Supplementary Information

for

Palladium/copper-cocatalyzed decarbonylative alkynylation of acyl fluorides with alkynylsilanes: synthesis of unsymmetrical diarylethynes

Qiang Chen,[a] Liyan Fu,[a] and Yasushi Nishihara*[b]

[a] *Graduate School of Natural Science and Technology, Okayama University,*
3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan
[b] *Research Institute for Interdisciplinary Science, Okayama University,*
3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan

Phone: +81-86-251-7855
Fax: +81-86-251-7855
Email: ynishiha@okayama-u.ac.jp

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1. General

Instrumentation

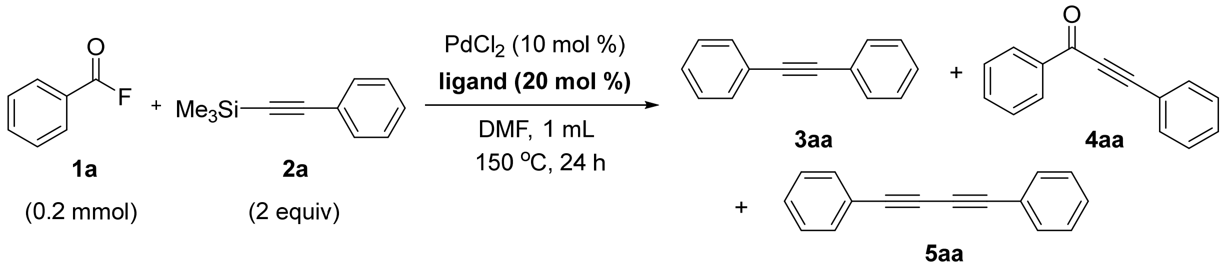
Unless otherwise noted, all the reactions were carried out under Ar atmosphere using standard Schlenk techniques. Solvents were employed as eluents for all other routine operation, as well as dehydrated solvent were purchased from commercial suppliers and employed without any further purification. Glassware was dried in an oven (130 °C) and heated under reduced pressure before use. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. Silica gel column chromatography was carried out using Silica gel 60 N (spherical, neutral, 40–100 μm) from Kanto Chemicals Co., Ltd. NMR spectra (^1H, $^{13}C\{^1H\}$, and $^{19}F\{^1H\}$) were recorded on Mercury-400 (400 MHz) spectrometers. Chemical shifts (δ) are in parts per million relative to $CDCl_3$ at 7.26 ppm for ^1H and at 77.16 ppm for $^{13}C\{^1H\}$, respectively. The $^{19}F\{^1H\}$ NMR spectra were measured by using CCl_3F (δ = 0.00 ppm) as an external standard. The GC yields were determined by GC analysis of the crude mixture, using *1-tetradecene* as an internal standard. GC analyses were performed on a Shimadzu GC-14A equipped with a flame ionization detector using Shimadzu Capillary Column (CBP1-M25-025) and Shimadzu C-R6A-Chromatopac integrator. Infrared spectra were recorded on a Shimadzu IR Prestige-21 spectrophotometer. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN elemental analyzer at Okayama University.

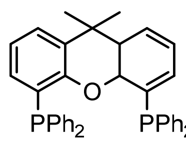
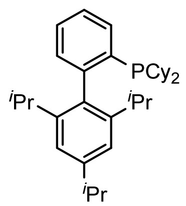
Chemicals

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Palladium(II)chloride and dimethyl sulfoxide (super dehydrated) was purchased from Wako Chemical Co. 1,3-Bis(diphenylphosphino)propane and benzoyl fluoride (**1a**) (purity > 98%) were purchased from TCI. Acyl fluorides **1b-1x**[1] and alkynylsilanes[2] were prepared according to the literatures and showed the identical spectra reported.

2. Optimization of Reaction Conditions

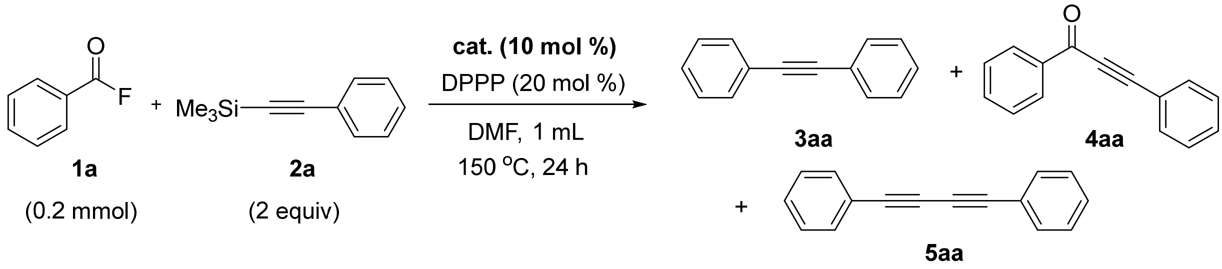
Table S1. Screening of the Ligands[a]



entry	ligand (20 mol %)	yield (%)[b]			
		2a	3aa	4aa	5aa
1	DPPE	40	24	3	8
2	DPPP	15	58	0	3
3	DPPB	41	27	0	2
4	DPPF	22	23	4	4
5	DCYPE	39	13	11	11
6		21	8	0	0
7	PPh_3 (40 mol %)	37	17	1	0
8	PCy_3 (40 mol %)	31	7	5	4
9	 (40 mol %)	23	11	0	0

[a]Reactions were carried out with **1a** (0.2 mmol, 1 equiv), **2a** (0.4 mmol, 2 equiv), $PdCl_2$ (0.02 mmol, 10 mol %), and ligand (0.04 mmol, 20 mol %) in DMF (1 mL) at 150 °C for 24 h. [b]GC yields using 1-tetradecene as an internal standard.

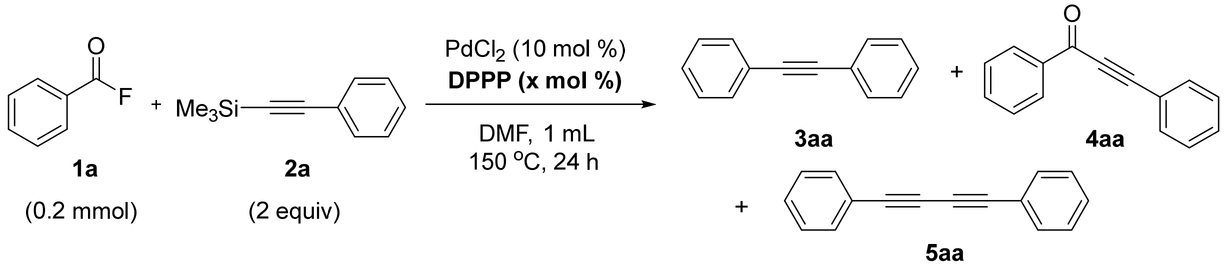
Table S2. Screening of the Catalyst[a]



entry	cat. (10 mol %)	yield (%)[b]			
		2a	**3aa**	**4aa**	**5aa**
1	$Pd(OAc)_2$	11	54	0	1
2	$PdCl_2$	15	58	0	3
3	$Pd(acac)_2$	0	25	0	0
4	$Pd_2(dba)_3$ C_6H_6 (5 mol %)	0	56	0	5
5[c]	$PdCl_2(PPh_3)_2$ (5 mol %)	36	14	5	2
6[d]	$Pd(PPh_3)_4$ (5 mol %)	23	17	44	0
7	$Ni(cod)_2$	-	25	0	4
8[e]	$Ni(cod)_2$	52	94	0	1

[a]Reactions were carried out with **1a** (0.2 mmol, 1 equiv), **2a** (0.4 mmol, 2 equiv), catalyst (0.02 mmol, 10 mol %), and DPPP (0.04 mmol, 20 mol %) in DMF (1 mL) at 150 °C for 24 h. [b]GC yields using 1-tetradecene as an internal standard. [c]PPh_3 (10 mol %) instead of DPPP. [d]Without DPPP. [e]**2a** (3 equiv), CuI (5 mol %).

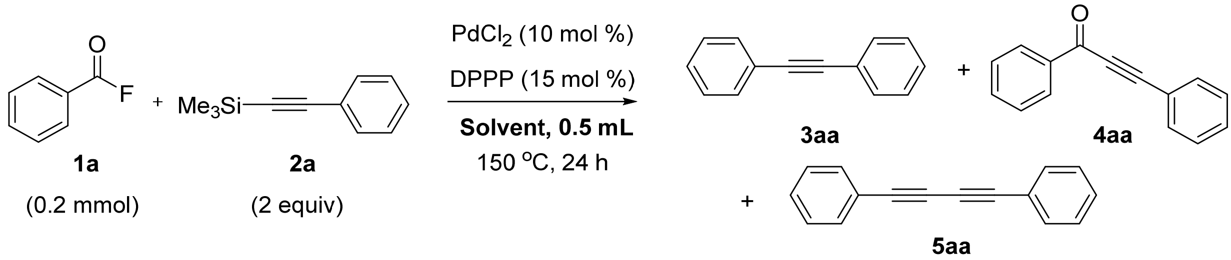
Table S3. Screening of the Amount of DPPP[a]



entry	DPPP (x mol %)	yield (%)[b]			
		2a	**3aa**	**4aa**	**5aa**
1	10	62	9	7	2
2	15	28	54	0	2
3[c]	15	27	61	2	6
4	30	33	51	0	2

[a]Reactions were carried out with **1a** (0.2 mmol, 1 equiv), **2a** (0.4 mmol, 2 equiv), $PdCl_2$ (0.02 mmol, 10 mol %), and DPPP (x mol %) in DMF (1 mL) at 150 °C for 24 h. [b]GC yields using 1-tetradecene as an internal standard. [c] DMF (0.5 mL).

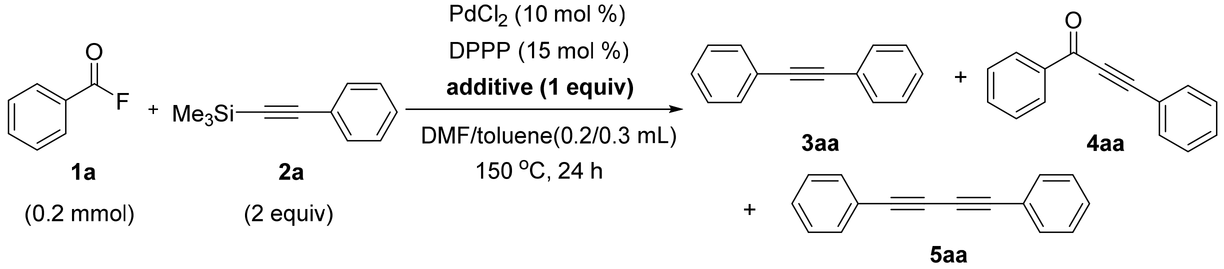
Table S4. Screening of Solvent[a]



entry	**solvent**	yield (%)[b]			
		2a	**3aa**	**4aa**	**5aa**
1	DMF/toluene (4/1)	16	65	1	6
2	DMF/toluene (3/2)	25	71	0	5
3	DMF/toluene (2/3)	19	74	0	5
4	toluene	139	0	0	0
5[c]	DMF/toluene (2/3)	99	74	0	4
6	DMF/DMSO (2/3)	20	0	1	6
7	DMF/1,4-dioxane (2/3)	30	66	0	3

[a]Reactions were carried out with **1a** (0.2 mmol, 1 equiv), **2a** (0.4 mmol, 2 equiv), $PdCl_2$ (0.02 mmol, 10 mol %), and DPPP (0.03 mmol, 15 mol %) in solvent (0.5 mL) at 150 °C for 24 h. [b]GC yields using 1-tetradecene as an internal standard. [c]**2a** (3 equiv).

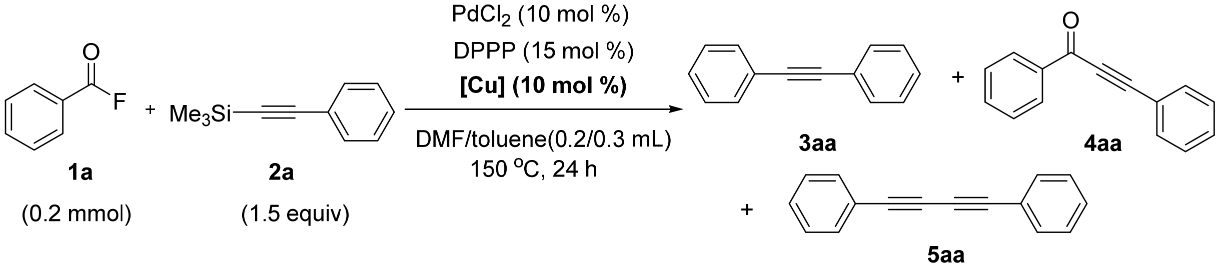
Table S5. Screening of Additive[a]



entry	additive (1 equiv)	yield (%)[b]			
		2a	3aa	4aa	5aa
1[c]	CuI	10	>99	0	0
2	PhCOONa	0	83	0	0
3	AcONa	0	2	0	0
4	PhCOOLi	5	38	2	8
5	PhCOOK	6	74	0	1
6[d]	PhCOONa	0	76	0	0
7[e]	PhCOONa	12	81	0	3

[a]Reactions were carried out with **1a** (0.2 mmol, 1 equiv), **2a** (0.4 mmol, 2 equiv), $PdCl_2$ (0.02 mmol, 10 mol %), DPPP (0.03 mmol, 15 mol %), and additive (1 equiv) in DMF/toluene (2 mL/3 mL) at 150 °C for 24 h. [b]GC yields using 1-tetradecene as an internal standard. [c]10 mol %. [d]0.5 equiv. [e]1.5 equiv.

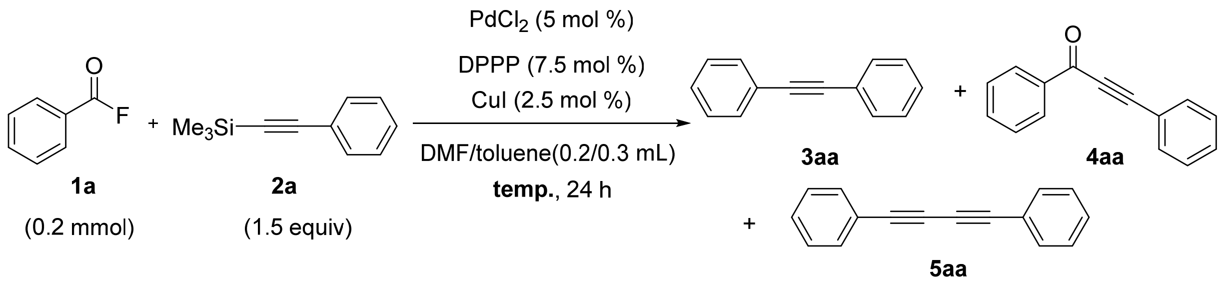
Table S6. Screening of Copper Source[a]



entry	[Cu] (10 mol %)	yield (%)[b]			
		2a	**3aa**	**4aa**	**5aa**
1	CuI	0	89	0	2
2	CuTC	0	77	1	2
3	CuCl	4	64	0	2
4	CuBr	0	66	1	3
5	$CuBr\cdot SMe_2$	0	83	0	1
6	Cu(OAc)	0	90	0	0
7	$Cu(OAc)_2$	0	56	1	1
8	CuF_2	0	83	0	0
9[c]	Cu(OAc)	0	85	0	0
10[d]	CuI	4	98 (84)	0	1
11[d, e]	CuI	0	80	0	1
12[f]	CuI	0	94	0	1
13[f, g]	CuI	7	58	1	3

[a]Reactions were carried out with **1a** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), $PdCl_2$ (0.02 mmol, 10 mol %), DPPP (0.03 mmol, 15 mol %), and copper source (10 mol %) in DMF/toluene (2/3) at 150 °C for 24 h. [b]GC yields using 1-tetradecene as an internal standard. [c]Cu(OAc) (5 mol %). [d]CuI (5 mol %). [e]**2a** (1.2 equiv). [f]$PdCl_2$ (5 mol %), CuI (2.5 mol %), DPPP (7.5 mol %). [g]18 h.

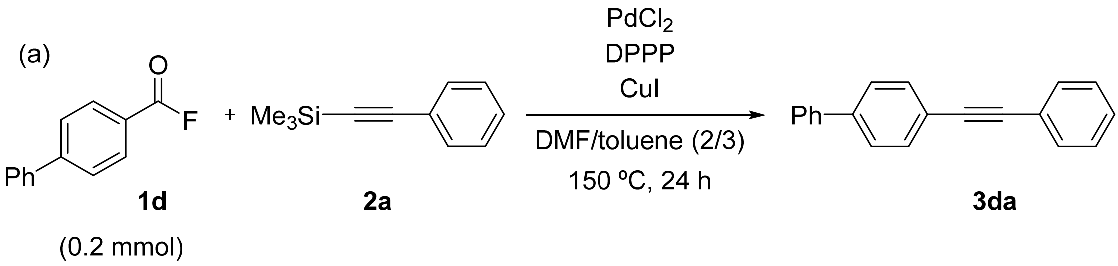
Table S7. Screening of the Reaction Temperature[a]



entry	**temp (ºC)**	yield (%)[b]			
		2a	**3aa**	**4aa**	**5aa**
1[c]	130	10	77	0	5
2	140	6	90	0	2
3	150	0	94	0	1
4	160	3	92	2	0

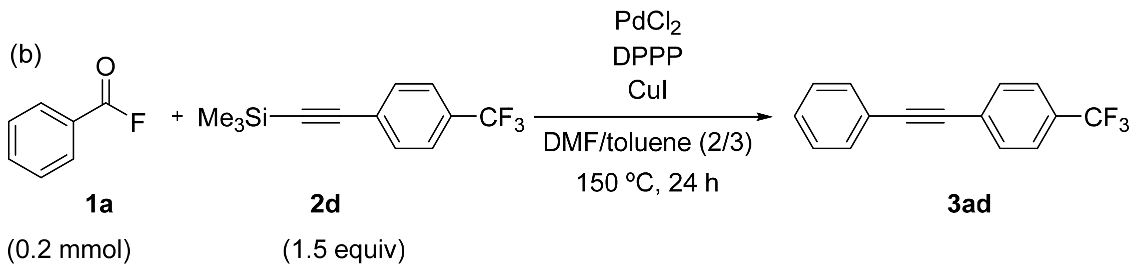
[a]Reactions were carried out with **1a** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), $PdCl_2$ (0.01 mmol, 5 mol %), DPPP (0.015 mmol, 7.5 mol %), and CuI (0.005 mmol, 2.5 mol %) in DMF/toluene (2 mL/3 mL) for 24 h. [b]GC yields using 1-tetradecene as an internal standard.

Table S8. The Comparison of Different Reaction Conditions[a]



entry	reaction condition	yield of **3da** (%)[a]
1	$PdCl_2$ (5 mol %), CuI (2.5 mol %), DPPP (7.5 mol %), **2a** (1.5 equiv)	52
2	**$PdCl_2$ (10 mol %), CuI (5 mol %), DPPP (15 mol %)**, **2a (1.5 equiv)**	**80**
3	$PdCl_2$ (10 mol %), CuI (10 mol %), DPPP (15 mol %), **2a** (2 equiv)	75

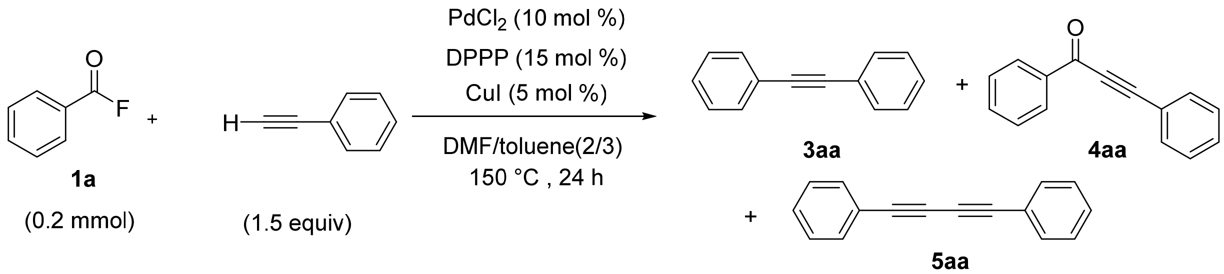
[a]Isolated yields.



entry	Reaction condition	yield of **3ad** (%)[a]
1	$PdCl_2$ (5 mol %), CuI (2.5 mol %), DPPP (7.5 mol %), **2a** (1.5 equiv)	72
2	$PdCl_2$ (10 mol %), CuI (5 mol %), DPPP (15 mol %), **2a** (1.5 equiv)	75
3	**$PdCl_2$ (10 mol %), CuI (10 mol %), DPPP (15 mol %), 2a (2 equiv)**	**80**

[a]Isolated yields.

Table S9. Reactions with a Terminal Alkyne in the Presence of the Base[a]

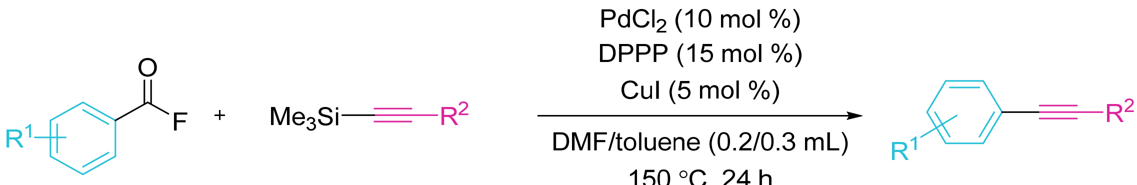


entry	base (1.5 equiv)	yield (%)[b]		
		3aa	**4aa**	**5aa**
1	Et_3N	16	0	4
2	K_3PO_4	16	0	0
3	K_2CO_3	32	0	0

[a]Reactions were carried out with **1a** (0.2 mmol, 1 equiv), phenylethyne (0.3 mmol, 1.5 equiv), $PdCl_2$ (0.02 mmol, 10 mol %), DPPP (0.03 mmol, 15 mol %), and CuI (5 mol %) in DMF/toluene (2 mL/3 mL) at 150 °C for 24 h. [b]GC yields using 1-tetradecene as an internal standard.

3. Experimental Procedures and Spectroscopic Data for the Desired Products

3.1 General Procedure for Palladium/Copper-cocatalyzed Decarbonylative Alkynylation of Acyl Fluorides 1 with Alkynylsilanes 2.

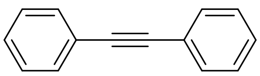


1 (0.2 mmol) **2** (1.5 equiv) **3**

An oven-dried 20 mL of Schlenk tube containing a magnetic stirring bar was charged with $PdCl_2$ (3.6 mg, 0.02 mmol, 10 mol %), DPPP (12.4 mg, 0.03 mmol, 15 mol %), CuI (1.8 mg, 0.01 mmol, 5 mol %), toluene (0.3 mL), DMF (0.2 mL) under argon, which was stirred for 30 seconds at room temperature. Then, acyl fluorides **1** (0.2 mmol) and alkynylsilanes **2** (0.3 mmol) were added. The mixture was heated at 150 ºC in a heating block with stirring for 24 h. After being at room temperature, the mixture was quenched with saturated NH_4Cl and then aqueous solution was extracted with diethyl ether. The combined organic phase was dried over anhydrous $MgSO_4$, and evaporated under vacuum to remove the volatiles. The residue was purified by column chromatography (EtOAc/hexane) on silica gel to afford the corresponding products **3**.

3.2 Spectroscopic Data for the Products

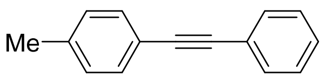
1,3-Diphenylpropane (3aa)[3]



3aa

Colorless solid. R_f = 0.50 (hexane). Isolated yield is 84% (30.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.41 (m, 6H), 7.55-7.59 (m, 4H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 89.5, 123.3, 128.4, 128.5, 131.7.

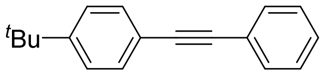
1-Methyl-4-(phenylethynyl)benzene (3ba)[3]



3ba

Colorless solid. R_f = 0.38 (hexane). Isolated yield is 67% (25.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H), 7.17 (d, J = 8 Hz, 2H), 7.33-7.38 (m, 3H), 7.45 (d, J = 8 Hz, 2H), 7.53-7.56 (m, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 21.7, 88.8, 89.7, 120.3, 123.6, 128.2, 128.5, 129.3, 131.6, 131.7, 138.5.

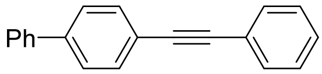
1-(*tert*-Butyl)-4-(phenylethynyl)benzene (3ca)[4]



3ca

Colorless solid. R_f = 0.52 (hexane). Isolated yield is 71% (33.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 9H), 7.33-7.40 (m, 5H), 7.49 (d, J = 8 Hz, 2H), 7.53-7.57 (m, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 31.3, 34.9, 88.9, 89.7, 120.4, 123.6, 125.5, 128.2, 128.4, 131.5, 131.7, 151.7.

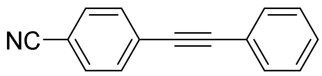
4-(Phenylethynyl)-1,1'-biphenyl (3da)[3]



3da

Colorless solid. R_f = 0.42 (hexane/EtOAc = 10/1). Isolated yield is 80% (40.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.41 (m, 4H), 7.46-7.50 (m, 2H), 7.57-7.65 (m, 8H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 89.4, 90.2, 122.3, 123.4, 127.2 (2 carbons), 127.8, 128.4, 128.5, 129.0, 131.7, 132.2, 140.5, 141.1.

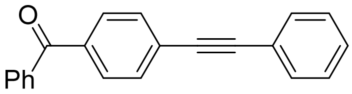
4-(Phenylethynyl)benzonitrile (3ea)[4]



3ea

Colorless solid. R_f = 0.21 (hexane/EtOAc = 50/1). Isolated yield is 63% (25.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.40 (m, 3H), 7.53-7.56 (m, 2H), 7.59-7.65 (m, 4H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 87.9, 93.9, 111.6, 118.7, 122.3, 128.4, 128.6, 129.3, 131.9, 132.1, 132.2.

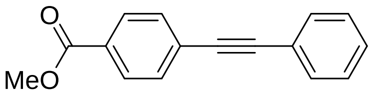
Phenyl(4-(phenylethynyl)phenyl)methanone (3fa)[5]



3fa

Colorless solid. R_f = 0.38 (hexane/EtOAc = 1/1). Isolated yield is 83% (46.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.39 (m, 3H), 7.48-7.52 (m, 2H), 7.56-7.61 (m, 3H), 7.62-7.66 (m, 2H), 7.79-7.83 (m, 4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 88.8, 92.6, 122.8, 127.7, 128.5, 128.6, 128.9, 130.1, 130.2, 131.5, 131.9, 132.6, 136.8, 137.5, 196.0.

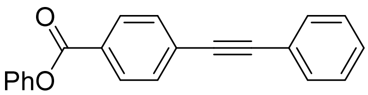
Methyl 4-(phenylethynyl)benzoate (3ga)[6]



3ga

Colorless solid. R_f = 0.38 (hexane/EtOAc = 10/1). Isolated yield is 76% (35.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.93 (s, 3H), 7.36-7.38 (m, 3H), 7.54-7.56 (m, 2H), 7.58-7.60 (m, 2H), 8.01-8.04 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 52.4, 88.8, 92.5, 122.8, 128.1, 128.6, 128.9, 129.6, 129.6, 131.6, 131.9, 166.7.

