Supporting Information

Nickel-Catalyzed Oxidative Coupling Reactions of Two Different Terminal Alkynes Using O_2 as the Oxidant at Room Temperature: Facile Syntheses of Unsymmetric 1,3-Diynes

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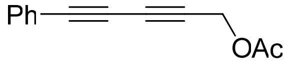
Experimental Details

General Information

Tetrahydrofuran (THF) was dried and distilled from sodium/benzophenone immediately prior to use under nitrogen atmosphere. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (boiling point is between 60-90 ^{o}C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they are listed as volume/volume ratios.

^{1}H and ^{13}C NMR data were recorded with a Varian Mercury (300 MHz) spectrometer with tetramethylsilane as an internal standard. All ^{1}H NMR spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants were reported in Hertz (Hz). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument or a Waters Q-Tof Premier instrument, accurate masses were reported for the molecular ion ($[M]^{+}$, $[M+1]^{+}$). Analytical gas chromatography (GC) was performed using a Varian 3900 Gas Chromatography fitted with a flame ionization detector. For the ReactIR kinetic experiments, the reaction spectra were recorded using a ReactIR 4000 from Mettler-Toledo AutoChem fitted with a silicon-tipped (SiComp) probe. Data manipulation was carried out using the iC IR software, version 1. 05.

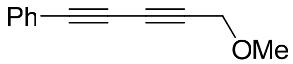
General procedures for synthesizing unsymmetric 1,3-diynes under air:



2a

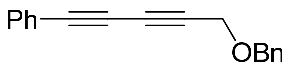
5-phenylpenta-2,4-diynyl acetate (2a).[1] The CuI (5 mol%) and $NiCl_2 \cdot 6H_2O$ (5 mol%) were dissolved in THF(4 mL) and TMEDA (20 mol%), and the solution was stirred for 2 min at room temperature. Phenylacetylene **1a** (5 mmol**)** and prop-2-ynyl acetate **1b** (1 mmol) were added subsequently and the reaction mixture was stirred under air for 12 hours at room temperature. After completion of the reaction, as indicated by TLC, the mixture was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (petroleum/ethyl acetate = 100/1, v/v) to afford pure **2a** in 86% yield (170.3 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47-7.44 (m, 2H), 7.31-7.28 (m, 3H), 4.78 (s, 2H), 2.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.25, 132.87, 129.74, 128.69, 121.36, 79.00, 76.45, 73.28, 71.35, 52.76, 20.86.
All remaining unsymmetric diynes were prepared using a procedure similar to that used to synthesize **2a**.

Unsymmetric 1,3-diynes



2b

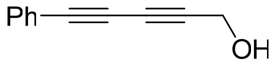
(5-methoxypenta-1,3-diynyl)benzene (2b).[2] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51-7.48 (m, 2H), 7.37-7.32 (m, 3H), 4.25 (s, 2H), 3.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.84, 129.59, 128.68, 121.61, 78.92, 78.30, 73.56, 71.31, 60.58, 58.09.



2c

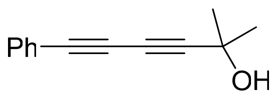
(5-(benzyloxy)penta-1,3-diynyl)benzene (2c). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52-7.50 (m, 2H), 7.39-7.37 (m, 8H), 4.66 (s, 2H), 4.34 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.36, 132.89, 130.13, 129.62, 128.72, 128.45, 121.64, 78.98, 78.37,

73.60, 71.98, 71.41, 58.00; HRMS (APCI) calcd for $C_{18}H_{14}O$ $[M]^+$: 246.1045; found 246.1048.



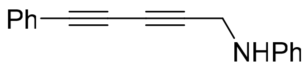
2d

5-phenylpenta-2,4-diyn-1-ol (2d).[3] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49-7.47 (m, 2H), 7.35-7.27 (m, 3H), 4.42 (s, 2H), 2.66 (b, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.83, 129.58, 128.65, 121.54, 80.75, 78.76, 73.44, 70.55, 51.74.



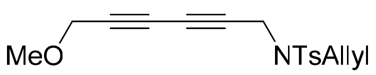
2e

2-methyl-6-phenylhexa-3,5-diyn-2-ol (2e).[4] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49-7.47 (m, 2H), 7.33-7.30 (m, 3H), 2.50 (b, 1H), 1.59 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.75, 129.49, 128.67, 121.75, 86.96, 79.00, 73.42, 67.29, 65.98, 31.34.



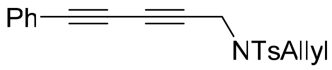
2f

N-(5-phenylpenta-2,4-diynyl)benzenamine (2f).[5] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.34 (m, 2H), 7.22-7.10 (m, 5H), 6.73-6.68 (m, 1H), 6.59-6.57 (m, 2H), 3.94 (s, 2H), 3.78 (b, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.77, 132.76, 129.51, 129.42, 128.61, 121.65, 118.95, 113.76, 80.65, 77.15, 73.92, 67.92, 34.60.



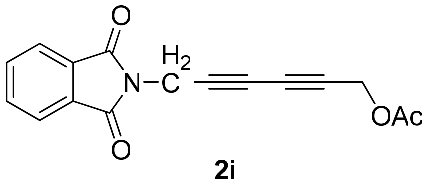
2g

N-allyl-N-(6-methoxyhexa-2,4-diynyl)-4-methylbenzenesulfonamide (2g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 5.70-5.65 (m, 1H), 5.29-5.21 (m, 2H), 4.12-4.18 (m, 4H), 3.77 (d, J = 6.6 Hz, 2H), 3.33 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.11, 135.57, 131.88, 129.86, 127.92, 120.60, 74.69, 72.28, 70.32, 69.78, 60.23, 58.07, 49.63, 36.70, 21.78; HRMS (APCI) calcd for $C_{10}H_{11}NO$ $[M\text{-}Ts\text{-}H]^+$: 161.0841; found 161.0846.



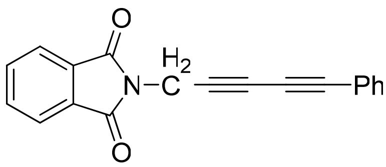
2h

N-allyl-4-methyl-N-(5-phenylpenta-2,4-diynyl)benzenesulfonamide (2h). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.43-7.40 (m, 2H), 7.33-7.29 (m, 5H), 5.73-5.67 (m, 1H), 5.30 (d, J = 17.1 Hz, 1H), 5.24 (d, J = 9.9 Hz, 1H), 4.19 (s, 2H), 3.82 (d, J = 6.3 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.19, 135.59, 132.74, 131.95, 129.90, 129.74, 128.76, 127.98, 121.36, 120.61, 75.71, 74.18, 73.30, 70.47, 49.72, 37.02, 21.85; HRMS (APCI) calcd for $C_{21}H_{19}NO_2S$ $[M]^+$: 349.1136; found 349.1134.



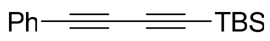
2i

6-(1-oxoisoindolin-2-yl)hexa-2,4-diynyl acetate (2i). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, *J* = 0.9 Hz, 2H), 7.76 (d, *J* = 0.9 Hz, 2H), 4.69 (s, 2H), 4.54 (s, 2H), 2.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.19, 166.97, 134.56, 132.08, 123.87, 73.61, 72.51, 70.69, 67.33, 52.41, 27.79, 20.82; HRMS (APCI) calcd for $C_{15}H_8NO_4$ $[M-CH_3]^+$: 266.0453; found 266.0455.



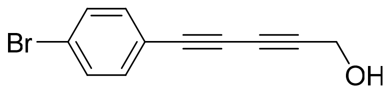
2j

2-(5-phenylpenta-2,4-diynyl)isoindoline-1,3-dione (2j). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91-7.88 (m, 2H), 7.77-7.74 (m, 2H), 7.46-7.44 (m, 2H), 7.33-7.29 (m, 2H), 4.61 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.07, 134.53, 132.84, 132.13, 129.60, 128.62, 123.85, 121.43, 77.72, 76.23, 73.52, 68.19, 28.10; HRMS (APCI) calcd for $C_{19}H_{11}NO_2$ $[M]^+$: 285.0790; found 285.0801.



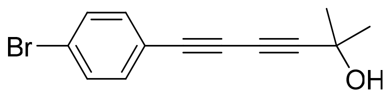
2k

Tert-butyldimethyl(phenylbuta-1,3-diynyl)silane (2k).[6] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (m, 2H), 7.33 (m, 3H), 1.00 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.9, 129.6, 128.7, 121.6, 89.6, 88.7, 76.5, 74.6, 26.3, 17.0, -4.5.



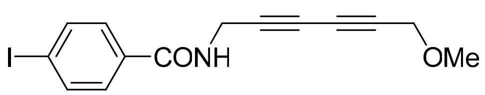
2l

5-(4-bromophenyl)penta-2,4-diyn-1-ol (2l). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 4.41 (d, *J* = 6.3 Hz, 2H), 1.74 (t, *J* = 6.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.16, 131.99, 124.10, 120.52, 81.25, 77.63, 74.47, 70.47, 51.90; HRMS (APCI) calcd for $C_{11}H_7BrO$ $[M]^+$: 233.9680; found 233.9688.



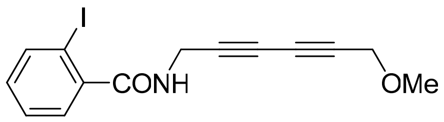
2m

6-(4-bromophenyl)-2-methylhexa-3,5-diyn-2-ol (2m). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 1.57 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.09, 131.99, 123.96, 120.71, 87.60, 77.85, 74.55, 67.11, 66.00, 31.31; HRMS (APCI) calcd for $C_{13}H_{11}BrO$ $[M]^+$: 261.9993; found 261.9996.



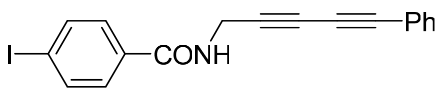
2n

4-iodo-N-(6-methoxyhexa-2,4-diynyl)benzamide (2n). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 6.39 (b, 1H), 4.33 (d, *J* = 5.1 Hz, 2H), 4.16 (s, 2H), 3.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.52, 138.12, 133.12, 128.84, 99.28, 74.95, 74.85, 70.64, 68.15, 60.33, 58.11, 30.65; HRMS (APCI) calcd for $C_{14}H_{12}INO_2$ $[M]^+$: 352.9913; found 352.9908.



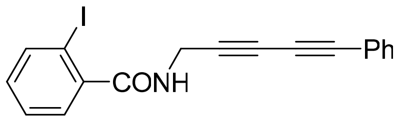
2o

2-iodo-N-(6-methoxyhexa-2,4-diynyl)benzamide (2o). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.8 Hz, 1H), 7.40-7.38 (m, 2H), 7.15-7.10 (m, 1H), 6.13 (b, 1H), 4.34 (d, *J* = 5.1 Hz, 2H), 4.16 (s, 2H), 3.38(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.03, 141.30, 140.21, 131.73, 128.62, 128.44, 92.57, 74.86, 74.54, 70.73, 68.30, 60.34, 58.11, 30.60; HRMS (APCI) calcd for $C_{14}H_{12}INO_2$ $[M]^+$: 352.9913; found 352.9908.



2p

4-iodo-N-(5-phenylpenta-2,4-diynyl)benzamide (2p). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.53-7.48 (m, 4H), 7.36-7.32 (m, 3H), 6.28 (s, 1H), 4.42 (d, *J* = 5.1 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-D_6): δ 166.13, 138.00, 133.62, 133.13, 130.58, 129.93, 129.56, 121.00, 100.13, 82.21, 77.32, 74.13, 66.63, 30.19; HRMS (APCI) calcd for $C_{18}H_{12}INO$ $[M]^+$: 384.9964; found 384.9965.

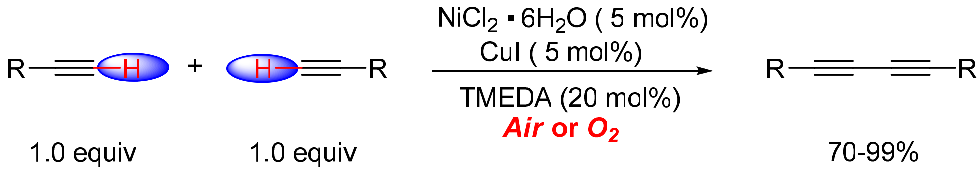


2q

2-iodo-N-(5-phenylpenta-2,4-diynyl)benzamide (2q). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.50- 7.48 (m, 2H), 7.40-7.26 (m, 5H), 7.14-7.08 (m, 1H), 6.20 (b, 1H), 4.41 (d, *J* = 5.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.03, 141.34, 140.23, 132.87, 131.72, 129.63, 128.67, 128.45, 121.50, 92.59, 77.85, 77.77, 73.53, 68.97, 30.91; HRMS (APCI) calcd for $C_{18}H_{12}INO$ $[M]^+$: 384.9964; found 384.9966.

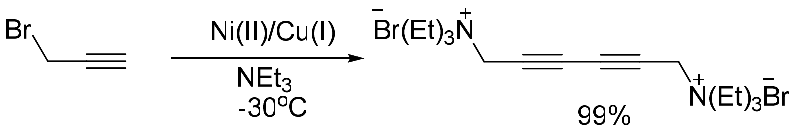
General procedures for synthesizing symmetric 1,3-diynes under air:

Homocoupling of terminal alkynes under our conditions also could get perfect outcomes.



The scope of substrates for this Ni/Cu catalyzed diyne syntheses was examined and the results were listed in table 1. Alkynes based on propargylic alcohols and amines were successfully coupled in high yields, no matter the substituents were electron-withdrawing or electron-donating (Table 1, entries 2-7, 11-12). Terminal alkene group was well tolerated, and 1,6-enynes with O-, C- and N- tether were coupled in good yields (Table 1, entries 8-10). Arylacetylenes with methoxy substituent as well as sensitive chloro, bromo and iodo groups on the phenyl ring were suitable substrates too, and the halo groups remained intact in the reaction process, providing reactive sites for further transformation (Table 1, entries 13-17).

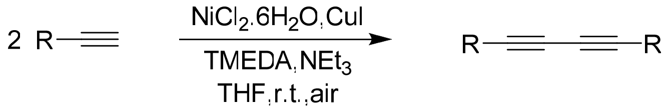
Propargyl bromide failed to be coupled under the above conditions due to its high reactivity. Yet the reaction proceeded readily in the presence of NEt_3 at -30°C to generate diamminum bromide salt in 99% yield (eq 1). All attempts at room temperature or 0°C led to black mixtures, probably rising from the sensitivity of the bromo group under the reaction conditions.

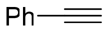
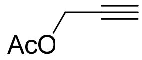
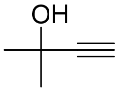
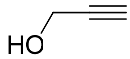
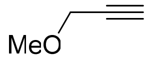
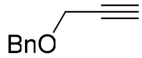
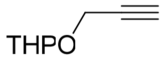
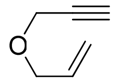
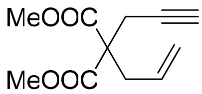
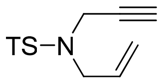
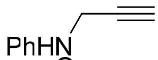
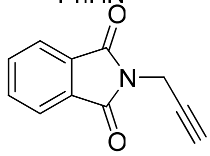
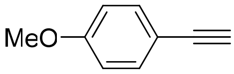
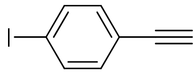
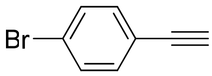
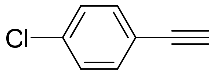
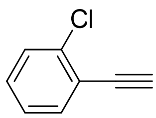


(1)

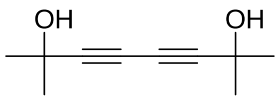
N1,N1,N1,N6,N6,N6-hexaethylhexa-2,4-diyne-1,6-diaminium bromide. ^{1}H NMR (300 MHz, D_2O): δ 3.96 (s, 4H), 3.25 (q, J = 7.2 Hz, 12H), 1.14 (t, J = 7.2 Hz, 18H); ^{13}C NMR (75 MHz, D_2O): δ 80.94, 70.53, 53.50, 47.74, 7.23; HRMS (ESI) calcd for $C_{18}H_{34}Br_2N_2$ $[M + H]^+$: 437.1167; found 437.1813.

Table 1. Homocoupling of Alkynes Catalyzed by Ni/Cu[a]



entry	substrate	product	yield (%)
1		**3a**	99
2		**3b**	99
3		**3c**	99
4		**3d**	92
5		**3e**	83
6		**3f**	98
7		**3g**	82
8		**3h**	76
9		**3i**	91
10		**3j**	80
11		**3k**	70
12		**3l**	76
13		**3m**	75
14		**3n**	99
15		**3o**	99
16		**3p**	99
17		**3q**	99

[a] Unless otherwise indicated, the reaction conditions were as follows: **1** (1 mmol), $NiCl_2 \cdot 6H_2O$ (0.05 mmol), CuI (0.05 mmol), TMEDA (0.2 mmol), NEt_3 (3.0 mmol) and THF (4 mL) at room temperature under aerobic conditions. Isolated yields.

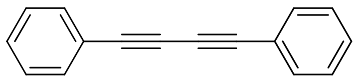


3c

2,7-dimethylocta-3,5-diyne-2,7-diol (3c).[7] A mixture of 2-methylbut-3-yn-2-ol (2 mmol), TMEDA (20 mol%), CuI (5 mol%) and $NiCl_2 \cdot 6H_2O$ (5 mol%) in THF (4 mL) was stirred in air at room temperature. After completion of the reaction, as indicated by TLC, the mixture was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel to afford **3c** in 99% yield. ^{1}H NMR (300 MHz, DMSO-D_6): δ 5.52 (s, 2H), 1.35 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 84.19, 66.53, 65.80, 31.26.

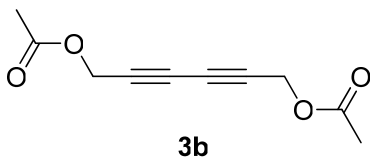
All remaining symmetric diynes were prepared using a procedure similar to that used to synthesize **3c**.

Symmetric 1,3-diynes:



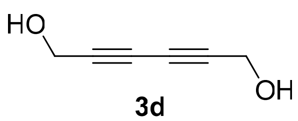
3a

1,4-diphenylbuta-1,3-diyne (3a).[8] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54-7.52 (m, 4H), 7.36-7.33 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.73, 129.44, 128.67, 122.03, 81.78, 74.14.



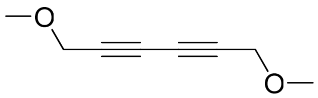
3b

Hexa-2,4-diyne-1,6-diyl diacetate (3b).[9] ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.74 (s, 4H), 2.11 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.20, 73.81, 70.42, 52.41, 20.82.



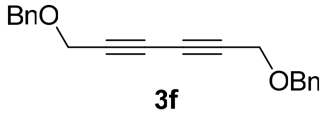
3d

Hexa-2,4-diyne-1,6-diol (3d).[10] ^{1}H NMR (300 MHz, DMSO-D_6): δ 5.39 (b, 2H), 4.15 (s, 4H); ^{13}C NMR (75 MHz, DMSO-D_6): δ 80.22, 68.58, 50.00.



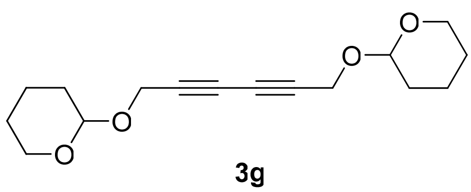
3e

1, 6-dimethoxyhexa-2,4-diyne (3e).[9] ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.18 (s, 4H), 3.39 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 75.05, 70.12, 59.74, 57.40.



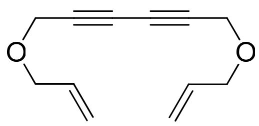
3f

1,6-bis(benzyloxy)hexa-2,4-diyne (3f).[11] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.35 (m, 10H), 4.65 (s, 4H), 4.28 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.31, 128.90, 128.44, 128.33, 75.71, 72.00, 70.91, 57.82.



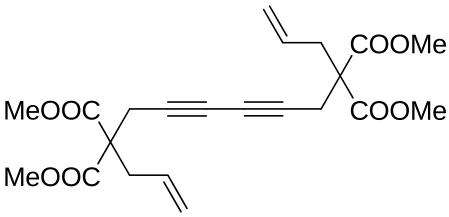
3g

1,6-bis(tetrahydro-2H-pyran-2-yloxy)hexa-2,4-diyne (3g).[12] ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.80 (m, 2H), 4.33(s, 4H), 3.85–3.52 (m, 2H), 3.57-3.52 (m, 2H), 1.80-1.56 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 96.99, 75.38, 70.08, 62.05, 54.48, 30.28, 25.45, 19.06.



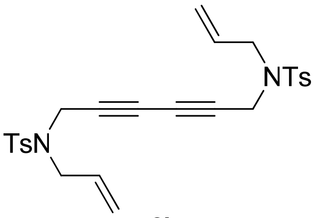
3h

1,6-bis(allyloxy)hexa-2,4-diyne (3h).[13] ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.88-5.79 (m, 2H), 5.28-5.15 (m, 4H), 4.16(s, 4H), 4.00 (d, J = 5.7 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.86, 118.44, 75.52, 71.01, 70.60, 57.76.



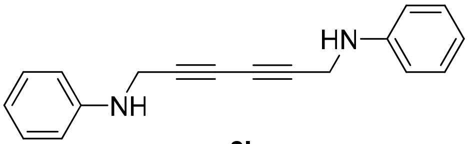
3i

Tetramethyl tetradeca-1,13-dien-6,8-diyne-4,4,11,11-tetracarboxylate (3i).[14] ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.58-5.46 (m, 2H), 5.14-5.06 (m, 4H), 3.68 (s, 12H), 2.80 (s, 4H), 2.71 (d, *J* = 7.2 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$)): δ 169.65, 131.24, 119.91, 72.19, 67.82, 56.57, 52.66, 36.56, 23.31.



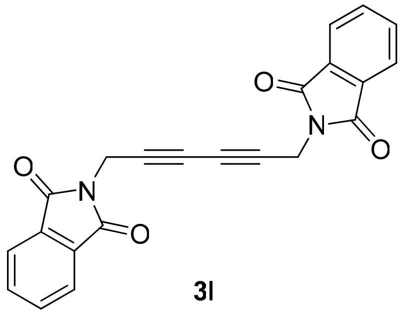
3j

N,N'-(hexa-2,4-diyne-1,6-diyl)bis(N-allyl-4-methylbenzenesulfonamide) (3j).[13] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.8 Hz, 4H), 7.29 (d, *J* = 7.8 Hz, 4H), 5.73-5.65 (m, 2H), 5.27–5.23 (m, 4H), 4.11 (s, 4H), 3.75 (d, *J* = 6.3 Hz, 4H), 2.43 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.11, 135.79, 131.86, 129.83, 127.80, 120.44, 71.93, 69.46, 49.01, 36.66, 21.78.



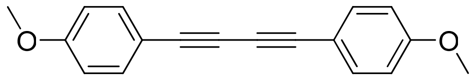
3k

N1,N6-diphenylhexa-2,4-diyne-1,6-diamine (3k).[5] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26-7.19 (m, 4H), 6.82-6.79 (m, 2H), 6.67-6.65 (m, 4H), 3.99 (s, 4H), 3.86 (b, 2H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 146.76, 129.51, 119.01, 113.75, 75.84, 67.66, 34.43.



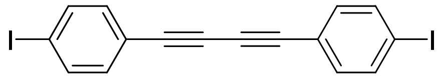
3l

2,2'-(hexa-2,4-diyne-1,6-diyl)diisoindoline-1,3-dione (3l).[15] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86-7.85 (m, 4H), 7.76-7.74 (m, 4H), 4.49 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.96, 134.50, 132.12, 123.86, 72.31, 67.57, 27.76.



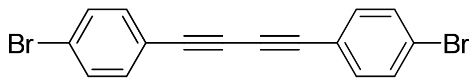
3m

1,4-bis(4-methoxyphenyl)buta-1,3-diyne (3m).[16,17] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (d, J = 8.4 Hz, 4H), 6.85 (d, J = 8.4 Hz, 4H), 3.81 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 160.42, 134.23, 114.32, 114.11, 81.42, 73.14, 55.52.



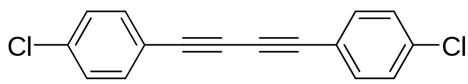
3n

1,4-bis(4-iodophenyl)buta-1,3-diyne (3n).[17] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71–7.68 (m, 4H), 7.25–7.22 (m, 4H); very insoluble in common organic solvents.[18]



3o

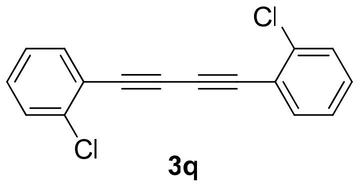
1,4-bis(4-bromophenyl)buta-1,3-diyne (3o).[18] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 (d, J = 8.1 Hz, 4H), 7.38 (d, J = 8.1 Hz, 4H); very insoluble in common organic solvents.[18]



3p

1,4-bis(4-chlorophenyl)buta-1,3-diyne (3p).[19] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46

(d, J = 8.1 Hz, 4H), 7.32 (d, J = 8.1 Hz, 4H); very insoluble in common organic solvents.[18]



3q

1,4-bis(2-chlorophenyl)buta-1,3-diyne (3q).[20] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59-7.56 (m, 2H), 7.44-7.41 (m, 2H), 7.34-7.22 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.20, 134.61, 130.53, 129.69, 126.79, 122.03, 79.64, 78.59.

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General ReactIR Experimental Details

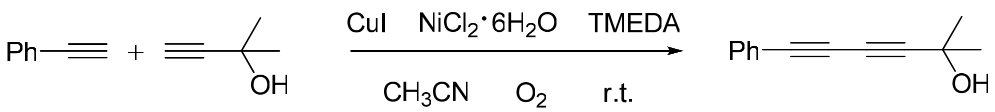
All kinetic experiments were run at 25 ± 1 ^{o}C. For the ReactIR kinetic experiments, the reaction spectra were recorded using a ReactIR 4000 from Mettler-Toledo AutoChem fitted with a silicon-tipped (SiComp) probe. The spectra were acquired in 2 scans at a gain of one and a resolution of two using system ReactIR 3.0 software. Data manipulation was carried out using the iC IR software, version 1. 05.

The experimental details:

The reaction was carried out as follows: an oven-dried three necked reaction vessel was fitted with a magnetic stirring bar. The IR probe was inserted through an adapter into the middle neck; the other two necks were capped by septa for injections and an oxygen line. The reaction vessel was kept at room temperature. Following evacuation under vacuum and flushing with oxygen, the three necked vessel was charged with 2.0 mL CH_3CN solution containing $NiCl_2{\cdot}6H_2O$ (5 %), CuI (5 %) and TMEDA (20 %). Then the two alkynes were added to initiate the reaction, and IR spectra were recorded over the course of the reaction.

Apparent kinetics of the hetero-couplings:

To gain more information of the reaction, the hetero-coupling reaction of phenylacetylene **1a** and 2-methylbut-3-yn-2-ol **1f** was monitored by in situ IR (eq 2). Figure 1 listed parts of the region of recorded spectrum of the reaction, in which the increasing of peak near 955 cm^{-1}, and declining of peak near 964 cm^{-1} clearly show the progress of the reaction.



(2)

1a **1f** **2e**

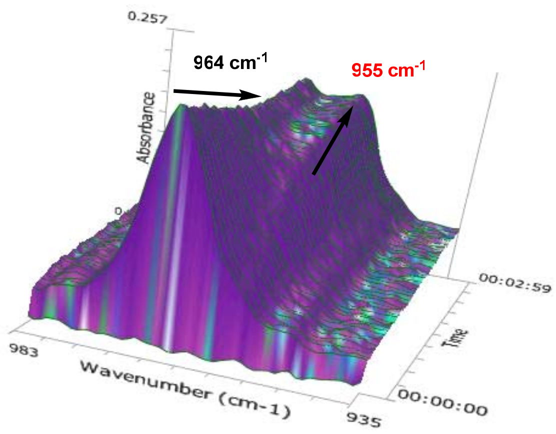


Figure 1. The time-resolution IR spectra of the reaction of **1a** and **1f** in the presence of Ni/Cu/O_2.

The kinetic profiles of component **1** and **2**, exhibited the trends of two species in the reaction with time (Figure 2A). Compared with the authentic samples shown in Figure 2B, the component **1** was assigned as alkyne **1f**, and the component **2** was the cross-coupled diyne **2e**.

