-3-phenoxyazetidin-2-one (3ie):



employing General Procedure, with 1-benzyl-4-(4-iodophenyl)-3-phenoxyazetidin-2-one (**1i**) (30 mg, 0.066 mmol) as starting material and (4-chlorophenyl)triethoxysilane (**2e**), desired product **3ie** was isolated in 90% yield.

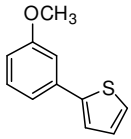
Characterization of **3ie**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.91

(d, *J* = 14.7 Hz, 1H), 4.79 (d, *J* = 4.5 Hz, 1H), 4.91 (d, *J* = 14.7 Hz, 1H), 5.42 (d, *J* = 4.5 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 2H), 6.87 (t, *J* = 7.38 Hz, 1H), 7.09-7.14 (m, 2H), 7.18-7.20 (m, 2H), 7.32-7.41 (m, 7H), 7.46-7.49 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 44.2, 61.1, 82.2, 115.6, 122.0, 126.8, 128.0, 128.2, 128.6, 128.9, 128.9, 129.2, 132.1, 133.6, 134.7, 138.8, 140.2, 156.9, 165.5. HRMS (ESI) m/z 462.12404 [(M + Na^+); calcd for $C_{28}H_2ClNaO_2$: 462.12313].



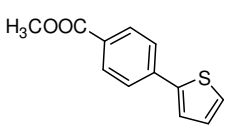
3-(3-methoxyphenyl)pyridine (3ja): employing General Procedure, with 3-iodopyridine (**1j**) (30 mg, 0.15 mmol) as starting material and triethoxy(3-methoxyphenyl)silane (**2a**), desired product **3ja** was isolated in 87% yield.

Characterization of **3ja**:[2] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.87 (s, 3H), 6.95 (ddd, *J* = 8.3, 2.4 and 0.9 Hz, 1H), 7.10 (t, *J* = 2.4 Hz, 1H), 7.15-7.18 (m, 1H), 7.33-7.42 (m, 2H), 7.85 (dt, *J* = 7.9 and 1.6 Hz, 1H), 8.59 (dd, *J* = 4.8 and 1.6 Hz, 1H), 8.85 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 55.3, 112.9, 113.4, 119.6, 123.5, 130.1, 134.4, 136.5, 139.3, 148.3, 148.6, 160.1. GC/MS: ^{t}R 17.15 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 185 (M^+, 100).



2-(3-methoxyphenyl)thiophene (3ka): employing General Procedure, with 2-iodothiophene (**1k**) (38 mg, 0.18 mmol) as starting material and triethoxy(3-methoxyphenyl)silane (**2a**), desired product **3ka** was isolated in 93% yield.

Characterization of **3ka**:[16] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.86 (s, 3H), 6.85 (ddd, *J* = 8.0, 2.4 and 0.9 Hz, 1H), 7.08 (dd, *J* = 5.0 and 3.6 Hz, 1H), 7.17 (ta, *J* = 2.1 Hz, 1H), 7.21-7.24 (m, 1H), 7.28-7.33 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 55.3, 111.6, 112.9, 118.6, 123.3, 124.9, 127.9, 129.9, 135.7, 144.2, 159.9. GC/MS: ^{t}R 16.55 min (50℃ (3 min), 10 ℃/min, 300℃, 49.6 kPa). *m/z* (%) 190 (M^+, 100).



2-(4-methoxycarbonylphenyl)thiophene (3ag): employing General Procedure, with methyl 4-iodobenzoate (**1a**) (30 mg, 0.11 mmol) as starting material and triethoxy(thiophen-2-yl)silane (**2g**), desired product **3ag** was isolated in 88% yield.

Characterization of **3ag**:[17] ^{1}H NMR ($CDCl_3$, 300 Hz) 3.93 (s, 3 H) 7.11 (dd, *J* = 5.3 and 3.8 Hz, 1H), 7.35-737 (m, 1H) 7.41-7.43 (m, 1H) 7.67 (d, *J* = 8.4 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 52.1, 124.5, 125.5, 1126.3, 128.3, 128.8, 130.3, 138.6, 143.1, 166.7. GC/MS: ^{t}R 18.97 min (50 ℃ (3 min), 10 ℃/min, 300 ℃, 49.6 kPa). *m/z* (%) 187 (100), 218 (M^+).

2.- References

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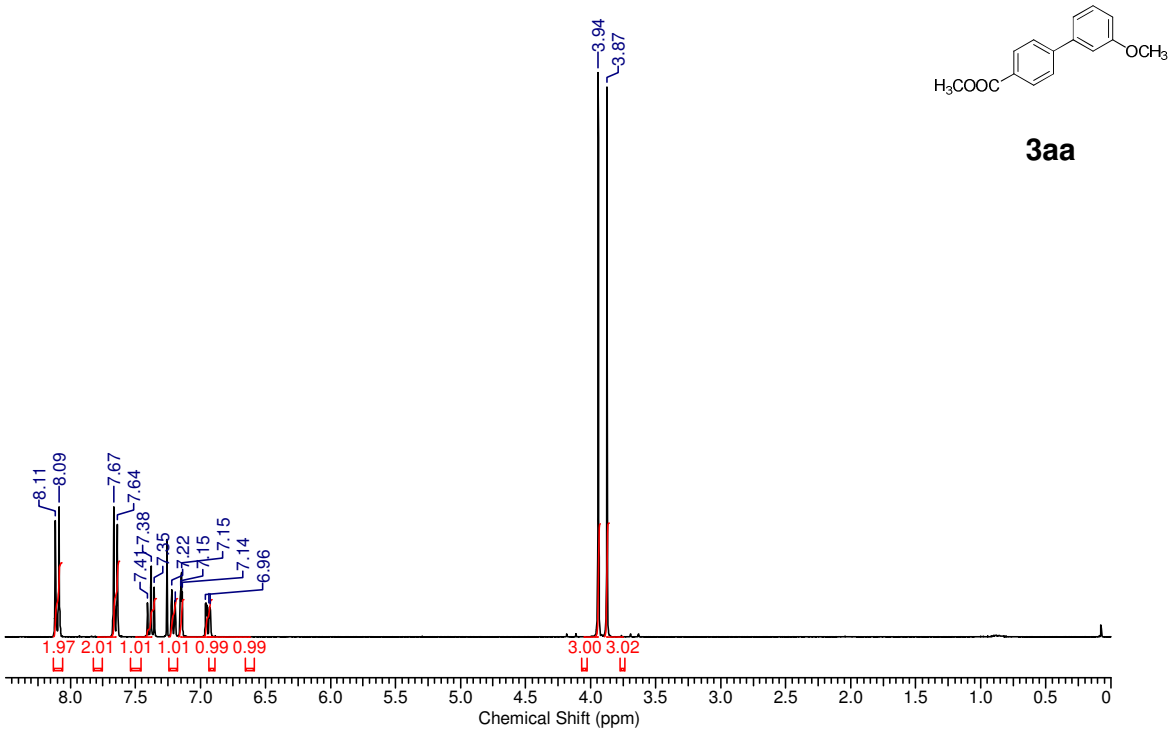
3.- ^{1}H NMR and ^{13}C NMR Spectra



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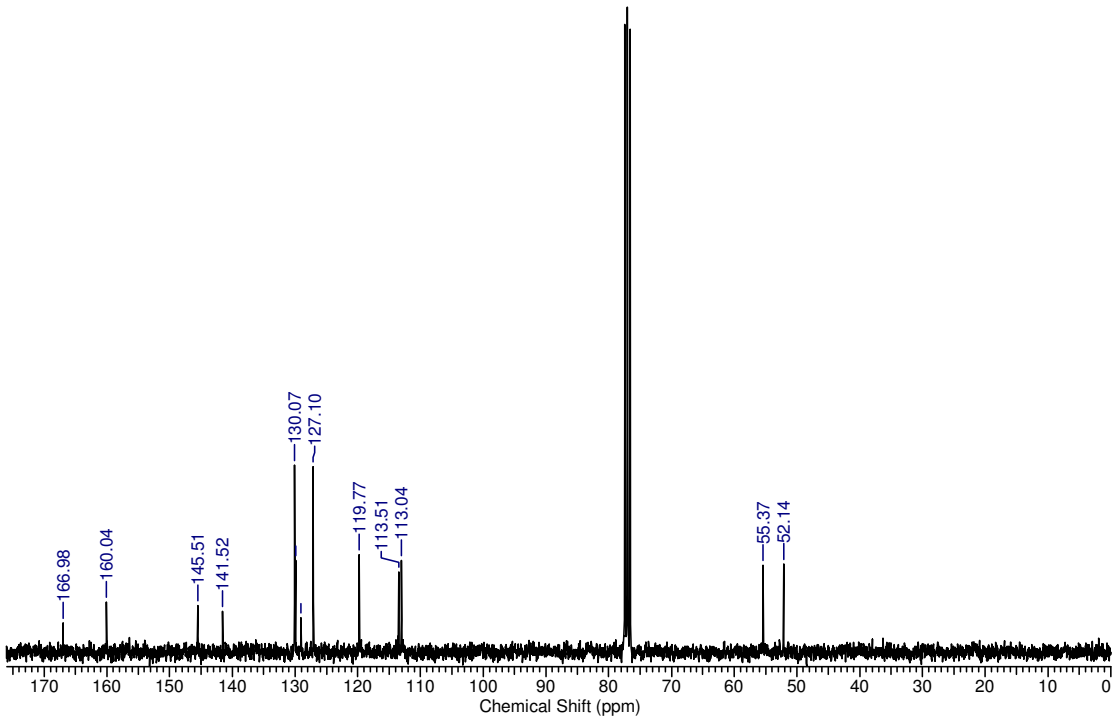

