SCIENCE CHINA
Chemistry

• ARTICLES •

July 2013 Vol.56 No.7: 945–951
doi: 10.1007/s11426-013-4843-7

Synthesis of naphthalene derivatives through inexpensive $BF_3·Et_2O$-catalyzed annulation reaction of arylacetaldehydes with arylalkynes

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Received November 11, 2012; accepted December 26, 2012; published online February 21, 2013

An inexpensive $BF_3·Et_2O$-catalyzed annulation reaction of arylacetaldehydes with arylalkynes has been developed. Various substituted phenylacetaldehydes and phenylacetylenes can undergo this reaction, producing corresponding α-aryl substituted naphthalene derivatives. Use of inexpensive and readily available $BF_3·Et_2O$ catalyst constitutes the most attractive advantage of this transformation.

naphthalene derivatives, $BF_3·Et_2O$, arylacetaldehydes, arylalkynes, annulation reaction

1 Introduction

The naphthalene unit is a ubiquitous skeleton in chemical and pharmaceutical industries as well as optical and electronic materials [1]. In the past decades, the development of some new and efficient methodologies for the synthesis of polysubstituted naphthalene derivatives has aroused great interest of organic chemists [2–5]. Among these methodologies, the acid-catalyzed annulation reaction of α-aryl-substituted carbonyl compounds with alkynes is quite an efficient approach for the synthesis of naphthalene derivatives. In 2002, Li and co-workers [3] realized a highly regioselective synthesis of polysubstituted naphthalene derivatives through $GaCl_3$-catalyzed annulation reaction of phenylacetaldehydes (and ketones) with alkynes (Eq. (1)). In spite of the moderate yields and the application of expensive $GaCl_3$ catalyst, this annulation reaction was discovered by them for the first time. Next year, Kabalka and co-workers [4] reported a $TiCl_4$-mediated annulation reaction of α-aryl-substituted carbonyl compounds with alkynes. Kabalka's method greatly improved the yields of naphthalene derivatives, but required the use of quantitative $TiCl_4$ for this transformation. In 2009, the catalytic system of $AuCl_3/AgSbF_6$ was utilized by Balamurugan group to achieve the similar transformation to synthesize polysubstituted naphthalene derivatives (Eq. (2)) [5]. This approach is very effective, however, use of expensive $AuCl_3/AgSbF_6$ catalyst limited its broad application.

Inexpensive $BF_3·Et_2O$ is widely used as a Lewis acid catalyst in organic synthesis [6]. Recently, we developed a $BF_3·Et_2O$/ammonium salt cocatalyzed alkenylation reaction of indoles with α,β-unsaturated ketones [7]. The combination of inexpensive and readily available $BF_3·Et_2O$ and an ammonium salt as the efficient cocatalyst constitutes the attractive advantage of the reaction. Herein, we wish to report a new annulation reaction of arylacetaldehydes with arylalkynes catalyzed by inexpensive $BF_3·Et_2O$ to give naphthalene derivatives (Eq. (3)).

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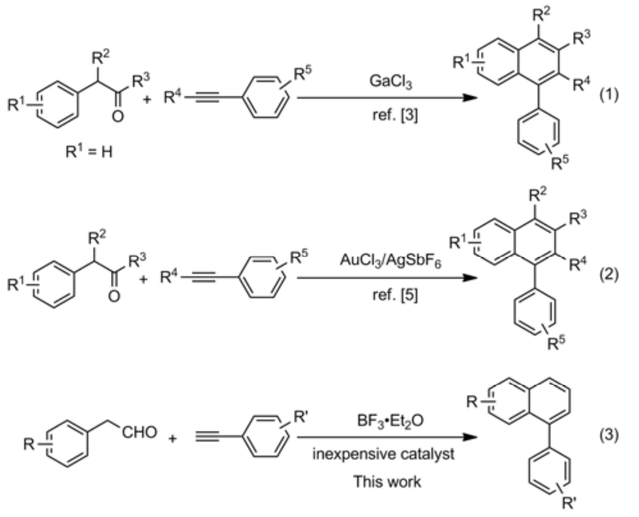
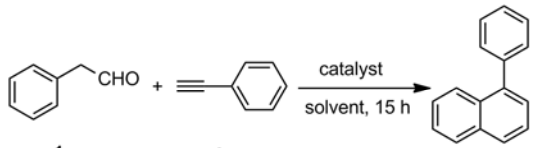


2 Results and discussion

Initially, we investigated the annulation reaction of phenylacetaldehyde **1a** and phenylacetylene **2a** in the presence of 5 mol% of $FeCl_3$. Gratifyingly, 58% of 1-phenylnaphthalene **3aa** was obtained when dichloroethane (DCE) was used as the solvent (entry 1, Table 1). Although other Lewis acid catalysts or Brønsted acid catalysts such as $FeCl_2{\cdot}4H_2O$, AgOTf, and CH_3SO_3H also promoted this transformation, their efficiencies were lower than $FeCl_3$ (entries 2–4, Table 1). TsOH hardly led to any desired product (entry 5, Table 1). Notably, the yield was improved to 74% when $BF_3{\cdot}Et_2O$ was used as a catalyst (entry 6, Table 1).

Table 1 Annulation reaction of phenylacetaldehyde (**1a**) with phenylacetylene (**2a**) under different conditions [a)]



1a **2a** **3aa**

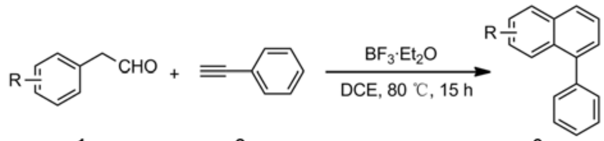
Entry	Catalyst (mmol%)	Solvent (mL)	*T* (℃)	Yield (%) [b)]
1	$FeCl_3$ (5)	DCE	80	58
2	$FeCl_2{\cdot}H_2O$ (5)	DCE	80	27
3	AgOTf (5)	DCE	80	27
4	CH_3SO_3H (5)	DCE	80	28
5	TsOH (5)	DCE	80	trace
6	$BF_3{\cdot}Et_2O$ (5)	DCE	80	74
7	$BF_3{\cdot}Et_2O$ (5)	PhCl	80	42
8	$BF_3{\cdot}Et_2O$ (5)	toluene	80	26
9	$BF_3{\cdot}Et_2O$ (5)	MeCN	80	38
10	$BF_3{\cdot}Et_2O$ (5)	$MeNO_2$	80	37
11	$BF_3{\cdot}Et_2O$ (5)	DMF	80	ND [c)]
12	$BF_3{\cdot}Et_2O$ (5)	DCE	50	30
13	$BF_3{\cdot}Et_2O$ (5)	DCE	rt	ND [c)]
14[d]	$BF_3{\cdot}Et_2O$ (5)	DCE	80	82

a) All the reactions were carried out in the scale of 0.3 mmol **1a**, 0.3 mmol **2a**, 5 mmol% catalyst in 1.0 mL solvent if without further note; b) the yields were isolated yields; c) ND = not detected; d) 0.36 mmol **2a** was used.

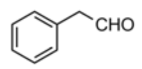
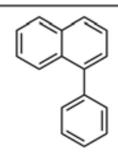
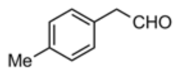
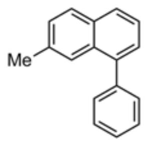
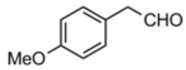
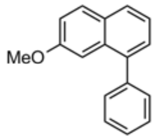
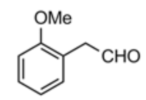
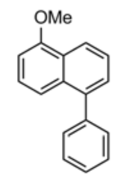
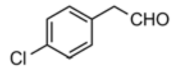
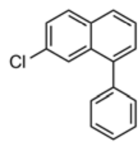
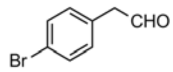
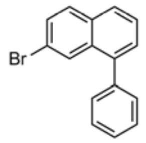
Different solvents were then screened, indicating DCE as the best reaction medium (entries 6–11, Table 1). In addition, the reaction temperature was also critical for this annulation reaction (cf. entries 6, 12 and 13, Table 1). Finally, the best result of 82% yield was achieved by increasing the amount of phenylacetylene to 1.2 equivalents (entry 14, Table 1).

The scope of annulation reaction was expanded to a variety of substituted phenylacetaldehydes **1** and phenylacetylenes **2** (Tables 2 and 3). Phenylacetaldehydes **1** with both electron-donating groups and electron-withdrawing groups in the benzene ring smoothly underwent this kind of transformation, generating naphthalene derivatives **3** in moderate

Table 2 Annulation reaction of substituted phenylacetaldehydes (**1**) with phenylacetylene (**2a**) [a)]

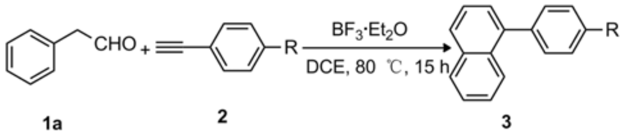


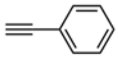
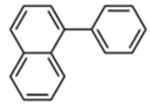
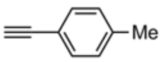
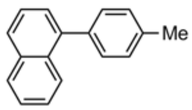
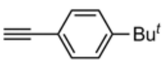
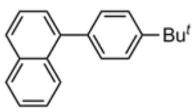
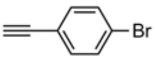
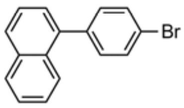
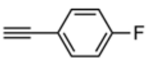
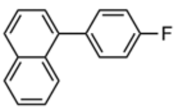
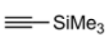
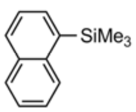
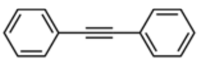
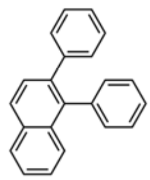
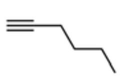
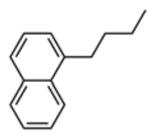
1 **2a** **3**

entry	1		3		yield (%)
1		**1a**		**3aa**	82
2		**1b**		**3ba**	58
3		**1c**		**3ca**	60
4[b]		**1d**		**3da**	30
5		**1e**		**3ea**	53
6		**1f**		**3fa**	64

a) All the reactions were carried out in the scale of 0.3 mmol **1**, 0.36 mmol **2a**, 5 mmol% $BF_3{\cdot}Et_2O$ in 1.0 mL DCE at 80 °C if without further note. The yields were isolated yields; b) the reactions were carried out at 90 °C. 10 mmol% $BF_3{\cdot}Et_2O$ was used.

Table 3 Annulation reaction of phenylacetaldehydes (**1a**) with various phenylacetylenes (**2**) [a)]

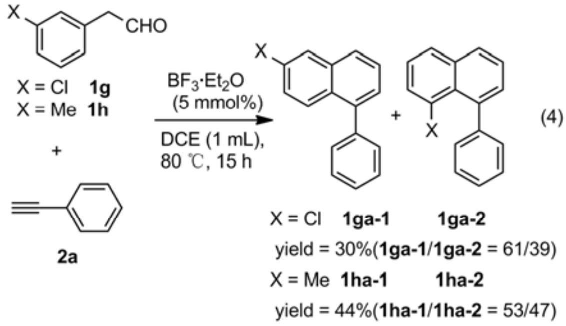


entry	2		3		yield (%)
1		2a		3aa	82
2		2b		3ab	73
3		2c		3ac	78
4 [b)]		2d		3ad	55
5 [b)]		2e		3ae	61
6		2f		3af	0
7		2g		3ag	0
8		2h		3ah	trace

a) All the reactions were carried out in the scale of 0.3 mmol **1a**, 0.36 mmol **2**, 5 mmol% $BF_3{\cdot}Et_2O$ in 1.0 mL DCE at 80 °C if without further note. The yields were isolated yields; b) the reactions were carried out in PhCl (1 mL) instead of DCE at 110 °C. 20 mmol% $BF_3{\cdot}Et_2O$ was used.

to excellent yields 30–82% (entries 1–6, Table 2). It is noteworthy that electronic effect of the arylacetaldehydes component had some influence on the reaction, but the regularity was not obvious (entries 1–6, Table 2). The substituents Cl and Br were compatible under these conditions, which could be further transformed into other functionalities (entries 5 and 6, Table 2).