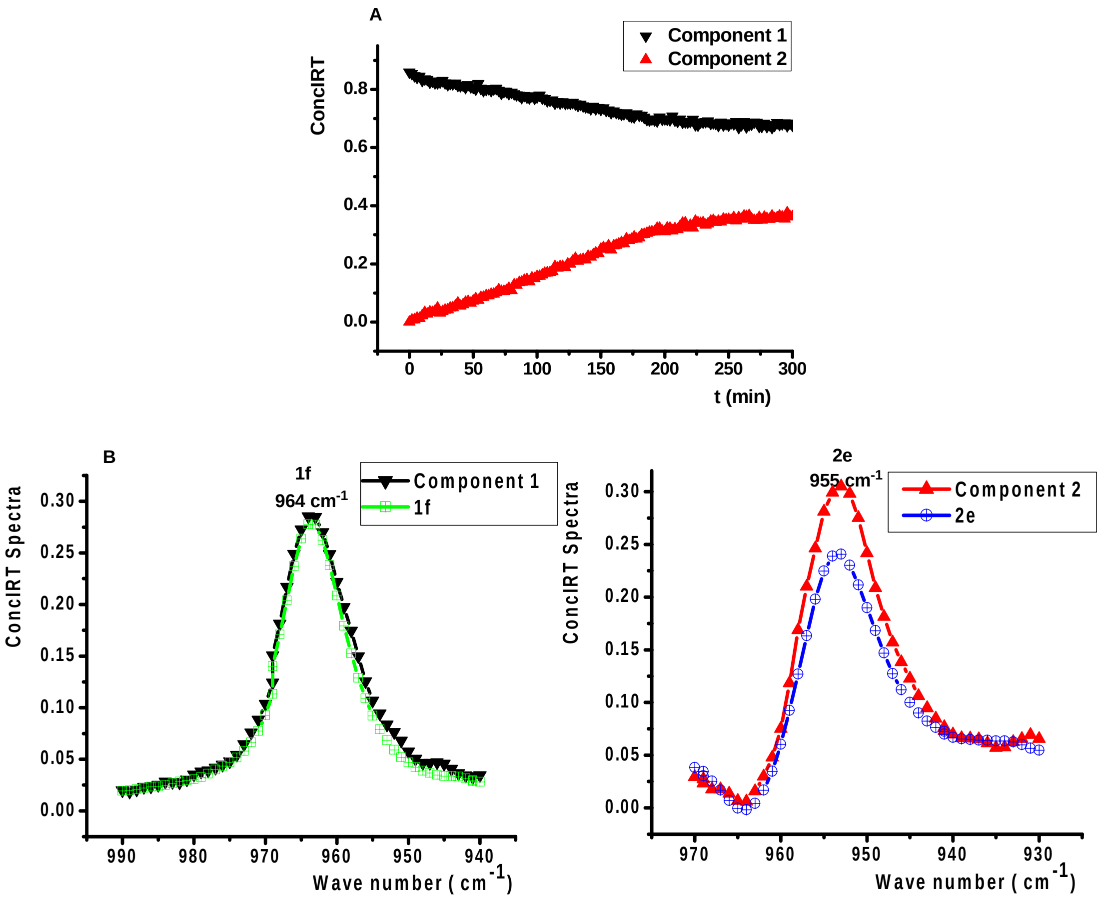


Figure 2. A: Kinetic profiles of the reaction between **1a** and **1f** monitored by in-situ IR. **B**: Component **1** and **2** comparison between authentic samples **1f** and **2e**.

Figure 3A listed the kinetic profile of the cross-coupled diyne 2**e** with time in the reaction of 5.0 equiv **1f** with 1.0 equiv **1a** in the presence of Ni/Cu catalysts, which is interested since it showed a liner region from beginning till the end. Similar kinetic trends were observed in the reaction of 1.0 equiv **1f** with 5.0 equiv **1a** in the presence of Ni/Cu catalysts (Figure 3B). However, the kinetic curve of the reaction of 5.0 equiv **1f** with 1.0 equiv **1a** in only presence of Cu catalyst, but no Ni-catalyst (Figure 3C) was completely different with the one listed in the Figure 3A. The preliminary kinetic data clearly clarified that the formation of cross-coupled diynes from the catalyst system of Ni/Cu was different from the only Cu-catalyst system again.

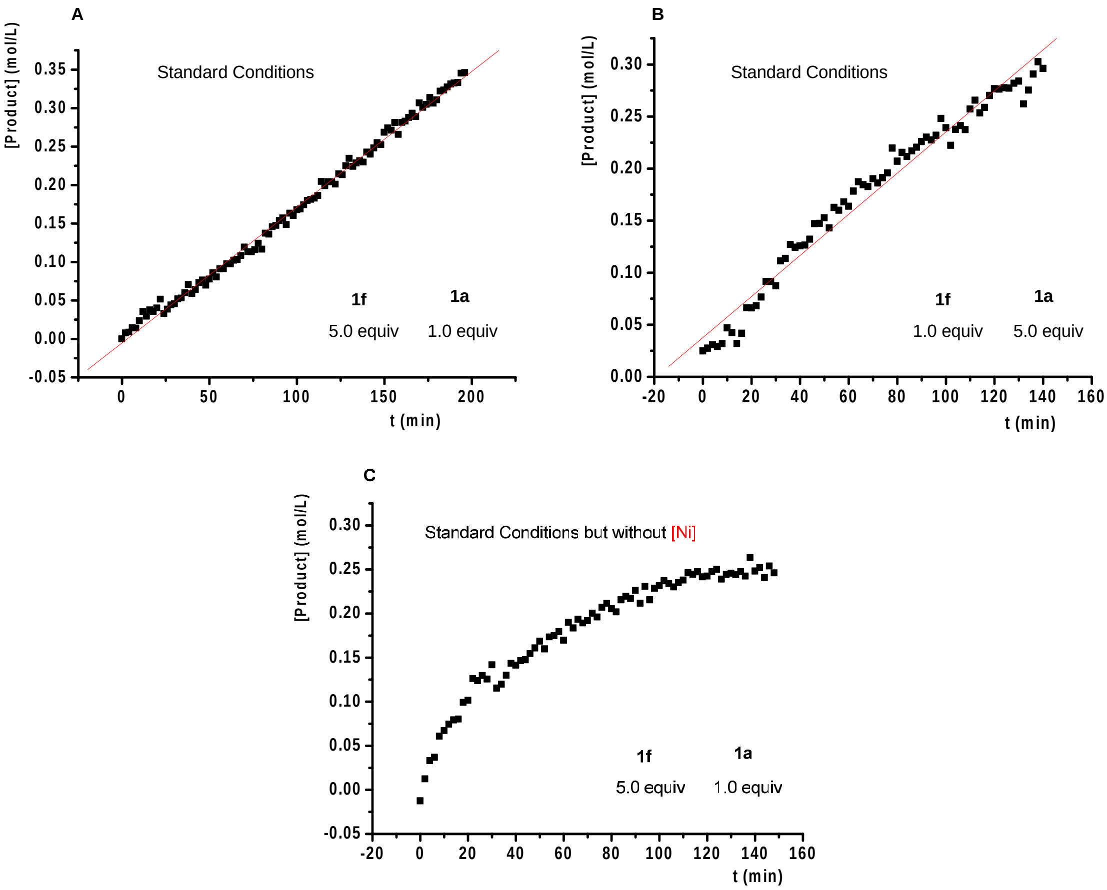
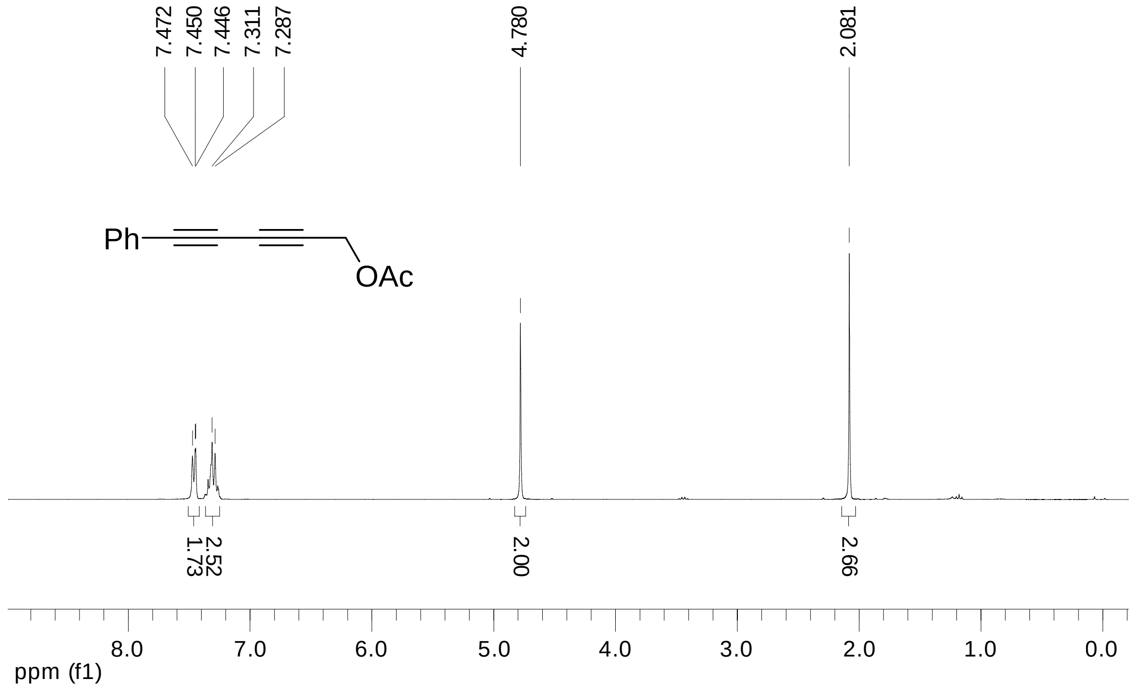
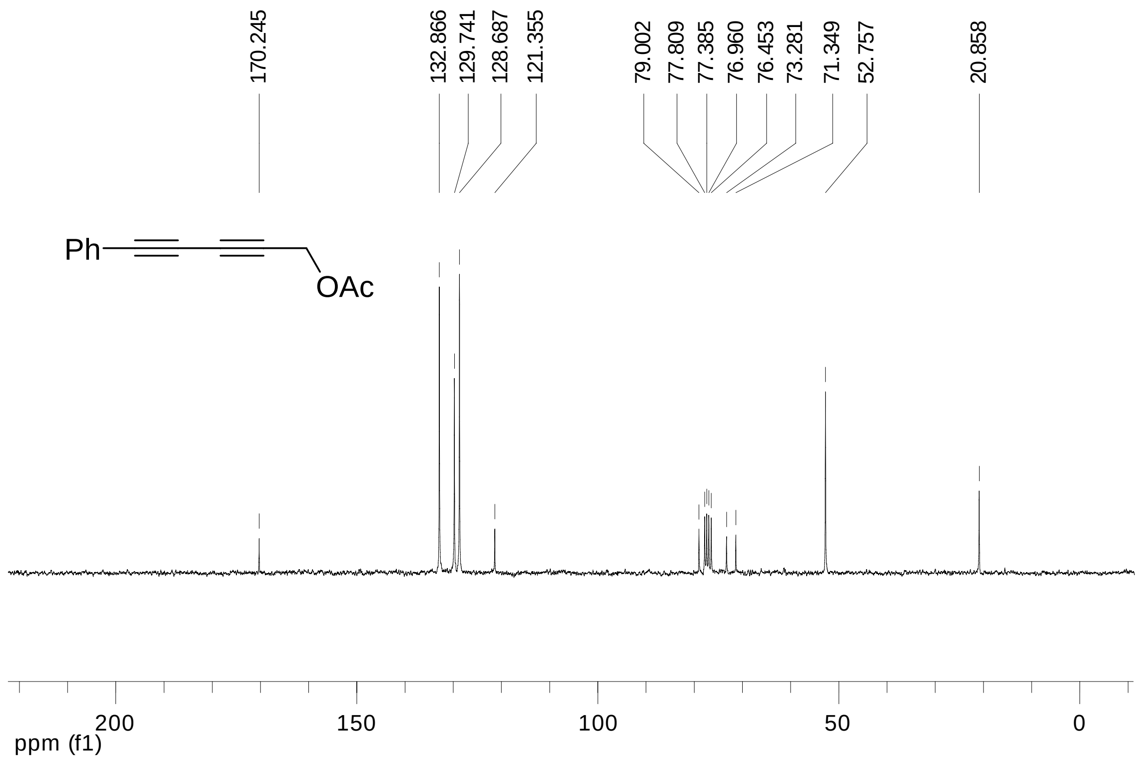


Figure 3. Time profiles of hetero-coupling of phenylacetylene **1a** and 2-methylbut-3-yn-2-ol **1f**. Standard conditions: Ni(II) / Cu(I) [$NiCl_2 \cdot 6H_2O$ (5 mol%), CuI (5 mol%)], TMEDA (20 mol%), 2 mL CH_3CN, O_2 at room temperature. **A**: 2-methylbut-3-yn-2-ol **1f** (5.0 equiv); **B**: phenylacetylene **1a** (5.0 equiv); **C**: 2-methylbut-3-yn-2-ol **1f** (5.0 equiv) without [Ni].

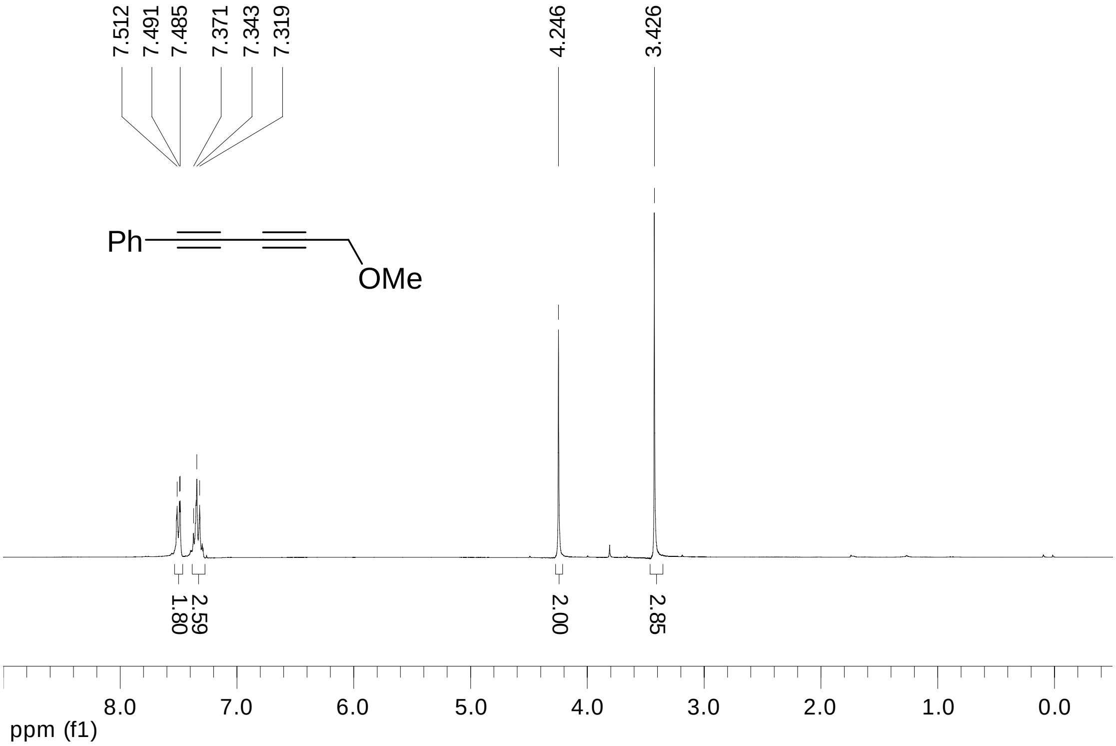
Spectrum

2a

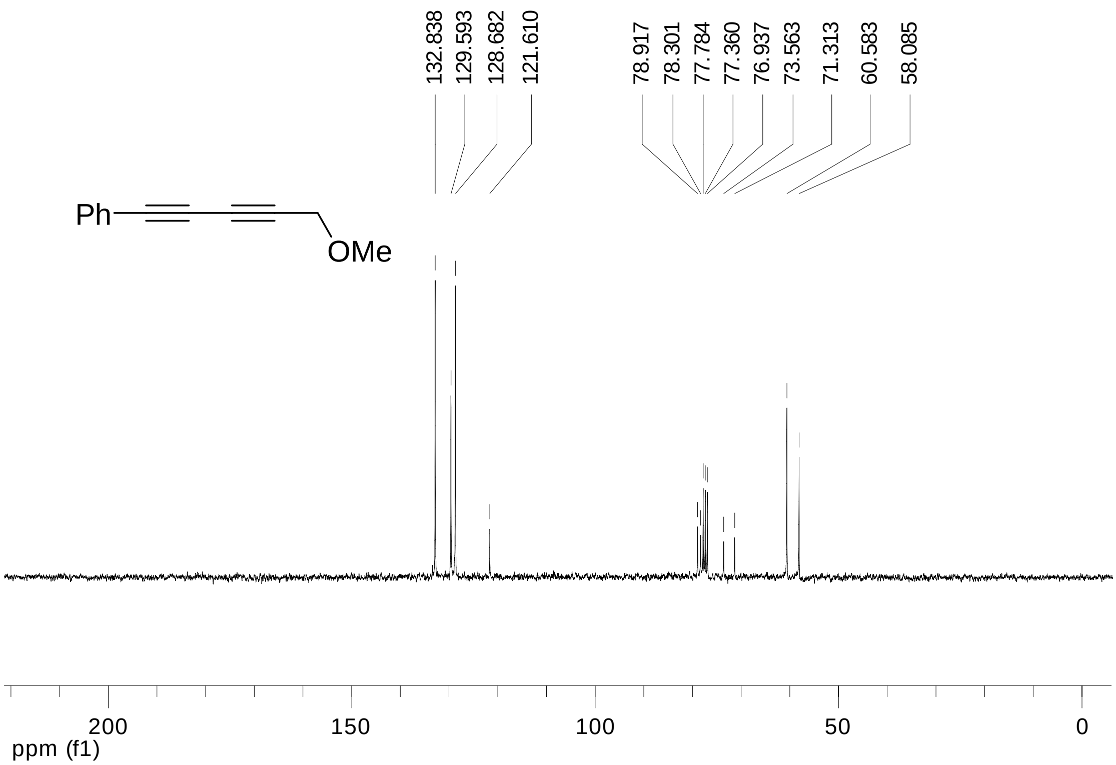

7.472
7.450
7.446
7.311
7.287
4.780
2.081
Ph
OAc
1.73
2.52
2.00
2.66
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


170.245
132.866
129.741
128.687
121.355
79.002
77.809
77.385
76.960
76.453
73.281
71.349
52.757
20.858
Ph
OAc
200
150
100
50
0
ppm (f1)

2b

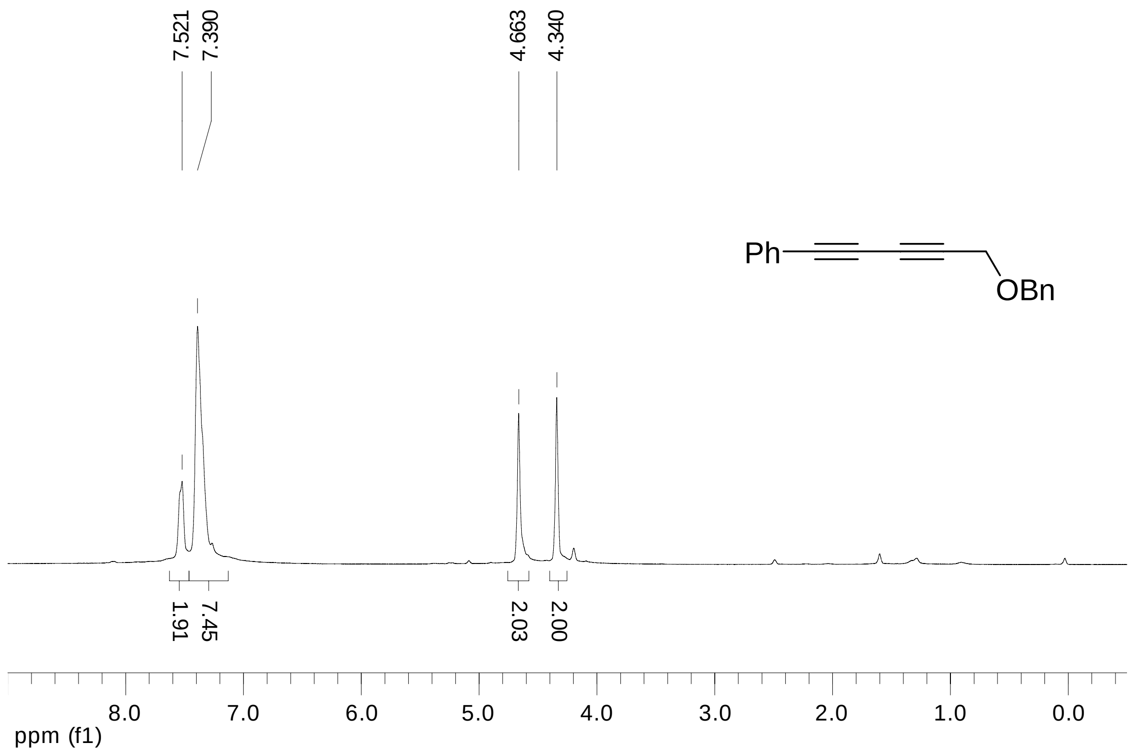


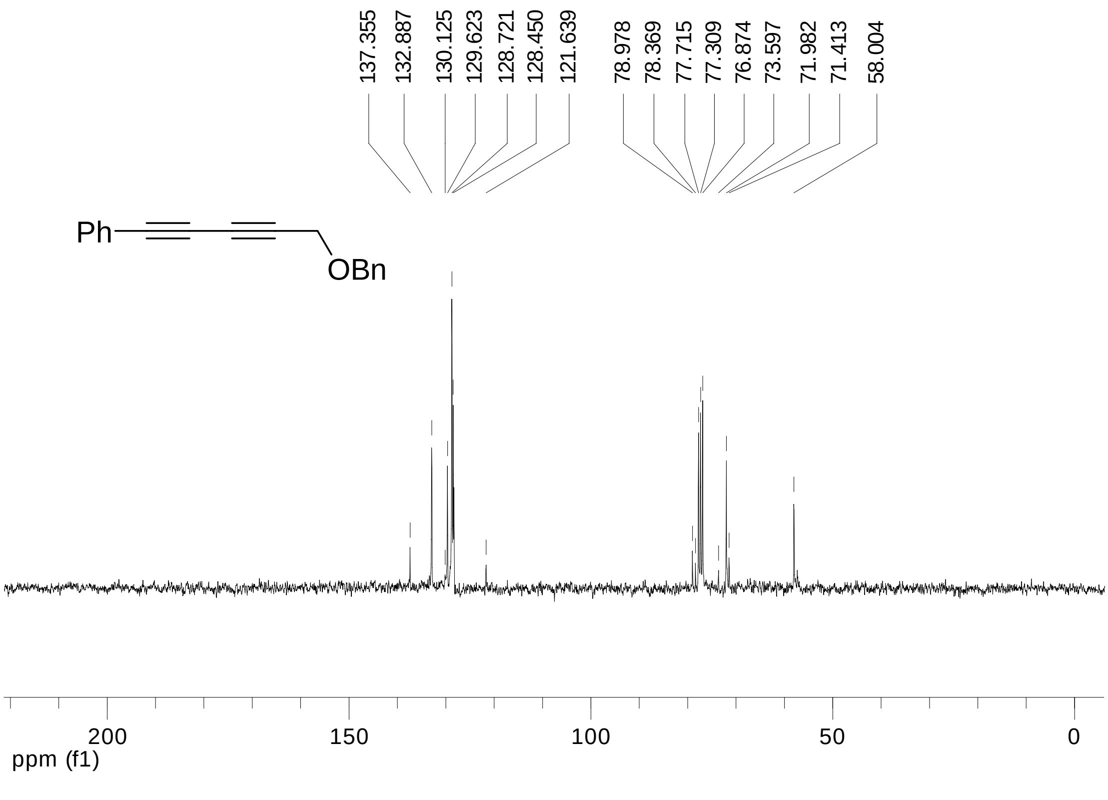
7.512
7.491
7.485
7.371
7.343
7.319
4.246
3.426
Ph
OMe
1.80
2.59
2.00
2.85
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)



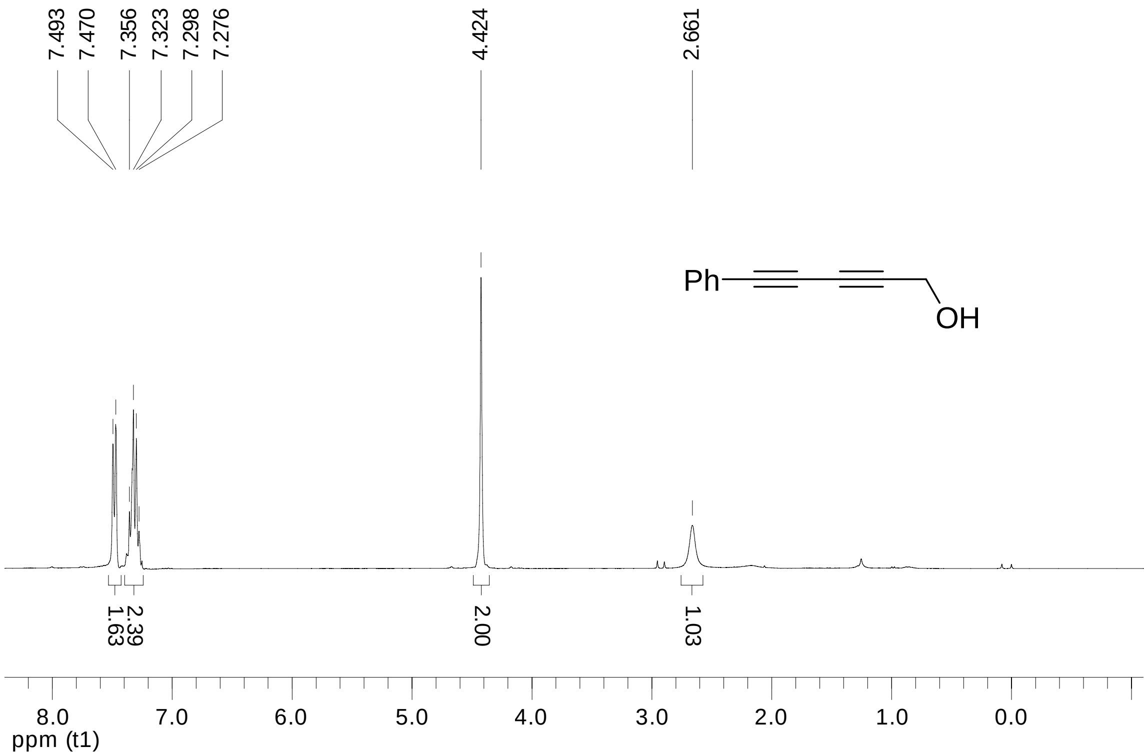
132.838
129.593
128.682
121.610
78.917
78.301
77.784
77.360
76.937
73.563
71.313
60.583
58.085
Ph
OMe
200
150
100
50
0
ppm (f1)

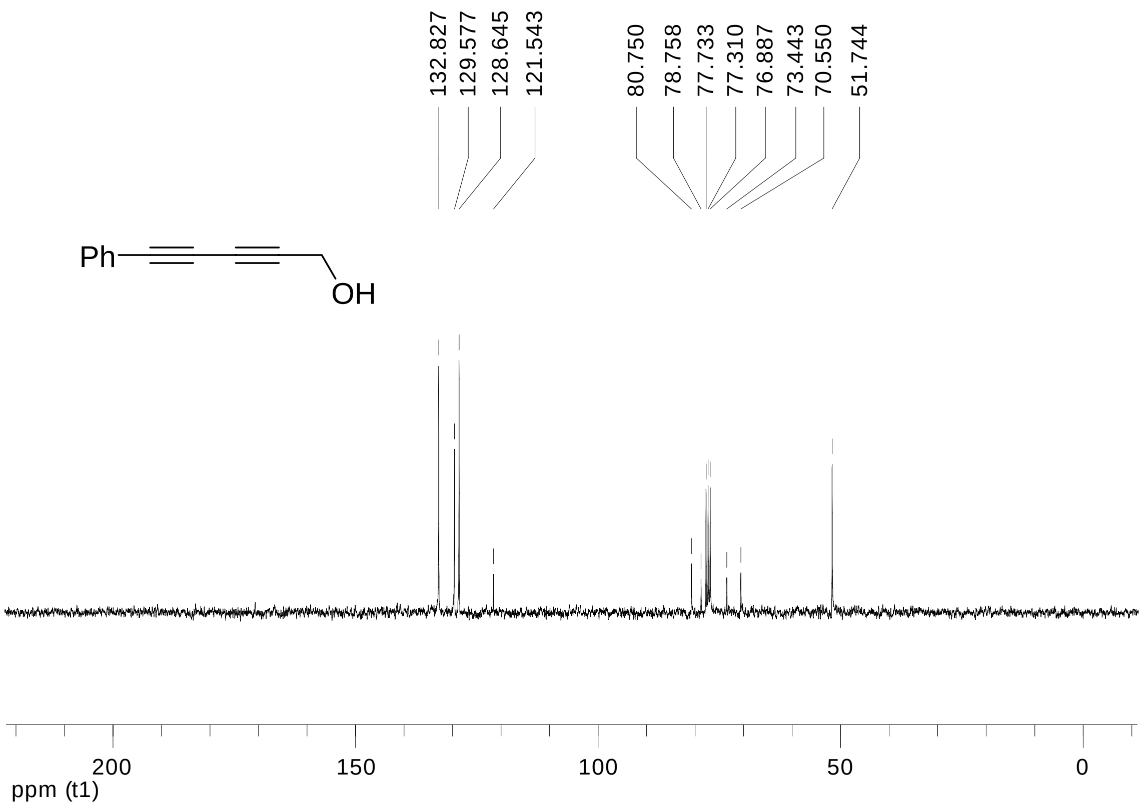
2c


7.521
7.390
4.663
4.340
Ph
OBn
1.91
7.45
2.03
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

