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Electronic Supplementary Information

Palladium-catalyzed cross-coupling of arylcarboxylic acid 2-pyridyl esters with terminal alkynes

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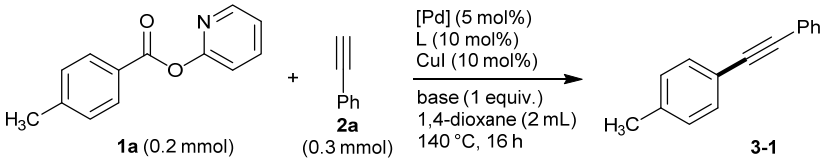
I. Optimization of reaction conditions

Table S1. Optimization of reaction conditions[a]



Entry	[Pd]	L	Base	Solvent	Yield[b] (%)
1	$Pd(OAc)_2$	iMes·HCl	Na_2CO_3	dioxane	0
2	$Pd(OAc)_2$	PPh_3	Na_2CO_3	dioxane	7
3	$Pd(OAc)_2$	dppe	Na_2CO_3	dioxane	20
4	$Pd(OAc)_2$	dppp	Na_2CO_3	dioxane	56
5	$Pd(OAc)_2$	dppf	Na_2CO_3	dioxane	36
6	$Pd(OAc)_2$	dcype	Na_2CO_3	dioxane	trace
7	$Pd(OAc)_2$	xantphos	Na_2CO_3	dioxane	trace
8	$PdCl_2$	dppp	Na_2CO_3	dioxane	37
9	$PdCl_2(CH_3CN)_2$	dppp	Na_2CO_3	dioxane	39
10	$[Pd(\pi\text{-allyl})Cl]_2$	dppp	Na_2CO_3	dioxane	41
11	PEPPSI-IPr	dppp	Na_2CO_3	dioxane	34
12	$PdCl_2(PPh_3)_2$	dppp	Na_2CO_3	dioxane	37
13	$PdCl_2(PCy_3)_2$	dppp	Na_2CO_3	dioxane	38
14	$PdCl_2$(dppf)	dppp	Na_2CO_3	dioxane	71
15	Pd_2dba_3	dppp	Na_2CO_3	dioxane	63
16	$Pd(PPh_3)_4$	dppp	Na_2CO_3	dioxane	47
17	$PdCl_2$(dppf)	dppp	K_2CO_3	dioxane	<5
18	$PdCl_2$(dppf)	dppp	Cs_2CO_3	dioxane	trace
19	$PdCl_2$(dppf)	dppp	$NaHCO_3$	dioxane	53
20	$PdCl_2$(dppf)	dppp	NaOAc	dioxane	54
21	$PdCl_2$(dppf)	dppp	*t*BuONa	dioxane	11
22	$PdCl_2$(dppf)	dppp	Na_2CO_3	toluene	46
23	$PdCl_2$(dppf)	dppp	Na_2CO_3	THF	47
24	$PdCl_2$(dppf)	dppp	Na_2CO_3	DME	37
25[c]	$PdCl_2$(dppf)	dppp	Na_2CO_3	dioxane	88
26[d]	$PdCl_2$(dppf)	dppp	Na_2CO_3	dioxane	>99
27[e]	$PdCl_2$(dppf)	dppp	Na_2CO_3	dioxane	49
28[d,f]	$PdCl_2$(dppf)	dppp	Na_2CO_3	dioxane	90
29[d,g]	$PdCl_2$(dppf)	dppp	Na_2CO_3	dioxane	81
30[d,h]	$PdCl_2$(dppf)	dppp	Na_2CO_3	dioxane	>99

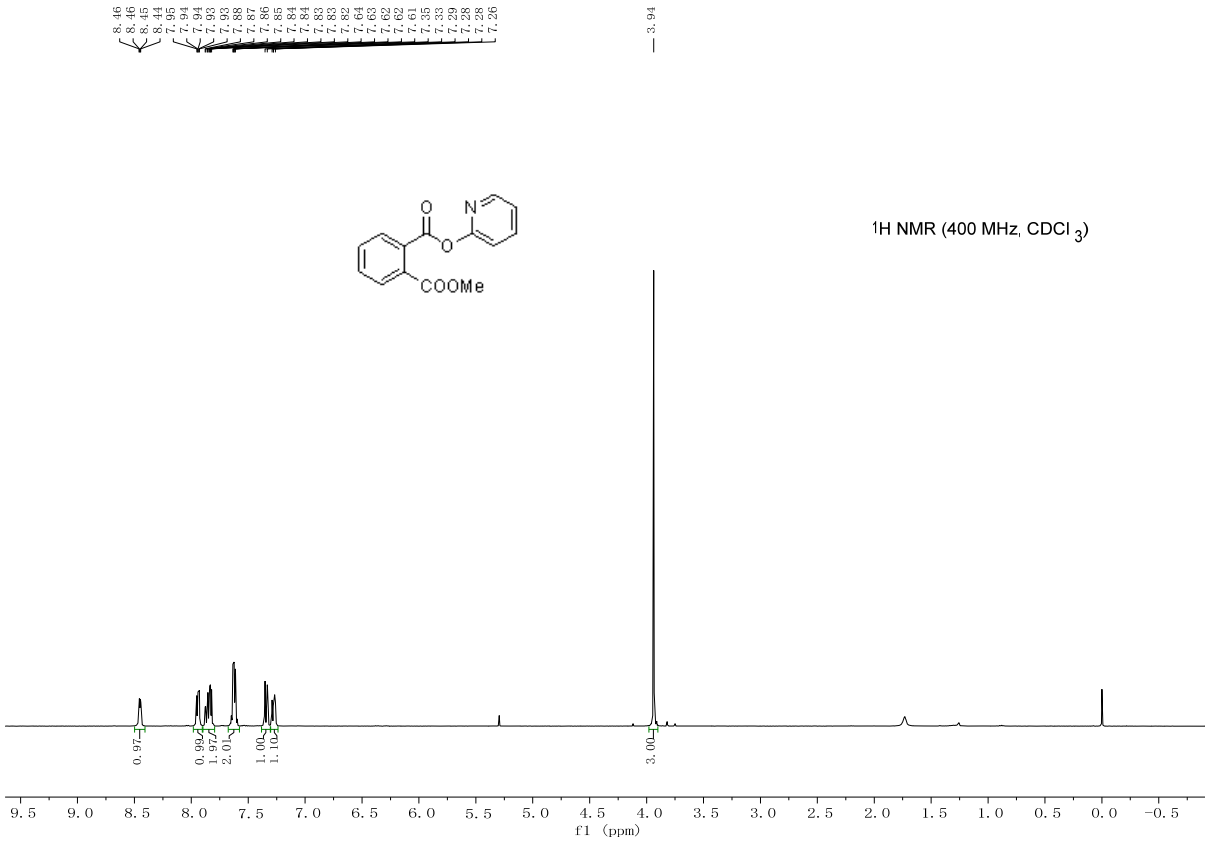
31[d]	$PdCl_2$(dppf)	dppp	-	dioxane	13
32[d,h,i]	$PdCl_2$(dppf)	dppp	Na_2CO_3	dioxane	86
33[d,h,j]	$PdCl_2$(dppf)	dppp	Na_2CO_3	dioxane	76
34[d,h]	-	dppp	Na_2CO_3	dioxane	0
35[d,h,k]	$PdCl_2$(dppf)	dppp	Na_2CO_3	dioxane	67

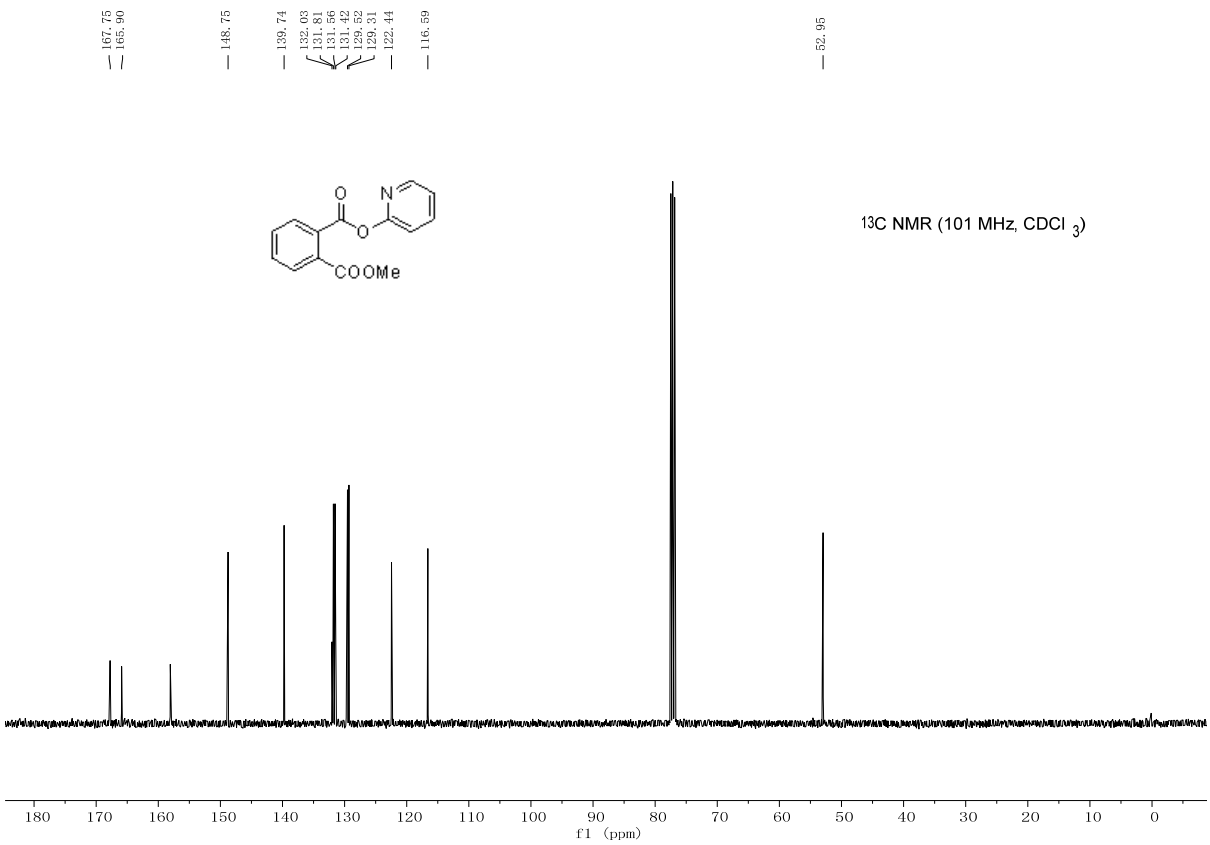
[a] Unless otherwise noted, the reactions were carried out according to the conditions indicated in the above equation. [b] Yields were determined by ^{1}H NMR spectral analysis with tetrachloroethane as an internal standard. [c] 2 equiv. of **2a** were used. [d] 3 equiv. of **2a** were used. [e] 0.3 mmol **1a** and 0.2 mmol **2a** were used. [f] 5 mol% CuI was used. [g] The reaction temperature was 130 °C. [h] 0.5 equiv. of Na_2CO_3 was used. [i] 5 mol% of dppp were used. [j] 2.5 mol% $PdCl_2$(dppf) and 5 mol% dppp were used. [k] The reaction was carried out in air.

II. NMR spectral copies of unreported reactants and the cross-coupling products

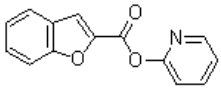
1. NMR spectral copies of the unreported pyridyl esters

(1) methyl pyridin-2-yl phthalate (**1j**)

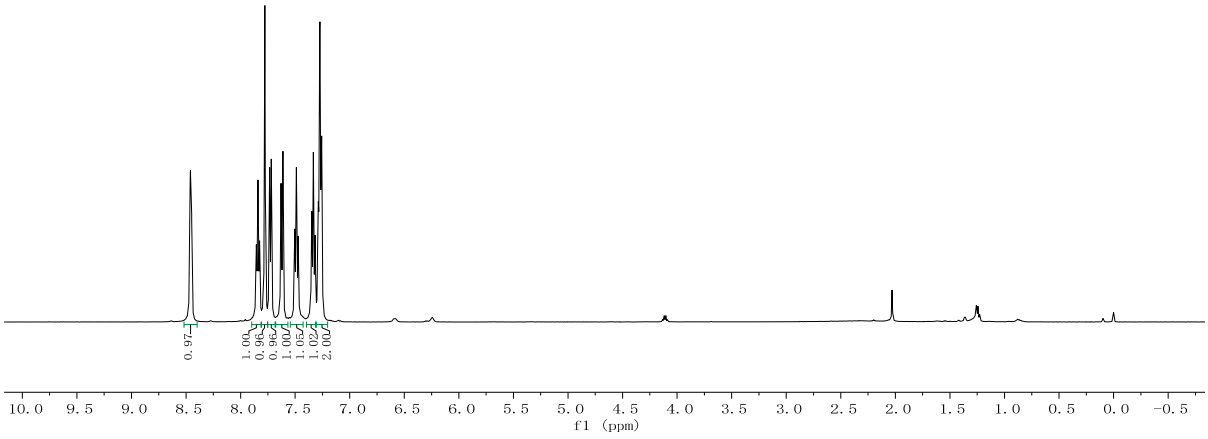


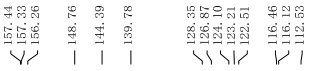


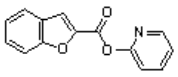
(2) pyridin-2-yl benzofuran-2-carboxylate (**1r**)



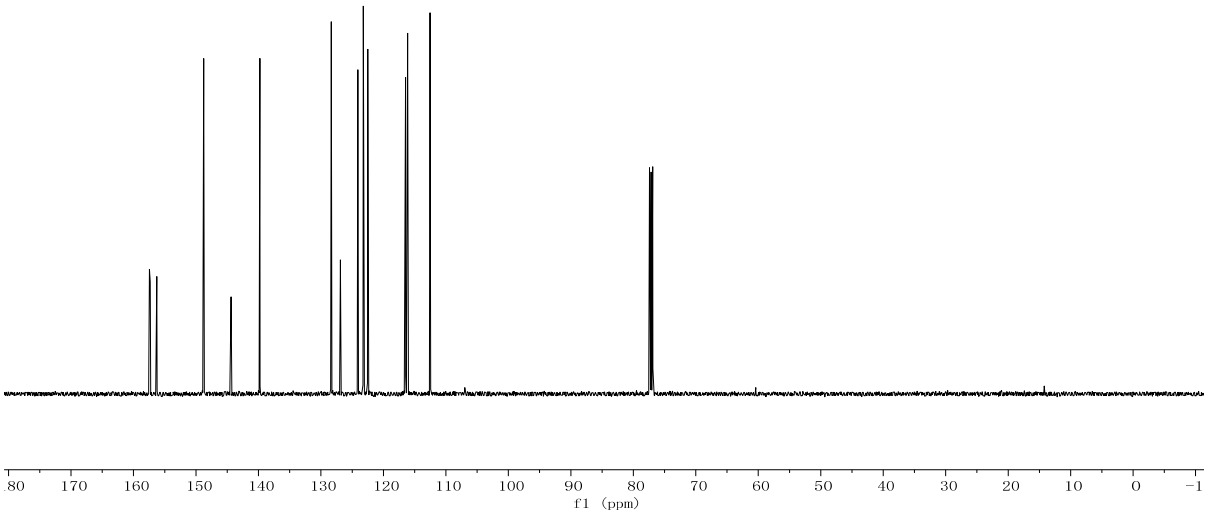
^{1}H NMR (500 MHz, CDCl $_{3}$)



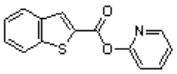


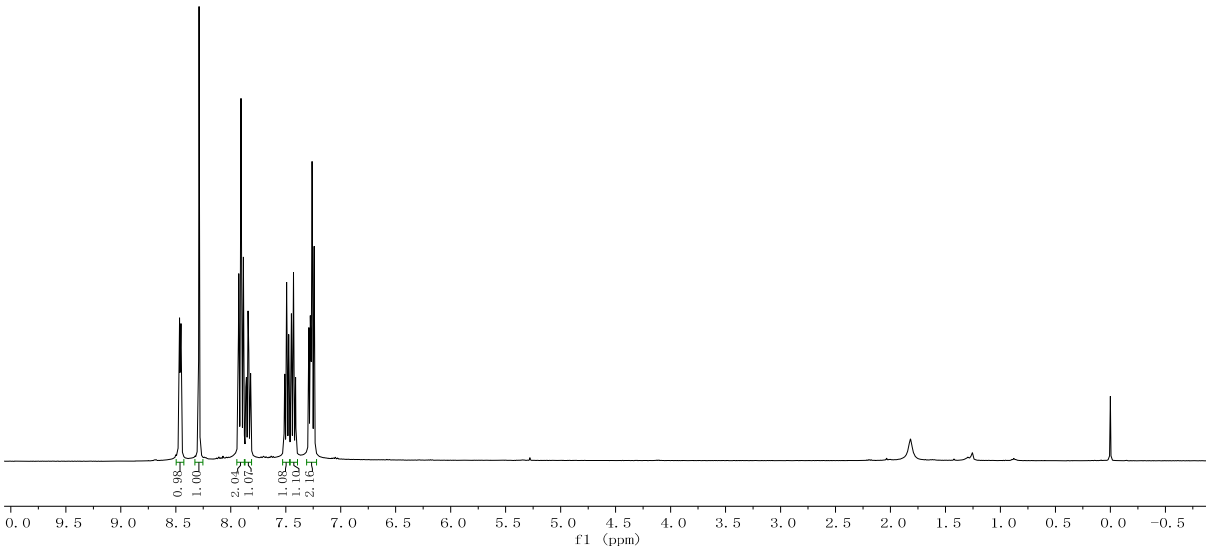


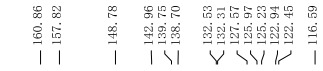
^{13}C NMR (126 MHz, CDCl $_{3}$)

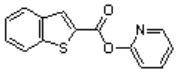


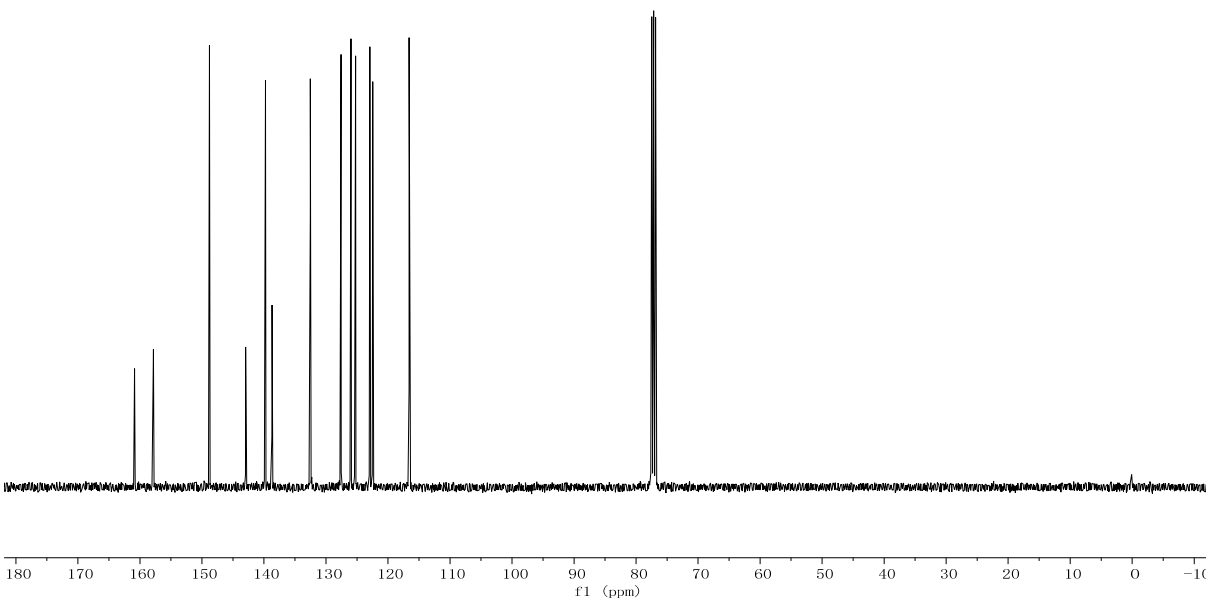
(3) pyridin-2-yl benzo[*b*]thiophene-2-carboxylate (**1s**)



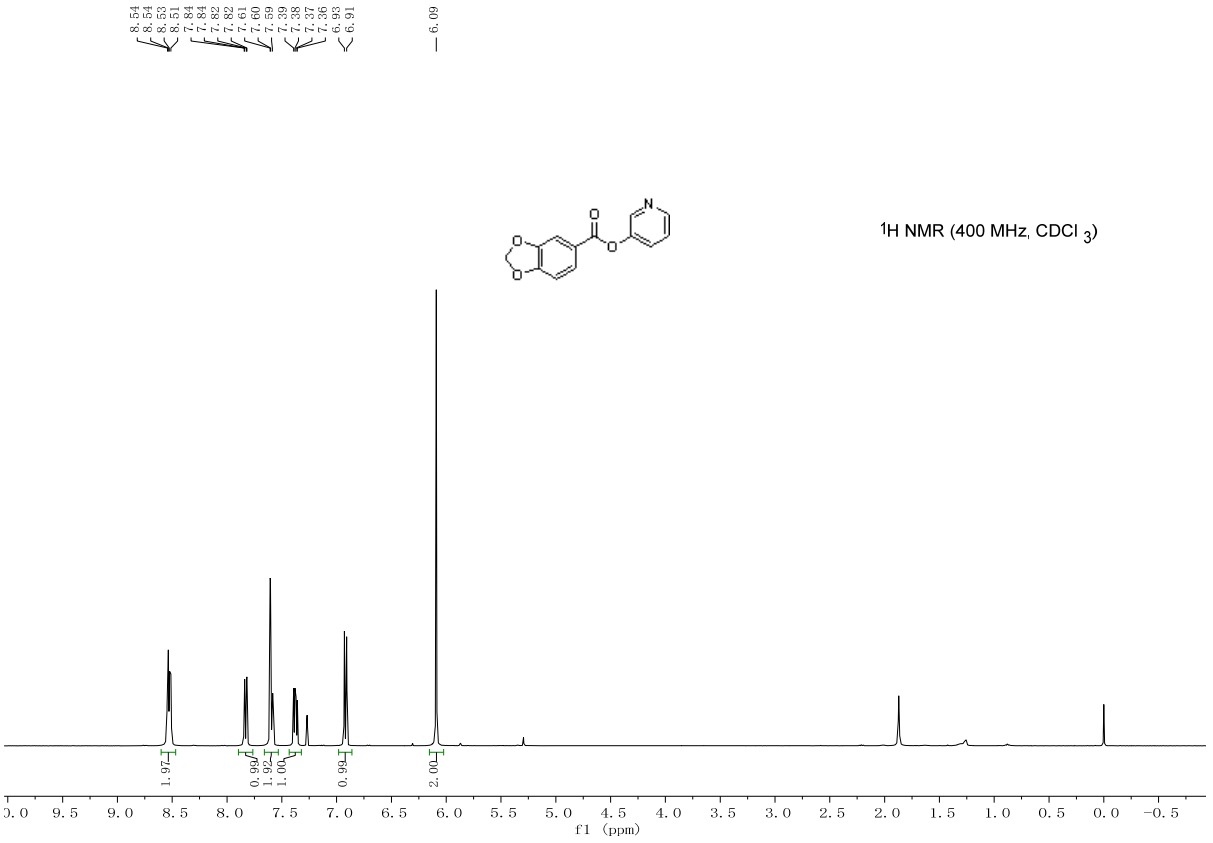


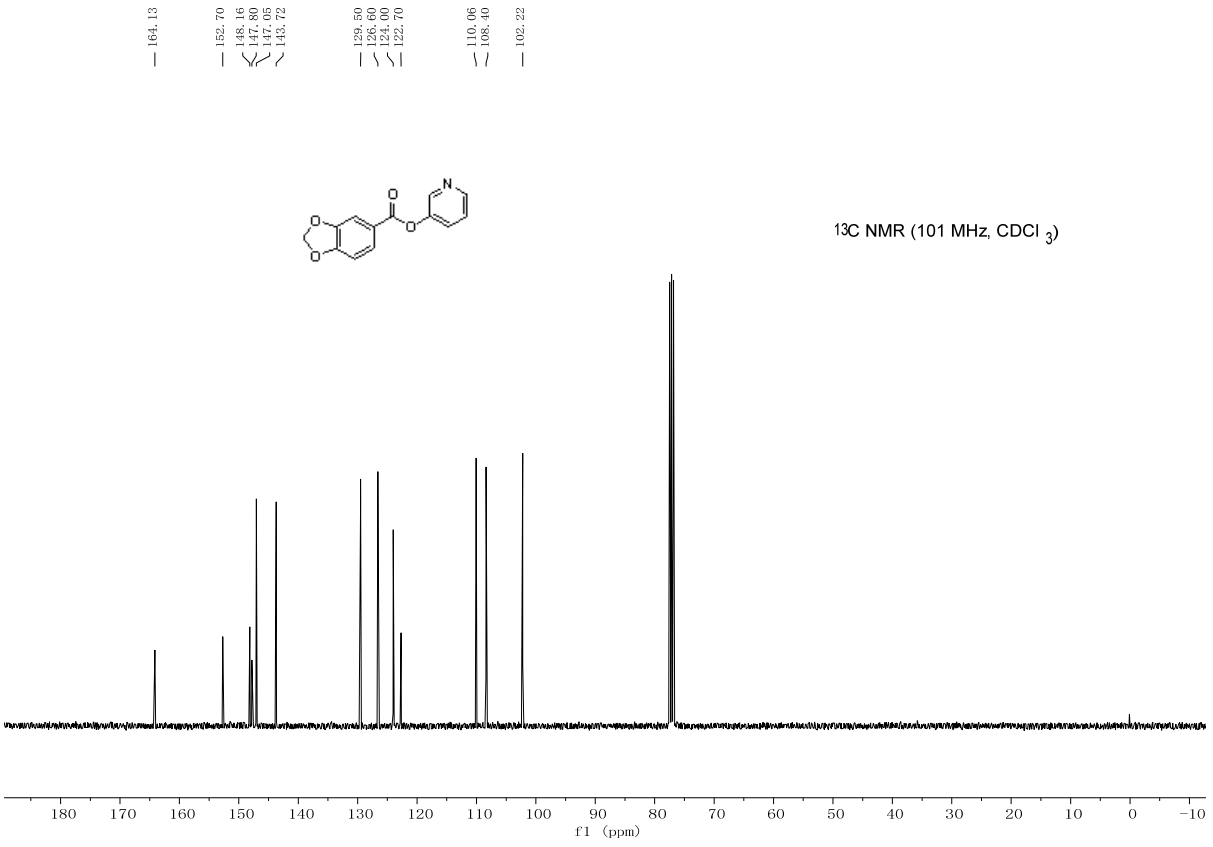




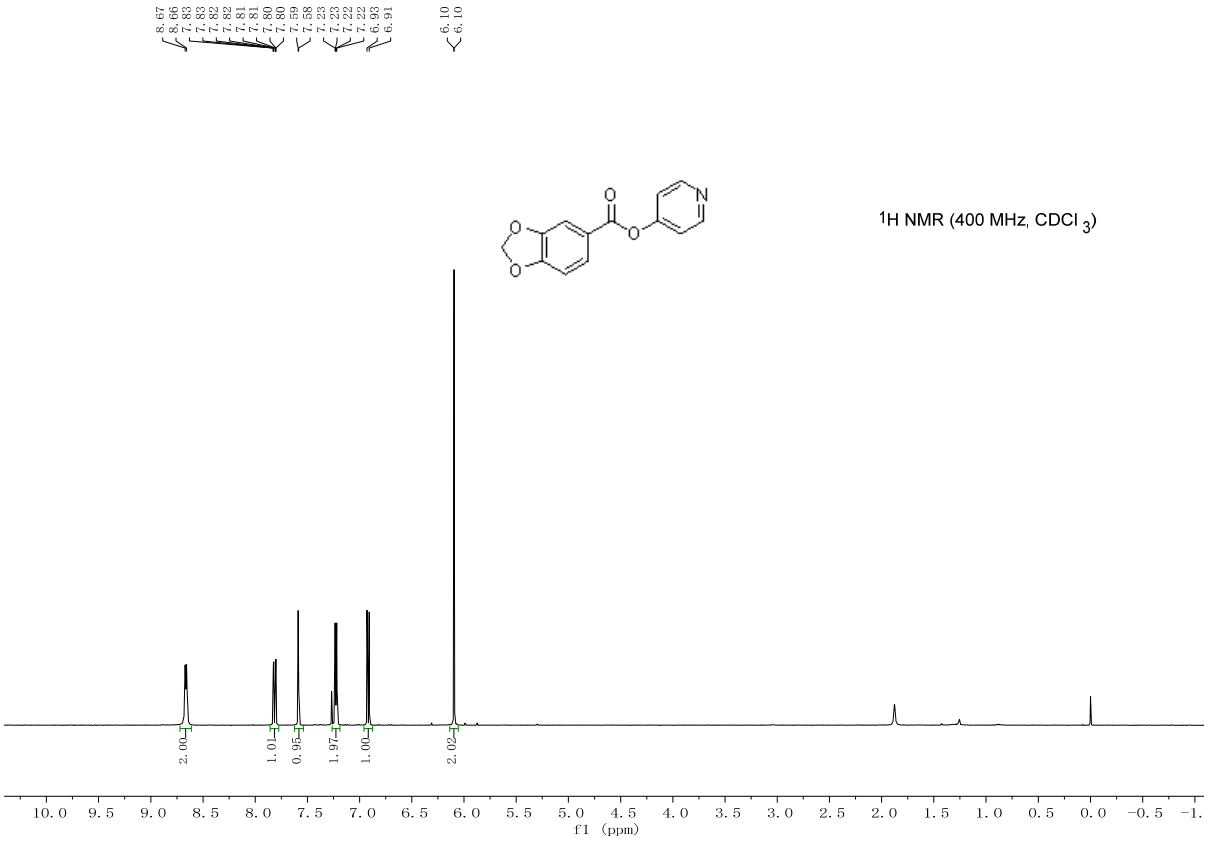


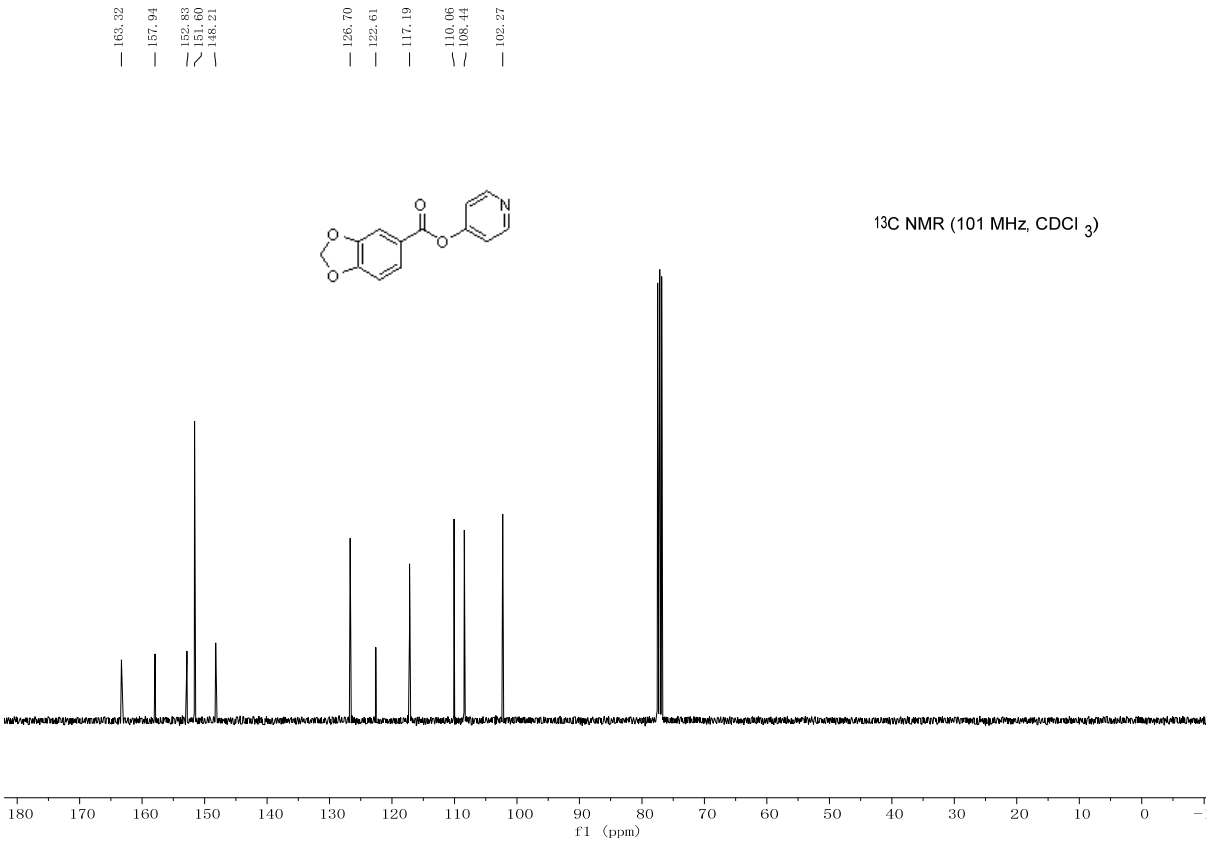
(4) pyridin-3-yl benzo[*d*][1,3]dioxole-5-carboxylate (**1w**)



