Supplementary Information

N-Heterocycle Carbene Copper Catalyzed Direct Alkylation of Terminal Alkynes with Nonactivated Alkyl Triflates

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1. General

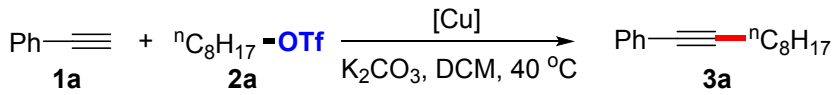
All reactions were carried out under nitrogen atmosphere unless otherwise noted. All ^{1}H and ^{13}C NMR spectra were recorded on Bruker ADVANCE III 500 MHz spectrometer in deuterium solvents with tetramethylsilane (TMS) as internal standard. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad signal. Chemical shifts are given in ppm and are referenced to TMS (^{1}H, ^{13}C). All spectra were obtained at 25 °C in the solvent indicated. Coupling constants *J* are given in Hz. GC analyses were performed on Agilent 6890 instrument with FID detector using an HP-5 capillary column (30 m x 0.32 mm (i.d.), 0.25 μ). High-resolution mass spectra were recorded in the EI mode on Waters GCT Premier TOF MS. Reactions rates were acquired by Mettler-Toledo ReactIR™15 with iC IR software. Melting points were determined on BUCHI M-565 apparatus. Single crystal X-ray diffraction data were collected on a Bruker Apex II CCD detector using Mo-Kα radiation (λ = 0.71073 Å). Flash column chromatography was performed on neutral silica gel (200-300 mesh) with ethyl acetate/petroleum ether as eluent. All solvents were used after dried and distillation. N-heterocycle carbene copper chlorides (NHCCuCl) were synthesized according to the reported methods.[1] All bases were commercial available and used directly. Most terminal alkynes were commercial available and used directly. Alkyne **1e** was prepared through Pd-catalyzed coupling between 2,6-dibromobenzene and 2-methyl-3-butyn-2-ol, followed by the basic cleavage of the protecting group.[2] **1p**,[3] **1q**,[3] and **1j**[4] were prepared through Pd-catalyzed coupling of the corresponding aryl bromide and (trimethylsilyl)acetylene and following desilylations.[5] **5f** was synthesized starting from phenol and 5-chloropentyne.[6] Alkyl sulfonate esters were synthesized from the corresponding alcohols according to the literature procedures.[7]

2. General procedure for Cu-catalyzed alkylations of terminal alkynes

The Young tube was charged with IMesCuCl (20.2 mg, 5 mol%), *t*-AmONa (165 mg, 1.5 mmol) and CH_2Cl_2 (3 mL). Then, terminal alkyne (1 mmol) and alkyl triflates (1.5 mmol) were added. After stirring the resultant mixture at 40 °C for 12 h, the solvent was removed in vacuo and the desired product was isolated by column chromatography.

For aliphatic alkynes, the reactions were conducted as the similar procedure with 10 mol% of IMesCuCl as the catalyst.

3. Reaction optimization of NHC-Copper catalyzed coupling of phenylacetylene with octyl triflate



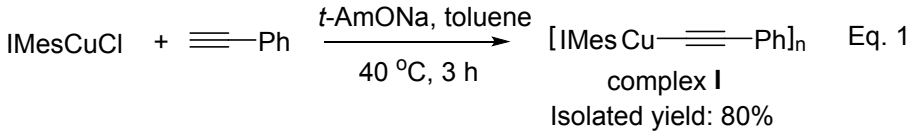
Entry	[Cu]	Base	Solvent	Yield (%)[b]
1	SIPrCuCl	K_2CO_3	toluene	36
2	SIPrCuCl	K_2CO_3	hexane	27
3	SIPrCuCl	K_2CO_3	DMF	2
4	SIPrCuCl	K_2CO_3	THF	14
5	SIPrCuCl	Cs_2CO_3	DCM	27
6	SIPrCuCl	$NaHCO_3$	DCM	0
7	SIPrCuCl	Et_3N	DCM	0
8	SIPrCuCl	*t*-BuONa	DCM	51
9	SIPrCuCl	*t*-AmONa	DCM	76
10	IPrCuCl	*t*-AmONa	DCM	79
11	SIMesCuCl	*t*-AmONa	DCM	71
12	**IMesCuCl**	***t*-AmONa**	**DCM**	**84(76[c])**
13	CuI	*t*-AmONa	DCM	60
14	CuCl	*t*-AmONa	DCM	38
15	no [Cu]	*t*-AmONa	DCM	17

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), catalyst (5 mol%), base (0.45 mmol), solvent (1 mL), 12 h.

[b] Yield was determined by GC using biphenyl as an internal standard. [c] Isolated yield in the parenthesis.

Initial screening of the solvents suggested that changing dichloromethane to others, like toluene or hexane, slightly lowered the yields of the target product (entry 1 and 2). When using DMF and THF, the yield dropped substantially (entry 3 and 4). Then, in dichloromethane, changing the base to a stronger one, such as ^{t}BuONa, increased the yield of the cross-coupling product **3a** to 51% (entry 8). To our delight, using ^{t}AmONa instead led to the desired product **3a** in up to 76% yield (entry 9), presumably due to the better solubility of ^{t}AmONa in dichloromethane. Unfortunately, exploring other bases gave clear detrimental effects (entries 5-7). On switching to other NHC ligands, IPr and SIMes had only marginal effects on the reaction (entry 10 and 11). Notably, IMes clearly proved to be superior with a good GC yield of 84% and 76% isolated (entry 12). Other generally used cuprous salts CuI and CuCl were also tested, which delivering lower yield to 60% and 38%, respectively (entry 13 and 14). Meanwhile, a control experiment without the addition of copper was remarkably inhibited (entry 15)

4. Mechanistic studies



Eq. 1

4.1 Procedure for the reaction of phenyl acetylene and IMesCuCl

To a Schlenk tube, IMesCuCl (468.2 mg, 1.0 mmol), *t*-AmONa (111.2 mg, 1.0 mmol), phenyl acetylene (99.0 mg, 0.97 mmol) and toluene (5 mL) were added. The mixture was then heated at 40 °C for 3 h. After filtration and 3 mL of toluene wash of the filter twice, the filtrate was concentrated. Wash the crude product with hexane for three times, and dry under vacuo. Pale while solid was obtained as the copper acetylide. Yield (376.0 mg, 80%). Crystals were grown by slow diffusion of pentane to the saturated solution in dichloromethane. The structure details were shown as follows.

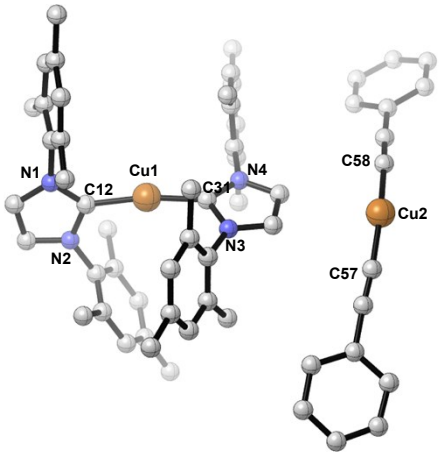


Figure S1. X-ray diffraction of copper acetylide (**S-I**) in the solid state. Hydrogen atoms were emitted for clarity.

Table S1. Crystal data and structure refinement for **S-I**.

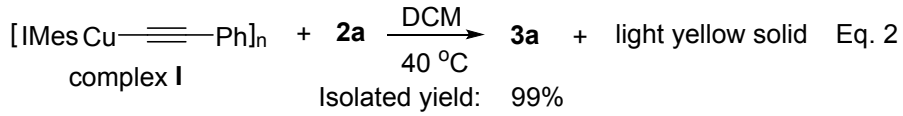
Identification code	20161206ZJA_0m_a	
Empirical formula	C58 H58 Cu2 N4 O0	
Formula weight	938.16	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 19.5091(12) Å	α= 90°.
	b = 19.9327(12) Å	β= 90°.
	c = 26.1996(16) Å	γ = 90°.
Volume	10188.2(11) $Å^3$	
Z	8	
Density (calculated)	1.223 Mg/m^3	
Absorption coefficient	0.875 mm^{-1}	
F(000)	3936	
Crystal size	0.270 x 0.250 x 0.220 mm^3	
Theta range for data collection	2.043 to 25.008°.	
Index ranges	-23<=h<=21, -21<=k<=23, -31<=l<=31	
Reflections collected	31496	
Independent reflections	8870 [R(int) = 0.0593]	
Completeness to theta = 25.008°	98.8 %	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	8870 / 36 / 589
Goodness-of-fit on F^2	1.358
Final R indices [I>2sigma(I)]	R1 = 0.1987, wR2 = 0.3723
R indices (all data)	R1 = 0.2486, wR2 = 0.4024
Extinction coefficient	n/a
Largest diff. peak and hole	0.777 and -0.817 e.Å^{-3}

Table S2. Selected bond lengths [Å] and angles [°] for **S-I**.

selected bond lengths [Å]		selected angles [°]	
C(12)-Cu(1)	1.911(14)	N(1)-C(12)-Cu(1)	135.4(12)
C(12)-N(1)	1.353(18)	N(2)-C(12)-Cu(1)	120.4(10)
C(12)-N(2)	1.35(2)	N(4)-C(31)-Cu(1)	134.8(11)
C(31)-N(4)	1.347(18)	N(3)-C(31)-Cu(1)	122.4(10)
C(31)-N(3)	1.402(19)	C(31)-Cu(1)-C(12)	171.1(7)
C(31)-Cu(1)	1.879(14)	C(58)-Cu(2)-C(57)	167.8(7)
C(57)-Cu(2)	1.887(15)		
C(58)-Cu(2)	1.86(2)		

4.2 Procedure for the reaction of copper acetylide and 2a



Eq. 2

To a Schlenk tube was added octyl triflate (167.9 mg, 0.64 mmol) and dichloromethane (0.5 mL). The solution of complex **1** in dichloromethane (1.5 mL) was added to the tube dropwise at 40 °C. After 30 min, removed the solvent in vacuo and washed the residue with 5 mL of pentane for three times. The pentane filtrate was collected and concentrated. **3a** (92.0 mg, 99% yield) was obtained after column chromatography with petroleum ether as the eluent. The solid that could not dissolve in pentane was isolated as light yellow solid (159.6 mg). Crystals were grown by slow

diffusion of pentane to the saturated solution in dichloromethane and light yellow precipitation left in the bottom. The X-Ray diffraction confirmed that the crystals are $(IMes)_2CuOTf$ (**S-II**), which might be produced from the decomposition of the expected (IMes)CuOTf. The structure details were shown as follows, which match well with the reference report for the same structure.[8]

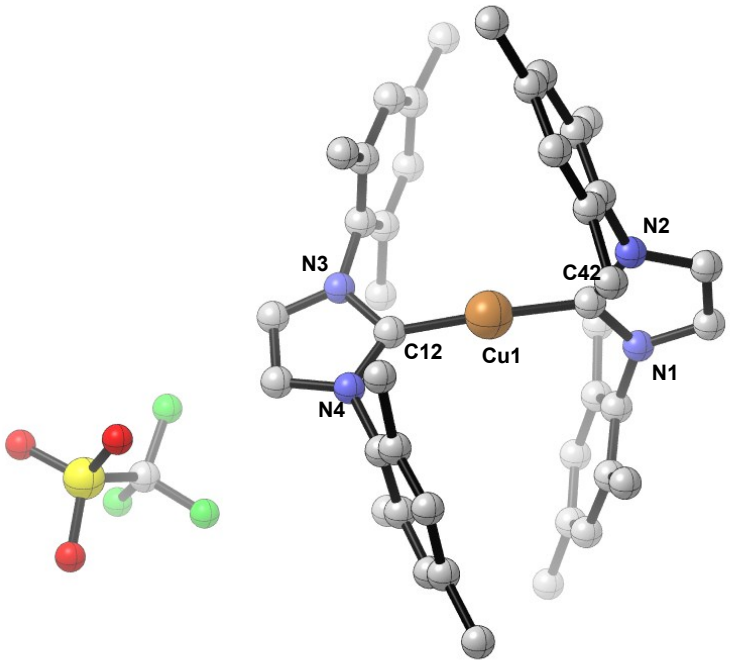


Figure S2. X-ray diffraction of the complex (**S-II)** which was crystalized from the reaction of Eq.2. Hydrogen atoms were emitted for clarity.

Table S3. Crystal data and structure refinement for **S-II**.

Empirical formula	C43 H48 Cu F3 N4 O3 S	
Formula weight	821.45	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.9135(13) Å	α= 83.675(4)°.
	b = 12.1519(13) Å	β= 80.838(4)°.
	c = 32.864(4) Å	γ = 86.977(4)°.
Volume	4273.9(8) $Å^3$	
Z	4	
Density (calculated)	1.277 Mg/m^3	

Absorption coefficient	0.615 mm^{-1}
F(000)	1720
Crystal size	0.260 x 0.220 x 0.190 mm^3
Theta range for data collection	2.084 to 25.009°.
Index ranges	-12<=h<=12, -14<=k<=14, -32<=l<=39
Reflections collected	30822
Independent reflections	14944 [R(int) = 0.0821]
Completeness to theta = 25.009°	99.3 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14944 / 32 / 1009
Goodness-of-fit on F^2	1.211
Final R indices [I>2sigma(I)]	R1 = 0.1509, wR2 = 0.3243
R indices (all data)	R1 = 0.2034, wR2 = 0.3466
Extinction coefficient	n/a
Largest diff. peak and hole	2.446 and -1.009 e.$Å^{-3}$

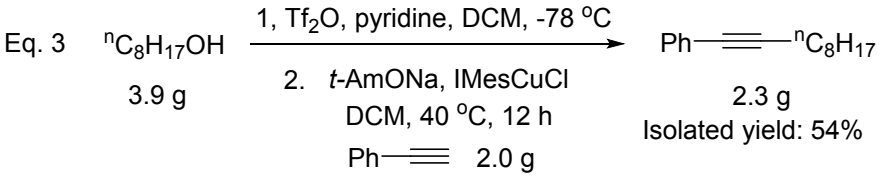
Table S4. Selected bond lengths [Å] and angles [°] for **S-II**.

selected bond lengths [Å]		selected angles [°]	
C(12)-Cu(1)	1.857(8)	N(1)-C(42)-Cu(1)	123.8(6)
C(42)-Cu(1)	1.872(8)	N(2)-C(42)-Cu(1)	130.9(6)
C(12)-N(3)	1.419(10)	N(3)-C(12)-Cu(1)	125.9(6)
C(12)-N(4)	1.321(10)	N(4)-C(12)-Cu(1)	131.7(6)
C(42)-N(2)	1.333(10)	C(12)-Cu(1)-C(42)	177.0(4)
C(42)-N(1)	1.377(11)		

4.3 Procedure for kinetic studies

To a three neck flask charging with React IR tube, IMesCuCl (20.0 mg, 5 mol%) and t-AmONa (165.2 mg, 1.5 mmol) was added phenyl acetylene (102.0 mg, 1 mmol), octyl triflates (393.5 mg, 1.5 mmol) and dichloromethane (3.0 mL). At the same time, started to monitor the accumulation of the product. At 40 °C for 3.5 h, stopped and quenched the reaction with diluted HCl aq. GC yield was obtained with naphthalene as the internal standard. Data analysis by iC IR could give the reaction rate.

5. Scale-up reactions

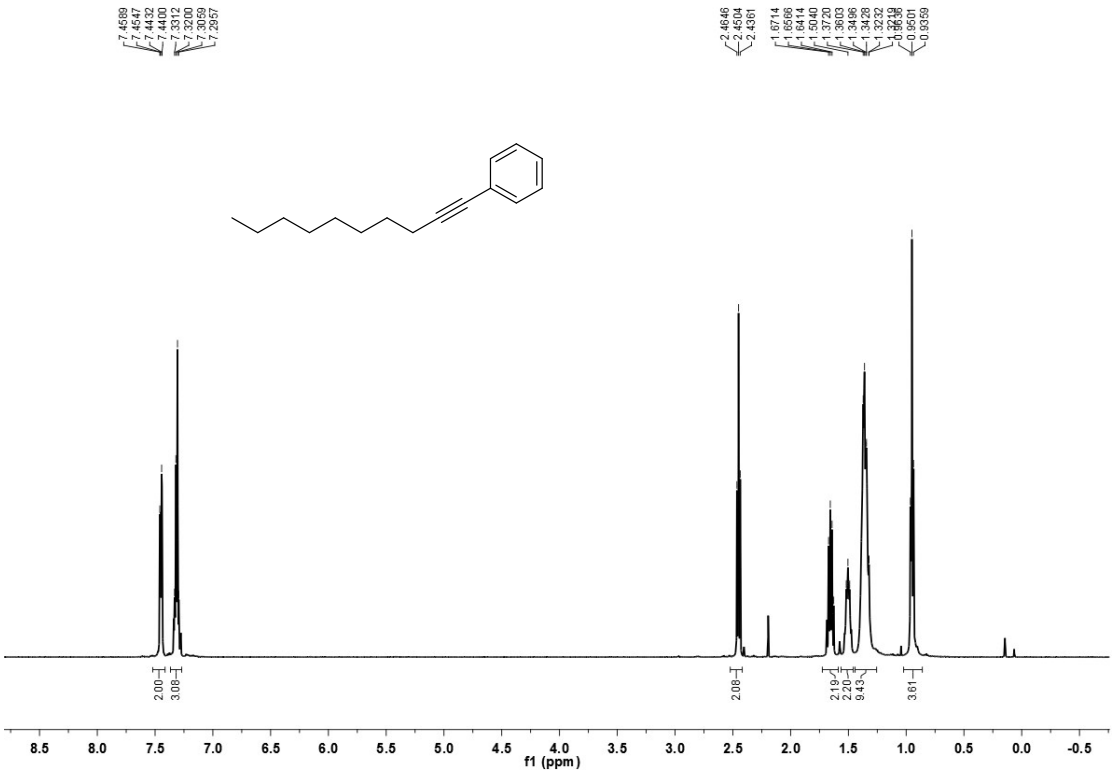


Step 1: To a Schlenk tube were added 1-octanol (3.9 g, 30 mmol), pyridine (2.3 g, 28.5 mmol) and dichloromethane (50 mL) at -78 °C. Triflic anhydride (8.0 g, 28.5 mmol) was then added dropwise. After 10 mins, removed the cold bath and increased the temperature to room temperature and stirred for 3 h. After simple filtration and washed by pentane (50 mL), concentrated the filtrate affording the octyl triflate for the next step.