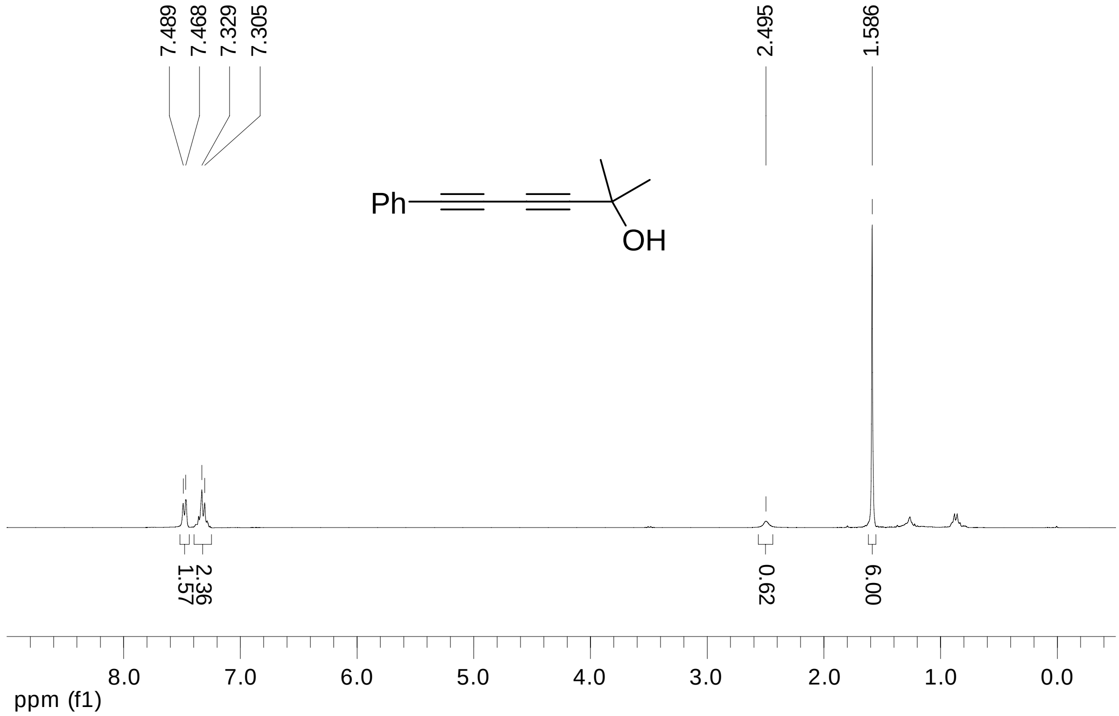

137.355
132.887
130.125
129.623
128.721
128.450
121.639
78.978
78.369
77.715
77.309
76.874
73.597
71.982
71.413
58.004
Ph
OBn
200
150
100
50
0
ppm (f1)

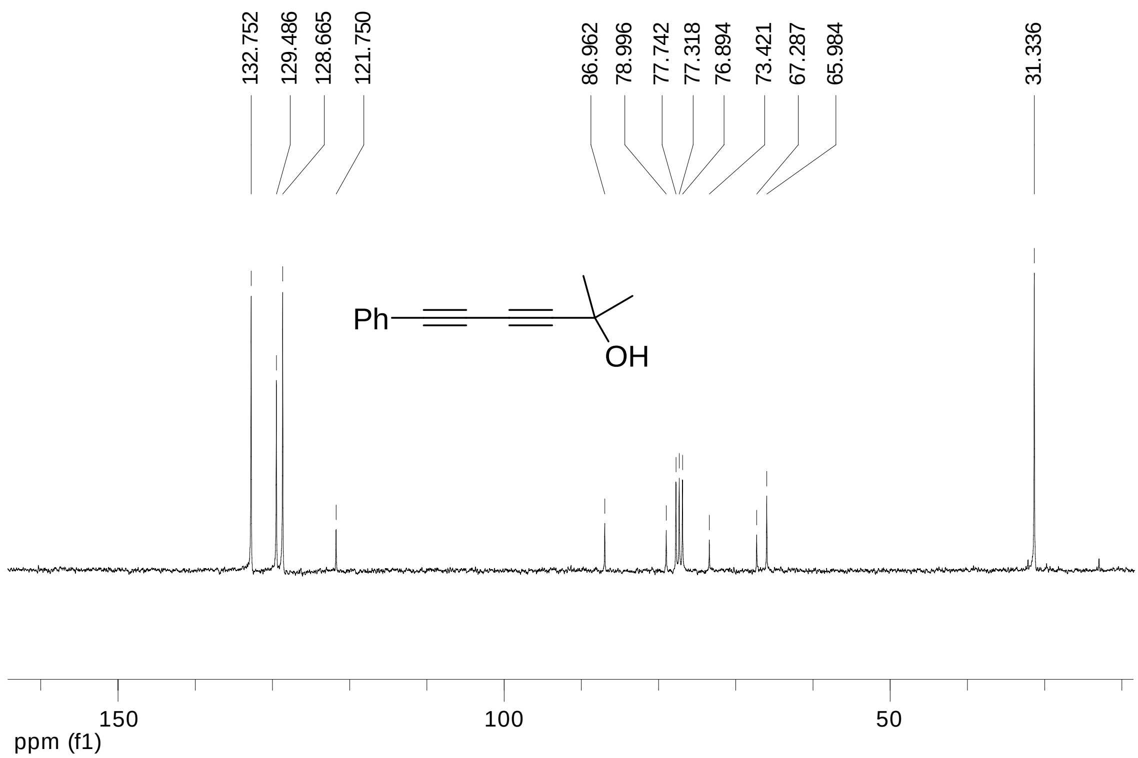
2d


7.493
7.470
7.356
7.323
7.298
7.276
4.424
2.661
Ph
OH
1.63
2.39
2.00
1.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

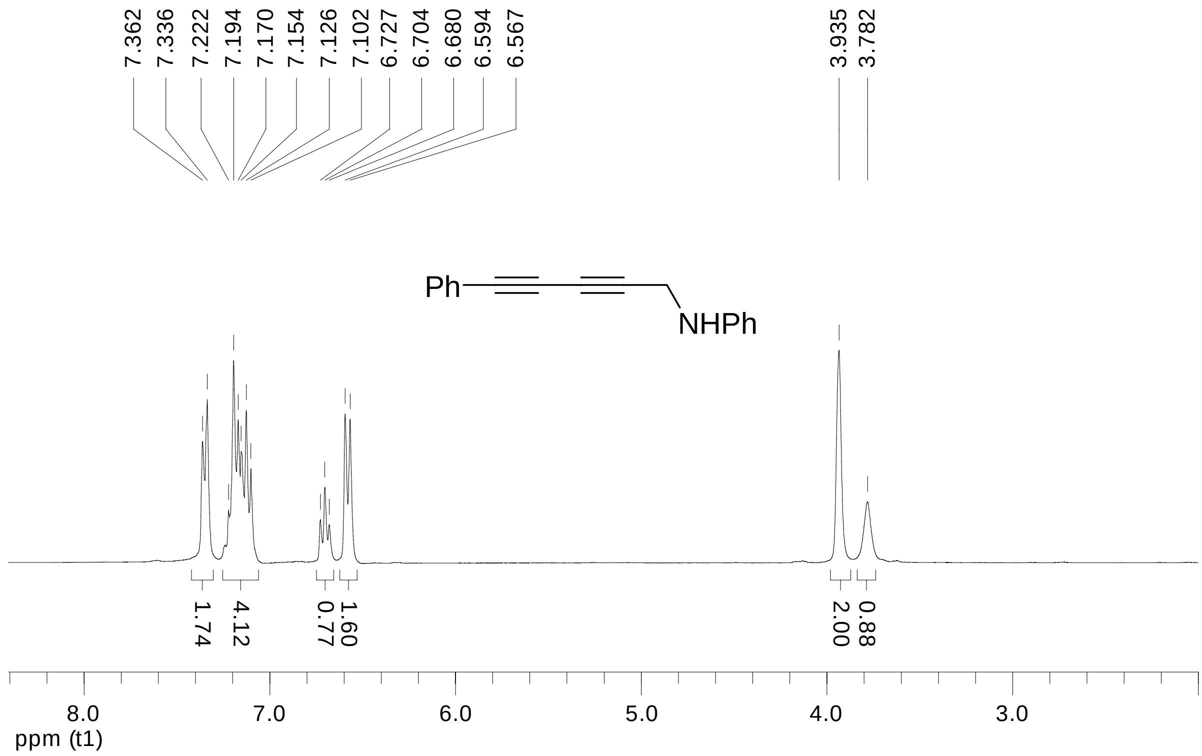

132.827
129.577
128.645
121.543
80.750
78.758
77.733
77.310
76.887
73.443
70.550
51.744
Ph
OH
200
150
100
50
0
ppm (t1)

2e

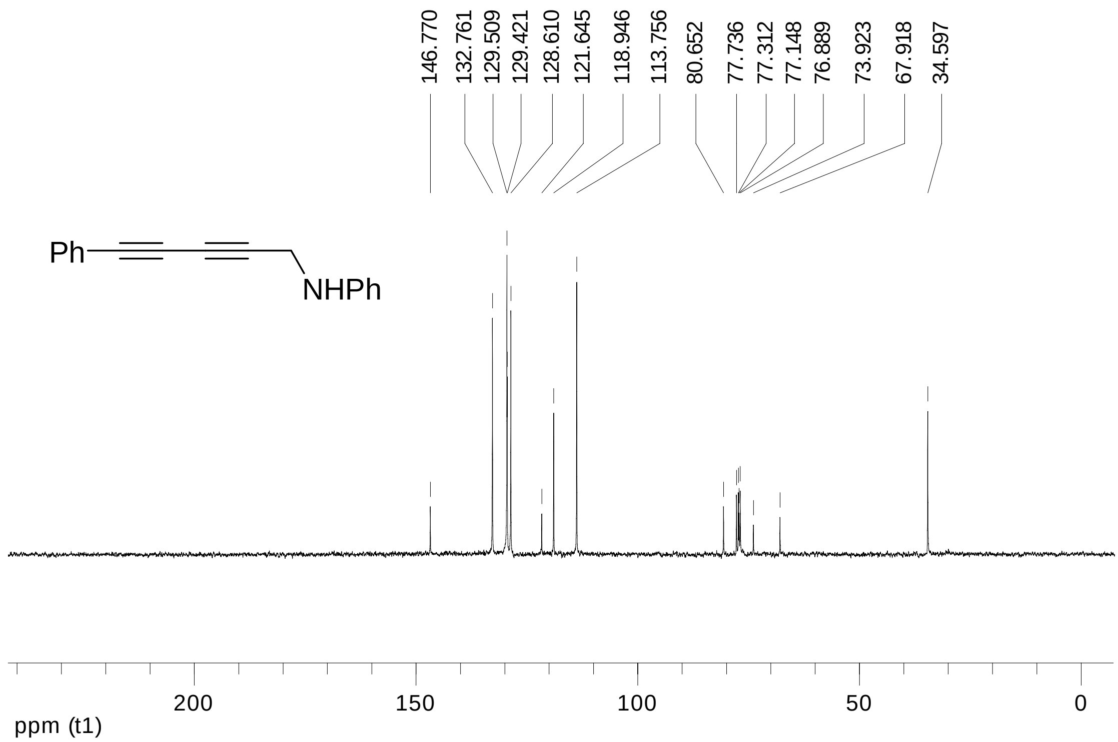

7.489
7.468
7.329
7.305
2.495
1.586
Ph
OH
1.57
2.36
0.62
6.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


132.752
129.486
128.665
121.750
86.962
78.996
77.742
77.318
76.894
73.421
67.287
65.984
31.336
Ph
OH
150
100
50
ppm (f1)

2f

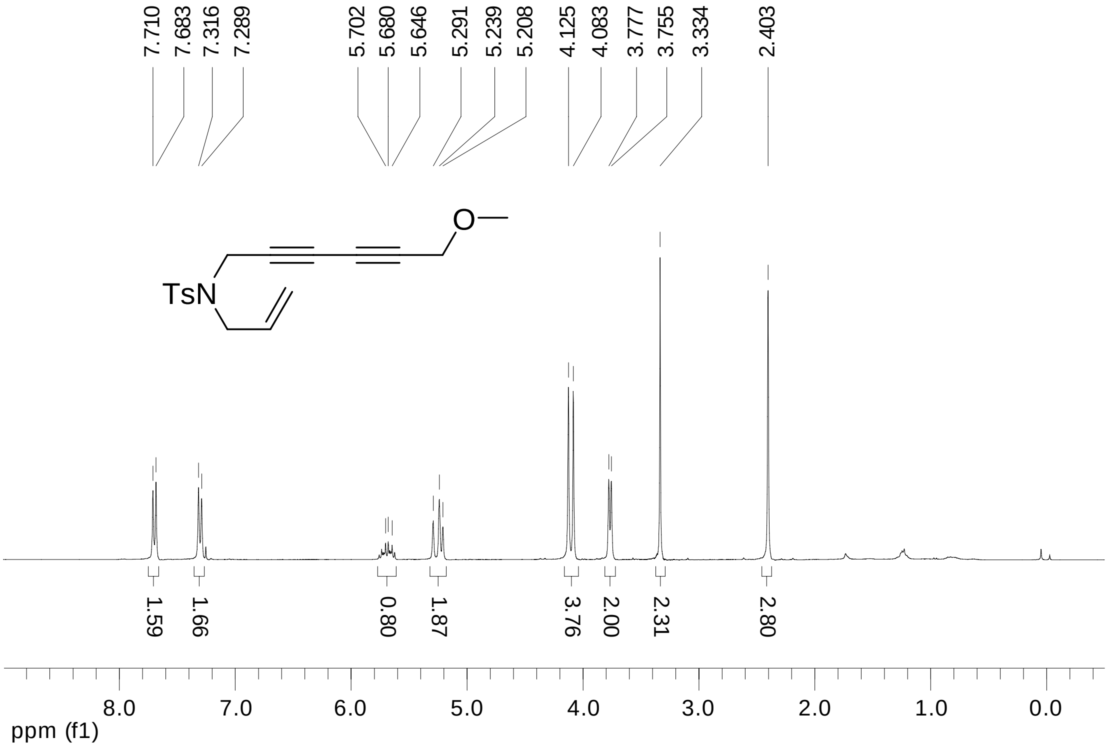


7.362
7.336
7.222
7.194
7.170
7.154
7.126
7.102
6.727
6.704
6.680
6.594
6.567
3.935
3.782
Ph
NHPh
1.74
4.12
0.77
1.60
2.00
0.88
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

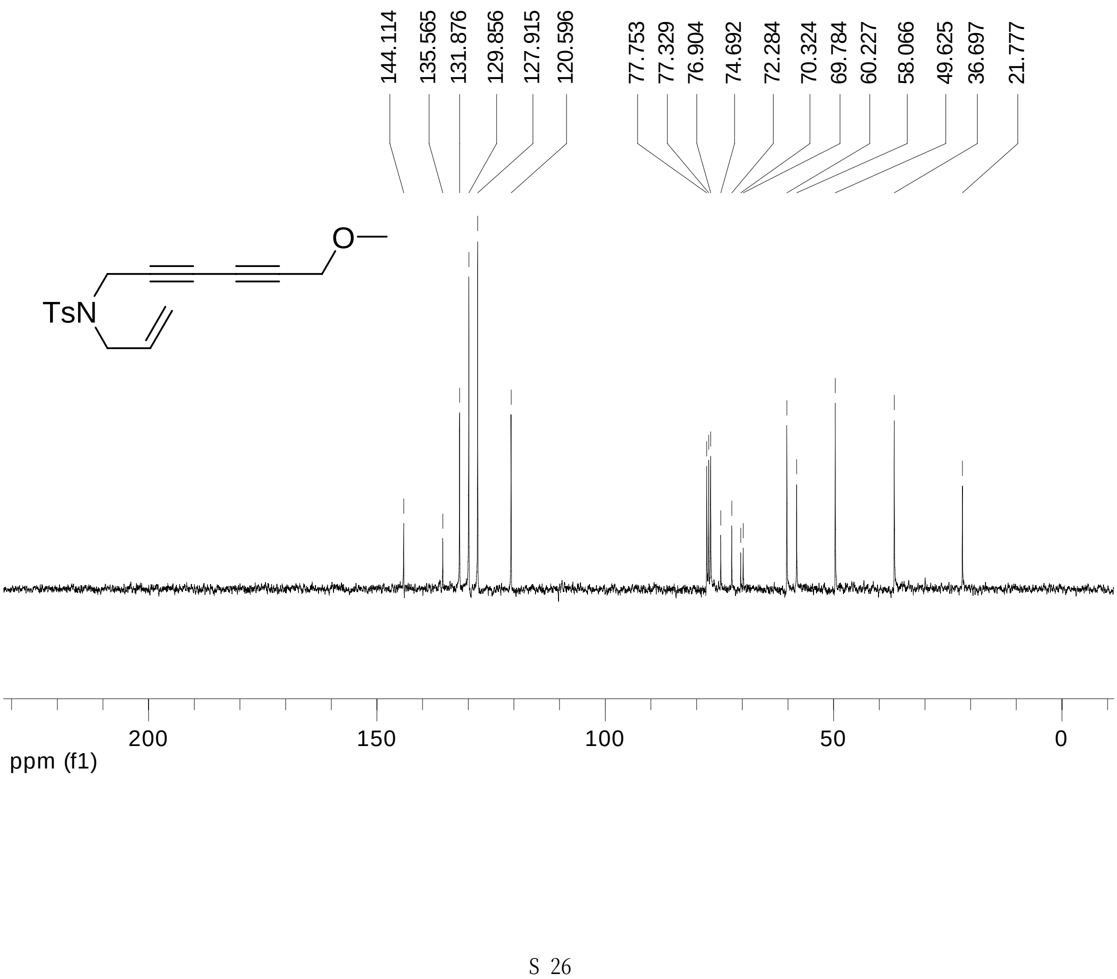


146.770
132.761
129.509
129.421
128.610
121.645
118.946
113.756
80.652
77.736
77.312
77.148
76.889
73.923
67.918
34.597
Ph
NHPh
200
150
100
50
0
ppm (t1)

2g

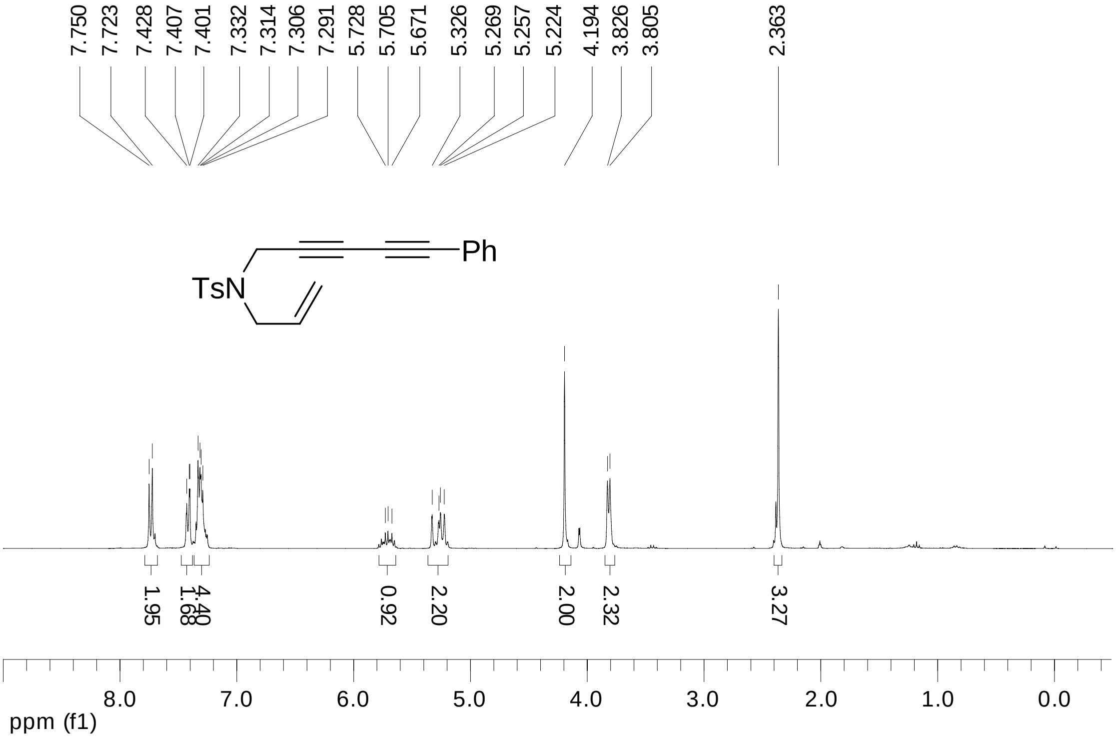


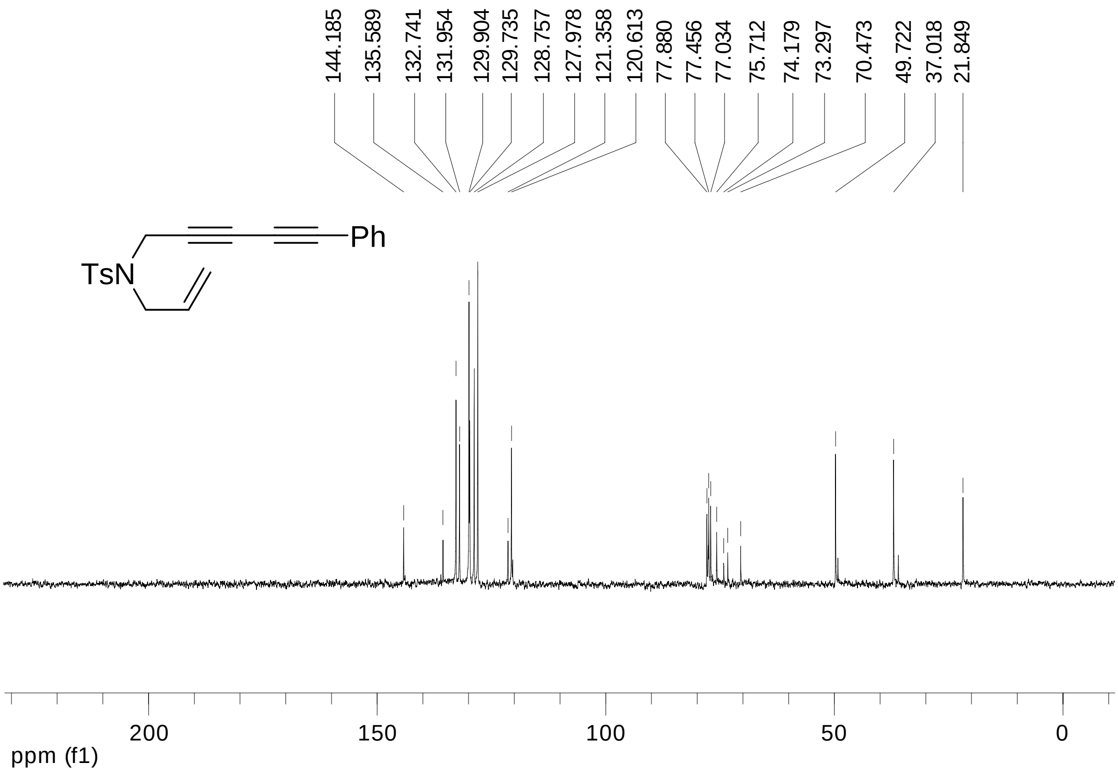
7.710
7.683
7.316
7.289
5.702
5.680
5.646
5.291
5.239
5.208
4.125
4.083
3.777
3.755
3.334
2.403
TsN
O
1.59
1.66
0.80
1.87
3.76
2.00
2.31
2.80
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)



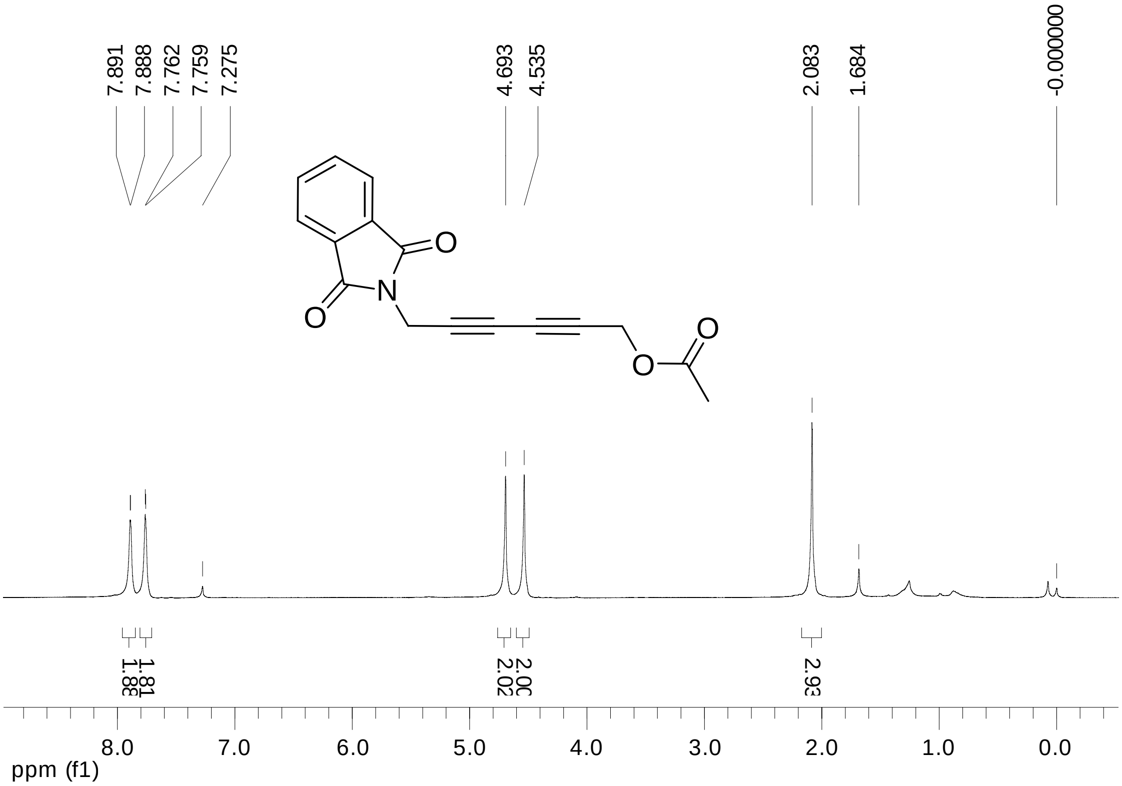
144.114
135.565
131.876
129.856
127.915
120.596
77.753
77.329
76.904
74.692
72.284
70.324
69.784
60.227
58.066
49.625
36.697
21.777
TsN
O
200
150
100
50
0
ppm (f1)