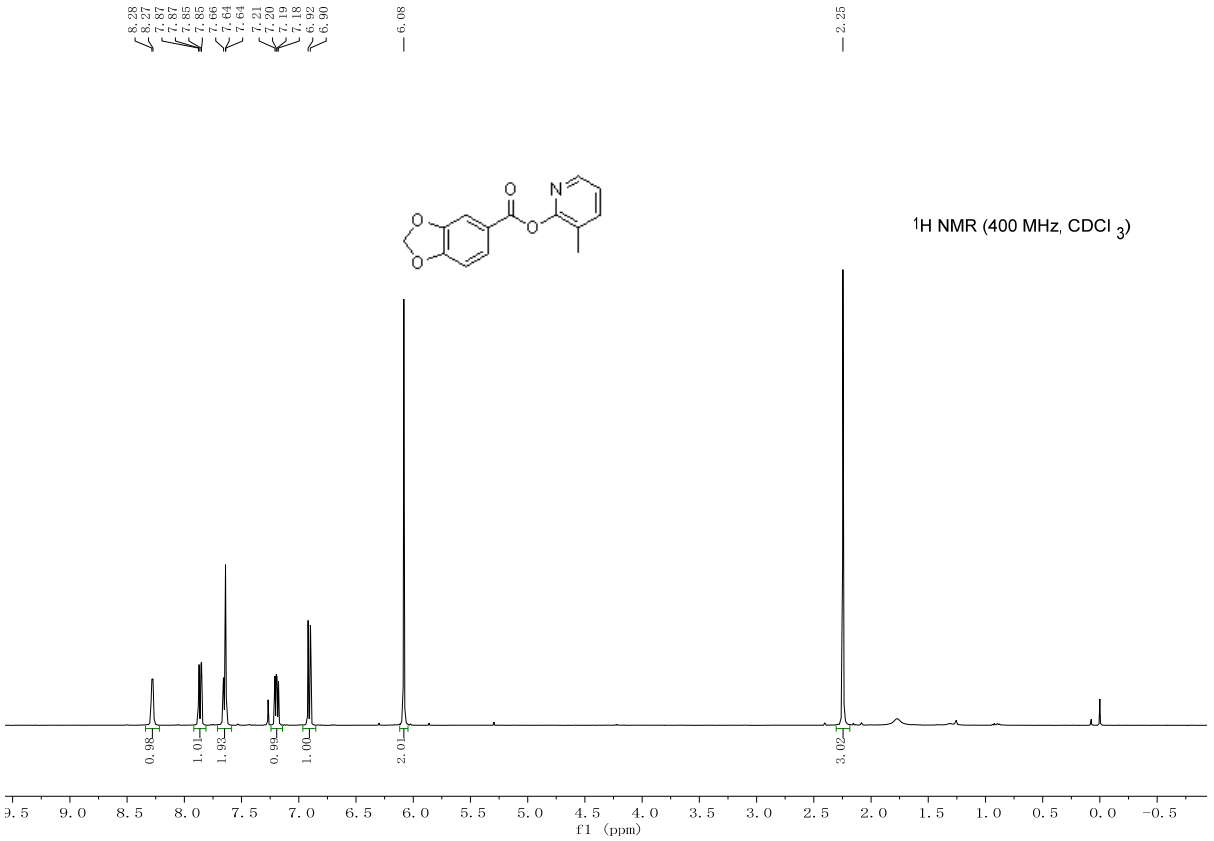


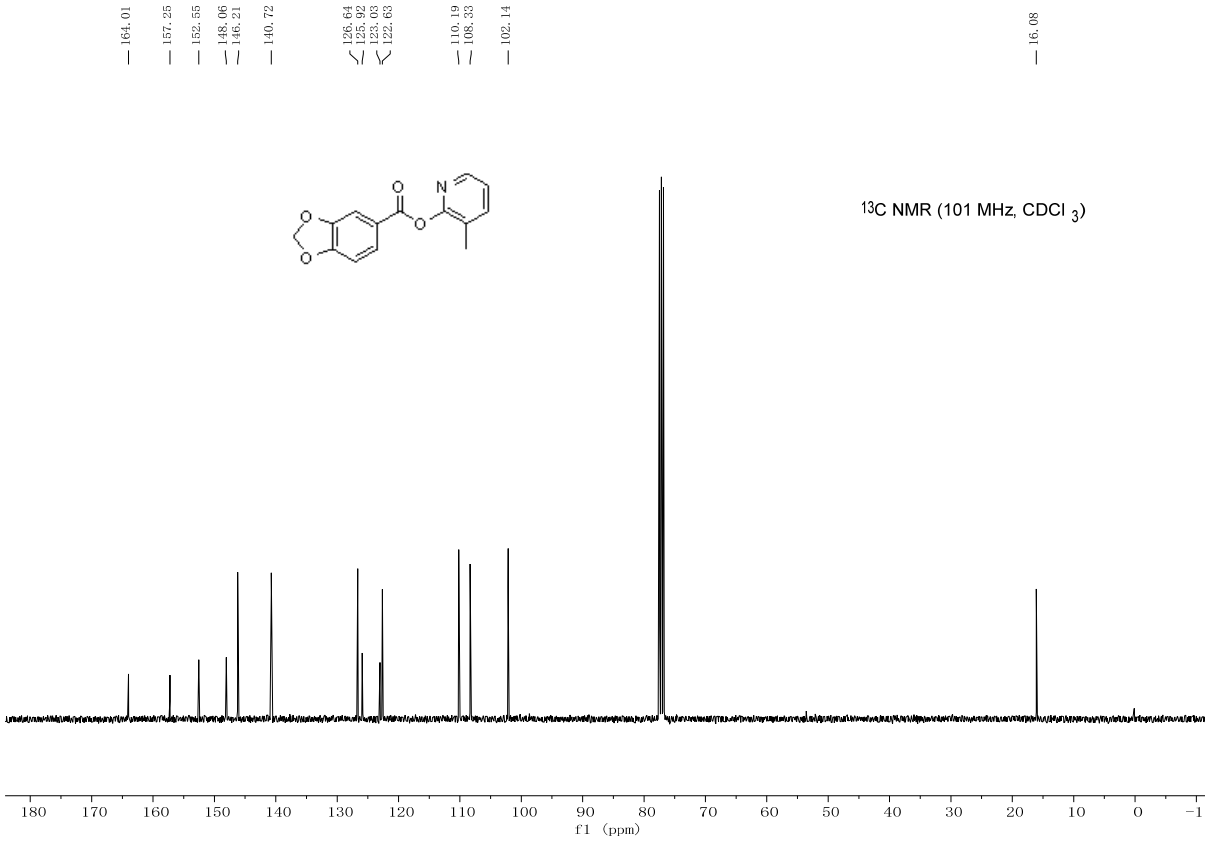
(5) pyridin-4-yl benzo[*d*][1,3]dioxole-5-carboxylate (**1x**)





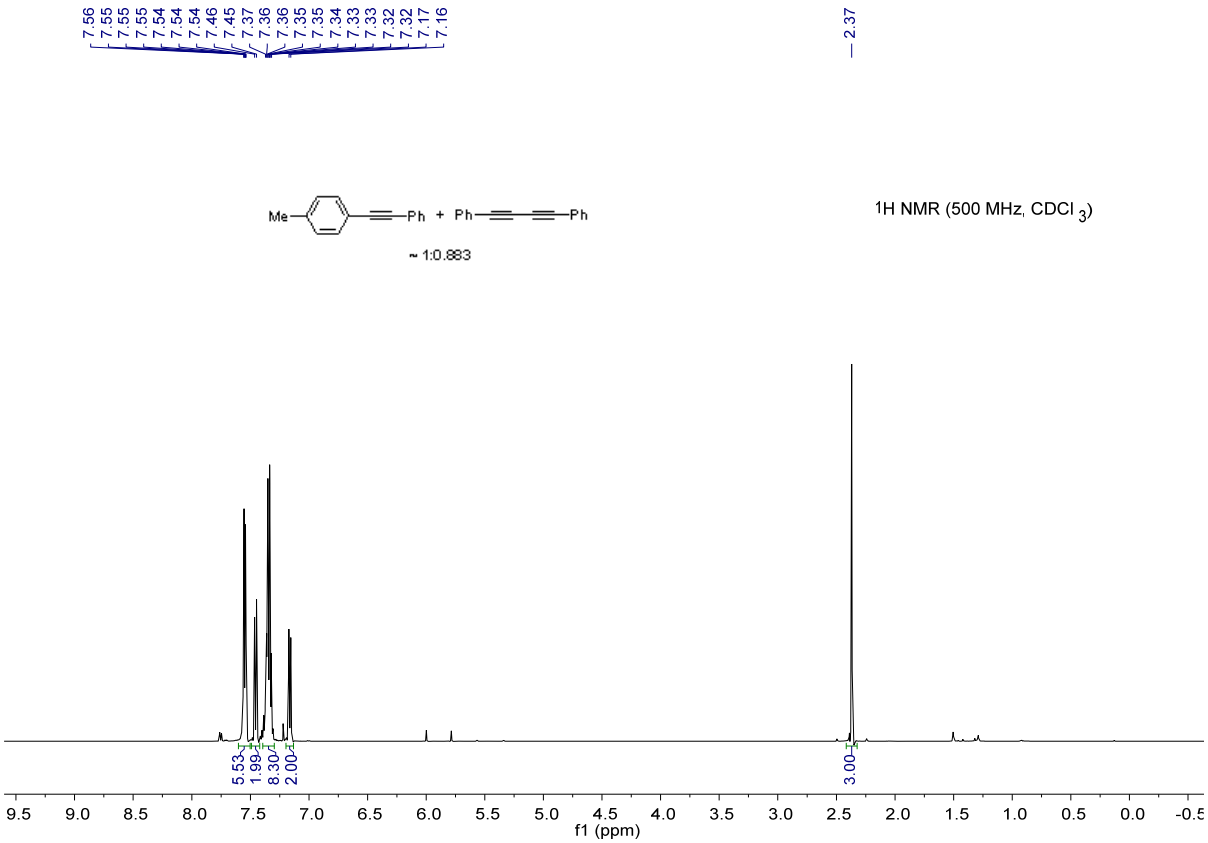
(6) 3-methylpyridin-2-yl benzo[*d*][1,3]dioxole-5-carboxylate (**1y**)

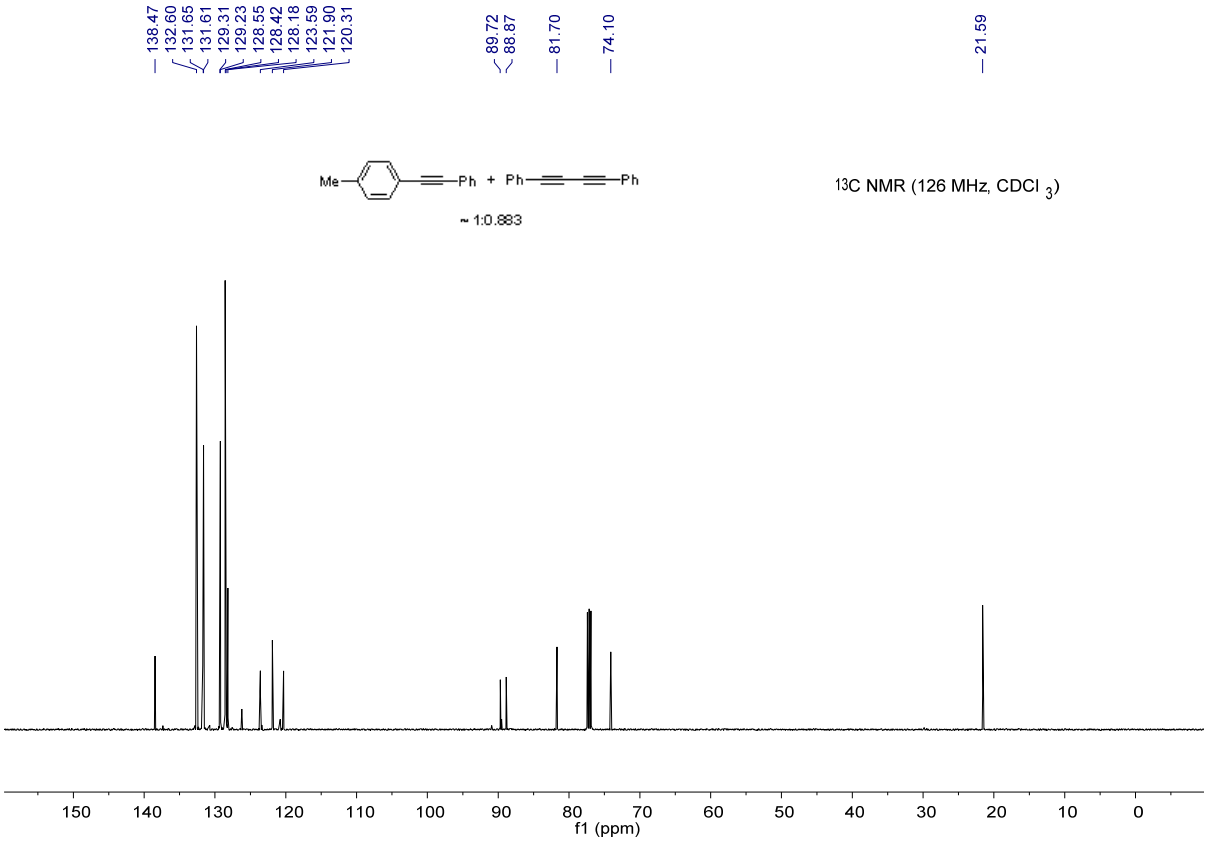




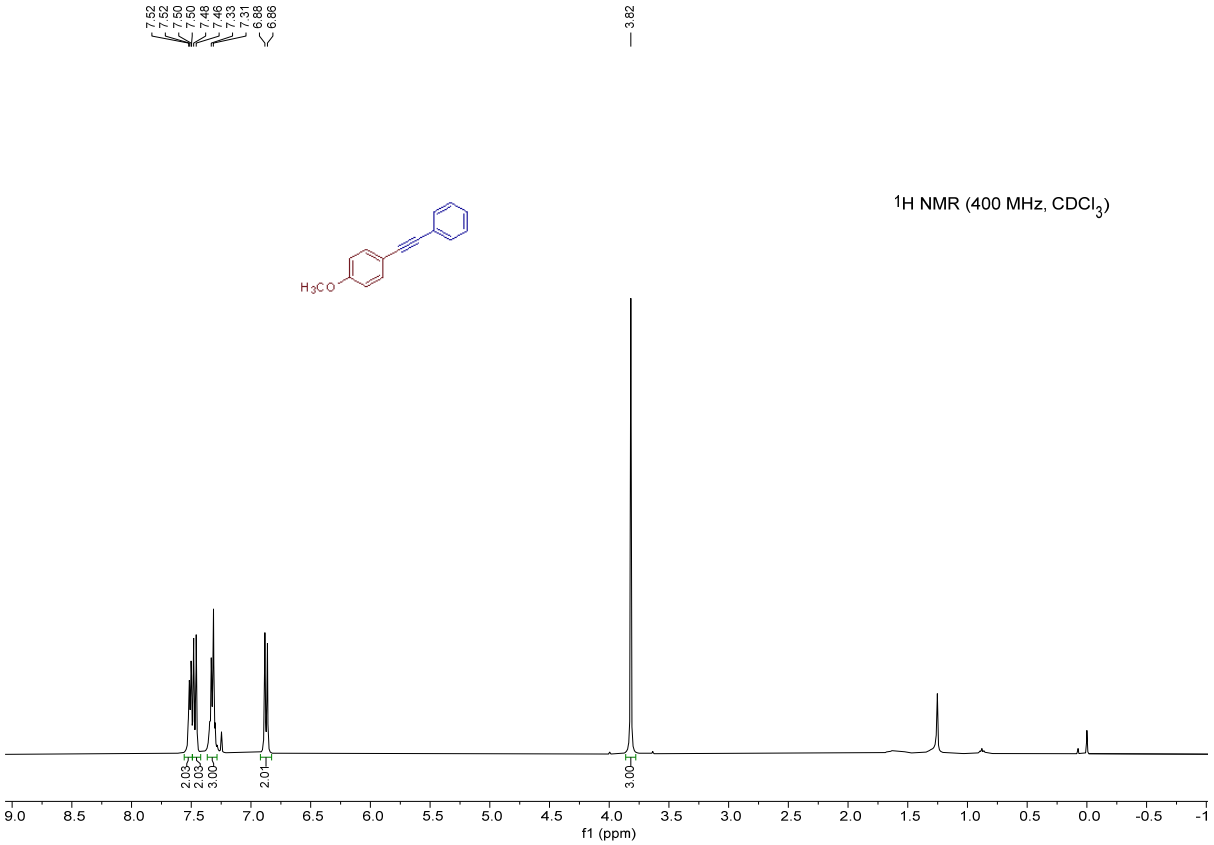
2. NMR spectral copies of the cross-coupling products

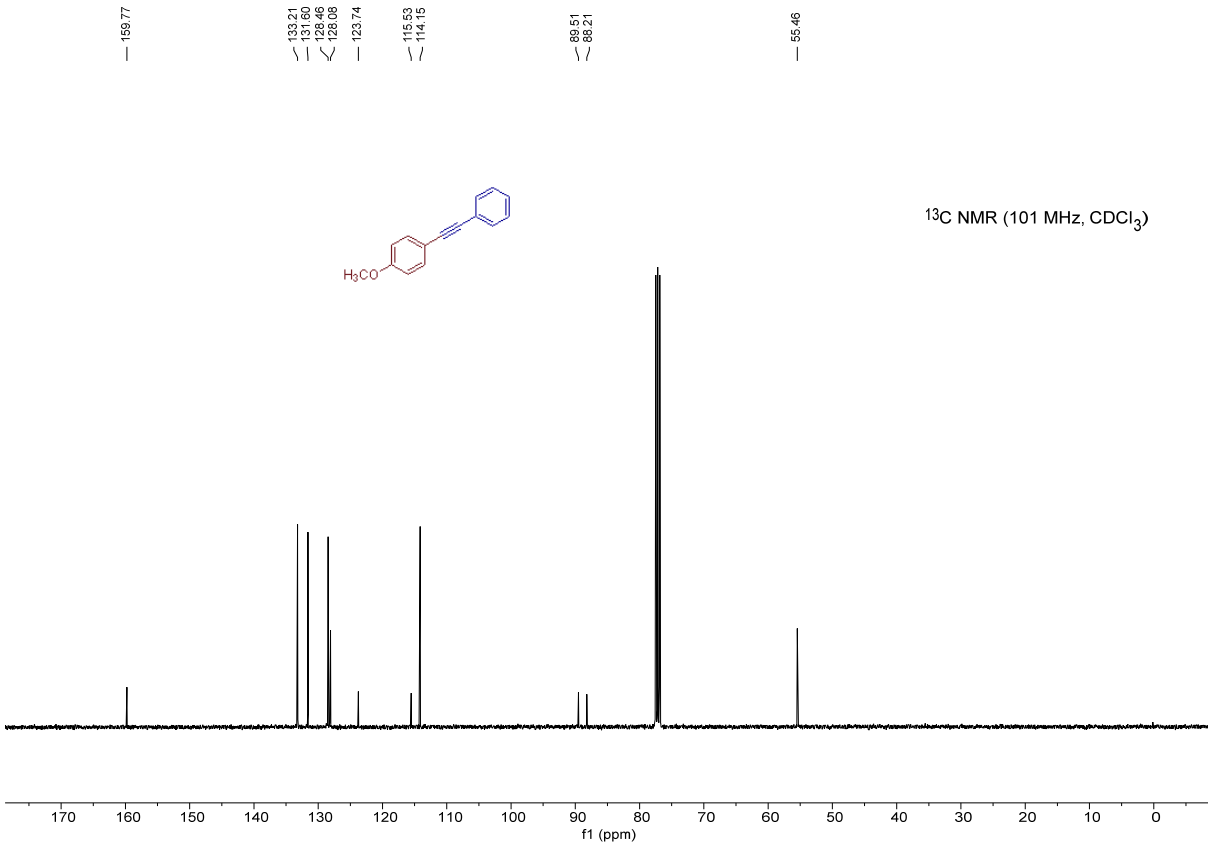
(1) 1-methyl-4-(phenylethynyl)benzene (**3-1**) and 1,4-diphenylbuta-1,3-diyne



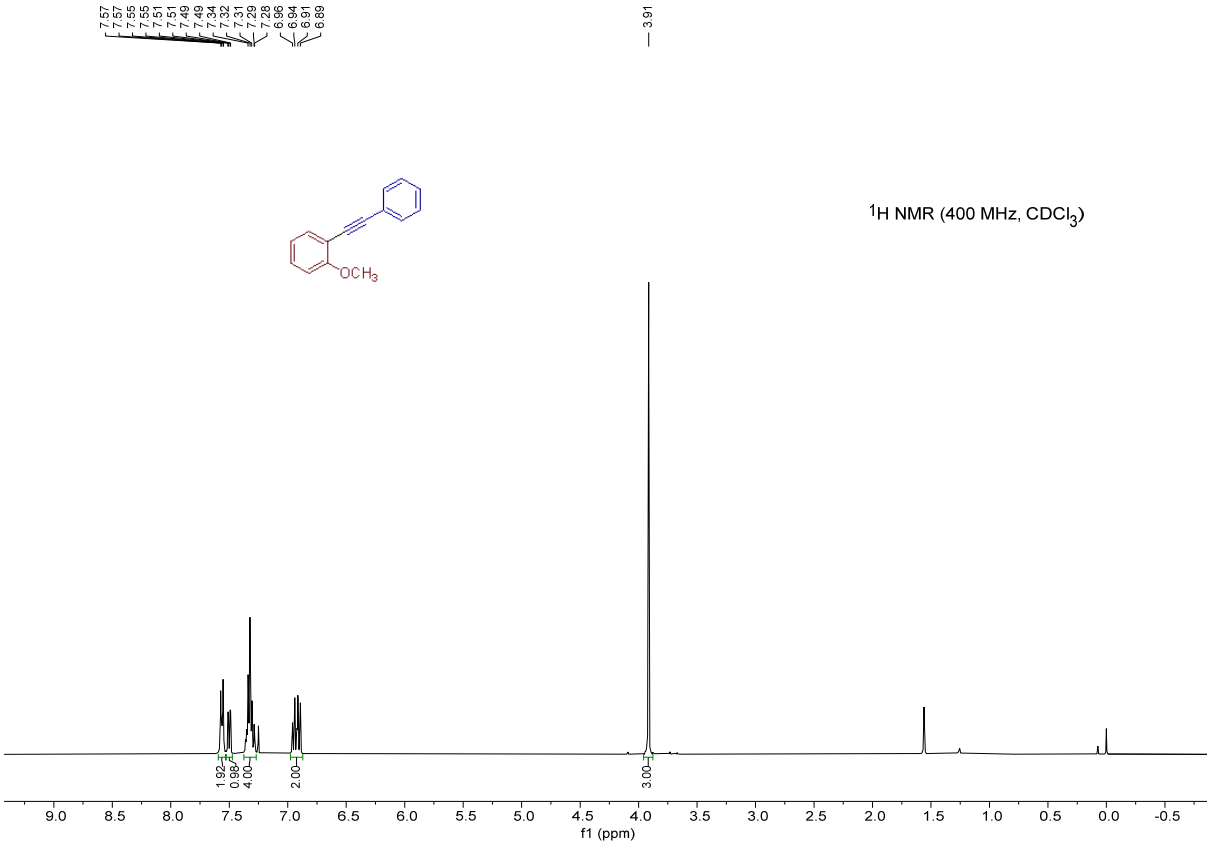


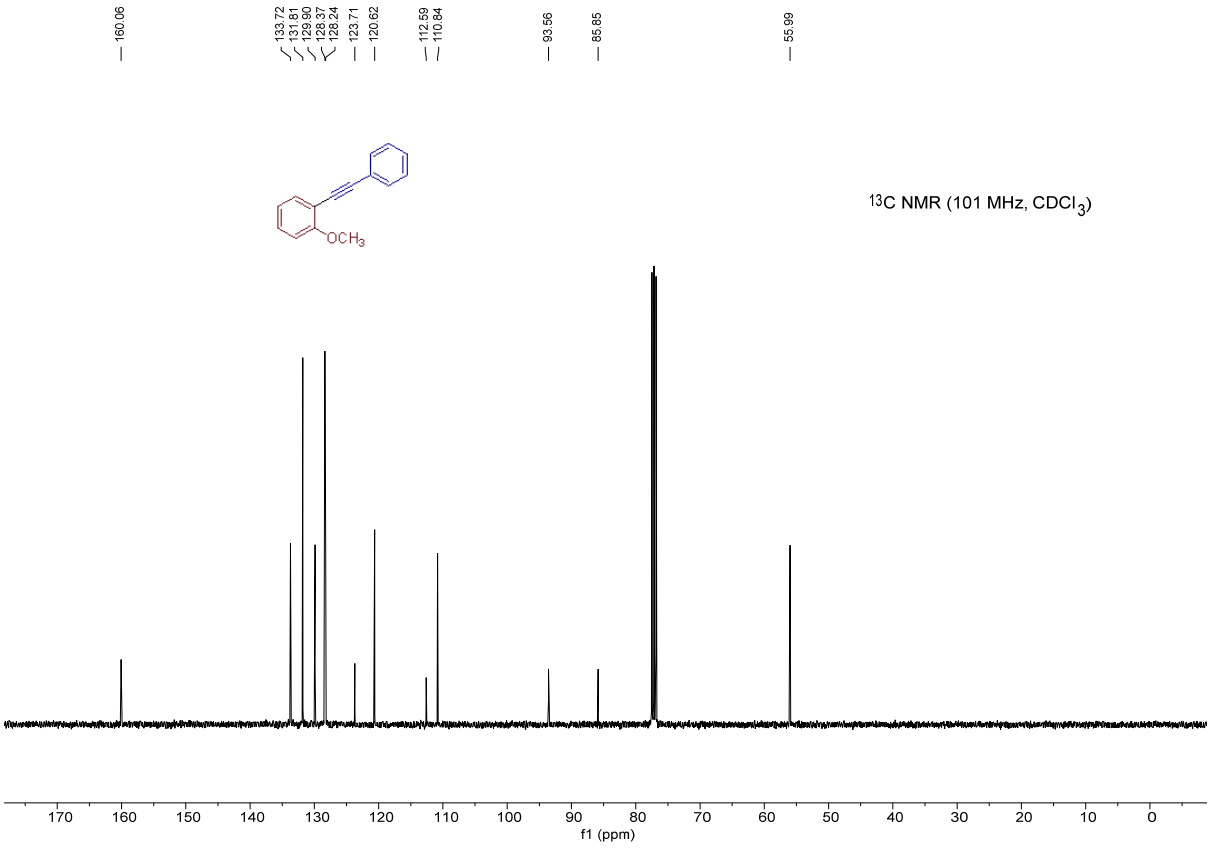
(2) 1-methoxy-4-(phenylethynyl)benzene (**3-2**)



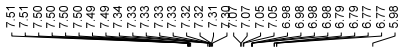


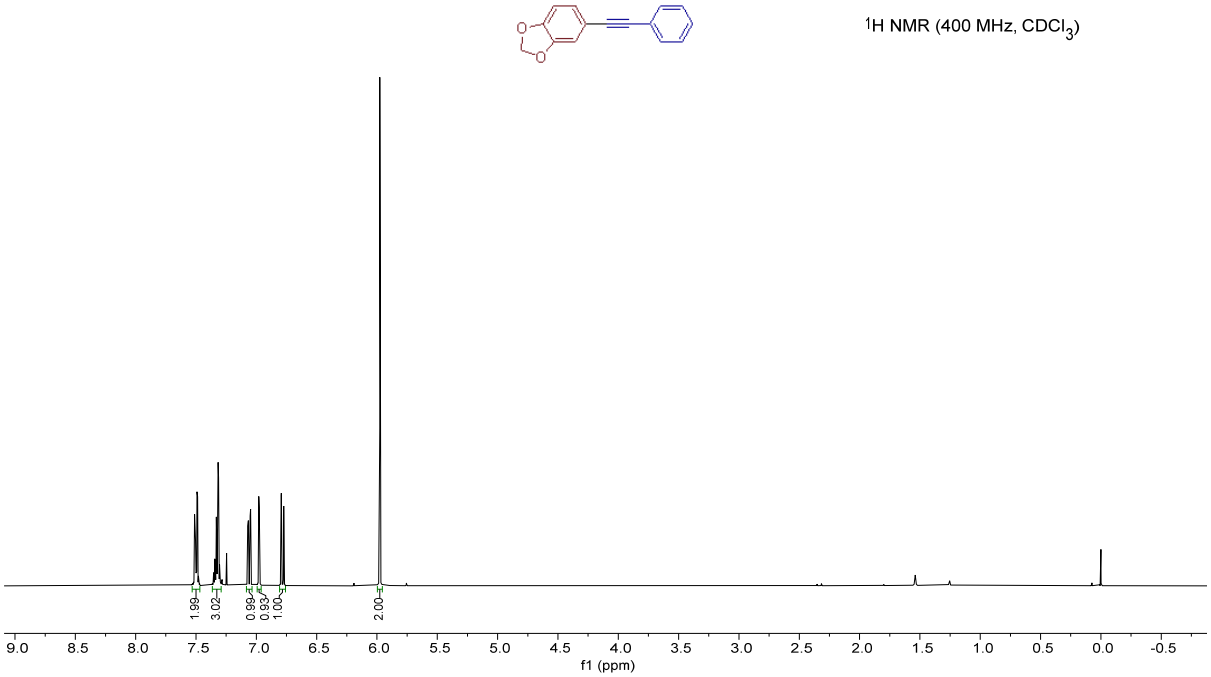
(3) 1-methoxy-2-(phenylethynyl)benzene (**3-3**)

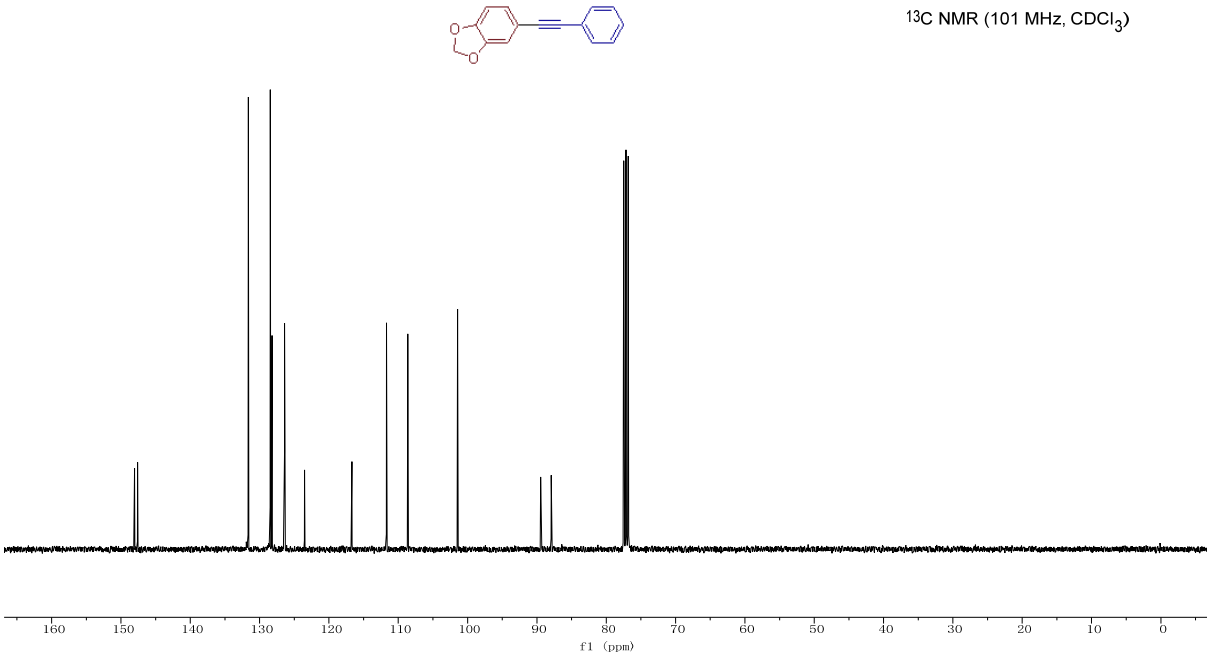




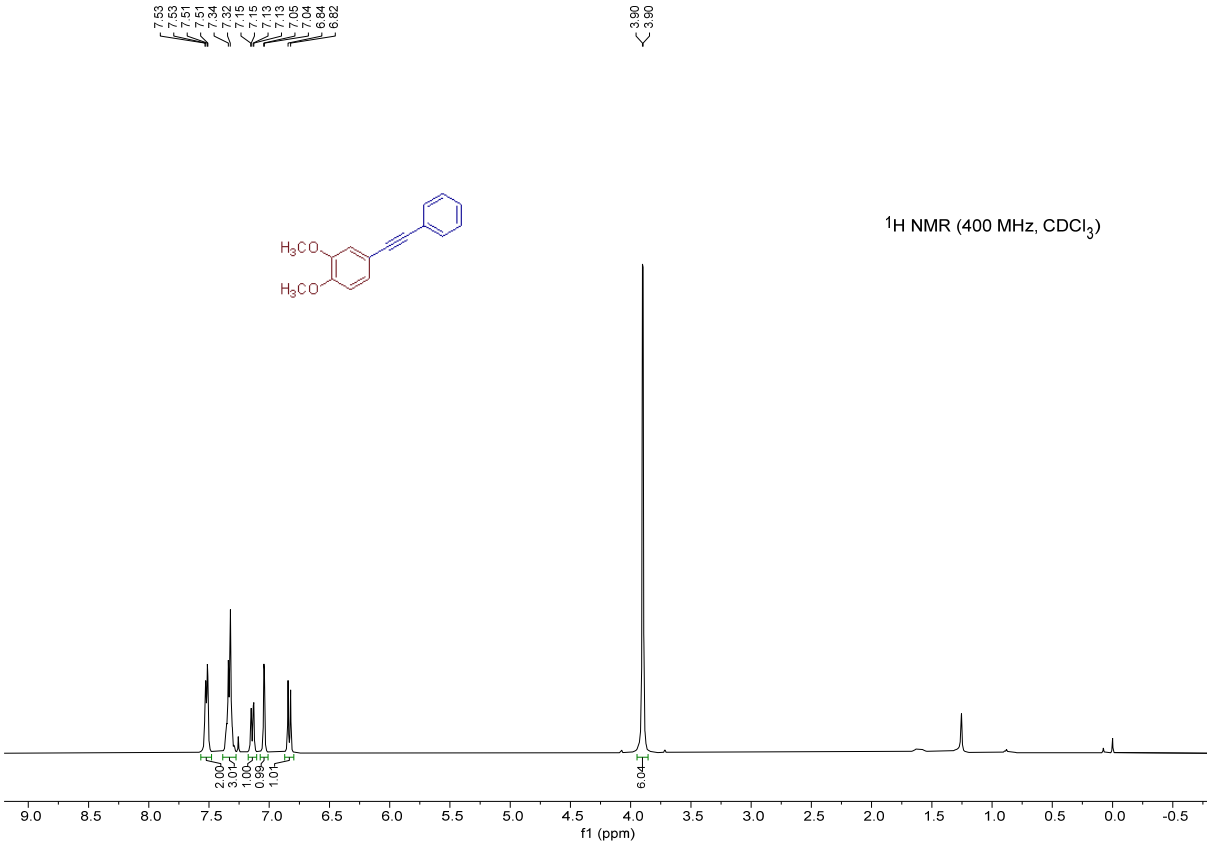
(4) 5-(phenylethynyl)-1,3-benzodioxole (**3-4**)

