Photoredox mediated synthesis of propargylic sulfoxides: A one-step aerobic approach

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1. General information:

Materials: All the reagents except Propargyl Chlorides were purchased commercially and used as received. Reactions were carried out in oven-dried glassware. The solvents used for chromatography were purified by distillation.

NMR spectra: ^{1}H and ^{13}C NMR spectra were recorded on FT-NMR 500 and 400 MHz instruments. Chemical data for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent ($CDCl_3$, 7.26 ppm). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 125 MHz or 100 MHz: chemical data for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent. ^{19}F NMR spectra are not calibrated by an internal reference. Coupling constants (J) are quoted in Hz.

High-Resolution Mass Spectrometry (HRMS): All samples were recorded using a QTOF-LC/MS spectrometer with electron spray ionization.

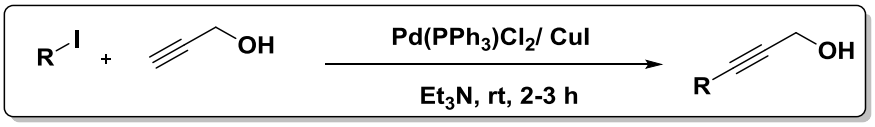
Electrochemical measurements were carried out using a Bio-Logic SAS potentiostat (Model SP-150) with a glassy carbon electrode as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl (3 M NaCl) reference electrode in CH3CN solvent, using NBu4PF6 as the supporting electrolyte at a scan rate of 100 mV/s.

Set-up for Photochemical reaction: The Penn PhD Photoreactor M2 (450 nm) is used for reaction irradiation, which was commercially purchased from Sigma-Aldrich. The LED intensity for irradiation is typically set to 100% with stirring at 200 RPM and a 4000 RPM fan speed. The reaction was performed at room temperature (25°C) under these conditions.

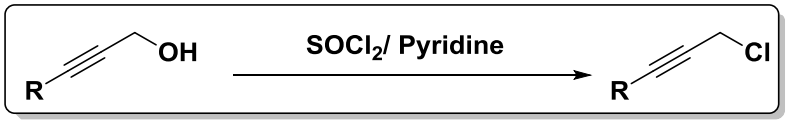
Figure **S1**: The Penn PhD Photoreactor M2

2. General Synthesis of Phenyl Propargyl Chlorides:

2.1. General Procedure for the Sonogashira Coupling of Propargyl Alcohol with Aryl Iodides (GP1): General procedure reported from the previous literature.[1] Iodobenzene (1 equiv.) was added to an oven-dried 50 mL round bottom flask and dissolved in Triethylamine (10 mL), $Pd(PPh_3)_2Cl_2$ (0.01 mol%), CuI (0.02 mol%), and propargyl alcohol (1.5 equiv.) were added to the flask and the mixture was cooled to 0 ºC. After 2-4 hours, TLC analysis showed consumption of the iodobenzene. Evaporating the solvent under reduced pressure yielded a thick brown paste which was filtered through a plug of silica gel (100% EtOAc). The crude material was then purified by column chromatography with hexane/ethyl acetate as solvent system.



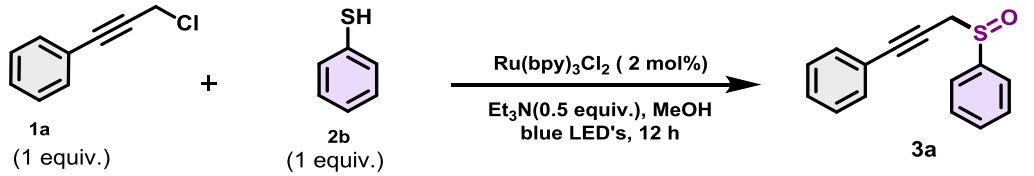
2.2. Functional group interconversion of Propargyl Alcohols to Propargyl Chlorides (GP2): General procedure was reported from the previous literature.[2] A 50 mL round-bottom flask was charged with anhydrous CH_2Cl_2 (20 mL), propargyl alcohol (1 equiv.) and Pyridine (1.2 equiv.), and the mixture was cooled with an ice bath. To the solution, $SOCl_2$ (1.1 equiv.) was added dropwise and the mixture was stirred at 0 ^oC for 30 minutes. The mixture was allowed to warm up to room temperature and stirred overnight at room temperature. The resulting mixture was diluted with ether (20 mL) and washed with 1N HCl Solution (15 mL×3). The water layer was extracted with Et_2O (20 mL×3). The combined organic extracts were washed with saturated $NaHCO_3$ aq. (15 mL ×3). The organic layer was dried over $MgSO_4$. After filtration and removal of the solvents in vacuo, the crude material was then purified by column chromatography using hexane as solvent to obtain the desired product.



3. General procedure for the synthesis of sulfoxides (GP3):

To an oven-dried 30 ml glass vial was added 3-chloro-1-phenyl-1-propyne **1** (100 µL, 0.67 mmol) in 2 mL MeOH followed by addition of $Ru(bpy)_3Cl_2$ (10 mg, 2 mol%), thiophenol (73 µL, 0.67 mmol) and Triethylamine (33.8 µL, 0.33 mmol) with continuous stirring under air. The reaction mixture was then irradiated under blue light sourced from Penn PhD Photoreactor M2 for 12 h. After the completion of the reaction, as monitored by TLC, the reaction mixture was extracted with ethyl acetate and water. The aqueous layers were washed with aq. HCl and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated under a vacuum. The crude mixture was purified by silica gel column chromatography to obtain product **3** as a brownish liquid (125.4µL, 78% yield) using distilled hexane/ethyl acetate (75:25) as a solvent system.

4. Optimization Table (Table S1)

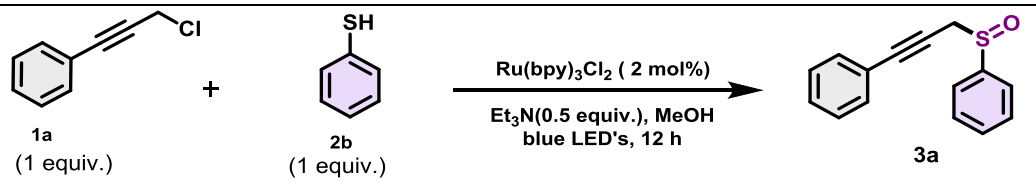


entry	deviation from standard conditions	yield (%)
1	none	78
2	Mes-Acr^{+}ClO_4^{-} as photocatalyst	traces
3	rose bengal as photocatalyst	16
4	eosin-Y as photocatalyst	23
5	DMSO instead of CH_3CN	32
6	CH_3CN instead of MeOH	41
7	DCM , DCE instead of CH_3CN	traces
8	DMF, THF instead of CH_3CN	traces
9	No triethylamine	21
10	no light, photocatalyst or thiophenol	n.d

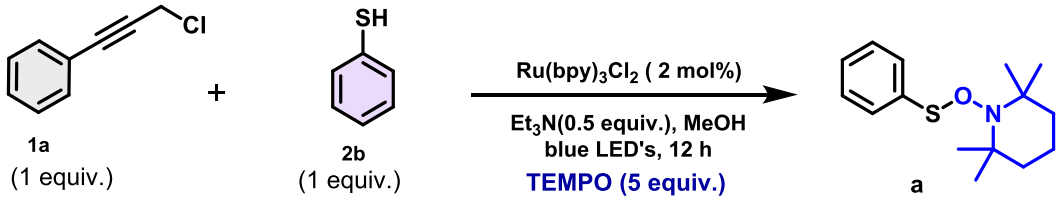
[a]Reaction conditions: 3-chloroprop-1-yn-1-yl)benzene (**1a**, 1 equiv.), thiophenol (**2a**, 1 equiv.), triethylamine (0.5 equiv.), photocatalyst (2 mol %), CH_3OH (2 mL), irradiation under air atmosphere, blue LEDs, room temperature: 25 ^{o}C, time 12 h.

5. Control Experiment:

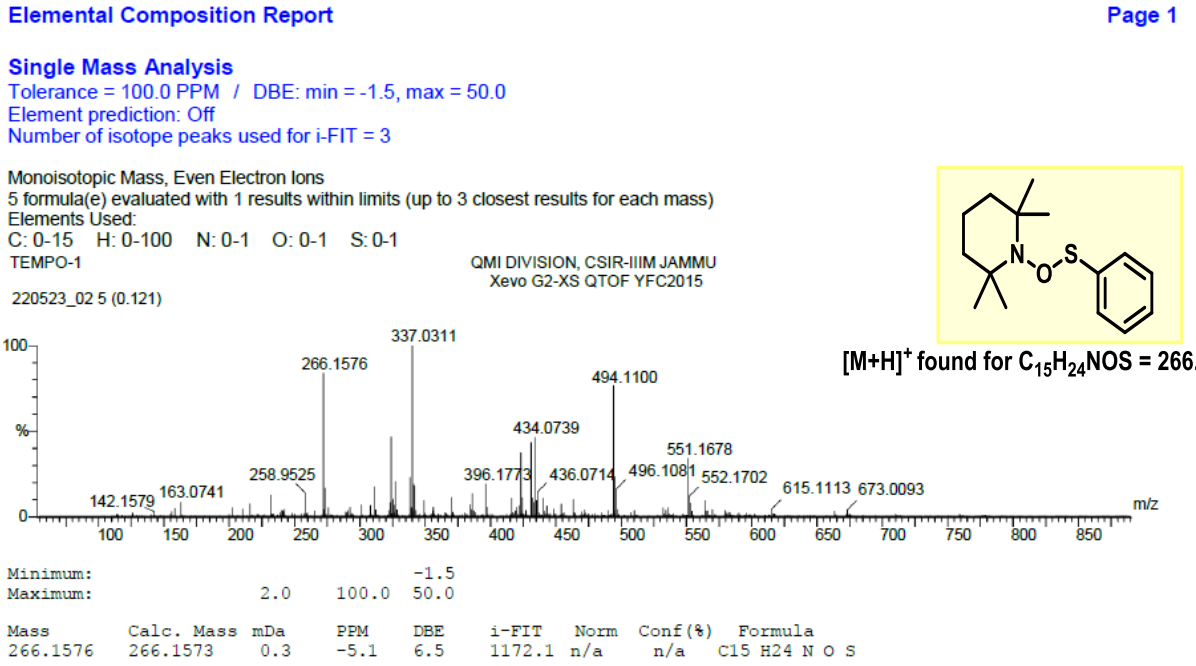
Table S2:



Entry	Deviation	Yield (%)
1	+ TEMPO (5 eq.)	traces
2	Degassed conditions	traces



HRMS (ESI) (m/z) of compound **a**



$[M+H]^+$ found for $C_{15}H_{24}NOS$ = 266.1576

6. Photoredox Studies:

To further validate the proposed reaction mechanism, luminescence quenching, absorption binding propensities and cyclic voltammetry studies were performed. The evaluation of the reaction components affinities for single-electron transfer (SET) with $[Ru(bpy)_3]Cl_2$ was determined through their luminescence quenching constants. Stern-Volmer plots reveal that the quenching efficiency follows the trend: thiophenol (PhSH) > propargyl chloride (PC) > triethylamine (TEA).The relative degradation data of $[Ru(bpy)_3]Cl_2$ by thiophenol(PhSH) > propargyl chloride (PC) > triethylamine (TEA) solved in first order kinetics with the calculated first order rate constant in the order: thiophenol(PhSH) > propargyl chloride (PC) > triethylamine (TEA). This observed kinetic order can be corroborated with the relative propensity of reaction ingredients towards single electron transfer reaction and the significantly high quenching rate observed for thiophenol supports its role in the initial step of the reaction, indicating its involvement in the reductive quenching of the photocatalyst. Moreover, changes in the cyclic voltammograms upon adding thiophenol suggest a thermodynamic preference for electron transfer through reductive pathways. Additionally, light on-off experiments confirm that continuous irradiation is necessary for the reaction to proceed.

6.1. Absorption Studies:

Absorption variations were examined by introducing quenchers into binary mixtures containing a fixed 7 μM concentration of the photocatalyst $[Ru(bpy)_3]Cl_2$ in MeOH at room temperature. These mixtures were exposed to blue LED irradiation while the quencher concentrations were systematically adjusted (Figure S1). The observed degradation of $[Ru(bpy)_3]Cl_2$ in the presence of thiophenol (PhSH) > propargyl chloride (PC) > triethylamine (TEA) aligns with their respective tendencies for single-electron transfer (SET) reactions. The binding affinity was determined using the Benesi–Hildebrand equation.

$$\frac{1}{(A - A_0)} = \frac{1}{(A_{max} - A)} + \frac{1}{K(A_{max} - A)[M]} \qquad (1)$$

Data analysis reveals that thiophenol exhibits a greater affinity for the $[Ru(bpy)_3]Cl_2$ catalyst compared to the other reactants, confirming its role as the primary reagent in the single-electron transfer reaction with the photoexcited $[Ru(bpy)_3]Cl_2$ catalyst(Figure S1).The relative degradation data of $[Ru(bpy)_3]Cl_2$ by thiophenol(PhSH) , propargyl chloride (PC) triethylamine (TEA) solved in first order kinetics with the calculated first order rate constant in the order: thiophenol (PhSH) > propargyl chloride (PC) > triethylamine (TEA) (Figure S2).This observed kinetic order can be corroborated with the relative propensity of reaction ingredients towards single electron transfer reaction with photoexcited $[Ru(bpy)_3]Cl_2$.

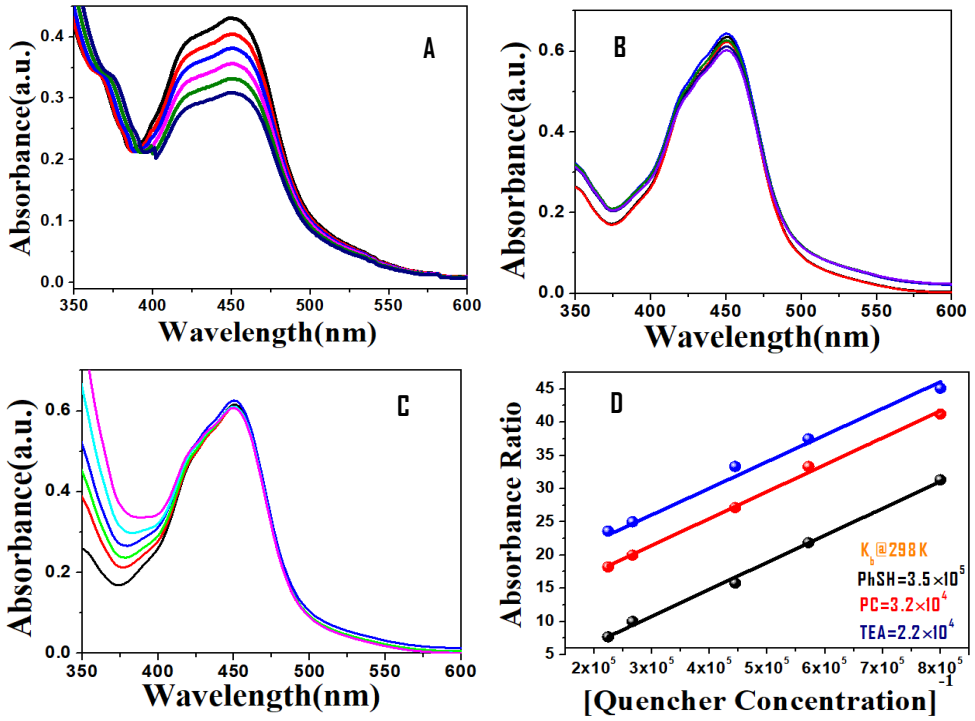


Figure S1 Absorption studies for the photocatalytic degradation with the incremental titration of reaction ingredients (A) thiophenol(PhSH),(B) propargyl chloride (PC) ,(C) triethylamine (TEA) and (D) comparative binding propensities of reaction ingredients with of $[Ru(bpy)_3]Cl_2$.

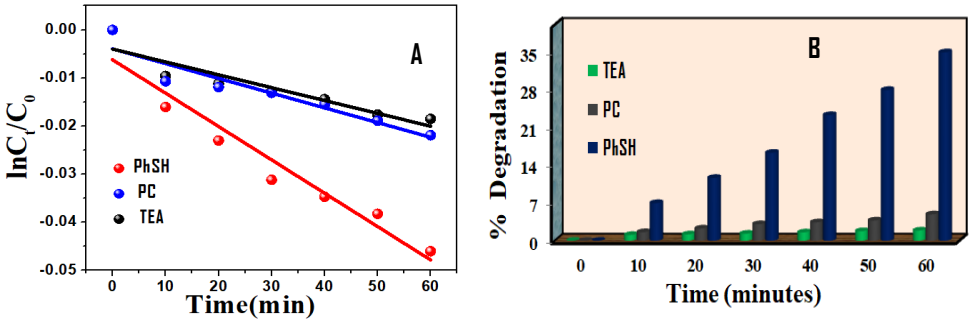


Figure S2 The first order kinetics (A) and relative degradation data (B) of $[Ru(bpy)_3]Cl_2$ with the order: thiophenol (PhSH) > propargyl chloride (PC) > triethylamine (TEA).

6.2. Fluorescence Studies:

Fluorescence quenching studies were conducted using a 7 µM solution of $[Ru(bpy)_3]Cl_2$ with increasing concentrations of quenchers thiophenol (PhSH),propargyl chloride (PC), triethylamine (TEA) in MeOH at room temperature. The solutions were exposed to blue LED light at an excitation wavelength of 450 nm, and luminescence was recorded at 552 nm, corresponding to the maximum emission wavelength of the $[Ru(bpy)_3]Cl_2$ photocatalyst. Stern-Volmer analysis of the quenching data was performed to determine the comparative quenching constants (Figure S3). The calculated values showed strong agreement with absorption data, further confirming thiophenol as an effective reagent for initiating a single-electron transfer reaction with the photoexcited $[Ru(bpy)_3]Cl_2$ catalyst. Additionally, the light on-off experiment highlights the necessity of continuous blue LED irradiation for the reaction to proceed (Figure S4).

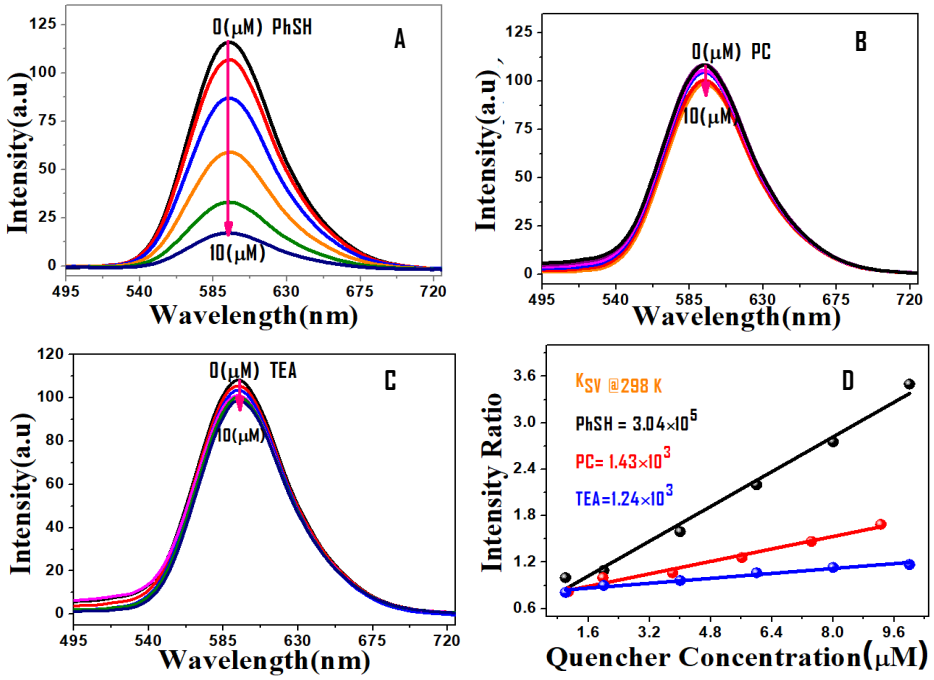


Figure S3 Fluorescence quenching studies of [Ru(bpy)3]Cl2 with reaction precursors, (A) thiophenol(PhSH),(B) propargyl chloride (PC) ,(C) triethylamine (TEA) and (D) Their relative Stern-Volmer plots at room temperature confirming thiophenol as an effective reagent for initiating a single-electron transfer reaction with the photoexcited $[Ru(bpy)_3]Cl_2$ catalyst.

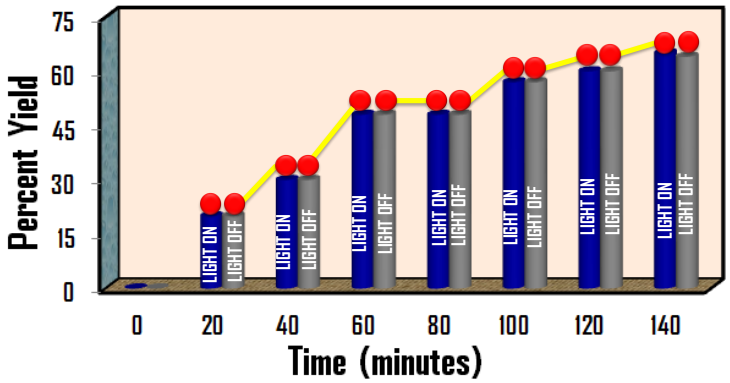


Figure S4 Light on-off experiment suggests requirement of continuous exposure of blue LED.

6.3. Electrochemical Studies:

Electrochemical measurements were performed using a Bio-Logic SAS potentiostat (Model SP-150) with a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. The experiments were conducted at a scan rate of 100 mV/s in MeOH. All measurements were carried out using a fixed 7 µM concentration of $[Ru(bpy)_3]Cl_2$ under blue LED irradiation while varying the concentrations of reactants. The well-defined redox potential of $[Ru(bpy)_3]Cl_2$ displayed a significant shift toward higher potential, accompanied by an increase in peak current, upon the addition of 5 µM thiophenol (Figure S5). This shift in peak potential supports the hypothesis that thiophenol facilitates the single-electron reduction of the photocatalyst. In contrast, the addition of propargyl chloride, whether individually or in combination, did not induce notable changes in the redox behavior of $[Ru(bpy)_3]Cl_2$.This absence of significant alterations suggests that these reactants have minimal influence on the redox properties of the photocatalyst under the given experimental conditions. Overall, the electrochemical data, particularly the redox potential shift observed with thiophenol, reinforce the proposed reaction mechanism involving the single-electron reduction of the photocatalyst. Meanwhile, propargyl chloride appear to have a negligible effect on the redox behavior of $[Ru(bpy)_3]Cl_2$ under the studied conditions.

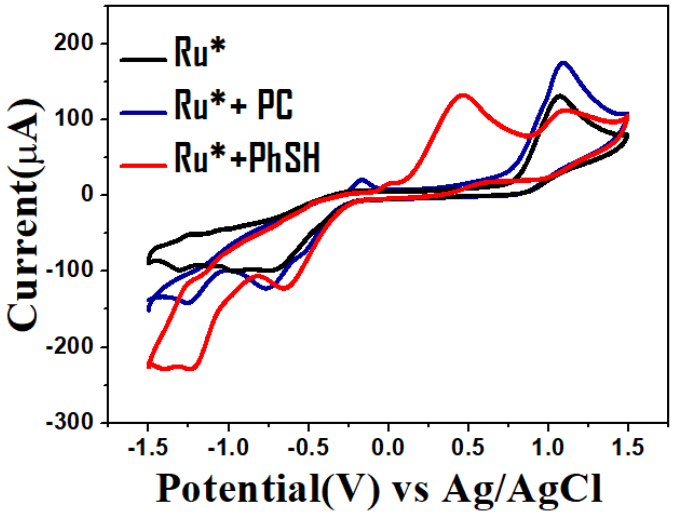
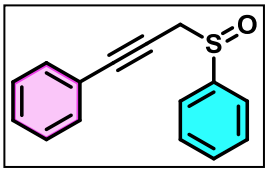


Figure S5 Cyclic voltammograms of photocatalyst with binary reaction combinations displayed a significant shift toward higher potential, accompanied by an increase in peak current, upon the addition of 5 µM thiophenol(PhSH).

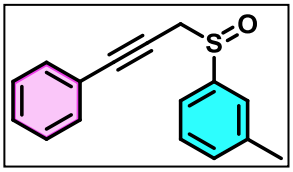
7. Characterization data:

((3-phenylprop-2-yn-1-yl)sulfinyl)benzene (3a):



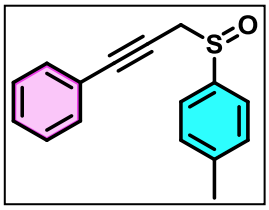
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), thiophenol (73.7 µL, 0.13 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as brownish liquid (125.4 µL, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.71 – 7.68 (m, 2H), 7.48 (dd, J = 5.1, 1.8 Hz, 3H), 7.27 – 7.19 (m, 5H), 3.88 (d, J = 15.6 Hz, 1H), 3.75 (d, J = 15.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 143.0, 131.8, 131.7, 129.0, 128.8, 128.3, 124.6, 122.1, 88.2, 78.0, 49.0. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{13}OS^+$,241.0682; found:241.0686

1-methyl-3-((3-phenylprop-2-yn-1-yl)sulfinyl)benzene (4a):



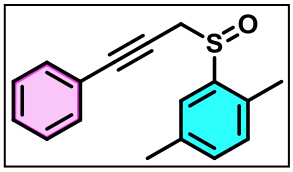
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), 4-methylthiophenol (83.08 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as brownish liquid (129.3 µL, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 – 7.64 (m, 2H), 7.35 (m, 3H), 7.31 (m, 5H), 3.95 (d, *J* = 15.5 Hz, 1H), 3.80 (d, *J* = 15.5 Hz, 1H), 2.44 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.3, 139.8, 131.8, 129.7, 128.8, 128.3, 124.6, 122.2, 88.0, 78.2, 49.0, 21.6. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{16}H_{15}OS^+$:255.0838; found: 255.0832

1-methyl-4-((3-phenylprop-2-yn-1-yl)sulfinyl)benzene (5a):



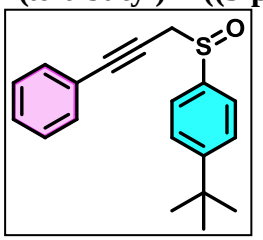
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), 3-methylthiophenol (83.8 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as brownish liquid (137.8 µL, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 – 7.75 (m, 2H), 7.57 – 7.53 (m, 3H), 7.23 – 7.20 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 3.95 (d, *J* = 15.5 Hz, 1H), 3.81 (d, *J* = 15.5 Hz, 1H), 2.34 (s, 3H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.9, 139.2, 132.6, 131.8, 128.8, 128.3, 124.9, 122.1, 121.8, 88.1, 78.2, 49.0, 21.4. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{16}H_{15}OS^+$:255.0838; found: 255.0868

1,4-dimethyl-2-((3-phenylprop-2-yn-1-yl)sulfinyl)benzene (6a):



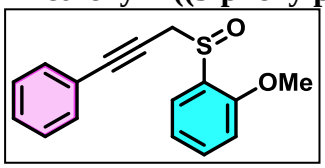
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), 2,5-dimethylthiophenol (92.5 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as brown liquid (138.2 µL, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.35 (m, 2H), 7.34 – 7.26 (m, 5H), 7.17 – 7.15 (m, 1H), 3.93 (d, *J* = 15.5 Hz, 1H), 3.80 (d, *J* = 15.5 Hz, 1H), 2.37 (s, 6H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.6, 139.0, 133.5, 131.8, 130.0, 128.7, 128.3, 122.1, 88.1, 78.4, 48.9, 21.3. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{17}H_{17}OS^+$:269.0995; found: 269.0102

1-(*tert*-butyl)-4-((3-phenylprop-2-yn-1-yl)sulfinyl)benzene (7a):



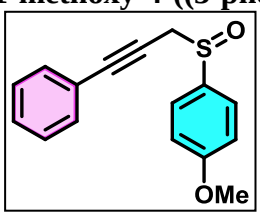
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), 4-*tert*-butylthiophenol (111.2 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as brown liquid (142.8 µL, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 – 7.66 (m, 2H), 7.58 – 7.54 (m, 2H), 7.32 – 7.26 (m, 5H), 3.95 (d, *J* = 15.6 Hz, 1H), 3.81 (d, *J* = 15.6 Hz, 1H), 1.36 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.4, 139.8, 131.8, 128.7, 128.3, 126.1, 124.5, 122.2, 88.0, 78.5, 49.0, 35.1, 31.4. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{19}H_{21}OS^+$:297.1308; found: 297.1301

1-methoxy-2-((3-phenylprop-2-yn-1-yl)sulfinyl)benzene (8a):



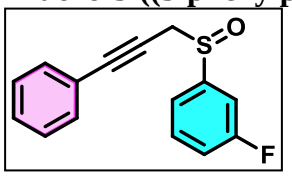
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), 2-methoxythiophenol (93.8 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as creamish brown liquid (123 µL, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.29 – 7.18 (m, 6H), 6.94 (d, *J* = 8.2 Hz, 1H), 4.10 (d, *J* = 16.1 Hz, 1H), 3.98 (d, *J* = 16.6 Hz, 1H), 3.89 (s, 3H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.2, 133.6, 132.5, 131.9, 128.5, 128.2 , 126.4, 121.1, 119.5, 87.5, 78.8, 55.8, 45.5. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{16}H_{15}O_2S^+$:271.0878; found:271.0874

1-methoxy-4-((3-phenylprop-2-yn-1-yl)sulfinyl)benzene (9a):



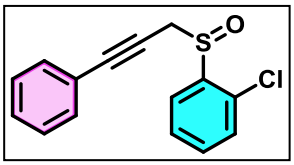
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), 4-methoxythiophenol (93.8 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as brownish liquid (132 µL, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 – 7.67 (m, 2H), 7.34 – 7.27 (m, 5H), 7.07 – 7.02 (m, 2H), 3.95 (d, *J* = 15.5 Hz, 1H), 3.87 (s, 3H), 3.77 (d, *J* = 15.5 Hz, 1H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.5, 134.0, 131.8, 128.8, 128.3, 126.5, 122.2, 88.0, 78.3, 55.6, 49.0. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{16}H_{15}O_2S^+$:271.0878; found: 271.0876

1-fluoro-3-((3-phenylprop-2-yn-1-yl)sulfinyl)benzene (10a):



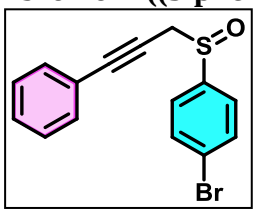
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), 3-fluorothiophenol (85.8 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as reddish brown liquid (112.4 µL, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.48 (m, 3H), 7.38 – 7.28 (m, 5H), 7.25 (m, 1H), 3.96 (d, *J* = 15.6 Hz, 1H), 3.84 (d, *J* = 15.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.0 (d, J = 251.7 Hz), 145.6, 131.8, 130.7 (d, J = 7.7 Hz), 129.0, 128.4, 121.9, 120.4(d, J = 3.2 Hz), 118.9 (d, J = 21.5 Hz), 111.9 (d, J = 23.9 Hz), 88.62, 77.5, 49.0. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{12}OFS^+$:259.0587; found: 259.0581

1-chloro-2-((3-phenylprop-2-yn-1-yl)sulfinyl)benzene (11a):