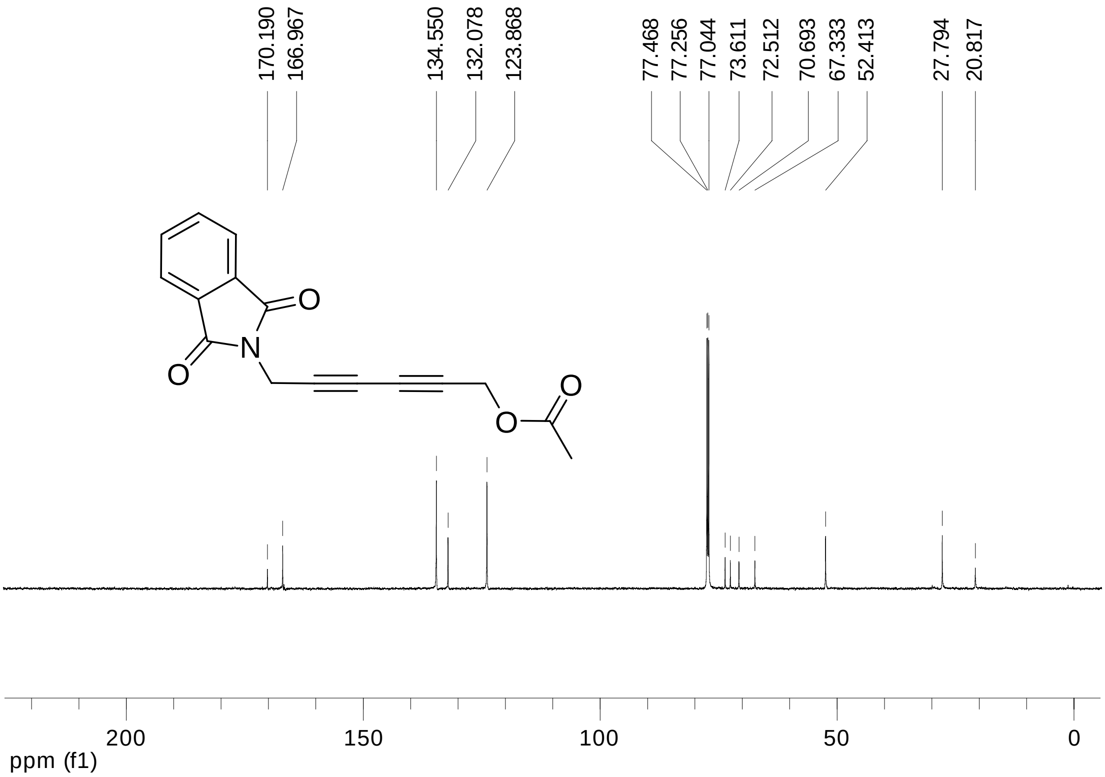
2h



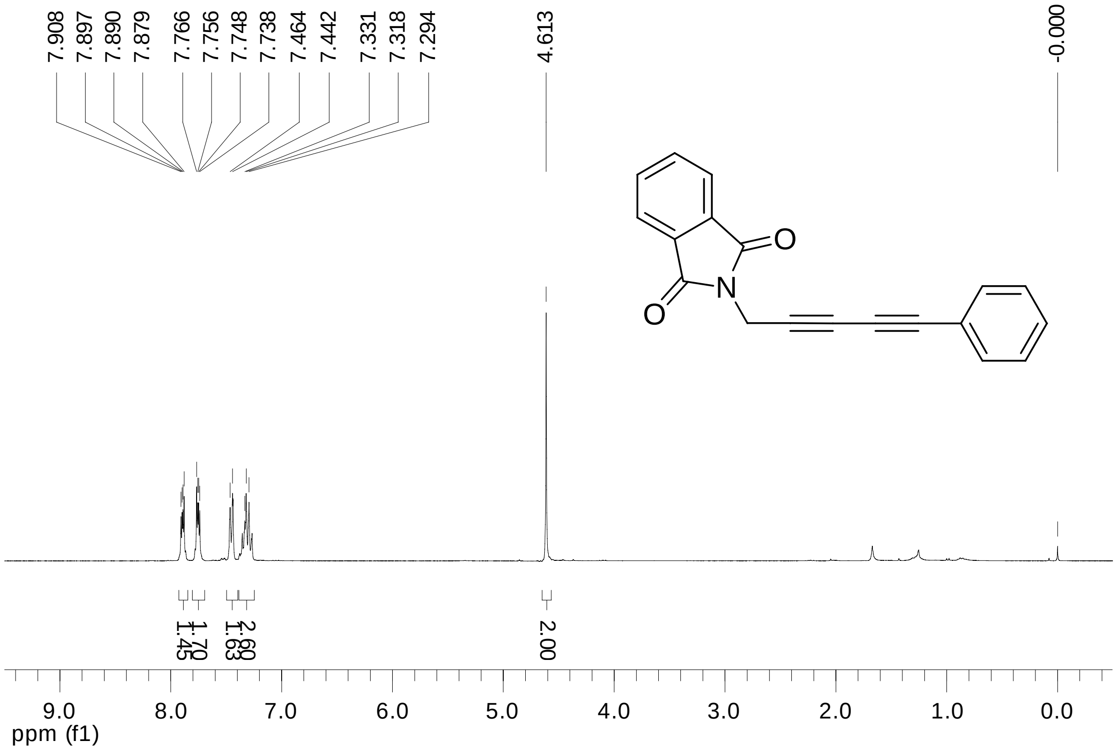


2i

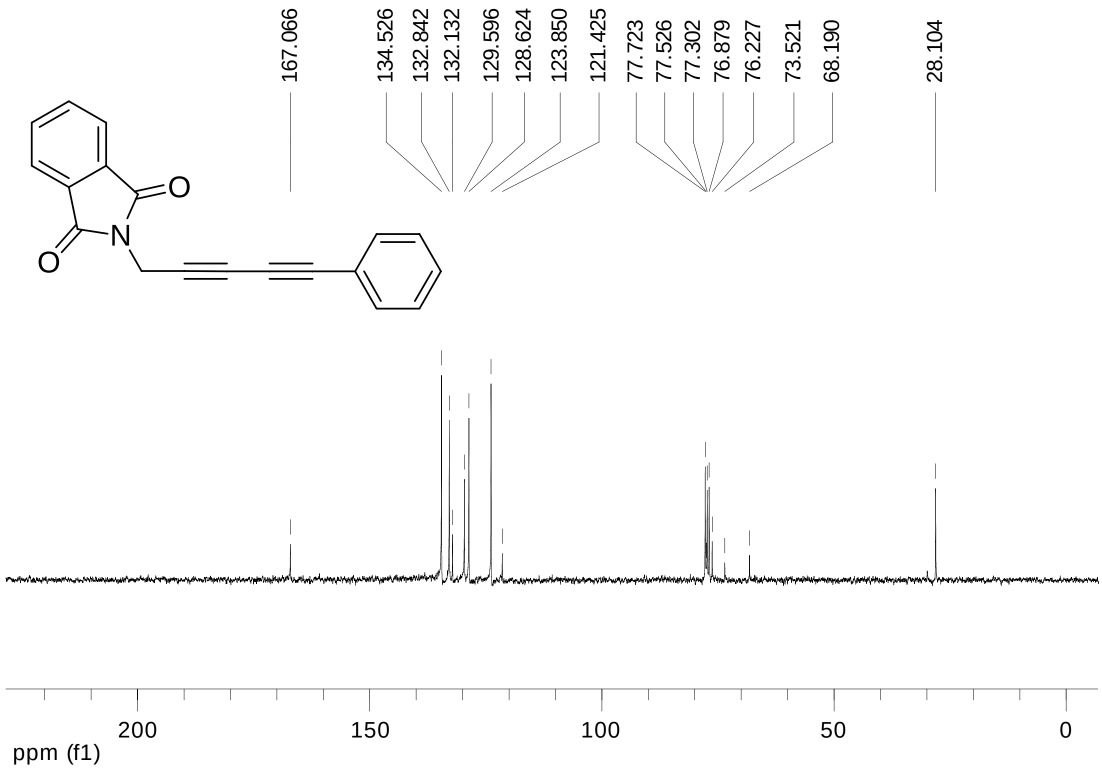

7.891
7.888
7.762
7.759
7.275
4.693
4.535
2.083
1.684
-0.000000
O
N
O
O
O
1.83
1.81
2.02
2.00
2.93
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


170.190
166.967
134.550
132.078
123.868
77.468
77.256
77.044
73.611
72.512
70.693
67.333
52.413
27.794
20.817
O
N
O
O
O
200
150
100
50
0
ppm (f1)

2j

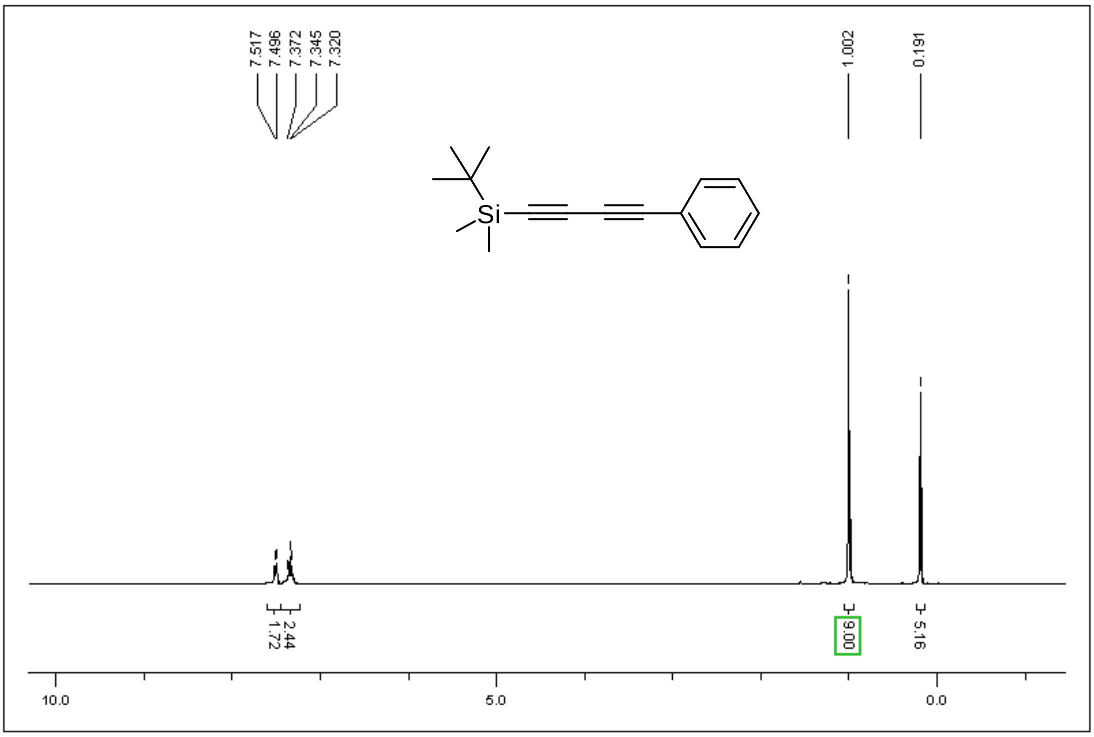


7.908
7.897
7.890
7.879
7.766
7.756
7.748
7.738
7.464
7.442
7.331
7.318
7.294
4.613
-0.000
O
N
O
1.45
1.70
1.63
2.60
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

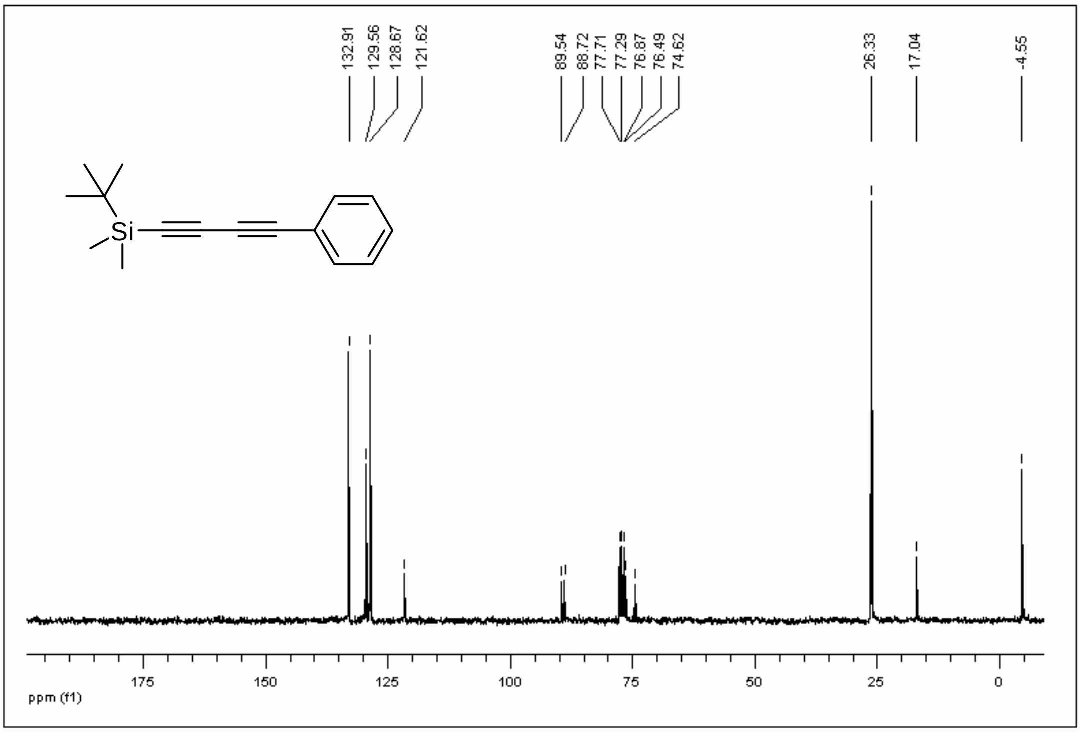


167.066
134.526
132.842
132.132
129.596
128.624
123.850
121.425
77.723
77.526
77.302
76.879
76.227
73.521
68.190
28.104
O
N
O
200
150
100
50
0
ppm (f1)

2k

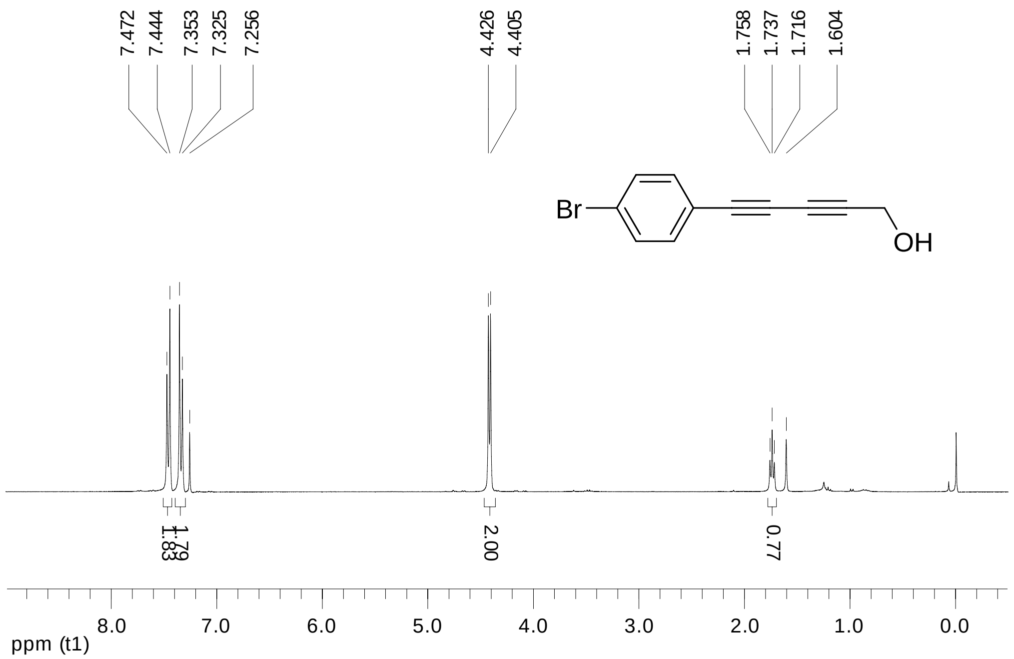


7.517
7.496
7.372
7.345
7.320
1.002
0.191
Si
1.72
2.44
9.00
5.16
10.0
5.0
0.0

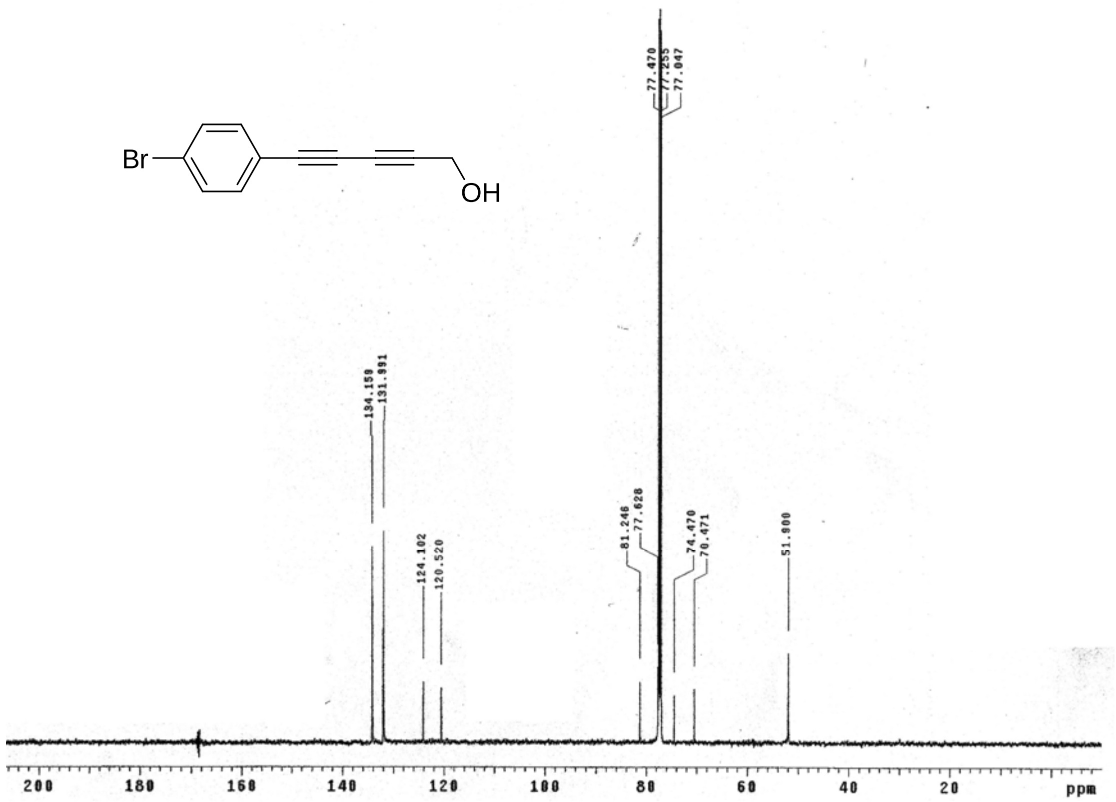


132.91
129.56
128.67
121.62
89.54
88.72
77.71
77.29
76.87
76.49
74.62
26.33
17.04
-4.55
Si
175
150
125
100
75
50
25
0
ppm (f1)

2l

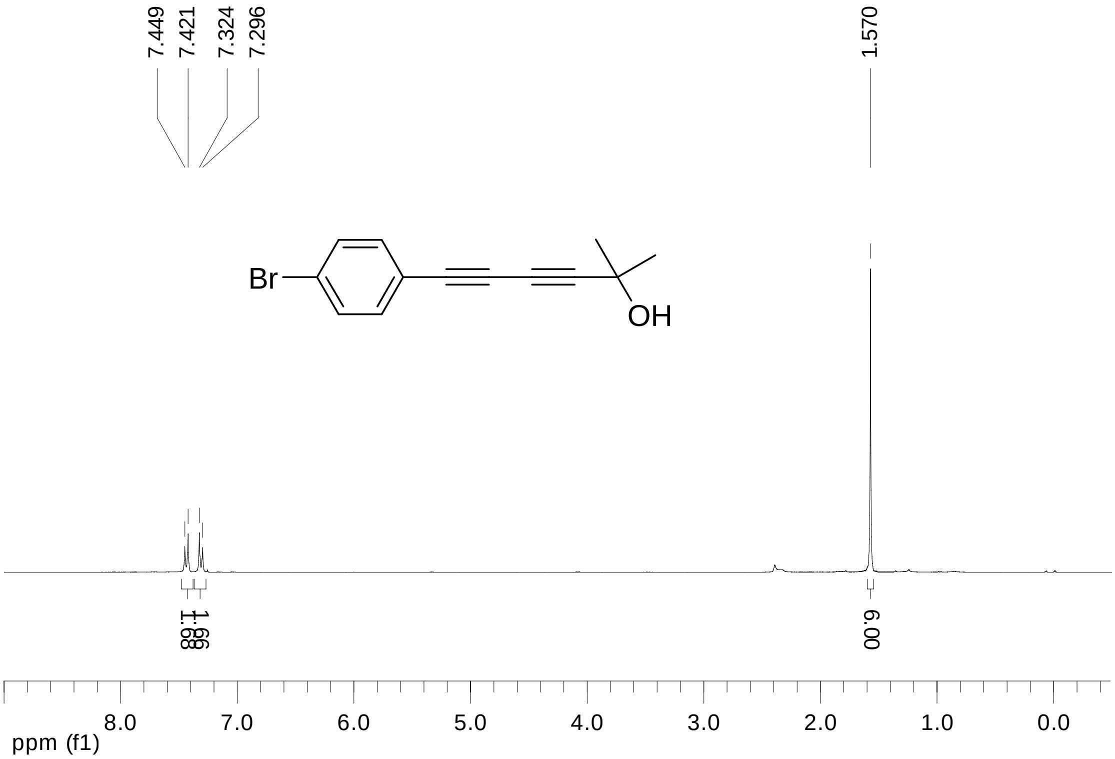


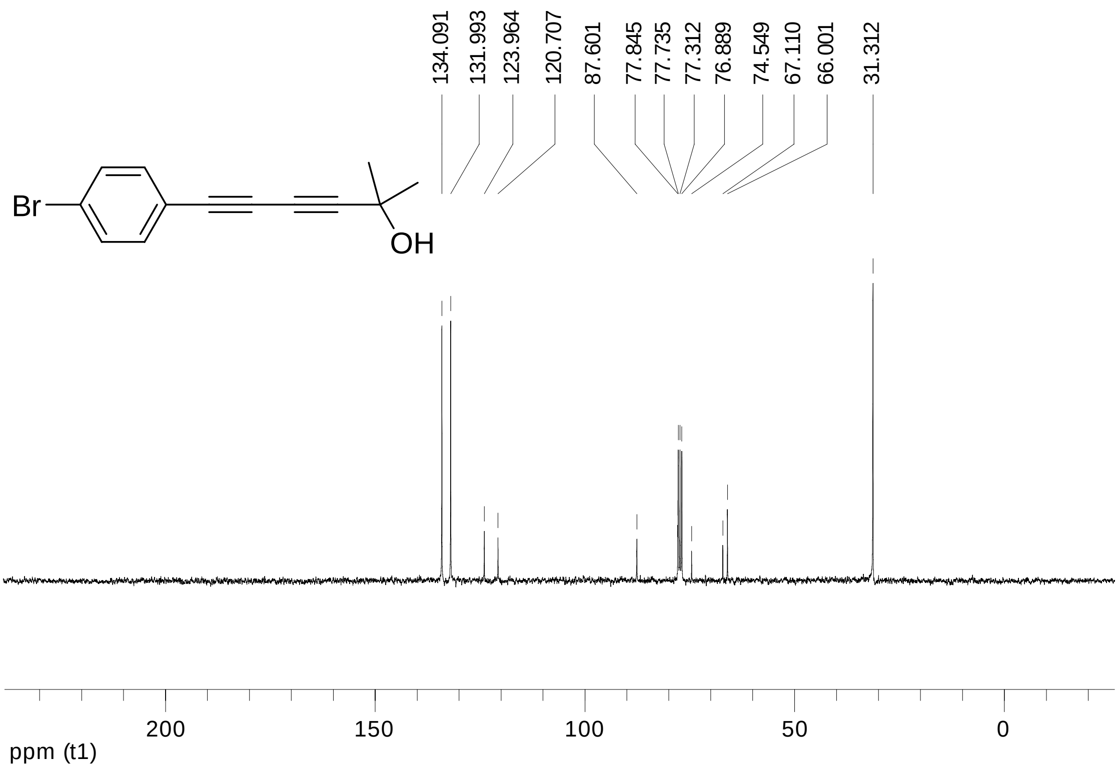
7.472
7.444
7.353
7.325
7.256
4.426
4.405
1.758
1.737
1.716
1.604
Br
OH
1.83
1.79
2.00
0.77
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)



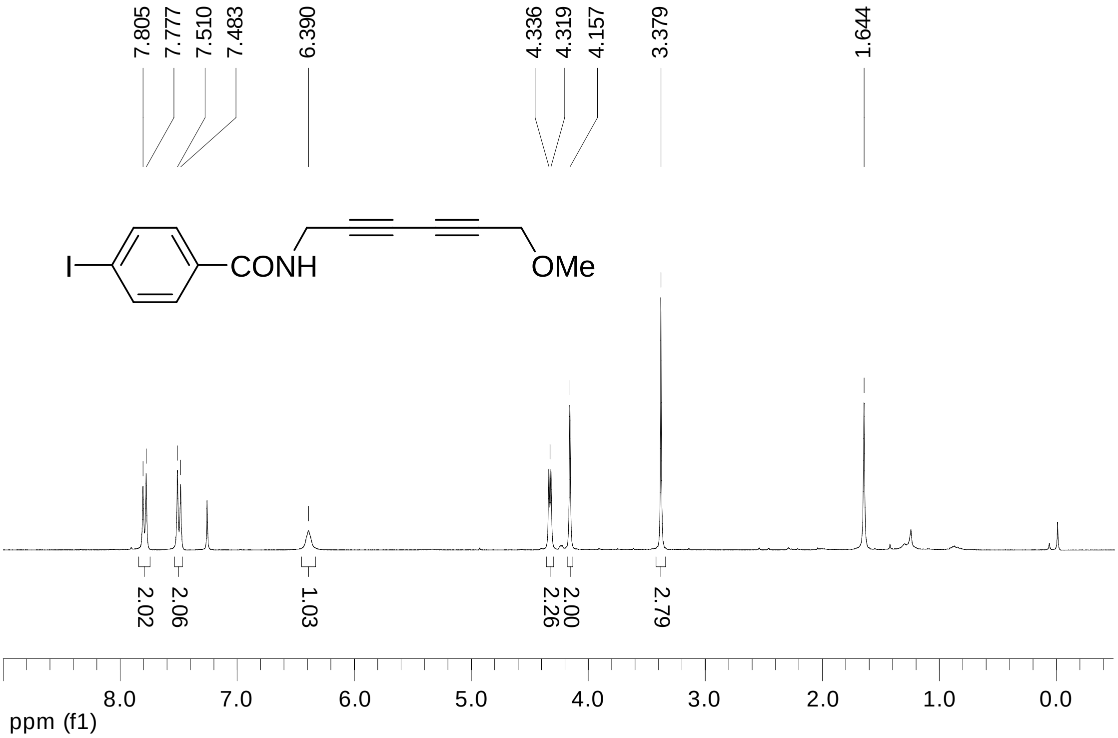
77.470
77.255
77.047
Br
OH
134.150
131.991
124.102
120.520
81.246
77.628
74.470
70.471
51.800
200
180
160
140
120
100
80
60
40
20
ppm

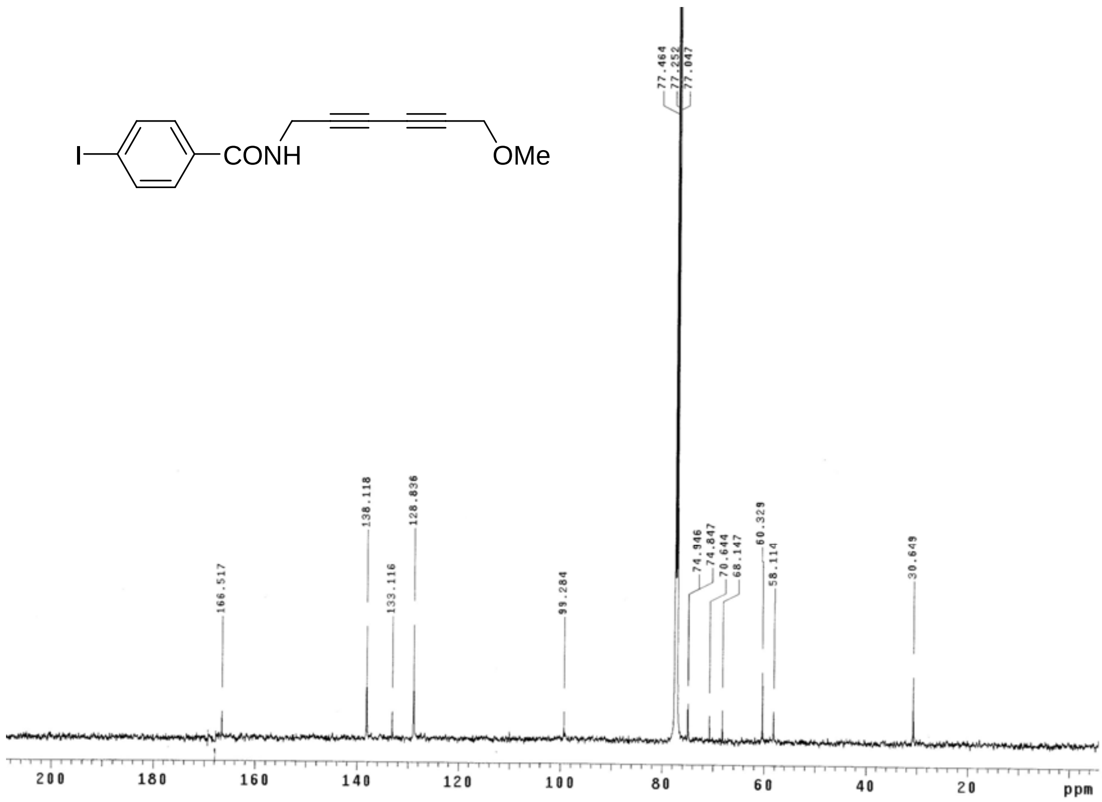
2m


7.449
7.421
7.324
7.296
1.570
Br
OH
1.68
1.66
6.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