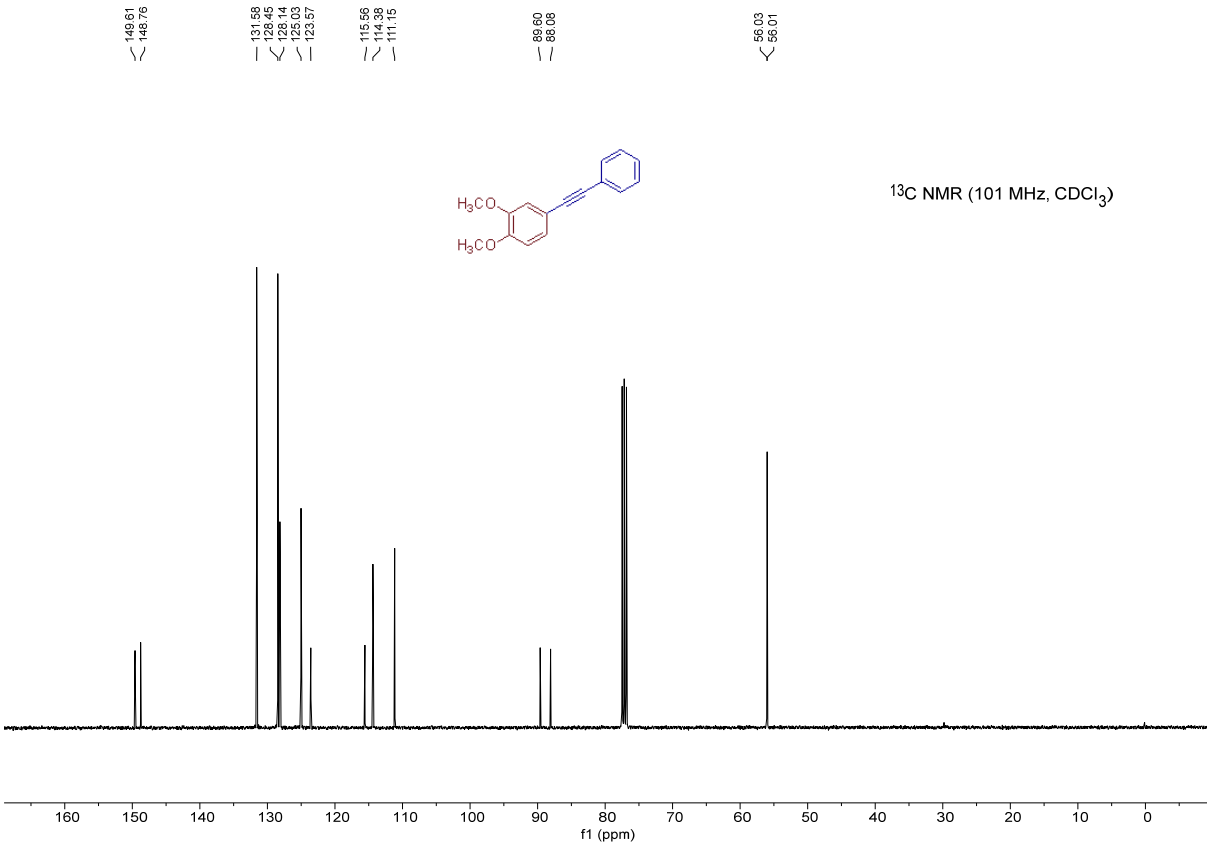




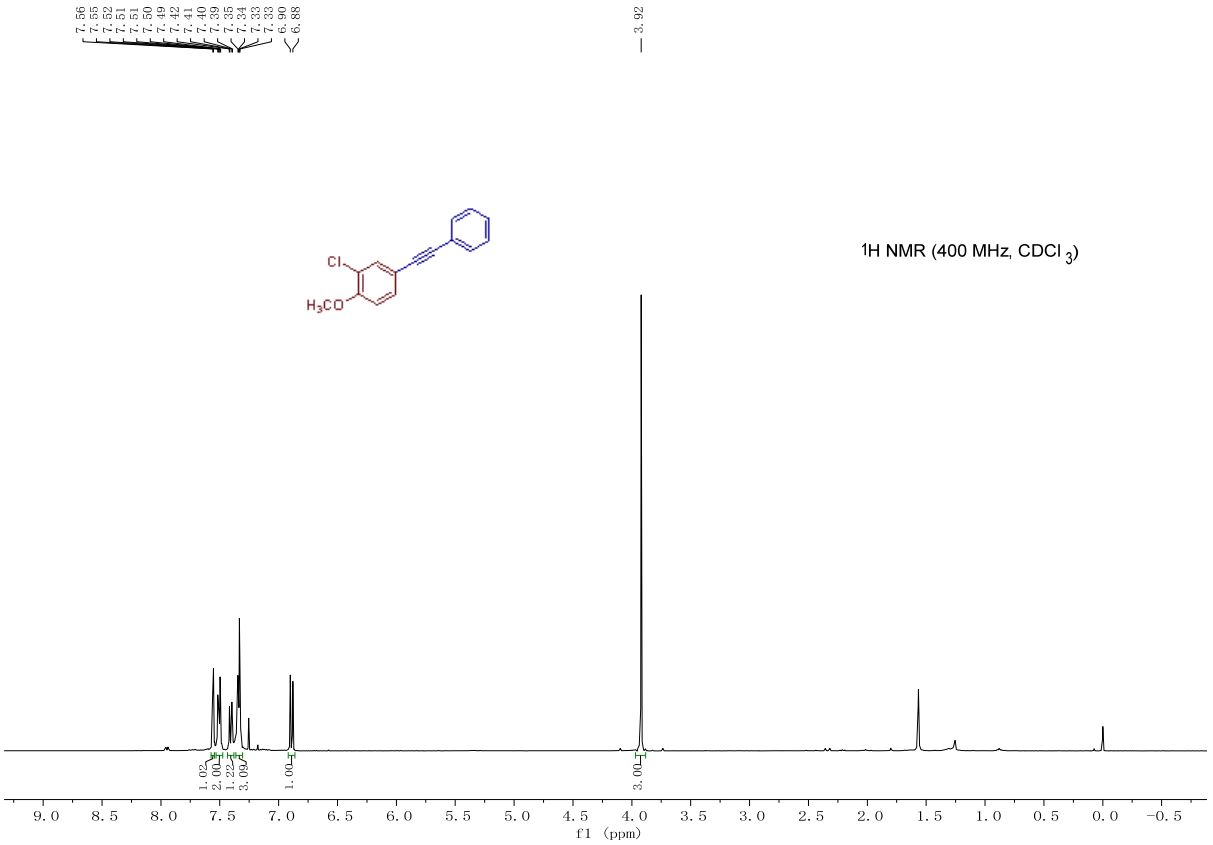


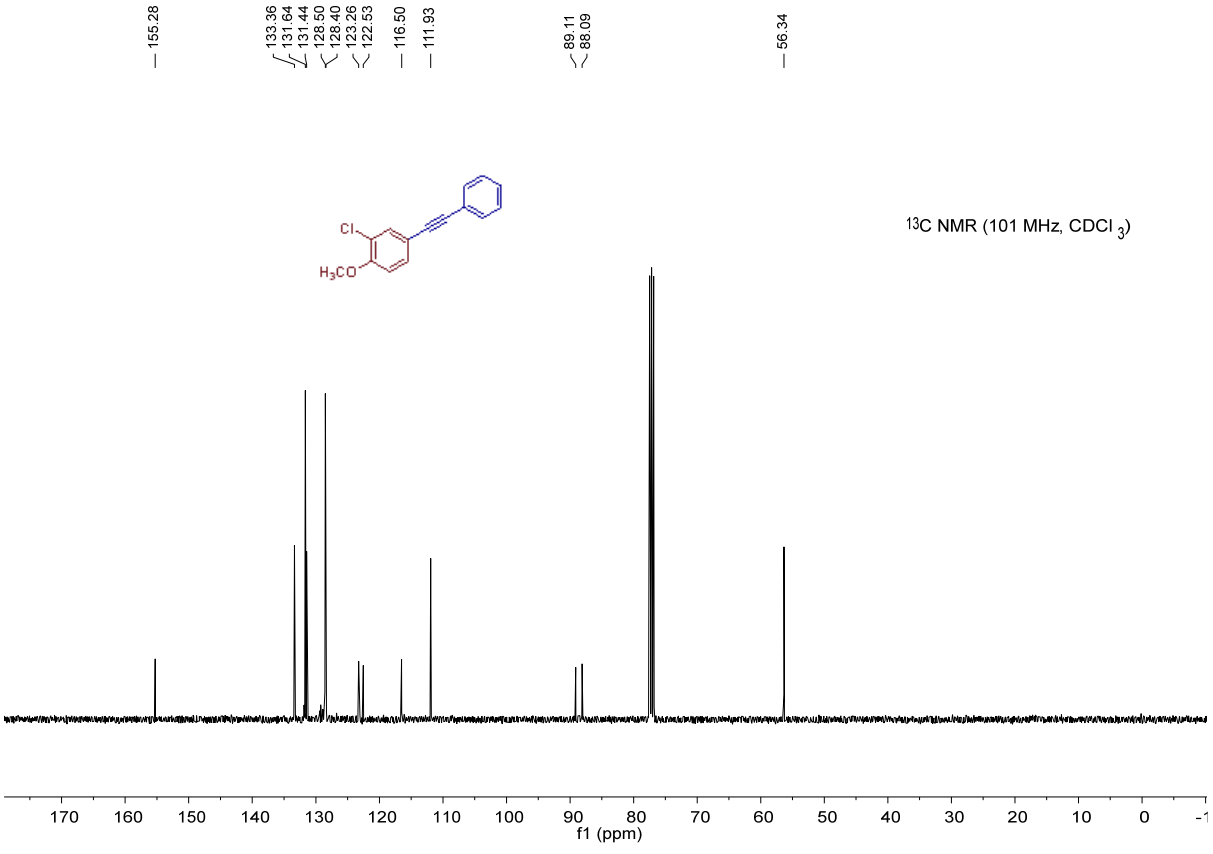
(5) 1,2-dimethoxy-4-(phenylethynyl)benzene (**3-5**)



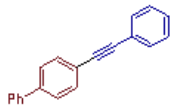


(6) 2-chloro-1-methoxy-4-(phenylethynyl)benzene (**3-6**)

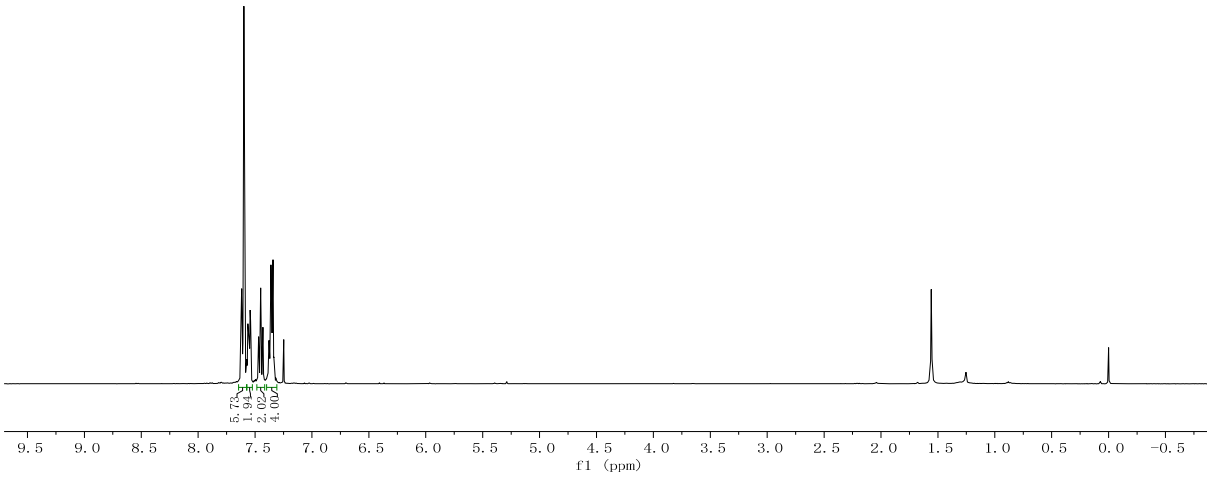


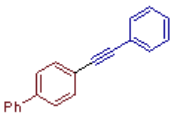


(7) 1-phenyl-4-(phenylethynyl)benzene (**3-7**)

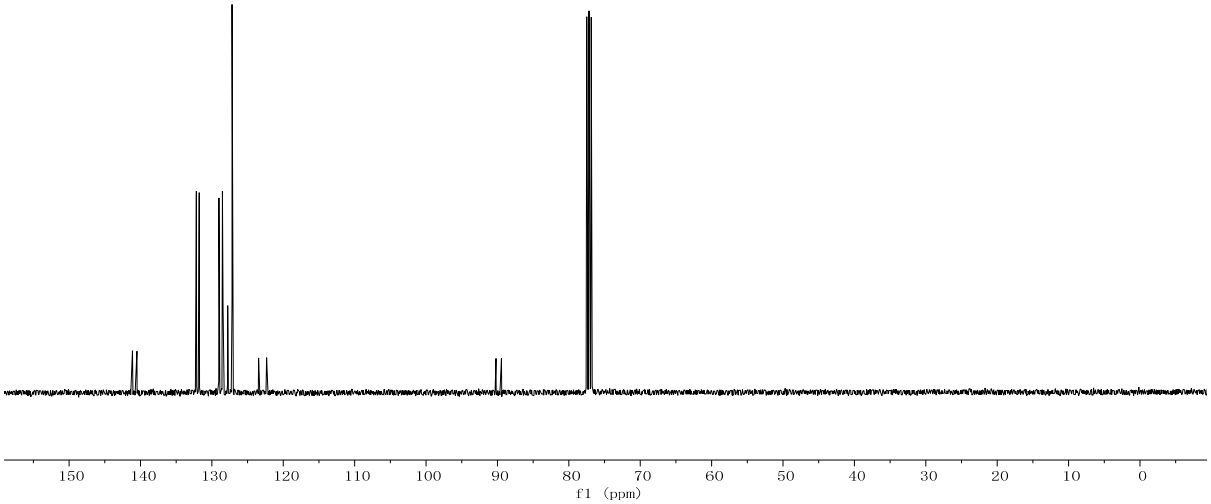


^{1}H NMR (400 MHz, $CDCl_3$)

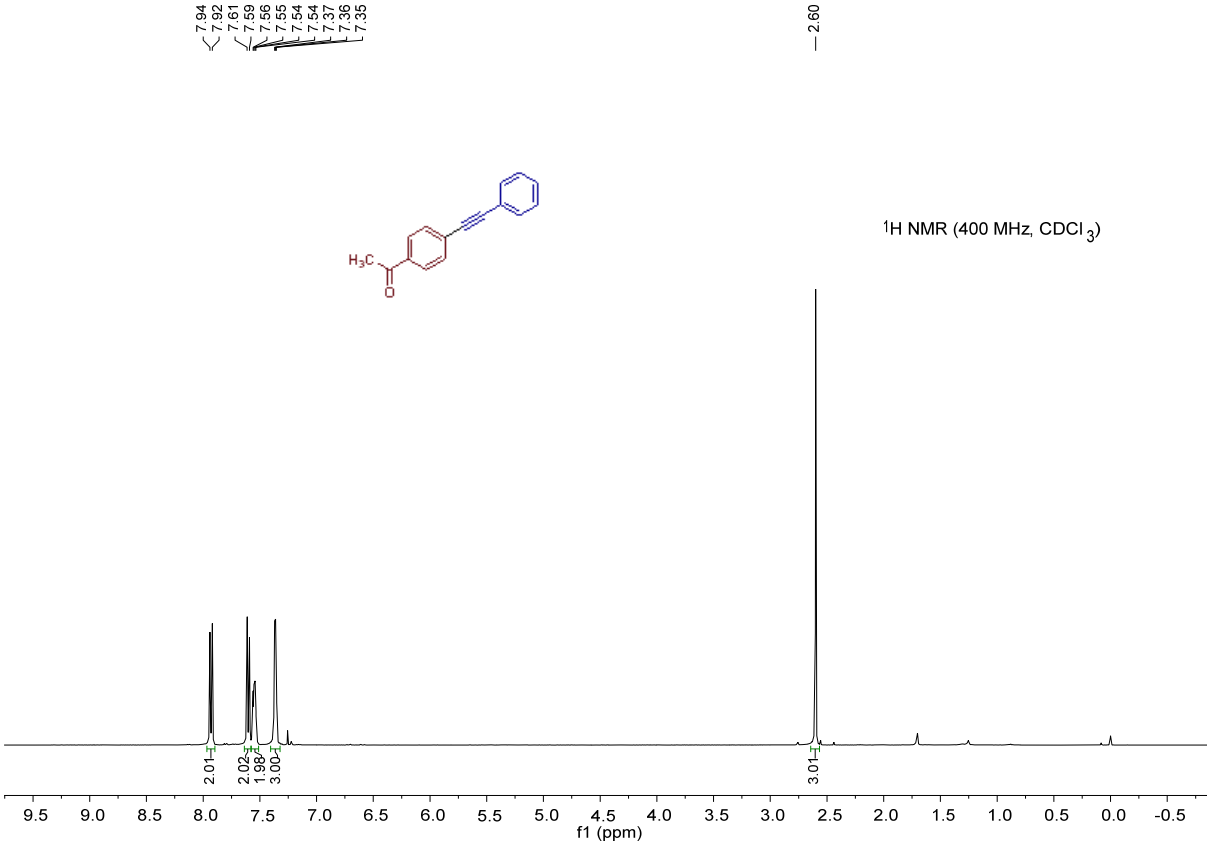


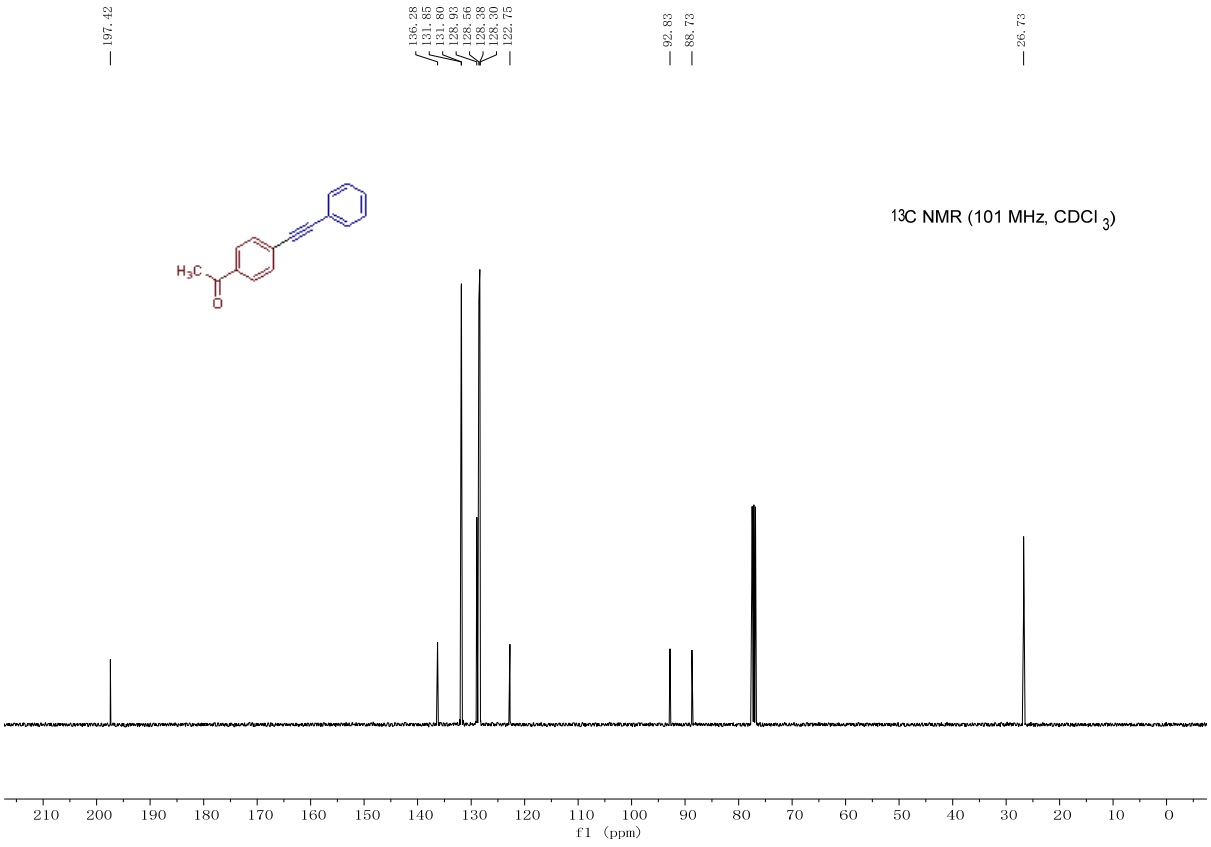


^{13}C NMR (101 MHz, $CDCl_3$)

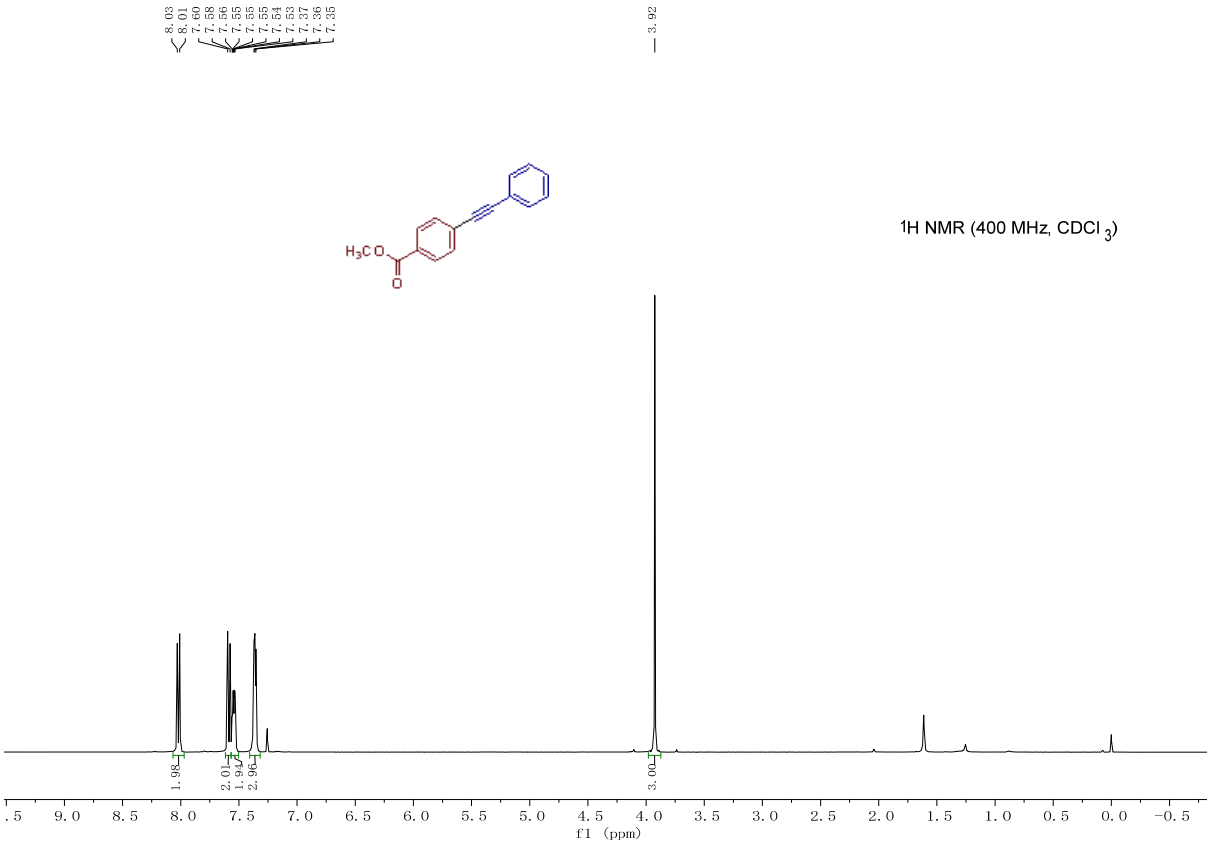


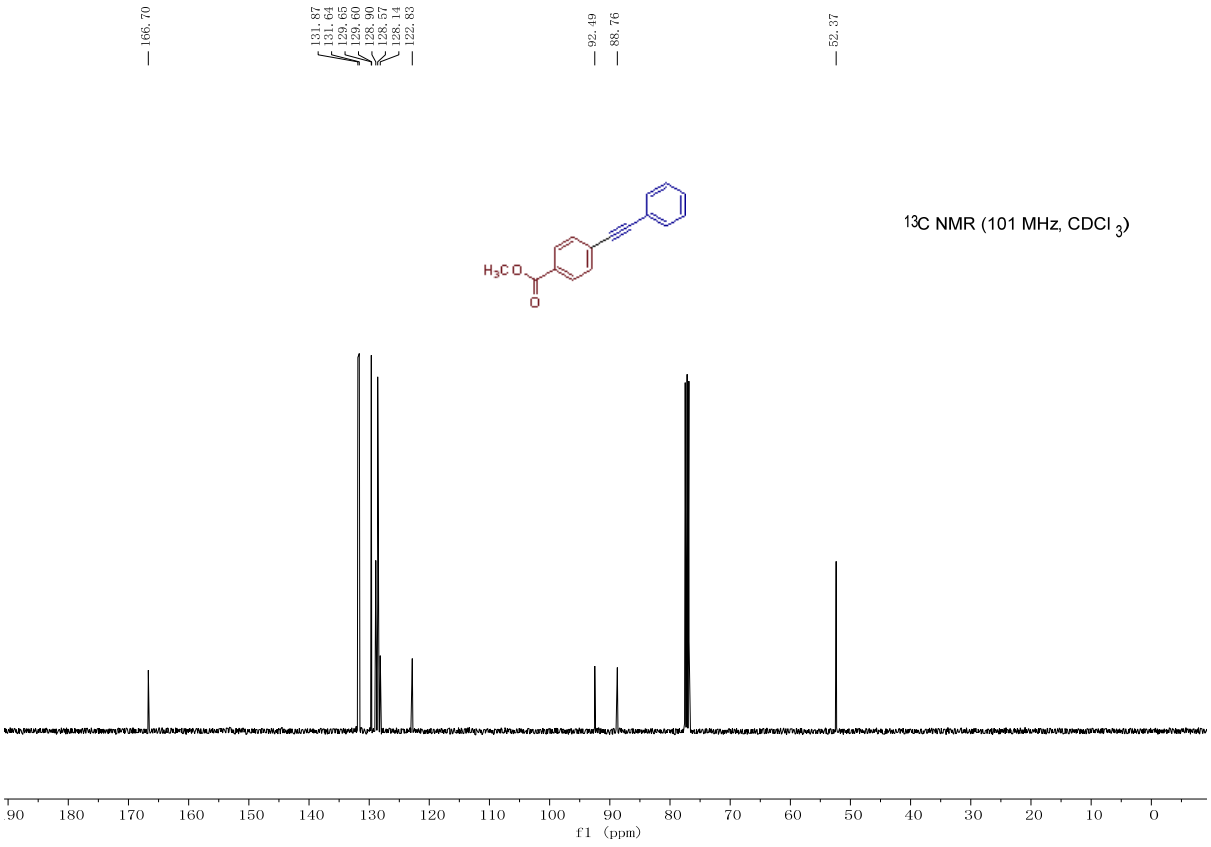
(8) 4-(phenylethinyl)acetophenone (**3-8**)



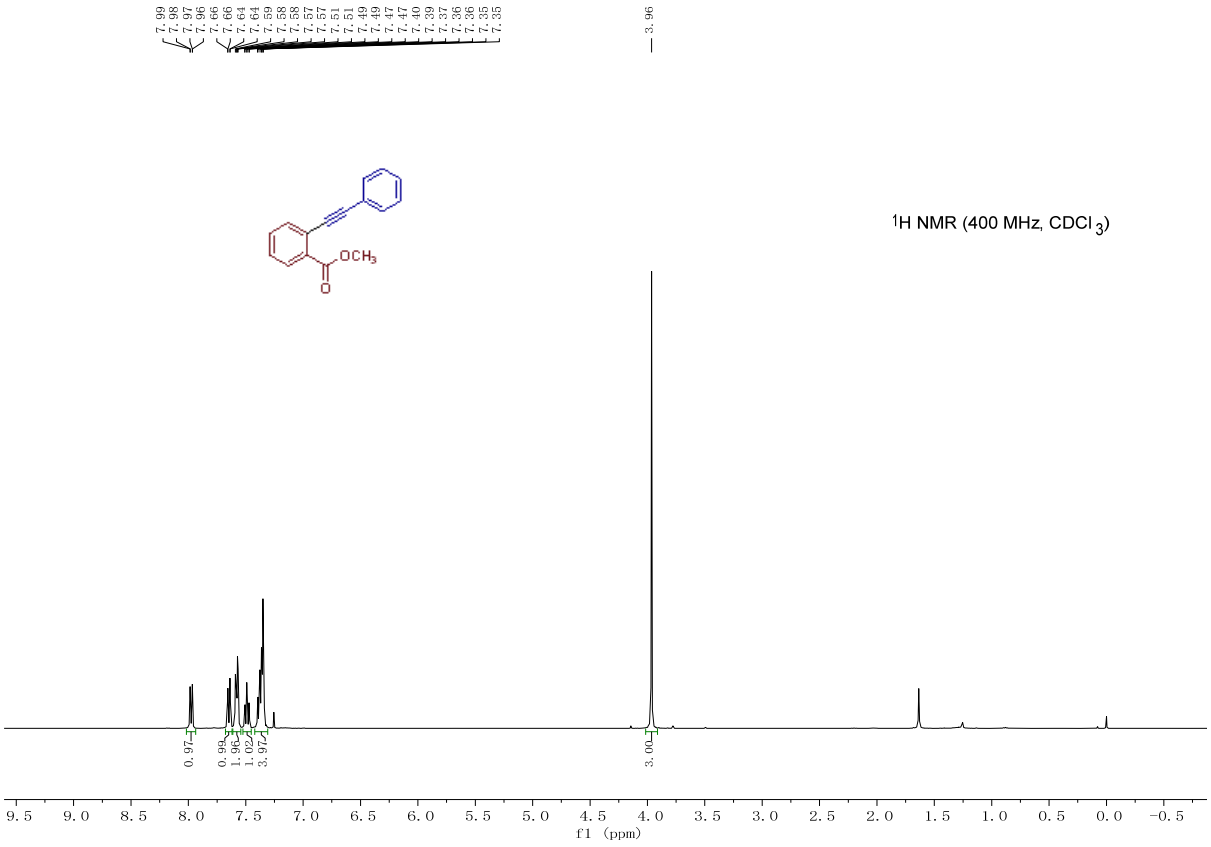


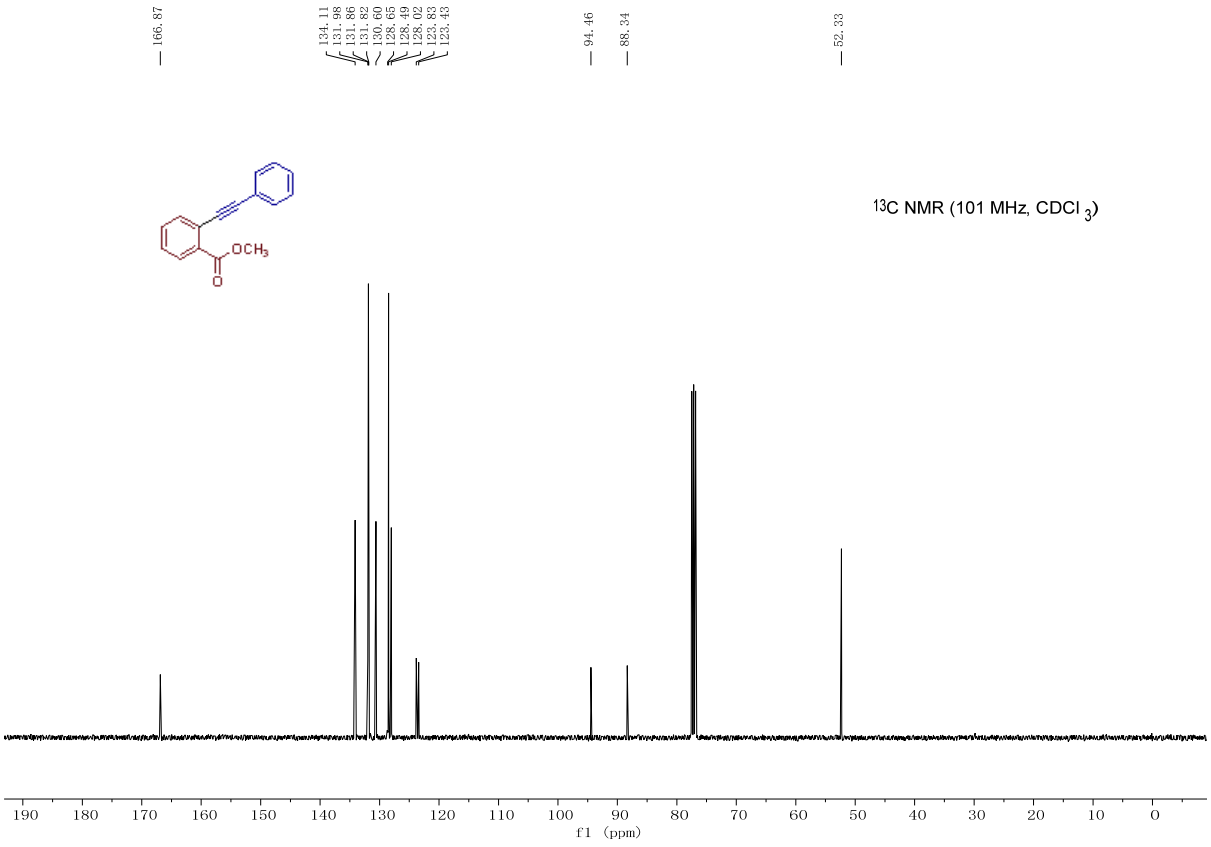
(9) methyl 4-(phenylethynyl)benzoate (**3-9**)



