Supporting for

Recyclable Cu/C_3N_4 composite materials catalyzed homo- and cross-coupling of terminal alkynes under mild conditions

Hang Xu[a], KeyingWu[a], Jing Tian[a], Li Zhu[b,*] and Xiaoquan Yao[a,*]

[a] *Department of Applied Chemistry, College of Material Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, PR China*

[b] *Department of Chemistry, School of Pharmacy, Nanjing Medical University, Nanjing 211166, PR China*

Fax: +86-25-52112626; Phone: +86-25-52112902; e-mail: yaoxq@nuaa.edu.cn

Table of contents

1. Preparation and characterization of catalyst

The Cu/C_3N_4 catalyst was synthesized following the reported method.[s1] Typically, melamide (2g) was uniformly mixed with copper(II) acetate (625mg). The resulting mixture was then heated to 550 ^oC with 2^oC/min in a tube furnace under N_2 atmosphere and kept for 2 h. After cooling to room temperature, the final solid product (Cu-doped C_3N_4) was collected without further purification.

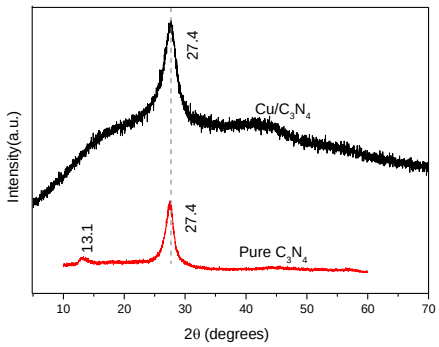


Figure S1. XRD patterns of pure C_3N_4 and Cu/C_3N_4.

Figure S1 shows the XRD patterns of pure C_3N_4 and 20% Cu/C_3N_4. It was found that the XRD pattern of 20% Cu/C_3N_4 was similar to pure C_3N_4. This result indicates that the structure of C_3N_4 remains unchanged when copper species were host by coordination with the N atom.[s1]

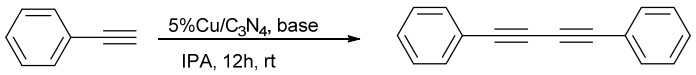
2. Experimental section

2.1 General information

All experiments were carried out under oxygen atmosphere. Flash column chromatography was performed over silica gel 200-300 mesh. ^{1}H NMR spectra were acquired by 400 MHz, and ^{13}C NMR spectra were acquired by 101 MHz. Compound **3g** and **3j** are unknown compounds and were characterized by m.p., ^{1}H & ^{13}C NMR, LR & HR MS. All of the known compounds described in the paper were characterized by comparing their ^{1}H & ^{13}C NMR to the previously reported data.

2.2 Condition optimization for the homo-coupling of phenylacetylene(1a)

Table S1 Screening bases for the homo-coupling of phenylacetylene catalyzed by 5% Cu/C_3N_4 [a].



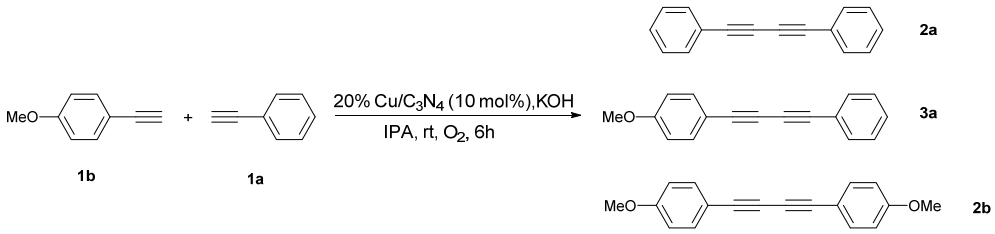
1a **2a**

Entry	Base	Yield(%) [b]
1	None	0
2	K_2CO_3	trace
3	$NaHCO_3$	10
4	Na_2CO_3	trace
5	Et_3N	15
6	NaOH	70
7	Py	trace
8	KOH	74
9 [c]	KOH	65

[a] The reaction was carried out using **1a** (0.2 mmol) and base (2 eq) in the presence of catalyst (10 mol%) in IPA (0.5 mL) at rt under O_2. [b] Isolated yields. [c] KOH 1eq.

2.3 Condition optimization for the cross-coupling of phenylacetylene (1a) and *p*-Methoxyphenlacetylene (1b)

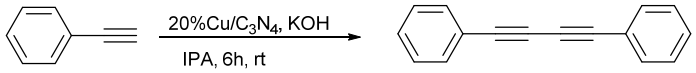
Table S2 Screening ratio for the cross-coupling of phenylacetylene and *p*-Methoxyphenlacetylene catalyzed by 20% Cu/C_3N_4 [a].



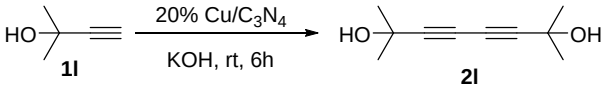
Entry	**1b** (mmol)	**1a** (mmol)	**3a** Yield(%) [b]	**2a** Yield(%) [c]	**2b** Yield(%) [d]
1	0.1	0.1	43 (0.043)	49 (0.025)	38 (0.019)
2	0.1	0.2	60 (0.060)	59 (0.059)	38 (0.019)
3	0.1	0.5	78 (0.078)	65 (0.163)	15 (0.011)
4	0.5	0.1	65 (0.065)	30 (0.015)	61 (0.076)
5[e]	0.1	0.5	65 (0.065)	65 (0.163)	8 (0.008)
6[f]	0.1	0.5	trace	34 (0.084)	8 (0.008)
7[g]	0.1	0.5	trace	trace	trace

[a] The reaction was carried out using 20% Cu/C_3N_4 (10 mmol%) and KOH (2 eq) in IPA (0.5 mL) at rt under O_2; Isolated yield. [b] the numbers in the parentheses are amounts of **3a** (mmol). [c] Yields based on **1a**; the numbers in the parentheses are amounts of **2a** (mmol). [d] Yields based on **1b**; the numbers in the parentheses are amounts of **2b** (mmol). [e] With 4 equiv. of IPA. [f] Neat. [g] CH_3CN (0.5 mL) as solvent.

2.4 Typical procedure for the synthesis of symmetric 1,3-diynes

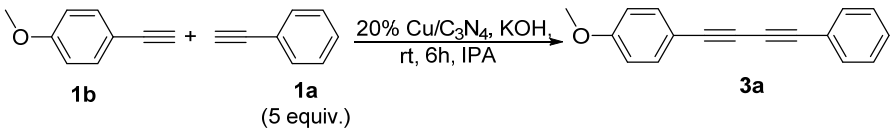


Phenylacetylene (**1a**, 0.2 mmol), 20% Cu/C_3N_4 (10 mol%), KOH (2 eq) and 0.5 mL of isopropanol (0.5 mL) were added into a 10 mL sealed tube under O_2. The mixture was stirred at room temperature for 6 hours. Then, the reaction was stopped, and the reaction mixture was purified by flash column chromatography on silica gel (pure hexanes). Compound **2a** was obtained in 99% of yield.



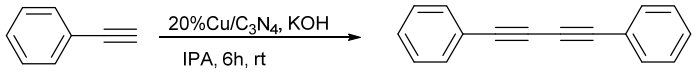
2-Methylbut-3-yn-2-ol (**1l,** 1 mmol), 20% Cu/C_3N_4 (10 mol%), KOH (2 eq) were added into a 10 mL sealed tube under O_2. The mixture was stirred at room temperature for 6 hours. Then, the reaction was stopped, and the reaction mixture was purified by flash column chromatography on silica gel (hexanes/ethyl acetate=5:1). Compound **2l** was obtained in 55% of yield.

2.5 Typical procedure for the synthesis of unsymmetrical 1,3-diynes



Phenylacetylene (**1a**, 0.5 mmol), p-methoxyphenylacetylene (**1b**, 0.1 mmol), 20% Cu/C_3N_4 (10 mol%), KOH (2 eq) and 0.5 mL of isopropanol (0.5 mL) were added into a 10 mL sealed tube under O_2. The mixture was stirred at room temperature for 6 hours. Then, the reaction was stopped, and the reaction mixture was purified by flash column chromatography on silica gel (pure hexanes). Compound **3a** was obtained in 78% of yield.

2.6 The experiments of catalyst recycle



1a
(1 mmol scale)

2a

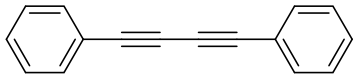
Phenylacetylene (**1a**, 1 mmol), 20% Cu/C_3N_4 (10 mol%), KOH (2 eq) and 2 mL of isopropanol (0.5 mL) were added into a 10 mL sealed tube under O_2. The mixture was stirred at room temperature for 6 hours. After completion of the reaction, the catalyst was separated by centrifugation and washed by water and ether, and then, dried under vacuum at 60 ^oC. The recovered catalyst was reused for the next cycle with fresh starting materials and solvent.

Table S3. Recycling of the Cu/C_3N_4 catalyst [a]

Run	Fresh	1	2	3	4	5	6	7	8	9	10
Yield(%)[b]	98	97	98	97	93	91	91	92	93	92	91

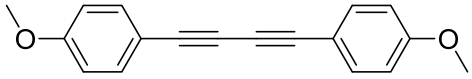
[a] The reaction was carried out using **1a** (1.0 mmol) and KOH (2eq) in the presence of 20% Cu/C_3N_4 (10mol%) in IPA (2 mL) at rt under O_2. [b] Isolated yields

Characterization for compounds 2 & 3



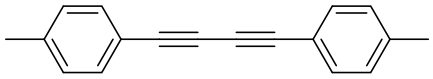
2a

1,4-diphenyl buta-1,3-diyne (2a) [s2]: White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54-7.51 (m, 4 H), 7.36-7.31 (m, 6 H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 132.79, 129.09, 128.45, 121.82, 81.56, 73.92.



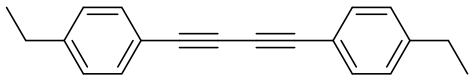
2b

1,4-bis(p-methoxyphenyl)buta-1,3-diyne (2b) [s2]: White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 9.2 Hz, 4 H), 6.85 (d, *J* = 8.8 Hz, 4 H), 3.82 (s, 6 H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 160.25, 134.05, 114.14, 113.97, 81.32, 72.95, 55.35.



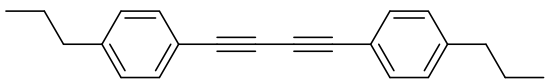
2c

1,4-Bis(4-ethylphenyl)buta-1,3-diyne (2c) [s3]**:** White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 7.6 Hz, 4 H), 7.14 (d, *J* =7.6 Hz, 4 H), 2.36 (s, 6 H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 139.53, 132.43, 129.25, 118.84, 81.58, 73.48, 21.66.



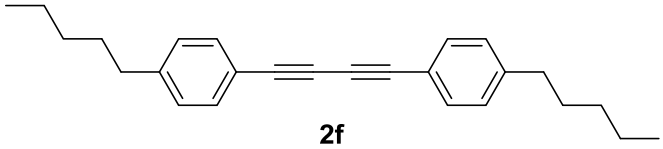
2d

1,4-Bis(4-ethylphenyl)buta-1,3-diyne (2d) [s2]**:** White solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.44 (d, *J* = 8.0 Hz, 4 H), 7.16 (d, *J* = 8.4 Hz, 4 H), 2.64 (q, *J* = 7.6 Hz, 4 H), 1.23 (t, *J* = 7.6 Hz, 6 H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 145.67, 132.50, 128.03, 119.41, 81.58, 73.38, 28.93, 15.25.



2e

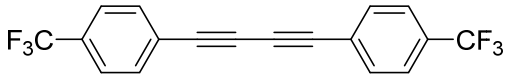
1,4-Bis(4-n-propylphenyl)buta-1,3-diyne (2e) [s2]**:** Yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.43 (d, *J* = 7.6 Hz, 4 H), 7.14 (d, *J* = 7.6 Hz, 4 H), 2.59 (t, *J* = 7.6 Hz, 4 H), 1.68-1.59 (m, 4 H), 0.94 (t, *J* = 7.2 Hz, 4 H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 144.24, 132.40, 128.62, 119.05, 81.58, 73.48, 38.05, 24.27, 13.76.



2f

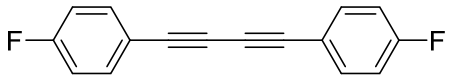
1,4-Bis(4-n-pentylphenyl)buta-1,3-diyne (2f) [s3]**:** Yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.43 (d, *J* = 8.0 Hz, 4 H), 7.14 (d, *J* = 7.6 Hz, 4 H), 2.60 (t, *J* = 7.6 Hz, 4 H), 1.64-1.57 (m, 4 H), 1.32 (m, 8 H), 0.90-0.87 (m, 6 H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ

144.51, 132.42, 128.57, 119.05, 81.59, 73.48, 35.97, 31.44, 30.86, 22.51, 14.01.



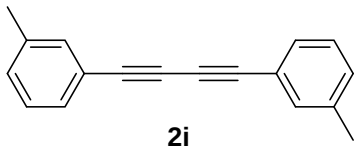
2g

1,4-Bis(4-trifluoromethyl)buta-1,3-diyne (2g) [s4]: Yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.63 (q, *J* = 8.4 Hz, J = 4.0 Hz, 8 H); **^{13}C NMR** ($CDCl_3$, 101 MHz): 132.83, 131.13 (q, *J* = 33.0 Hz), 125.48 (q, *J* = 3.7 Hz), 123.70 (q, *J* = 273.4 Hz), 80.98, 75.65.



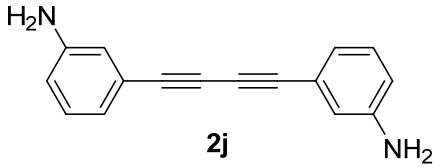
2h

1,4-Bis(4-fluorophenyl)buta-1,3-diyne (2h) [s2]**:** White solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.53-7.50 (m, 4 H), 7.04 (t, *J* = 8.4 Hz, 4 H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 163.1, 134.57(d, *J* = 8.0 Hz), 117.86 (d, *J* = 3.0 Hz), 115.94 (d, *J* = 22.2 Hz), 80.46, 73.57.



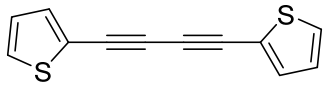
2i

1,4-bis(m-methylphenyl)buta-1,3-diyne (2i) [s2]**:** White solid. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.28-7.25 (m, 4 H), 7.17-7.10 (m, 4 H), 2.27 (s, 6 H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 138.1, 133.0, 130.1, 129.6, 128.3, 121.7, 81.6, 73.7, 21.2.



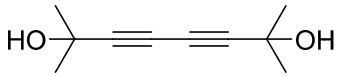
2j

3,3'-(Buta-1,3-diyne-1,4-diyl)dibenzenamine (2j) [s2]**:** Yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.11 (t, *J* = 7.6 Hz, 2 H), 6.93 (d, *J* = 7.6 Hz, 2 H), 6.82 (s, 2 H), 6.68 (d, *J* = 8.0 Hz, 2 H), 3,71 (s, 4 H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 146.34, 129.41, 123.00, 122.51, 118.44, 116.30, 81.68, 73.42.



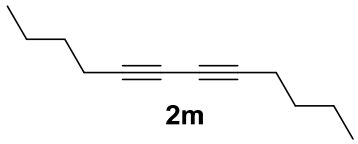
2k

1,4-Bis(2-thienyl) buta-1,3-diyne (2i) [s2]**:** Yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.35-7.31 (m, 4H), 7.00-6.98 (m, 2H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 134.41, 128.92, 127.22, 121.91, 77.83, 76.64.



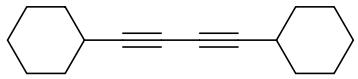
2l

2,7-dimethyl octa-3,5-diyne-2,7-diol (2l) [s5]**:** Colorless liquid; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 1.47 (s, 12 H), 1.36 (s, 2 H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 83.99, 66.33, 65.59, 31.05.



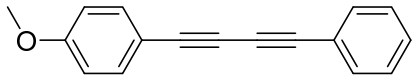
2m

Dodeca-5,7-diyne (2m) [s2]: Yellow liquid; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 2.18 (t, *J* = 6.8 Hz, 4 H), 1.47-1.30 (m, 8 H), 0.83 (t, *J* = 7.2 Hz, 6 H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 77.49, 65.26, 30.41, 21.94, 18.90, 13.54.



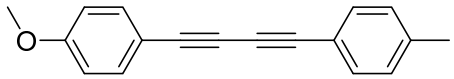
2n

1,4-dicyclohexylbuta-1,3-diyne (2n) [s5]**:** Colorless liquid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.46-2.40 (m, 2 H), 1.81-1.77 (m, 4 H), 1.71-1.68 (m, 4 H), 1.49-1.41 (m, 6 H), 1.33-1.26 (m, 6 H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 80.86, 64.08, 31.27, 28.48, 24,47, 23.77.



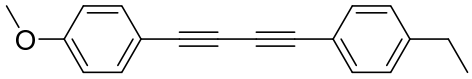
3a

1-methoxy-4-(phenylbuta-1, 3-diyn-1-yl) benzene (3a) [s2]**:** Colorless solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 6.8 Hz, 2 H), 7.47 (d, *J* = 8.4 Hz, 2 H), 7.36-7.31 (m, 3 H), 6.86 (d, *J* = 8.4 Hz, 2 H), 3.83 (s, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 160.38, 134.13, 132.44, 129.02, 128.42, 122.03, 114.17, 113.72, 81.82, 81.03, 74.18, 72.74, 55.35.



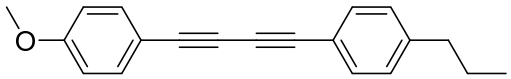
3b

1-((4-methoxyphenyl)buta-1,3-diynyl)-4-methylbenzene (3b) [s2]**:** White solid; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.39 (d, *J* =8.8 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 6.78 (d, *J* = 8.8 Hz, 2 H), 3.74 (s, 3 H), 2.29 (s, 3 H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 160.30, 139.41, 134.09, 132.36, 129.21, 118.89, 114.08, 113.86, 81.46, 81.32, 73.52, 72.86, 55.35, 21.63.



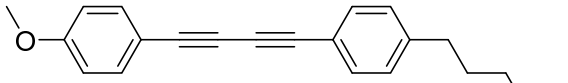
3c

1-Ethyl-4-((4-methoxyphenyl)buta-1,3-diynyl)benzene (3c) [s2]**:**White solid; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.45 (t, *J* = 9.2 Hz, 4 H), 7.16 (d, *J* = 7.6 Hz, 2 H), 6.86 (d, *J* = 8.0 Hz, 2 H), 3.83 (s, 3 H), 2.66 (q, *J* = 7.6 Hz, 2 H), 1.25-1.21(m, 3 H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 160.30, 145.67, 134.09, 132.46, 128.02, 119.11, 114.15, 113.86, 81.45, 81.36, 73.51, 72.89, 55.35, 28.92, 15.26.



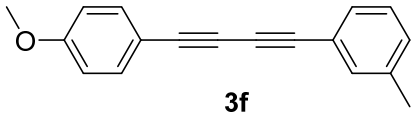
3d

1-Propyl-4-((4-methoxyphenyl)buta-1,3-diynyl)benzene (3d) [s2]**:** Yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.48-7.42 (m, 4 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 6.85 (d, *J* = 8.4 Hz, 2 H), 3.82 (s, 3 H), 2.59 (t, *J* = 7.6 Hz, 2 H), 1.68-1.59 (m, 2 H), 0.93 (t, *J* = 7.2Hz, 3 H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 160.33, 144.19, 134.12, 132.40, 128.65, 119.15, 114.18, 113.90, 81.49, 81.41, 73.57, 72.94, 55.38, 38.08, 24.31, 13.79.



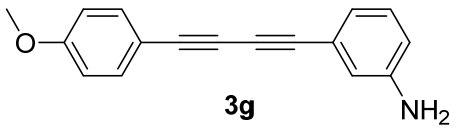
3e

1-methoxy-4-((4-pentylphenyl)buta-1,3-diynyl)benzene (3e) [s6]**:** Yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.48-7.42 (m, 4 H), 7.14 (d, *J* = 7.2 Hz, 2 H), 6.86 (d, *J* = 8.0 Hz 2 H), 3.83 (s, 3 H), 2.60 (t, *J* = 7.6 Hz, 2 H), 1.64-1.57 (m, 2 H), 1.36-1.31 (m, 4 H), 0.91-0.87 (m, 3 H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 160.39, 144.48, 134.09, 132.38, 128.56, 119.07, 114.02, 81.42, 73.53, 72.91, 55.35, 35.97, 31.43, 30.86, 22.51, 14.07.



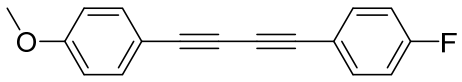
3f

1-(4-Methoxyphenyl)-4-(*m*-toluenyl)-buta-1,3-diyne (3f) [s7]**:** White solid; **^{1}H NMR** (CDCl3, 400 MHz): δ = 7.47 (d, *J* = 8.4 Hz, 2 H), 7.34-7.32 (m, 2 H), 7.24-7.16 (m, 2 H), 6.86 (d, *J* = 8.4 Hz, 2 H), 3.82 (s, 3 H), 2.33 (s, 3 H); **^{13}C NMR** ($CDCl_3$, 101MHz): δ 160.34, 138.14, 134.12, 132.93, 129.99, 129.56, 128.31, 121.80, 114.16, 113.80, 81.61, 81.27, 73.81, 72.82, 55.35, 21.22.