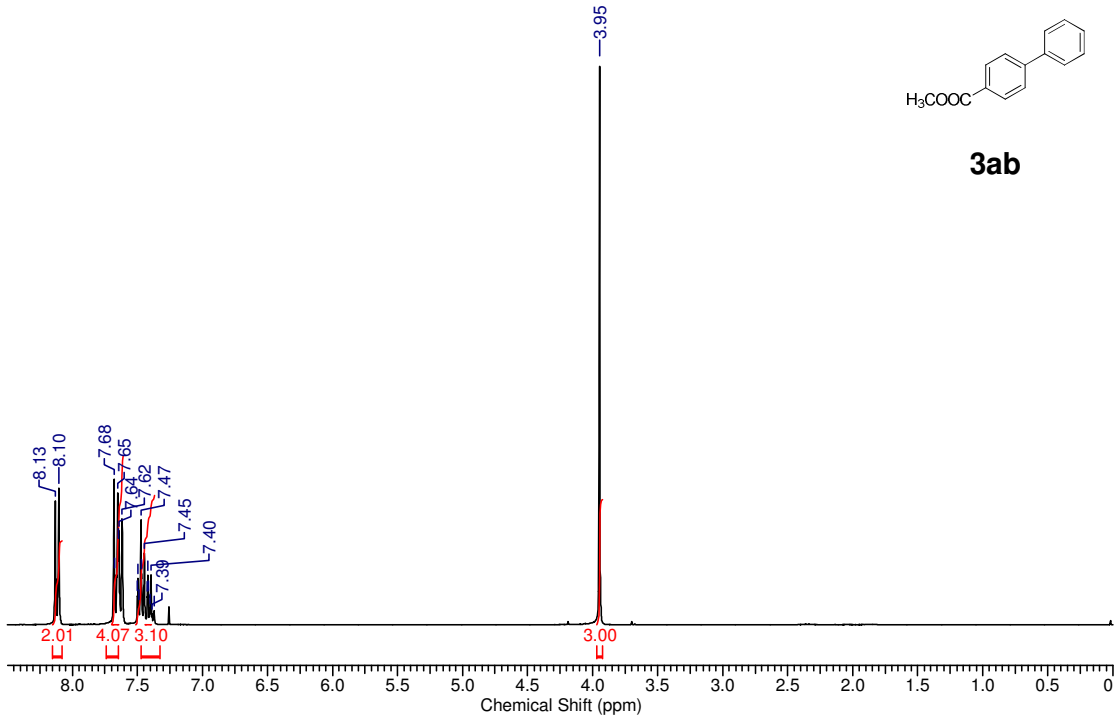

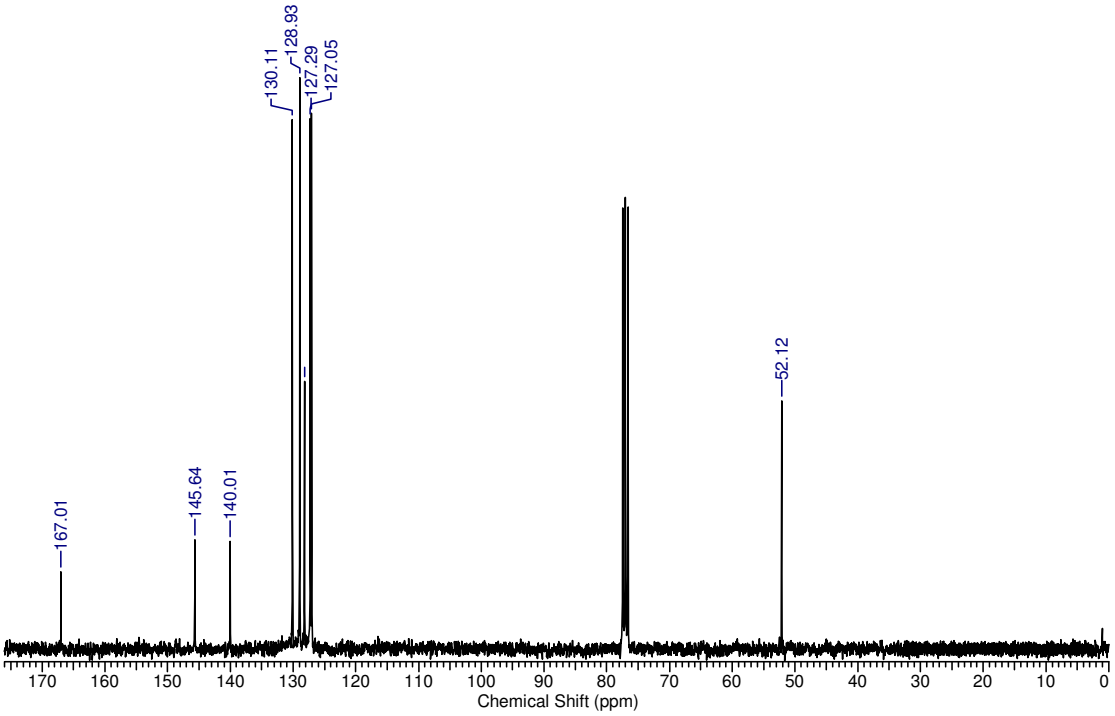

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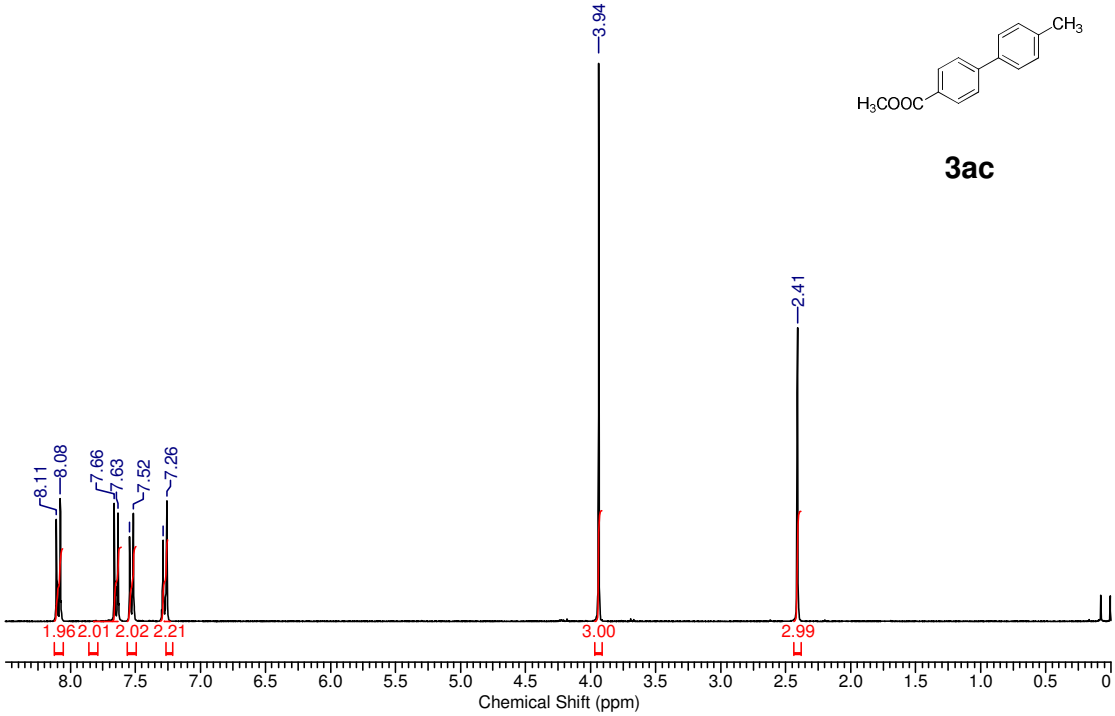

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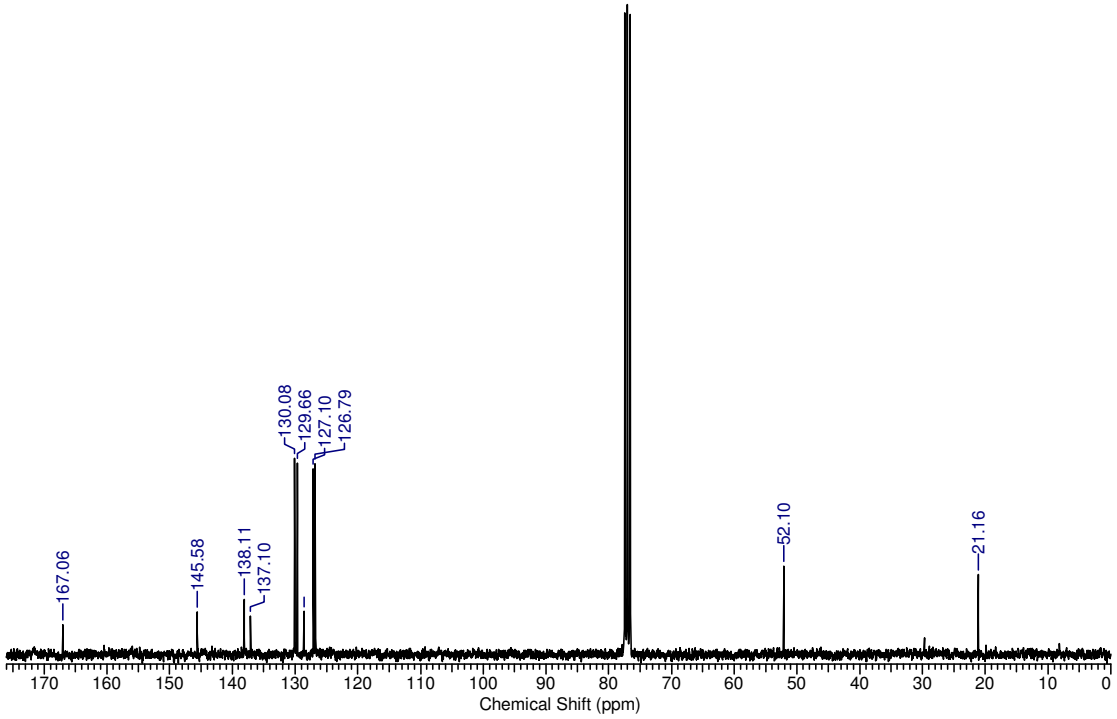

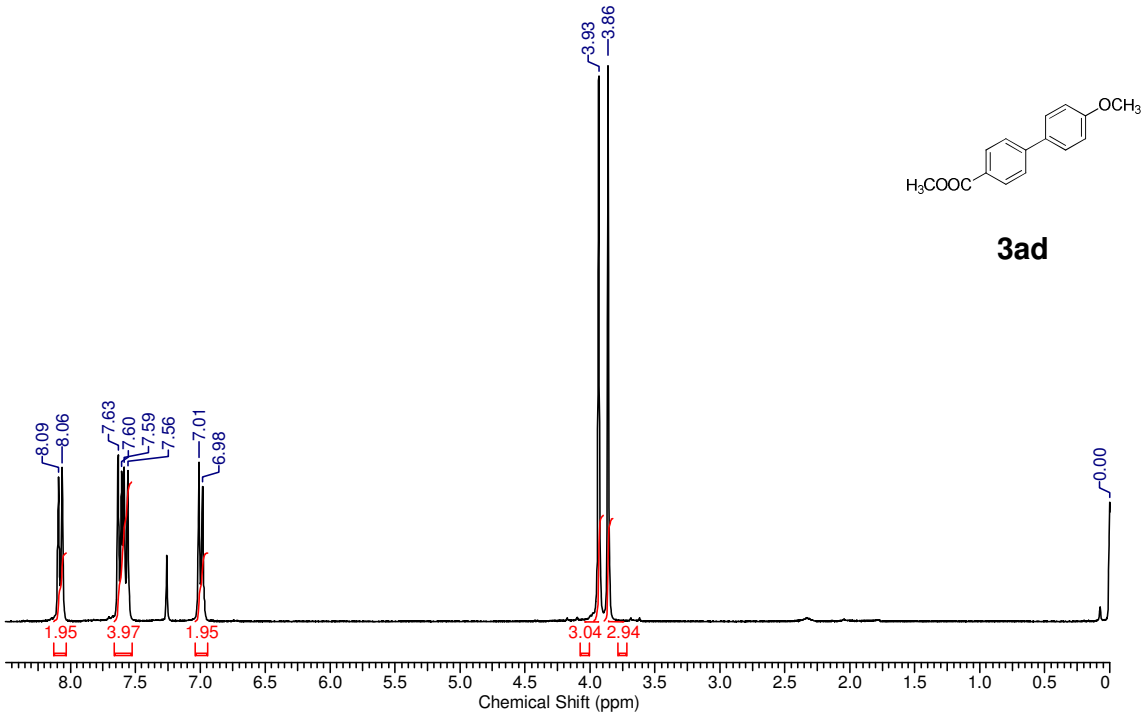

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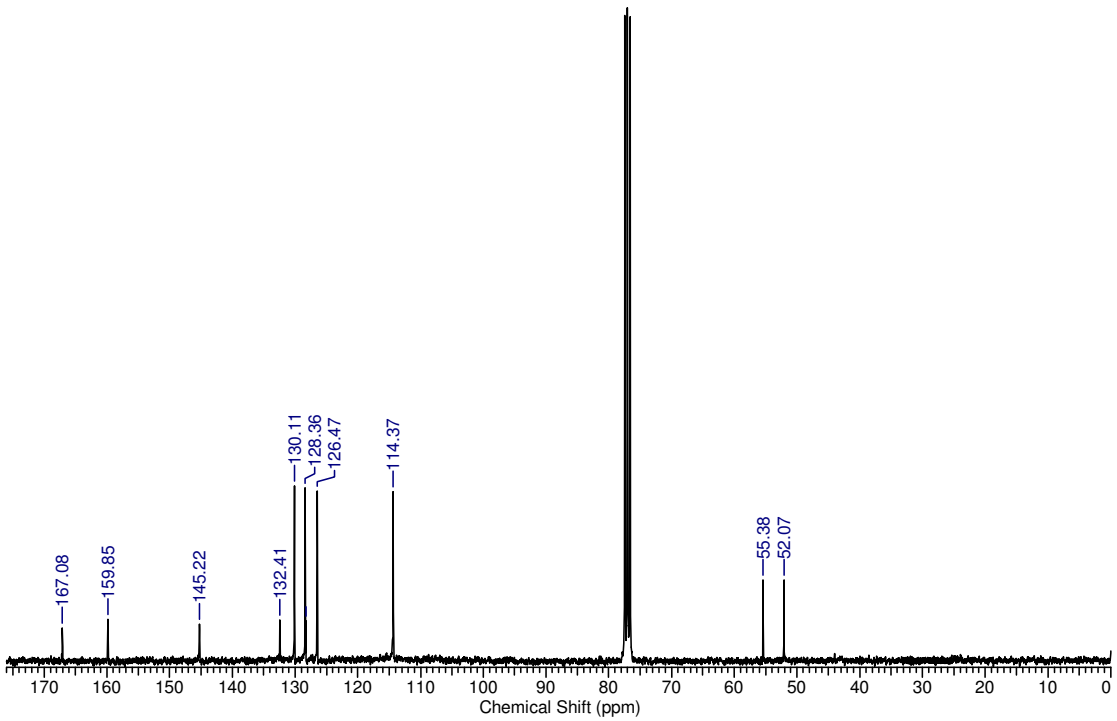
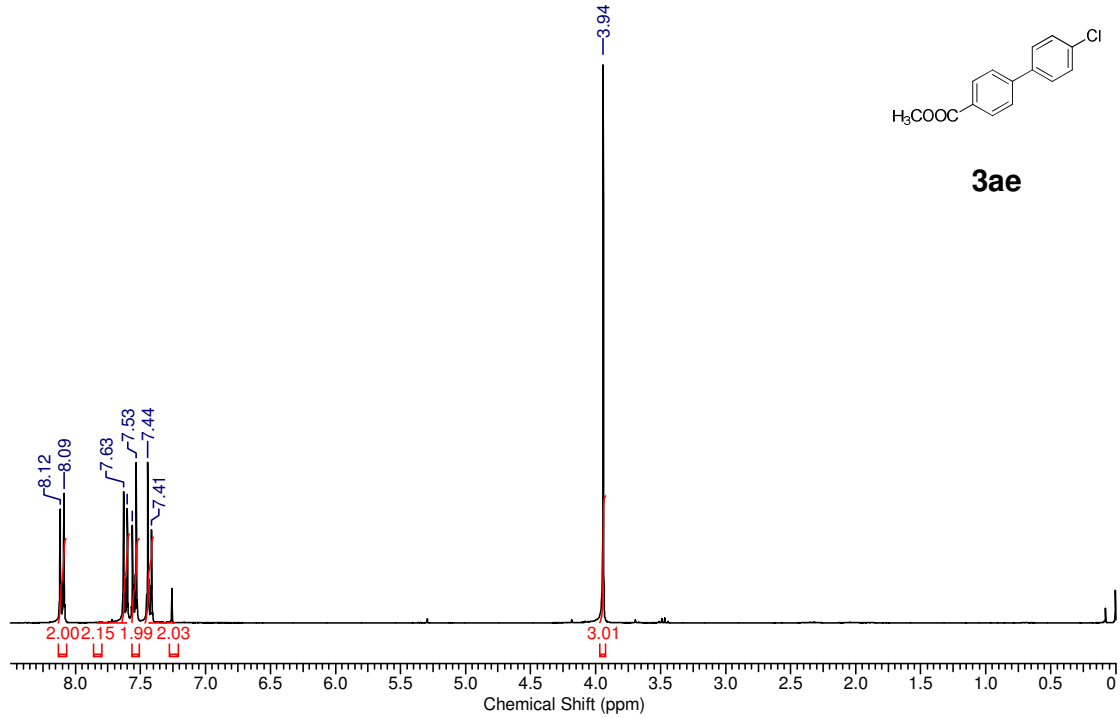
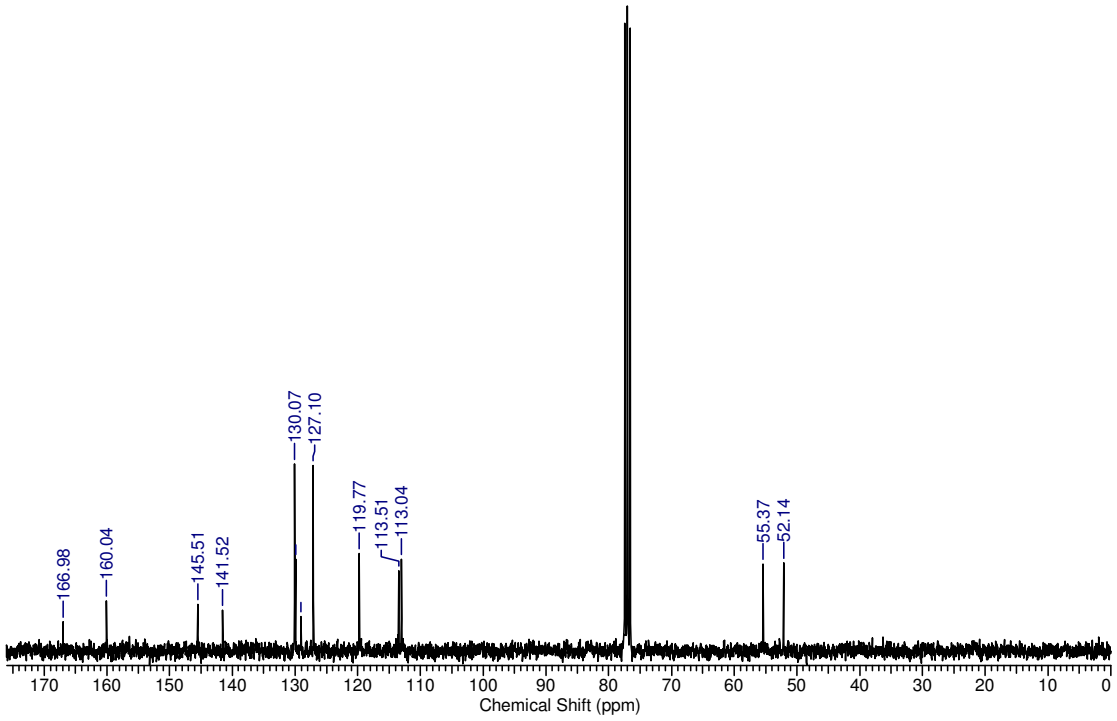
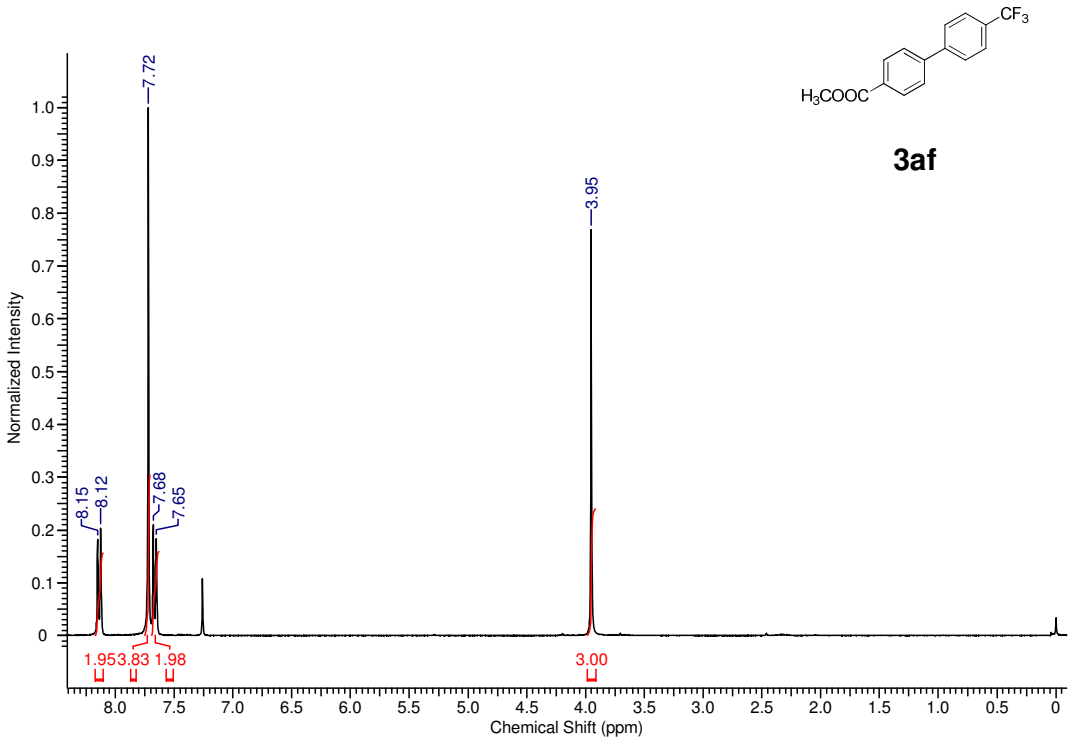
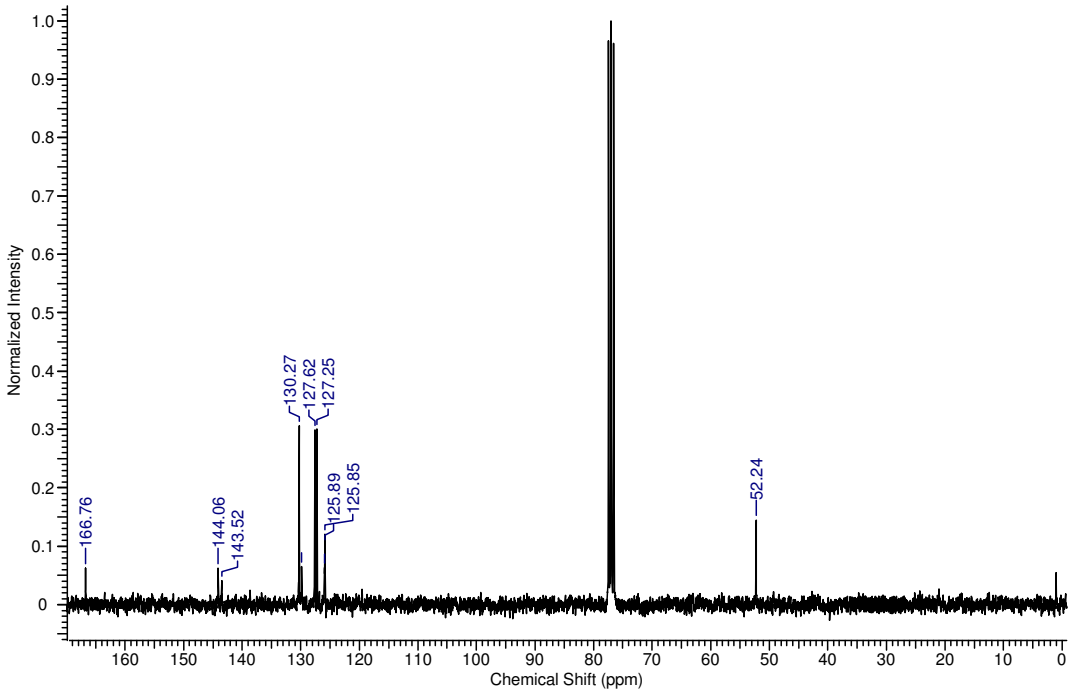


