Supporting Information

Highly Dispersed Ni_2P Nanoparticles on N,P-codoped Carbon for Efficient Cross-Dehydrogenative Coupling to Access Alkynyl Thioethers

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Table Contents

1. General considerations

Unless otherwise noted, all reagents were purchased commercially from Sigma-Aldrich, or Aladdin and used as received without further purification. The fresh bamboo shoots were obtained from Anhui Taiping Test Centre, International Centre for Bamboo and Rattan, Anhui Province, China. All operations were carried out in an argon atmosphere using glovebox and Schlenk techniques unless otherwise specified. The X-ray diffraction (XRD) patterns of all the catalysts were obtained on a Bruker D8 Advance X-ray diffraction diffractometer equipped with Cu Ka radiation (λ= 1.5147 Å). The morphology of catalysts was examined by an H-7600 transmission electron microscopy (TEM), a Tecnai G2 F30 high-resolution TEM (HRTEM) and a FEI Tecnai G2 F20 scanning transmission electron microscopy (STEM). Nitrogen adsorption–desorption data were obtained on a Micromeritics ASAP 2020 static volumetric sorption analyzer. The specific surface area of the samples was calculated by the Brunauer-Emmet-Teller (BET) method. The micropore volume was calculated by t-plot method. The pore size distributions were determined by non-local density functional theory (NLDFT). The X-ray photoelectron spectroscopy (XPS) data was collected on an ESCALAB 250Xi (Thermo Scientific, UK) instrument equipped with a monochromatized Al Ka line source. All the binding energies obtained were calibrated based on the C 1s peak at 284.8 eV. The elemental composition analysis of the catalysts was conducted on Vario El elemental analyzer. Ion Chromatography was conducted on a Thermo Scientific Dionex ICS-5000 equipped with CS-12 column with methanesulfonic acid (20 mM) as an eluent. Raman spectra were obtained on a Horiba Jobin Yvon LabRAM HR800 Raman spectrometer system using a 532 nm wavelength laser at room temperature. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was conducted on a PerkinElmer Optima 5300 DV instrument. Gas chromatography analysis was performed on an Agilent HP-7890 instrument with a flame ionization detector (FID) and an HP-5MS capillary column (30 m, 0.25 mm i.d., 0.25 μm film thicknesses) using helium as the carrier gas. Gas chromatography-mass spectrometry analysis was carried out on an Agilent HP-7890 instrument with an

Agilent HP-5975 with triple-axis detector and HP-5 capillary column using helium carrier gas. NMR spectra were from a Bruker DRX-400, or DRX-600, instrument and calibrated using residual non-deuterated solvent ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; DMSO-d_6, δ_H = 2.50 ppm, δ_C = 39.60 ppm) as an internal reference. High-resolution mass data were recorded on Bruke Maxis UHR TOF mass spectrometers in ESI mode.

2. Preparation of catalysts

The hydrochars were firstly prepared by hydrothermal method using bamboo shoots as raw material. The fresh bamboo shoots were cut into slices, dried and ground into a powder. 2 g of the dried bamboo shoots were added to 20 mL of deionized water in a 100 mL Teflon-inner stainless steel autoclave, which was sealed and heated at 180 ^oC for 5.5 h. The resulting solids were obtained by filtration, washed thoroughly using distilled water to remove any soluble metals, and dried by vacuum freeze-drying. After that, 1 g of the obtained hydrochars were mixed with 20 mL of $Ni(OAc)_2$ aqueous solution (0.4 mmol Ni) and 120 μL phytic acid (PA, 1.1 mol/L), the suspension was stirred at 60 ^oC for 2 h and then dried at 100 ^oC for 10 h to remove water. Afterward, the solids were grinded to fine powders and heated to 700, 800 or 900 ^oC at a rate of 5 ^oC/min and maintained at this temperature for 2 h under N_2 atmosphere. The obtained catalyst was named as Ni_2P@NPC-T, where T represents the calcination temperature. For comparison, the catalysts Ni@NC-800 without addition of PA and Ni@NPC-800-X (X represent the amount of PA) with addition of different amount of PA were prepared in the same procedure.

3. Characterization results

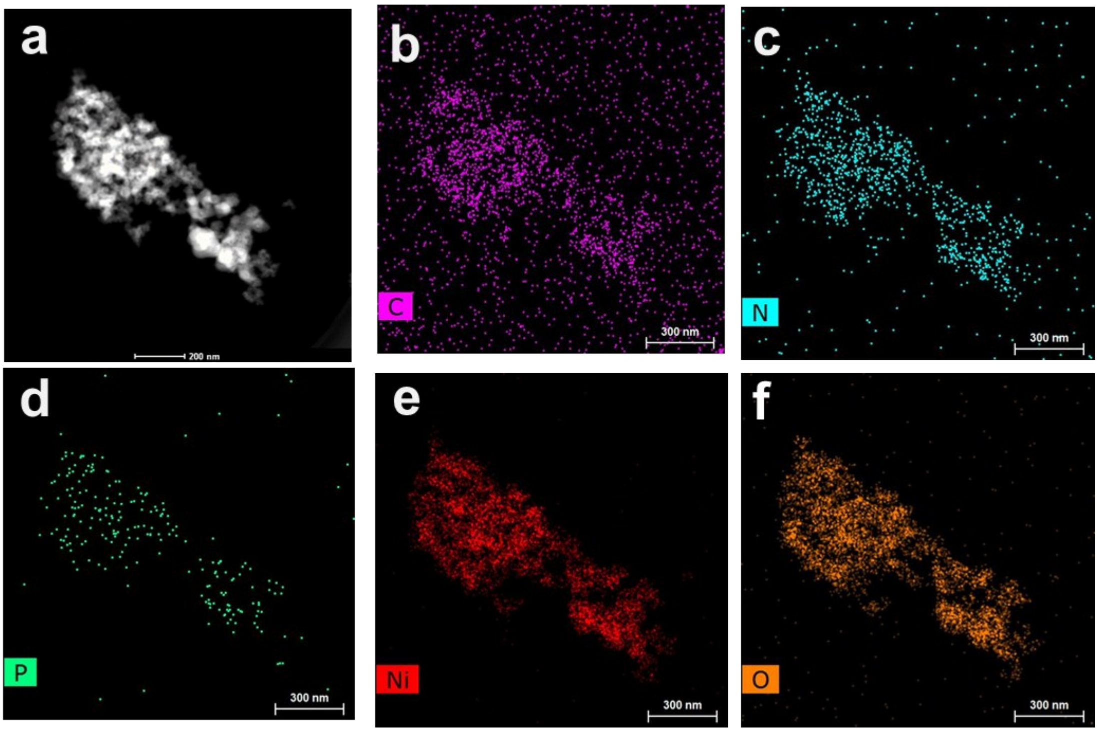


Figure S1. (a) HAADF STEM image, and (b-f) EDX mapping of C, N, P, and Ni of Ni_2P@NPC-800.

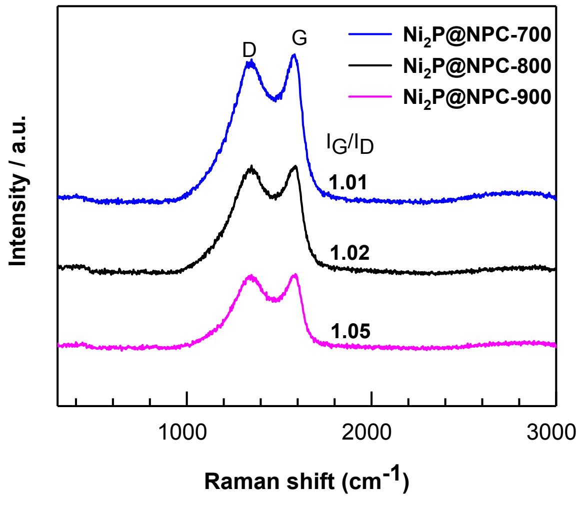


Figure S2. Raman spectra of the catalysts Ni_2P@NPC-700, Ni_2P@NPC-800, and Ni_2P@NPC-900.

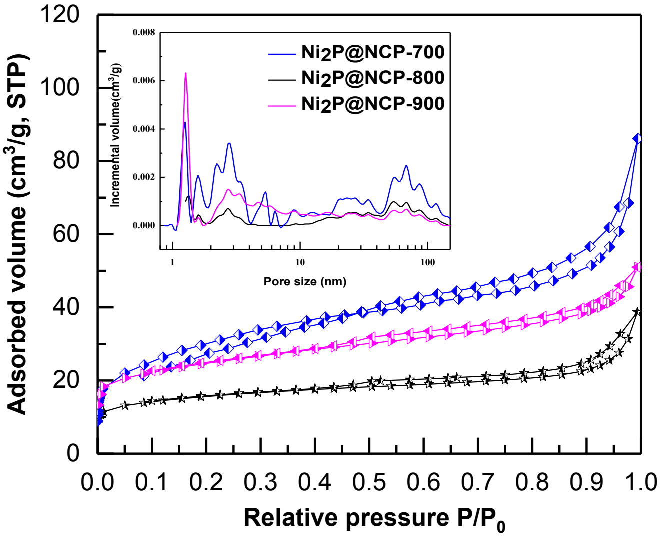


Figure S3. N_2 sorption isotherms and pore size distribution calculated using a nonlocal density function theory (NLDFT) method for the catalysts Ni_2P@NPC-700, Ni_2P@NPC-800, and Ni_2P@NPC-900.

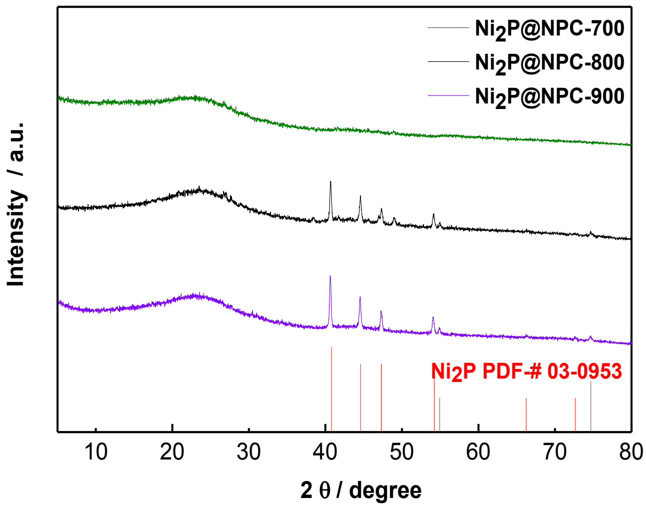


Figure S4. XRD patterns of Ni_2P@NPC-700, Ni_2P@NPC-800, and Ni_2P@NPC-900.

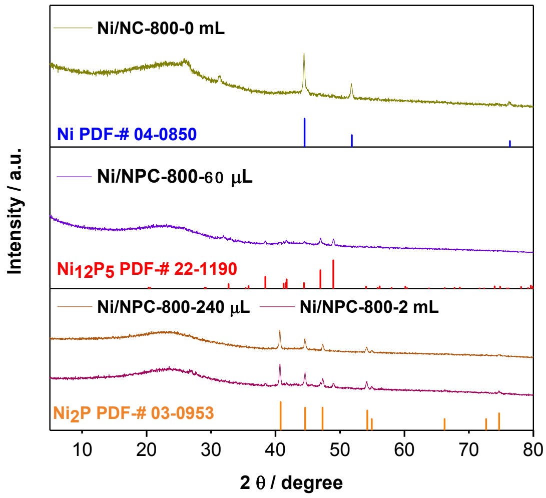


Figure S5. XRD patterns of the catalysts with different amount of phytic acid under 800°C

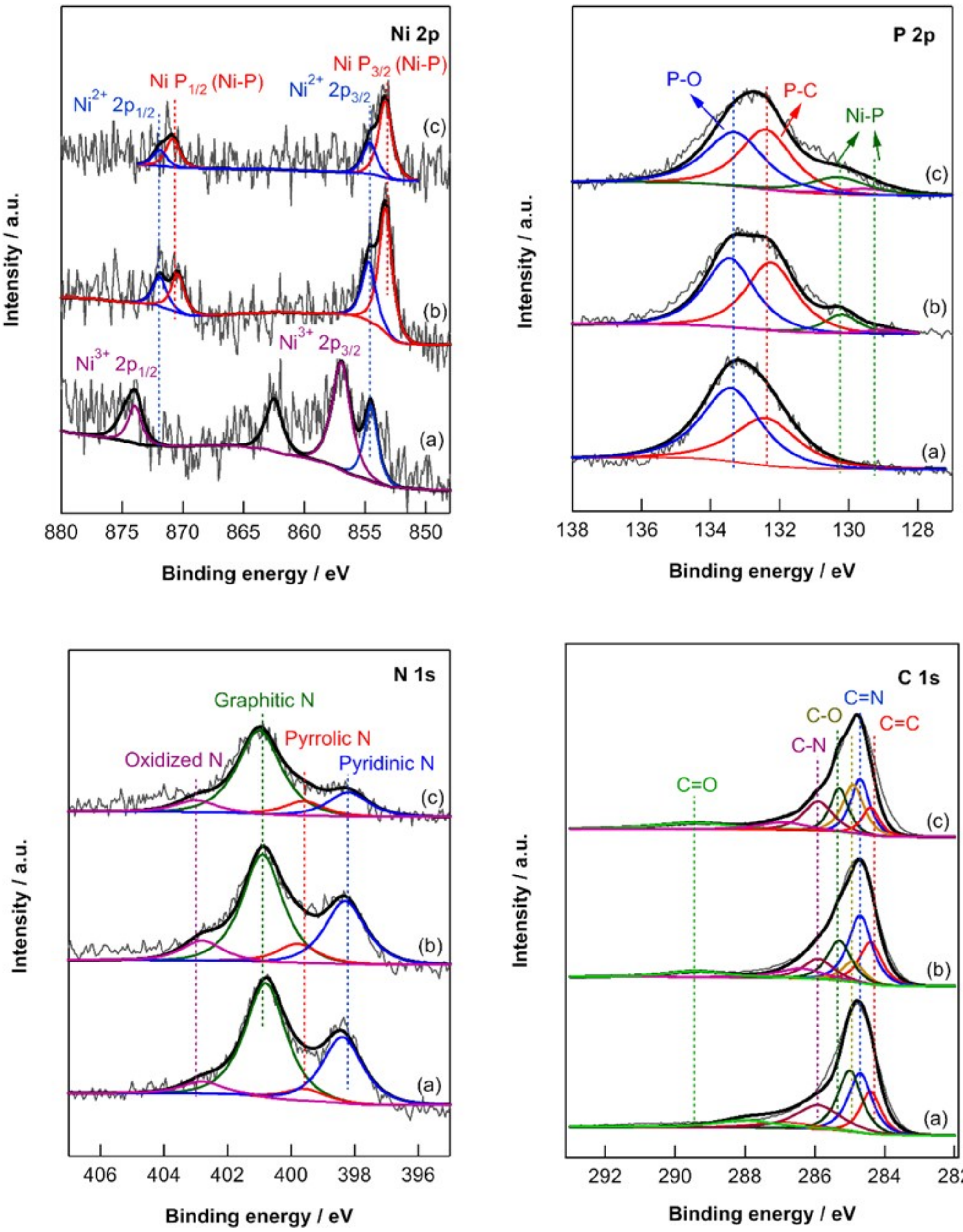


Figure S6. Ni 2p, P 2p, N 1s, C 1s XPS spectra of the catalysts Ni_2P@NPC-700, Ni_2P@NPC-800, Ni_2P@NPC-900.

Table S1. Chemical composition and texture properties of the catalyst Ni/NCP-T.

Sample	Ni[a] content (wt%)	P[a] content (wt%)	Elemental analysis		BET analysis		Catalyst yield (wt%)	Content of Ni_2P in catalyst (wt%)[c]
			C(wt%)	N(wt%)	S_{BET}[b] (m^2 g^{-1})	Pore volume (cm^3 g^{-1})		
Ni/NC-800	4.27	0	84.20	3.72	155.5	0.121	22.2	-
Ni_2P/NPC-700-120μL	3.05	3.52	75.48	5.01	106.9	0.089	24.0	-
Ni_2P /NPC-800-120μL	4.58	2.50	75.50	5.01	51.3	0.040	22.7	3.15
Ni_2P /NPC-900-120 μL	4.96	2.30	76.44	3.36	81.9	0.065	18.5	3.23
Ni/NPC-800-60μL	4.98	1.41	80.56	5.17	-	-	-	-
Ni/NPC-800-240μL	3.24	4.25	68.32	3.96	-	-	-	-
Ni/NPC-800-2 mL	1.99	8.94	59.96	3.24	-	-	-	-

[a]Determined by ICP-OES. [b]Specific surface areas were determined by the BET multipoint method. [c]Determined by XPS.

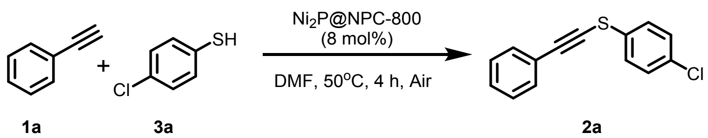
4. General procedure for synthesis of alkynyl thioethers.

A 25 mL sealing tube was charged with a magnetic stirring bar, alkyne (0.2 mmol) , thiol (0.3 mmol), Ni_2P@NPC-800 (20 mg, 8 mol% of Ni), 2 mL DMF. The reaction was stirred for 4 h at 50°C under atmospheric air. After completion of the reaction, the reaction mixture was cooled to room temperature and the conversion and selectivity was analyzed by GC-MS. The products were purified by column chromatography and structurally confirmed by NMR.

5. Catalytic studies

5.1. Recyclability of catalyst

The synthesis of alkynyl thioethers was chosen as the model reaction to investigate the recyclability of the catalyst Ni_2P@NPC-800. A 25 mL sealing tube was charged with a magnetic stirring bar, phenylacetylene (0.2 mmol), *para*-chlorobenzenethiol (0.3 mmol), Ni_2P@NPC-800 (20 mg, 8 mol% of Ni), 2 mL DMF. The reaction was stirred for 4 h at 50 °C under atmospheric air. After completion of the reaction, the reaction mixture was cooled to room temperature and the conversion and selectivity was analyzed by GC-MS. The residue was dispersed in 5 mL of ethanol and the resulting mixture was stirred for 10 min, the catalyst were separated by centrifuge. Such operation was repeated for 3 times. Finally, the obtained black solid was dried under vacuum at 40°C overnight for successive use.



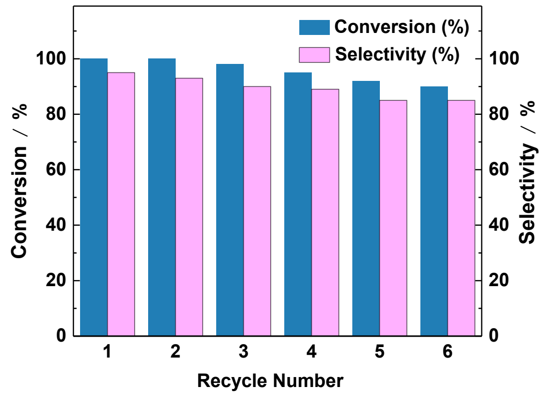
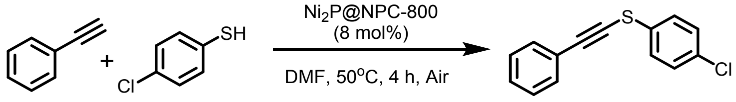


Figure S7. Recyclability of the catalyst Ni_2P@NPC-800 for the synthesis of alkynyl thioethers via CDC strategy.

5.2 Effect of removal of the Ni_2P@NPC-800 catalyst during the reaction.



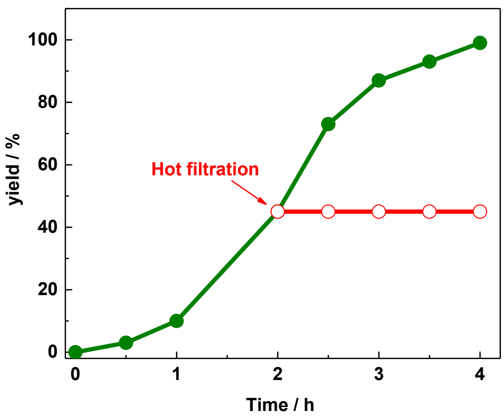
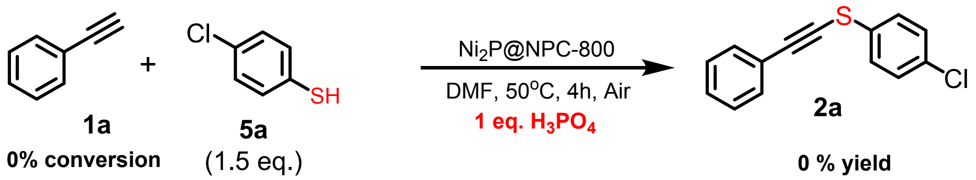


Figure S8. Effect of removal of the Ni_2P@NPC-800 catalyst during the reaction. (○) after removal of Ni_2P@NPC-800 and (●) without removal of Ni_2P@NPC-800. The arrow indicates the time when the Ni_2P@NPC-800 catalyst was removed from the reaction mixture.

5.3 Poisoning experiment.



A 25 mL sealing tube was charged with a magnetic stirring bar, Ni_2P@NPC-800 (20 mg, 8 mol% of Ni), H_3PO_4 (0.2 mmol), 2 mL DMF, the mixture was stirred 1h. Then phenylacetylene (0.2 mmol), *para*-chlorobenzenethiol (0.3 mmol) were added, the reaction was stirred for 4 h at 50 °C under atmospheric air.

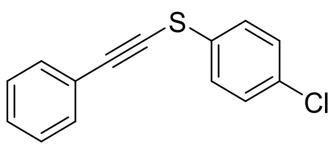
5.4 Comparison of catalytic performance for this work with other previous reports for synthesis of alkynyl thioethers via CDC strategy.

Table S2. Comparison of catalytic performance for this work with other previous reports for synthesis of alkynyl thioethers via CDC strategy.

