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Article

Metal-Free Synthesis of Indanes by Iodine(III)-Mediated Ring Contraction of 1,2-Dihydronaphthalenes

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Um protocolo livre de metais foi desenvolvido para sintetizar indanos através da contração de anel de 1,2-di-hidronaftalenos promovida por PhI(OH)OTs (HTIB ou reagente de Koser). Este rearranjo oxidativo pode ser realizado em diversos solventes (MeOH, CH_3CN, 2,2,2-trifluoroetanol (TFE), 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), e uma mistura 1:4 de TFE:CH_2Cl_2) em condições brandas. A contração de anel fornece indanos *trans*-1,3-dissubstituídos diastereosseletivamente, os quais são difíceis de obter em química orgânica sintética.

A metal-free protocol was developed to synthesize indanes by ring contraction of 1,2-dihydronaphthalenes promoted by PhI(OH)OTs (HTIB or Koser's reagent). This oxidative rearrangement can be performed in several solvents (MeOH, CH_3CN, 2,2,2-trifluoroethanol (TFE), 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), and a 1:4 mixture of TFE:CH_2Cl_2) under mild conditions. The ring contraction diastereoselectively gives functionalized *trans*-1,3-disubstituted indanes, which are difficult to obtain in synthetic organic chemistry.

Keywords: indanes, hypervalent iodine, ring contraction, 1,2-dihydronaphthalenes, rearrangements

Introduction

The indane ring system is present in several natural products and in non-natural compounds with remarkable biological activity.[1] Consequently, efforts have continuously been made to develop new routes to obtain molecules with this unit.[2] A typical strategy to synthesize a functionalized indane is by selecting an appropriate indanone, which is then elaborated into the target molecule.[2,3] As tetralones are usually cheaper than indanones, the preparation of indanes starting from a tetralone (or a derivative) through a ring contraction rearrangement could be advantageous.[4]

In the last years, hypervalent iodine reagents have become an essential tool in synthetic organic chemistry due to the plethora of reactions that can be performed with them in excellent yield and selectivities.[5] Moreover, hypervalent iodine compounds represent in many cases an alternative to toxic heavy metals.[5] Although the oxidative rearrangement of alkenes mediated by iodine(III) has been described in some papers,[6] the ring contraction of 1,2-dihydronaphthalenes was reported for a few substrates using only *p*-Me-C_6H_4-IF_2,[6] which led to fluorinated indanes.

Herein, we describe an efficient metal-free protocol for the synthesis of indanes under mild conditions. In a preliminary communication, we report the ring contraction of 1,2-dihydronaphthalenes (which are obtained from 1-tetralones) mediated by PhI(OH)OTs (HTIB or Koser's reagent) for a few substrates.[7] In this article, the oxidation of several additional substrates is presented, better defining the reaction scope. Additionally, other reaction conditions were

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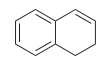
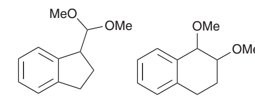
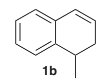
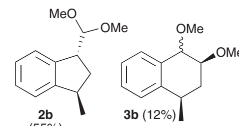
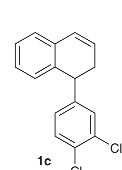
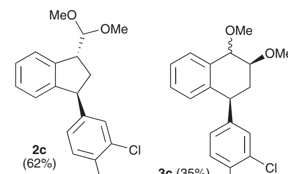
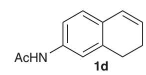
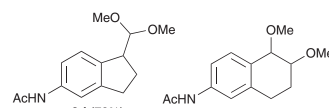
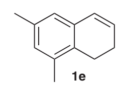
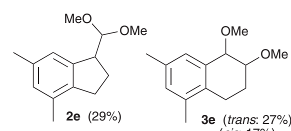
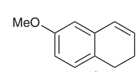
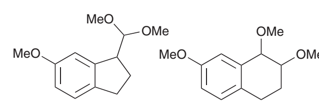
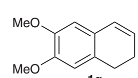
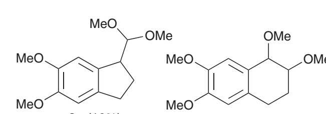
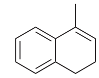
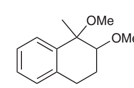
discovered using fluoroalcohols as solvent, which highly improved isolated yields. The best condition employed a 4:1 mixture of CH_2Cl_2-TFE that led to indanes in very good yield and with high diastereoselectivity.

Results and Discussion

Ring contractions in methanol

The required 1,2-dihydronaphthalenes are readily available substrates that can be prepared from 1-tetralones by reduction or Grignard reaction followed by dehydration[7,8] (see Supplementary Information, SI, for details). This work was initiated studying the oxidation of **1a** with the readily available iodine(III) reagents HTIB, $PhI(OAc)_2$, and $PhI(OCOCF_3)_2$ in methanol. Mixtures of several compounds and/or starting material were obtained using $PhI(OAc)_2$ or $PhI(OCOCF_3)_2$. Albeit the addition product **3a** was isolated as the major component, the desired indane **2a** was isolated using HTIB (Table 1, entry 1). Thus, HTIB was selected for further tests. When the reaction was performed at −10 °C, the overall isolated yield was lower (**2a**: 24%, *trans*-**3a**: 20%, *cis*-**3a**: 15%) than at room temperature. The use of trimethylorthoformate (TMOF) as solvent, instead of MeOH, also decreased the global yield (**2a**: 14%, *trans*-**3a**: 12%, *cis*-**3a**: 2%). These two trends are opposite to that observed in analogous thallium(III) promoted oxidation of 1,2-dihydronaphthalenes.[9] Although indane **2a** was obtained in only 36%, we decided to study the behavior of the methyl-substituted 1,2-dihydronaphthalene **1b**, hoping to obtain a higher yield of the ring contraction product.[9] Indeed, when **1b** was treated with HTIB, the desired *trans*-indane **2b** was obtained in 55% yield, together with the addition products **3b** (entry 2). The ring contraction of 1,2-dihydronaphthalene **1c** was performed with 3.6 equiv. of HTIB, which delivered indane **2c** in 62% yield, as a single diastereomer, together with the addition product **3c** in 35% yield (entry 3). With a lower amount of HTIB, the yield of **2c** is smaller. A similar pattern was also observed in Tl(III) reactions, where an excess of the oxidant increased the yield of the indane.[8] It is important to note that the diastereoselective synthesis of *trans*-1,3-disubstituted indanes is a difficult task in synthetic organic chemistry.[10] Compound **2c** is a synthetic intermediate in the synthesis of (±)–indatraline, which displays several interesting biological activities.[7] The presence of donating groups at the aromatic ring may facilitate the rearrangement of 1,2-dihydronaphthalenes by increasing the migratory aptitude of the migrating carbon.[8] Indeed, the oxidation of alkene **1d**, that bears an amide group *para* to the migrating carbon, with HTIB gave the desired acetal **2d** in much higher yield than the corresponding non-substituted substrate **1a**

Table 1. Oxidation of 1,2-dihydronaphthalenes with HTIB in MeOH

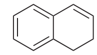
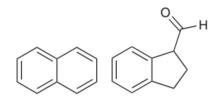
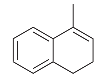
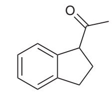
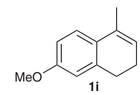
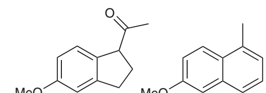
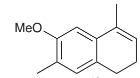
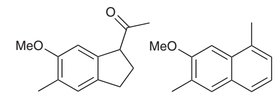
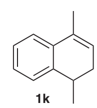
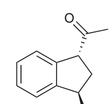
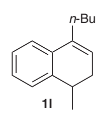
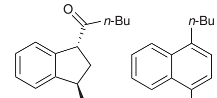
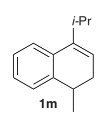
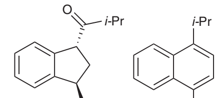
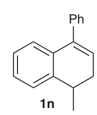
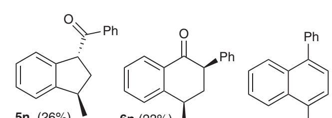
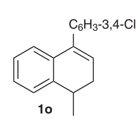
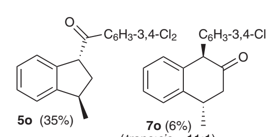
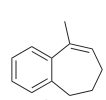
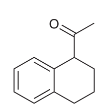
entry	Substrate	Product (yield)
1	 **1a**	 **2a** (36%); **3a** (*trans*: 28%) (*cis*: 14%)
2	 **1b**	 **2b** (55%); **3b** (12%) (*cis:trans* = 3:4)
3	 **1c**	 **2c** (62%); **3c** (35%) (*cis:trans* =1:4)
4	 **1d**	 **2d** (72%); **3d** (*trans*: 10%) (*cis*: 7%)
5	 **1e**	 **2e** (29%); **3e** (*trans*: 27%) (*cis*: 17%)
6	 **1f**	 **2f** (3%); **3f** (*trans*: 26%) (*cis*: 17%)
7	 **1g**	 **2g** (12%); **3g** (*trans*: 8%)
8	 **1h**	 **3h** (*trans*: 60%) (*cis*: 31%)

(entry 4). However, the treatment of alkene **1e** with HTIB gave indane **2e** in comparable yield to that obtained for the substrate **1a** (*cf.* entries 1 and 5). When HTIB was added to a methanol solution of substrates **1f-g**, which bear a methoxy group at the aromatic ring, the mixture immediately became black, leading to indanes **2f-g** in low yield (entries 6 and 7). Low yields in iodine(III)-mediated oxidation of methoxy-substituted substrates has also been observed by others.[11,12] Considering our experience in the oxidations of alkenes mediated by Tl(III),[9] we expected that the trisubstituted 1,2-dihydronaphthalene **1h** would have a different behavior toward HTIB from that of the disubstituted alkene **1a**. Indeed, when **1h** was treated with HTIB in MeOH only the addition product **3h** was isolated (entry 8). It is important to note that the acetal moiety in indanes like **2a**-**g** can be easily transformed without epimerization into the corresponding aldehyde.[2]

Ring contractions in acetonitrile

The conditions used by Kirschning and co-workers[6] in the oxidation of carbohydrates were also applied in the oxidation of 1,2-dihydronaphthalenes. Naphthalene (**4a**) was isolated in 30% yield when **1a** was treated with HTIB in CH_3CN (Table 2, entry 1). NMR analysis of the crude product indicates the presence of indane **5a** as a minor component, which decomposed during the purification step.[13] Similarly, **4a** was obtained in 48% yield when the reaction was performed in CH_2Cl_2, as solvent. However, when **1h** was treated with HTIB in CH_3CN indane **5h** was isolated in 51% yield (entry 2), which should be compared to exclusive formation of addition products in MeOH reactions (Table 1, entry 8). Ring contractions of epoxides can also be performed by treatment with Brønsted or Lewis acids.[4] However, compound **5h** can not be prepared in this manner, as no ring contraction product was obtained from the epoxide prepared from **1h**.[14-17] The oxidative rearrangement of other 4-alkyl-1,2-dihydronaphthalenes was also investigated. The reaction of alkenes **1i** and **1g**, which bear a methoxy group in the aromatic ring, with HTIB in CH_3CN furnished indanes **5i** and **5g**, respectively, in low yield (Table 2, entries 3 and 4), similarly to the disubstituted alkenes (Table 1, entries 6-7). Trisubstituted alkenes **1k-m** were transformed into indanes **5k-m**[13] in good yield (entries 5-7). Thus, the ring contraction is not precluded by the presence of bulky alkyl groups. The behavior of alkene **1n** is slightly different to that observed for other substrates. The reaction of **1n** with HTIB in CH_3CN led mainly to indane **5n** and ketone **6n**[18] in 26 and 23% yield, respectively. The tetralone **6n** is formed by migration of the phenyl group.[6] The reaction of **1n** with HTIB led to a nearly 1:1 mixture of the rearrangement products **5n** and **6n**, because the aromatic rings have similar migratory aptitude. In theory, if the migratory aptitude of the aromatic rings was different, the ratio of the rearrangement products could be modified. Indeed, when **1o**, which has two Cl atoms in one of the rings, was treated with HTIB, *trans*-indane **5o** was isolated and the product of migration of the $C_6H_3Cl_2$ group was not formed, because of the low migratory aptitude of $C_6H_3Cl_2$. However, a small amount of the tetralone **7o**, which is formed by migration of hydride,[13,16] was isolated (entry 9). Finally, we investigated the ring contraction in a seven-membered ring substrate. When alkene **1p** was treated with HTIB in CH_3CN, the substituted tetralin **5p** was obtained in good yield (entry 10). The ring contractions in CH_3CN were performed under inert atmosphere and in the presence of molecular sieves. When these conditions were

Table 2. Oxidation of 1,2-dihydronaphthalenes with HTIB in CH_3CN

entry	Substrate	Product (yield)
1	 **1a**	 **4a** (30%) **5a**[a]
2	 **1h**	 **5h** (51%)
3	 **1i**	 **5i** (12%) **4i**[b]
4	 **1j**	 **5j** (20%) **4j** (20%)
5	 **1k**	 **5k** (60%) (*trans:cis* = 10:1)
6	 **1l**	 **5l** (49%) (*trans:cis* = 10:1) **4l** (2%)
7	 **1m**	 **5m** (48%) (*trans:cis* = 5:1) **4m** (13%)
8	 **1n**	 **5n** (26%) **6n** (23%) (*cis:trans* 6:1) **4n** (4%)
9	 **1o**	 **5o** (35%) **7o** (6%) (*trans:cis* = 11:1)
10	 **1p**	 **5p** (52%)

[a]Yield not determined; [b]together with **1i**, *ca.* 20%.

not followed, lower yields were observed. The preparation of indanes analogues to **5** from 1,2-dihydronaphthalenes has been reported in a two-step protocol using NBS/water followed by reaction with Et_2Zn, which requires anhydrous conditions.[17]

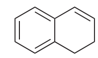
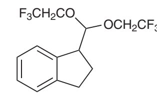
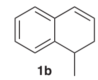
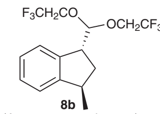
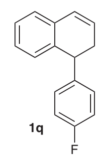
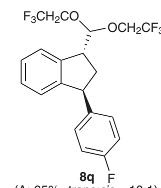
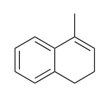
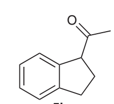
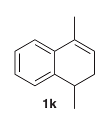
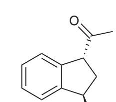
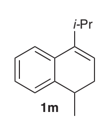
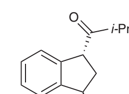
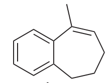
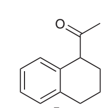
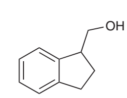
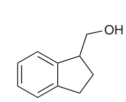
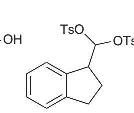
Ring contractions in fluorinated solvents

After investigating the oxidation of 1,2-dihydronaphthalenes with HTIB in methanol and in acetonitrile, we focused on the more polar solvents 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) because we envisioned that the formation of by products could be decreased performing the reaction in these high polar low nucleophilic solvents. Since the first report by Kita *et al.*,[19] the fluoroalcohols TFE[20] and HFIP[21] have been used as solvent in several reactions with hypervalent iodine compounds. However, TFE and HFIP have never been used in the oxidative rearrangement of alkenes.[5,6]

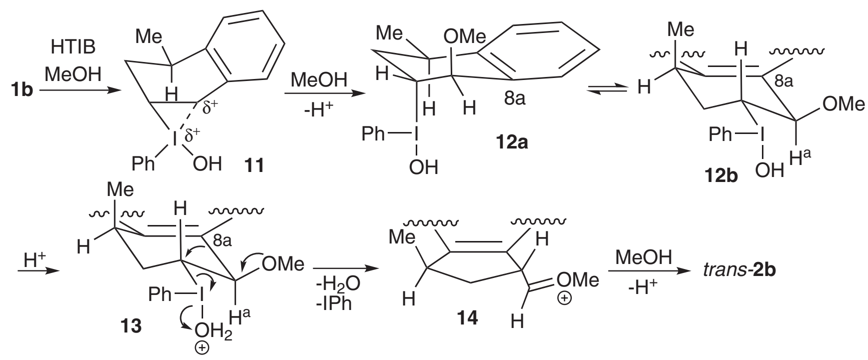
For the alkene **1a**, the yield of the desired product jumped from 36% (*cf.* entry 1, Table 1) to more than the double (73%, Table 3, entry 1). The reaction of **1b** with HTIB in TFE led to indane **8b** in higher yield than in MeOH (55% *vs.* 70%), although the diastereoselectivity is lower (entry 2 of Tables 1 and 3, respectively). The ring contraction of **1q** in TFE led to **8q** in 65% yield, as a 10:1 mixture of *trans*:*cis* diastereomers, respectively. Considering our previous work on the synthesis of 3-phenyl-1-indanamines,[7] the indane **8q** could be used as an intermediate in the synthesis of (±)-irindalone.[22] Moreover, this new method to obtain fluorinated acetals, which have different applications,[23] is more efficient than the previous described.[24-26] The oxidation of trisubstituted alkenes **1h** and **1p** with HTIB in TFE gave indanes **5h** and **5p**, respectively, in higher yield than using acetonitrile (*cf.* Table 2, entries 2 and 10 with entries 4 and 7 of Table 3). On the other hand, **1k** led to **5k** in lower yield and diastereoselectivity than in acetonitrile (entry 5 of Tables 2 and 3).

Although the HTIB-mediated oxidation of 1,2-dihydronaphthalenes in TFE led to the rearrangement products in higher yields than in other solvents, the diastereoselectivity is lower. Thus, several conditions were tested trying to optimize the diastereoselectivity, without decreasing the isolated yields. Eventually, this goal was achieved by performing the reaction in a 4:1 mixture of CH_2Cl_2:TFE as solvent. Although CH_2Cl_2 is the major component of the mixture, TFE must have a crucial role because the reaction of **1a** with HTIB in pure CH_2Cl_2 gave naphthalene (*cf.* entry 1, Table 2). The indane **8a** was obtained from **1a** in a yield comparable to the reaction in only TFE (73% *vs.* 67% yield, entry 1, Table 3). The alkene **1q** gave the indane **8q** in 69% yield, as a *trans*:*cis*

Table 3. Reaction of 1,2-dihydronaphthalenes with HTIB in fluoroalcohols[a]

Entry	Substrate	Product (isolated yield)
1	 **1a**	 **8a** (A: 73%) (B: 67%)
2	 **1b**	 **8b** (A: 70%, *trans:cis* = 5:1)
3	 **1q**	 **8q** (A: 65%, *trans:cis* = 10:1) (B: 69%, *trans:cis* = 17:1)
4	 **1h**	 **5h** (A: 72%)
5	 **1k**	 **5k** (A: 53%, *trans:cis* = 2:1) (B: 76%, *trans:cis* = 7:1)
6	 **1m**	 **5m** (B: 62%, *trans:cis* = 9:1)
7	 **1p**	 **5p** (A: 62%)
8	**1a**	**5a** (C: 58%)
9	**1a**	 **9a** (D: 34%)
10	**1a**	 **9a** (E: 48%)  **10a** (E: 17%)
11	**1a**	**9a** (F: 74%)

[a]A: TFE; B: 4:1 mixture of CH_2Cl_2/TFE; C: HFIP; D: *i*) HFIP, *ii*) $NaBH_4$; E: *i*) CH_2Cl_2:HFIP (4:1), *ii*) $NaBH_4$; F: *i*) 22 equiv. H_2O, CH_2Cl_2:HFIP (4:1), *ii*) $NaBH_4$.



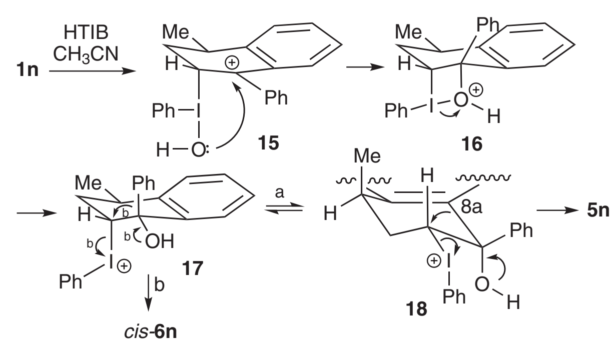
Scheme 1. Mechanism for the ring contraction of **1b** in MeOH.

ratio of 17:1, i.e., in better yield and selectivity than using only TFE (entry 3, Table 3). The reaction in CH_2Cl_2/TFE is also appropriate for trisubstituted alkenes. Ketones **5k** and **5m** were obtained in higher yield than in acetonitrile or in TFE. Furthermore, the diastereoselectivity is higher than in TFE and comparable to the reaction in acetonitrile (*cf.* entries 5 and 7 of Table 2 and entries 5 and 6 of Table 3). In summary, treatment of 1,2-dihydronaphthalenes with HTIB in TFE or in CH_2Cl_2/TFE gave the desired indanes in higher yields than using MeOH or CH_3CN for either di- or trisubstituted double bonds.

Considering the very good results with TFE, the obvious extension would be the study of the reaction in the even more polar solvent HFIP. The oxidation of alkene **1a** in HFIP was very fast and led to indane **5a**. The yield of the ring contraction product was, however, lower than in TFE (*cf.* entries 1 and 8, Table 3). In the presence of the bulky and low nucleophilic solvent HFIP an aldehyde (**5a**) is isolated instead of acetals, as in MeOH or in TFE (**2a** and **8a**). Aldehyde **5a** is not very convenient for manipulation and storage because it decomposes. We thus investigated if **5a** could be reduced *in situ*, giving a stable alcohol. The reaction of **1a** with HTIB in HFIP followed by addition of $NaBH_4$ gave the desired alcohol **9a** in only 34% yield (entry 9). Changing the solvent to a mixture of CH_2Cl_2:HFIP (4:1), the alcohol **9a** was isolated in better yield, however together with the gem ditosylate **10a**[6] in 17% yield (entry 10). We envisioned that the addition of H_2O could favor the formation of **9a**, avoiding the undesired product **10a**. Indeed, a smooth ring contraction/reduction was observed when **1a** was treated with HTIB in the presence of H_2O in CH_2Cl_2/HFIP (4:1) as solvent, followed by addition of $NaBH_4$, giving **9a** in 74% isolated yield (entry 11).

Mechanism discussion

The exclusive formation of *trans*-1,3-disubstituted indanes in the ring contractions in methanol can be explained by the mechanism detailed below. The electrophilic *anti*-addition of HTIB to the double bond would lead to **12a**, through the cyclic organoiodine intermediate **11**. The approach of the electrophile occurs opposite to the remote methyl group,[27-29] explaining the stereoselectivity of this ring contraction, as well as of the other reactions discussed below. The adduct **12a** would equilibrate to its more stable conformational isomer **12b**, on which the required *anti*-periplanarity for the rearrangement is achieved. Migration of the aryl group (carbon 8a) on **13** would displace PhI giving the oxonium **14**, which would furnish the *trans*-indane **2b** after addition of MeOH (Scheme 1). The diastereoselective formation of the *trans* products in ring contractions in TFE or in CH_2Cl_2/TFE can be explained by similar mechanisms. However, considering the anhydrous conditions of the ring contraction in CH_3CN, the mechanism is probably different, as shown in Scheme 2 for **1n**. The stereoselective electrophilic addition of HTIB to the alkene **1n** would give the *bis*-benzylic carbocation **15**. The hydroxyl group would attack the C1 position of **15**, giving the four-membered ring intermediate **16**,[6] which would ring open to form **17**. The ring contraction would take place on its conformer (**18**) giving *trans*-**5n** (path a, Scheme 2). The solvent may have some influence in the stereoselectivity of the electrophilic addition of the iodine(III), explaining the formation of

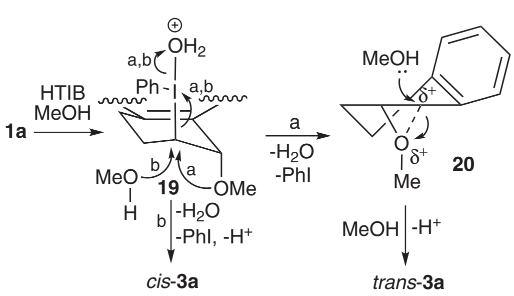


Scheme 2. Rearrangements of **1n** in CH_3CN.

cis-1,3-disubstituted indanes. Alternatively, the *cis* indanes can be formed by epimerization of the ketone moiety of the corresponding *trans* isomers. Starting from trisubstituted double bonds, the ring contraction lead to ketones which are always obtained as a free carbonyl. Aldehydes are formed from disubstituted alkenes. In the presence of a nucleophilic solvent, such as MeOH or TFE, acetals were isolated. On the other hand, free aldehydes were obtained in CH_3CN or in HFIP.