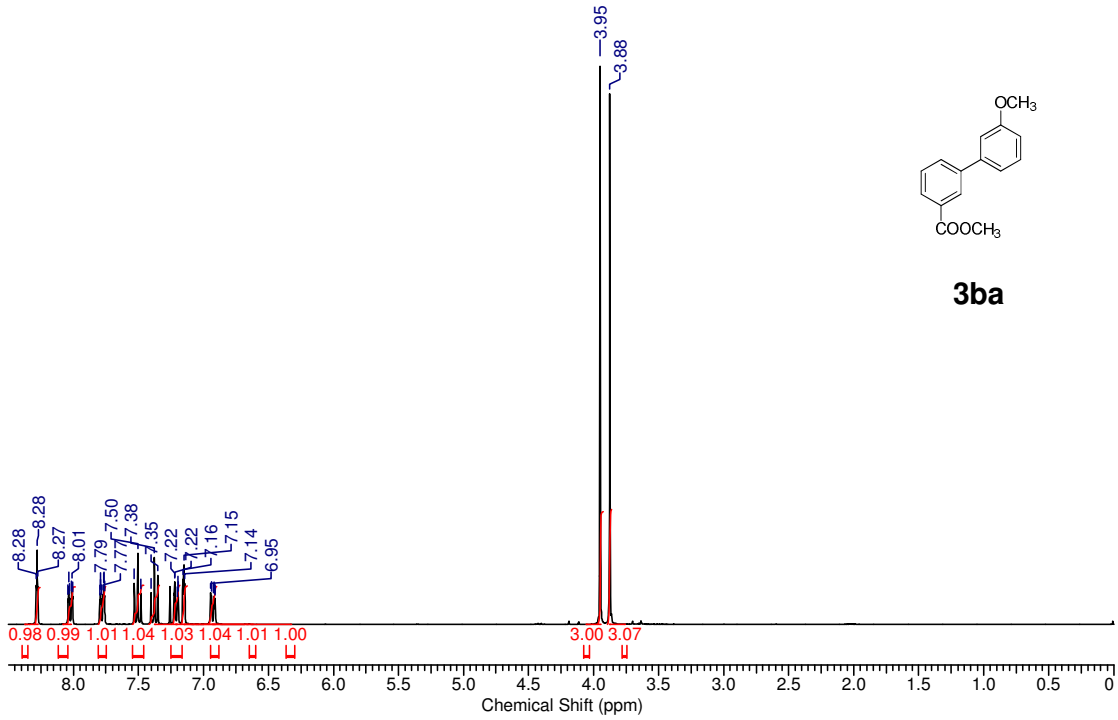


3ae









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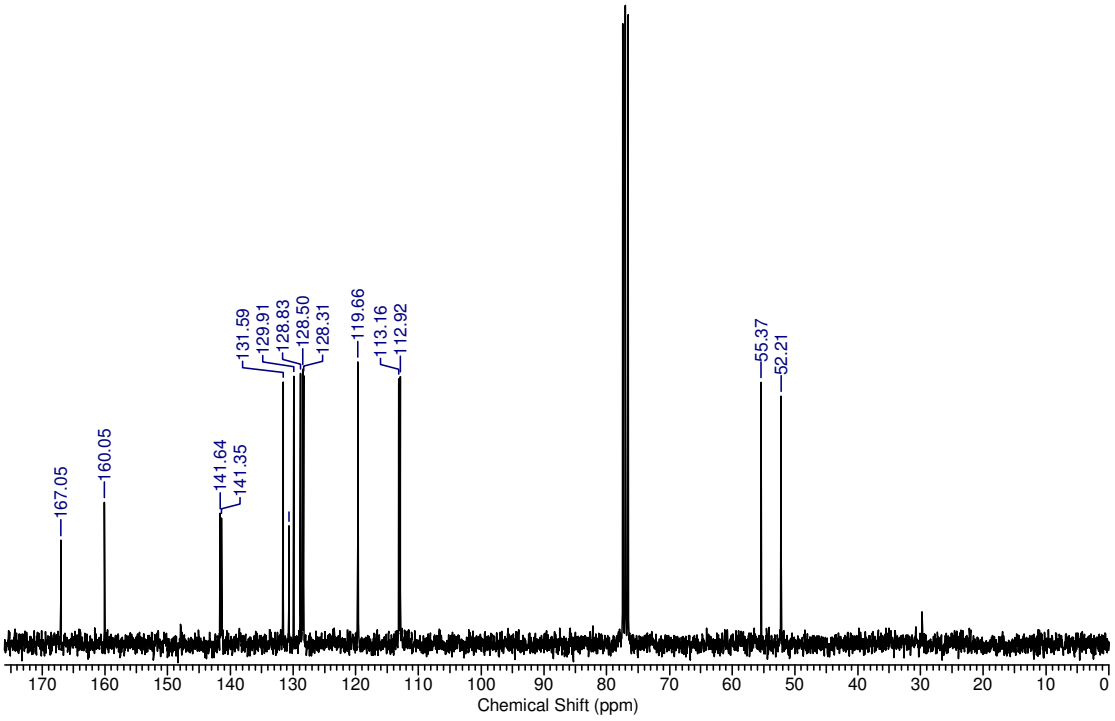

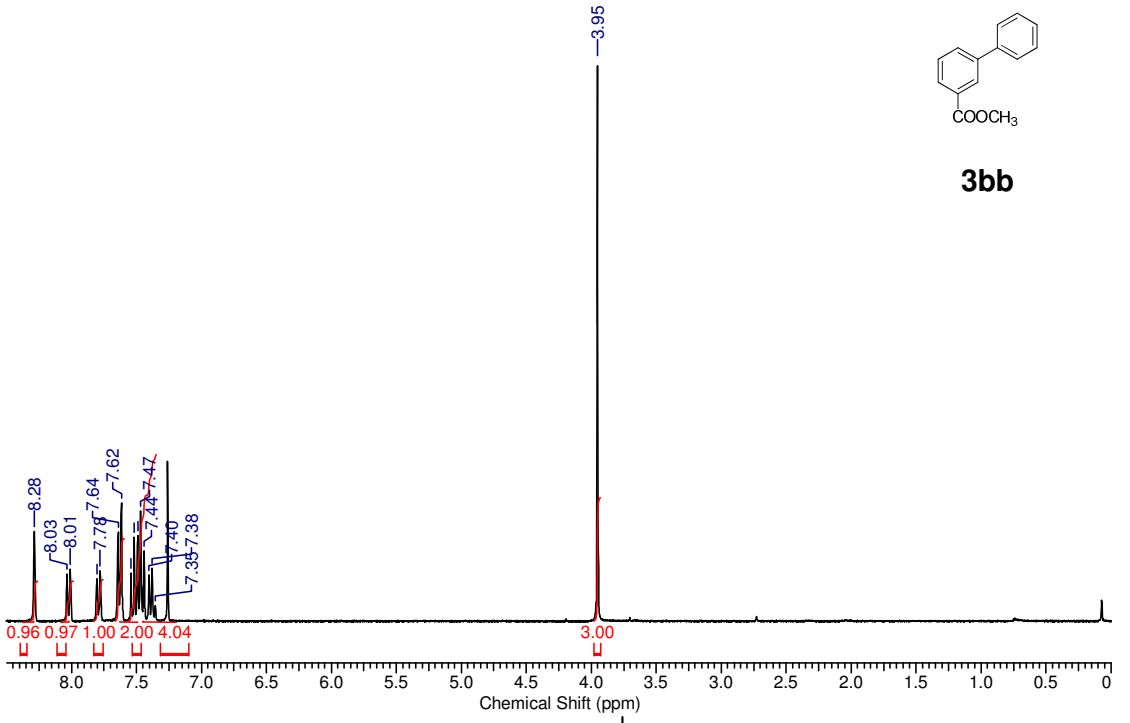

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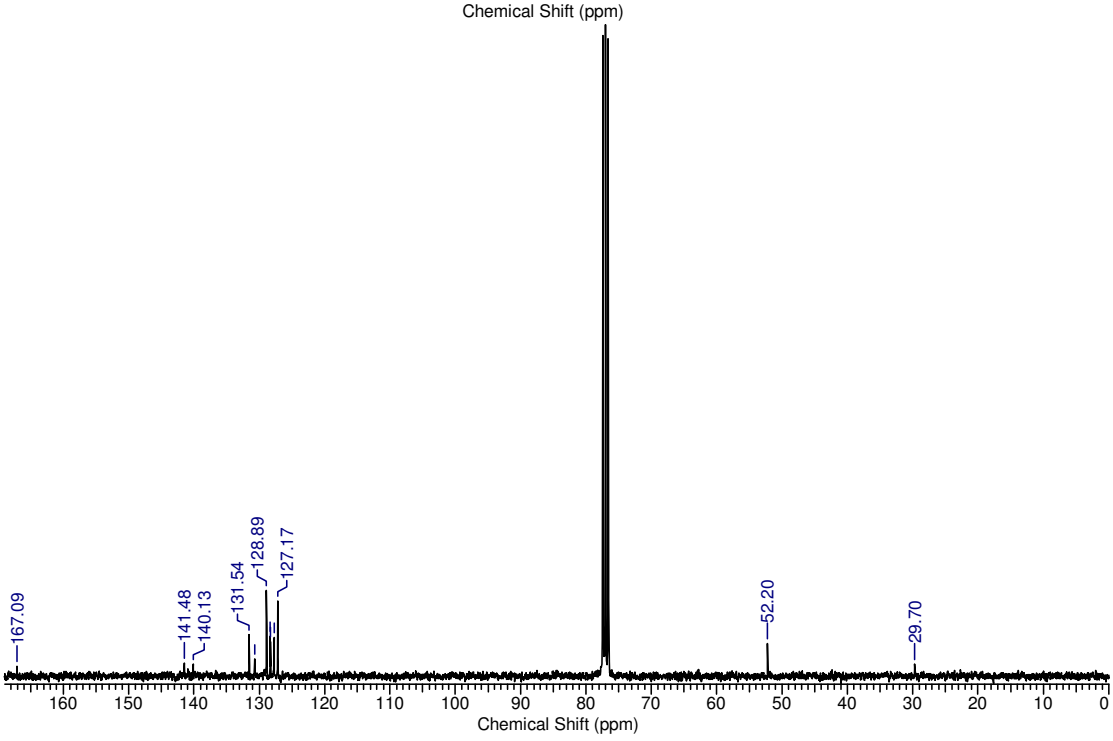

