Electronic Supplementary Material (ESI) for ChemComm.

Palladium(II)-Catalyzed *meta*-Selective Direct Arylation of *O*-*β*-Naphthyl Carbamate

Jingchang Zhang,[a] Qingwen Liu,[a] Xufei Liu[b], Suoqin Zhang,*[a], Pingping Jiang, [a], Yanxiang Wang,[a] Shengyuan Luo, [a] Yang Li[a] and Qifeng Wang*[a], [b]

Table of cotents

(A) General information S2

(B) Optimisation for the palladium-catalyzed Coupling Reaction S2

(C) Genaral Procedure for Coupling Reaction S3

(D) Experimental data of isolated compound.....S4

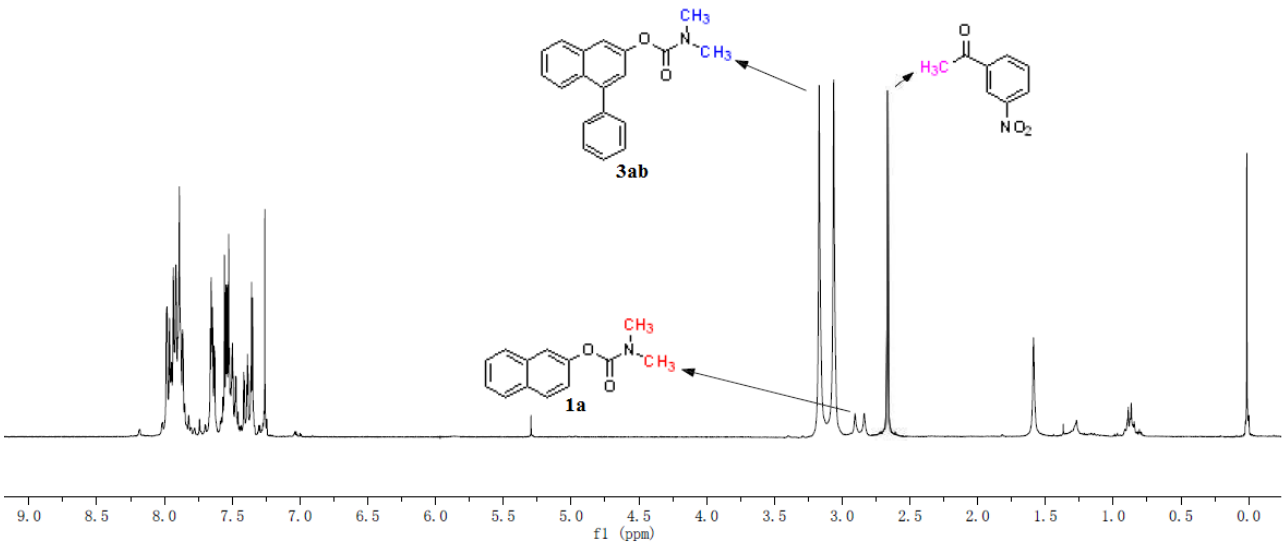
(E) Copies of ^{1}H and ^{13}C spectra S12

(A) General information

Unless otherwise noted, all the reactions were performed under N_2 atmosphere using Schlenk technique. All reagents were used without purification as commercially available. All reactions were monitored by thin layer chromatography. Purification of reaction products were carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. The melting point was recorded on a melting point apparatus (MPA100, Stanford Research Systems, Inc.). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 300 MHz spectrometers (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR). Chemical shifts of ^{1}H and ^{13}C signals were given in δ relative to the solvents residual ^{1}H-signal (CH-Cl_3, δ(H) 7.26, DMSO, δ(H) 2.50) or to Me_4Si (δ 0.0). CDCl3 resonance in the ^{13}C spectrum is 77.2 ppm and DMSO resonance in the ^{13}C spectrum is 39.5 ppm. The following abbreviations are used: s, singlet, d, doublet, t, triplet, q, quartet, quint, quintuplet, m, multiplet, br, broad. High-resolution mass spectral analysis (HRMS) datas were measured on a Bruker ApexII mass spectrometer by means of the ESI technique.

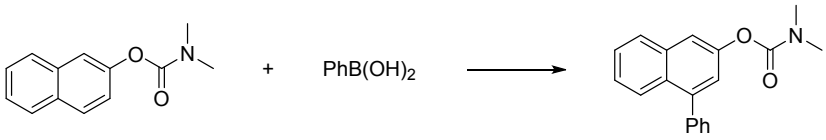
(B) Optimization of the reaction conditions for *meta*-C-H bond direct arylation.

O-*β*-naphthyl dimethylcarbamate (43.0 mg, 0.2 mmol) **1a**, phenyl boronic acid (73.2 mg, 0.6 mmol) **2a**, Oxidants and $Pd(OAc)_2$ (2.24 mg, 0.01 mmol) were added to a Schlenk tube. The tube was degassed and refilled with N_2 for three times. Then solvent (1 ml, 0.2 M) was added by syringe. The reaction mixture was stirred at room temperature for the indicated length of time in Table 1. Then the reaction mixture was filtered through celite and washed with CH_2Cl_2. The mixture was neutralized with saturated K_2CO_3 aqueous solution. The aqueous phase was re-extracted with CH_2Cl_2 (3 × 10 ml). The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. 1-(3-nitrophenyl) ethanone (33.0mg, 0.2mmol) was added and the mixture was dissolved in 1ml $CDCl_3$. An aliquot was removed and the yield was determined by ^{1}H NMR spectroscopy. Chemical shifts of methyl groups in **1a**, **3ab** and internal standard were given in Scheme 1.



Scheme 1. Chemical shifts of methyl groups in 1a, 3ab and internal standard. NMR yields were calculated according to the integration of methyl groups.

Table 1. Optimization of the reaction conditions for *meta*-C-H bond direct arylation.



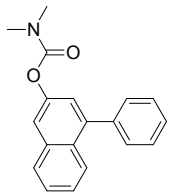
Entry	Catalyst(mol%)	Oxidant(equvi)	Solvent	Additive(equiv)	T(°C)	Time(h)	Yield(%)
1	$Pd(OAc)_2$(5)	$Cu(TfO)_2$(2)/ Ag_2O(0.5)	Toluene	-	120	24	--
2	$Pd(OAc)_2$(5)	BQ(2)/O_2 (1atm)	t-BuOH	K_2HPO_4(1.5)	100	24	--
3	$Pd(OAc)_2$(5)	$Cu(OAc)_2$(2)	TFA	O_2(1 atm)	25	24	--
4[b]	$Pd(OAc)_2$(5)	AgOAc(2)	TFA	-	50	36	--
5[b]	$Pd(OAc)_2$(5)	AgOAc(2)	TFA	-	100	36	< 5
6	$Pd(OAc)_2$(5)	$K_2S_2O_8$(6)	TFA	-	70	36	15
7	$Pd(OAc)_2$(5)	$K_2S_2O_8$(6)	TFA	-	50	36	42
8	$Pd(OAc)_2$(5)	$K_2S_2O_8$(6)	TFA	-	25	36	45
9	$Pd(OAc)_2$(5)	$K_2S_2O_8$(6)	TFA	AgOAc(0.05)	25	36	56
10	$Pd(OAc)_2$(5)	$K_2S_2O_8$(6)	TFA:HOAc=1:1	AgOAc(0.05)	25	36	72
11	$Pd(OAc)_2$(5)	$K_2S_2O_8$(6)	TFA:HOAc=2:1	AgOAc(0.05)	25	36	84
12	$Pd(OAc)_2$(5)	$K_2S_2O_8$(6)	TFA:HOAc=3:1	AgOAc(0.05)	25	36	70
13	$Pd(OAc)_2$(5)	$K_2S_2O_8$(3)	TFA:HOAc=2:1	AgOAc(0.05)	25	36	74
14	$Pd(OAc)_2$(5)	$K_2S_2O_8$(6)	TFA:HOAc=2:1	AgOAc(0.05)	25	12	64
15	$Pd(OAc)_2$(5)	$K_2S_2O_8$(6)	TFA:HOAc=2:1	AgOAc(0.05)	25	48	75

[a] Yields were determined by ^1H NMR using 1-(3-nitrophenyl) ethanone as an internal standard. [b] Using PhI (3 eq.) to replace $PhB(OH)_2$.

(C) Genaral Procedure for *meta*-direct arylation.

O-*β*-naphthyl dimethylcarbamate (**1a**) (1.0 mmol), aryl boronic acid (3 mmol), $K_2S_2O_8$ (6 mmol), AgOAc (0.05 mmol) and $Pd(OAc)_2$ (0.05 mmol) were added to a Schlenk tube. The tube was degassed and refilled with N_2 for three times. Then solvent (TFA:AcOH=2:1, v/v, 5ml) was added by syringe, The reaction mixture was stirred at room temperature and monitored by TLC analysis. After the starting material was completely consumed, the reaction mixture was filtrated through celite and washed with CH_2Cl_2. The mixture was neutralized with saturated K_2CO_3 aqueous solution. The aqueous phase was extracted with CH_2Cl_2 (3 × 20 ml). The combined organic phase were dried over Na_2SO_4 and concentrated under reduced pressure, the residue was purified by flash chromatography on silica gel (petroleum ether/dichloromethane as an eluent) to afford the *meta*-arylated product.

(D) Experimental data of isolated compounds



3ab

4-phenylnaphthalen-2-yl dimethylcarbamate (3ab)

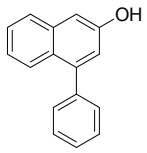
The reaction was performed according to the general procedure for 36 hours. Flash chromatography (petroleum ether: dichloromethane=1:1) yielded the product **3ab** (216.6 mg, 74%), Colorless oil.

^{1}H NMR (300 MHz, dmso) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 2.1 Hz, 1H), 7.58 – 7.44 (m, 7H), 7.24 (d, *J* = 2.4 Hz, 1H), 3.10 (s, 3H), 2.94 (s, 3H).

^{13}C NMR (75 MHz, dmso) δ(ppm) 154.0, 148.3, 140.8, 139.0, 133.9, 129.5(2C), 128.5, 128.4 (2C), 127.9, 127.6, 126.4, 125.7, 125.1, 122.5, 117.9 , 36.2, 36.1.

HRMS (ESI) m/z calcd for $C_{19}H_{17}NO_2$ ([M+H]$^+$):292.1332, found: 292.1334.

To confirm the structure of **3ab** data is *meta*-arylated product, we removed the carbamate group and procedure and the NMR data is shown below:



3ab-OH

4-phenylnaphthalen-2-ol (3ab-OH)

To a flask was added **3ab** (87.4 mg, 0.3 mmol), NaOH (120 mg, 3 mmol), EtOH (3ml), the mixture was refluxed for overnight. After that, the reaction mixture was diluted with CH_2Cl_2 through celite and washed with water (1 × 5 ml). The aqueous phase was re-extracted with CH_2Cl_2 (3 × 5 ml). The combined organic phase were dried over Na_2SO_4 and concentrated under reduced pressure, the residue was purified by flash chromatography (petroleum ether: ethyl acetate=7:1) to afford the product **3ab-OH** (60.1 mg, 91%), Red oil.

^{1}H NMR (300 MHz, cdcl$_3$) δ 7.80 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.51 – 7.42 (m, 6H), 7.30 – 7.26 (m, 1H), 7.18 (d, *J* = 2.7 Hz, 1H), 7.07 (d, *J* = 2.7 Hz, 1H), 5.16 (br, 1H).

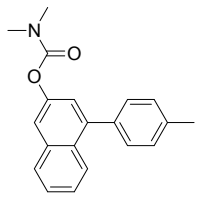
^{13}C NMR (75 MHz, cdcl$_3$) δ 152.8, 142.6, 140.3, 135.4, 130.1 (2C), 128.4 (2C), 127.6, 127.5, 127.0, 126.6, 126.2, 123.9, 118.9, 109.4.

HRMS (ESI) m/z calcd for $C_{16}H_{12}O$ ([M+H]$^+$):221.2733, found: 221.2730.

The NMR data is consistent with that reported in the literature. [1]

In ^{13}C NMR of **3ab**, the chemical shifts of 117.9 and 122.5 ppm are assigned to *ortho*-sites of carbamate group. In its substrate *O*-*β*-naphthyl dimethylcarbamate **1a**, the corresponding chemical shifts are 118.3 and 121.5. From the chemical shifts and height of the peaks, we can confirm the *ortho*-sites of carbamate group in **3ab** are C-H bonds without any substitution. In the examples below,

these two chemical shifts exist in acceptable changes. Also to confirm again the structure, **3ae** was converted to its corresponding **3ae-OH** and the structure is consistent with that reported in the literature. [1]



3ac

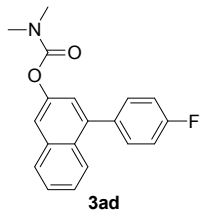
4-(p-tolyl)naphthalen-2-yl dimethylcarbamate (3ac)

The reaction was performed according to the general procedure for 40 hours. Flash chromatography (petroleum ether: dichloromethane=1:1) yielded the product **3ac** (186.3 mg, 61%), Colorless oil.

^{1}H NMR (300 MHz, cdcl$_3$) δ(ppm) 7.89 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.50 – 7.35 (m, 4H), 7.30 (s, 1H), 7.28 (d, *J* = 0.3 Hz, 1H), 7.24 (dd, *J* = 2.4, 0.6 Hz, 1H), 3.16 (s, 3H), 3.05 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (75 MHz, cdcl$_3$) δ (ppm)155.1, 148.7, 142.0, 137.3, 137.1, 134.6, 130.0 (2C), 129.8, 129.1(2C), 128.1, 126.4, 126.2, 125.5, 122.6, 118.0, 36.9, 36.6, 21.4.

HRMS (ESI) m/z calcd for $C_{20}H_{19}NO_2$ ([M+H]$^+$):306.1489, found: 306.1484.



3ad

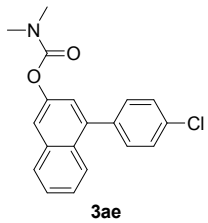
4-(4-fluorophenyl)naphthalen-2-yl dimethylcarbamate (3ad)

The reaction was performed according to the general procedure for 14 hours. Flash chromatography (petroleum ether: dichloromethane=1:1) yielded the product **3ad** (213.4 mg, 69%), Colorless oil.

^{1}H NMR (300 MHz, cdcl$_3$) δ 7.85 (d, *J* = 8.7 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.51 – 7.37 (m, 4H), 7.22 (d, *J* = 2.1 Hz, 1H), 7.21 – 7.13 (m, 2H), 3.16 (s, 3H), 3.05 (s, 3H).

^{13}C NMR (75 MHz, cdcl$_3$) δ(ppm) 162.5 (d, $^1J_{C\text{-}F}$=245Hz), 155.1, 148.6, 140.7, 136.0 (d, $^4J_{C\text{-}F}$=3Hz), 134.5, 131.7 (d, $^3J_{C\text{-}F}$ = 7.5 Hz, 2C), 129.7, 128.2, 126.5, 125.8, 125.7, 122.8, 118.3, 115.3(d, $^2J_{C\text{-}F}$=21Hz, 2C), 36.9, 36.6.

HRMS (ESI) m/z calcd for $C_{19}H_{16}FNO_2$ ([M+H]$^+$):310.1238, found: 310.1234.



3ae

4-(4-chlorophenyl)naphthalen-2-yl dimethylcarbamate (3ae)

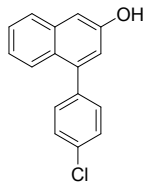
The reaction was performed according to the general procedure for 17 hours. Flash chromatography (petroleum ether: dichloromethane=1:1) yielded the product **3ae** (224.8 mg, 69%), Colorless oil.

^{1}H NMR (300 MHz, cdcl$_3$) δ (ppm) 7.85 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.52 – 7.37 (m, 6H), 7.23 (d, *J* = 2.4 Hz, 1H), 3.16 (s, 3H), 3.05 (s, 3H).

^{13}C NMR (75 MHz, cdcl$_3$) δ (ppm) 155.0, 148.6, 140.5, 138.5, 134.5, 133.7, 131.4 (2C), 129.5, 128.6 (2C), 128.2, 126.6, 125.8, 125.7, 122.7, 118.5, 36.9, 36.6.