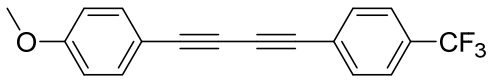
3g

3-((4-methoxyphenyl)buta-1,3-diyn-1-yl)aniline (3g): Yellow solid; MP. 78-81℃ **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.46 (d, *J* = 8.4 Hz, 2 H), 7.13-7.09 (m, 2 H), 6.93 (d, *J* = 7.6 Hz, 1 H), 6.87-6.82 (m, 3 H), 3.82 (s, 3 H), 3.70 (s, 2 H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 160.33, 146.28, 134.11, 129.35, 122.93, 122.64, 118.36, 116.13, 114.15, 1113.80, 81.52, 81.36, 73.52, 72.84, 55.35; MS (EI) m/z (%): 247(M^+), 232, 205(100), 190, 149, 121. HRMS calcd for C17H13NO: 247.0997; found 247.0999.



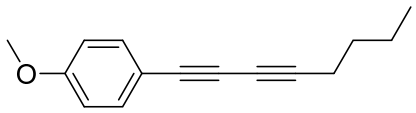
3h

1-(4-Methoxyphenyl)-4-(4-fluorophenyl)-buta-1,3-diyne (3h) [s2]: White solid; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.48 (m, 4 H), 7.03-7.00 (m, 2 H), 6.89-6.85 (m, 2 H), 3.83 (s, 3 H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 162.93 (d, *J* = 250 Hz), 160.44, 134.44 (d, *J* = 8.0 Hz), 134.15, 118.16 (d, *J* = 8.0 Hz), 115.85 (d, *J* = 22 Hz), 114.2, 113.61, 81.82, 79.92, 73.96, 72.59, 55.36.



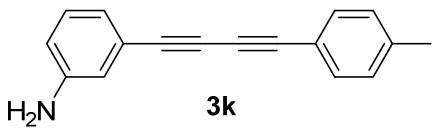
3i

1-(4-Methoxyphenyl)-4-(4-trifluorophenyl)-buta-1,3-diyne (3i) [s8]: Yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.53 (dd, J_1 = 8.6 Hz, J_2 = 11.4 Hz, 4 H), 7.41 (d, *J* = 8.3 Hz, 2 H), 6.80 (d, *J* = 8.3 Hz, 2 H), 3.76 (s, 3 H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 160.68, 134.30, 132.64, 130.58 (q, *J* = 32.9 Hz), 125.99 (d, *J* = 1.1 Hz), 125.38 (dd, J_1 = 3.7 Hz, J_2 = 7.5 Hz), 123.82 (q, *J* = 273.3 Hz), 114.28, 113.28, 83.24, 79.36, 76.60, 72.36, 55.40.



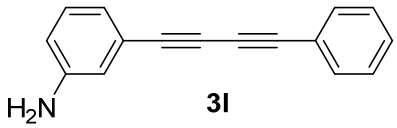
3j

1-(4-Methylphenyl)-1,3-octadiyne (3j) [s9]: White liquid; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.34 (d, *J* = 8.4 Hz, 2 H), 6.75 (d, *J* = 8.0 Hz, 2 H), 3.74 (s, 3 H), 2.29 (t, *J* = 6.8 Hz, 2 H), 1.50-1.45 (m, 2 H), 1.42-1.33(m, 2 H), 0.85 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 160.06, 134.08, 114.07, 84.19, 74.85, 73.16, 65.22, 55.34, 30.38, 29.74, 21.98, 19.31, 13.57.



3k

3-(p-tolylbuta-1,3-diyn-1-yl)aniline (3k)： Yellow solid; MP. 105-107 ºC. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.41 (d, J = 7.6 Hz, 2 H), 7.15-7.09 (m, 3 H), 6.93 (*d*, J = 7.6 Hz, 1 H), 6.82 (s, 1 H, J = 8.0 Hz), 6.68 (*d*, J = 8.0 Hz, 1 H), 3.70 (s, 2 H), 2.36 (s, 3 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 146.35, 139.60, 132.45, 129.41, 129.27, 122.98, 118.77, 118.42, 116.26, 81.65, 81.52, 73.47, 21.67; MS (EI) m/z (%): 231(M^+, 100), 202, 163, 139, 115, 101, 88. HRMS calcd for C17H13N: 231.1048; found 231.1047.



3l

3-(phenylbuta-1,3-diyn-1-yl)aniline (3l) [s10]: Yellow solid ; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45 (d, J = 6.8 Hz, 2 H), 7.31-7.24 (m, 3 H), 7.04 (t, J = 7.2 Hz, 1 H), 6.86 (d, J = 7.6 Hz, 1 H), 6.76 (s, 1 H), 6.62 (d, J = 7.6 Hz, 1 H), 3.65 (s, 2 H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 145.29, 131.47, 128.37, 128.13, 127.41, 121.96, 121.40, 120.86, 117.38, 115.29, 80.91, 80.26, 73.02, 72.25.

References:

S1. X. Zou, R. Silva, A. Goswami and T. Asefa, *Appl. Surf. Sci.,* 2015, **357**, 221.

S2. Y. Liu, C. Wang, X. Wang and J. Wan, *Tetrahedron lett.*, 2013, **54**, 3953.

S3. X. Jia, K. Yin, C. Li, J. Li and H. Bian, *Green Chem.*, 2011, **13**, 591.

S4. O. Takamichi, K. Yamaguchi and N. Mizuno, *ACS Catal.*, 2011, **1**, 1351.

S5. A. Sagadevan, V. P. Charpe and C. H. Kuo, *Catal. Sci. Tech.*, 2016, **6**, 7688.

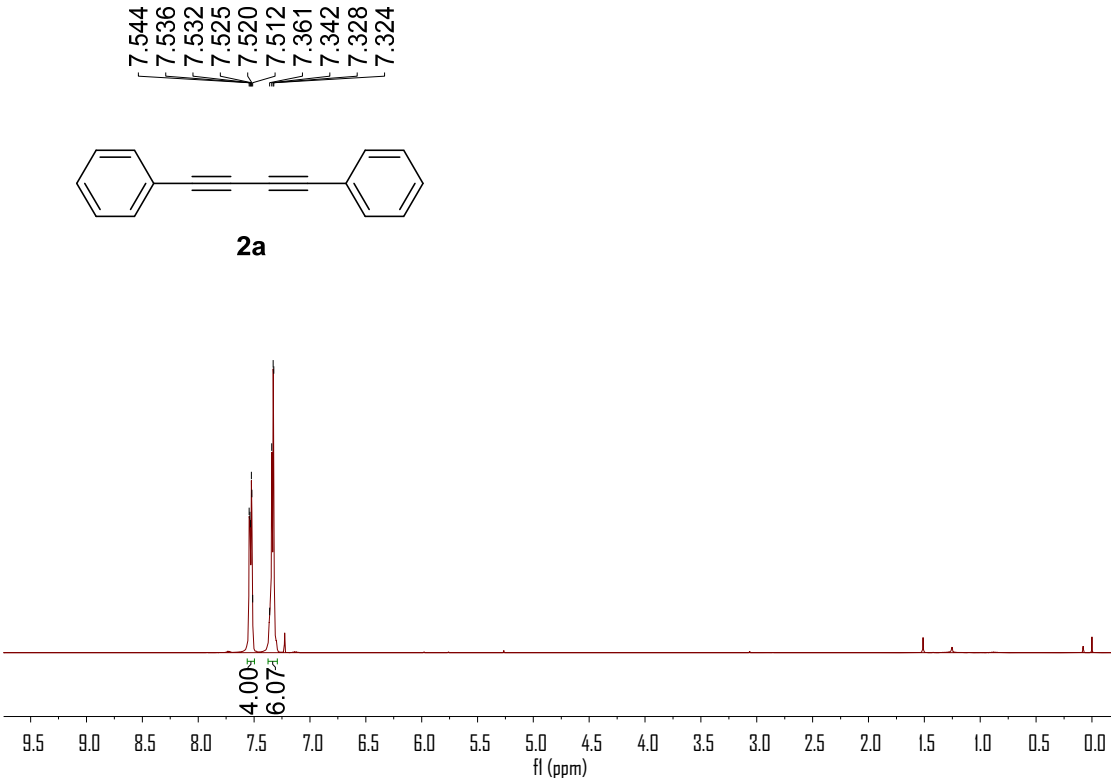
S6. N. Mukherjee, D. Kundu and B. C. Ranu, *Chem. Commun.*, 2014, **50**,15784.

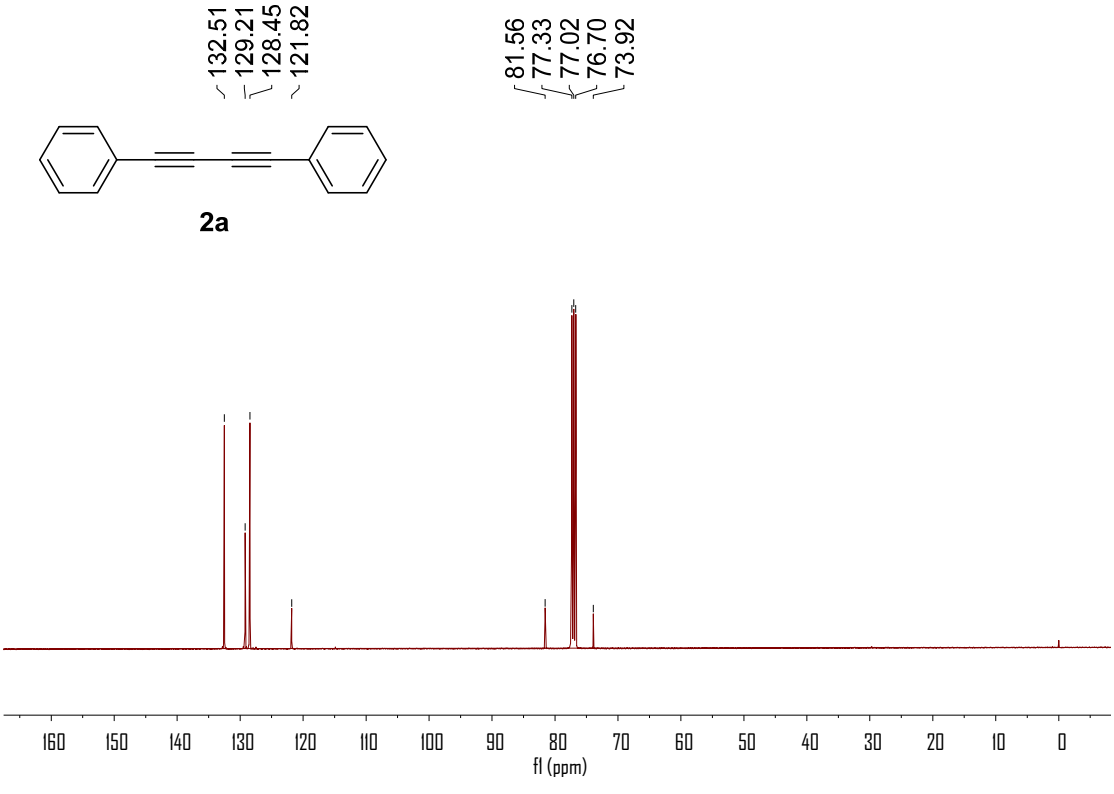
S7. M. Yu, D. Pan, W. Jia, W. Chen and N. Jiao, *Tetrahedron Lett.,* 2010, ***51***, 1287.

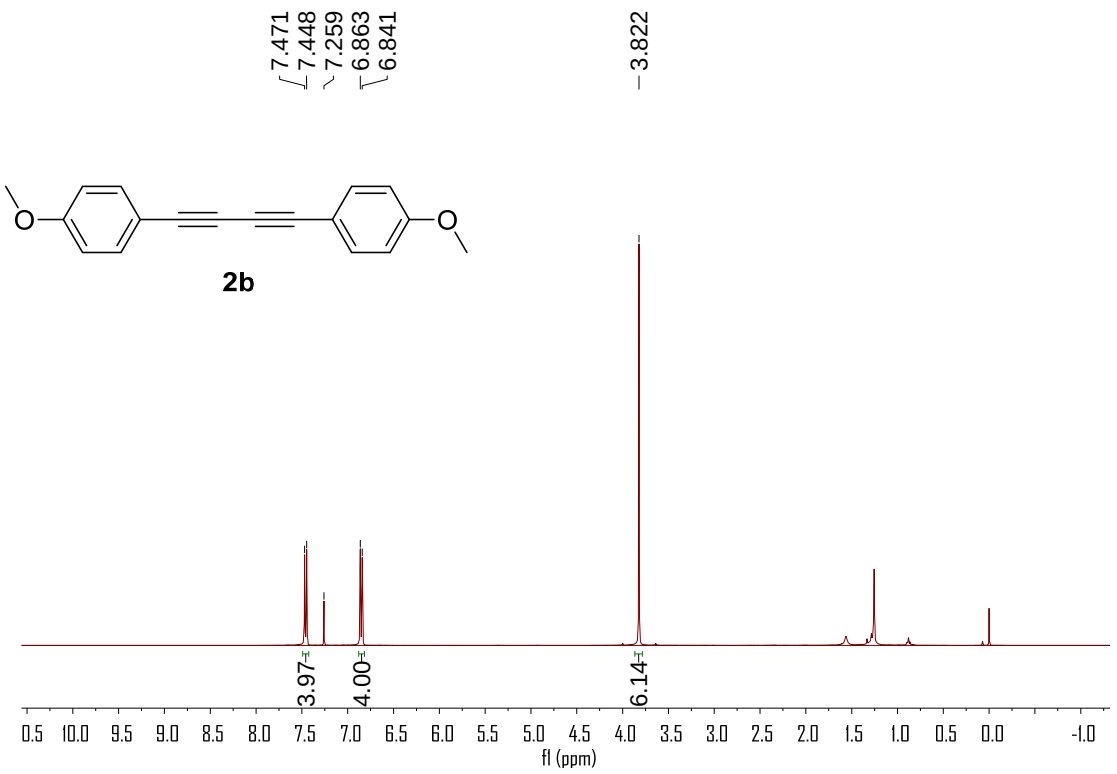
S8. S.V. Damle, D. Seomoon and P. H. Lee, *J. Org. Chem.,* 2003, **68**, 7085.

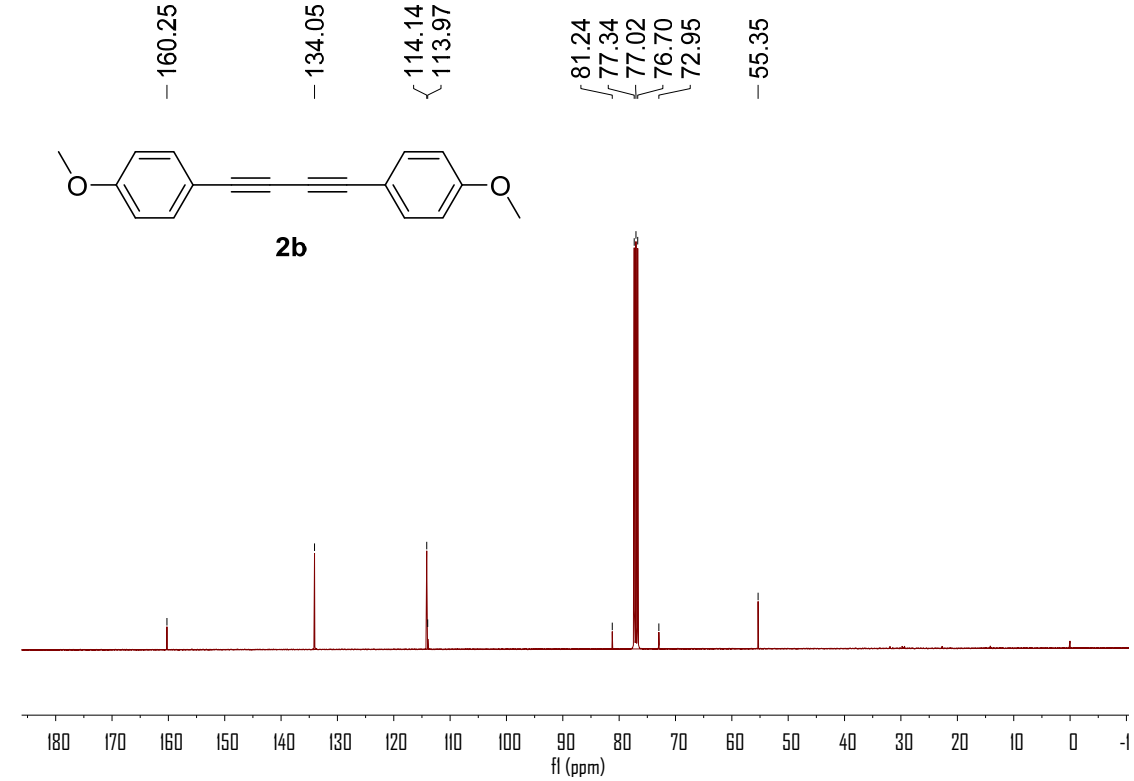
S9. S. T. Li, T. Schnabel, S. Lysenko, K. Brandhorst and M. Tamm, *Chem. Commun.,* 2013, ***49***, 7189.

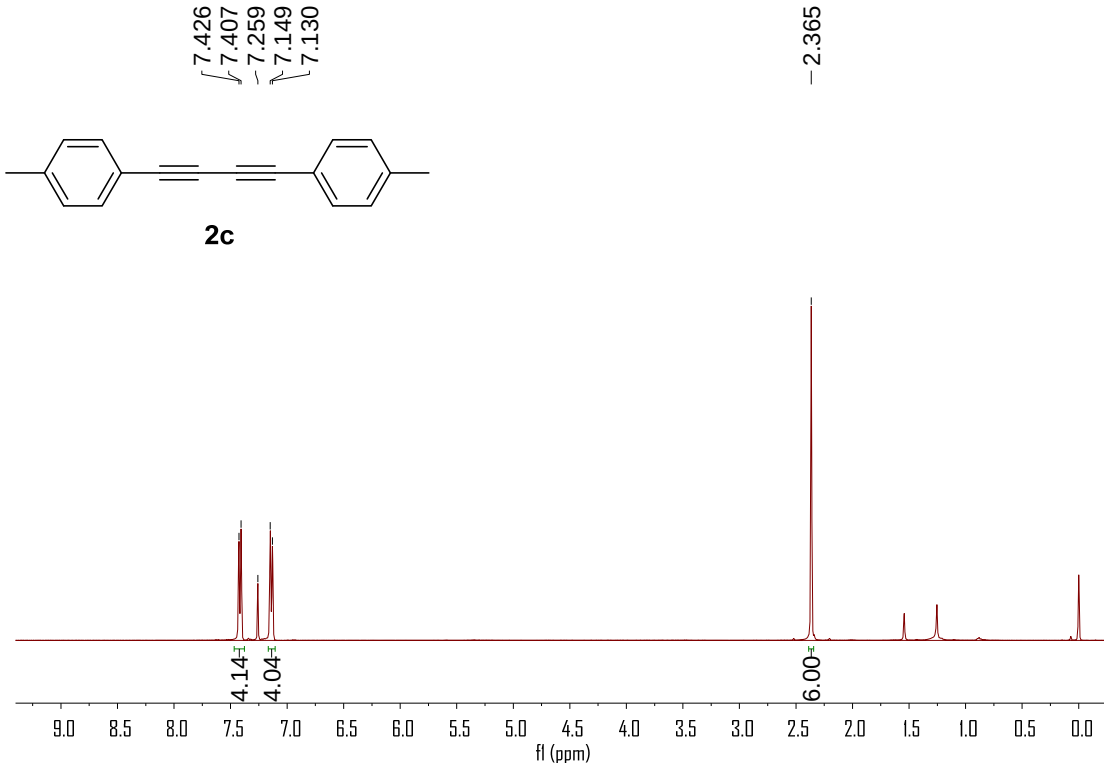
S10. Y. Liu, P. Liu, N. Gu, J. Xie, Y. Liu and B. Dai, *Chin. J. Chem.*, 2016, ***34***, 895.