The formation of the *cis*-2,4-disubstituted-1-tetralone **6n** can be explained by the mechanism shown in path b of Scheme 2. The Ph group would migrate on intermediate **17**, with the exit of PhI, leading to *cis*-**6n**. *trans*-**6n** can be formed either by isomerization of *cis*-isomer or the addition of I(III) to **1n** could take place by the other face. In acetonitrile oxidations, small amounts of naphthalenes were isolated in some reactions, which are formed by addition followed by elimination.[13]

A plausible mechanism to explain the formation of the products of addition of MeOH is shown in Scheme 3, using substrate **1a** as example.[6,8] The methoxy group of **19** would intramolecularly displace PhI, giving the oxonium **20**. Methanol would attack the C1 benzylic position of **20**, furnishing *trans*-**3a** (path a). Alternatively, the intermolecular displacement of PhI by MeOH in the intermediate **19** would lead to *cis*-**3a** (path b). The preferential formation of the *trans* isomers (Table 1) indicates that the intramolecular process is favored. The formation of *cis*- and *trans*-isomers has also been observed in the reaction of indene with iodosobenzene derivatives in methanol.[30] However, the oxidation of cyclohexenes with iodine(III) led to rearrangement products,[6] *cis*-isomers[6,31-33] or *trans*-isomers,[31,34] depending mainly on the reaction conditions.



Scheme 3. Mechanism for the formation of addition products **3a**.

As described above, the solvent has a crucial role in the oxidation of 1,2-dihydronaphthalenes with HTIB. In methanol, ring contraction is favored toward the addition of solvent for disubstituted double bonds. However, for trisubstituted substrates, the nucleophilic attack of MeOH is faster, probably because the required conformations for the rearrangements are disfavored with an additional methyl group (**12b** and **13** with Me instead H^a in Scheme 1). In anhydrous acetonitrile, there is no good nucleophile and ring contraction of trisubstituted alkenes occurs through the formation of a tertiary benzylic carbocation (like **15**). For disubstituted double bonds, the ring contraction would occur through a less favored secondary benzylic carbocation and, thus, the formation of naphthalenes predominates. In TFE or in CH_2Cl_2/TFE, ring contraction was observed for either di- or trisubstituted 1,2-dihydronaphthalenes. The mechanism described for MeOH is the major pathway, as acetals are isolated for disubstituted alkenes. Ring contraction also takes place with trisubstituted substrates, because a less nucleophilic species is present, making the formation of addition products more difficult.

Conclusions

A one-step, fast, mild and metal-free protocol was developed for the synthesis of indanes through ring contraction of readily available 1,2-dihydronaphthalenes mediated by HTIB. This oxidative rearrangement is diastereoselective giving 1,3-*trans*-disubstituted indanes preferentially or exclusively. The developed methodology facilitates the access to this structural motif, which is difficult to construct. Moreover, indanes bearing different functional groups can be easily obtained by changing the reaction conditions. In summary, the protocol herein presented will be useful in synthetic organic chemistry and in medicinal chemistry to access functionalized indanes in an expeditious manner. The protocol represents a green alternative to the analogous reaction using toxic thallium(III) salts.[8,9,13,35,36]

Experimental

General procedure

Synthesis of 4-(4-fluorophenyl)-3,4-dihydronaphthalen-1(2H)-one

To a dry round bottom flask under nitrogen atmosphere, $AlCl_3$ (7.8 g, 59 mmol) was added followed by the addition of fluorobenzene (10.8 mL, 11.1 g, 115 mmol). After cooling the flask to 0 °C, 1-naftol (3.0 g, 20.8 mmol) was added portion-wise under strong stirring (cake forms). After the addition, the flask was charged with a condenser and stirred at 75 °C for 1.5 h. The reaction was again cooled to 0 °C and quenched by adding ice through the condenser (strongly exothermic), until no gas evolution could be observed. The reaction mixture was extracted with CH_2Cl_2 (3 × 25 mL), the organics washed with 1 mol L^{-1} NaOH

(2 × 20 mL) and brine, dried with Na_2SO_4, filtered and concentrated to give a thick brown oil (5.48 g). The crude oil was purified by column chromatography (10% Et_2O in hexane), where the *o*-isomer elutes first followed by the *m*- and *p*-isomers. As the *m*- and *p*-isomers have the same R_f value, the mixed fractions were checked by GC to collect fractions with pure *p*-product 4-(4-fluorophenyl)-3,4-dihydronaphthalen-1(2*H*)-one[37] (1.14 g, 4.75 mmol, 23%).

*Synthesis of 1-(4-fluorophenyl)-1,2-dihydronaphthalene (**1c**)*

4-(4-fluorophenyl)-3,4-dihydronaphthalen-1(2*H*)-one (806 µL, 3.36 mmol) was added to a round bottom flask, diluted with MeOH (25 mL) followed by cooling to 0 °C and addition of $NaBH_4$ (140 mg, 3.68 mmol). The reaction was quenched with H_2O after 1 h and adjusted to pH 5 with 10% HCl. After evaporation of the MeOH, the aqueous phase was extracted with EtOAc (3 × 15 mL), followed by the washing of the organics with brine, dried with Na_2SO_4, filtered and concentrated to give a crude yellow oil of 4-(4-fluorophenyl)-1,2,3,4-tetrahydronaphthalen-1-ol (928 mg), which was used in the next step without any further purification. The crude tetralol (928 mg) was added to a dry round bottom flask, followed by dry toluene (20 mL) and a few crystals of *p*-TsOH (cat.). The flask was equipped with a dean-stark trap and refluxed until no alcohol remained according to TLC (*ca.* 1.5 h). The reaction was quenched with a saturated $NaHCO_3$ solution and diluted with EtOAc. The organic phase was washed with saturated $NaHCO_3$ (2 × 15 mL), brine (2 × 15 mL), dried with Na_2SO_4, filtered and concentrated to give a crude brown oil (761 mg). It was purified by column chromatography (hexane) to afford **1c** as colorless oil (728 mg, 3.25 mmol, 97% over 2 steps); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 (dddd, 1H, *J* 13.8, 9.7, 4.2 and 2.0 Hz), 2.67 (dddd, 1H, *J* 12.1, 7.4, 4.6 and 1.8 Hz), 4.12 (dd, 1H, *J* 9.3 and 7.7 Hz), 5.99 (dt, 1H, *J* 9.6 and 4.4 Hz), 6.55 (dt, 1H, *J* 9.6 and 1.5 Hz), 6.81 (d, 1H, *J* 7.7 Hz), 7.03-6.95 (m, 2H), 7.14-7.07 (m, 2H), 7.22-7.14 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.2, 43.2, 115.3 (d, *J* 21 Hz), 126.4, 127.1, 127.1, 127.5, 127.9, 128.2, 129.9 (d, *J* 8 Hz), 134.2, 137.8, 140.3 (d, *J* 3 Hz), 161.7 (d, *J* 245 Hz); HRMS (*m/z*) calcd. for $C_{16}H_{13}F$ 247.0893 [M + Na]$^+$, found 247.0901.

*Reaction of 1,2-dihydro-6-methoxynaphthalene (**1f**) with HTIB in MeOH*

To a solution of **1f** (0.328 g, 2.05 mmol) in MeOH (8 mL) was added HTIB (0.941 g, 2.40 mmol) at 0 °C. Immediately after addition of HTIB the reaction became dark. The mixture was stirred at room temperature for 1 h. The reaction was extracted with EtOAc, washed with H_2O, with brine, and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The crude product was purified by column (0-25% EtOAc in hexane), affording **2f**[9] (0.0137 g, 0.0616 mmol, 3%), as colorless oil, *trans*-**3f**[9] (0.117 g, 0.526 mmol, 26%) and *cis*-**3f** (0.0779 g, 0.350 mmol, 17%), both as yellow oils. *cis*-1,2,3,4-Tetrahydro-1,2,7-trimethoxynaphthalene (**3f**): colorless oil; IR ν_{max}/cm^{-1} (film) 1101, 1249, 1499, 2834, 2933; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.91-1.94 (m, 1H), 2.16-2.23 (m, 1H), 2.67-2.74 (m, 1H), 2.92-2.96 (m, 1H), 3.47 (s, 3H), 3.50 (m, 3H,), 3.61-3.69 (m, 1H), 3.79 (s, 3H), 4.30 (d, 1H, *J* 3.1 Hz), 6.80 (dd, 1H, *J* 8.3, 2.6 Hz), 6.86 (d, 1H, *J* 2.6 Hz), 7.04 (d, 1H, *J* 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.7, 26.1, 55.3, 56.5, 57.4, 77.9, 78.2, 114.3, 114.4, 128.5, 129.7, 135.7, 157.5; LRMS (*m/z*, %) 222 ($M^{+\bullet}$, 17), 191 (7), 190 (52); 189 (9), 164 (100); HRMS (*m/z*) calcd. for $C_{13}H_{18}O_3$ [M + Na]$^+$ 245.1148, found 245.1141.

*Reaction of 1,2-dihydro-6,7-dimethoxynaphthalene (**1g**) with HTIB in MeOH*

As **1f**, but using **1g** (0.0744 g, 0.391 mmol), HTIB (0.153 g, 0.391 mmol), and MeOH (2.0 mL). The reaction was stirred for 1 h at 0 ºC. The crude product was purified by column (0-30% EtOAc in hexane), affording **2g**[8] (0.0116 g, 0.0460 mmol, 12%) and *trans*-**3g** (0.0080 g, 0.032 mmol, 8%), both as a colorless oil. *trans*-1,2,3,4-Tetrahydro-1,2,6,7-tetramethoxynaphthalene (**3g**): colorless oil; IR ν_{max}/cm^{-1} (film) 1121, 1258, 1515, 2830, 2934; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.88-1.97 (m, 1H), 2.05-2.15 (m, 1H), 2.62-2.82 (m, 2H), 3.44 (s, 3H), 3.51 (s, 3H), 3.71 (ddd, 1H, *J* 7.2, 4.8, 2.7 Hz), 3.84 (s, 3H), 3.87 (3H, s), 4.21 (d, 1H, *J* 4.8 Hz), 6.58 (1H), 6.83 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.4, 25.1, 55.9, 56.0, 56.7, 57.2, 77.2, 79.5, 111.1, 112.4, 126.5, 129.3, 147.5, 148.7; HRMS (*m/z*) calcd. for $C_{14}H_{20}O_4$ [M + Na]$^+$ 275.1254, found 275.1252.

*Synthesis of 1-(dimethoxymethyl)-5-acetamido-indane (**2d**)*

To a stirred mixture of **1d** (0.254 g, 1.36 mmol) and MeOH (27 mL), was added HTIB (0.590 g, 1.50 mmol) at once at 0 °C. After 35 min the reaction was quenched with saturated solution of $NaHCO_3$. The aqueous phase was extracted with EtOAc (3 × 10 mL), washed with brine (2 × 10 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The crude product was purified by column (hexane:EtOAc, 3:7) giving **2d** (72%, 0.244 g, 0.98 mmol) as a yellow solid, *trans*-**3d** (10%, 0.035 g, 0.14 mmol) as a solid and *cis*-**3d** (7%, 0.025 g, 0.10 mmol) as a solid. 1-(Dimethoxymethyl)-5-acetamido-indane (**2d**): mp 68.4-69.3 ºC; IR ν_{max}/cm^{-1} (film) 828, 1058, 1124, 1372, 1426, 1492, 1546, 1602, 1667; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.85-2.28 (m, 3H), 2.13 (s, 3H), 2.70-2.90 (m, 2H), 3.37 (s, 3H), 3.41 (s, 3H), 4.27 (d, 1H, *J* 7.4 Hz), 7.16 (dd, 1H, *J* 1.4, 8.2 Hz), 7.32 (d, 1H, *J* 8.0 Hz), 7.46 (s, 1H), 7.84 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.3, 27.5, 31.4, 47.0, 52.9, 54.2, 107.2, 116.4, 118.2, 125.6, 136.8, 138.7, 145.6, 168.6; LRMS (*m/z*, %) 249 ($M^{+\bullet}$, 2.4%), 218 (6), 186 (3), 174 (4), 144 (6), 132 (13), 115 (5), 103 (3), 75 (100); HRMS (*m/z*) calcd. for $C_{14}H_{19}NO_3$ [M + H]$^+$ 250.1438, found 250.1440. *N*-(*trans*-5,6-dimethoxy-5,6,7,8-tetrahydronaphthalen-2-yl)acetamide (*trans*-**3d**): mp 108.7-110.5 °C; IR ν_{max}/cm^{-1} (film) 830, 915, 1091, 1331, 1372, 1419, 1505, 1544, 1598, 1614, 1671, 2934, 3302, 3507; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.81-2.18 (m, 2H), 2.13 (s, 3H), 2.58-2.90 (m, 2H), 3.44 (s, 3H), 3.48 (s, 3H), 3.67-3.74 (m, 1H) 4.21 (d, 1H, *J* 4.8 Hz), 7.21-7.27 (m, 2H), 7.34 (s, 1H), 7.56 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.3, 24.5, 25.5, 56.5, 57.3, 77.8, 79.2, 117.5, 119.4, 130.5, 130.6, 137.3, 137.9, 168.3; LRMS (*m/z*, %) 249 ($M^{+\bullet}$, 23%), 217 (27), 191 (100); HRMS (*m/z*) calcd. for $C_{14}H_{19}NO_3$ [M + Na]$^+$ 272.1257, found 272.1262. *N*-(*cis*-5,6-dimethoxy-5,6,7,8-tetrahydronaphthalen-2-yl) acetamide (*cis*-**3d**): IR ν_{max}/cm^{-1} (film) 817, 882, 1081, 1106, 1372, 1419, 1505, 1544, 1602, 1614, 1671, 2933, 3311, 3509; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.86-2.30 (m, 2H), 2.16 (s, 3H), 2.68-3.07 (m, 2H), 3.45 (s, 3H), 3.47 (s, 3H), 3.57-3.67 (m, 1H), 4.32 (d, 1H, *J* 2.8 Hz), 7.25-7.34 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.3, 24.6, 27.3, 56.4, 57.1, 77.5, 78.2, 117.1, 119.8, 130.5, 130.6, 137.6, 137.7, 168.3.; LRMS (*m/z*, %) 249 ($M^{+\bullet}$, 21%), 217 (28), 191 (100); HRMS (*m/z*) calcd. for $C_{14}H_{19}NO_3$ [M + Na]$^+$ 272.1257, found 272.1260.

*Syntheses of cis and trans-1-(2,3)-dihydro-1-metyl-1H-inden-3-yl)pentan-1-one (**5l**)*

To a solution of **1l** (0.129 g, 0.647 mmol) and molecular sieves (3 Å, 0.065 g) in anhydrous CH_3CN (6.5 mL) under N_2 was added HTIB (0.489 g, 1.25 mmol) at 0 °C. The reaction was stirred for 15 min at 0 °C. A saturated solution of $NaHCO_3$ was added until pH 7. The organic phase was washed with H_2O, with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The crude product was purified by column (0-10% EtOAc in hexane), affording **5l** (0.0681 g, 0.315 mmol, 49%) as a *trans*:*cis* (10:1) mixture. Naphthalene **4l**[9] (0.0031 g, 0.016 mmol, 2%) was also isolated as a colorless oil. *cis* and *trans*-**5l**: yellow oil; IR ν_{max}/cm^{-1} (film) 755, 1460, 1711, 2870, 2931, 2959; ^{1}H NMR (300 MHz, $CDCl_3$) δ (*trans* isomer) 0.87 (t, 3H, *J* 7.3 Hz), 1.21-1.25 (m, 1H), 1.28 (d, 3H, *J* 6.9 Hz), 1.51-1.56 (m, 2H), 2.41-2.62 (m, 3H), 3.40 (sext, 1H, *J* 6.8 Hz), 4.08 (dd, 1H, *J* 8.7, 3.4 Hz), 7.14-7.28 (m, 4H), (*cis* isomer) 0.91 (t, 3H, *J* 7.5 Hz), 1.35 (d, 3H, *J* 6.9 Hz), 1.81-1.85 (m, 2H), 3.21 (sext, 1H, *J* 7.2 Hz) (other signals overlap with the *trans* form); ^{13}C NMR (75 MHz, $CDCl_3$) δ (*trans* isomer) 13.8, 20.2, 22.3, 25.8, 37.8, 38.5, 40.1, 57.0, 123.8, 124.7, 126.6, 127.6, 140.7, 149.3, 210.8, (*cis* isomer) 13.9, 19.7, 22.4, 25.9, 38.3, 40.8, 123.5, 124.6, 127.4, 141.0, 148.8, 211.3 (other signals overlap with the *trans* form); LRMS (*m/z*, %) 216 ($M^{+\bullet}$, 5), 131 (100); HRMS (*m/z*) calcd. for $C_{15}H_{20}O$ [M + H]$^+$ 217.1587, found 217.1586.

*Reaction of 4-isopropyl-1-methyl-1,2-dihydronaphthalene (**1m**) with HTIB in CH_3CN*

The typical procedure for reactions in CH_3CN was followed, but using **5m** (0.187 g, 1.00 mmol). The crude product was purified by flash column chromatography (gradient elution, 0-20% EtOAc in hexanes), affording indane **5m** (0.0981 g, 0.485 mmol, 48%)[13] as a *trans*:*cis* (5:1 by ^{1}H NMR after purification) mixture, as yellow oil. Naphthalene **4m** (0.0244 g, 0.132 mmol, 13%)[38] was also isolated as colorless oil.

*Reaction of 1,2-dihydro-7-methoxy-4-methylnaphthalene (**1i**) with HTIB in CH_3CN*

To a solution of **1i** (0.178 g, 1.02 mmol) and molecular sieves (3 Å, 0.100 g) in CH_3CN (10 mL) under N_2 was added HTIB (0.442 g, 1.13 mmol) at 0 °C. The ice bath was removed. The mixture was stirred for 15 min at room temperature. A saturated solution of $NaHCO_3$ was added until pH 7. The organic phase was washed with H_2O, with brine and dried over anhydous $MgSO_4$. The solvent was removed under reduced pressure. The crude product was purified by column (0-40% EtOAc in hexane), affording **5i**[39] (0.0231 g, 0.121 mmol, 12%), as a yellow oil and a mixture 1:1 of **4i**[40] and starting material (0.0361 g), as a colorless oil.

*Reaction of 1,2-dihydro-6-methoxy-4,7-dimethynaphthalene (**1j**) with HTIB in CH_3CN*

As for **1i**, but using **1j** (0.197 g, 1.05 mmol), molecular sieves (3 Å, 0.100 g), HTIB (0.489 g, 1.25 mmol), CH_3CN (10 mL). The mixture was stirred for 30 min at room temperature. The crude product was purified by column (0-40% EtOAc in hexane) affording **5j**[8] (0.0420 g, 0.204 mmol, 20%) and impure **4j** (0.0594 g). Impure **4j** was purified by column (10% EtOAc in hexane), affording **4j**[41] (0.0381 g, 0.205 mmol, 20%).

*Reaction of 1,2-dihydro-1-methyl-4-phenylnaphthalene (**1n**) with HTIB in CH_3CN*

As for **5l**, but using **1n** (0.165 g, 0.750 mmol), molecular sieves (3 Å, 0.0750 g), HTIB (0.353 g, 0.901 mmol), and

CH_3CN (7.5 mL). The mixture was stirred for 20 min at room temperature. The product crude was purified by column (0-10% EtOAc in hexane) affording **5n** (0.0452 g, 0.191 mmol, 26%),[13] and **6n** (0.0414 g, 0.175 mmol, 23%),[18] as yellow oil and as a *cis*:*trans* mixture (6:1). **4n** (7.00 mg, 0.0321 mmol, 4%)[42] was isolated, as a colorless oil.

*Reaction of 4-(3,4-dichlorophenyl)-1-methyl-1,2-dihydronaphthalene (**1o**) with HTIB in CH_3CN*

As for **1i**, but using **1o** (0.118 g, 0.408 mmol), molecular sieves (3 Å, 0.0413 g), HTIB (0.194 g, 0.495 mmol), and CH_3CN (4.0 mL). The mixture was stirred for 20 min at room temperature. The product was purified by column (0-30% EtOAc in hexane) affording **5o** (0.0430 g, 0.141 mmol, 35%) and **7o** (0.0070 g, 0.023 mmol, 6%), both as a yellow oil. *trans*-(3,4-Dichlorophenyl)-2,3-dihydro-1-methyl-1*H*-inden-3-yl)methanone (**5o**): IR ν_{max}/cm^{-1} (film) 755, 1030, 1206, 1687, 2867, 2925, 2958; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (d, 3H, *J* 6.9 Hz), 2.0.2 (ddd, 1H, *J* 12.8, 7.6, 8.7 Hz), 2.68 (ddd, 1H, *J* 12.5, 7.8, 4.0 Hz), 3.49 (sext, 1H, *J* 7.2 Hz), 4.95 (dd, 1H, *J* 8.8, 3.9 Hz), 7.04 (d, 1H, *J* 7.5 Hz), 7.11-7.14 (m, 1H), 7.24-7.25 (m, 2H), 7.59 (d, 1H, *J* 8.4 Hz), 7.86 (dd, 1H, *J* 8.3, 2.0 Hz), 8.11 (d, 1H, *J* 2.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.4, 38.4, 38.5, 51.3, 124.0, 124.0, 126.6, 127.9, 127.9, 130.8, 130.8, 133.5, 136.4, 137.7, 140.0, 149.4, 198.2; LRMS (*m/z*, %) 305 ($M^{+\bullet}$, 1%), 131 (100); HRMS (*m/z*) calcd. for $C_{17}H_{14}Cl_2O$ $[M + H]^+$ 305.0494, found 305.0486. 1-(3,4-Dichlorophenyl)-3,4-dihydro-4-methylnaphthalen-2(1*H*)-one (**7o**): IR ν_{max}/cm^{-1} (film) 755, 1030, 1206, 1687, 2867, 2925, 2958; 760, 1031, 1175, 1380, 1467, 1722, 2928, 2963; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31 (dd, 1H, *J* 16.8, 7.5 Hz), 2.98 (dd, 1H, *J* 16.8, 6.6 Hz), 3.12 (sext, 1H, *J* 6.9 Hz), 4.77 (s, 1H), 6.88 (dd, 1H, *J* 8.4, 2.4 Hz), 7.16 (d, 1H, *J* 2.1 Hz), 7.30-7.47 (m, 4H), 7.62-7.71 (m, 1H,); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.1, 32.5, 41.8, 54.2, 125.5, 126.5, 127.5, 127.8, 128.9, 129.2, 130.6, 132.8, 133.9, 137.2, 140.2, 141.1, 208.8; HRMS (*m/z*) calcd. for $C_{17}H_{14}Cl_2O$ $[M + H]^+$ 305.0494, found 305.0486.

*Reaction of 9-methyl-6,7-dihydro-5H-benzo[7]annulene (**1p**) with HTIB in CH_3CN*

The typical procedure for reactions in CH_3CN was followed, but using **1p** (0.0416 g, 0.263 mmol), molecular sieves (3 Å, 0.0179 g), HTIB (0.118 g, 0.301 mmol) in anhydrous CH_3CN (2.5 mL). The mixture was stirred for 15 min at room temperature. The crude product was purified by flash column chromatography (15% EtOAc in hexanes) affording **5p**[43] (0.0241 g, 0.138 mmol, 52%), as a colorless oil.

*Synthesis of 1-[bis(trifluoromethoxy)methyl]-2,3-dihydro-1H-indene (**8a**)*

To a stirred mixture of **1a** (0.102 g, 0.78 mmol) and TFE (6 mL), was added HTIB (0.34 g, 0.86 mmol) at once at 0 °C. After 30 min the reaction was quenched with saturated solution of $NaHCO_3$ until pH 7. The aqueous phase was extracted with EtOAc (3 × 10 mL), washed with brine (2 × 10 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The crude product was purified by column (hexane:EtOAc, 9:1) giving **8a** (73%, 0.19 g, 0.57 mmol) as a light yellow oil; IR ν_{max}/cm^{-1} (film) 2949, 2855, 1460, 1281, 1164, 1078; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.96-2.08 (m, 1H), 2.18-2.30 (m, 1H), 2.82-3.03 (m, 2H), 3.47 (q, 1H, *J* 7.9 Hz), 3.86-4.07 (m, 4H), 4.70 (d, 1H, *J* 7.9 Hz), 7.15-7.24 (m, 3H), 7.38-7.41 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.1, 31.2, 47.2, 61.9 (q, *J* 34.9 Hz), 63.4 (q, *J* 34.9 Hz), 105.4, 123.7 (q, *J* 276 Hz), 123.8 (q, *J* 276 Hz), 124.6, 125.5, 126.5, 127.6, 140.8, 144.6; LRMS (*m/z*, %) 328 ($M^{+\bullet}$, 1.3%), 211 (70), 129 (21), 117 (100); HRMS (*m/z*) calcd. for $C_{14}H_{14}F_6O_2$ $[M + Na]^+$ 351.0790, found 351.0801.