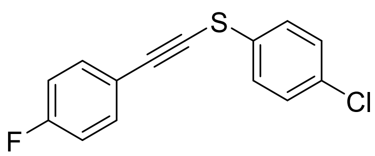
Catalyst	Reaction condition	Substrate scopes	Yield	Ref.
$RhH(PPh_3)_4$ + dppf	terminal alkyne (0.25 mmol), disulfide (0.75 mmol), $RhH(PPh_3)_4$ (2 mol%), dppf (2-4 mol%), acetone (0.5 mL), Ar atmosphere, reflux for 1 h.	Ar–≡–S–Ar	81%	[9a]
		Ar–≡–S–Alkyl	64%	
		Alkyl–≡–S–Ar	79-86%	
		Alkyl–≡–S–Alkyl	54-86%	
MCM-41-2N-CuCl Complexes	terminal alkyne (0.5 mmol), thiol (0.55 mmol), MCM-41-2N-CuCl (5 mol%), K_2CO_3 (10 mol%), DMSO (2 mL), 70 °C, 1 atm O_2, 1 h. (The heterogeneous catalyst can be recycled 10 times without any decreases in activity)	Ar–≡–S–Ar	76-95%	[9b]
		Ar–≡–S–Alkyl	-	
		Alkyl–≡–S–Ar	74-90%	
		Alkyl–≡–S–Alkyl	-	
CuCl	terminal alkyne (0.5 mmol), thiol (0.55 mmol), CuCl (5 mol%), K_2CO_3 (10 mol%), DMSO (2 mL), 70 °C,1 atm O_2, 1 h.	Ar–≡–S–Ar	14-97%	[9c]
		Ar–≡–S–Alkyl	58-71%	
		Alkyl–≡–S–Ar	91-93%	
		Alkyl–≡–S–Alkyl	34%	

CuI	terminal alkyne (0.25 mmol), disulfide (0.125 mmol), CuI (4 mol%), K_2CO_3 (0.5 mmol), DMSO (2 mL), 70°C, 1 atm O_2, 1 h.	Ar—≡—S–Ar	-	[9d]
		Ar—≡—S–Alkyl	-	
		Alkyl—≡—S–Ar	30-92%	
		Alkyl—≡—S–Alkyl	-	
Ni_2P@NPC-800	terminal alkyne (0.2 mmol), thiol (0.3 mmol), Ni_2P@NPC-800 (8 mol% of Ni), DMF (2 mL), air atmosphere, 50°C, 4h	Ar—≡—S–Ar	71-93%	This work
		Ar—≡—S–Alkyl	61-67%	
		Alkyl—≡—S–Ar	72%-82%	
		Alkyl—≡—S–Alkyl	52-57%	

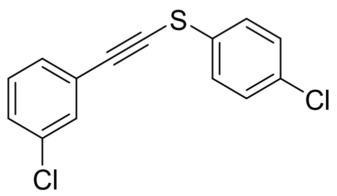
6. Characterization of products



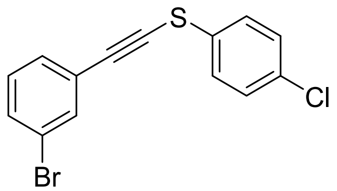
(4-chlorophenyl)(phenylethynyl)sulfane (2a), yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53-7.49 (m, 2H), 7.41 (d, J = 8.6 Hz, 3H), 7.37-7.30 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 132.5, 131.8, 131.6, 129.4, 128.9, 128.5, 127.5, 122.6, 98.4, 74.8. HRMS: calcd. for $C_{14}H_9ClS$ [M], 244.0013; found,244.0115.



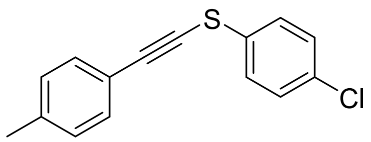
(4-chlorophenyl)((4-fluorophenyl)ethynyl)sulfane (2b), yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52-7.48 (m, 2H), 7.41-7.37 (m, 2H), 7.34-7.30 (m, 2H), 7.07-7.02 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 162.89 (d, J = 250.8 Hz), 134.01 (d, J = 8.6 Hz), 132.6, 131.4, 129.4, 127.6, 118.73 (d, J = 3.6 Hz), 115.83 (d, J = 22.2 Hz), 97.2, 74.6. HRMS: calcd. for $C_{14}H_{18}ClFS$ [M], 262.0019; found,262.0023.



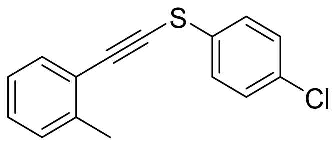
(4-chlorophenyl)((3-chlorophenyl)ethynyl)sulfane (2c), yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.43-7.38 (m, 3H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 134.3, 132.8, 131.9, 130.9, 130.2, 129.9, 129.5, 127.7, 124.6, 122.3, 96.6. HRMS: calcd. for $C_{14}H_{18}Cl_2S$ [M], 277.9724; found,277.9717.



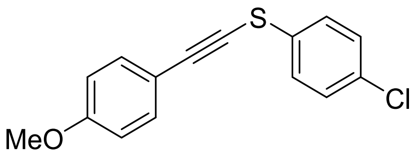
((3-bromophenyl)ethynyl)(4-chlorophenyl)sulfane (2d), yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.47-7.41 (m, 3H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.25 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 134.4, 132.9, 131.9, 131.1, 130.2, 129.9, 129.6, 127.8, 124.7, 122.3. 96.7. HRMS: calcd. for $C_{14}H_{18}BrClS$ [M], 321.9219; found, 321.9221.



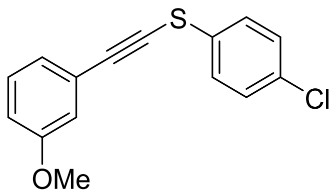
(4-chlorophenyl)(p-tolylethynyl)sulfane (2e), White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44 (dt, *J* = 4.6, 4.0 Hz, 4H), 7.37-7.33 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.3, 132.4, 131.9, 131.8, 129.4, 129.3, 127.4, 119.7, 119.5, 98.67, 73.8, 21.6. HRMS: calcd. for $C_{15}H_{11}ClS$ [M], 258.0270; found, 258.0271.



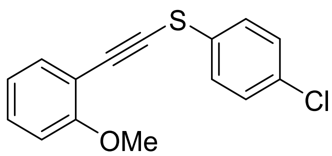
(4-chlorophenyl)(o-tolylethynyl)sulfane (2f), Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.6 Hz, 1H), 7.44-7.40 (m, 2H), 7.34-7.29 (m, 2H), 7.24 (ddd, *J* = 17.1, 10.3, 3.8 Hz, 2H), 7.19-7.14 (m, 1H), 2.47 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.5, 132.5 132.2, 131.9, 129.6, 129.4, 128.9, 127.4, 125.7, 122.5, 97.4, 78.2, 20. 9. HRMS: calcd. for $C_{15}H_{11}ClS$ [M], 258.0270; found, 258.0273.



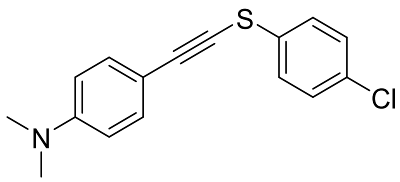
(4-chlorophenyl)((4-methoxyphenyl)ethynyl)sulfane (2g), colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49-7.40 (m, 2H), 7.41-7.33 (m, 2H), 7.33-7.19 (m, 2H), 6.92-6.78 (m, 2H), 3.79 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.3, 133.9, 132.3, 132.1, 129.4, 127.3, 114.7, 114.1, 98.6, 72.9, 55.4. HRMS: calcd. for $C_{15}H_{11}ClOS$ [M], 274.0219; found, 274.0216.



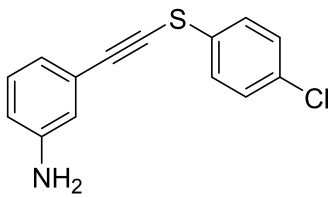
(4-chlorophenyl)((3-methoxyphenyl)ethynyl)sulfane (2h), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.36 (m, 2H), 7.34-7.26 (m, 2H), 7.29-7.21 (m, 1H), 7.14-7.07 (m, 1H), 7.02 (dd, *J* = 2.3, 1.5 Hz, 1H), 6.97-6.85 (m, 1H), 3.80 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 159.4, 132.6, 131.5, 129.6, 129.4, 127.5, 124.4, 123.6, 116.6, 115.5, 98.4, 55.4. HRMS: calcd. for $C_{15}H_{11}ClOS$ [M], 274.0219; found, 274.0219.



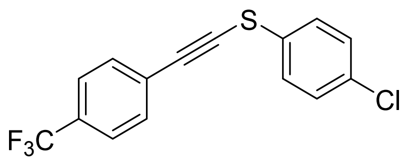
(4-chlorophenyl)((2-methoxyphenyl)ethynyl)sulfane (2i), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.39 (m, 3H), 7.35-7.26 (m, 3H), 6.91 (ddd, J = 16.9, 11.8, 4.5 Hz, 2H), 3.89 (s, J = 3.0 Hz, 3H).. ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.3, 133.3, 132.2, 132.0, 130.3, 129.3, 127.3, 120.6, 111.9, 110.7, 95.3, 78.4, 55.8. HRMS: calcd. for $C_{15}H_{11}ClOS$ [M], 274.0219; found, 274.02120.



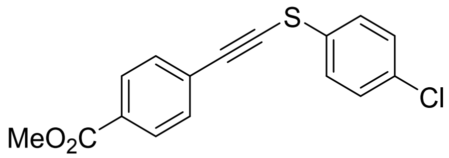
4-(((4-chlorophenyl)thio)ethynyl)-N,N-dimethylaniline (2j), yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.45-7.35 (m, 4H), 7.31-7.26 (m, 2H), 6.66-6.62 (m, 2H), 3.00 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 150.7, 133.9, 132.9, 131.9, 129.2, 127.1, 111.7, 108.9, 100.1, 71.3, 40.2. HRMS: calcd. for $C_{16}H_{14}ClNS$ [M], 287.0535; found, 287.0536.



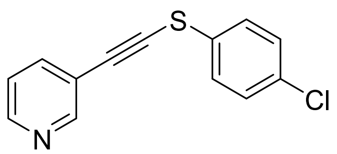
3-(((4-chlorophenyl)thio)ethynyl)aniline (2k), colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52-7.35 (m, 2H), 7.35-7.27 (m, 2H), 7.11 (t, J = 7.8 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 6.70-6.61 (m, 1H), 3.69 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 146.4, 132.4, 131.7, 129.4, 129.3, 127.4, 123.3, 122.2, 117.8, 115.9, 98.8, 74.0. HRMS: calcd. for $C_{14}H_{10}ClNS$ [M], 259.0222, 259.0224.



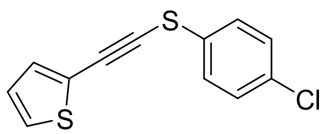
2-(thiophen-3-yl)quinazoline (2l), colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 (q, J = 8.5 Hz, 4H), 7.40 (t, J = 8.9 Hz, 2H), 7.33 (d, J = 8.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 133.0, 131.6, 130.7, 130.27 (d, J = 32.8 Hz), 129. 6, 129.3, 127.8, 125.40 (q, J = 3.8 Hz), 123.84 (d, J = 272.3 Hz), 96.8, 78.4. HRMS: calcd. for $C_{15}H_8ClF_3S$ [M], 311.9987; found, 311.9989.



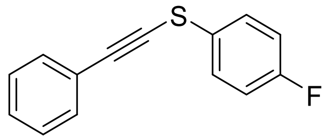
methyl 4-(((4-chlorophenyl)thio)ethynyl)benzoate (2m), White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 3.93 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 166.4, 132.9, 131.2, 130.8, 129.8, 129.6, 129.6, 127.8, 127.3 98.9, 78.8, 52.3. HRMS: calcd. for $C_{16}H_{11}ClO_2S$ [M], 302.0168; found,302.0169.



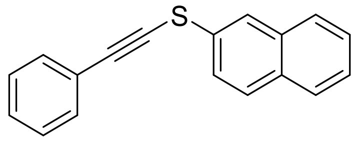
3-(((4-chlorophenyl)thio)ethynyl)pyridine (2n), yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.73 (d, J = 1.5 Hz, 1H), 8.56 (dd, J = 4.9, 1.6 Hz, 1H), 7.77 (dt, J = 7.9, 1.9 Hz, 1H), 7.45-7.39 (m, 2H), 7.37-7.32 (m, 2H), 7.31-7.24 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 152.3, 149.0, 138.6, 133.0, 130.7, 129.6, 127.8, 123.1, 119.9, 94.7, 79.1. HRMS: calcd. for $C_{13}H_8ClNS$ [M], 245.0066; found,245.0067.



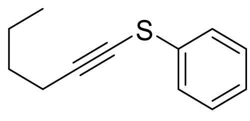
2-(((4-chlorophenyl)thio)ethynyl)thiophene (2o), yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40-7.27 (m, 6H), 7.00 (dd, J = 5.0, 3.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 134.2, 132.7, 131.5, 129.4, 129.0, 127.6, 127.2, 122.7, 91.2, 76.9. HRMS: calcd. for $C_{12}H_7ClS_2$ [M], 249.9678; found, 249.9676.



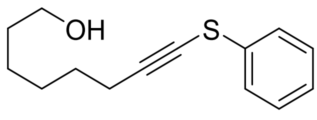
(4-fluorophenyl)(phenylethynyl)sulfane (2p), White solid; [1]H NMR (400 MHz, $CDCl_3$): δ 7.45-7.34 (m, 4H), 7.29-7.22 (m, 3H), 7.02-6.94 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.90 (d, *J* = 246.5 Hz), 131.8, 128.8, 128.5, 128.5, 128.4, 127.90 (d, *J* = 3.3 Hz), 122.8, 116.50 (d, *J* = 22.4 Hz), 97.6, 75.7. HRMS: calcd. for $C_{14}H_9FS$ [M], 228.0409; found, 228.0410.



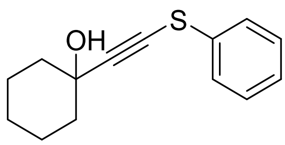
naphthalen-2-yl(phenylethynyl)sulfane (2q), white solid; ^1H NMR (400 MHz, $CDCl_3$):δ 7.95 (d, *J* = 1.4 Hz, 1H), 7.86-7.77 (m, 3H), 7.58-7.53 (m, 3H), 7.53-7.44 (m, 2H), 7.40-7.34 (m, 3H). ^{13}C (101 MHz, $CDCl_3$): δ 132.1, 131.8, 130.3, 129.0, 128.7, 128.5, 127.8, 127.2, 126.9, 126.0, 124.6, 124.2. HRMS: calcd. for $C_{18}H_{12}S$ [M], 260.0660; found, 260.0667.



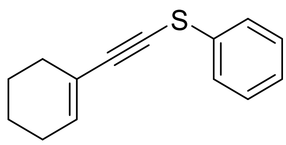
hex-1-yn-1-yl(phenyl)sulfane (2r), colorless oil; ^1H NMR (600 MHz, $CDCl_3$): δ 7.50-6.92 (m, 4H), 2.45 (t, *J* = 7.1 Hz, 2H), 1.72-1.51 (m, 2H), 1.50-1.32 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 132.5, 131.9, 129.2, 127.0, 100.7, 64.0, 30.7, 22.0, 20.01, 13.6. HRMS: calcd. for $C_{12}H_{14}S$ [M], 190.0816; found,190.0818.



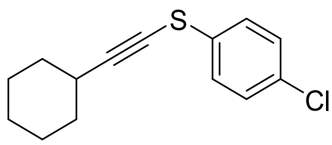
8-(phenylthio)oct-7-yn-1-ol (2s), colorless oil; ^1H NMR (600 MHz, $CDCl_3$): δ 7.34-7.25 (m, 4H), 3.63 (t, *J* = 6.6 Hz, 2H), 2.45 (t, *J* = 7.1 Hz, 2H), 1.59 (ddd, *J* = 15.0, 10.8, 7.5 Hz, 4H), 1.49-1.37 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.4, 131.9, 129.2, 127.0, 100.6, 64.2, 62.7, 40.8, 32.6, 28.7, 28.5, 25.3, 20.2. HRMS: calcd. for $C_{14}H_{18}OS$ [M], 234.1078; found, 234.1079.



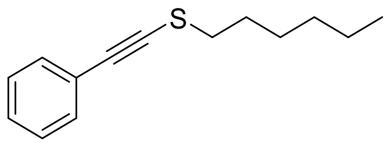
1-((phenylthio)ethynyl)cyclohexan-1-ol (2t), colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36-7.28 (m, 4H), 2.07-1.91 (m, 2H), 1.73 (dt, J = 11.8, 8.3 Hz, 2H), 1.70-1.62 (m, 4H), 1.61-1.52 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 132.5, 131.4, 129.4, 127.3, 39.8, 34.7, 25.3, 25.1, 23.3, 21.5. HRMS: calcd. for $C_{14}H_{16}OS$ [M], 232.0922; found, 232.0924.



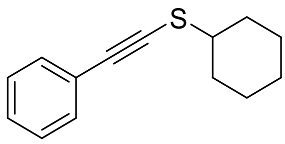
(cyclohex-1-en-1-ylethynyl)(phenyl)sulfane (2u), colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38-7.27 (m, 4H), 6.23 (td, J = 4.0, 2.0 Hz, 1H), 2.19 (tt, J = 6.2, 2.3 Hz, 2H), 2.16-2.12 (m, 2H), 1.70-1.64 (m, 2H), 1.63-1.58 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 136.7, 132.3, 132.1, 129.3, 127.1, 120.6, 100.6, 71.3, 29.1, 25.8, 22.2, 21.4. HRMS: calcd. for $C_{14}H_{14}S$ [M], 214.0816; found, 214.0811.



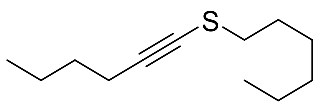
(4-chlorophenyl)(cyclohexylethynyl)sulfane (2v), colorless oil; 1H NMR (600 MHz, $CDCl_3$): δ 7.30 (dd, J = 25.2, 8.6 Hz, 4H), 2.67-2.58 (m, 1H), 1.87 (d, J = 7.0 Hz, 2H), 1.76-1.71 (m, 2H), 1.54 (dd, J = 11.1, 8.2 Hz, 3H), 1.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.6, 131.9, 129.2, 126.9, 104.7, 64.1, 32.6, 30.6, 25.8, 24.8. HRMS: calcd. for $C_{14}H_{15}ClS$ [M], 250.0583; found, 250.0588.



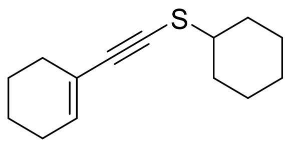
hexyl(phenylethynyl)sulfane (2w), colorless oil; [1]H NMR (400 MHz, $CDCl_3$): δ 7.44-7.35 (m, 2H), 7.31-7.23 (m, 3H), 2.84-2.73 (m, 2H), 1.79 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.49-1.38 (m, 2H), 1.37-1.23 (m, 4H), 0.89 (dd, *J* = 8.8, 5.2 Hz, 4H). [13]C NMR (101 MHz, $CDCl_3$): δ 131.4, 128.3, 127.9, 123.6, 92.9, 79.7, 35.8, 31.3, 29.4, 28.0, 22.5, 14.1. HRMS: calcd. for $C_{14}H_{18}S$ [M], 218.1129; found, 218.1131.



cyclohexyl(phenylethynyl)sulfane (2x), colorless oil; [1]H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 6.5, 3.2 Hz, 2H), 7.35-7.23 (m, 3H), 3.00 (tt, *J* = 10.9, 3.8 Hz, 1H), 2.19-2.00 (m, 2H), 1.89-1.76 (m, 2H), 1.63 (ddd, *J* = 11.9, 7.6, 3.7 Hz, 1H), 1.57 (d, *J* = 3.5 Hz, 1H), 1.43-1.32 (m, 2H), 1.27 (ddd, *J* = 11.5, 8.3, 3.1 Hz, 2H). [13]C NMR (101 MHz, $CDCl_3$): δ 131.4, 128.3, 127.9, 123.7, 94.4, 78.6, 47.7, 33.0, 26.1, 25.5. HRMS: calcd. for $C_{14}H_{16}S$ [M], 216.0973; found, 216.0977.