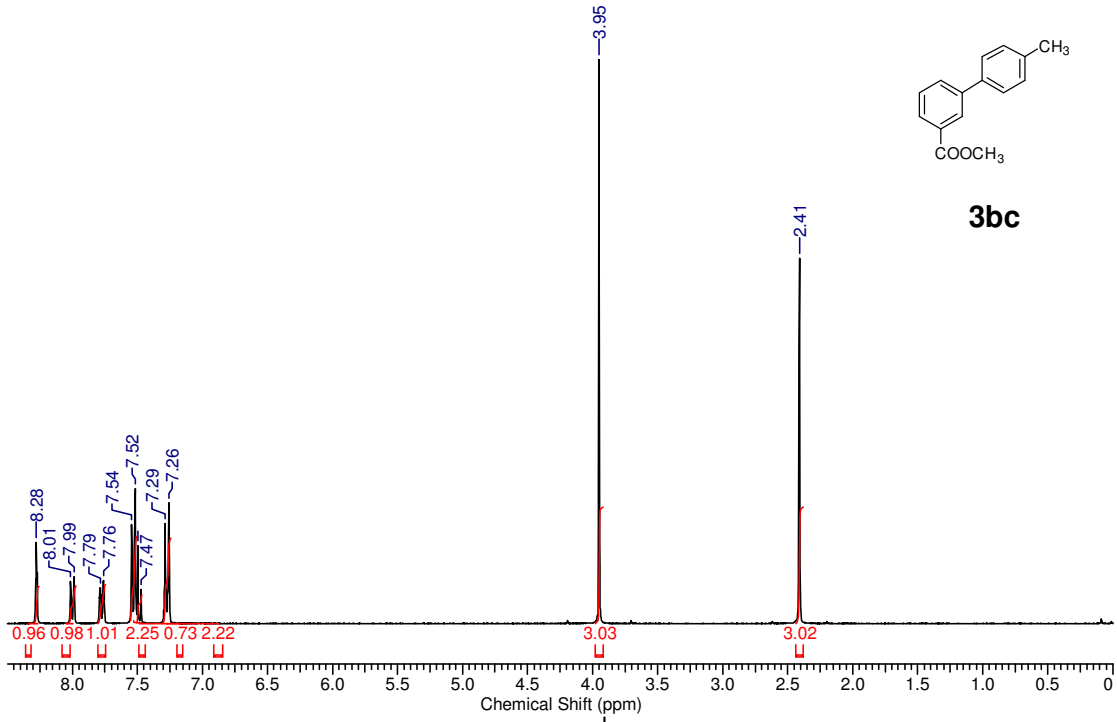

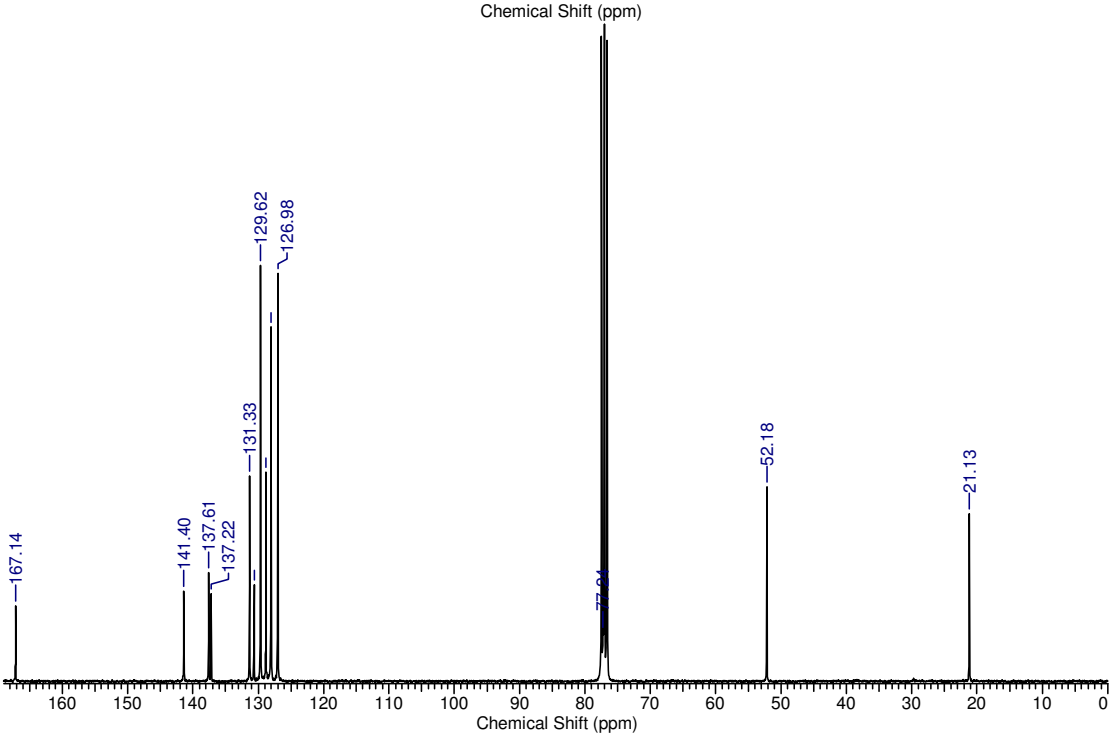

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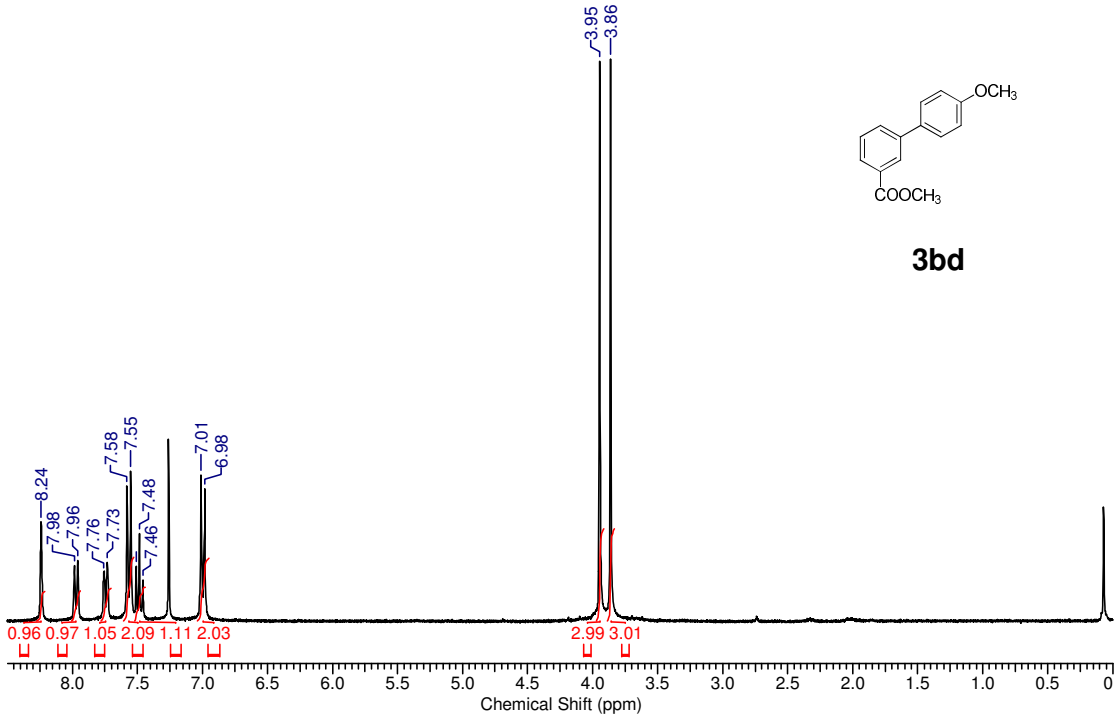

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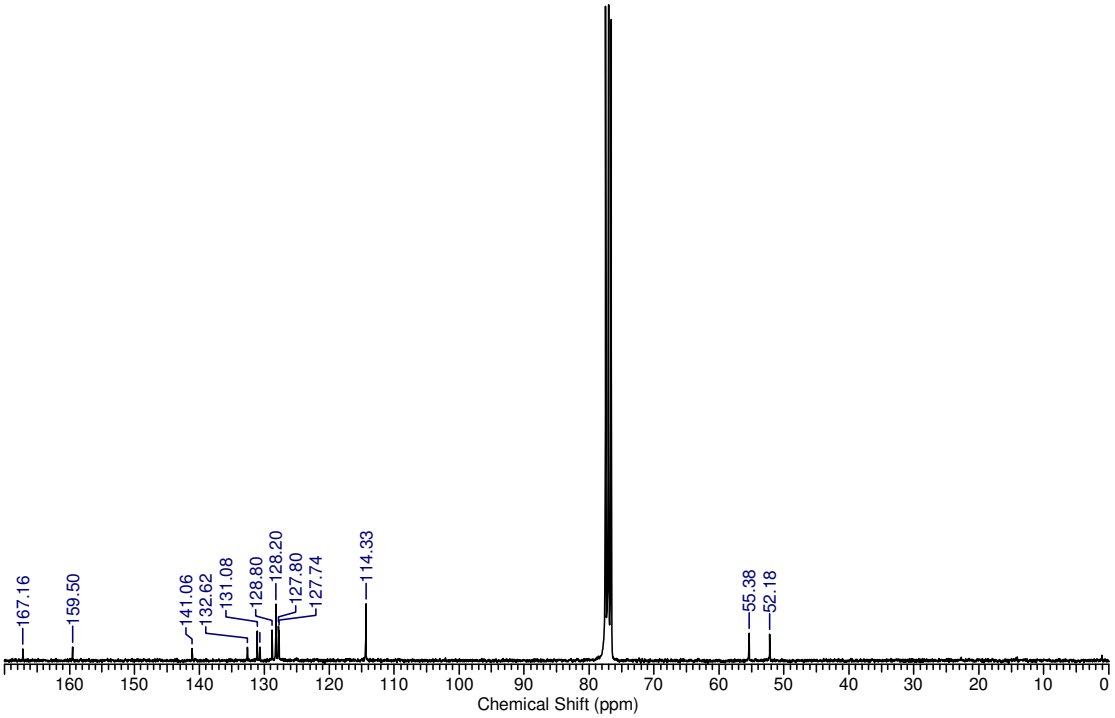