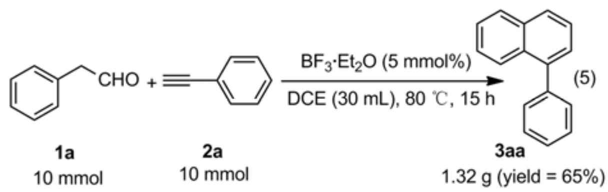
In addition, both electron-rich and electron-deficient arylacetylenes were tolerable as the annulation reaction partners with the yields of 55–82% (entries 1–5, Table 3). Notably, the electron-rich arylacetylenes gave the desired products in higher yields than the electron-deficient ones (entries 2–5, Table 3). It is regretful that both (trimethylsilyl)acetylene and internal alkyne can not undergo this transformation to give the desired product (entries 6 and 7, Table 3). The internal alkynes failed to undergo the reaction possibly due to the following two reasons: i) The diphenylacetylene has a weaker nucleophilicity than phenylacetaldehyde; ii) The Lewis acidity of $BF_3{\cdot}Et_2O$ is lower than $GaCl_3$ or $AuCl_3/AgSbF_6$. Furthermore, the 1-hexyne **2h** was examined and gave only trace amount of product (entry 8, Table 3).



(4)

Two meta-substituted arylacetaldehydes (**1g**, **1h**) was employed to study the selectivity of the reaction (Eq. (4)). The results showed that the selectivity is terrible.

To explore the application of such transformations, this annulation reaction was scaled up to 10 mmol (Eq. (5)). When 10 mmol of phenylacetaldehyde **1a** and phenylacetylene **2a** were used as substrates, 1.32 g of 1-phenylnaphthalene **3aa** was obtained with the good yield of 65%. The result indicated that the catalytic method was very efficient.

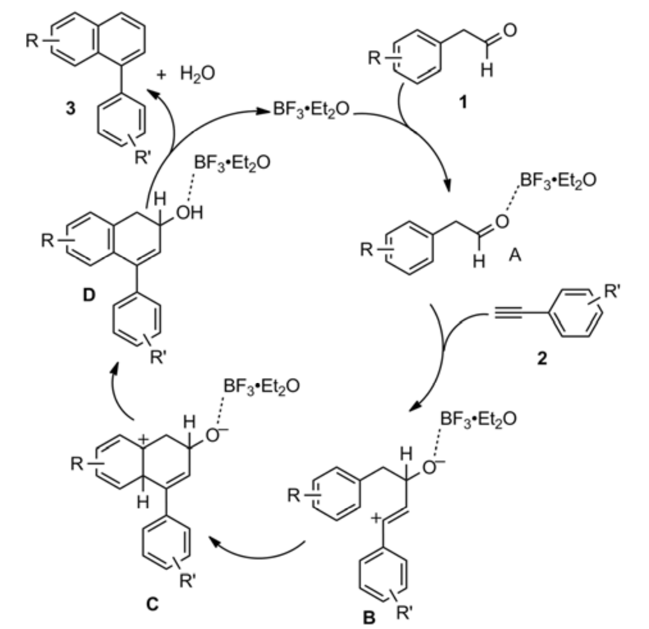


(5)

A possible mechanism for this catalytic transformation is illustrated in Scheme 1. Initially, $BF_3{\cdot}Et_2O$ coordinates with the carbonyl oxygen to form the aldehyde-Lewis acid complex **A** [3, 5, 6]. Electrophilic attack of the carbonyl carbon in complex **A** on the arylalkyne **2** takes place to generate complex **B** with a vinyl carbocation stabilized by the aryl group. Intramolecular electrophilic attack of the formed vinyl carbocation to the aromatic ring followed by elimination of a proton generates the cyclization product **D**. Finally, the complex **D** can aromatize by dehydration to form the corresponding naphthalene derivative **3**, releasing the catalyst at the completion of catalytic cycle.

3 Conclusions

In summary, we developed an inexpensive $BF_3{\cdot}Et_2O$-catalyzed annulation reaction of arylacetaldehydes with arylalkynes.



Scheme 1 Proposed mechanism for this catalytic transformation.

Various substituted phenylacetaldehydes and phenylacetylenes can undergo this reaction, providing an alternative approach for the synthesis of naphthalene derivatives. Use of inexpensive and readily available $BF_3{\cdot}Et_2O$ catalyst constitutes the most attractive advantage of this transformation. Development of other methodologies for the synthesis of naphthalene derivatives is ongoing in our laboratory.

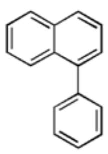
4 Experimental

4.1 General experimental section

All manipulations were conducted with Schlenk tube. ^{1}H NMR spectra were recorded on the Varian 400 MHz WB spectrometers. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. ^{13}C NMR spectra were obtained by the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). Mass spectra were obtained using Electron Impact (EI) mass spectrometer. Arylacetaldehydes **1b**–**f** were synthesized according to literature method [8]. Unless otherwise noted, materials and solvents from commercial suppliers were used without further purification.

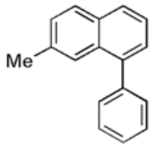
4.2 Experimental procedures and characterization of products

*1-Phenylnaphthalene (**3aa**)*



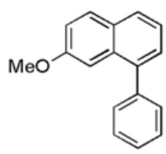
Typical procedure: phenylacetaldehyde (36.0 mg, 0.3 mmol) and phenylacetylene (36.7 mg, 0.36 mmol), $BF_3{\cdot}Et_2O$ (2.1 mg, 0.015 mmol) and DCE (1 mL) were mixed in a Schlenck tube. The reaction mixture was stirred for 15 h at 80 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, *v*/*v* = 70:1) to afford 50.2 mg (82%) of **3aa**. IR:(KBr) ν_{max} 3056, 2921, 2851 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.91–7.88 (m, 2H), 7.85–7.82 (m, 1H), 7.48–7.40 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.7, 140.2, 133.7, 131.6, 130.0, 128.2, 127.6, 127.2, 126.9, 126.0, 125.7, 125.4; MS (70 eV), *m*/*z* (%): 204.4 (72) [M]$^+$, 203.2 (100).

*7-Methyl-1-phenylnaphthalene (**3ba**)*



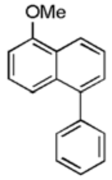
2-*p*-Tolylacetaldehyde (40.2 mg, 0.3 mmol) and phenylacetylene (36.7 mg, 0.36 mmol), $BF_3{\cdot}Et_2O$ (2.1 mg, 0.015 mmol) and DCE (1 mL) were mixed in a Schlenck tube. The reaction mixture was stirred for 15 h at 80 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, *v*/*v* = 70:1) to afford 37.9 mg (58%) of **3ba**. IR(KBr): ν_{max} 3052, 2917, 2855, 2732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.66 (s, 1H), 7.50–7.45 (m, 4H), 7.44–7.41 (m, 2H), 7.38–7.36 (m, 1H), 7.33–7.30 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.0, 139.5, 135.7, 132.0, 131.7, 130.0, 128.2, 128.1, 128.0, 127.4, 127.1, 127.0, 124.8, 124.5, 21.9; MS (70 eV), *m*/*z* (%): 218.0 (100) [M]$^+$.

*7-Methoxy-1-phenylnaphthalene (**3ca**)*



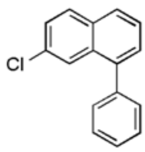
2-(4-Methoxyphenyl)acetaldehyde (45.0 mg, 0.3 mmol) and phenylacetylene (36.7 mg, 0.36 mmol), $BF_3{\cdot}Et_2O$ (2.1 mg, 0.015 mmol) and DCE (1 mL) were mixed in a Schlenck tube. The reaction mixture was stirred for 15 h at 80 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, *v*/*v* = 5:1) to afford 42.1 mg (60%) of **3ca** with two isomers in 92:8 ratio. IR(KBr) ν_{max} 3054, 3022, 2956, 2936, 2878, 2831 cm^{-1}; ^{1}H NMR of major product (400 MHz, $CDCl_3$, ppm) δ 7.81–7.79 (m, 2H), 7.52–7.46 (m, 4H), 7.43–7.41 (m, 1H), 7.39–7.36 (m, 2H), 7.23 (s, 1H), 7.16 (d, *J* = 8.8 Hz, 1H), 3.75 (s, 3H); MS (70 eV), *m*/*z* (%): 234.1 (100) $[M]^+$.

*1-Methoxy-5-phenylnaphthalene (**3da**)*



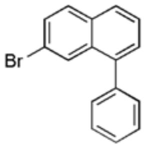
2-(2-Methoxyphenyl)acetaldehyde (45.0 mg, 0.3 mmol) and phenylacetylene (36.7 mg, 0.36 mmol), $BF_3{\cdot}Et_2O$ (4.2 mg, 0.03 mmol) and DCE (1 mL) were mixed in a Schlenck tube. The reaction mixture was stirred for 15 h at 90 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, *v*/*v* = 5:1) to afford 21.1 mg (30%) of **3da**. IR(KBr) ν_{max} 3031, 3006, 2966, 2934, 2853, 2833 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.33–8.29 (m, 1H), 7.53–7.41 (m, 8H), 7.33–7.28 (m, 1H), 6.81 (d, *J* = 7.2 Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 155.5, 141.1, 139.8, 132.6, 130.1, 128.1, 127.5, 127.1, 125.9, 125.8, 124.7, 121.5, 118.3, 103.6, 55.6; MS (70 eV), *m*/*z* (%): 234.2 (100) $[M]^+$.

*7-Chloro-1-phenylnaphthalene (**3ea**)*



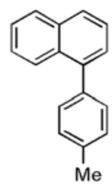
2-(4-Chlorophenyl)acetaldehyde (46.4 mg, 0.3 mmol) and phenylacetylene (36.7 mg, 0.36 mmol), $BF_3{\cdot}Et_2O$ (2.1 mg, 0.015 mmol) and DCE (1 mL) were mixed in a Schlenck tube. The reaction mixture was stirred for 15 h at 80 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, *v*/*v* = 70:1) to afford 41.6 mg (58%) of **3ea**. IR(KBr) ν_{max} 3056, 2924, 2853 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.87–7.81 (m, 3H), 7.51–7.44 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.0, 139.6, 132.3, 132.01, 131.99, 129.93, 129.86, 128.4, 127.9, 127.5, 127.4, 126.7, 125.6, 124.9; MS (70 eV), *m*/*z* (%): 238.0 (100) $[M]^+$.

*7-Bromo-1-phenylnaphthalene (**3fa**)*



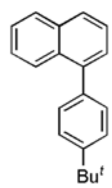
2-(4-Bromophenyl)acetaldehyde (59.7 mg, 0.3 mmol) and phenylacetylene (36.7 mg, 0.36 mmol), $BF_3{\cdot}Et_2O$ (2.1 mg, 0.015 mmol) and DCE (1 mL) were mixed in a Schlenck tube. The reaction mixture was stirred for 15 h at 80 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, *v*/*v* = 70:1) to afford 54.0 mg (64%) of **3fa**. IR(KBr) ν_{max} 3056, 2922, 2851 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.04 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.57–7.43 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.0, 139.5, 132.7, 132.2, 129.9, 129.2, 128.5, 128.1, 127.9, 127.53, 127.48, 125.8, 120.4; MS (70 eV), *m*/*z* (%): 282.0 (100) $[M]^+$.

