Supporting Information

Remote Radical Alkynylation of Unactivated C(sp3)−H Bonds of Ethynesulfonamides

Pan Zhou,[a,c] Mengru Guo,[a,c] Jiawei Li,[a] Xu Li,[a] Danyang Xie,[b]* Bo Qin[a]* and Yong Xia[a]*

[a] School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China.
[b] School of Smart Health, Chongqing College of Electronic Engineering, Chongqing 401331, China.
[c] P. Zhou and M. Guo contributed equally to this work.

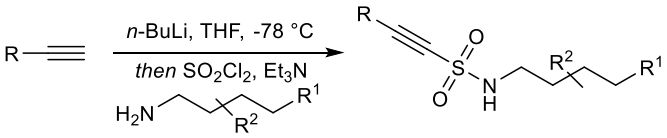
E-mail: xiedanyang@cqcet.edu.cn; qinbo@cqu.edu.cn; xiayong@cqu.edu.cn

Table of contents

1. General information

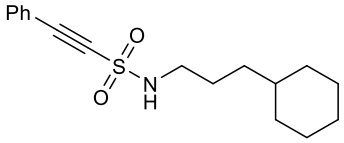
All reactions were carried out using oven-dried glassware and magnetic stirring under an inert atmosphere (N_2). All chemical were obtained from commercial supplier and were used without further purification unless otherwise stated. All solvents were dried and distilled under N_2 prior to use. Solvents for chromatography were of technical grade and distilled prior to use. Analytical thin layer chromatography was carried out using silica gel GF254, visualized under UV light (at 254 nm). ^{1}H NMR (TMS as internal reference) and ^{13}C NMR spectra were recorded on Bruker 400 (400, 101 MHz). Chemical shifts were referenced relative to internal reference or residual solvent. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, coupling constant (Hz). ^{13}C spectra were reported as chemical shifts in ppm and multiplicity where appropriate. Melting points were measured using a melting point apparatus in open glass capillaries.High resolution mass spectra were acquired on an LTQ Orbitrap Elite mass spectrometer (ESI). TLC was performed using silica, detection of compounds with UV light or dipping into asolution of $KMnO_4$ (1.5 g in 400 mL H_2O, 5.0 g $NaHCO_3$), followed by heating. Flash column chromatography (FC) was performed using Qingdao Haiyang silica gel 60 (40-63 μm) applying a pressure of about 0.2 bar.

2. General procedure for the preparation of ethynesulfonamides from the corresponding amines (GP1).



To a solution of the corresponding acetylene (10.0 mmol, 1 equiv) in THF (50 mL) at -78 ℃ was added *n*-BuLi (11.0 mmol, 1.1 equiv) dropwise. After stirring at this temperature for 0.5 hours, sulfuryl chloride (10.0 mmol) was added to the reaction mixture. The resulting mixture was stirred for 2 hours. Then, Et_3N (10.0 mmol) and alkylamine (10.0 mmol) were added. Upon completion of the reaction, the mixture was diluted with EA and washed with 1N HCl solution (10.0 mL), H_2O (13.0 mL) and brine (13.0 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting residue was purified by chromatography on silica gel to provide the corresponding ethynesulfonamides. Note: Alkylamines were synthesized according to relevant literatures [1-5] and directly used in the next reaction!

***N*-(3-Cyclohexylpropyl)-2-phenylethyne-1-sulfonamide (S1)**



Prepared according to GP1 starting from phenylacetylene (1.02 g, 10 mmol), *n*-BuLi

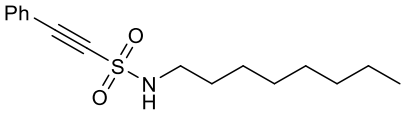
(4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and 3-cyclohexyl-1-propanamine (1.41 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20:1), giving the product **S1** as yellow solid in 52% yield (1.58 g). **TLC** R_f = 0.6 (PE:EA = 7:1). mp 147–149 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.51 (m, 2H), 7.51 – 7.46 (m, 1H), 7.43 – 7.36 (m, 2H), 4.69 (t, *J* = 6.1 Hz, 1H), 3.29 – 3.21 (m, 2H), 1.71 – 1.61 (m, 7H), 1.26 – 1.11 (m, 6H), 0.91 – 0.84 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.7, 131.2, 128.7, 118.3, 88.5, 83.6, 44.2, 37.2, 34.3, 33.2, 26.7, 26.6, 26.3.

HRMS (ESI) m/z calcd for $C_{17}H_{23}NNaO_2S$ $[M+Na]^+$ 328.1342, found 328.1341.

***N*-Octyl-2-phenylethyne-1-sulfonamide (S2)**



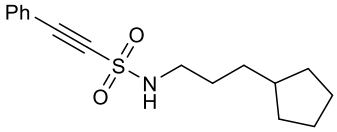
Prepared according to GP1 starting from phenylacetylene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and octan-1-amine (1.29 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **S2** as yellow oil in 54% yield (1.51 g). **TLC** R_f = 0.6 (PE:EA = 7:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.39 (m, 2H), 7.39 – 7.33 (m, 1H), 7.31 – 7.22 (m, 2H), 5.27 (t, *J* = 6.0 Hz, 1H), 3.24 – 3.08 (m, 2H), 1.62 – 1.50 (m, 2H), 1.32 – 1.24 (m, 2H), 1.22 – 1.10 (m, 8H), 0.77 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.6, 131.1, 128.7, 118.3, 88.5, 83.6, 43.9, 31.7, 29.2, 29.1, 29.1, 26.6, 22.6, 14.1.

HRMS (ESI) m/z calcd for $C_{16}H_{23}NNaO_2S$ $[M+Na]^+$ 316.1342, found 316.1346.

***N*-(3-Cyclopentylpropyl)-2-phenylethyne-1-sulfonamide (S3)**



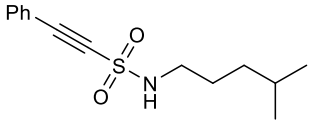
Prepared according to GP1 starting from ethynylbenzene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and 3-cyclopentylpropan-1-amine (1.27 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **S3** as pale yellow solid in 20% yield (0.56 g). **TLC** R_f = 0.3 (PE:EA = 20:3). mp 143–145 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 2H), 7.50 – 7.45 (m, 1H), 7.41 – 7.35 (m, 2H), 5.13 (t, *J* = 6.0 Hz, 1H), 3.28 – 3.22 (m, 2H), 1.79 – 1.71 (m, 3H), 1.70 – 1.63 (m, 2H), 1.61 – 1.53 (m, 2H), 1.53 – 1.44 (m, 2H), 1.42 – 1.36 (m, 2H), 1.11 – 1.01 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.6, 131.2, 128.7, 118.3, 88.5, 83.6, 44.1, 39.7, 33.0, 32.6, 28.5, 25.1.

HRMS (ESI) m/z calcd for $C_{16}H_{21}NNaO_2S$ $[M+Na]^+$ 314.1185, found 314.1193.

***N*-(4-Methylpentyl)-2-phenylethyne-1-sulfonamide (S4)**



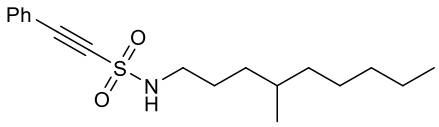
Prepared according to GP1 starting from ethynylbenzene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and 4-methylpentan-1-amine (1.01 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1), giving the product **S4** as yellow oil in 42% yield (1.10 g). **TLC** R_f = 0.5 (PE:EA = 7:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.42 – 7.38 (m, 1H), 7.34 – 7.27 (m, 2H), 4.92 (t, *J* = 6.1 Hz, 1H), 3.20 – 3.13 (m, 2H), 1.62 – 1.55 (m, 2H), 1.53 – 1.42 (m, 1H), 1.22 – 1.16 (m, 2H), 0.81 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.6, 131.2, 128.7, 118.3, 88.5, 83.5, 44.1, 35.7, 27.7, 27.2, 22.5.

HRMS (ESI) m/z calcd for $C_{14}H_{19}NNaO_2S$ $[M+Na]^+$ 288.1029, found 288.1030.

***N*-Nonyl-2-phenylethyne-1-sulfonamide (S5)**



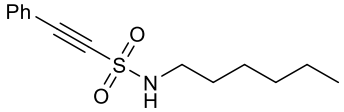
Prepared according to GP1 starting from ethynylbenzene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and 4-methylnonan-1-amine (1.57 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1), giving the product **S5** as yellow solid in 58% yield (1.78 g). **TLC** R_f = 0.6 (PE:EA = 7:1). mp 32–34 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.49 – 7.44 (m, 1H), 7.40 – 7.32 (m, 2H), 5.30 (t, *J* = 6.0 Hz, 1H), 3.29 – 3.20 (m, 2H), 1.71 – 1.60 (m, 2H), 1.47 – 1.31 (m, 3H), 1.30 – 1.18 (m, 8H), 0.89 – 0.82 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.6, 131.1, 128.7, 118.3, 88.5, 83.6, 44.3, 36.8, 33.9, 32.4, 32.2, 26.8, 26.7, 22.7, 19.5, 14.1.

HRMS (ESI) m/z calcd for $C_{18}H_{27}NNaO_2S$ $[M+Na]^+$ 344.1655, found 344.1663.

***N*-Hexyl-2-phenylethyne-1-sulfonamide (S6)**



Prepared according to GP1 starting from ethynylbenzene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and hexan-1-amine (1.01 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1), giving the product **S6** as yellow oil in 45% yield (1.18 g). **TLC** R_f = 0.33

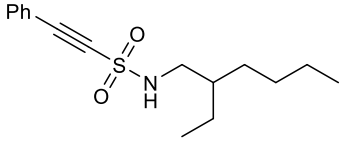
(PE:EA = 20:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.50 – 7.46 (m, 1H), 7.42 – 7.34 (m, 2H), 4.99 (t, *J* = 6.1 Hz, 1H), 3.31 – 3.22 (m, 2H), 1.69 – 1.62 (m, 2H), 1.42 – 1.36 (m, 2H), 1.33 – 1.25 (m, 4H), 0.91 – 0.84 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.6, 131.2, 128.7, 118.3, 88.5, 83.5, 43.9, 31.3, 29.2, 26.3, 22.5, 14.0.

HRMS (ESI) m/z calcd for $C_{14}H_{19}NNaO_2S$ $[M+Na]^+$ 288.1029, found 288.1035.

***N*-(2-Ethylhexyl)-2-phenylethyne-1-sulfonamide (S7)**



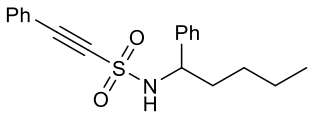
Prepared according to GP1 starting from ethynylbenzene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and 2-ethylhexan-1-amine (1.29 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **S7** as yellow oil in 48% yield (1.43 g). **TLC** R_f = 0.60 (PE:EA = 20:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 2H), 7.42 – 7.37 (m, 1H), 7.32 – 7.25 (m, 2H), 5.02 (t, *J* = 6.2 Hz, 1H), 3.15 – 3.06 (m, 2H), 1.54 – 1.46 (m, 1H), 1.36 – 1.30 (m, 2H), 1.28 – 1.18 (m, 6H), 0.85 – 0.77 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.6, 131.1, 128.7, 118.3, 88.5, 83.5, 46.4, 39.0, 30.7, 28.8, 24.0, 22.9, 14.0, 10.7.

HRMS (ESI) m/z calcd for $C_{16}H_{23}NNaO_2S$ $[M+Na]^+$ 316.1342, found 316.1346.

2-Phenyl-*N*-(1-phenylhexyl)ethyne-1-sulfonamide (S8)



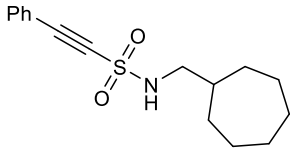
Prepared according to GP1 starting from ethynylbenzene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and 1-phenylpentan-1-amine (1.63 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1), giving the product **S8** as yellow oil in 28% yield (0.92 g). **TLC** R_f = 0.33 (PE:EA = 20:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 3H), 7.27 (m, 4H), 7.23 – 7.16 (m, 3H), 5.91 (d, *J* = 8.4 Hz, 1H), 4.61 – 4.51 (m, 1H), 1.97 – 1.88 (m, 1H), 1.84 – 1.74 (m, 1H), 1.43 – 1.25 (m, 4H), 0.83 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 132.5, 130.9, 128.7, 128.4, 127.8, 126.8, 118.2, 88.6, 84.3, 59.2, 37.3, 28.1, 22.3, 13.9.

HRMS (ESI) m/z calcd for $C_{19}H_{21}NNaO_2S$ $[M+Na]^+$ 350.1185, found 350.1193.

***N*-(Cycloheptylmethyl)-2-phenylethyne-1-sulfonamide (S9)**



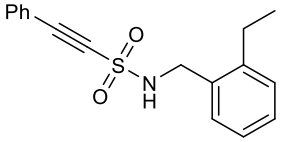
Prepared according to GP1 starting from ethynylbenzene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and cycloheptylmethanamine (1.27 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1), giving the product **S9** as yellow oil in 24% yield (0.69 g). **TLC** R_f = 0.33 (PE:EA = 20:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.51 – 7.45 (m, 1H), 7.42 – 7.36 (m, 2H), 4.92 (t, *J* = 6.3 Hz, 1H), 3.13 – 3.07 (m, 2H), 1.84 – 1.76 (m, 3H), 1.72 – 1.63 (m, 2H), 1.59 – 1.40 (m, 6H), 1.29 – 1.21 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.6, 131.1, 128.7, 118.3, 88.5, 83.6, 50.2, 39.1, 31.9, 28.3, 26.2.

HRMS (ESI) m/z calcd for $C_{16}H_{21}NO_2S$ $[M+Na]^+$ 314.1185, found 314.1190.

***N*-(2-Ethylbenzyl)-2-phenylethyne-1-sulfonamide (S10)**



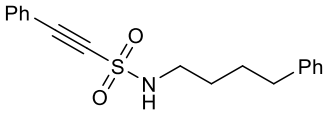
Prepared according to GP1 starting from ethynylbenzene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and (2-ethylphenyl)methanamine (1.35 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1), giving the product **S10** as yellow oil in 47% yield (1.39 g). **TLC** R_f = 0.33 (PE:EA = 20:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.46 (m, 3H), 7.44 – 7.32 (m, 3H), 7.30 – 7.17 (m, 3H), 4.90 (t, *J* = 5.8 Hz, 1H), 4.45 (d, *J* = 5.8 Hz, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 132.7, 132.5, 131.3, 129.5, 129.1, 128.9, 128.8, 126.4, 118.2, 89.1, 83.2, 45.5, 25.3, 15.3.

HRMS (ESI) m/z calcd for $C_{17}H_{17}NNaO_2S$ $[M+Na]^+$ 322.0872, found 322.0881.

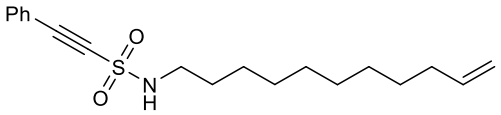
2-Phenyl-N-(4-phenylbutyl)ethyne-1-sulfonamide (S11)



Prepared according to GP1 starting from ethynylbenzene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and 4-phenylbutan-1-amine (1.49 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **S11** as yellow oil in 50% yield (1.57 g). **TLC** R_f = 0.3 (PE:EA = 7:1).

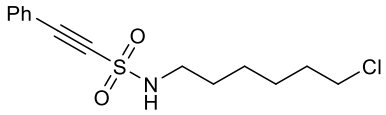
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.39 – 7.33 (m, 1H), 7.30 – 7.23 (m, 2H), 7.19 – 7.13 (m, 2H), 7.12 – 7.03 (m, 3H), 4.98 (t, *J* = 6.1 Hz, 1H), 3.23 – 3.13 (m, 2H), 2.55 (t, *J* = 7.1 Hz, 2H), 1.65 – 1.53 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 132.7, 131.2, 128.8, 128.4, 126.0, 118.2, 88.6, 83.5, 43.7, 35.3, 28.8, 28.3.
HRMS (ESI) m/z calcd for $C_{18}H_{19}NNaO_2S$ $[M+Na]^+$ 336.1029, found 336.1036.

2-Phenyl-N-(undec-10-en-1-yl)ethyne-1-sulfonamide (S12)



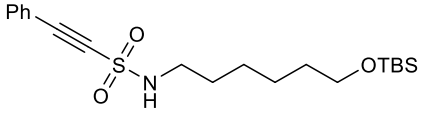
Prepared according to GP1 starting from ethynylbenzene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and undec-10-en-1-amine (1.69 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **S12** as yellow oil in 50% yield (1.57 g). **TLC** R_f = 0.15 (PE:EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 2H), 7.51 – 7.46 (m, 1H), 7.43 – 7.37 (m, 2H), 5.87 – 5.73 (m, 1H), 5.03 – 4.90 (m, 2H), 4.76 (t, *J* = 6.1 Hz, 1H), 3.31 – 3.21 (m, 2H), 2.06 – 2.00 (m, 2H), 1.69 – 1.63 (m, 2H), 1.43 – 1.33 (m, 6H), 1.30 – 1.24 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 132.6, 131.2, 128.7, 118.3, 114.2, 88.5, 83.5, 43.9, 33.8, 29.4, 29.4, 29.3, 29.1, 29.1, 28.9, 26.6.
HRMS (ESI) m/z calcd for $C_{19}H_{27}NNaO_2S$ $[M+Na]^+$ 356.1655, found 356.1663.

***N*-(6-Chlorohexyl)-2-phenylethyne-1-sulfonamide (S13)**



Prepared according to GP1 starting from ethynylbenzene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and 6-chlorohexan-1-amine (1.35 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **S13** as yellow oil in 38% yield (1.14 g). **TLC** R_f = 0.3 (PE:EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.43 (m, 2H), 7.42 – 7.36 (m, 1H), 7.35 – 7.25 (m, 2H), δ 5.03 (t, *J* = 6.2 Hz, 1H). 3.44 (t, *J* = 6.6 Hz, 2H), 3.27 – 3.09 (m, 2H), 1.71 – 1.64 (m, 2H), 1.63 – 1.55 (m, 2H), 1.43 – 1.29 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 132.7, 131.2, 128.8, 118.2, 88.6, 83.5, 44.8, 43.7, 32.3, 29.2, 26.4, 25.9.
HRMS (ESI) m/z calcd for $C_{14}H_{18}Cl^{35}NNaO_2S$ $[M+Na]^+$ 322.0639, found 322.0641. $C_{14}H_{18}Cl^{37}NNaO_2S$ $[M+Na]^+$ 324.0609, found 324.0610.

***N*-(6-((*tert*-Butyldimethylsilyl)oxy)hexyl)-2-phenylethyne-1-sulfonamide (S14)**



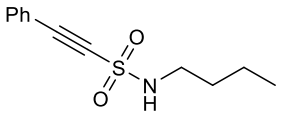
Prepared according to GP1 starting from ethynylbenzene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and 6-((tert-butyldimethylsilyl)oxy)hexan-1-amine (2.31 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **S14** as yellow oil in 39% yield (0.77 g). **TLC** R_f = 0.3 (PE:EA = 7:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 2H), 7.51 – 7.45 (m, 1H), 7.44 – 7.35 (m, 2H), 4.86 (brs, 1H), 3.58 (t, *J* = 6.4 Hz, 2H), 3.32 – 3.21 (m, 2H), 1.69 – 1.64 (m, 2H), 1.54 – 1.47 (m, 2H), 1.45 – 1.33 (m, 4H), 0.88 (s, 9H), 0.03 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.6, 131.2, 128.7, 118.3, 88.5, 83.5, 63.0, 43.8, 32.6, 29.3, 26.4, 26.0, 25.4, 18.4, -5.3.

HRMS (ESI) m/z calcd for $C_{20}H_{33}NNaO_3SSi$ $[M+Na]^+$ 418.1843, found 418.1850.

***N*-Butyl-2-phenylethyne-1-sulfonamide (S15)**



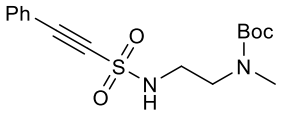
Prepared according to GP1 starting from ethynylbenzene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and butan-1-amine (0.73 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1), giving the product **S15** as yellow oil in 50% yield (1.18 g). **TLC** R_f = 0.30 (PE:EA = 20:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.50 – 7.45 (m, 1H), 7.41 – 7.34 (m, 2H), 5.17 (t, *J* = 6.1 Hz, 1H), 3.30 – 3.23 (m, 2H), 1.68 – 1.60 (m, 2H), 1.47 – 1.38 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.6, 131.2, 128.7, 118.3, 88.5, 83.5, 43.5, 31.2, 19.8, 13.6.

HRMS (ESI) m/z calcd for $C_{12}H_{15}NNaO_2S$ $[M+Na]^+$ 260.0716, found 260.0717.

***tert*-Butyl methyl(2-((phenylethynyl)sulfonamido)ethyl)carbamate (S16)**



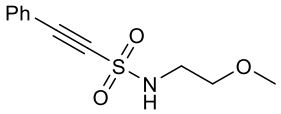
Prepared according to GP1 starting from ethynylbenzene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and tert-butyl (2-aminoethyl)(methyl)carbamate (1.74 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 4/1), giving the product **S16** as yellow solid in 4% yield (0.14 g). **TLC** R_f = 0.1 (PE:EA = 4:1). mp 113–115 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ 7.61 – 7.53 (m, 2H), 7.52 – 7.46 (m, 1H), 7.40 (m, 2H), 6.13 (brs, 1H), 3.52 – 3.46 (m, 2H), 3.45 – 3.38 (m, 2H), 2.92 (s, 3H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ 157.1, 155.6, 132.6, 131.2, 128.7, 118.3, 88.0, 83.6, 80.5, 48.5, 47.7, 42.5, 35.2, 28.4.

HRMS (ESI) m/z calcd for $C_{16}H_{22}N_2NaO_4S$ $[M+Na]^+$ 361.1192, found 361.1199.

***N*-(2-Methoxyethyl)-2-phenylethyne-1-sulfonamide (S17)**



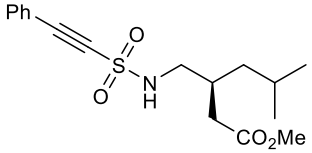
Prepared according to GP1 starting from ethynylbenzene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and 2-methoxyethan-1-amine (0.75 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 5/1), giving the product **S17** as yellow oil in 73% yield (1.75 g). **TLC** R_f = 0.1 (PE:EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.52 – 7.47 (m, 1H), 7.43 – 7.38 (m, 2H), 5.21 (brs, 1H), 3.62 (t, *J* = 5.0 Hz, 2H), 3.46 – 3.41 (m, 2H), 3.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.7, 131.2, 128.8, 118.2, 88.8, 83.3, 70.0, 58.9, 43.5.

HRMS (ESI) m/z calcd for $C_{11}H_{13}NNaO_3S$ $[M+Na]^+$ 262.0508, found 262.0515.

Methyl (*S*)-5-methyl-3-(((phenylethynyl)sulfonamido)methyl)hexanoate (S18)



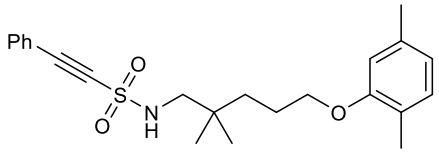
Prepared according to GP1 starting from ethynylbenzene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and methyl (*S*)-3-(aminomethyl)-5-methylhexanoate (1.73 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1), giving the product **S18** as yellow oil in 18% yield (0.61 g). **TLC** R_f = 0.3 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.51 (m, 2H), 7.51 – 7.46 (m, 1H), 7.43 – 7.35 (m, 2H), 5.35 (t, *J* = 6.4 Hz, 1H), 3.68 (s, 3H), 3.37 – 3.29 (m, 1H), 3.20 – 3.12 (m, 1H), 2.47 – 2.37 (m, 2H), 2.29 – 2.20 (m, 1H), 1.69 – 1.64 (m, 1H), 1.30 – 1.18 (m, 2H), 0.94 – 0.86 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 132.7, 131.2, 128.7, 118.3, 88.5, 83.5, 51.8, 47.2, 41.3, 36.9, 32.8, 25.1, 22.6, 22.5.

HRMS (ESI) m/z calcd for $C_{17}H_{23}NNaO_4S$ $[M+Na]^+$ 360.1240, found 360.1249.

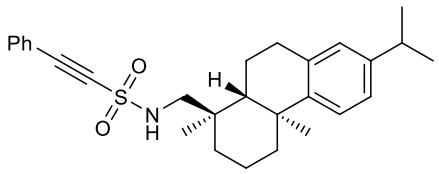
***N*-(5-(2,5-Bimethylphenoxy)-2,2-dimethylpentyl)-2-phenylethyne-1-sulfonamide (S19)**



Prepared according to GP1 starting from ethynylbenzene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and 5-(2,5-dimethylphenoxy)-2,2-dimethylpentan-1-amine (2.35 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1), giving the product **S19** as pale yellow solid in 39% yield (0.77 g). **TLC** R_f = 0.3 (PE:EA = 10:1). mp 139–141 ℃.

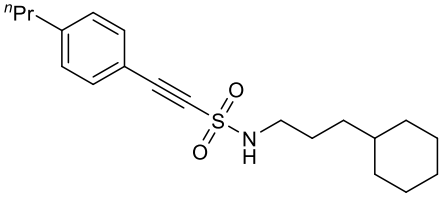
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.48 (m, 2H), 7.47 – 7.42 (m, 1H), 7.40 – 7.31 (m, 2H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 7.4 Hz, 1H), 6.59 (s, 1H), 5.12 (t, *J* = 6.7 Hz, 1H), 3.91 (t, *J* = 6.3 Hz, 2H), 3.06 (d, *J* = 6.7 Hz, 2H), 2.29 (s, 3H), 2.17 (s, 3H), 1.83 – 1.73 (m, 2H), 1.53 – 1.43 (m, 2H), 1.00 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 136.5, 132.7, 131.2, 130.4, 128.7, 123.6, 120.8, 118.3, 112.1, 88.7, 83.5, 68.2, 53.4, 35.8, 33.8, 25.0, 24.0, 21.4, 15.9.
HRMS (ESI) m/z calcd for $C_{23}H_{29}NNaO_3S$ $[M+Na]^+$ 422.1760, found 422.1768.

***N*-(((1*R*,4a*S*,10a*R*)-7-Isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-2-phenylethyne-1-sulfonamide (S20)**



Prepared according to GP1 starting from ethynylbenzene (1.02 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and ((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methanamine (2.85 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1), giving the product **S20** as yellow solid in 30% yield (1.35 g). **TLC** R_f = 0.1 (PE:EA = 10:1). mp 162–164 ℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.48 – 7.44 (m, 1H), 7.39 – 7.33 (m, 2H), 7.15 (d, *J* = 8.2 Hz, 1H), 7.00 – 6.96 (m, 1H), 6.87 (d, *J* = 2.0 Hz, 1H), 5.02 (t, *J* = 6.9 Hz, 1H), 3.17 – 3.11 (m, 1H), 3.04 – 2.98 (m, 1H), 2.93 – 2.87 (m, 2H), 2.85 – 2.77 (m, 1H), 2.31 – 2.25 (m, 1H), 1.81 – 1.78 (m, 1H), 1.77 – 1.73 (m, 1H), 1.71 – 1.68 (m, 1H), 1.56 (dd, *J* = 12.0, 2.7 Hz, 1H), 1.48 – 1.44 (m, 1H), 1.42 – 1.30 (m, 3H), 1.23 – 1.19 (m, 9H), 1.00 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 145.7, 134.6, 132.7, 131.2, 128.7, 126.9, 124.2, 123.9, 118.3, 88.8, 83.5, 54.4, 45.1, 38.2, 37.5, 37.0, 35.9, 33.5, 29.9, 25.3, 24.0, 24.0, 18.9, 18.6, 18.5.
HRMS (ESI) m/z calcd for $C_{28}H_{35}NNaO_2S$ $[M+Na]^+$ 472.2281, found 476.2285.