7.544
7.536
7.532
7.525
7.520
7.512
7.361
7.342
7.328
7.324
2a
4.00
6.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

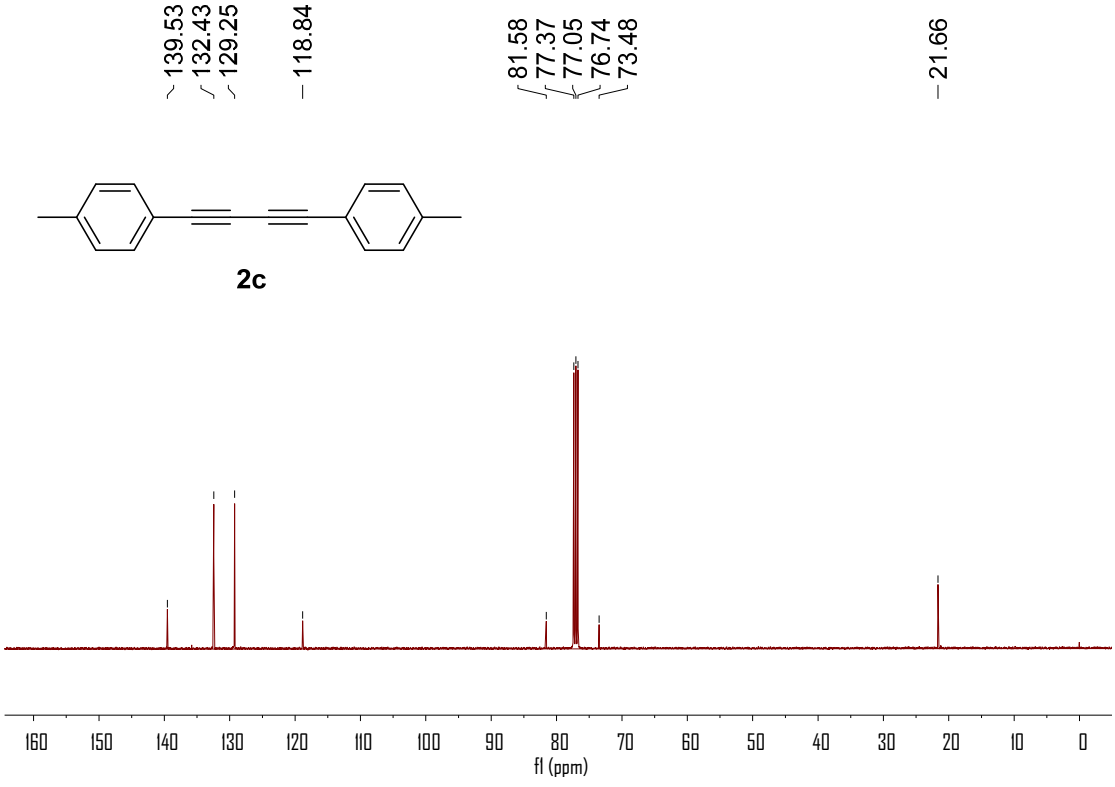

132.51
129.21
128.45
121.82
81.56
77.33
77.02
76.70
73.92
2a
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.471
7.448
7.259
6.863
6.841
3.822
2b
3.97
4.00
6.14
f1 (ppm)

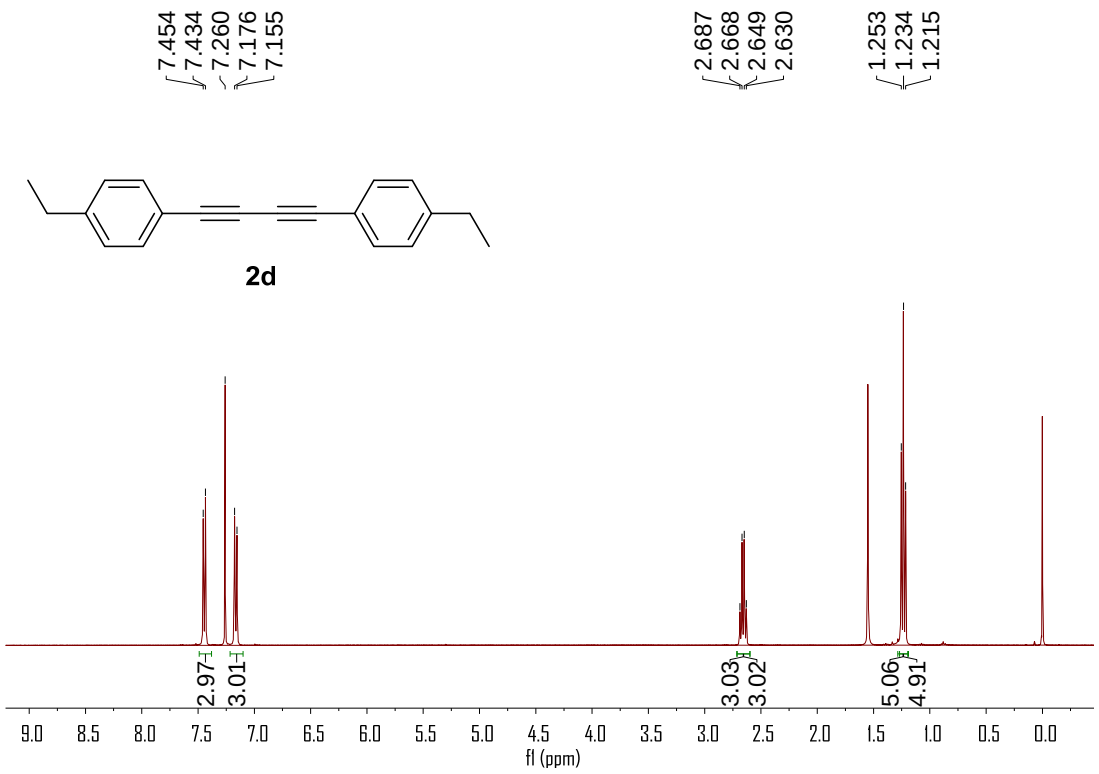

160.25
134.05
114.14
113.97
81.24
77.34
77.02
76.70
72.95
55.35
2b
f1 (ppm)

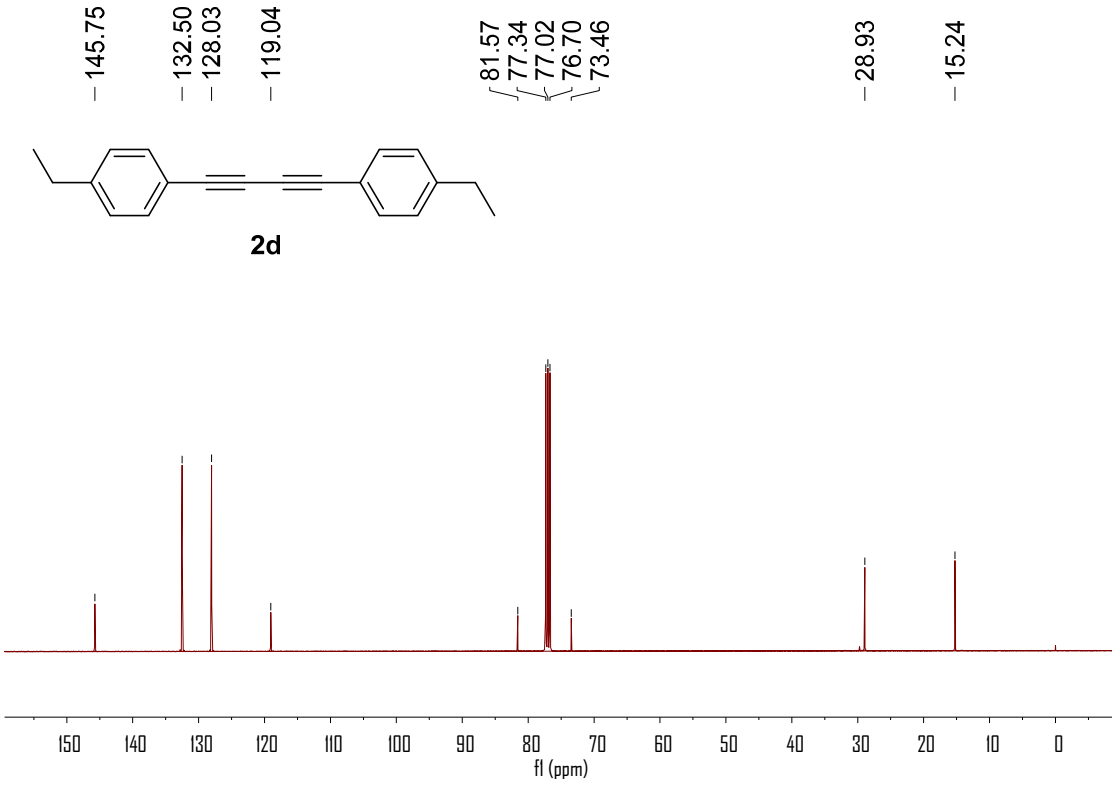

7.426
7.407
7.259
7.149
7.130
2.365
4.14
4.04
6.00
f1 (ppm)

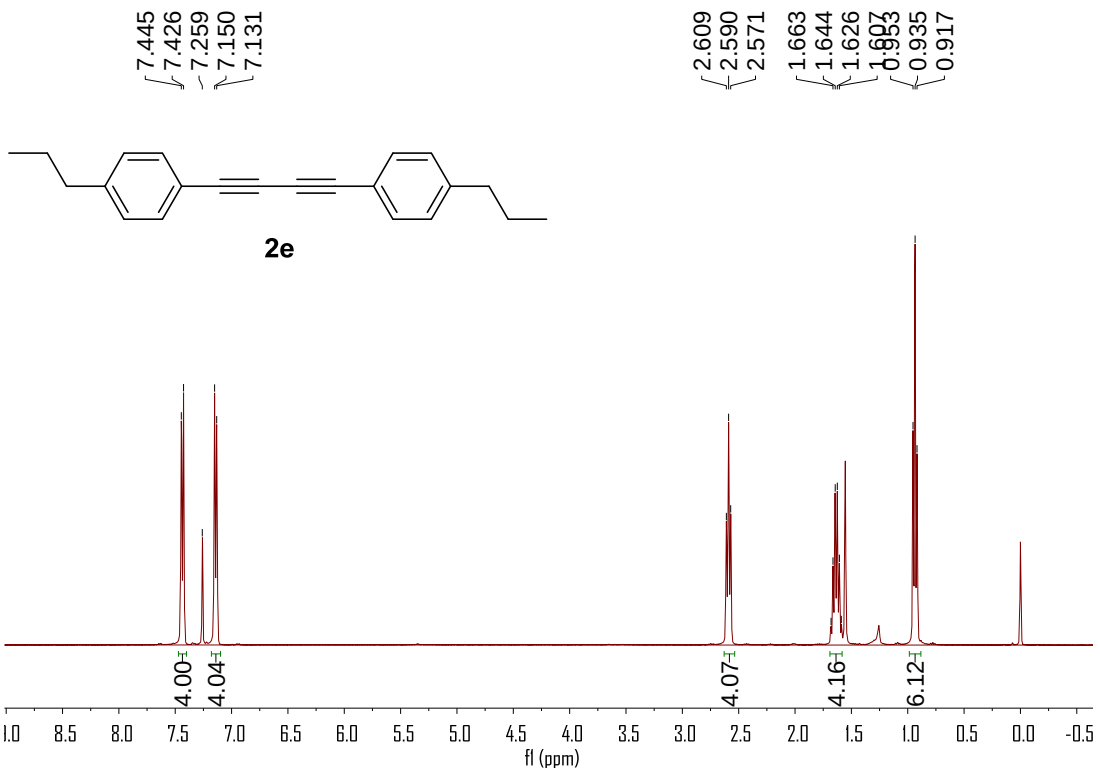
2c

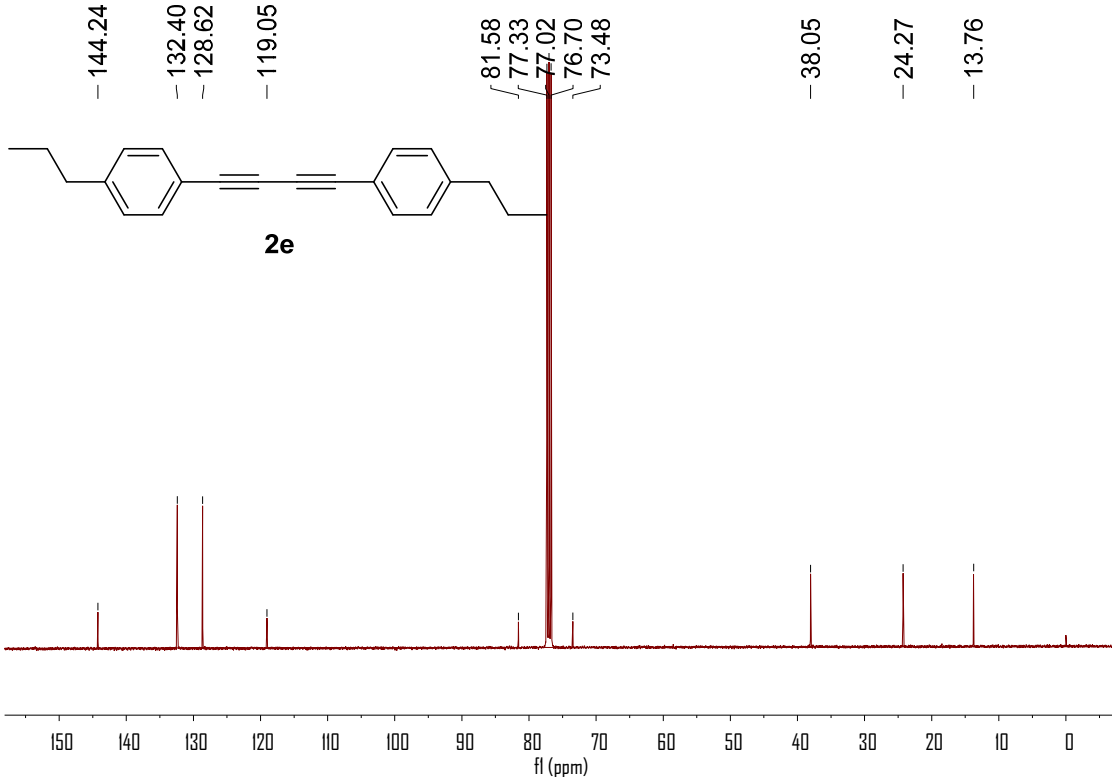

139.53
132.43
129.25
118.84
81.58
77.37
77.05
76.74
73.48
21.66
f1 (ppm)

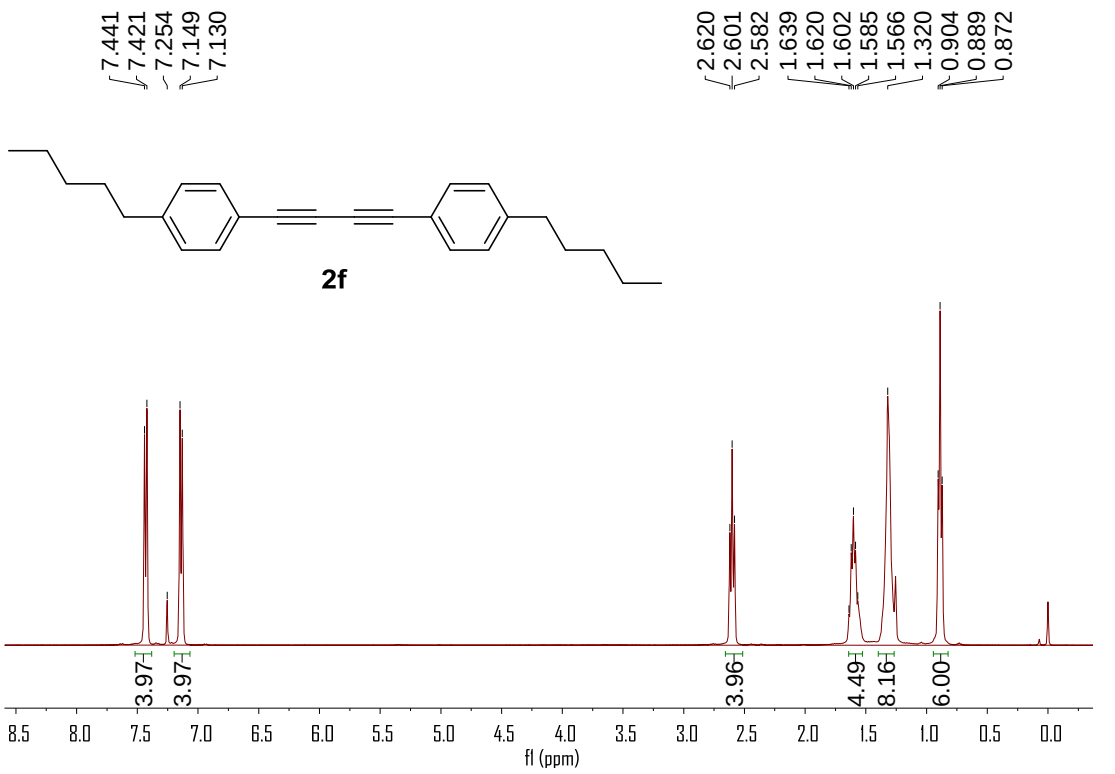
2c

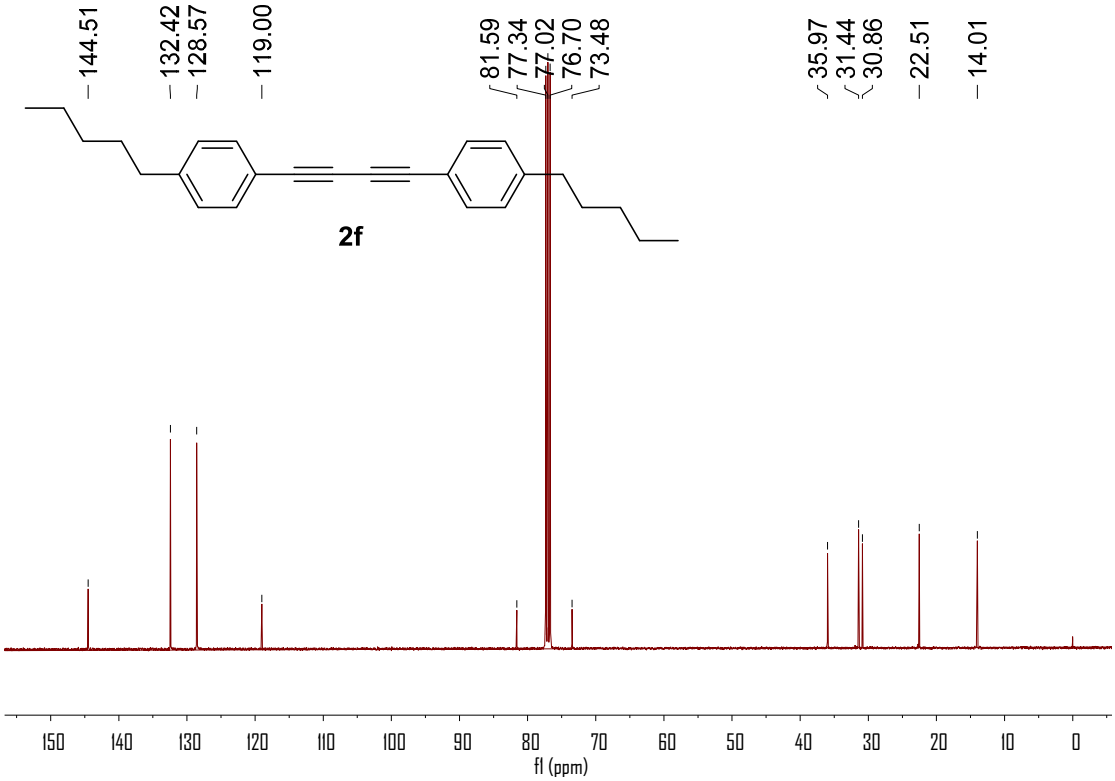

7.454
7.434
7.260
7.176
7.155
2.687
2.668
2.649
2.630
1.253
1.234
1.215
2d
2.97
3.01
3.03
3.02
5.06
4.91
f1 (ppm)

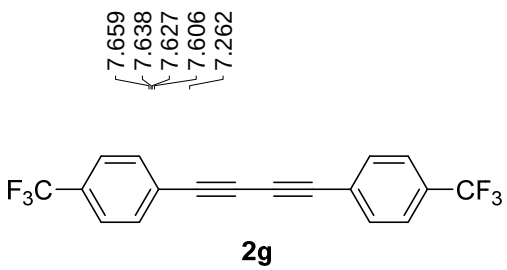

145.75
132.50
128.03
119.04
81.57
77.34
77.02
76.70
73.46
28.93
15.24
2d
f1 (ppm)


7.445
7.426
7.259
7.150
7.131
2.609
2.590
2.571
1.663
1.644
1.626
0.935
0.917
2e
4.00
4.04
4.07
4.16
6.12
f1 (ppm)

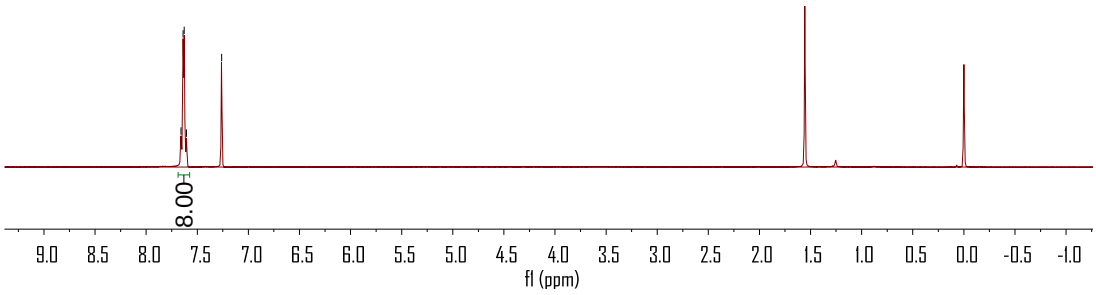

144.24
132.40
128.62
119.05
81.58
77.33
77.02
76.70
73.48
38.05
24.27
13.76
2e
f1 (ppm)

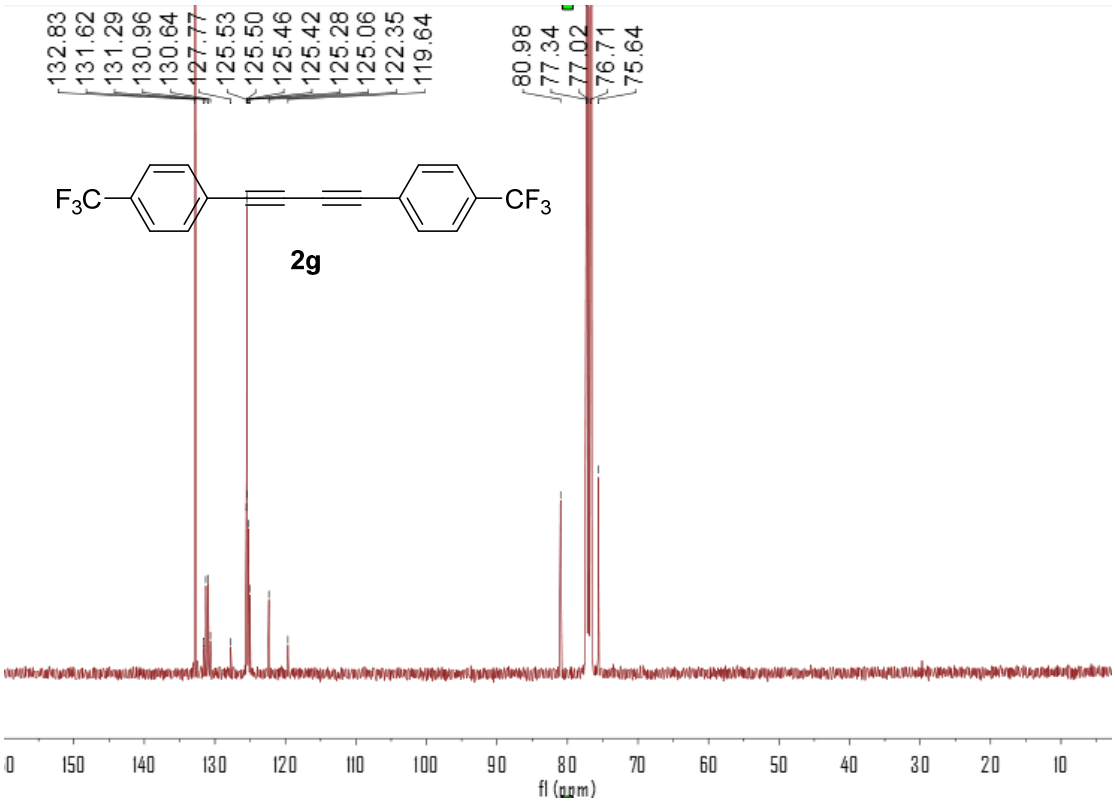

7.441
7.421
7.254
7.149
7.130
2.620
2.601
2.582
1.639
1.620
1.602
1.585
1.566
1.320
0.904
0.889
0.872
2f
3.97
3.97
3.96
4.49
8.16
6.00
f1 (ppm)