HRMS (ESI) m/z calcd for $C_{19}H_{16}ClNO_2$ ([M+H]$^+$):326.0942, found: 326.0942.

To confirm the structure of **3ae** is *meta*-arylated product again, we removed the carbamate group and procedure and the NMR data is shown below:



3ae-OH

4-(4-chlorophenyl)naphthalen-2-ol (3ae-OH)

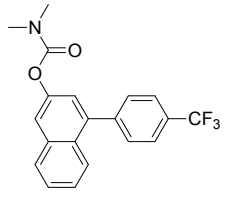
To a flask added **3ae** (97.7 mg, 0.3 mmol), NaOH (120 mg, 3 mmol), EtOH (3ml), the mixture was refluxed over night, After that, the reaction mixture was diluted with CH_2Cl_2 through celite and washed with water (1 × 5 ml). The aqueous phase was re-extracted with CH_2Cl_2 (3 × 5 ml). The combined organic phase were dried over Na_2SO_4 and concentrated under reduced pressure, the residue was purified by flash chromatography (petroleum ether: ethyl acetate=7:1) to afford the product **3ae-OH** (70.3 mg, 92%), pale purple oil.

^{1}H NMR (300 MHz, cdcl$_3$) δ7.76 – 7.72 (m, 2H), 7.49 – 7.38 (m, 5H), 7.32 – 7.26 (m, 1H), 7.19 (d, *J* = 2.4 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 4.36 (br, 1H).

^{13}C NMR (75 MHz, cdcl$_3$) δ 152.7, 141.2, 138.6, 135.3, 133.7, 131.3 (2C), 128.6 (2C), 127.3, 127.1, 126.8, 125.9, 124.2, 118.9, 109.8.

HRMS (ESI) m/z calcd for $C_{16}H_{11}ClO$ ([M+H]$^+$):255.0571, found: 255.0575.

The NMR data is consistent with that reported in the literature. [1]



3af

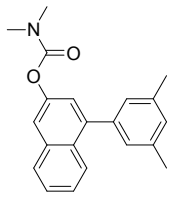
4-(4-(trifluoromethyl)phenyl)naphthalen-2-yl dimethylcarbamate (3af)

The reaction was performed according to the general procedure for 9 hours. Flash chromatography (petroleum ether: dichloromethane=1:1) yielded the product **3af** (258.7 mg, 72%), white oil.

^{1}H NMR (300 MHz, dmso) δ 8.01 (d, *J* = 7.8 Hz, 1H), 7.91 (s, 1H), 7.89 (s, 1H), 7.77 (d, *J* = 2.4 Hz, 1H), 7.75 – 7.71 (m, 3H), 7.61 – 7.55 (m, 1H), 7.52 – 7.46 (m, 1H), 7.31 (d, *J* = 2.4 Hz, 1H), 3.10 (s, 3H), 2.94 (s, 3H).

^{13}C NMR (75 MHz, cdcl$_3$) δ 154.9, 148.6, 143.7, 140.1, 134.5, 130.4 (3C), 129.2, 128.2, 126.6, 126.0, 125.5 (2C), 125.3, 122.8, 118.9, 107.7, 36.8, 36.5.

HRMS (ESI) m/z calcd for $C_{20}H_{16}F_3NO_2$ ([M+H]$^+$):360.1206, found: 360.1205.



3ag

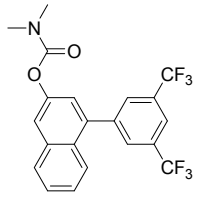
4-(3,5-dimethylphenyl)naphthalen-2-yl dimethylcarbamate (3ag)

To a Schlenk tube under N_2 atmosphere added **1a** (215.2 mg, 1 mmol), (3, 5-dimethylphenyl) boronic acid (449.9 mg, 3 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), $K_2S_2O_8$ (1622 mg, 6 mmol), AgOAc (8.3 mg, 0.05 mmol), TFA (5ml). The mixture was stirred for 6 hours at room temperature under N_2. Then the reaction mixture was neutralized with saturated K_2CO_3 aqueous solution and extracted with CH_2Cl_2 (20 ml × 3). The combined organic phase were dried over Na_2SO_4 and concentrated under reduced pressure, the residue was purified by flash chromatography (petroleum ether: dichloromethane=1:1) to afford the product **3ag** (201.2 mg, 63%), Yellow oil.

^{1}H NMR (300 MHz, dmso) δ(ppm) 7.96 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 2.4 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.48 – 7.43 (m, 1H), 7.19 (d, *J* = 2.1 Hz, 1H), 7.10 (s, 1H), 7.07 (s, 2H), 3.09 (s, 3H), 2.94 (s, 3H), 2.35 (s, 6H).

^{13}C NMR (75 MHz, cdcl$_3$) δ(ppm) 155.1, 148.6, 142.2, 139.9, 137.8 (2C), 134.5, 129.7, 129.1, 128.1, 127.9 (2C), 126.3 C, 126.3, 125.4, 122.4, 117.9, 36.8, 36.6, 21.4 (2C).

HRMS (ESI) m/z calcd for $C_{21}H_{21}NO_2$ ([M+H]$^+$):320.1645, found: 320.1652.



3ah

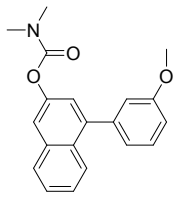
4-(3,5-bis(trifluoromethyl)phenyl)naphthalen-2-yl dimethylcarbamate (3ah)

The reaction was performed according to the general procedure for 3 hours. Flash chromatography (petroleum ether: ethyl acetate=10:1) yielded the product **3ah** (306.2 mg, 71%), White solid, mp.92-93^{0}C.

^{1}H NMR (300 MHz, dmso) δ(ppm) 8.25 (s, 1H), 8.17 (s, 2H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 1.8 Hz, 1H), 7.67 – 7.58 (m, 2H), 7.56 – 7.50 (m, 1H), 7.45 (d, *J* = 2.4 Hz, 1H), 3.11 (s, 3H), 2.95 (s, 3H).

^{13}C NMR (75 MHz, cdcl$_3$) δ(ppm) 155.0, 148.6, 142.2, 138.4, 134.7, 132.2, 131.7, 130.3 (2C), 129.1, 128.6, 127.0 (2C), 126.6, 124.9, 123.3, 121.6 (2C), 119.7, 36.9, 36.7.

HRMS (ESI) m/z calcd for $C_{21}H_{15}F_6NO_2$ ([M+H]$^+$):428.1080, found: 428.1081.



3ai

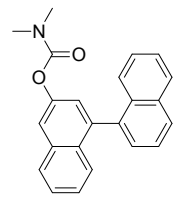
4-(3-methoxyphenyl)naphthalen-2-yl dimethylcarbamate (3ai)

To a Schlenk tube under N_2 atmosphere added 2-naphthyl dimethylcarbamate (215.2 mg, 1 mmol), (3-methoxyphenyl) boronic acid (455.9 mg, 3 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), $K_2S_2O_8$ (1622 mg, 6 mmol), AgOAc (8.3 mg, 0.05 mmol), TFA (5ml). The mixture was stirred for 8 hours at room temperature under N_2. Then the reaction mixture was neutralized with saturated K_2CO_3 aqueous solution and extracted with CH_2Cl_2 (20 ml × 3). The combined organic phase were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether: dichloromethane=1:1) to afford the product **3ai** (202.5 mg, 63%), White oil.

^{1}H NMR (300 MHz, cdcl$_3$) δ(ppm) 7.89 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 2.1 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.41 – 7.36 (m, 2H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.10 – 7.07 (m, 1H), 7.05 – 7.04 (m, 1H), 6.99 – 6.95 (m, 1H), 3.85 (s, 3H), 3.15 (s, 3H), 3.05 (s, 3H).

^{13}C NMR (75 MHz, cdcl$_3$) δ (ppm)159.6, 155.1, 148.6, 141.7, 141.4, 134.5, 129.6, 129.3, 128.1, 126.4, 126.1, 125.6, 122.6, 122.5, 118.2, 115.5, 113.3, 55.4, 36.8, 36.6.

HRMS (ESI) m/z calcd for $C_{20}H_{19}NO_3$ ([M+H]$^+$):322.1438, found: 322.1436.



3aj

.

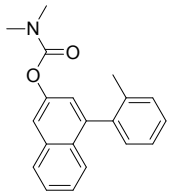
[1,1'-binaphthalen]-3-yl dimethylcarbamate (3aj)

The reaction was performed according to the general procedure for 4 hours. Flash chromatography (petroleum ether: dichloromethane=1:1) yielded the product **3aj** (200.5 mg, 59%), yellow oil.

^{1}H NMR (300 MHz, dmso) δ(ppm) 8.08 – 8.01 (m, 3H), 7.82 (d, *J* = 2.1 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.56 – 7.49 (m, 3H), 7.39 – 7.30 (m, 3H), 7.24 – 7.17 (m, 2H), 3.09 (s, 3H), 2.93 (s, 3H).

^{13}C NMR (75 MHz, cdcl$_3$) δ(ppm) 155.1, 148.8, 140.2, 137.7, 134.3, 133.7, 132.9, 130.9, 128.3 (2C), 128.1, 128.0, 126.7, 126.7, 126.5, 126.3, 126.0, 125.6, 125.4, 123.6, 118.5, 36.9, 36.7.

HRMS (ESI) m/z calcd for $C_{23}H_{19}NO_2$ ([M+H]$^+$):342.1489, found: 342.1485.



3ak

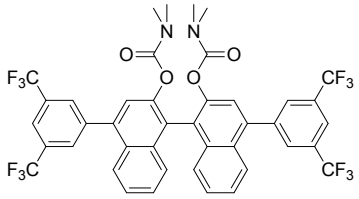
4-(o-tolyl)naphthalen-2-yl dimethylcarbamate (3ak)

The reaction was performed according to the general procedure for 36 hours. Flash chromatography (petroleum ether: dichloromethane=1:1) yielded the product **3ak** (201.5 mg, 66%), Colorless oil.

^{1}H NMR (300 MHz, cdcl$_3$) δ 7.88 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 2.4 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.38 – 7.29 (m, 5H), 7.21 (d, *J* = 2.1 Hz, 1H), 3.16 (s, 3H), 3.07 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (75 MHz, cdcl$_3$) δ 154.9, 148.6, 141.3, 139.4, 136.7, 134.1, 130.3, 129.9 (2C), 128.0, 127.8, 126.3, 126.0, 125.6, 125.5, 122.4, 117.8, 36.7, 36.5, 20.1.

HRMS (ESI) m/z calcd for $C_{20}H_{19}NO_2$ ([M+H]$^+$):306.1489, found: 306.1487.



3bh

4,4'-bis(3,5-bis(trifluoromethyl)phenyl)-[1,1'-binaphthalene]-2,2'-diyl bis(dimethylcarbamate) (3bh)

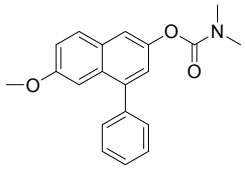
To a Schlenk tube under N_2 atmosphere added [1, 1'-binaphthalene]-2, 2'-diyl bis (dimethylcarbamate) (85.7 mg, 0.2 mmol), (3, 5-bis (trifluoromethyl) phenyl) boronic acid (305.5 mg, 1.2 mmol), Pd(OAc)$_2$ (4.5 mg, 0.02 mmol), $K_2S_2O_8$ (324.4 mg, 1.2 mmol), AgOAc (1.7 mg, 0.01 mmol), TFA (0.6ml). The mixture was stirred for 36 hours at room temperature under N_2. Then the reaction mixture was neutralized with saturated K_2CO_3 aqueous solution and extracted with CH_2Cl_2 (3 × 5 ml). The combined organic phase were dried over Na_2SO_4 and concentrated under reduced pressure, the residue was purified by flash chromatography (petroleum ether: ethyl acetate=15:1) to afford the product **3bh** (68.2 mg, 40%), White oil.

^{1}H NMR (300 MHz, cdcl$_3$) δ(ppm) 8.10 (s, 4H), 8.06 (s, 2H), 7.99 (d, *J* = 8.1 Hz, 2H), 7.88 (s, 2H), 7.56 – 7.50 (m, 2H), 7.39 (s, 4H), 2.38 (brs, 12H).

^{13}C NMR (75 MHz, cdcl$_3$) δ(ppm) 153.1 (2C), 145.1 (2C), 140.7 (2C), 133.6 (2C), 132.5 (2C), 132.1 (2C), 131.6 (2C), 130.5 (2C), 129.4 (4C), 128.2 (2C), 127.6 (2C), 126.7 (4C), 125.4 (2C), 121.8 (2C), 121.2 (4C), 118.2 (2C), 36.2 (2C), 35.7 (2C).

HRMS (ESI) m/z calcd for $C_{42}H_{28}F_{12}N_2O_2$ ([M+H]$^+$):853.1930, found: 853.1932.

Since the chemical shifts around 118 and δ 122 ppm which are assigned to *ortho*-sites of carbamate group exist in all the above examples, we can confirm the structure are not *ortho*-arylated.



3cb

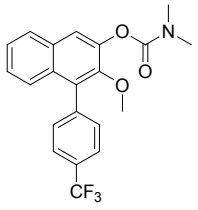
6-methoxy-4-phenylnaphthalen-2-yl dimethylcarbamate (3cb)

The reaction was performed according to the general procedure for 5 hours. Flash chromatography (petroleum ether: dichloromethane=1:3) yieled the product **3cb** (189.2 mg, 59%), White solid, mp.106-107^{0}C.

^{1}H NMR (300 MHz, cdcl$_3$) δ(ppm) 7.75 (d, *J* = 8.7 Hz, 1H), 7.55 – 7.39 (m, 6H), 7.22 (s, 1H), 7.21 (s, 1H), 7.17 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.75 (s, 3H), 3.15 (s, 3H), 3.05 (s, 3H).

^{13}C NMR (75 MHz, cdcl$_3$) δ(ppm) 157.6, 155.3, 147.1, 140.5, 140.3, 130.7, 129.9 (2C), 129.8, 129.6, 128.5 (2C), 127.5, 123.1, 118.9, 118.1, 104.8, 55.3, 36.8, 36.6.

HRMS (ESI) m/z calcd for $C_{20}H_{19}NO_3$ ([M+H]$^+$):322.1438, found: 322.1438.



3df

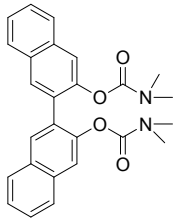
3-methoxy-4-(4-(trifluoromethyl)phenyl)naphthalen-2-yl dimethylcarbamate (3df)

To a Schlenk tube under N_2 atmosphere added 3-methoxyl-2-naphthyl dimethylcarbamate (245.3 mg,1 mmol), (4-(trifluoromethyl) phenyl) boronic acid (569.8 mg, 3 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), $K_2S_2O_8$ (1622 mg, 6 mmol), AgOAc (8.3 mg, 0.05 mmol) , TFA (5ml). The mixture was stirred for 9 hours at 50^{0}C under N_2. Then the reaction mixture was neutralized with saturated K_2CO_3 aqueous solution and extracted with CH_2Cl_2 (20 ml × 3). The combined organic phase were dried over Na_2SO_4 and concentrated under reduced pressure, the residue was purified by flash chromatography (petroleum ether: dichloromethane=1:1) to afford the product **3df** (194.7 mg, 50%), yellow oil.

^{1}H NMR (300 MHz, cdcl$_3$) δ 7.95 – 7.92 (m, 1H), 7.84 – 7.70 (m, 5H), 7.66 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.22 (s, 1H), 3.98 (s, 3H), 3.19 (s, 3H), 3.05 (s, 3H).

^{13}C NMR (75 MHz, cdcl$_3$) δ 154.9, 151.9, 144.9, 142.0, 135.5, 132.2, 130.4, 128.9, 128.3, 127.8, 127.6 (2C), 127.5, 125.9 (2C), 125.3, 121.3, 107.2, 56.2, 37.0, 36.9.