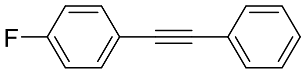
Phenyl 4-(phenylethynyl)benzoate (3ha)[7]



3ha

Colorless solid. R_f = 0.38 (hexane/EtOAc = 10/1). Isolated yield is 62% (36.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.26 (m, 2H), 7.28-7.32 (m, 1H), 7.38-7.41 (m, 3H), 7.43-7.48 (m, 2H), 7.57-7.61 (m, 2H), 7.66-7.69 (m, 2H), 8.19-8.22 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 88.7, 93.0, 121.8, 122.7, 126.1, 128.6, 128.8, 129.0, 129.0, 129.7, 130.2, 131.8, 131.9, 151.0, 164.8.

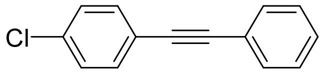
1-Fluoro-4-(phenylethynyl)benzene (3ia)[3]



3ia

Colorless solid. R_f = 0.48 (hexane). Isolated yield is 86% (34.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (t, J = 9 Hz, 2H), 7.34-7.39 (m, 3H), 7.50-7.57 (m, 4H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 88.4, 89.2, 115.7 (d, J_{C-F} = 21 Hz), 119.5 (d, J_{C-F} = 4 Hz), 123.2, 128.4, 128.5, 131.7, 133.6 (d, J_{C-F} = 9 Hz), 162.6 (d, J_{C-F} = 250 Hz); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –110.9.

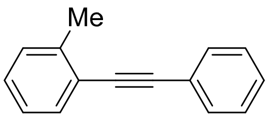
1-Chloro-4-(phenylethynyl)benzene (3ja)[8]



3ja

Colorless solid. R_f = 0.46 (hexane). Isolated yield is 74% (31.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.38 (m, 5H), 7.46-7.49 (m, 2H), 7.53-7.56 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 88.4, 90.4, 121.9, 123.1, 128.5, 128.6, 128.8, 131.7, 132.9, 134.4.

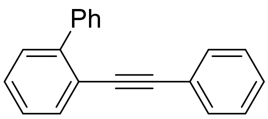
1-Methyl-2-(phenylethynyl)benzene (3ka)[4]



3ka

Colorless oil. R_f = 0.36 (hexane). Isolated yield is 72% (27.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.55 (s, 3H), 7.19-7.22 (m, 1H), 7.25-7.27 (m, 2H), 7.35-7.41 (m, 3H), 7.52-7.54 (m, 1H), 7.55-7.59 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 20.9, 88.5, 93.5, 123.1, 123.7, 125.7, 128.3, 128.4, 128.5, 129.6, 131.6, 132.0, 140.3.

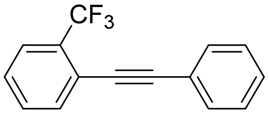
2-(Phenylethynyl)-1,1'-biphenyl (3la)[4]



3la

Colorless oil. R_f = 0.20 (hexane). Isolated yield is 53% (27.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.33 (m, 3H), 7.36-7.39 (m, 3H), 7.41-7.52 (m, 5H), 7.68-7.73 (m, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 89.5, 92.3, 121.7, 123.5, 127.2, 127.6, 128.0, 128.2, 128.4, 128.7, 129.5, 129.6, 131.5, 133.0, 140.6, 144.0.

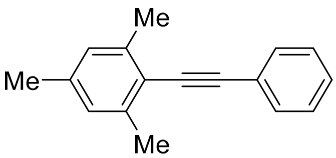
1-(Phenylethynyl)-2-(trifluoromethyl)benzene (3ma)[9]



3ma

Colorless oil. R_f = 0.36 (hexane). Isolated yield is 69% (33.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.41 (m, 3H), 7.42-7.44 (m, 1H), 7.51-7.55 (m, 1H), 7.58-7.61 (m, 2H), 7.68-7.73 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 85.5, 95.1, 121.7, 122.4, 122.9, 125.1, 126.0 (q, J_{C-F} = 5 Hz), 128.1, 128.5, 129.0, 131.5, 131.9, 133.8; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, rt): δ –62.8.

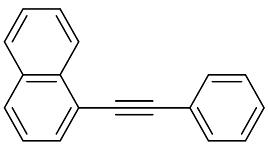
1,3,5-Trimethyl-2-(phenylethynyl)benzene (3na)[10]



3na

Colorless solid. R_f = 0.41 (hexane). Isolated yield is 27% (12.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H), 2.59 (s, 6H), 6.98 (brs, 2H), 7.37-7.46 (m, 3H), 7.61-7.65 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 21.1, 21.4, 87.5, 97.2, 120.1, 124.2, 127.7, 128.0, 128.4, 131.4, 137.9, 140.2.

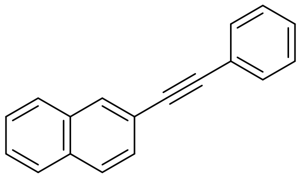
1-(Phenylethynyl)naphthalene (3oa)[3]



3oa

Colorless solid. R_f = 0.29 (hexane). Isolated yield is 74% (33.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.47 (m, 3H), 7.50 (dd, J = 8.0, 7.2 Hz, 1H), 7.56-7.60 (m, 1H), 7.63-7.67 (m, 1H), 7.70-7.73 (m, 2H), 7.83 (dd, J = 7.2, 1.6 Hz, 1H), 7.87-7.92 (m, 2H), 8.50-8.53 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 87.7, 94.4, 121.0, 123.5, 125.4, 126.3, 126.6, 126.9, 128.4, 128.5, 128.6, 128.9, 130.5, 131.8, 133.3, 133.4.

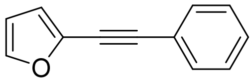
2-(Phenylethynyl)naphthalene (3pa)[3]



3pa

Colorless solid. R_f = 0.23 (hexane). Isolated yield is 57% (26.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.42 (m, 3H), 7.51-7.53 (m, 2H), 7.60-7.63 (m, 3H), 7.82-7.86 (m, 3H), 8.09 (s, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 89.8, 89.9, 120.7, 123.4, 126.7, 126.8, 127.9$_0$, 127.9$_1$, 128.1, 128.4$_5$, 128.5$_2$, 128.5$_5$, 131.6, 131.8, 132.9, 133.1.

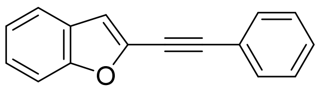
2-(Phenylethynyl)furan (3qa)[11]



3qa

Colorless solid. R_f = 0.40 (hexane). Isolated yield is 59% (19.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.44 (dd, J = 3.6, 2.0 Hz, 1H), 6.67 (dd, J = 2.7, 0.8 Hz. 1H), 7.34-7.37 (m, 3H), 7.44 (dd, J = 2.0, 0.8 Hz, 1H), 7.52-7.55 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 79.5, 93.4, 111.2, 115.4, 122.4, 128.5, 128.8, 131.6, 137.3, 143.8.

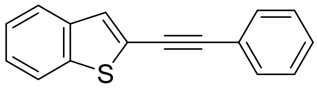
2-(Phenylethynyl)benzofuran (3ra)[3]



3ra

Colorless solid. R_f = 0.33 (hexane). Isolated yield is 62% (27.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (d, J = 4.0 Hz, 1H), 7.25-7.29 (m, 1H), 7.34-7.42 (m, 4H), 7.49-7.52 (m, 1H), 7.58-7.63 (m, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 79.7, 95.2, 111.4, 111.7, 121.3, 121.9, 123.4, 125.7, 127.8, 128.6, 129.3, 131.8, 138.8, 155.0.

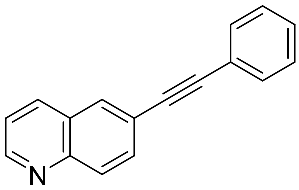
2-(Phenylethynyl)benzo[b]thiophene (3sa)[3]



3sa

Colorless solid. R_f = 0.45 (hexane). Isolated yield is 71% (33.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.41 (m, 5H), 7.52 (s, 1H), 7.54-7.59 (m, 2H), 7.76-7.81 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 83.1, 95.0, 122.1, 122.7, 123.4, 123.9, 124.9, 125.5, 128.6, 128.8, 128.9, 131.7, 139.3, 140.4.

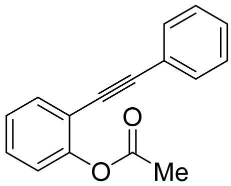
6-(Phenylethynyl)quinoline (3ta)[4]



3ta

Colorless solid. R_f = 0.1 (EtOAc/hexane = 1/4). Isolated yield is 81% (37.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.39 (m, 3H), 7.42 (dd, J = 8.4, 4.4 Hz, 1H), 7.57-7.59 (m, 2H), 7.82 (dd, J = 8.8, 1.6 Hz, 1H), 8.01 (d, J = 4.0 Hz, 1H), 8.09-8.15 (m, 2H), 8.90 (dd, J = 4.0, 1.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 89.0, 90.9, 121.8, 121.9, 123.0, 128.2, 128.6, 128.7, 129.4, 131.2, 131.8, 132.5, 136.2, 147.3, 150.7.

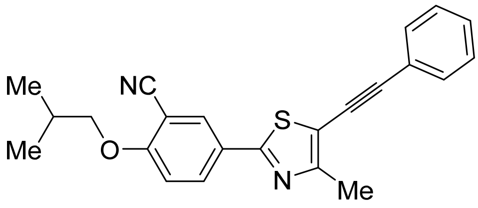
2-(Phenylethynyl)phenyl acetate (3ua)[12]



3ua

Brown oil. R_f = 0.50 (hexane). Isolated yield is 55% (26.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H), 7.12-7.15 (m, 1H), 7.22-7.26 (m, 1H), 7.34-7.39 (m, 4H), 7.49-7.52 (m, 2H), 7.57-7.60 (m, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 21.0, 84.4, 94.3, 117.6, 122.4, 123.1, 126.1, 128.5, 128.7, 129.6, 131.7, 133.1, 151.7, 169.1.

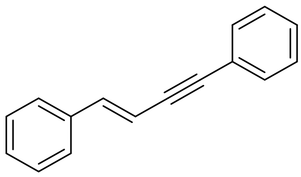
2-Isobutoxy-5-(4-methyl-5-(phenylethynyl)thiazol-2-yl)benzonitrile (3va)



3va

Yellow solid. Melting point: 145-147 °C. R_f = 0.35 (EtOAc/hexane = 1/5). Isolated yield is 52% (38.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (d, J = 6.8 Hz, 6H), 2.19 (sext, J = 6.8 Hz, 1H), 2.59 (s, 3H), 3.87 (d, J = 4.0 Hz, 2H), 6.98 (d, J = 8.0 Hz, 1H), 7.36-7.38 (m, 3H), 7.51-7.53 (m, 2H), 8.04 (dd, J = 8.8, 2.0 Hz, 1H), 8.10 (d, J = 2.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 16.6, 19.2, 28.3, 75.7, 79.8, 98.3, 102.9, 112.7, 113.7, 115.7, 122.6, 126.4, 128.6, 128.9, 131.5, 131.8, 132.3, 158.2, 162.1, 163.7. FT-IR (cm^{-1}): 688.6 (s), 754.2 (s), 1014.1 (s), 1129.1 (s), 1296.2 (s), 1440.8 (s), 1504.3 (s), 1606.7 (s), 2227.7 (s), 2954.9 (s). Anal. Calcd for $C_{23}H_{20}N_2OS$: C, 74.16; H, 5.41; N 7.52%. Found: C, 73.85; H, 5.29; N 7.28%.

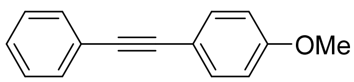
(*E*)-But-1-en-3-yne-1,4-diyldibenzene (3wa)[11]



3wa

Colorless solid. R_f = 0.30 (hexane). Isolated yield is 27% (11.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.41 (d, J = 16.0 Hz, 1H), 7.07 (d, J = 16.0 Hz, 1H), 7.29-7.39 (m, 6H), 7.44-7.46 (m, 2H), 7.49-7.52 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 89.0, 91.9, 108.3, 123.6, 126.5, 128.3, 128.5, 128.8, 128.9, 131.7, 136.5, 141.4.

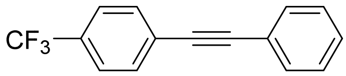
1-Methoxy-4-(phenylethynyl)benzene (3ac)[4]



3ac

Colorless solid. R_f = 0.18 (hexane). Isolated yield is 83% (34.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.89 (d, J = 8.8 Hz, 2H), 7.32-7.35 (m, 3H), 7.48 (d, J = 8.8 Hz, 2H), 7.50-7.54 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 55.4, 88.2, 89.5, 114.1, 115.5, 123.7, 128.1, 128.4, 131.6, 133.2, 159.7.

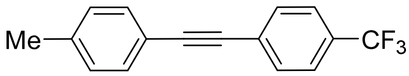
1-(Phenylethynyl)-4-(trifluoromethyl)benzene (3ad)[13]



3ad

Colorless solid. R_f =0.54 (hexane). Isolated yield is 75% (36.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.40 (m, 3H), 7.54-7.58 (m, 2H), 7.60-7.65 (m, 4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 88.1, 91.9, 122.7$_0$, 122.7$_5$, 125.4 (q, J_{C-F} = 4 Hz), 127.2$_5$, 127.2$_7$, 129.0, 130.0 (q, J_{C-F} = 33 Hz), 131.8$_9$, 131.9$_4$; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, rt): δ –62.7.

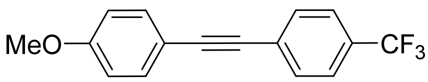
1-Methyl-4-((4-(trifluoromethyl)phenyl)ethynyl)benzene (3xb)[14]



3xb

Colorless solid. R_f = 0.50 (hexane). Isolated yield is 71% (37.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H), 7.19 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.59-7.64 (m, 4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 21.7, 87.5, 92.2, 119.6, 122.8, 125.4 (q, J_{C-F} = 4 Hz), 127.5, 129.4, 129.8 (q, J_{C-F} = 32 Hz), 131.8, 131.9, 139.2; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, rt): δ –63.1.

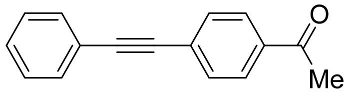
1-Methoxy-4-((4-(trifluoromethyl)phenyl)ethynyl)benzene (3xc)[8]



3xc

Colorless solid. R_f = 0.20 (hexane). Isolated yield is 81% (44.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.91 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 7.59-7.64 (m, 4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 55.4, 87.0, 92.1, 114.2, 114.7, 122.8, 125.4 (q, J_{C-F} = 4 Hz), 127.6, 129.6, (q, J_{C-F} = 33 Hz), 131.7, 133.4, 160.2; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, rt): δ –63.0.

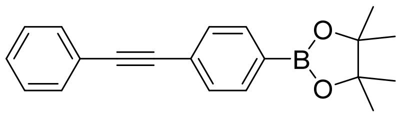
1-(4-(Phenylethynyl)phenyl)ethan-1-one (3ae)[4]



3ae

Colorless solid. R_f = 0.22 (EtOAc/hexane = 1/10). Isolated yield is 43% (19.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.61 (s, 3H), 7.36-7.38 (m, 3H), 7.54-7.57 (m, 2H), 7.61 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 26.8, 88.7, 92.8, 122.8, 128.3, 128.4, 128.6, 129.0, 131.8, 131.9, 136.3, 197.5.

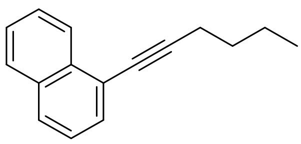
4,4,5,5-Tetramethyl-2-(4-(phenylethynyl)phenyl)-1,3,2-dioxaborolane (3af) [15]



3af

Colorless solid. R_f = 0.2 (EtOAc/hexane = 1/50). Isolated yield is 50% (32.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (s, 12H), 7.34-7.37 (m, 3H), 7.52-7.55 (m, 4H), 7.79 (d, J = 8.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 25.0, 84.1, 89.7, 90.8, 123.3, 126.1, 128.5_0, 128.5_2, 130.9, 131.8, 134.7. The carbon signal attached to B was not observed due to low intensity.

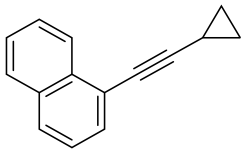
1-(Hex-1-yn-1-yl)naphthalene (3og)[16]



3og

Colorless oil. R_f = 0.50 (hexane). Isolated yield is 54% (22.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (t, J = 7.2 Hz, 3H), 1.56-1.62 (m, 2H), 1.68-1.74 (m, 2H), 2.60 (t, J = 7.2 Hz, 2H), 7.41 (dd, J = 8.0, 7.2 Hz, 1H), 7.49-7.59 (m, 2H), 7.64 (dd, J = 6.8, 1.2 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.83-7.86 (m, 1H), 7.35-7.38 (m, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 13.8, 19.6, 22.3, 31.2, 78.7, 95.7, 121.9, 125.4, 126.3, 126.4, 126.6, 128.0, 128.3, 130.1, 133.3, 133.7.

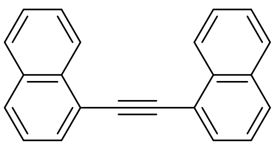
1-(Cyclopropylethynyl)naphthalene (3oh)[17]



3oh

Colorless oil. $R_f = 0.26$ (hexane). Isolated yield is 52% (20.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92-1.00 (m, 4H), 1.59-1.66 (m, 1H), 7.40 (dd, J = 8.0, 6.8 Hz, 1H), 7.49-7.58 (m, 2H), 7.62 (dd, J = 7.2, 1.2 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.82-7.85 (m, 1H), 7.31-8.34 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 0.6, 9.1, 73.9, 98.7, 121.7, 125.4, 126.3, 126.4, 126.6, 128.0, 128.3, 130.2, 133.3, 133.7.

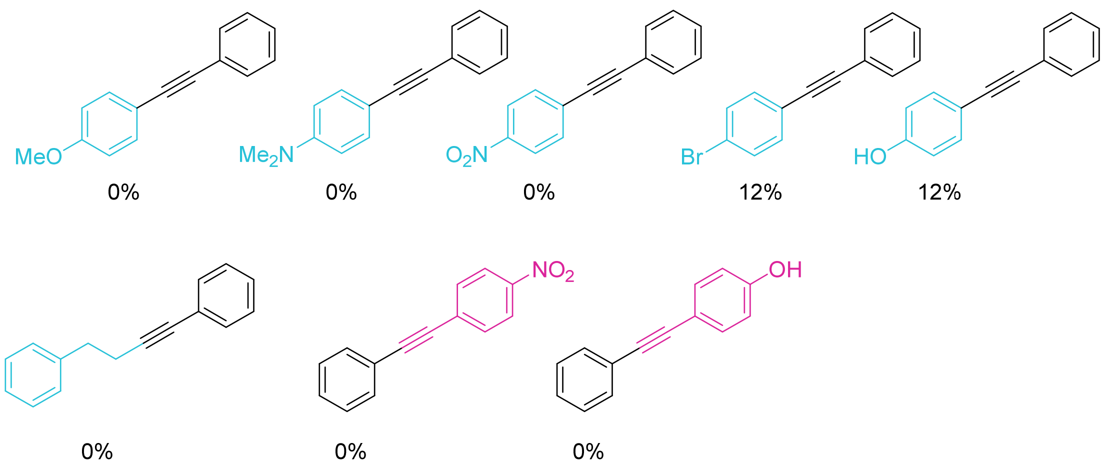
1,2-Di(naphthalen-1-yl)ethyne (5)[18]



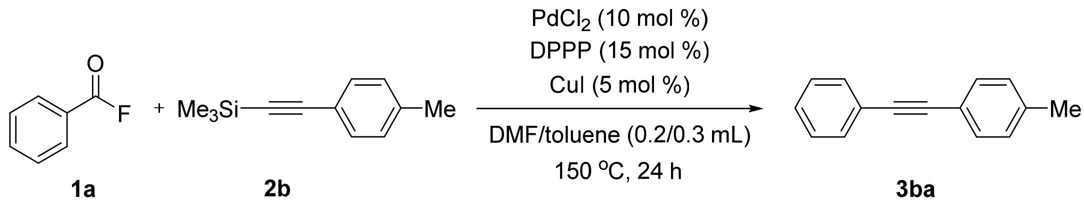
5

Colorless solid. $R_f = 0.30$ (hexane). Isolated yield is 52% (28.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (dd, J = 8.4, 7.2 Hz, 2H), 7.58-7.62 (m, 2H), 7.66-7.70 (m, 2H), 7.90-7.94 (m, 6H), 8.61-8.64 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 92.6, 121.2, 125.5, 126.4, 126.6, 127.1, 128.5, 129.0, 130.7, 133.4 (2 carbons).

Substrate scope



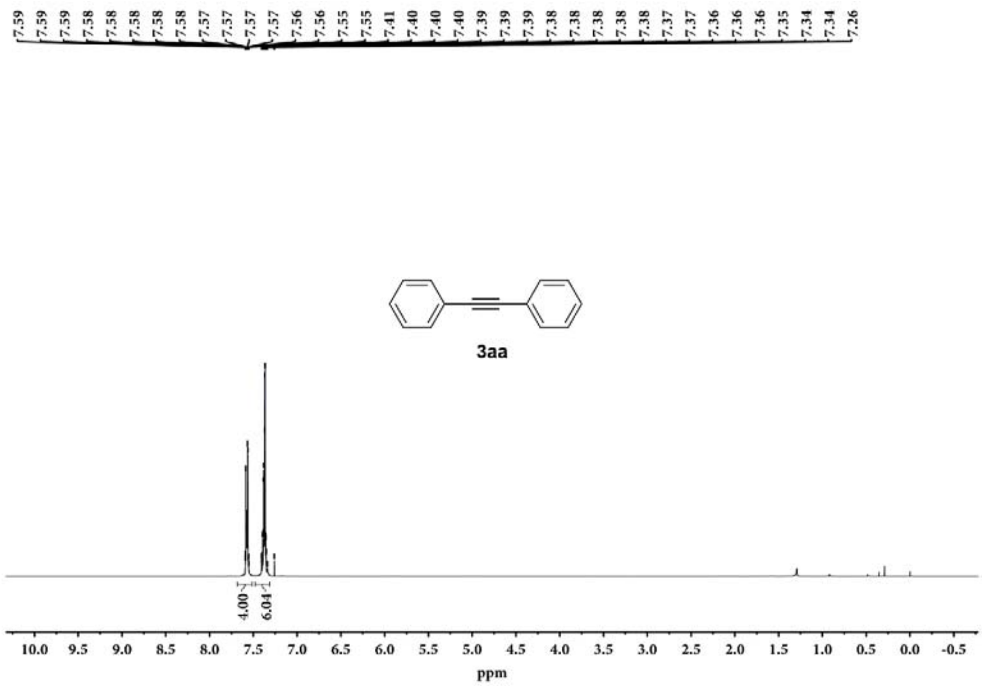
3.3 Gram-scale Synthesis

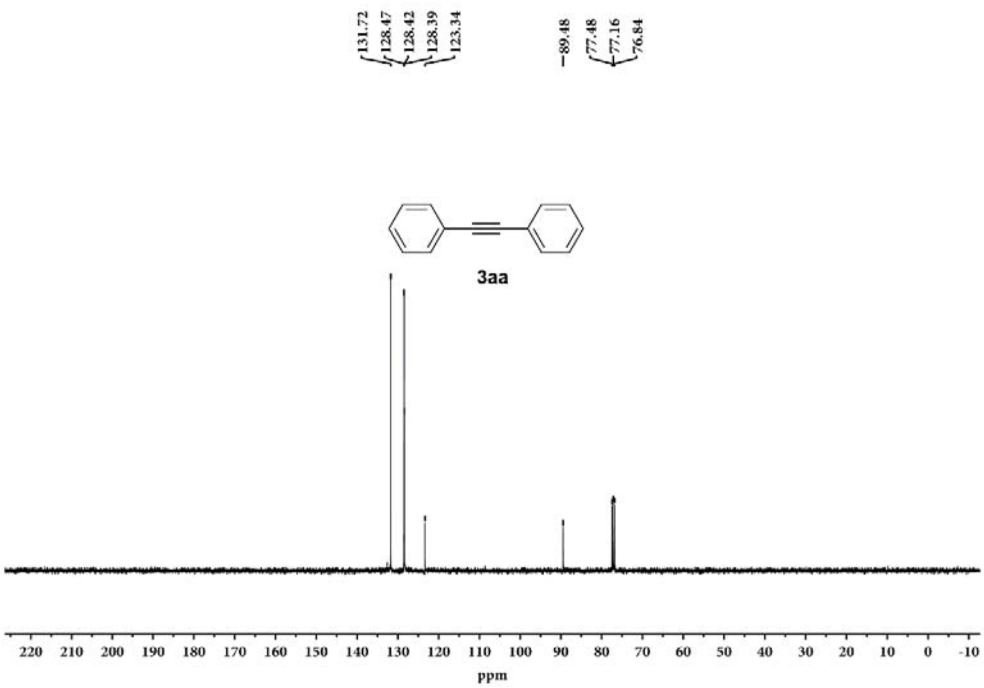


1a 2b 3ba

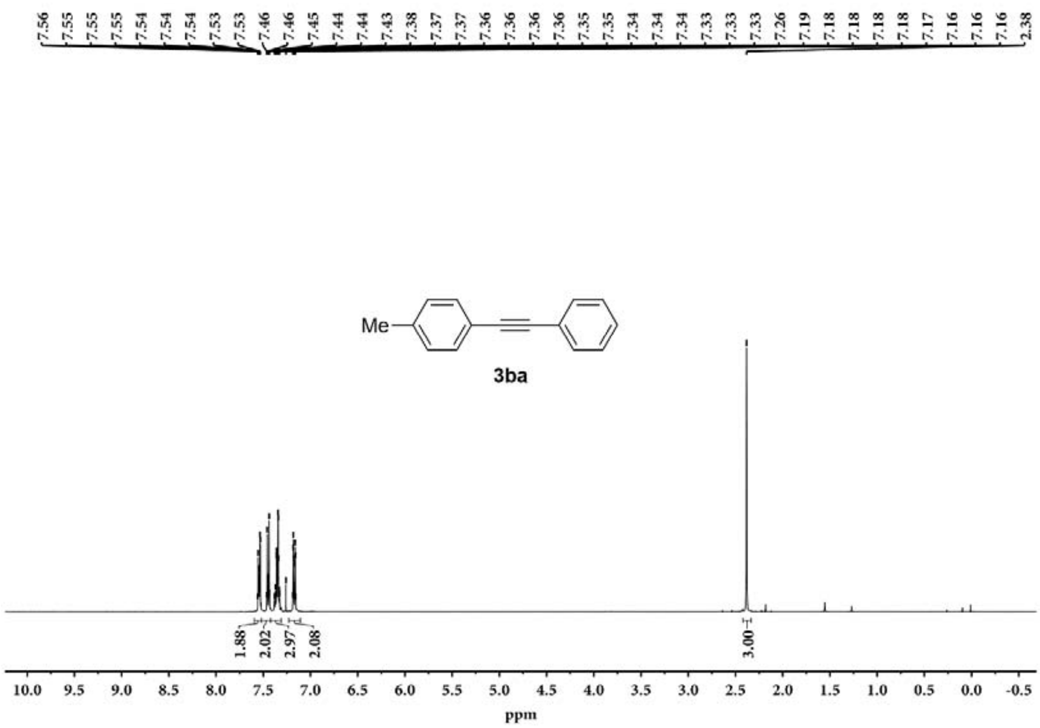
An oven-dried 50 mL of Schlenk tube containing a magnetic stirring bar was charged with $PdCl_2$ (90.0 mg, 0.5 mmol, 5 mol %), DPPP (309.3 mg, 0.75 mmol, 7.5 mol %), DMF (4 mL), and toluene (6 mL) under argon, which was stirred for 30 seconds at room temperature. Benzoyl fluoride (**1a**) (10 mmol) and trimethyl(4-tolylethynyl)silane (**2b**) (15 mmol) were added. The mixture was heated at 150 ºC in a heating block with stirring for 24 h. After being at room temperature, the mixture was quenched with saturated NH_4Cl and the aqueous solution was extracted with diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and evaporated under vacuum to obtain the crude product which was purified by column chromatography (hexane; R_f = 0.38) on silica gel to afford the product **3ba** (1.10 g, 5.7 mmol) in 57% yield as colorless solid.