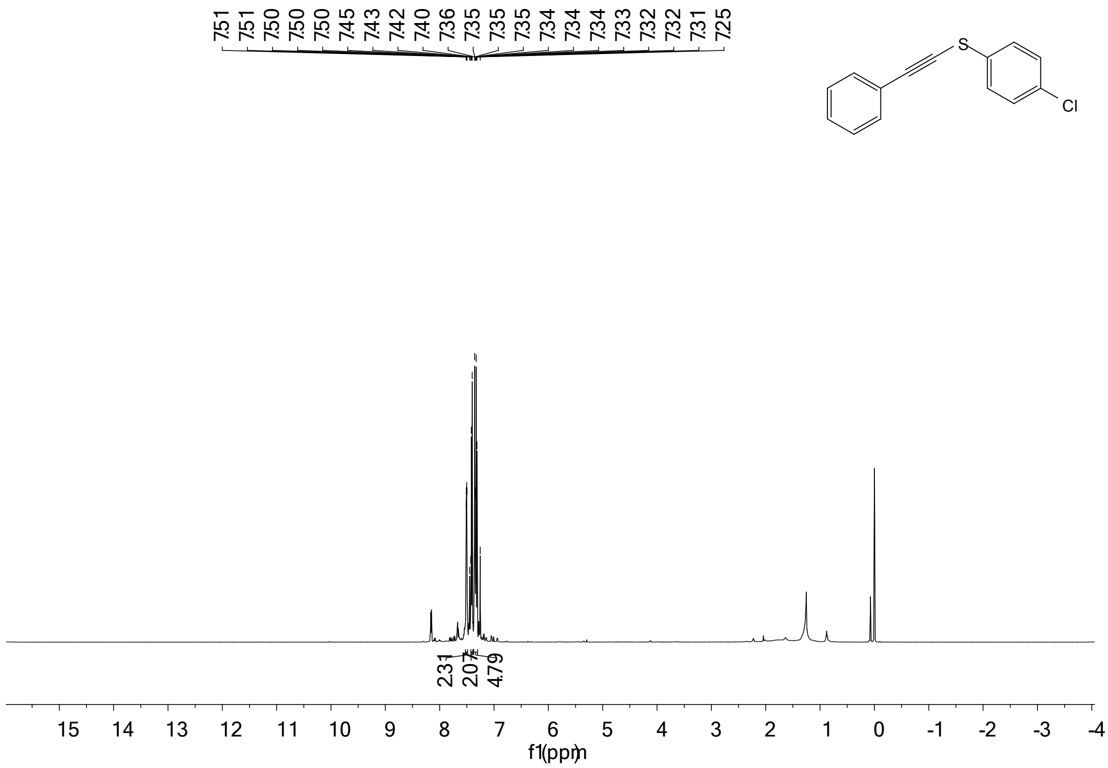
hex-1-yn-1-yl(hexyl)sulfane (2y), colorless oil; [1]H NMR (400 MHz, $CDCl_3$) δ 2.75-2.58 (m, 2H), 2.30 (t, *J* = 6.9 Hz, 2H), 1.71 (dt, *J* = 14.8, 7.3 Hz, 2H), 1.54-1.46 (m, 2H), 1.45-1.36 (m, 2H), 1.36-1.28 (m, 4H), 0.96-0.84 (m, 4H). [13]C NMR (101 MHz, $CDCl_3$): δ 94.2, 68.3, 35.5, 31.4, 30.9, 29.2, 27.9, 22.5, 21.9, 19.8, 14.0, 13.6. HRMS: calcd. for $C_{12}H_{22}S$ [M], 198.1442; found, 198.1447.

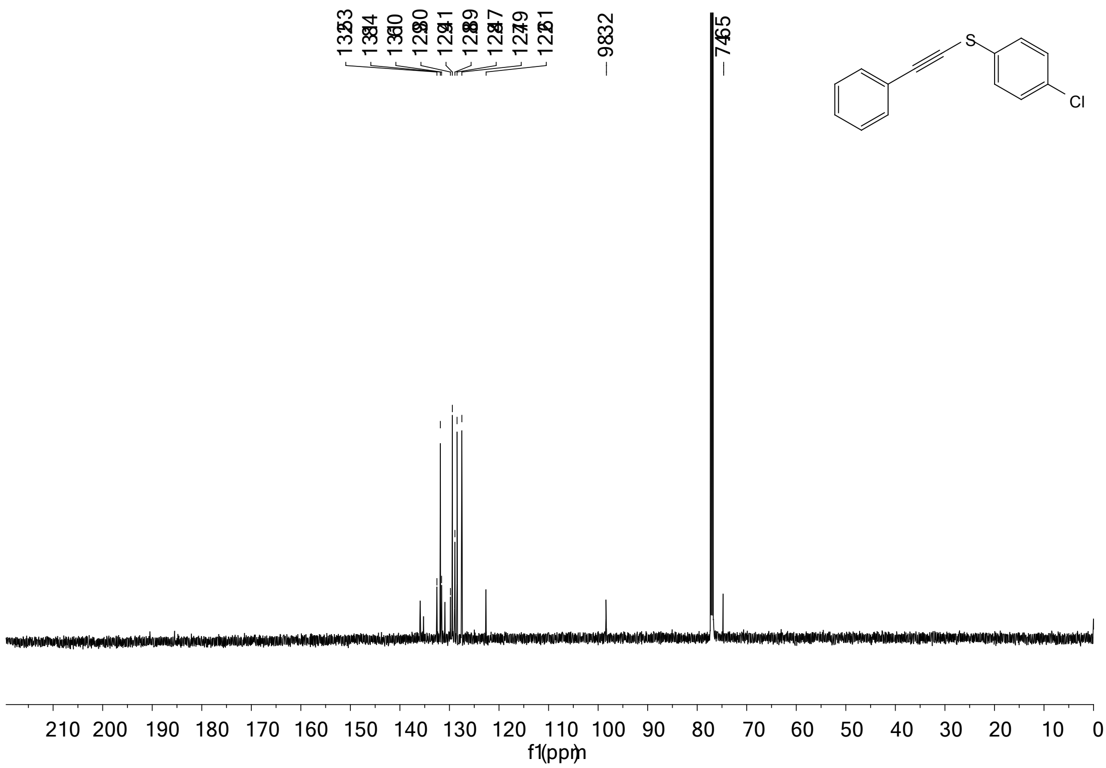


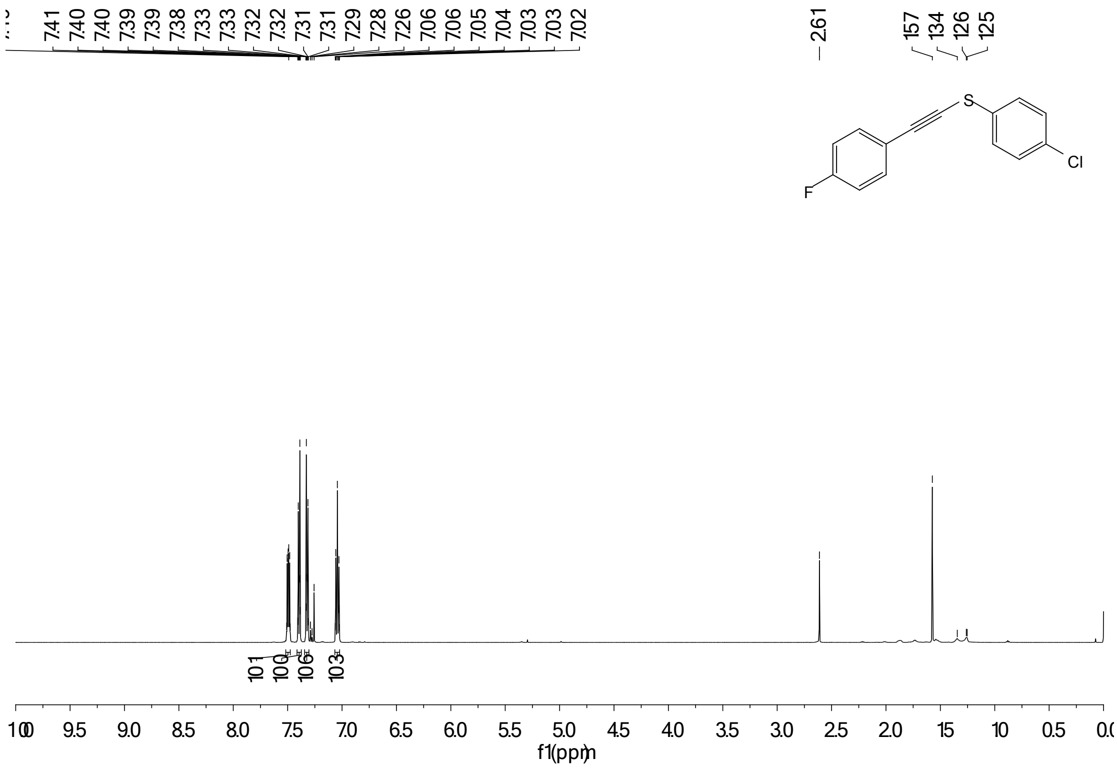
(cyclohex-1-en-1-ylethynyl)(cyclohexyl)sulfane (2z), colorless oil; [1]H NMR (400

MHz, $CDCl_3$): δ 6.07-5.92 (m, 1H), 2.82 (tt, *J* = 10.8, 3.7 Hz, 1H), 2.05-1.97 (m, 4H), 1.77-1.67 (m, 4H), 1.57-1.51 (m, 4H), 1.46-1.36 (m, 2H), 1.26 -1.21 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 134.3, 121.1, 96.3, 74.6, 32.91, 32.87, 29.3, 26.1, 25.7, 25.5, 22.3, 21.5. HRMS: calcd. for $C_{14}H_{20}S$ [M], 220.1286; found, 220.1286.

7. [1]H and [13]C NMR spectra of products



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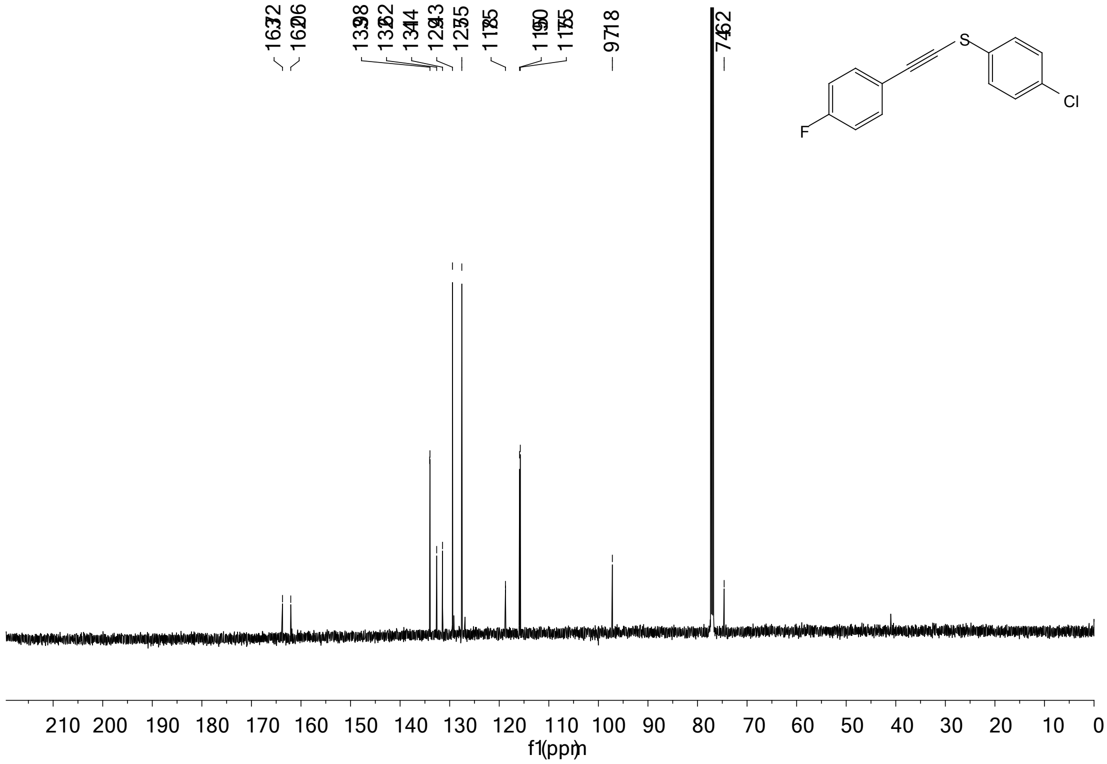
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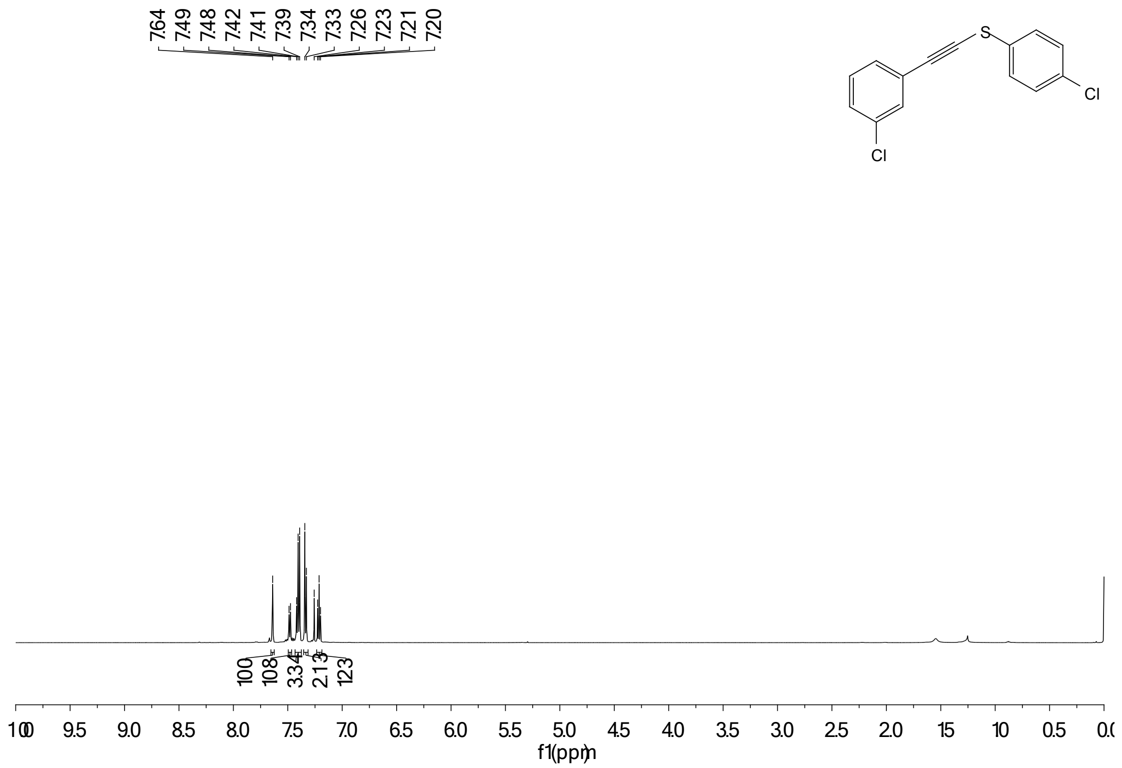