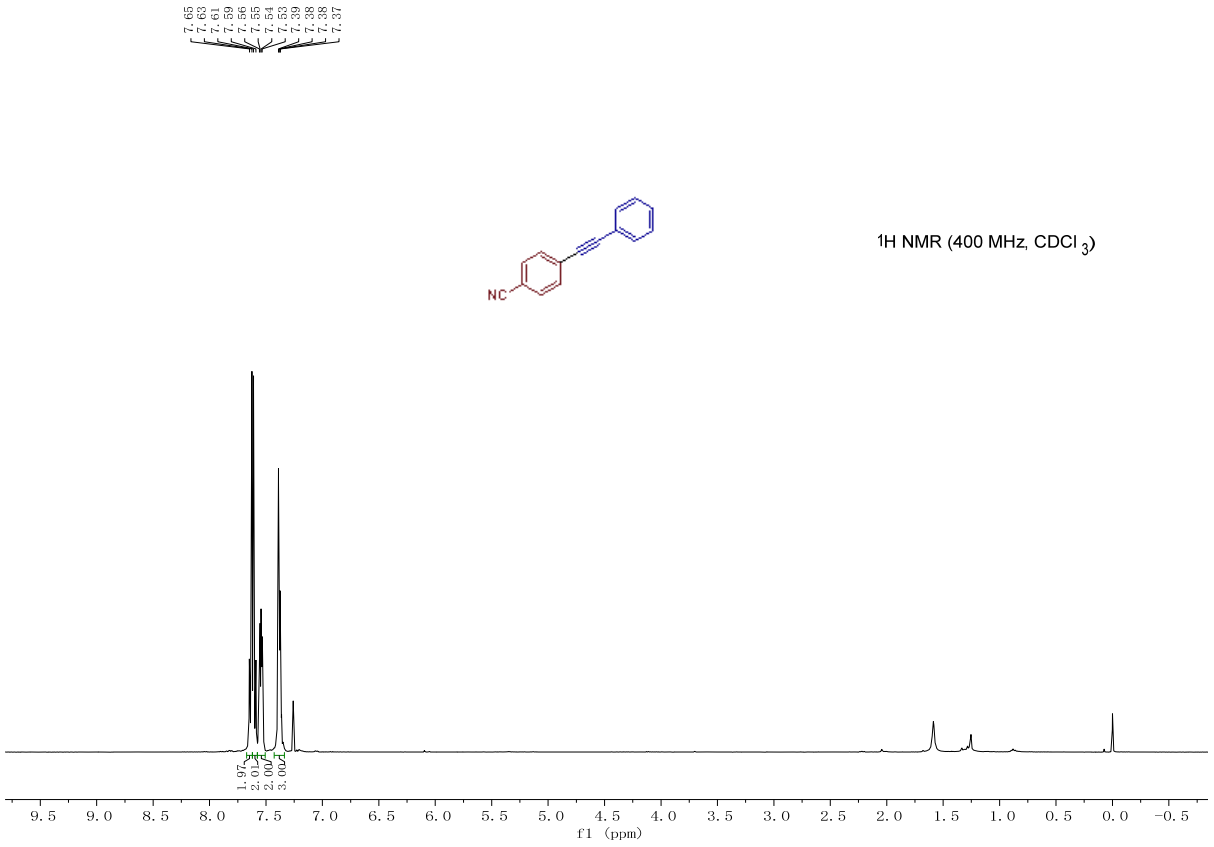


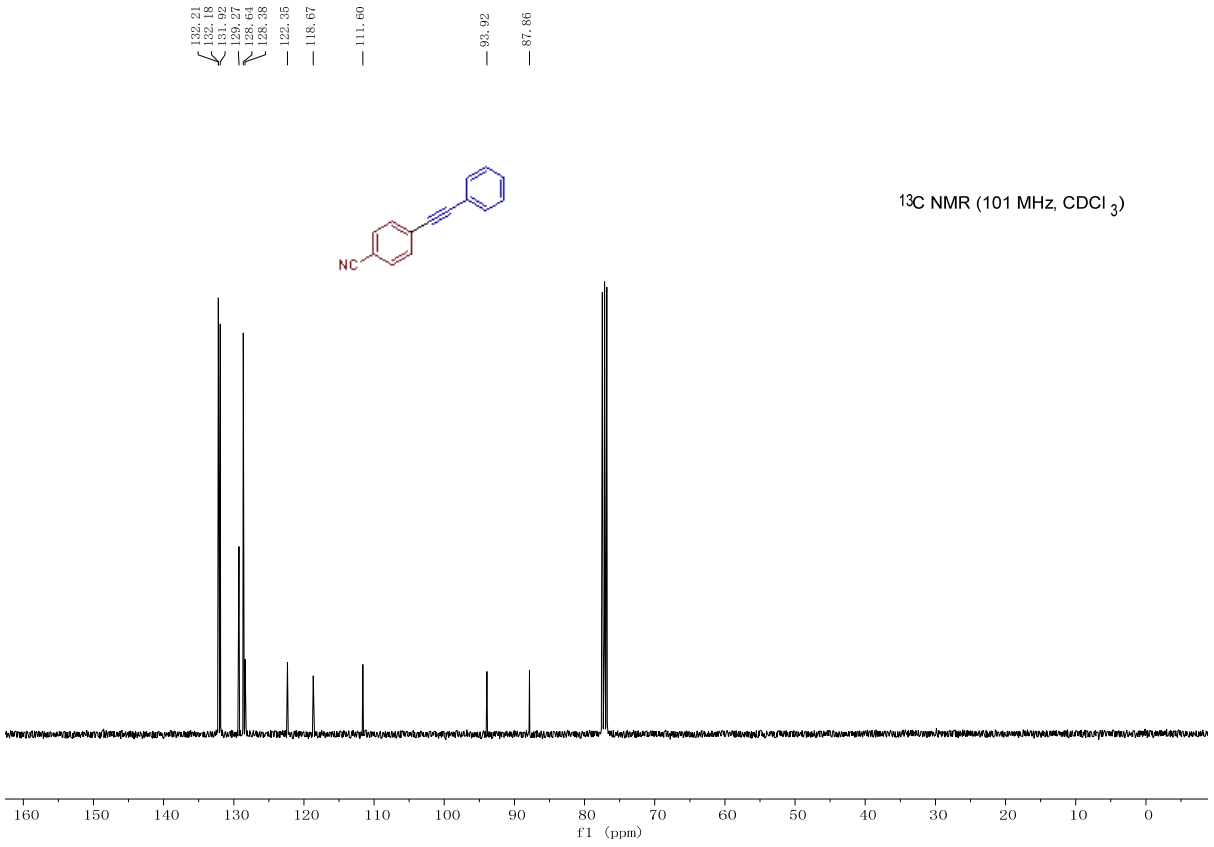
(10) methyl 2-(phenylethynyl)benzoate (**3-10**)



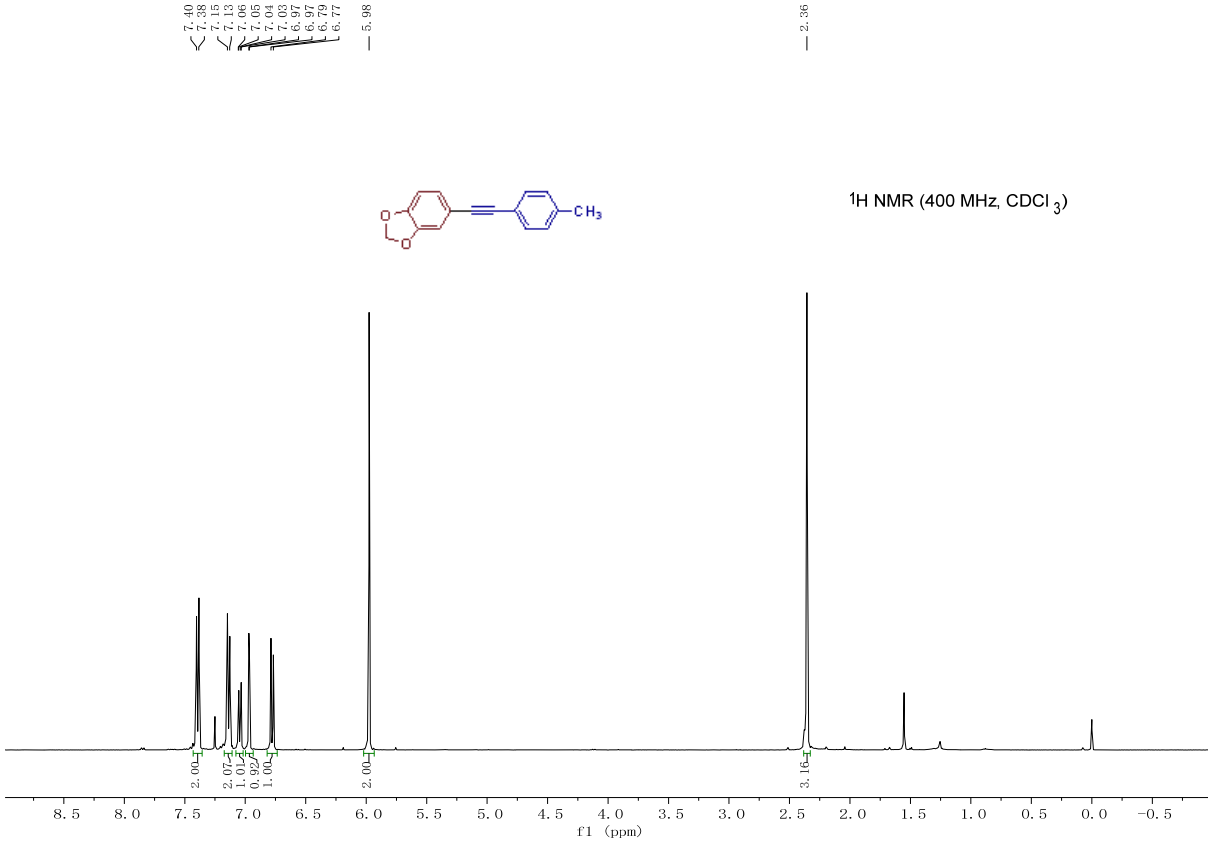


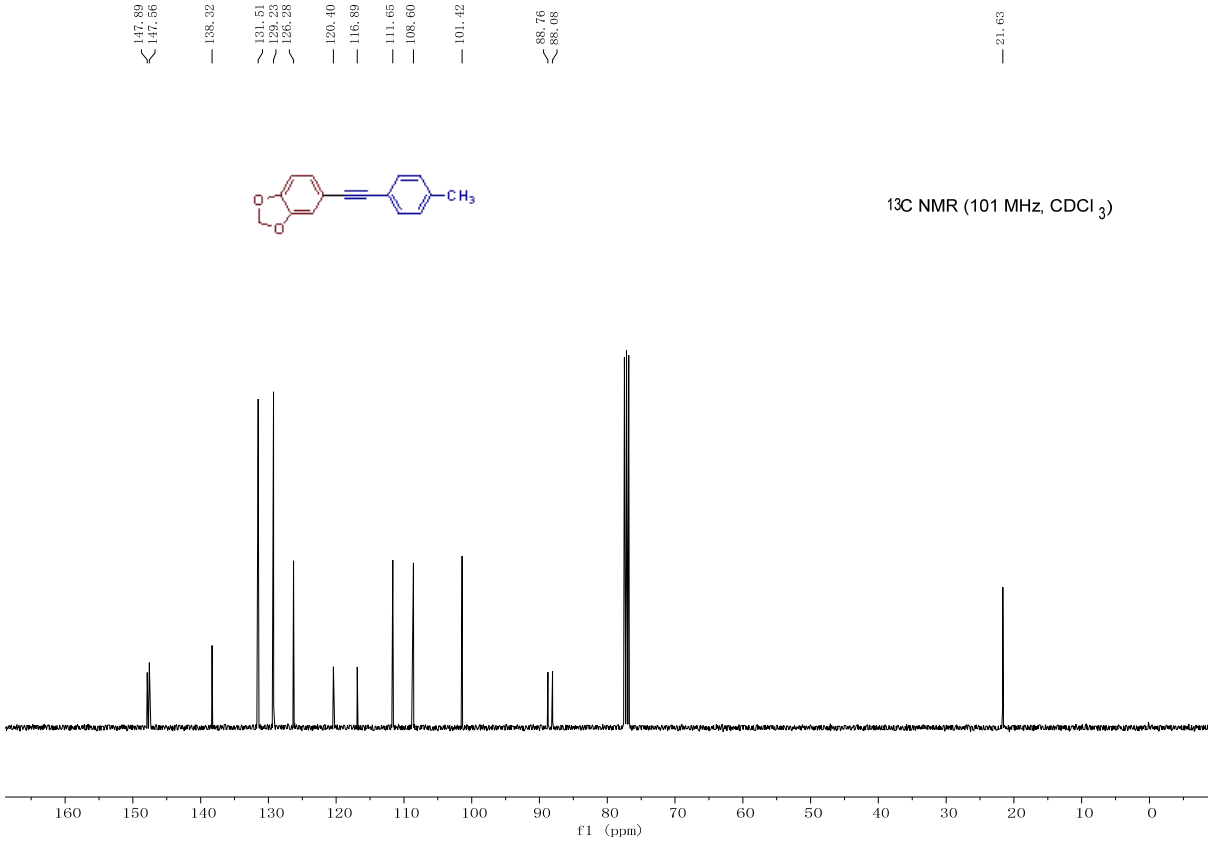
(11) 4-(2-phenylethynyl)benzonitrile (**3-11**)



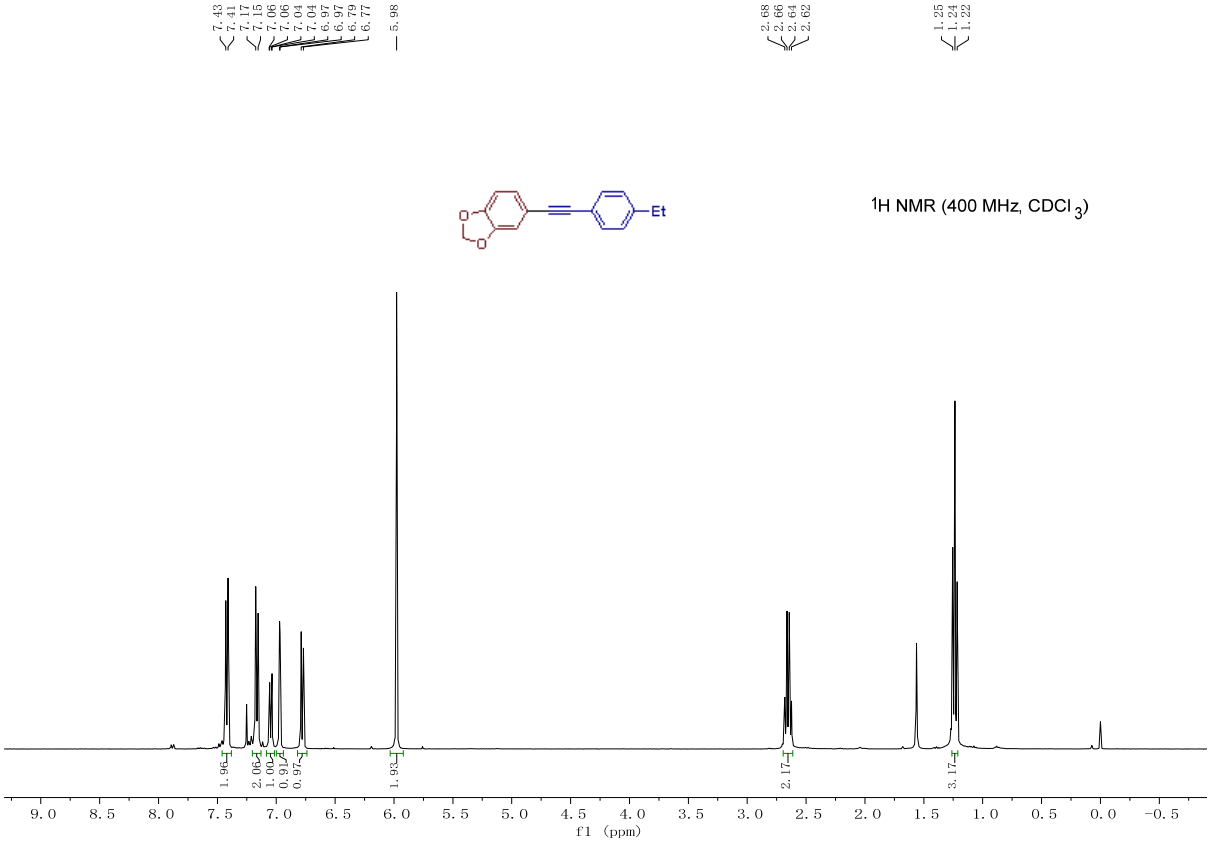


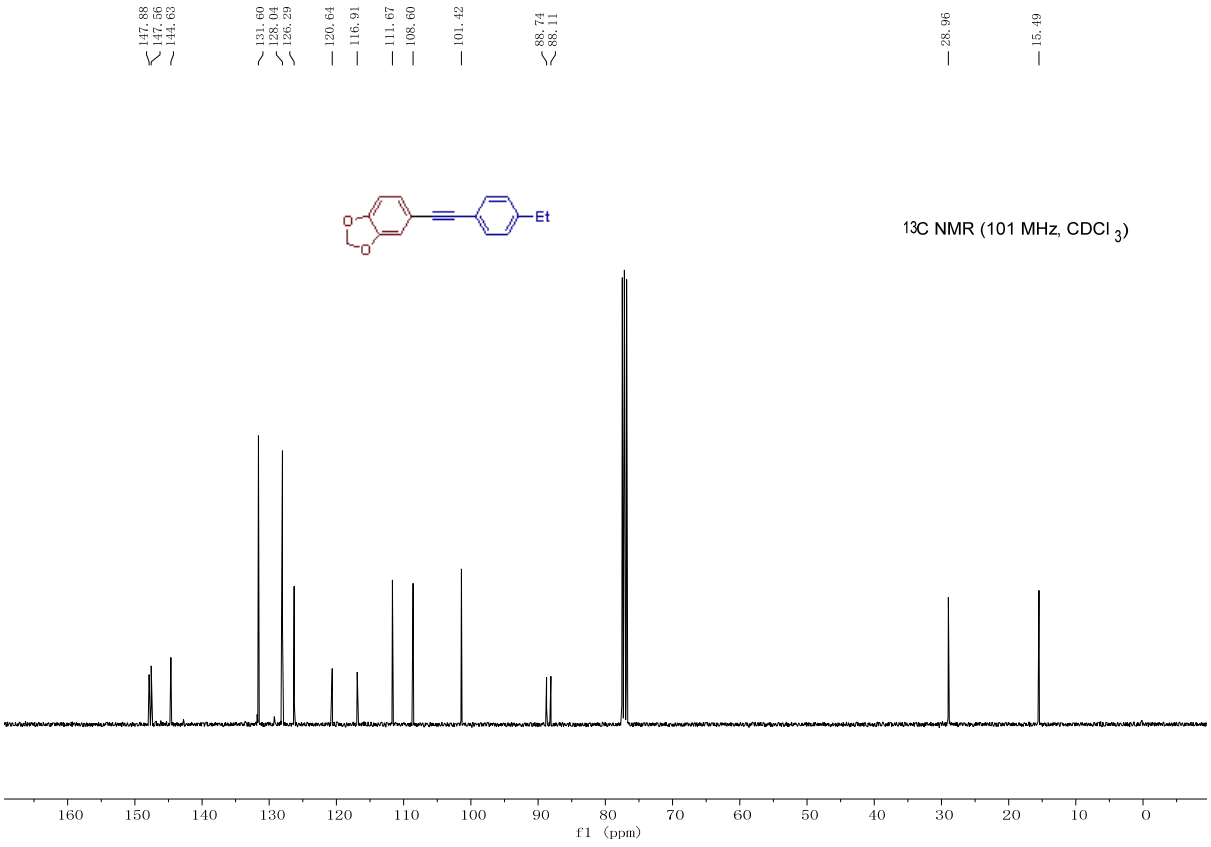
(12) 5-((4-methylphenyl)ethynyl)-1,3-benzodioxole (**3-12**)



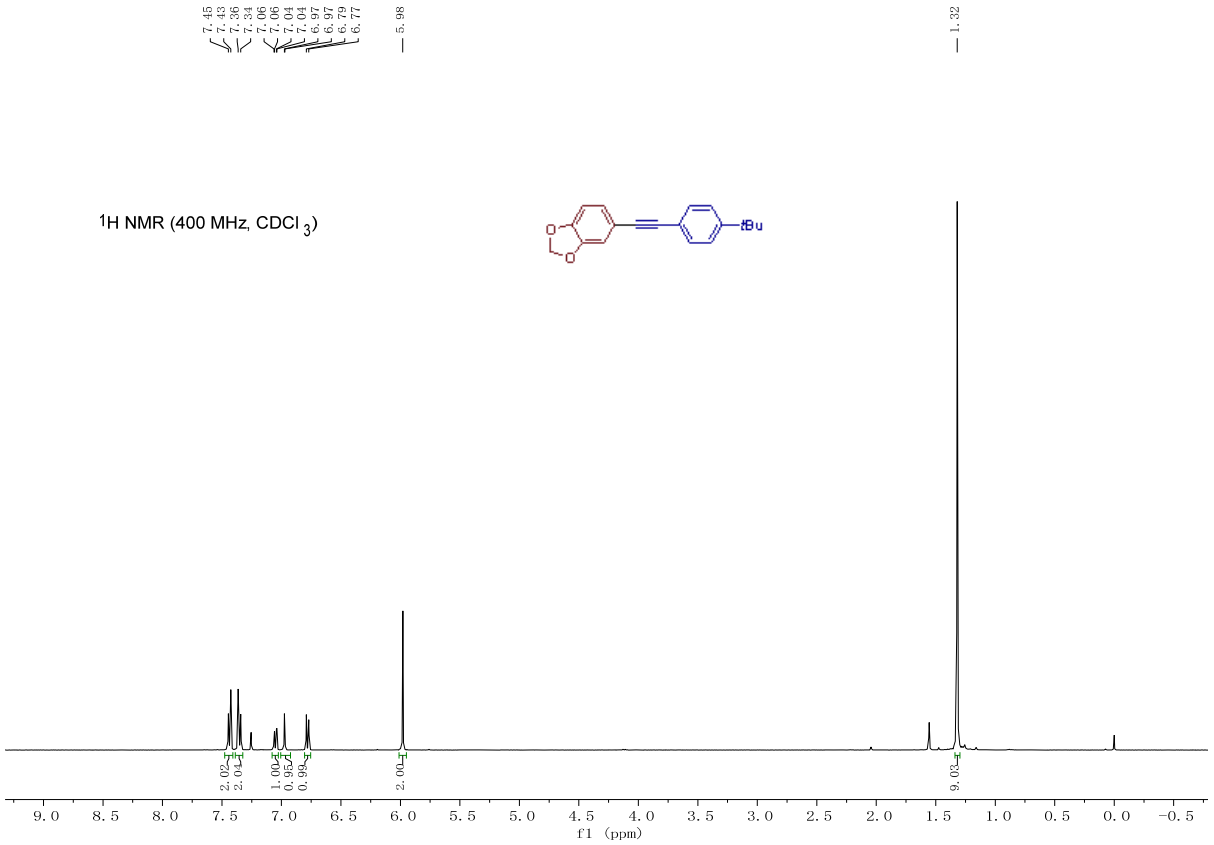


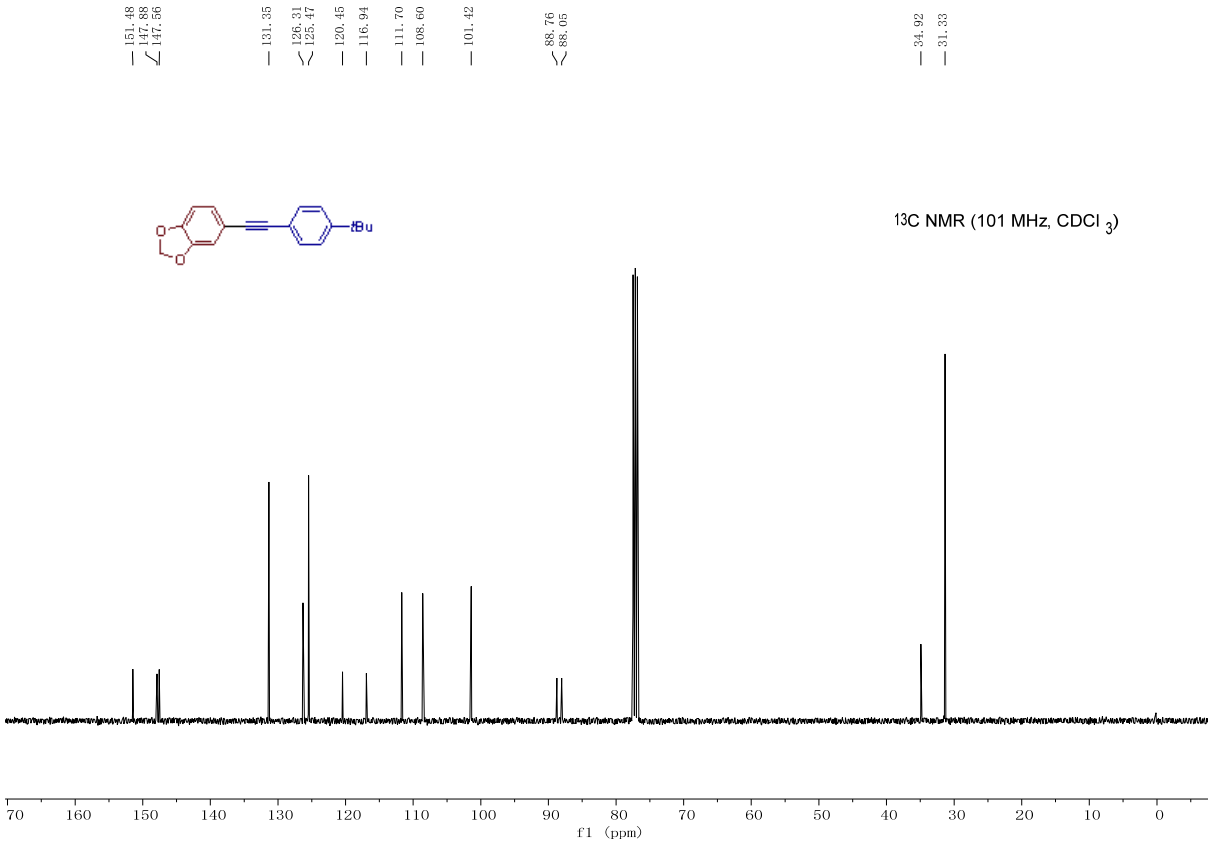
(13) 5-((4-ethylphenyl)ethynyl)-1,3-benzodioxole (**3-13**)



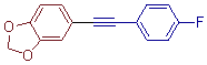


(14) 5-((4-*tert*-butylphenyl)ethynyl)-1,3-benzodioxole (**3-14**)

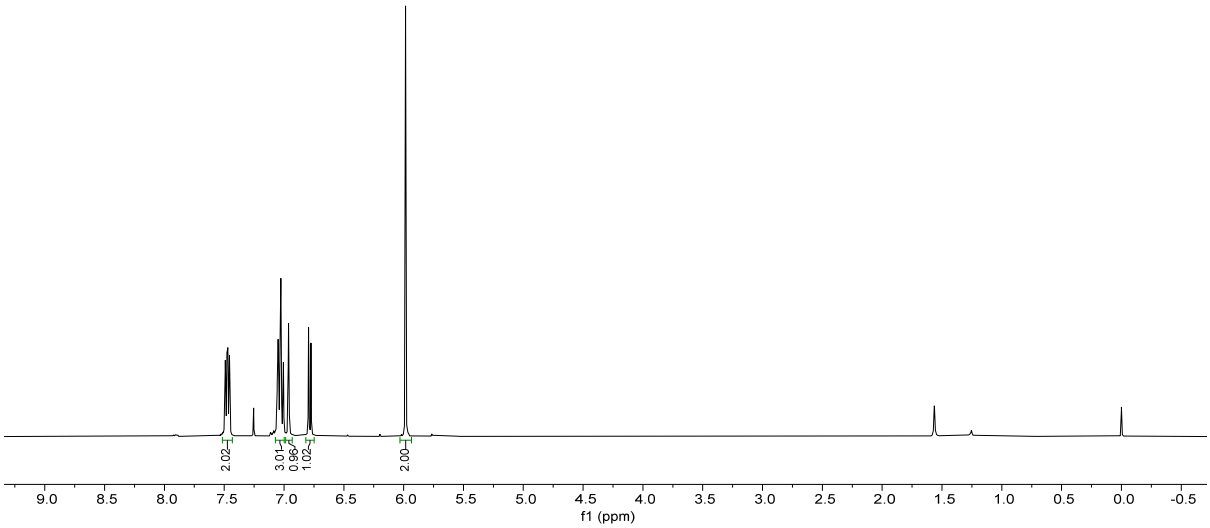


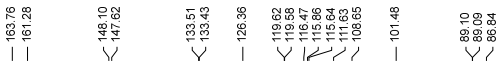


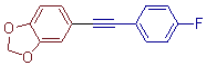
(15) 5-((4-fluorophenyl)ethynyl)-1,3-benzodioxole (**3-15**)



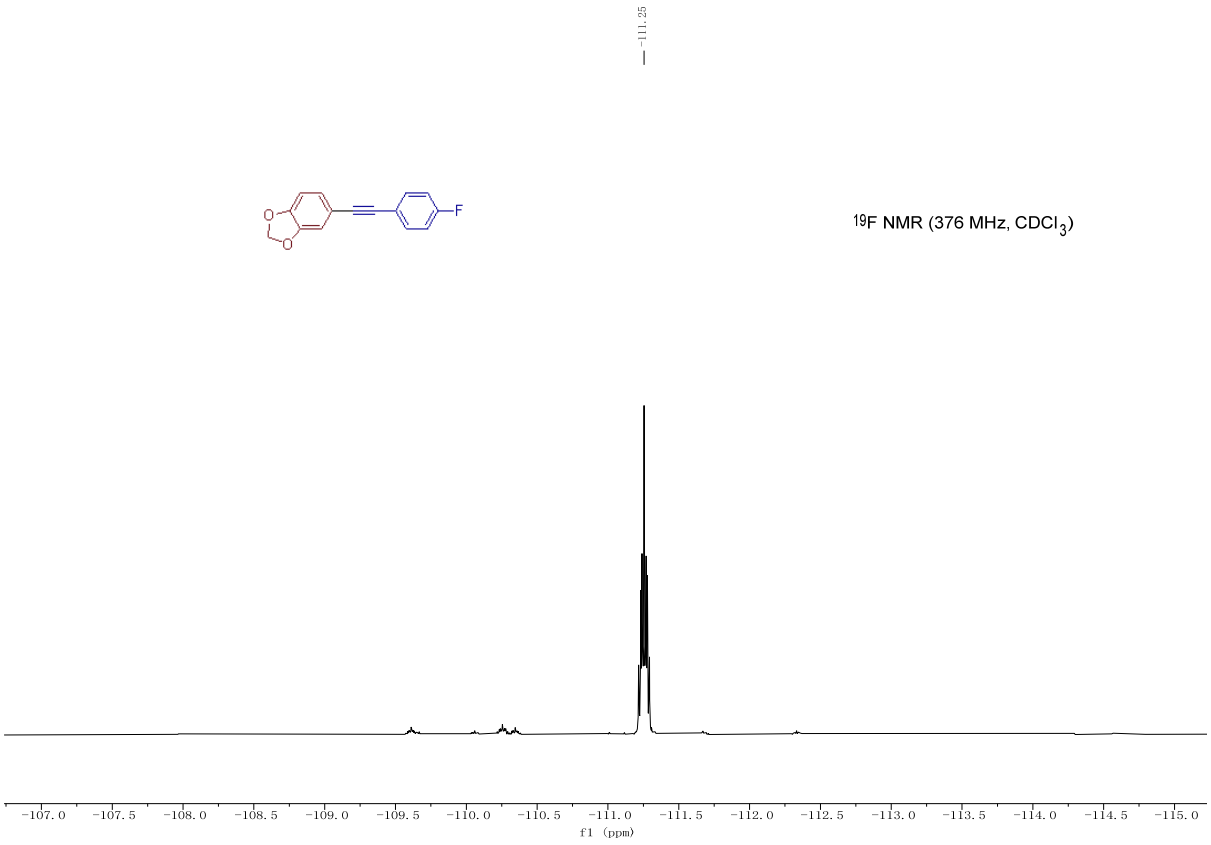
^{1}H NMR (400 MHz, $CDCl_3$)



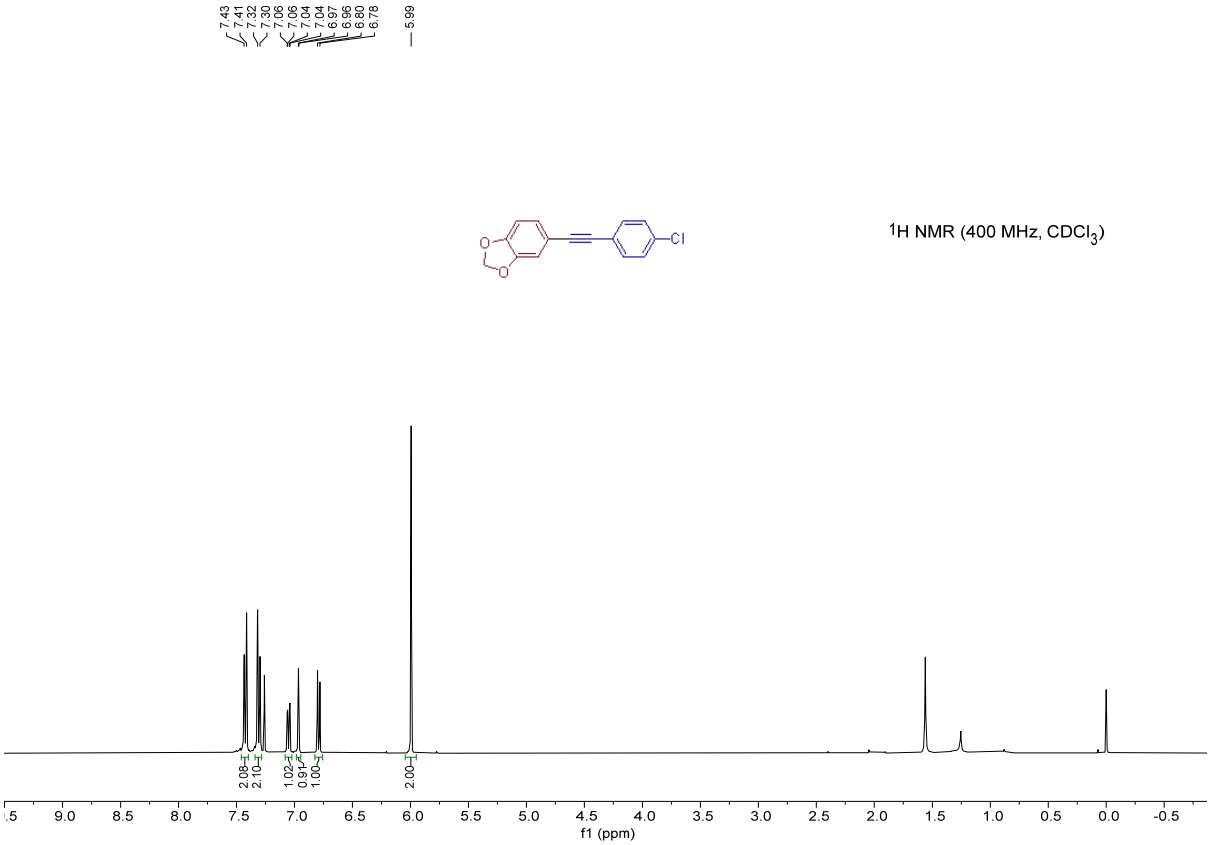


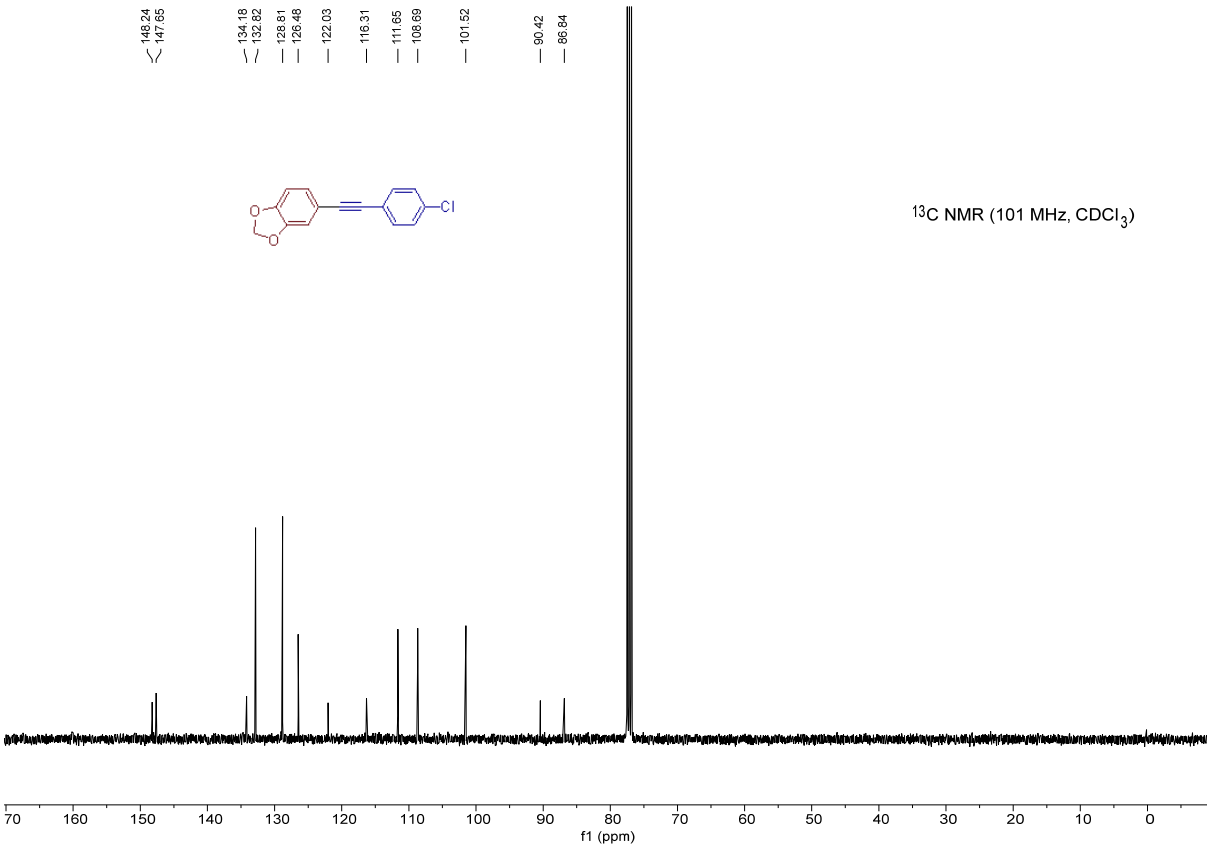


^{13}C NMR (101 MHz, $CDCl_3$)

