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Graphical Abstract

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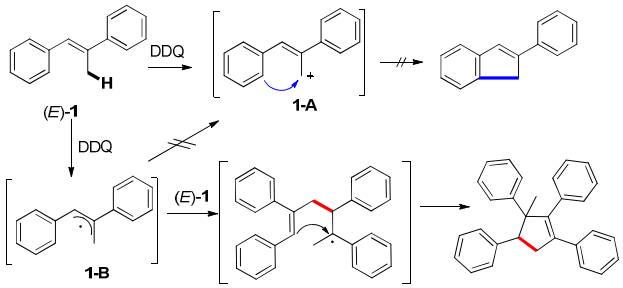
ABSTRACT

A direct DDQ-mediated dehydrogenative intramolecular cyclization of (Z)-1,2,3-triaryl substituted propylenes promoted by $Cu(OAc)_2$ was developed, providing 1,2-diarylindene derivatives in moderate to good yields (up to 92%) under mild conditions. This protocol provides a straightforward access to 1,2-diarylindenes *via* DDQ-mediated benzylic/ allylic sp^3 C-H bond activation.

1. Introduction

Indene derivatives are important cyclic compounds that serve as building blocks for biologically active compounds,[1] valuable ligands for indenyl metal complexes,[2] as well as functional materials.[3] Thus, a great number of approaches for constructing indene have been well developed. For example, intramolecular cyclization of phenyl-substituted allylic alcohols, *via* an *in-situ* formed allylic cation key intermediate, can generate indenes in good to excellent yields in the presence of strong acid or boron trifluoride etherate.[4] In addition, transition metals were also widely used for the intermolecular[5] or intramolecular[6] cyclization to form indene derivatives. Moreover, transition metals-catalyzed carbocyclization *via* C-H activation[7] represents a straightforward and powerful method. However, most of the carbocyclization reactions for indene formation were rhodium-catalyzed intermolecular reaction of alkynes with different arene substrates. To the best of our knowledge, direct intramolecular cyclization for the synthesis of indene *via* catalyzed C-H activation has been rarely reported.[7c]

Recently, we were dedicated to testing the feasibility of direct intramolecular dehydrogenative cyclization by employing 1,2-diarylpropylene substrate (*E*)-**1** as model substrate to construct indene compound *via* DDQ-mediated oxidative activation of terminal allylic C–H bond. Interestingly, an unexpected product 1,2,3,4-tetraphenyl cyclopentene was obtained instead of ~~desired in~~dene compound (Scheme 1).[8]



Scheme 1. Intermolecular cyclization of (*E*)-**1** *via* oxidative activation of terminal allylic C-H bond.

We proposed that the initially formed allylic radical **1-B** is active enough for coupling to another equivalent of (*E*)-**1**, followed by forming the cyclopentene, instead of generating the allylic cation **1-A** *via* further oxidation. Therefore, we further envisaged that introduction of a proper substituent on the terminal methyl group of (*E*)-**1** could inhibit the intermolecular coupling of allylic radical **1-B**. Thus, this relative stable radical of **1-B** analog could then be subjected to a further SET process to form an allyic cation species, which may facilitate the direct intramolecular dehydrogenative cyclization. In this paper, we would like to demonstrate an efficient approach to 1,2-diarylindene derivatives *via* DDQ-mediated dehydrogenative intramolecular cyclization of (*Z*)-1,2,3-triaryl substituted propylenes promoted by $Cu(OAc)_2$.

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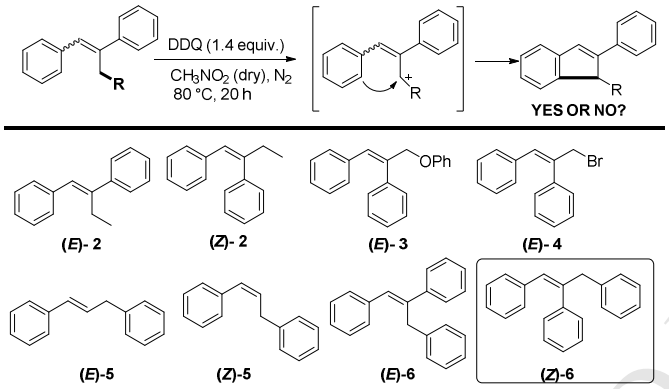
2. Results and discussion

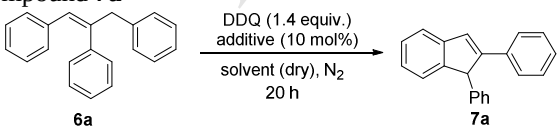
Initially, a series of substituted propenes **2-6** were prepared to test the feasibility of direct cyclization to construct indene ring as shown in scheme 2. Unfortunately, (*E*)- and (Z)-**2**, as well as (*E*)- and (Z)-**5** all failed to give desired indene products, while (*Z*)-**2** and (*E*)-**5** were found to afford ketone products presumably *via* the nucleophilic attack to *in-situ* formed cations by water instead of the cyclization. Phenoxy and bromide substituted compounds (*E*)-**3** and (*E*)-**4** were found not proper for the intramolecular oxidative cyclization. It should be pointed out that Batey and his coworkers[4c] recently reported a synthesis of highly substituted indenes by treating 1,3-diaryl substituted allylic alcohols with Lewis acids. They found that 2-unsubstituted (*E*)-1,3-diphenylprop-2-en-1-ol was not suitable for the indene formation as well. To our delight, the cyclization of (*Z*)-1,2,3-triphenyl propylene **6** was successful to provide 1,2-diphenyl indene **7** in 44% yield (Table 1, entry 1), although (*E*)-isomer **6** failed to afford the desired product **7** presumably due to the steric hindrance from three adjacent phenyl groups in the step of DDQ-mediated cation formation.



Scheme 2. Substrates investigation for intramolecular dehydrogenative cyclization.

Encouraged by this result, we then turned to optimize the reaction condition as shown in table 1. Initially, palladium salts which are commonly used in the sp^3 C-H bond activation[9] were tested as promoter. To our delight, the yield of **7a** was improved to 70% from 44% by using 10 mol% of $PdCl_2$ at 60 °C (Table 1, entries 1-3). However, $Pd(OAc)_2$ was found not effective (Table 1, entry 5). Further screening of a series of Fe and Cu salts turned out that **7a** can be obtained in 92% of yield in the presence of $Cu(OAc)_2•H_2O$ (Table 1, entries 6-10). Other solvents were tested and nitromethane was found most suitable (Table 1, entries 11-17). Moreover, decreasing the amount of DDQ or $Cu(OAc)_2•H_2O$ slightly decreased the yield (Table 1, entries 18-19).

Table 1. Optimization of reaction conditions for the formation of compound **7a**[a]



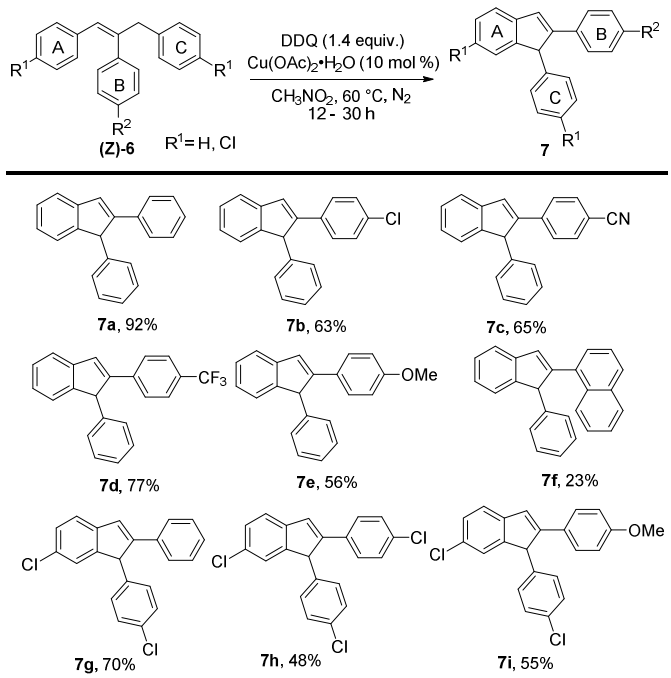
Entry	Additive	Solvent	Temp. (°C)	Yield (%)[b]
1	/	CH_3NO_2	80	44
2	$PdCl_2$	CH_3NO_2	80	68
3	$PdCl_2$	CH_3NO_2	60	70
4	$PdCl_2$	CH_3NO_2	r.t.	46
5	$Pd(OAc)_2$	CH_3NO_2	60	44
6	$FeCl_2$	CH_3NO_2	60	24
7	$FeCl_3$	CH_3NO_2	60	20
8	CuBr	CH_3NO_2	60	42
9	$CuCl_2$	CH_3NO_2	60	69
10	**$Cu(OAc)_2•H_2O$**	**CH_3NO_2**	**60**	**92**
11	$Cu(OAc)_2•H_2O$	Toluene	60	trace
12	$Cu(OAc)_2•H_2O$	THF	60	trace
13	$Cu(OAc)_2•H_2O$	DMSO	60	N.R.
14	$Cu(OAc)_2•H_2O$	1,4-Dioxane	60	N.R.
15	$Cu(OAc)_2•H_2O$	DCM	60	43
16	$Cu(OAc)_2•H_2O$	DCE	60	70
17	$Cu(OAc)_2•H_2O$	CH_3CN	60	80
18[c]	$Cu(OAc)_2•H_2O$	CH_3NO_2	60	85
19[d]	$Cu(OAc)_2•H_2O$	CH_3NO_2	60	85

[a] Unless otherwise noted, the reaction was performed under N_2 atmosphere, with **6a** (0.2 mmol) and DDQ (1.4 equiv.), in the presence of 10 mol% of catalyst in 2 mL of solvent. [b] Isolated yields. [c] 5 mol% of catalyst was used. [d] DDQ (1.2 equiv.) was used.

With optimized reaction conditions in hand, a series of 1, 2, 3-triaryl propylene derivatives **6b-i** were then investigated. Substrates with different substituted at *para* position of ring B were explored since substituent at C-2 of propylene was necessary as mentioned before. It was found that substrates with strong electron-withdrawing groups such as CN and CF_3 afforded slightly higher yields than 4-Cl substituted compound (Scheme 3, **7b-7d**). Interestingly, the transformation of substrates with strong electron-donating substituent such as methoxy group was also successful (Scheme 3, **7e**), unlike the cases of naphthalenes[8a] and cyclopentenes[8b] synthesis, in which the substrates with methoxy group on aryl ring failed to afford the desired products. It was also found that bulky 2-naphthyl indene **7f** can be obtained, albeit in lower yield (Scheme 3, 23%). The reaction of substrate **6g** with 4-Cl substituent on both ring A and C underwent also smoothly, affording the corresponding product in 70% yield (Scheme 3, **7g**). However, only moderate yields were obtained when substrates containing substituent on all three aryl rings. (Scheme 3, **7h-7i**).

Further investigation of mono-substituted substrates suggested a substituent effect on regioselectivity of cyclization. It should be noticed that cyclization of **6j-6s** generated the inseparable mixture of regioisomers in moderate overall yields. For *ortho*- and *para*-substituted substrates with electron-withdrawing groups, cyclization occurred preferentially at the non-substituted ring (Table 2, entries 1-5), while reaction of **6o** with a *p*-F group afforded an exclusive regioisomer product **7o** (Table 2, entry 6). In contrast, *p*-methyl-substituted substrate **6p** showed the opposite selectivity because of the rich electron density of electron-donating group substituted ring (Table 2, entry 7). For the substrates with *meta*-substituent, **6q** and **6r**, three isomers were found with poor regioselectivity, and the structure

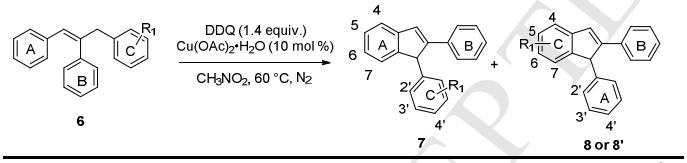
assignment for **8** over **8'** was not determined (Table 2, entries 8-9). Similarly, transformation of di-fluoro substituted **6s** gave two iosmers with poor selectivity of regioisomer of **7s** and **8s** (Table 2, entry 10).



Scheme 3. Indene formation from (*Z*)- triaryl substituted propylenes **6**.

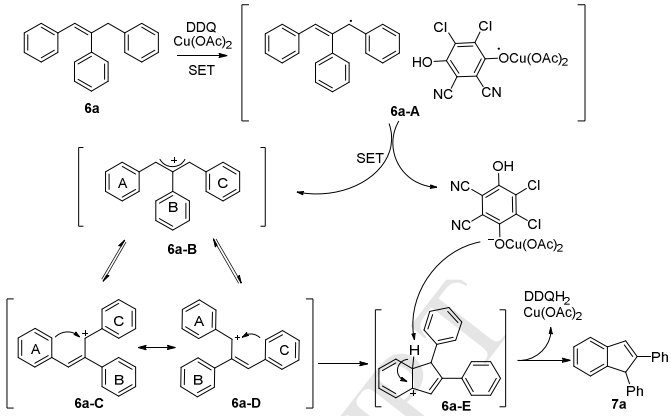
To further understand this intramolecular dehydrogenative cyclization reaction, excess amount of TEMPO was added to the reaction of **6a** and the yield of product **7a** decreased significantly to 29% under the optimal reaction condition. Moreover, the reaction was fully suppressed by TEMPO without the additive, which implies that a radical process was involved in the initial oxidative step.

Table 2. Regioselectivity study of the cyclization of various substituted **6** [a]



Entry	R^1	Isolated indene 7/ 8/ 8'	Ratio[b]	Yield[c] (%)
1	2-F (**6j**)	**7j** (2'-F)/ **8j** (4-F)	5:1	68
2	2-Br (**6k**)	**7k** (2'-Br)/ **8k** (4-Br)	2.8:1	62
3	4-Cl (**6l**)	**7l** (4'-Cl)/ **8l** (6-Cl)	2.2:1	40
4	4-Br (**6m**)	**7m** (4'-Br)/ **8m** (6-Br)	1.7:1	45
5	4-CF_3 (**6n**)	**7n** (4'-CF_3)/ **8n** (6-CF_3)	5:1	49
6	4-F(**6o**)	**7o** (4'-F)	100:0	53
7	4-Me (**6p**)	**7p** (4'-Me)/ **8p** (6-Me)	1:2	30
8	3-F (**6q**)	**7q** (3'-F)/ **8q** (5-F)/ **8'q** (7-F)	7.4:9.1:1	60
9	3-Br (**6r**)	**7r** (3'-Br)/ **8r** (5-Br)/ **8'r** (7-Br)	10:3.5:1	57
10	3,5-F (**6s**)	**7s** (3',5'-F)/ **8s** (5,7-F)	1.6:1	66

[a] Unless otherwise noted, the reaction was performed under N_2 atmosphere, with **6** (0.2 mmol) and DDQ (1.4 equiv.), in the presence of 10 mol% of $Cu(OAc)_2•H_2O$ in 2 mL of CH_3NO_2.[b] Crude ratio was calculated from ^1H NMR analysis, according to the empirical regularity of ref. 4c. [c] Overall yields. A mixture of regioisomers which cannot be separated was isolated together following silica gel column chromatographic purification.



Scheme 4. Proposed reaction mechanism.

On the basis of these observations, a tentative mechanism was proposed in scheme 4. Initially, substrate **6a** underwent hydrogen abstraction through a copper-promoted single electron transfer process by DDQ to form the radical specie **6a-A**.[10] The radical species **6a-A** was then further oxidized to generate "M" conformation of allylic cation **6a-B** which cannot directly undergo cyclization.[4c] Isomerization of **6a-B** through bond rotation gave "S" conformation of intermediate **6a-C** and **6a-D**, followed by Friedel–Crafts cyclization,[5e] and subsequent proton elimination afforded the final indene product **7a**. In the case that ring **A** is different from ring **C**, cyclization of intermediate **6a-C** and **6a-D** would generate regioisomers as mentioned before, and the regioselectivity is mainly depended on the electronical effect of the substituent. For example, substrate **6o** with strong electron-withdrawing group underwent Friedel–Crafts cyclization to afford **7o** with an exclusive regioselectivity.

3. Conclusion

In conclusion, an efficient copper-promoted dehydrogenative intramolecular cyclization was developed for the synthesis of 1,2-diarylindenes in moderate to excellent yields from (*Z*)-1,2,3-triaryl substituted propylenes. This protocol provides a straightforward approach to 1,2-diarylindenes *via* DDQ-mediated benzylic/ allylic sp^3 C-H bond activation. Further studies on the scope, mechanism and applications of this transformation are in progress in our laboratory.

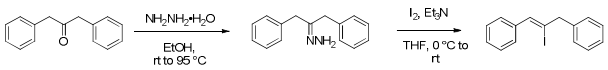
4. Experimental section

4-1 General methods

Melting points were obtained in open capillary tubes using a micro melting point apparatus SGW X-4, which were uncalibrated. Mass spectra were recorded by the HP5989A service; HRMS (EI) spectra were obtained on a Finigann MAT8401 instrument. ^1H nuclear magnetic resonance (NMR) spectra were recorded using an internal deuterium lock for the residual protons in $CDCl_3$ ($\delta_H = 7.26$) at ambient temperatures on the following instruments: Bruker AVANCE DPX-400 (400 MHz). Data are presented as follows: Chemical shift (in ppm on the scale relative to $\delta_{TMS} = 0$), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet), coupling constant (*J*/ Hz) and interpretation. ^{13}C NMR spectra were recorded by broadband spin decoupling using an internal deuterium lock for $CDCl_3$ ($\delta = 77.2$) at ambient temperatures on the following instruments: Bruker AVANCE DPX-400 (100 MHz). Chemical shift values are reported in ppm on the scale

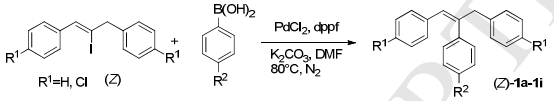
(δ_{TMS} = 0). All reagents and solvents were used as purchased if not otherwise stated.