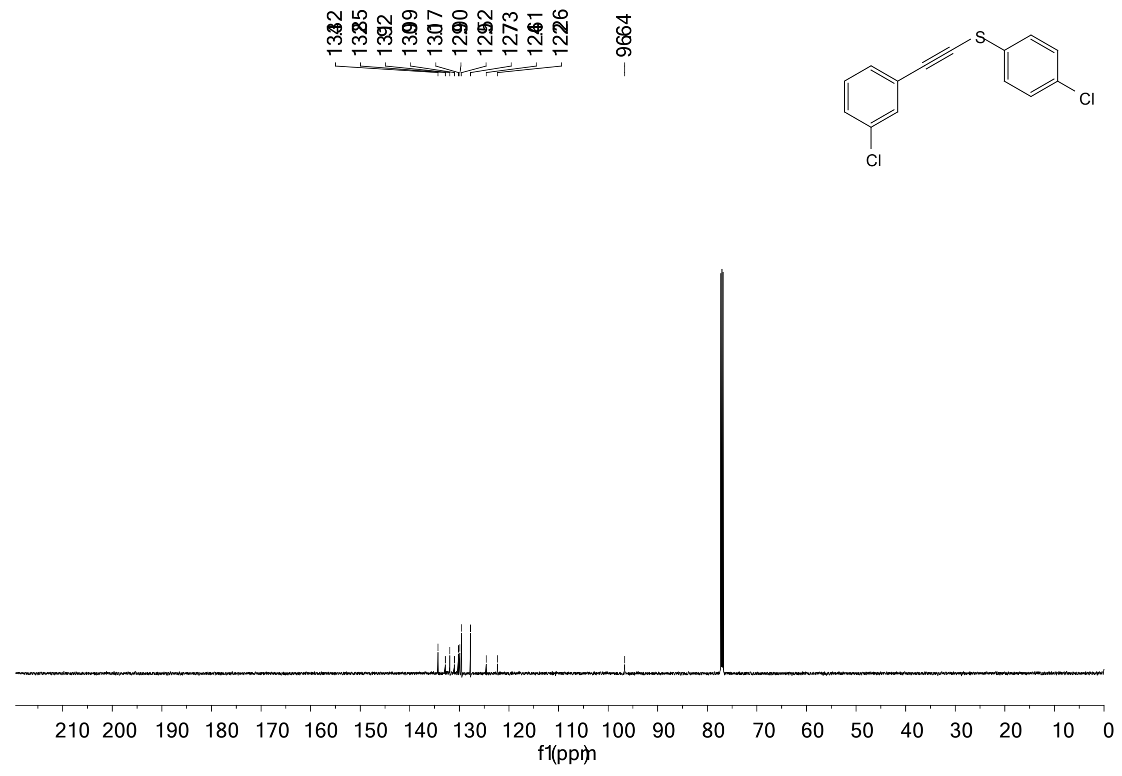

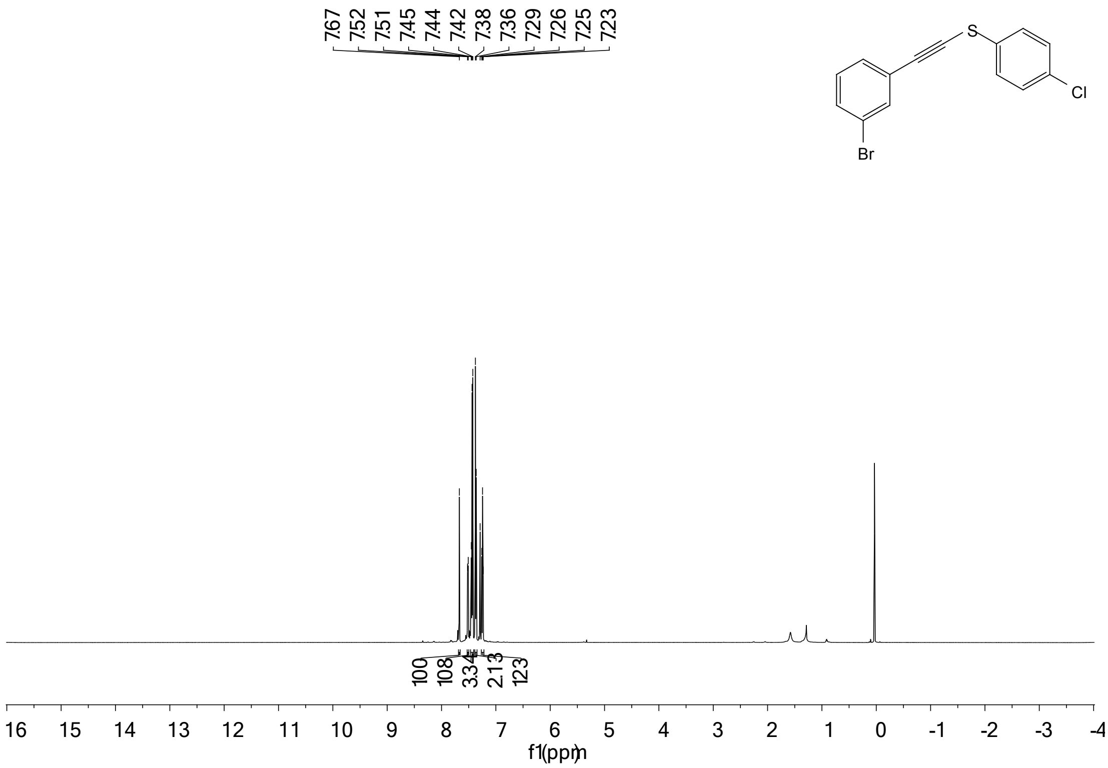
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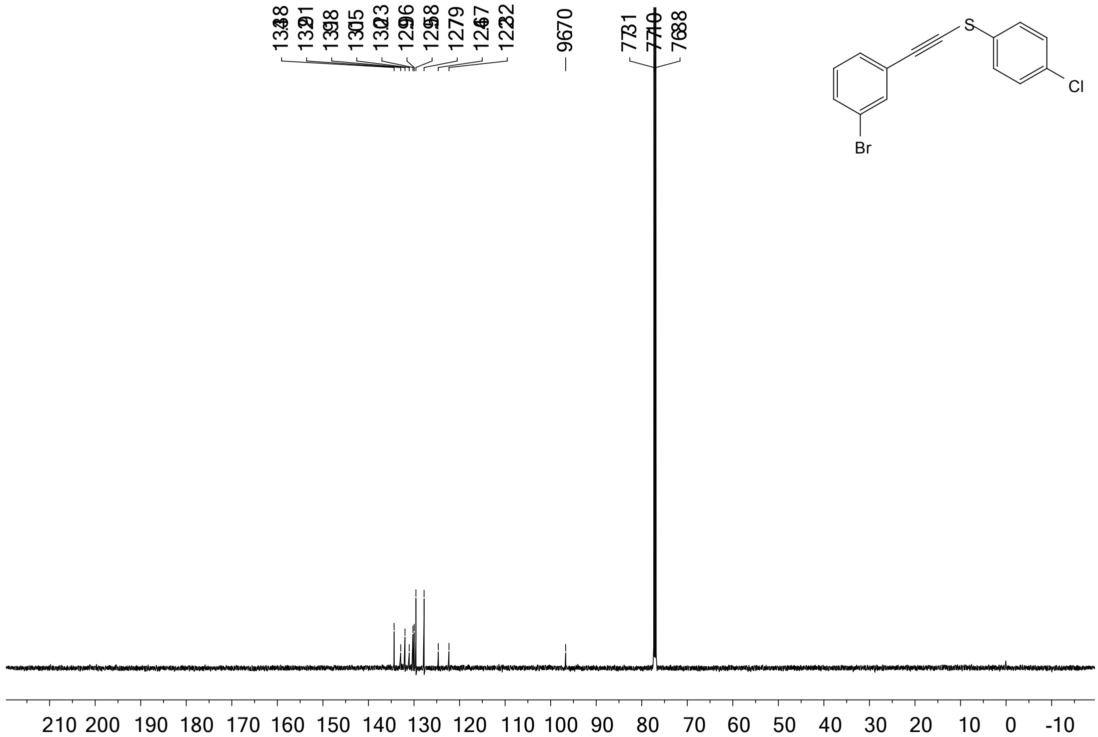
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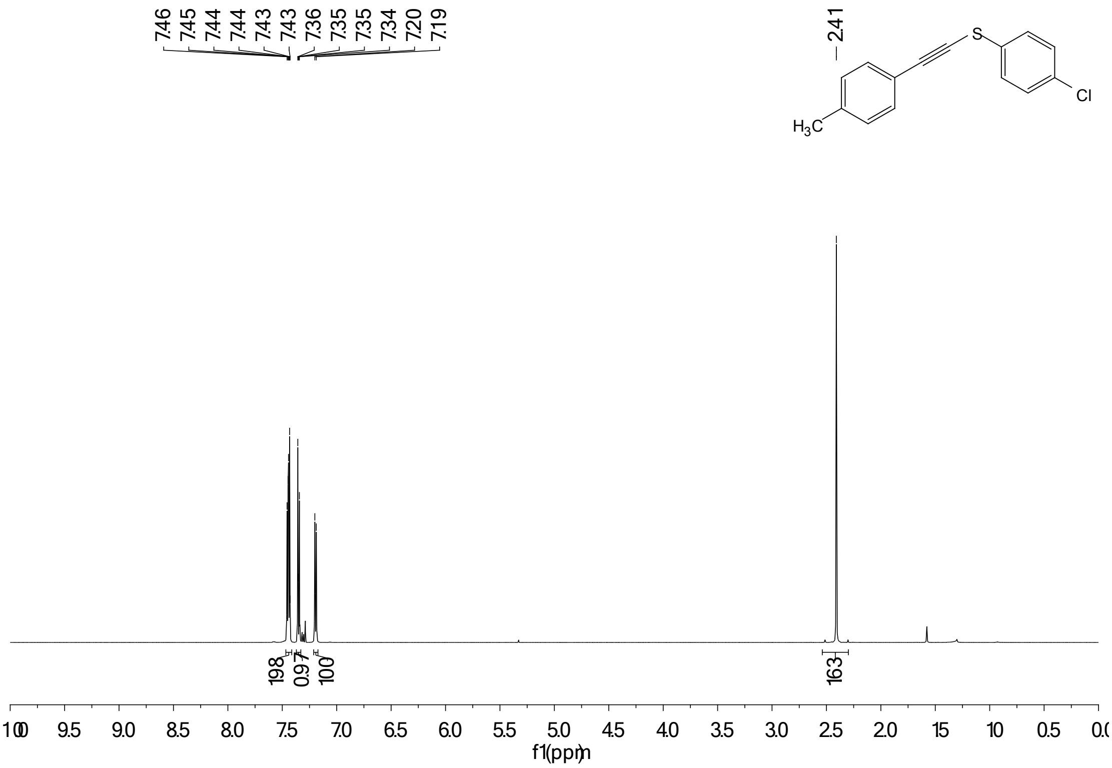
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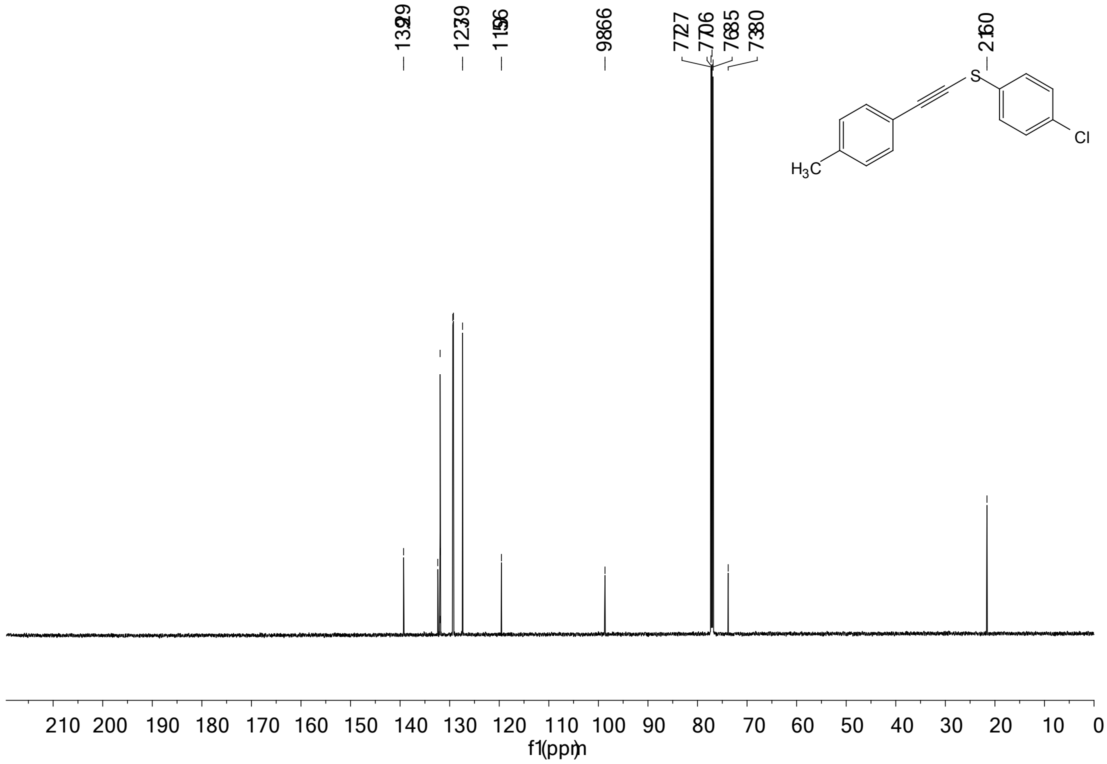
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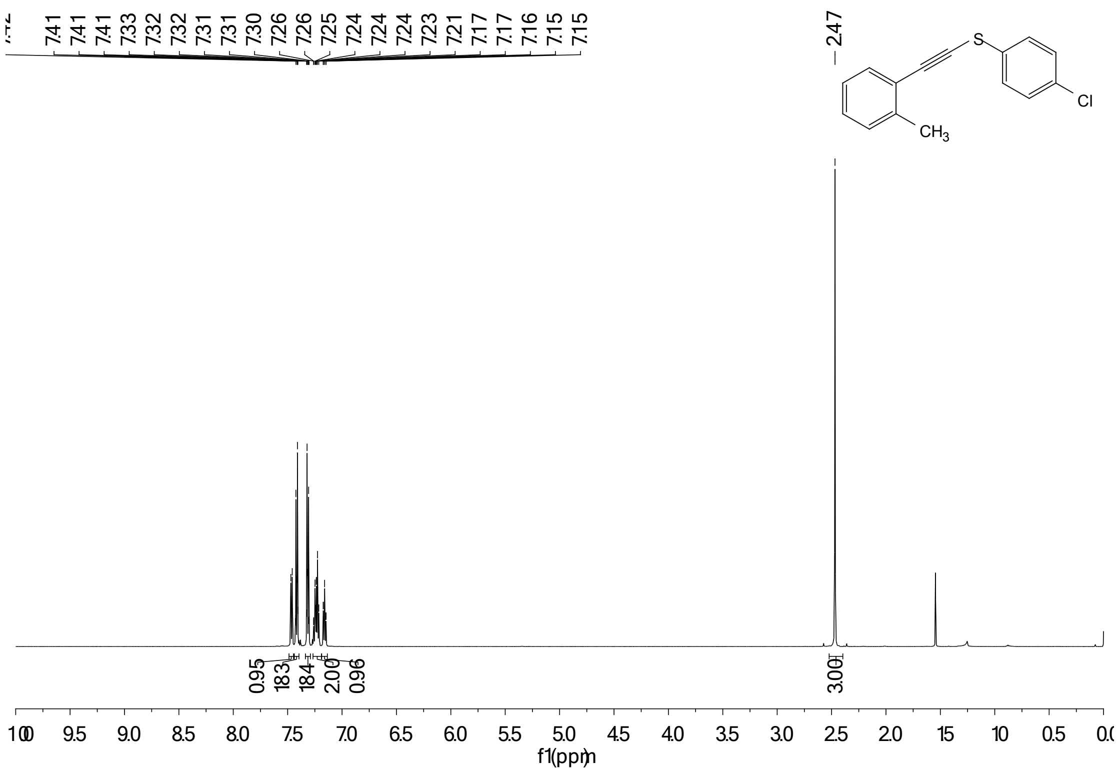

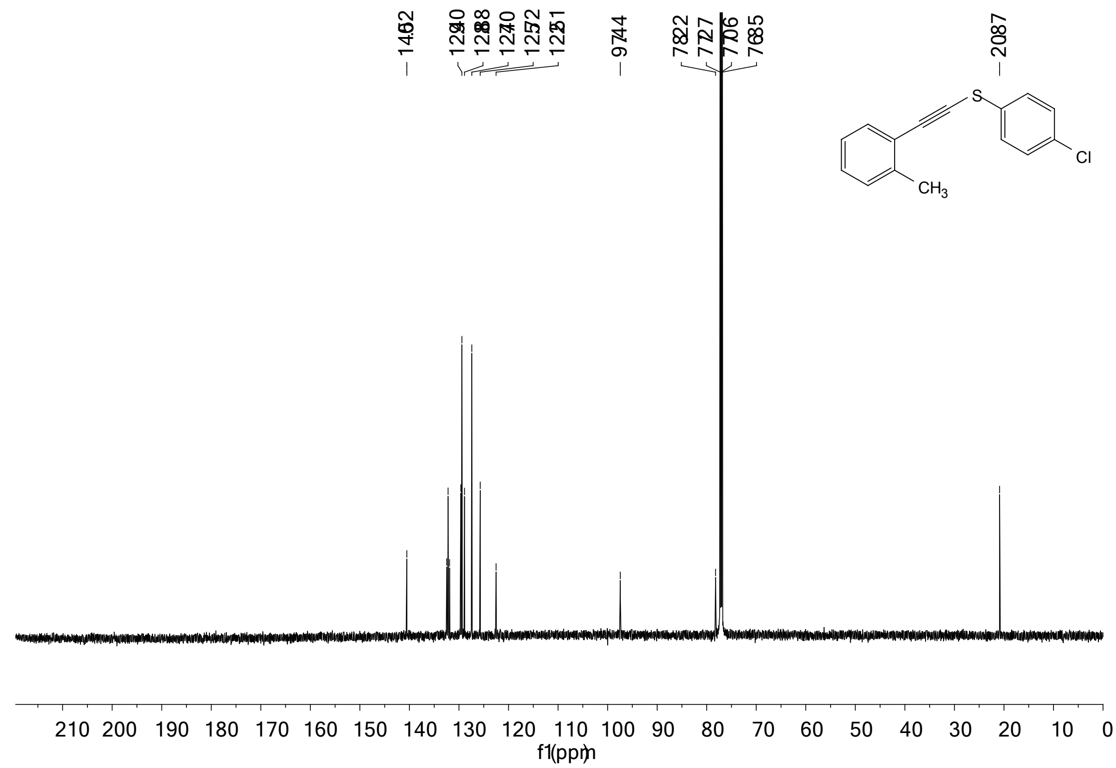

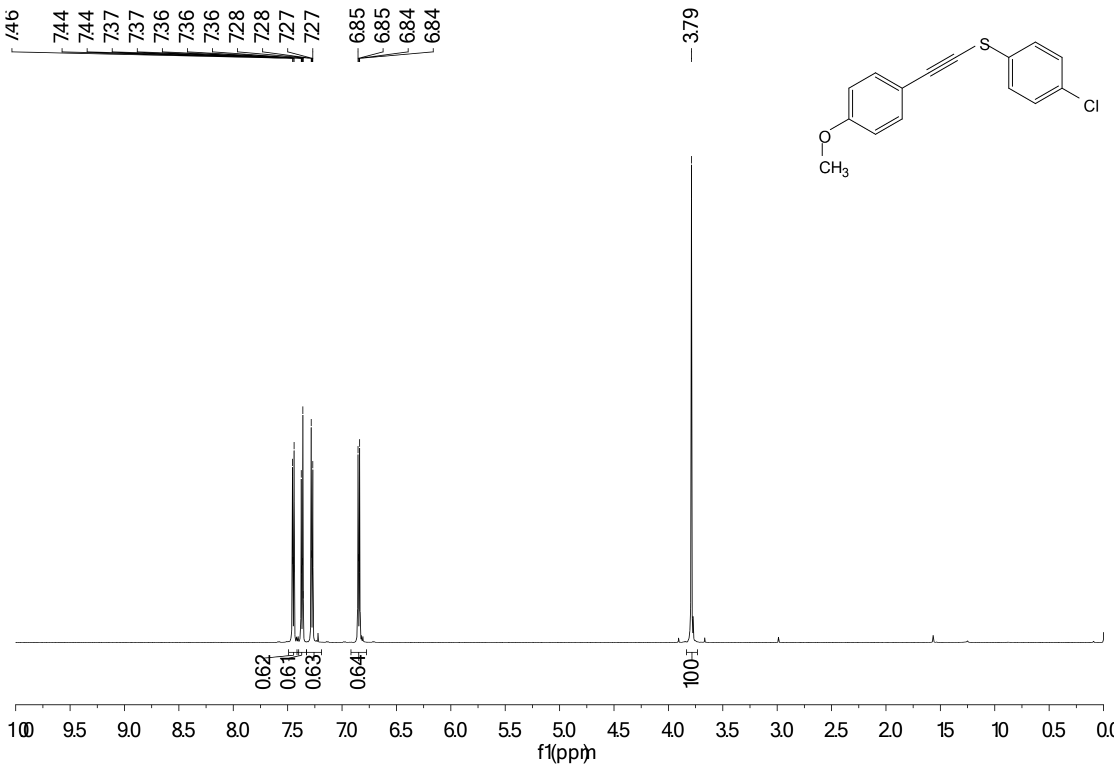

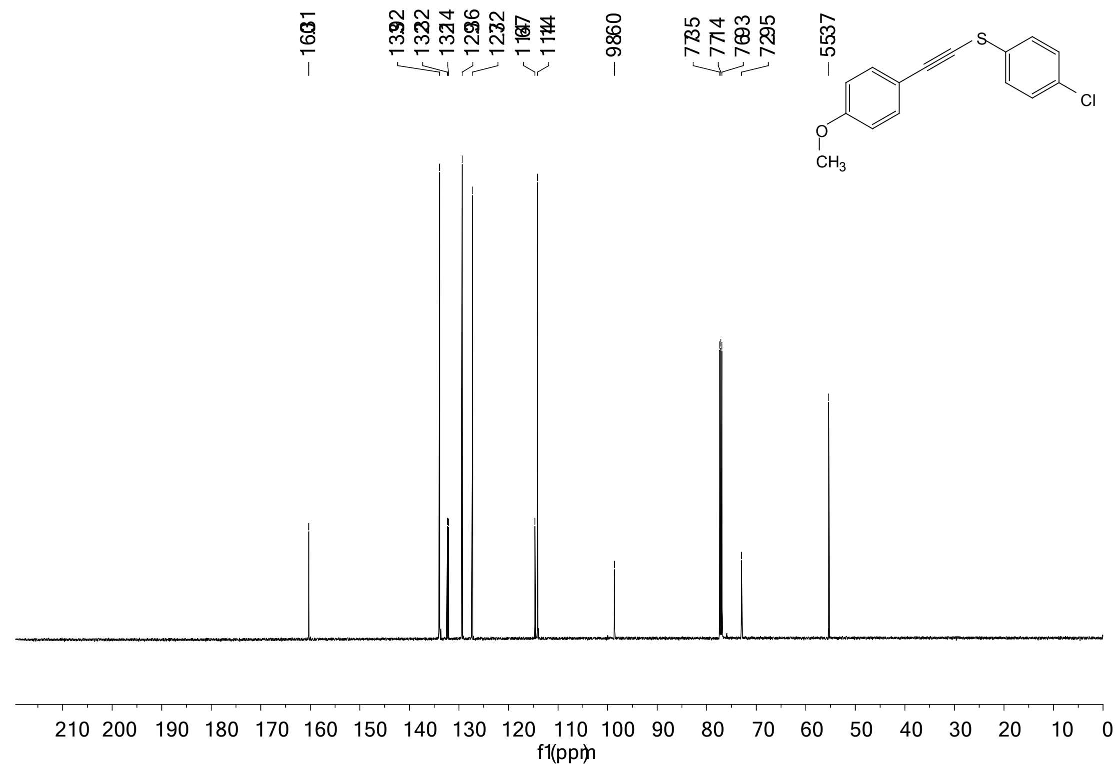

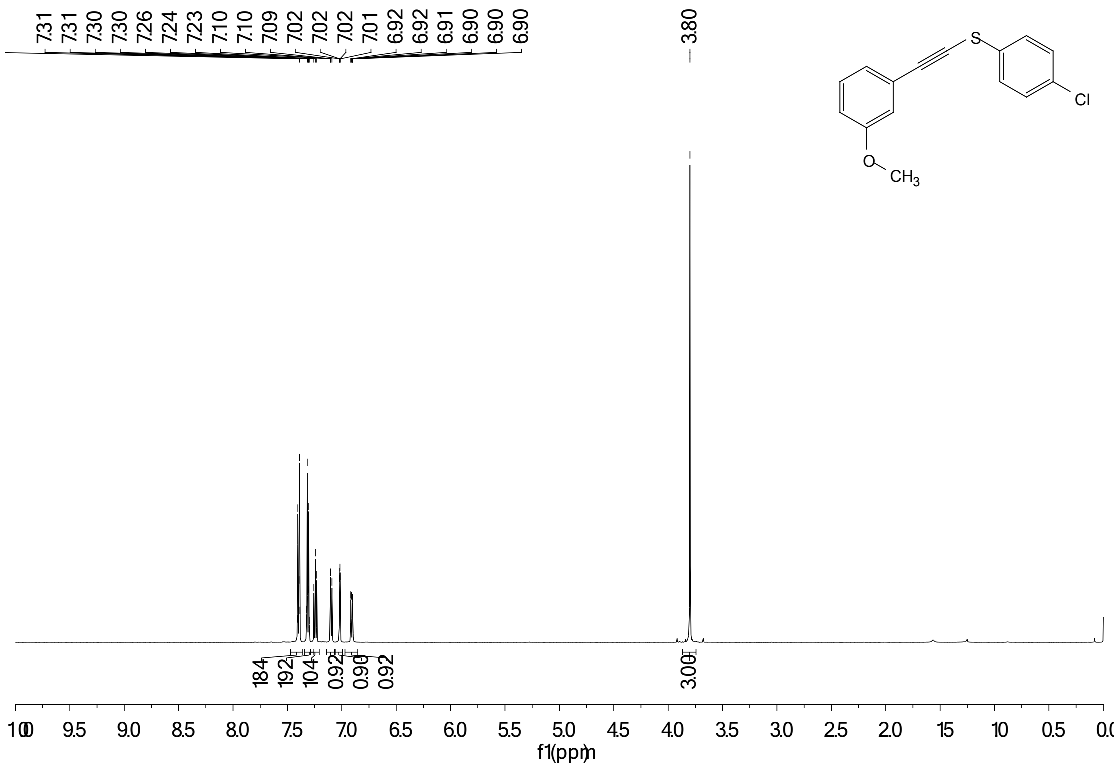
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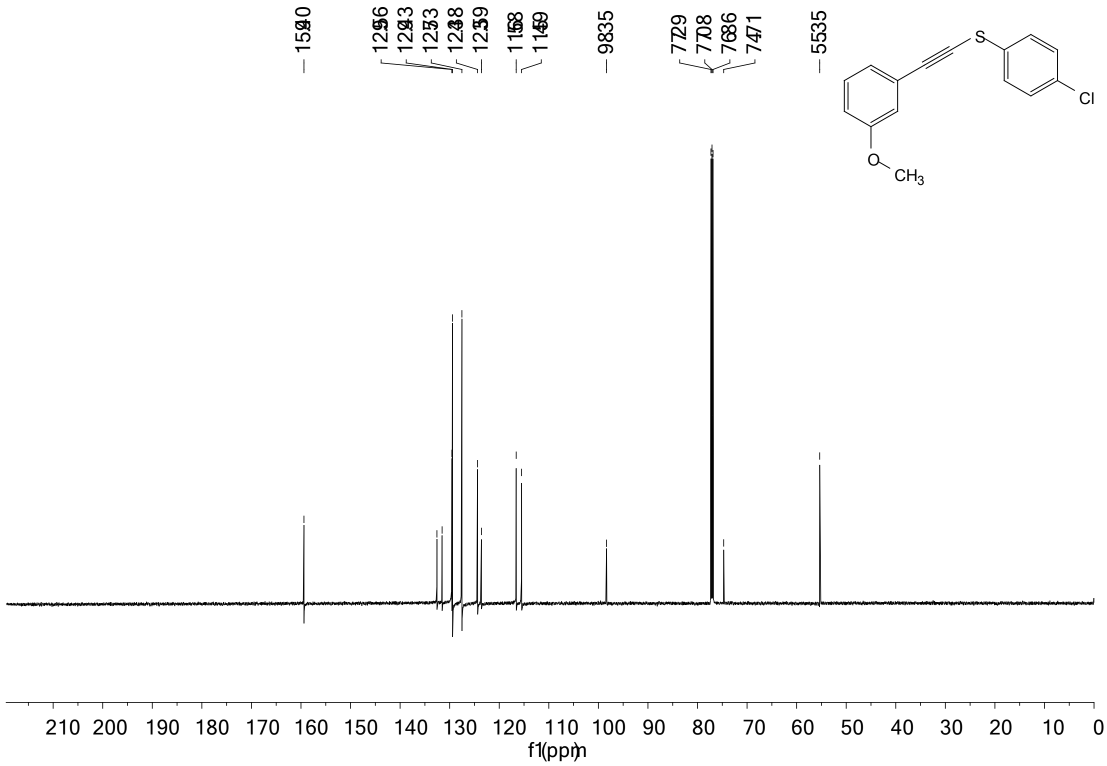
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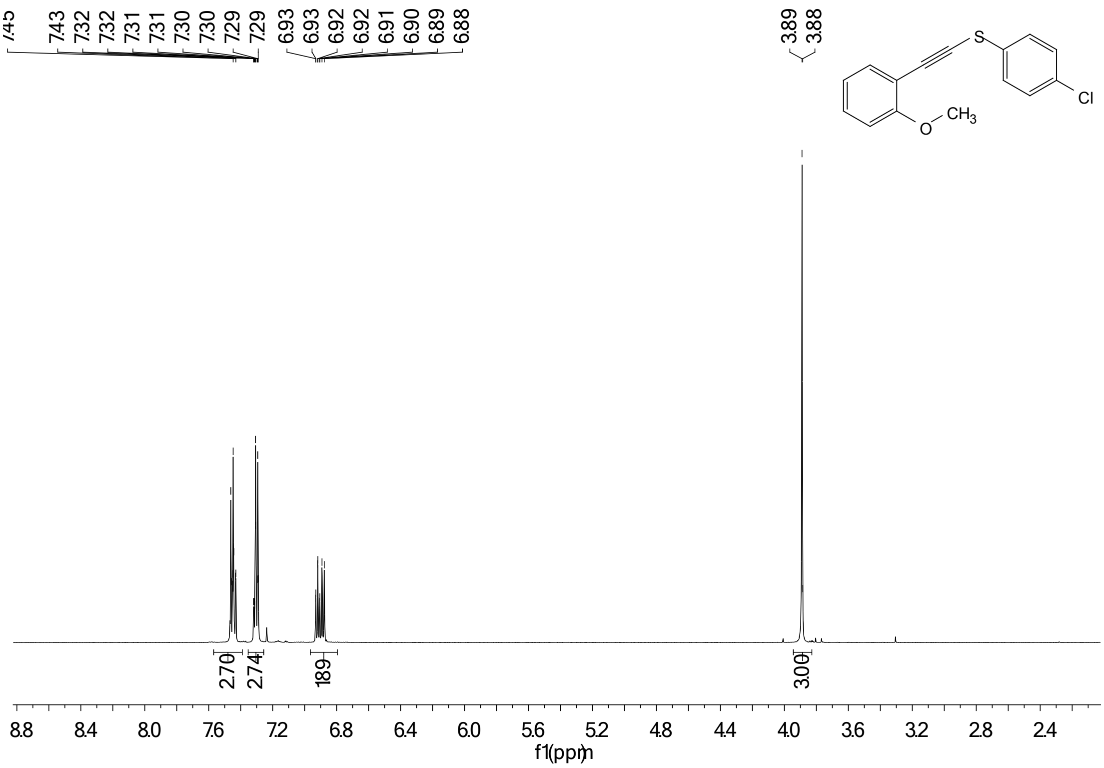