***N*-(3-Cyclohexylpropyl)-2-(4-propylphenyl)ethyne-1-sulfonamide (S21)**



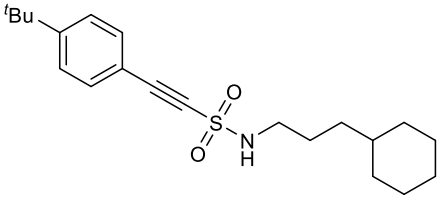
Prepared according to GP1 starting from 1-ethynyl-4-propylbenzene (1.44 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and 3-cyclohexyl-1-propanamine (1.41 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **S21** as white solid in 51% yield (1.75 g). **TLC** R_f = 0.6 (PE:EA = 7:1). mp 153–155 ℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.13

(brs, 1H), 3.23 (t, *J* = 7.3 Hz, 2H), 2.63 – 2.58 (m, 2H), 1.70 – 1.60 (m, 9H), 1.28 – 1.10 (m, 6H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.90 – 0.80 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 132.6, 128.9, 115.4, 89.2, 83.1, 44.2, 38.1, 37.2, 34.3, 33.2, 26.6, 26.6, 26.3, 24.2, 13.7.

HRMS (ESI) m/z calcd for $C_{20}H_{29}NNaO_2S$ $[M+Na]^+$ 370.1811, found 370.1818.

2-(4-(*tert*-Butyl)phenyl)-*N*-(3-cyclohexylpropyl)ethyne-1-sulfonamide (S22)



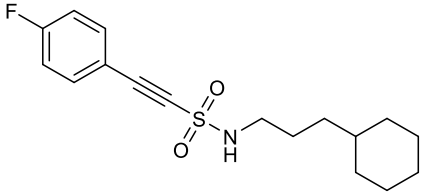
Prepared according to GP1 starting from 1-(*tert*-butyl)-4-ethynylbenzene (1.58 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and 3-cyclohexyl-1-propanamine (1.41 g, 10.0 mmol). The residue was purified by column chromatography petroleum ether/ethyl acetate = 20/1), giving the product **S22** as white solid in 52% yield (1.65 g). **TLC** R_f = 0.6 (PE:EA = 7:1). mp 147–149 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.43 – 7.38 (m, 2H), 4.99 (t, *J* = 6.1 Hz, 1H), 3.27 – 3.19 (m, 2H), 1.71 – 1.60 (m, 7H), 1.32 (s, 9H), 1.29 – 1.19 (m, 4H), 1.18 – 1.14 (m, 2H), 0.90 – 0.80 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 132.5, 125.8, 115.2, 89.2, 83.1, 44.2, 37.2, 35.1, 34.3, 33.2, 31.0, 26.6, 26.6, 26.3.

HRMS (ESI) m/z calcd for $C_{21}H_{31}NNaO_2S$ $[M+Na]^+$ 384.1968, found 384.1973.

***N*-(3-Cyclohexylpropyl)-2-(4-fluorophenyl)ethyne-1-sulfonamide (S23)**



Prepared according to GP1 starting from 1-ethynyl-4-fluorobenzene (1.20 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and 3-cyclohexyl-1-propanamine (1.41 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **S23** as pale yellow solid in 13% yield (0.43 g). **TLC** R_f = 0.45 (PE:EA = 7:1). mp 124–126 ℃.

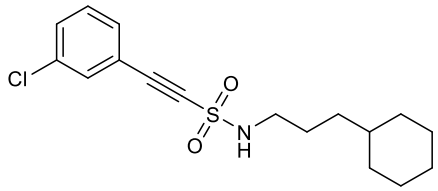
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.49 (m, 2H), 7.14 – 7.05 (m, 2H), 4.87 (t, *J* = 6.1 Hz, 1H), 3.29 – 3.18 (m, 2H), 1.71 – 1.64 (m, 6H), 1.31 – 1.07 (m, 7H), 0.91 – 0.82 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2 (d, *J* = 255.4 Hz), 135.0 (d, *J* = 10.0 Hz), 116.3 (d, *J* = 22.5 Hz), 114.4 (d, *J* = 3.4 Hz), 87.4, 83.5, 44.2, 37.2, 34.3, 33.2, 26.7, 26.6, 26.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ -105.3.

HRMS (ESI) m/z calcd for $C_{17}H_{22}FNNaO_2S$ $[M+Na]^+$ 346.1247, found 346.1252.

2-(3-Chlorophenyl)-*N*-(3-cyclohexylpropyl)ethyne-1-sulfonamide (S24)



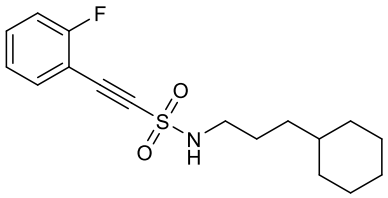
Prepared according to GP1 starting from 1-chloro-3-ethynylbenzene (1.36 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and 3-cyclohexyl-1-propanamine (1.41 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **S24** as pale yellow solid in 14% yield (0.47 g). **TLC** R_f = 0.6 (PE:EA = 7:1). mp 134–136 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 1H), 7.49 – 7.42 (m, 2H), 7.37 – 7.31 (m, 1H), 4.96 (t, *J* = 6.0 Hz, 1H), 3.28 – 3.20 (m, 2H), 1.71 – 1.63 (m, 7H), 1.27 – 1.10 (m, 6H), 0.92 – 0.83 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.7, 132.3, 131.5, 130.7, 130.0, 120.1, 86.4, 84.5, 44.2, 37.2, 34.3, 33.3, 26.7, 26.6, 26.3.

HRMS (ESI) m/z calcd for $C_{17}H_{22}Cl^{35}NNaO_2S$ $[M+Na]^+$ 362.0952, found 362.0955. $C_{17}H_{22}Cl^{37}NNaO_2S$ $[M+Na]^+$ 364.0922, found 364.0926.

***N*-(3-Cyclohexylpropyl)-2-(2-fluorophenyl)ethyne-1-sulfonamide (S25)**



Prepared according to GP1 starting from 1-ethynyl-2-fluorobenzene (1.20 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and 3-cyclohexyl-1-propanamine (1.41 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **S25** as pale yellow solid in 12% yield (0.39 g). **TLC** R_f = 0.45 (PE:EA = 7:1). mp 69–71 ℃.

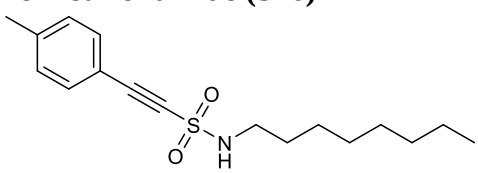
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.44 (m, 2H), 7.23 – 7.10 (m, 2H), 4.71 (t, *J* = 6.2 Hz, 1H), 3.32 – 3.21 (m, 2H), 1.74 – 1.61 (m, 7H), 1.26 – 1.08 (m, 6H), 0.90 – 0.84 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 (d, *J* = 257.0 Hz), 134.2, 133.2 (d, *J* = 8.2 Hz), 124.4 (d, *J* = 3.8 Hz), 116.0 (d, *J* = 20.2 Hz), 107.4 (d, *J* = 15.0 Hz), 88.2 (d, *J* = 3.3 Hz), 82.1, 44.2, 37.2, 34.2, 33.2, 26.6, 26.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ -106.9.

HRMS (ESI) m/z calcd for $C_{17}H_{22}FNNaO_2S$ $[M+Na]^+$ 346.1247, found 346.1254.

***N*-Octyl-2-(p-tolyl)ethyne-1-sulfonamide (S26)**



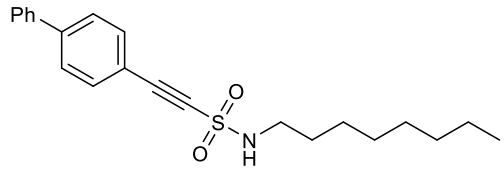
Prepared according to GP1 starting from 1-ethynyl-4-methylbenzene (1.16 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and octan-1-amine (1.29 g, 1 0.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **S26** as yellow solid in 63% yield (1.93 g). **TLC** R_f = 0.6 (PE:EA = 7:1). mp 138–140 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.99 (t, *J* = 6.1 Hz, 1H), 3.28 – 3.21 (m, 2H), 2.39 (s, 3H), 1.68 – 1.61 (m, 2H), 1.41 – 1.35 (m, 2H), 1.30 – 1.21 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 132.6, 129.5, 115.2, 89.1, 83.1, 43.8, 31.7, 29.2, 29.1, 29.1, 26.6, 22.6, 21.7, 14.1.

HRMS (ESI) m/z calcd for $C_{17}H_{25}NNaO_2S$ $[M+Na]^+$ 330.1498, found 330.1493.

2-([1,1'-Biphenyl]-4-yl)-*N*-octylethyne-1-sulfonamide (S27)



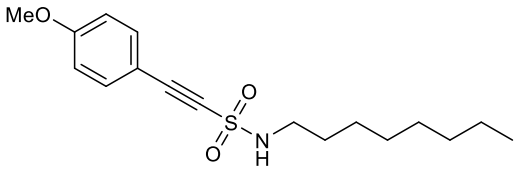
Prepared according to GP1 starting from 4-ethynyl-1,1'-biphenyl (1.78 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and octan-1-amine (1.29 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **S27** as yellow solid in 47% yield (1.73 g). **TLC** R_f = 0.6 (PE:EA = 7:1). mp 99–101 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 4H), 7.59 – 7.56 (m, 1H), 7.56 – 7.54 (m, 1H), 7.47 – 7.43 (m, 2H), 7.41 – 7.38 (m, 1H), 5.00 (t, *J* = 6.1 Hz, 1H), 3.31 – 3.24 (m, 2H), 1.70 – 1.63 (m, 2H), 1.44 – 1.36 (m, 2H), 1.31 – 1.22 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 139.6, 133.1, 129.0, 128.3, 127.3, 127.1, 117.0, 88.6, 84.1, 43.9, 31.8, 29.3, 29.2, 29.1, 26.6, 22.6, 14.1.

HRMS (ESI) m/z calcd for $C_{22}H_{27}NNaO_2S$ $[M+Na]^+$ 392.1655, found 392.1662.

2-(4-Methoxyphenyl)-*N*-octylethyne-1-sulfonamide (S28)



Prepared according to GP1 starting from 1-ethynyl-4-methoxybenzene (1.32 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and octan-1-amine (1.29 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **S28** as yellow solid in 43% yield (1.39 g). **TLC** R_f = 0.6 (PE:EA = 7:1). mp 71–73 ℃.

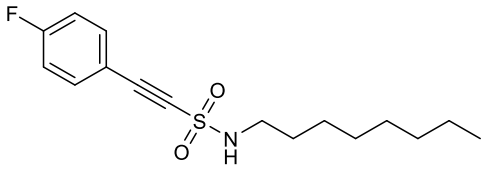
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.86

(t, *J* = 6.1 Hz, 1H), 3.84 (s, 3H), 3.28 – 3.20 (m, 2H), 1.68 – 1.58 (m, 2H), 1.42 – 1.35 (m, 2H), 1.31 – 1.22 (m, 8H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 134.5, 114.4, 110.0, 89.5, 82.7, 55.5, 43.8, 31.7, 29.2, 29.1, 29.1, 26.6, 22.6, 14.1.

HRMS (ESI) m/z calcd for $C_{17}H_{25}NNaO_3S$ $[M+Na]^+$ 346.1447, found 346.1451.

2-(4-Fluorophenyl)-*N*-octylethyne-1-sulfonamide (S29)



Prepared according to GP1 starting from 1-ethynyl-4-fluorobenzene (1.20 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and octan-1-amine (1.29 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **S29** as pale yellow solid in 12% yield (0.18 g). **TLC** R_f = 0.5 (PE:EA = 7:1). mp 97–99 ℃.

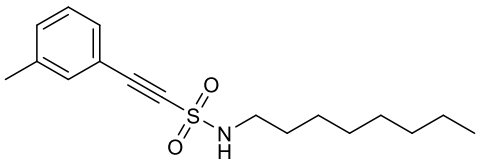
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.51 (m, 2H), 7.16 – 7.06 (m, 2H), 4.76 (t, *J* = 6.1 Hz, 1H), 3.31 – 3.21 (m, 2H), 1.70 – 1.62 (m, 2H), 1.42 – 1.25 (m, 10H), 0.87 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2 (d, *J* = 255.5 Hz), 134.9 (d, *J* = 9.0 Hz), 116.4 (d, *J* = 22.5 Hz), 114.4 (d, *J* = 3.6 Hz), 87.4, 83.5, 43.9, 31.7, 29.3, 29.1, 29.1, 26.6, 22.6, 14.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ -105.3.

HRMS (ESI) m/z calcd for $C_{16}H_{22}FNNaO_2S$ $[M+Na]^+$ 334.1247, found 334.1256.

2-(4-Methoxyphenyl)-*N*-octylethyne-1-sulfonamide (S30)



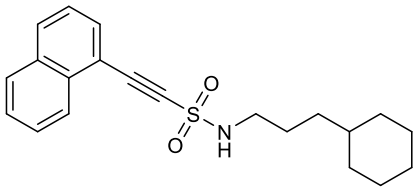
Prepared according to GP1 starting from 1-ethynyl-4-methoxybenzene (1.16 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and octan-1-amine (1.29 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **S30** as yellow oil in 34% yield (0.92 g). **TLC** R_f = 0.6 (PE:EA = 7:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.31 – 7.26 (m, 2H), 4.78 (brs, 1H), 3.29 – 3.22 (m, 2H), 2.36 (s, 3H), 1.69 – 1.62 (m, 3H), 1.41 – 1.26 (m, 9H), 0.89 – 0.84 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 133.1, 132.1, 129.8, 128.6, 118.1, 88.9, 83.2, 43.9, 31.7, 29.3, 29.1, 29.1, 26.6, 22.6, 21.2, 14.1.

HRMS (ESI) m/z calcd for $C_{17}H_{25}NNaO_2S$ $[M+Na]^+$ 330.1498, found 330.1506.

***N*-(3-Cyclohexylpropyl)-2-(naphthalen-1-yl)ethyne-1-sulfonamide (S31)**



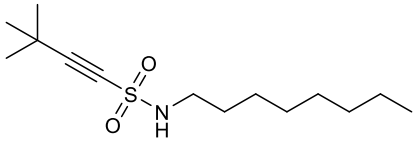
Prepared according to GP1 starting from 1-ethynyl-2-fluorobenzene (1.52 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and 3-cyclohexyl-1-propanamine (1.41 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **S31** as yellow solid in 4% yield (0.1 g). **TLC** R_f = 0.6 (PE:EA = 7:1). mp 118–120 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.88 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.80 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.45 (dd, *J* = 8.2, 7.2 Hz, 1H), 5.04 (t, *J* = 6.0 Hz, 1H), 3.35 – 3.28 (m, 2H), 1.73 – 1.61 (m, 7H), 1.30 – 1.24 (m, 2H), 1.22 – 1.05 (m, 4H), 0.88 – 0.78 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.2, 133.0, 132.9, 131.8, 128.6, 128.0, 127.1, 125.4, 125.0, 115.8, 88.1, 87.3, 44.3, 37.2, 34.3, 33.2, 26.7, 26.5, 26.2.

HRMS (ESI) m/z calcd for $C_{21}H_{25}NNaO_2S$ $[M+Na]^+$ 378.1498, found 378.1502.

3,3-Dimethyl-*N*-octylbut-1-yne-1-sulfonamide (S32)



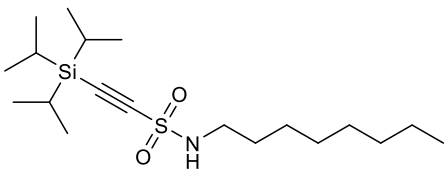
Prepared according to GP1 starting from 3,3-dimethylbut-1-yne (0.82 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and octan-1-amine (1.29 g, 10.0 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **S32** as pale yellow oil in 78% yield (2.12 g). **TLC** R_f = 0.6 (PE:EA = 7:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 (t, *J* = 6.1 Hz, 1H), 3.20 – 3.13 (m, 2H), 1.67 – 1.59 (m, 2H), 1.38 – 1.25 (m, 19H), 0.91 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 98.9, 74.7, 43.8, 31.7, 29.7, 29.2, 29.1, 29.1, 27.7, 26.6, 22.6, 14.1.

HRMS (ESI) m/z calcd for $C_{14}H_{27}NNaO_2S$ $[M+Na]^+$ 296.1655, found 296.1660.

***N*-octyl-2-(triisopropylsilyl)ethyne-1-sulfonamide (S33)**



Prepared according to GP1 starting from ethynyltriisopropylsilane (1.82 g, 10 mmol), *n*-BuLi (4.40 mL, 2.5M in hexanes, 11.0 mmol), sulfuryl chloride (0.81 mL, 10.0 mmol), triethylamine (1.40 mL, 10.0 mmol), and octan-1-amine (1.29 g, 10.0 mmol).

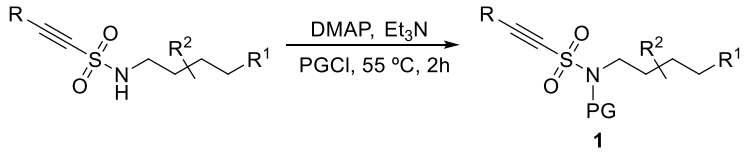
The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1), giving the product **S33** as pale yellow oil in 65% yield (2.42 g). **TLC** R_f = 0.35 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.52 (t, *J* = 6.1 Hz, 1H), 3.17 – 3.07 (m, 2H), 1.59 – 1.54 (m, 2H), 1.32 – 1.18 (m, 11H), 1.13 – 1.01 (m, 20H), 0.81 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 98.7, 93.9, 43.8, 31.8, 29.2, 29.1, 29.1, 26.6, 22.6, 18.4, 14.1, 10.9.

HRMS (ESI) m/z calcd for $C_{19}H_{39}NNaSiO_2S$ $[M+Na]^+$ 396.2363, found 396.2369.

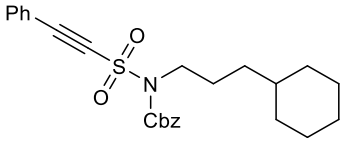
3. General procedure for the preparation of N-protected ethynesulfonamides from the corresponding ethynesulfonamides (GP2)



1

DMAP (0.03 mmol, 0.01 equiv) and Et_3N (7.5 mmol, 2.50 equiv) in a dry 50 mL flask equipped with stir bar was added slowly to a solution of the ethynesulfonamides (1.0 equiv, 3.0 mmol) in isopropyl acetate (7.0 mL). The solution was heated to 55 °C under N_2 atmosphere. A solution of acyl chloride (3.3 mmol, 1.10 equiv) in toluene (2.0 mL) was then dropped into the above solution at 55 °C over 1 h by syringe pump. After the addition was completed, the mixture was stirred for additional 1.5 h at 55 °C. After cooling to room temperature, the mixture was quenched with distilled water (1.0 mL). The resulting mixture was washed with 1N HCl solution (7 mL) and extracted with DCM (10.0 mL × 3 times). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel to provide N-protected ethynesulfonamides **1**.

Benzyl (3-cyclohexylpropyl)((phenylethynyl)sulfonyl)carbamate (1a)



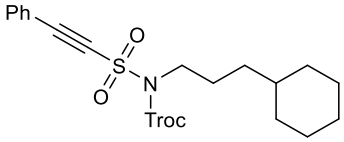
Prepared according to GP2 starting from *N*-(3-cyclohexylpropyl)-2-phenylethyne-1-sulfonamide (0.92 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 40/1), giving the product **1a** as a yellow solid in 82% yield (1.08 g). **TLC** R_f = 0.35 (PE:EA = 20:1). mp 104–106 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.29 (m, 10H), 5.34 (s, 2H), 3.84 (t, *J* = 7.6 Hz, 2H), 1.80 – 1.60 (m, 7H), 1.23 – 1.08 (m, 6H), 0.88 – 0.79 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 134.8, 132.9, 131.6, 128.7, 128.6, 128.6, 128.2, 117.6, 90.1, 83.3, 69.4, 48.6, 37.2, 34.1, 33.2, 26.8, 26.6, 26.3.

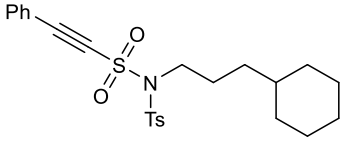
HRMS (ESI) m/z calcd for $C_{24}H_{29}NNaO_4S$ $[M+Na]^+$ 462.1710, found 462.1711.

2,2,2-Trichloroethyl (3-cyclohexylpropyl)((phenylethynyl)sulfonyl)carbamate (1b)



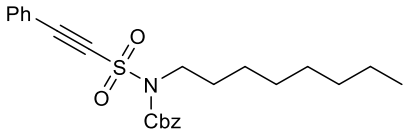
Prepared according to GP2 starting from *N*-(3-cyclohexylpropyl)-2-phenylethyne-1-sulfonamide (0.92 g, 3.0 mmol), 2,2,2-trichloroethyl chloroformate (0.46 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 40/1), giving the product **1b** as a pale yellow solid in 47% yield (0.68 g). **TLC** R_f = 0.3 (PE:EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 2H), 7.55 – 7.49 (m, 1H), 7.44 – 7.39 (m, 2H), 4.91 (s, 2H), 3.91 (t, *J* = 7.6 Hz, 2H), 1.86 – 1.78 (m, 2H), 1.72 – 1.67 (m, 3H), 1.64 – 1.59 (m, 1H), 1.34 – 1.07 (m, 7H), 0.91 – 0.82 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 133.0, 131.9, 128.8, 117.5, 94.1, 90.9, 82.8, 76.1, 49.1, 37.2, 34.1, 33.3, 26.8, 26.6, 26.3.
HRMS (ESI) m/z calcd for $C_{20}H_{24}Cl^{35}{}_3NNaO_4S$ $[M+Na]^+$ 502.0384, found 502.0391. $C_{20}H_{24}Cl^{35}{}_2Cl^{37}NNaO_4S$ $[M+Na]^+$ 504.0354, found 504.0359. $C_{20}H_{24}Cl^{35}Cl^{37}{}_2NNaO_4S$ $[M+Na]^+$ 506.0325, found 506.0326. $C_{20}H_{24}Cl^{37}{}_3NNaO_4S$ $[M+Na]^+$ 508.0295, found 508.0291.

***N*-(3-Cyclohexylpropyl)-4-methyl-*N*-((phenylethynyl)sulfonyl)benzenesulfonamide (1c)**



Under a nitrogen atmosphere, the *N*-(3-cyclohexylpropyl)-2-phenylethyne-1-sulfonamide (0.92 g, 3.0 mmol) was dissolved in THF (15.0 mL) and placed at -78 ℃. *n*-BuLi (1.32 mL, 2.5 M, 3.3 mmol) was added dropwise to the solution. After stirring at -78 ℃ for 0.5 hours, tosyl chloride (0.63 g, 3.3 mmol) was added to the rection mixture which was then warmed to room temperature and stirred for further 3 hours. The reaction mixture was quenched with water (1.0 mL), washed with 1N HCl solution (7 mL) and extracted with EtOAc (7 mL × 3 times). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1), giving the product **1c** as a white solid in 65% yield (0.90 g). **TLC** R_f = 0.32 (PE:EA = 10:1). mp 188–190 ℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.86 (m, 2H), 7.58 – 7.46 (m, 3H), 7.45 – 7.37 (m, 2H), 7.35 – 7.29 (m, 2H), 3.79 (t, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 1.96 – 1.83 (m, 2H), 1.71 – 1.61 (m, 5H), 1.29 – 1.25 (m, 1H), 1.23 – 1.10 (m, 5H), 0.91 – 0.80 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 136.4, 132.9, 131.7, 129.7, 128.7, 128.4, 117.6, 90.9, 83.4, 50.6, 37.2, 34.1, 33.2, 27.4, 26.6, 26.3, 21.7.
HRMS (ESI) m/z calcd for $C_{24}H_{29}NNaO_4S_2$ $[M+Na]^+$ 482.1430, found 482.1436.

Benzyl octyl((phenylethynyl)sulfonyl)carbamate (1d)



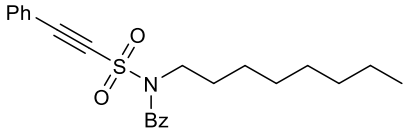
Prepared according to GP2 starting from *N*-octyl-2-phenylethyne-1-sulfonamide (0.88 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1d** as a yellow oil in 88% yield (1.08 g). **TLC** R_f = 0.25 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38– 7.33 (m, 1H), 7.33 – 7.27 (m, 2H), 7.27 – 7.20 (m, 4H), 7.21 – 7.08 (m, 3H), 5.22 (s, 2H), 3.76 (t, *J* = 7.5 Hz, 1H)., 1.68 – 1.59 (m, 2H), 1.29 – 1.10 (m, 10H), 0.76 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 134.8, 132.8, 131.7, 128.7, 128.7, 128.6, 128.2, 117.6, 90.1, 83.3, 69.4, 48.3, 31.8, 29.4, 29.2, 29.1, 26.6, 22.6, 14.1.

HRMS (ESI) m/z calcd for $C_{24}H_{29}NNaO_4S$ $[M+Na]^+$ 450.1710, found 450.1712.

***N*-Octyl-*N*-((phenylethynyl)sulfonyl)benzamide (1e)**



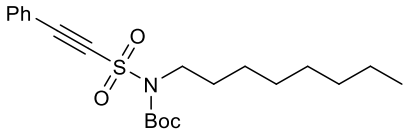
Prepared according to GP2 starting from *N*-octyl-2-phenylethyne-1-sulfonamide (0.88 g, 3.0 mmol), benzoyl chloride (0.39 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1e** as a yellow oil in 67% yield (0.77 g). **TLC** R_f = 0.3 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 1H), 7.49 – 7.47 (m, 1H), 7.48 – 7.42 (m, 1H), 7.42 – 7.38 (m, 2H), 7.38 – 7.36 (m, 2H), 7.36 – 7.32 (m, 3H), 3.79 (t, *J* = 7.6 Hz, 2H), 1.73 – 1.64 (m, 2H), 1.22 – 1.11 (m, 10H), 0.79 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 134.9, 132.9, 132.4, 131.8, 128.9, 128.6, 128.4, 117.6, 91.1, 83.2, 48.9, 31.7, 29.1, 29.0, 28.8, 26.7, 22.6, 14.1.

HRMS (ESI) m/z calcd for $C_{23}H_{27}NNaO_3S$ $[M+Na]^+$ 420.1604, found 420.1602.