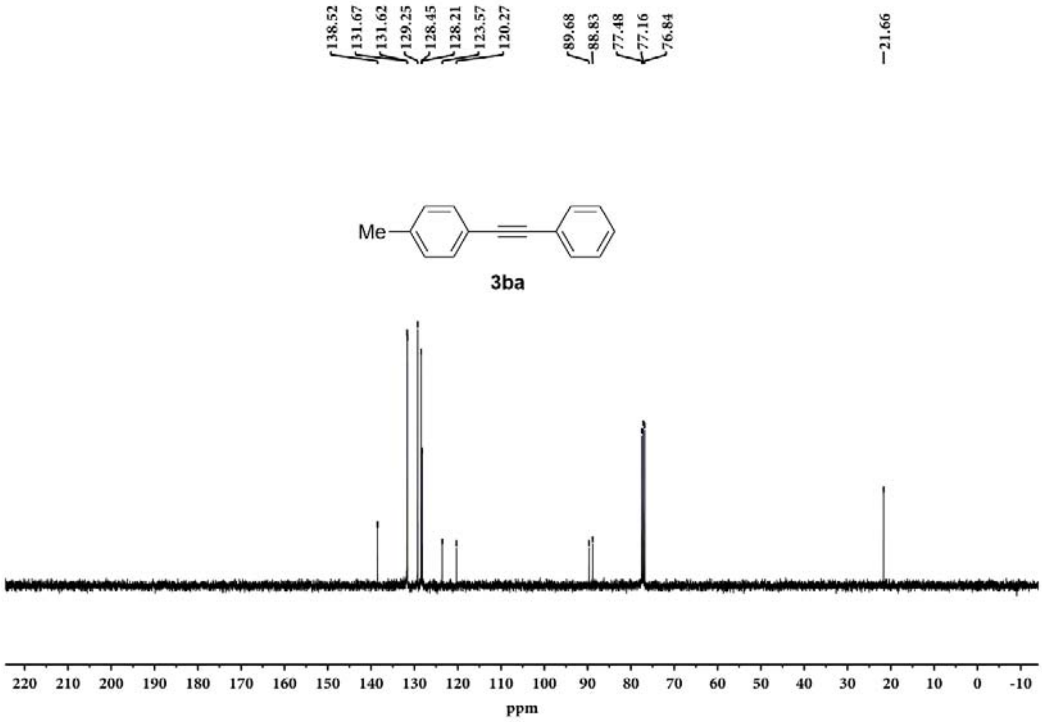
4. ***Copies of ^{1}H, $^{13}C\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR Charts for the Desired Products***



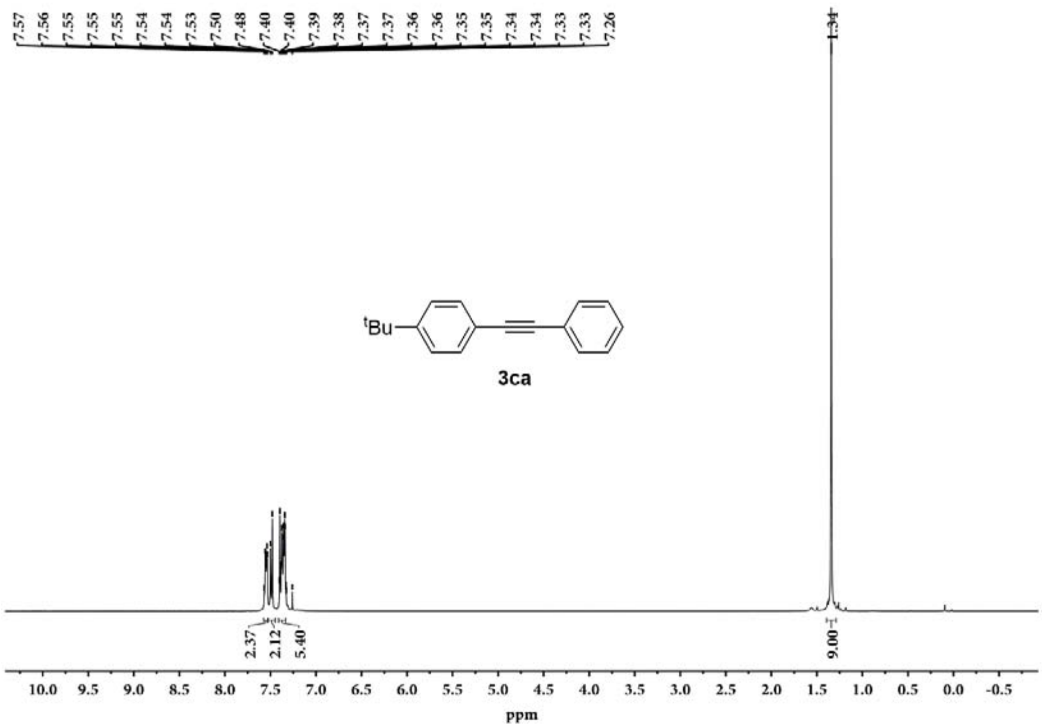


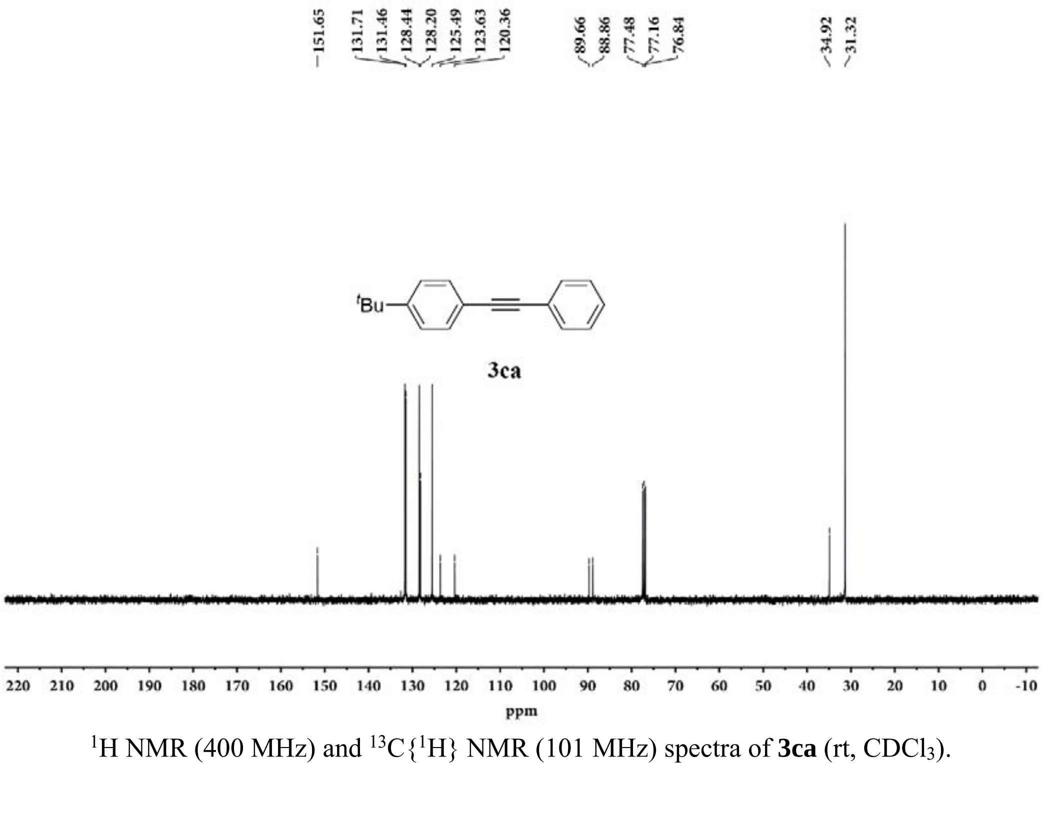
[1]H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **3aa** (rt, $CDCl_3$).



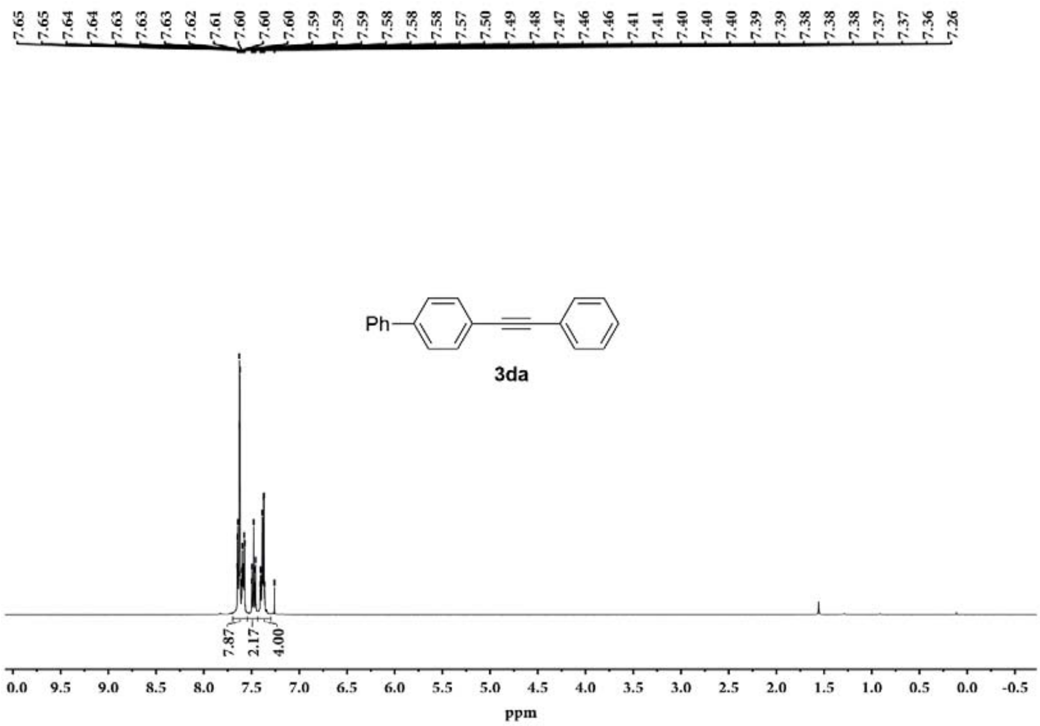


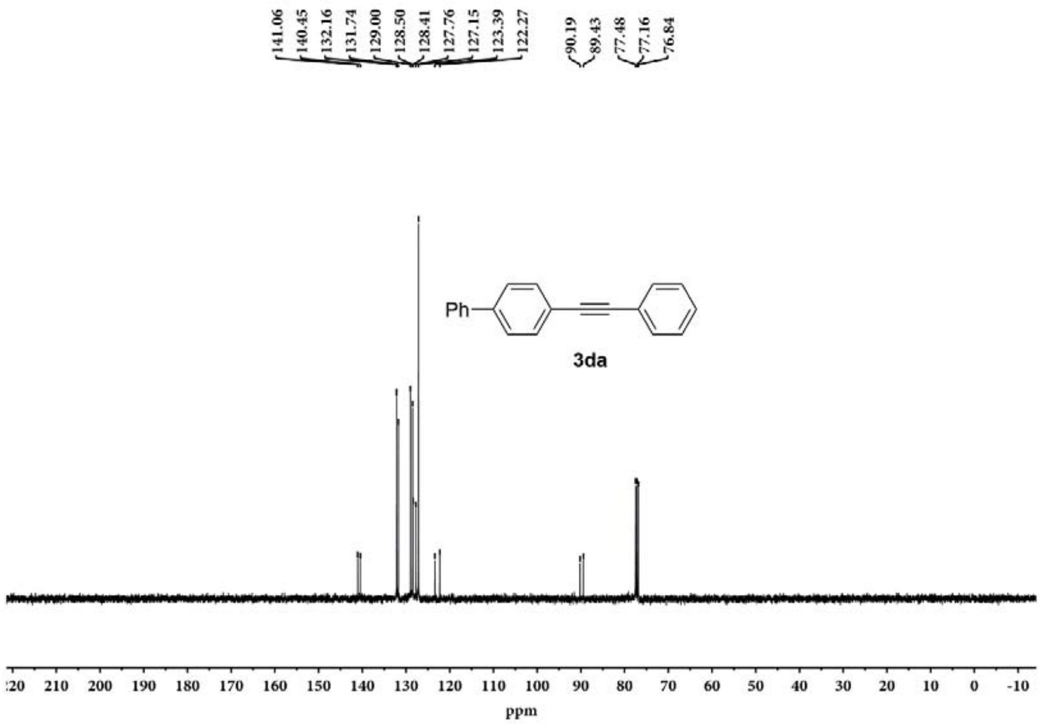
[1]H NMR (400 MHz) and $^{13}C\{^1H\}$ NMR (101 MHz) spectra of **3ba** (rt, $CDCl_3$).



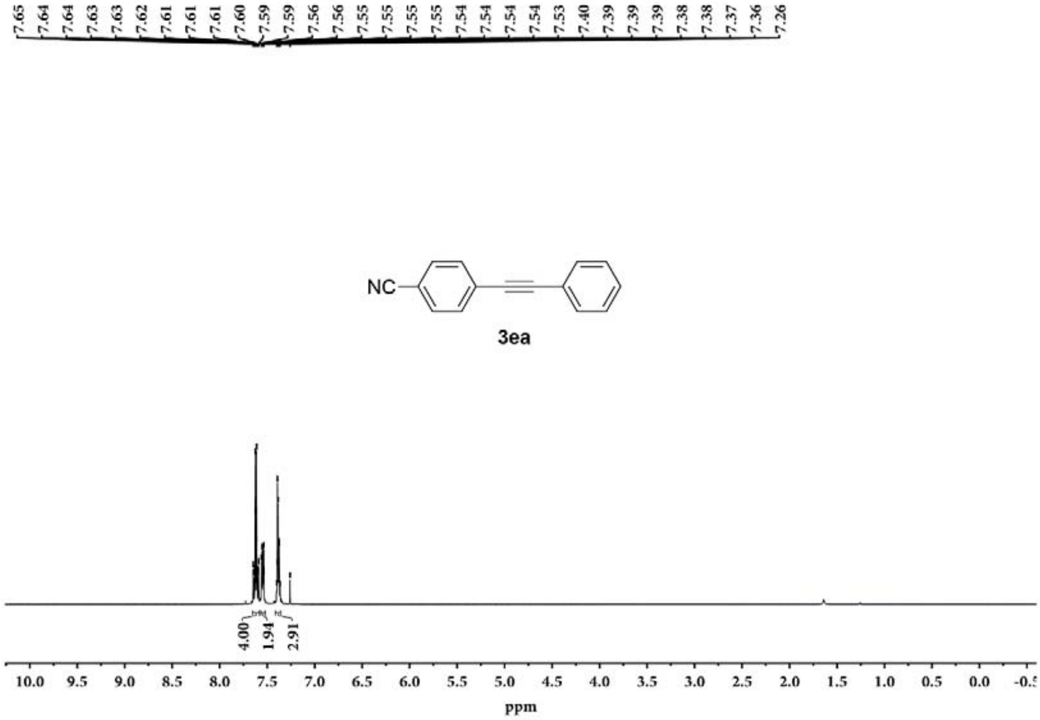


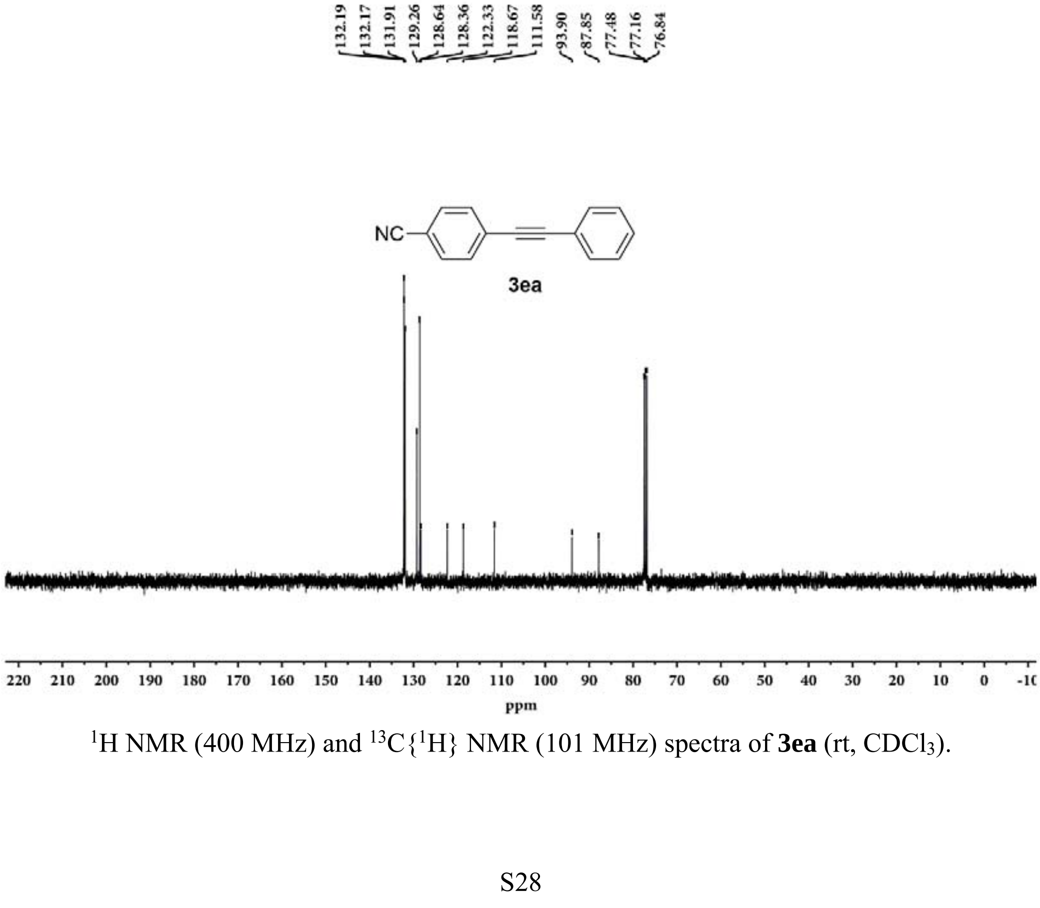
[1]H NMR (400 MHz) and $^{13}C\{^1H\}$ NMR (101 MHz) spectra of **3ca** (rt, $CDCl_3$).



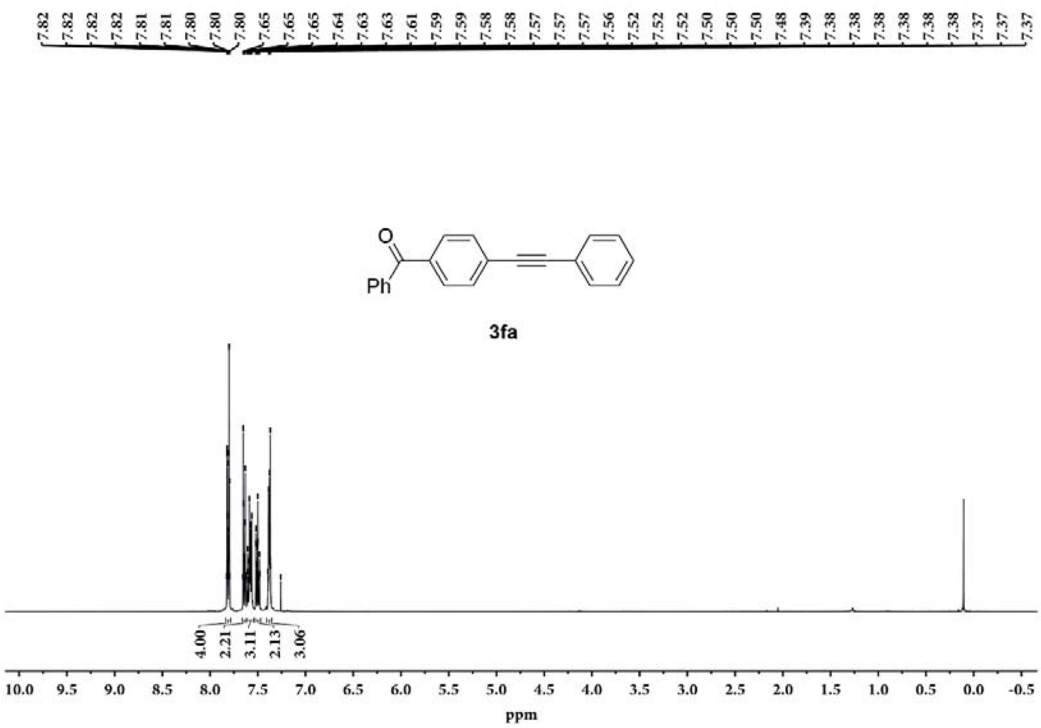


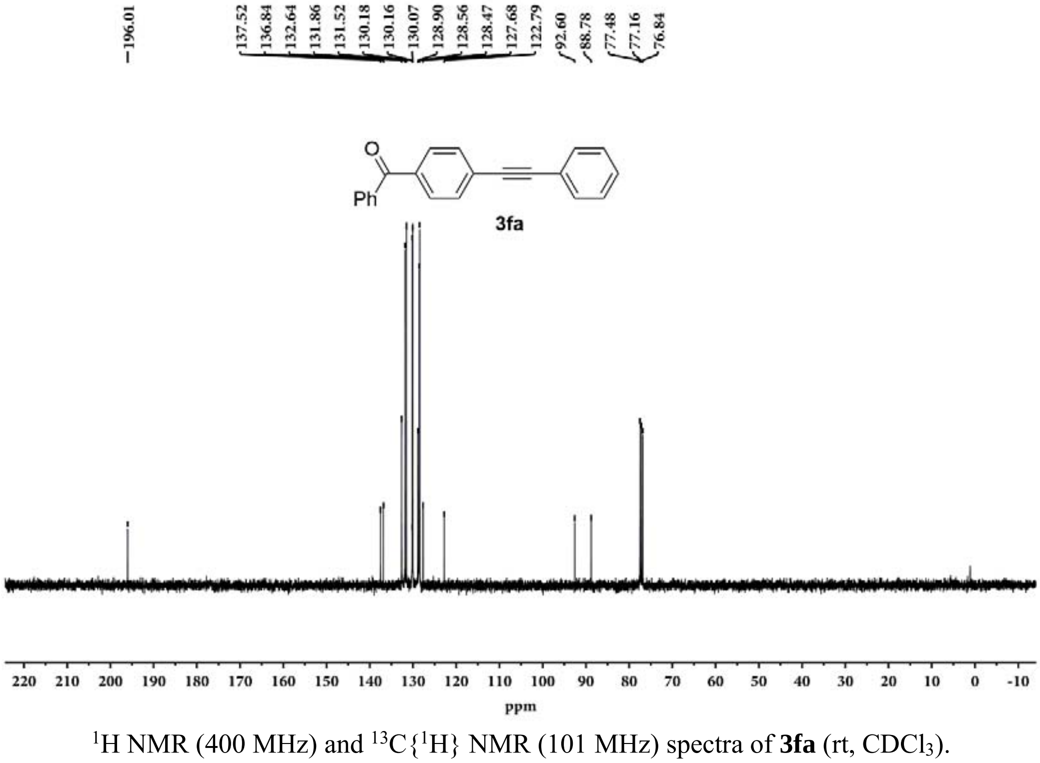
^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **3da** (rt, $CDCl_3$).



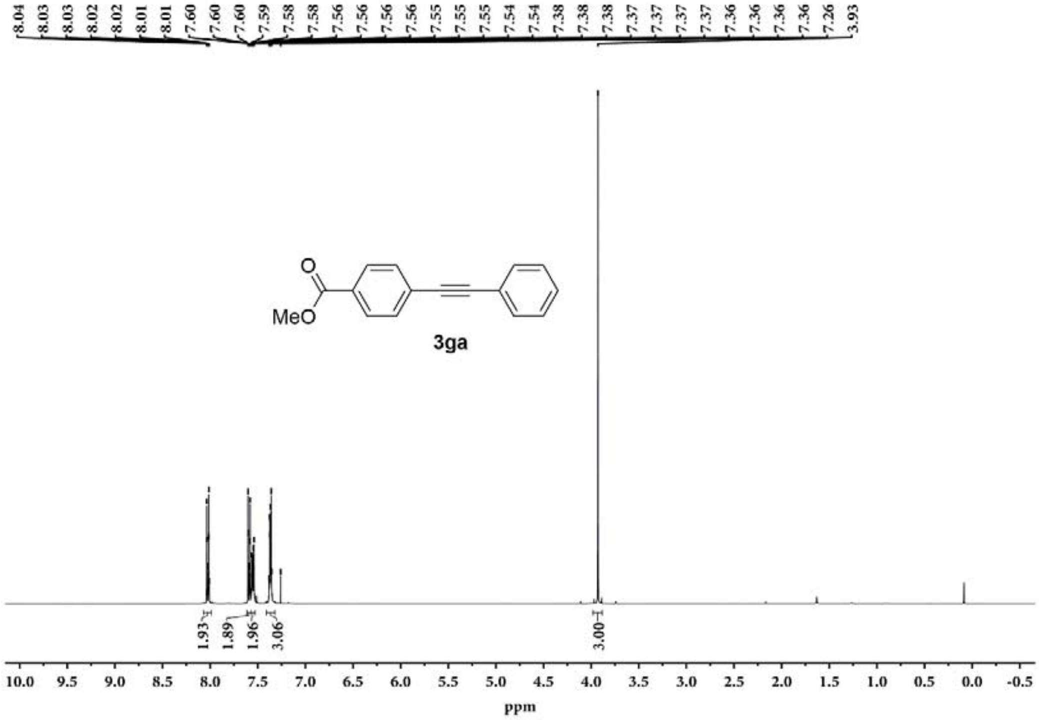


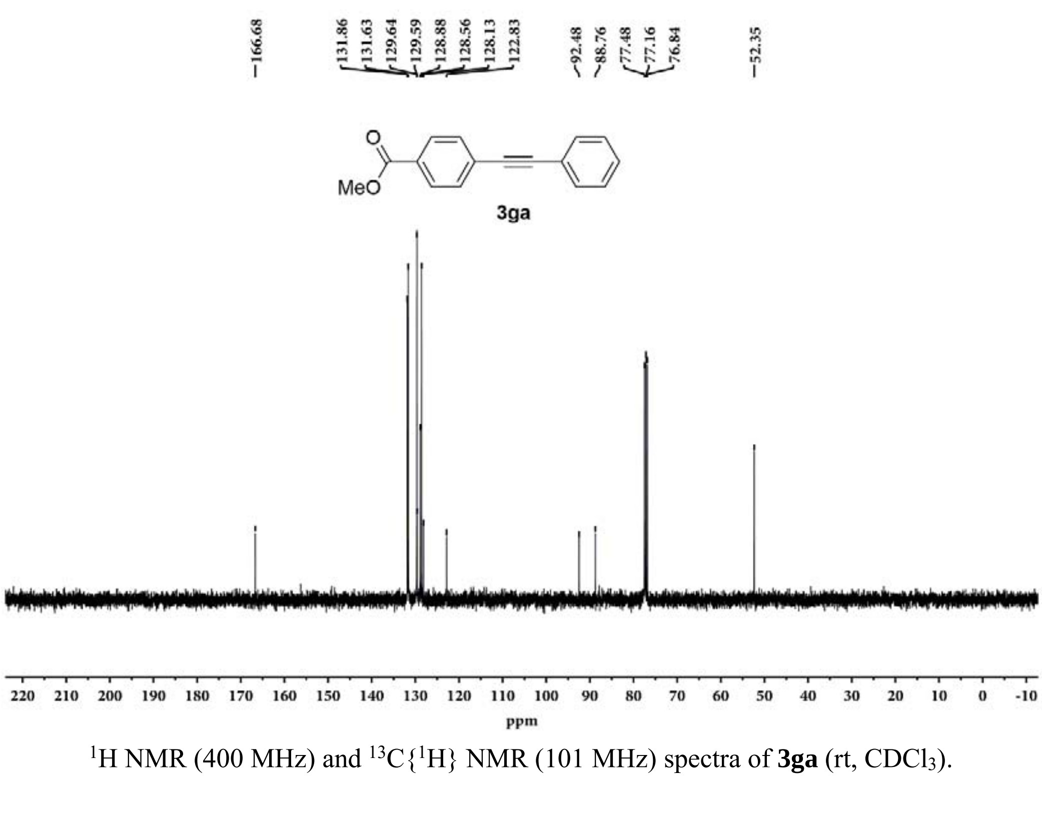
^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **3ea** (rt, $CDCl_3$).