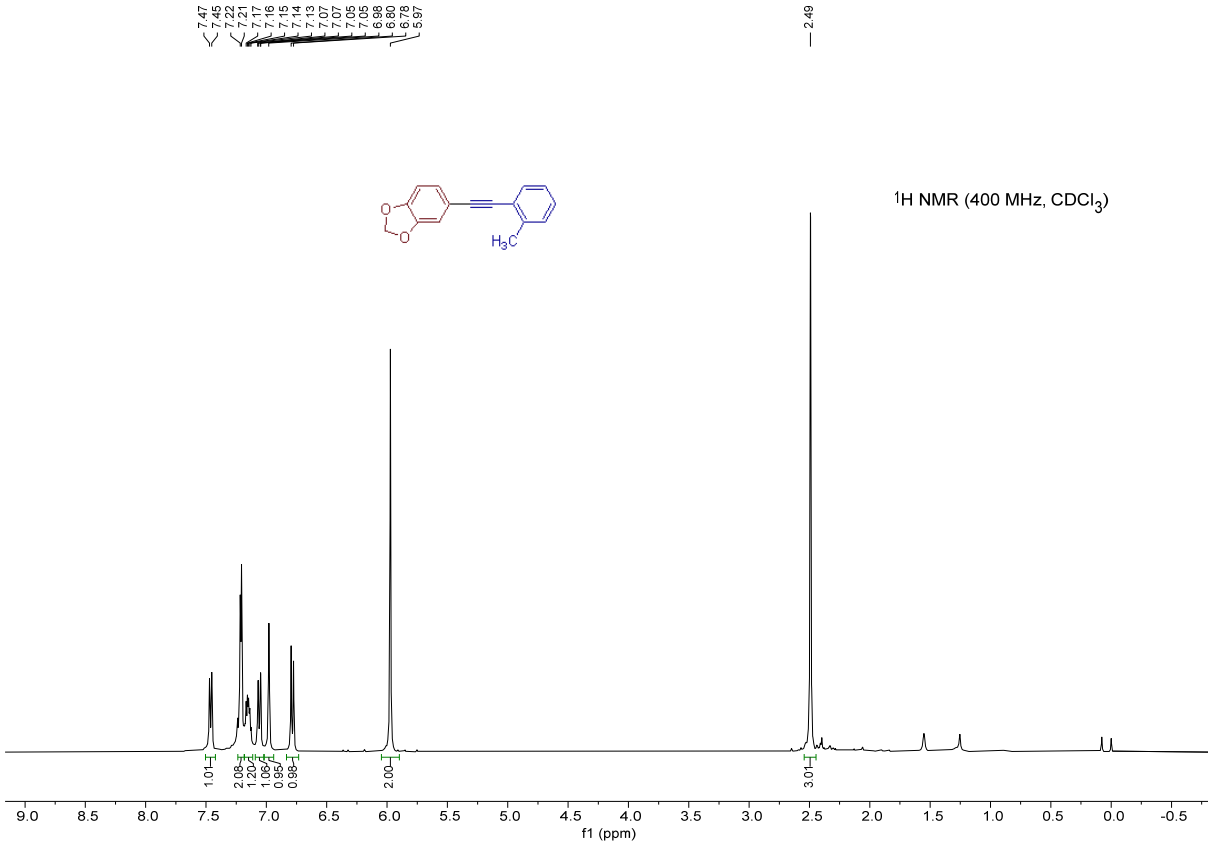

-111.25
F
19F NMR (376 MHz, CDCl3)
-107.0
-107.5
-108.0
-108.5
-109.0
-109.5
-110.0
-110.5
-111.0
-111.5
-112.0
-112.5
-113.0
-113.5
-114.0
-114.5
-115.0
f1 (ppm)

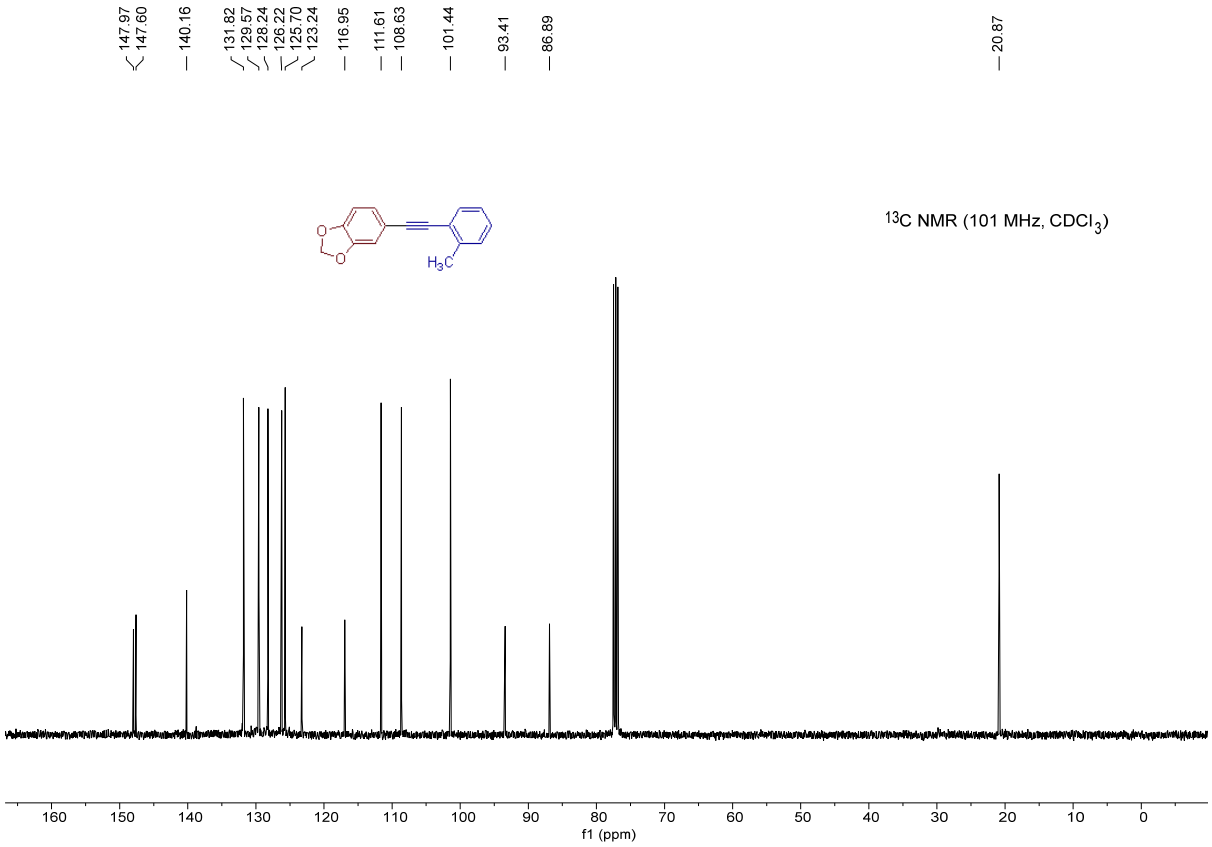
(16) 5-((4-chlorophenyl)ethynyl)-1,3-benzodioxole (**3-16**)



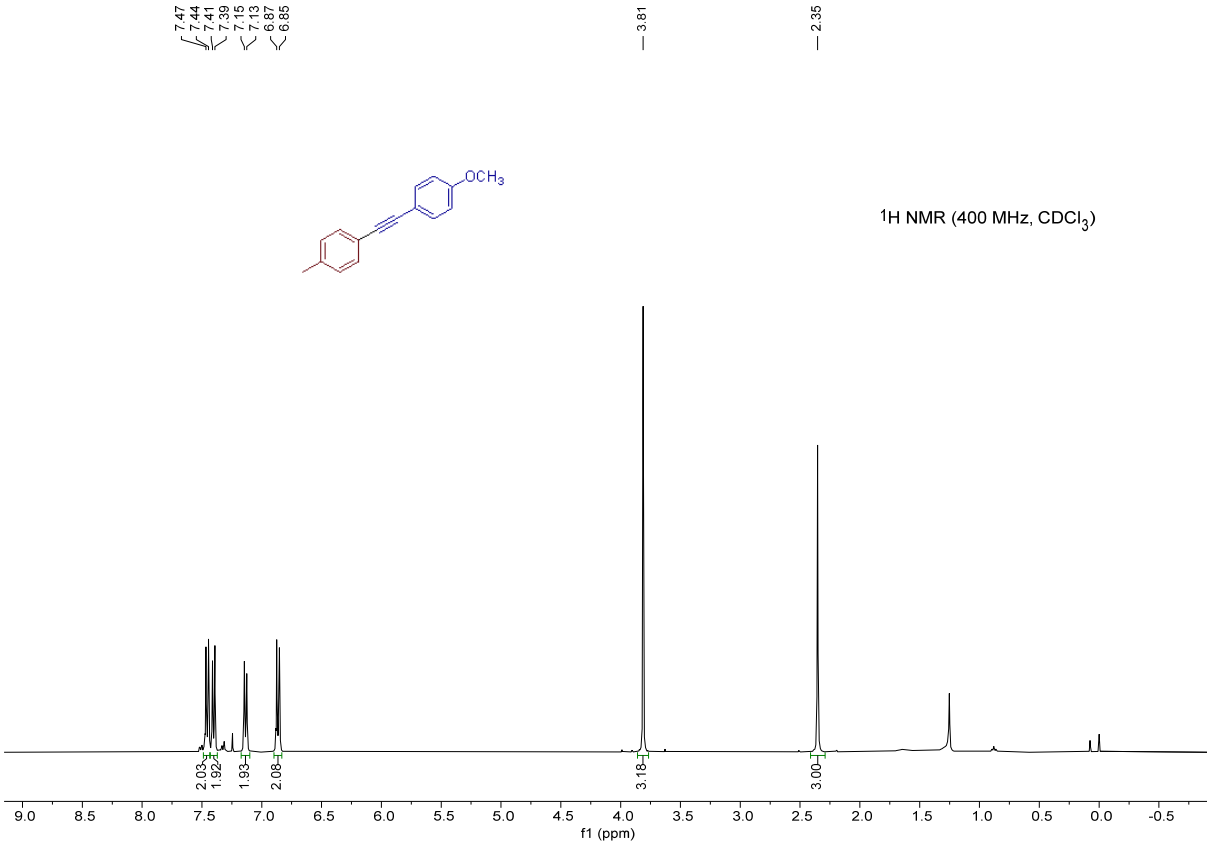


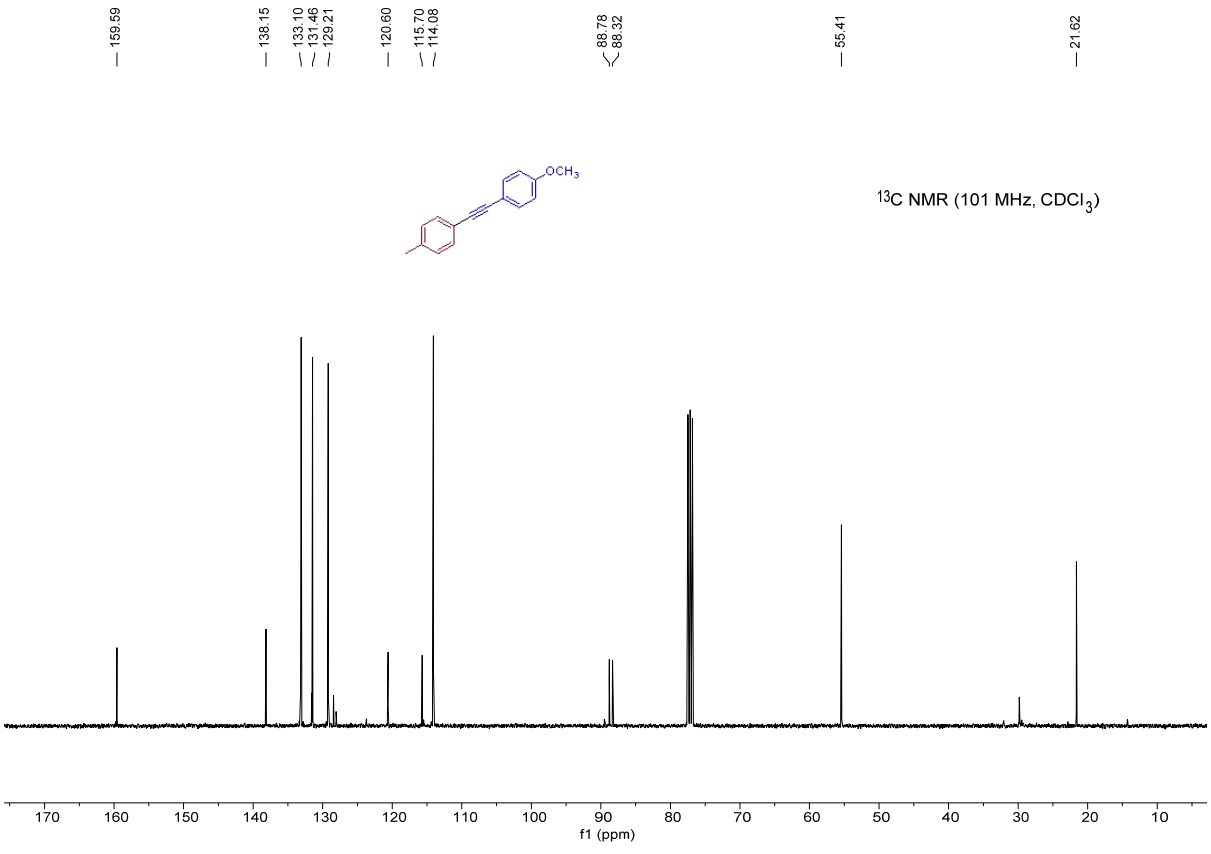
(17) 5-((2-methylphenyl)ethynyl)-1,3-benzodioxole (**3-18**)



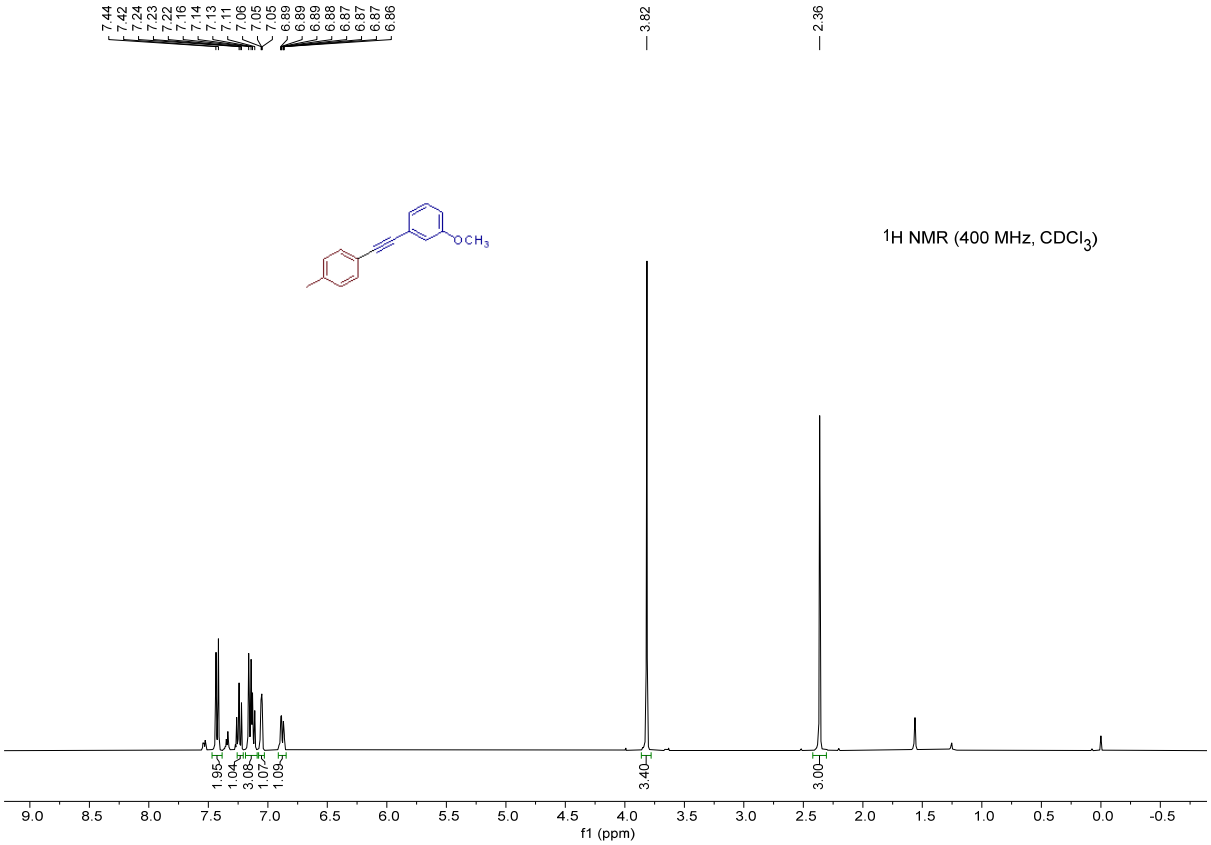


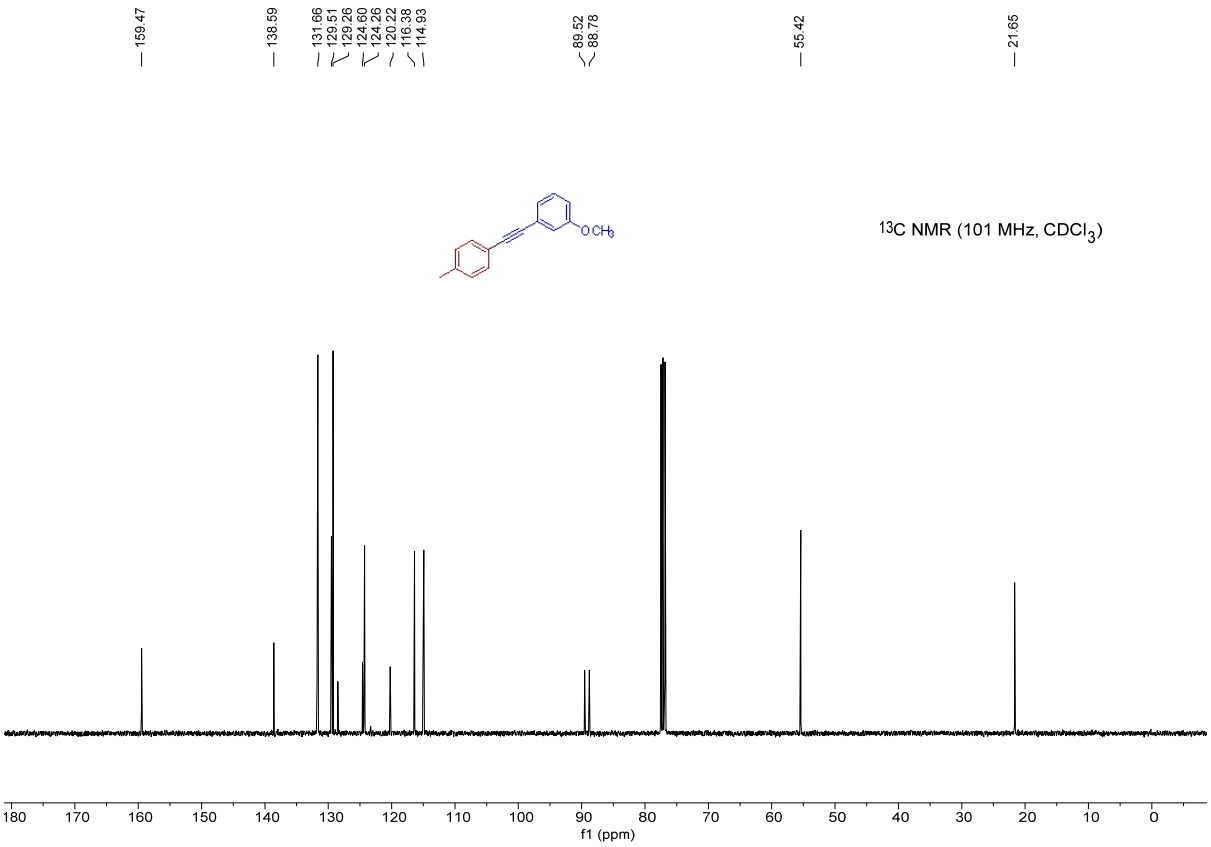
(18) 1-methoxy-4-((4-methylphenyl)ethynyl)benzene (**3-19**)



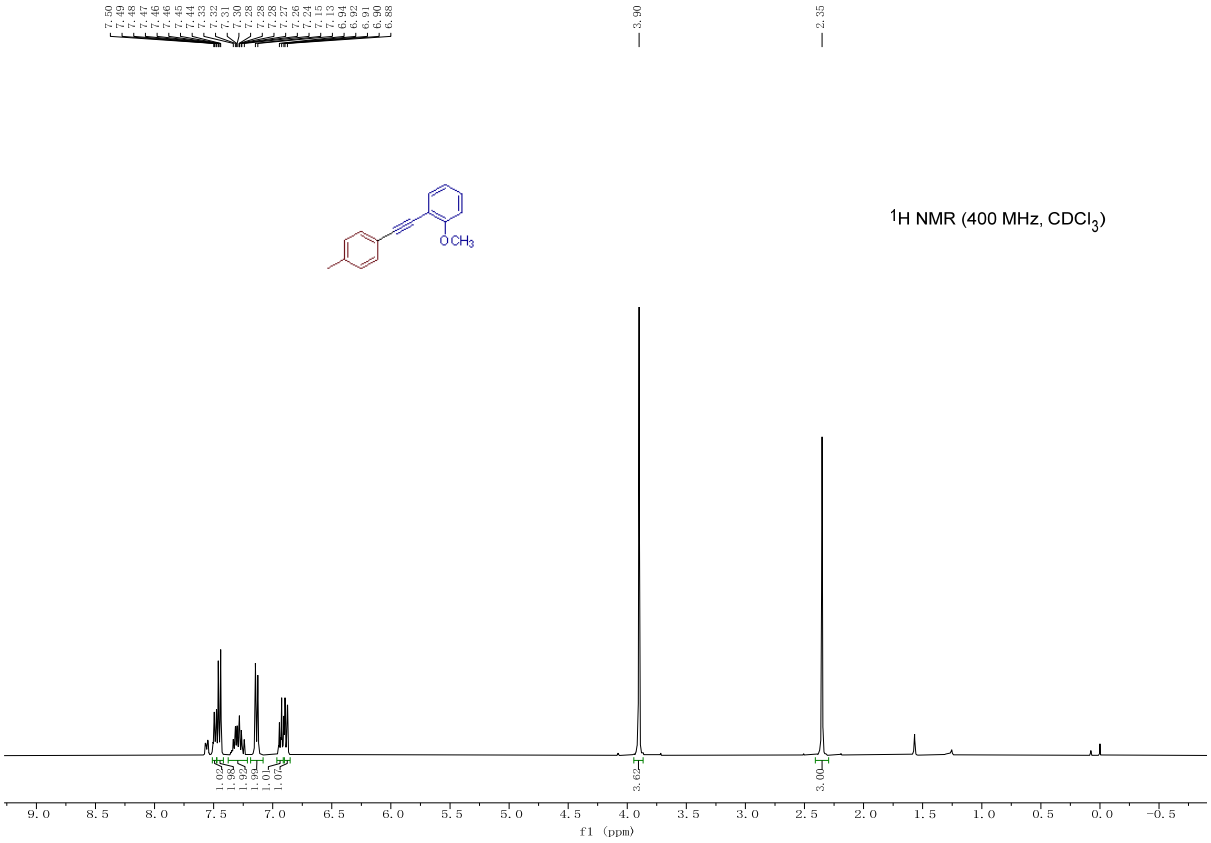


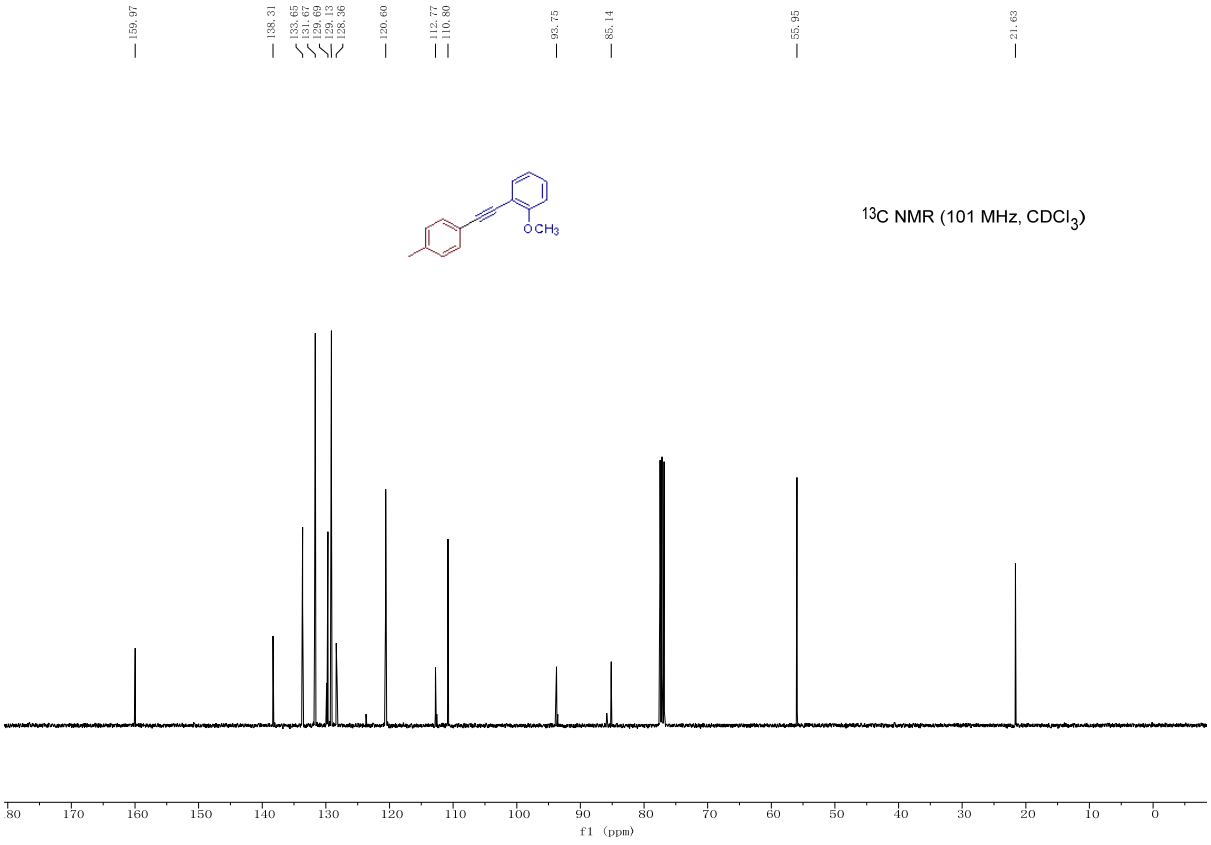
(19) 1-methoxy-3-((4-methylphenyl)ethynyl)benzene (**3-20**)



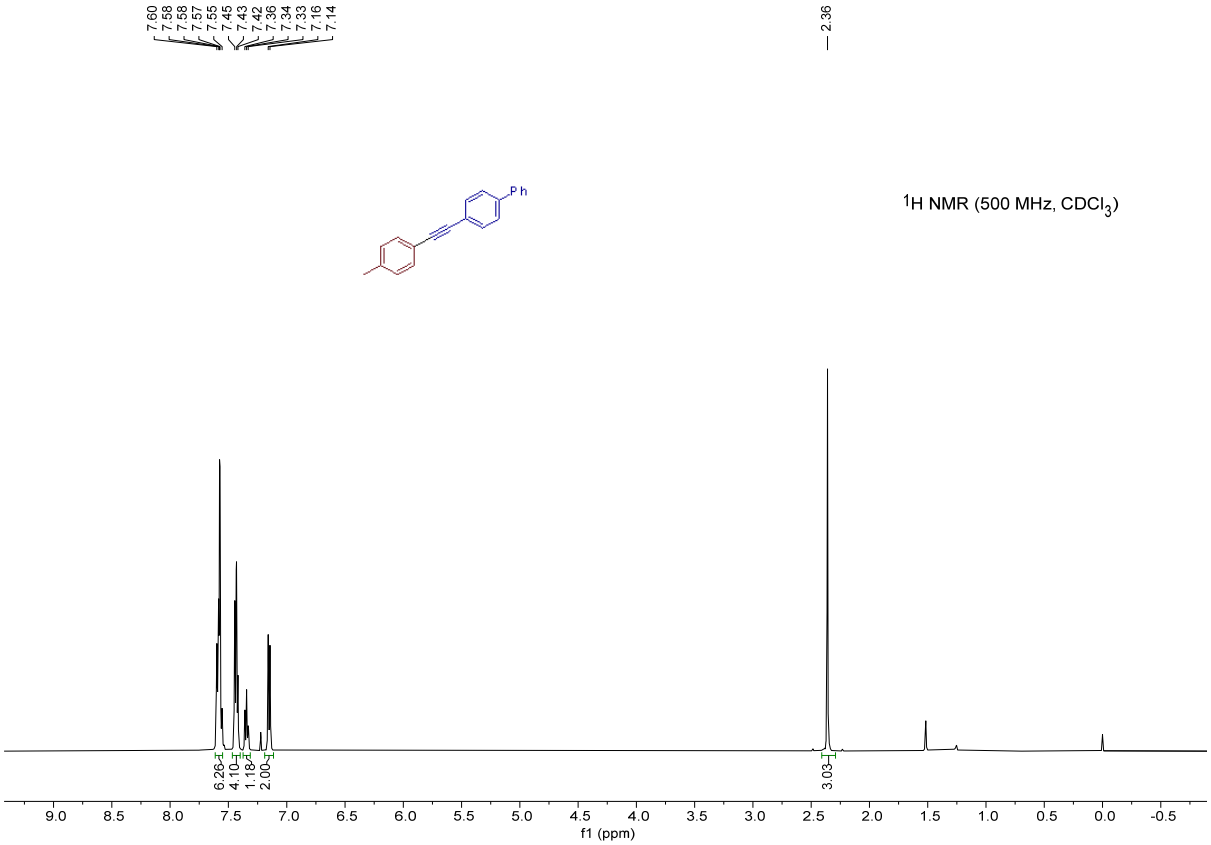


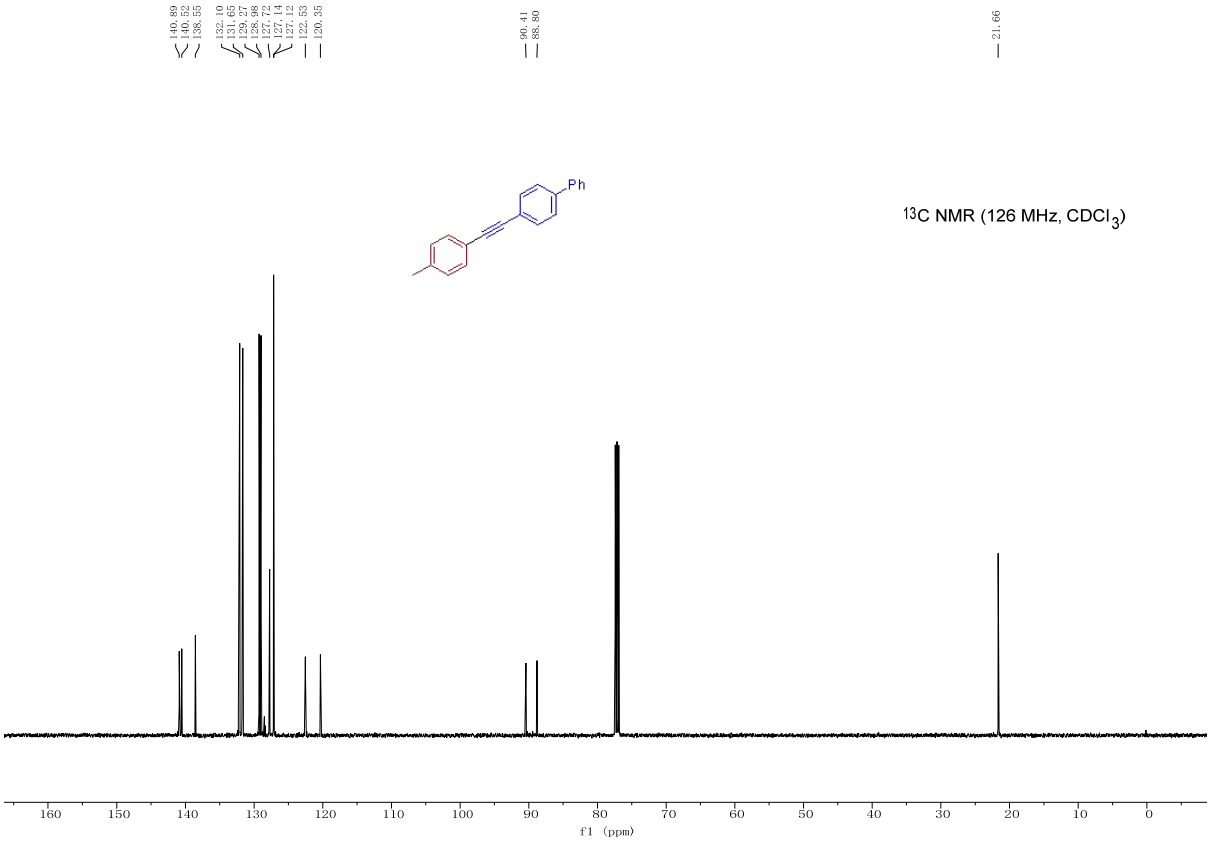
(20) 1-methoxy-2-((4-methylphenyl)ethynyl)benzene (**3-21**)