***Tert*-Butyl octyl((phenylethynyl)sulfonyl)carbamate (1f)**

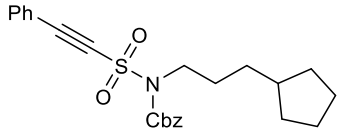


Prepared according to GP2 starting from *N*-octyl-2-phenylethyne-1-sulfonamide (0.88 g, 3.0 mmol), di-*tert*-butyl dicarbonate (0.76 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 40/1), giving the product **1f** as a yellow oil in 87% yield (1.03 g). **TLC** R_f = 0.2 (PE:EA = 40:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.39 (m, 2H), 7.38 – 7.28 (m, 3H), 3.77 – 3.64 (m, 2H), 1.68 – 1.60 (m, 2H), 1.46 (s, 9H), 1.24 – 1.10 (m, 10H), 0.80 – 0.72 (m, 3H).

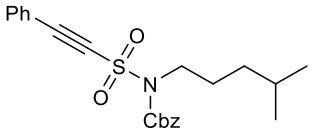
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 132.6, 131.5, 128.8, 117.9, 89.0, 84.9, 47.7, 31.7, 29.4, 29.2, 29.1, 28.4, 28.0, 26.6, 22.6, 14.1.
HRMS (ESI) m/z calcd for $C_{21}H_{31}NNaO_4S$ $[M+Na]^+$ 416.1866, found 416.1864.

Benzyl (3-cyclopentylpropyl)((phenylethynyl)sulfonyl)carbamate (1g)



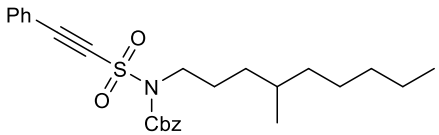
Prepared according to GP2 starting from *N*-(3-cyclopentylpropyl)-2-phenylethyne-1-sulfonamide (0.87 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1g** as a yellow solid in 76% yield (0.97 g). **TLC** R_f = 0.25 (PE:EA = 20:1). mp 90–92 ℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 1H), 7.44 – 7.40 (m, 2H), 7.39 – 7.33 (m, 4H), 7.32 – 7.27 (m, 3H), 5.34 (s, 2H), 3.86 (t, *J* = 7.5 Hz, 2H), 1.79 – 1.68 (m, 5H), 1.59 – 1.51 (m, 2H), 1.50 – 1.40 (m, 2H), 1.36 – 1.29 (m, 2H), 1.09 – 0.99 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 134.8, 132.9, 131.6, 128.7, 128.7, 128.6, 128.2, 117.6, 90.1, 83.2, 69.4, 48.5, 39.7, 32.9, 32.6, 28.6, 25.2.
HRMS (ESI) m/z calcd for $C_{24}H_{27}NNaO_4S$ $[M+Na]^+$ 448.1553, found 448.1552.

Benzyl (4-methylpentyl)((phenylethynyl)sulfonyl)carbamate (1h)



Prepared according to GP2 starting from N-(4-methylpentyl)-2-phenylethyne-1-sulfonamide (0.80 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1h** as a yellow oil in 87% yield (1.04 g). **TLC** R_f = 0.25 (PE:EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 1H), 7.36 – 7.31 (m, 2H), 7.30 – 7.24 (m, 4H), 7.24 – 7.15 (m, 3H), 5.23 (s, 2H), 3.77 (t, *J* = 7.5 Hz, 2H), 1.70 – 1.61 (m, 2H), 1.51 – 1.41 (m, 1H), 1.16 – 1.09 (m, 2H), 0.77 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 134.8, 132.9, 131.6, 128.7, 128.7, 128.6, 128.2, 117.6, 90.1, 83.2, 69.4, 48.5, 35.6, 27.7, 27.3, 22.5.
HRMS (ESI) m/z calcd for $C_{22}H_{25}NNaO_4S$ $[M+Na]^+$ 422.1397, found 422.1401.

Benzyl (4-methylnonyl)((phenylethynyl)sulfonyl)carbamate (1i)



Prepared according to GP2 starting from *N*-(4-methylnonyl)-2-phenylethyne-1-sulfonamide (0.96 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by

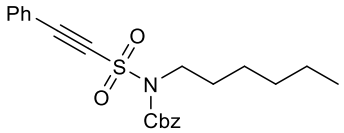
column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1i** as a yellow oil in 66% yield (0.88 g). **TLC** R_f = 0.25 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 1H), 7.44 – 7.40 (m, 2H), 7.39 – 7.33 (m, 4H), 7.33 – 7.28 (m, 3H), 5.34 (s, 2H), 3.85 (t, *J* = 7.5 Hz, 2H), 1.80 – 1.68 (m, 2H), 1.40 – 1.35 (m, 1H), 1.33 – 1.14 (m, 9H), 1.10 – 1.04 (m, 1H), 0.89 – 0.82 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 134.8, 132.9, 131.6, 128.7, 128.6, 128.6, 128.2, 117.6, 90.1, 83.2, 69.4, 48.6, 36.9, 33.7, 32.4, 32.2, 27.0, 26.7, 22.7, 19.5, 14.1.

HRMS (ESI) m/z calcd for $C_{26}H_{33}NNaO_4S$ $[M+Na]^+$ 478.2023, found 478.2030.

Benzyl hexyl((phenylethynyl)sulfonyl)carbamate (1j)



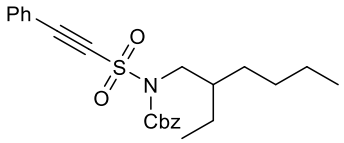
Prepared according to GP2 starting from *N*-hexyl-2-phenylethyne-1-sulfonamide (0.80 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1j** as a yellow oil in 45% yield (0.54 g). **TLC** R_f = 0.2 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 1H), 7.44 – 7.39 (m, 2H), 7.39 – 7.32 (m, 4H), 7.32 – 7.27 (m, 3H), 5.33 (s, 2H), 3.86 (t, *J* = 7.6 Hz, 2H), 1.78 – 1.70 (m, 2H), 1.36 – 1.25 (m, 6H), 0.89 – 0.83 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 134.8, 132.9, 131.6, 128.7, 128.7, 128.6, 128.2, 117.6, 90.1, 83.2, 69.4, 48.4, 31.3, 29.4, 26.2, 22.5, 14.0.

HRMS (ESI) m/z calcd for $C_{22}H_{25}NNaO_4S$ $[M+Na]^+$ 422.1397, found 422.1399.

Benzyl (2-ethylhexyl)((phenylethynyl)sulfonyl)carbamate (1k)



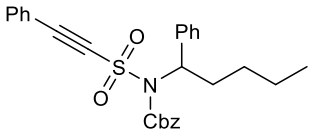
Prepared according to GP2 starting from *N*-(2-ethylhexyl)-2-phenylethyne-1-sulfonamide (0.88 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1k** as a yellow oil in 90% yield (1.15 g). **TLC** R_f = 0.2 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 1H), 7.36 – 7.31 (m, 2H), 7.30 – 7.24 (m, 4H), 7.24 – 7.17 (m, 3H), 5.25 (s, 2H), 3.70 (d, *J* = 7.4 Hz, 2H), 1.80 – 1.69 (m, 1H), 1.32 – 1.23 (m, 2H), 1.23 – 1.12 (m, 6H), 0.81 – 0.73 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 134.7, 132.8, 131.6, 128.7, 128.6, 128.6, 128.3, 117.6, 90.1, 83.2, 69.5, 51.9, 38.8, 30.2, 28.5, 23.5, 23.0, 14.0, 10.5.

HRMS (ESI) m/z calcd for $C_{24}H_{29}NNaO_4S$ $[M+Na]^+$ 450.1710, found 450.1714.

Benzyl ((phenylethynyl)sulfonyl)(1-phenylpentyl)carbamate (1l)



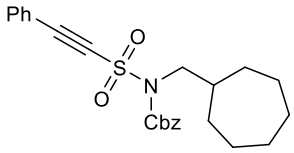
Prepared according to GP2 starting from 2-phenyl-*N*-(1-phenylpentyl)ethyne-1-sulfonamide (0.98 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1l** as a yellow oil in 80% yield (1.01 g). **TLC** R_f = 0.2 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 3H), 7.37 – 7.23 (m, 12H), 5.61 (dd, *J* = 10.0, 5.6Hz, 1H), 5.20 (s, 2H), 2.51 – 2.40 (m, 1H), 2.20 – 2.09 (m, 1H), 1.50 – 1.33 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 139.0, 134.6, 132.8, 131.6, 128.7, 128.5, 128.5, 128.3, 127.8, 127.7, 117.6, 90.3, 83.4, 69.2, 63.1, 30.7, 29.1, 22.4, 14.0.

HRMS (ESI) m/z calcd for $C_{27}H_{27}NNaO_4S$ $[M+Na]^+$ 484.1553, found 484.1560.

Benzyl (cycloheptylmethyl)((phenylethynyl)sulfonyl)carbamate (1m)



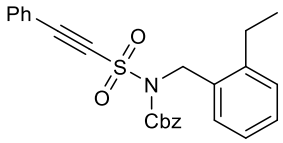
Prepared according to GP2 starting from *N*-(cycloheptylmethyl)-2-phenylethyne-1-sulfonamide (0.87 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1m** as a yellow oil in 39% yield (0.48 g). **TLC** R_f = 0.2 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 1H), 7.44 – 7.40 (m, 2H), 7.39 – 7.33 (m, 4H), 7.33 – 7.27 (m, 3H), 5.34 (s, 2H), 3.71 (d, *J* = 7.6 Hz, 2H), 2.08 – 1.98 (m, 1H), 1.77 – 1.70 (m, 2H), 1.69 – 1.57 (m, 3H), 1.55 – 1.35 (m, 5H), 1.23 – 1.13 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 134.7, 132.8, 131.6, 128.7, 128.6, 128.6, 128.2, 117.6, 90.2, 83.2, 69.5, 53.8, 39.0, 31.5, 28.3, 25.9.

HRMS (ESI) m/z calcd for $C_{24}H_{27}NNaO_4S$ $[M+Na]^+$ 448.1553, found 448.1552

Benzyl (2-ethylbenzyl)((phenylethynyl)sulfonyl)carbamate (1n)

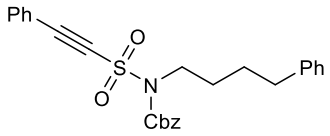


Prepared according to GP2 starting from *N*-(2-ethylbenzyl)-2-phenylethyne-1-sulfonamide (0.90 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1n** as a yellow oil in 81% yield (1.12 g). **TLC** R_f = 0.2 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 1H), 7.42 – 7.24 (m, 10H), 7.23 – 7.12

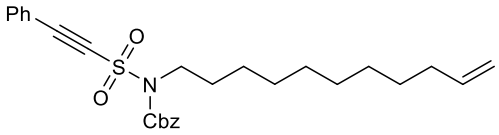
(m, 3H), 5.30 (s, 2H), 5.13 (s, 2H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.19 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 141.1, 134.5, 133.5, 132.9, 131.7, 128.7, 128.6, 128.6, 128.6, 128.3, 127.6, 126.2, 126.1, 117.5, 90.9, 83.0, 69.7, 48.2, 25.5, 14.7.
HRMS (ESI) m/z calcd for $C_{25}H_{23}NNaO_4S$ $[M+Na]^+$ 456.1240, found 456.1246.

Benzyl (4-phenylbutyl)((phenylethynyl)sulfonyl)carbamate (1o)



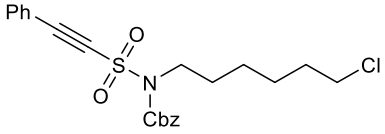
Prepared according to GP2 starting from 2-phenyl-*N*-(4-phenylbutyl)ethyne-1-sulfonamide (0.94 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1), giving the product **1o** as a yellow oil in 85% yield (1.14 g). **TLC** R_f = 0.40 (PE:EA = 5:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 1H), 7.30 – 7.26 (m, 2H), 7.24 – 7.18 (m, 4H), 7.18 – 7.14 (m, 3H), 7.14 – 7.09 (m, 2H), 7.06 – 6.99 (m, 3H), 5.20 (s, 2H), 3.80 (t, *J* = 7.2 Hz, 2H), 2.50 (t, *J* = 7.7 Hz, 2H), 1.72 – 1.63 (m, 2H), 1.59 – 1.51 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 142.0, 134.8, 132.9, 131.7, 128.8, 128.7, 128.7, 128.5, 128.4, 128.3, 125.9, 117.5, 90.3, 83.3, 69.5, 48.1, 35.5, 29.1, 28.4.
HRMS (ESI) m/z calcd for $C_{26}H_{25}NNaO_4S$ $[M+Na]^+$ 470.1397, found 470.1401.

Benzyl ((phenylethynyl)sulfonyl)(undec-10-en-1-yl)carbamate (1p)



Prepared according to GP2 starting from 2-phenyl-*N*-(undec-10-en-1-yl)ethyne-1-sulfonamide (1.00 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1p** as a yellow oil in 47% yield (0.66 g). **TLC** R_f = 0.30 (PE:EA = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 1H), 7.45 – 7.40 (m, 2H), 7.39 – 7.35 (m, 4H), 7.32 – 7.29 (m, 3H), 5.85 – 5.77 (m, 1H), 5.34 (s, 2H), 5.01 – 4.91 (m, 2H), 3.86 (t, *J* = 7.6 Hz, 2H), 2.05 – 2.00 (m, 2H), 1.78 – 1.69 (m, 2H), 1.41 – 1.26 (m, 10H), 1.23 – 1.17 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 139.2, 134.7, 132.9, 131.6, 128.7, 128.6, 128.6, 128.2, 117.6, 114.2, 90.1, 83.2, 69.4, 48.4, 33.8, 29.4, 29.4, 29.4, 29.1, 29.1, 28.9, 26.6.
HRMS (ESI) m/z calcd for $C_{27}H_{33}NNaO_4S$ $[M+Na]^+$ 490.2023, found 490.2022.

Benzyl (6-chlorohexyl)((phenylethynyl)sulfonyl)carbamate (1q)



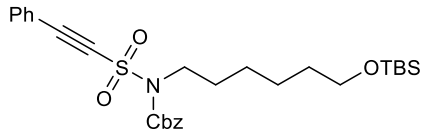
Prepared according to GP2 starting from *N*-(6-chlorohexyl)-2-phenylethyne-1-sulfonamide (0.90 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1q** as a yellow oil in 74% yield (0.96 g). **TLC** R_f = 0.30 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 1H), 7.44 – 7.41 (m, 2H), 7.40 – 7.33 (m, 4H), 7.33 – 7.27 (m, 3H), 5.34 (s, 2H), 3.87 (t, *J* = 7.4 Hz, 2H), 3.49 (t, *J* = 6.7 Hz, 2H), 1.80 – 1.70 (m, 4H), 1.49 – 1.41 (m, 2H), 1.40 – 1.32 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 134.7, 132.9, 131.7, 128.7, 128.7, 128.6, 128.3, 117.5, 90.2, 83.1, 69.5, 48.1, 44.9, 32.4, 29.2, 26.4, 25.8.

HRMS (ESI) m/z calcd for $C_{22}H_{24}ClNNaO_4S$ $[M+Na]^+$ 456.1006, found 456.1011.

Benzyl (6-((*tert*-butyldimethylsilyl)oxy)hexyl)((phenylethynyl)sulfonyl)carbamate (1r)



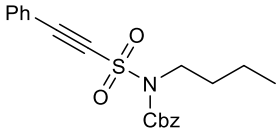
Prepared according to GP2 starting from *N*-(6-((*tert*-butyldimethylsilyl)oxy)hexyl)-2-phenylethyne-1-sulfonamide (1.19 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1), giving the product **1r** as a yellow oil in 41% yield (0.65 g). **TLC** R_f = 0.35 (PE:EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 1H), 7.44 – 7.40 (m, 2H), 7.39 – 7.34 (m, 4H), 7.33 – 7.29 (m, 3H), 5.34 (s, 2H), 3.86 (t, *J* = 7.6 Hz, 2H), 3.57 (t, *J* = 6.5 Hz, 2H), 1.78 – 1.71 (m, 2H), 1.52 – 1.46 (m, 2H), 1.38 – 1.32 (m, 4H), 0.89 (s, 9H) 0.04 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 134.7, 132.9, 131.6, 128.7, 128.6, 128.6, 128.2, 117.6, 90.1, 83.2, 69.4, 63.1, 48.3, 32.7, 29.4, 26.4, 26.0, 25.4, 18.4, -5.3.

HRMS (ESI) m/z calcd for $C_{28}H_{39}NNaO_5SSi$ $[M+Na]^+$ 552.2210, found 552.2211.

Benzyl butyl((phenylethynyl)sulfonyl)carbamate (1s)



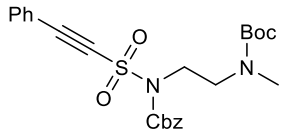
Prepared according to GP2 starting from *N*-butyl-2-phenylethyne-1-sulfonamide (0.72 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1), giving the product **1s** as a yellow oil in 76% yield (0.85 g). **TLC** R_f = 0.2 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 1H), 7.44 – 7.40 (m, 2H), 7.38 – 7.33 (m, 4H), 7.32 – 7.28 (m, 3H), 5.33 (s, 2H), 3.87 (t, *J* = 7.6 Hz, 2H), 1.76 – 1.69 (m, 2H), 1.40 – 1.33 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 134.8, 132.9, 131.6, 128.7, 128.7, 128.6, 128.2, 117.6, 90.1, 83.2, 69.4, 48.1, 31.5, 19.8, 13.7.

HRMS (ESI) m/z calcd for $C_{20}H_{21}NNaO_4S$ $[M+Na]^+$ 394.1084, found 394.1092.

***tert*-Butyl (2-((*N*-((benzyloxy)carbonyl)-2-phenylethynyl)sulfonamido)ethyl)(methyl)carbamate (1t)**



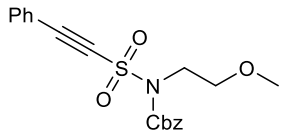
Prepared according to GP2 starting from *N*-(3-cyclopentylpropyl)-2-phenylethyne-1-sulfonamide (0.87 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1t** as a yellow oil in 60% yield (0.85 g). **TLC** R_f = 0.60 (PE:EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 1H), 7.45 – 7.41 (m, 2H), 7.41 – 7.34 (m, 4H), 7.34 – 7.28 (m, 3H), 5.35 (s, 2H), 4.06 – 3.96 (m, 2H), 3.55 – 3.46 (m, 2H), 2.87 (s, 3H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 151.9, 134.5, 133.0, 131.7, 130.5, 128.7, 128.4, 128.3, 117.4, 90.2, 82.8, 80.0, 69.7, 48.0, 45.6, 34.9, 28.4.

HRMS (ESI) m/z calcd for $C_{24}H_{28}N_2NaO_6S$ $[M+Na]^+$ 495.1560, found 495.1564.

Benzyl (2-methoxyethyl)((phenylethynyl)sulfonyl)carbamate (1u)



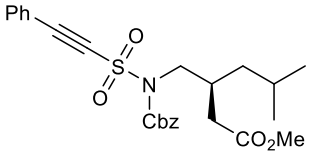
Prepared according to GP2 starting from *N*-(2-methoxyethyl)-2-phenylethyne-1-sulfonamide (0.72 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1), giving the product **1u** as a yellow oil in 40% yield (0.45 g). **TLC** R_f = 0.35 (PE:EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 1H), 7.45 – 7.41 (m, 2H), 7.39 – 7.34 (m, 4H), 7.33 – 7.27 (m, 3H), 5.35 (s, 2H), 4.08 (t, *J* = 5.7 Hz, 2H), 3.62 (t, *J* = 5.7 Hz, 2H), 3.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 134.7, 132.9, 131.6, 128.7, 128.6, 128.6, 128.2, 117.6, 90.3, 83.0, 70.0, 69.5, 58.9, 47.0.

HRMS (ESI) m/z calcd for $C_{19}H_{19}NNaO_5S$ $[M+Na]^+$ 396.0876, found 396.0882.

Methyl (*S*)-3-(((*N*-((benzyloxy)carbonyl)-2-phenylethynyl)sulfonamido)methyl)-5-methylhexanoate (1v)



Prepared according to GP2 starting from methyl (*R*)-5-methyl-3-(((phenylethynyl)sulfonamido)methyl)hexanoate (1.01 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum

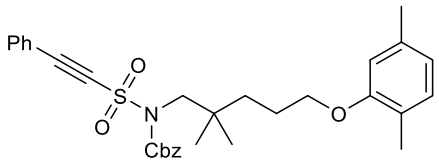
ether/ethyl acetate = 20/1), giving the product **1v** as a yellow solid in 24% yield (0.34 g). **TLC** R_f = 0.10 (PE:EA = 20:1). mp 113–115 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 1H), 7.45 – 7.41 (m, 2H), 7.39 – 7.34 (m, 4H), 7.32 – 7.29 (m, 3H), 5.34 (s, 2H), 3.89 – 3.78 (m, 2H), 3.62 (s, 3H), 2.50 – 2.39 (m, 2H), 2.32 – 2.25 (m, 1H), 1.67 – 1.60 (m, 1H), 1.20 (t, *J* = 6.9 Hz, 2H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.84 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 152.3, 134.6, 132.9, 131.7, 128.7, 128.7, 128.6, 128.4, 117.5, 90.5, 82.9, 69.7, 51.7, 51.5, 41.4, 37.0, 33.1, 25.3, 22.6, 22.6.

HRMS (ESI) m/z calcd for $C_{22}H_{24}ClNNaO_4S$ $[M+Na]^+$ 494.1608, found 494.1609.

Benzyl (5-(2,5-dimethylphenoxy)-2,2-dimethylpentyl)((phenylethynyl)sulfonyl)carbamate (1w)



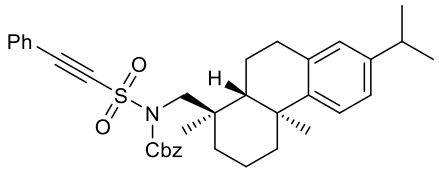
Prepared according to GP2 starting from *N*-(5-(2,5-dimethylphenoxy)-2,2-dimethylpentyl)-2-phenylethyne-1-sulfonamide (1.20 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1w** as a yellow oil in 25% yield (0.42 g). **TLC** R_f = 0.25 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 1H), 7.44 – 7.40 (m, 2H), 7.32 (d, *J* = 4.4 Hz, 4H), 7.30 – 7.26 (m, 3H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.65 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.60 (d, *J* = 1.6 Hz, 1H), 5.33 (s, 2H), 3.91 – 3.83 (m, 4H), 2.30 (s, 3H), 2.15 (s, 3H), 1.83 – 1.75 (m, 2H), 1.48 – 1.41 (m, 2H), 0.99 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 153.0, 136.5, 134.6, 132.8, 131.6, 130.3, 128.7, 128.6, 128.6, 128.4, 123.6, 120.7, 117.6, 112.1, 90.4, 83.2, 69.7, 68.4, 56.5, 36.7, 35.8, 25.3, 24.2, 21.4, 15.8.

HRMS (ESI) m/z calcd for $C_{31}H_{35}NNaO_5S$ $[M+Na]^+$ 556.2128, found 556.2132.

Benzyl (((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)((phenylethynyl)sulfonyl)carbamate (1x)



Prepared according to GP2 starting from N-(((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-2-phenylethyne-1-sulfonamide (1.35 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1x** as a yellow oil in 21% yield (0.37 g). **TLC** R_f = 0.25 (PE:EA = 20:1).

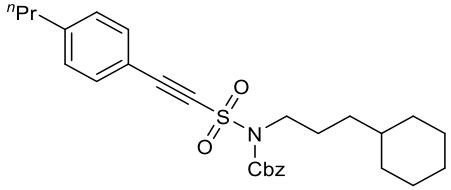
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.20 (m, 9H), 7.16 – 7.08 (m, 1H), 7.03 – 6.96 (m, 2H), 6.94 – 6.85 (m, 1H), 5.39 – 5.23 (m, 2H), 4.05 – 3.80 (m, 2H), 3.11 – 2.73

(m, 3H), 2.29 – 2.16 (m, 1H), 2.01 – 1.93 (m, 1H), 1.77 – 1.51 (m, 6H), 1.26 – 1.19 (m, 8H), 0.99 (s, 3H), 0.90 – 0.82 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 147.2, 145.6, 135.0, 134.6, 132.8, 131.4, 128.6, 128.5, 128.3, 127.0, 124.0, 123.7, 117.5, 90.5, 83.2, 69.7, 57.0, 45.2, 39.4, 38.2, 37.8, 36.4, 33.5, 30.0, 26.0, 24.1, 24.0, 19.5, 18.6, 18.5.

HRMS (ESI) m/z calcd for $C_{36}H_{41}NNaO_4S$ $[M+Na]^+$ 606.2649, found 606.2650.

enzyl (3-cyclohexylpropyl)(((4-propylphenyl)ethynyl)sulfonyl)carbamate (1aa)



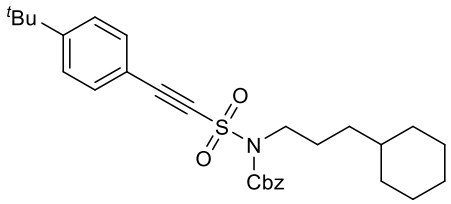
Prepared according to GP2 starting from *N*-(3-cyclohexylpropyl)-2-(4-propylphenyl)ethyne-1-sulfonamide (1.04 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1aa** as a white solid in 80% yield (1.16 g). **TLC** R_f = 0.25 (PE:EA = 20:1). mp 109–111 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.34 – 7.27 (m, 5H), 7.19 – 7.13 (m, 2H), 5.33 (s, 2H), 3.83 (t, *J* = 7.6 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.78 – 1.71 (m, 2H), 1.69 – 1.59 (m, 7H), 1.24 – 1.10 (m, 6H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.88 – 0.78 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 147.2, 134.8, 132.9, 128.9, 128.6, 128.5, 128.2, 114.7, 90.9, 82.9, 69.3, 48.6, 38.1, 37.2, 34.1, 33.2, 26.8, 26.6, 26.3, 24.2, 13.7.

HRMS (ESI) m/z calcd for $C_{28}H_{35}NNaO_4S$ $[M+Na]^+$ 504.2179, found 504.2182.

Benzyl (((4-(*tert*-butyl)phenyl)ethynyl)sulfonyl)(3-cyclohexylpropyl)carbamate (1ab)



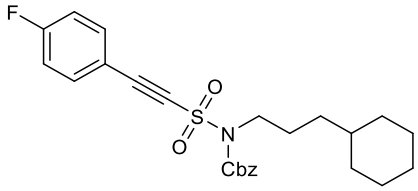
Prepared according to GP2 starting from 2-(4-(tert-butyl)phenyl)-*N*-(3-cyclohexylpropyl)ethyne-1-sulfonamide (1.08 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1ab** as a yellow oil in 76% yield (1.13 g). **TLC** R_f = 0.25 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.39 – 7.30 (m, 7H), 5.33 (s, 2H), 3.84 (t, *J* = 7.6 Hz, 2H), 1.78 – 1.70 (m, 2H), 1.68 – 1.60 (m, 5H), 1.32 (s, 9H), 1.24 – 1.10 (m, 6H), 0.88 – 0.80 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 152.2, 134.8, 132.8, 128.6, 128.5, 128.2, 125.7, 114.5, 90.9, 82.8, 69.3, 48.6, 37.2, 35.2, 34.1, 33.2, 31.0, 26.8, 26.6, 26.3.

