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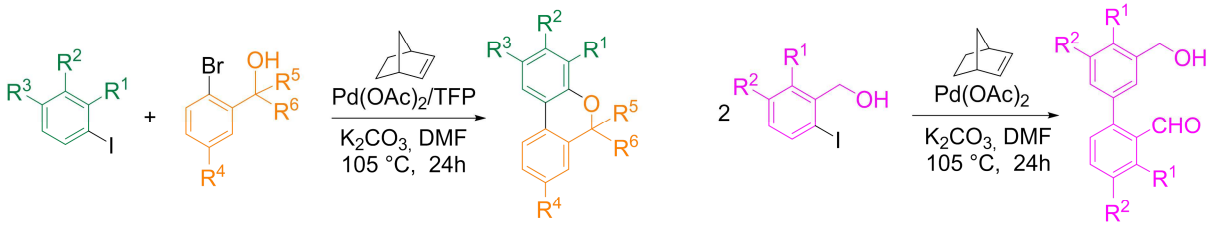

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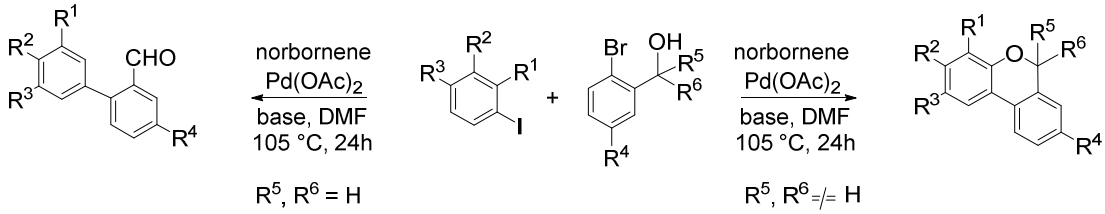
ABSTRACT

Developments are reported in the catalytic synthesis of biaryls containing an *ortho*-carbaldehyde or 6*H*-dibenzopyrans in the presence of palladium/norbornene as catalyst. The reaction of o-substituted aryl iodides and o-bromobenzyl alcohols proceeds by unsymmetrical aryl-aryl coupling to form a seven-membered oxapalladacycle intermediate, which may undergo an intramolecular redox process to form carbonyl groups or a C–O coupling to six-membered cyclic ethers. The predominant formation of dibenzopyrans as well as of biaryl structures containing the oxidized CHO group in one ring and the reduced CH_2OH in the other is described along with some mechanistic insights.

1. Introduction

Organopalladium chemistry is one of the most versatile and powerful techniques for the synthesis of organic compounds.[1] In particular great attention has been focused on sequential reactions that are highly selective, have mild reaction conditions, use commercially accessible starting materials and tolerate a great variety of functional groups.[2] In the course of our studies aimed at the development of new synthetic procedures based on the use of palladium/norbornene as a unique catalytic system, we have shown that it is possible to selectively form substituted biaryl structures by unsymmetrical coupling of aryl iodides and aryl bromides followed by an irreversible inter- or intramolecular step. In order to achieve this goal it is essential to correctly tune the reactivity of the two aryl halides towards palladium species in the oxidation state (0) and (II). It has been ascertained that o-substituted aryl iodides bearing an electron-releasing group and aryl bromides containing an electron-withdrawing substituent, or an ortho chelating group, could be a winning combination for the selective construction of unsymmetrical biaryl derivatives.[3]

We have recently reported[4] that a biaryl structure containing an ortho carbaldehyde or a 6*H*-dibenzopyran derivative could be conveniently obtained through the one-pot reaction of an ortho-substituted aryl iodide with a 2-bromobenzyl alcohol derivative. terminated either by an intramolecular redox process, which affects both rings of the biaryl structure, or by ring closure across the two aromatic rings. Under the conditions previously reported the chemoselectivity of the process was essentially determined by the alcohol moiety: primary and tertiary alcohols selectively led to o-biaryl aldehydes and dibenzopyrans, respectively, while secondary alcohols gave rise to a mixture of ketones and dibenzopyran derivatives (Scheme 1).



Scheme 1. Palladium/norbornene catalyzed synthesis of o-biaryl carbaldehydes and dibenzopyran derivatives.

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In continuation of this work we have found that dibenzopyran derivatives could also be obtained predominantly either from primary or secondary benzyl alcohols and that interesting biaryl derivatives containing an aldehyde group in one ring and a hydroxymethyl in the other could be readily prepared through unsymmetrical aryl-aryl coupling of two molecules of o-iodobenzyl alcohols. In this manuscript developments of the catalytic reactions are described and some mechanistic aspects involved in the process are discussed.

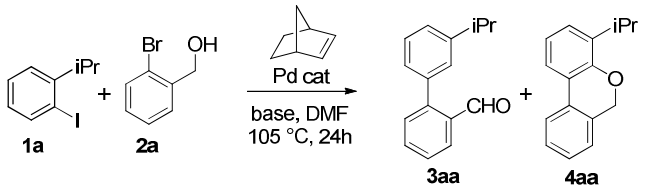
2. Results and Discussion

2.1. Primary o-bromobenzyl alcohols

2.1.1. Synthesis of o-biaryl carbaldehydes

In our initial studies, the reaction of 1-iodo-2-isopropylbenzene (**1a**) with 2-bromobenzyl alcohol (**2a**) in the presence of palladium and norbornene as catalysts was chosen as model to investigate the reaction conditions for the selective synthesis of the o-biaryl carbaldehyde **3aa**. The results are summarized in Table 1.

Table 1
Screening of reaction conditions for the synthesis of o-biaryl carbaldehyde **3aa** from 1-iodo-2-isopropylbenzene **1a** and o-bromobenzyl alcohol **2a**[a]



entry	catalyst	base	**3aa** yield (%)[b]	**4aa** yield (%)[b]
1	$PdCl_2$	K_2CO_3	29	12
2	$PdCl_2(MeCN)_2$	K_2CO_3	39	6
3	$Pd_2(dba)_3$	K_2CO_3	11	-
4	$Pd(OAc)_2$	K_2CO_3	32	24
5	$Pd(OAc)_2$	Cs_2CO_3	35	21
6	$Pd(OAc)_2$	Na_2CO_3	15	-
7	$Pd(OAc)_2$	K_3PO_4	25	18
8	$Pd(OAc)_2$	NEt_3[c]	-	-
9	$Pd(OAc)_2$	KOAc	35	-
10	$Pd(OAc)_2$	KOPiv	67	-
11	$Pd(OAc)_2$	CsOPiv	74	-
12[d]	$Pd(OAc)_2$	CsOPiv	72	-
13[e]	$Pd(OAc)_2$	CsOPiv	41	5
14[f]	$Pd(OAc)_2$	CsOPiv	32	-
15[g]	$Pd(OAc)_2$	CsOPiv	57	5
16[h]	$Pd(OAc)_2$	CsOPiv	95	-

[a] Reaction conditions: molar ratio of **1a**, **2a**, Pd catalyst, norbornene and base 20:20:1:20:50; 2.2×10^{-3} mmol Pd/mL DMF; under N_2, 105 °C, 24 h.

[b] GC and/or ^1H NMR yield on the charged amount of **1a**.

[c] molar ratio of the base to palladium 100:1.

[d] DMA

[e] MeCN, refluxing

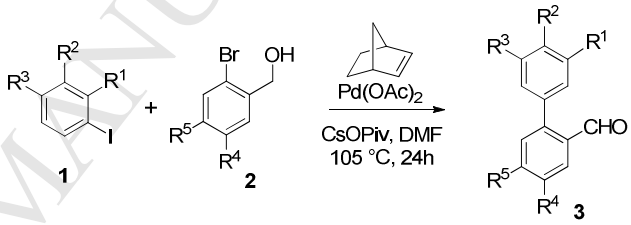
[f] 80 °C

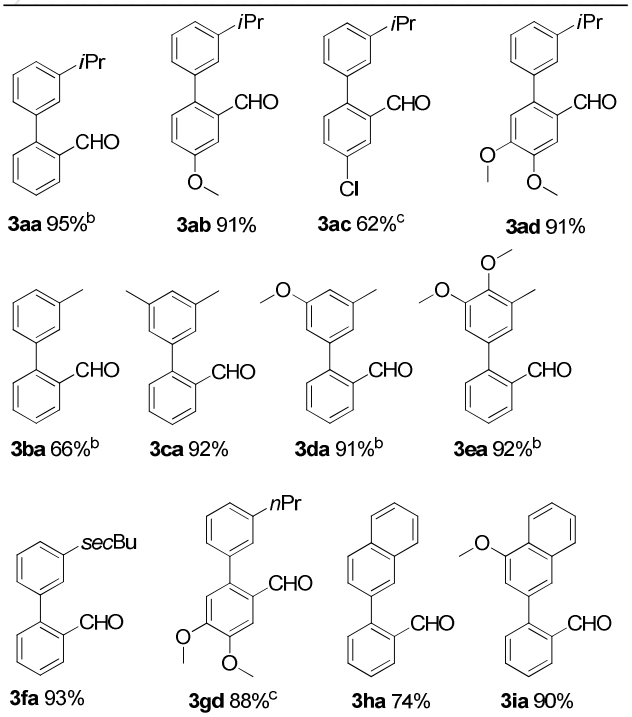
[g] 120 °C

[h] molar ratio norbornene to Pd 5:1

Pd(0) precursors such as $PdCl_2$, $PdCl_2(MeCN)_2$, $Pd(OAc)_2$ and $Pd_2(dba)_3$ were initially tested in DMF using K_2CO_3 as a base (entries 1–4). Among these, $Pd(OAc)_2$ gave the best results in terms of yield and halide conversion, but not in terms of selectivity; both compounds **3aa** and **4aa** were obtained in comparable yields (entry 4). The effect of the bases was evaluated using $Pd(OAc)_2$ in DMF. Cs_2CO_3 gave results similar to K_2CO_3, while Na_2CO_3 or $NaHCO_3$ afforded very low yields and conversions (entries 4–6). Cesium pivalate (CsOPiv) was found to be the best base leading to the formation of only the *o*-biaryl carbaldehyde **3aa** (74% yield); dibenzopyran derivative **4aa** was not detected in the reaction mixture by GC analysis (entry 11). All other bases afforded either comparable or lower yields (entries 7–10). Different temperatures, reaction times and solvents were tested using $Pd(OAc)_2$ as catalyst and CsOPiv as a base. DMA performed similarly to DMF while acetonitrile led to modest conversion (entries 12 and 13). The best temperature was 105°C; low conversion was obtained at 80°C and poor selectivity at 120°C (entries 14–15). The amount of norbornene was crucial and reducing the molar ratio to Pd from 20:1 to 5:1 gave carbaldehyde **3aa** in 95% yield (entry 16).

Table 2
Synthesis of o-biaryl carbaldehydes **3**: selected significant examples[a,4]





[a] Reaction conditions: aryl iodide **1** (0.36 mmol), o-bromobenzyl alcohol **2** (0.36 mmol), norbornene (0.18 mmol), $Pd(OAc)_2$ (0.018 mmol), CsOPiv (0.90 mmol) in DMF (8 mL), under N_2 at 105° C for 24 h; isolated yields based on the charged amount of the aryl iodide.

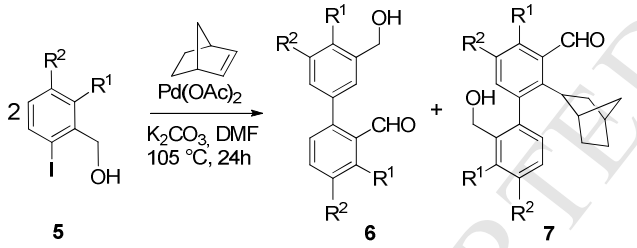
[b] Molar ratio of norbornene to Pd = 5:1.

[c] Molar ratio of norbornene to Pd = 20:1.

Under our best conditions the scope of the reaction was evaluated by using different o-substituted aryl iodides and o-bromobenzyl alcohols. It was noticed, however, that a reduced amount of norbornene (5:1 molar ratio to Pd), although appropriate for 1-iodo-2-isopropylbenzene, led to poor results with some other substrates. Thus norbornene was used in a molar ratio to palladium ranging from 5:1 to 20:1. Table 2 reports significant examples obtained with different substituents in the starting aryl iodides and o-bromobenzyl alcohols.[4] The reaction afforded biarylaldehydes **3** in good to excellent yields. Better yields were observed especially in the presence of bulky ortho groups on the starting aryl iodides and when electron-donating substituents were present in both of the aryl rings.

Interesting biaryl derivatives containing a CH_2OH group on one aromatic ring and a CHO on the other were obtained when two molecules of o-iodobenzyl alcohol were allowed to react under the conditions reported in Table 3. In addition to the straightforward synthesis of these 3'-hydroxymethyl-[1,1']-biphenyl-2-carbaldehydes,[5] which occurs with satisfactory yields both in the presence of electron-donating and electron-withdrawing groups (entries 2–3 and 4), the selective oxidation of only the ortho CH_2OH group has some bearing on the reaction mechanism (see infra). In this case, however, formation of o-biaryl carbaldehyde **6** was accompanied by anomalous compound **7**, which still retains a norbornyl group as shown in Table 3. Decreasing the amount of norbornene did not bias the outcome of the reaction toward compounds **6**.

Table 3
Reaction of *o*-iodobenzyl alcohols in the presence of $Pd(OAc)_2$ and norbornene[a]



5 6 7

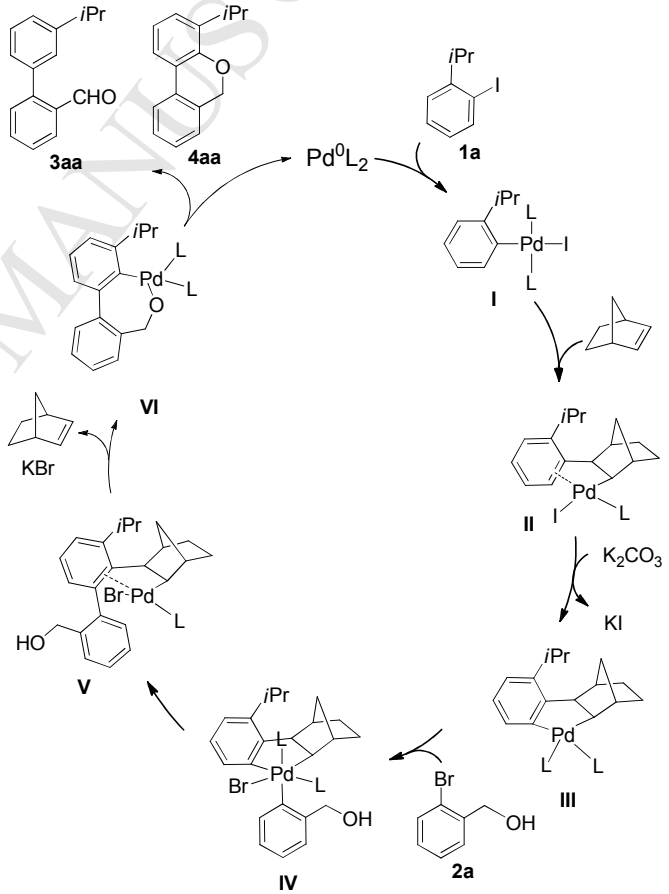
Entry	R^1, R^2	**6** yield (%)[b]	**7** yield (%)[b,c]
1	H, H	73%	13%
2	H, OMe	61%	12%
3	OMe, OMe	51%	13%
4	H, CO_2Me	71%	13%

[a] Reaction conditions: o-iodobenzyl alcohol **5** (0.72 mmol), norbornene (0.36 mmol), $Pd(OAc)_2$ (0.018 mmol), K_2CO_3 (0.90 mmol) in DMF (8 mL), under N_2 at 105° C for 24 h.

[b] Isolated yield based on the charged amount of the o-iodobenzyl alcohol **5**.

[c] Two diastereoisomers in 1:1 molar ratio.

The Scheme reported shows the proposed reaction pathway for the formation of o-biarylcarbaldehydes **3** and 6*H*-dibenzopyran derivatives **4** from aryl iodides **1** and primary o-bromobenzyl alcohols **2** under our palladium/norbornene catalysis conditions.



Scheme 2. Proposed reaction pathway to *o*-biarylcarbaldehyde **3aa** and dibenzopyran **4aa** (L = solvent or coordinating substrates).

The proposed mechanism for the reaction of 1-iodo-2-isopropylbenzene **1a** and o-bromobenzyl alcohol **2a**, is relevant to interpret the role of norbornene along with other reaction components and to facilitate in the discussion of mechanistic insights that have been elucidated in the present work.

The reaction starts with the oxidative addition of Pd(0) to aryl iodide **1a** to form arylpalladium complex **I**.[6] Norbornene stereoselectively inserts into the C–C bond of **I** generating

cis,exo arylnorbornylpalladium iodide **II**,[7] which in turn gives rise to palladacycle **III**[8,3i] through aryl C–H bond activation.[9] Oxidative addition of o-bromobenzyl alcohol **2a** to metallacycle **III** affords the Pd(IV) intermediate **IV**,[10] which undergoes reductive elimination to complex **V**[11] by selective aryl-aryl coupling. Norbornene deinsertion from **V** gives an aryl-Pd(II) intermediate that contains the benzylic OH group in appropriate position to form the oxapalladacycle **VI**.[12] Depending on the reaction conditions, complex **VI** can deliver either the carbaldehyde **3aa** or cyclic derivative **4aa** while regenerating Pd(0) catalyst. While the cyclic compound is formed by C–O coupling,[13] the o-biaryl carbaldehyde is obtained by an intramolecular redox process, with migration of a hydrogen atom from the benzylic group to the aryl carbon of the adjacent ring.

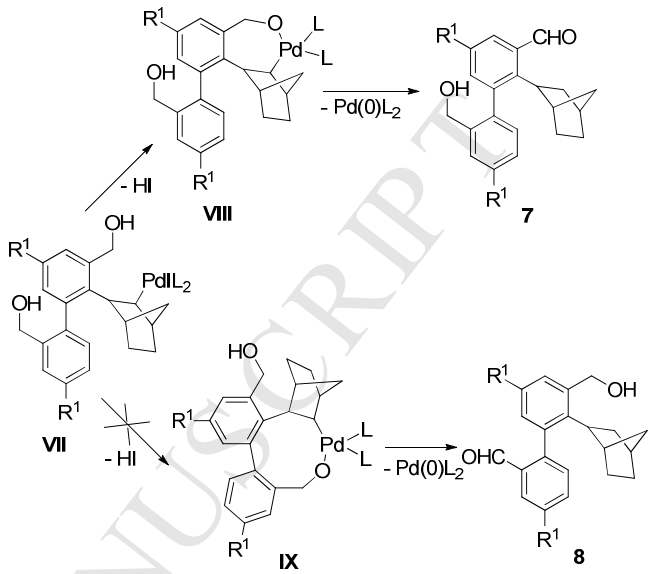
A critical feature of the reaction pathway is the catalytic character of norbornene participation.[3a-c] As shown in Scheme 2, norbornene is inserted at the beginning of the cycle and expelled towards the end. The quantity of norbornene in the reaction mixture is quite crucial since at high concentration it favors the insertion step (from **I** to **II**) while making the deinsertion difficult (from **V** to **VI**). Each substrate may have different requirements and the proper concentration is found experimentally.

As mentioned in the introduction, it is also appropriate to stress the need for an accurate balance of the species that give rise to palladium complex **VI**. In order to achieve a high yield of the desired products complex **VI** must result from comparable reaction rates of the Pd(II) intermediate **I** with norbornene to give the initial palladacycle **III** on the one hand, and of the hydroxymethyl bromoarene to afford the palladium(IV) complex **IV** on the other. If complex **VI** is not formed in a timely fashion, one of the two coupling partners, in particular the iodoarene, that is usually the most reactive, will undergo cyclization with norbornene and/or with itself through palladacycle **III** according to previously described pathways.[3a-c,14] This trend could be counteracted either by decreasing the norbornene concentration by up to one fourth (as shown in some experiments of Table 2) and/or by introducing electron-releasing substituents on the iodoarene to curtail its reactivity towards the oxidative addition of palladium(0).

Another important aspect of the reaction is connected with the dual reactivity of the oxapalladacycle **VI**: hydrogen transfer from the benzylic group to the palladium-bonded aryl carbon of the neighboring ring or reductive elimination by C-O bond formation, to form carbaldehyde **3aa** or dibenzopyran derivative **4aa**, respectively.

As previously mentioned, the first evidence for an intramolecolar redox reaction was evidenced by the fact that the unsymmetrical aryl coupling reaction of two molecules of an o-iodobenzyl alcohol led to the formation of the o-biarylcarbaldehyde **6** (Table 3), as the major product, in accord with the proposed mechanism of Scheme 2. In this case, however, both of the aryl rings involved in the redox process (Scheme 2, type **VI** intermediate) bear a hydroxymethyl group and only one is oxidized, giving rise to compound **6** (Table 3) containing both an aldehyde and an unreacted hydroxymethyl group. Had an intermolecular reaction occurred, the hydroxymethyl groups of the two rings would have been transformed by oxidation with unbiased selectivity.

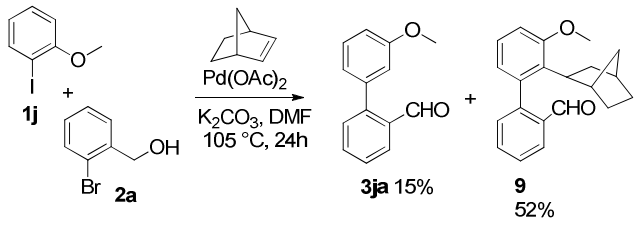
Moreover, in this case we observe the formation of compound **7** (Table 3), which still retains a norbornyl group in spite of the fact that norbornene deinsertion is usually observed in the mechanism of Scheme 2 (from **V** to **VI**) in the presence of bulky groups adjacent to the aryl-norbornyl bond. This behavior is likely to be due to the coordinating ability of the hydroxymethyl group of complex **VII** (Scheme 3) to form a ring with the norbornylpalladium species (complex **VIII**), thus making deinsertion more difficult. The subsequent formation of aryl carbaldehyde **7** must therefore be attributed to the migration of a hydrogen atom from the hydroxymethyl group to the norbornyl carbon now bonded to palladium, via the oxapalladacycle **VIII**, as represented in Scheme 3.



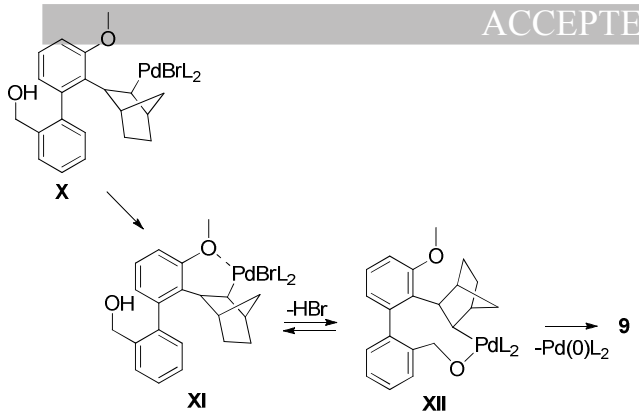
Scheme 3. Oxapalladacycle **VIII** precludes norbornene deinsertion and allows benzylic hydrogen transfer to the palladium-bonded norbornyl group.

Although an intramolecular reaction could hypothetically take place with the hydroxymethyl group of the other ring, no aldehyde groups at the 2-position of the biaryl systems were observed, presumably because the smaller 7-membered oxapalladacycle **VIII** is preferred to the larger 9-membered one **IX**. This observation lends further support to the proposed intramolecular mechanism.

Retention of the norbornyl group is also observed in the absence of the hydroxymethyl group. Other coordinating groups such as the methoxy have a similar effect (Scheme 4). By allowing 2-iodoanisole and 2-bromobenzylalcohol to react in the presence of $Pd(OAc)_2$ and norbornene as catalysts with K_2CO_3 as a base in DMF at 105 °C, compound **9**, containing the norbornyl moiety, was isolated as the major product in 52% yield together with 15% of carbaldehyde **3ja**. Lowering the ratio of norbornene to $Pd(OAc)_2$ from 20:1 to 10:1 did not increase the selectivity with regard to the formation of **3ja**, which was recovered in only 11% yield together with 34% of compound **9**. As shown in Scheme 5, compound **9** originates from the less favored 9-membered oxapalladacycle ring **XII**, that appears to be the only intermediate allowing an easy termination pathway to the sequential process.



Scheme 4. Anomalous behavior caused by the methoxy group.

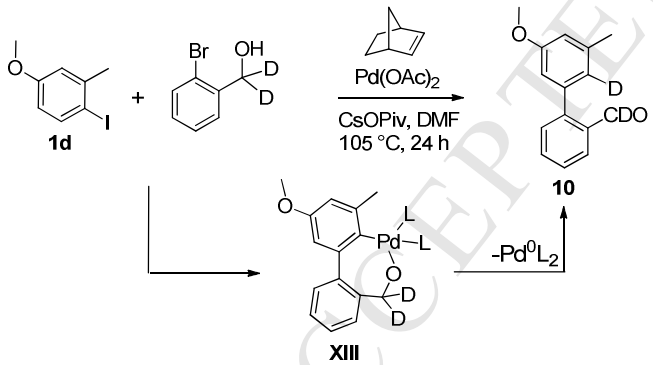


Scheme 5. Oxapalladacycles **XI** and **XII** inhibit norbornene expulsion.

Also noteworthy is that o-bromobenzaldehydes expected from intermolecular hydrogen transfer, as well as their possible reaction products with substrates present in solution, have never been detected. It is well known, however, that intermolecular hydrogen transfer reactions can readily terminate a palladium catalyzed reaction sequence.[15]

2.1.2. Deuterium labelling experiment

To probe the intramolecular hydrogen transfer from the benzylic group of oxapalladacycle of type **VI** (Scheme 2) to the ortho aromatic carbon of the adjacent ring unequivocally, a control reaction was carried out using (2-bromophenyl)methan-d_2-ol as a coupling partner with 1-iodo-4-methoxy-2-methylbenzene **1d** (Scheme 6). As revealed by ^{1}H NMR experiments, the resulting ortho biaryl carbaldehyde **10** (85% yield) contained one deuterium atom on the aldehydic group and another in the ortho position of the adjacent aryl ring with almost complete incorporation of deuterium within the limits of experimental error.[16]

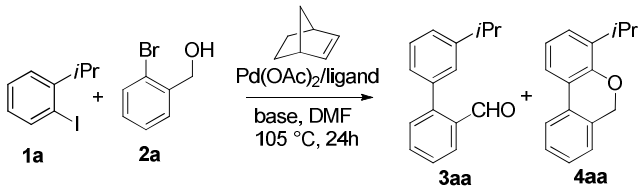


Scheme 6. Reaction of 1-iodo-4-methoxy-2-methylbenzene and (2-bromophenyl)methan-d_2-ol.

2.1.3. o-Bromobenzyl alcohol 2a: synthesis of dibenzopyran derivatives

We then attempted to bias the selectivity of the reaction towards the formation of dibenzopyran derivatives and investigated the reaction conditions while consistently using 1-iodo-2-isopropylbenzene (**1a**) and 2-bromobenzyl alcohol (**2a**) as model substrates. The results are summarized in Table 4.

Table 4
Screening of reaction conditions for the synthesis of dibenzopyran **4aa** from 1-iodo-2-isopropylbenzene **1a** and o-bromobenzyl alcohol **2a**[a]



entry	base	ligand	**3aa** yield (%)[b]	**4aa** yield (%)[b]
1	K_2CO_3	TPP	27	29
2	Cs_2CO_3	TPP	31	29
3	K_3PO_4	TPP	25	22
4	KOAc	TPP	29	17
5	KOPiv	TPP	60	-
6	CsOPiv	TPP	64	-
7	K_2CO_3	TFP	12	64
8	KOPiv	TFP	38	-
9	CsOPiv	TFP	35	5
10	K_2CO_3	mTCPP	10	56
11	CsOPiv	mTCPP	38	-
12	K_2CO_3	pTCPP	12	54
13	KOPiv	pTCPP	38	-
14	CsOPiv	pTCPP	35	5

[a] Reaction conditions: molar ratio of **1a**, **2a**, $Pd(OAc)_2$, norbornene, ligand and base 20:20:1:20:2:50; 2.2×10^{-3} mmol Pd/mL DMF; under N_2, 105 °C, 24 h.

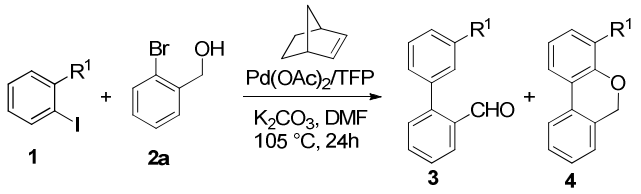
[b] GC and/or ^{1}H NMR yield on the charged amount of the aryl iodide **1a**.

The effect of ligands, bases and other parameters were investigated using $Pd(OAc)_2$/norbornene as the catalytic system in DMF at 105 °C for 24 h (Table 4). The addition of a phosphine ligand such as TPP (triphenylphosphine) in the presence of different bases such as K_2CO_3, Cs_2CO_3, K_3PO_4 and KOAc led to the formation of the o-biaryl carbaldehyde **3aa** and cyclic compound **4aa** in comparable amounts (entries 1-4). Switching to TFP (trifurylphosphine) as the ligand in combination with K_2CO_3 as a base proved beneficial with regard to the formation of dibenzopyran derivative **4aa** which was obtained in 64% yield along with 12% of compound **3aa** (entry 7). A similar trend was observed with mTCPP and pTCPP (meta- and para-chloro triphenylphosphines) with slightly lower yields (entries 10 and 12). The use of KOPiv or CsOPiv as a base offset the positive effect of TFP, mTCPP and pTCPP with regards to dibenzopyran formation (entries 8-9, 11 and 13-14). The best molar ratio of norbornene to $Pd(OAc)_2$ was found to be 20:1.