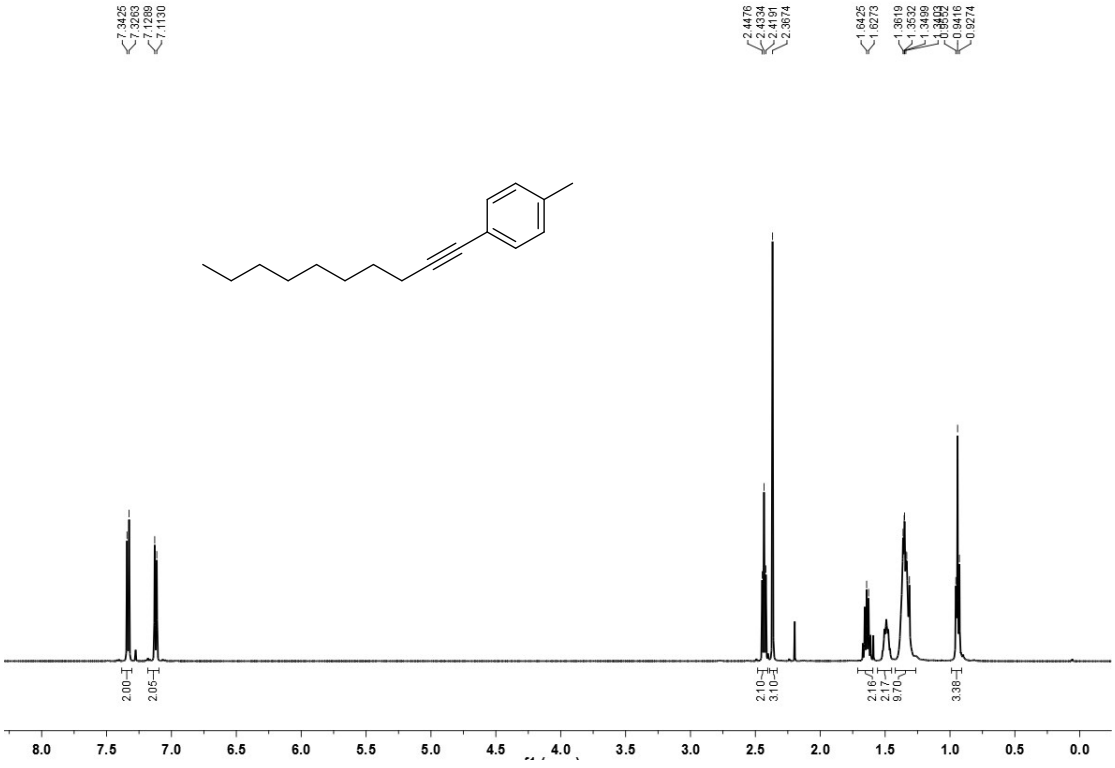
Step 2: To a three-necked flask were added IMesCuCl (80.7 mg，1 mol%), phenyl acetylene (20.4 g，20 mmol) and 10 mL of dichloromethane. *t*-AmONa (3.3 g, 30 mmol) in 55 mL of dichloromethane and the resulted octyl triflate from step 1 in 50 mL of dichloromethane were added dropwise to the flask at 40 °C. 12 h later, stopped the reaction. 2.3 g of the desired product was isolated by column chromatography after usual work-up. Yield (54%)

6. NMR spectra of coupling products and copper complexes

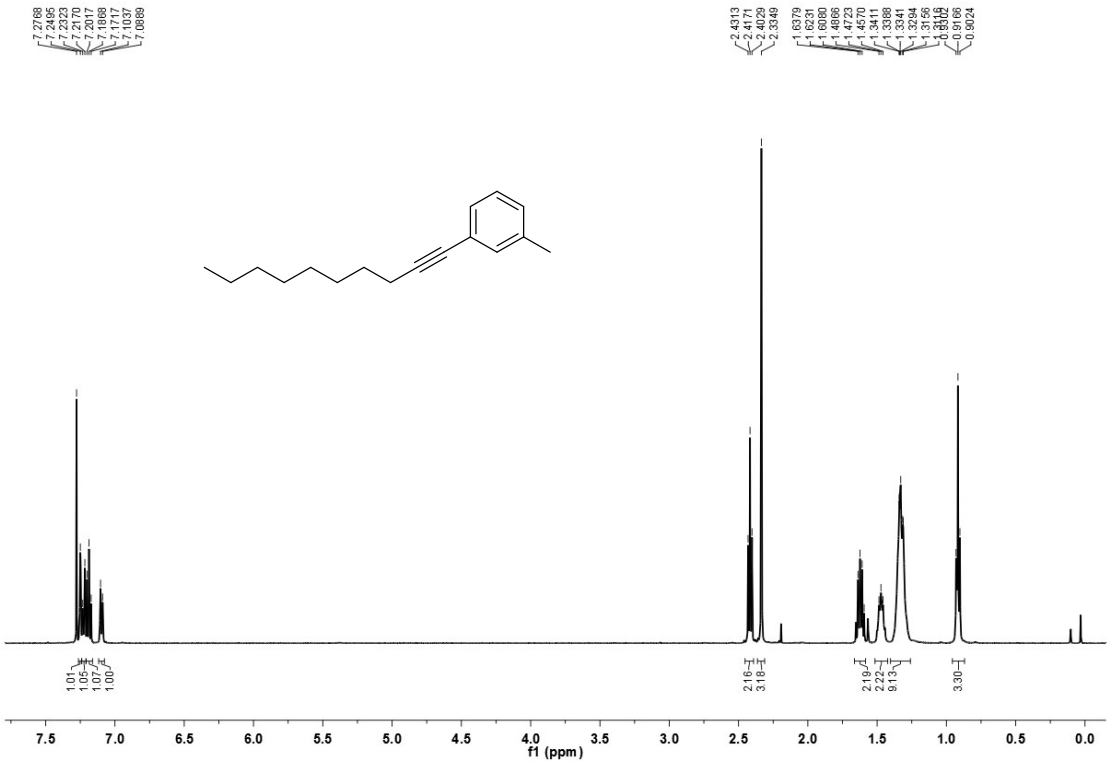
1-Phenyl-1-decyne (**3a**)[9]: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45 (d, J = 7.7 Hz, 2H), 7.34-7.27 (m, 3H), 2.45 (t, J = 7.1 Hz, 2H), 1.66 (sept, J = 7.7 Hz,, 2H), 1.55-1.45 (m, 2H), 1.43-1.28 (m, 8H), 0.95 (t, J = 6.8 Hz, 3H).

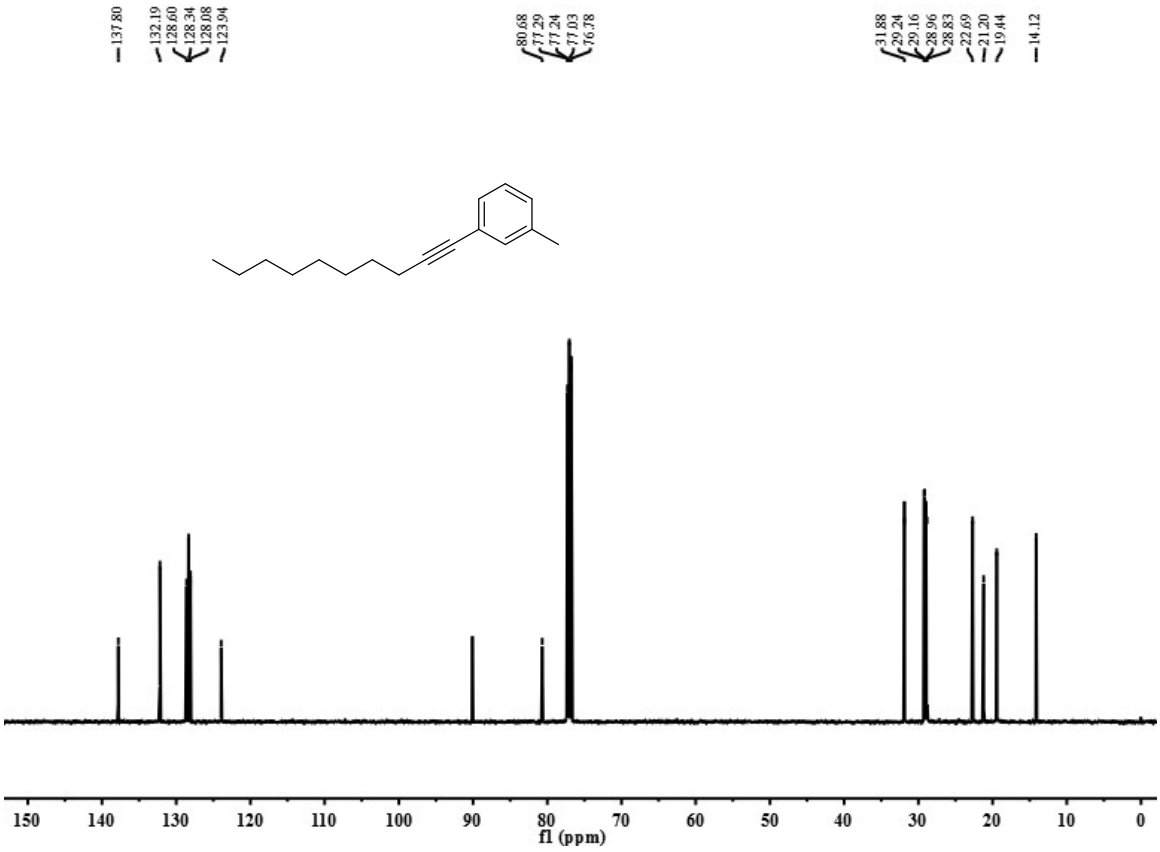


1-(4-Methyl)-phenyl-1-decyne (**3b**)[10]: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.33 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 2.43 (t, J = 7.1 Hz, 2H), 2.37 (s, 3H), 1.68-1.60 (m, 2H), 1.52-1.45 (m, 2H), 1.41-1.32 (m, 8H), 0.94 (t, J = 6.8 Hz, 3H).

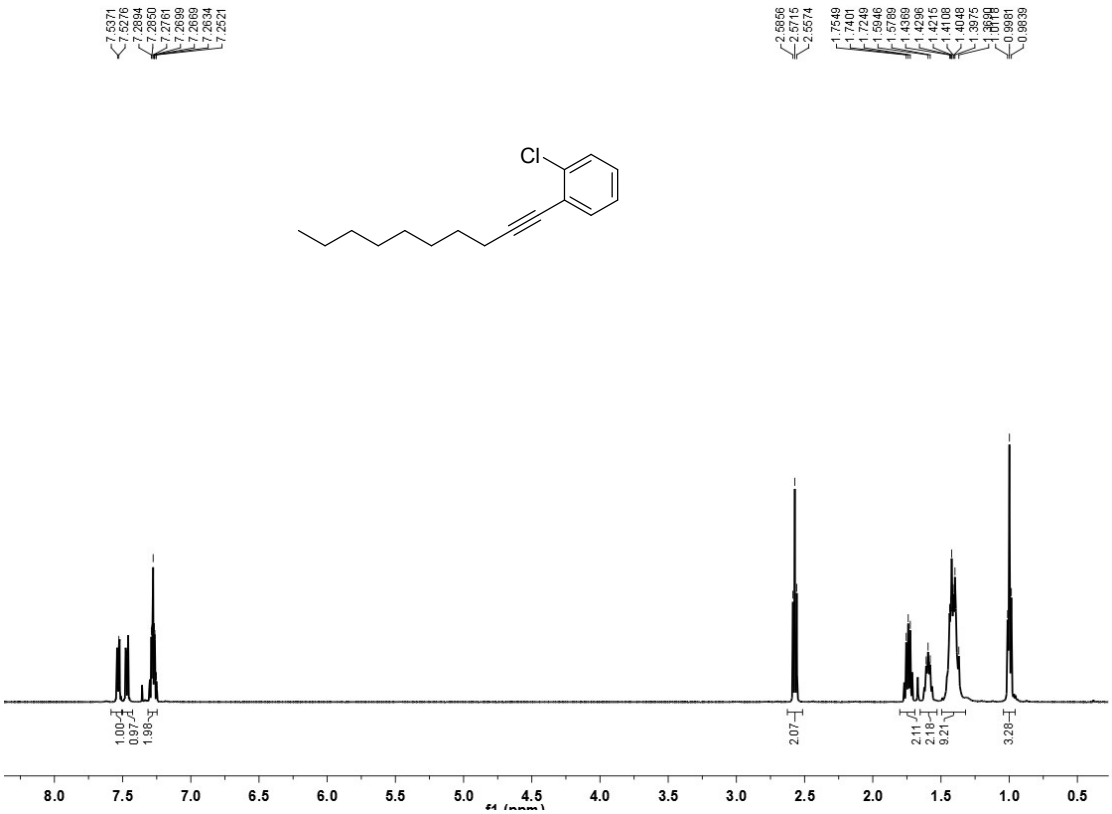


1-(3-Methyl)-phenyl-1-decyne (**3c**): ^{1}H NMR ($CDCl_3$, 500 MHz):δ 7.24 (s, 1 H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 2.42 (t, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 1.62 (sept, *J* = 7.1 Hz, 2H), 1.52-1.45 (m, 2H), 1.39-1.28 (m, 8H), 0.91 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz):δ 137.8, 132.1, 128.6, 128.3, 128.1, 123.9, 90.1, 80.7, 31.9, 29.2, 29.1, 29.0, 28.8, 22.7, 21.2, 19.4, 14.1. HRMS (EI-TOF): m/z calculated for $C_{17}H_{24}$ 228.1878, found 228.1896.

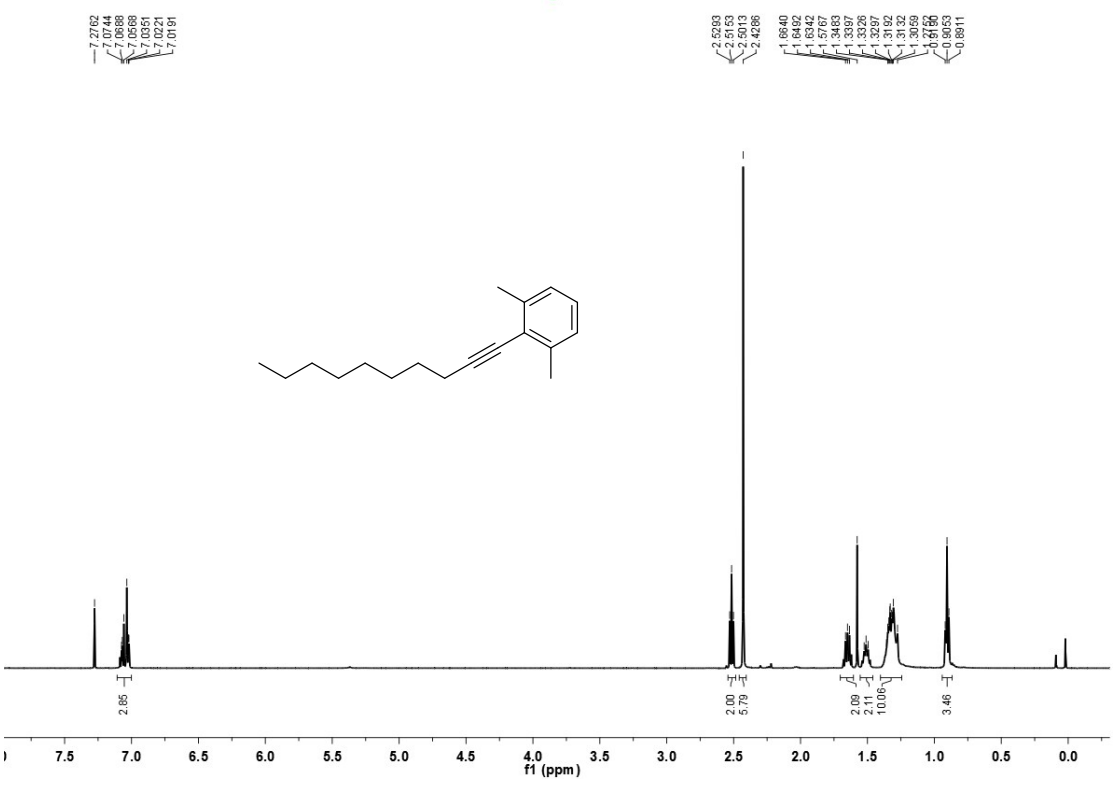


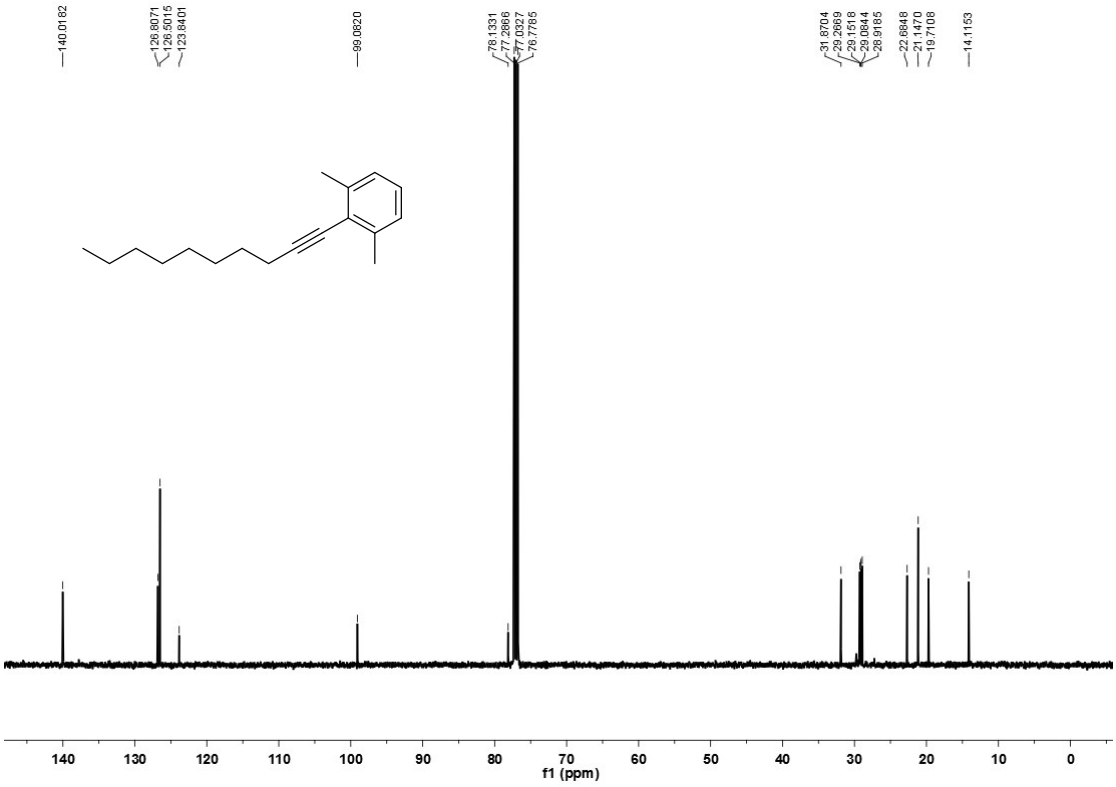


1-(2-Chloro)-phenyl-1-decyne (**3d**)[11]: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.53 (d, J = 6.6 Hz, 1H), 7.47 (d, J = 6.6 Hz, 1H), 7.30-7.25 (m, 2H), 2.57 (t, J = 7.0 Hz, 2H), 1.74 (sept, J = 7.4 Hz, 2H), 1.63-1.55 (m, 2H), 1.47-1.33 (m, 8H), 0.99 (t, J = 6.8 Hz, 3H).



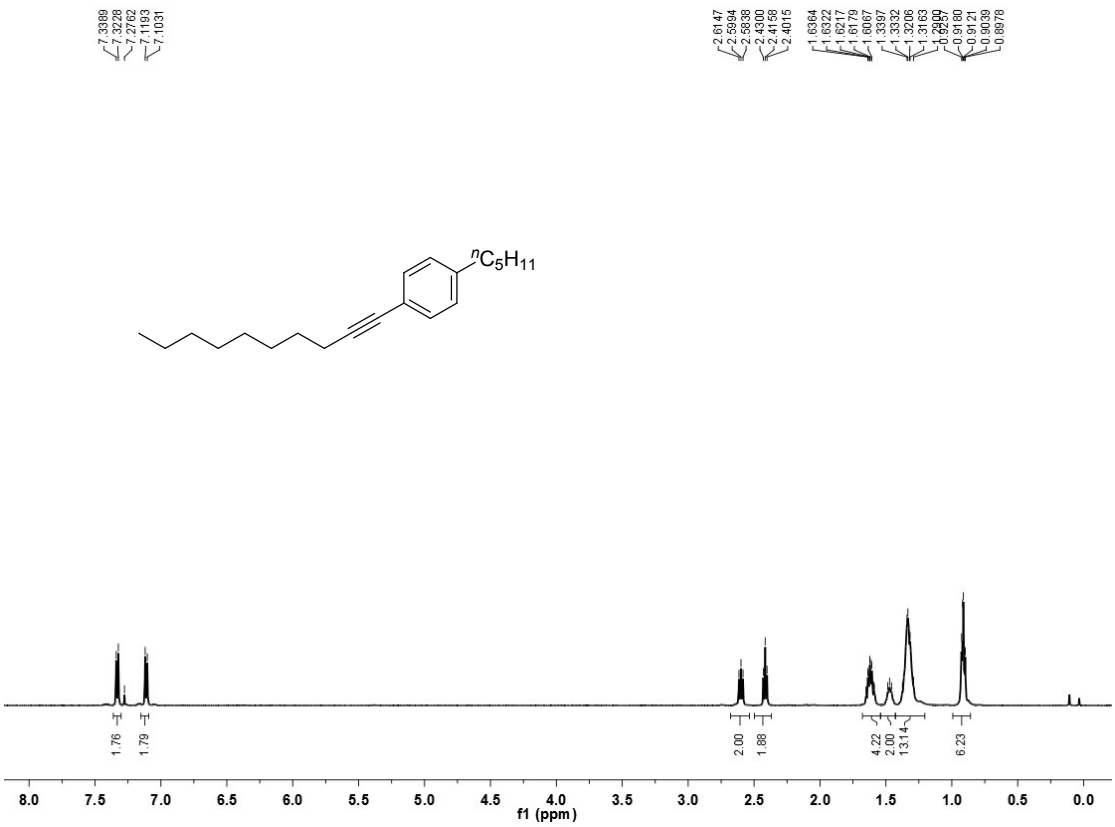
1-(2,6-Dimethyl)-phenyl-1-decyne (**3e**): ^{1}H NMR ($CDCl_3$, 500 MHz):δ 7.10-7.00 (m, 3H), 2.51 (t, *J* = 7.0 Hz, 2H), 2.42 (s, 6H), 1.65 (sept, *J* = 7.4 Hz, 2H), 1.55-1.46 (m, 2H), 1.36-1.27 (m, 8H), 0.91 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 140.0, 126.8, 126.5, 123.8, 99.1, 78.1, 31.9, 29.3, 29.2, 29.1, 28.9, 22.9, 21.2, 19.7, 14.1. HRMS (EI-TOF): m/z calculated for $C_{18}H_{26}$ 242.2035, found 242.2045.