*Synthesis of 1-[bis(trifluoromethoxy)methyl]-2,3-dihydro-3-methyl-1H-indene (**8b**)*

As for **1a**, but using **1b** (0.146 g, 1.01 mmol). HTIB was added at once. The reaction was quenched after 7 min. Compound **8b** was obtained as a yellow oil (70%, 0.243 g, 0.710 mmol) as a 5:1 *trans*:*cis* mixture; IR ν_{max}/cm^{-1} (film) 2961, 2932, 2872, 1458, 1281, 1174, 1078, 758; ^{1}H NMR (300 MHz, $CDCl_3$) δ (*trans* isomer) 1.27 (d, 3H, *J* 6.9 Hz), 1.81 (ddd, 1H, *J* 13.2, 8.5, 7.3 Hz), 2.32 (ddd, 1H, *J* 13.2, 7.8, 4.2 Hz), 3.22-3.34 (m, 1H), 3.43-3.50 (m, 1H), 3.82-4.06 (m, 4H), 4.64 (d, 1H, *J* 8.1 Hz), 7.18-7.36 (m, 4H), (*cis* isomer) 1.33 (d, 3H, *J* 6.9 Hz), 2.40-2.55 (m, 1H), 4.75 (d, 1H, *J* 8.4 Hz), 7.08-7.13 (m, 1H), 7.41-7.44 (m, 1H), 7.68-7.72 (m, 1H) (other signals overlap with the *trans* form); ^{13}C NMR (75 MHz, $CDCl_3$) δ (*trans* isomer) 20.5, 35.9, 37.6, 46.0, 61.6 (q, *J* 34.7 Hz), 63.8 (q, *J* 34.7 Hz), 105.1, 123.5, 123.6 (q, *J* 276 Hz), 123.8 (q, *J* 276 Hz), 125.8, 126.6, 127.8, 140.3, 149.2, (*cis* isomer) 19.7, 36.9, 37.7, 45.6, 105.7, 123.3, 124.8, 126.7, 127.6, 130.2, 137.5 (other signals overlap with the *trans* form); LRMS (*m/z*, %) (major diastereomer) 242 ($M^{+\bullet}$ - CF_3CH_2OH, 17%), 211 (69), 131 (100), (minor diastereomer) 342 ($M^{+\bullet}$, 3%), 242 (9), 211 (75), 131 (100); HRMS (*m/z*) calcd. for $C_{15}H_{16}F_6O_2$ $[M + Na]^+$ 365.0947, found 365.0960.

*Synthesis of 1-(2,3-dihydro-1H-inden-3-yl)ethanone (**5h**)*

As for **1a**, but using **1h** (0.158 g, 1.10 mmol). The reaction was quenched after 30 min. The crude product was purified by column (5-10% EtOAc in hexane) affording **5h**[7] (72%, 0.127 g, 0.791 mmol), as a light yellow oil.

*Synthesis of 1-(1,2,3,4-tetrahydronaphthalene-4-yl) ethanone (**5p**)*

As for **1a**, but using **1p** (0.158 g, 1.00 mmol). The reaction was quenched after 20 min. The crude product was purified using column (hexane:EtOAc, 9:1) giving **5p**[13] (62%, 0.107 g, 0.62 mmol), as a light yellow oil.

*Synthesis of 1-(bis(2,2,2-trifluoroethoxy)methyl)-3-(4-fluorophenyl)-2,3-dihydro-1H-indene (**8q**)*

A dry round bottom flask was charged with **1q** (240 mg, 1.07 mmol), CH_2Cl_2/TFE (4:1 v/v) followed by HTIB (550 mg, 1.40 mmol) at room temperature. The reaction color changed towards yellow within a minute. After 10 min at room temperature, the reaction was quenched with H_2O, washed with H_2O (2 × 20 mL), with 50% $NaHCO_3$ solution (2 × 20 mL), with H_2O (20 mL), with brine (2 × 20 mL), dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under reduced pressure to give a brownish oil. The crude product was purified by column (0-25% EtOAc in hexane) giving **8q** (312 mg, 0.739 mmol, 69%), as a *trans*:*cis* (17:1) mixture as colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ (*trans* isomer) 2.18 (ddd, 1H, 13.5, 8.5, 7.7 Hz), 2.60 (ddd, 1H, *J* 13,5, 8.2, 4.2 Hz), 3.58 (dt, 1H, *J* 8.2, 4.2 Hz), 4.11-3.80 (m, 4H), 4.43 (t, 1H, *J* 8.0 Hz), 4.74 (d, 1H, *J* 7.9 Hz), 7.03-6.93 (m, 3H), 7.10-7.03 (m, 2H), 7.29-7.20 (m, 2H), 7.47-7.39 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (*trans* isomer) 38.0, 46.5, 49.2, 62.0 (q, *J* 35 Hz), 64.1 (q, *J* 35 Hz), 105.3, 115.5 (d, *J* 21 Hz), 123.8 (q, *J* 278 Hz), 123.9 (q, *J* 278 Hz), 125.4, 126.0, 127.4, 128.3, 129.5 (d, *J* 8 Hz), 140.8 (d, *J* 3 Hz), 141.2, 147.2, 161.8 (d, *J* 245 Hz); HRMS (*m/z*) calcd. for $C_{20}H_{17}F_7O_2$ $[M + Na]^+$ 445.1009, found 445.1017.

*Synthesis of 1-(bis(2,2,2-trifluoroethoxy)methyl)-2,3-dihydro-1H-indene (**8a**)*

As for **1q**, but using **1a** (0.130 g, 1.00 mmol). HTIB (0.510 g, 1.30 mmol) was added at 0 °C. The reaction was stirred for 10 min at room temperature. The crude product was purified by column (1-10% EtOAc in hexane) affording **8a** (67%, 0.221 g, 0.673 mmol), as a yellow oil.

*Synthesis of 1-(2,3-dihydro-1-methyl-1H-inden-3-yl) ethanone (**5k**)*

As for **1q**, but using **1k** (0.158 g, 1.00 mmol). HTIB (1.3 equiv.) was added at 0 °C. The reaction was stirred for 10 min at room temperature. The crude product was purified by column (1-20% EtOAc in hexane) affording **5k**[7] (76%, 0.132 g, 0.758 mmol), as a light yellow oil.

*Synthesis of 1-(2,3-dihydro-1-methyl-1H-inden-3-yl)-2-methylpropan-1-one (**5m**)*

As for **1q**, but using **1m** (0.108 g, 0.580 mmol). HTIB (1.3 equiv.) was added at 0 °C and the reaction was quenched after 2 min at 0 °C. The crude product was purified by column (2-30% EtOAc in hexane) affording **5m**[13] (62%, 0.073 g, 0.359 mmol), as a light yellow oil.

*Synthesis of 2,3-dihydro-1H-indene-1-carbaldehyde (**5a**)*

To a stirred solution of **1a** (0.122 g, 0.937 mmol) in HFIP (4.0 mL) was added HTIB (0.404 g, 1.04 mmol) at 0 °C. After 1 min the reaction was quenched with saturated solution of $Na_2S_2O_3$ (5.0 mL). The resulting mixture was extracted with EtOAc (3 × 10 mL). The organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduce pressure and the crude product was purified by column (5-10% EtOAc in hexane) giving **5a**[13] (58%, 0.080 g, 0.55 mmol) as a light yellow oil.

*Reaction of 1,2-dihydronaphthalene (**1a**) with HTIB in HFIP/CH_2Cl_2 followed by in situ reduction with $NaBH_4$*

To a stirred solution of **1a** (0.050 g, 0.38 mmol) in HFIP (0.8 mL) and CH_2Cl_2 (3.2 mL) was added at 0 °C HTIB (0.19 g, 0.49 mmol). The mixture was stirred for 15 min. Then, $NaBH_4$ (0.72 g, 1.9 mmol) was added and the reaction was allowed to reach room temperature while stirring for 20 min. Alcohol **9a** was obtained as a mixture with ditosilate **10a** as a yellow oil after column chromatography (AcOEt in hexanes, 1 to 30%). A second column chromatography (20% AcOEt in hexanes) allowed complete separation of the products giving **9a**[44] (48%, 0.027 g, 0.18 mmol) as a yellow oil and **10a** (17%, 0.031 g, 0.066 mmol) as a white solid. (2,3-dihydro-1*H*-inden-1-yl)methylene *bis*(4-methylbenzenesulfonate) (**10a**): IR ν_{max}/cm^{-1} (film) 1376, 1193, 1178, 750 cm^{-1}; ^1H RMN (200 MHz, $CDCl_3$) δ 2.10-2.21 (m, 2H), 2.41 (s, 3H), 2.44 (s, 3H), 2.75-2.87 (m, 2H), 3.55-3.64 (m, 1H), 6.50 (d, *J* 3.8 Hz, 1,H), 6.99-7.20 (m, 6H), 7.28-7.32 (m, 2H), 7.44-7.50 (m, 2H), 7.71-7.77 (m, 2H); ^{13}C RMN (75 MHz, $CDCl_3$) δ 21.7, 21.7, 25.3, 31.3, 50.2, 100.6, 124.7, 125.2, 126.3, 127.8, 128.1, 129.6, 129.7, 133.2, 133.5; 138.5, 145.0, 145.1, 145.2; HRMS (*m/z*) calcd. for $C_{24}H_{24}O_6S_2$ $[M + Na]^+$ 495.0907, found 495.0910.

*Synthesis of (2,3-dihydro-1H-inden-1-yl)methanol (**9a**)*

To a stirred mixture of **1a** (0.13 g, 1.0 mmol) and H_2O (0.40 mL, 22 mmol) was added CH_2Cl_2/HFIP (16 mL/4 mL) at 0 °C. HTIB (0.51 g, 1.3 mmol) was added dropwise. The mixture was stirred for 5 min at the same temperature. $NaBH_4$ was added (0.19 g, 5.0 mmol) at room temperature. The mixture was stirred for 70 min and H_2O was added. The resulting mixture was extracted with EtOAc. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduce pressure and the crude product was purified by column (0-20% EtOAc in hexane) giving **9a**[44] (0.109 g, 0.736 mmol, 74%) as a light yellow oil.

Supplementary Information

Supplementary information concerning spectroscopic data, experimental procedures and NMR copies are available free of charge at http://jbcs.sbq.org.br as PDF file.

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Supplementary Information

Metal-Free Synthesis of Indanes by Iodine(III)-Mediated Ring Contraction of 1,2-Dihydronaphthalenes

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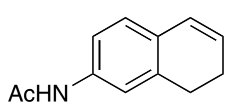
Experimental

General information

HTIB was used as received. Methanol and acetonitrile were distilled from magnesium turnings and CaH_2, respectively. These solvents were storaged in a bottle containing 4 Å molecular sieves. THF and Et_2O were freshly distilled from sodium/benzophenone. Column chromatography was performed using silica gel 200-400 mesh. TLC analyses were performed using silica gel plates, using solutions of phosphomolybdic acid and *p*-anisaldehyde for visualization. NMR spectra were recorded using $CDCl_3$ as solvent and TMS as internal pattern. The substrates **1a**, **1b**, **1c**, **1e**, **1g**, **1h**, **1j** and **1k** were prepared as previously described.[1-3] See the previous communication for experimental procedures of the HTIB oxidations in MeOH with **1a**, **1b**, **1c**, **1d** and **1g**, and in MeCN with **1a**, **1g** and **4l**.[4]

Preparation of 1,2-dihydronaphthalenes

*7-Acetamido-1,2-dihydronaphthalene (**1d**)*



In a solution of 6-amino-1-tetralone (1.00 g, 6.21 mmol) and DMAP (0.020 g) in Et3N (25 mL) was added Ac_2O (2.0 mL). The mixture was stirred for 1 h at room temperature. The reaction was quenched with MeOH (10 mL) and H2O (15 mL), extracted with EtOAc (3 × 15 mL), washed with brine (2 × 10 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (silica gel 200-400 mesh, 60% EtOAc in hexanes) giving 6-acetamido-1-tetralone[5] (92%, 1.16 g, 5.72 mmol) as a light-yellow solid; mp 124.5-126.7 ºC (124.5-125 ºC)[5]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.02-2.17 (m, 2H), 2.22 (s, 3H), 2.62 (t, 2H, *J* 6.5 Hz), 2.92 (t, 2H, *J* 6.0 Hz), 7.27 (dd, 1H, *J* 2.4 and 8.6 Hz), 7.72 (s, 1H), 7.96 (d, 1H, *J* 8.4 Hz), 8.31 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.2, 24.7, 29.9, 38.9, 117.5, 118.5, 128.4, 142.7, 146.3, 169.0, 197.7.

To a stirred solution of 6-acetamido-1-tetralone (1.12 g, 5.50 mmol) in anhydrous MeOH (70 mL) was added $NaBH_4$ (0.25 g, 6.61 mmol) in portions at 0 ºC. The mixture was stirred for 1 h at room temperature. The reaction was quenched with H_2O (20 mL) and a 10% aqueous solution of HCl was added dropwise until pH *ca.* 7. The resulting solution was extracted with EtOAc (3 × 15 mL), washed with brine (20 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure giving 6-acetamido-1-tetralol (78%, 0.882 mg, 4.30 mmol) as a pale-yellow solid. The 1-tetralol (0.841 g, 4.10 mmol) was used without purification in a dehydration reaction using toluene (45 mL), a few crystals of *p*-TsOH and reaction time of 3 h at 130 ºC, using a Dean-Stark apparatus. The resulting residue was purified by flash chromatography (silica gel 200-400 mesh, 80% EtOAc in hexanes) affording **1d**[6] (95%, 0.728 g, 3.89 mmol) as a pale-yellow solid. Experimental data has not been previously reported: mp: 89.3-90.6 ºC; IR ν_{max}/cm^{-1} (film) 497, 566, 684, 834, 883, 1018, 1266, 1328, 1370, 1421, 1536, 1594, 1666, 2829, 2883, 2933, 3032,

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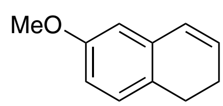
[§]Dedicated with deep respect to Prof. Miuako K. Kuya

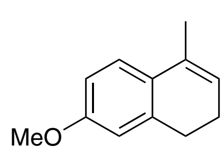
3297; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.14 (s, 3H), 2.20-2.31 (m, 2H), 2.72 (t, 2H, *J* 8.1 Hz), 5.90-5.99 (m, 1H), 6.40 (d, 1H, *J* 9.6 Hz), 6.92 (d, 1H, *J* 8.0 Hz), 7.23 (dd, 1H, *J* 2.2 and 8.0 Hz), 7.31 (s, 1H), 7.89 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.9, 24.4, 27.6, 117.8, 119.4, 126.1, 127.0, 127.6, 130.4, 136.3, 136.5, 168.6; LRMS *m/z* (%) 187 ($M^{+\bullet}$, 72%), 146 (9), 145 (61), 144 (100), 130 (29), 115 (24), 91 (8), 77 (6), 51 (5), 43 (23); HRMS (*m/z*) calcd. for $C_{12}H_{13}NO$ $[M + H]^+$ 188.1070, found 188.1067.

*1,2-Dihydro-6-methoxynaphthalene (**1f**)*



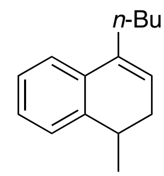
$NaBH_4$ (0.455 g, 12.0 mmol) was added dropwise to a solution of 7-methoxy-1-tetralone (1.52 g, 8.63 mmol) in MeOH (50 mL) at 0 ºC. The mixture was stirred at room temperature. After 2 h, the reaction was quenched with H_2O and a 10% aqueous solution of HCl was added dropwise until pH *ca.* 5. The MeOH was removed under reduced pressure and the residue was extracted with EtOAc, washed with brine, and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The crude corresponding 1-tetralol was dissolved in THF (10 mL) and H_3PO_4 85% (4.5 mL) was added dropwise at room temperature. The mixture was refluxed at 95 ºC for 2 h. The crude product was transferred to an Erlenmeyer and diluted with Et_2O. A sat. solution of $NaHCO_3$ was added until *ca.* pH 7. The solution was extracted with Et_2O, washed with sat. solution of NaCl and dried over anhydrous $MgSO_4$. The residue was purified by flash column chromatography (gradient elution, 0-30% EtOAc in hexanes), affording **1f**[2] (0.885 g, 5.52 mmol, 64%), as a colorless oil. Starting material was also recovered (0.0089 g, 0.0555 mmol, 1%), as a colorless oil.

*1,2-Dihydro-7-methoxy-4-methylnaphthalene (**1i**)*



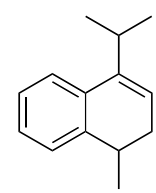
A solution of 6-methoxy-1-tetralone (1.76 g, 10.0 mmol) in Et_2O (7.0 mL) was added to a solution of MeMgI [prepared from MeI (1.7 mL, 27.0 mmol), Mg (0.673 g, 27.7 mmol) and I_2 (some crystals) in anhydrous Et_2O (7.0 mL)]. The mixture was refluxed for 4.5 h. After that, a solution of HCl 6 mol L^{-1} (6 mL) was added dropwise at 0 °C. The solution was stirred for 15 min at room temperature. The organic layer was extracted with Et_2O, washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (gradient elution, 0-30% of EtOAc in hexanes), affording **5j**[7] (1.08 g, 6.20 mmol, 62%), as a colorless oil.

*4-n-Butyl-1,2-dihydro-1-methylnaphthalene (**1l**)*



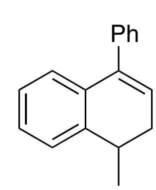
The reaction was performed as indicated for **1i**. A mixture of 4-methyl-1-tetralone (1.42 g, 8.86 mmol) in Et_2O (12.0 mL) was added to a solution of *n*-BuMgI [prepared from 1-bromobutane (1,46 g, 10.6 mmol), Mg (0.245 g, 10.1 mmol), I_2 (some crystals) and anhydrous Et_2O (12.0 mL)]. The mixture was refluxed for 3 h. The crude product was purified by flash column chromatography (gradient elution, 0-5% of EtOAc in hexanes), affording the olefin **1l**[2] (0.805 g, 4.02 mmol, 45%), as a colorless oil. Starting material was recovered (0.214 g, 1.34 mmol, 15%).

*1,2-Dihydro-4-isopropyl-1-methylnaphthalene (**1m**)*



The reaction was performed as indicated for **1i**. A mixture of 4-methyl-1-tetralone (0.961 g, 6.00 mmol) in Et_2O (4.0 mL), *i*-PrMgI [prepared from 2-bromopropane (1.93 g, 15.7 mmol), Mg (0.321 g, 13.2 mmol), I_2 (some crystals) in anhydrous Et_2O (6.0 mL)] was stirred for 5.5 h. The crude product was purified by flash column chromatography (gradient elution, 0-20% of EtOAc in hexanes), affording **1m**[8] (0.387 g, 2.08 mmol, 35%) as a colorless oil.

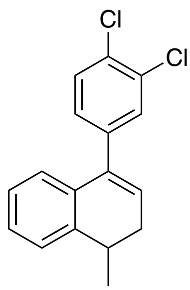
*1,2-Dihydro-1-methyl-4-phenylnaphthalene (**1n**)*



The reaction was performed as indicated for **1i**. A mixture of 4-methyl-1-tetralone (0.641 g, 4.00 mmol) in Et_2O (0.5 mL) and PhMgBr [prepared from bromobenzene

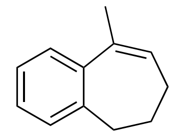
(0.792 g, 5.04 mmol), Mg (0.117 g, 4.81 mmol), I_2 (some crystals) in anhydrous Et_2O (1.0 mL)] was refluxed for 1.5 h. The crude product was purified by flash column chromatography (gradient elution, 10-15% of EtOAc in hexanes), affording the 1,2-dihydronaphthalene **1n**[9] (0.682 g, 3.10 mmol, 78%), as a colorless oil.

*4-(3,4-Dichlorophenyl)1,2-dihydro-1-methylnaphthalene (**1o**)*



The reaction was performed as indicated for **1i**. A mixture of 4-methyl-1-tetralone (0.645 g, 4.03 mmol) in Et_2O (0.5 mL) and 1,2-ClPhMgBr [prepared from 4-bromo-1,2-dichlorobenzene (1.15 g, 5.09 mmol), Mg (0.117 g, 4.81 mmol), I_2 (some crystals) in anhydrous Et_2O (1.0 mL)] was refluxed for 2 h. The crude product was purified by flash column chromatography (gradient elution, 10-30% of EtOAc in hexanes), affording the 1-(3,4-dichloropheny)-1,2,3,4-tetrahydro-4-methylnaphthalen-1-ol (0.870 g, 2.83 mmol, 70%), as a colorless oil. The isolated alcohol was dissolved in anhydrous toluene (3.5 mL). Some crystals of *p*-toluenesulfonic acid were added to that solution. The reaction was refluxed for 6 h. The reaction was extracted with EtOAc. The organic phase was washed with H_2O, saturated solution of $NaHCO_3$, saturated solution of NaCl and dried over anhydrous $MgSO_4$. The crude product was purified by flash column chromatography (isocratic elution with hexanes), furnishing the desired alkene **1o** (0.385 g, 1.33 mmol, 56%), as a colorless oil; IR ν_{max}/cm^{-1} (film) 1121, 1258, 1515, 2830, 2934; ^1H NMR (300 MHz, $CDCl_3$) δ 1.30 (d, 1H, *J* 7,0 Hz), 2.22 (ddd, 1H, *J* 16.8, 7.7 and 5.0 Hz), 2.55 (ddd, 1H, *J* 16.8, 6.5 and 4.4 Hz), 2.98 (sext, 1H, *J* 7.0 Hz), 6.00 (t, 1H, *J* 4.7 Hz), 6.93-6.96 (m, 1H), 7.10-7.26 (m, 4H), 7.42-7.46 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.8, 31.4, 32.1, 125.3, 126.2, 126.2, 127.4, 127.7, 128.1, 130.2, 130.5, 131.0, 132.3, 133.4, 137.5, 140.9, 141.5; HRMS (*m/z*) calcd. for $C_{14}H_{20}O_4$ $[M + Na]^+$ 275.1254, found 275.1252.

*6,7-Dihydro-9-methyl-5H-benzo[7]annulene (**1p**)*



The reaction was performed as indicated for **1i**. A mixture of 1-benzosuberone (0.481 g, 3.00 mmol) in anhydrous Et_2O (2.0 mL), MeMgI [prepared from MeI (0.5 mL, 8.10 mmol), Mg (0.202 g, 8.31 mmol) and I_2 (some crystals) in anhydrous Et_2O (2.0 mL)] was stirred for 4 h under reflux. The crude product was purified by flash column chromatography (gradient elution, 0-10% of EtOAc in hexanes), affording **1p**[10] (0.403 g, 2.55 mmol, 85%), as a colorless oil.

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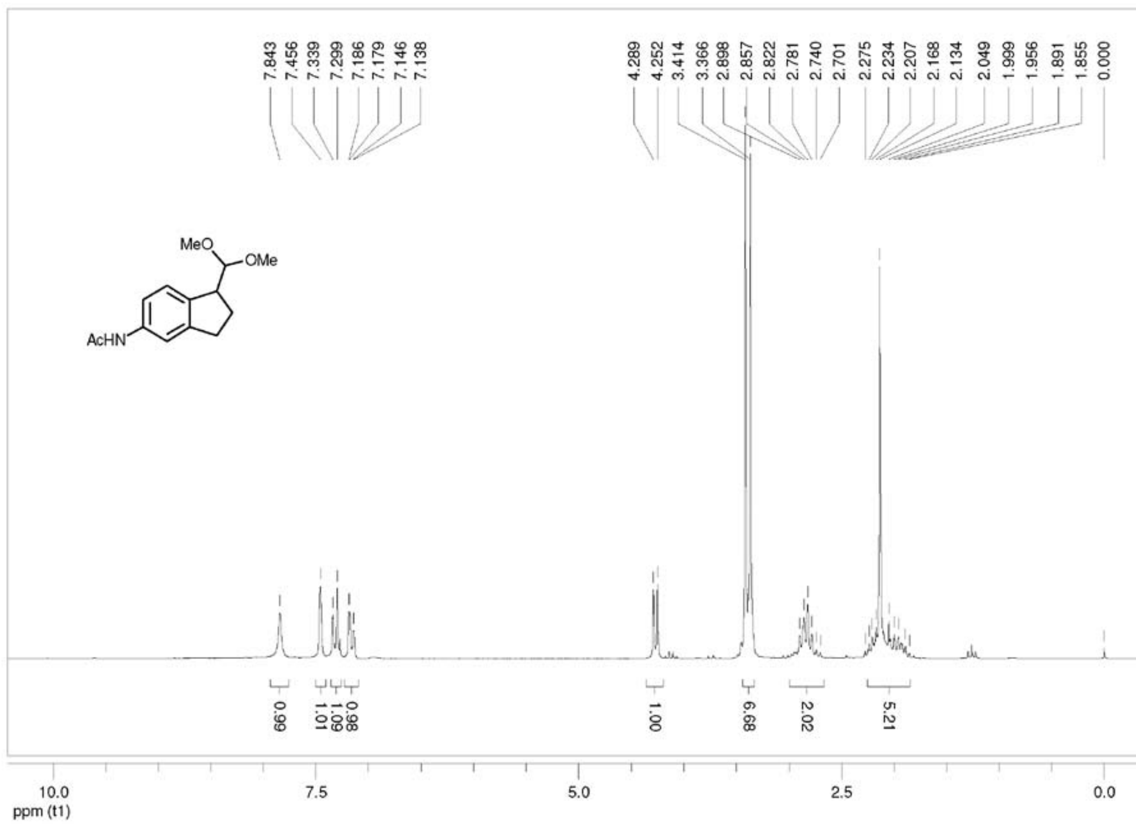

Figure S1. ^{1}H NMR spectrum of **2d** ($CDCl_3$, TMS, 200 MHz, δ).