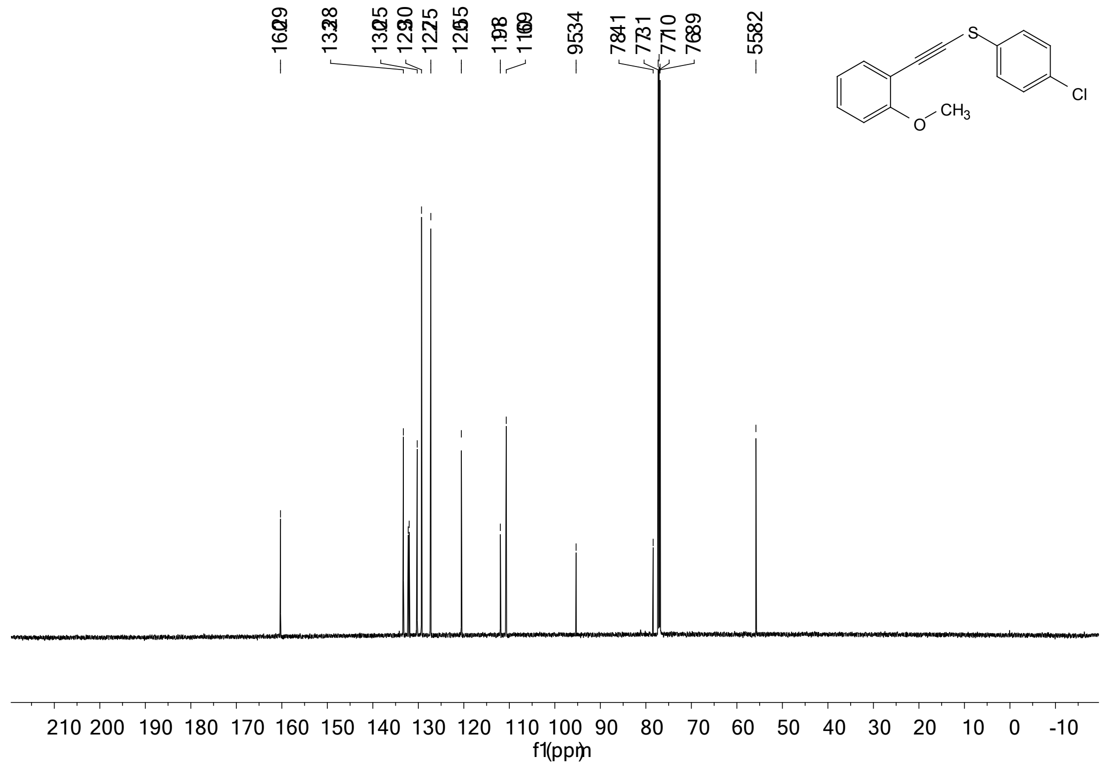

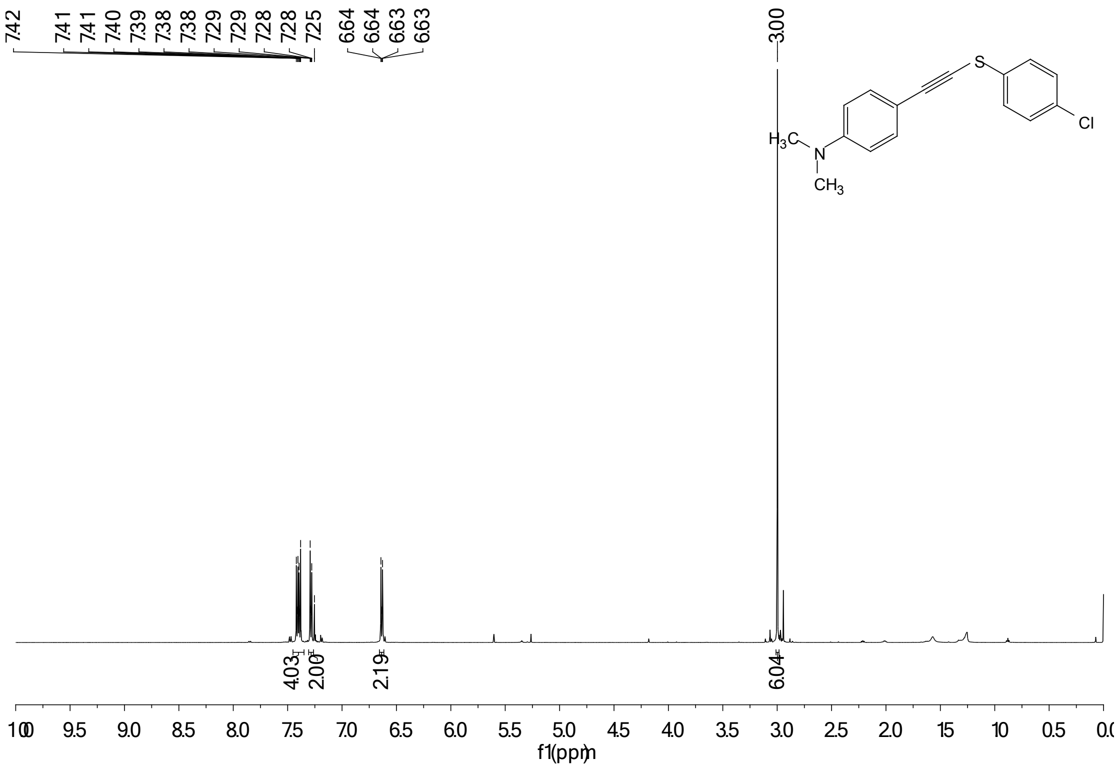
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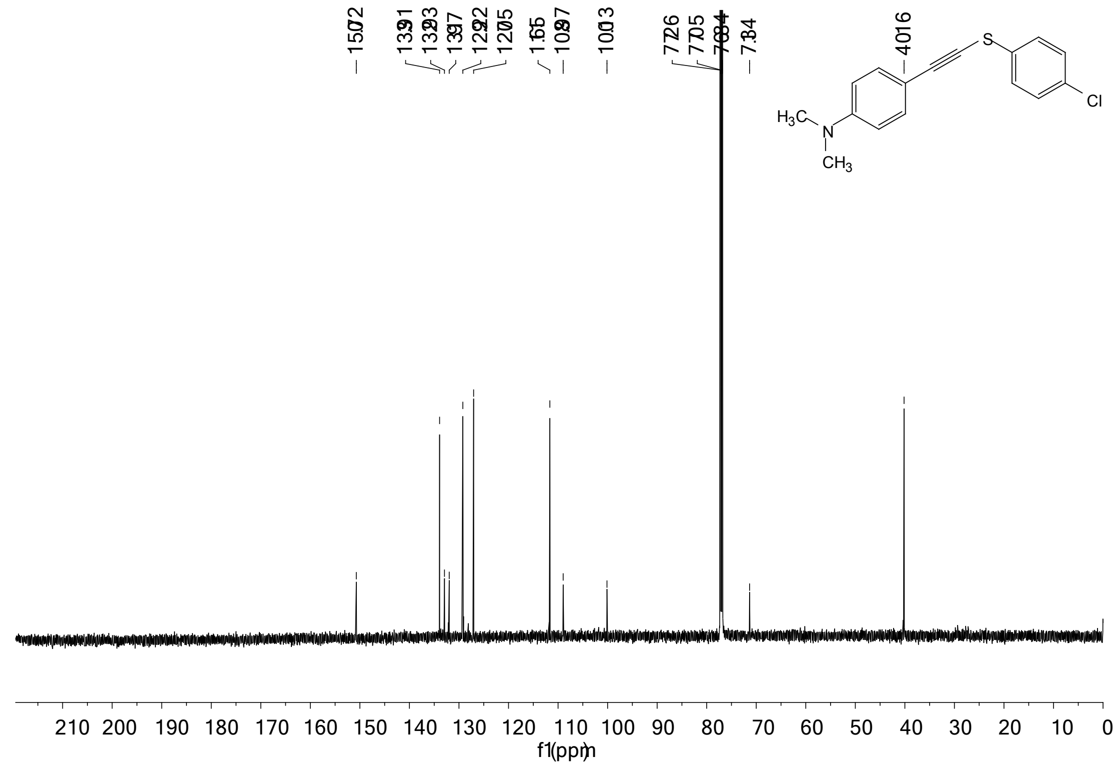
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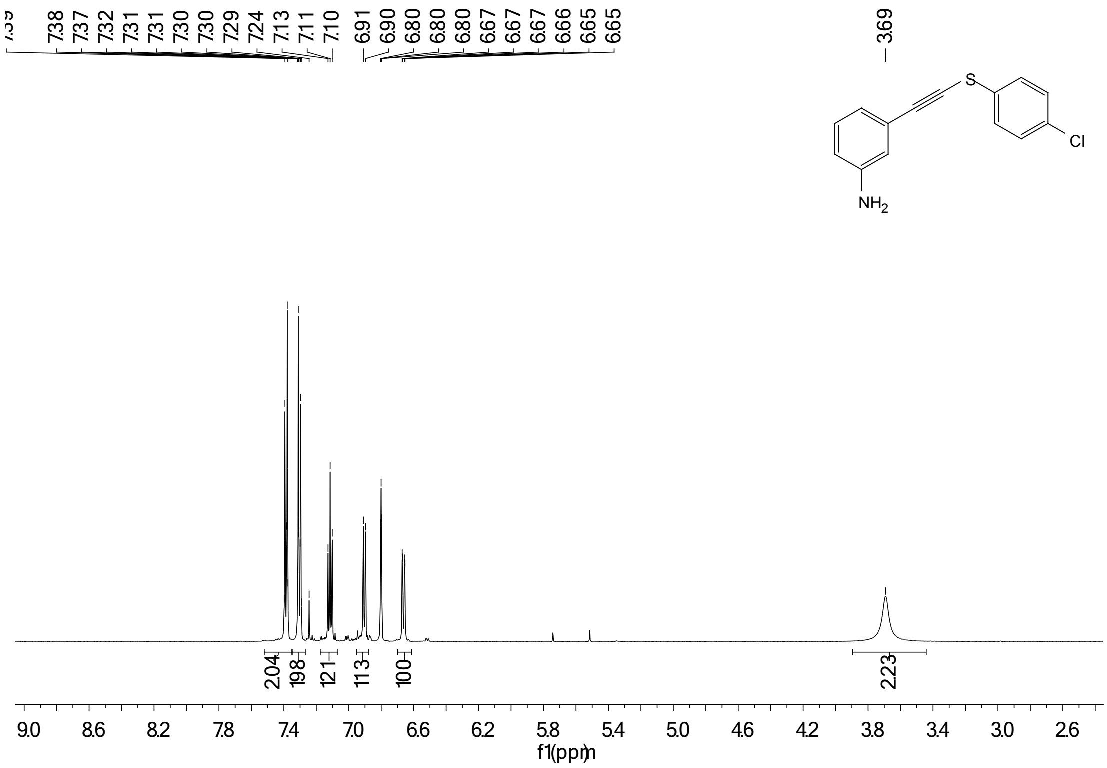