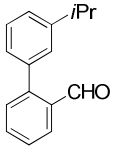
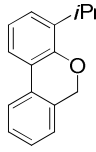
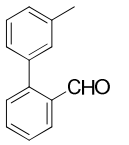
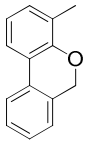
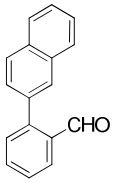
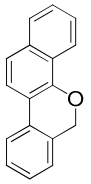
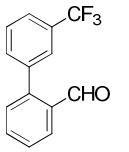
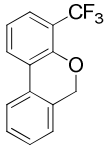
With our optimized conditions in hand we next studied the scope of the reaction using ortho-substituted aryl iodides as cross-coupling partners of o-bromobenzyl alcohol **2a** (Table 5). In agreement with previously reported data,[14] also 1-iodo-2-(trifluoromethyl) benzene containing an electron-withdrawing CF_3 group led to the corresponding dibenzopyran derivative in satisfactory yield.

Table 5

Synthesis of dibenzopyrans **4** from *ortho*-substituted aryl iodides **1** and o-bromobenzyl alcohol **2a**[a]



1 **2a** **3** **4**

Entry	R^1	**3** yield (%)[b]	**4** yield (%)[b]
1	*i*-Pr	 **3aa** 12%	 **4aa** 64%
2	Me	 **3ba** 10%	 **4ba** 61%
3	$(CH=CH)_2$	 **3ha** 8%	 **4ha** 77%
4	CF_3	 **3ka** 6%	 **4ka** 58%

[a] Reaction conditions: aryl iodide **1** (0.36 mmol), o-bromobenzyl alcohol **2a** (0.36 mmol), norbornene (0.36 mmol), $Pd(OAc)_2$ (0.018 mmol), TFP (0.036 mmol) and K_2CO_3 (0.90 mmol) in DMF (8 mL), under N_2 at 105° C for 24 h.

[b] Isolated yield on the charged amount of the aryl iodide **1**.

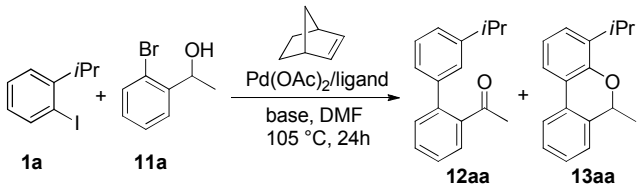
2.2. Secondary benzyl alcohols

2.2.1. Synthesis of dibenzopyran derivatives

As previously observed the reaction of ortho-substituted aryl iodides with secondary o-bromobenzyl alcohols carried out in the absence of any stabilizing ligands led to the formation of a mixture of ketones and dibenzopyran derivatives.[4] We have found that TFP as well as mTCPP and pTCPP had a positive effect on the C–O reductive elimination pathway of oxapalladacycle of type **VI** (Scheme 2) leading predominantly to the formation of dibenzopyran derivatives. Optimization of the reaction conditions was carried out using 1-iodo-2-isopropylbenzene **1a** and 1-(2-bromophenyl)ethanol **11a** as model substrates (Table 6). Satisfactory to good results were obtained except when highly electron rich aryl iodides such as 1-iodo-4-methoxy-2-methyl and 1-iodo-3,4-dimethoxy-2-methyl-benzene were used (Table 7, entries 4 and 5).

Table 6

Screening of reaction conditions for the synthesis of dibenzopyran **13aa** from 1-iodo-2-isopropylbenzene **1a** and 1-(2-bromophenyl)ethanol **11a**[a]



1a **11a** **12aa** **13aa**

Entry	base	ligand	**12aa** yield (%)[b]	**13aa** yield (%)[b]
1	K_2CO_3	-	41	44
2	Cs_2CO_3	-	31	24
3	CsOPiv	-	35	31
4	KOPiv	-	33	29
5	KOAc	-	35	20
6	K_2CO_3	TPP	43	48
7	CsOPiv	TPP	37	31
8	K_2CO_3	TFP	7	82
9	CsOPiv	TFP	35	39
10	K_2CO_3	mTCPP	14	62
11	K_2CO_3	pTCPP	13	67
12[d]	K_2CO_3	-	37	34
13[d]	K_2CO_3	TFP	15	77
14[e]	K_2CO_3	TFP	9	51
15[f]	K_2CO_3	TFP	6	69
16[g]	K_2CO_3	TFP	9	77

[a] Reaction conditions: molar ratio of **1a**, **11a**, $Pd(OAc)_2$, norbornene, ligand and base 20:20:1:10:2:50; 2.2×10^{-3} mmol Pd/mL; DMF as solvent, under N_2, 105 °C, 24 h.

[b] GC and/or ^1H NMR yield on the charged amount of the aryl iodide **1a**.

[c] molar ratio of the base to palladium 40:1.

[d] DMA

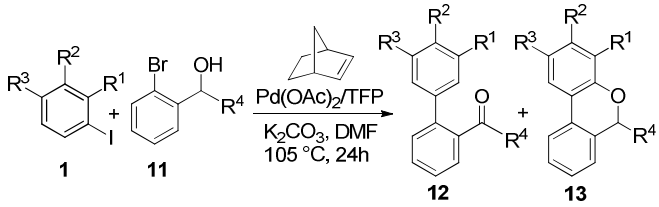
[e] MeCN

[f] 80 °C

[g] 120 °C

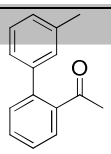
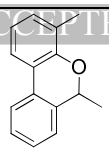
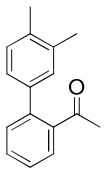
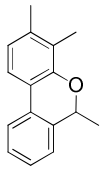
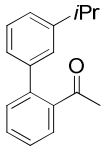
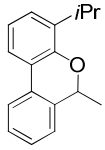
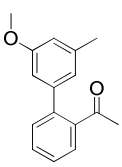
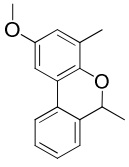
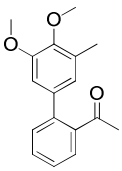
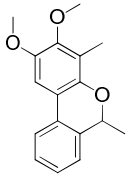
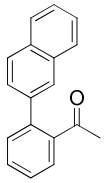
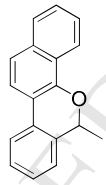
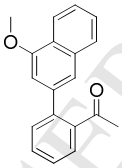
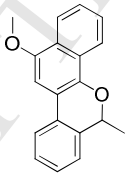
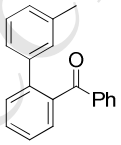
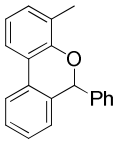
Table 7

Synthesis of dibenzopyrans **13** from *ortho*-substituted aryl iodides **1** and secondary o-bromobenzyl alcohol **11**[a]



1 **11** **12** **13**

Entry	R^1, R^2. R^3	R^4	**12** yield (%)[b]	**13** yield (%)[b]

1	Me, H, H	Me	 **12ba** 8%	 **13ba** 79%
2	Me, Me, H	Me	 **12ia** 9%	 **13la** 75%
3	*i*Pr, H, H	Me	 **12aa** 7%	 **13aa** 82%
4	Me, H, OMe	Me	 **12da** 16%	 **13da** 68%
5	Me, OMe, OMe	Me	 **12ea** 21%	 **13ea** 61%
6	$(CH=CH)_2$, H	Me	 **12ha** 4%	 **13ha** 88%
7	$(CH=CH)_2$, OMe	Me	 **12ia** 17%	 **13ia** 73%
8	Me, H, H	Ph	 **12bb** 9%	 **13bb** 69%

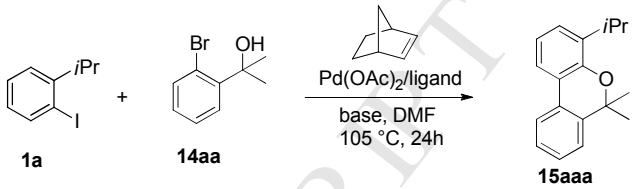
[a] Reaction conditions: aryl iodide **1** (0.36 mmol), o-bromobenzyl alcohol **11** (0.36 mmol), norbornene (0.36 mmol), $Pd(OAc)_2$ (0.018 mmol), TFP (0.036 mmol) and K_2CO_3 (0.90 mmol) in DMF (8 mL), under N_2 at 105° C for 24 h.

[b] Isolated yield on the charged amount of the aryl iodide **1**.

*2.3. Tertiary benzyl alcohols: Synthesis of dibenzopyrans **15***

Not surprisingly, given the lack of benzylic hydrogens, the synthesis of dibenzopyran derivatives starting from tertiary o-bromobenzyl alcohols and ortho-substituted aryl iodides was very efficient in terms of both yield and selectivity. The reaction of 1-iodo-2-isopropylbenzene (**1a**) and 2-(2-bromophenyl)propan-2-ol (**14aa**), in the presence of $Pd(OAc)_2$ and norbornene as catalysts, K_2CO_3 as a base, at 105 °C for 24 h, afforded cyclic compound **15aaa** in 83% yield (Table 8, entry 1). In our initial studies, this reaction was chosen as a model to optimize the reaction conditions. The results are summarized in Table 8.

Table 8
Screening of reaction conditions for the synthesis of dibenzopyran **15aaa** from 1-iodo-2-isopropylbenzene **1a** and 2-(2-bromophenyl)propan-2-ol **14aa**[a]



Entry	base	ligand	**15aaa** yield (%)[b]
1	K_2CO_3	-	83
2	CsOPiv	-	77
3	KOPiv	-	78
4	K_2CO_3	TPP	80
5	K_2CO_3	TFP	83
6	K_2CO_3	pTCPP	80
7[c]	K_2CO_3	-	67
8[d]	K_2CO_3	-	65
9[e]	K_2CO_3	-	82
10[f]	K_2CO_3	-	74
11[g]	K_2CO_3	-	75

[a] Reaction conditions: molar ratio of **1a**, **14aa**, $Pd(OAc)_2$, norbornene, ligand and base 20:20:1:20:2:50; 2.2×10^{-3} mmol Pd/mL DMF; under N_2, 105 °C, 24 h.

[b] GC and/or ^{1}H NMR yield based on the charged amount of **1a**.

[c] DMA

[d] MeCN

[e] 80 °C

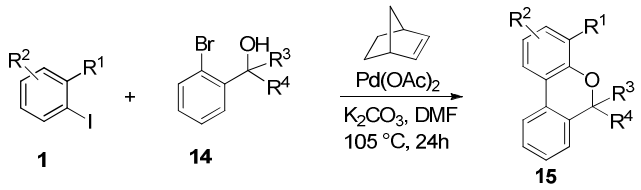
[f] 120 °C

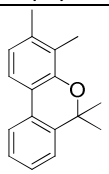
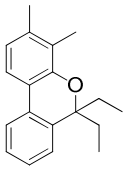
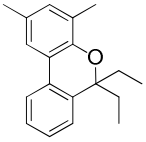
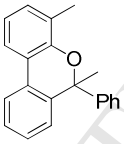
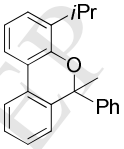
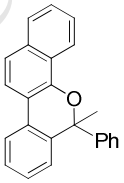
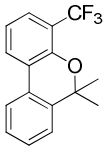
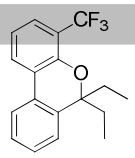
[g] molar ratio of norbornene to palladium 10:1

K_2CO_3 was found to be the base of choice in terms of dibenzopyran yield and selectivity (entries 1-3); phosphine ligands, which proved to be crucial for the synthesis of dibenzopyran rings resulting from primary or secondary benzyl alcohols, as well as solvent, temperature, amount of norbornene and base did not significantly affect the yield of dibenzopyran **15** (entries 4-11). As expected due to the absence of benzylic hydrogens, only the geminal groups have a dramatic effect on ring closure.[17] Dibenzopyran heterocycles **15** containing the electron-withdrawing trifluoromethyl group were also prepared (entries 7–8, Table 9) with good yields starting from the corresponding bromide. Less desirable results were observed with the corresponding aryl iodide likely because of its increased reactivity as compared to aryl bromides. The yields were further increased by using CsOPiv as a base (entries 7-8). The trend

observed for the substituent effect is similar to that reported in Table 1.

Table 9
Synthesis of dibenzopyrans **15** from *ortho*-substituted aryl iodides **1** and tertiary o-bromobenzyl alcohol **14**[a]



Entry	R^1	R^2	R^3	R^4	**15** yield (%)[b]
1	Me	3-Me	Me	Me	 **15laa** 86%
2	Me	3-Me	Et	Et	 **15lbb** 98%
3	Me	4-Me	Et	Et	 **15cbb** 98%
4	Me	H	Me	Ph	 **15bac** 86%
5	*i*Pr	H	Me	Ph	 **15aac** 93%
6	$(CH=CH)_4$		Me	Ph	 **15hac** 88%
7	CF_3	H	Me	Me	 **15kaa** 59,72[c],88[d]%
8	CF_3	H	Et	Et	 **15kbb** 71,80[c],99[d]%

[a] Reaction conditions: aryl iodide **1** (0.36 mmol), o-bromobenzyl alcohol **14** (0.36 mmol), norbornene (0.36 mmol), $Pd(OAc)_2$ (0.018 mmol), K_2CO_3 (0.90 mmol) in DMF (8 mL), under N_2 at 105° C for 24 h;

[b] Isolated yields based on the charged amount of **1**.

[c] 1-bromo-2-(trifluoromethyl)benzene in place of 1-iodo-2-(trifluoromethyl)benzene

[d] CsOPiv as base; 1-bromo-2-(trifluoromethyl)benzene in place of 1-iodo-2-(trifluoromethyl)benzene

In all cases no reaction was observed in the absence of norbornene. All the steps involved in the formations of o-biaryl carbaldehydes and dibenzopyran derivatives worked nicely and led to the desired final products in satisfactory to good yields. In spite of its complexity the overall reaction can be carried out under simple and mild conditions, starting from simple building blocks thus offering a valuable synthetic tool. In particular the dibenzopyrans presented here are not easily accessible by other routes including those recently reported.[18]

3. Conclusions

In conclusion, we have developed a methodology for the synthesis of selectively substituted o-biaryl carbaldehydes and probed that the reaction mechanism proceeds through an intramolecular redox process by robust deuterium labelling experiments and substantial chemical evidence. The predominant formation of dibenzopyran derivatives starting either from primary or secondary o-bromobenzyl alcohols as partner of ortho-substituted aryl iodides has been obtained taking advantage of the positive effect exerted by TFP. Ligands were not required when tertiary o-bromobenzyl alcohols were used since ring closure is strongly favored by the geminal group effect.

4. Experimental section

4.1. General

Most starting materials were commercially available and were used without further purification. 1-Iodo-2-isopropyliodobenzene, 1-iodo-4-methoxy-2-methylbenzene were prepared by iodination of the corresponding diazonium salt according to the literature.[19] 1-Iodo-3,4-dimethoxy-2-methylbenzene,[20] 1-iodo-4-methoxynaphthalene,[21] (2-bromophenyl)phenylmethanol,[22] 3-(2-bromophenyl)pentan-3-ol,[17a] 2-bromobenzenemethan-d_2-ol,[23] 1-(2-bromophenyl)-1-phenylethanol,[24] (2-iodo-5-methoxyphenyl)methanol,[25] (6-iodo-2,3-dimethoxyphenyl)methanol,[25] were prepared according to procedures adapted from the literature. (5-Carbomethoxy-2-iodophenyl)methanol was prepared starting from methyl 4-amino-3-methylbenzoate by diazotization, followed by bromination of the benzylic group and final hydrolysis.[26]

All palladium-catalyzed reactions were carried out under nitrogen using standard Schlenk techniques. DMF was dried and stored over 4 Å molecular sieves under nitrogen. Gas chromatographic analyses were performed with an Agilent Technologies 7820A GC System using a 30 m SE-30 capillary

column. Flash column chromatography was carried out on Merck Kieselgel 60 and TLC on Merck $60F_{254}$ plates.

Mass spectra (EI) were obtained with a Hewlett Packard instrument working at 70 eV ionization energy. NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE 400 spectrometer, unless otherwise indicated. Chemical shifts are reported in parts per million using the solvent as internal reference (7.26 and 77.00 ppm, respectively for ^1H and ^{13}C NMR). The reported assignments are based on decoupling, COSY, NOESY, HMQC and HMBC correlation experiments. Interchangeable assignments are marked by an asterisk. IR spectra were recorded on a Nicolet FT-IR 5700 spectrophotometer (Thermo Electron Corporation). Melting points were determined with an Electrothermal apparatus and are uncorrected. Elemental analyses were performed with a Carlo Erba EA 1108-Elemental Analyzer.

4.2. General procedure

4.2.1. General procedure for the reaction of o-iodobenzyl alcohols in the presence of norbornene, $Pd(OAc)_2$ and K_2CO_3 in DMF

A DMF solution (8 mL) of the *o*-iodobenzyl alcohol (0.72 mmol) and norbornene (34 mg, 0.36 mmol) was added under nitrogen to a Schlenck-type flask containing $Pd(OAc)_2$ (4 mg, 0.018 mmol) and K_2CO_3 (124 mg, 0.90 mmol). The reaction mixture was stirred at 105 °C for 24h. After cooling to room temperature the organic layer was diluted with EtOAc (20 mL), washed twice with water (20 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography on silica gel using mixtures of hexane-EtOAc as eluent.

4.2.2. General procedure for the reaction of o-substituted aryl iodides with primary, secondary or tertiary 2-bromobenzyl alcohols in the presence of norbornene, $Pd(OAc)_2$, a ligand and a base in DMF

A DMF solution (8 mL) of the *o*-substituted aryl iodide (0.36 mmol), the o-bromobenzyl alcohol (0.36 mmol) and norbornene (34 mg, 0.36 mmol) was added under nitrogen to a Schlenck-type flask, containing $Pd(OAc)_2$ (4 mg, 0.018 mmol), the phosphine (0.036 mmol), when required, and K_2CO_3 (124 mg, 0.90 mmol) or CsOPiv (211 mg, 0.90). The reaction mixture was stirred at 105 °C for 24h. After cooling to room temperature the organic layer was diluted with EtOAc (20 mL), washed twice with water (20 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography on silica gel using mixtures of hexane-EtOAc as eluent.

*4.2.2.1. 3'-i-Propyl-[1,1']-biphenyl-2-carbaldehyde (**3aa**, Table 5, entry 1)*[4]

From 1-iodo-2-isopropylbenzene (89 mg, 0.36 mmol), (2-bromophenyl)methanol (67 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **3aa** was obtained in 12% yield (10 mg). Eluent: hexane.

*4.2.2.2. 4-i-Propyl-6H-dibenzo[b,d]pyran (**4aa**, Table 5, entry 1)*[4]

From 1-iodo-2-isopropylbenzene (89 mg, 0.36 mmol), (2-bromophenyl)methanol (67 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **4aa** was obtained in 64% yield (56 mg). Eluent: hexane.

*4.2.2.3. 3'-Methyl-[1,1']-biphenyl-2-carbaldehyde (**3ba**, Table 5, entry 2)*[4]

From 2-iodotoluene (79 mg, 0.36 mmol), (2-bromophenyl)methanol (67 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **3ba** was obtained in 10% yield (7 mg). Eluent: hexane.

*4.2.2.4. 4-Methyl-6H-dibenzo[b,d]pyran (**4ba**, Table 5, entry 2)*[27]

From 2-iodotoluene (79 mg, 0.36 mmol), (2-bromophenyl)methanol (67 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **4ba** was obtained in 61% yield (43 mg). Eluent: hexane.

*4.2.2.5. 2-(Naphthalen-2'-yl)benzaldehyde (**3ha**, Table 5, entry 3)*[4]

From 2-iodonaphthalene (91 mg, 0.36 mmol), (2-bromophenyl)methanol (67 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **3ha** was obtained in 8% yield (7 mg). Eluent: hexane.

*4.2.2.6. 6H-Benzo[d]naphtho[1,2-b]pyran (**4ha**, Table 5, entry 3)*[4]

From 2-iodonaphthalene (91 mg, 0.36 mmol), (2-bromophenyl)methanol (67 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **4ha** was obtained in 77% yield (64 mg). Eluent: hexane.

*4.2.2.7. 3'-(Trifluoromethyl)-[1,1']-biphenyl-2-carbaldehyde (**3ka**, Table 5, entry 4)*[4]

From 1-iodo-2-(trifluoromethyl)benzene - (98 mg, 0.36 mmol), (2-bromophenyl)methanol (67 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **3ka** was obtained in 6% yield (5 mg). Eluent: hexane.

*4.2.2.8. 4-(Trifluoromethyl)-6H-dibenzo[b,d]pyran (**4ka**, Table 5, entry 4)*[4]

From 1-iodo-2-(trifluoromethyl)benzene (98 mg, 0.36 mmol), (2-bromophenyl)methanol (67 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.9 mmol) and TFP (8.3 mg, 0.036 mmol), product **4ka** was obtained in 58% yield (52 mg). Eluent: hexane.

*4.2.2.9. 1-(3'-Methyl-[1,1'-biphenyl]-2-yl)ethanone (**12ba**, Table 7, entry 1)*[4]

From 2-iodotoluene (79 mg, 0.36 mmol), 1-(2-bromophenyl)ethanol (72 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **12ba** was obtained in 8% yield (6 mg). Eluent: hexane.

*4.2.2.10. 4,6-Dimethyl-6H-dibenzo[b,d]pyran (**13ba**, Table 7, entry 1)*[4]

From 2-iodotoluene (79 mg, 0.36 mmol), 1-(2-bromophenyl)ethanol (72 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **13ba** was obtained in 79% yield (60 mg). Eluent: hexane.

*4.2.2.11. 1-(3'-Methoxy-5'-methyl-[1,1'-biphenyl]-2-yl)ethanone (**12da**, Table 7, entry 4)*[4]

From 1-iodo-4-methoxy-2-methylbenzene (89 mg, 0.36 mmol), 1-(2-bromophenyl)ethanol (72 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **12da** was obtained in 16% yield (14 mg). Eluent: hexane.

*4.2.2.12. 2-Methoxy-4,6-dimethyl-6H-dibenzo[b,d]pyran (**13da**, Table 7, entry 4)*[4]

From 1-iodo-4-methoxy-2-methylbenzene (89 mg, 0.36 mmol), 1-(2-bromophenyl)ethanol (72 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **13da** was obtained in 68% yield (59 mg). Eluent: hexane.

*4.2.2.13. 1-(3',4'-Dimethoxy-5'-methyl-[1,1'-biphenyl]-2-yl)ethanone (**12ea**, Table 7, entry 5)*[4]

From 1-iodo-3,4-dimethoxy-2-methylbenzene (99 mg, 0.36 mmol), 1-(2-bromophenyl)ethanol (72 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **12ea** was obtained in 21% yield (20 mg). Eluent hexane/EtOAc 97:3

*4.2.2.14. 2,3-Dimethoxy-4,6-dimethyl-6H-dibenzo[b,d]pyran (**13ea**, Table 7, entry 5)*[4]

From 1-iodo-3,4-dimethoxy-2-methylbenzene (99 mg, 0.36 mmol), 1-(2-bromophenyl)ethanol (72 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **13ea** was obtained in 61% yield (58 mg). Eluent hexane/EtOAc 97:3

*4.2.2.15. 1-[2-(Naphthalen-2-yl)phenyl]ethanone (**12ha**, Table 7, entry 6)*[4]

From 1-iodonaphthalene (91 mg, 0.36 mmol), 1-(2-bromophenyl)ethanol (72 mg, 0.36 mmol) using K_2CO_3 as a base (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **12ha** was obtained in 4% yield (4 mg). Eluent: hexane.

*4.2.2.16. 6-Methyl-6H-benzo[d]naphtho[1,2-b]pyran (**13ha**, Table 7, entry 6)*[4]

From 1-iodonaphthalene (91 mg, 0.36 mmol), 1-(2-bromophenyl)ethanol (72 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **13ha** was obtained in 88% yield (88 mg). Eluent: hexane.

*4.2.2.17. 1-[2-(4-Methoxynaphthalen-2-yl)phenyl]ethanone (**12ia**, Table 7, entry 7)*[4]

From 1-iodo-4-methoxyonaphthalene (102 mg, 0.36 mmol), 1-(2-bromophenyl)ethanol (72 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **12ia** was obtained in 17% yield (17 mg). Eluent: hexane/EtOAc 97:3.

*4.2.2.18. 12-Methoxy-6-methyl-6H-Benzo[d]naphtho[1,2-b]pyran (**13ia**, Table 7, entry 7)*[4]

From 1-iodo-4-methoxyonaphthalene (102 mg, 0.36 mmol), 1-(2-bromophenyl)ethanol (72 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **13ia** was obtained in 73% yield (74 mg). Eluent: hexane/EtOAc 97:3.

*4.2.2.19. 3'-Methyl-[1,1'-biphenyl]-2-yl)(phenyl)methanone (**12bb**, Table 7, entry 8)*[4]

From 2-iodotoluene (79 mg, 0.36 mmol), (2-bromophenyl)phenylmethanol (95 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **12bb** was obtained in 9% yield (9 mg). Eluent: hexane/EtOAc 95:5.

*4.2.2.20. 4-Methyl-6-phenyl-6H-dibenzo[b,d]pyran (**13bb**, Table 7, entry 8)*[4]

From 2-iodotoluene (79 mg, 0.36 mmol), (2-bromophenyl)phenylmethanol (95 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.90 mmol) and TFP (8.3 mg, 0.036 mmol), product **13bb** was obtained in 69% yield (70 mg). Eluent: hexane/EtOAc 95:5.

*4.2.2.21. 4-i-Propyl-6,6-dimethyl-6H-dibenzo[b,d]pyran (**15aaa**, Table 8)*[4]

From 1-iodo-2-isopropylbenzene (89 mg, 0.36 mmol), 2-(2-bromophenyl)propan-2-ol (77 mg, 0.36 mmol) using K_2CO_3 (124 mg, 0.9 mmol), product **15aaa** was obtained in 83% yield (75 mg). Eluent: hexane.

4.3. Characterization data

*4.3.1. 3'-Hydroxymethyl-[1,1']-biphenyl-2-carbaldehyde (**6**, R^1,R^2 = H, Table 3, entry 1)*

From (2-iodophenyl)methanol (168 mg, 0.72 mmol) using norbornene (34 mg, 0.36 mmol), product **6** was obtained in 73% yield (55 mg). Eluent: hexane/EtOAc 9:1. Mp. (hexane): 66 °C.

^{1}H NMR: δ 9.94 (1H, s, CHO), 8.01 (1H, dd, J = 7.8, 1.4 Hz, H3), 7.63 (1H, td, J = 7.5, 1.4 Hz, H5), 7.53–7.40 (4H, m, H4, H5', H4', H6), 7.38 (1H, br s, H2'), 7.31–7.24 (1H, m, H6'), 4.75 (2H, s, CH_2OH), 2.88 (1H, br s, OH); ^{13}C NMR: δ 192.5 (CHO), 145.8 (C1), 141.2 (C3'), 137.9 (C1'), 133.6 (C5), 133.5 (C2), 130.7 (C6), 129.3 (C6'), 128.5 (C5'), 128.4 (C2'), 127.8 (C4), 127.6 (C3), 126.6 (C4'), 64.8 (CH_2OH); MS (EI, 70 eV): M^+ 212 (52), m/z 194 (21), 181 (100), 166 (40), 165 (91), 153 (47), 152 (72), 77 (37), 76 (27). IR (neat, cm^{-1}): ν 1693. Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70 Found: C, 79.14; H, 5.72.

*4.3.2. 2'-Hydroxymethyl-2-(2"-exo-norbornyl)-[1,1']-biphenyl-3-carbaldehyde (**7**, R^1, R^2 = H, Table 3, entry 1)*

From (2-iodophenyl)methanol (168 mg, 0.72 mmol) using norbornene (34 mg, 0.36 mmol), product **7** was obtained in 13% yield (13 mg). Eluent: hexane/EtOAc 9:1. Colorless oil. A 1:1 mixture of two stereoisomers.

^{1}H NMR: δ 10.75, 10.72 (1H, 2s, CHO), 7.86 (1H, 2dd, J = 7.4, 1.9 Hz), 7.56 (1H, d further split), 7.42 (1H, t, J = 7.5Hz), 7.35–7.33 (1H, m), 7.29–7.21 (2H, m), 7.18–7.10, (1H, m), 4.40, 4.39 (2H, 2s, CH_2OH), 3.14, 3.04 (1H, 2 pst, J ≅ 8.5 Hz), 2.39–2.34, 2.28–2.21 (1H, 2m), 2.21–2.16 (1H, m), 1.71–0.8 (9H, m); ^{13}C NMR: δ 194.0,193.7, 146.8, 146.6, 141.2, 141.1, 140.8, 140.6, 138.4, 138.1, 136.4, 136.3, 135.8, 135.7, 130.3, 129.9, 129.3, 129.2, 128.0, 127.9, 127.3, 127.2, 127.1, 127.0, 125.6, 125.5, 63.1, 63.0, 45.7, 45.6, 43.5, 42.5, 42.3, 42.1, 38.1, 37.5, 37.1, 36.9, 32.7, 31.9, 28.2, 27.8. MS (EI, 70 eV): (M^+ - 18) 288 (3), m/z 219 (34), 211 (100), 179 (53), 178 (52), 165 (60), 67 (36). IR (neat, cm^{-1}): ν 1691. Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24 Found: C, 82.22; H, 7.14.