4-2 Typical procedure for synthesis of substrates ***6a-6i***



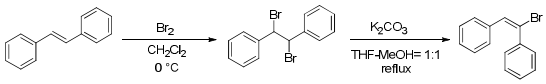
Into a 2-necked 100 mL round-bottomed flask equipped with a magnetic stirring bar, condenser, and addition funnel was added hydrazine hydrate (160 mmol). A solution of 1,3-diphenylpropan-2-one (20 mmol) in absolute ethanol (25 mL) was added very slowly to the hydrazine hydrate with vigorous stirring. After the addition was complete, the contents of the flask were heated to reflux for 1 h and then cooled to room temperature, after which most of the ethanol was removed under aspirator pressure. The reaction mixture was then extracted with chloroform (2 × 25 mL). The combined chloroform layers were washed successively with saturated brine (2 × 10 mL) and dried over anhydrous sodium sulfate. Filtered, and concentrated *in vacuo* without further purification.[11]

A solution of above hydrazone (20 mmol) in dry triethylamine (30 mL) was placed into a 100 mL round-bottomed flask equipped with an addition funnel, magnetic stirring bar, and calcium sulfate drying tube. The flask was cooled to 0 °C in an ice bath and a saturated solution of iodine in THF, which had been distilled with $LiAlH_4$, was added rapidly *via* the addition funnel to the hydrazone solution with vigorous stirring until the evolution of nitrogen ceased. The reaction mixture was stirred at room temperature for 1 h and then poured into 100 mL ice solution of sodium thiosulfate. The aqueous layer was extracted with PE (3 × 25 mL) and the combined organic layers were washed with cold 1 N hydrochloric acid (3 × 25 mL). The organic layer was then washed with one 25 mL portion each of saturated $NaHCO_3$, saturated brine, dried over anhydrous sodium sulfate, and filtered. Removal of the solvent and purification by flash chromatography on silica gel with petroleum ether as a dilute afforded pure (*Z*)-(2-iodoprop-1-ene-1,3-diyl) dibenzene as colorless oil.[11]



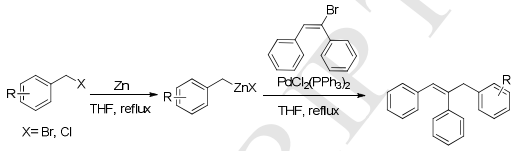
To a 25 mL Schlenk tube was added (*Z*)-2-iodoprop-1-enes (1.0 mmol), arylboronic acid (2.0 mmol), palladium chloride (0.1 mmol), 1,1'-bis(diphenylphosphino)ferrocene (0.1 mmol) and potassium carbonate (5.5 mmol) under N_2, followed by DMF (8 mL). The mixture was then heated to 80 °C for 24 hours until TLC analysis showed complete conversion of starting material. After cooled to room temperature, the reaction solution was filtered with EA through a short flash chromatography on silica gel to remove the undesired salts. The solvent was washed by 50 mL of water, exacted by ethyl acetate (3 × 20 mL) and washed with saturated brine, dried over anhydrous sodium sulfate, and filtered. Removal of the solvent and purification by flash chromatography on silica gel with petroleum ether as a dilute afforded pure (*Z*)-1,2,3-triphenyl substituted propylene **6a**- **6i**.

4-3 Typical procedure for synthesis of substrates ***6j-6s***



To a 100 mL round-bottomed flask was added (*E*)-1,2-diphenylethene (30 mmol), DCM (60 mL). Bromine (30 mmol) was added dropwise under ice bath and stirred for another 4 hours. After completion, the reaction mixture was quenched with saturated K_2CO_3, extracted by DCM. The organic layers washed by saturated brine, dried over anhydrous sodium sulfate. Remove the solvent to obtain crude 1,2-dibromo-1,2-diphenylethane.[12]

To a 40 mL solutiom of THF/ MeOH (1: 1) was added 1, 2-dibromo-1, 2-diphenylethane (6 mmol), and K_2CO_3 (12 mmol) in one portion. The resulting solution was heated to reflux for 1 hour. After completion, the reaction mixture was quenched with saturated ammonium chloride, extracted by ethyl acetate. The organic layers were washed by saturated brine, dried over anhydrous sodium sulfate. Remove the solvent to obtain (*E*)-(1-bromoethene-1, 2-diyl) dibenzene.



Substituted benzyl halide (4.5 mmol) in THF (20 mL) was added dropwise to the suspension of Zn dust (6.75 mmol) in 50 mL of dry THF under N_2. The reaction mixture was heated to reflux for half an hour. The reaction mixture was then transferred to another Schlenk tube containing (*E*)-(1-bromoethene-1,2-diyl) dibenzene (3.0 mmol) and $PdCl_2(PPh_3)_2$ (0.03 mmol) and refluxed until the complete consumption of the starting material, quenched with saturated ammonium chloride, extracted by ethyl acetate. The organic layers were washed by saturated brine, dried over anhydrous sodium sulfate. After the mixture was filtered and evaporated, the residue was purified by flash column chromatography, recrystallized by EtOH to provide desired substrate **6j-6s**.[13]

4-4 Typical procedure for synthesis of indene ***7/ 8/ 8'***

To a flame-dried 10 mL Schlenk tube under N_2 was added **6** (0.20 mmol), $Cu(OAc)_2•H_2O$ (0.02 mmol), followed by CH_3NO_2 (2 mL). DDQ (1.4 equiv.) was added after the starting material was dissolved. The reaction mixture was then heated at 60 ºC. After completion determined by TLC, the solvent was removed by rotary evaporator and the reaction residue was purified by column chromatography to afford the desired product **7**/ **8**/ **8'**.

4-4-1. 1,2-diphenyl-1H-indene ***7a***[14]

White solid (92%). Mp: 186 – 187 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.48 (m, 2H), 7.41 (d, J = 7.5 Hz, 1H), 7.36 (s, 1H), 7.28 – 7.07 (m, 11H), 4.97 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 149.4, 143.4, 140.2, 135.2, 129.1, 128.7, 128.2, 128.1, 127.5, 127.2, 126.9, 126.8, 125.7, 124.0, 121.3, 56.4.

4-4-2. 2-(4-chlorophenyl)-1-phenyl-1H-indene ***7b***

White solid (63%). Mp: 186 – 187 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.38 (m, 3H), 7.34 (s, 1H), 7.28 – 7.08 (m, 10H), 4.92 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 148.8, 143.2, 139.8, 133.7, 133.2, 129.2, 128.9, 128.7, 128.0, 127.3, 127.1, 125.9, 124.1, 121.4, 56.4. HRMS (EI): calcd for $C_{21}H_{15}Cl$ ($[M]^+$): 302.0862, found 302.0859.

4-4-3. 4-(1-phenyl-1H-inden-2-yl)benzonitrile ***7c***

Pale yellow solid (65%). Mp: 152 – 153 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.44 (m, 6H), 7.32 – 7.08 (m, 8H), 4.95 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 147.7, 142.3, 139.3, 138.9, 132.2, 131.4, 129.1, 127.6, 127.3, 127.1, 126.8, 126.5, 123.9, 121.8, 119.0, 110.2, 56.1. HRMS (EI): calcd for $C_{22}H_{15}N$ ($[M]^+$): 293.1204, found 293.1205.

4-4-4. 1-phenyl-2-(4-(trifluoromethyl)phenyl)-1H-indene ***7d***

White solid (77%). Mp: 141 – 142 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.45

(d, *J* = 8.5 Hz, 2H), 7.30 – 7.10 (m, 8H), 4.97 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 149.5, 148.5, 142.8, 139.5, 138.6, 130.5, 129.2, 128.9, 128.0, 127.4, 127.2, 126.8, 126.4, 125.7, 125.6 (q, *J* = 3.8 Hz), 124.2, 121.8, 56.4. HRMS (EI): calcd for $C_{22}H_{15}F_3$ ($[M]^+$): 336.1126, found 336.1127.

4-4-5. 2-(4-methoxyphenyl)-1-phenyl-1H-indene ***7e***

Pale yellow solid (56%). Mp: 184 – 185 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.43 (d, *J* = 8.9 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.24 – 7.19 (m, 4H), 7.18 – 7.12 (m, 4H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.9 Hz, 2H), 4.92 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 159.1, 149.7, 149.1, 143.7, 140.5, 129.0, 128.0(4), 128.0(1), 127.1, 126.8, 126.3, 125.2, 123.9, 120.9, 114.1, 56.6, 55.4. HRMS (EI): calcd for $C_{22}H_{18}O$ ($[M]^+$): 298.1358, found 298.1354.

4-4-6. 1-(1-phenyl-1H-inden-2-yl)naphthalene ***7f***

Orange oil (23%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.32 (d, *J* = 8.7 Hz, 1H), 7.82 (d, *J* = 6.8 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.41 (m, 3H), 7.38 – 7.31 (m, 2H), 7.30 – 7.24 (m, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.14 (s, 1H), 7.11 – 7.00 (m, 5H), 5.19 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 150.2, 148.7, 144.2, 139.2, 134.5, 134.1, 132.2, 128.7, 128.6, 128.3, 127.7, 127.3, 126.8(84), 126.8(78), 126.2, 125.9, 125.8, 125.7, 125.3, 124.3, 121.3, 59.5. HRMS (EI): calcd for $C_{25}H_{18}$ ($[M]^+$): 318.1409, found 318.1400.

4-4-7. 6-chloro-1-(4-chlorophenyl)-2-phenyl-1H-indene ***7g***

Yellow solid (70%). Mp: 171 – 172 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.44 (d, *J* = 7.3 Hz, 2H), 7.33 – 7.17 (m, 8H), 7.11 (s, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 4.92 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 150.4, 150.2, 141.9, 137.9, 134.5, 132.9, 131.6, 129.4, 129.3, 128.8, 128.0, 127.7, 127.5, 126.8, 124.5, 122.2, 55.6. HRMS (EI): calcd for $C_{21}H_{14}Cl_2$ ($[M]^+$): 336.0473, found 336.0468.

4-4-8. 6-chloro-1,2-bis(4-chlorophenyl)-1H-indene ***7h***

White solid (48%). Mp: 170 – 171 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.35 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.19 (m, 5H), 7.11 (s, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 4.88 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 150.2, 148.9, 141.5, 137.4, 133.7, 133.1, 132.9, 131.8, 129.5, 129.2, 129.0, 127.9(91), 127.9(88), 127.7, 124.4, 122.3, 55.5. HRMS (EI): calcd for $C_{21}H_{13}Cl_3$ ($[M]^+$): 370.0083, found 370.0085.

4-4-9. 6-chloro-1-(4-chlorophenyl)-2-(4-methoxyphenyl)-1H-indene ***7i***

Orange solid (55%). Mp: 112 – 113 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.36 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.17 (m, 4H), 7.14 (s, 1H), 7.08 (s, 1H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.79 (d, *J* = 8.1 Hz, 2H), 4.85 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 159.4, 150.1, 149.8, 142.2, 138.2, 132.8, 131.0, 129.4, 129.3, 128.0, 127.5, 127.2, 125.5, 124.3, 121.7, 114.2, 55.6, 55.4. HRMS (EI): calcd for $C_{22}H_{16}OCl_2$ ($[M]^+$): 366.0578, found 366.0580.

4-4-10. Indene ***7j*** *and* ***8j***

Yellow solid (68%), **7j**/ **8j** = 5:1; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.49 (d, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.36 (s, 1H), 7.29 – 7.08 (m, 8H), 6.86 – 6.78 (m, 1H), 6.69 (t, *J* = 7.2 Hz, 1H), 5.43 (s, 1H) (**7j**); 7.49 (d, *J* = 7.5 Hz, 2H), 7.45 (s, 1H), 7.31 (d, *J* = 4.3 Hz, 1H), 7.29 – 7.08 (m, 7H), 7.07 – 7.02 (m, 1H), 6.99 – 6.89 (m, 2H), 5.01 (s, 1H) (**8j**). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 162.6, 160.1, 149.5, 148.5, 143.6, 139.5, 134.8, 134.7, 129.1, 128.71, 128.7 (65), 128.5, 128.4, 128.3, 127.9, 127.8, 127.6, 127.3, 127.1 (d, *J* = 1.8 Hz), 127.0, 126.9 (94), 126.9 (87), 126.6, 125.7, 124.7 (d, *J* = 3.5 Hz), 123.9, 123.9 (d, *J* = 1.2 Hz), 122.4 (d, *J* = 1.7 Hz), 121.3, 119.9 (d, *J* = 3.3 Hz), 115.9, 115.7, 113.8, 113.6, 56.8, 48.1. HRMS (EI): calcd for $C_{21}H_{15}F$ ($[M]^+$): 286.1158, found 286.1158.

4-4-11. Indene ***7k*** *and* ***8k***

Yellow oil (62%), **7k**/ **8k** = 2.8:1; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.65 (d, *J* = 7.9 Hz, 1H) (**7k**), 7.50 (d, *J* = 7.6 Hz, 0.78H) (**8k**), 7.47-7.41 (m, 3H), 7.40 – 7.36 (t, *J* = 5.4 Hz, 2H) (**7k**), 7.34 (d, *J* = 7.0 Hz, 1H) (**7k**), 7.28 – 7.06 (m, 7.6H), 7.01 – 6.90 (m, 2.6H), 6.60 (dd, *J* = 7.6, 1.6 Hz, 1H) (**7k**), 5.68 (s, 1H) (**7k**), 5.03 (s, 0.36H) (**8k**). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 151.0, 150.6, 150.0, 148.6, 143.6, 143.4, 139.8, 139.3, 134.7, 134.6, 133.1, 130.3, 129.2, 128.8, 128.7, 128.5(50), 128.5(47), 128.3, 128.2, 128.0(00), 128.0(96), 127.7, 127.4, 127.3, 127.2, 127.1, 127.0, 126.7, 125.7, 125.2, 123.9, 122.9, 121.5, 115.2, 57.4, 54.7. HRMS (EI): calcd for $C_{21}H_{15}Br$ ($[M]^+$): 346.0357, found 346.0355.

4-4-12. Indene ***7l*** *and* ***8l***

Yellow solid (40%), **7l**/ **8l** = 2.2:1; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.48 – 7.44 (m, 2.9H), 7.40 (d, *J* = 7.5 Hz, 1H) (**7l**), 7.33 (s, 1H) (**7l**), 7.31 – 7.26 (m, 2.3H), 7.24 – 7.08 (m, 11H), 7.06 (d, *J* = 8.4 Hz, 2H) (**7l**), 4.94 (s, 0.45H) (**8l**), 4.93 (s, 1H) (**7l**). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 150.8, 150.4, 149.7, 148.8, 143.3, 141.8, 139.2, 138.7, 137.6, 134.8, 134.7, 132.5, 131.4, 129.3, 129.2(18), 129.2(16), 128.7, 128.6, 128.4, 127.9, 127.7, 127.4, 127.3, 127.2, 127.1, 126.8, 126.7, 125.7, 124.5 123.9, 122.0, 121.4, 56.3, 55.6. HRMS (EI): calcd for $C_{21}H_{15}Cl$ ($[M]^+$): 302.0862, found 302.0863.

4-4-13. Indene ***7m*** *and* ***8m***

Yellow solid (45%), **7m**/ **8m** = 1.7:1; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.50 – 7.44 (m, 3.3H), 7.41 (d, *J* = 7.5 Hz, 1H) (**7m**), 7.37 (d, *J* = 8.2 Hz, 0.6H) (**8m**), 7.35 – 7.31 (m, 3.2H), 7.30 – 7.16 (m, 9H), 7.15 – 7.09 (m, 3.2H), 7.02 (d, *J* = 8.2 Hz, 2H) (**7m**), 4.95 (s, 0.6H) (**8m**), 4.93 (s, 1H) (**7m**). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 151.1, 150.5, 149.6, 148.7, 143.3, 142.3, 139.3, 139.1, 134.8, 134.7, 132.1, 130.2, 129.7, 129.2, 128.6(8), 128.6(6), 128.4, 127.89, 127.8, 127.7, 127.4, 127.3, 127.2, 127.2(15), 126.8, 126.7, 125.7, 123.9, 122.4, 121.4, 120.6, 119.4, 56.4, 55.6. HRMS (EI): calcd for $C_{21}H_{15}Br$ ($[M]^+$): 346.0357, found 346.0354.

4-4-14. Indene ***7n*** *and* ***8n***

Yellow solid (49%), **7n**/ **8n** = 5:1; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.52 – 7.44 (m, 5H), 7.43 (d, J = 7.5 Hz, 1H) (**7n**), 7.40 – 7.35 (m, 1.5H), 7.30 – 7.23 (m, 5H), 7.21 – 7.15 (m, 2H), 7.14 – 7.10 (m, 2H), 5.02 (s, 1H) (**7n**), 5.01 (s, 0.2H) (**8n**). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 153.0, 149.5, 149.3, 148.4, 144.5, 143.4, 143.0, 138.8, 134.7, 134.4, 130.0, 129.4, 129.3, 129.2, 129.0, 128.8, 127.7(72), 127.7(67), 128.5(52), 128.5(48), 128.4, 128.3, 128.2, 128.0, 127.8, 127.5, 127.3, 127.0, 126.7, 126.0 (q, *J* = 3.8 Hz), 125.8, 125.6, 123.9, 123.8, 122.9, 121.5, 121.1, 56.4, 55.9. HRMS (EI): calcd for $C_{22}H_{15}F_3$ ($[M]^+$): 336.1126, found 336.1128.

4-4-15. Indene ***7o***

Yellow solid (53%). Mp: 128 – 129 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.49-7.44 (m, 2H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.35 – 7.06 (m, 9H), 6.97 – 6.86 (m, 2H), 4.95 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 162.7, 160.3, 142.3, 139.2, 137.8, 135.4, 130.6, 129.9, 129.8, 128.7, 128.6, 127.6, 127.3, 126.7, 115.6, 115.4, 35.5. HRMS (EI): calcd for $C_{21}H_{15}F$ ($[M]^+$): 286.1158, found 286.1154.

4-4-16. Indene ***7p*** *and* ***8p***

Yellow solid (30%), **7p**/ **8p** = 1:2; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.52 – 7.45 (m, 3H) (**8p**), 7.39 (d, *J* = 7.5 Hz, 1H) (**8p**), 7.34 – 7.31 (m, 1.5H) (**7p**), 7.25 – 7.12 (m, 8H), 7.10 (d, *J* = 7.3 Hz, 1H) (**8p**), 7.06 (d, *J* = 4.5 Hz, 0.5H) (**7p**), 7.05 – 6.99 (m, 5H),

4.94 (s, 1H) (**8p**), 4.92 (s, 0.5H) (**7p**), 2.29 (s, 1.5H) (**7p**), 2.25 (s, 3H) (**8p**). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 149.6, 149.5, 149.0, 143.3, 140.7, 140.4, 137.0, 136.3, 135.4, 135.3, 135.2, 129.7, 129.0, 128.6, 128.5, 128.1, 128.0, 127.9, 127.8, 127.4, 127.2, 127.0, 126.8, 126.7, 126.6, 125.6, 124.8, 123.9, 121.2, 120.9, 56.2, 56.0, 21.7, 21.2. HRMS (EI): calcd for $C_{22}H_{18}$ ($[M]^+$): 282.1409, found 282.1411.