*1-p-Tolylnaphthalene (**3ab**)*



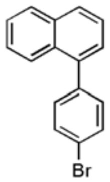
Phenylacetaldehyde (36.0 mg, 0.3 mmol) and 1-ethynyl-4-methylbenzene (41.8 mg, 0.36 mmol), $BF_3{\cdot}Et_2O$ (2.1 mg, 0.015 mmol) and DCE (1 mL) were mixed in a Schlenck tube. The reaction mixture was stirred for 15 h at 80 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, *v*/*v* = 70:1) to afford 47.7 mg (73%) of **3ab**. IR(KBr) ν_{max} 3037, 2963, 2918, 2857 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.92–7.85 (m, 3H), 7.51–7.41 (m, 6H), 7.31 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 137.8, 136.9, 133.8, 131.7, 130.0, 129.0, 128.3, 127.4, 126.9, 126.1, 125.9, 125.7, 125.4, 21.3; MS (70 eV), *m*/*z* (%): 218.2 (100) $[M]^+$.

*1-(4-Tert-butylphenyl)naphthalene (**3ac**)*



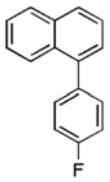
Phenylacetaldehyde (36.0 mg, 0.3 mmol) and 1-*tert*-butyl-4-ethynylbenzene (57.0 mg, 0.36 mmol), $BF_3{\cdot}Et_2O$ (2.1 mg, 0.015 mmol) and DCE (1 mL) were mixed in a Schlenck tube. The reaction mixture was stirred for 15 h at 80 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, *v*/*v* = 70:1) to afford 60.9 mg (78%) of **3ac**. IR(KBr) ν_{max} 3063, 3039, 2958, 2900, 2863 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.96 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.53–7.48 (m, 4H), 7.47–7.40 (m, 4H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 150.1, 140.2, 137.7, 133.8, 131.7, 129.7, 128.2, 127.4, 126.9, 126.2, 125.9, 125.7, 125.4, 125.2, 34.6, 31.5; MS (70 eV), m/z (%): 260.0 (100) $[M]^+$.

*1-(4-Bromophenyl)naphthalene (**3ad**)*



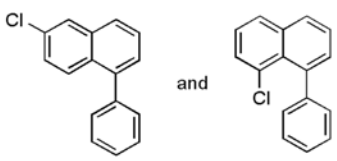
Phenylacetaldehyde (36.0 mg, 0.3 mmol) and 1-bromo-4-ethynylbenzene (65.2 mg, 0.36 mmol), $BF_3 \cdot Et_2O$ (8.2 mg, 0.06 mmol) and PhCl (1 mL) were mixed in a Schlenck tube. The reaction mixture was stirred for 15 h at 110 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, v/v = 70:1) to afford 46.7 mg (55%) of **3ad**. IR(KBr) ν_{max} 3058, 2924 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.90–7.81 (m, 3H), 7.61–7.58 (m, 2H), 7.49–7.47 (m, 2H), 7.44–7.41 (m, 1H), 7.35–7.33 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 139.6, 138.9, 133.7, 131.7, 131.4, 131.3, 128.3, 128.0, 126.8, 126.2, 125.9, 125.6, 125.3, 121.4; MS (70 eV), m/z (%): 282.2 (100) $[M]^+$.

*1-(4-Fluorophenyl)naphthalene (**3ae**)*



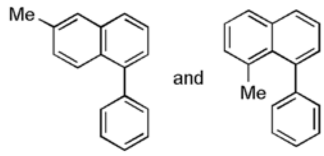
Phenylacetaldehyde (36.0 mg, 0.3 mmol) and 1-ethynyl-4-fluorobenzene (43.2 mg, 0.36 mmol), $BF_3 \cdot Et_2O$ (8.4 mg, 0.06 mmol) and PhCl (1 mL) were mixed in a Schlenck tube. The reaction mixture was stirred for 15 h at 110 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, v/v = 70:1) to afford 40.6 mg (61%) of **3ae**. IR(KBr) ν_{max} 3042, 2929, 2850 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.91–7.84 (m, 3H), 7.52–7.36 (m, 6H), 7.19–7.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2 (d, J = 244.4 Hz), 139.1, 136.63, 136.59, 133.7, 131.6, 131.5, 128.3, 127.8, 127.0, 126.1, 125.8, 125.7, 125.3, 115.3, 115.0; MS (70 eV), m/z (%): 222.4 (74) $[M]^+$, 221.1 (100).

*6-Chloro-1-phenylnaphthalene (**3ga-1**) and 1-chloro-8-phenylnaphthalene (**3ga-2**)*



2-(3-Chlorophenyl)acetaldehyde (46.4 mg, 0.3 mmol) and phenylacetylene (36.7 mg, 0.36 mmol), $BF_3 \cdot Et_2O$ (2.1 mg, 0.015 mmol) and DCE (1 mL) were mixed in a Schlenck tube. The reaction mixture was stirred for 15 h at 80 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, v/v = 70:1) to afford 21.4 mg (30%) of **3ga** (**3ga-1/3ga-2 =** 61/39). **3ga-1:** ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.867 (d, J = 2.0 Hz, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.55–7.39 (m, 7H), 7.34 (dd, J_1 = 9.6 Hz, J_2 = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.4, 140.2, 134.5, 131.6, 129.93, 129.0, 128.3, 127.8, 127.5, 127.1, 126.8, 126.7, 126.5; MS (70 eV), m/z (%): 237.7 (100) $[M]^+$. **3ga-2:** ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.88–7.82 (m, 2H), 7.52–7.47 (m, 2H), 7.41–7.32 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.5, 139.5, 136.0, 131.4, 131.0, 129.6, 129.4, 128.7, 128.6, 128.2, 127.2, 126.7, 125.6, 125.4; MS (70 eV), m/z (%): 238.7 (100) $[M]^+$.

*6-Methyl-1-phenylnaphthalene (**3ha-1**) and 1-methyl-8-phenylnaphthalene (**3ha-2**)*



2-*m*-Tolylacetaldehyde (40.2 mg, 0.3 mmol) and phenylacetylene (36.7 mg, 0.36 mmol), $BF_3 \cdot Et_2O$ (2.1 mg, 0.015 mmol) and DCE (1 mL) were mixed in a Schlenck tube. The reaction mixture was stirred for 15 h at 80 °C. The solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, v/v = 70:1) to afford 28.8 mg (44%) of **3ha** (**3ha-1/3ha-2 =** 53/47). ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.66 (s, 1H); MS (70 eV), m/z (%): 218.2 (100) $[M]^+$.

We are grateful for the financial supports from Sichuan Provincial Department of Education (11ZA108), National Natural Science Foundation of China (21202109 and 21072140), Special Funds of Sichuan Normal University for Sharing the Large Precision Equipments (DJ2012-07, DJ2011-16) and Sichuan Normal University.

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July 2013 Vol.56 No.7: 1–9
doi: 10.1007/s11426-013-4843-7

Synthesis of naphthalene derivatives through inexpensive $BF_3 \cdot Et_2O$-catalyzed annulation reaction of arylacetaldehydes with arylalkynes

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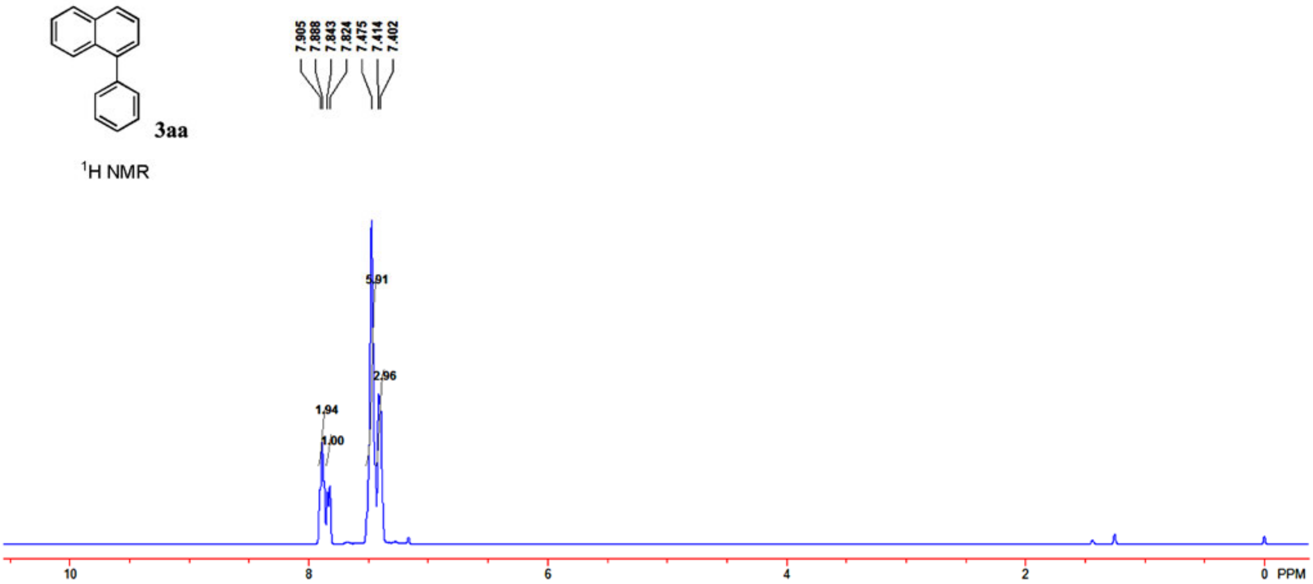
Received November 11, 2012; accepted December 26, 2012; published online February 21, 2013