HRMS (ESI) m/z calcd for $C_{29}H_{37}NNaO_4S$ $[M+Na]^+$ 518.2336, found 518.2343.

Benzyl (3-cyclohexylpropyl)(((4-fluorophenyl)ethynyl)sulfonyl)carbamate (1ac)



Prepared according to GP2 starting from *N*-(3-cyclohexylpropyl)-2-(4-fluorophenyl)ethyne-1-sulfonamide (0.97 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1ac** as a pale yellow solid in 55% yield (0.75 g). **TLC** R_f = 0.2 (PE:EA = 20:1). mp 107–109 °C.

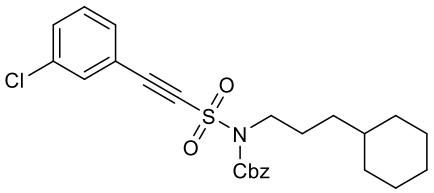
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.38 – 7.34 (m, 2H), 7.33 – 7.31 (m, 3H), 7.07 – 7.02 (m, 2H), 5.33 (s, 2H), 3.83 (t, *J* = 7.4 Hz, 2H), 1.77 – 1.71 (m, 2H), 1.68 – 1.63 (m, 5H), 1.23 – 1.17 (m, 4H), 1.15 – 1.06 (m, 2H), 0.88 – 0.79 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4 (d, *J* = 256.3 Hz), 152.1, 135.2 (d, *J* = 9.2 Hz), 134.7, 128.7, 128.6, 128.3, 116.3 (d, *J* = 22.6 Hz), 113.7 (d, *J* = 3.7 Hz), 89.0, 83.2, 69.4, 48.6, 37.2, 34.1, 33.2, 26.8, 26.6, 26.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ 104.3.

HRMS (ESI) m/z calcd for $C_{25}H_{28}FNNaO_4S$ $[M+Na]^+$ 480.1615, found 480.1620.

Benzyl (((3-chlorophenyl)ethynyl)sulfonyl)(3-cyclohexylpropyl)carbamate (1ad)



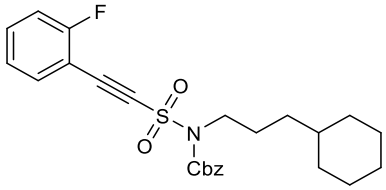
Prepared according to GP2 starting from 2-(3-chlorophenyl)-*N*-(3-cyclohexylpropyl)ethyne-1-sulfonamide (1.02 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1ad** as a yellow oil in 38% yield (0.54 g). **TLC** R_f = 0.2 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 3H), 7.34 – 7.31 (m, 3H), 7.31 – 7.23 (m, 3H), 5.34 (s, 2H), 3.84 (t, *J* = 7.6 Hz, 2H), 1.78 – 1.71 (m, 2H), 1.69 – 1.64 (m, 5H), 1.23 – 1.10 (m, 6H), 0.88 – 0.80 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 134.7, 134.6, 132.5, 131.9, 130.9, 130.0, 128.7, 128.7, 128.3, 119.3, 87.9, 84.0, 69.5, 48.6, 37.2, 34.1, 33.3, 26.8, 26.6, 26.3.

HRMS (ESI) m/z calcd for $C_{25}H_{28}Cl^{35}NNaO_4S$ $[M+Na]^+$ 496.1320, found 496.1322. $C_{25}H_{28}Cl^{37}NNaO_4S$ $[M+Na]^+$ 498.1290, found 498.1294.

Benzyl (3-cyclohexylpropyl)(((2-fluorophenyl)ethynyl)sulfonyl)carbamate (1ae)



Prepared according to GP2 starting from *N*-(3-cyclohexylpropyl)-2-(2-fluorophenyl)ethyne-1-sulfonamide (0.97 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1ae** as a pale yellow oil in 36% yield (0.50 g). **TLC** R_f = 0.2 (PE:EA = 20:1).

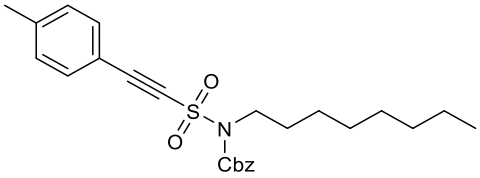
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 1H), 7 .44 – 7.40 (m, 2H), 7.37 – 7.27 (m, 4H), 7.19 – 7.08 (m, 2H), 5.34 (s, 2H), 3.85 (t, *J* = 7.6 Hz, 2H), 1.78 – 1.72 (m, 2H), 1.68 – 1.61 (m, 5H), 1.26 – 1.11 (m, 6H), 0.89 – 0.79 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6 (d, *J* = 258.5 Hz), 152.1, 134.7, 134.4, 133.7 (d, *J* = 8.2 Hz), 128.6, 128.5, 128.2, 124.4 (d, *J* = 3.8 Hz), 116.0 (d, *J* = 20.0 Hz), 106.8 (d, *J* = 15.3 Hz), 87.7, 83.7, 69.4, 48.7, 37.2, 34.1, 33.2, 26.7, 26.6, 26.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ 106.1.

HRMS (ESI) m/z calcd for $C_{25}H_{28}FNNaO_4S$ $[M+Na]^+$ 480.1615, found 480.1617.

Benzyl octyl((*p*-tolylethynyl)sulfonyl)carbamate (1af)



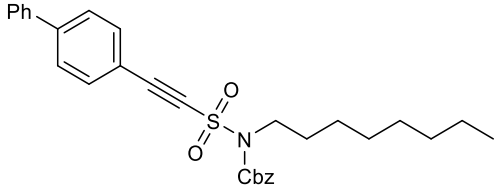
Prepared according to GP2 starting from *N*-octyl-2-(*p*-tolyl)ethyne-1-sulfonamide (0.92 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1af** as a yellow oil in 89% yield (1.18 g). **TLC** R_f = 0.25 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 2H), 7.29 – 7.20 (m, 3H), 7.19 – 7.14 (m, 2H), 7.09 – 7.01 (m, 2H), 5.24 (s, 2H), 3.77 (t, *J* = 7.6 Hz, 2H), 2.29 (s, 3H), 1.68 – 1.59 (m, 2H), 1.24 – 1.09 (m, 10H), 0.77 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 142.5, 134.8, 132.8, 129.5, 128.6, 128.5, 128.2, 114.4, 90.8, 82.9, 69.3, 48.3, 31.8, 29.4, 29.2, 29.1, 26.6, 22.6, 21.8, 14.1.

HRMS (ESI) m/z calcd for $C_{25}H_{31}NNaO_4S$ $[M+Na]^+$ 464.1866, found 464.1869.

Benzyl (([1,1'-biphenyl]-4-ylethynyl)sulfonyl)(octyl)carbamate (1ag)



Prepared according to GP2 starting from 2-([1,1'-biphenyl]-4-yl)-*N*-octylethyne-1-

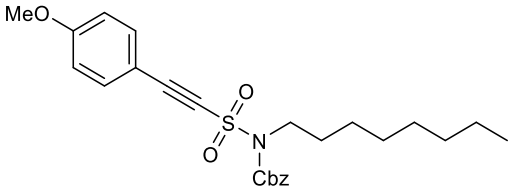
sulfonamide (1.11 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1ag** as a yellow solid in 82% yield (1.24 g). **TLC** R_f = 0.25 (PE:EA = 20:1). mp 40–42 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 4H), 7.50 – 7.39 (m, 7H), 7.35 – 7.27 (m, 3H), 5.35 (s, 2H), 3.88 (t, *J* = 7.5 Hz, 2H), 1.79 – 1.70 (m, 2H), 1.35 – 1.20 (m, 10H), 0.86 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 144.4, 139.5, 134.8, 133.4, 129.1, 128.7, 128.6, 128.5, 128.2, 127.3, 127.2, 116.2, 90.3, 83.8, 69.4, 48.4, 31.8, 29.5, 29.2, 29.2, 26.6, 22.7, 14.1.

HRMS (ESI) m/z calcd for $C_{30}H_{33}NNaO_4S$ $[M+Na]^+$ 526.2023, found 526.2024.

Benzyl (((4-methoxyphenyl)ethynyl)sulfonyl)(octyl)carbamate (1ah)



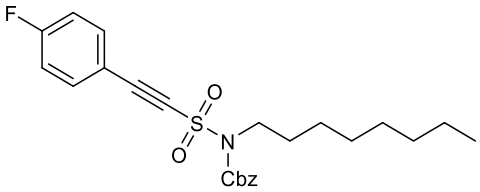
Prepared according to GP2 starting from 2-(4-methoxyphenyl)-*N*-octylethyne-1-sulfonamide (0.97 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1ah** as a yellow oil in 89% yield (1.22 g). **TLC** R_f = 0.25 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2H), 7.36 – 7.25 (m, 5H), 6.88 – 6.79 (m, 2H), 5.33 (s, 2H), 3.85 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.77 – 1.69 (m, 2H), 1.40 – 1.16 (m, 10 H), 0.86 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 152.2, 134.8, 128.6, 128.5, 128.2, 114.4, 109.2, 91.3, 82.6, 69.3, 55.5, 48.3, 31.8, 29.4, 29.2, 29.1, 26.6, 22.6, 14.1.

HRMS (ESI) m/z calcd for $C_{25}H_{31}NNaO_5S$ $[M+Na]^+$ 480.1815, found 480.1819.

Benzyl (((4-fluorophenyl)ethynyl)sulfonyl)(octyl)carbamate (1ai)



Prepared according to GP2 starting from 2-(4-fluorophenyl)-*N*-octylethyne-1-sulfonamide (0.93 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1ai** as a pale yellow oil in 30% yield (0.40 g). **TLC** R_f = 0.2 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.36 – 7.29 (m, 5H), 7.07 – 7.01 (m, 2H), 5.34 (s, 2H), 3.86 (t, *J* = 7.6 Hz, 2H), 1.77 – 1.68 (m, 2H), 1.31 – 1.22 (m, 10H), 0.86 (t, *J* = 6.9 Hz, 3H).

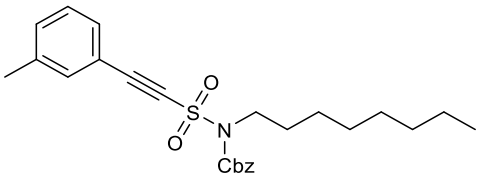
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4 (d, *J* = 256.3 Hz), 152.1, 135.2 (d, *J* = 9.1 Hz),

134.8, 128.6, 128.6, 128.2, 116.3 (d, *J* = 22.6 Hz), 113.8 (d, *J* = 3.5 Hz), 89.0, 83.2, 69.4, 48.3, 31.7, 29.4, 29.1, 29.1, 26.6, 22.6, 14.0.

^{19}F NMR (377 MHz, $CDCl_3$) δ 104.3.

HRMS (ESI) m/z calcd for $C_{24}H_{28}FNNaO_4S$ $[M+Na]^+$ 468.1615, found 468.1618.

Benzyl octyl((*m*-tolylethynyl)sulfonyl)carbamate (1aj)



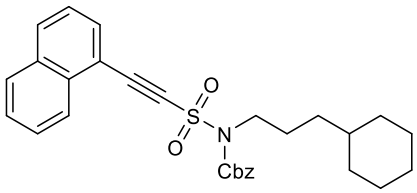
Prepared according to GP2 starting from N-octyl-2-(*m*-tolyl)ethyne-1-sulfonamide (0.92 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1aj** as a yellow oil in 34% yield (0.45 g). **TLC** R_f = 0.25 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.33 – 7.22 (m, 5H), 7.22 – 7.17 (m, 2H), 5.34 (s, 2H), 3.86 (t, *J* = 7.6 Hz, 2H), 2.32 (s, 3H), 1.77 – 1.69 (m, 2H), 1.33 – 1.21 (m, 10H), 0.86 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 138.6, 134.8, 133.2, 132.5, 130.0, 128.6, 128.6, 128.5, 128.2, 117.4, 90.5, 82.9, 69.4, 48.3, 31.8, 29.4, 29.2, 29.1, 26.6, 22.6, 21.1, 14.1.

HRMS (ESI) m/z calcd for $C_{25}H_{31}NNaO_4S$ $[M+Na]^+$ 464.1866, found 464.1869.

Benzyl (3-cyclohexylpropyl)((naphthalen-1-ylethynyl)sulfonyl)carbamate (1ak)



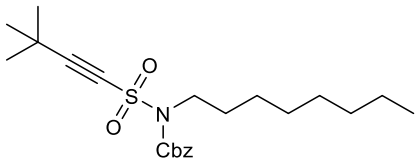
Prepared according to GP2 starting from *N*-(3-cyclohexylpropyl)-2-(naphthalen-1-yl)ethyne-1-sulfonamide (1.07 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1ak** as a yellow oil in 81% yield (1.19 g). **TLC** R_f = 0.25 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.88 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.64 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.46 – 7.38 (m, 3H), 7.25 – 7.22 (m, 3H), 5.35 (s, 2H), 3.90 (t, *J* = 7.6 Hz, 2H), 1.83 – 1.75 (m, 2H), 1.69 – 1.59 (m, 5H), 1.26 – 1.22 (m, 2H), 1.21 – 1.14 (m, 2H), 1.14 – 1.03 (m, 2H), 0.87 – 0.77 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 134.7, 133.4, 133.3, 132.9, 132.4, 128.6, 128.6, 128.5, 128.1, 127.2, 125.4, 125.0, 115.1, 89.1, 87.7, 69.4, 48.7, 37.3, 34.1, 33.2, 26.8, 26.6, 26.3.

HRMS (ESI) m/z calcd for $C_{29}H_{31}NNaO_4S$ $[M+Na]^+$ 512.1866, found 512.1863.

Benzyl ((3,3-dimethylbut-1-yn-1-yl)sulfonyl)(octyl)carbamate (1al)



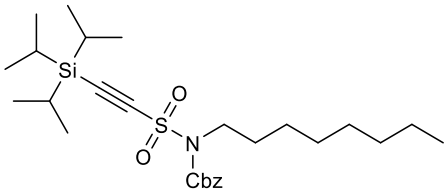
Prepared according to GP2 starting from 3,3-dimethyl-*N*-octylbut-1-yne-1-sulfonamide (0.82 g, 3.0 mmol), benzyl chloroformate (0.47 mL, 3.3 mmol), DMAP (3.7 mg, 0.03 mmol) and Et_3N (1.04 mL, 7.5 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 30/1), giving the product **1al** as a pale yellow oil in 55% yield (0.67 g). **TLC** R_f = 0.32 (PE:EA = 30:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.38 – 7.33 (m, 3H), 5.31 (s, 2H), 3.80 (t, *J* = 7.6 Hz, 2H), 1.72 – 1.65 (m, 2H), 1.31 – 1.25 (m, 10H), 1.16 (s, 9H), 0.87 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 134.9, 128.6, 128.5, 128.1, 100.5, 74.7, 69.2, 48.2, 31.8, 29.2, 29.2, 29.1, 27.7, 26.6, 22.6, 14.1.

HRMS (ESI) m/z calcd for $C_{22}H_{33}NNaO_4S$ $[M+Na]^+$ 430.2023 found 430.2018.

Benzyl octyl(((triisopropylsilyl)ethynyl)sulfonyl)carbamate (1am)



Prepared according to GP2 starting from *N*-octyl-2-(triisopropylsilyl)ethyne-1-sulfonamide (2.58 g, 6.9 mmol), benzyl chloroformate (1.08 mL, 7.6 mmol), DMAP (8.5 mg, 0.07 mmol) and Et_3N (2.39 mL, 17.3 mmol). The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1), giving the product **1am** as a yellow oil in 90% yield (3.15 g). **TLC** R_f = 0.60 (PE:EA = 20:1).

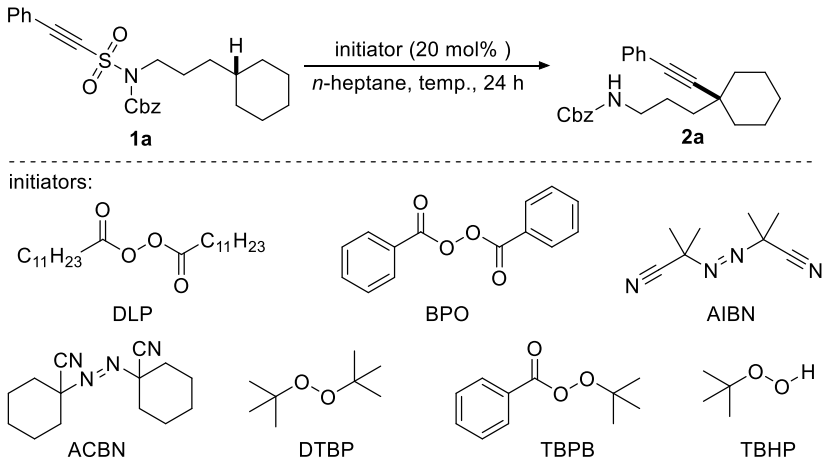
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 5H), 5.29 (s, 2H), 3.82 (t, *J* = 7.6 Hz, 2H), 1.74 – 1.65 (m, 2H), 1.31 – 1.22 (m, 10H), 1.07 – 0.99 (m, 21H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 134.7, 128.6, 128.5, 127.9, 97.8, 96.5, 69.4, 48.2, 31.8, 29.1, 26.6, 22.6, 18.3, 14.1, 10.8.

HRMS (ESI) m/z calcd for $C_{27}H_{45}NNaSiO_4S$ $[M+Na]^+$ 530.2731, found 530.2734.

4. Optimization of the reaction conditions and control experiments

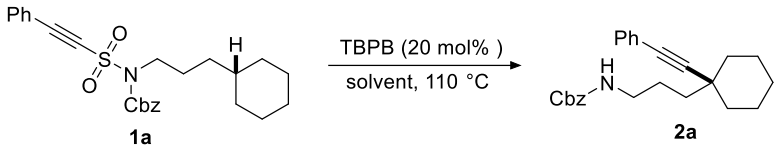
4.1 Screenings of radical initiators



Entry[a]	Solvent	Initiator	Temperature (℃)	Yield (%)[b]
1	heptane	DLP	85	46
2	heptane	AIBN	85	41
3	heptane	BPO	85	34
4	heptane	ACCN	85	41
5	heptane	TPHP	85	23
6	heptane	DTBP	110	63
7	heptane	TBPB	110	84

[a] Reaction conditions: **1a** (0.1 mmol) and initiator (20 mol%) in heptane (0.5 mL) were stirred at the indicated temperature for 24 h under N_2. [b] Yields were determined by ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard.

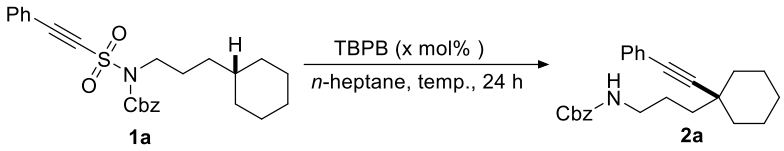
4.2 Screenings of solvents



Entry	Eolvent	Initiator	Yield (%)
1	EtOAc	TBPB	67
2	MeCN	TBPB	55
3	toluene	TBPB	53
4	DMF	TBPB	N.D.
5	THF	TBPB	54
6	DCE	TBPB	70
7	DME	TBPB	56
8	DCM	TBPB	57
9	chlorobenzene	TBPB	52

[a] Reaction conditions: **1a** (0.1 mmol) and TBPB (20 mol%) in solvent (0.5 mL) were stirred at 110 °C for 24 h under N_2. [b] Yields were determined by ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard.

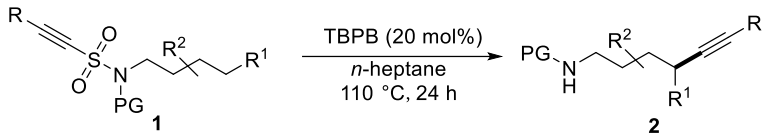
4.3 Screenings of reaction temperature and initiator loading



Entry[a]	Initiator loading (mol%)	Temp (℃)	Yield (%)[b]
1	20	80	15
2	20	100	72
3	20	120	73
4	20	140	72
5	10	110	62
6	30	110	49
7	50	110	47

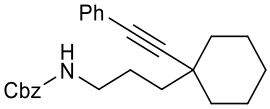
[a] Reaction conditions: **1a** (0.1 mmol) and initiator (x mol %) in *n*-heptane (0.5 mL) were stirred at the indicated temperature for 24 h under N_2. [b] Yields were determined by ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard.

5. General procedure and characterization data for the alkynylation products GP3.



To a solution of *N*-protected ethynesulfonamides **1** (0.20 mmol, 1.0 equiv) in 1.0 mL of heptane under argon was added *tert*-butyl peroxybenzoate (0.04 mmol, 20 mol%). The reaction mixture was stirred at 110 ºC for 24 hours. The product was purified by flash column chromatography on silica gel with *n*-pentane/ethyl ether as an eluent to give the corresponding product **2**.

Benzyl (3-(1-(phenylethynyl)cyclohexyl)propyl)carbamate (2a)



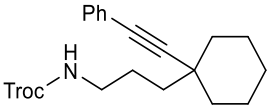
Prepared according to GP3 starting from benzyl (3-cyclohexylpropyl)((phenylethynyl)sulfonyl)carbamate (87.9 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2a** as a yellow oil in 88% yield (66.1 mg). **TLC** R_f = 0.40 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.30 – 7.25 (m, 5H), 7.20 – 7.18 (m, 3H), 5.02 (s, 2H), 4.71 (brs, 1H), 3.21 – 3.14 (m, 2H), 1.79 – 1.72 (m, 2H), 1.71 – 1.57 (m, 5H), 1.55 – 1.52 (m, 1H), 1.43 – 1.37 (m, 2H), 1.25 – 1.02 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 136.7, 131.6, 128.5, 128.2, 128.1, 128.1, 127.5, 123.6, 95.0, 83.5, 66.6, 41.5, 40.1, 37.9, 37.0, 26.2, 25.1, 23.7.

HRMS (ESI) m/z calcd for $C_{22}H_{25}NNaO_2$ $[M+Na]^+$ 398.2091, found 398.2092.

2,2,2-Trichloroethyl (3-(1-(phenylethynyl)cyclohexyl)propyl)carbamate (2b)



Prepared according to GP3 starting from 2,2,2-trichloroethyl (3-cyclohexylpropyl)((phenylethynyl)sulfonyl)carbamate (96.2 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2b** as a yellow oil in 46% yield (38.3 mg). **TLC** R_f = 0.40 (PE:EA = 10:1).

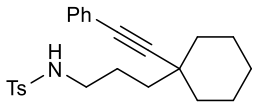
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 2H), 7.29 – 7.26 (m, 3H), 5.02 (t, *J* = 6.3 Hz, 1H), 4.72 (s, 2H), 3.32 – 3.26 (m, 2H), 1.87 – 1.77 (m, 4H), 1.73 – 1.66 (m, 3H), 1.64 – 1.59 (m, 2H), 1.52 – 1.47 (m, 2H), 1.24 – 1.15 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 131.6, 128.2, 127.5, 124.0, 95.7, 94.9, 83.6, 74.5, 41.7, 40.0, 38.0, 37.0, 26.2, 25.0, 23.2.

HRMS (ESI) m/z calcd for $C_{20}H_{24}Cl^{35}{}_3NNaO_2$ $[M+Na]^+$ 438.0765, found 438.0768. $C_{20}H_{24}Cl^{35}{}_2Cl^{37}NNaO_2$ $[M+Na]^+$ 440.0735, found 440.0738. $C_{20}H_{24}Cl^{35}Cl^{37}{}_2NNaO_2$

$[M+Na]^+$ 442.0706, found 442.0706. $C_{20}H_{24}Cl^{37}{}_3NNaO_2$ $[M+Na]^+$ 444.0676, found 438.0782.

4-Methyl-*N*-(3-(1-(phenylethynyl)cyclohexyl)propyl)benzenesulfonamide (2c)



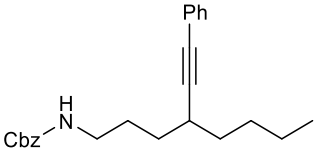
Prepared according to GP3 starting from *N*-(3-cyclohexylpropyl)-4-methyl-*N*-((phenylethynyl)sulfonyl)benzenesulfonamide (91.9 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2c** as a white solid in 59% yield (46.7 mg). **TLC** R_f = 0.20 (PE:EA = 10:1). mp 153–155 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2H), 7.40 – 7.32 (m, 2H), 7.31 – 7.23 (m, 5H), 4.71 (t, *J* = 6.2 Hz, 1H), 3.08 – 2.92 (m, 2H), 2.38 (s, 3H), 1.77 – 1.62 (m, 7H), 1.60 – 1.54 (m, 2H), 1.43 – 1.37 (m, 2H), 1.17 – 1.08 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 137.1, 131.6, 129.7, 128.2, 127.5, 127.1, 124.0, 94.8, 83.6, 43.7, 39.9, 37.9, 36.8, 26.2, 24.8, 23.2, 21.5.

HRMS (ESI) m/z calcd for $C_{24}H_{29}NNaO_2S$ $[M+Na]^+$ 418.1811, found 418.1819.

Benzyl (4-(phenylethynyl)octyl)carbamate (2d)



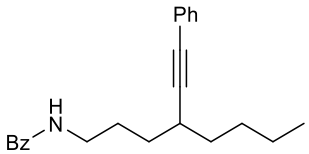
Prepared according to GP3 starting from benzyl octyl((phenylethynyl)sulfonyl)carbamate (85.5 mg, 0.2 mmol) and tert-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2d** as a yellow oil in 63% yield (45.8 mg). **TLC** R_f = 0.40 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H), 7.28 – 7.25 (m, 4H), 7.25 – 7.22 (m, 1H), 7.20 – 7.16 (m, 3H), 5.02 (s, 2H), 4.74 (brs, 1H), 3.21 – 3.13 (m, 2H), 2.49 – 2.42 (m, 1H), 1.75 – 1.65 (m, 1H), 1.61 – 1.52 (m, 1H), 1.48 – 1.40 (m, 5H), 1.36 – 1.21 (m, 3H), 0.84 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 136.7, 131.6, 128.5, 128.2, 128.1, 128.1, 127.6, 124.0, 93.1, 82.2, 66.6, 41.0, 35.0, 32.3, 32.1, 29.7, 28.0, 22.6, 14.1.

HRMS (ESI) m/z calcd for $C_{24}H_{29}NNaO_2$ $[M+Na]^+$ 386.2091, found 386.2094.

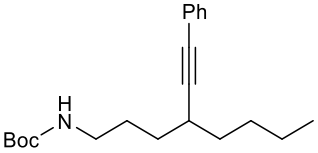
***N*-(4-(Phenylethynyl)octyl)benzamide (2e)**



Prepared according to GP3 starting from *N*-octyl-*N*-((phenylethynyl)sulfonyl)benzamide (79.5 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2e** as yellow oil in 54% yield (36.0 mg). **TLC** R_f = 0.40 (PE:EA = 10:1).