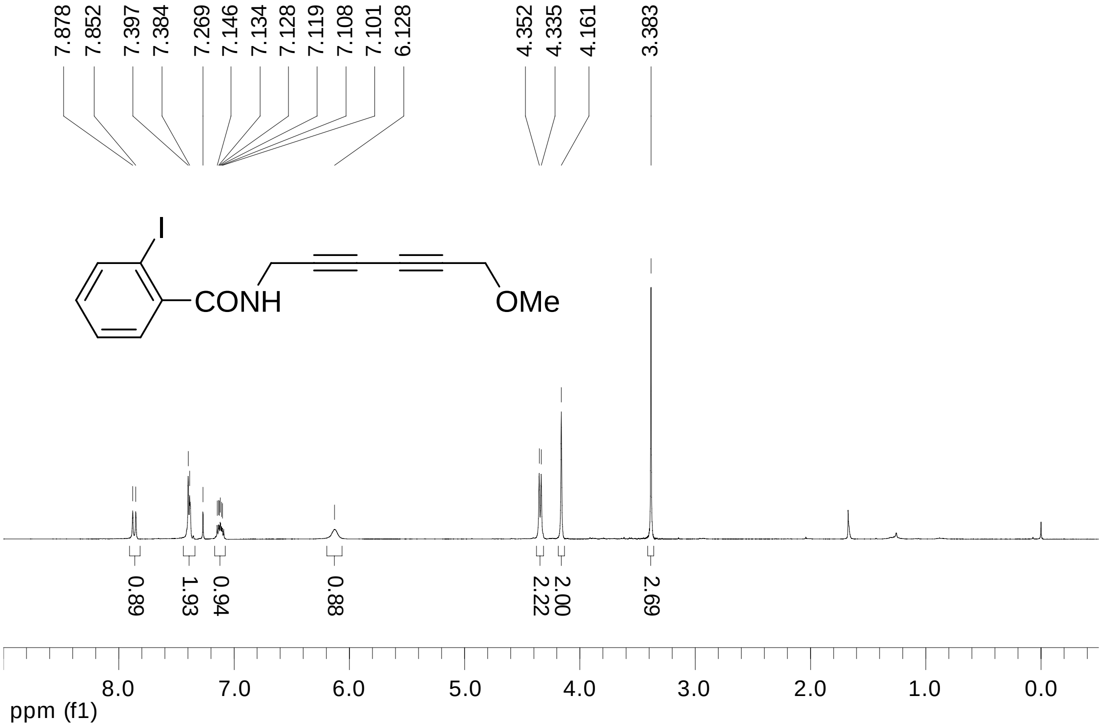

134.091
131.993
123.964
120.707
87.601
77.845
77.735
77.312
76.889
74.549
67.110
66.001
31.312
Br
OH
200
150
100
50
0
ppm (t1)

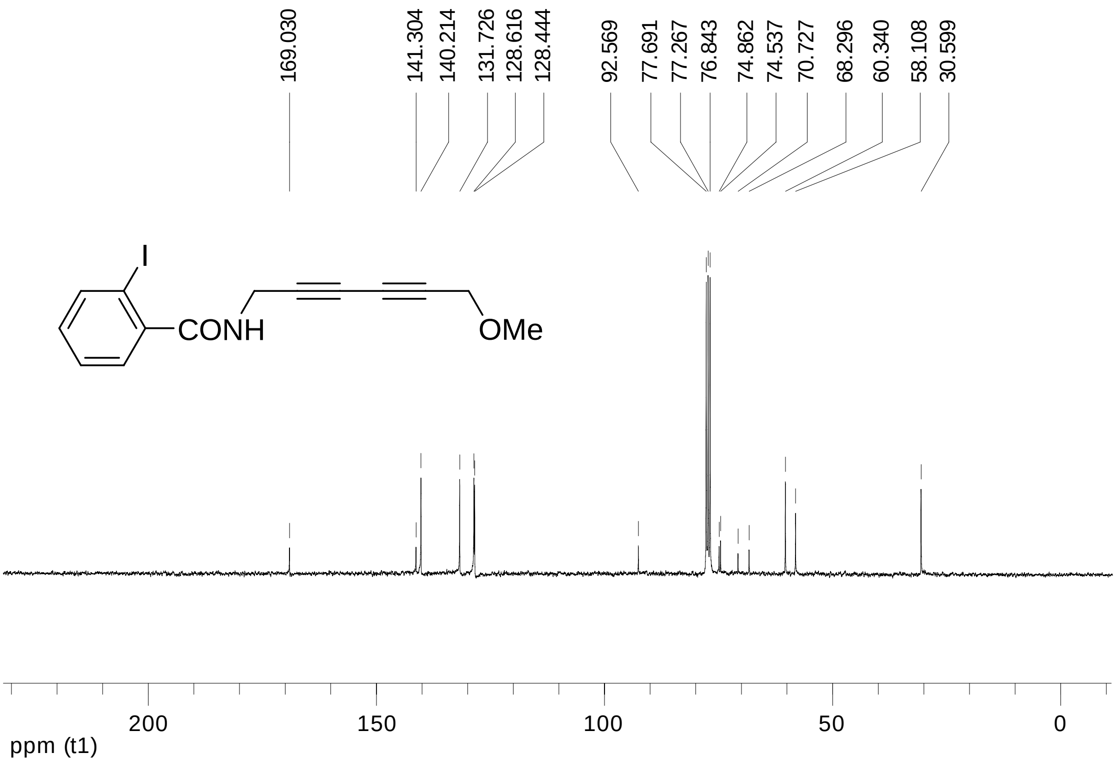
2n


7.805
7.777
7.510
7.483
6.390
4.336
4.319
4.157
3.379
1.644
I
CONH
OMe
2.02
2.06
1.03
2.26
2.00
2.79
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

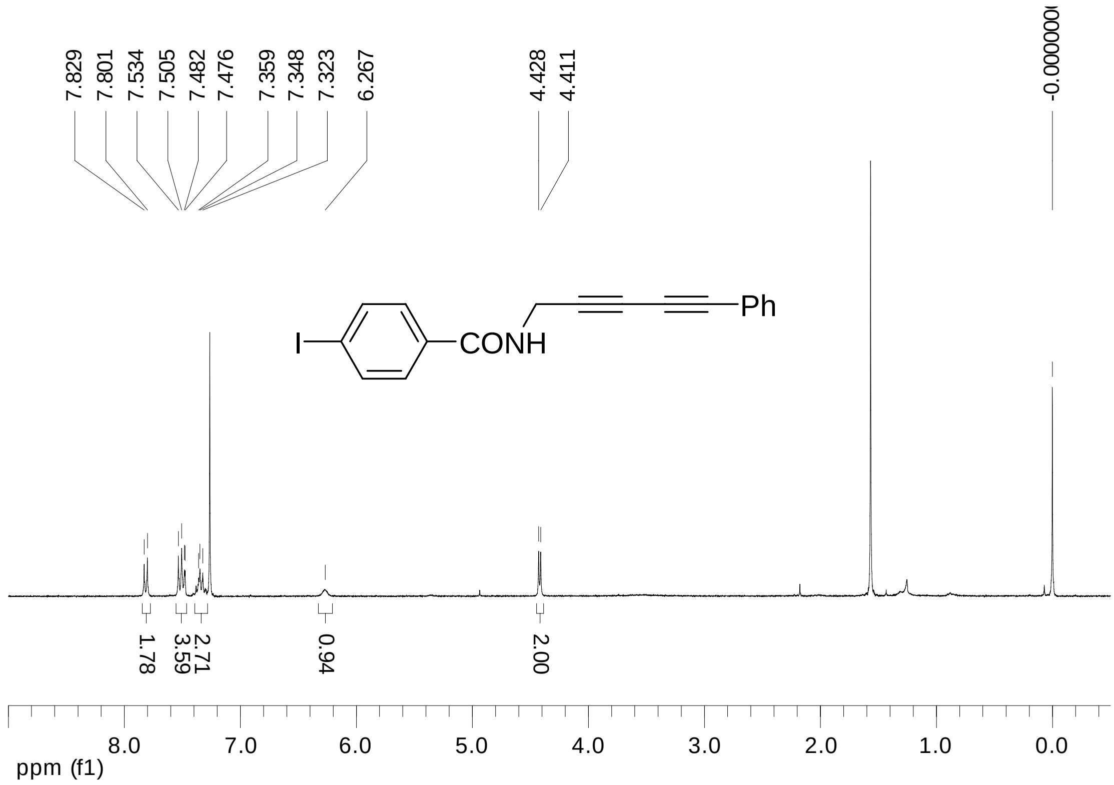

I
CONH
OMe
77.464
77.252
77.047
166.517
138.118
133.116
128.836
99.284
74.946
74.847
70.644
68.147
60.329
58.114
30.649
200
180
160
140
120
100
80
60
40
20
ppm

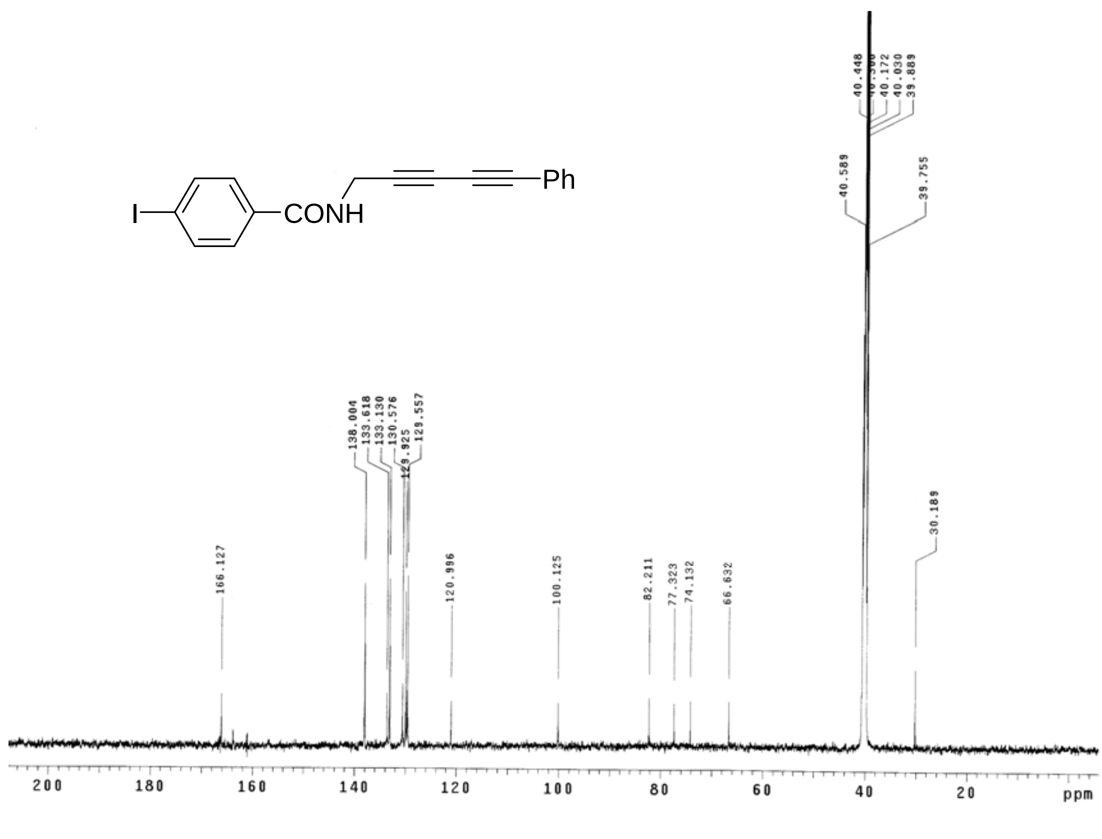
2o


7.878
7.852
7.397
7.384
7.269
7.146
7.134
7.128
7.119
7.108
7.101
6.128
4.352
4.335
4.161
3.383
CONH
OMe
I
0.89
1.93
0.94
0.88
2.22
2.00
2.69
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

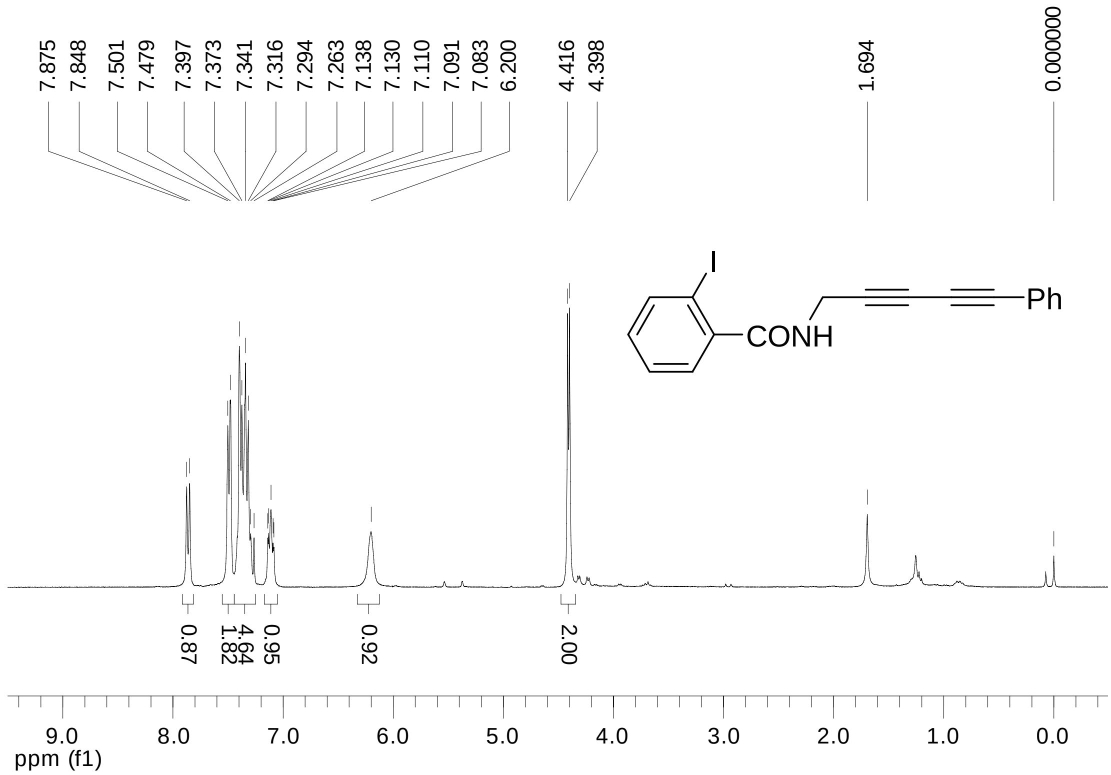

169.030
141.304
140.214
131.726
128.616
128.444
92.569
77.691
77.267
76.843
74.862
74.537
70.727
68.296
60.340
58.108
30.599
I
CONH
OMe
200
150
100
50
0
ppm (t1)

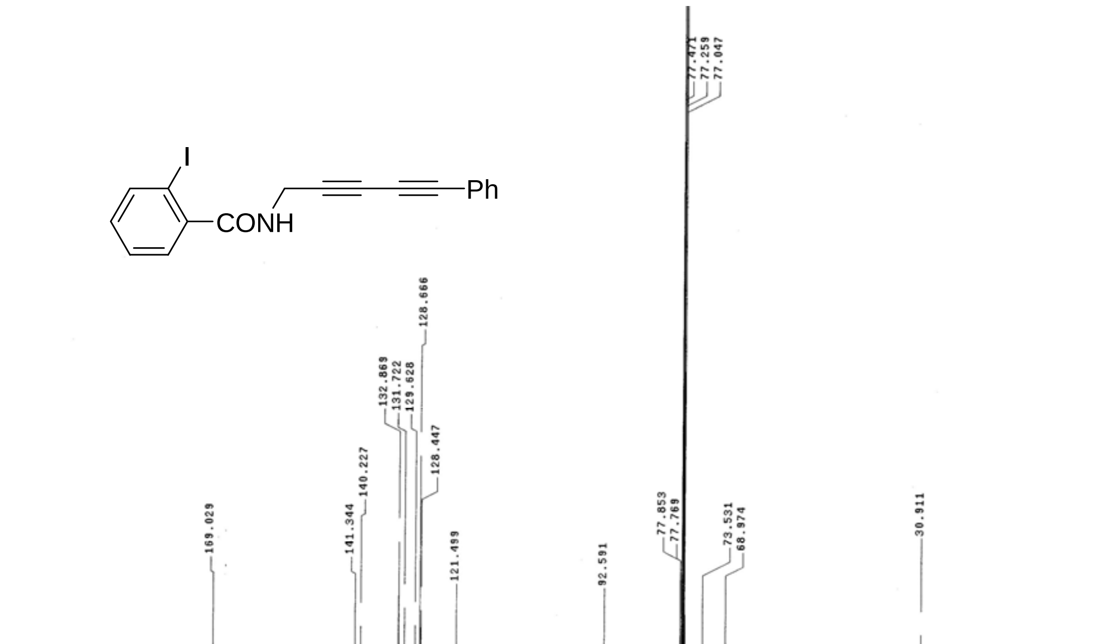
2p


7.829
7.801
7.534
7.505
7.482
7.476
7.359
7.348
7.323
6.267
4.428
4.411
-0.000000
I
CONH
Ph
1.78
3.59
2.71
0.94
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

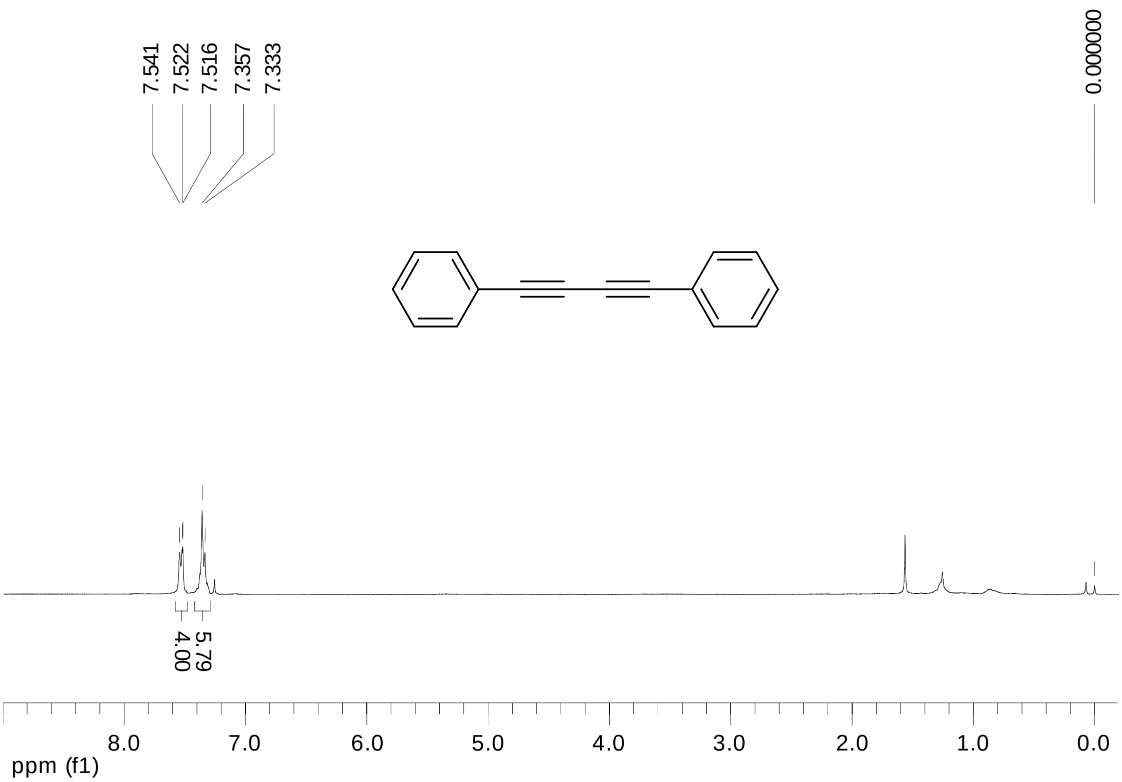

40.448
40.172
40.030
39.889
40.589
39.755
I
CONH
Ph
138.004
133.618
133.130
130.576
129.925
129.557
166.127
120.996
100.125
82.211
77.323
74.132
66.632
30.189
200
180
160
140
120
100
80
60
40
20
ppm

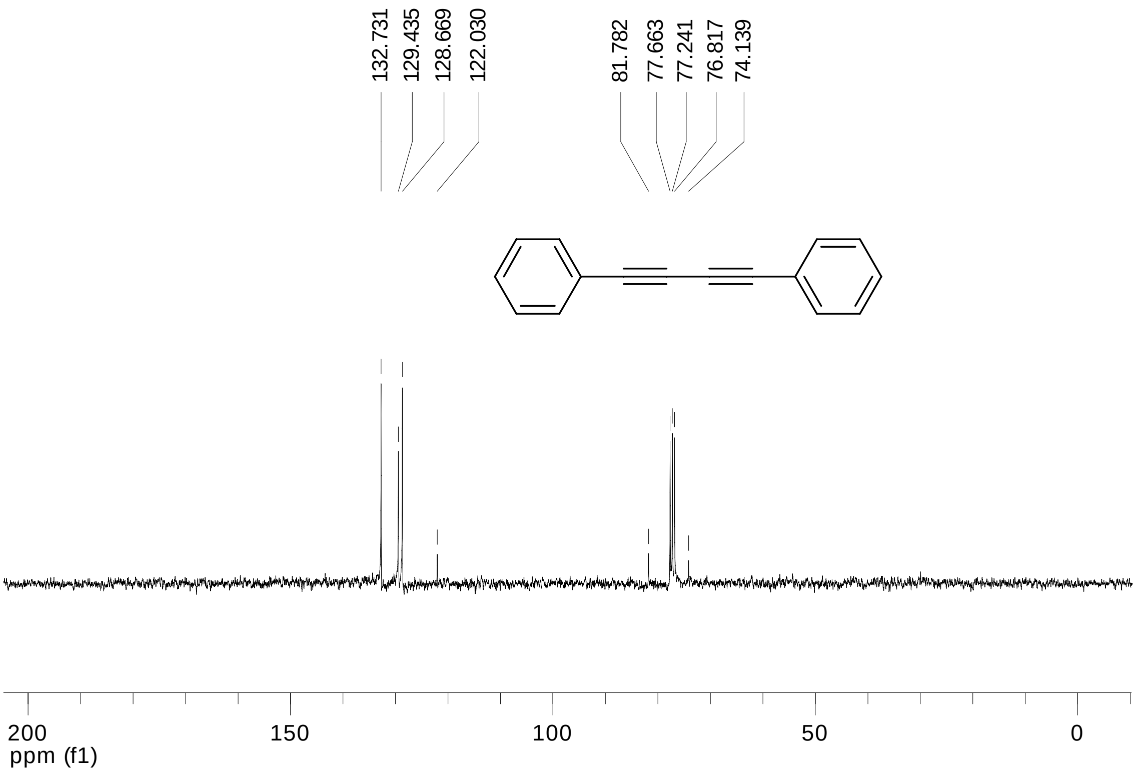
2q


7.875
7.848
7.501
7.479
7.397
7.373
7.341
7.316
7.294
7.263
7.138
7.130
7.110
7.091
7.083
6.200
4.416
4.398
1.694
0.000000
I
CONH
Ph
0.87
1.82
4.64
0.95
0.92
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

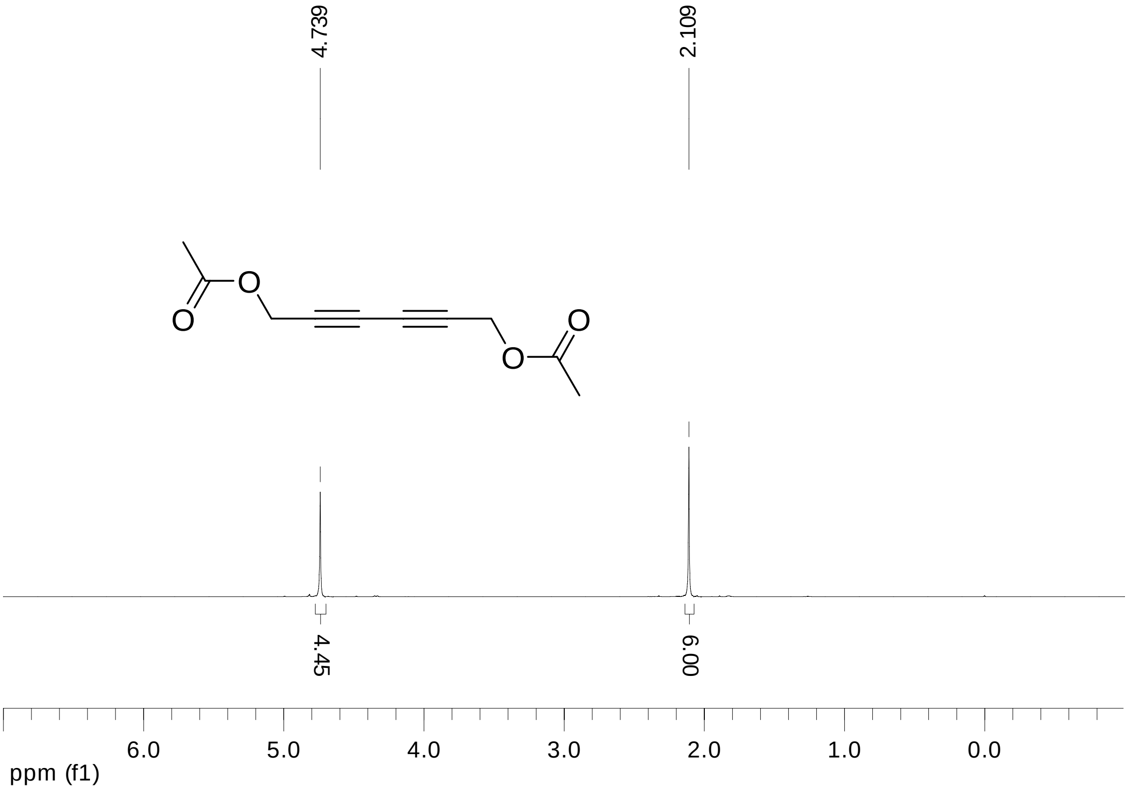

77.471
77.259
77.047
I
CONH
Ph
128.666
132.869
131.722
129.628
128.447
140.227
141.344
169.029
121.499
92.591
77.853
77.769
73.531
68.974
30.911
200
180
160
140
120
100
80
60
40
20
ppm