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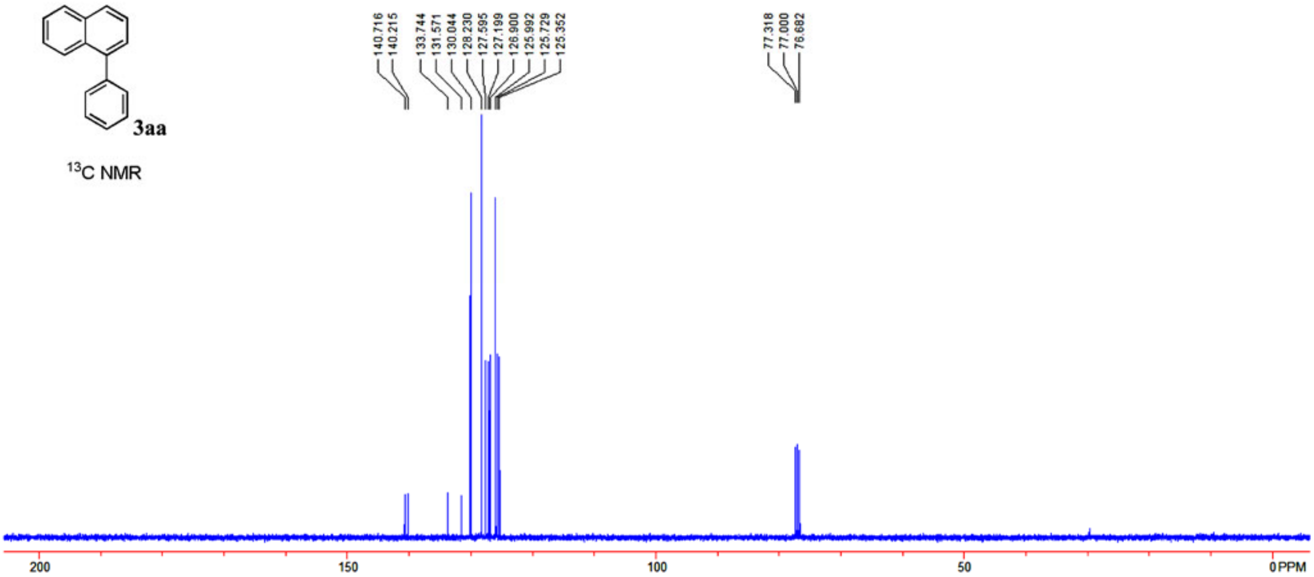
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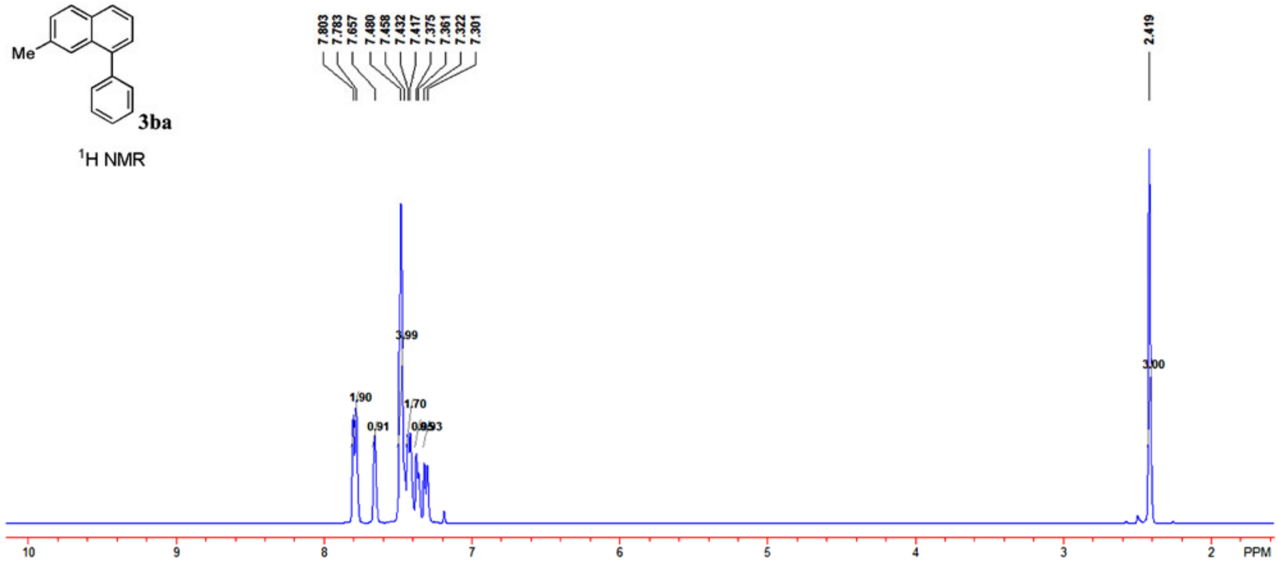
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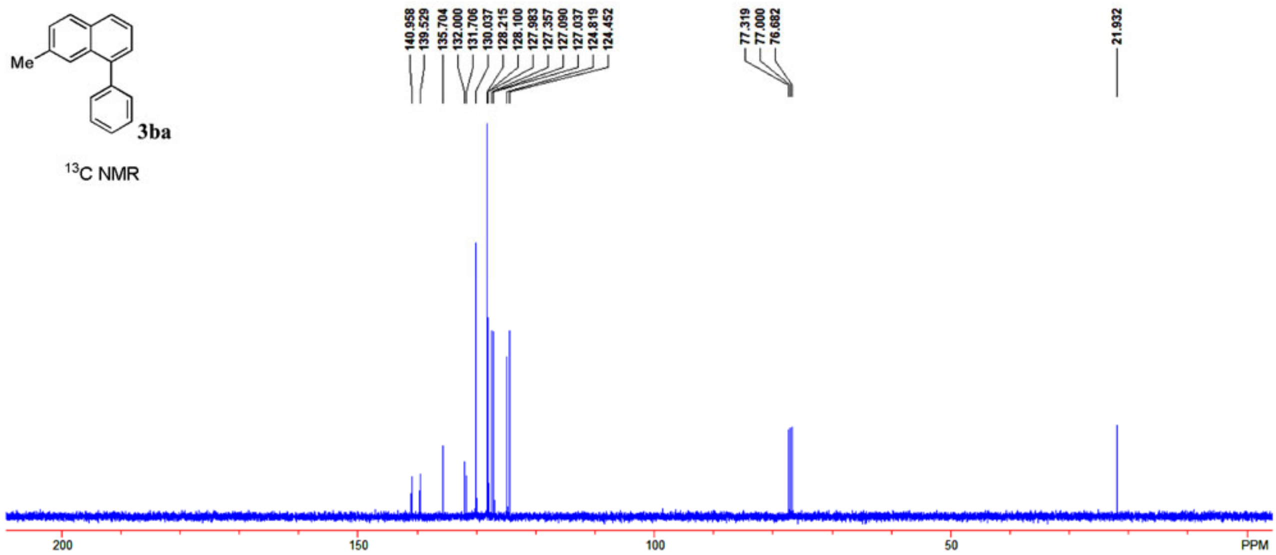
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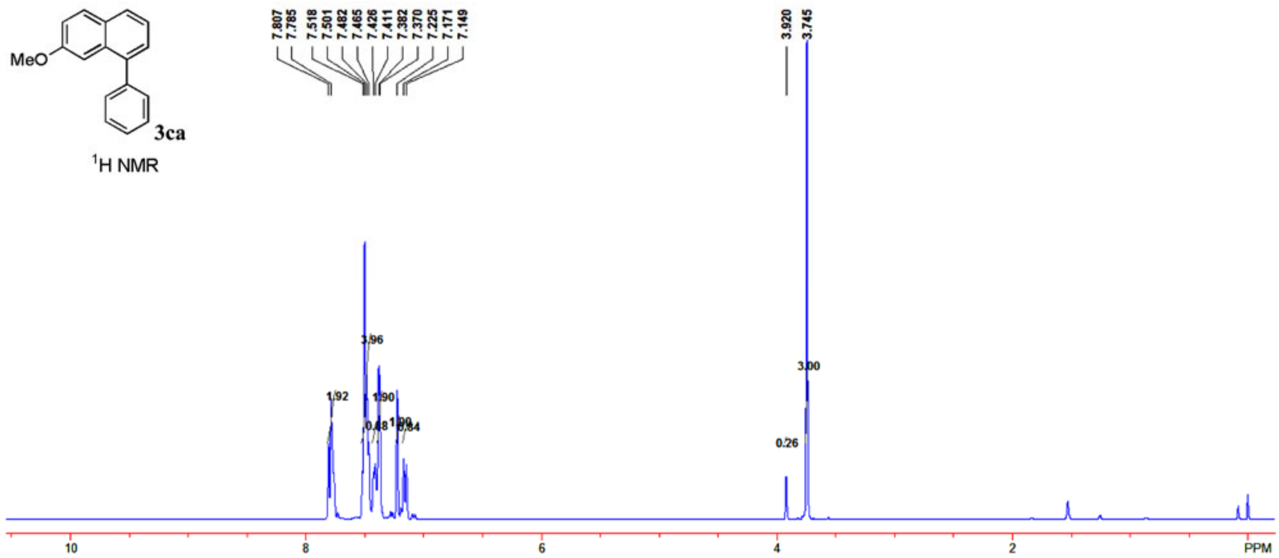
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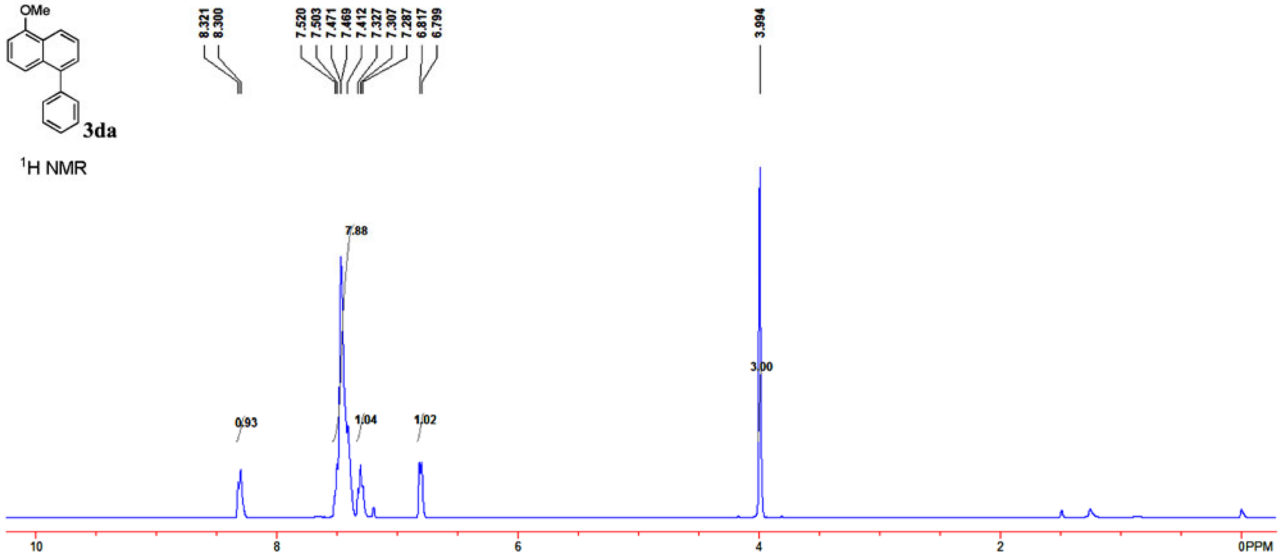
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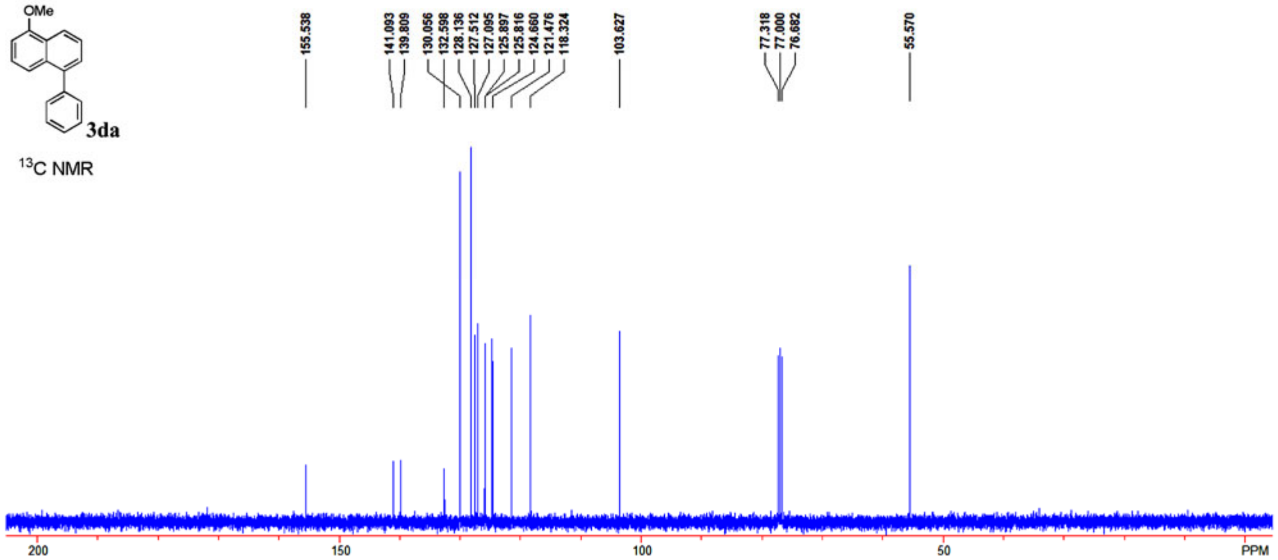
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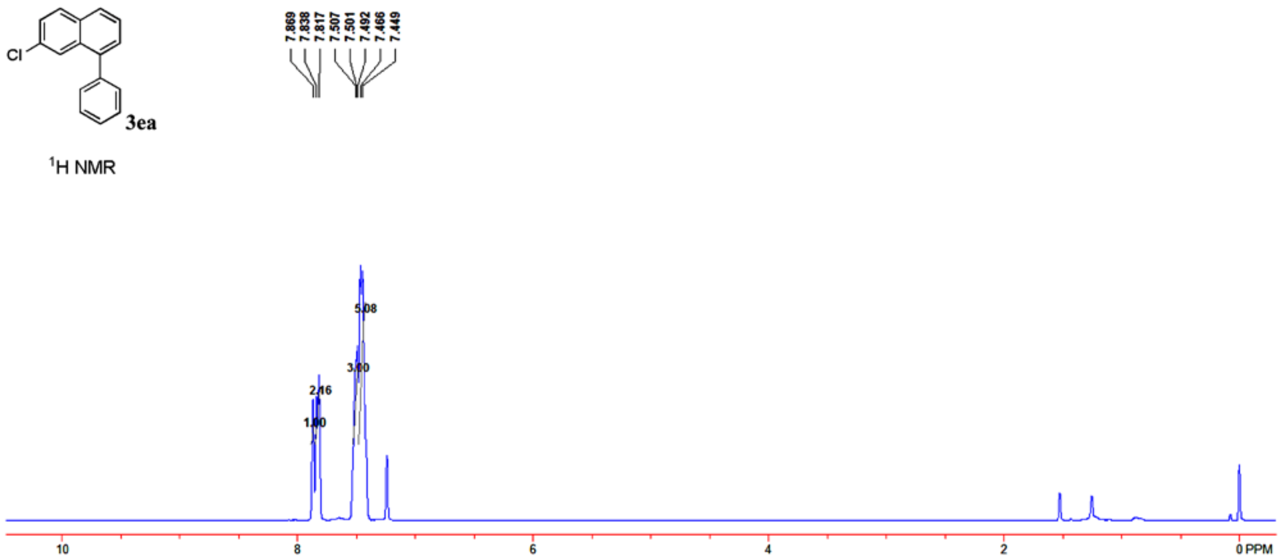