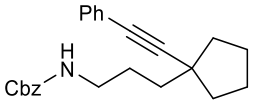
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.52 (m, 2H), 7.46 – 7.34 (m, 1H), 7.32 – 7.20 (m, 4H), 7.21 – 6.99 (m, 3H), 6.25 (brs, 1H), 3.50 – 3.32 (m, 2H), 2.58 – 2.38 (m, 1H), 1.83 – 1.68 (m, 2H), 1.61 – 1.49 (m, 2H), 1.46 – 1.42 (m, 2H), 1.37 – 1.31 (m, 1H), 1.31 – 1.22 (m, 2H), 1.20 – 1.16 (m, 1H), 0.84 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 134.8, 131.6, 131.3, 128.5, 128.2, 127.6, 126.9, 123.9, 93.2, 82.2, 40.0, 35.0, 32.5, 32.2, 29.7, 27.0, 22.6, 14.1.
HRMS (ESI) m/z calcd for $C_{23}H_{27}NNaO$ $[M+Na]^+$ 356.1985, found 356.1987.

***tert*-Butyl (4-(phenylethynyl)octyl)carbamate (2f)**



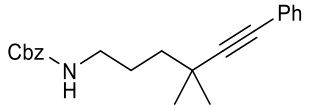
Prepared according to GP3 starting from *tert*-butyl octyl((phenylethynyl)sulfonyl)carbamate (78.7 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2f** as a yellow oil in 54% yield (35.6 mg). **TLC** R_f = 0.40 (PE:EA = 10:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.22 – 7.18 (m, 3H), 4.49 (brs, 1H), 3.13 – 3.05 (m, 2H), 2.50 – 2.41 (m, 1H), 1.76 – 1.61 (m, 2H), 1.60 – 1.54 (m, 1H), 1.48 – 1.43 (m, 4H), 1.37 (s, 9H), 1.31 – 1.24 (m, 2H), 1.21 – 1.15 (m, 1H), 0.85 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 131.6, 128.2, 127.5, 124.0, 93.2, 82.1, 79.1, 40.5, 35.0, 32.3, 32.1, 29.6, 28.4, 28.1, 22.6, 14.1.
HRMS (ESI) m/z calcd for $C_{21}H_{31}NNaO_2$ $[M+Na]^+$ 352.2247, found 352.2255.

Benzyl (3-(1-(phenylethynyl)cyclopentyl)propyl)carbamate (2g)



Prepared according to GP3 starting from benzyl (3-cyclopentylpropyl)((phenylethynyl)sulfonyl)carbamate (85.1 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2g** as a pale yellow solid in 88% yield (63.6 mg). **TLC** R_f = 0.40 (PE:EA = 10:1). mp 94–96 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 6H), 7.31 – 7.25 (m, 2H), 7.24 – 7.22 (m, 2H), 5.09 (s, 2H), 4.86 (brs, 1H), 3.28 – 3.20 (m, 2H), 2.00 – 1.93 (m, 2H), 1.87 – 1.81 (m, 2H), 1.78 – 1.72 (m, 2H), 1.70 – 1.63 (m, 2H), 1.58 – 1.49 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 136.7, 131.6, 128.5, 128.2, 128.1, 128.1, 127.5, 124.1, 96.8, 81.3, 66.6, 43.0, 41.4, 40.2, 37.9, 27.2, 24.2.
HRMS (ESI) m/z calcd for $C_{24}H_{27}NNaO_2$ $[M+Na]^+$ 384.1934, found 384.1939.

Benzyl (4,4-dimethyl-6-phenylhex-5-yn-1-yl)carbamate (2h)



Prepared according to GP2 starting from benzyl (4-

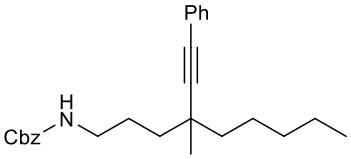
methylpentyl)((phenylethynyl)sulfonyl)carbamate (80.0 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2h** as a yellow oil in 74% yield (49.6 mg). **TLC** R_f = 0.40 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 6H), 7.22 – 7.13 (m, 4H), 5.02 (s, 2H), 4.73 (brs, 1H), 3.21 – 3.15 (m, 2H), 1.69 – 1.62 (m, 2H), 1.44 – 1.39 (m, 2H), 1.20 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 136.7, 131.6, 128.5, 128.2, 128.1, 128.1, 127.6, 123.8, 96.8, 80.7, 66.6, 41.4, 40.4, 31.5, 29.3, 26.2.

HRMS (ESI) m/z calcd for $C_{22}H_{25}NNaO_2$ $[M+Na]^+$ 358.1777, found 358.1775.

Benzyl (4-methyl-4-(phenylethynyl)nonyl)carbamate (2i)



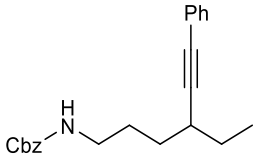
Prepared according to GP3 starting from benzyl (4-methylnonyl)((phenylethynyl)sulfonyl)carbamate (91.1 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2i** as a yellow oil in 86% yield (67.3 mg). **TLC** R_f = 0.40 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 6H), 7.33 – 7.30 (m, 1H), 7.27 – 7.24 (m, 3H), 5.10 (s, 2H), 4.79 (brs, 1H), 3.29 – 3.21 (m, 2H), 1.76 – 1.67 (m, 2H), 1.55 – 1.49 (m, 2H), 1.48 – 1.38 (m, 4H), 1.36 – 1.28 (m, 4H), 1.22 (s, 3H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 136.7, 131.6, 128.5, 128.2, 128.1, 127.5, 124.0, 96.1, 81.7, 66.6, 41.8, 41.5, 38.7, 35.2, 32.3, 26.5, 25.7, 24.6, 22.6, 14.1.

HRMS (ESI) m/z calcd for $C_{26}H_{33}NNaO_2$ $[M+Na]^+$ 414.2404, found 414.2404.

Benzyl (4-ethyl-6-phenylhex-5-yn-1-yl)carbamate (2j)



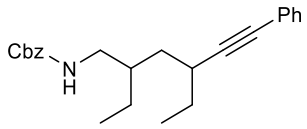
Prepared according to GP3 starting from benzyl hexyl((phenylethynyl)sulfonyl)carbamate (79.9 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2j** as a yellow oil in 71% yield (50.9 mg). **TLC** R_f = 0.35 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 2H), 7.36 – 7.33 (m, 4H), 7.33 – 7.27 (m, 3H), 7.26 – 7.24 (m, 1H), 5.10 (s, 2H), 4.79 (brs, 1H), 3.30 – 3.22 (m, 2H), 2.53 – 2.43 (m, 1H), 1.82 – 1.74 (m, 1H), 1.71 – 1.64 (m, 1H), 1.58 – 1.51 (m, 4H), 1.05 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 136.6, 131.6, 128.5, 128.2, 128.1, 127.6, 123.9, 92.9, 82.3, 66.6, 41.0, 33.8, 31.9, 28.3, 28.0, 11.9.

HRMS (ESI) m/z calcd for $C_{22}H_{25}NNaO_2$ $[M+Na]^+$ 358.1777, found 358.1777.

Benzyl (2,4-diethyl-6-phenylhex-5-yn-1-yl)carbamate (2k)



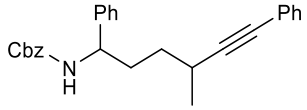
Prepared according to GP3 starting from benzyl (2-ethylhexyl)((phenylethynyl)sulfonyl)carbamate (85.5 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2k** as a yellow oil in 68% yield (49.4 mg, 1.3:1 dr). **TLC** R_f = 0.40 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$, mixture of diastereoisomers) δ 7.33 – 7.28 (m, 2H), 7.28 – 7.21 (m, 5H), 7.20 – 7.14 (m, 3H), 5.01 (s, 2H, major diastereoisomer), 5.00 (s, 2H, minor diastereoisomer), 4.80 (brs, 1H), 3.26 – 3.07 (m, 2H), 2.57 – 2.39 (m, 1H), 1.74 – 1.66 (m, 1H), 1.51 – 1.38 (m, 3H), 1.36 – 1.21 (m, 3H), 1.02 – 0.94 (m, 3H), 0.88 – 0.82 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, mixture of diastereoisomers) δ 156.6, 136.7, 131.6, 131.6, 128.5, 128.2, 128.1, 128.1, 127.6, 123.9, 123.9, 93.2, 93.1, 82.4, 82.3, 66.6, 44.2, 43.4, 38.2, 38.1, 37.0, 36.7, 32.1, 31.7, 28.9, 28.9, 28.8, 28.8, 25.1, 23.9, 11.9, 11.2, 10.7.

HRMS (ESI) m/z calcd for $C_{24}H_{29}NNaO_2$ $[M+Na]^+$ 386.2091, found 386.2092.

Benzyl (4-methyl-1,6-diphenylhex-5-yn-1-yl)carbamate (2l)



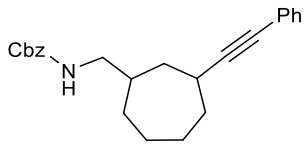
Prepared according to GP3 starting from benzyl ((phenylethynyl)sulfonyl)(1-phenylpentyl)carbamate (92.3 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2l** as a pale yellow solid in 78% yield (62.0 mg, 1.1:1 dr). **TLC** R_f = 0.30 (PE:EA = 10:1). mp 133–135 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, mixture of diastereoisomers) δ 7.38 – 7.23 (m, 15H), 5.13 – 5.00 (m, 3H), 4.82 – 4.64 (m, 1H), 2.70 – 2.59 (m, 1H), 2.09 – 1.88 (m, 2H), 1.59 – 1.38 (m, 2H), 1.25 – 1.18 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, mixture of diastereoisomers) δ 155.8, 142.6, 136.5, 131.6, 128.7, 128.7, 128.5, 128.2, 127.6, 127.5, 127.4, 126.5, 126.3, 123.8, 93.9, 81.3, 66.8, 55.5, 55.2, 34.7, 34.4, 33.5, 33.4, 26.5, 26.3, 21.2, 21.1.

HRMS (ESI) m/z calcd for $C_{27}H_{27}NNaO_2$ $[M+Na]^+$ 420.1934, found 420.1939.

Benzyl ((3-(phenylethynyl)cycloheptyl)methyl)carbamate (2m)



Prepared according to GP3 starting from benzyl (3-cycloheptylpropyl)((phenylethynyl)sulfonyl)carbamate (85.1 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column

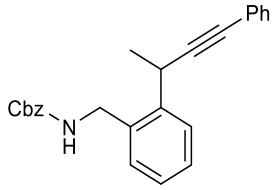
chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2m** as a yellow oil in 37% yield (26.8 mg, 1.2:1 dr). **TLC** R_f = 0.40 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$, mixture of diastereoisomers) δ 7.38 – 7.23 (m, 10H), 5.14 – 5.03 (m, 2H), 5.00 – 4.88 (m, 1H, minor diastereoisomer), 4.88 – 4.76 (m, 1H, major diastereoisomer), 3.15 – 2.96 (m, 3H), 2.07 – 1.89 (m, 2H), 1.81 – 1.61 (m, 5H), 1.59 – 1.43 (m, 3H), 1.30 – 1.20 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, mixture of diastereoisomers) δ 156.6, 156.6, 136.7, 136.7, 131.6, 131.5, 128.6, 128.5, 128.3, 128.2, 128.2, 128.1, 128.1, 128.1, 127.5, 127.5, 124.0, 95.1, 94.0, 81.7, 80.7, 66.7, 66.7, 47.6, 47.4, 38.8, 37.2, 36.3, 35.2, 34.4, 32.0, 31.6, 31.2, 29.4, 26.8, 25.9, 25.6, 25.6.

HRMS (ESI) m/z calcd for $C_{24}H_{27}NNaO_2$ $[M+Na]^+$ 384.1934, found 384.1930.

Benzyl (2-(4-phenylbut-3-yn-2-yl)benzyl)carbamate (2n)



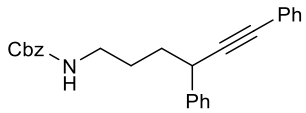
Prepared according to GP3 starting from benzyl (2-ethylbenzyl)((phenylethynyl)sulfonyl)carbamate (86.7 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2n** as a pale yellow solid in 69% yield (51.0 mg). **TLC** R_f = 0.40 (PE:EA = 10:1). mp 139–141 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 1H), 7.42 – 7.36 (m, 2H), 7.35 – 7.26 (m, 7H), 7.26 – 7.19 (m, 4H), 5.21 – 5.13 (m, 1H), 5.11 (s, 2H), 4.56 – 4.42 (m, 2H), 4.20 (q, *J* = 7.0 Hz, 1H), 1.56 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 141.5, 136.5, 134.8, 131.6, 129.4, 128.6, 128.5, 128.2, 128.1, 128.1, 127.9, 127.6, 127.2, 123.5, 92.8, 82.0, 66.9, 42.7, 28.6, 23.5.

HRMS (ESI) m/z calcd for $C_{25}H_{23}NNaO_2$ $[M+Na]^+$ 392.1621, found 392.1623.

Benzyl (4,6-diphenylhex-5-yn-1-yl)carbamate (2o)



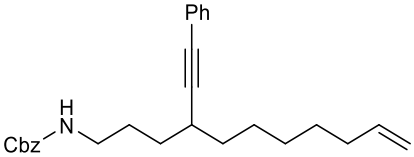
Prepared according to GP3 starting from benzyl (4-phenylbutyl)((phenylethynyl)sulfonyl)carbamate (89.5 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2o** as a yellow oil in 63% yield (48.3 mg). **TLC** R_f = 0.40 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.38 (m, 4H), 7.36 – 7.32 (m, 6H), 7.31 – 7.28 (m, 3H), 7.27 – 7.25 (m, 2H), 5.09 (s, 2H), 4.77 (brs, 1H), 3.81 (t, *J* = 7.2 Hz, 1H), 3.30 – 3.20 (m, 2H), 1.89 – 1.81 (m, 2H), 1.77 – 1.65 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 141.7, 136.6, 131.7, 128.6, 128.5, 128.4, 128.4, 128.2, 128.1, 127.9, 127.5, 126.9, 90.9, 83.7, 66.7, 40.7, 38.0, 35.6, 27.9.

HRMS (ESI) m/z calcd for $C_{26}H_{25}NNaO_2$ $[M+Na]^+$ 406.1777, found 406.1779.

Benzyl (4-(phenylethynyl)undec-10-en-1-yl)carbamate (2p)



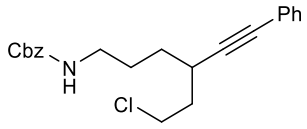
Prepared according to GP3 starting from benzyl ((phenylethynyl)sulfonyl)(undec-10-en-1-yl)carbamate (93.5 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2p** as a yellow oil in 46% yield (37.1 mg). **TLC** R_f = 0.40 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 6H), 7.32 – 7.30 (m, 1H), 7.28 – 7.24 (m, 3H), 5.91 – 5.68 (m, 1H), 5.09 (s, 2H), 5.06 – 4.86 (m, 2H), 4.79 (brs, 1H), 3.29 – 3.20 (m, 2H), 2.59 – 2.47 (m, 1H), 2.11 – 1.98 (m, 2H), 1.82 – 1.68 (m, 2H), 1.57 – 1.47 (m, 5H), 1.47 – 1.29 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 139.1, 136.7, 131.6, 128.5, 128.2, 128.1, 128.1, 127.6, 123.9, 114.3, 93.1, 82.2, 66.6, 41.0, 35.2, 33.8, 32.3, 32.1, 29.0, 28.8, 28.0, 27.3.

HRMS (ESI) m/z calcd for $C_{27}H_{33}NNaO_2$ $[M+Na]^+$ 426.2404, found426.2404.

Benzyl (4-(2-chloroethyl)-6-phenylhex-5-yn-1-yl)carbamate (2q)



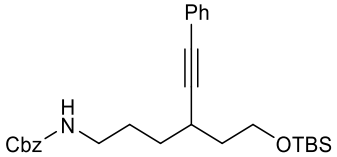
Prepared according to GP2 starting from benzyl (4-chlorobutyl)((phenylethynyl)sulfonyl)carbamate (86.8 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2q** as a yellow oil in 48% yield (35.5 mg). **TLC** R_f = 0.40 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.29 – 7.27 (m, 3H), 7.26 – 7.22 (m, 2H), 7.22 – 7.16 (m, 3H), 5.03 (s, 2H), 4.72 (brs, 1H), 3.67 (t, *J* = 6.6 Hz, 2H), 3.24 – 3.13 (m, 2H), 2.82 – 2.69 (m, 1H), 1.94 – 1.80 (m, 2H), 1.77 – 1.68 (m, 1H), 1.69 – 1.60 (m, 1H), 1.53 – 1.44 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 136.6, 131.6, 128.5, 128.3, 128.1, 127.9, 123.3, 90.8, 83.2, 66.7, 43.0, 40.8, 38.0, 32.0, 29.7, 27.9.

HRMS (ESI) m/z calcd for $C_{22}H_{24}Cl^{35}NNaO_2$ $[M+Na]^+$ 392.1387, found 392.1384. $C_{22}H_{24}Cl^{37}NNaO_2$ $[M+Na]^+$ 394.1358, found 394.1368.

Benzyl (4-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-6-phenylhex-5-yn-1-yl)carbamate (2r)



Prepared according to GP3 starting from benzyl (6-((*tert*-butyldimethylsilyl)oxy)hexyl)((phenylethynyl)sulfonyl)carbamate (105.9 mg, 0.2

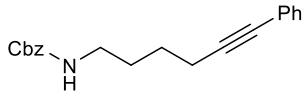
mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2r** as a yellow oil in 59% yield (55.0 mg). **TLC** R_f = 0.30 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 5H), 7.32 – 7.24 (m, 5H), 5.09 (s, 2H), 4.81 (brs, 1H), 3.83 – 3.79 (m, 2H), 3.30 – 3.23 (m, 2H), 2.79 – 2.72 (m, 1H), 1.85 – 1.70 (m, 3H), 1.63 – 1.45 (m, 3H), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 136.7, 131.6, 128.5, 128.2, 128.1, 128.1, 127.6, 123.8, 92.4, 82.4, 66.6, 61.0, 41.0, 38.2, 32.3, 28.5, 28.0, 26.0, 18.4, -5.2, -5.3.

HRMS (ESI) m/z calcd for $C_{28}H_{39}NNaO_3Si$ $[M+Na]^+$ 488.2591, found 488.2595.

Benzyl (6-phenylhex-5-yn-1-yl)carbamate (2s)



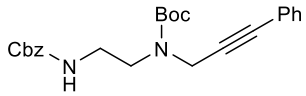
Prepared according to GP3 starting from benzyl butyl((phenylethynyl)sulfonyl)carbamate (74.3 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2s** as a pale yellow oil in 20% yield (12.3 mg). **TLC** R_f = 0.20 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 6H), 7.33 – 7.30 (m, 1H), 7.29 – 7.26 (m, 3H), 5.10 (s, 2H), 4.79 (brs, 1H), 3.30 – 3.23 (m, 2H), 2.44 (t, *J* = 6.5 Hz, 2H), 1.72 – 1.63 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 136.6, 131.6, 128.5, 128.2, 128.1, 127.6, 123.8, 89.6, 81.1, 66.7, 40.6, 29.2, 25.8, 19.1.

HRMS (ESI) m/z calcd for $C_{20}H_{21}NNaO_2$ $[M+Na]^+$ 330.1464, found 330.1467.

***tert*-Butyl (2-(((benzyloxy)carbonyl)amino)ethyl)(3-phenylprop-2-yn-1-yl)carbamate (2t)**



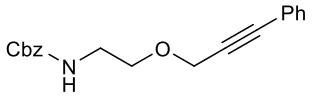
Prepared according to GP3 starting from tert-butyl (2-((*N*-((benzyloxy)carbonyl)-2-phenylethynyl)sulfonamido)ethyl)(methyl)carbamate (94.5 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 2/1), giving the product **2t** as a yellow oil in 57% yield (46.5 mg). **TLC** R_f = 0.10 (PE:EA = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$, mixture of ratomers) δ 7.62 – 7.51 (m, 1H), 7.42 – 7.39 (m, 1H), 7.36 – 7.31 (m, 6H), 7.30 – 7.26 (m, 2H), 6.12 (brs, 1H, minor ratomer), 5.36 (brs, 1H, major ratomer), 5.08 (s, 2H), 4.33 – 4.15 (m, 2H), 3.55 – 3.51 (m 1H), 3.47 – 3.43 (m, 1H), 3.43 – 3.31 (m, 2H), 1.49 – 1.45 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$, mixture of ratomers) δ 169.7, 156.6, 137.4, 136.6, 133.3, 131.8, 130.1, 129.9, 128.9, 128.5, 128.4, 128.3, 128.0, 126.5, 122.6, 84.9, 80.8, 80.5, 66.7, 46.8, 46.4, 39.9, 38.2, 28.4, 28.4.

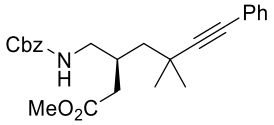
HRMS (ESI) m/z calcd for $C_{24}H_{28}N_2NaO_4$ $[M+Na]^+$ 431.1941, found 431.1944.

Benzyl (2-((3-phenylprop-2-yn-1-yl)oxy)ethyl)carbamate (2u)



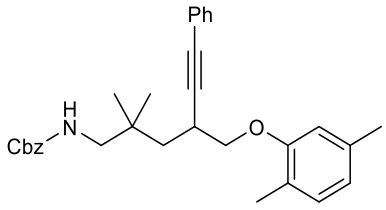
Prepared according to GP3 starting from benzyl (2-methoxyethyl)((phenylethynyl)sulfonyl)carbamate (74.7 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2u** as a pale yellow solid in 60% yield (37.1 mg). **TLC** R_f = 0.25 (PE:EA = 10:1). mp 42–44 ℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.39 – 7.26 (m, 8H), 5.21 (brs, 1H), 5.09 (s, 2H), 4.37 (s, 2H), 3.67 (t, *J* = 5.1 Hz, 2H), 3.50 – 3.40 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 136.6, 131.8, 128.6, 128.5, 128.3, 128.1, 122.4, 86.6, 84.7, 68.9, 66.7, 59.1, 40.9.
HRMS (ESI) m/z calcd for $C_{19}H_{19}NNaO_3$ $[M+Na]^+$ 332.1257, found 332.1263.

Methyl (*S*)-3-((((benzyloxy)carbonyl)amino)methyl)-5,5-dimethyl-7-phenylhept-6-ynoate (2v)



Prepared according to GP2 starting from methyl (*R*)-3-(((*N*-((benzyloxy)carbonyl)-2-phenylethynyl)sulfonamido)methyl)-5-methylhexanoate (94.2 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 1/1), giving the product **2v** as a yellow solid in 39% yield (31.8 mg). **TLC** R_f = 0.50 (PE:EA = 4:1). mp 57–59 ℃.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 7H), 7.27 – 7.20 (m, 3H), 5.11 (brs, 1H), 5.08 (s, 2H), 3.62 (s, 3H), 3.48 – 3.39 (m, 1H), 3.34 – 3.25 (m, 1H), 2.63 – 2.53 (m, 1H), 2.47 – 2.39 (m, 1H), 2.38 – 2.31 (m, 1H), 1.58 – 1.43 (m, 2H), 1.31 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 156.7, 136.6, 131.5, 128.5, 128.2, 128.1, 128.1, 127.7, 123.5, 96.7, 81.2, 66.7, 51.6, 45.2, 44.5, 38.2, 33.3, 31.0, 30.2, 29.5.
HRMS (ESI) m/z calcd for $C_{25}H_{29}NNaO_4$ $[M+Na]^+$ 430.1989, found 430.1990.

Benzyl (4-((2,5-dimethylphenoxy)methyl)-2,2-dimethyl-6-phenylhex-5-yn-1-yl)carbamate (2w)



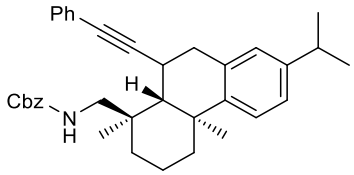
Prepared according to GP2 starting from methyl benzyl (5-(2,5-dimethylphenoxy)-2,2-dimethylpentyl)((phenylethynyl)sulfonyl)carbamate (106.7 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2w** as a yellow oil in 25% yield (23.5 mg, *rr* = 1.1:1). **TLC** R_f = 0.30 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$, mixture of regioisomers) δ 7.46 – 7.20 (m, 10H), 7.03 – 6.97 (m, 1H), 6.70 – 6.59 (m, 2H), 5.13 – 5.07 (m, 2H), 4.80 (brs, 1H), 4.12 – 3.85 (m, 1H), 3.26 – 3.17 (m, 1H), 3.12 – 3.00 (m, 2H), 2.31 (s, 3H, major regioisomer), 2.31 (s, 3H, minor regioisomer), 2.19 (s, 3H, major regioisomer), 2.16 (s, 3H, minor regioisomer), 1.78 – 1.68 (m, 2H), 1.04 (s, 3H, major regioisomer), 1.03 (s, 3H, minor regioisomer), 0.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, mixture of regioisomers) δ 157.0, 156.8, 156.8, 156.5, 136.6, 136.5, 131.5, 130.5, 130.3, 128.5, 128.5, 128.3, 128.1, 128.1, 128.0, 123.7, 123.6, 123.2, 121.3, 120.7, 112.3, 112.1, 91.0, 82.9, 71.0, 68.3, 66.7, 66.7, 50.9, 50.3, 41.3, 35.8, 34.9, 34.2, 29.7, 28.5, 26.1, 25.2, 24.8, 24.1, 21.4, 21.4, 15.9, 15.8.

HRMS (ESI) m/z calcd for $C_{31}H_{35}NNaO_3$ $[M+Na]^+$ 492.2509, found 492.2508.

Benzyl (((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-10-(phenylethynyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)carbamate (2x)



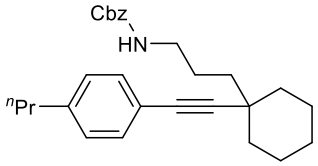
Prepared according to GP2 starting from benzyl (((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)((phenylethynyl)sulfonyl)carbamate (116.8 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2x** as a yellow oil in 48% yield (49.9 mg). **TLC** R_f = 0.40 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 3H), 7.27 – 7.25 (m, 2H), 7.24 – 7.20 (m, 3H), 7.18 – 7.12 (m, 3H), 7.07 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.98 (d, *J* = 2.0 Hz, 1H), 5.50 (dd, *J* = 10.0, 4.4 Hz, 1H), 5.09 (d, *J* = 12.3 Hz, 1H), 4.93 (d, *J* = 12.3 Hz, 1H), 3.48 – 3.39 (m, 2H), 3.28 – 3.20 (m, 2H), 2.98 (dd, *J* = 15.8, 3.6 Hz, 1H), 2.89 – 2.82 (m, 1H), 2.21 – 2.16 (m, 1H), 1.80 – 1.74 (m, 1H), 1.69 – 1.67 (m, 1H), 1.57 – 1.49 (m, 2H), 1.47 – 1.40 (m, 2H), 1.25 (s, 3H), 1.23 (d, *J* = 2.8 Hz, 6H), 1.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 147.1, 146.3, 136.7, 133.9, 131.4, 128.4, 128.3, 127.9, 127.9, 126.7, 124.5, 123.2, 122.3, 96.4, 81.5, 66.5, 51.5, 49.2, 39.3, 38.5, 38.2, 36.8, 36.7, 33.6, 25.6, 24.1, 24.1, 22.4, 19.6, 18.2.