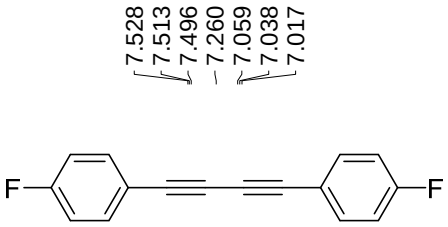

144.51
132.42
128.57
119.00
81.59
77.34
77.02
76.70
73.48
35.97
31.44
30.86
22.51
14.01
2f
f1 (ppm)


7.659
7.638
7.627
7.606
7.262
F3C
CF3

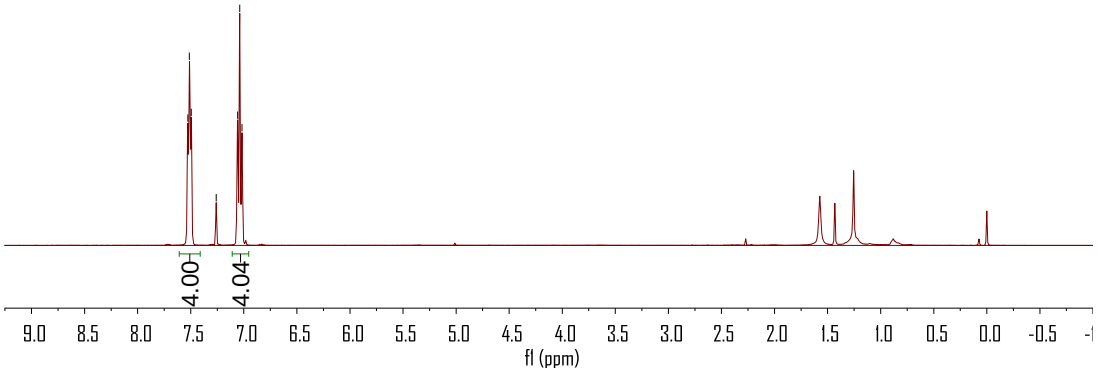
2g

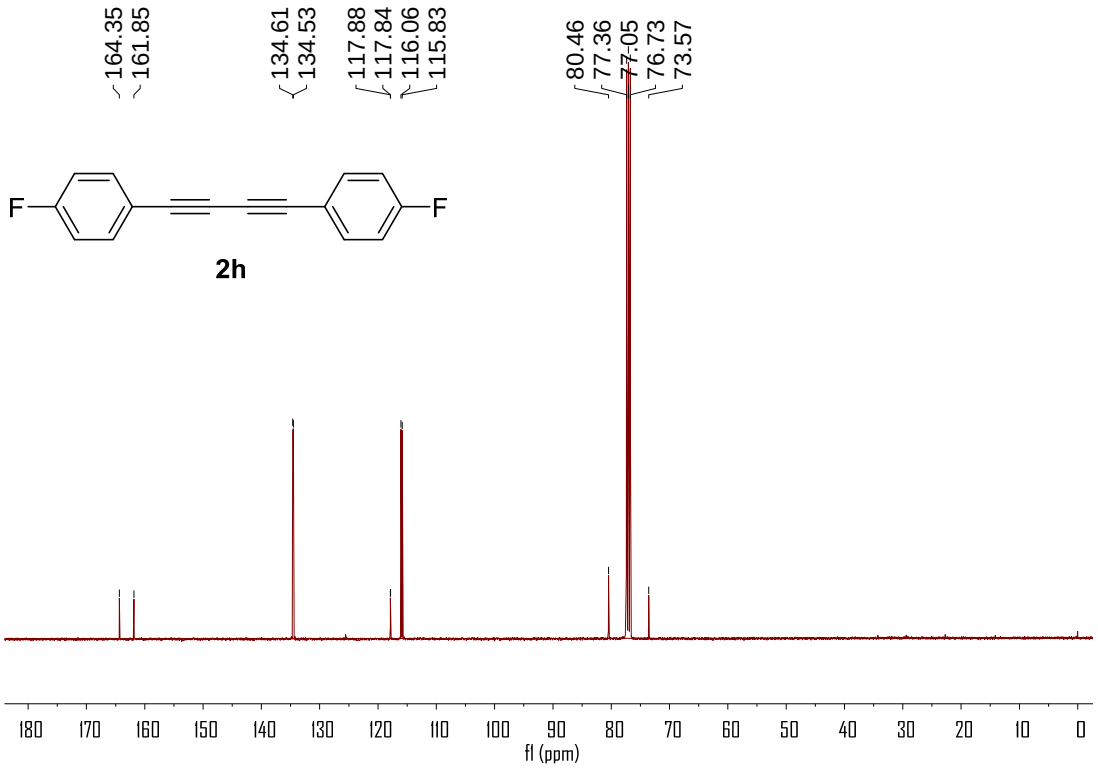

8.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


132.83
131.62
131.29
130.96
130.64
127.77
125.53
125.50
125.46
125.42
125.28
125.06
122.35
119.64
80.98
77.34
77.02
76.71
75.64
F3C
CF3
2g
0 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

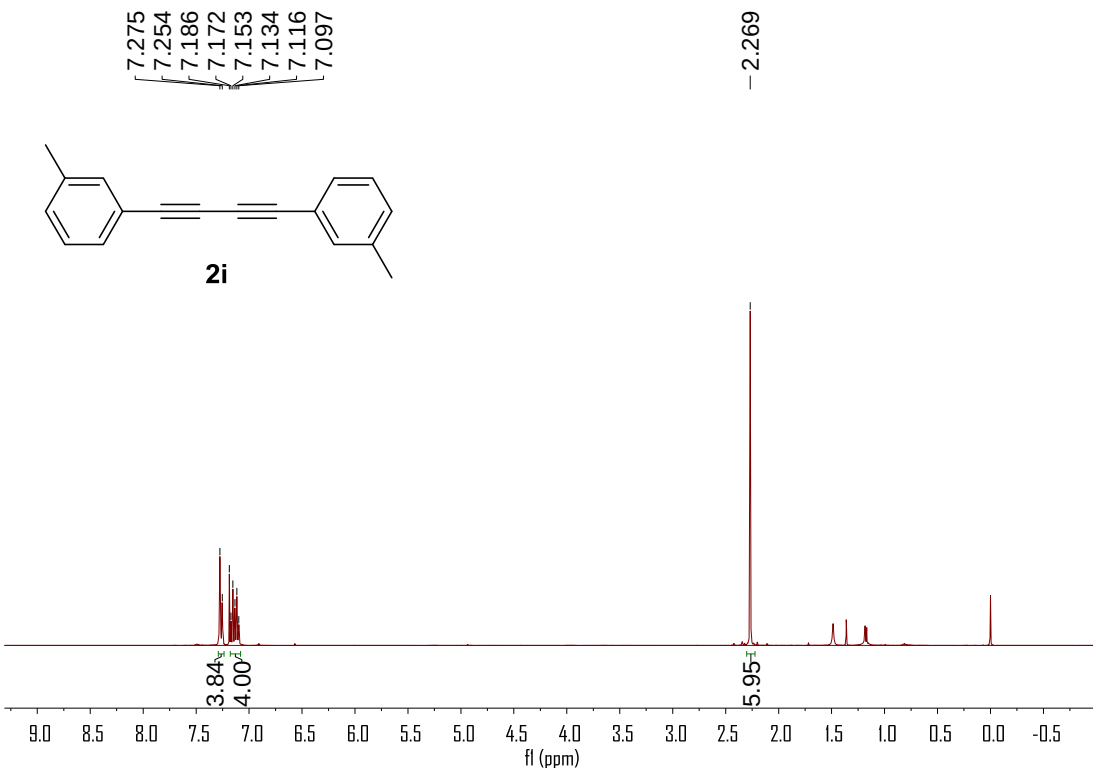

7.528
7.513
7.496
7.260
7.059
7.038
7.017
F
F

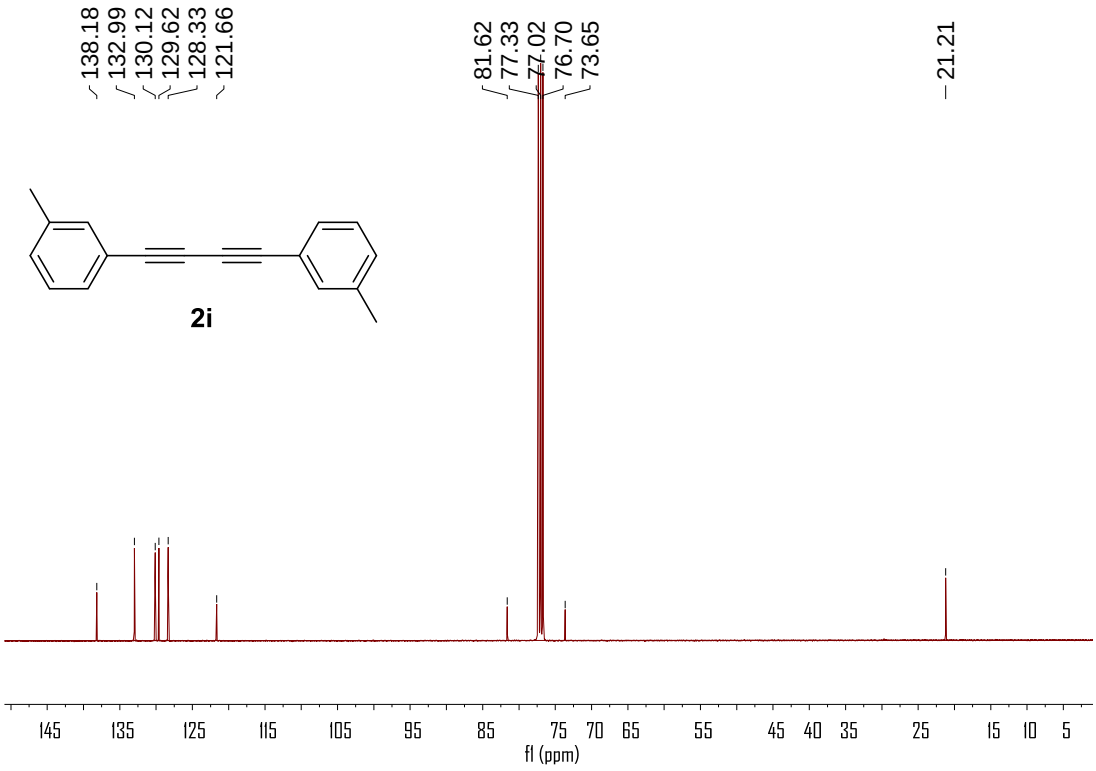
2h

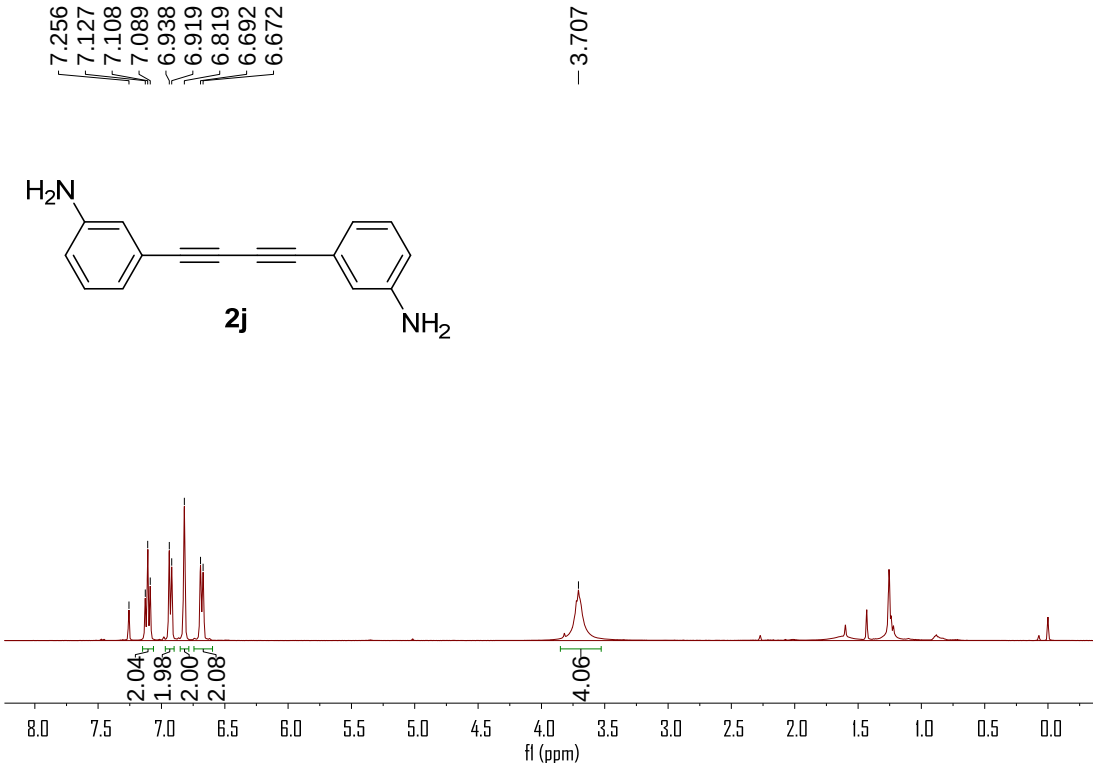

4.00
4.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

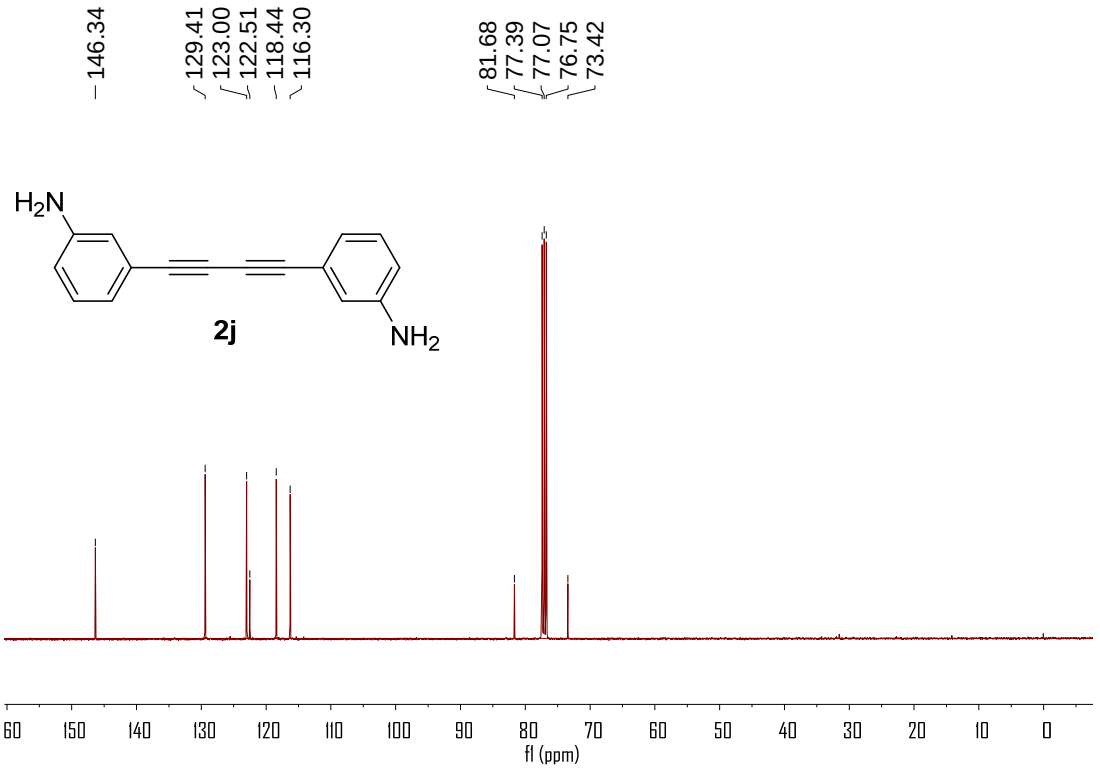

164.35
161.85
134.61
134.53
117.88
117.84
116.06
115.83
80.46
77.36
77.05
76.73
73.57
F
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

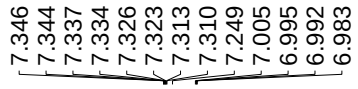
2h

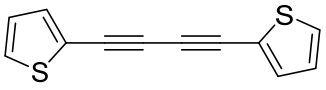

7.275
7.254
7.186
7.172
7.153
7.134
7.116
7.097
2.269
2i
3.84
4.00
5.95
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


138.18
132.99
130.12
129.62
128.33
121.66
81.62
77.33
77.02
76.70
73.65
21.21
2i
145 135 125 115 105 95 85 75 70 65 55 45 40 35 25 15 10 5
f1 (ppm)

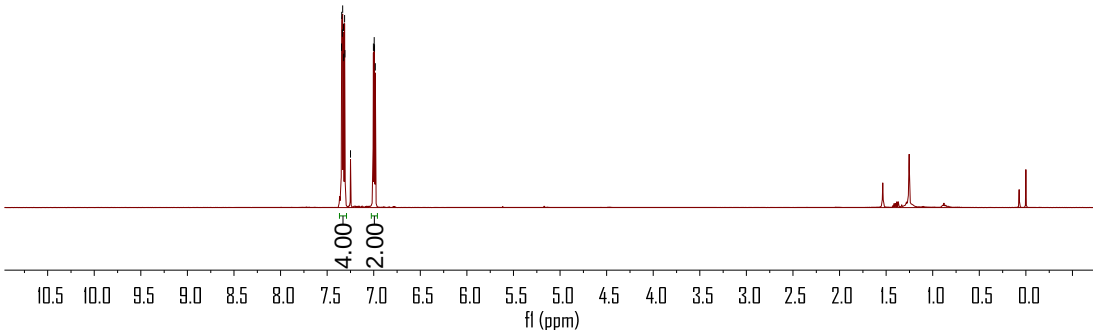

7.256
7.127
7.108
7.089
6.938
6.919
6.819
6.692
6.672
3.707
H2N
2j
NH2
2.04
1.98
2.00
2.08
4.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


146.34
129.41
123.00
122.51
118.44
116.30
81.68
77.39
77.07
76.75
73.42
H2N
2j
NH2
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.346
7.344
7.337
7.334
7.326
7.323
7.313
7.310
7.249
7.005
6.995
6.992
6.983