*4.3.3. 3'-Hydroxymethyl-4,5'-dimethoxy-[1,1']-biphenyl-2-carbaldehyde (**6**, R^1 = H, R^2= OMe, Table 3, entry 2)*

From (2-iodo-5-methoxyphenyl)methanol (191 mg, 0.72 mmol) using norbornene (34 mg, 0.36 mmol), product **6** was obtained in 61% yield (59 mg). Eluent: hexane/EtOAc 8:2. Colorless oil.

^{1}H NMR: δ 9.89 (1H, s, CHO), 7.44 (1H, brs), 7.31 (1H, d, J = 8.1 Hz), 7.14 (1H, d, J = 8.1 Hz), 6.95 (1H, s), 6.87 (1H, s), 6.75 (1H, s), 4.68 (2H, s, CH_2OH), 3.86 (3H, s), 3.80 (3H,s), 2.61 (1H, br s, OH); ^{13}C NMR: δ 192.0, 145.6, 141.0, 137.3, 133.4, 133.3, 130.3, 128.0, 127.8, 127.5, 126.6, 113.6, 110.9, 64.8, 55.5, 54.3; MS (EI, 70 eV): M^+ 272 (44), m/z 254 (15), 241 (100), 221 (20), 165 (90), 153 (41), 107 (65),76 (47). IR (neat, cm^{-1}): ν 1691. Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92 Found: C, 70.64; H, 5.82.

*4.3.4. 2'-Hydroxymethyl-4',5-dimethoxy-2-(2"-exo-norbornyl)-[1,1']-biphenyl-3-carbaldehyde (**7**, R^1 = H, R^2= OMe, Table 3, entry 2)*

From (2-iodo-5-methoxyphenyl)methanol (191 mg, 0.72 mmol) using norbornene (34 mg, 0.36 mmol), product **7** was obtained in 12% yield (15 mg). Eluent: hexane/EtOAc 8:2. Colorless oil. A 1:1 mixture of two stereoisomers.

^{1}H NMR: δ 10.67, 10.65 (1H, 2s, CHO), 7.35 (1H, br d, J = 2.5 Hz), 7.10 (1H, s), 7.03-7.00 (1H, m), 6.84–6.77 (2H, m), 4.33 (2H, s), 3.84 (3H, s), 3.77 (3H, s), 3.00, 2.91 (1H, 2 pst, J ≅ 8.3 Hz), 2.31–2.13 (2H, m), 1.81 (1H, s, OH) 1.55-0.9 (8H, m); ^{13}C NMR: δ 194.2, 193.9, 147.7, 147.6, 140.2, 140.0, 140.8, 140.7, 137.2, 137.0, 136.0, 135.8, 135.6, 135.5, 130.1, 129.9, 129.3, 129.1, 128.1, 127.9, 127.1, 127.0, 113.6, 113.4, 111.0, 110.9, 63.2, 63.1, 55.5, 55.2, 54.5, 54.3, 45.6, 45.5, 43.5, 42.4, 42.3, 42.1, 38.0, 37.5, 37.0, 36.9, 32.9, 31.9, 28.2, 27.7. MS (EI, 70 eV): (M^+ - 18) 348 (9), m/z 297 (13), 289 (100), 267 (65), 179 (13), 178 (38), 165 (54), 67 (19). IR (neat, cm^{-1}): ν 1693. Anal. Calcd for $C_{23}H_{26}O_4$: C, 75.38; H, 7.15 Found: C, 75.33; H, 7.01.

*4.3.5. 5'-Hydroxymethyl-3,4,3',4'-tetramethoxy-1,1'-biphenyl-2-carbaldehyde (**6**, R^1, R^2= OMe, Table 3, entry 3)*

From (6-iodo-2,3-dimethoxyphenyl)methanol, (212 mg, 0.72 mmol) using norbornene (34 mg, 0.36 mmol), product **6** was obtained in 51% yield (60 mg). Eluent: hexane/EtOAc 8:2. Colorless oil.

^{1}H NMR: δ 9.81 (1H, s, CHO), 7.44 (1H, brs),7.31 (1H, d, J = 7.8 Hz), 7.07 (1H, d, J =7.8 Hz), 6.87 (1H, s), 4.60 (2H, s, CH_2OH), 3.95 (3H, s), 3.87 (3H,s), 3.78 (3H, s), 3.80 (3H,s), 2.53 (1H, br s, OH); ^{13}C NMR: δ 192.2, 145.5, 141.0, 137.3, 133.3, 133.3, 130.0, 128.2, 127.5, 113.4, 113.1, 111.3, 110.9, 64.6, 55.5, 55.3, 54.7, 54.3. MS (EI, 70 eV): M^+ 332 (24), m/z 314 (35), 301 (100), 165 (88), 153 (51). IR (neat, cm^{-1}): ν 1693. Anal. Calcd for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07 Found: C, 65.00; H, 6.02.

*4.3.6.2'-Hydroxymethyl-4,5,3',4'-tetramethoxy-2-(2"-exo-norbornyl)-1,1'-biphenyl-3-carbaldehyde (**7**, R^1, R^2= OMe, Table 3, entry 3)*

From (6-iodo-2,3-dimethoxyphenyl)methanol, (212 mg, 0.72 mmol) using norbornene (34 mg, 0.36 mmol), product **7** was obtained in 13% yield (19 mg). Eluent: hexane/EtOAc 8:2. Colorless oil. A 1:1 mixture of two stereoisomers.

^{1}H NMR: δ 10.62, 10.60 (1H, 2s, CHO), 7.40 (1H, brs), 7.26 (1H, d, J = 7.9 Hz), 7.09 (1H, d, J = 7.9 Hz), 4.28 (2H, s), 3.84 (3H, s), 3.78 (3H, s), 3.72 (3H, s), 3.66 (3H, s), 3.03, 2.95 (1H, 2 pst, J ≅ 8.4 Hz), 2.30–2.12 (2H, m), 1.83 (1H, s, OH) 1.55–0.8 (8H, m); ^{13}C NMR: δ 192.2, 190.0, 145.7, 145.5, 141.1, 141.0, 137.3, 137.2, 133.3, 133.2, 133.1,133.0, 131.2, 130.0, 128.2, 120.0, 127.5. 127.3, 113.4, 113.3, 113.1,113.0, 111.3, 111.1, 111.0 110.9, 64.6, 64.5, 55.7, 55.6, 55.5, 55.3, 54.7, 54.6, 54.4, 54.3, 45.6, 45.5, 43.5, 42.4, 42.3, 42.1, 38.0, 37.5, 37.0, 36.9, 32.9, 31.9, 28.2, 27.7. MS (EI, 70 eV): (M^+ - 18) 408 (15), m/z 357 (19), 349 (100), 267 (35), 178 (38), 165 (45), 67 (22). IR (neat, cm^{-1}): ν 1691. Anal. Calcd for $C_{25}H_{30}O_6$: C, 70.40; H, 7.09 Found: C, 70.43; H, 7.06.

*4.3.7. 5'-Hydroxymethyl-4,3'-dicarbomethoxy-1,1'-biphenyl-2-carbaldehyde (**6**, R^1= H, R^2= CO_2Me, Table 3, entry 4)*

From (5-carbomethoxy-2-iodophenyl)methanol (210 mg, 0.72 mmol) using norbornene (34 mg, 0.36 mmol), product **6** was obtained in 71% yield (83 mg). Eluent: hexane/EtOAc 7:3. Colorless oil.

^{1}H NMR: δ 9.97 (1H, s, CHO), 8.04 (1H, d, J = 1.2 Hz), 8.01 (1H, d, J = 1.2 Hz), 7.91 (1H, dd, J = 8.1, 1.1 Hz), 7.72 (1H, s), 7.61 (1H, d, J = 8.1 Hz), 7. 54 (1H, s), 4.76 (2H, s, CH_2OH), 3.94 (3H, s), 3.88 (3H, s), 2.60 (1H, br s, OH); ^{13}C NMR: δ 192.5, 166.0, 165.7, 145.2, 141.5, 137.0, 133.2, 133.0, 130.9, 130.1, 128.0, 127.8, 127.4, 127.0, 126.7, 64.8, 52.0, 51.8; MS (EI, 70 eV): M^+ 328 (35), m/z 310 (19), 295 (100), 267 (29), 165 (82), 153 (52), 107 (61),76 (60). IR (neat, cm^{-1}): ν 1721, 1693. Anal. Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91 Found: C, 65.80; H, 4.82.

*4.3.8. 2'-Hydroxymethyl-4',5-dicarbomethoxy-2-(2"-exo-norbornyl)-1,1'-biphenyl-3-carbaldehyde (**7**, R^1= H, R^2= CO_2Me, Table 3, entry 4)*

From (5-carbomethoxy-2-iodophenyl)methanol (210 mg, 0.72 mmol) using norbornene (34 mg, 0.36 mmol), product **7** was obtained in 13% yield (15 mg). Eluent: hexane/EtOAc 7:3. Colorless oil. A 1:1 mixture of two stereoisomers.

^{1}H NMR: δ 10.76, 10.74 (1H, 2s, CHO), 8.05 (1H, s), 7.92 (1H, d further split, J = 8.1 Hz), 7.82 (1H, s), 7.78 (1H, s), 7.45 (1H, d, J = 8.1 Hz), 4.42 (2H, s), 3.93 (3H, s), 3.86 (3H, s), 3.08, 3.00 (1H, 2 pst, J ≅ 8.3 Hz), 2.30–2.11 (2H, m), 1.80 (1H, s, OH) 1.60–0.80 (8H, m); ^{13}C NMR: δ 194.0,193.8, 166.0, 165.8, 165.7, 165.5, 147.7, 147.6, 140.2, 140.0, 140.8, 140.7, 137.2, 137.0, 136.0, 135.8, 135.6, 135.5, 130.1, 129.9, 129.3, 129.1, 128.1, 127.9, 127.1, 127.0, 125.5, 125.4, 125.1, 125.0, 63.1, 63.1, 52.5, 52.2, 51.5, 51.3, 45.4, 45.2, 43.5, 42.2, 42.0, 41.8, 38.5, 37.9, 37.0, 36.8, 32.8, 31.9, 28.0, 27.8. MS (EI, 70 eV): (M^+ - 18) 404 (19), m/z 363 (41), 289 (100), 267 (45), 178 (18), 165 (36), 67 (9). IR (neat, cm^{-1}): ν 1721, 1693. Anal. Calcd for $C_{25}H_{26}O_6$: C, 71.07; H, 6.20 Found: C, 71.00; H, 6.23.

*4.3.9. 3-Methoxy-2-(2"-exo-norbornyl)-1,1'-biphenyl-2'-carbaldehyde (**9**, Scheme 4)*

From 2-iodoanisole (84 mg, 0.36 mmol) and (2-bromophenyl)methanol (67 mg, 0.36 mmol) using norbornene (34 mg, 0.36 mmol), product **9** was obtained in 52% yield (57 mg). Eluent: hexane/EtOAc 9:1. Colorless oil. A 1:1 mixture of two diastereoisomers.

^{1}H NMR: δ 9.79, 9.76 (1H, 2s further split), 8.03 (1H, d further split, J = 7.8, 1.5 Hz), 7.62 (1H, t, J = 7.8 Hz), 7.50 (1H, t, J = 7.8 Hz), 7.29 (1H, t, J = 8.0 Hz), 7.22–7.16 (1H, m), 6.95 (1H, d, J = 8.2 Hz), 6.76 (1H, td, J = 7.4, 1.2 Hz), 3.86 (3H, s), 2.43, 2.38 (1H, 2 pst, J ≅ 8.4 Hz), 2.23 (1H, br s), 2.14 (1H, br s), 1.96-1.85 (1H, m), , 1.49-1.14 (4H, m), 1.18-1.08 (1H, m), 0.94-0.62 (2H, m); ^{13}C NMR: δ 192.5, 192.3, 158.5, 158.4, 147.0, 146.8, 139.6, 139.5, 133.9, 133.4, 133.2, 133.0, 132.9, 131.0, 130.8, 127.7, 127.6, 126.7, 126.6, 126.0, 125.9, 123.2, 122.8, 111.5, 111.4, 54.8, 44.5, 44.4, 42.9, 42.0, 38.9, 37.9, 37.8, 37.7, 37.0, 36.9, 32.9, 32.4, 22.8, 27.7.MS (EI, 70 eV): M^+ 306 (89), m/z 225 (100), 165 (38), 115 (17). IR (neat, cm^{-1}): ν 1693. Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24 Found: C, 82.34; H, 7.16.

*4.3.10. 3'-Methoxy-[1,1']-biphenyl-2-carbaldehyde (**3ja**, Scheme 4)*

From 2-iodoanisole (84 mg, 0.36 mmol) and (2-bromophenyl)methanol (67 mg, 0.36 mmol) using norbornene (34 mg, 0.36 mmol), product **3ja** was obtained in 15% yield (11 mg). Eluent: hexane/EtOAc 9:1. Colorless oil.

^{1}H NMR: δ 10.02 (1H, s), 8.05 (1H, d further split, J = 7.8 Hz), 7.66 (1H, td, J = 7.6, 1.2 Hz), 7.55–7.43 (2H, m), 7.40 (1H, t, J = 7.6 Hz), 7.05-6.96 (3H, m), 3.88 (3H, s); ^{13}C NMR: δ 192.4, 146.0, 138.1, 137.7, 133.7, 133.5, 130.9, 130.7, 128.6, 128.2, 127.3, 116.7, 105.4, 55.2; IR (neat, cm^{-1}): ν 1693; MS (EI, 70 eV): M^+ 212 (29), m/z 196 (100), 183 (28), 152 (60).Anal.

Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 15.08. Found: C, 79.26; H, 15.00.

*4.3.11. 5'-Methoxy-3'-methyl-2'-d-[1,1']-biphenyl-2-carbaldehyde-formyl-d (**10**, Scheme 6)*

From 1-iodo-4-methoxy-3-methylbenzene (89 mg, 0.36 mmol) and 2-bromobenzenemethan-d2-ol (68 mg, 0.36 mmol) using norbornene (34 mg, 0.36 mmol), product **10** was obtained in 85% yield (69 mg). Eluent: hexane/EtOAc 97:3. Mp. (hexane): 66 °C.

^{1}H NMR: δ 8.04 (1H, dd further split, J = 7.8, 1.6 Hz, H3), 7.64 (1H, td, J = 7.6, 1.6 Hz, H5), 7.54 (1H, td further split, J = 7.6, 1.2 Hz, H4), 7.48 (1H, dd, J = 7.8, 1.2 Hz, H6), 6.81 (1H, d further split, J = 2.4 Hz, H4'), 6.75 (1H, further split, J = 2.4 Hz, H2'), 3.86 (3H, s), 2.42 (3H, s); ^{13}C NMR: δ 192.3 (1:1:1 t, $J_{C,D}$ = 26.6 Hz, CDO), 159.5 (C3'), 146.0 (C1), 139.5 (C3*), 138.8 (C1'*), 133.7 (C2), 133.5 (C5), 130.5 (C6), 127.7 (C4), 127.3 (C3), 123.6 (1:1:1 t, $J_{C,D}$ = 25.6 Hz, C6'), 114.5 (C4'), 112.8 (C2'), 55.3, 21.5; MS (EI, 70 eV): M^+ 228 (93), m/z 200 (100), 169 (47), 154 (42). IR (neat, cm^{-1}): ν 1690. Anal. Calcd for $C_{15}H_{12}D_2O_2$: C, 78.92; H, 7.06 Found: C, 78.99; H, 7.02.

*4.3.12. 3,4,6-Trimethyl-6H-dibenzo[b,d]pyran (**13la**, R^1, R^2= Me, R^3=H, R^4= Me, Table 7, entry 2).*

From 1-iodo-2,3-dimethylbenzene (84 mg, 0.36 mmol) and 1-(2-bromophenyl)ethanol (72 mg, 0.36 mmol) using norbornene (34 mg, 0.36 mmol), product **13la** was obtained in 75% yield (60 mg). Eluent: hexane. Mp. (hexane): 62 °C.

^{1}H NMR: δ 7.74 (1H, d, *J* = 7.6 Hz), 7.55 (1H, d, *J* = 7.6 Hz), 7.40 (1H, t, *J* = 7.6 Hz), 7.33 (1H, t, *J* = 7.2 Hz), 7.22 (1H, d further split, *J* = 7.2 Hz), 6.92 (1H, d, *J* = 8.0 Hz), 5.32 (1H, q, *J* = 6.2 Hz), 2.37 (3H, s), 2.28 (3H, s), 1.68 (3H, d, *J* = 6.2 Hz); ^{13}C NMR: δ 151.4, 138.3, 135.6, 130.2, 128.0, 127.2, 125.4, 123.9, 123.0, 122.1, 120.1, 120.0, 73.59, 20.20 (2C), 11.70. MS (EI, 70 eV): M^+ 224 (17), *m/z* 209 (100), 178 (9), 165 (31), 152 (18). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19 Found: C, 85.64; H, 7.12.

*4.3.13. 1-(3',4'-dimethyl-[1,1'-biphenyl]-2-yl)ethanone (**12la**, R^1, R^2= Me, R^3=H, R^4= Me, Table 7, entry 2).*

From 1-iodo-2,3-dimethylbenzene (84 mg, 0.36 mmol) and 1-(2-bromophenyl)ethanol (72 mg, 0.36 mmol) using norbornene (34 mg, 0.36 mmol), product **12la** was obtained in 9% yield (7 mg). Eluent: hexane. Colorless oil.

^{1}H NMR: δ 7.55 (1H, dd, *J* = 8.0, 1.8 Hz) 7.51 (1H, dt, *J* = 7.21, 1.6 Hz) 7.44-7.38 (2H, m), 7.21 (1H, d, *J* = 7.6 Hz), 7.15 (1H, brs), 7.09 (1H, dd, *J* = 7.6, 1.6 Hz), 2.34 (3H, s), 2.33 (3H, s), 2.04 (3H, s);^{13}C NMR: δ 205.3, 140.9, 140.7, 138.3, 137.0, 136.4 , 130.6, 130.2, 130.0, 129.9, 127.8, 127.1, 126.3, 30.4, 19.8, 19.5. MS (EI, 70 eV): M^+ 224 (100), *m/z* 178 (29), 165 (13), 152 (10). IR (neat, cm^{-1}): ν 1687. Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19 Found: C, 85.58; H, 7.24.

*4.3.14. 4-Isopropyl-6-methyl-6H-dibenzo[b,d]pyran (**13aa**, R^1= iPr, R^2,R^3=H, R^4= Me, Table 7, entry 3).*

From 1--iodo-2-isopropylbenzene (89 mg, 0.36 mmol) and 1-(2-bromophenyl)ethanol (72 mg, 0.36 mmol) using norbornene (34 mg, 0.36 mmol), product **13aa** was obtained in 82% yield (70 mg). Eluent: hexane. Colorless oil.

^{1}H NMR: δ 7.74 (1H, d, *J* = 7.6 Hz), 7.63 (1H, dd, *J* = 8.0, 1.6 Hz), 7.38 (1H, td, *J* = 7.6, 1.6 Hz), 7.32 (1H, td, *J* = 7.21, 1.6 Hz), 7.25–7.18 (2H, m), 7.05 (1H, t, J = 7.6), 5.30 (1H, quart, J = 6.4 Hz), 3.41 (1H, quint, J = 7.2 Hz), 1.66 (3H, d, J = 6.4 Hz), 1.31 (3H, d, J = 6.4 Hz), 1.30 (3H, d, J = 6.4 Hz);^{13}C NMR (100 MHz): δ 150.7, 137.6, 136.0, 130.0, 128.0, 127.5, 126.3, 123.8, 122.5, 122.4, 121.5, 120.7, 73.4, 27.1, 22.7, 22.6, 20.0¸ MS (EI, 70 eV): M^+ 238 (7), *m/z* 223 (100), 178 (19), 165 (26), 152 (11). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61 Found: C, 85.44; H, 7.52.

*4.3.15. 1-(3'-isopropyl-[1,1'-biphenyl]-2-yl)ethanone (**12aa**, R^1= iPr, R^2,R^3=H, R^4= Me, Table 7, entry 3).*

From 1-iodo-2-isopropylbenzene (89 mg, 0.36 mmol) and 1-(2-bromophenyl)ethanol (72 mg, 0.36 mmol) using norbornene (34 mg, 0.36 mmol), product **12aa** was obtained in 7% yield (6 mg). Eluent: hexane. Colorless oil.

^{1}H NMR: δ 7.60–7.55 (1H, m), 7.55–7.50 (1H, m), 7.47–7.41 (2H, m), 7.37 (1H, d, *J* = 8.0 Hz), 7.31–7.26 (1H, m), 7.22–7.20 (2H, m), 2.97 (1H, m, J = 6.8 Hz), 1.99 (3H, s) 1.30 (6H, d, *J* = 6.8 Hz); ^{13}C NMR: δ 205.2, 149.4, 141.1, 140.9, 140.6, 130.7, 130.1, 128.7, 127.8, 127.3, 127.2, 126.2, 126.1, 34.1, 30.4, 24.0 (2C). MS (EI, 70 eV): M^+ 238 (100), *m/z* 223 (65), 178 (34), 165 (67), 152 (54). IR (neat, cm^{-1}): ν 1688. Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61 Found: C, 85.34; H, 7.57.

*4.3.16. 3,4,6,6-Tetramethyl-6H-dibenzo[b,d]pyran (**15laa**, Table 9, entry 1).*

From 1-iodo-2,3-dimethylbenzene (84 mg, 0.36 mmol) and 2-(2-bromophenyl)propan-2-ol (77 mg, 0.36 mmol) using norbornene (34 mg, 0.36 mmol), product **15laa** was obtained in 86% yield (73 mg). Eluent: hexane. Colorless oil.

^{1}H NMR: δ 7.73 (1H, d, J = 7.8 Hz), 7.51 (1H, d, J = 7.9 Hz), 7.36 (1H, "t" further split, J = 7.6 Hz), 7.32–7.25 (2H, m), 6.88 (1H, d, J = 8.0 Hz), 2.34 (3H, s), 2.24 (3H, s), 1.68, 1.67 (6H, 2s); ^{13}C NMR: δ 150.6, 139.2, 138.1, 129.4, 127.5, 127.3, 125.6, 123.0, 122.6, 122.1, 119.9, 119.7, 77.3, 27.5 (2C), 20.1, 11.5; MS (EI, 70 eV): M^+ 238 (11), *m/z* 223 (100), 178 (14), 165 (19), 152 (12). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61 Found: C, 85.69; H, 7.58.

*4.3.17. 6,6-Diethyl-3,4-dimethyl-6H-dibenzo[b,d]pyran (**15lbb**, Table 9, entry 2).*

From 1-iodo-2,3-dimethylbenzene (84 mg, 0.36 mmol) and 3-(2-bromophenyl)pentan-3-ol (88 mg, 0.36 mmol) using norbornene (34 mg, 0.36 mmol), product **15lbb** was obtained in 86% yield (73 mg). Eluent: hexane. Colorless oil.

^{1}H NMR: δ 7.77 (1H, d, *J* = 7.6 Hz), 7.51 (1H, d, *J* = 8.0 Hz), 7.35 (1H, td, *J* = 7.6, 1.2 Hz), 7.29 (1H, td, *J* = 7.6, 1.2 Hz), 7.16 (1H, d further split, *J* = 7.2 Hz), 6.85 (1H, d, *J* = 8.0 Hz), 2.34 (3H, s), 2.26 (3H, s), 2.05–1.92 (4H, m), 0.95 (6H, t, *J* = 7.6 Hz);^{13}C NMR: δ 150.7, 138.1, 136.2, 130.2, 127.3, 126.8, 125.2, 124.6, 122.2, 122.0, 119.5, 119.2, 82.5, 30.5 (2C), 20.1, 11.5, 8.3 (2C); MS (EI, 70 eV): M^+ 266 (7), *m/z* 237 (100), 222 (9), 178 (14), 165 (10). Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.64; H, 8.35.

*4.3.18. 6,6-Diethyl-2,4-dimethyl-6H-dibenzo[b,d]pyran (**15cbb**, Table 9, entry 3).*

From 1-iodo-2,4-dimethylbenzene (84 mg, 0.36 mmol) and 3-(2-bromophenyl)pentan-3-ol (88 mg, 0.36 mmol) using norbornene (34 mg, 0.36 mmol), product **15cbb** was obtained in 98% yield (93 mg). Eluent: hexane. M.p.(hexane): 91 °C.

^{1}H NMR (300 MHz): δ 7.77 (1H, d, *J* = 7.6 Hz), 7.40 (1H, br s), 7.34 (1H, td, *J* = 7.6, 1.2 Hz), 7.29 (1H, td, *J* = 7.6, 1.2 Hz), 7.15 (1H, dd, *J* = 7.6, 1.6 Hz), 6.95 (1H, br s), 2.36 (3H, s), 2.28 (3H, s), 2.02–1.90 (4H, m), 0.93 (6H, t, *J* = 7.6 Hz); ^{13}C NMR: δ 148.8, 136.7, 131.4, 130.0, 129.3, 127.2, 127.0, 126.5, 124.7, 122.2, 120.9, 120.6, 82.2, 30.5 (2C), 20.9, 15.7, 8.3 (2C); MS (EI, 70 eV): M^+ 266 (5), *m/z* 237 (100), 222 (7), 178 (10), 165 (6). Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.74; H, 8.28.

*4.3.19. 4,6-Dimethyl-6-phenyl- -6H-dibenzo[b,d]pyran (**15bac**, Table 9, entry 4)*

From 2-iodotoluene (84 mg, 0.36 mmol) and 1-(2-bromophenyl)-1-phenylethanol (99 mg, 0.36 mmol) using norbornene (34 mg, 0.36 mmol), product **15bac** was obtained in 86% yield (88 mg). Eluent: hexane. Colorless oil.

^{1}H NMR: δ 7.79 (1H, d further split, J = 8.2 Hz), 7.55 (1H, d further split, J = 7.6 Hz), 7.45 (1H, td, J = 7.7, 1.5 Hz), 7.39 (1H, td, J = 7.2, 1.2 Hz), 7.36-7.30 (3H, m), 7.28-7.18 (3H, m), 7.10 (1H, d further split, J = 7.2 Hz), 6.90 (1H, t, J = 7.8 Hz), 2.42 (3H, s), 2.11 (3H, s); ^{13}C NMR: δ 151.1, 145.2, 137.2, 130.7, 130.0, 128.1, 127.9 (2C), 127.34, 127.33, 126.8, 126.2 (2C), 125.4, 122.8, 122.4, 121.1, 120.6, 81.0, 28.6, 16.1; MS (EI, 70 eV): 286 (36) (M^+), m/z 271 (100), 209 (32), 165 (10). Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.01; H, 6.39.

*4.3.20. 6-Methyl-6-phenyl-4-isopropyl-6H-dibenzo[b,d]pyran (**15aac**, Table 9, entry 5)*

From 1-iodo-2-isopropylbenzene (89 mg, 0.36 mmol) and 1-(2-bromophenyl)-1-phenylethanol (99 mg, 0.36 mmol) using norbornene (34 mg, 0.36 mmol), product **15aac** was obtained in 93% yield (104 mg). Eluent: hexane. Colorless oil.

^{1}H NMR: δ 7.80 (1H, dd, J = 7.8 Hz, 1.3 Hz), 7.58 (1H, dd, J = 7.7, 1. 5 Hz), 7.43 (1H, td, J = 7.8, 1.4 Hz), 7.4-7.32 (3H, m, with a triplet centered at 7.35 ppm, J = 7.4, 1.3 Hz), 7.32-7.18 (5H, m, with a dd centered at 7.20 ppm, J = 7.7, 1.3 Hz), 6.99 (1H, t, J = 7.7 Hz), 3.63 (1H, hept, J = 6.8 Hz), 2.09 (3H, s), 1.31 (3H, d; J = 6.8 Hz), 1.28 (3H, d, *J* = 6.8 Hz); ^{13}C NMR: δ 149.8, 145.0, 137.7, 137.5, 130.1, 128.1, 127.9 (2C), 127.4, 127.3, 126.6 (2C), 126.3, 125.4, 122.8, 122.4, 121.4, 120.4, 81.0, 27.9, 26.3, 23.6, 22.6; MS (EI, 70 eV): 314 (36) (M+), m/z 299 (100), 283 (15), 237 (28), 221 (12). Anal. Calcd for $C_{23}H_{22}O$: C, 87.86; H, 7.05. Found: C, 87.81; H, 7.00.

*4.3.21. 6-Methyl-6-phenyl-6H-benzo[d]naphtho[1,2-b]pyran (**15hac**, Table 9, entry 6)*

From 1-iodonaphthlene (91 mg, 0.36 mmol) and 1-(2-bromophenyl)-1-phenylethanol (99 mg, 0.36 mmol) using norbornene (34 mg, 0.36 mmol), product **15hac** was obtained in 88% yield (101 mg). Eluent: hexane. Colorless oil.

^{1}H NMR: δ 8.59 (1H, d, J = 7.6 Hz), 7.87–7.78 (3H, m), 7.63 (1H, td, J = 8.0, 1.2 Hz), 7.59–7.41 (7H, m), 7.27–7.21 (3H, m), 2.26 (3H, s); ^{13}C NMR: δ 148.3, 145.0, 136.6, 134.3, 129.8, 128.2, 128.2, 127.9, 127.8, 127.6, 127.3, 126.4, 125.9 (2C), 125.7, 125.4, 122.4, 122.2, 121.2, 120.6, 81.7, 28.5; MS (EI, 70 eV): 322 (48) (M+), m/z 307 (100), 245 (42), 215 (17), 202 (11). Anal. Calcd for $C_{24}H_{18}O$: C, 89.41; H, 5.63. Found: C, 89.56; H, 5.53.