*4-4-17. Indene **7q**, **8q** and **8' q***

Yellow solid (60%), **7q**/ **8q (5-F)**/ **8'q (7-F)** = 7.4:9.1: 1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 7.4 Hz, 4H) (**8q**), 7.33 (d, J = 7.5 Hz, 1H) (**8q**), 7.22 – 6.98 (m, 18H), 6.90 (d, J = 7.6 Hz, 1H) (**8q**), 6.79 – 6.67 (m, 3H), 5.08 (s, 0.11H) (**8'q**), 4.88 (s, 1H) (**8q**), 4.85 (s, 0.81H) (**7q**). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 163.9, 162.0, 161.5, 152.2, 149.5, 148.6, 145.1(14), 145.1(05), 144.6(d, J = 2.5 Hz), 143.3, 142.8, 142.7, 139.8, 134.8, 134.7, 130.5, 130.4, 129.1, 128.8, 128.7, 128.6(64), 128.6(60), 128.6(58), 128.4, 128.2, 127.9, 127.8, 127.6, 127.4, 127.3(d, J = 3.3 Hz), 127.0, 126.9, 126.8, 126.7, 125.7, 124.8, 124.7, 123.9, 123.8(d, J = 2.8 Hz), 121.4, 114.8, 114.5, 114.0, 113.8, 112.2, 120.0, 108.3, 108.1, 55.9, 55.8, 55.7. HRMS (EI): calcd for $C_{21}H_{15}F$ ($[M]^+$): 286.1158, found 286.1154

*4-4-18. Indene **7r**, **8r** and **8'r***

Yellow oil (57%), **7r**/ **8r (5-Br)**/ **8'r (7-Br)** = 10:3.5:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.8 Hz, 0.7H) (**8r**), 7.46 (d, J = 8.2 Hz, 2H) (**7r**), 7.39 (t, J = 10.3 Hz, 1H) (**7r**), 7.34 (s, 1H) (**7r**), 7.31 – 7.04 (m, 15.2H), 7.01 (d, J = 7.8 Hz, 0.36H) (**8r**), 5.26 (s, 0.1H) (**8'r**), 5.03 (s, 0.35H) (**8r**), 4.90 (s, 1H) (**7r**). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 151.7, 149.4, 148.5, 148.0, 147.9, 146.3, 145.4, 143.3, 142.6, 139.3, 136.9, 134.7, 134.6(58), 134.6(57), 130.9, 130.6, 130.1, 129.4, 129.2(22), 129.2(18), 129.1, 128.7, 128.6(65), 128.6(58), 128.5, 128.4, 128.2, 127.9(91), 127.9(89), 127.9(86), 127.7, 127.4, 127.1, 126.9(93), 126.9(90), 126.9(88), 126.8, 126.7(71), 126.7(66), 126.6, 125.8, 125.3, 124.2, 123.9, 122.9, 121.4, 121.1, 120.2, 119.7, 57.9, 56.0, 55.7. HRMS (EI): calcd for $C_{21}H_{15}Br$ ($[M]^+$): 346.0357, found 346.0359.

*4-4-19. Indene **7s**, and **8s***

Yellow solid (66%), **7s**/ **8s** = 1.6:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.36 (m, 5.4H), 7.33 (d, J = 7.5 Hz, 1.6H) (**7s**), 7.23 – 7.16 (m, 6.8H), 7.16 – 7.04 (m, 13.2H), 6.84 (d, J = 8.1 Hz, 1H) (**8s**), 6.60 (d, J = 6.5 Hz, 3.2H) (**7s**), 6.51 (t, J = 8.9 Hz, 1.6H) (**7s**), 6.43 (t, J = 9.4 Hz, 1H) (**8s**), 5.05 (s, 1H) (**8s**), 4.84 (s, 1.6H) (**7s**). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 162.1, 153.4, 149.1, 147.9, 144.3, 143.3, 137.7, 134.6, 134.1, 128.9, 128.8, 138.7, 128.3, 128.1, 127.9, 127.7, 127.0, 126.7, 125.9, 123.9, 121.6, 110.9 (d, J = 6.7 Hz), 110.7 (d, J = 6.8 Hz), 104.8 (d, J = 3.6 Hz), 104.6 (d, J = 3.6 Hz), 102.8, 102.6, 102.3, 101.2, 100.9, 100.7, 55.7, 53.7. HRMS (EI): calcd for $C_{21}H_{14}F_2$ ($[M]^+$): 304.1064, found 304.1066.

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14. Hu, Q.; Li, D.; Zhang, H.; Xi, Z. *Tetrahedron Lett.* **2007**, *35*, 6167.

Supplementary Material

The ^{1}H NMR and ^{13}C NMR copies of all compounds were attached as supplementary material.

Supporting Information

DDQ-mediated dehydrogenative intramolecular cyclization for the synthesis of 1,2-diarylindenes

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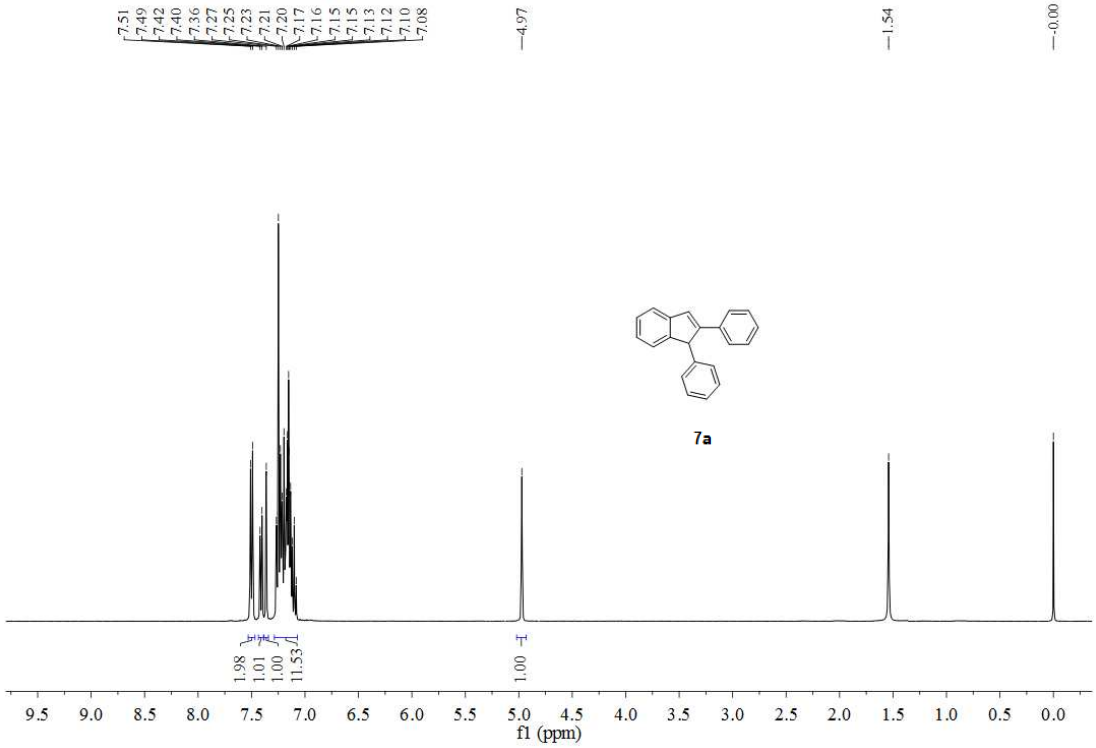
weiping_deng@ecust.edu.cn