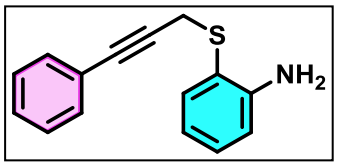
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), 2-chlorothiophenol (96.5 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as yellowish liquid (128.9 µL, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 – 7.64 (m, 2H), 7.50 – 7.47 (m, 5H), 7.34 (d, *J* = 7.9 Hz, 2H), 3.87 (d, *J* = 15.7 Hz, 1H), 3.80 (d, *J* = 15.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 143.0, 133.5, 131.8, 130.2, 129.0, 128.8, 128.5, 128.3, 124.6, 122.1, 88.2, 78.0, 49.0. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{12}OClS^+$:275.0292; found: 272.0294

1-bromo-4-((3-phenylprop-2-yn-1-yl)sulfinyl)benzene (12a):



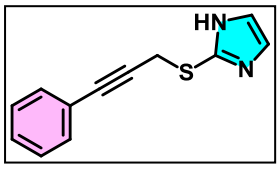
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), 4-bromothiophenol (126 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as brownish liquid (136.8 µL, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 – 7.67 (m, 2H), 7.66 – 7.62 (m, 2H), 7.36 – 7.30 (m, 5H), 3.96 (d, *J* = 15.6 Hz, 1H), 3.81 (d, *J* = 15.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.2, 132.2, 131.8, 129.5, 129.0, 128.9, 128.6, 128.4, 128.2, 126.4, 126.2, 83.9, 77.2, 49.0. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{12}OBrS^+$:318.9787; found:318.9791

2-((3-phenylprop-2-yn-1-yl)thio)aniline (13a):



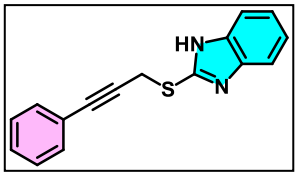
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), 2-aminothiophenol (83.1 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as brownish liquid (132.9 µL, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.6 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.28 – 7.23 (m, 3H), 7.15 (t, J = 7.7 Hz, 1H), 6.70 (dd, J = 11.0, 8.2 Hz, 2H), 4.42 (s, 2H), 3.65 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 138.3, 131.7, 128.6, 128.3, 124.0, 122.4, 84.7, 84.5, 24.9. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{14}NS^+$:240.0841; found: 240.0836

2-((3-phenylprop-2-yn-1-yl)thio)-1*H*-imidazole (14a):



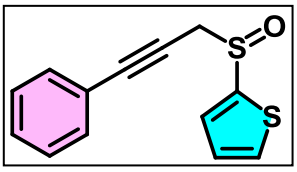
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), 1*H*-imidazole-2-thiol (67 mg, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as brownish liquid (123.3 µL, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 2H), 7.27 (d, J = 6.7 Hz, 3H), 7.18 (s, 2H), 3.90 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 138.2, 131.7, 128.4 ,128.2, 124.5, 122.6, 84.8, 84.4, 24.9. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{12}H_{11}N_2S^+$:215.0637; found: 215.0639

2-((3-phenylprop-2-yn-1-yl)thio)-1*H*-benzo[d]imidazole (15a):



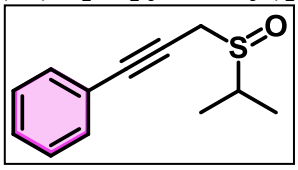
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), 1H-benzo[d]imidazole-2-thiol (100.5 mg, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as blackish liquid (145 µL, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.37 – 7.32 (m, 2H), 7.30 –7.27 (m, 4H), 7.24 – 7.20 (m, 3H), 4.27 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.6, 131.8, 128.6, 128.3, 122.7, 122.4, 84.4, 84.2, 22.6. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{16}H_{13}N_2S^+$:265.0794; found: 265.0791

2-((3-phenylprop-2-yn-1-yl)sulfinyl)thiophene (16a):



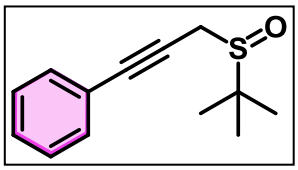
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), thiophene-2-thiol (77.7 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as brownish liquid (100.7 µL, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.75 (m, 1H), 7.58 – 7.54 (m, 2H), 7.34 – 7.27 (m, 5H), 3.96 (d, *J* = 15.5 Hz, 1H), 3.83 (d, *J* = 15.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 143.0, 131.8, 131.7, 129.0, 128.8, 128.3, 124.6, 122.1, 88.2, 78.0 49.0.HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{13}H_{11}OS_2^+$:247.0246; found: 247.0249

(3-(isopropylsulfinyl)prop-1-yn-1-yl)benzene (17a):



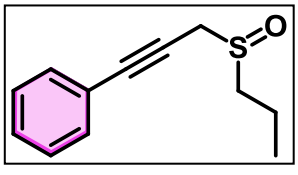
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), propane-2-thiol (51 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as yellowish liquid (120 µL, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.35 – 7.30 (m, 1H), 3.79 (s, 1H), 3.78 (s, 1H), 3.15 (dd, *J* = 13.8, 6.9 Hz, 1H), 1.38 (dd, *J* = 6.9, 4.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 132.0, 131.9, 128.8, 128.6, 128.4, 127.4, 122.1, 87.5, 77.9, 49.0, 40.4, 16.8, 13.3. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{12}H_{15}OS^+$:207.0838; found: 207.0835

(3-(*tert*-butylsulfinyl)prop-1-yn-1-yl)benzene (18a):



Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), *tert*-butylthiolol (60 µL, 0.67 mmol), TEA (38 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as yellowish liquid (120.8 µL, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.41 (m, 2H), 7.34 – 7.30 (m, 3H), 3.74 (s, 1H), 3.61 (s, 1H), 1.36 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 131.7, 128.7, 128.3, 122.4, 86.9, 79.7, 55.0, 38.9, 23.1.HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{13}H_{17}OS^+$:221.0995; found: 221.1002

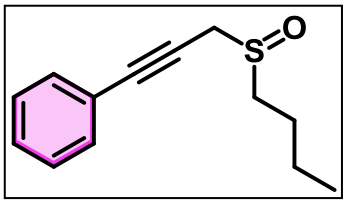
(3-(propylsulfinyl)prop-1-yn-1-yl)benzene (19a):



Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), propane-1-

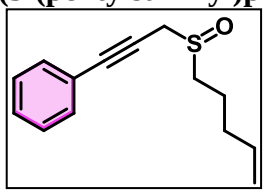
thiol (50.1 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as yellowish liquid (118.7 µL, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.42 (m, 2H), 7.36 – 7.30 (m, 3H), 3.86 (d, J = 15.9 Hz, 1H), 3.79 (d, J = 15.9 Hz, 1H), 3.06 – 2.83 (m, 2H), 1.95 – 1.82 (m, 2H), 1.13 (t, J = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ131.9, 128.9, 128.4, 122.0, 87.8, 77.7, 53.7, 43.2, 16.0, 13.5.HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{11}H_{13}OS^+$:207.0838; found: 207.0831

(3-(butylsulfinyl)prop-1-yn-1-yl)benzene (20a):



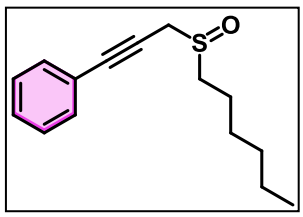
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), butane-1-thiol (60 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as yellowish liquid (123.8 µL, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.36 – 7.29 (m, 3H), 3.83 (s, 1H), 3.81 (s, 1H), 2.96 (m, 2H), 1.87 – 1.77 (m, 2H), 1.59 – 1.46 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ131.8, 128.9, 128.4, 122.0, 87.9, 77.7, 51.4, 43.1, 24.2, 22.1, 13.7. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{13}H_{17}OS^+$:221.0995; found:221.0992

(3-(pentylsulfinyl)prop-1-yn-1-yl)benzene (21a):



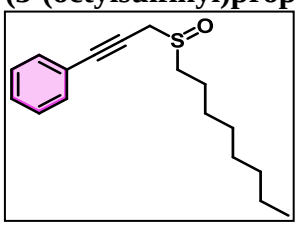
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), pentane-1-thiol (69.7 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as yellowish liquid (130 µL, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.42 (m, 2H), 7.36 – 7.30 (m, 3H), 3.85 (d, *J* = 15.9 Hz, 1H), 3.79 (d, *J* = 15.9 Hz, 1H), 2.95 (m, 2H), 1.89 – 1.80 (m, 2H), 1.53 – 1.32 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 131.9, 128.9, 128.4, 122.0, 87.8, 77.7, 51.7, 43.1, 31.0, 22.3, 21.9, 13.8.HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{14}H_{19}OS^+$:235.1151; found:235.1154

(3-(hexylsulfinyl)prop-1-yn-1-yl)benzene (22a):



Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), hexane-1-thiol (79 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as yellowish liquid (134.5 µL, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.42 (m, 2H), 7.36 – 7.29 (m, 3H), 3.86 (d, *J* = 15.9 Hz, 1H), 3.80 (d, *J* = 15.9 Hz, 1H), 2.96 (m, 2H), 1.88 – 1.78 (m, 2H), 1.49 (m, 2H), 1.38 – 1.29 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 131.9, 129.9, 128.9, 128.4, 122.0, 87.9, 77.7, 51.6, 43.0, 31.4, 28.5, 22.4, 22.2, 14.0.HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{21}OS^+$:249.1308; found:249.1305

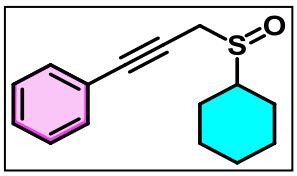
(3-(octylsulfinyl)prop-1-yn-1-yl)benzene (23a):



Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), octane-1-thiol (97.8 µL, 0.67 mmol), TEA (38 µL, 0.33 mmol),

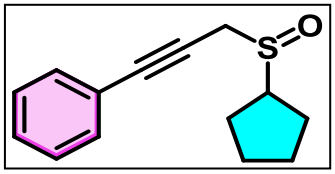
$[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as brownish liquid (155.3 µL, 84% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.42 (m, 2H), 7.36 – 7.29 (m, 3H), 3.85 (s, 1H), 3.82 (s, 1H), 3.05 – 2.84 (m, 2H), 1.84 (dt, *J* = 15.5, 7.7 Hz, 2H), 1.57 – 1.42 (m, 2H), 1.37 – 1.22 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 131.9, 129.9, 128.9, 128.4, 128.3, 122.0, 87.9, 77.7, 51.6, 43.0, 31.7, 29.1, 29.0, 28.8, 22.6, 22.2, 14.1. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{17}H_{25}OS^+$:277.1621; found: 277.1626

(3-(cyclohexylsulfinyl)prop-1-yn-1-yl)benzene (24a):



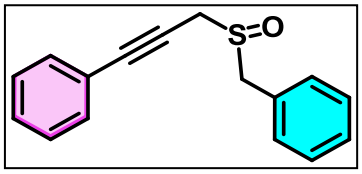
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), cyclohexanethiol (77.7 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as brownish liquid (130.1 µL, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.42 (m, 2H), 7.36 – 7.29 (m, 3H), 3.85 (d, *J* = 16.2 Hz, 1H), 3.78 (d, *J* = 16.2 Hz, 1H), 2.97 – 2.88 (m, 1H), 2.01 – 1.93 (m, 2H), 1.77 – 1.51 (m, 4H), 1.34 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 131.9, 128.8, 128.4, 122.2, 87.5, 78.0, 57.5, 40.0, 26.8, 25.6, 25.4, 25.2, 23.5. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{19}OS^+$:247.1151; found: 247.1148

(3-(cyclopentylsulfinyl)prop-1-yn-1-yl)benzene (25a):



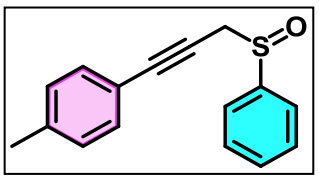
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), cyclpentanethiol (68.3 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as brownish liquid (119.6 µL, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.43 (m, 2H), 7.37 – 7.28 (m, 3H), 3.80 (d, *J* = 16.2 Hz, 1H), 3.76 (d, *J* = 16.2 Hz, 1H), 3.80 (d, *J* = 16.2 Hz, 1H), 3.77 (d, *J* = 16.2 Hz, 1H), 2.28 – 2.18 (m, 1H), 2.07 – 1.96 (m, 2H), 1.82 – 1.66 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 131.9, 129.9, 128.8, 128.4, 122.1, 87.4, 78.1, 58.2, 41.8, 27.8, 26.4, 25.8, 24.3. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{14}H_{17}OS^+$:233.0995; found: 233.0997

(3-(benzylsulfinyl)prop-1-yn-1-yl)benzene (26a):



Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), phenylmethanethiol (83 µL, 0.67 mmol), TEA (33.8 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography as white solid (139 µL, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.47 (m, 2H), 7.40 – 7.28 (m, 8H), 4.26 (d, *J* = 13.1 Hz, 1H), 4.09 (d, *J* = 13.1 Hz, 1H), 3.61 (d, *J* = 16.0 Hz, 1H), 3.56 (d, *J* = 16.0 Hz, 1H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 131.9, 130.4, 129.0, 128.6, 128.5, 122.1, 88.5, 78.0, 56.2, 41.2. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{16}H_{15}OS^+$:255.0838; found: 255.0837

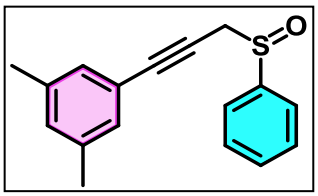
1-methyl-4-(3-(phenylsulfinyl)prop-1-yn-1-yl)benzene (27a):



Following the general procedure (**GP3)** the reaction was carried out with (1-(3-chloroprop-1-yn-1-yl)-4-methylbenzene (100 µL, 0.61 mmol), thiophenol (67.1 µL, 0.61 mmol), TEA (30.8 µL, 0.30 mmol),

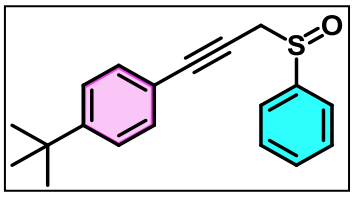
$[Ru(bpy)_3]Cl_2.6H_2O$ (9 mg, 2 mol%) and purified by column chromatography as brownish liquid (114 µL, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.74 (m, 2H), 7.57 – 7.52 (m, 3H), 7.23 – 7.19 (m, 2H), 7.10 (dt, *J* = 2.6, 2.1 Hz, 2H), 3.95 (d, *J* = 15.5 Hz, 1H), 3.81 (d, *J* = 15.6 Hz, 1H), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 143.1, 139.0, 131.7, 129.1, 129.0, 124.6, 119.0, 88.3, 77.3, 49.1, 21.5.HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{16}H_{15}OS^+$:255.0838; found: 255.0842

1,3-dimethyl-5-(3-(phenylsulfinyl)prop-1-yn-1-yl)benzene (28a):



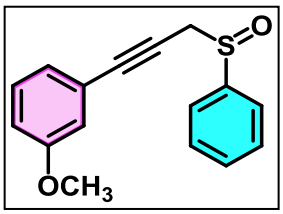
Following the general procedure (**GP3)** the reaction was carried out with 1-(3-chloroprop-1-yn-1-yl)-3,5-dimethylbenzene (100 µL, 0.56 mmol), thiophenol (61.6 µL, 0.56 mmol), TEA (28.3 µL, 0.28 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (8 mg, 2 mol%) and purified by column chromatography as brownish liquid (106 µL, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (m, 2H), 7.73 – 7.70 (m, 1H), 7.57 – 7.53 (m, 3H), 6.96 (d, *J* = 2.9 Hz, 2H), 3.96 (d, *J* = 15.5 Hz, 1H), 3.80 (d, *J* = 15.5 Hz, 1H), 2.27 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.8, 139.3, 132.6, 131.8, 129.0, 128.8, 128.3, 124.8, 122.1, 121.8, 88.1, 78.2, 49.0, 21.4.HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{17}H_{17}OS^+$:269.0995; found:269.0991

1-(*tert*-butyl)-4-(3-(phenylsulfinyl)prop-1-yn-1-yl)benzene (29a):



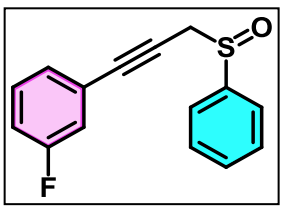
Following the general procedure (**GP3)** the reaction was carried out with 1-(*tert*-butyl)-4-(3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.48 mmol), thiophenol (52.8 µL, 0.48 mmol), TEA (24.2 µL, 0.24 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (7 mg, 2 mol%) and purified by column chromatography as brownish liquid (95 µL, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (dt, *J* = 2.1, 1.6 Hz, 2H), 7.31 (dq, *J* = 5.3, 1.6 Hz, 2H), 7.27 – 7.23 (m, 5H), 3.97 (d, *J* = 15.5 Hz, 1H), 3.81 (d, *J* = 15.5 Hz, 1H), 1.30 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.1, 143.0, 131.7, 131.5, 130.0, 129.0, 125.4, 124.7, 119.0, 88.3, 77.2, 49.1, 34.8, 31.1. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{19}H_{21}OS^+$:297.1308; found: 297.1313

1-methoxy-3-(3-(phenylsulfinyl)prop-1-yn-1-yl)benzene (30a):



Following the general procedure (**GP3)** the reaction was carried out with 1-(3-chloroprop-1-yn-1-yl)-3-methoxybenzene (100 µL, 0.55 mmol), thiophenol (60.5 µL, 0.55 mmol), TEA (27.3 µL, 0.27 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (8 mg, 2 mol%) and purified by column chromatography as brownish liquid (92 µL, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (m, 1H), 7.73 – 7.70 (m, 1H), 7.62 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.56 (dt, *J* = 2.2, 1.5 Hz, 2H), 7.22 – 7.13 (m, 1H), 6.93 – 6.82 (m, 3H), 3.97 (d, *J* = 15.5 Hz, 1H), 3.86 (d, *J* = 14.4 Hz, 1H), 3.78 (s, 3H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.1, 143.0, 131.7, 131.5, 130.0, 129.0, 125.4, 124.7, 119.0, 88.3, 77.2, 49.1, 34.8, 31.1. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{16}H_{15}O_2S^+$:271.0787; found: 271.0792

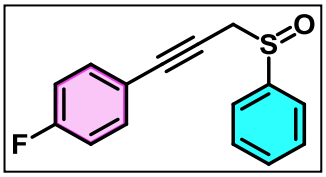
1-fluoro-3-(3-(phenylsulfinyl)prop-1-yn-1-yl)benzene (31a):



Following the general procedure (**GP3)** the reaction was carried out with 1-(3-chloroprop-1-yn-1-yl)-3-fluorobenzene (100 µL, 0.59 mmol),

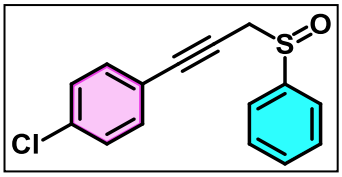
thiophenol (64.9 µL, 0.59 mmol), TEA (29.3 µL, 0.29 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (8 mg, 2 mol%) and purified by column chromatography as brownish liquid (100.4 µL, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dt, *J* = 9.7, 2.7 Hz, 2H), 7.60 – 7.54 (m, 3H), 7.28 – 7.22 (m, 1H), 7.12 – 6.97 (m, 3H), 3.92 (d, *J* = 15.6 Hz, 1H), 3.83 (d, *J* = 15.6 Hz, 1H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.2 (d, *J* = 247.1 Hz), 142.9, 131.8, 129.9, 129.1, 127.7, 124.6, 118.6 (d, *J* = 22.9 Hz), 116.2 (d, *J* = 21.0 Hz), 86.8, 79.1, 48.8. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{12}FOS^+$:259.0587; found: 259.0583

1-fluoro-4-(3-(phenylsulfinyl)prop-1-yn-1-yl)benzene (32a):



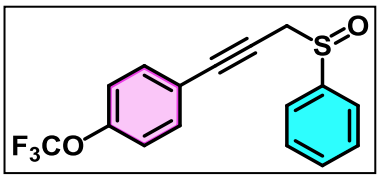
Following the general procedure (**GP3)** the reaction was carried out with 1-(3-chloroprop-1-yn-1-yl)-4-fluorobenzene (100 µL, 0.59 mmol), thiophenol (64.9 µL, 0.59 mmol), TEA (29.3 µL, 0.29 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (8 mg, 2 mol%) and purified by column chromatography as brownish liquid (103.5 µL, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.57 (dd, *J* = 4.1, 2.2 Hz, 3H), 7.28 – 7.21 (m, 2H), 7.12 – 6.96 (m, 4H), 3.93 (d, *J* = 15.6 Hz, 1H), 3.83 (d, *J* = 15.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.5 (d, *J* = 251.7 Hz), 146.2, 132.3, 131.2, 129.5, 129.0, 122.4, 120.9 (d, *J* = 3.2 Hz), 119.4 (d, *J* = 21.5 Hz), 89.2, 78.1, 49.6. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{12}FOS^+$:259.0587; found:259.0585

1-chloro-4-(3-(phenylsulfinyl)prop-1-yn-1-yl)benzene (33a):



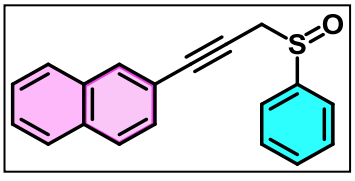
Following the general procedure (**GP3)** the reaction was carried out with 1-(3-chloroprop-1-yn-1-yl)-4-chlorobenzene (100 µL, 0.54 mmol), thiophenol (59.4 µL, 0.54 mmol), TEA (27.3 µL, 0.27 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (8 mg, 2 mol%) and purified by column chromatography as brownish liquid (102 µL, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.72 (m, 2H), 7.58 – 7.54 (m, 2H), 7.29 – 7.22 (m, 5H), 3.92 (d, *J* = 15.8 Hz, 1H), 3.83 (d, *J* = 15.6 Hz, 1H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 142.0, 130.8, 128.0, 127.8, 127.3, 123.6, 121.1, 87.1, 77.0, 48.0.HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{12}ClOS^+$:275.0292; found:275.0296

1-trifluoromethyl-4-(3-(phenylsulfinyl)prop-1-yn-1-yl)benzene (34a):



Following the general procedure (**GP3)** the reaction was carried out with 1-(3-chloroprop-1-yn-1-yl)-4-(trifluoromethoxy)benzene (100 µL, 0.43 mmol), thiophenol (47.4 µL, 0.43 mmol), TEA (21.7 µL, 0.21 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (6 mg, 2 mol%) and purified by column chromatography as brownish liquid (86.4 µL, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.73 (m, 2H), 7.59 – 7.53 (m, 5H), 7.42 (d, *J* = 8.5 Hz, 2H), 3.94 (d, *J* = 15.8 Hz, 1H), 3.87 (d, *J* = 15.8 Hz, 1H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 142.8, 132.0, 131.9, 130.7, 130.3, 129.1, 125.9, 125.3(q, *J* = 3.7 Hz), 124.5, 122.4, 86.7, 80.7, 48.7.HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{16}H_{12}F_3O_2S^+$:325.0505; found: 325.0501

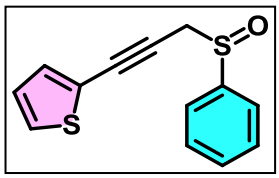
2-(3-(phenylsulfinyl)prop-1-yn-1-yl)naphthalene (35a):



Following the general procedure (**GP3)** the reaction was carried out with 2-(3-chloroprop-1-yn-1-yl)naphthalene (100 µL, 0.50 mmol),

thiophenol (55 μL, 0.50 mmol), TEA (25.2 μL, 0.25 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (6 mg, 2 mol%) and purified by column chromatography as brownish liquid (104 μL, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 – 7.95 (m, 1H), 7.85 – 7.78 (m, 3H), 7.58 – 7.36 (m, 8H), 4.12 (d, *J* = 15.5 Hz, 1H), 4.02 (d, *J* = 15.6 Hz, 1H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.1, 133.0, 131.8, 131.0, 129.3, 129.2, 128.3, 126.9, 126.5, 126.0, 125.1, 124.8, 119.7, 86.3, 82.6, 49.2.HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{19}H_{14}OS^+$:291.0836; found: 291.0839

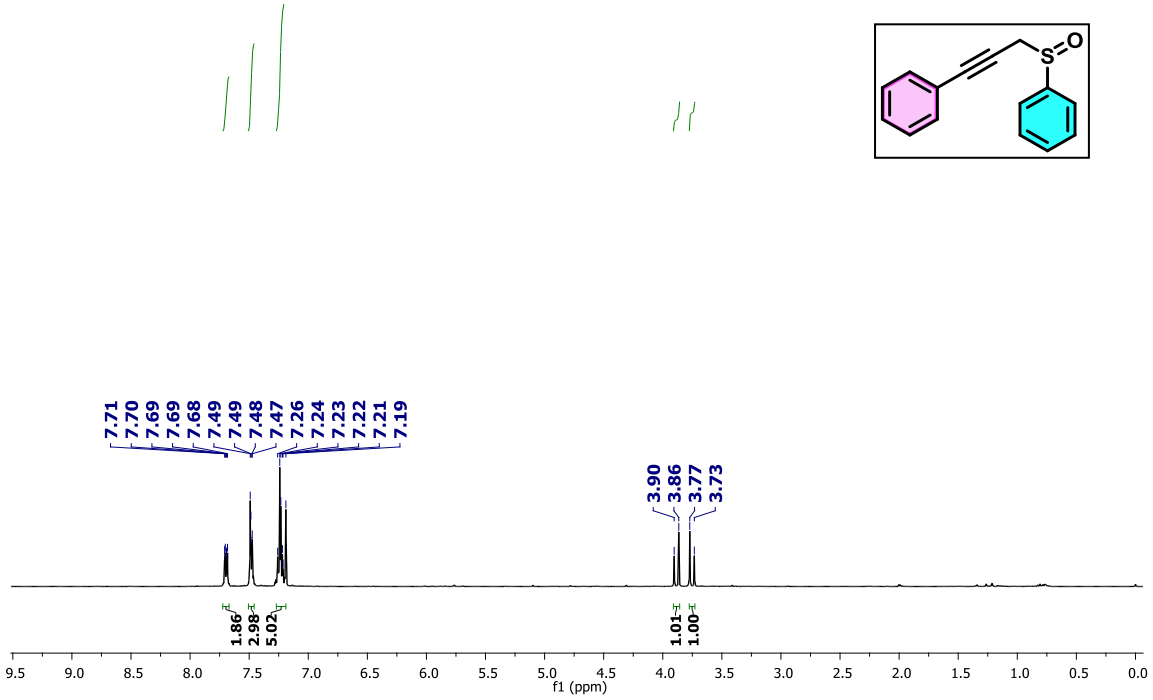
2-(3-(phenylsulfinyl)prop-1-yn-1-yl)thiophene (36a):



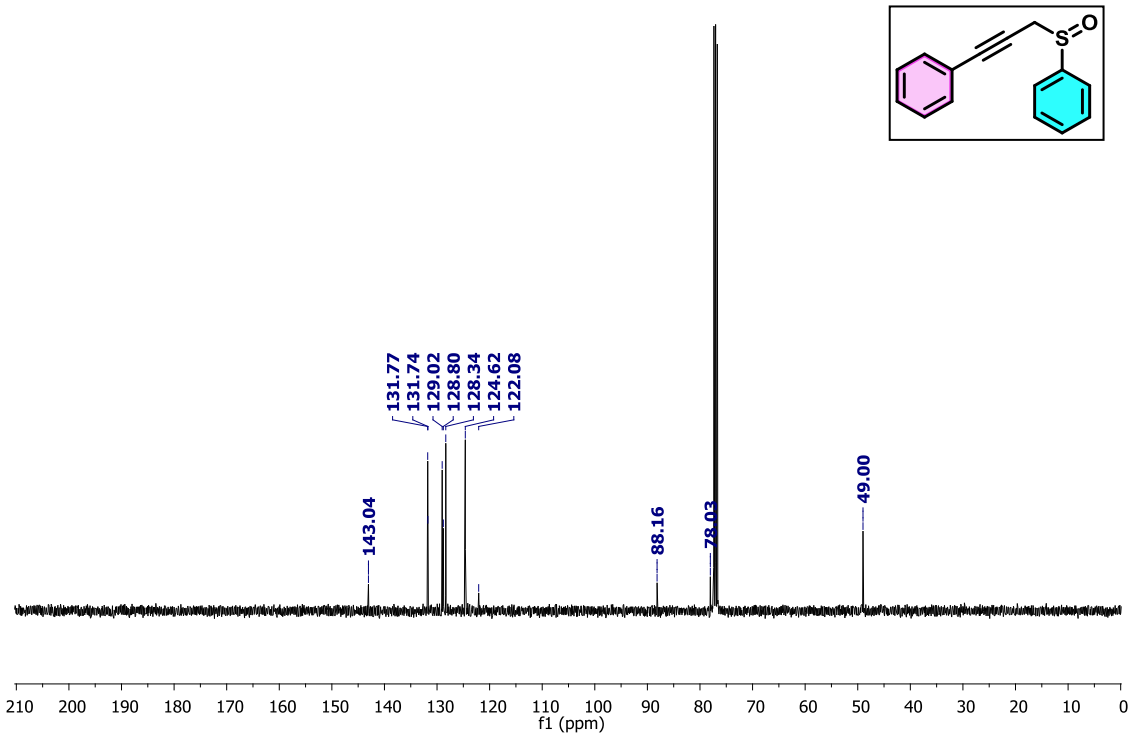
Following the general procedure (**GP3)** the reaction was carried out with 2-(3-chloroprop-1-yn-1-yl)thiophene (100 μL, 0.64 mmol), thiophenol (70.4 μL, 0.64 mmol), TEA (32.3 μL, 0.32 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (9 mg, 2 mol%) and purified by column chromatography as brownish liquid (107 μL, 68% yield).^{1}H NMR (400 MHz, $CDCl_3$): 7.56 – 7.51 (m, 2H), 7.36 – 7.30 (m, 5H), 7.28 – 7.24 (m, 1H), 3.96 (d, *J* = 15.6 Hz, 1H), 3.84 (d, *J* = 15.6 Hz, 1H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 142.0, 130.8, 128.0, 127.8, 127.3, 123.6, 121.1, 87.1, 77.0, 48.0. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{13}H_{11}OS^+$:247.0246; found: 247.0241