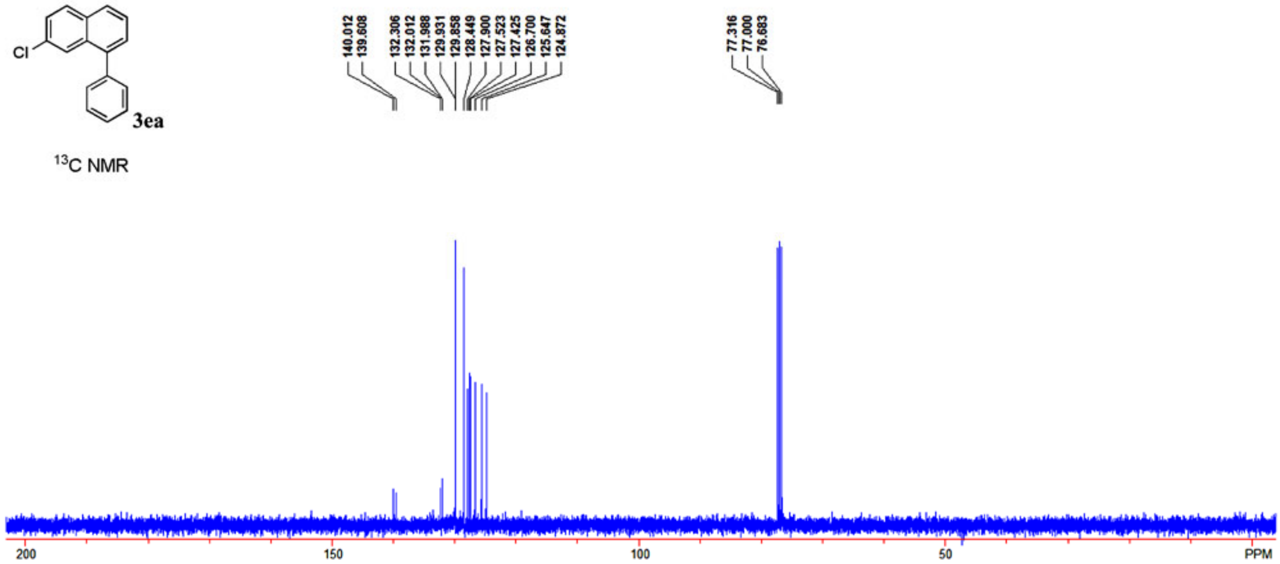

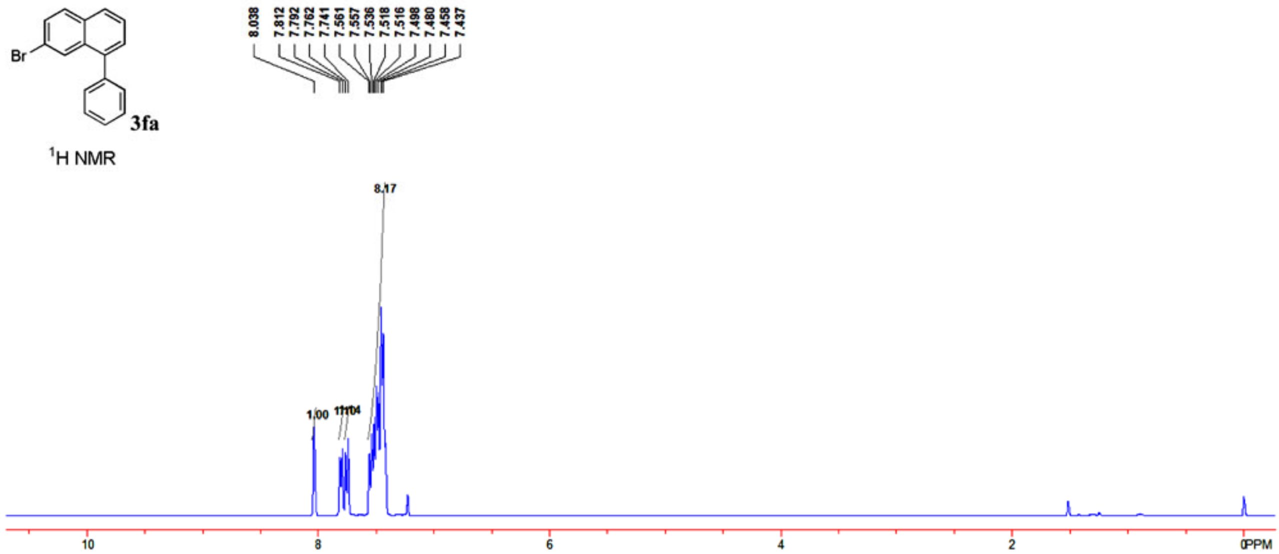

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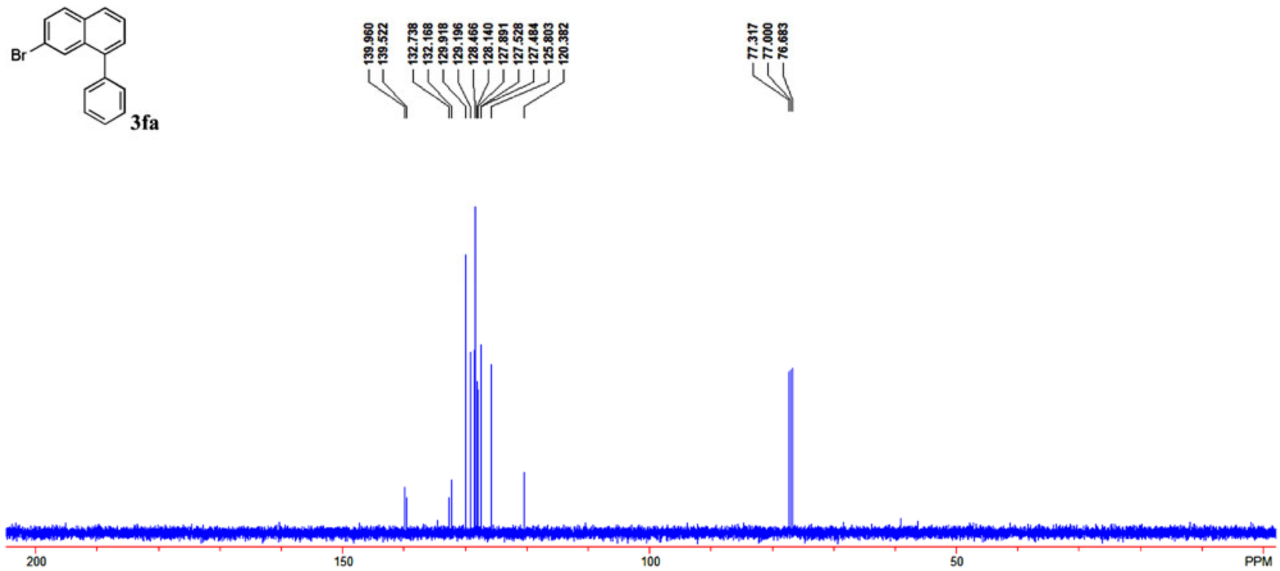
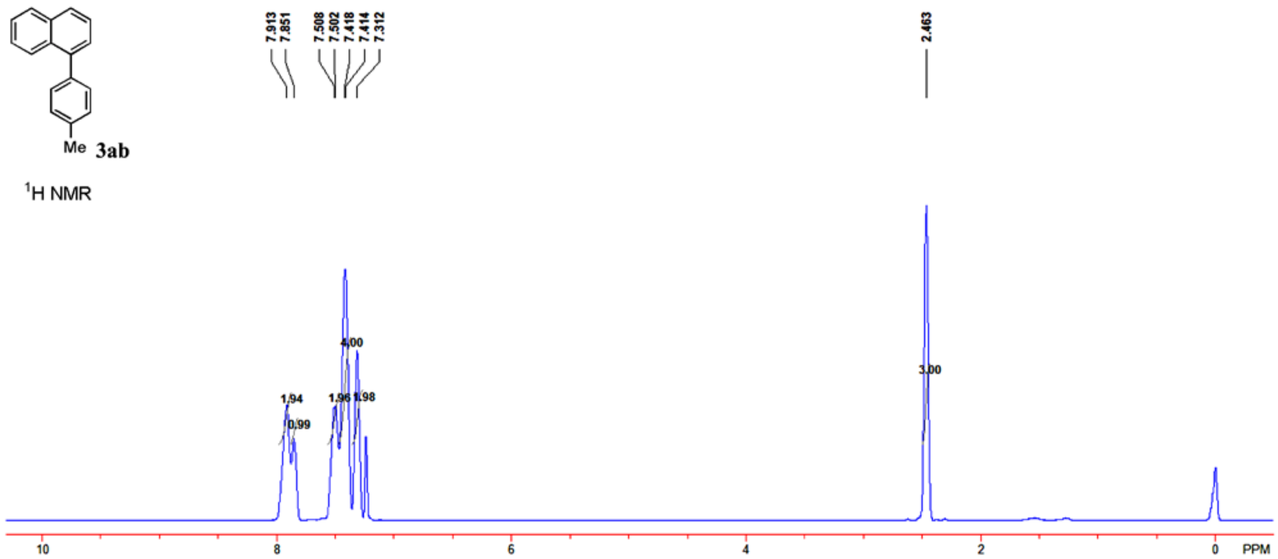
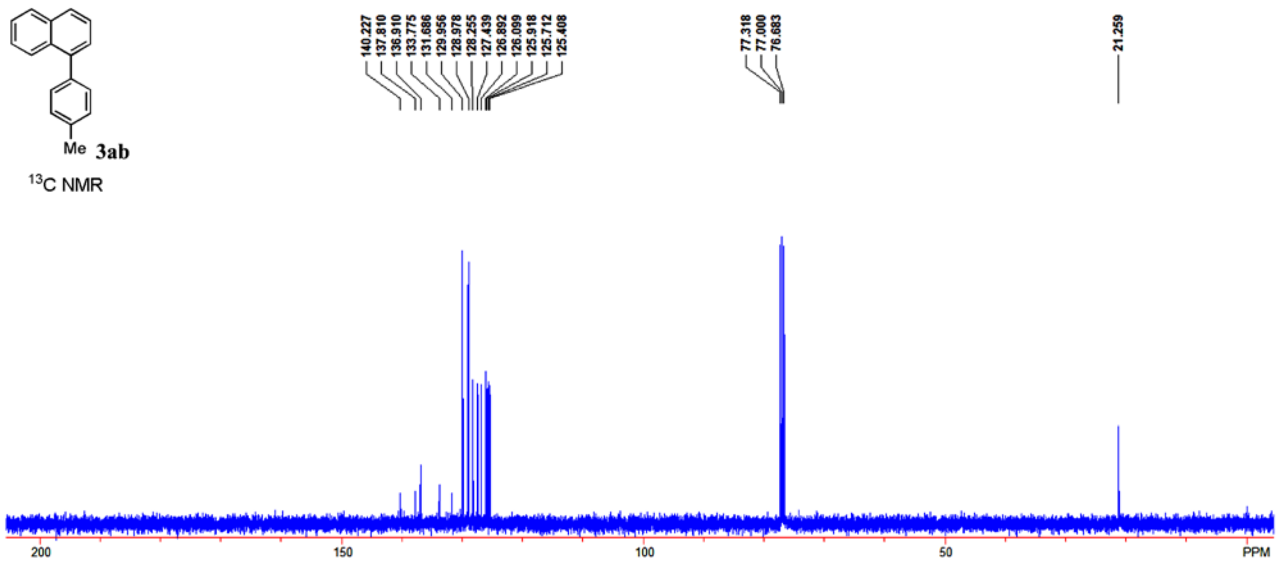
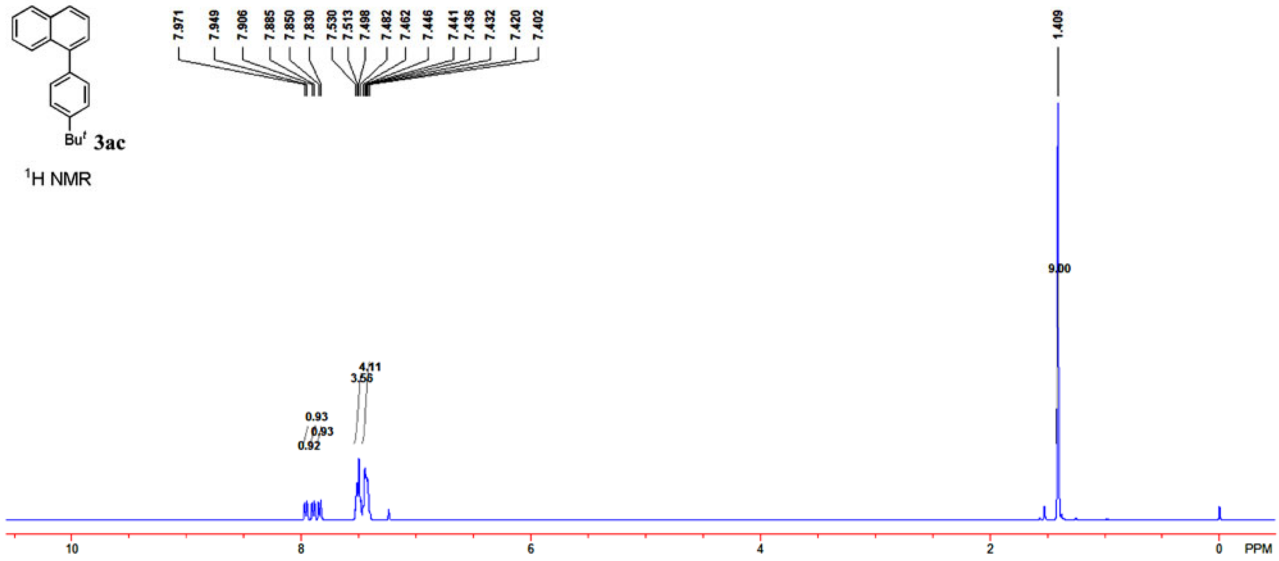
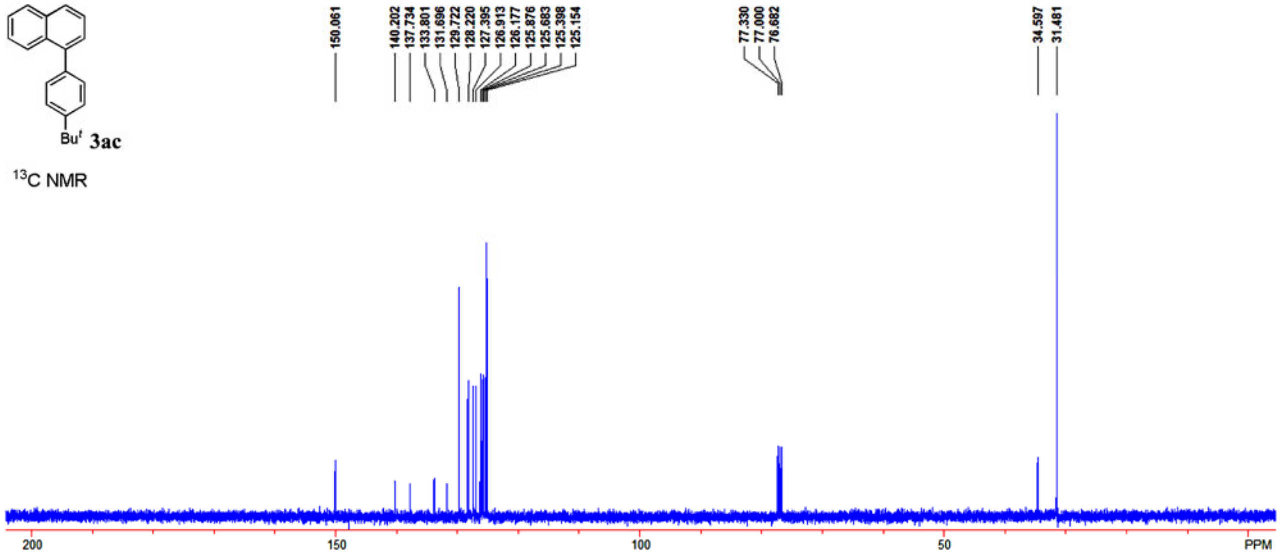