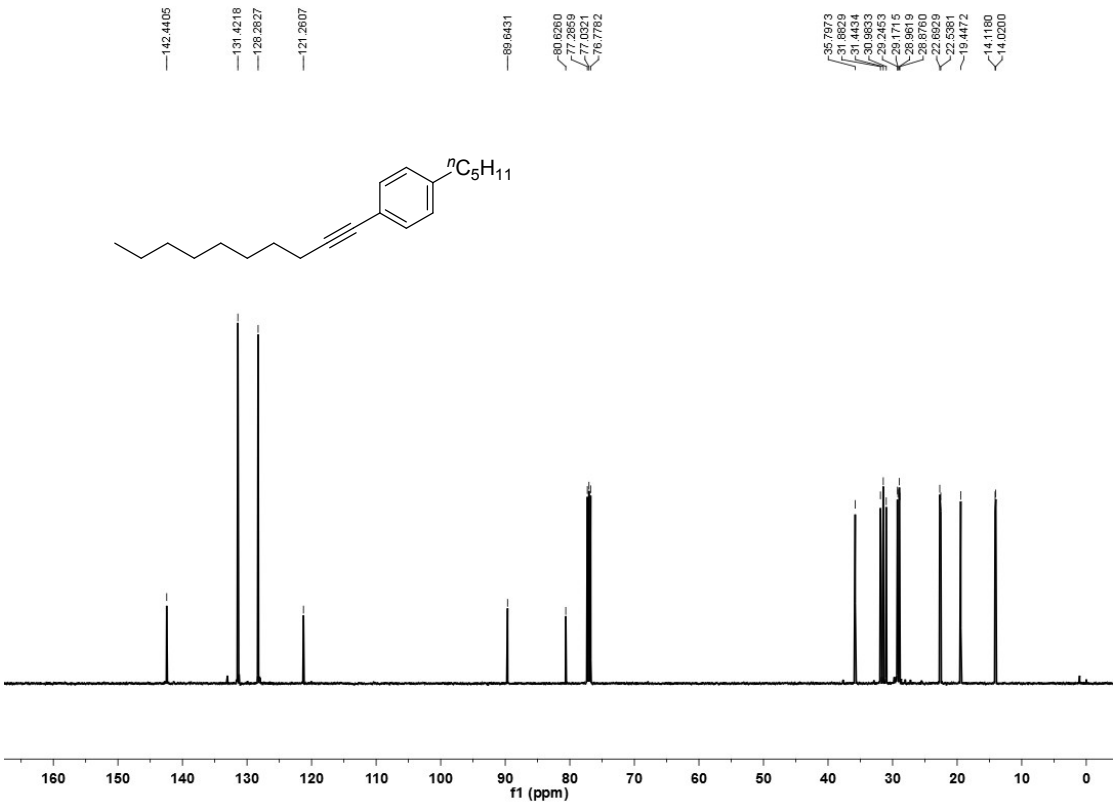




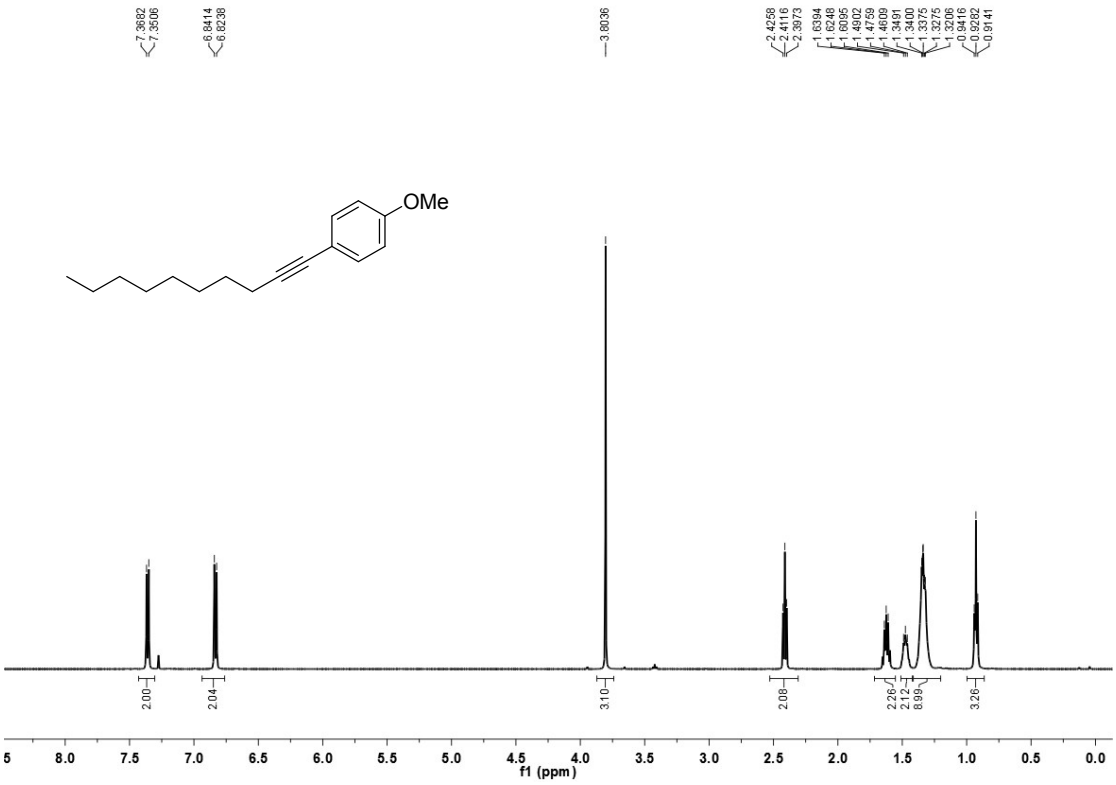
1-(4-Pentyl)-phenyl-1-decyne (**3f**): ^{1}H NMR ($CDCl_3$, 500 MHz):δ 7.33 (d, J = 7.9 Hz, 2H), 7.11 (d, J = 7.9 Hz, 2H), 2.59 (t, J = 7.8 Hz, 2H), 2.41 (t, J = 7.1 Hz, 2H), 1.67-1.55 (m, 4H), 1.51-1.42 (m, 2H), 1.40-1.28 (m, 14H), 0.96-0.86 (m, 6H). ^{13}C NMR

($CDCl_3$, 500 MHz): δ 142.4, 131.4, 128.3, 121.3, 89.6, 80.6, 35.8, 31.9, 31.4, 31.0, 29.2, 29.1, 29.0, 28.9, 22.9, 22.5, 19.4, 14.1, 14.0. HRMS (EI-TOF): m/z calculated for $C_{21}H_{32}$ 284.2504, found 284.2538.

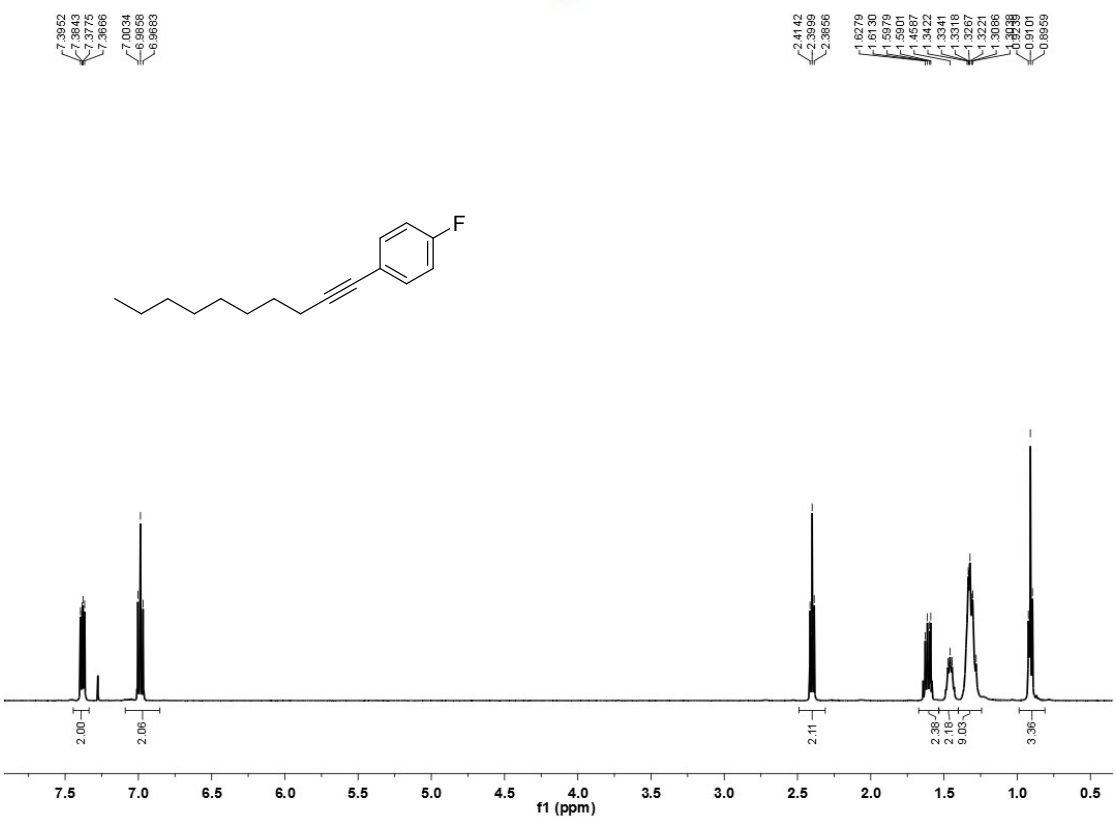




1-(4-Methoxyl)-phenyl-1-decyne (**3g**)[9]: ^{1}H NMR ($CDCl_3$, 500 MHz):δ 7.35 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 3.80 (s, 3H), 2.41 (t, J = 7.1 Hz, 2H), 1.62 (sept, J = 7.7 Hz, 2H), 1.52-1.42 (m, 2H), 1.36-1.23 (m, 8H), 0.92 (t, J = 6.8 Hz, 3H).



1-(4-Fluoro)-phenyl-1-decyne (**3h**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.38 (dd, *J* = 7.3 Hz, *J* = 5.4 Hz, 2H), 6.98 (t, *J* = 8.5 Hz, 2H), 2.39 (t, *J* = 7.1 Hz, 2H), 1.65 – 1.56 (m, 2H), 1.51-1.40 (m, 2H), 1.37-1.25 (m, 8H), 0.91 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 162.1 (d, *J* = 248.1 Hz), 133.3 (d, *J* = 8.1 Hz), 120.2 (d, *J* = 3.5 Hz), 115.3 (d, *J* = 21.8 Hz), 90.1, 79.5, 31.9, 29.3, 29.2, 29.0, 28.8, 22.7, 19.4, 14.1. HRMS (EI-TOF): m/z calculated for $C_{16}H_{21}F$ 232.1627, found 232.1609.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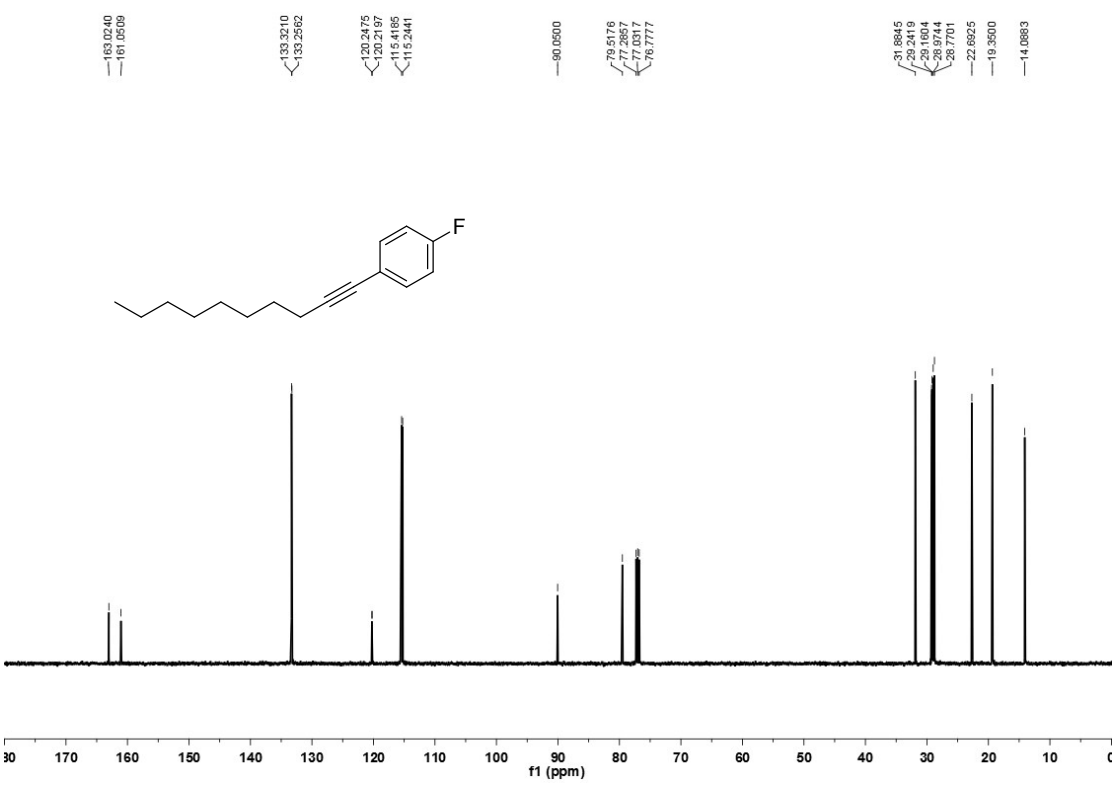
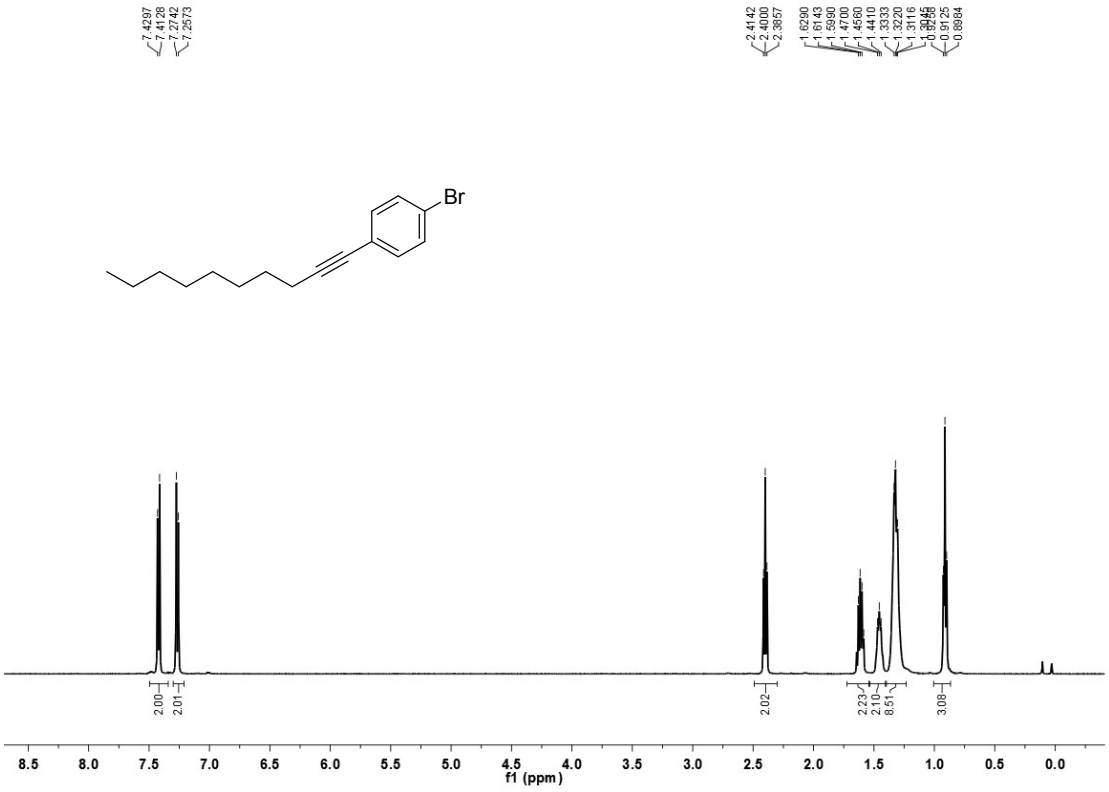
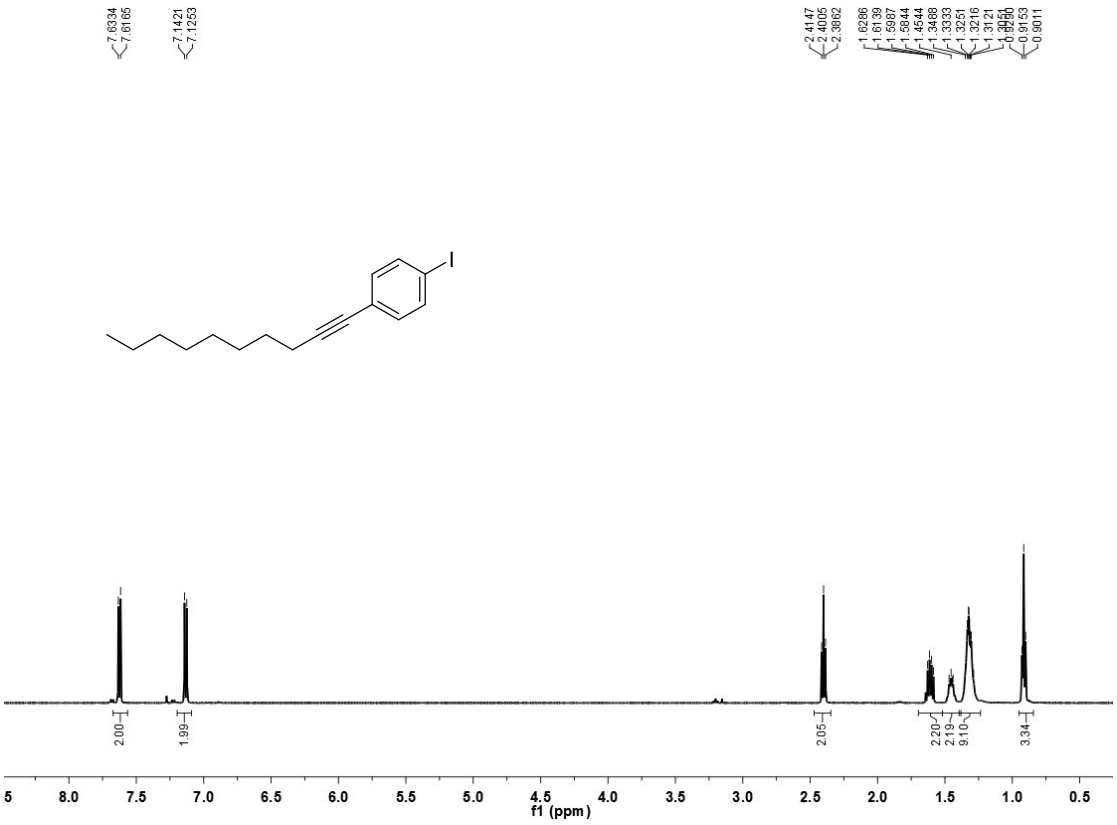
1.6130
1.5979
1.5901
1.4587
1.3422
1.3341
1.3318
1.3257
1.3071
1.3066
0.9101
0.8959
F
2.00
2.06
2.11
2.38
2.18
9.03
3.36
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