8. NMR Spectra:

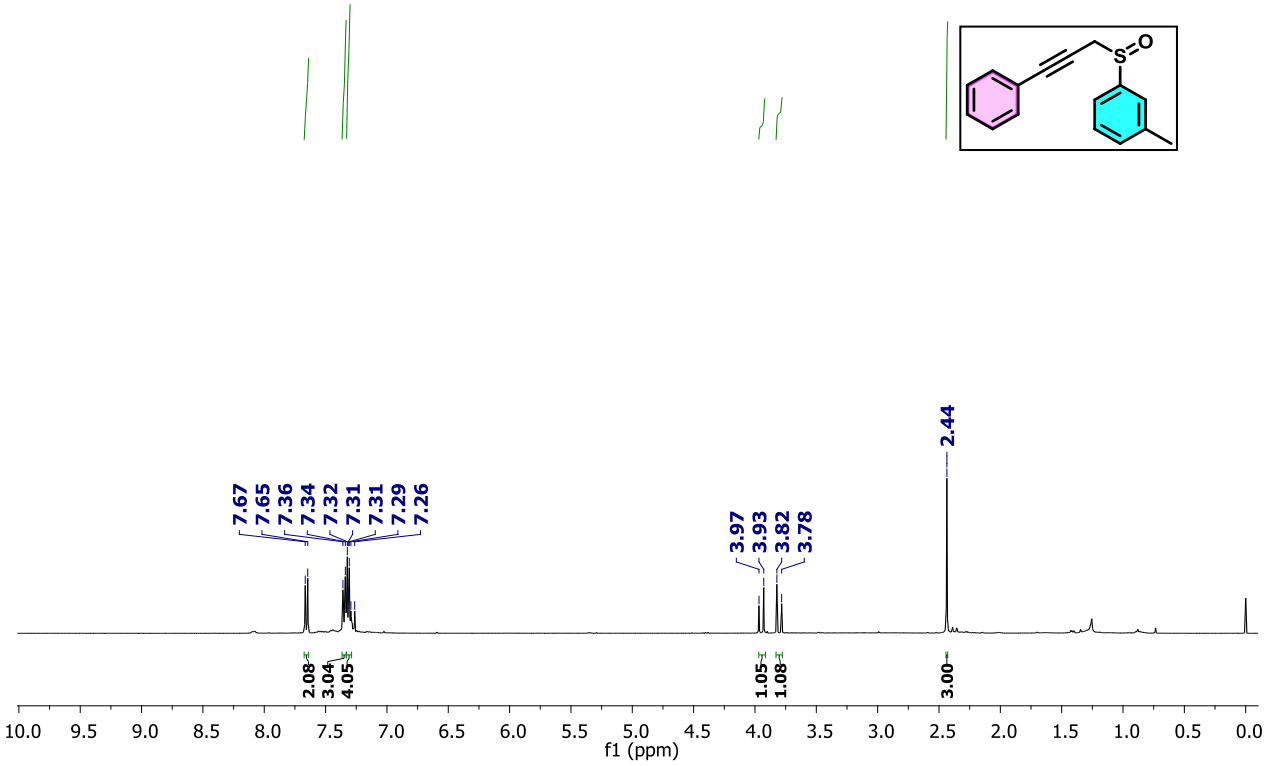
^{1}H-NMR (400 MHz, $CDCl_3$) of Compound **3a**



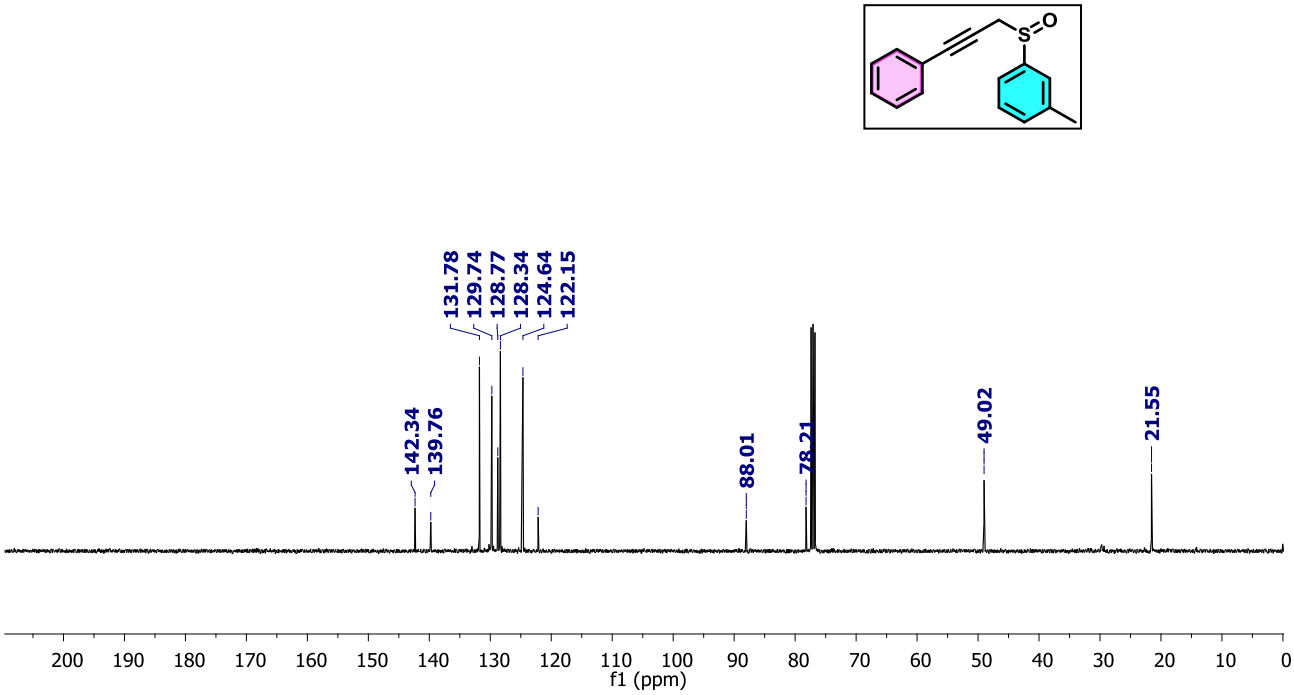
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) of Compound **3a**



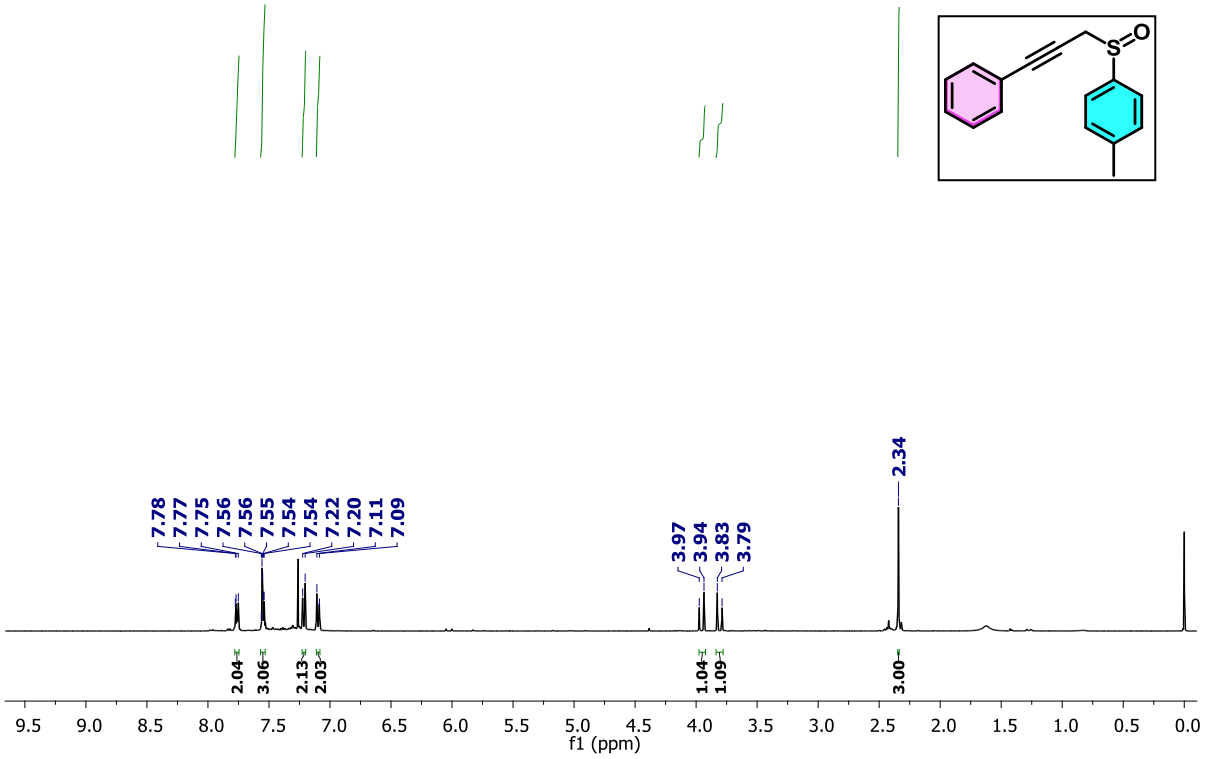
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **4a**



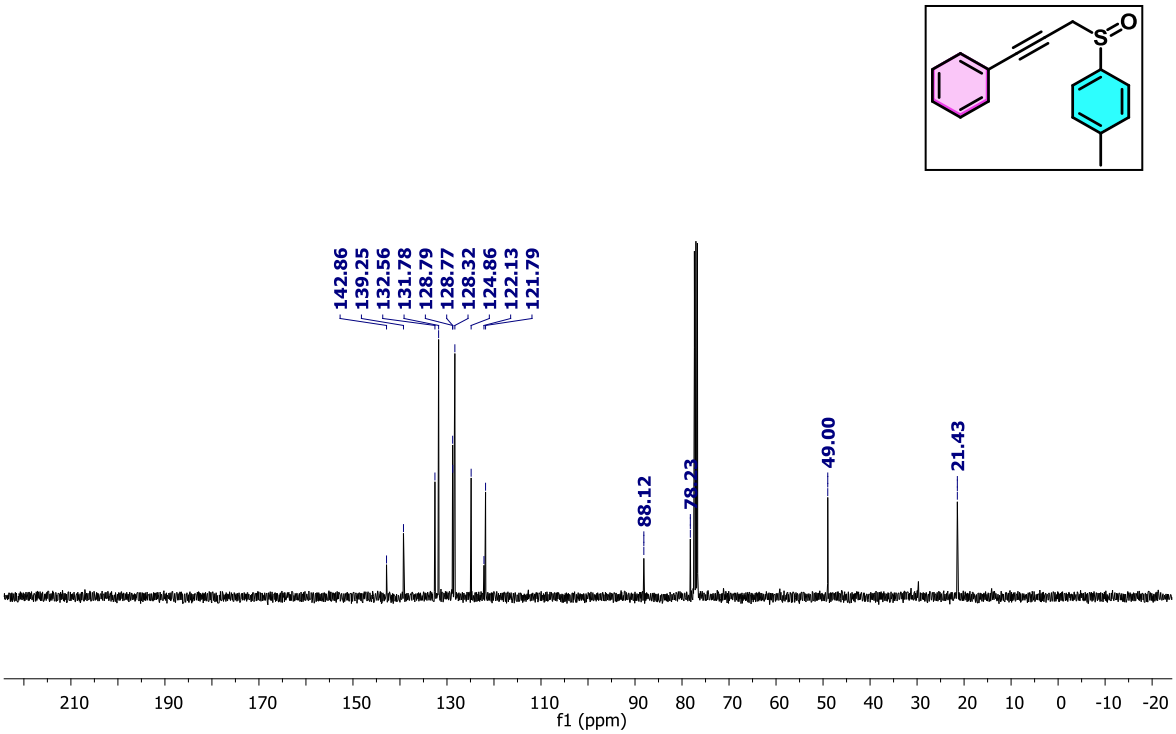
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **4a**



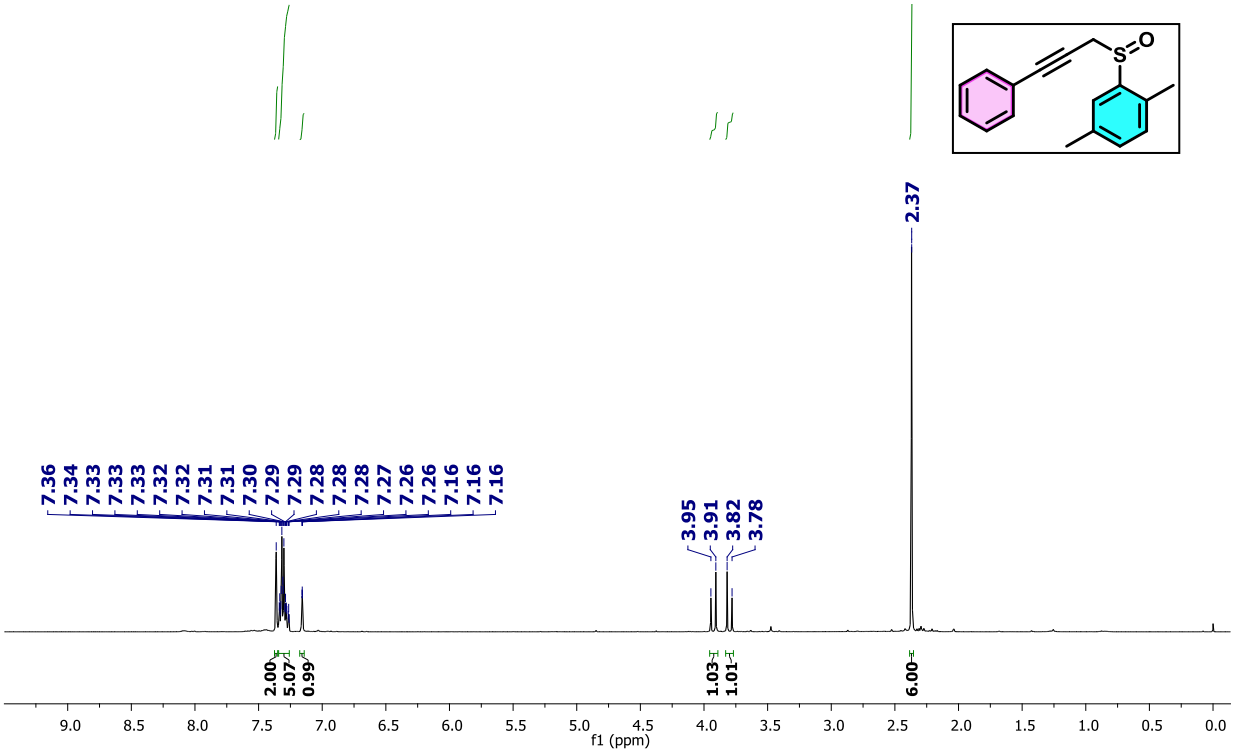
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **5a**



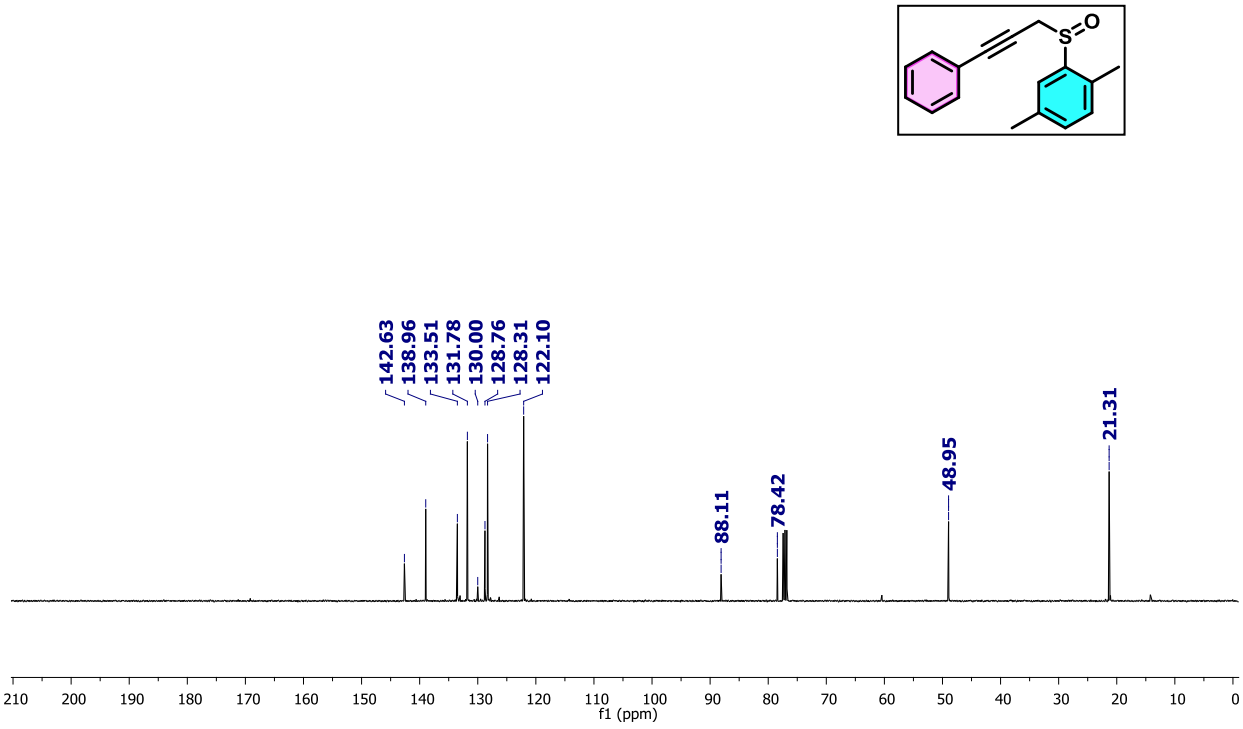
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **5a**



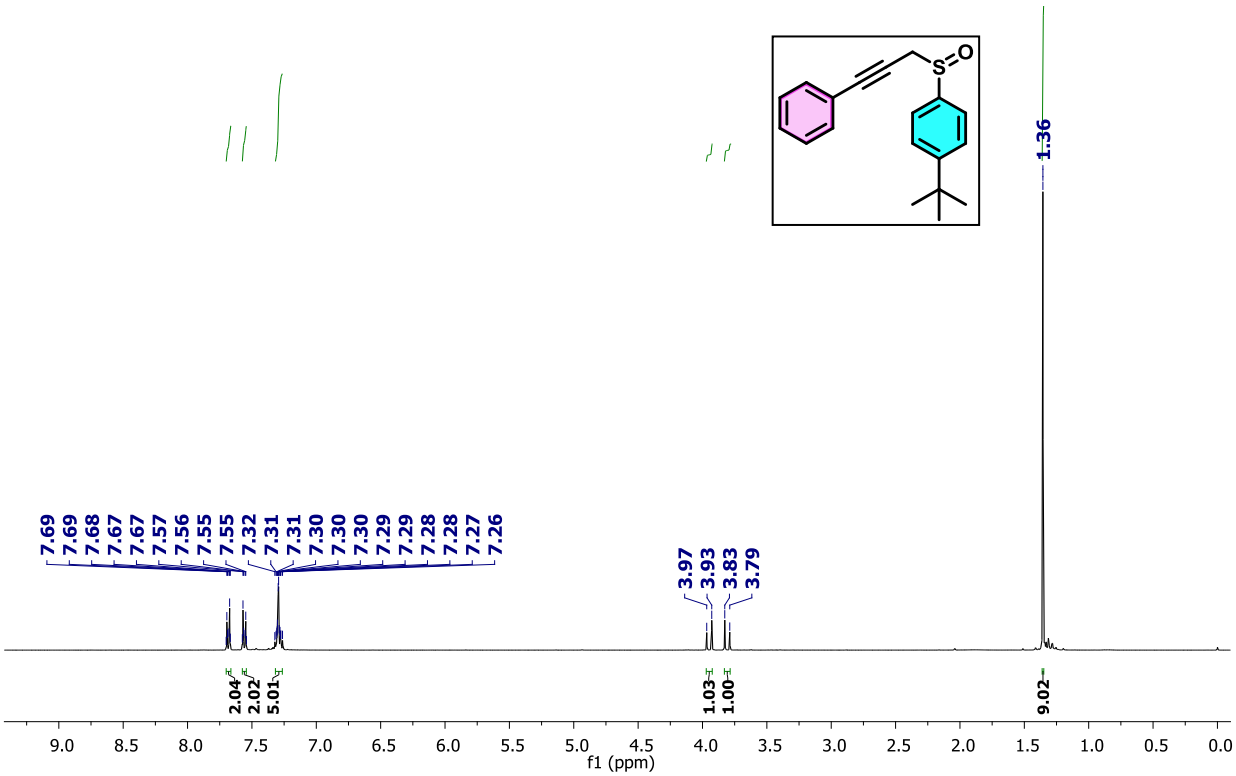
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **6a**



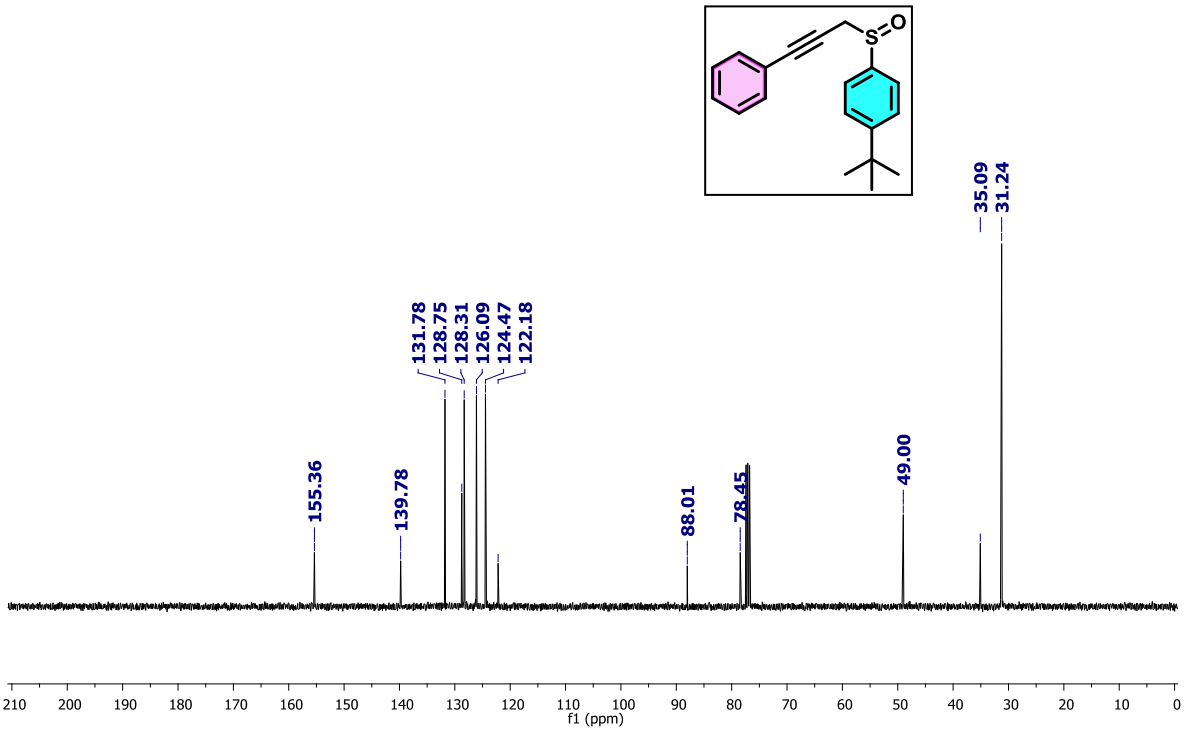
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **6a**



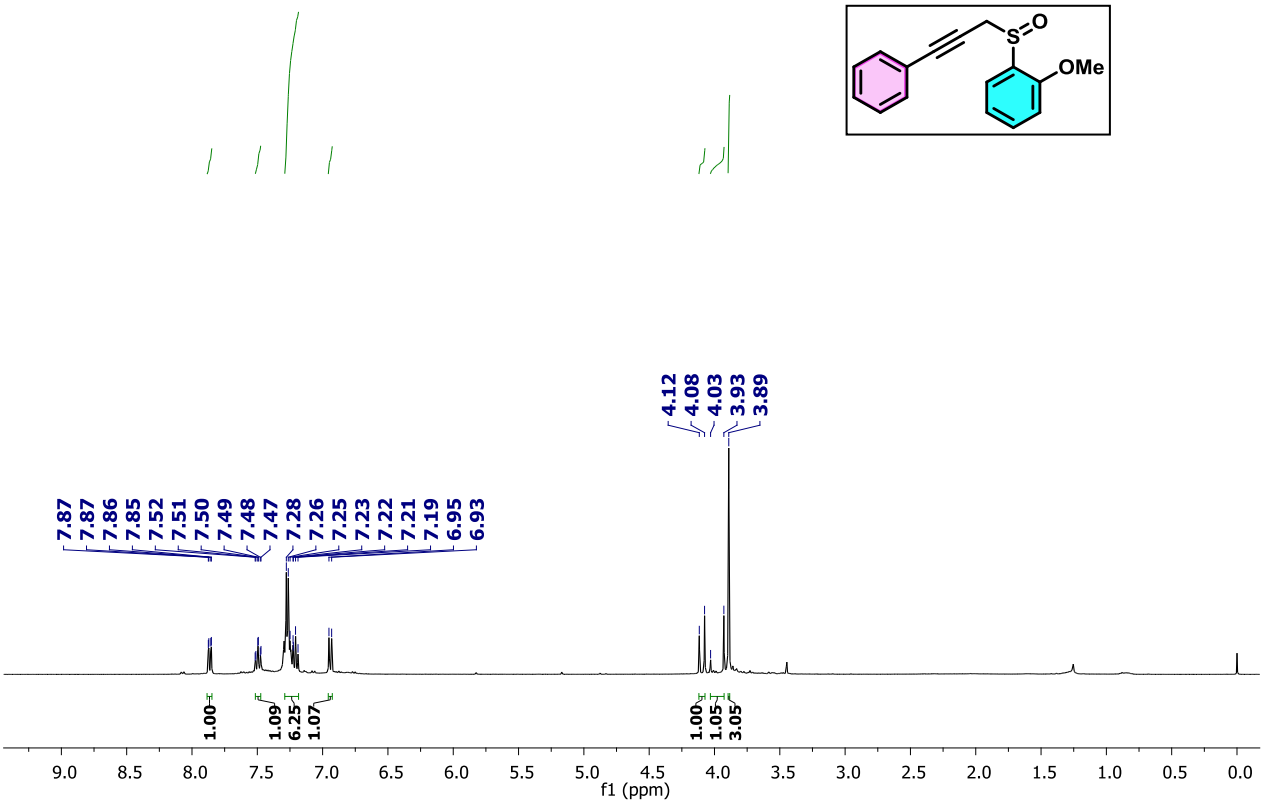
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **7a**



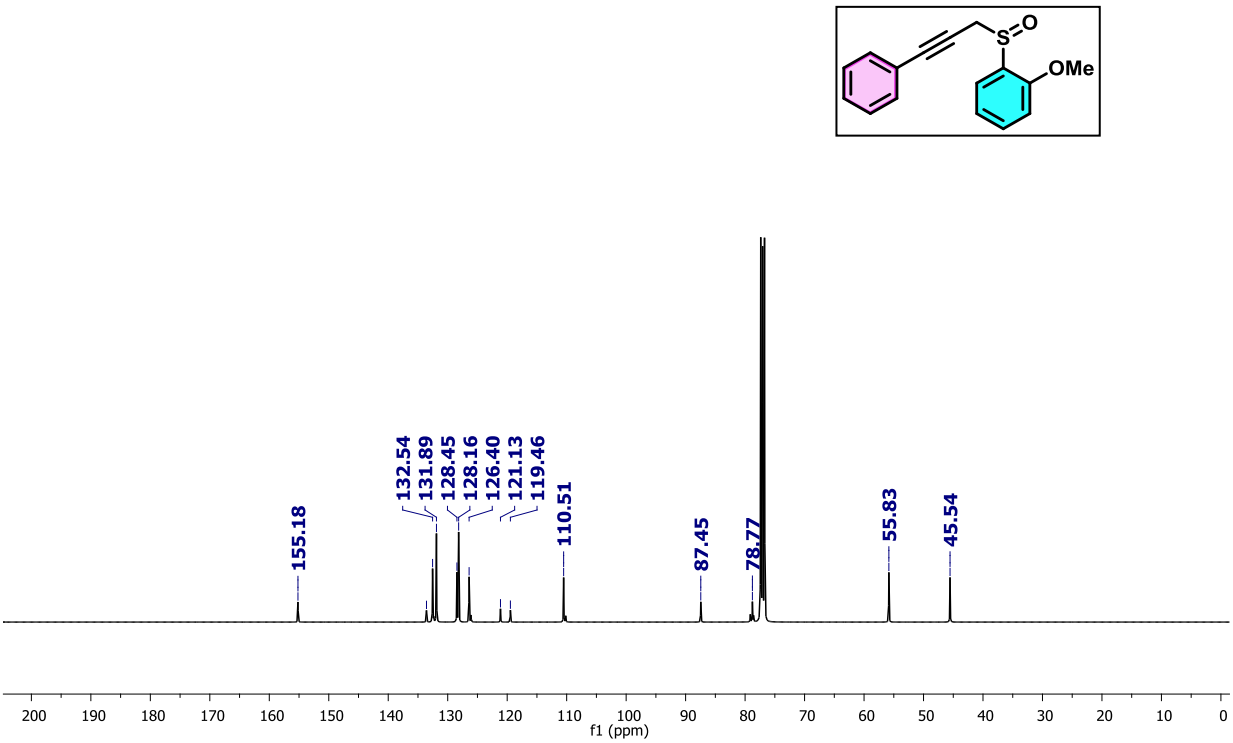
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) of Compound **7a**



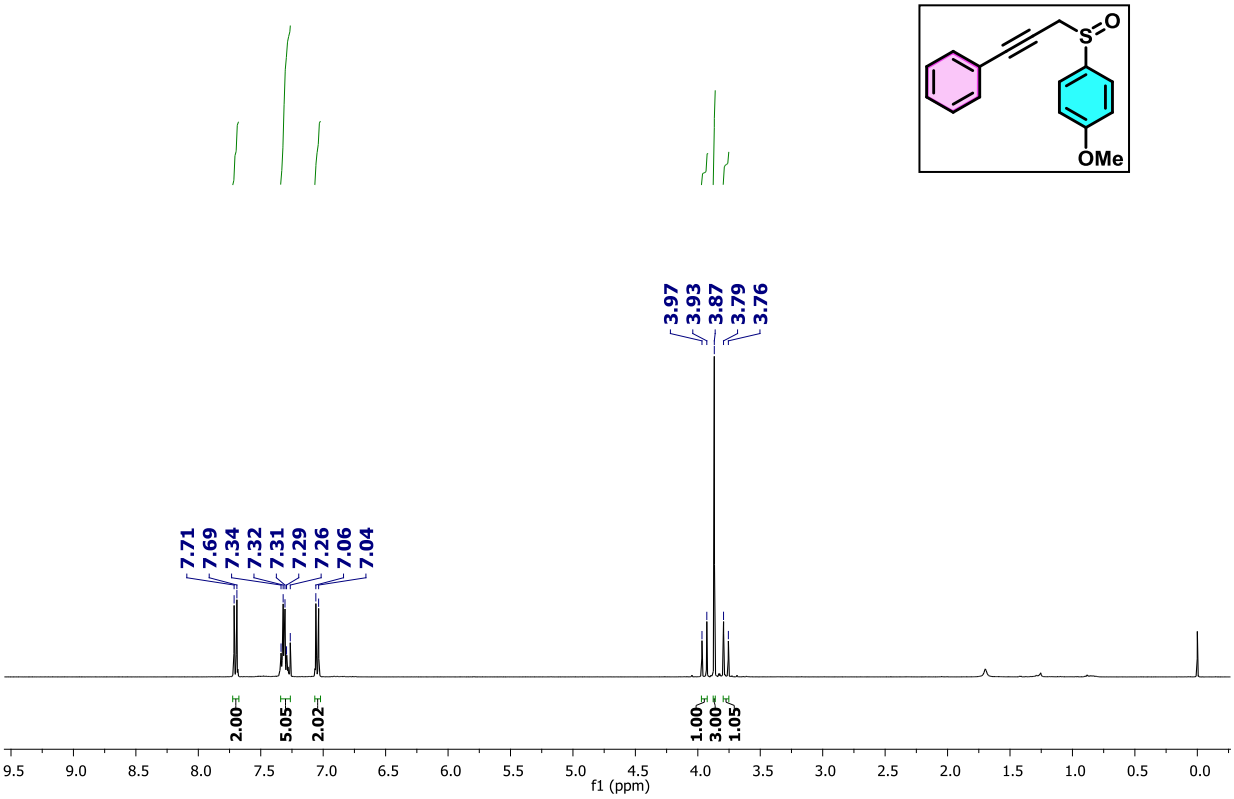
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **8a**