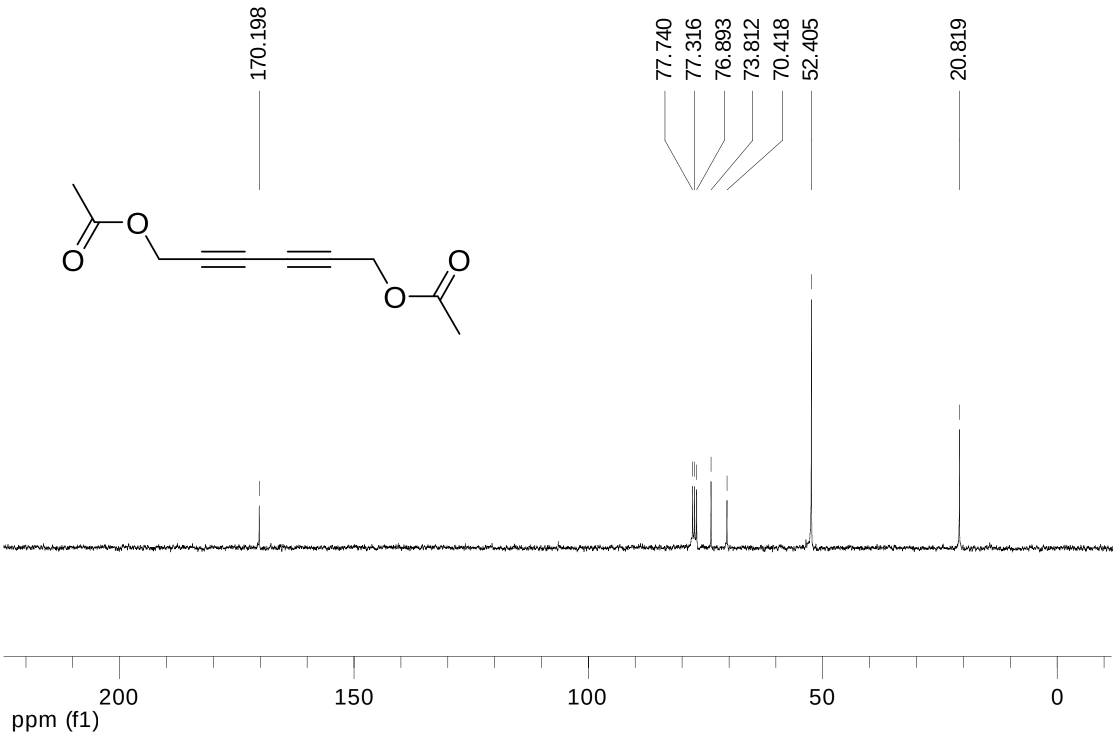
3a


7.541
7.522
7.516
7.357
7.333
0.000000
4.00
5.79
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

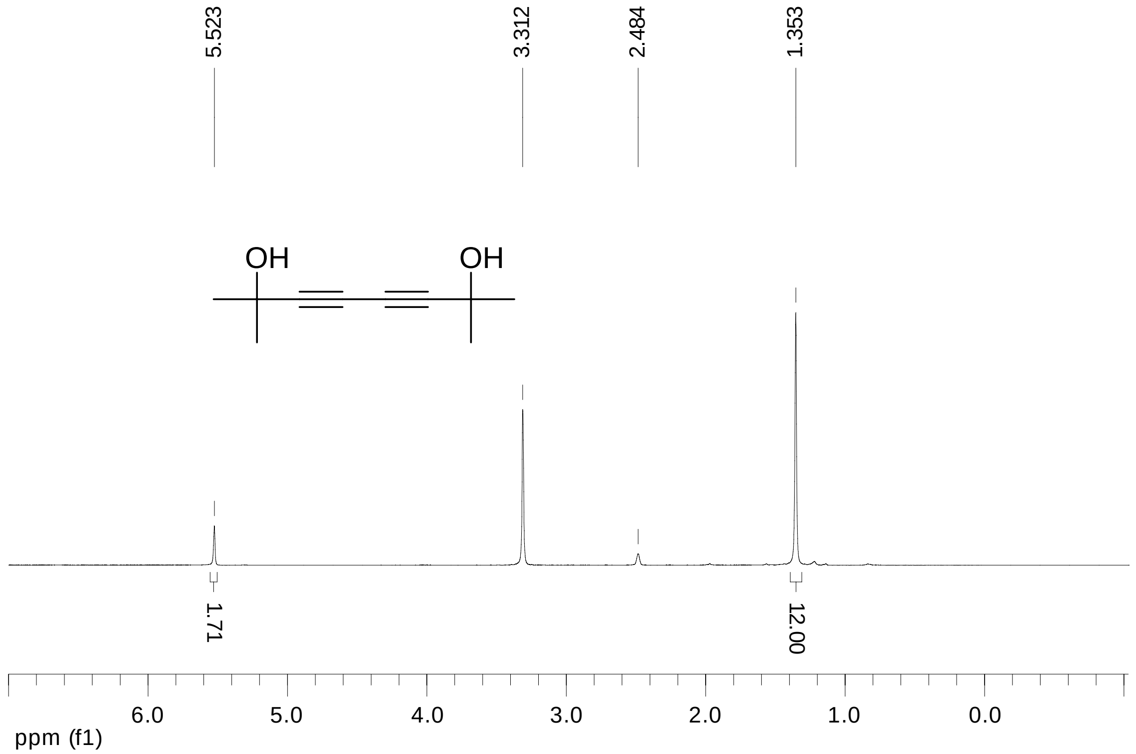

132.731
129.435
128.669
122.030
81.782
77.663
77.241
76.817
74.139
200
150
100
50
0
ppm (f1)

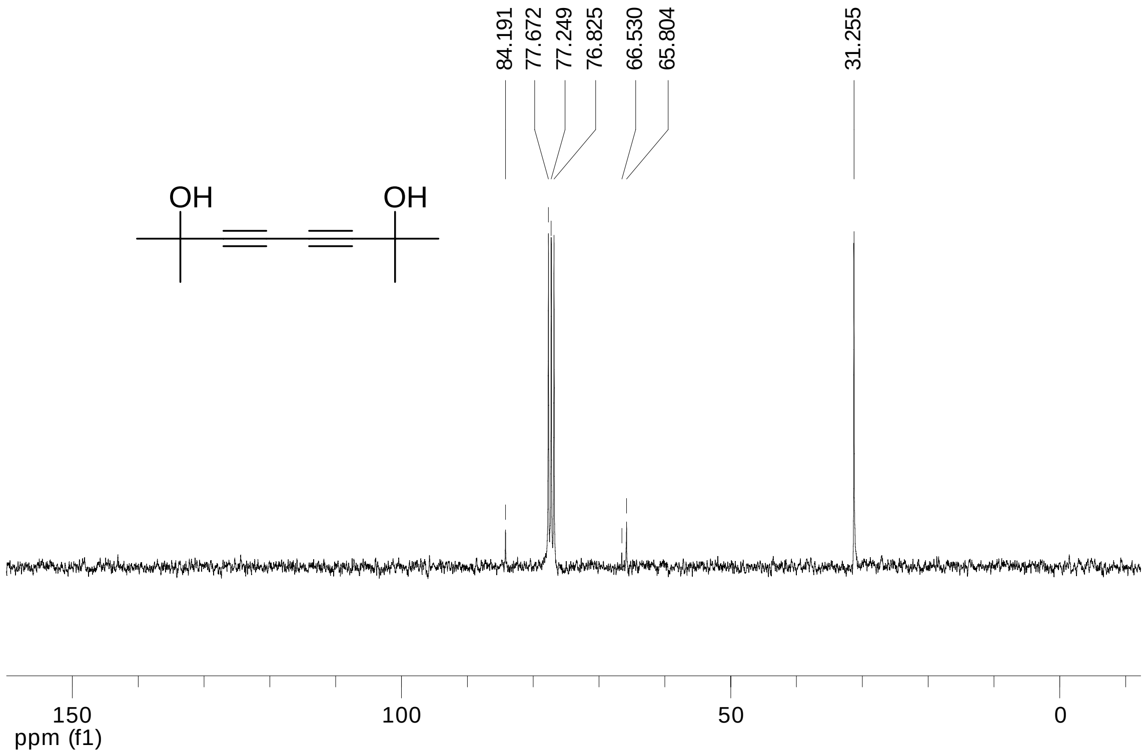
3b


4.739
2.109
4.45
6.00
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

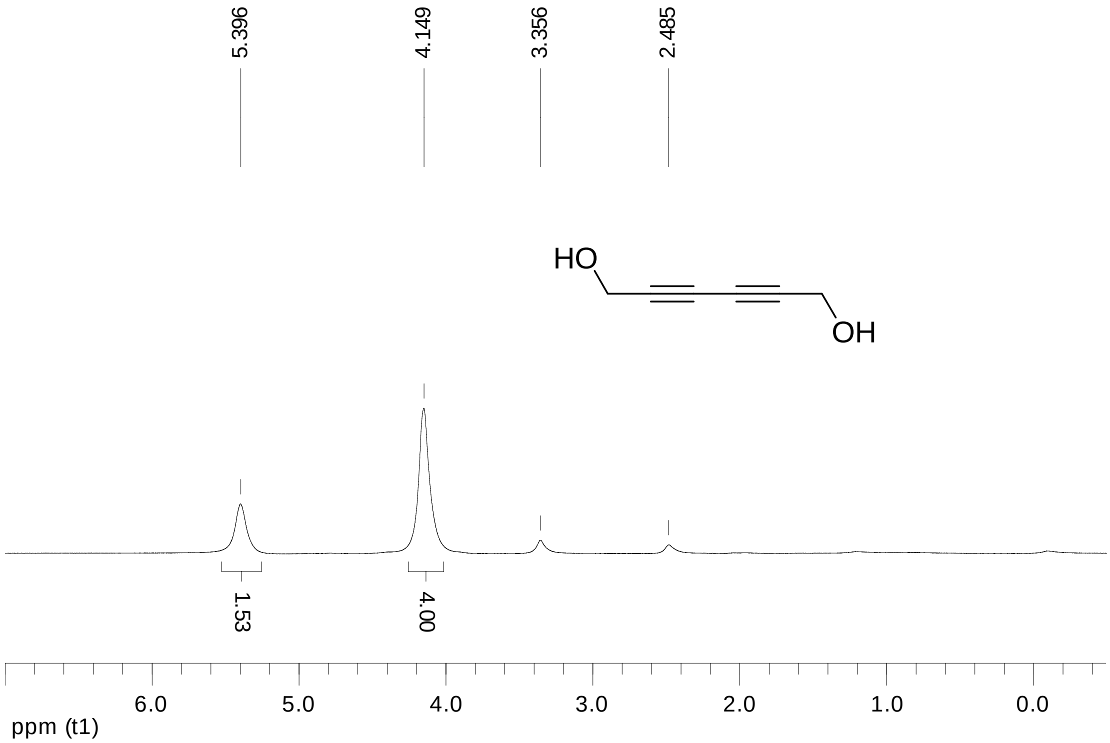

170.198
77.740
77.316
76.893
73.812
70.418
52.405
20.819
200
150
100
50
0
ppm (f1)

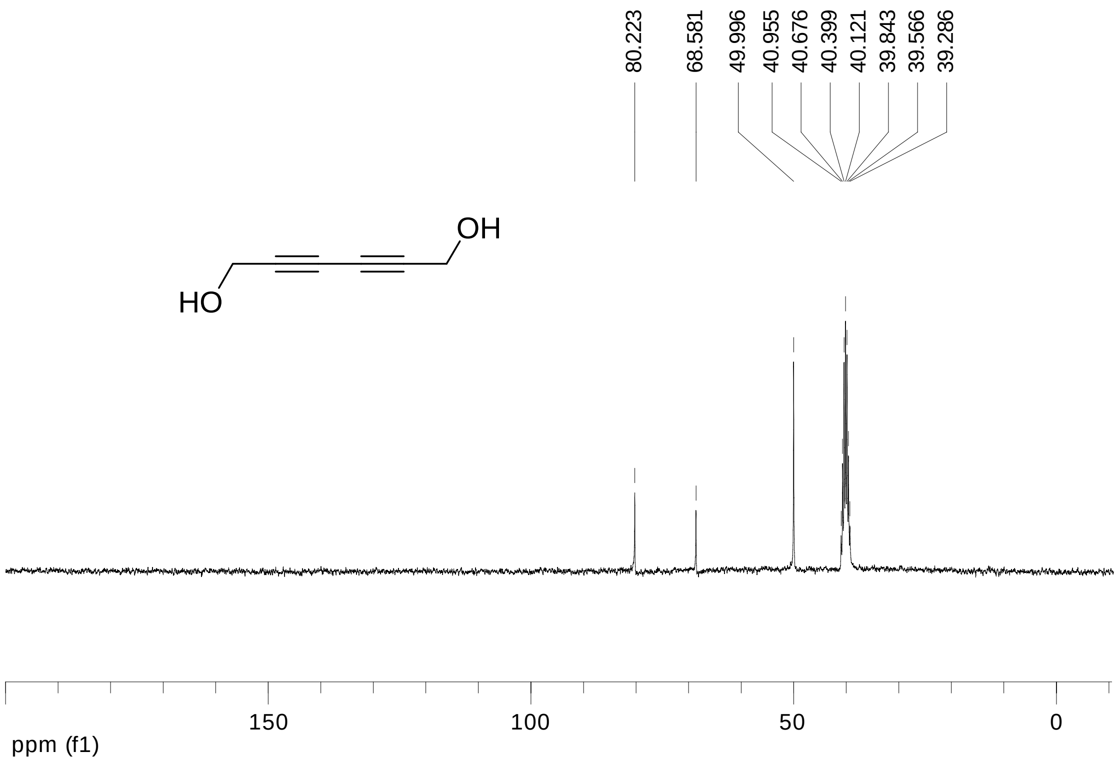
3c


5.523
3.312
2.484
1.353
OH
OH
1.71
12.00
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

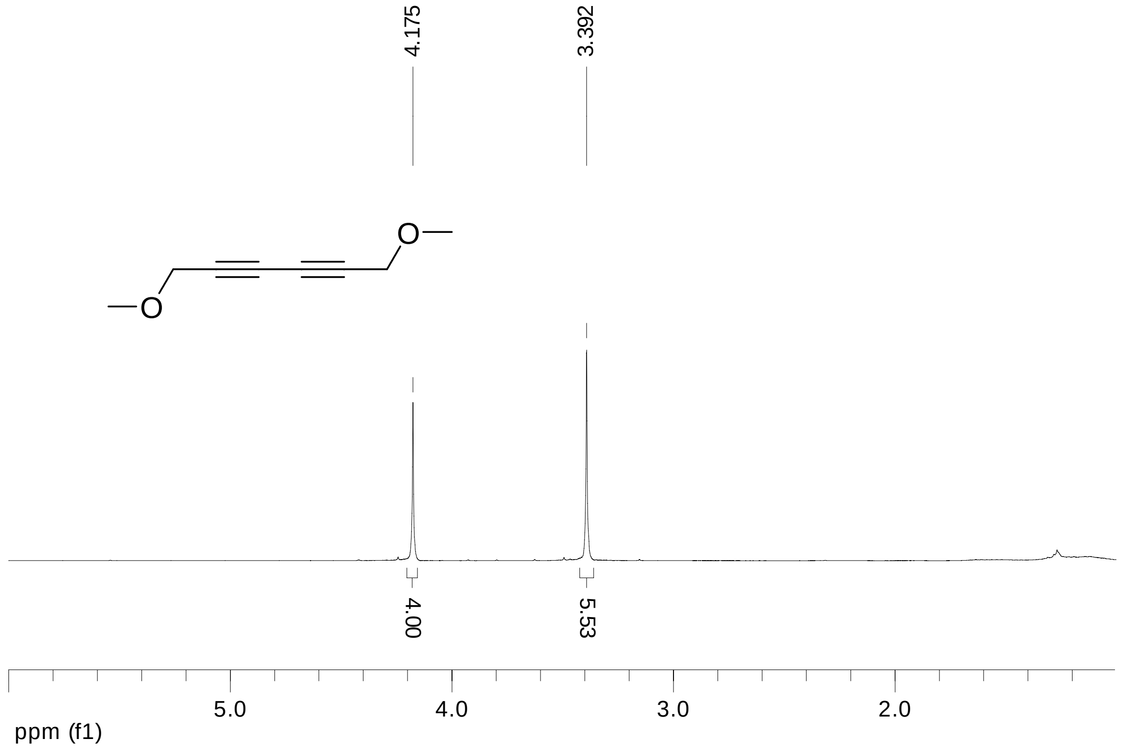

84.191
77.672
77.249
76.825
66.530
65.804
31.255
OH
OH
150
100
50
0
ppm (f1)

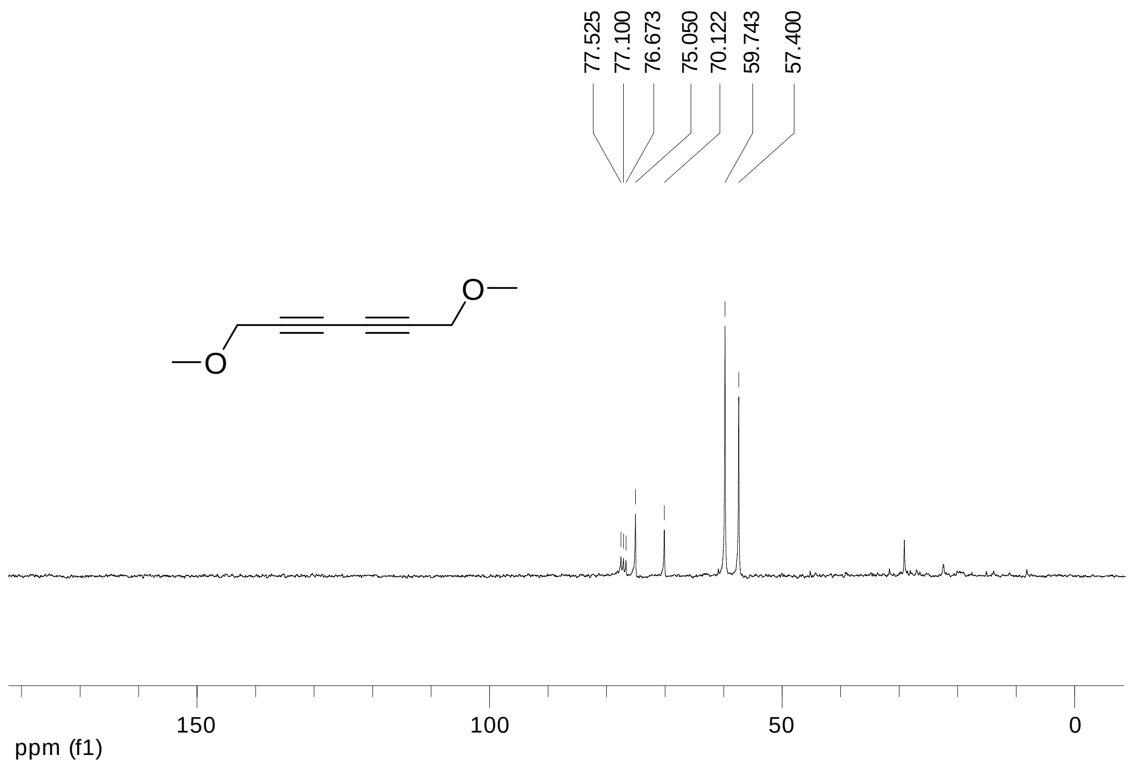
3d


5.396
4.149
3.356
2.485
HO
OH
1.53
4.00
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

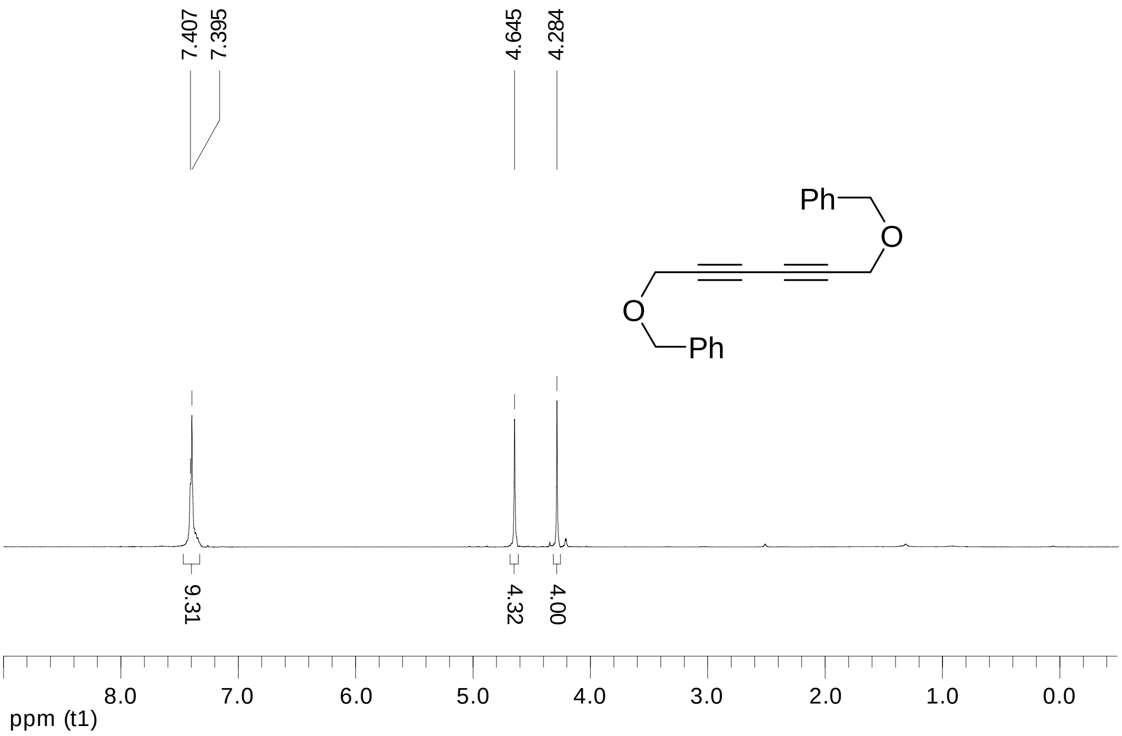

80.223
68.581
49.996
40.955
40.676
40.399
40.121
39.843
39.566
39.286
OH
HO
150
100
50
0
ppm (f1)

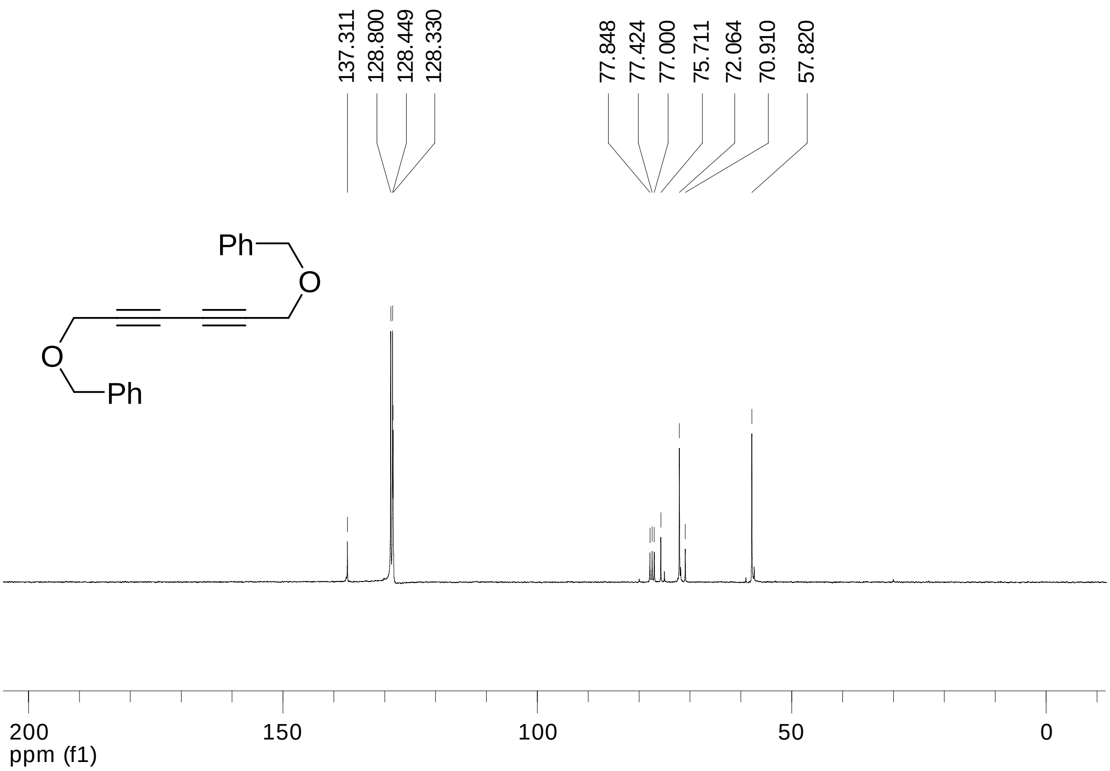
3e


4.175
3.392
4.00
5.53
5.0
4.0
3.0
2.0
ppm (f1)

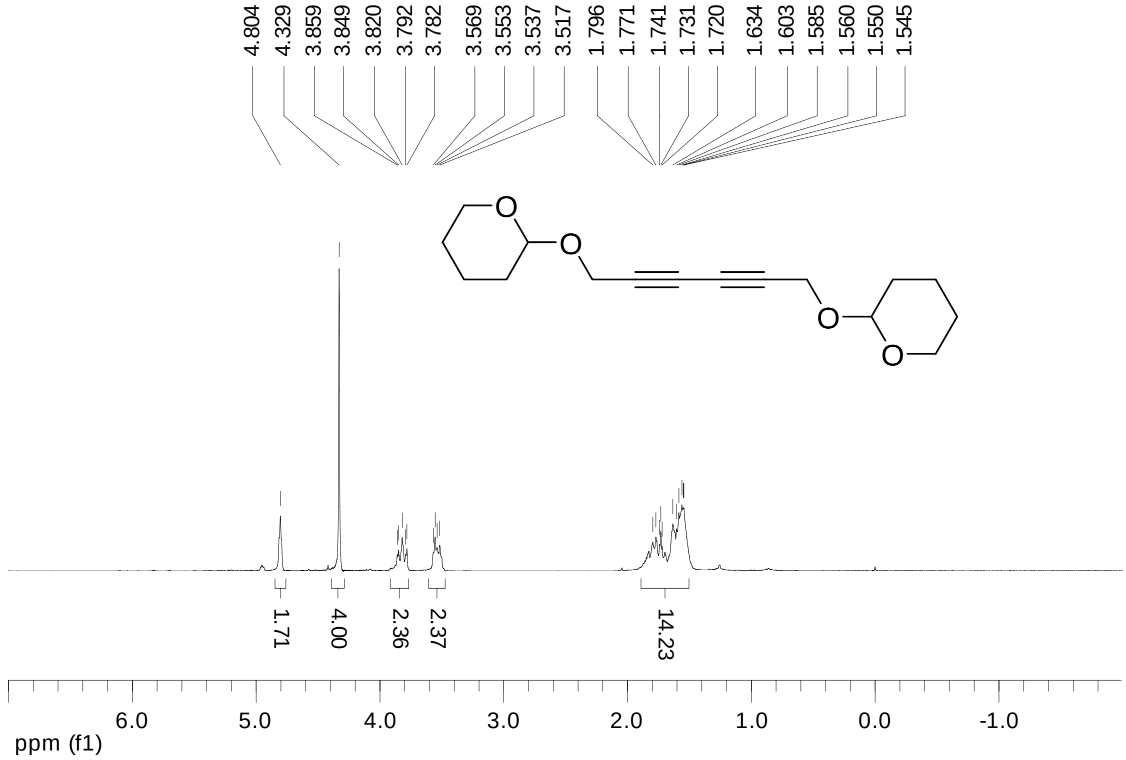

77.525
77.100
76.673
75.050
70.122
59.743
57.400
150
100
50
0
ppm (f1)

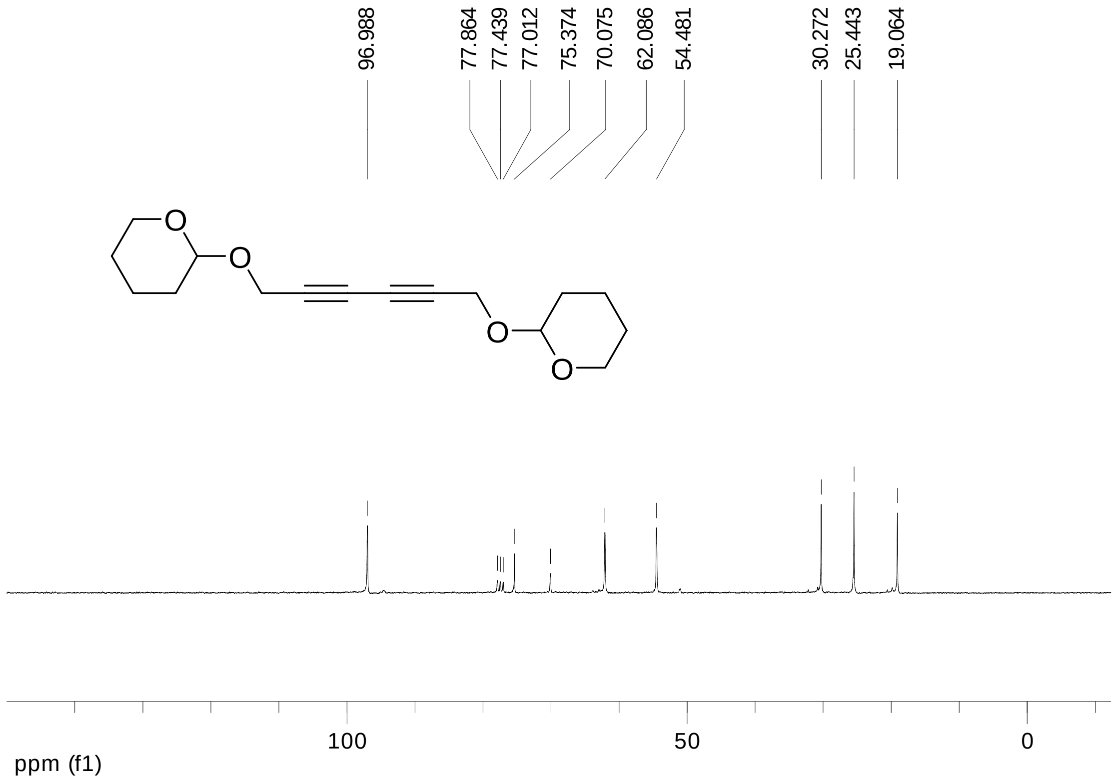
3f


7.407
7.395
4.645
4.284
Ph
O
O
Ph
9.31
4.32
4.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