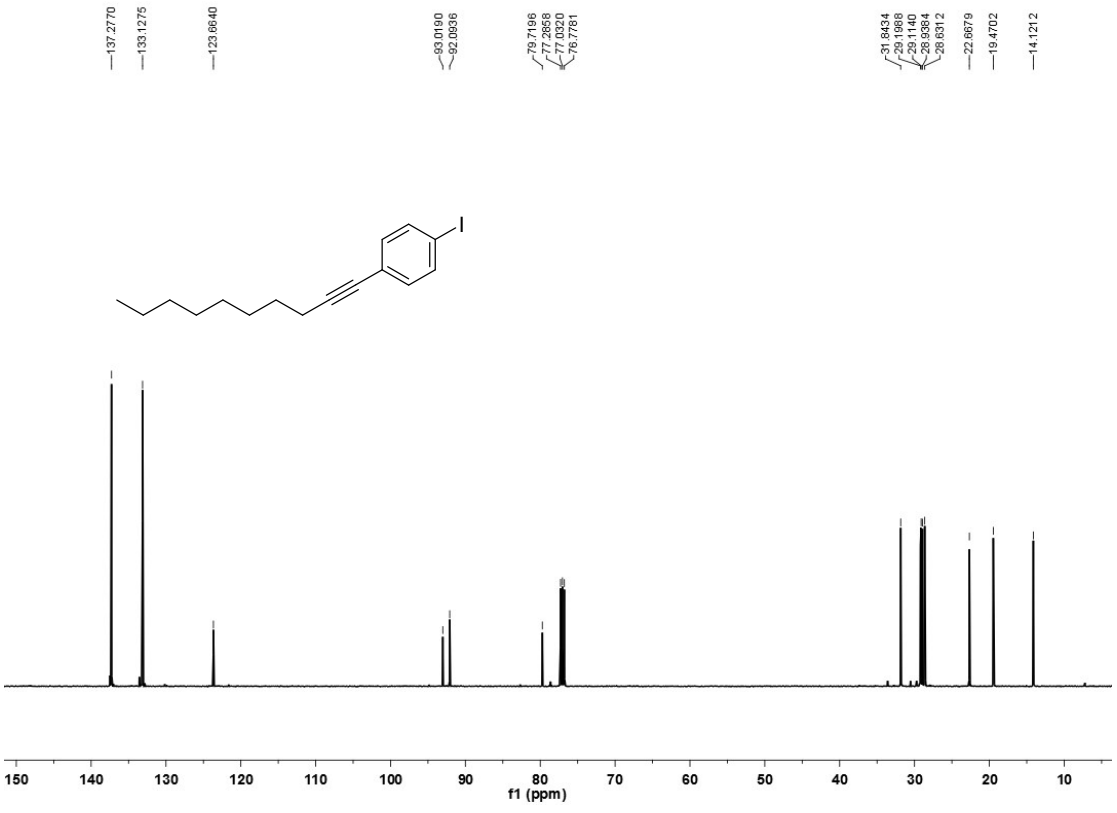

163.0240
161.0509
133.3210
133.2562
120.2475
120.2197
115.4165
115.2441
90.0500
79.5176
77.2857
77.0317
76.7777
31.8845
29.2419
29.1604
28.9744
28.7701
22.6925
19.3500
14.0883
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

1-(4-Bromo)-phenyl-1-decyne (**3i**)[10]: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 2.40 (t, *J* = 7.2 Hz, 2H), 1.68-1.55 (m, 2H), 1.51-1.40 (m, 2H), 1.39-1.25 (m, 8H), 0.91 (t, *J* = 6.8 Hz, 3H).

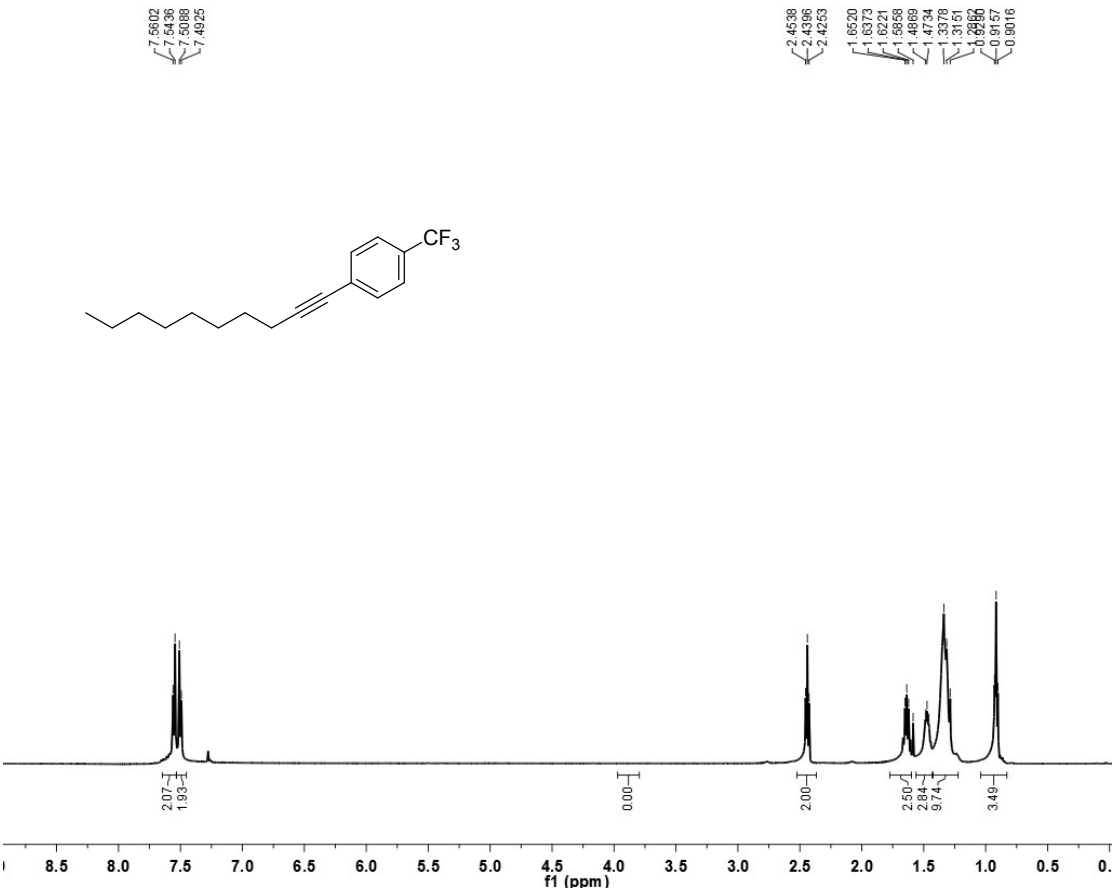


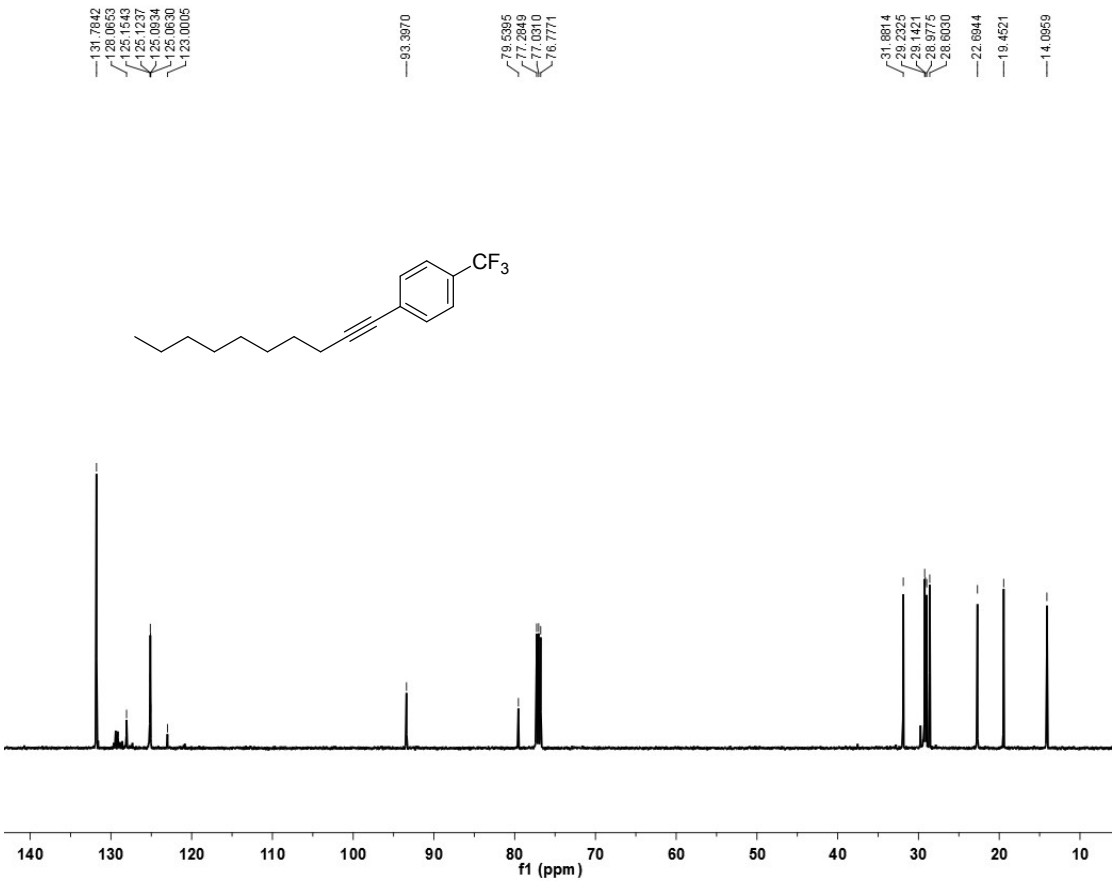
1-(4-Iodo)-phenyl-1-decyne (**3j**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 2.40 (t, *J* = 7.1 Hz, 2H), 1.61 (sept, *J* = 7.1 Hz, 2H), 1.50-1.40 (m, 2H), 1.39-1.26 (m, 8H), 0.91 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 137.3, 133.1, 123.7, 93.0, 92.1, 79.7, 31.9, 29.2, 29.1, 28.9, 28.6, 22.7, 19.5, 14.1. HRMS (EI-TOF): m/z calculated for $C_{16}H_{21}I$ 340.0688, found 340.0692.


7.6334
7.6165
7.1421
7.1253
2.4147
2.4005
2.3862
1.6286
1.6139
1.5987
1.5844
1.4544
1.3488
1.3333
1.3251
1.3216
1.3121
0.9153
0.9011
I
2.00
1.99
2.05
2.20
2.19
9.10
3.34
f1 (ppm)

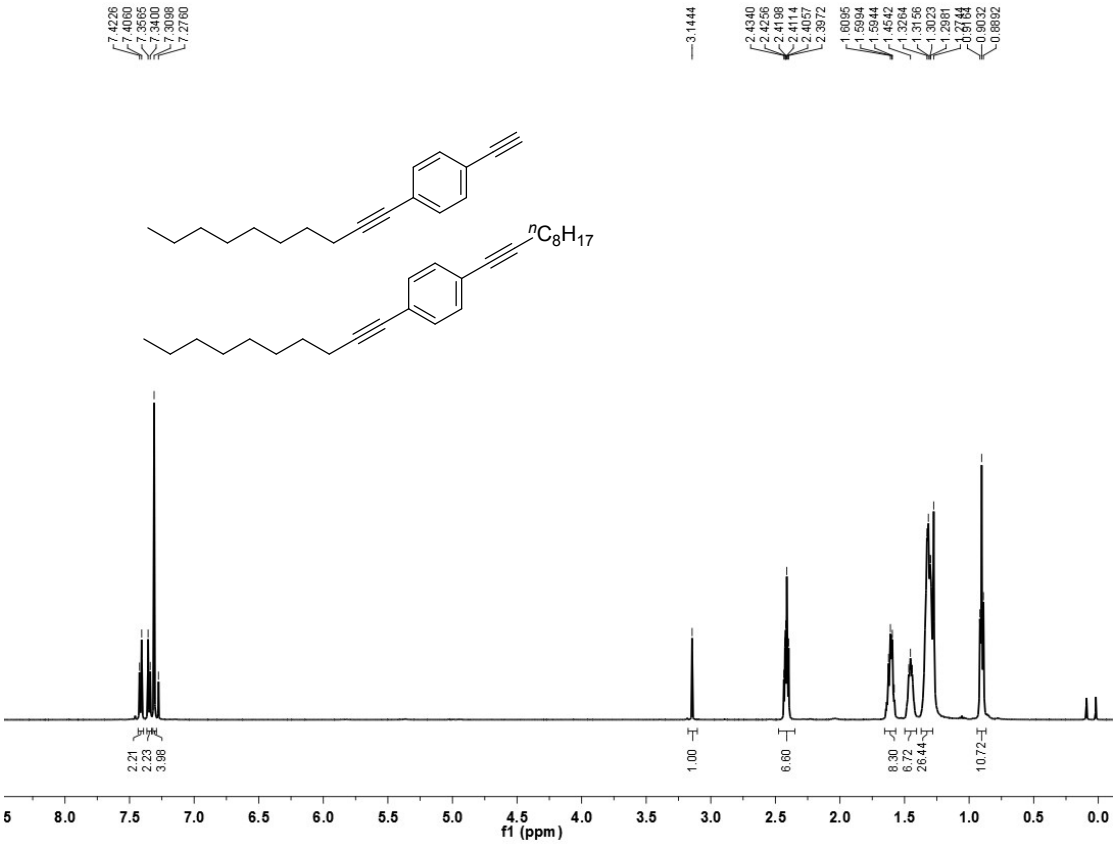

137.2770
133.1275
123.6640
93.0190
92.0936
79.7196
77.2858
77.0320
76.7781
31.9434
29.1968
29.1440
28.9384
28.8312
22.6679
19.4702
14.1212
I
f1 (ppm)

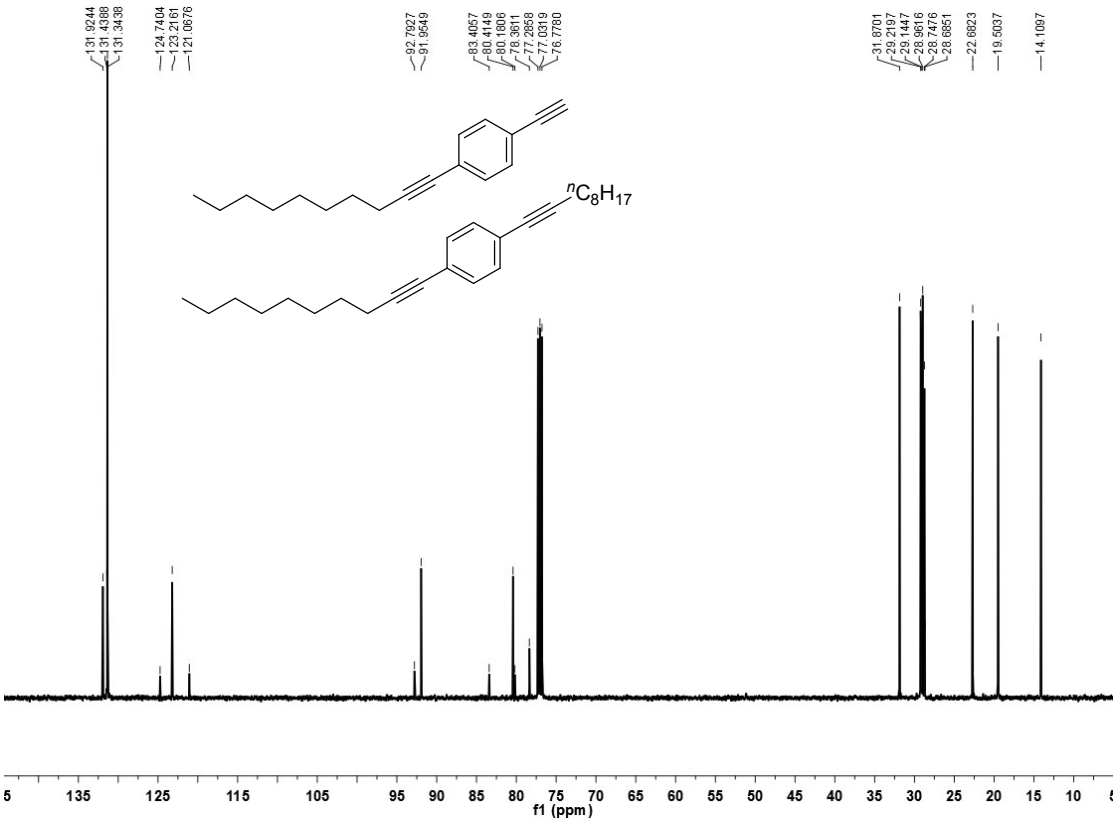
1-(4-Trifluoromethyl)-phenyl-1-decyne (**3k**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.55 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 2.44 (t, J = 7.1 Hz, 2H), 1.69-1.59 (m, 2H), 1.55-1.43 (m, 2H), 1.43-1.17 (m, 2H), 0.91 (t, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): 131.8, 129.3 (q, J = 32.5 Hz) 128.1, 125.1 (q, J = 3.5 Hz), 123.0, 93.4, 79.5, 31.9, 29.2, 29.1, 29.0, 28.6, 22.7, 19.5, 14.1. HRMS (EI-TOF): m/z calculated for $C_{17}H_{21}F_3$ 282.1595, found 282.1605.



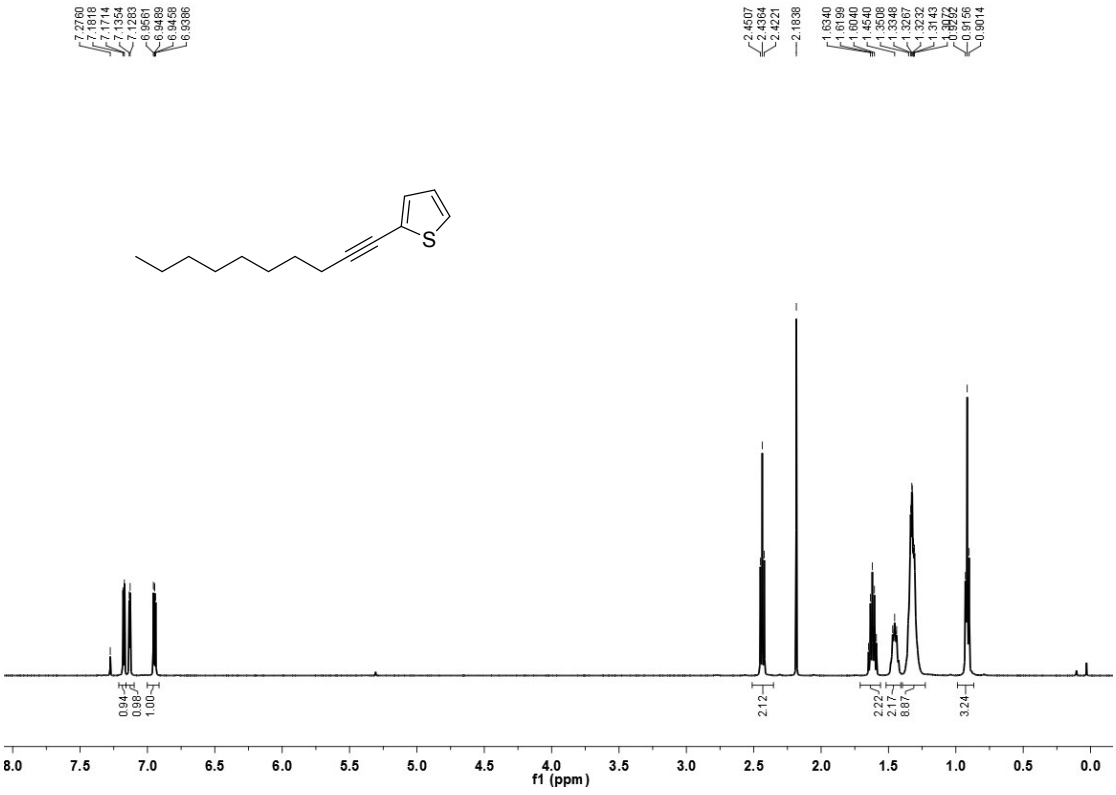


1-(4-Ethynyl)-phenyl-1-decyne and 1,4-didecynylbenzene (**3l**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.31 (s, 4H), 3.14 (s, 1H), 2.45-2.38 (m, 6H), 1.65-1.56 (m, 6H), 1.49-1.40 (m, 6H), 1.37-1.28 (m, 24H), 0.90 (t, *J* = 6.8 Hz, 9H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 131.9, 131.4, 131.3, 124.7, 123.2, 121.1, 92.8, 92.0, 83.4, 80.4, 80.2, 78.4, 31.9, 29.2, 29.1, 29.0, 28.7, 28.6, 22.7, 19.5, 14.1. HRMS (EI-TOF): m/z calculated for $C_{18}H_{22}$ 238.1722, found 238.1721. HRMS (EI-TOF): m/z calculated for $C_{26}H_{38}$ 350.2974, found 350.2973.