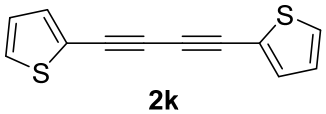

S
S

2k

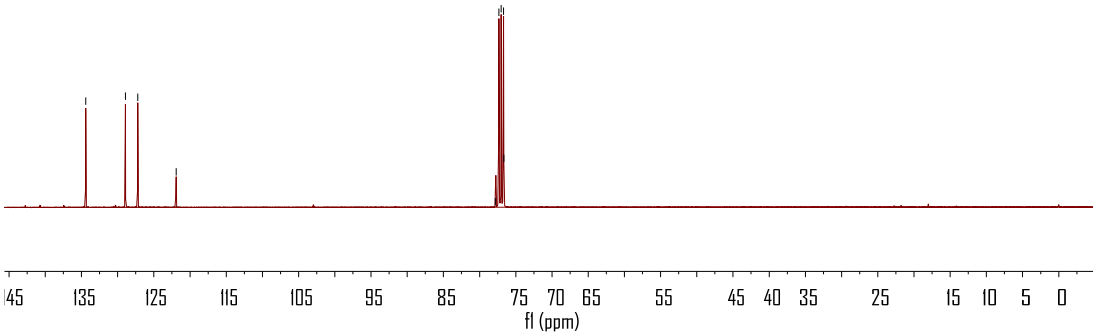

4.00
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

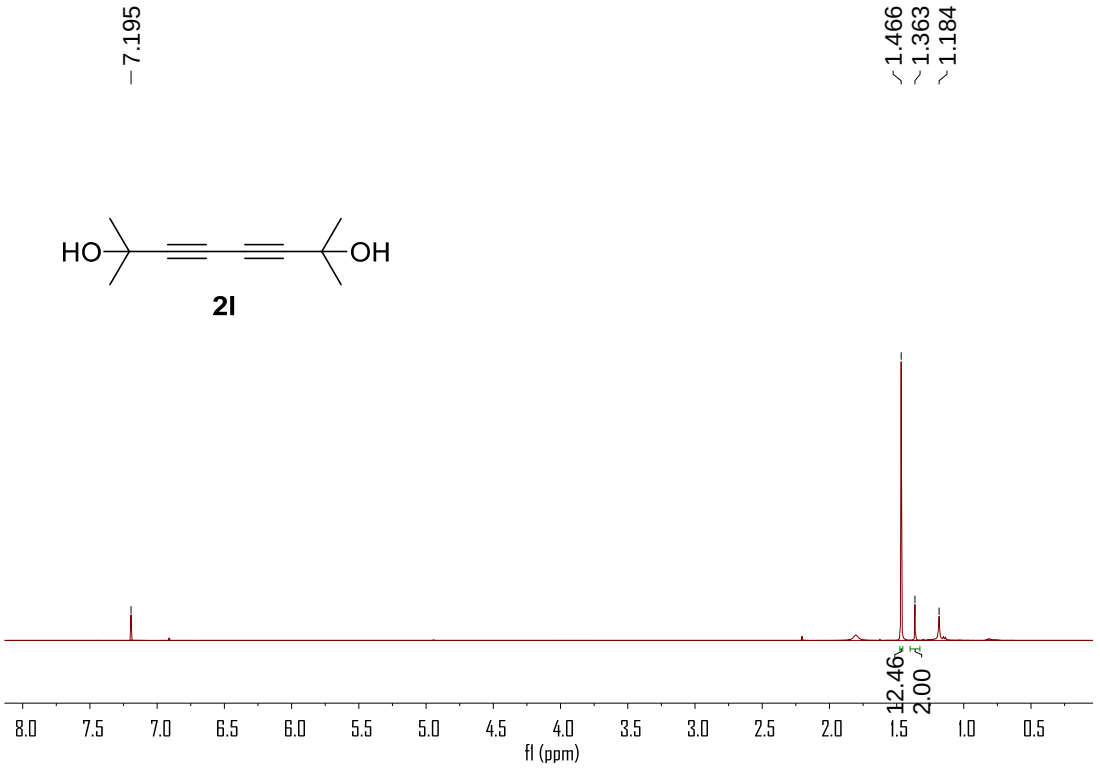

134.41
128.92
127.22
121.92

77.83
77.34
77.02
76.70
76.64

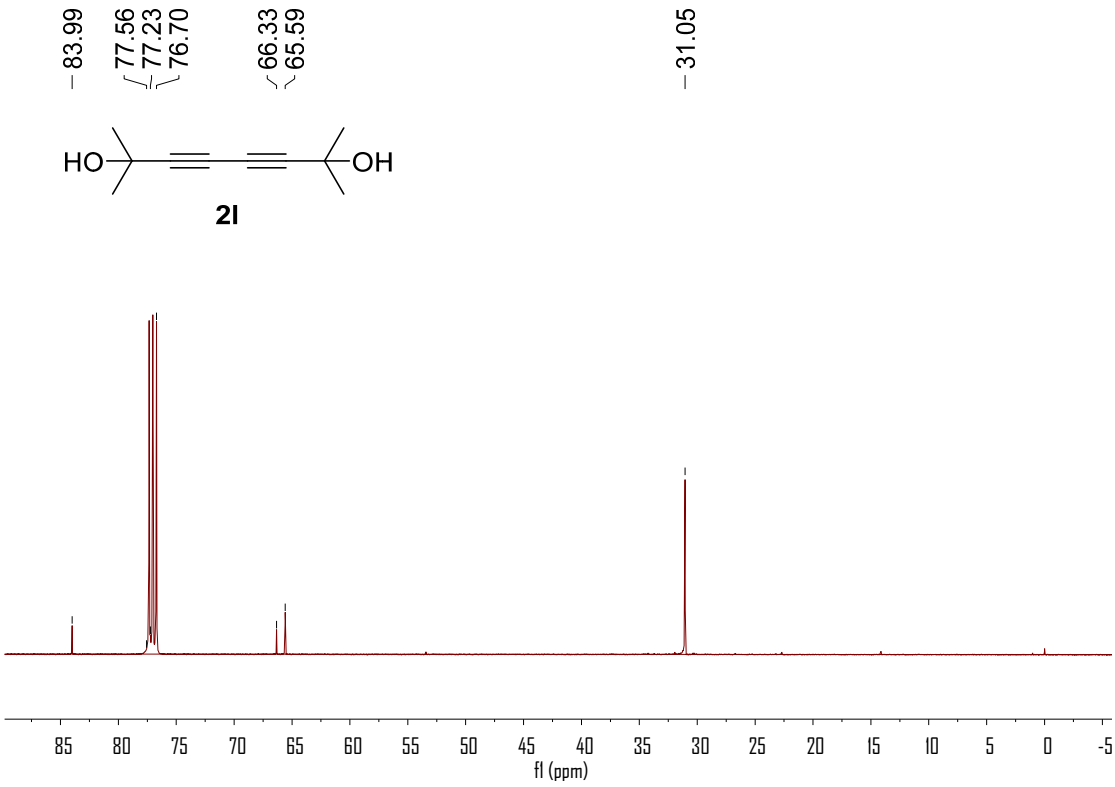

S
S

2k

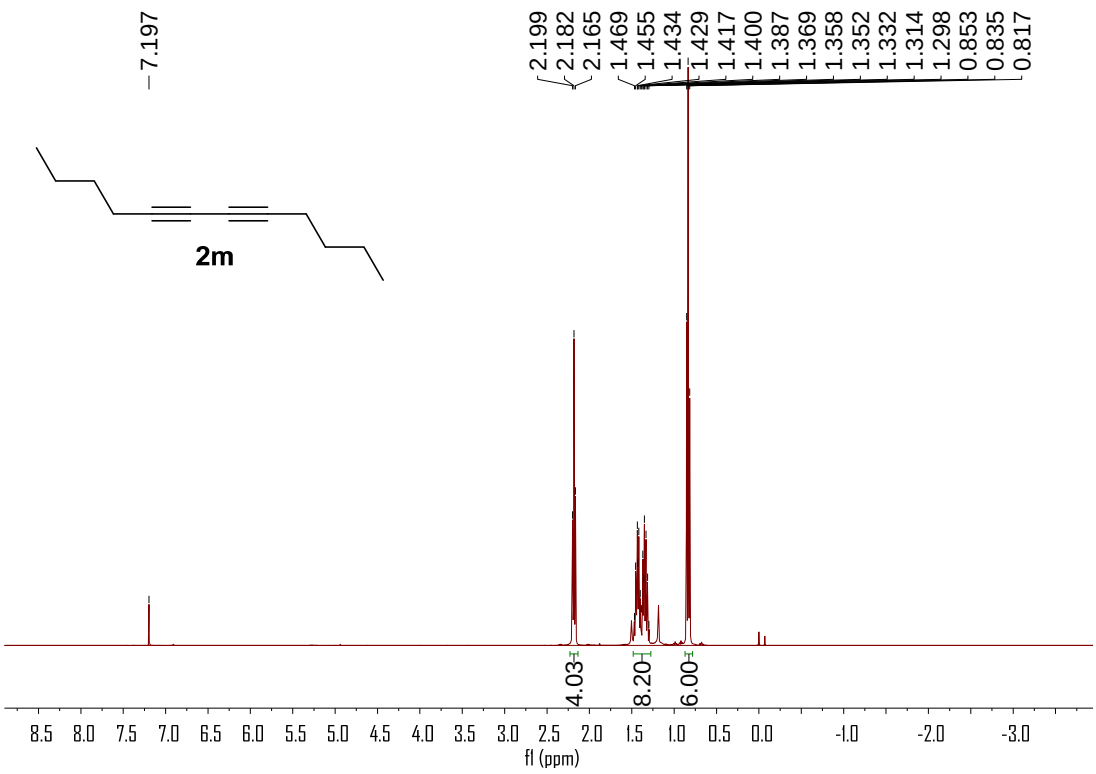

145 135 125 115 105 95 85 75 70 65 55 45 40 35 25 15 10 5 0
f1 (ppm)

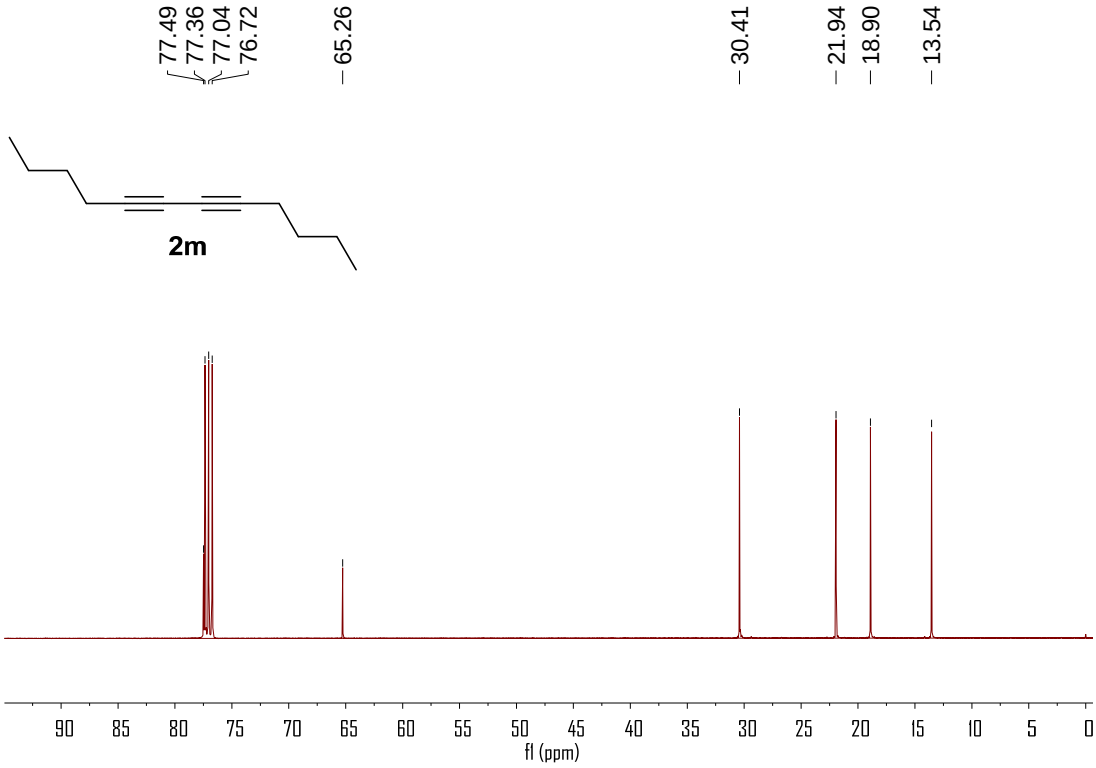

7.195
1.466
1.363
1.184
HO
OH
12.46
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

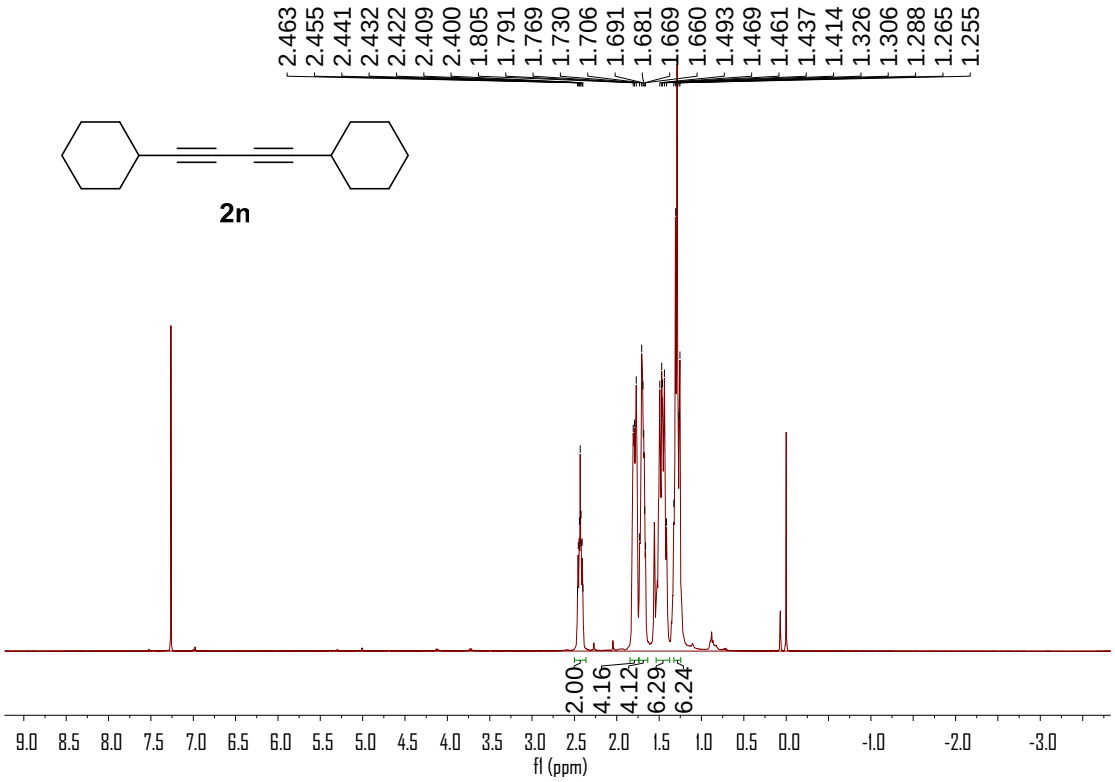
2l

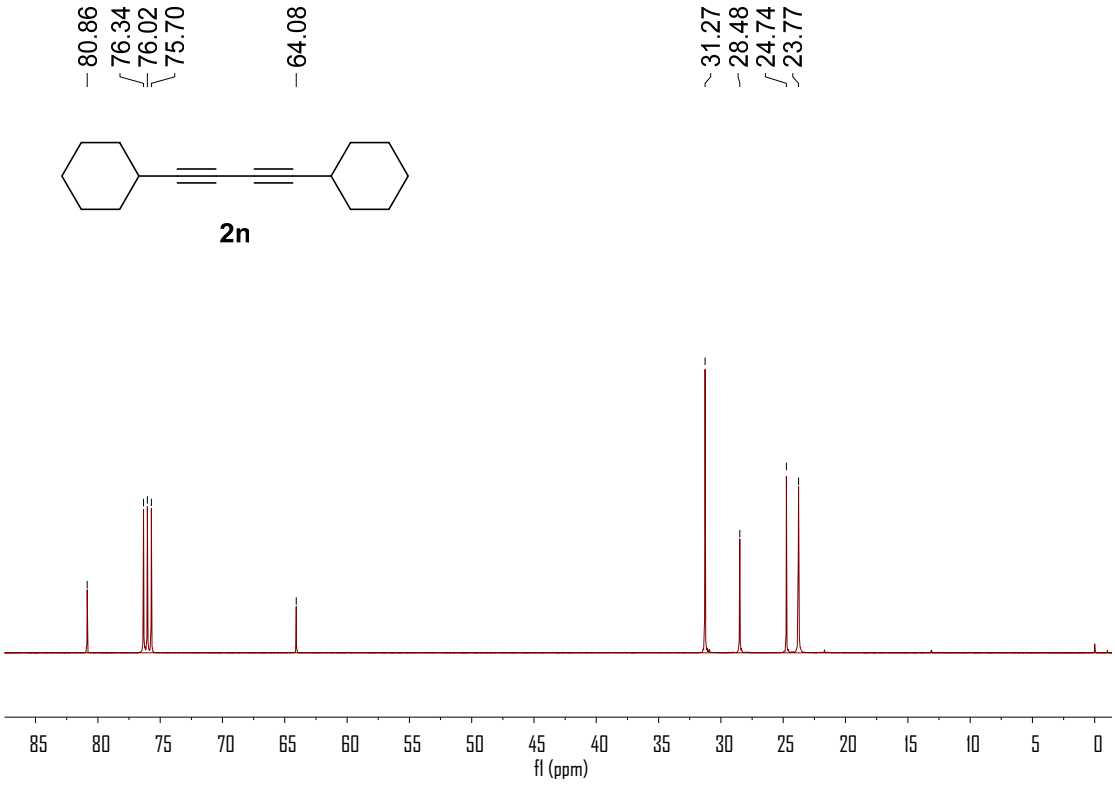

83.99
77.56
77.23
76.70
66.33
65.59
31.05
HO
OH
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
f1 (ppm)

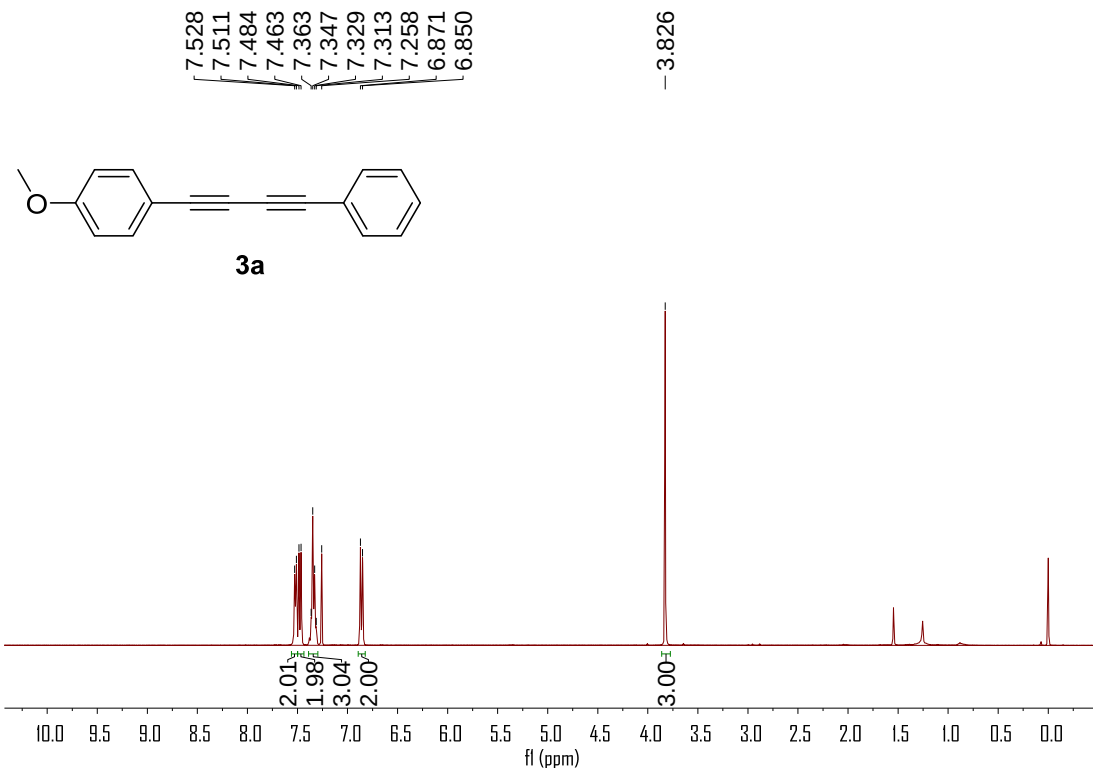
2l

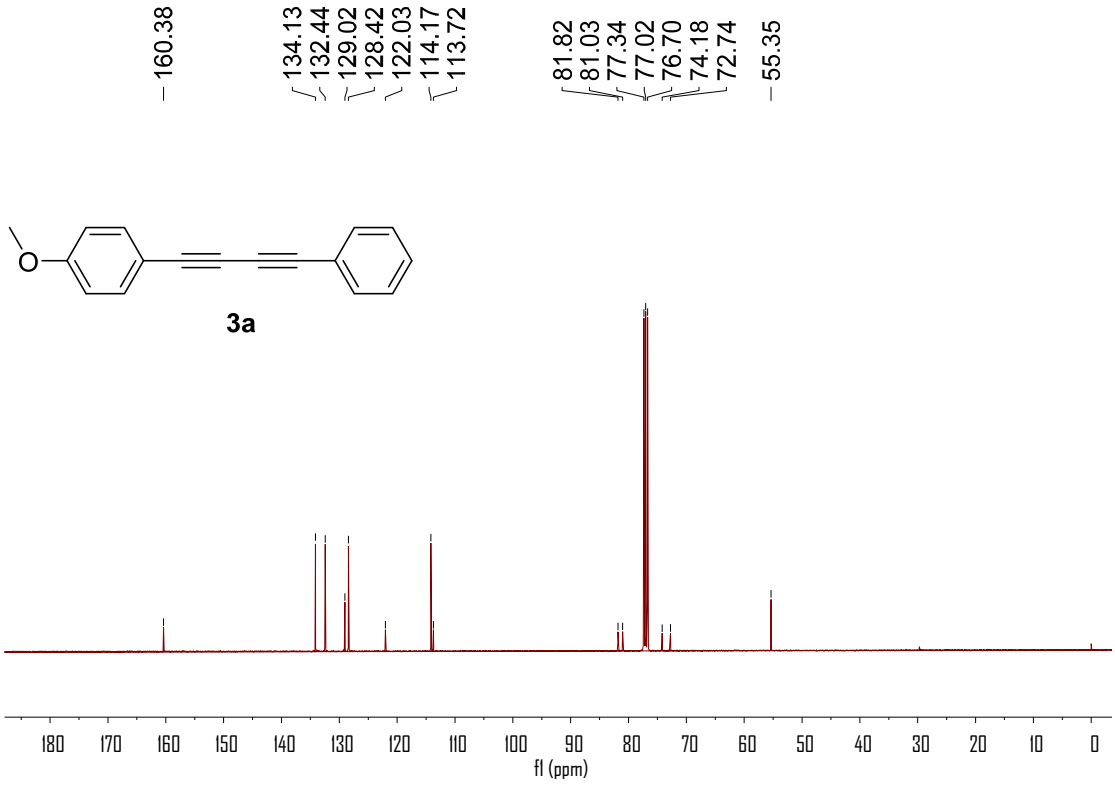

7.197
2.199
2.182
2.165
1.469
1.455
1.434
1.429
1.417
1.400
1.387
1.369
1.358
1.352
1.332
1.314
1.298
0.853
0.835
0.817
2m
4.03
8.20
6.00
f1 (ppm)