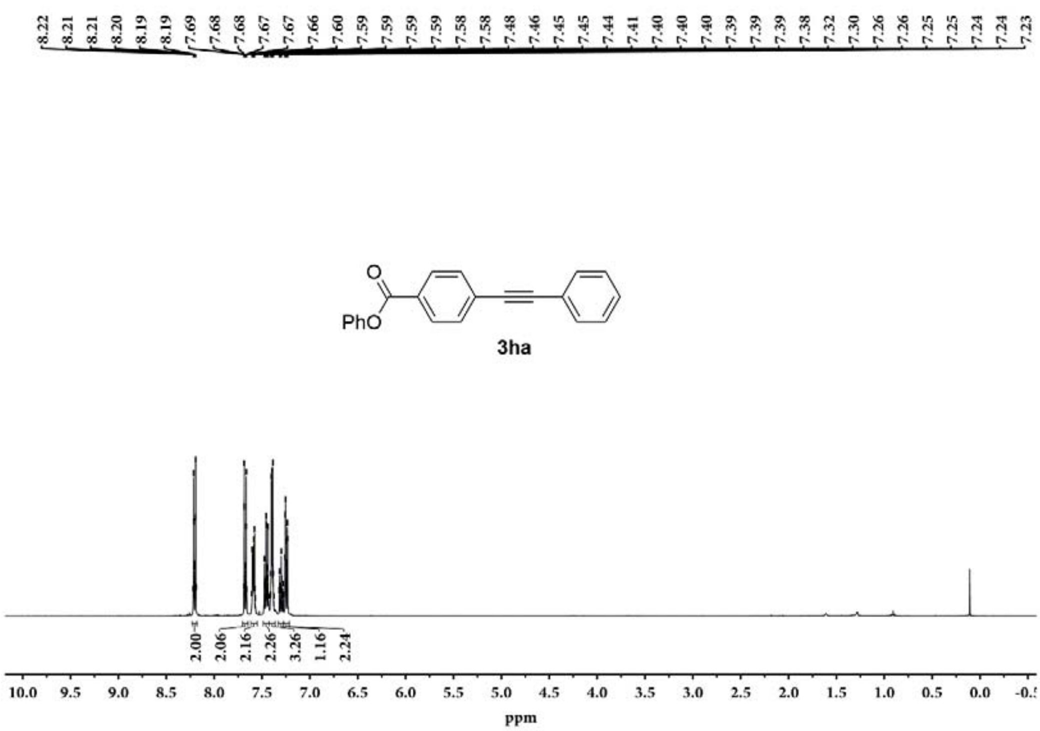


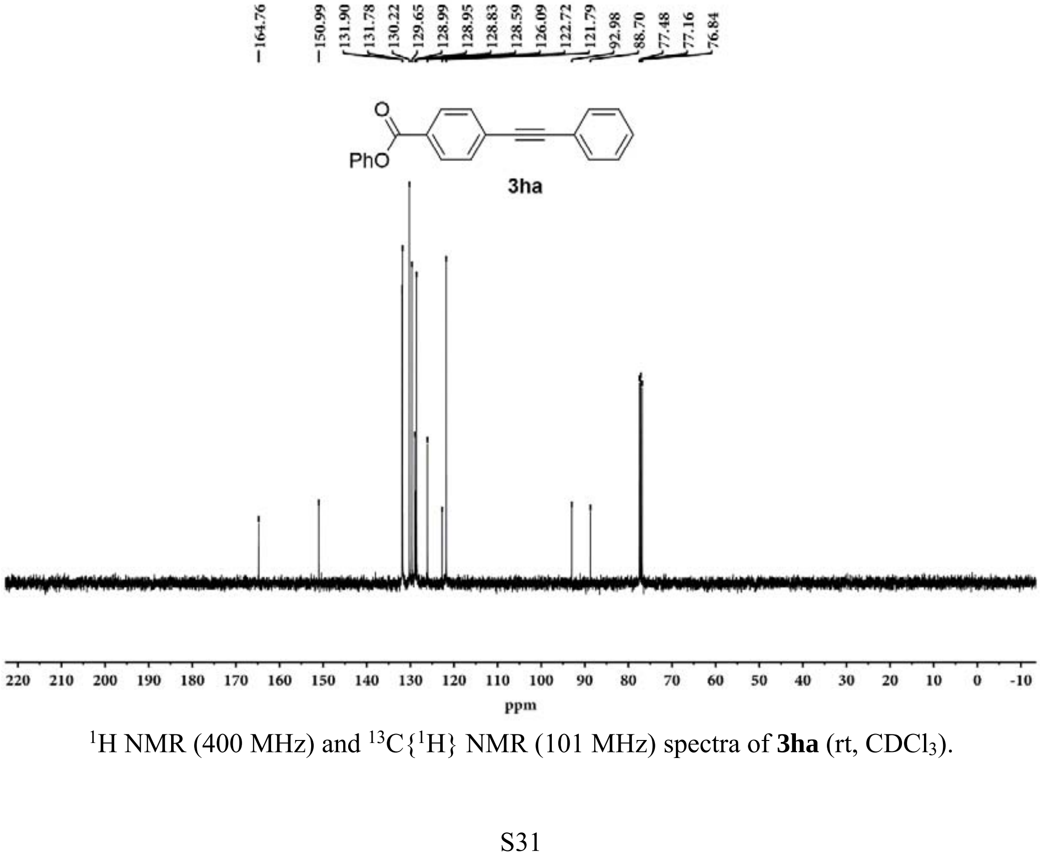
^{1}H NMR (400 MHz) and $^{13}C\{^1H\}$ NMR (101 MHz) spectra of **3fa** (rt, $CDCl_3$).



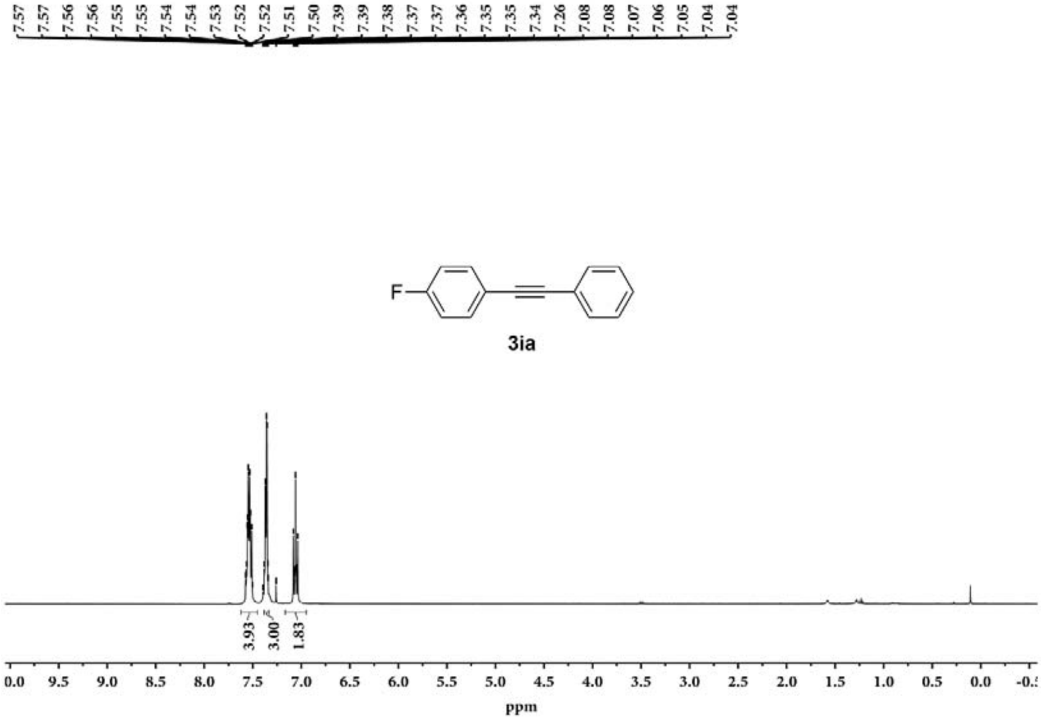


[1]H NMR (400 MHz) and [13]C{[1]H} NMR (101 MHz) spectra of **3ga** (rt, $CDCl_3$).





^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **3ha** (rt, $CDCl_3$).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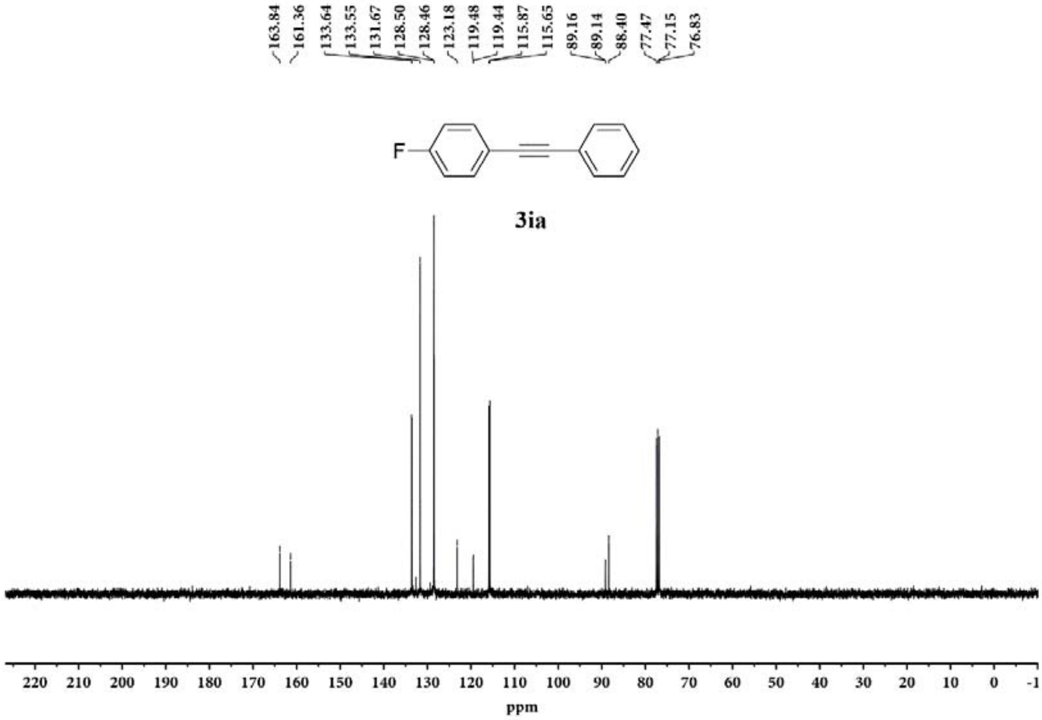
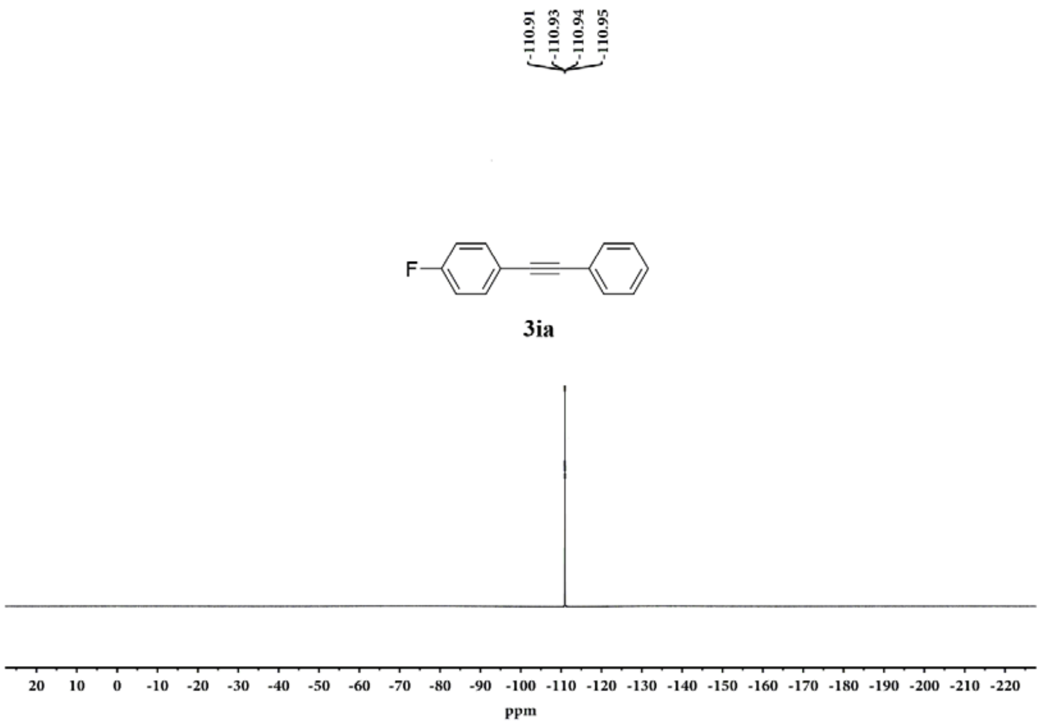
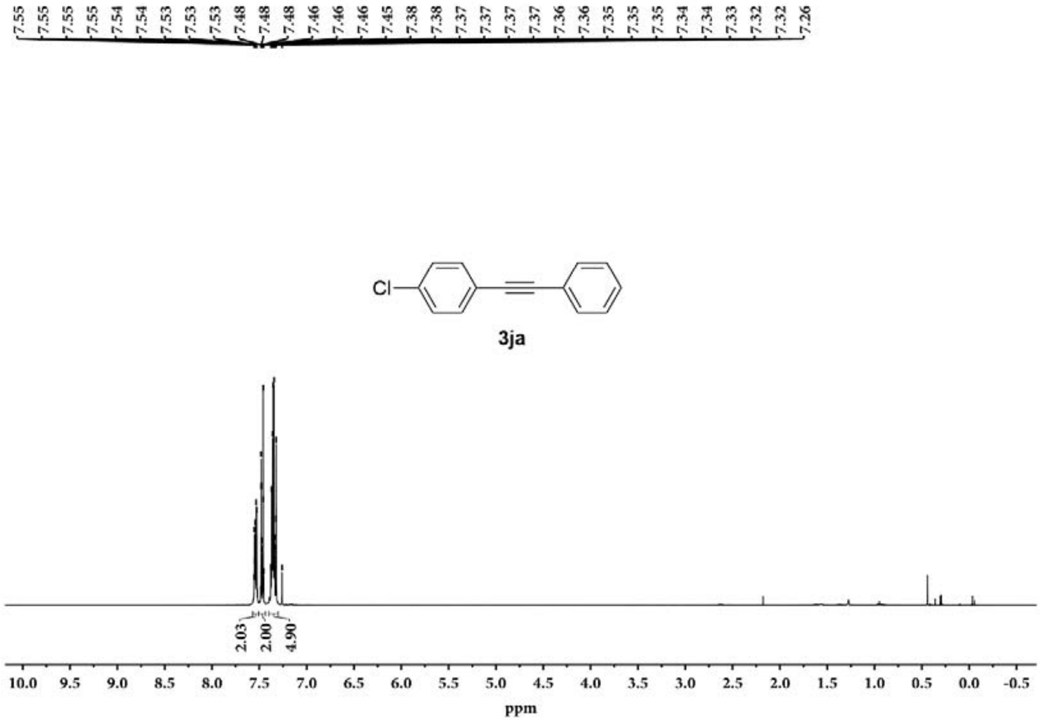
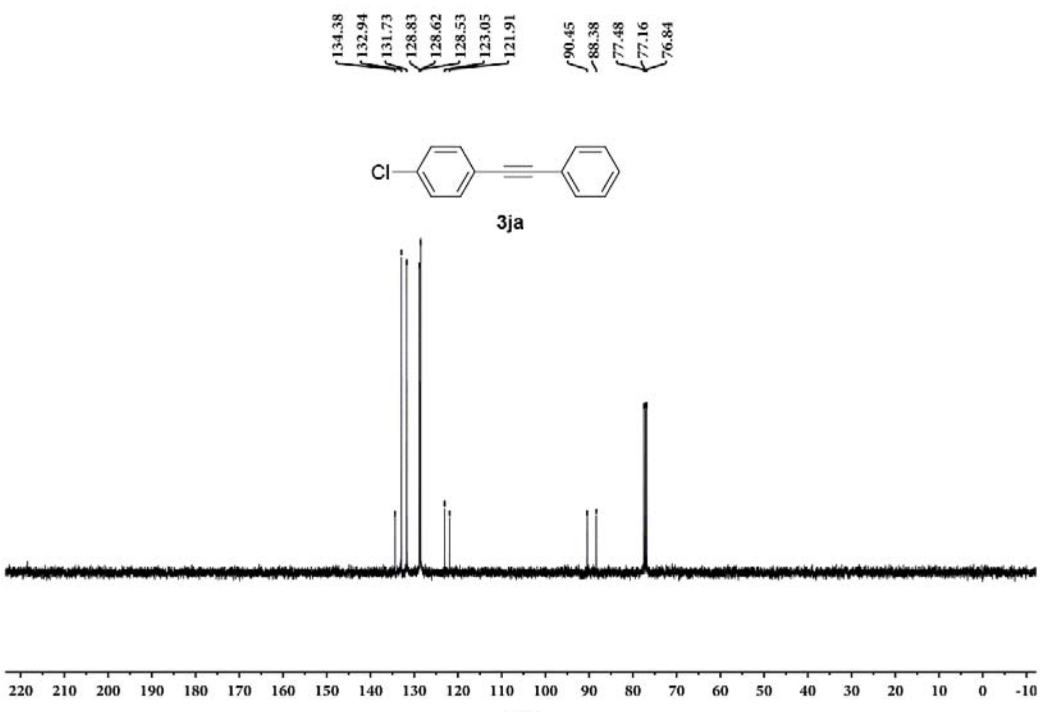
ppm


3ia
ppm

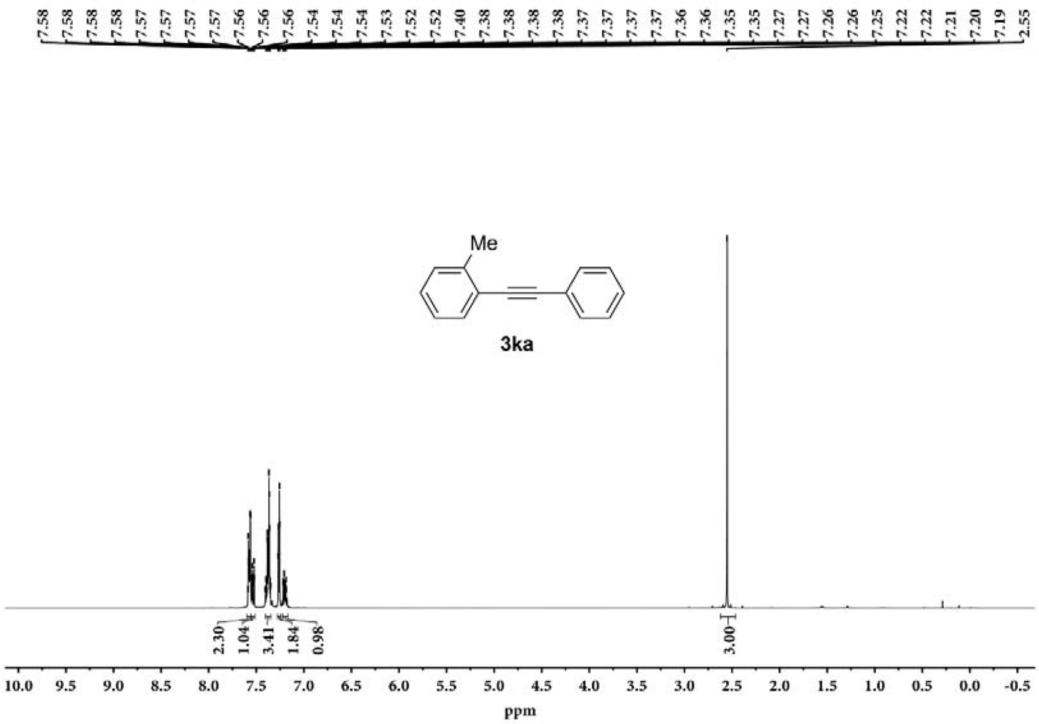


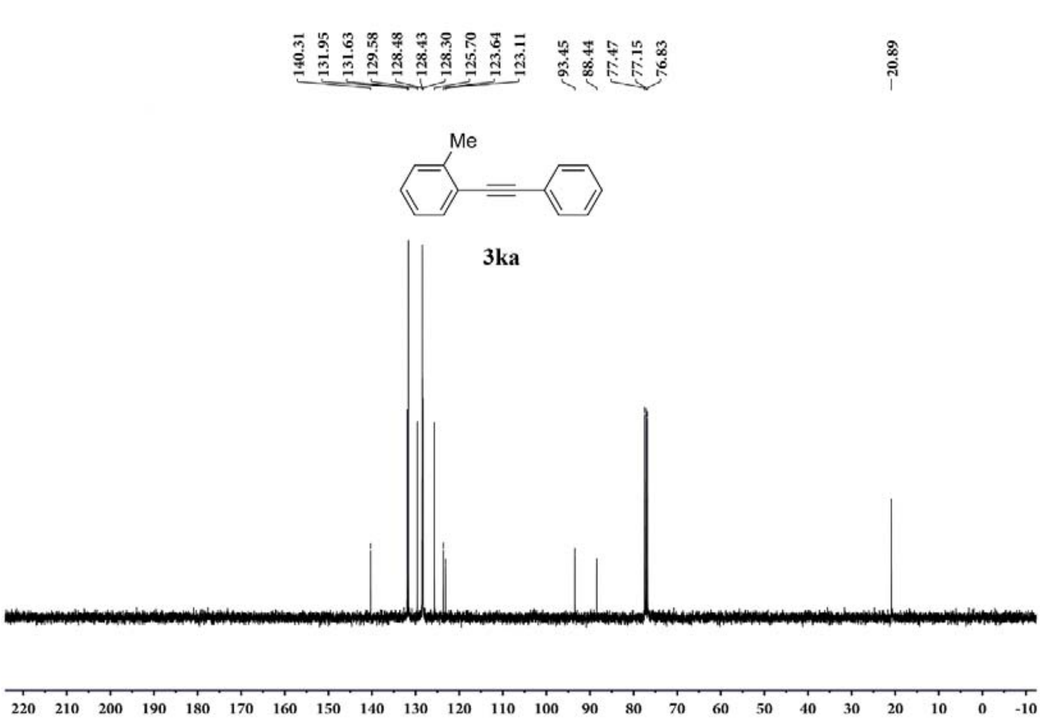
[1]H NMR (400 MHz), [13]C{[1]H} NMR (101 MHz), and [19]F{[1]H} NMR (376 MHz) spectra of **3ia** (rt, $CDCl_3$).



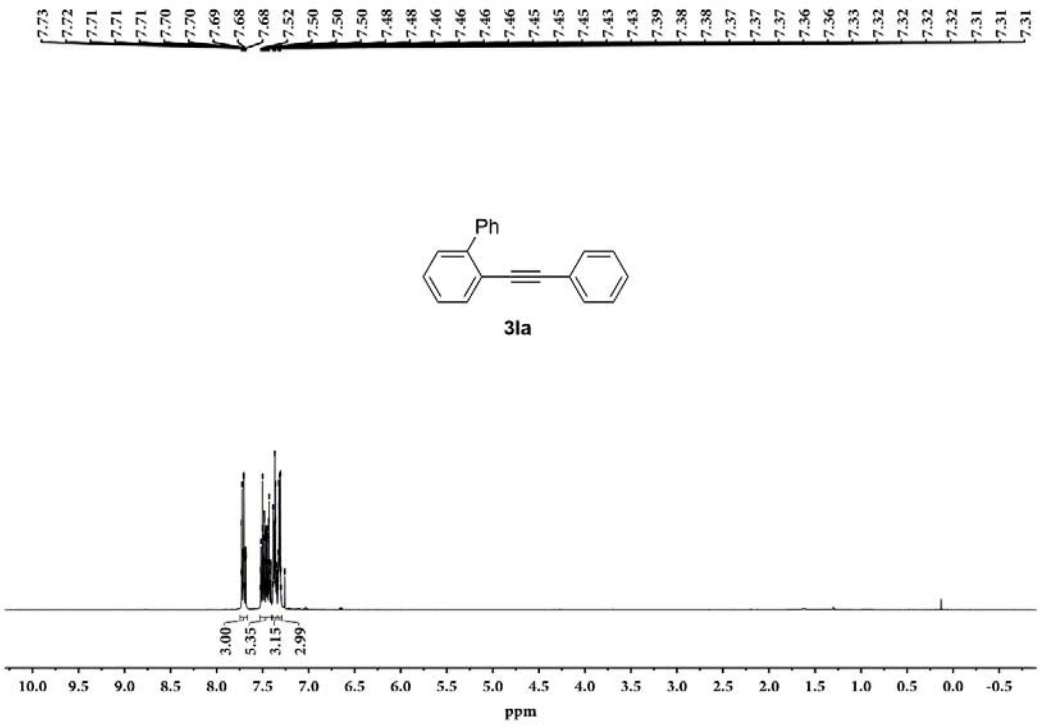


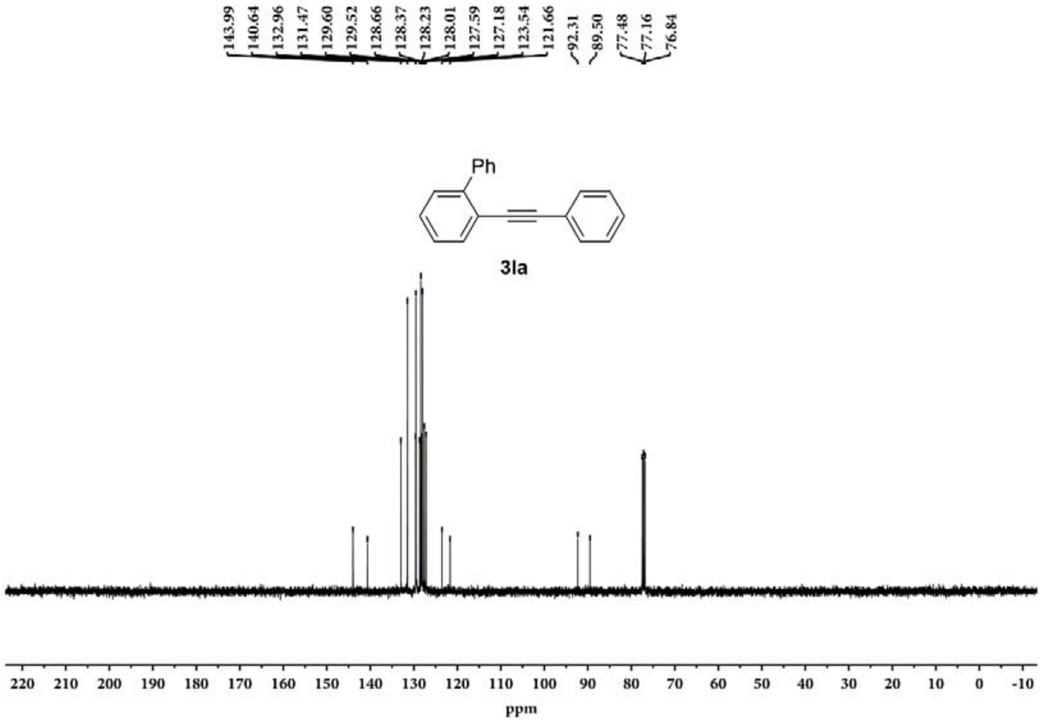
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of **3ja** (rt, $CDCl_3$).