HRMS (ESI) m/z calcd for $C_{36}H_{41}NNaO_2$ $[M+Na]^+$ 542.3030, found 542.3037.

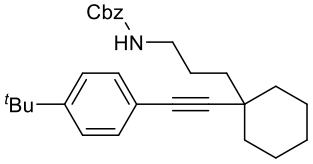
Benzyl (3-(1-((4-propylphenyl)ethynyl)cyclohexyl)propyl)carbamate (2aa)



Prepared according to GP3 starting from benzyl (3-cyclohexylpropyl)(((4-propylphenyl)ethynyl)sulfonyl)carbamate (96.3 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2aa** as a

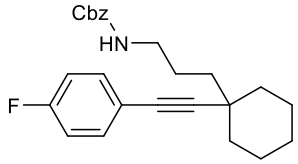
yellow oil in 79% yield (66.0 mg). **TLC** R_f = 0.40 (PE:EA = 10:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.25 (m, 7H), 7.13 – 6.99 (m, 2H), 5.09 (s, 2H), 4.80 (brs, 1H), 3.30 – 3.15 (m, 2H), 2.55 (t, *J* = 7.6 Hz, 2H), 1.88 – 1.78 (m, 2H), 1.78 – 1.69 (m, 4H), 1.69 – 1.64 (m, 2H), 1.64 – 1.52 (m, 4H), 1.50 – 1.42 (m, 2H), 1.21 – 1.14 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, CDCl3) δ 156.4, 142.3, 136.7, 131.5, 128.5, 128.4, 128.1, 128.1, 121.3, 94.2, 83.5, 66.6, 41.5, 40.2, 38.0, 37.9, 37.0, 26.3, 25.1, 24.4, 23.2, 13.7.
HRMS (ESI) m/z calcd for $C_{28}H_{35}NNaO_2$ $[M+Na]^+$ 440.2560, found 440.2567.

Benzyl (3-(1-((4-(*tert*-butyl)phenyl)ethynyl)cyclohexyl)propyl)carbamate (2ab)



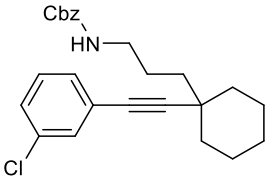
Prepared according to GP3 starting from benzyl (((4-(*tert*-butyl)phenyl)ethynyl)sulfonyl)(3-cyclohexylpropyl)carbamate (99.1 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2ab** as a yellow oil in 84% yield (72.5 mg). **TLC** R_f = 0.40 (PE:EA = 10:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 9H), 5.09 (s, 2H), 4.78 (brs, 1H), 3.29 – 3.18 (m, 2H), 1.88 – 1.63 (m, 8H), 1.49 – 1.43 (m, 2H), 1.31 – 1.25 (m, 10H), 1.22 – 1.14 (m, 3H).
^{13}C NMR (101 MHz, CDCl3) δ 156.4, 150.7, 136.7, 131.3, 128.5, 128.1, 128.1, 125.2, 121.1, 94.3, 83.5, 66.6, 41.5, 40.1, 38.0, 37.0, 34.7, 31.2, 26.3, 25.1, 23.2.
HRMS (ESI) m/z calcd for $C_{29}H_{37}NO_2$ $[M+Na]^+$ 454.2717, found 454.2725.

Benzyl (3-(1-((4-fluorophenyl)ethynyl)cyclohexyl)propyl)carbamate (2ac)



Prepared according to GP3 starting from benzyl (3-cyclohexylpropyl)(((4-fluorophenyl)ethynyl)sulfonyl)carbamate (91.5 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2ac** as a pale yellow oil in 66% yield (51.9 mg). **TLC** R_f = 0.30 (PE:EA = 10:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 7H), 6.99 – 6.92 (m, 2H), 5.09 (s, 2H), 4.82 (brs, 1H), 3.29 – 3.20 (m, 2H), 1.84 – 1.78 (m, 2H), 1.77 – 1.67 (m, 5H), 1.64 – 1.58 (m, 2H), 1.49 – 1.43 (m, 2H), 1.24 – 1.13 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (d, *J* = 249.0 Hz), 156.4, 136.7, 133.3 (d, *J* = 8.2 Hz), 128.5, 128.1, 120.1 (d, *J* = 3.4 Hz), 115.3 (d, *J* = 22.1 Hz), 94.7, 82.4, 66.6, 41.5, 40.1, 37.9, 36.9, 26.2, 25.1, 23.2.
^{19}F NMR (377 MHz, $CDCl_3$) δ -112.5.
HRMS (ESI) m/z calcd for $C_{25}H_{28}FNNaO_2$ $[M+Na]^+$ 416.1996, found 416.1999.

Benzyl (3-(1-((3-chlorophenyl)ethynyl)cyclohexyl)propyl)carbamate (2ad)



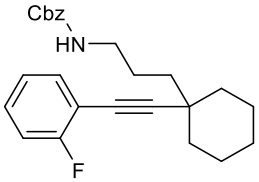
Prepared according to GP3 starting from benzyl (((3-chlorophenyl)ethynyl)sulfonyl)(3-cyclohexylpropyl)carbamate (94.8 mg, 0.2 mmol)and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2ad** as a yellow oil in 70% yield (57.4 mg). **TLC** R_f = 0.40 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 1H), 7.36 – 7.31 (m, 5H), 7.26 – 7.17 (m, 3H), 5.10 (s, 2H), 4.81 (brs, 1H), 3.27 – 3.21 (m, 2H), 1.84 – 1.79 (m, 2H), 1.75 – 1.67 (m, 4H), 1.65 – 1.57 (m, 3H), 1.49 – 1.44 (m, 2H), 1.23 – 1.15 (m, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 156.4, 136.7, 134.0, 131.5, 129.7, 129.4, 128.5, 128.1, 128.1, 127.8, 125.8, 96.5, 82.3, 66.6, 41.5, 40.0, 37.8, 37.0, 26.2, 25.1, 23.2.

HRMS (ESI) m/z calcd for $C_{25}H_{28}Cl^{35}NNaO_2$ $[M+Na]^+$ 432.1701, found 432.1703. $C_{25}H_{28}Cl^{37}NNaO_2$ $[M+Na]^+$ 434.1671, found 434.1675.

Benzyl (3-(1-((2-fluorophenyl)ethynyl)cyclohexyl)propyl)carbamate (2ae)



Prepared according to GP3 starting from benzyl (3-cyclohexylpropyl)(((2-fluorophenyl)ethynyl)sulfonyl)carbamate (91.5 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2ae** as a pale yellow oil in 74% yield (58.2 mg). **TLC** R_f = 0.30 (PE:EA = 10:1)

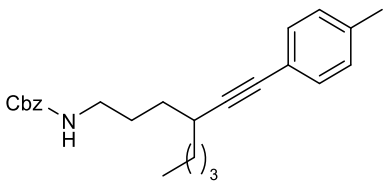
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 6H), 7.25 – 7.18 (m, 1H), 7.08 – 6.97 (m, 2H), 5.10 (s, 2H), 4.79 (brs, 1H), 3.30 – 3.16 (m, 2H), 1.88 – 1.81 (m, 2H), 1.79 – 1.67 (m, 5H), 1.65 – 1.56 (m, 2H), 1.52 – 1.44 (m, 2H), 1.26 – 1.12 (m, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 162.9 (d, *J* = 251.1 Hz), 156.4, 136.7, 133.4, 133.4, 129.1 (d, *J* = 7.8 Hz), 128.5, 128.1 (d, *J* = 3.5 Hz), 123.8, 123.7, 115.3 (d, *J* = 21.2 Hz), 112.5 (d, *J* = 15.9 Hz), 100.7, 66.6, 41.5, 40.0, 37.9, 37.3, 26.2, 25.1, 23.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ -110.6.

HRMS (ESI) m/z calcd for $C_{25}H_{28}FNNaO_2$ $[M+Na]^+$ 416.1996, found 416.1996.

Benzyl (4-(*p*-tolylethynyl)octyl)carbamate (2af)



Prepared according to GP3 starting from benzyl octyl((p-

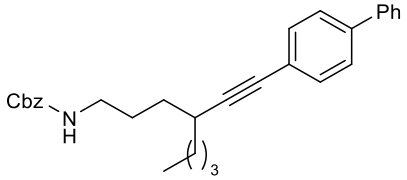
tolylethynyl)sulfonyl)carbamate (88.2 mg, 0.2 mmol) and tert-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2af** as yellow oil in 67% yield (50.6 mg). **TLC** R_f = 0.40 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 5H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 5.09 (s, 2H), 4.80 (brs, 1H), 3.29 – 3.19 (m, 2H), 2.56 – 2.48 (m, 1H), 2.32 (s, 3H), 1.82 – 1.73 (m, 1H), 1.69 – 1.64 (m, 1H), 1.55 – 1.46 (m, 5H), 1.40 – 1.27 (m, 3H), 0.91 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 137.5, 136.7, 131.5, 128.9, 128.5, 128.1, 120.9, 92.3, 82.2, 66.6, 41.0, 35.0, 32.3, 32.1, 29.7, 28.0, 22.6, 21.4, 14.1.

HRMS (ESI) m/z calcd for $C_{25}H_{31}NNaO_2$ $[M+Na]^+$ 400.2247, found 400.2253.

Benzyl (4-([1,1'-biphenyl]-4-ylethynyl)octyl)carbamate (2ag)



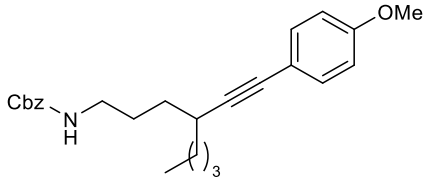
Prepared according to GP2 starting from benzyl (([1,1'-biphenyl]-4-ylethynyl)sulfonyl)(octyl)carbamate (100.7 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2ag** as yellow solid in 75% yield (65.9 mg). **TLC** R_f = 0.40 (PE:EA = 10:1). mp 146–148 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7. 59 – 7.55 (m, 2H), 7. 53 – 7.49 (m, 2H), 7.48 – 7.37 (m, 5H), 7.36 – 7.31 (m, 5H), 5.10 (s, 2H), 4.80 (brs, 1H), 3.30 – 3.22 (m, 2H), 2.59 – 2.52 (m, 1H), 1.83 – 1.75 (m, 1H), 1.72 – 1.60 (m, 2H), 1.57 – 1.49 (m, 5H), 1.42 – 1.34 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 140.5, 140.3, 136.7, 132.0, 128.8, 128.5, 128.1, 127.5, 127.0, 126.9, 122.9, 93.9, 82.0, 66.6, 41.0, 35.0, 32.3, 32.2, 29.7, 28.0, 22.6, 14.1.

HRMS (ESI) m/z calcd for $C_{30}H_{33}NNaO_2$ $[M+Na]^+$ 462.2404, found 462.2408.

Benzyl (4-((4-methoxyphenyl)ethynyl)octyl)carbamate (2ah)



Prepared according to GP2 starting from benzyl (((4-methoxyphenyl)ethynyl)sulfonyl)(octyl)carbamate (91.5, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2ah** as a yellow solid in 65% yield (51.2 mg). **TLC** R_f = 0.20 (PE:EA = 5:1). mp 55–57 ℃.

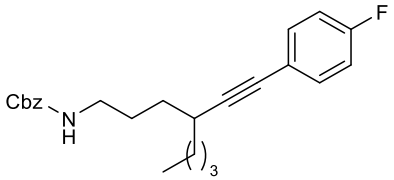
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 5H), 7.32 – 7.30 (m, 2H), 6.82 – 6.77 (m, 2H), 5.09 (s, 2H), 4.80 (brs, 1H), 3.79 (s, 3H), 3.28 – 3.18 (m, 2H), 2.54 – 2.48 (m, 1H), 1.80 – 1.72 (m, 1H), 1.71 – 1.65 (m, 1H), 1.55 – 1.47 (m, 5H), 1.42 – 1.30 (m,

3H), 0.92 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 156.4, 136.7, 132.9, 128.5, 128.1, 116.1, 113.8, 91.5, 81.8, 66.6, 55.3, 41.0, 35.1, 32.3, 32.1, 29.7, 28.0, 22.6, 14.1.

HRMS (ESI) m/z calcd for $C_{25}H_{31}NNaO_3$ $[M+Na]^+$ 416.2196, found 416.2201.

Benzyl (4-((4-fluorophenyl)ethynyl)octyl)carbamate (2ai)



Prepared according to GP3 starting from benzyl (((4-fluorophenyl)ethynyl)sulfonyl)(octyl)carbamate (89.0 mg, 0.2 mmol) and tert-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2ai** as a pale yellow oil in 46% yield (35.1 mg). **TLC** R_f = 0.30 (PE:EA = 10:1).

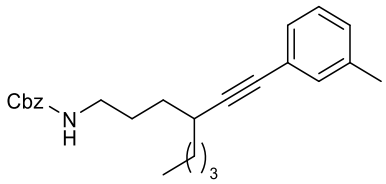
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 7H), 6.98 – 6.93 (m, 2H), 5.10 (s, 2H), 4.78 (brs, 1H), 3.28 – 3.21 (m, 2H), 2.55 – 2.48 (m, 1H), 1.80 – 1.73 (m, 1H), 1.70 – 1.62 (m, 2H), 1.58 – 1.51 (m, 2H), 1.50 – 1.46 (m, 2H), 1.41 – 1.28 (m, 3H), 0.92 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (d, *J* = 249.0 Hz), 156.4, 136.6, 133.3 (d, *J* = 8.3 Hz), 128.5, 128.1, 120.0 (d, *J* = 3.8 Hz), 115.4 (d, *J* = 21.9 Hz), 92.7, 81.1, 66.6, 41.0, 34.9, 32.2, 32.1, 29.6, 28.0, 22.6, 14.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ -112.3.

HRMS (ESI) m/z calcd for $C_{24}H_{28}FNNaO_2$ $[M+Na]^+$ 404.1996, found 404.1997.

Benzyl (4-(*m*-tolylethynyl)octyl)carbamate (2aj)



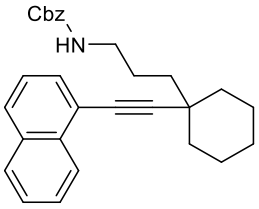
Prepared according to GP3 starting from benzyl octyl((*m*-tolylethynyl)sulfonyl)carbamate (88.3 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2aj** as a pale yellow oil in 48% yield (36.2 mg). **TLC** R_f = 0.40 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 7.23 – 7.13 (m, 3H), 7.09 – 7.03 (m, 1H), 5.09 (s, 2H), 4.81 (brs, 1H), 3.31 – 3.16 (m, 2H), 2.58 – 2.46 (m, 1H), 2.30 (s, 3H), 1.85 – 1.73 (m, 1H), 1.70 – 1.62 (m, 1H), 1.57 – 1.46 (m, 5H), 1.42 – 1.27 (m, 3H), 0.92 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 137.8, 136.7, 132.2, 128.6, 128.5, 128.4, 128.1, 123.7, 92.7, 82.3, 66.6, 41.0, 35.0, 32.3, 32.1, 29.6, 28.0, 22.6, 21.2, 14.1.

HRMS (ESI) m/z calcd for $C_{25}H_{31}NNaO_2$ $[M+Na]^+$ 400.2247, found 400.2248.

Benzyl (3-(1-(naphthalen-1-ylethynyl)cyclohexyl)propyl)carbamate (2ak)



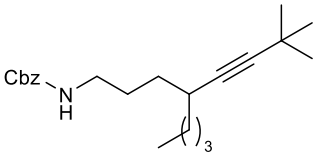
Prepared according to GP3 starting from benzyl (3-cyclohexylpropyl)((naphthalen-1-ylethynyl)sulfonyl)carbamate (97.9 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2ak** as a pale yellow oil in 61% yield (51.9 mg). **TLC** R_f = 0.40 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.3 Hz, 1H), 7.83 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 7.1 Hz, 1H), 7.57 – 7.48 (m, 2H), 7.41 – 7.27 (m, 6H), 5.09 (s, 2H), 4.78 (brs, 1H), 3.33 – 3.23 (m, 2H), 1.98 – 1.92 (m, 2H), 1.90 – 1.79 (m, 4H), 1.79 – 1.64 (m, 4H), 1.61 – 1.59 (m, 1H), 1.33 – 1.22 (m, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 156.4, 136.7, 133.5, 133.3, 130.2, 128.5, 128.3, 128.1, 127.9, 126.6, 126.2, 125.3, 121.8, 100.2, 81.4, 66.6, 41.6, 40.3, 38.1, 37.5, 26.3, 25.3, 23.4.

HRMS (ESI) m/z calcd for $C_{29}H_{31}NNaO_2$ $[M+Na]^+$ 448.2247, found 448.2245.

Benzyl (4-butyl-7,7-dimethyloct-5-yn-1-yl)carbamate (2al)



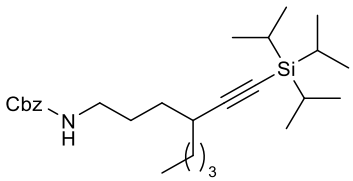
Prepared according to GP3 starting from benzyl ((3,3-dimethylbut-1-yn-1-yl)sulfonyl)(octyl)carbamate (81.5 mg, 0.2 mmol) and *tert*-butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2al** as a colorless oil in 65% yield (44.7 mg). **TLC** R_f = 0.35 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 5H), 5.09 (s, 2H), 4.78 (brs, 1H), 3.25 – 3.18 (m, 2H), 2.30 – 2.19 (m, 1H), 1.42 – 1.24 (m, 10H), 1.18 (s, 9H), 0.89 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 156.4, 136.7, 128.5, 128.1, 128.1, 90.6, 81.3, 66.6, 41.0, 35.3, 32.5, 31.5, 31.3, 29.5, 27.8, 27.3, 22.5, 14.1.

HRMS (ESI) m/z calcd for $C_{22}H_{33}NNaO_2$ $[M+Na]^+$ 366.2404, found 366.2408.

Benzyl (4-((triisopropylsilyl)ethynyl)octyl)carbamate (2am)



Prepared according to GP2 starting from benzyl octyl(((triisopropylsilyl)ethynyl)sulfonyl)carbamate (101.6 mg, 0.2 mmol) and *tert*-

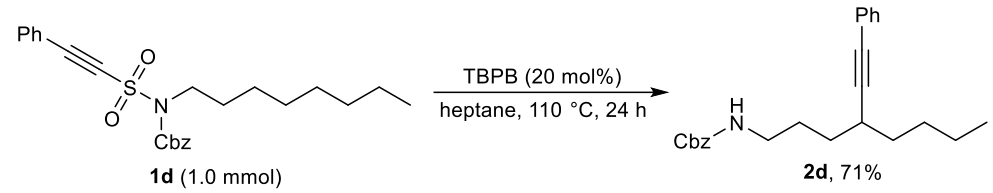
butyl peroxybenzoate (7.6 μL, 0.04 mmol). The residue was purified by column chromatography (petroleum ether/diethyl ether = 4/1), giving the product **2am** as a yellow oil in 74% yield (65.7 mg). **TLC** R_f = 0.40 (PE:EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 5.09 (s, 2H), 4.76 (brs, 1H), 3.26 – 3.16 (m, 2H), 2.41 – 2.31 (m, 1H), 1.80 – 1.68 (m, 1H), 1.66 – 1.57 (m, 1H), 1.51 – 1.25 (m, 8H), 1.09 – 0.99 (m, 21H), 0.89 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 136.7, 128.5, 128.1, 128.1, 112.1, 81.4, 66.6, 40.9, 35.0, 32.4, 32.3, 29.5, 27.8, 22.5, 18.7, 14.0, 11.3.

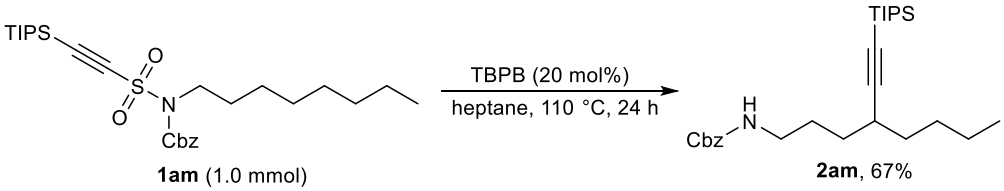
HRMS (ESI) m/z calcd for $C_{27}H_{45}NNaSiO_2$ $[M+Na]^+$ 466.3112, found 466.3114.

6. Scale-up reaction



1d (1.0 mmol) **2d**, 71%

A dry flask equipped with a stirring bar was charged with benzyl octyl((phenylethynyl)sulfonyl)carbamate **1d** (427.0 mg, 1.0 mmol). It was capped with a rubber septum, evacuated and backfilled with N_2. Then, heptane (10.0 mL) and *tert*-butyl peroxybenzoate (38 μL, 0.2 mmol) was added. The reaction mixture was stirred at 110 °C for 24 h. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (petroleum ether/diethyl ether = 4/1) to afford the benzyl (4-(phenylethynyl)octyl)carbamate **2d** in 71% yield (257.0 mg).

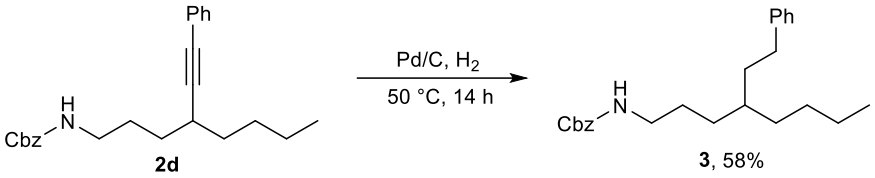


1am (1.0 mmol) **2am**, 67%

A dry flask equipped with a stirring bar was charged with benzyl octyl(((triisopropylsilyl)ethynyl)sulfonyl)carbamate **1am** (507.8 mg, 1.0 mmol). It was capped with a rubber septum, evacuated and backfilled with N_2. Then, heptane (10 mL) and *tert*-butyl peroxybenzoate (38 μL, 0.2 mmol) was added. The reaction mixture was stirred at 110 °C for 24 h. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (petroleum ether/diethyl ether = 4/1) to afford the benzyl (4-((triisopropylsilyl)ethynyl)octyl)carbamate **2am** in 67% yield (297.3 mg).

7. Synthetic transformations of the alkynylated products

7.1 Hydrogenation



2d **3**, 58%

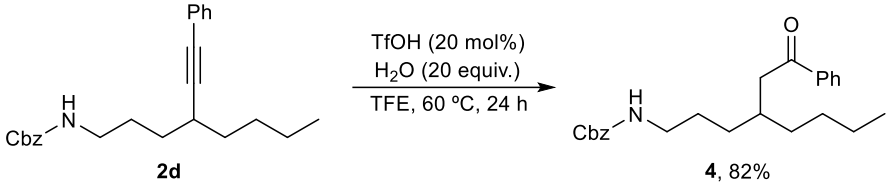
A mixture of benzyl (4-(phenylethynyl)octyl)carbamate **2d** (72.6 mg, 0.2 mmol) and Pd/C (10 w/w%, 30 mg) in EtOAc (1.0 mL) was stirred under a hydrogen atmosphere at 50 °C for 14 h. The catalyst was filtered through celite, and the filtrate was concentrated in vacuo to yield benzyl (4-phenethyloctyl)carbamate **3** in 58% yield (42.5 mg) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.26 (m, 4H), 7.24 – 7.20 (m, 1H), 7.20 – 7.15 (m, 2H), 7.10 – 7.05 (m, 3H), 5.02 (s, 2H), 4.67 (brs, 1H), 3.13 – 3.06 (m, 2H), 2.51 – 2.45 (m, 2H), 1.49 – 1.43 (m, 2H), 1.43 – 1.37 (m, 2H), 1.25 – 1.17 (m, 9H), 0.84 – 0.80 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 143.0, 136.7, 128.5, 128.3, 128.3, 128.1, 128.1, 125.6, 66.6, 41.5, 36.9, 35.5, 33.1, 33.0, 30.5, 28.8, 27.1, 23.1, 14.2.

HRMS (ESI) m/z calcd for $C_{24}H_{33}NNaO_2$ $[M+Na]^+$ 390.2403, found 390.2401.

7.2 Synthesis of benzyl (4-(2-oxo-2-phenylethyl)octyl)carbamate

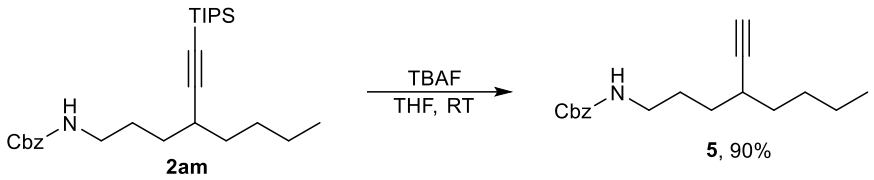


2d **4**, 82%

To a stirred solution of benzyl (4-(phenylethynyl)octyl)carbamate **2d** (56.0 mg, 0.15 mmol) in 2,2,2-trifluoroethan-1-ol (TFE, 1.0 mL) was added H_2O (54 μL, 3.0 mmol, 20 equiv.) and trifluoromethanesulfonic acid (TfOH, 2.7 μL, 0.03 mmol, 20 mol%) at room temperature and the mixture was stirred at 60 °C for 24 h. Then, the mixture was transferred into a 50.0 mL separating funnel which contained 10.0 mL of sat. $NaHCO_3$ and extracted twice by DCM (10.0 mL each). The combined organic layers were dried by $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure to give the crude product, which was purified by flash chromatography on silica gel (EtOAc : pentane = 1:10) to give benzyl (4-(2-oxo-2-phenylethyl)octyl)carbamate **4** in 82% yield (46.9 mg) as a colorless oil. **TLC** R_f = 0.30 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 2H), 7.58 – 7.52 (m, 1H), 7.48 – 7.43 (m, 2H), 7.37 – 7.27 (m, 5H), 5.09 (s, 2H), 4.88 (brs, 1H), 3.23 – 3.12 (m, 2H), 2.96 – 2.80 (m, 2H), 2.15 – 2.06 (m, 1H), 1.57 – 1.47 (m, 2H), 1.38 – 1.26 (m, 8H), 0.90 – 0.85 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.4, 156.4, 137.4, 136.7, 132.9, 128.6, 128.5, 128.1, 66.6, 43.3, 41.2, 33.7, 33.7, 31.1, 28.9, 27.1, 22.9, 14.1. **HRMS (ESI)** m/z calcd for $C_{24}H_{31}NNaO_3$ $[M+Na]^+$ 404.2196, found 404.2197.