*4.3.22. 6,6-Dimethyl-4-trifluoromethyl-6H-dibenzo[b,d]pyran (**15kaa**, Table 9, entry 7)*

From 1-iodo-2-(trifluoromethyl)benzene (98 mg, 0.36 mmol) and 2-(2-bromophenyl)propan-2-ol (77 mg, 0.36 mmol) using norbornene (34 mg, 0.36 mmol), product **15kaa** was obtained in 88% yield (87 mg). Eluent: hexane. Colorless oil.

^{1}H NMR: δ 7.89 (1H, d, J = 7.6 Hz), 7.80–7.75 (1H, m), 7.51 (1H, d further split, J = 8.0 Hz), 7.34, 7.31 (2H partly overlapped, td, J = 7.5, 1.6 Hz, td, J = 7.6, 1.6 Hz), 7.20–7.13 (1H, m), 7.04 (1H, t, J = 7.8 Hz), 1.57 (6H, s); ^{13}C NMR: δ 150.4, 135.7, 128.0, 128.1, 127.4, 126.2 (quart, $J_{C,F}$ = 5.0 Hz), 126.1, 125.0, 123.9 (quart, $J_{C,F}$ = 270.9 Hz), 122.8, 122.2, 120.1, 119.4 (quart, $J_{C,F}$ = 30.5 Hz), 84.0, 27.5 (2C); MS (EI, 70 eV): M^+ 278 (7), *m/z* 249 (100), 232 (10), 221 (23), 165 (14). Anal. Calcd for $C_{16}H_{13}F_3O$: C, 69.06; H, 4.71. Found: C, 69.12; H, 4.53.

*4.3.23. 6,6-Diethyl-4-trifluoromethyl-6H-dibenzo[b,d]pyran (**15kbb**, Table 9, entry 8)*

From 1-iodo-2-(trifluoromethyl)benzene (98 mg, 0.36 mmol) and 3-(2-bromophenyl)pentan-3-ol (88 mg, 0.36 mmol) using norbornene (34 mg, 0.36 mmol), product **15kbb** was obtained in 80% yield (87 mg). Eluent: hexane. Colorless oil.

^{1}H NMR: δ 7.88 (1H, d, J = 7.6 Hz), 7.81–7.73 (1H, m), 7.51 (1H, d further split, J = 8.0 Hz), 7.38, 7.36 (2H partly overlapped, td, J = 7.6, 1.6 Hz, td, J = 7.7, 1.6 Hz), 7.20–7.13 (1H, m), 7.03 (1H, t, J = 7.9 Hz), 2.01 (4H, quart, J = 7.6 Hz), 0.91 (6H, t, J = 7.6 Hz); ^{13}C NMR: δ 151.4, 136.0, 128.2, 128.1, 127.6, 126.5 (quart, $J_{C,F}$ = 5.0 Hz), 126.2, 125.0, 123.7 (quart, $J_{C,F}$ = 270.9 Hz), 122.9, 122.2, 120.0, 119.1 (quart, $J_{C,F}$ = 30.5 Hz), 84.2, 30.9 (2C), 7.9 (2C); MS (EI, 70 eV): M^+ 306 (3), *m/z* 277 (100), 262 (12), 249 (10), 165 (9). Anal. Calcd for $C_{18}H_{17}F_3O$: C, 70.58; H, 5.59. Found: C, 70.60; H, 5.53.

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References and notes

1. (a) Tsuji, J. In *Palladium Reagents and Catalysts: New Perspectives for the 21st Century*; Wiley, 2004; (b) *Palladium in Organic Synthesis* Tsuji, J., Ed.; Springer: Berlin, 2005.
2. (a) *Domino Reactions: Concepts for Efficient Organic Synthesis*; Tietze, L.F., Ed.; Wiley-VCH, Weinheim 2014; (b) *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E.-I., Ed.; Wiley: New York, 2002.
3. (a) Catellani, M.; Motti, E.; Della Ca', N. *Acc. Chem. Res.* **2008**, *41*, 1512; (b) Catellani M. In *Palladium in Organic Synthesis*; Tsuji, J. Ed.; Springer, Berlin, 2005, 21; (c) Chiusoli, G. P.; Catellani, M.; Costa, M.; Motti, E.; Della Ca', N.; Maestri, G. *Coord. Chem. Rev.* **2010**, *254*, 456; (d) Martins, A.; Mariampillai, B.; Lautens, M. *Top. Curr. Chem.* **2010**, *292*, 1; (e) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174; (f) Sehnal, P.; Taylor, R. J. K.; Fairlamb, I. J. S. *Chem. Rev.* **2010**, *110*, 824; (g) Xu, L.-M.; Li, B.-J.; Yang, Z.; Shi, Z.-J. *Chem. Soc. Rev.* **2010**, *39*, 712; (h) Muñiz, K. *Angew. Chem. Int. Ed.* **2009**, *48*, 9412; (i) Johnson, J. B.; Rovis, T. *Angew. Chem. Int. Ed.* **2008**, *47*, 840; (j) Jiao, L.; Herdtweck, E.; Bach, T. *J. Am. Chem. Soc.* **2012**, *134*, 14563; (k) Ferraccioli, R. *Synthesis* **2013**, *45*, 581; (l) Sui, X.; Zhu, R.; Gu, Z. *Synlett* **2013**, *24*, 2013; (m) Rossi, R.; Bellina, F.; Lessi, M.; Manzini, C. *Adv. Synth. Catal.* **2014**, *356*, 17.
4. Motti, E.; Della Ca', N.; Xu, D.; Piersimoni, A.; Bedogni, E.; Zhou, Z.-M.; Catellani, M. *Org. Lett.* **2012**, *14*, 5792.
5. (a) Guo, M.; Zhu, Z.; Huang, H.; Zhang, Q. *Catalysis Commun.* **2009**, *10*, 865 and references therein. (b) Gürbüz, N.; Özdemir, I.; Çetinkaya, B. *Tetrahedron Lett.* **2005**, *46*, 2273. (c) Tredwell, M. J.; Gulias, M.; Gaunt Bremeyer, N.; Johansson, C. C. C.; Collins, B. S. L.; Gaunt, M. J. *Angew. Chem. Int. Ed.* **2011**, *50*, 1076.
6. (a) Fitton, P.; Rick, E. A. *J. Organomet. Chem.* **1971**, *28*, 287; (b) Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 13944; (c) Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*,

8375; (d) Goossen, L. J.; Koley, D.; Hermann, H. L.; Thiel, W. *Organometallics* **2005**, *24*, 2398.
7. (a) Horino, H.; Arai M.; Inoue, N. *Tetrahedron Lett*. **1974**, *15*, 647; (b) Li, C.-S.; Cheng, C.-H.; Liao, F.-L.; Wang, S.-L. *J. Chem. Soc. Chem. Commun*. **1991**, 710; (c) Portnoy, M.; Ben-David, Y.; Rousso, I.; Milstein, D. *Organometallics* **1994**, *13*, 3465; (d) Catellani, M.; Mealli, C.; Motti, E.; Paoli, P.; Perez-Carreno, E.; Pregosin, P. S. *J. Am. Chem. Soc*. **2002**, *124*, 4336.
8. (a) Catellani, M.; Chiusoli, G. P. *J. Organomet. Chem*. **1988**, *346*, C27; (b) Liu, C.-H.; Li, C.-S.; Cheng, C.-H. *Organometallics* **1994**, *13*, 18; (c) Chai, D. I.; Thansandote, P.; Lautens, M. *Chem. Eur. J*. **2011**, *17*, 8175; (d) Malinakova, H. C. *Top. Organomet. Chem*. **2011**, *35*, 85; (e) Della Ca', N.; Catellani, M.; Massera, C.; Motti, E. *Inorg. Chim. Acta*, 2015, doi:10.1016/j.ica.2015.03.022.
9. (a) Dyker, G. *Angew. Chem. Int. Ed*. **1999**, *38*, 1698; (b) Dyker, G. In *Handbook of C–H Transformation*; Dyker, G. Ed.; Wiley-VCH: Weinheim, 2005, 2, 465; (c) Kakiuchi, F.; Chatani, N. *Adv. Synth. Catal*. **2003**, *345*, 1077; (d) Beletskaya, I. P.; Cheprakov, A. V. *J. Organometal. Chem.* **2004**, *689*, 4055; (e) Neufeldt, S. R.; Sanford, M. S. *Acc. Chem. Res*. **2012**, *45*, 936; (f) Livendahl, M.; Echavarren, A. M. *Isr. J. Chem*. **2010**, *50*, 630; (g) De Mendoza, P.; Echavarren, A. M. In *Modern Arylation Methods*; Ackermann, L. Ed.; Wiley-VCH: Weinheim, 2009, 363; (h) Gorelsky, S.; Lapointe, D.; Fagnou, K. *J. Am. Chem. Soc*. **2008**, *130*, 10848; (i) Rousseaux, S.; Davi, M.; Sofack-Kreutzer, J.; Pierre, C.; Kefalidis, C. E.; Clot, E.; Fagnou, K.; Baudoin, O. *J. Am. Chem. Soc*. **2010**, *132*, 10706; (j) Zheng, H.; Zhu,Y.; Shi, Y. *Angew. Chem. Int. Ed*. **2014**, *53*, 11280; (k) McMurray, L.; O'Hara, F.; Gaunt, M. J. *Chem. Soc. Rev*. **2011**, *40*, 1885; (l) Wencel-Delord, J.; Drçge, T.; Liu, F.; Glorius, F. *Chem. Soc. Rev*. **2011**, *40*, 4740.
10. (a) Canty, A. J. *Acc. Chem. Res*. **1992**, *25*, 83; (b) Powers, D. C.; Lee, E.; Ariafard, A.; Sanford, M. S.; Yates, B. F.; Canty, A. J.; Ritter, T. *J. Am. Chem. Soc*. **2012**, *134*, 12002, (c) Hickman, A. J.; Sanford, M. S. *Nature* **2012**, *484*, 177; (d) Vicente, J.; Arcas, A.; Juliá-Hernández, F.; Bautista, D. *Angew. Chem. Int. Ed.* **2011**, *50*, 6896; (e) Julia-Hernandez, F.; Arcas, A.; Vicente, J. *Chem. Eur. J*. **2012**, *18*, 7780; (f) Catellani, M.; Fagnola, M. C. *Angew. Chem. Int. Ed. Engl*. **1994**, *33*, 2421; (g) Catellani, M.; Mann, B. E. *J. Organomet. Chem*. **1990**, *390*, 251; (h) Bocelli, G.; Catellani, M.; Ghelli, S. *J. Organomet. Chem*. **1993**, *458*, C12; (i) Amatore, C.; Catellani, M.; Deledda, S.; Jutand, A.; Motti, E. *Organometallics* **2008**, *27*, 4549.
11. (a) Maestri, G.; Motti, E.; Della Ca', N.; Malacria, M.; Derat, E.; Catellani, M. *J. Am. Chem. Soc*. **2011**, *133*, 8574; (b) Catellani, M.; Motti, E. *New J. Chem*. **1998**, *22*, 759; (c) Catellani, M.; Motti, E.; Baratta, S. *Org. Lett*. **2001**, *3*, 3611.
12. (a) Urriolabeitia, E. P. In *Palladacycles, Synthesis, Characterization and Application*; Dupont, J.; Pfeffer, M. Eds.; Wiley-VCH, Weinheim, 2008, 35; (b) Alsters, P. L.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 1639; (c) Fernández-Rivas, C.; Cárdenas, D. J.; Martín-Matute, B.; Monge, A.; Gutiérrez-Puebla, E.; Echavarren, A. M. *Organometallics* **2001**, *20*, 2998; (d) Widenhoefer, R. A.; Annita Zhong, H.; Buchwald, S. L. *J. Am. Chem. Soc*. **1997**, *119*, 6787.
13. (a) Terao, Y.; Wakui, H.; Satoh, T.; Miura, M.; Nomura, M. *J. Am. Chem. Soc*. **2001**, *123*, 10407; (b) Terao, Y.; Wakui, H.; Nomoto, M.; Satoh, T.; Miura, M.; Nomura, M. *J. Org. Chem*. **2003**, *68*, 5236; (c) Hartwig, J. F. *Angew. Chem., Int. Ed. Engl*. **1998**, *37*, 2046; (d) Mann, G.; Hartwig, J. F. *J. Am. Chem. Soc*. **1996**, *118*, 13109; (e) Kuwabe, S.-I.; Torraca, K. E.; Buchwald, S. L. *J. Am. Chem. Soc*. **2001**, *123*, 12202; (f) Palucki, M.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996,** *118*, 10333.
14. (a) Motti, M.; Ippomei, G.; Deledda, S.; Catellani, M. *Synthesis* **2003**, 2671. (b) Faccini, F.; Motti, E.; Catellani, M. *J. Am. Chem. Soc*. **2004**, *126*, 78.
15. (a) Zoran, A.; Sasson, Y.; Blum, J. *J. Mol. Cat*. **1984**, *27*, 349; (b) Deledda, S.; Motti, E.; Catellani, M. *Can. J. Chem*. **2005**, *83*, 741; (c) Martins, A.; Lautens, M. *Org. Lett*. **2008**, *10*, 5095.
16. ^{1}H and ^{13}C NMR spectra were carried out under "standard conditions". Since a routine NMR spectrum yields integrals with an accuracy of +/-10% the experimental error can be estimated in the same order.
17. Jung, M. E.; Piizzi, G. *Chem. Rev*. **2005**, *105*, 1735.
18. (a) Mahendar, L.; Krishna, J.; Reddy, A. G. K.; Ramulu, B. V.; Satyanarayana, G. *Org. Lett*. **2012**, *14*, 628; (b) Mahendar, L.; Satyanarayana, G. *J. Org. Chem*. **2014**, *79*, 2059; (c) Motti, E.; Faccini, F.; Ferrari, I.; Catellani, M.; Ferraccioli, R. *Org. Lett*. **2006**, *8*, 3967; (d) Xu, D.; Dai, L.; Catellani, M.; Motti, E.; Della Ca', N.; Zhou, Z. *Org. Biomol. Chem.* **2015**, *13*, 2260.
19. Lesslie, M. S.; Mayer, U. J. H. *J. Chem. Soc.* **1961**, 611.
20. Della Ca', N.; Motti, E.; Mega, A.; Catellani, M . *Adv. Synth. Catal*. **2010**, *352*, 1451.
21. Carreño, M. C.; García Ruano, J. L.; Sanz, G.; Toledo M. A.; Urbano, A. *Tetrahedron Lett.* **1996**, *37*, 4081.
22. Yumei L.; Herndon J. W.; Cervantes-Lee F. *J. Am Chem. Soc.* **2003**, *125*, 12720.
23. Tsai, S.-C.; Klinman, J. P. *Biochemistry*, **2001**, *40*, 2303.
24. Nicolai, S.; Erard, S.; Gonzalez, D. F.; Waser, J. *Org. Lett*. **2012**, *12*, 384.
25. Cowell, A.; Stille, J. K. *J. Am. Chem. Soc*. **1980**, *102*, 4193.
26. Smith, J. G.; Dibble, P. W.; Sandborn, R. E. *J .Org .Chem.* **1986**, 51, 3762.
27. Zhou, J.; Huang, L.-Z.; Li, Y.-Q.; Du, Z.-T. *Tetrahedron Lett*., **2012**, 53, 7036.

Supplementary Material

Supplementary data associated with this article can be found in the online version, at

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Supplementary Data

for

Formation of a carbonyl group *ortho* to a biaryl structure or a 6*H*-dibenzopyran by a palladium/norbornene-catalyzed ordered reaction sequence

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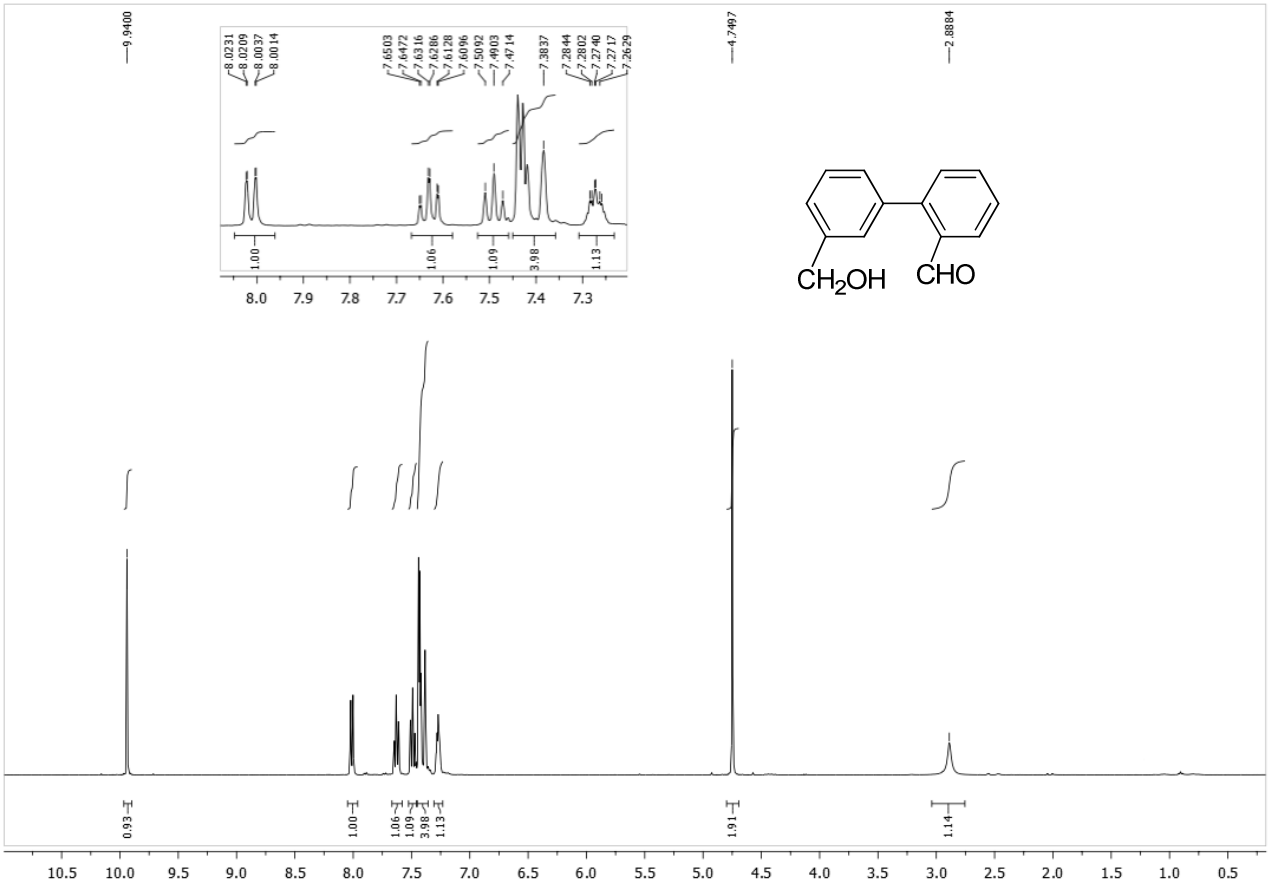
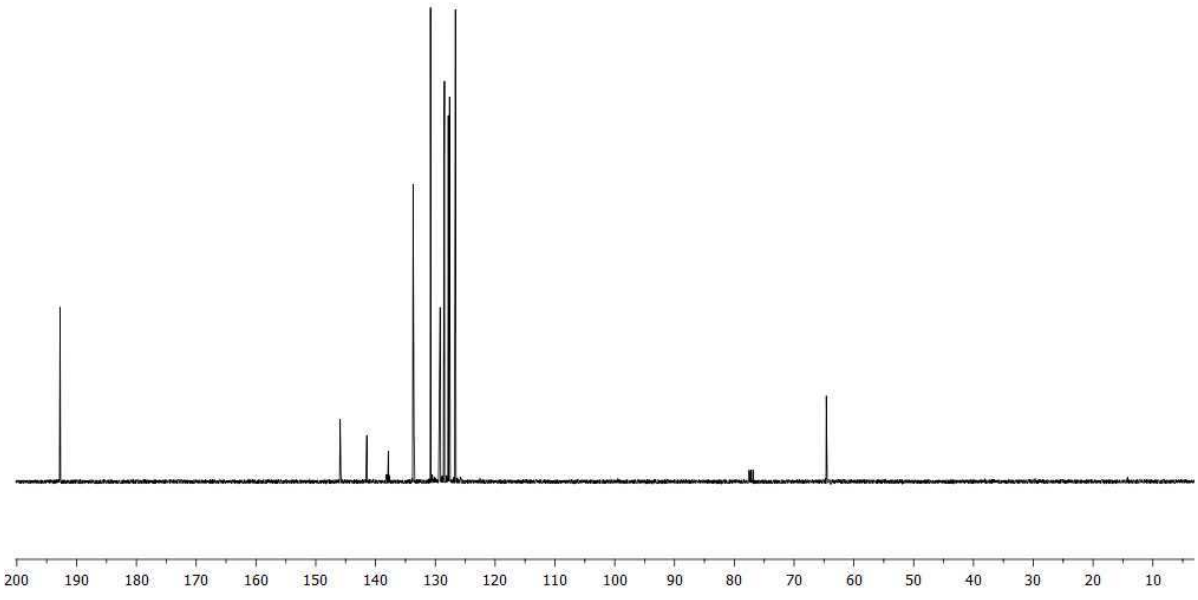
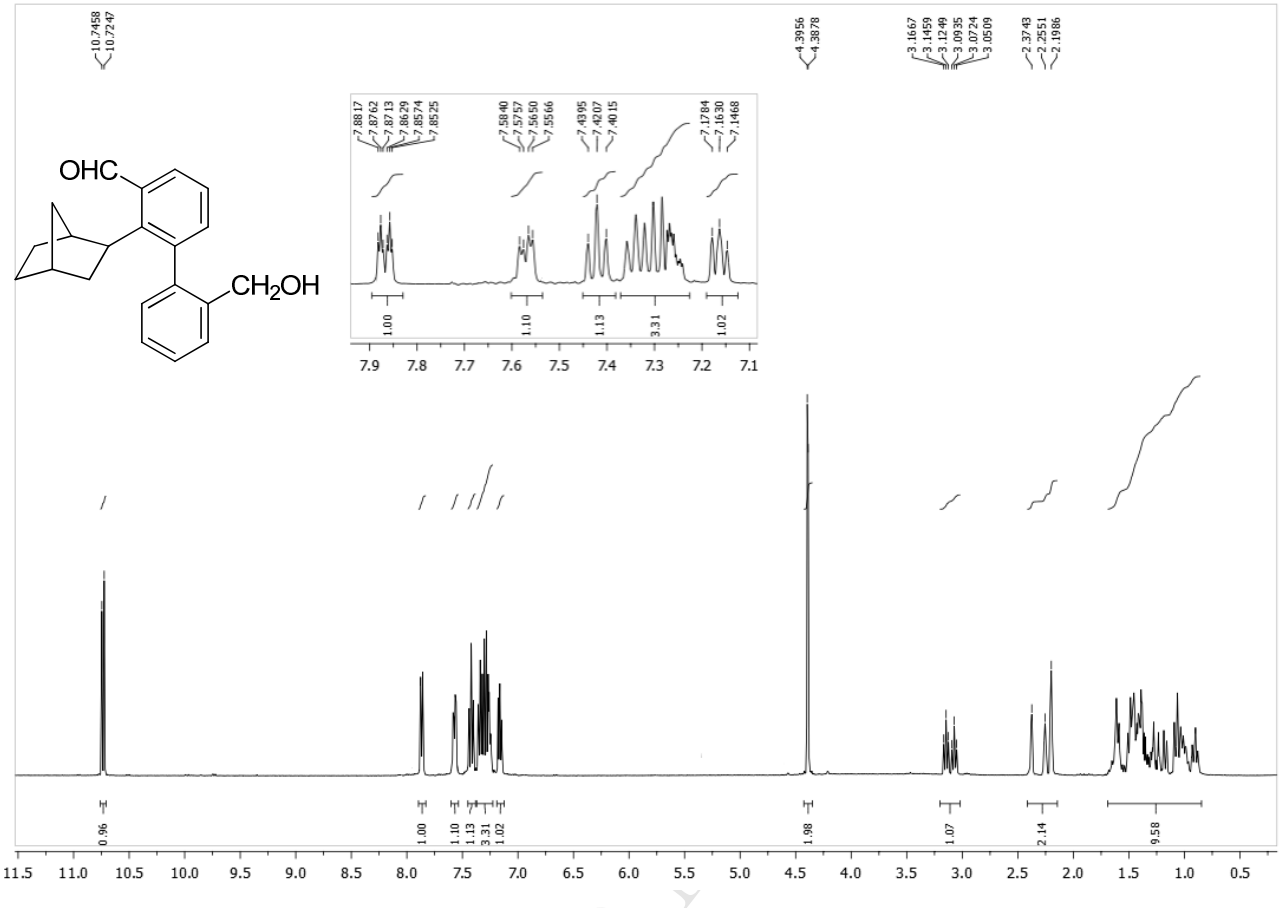
Copies of ^{1}H NMR and ^{13}C NMR spectra

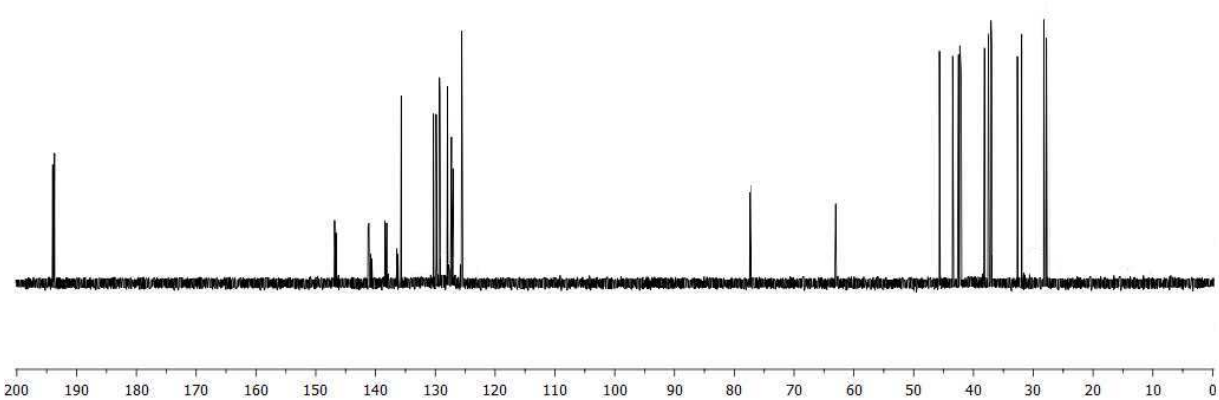
3’-Hydroxymethyl-1,1’-biphenyl-2-carbaldehyde (**6**, R^1, R^2 = H, Table 3)





2’-Hydroxymethyl-2-(2”-exo-norbornyl)-1,1’-biphenyl-3-carbaldehyde (**7**, R^1,R^2 = H, Table 3)