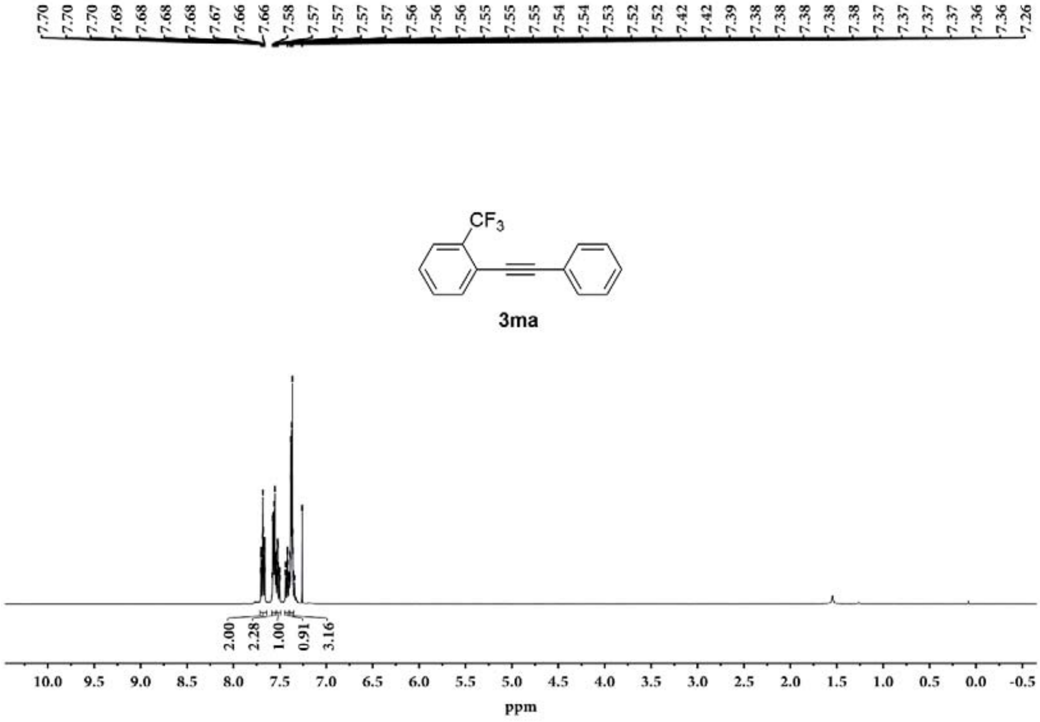


^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **3ka** (rt, $CDCl_3$).





^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of **3la** (rt, $CDCl_3$).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CF3
3ma
2.00 2.28 1.00 0.91 3.16
10.0 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
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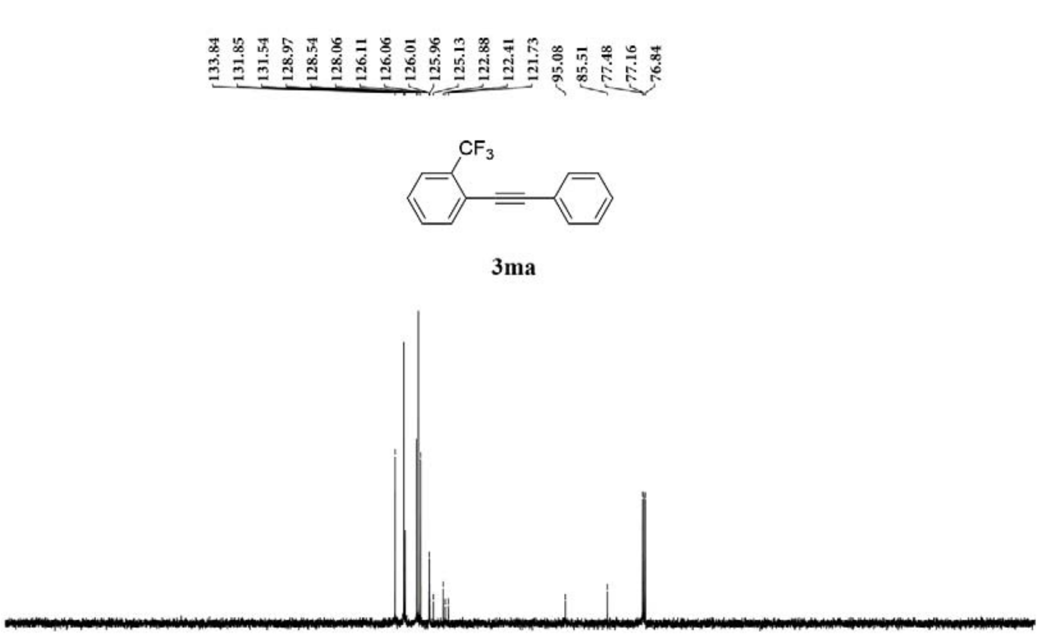
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CF3
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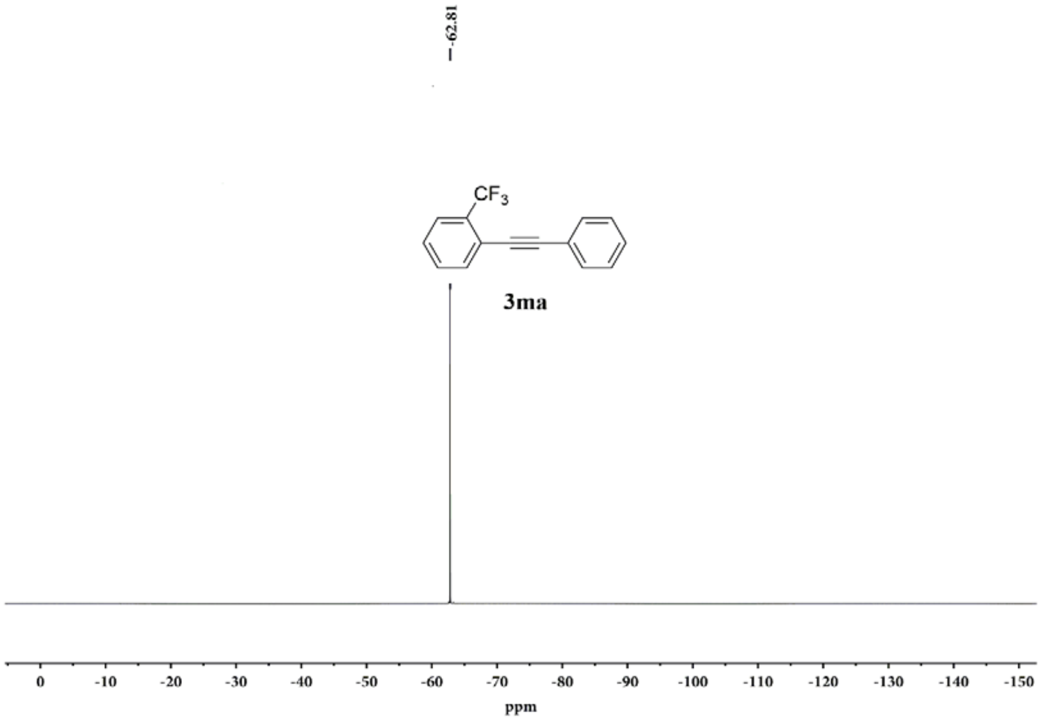
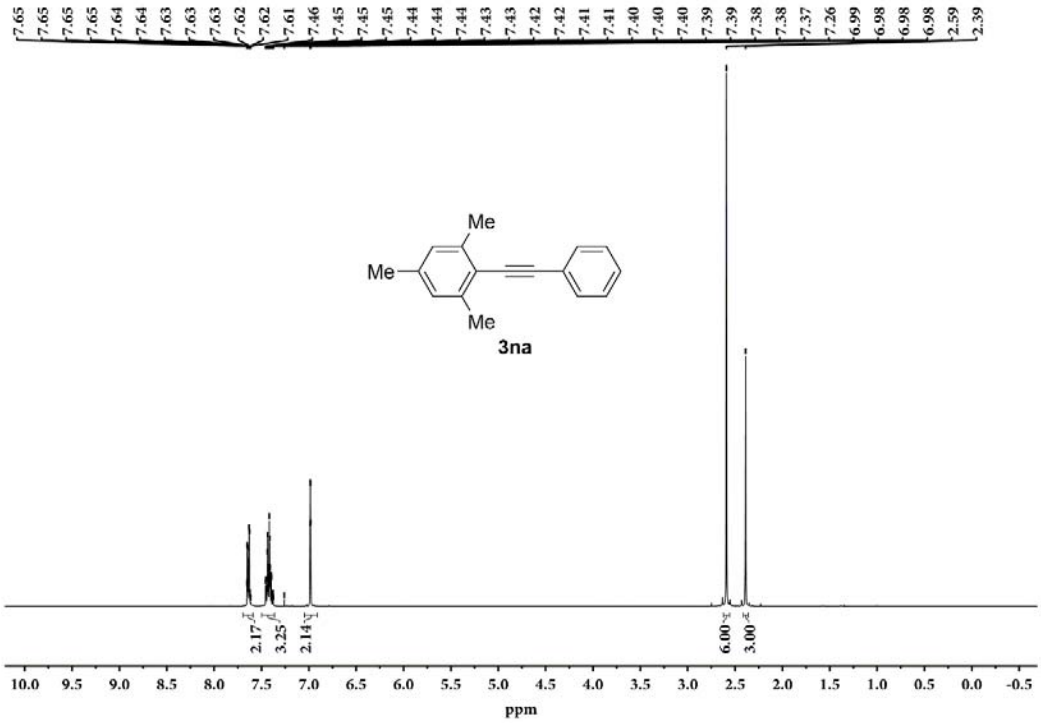
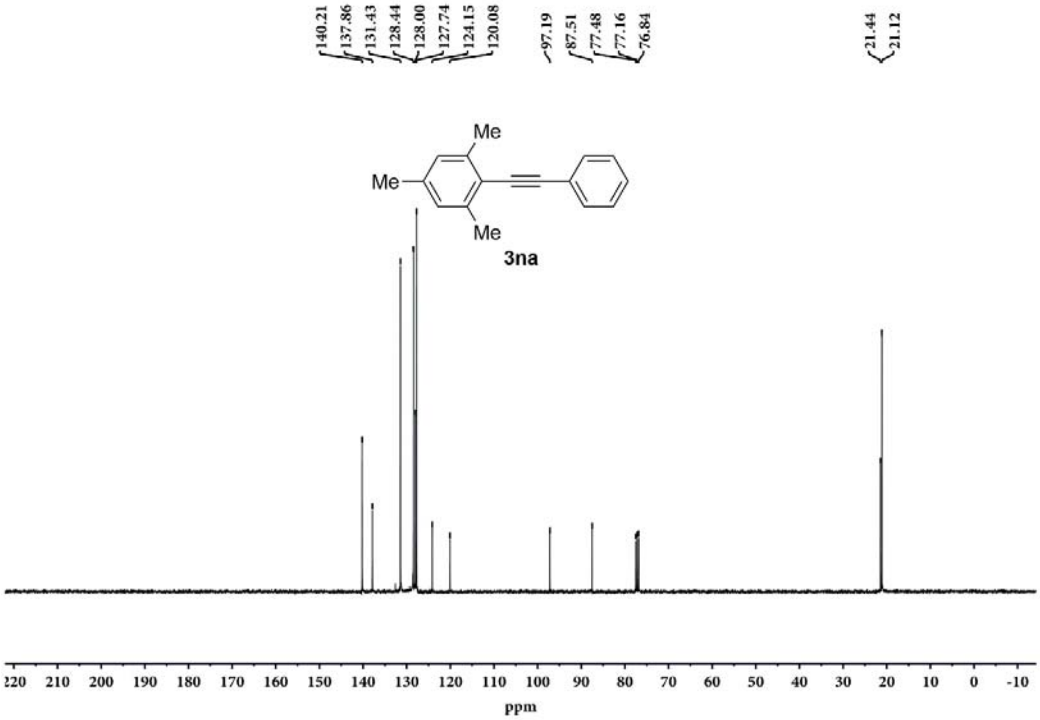
ppm

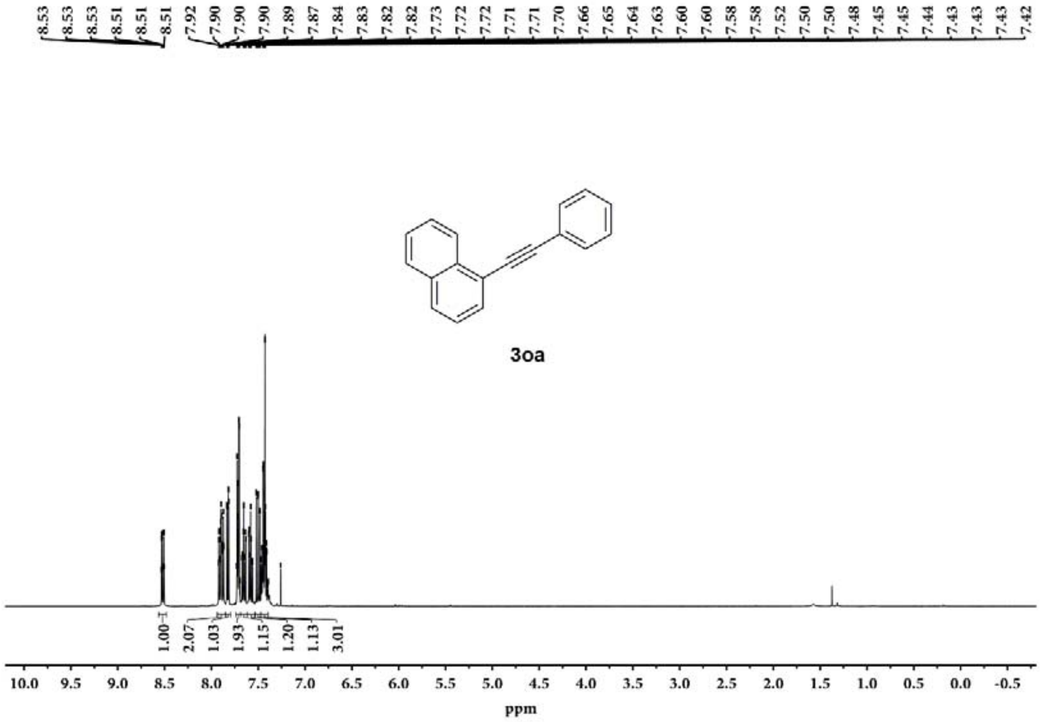


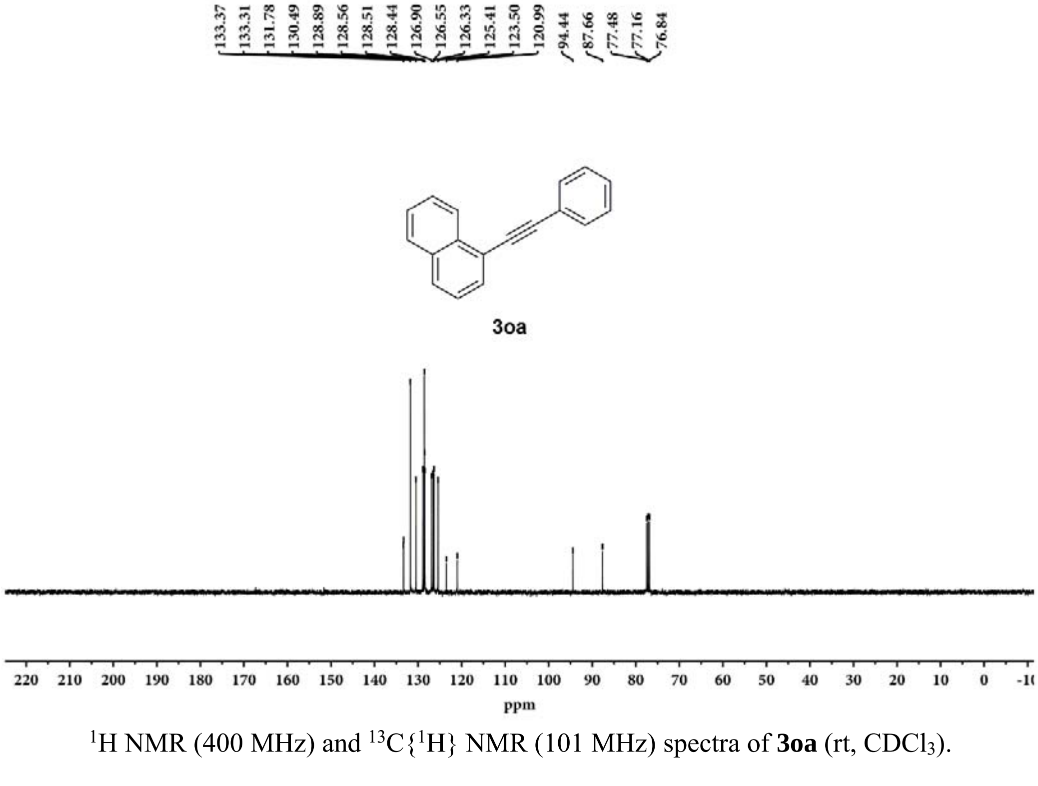
[1]H NMR (400 MHz), [13]C{[1]H} NMR (101 MHz), and [19]F{[1]H} NMR (376 MHz) spectra of **3ma** (rt, $CDCl_3$).



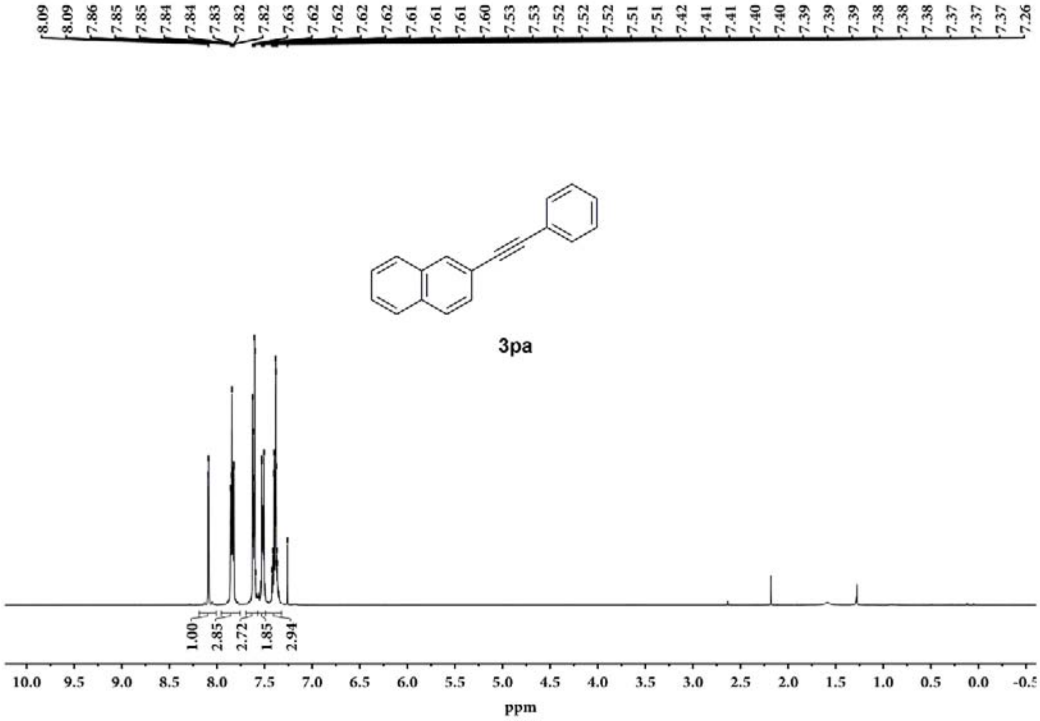


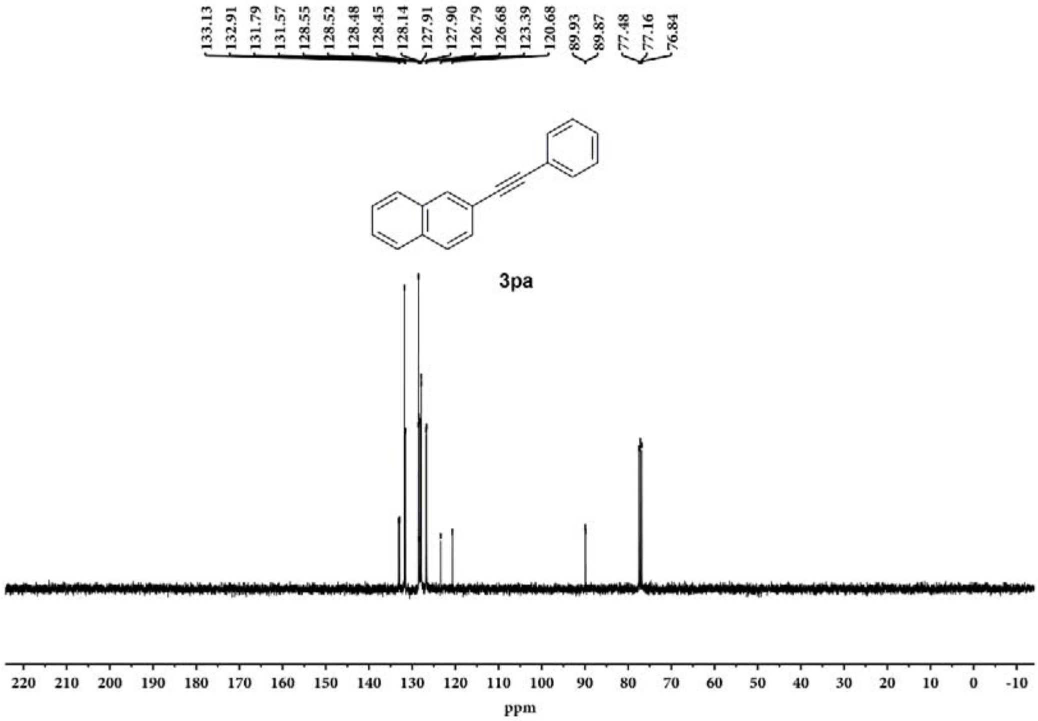
^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **3na** (rt, $CDCl_3$).



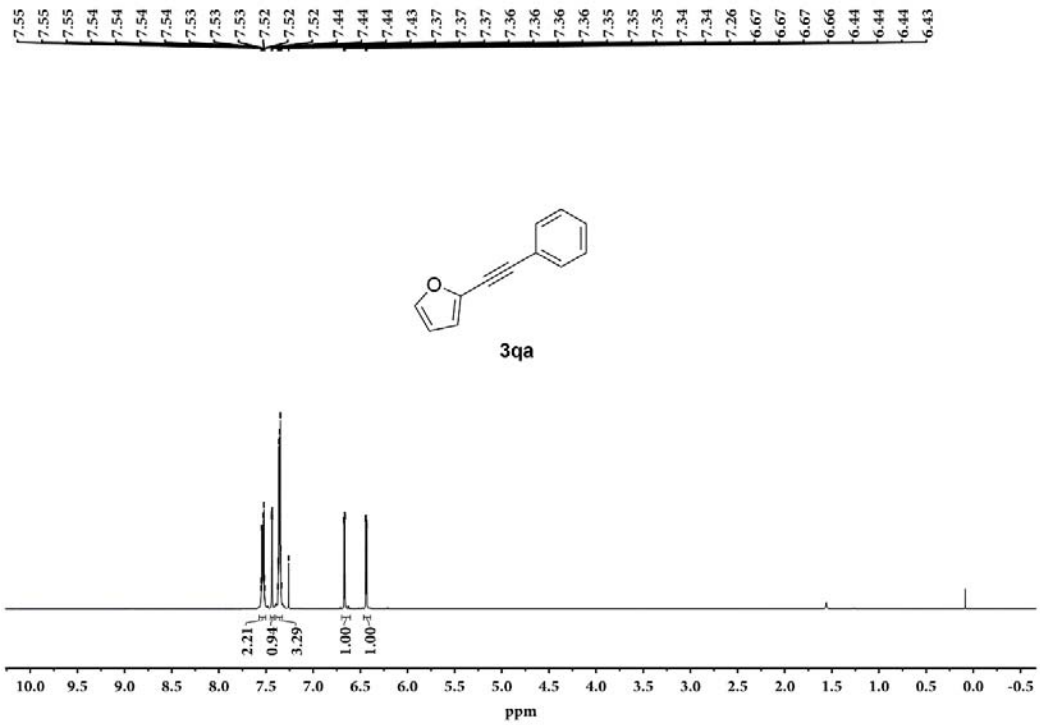


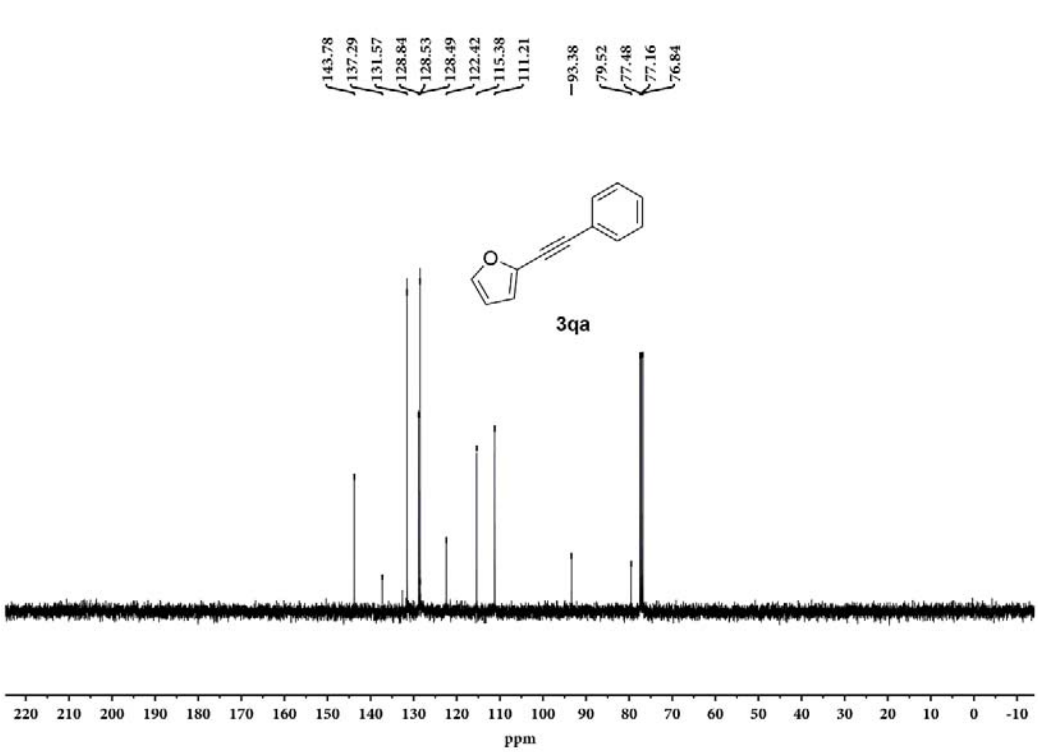
^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **3oa** (rt, $CDCl_3$).