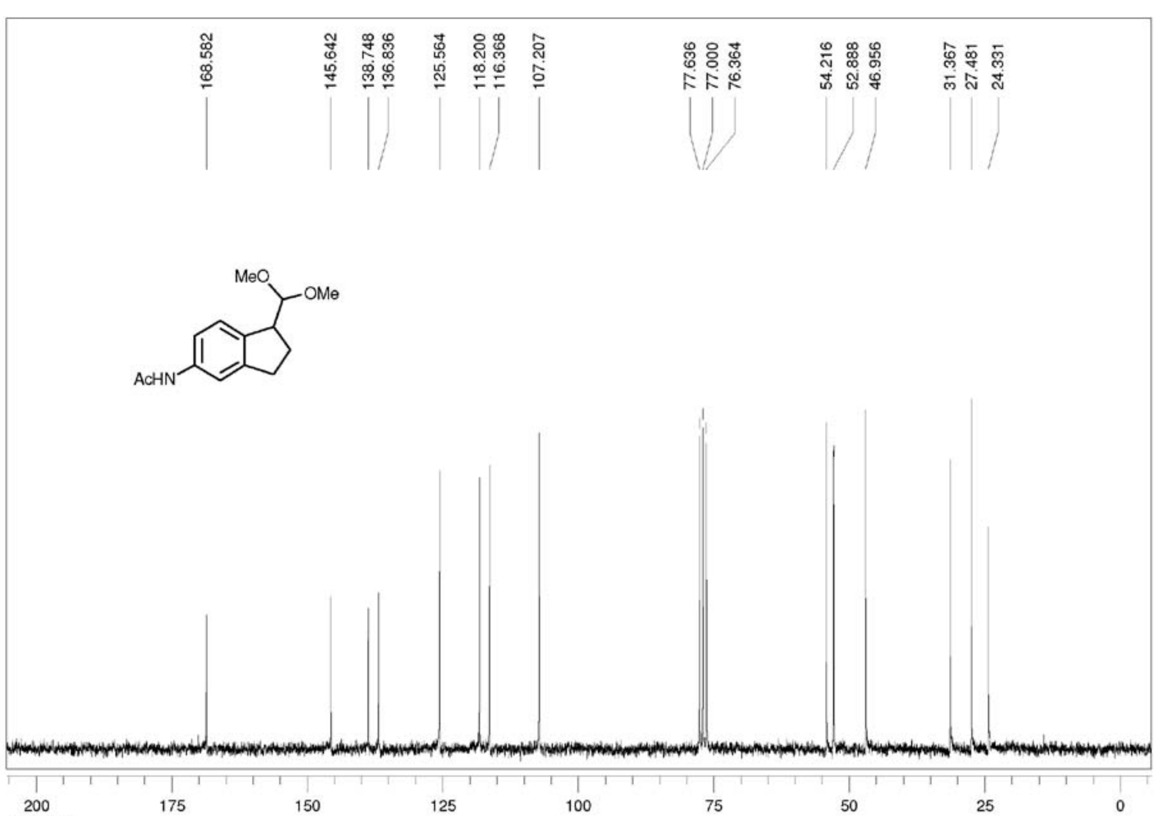

Figure S2. ^{13}C NMR spectrum of **2d** ($CDCl_3$, TMS, 50 MHz, δ).

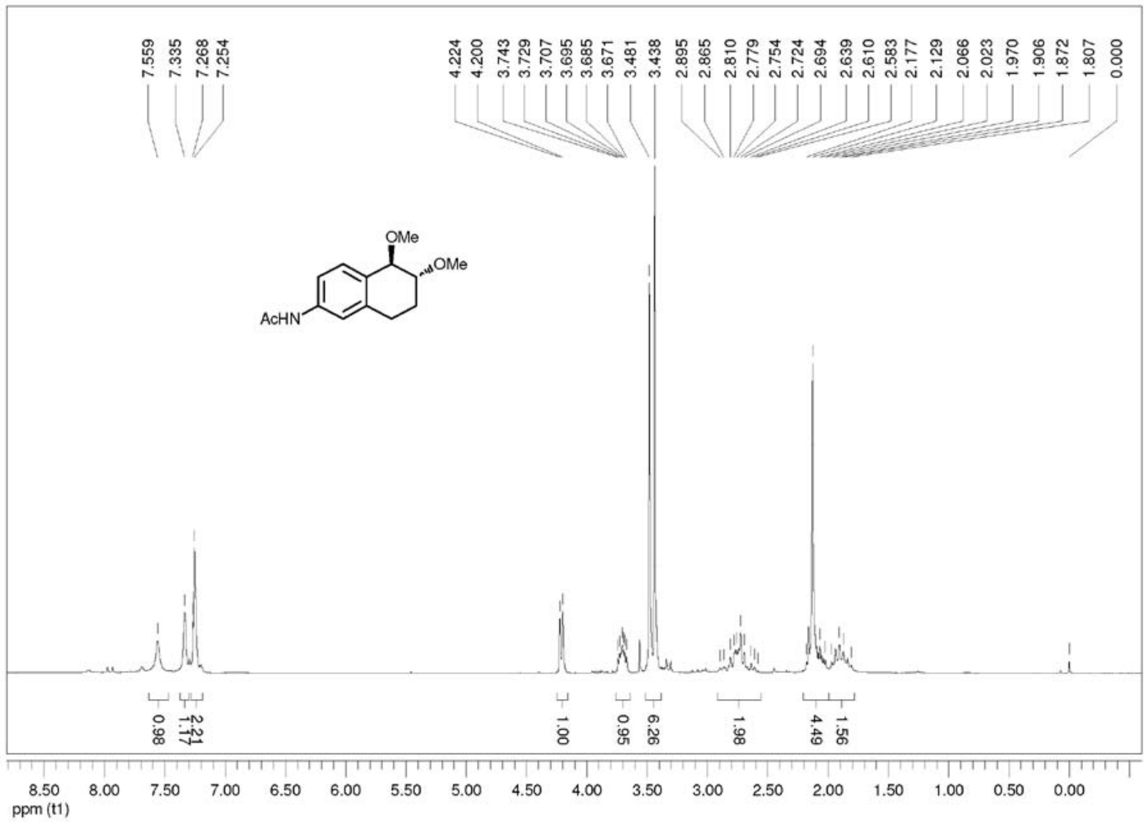

Figure S3. [1]H NMR spectrum of *trans*-**3d** ($CDCl_3$, TMS, 200 MHz, δ).

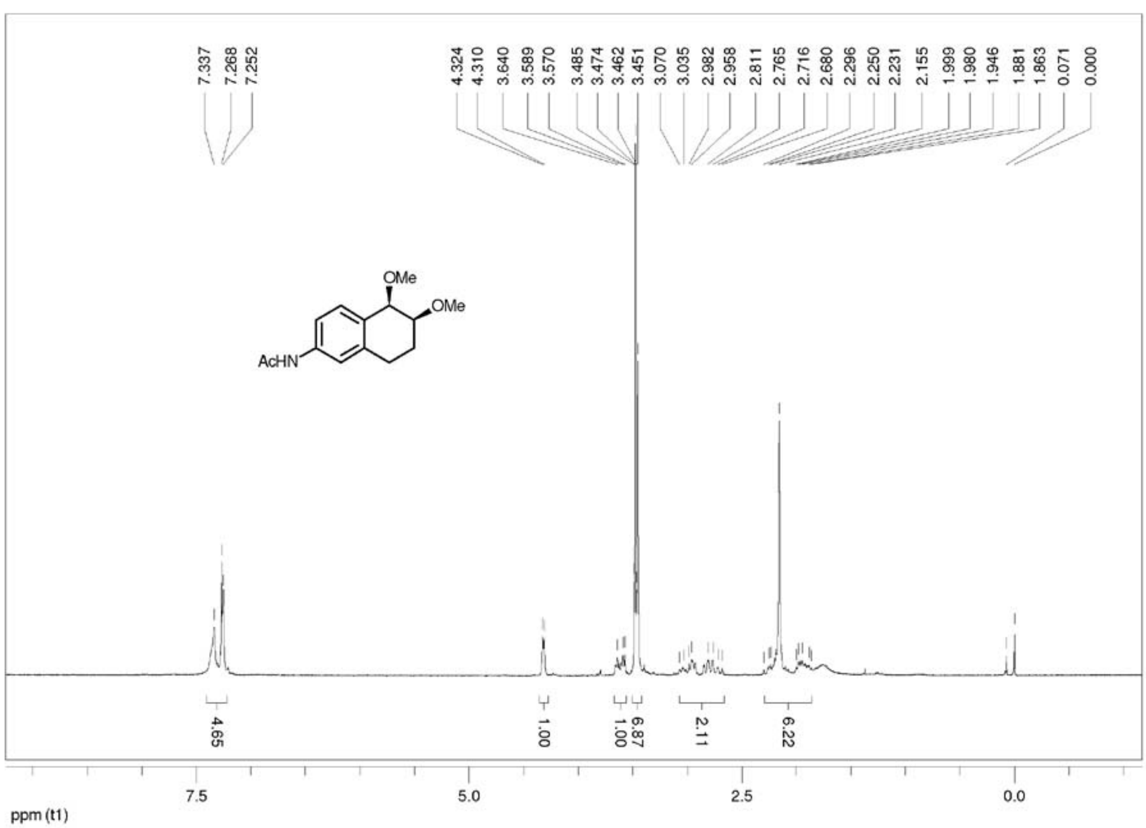

Figure S4. [1]H NMR spectrum of *cis*-**3d** ($CDCl_3$, TMS, 200 MHz, δ).

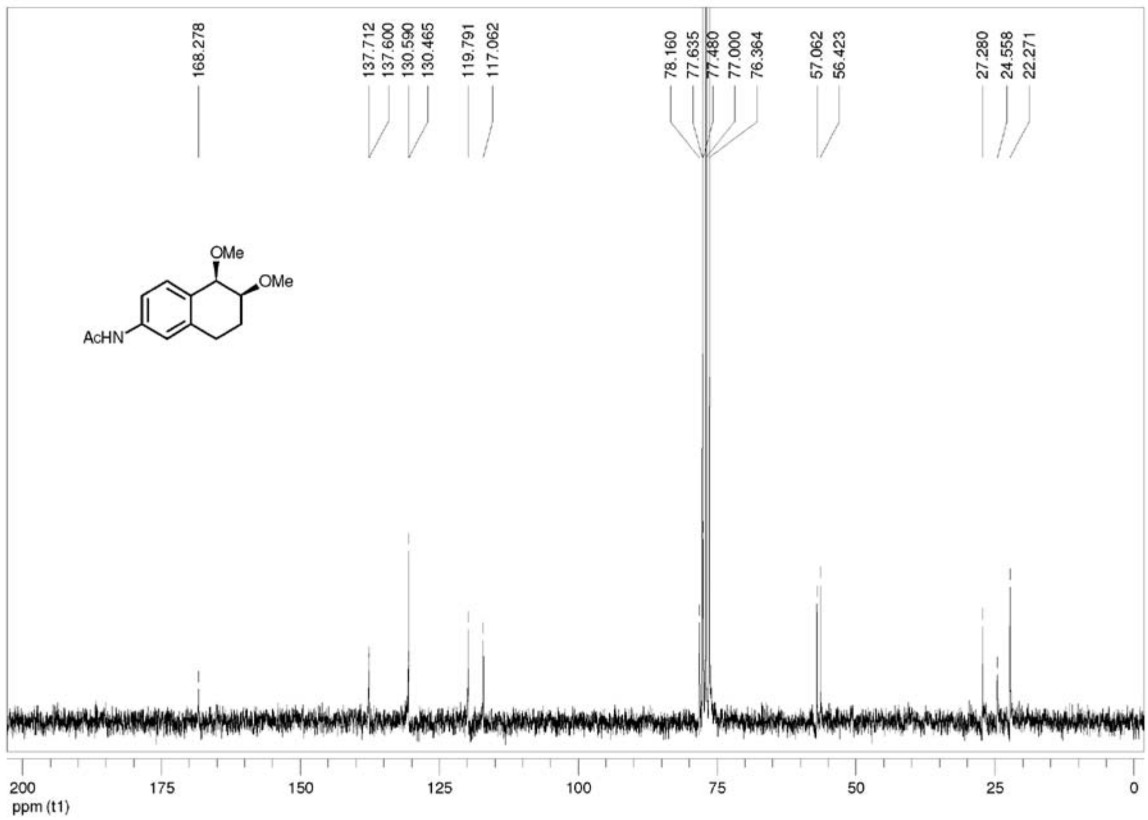

Figure S5. ^{13}C NMR spectrum of *cis*-**3d** ($CDCl_3$, TMS, 75 MHz, δ).

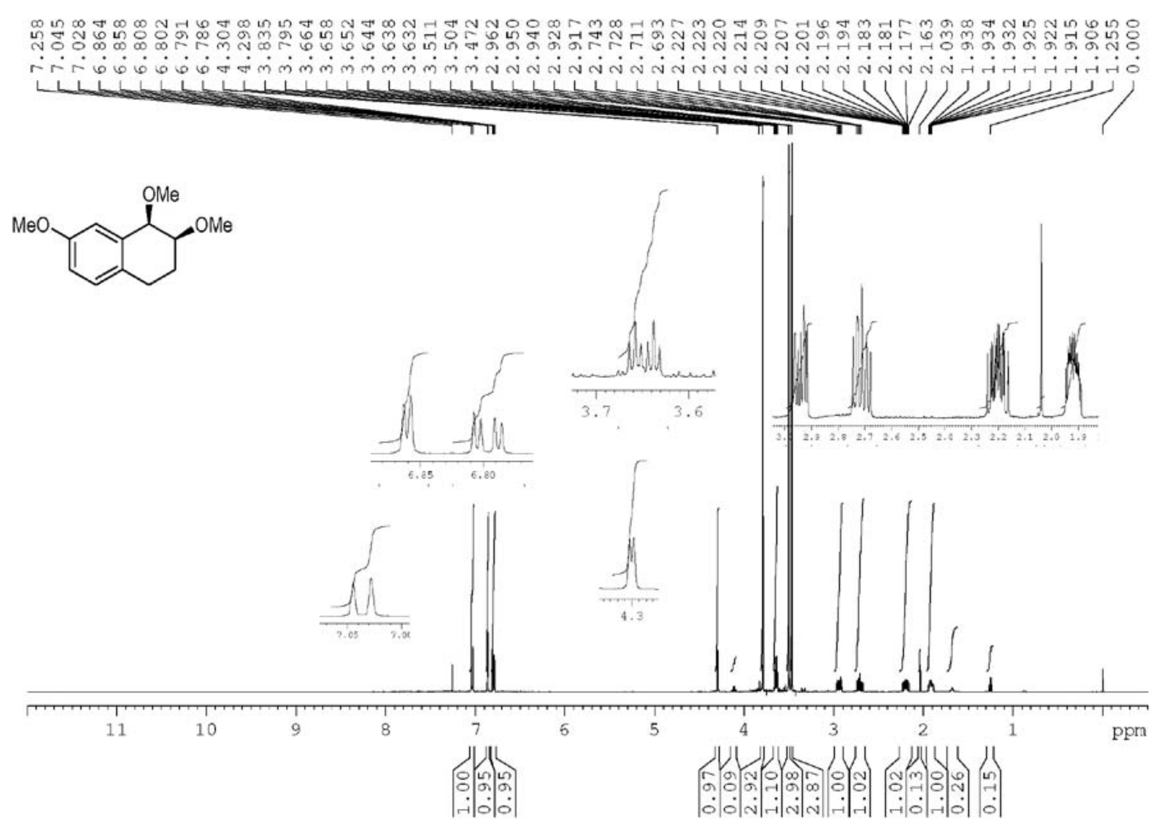

Figure S6. ^{1}H NMR spectrum of *cis*-**3f** ($CDCl_3$, TMS, 500 MHz, δ).

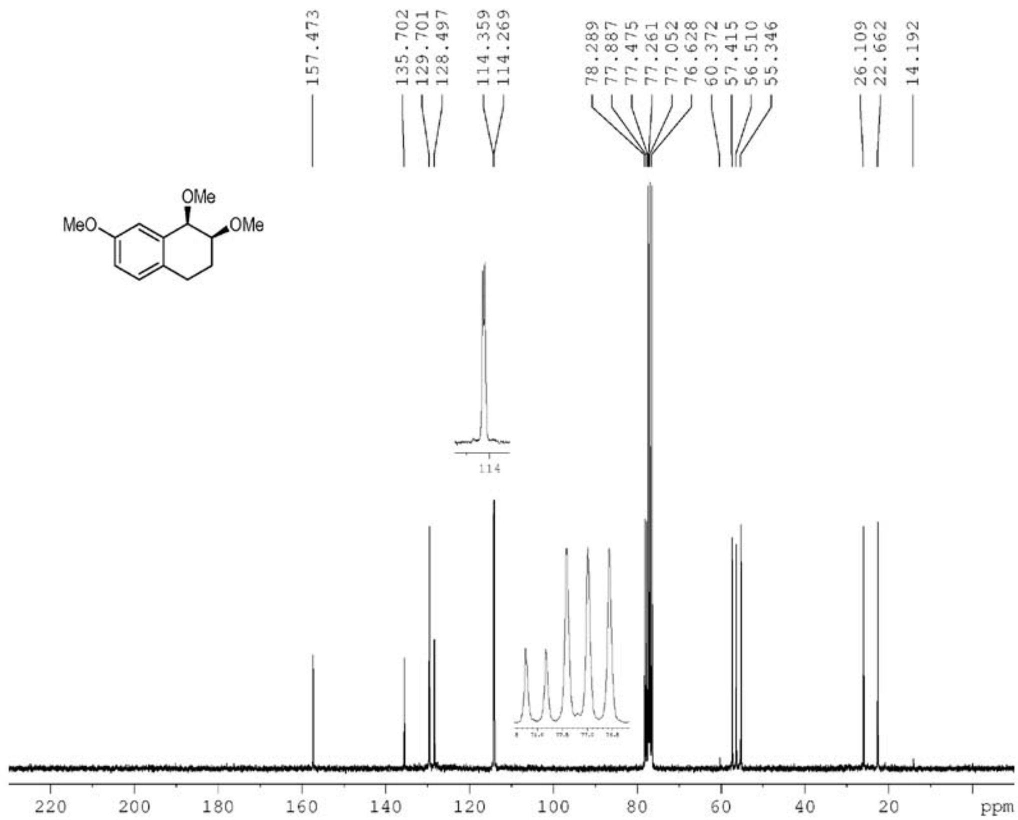

Figure S7. ^{13}C NMR spectrum of *cis*-**3f** ($CDCl_3$, TMS, 75 MHz, δ).

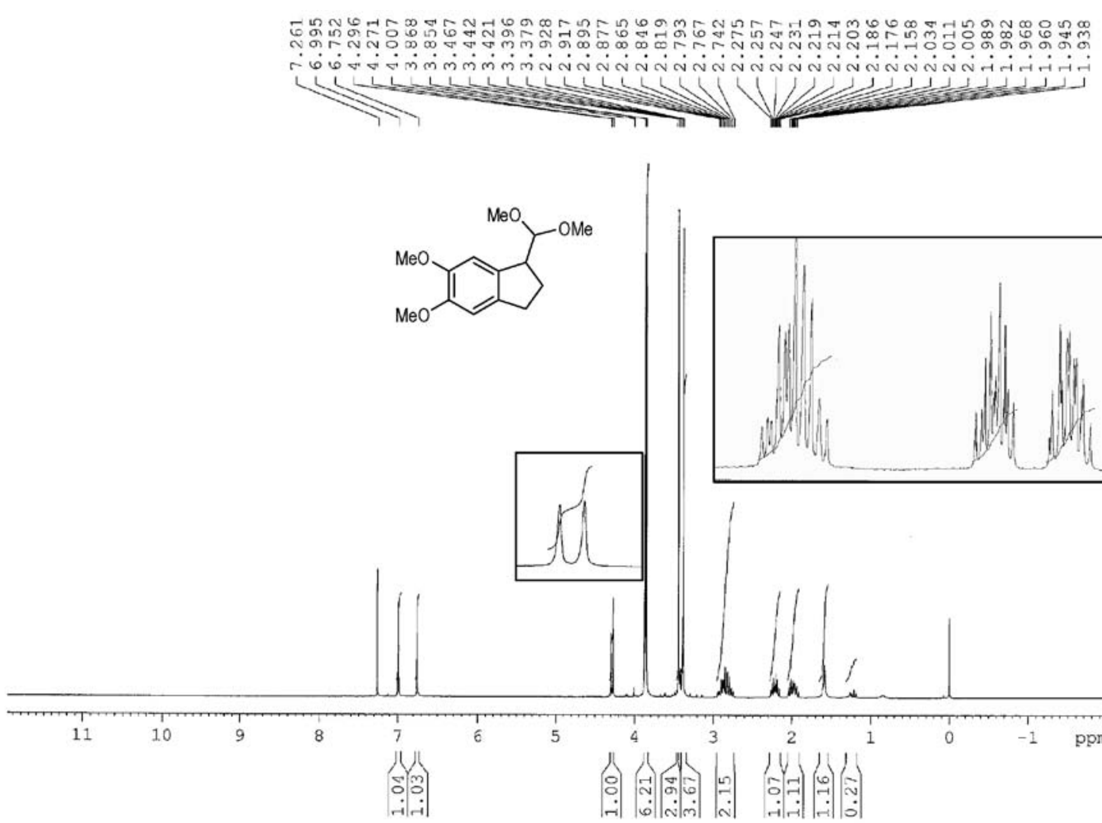

Figure S8. ^{1}H NMR spectrum of **2g** ($CDCl_3$, TMS, 300 MHz, δ).

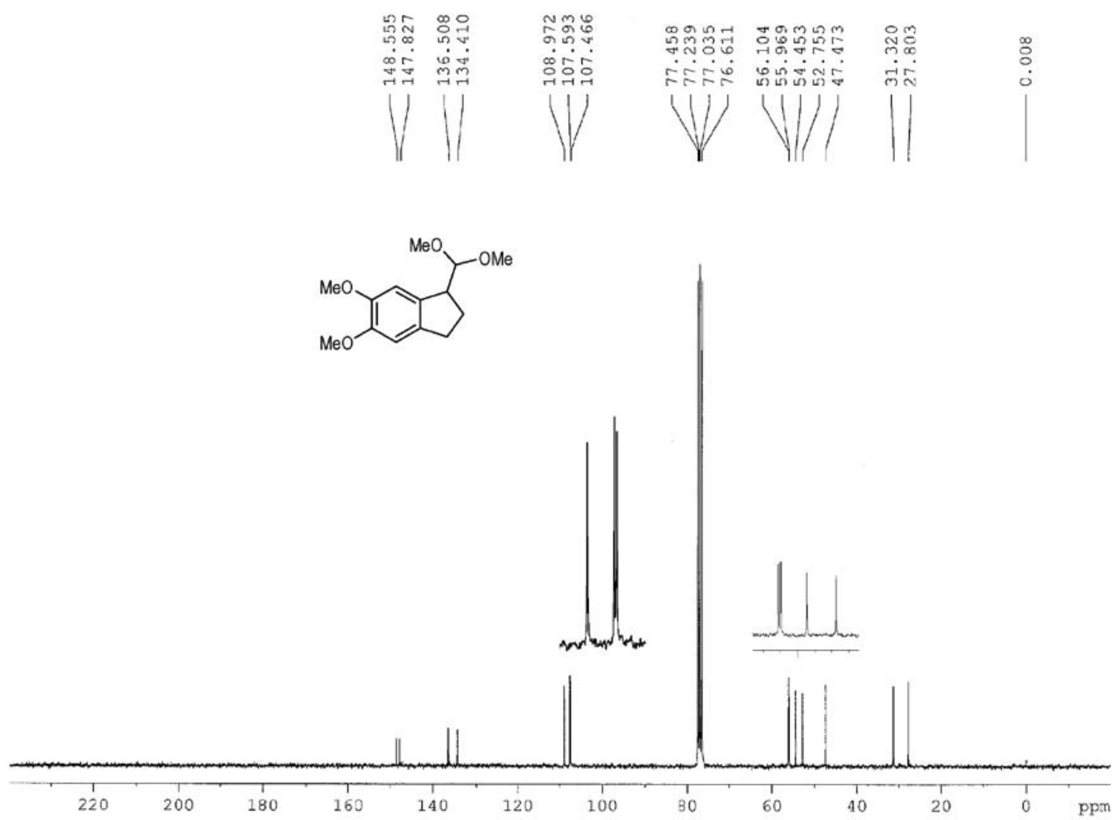

Figure S9. ^{13}C NMR spectrum of **2g** ($CDCl_3$, TMS, 75 MHz, δ).