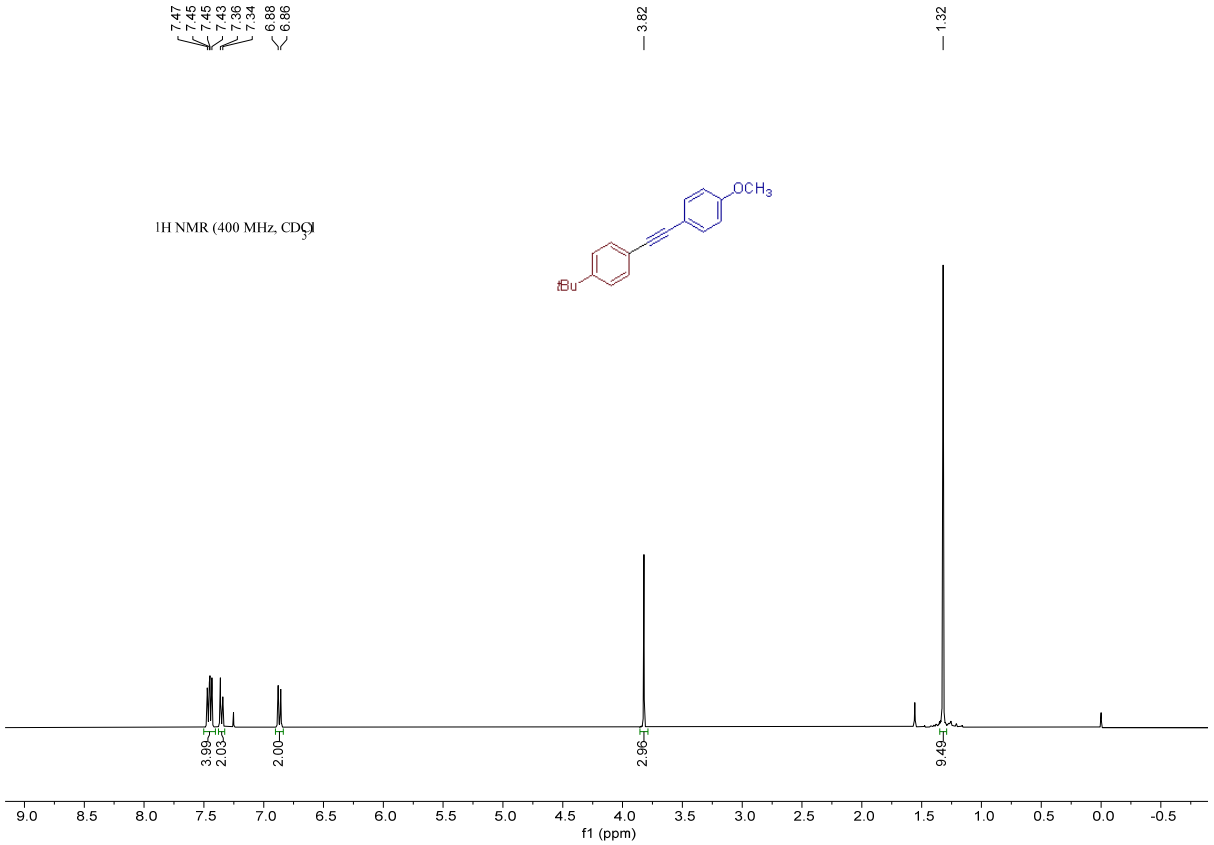


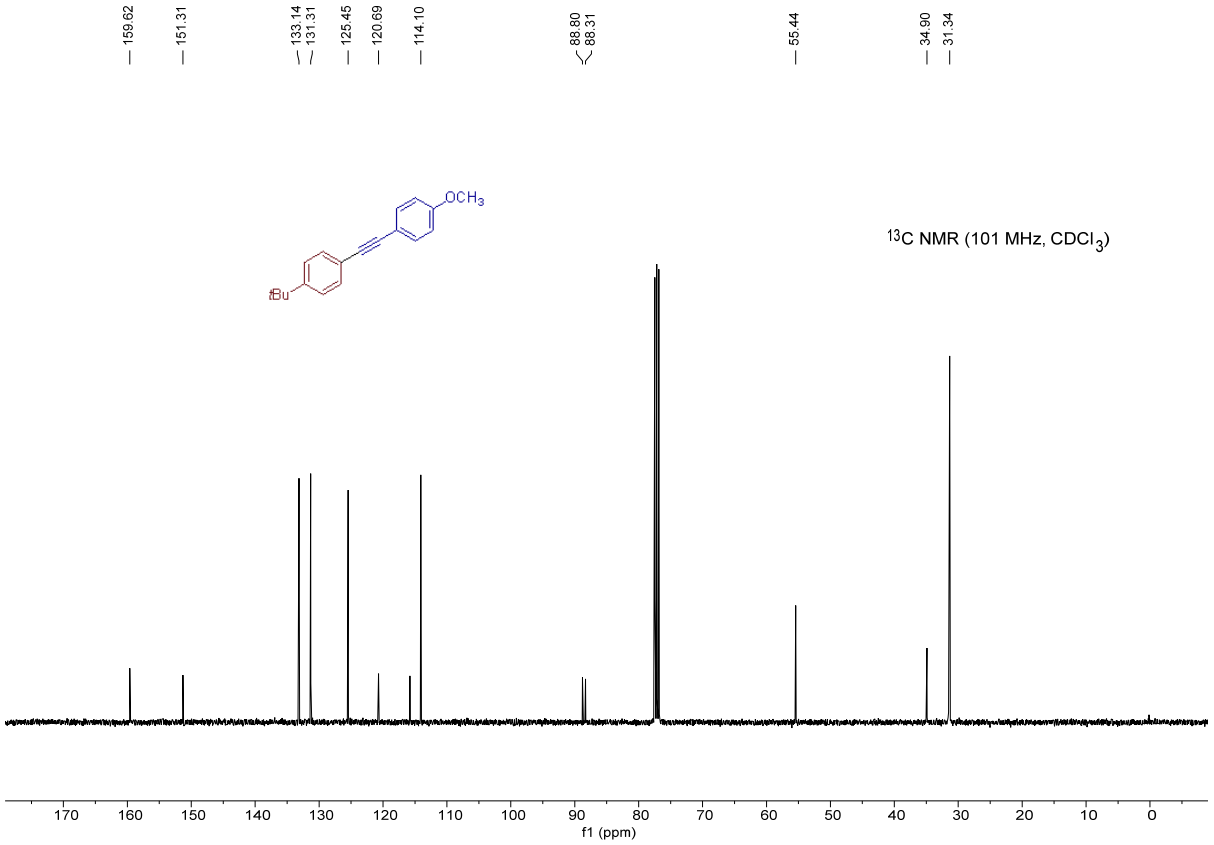
(21) 1-methyl-4-((4-phenylphenyl)ethynyl)benzene (**3-22**)



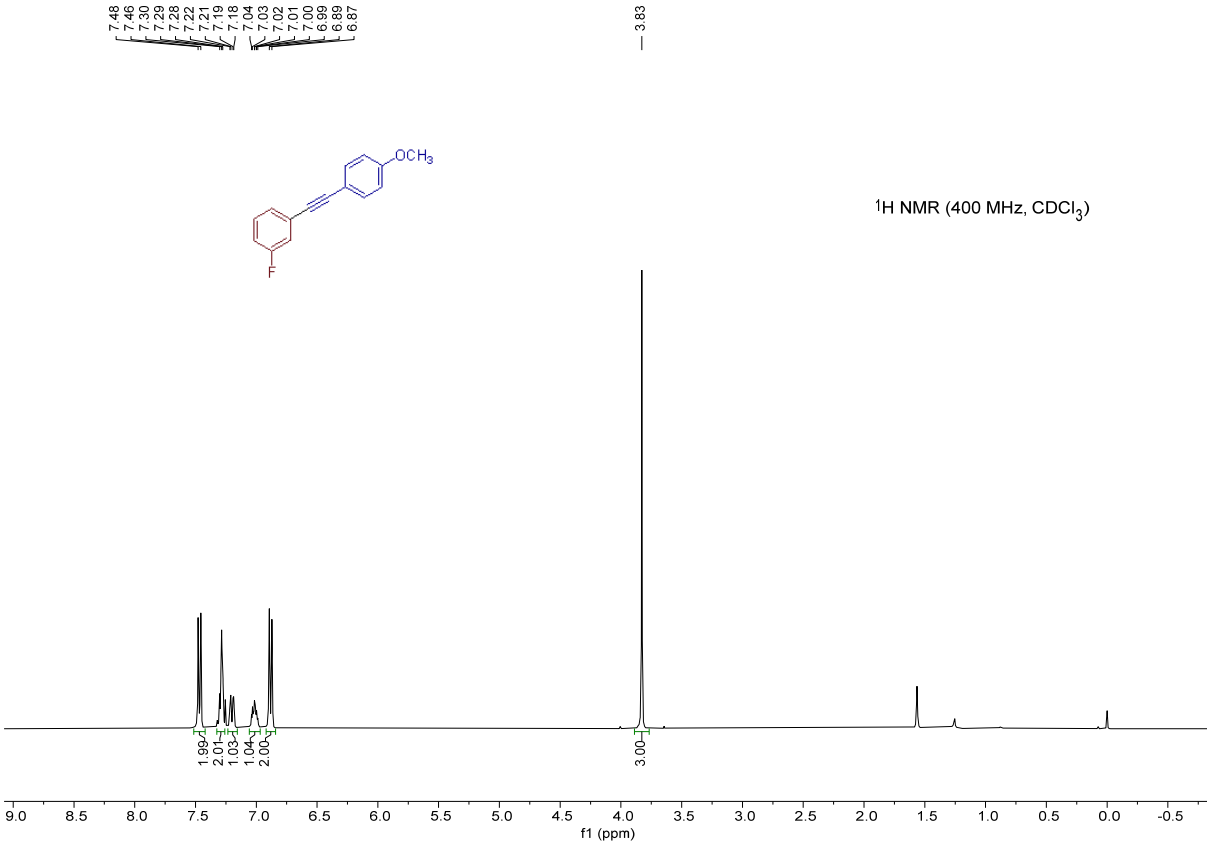


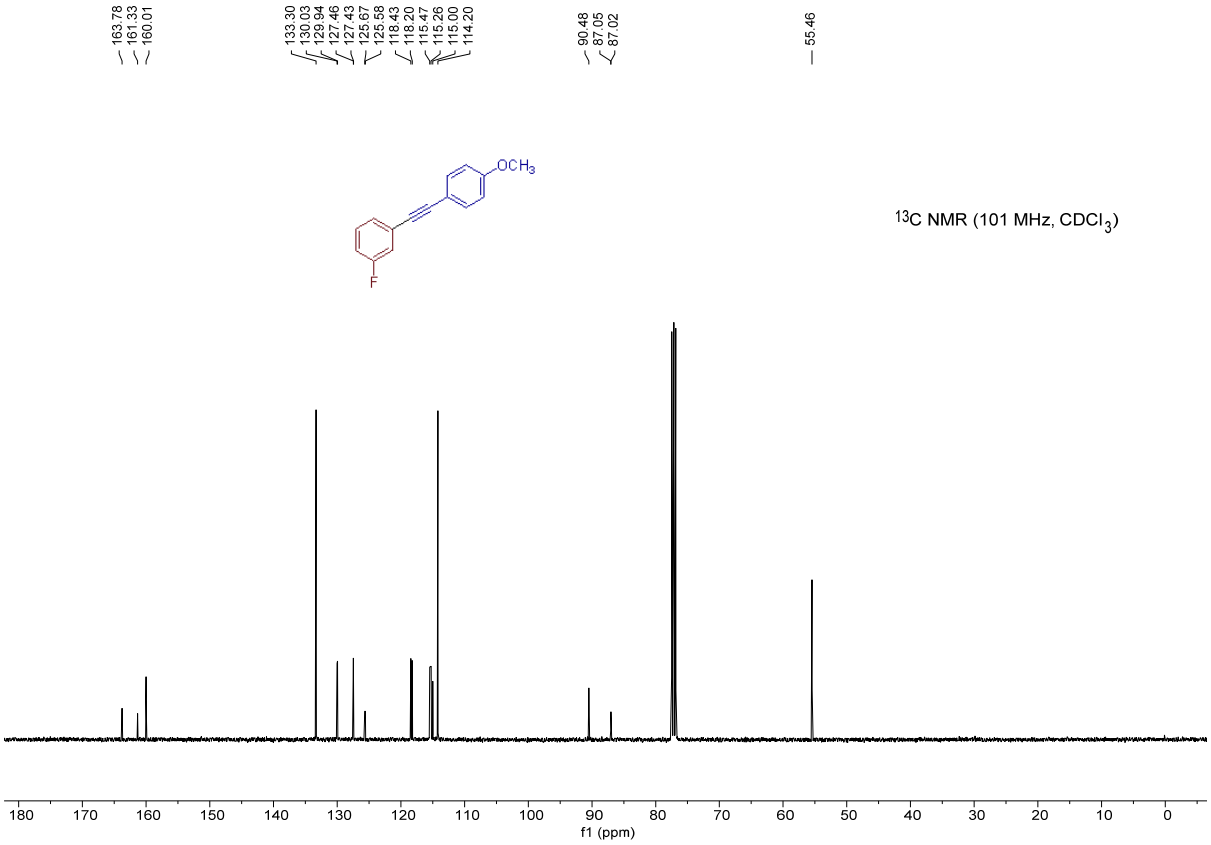
(22) 1-(*tert*-butyl)-4-((4-methoxyphenyl)ethynyl)benzene (**3-23**)

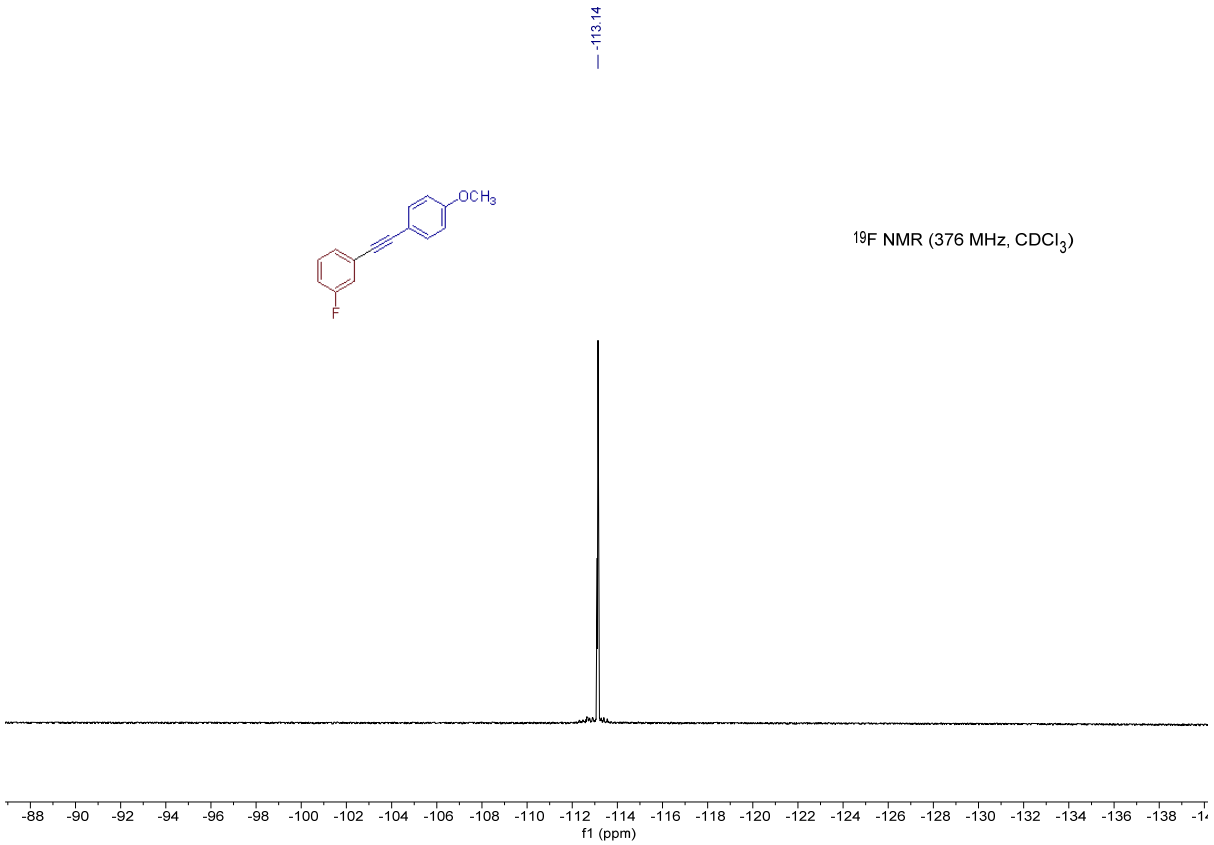




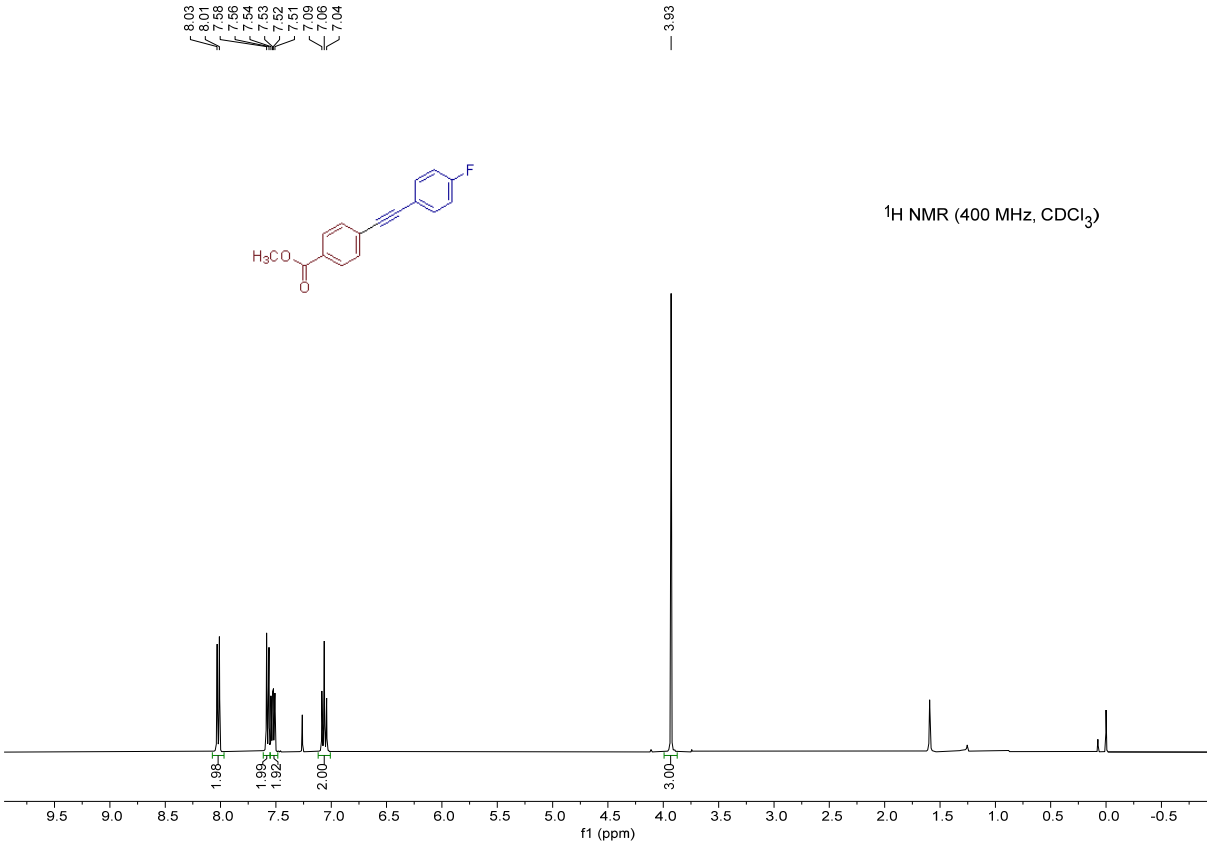
(23) 1-fluoro-3-((4-methoxyphenyl)ethynyl)benzene (**3-24**)

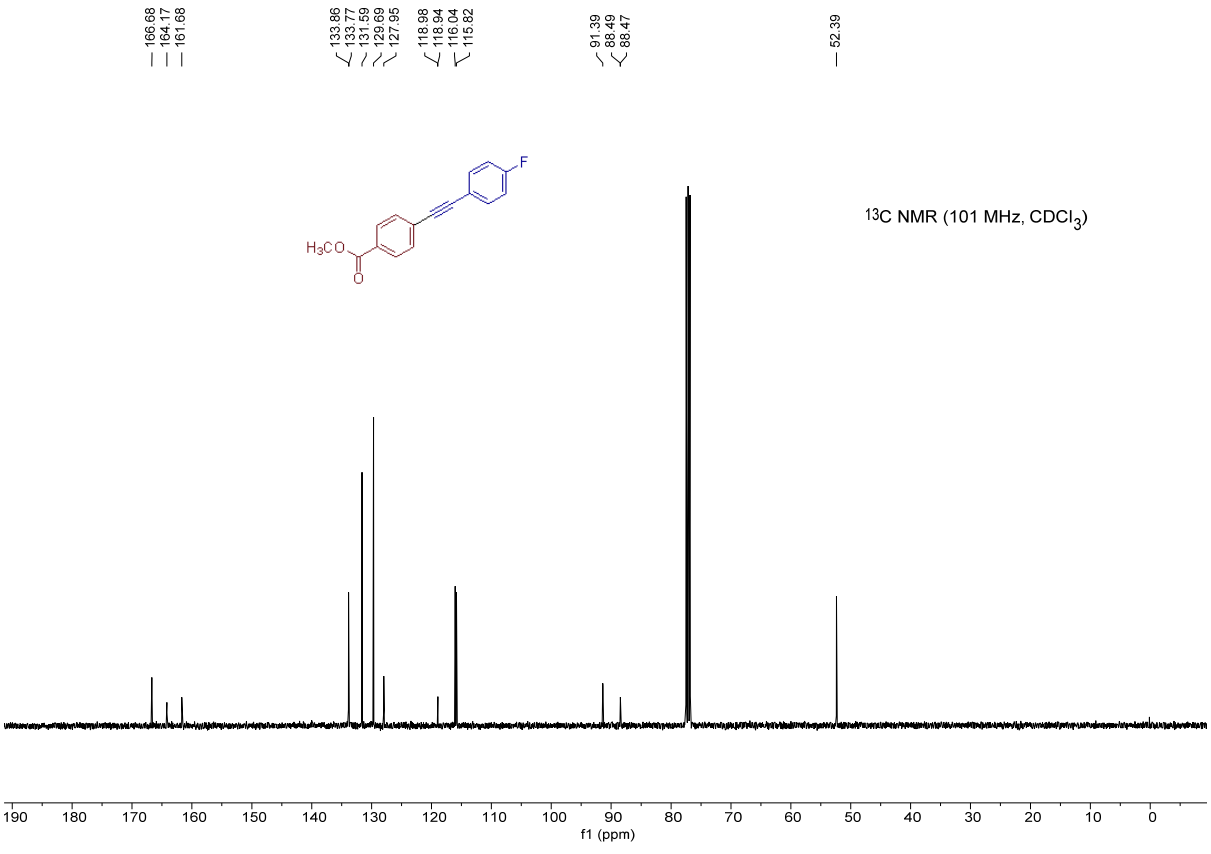


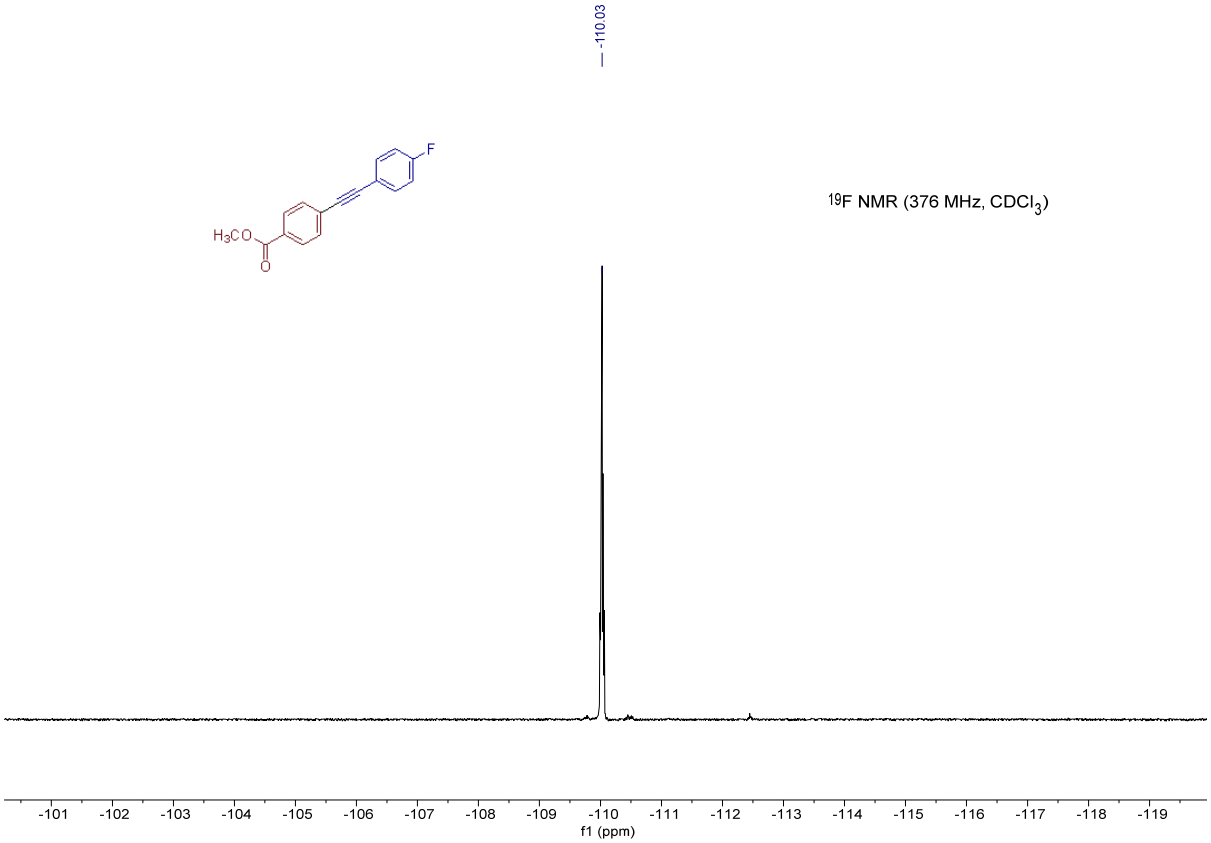



-113.14
OCH3
F
19F NMR (376 MHz, CDCl3)
-88 -90 -92 -94 -96 -98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138
f1 (ppm)

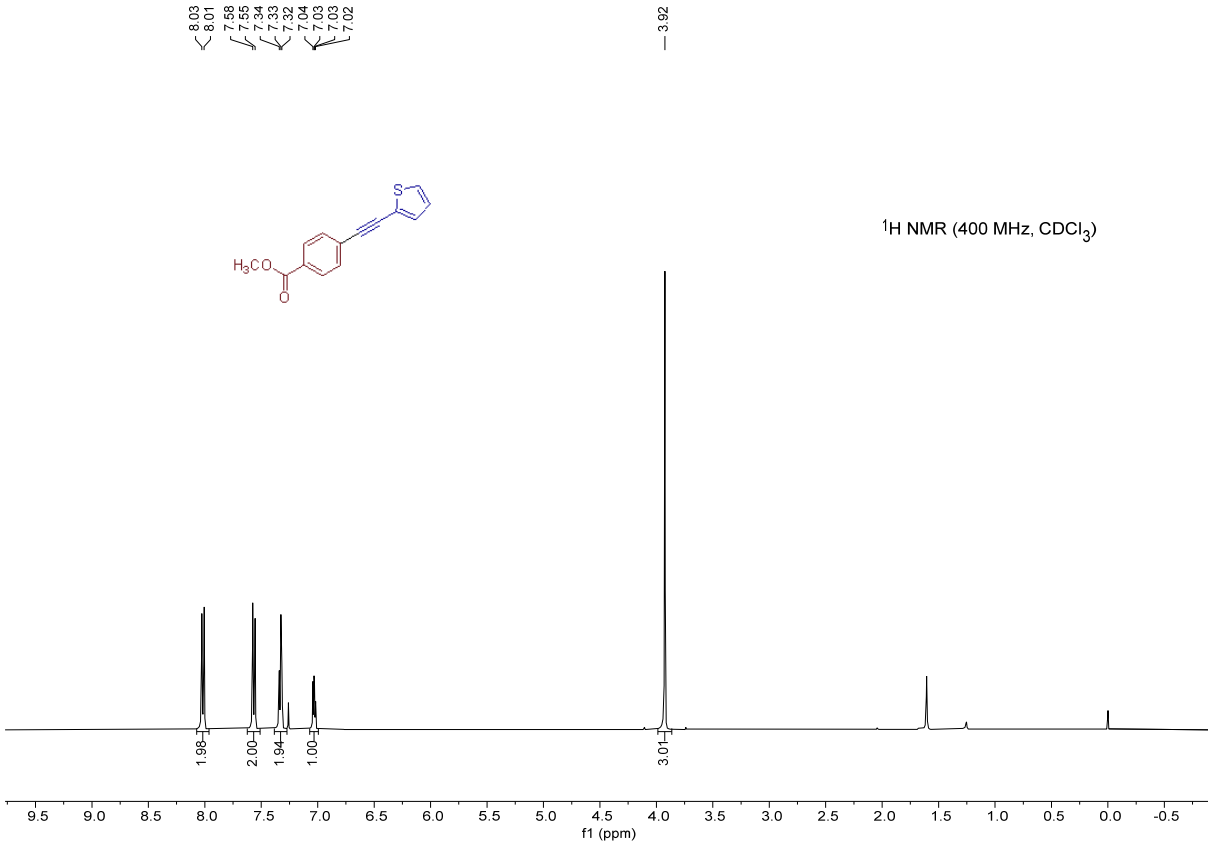
(24) methyl 4-((4-fluorophenyl)ethynyl)benzoate (**3-25**)

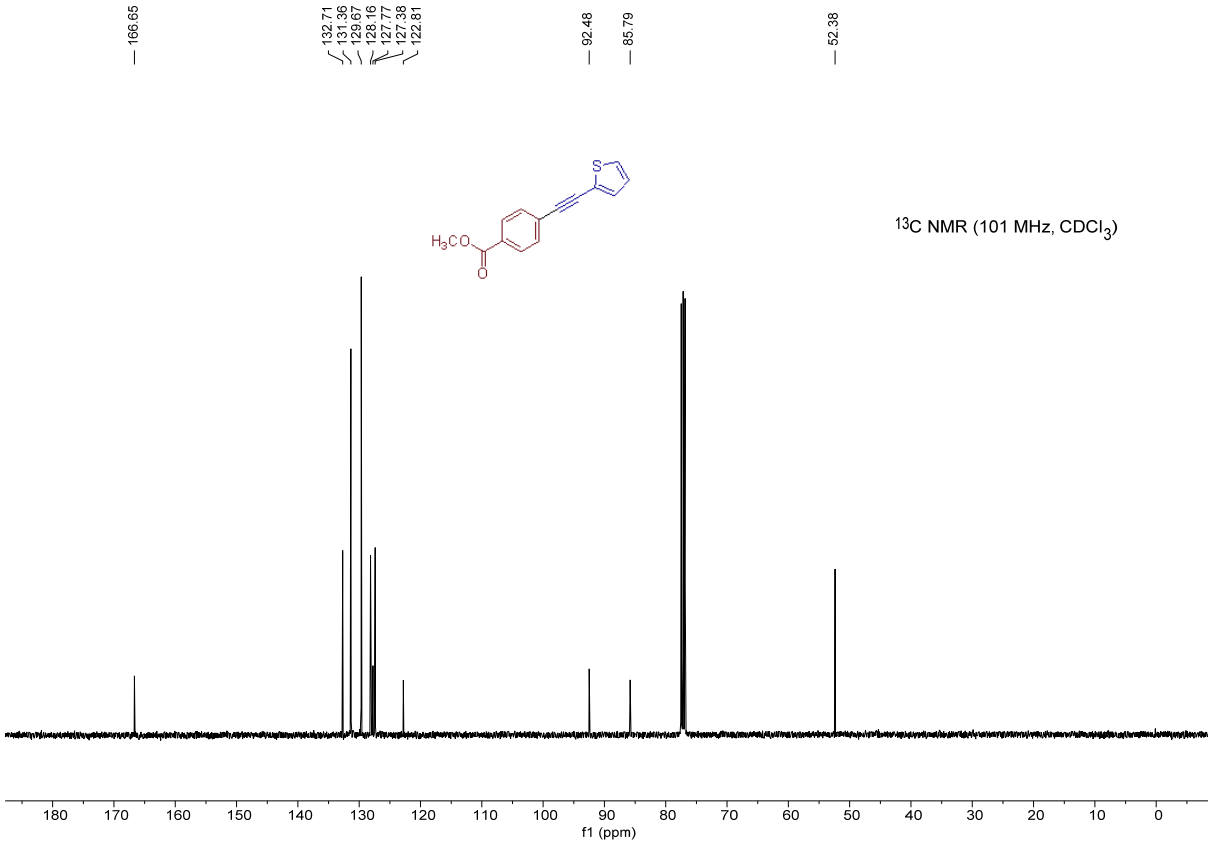




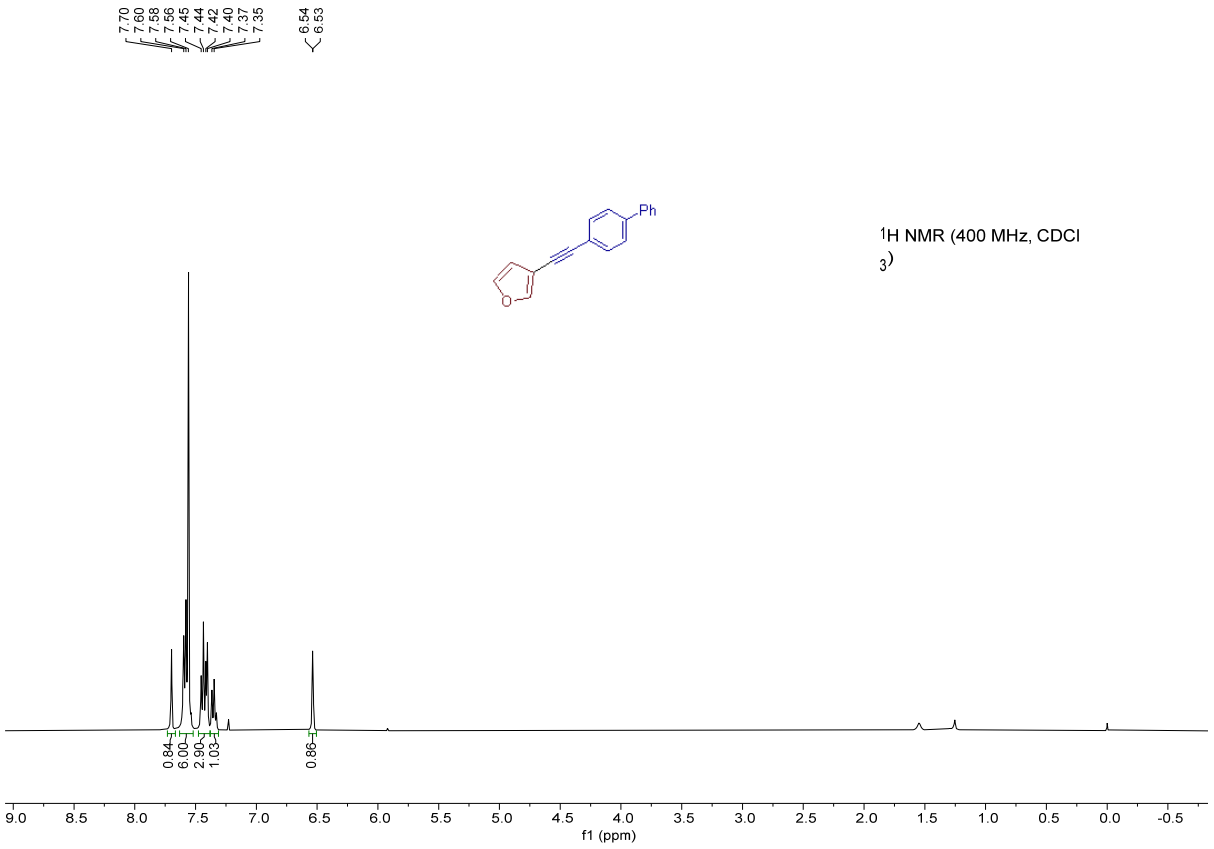

-110.03
F
H3CO
O
19F NMR (376 MHz, CDCl3)
-101
-102
-103
-104
-105
-106
-107
-108
-109
-110
-111
-112
-113
-114
-115
-116
-117
-118
-119
f1 (ppm)