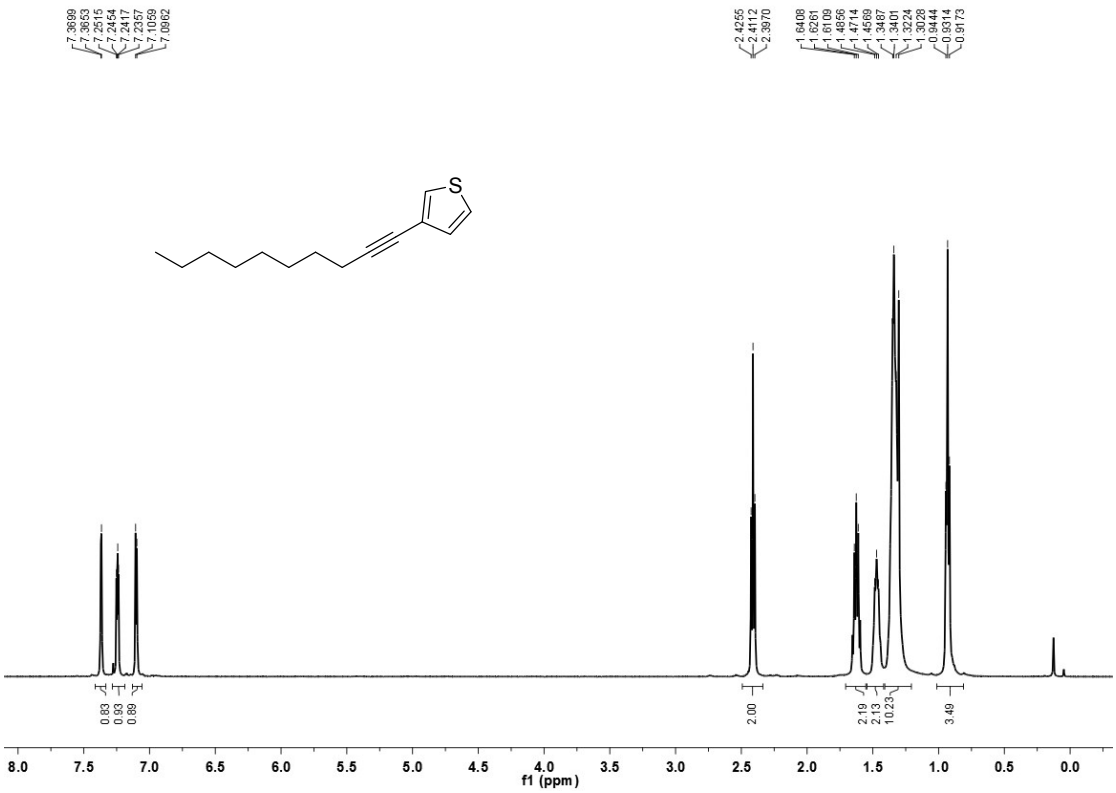

7.4226
7.4060
7.3565
7.3400
7.3098
7.2760
3.1444
2.4340
2.4256
2.4198
2.4114
2.4057
2.3972
1.6095
1.5994
1.5944
1.4542
1.3264
1.3156
1.3023
1.2981
0.9032
0.8892
$^{n}C_8H_{17}$
2.21
2.23
3.98
1.00
6.60
8.30
6.72
26.44
10.72
f1 (ppm)


131.9244
131.4388
131.3436
124.7404
123.2161
121.0676
92.7927
91.9549
83.4057
80.4149
80.1806
78.3611
77.2858
77.0319
76.7780
31.8701
29.2197
29.1447
28.9616
28.7476
28.6851
22.6823
19.5037
14.1097
$^{n}C_8H_{17}$
f1 (ppm)

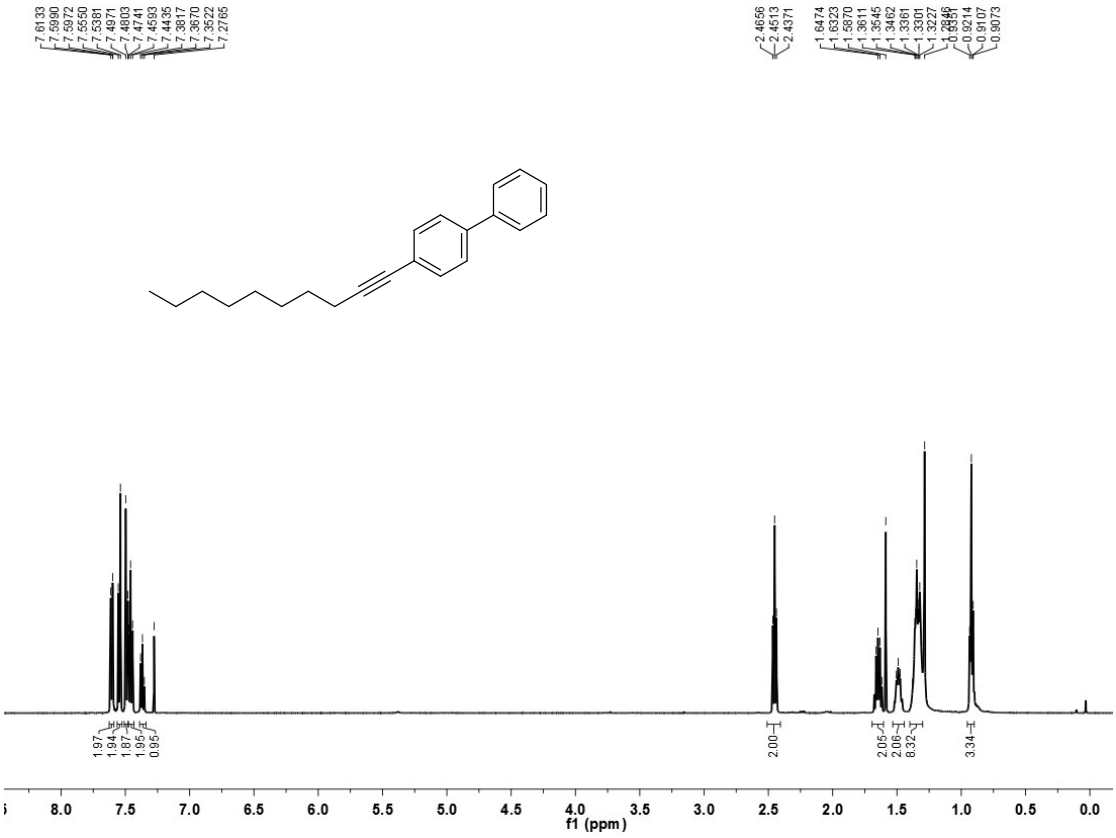
2-(Dec-1-yn-1-yl)thiophene (**3m**)[12]: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.19-7.15 (d, J = 5.3 Hz, 1H), 7.13 (d, J = 3.6 Hz, 1H), 6.95 (dd, J_1 = 5.3 Hz, J_2 = 3.5 Hz, 1H), 2.43 (t, J = 7.2 Hz, 2H), 1.62 (sept, J = 7.8 Hz, 2H), 1.49-1.39 (m, 2H), 1.38-1.23 (m, 8H), 0.91 (t, J = 6.8 Hz, 3H).

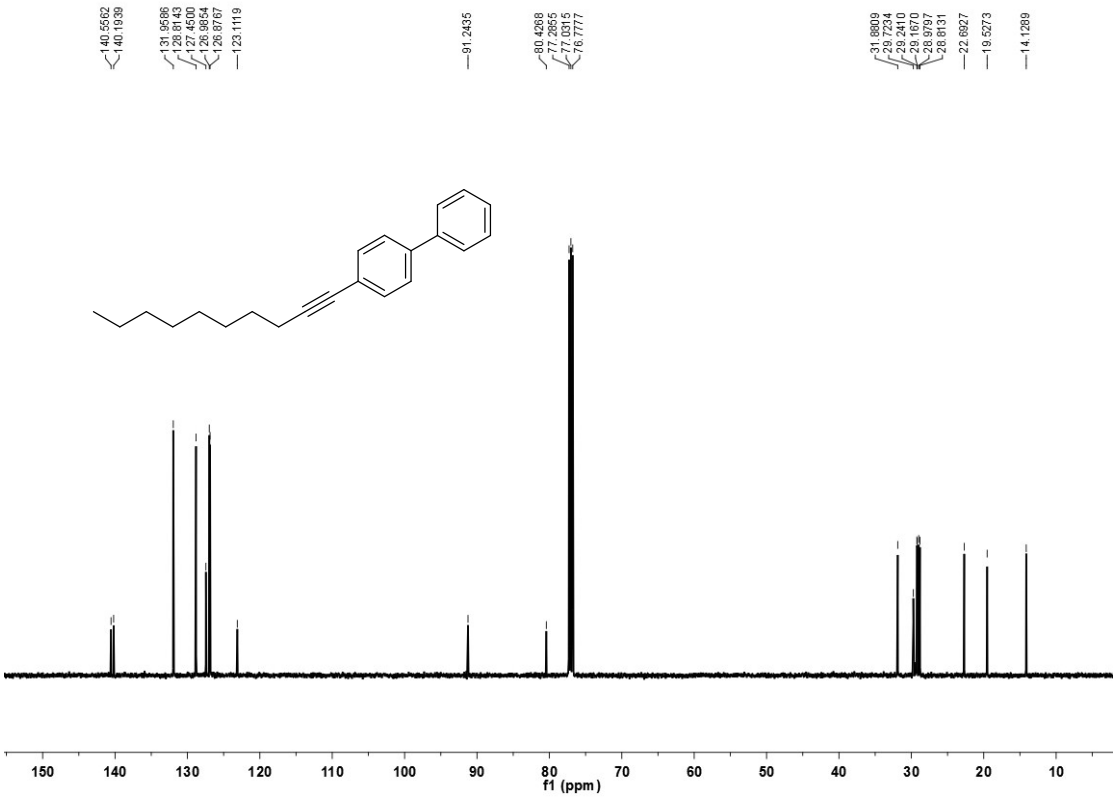


3-(Dec-1-yn-1-yl)thiophene (**3n**)[13]: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.37 (d, J = 2.9 Hz, 1H), 7.24 (dd, J_1 = 5.1 Hz, J_2 = 2.9 Hz, 1H), 7.10 (d, J = 5.1 Hz, 1H), 2.41 (t, J = 7.1 Hz, 2H), 1.63 (sept, J = 7.7 Hz, 2H), 1.52-1.41 (m, 2H), 1.40-1.30 (m, 8H), 0.93 (t, J = 6.8 Hz, 3H).



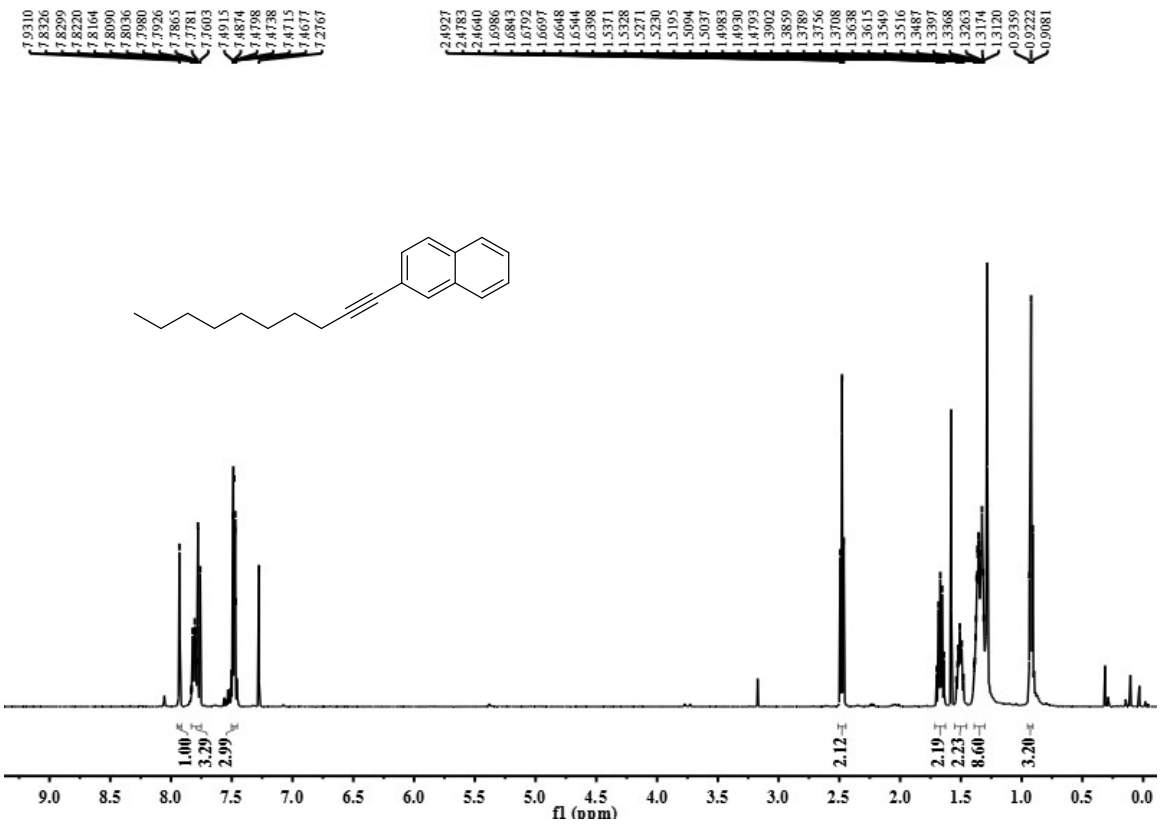
4-(Dec-1-yn-1-yl)-1,1'-biphenyl (**3o**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.60 (d, *J* = 7.5 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 2.45 (t, *J* = 7.1 Hz, 2H), 1.64 (sept, *J* = 7.1 Hz, 2H), 1.53-1.43 (m, 2H), 1.40-1.30 (m, 9H), 0.92 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 140.6, 140.2, 132.0, 128.8, 127.5, 127.0, 126.9, 123.1, 91.2, 31.9, 29.7, 29.2, 29.1, 29.0, 28.8, 22.7, 19.5, 14.1. HRMS (EI-TOF): m/z calculated for $C_{22}H_{26}$ 290.2035, found 290.2049.

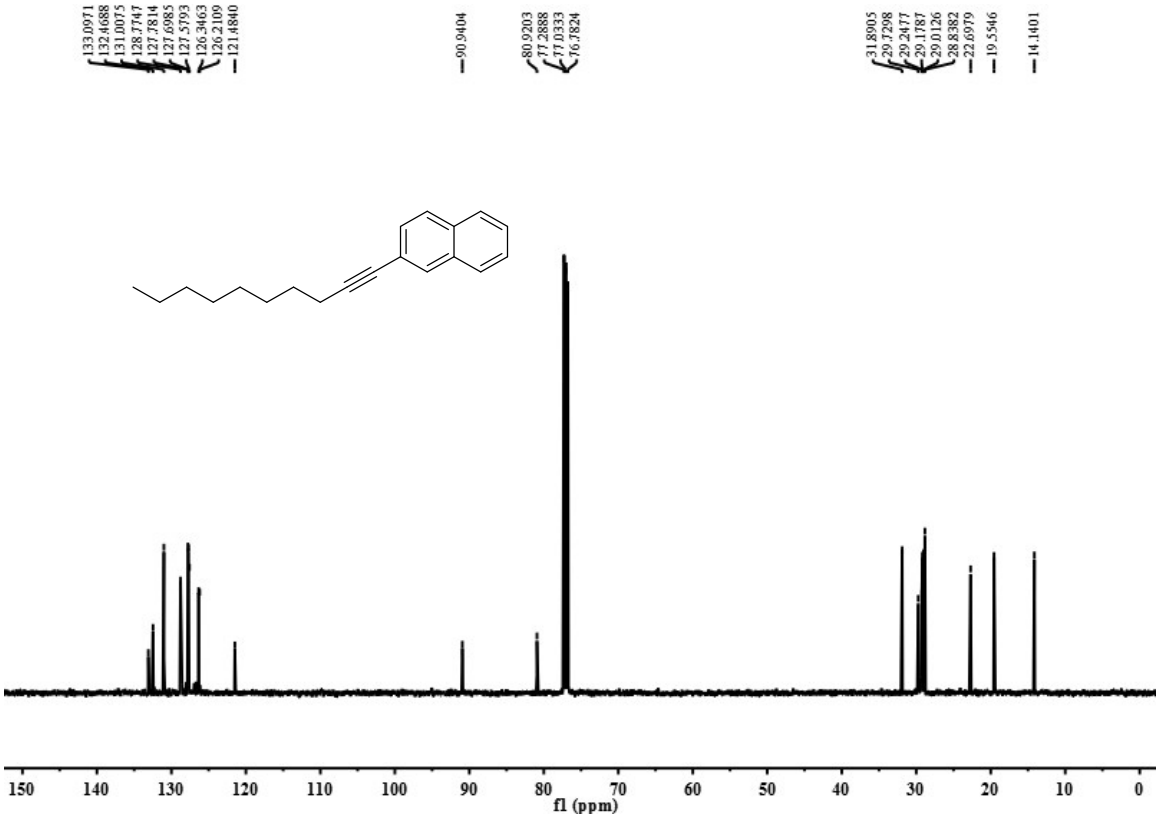




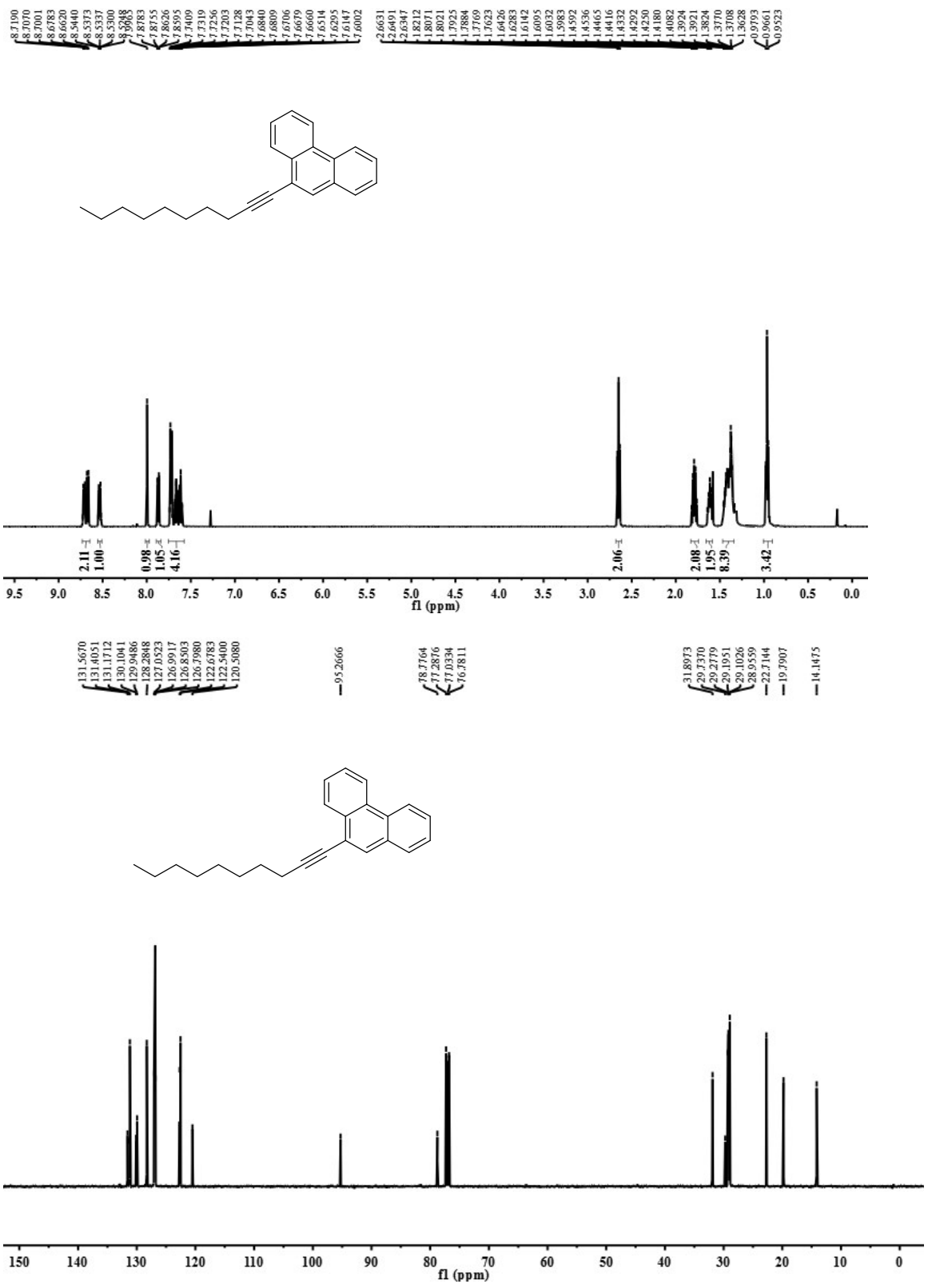
2-(Dec-1-yn-1-yl)naphthalene (**3p**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.93 (s, 1H), 7.83 – 7.75 (m, 3H), 7.50 – 7.45 (m, 3H), 2.48 (t, *J* = 7.2 Hz, 2H), 1.67 (sept, *J* = 7.6 Hz,

2H), 1.55-1.45 (m, 2H), 1.39-1.30 (m, 8H), 0.92 (t, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 133.1, 132.5, 131.0, 128.8, 127.8, 127.7, 127.6, 126.3, 126.2, 121.5, 90.9, 31.9, 29.7, 29.2, 29.1, 29.0, 28.8, 22.7, 19.6, 14.1. HRMS (EI-TOF): m/z calculated for $C_{20}H_{24}$ 264.1878, found 264.1892.