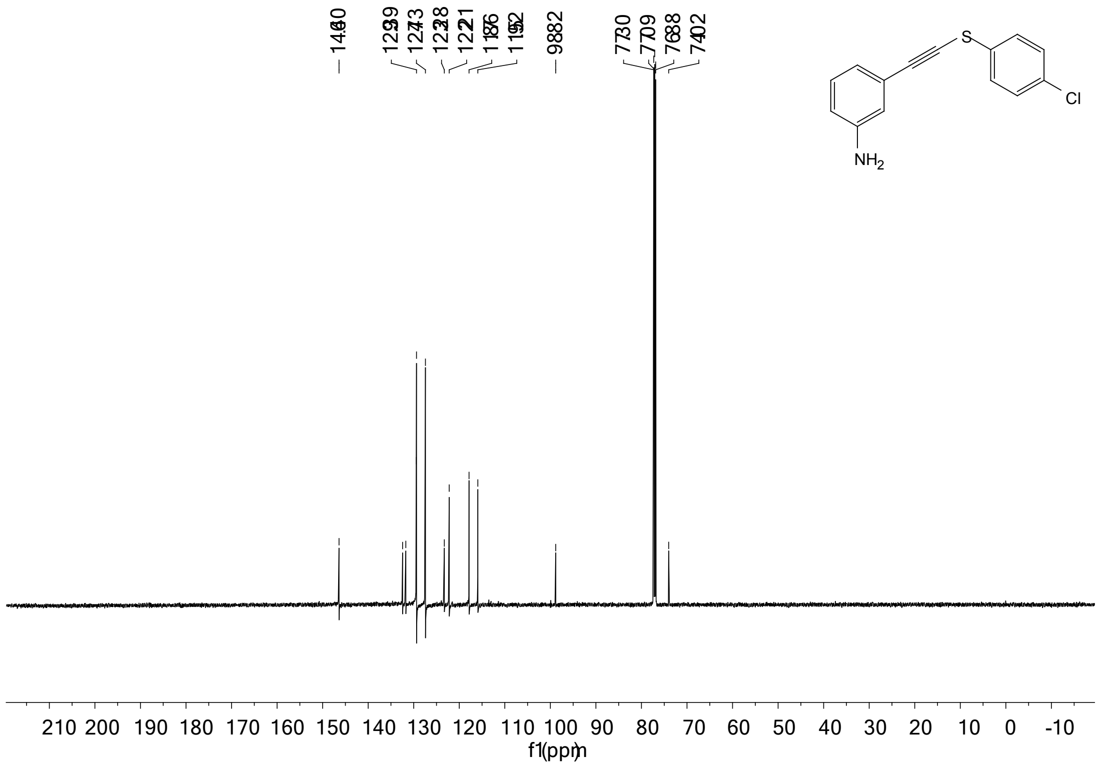

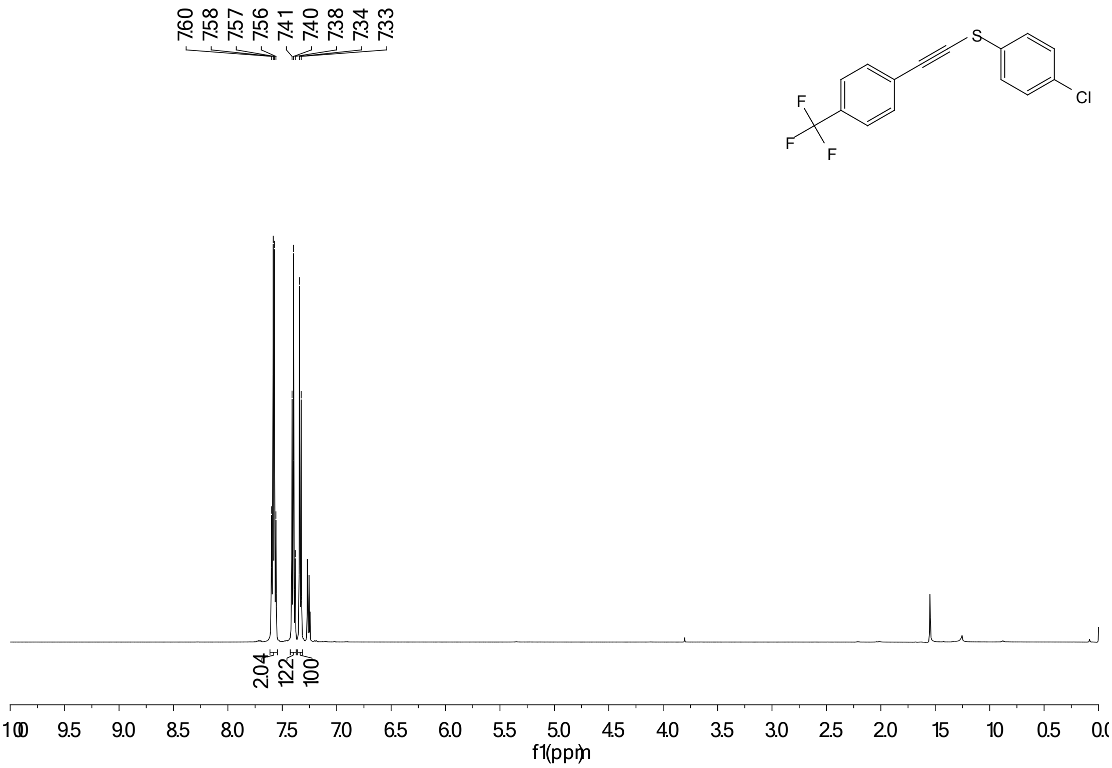
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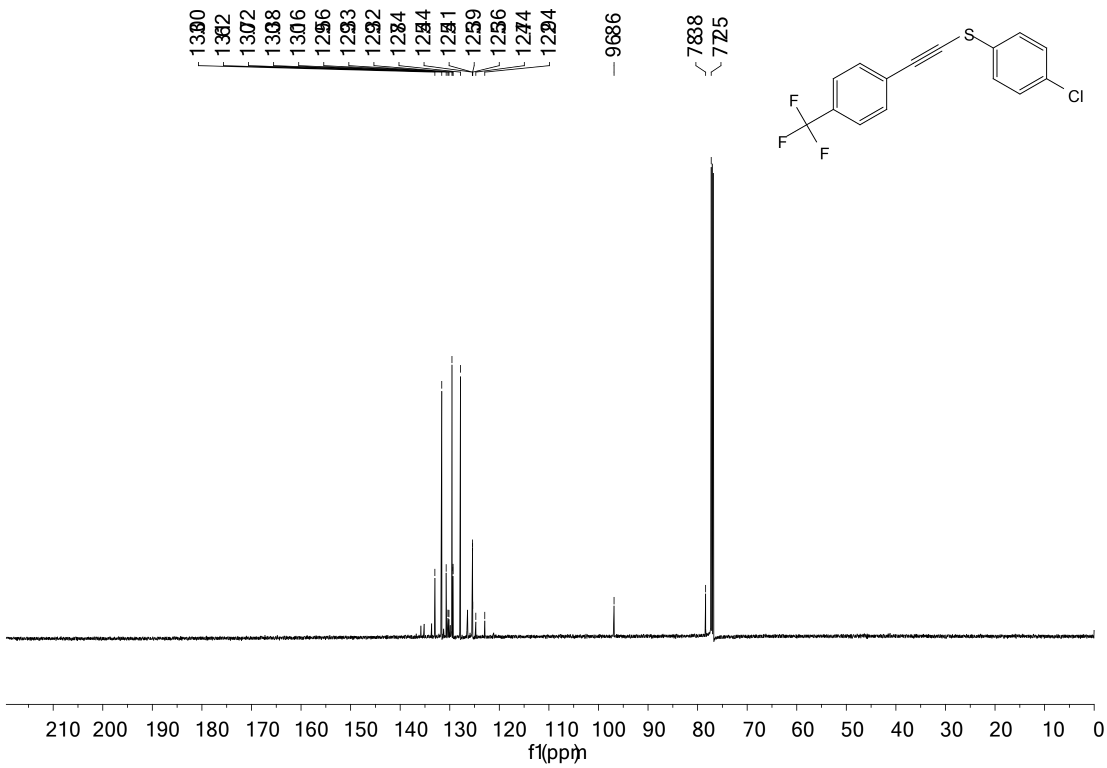
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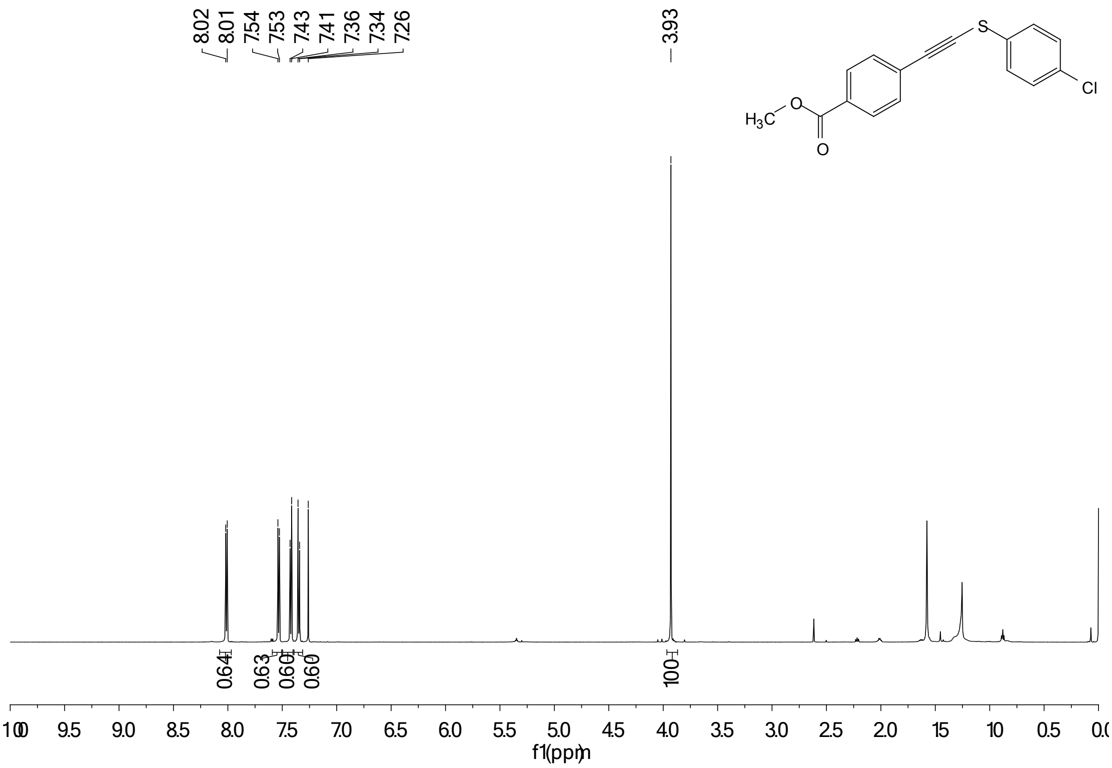
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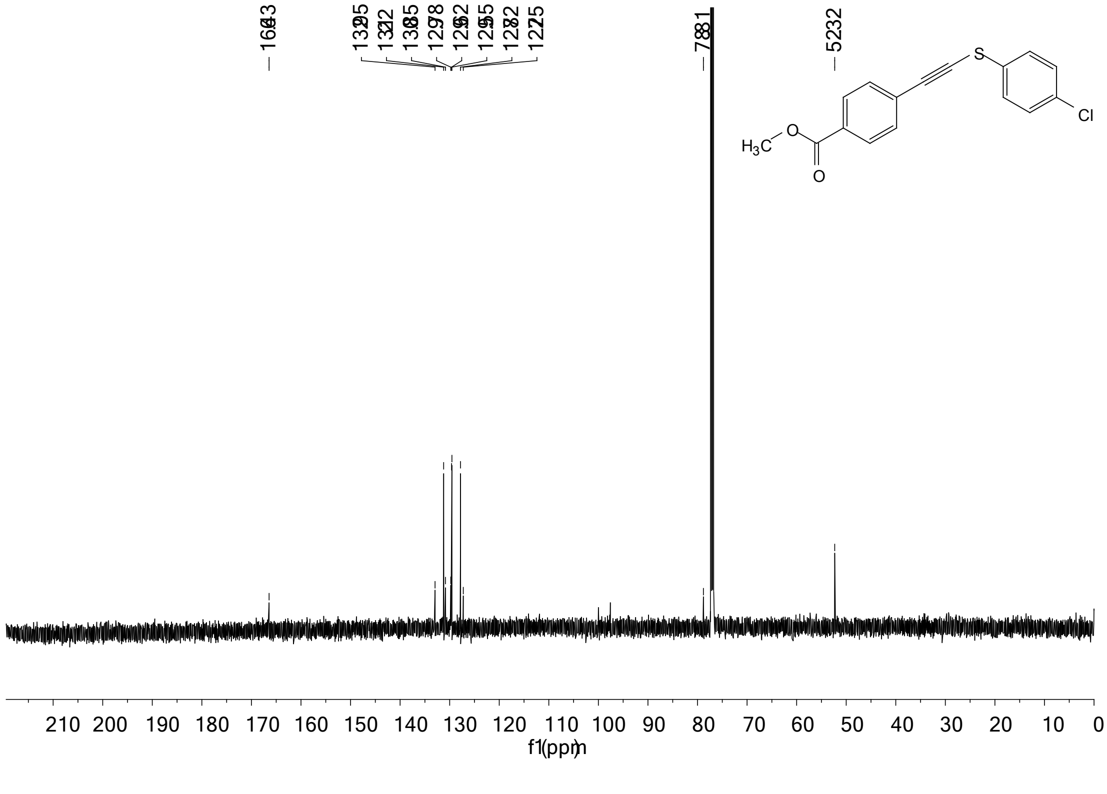
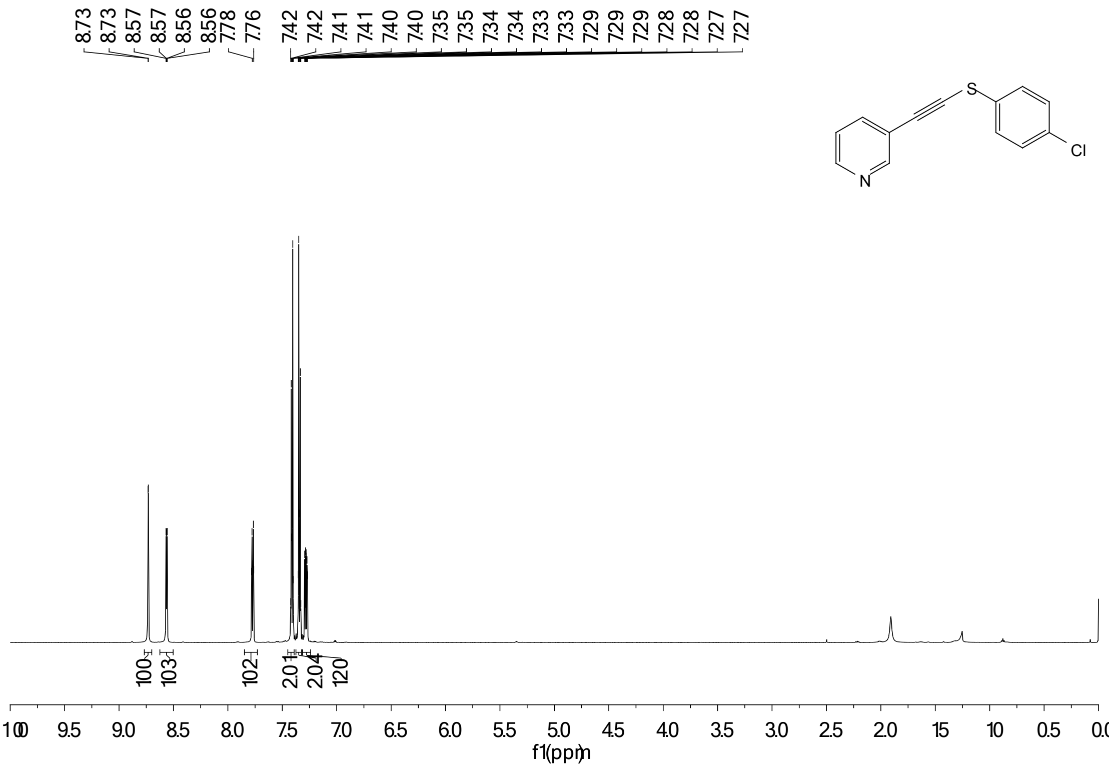
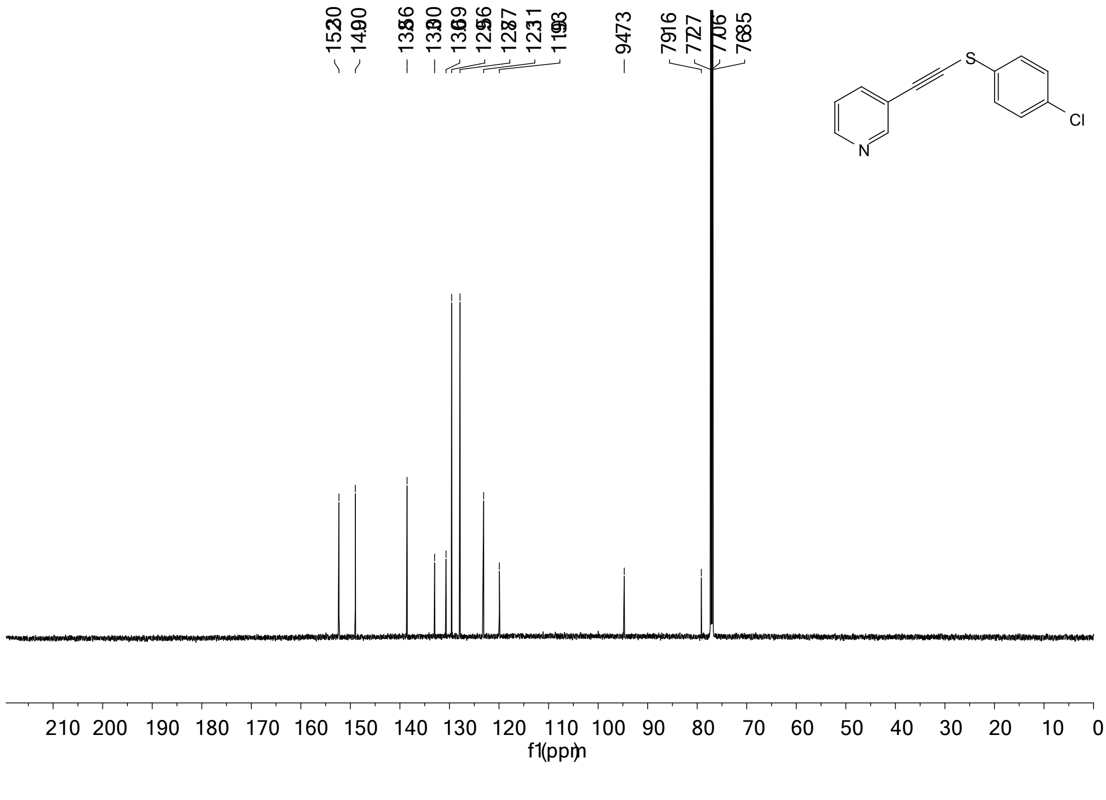
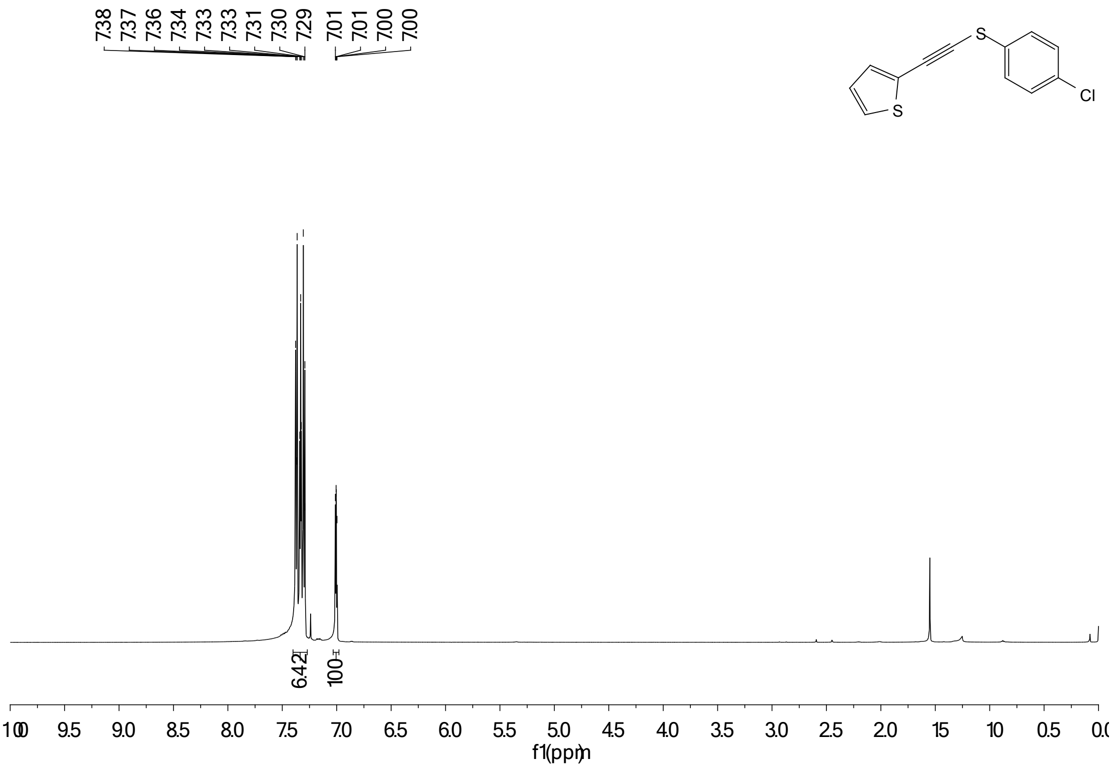
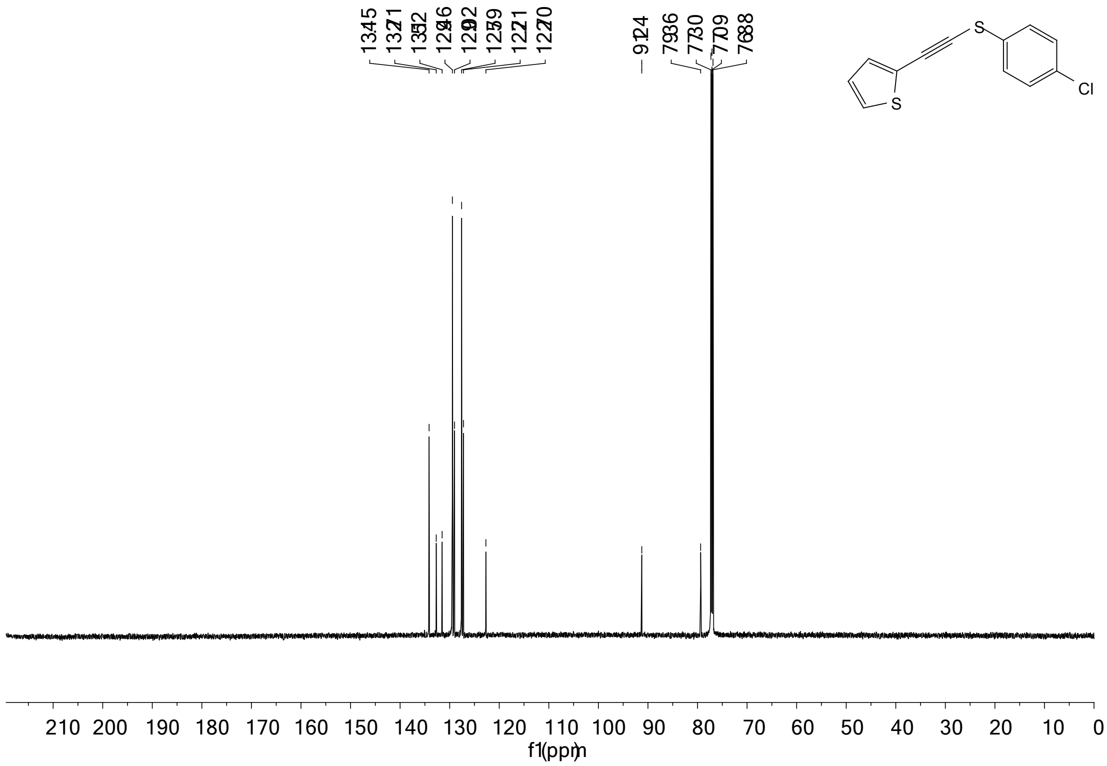
0.60
f1 (ppm)


S
Cl
O
O
f1 (ppm)






f1 (ppm)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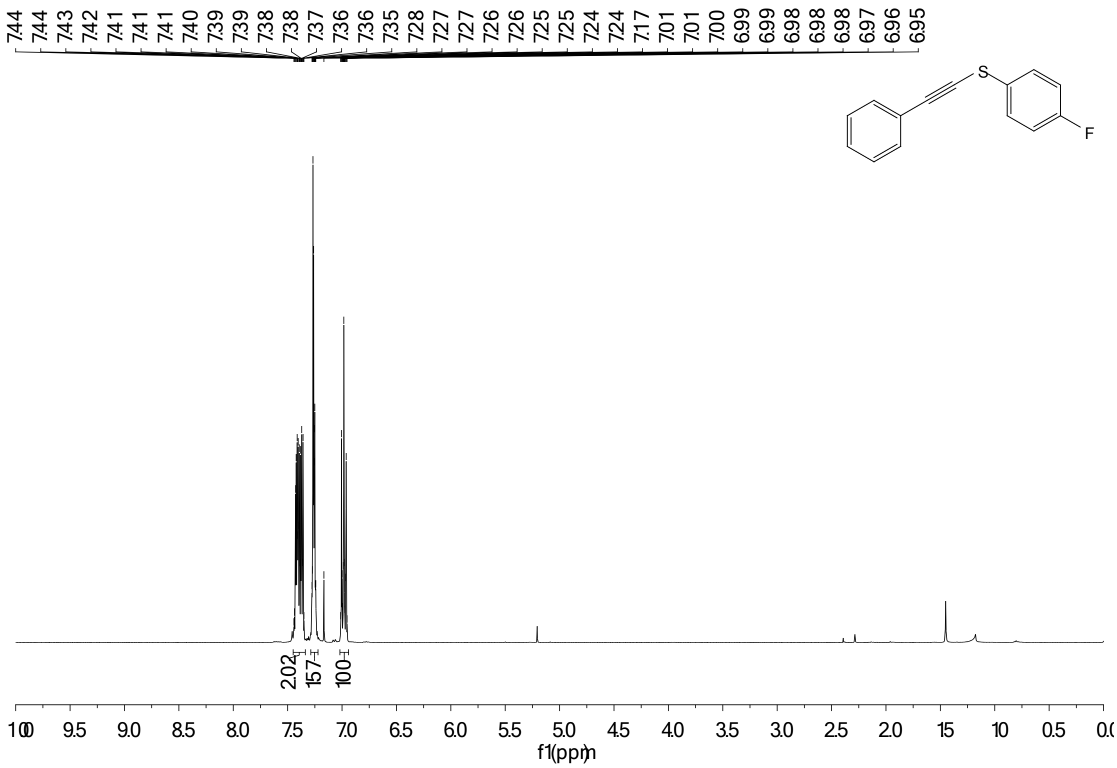
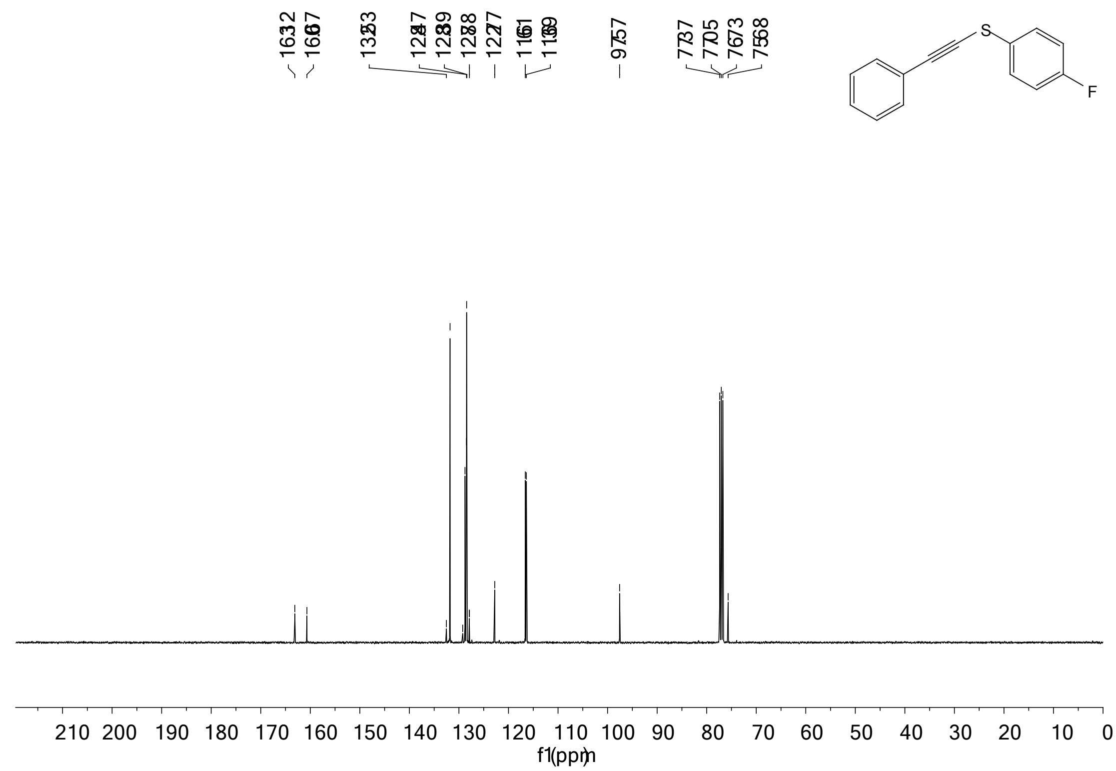
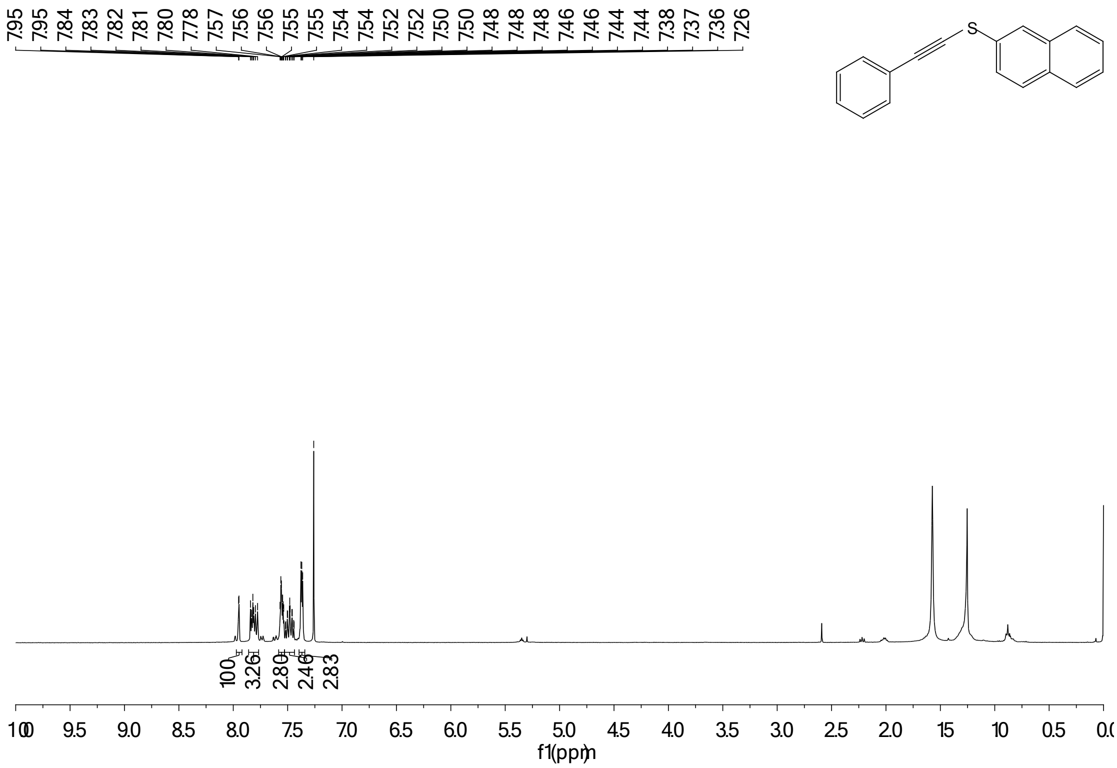