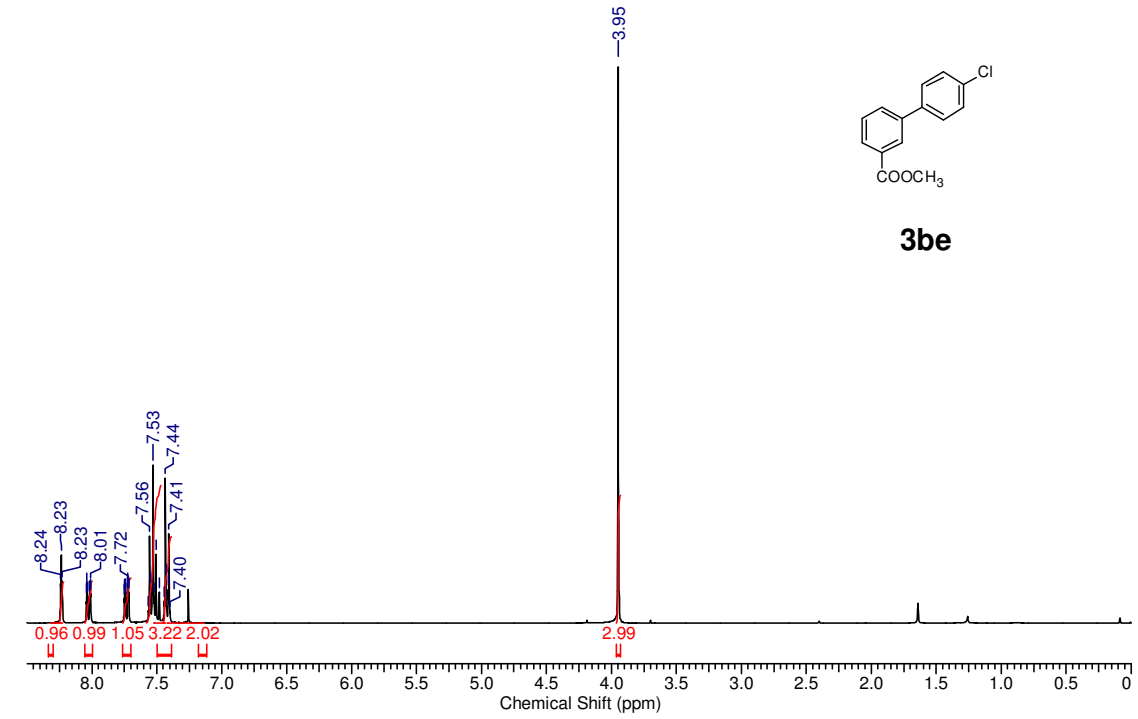

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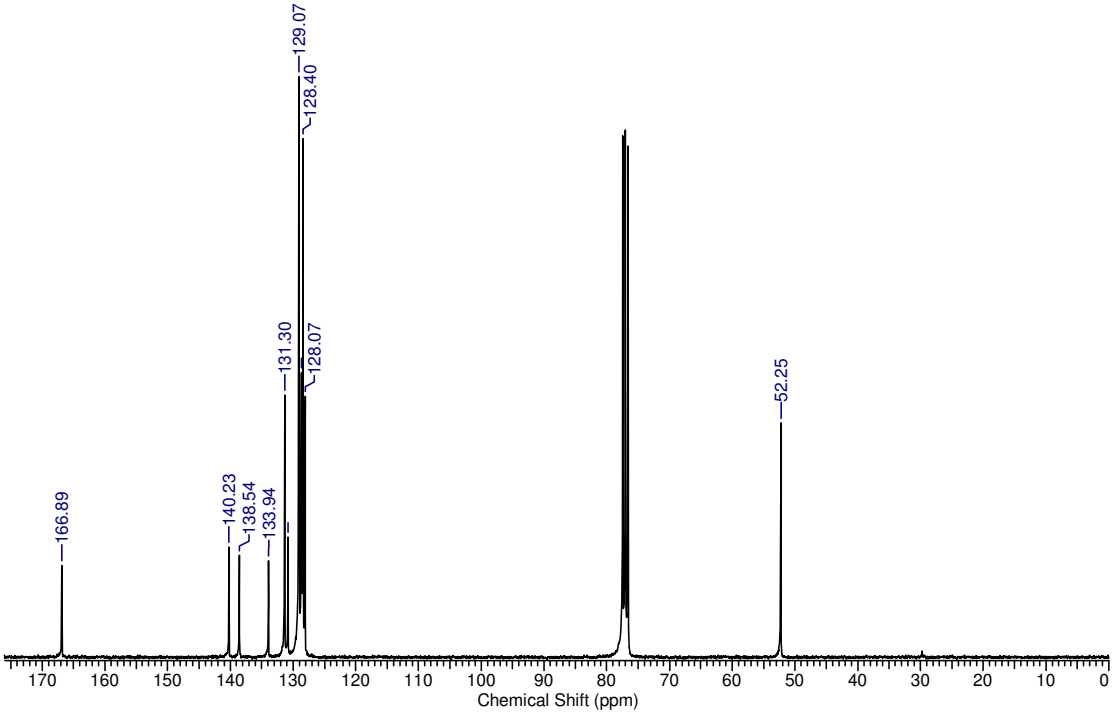

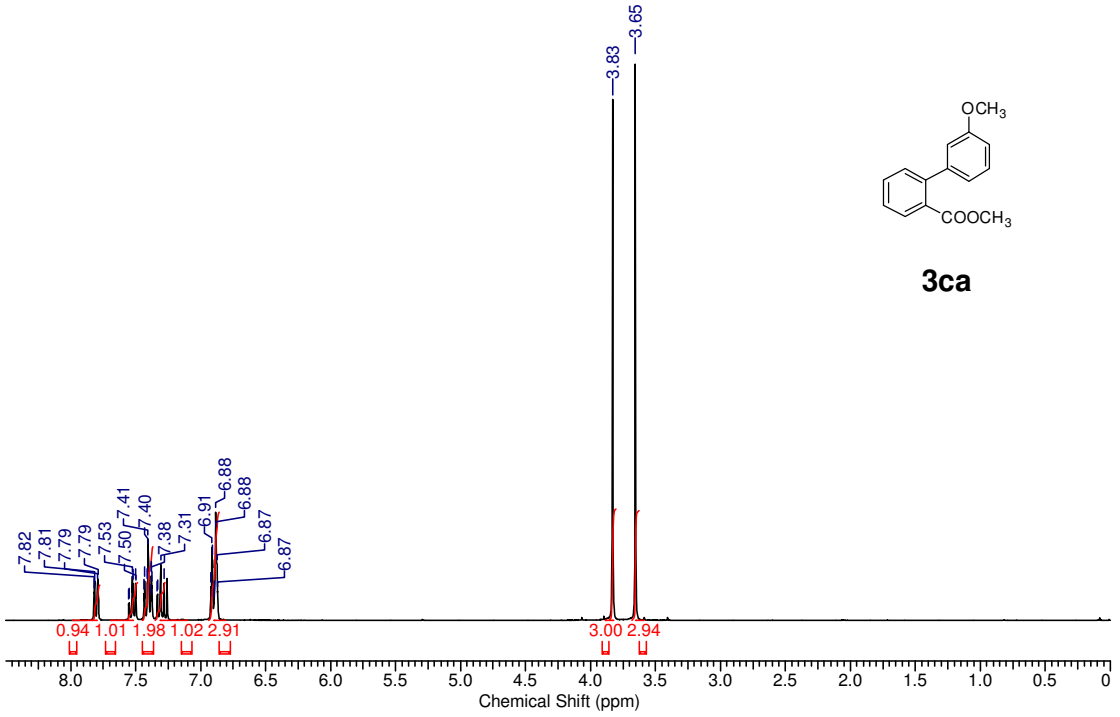

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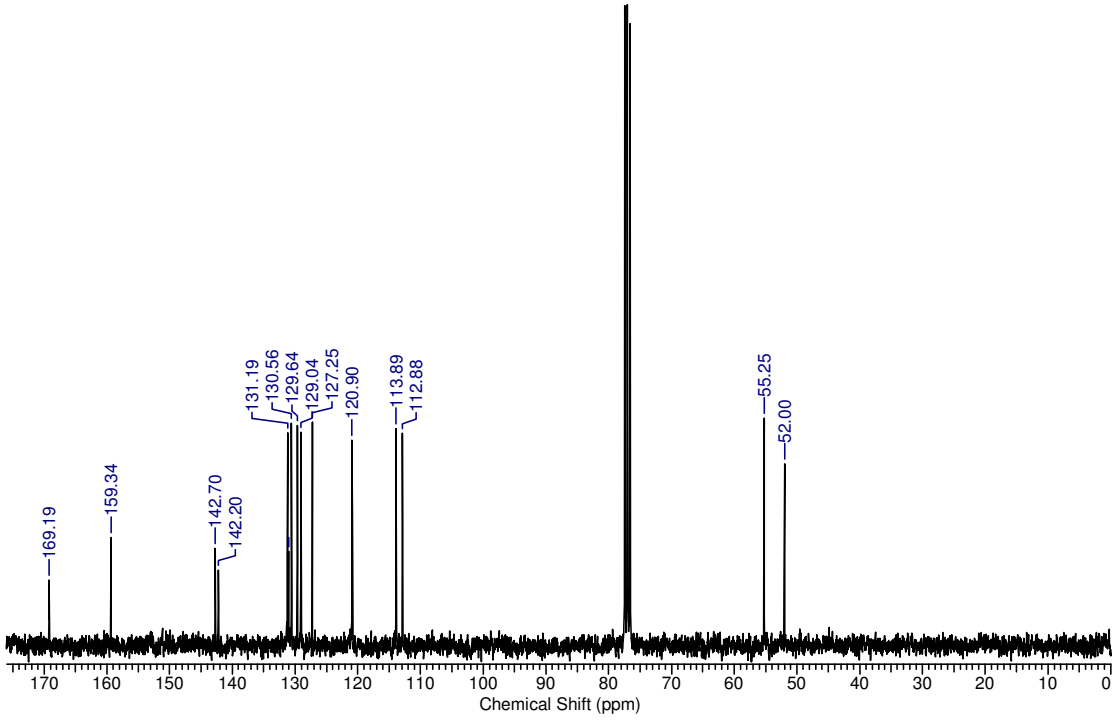

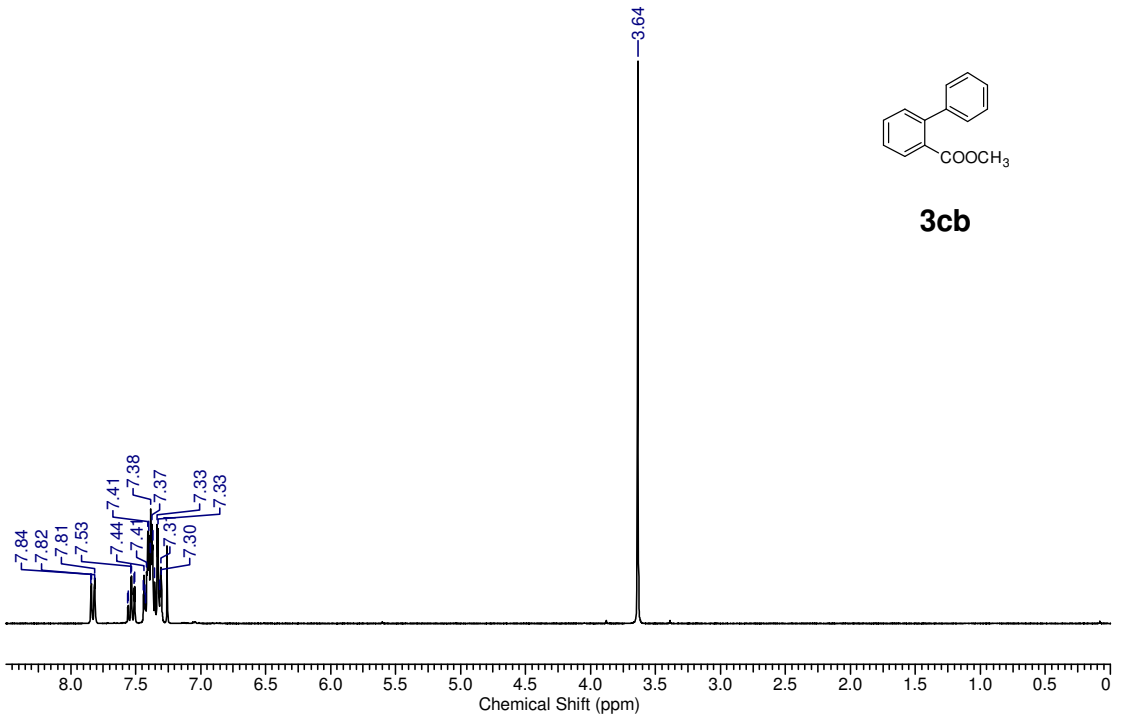

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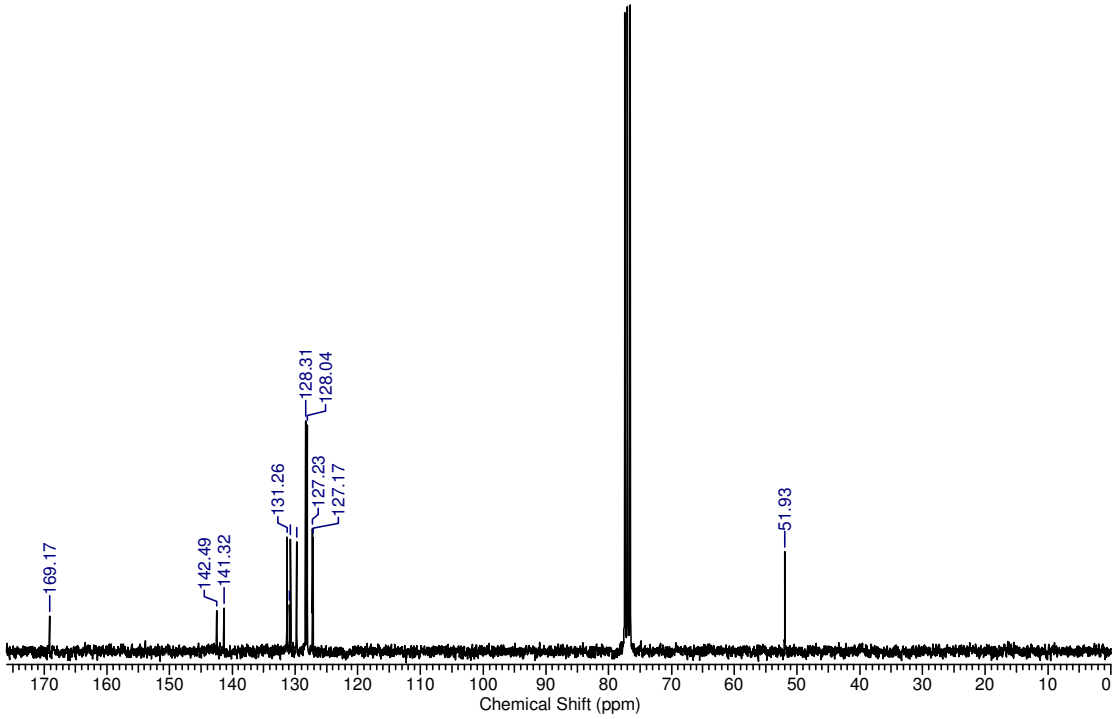