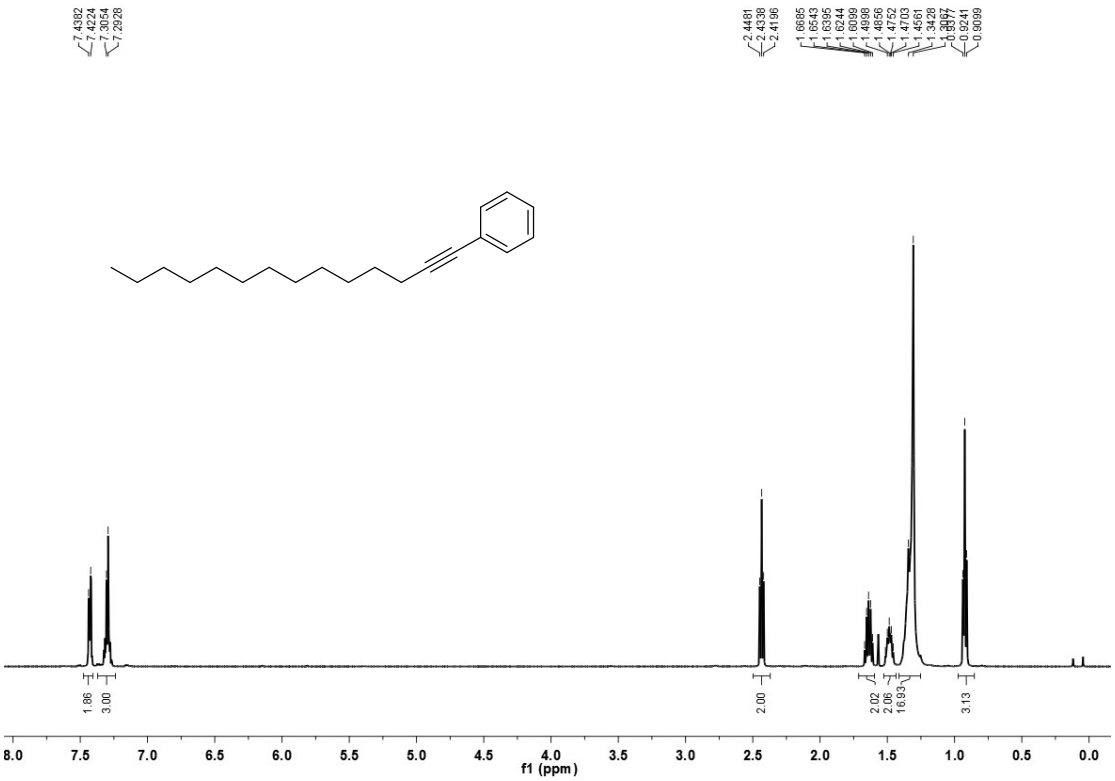




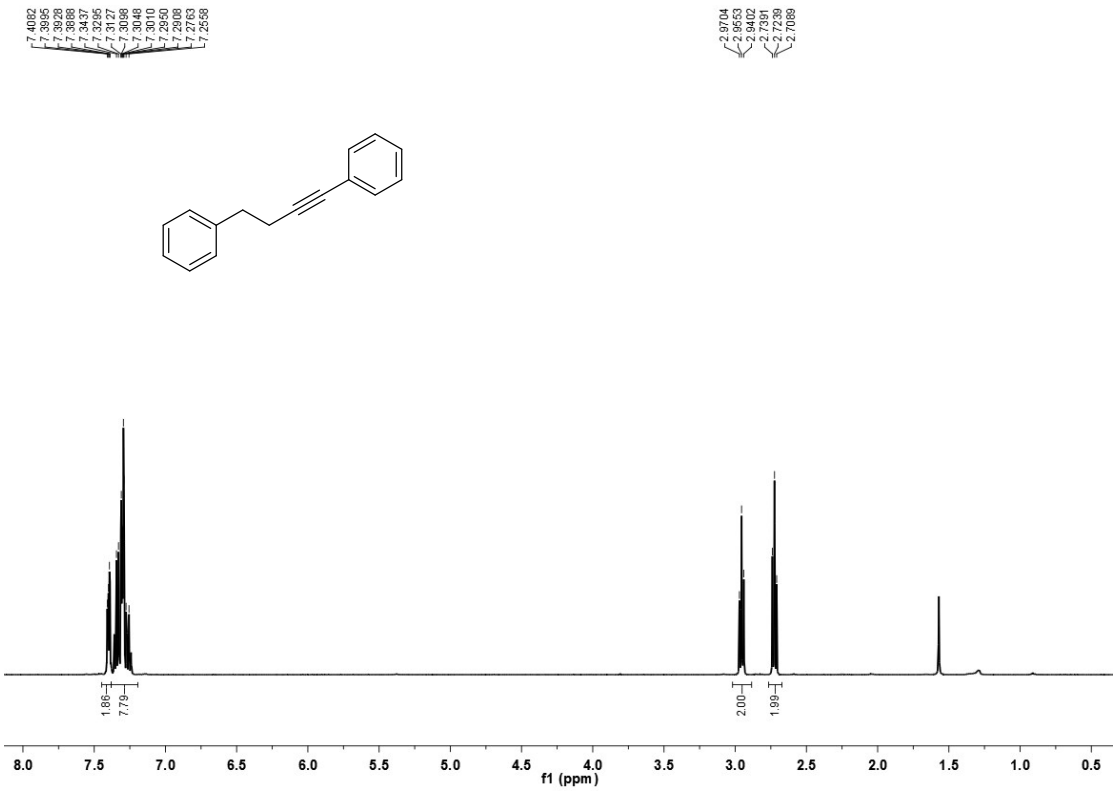
9-(Dec-1-yn-1-yl)phenanthrene (**3q**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.73-8.69 (m, 1H), 8.67 (d, *J* = 8.1 Hz, 1H), 8.56-8.51 (m, 1H), 8.00 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.75-7.68 (m, 2H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 2.65 (t, *J* = 7.1 Hz, 2H), 1.79 (sept, *J* = 7.6 Hz, 2H), 1.66-1.59 (m, 2H), 1.47-1.34 (m, 8H), 0.97 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz):δ 131.6, 131.4, 131.2, 130.1, 129.9, 128.3, 127.0, 126.9, 126.8, 126.7, 122.7, 122.5, 120.5, 95.3, 78.8, 31.9, 29.7, 29.3, 29.2, 29.1, 29.0, 22.7, 19.8, 14.1. HRMS (EI-TOF): m/z calculated for $C_{24}H_{26}$ 314.2035, found 314.2047.



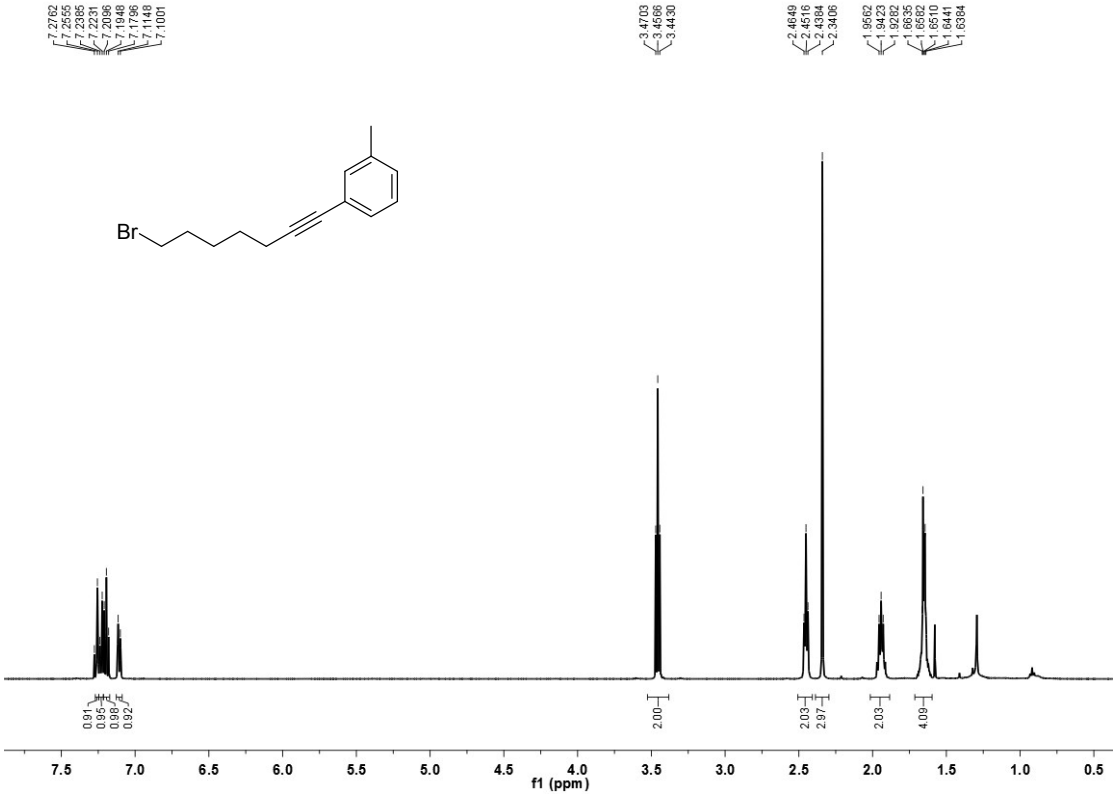
1-Phenyl-tetradecyne (**4a**)[14]: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43 (d, J = 7.4 Hz, 2H), 7.33-7.25 (m, 3H), 2.43 (t, J = 7.1 Hz, 2H), 1.64 (sept, J = 7.4 Hz, 2H), 1.52-1.43 (m, 2H), 1.40-1.20 (m, 16H), 0.92 (t, J = 6.8 Hz, 3H).

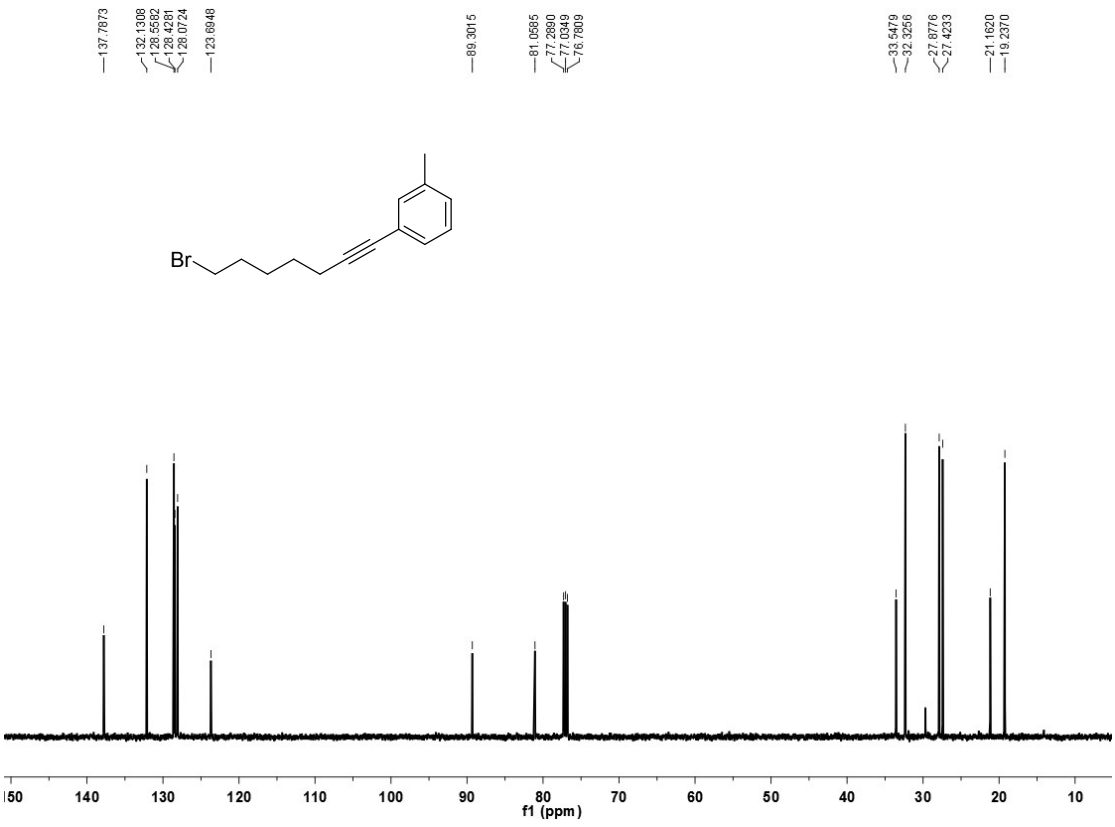


1,4-Diphenyl-butyne (**4b**)[14]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.41-7.37 (m, 2H), 7.37-7.23 (m, 8H), 2.96 (t, *J* = 7.5 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H).

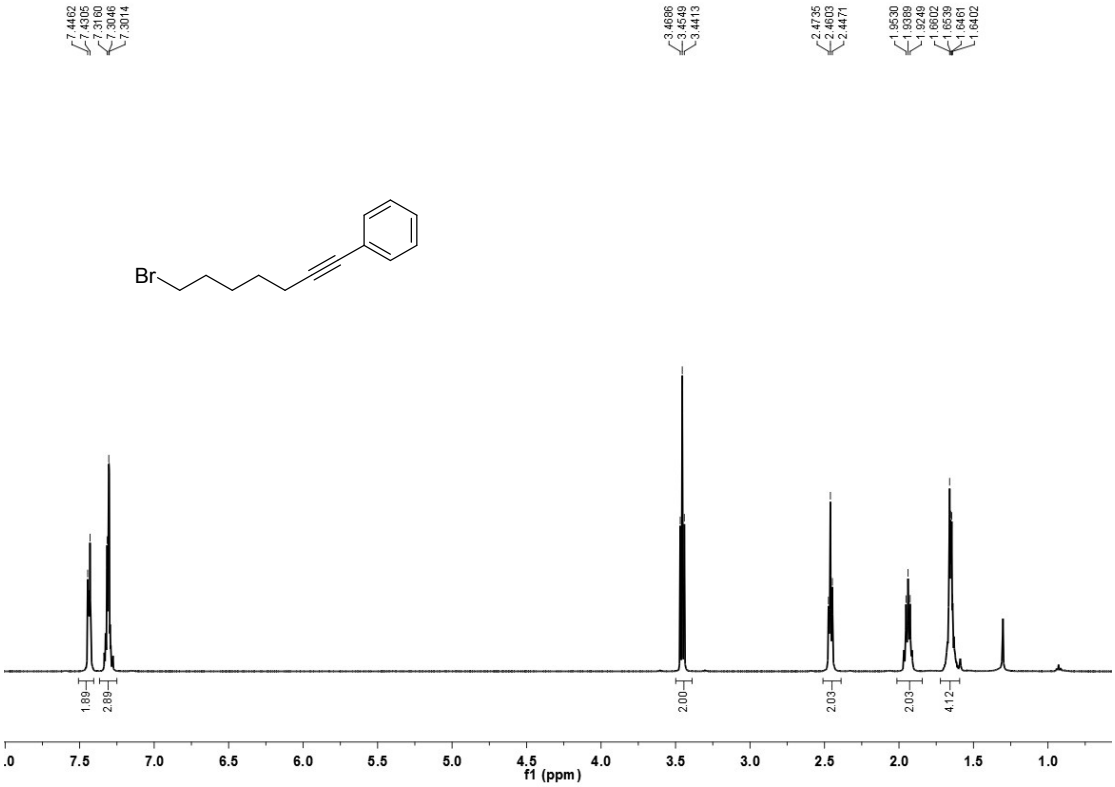


1-(7-Bromoheptynyl)-3-methylbenzene (**4c**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.26 (s, 1H), 7.23 (d, *J* = 7.5, 1H), 7.20 (t, *J* = 7.5, 1H), 7.11 (d, *J* = 7.5, 1H), 3.46 (t, *J* = 6.8 Hz, 2H), 2.49-2.41 (m, 2H), 2.34 (s, 3H), 1.97-1.90 (m, 2H), 1.71-1.60 (m, 4H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 137.8, 132.1, 128.6, 128.4, 128.1, 123.7, 89.3, 81.1, 33.5, 32.3, 27.9, 27.4, 21.2, 19.2. HRMS (EI-TOF): m/z calculated for $C_{14}H_{17}Br$ 264.0514, found 264.0507.