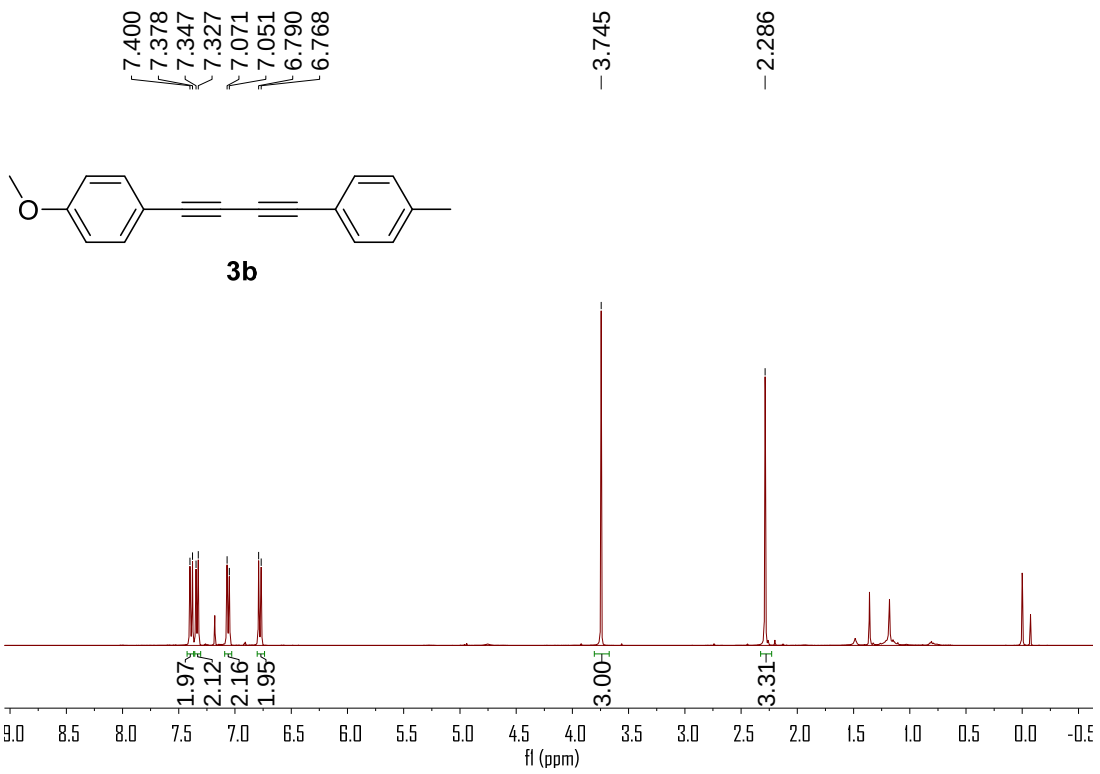

77.49
77.36
77.04
76.72
65.26
30.41
21.94
18.90
13.54
2m
f1 (ppm)

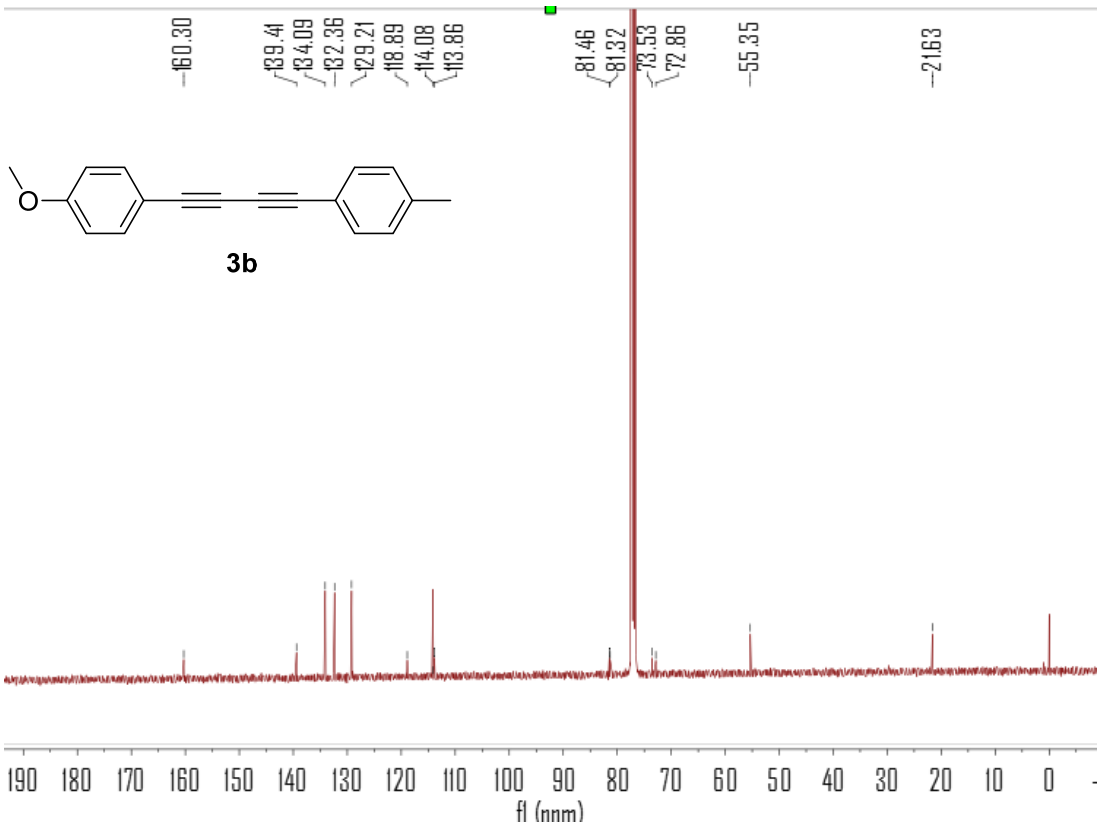

2.463
2.455
2.441
2.432
2.422
2.409
2.400
1.805
1.791
1.769
1.730
1.706
1.691
1.681
1.669
1.660
1.493
1.469
1.461
1.437
1.414
1.326
1.306
1.288
1.265
1.255
2n
2.00
4.16
4.12
6.29
6.24
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0 -2.0 -3.0
f1 (ppm)

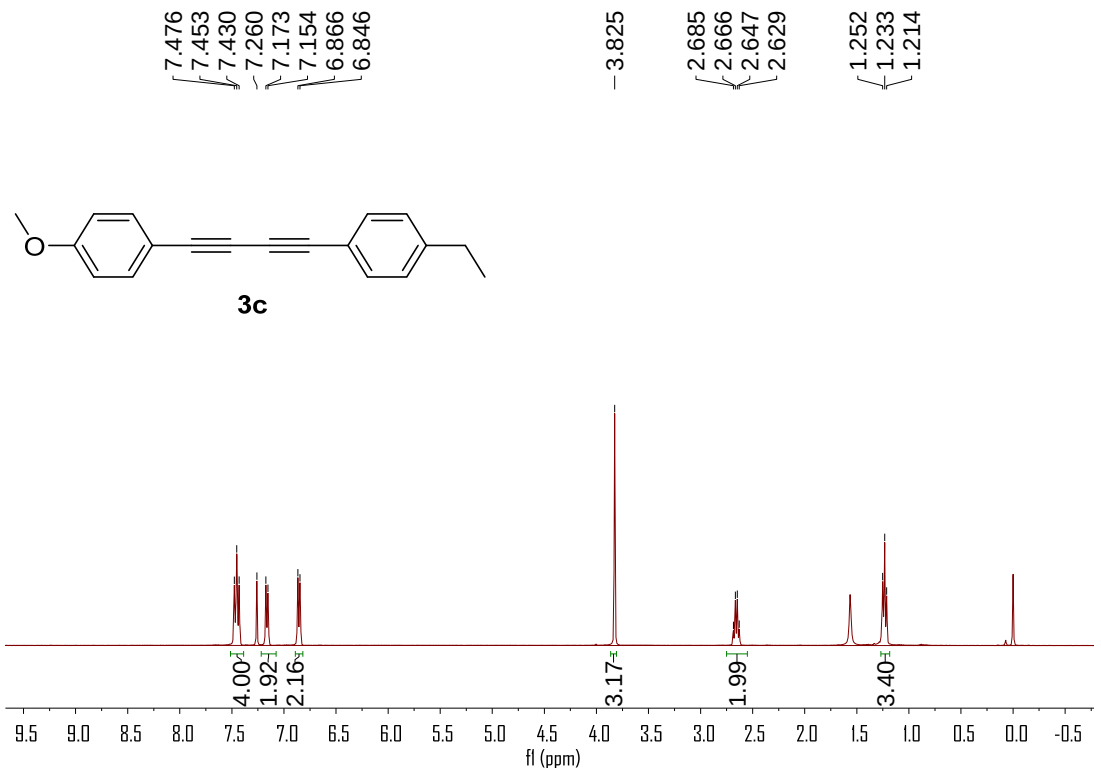

80.86
76.34
76.02
75.70
64.08
31.27
28.48
24.74
23.77
2n
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

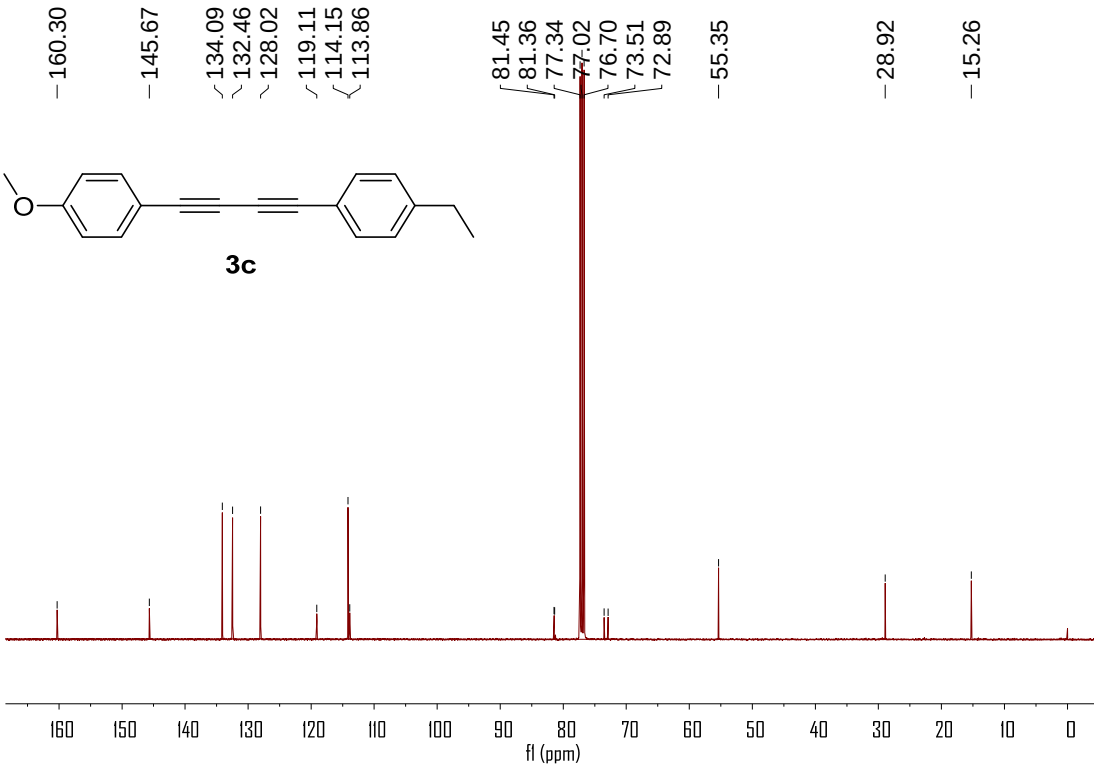

7.528
7.511
7.484
7.463
7.363
7.347
7.329
7.313
7.258
6.871
6.850
3.826
3a
2.01
1.98
3.04
2.00
3.00
f1 (ppm)

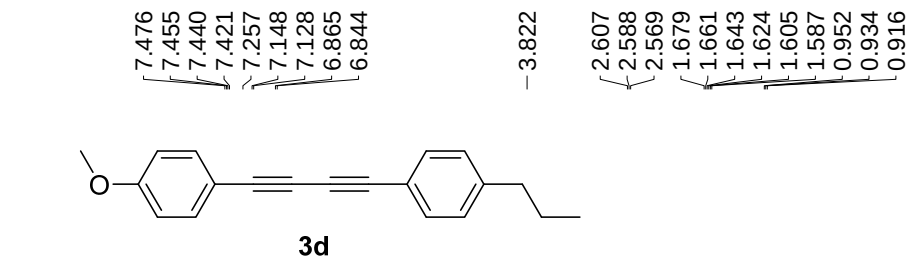

160.38
134.13
132.44
129.02
128.42
122.03
114.17
113.72
81.82
81.03
77.34
77.02
76.70
74.18
72.74
55.35
3a
f1 (ppm)


7.400
7.378
7.347
7.327
7.071
7.051
6.790
6.768
3.745
2.286
3b
1.97
2.12
2.16
1.95
3.00
3.31
f1 (ppm)

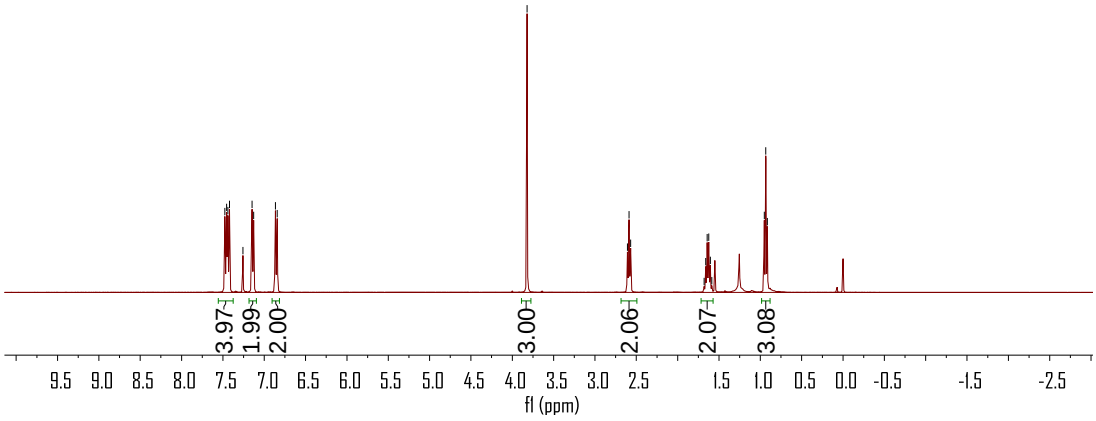

160.30
139.41
134.09
132.36
129.21
118.89
114.08
113.86
81.46
81.32
73.53
72.86
55.35
21.63
3b
f1 (nnm)

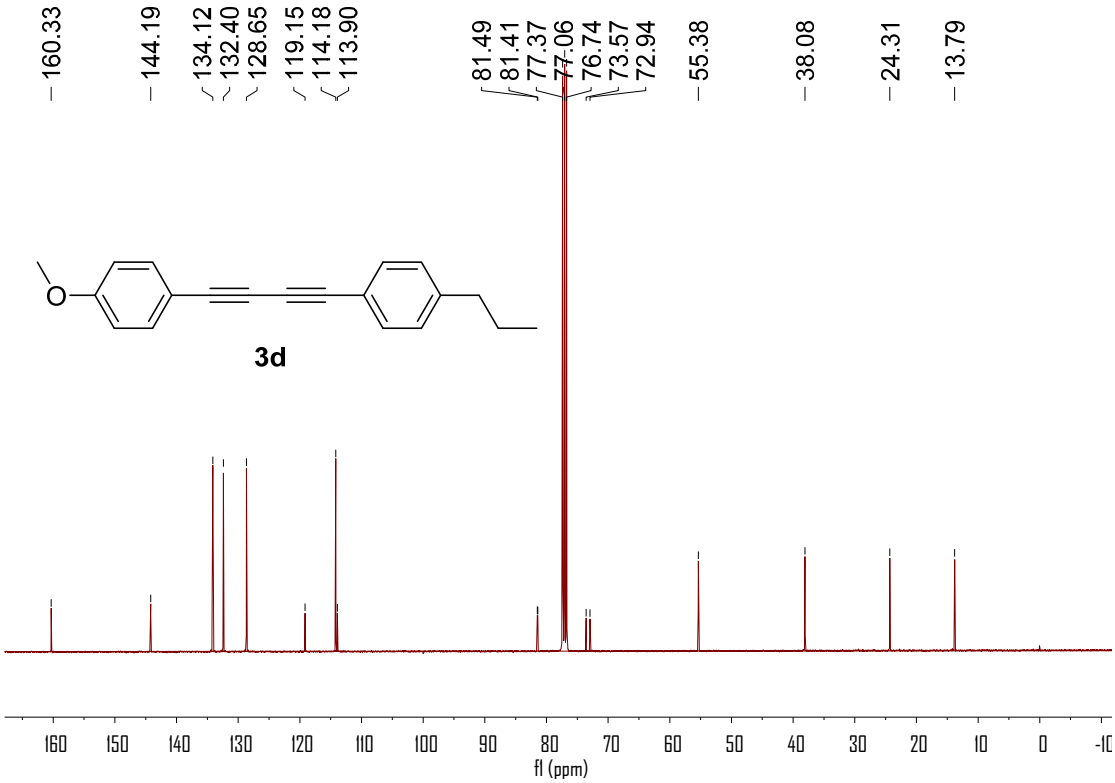

7.476
7.453
7.430
7.260
7.173
7.154
6.866
6.846
3.825
2.685
2.666
2.647
2.629
1.252
1.233
1.214
3c
4.00
1.92
2.16
3.17
1.99
3.40
f1 (ppm)


160.30
145.67
134.09
132.46
128.02
119.11
114.15
113.86
81.45
81.36
77.34
77.02
76.70
73.51
72.89
55.35
28.92
15.26
3c
f1 (ppm)

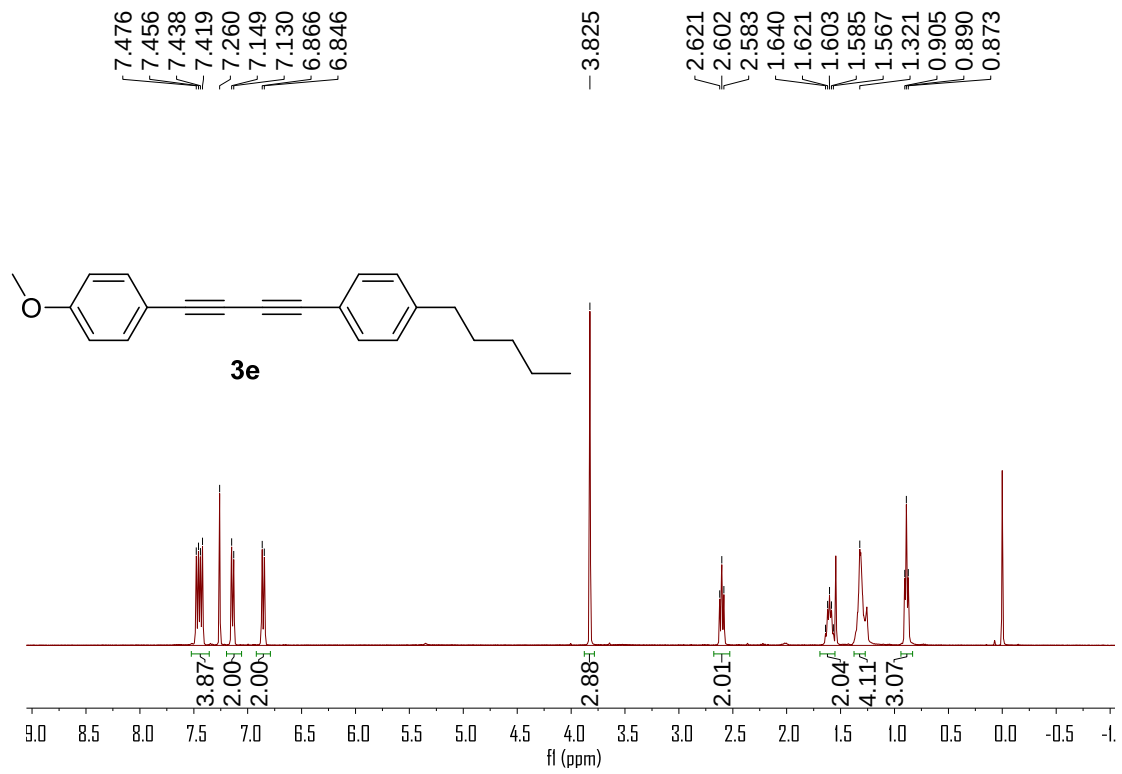

7.476
7.455
7.440
7.421
7.257
7.148
7.128
6.865
6.844
3.822
2.607
2.588
2.569
1.679
1.661
1.643
1.624
1.605
1.587
0.952
0.934
0.916
O