HRMS (ESI) m/z calcd for $C_{21}H_{18}F_3NO_3$ ([M+H]$^+$):390.1312, found: 390.1314.



4a

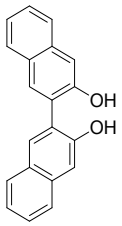
[2,2'-binaphthalene]-3,3'-diyl bis(dimethylcarbamate) (4a)

The reaction was performed according to the general procedure without aryl boronic acid for 2 hours. Flash chromatography (petroleum ether: ethyl acetate=3:1) yielded the product **4a** (321.3 mg, 75%) , Colorless oil.

^{1}H NMR (300 MHz, cdcl$_3$) δ 7.87 – 7.84 (m, 6H), 7.80 (s, 2H), 7.54 – 7.45 (m, 4H), 2.78 (s, 6H), 2.68 (s, 6H).

^{13}C NMR (75 MHz, cdcl$_3$) δ 154.4, 147.6, 133.7, 131.2, 130.9, 130.6, 128.0, 127.7, 126.6, 125.7, 119.3, 36.7, 36.2.

HRMS (ESI) m/z calcd for $C_{26}H_{24}N_2O_4$ ([M+H]$^+$):429.4872, found: 429.4875.



5a

[2,2'-binaphthalene]-3,3'-diol (5a)

To a flask added **4a** (321.3 mg, 0.75 mmol), NaOH (300mg, 7.5 mmol), EtOH (7.5ml), the mixture was refluxed over night, After that, the reaction mixture was diluted with CH_2Cl_2 through celite and washed with water (1 × 5 ml). The aqueous phase was re-extracted with CH_2Cl_2 (3 × 5 ml). The combined organic phase were dried over Na_2SO_4 and concentrated under reduced pressure, the residue was purified by flash chromatography (petroleum ether: ethyl acetate=3:1) to afford the product **5a** (189 mg, 88%), White solid, mp.180-182^{0}C.

^{1}H NMR (300 MHz, cdcl$_3$) δ 7.87 (s, 2H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.53 – 7.47 (m, 2H), 7.43 (s, 2H), 7.43 – 7.37 (m, 2H), 5.58 (br, 2H).

^{13}C NMR (75 MHz, cdcl$_3$) δ 151.4, 135.1, 131.3, 129.4, 128.1, 127.2, 126.6, 126.0, 124.6, 111.6.

HRMS (ESI) m/z calcd for $C_{20}H_{14}O_2$ ([M+H]$^+$):287.3314, found: 287.3310.

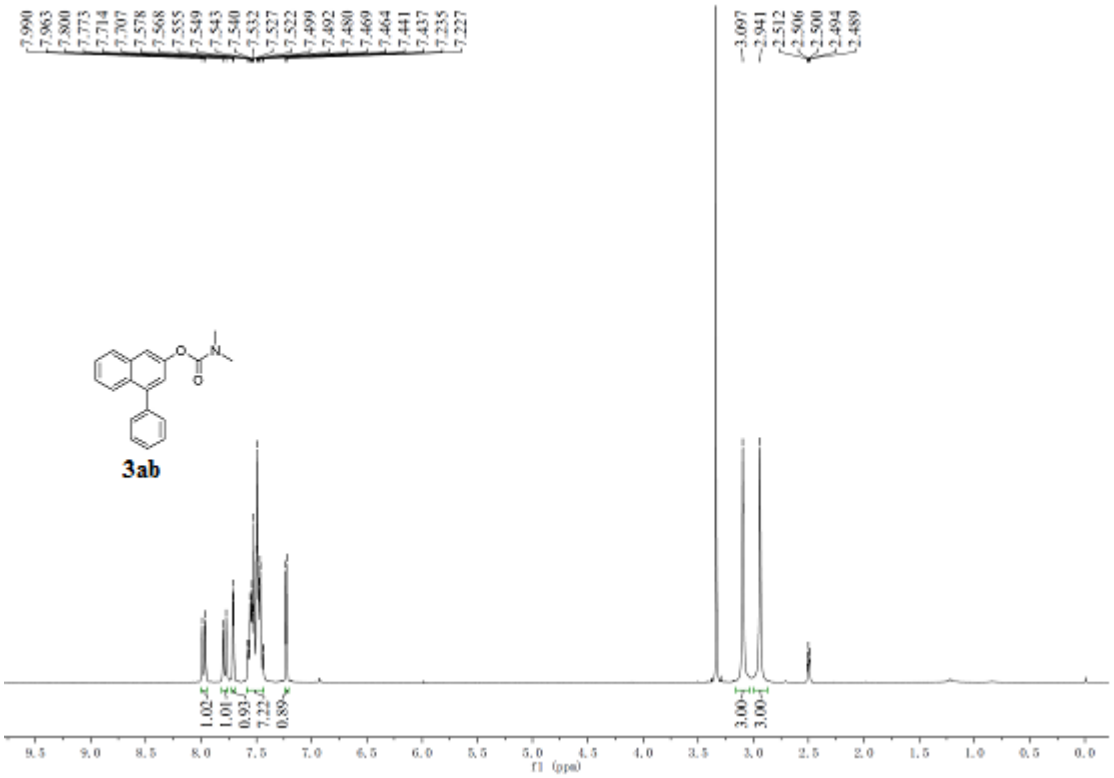
The NMR data is consistent with that reported in the literature. [2]

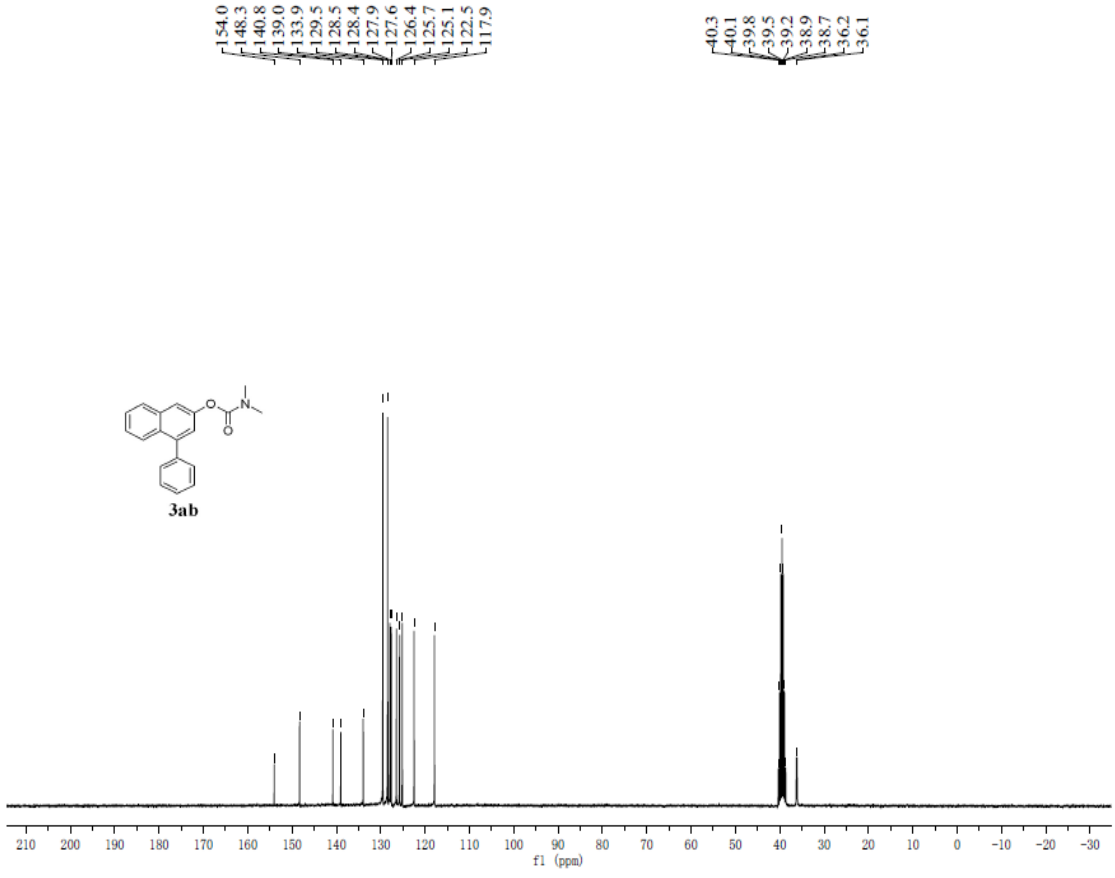
References

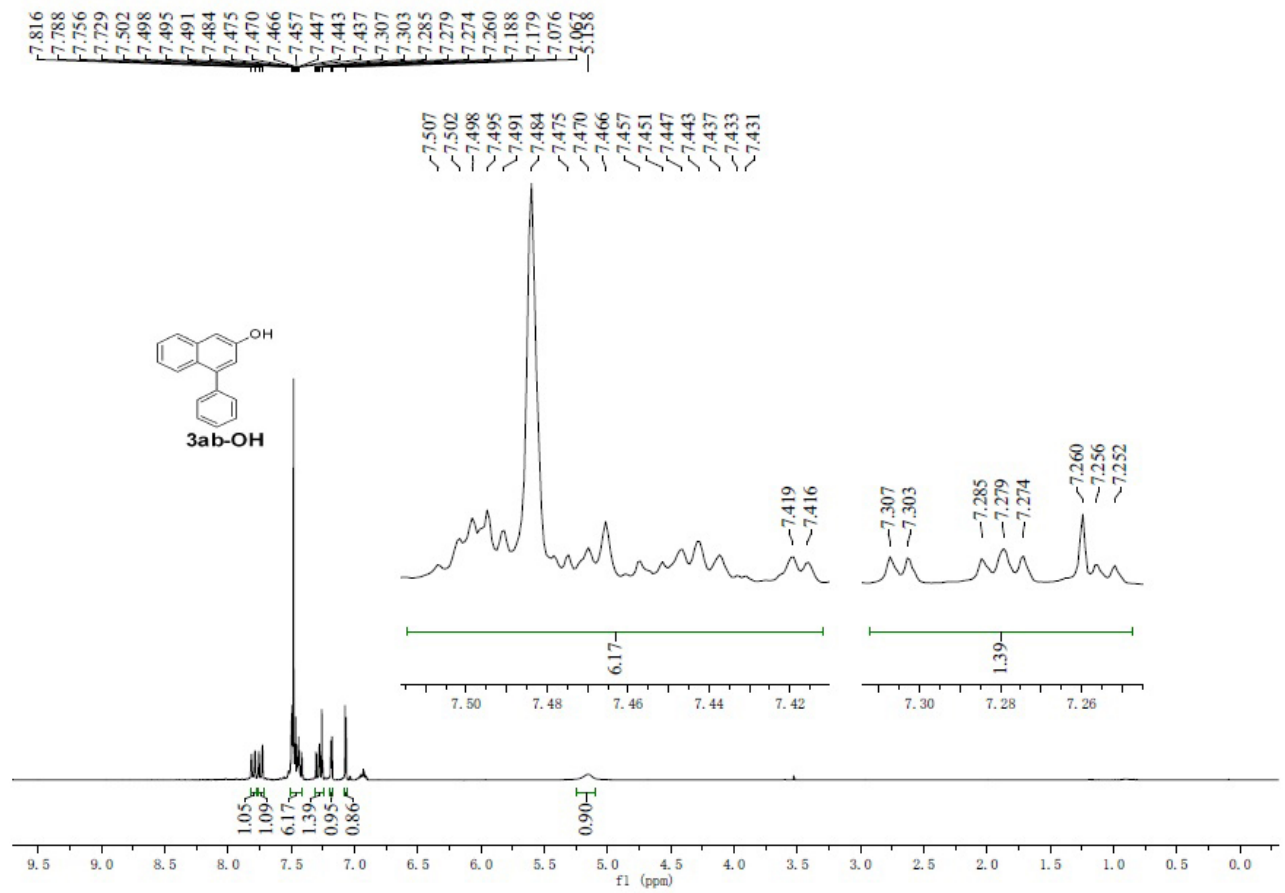
[1] K. Okuma, R. Itoyama, A. Sou, N. Nagahora, K. Shioj, *Chem. Commun*., 2012, **48**, 11145–11147.

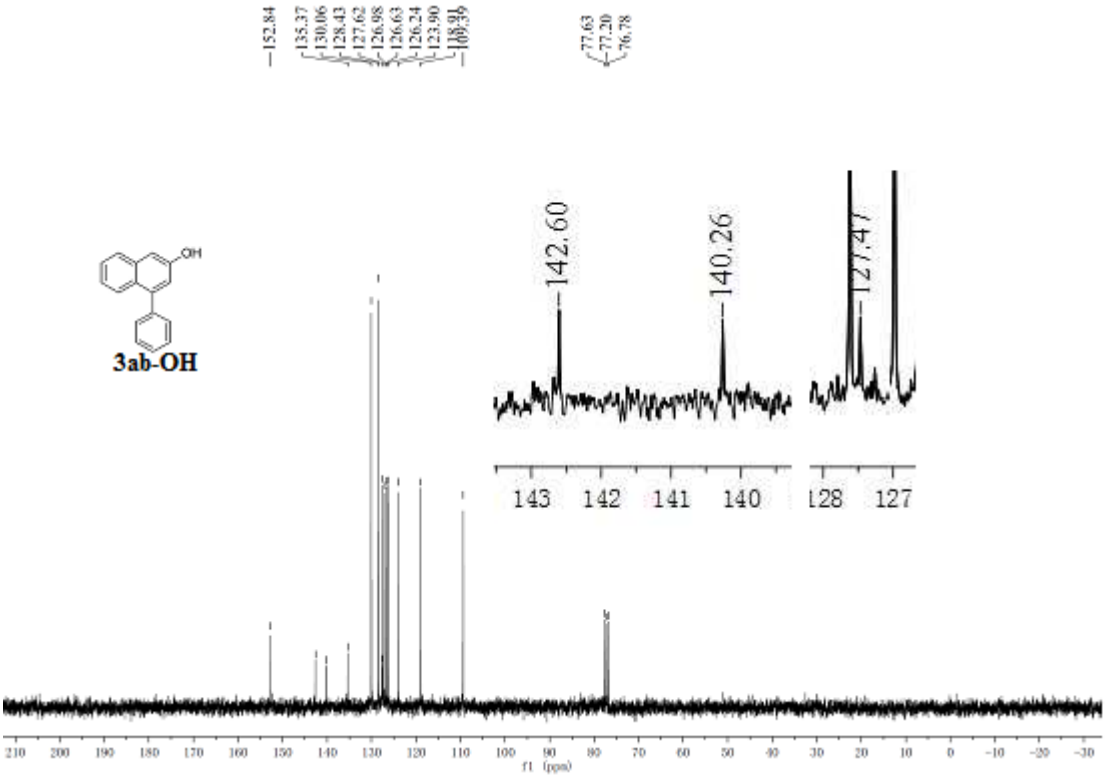
[2] T. Okamoto, C. Mitsui, M. Yamagishi, K. Nakahara, J. Soeda, Y. Hirose, K. Miwa, H. Sato, A. Yamano, T. Matsushita, T. Uemura, J. Takeya, *Adv. Mater.,* 2013, **25**, 6392–6397.