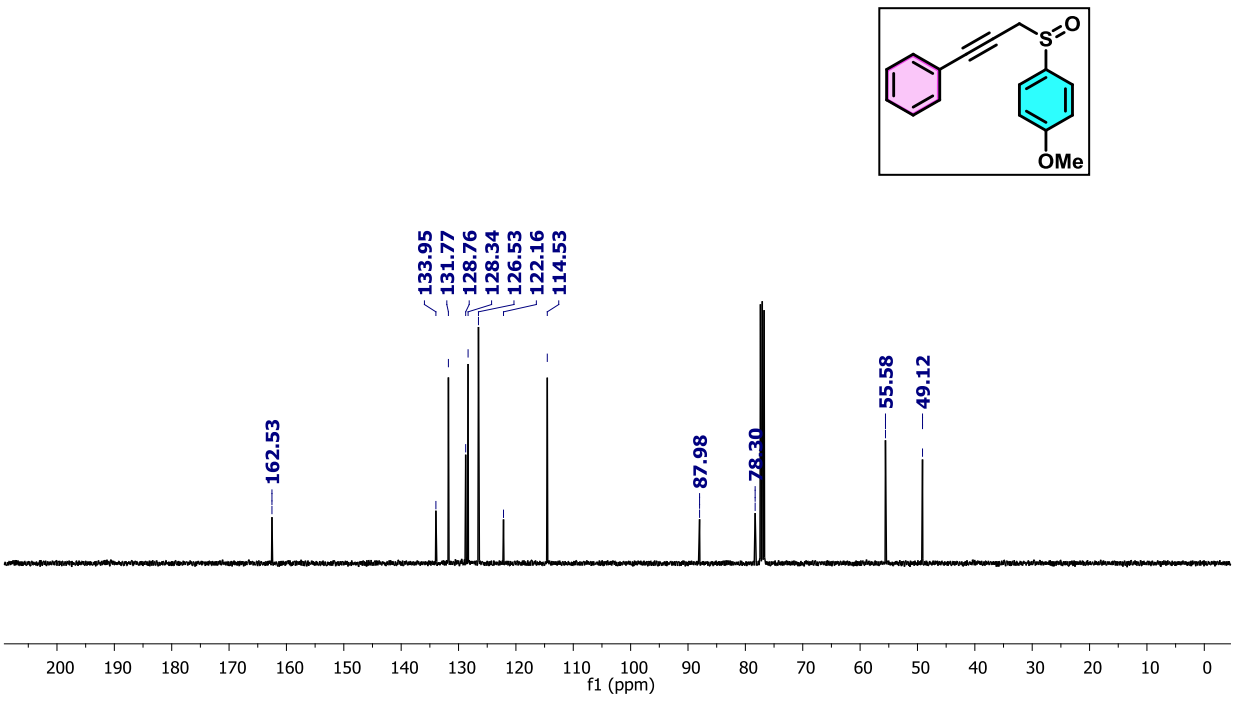
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **8a**



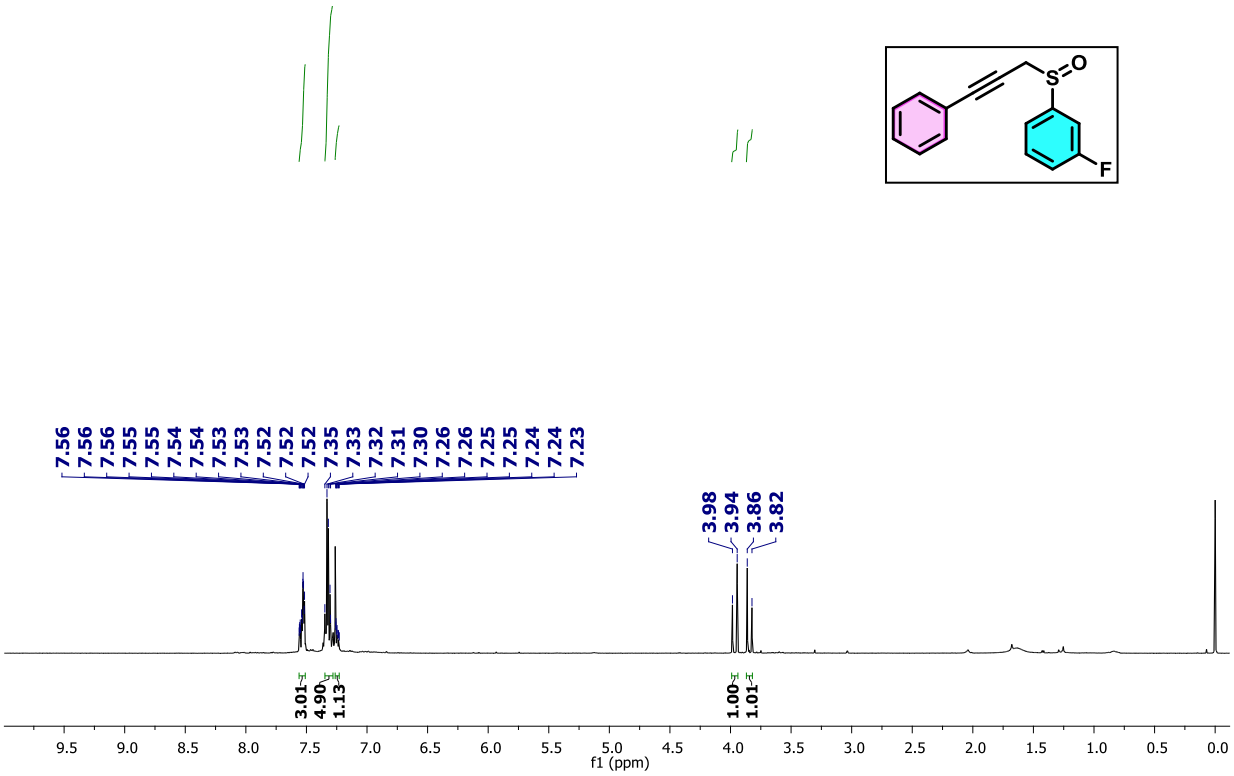
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **9a**



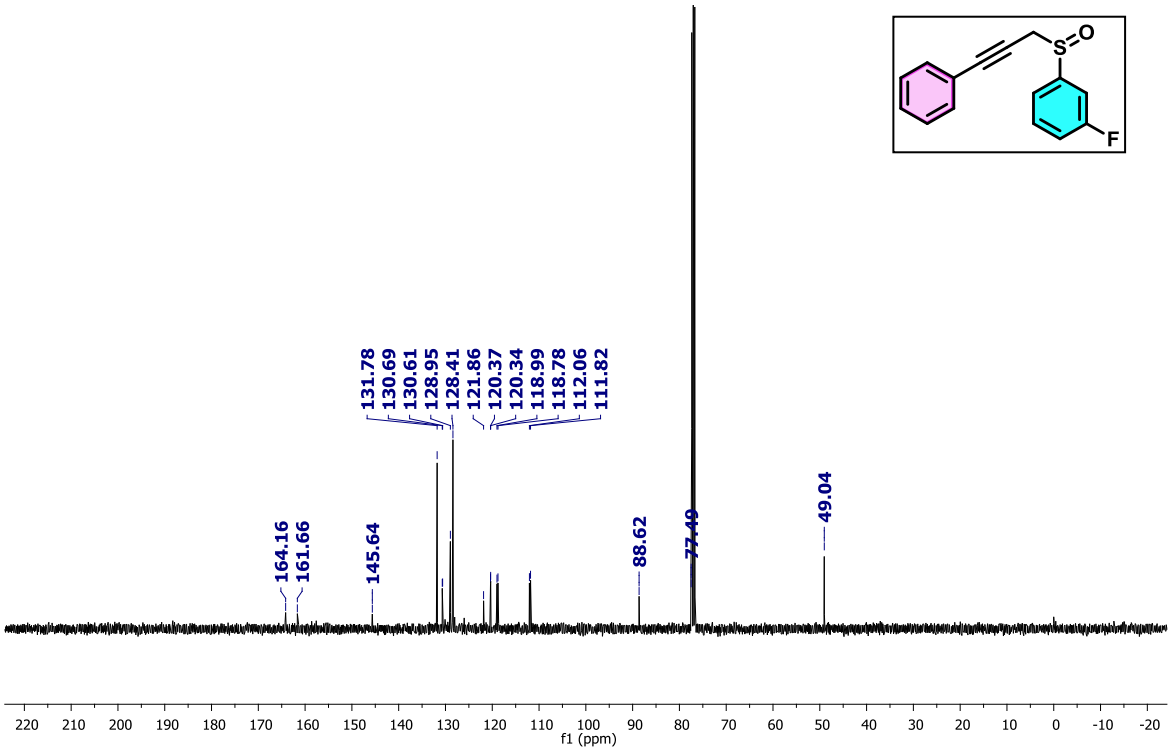
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **9a**



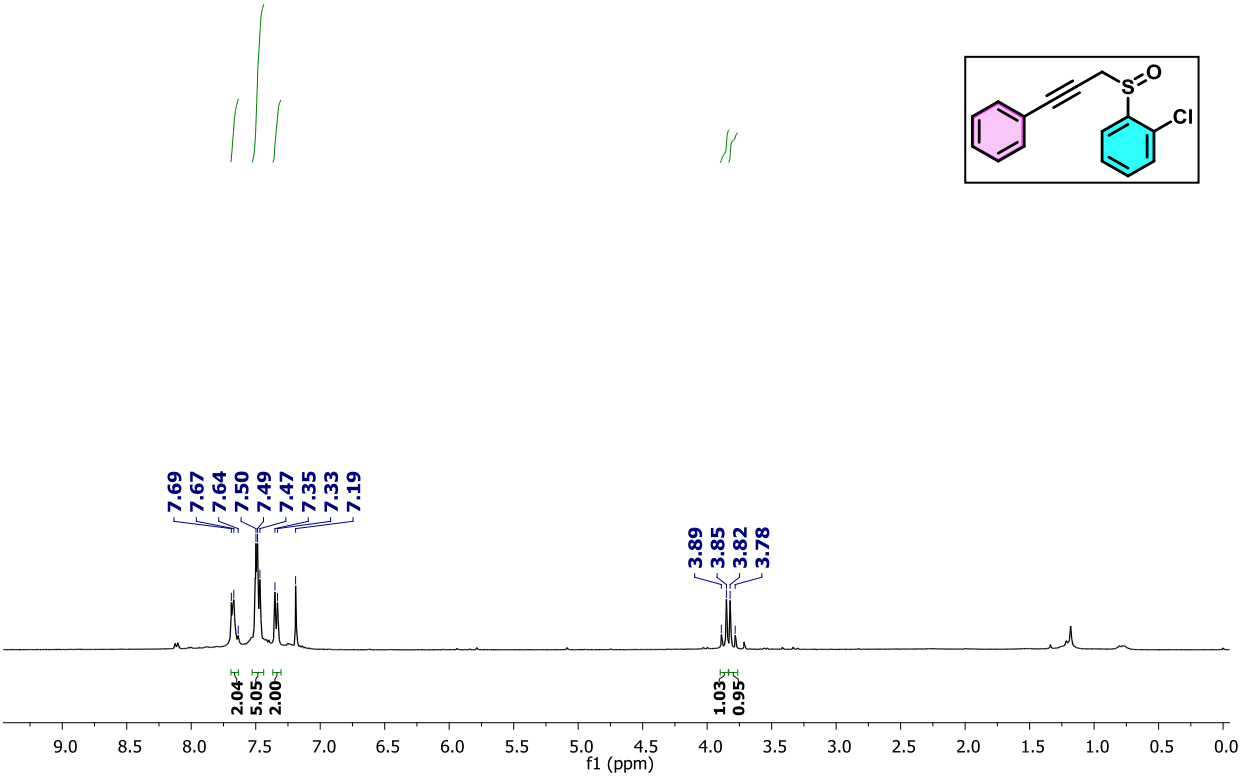
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **10a**



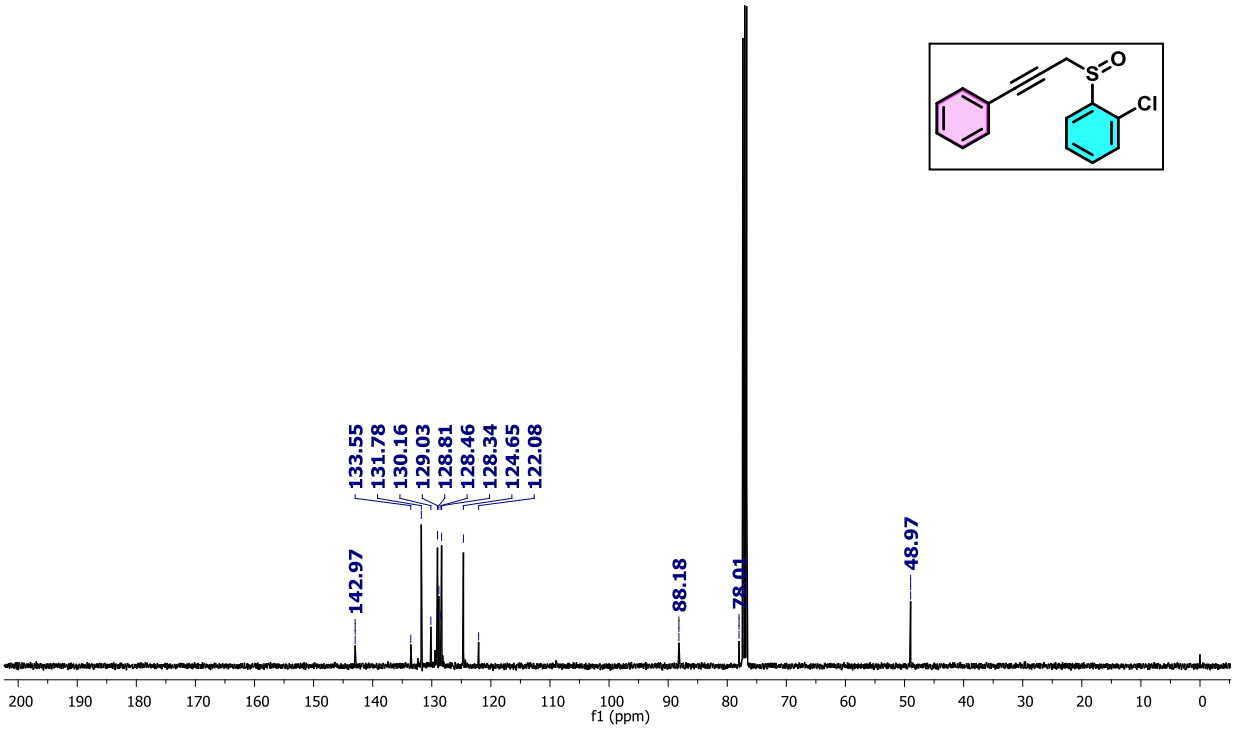
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **10a**



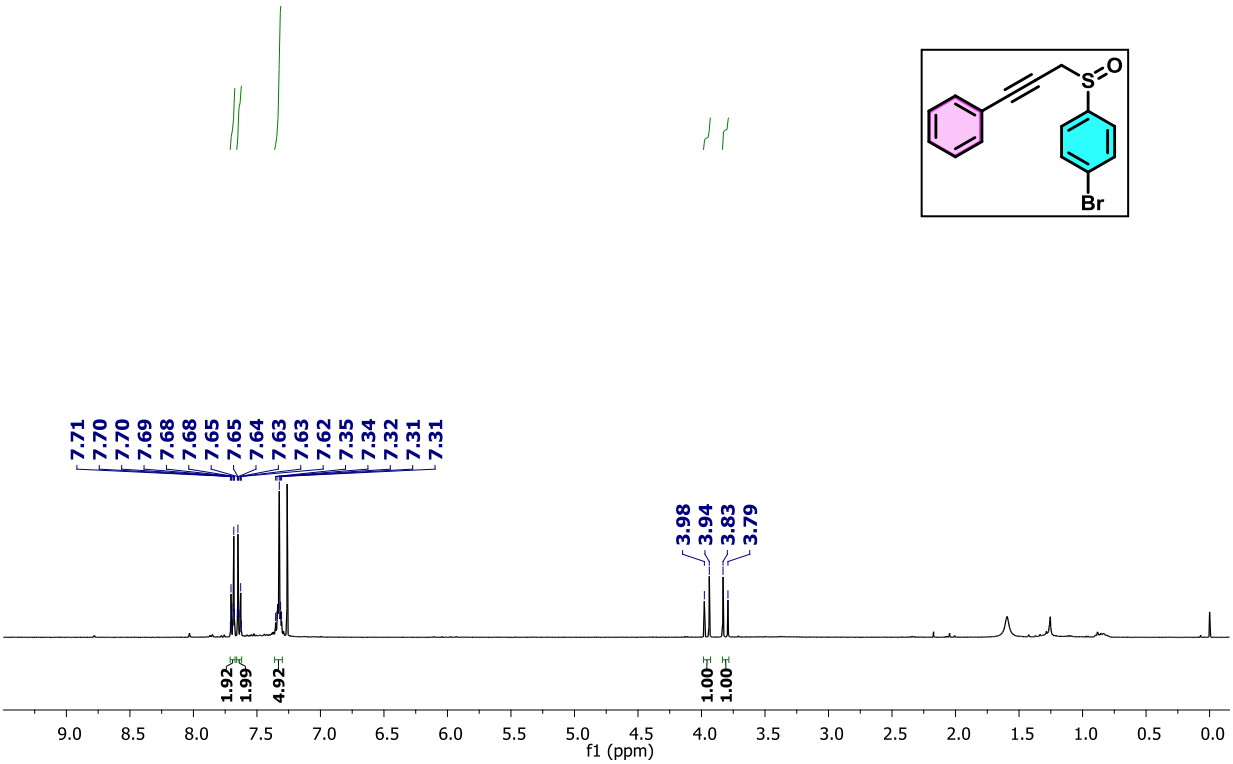
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **11a**



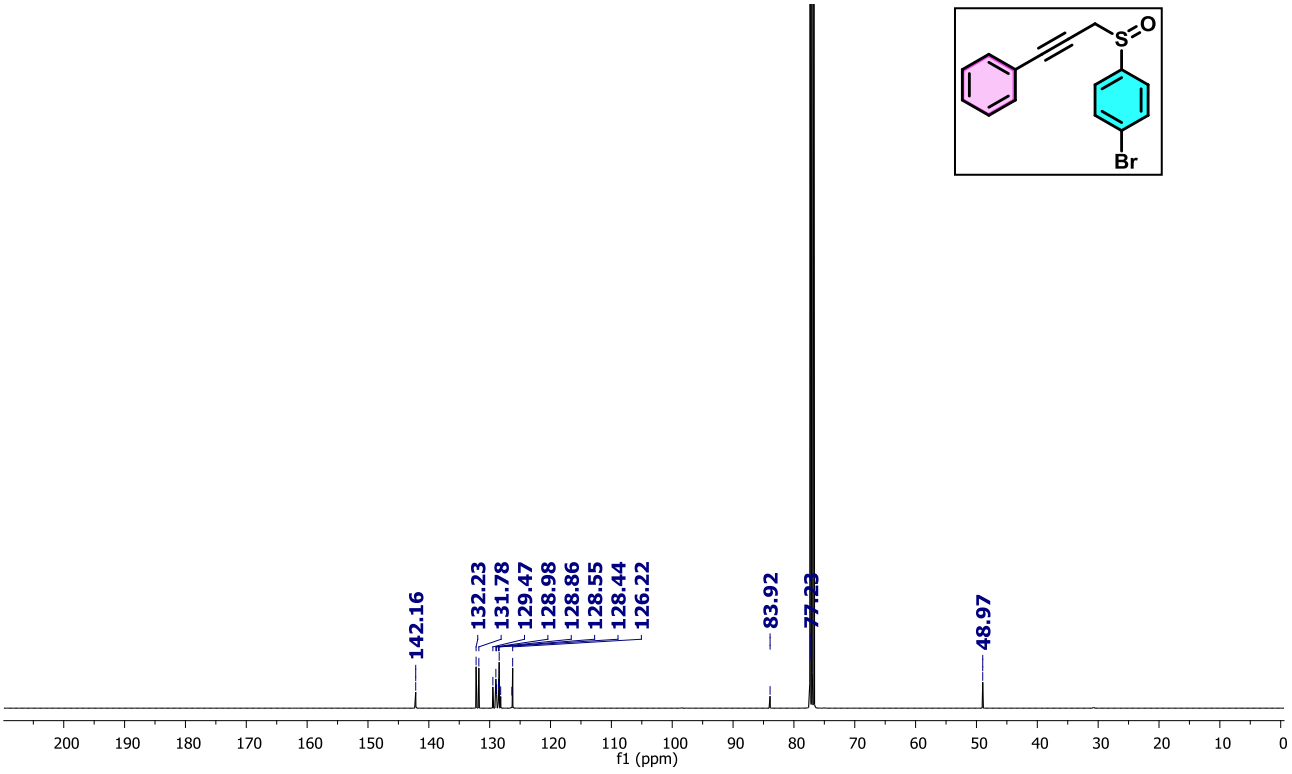
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **11a**



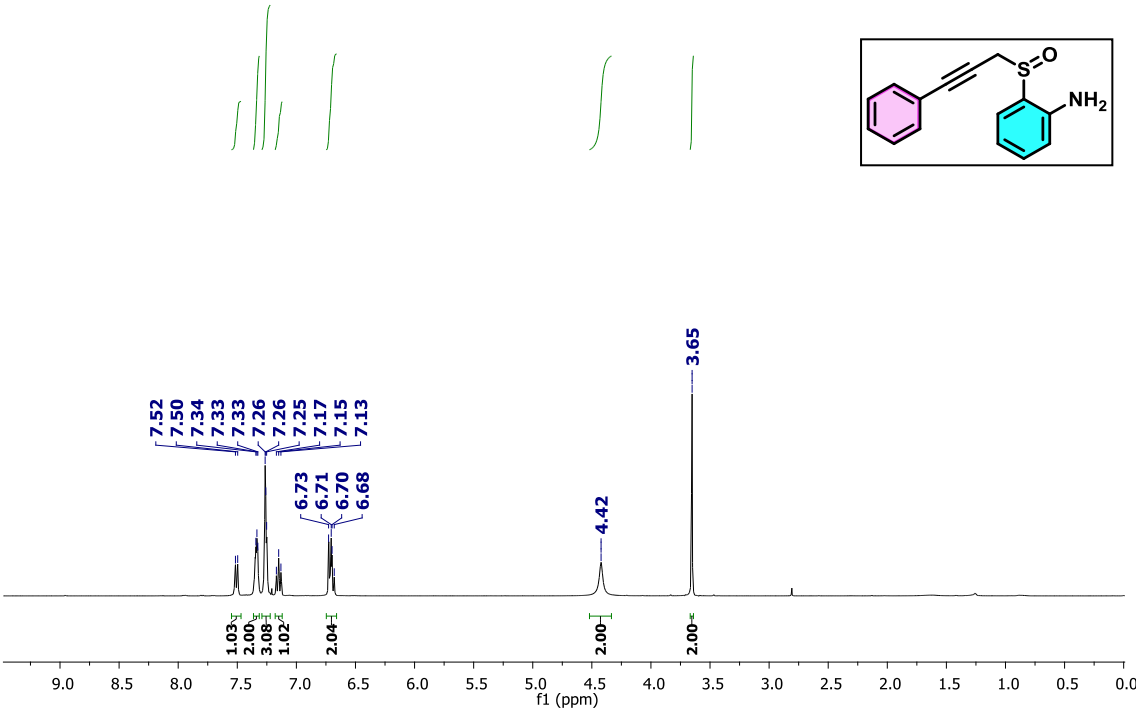
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **12a**



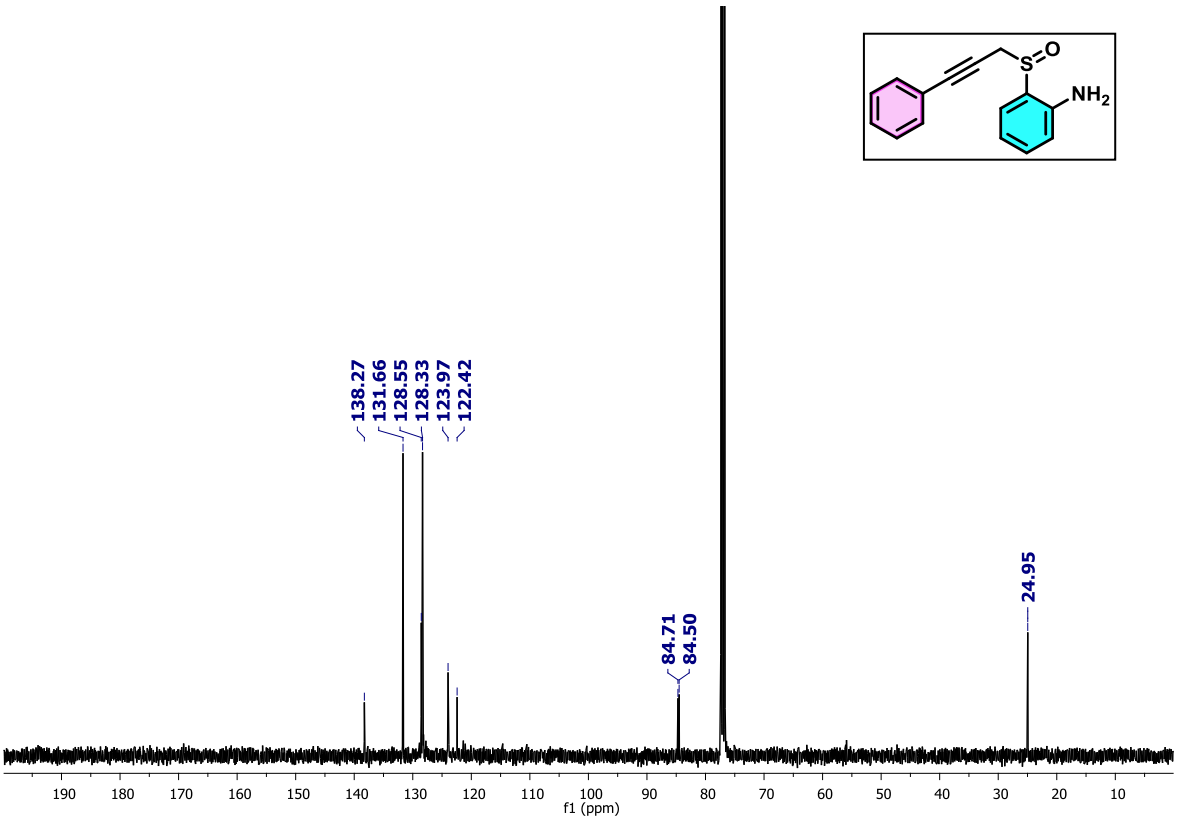
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **12a**



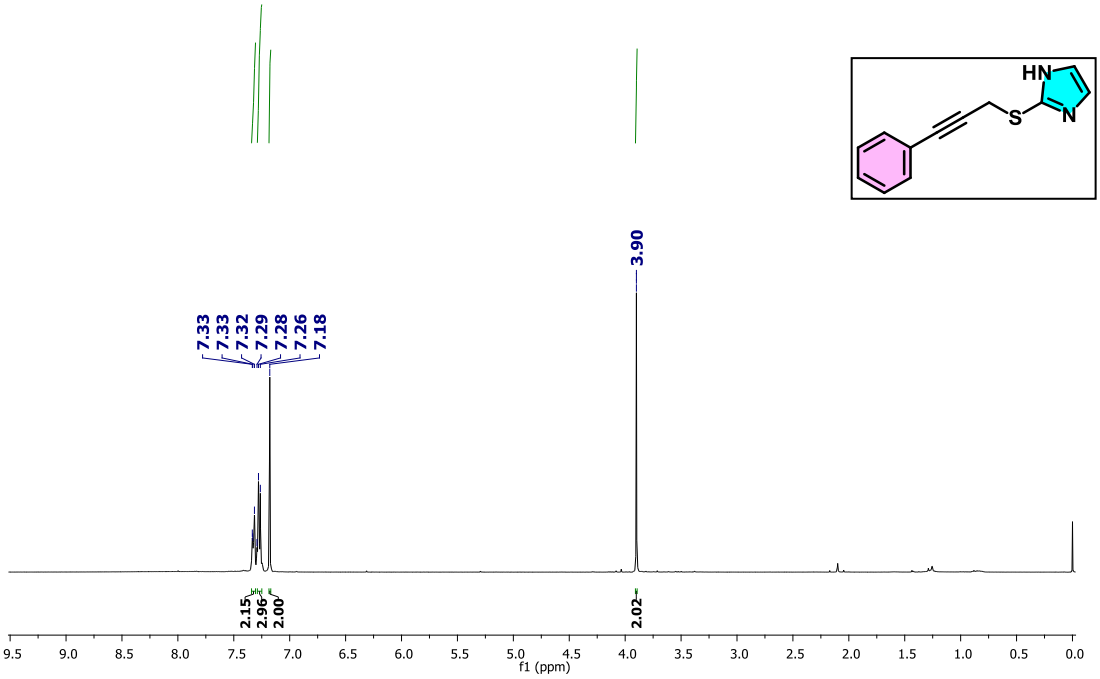
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **13a**



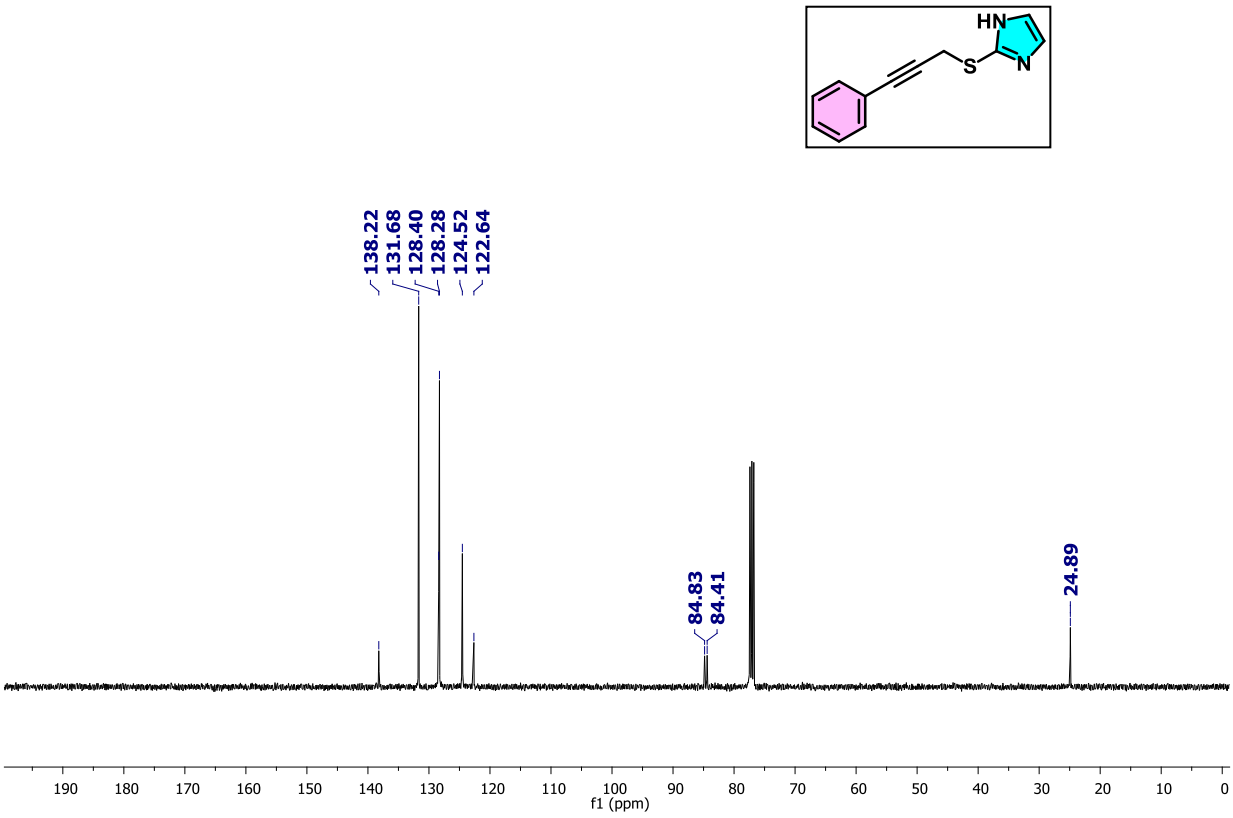
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **13a**