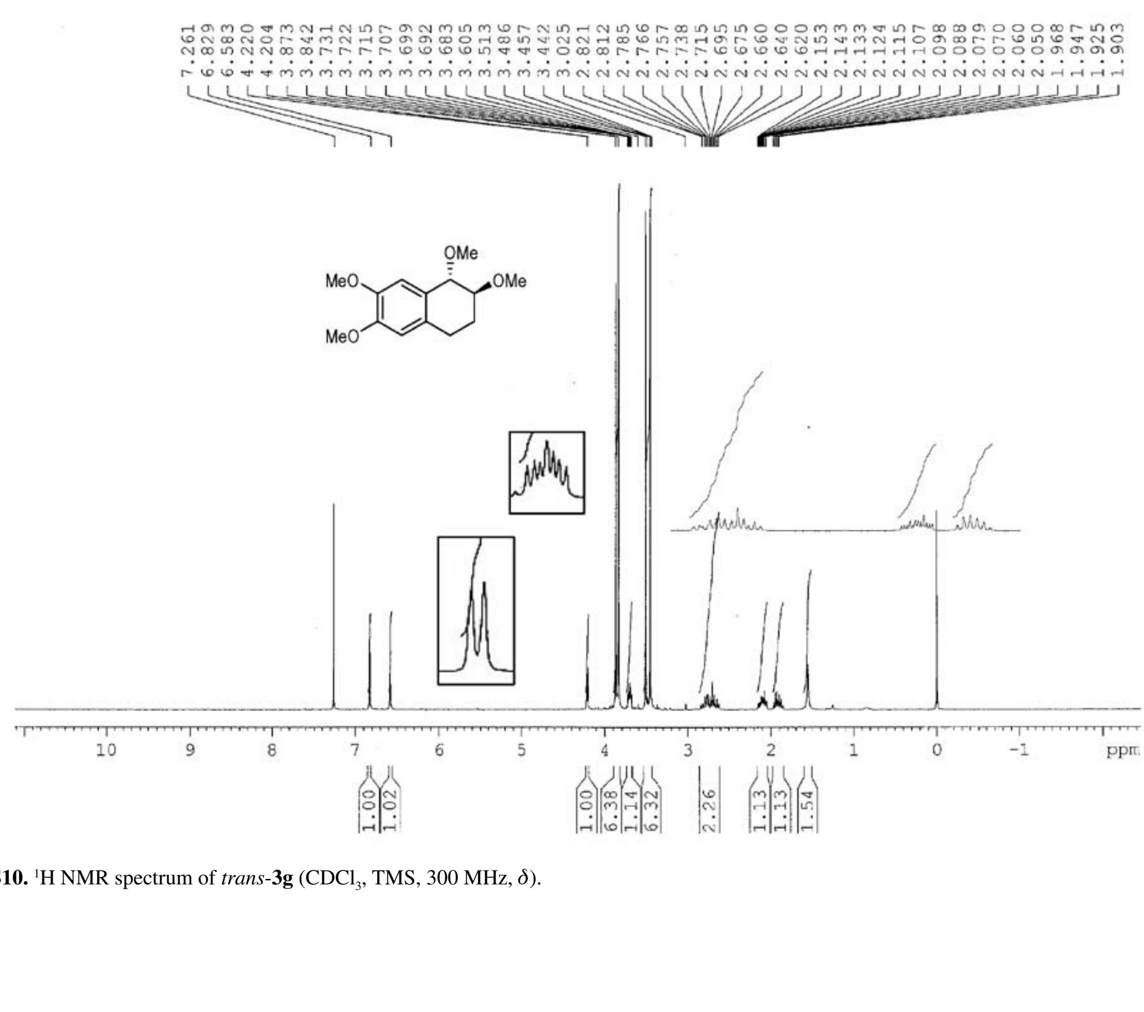

Figure S10. ^{1}H NMR spectrum of *trans*-**3g** ($CDCl_3$, TMS, 300 MHz, δ).

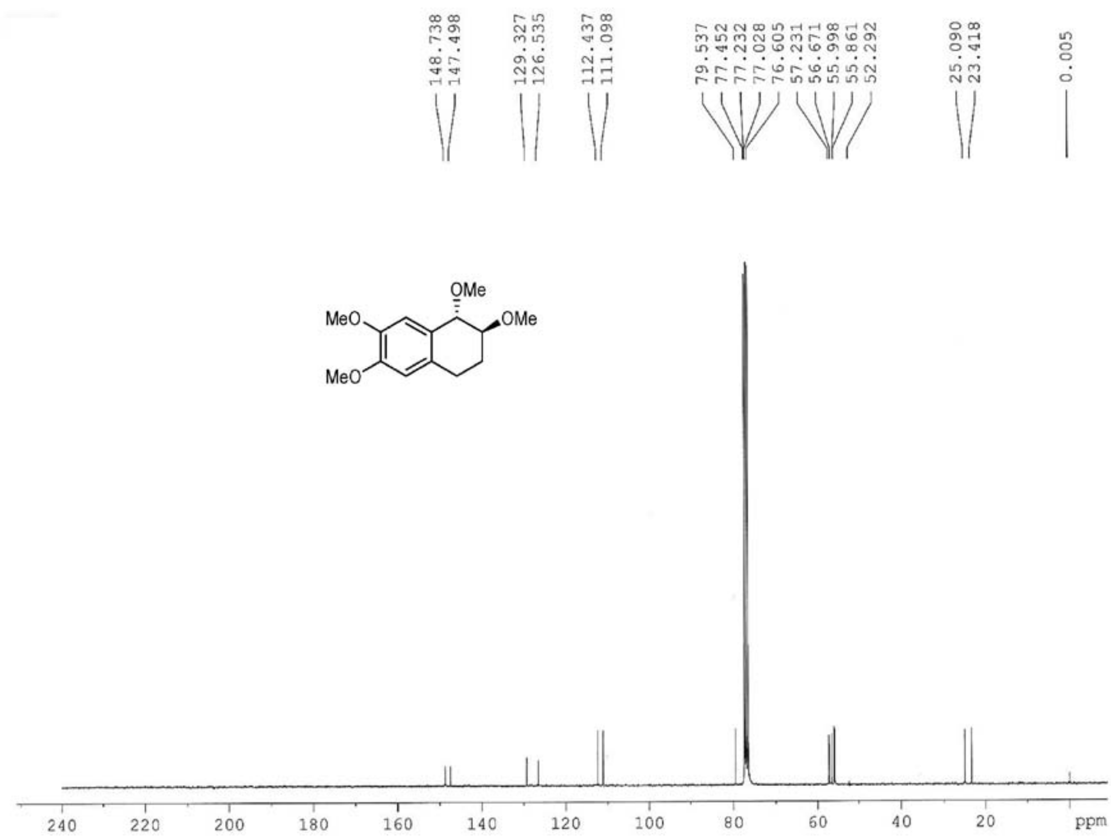

Figure S11. ^{13}C NMR spectrum of *trans*-**3g** ($CDCl_3$, TMS, 75 MHz, δ).

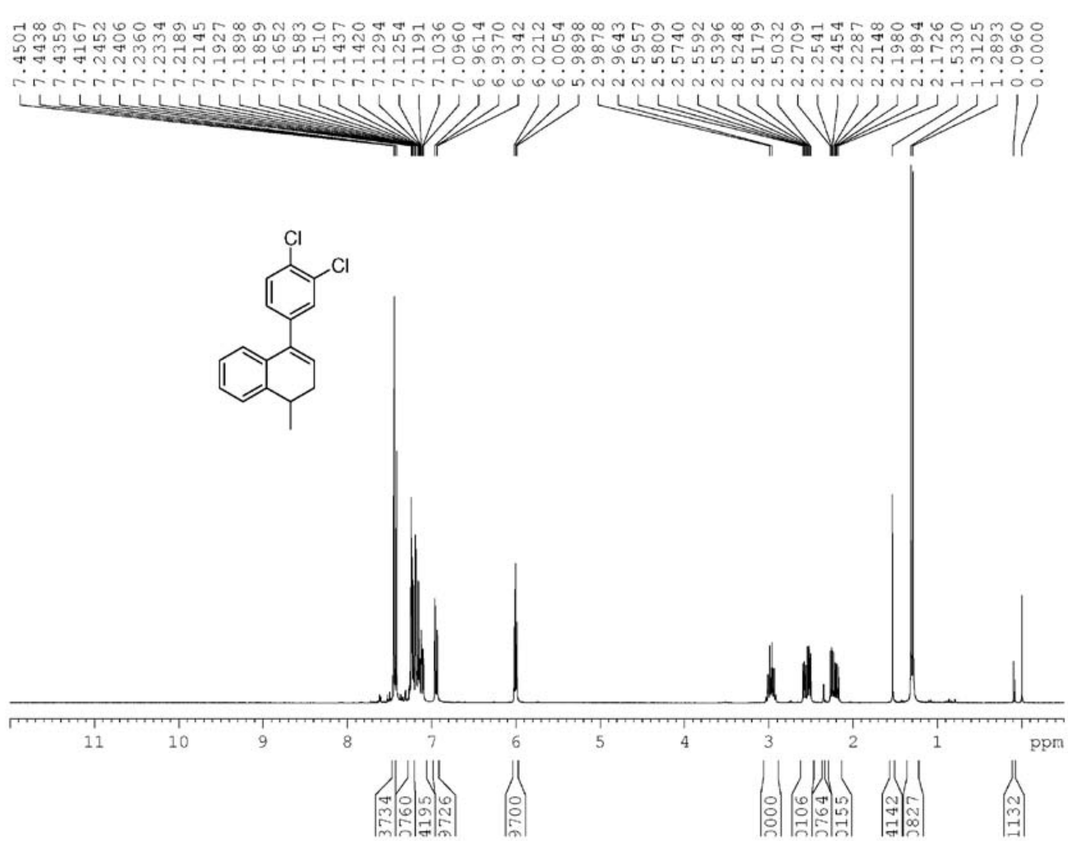

Figure S12. ^{1}H NMR spectrum of **1o** ($CDCl_3$, TMS, 300 MHz, δ).

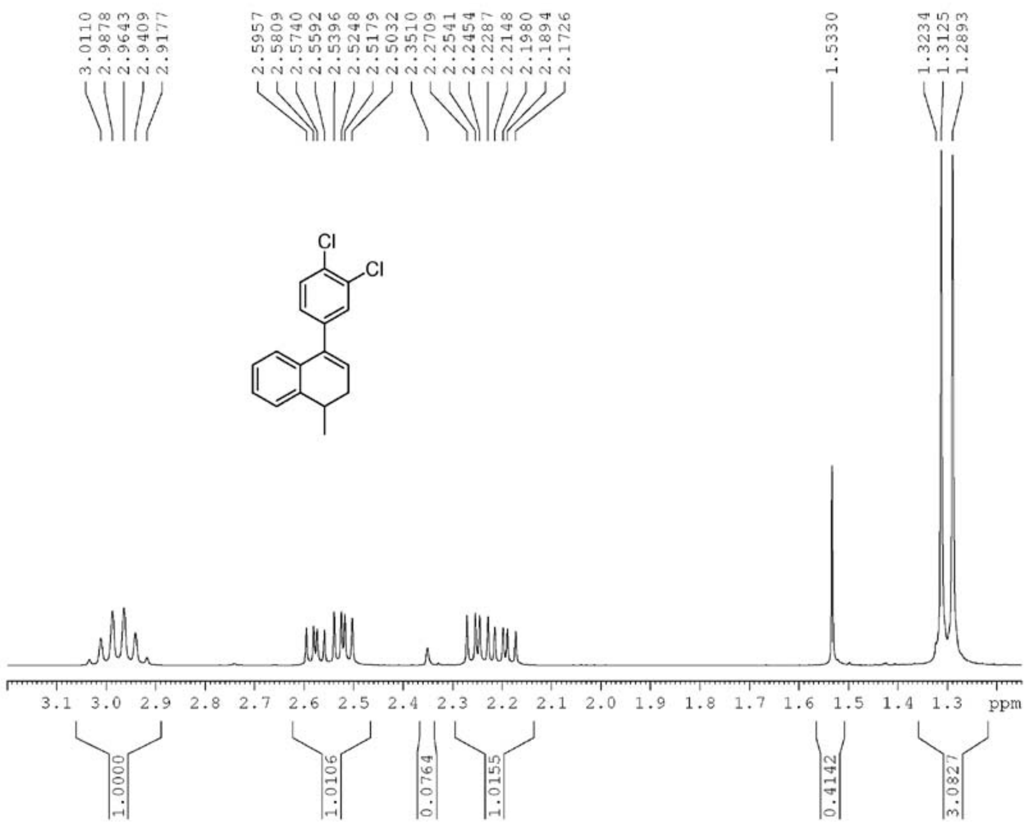

Figure S13. [1]H NMR spectrum of **1o** ($CDCl_3$, TMS, 300 MHz, δ) - expansion.

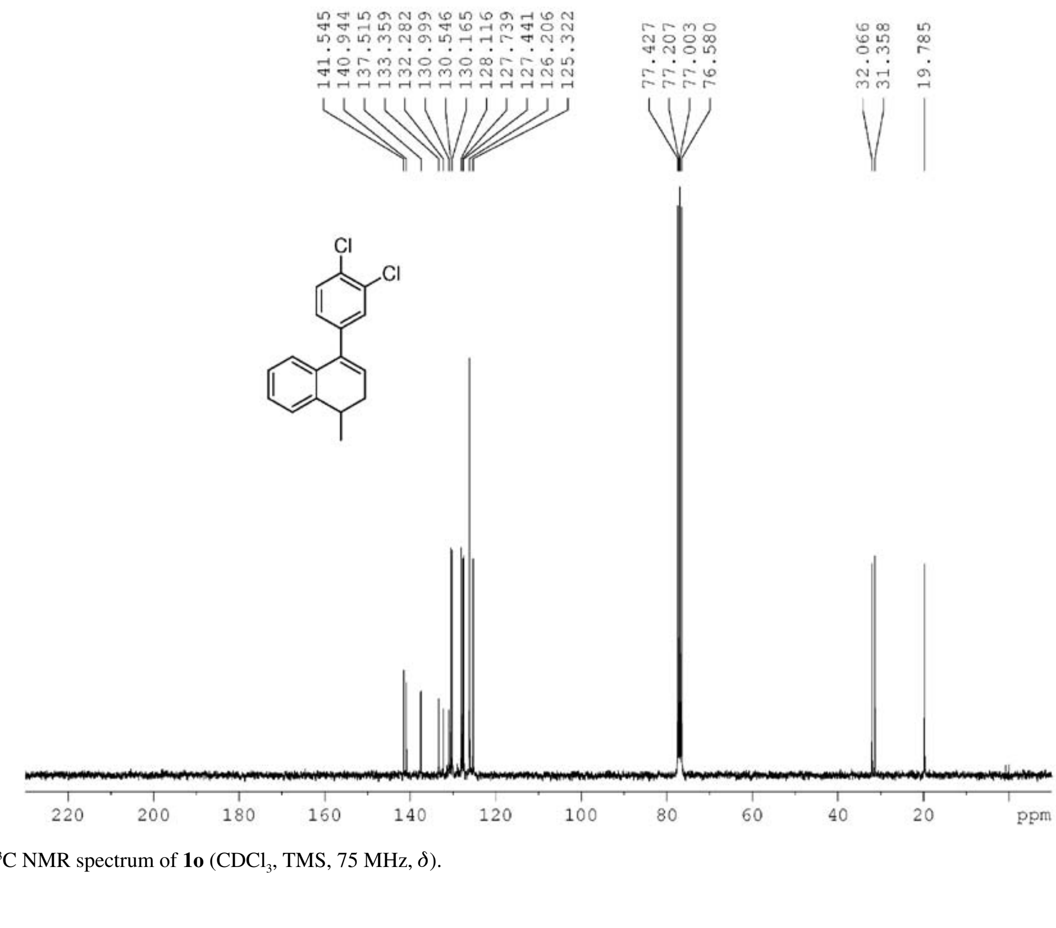

Figure S14. [13]C NMR spectrum of **1o** ($CDCl_3$, TMS, 75 MHz, δ).

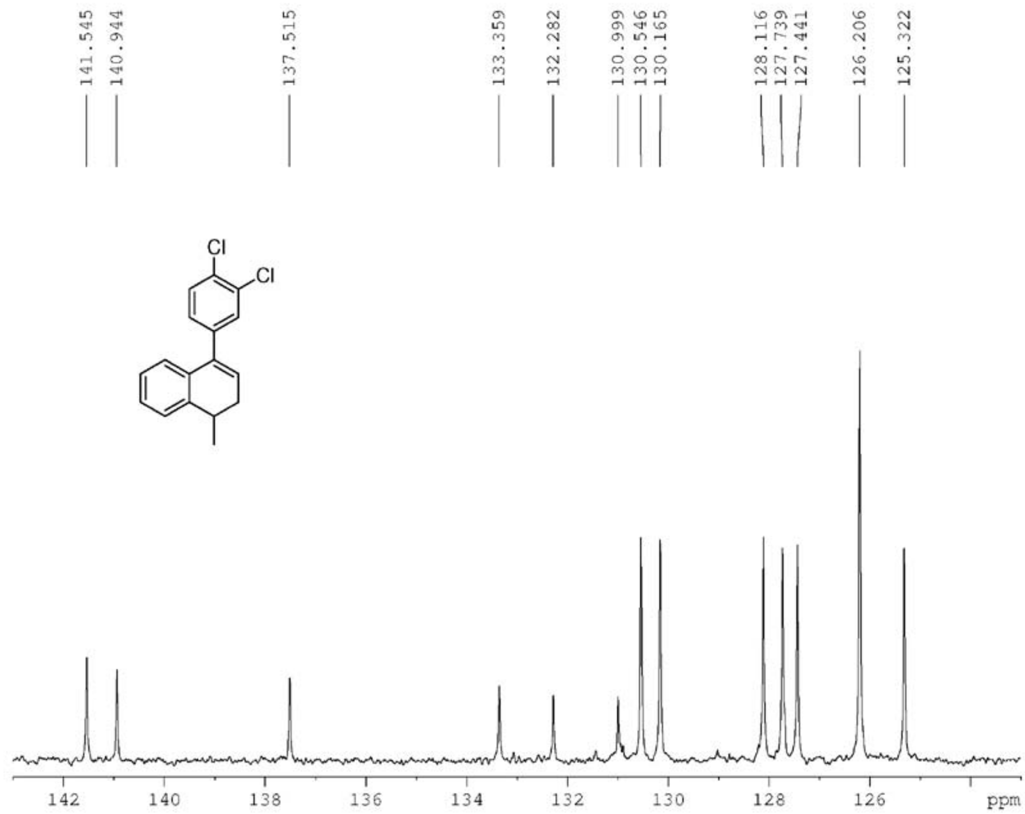

Figure S15. ^{13}C NMR spectrum of **1o** ($CDCl_3$, TMS, 75 MHz, δ) - expansion.

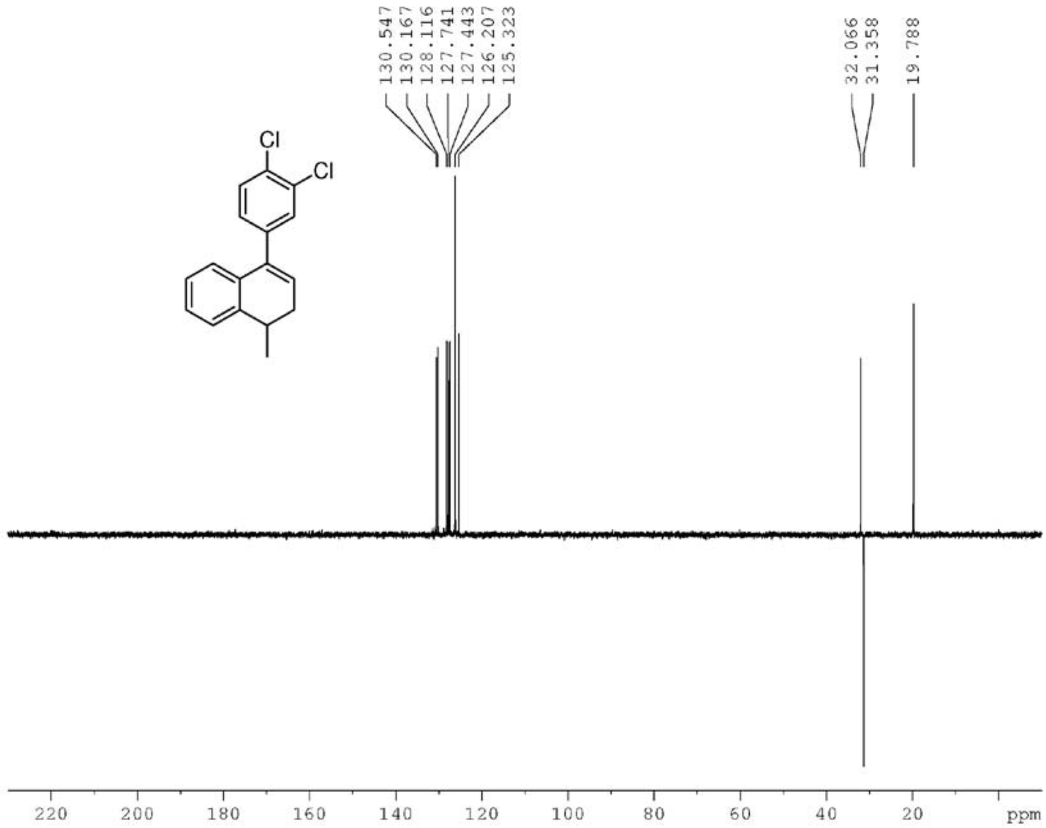

Figure S16. DEPT 135 spectrum of **1o** ($CDCl_3$, TMS, 75 MHz, δ).

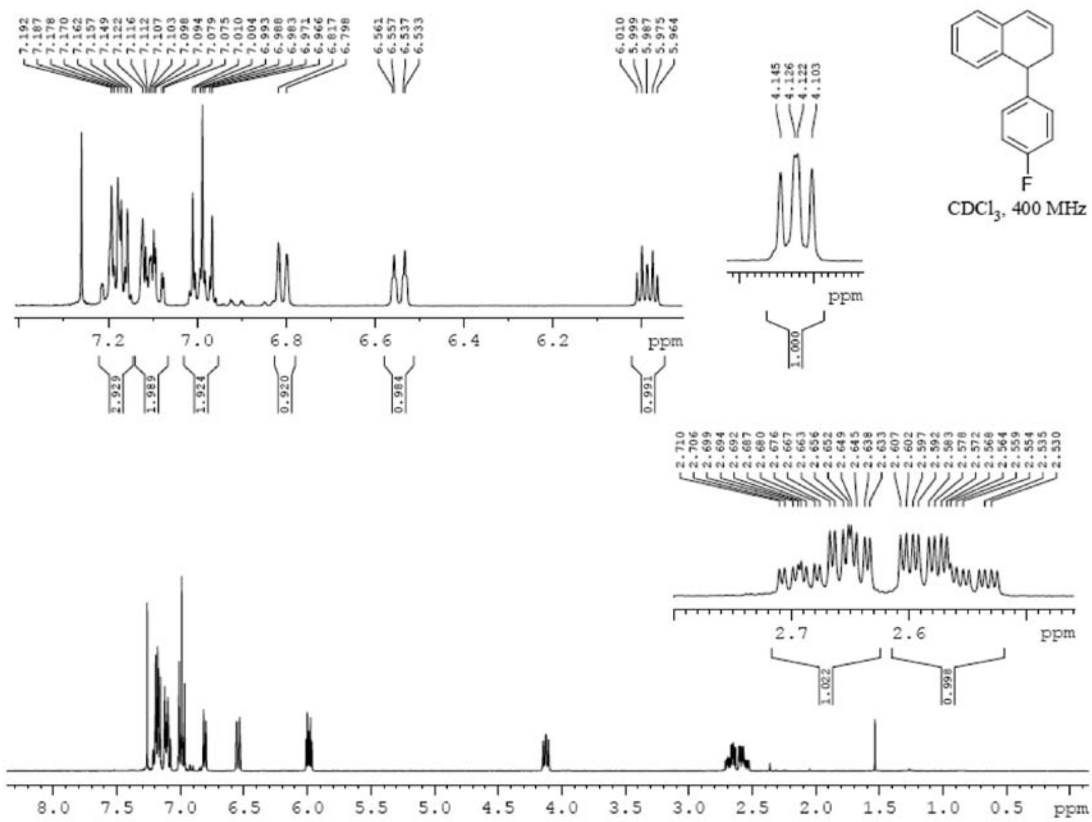

Figure S17. ^{1}H NMR spectrum of **1q** ($CDCl_3$, TMS, 400 MHz, δ).

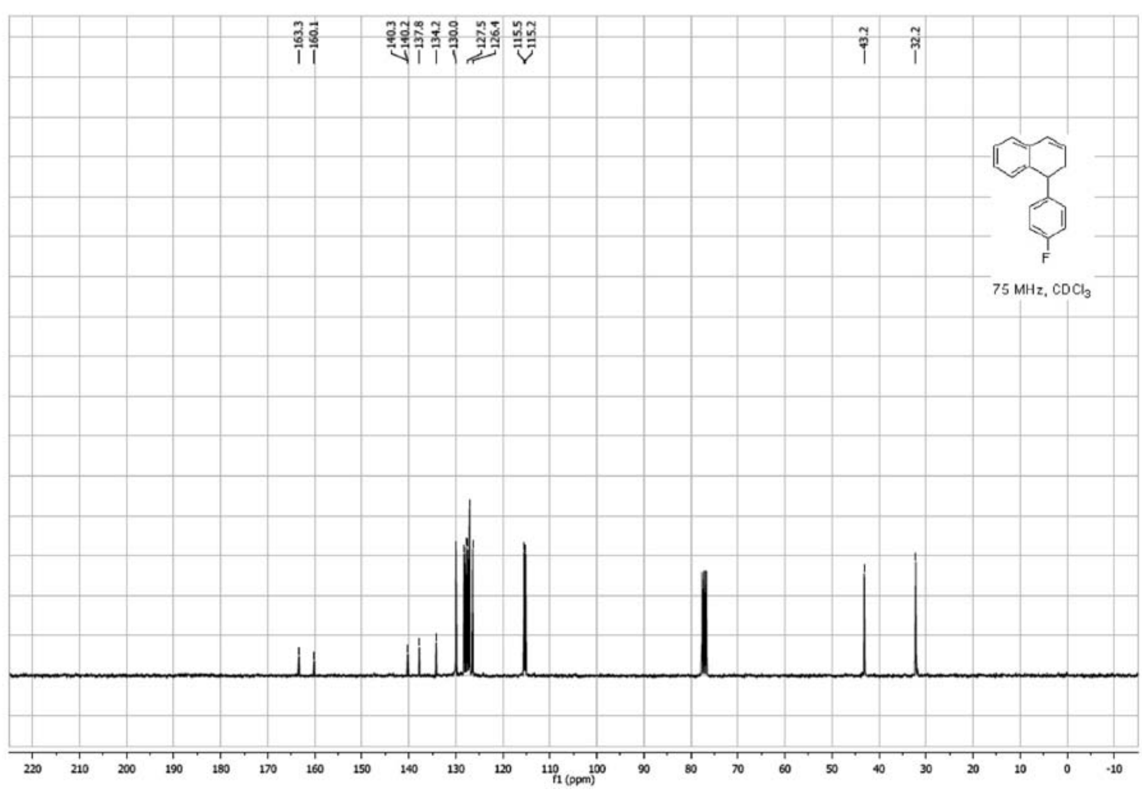

Figure S18. ^{13}C NMR spectrum of **1q** ($CDCl_3$, TMS, 75 MHz, δ).