^{1}H NMR and ^{13}C NMR spectra for compounds 7 and 8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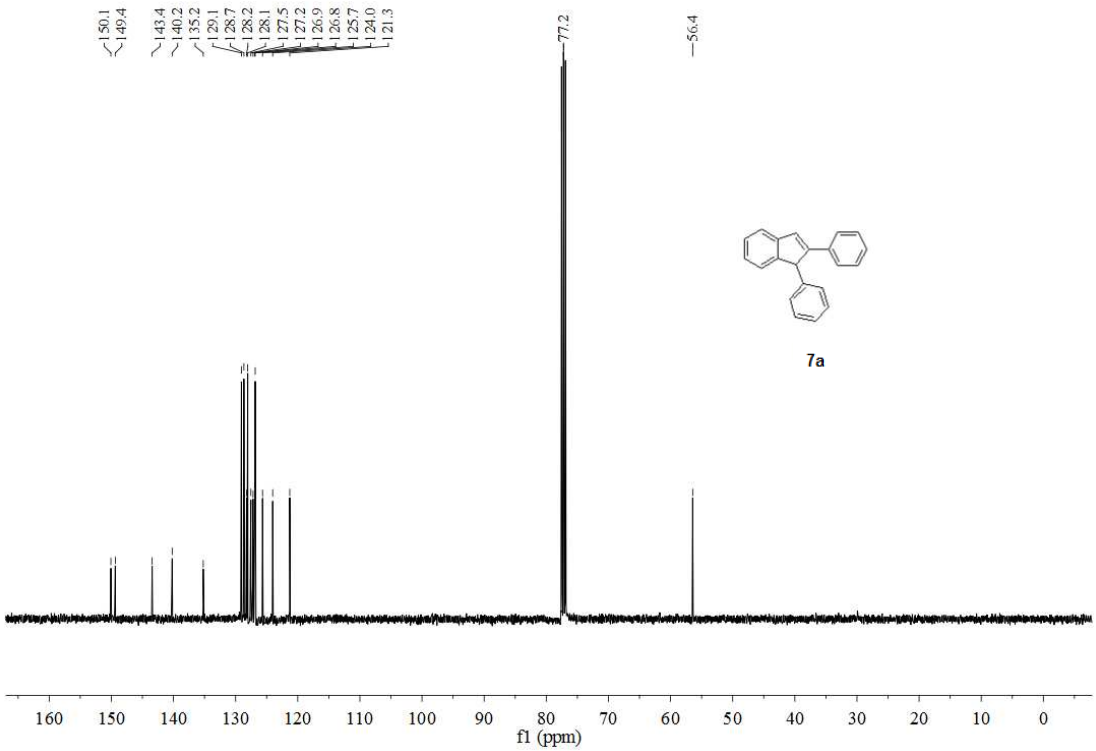
7.16
7.15
7.15
7.13
7.12
7.10
7.08
4.97
1.54
0.00
1.98
1.01
1.00
11.53
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
7a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128.2
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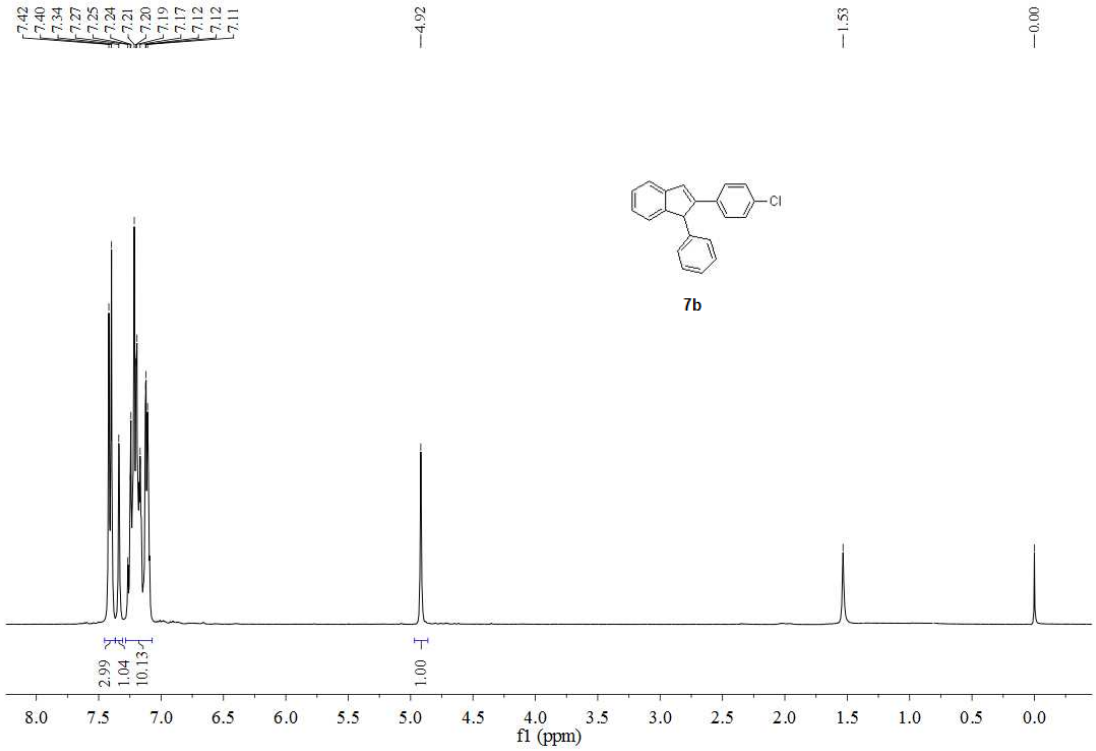
126.8
125.7
124.0
121.3
77.2
56.4
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
7a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7.12
7.11
4.92
1.53
0.00
Cl
7b
2.99
1.04
10.13
1.00
8.0
7.5
7.0
6.5
6.0
5.5
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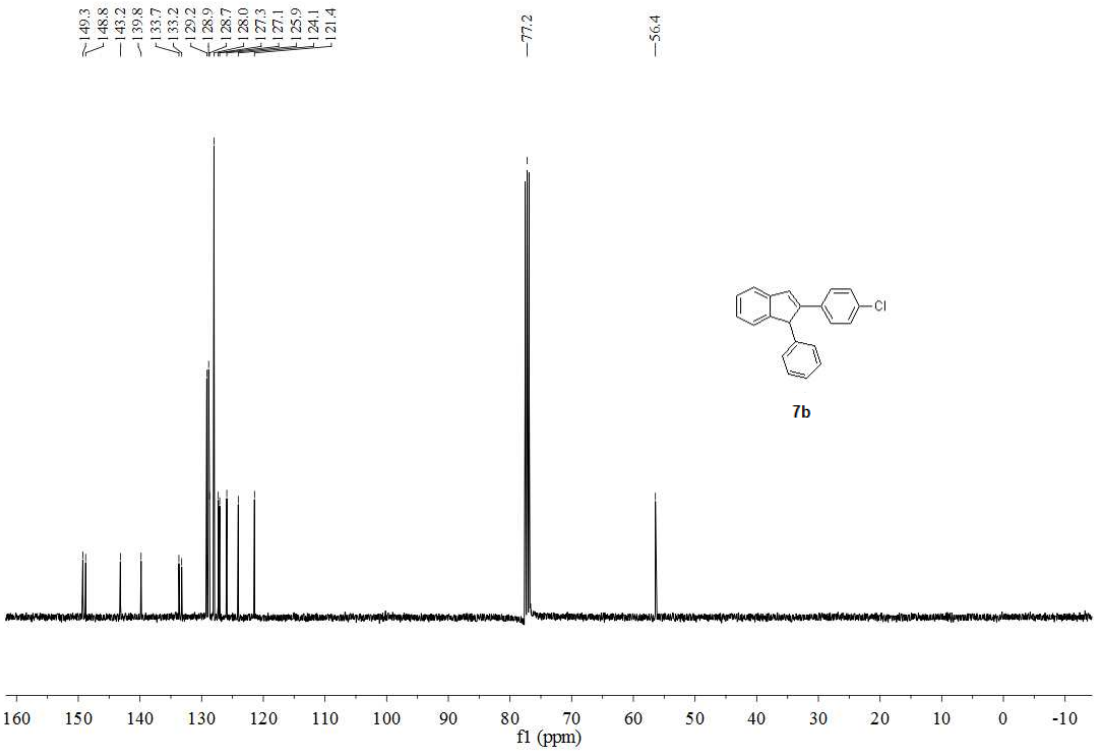
f1 (ppm)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128.9
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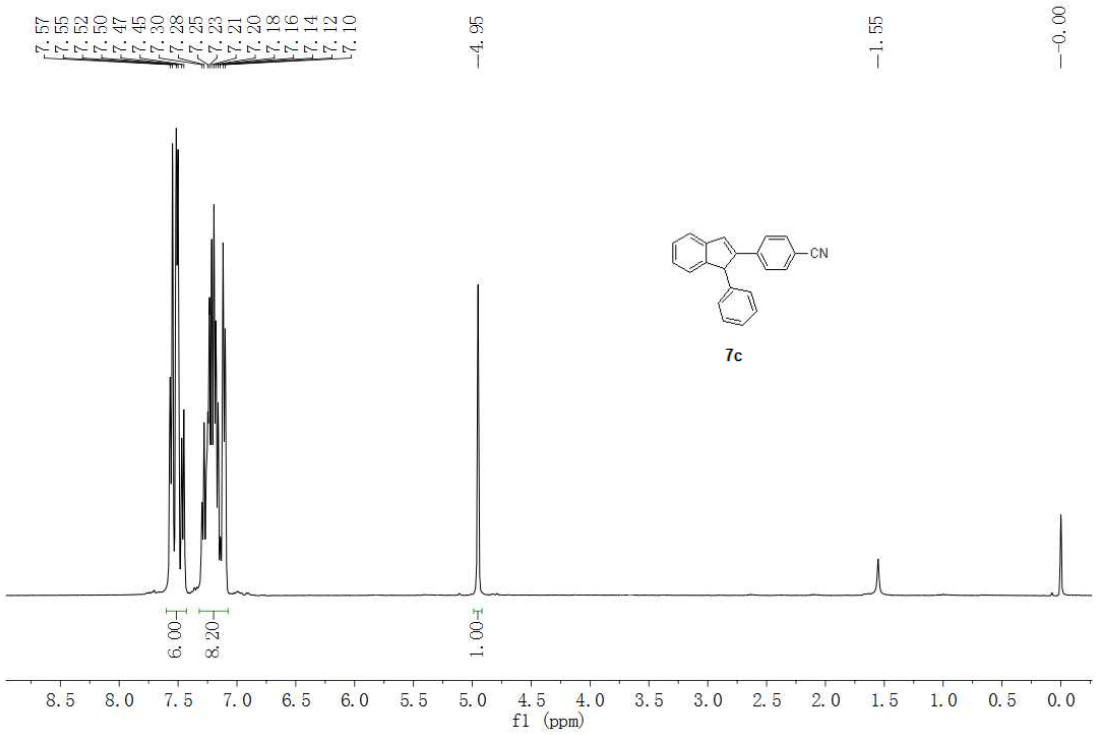
127.1
125.9
124.1
121.4
77.2
56.4
Cl
7b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.18
7.16
7.14
7.12
7.10
4.95
1.55
0.00
CN
7c
6.00
8.20
1.00
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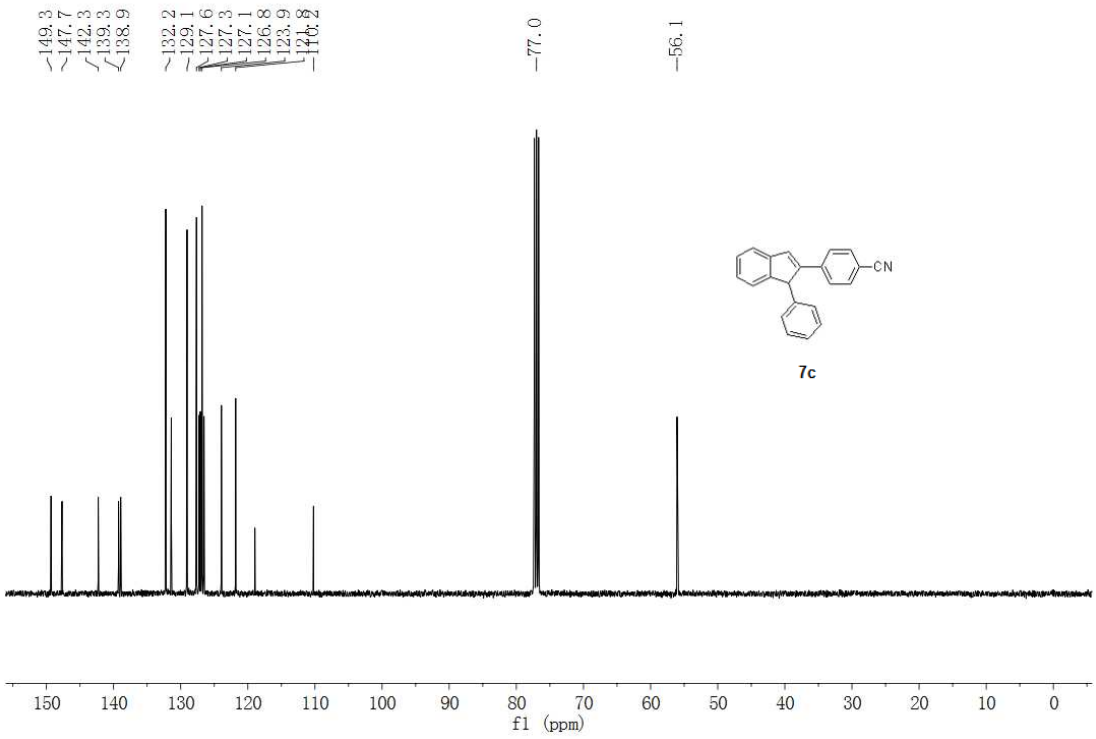
f1 (ppm)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129.1
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123.9
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56.1
CN
7c
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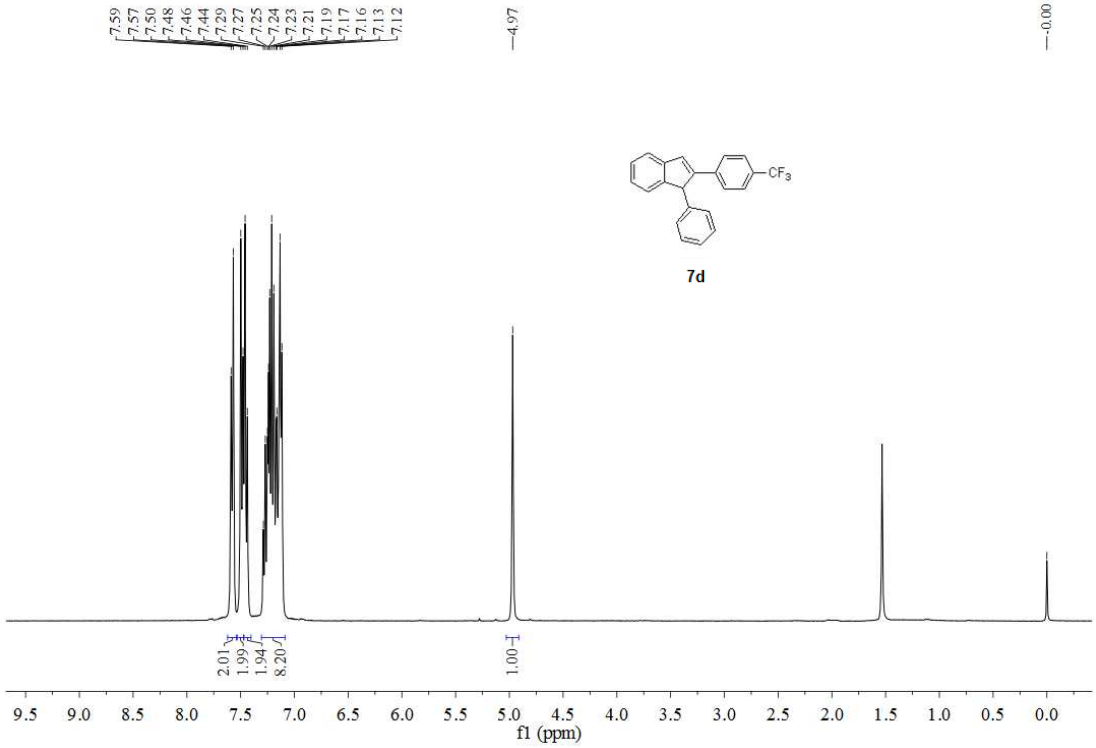
f1 (ppm)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7.16
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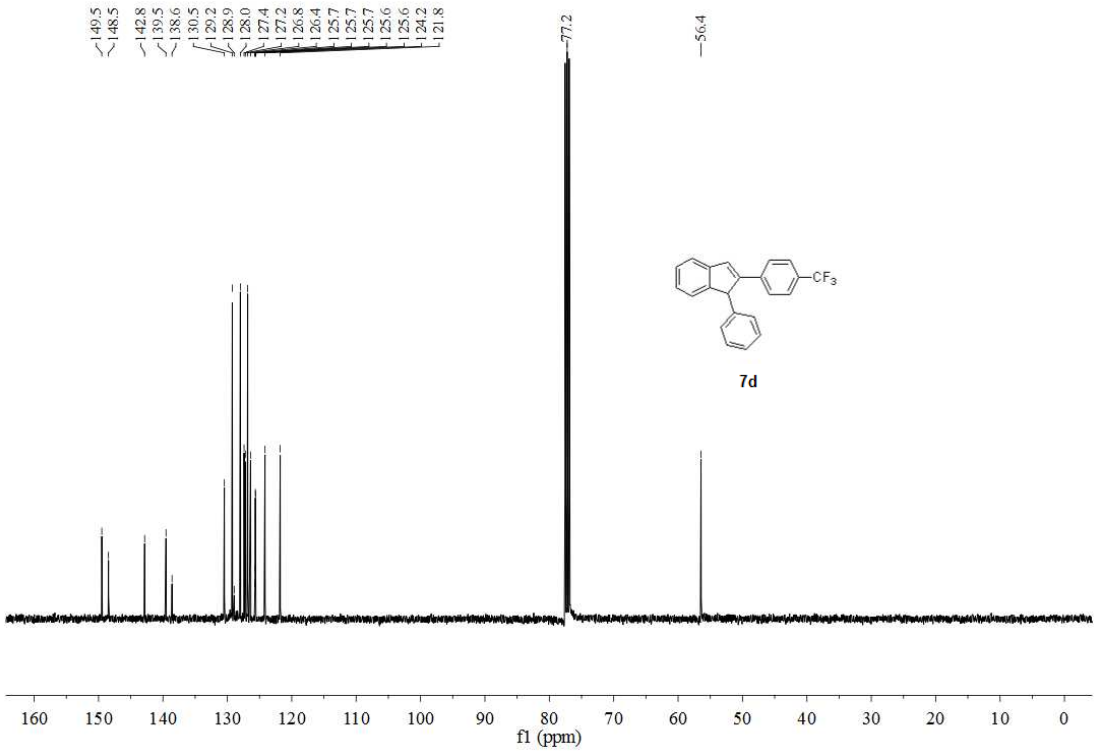
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126.4
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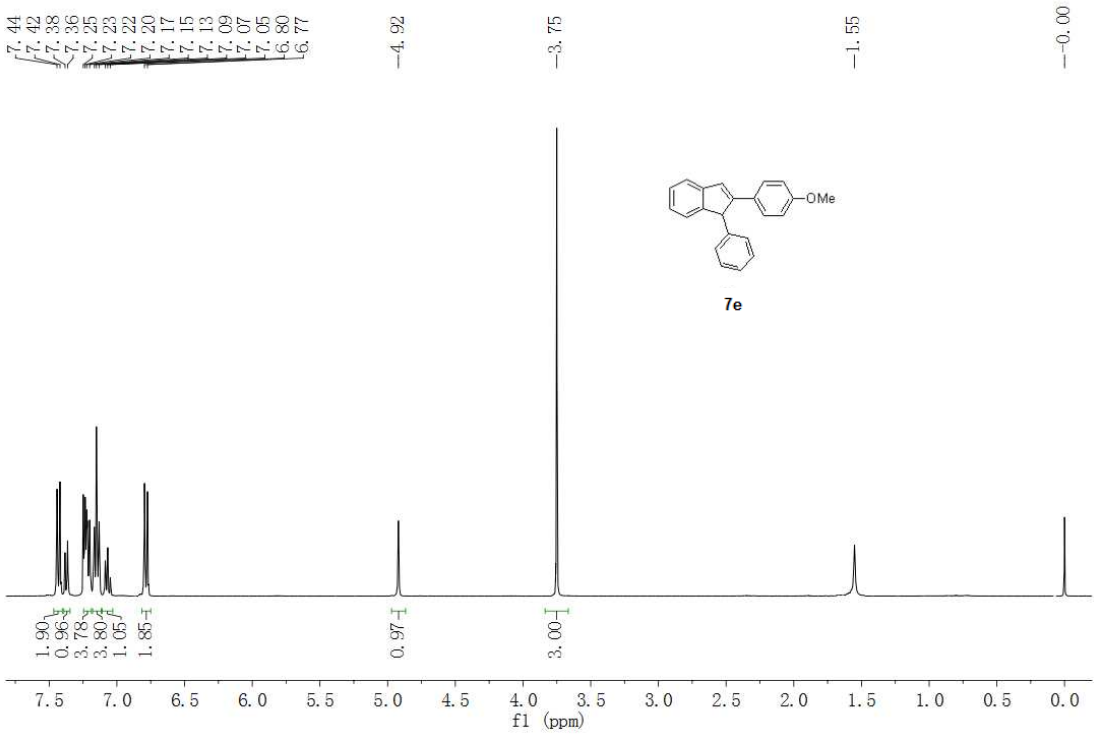
125.6
125.6
124.2
121.8
77.2
56.4
CF3
7d
f1 (ppm)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7.05
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6.77
4.92
3.75
1.55
0.00
OMe
7e
1.90
0.96
3.78
3.80
1.05
1.85
0.97
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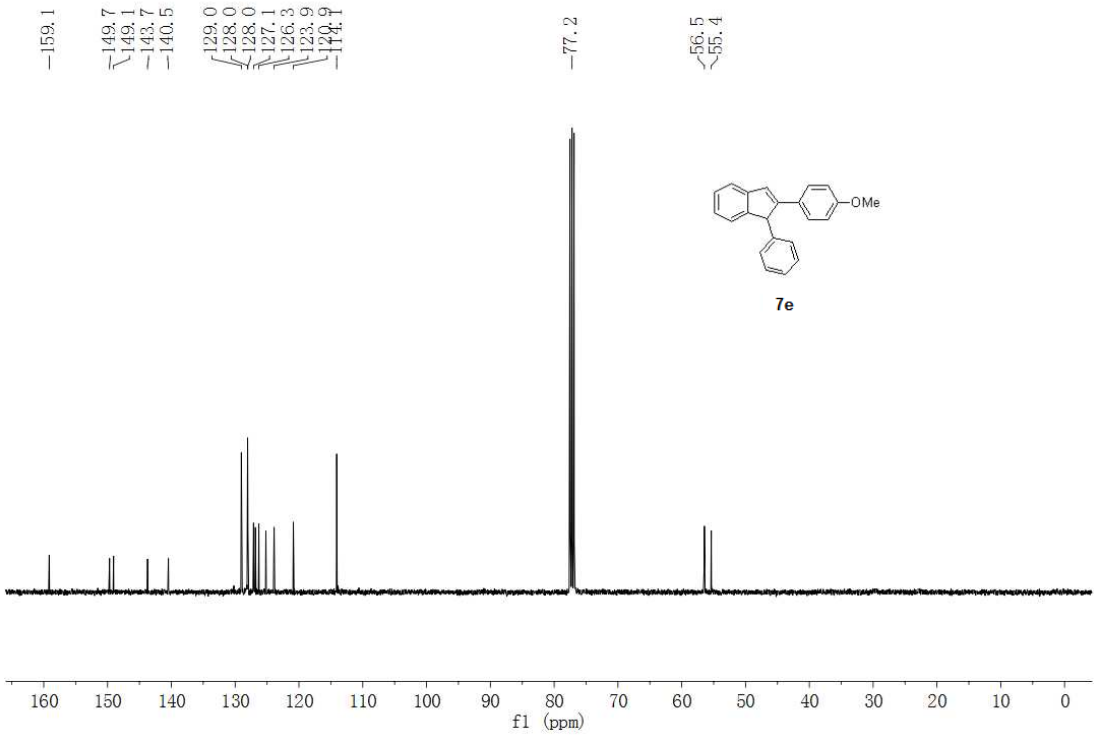
f1 (ppm)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128.0
127.1
126.3
123.9
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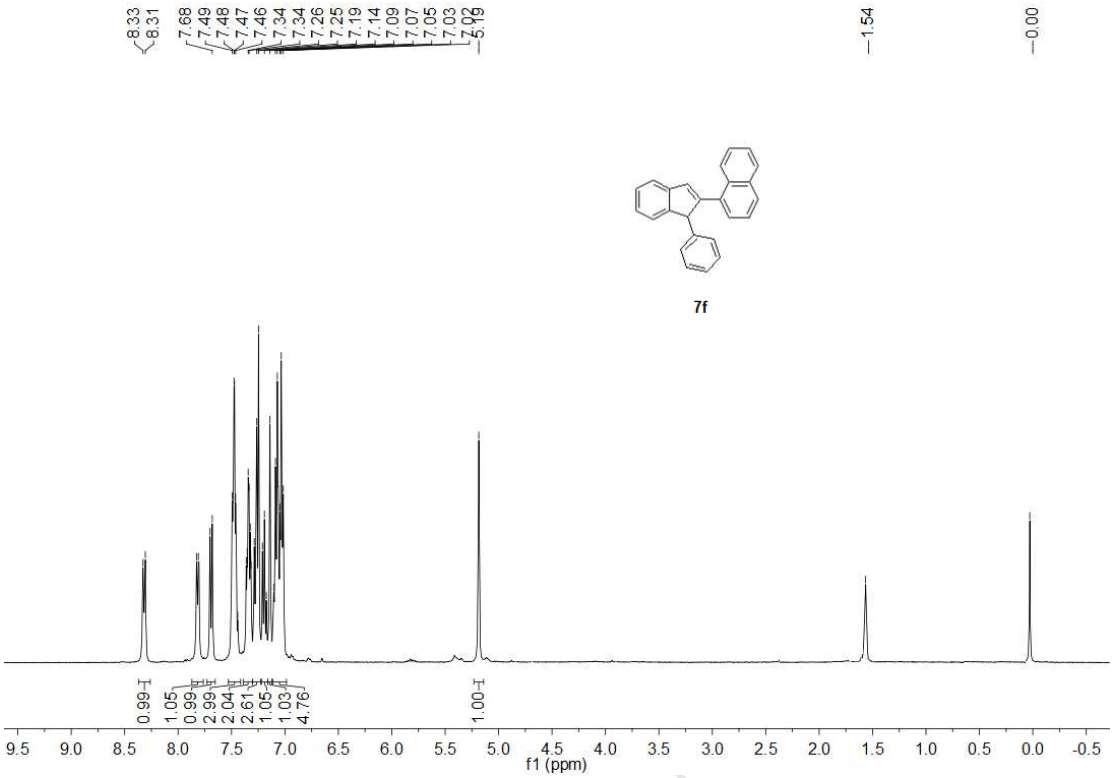
77.2
56.5
55.4
OMe
7e
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.19
7.14
7.09
7.07
7.05
7.03
7.02
5.19
1.54
0.00
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1.03
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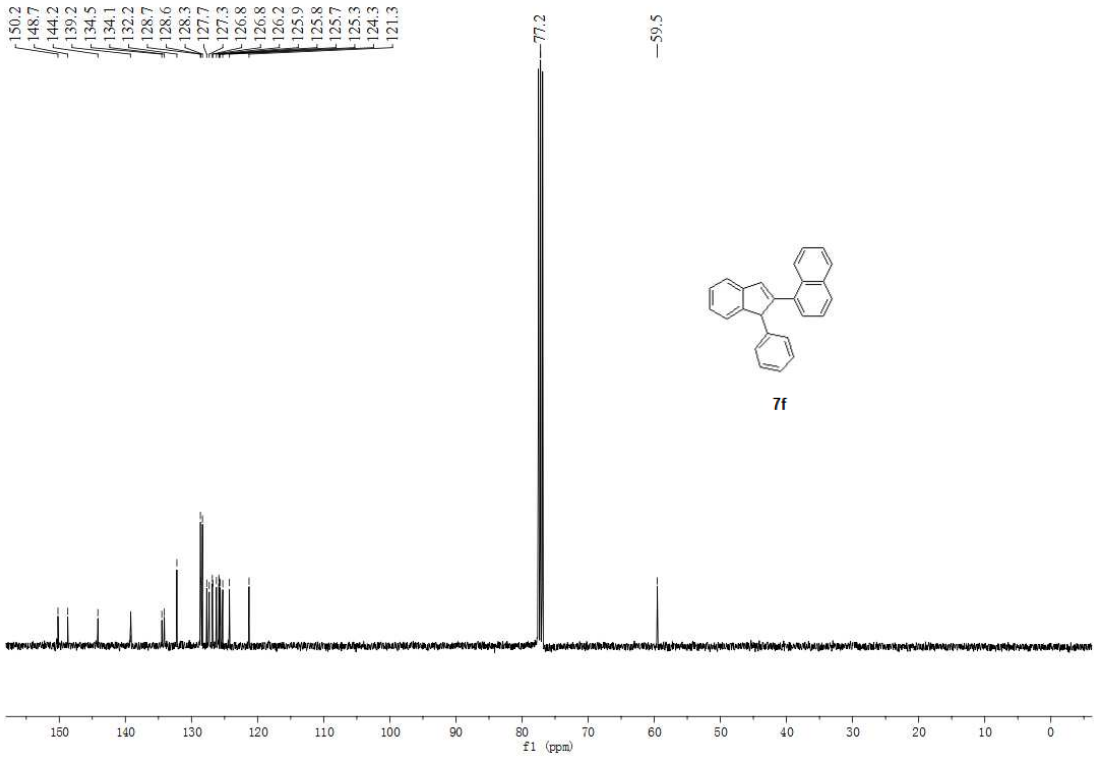
1.00
f1 (ppm)