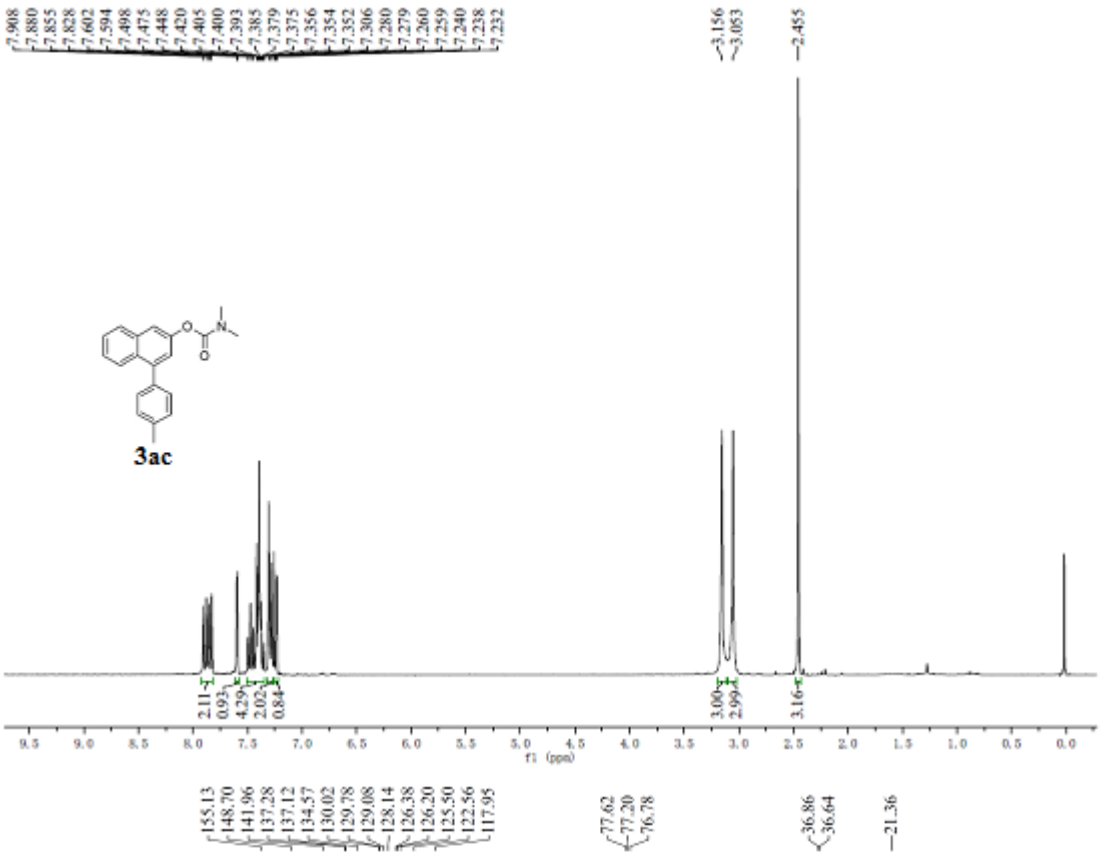
(E) Copies of ^{1}H and ^{13}C spectra

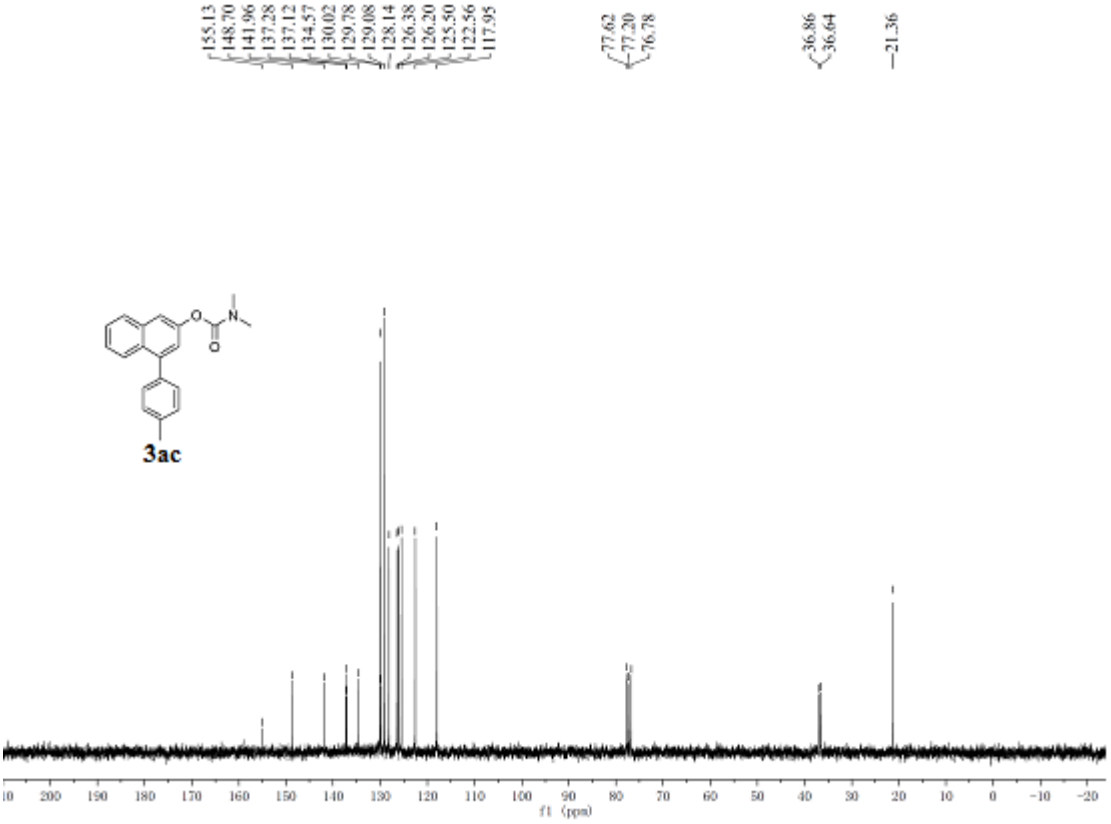


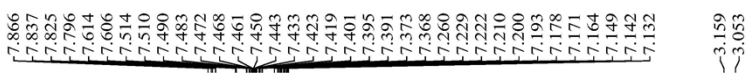


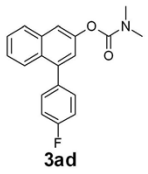

7.816
7.788
7.756
7.729
7.502
7.498
7.495
7.491
7.484
7.475
7.470
7.466
7.457
7.447
7.443
7.437
7.307
7.303
7.285
7.279
7.274
7.260
7.188
7.179
7.076
7.067
5.158
OH
3ab-OH
7.507
7.502
7.498
7.495
7.491
7.484
7.475
7.470
7.466
7.457
7.451
7.447
7.443
7.437
7.433
7.431
7.419
7.416
7.307
7.303
7.285
7.279
7.274
7.260
7.256
7.252
6.17
1.39
7.50
7.48
7.46
7.44
7.42
7.30
7.28
7.26
1.05
1.09
6.17
1.39
0.95
0.86
0.90
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)


152.84
135.37
130.06
128.43
127.62
126.98
126.63
126.24
123.90
118.91
110.39
77.63
77.20
76.78
OH
3ab-OH
142.60
140.26
127.47
143
142
141
140
128
127
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)

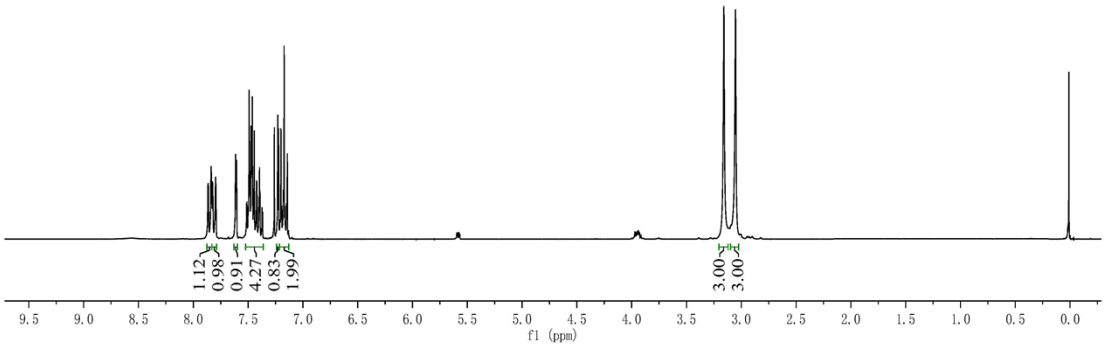

7.908
7.880
7.855
7.828
7.602
7.594
7.498
7.475
7.448
7.420
7.405
7.400
7.393
7.385
7.379
7.375
7.356
7.354
7.352
7.306
7.280
7.279
7.260
7.259
7.240
7.238
7.232
3.156
3.053
2.455
3ac
2.11
0.93
4.29
2.02
0.84
3.00
2.99
3.16
f1 (ppm)

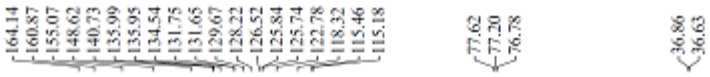

155.13
148.70
141.96
137.28
137.12
134.57
130.02
129.78
129.08
128.14
126.38
126.20
125.50
122.56
117.95
77.62
77.20
76.78
36.86
36.64
21.36
3ac
f1 (ppm)

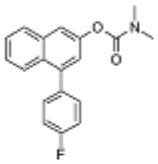

7.866
7.837
7.825
7.796
7.614
7.606
7.514
7.510
7.490
7.483
7.472
7.468
7.461
7.450
7.443
7.433
7.423
7.419
7.401
7.395
7.391
7.373
7.368
7.260
7.229
7.222
7.210
7.200
7.193
7.178
7.171
7.164
7.149
7.142
7.132
3.159
3.053



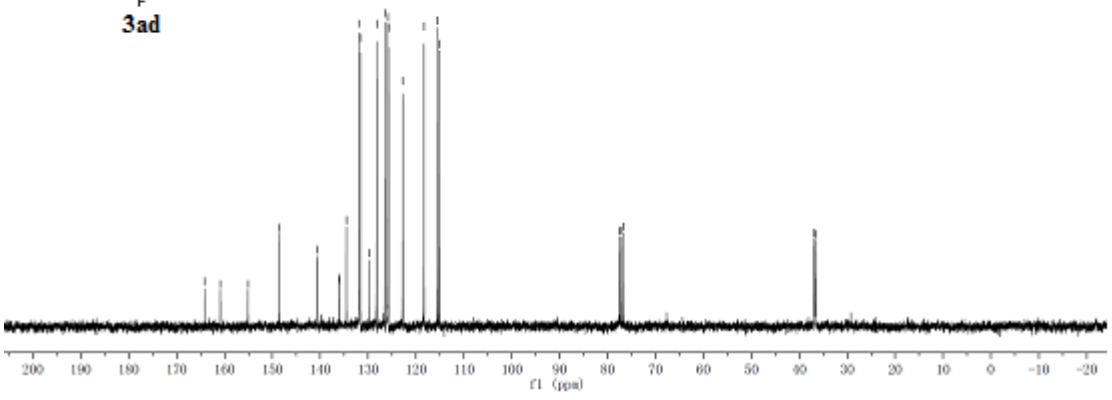
3ad

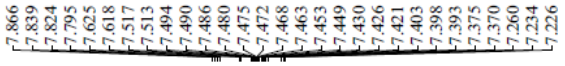

1.12
0.98
0.91
4.27
0.83
1.99
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

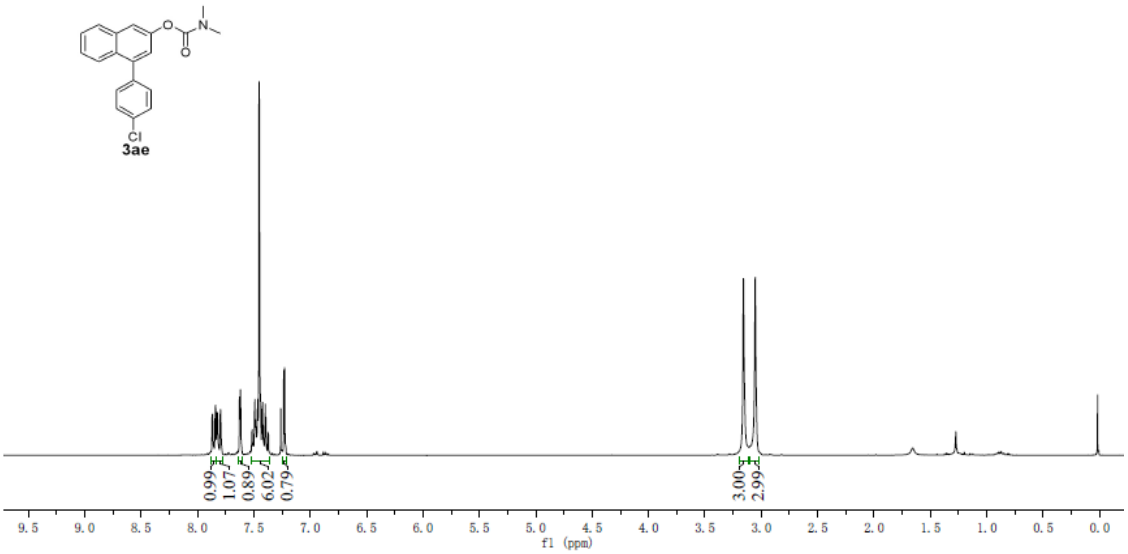

164.14
160.87
155.07
148.62
140.73
135.99
135.95
134.54
131.75
131.65
129.67
128.22
126.52
125.84
125.74
122.78
118.32
115.46
115.18
77.62
77.20
76.78
36.86
36.63

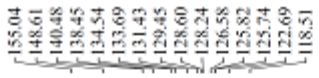


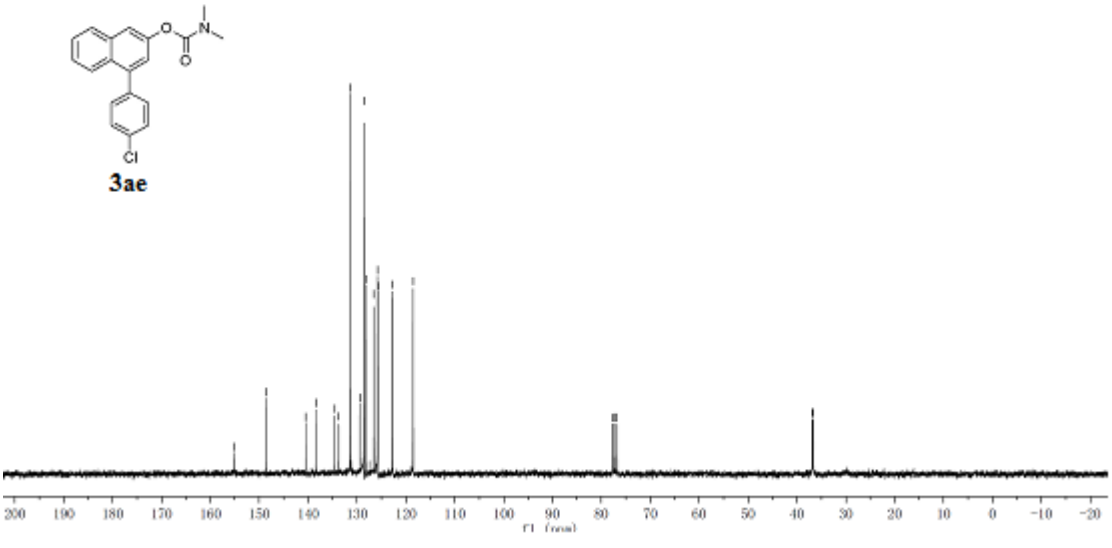
3ad


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

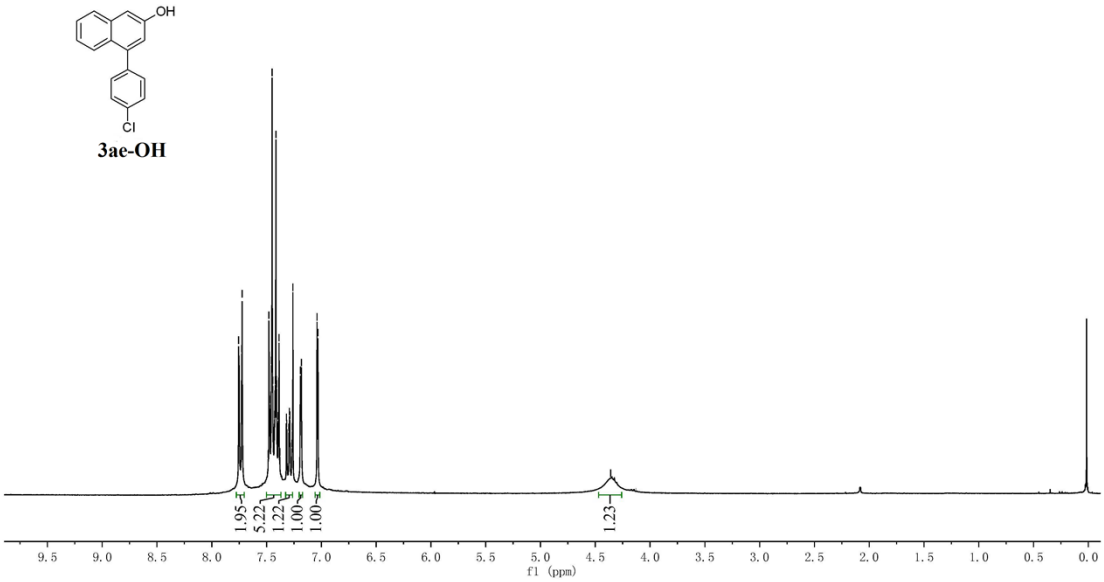

7.866
7.839
7.824
7.795
7.625
7.618
7.517
7.513
7.494
7.490
7.486
7.480
7.475
7.472
7.468
7.463
7.453
7.449
7.430
7.426
7.421
7.403
7.398
7.393
7.375
7.370
7.260
7.234
7.226
3.158
3.054