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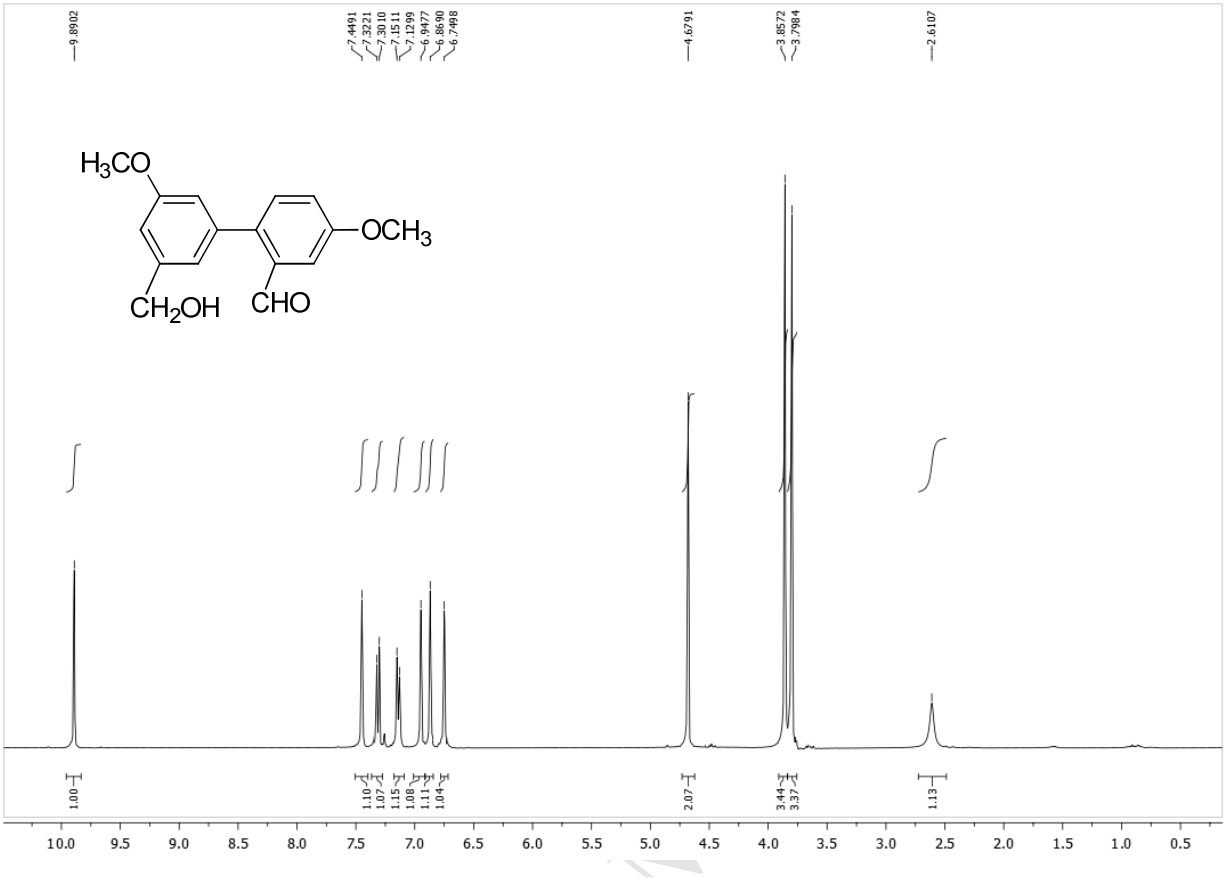
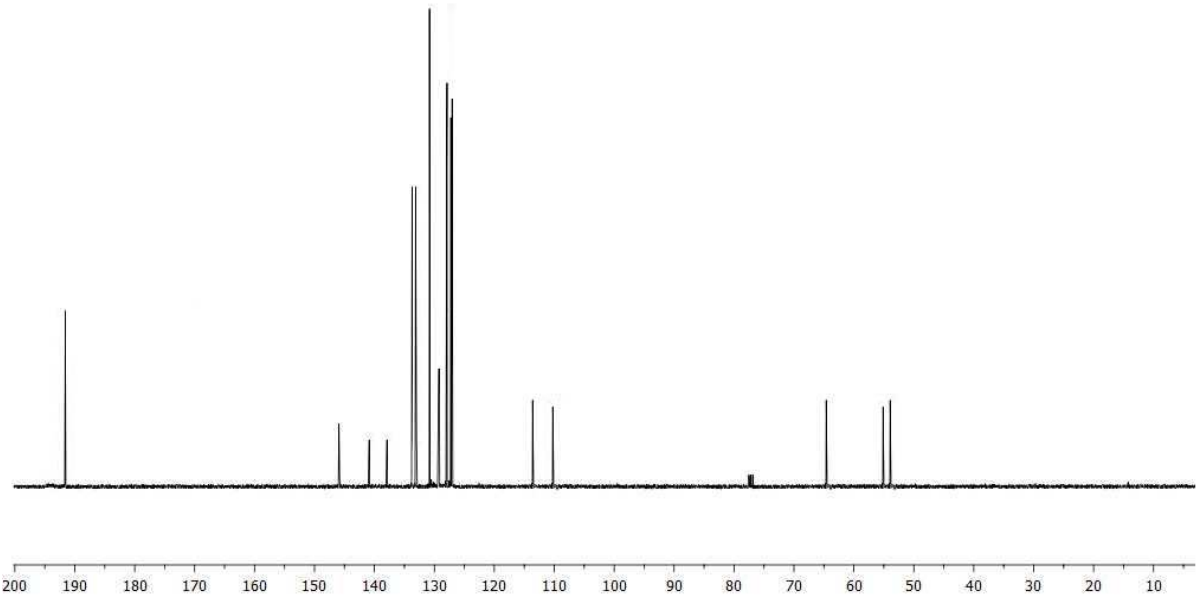
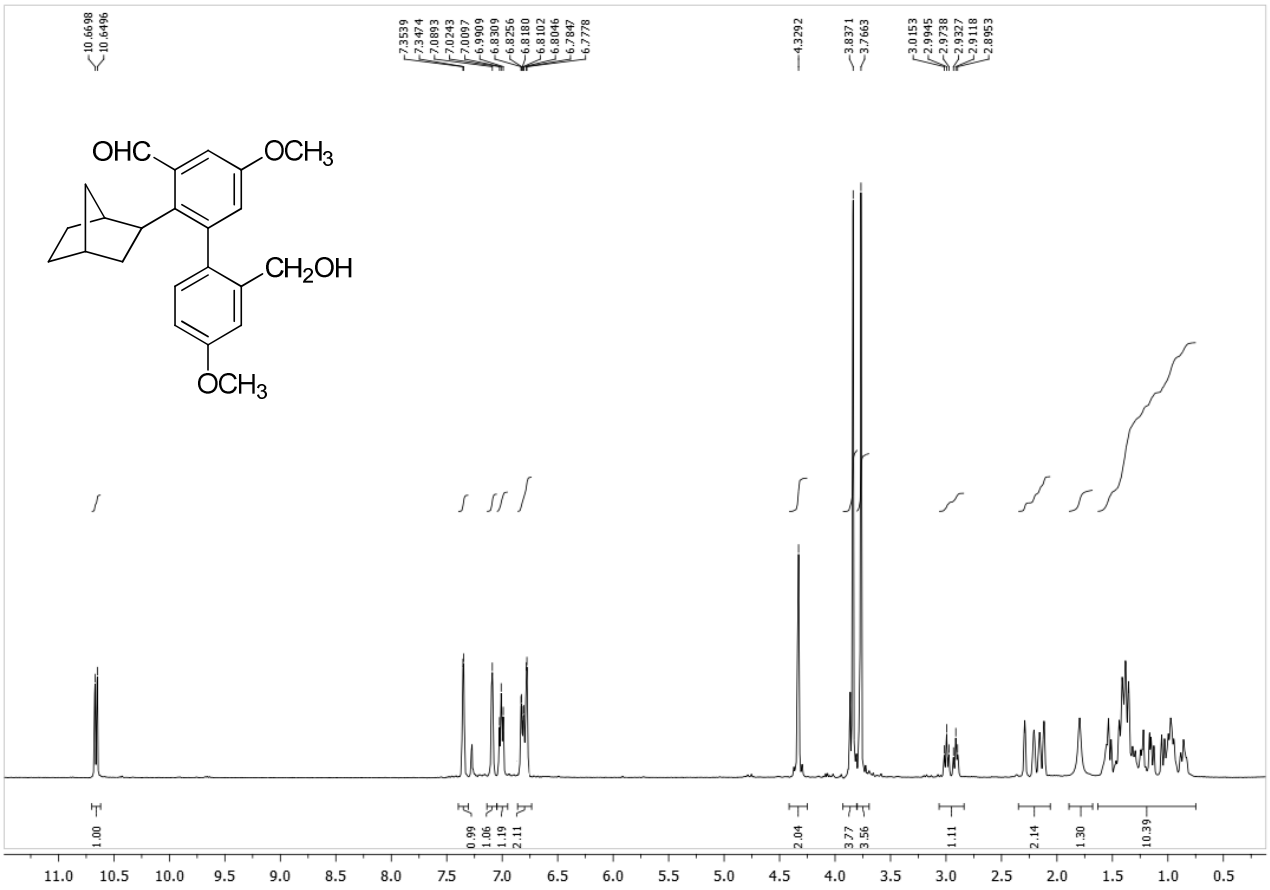
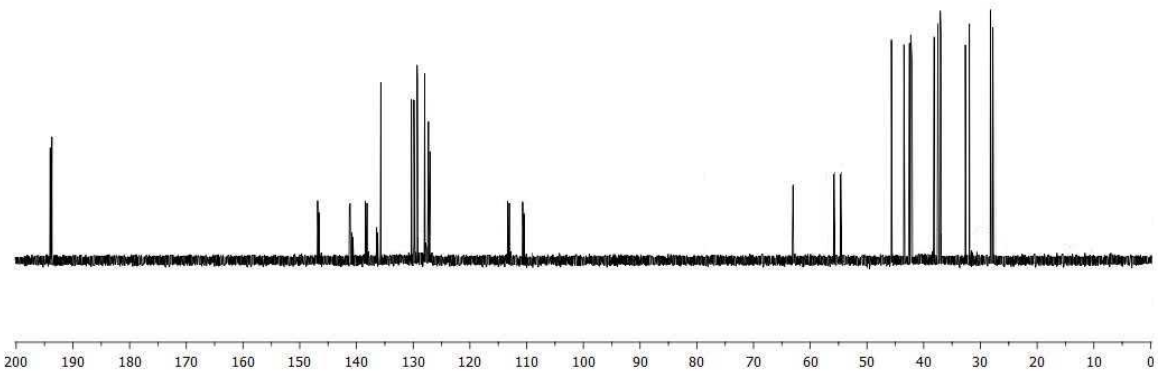




2’-Hydroxymethyl-4’,5-dimethoxy-2-(2”-exo-norbornyl)-1,1’-biphenyl-3-carbaldehyde (**7**, R^1 = H, R^2 = OMe, Table 3)





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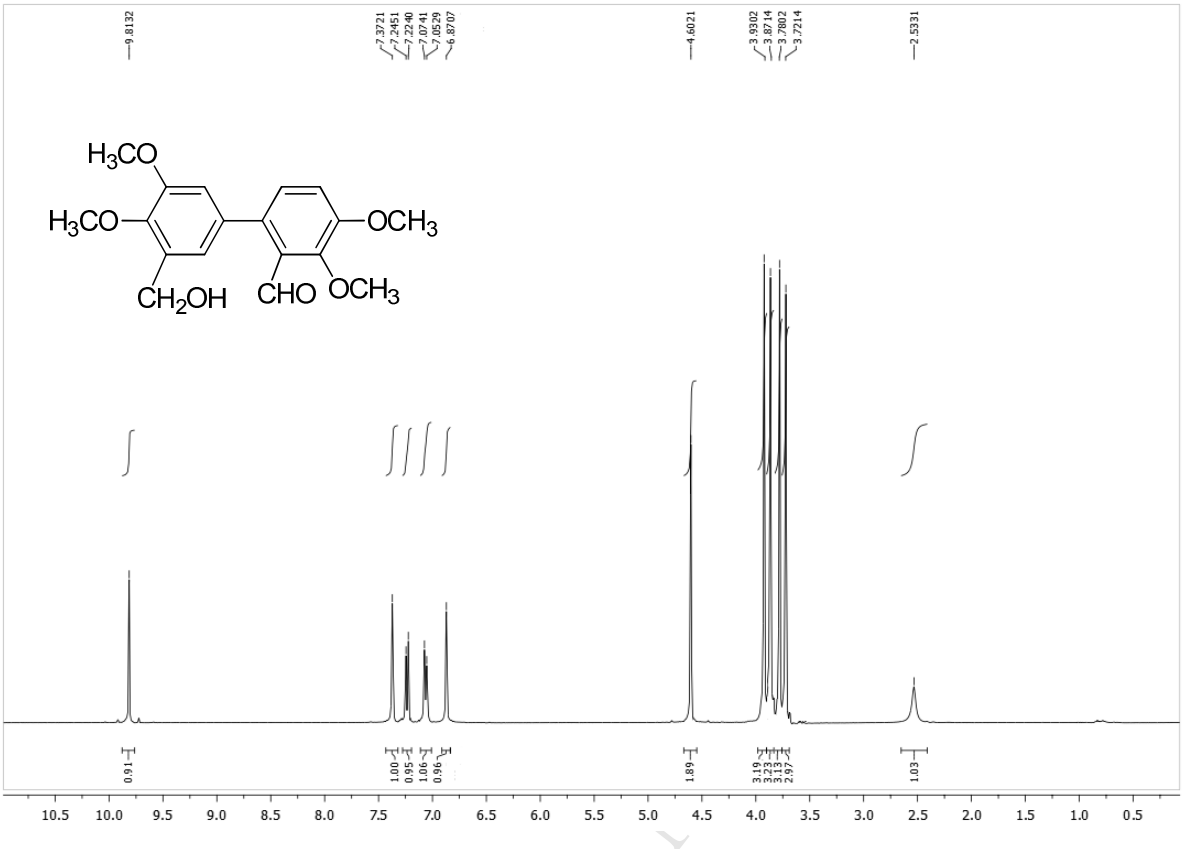
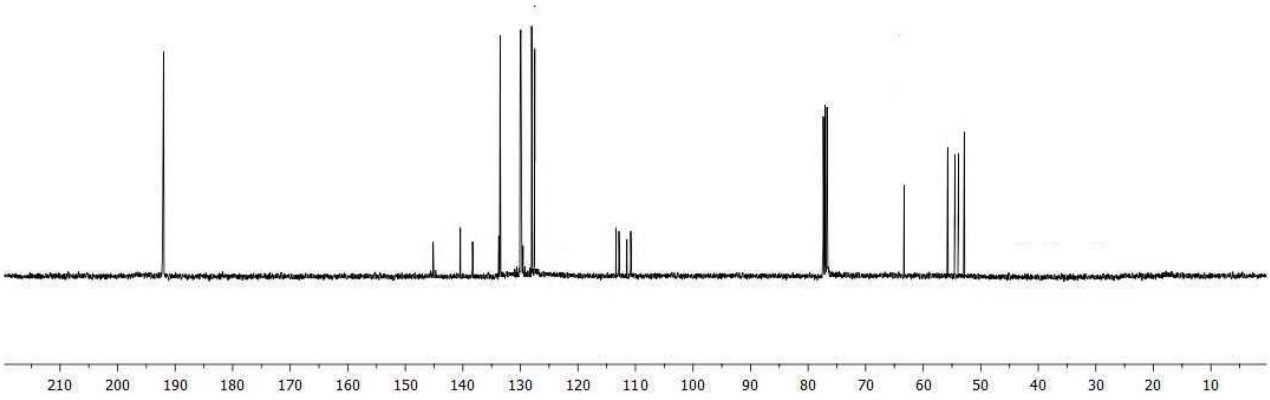
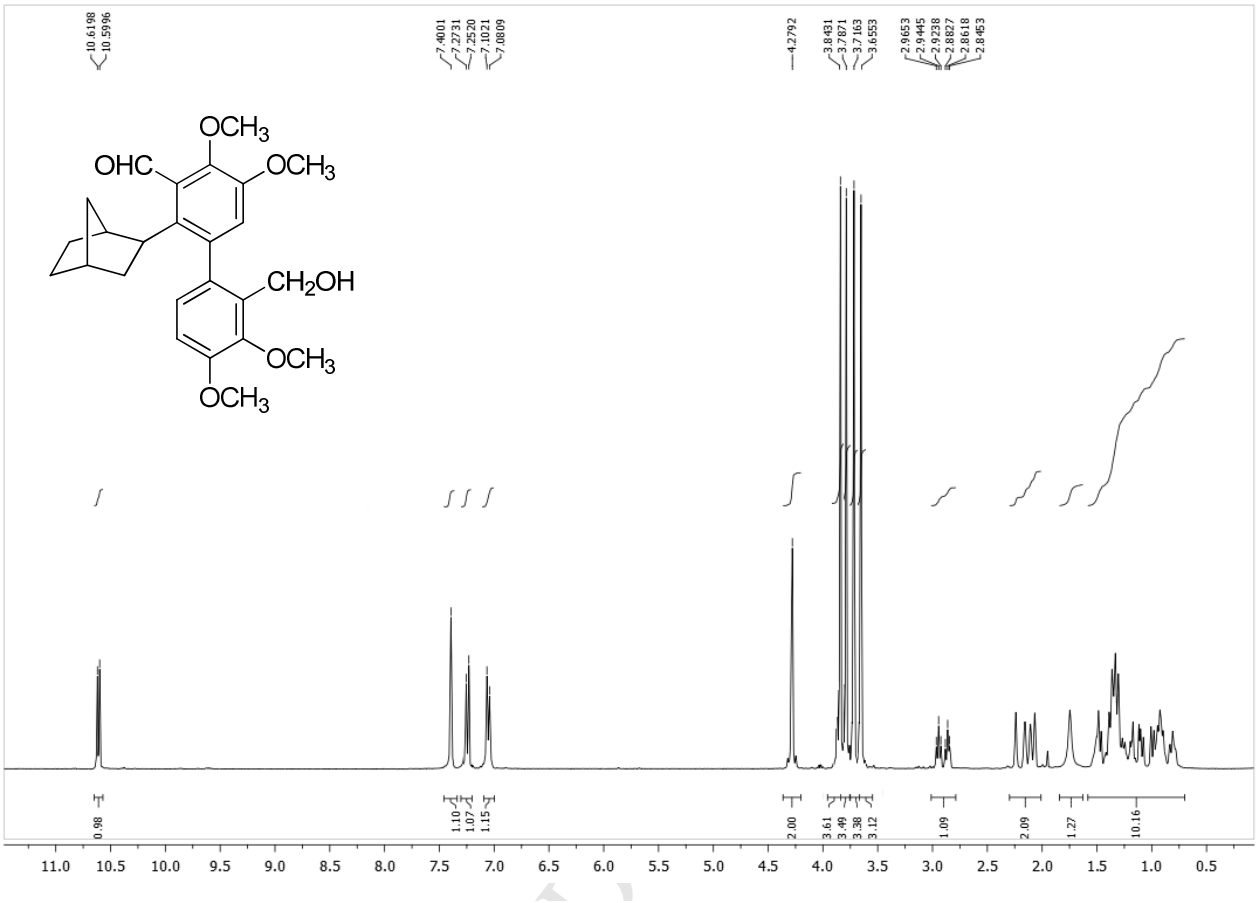
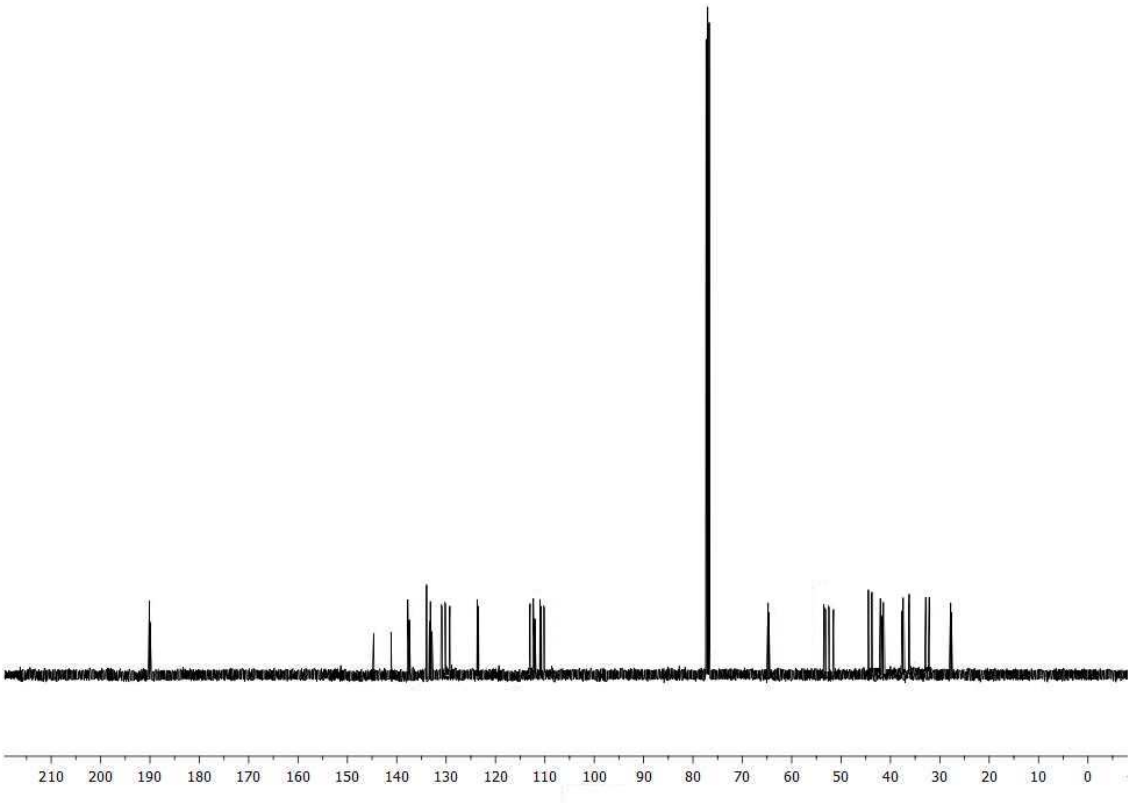




2’-Hydroxymethyl-4,5,3’,4’-tetramethoxy-2-(2”-exo-norbornyl)-1,1’-biphenyl-3-carbaldehyde (**7**, R^1, R^2 = OMe, Table 3)





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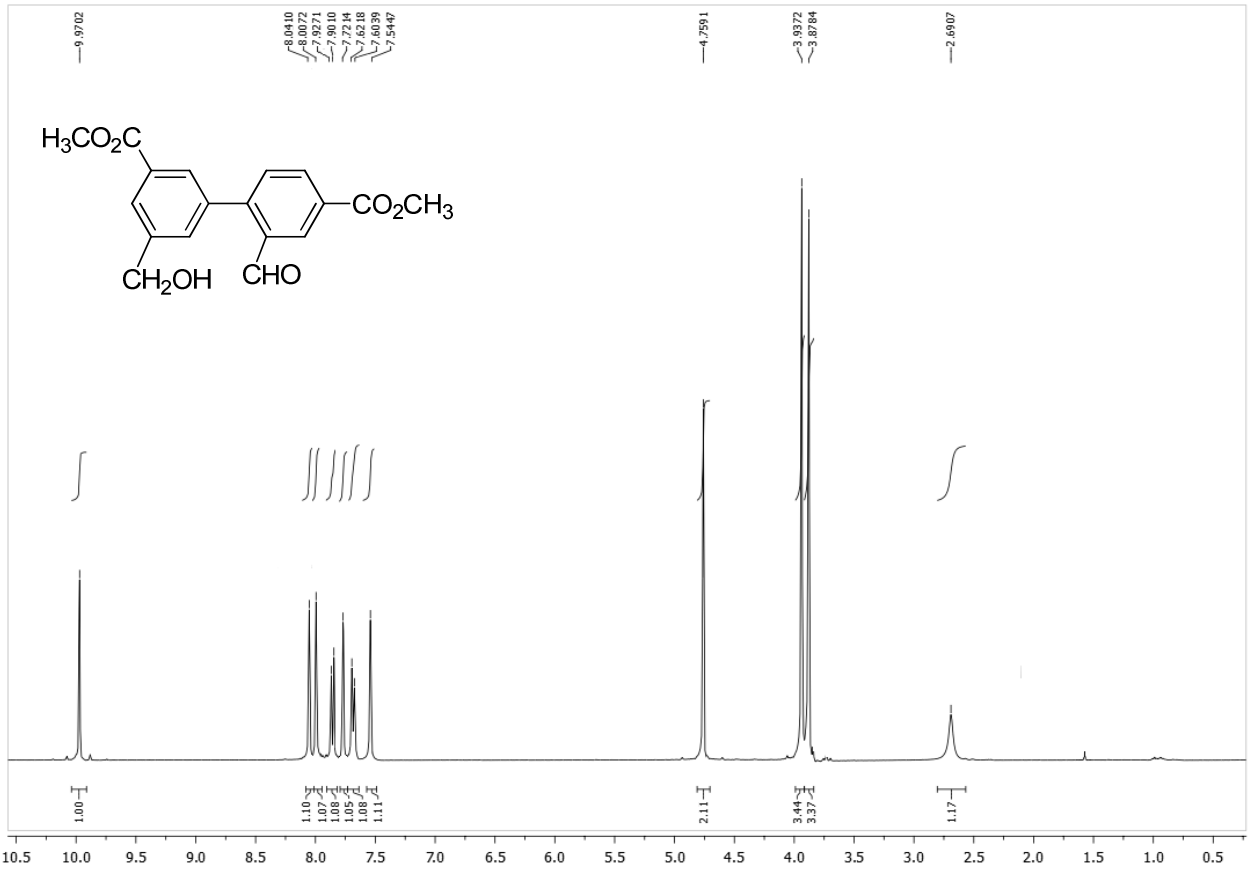
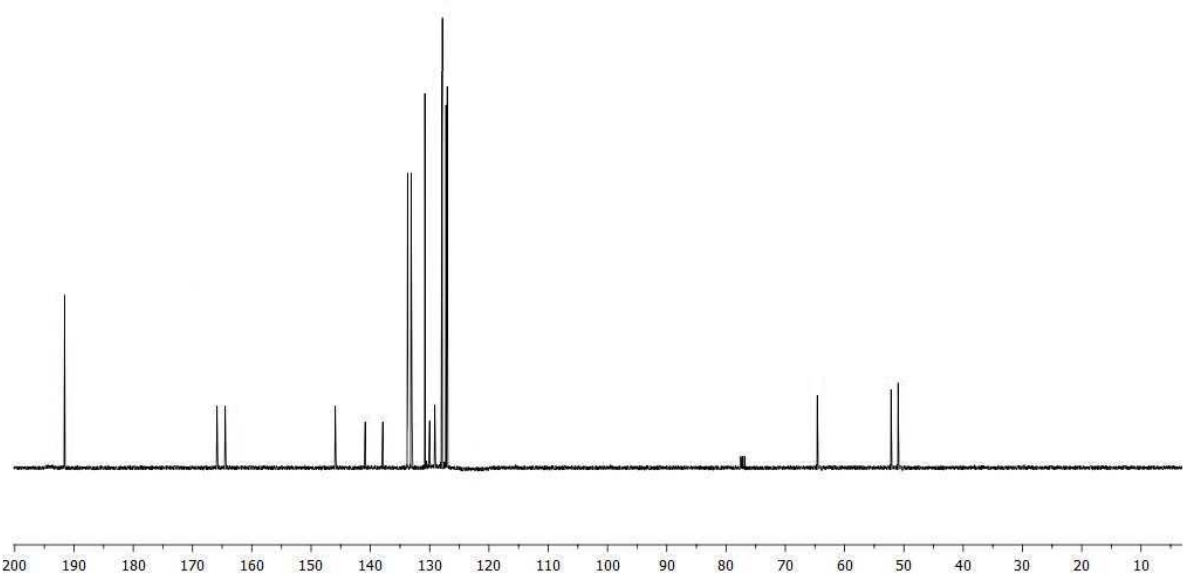
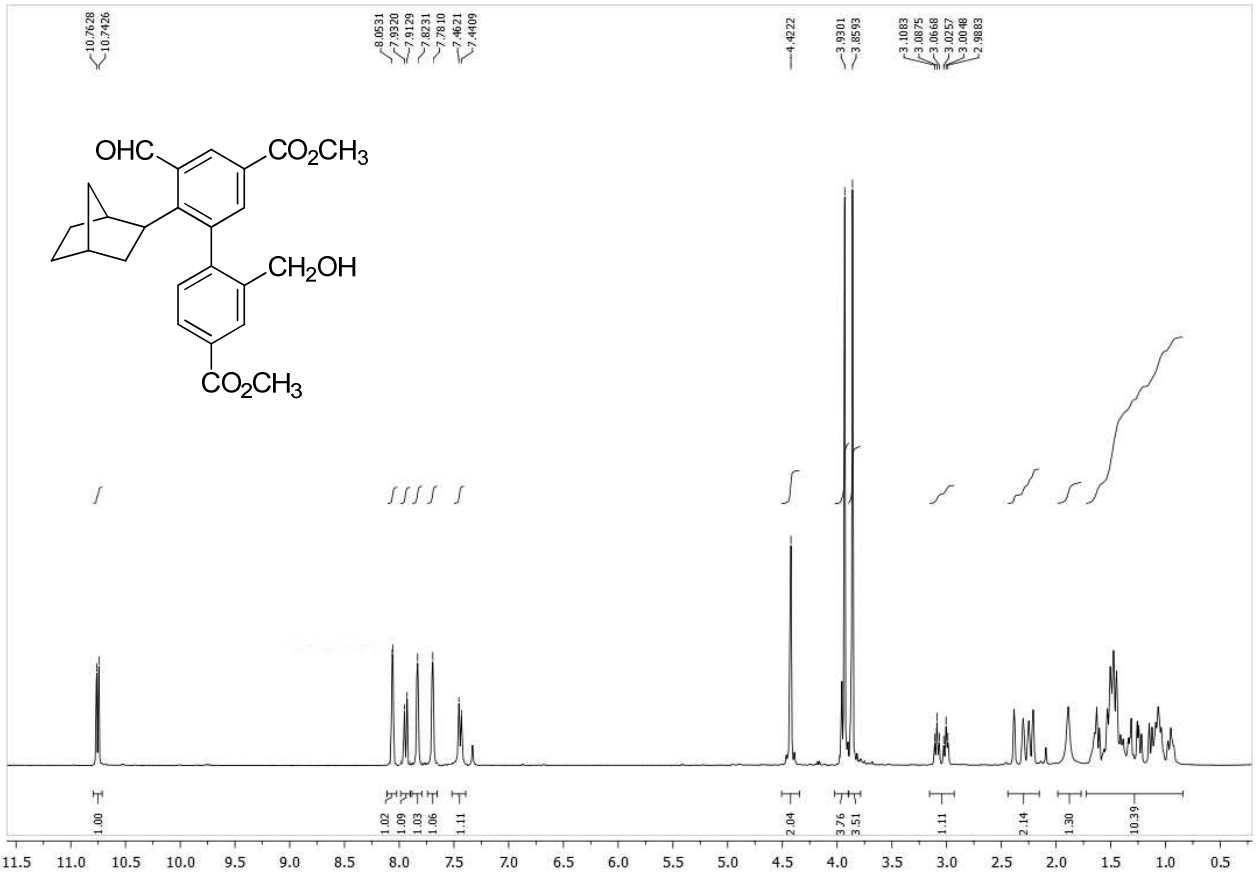
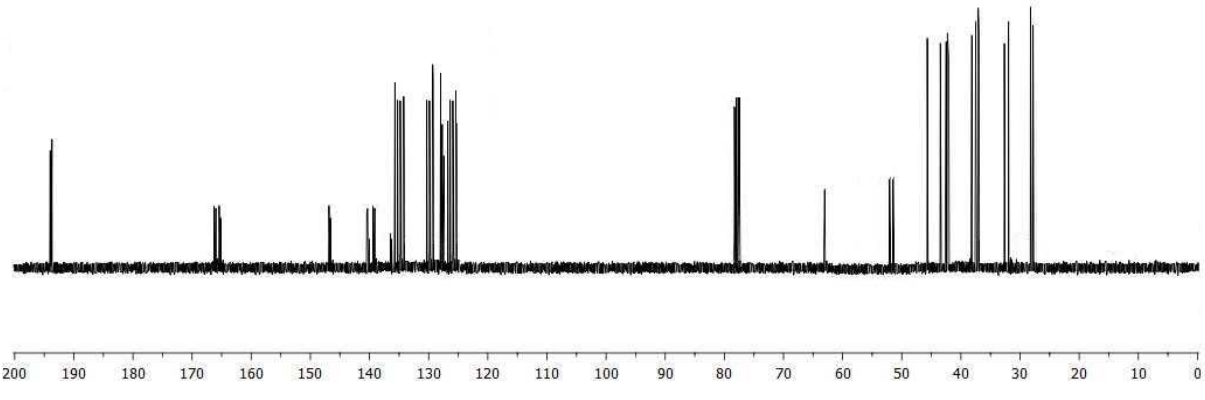