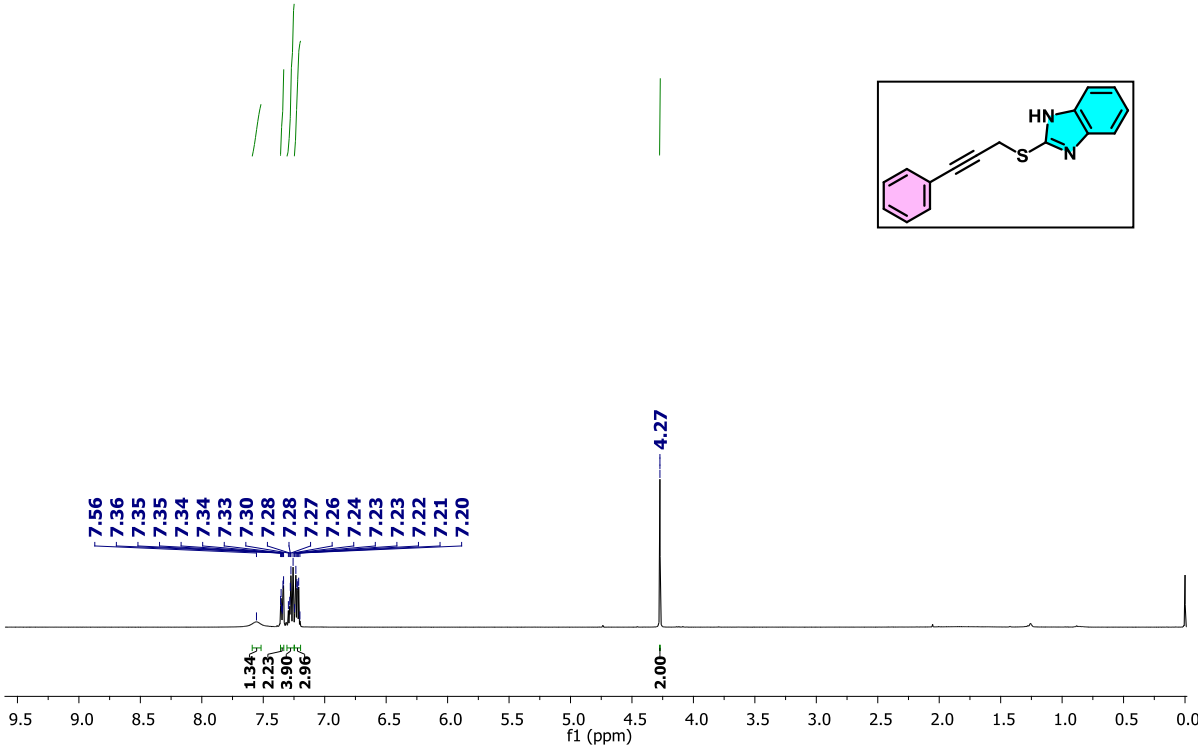
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **14a**



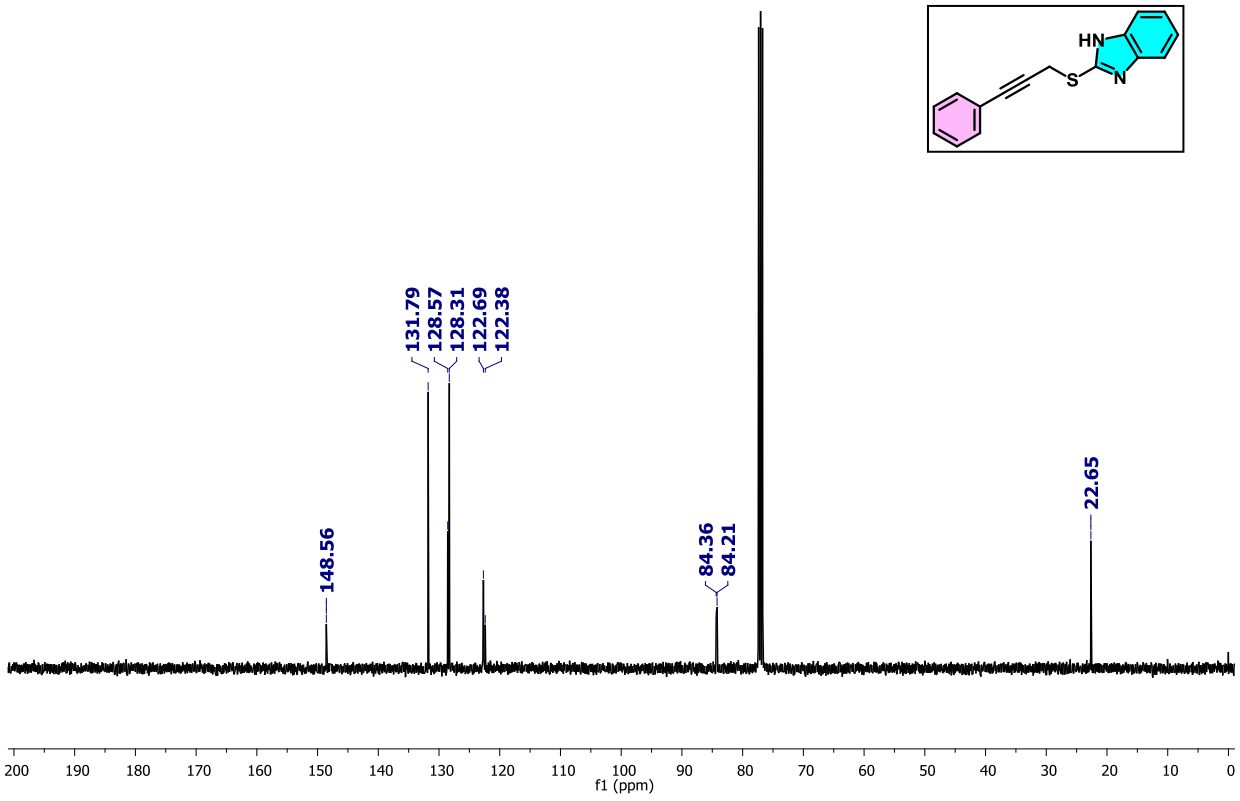
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) of Compound **14a**



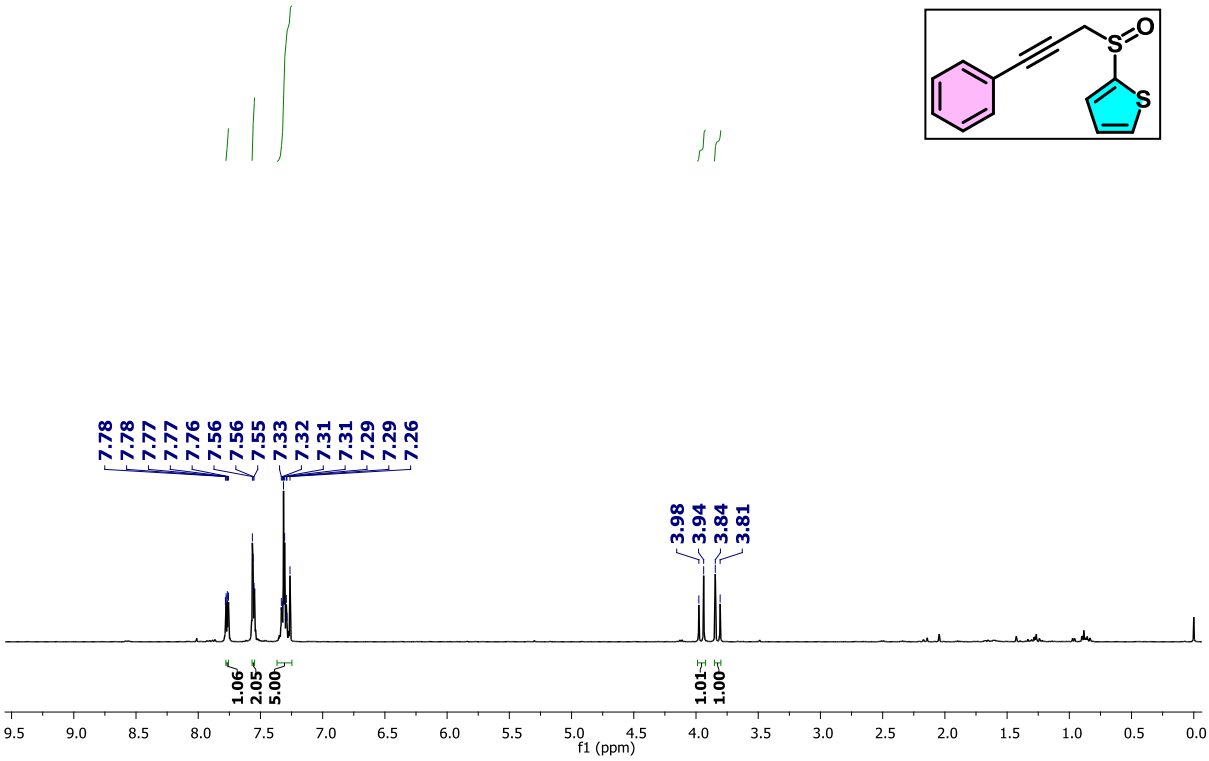
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **15a**



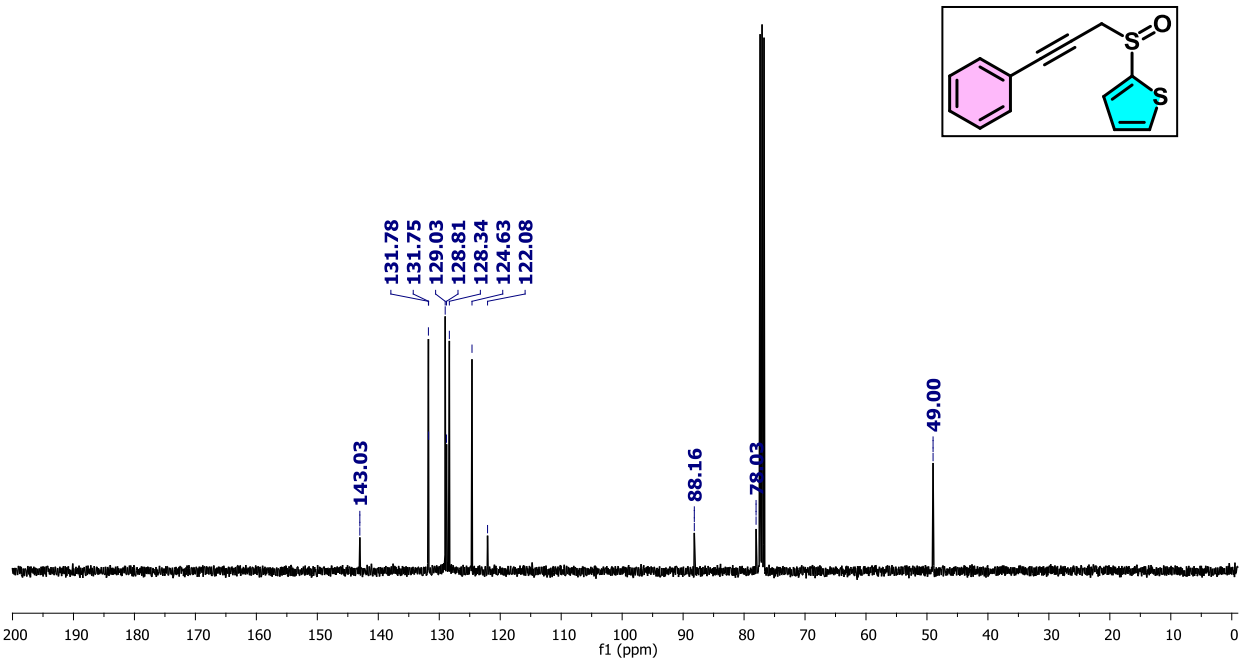
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **15a**



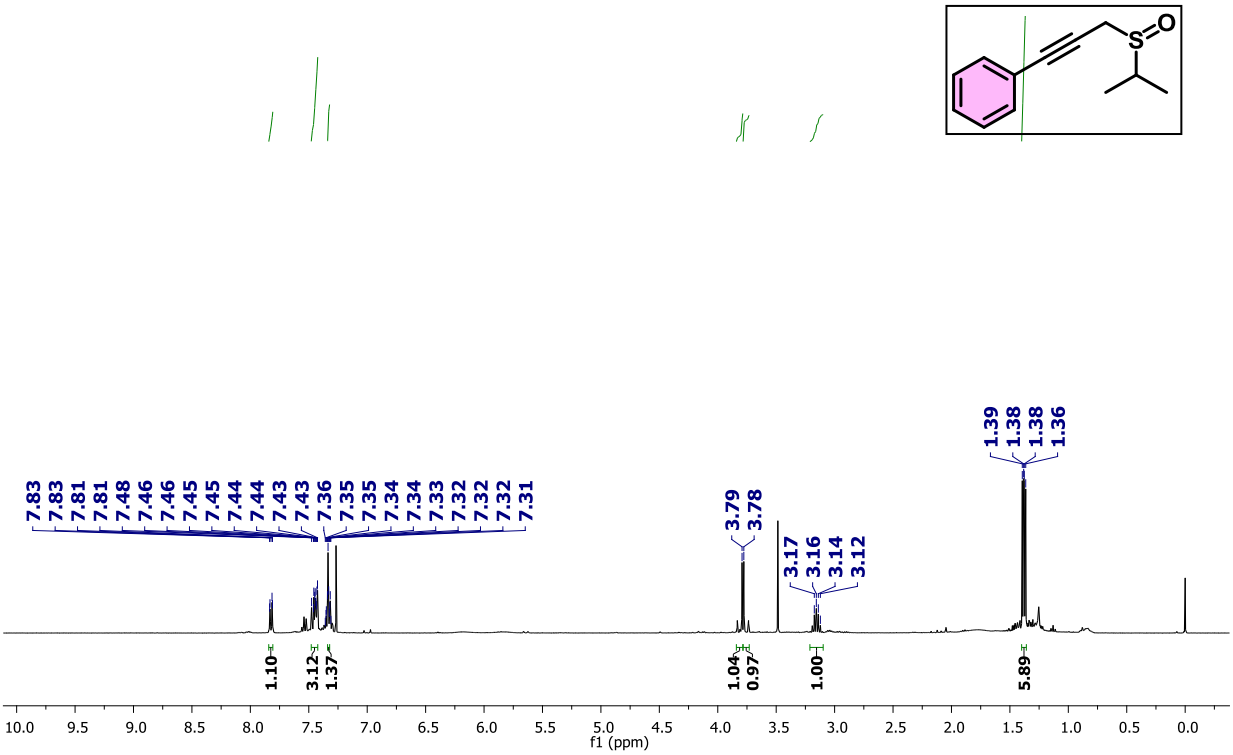
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **16a**



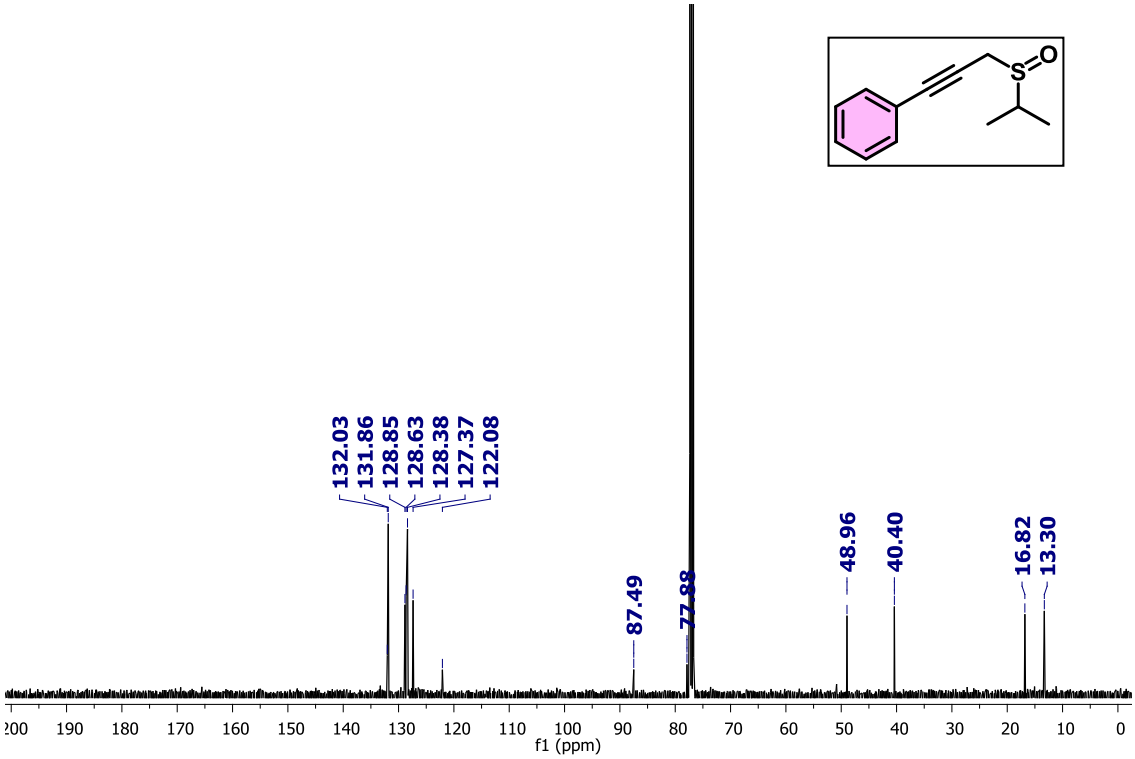
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **16a**



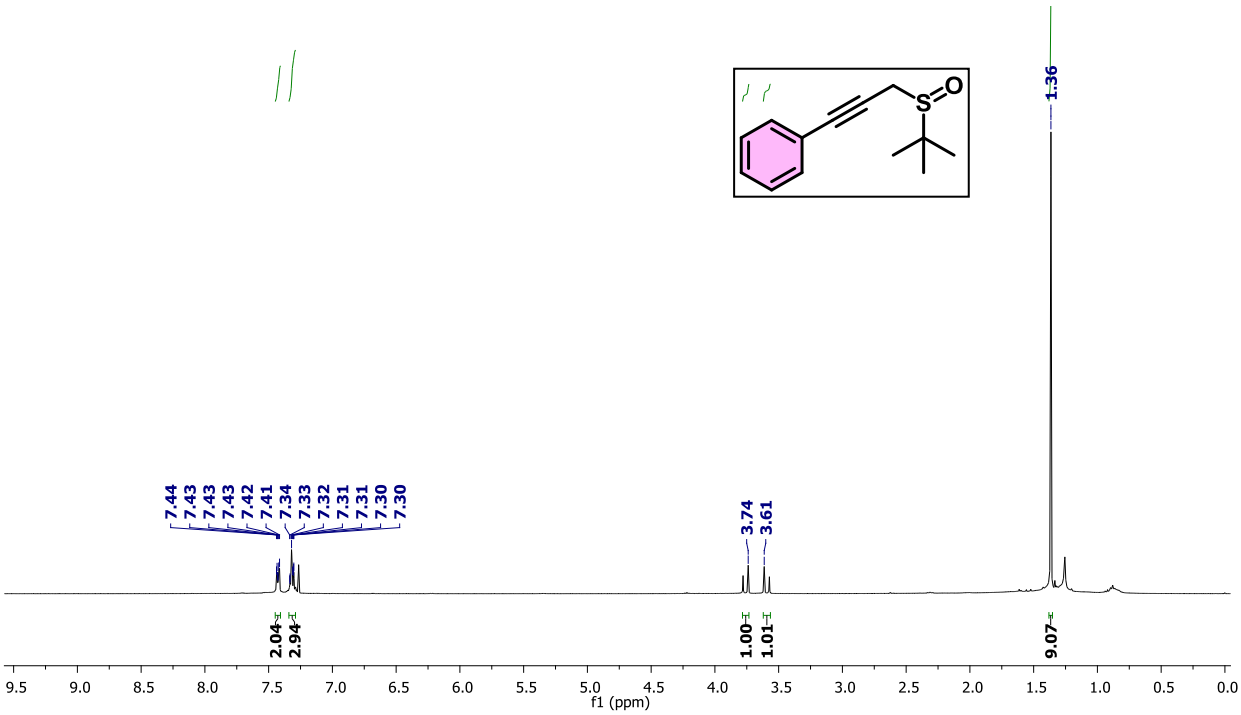
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **17a**



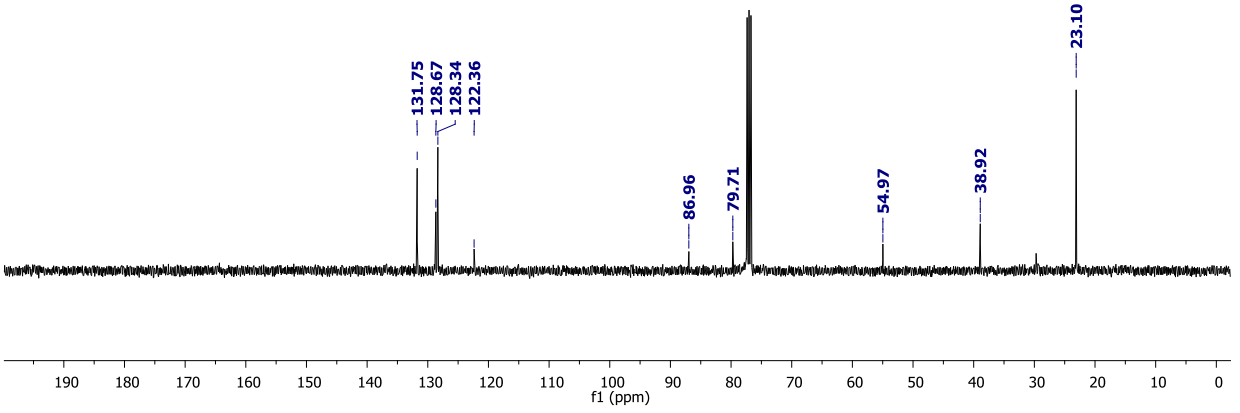
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **17a**



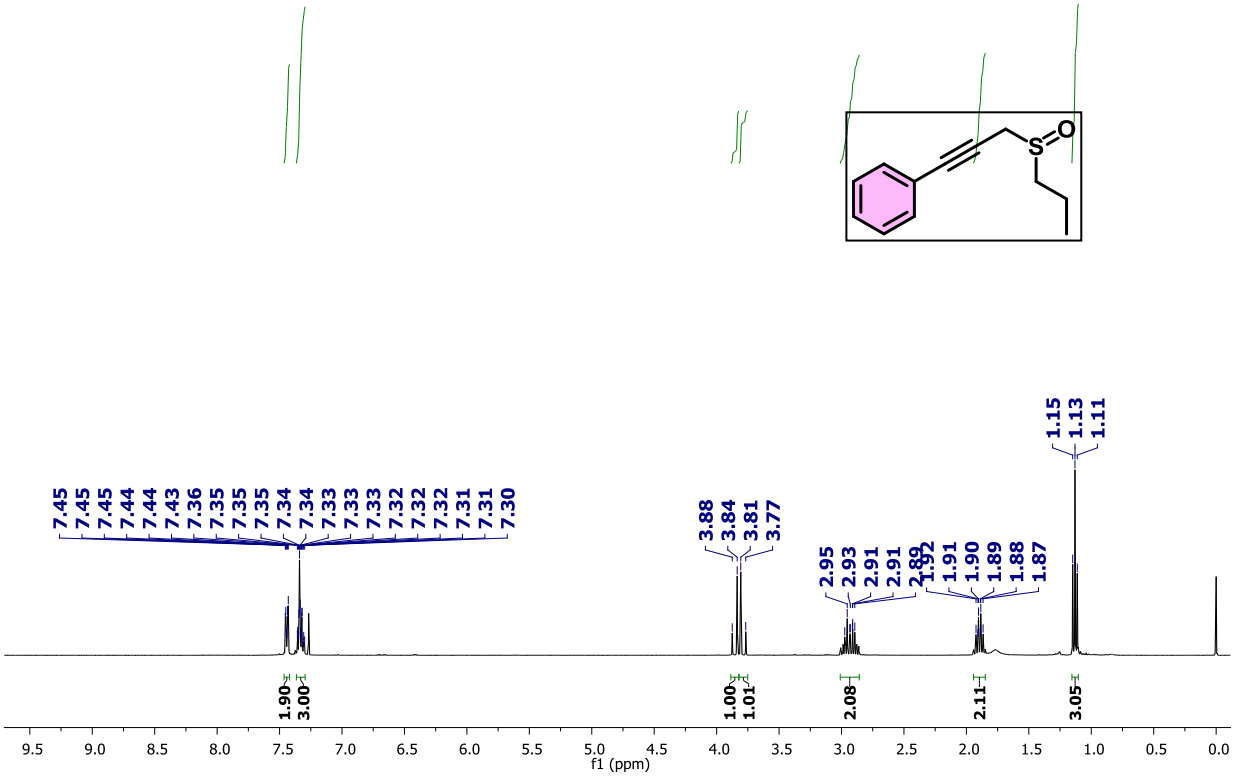
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **18a**



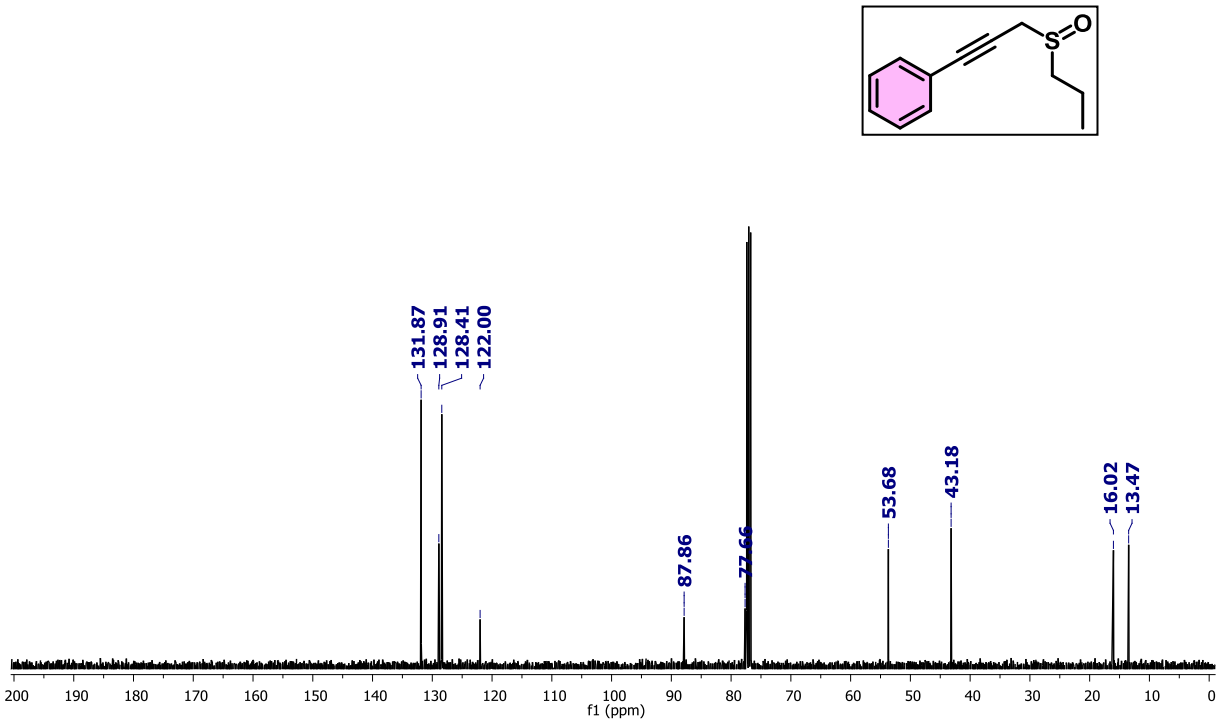
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **18a**



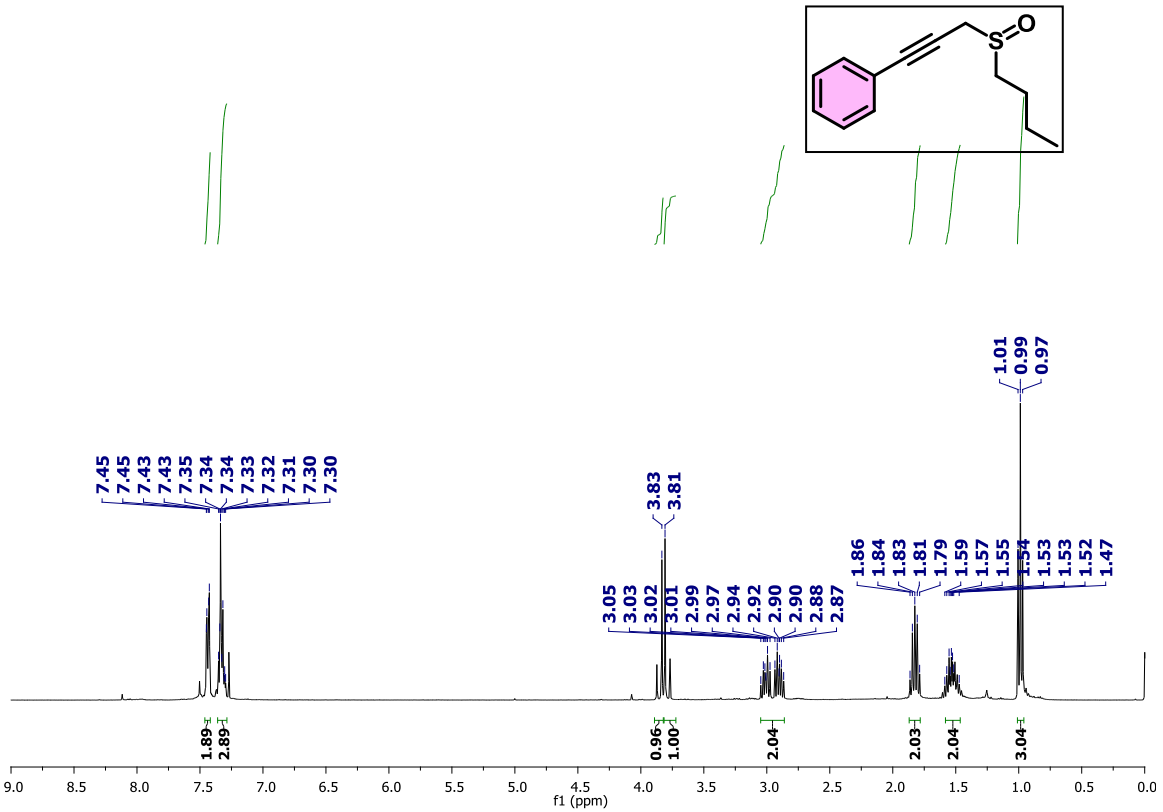
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **19a**