7f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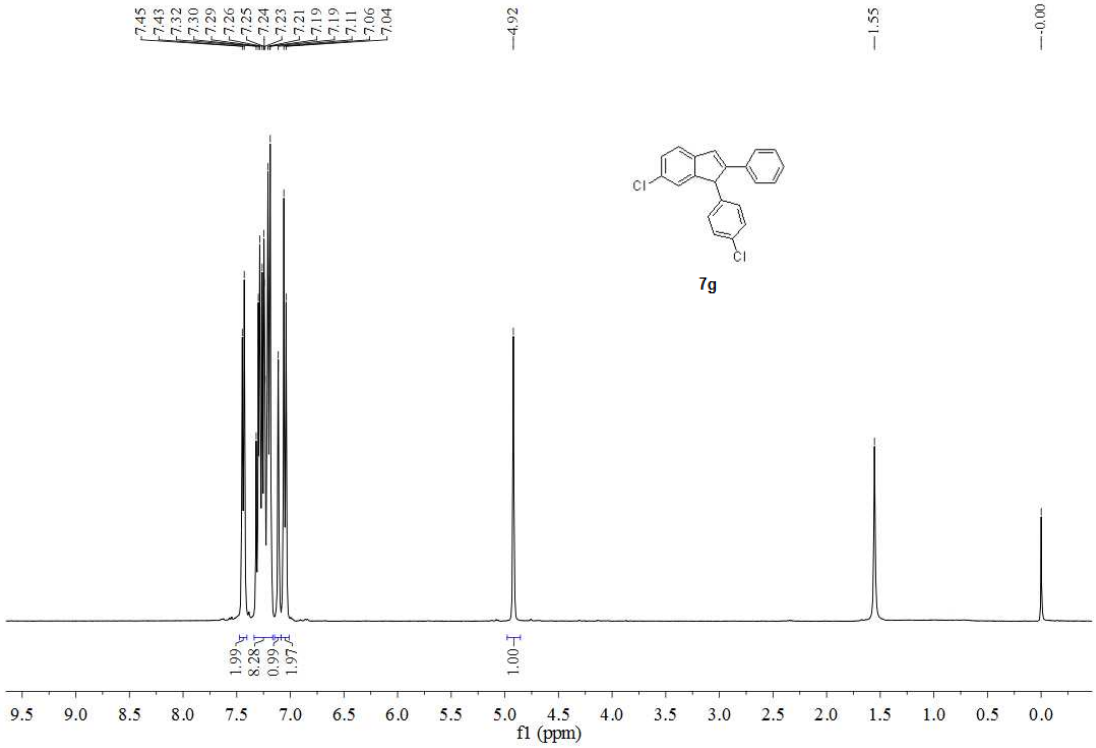
128.3
127.7
127.3
126.8
126.8
126.2
125.9
125.8
125.7
125.3
124.3
121.3
77.2
59.5
f1 (ppm)