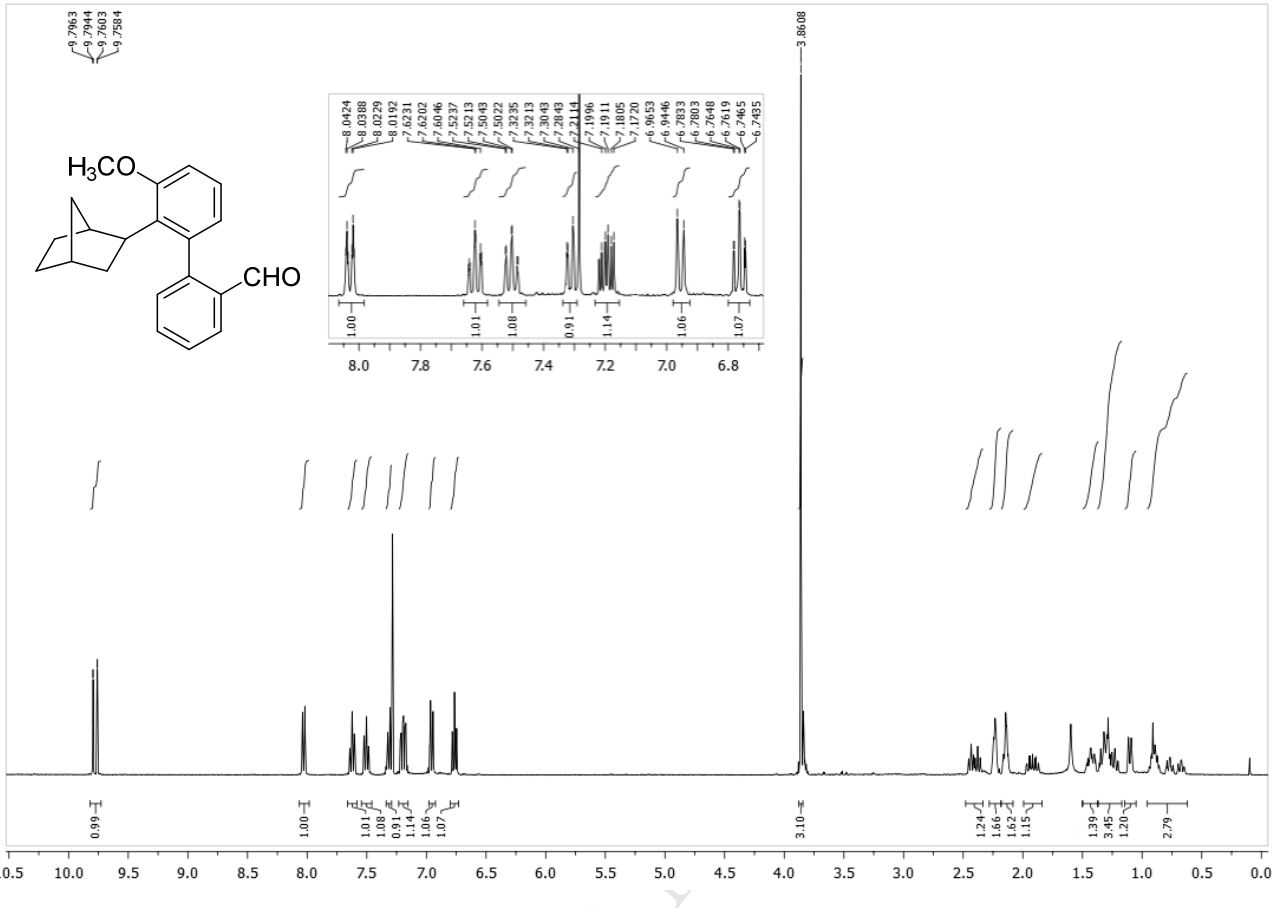


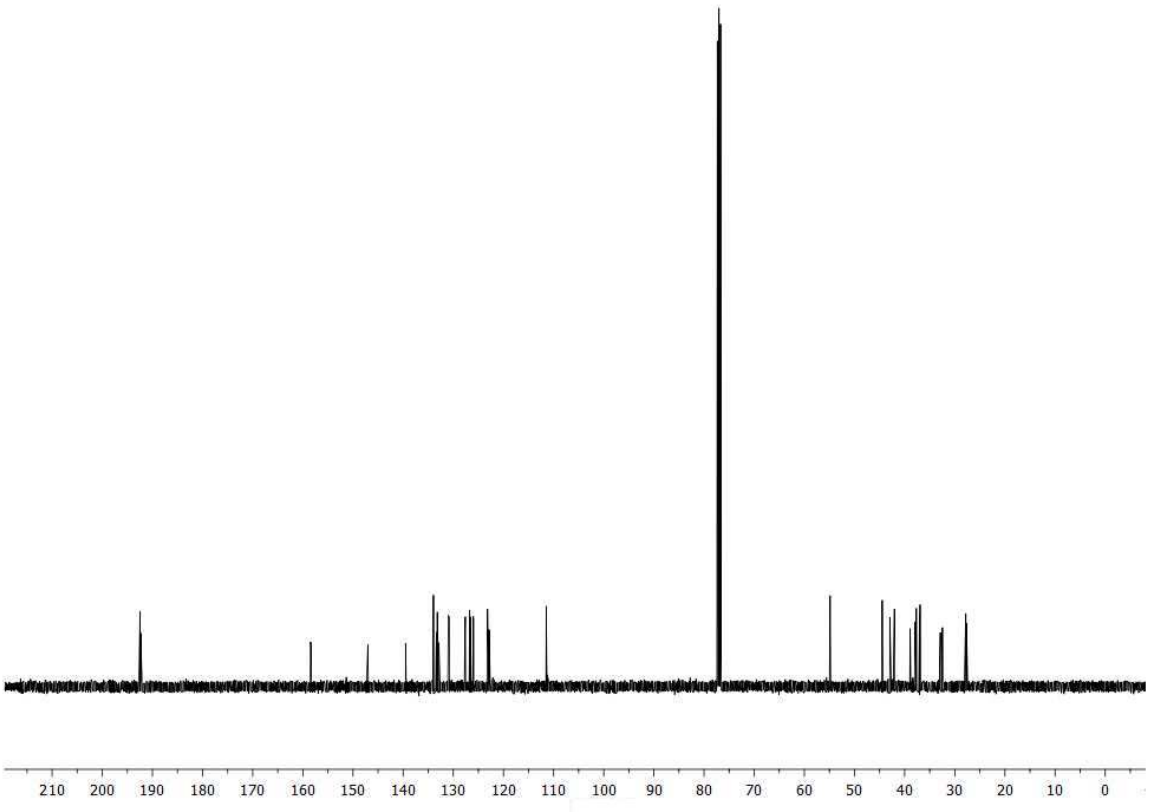
2’-Hydroxymethyl-4’,5-dicarbomethoxy-2-(2”-exo-norbornyl)-1,1’-biphenyl-3-carbaldehyde (**7**, R^1 = H, R^2 = CO_2Me, Table 3)



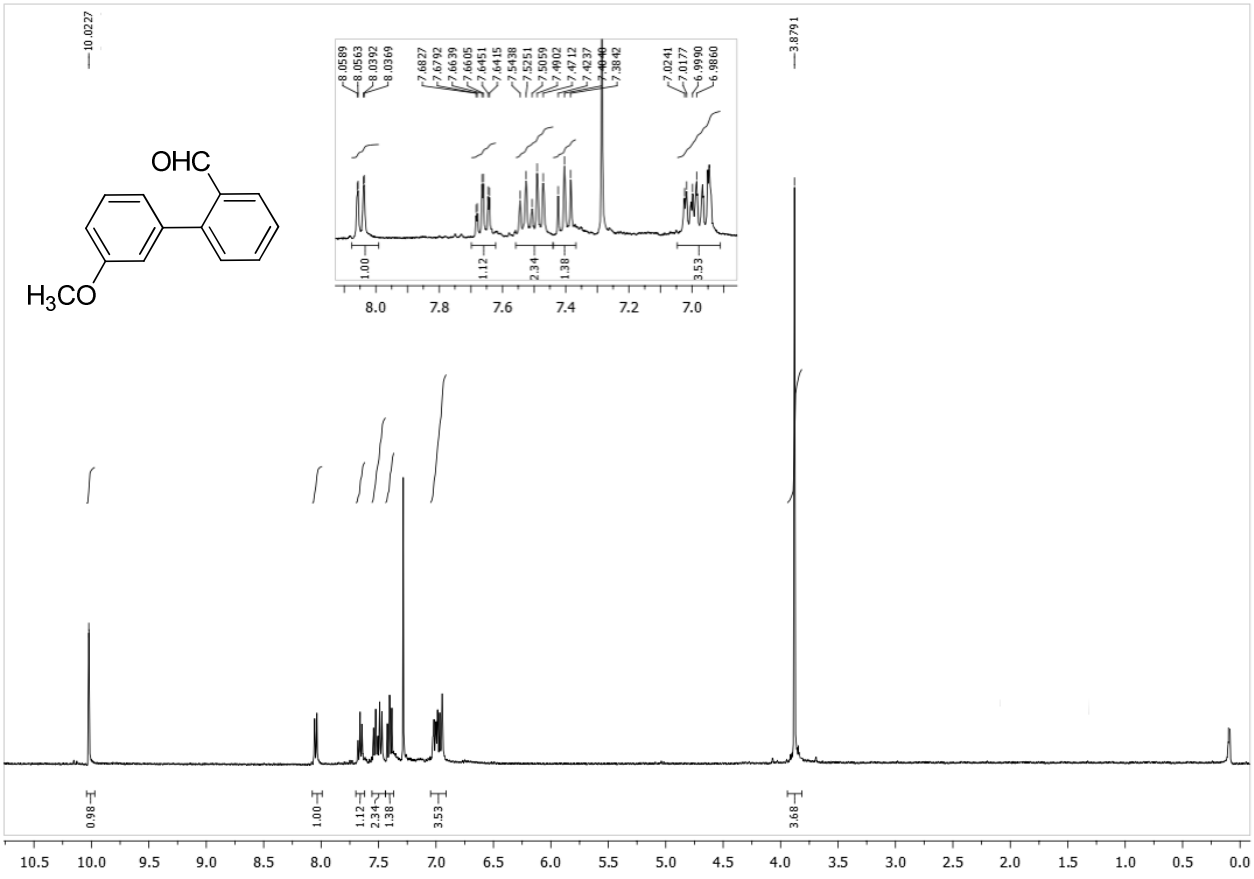


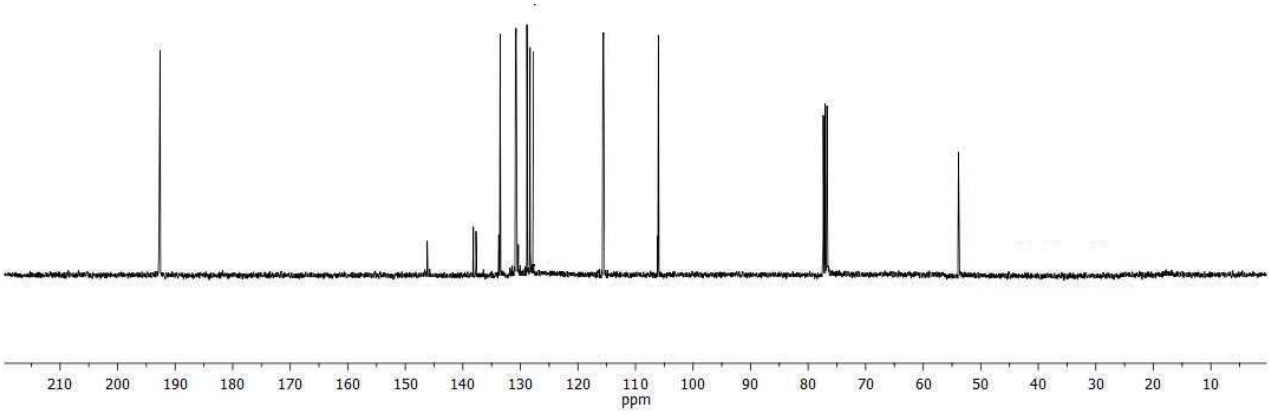
3-Methoxy-2-(2”-exo-norbornyl)-1,1’-biphenyl-2’-carbaldehyde (**9**, Scheme 4)





3’-Methoxy-[1,1’]-biphenyl-2-carbaldehyde (**3ja**, Scheme 4)





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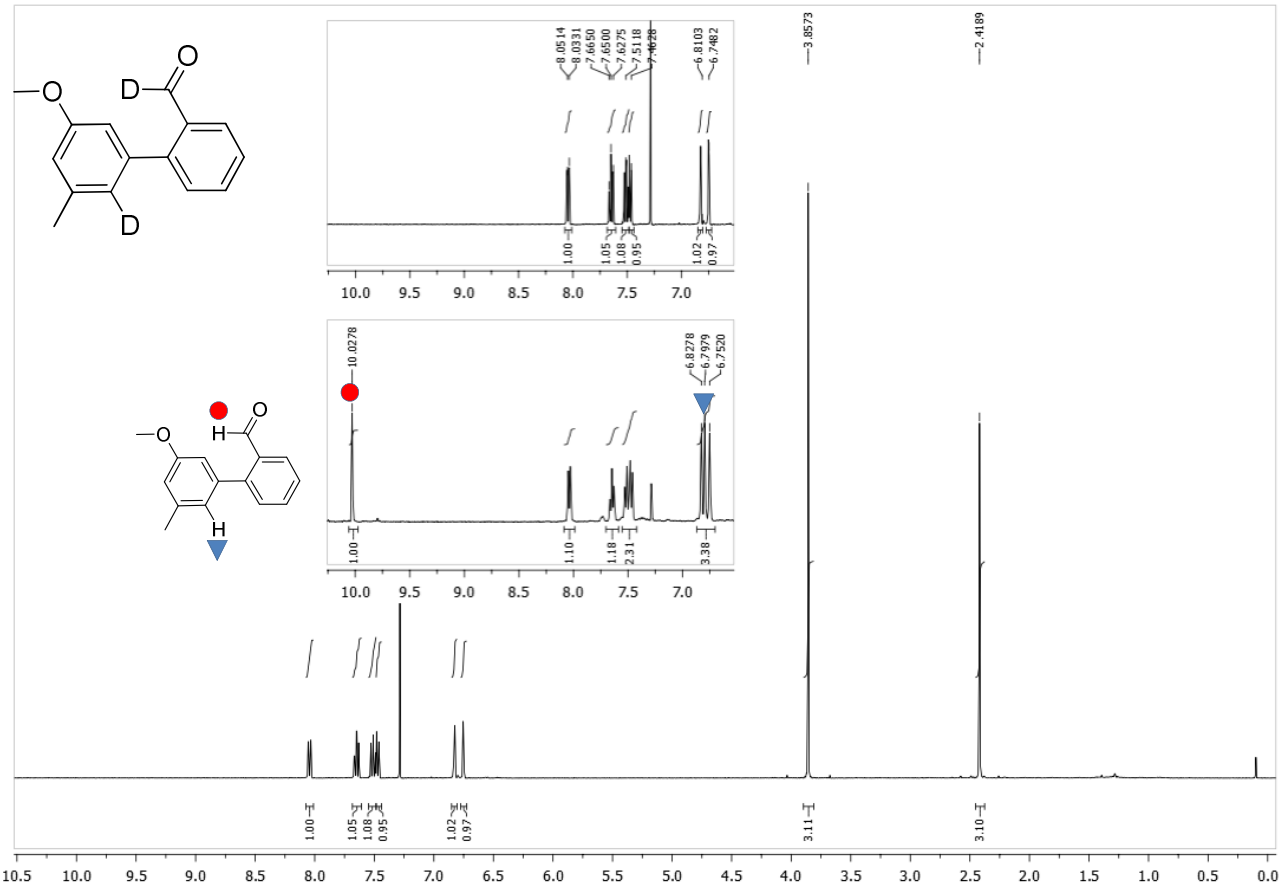
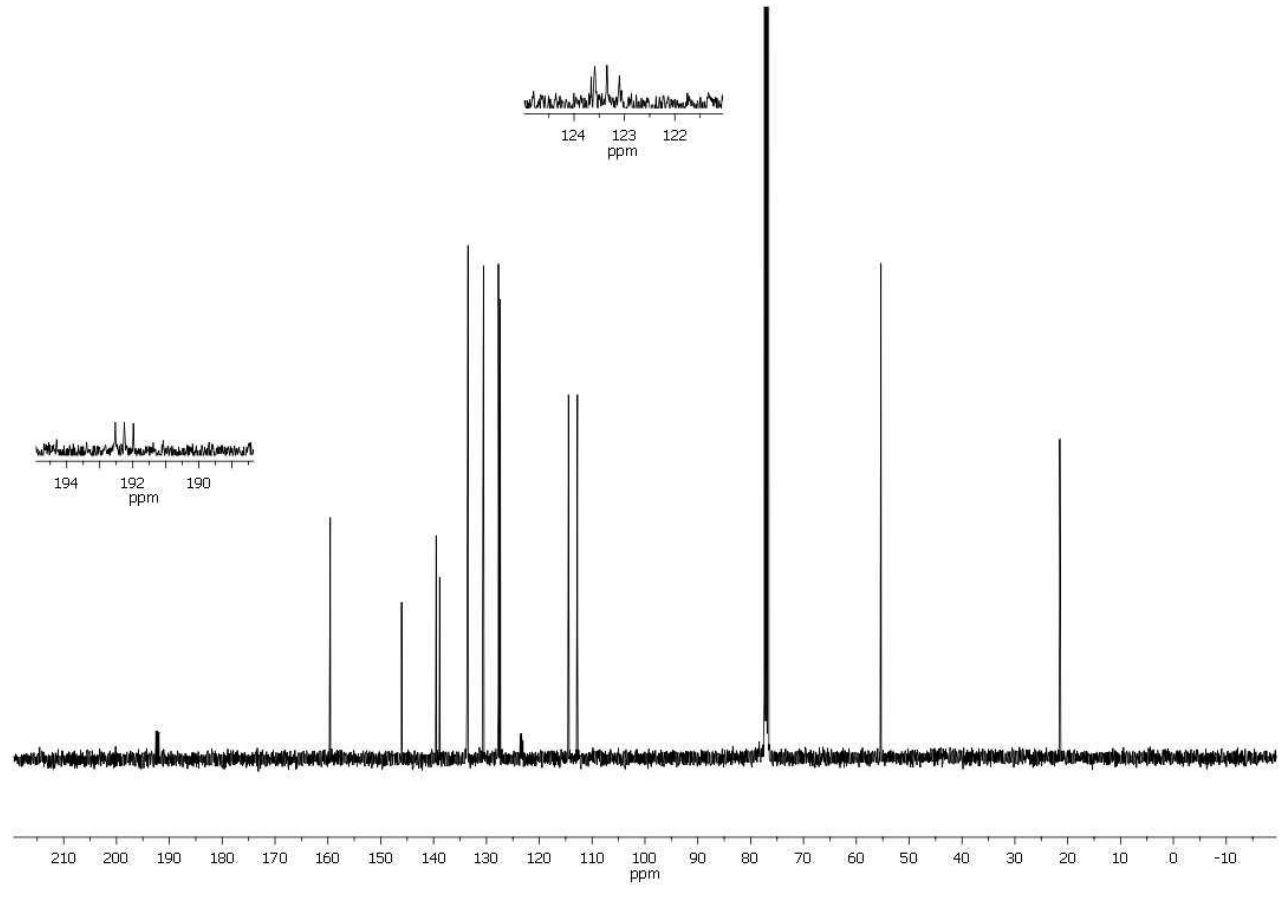
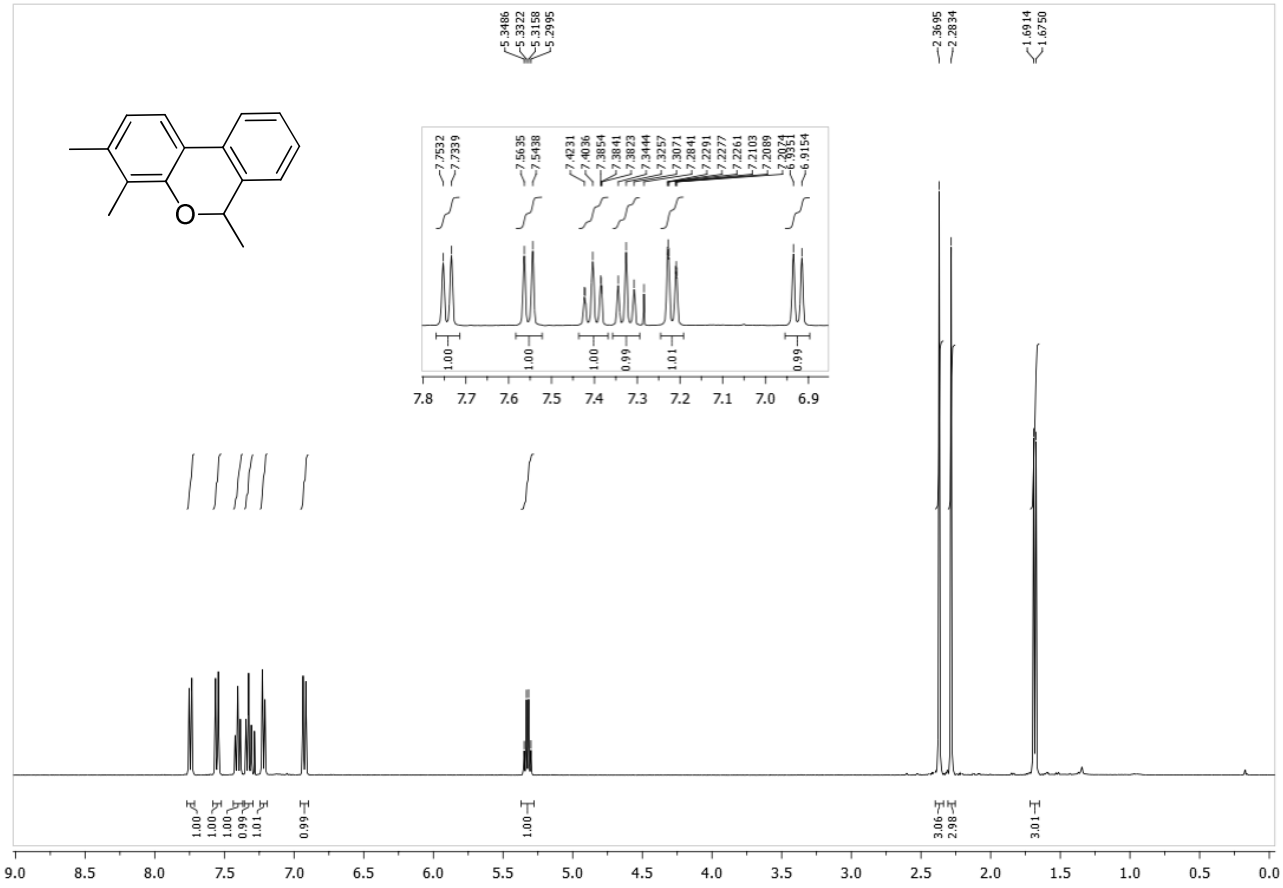
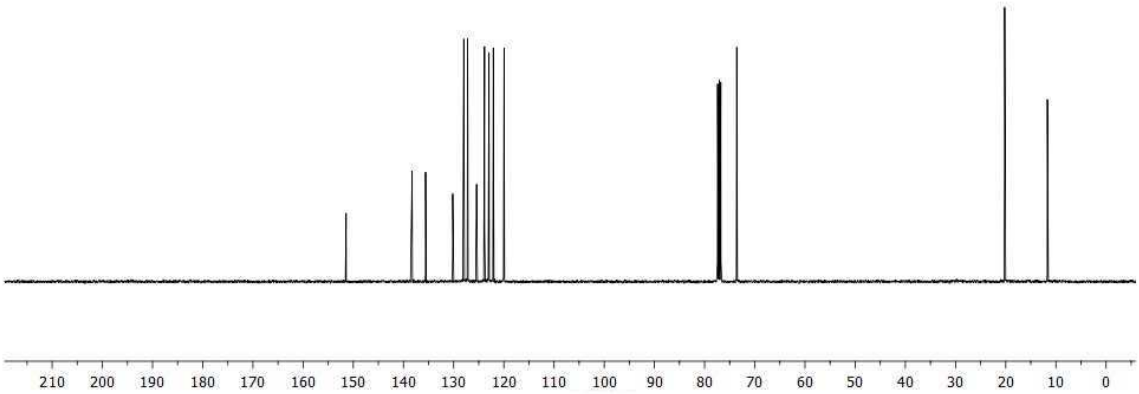




3,4,6-Trimethyl-6H- dibenzo[b,d]pyran (**13la**, R^1, R^2 = Me, R^3 = H, R^4 = Me, Table 7)