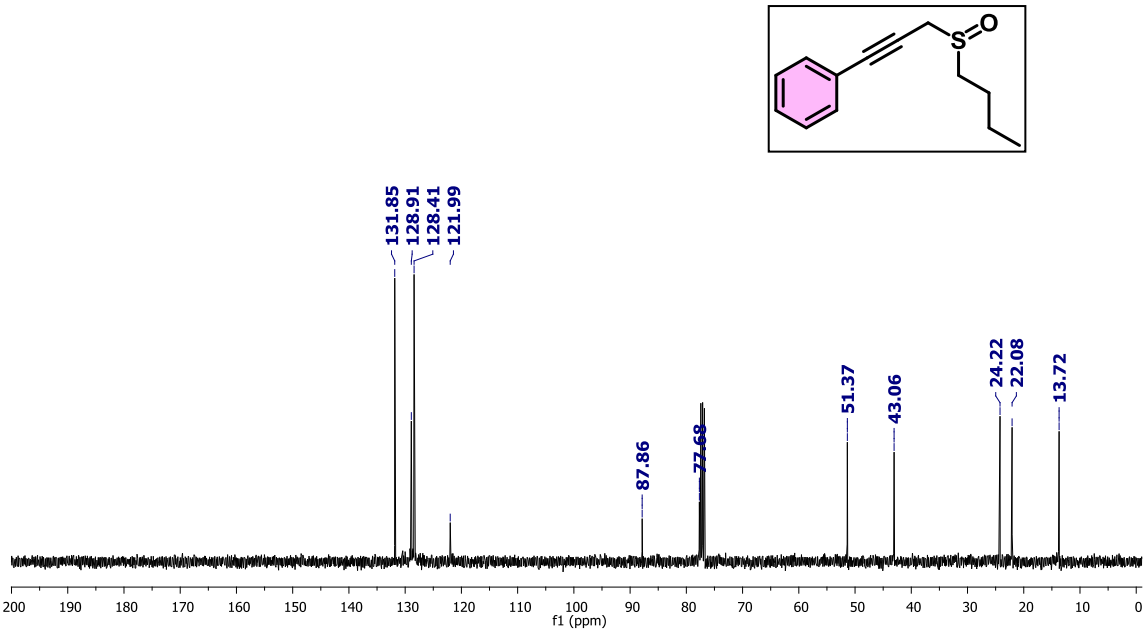
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **19a**



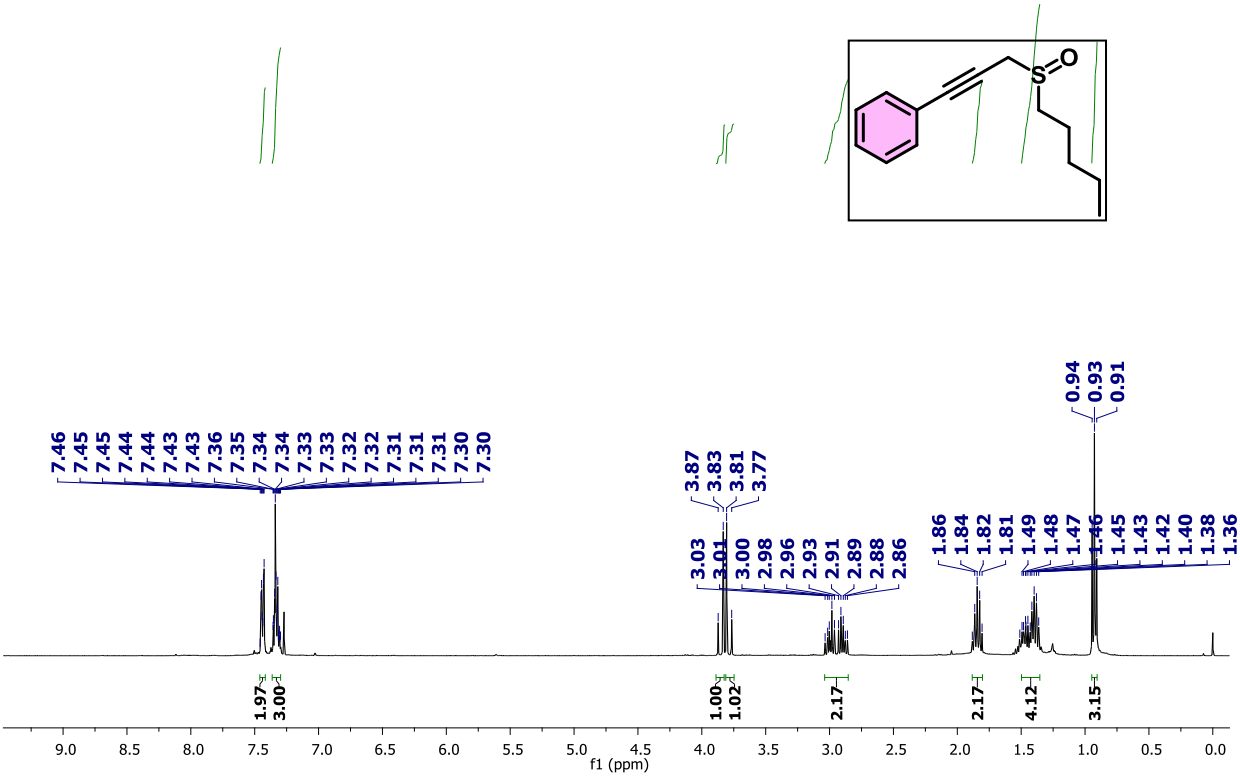
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **20a**



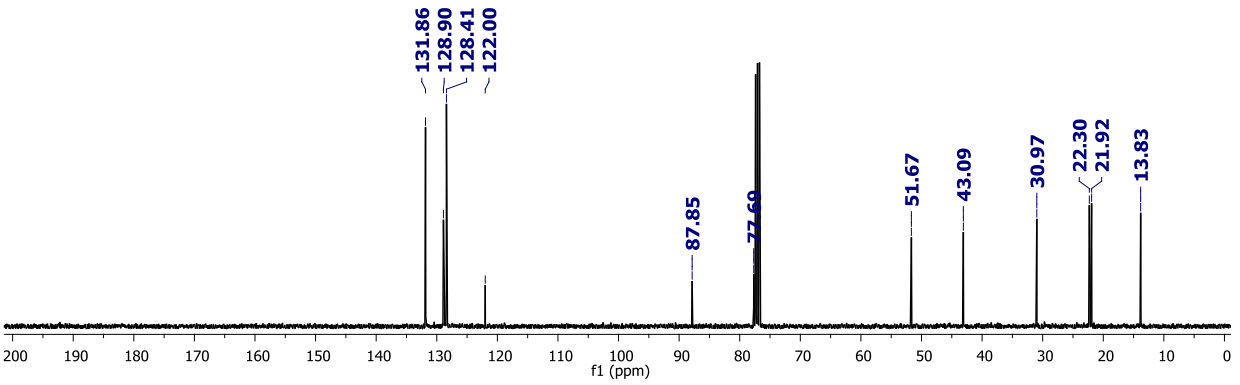
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **20a**



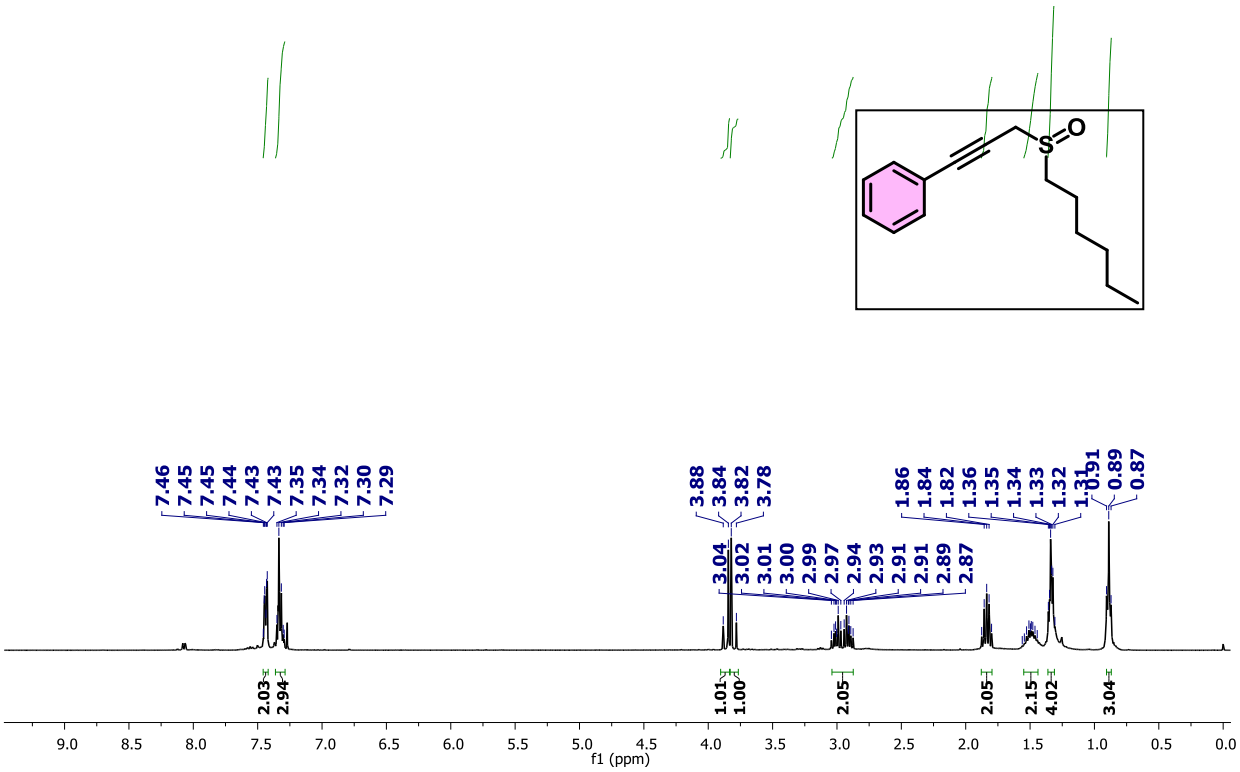
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **21a**



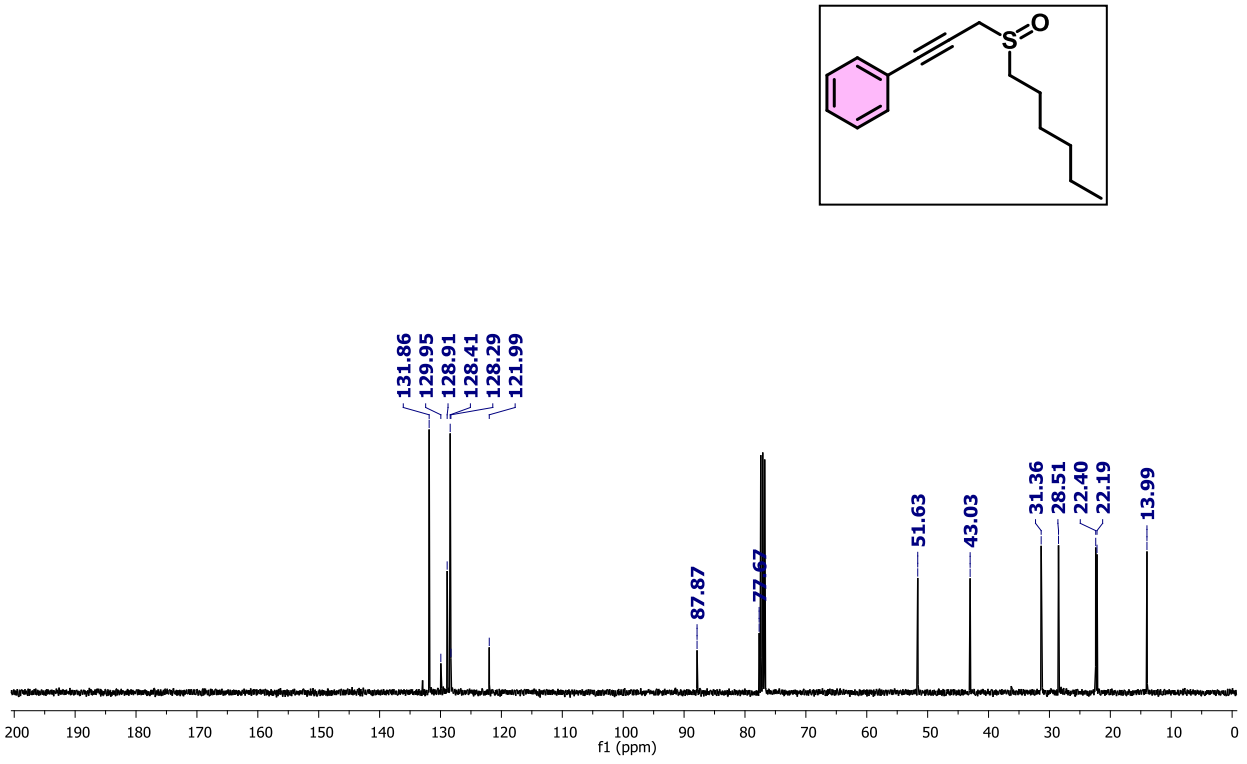
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **21a**



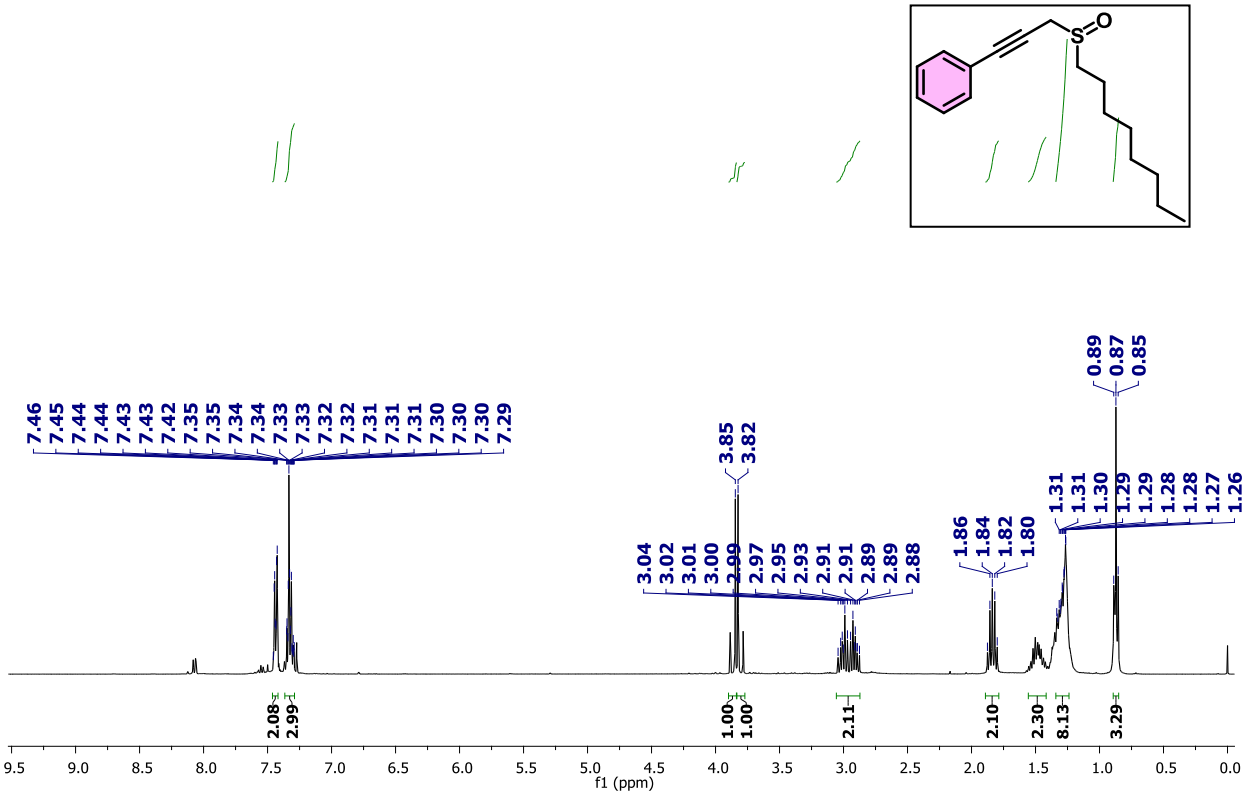
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **22a**



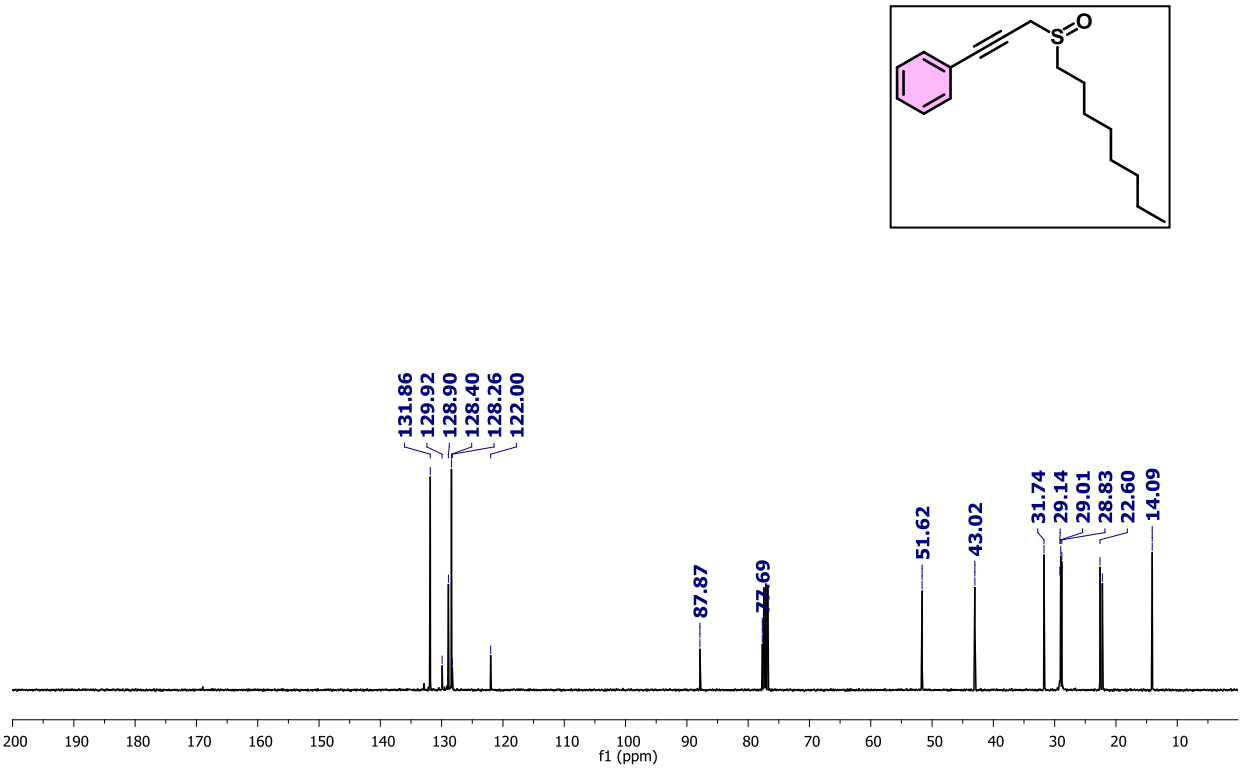
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **22a**



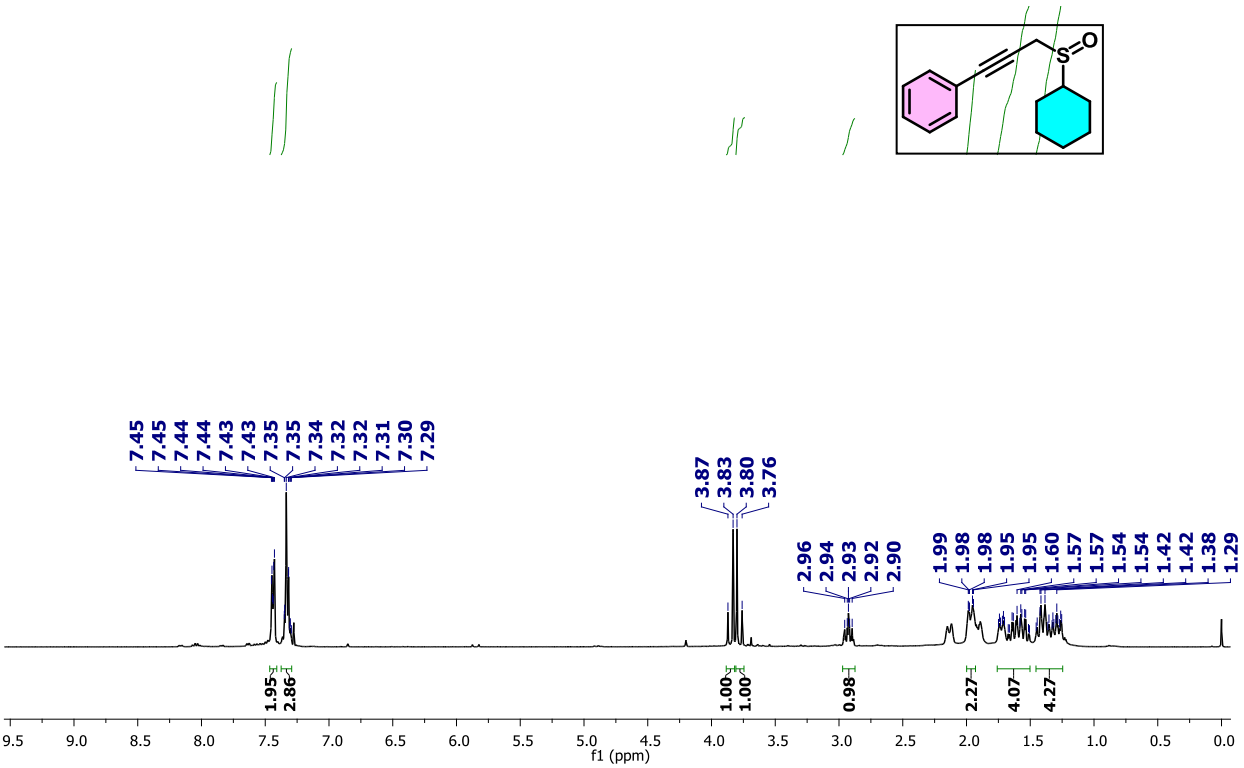
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **23a**



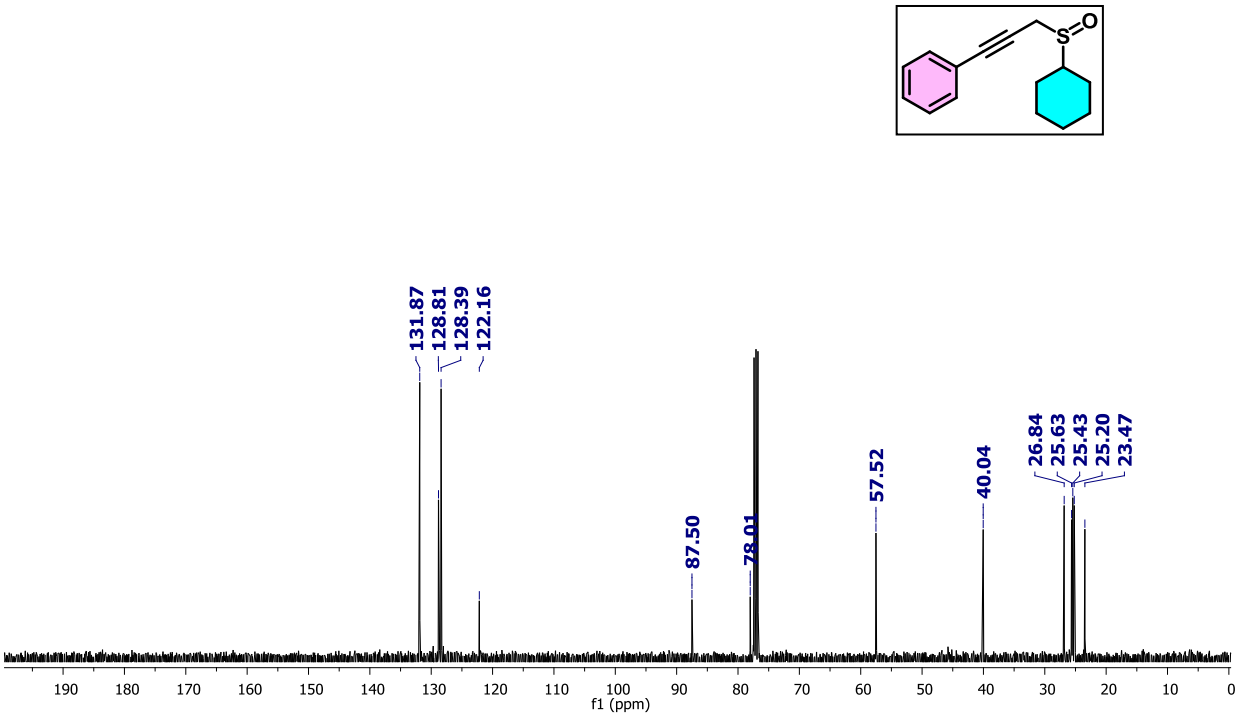
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **23a**



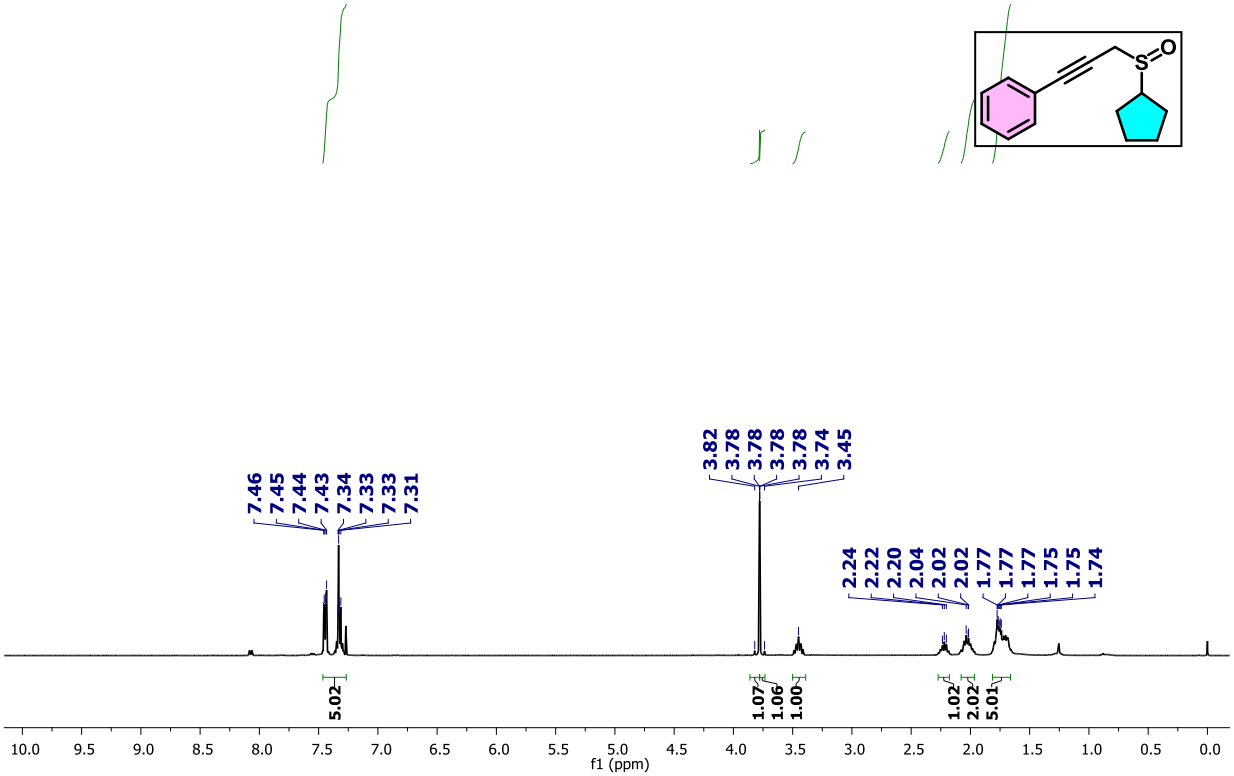
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **24a**



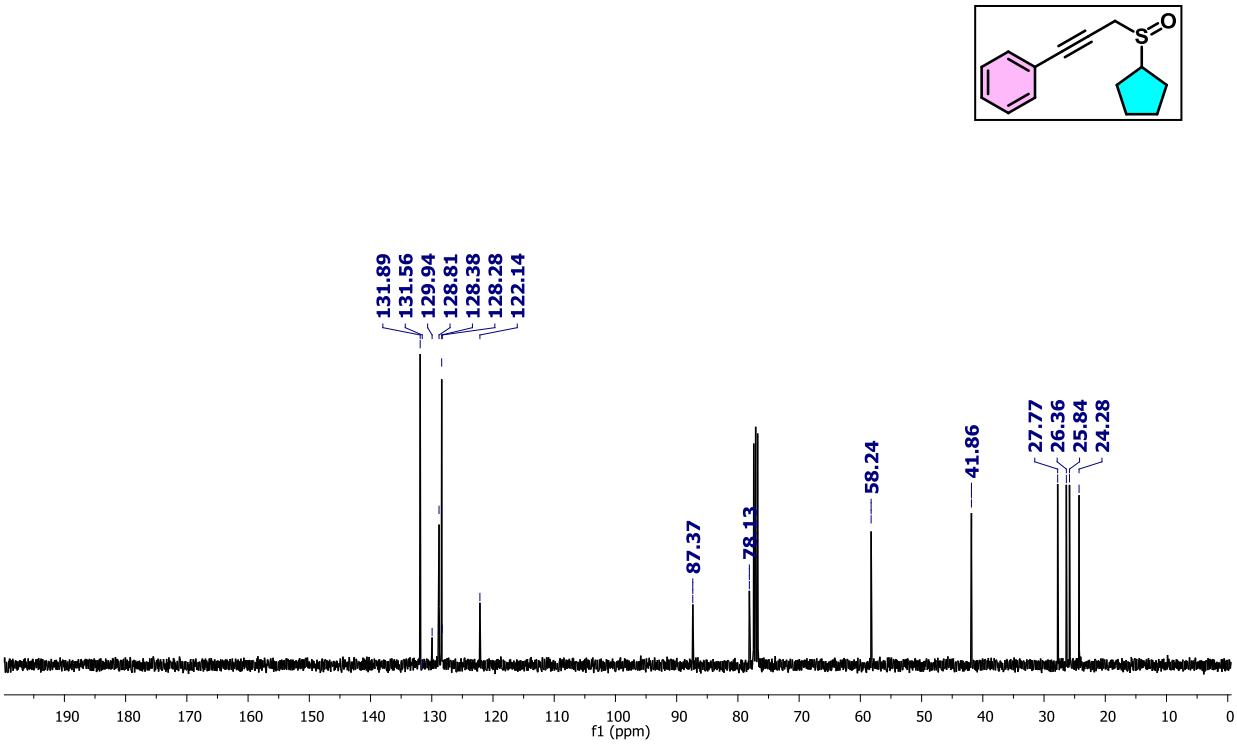
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **24a**