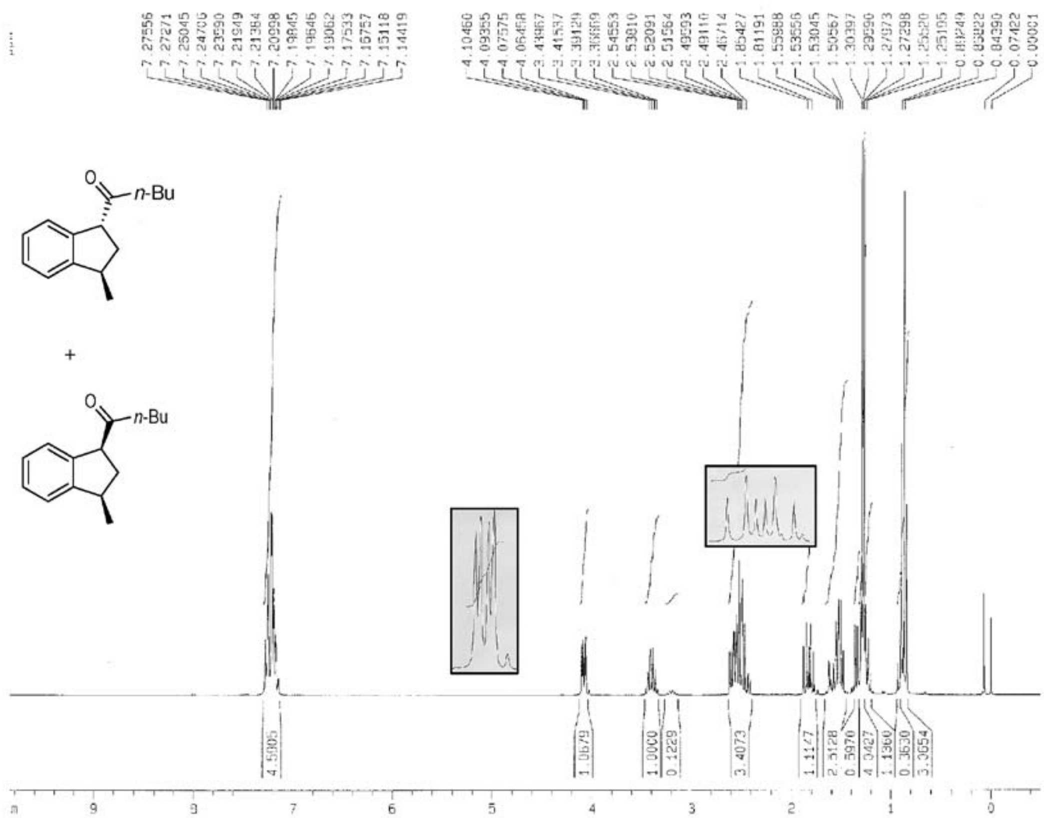

Figure S19. ^{1}H NMR spectrum of **5l** ($CDCl_3$, TMS, 300 MHz, δ).

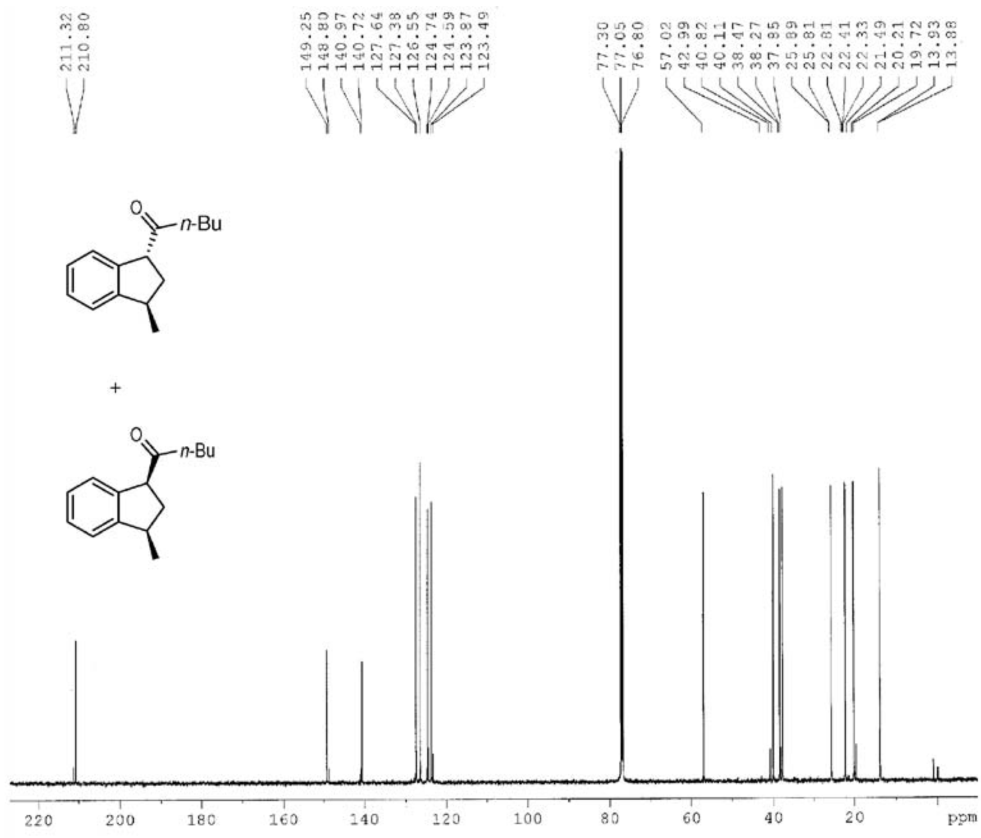

Figure S20. ^{13}C NMR spectrum of **5l** ($CDCl_3$, TMS, 75 MHz, δ).

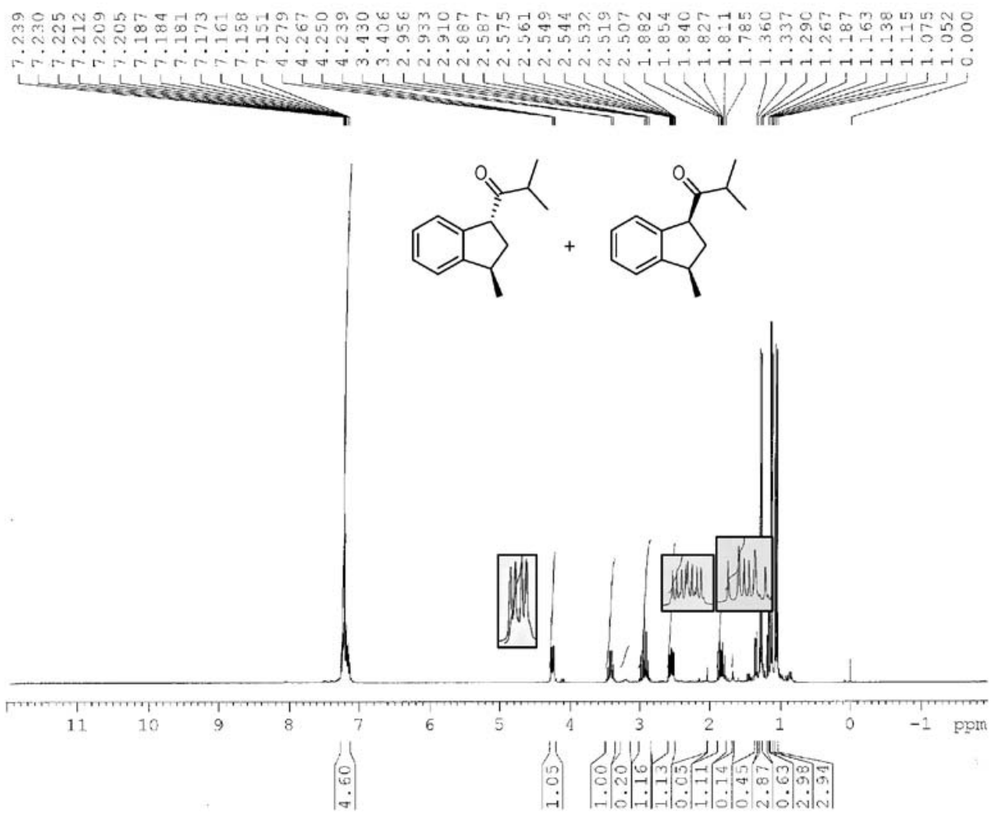

Figure S21. [1]H NMR spectrum of **5m** ($CDCl_3$, TMS, 300 MHz, δ).

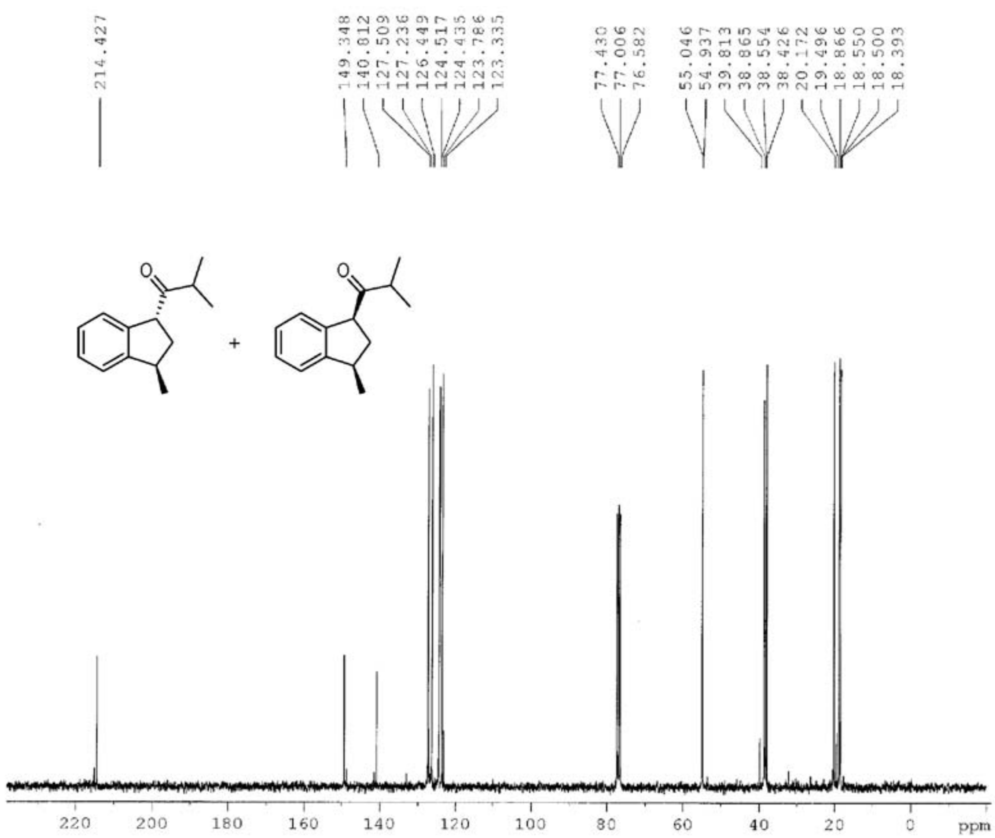

Figure S22. [13]C NMR spectrum of **5m** ($CDCl_3$, TMS, 75 MHz, δ).

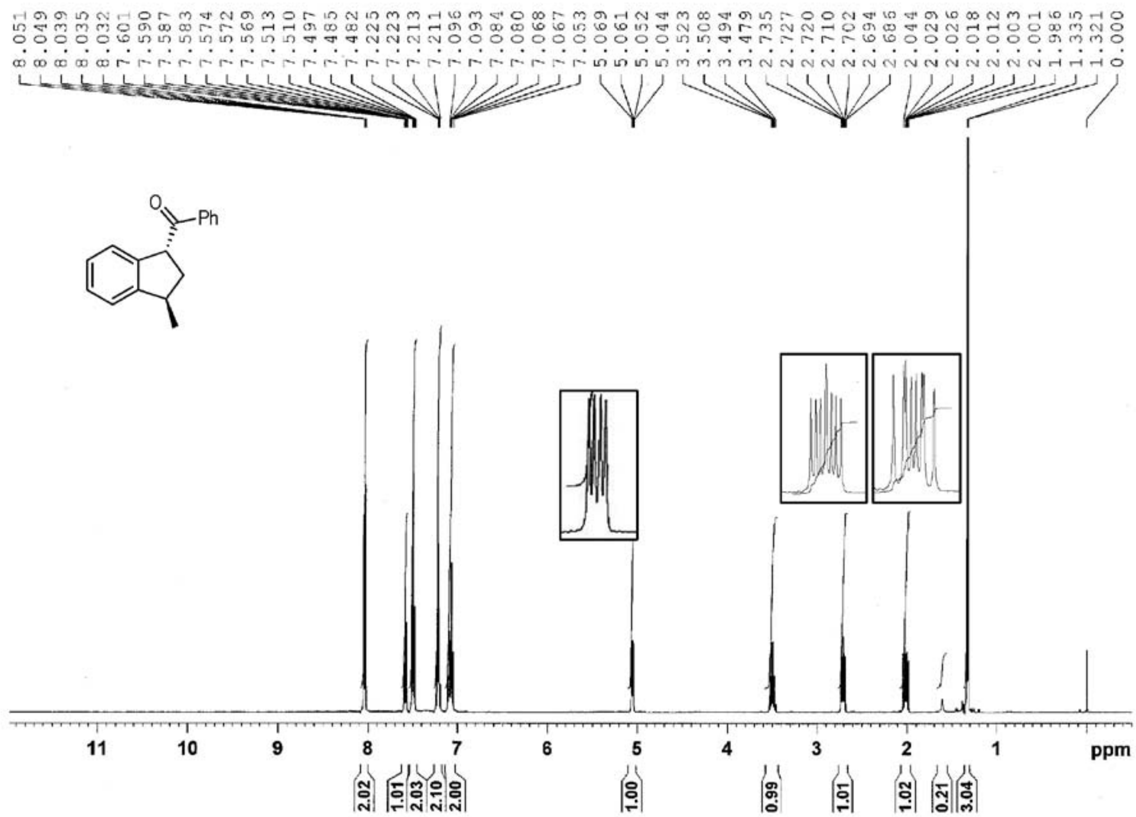

Figure S23. [1]H NMR spectrum of **5n** ($CDCl_3$, TMS, 500 MHz, δ).

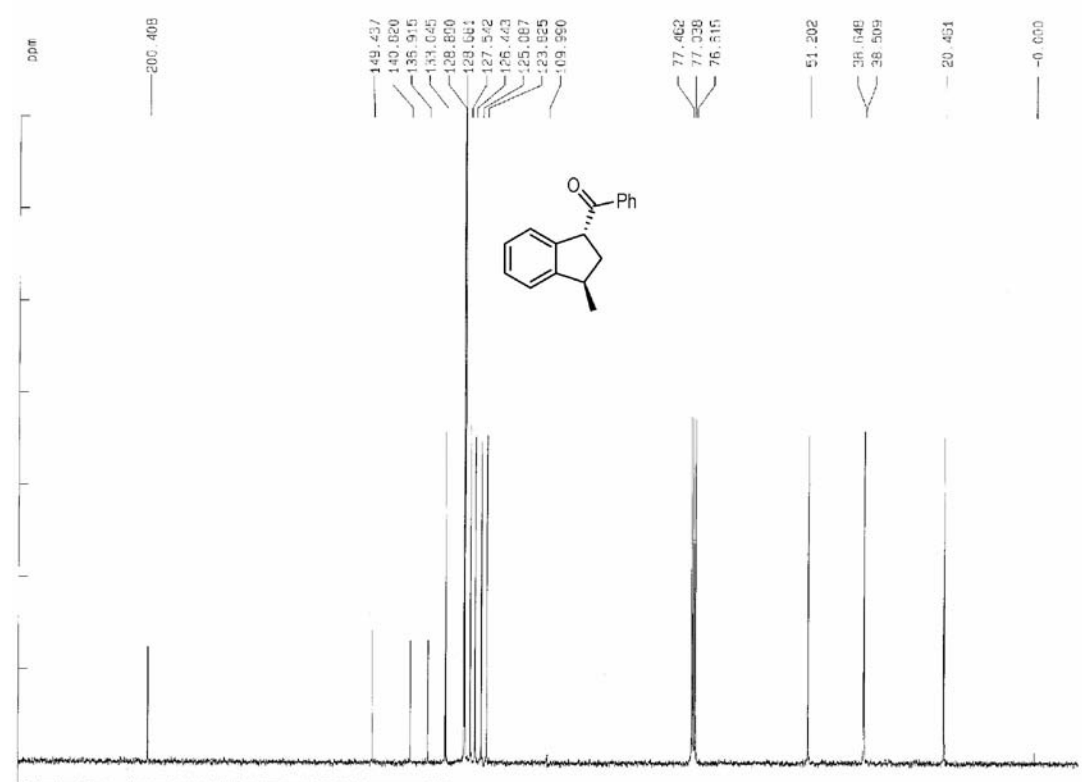

Figure S24. [13]C NMR spectrum of **5n** ($CDCl_3$, TMS, 75 MHz, δ).

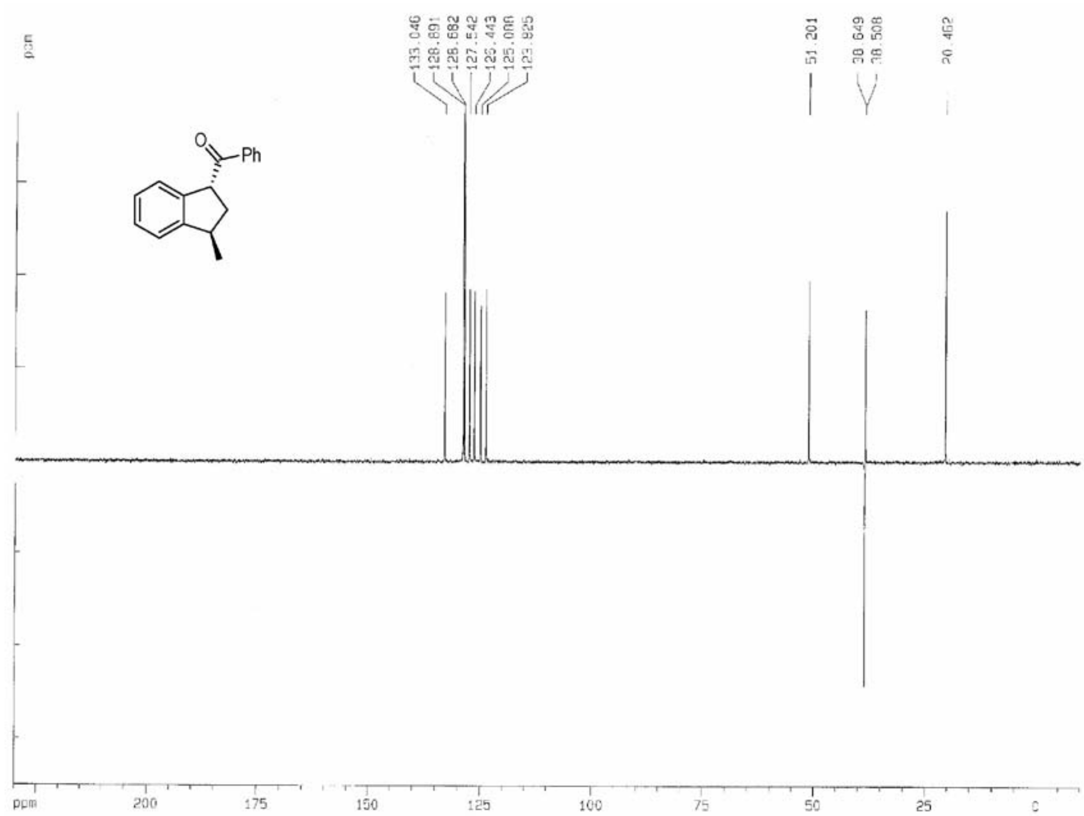

Figure S25. DEPT 135 spectrum of **5n** ($CDCl_3$, TMS, 75 MHz, δ).

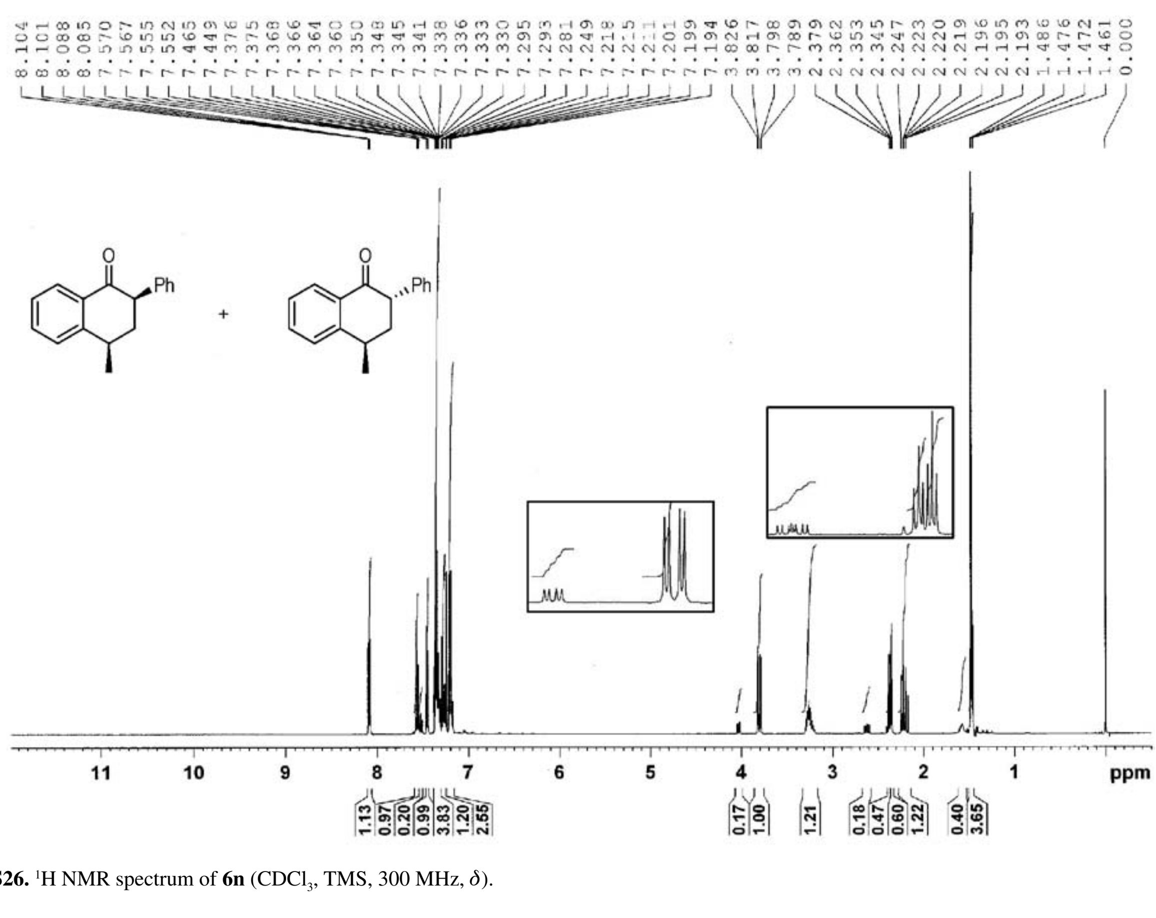

Figure S26. [1]H NMR spectrum of **6n** ($CDCl_3$, TMS, 300 MHz, δ).