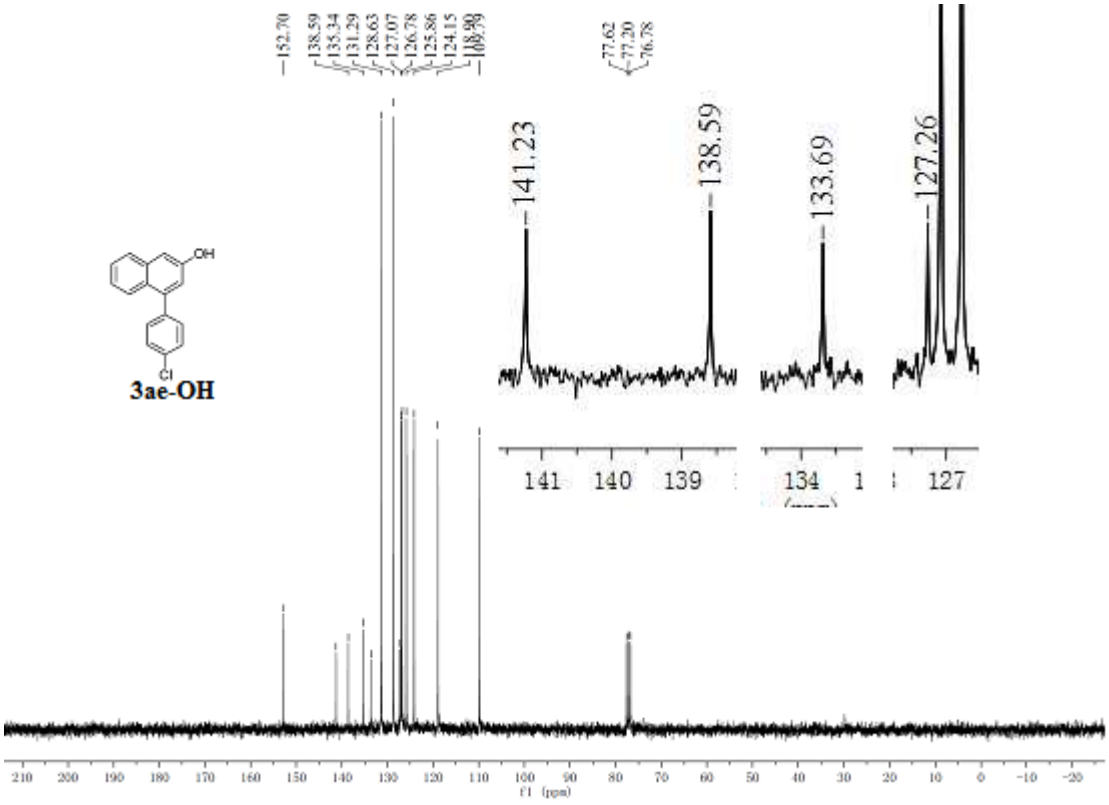

Cl
3ae
0.99
1.07
0.89
6.02
0.79
3.00
2.99
f1 (ppm)

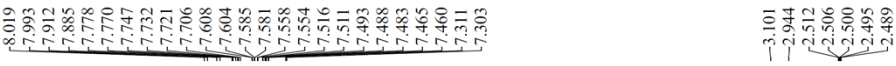

155.04
148.61
140.48
138.45
134.54
133.69
131.43
129.45
128.60
128.24
126.58
125.82
125.74
122.69
118.51
77.63
77.20
76.78
36.87
36.63

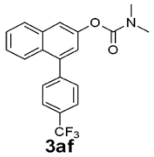

Cl
3ae


7.755
7.751
7.726
7.723
7.485
7.478
7.471
7.455
7.450
7.443
7.427
7.422
7.415
7.408
7.393
7.386
7.380
7.319
7.315
7.297
7.292
7.287
7.268
7.264
7.260
7.191
7.183
7.039
7.031
4.359

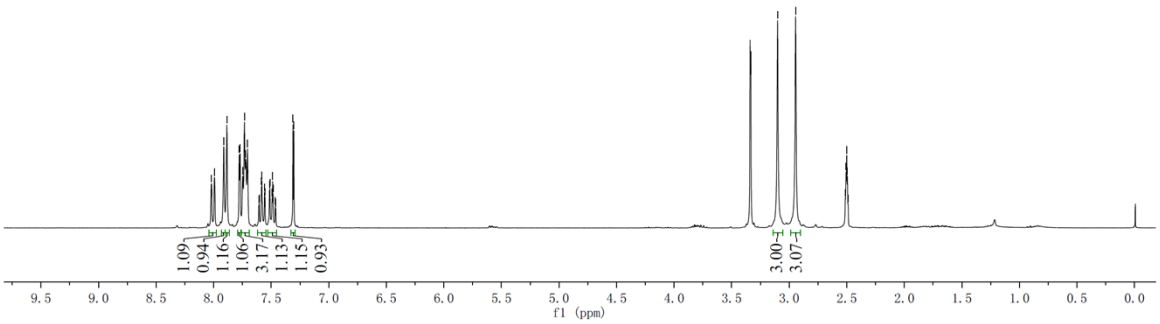

OH
Cl
3ae-OH
1.95
5.22
1.22
1.00
1.00
1.23
f1 (ppm)


152.70
138.59
133.34
131.29
128.63
127.07
126.78
125.86
124.15
77.62
77.20
76.78
141.23
138.59
133.69
127.26
OH
Cl
3ae-OH
f1 (ppm)

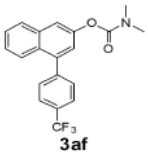

8.019
7.993
7.912
7.885
7.778
7.770
7.747
7.732
7.721
7.706
7.608
7.604
7.585
7.581
7.558
7.554
7.516
7.511
7.493
7.488
7.483
7.465
7.460
7.311
7.303
3.101
2.944
2.512
2.506
2.500
2.495
2.489


O
N
O
CF3

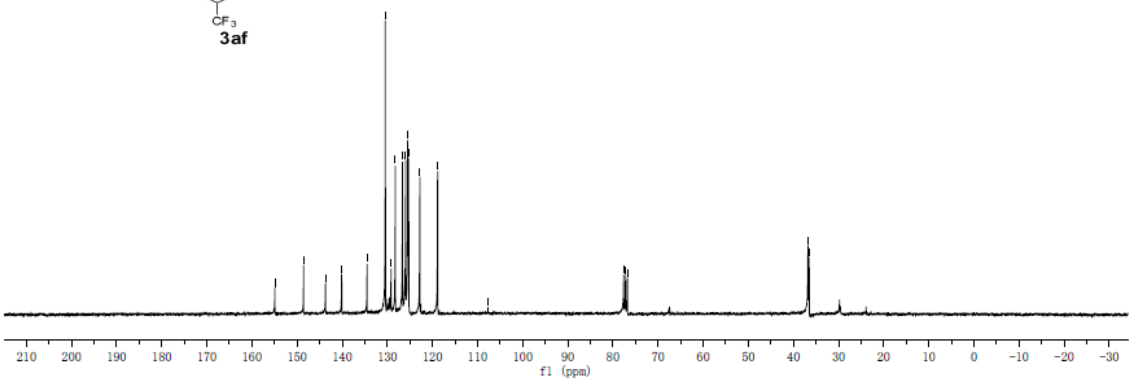
3af

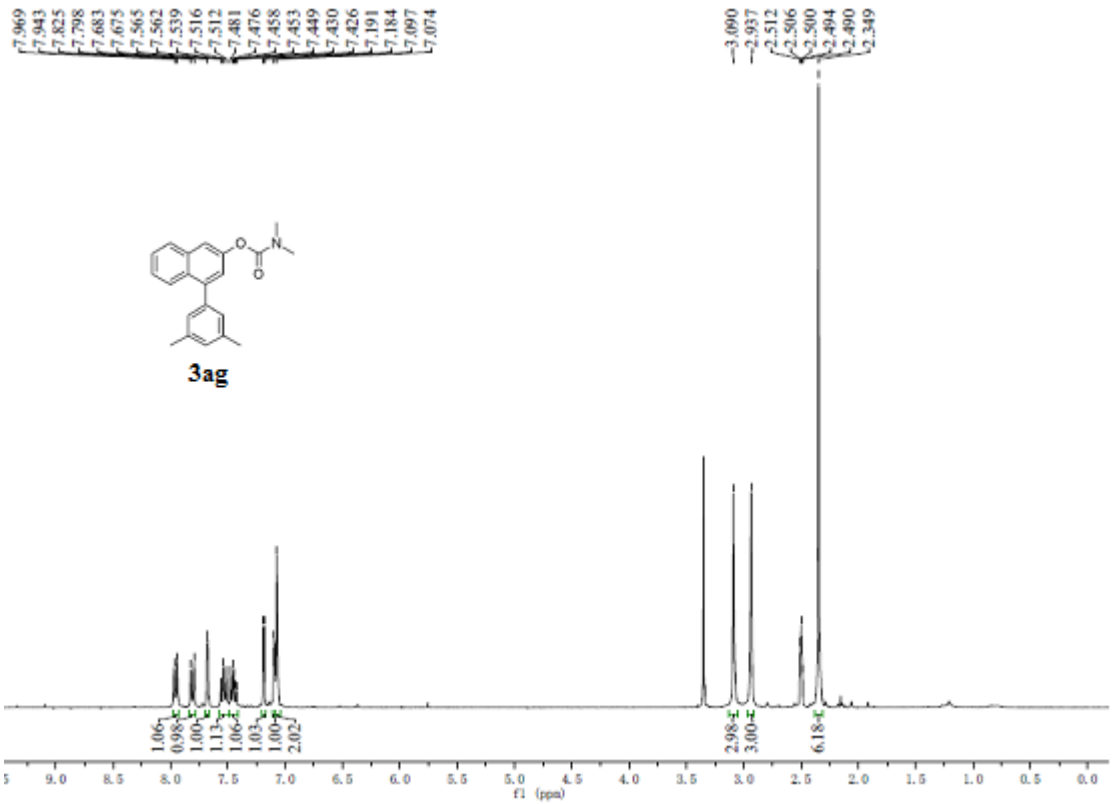

1.09
0.94
1.16
1.06
3.17
1.13
1.15
0.93
3.00
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


154.93
148.56
143.70
140.12
134.50
130.44
129.18
128.23
126.64
125.95
125.47
125.31
122.80
118.85
107.70
77.62
77.20
76.78
36.77
36.52

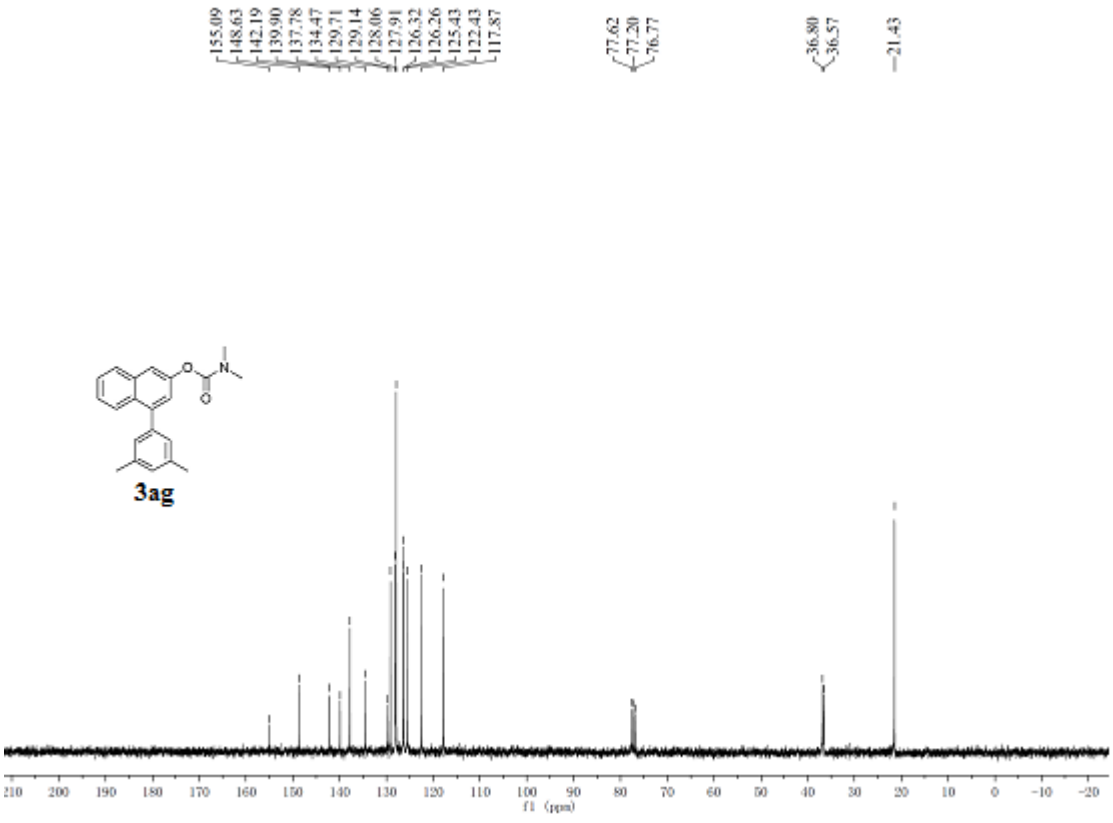

O
N
O
CF3

3af

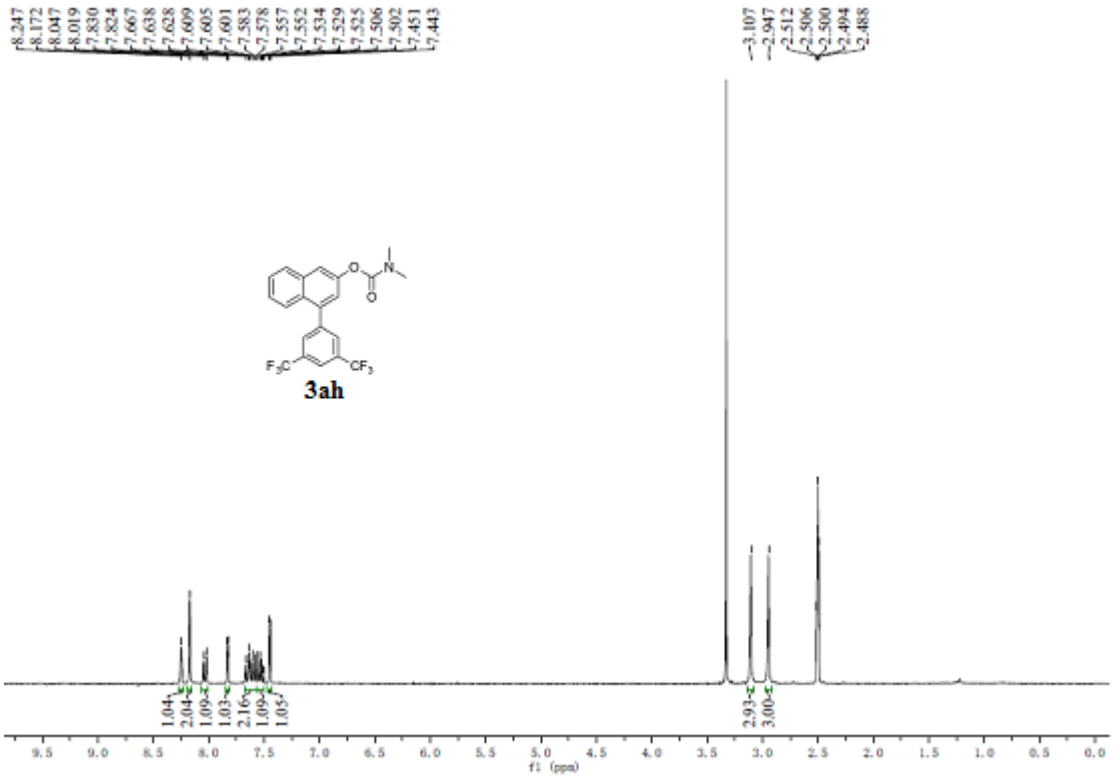

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


7.969
7.943
7.825
7.798
7.683
7.675
7.565
7.562
7.539
7.516
7.512
7.481
7.476
7.458
7.453
7.449
7.430
7.426
7.191
7.184
7.097
7.074
3.090
2.937
2.512
2.506
2.500
2.494
2.490
2.349
1.06
0.98
1.00
1.13
1.06
1.03
1.00
2.02
2.98
3.00
6.18
f1 (ppm)