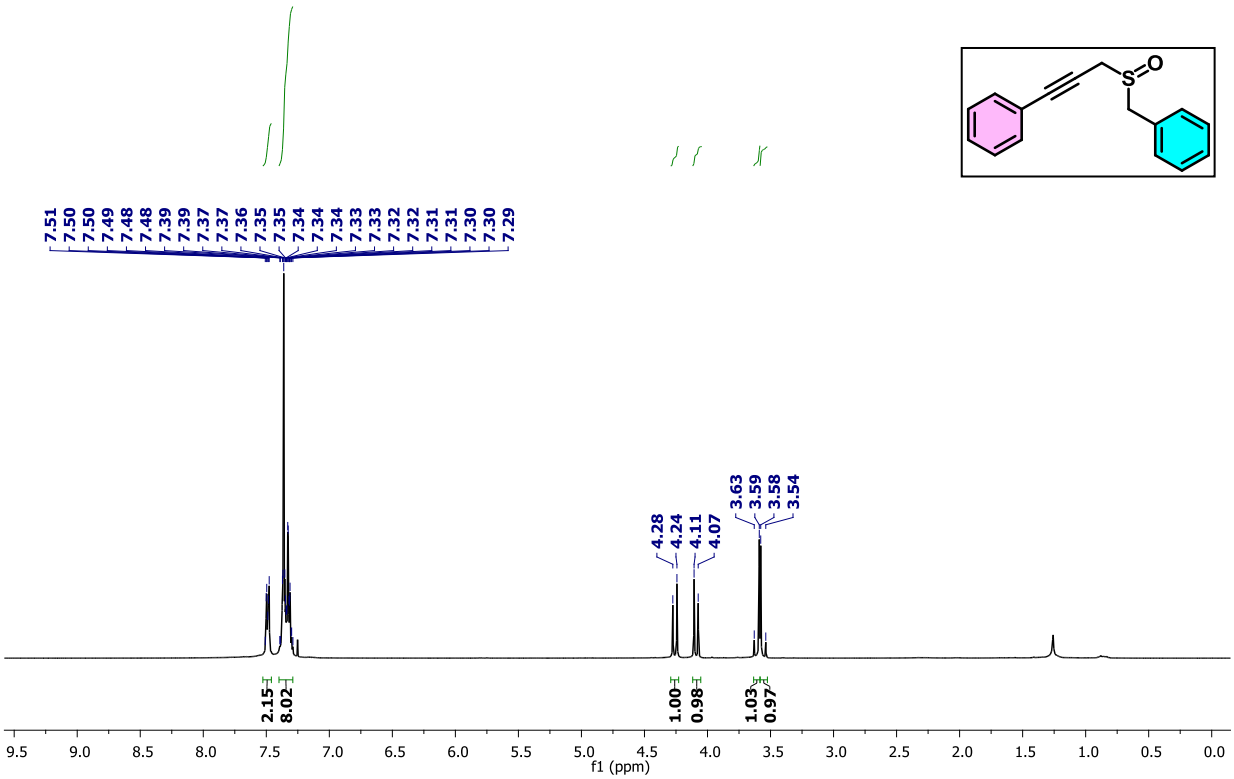
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **25a**



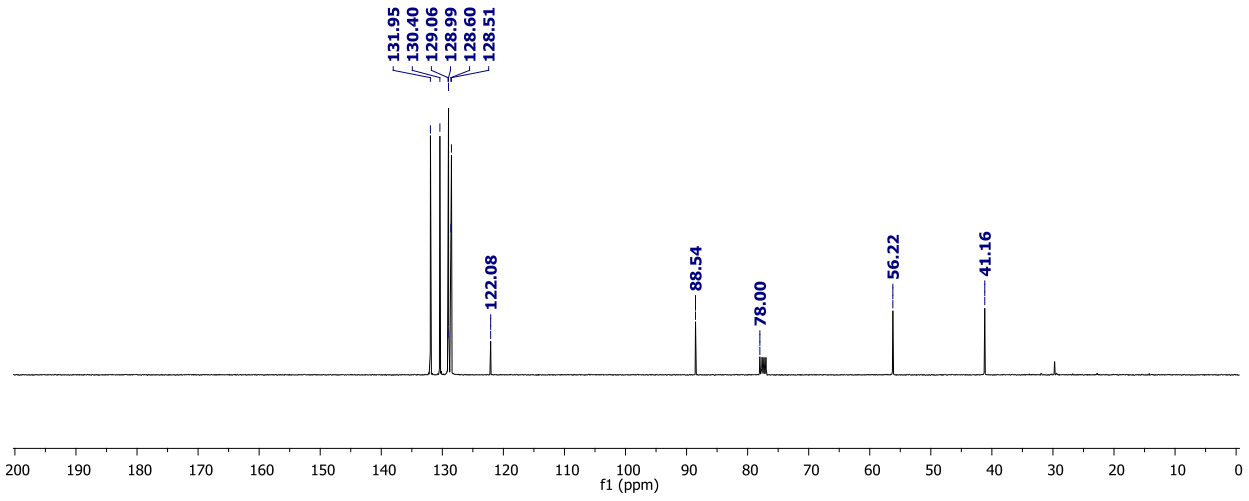
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **25a**



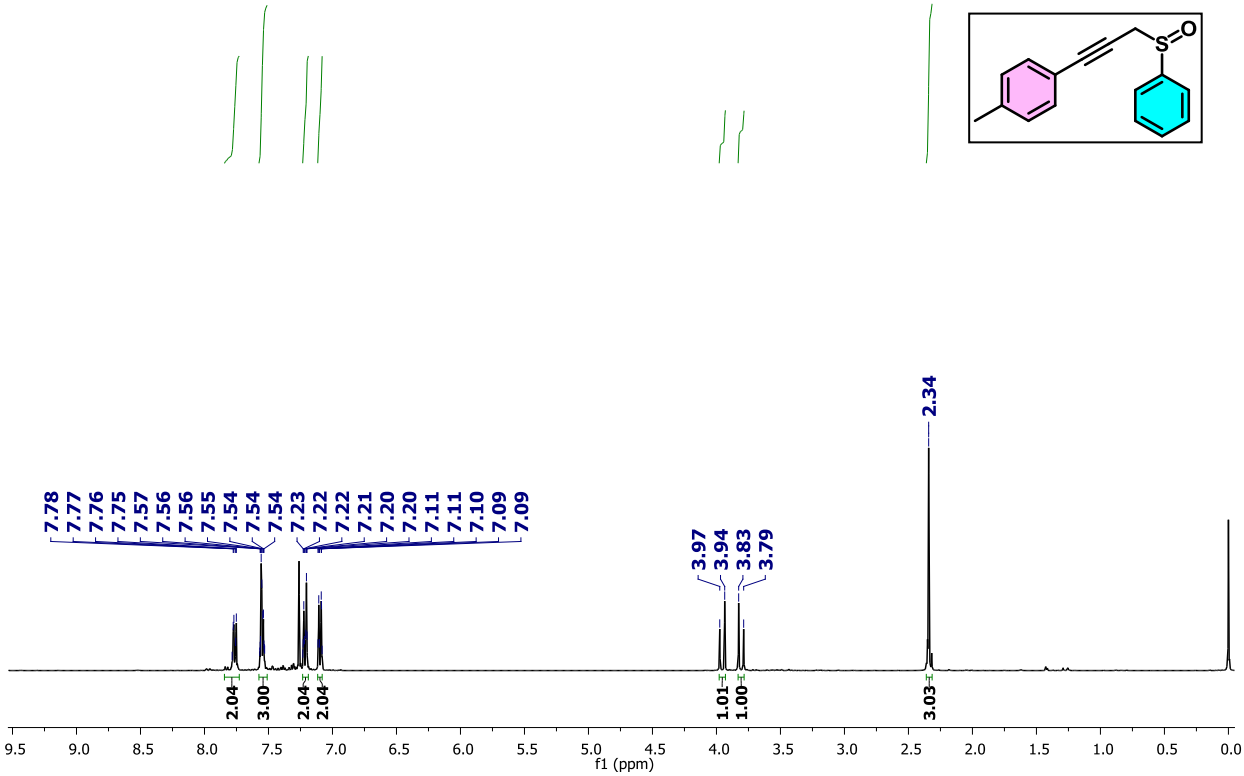
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **26a**



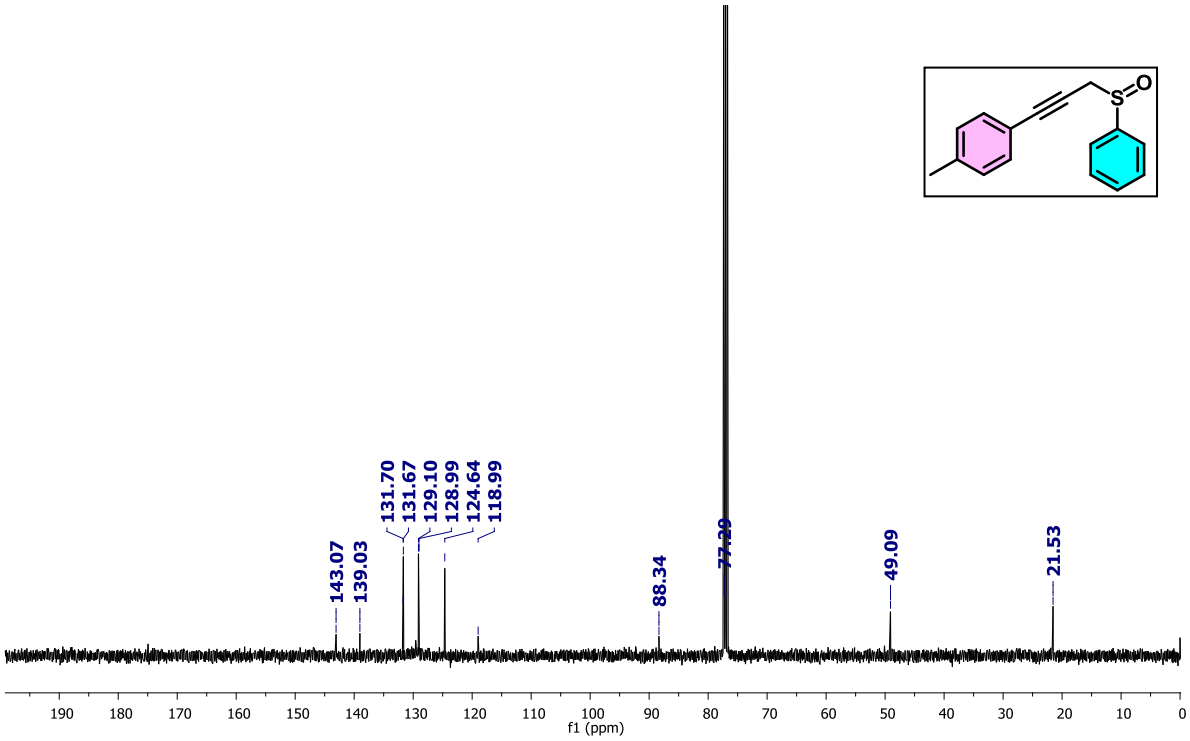
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **26a**



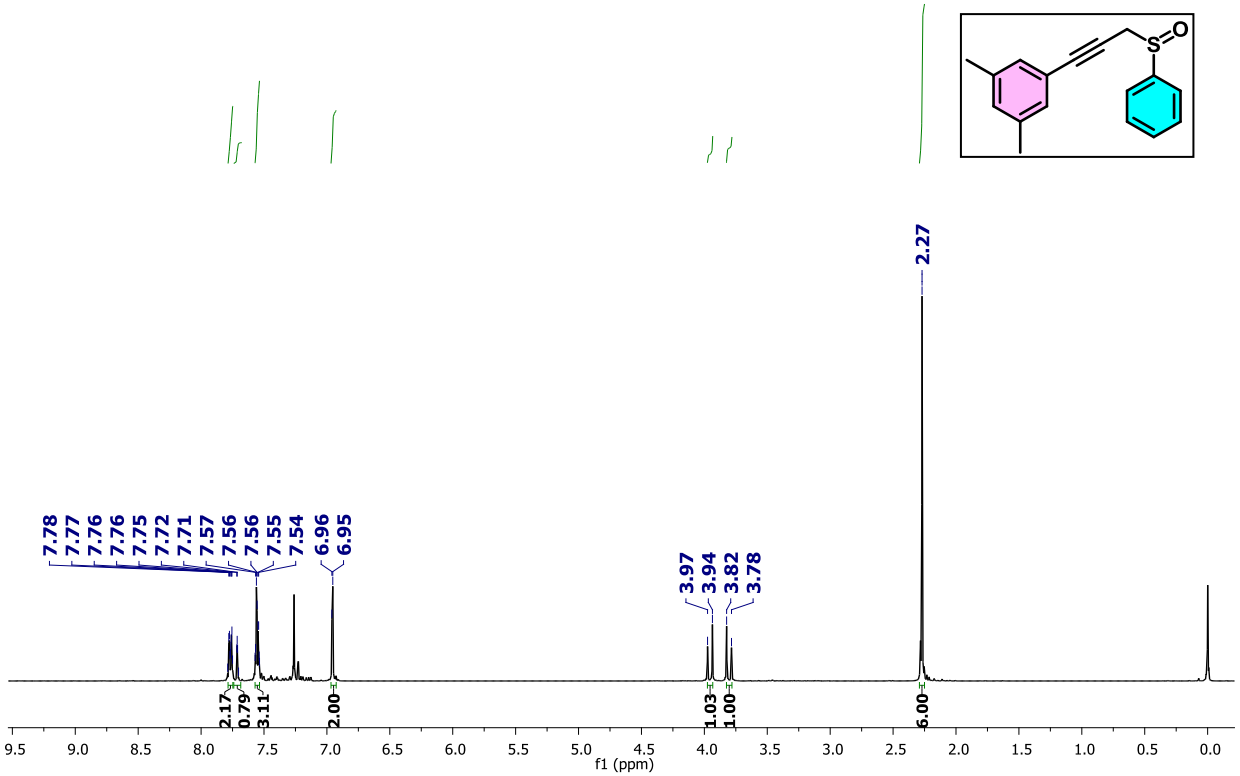
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **27a**



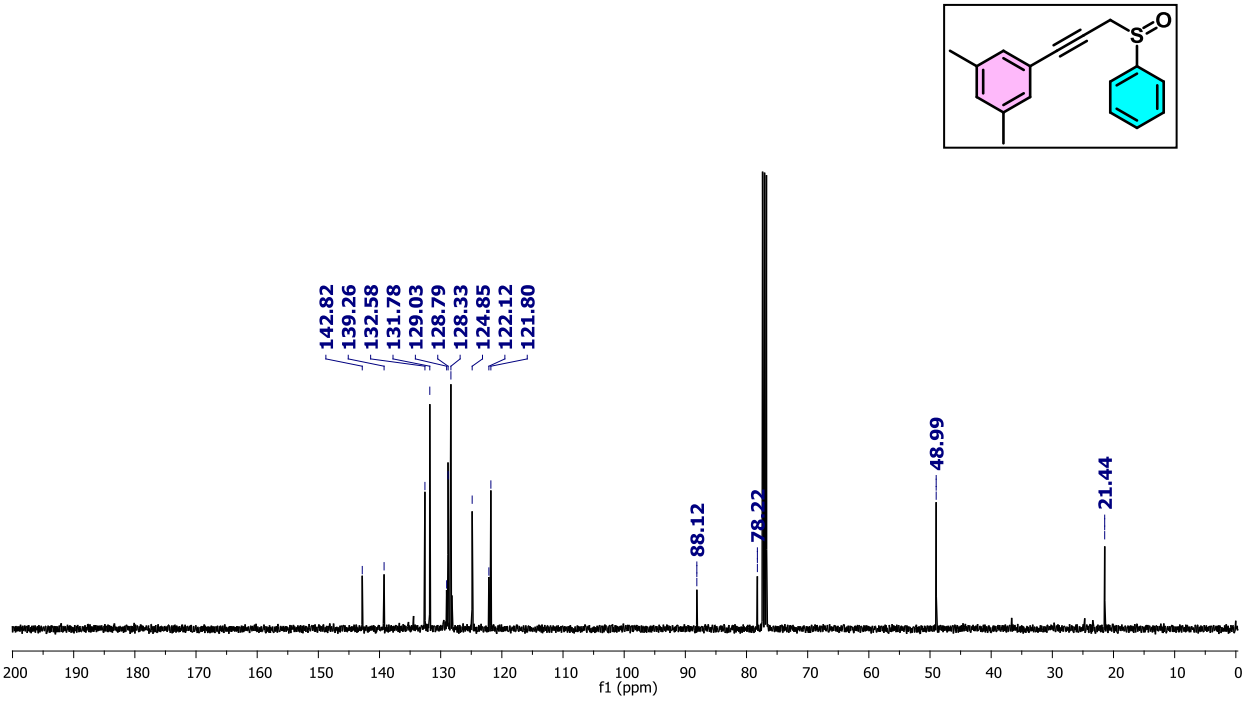
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **27a**



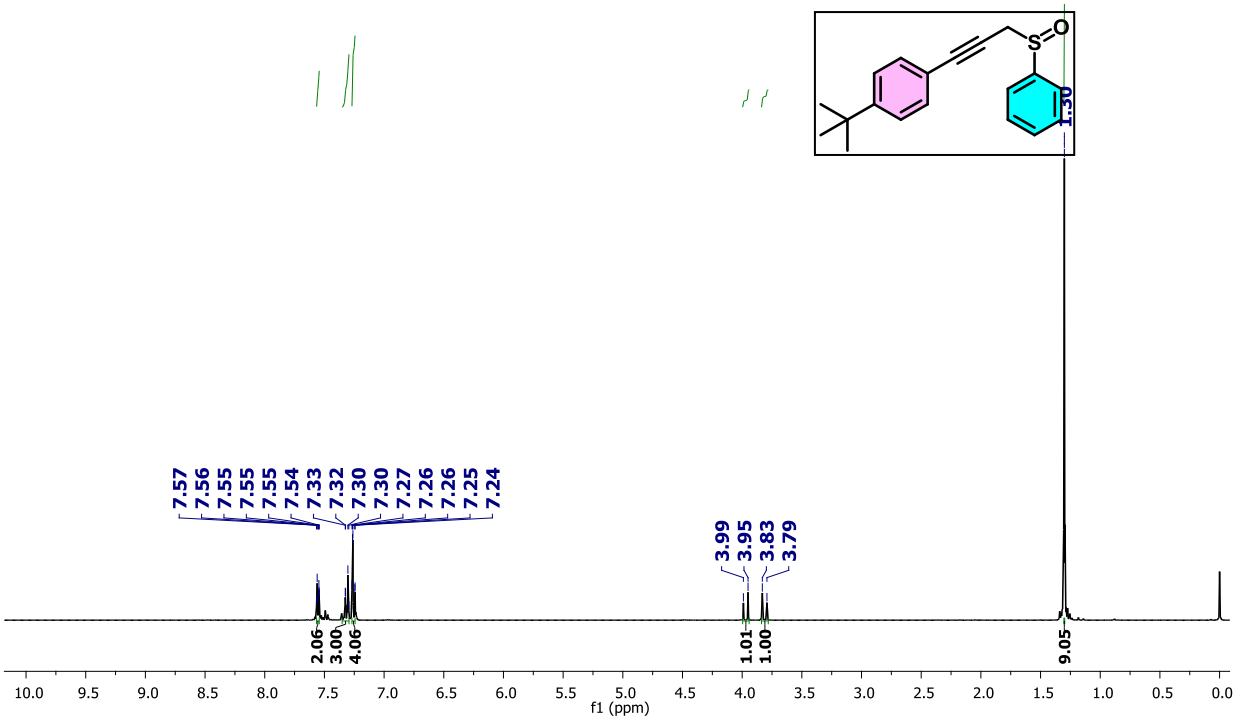
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **28a**



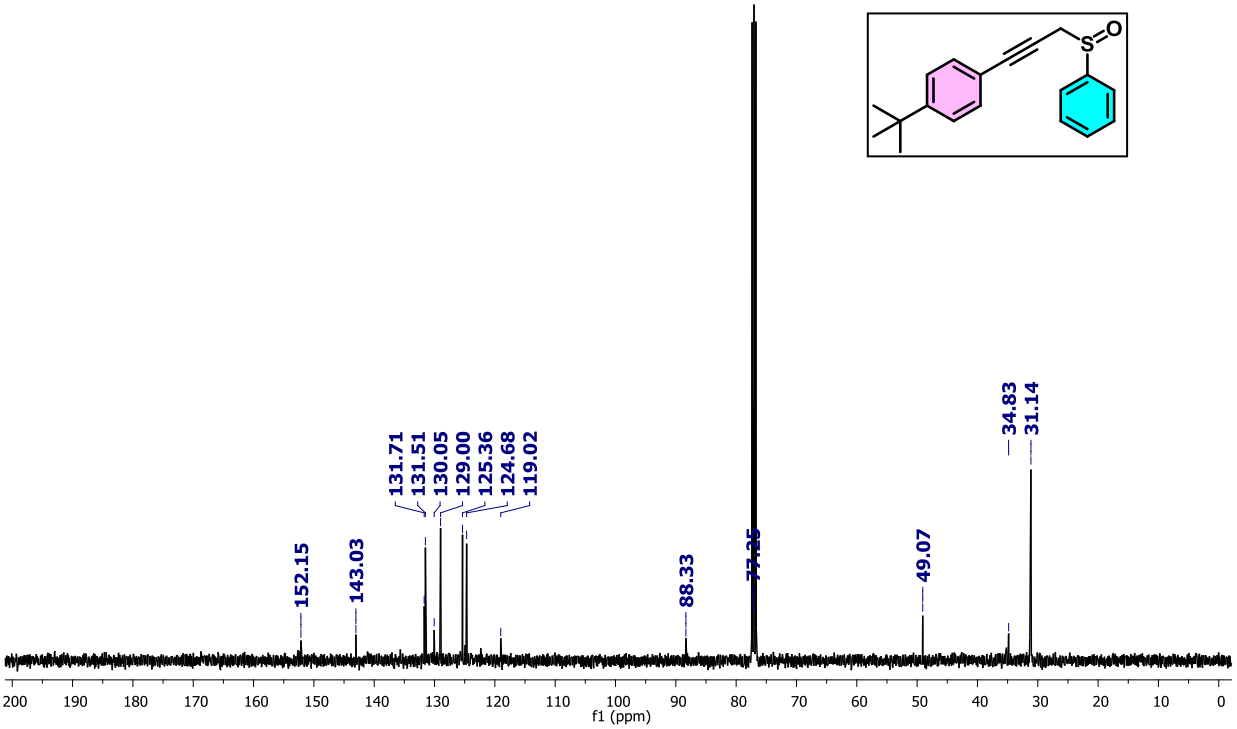
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **28a**



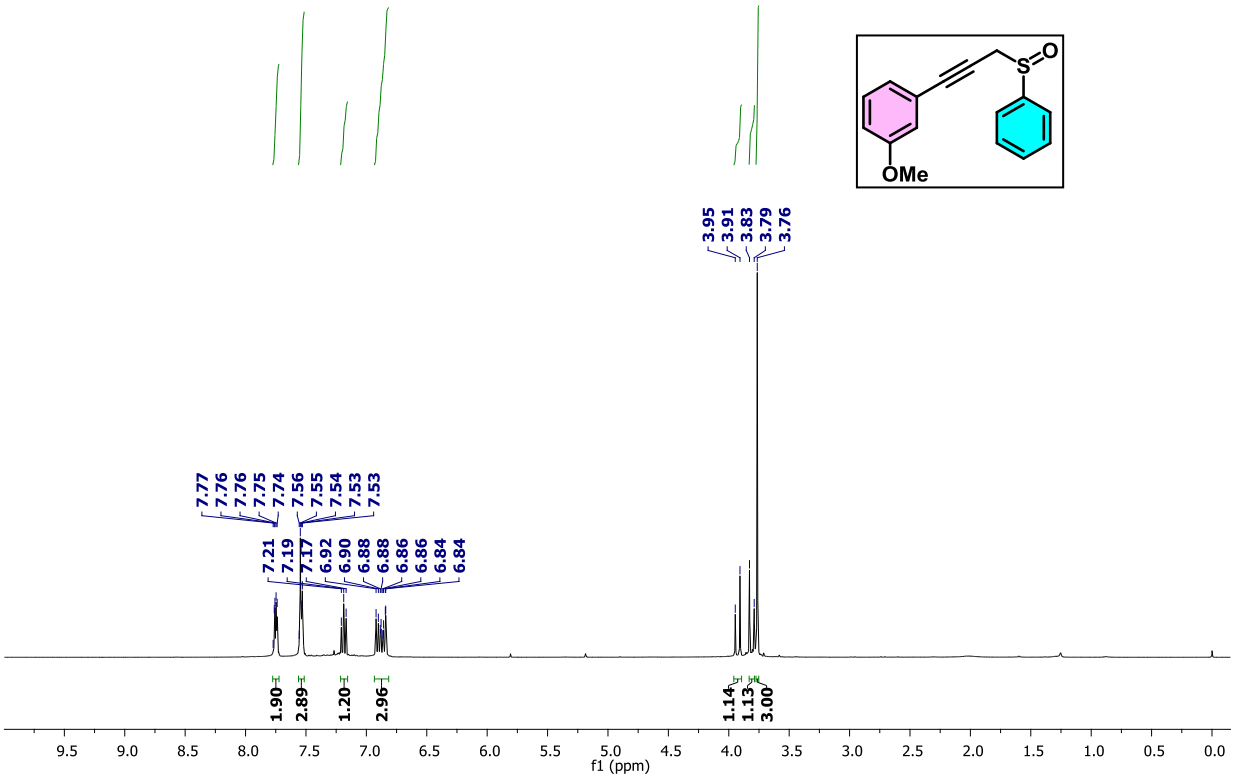
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **29a**



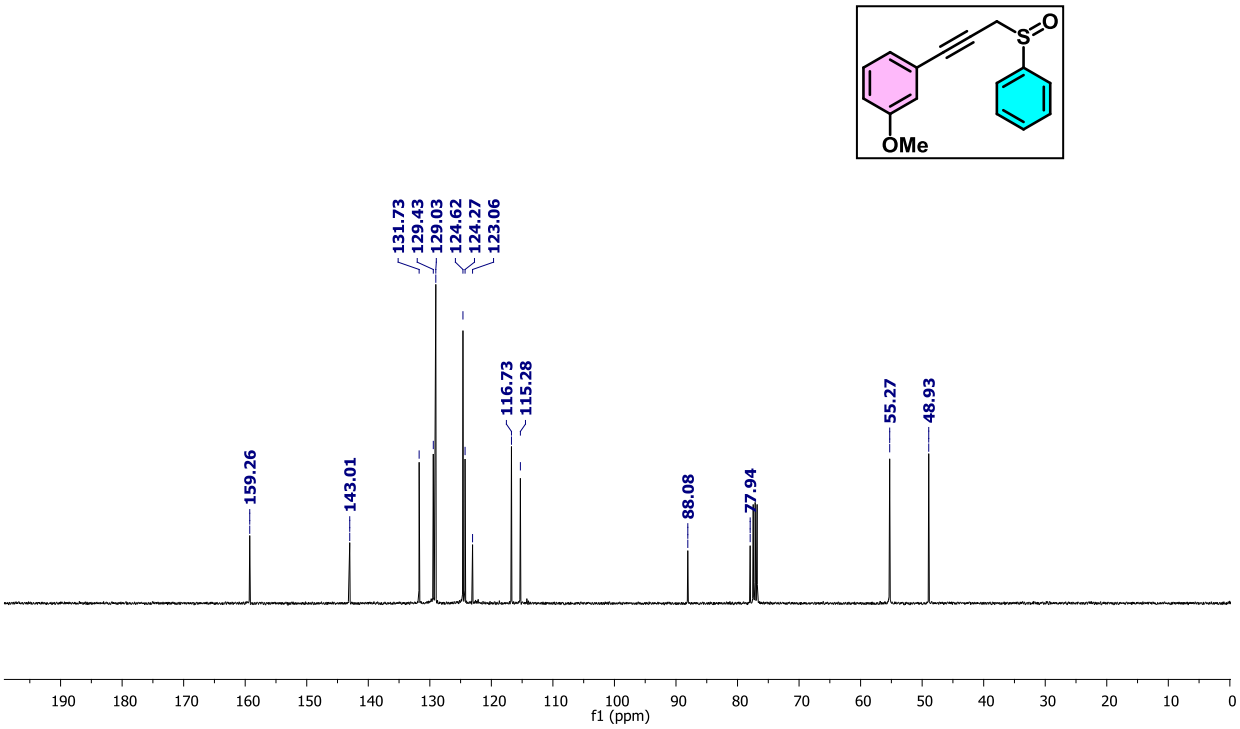
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **29a**



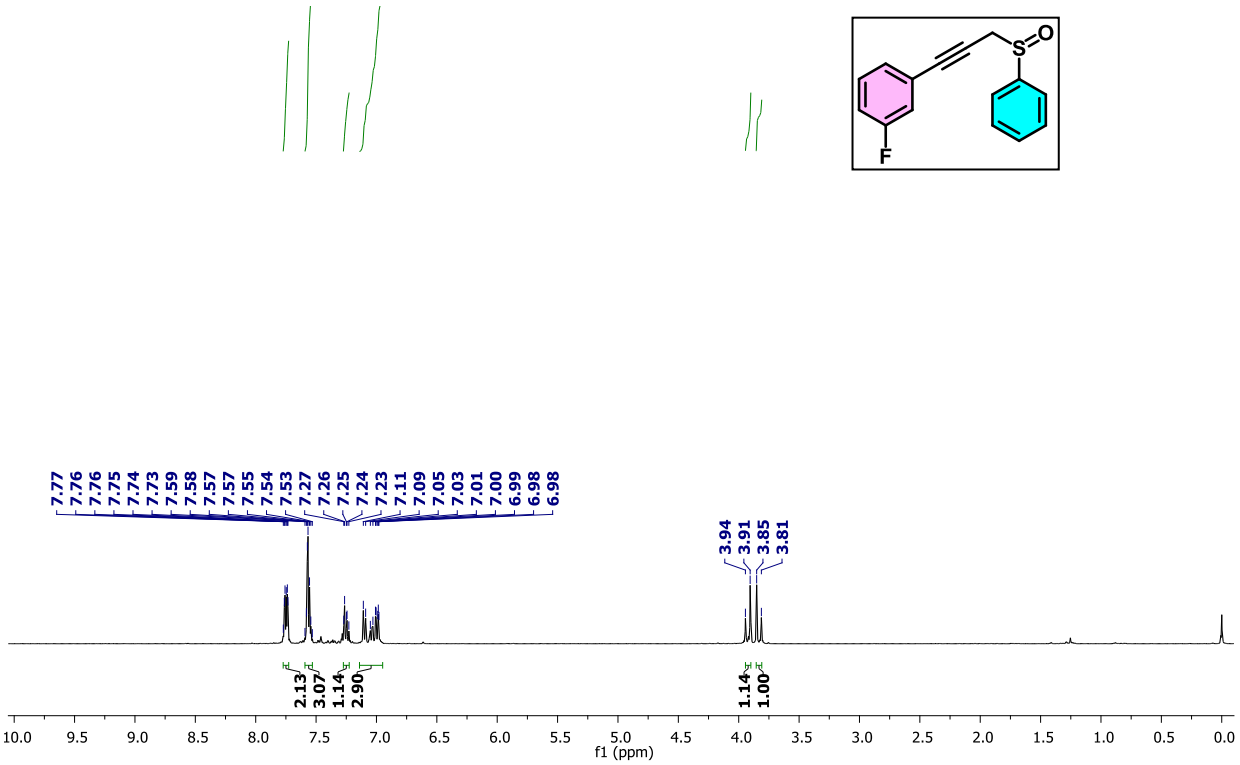
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **30a**