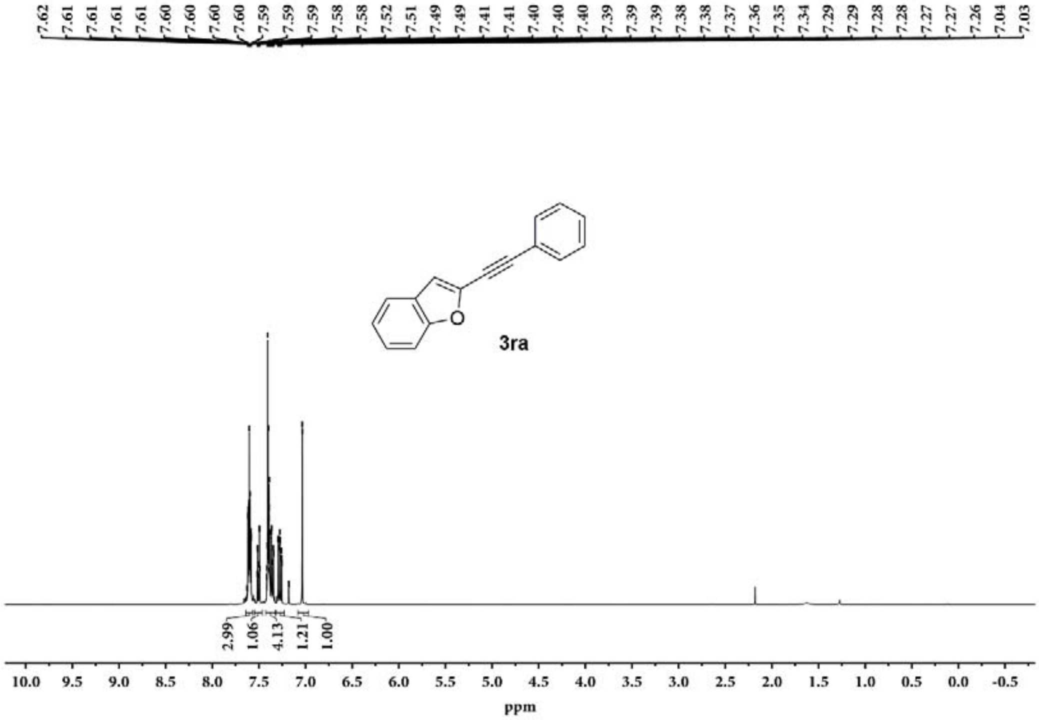


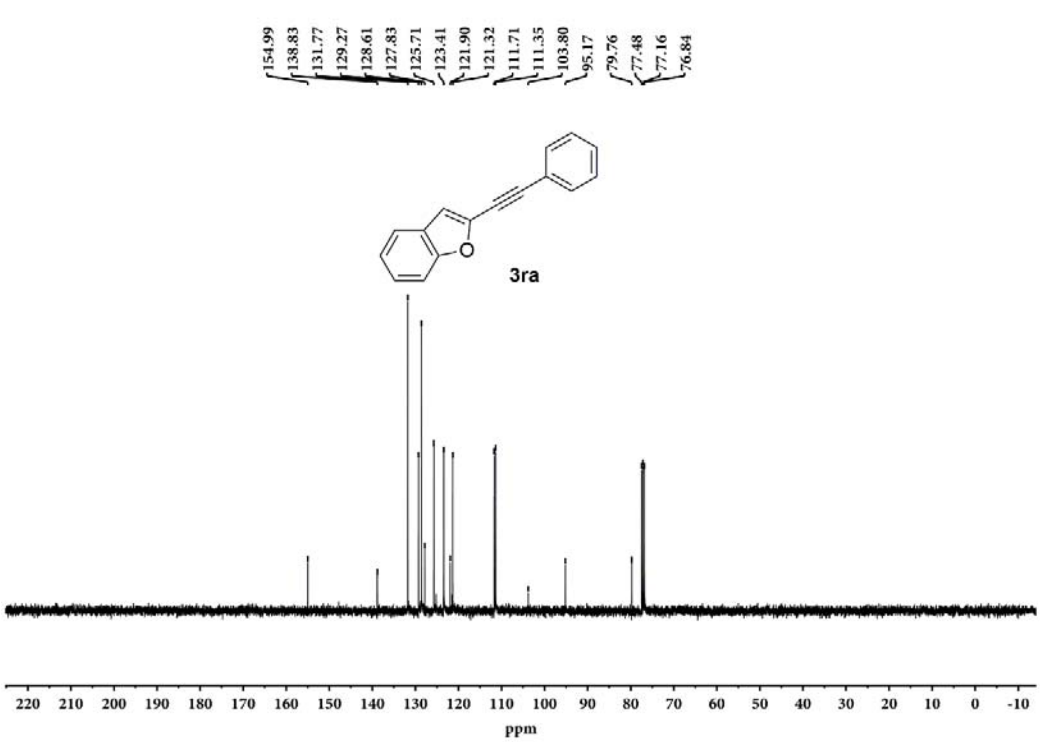
^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **3pa** (rt, $CDCl_3$).



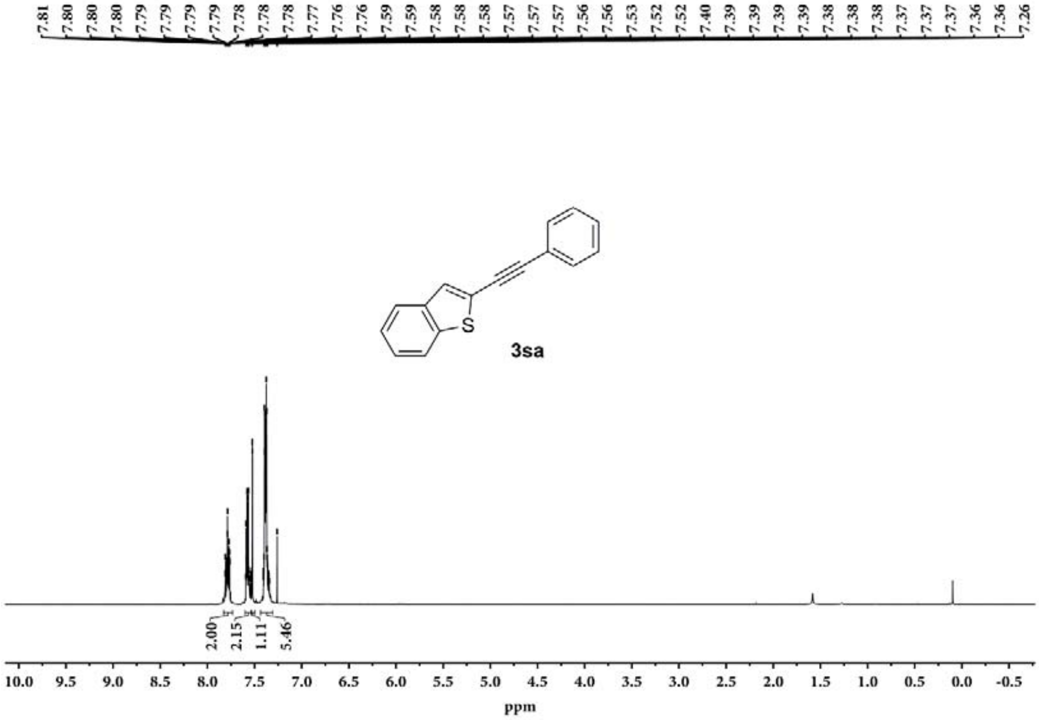


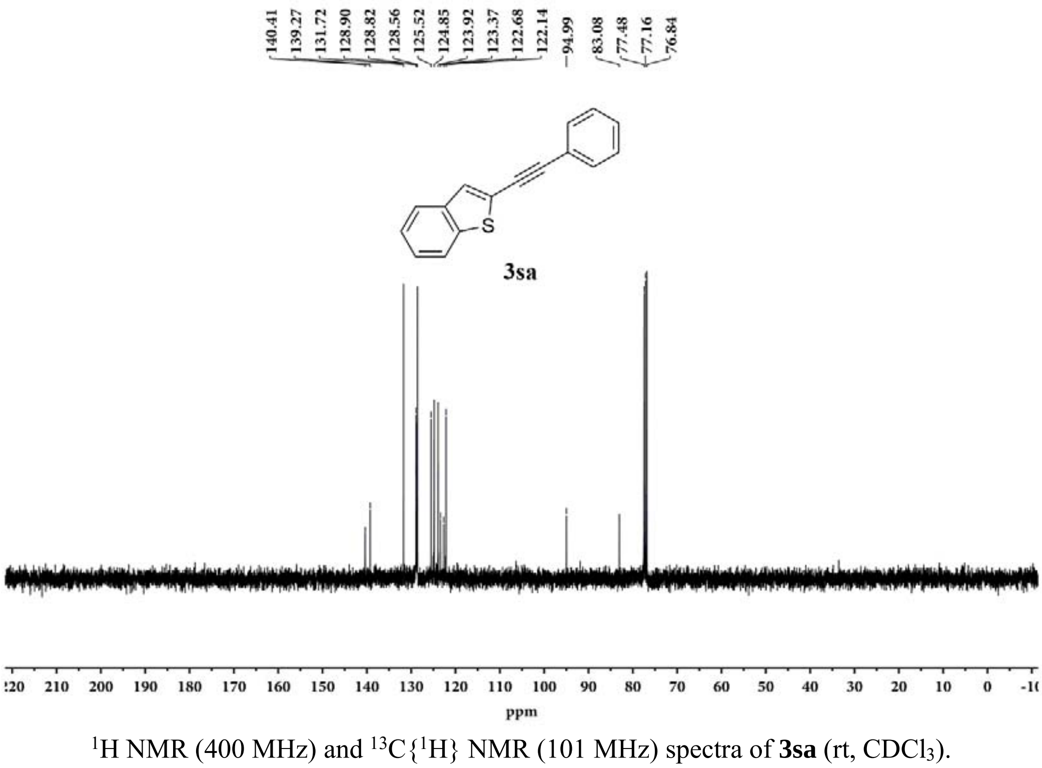
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of **3qa** (rt, $CDCl_3$).



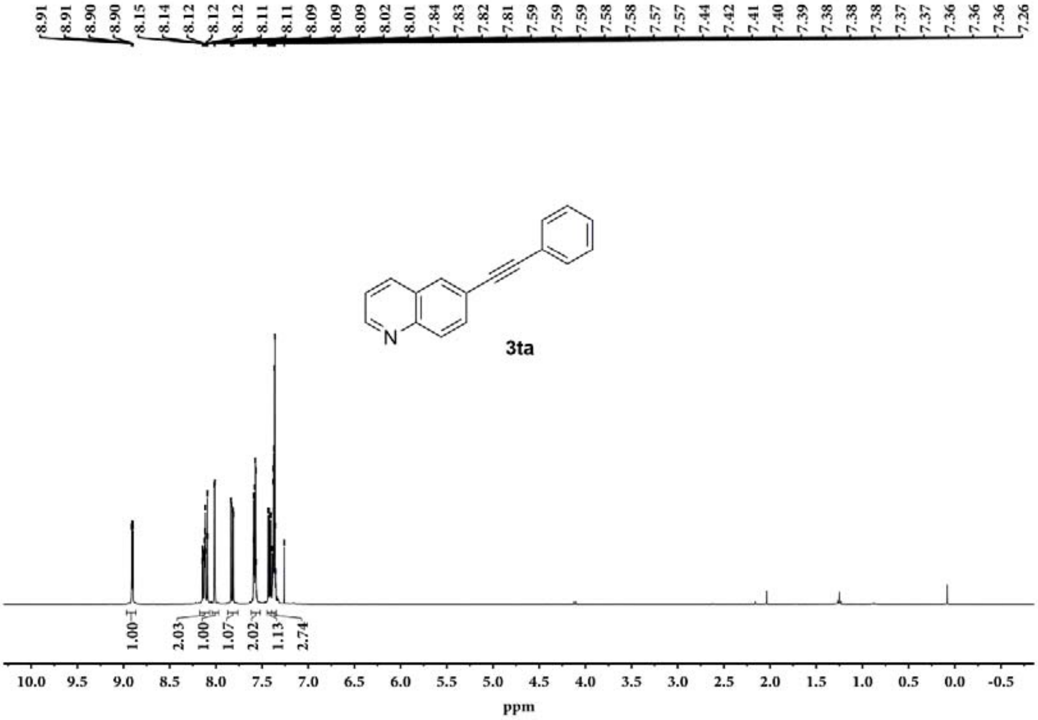


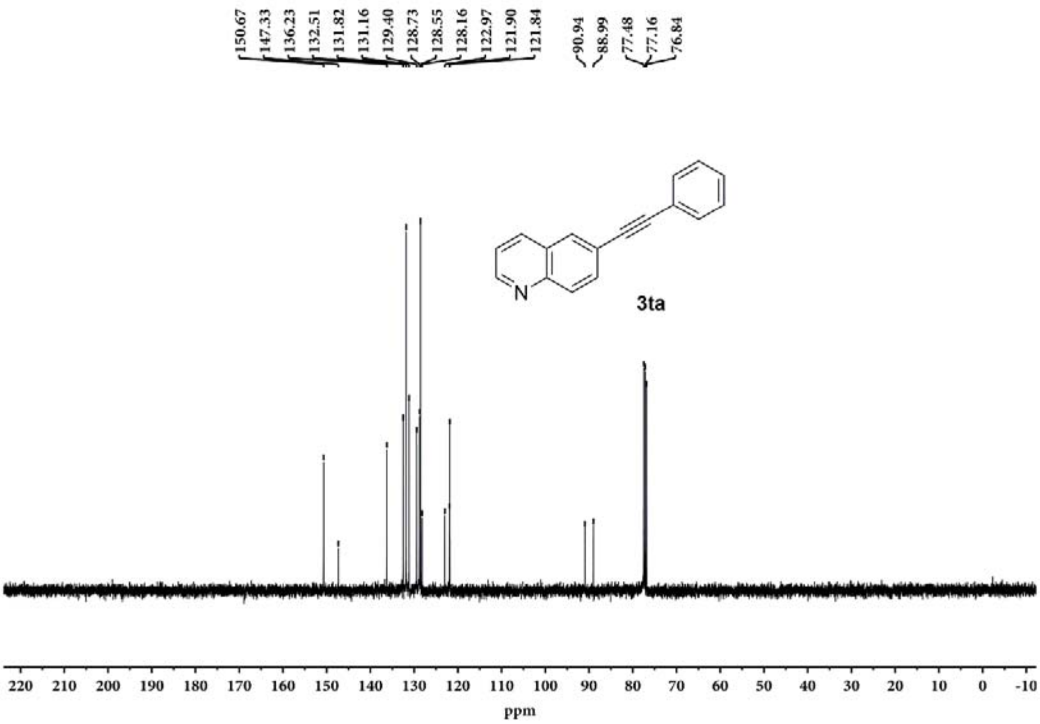
[1]H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **3ra** (rt, $CDCl_3$).



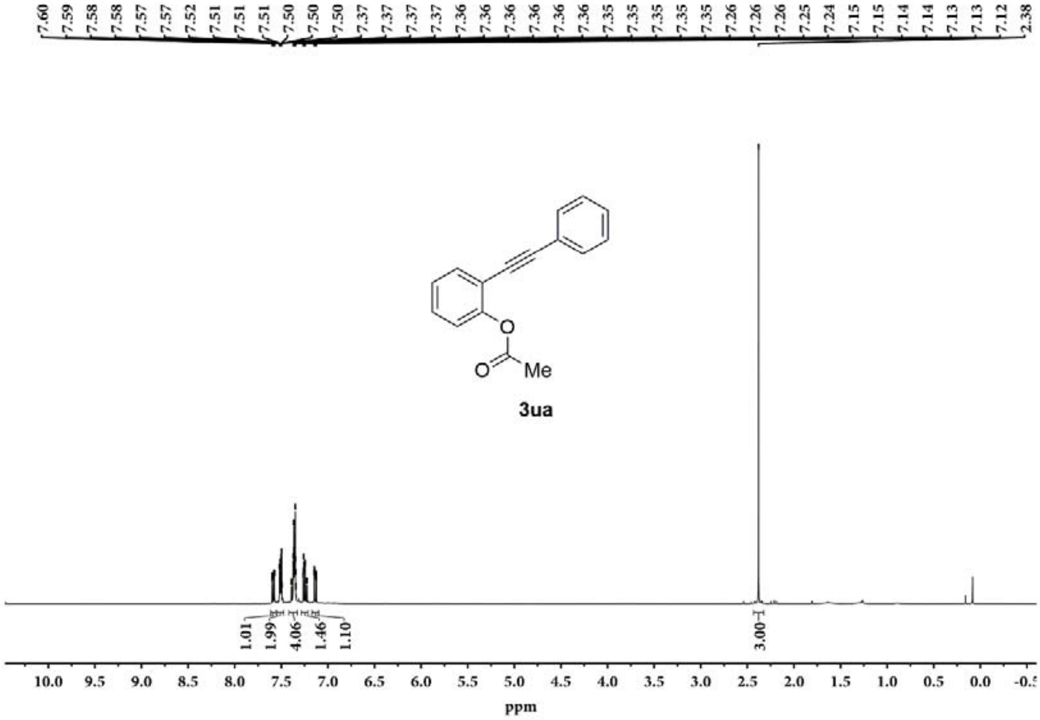


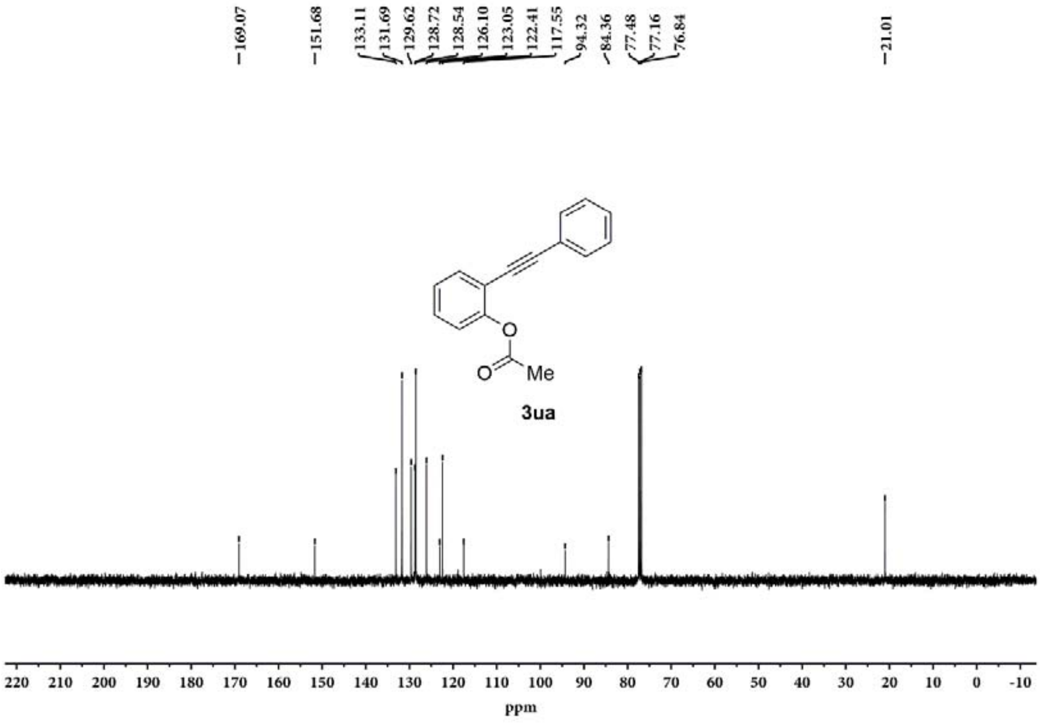
^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **3sa** (rt, $CDCl_3$).



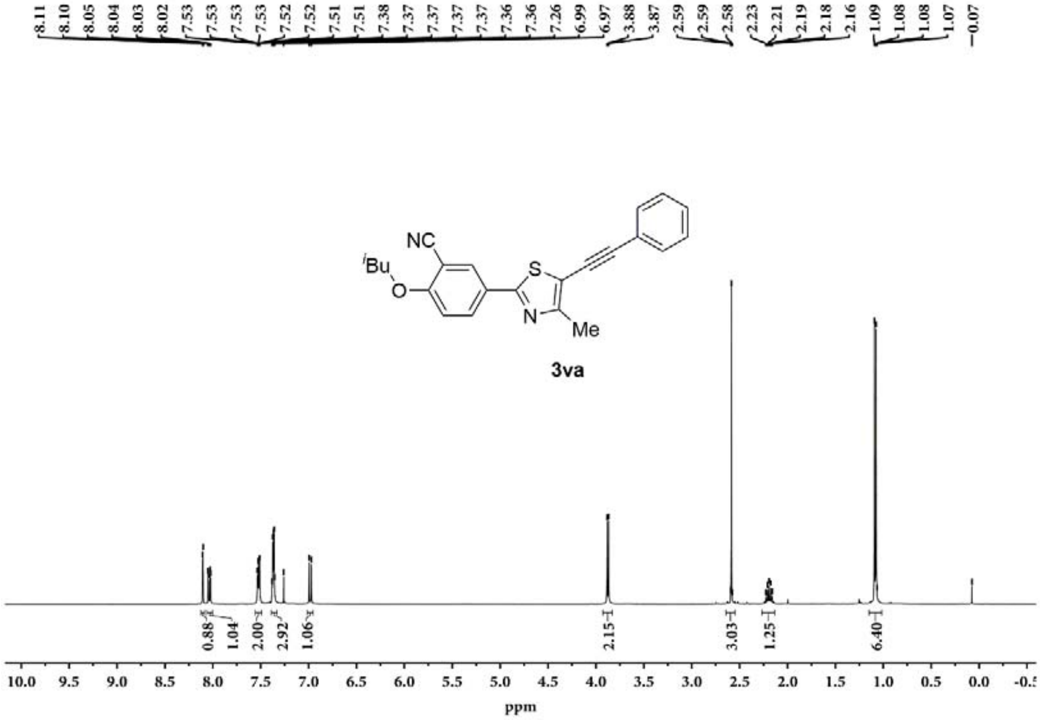


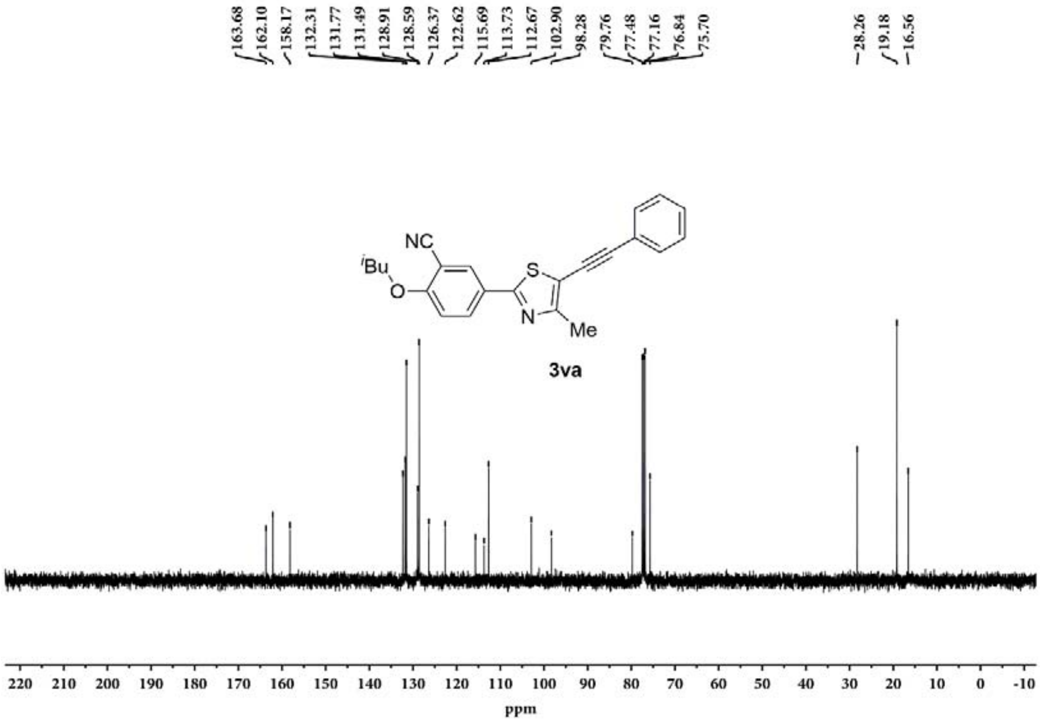
^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **3ta** (rt, $CDCl_3$).