7.3 Synthesis of ethyl 4-(4-(1-(((benzyloxy)carbonyl)amino)octan-4-yl)-1H-1,2,3-triazol-1-yl)butanoate[6]

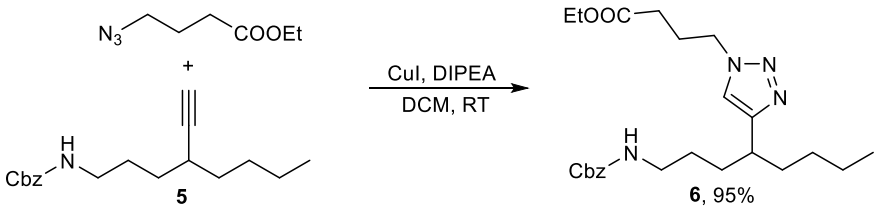


To a stirred solution of benzyl (4-((triisopropylsilyl)ethynyl)octyl)carbamate (443.7 mg, 1.0 mmol) in anhydrous THF (5.0 mL) at 0 °C was added dropwise a solution of TBAF in THF (2.0 mL, 1M in THF, 2 mmol). After the addition was complete, the mixture was warmed to room temperature and stirred for 16 h. Sat. aq. NH_4Cl (10 mL) was added to the mixture and extracted with Et_2O (3 × 5.0 mL). The combined organic extracts were successively washed with 1 M HCl (2.0 mL), water (10.0 mL), brine (10.0 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (EtOAc : pentane = 1:10) to afford benzyl (4-ethynyloctyl)carbamate **5** in 90% yield (258.7 mg). **TLC** R_f = 0.3 (PE:EA = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ 7.40 – 7.26 (m, 5H), 5.09 (s, 2H), 4.79 (brs, 1H), 3.27 – 3.15 (m, 2H), 2.37 – 2.27 (m, 1H), 2.09 – 1.99 (m, 1H), 1.80 – 1.70 (m, 1H), 1.65 – 1.55 (m, 1H), 1.51 – 1.29 (m, 8H), 0.90 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ 156.4, 136.6, 128.5, 128.1, 128.1, 87.6, 69.6, 66.6, 40.9, 34.7, 32.0, 31.3, 29.4, 27.8, 22.5, 14.1.

HRMS (ESI) m/z calcd for $C_{18}H_{25}NNaO_2$ $[M+Na]^+$ 310.1777, found 310.1782.



A suspension of benzyl (4-ethynyloctyl)carbamate **5** (57.5 mg, 0.2 mmol), CuI (1.9 mg, 0.01 mmol), DIPEA (0.18 mL, 5 mmol), and ethyl 4-azidobutanoate (31.4 mg, 0.2 mmol) was heated through a heating block in CH_2Cl_2 (2.0 mL) for 24 h, after which time the typical IR band for azide (2095 cm^{-1}) had completely disappeared. The precipitate was filtered, washed with methanol, and dried under vacuum to yield ethyl 4-(4-(1-(((benzyloxy)carbonyl)amino)octan-4-yl)-1H-1,2,3-triazol-1-yl)butanoate as a colorless oil **6** in 95% yield (84.4 mg). **TLC** R_f = 0.10 (PE:EA = 2:1).

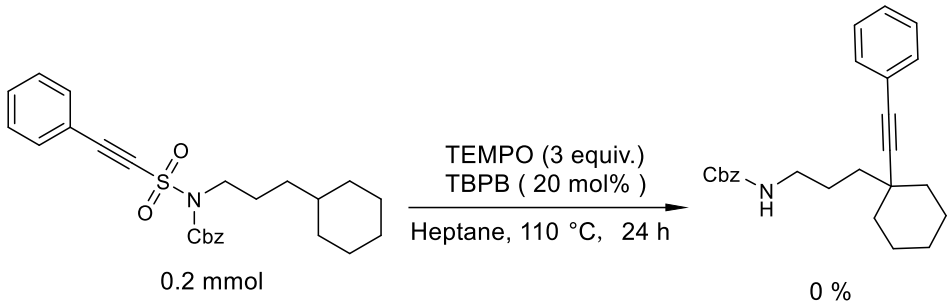
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 7.25 (s, 1H), 5.07 (s, 2H), 4.96 (brs, 1H), 4.41 – 4.32 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.19 – 3.08 (m, 2H), 2.83 – 2.73 (m, 1H), 2.35 – 2.28 (m, 2H), 2.23 – 2.18 (m, 2H), 1.71 – 1.58 (m, 4H), 1.49 – 1.37 (m, 2H), 1.30 – 1.14 (m, 7H), 0.84 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 156.4, 151.7, 136.7, 128.5, 128.1, 120.5, 66.5, 60.7, 49.1, 41.0, 36.5, 35.1, 32.4, 30.8, 29.4, 27.7, 25.5, 22.7, 14.2, 14.0.

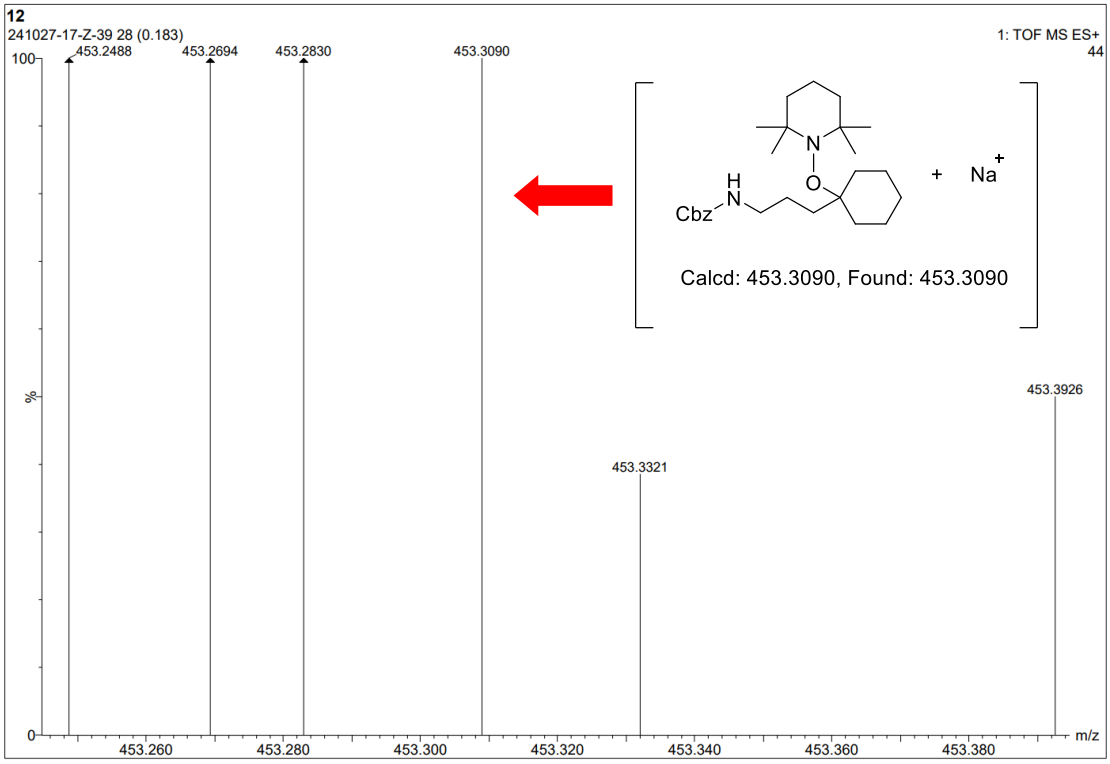
HRMS (ESI) m/z calcd for $C_{24}H_{36}N_4NaO_4$ $[M+Na]^+$ 467.2629, found 467.2629

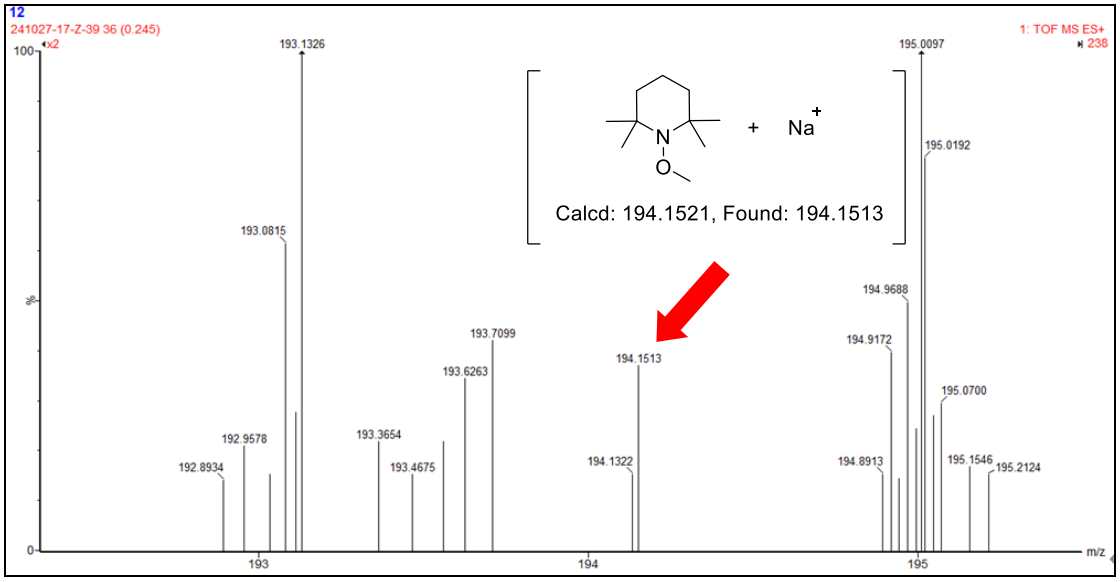
8. Control experiments

8.1 Radical trapping experiments



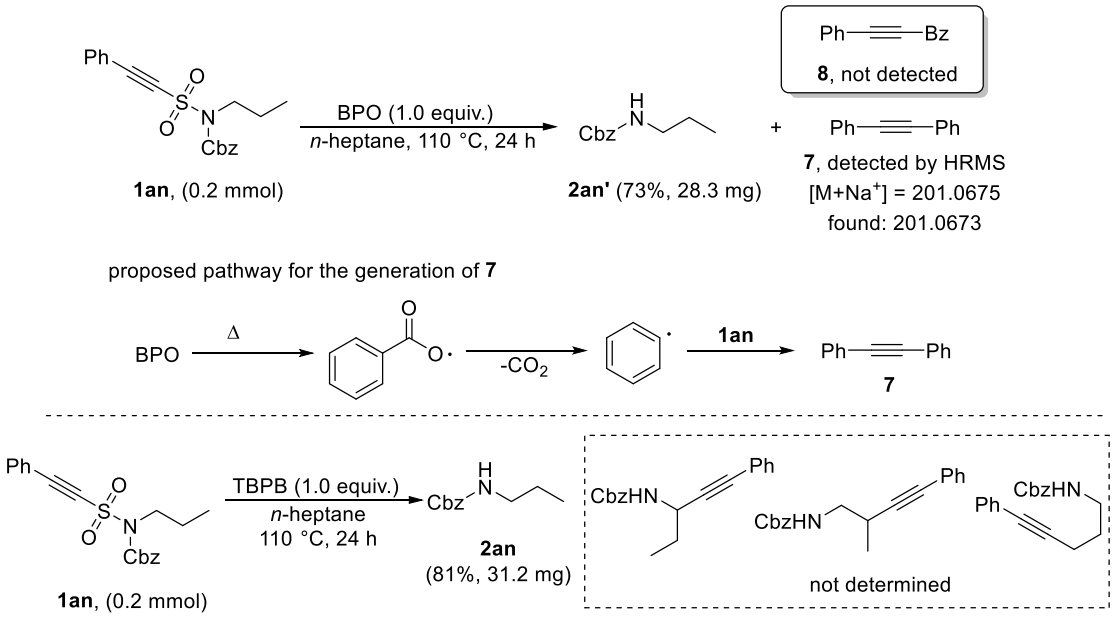
The radical scavenger TEMPO (2,2,6,6 tetromethyl-1-piperidinyloxy, 3.0 equiv) was added under the standard conditions. After 24 h, no desired product was observed by TLC, indicating that the reaction was completely inhibited. The mixture was detected by HRMS (see below).

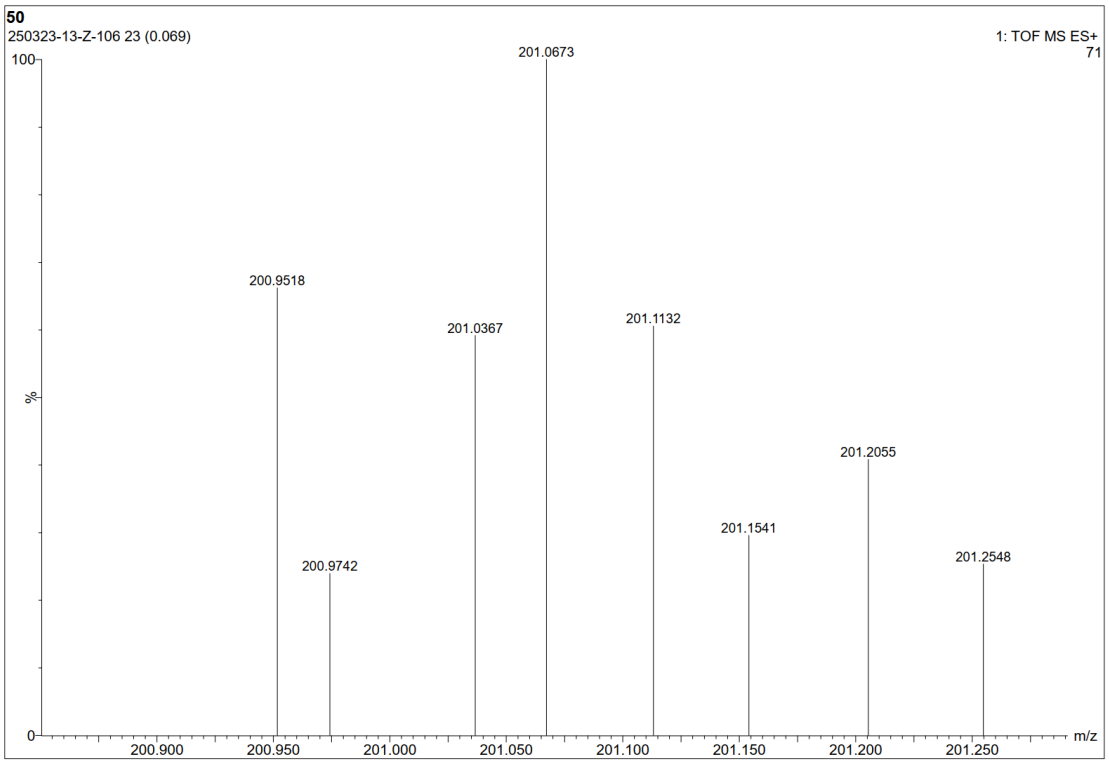




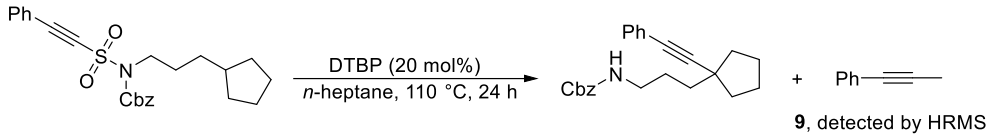
8.2 Control experments

We performed the reaction of **1an** by using BPO as the initiator. After 24 h,the redutive **2an'** was generated. The mixture was detected by HRMS (see below), indicating that phenyl radical initiate the radical chain by using BPO as the initiator.
We conducted the reaction of N-propyl derived ethynylsulfonamide **1an** by using 1.0 equivalents of tert-butyl peroxybenzoate (TBPB). However, we did observe any alkylated products.





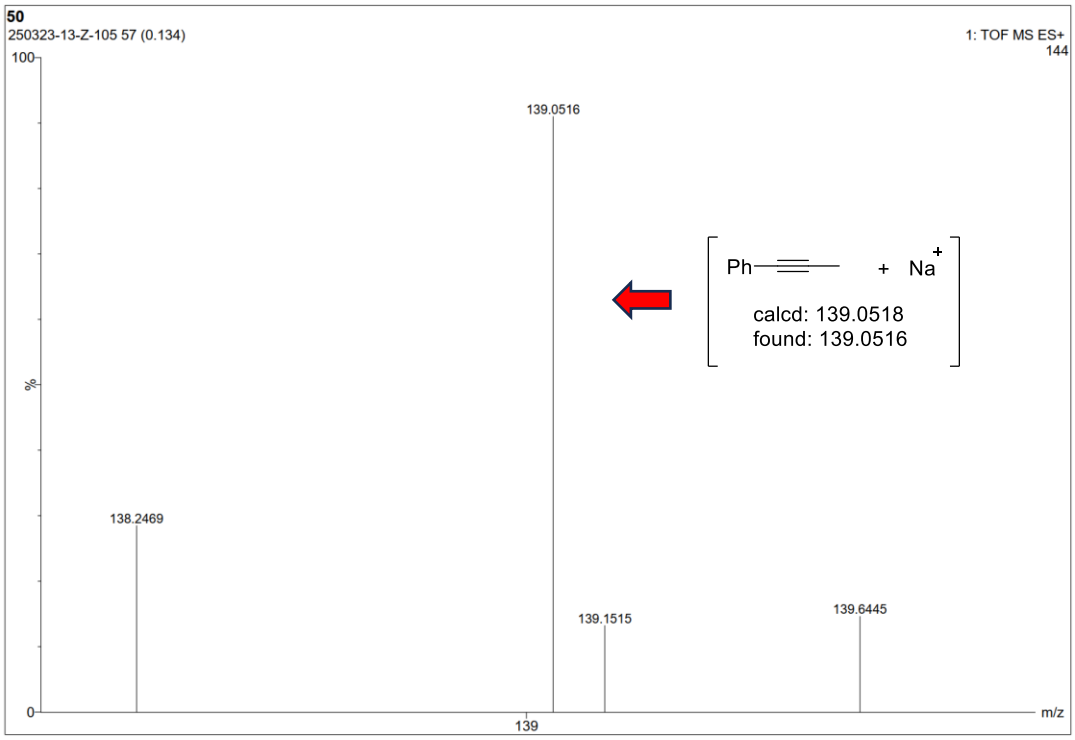
We used ethynylsulfonamide (**1g**) as the substrate, and di-tert-butyl peroxide (DTBP) was used as the initiator instead of TBPB. The target **2g** was isolated in 85% yield. When the reaction mixture was directly detected by HRMS (parallel experiment), prop-1-yn-1-ylarene **9** (HRMS (ESI) m/z calcd for C_9H_8Na [M+Na]+ 139.0518, found 139.0516) was observed.



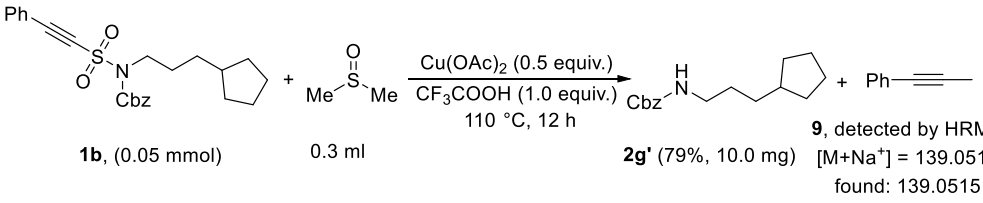
1g, (0.05 mmol)

2g (85%, 15.1 mg)

9, detected by HRMS
[M+Na$^+$] = 139.0518
found: 139.0516



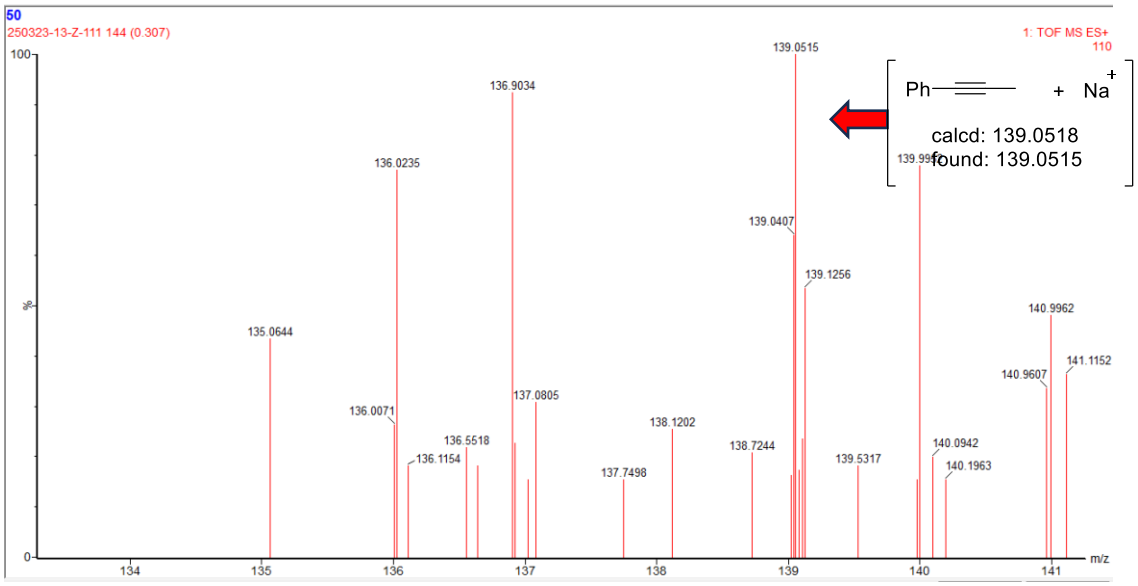
Then we performed the reaction of ethynylsulfonamide (**1g**) under Tan's methyl radical generation condition (*Chem. Commun.*, 2015, **51**, 1823) and found that the reductive carbamate **2g'** was formed in 79% yield, along with the observation of prop-1-yn-1-ylarene **9** by HRMS.



1b, (0.05 mmol) 0.3 ml **2g'** (79%, 10.0 mg) **9**, detected by HRMS

$[M+Na^+]$ = 139.0518

found: 139.0515

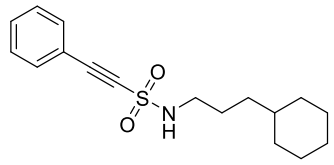


9 References

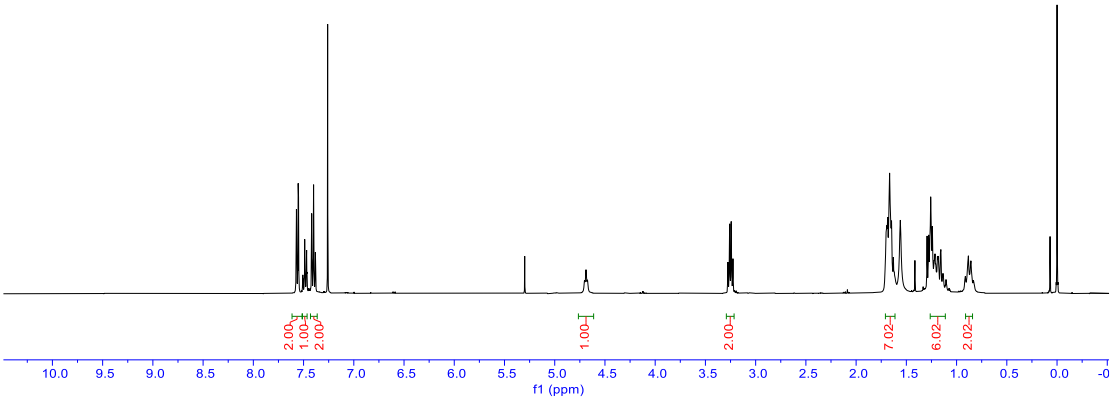
[1] Q. P. Hu, J. Cheng, Y. Wang, J. Shi, B. Q. Wang, P. Hu, K. Q. Zhao and F. Pan. *Org. Lett.* 2021, **23**, 4457.
[2] T. Utsumi, K. Noda, D. Kawauchi, H. Ueda and H. Tokuyama. *Adv. Synth. Catal.* 2020, **362**, 3583.
[3] L. Steemers, M. J. Wanner, M. Lutz, H. Hiemstra and J. H. van. Maarseveen. *Nat Commun.* 2017, **8**, 15392.
[4] E. Palomo, A. K. Sharma, Z. F. Wang, L. Y. Jiang, F. Maseras and M. G. Suero. *J. Am. Chem. Soc.* 2023, **145**, 4975.
[5] S. Y. Meng, W. T. Guo, J. Liu, J. Zheng and Q. R. Wang. *ChemistrySelect* 2022, **7**, e202202760.
[6] S. Jain and O. Reiser. *ChemSusChem.* 2008, **1**, 534.