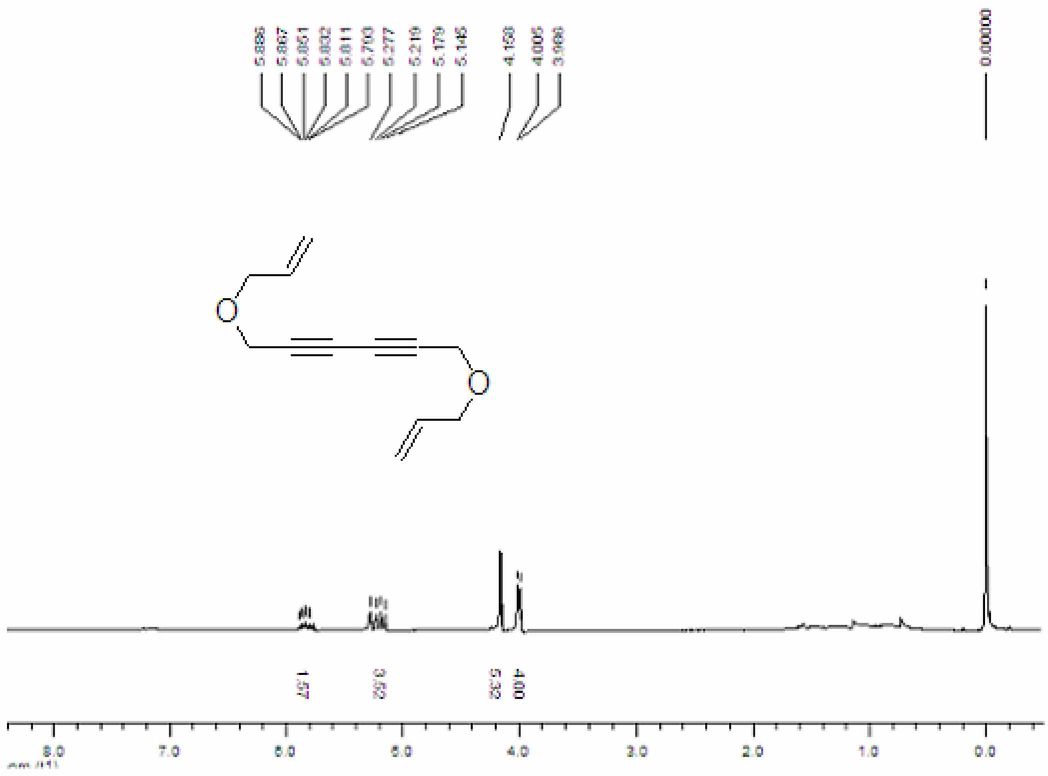

137.311
128.800
128.449
128.330
77.848
77.424
77.000
75.711
72.064
70.910
57.820
Ph
O
O
Ph
200
150
100
50
0
ppm (f1)

3g

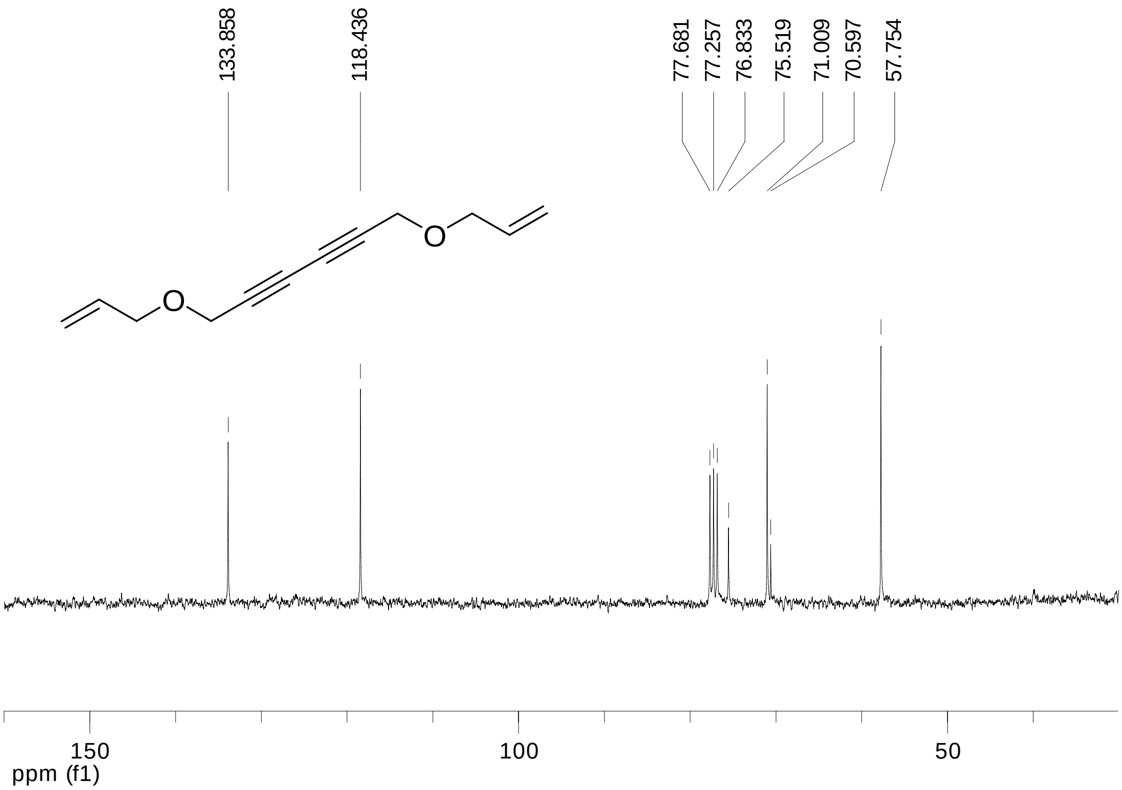

4.804
4.329
3.859
3.849
3.820
3.792
3.782
3.569
3.553
3.537
3.517
1.796
1.771
1.741
1.731
1.720
1.634
1.603
1.585
1.560
1.550
1.545
O
O
O
O
1.71
4.00
2.36
2.37
14.23
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (f1)


96.988
77.864
77.439
77.012
75.374
70.075
62.086
54.481
30.272
25.443
19.064
O
O
O
O
100
50
0
ppm (f1)

3h

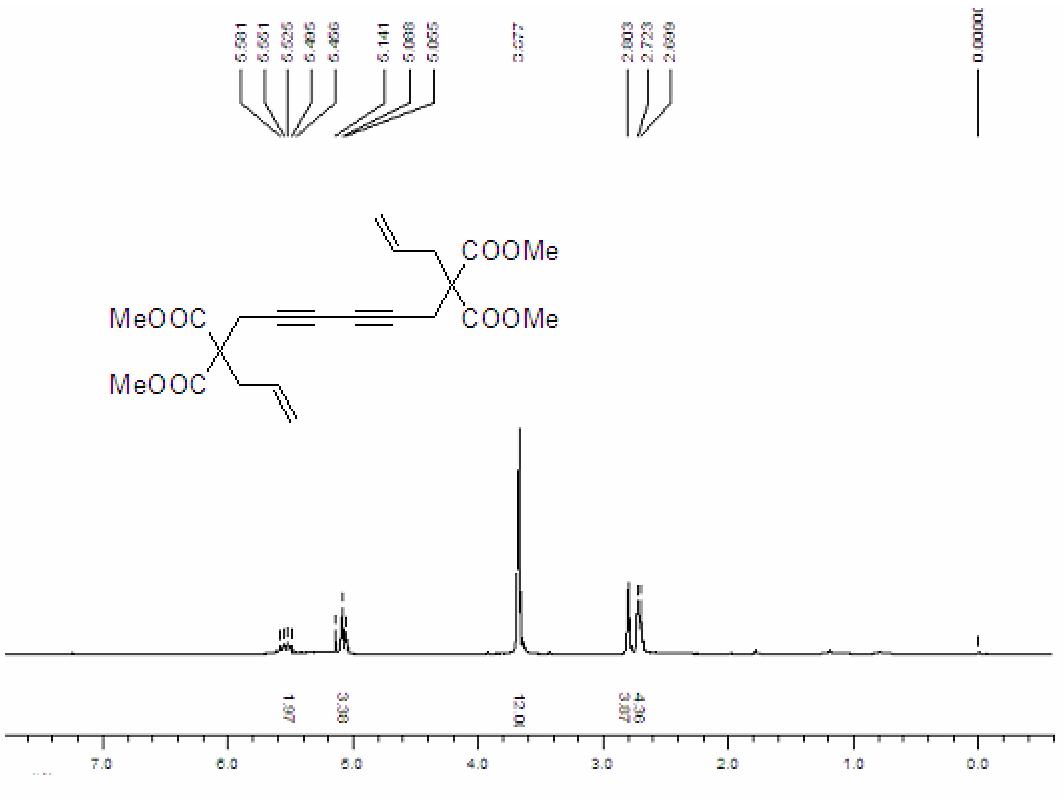


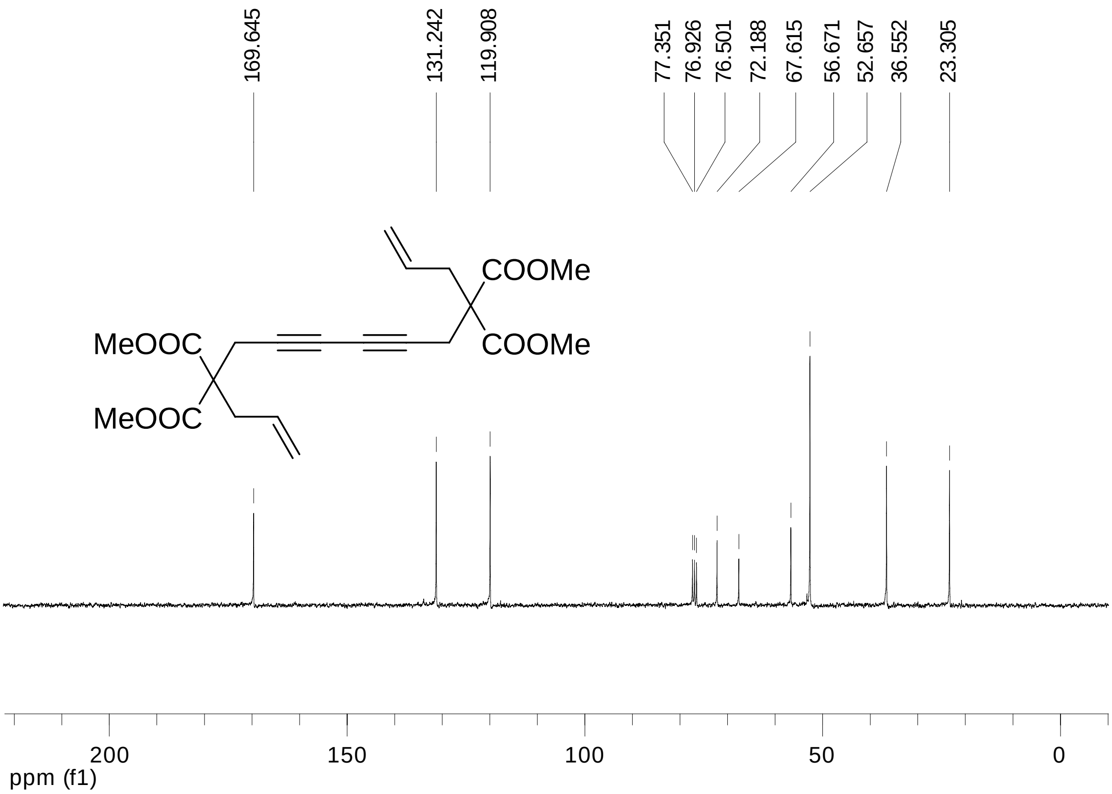
5.886
5.867
5.851
5.832
5.811
5.793
5.277
5.219
5.179
5.145
4.158
4.005
3.986
0.0000
1.57
3.52
5.32
4.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
O
O



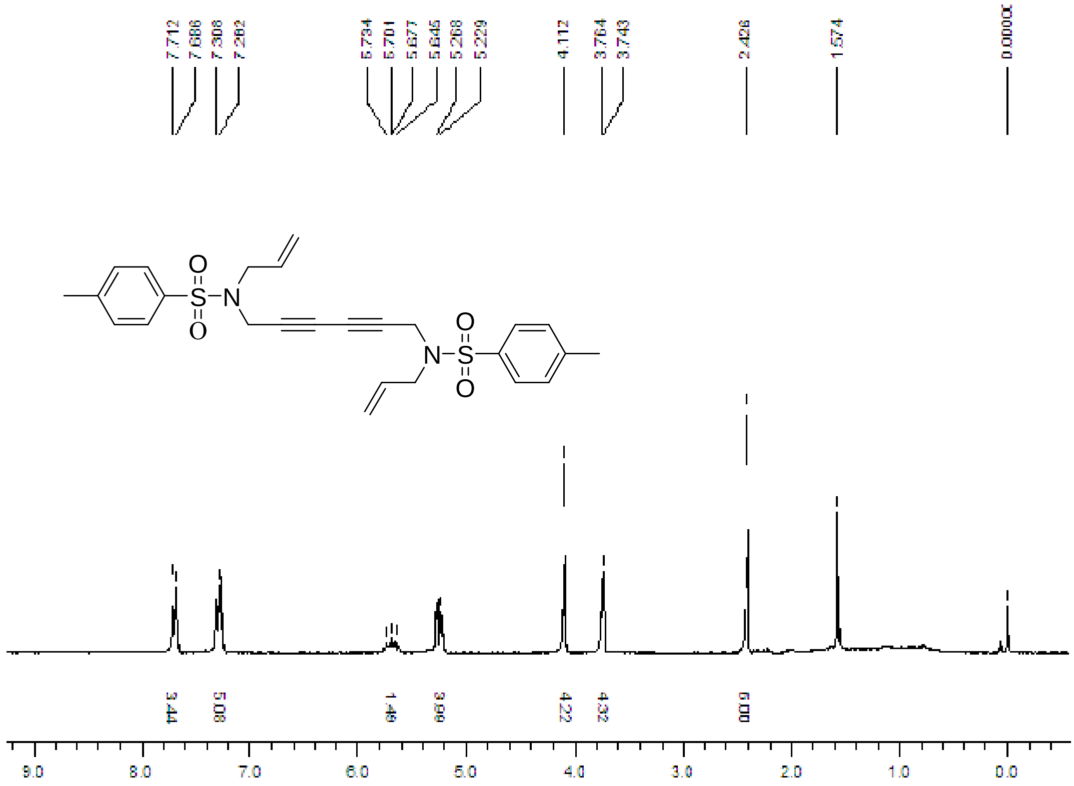
133.858
118.436
77.681
77.257
76.833
75.519
71.009
70.597
57.754
O
O
150
100
50
ppm (f1)

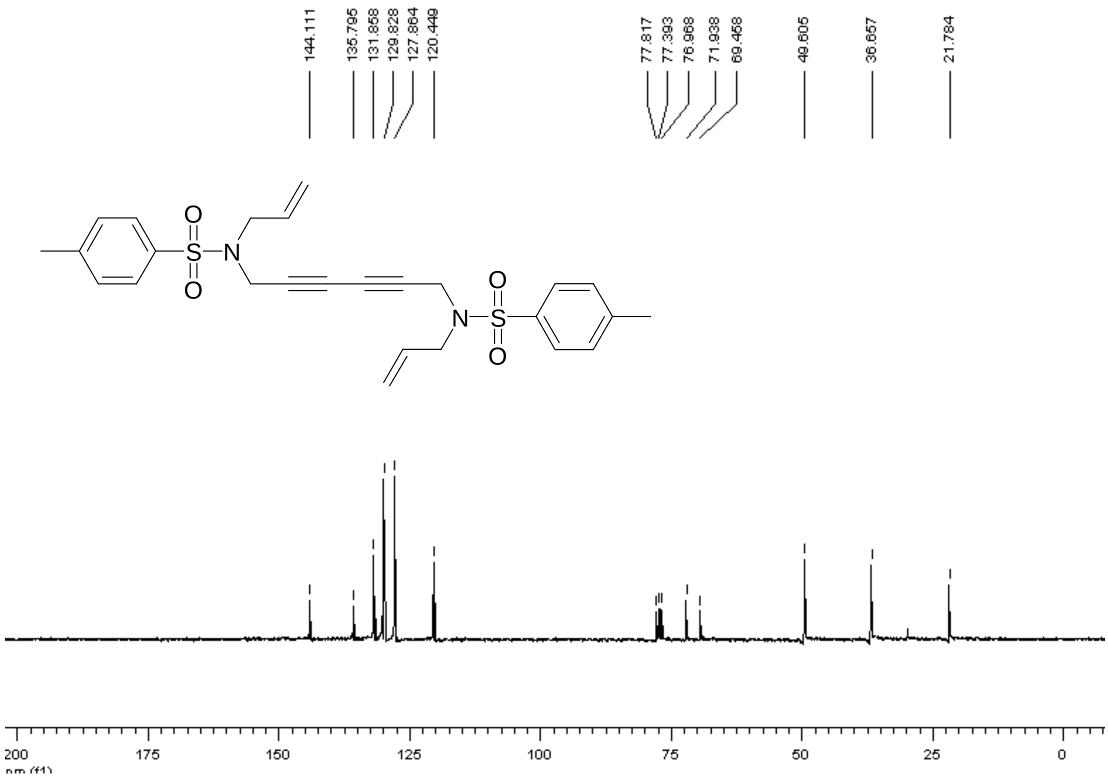
3i


5.581
5.561
5.526
5.495
5.456
5.141
5.088
5.055
3.677
2.803
2.723
2.699
0.00000
COOMe
MeOOC
COOMe
MeOOC
1.97
3.38
12.0
4.36
3.87
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

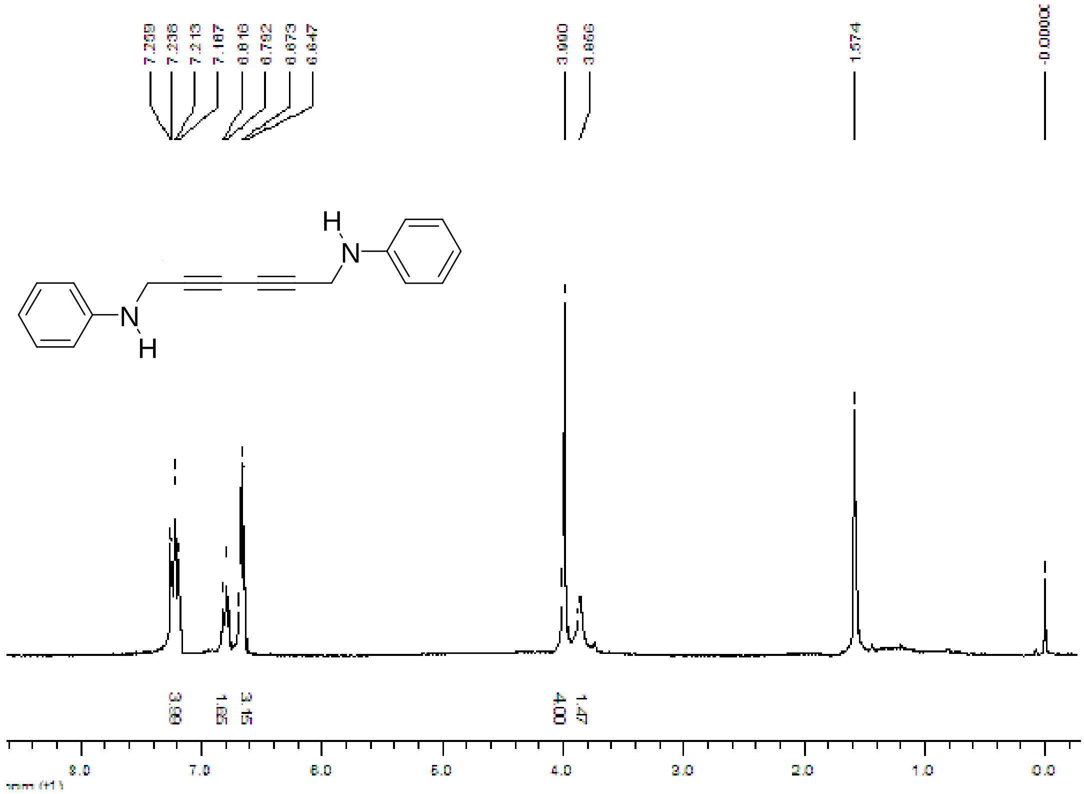

169.645
131.242
119.908
77.351
76.926
76.501
72.188
67.615
56.671
52.657
36.552
23.305
COOMe
MeOOC
COOMe
MeOOC
200
150
100
50
0
ppm (f1)

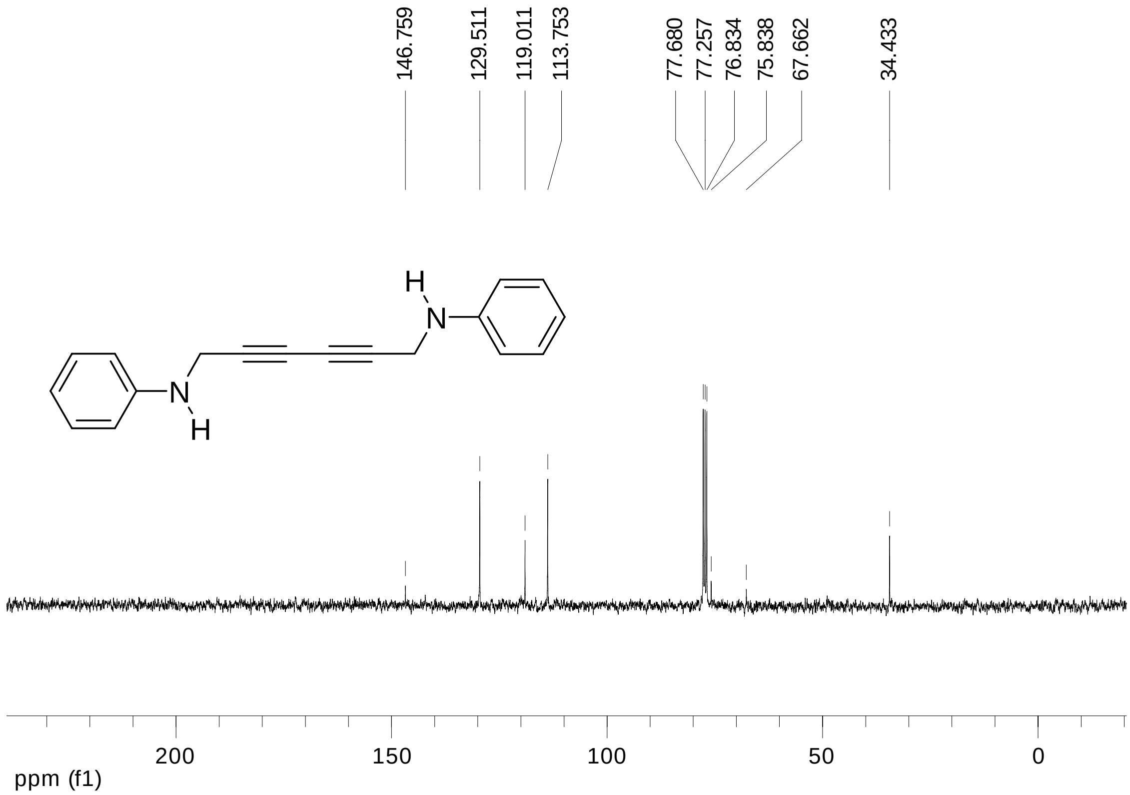
3j


7.712
7.686
7.306
7.282
5.734
5.701
5.677
5.645
5.268
5.229
4.112
3.764
3.743
2.426
1.574
0.0000
3.44
5.08
1.49
3.99
4.22
4.32
6.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

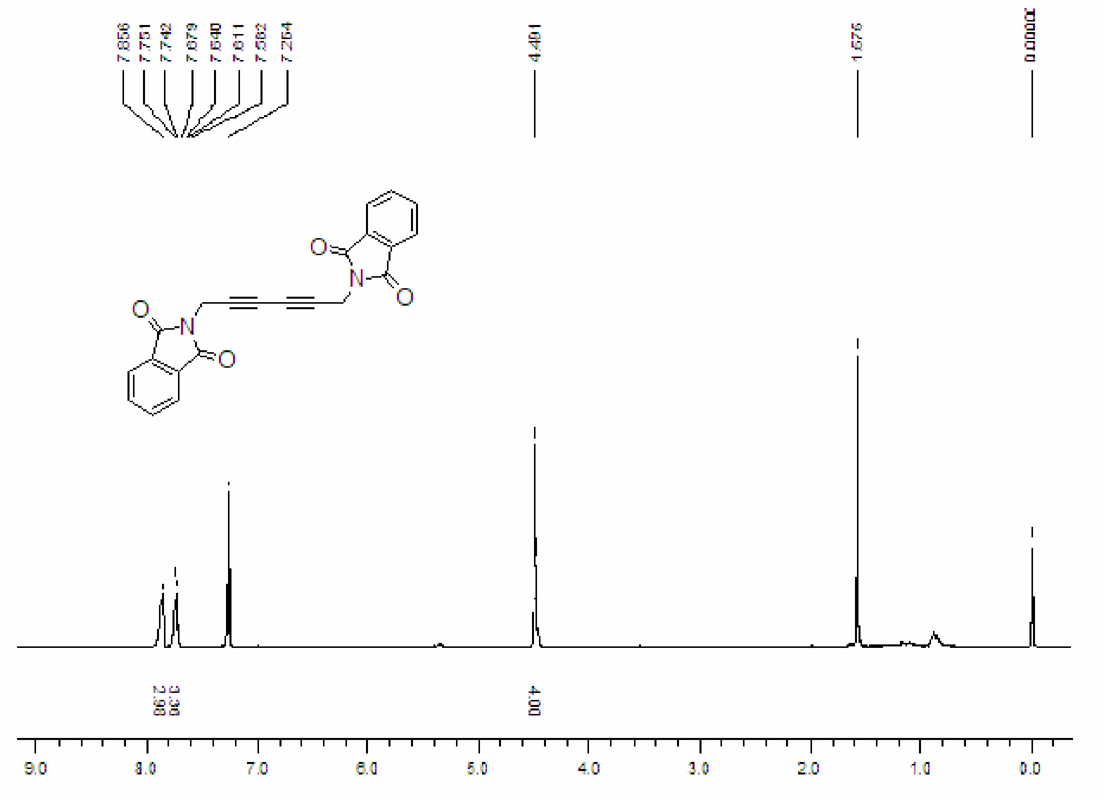

144.111
135.795
131.858
129.828
127.864
120.449
77.817
77.393
76.968
71.938
69.458
49.605
36.657
21.784
200
175
150
125
100
75
50
25
0