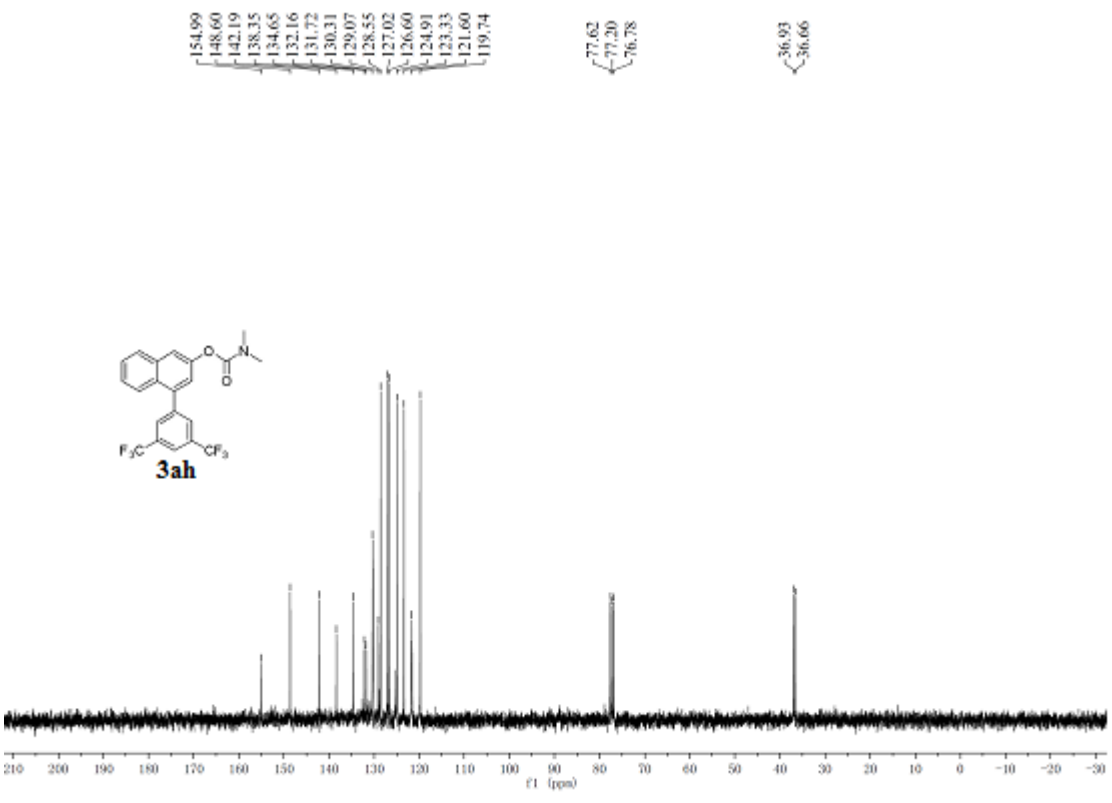
3ag


155.09
148.63
142.19
139.90
137.78
134.47
129.71
129.14
128.06
127.91
126.32
126.26
125.43
122.43
117.87
77.62
77.20
76.77
36.80
36.57
21.43
f1 (ppm)

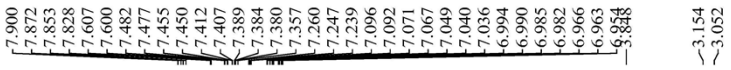
3ag

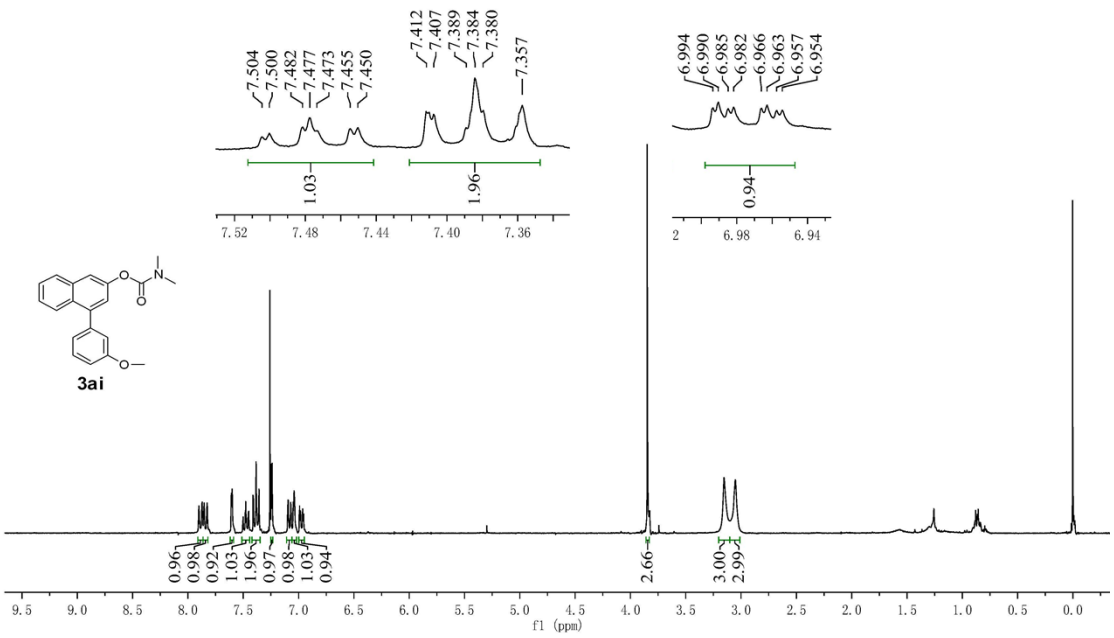

8.347
8.172
8.047
8.019
7.830
7.824
7.667
7.638
7.628
7.609
7.605
7.601
7.583
7.578
7.557
7.552
7.534
7.529
7.525
7.506
7.502
7.451
7.443
3.107
2.947
2.512
2.506
2.500
2.494
2.488
1.04
2.04
1.09
1.03
2.16
1.09
1.05
2.93
3.00
f1 (ppm)

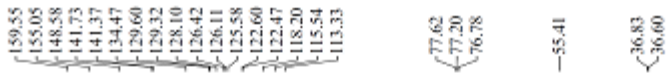
3ah

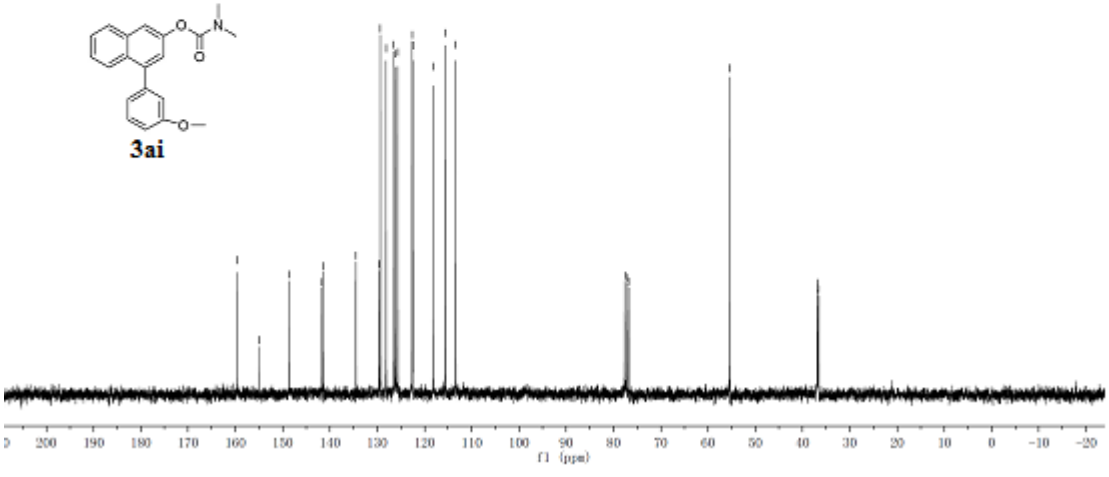

154.99
148.60
142.19
138.35
134.65
132.16
131.72
130.31
129.07
128.55
127.02
126.60
124.91
123.33
121.60
119.74
77.62
77.20
76.78
36.93
36.66
f1 (ppm)

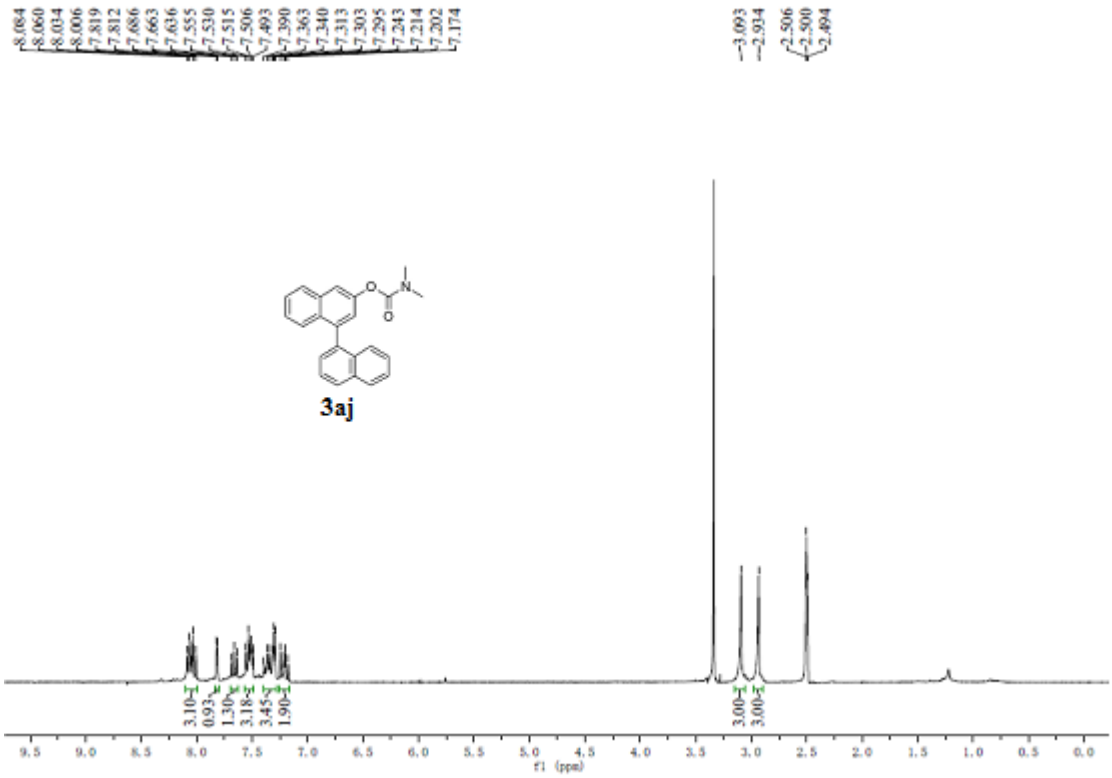
3ah

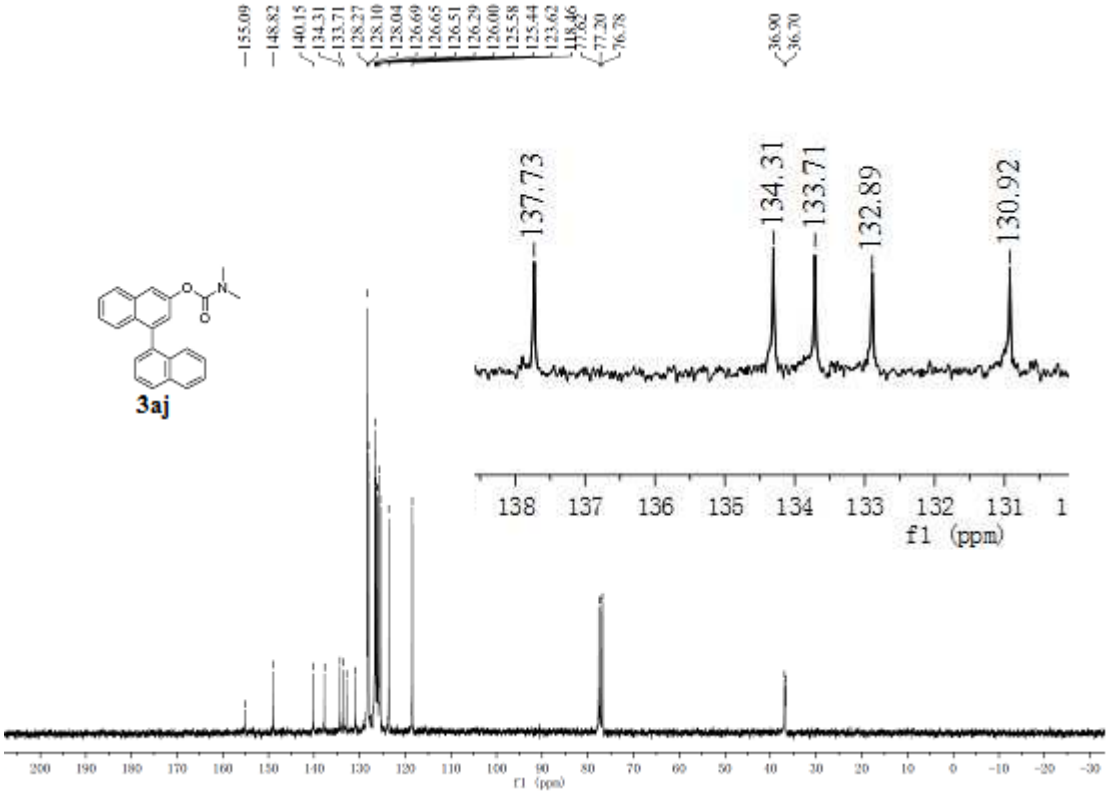

7.900
7.872
7.853
7.828
7.607
7.600
7.482
7.477
7.455
7.450
7.412
7.407
7.389
7.384
7.380
7.357
7.260
7.247
7.239
7.096
7.092
7.071
7.067
7.049
7.040
7.036
6.994
6.990
6.985
6.982
6.966
6.963
6.954
3.848
3.154
3.052