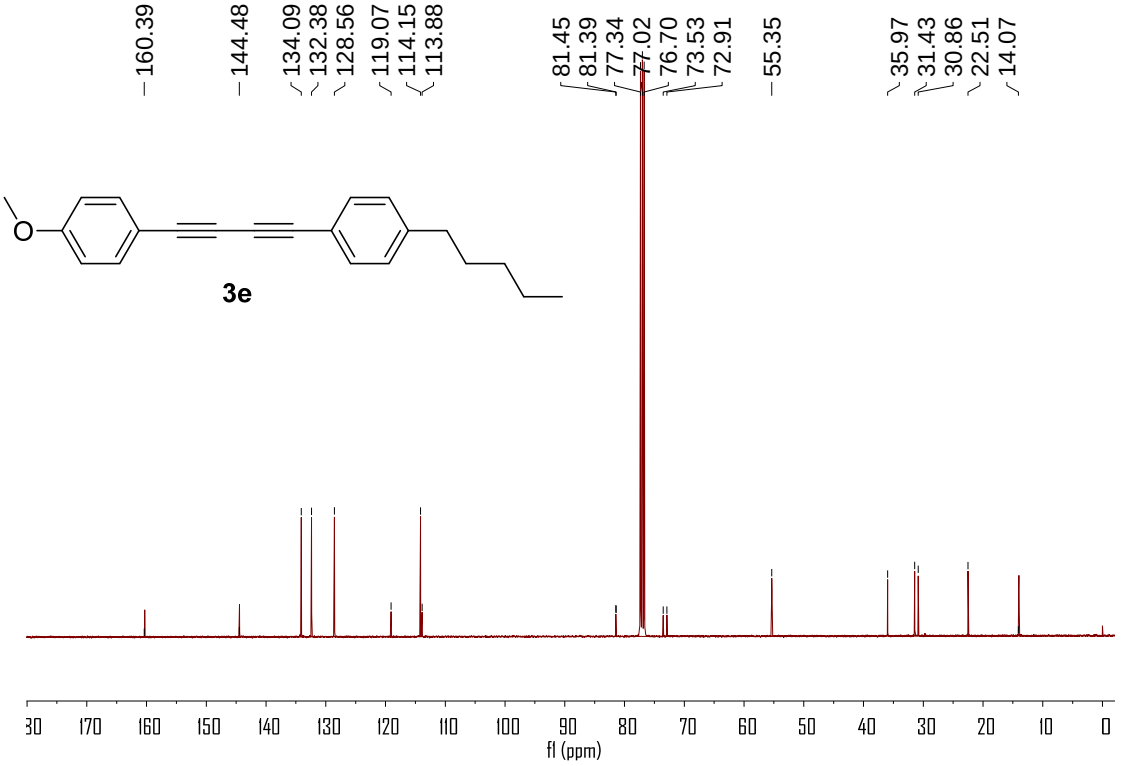
3d

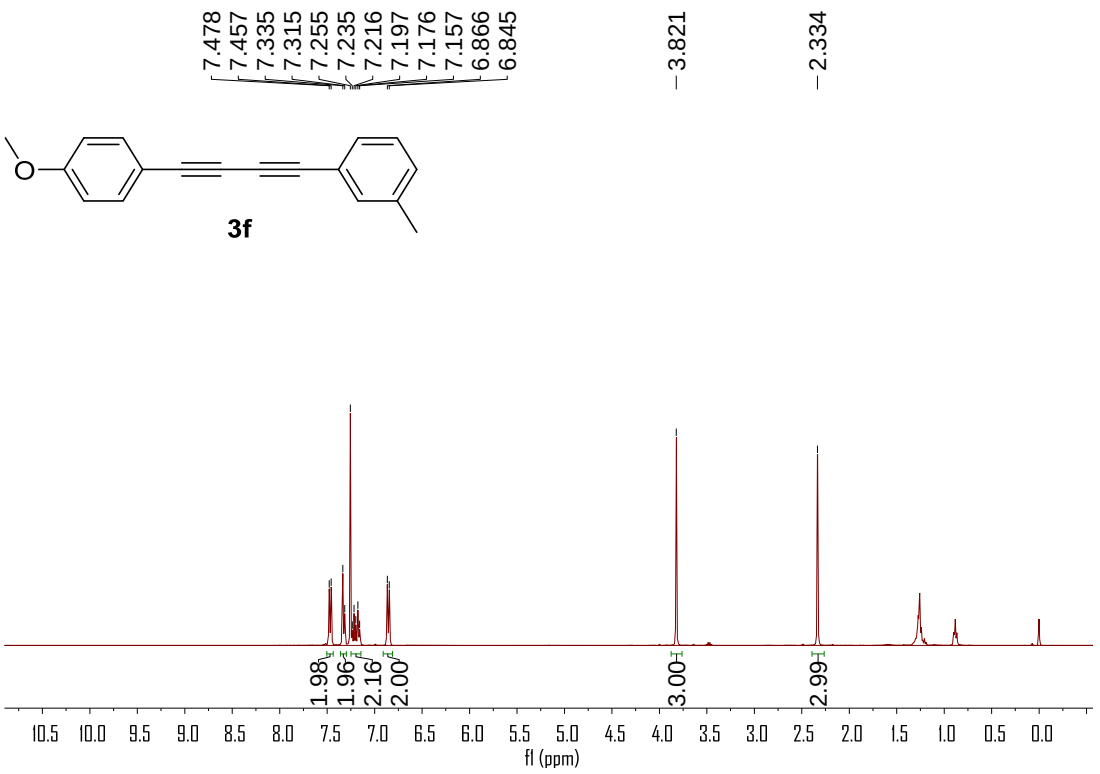

3.97
1.99
2.00
3.00
2.06
2.07
3.08
f1 (ppm)

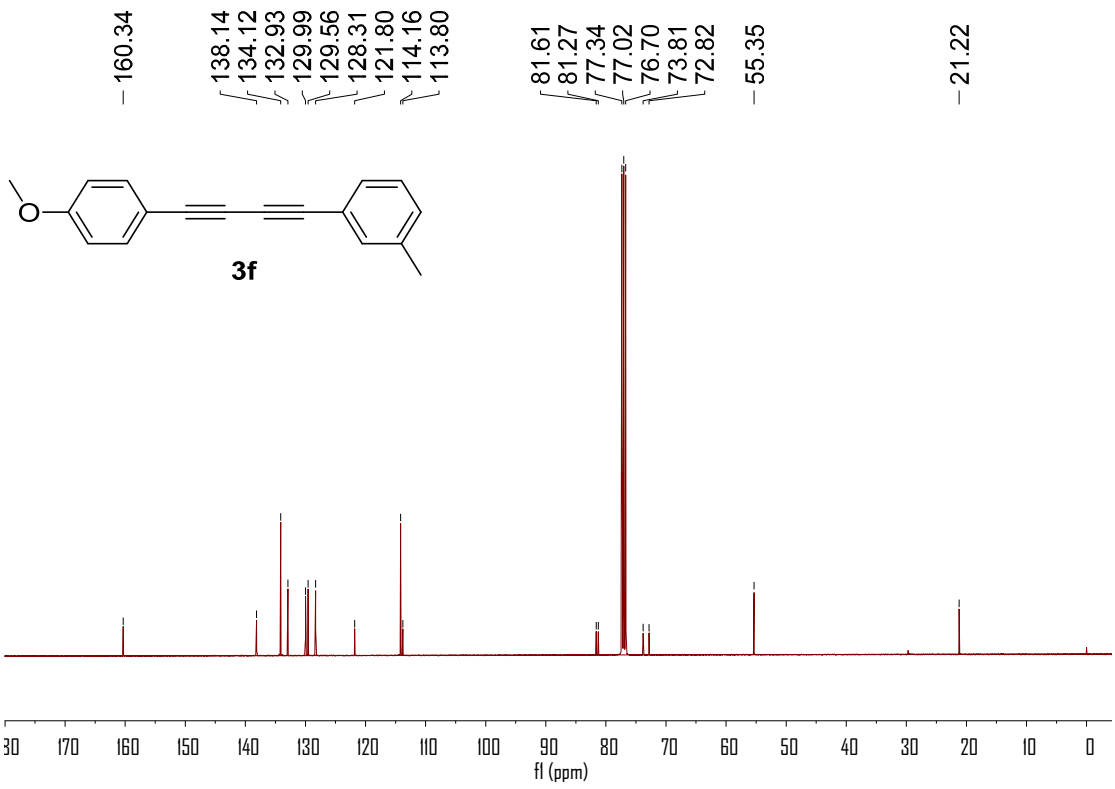

160.33
144.19
134.12
132.40
128.65
119.15
114.18
113.90
81.49
81.41
77.37
77.06
76.74
73.57
72.94
55.38
38.08
24.31
13.79
O
f1 (ppm)

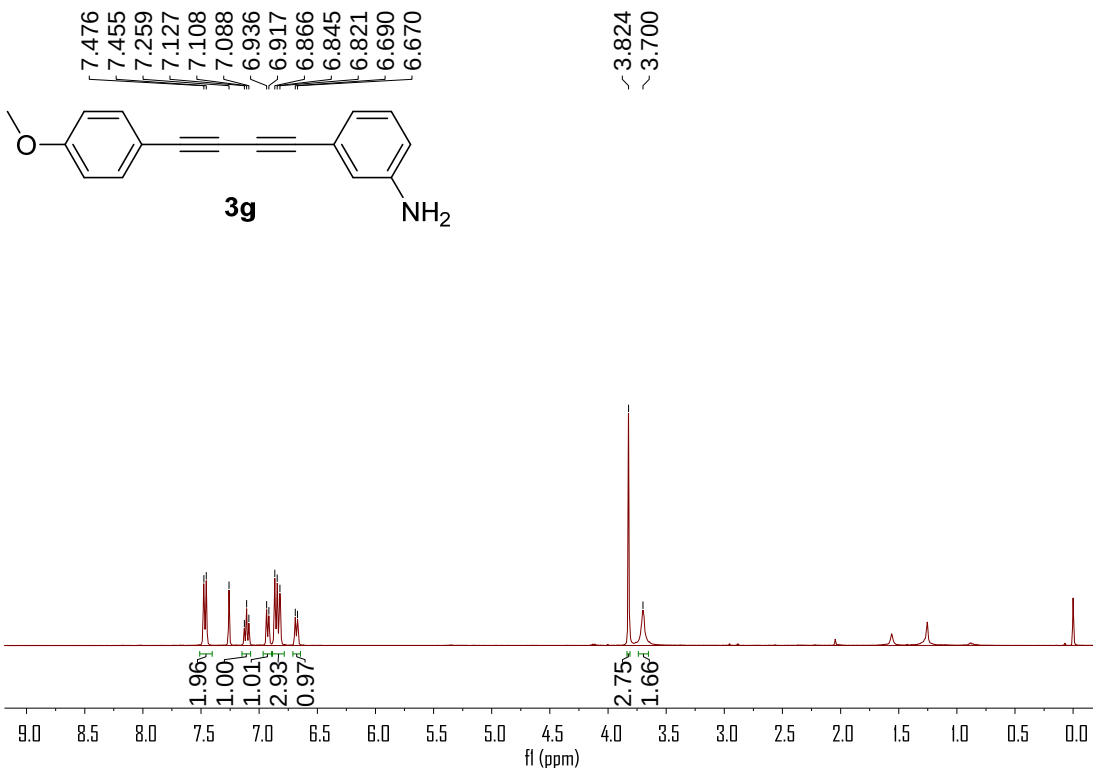
3d

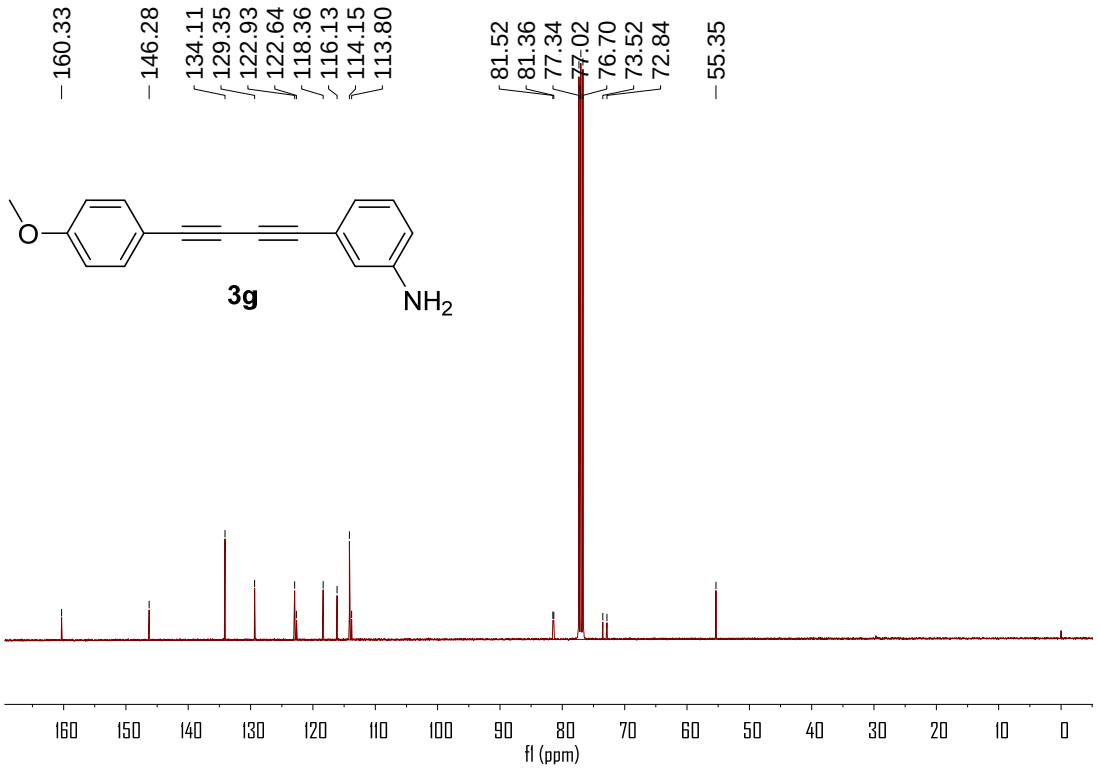

7.476
7.456
7.438
7.419
7.260
7.149
7.130
6.866
6.846
3.825
2.621
2.602
2.583
1.640
1.621
1.603
1.585
1.567
1.321
0.905
0.890
0.873
O
3e
3.87
2.00
2.00
2.88
2.01
2.04
4.11
3.07
f1 (ppm)

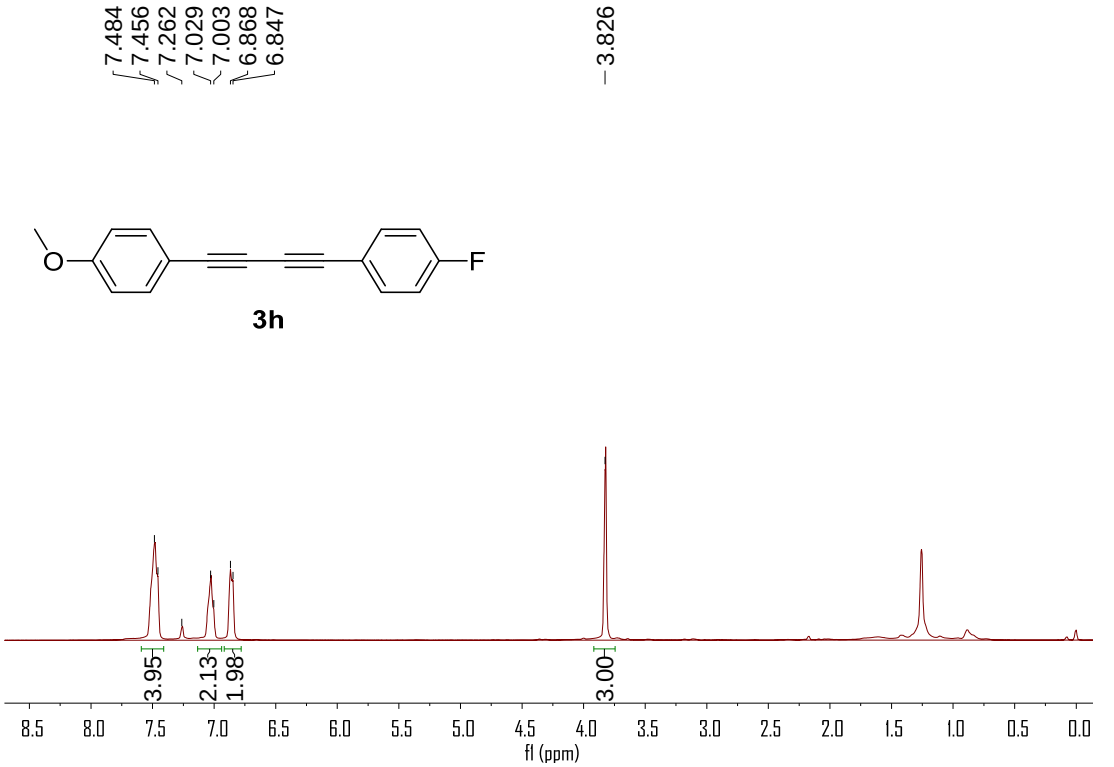

160.39
144.48
134.09
132.38
128.56
119.07
114.15
113.88
81.45
81.39
77.34
77.02
76.70
73.53
72.91
55.35
35.97
31.43
30.86
22.51
14.07
O
3e
f1 (ppm)

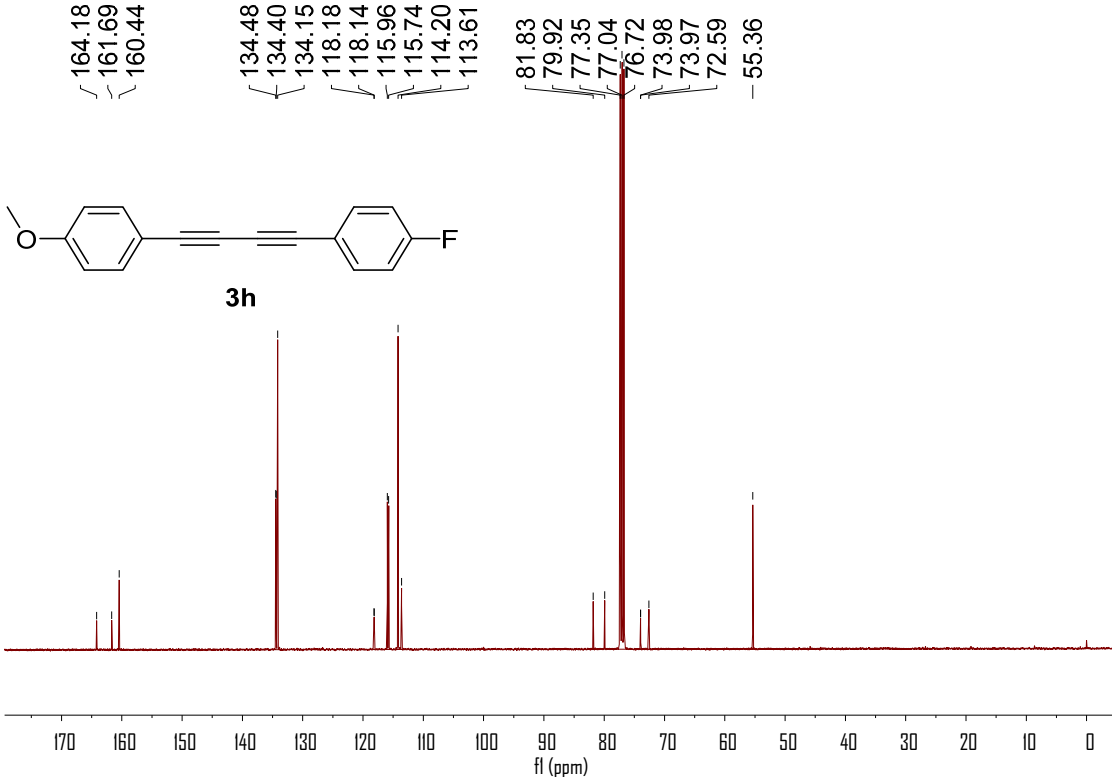

7.478
7.457
7.335
7.315
7.255
7.235
7.216
7.197
7.176
7.157
6.866
6.845
3.821
2.334
O
3f
1.98
1.96
2.16
2.00
3.00
2.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

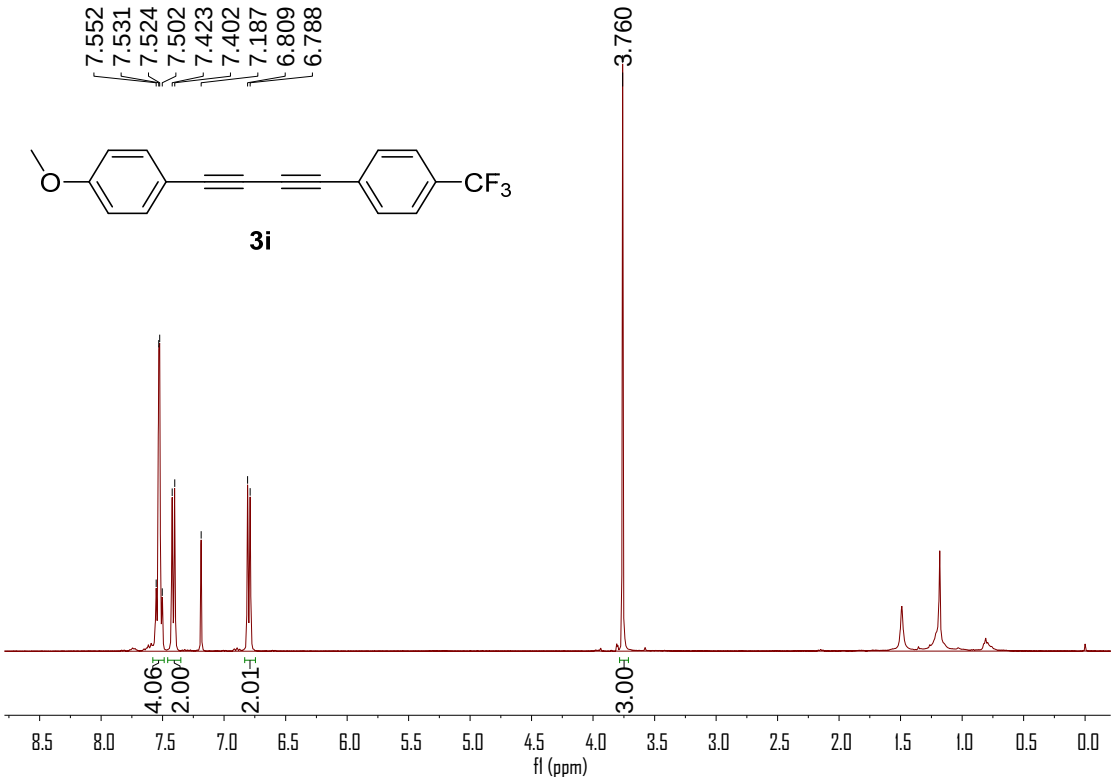

160.34
138.14
134.12
132.93
129.99
129.56
128.31
121.80
114.16
113.80
81.61
81.27
77.34
77.02
76.70
73.81
72.82
55.35
21.22
O
3f
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