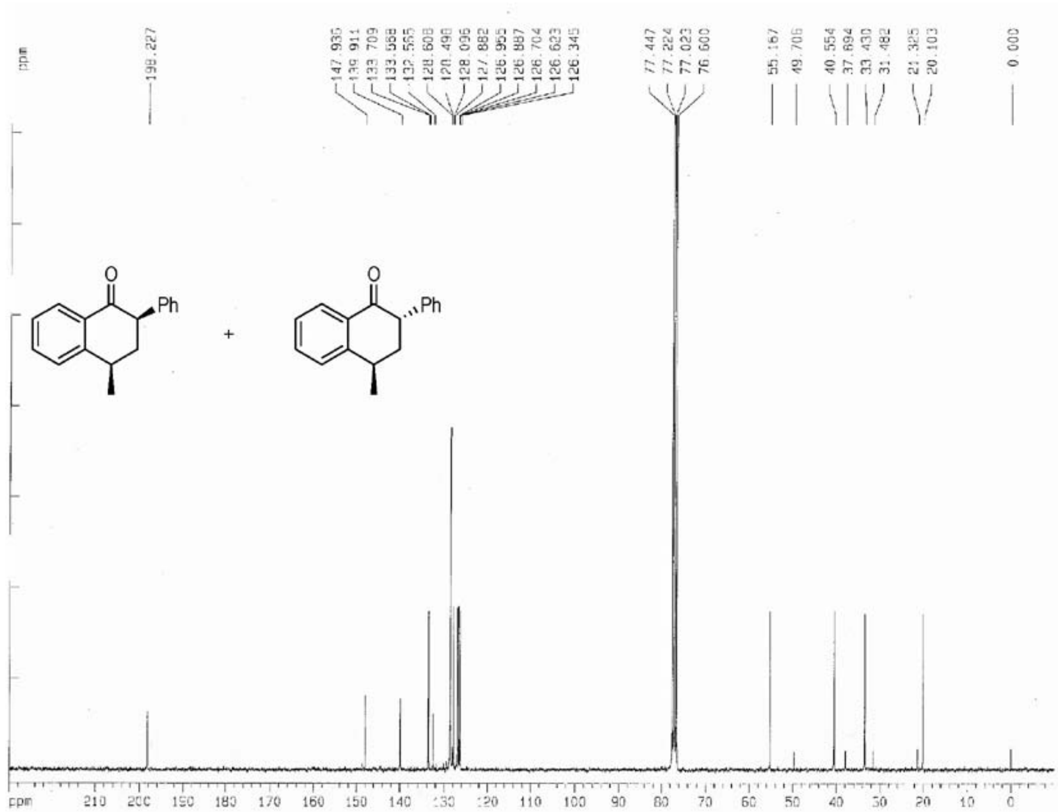

Figure S27. ^{13}C NMR spectrum of **6n** ($CDCl_3$, TMS, 75 MHz, δ).

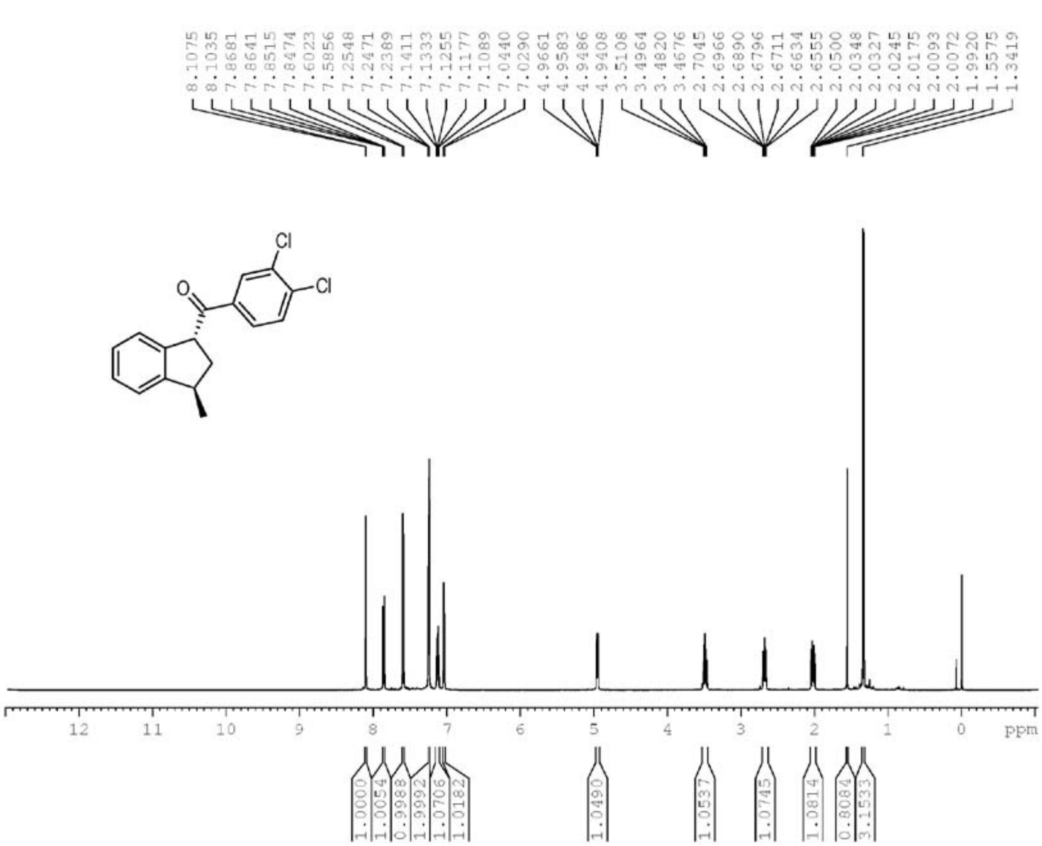

Figure S28. ^{1}H NMR spectrum of **5o** ($CDCl_3$, TMS, 500 MHz, δ).

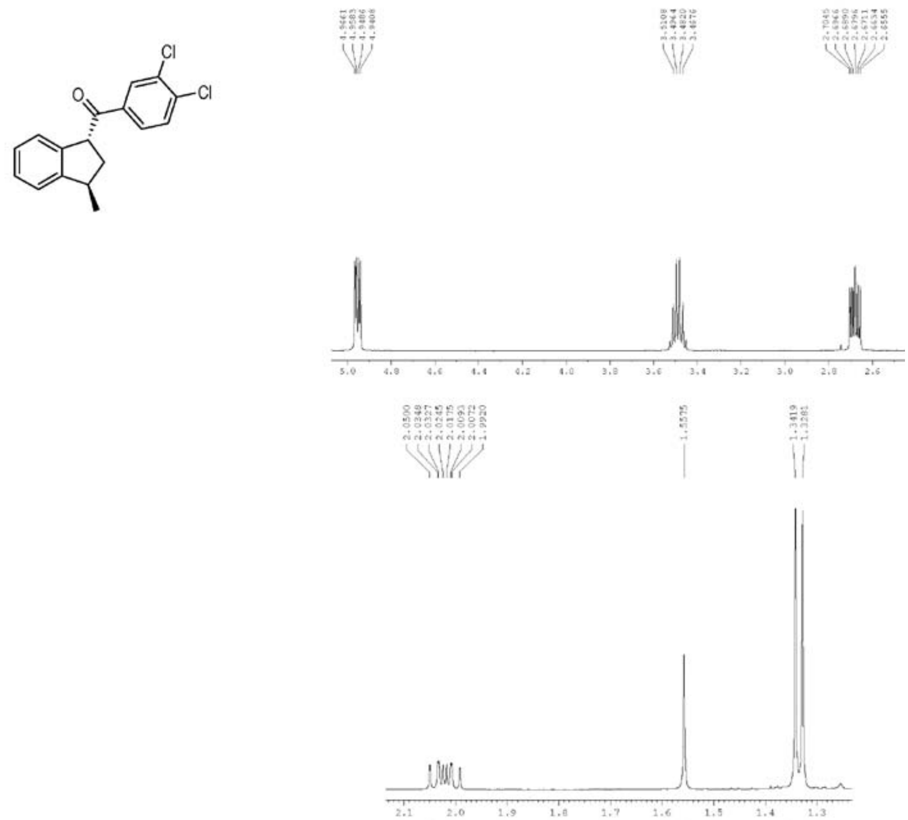

Figure S29. ¹H NMR spectrum of **5o** ($CDCl_3$, TMS, 500 MHz, δ) - expansion.

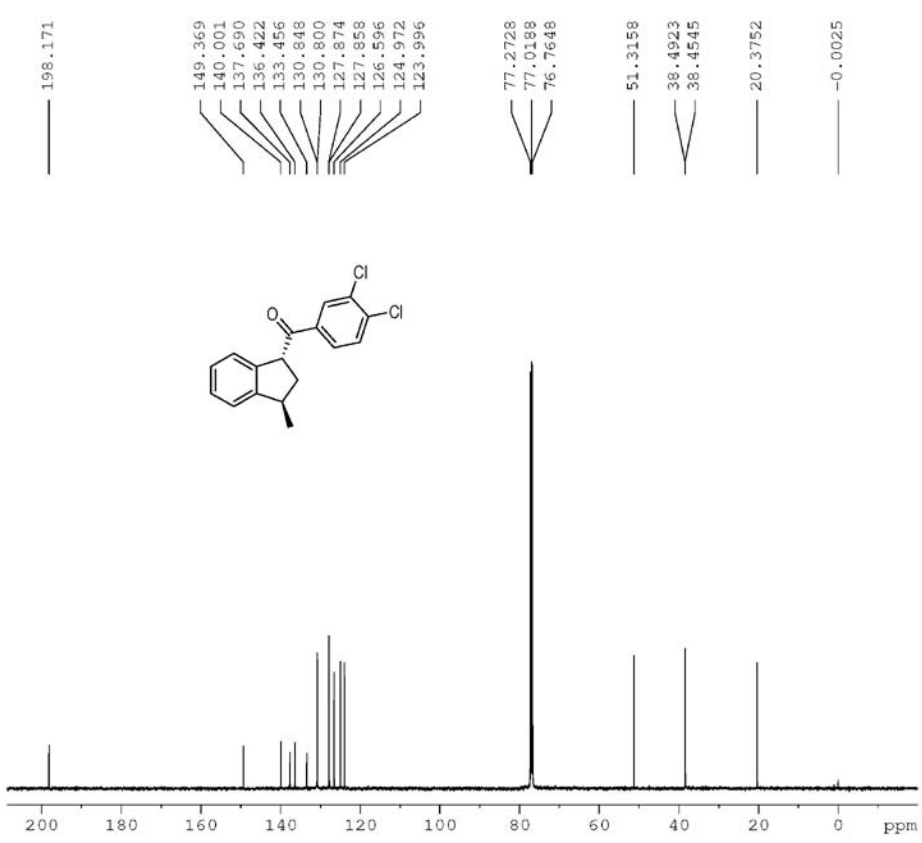

Figure S30. ¹³C NMR spectrum of **5o** ($CDCl_3$, TMS, 125 MHz, δ).

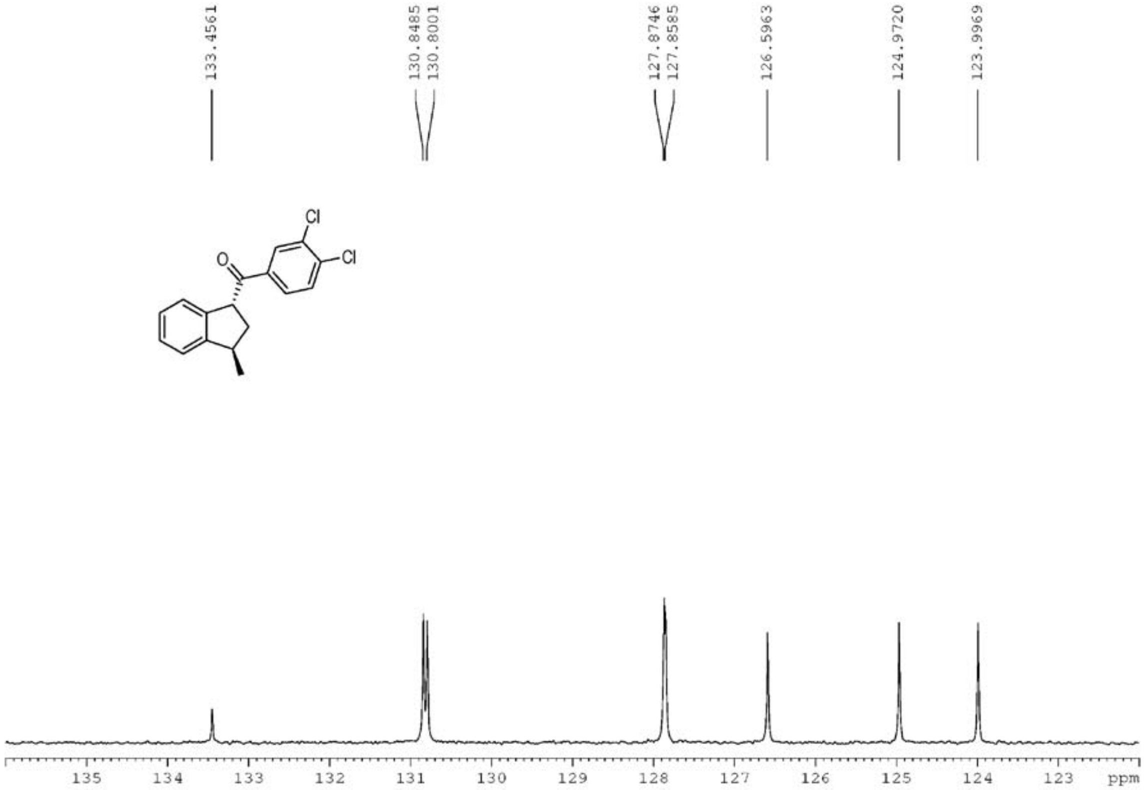

Figure S31. ^{13}C NMR spectrum of **5o** ($CDCl_3$, TMS, 125 MHz, δ) - expansion.

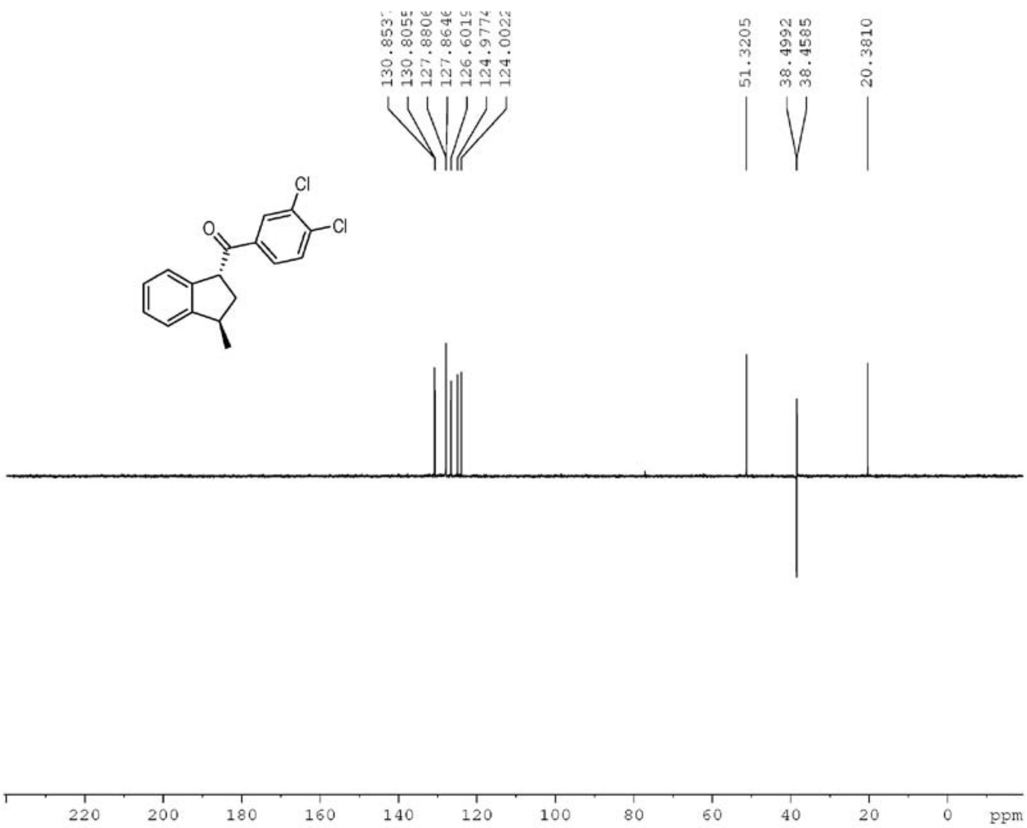

Figure S32. DEPT 135 spectrum of **5o** ($CDCl_3$, TMS, 125 MHz, δ).

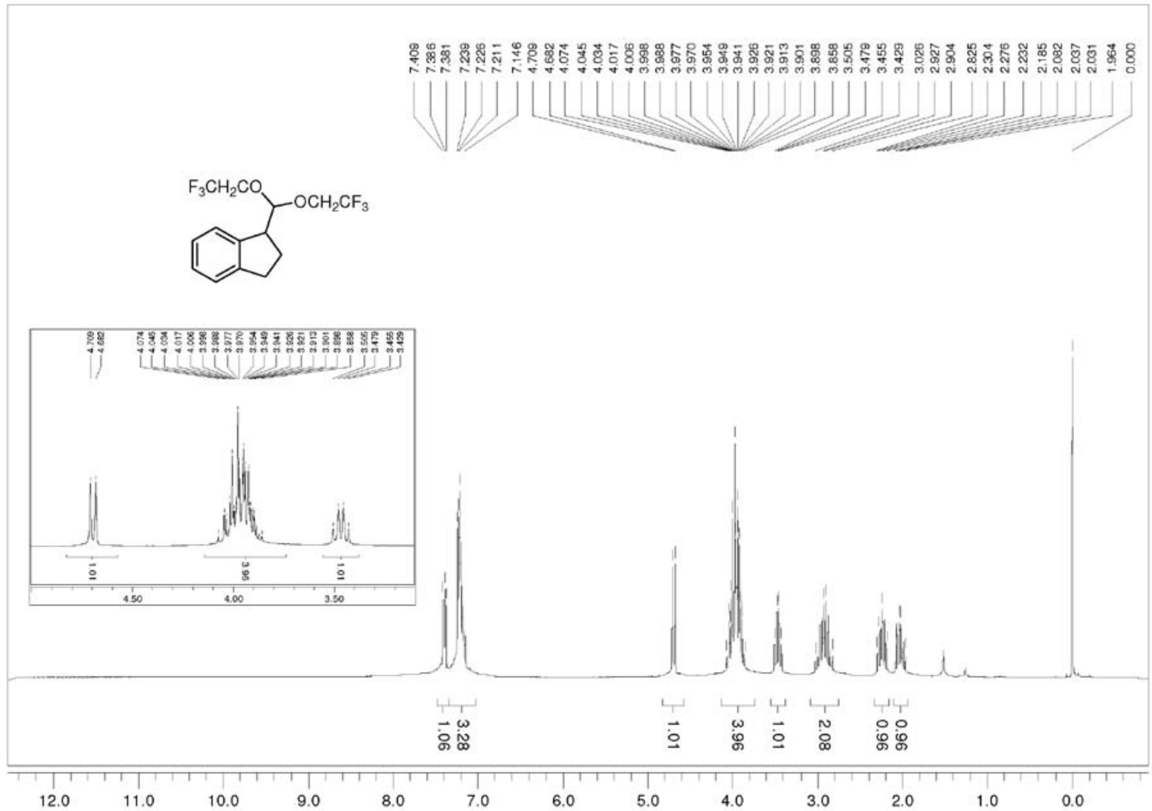

Figure S33. ^{1}H NMR spectrum of **8a** ($CDCl_3$, TMS, 300 MHz, δ).

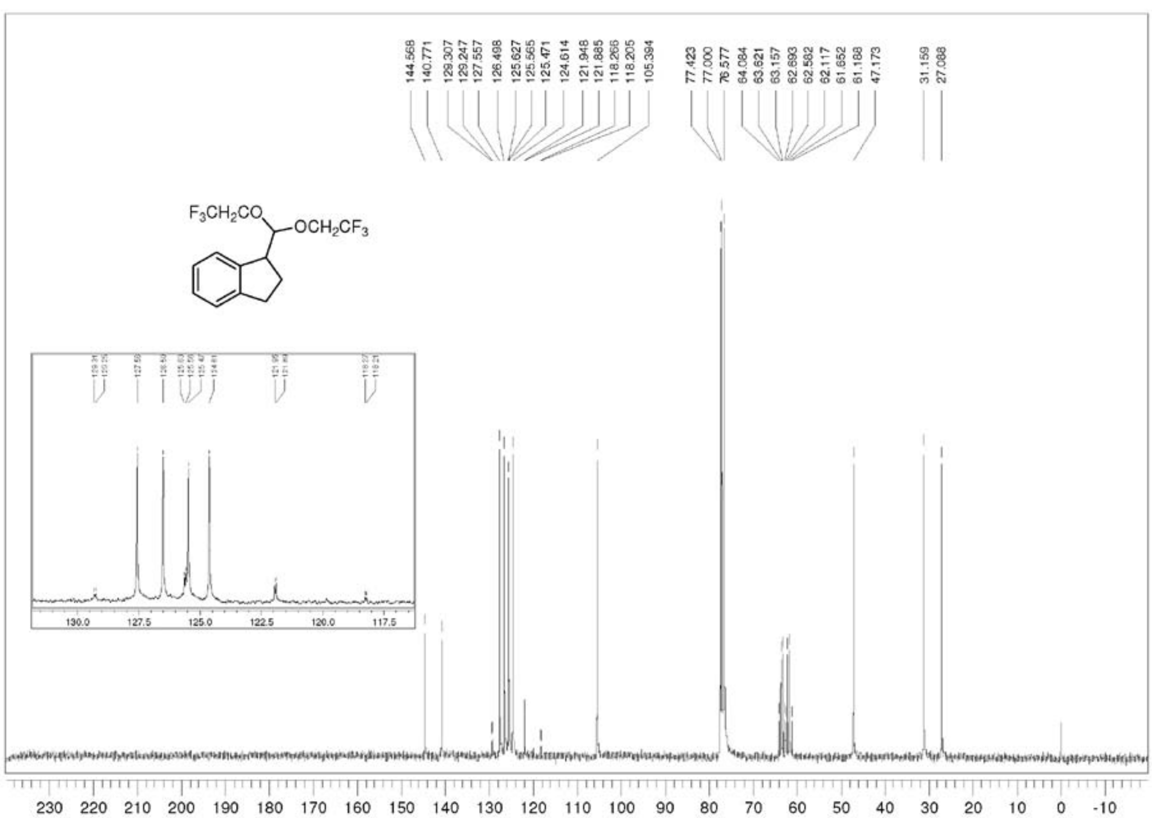

Figure S34. ^{13}C NMR spectrum of **8a** ($CDCl_3$, TMS, 75 MHz, δ).

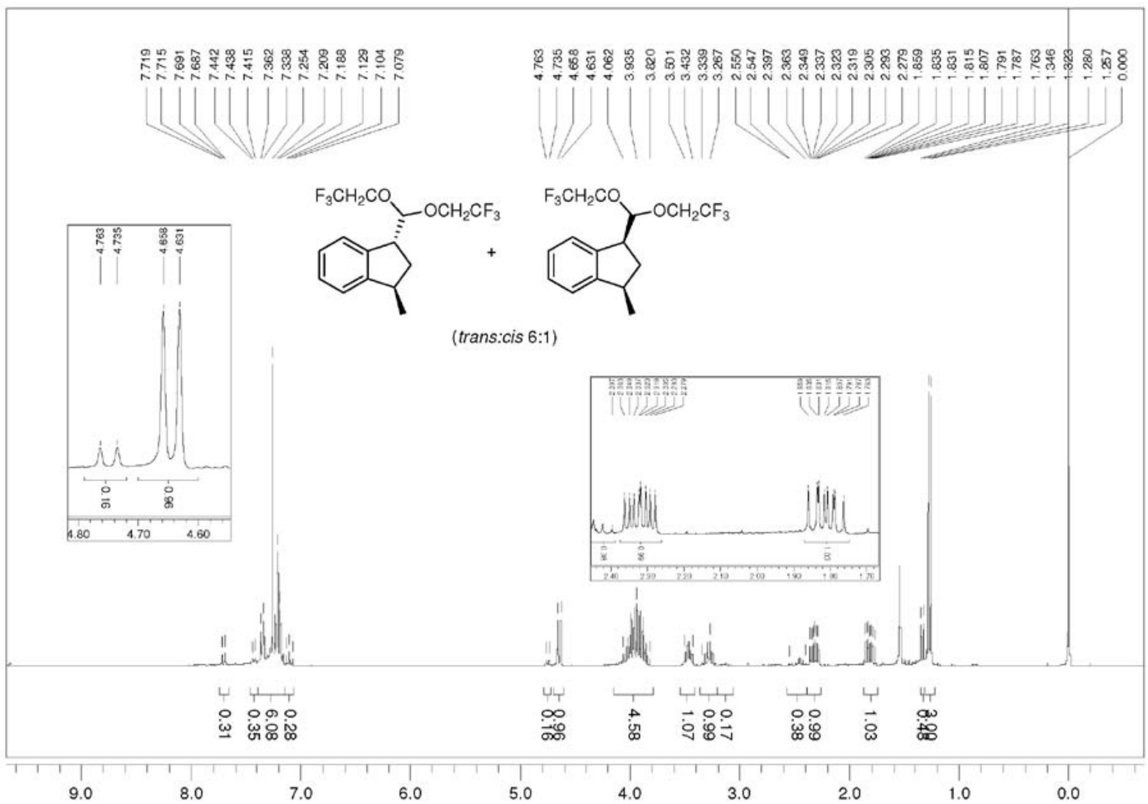

Figure S35. ^1H NMR spectrum of **8b** ($CDCl_3$, TMS, 300 MHz, δ).