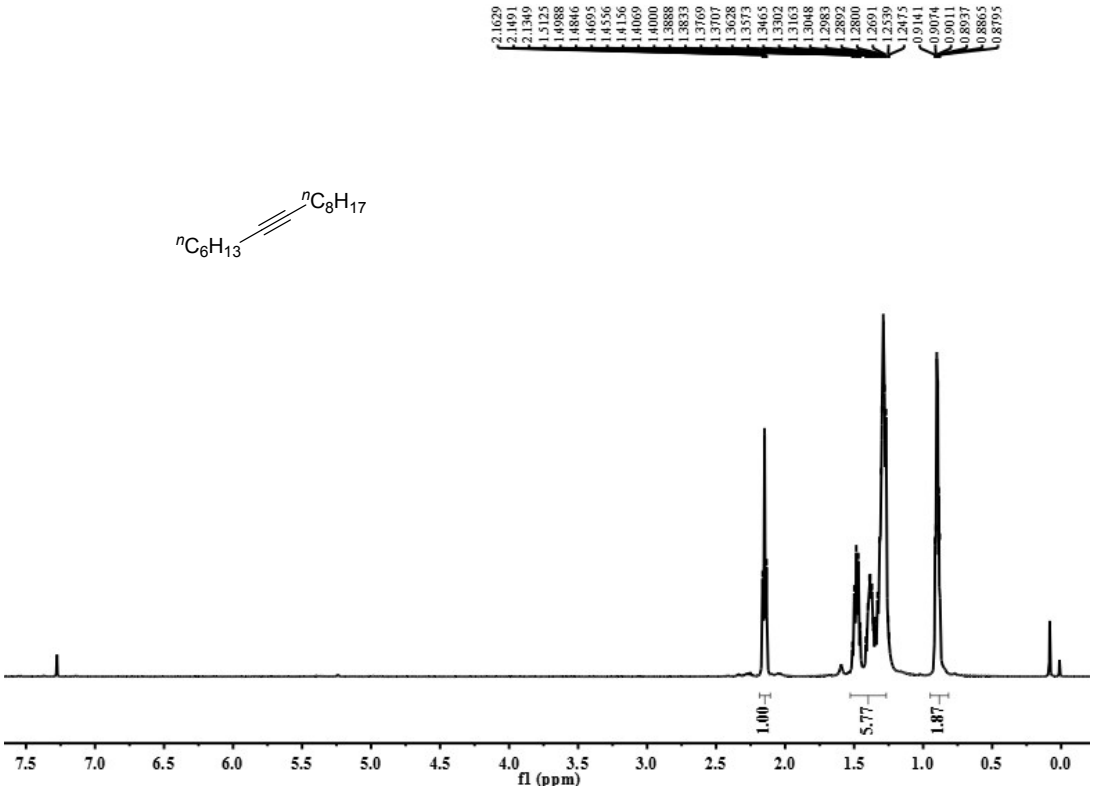




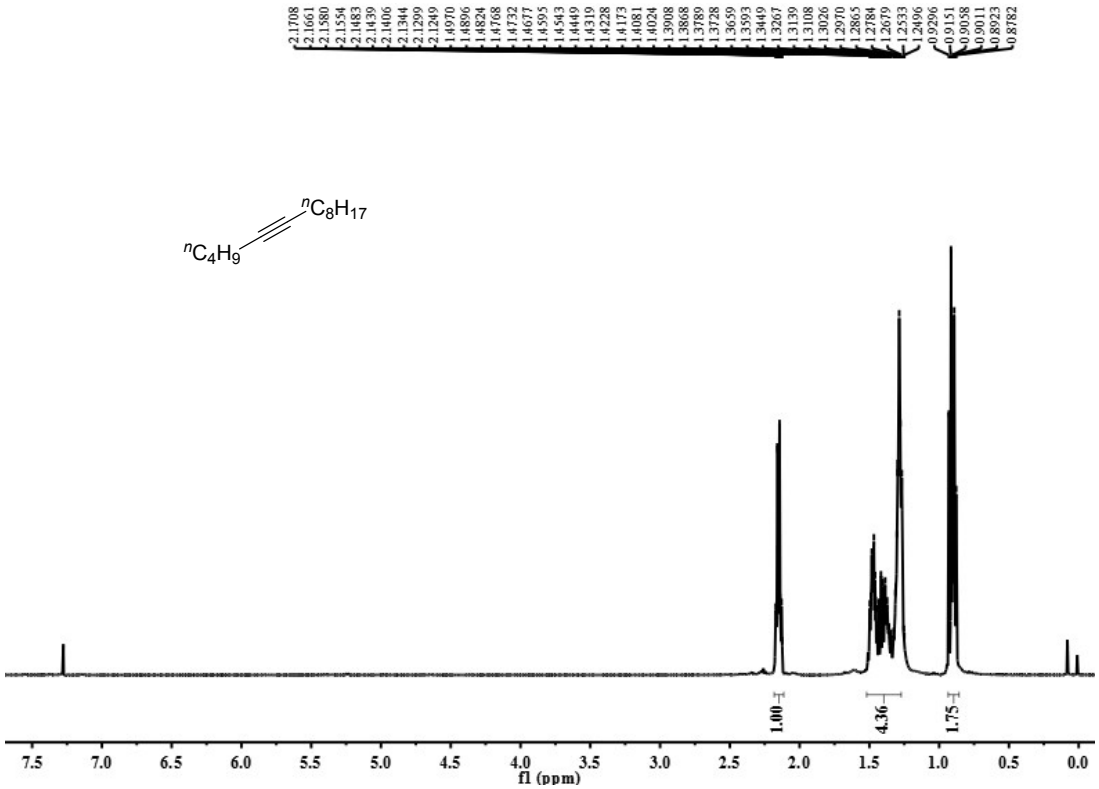
(7-Bromohept-1-yn-1-yl)benzene (**4d**)[15]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.44 (d, *J*= 7.4 Hz, 2H), 7.34-7.26 (m , 3H), 3.46 (t, *J*= 6.7 Hz, 2H), 2.46 (t, *J* = 6.5 Hz, 2H), 1.98-1.88 (m, 2H), 1.71-1.57 (m, 4H).



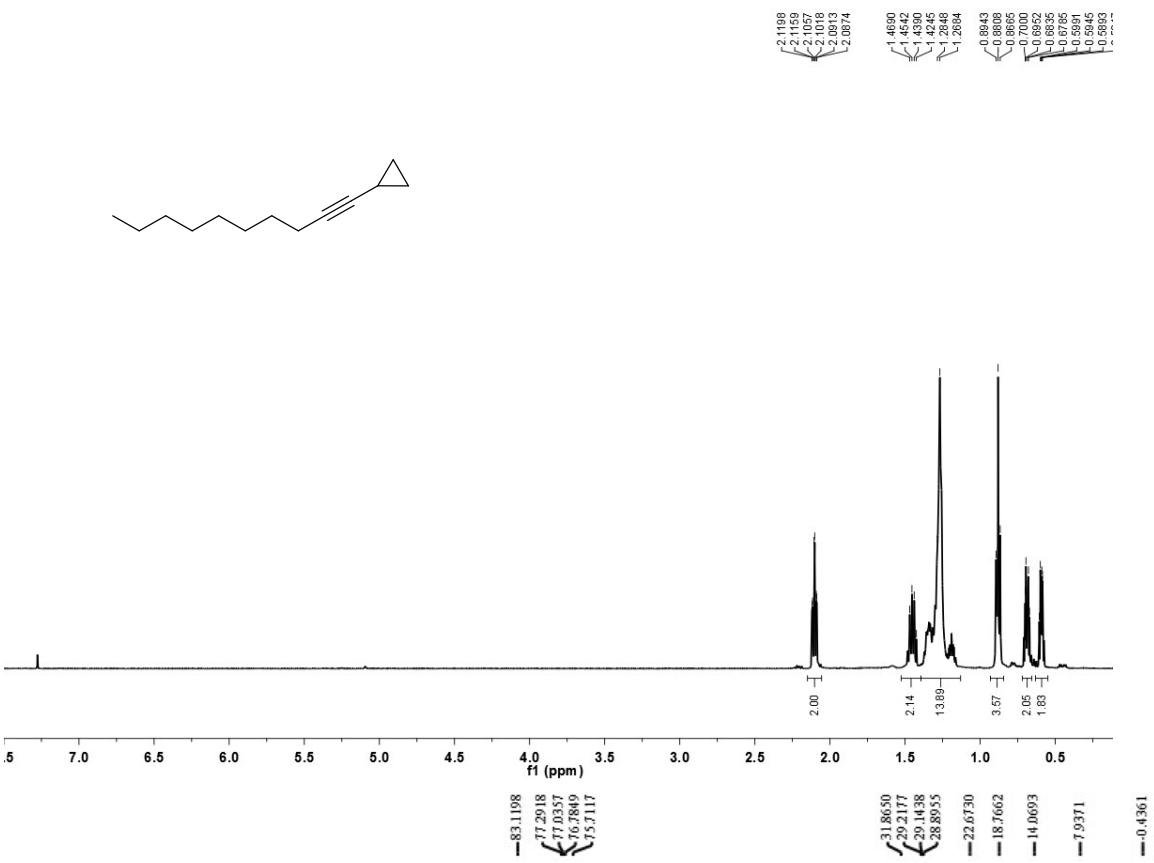
Hexadec-7-yne (**5a**)[9]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.5 (t, J = 6.9 Hz, 4H), 1.53-1.27 (m, 20H), 0.94-0.80 (m, 6H).

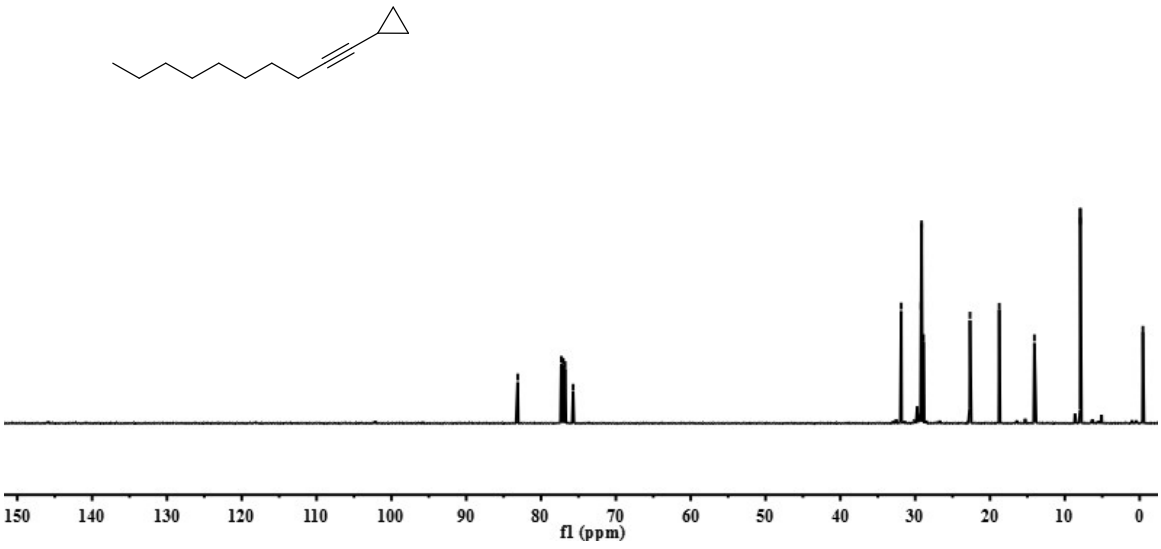


Tetradec-5-yne (**5b**)[16]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.20-2.10 (m, 4H), 1.52-1.28 (m, 16H), 0.95-0.86 (m, 6H).



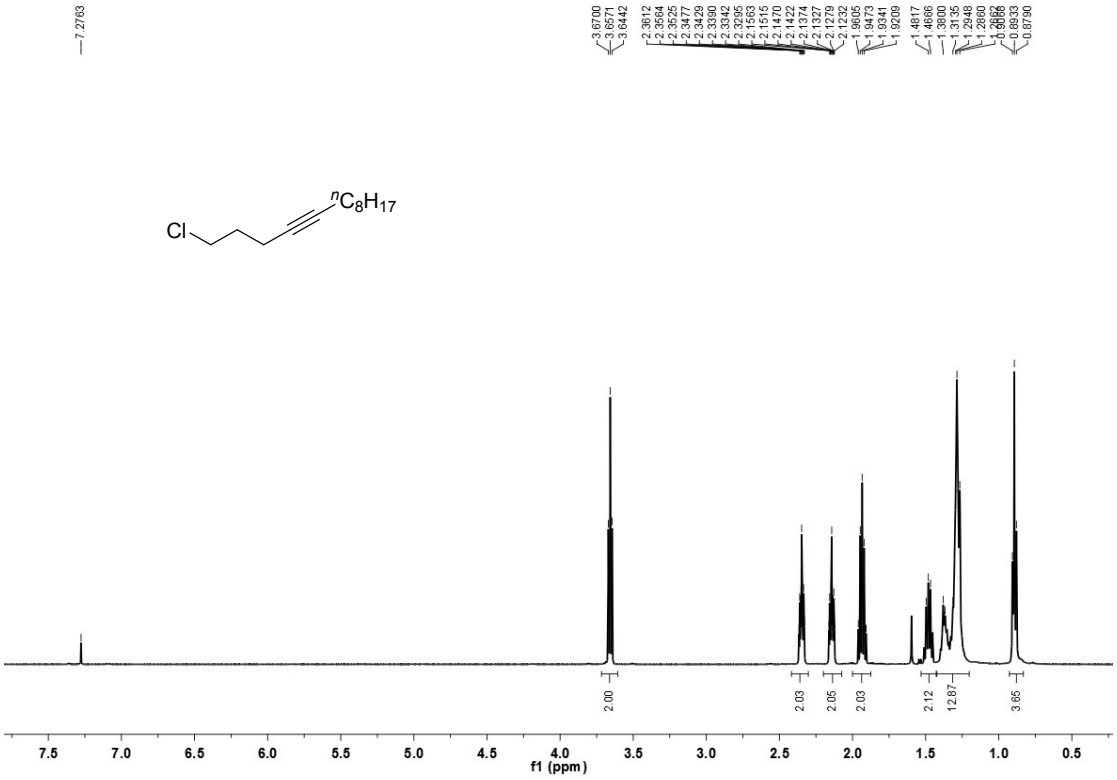
1-Cyclopropyl-decyne (**5c**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.10 (t, J = 7.3 Hz, 2H), 1.52-1.41 (m, 2H), 1.38-1.22 (m, 11H), 0.88 (t, J = 6.8 Hz, 3H), 0.72-0.66 (m, 2H), 0.61-0.55 (m, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 83.1, 75.7, 31.9, 29.2, 29.1, 28.9, 22.7, 18.8, 14.1, 7.9. HRMS (EI-TOF): m/z calculated for $C_{13}H_{22}$ 178.1722, found 178.1727.

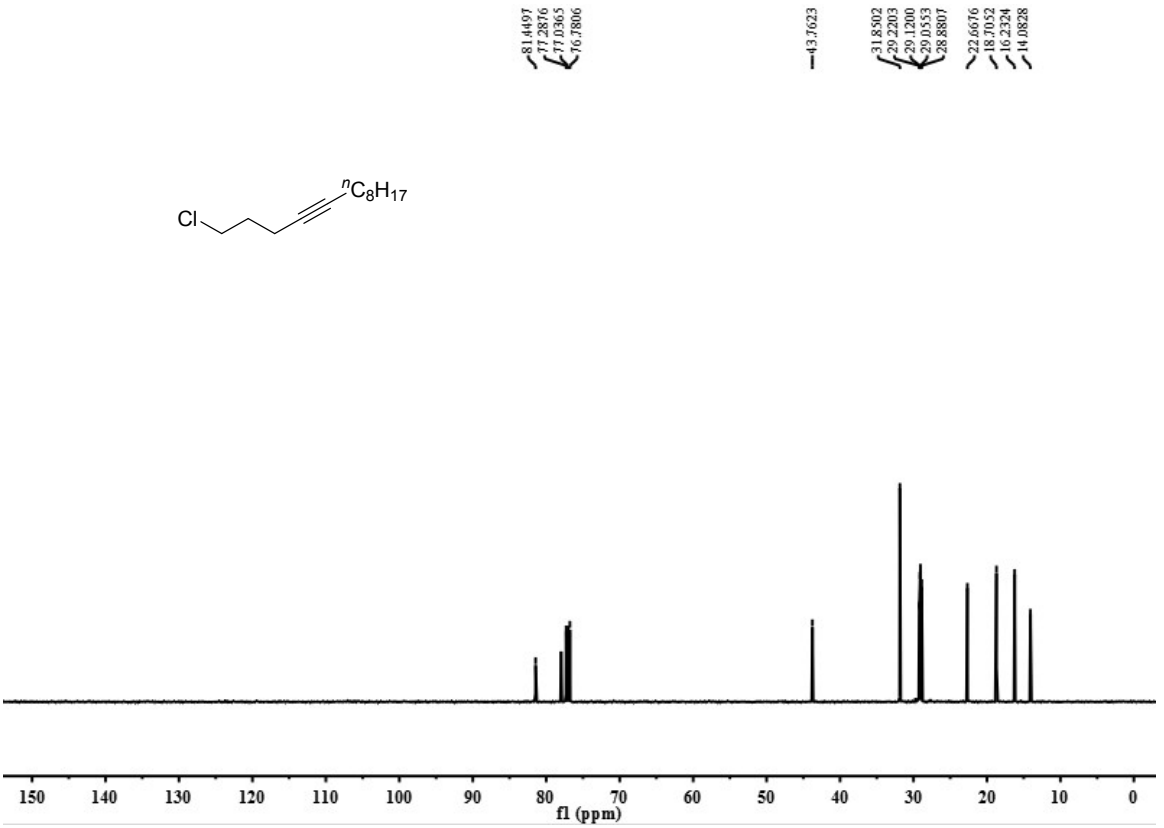




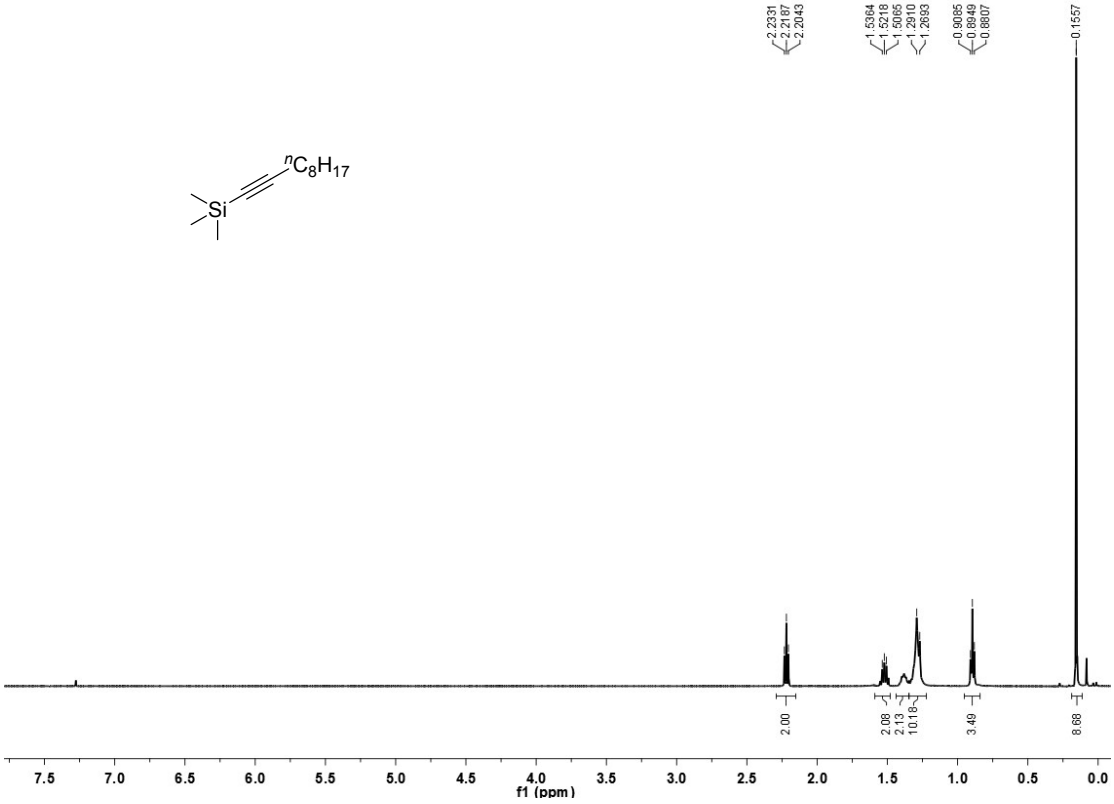
Chlorotridec-4-yne (**5d**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.66 (t, J = 6.5 Hz, 2H), 2.37-2.31 (m, 2H), 2.17-2.11 (m, 2H), 1.97-1.88 (m, 2H), 1.52-1.44 (m, 2H), 1.41-1.27 (m, 10H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 81.4, 78.0,

43.8, 31.8, 29.2, 29.1, 29.0, 28.9, 22.7, 18.7, 16.2, 14.1. HRMS (EI-TOF): m/z calculated for $C_{13}H_{23}Cl$ 179.1800, found 179.1810.