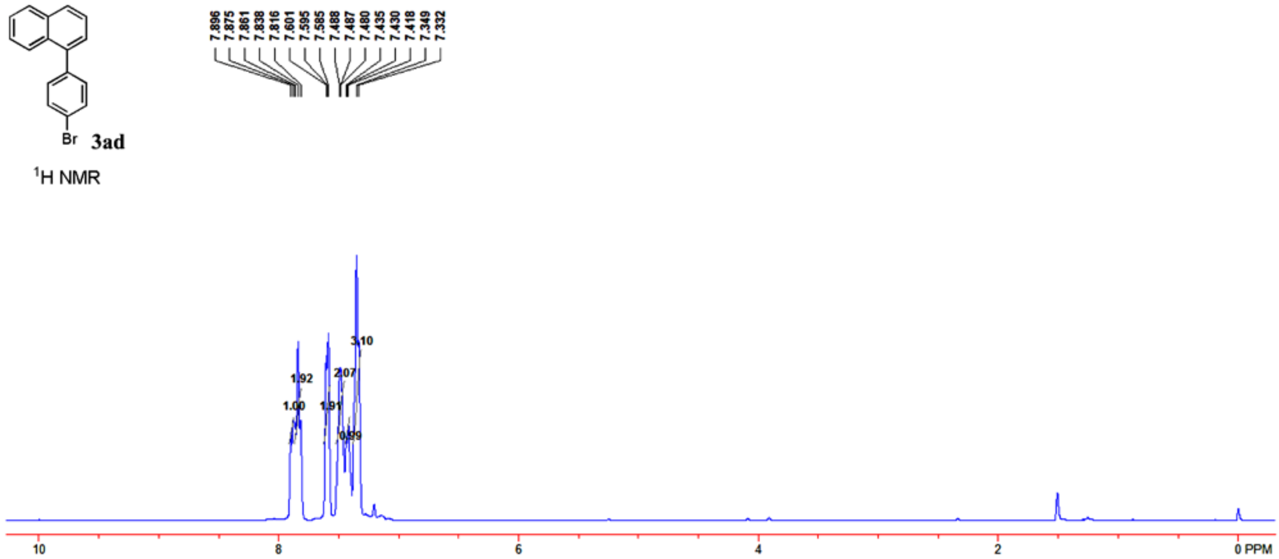

Br
3fa
139.960
139.522
132.738
132.168
129.918
129.196
128.466
128.140
127.891
127.528
127.484
125.803
120.382
77.317
77.000
76.683
200
150
100
50
PPM

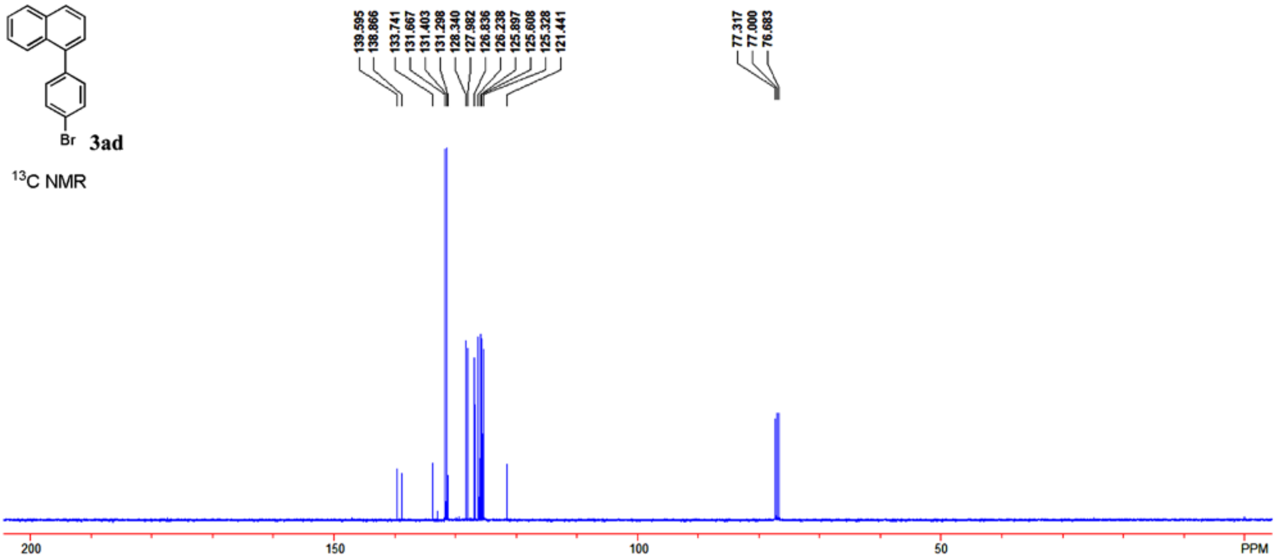

Me
3ab
^{1}H NMR
7.913
7.851
7.508
7.502
7.418
7.414
7.312
2.463
1.94
0.99
1.96
4.00
1.98
3.00
10
8
6
4
2
0
PPM