S
F
f1 (ppm)


S
F
f1 (ppm)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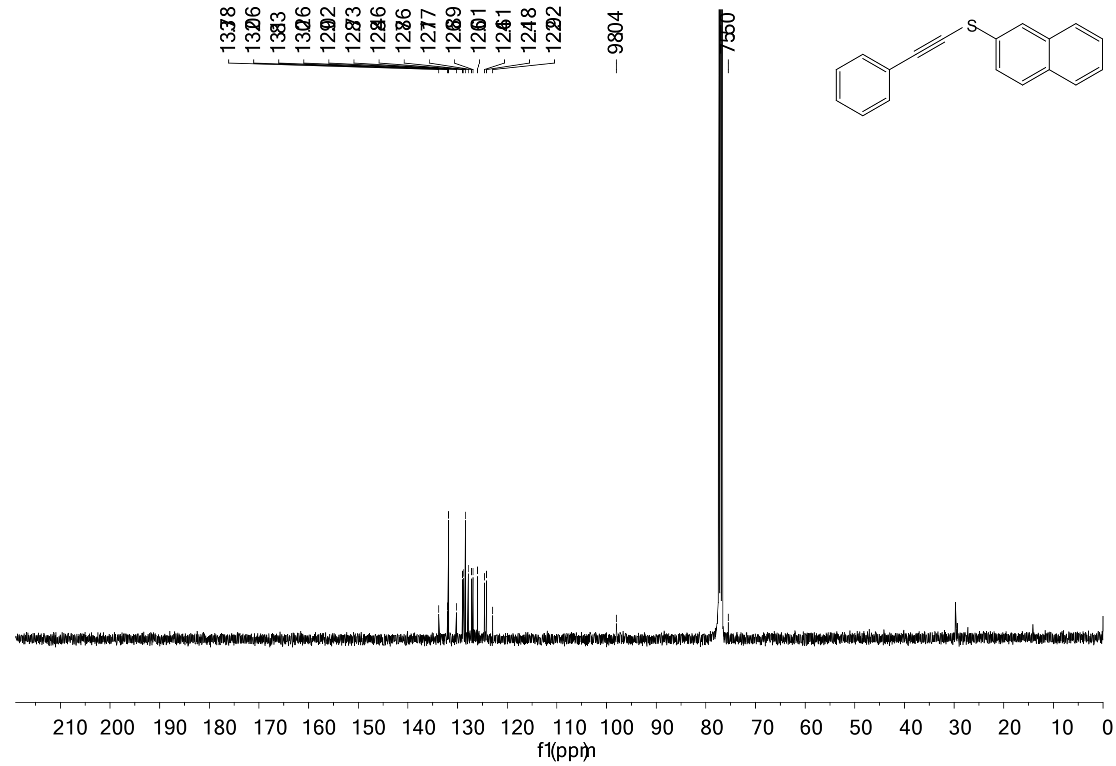
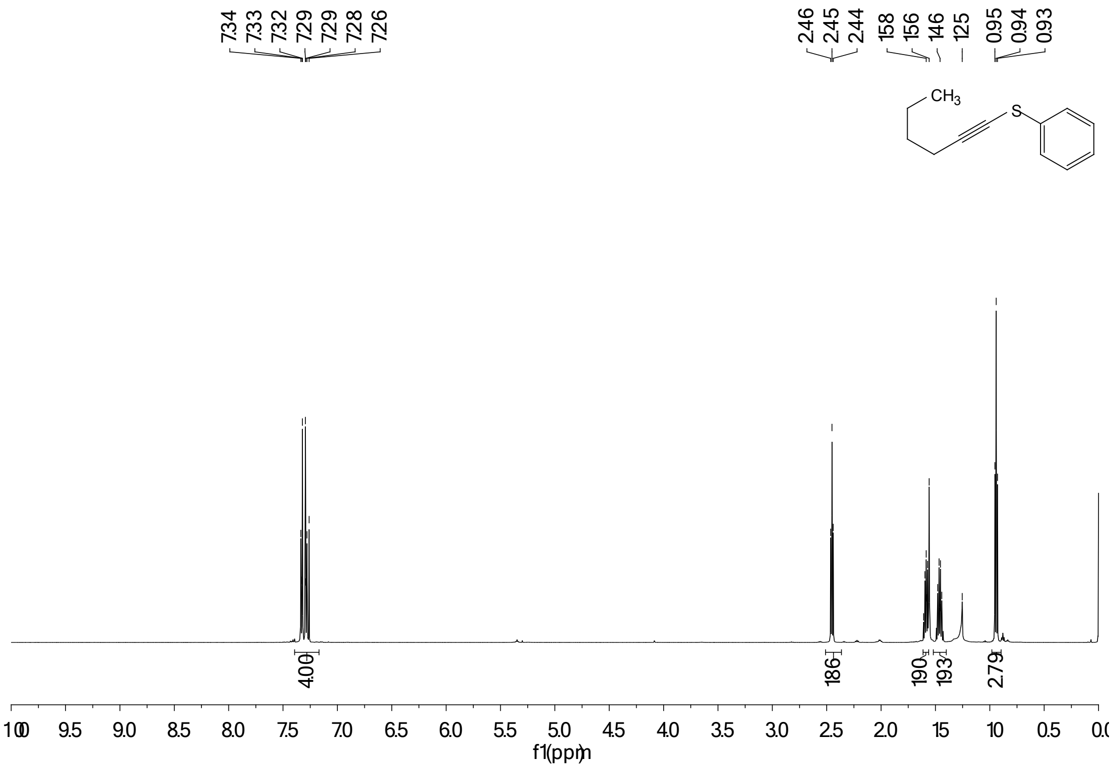
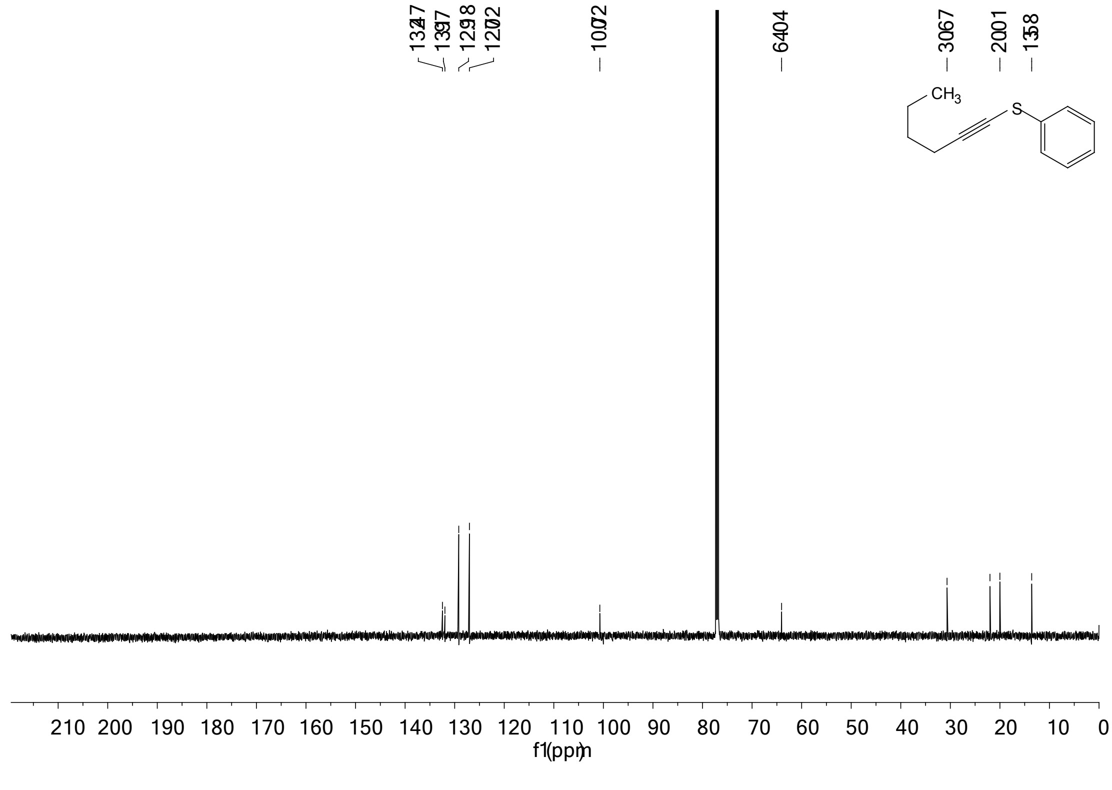
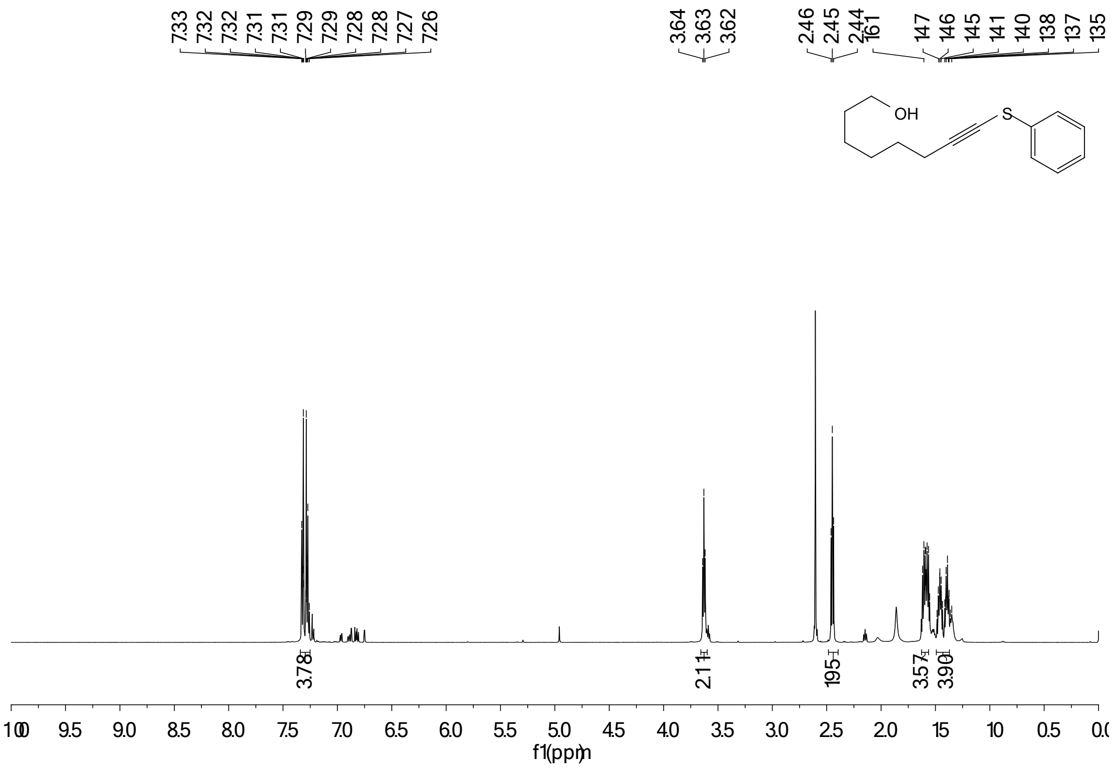
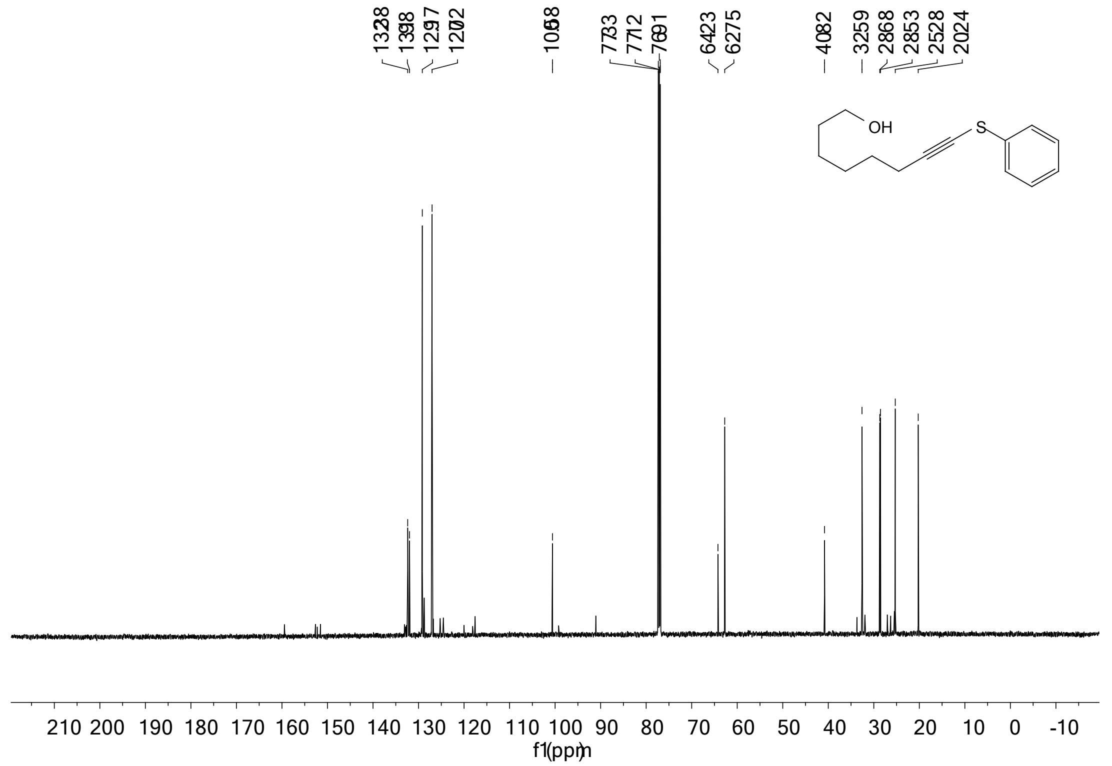
S
1.00
3.26
2.80
2.40
2.83
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

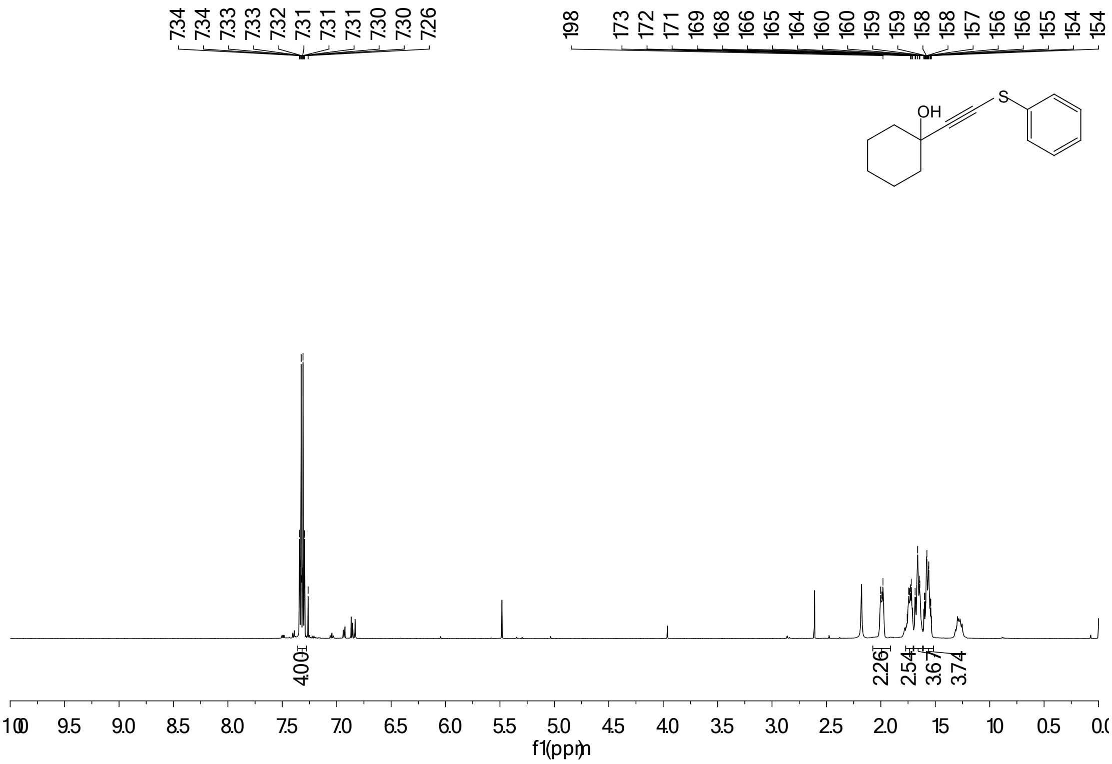

98.04
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.34
7.33
7.32
7.29
7.29
7.28
7.26
2.46
2.45
2.44
1.58
1.56
1.46
1.25
0.95
0.94
0.93
CH3
S
4.00
1.86
1.90
1.93
2.79
f1 (ppm)


100.72
64.04
30.67
20.01
CH3
S
f1 (ppm)


OH
S
f1 (ppm)


OH
S
f1 (ppm)