(25) methyl 4-(thiophen-2-ylethynyl)benzoate (**3-26**)

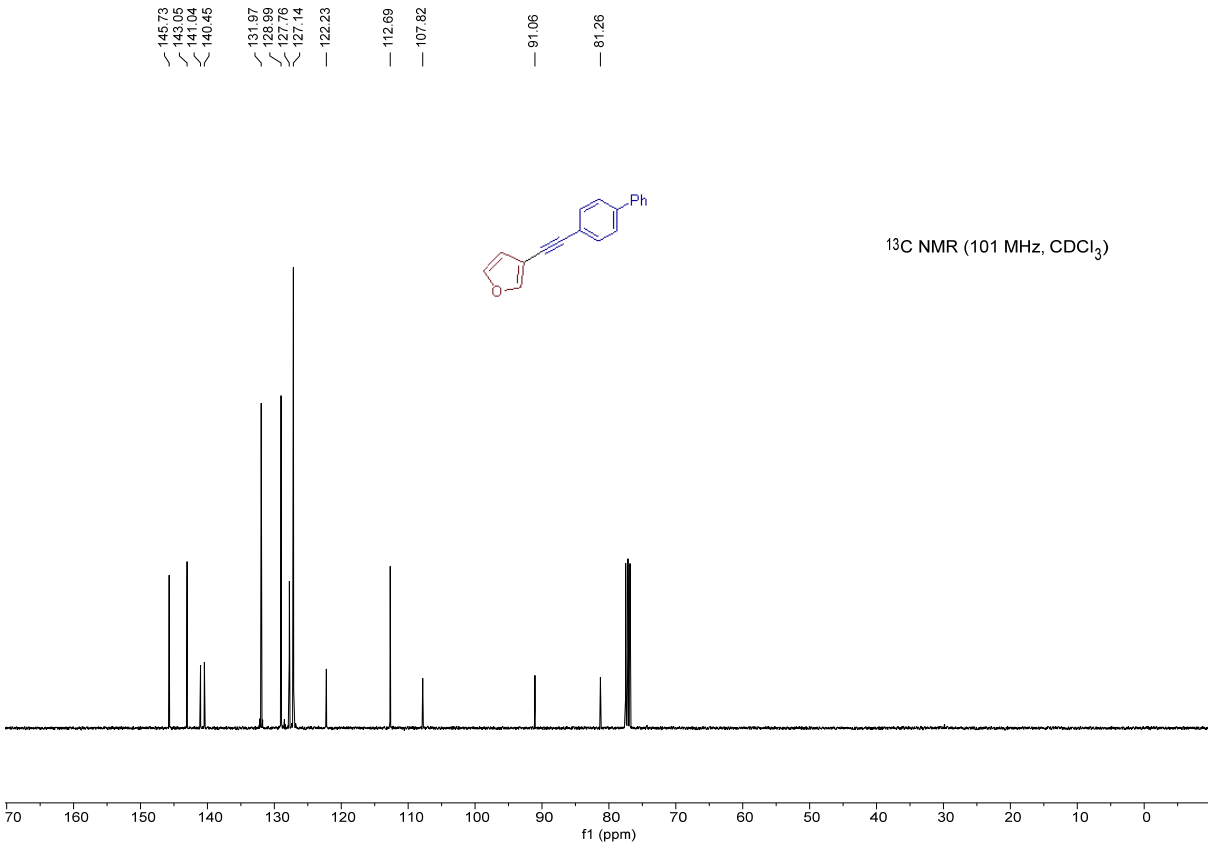




(26) 3-([1,1'-biphenyl]-4-ylethynyl)furan (**3-27**)

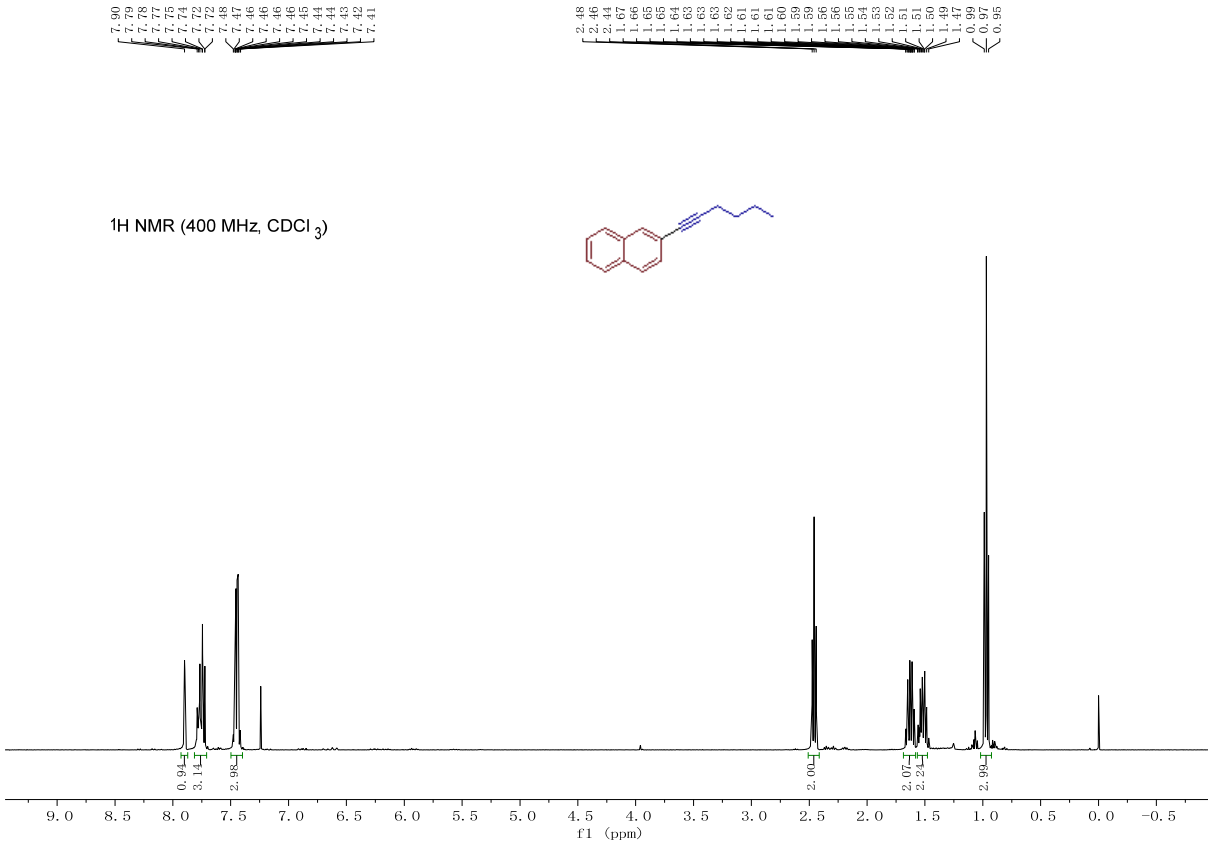


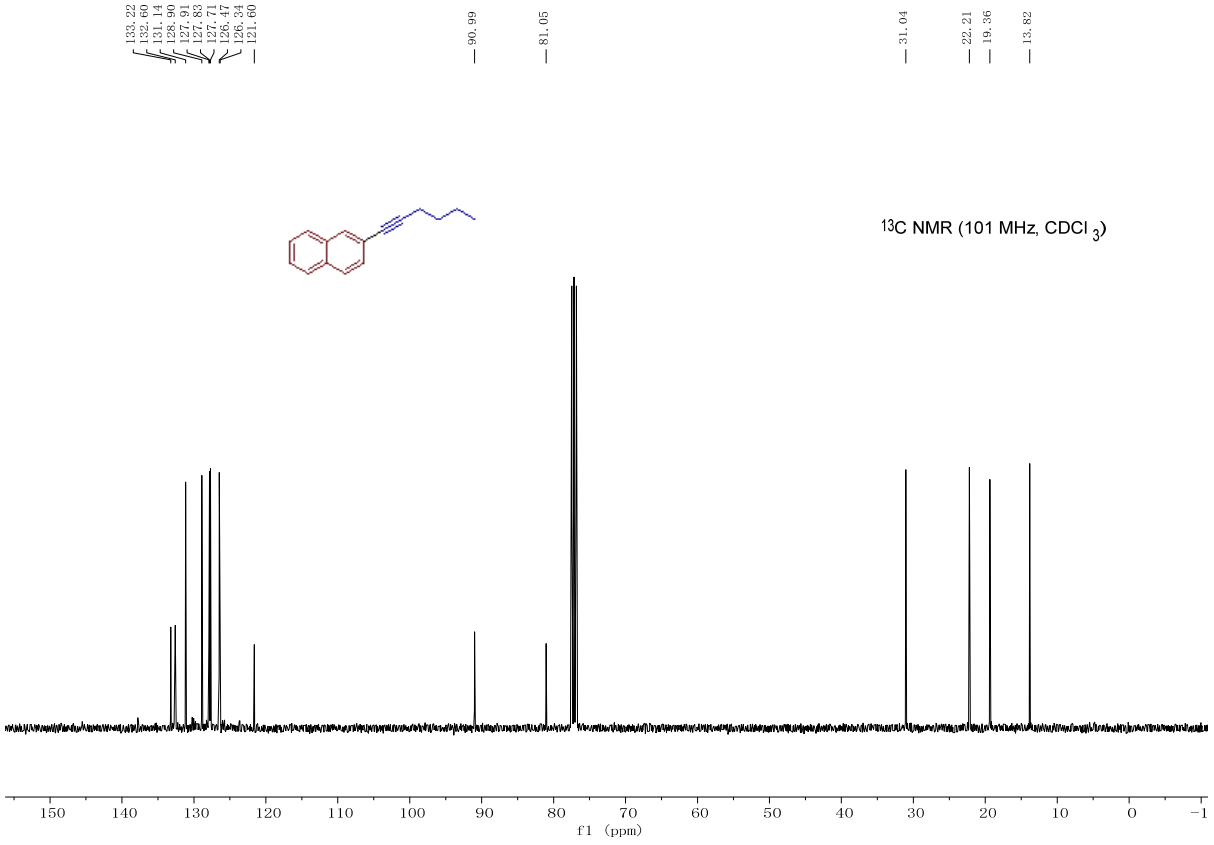
^{1}H NMR (400 MHz, $CDCl_3$)



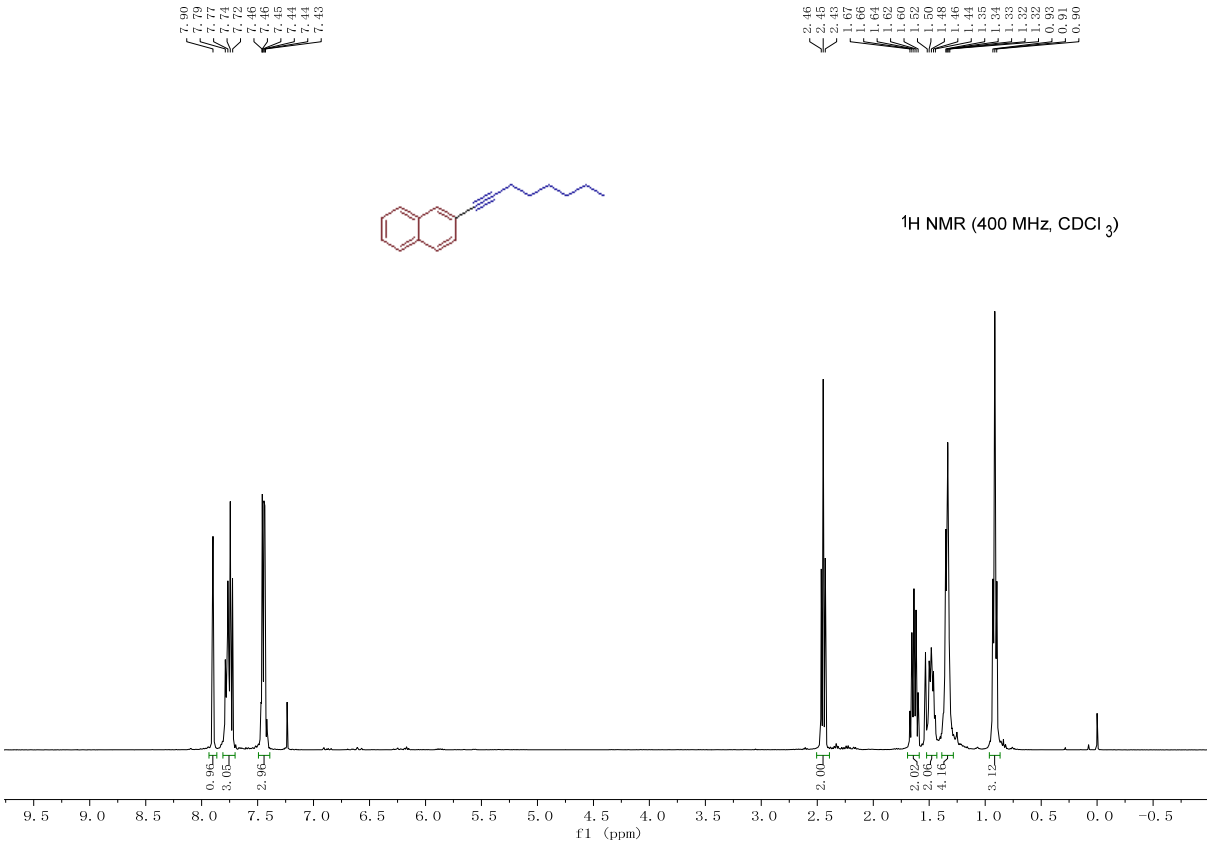
^{13}C NMR (101 MHz, $CDCl_3$)

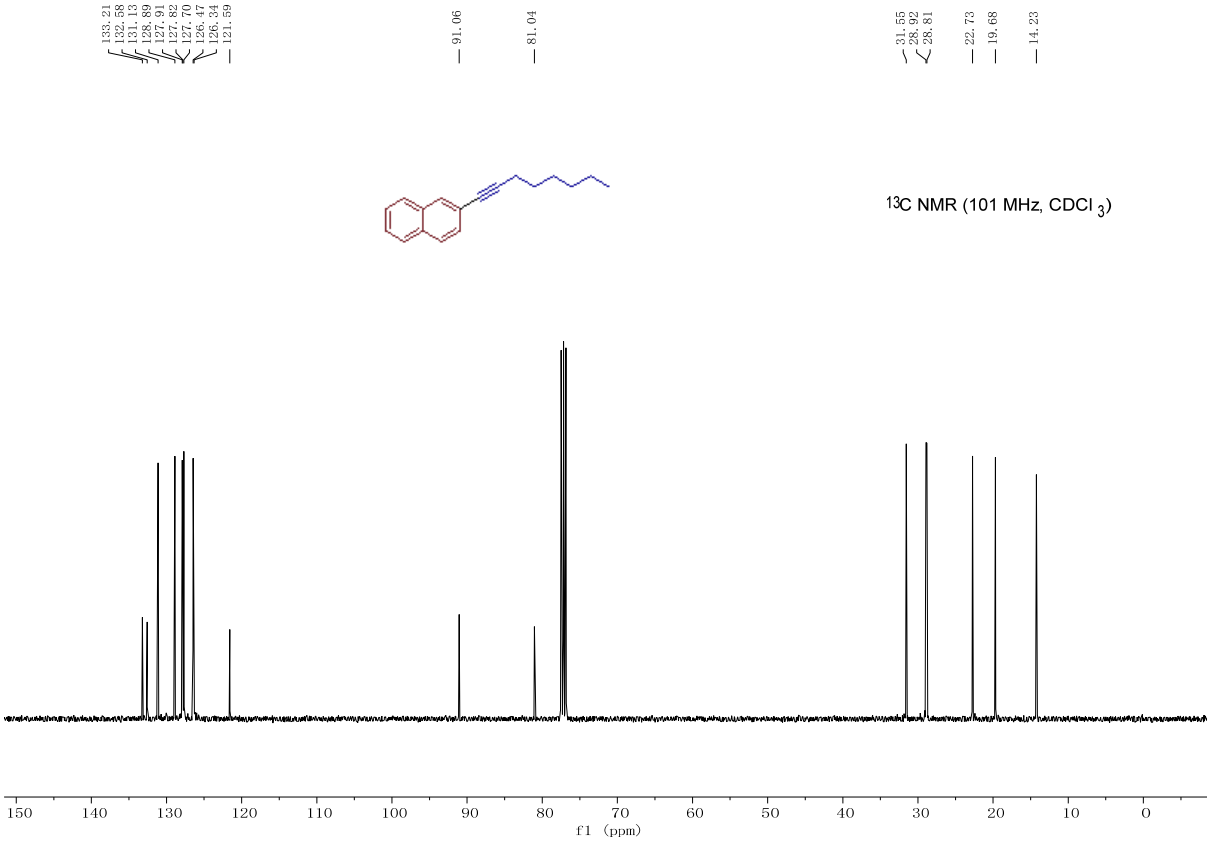
(27) 2-(hex-1-ynyl)naphthalene (**3-28**)



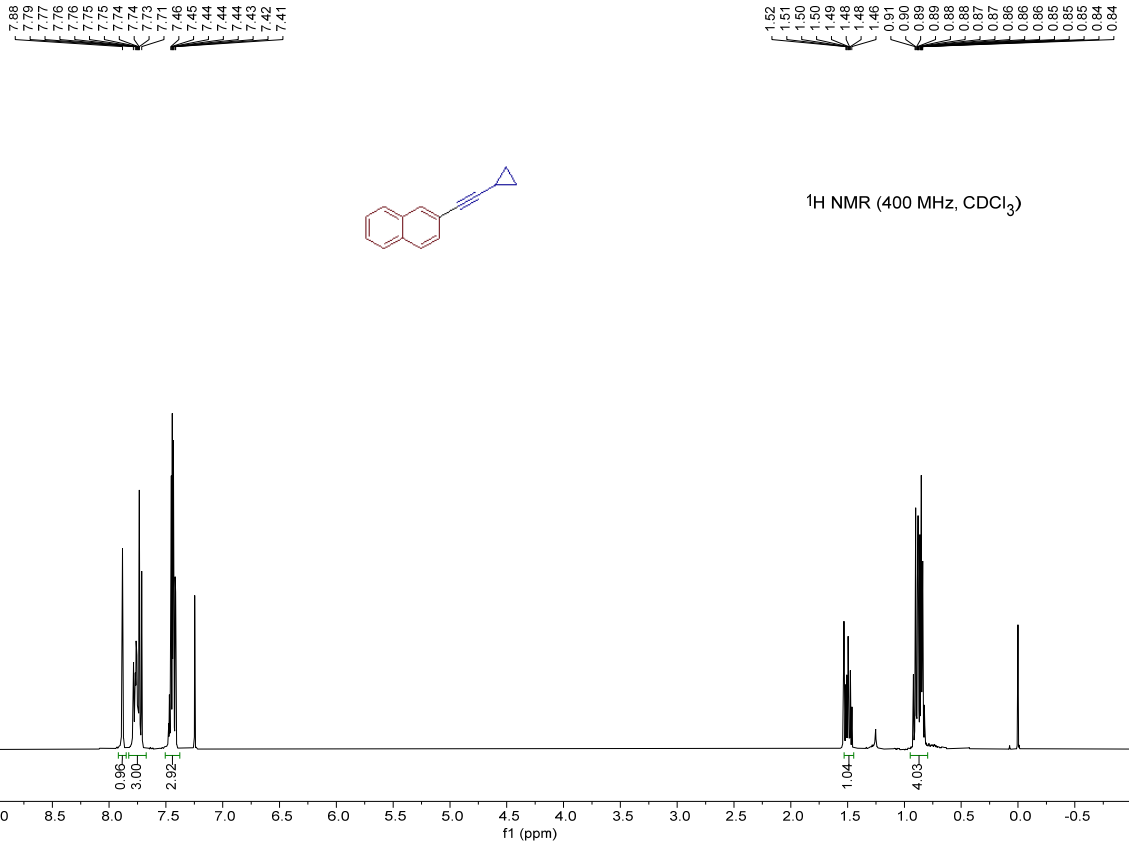


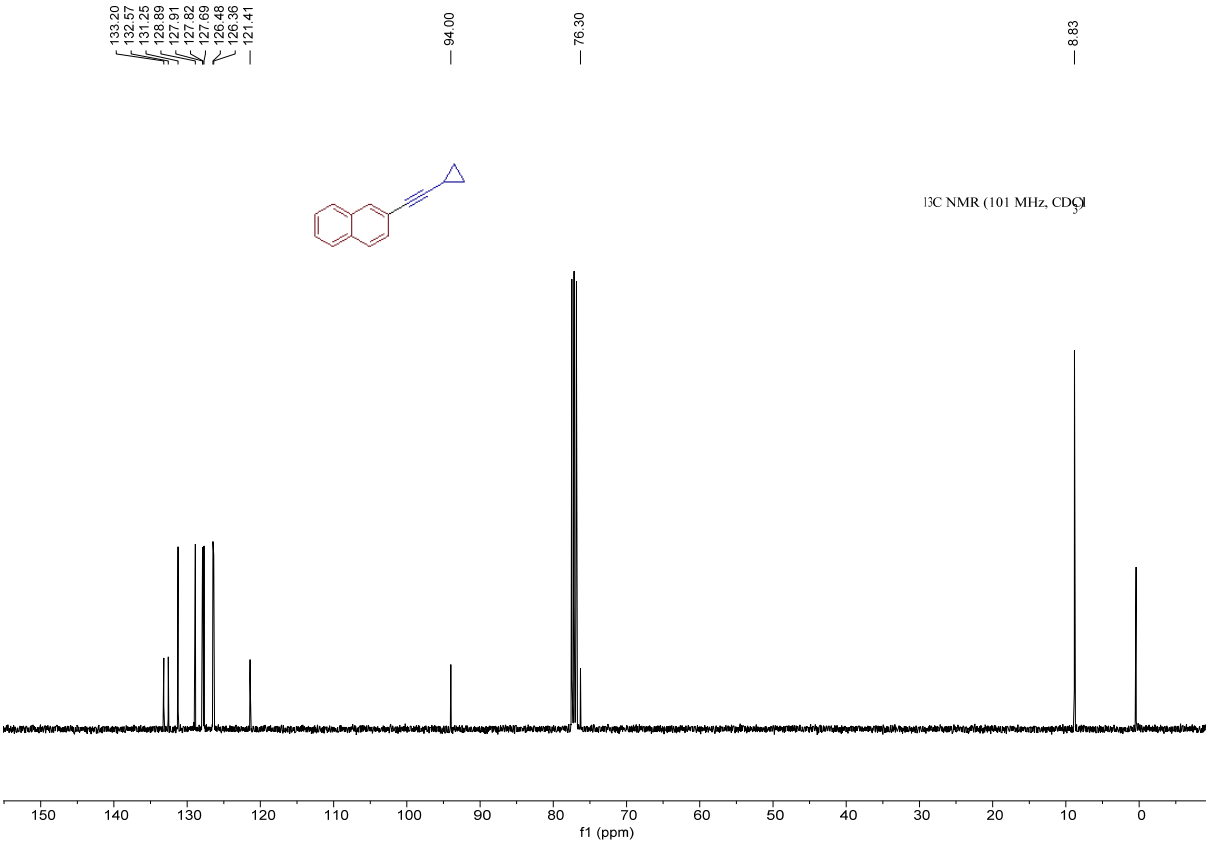
(28) 2-(oct-1-yn-1-yl)naphthalene (**3-29**)



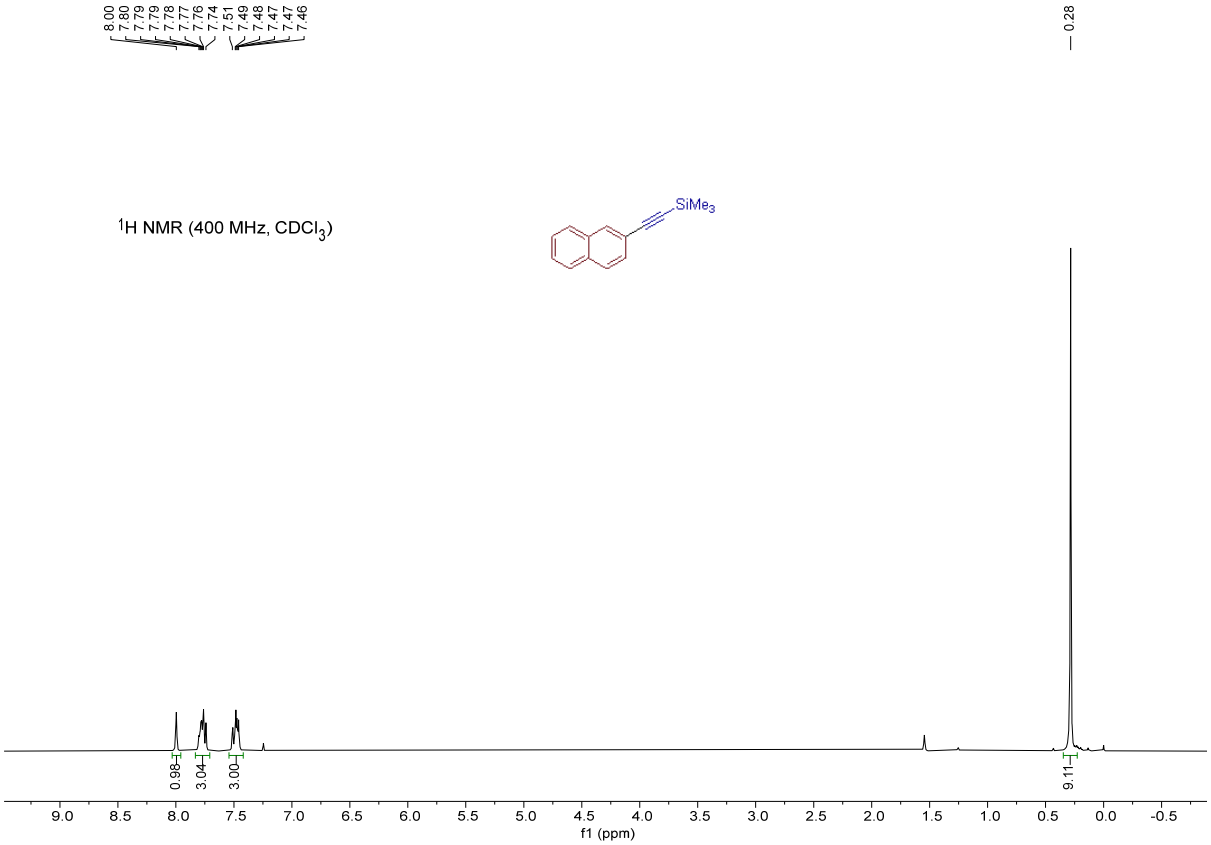


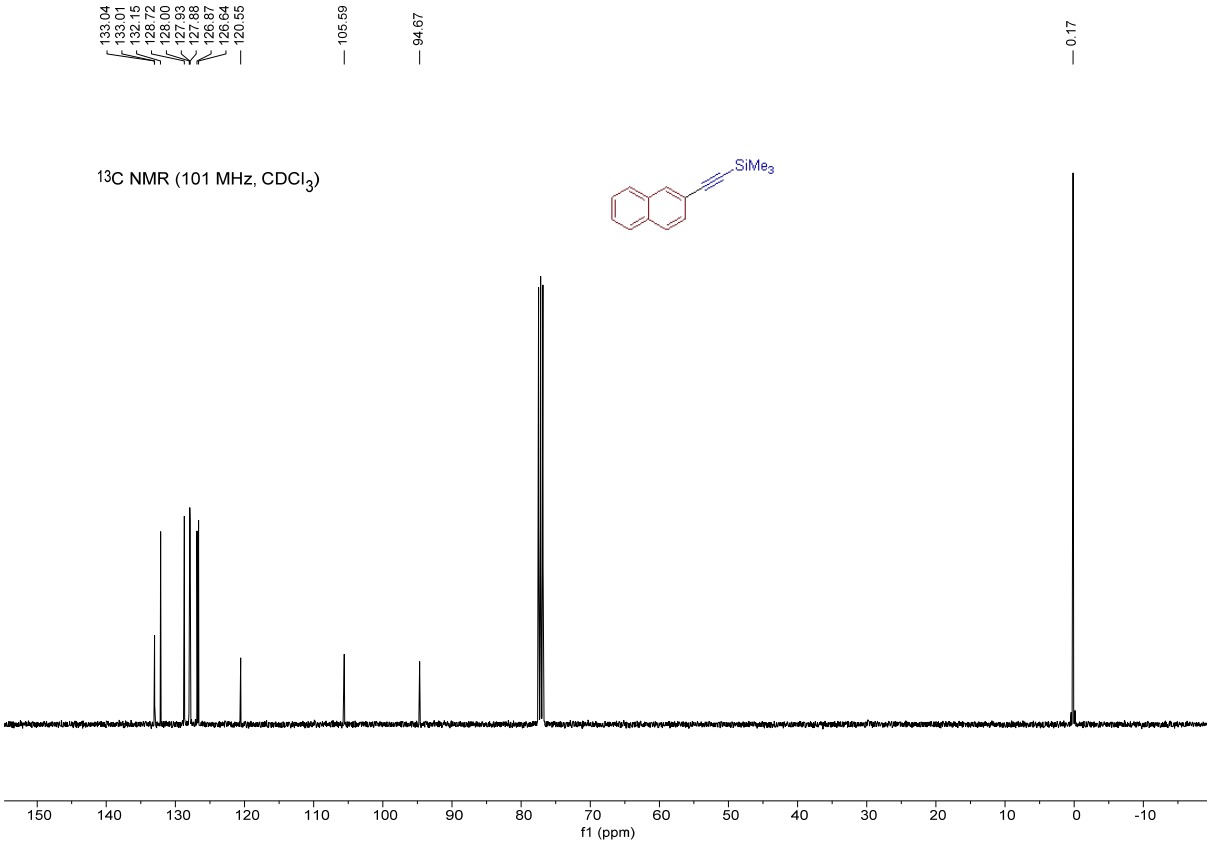
(29) 2-(cyclopropylethynyl)naphthalene (**3-30**)