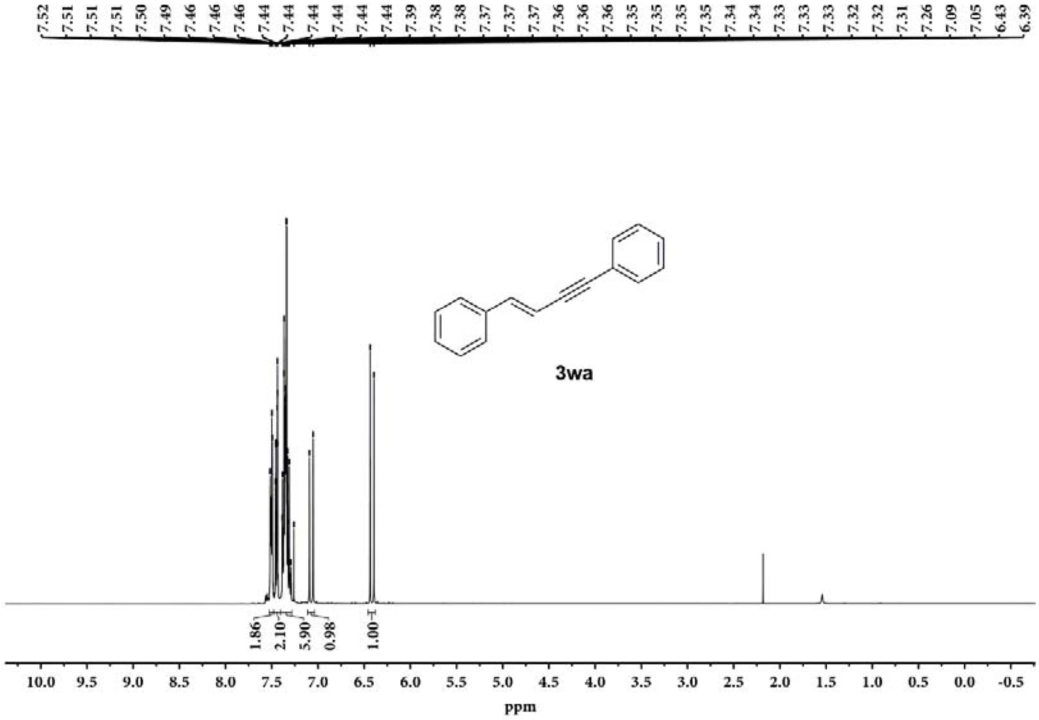


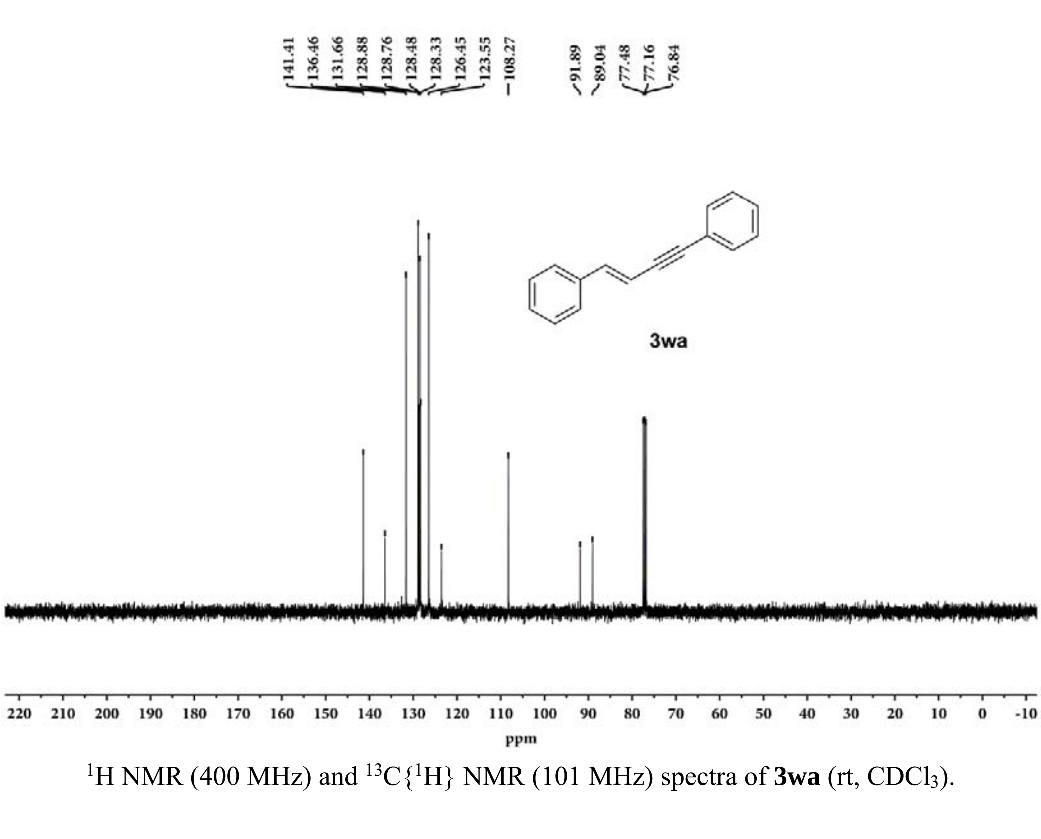
[1]H NMR (400 MHz) and $^{13}C\{^1H\}$ NMR (101 MHz) spectra of **3ua** (rt, $CDCl_3$).



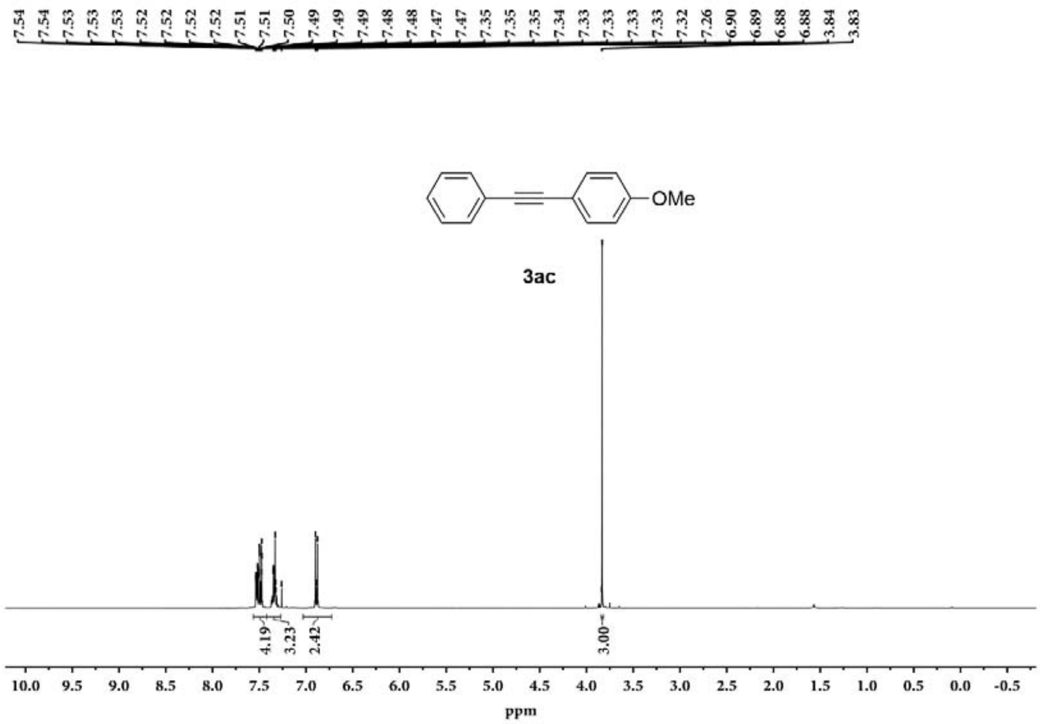


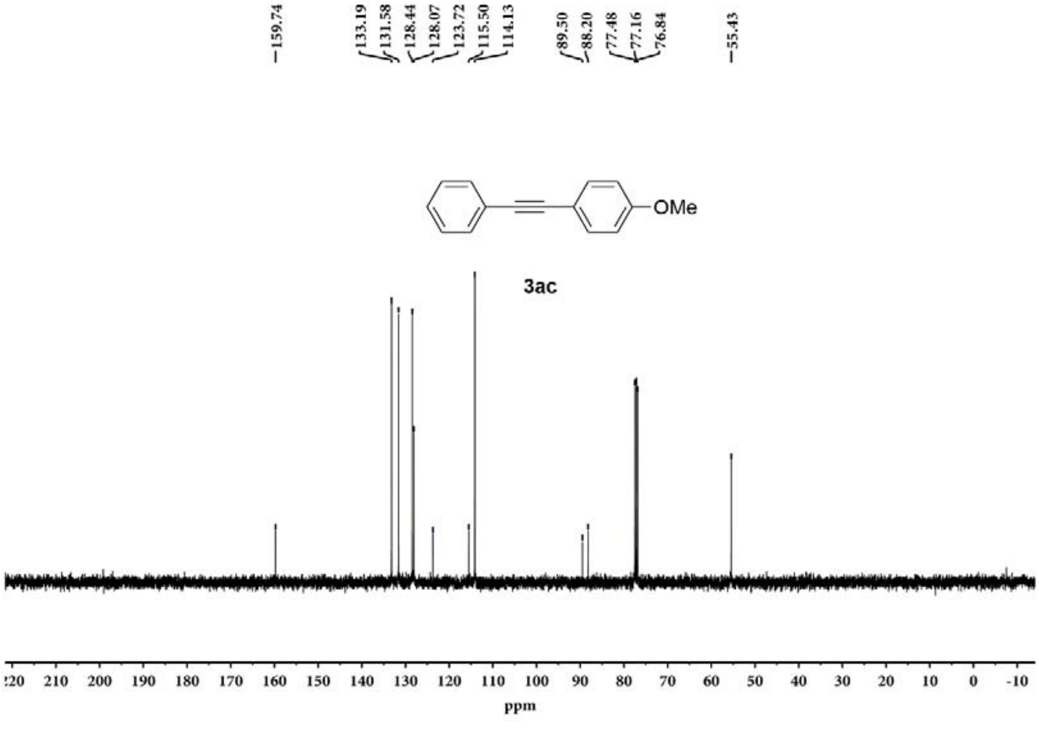
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of **3va** (rt, $CDCl_3$).



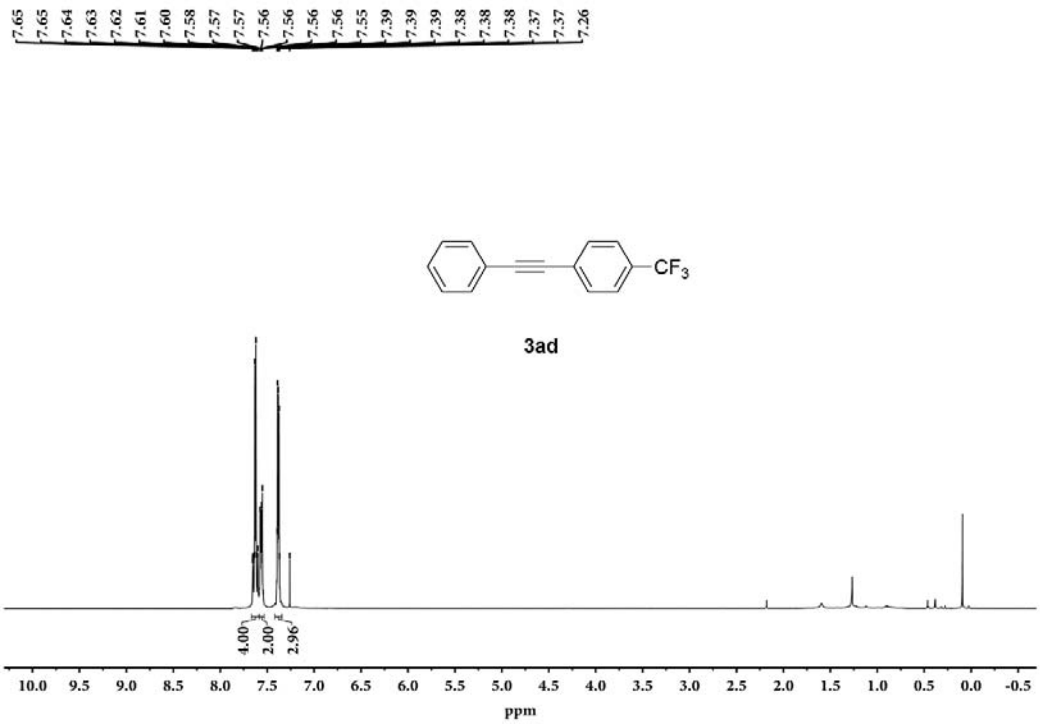


[1]H NMR (400 MHz) and [13]C{[1]H} NMR (101 MHz) spectra of **3wa** (rt, $CDCl_3$).





[1]H NMR (400 MHz) and [13]C{[1]H} NMR (101 MHz) spectra of **3ac** (rt, $CDCl_3$).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CF3
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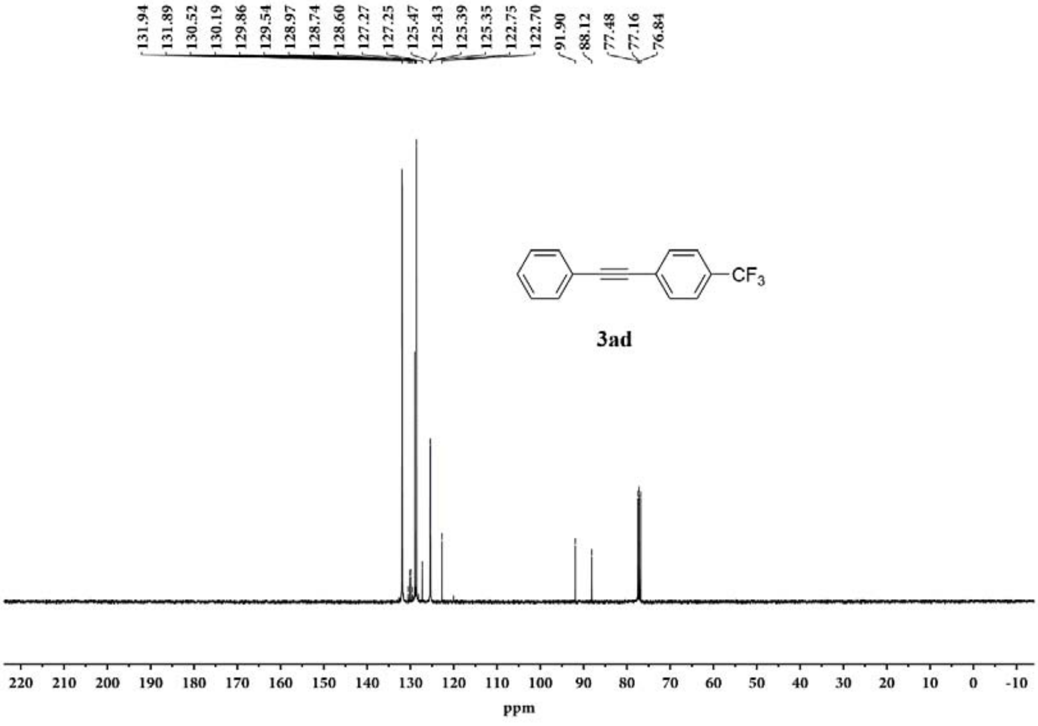
4.00
2.00
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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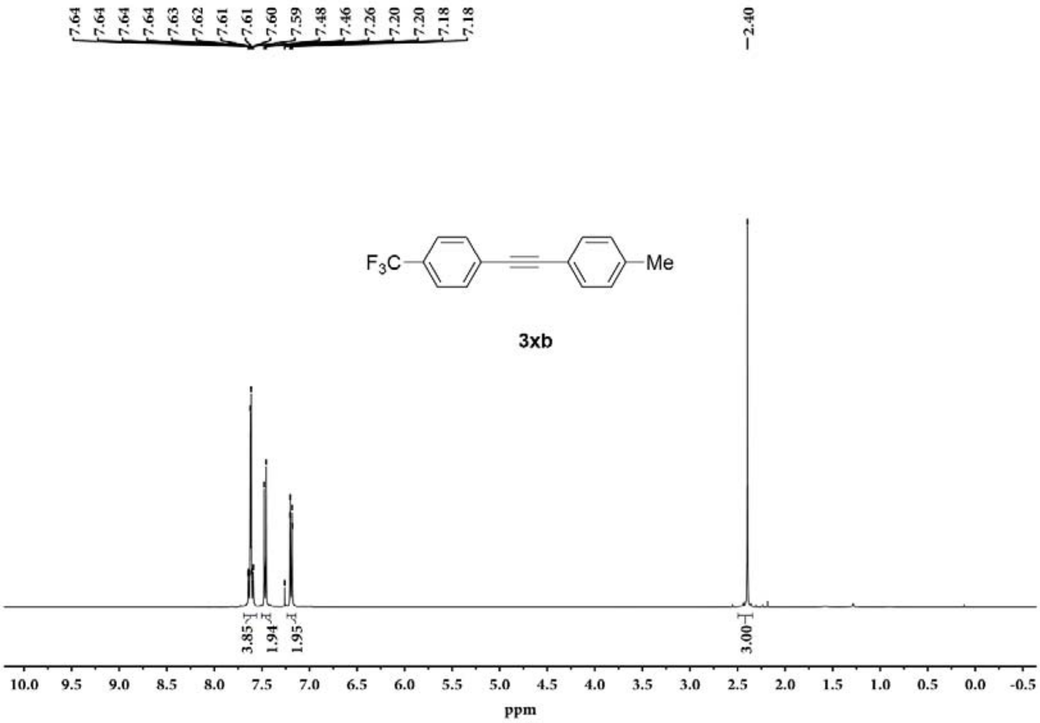
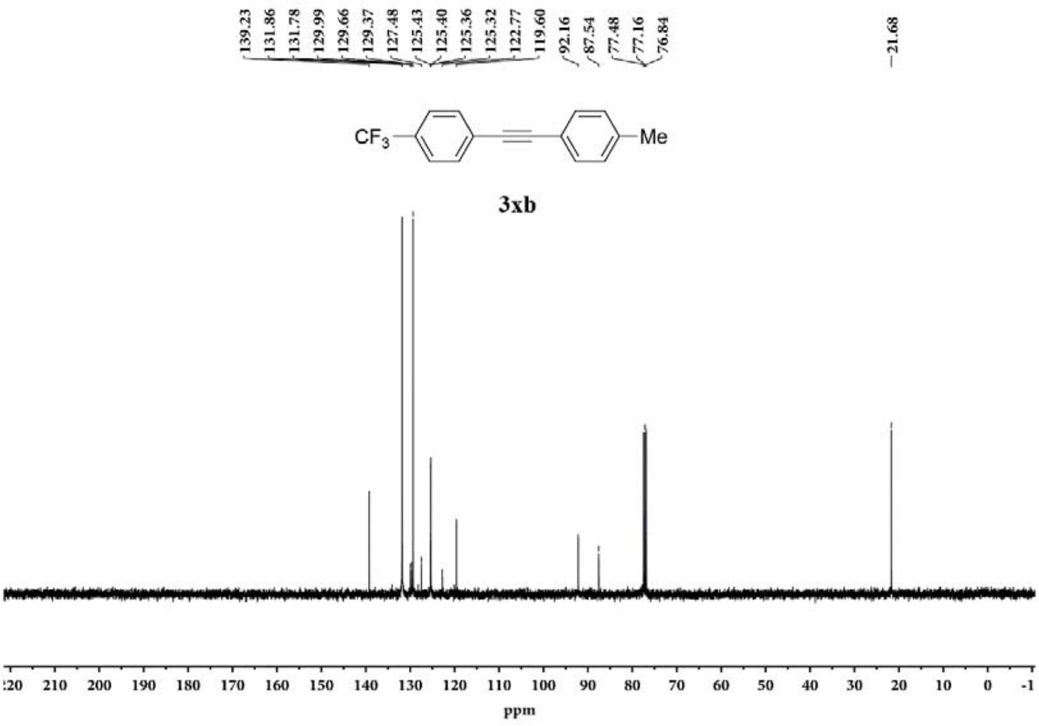
91.90 88.12
77.48 77.16 76.84
CF3
3ad
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

^{1}H NMR (400 MHz) ^{13}C{^{1}H} NMR (101 MHz), and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3ad** (rt, $CDCl_3$).


7.64
7.64
7.64
7.64
7.63
7.62
7.61
7.61
7.60
7.59
7.48
7.46
7.26
7.20
7.20
7.18
7.18
2.40
F3C
Me
3xb
3.85
1.94
1.95
3.00
10.0 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
ppm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125.43
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125.36
125.32
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92.16
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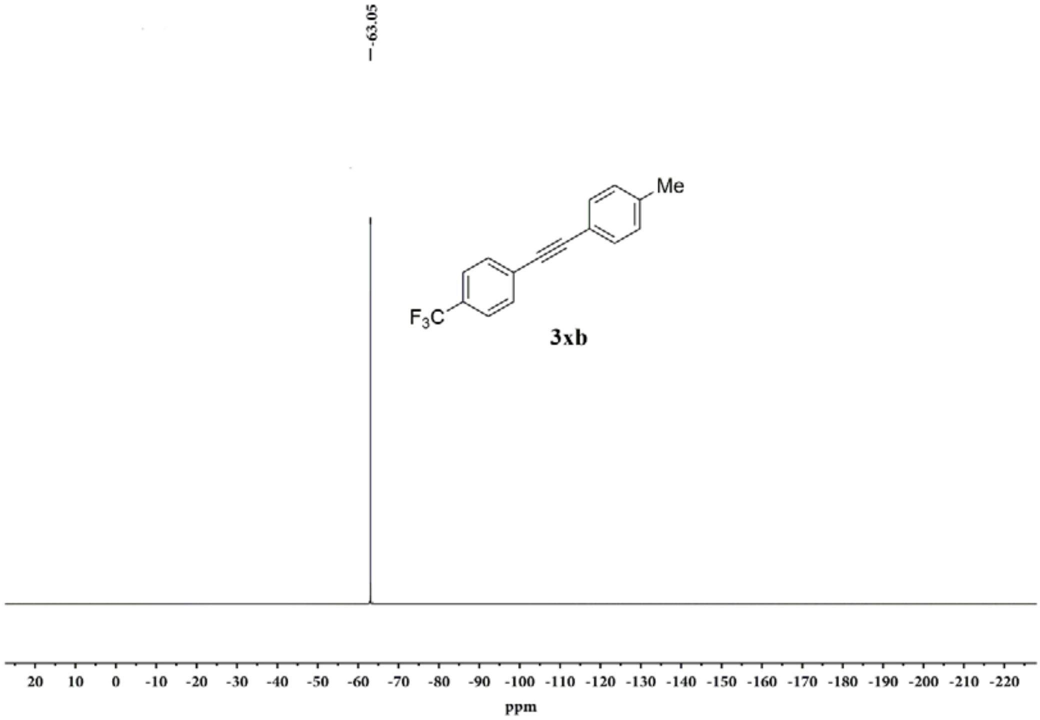
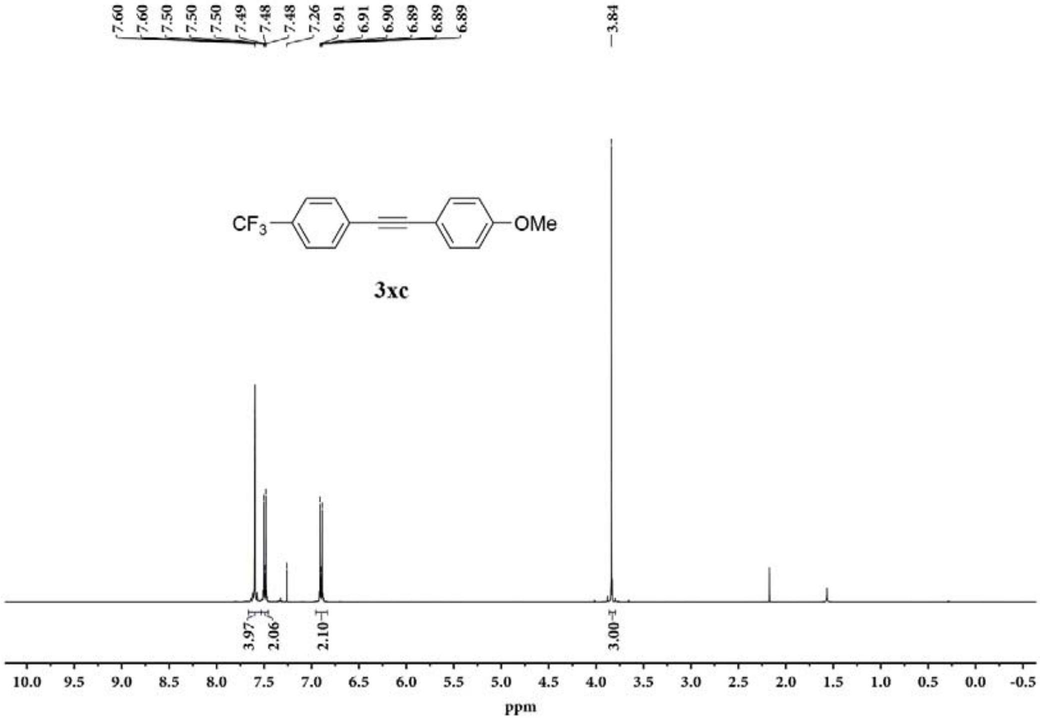
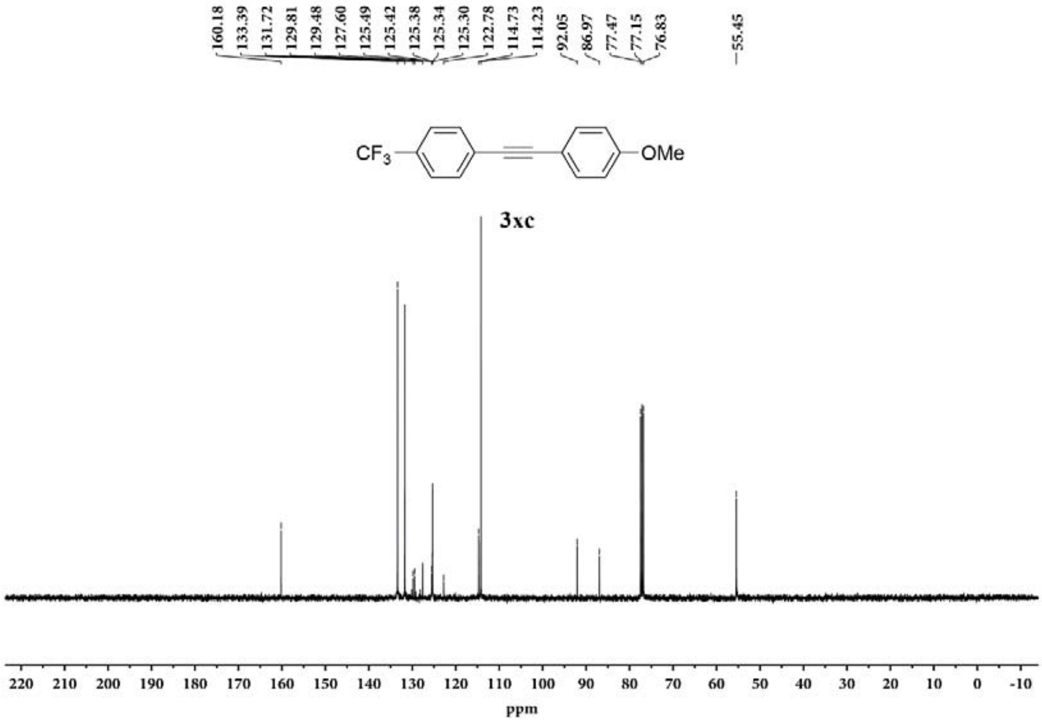
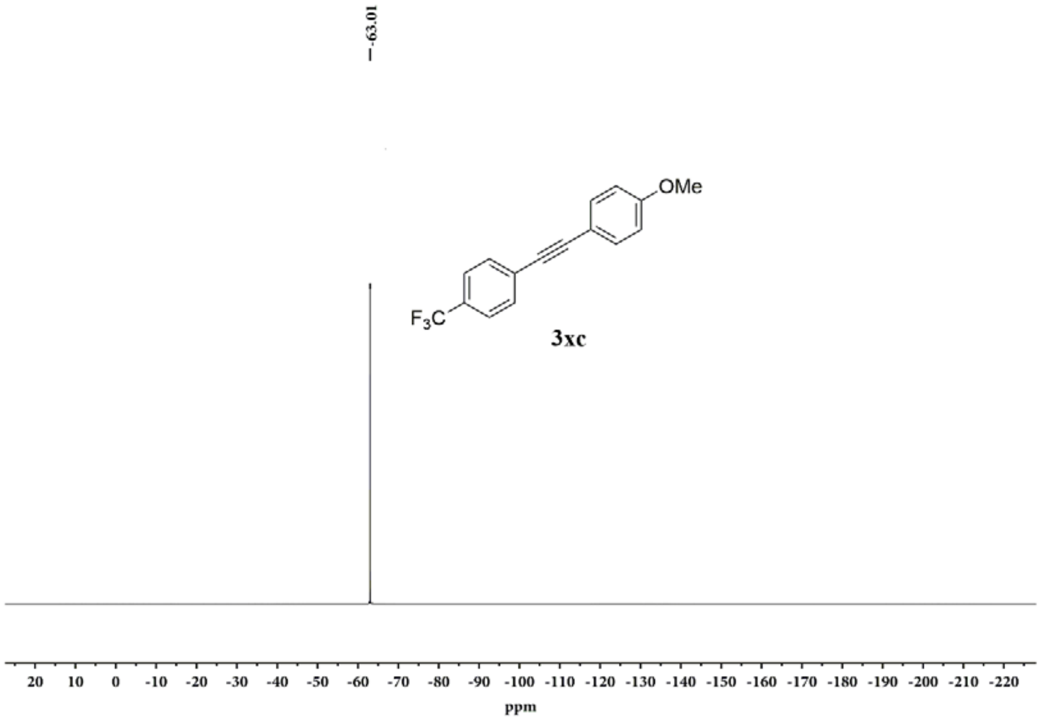
77.48
77.16
76.84
21.68
CF3
Me
3xb
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
ppm



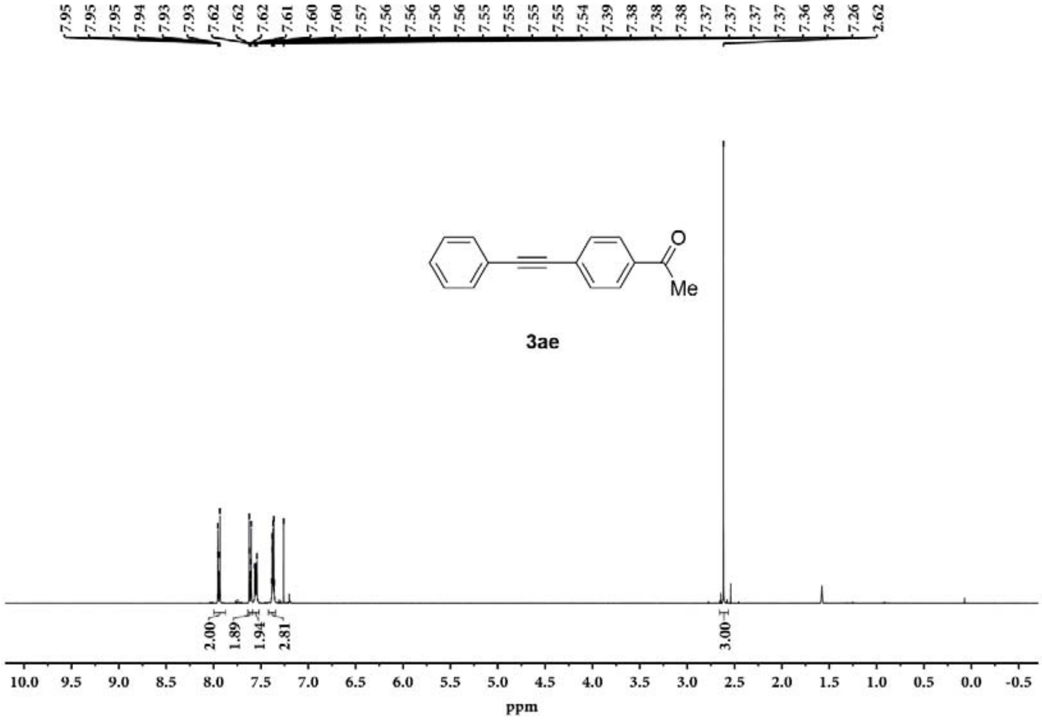
^{1}H NMR (400 MHz), $^{13}C\{^{1}H\}$ NMR (101 MHz), and $^{19}F\{^{1}H\}$ NMR (376 MHz) spectra of **3xb** (rt, $CDCl_3$).