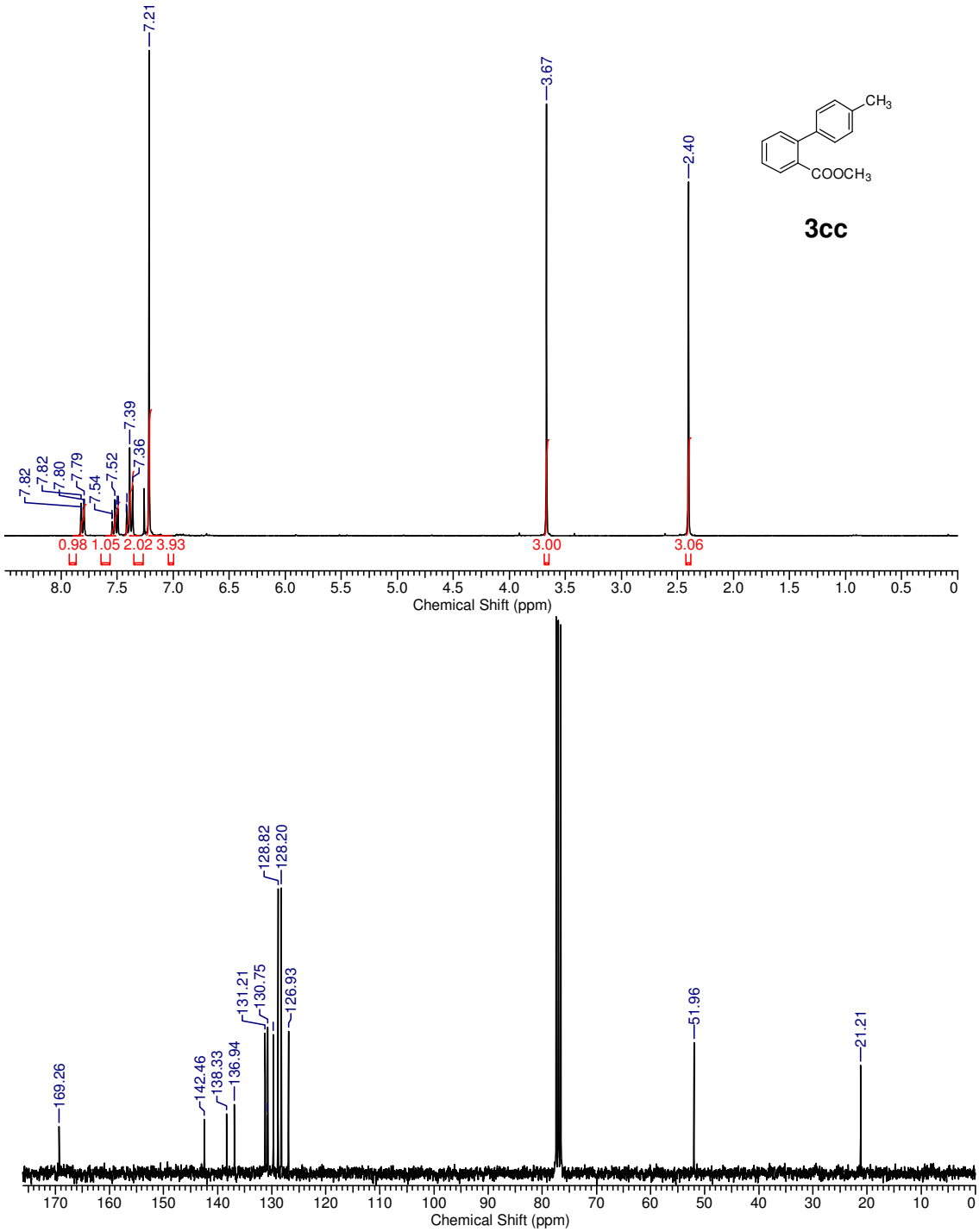

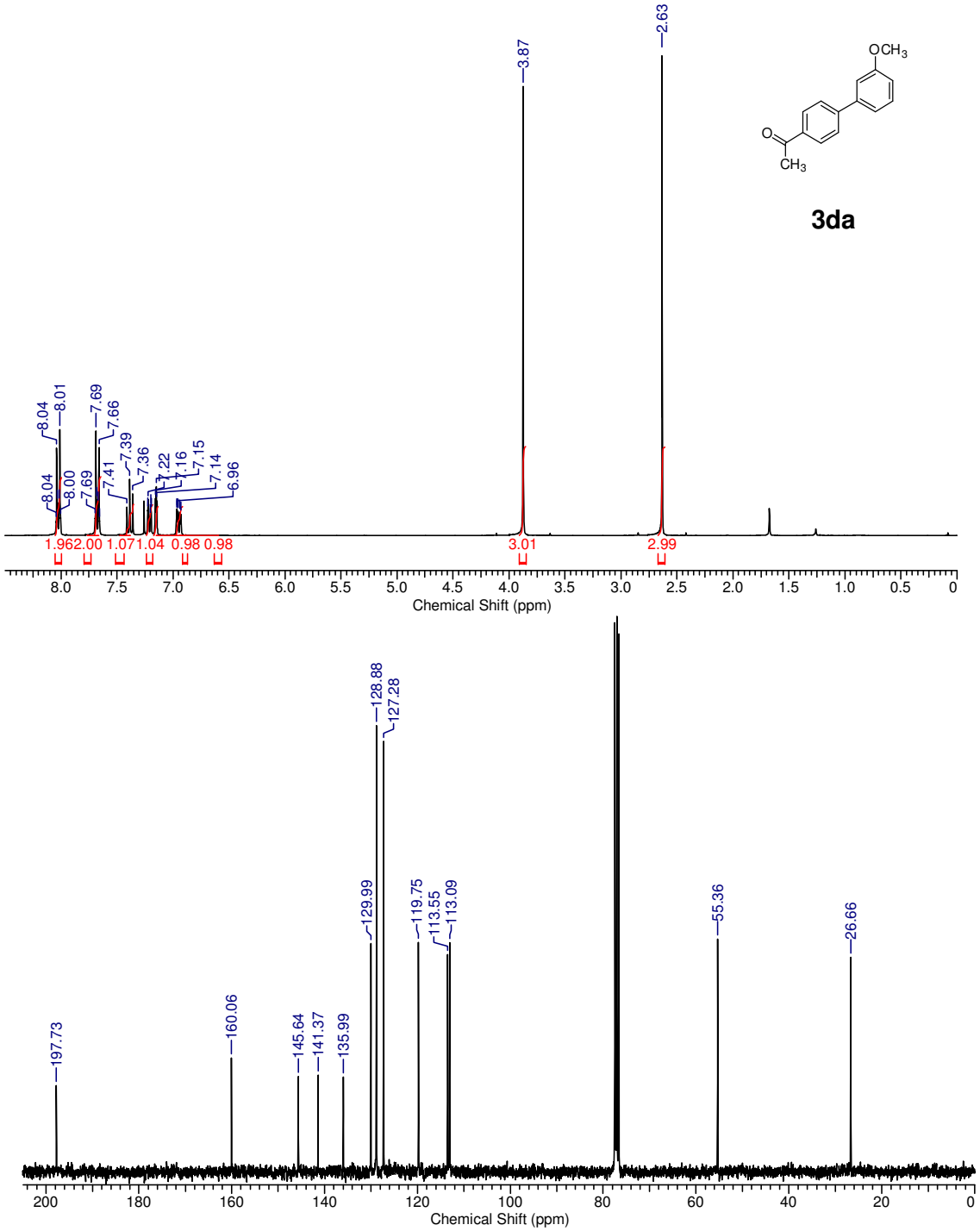

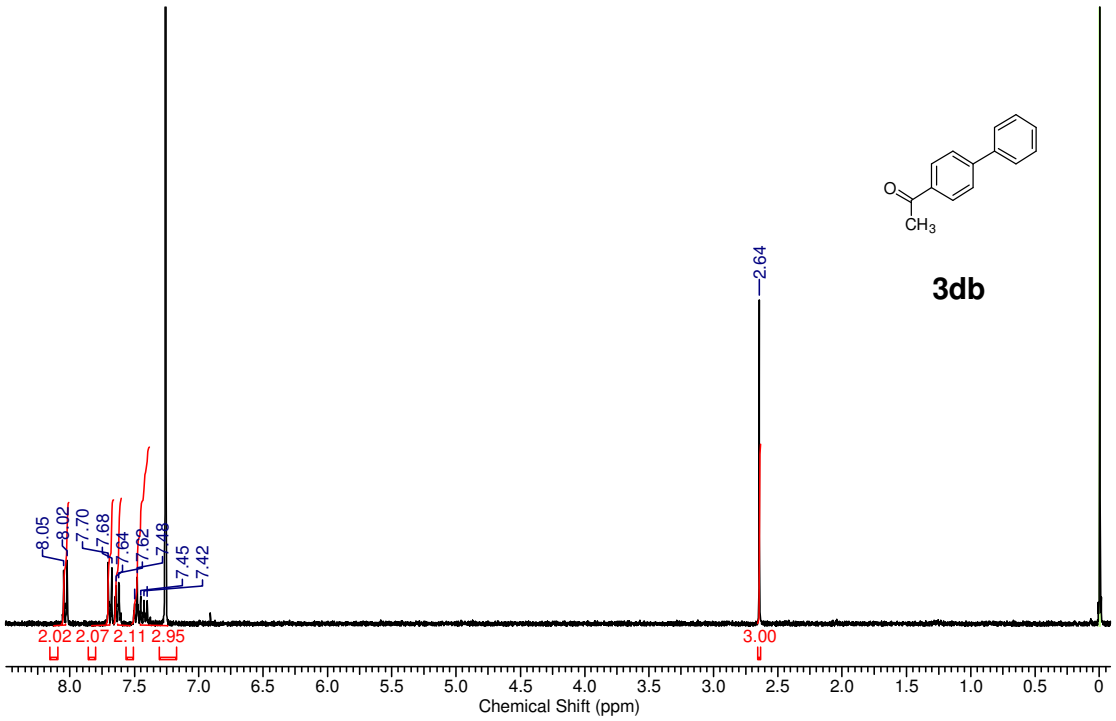

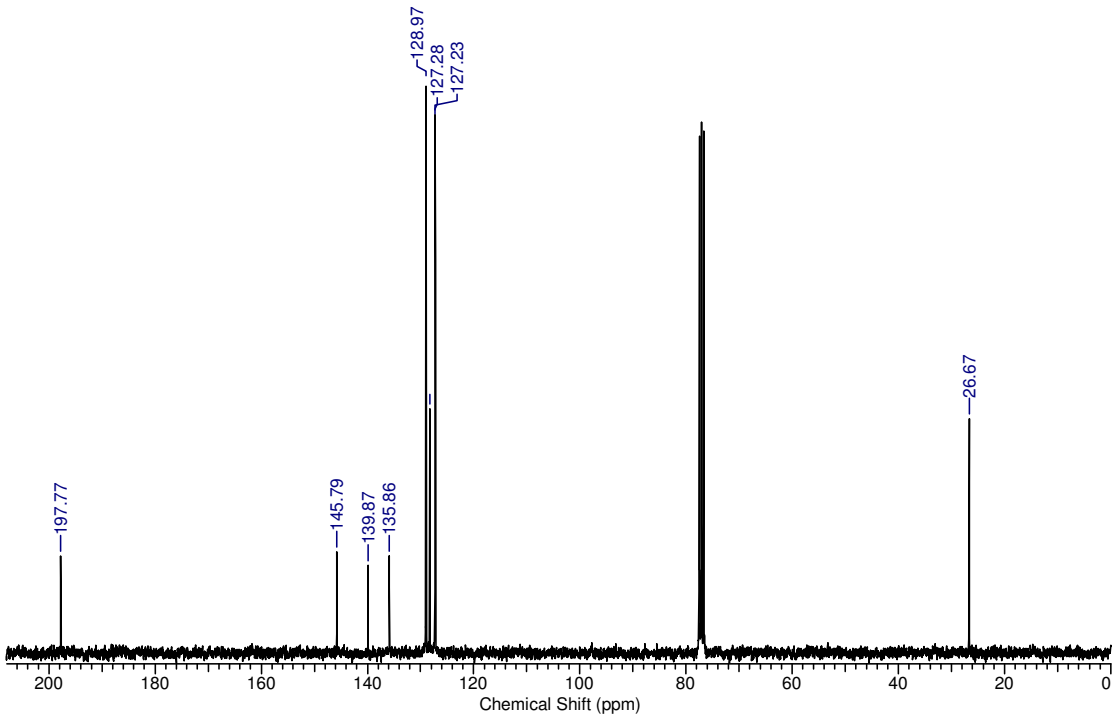

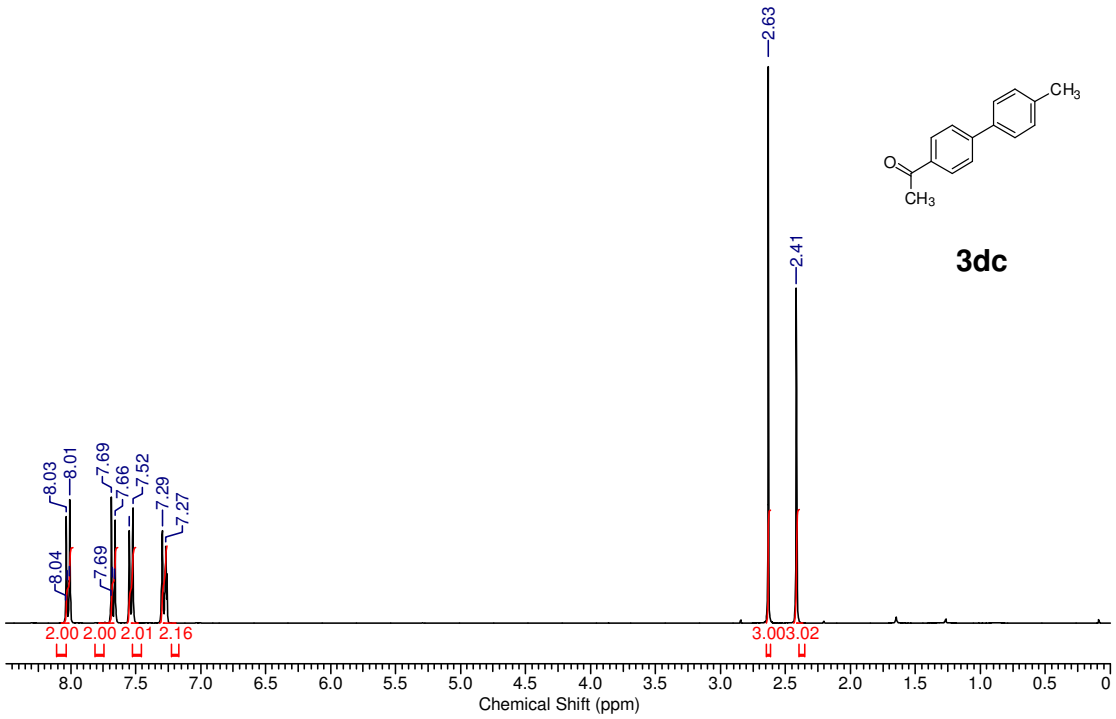

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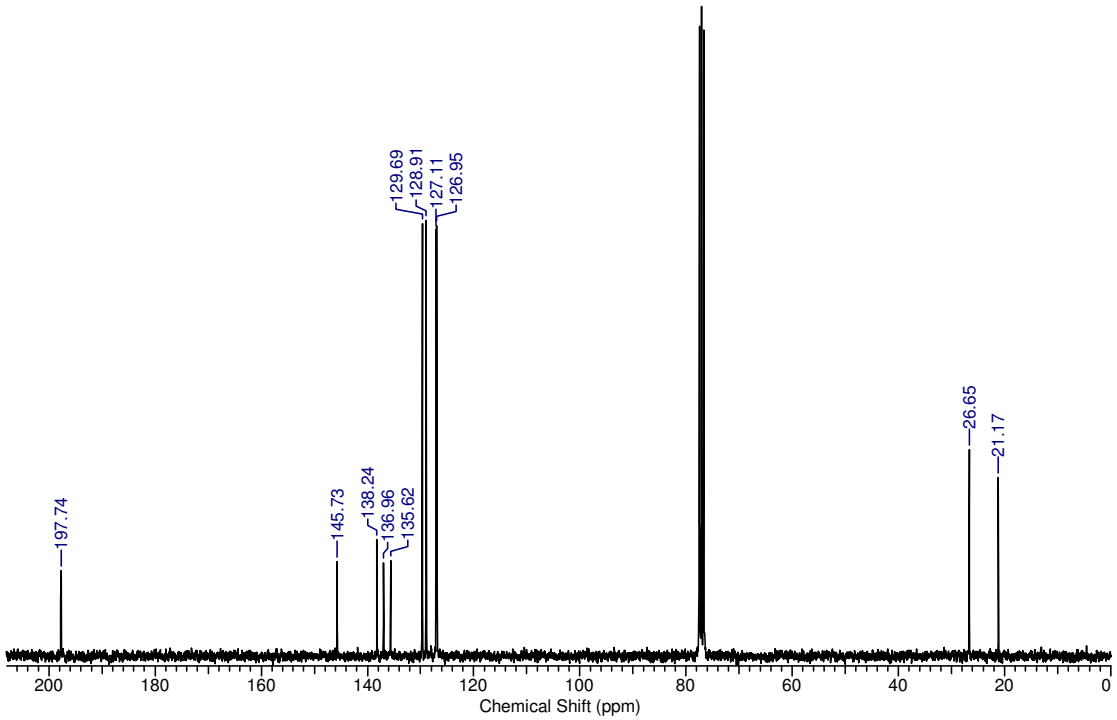