7f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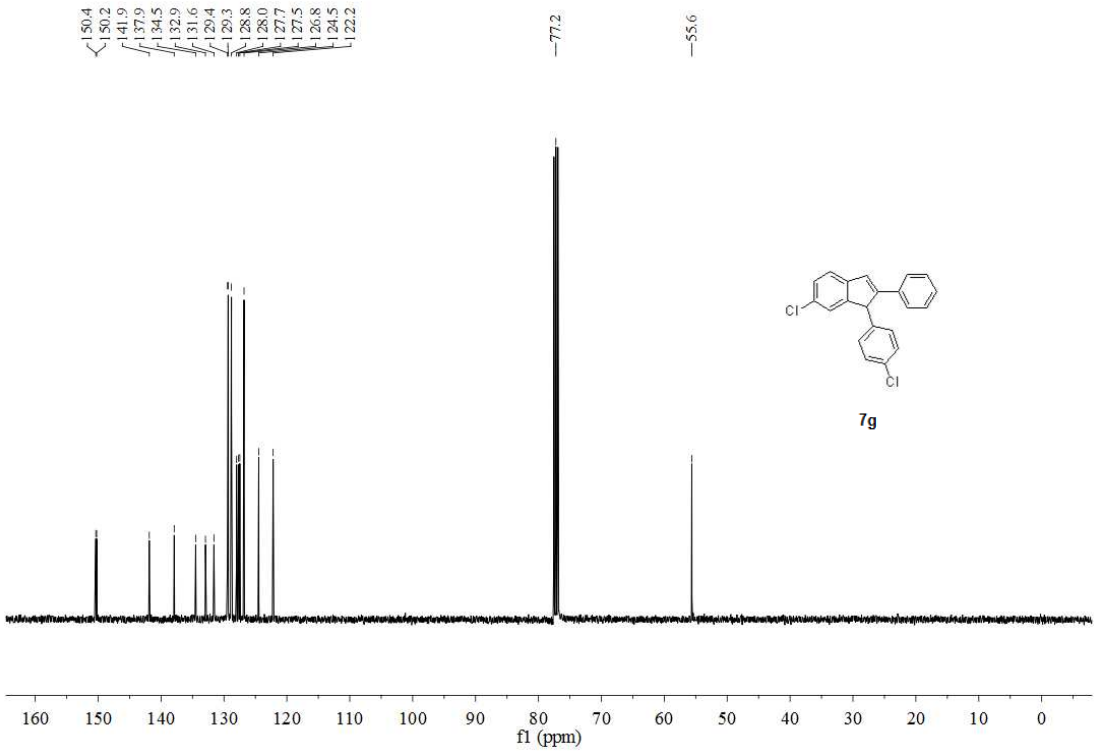
7.19
7.19
7.11
7.06
7.04
4.92
1.55
0.00
Cl
Cl
7g
1.99
8.28
0.99
1.97
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.7
127.5
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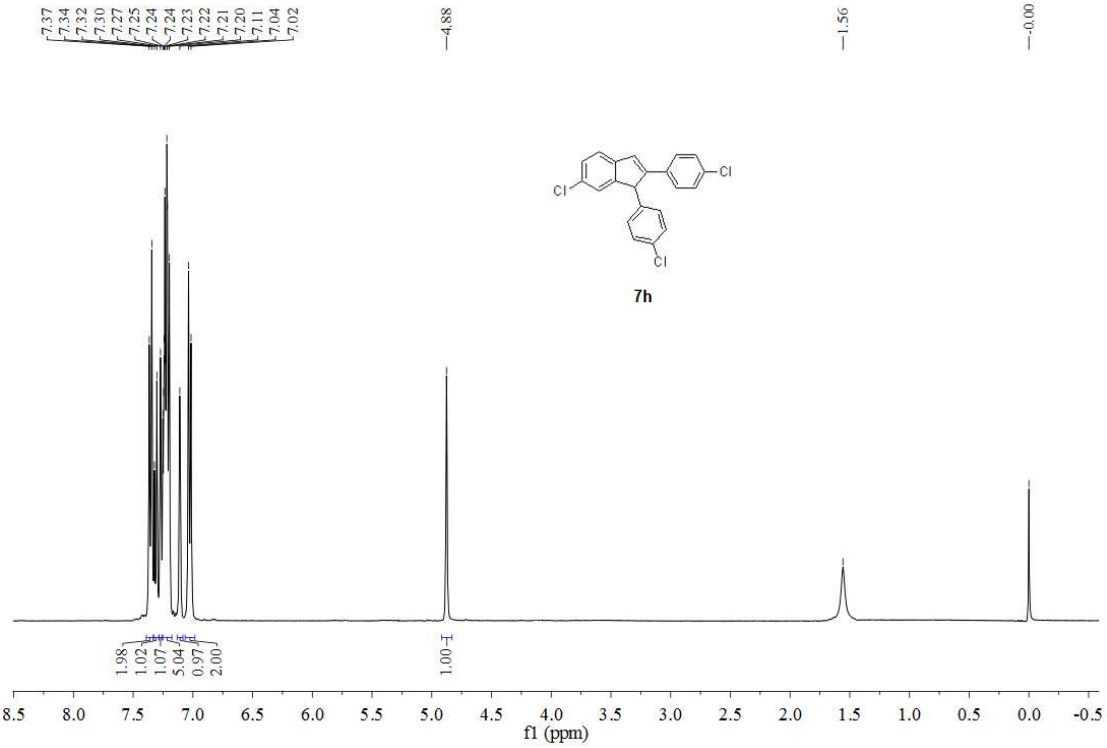
122.2
77.2
55.6
Cl
Cl
7g
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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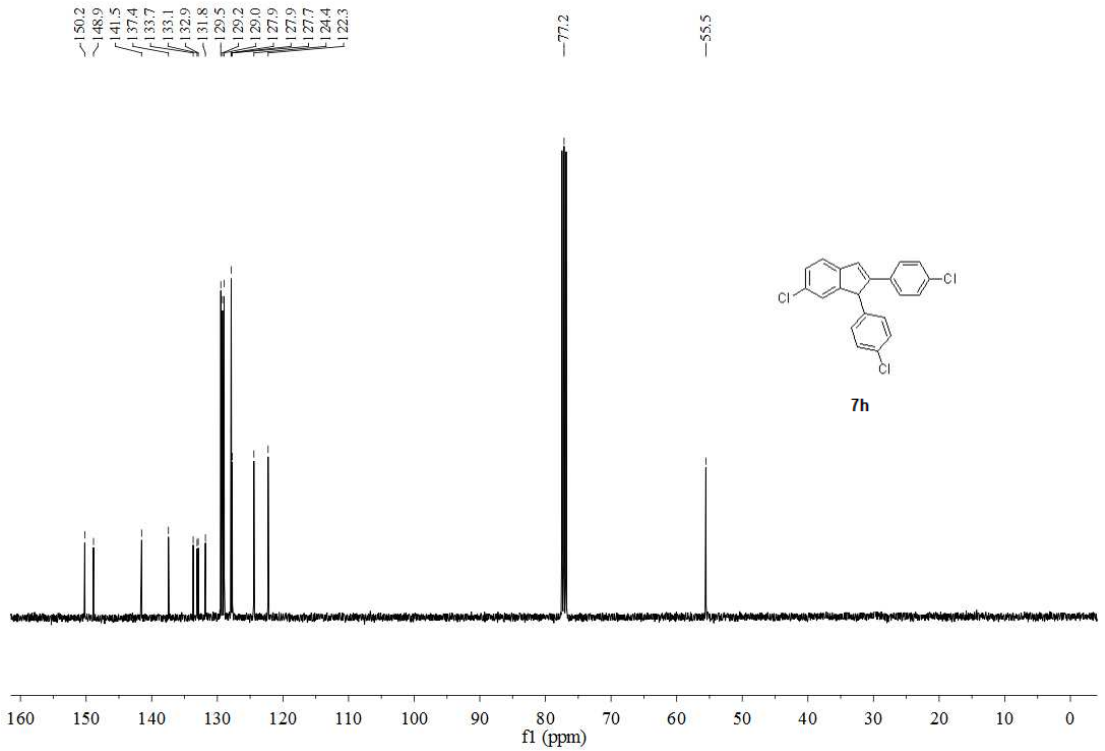
7.04
7.02
4.88
1.56
0.00
Cl
Cl
Cl
7h
1.98
1.02
1.07
5.04
0.97
2.00
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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137.4
133.7
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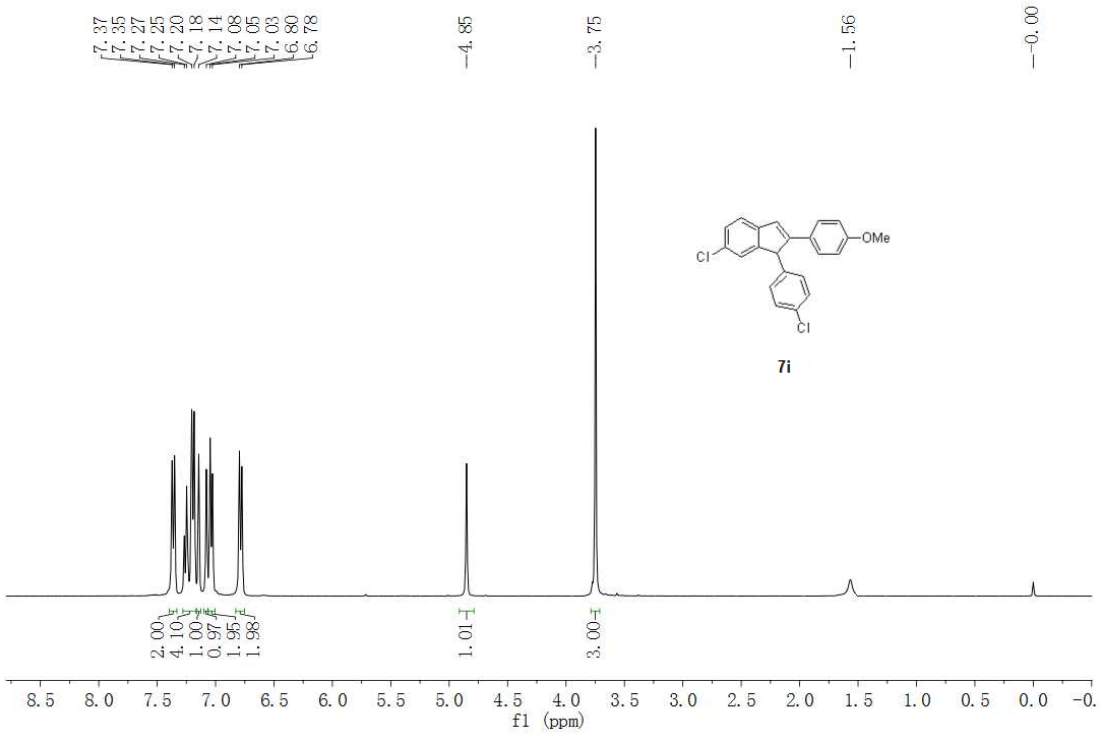
132.9
131.8
129.5
129.2
129.0
127.9
127.9
127.7
124.4
122.3
77.2
55.5
Cl
Cl
Cl
7h
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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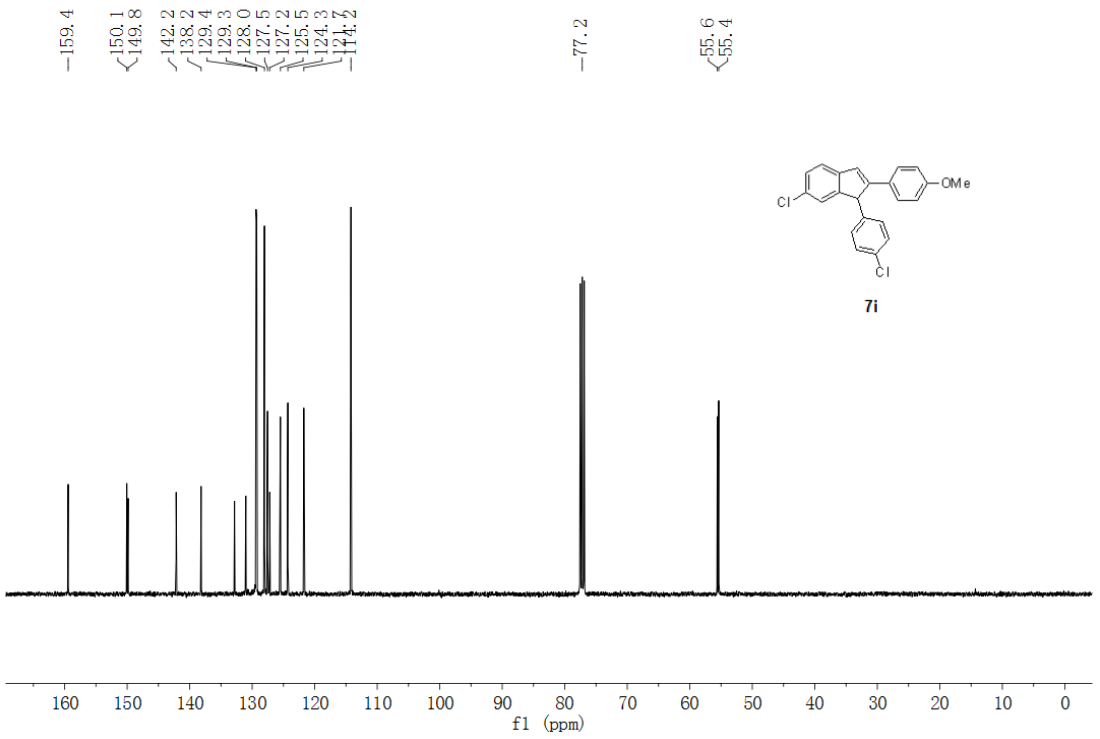
7.05
7.03
6.80
6.78
4.85
3.75
1.56
0.00
OMe
Cl
Cl
7i
2.00
4.10
1.00
0.97
1.95
1.98
1.01
3.00
f1 (ppm)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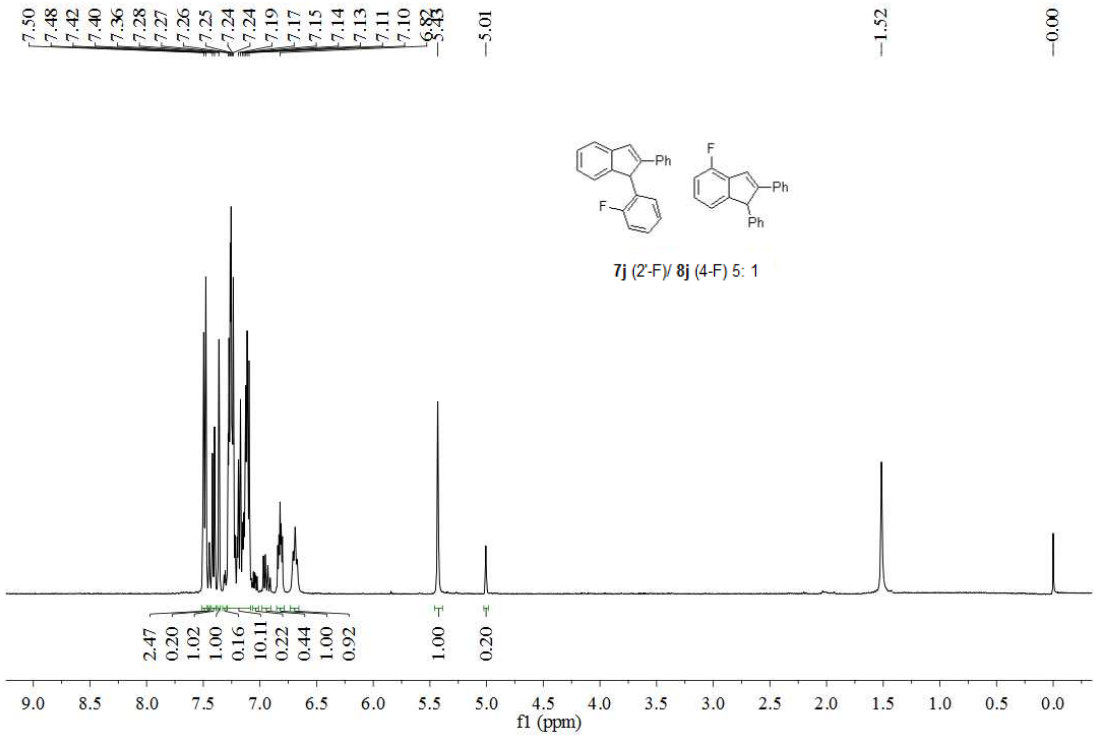
149.8
142.2
138.2
129.4
129.3
128.0
127.5
127.2
125.5
124.3
121.7
114.2
77.2
55.6
55.4
OMe
Cl
Cl
7i
f1 (ppm)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7.17
7.15
7.14
7.13
7.11
7.10
6.82
5.43
5.01
1.52
0.00
Ph
F
F
Ph
Ph
7j (2'-F)/ 8j (4-F) 5: 1
2.47
0.20
1.02
1.00
0.16
10.11
0.22
0.44
1.00
0.92
1.00
0.20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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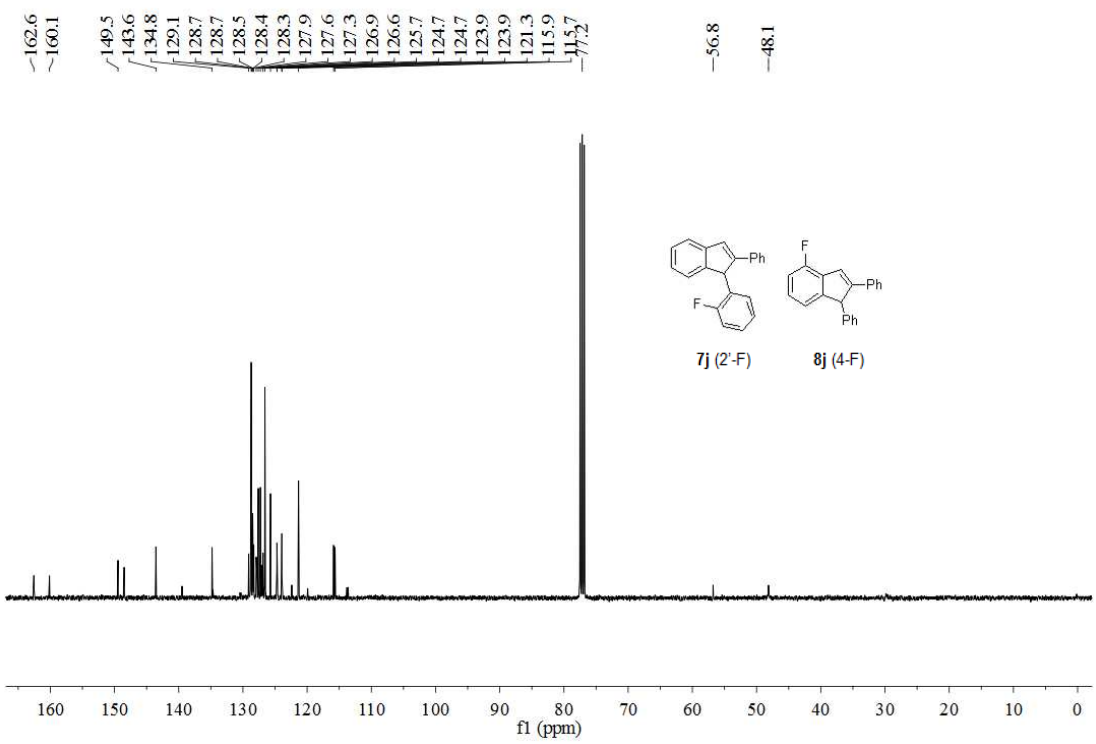
f1 (ppm)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128.7
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128.3
127.9
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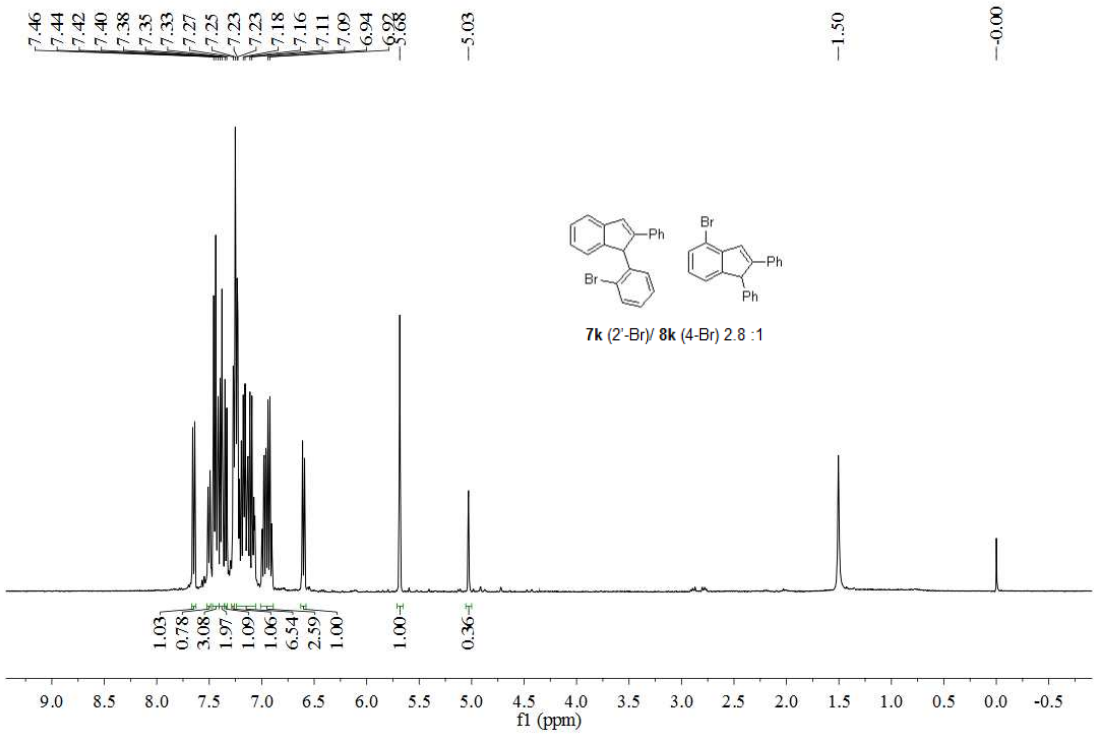
127.3
126.9
126.6
125.7
124.7
124.7
123.9
123.9
121.3
115.9
115.7
77.2
56.8
48.1
Ph
F
F
Ph
Ph
7j (2'-F)
8j (4-F)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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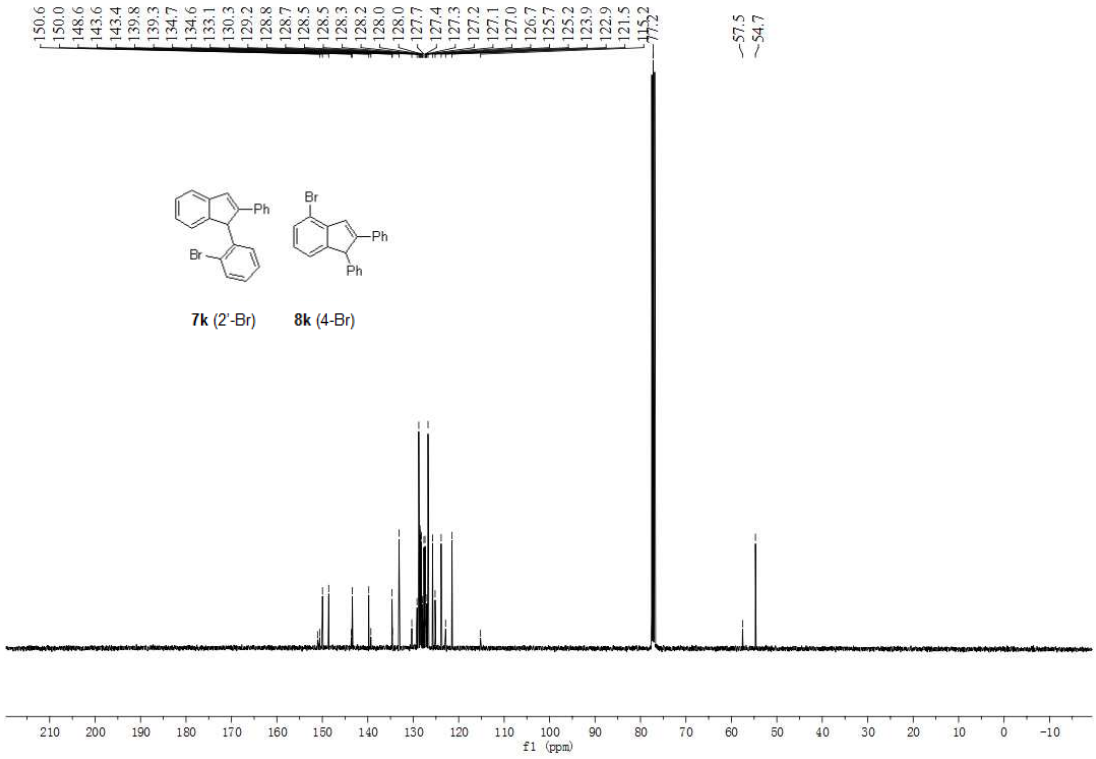
7.25
7.23
7.23
7.18
7.16
7.11
7.09
6.94
6.92
5.68
5.03
1.50
0.00
Ph
Br
Br
Ph
Ph
7k (2'-Br)/ 8k (4-Br) 2.8 :1
1.03
0.78
3.08
1.97
1.09
1.06
6.54
2.59
1.00
1.00
0.36
f1 (ppm)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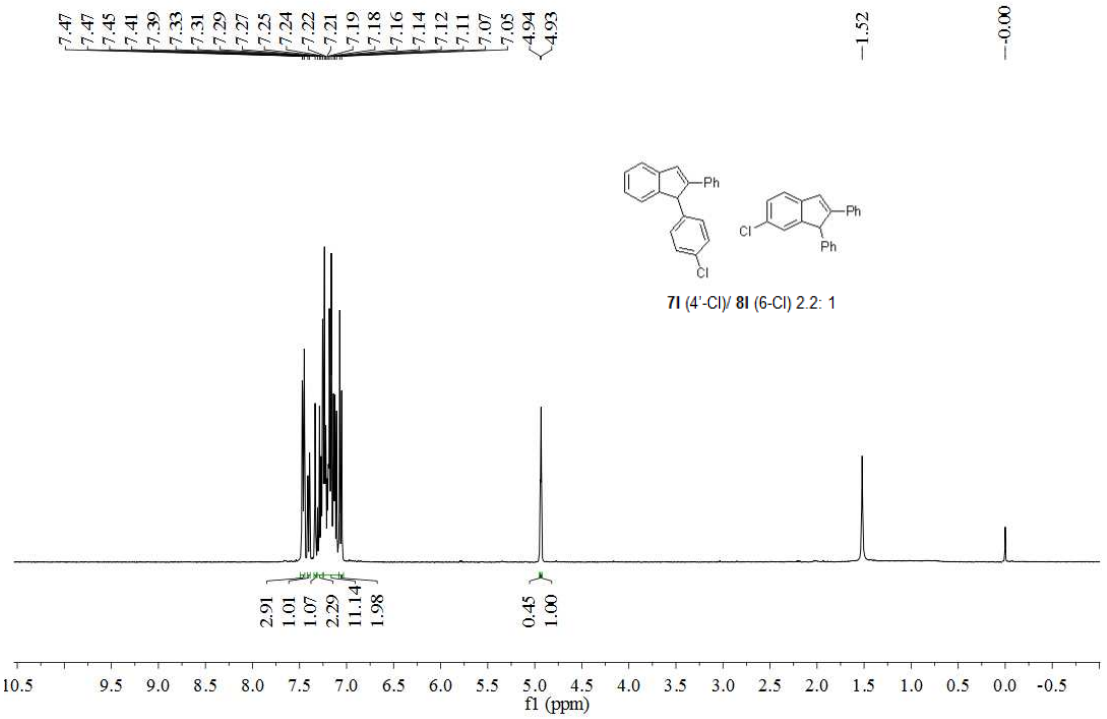
128.7
128.5
128.5
128.3
128.2
128.0
128.0
127.7
127.4
127.3
127.2
127.1
127.0
126.7
125.7
125.2
123.9
122.9
121.5
115.2
77.2
57.5
54.7
Ph
Br
Br
Ph
Ph
7k (2'-Br)
8k (4-Br)
f1 (ppm)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7.22
7.21
7.19
7.18
7.16
7.14
7.12
7.11
7.07
7.05
4.94
4.93
1.52
0.00
Ph
Cl
Cl
Ph
Ph
7l (4'-Cl)/ 8l (6-Cl) 2.2: 1
2.91
1.01
1.07
2.29
11.14
1.98
0.45
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
2.0
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1.0
0.5
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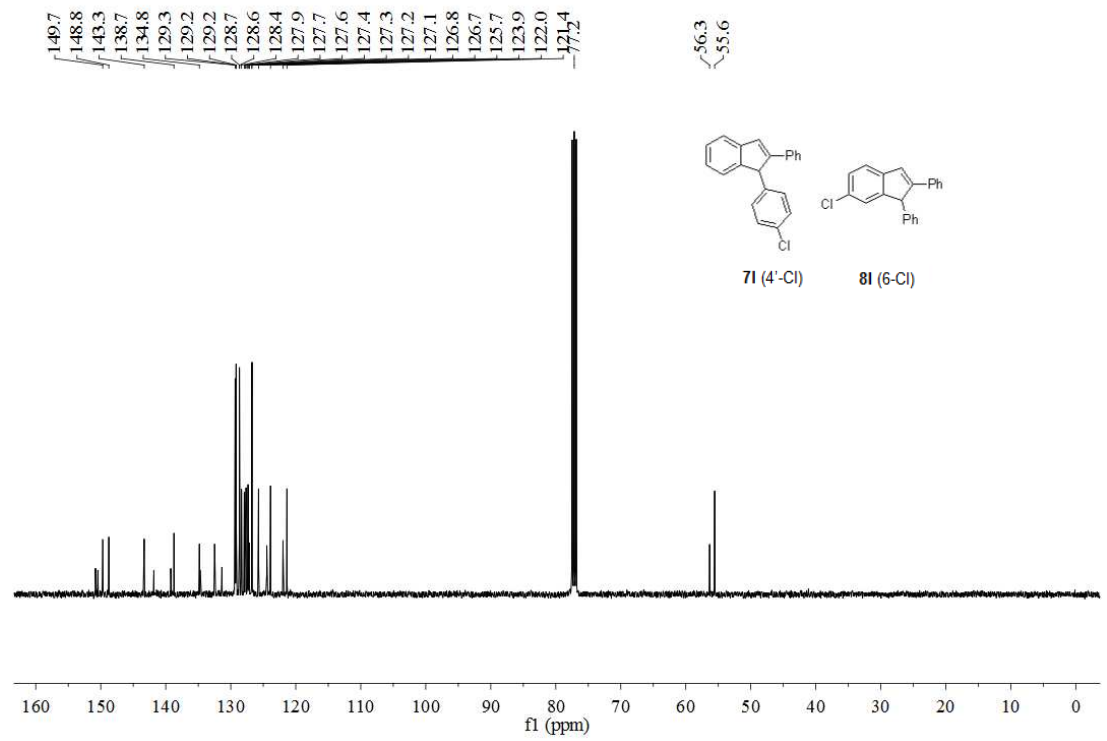
-0.5
f1 (ppm)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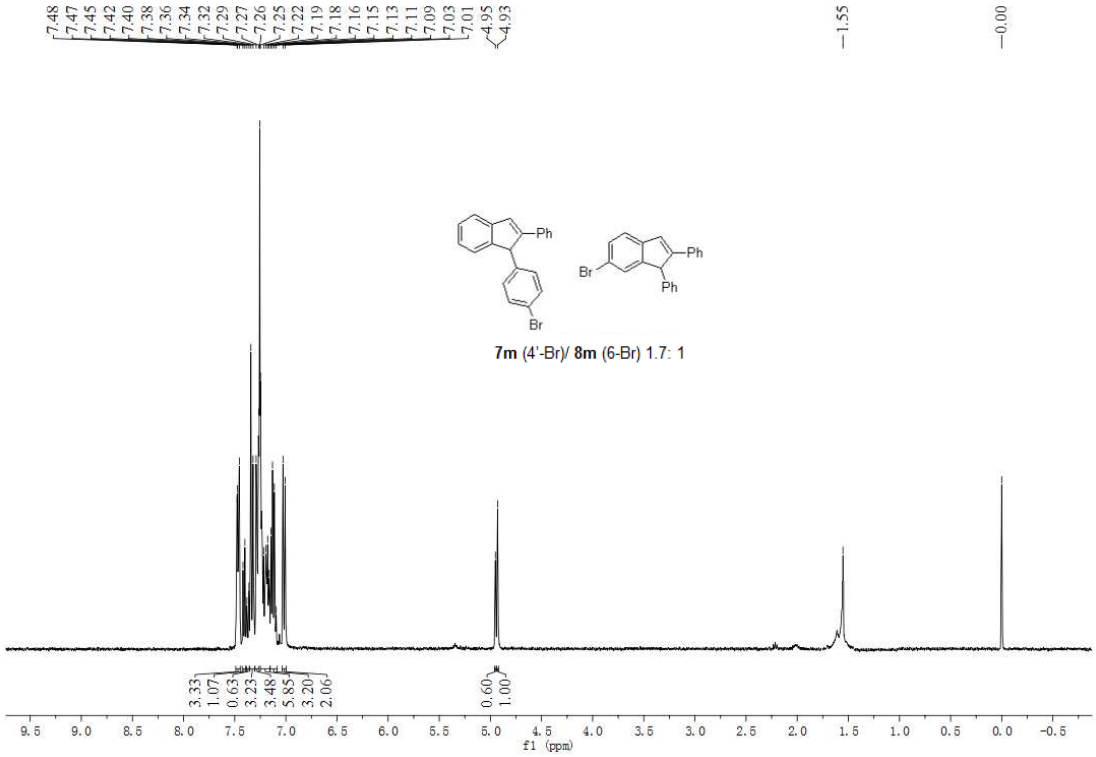
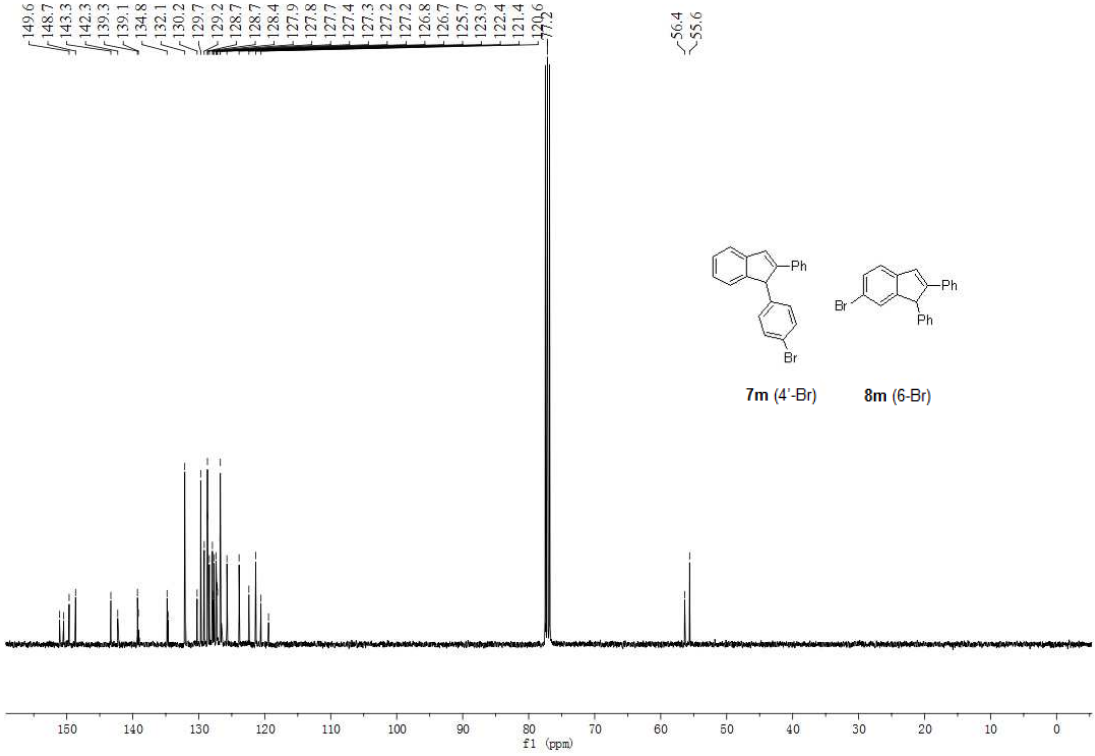
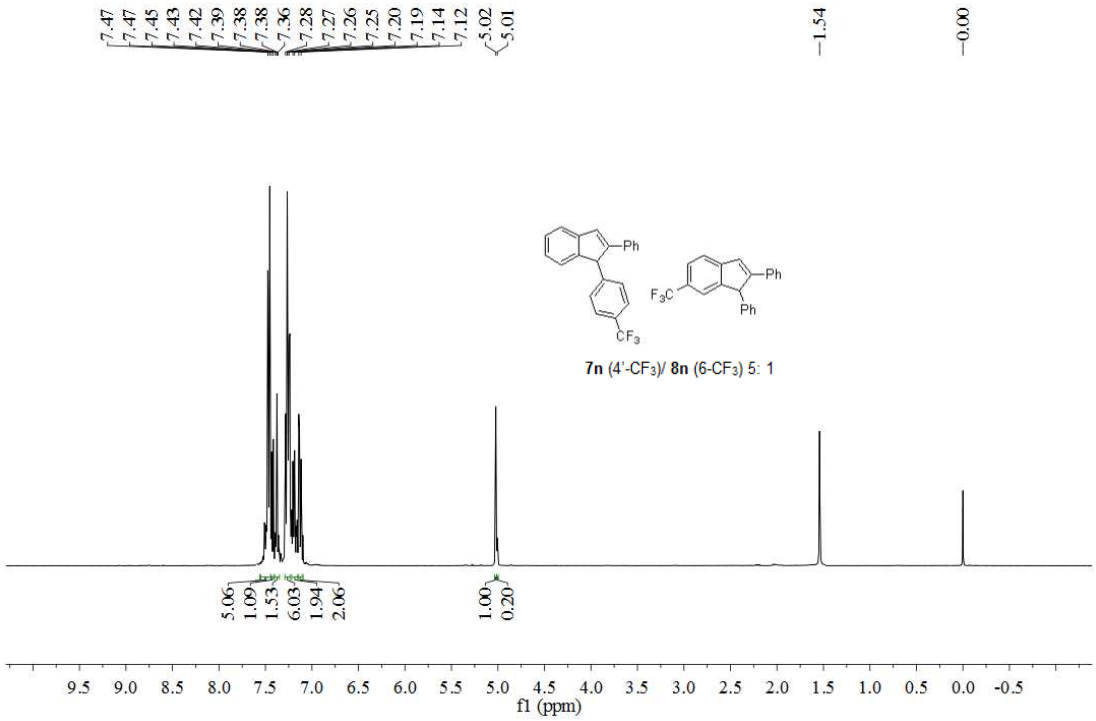
129.2
128.7
128.6
128.4
127.9
127.7
127.6
127.4
127.3
127.2
127.1
126.8
126.7
125.7
123.9
122.0
121.4
77.2
56.3
55.6
Ph
Cl
Cl
Ph
Ph
7l (4'-Cl)
8l (6-Cl)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