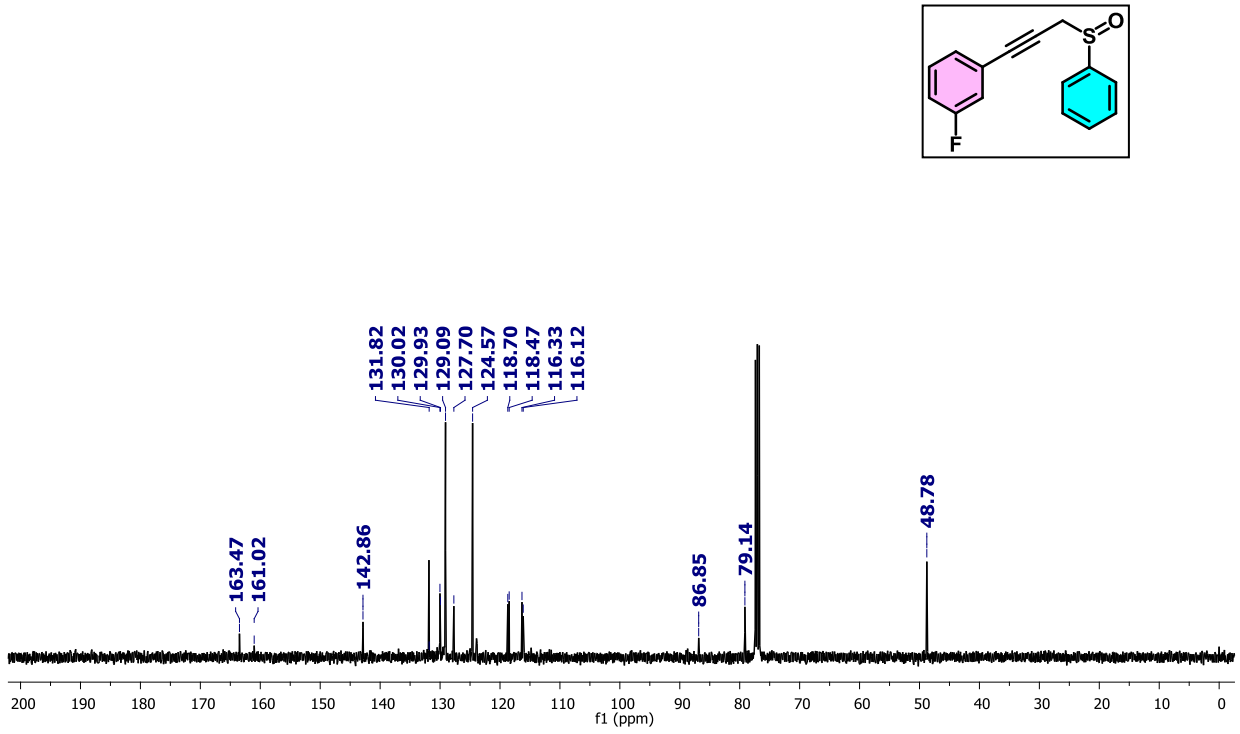
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **30a**



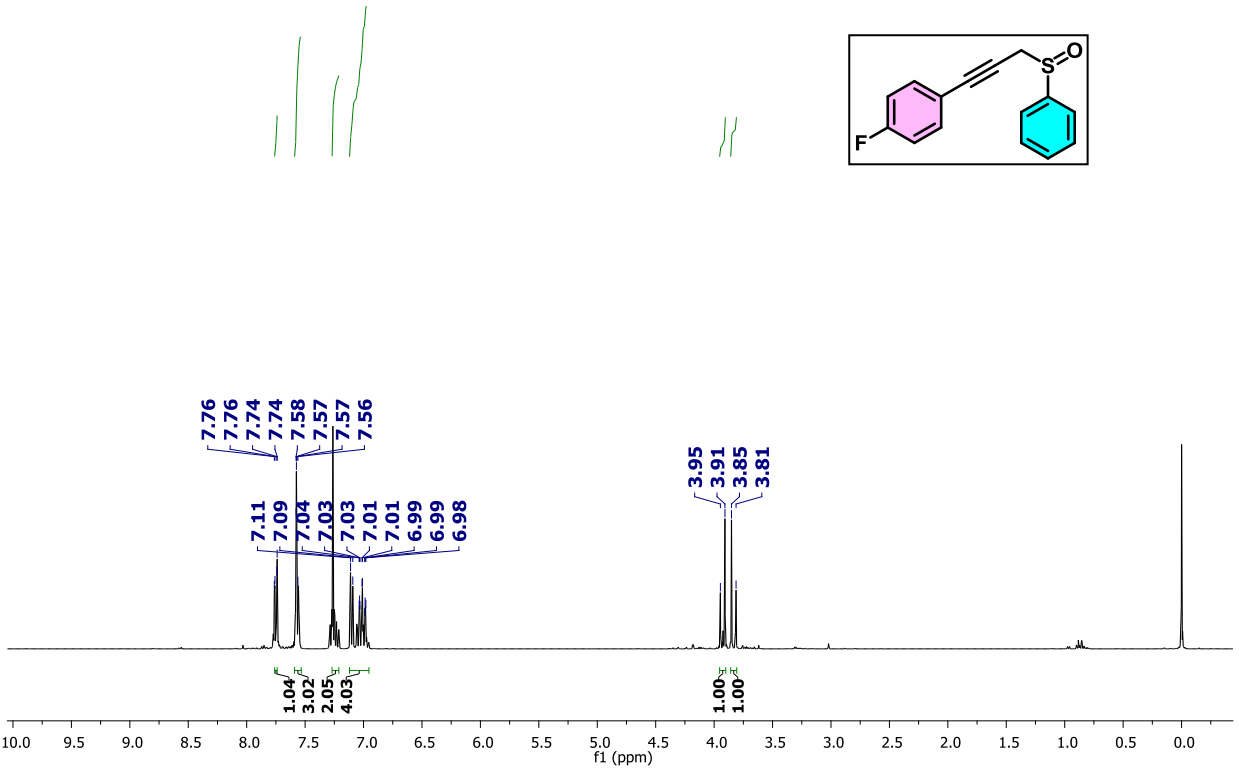
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **31a**



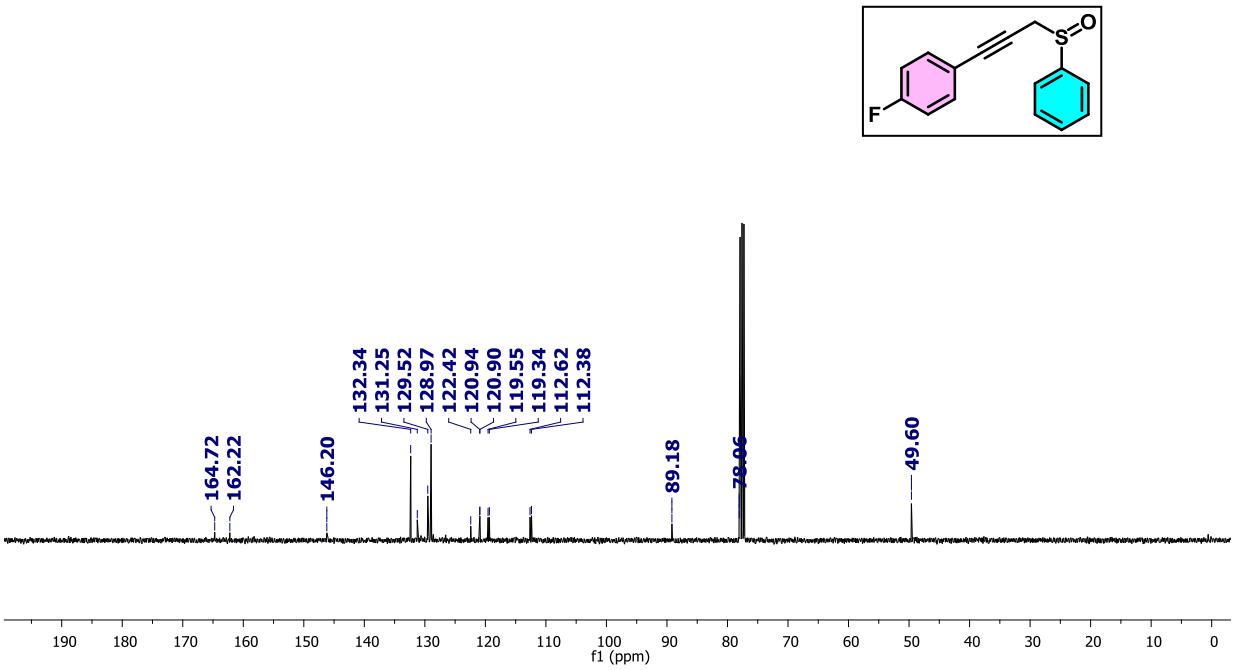
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **31a**



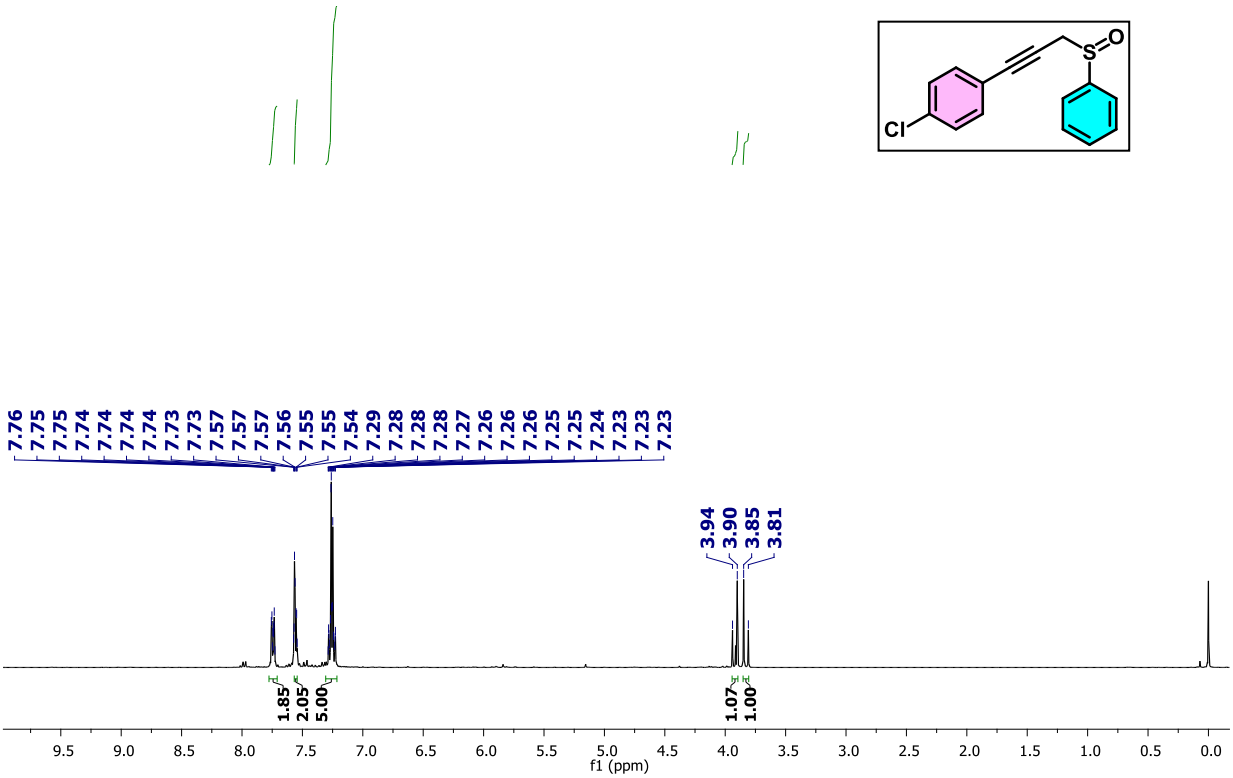
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **32a**



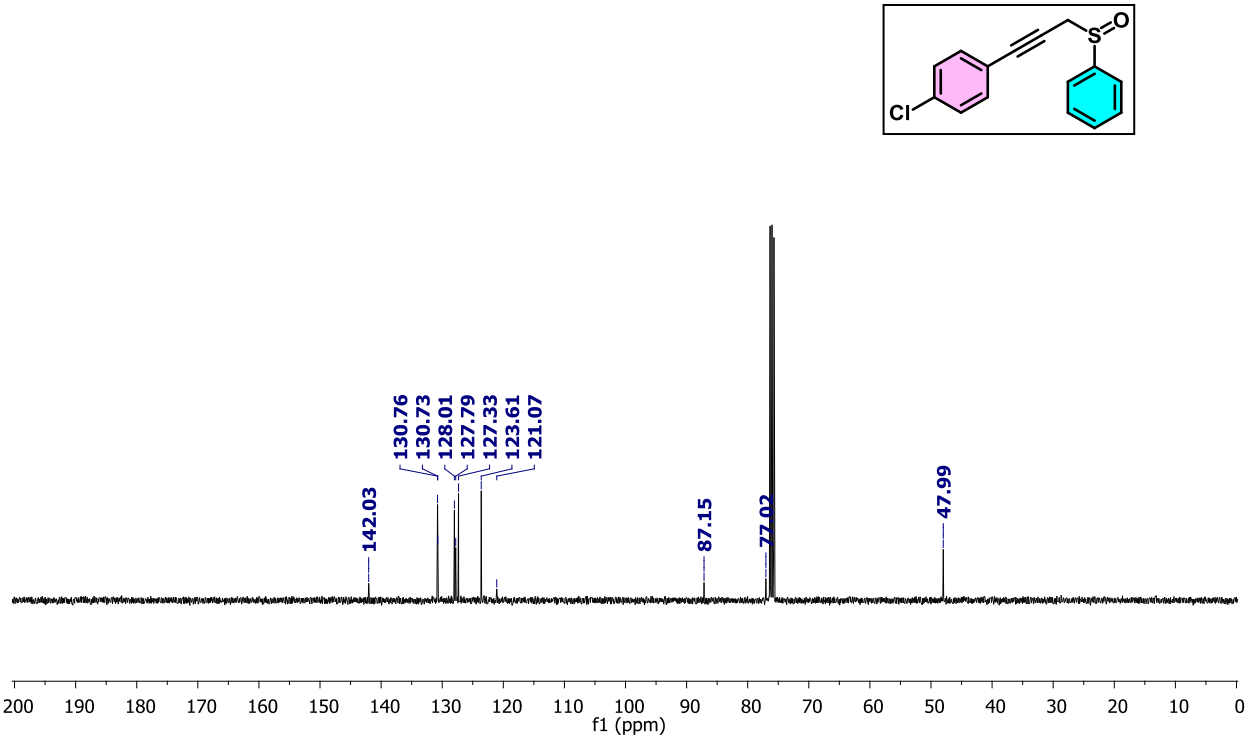
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **32a**



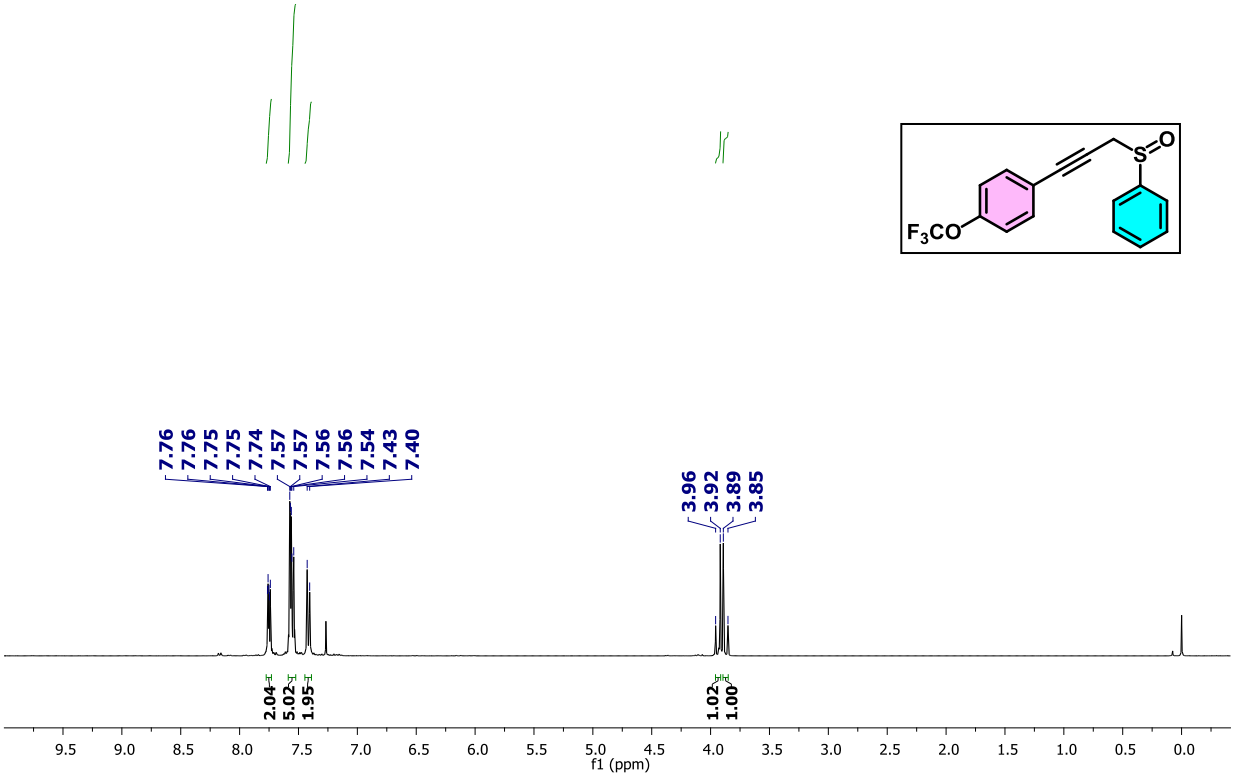
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **33a**



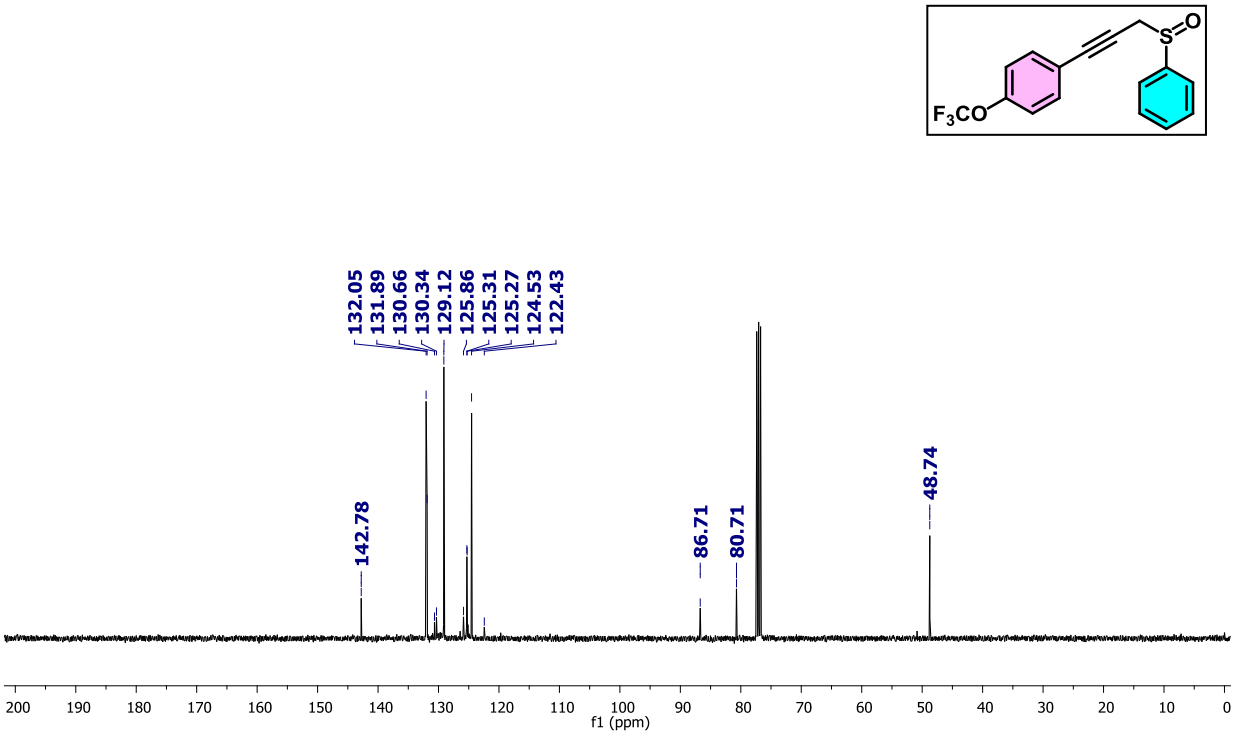
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **33a**



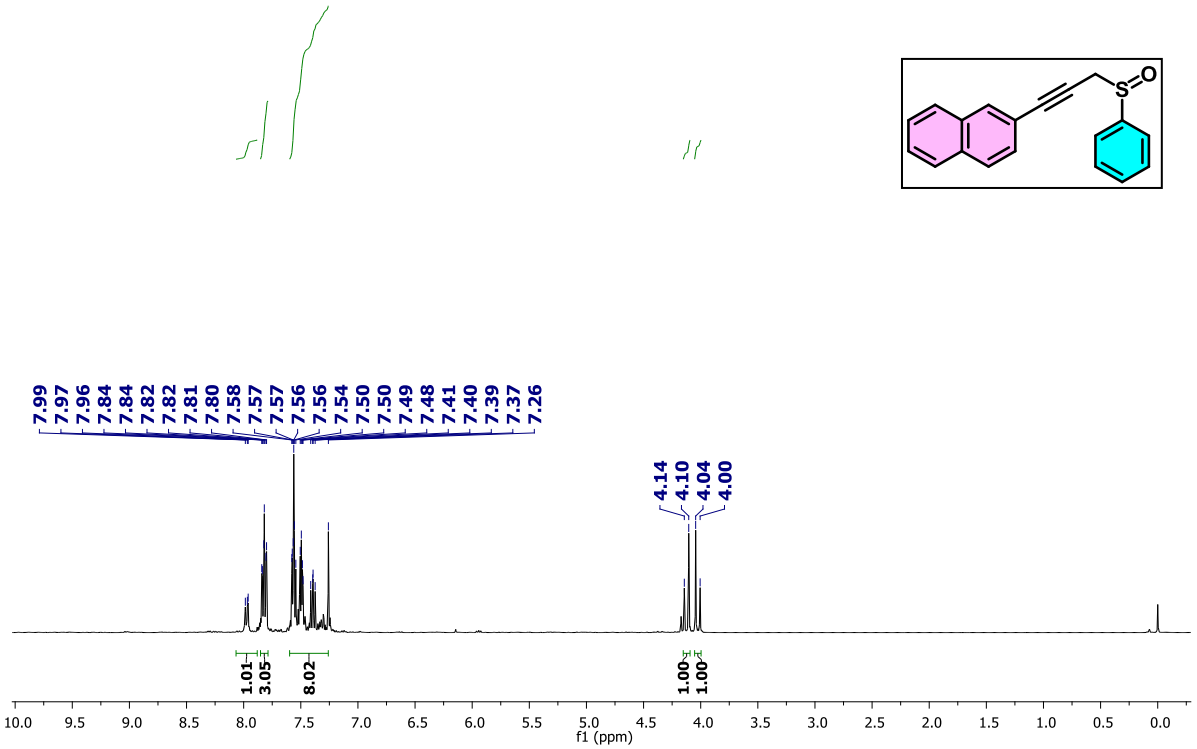
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **34a**



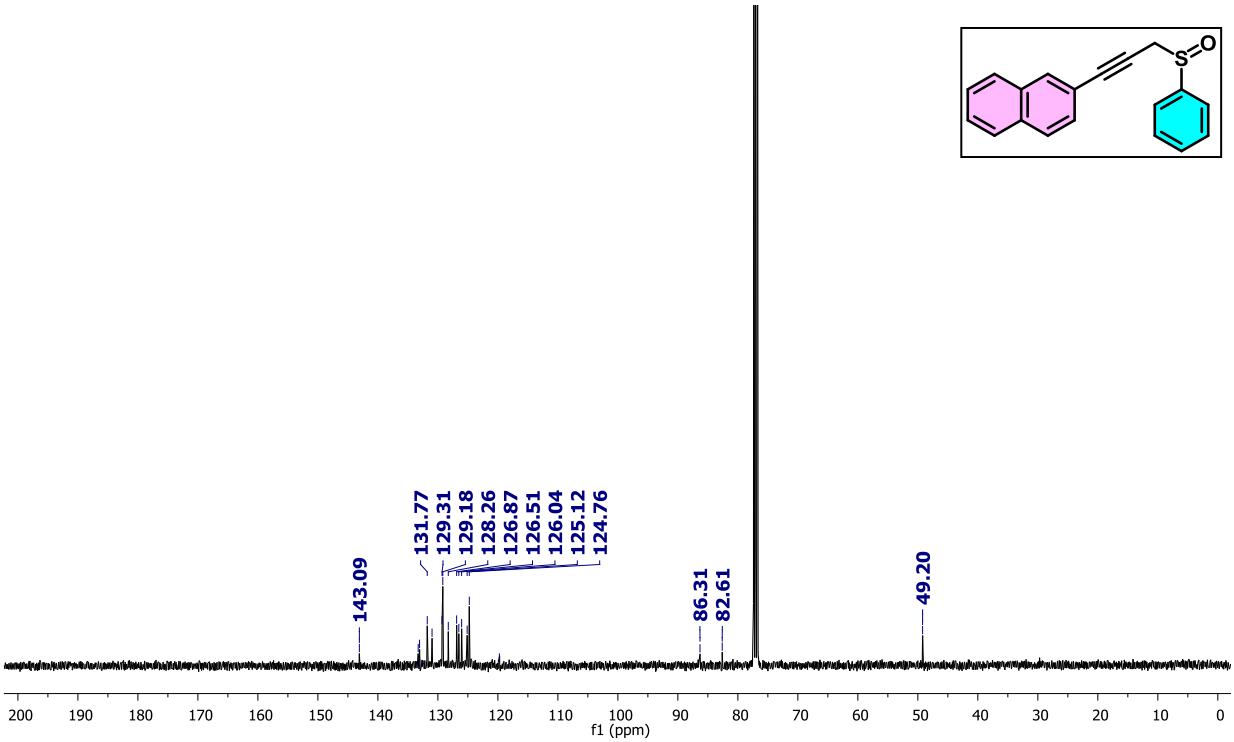
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **34a**



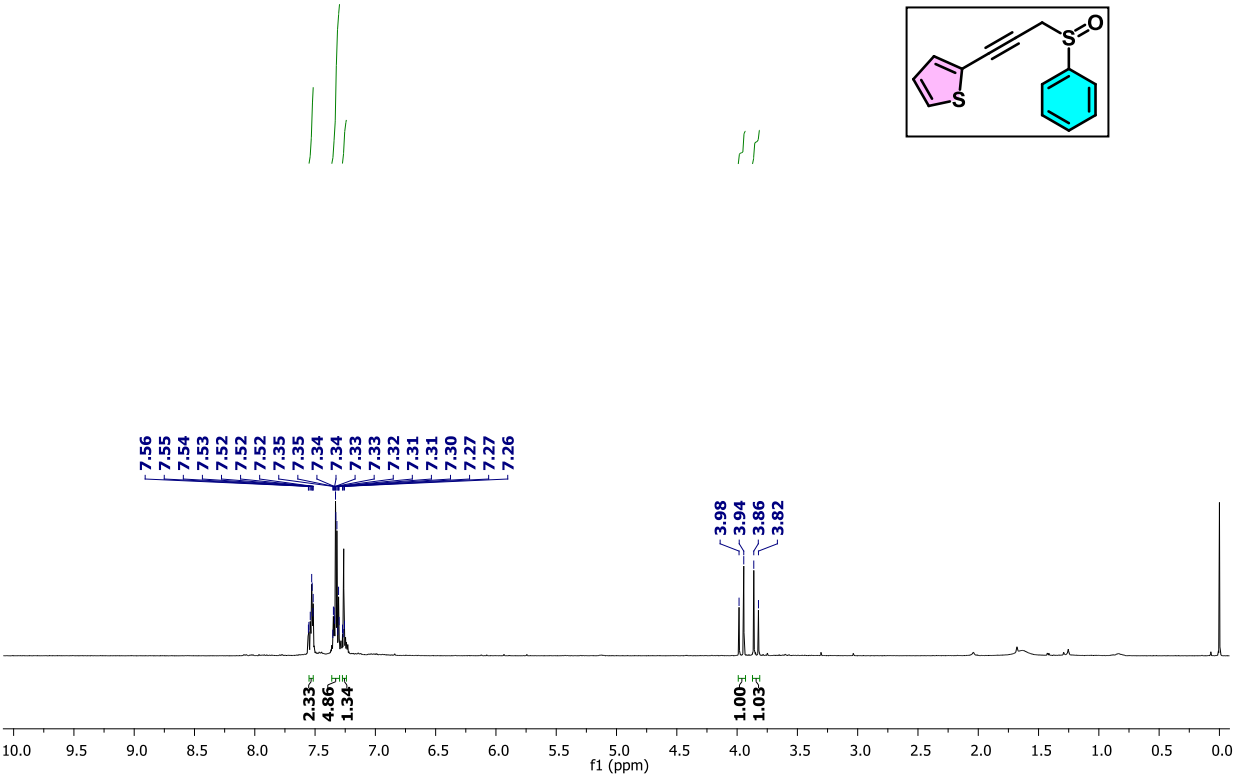
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **35a**



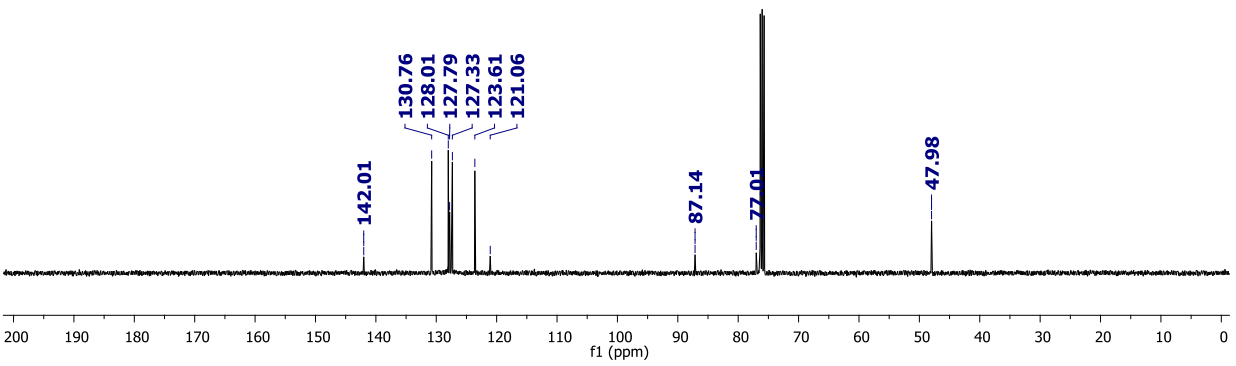
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **35a**



^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **36a**



^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **36a**



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