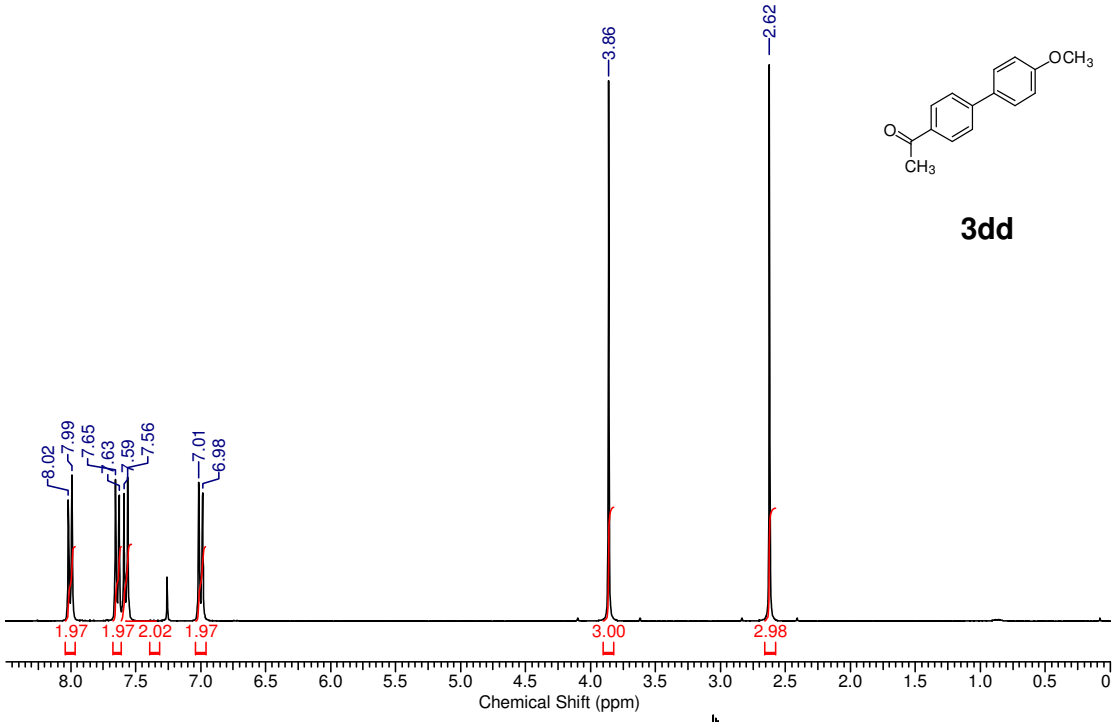

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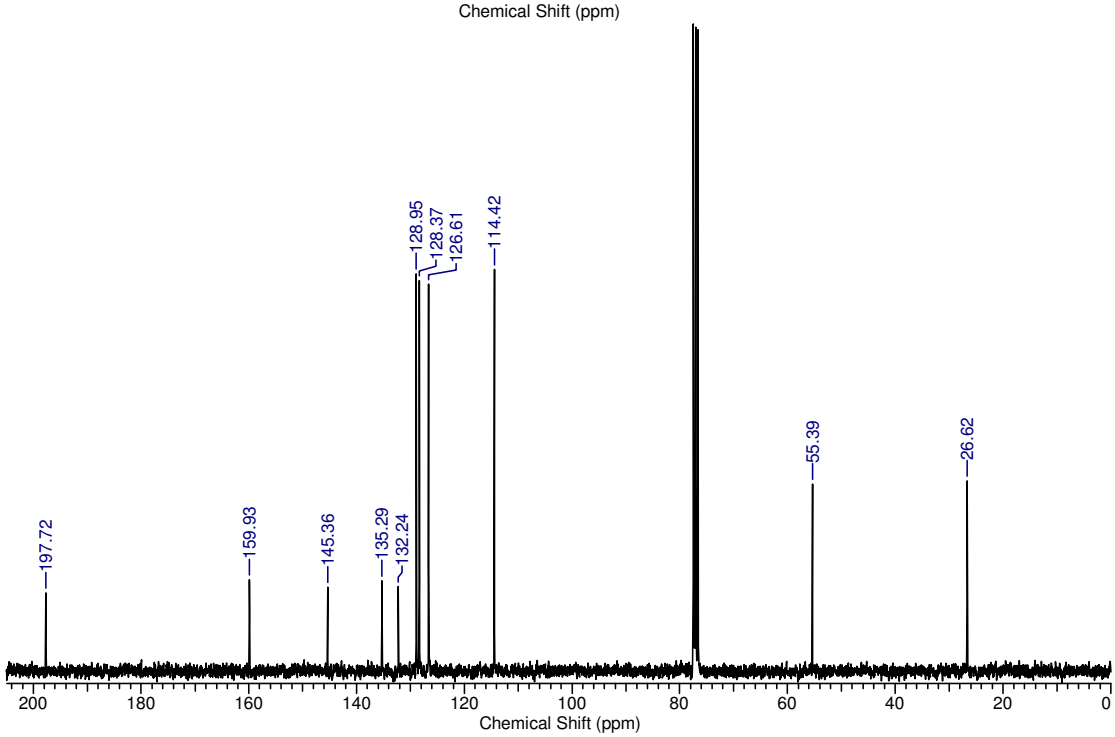

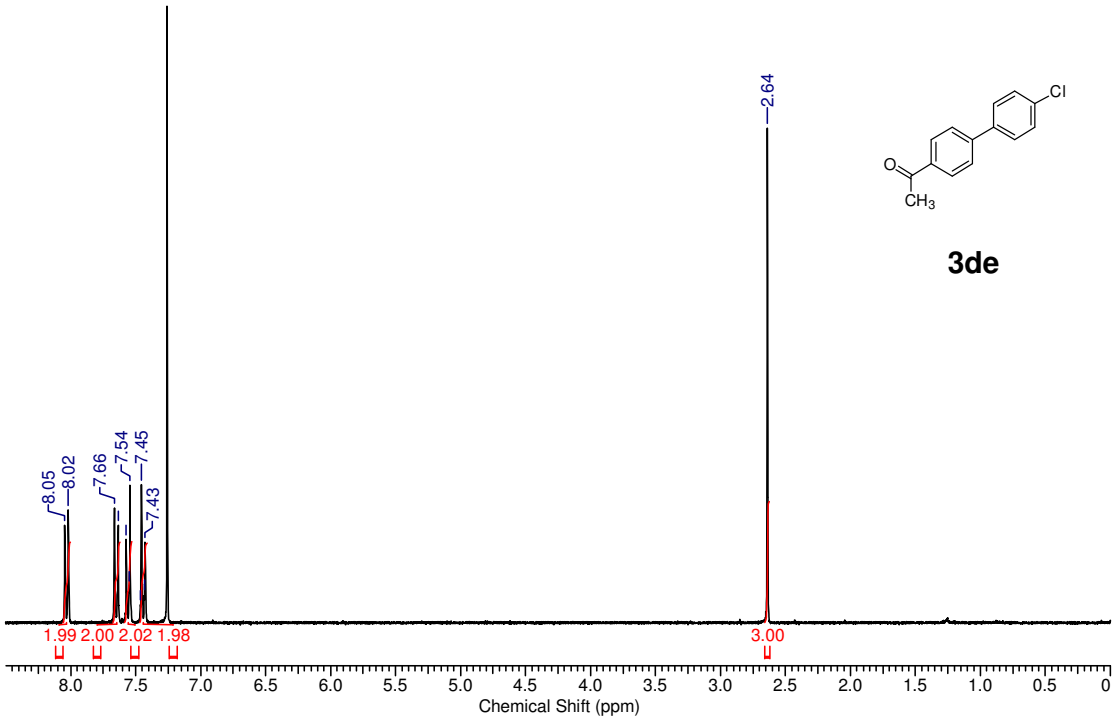

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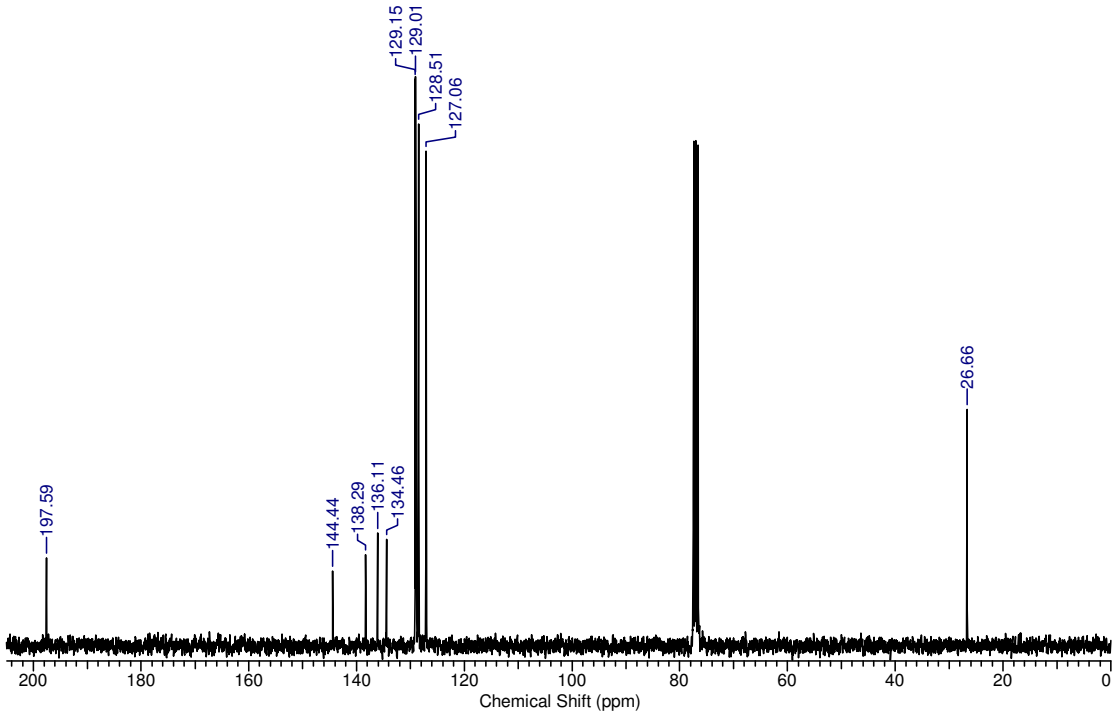