Me
3ab
^{13}C NMR
140.227
137.810
136.910
133.775
131.686
129.956
128.978
128.255
127.439
126.892
126.099
125.918
125.712
125.408
77.318
77.000
76.683
21.259
200
150
100
50
PPM


Bu^t 3ac
^{1}H NMR
7.971 7.949 7.906 7.885 7.850 7.830 7.530 7.513 7.498 7.482 7.462 7.446 7.441 7.436 7.432 7.420 7.402
1.409
9.00
4.11
3.56
0.93
0.93
0.92
10 8 6 4 2 0 PPM


Bu^t 3ac
^{13}C NMR
150.061
140.202 137.734 133.801 131.696 129.722 128.220 127.395 126.913 126.177 125.876 125.683 125.398 125.154
77.330 77.000 76.682
34.597 31.481
200 150 100 50 PPM


Br 3ad
^{1}H NMR
7.896 7.875 7.861 7.838 7.816 7.601 7.595 7.585 7.488 7.487 7.480 7.435 7.430 7.418 7.349 7.332
3.10
1.92
2.07
1.00
1.91
0.99
10 8 6 4 2 0 PPM


Br
3ad
^{13}C NMR
139.595
138.866
133.741
131.667
131.403
131.298
128.340
127.982
126.836
126.238
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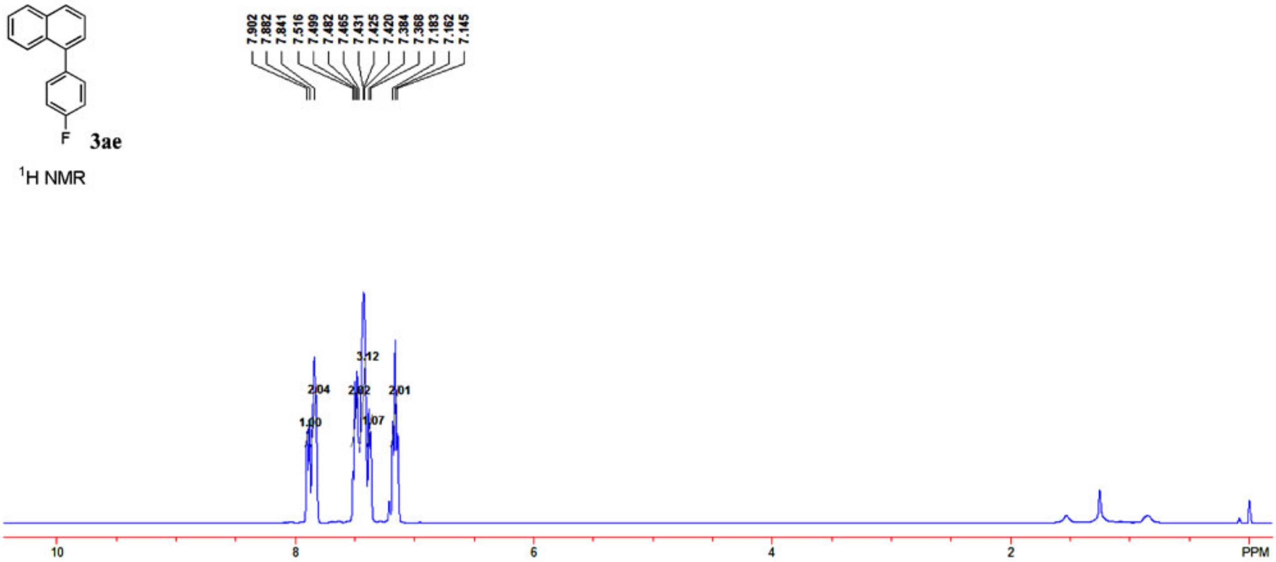
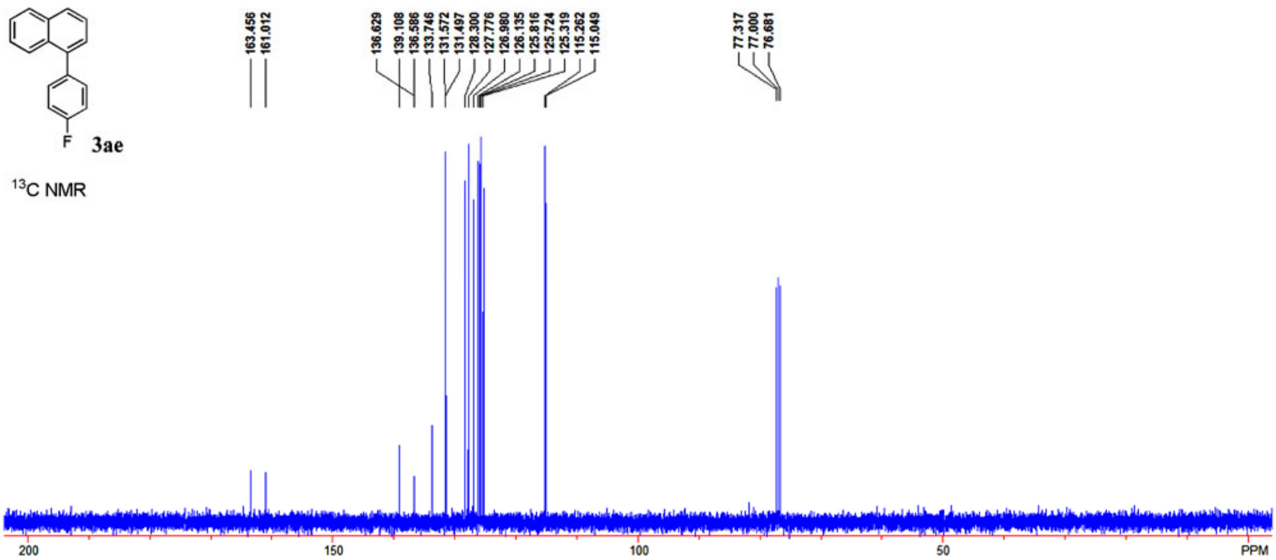
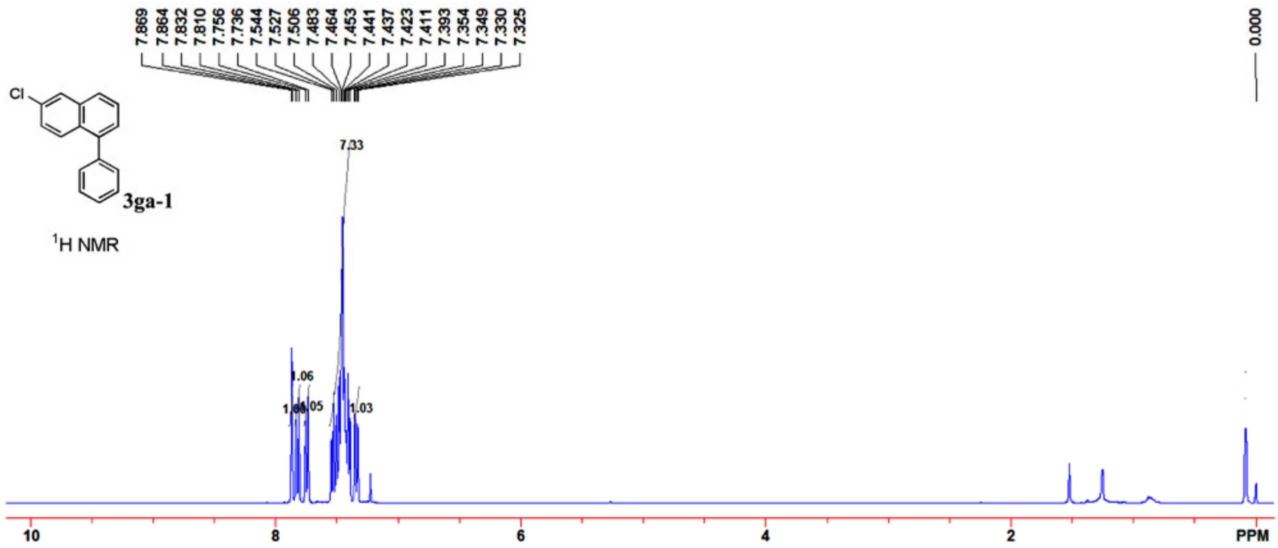
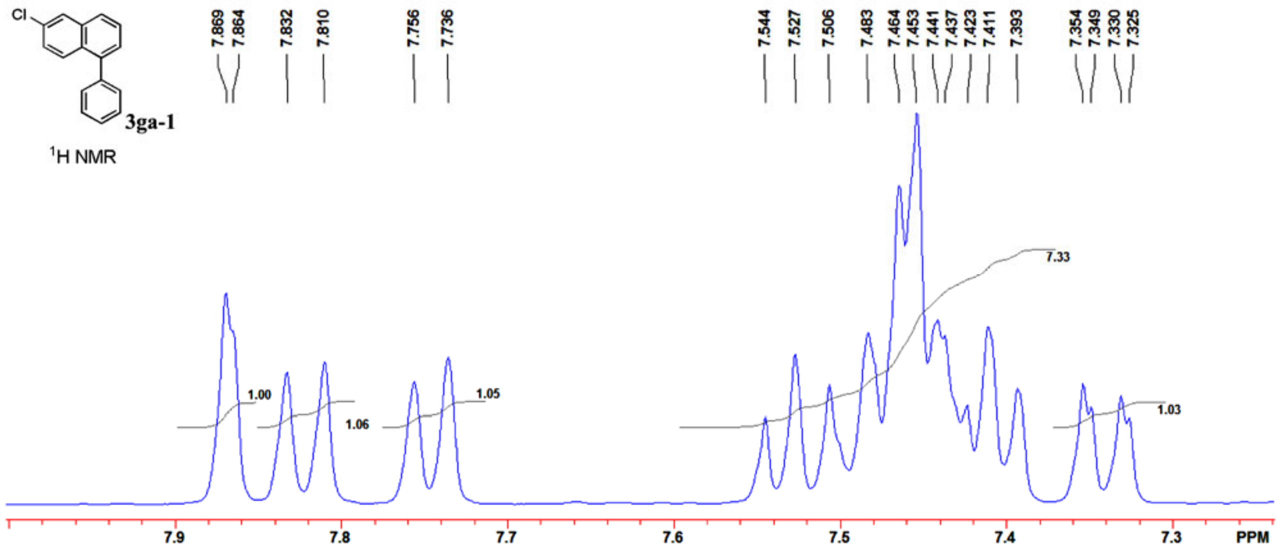
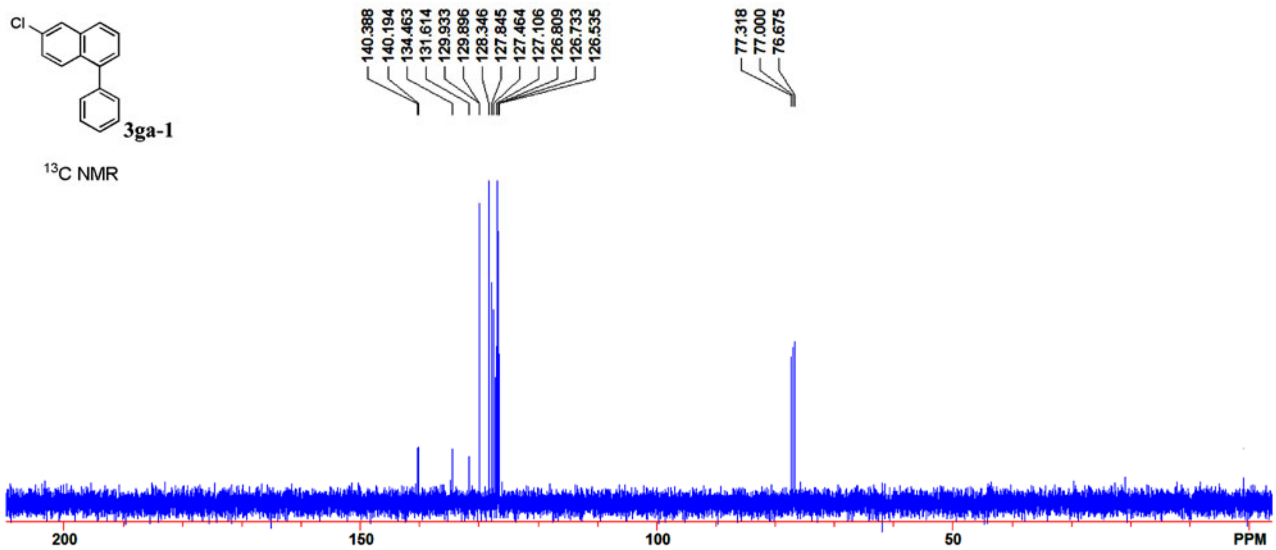
125.608
125.328
121.441
77.317
77.000
76.683
200
150
100
50
PPM