7m (4'-Br)/ **8m** (6-Br) 1.7: 1



7m (4'-Br) **8m** (6-Br)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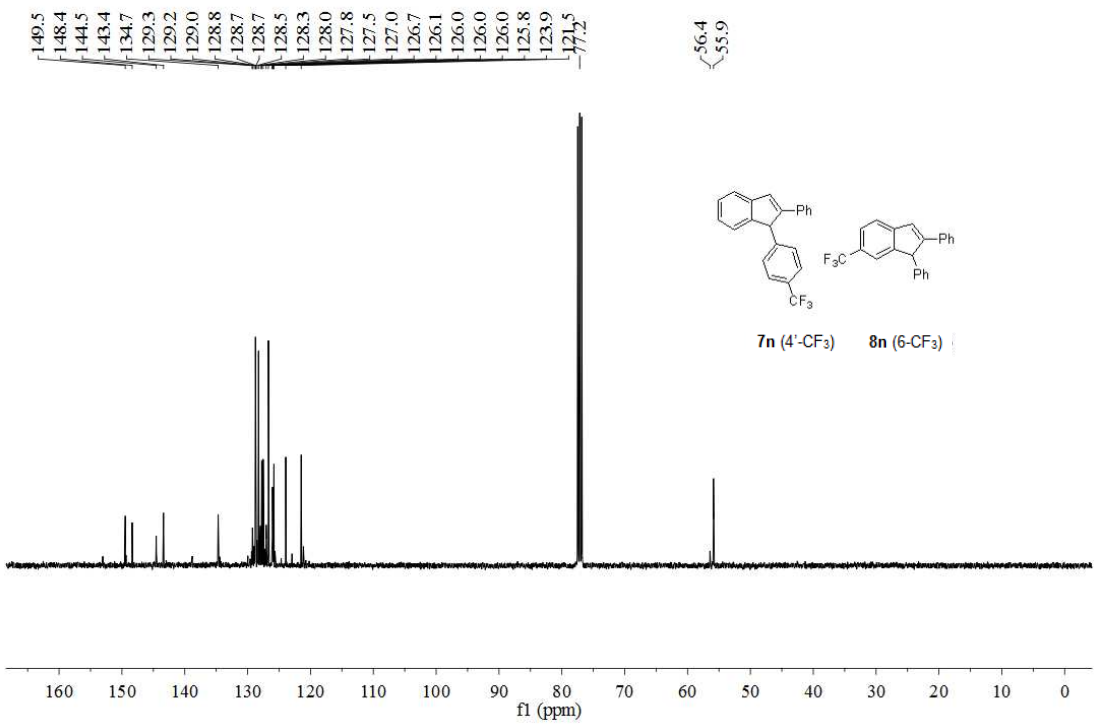
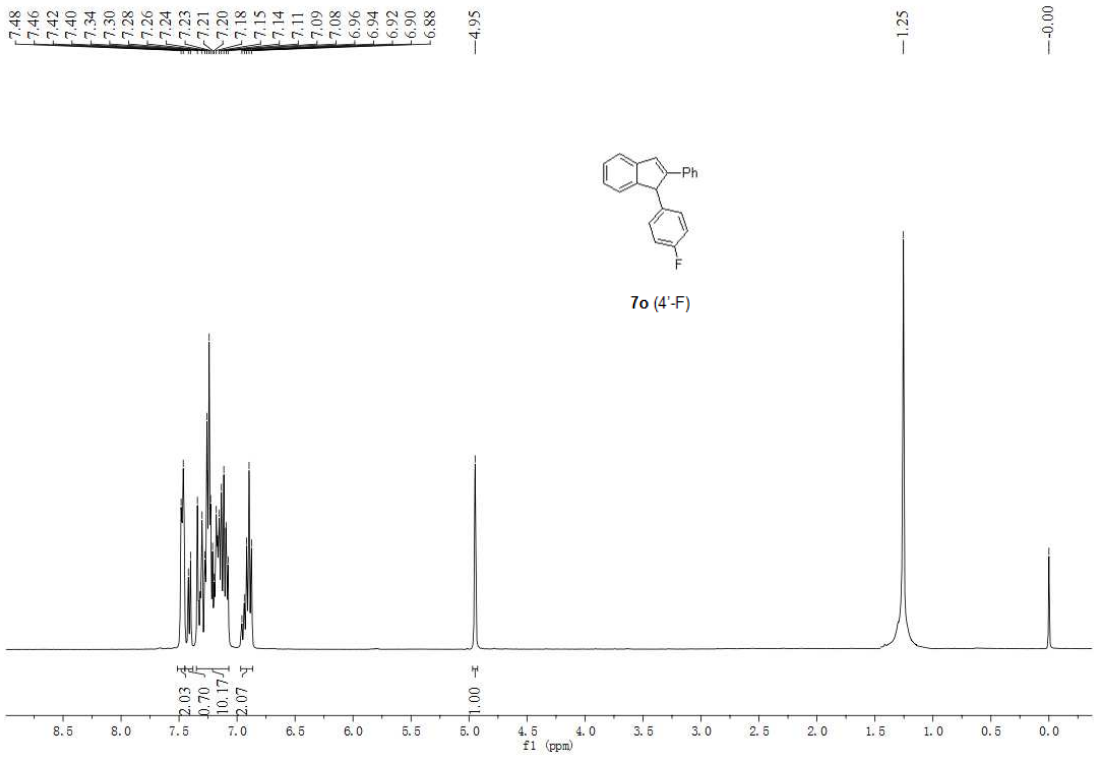
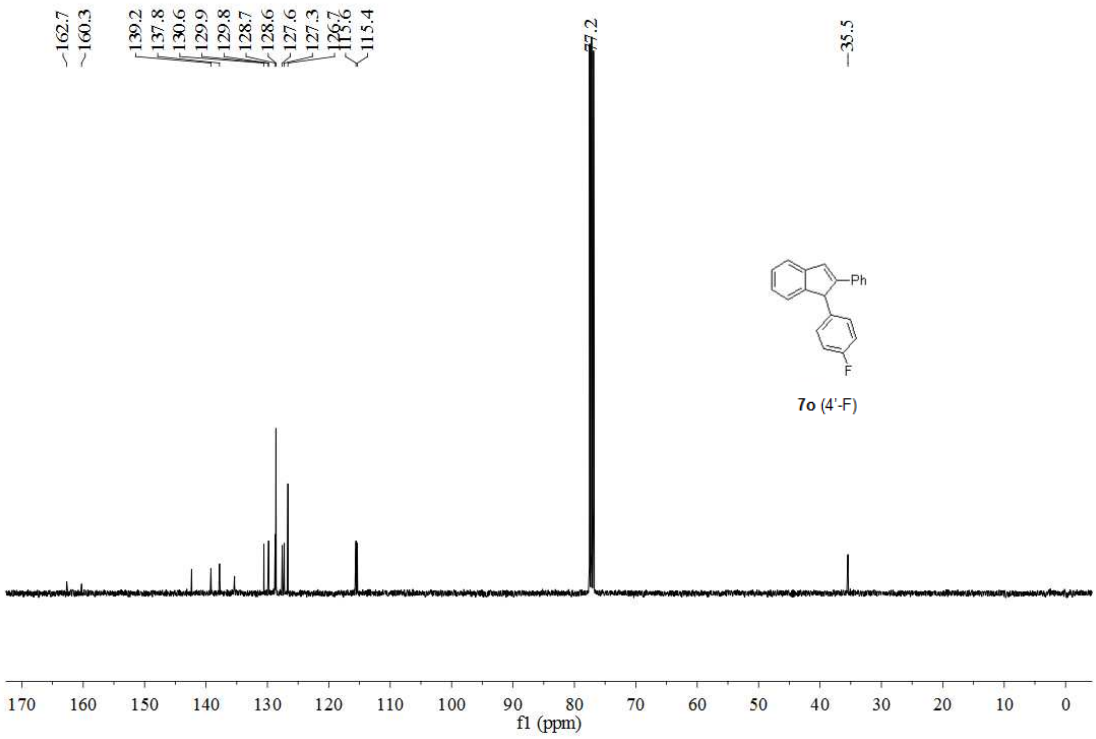
7.20
7.19
7.14
7.12
5.02
5.01
1.54
0.00
Ph
CF3
F3C
Ph
Ph
7n (4'-CF3)/ 8n (6-CF3) 5: 1
5.06
1.09
1.53
6.03
1.94
2.06
1.00
0.20
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

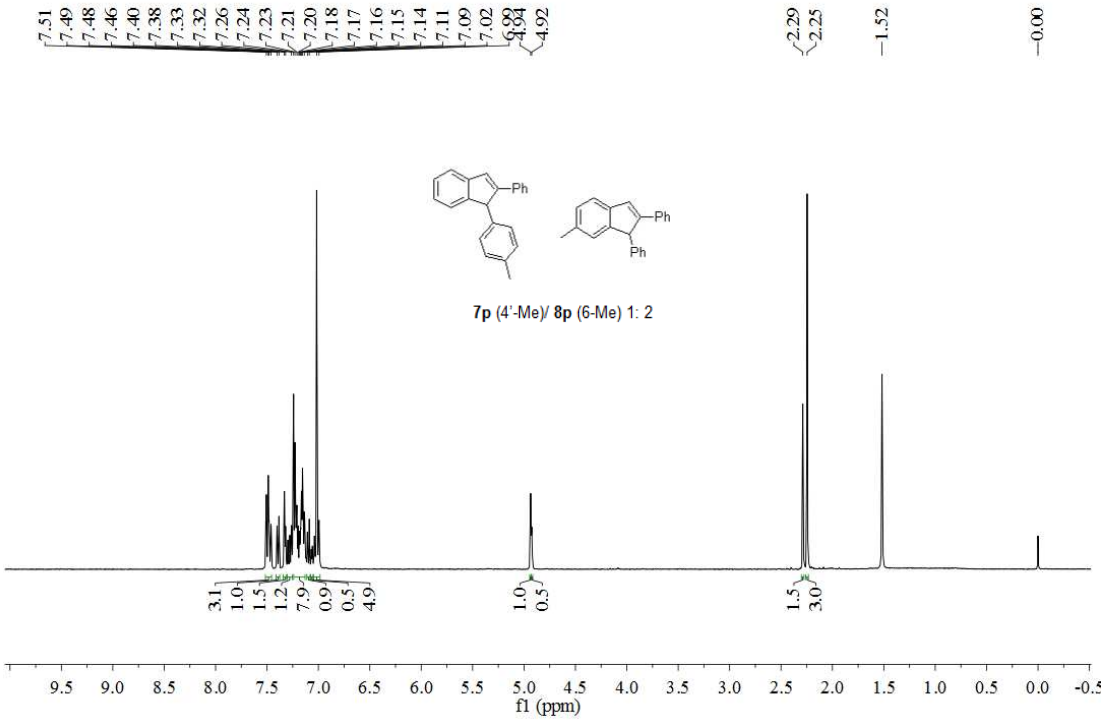

149.5
148.4
144.5
143.4
134.7
129.3
129.2
129.0
128.8
128.7
128.7
128.5
128.3
128.0
127.8
127.5
127.0
126.7
126.1
126.0
126.0
126.0
125.8
123.9
121.5
77.2
56.4
55.9
Ph
CF3
F3C
Ph
Ph
7n (4'-CF3)
8n (6-CF3)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

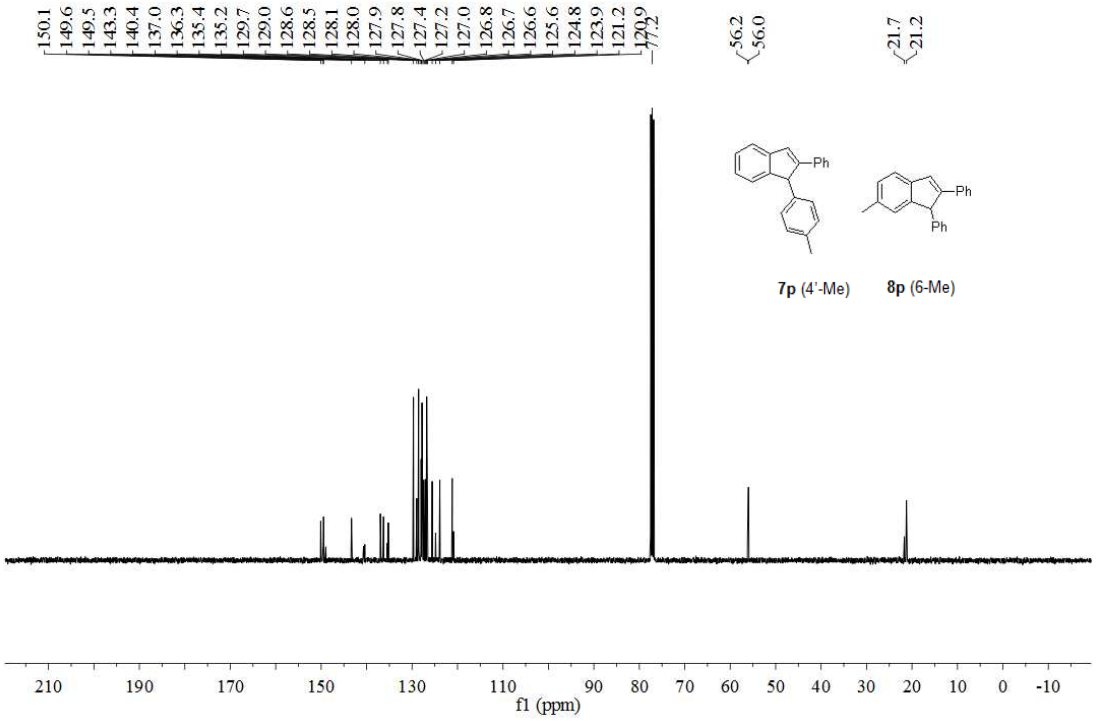

7.48
7.46
7.42
7.40
7.34
7.30
7.28
7.26
7.24
7.23
7.21
7.20
7.18
7.15
7.14
7.11
7.09
7.08
6.96
6.94
6.92
6.90
6.88
4.95
1.25
0.00
Ph
F
2.03
0.70
10.17
2.07
1.00
f1 (ppm)