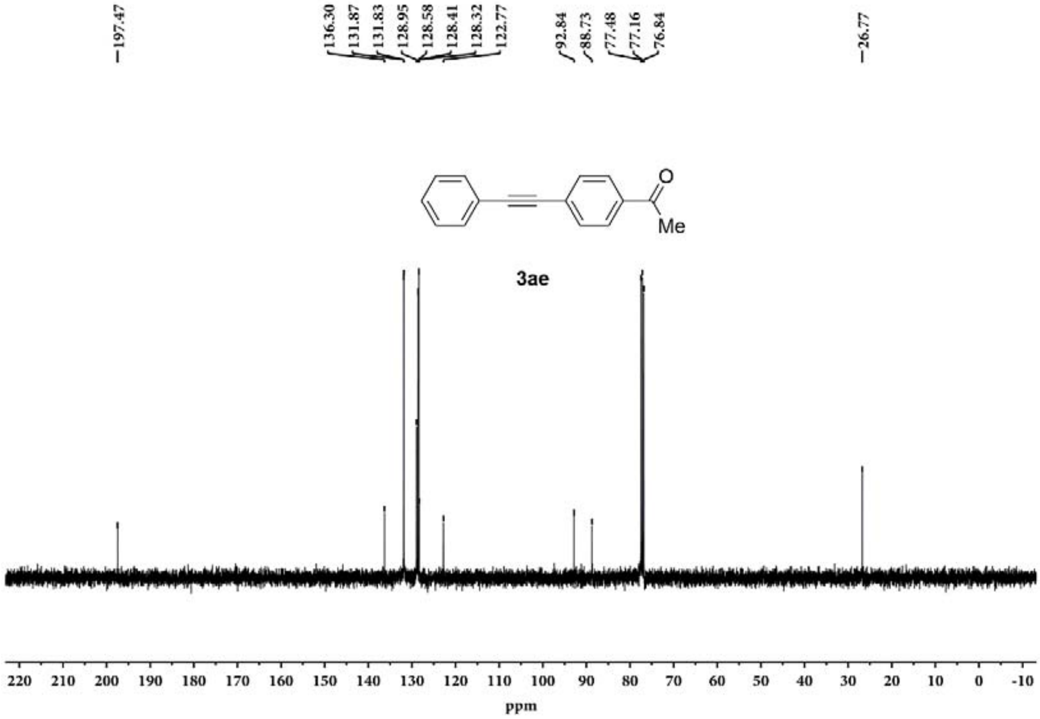

7.60 7.60 7.50 7.50 7.50 7.49 7.48 7.48 7.26 6.91 6.91 6.90 6.89 6.89 6.89
3.84
CF3 OMe
3xc
3.97 2.06 2.10 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


160.18 133.39 131.72 129.81 129.48 127.60 125.49 125.42 125.38 125.34 125.30 122.78 114.73 114.23
92.05 86.97 77.47 77.15 76.83
55.45
CF3 OMe
3xc
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

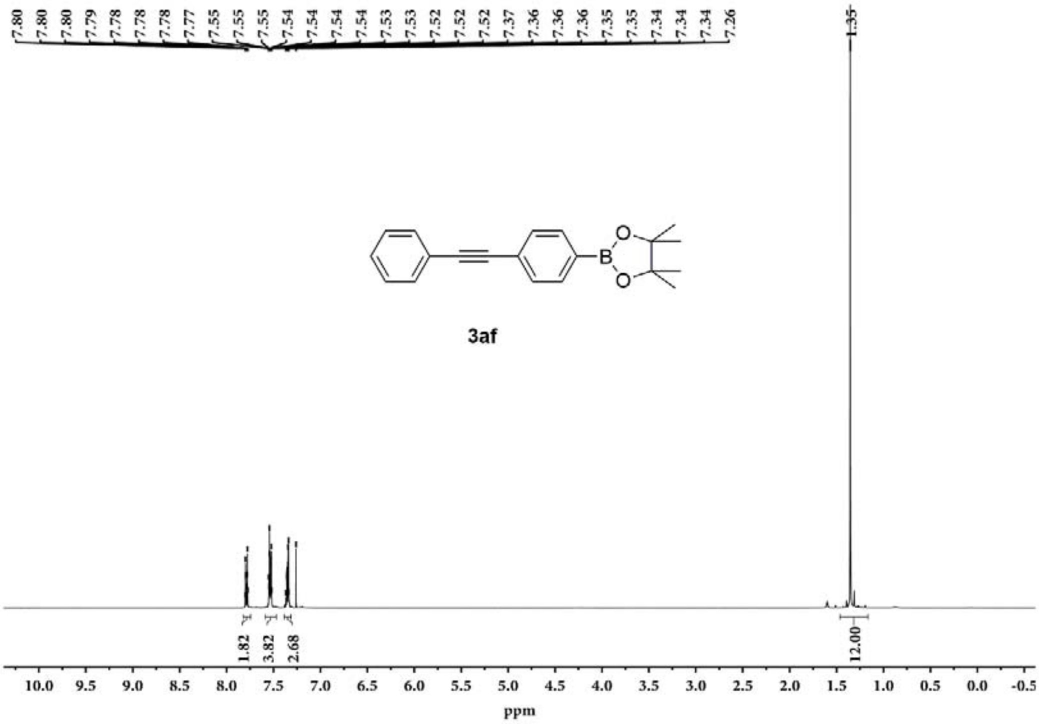


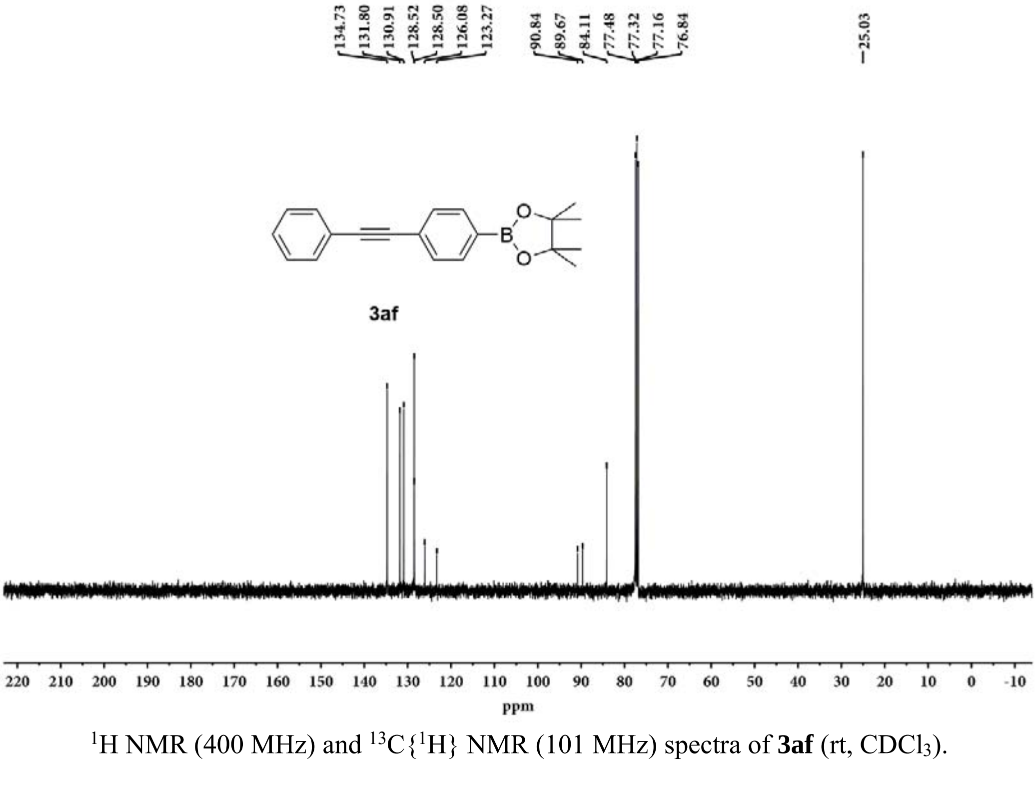
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3xc** (rt, $CDCl_3$).



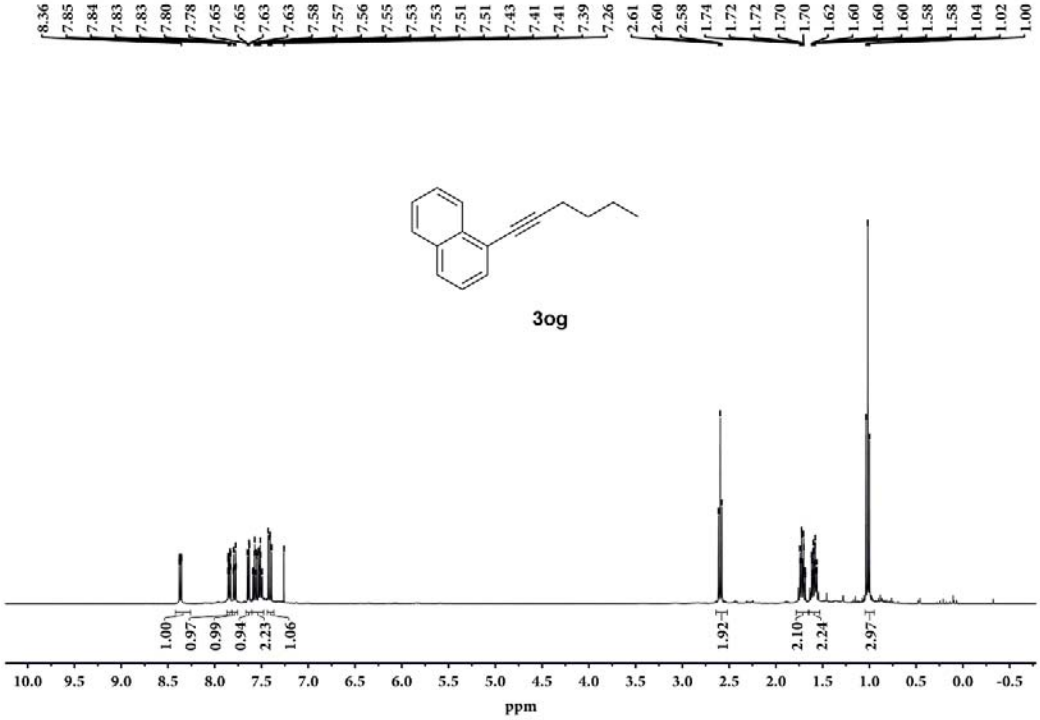


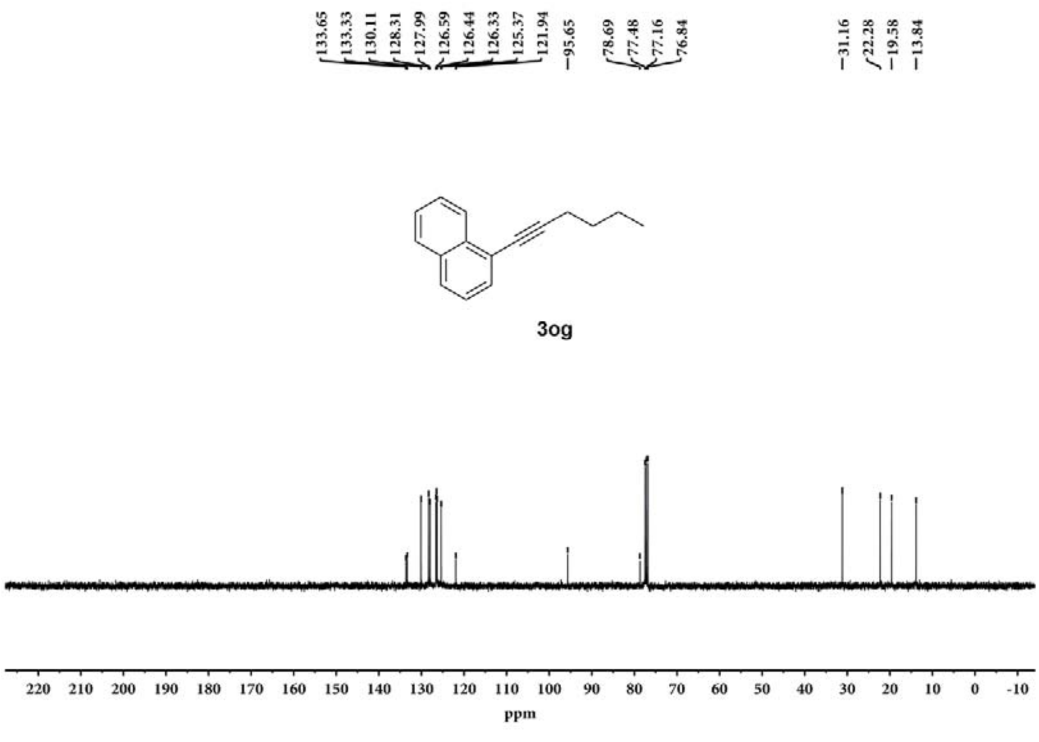
[1]H NMR (400 MHz) and $^{13}C\{^1H\}$ NMR (101 MHz) spectra of **3ae** (rt, $CDCl_3$).



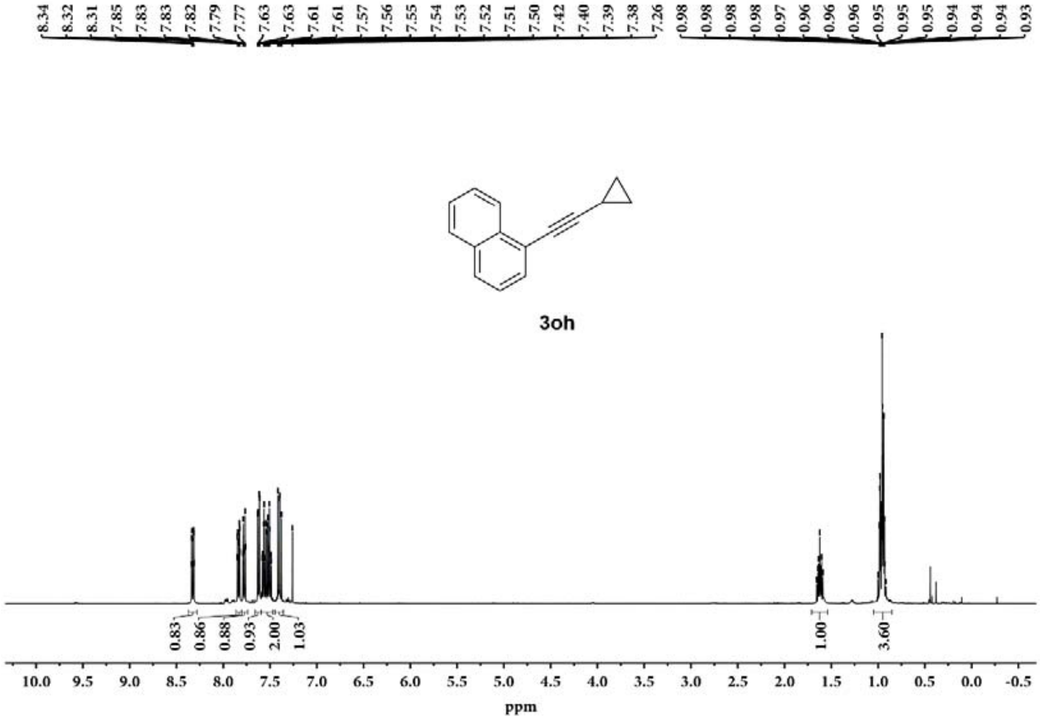


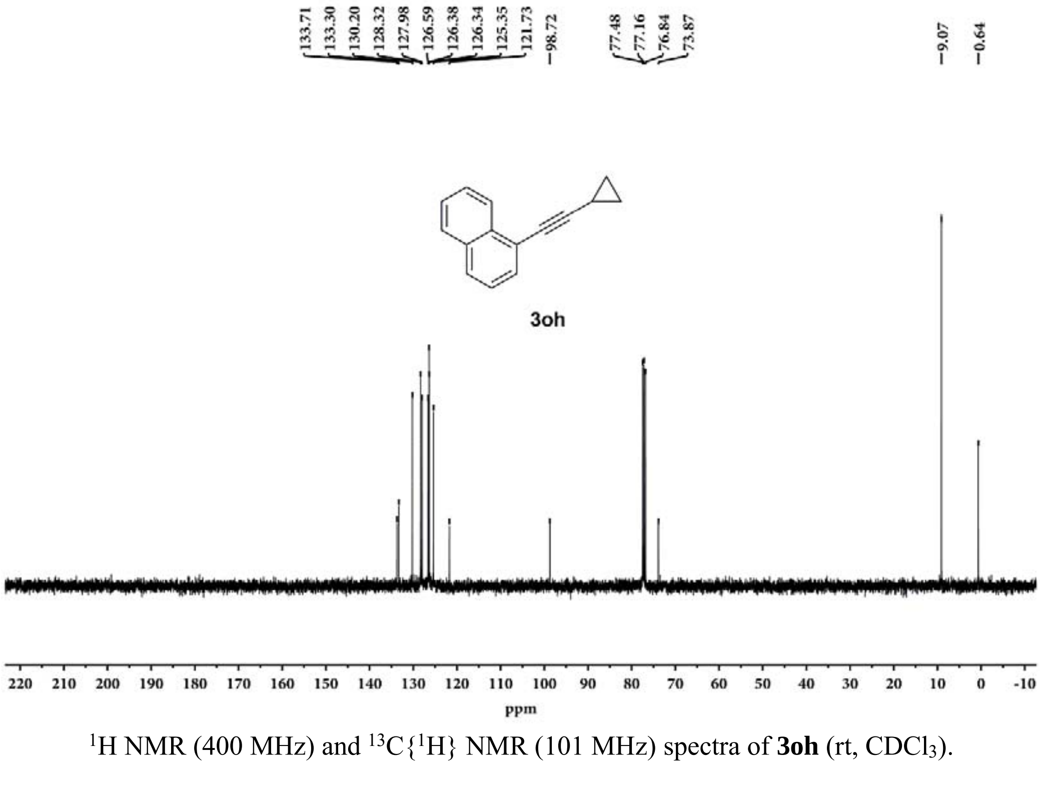
^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **3af** (rt, $CDCl_3$).



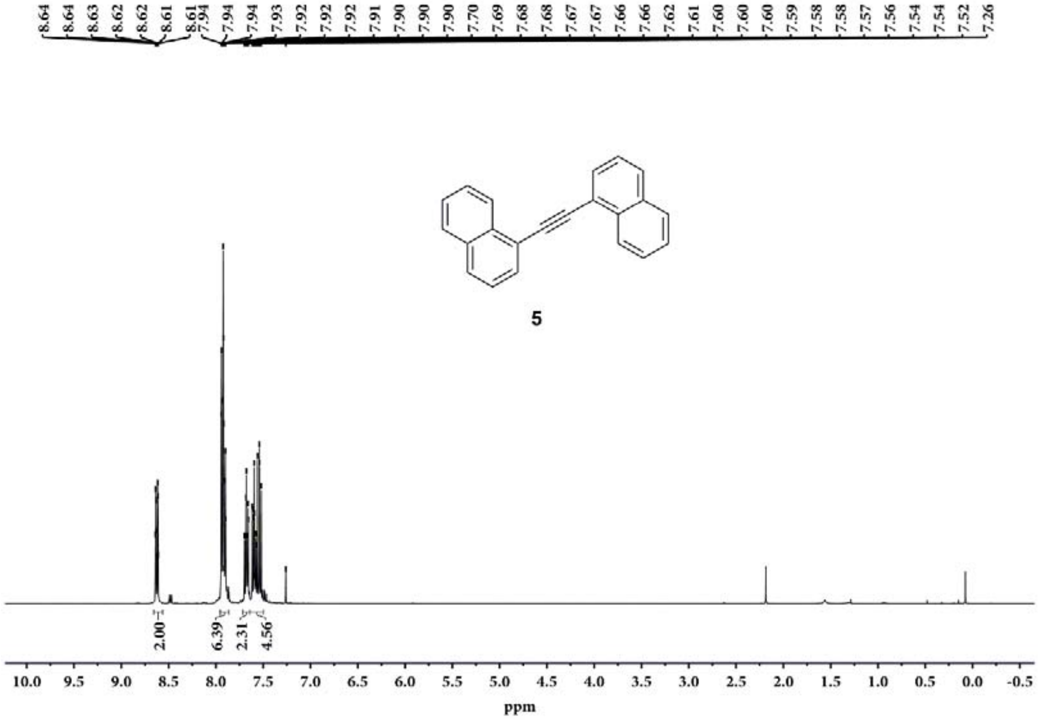


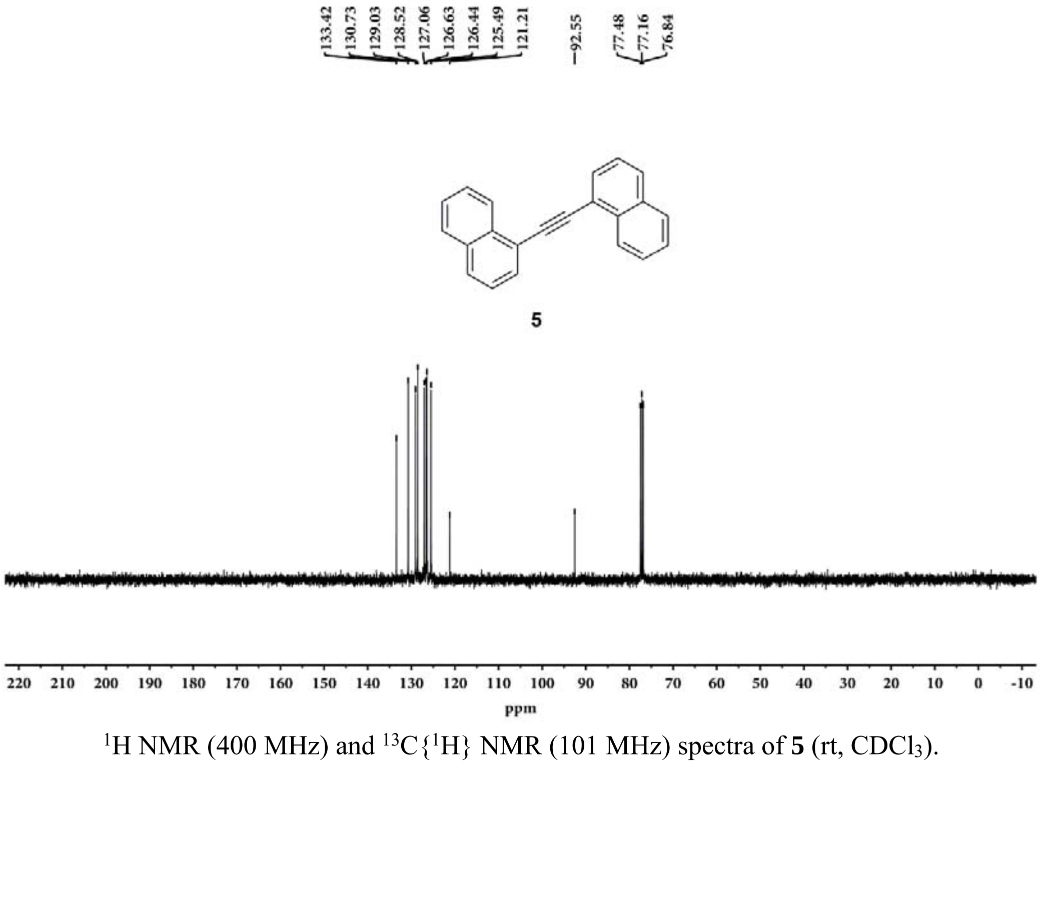
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of **3og** (rt, $CDCl_3$).





^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of **3oh** (rt, $CDCl_3$).





^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **5** (rt, $CDCl_3$).

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