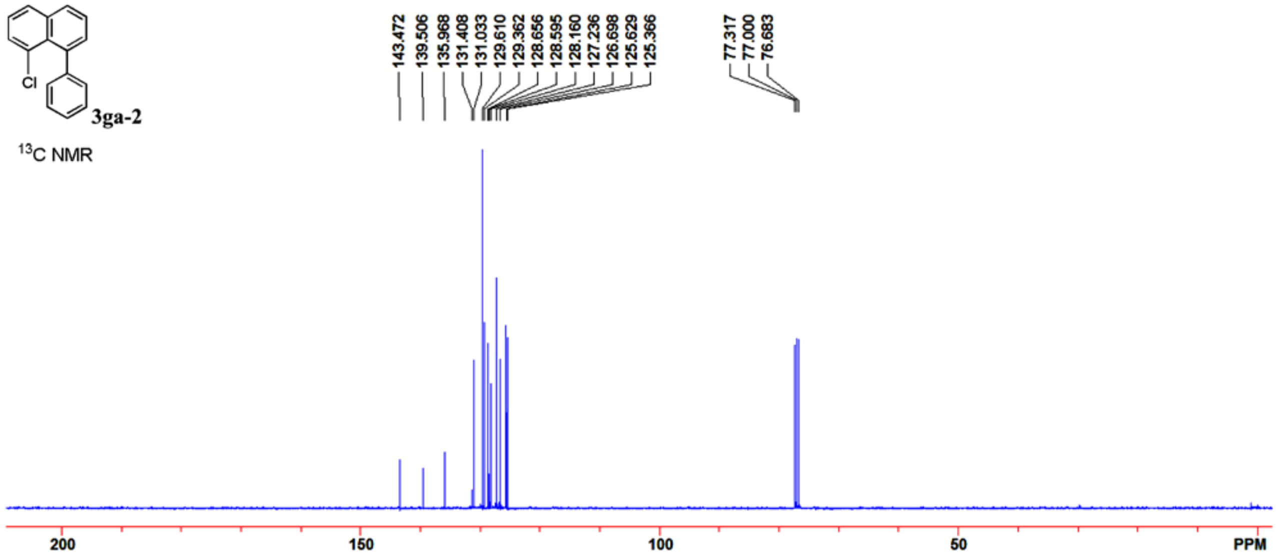

F
3ae
^{1}H NMR
7.902
7.882
7.841
7.516
7.499
7.482
7.465
7.431
7.425
7.420
7.384
7.368
7.183
7.162
7.145
1.00
2.04
2.02
3.12
1.07
2.01
10
8
6
4
2
PPM


F
3ae
^{13}C NMR
163.456
161.012
136.629
139.108
136.586
133.746
131.572
131.497
128.300
127.776
126.980
126.135
125.816
125.724
125.319
115.262
115.049
77.317
77.000
76.681
200
150
100
50
PPM

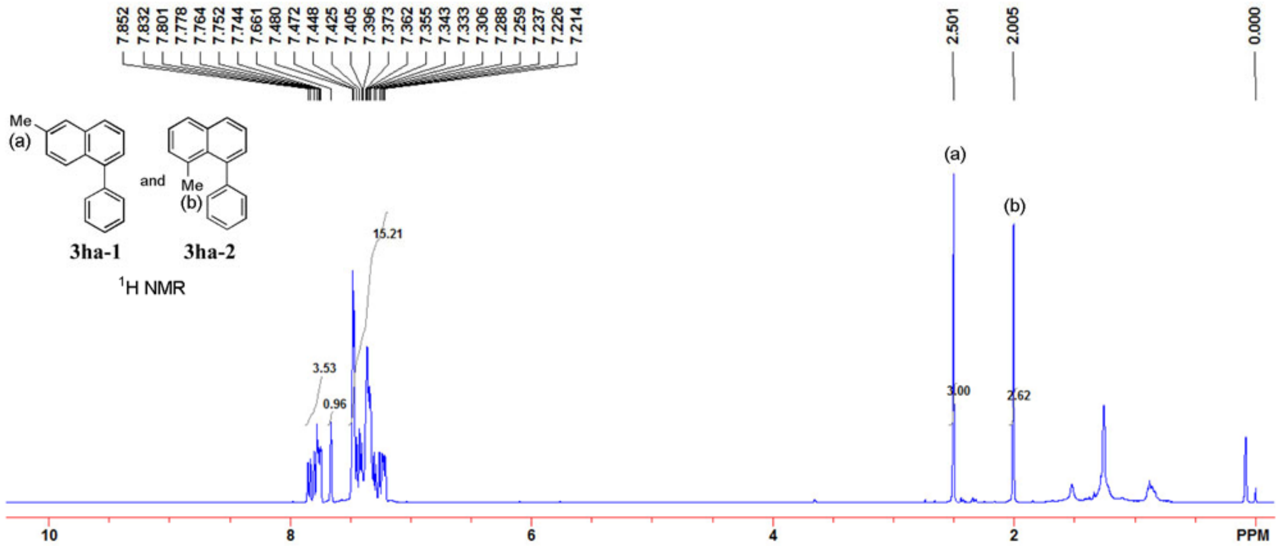

Cl
3ga-1
1H NMR
7.869 7.864 7.832 7.810 7.756 7.736 7.544 7.527 7.506 7.483 7.464 7.453 7.441 7.437 7.423 7.411 7.393 7.354 7.349 7.330 7.325
0.000
7.33
1.06
1.05
1.03
10 8 6 4 2 PPM


Cl
3ga-1
1H NMR
7.869 7.864 7.832 7.810 7.756 7.736 7.544 7.527 7.506 7.483 7.464 7.453 7.441 7.437 7.423 7.411 7.393 7.354 7.349 7.330 7.325
1.00
1.06
1.05
7.33
1.03
7.9 7.8 7.7 7.6 7.5 7.4 7.3 PPM

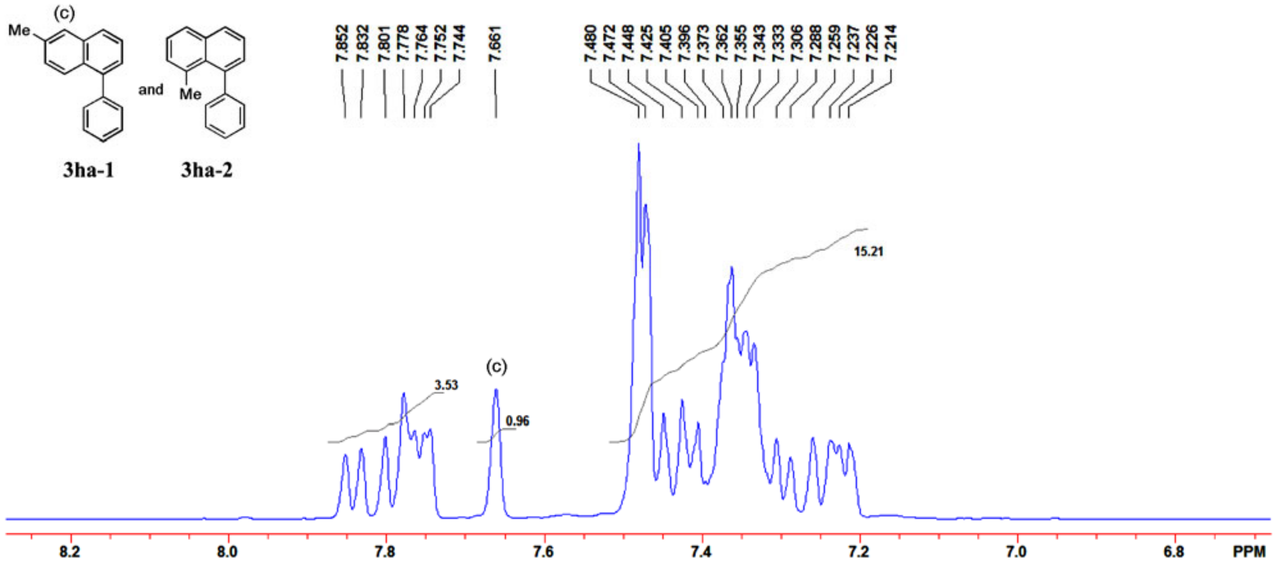

Cl
3ga-1
13C NMR
140.388 140.194 134.463 131.614 129.933 129.896 128.346 127.845 127.464 127.106 126.809 126.733 126.535
77.318 77.000 76.675
200 150 100 50 PPM



Cl
3ga-2
13C NMR
143.472
139.506
135.968
131.408
131.033
129.610
129.362
128.656
128.595
128.160
127.236
126.698
125.629
125.366
77.317
77.000
76.683
200
150
100
50
PPM



Me
(a)
and
Me
(b)
3ha-1
3ha-2
1H NMR
7.852
7.832
7.801
7.778
7.764
7.752
7.744
7.661
7.480
7.472
7.448
7.425
7.405
7.396
7.373
7.362
7.355
7.343
7.333
7.306
7.288
7.259
7.237
7.226
7.214
2.501
2.005
0.000
(a)
(b)
15.21
3.53
0.96
3.00
2.62
10
8
6
4
2
PPM



(c)
Me
and
Me
3ha-1
3ha-2
7.852
7.832
7.801
7.778
7.764
7.752
7.744
7.661
7.480
7.472
7.448
7.425
7.405
7.396
7.373
7.362
7.355
7.343
7.333
7.306
7.288
7.259
7.237
7.226
7.214
15.21
3.53
(c)
0.96
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
PPM