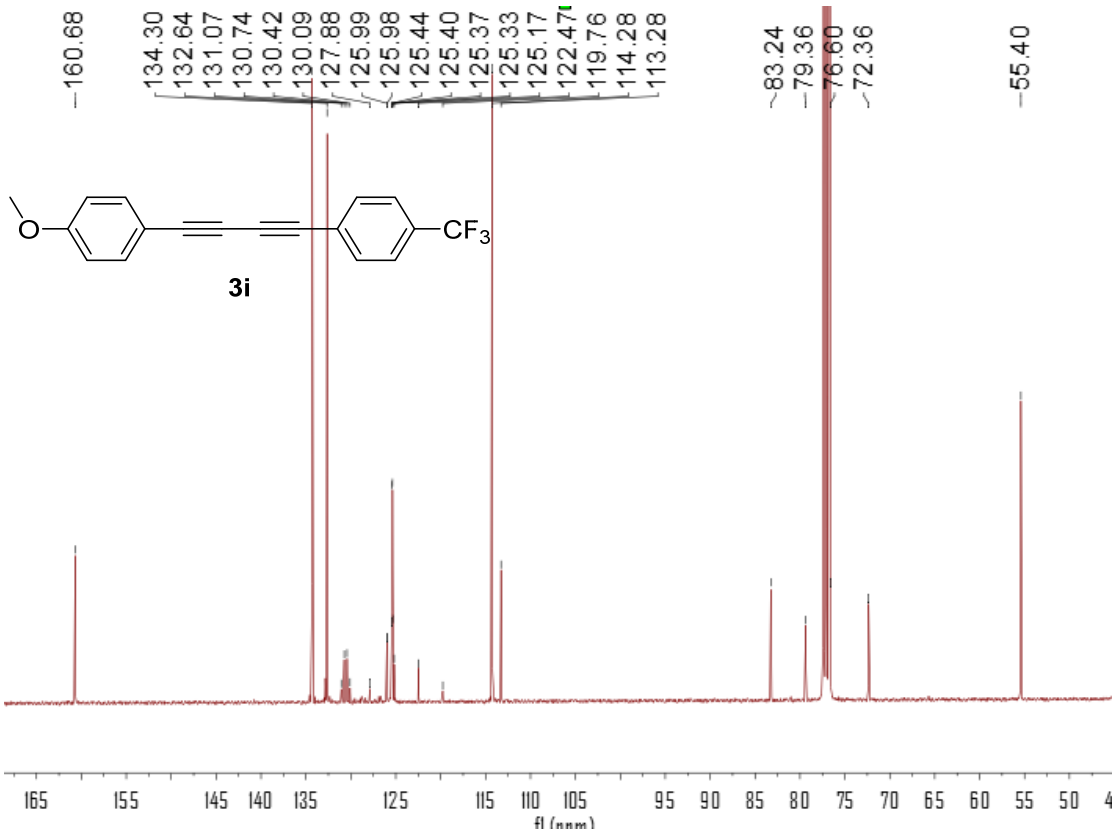

7.476
7.455
7.259
7.127
7.108
7.088
6.936
6.917
6.866
6.845
6.821
6.690
6.670
3.824
3.700
O
NH2
3g
1.96
1.00
1.01
2.93
0.97
2.75
1.66
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

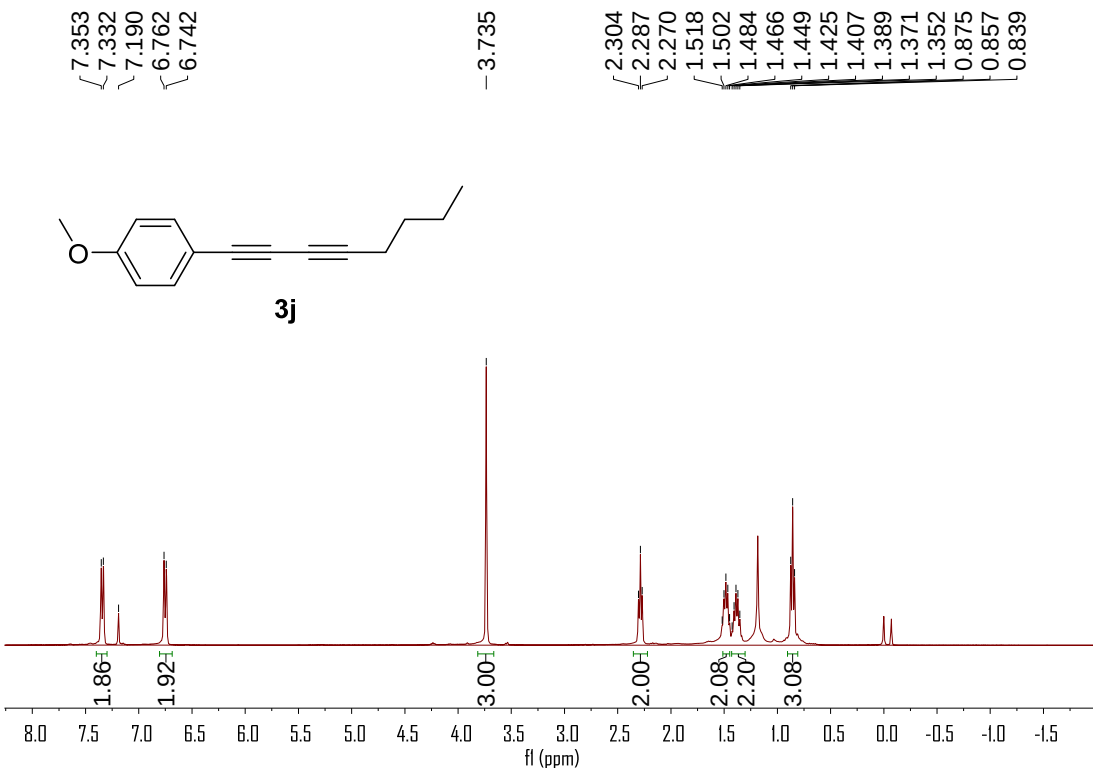

160.33
146.28
134.11
129.35
122.93
122.64
118.36
116.13
114.15
113.80
81.52
81.36
77.34
77.02
76.70
73.52
72.84
55.35
O
NH2
3g
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

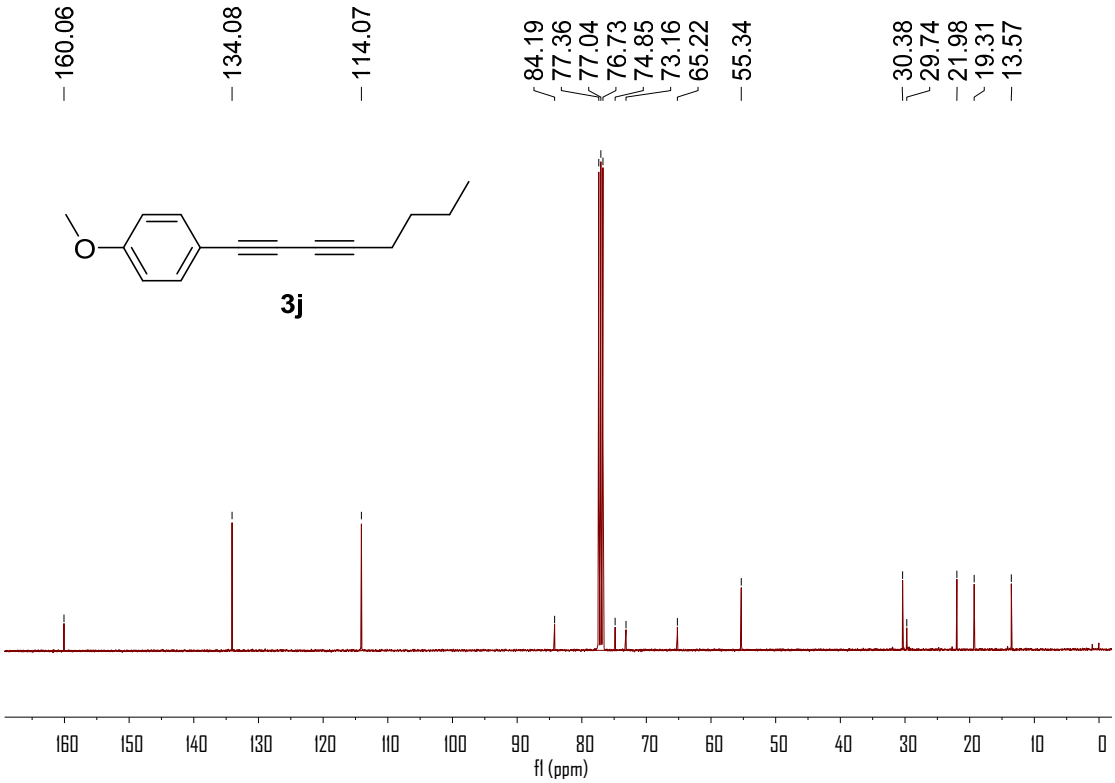

7.484
7.456
7.262
7.029
7.003
6.868
6.847
3.826
O
F
3h
3.95
2.13
1.98
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

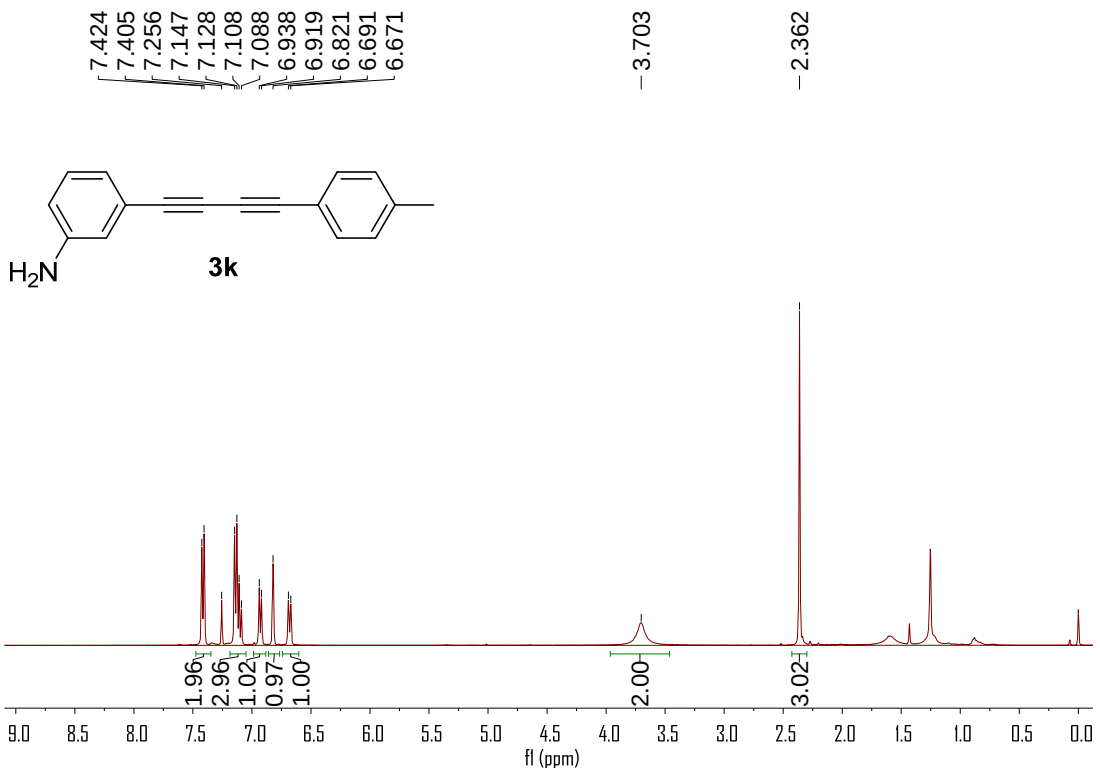

164.18
161.69
160.44
134.48
134.40
134.15
118.18
118.14
115.96
115.74
114.20
113.61
81.83
79.92
77.35
77.04
76.72
73.98
73.97
72.59
55.36
O
F
3h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

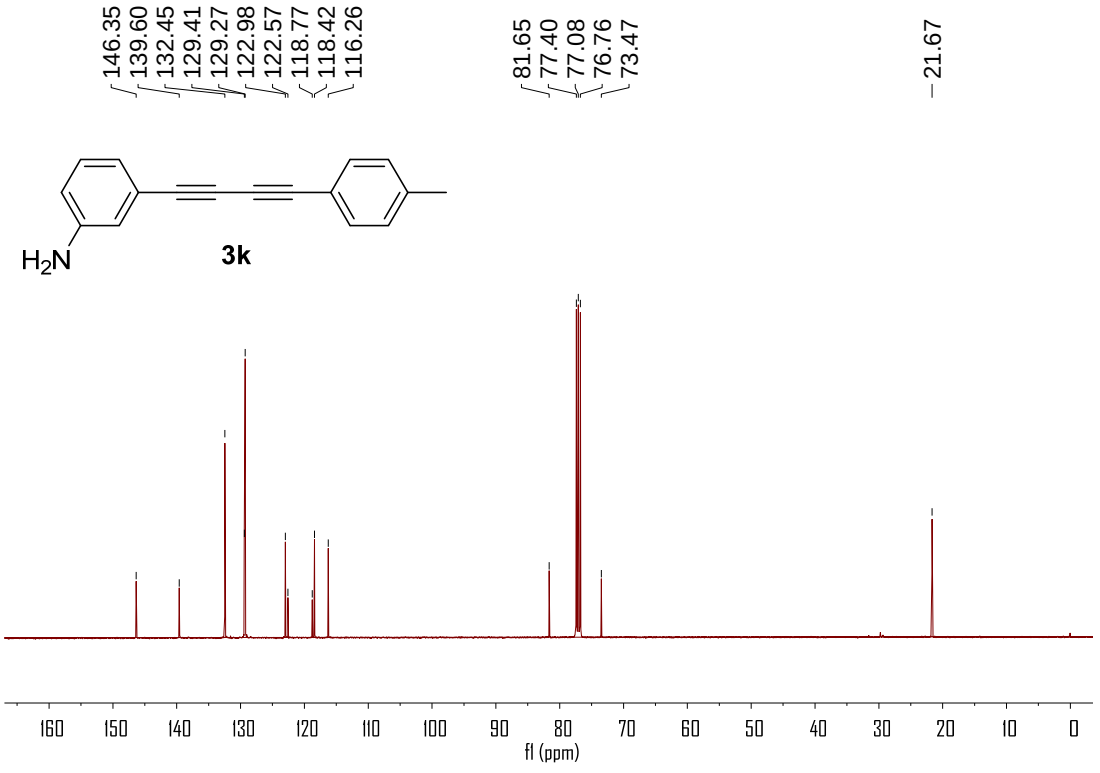

7.552
7.531
7.524
7.502
7.423
7.402
7.187
6.809
6.788
3.760
O
CF3
3i
4.06
2.00
2.01
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

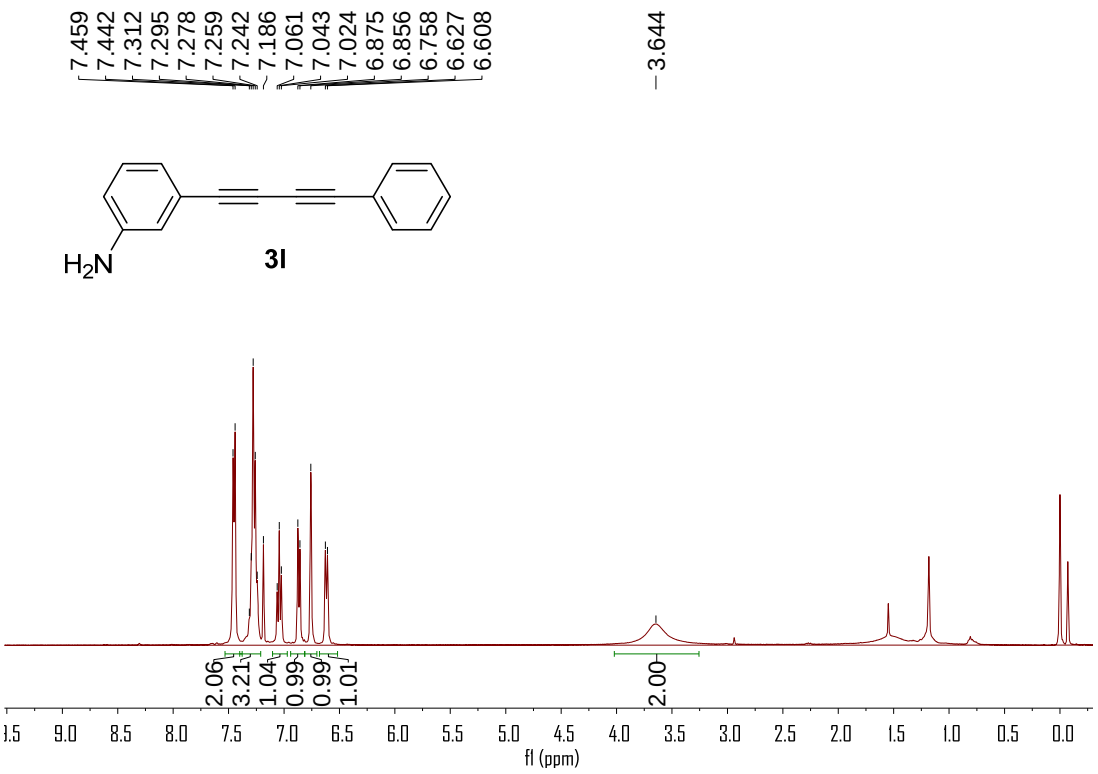

160.68
134.30
132.64
131.07
130.74
130.42
130.09
127.88
125.99
125.98
125.44
125.40
125.37
125.33
125.17
122.47
119.76
114.28
113.28
83.24
79.36
76.60
72.36
55.40
O
CF3
3i
165 155 145 140 135 125 115 110 105 95 90 85 80 75 70 65 60 55 50
f1 (ppm)

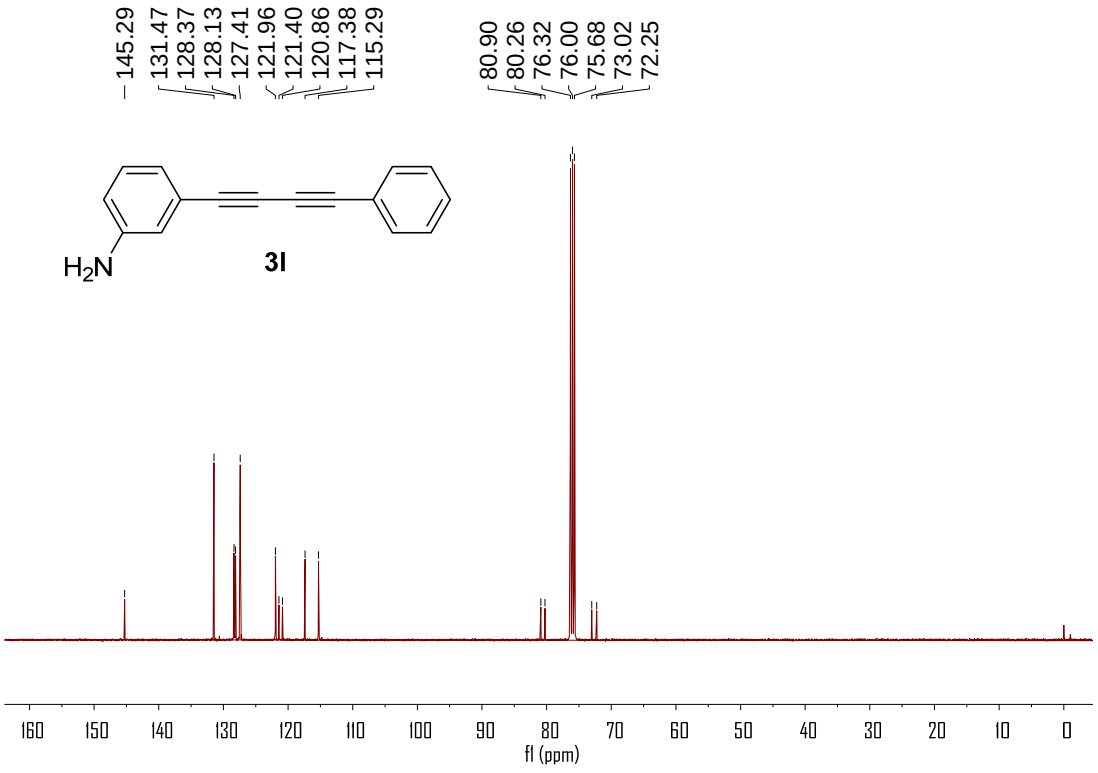

7.353
7.332
7.190
6.762
6.742
3.735
2.304
2.287
2.270
1.518
1.502
1.484
1.466
1.449
1.425
1.407
1.389
1.371
1.352
0.875
0.857
0.839
O
3j
1.86
1.92
3.00
2.00
2.08
2.20
3.08
f1 (ppm)


160.06
134.08
114.07
84.19
77.36
77.04
76.73
74.85
73.16
65.22
55.34
30.38
29.74
21.98
19.31
13.57
O
3j
f1 (ppm)


7.424
7.405
7.256
7.147
7.128
7.108
7.088
6.938
6.919
6.821
6.691
6.671
3.703
2.362
H2N
3k
1.96
2.96
1.02
0.97
1.00
2.00
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


146.35
139.60
132.45
129.41
129.27
122.98
122.57
118.77
118.42
116.26
81.65
77.40
77.08
76.76
73.47
21.67
H2N
3k
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.459
7.442
7.312
7.295
7.278
7.259
7.242
7.186
7.061
7.043
7.024
6.875
6.856
6.758
6.627
6.608
3.644
H2N
3l
2.06
3.21
1.04
0.99
0.99
1.01
2.00
f1 (ppm)


145.29
131.47
128.37
128.13
127.41
121.96
121.40
120.86
117.38
115.29
80.90
80.26
76.32
76.00
75.68
73.02
72.25
H2N
3l
f1 (ppm)