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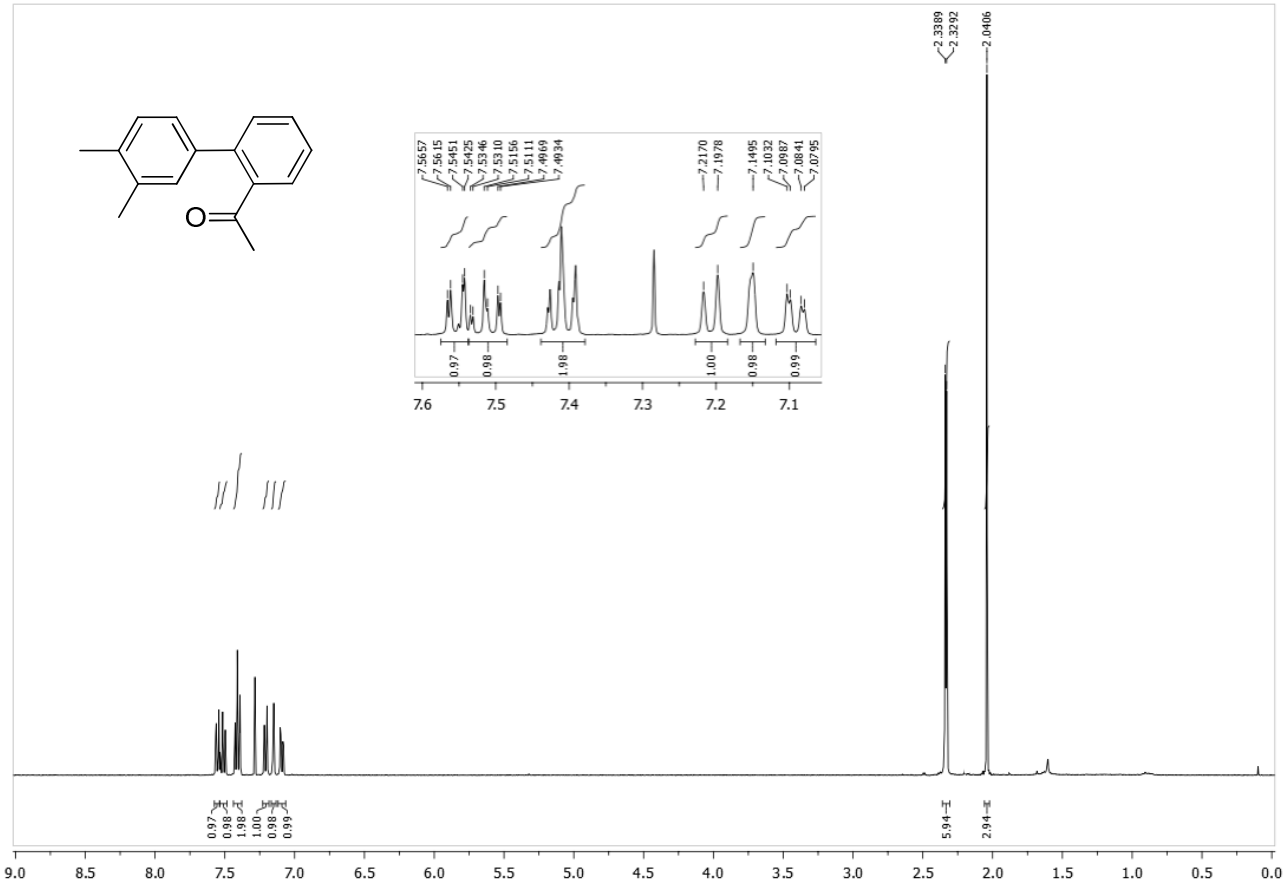
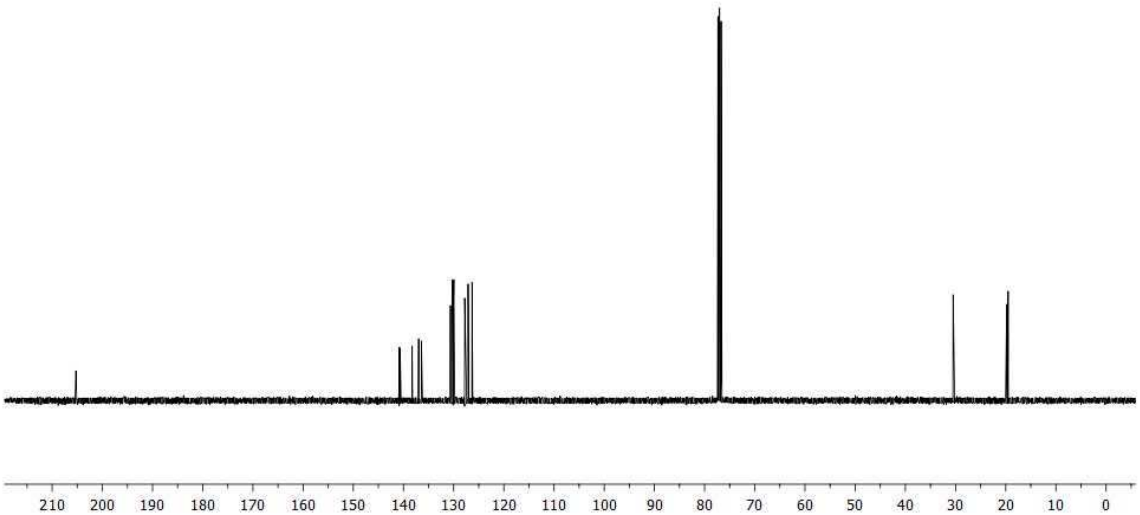
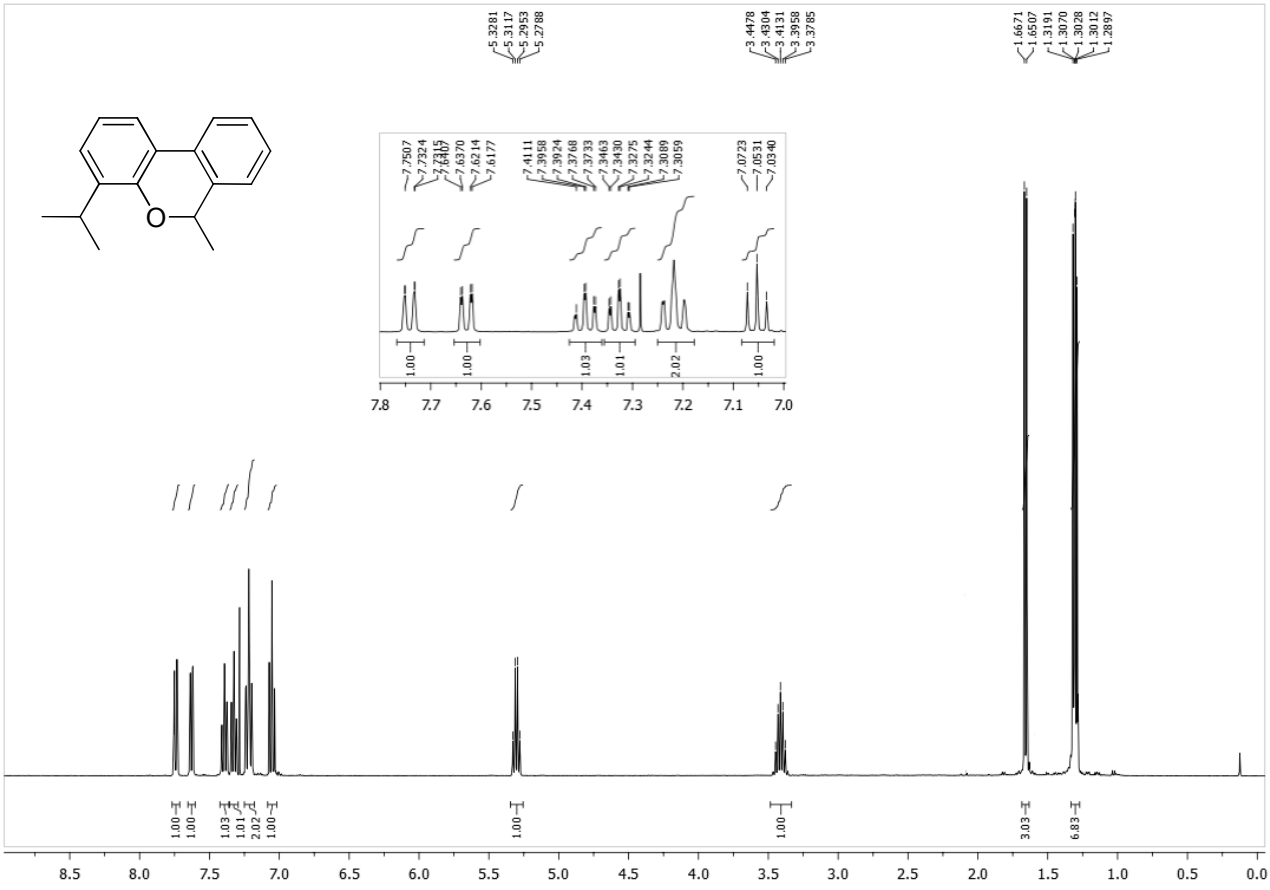
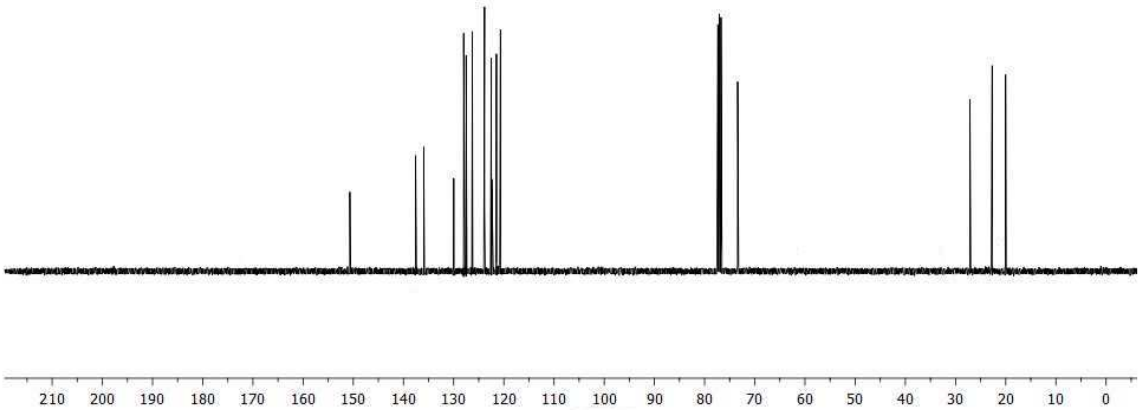


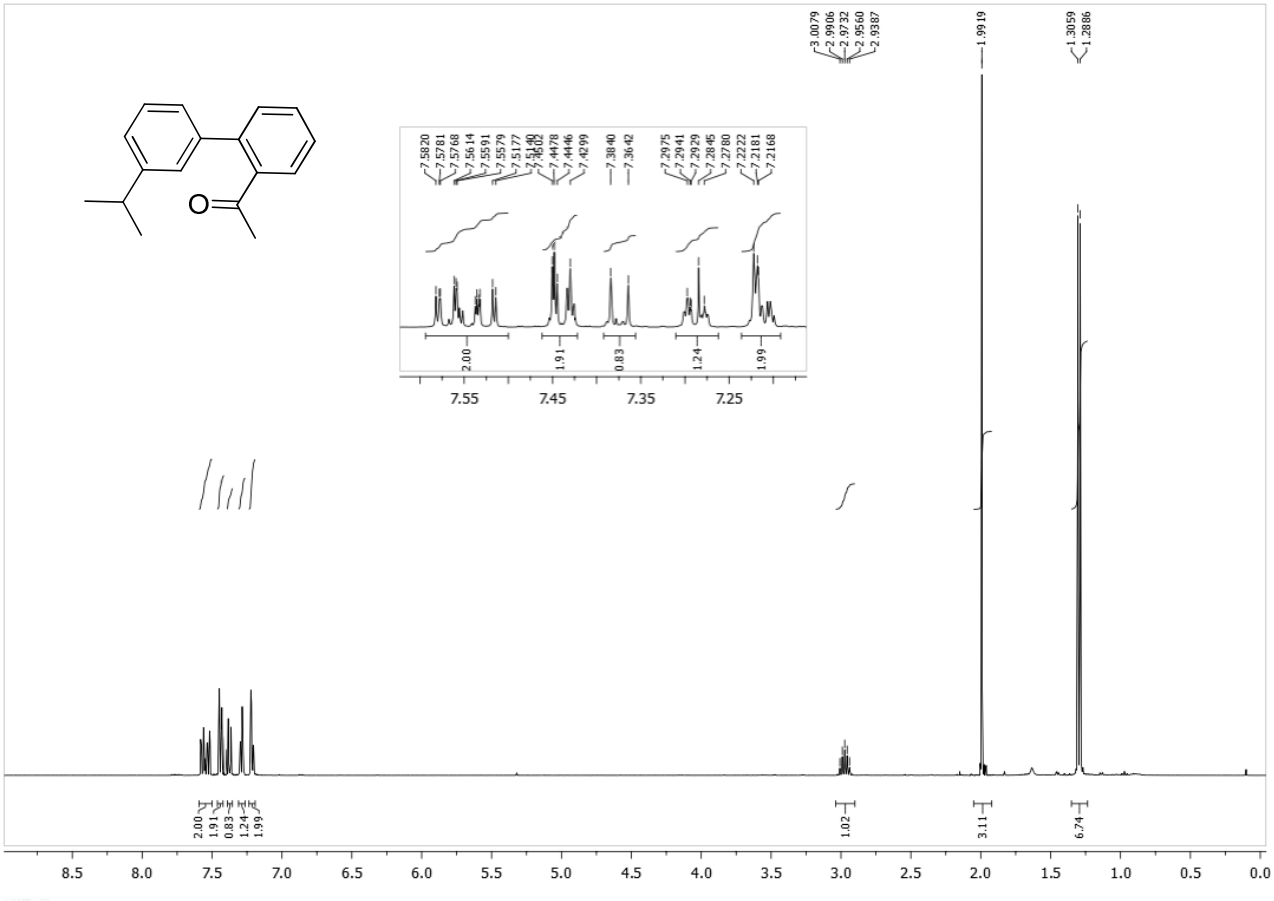


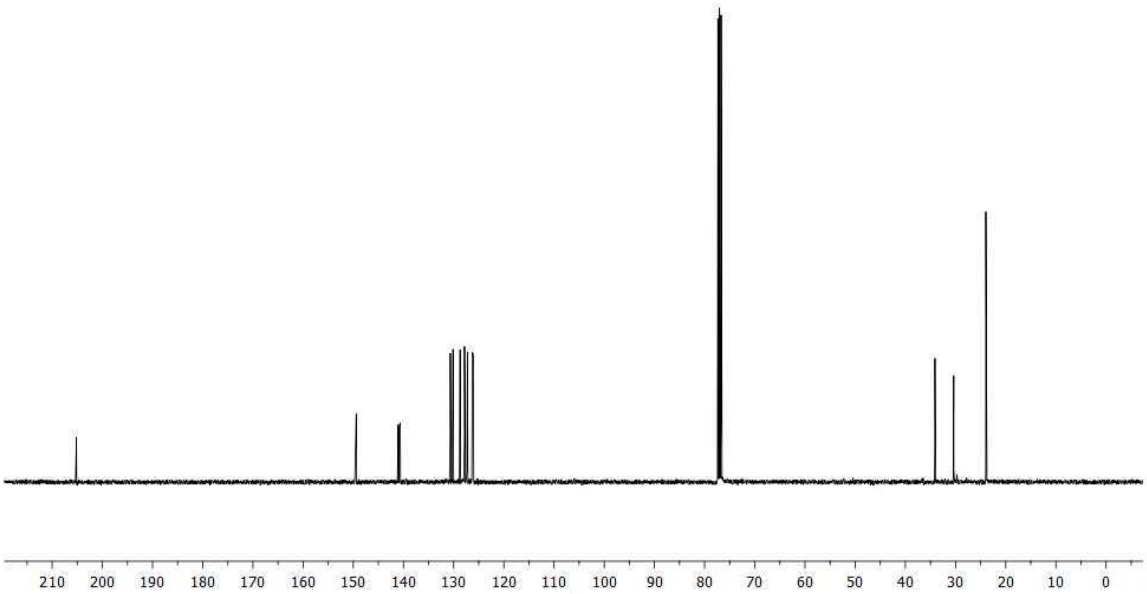
4-Isopropyl-6-methyl-6H-dibenzo[b,d]pyran (**13aa**, R^1 = iPr, R^2, R^3 = H, R^4 = Me, Table 7)



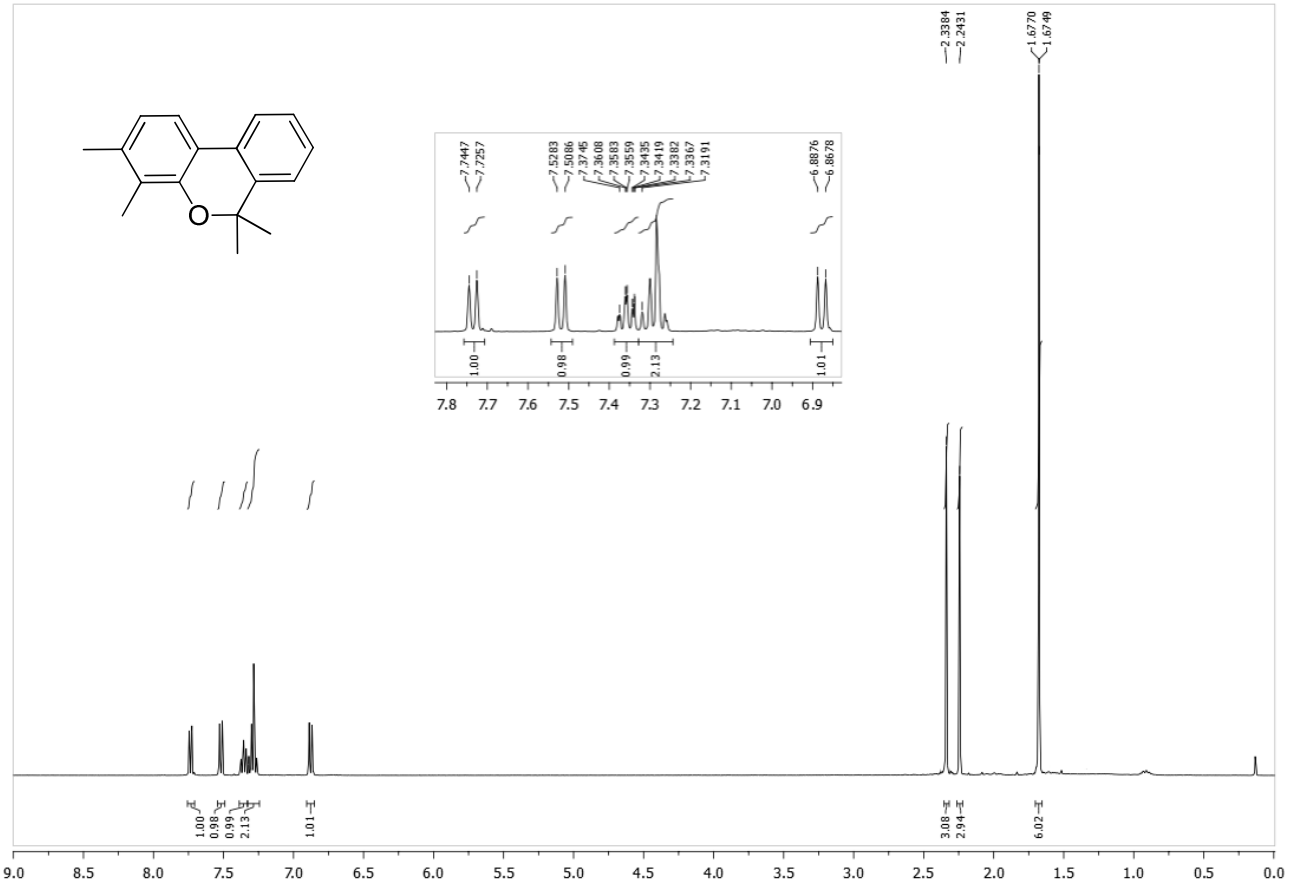


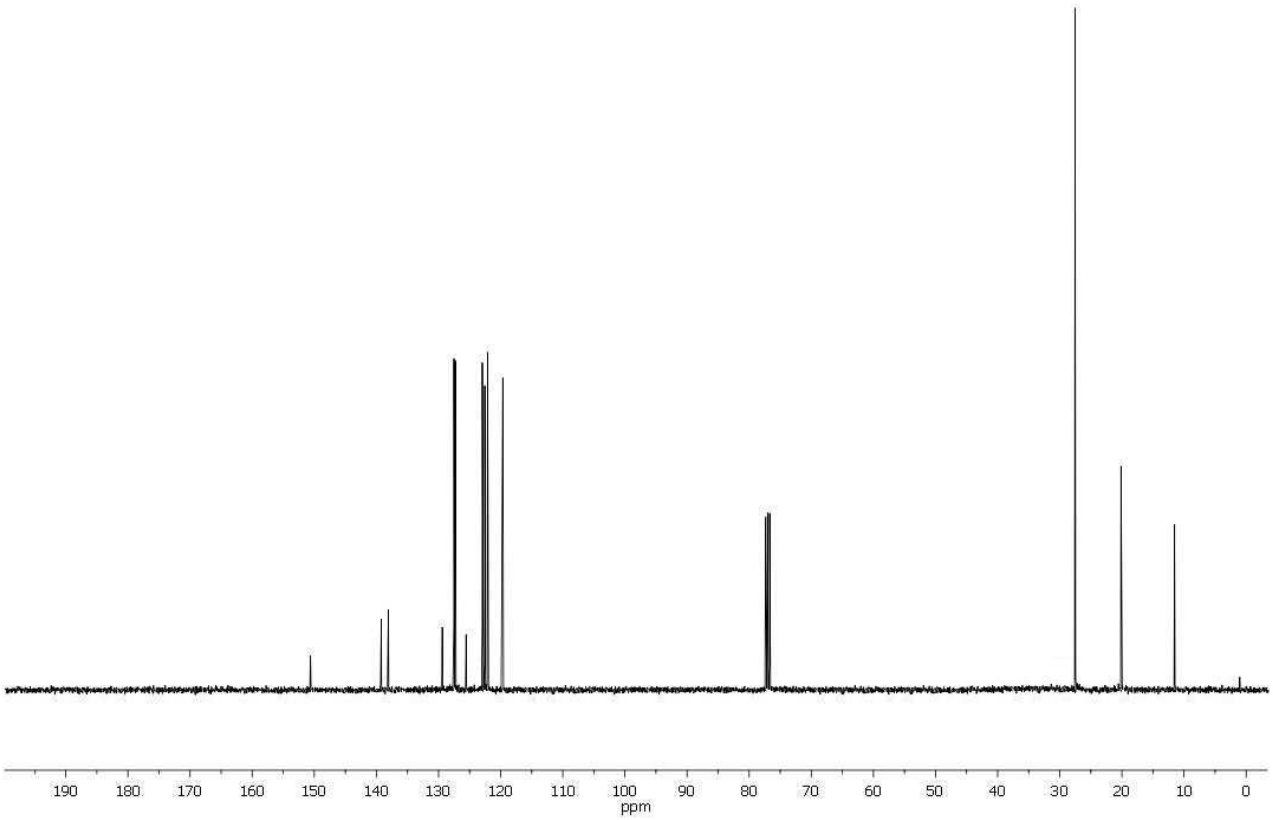
1-(3'-isopropyl-[1,1'-biphenyl]-2-yl)ethanone (**12aa**, R^1 = iPr, R^2, R^3 = H, R^4 = Me, Table 7)



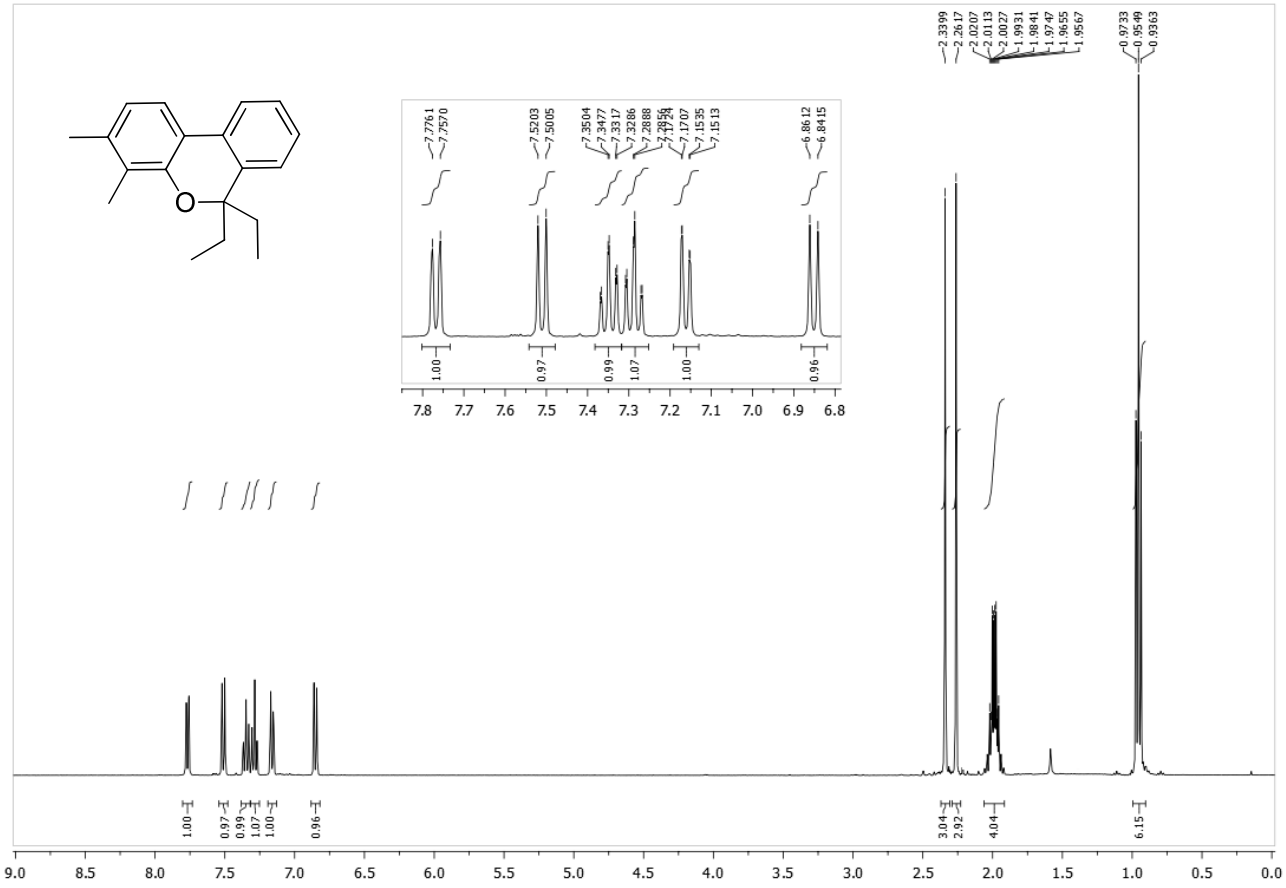


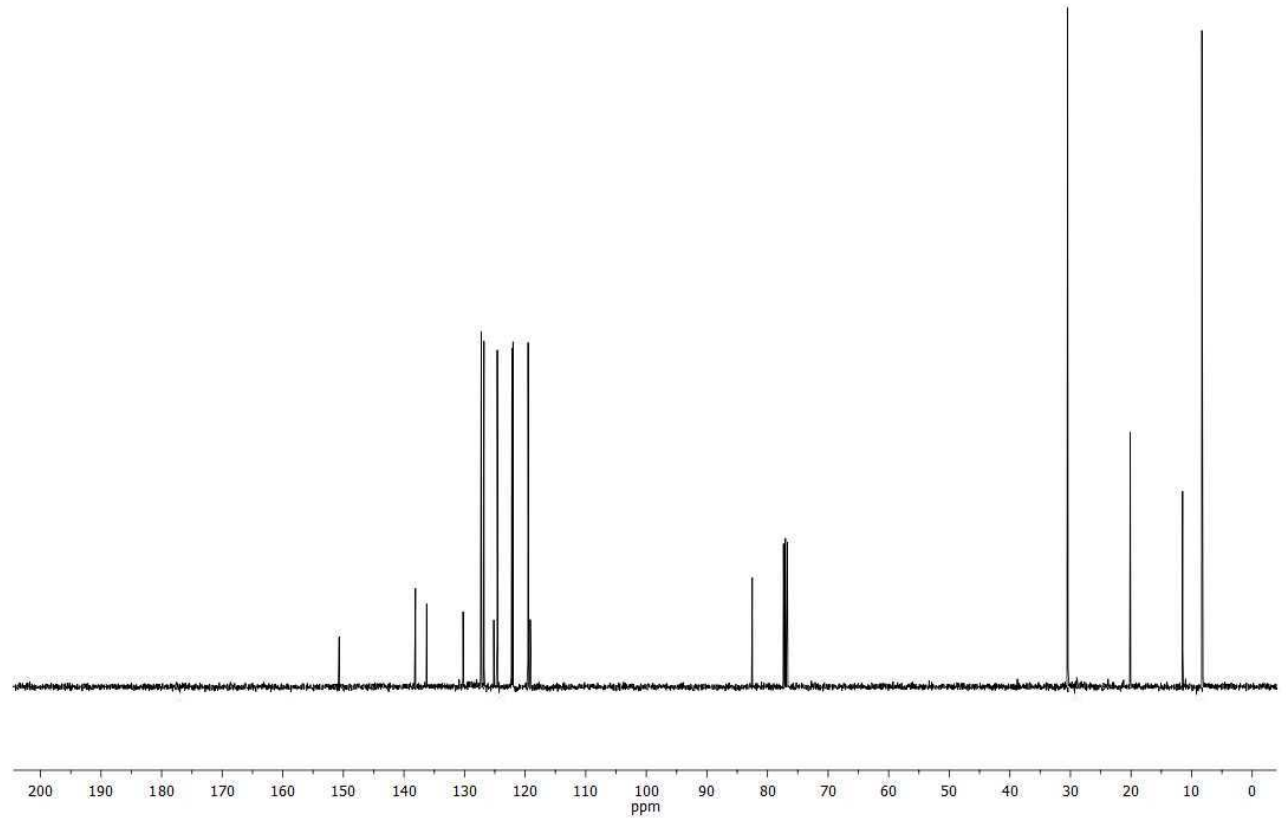
3,4,6,6-Tetramethyl-6H-dibenzo[b,d]pyran (**15laa**, Table 9)