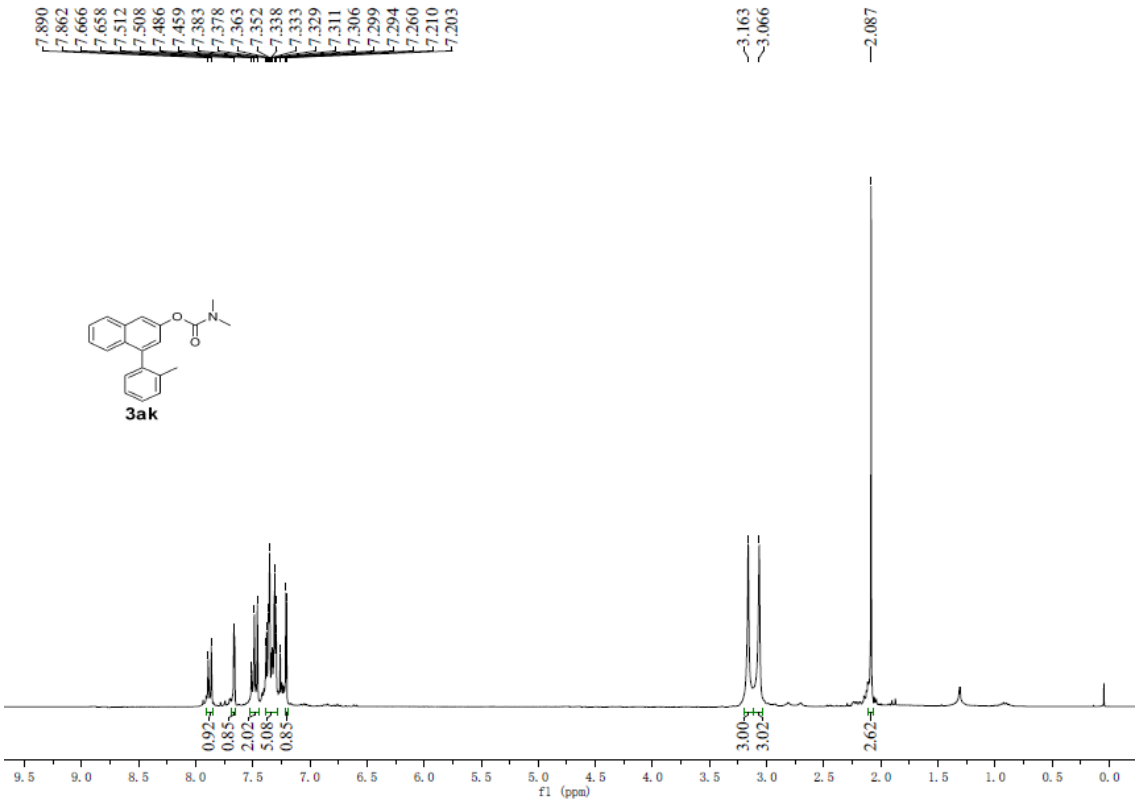

7.504
7.500
7.482
7.477
7.473
7.455
7.450
7.412
7.407
7.389
7.384
7.380
7.357
6.994
6.990
6.985
6.982
6.966
6.963
6.957
6.954
1.03
1.96
0.94
3ai
0.96
0.98
0.92
1.03
1.96
0.97
0.98
1.03
0.94
2.66
3.00
2.99
f1 (ppm)


159.55
155.05
148.58
141.73
141.37
134.47
129.60
129.32
128.10
126.42
126.11
125.58
122.60
122.47
118.20
115.54
113.33
77.62
77.20
76.78
55.41
36.83
36.60

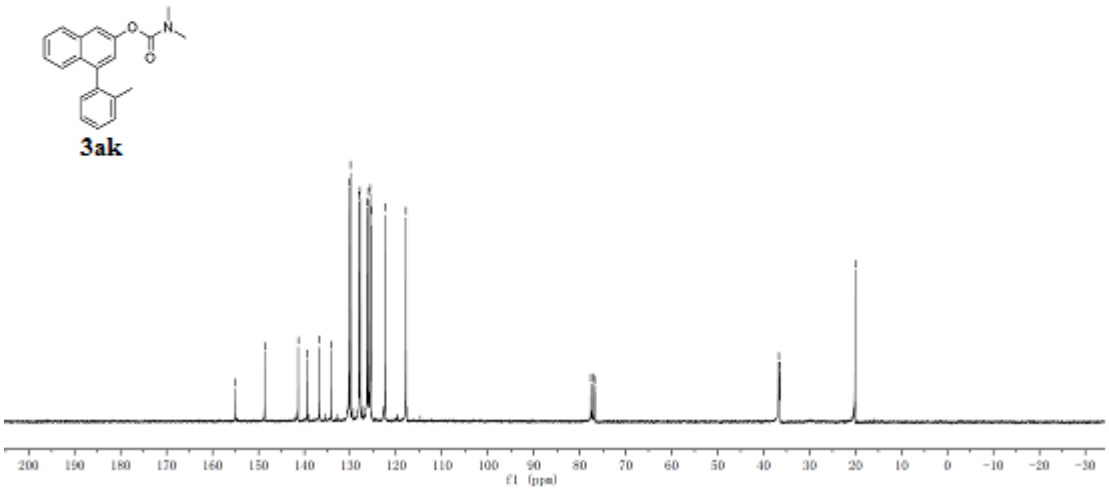

3ai
f1 (ppm)


8.064
8.060
8.034
8.006
7.819
7.812
7.686
7.663
7.636
7.555
7.530
7.515
7.506
7.493
7.390
7.363
7.340
7.313
7.303
7.295
7.243
7.214
7.202
7.174
3.093
2.934
2.506
2.500
2.494
3aj
3.10
0.93
1.30
3.18
3.45
1.90
3.00
3.00
f1 (ppm)

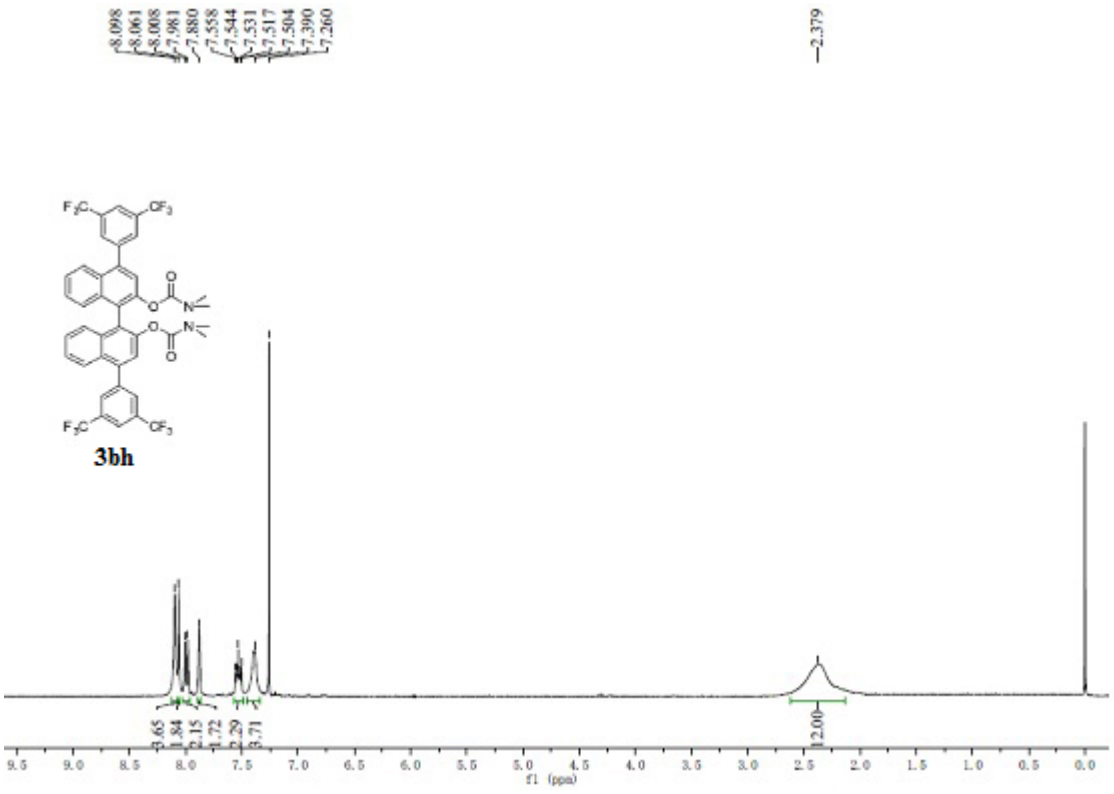

155.09
148.82
140.15
134.31
133.71
128.27
128.10
128.04
126.69
126.65
126.51
126.29
126.00
125.58
125.44
123.62
118.46
77.62
77.20
76.78
36.90
36.70
3aj
137.73
134.31
133.71
132.89
130.92
138 137 136 135 134 133 132 131 1
f1 (ppm)
f1 (ppm)

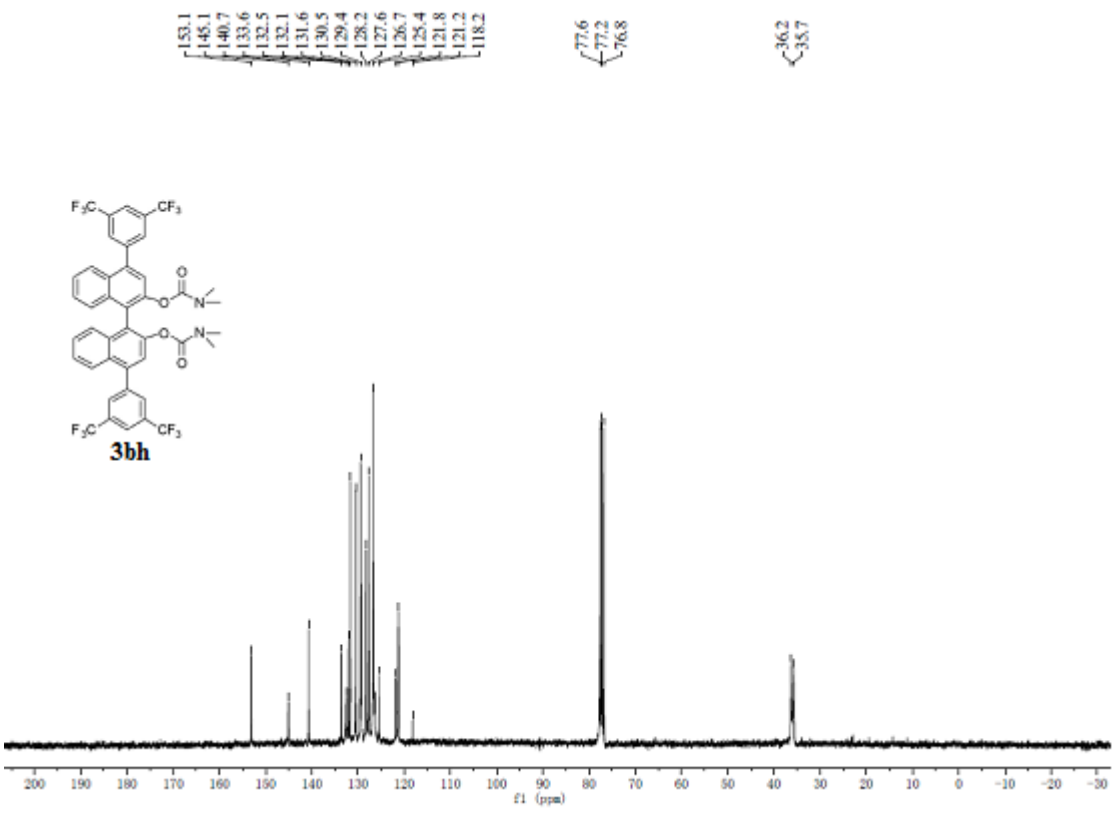

7.890
7.862
7.666
7.658
7.512
7.508
7.486
7.459
7.383
7.378
7.363
7.352
7.338
7.333
7.329
7.311
7.306
7.299
7.294
7.260
7.210
7.203
3.163
3.066
2.087
0.92
0.85
2.02
5.08
0.85
3.00
3.02
2.62
f1 (ppm)

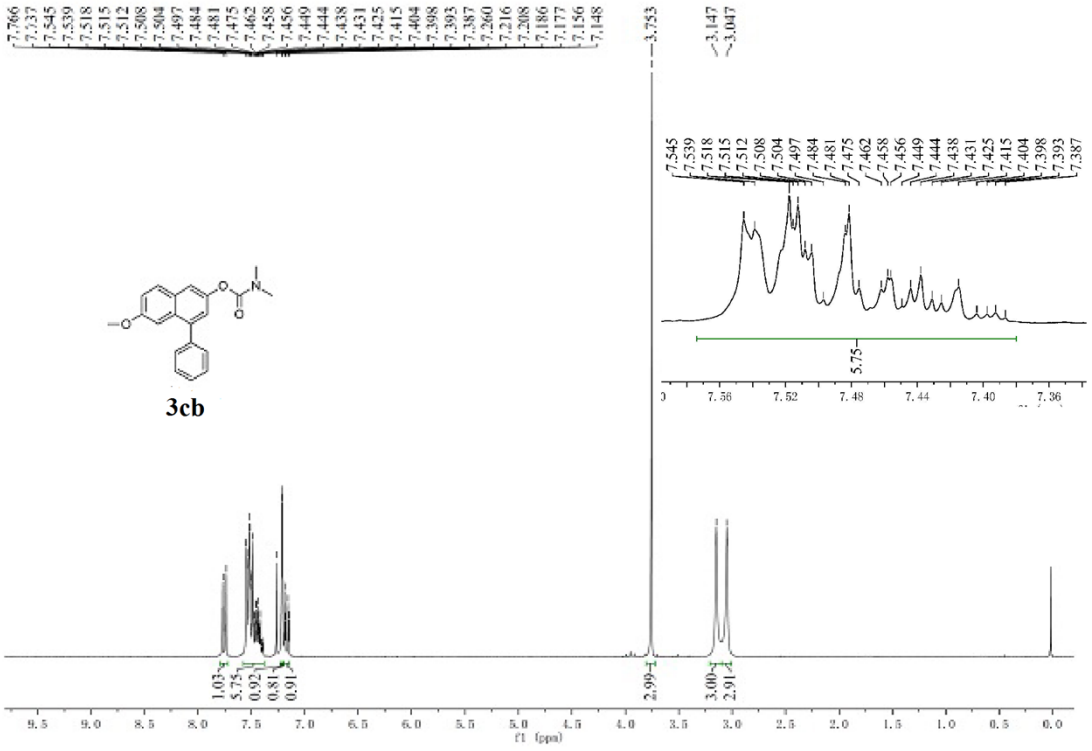
3ak


154.9
148.6
141.3
139.4
136.7
134.1
130.3
129.9
128.0
127.8
126.3
126.0
125.6
125.5
122.4
117.8
77.6
77.2
76.8
36.7
36.5
20.1
f1 (ppm)