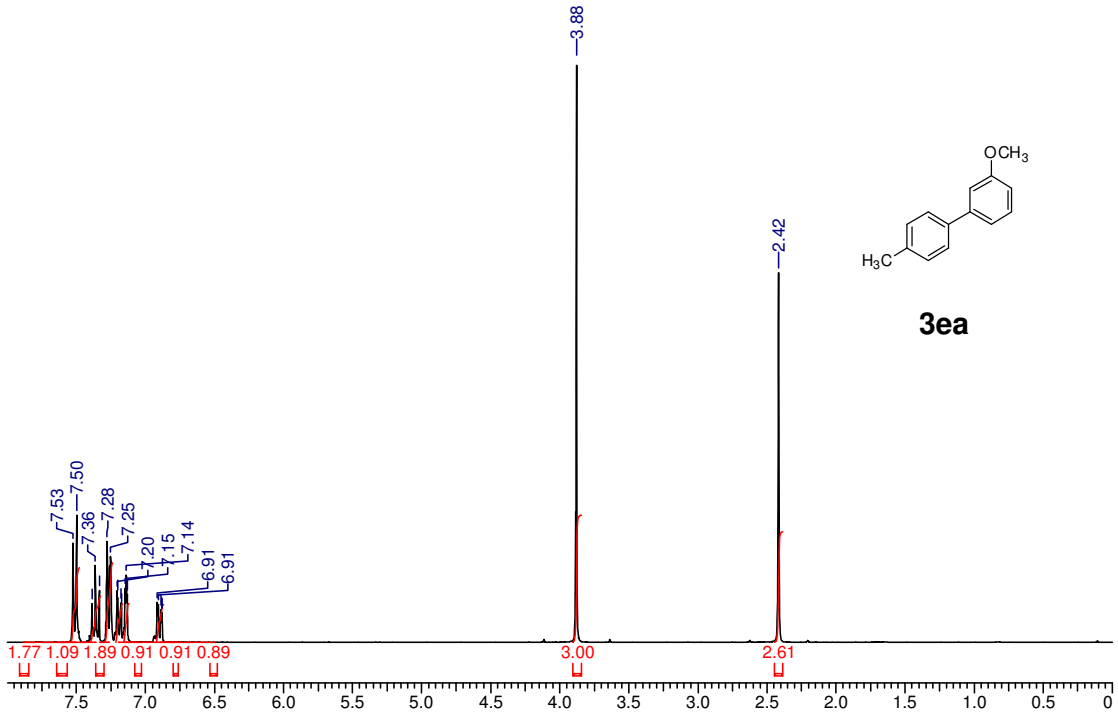

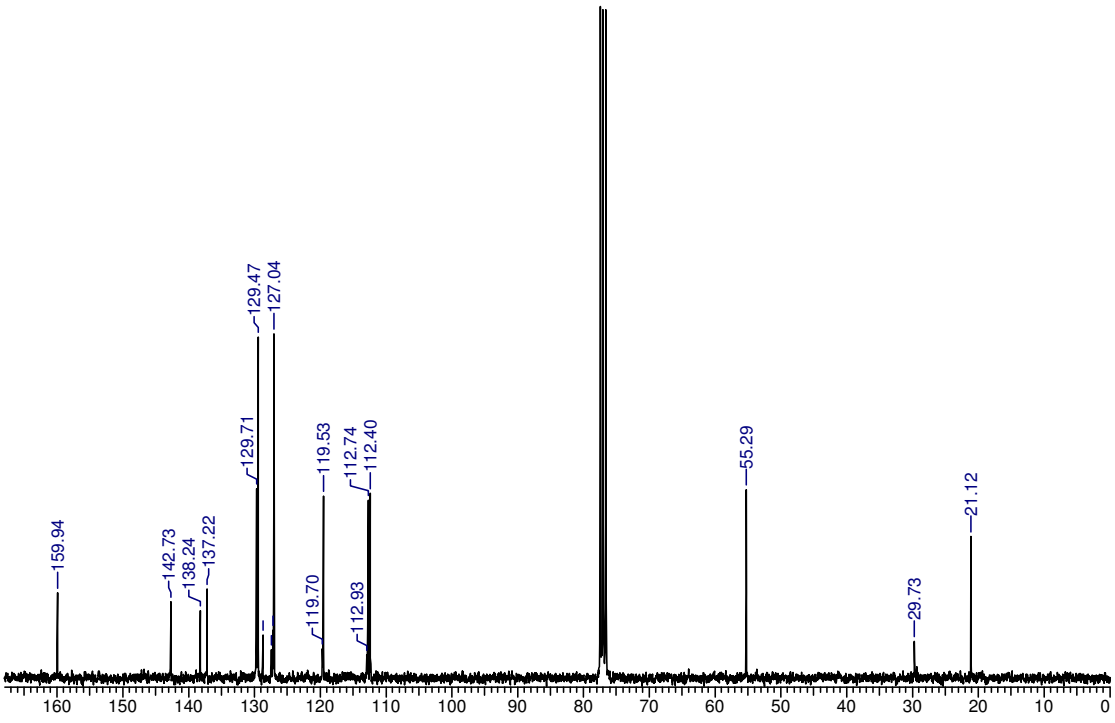

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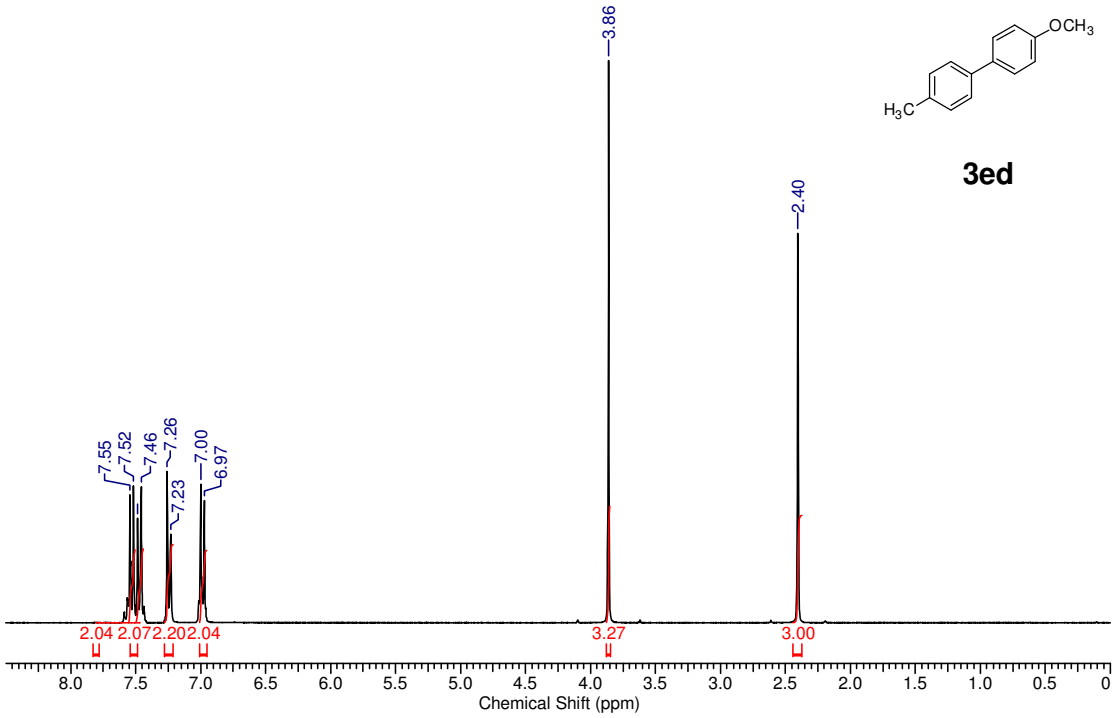

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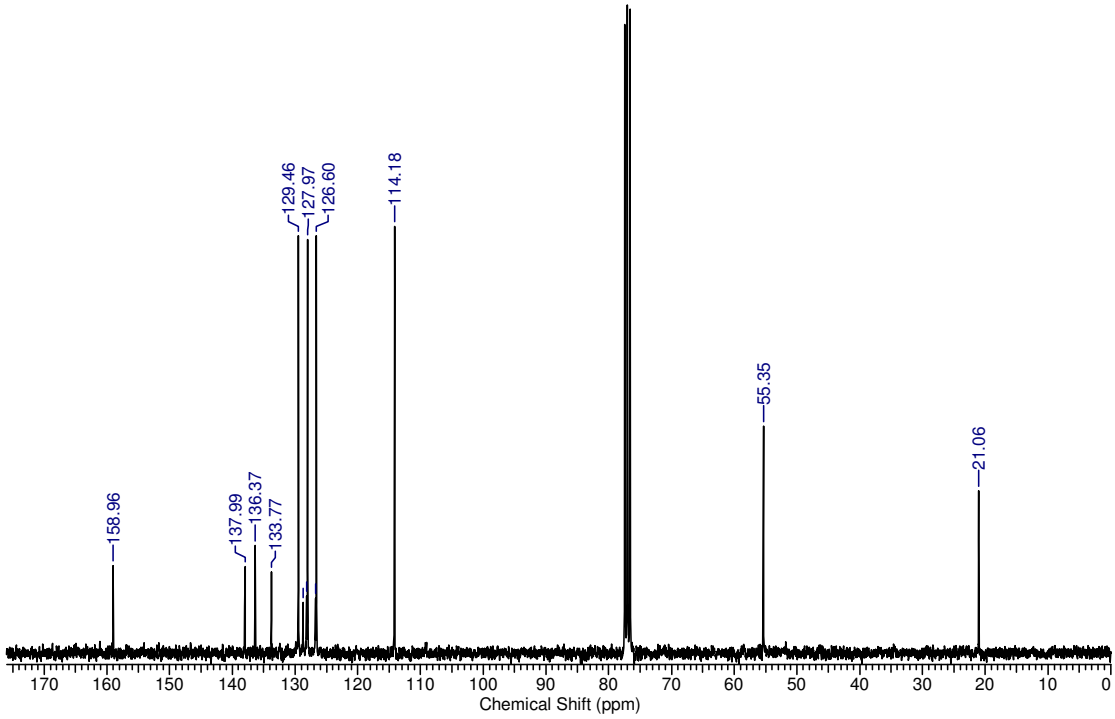

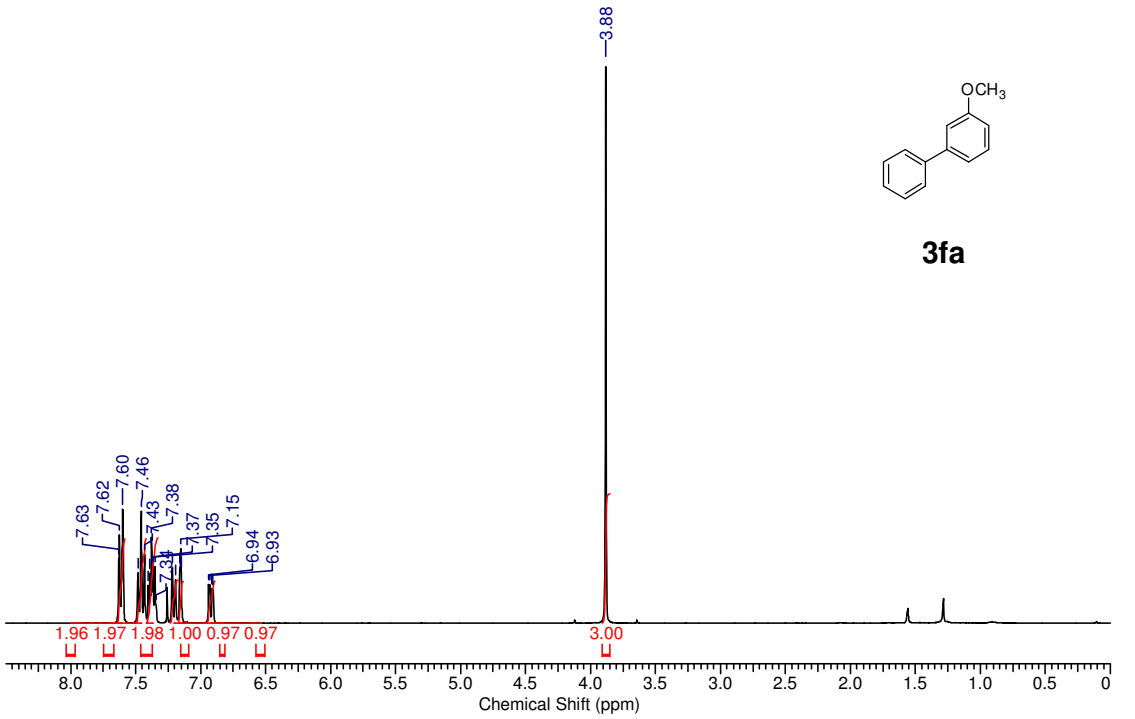

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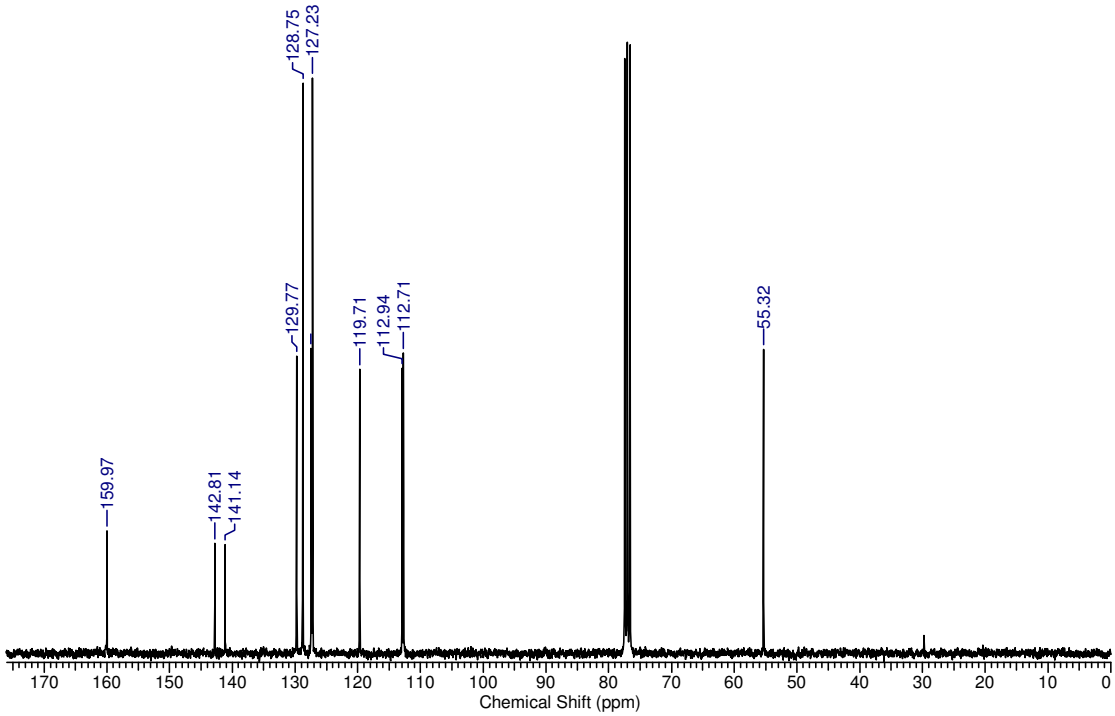

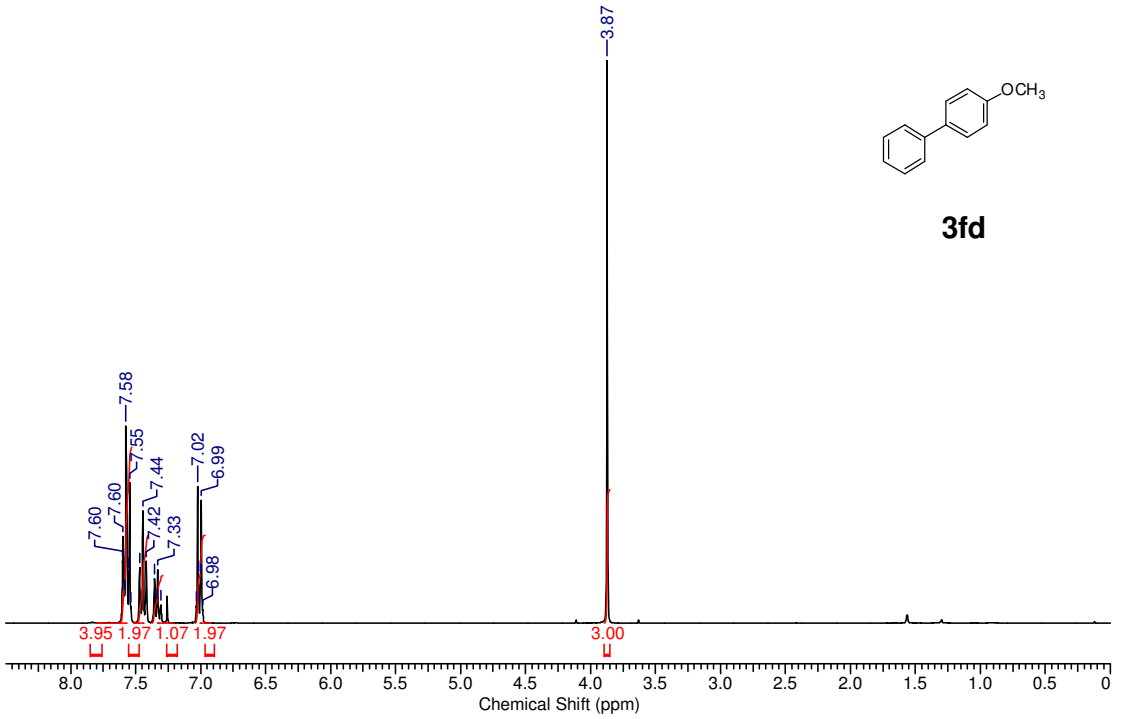

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