7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.31
7.30
7.30
7.26
OH
S
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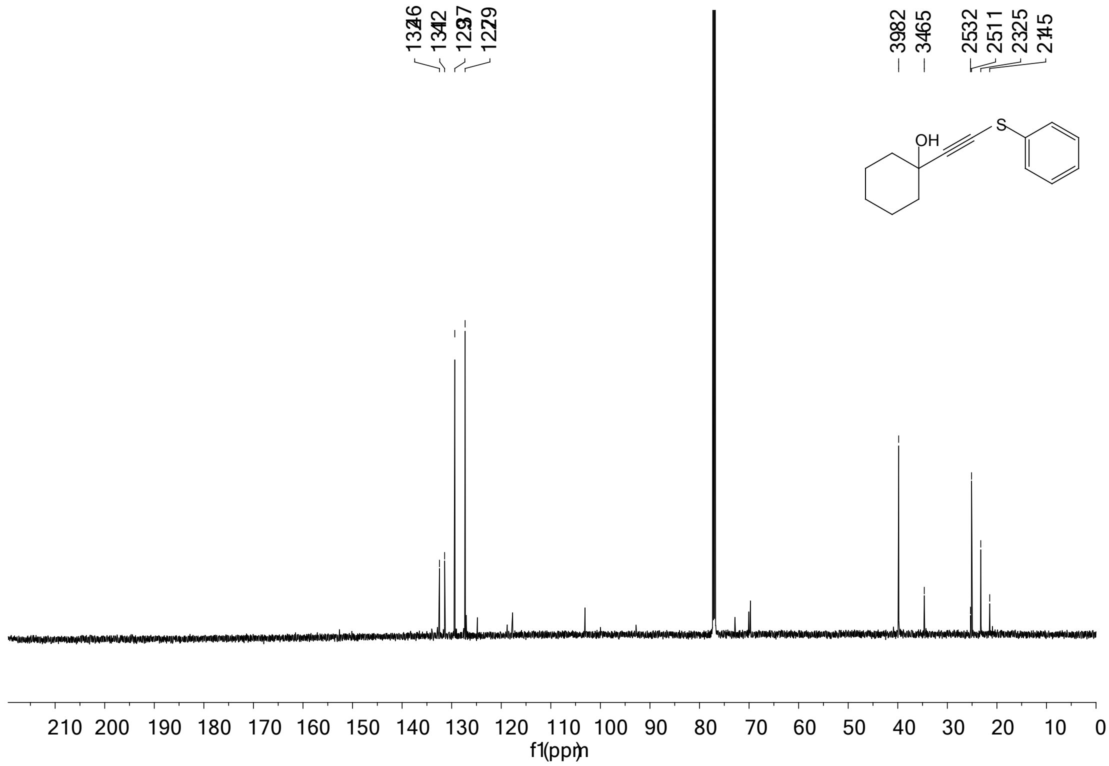
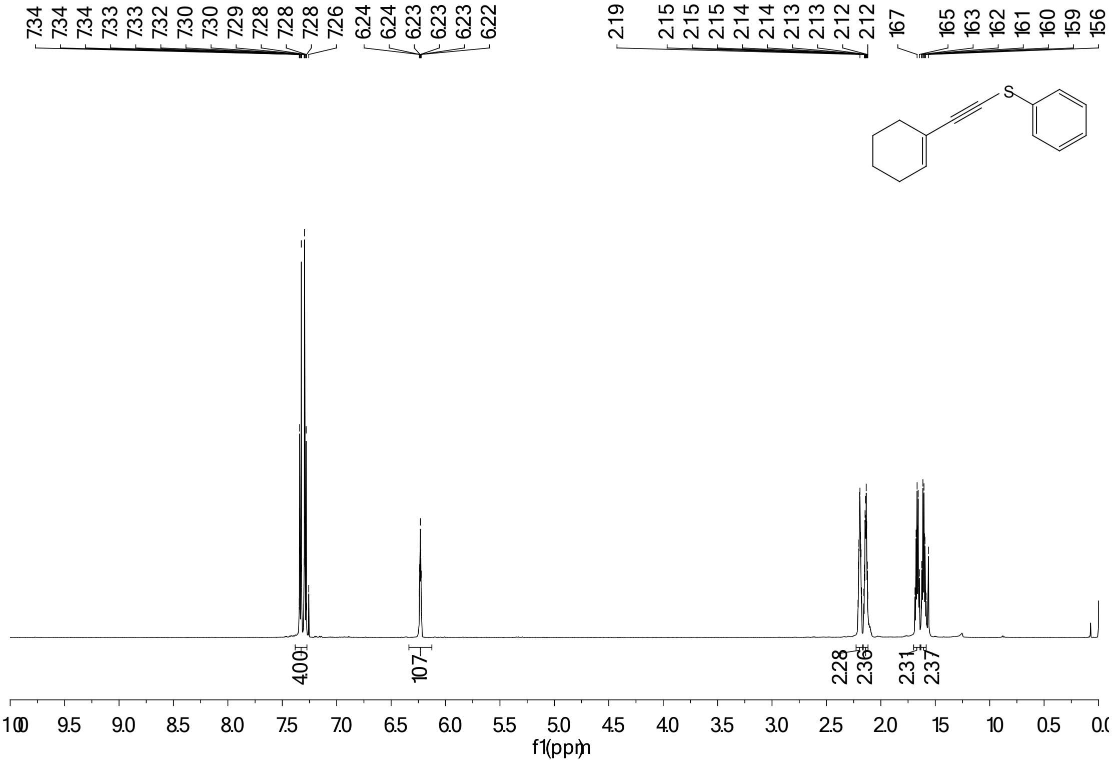
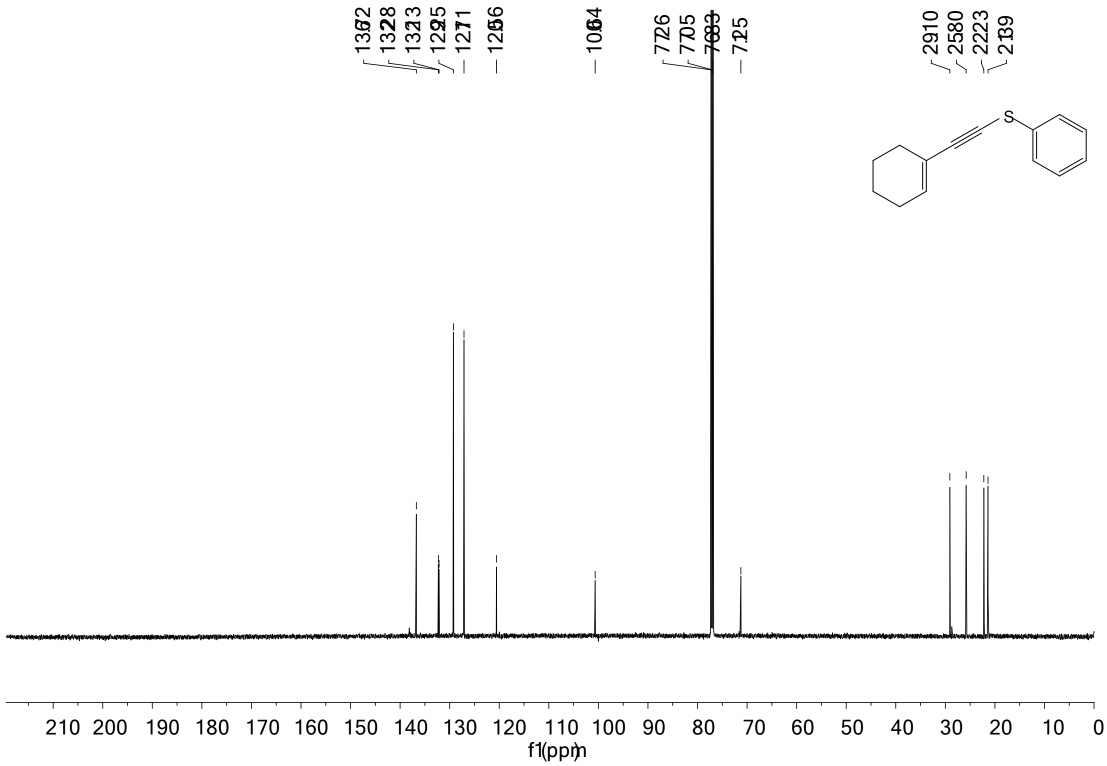
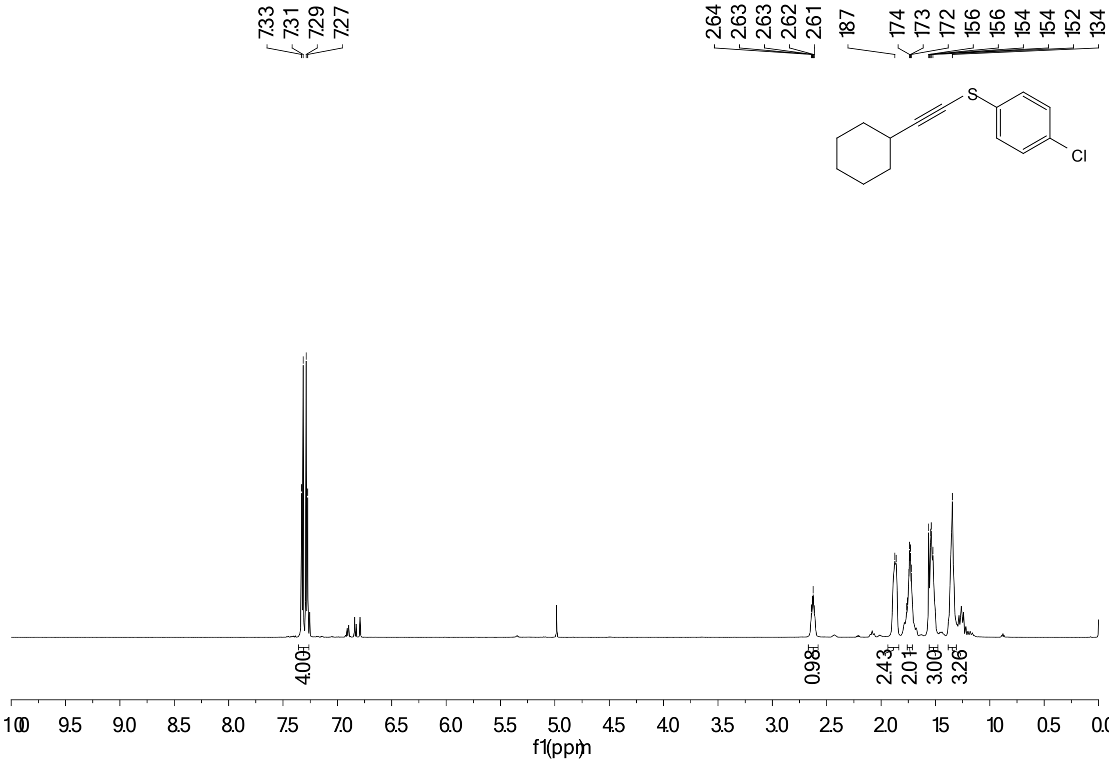
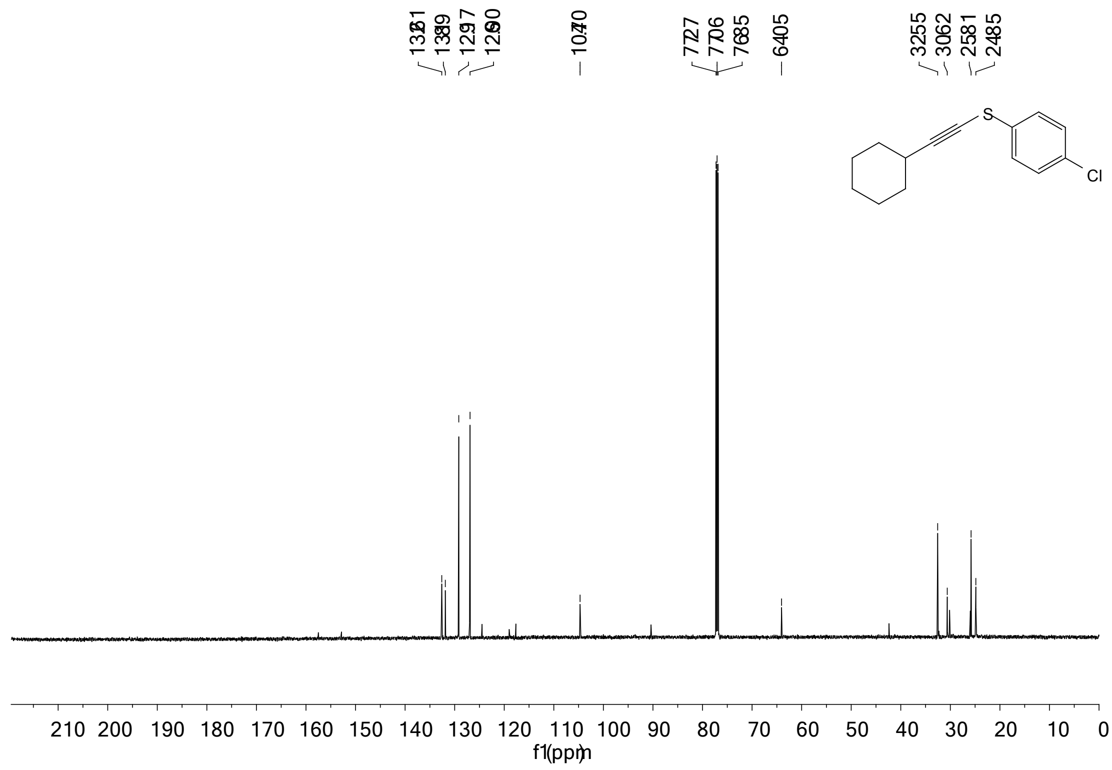
3.67
3.74
f1 (ppm)

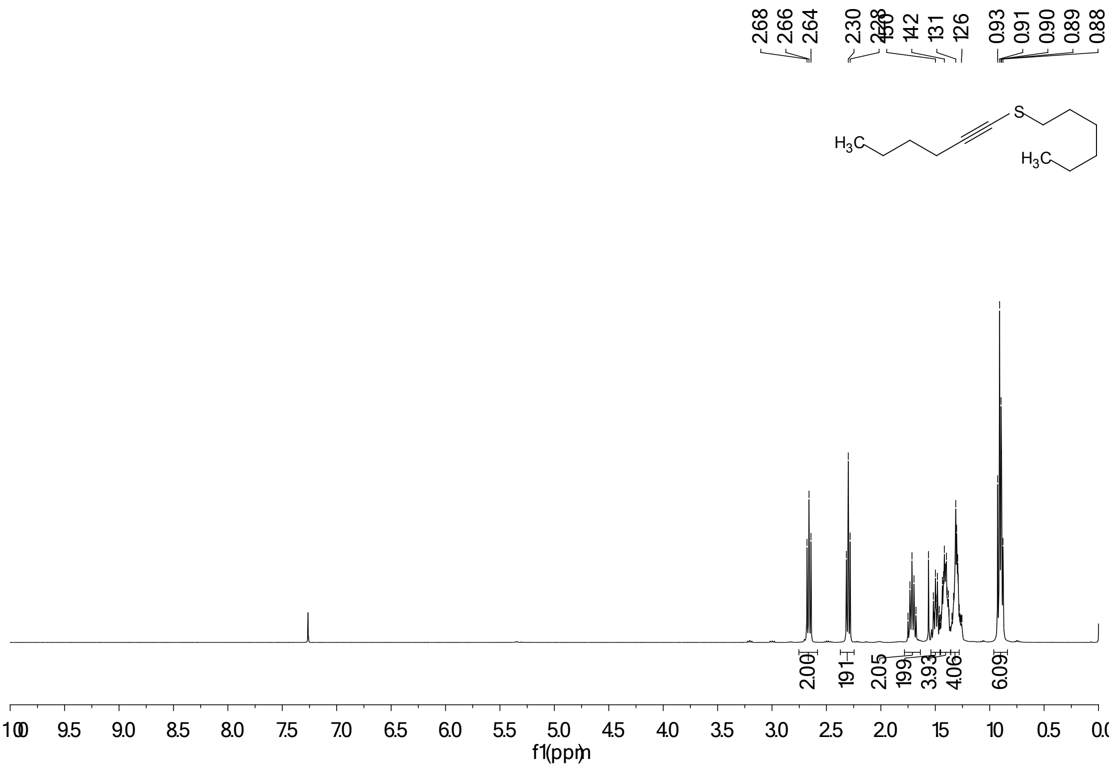

OH
S
f1 (ppm)

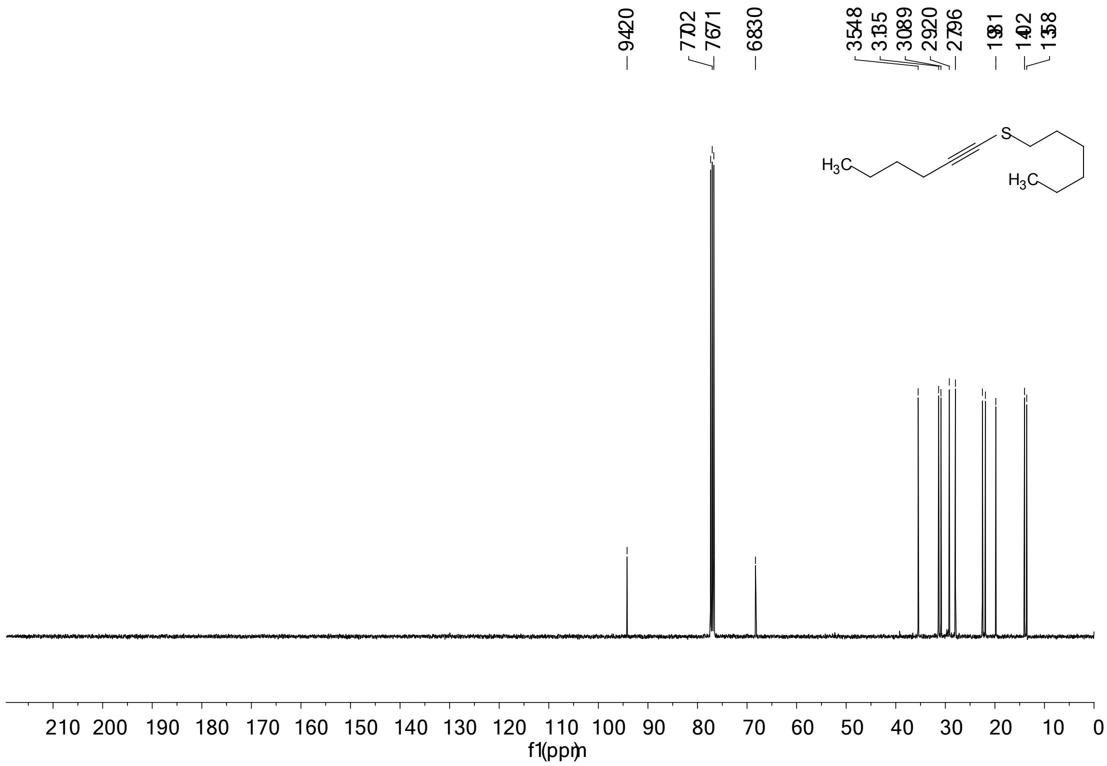


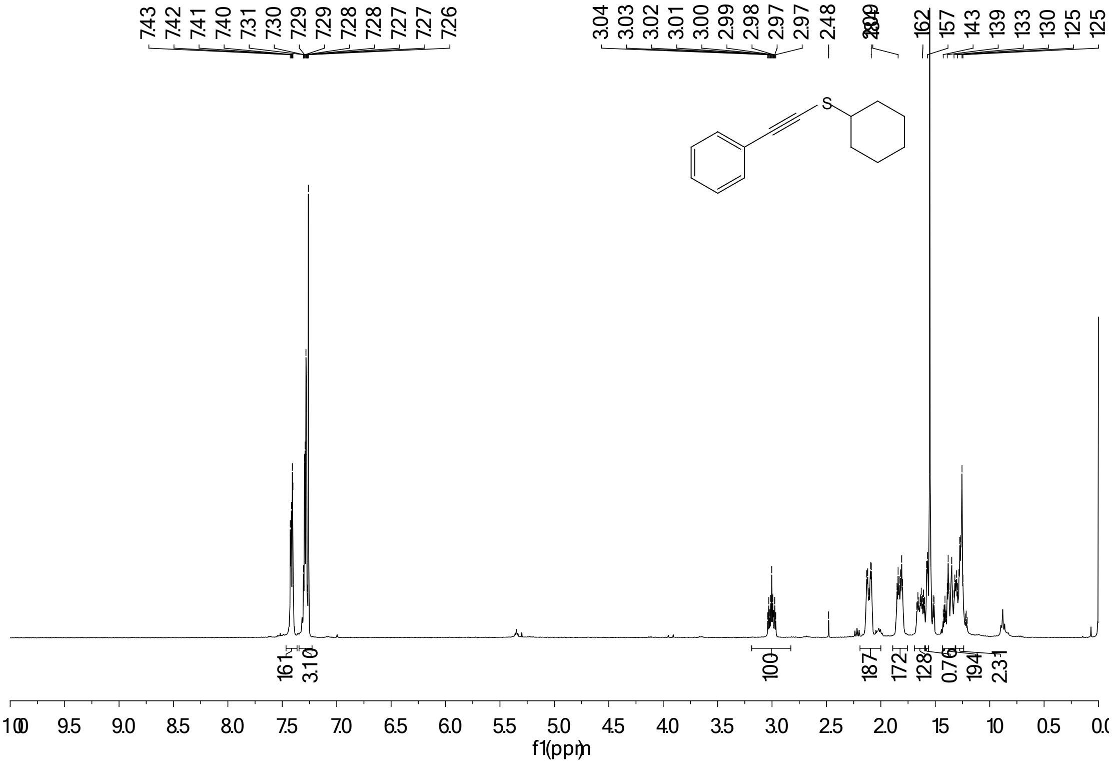


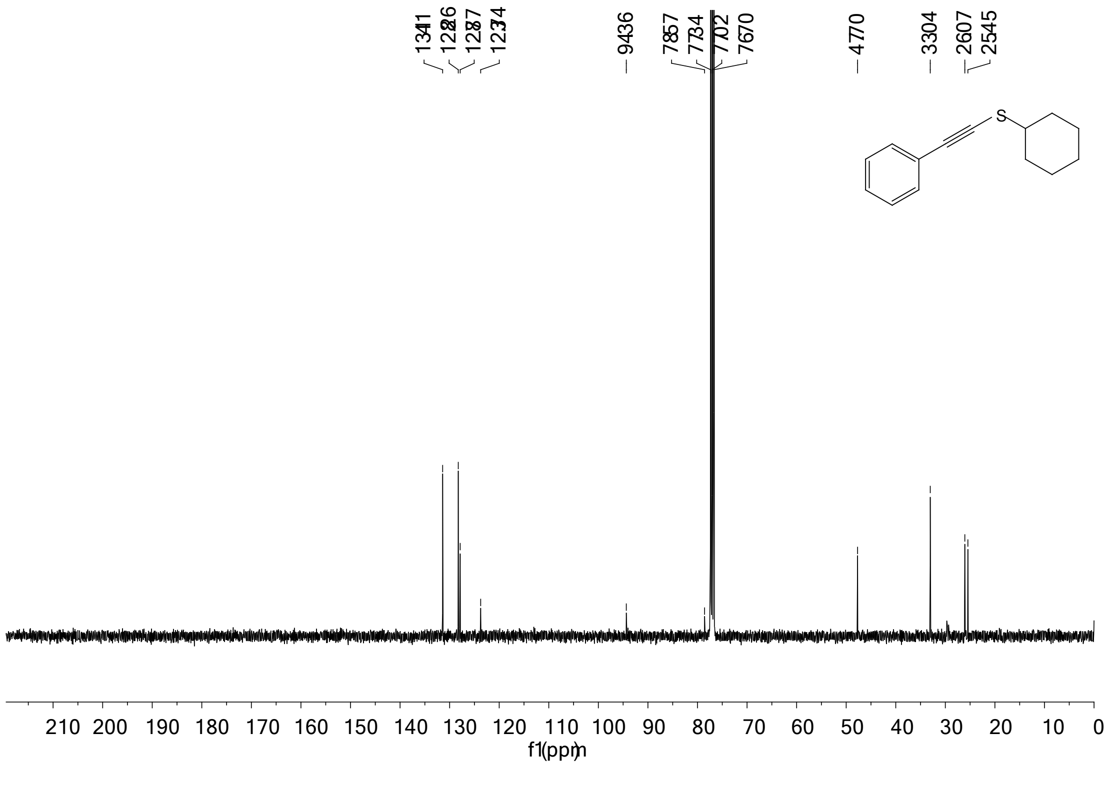





H3C
S
H3C
f1 (ppm)


H3C
S
H3C
f1 (ppm)


S
f1 (ppm)


S
f1 (ppm)