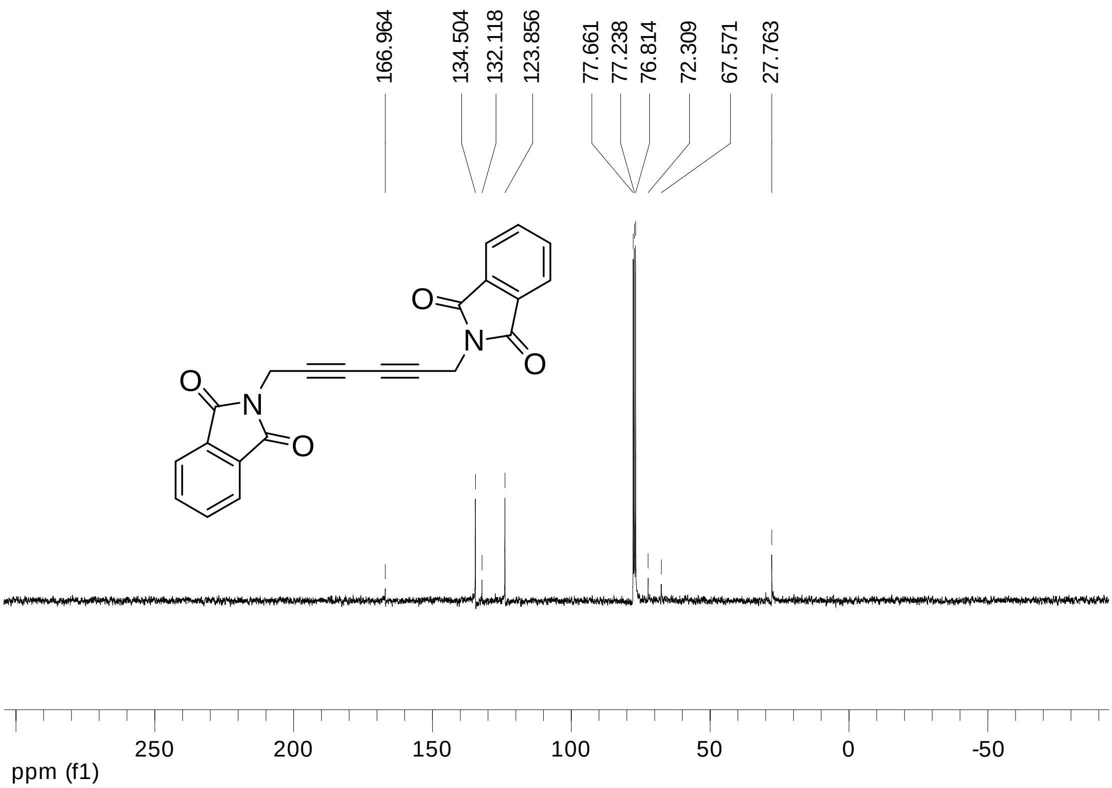
3k


7.259
7.238
7.213
7.187
6.816
6.792
6.673
6.647
3.990
3.856
1.574
0.0000
H
N
N
H
3.89
1.85
3.15
4.00
1.47
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

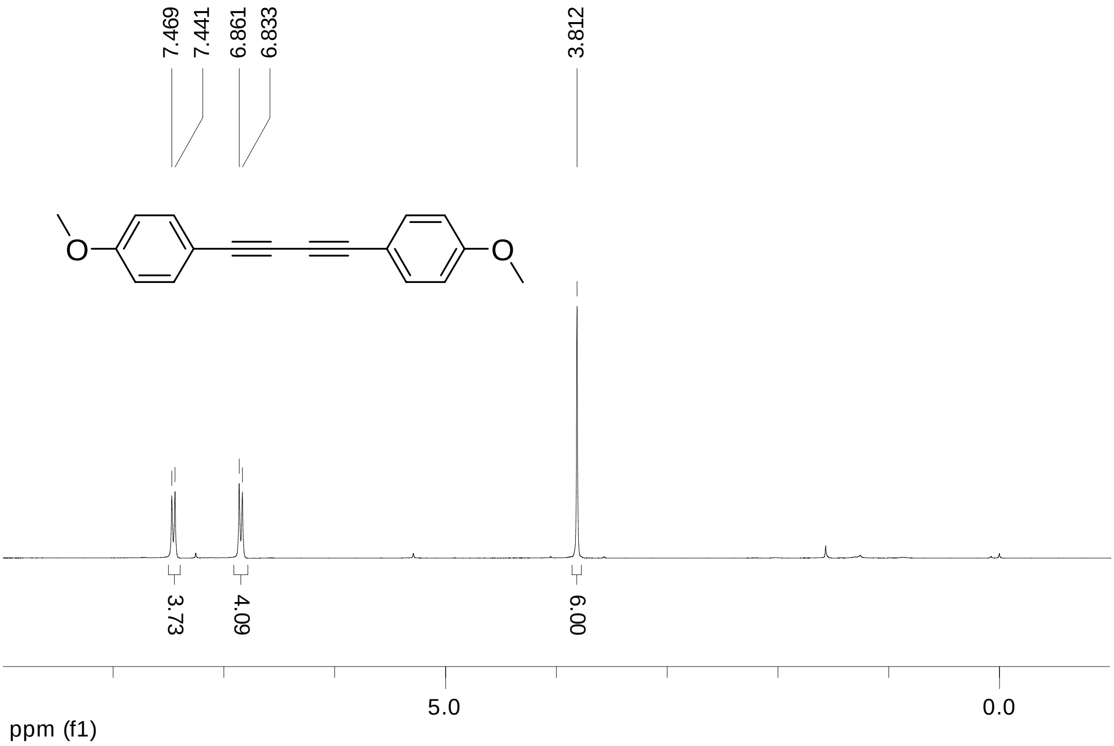

146.759
129.511
119.011
113.753
77.680
77.257
76.834
75.838
67.662
34.433
H
N
N
H
200
150
100
50
0
ppm (f1)

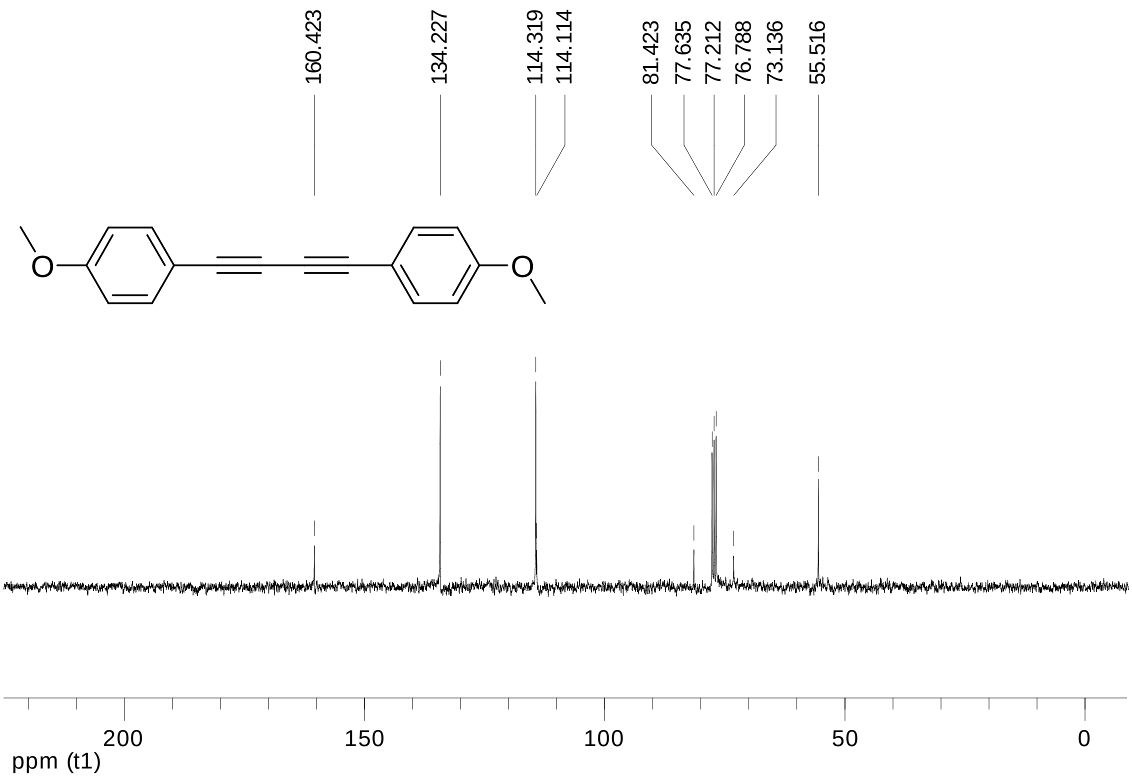
3l


7.856
7.751
7.742
7.679
7.640
7.611
7.562
7.264
4.491
1.575
0.0000
2.98
3.30
4.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

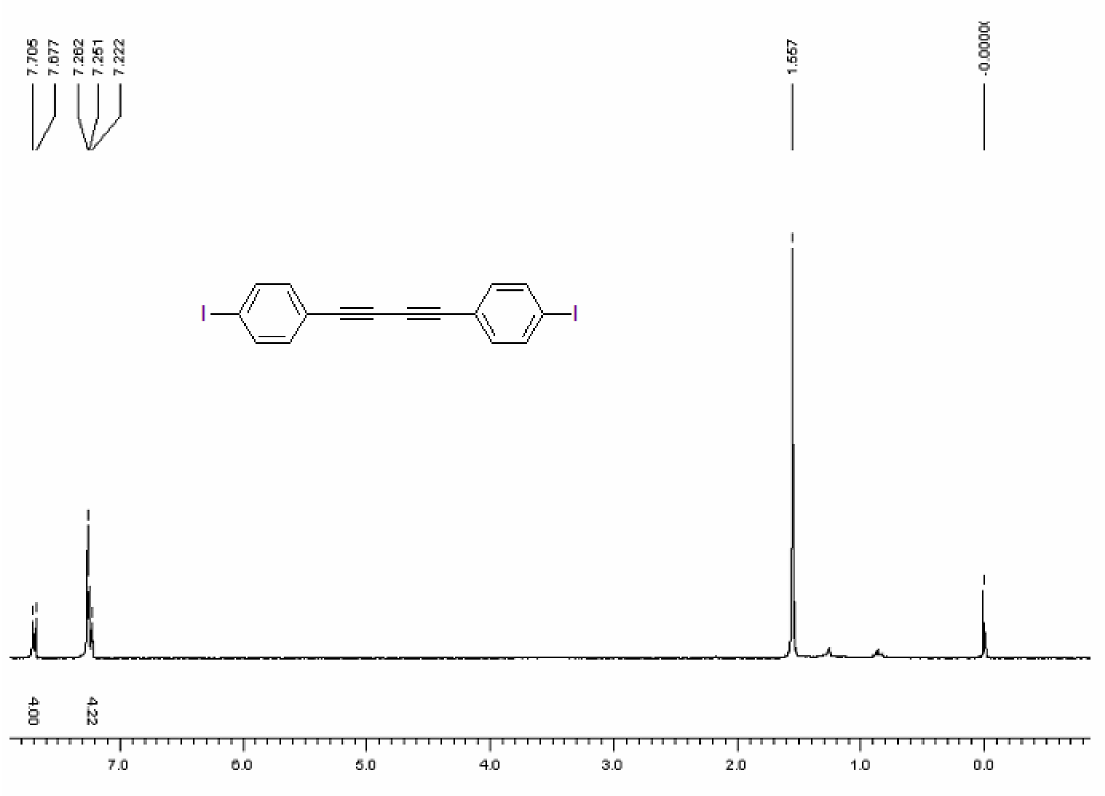

166.964
134.504
132.118
123.856
77.661
77.238
76.814
72.309
67.571
27.763
250
200
150
100
50
0
-50
ppm (f1)

3m

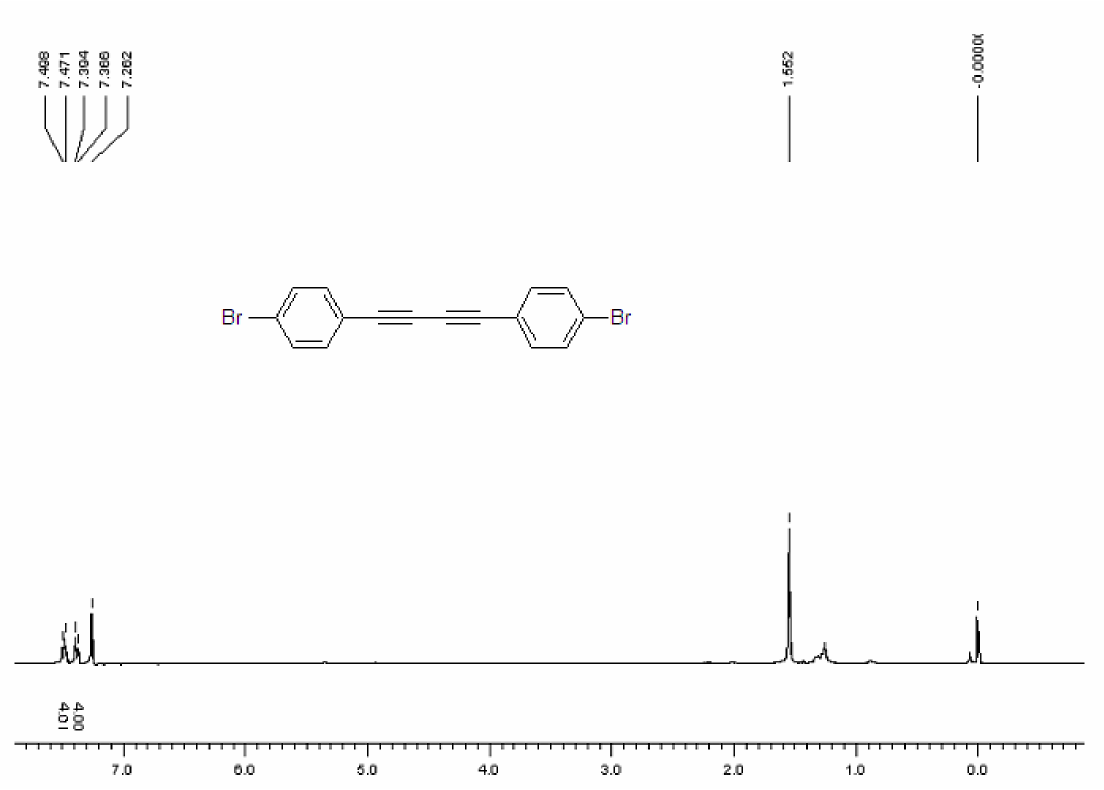

7.469
7.441
6.861
6.833
3.812
O
O
3.73
4.09
6.00
5.0
0.0
ppm (f1)


160.423
134.227
114.319
114.114
81.423
77.635
77.212
76.788
73.136
55.516
O
O
200
150
100
50
0
ppm (t1)

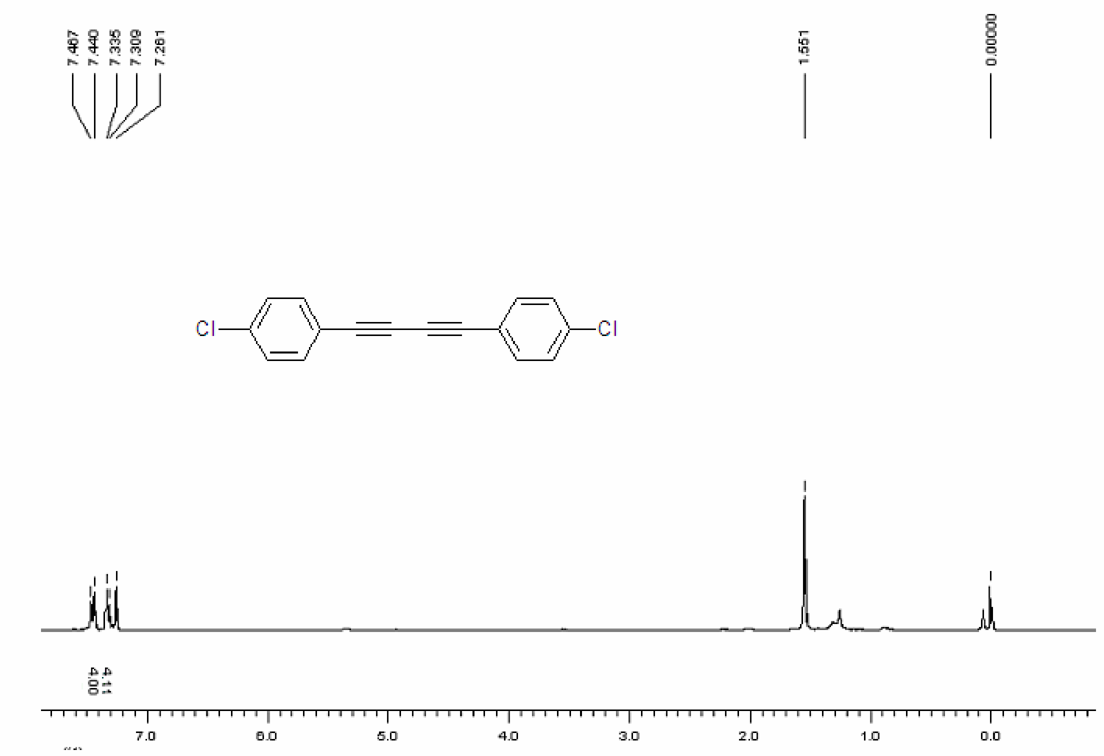
3n


7.705
7.677
7.262
7.251
7.222
1.557
-0.0000
I
I
4.00
4.22
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

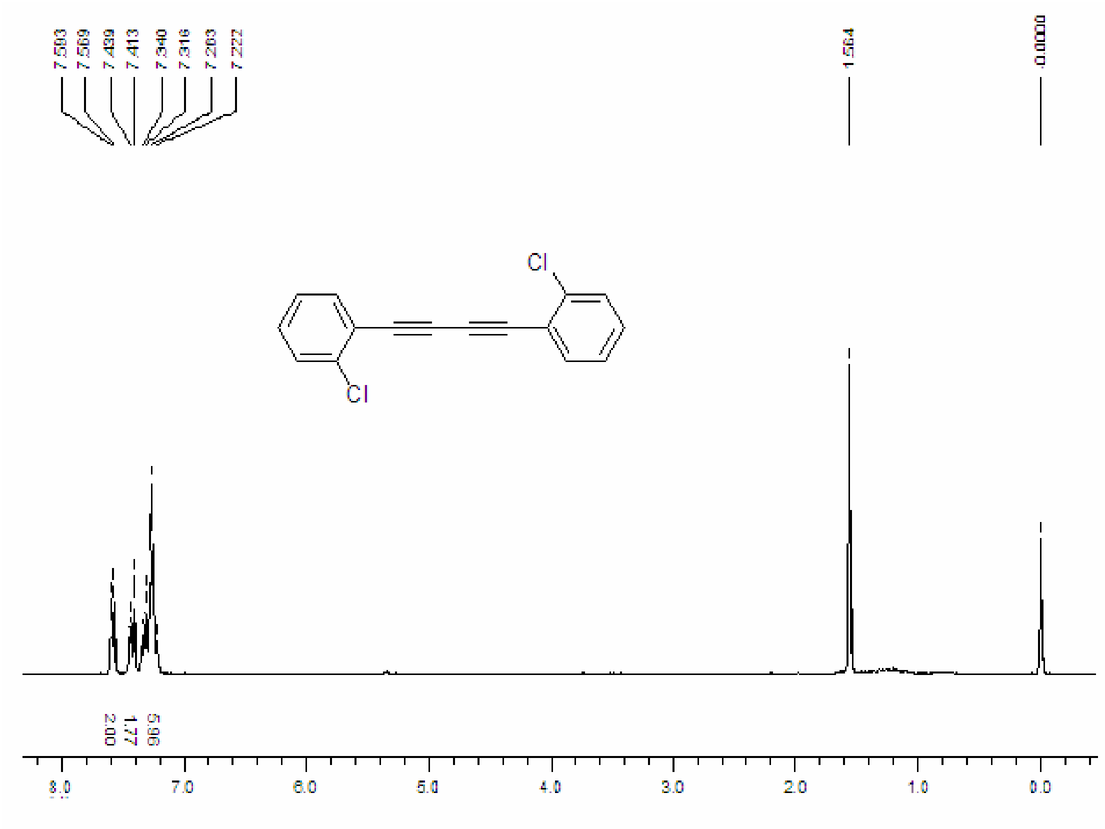
3o

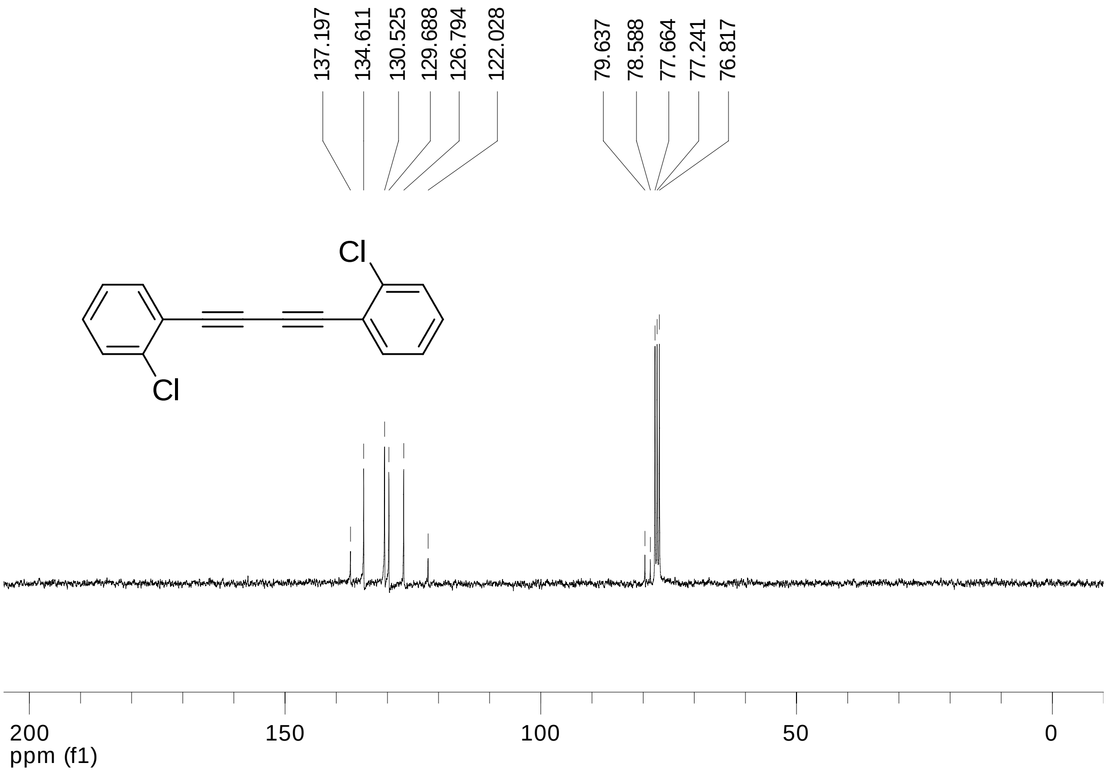

7.498
7.471
7.394
7.366
7.262
1.552
-0.0000
Br
Br
4.00
4.01
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

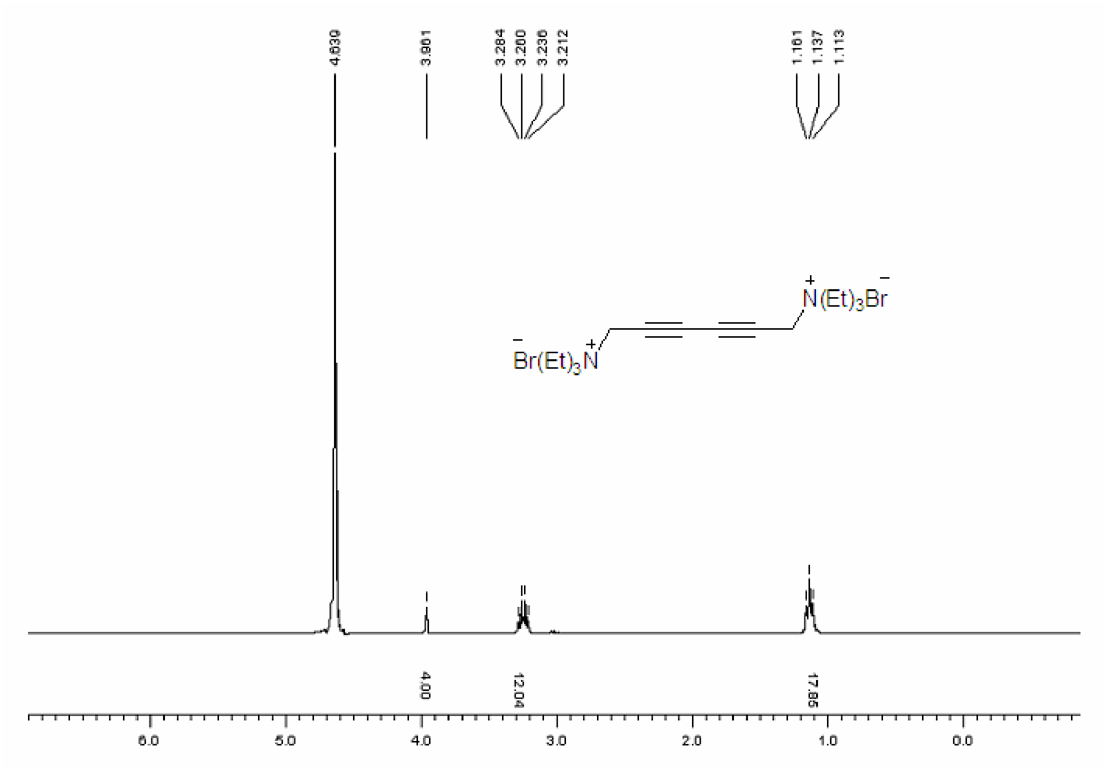
3p

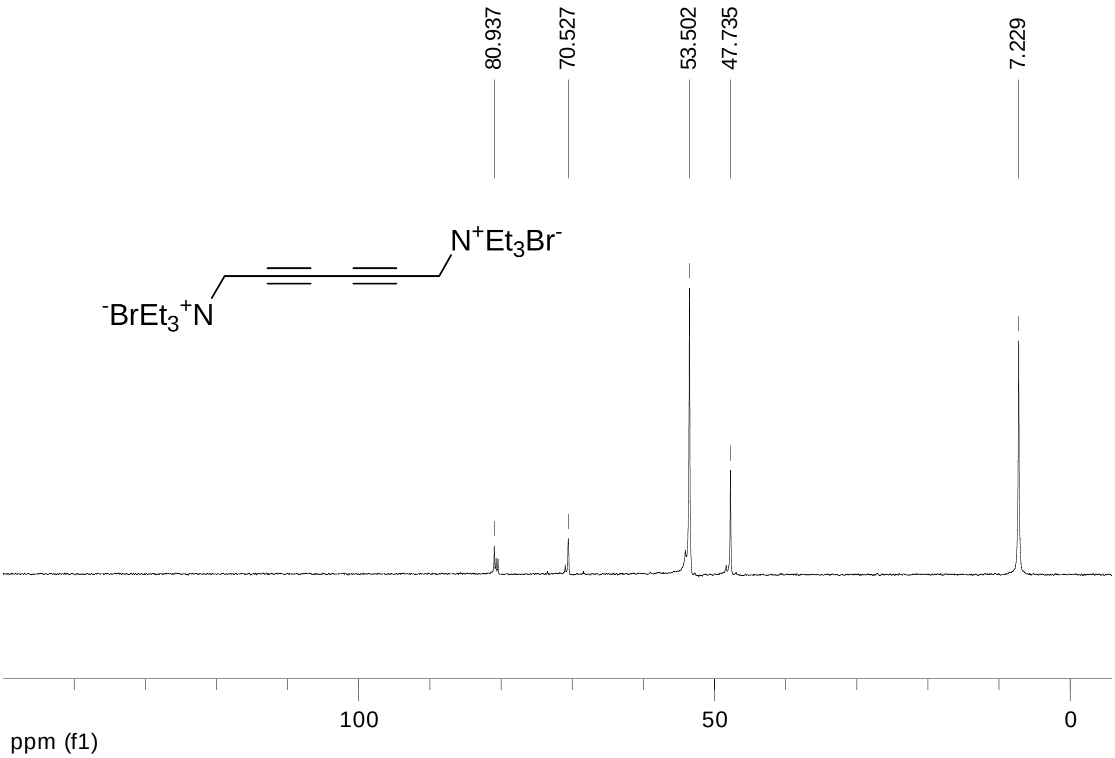

7.467
7.440
7.335
7.309
7.261
1.551
0.00000
Cl
Cl
4.11
4.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

3q


7.583
7.569
7.439
7.413
7.340
7.316
7.263
7.222
1.564
0.0000
Cl
Cl
2.00
1.77
5.96
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


137.197
134.611
130.525
129.688
126.794
122.028
79.637
78.588
77.664
77.241
76.817
Cl
Cl
200
150
100
50
0
ppm (f1)


4.639
3.961
3.284
3.260
3.236
3.212
1.161
1.137
1.113
N(Et)3Br
Br(Et)3N
4.00
12.04
17.85
6.0
5.0
4.0
3.0
2.0
1.0
0.0


80.937
70.527
53.502
47.735
7.229
N+Et3Br-
-BrEt3+N
100
50
0
ppm (f1)