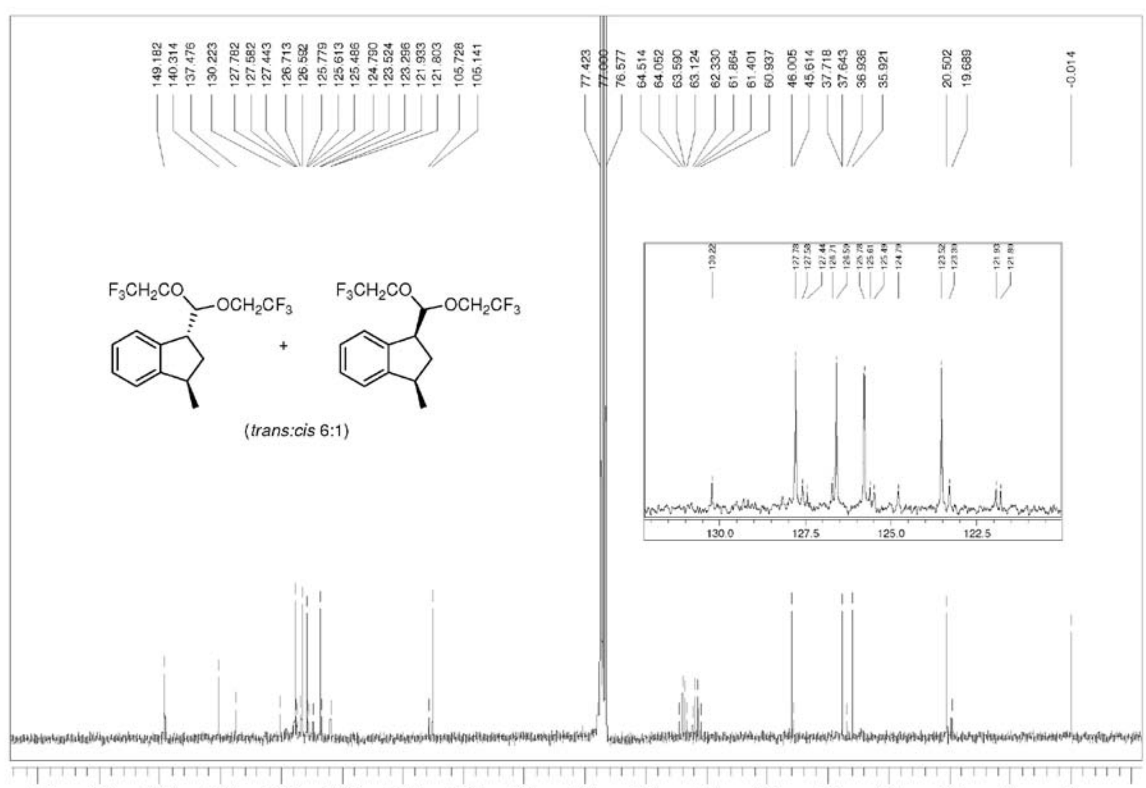

Figure S36. ^{13}C NMR spectrum of **8b** ($CDCl_3$, TMS, 75 MHz, δ).

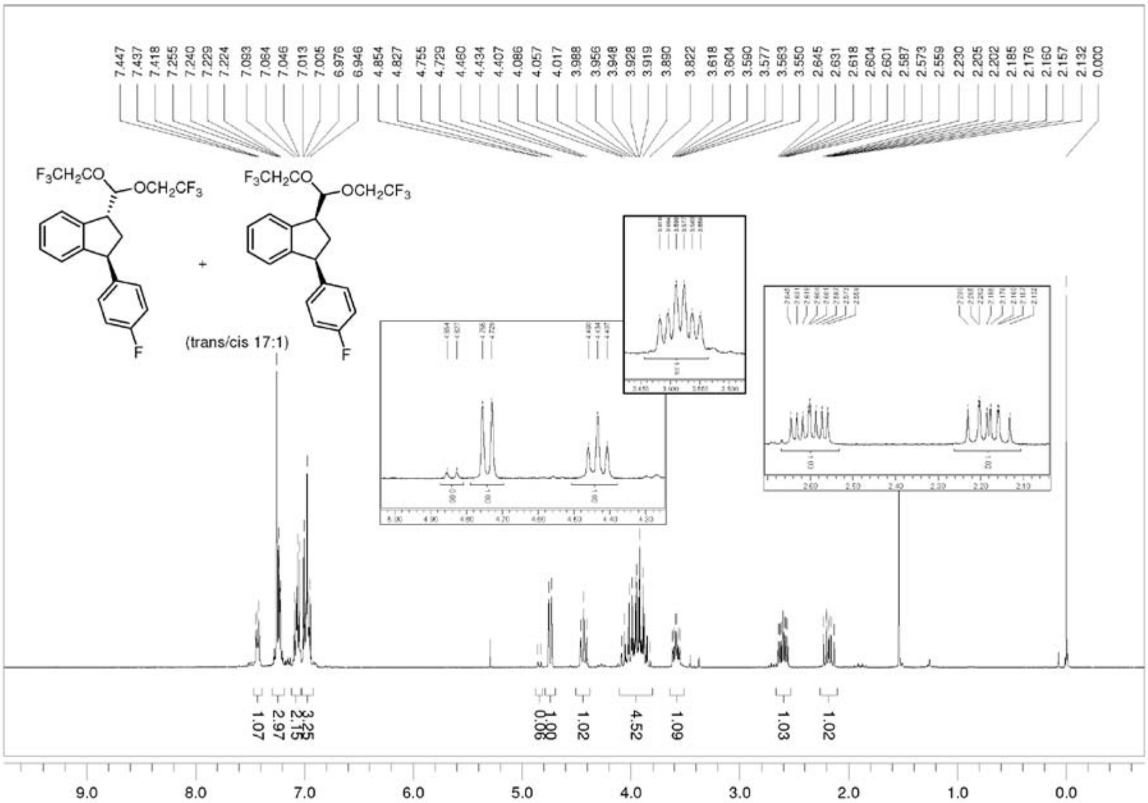

Figure S37. ^{1}H NMR spectrum of **8q** ($CDCl_3$, TMS, 300 MHz, δ).

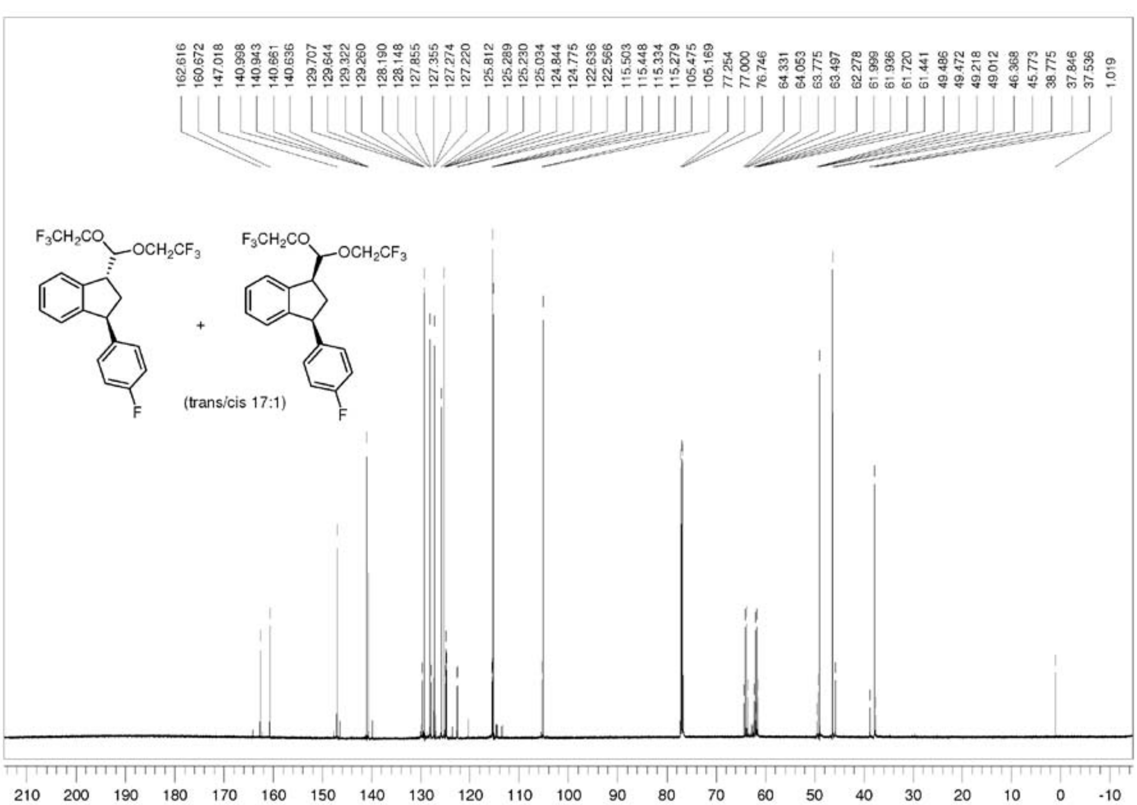

Figure S38. ^{13}C NMR spectrum of **8q** ($CDCl_3$, TMS, 125 MHz, δ).

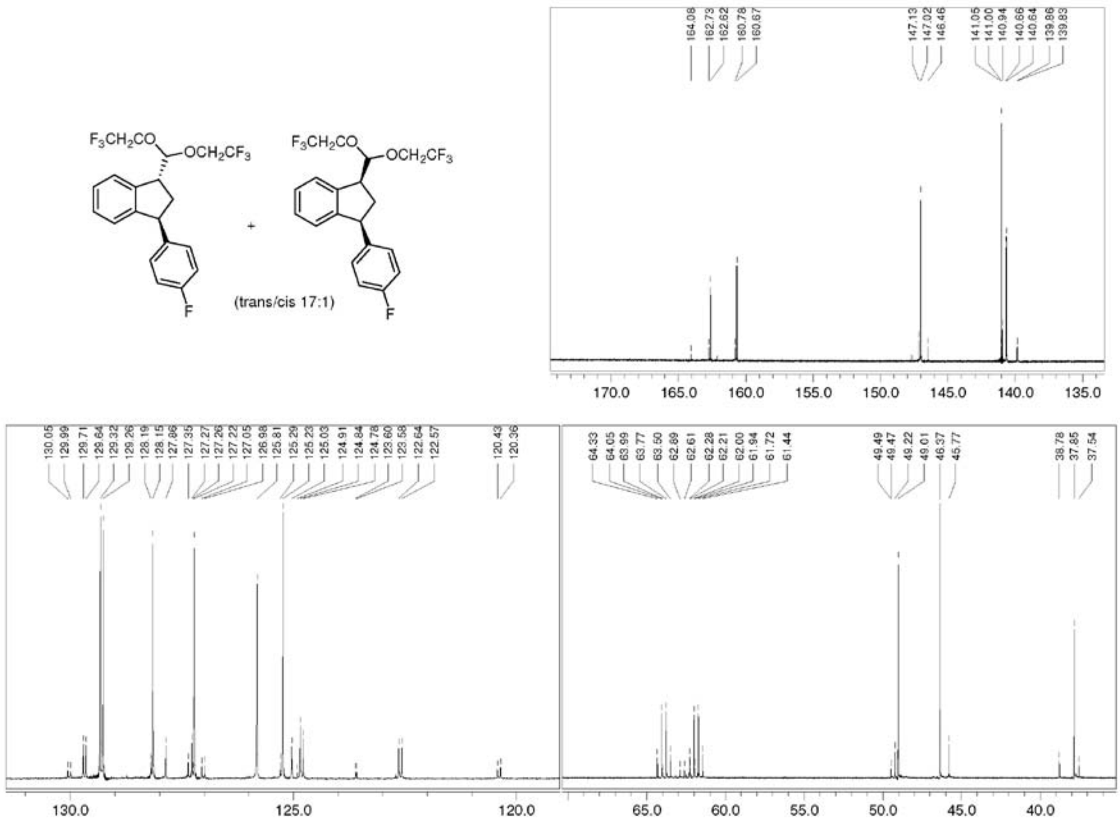

Figure S39. ^{13}C NMR spectrum of **8q** ($CDCl_3$, TMS, 125 MHz, δ) – expansions.

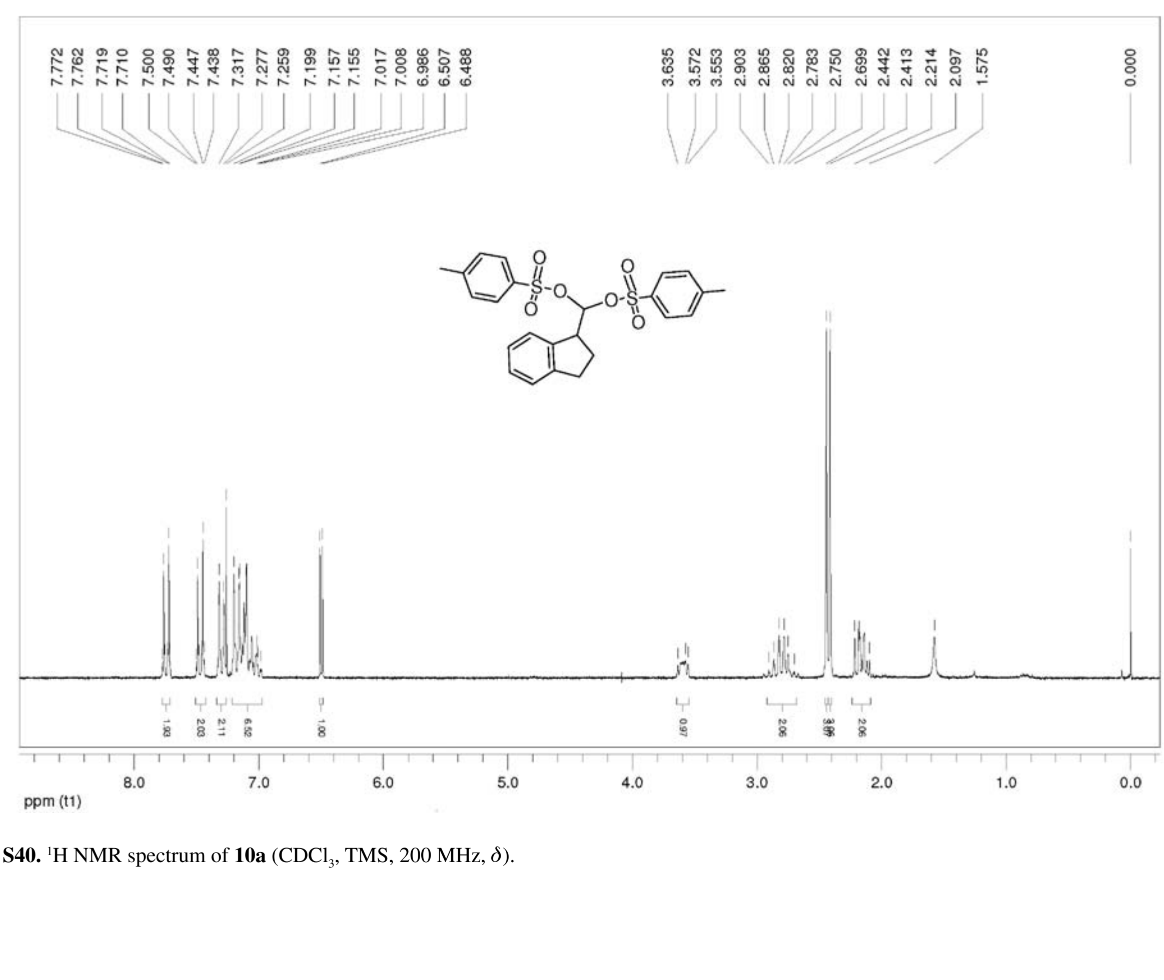

Figure S40. ^1H NMR spectrum of **10a** ($CDCl_3$, TMS, 200 MHz, δ).

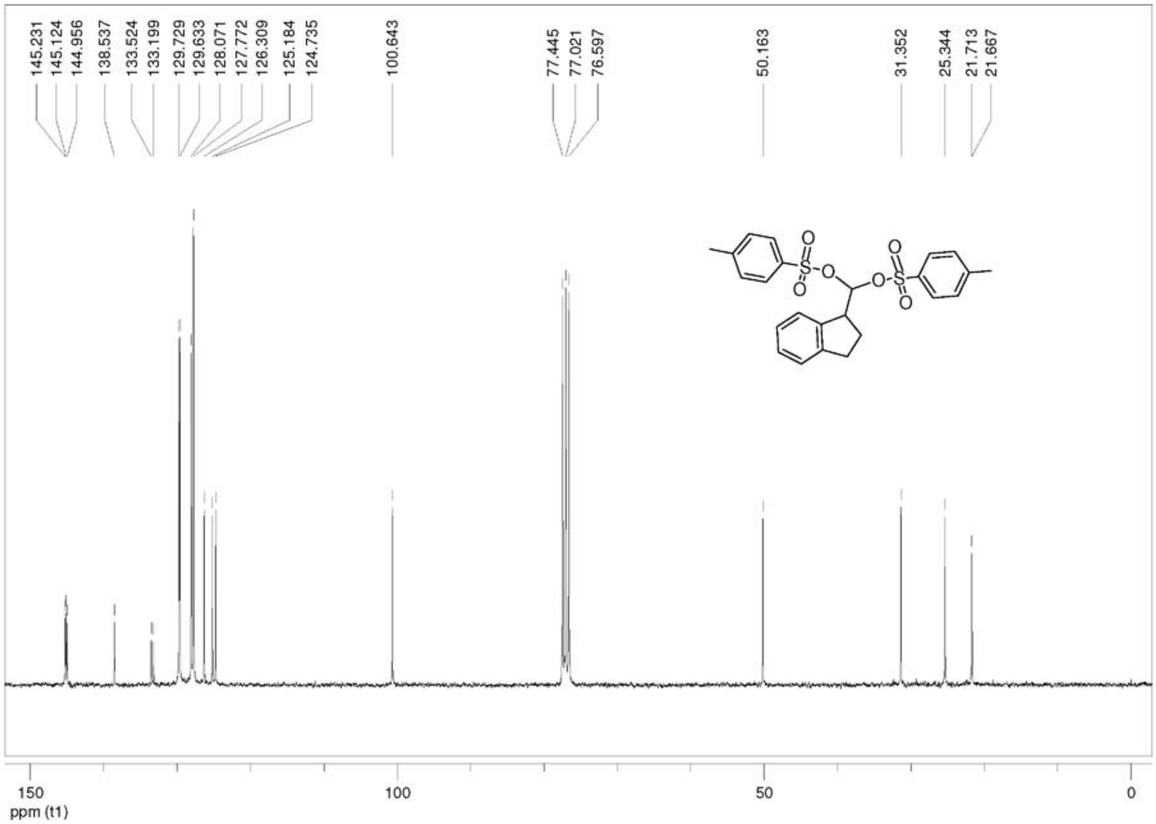

Figure S41. ^{13}C NMR spectrum of **10a** ($CDCl_3$, TMS, 50 MHz, δ).

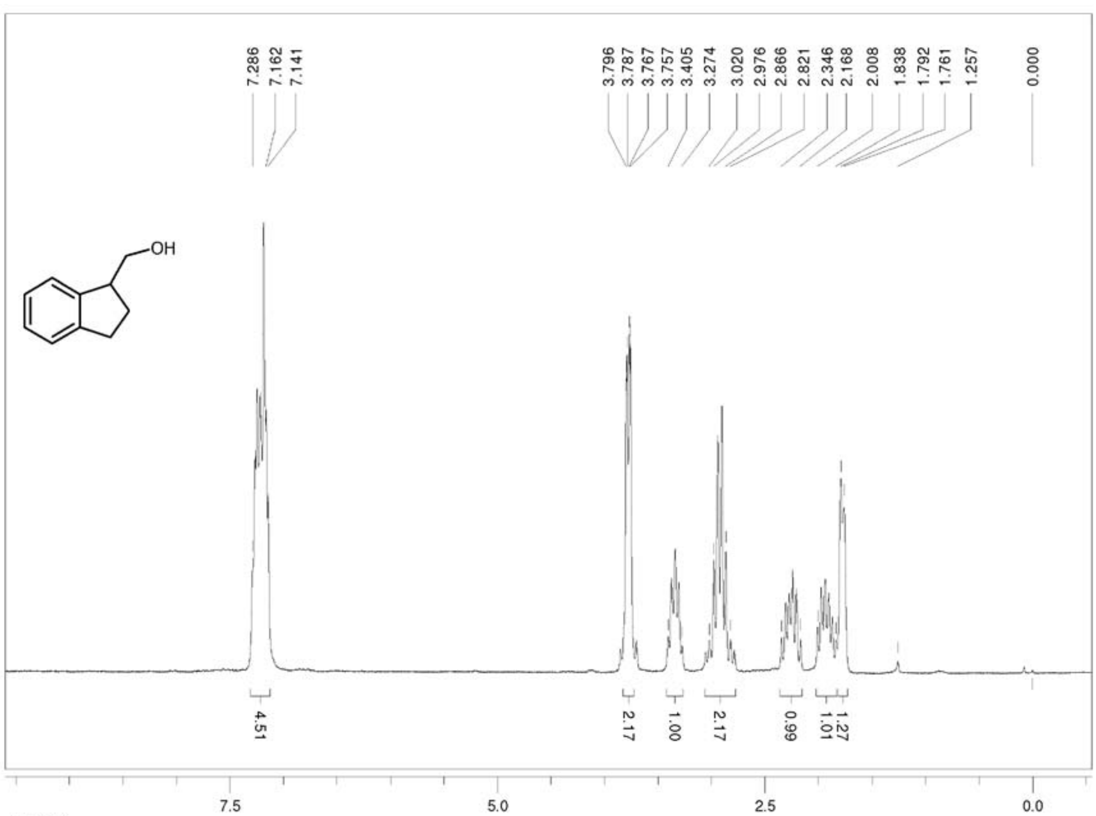

Figure S42. ^{1}H NMR spectrum of **9a** ($CDCl_3$, TMS, 200 MHz, δ).

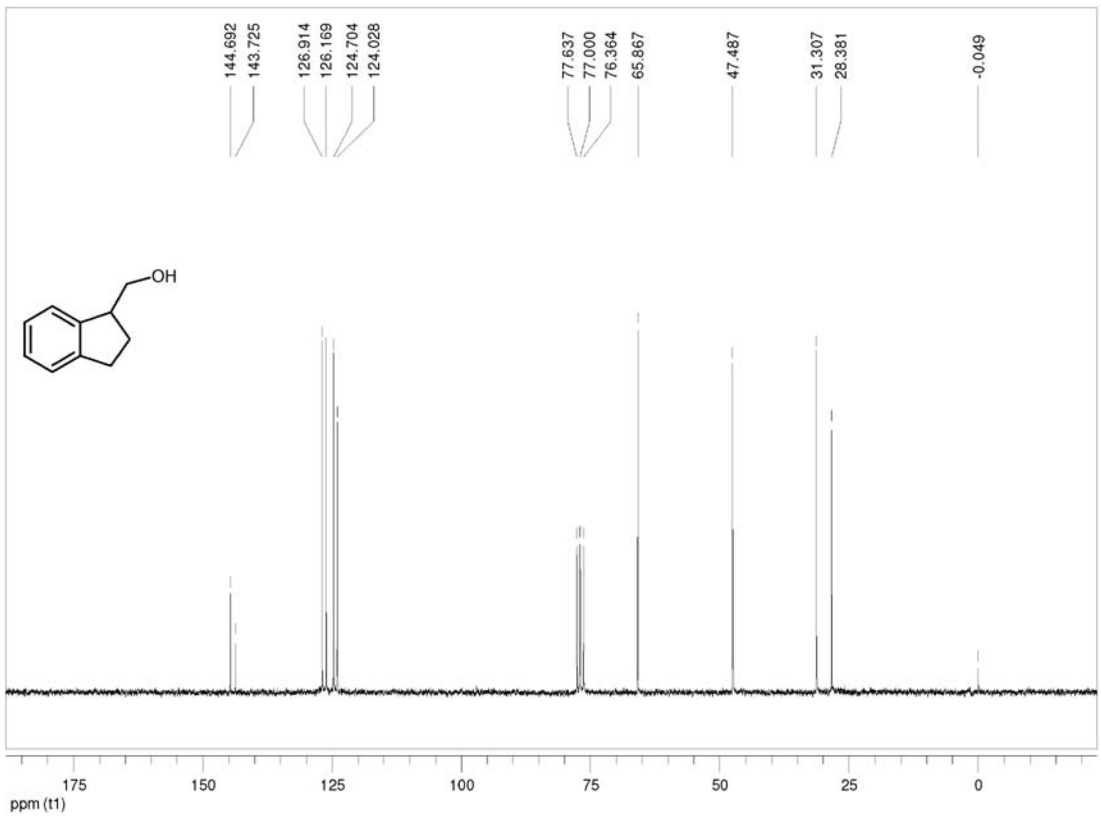

Figure S43. ^{13}C NMR spectrum of **9a** ($CDCl_3$, TMS, 50 MHz, δ).