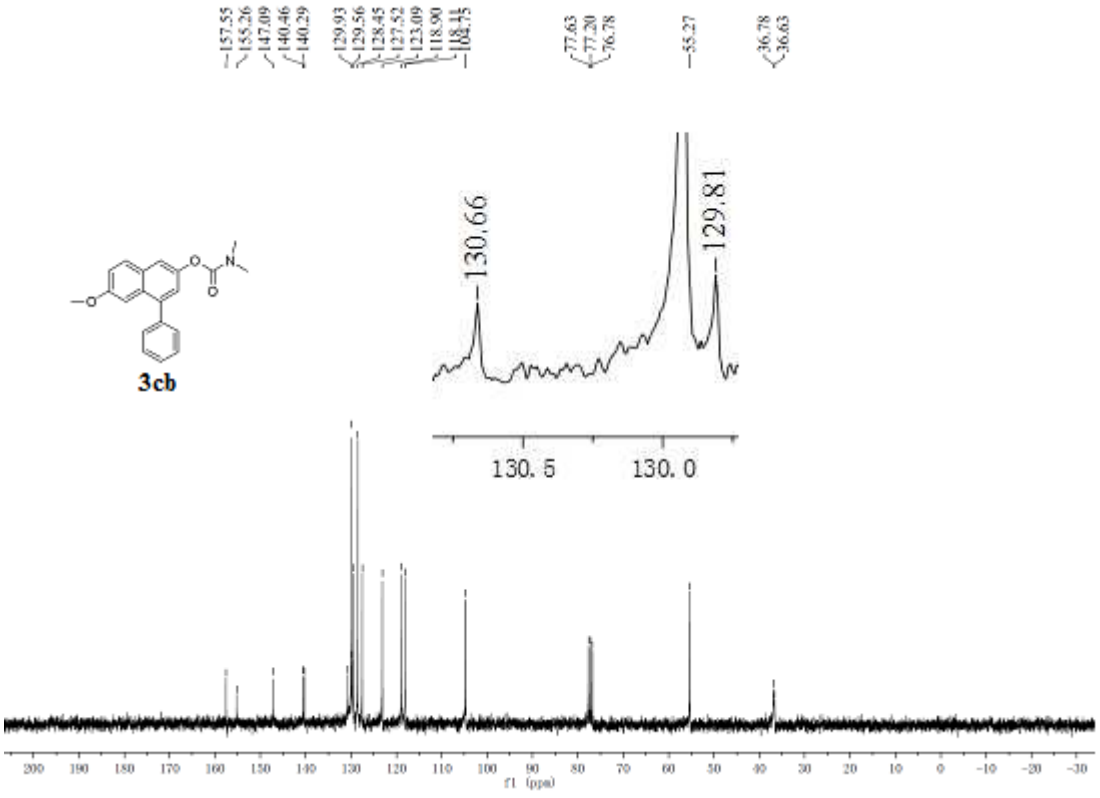
3ak


8.098
8.061
8.008
7.981
7.880
7.558
7.544
7.531
7.517
7.504
7.390
7.260
2.379
3bh
3.65
3.84
2.15
1.72
2.29
3.71
12.00
f1 (ppm)

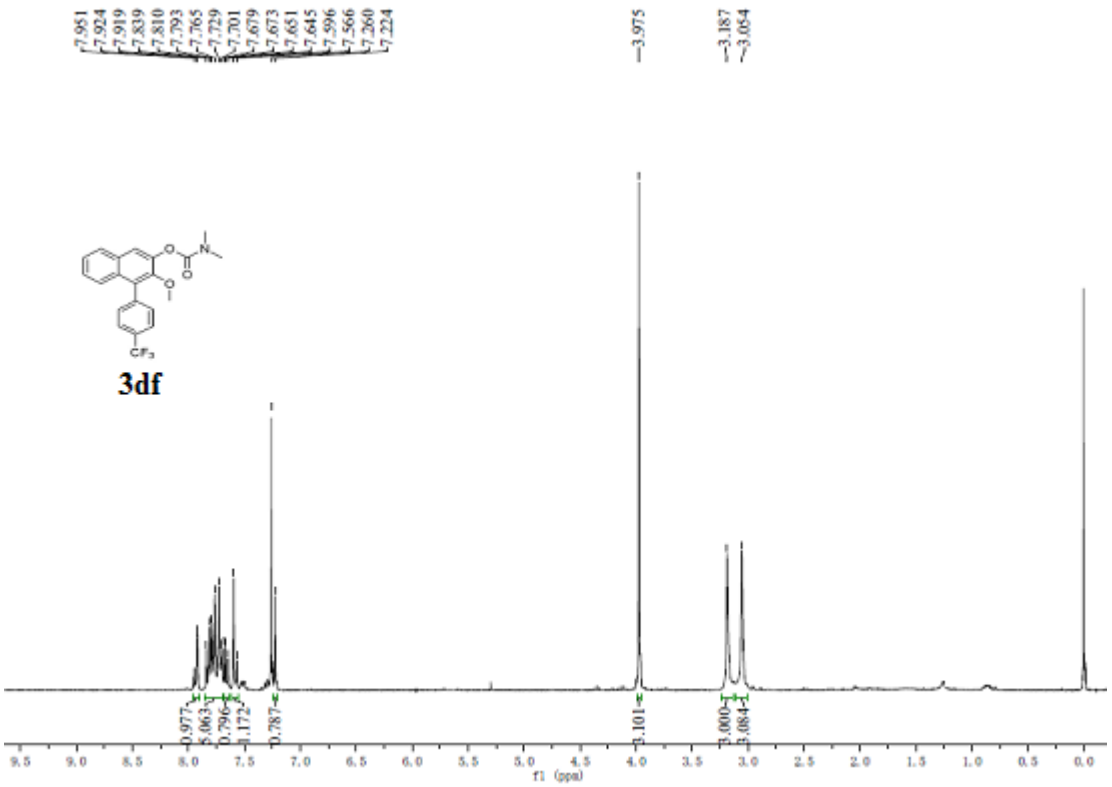

153.1
145.1
140.7
133.6
132.5
132.1
131.6
130.5
129.4
128.2
127.6
126.7
125.4
121.8
121.2
118.2
77.6
77.2
76.8
36.2
35.7
3bh
f1 (ppm)


7.766
7.737
7.545
7.539
7.518
7.515
7.512
7.508
7.504
7.497
7.484
7.481
7.475
7.462
7.458
7.456
7.449
7.444
7.438
7.431
7.425
7.415
7.404
7.398
7.393
7.387
7.260
7.216
7.208
7.186
7.177
7.156
7.148
3.753
3.147
3.047
5.75
1.03
5.75
0.92
0.81
0.91
2.99
3.00
2.91
f1 (ppm)

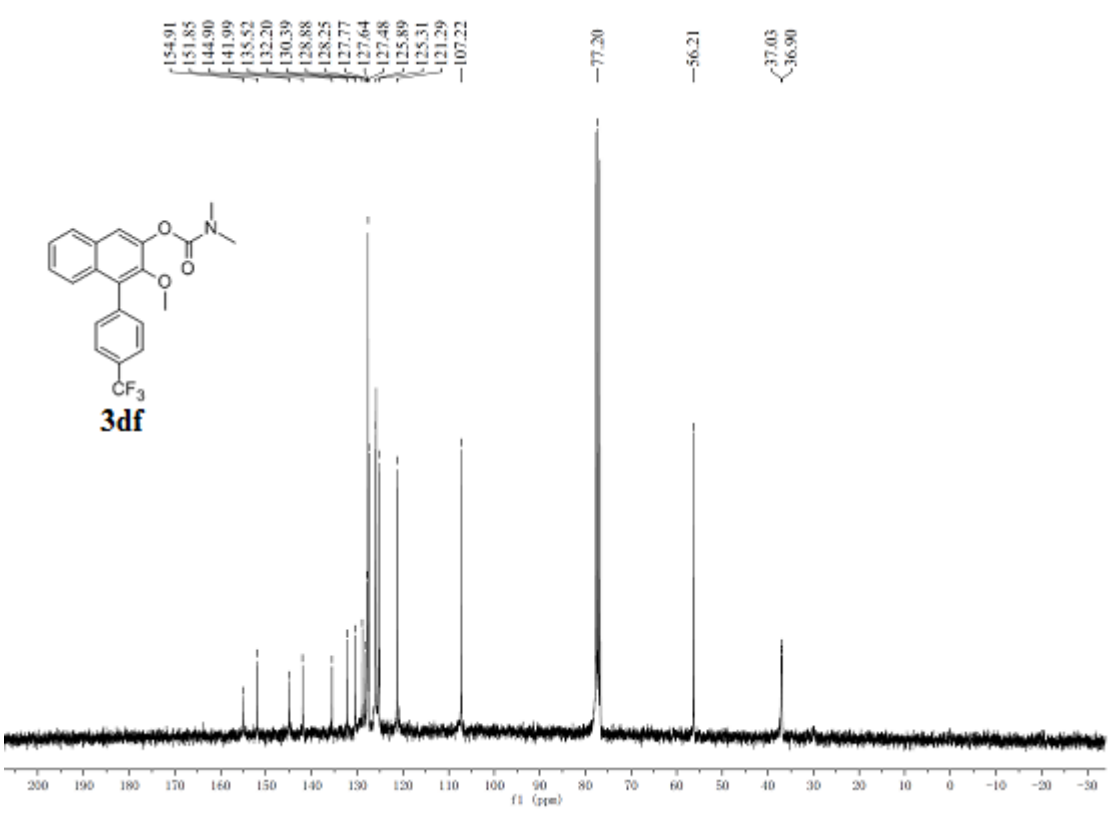
3cb


157.55
155.26
147.09
140.46
140.29
129.93
129.56
128.45
127.52
123.09
118.90
77.63
77.20
76.78
55.27
36.78
36.63
130.66
129.81
130.5
130.0
f1 (ppm)

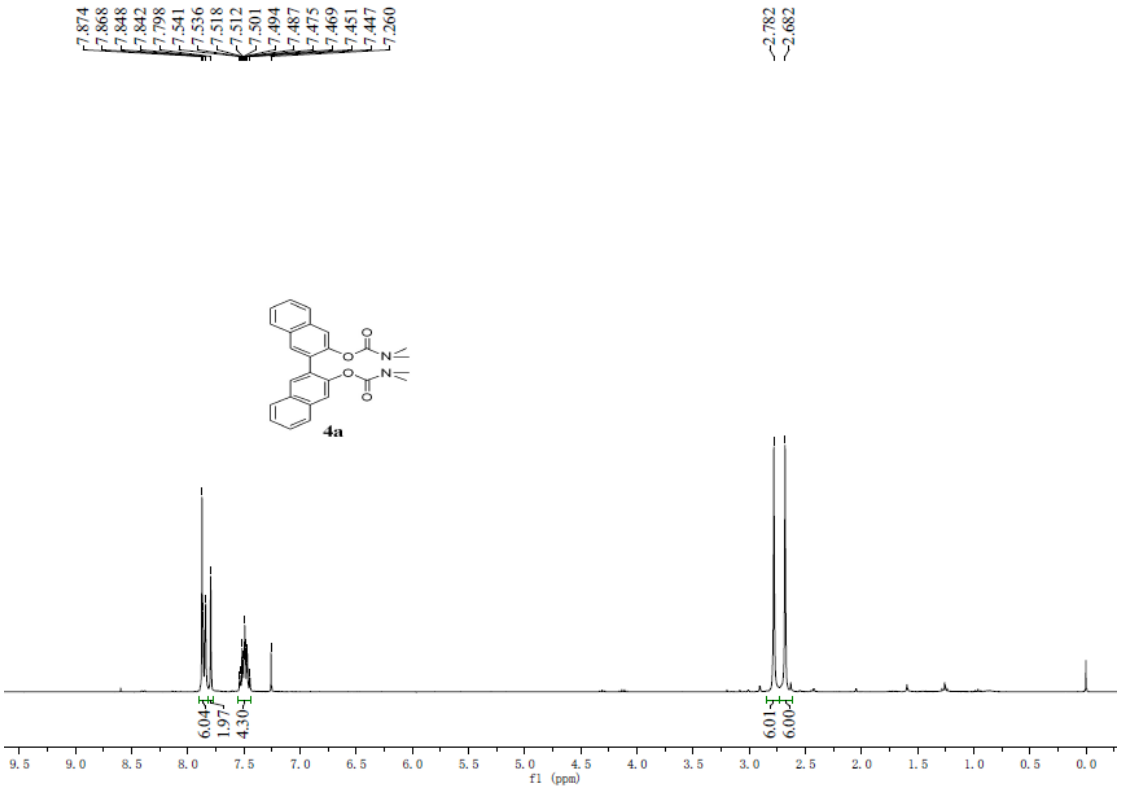
3cb

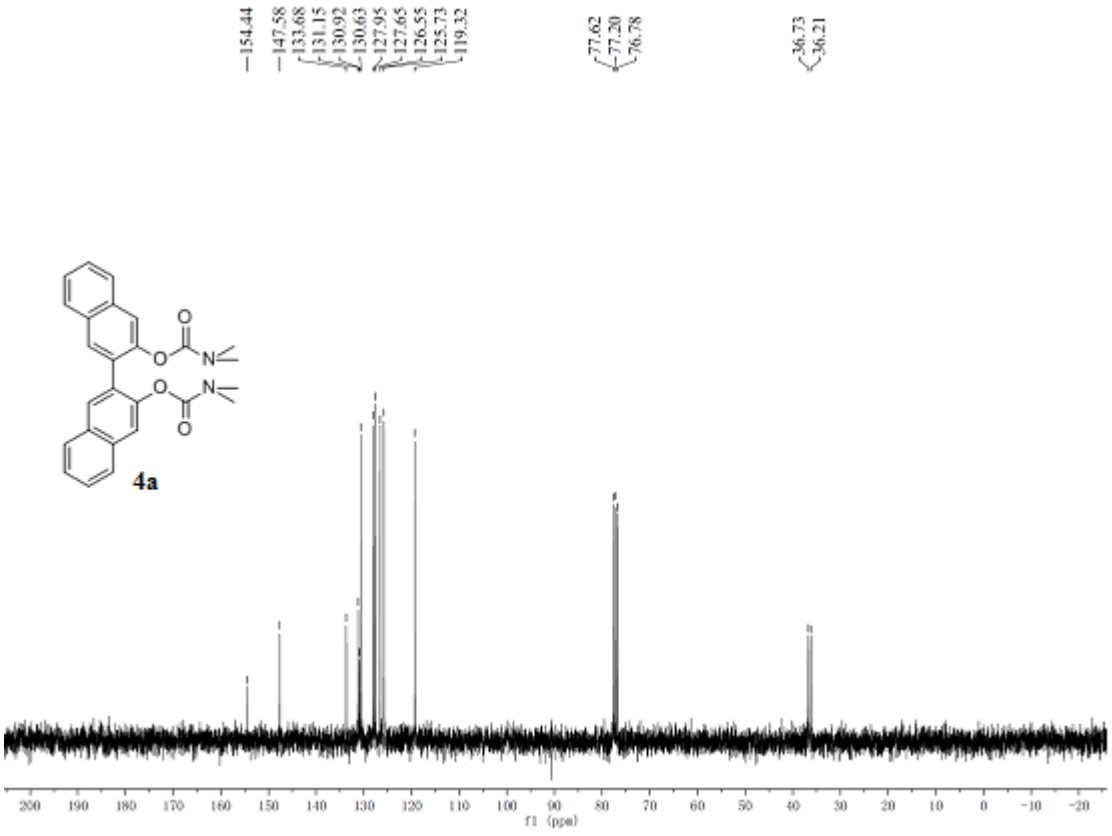

7.951
7.924
7.919
7.839
7.810
7.793
7.765
7.729
7.701
7.679
7.673
7.651
7.645
7.596
7.566
7.260
7.224
3.975
3.187
3.054
0.977
5.063
0.796
1.172
0.787
3.101
3.000
3.084
f1 (ppm)

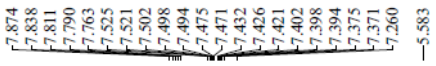
3df

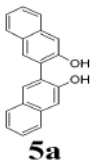

154.91
151.85
144.90
141.99
135.52
132.20
130.39
128.88
128.25
127.77
127.64
127.48
125.89
125.31
121.29
107.22
77.20
56.21
37.03
36.90
f1 (ppm)

3df


7.874
7.868
7.848
7.842
7.798
7.541
7.536
7.518
7.512
7.501
7.494
7.487
7.475
7.469
7.451
7.447
7.260
2.782
2.682
4a
6.04
1.97
4.30
6.01
6.00
f1 (ppm)

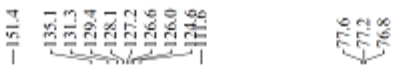

154.44
147.58
133.68
131.15
130.92
130.63
127.95
127.65
126.55
125.73
119.32
77.62
77.20
76.78
36.73
36.21
4a
f1 (ppm)

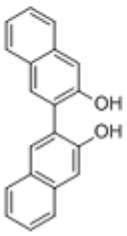

7.874
7.838
7.811
7.790
7.763
7.525
7.521
7.502
7.498
7.494
7.475
7.471
7.432
7.426
7.421
7.402
7.398
7.394
7.375
7.371
7.260
5.583


OH
OH

5a

2.00
2.04
2.01
2.02
1.73
2.23
1.82
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)


151.4
135.1
131.3
129.4
128.1
127.2
126.6
126.0
124.6
111.6
77.6
77.2
76.8


OH
OH

5a

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)