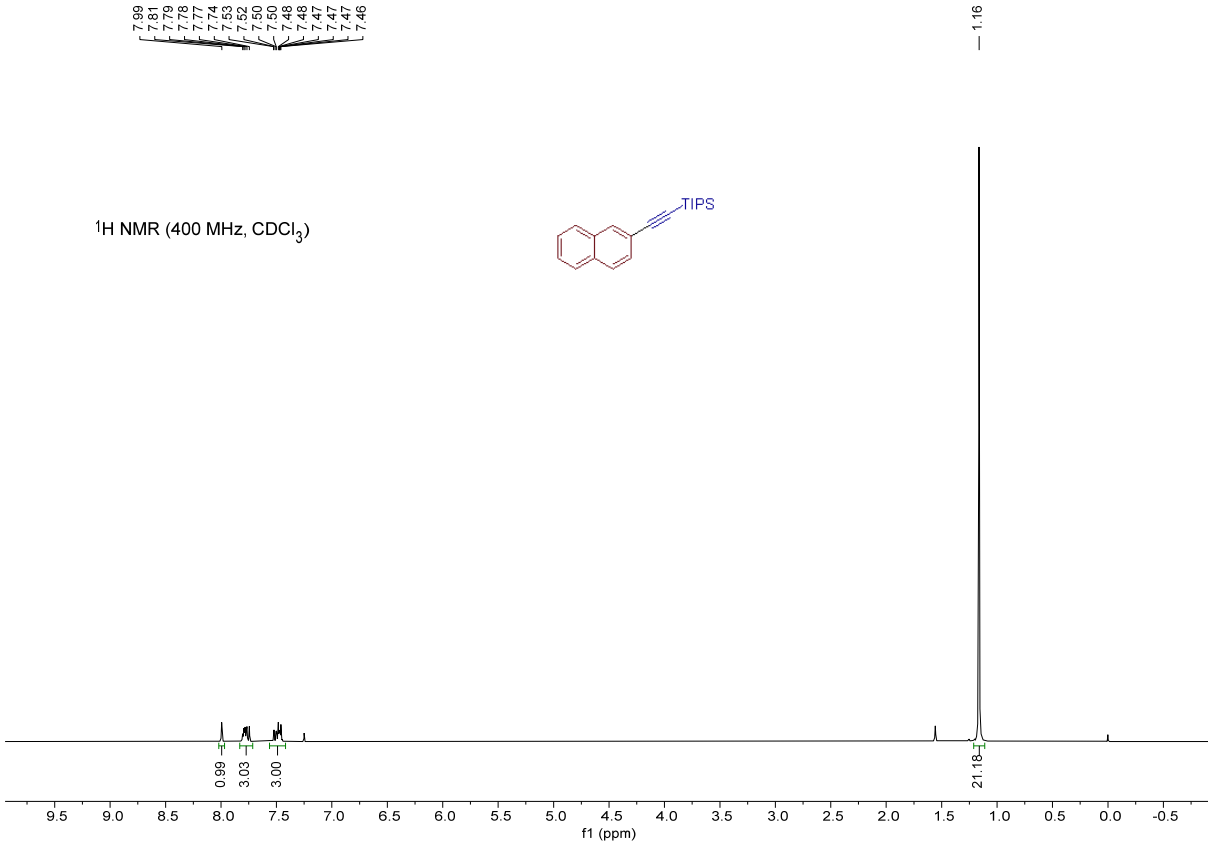


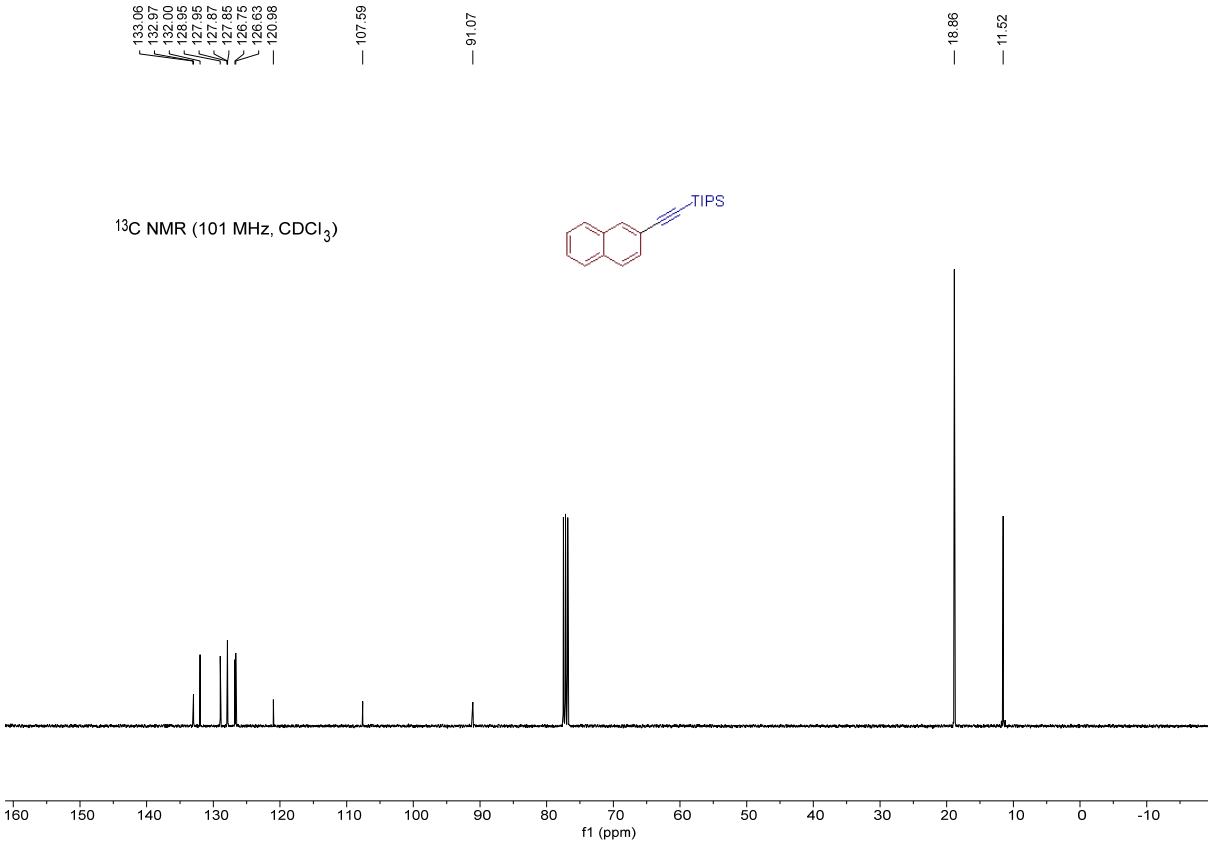
(30) trimethyl(naphthalen-2-ylethynyl)silane (**3-31**)



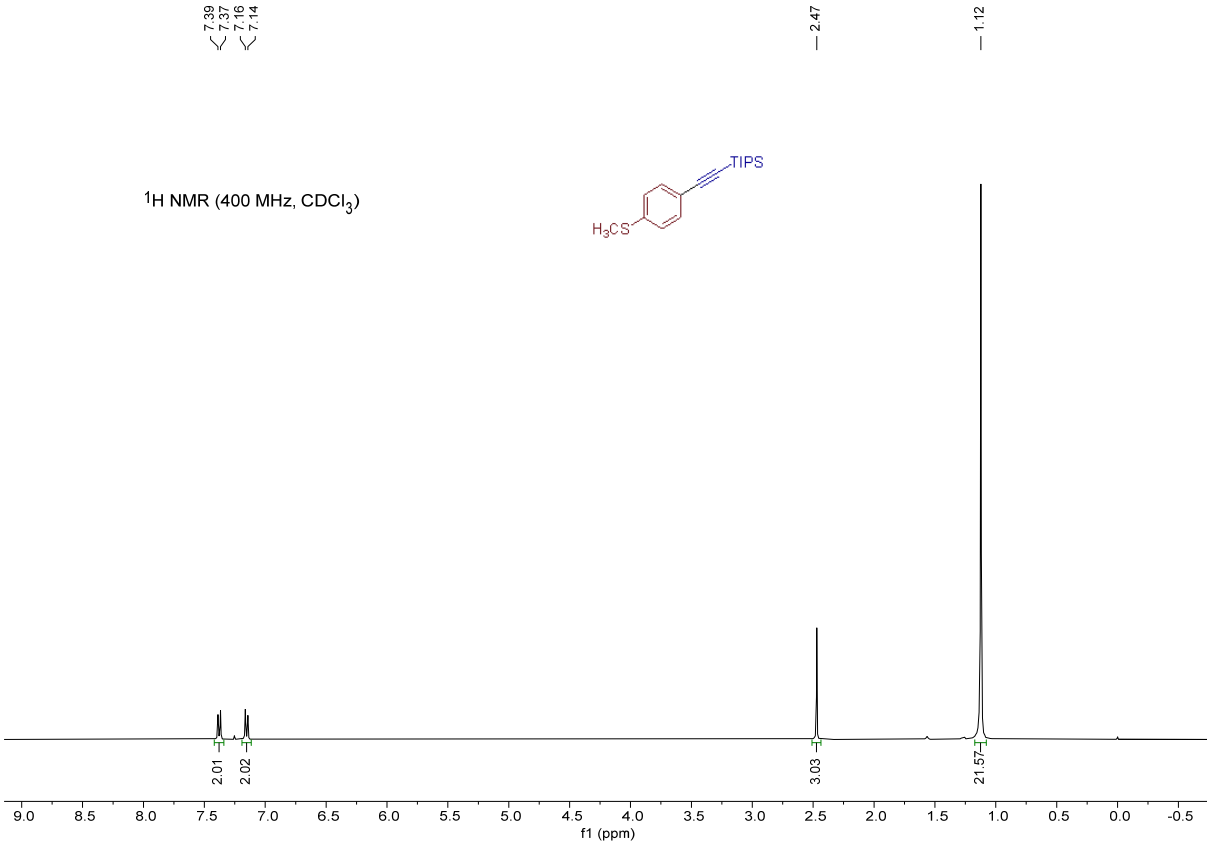


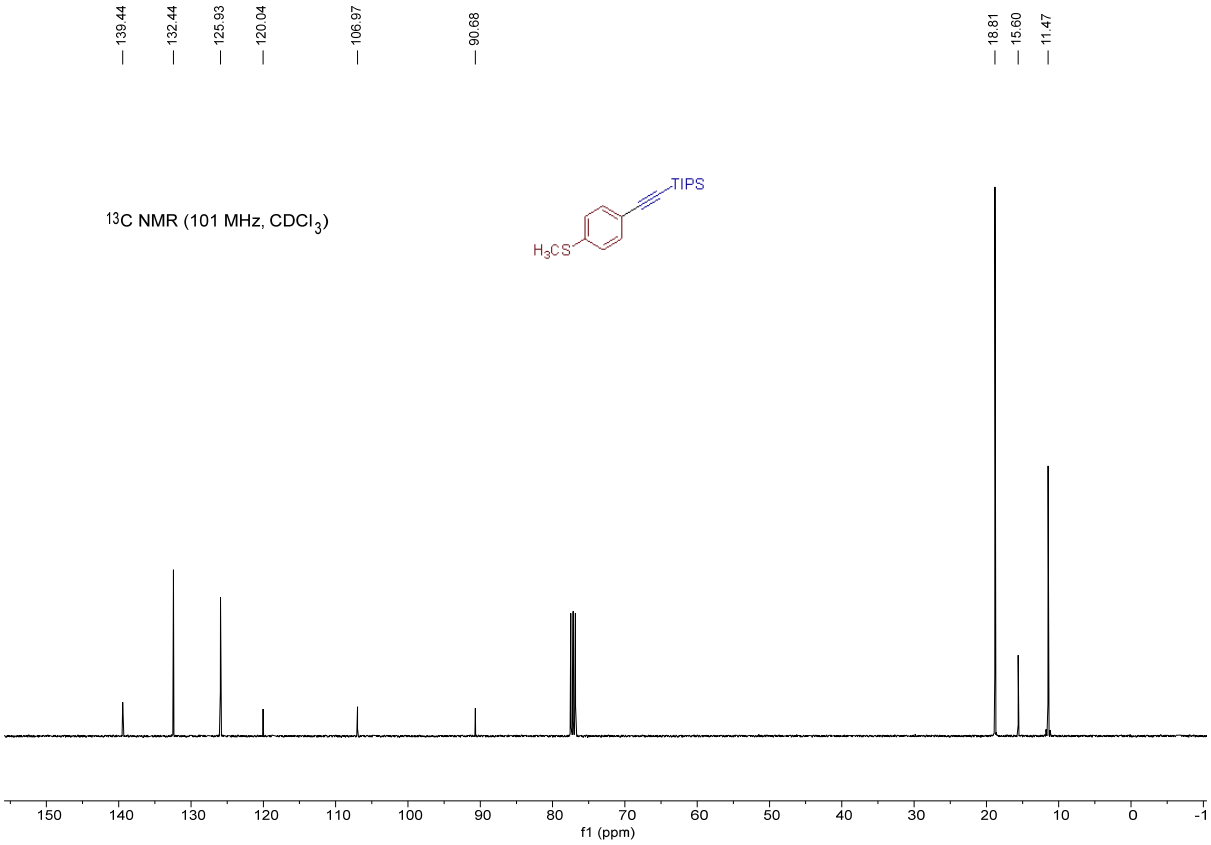
(31) (naphthalen-2-ylethynyl)(tripropan-2-yl)silane (**3-32**)



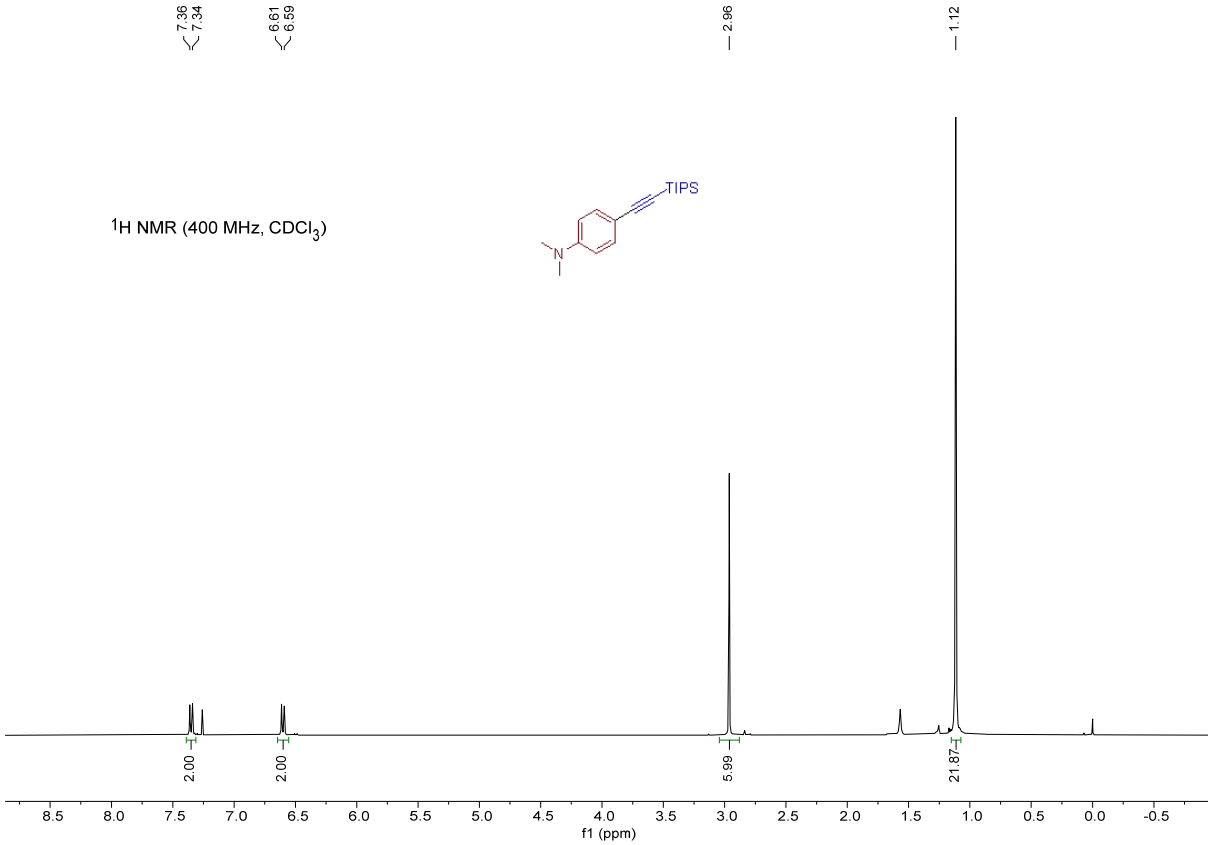


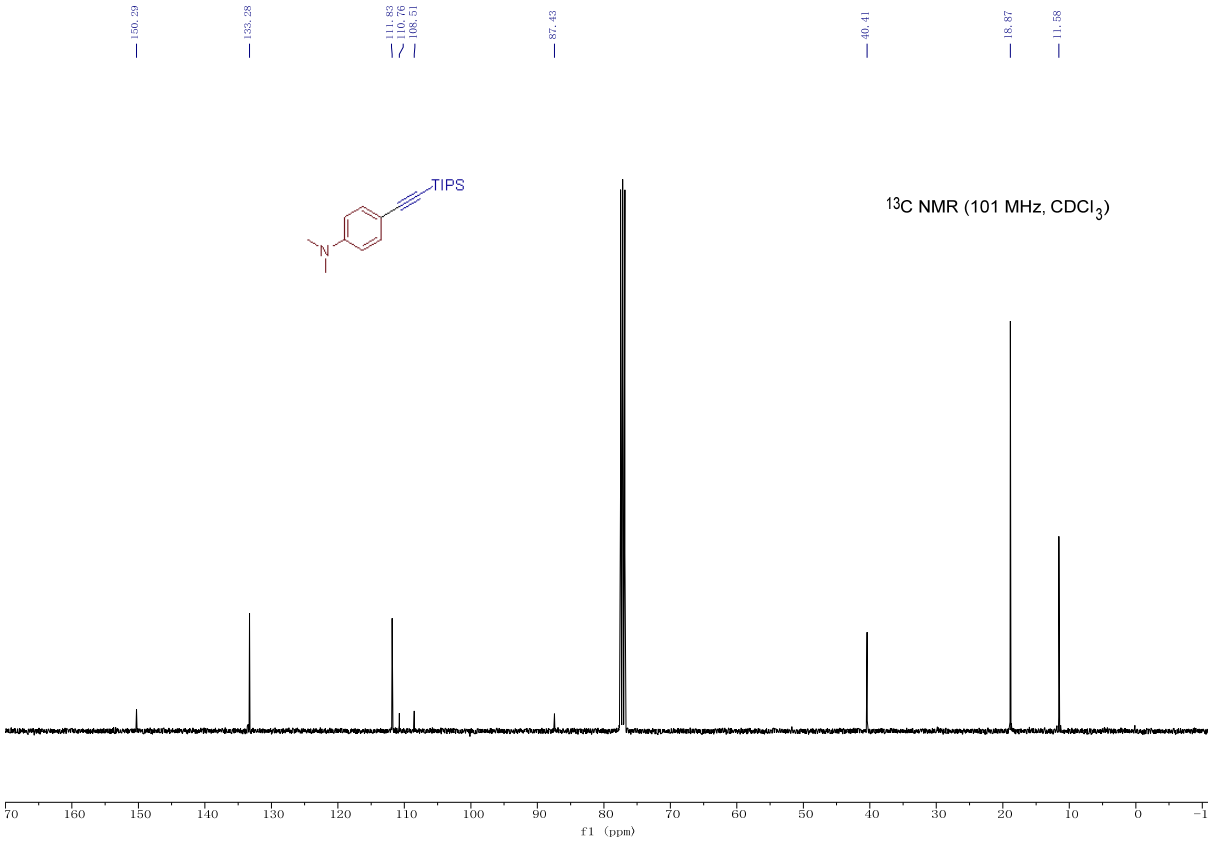
(32) ((4-(methylsulfanyl)phenyl)ethynyl)(tripropan-2-yl)silane (**3-33**)



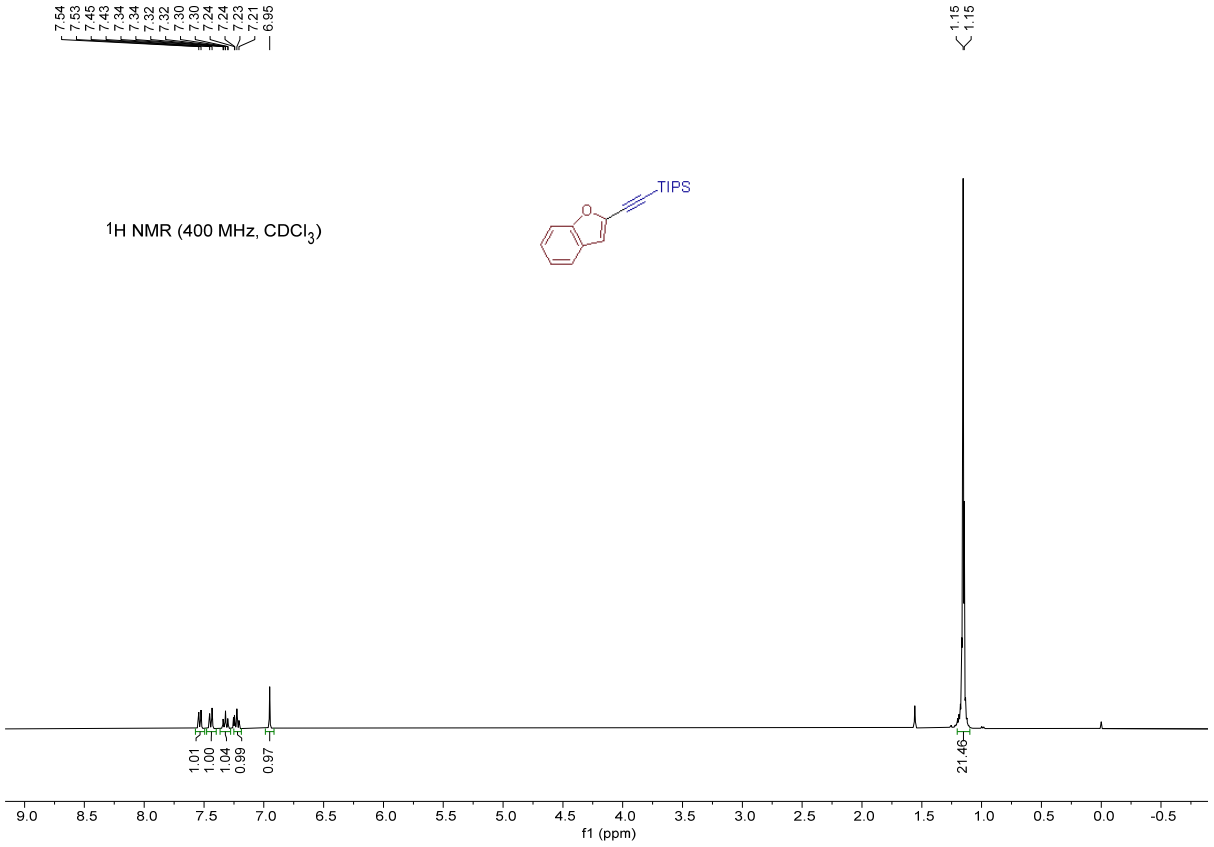


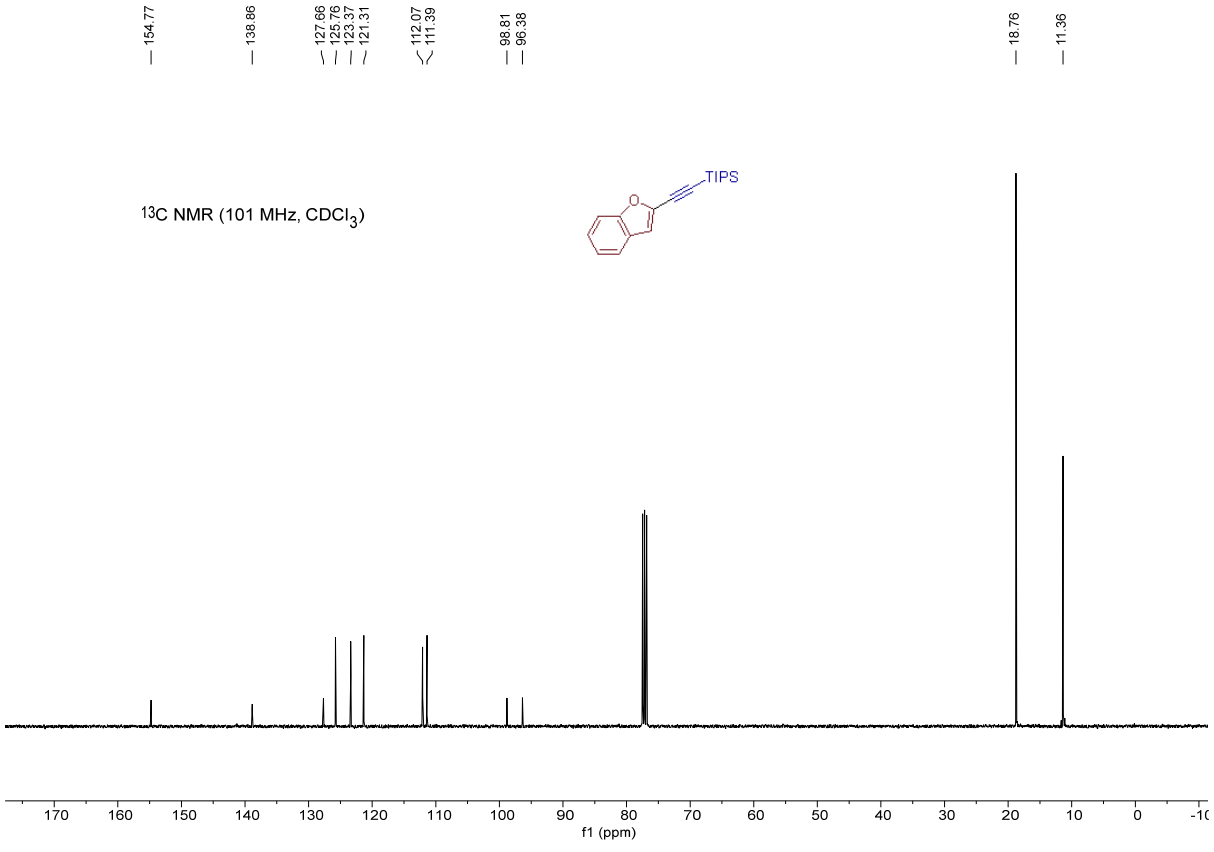
(33) N,N-dimethyl-4-((triisopropylsilyl)ethynyl)aniline (**3-34**)



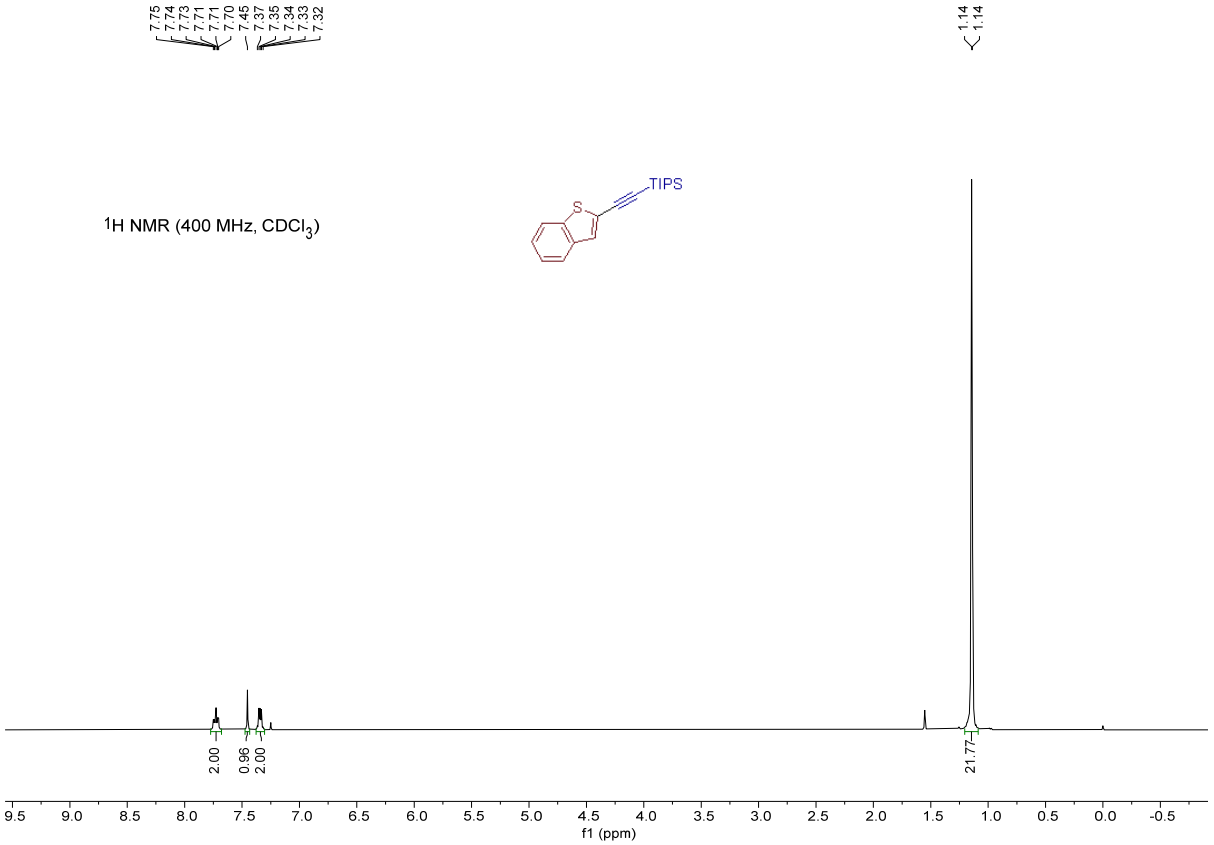


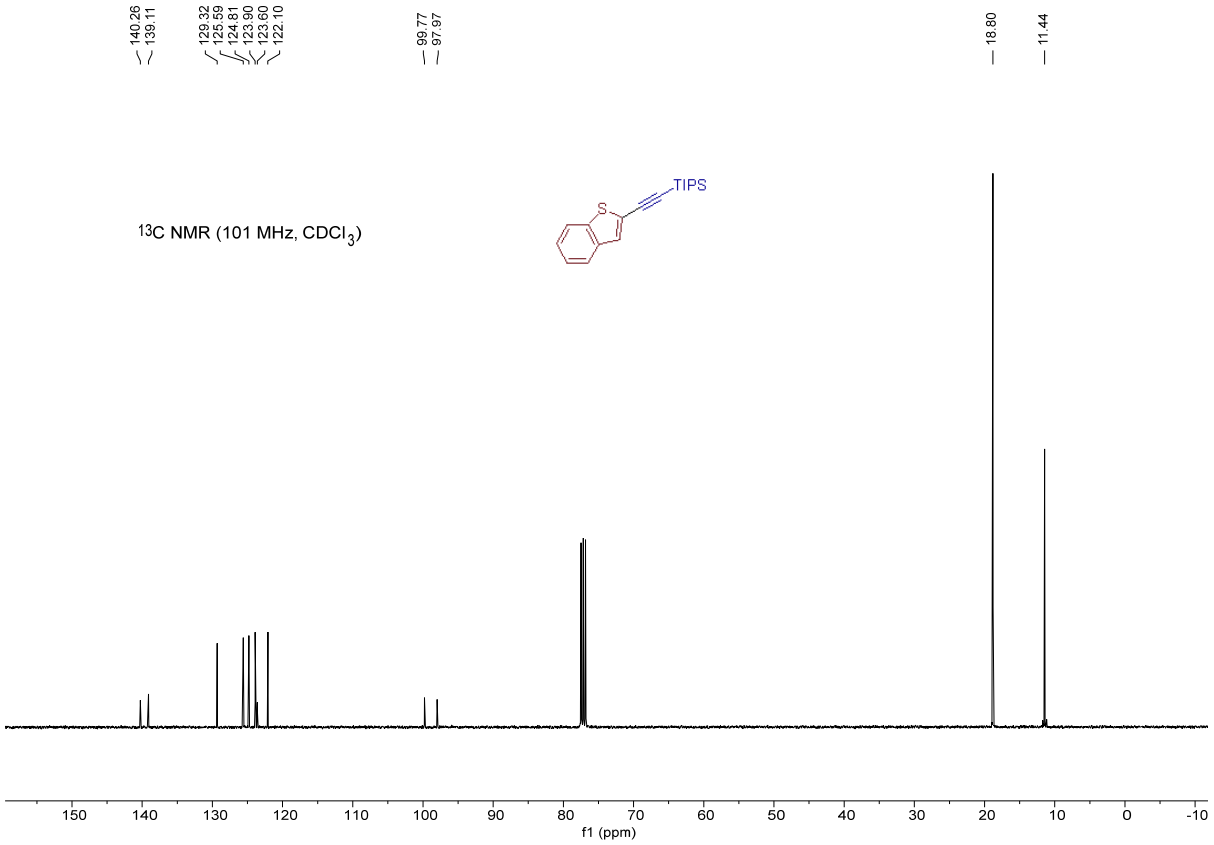
(34) (benzofuran-2-ylethynyl)triisopropylsilane (**3-35**)



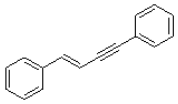


(35) (benzo[b]thiophen-2-ylethynyl)triisopropylsilane (**3-36**)

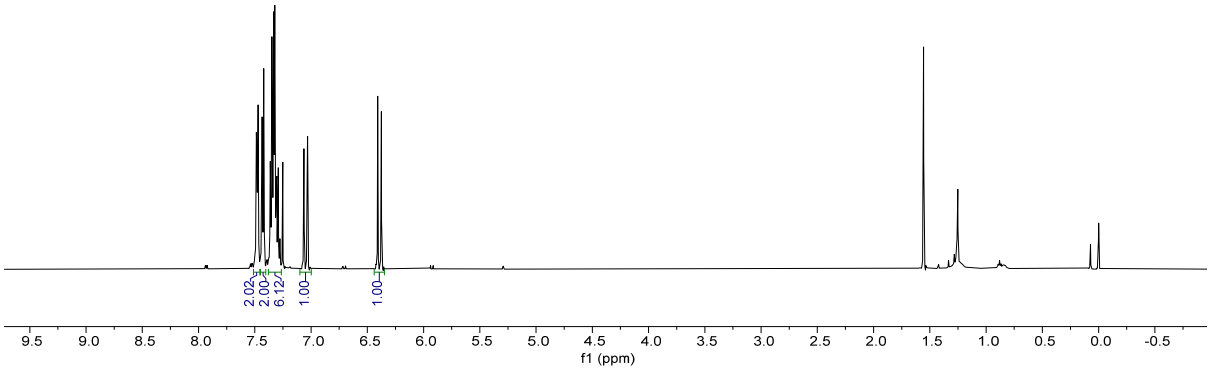


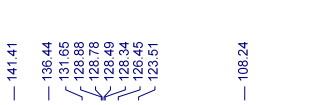


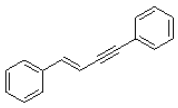
(36) (E)-but-1-en-3-yne-1,4-diyldibenzene (**3-37**)



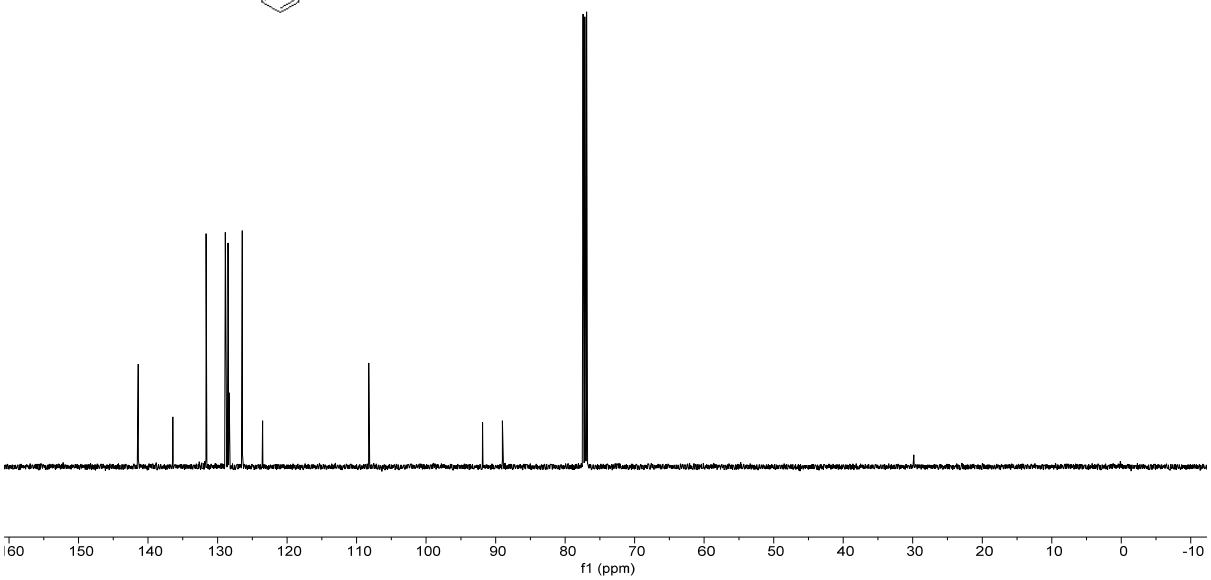
^{1}H NMR (500 MHz, $CDCl_3$)







^{13}C NMR (126 MHz, $CDCl_3$)



(37) A mixture of (*E*)-pent-3-en-1-yn-1-ylbenzene (**3-38**) and 1,4-diphenylbuta-1,3-diyne