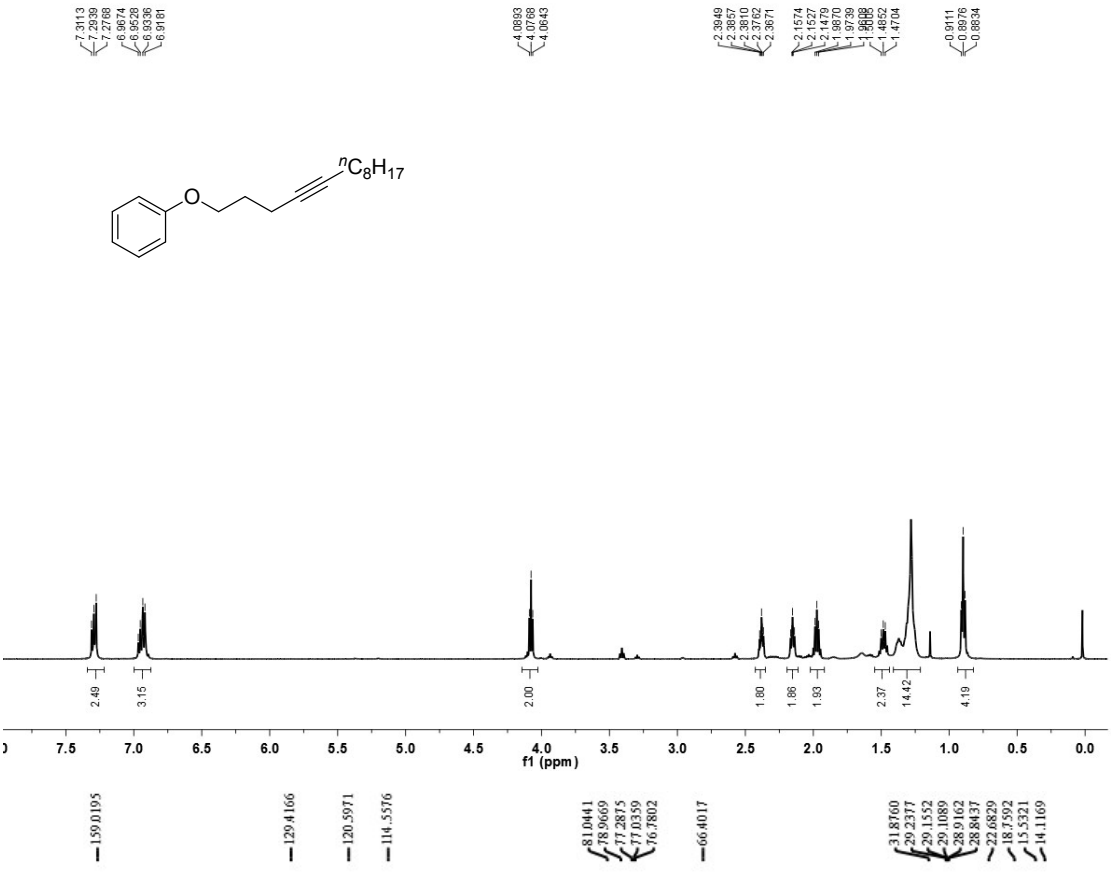


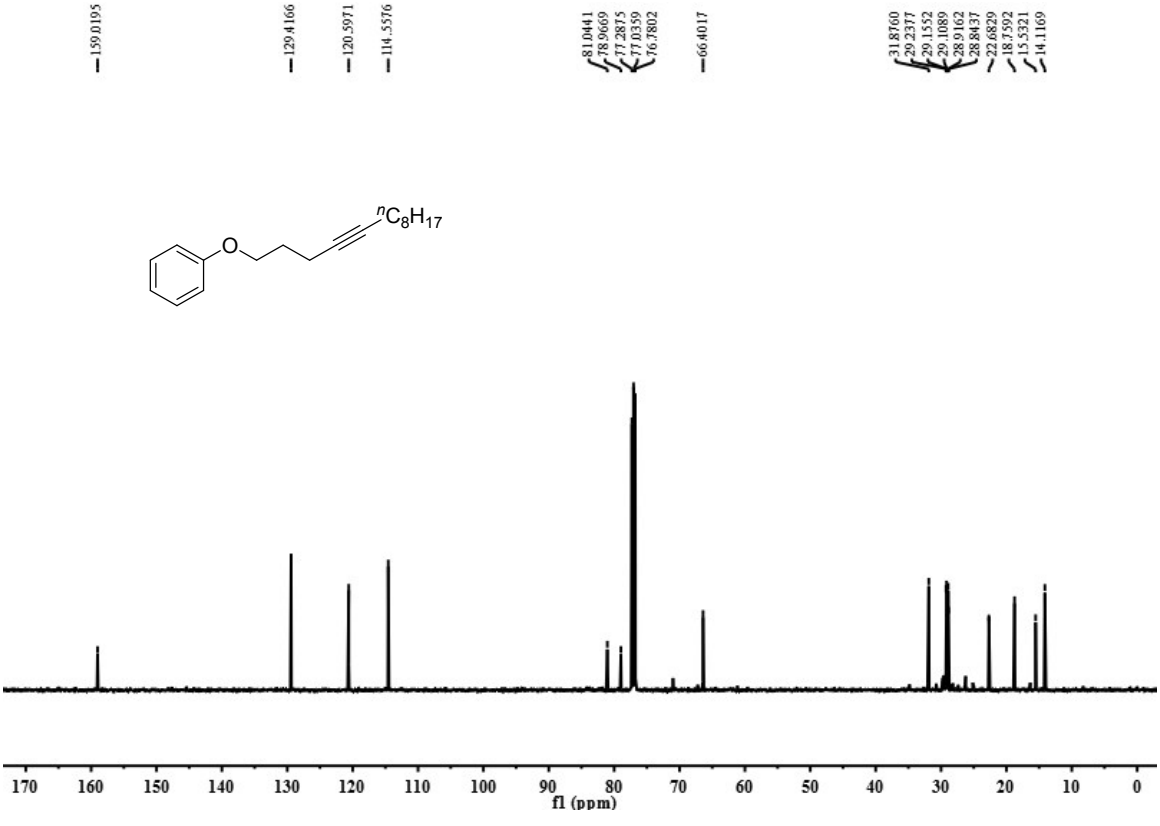


1-Trimethylsilyl-decyne (**5e**)[17]: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.21 (t, *J* = 7.2 Hz, 2H), 1.57-1.47 (m, 2H), 1.43-1.18 (m, 10H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.15 (s, 9H).

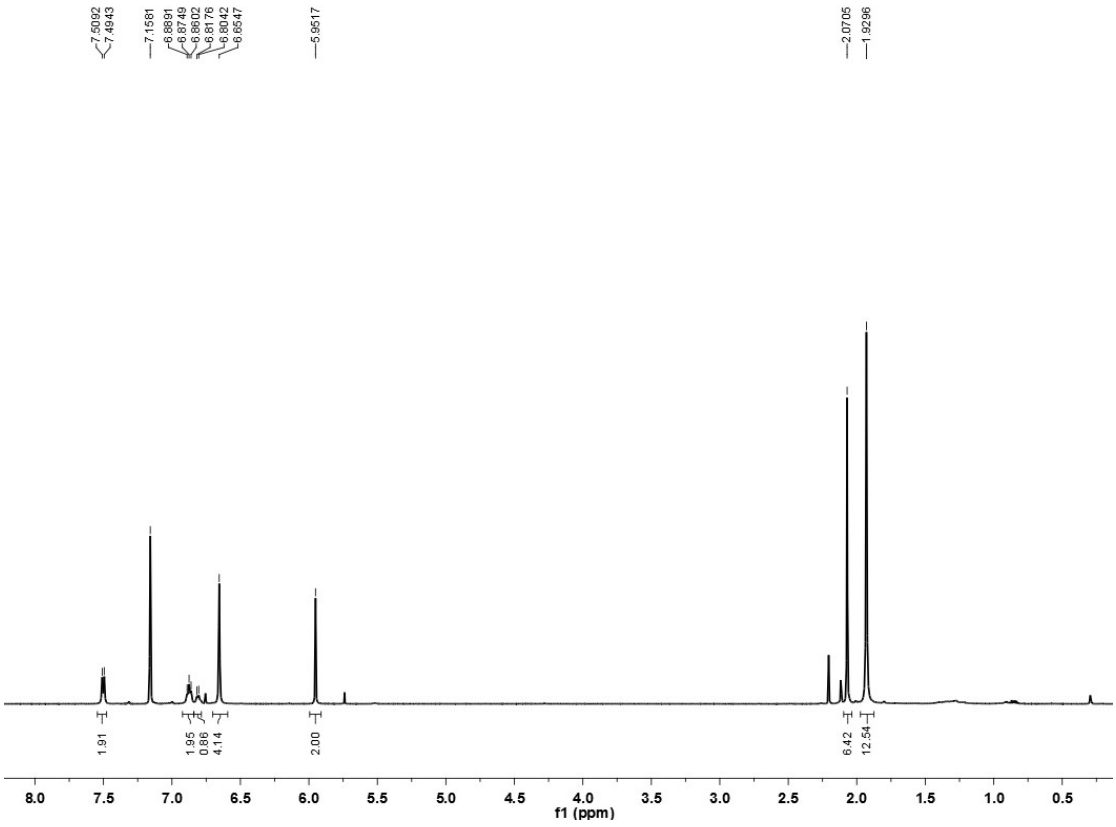


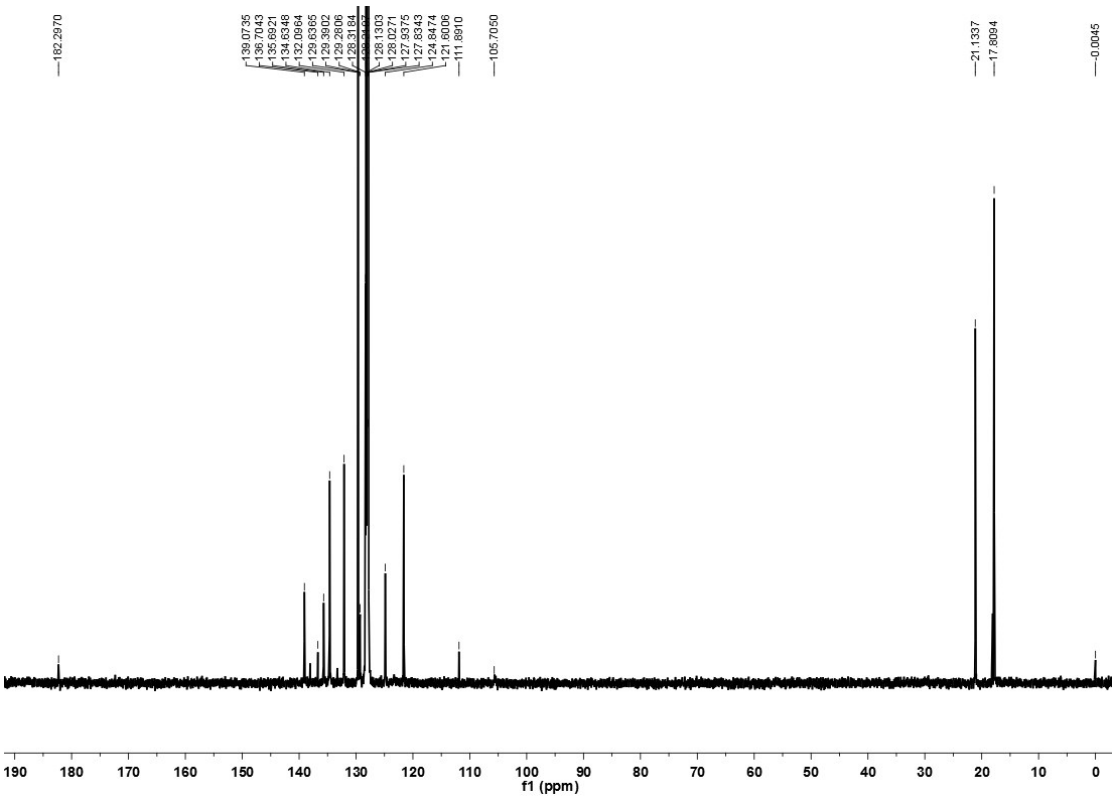
1-(3-Phenoxyl)-propyl-decyne (**5f**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32-7.25 (m, 2H), 6.99-6.87 (m, 3H), 4.08 (t, *J* = 6.2 Hz, 2H), 2.44-2.32 (m, 2H), 2.19-2.12 (m, 2H), 2.00-1.92 (m, 2H), 1.53-1.43 (m, 2H), 1.42-1.34 (m, 2H), 1.30-1.20 (m, 8H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 159.0, 129.4, 120.6, 114.6, 81.0, 79.0, 66.4, 31.9, 29.2, 29.1, 29.0, 28.9, 28.8, 22.7, 18.8, 15.5, 14.1. HRMS (EI-TOF): m/z calculated for $C_{19}H_{28}O$ 272.2140, found 272.2131.


7.3113
7.2939
7.2768
6.9674
6.9528
6.9336
6.9181
4.0893
4.0768
4.0643
2.3949
2.3857
2.3810
2.3762
2.3671
2.1574
2.1527
2.1479
1.9870
1.9739
1.4952
1.4704
0.9111
0.8976
0.8834
$^{n}C_8H_{17}$
O
2.49
3.15
2.00
1.80
1.86
1.93
2.37
14.42
4.19
f1 (ppm)

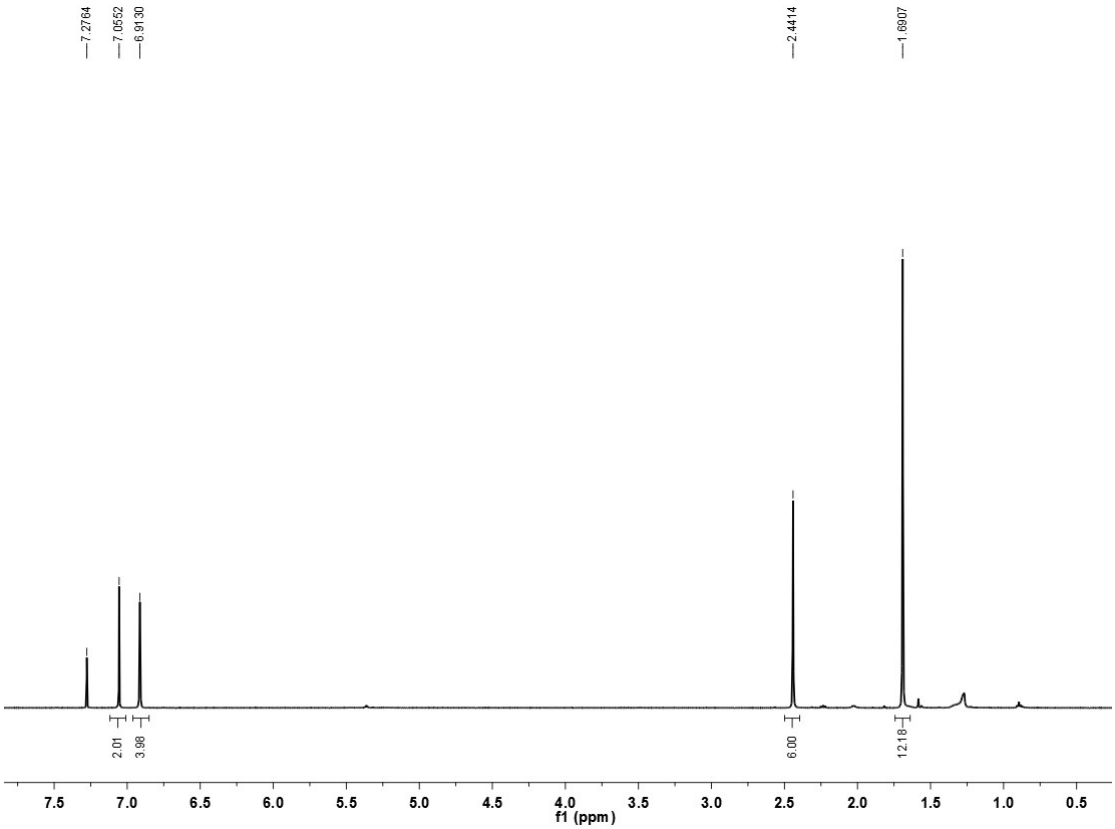

159.0195
129.4166
120.5971
114.5576
81.0441
78.9669
77.2875
77.0359
76.7802
66.4017
31.8760
29.2377
29.1552
29.1089
28.9162
28.8437
22.6829
18.7592
15.5321
14.1169
$^{n}C_8H_{17}$
O
f1 (ppm)

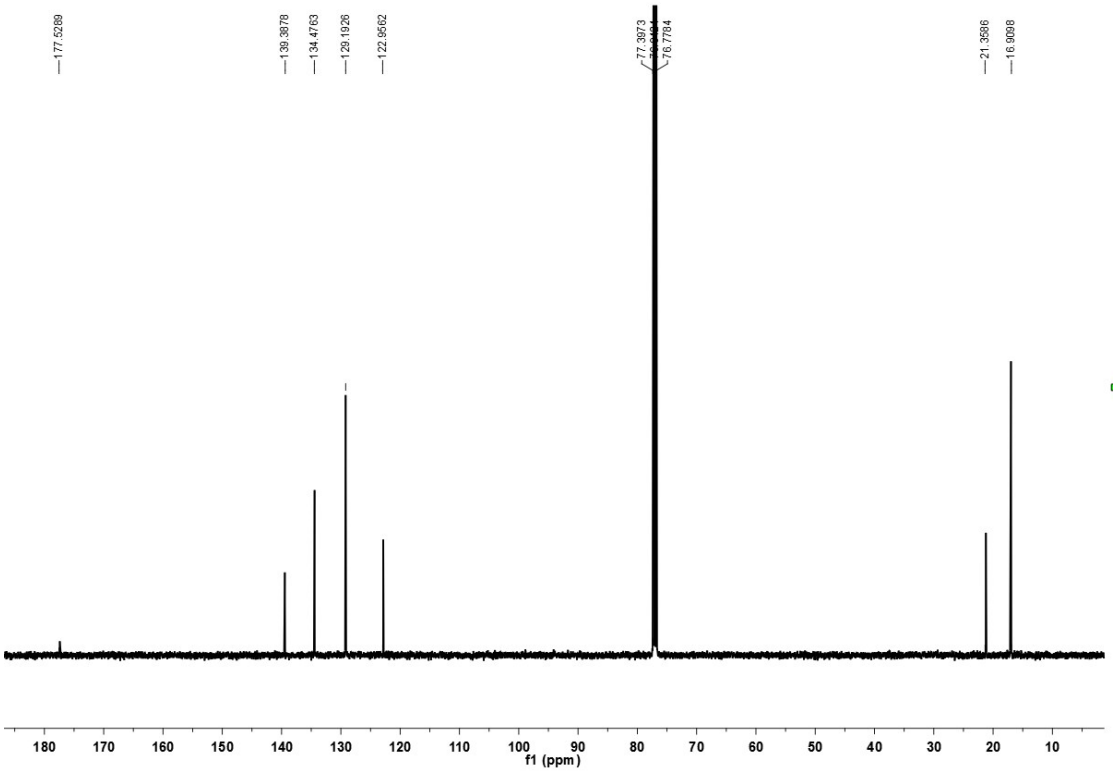
Complex **S-I**: ^{1}H NMR (C_6D_6, 500 MHz): δ 7.50 (d, *J* = 7.5 Hz, 2H), 6.87 (t, *J* = 7.5 Hz, 2H), 6.80 (t, *J* = 7.5 Hz, 1H), 6.65 (s, 4H), 5.95 (s, 1H), 2.07 (s, 6H), 1.92 (s, 12H). ^{13}C NMR (C_6D_6, 126 MHz): δ 182.3, 139.1, 136.7, 135.7, 134.6, 132.1, 129.4, 129.3, 124.8, 121.6, 111.9, 105.7, 21.1, 17.8. (Weak signals were also detected between 140 ppm to 115 ppm, which suggest the presence of different/additional species in solution.[18]) *m.p.* 130 °C (dec.) HRMS (ESI-MS): m/z calculated for $C_{42}H_{48}CuN_4$ ([(IMes)$_2$Cu]$^+$) 671.3175, found 671.3185. m/z calculated for $C_{23}H_{27}CuN_3$ ([(IMes) Cu]$^+$$CH_3CN$) 408.1501, found 408.1500.





Complex **S-II**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.06 (s, 2H), 6.91 (s, 4H), 2.44 (s, 6H), 1.69 (s, 12H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 177.5, 139.4, 134.5, 129.2, 123.0, 21.4, 16.9. *m.p.* 215 ^{o}C (dec.)


7.2764
7.0552
6.9130
2.4414
1.6907
2.01
3.98
6.00
12.18
f1 (ppm)


177.5289
139.3878
134.4763
129.1926
122.9562
77.3973
76.7784
21.3586
16.9098
f1 (ppm)

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