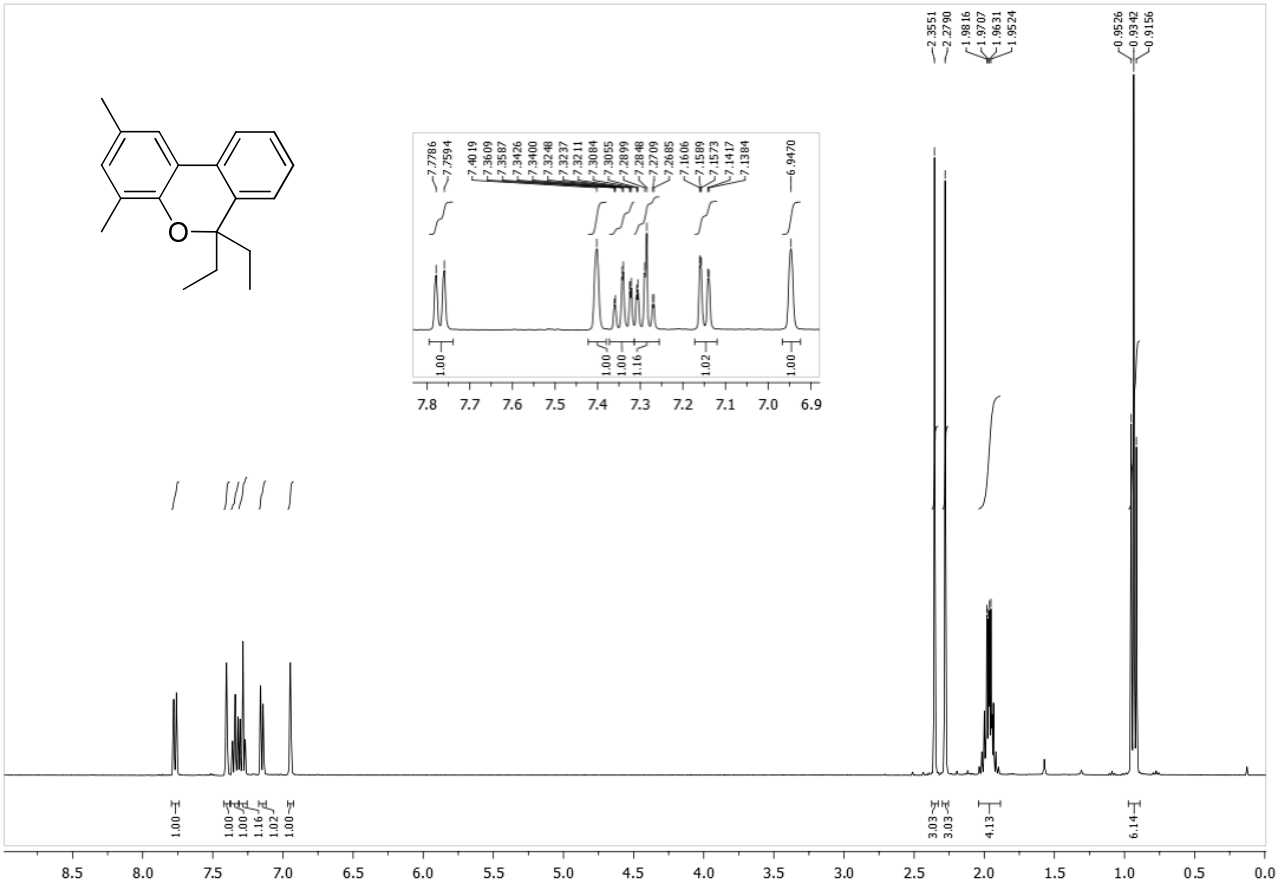


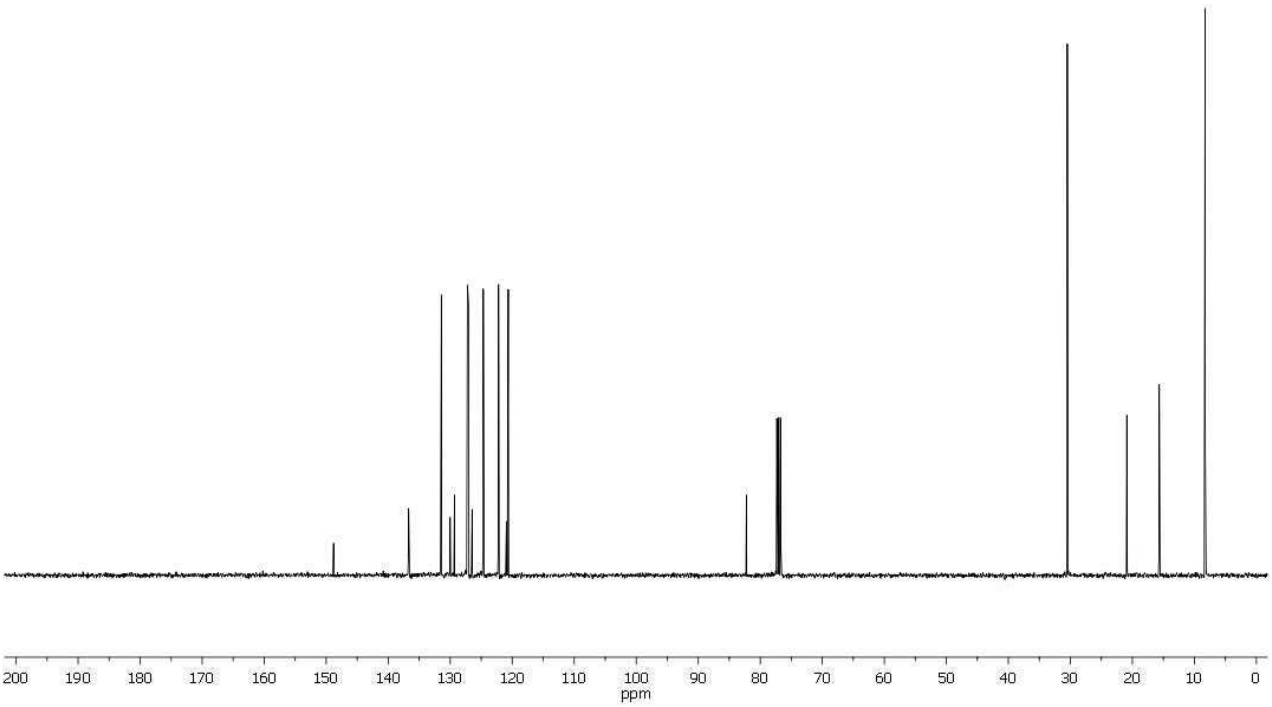
6,6-Diethyl-3,4-dimethyl-6H-dibenzo[b,d]pyran (**15lbb**, Table 9)



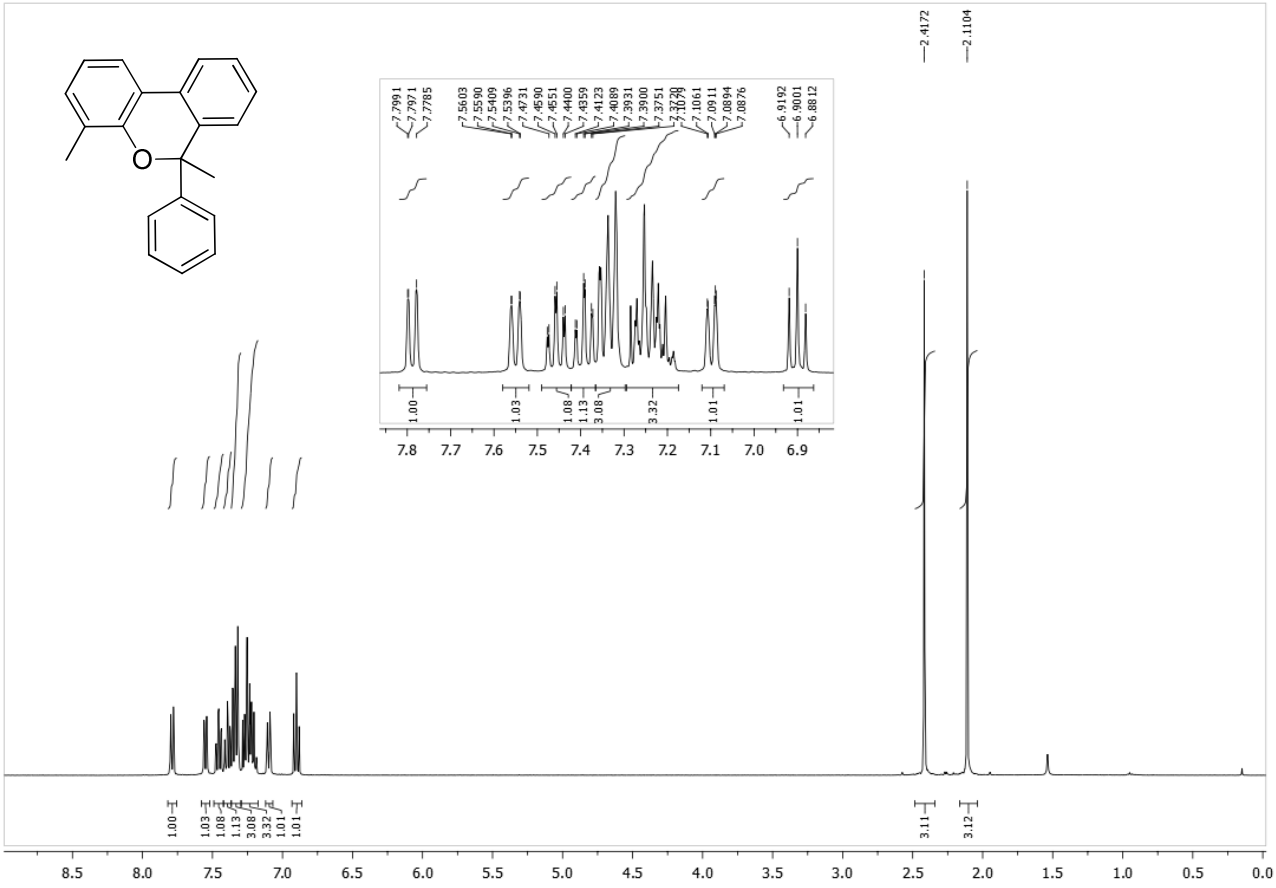


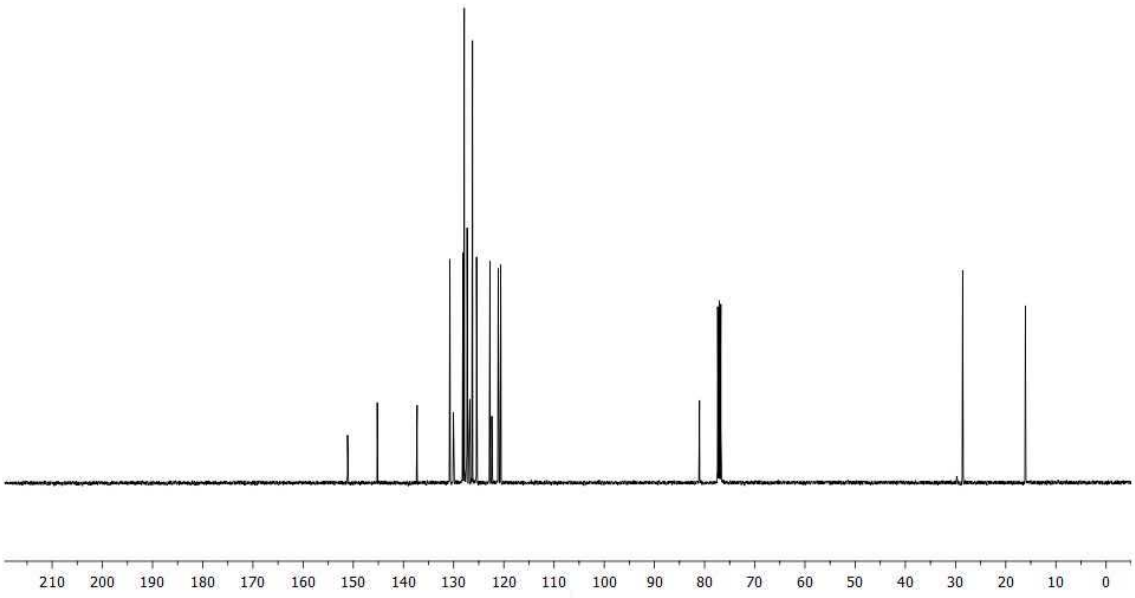
6,6-Diethyl-2,4-dimethyl-6H-dibenzo[b,d]pyran (**15cbb**, Table 9)



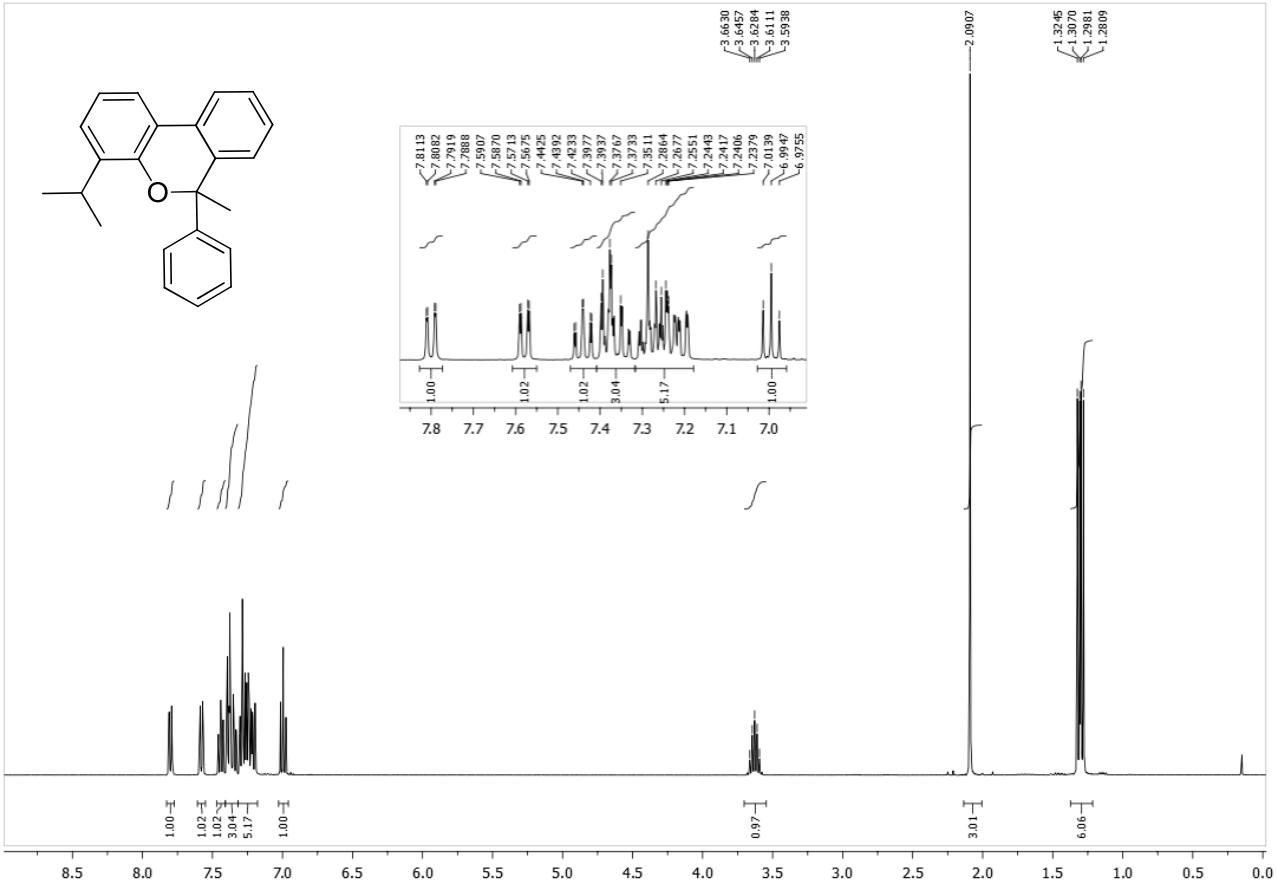


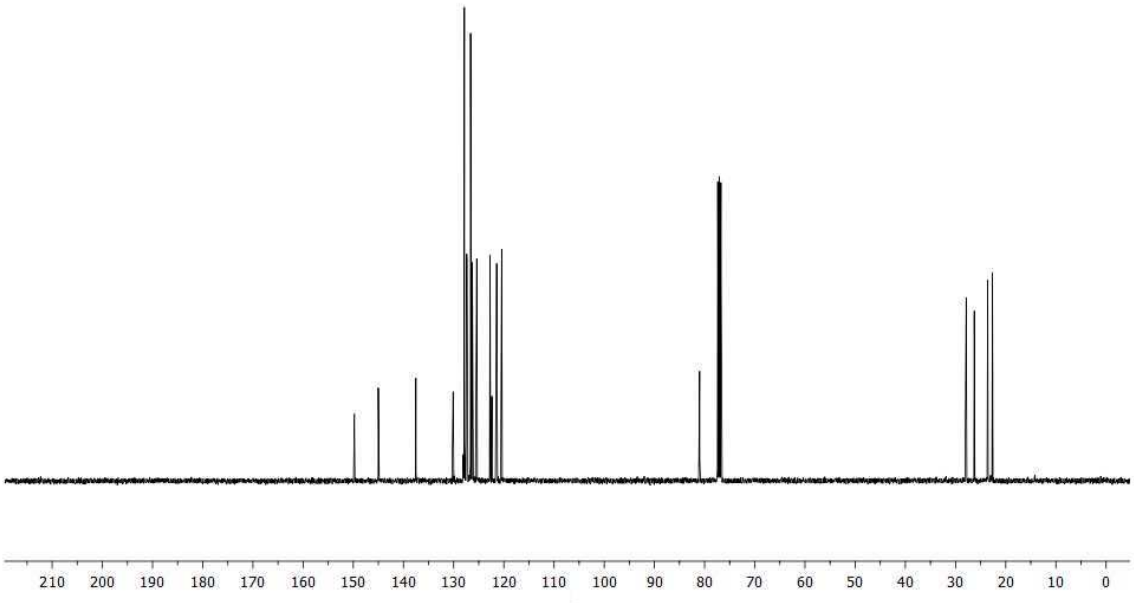
6-Methyl-6-phenyl-4-methyl-6H-dibenzo[b,d]pyran (**15bac**, Table 9)



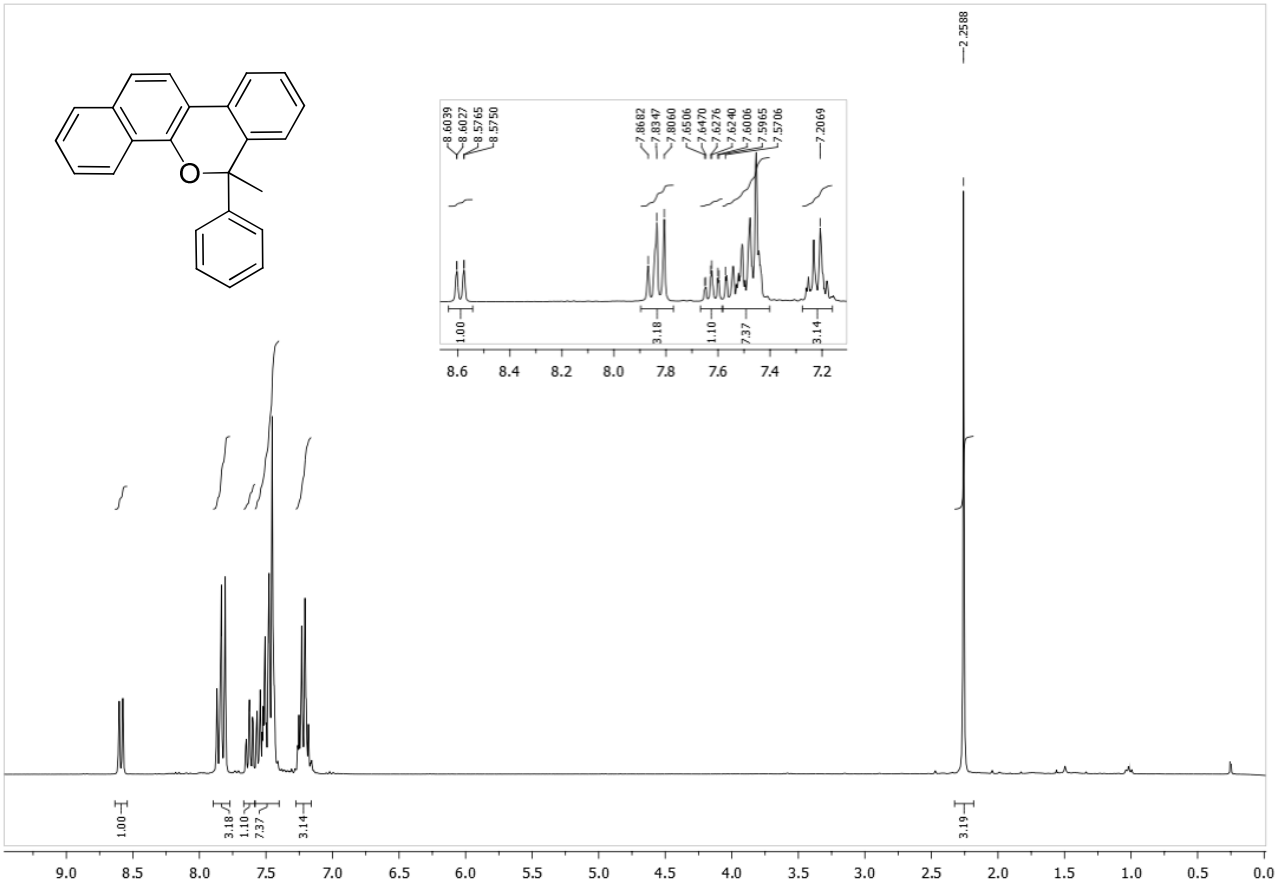


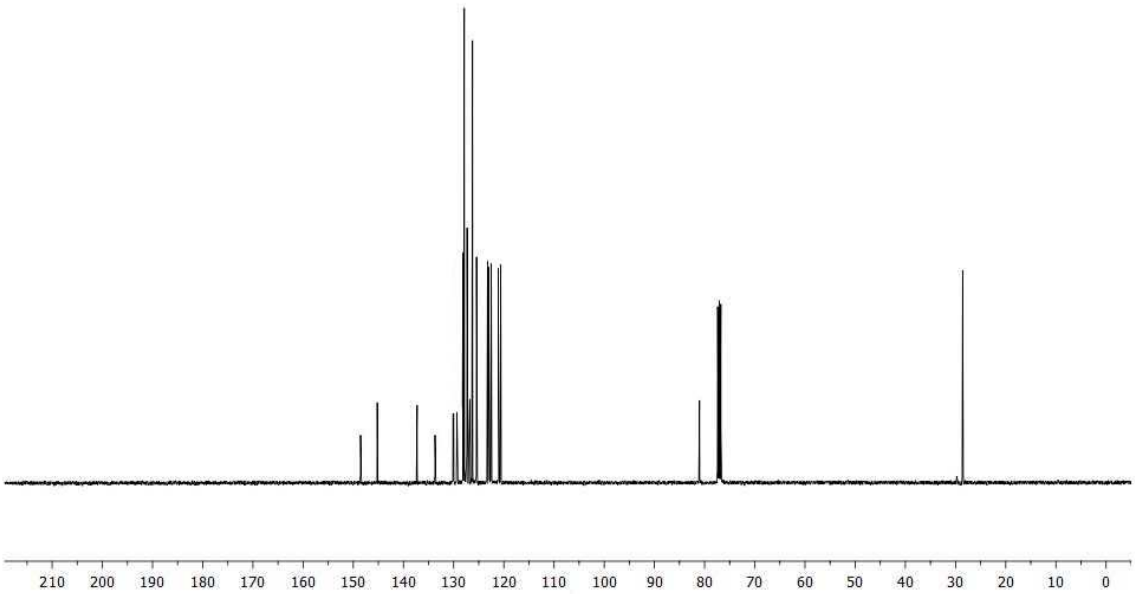
6-Methyl-6-phenyl-4-isopropyl-6H-dibenzo[b,d]pyran (**15aac**, Table 9)



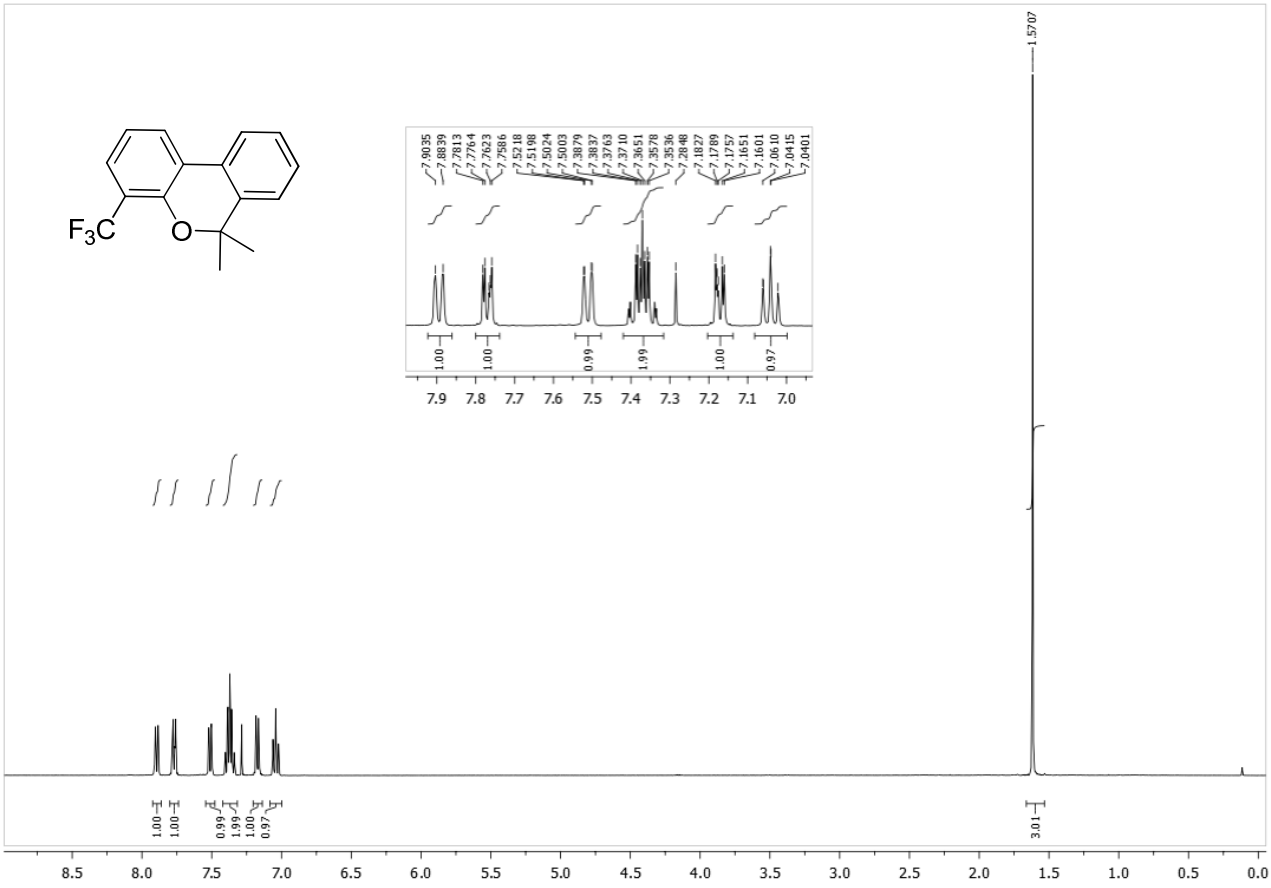


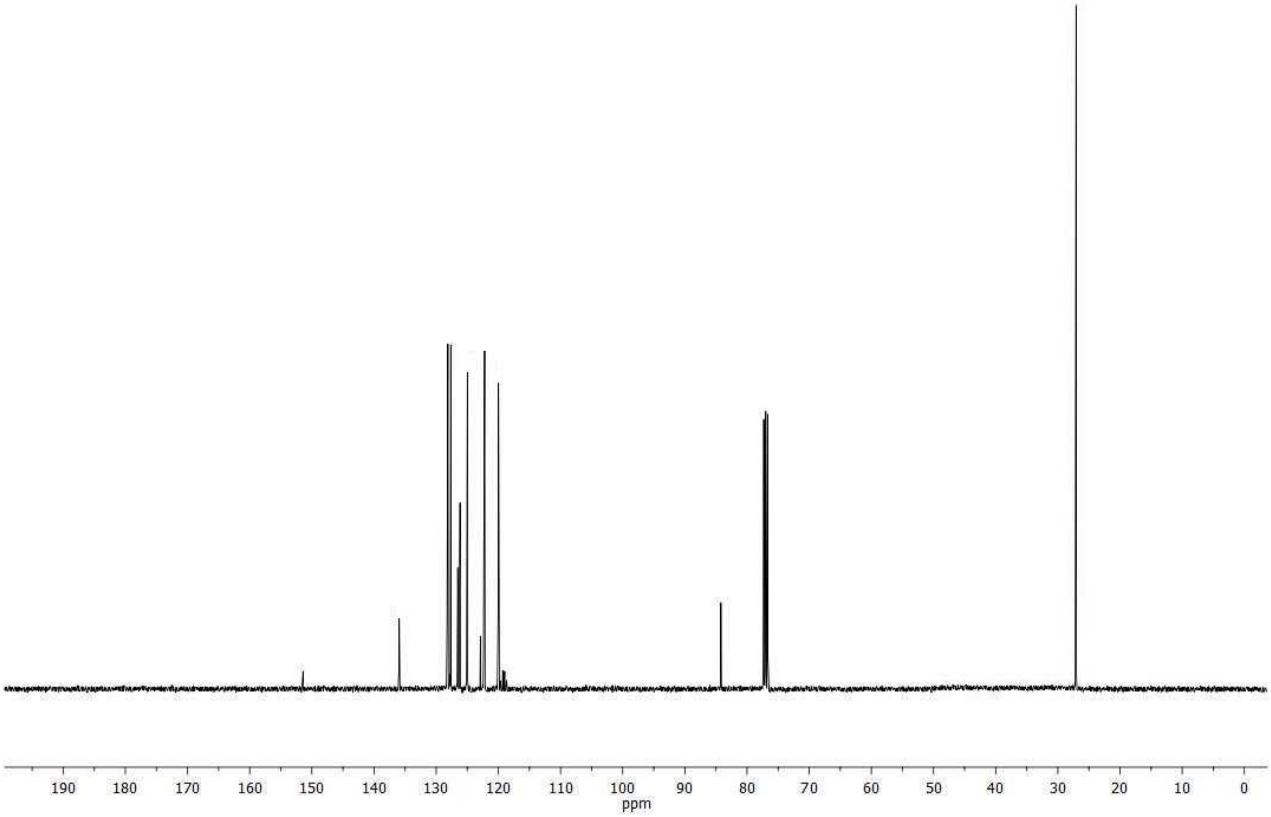
6-Methyl-6-phenyl-6H-benzo[d]naphtho[1,2-b]pyran (**15hac**, Table 9)





6,6-Dimethyl-4-trifluoromethyl-6H-dibenzo[b,d]pyran (**15kaa**, Table 9)





6,6-Diethyl-4-trifluoromethyl-6H-dibenzo[b,d]pyran (**15kbb**, Table 9)