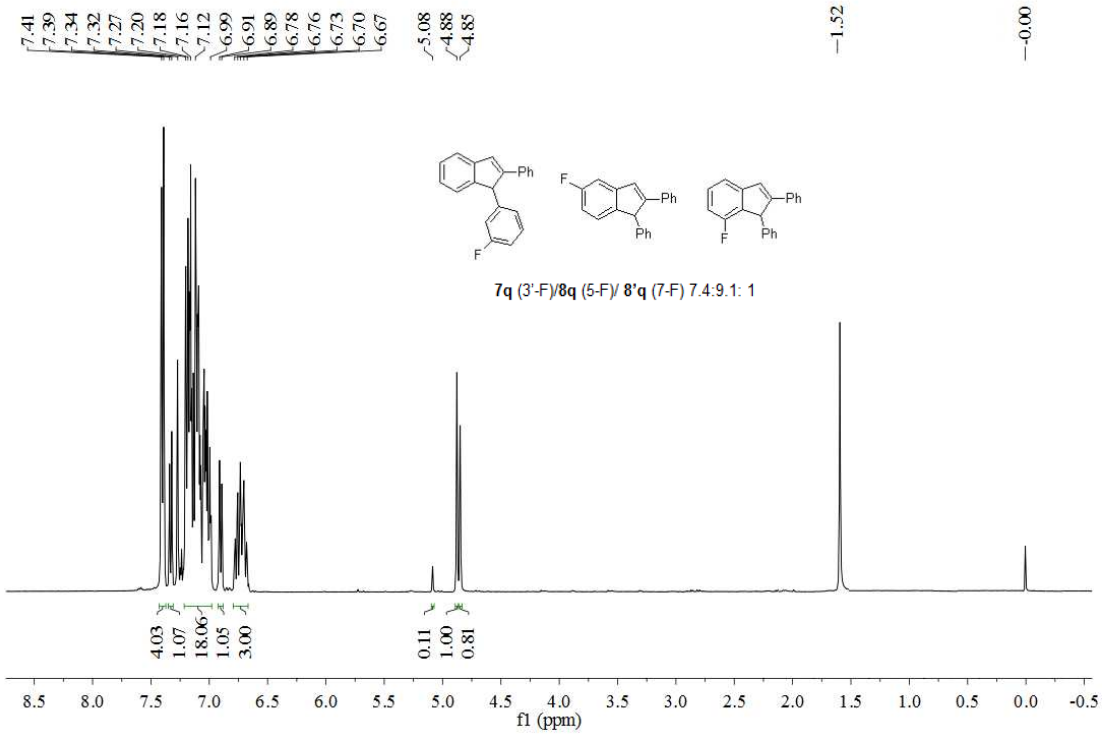
7o (4'-F)

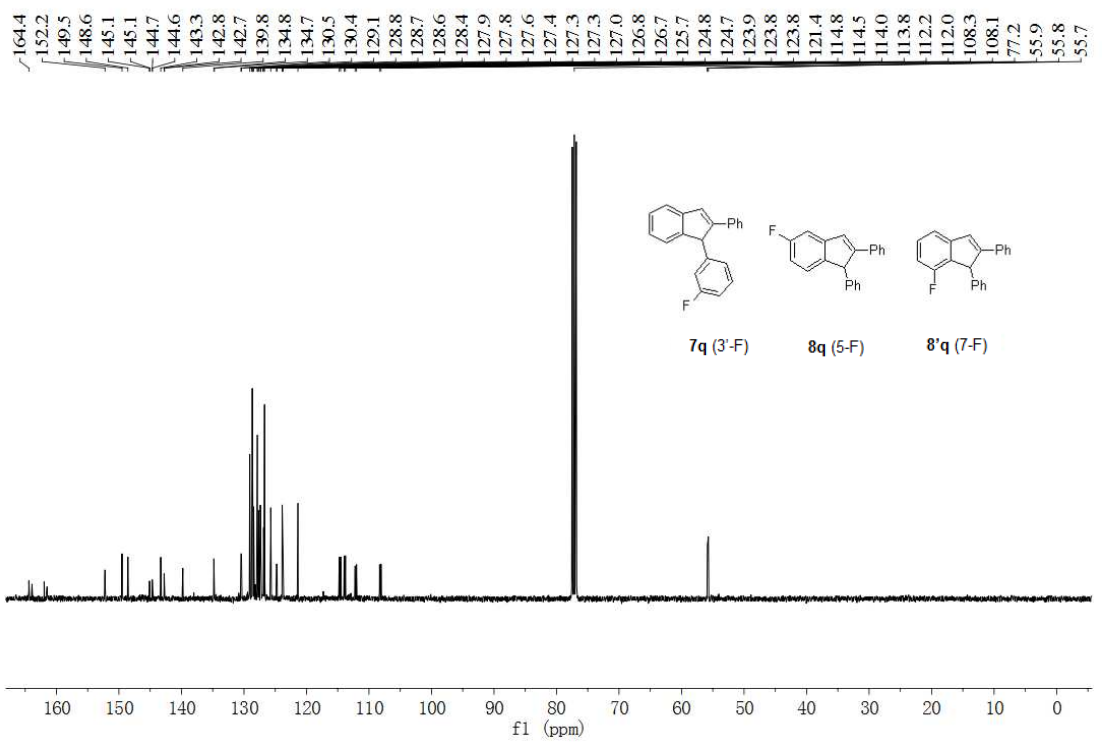

162.7
160.3
139.2
137.8
130.6
129.9
129.8
128.7
128.6
127.6
127.3
126.7
115.6
115.4
77.2
35.5
Ph
F
f1 (ppm)

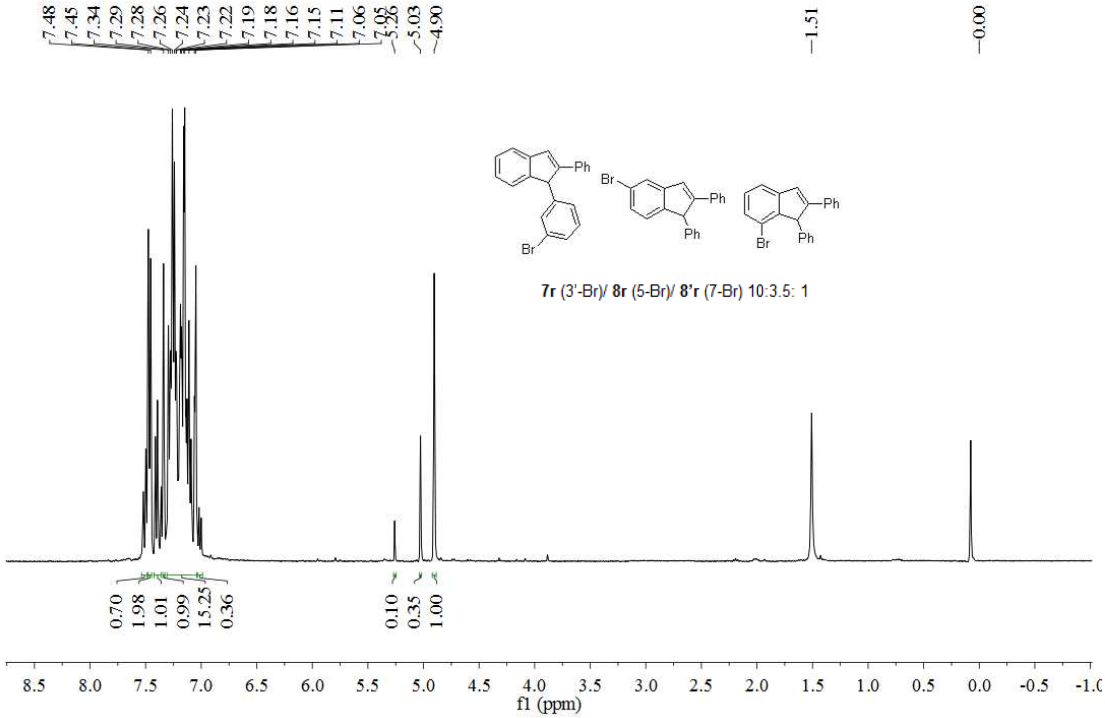
7o (4'-F)

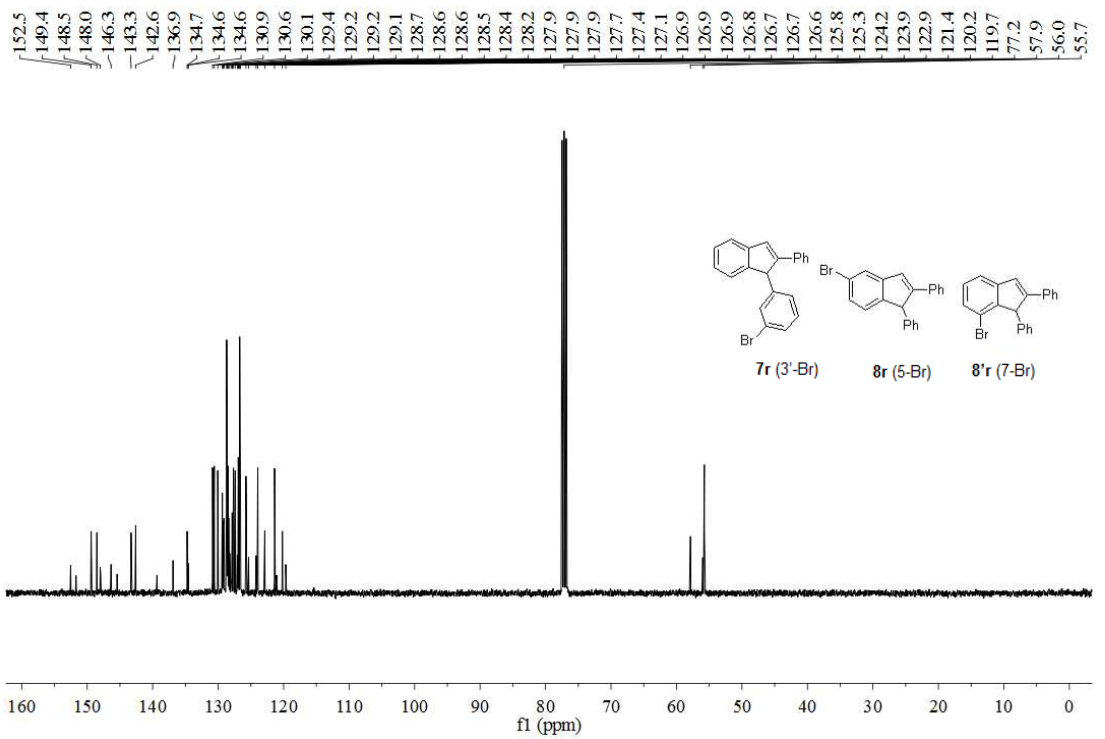

7.51
7.49
7.48
7.46
7.40
7.38
7.33
7.32
7.26
7.24
7.23
7.21
7.20
7.18
7.17
7.16
7.15
7.14
7.11
7.09
7.02
6.99
6.94
4.92
2.29
2.25
1.52
0.00
Ph
Ph
Ph
7p (4'-Me)/ 8p (6-Me) 1: 2
3.1
1.0
1.5
1.2
7.9
0.9
0.5
4.9
1.0
0.3
1.5
3.0
f1 (ppm)

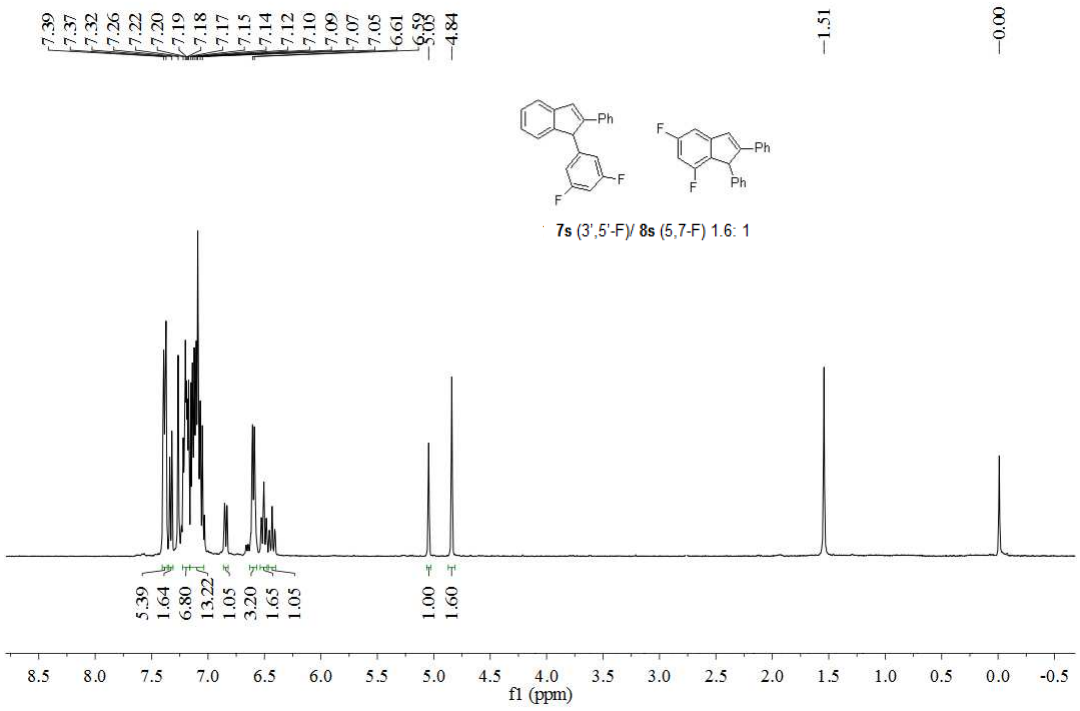

150.1
149.6
149.5
143.3
140.4
137.0
136.3
135.4
135.2
129.7
129.0
128.6
128.5
128.1
128.0
127.9
127.8
127.4
127.2
127.0
126.8
126.7
126.6
125.6
124.8
123.9
121.2
120.9
77.2
56.2
56.0
21.7
21.2
Ph
Ph
Ph
7p (4'-Me)
8p (6-Me)
f1 (ppm)

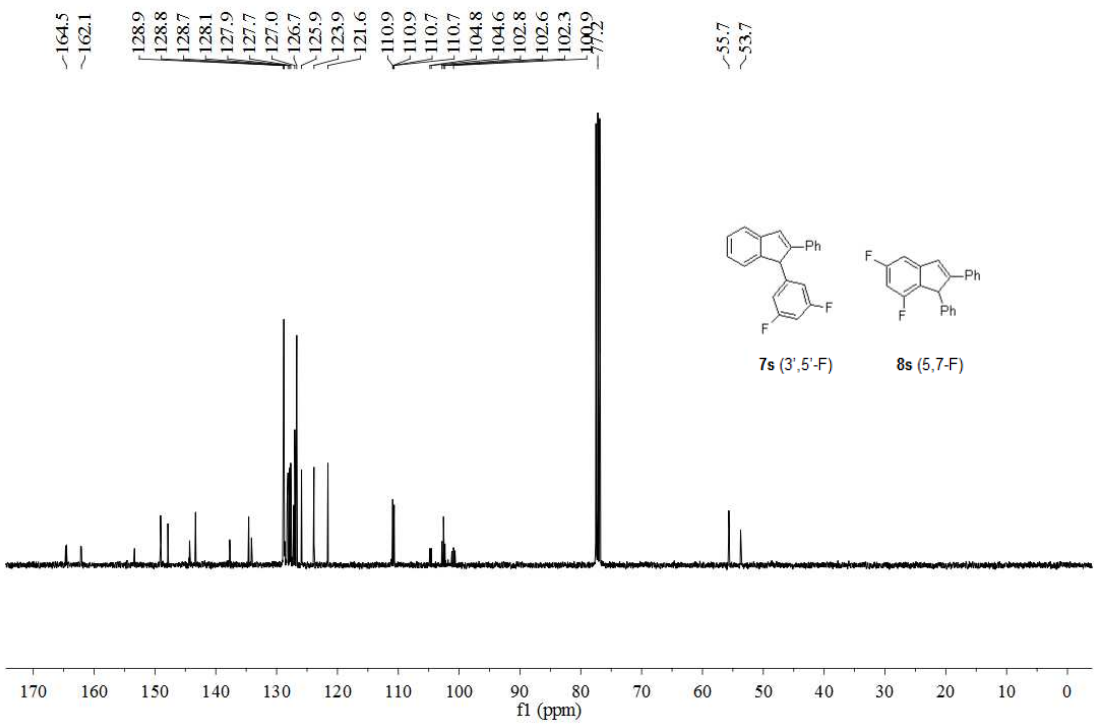

7.41
7.39
7.34
7.32
7.27
7.20
7.18
7.16
7.12
6.99
6.91
6.89
6.78
6.76
6.73
6.70
6.67
5.08
4.88
4.85
1.52
0.00
Ph
F
Ph
F
Ph
Ph
Ph
F
Ph
7q (3'-F)/8q (5-F)/ 8'q (7-F) 7.4:9.1: 1
4.03
1.07
18.06
1.05
3.00
0.11
1.00
0.81
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


164.4
152.2
149.5
148.6
145.1
145.1
144.7
144.6
143.3
142.8
142.7
139.8
134.8
134.7
130.5
130.4
129.1
128.8
128.7
128.6
128.4
127.9
127.8
127.6
127.4
127.3
127.3
127.0
126.8
126.7
125.7
124.8
124.7
123.9
123.8
123.8
121.4
114.8
114.5
114.0
113.8
112.2
112.0
108.3
108.1
77.2
55.9
55.8
55.7
Ph
F
Ph
F
Ph
Ph
Ph
F
Ph
7q (3'-F)
8q (5-F)
8'q (7-F)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.48
7.45
7.34
7.29
7.28
7.26
7.24
7.23
7.22
7.19
7.18
7.16
7.15
7.11
7.06
5.05
5.03
4.90
1.51
0.00
Ph
Br
Ph
Ph
Br
Ph
Ph
Br
Ph
7r (3'-Br)/ 8r (5-Br)/ 8'r (7-Br) 10:3.5: 1
0.70
1.98
1.01
0.99
15.25
0.36
0.10
0.35
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


152.5
149.4
148.5
148.0
146.3
143.3
142.6
136.9
134.7
134.6
134.6
130.9
130.6
130.1
129.4
129.2
129.2
129.1
128.7
128.6
128.6
128.5
128.4
128.2
127.9
127.9
127.9
127.7
127.4
127.1
126.9
126.9
126.9
126.8
126.7
126.7
126.6
125.8
125.3
124.2
123.9
122.9
121.4
120.2
119.7
77.2
57.9
56.0
55.7
Ph
Br
Br
Ph
Ph
Br
Ph
Ph
7r (3'-Br)
8r (5-Br)
8'r (7-Br)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.39
7.37
7.32
7.26
7.22
7.20
7.19
7.18
7.17
7.15
7.14
7.12
7.10
7.09
7.07
7.05
6.61
5.59
5.05
4.84
1.51
0.00
Ph
F
F
F
Ph
F
Ph
7s (3',5'-F)/ 8s (5,7-F) 1.6: 1
5.39
1.64
6.80
13.22
1.05
3.20
1.65
1.05
1.00
1.60
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


164.5
162.1
128.9
128.8
128.7
128.1
127.9
127.7
127.0
126.7
125.9
123.9
121.6
110.9
110.9
110.7
110.7
104.8
104.6
102.8
102.6
102.3
100.9
77.2
55.7
53.7
Ph
F
F
F
Ph
F
Ph
7s (3',5'-F)
8s (5,7-F)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)