10. NMR spectra of the starting materials and products

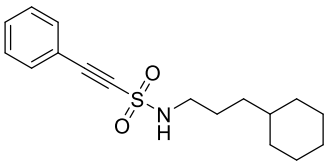
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S1



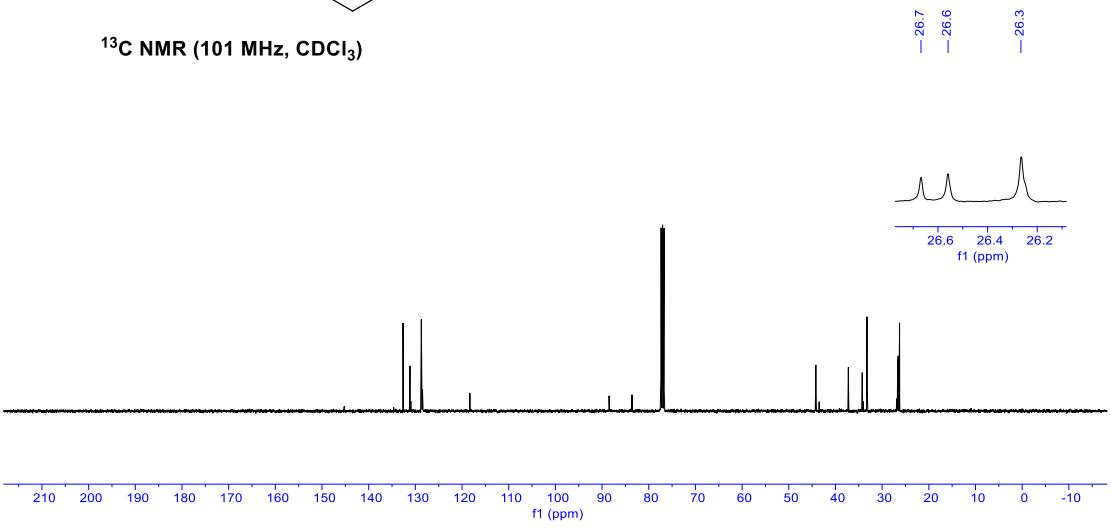
^{1}H NMR (400 MHz, $CDCl_3$)



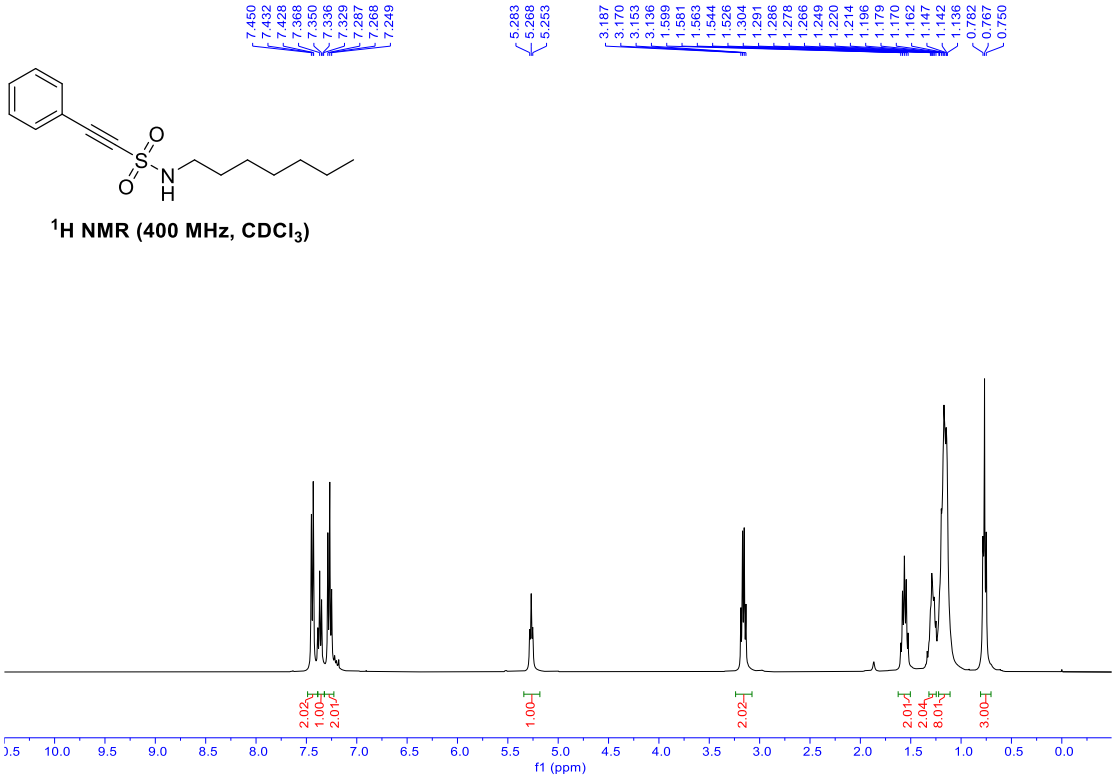
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S1



^{13}C NMR (101 MHz, $CDCl_3$)

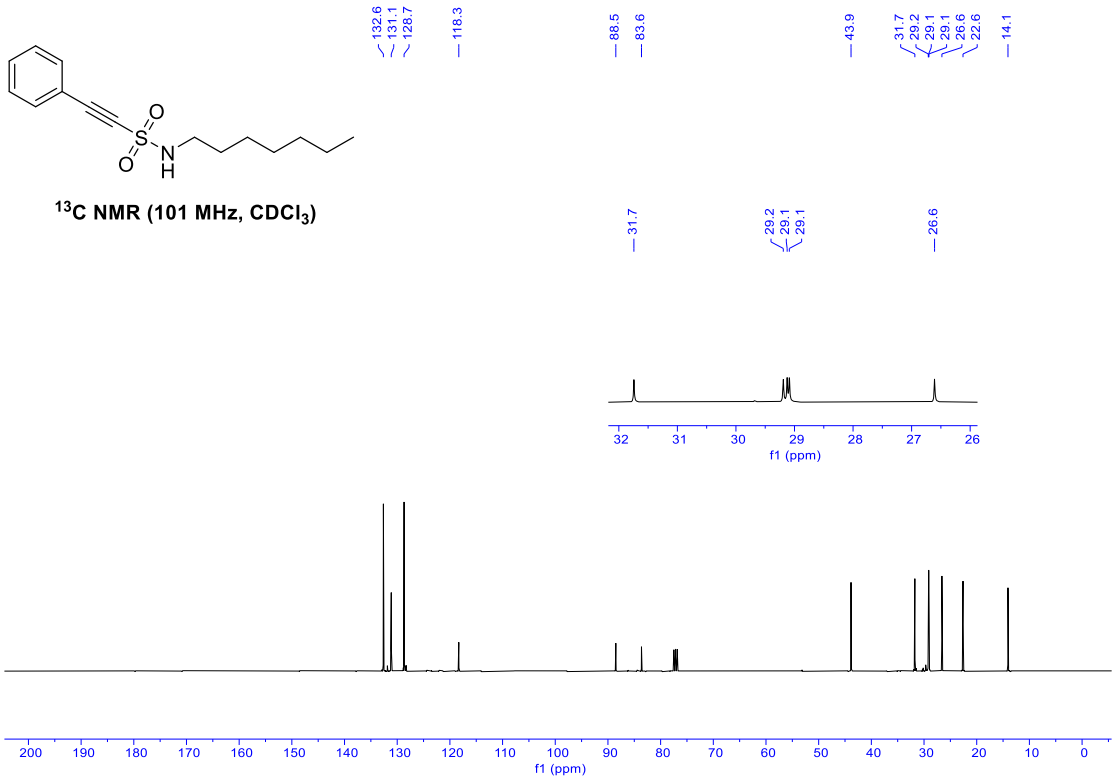


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S2



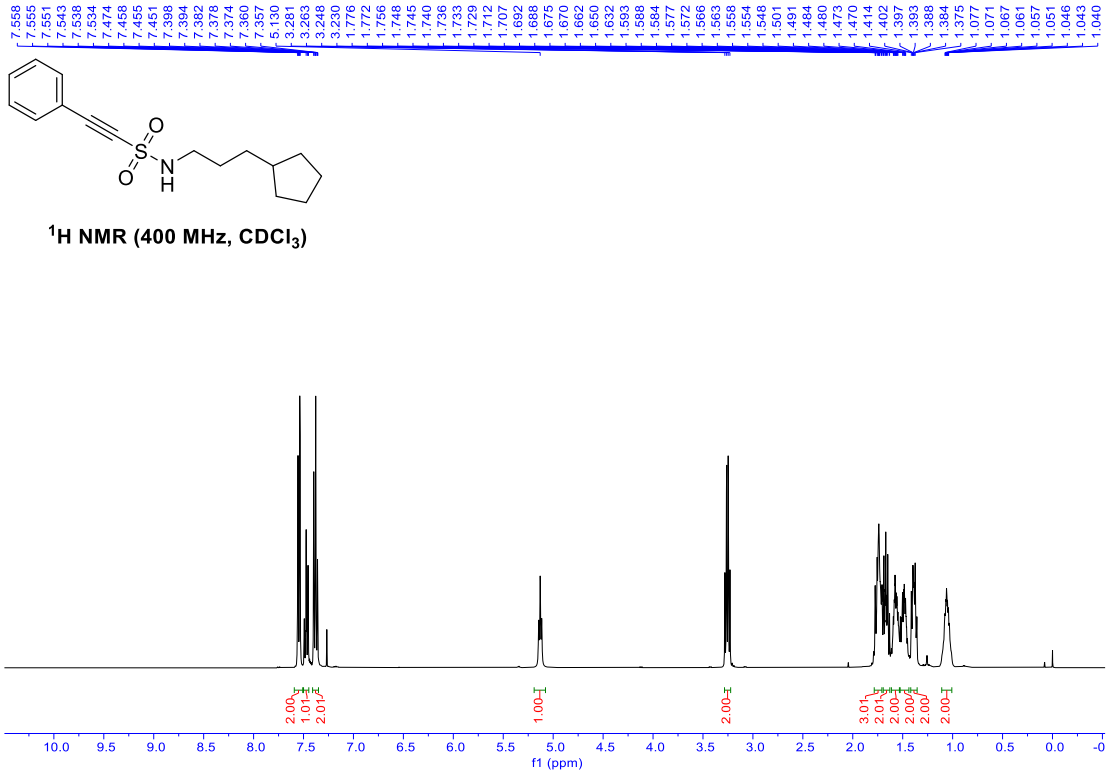
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S2



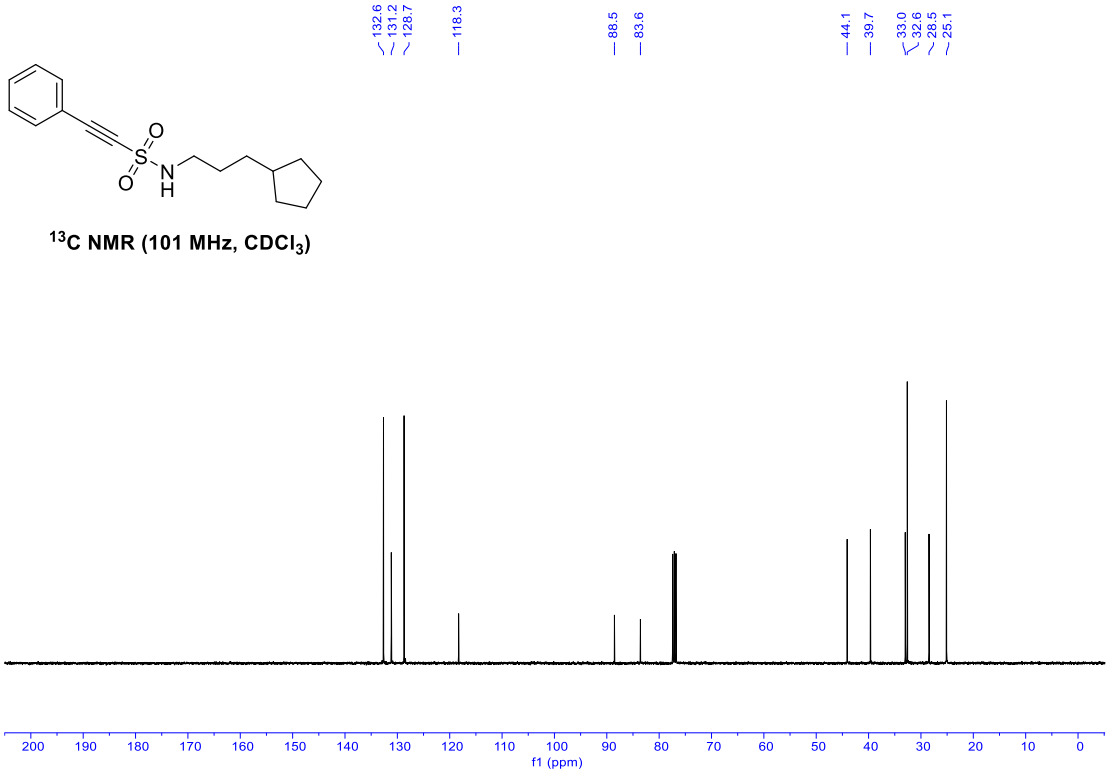
^{13}C NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S3



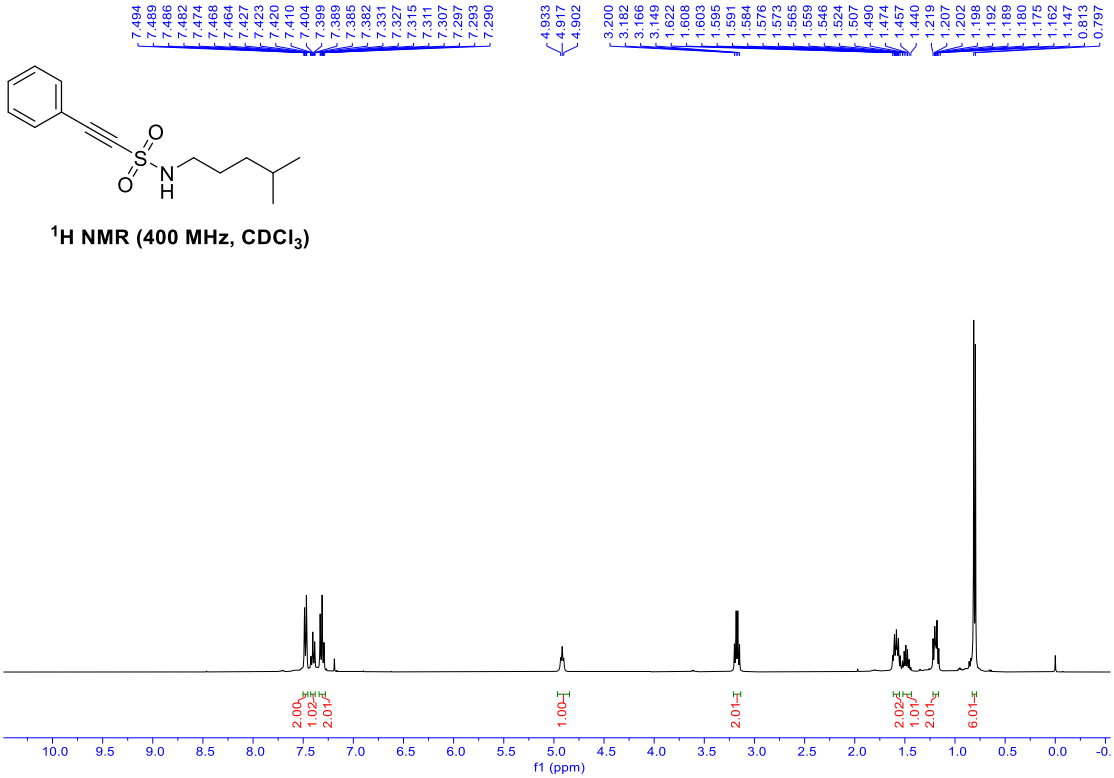
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S3



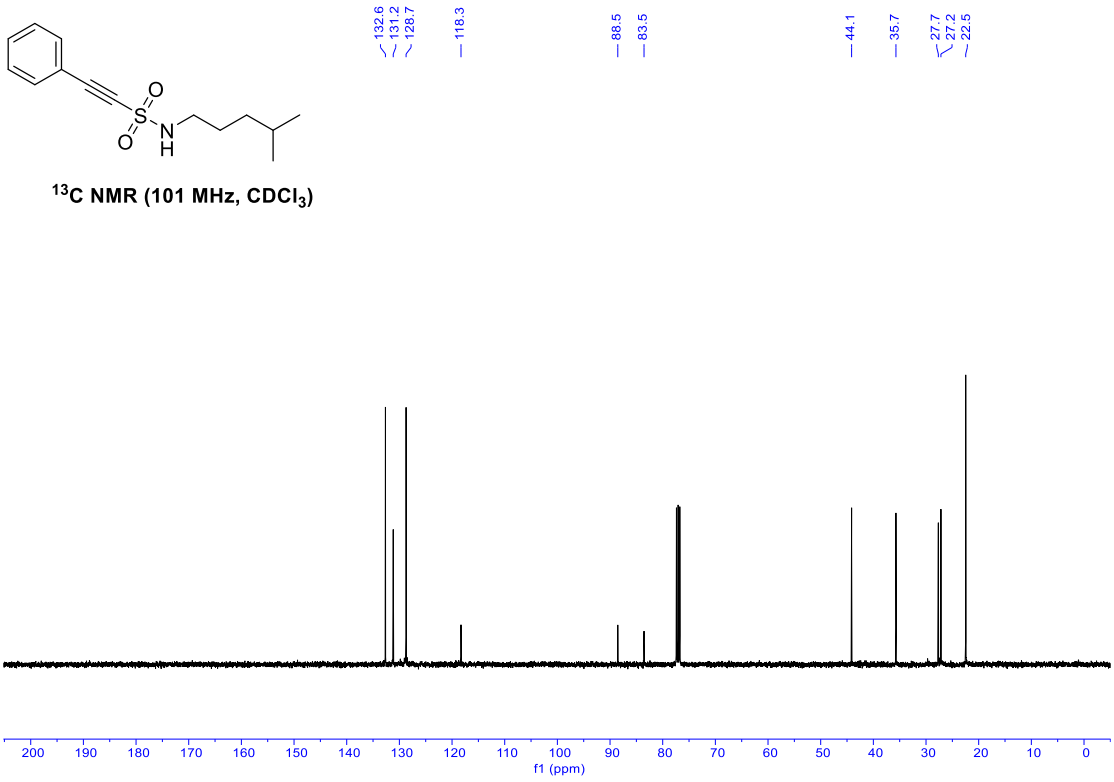
^{13}C NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S4



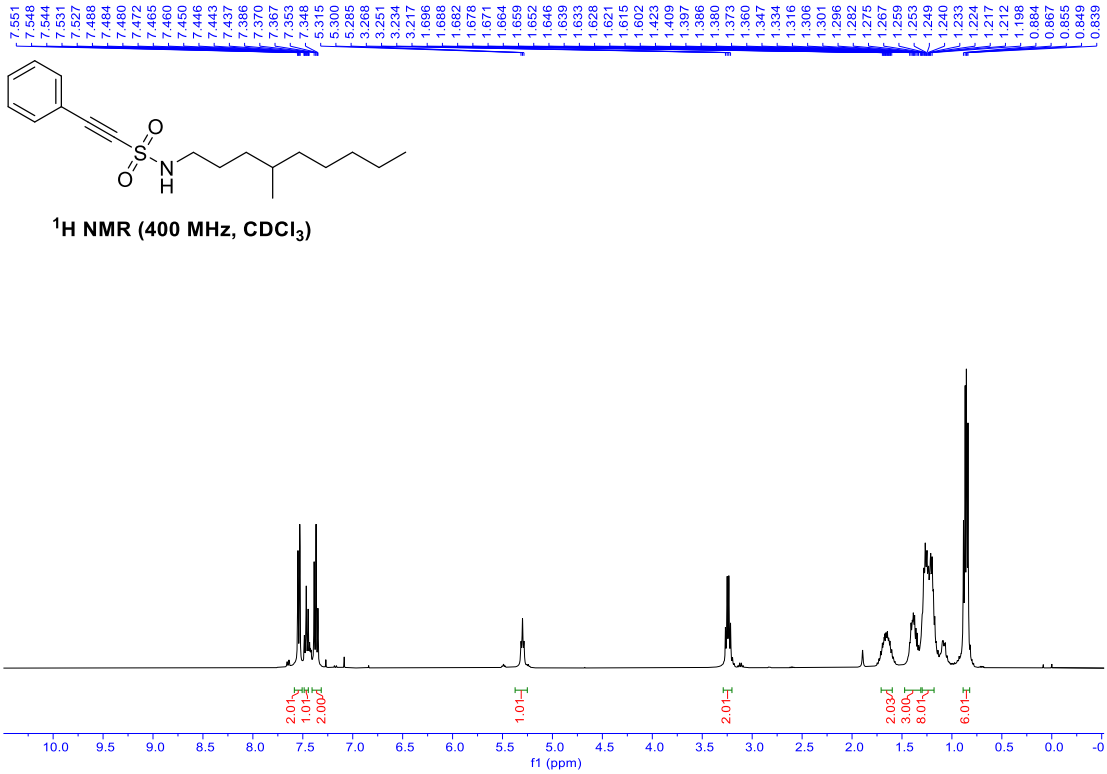
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S4

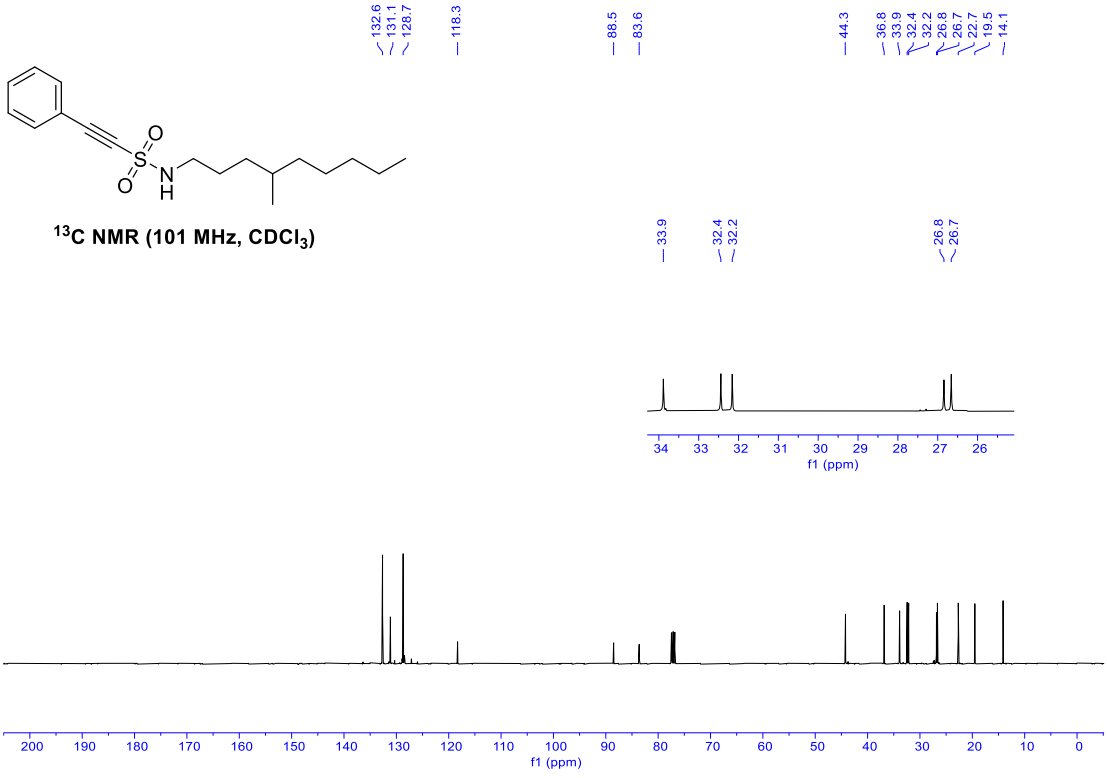


^{13}C NMR (101 MHz, $CDCl_3$)

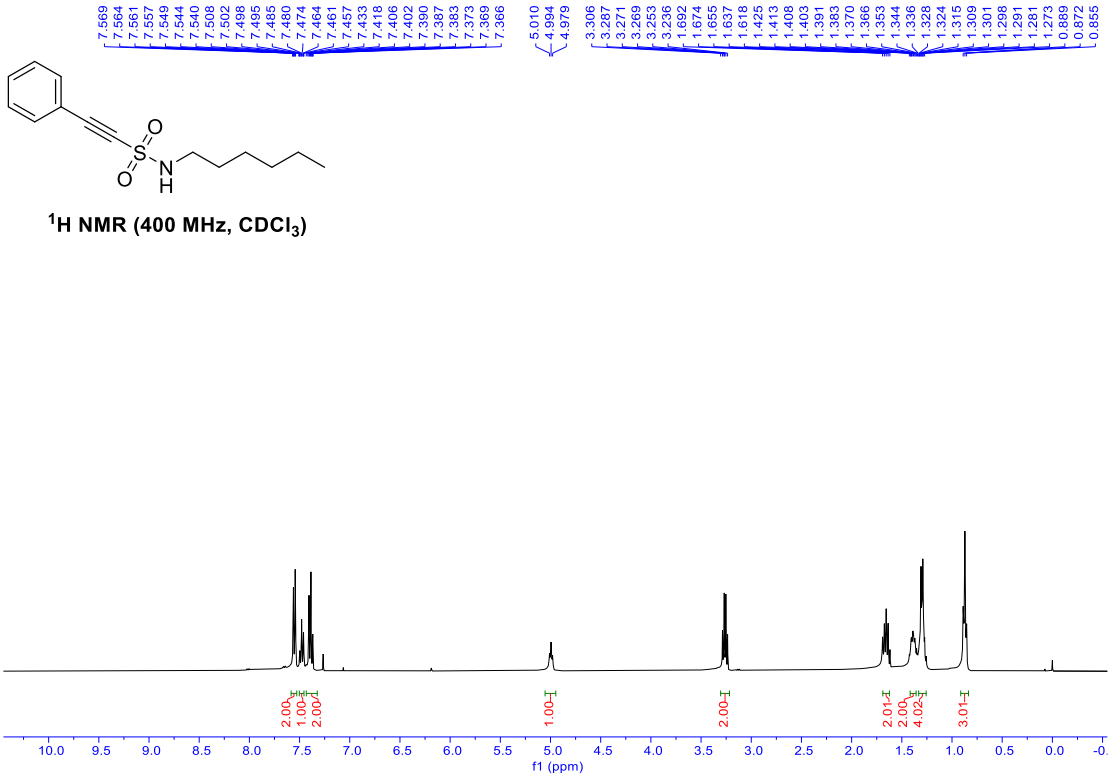
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S5



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S5

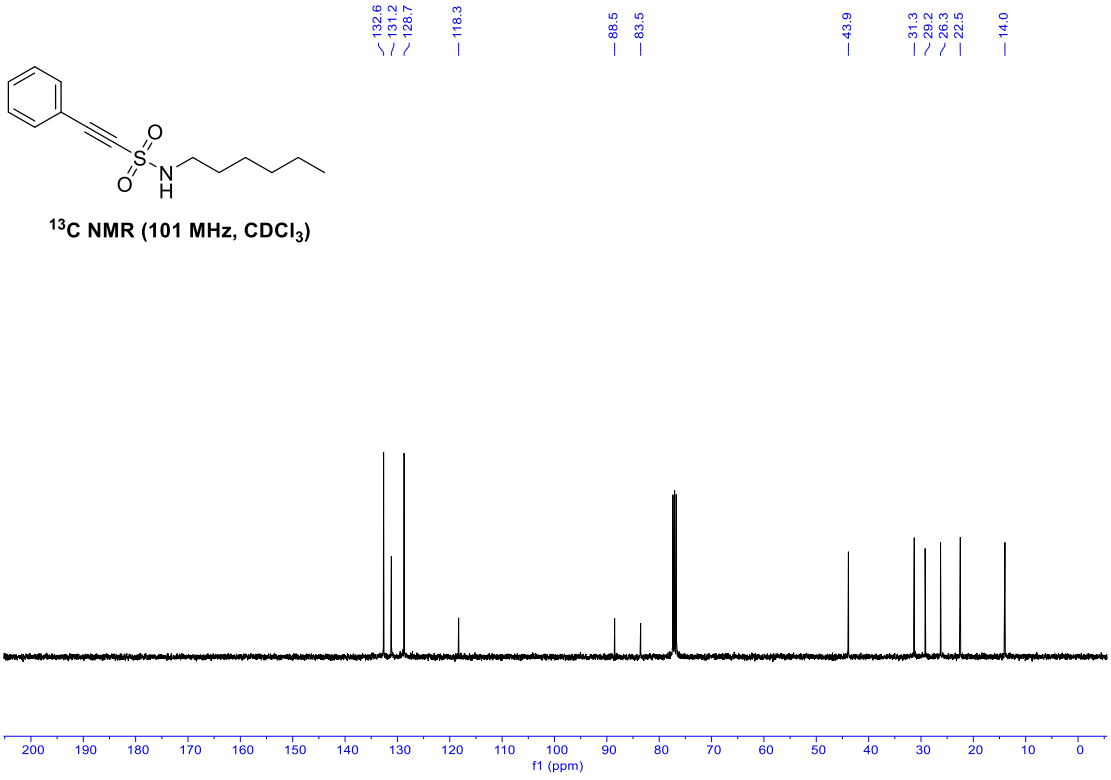


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S6



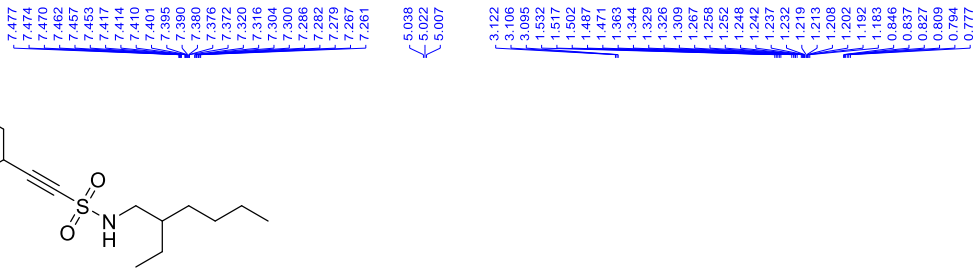
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S6

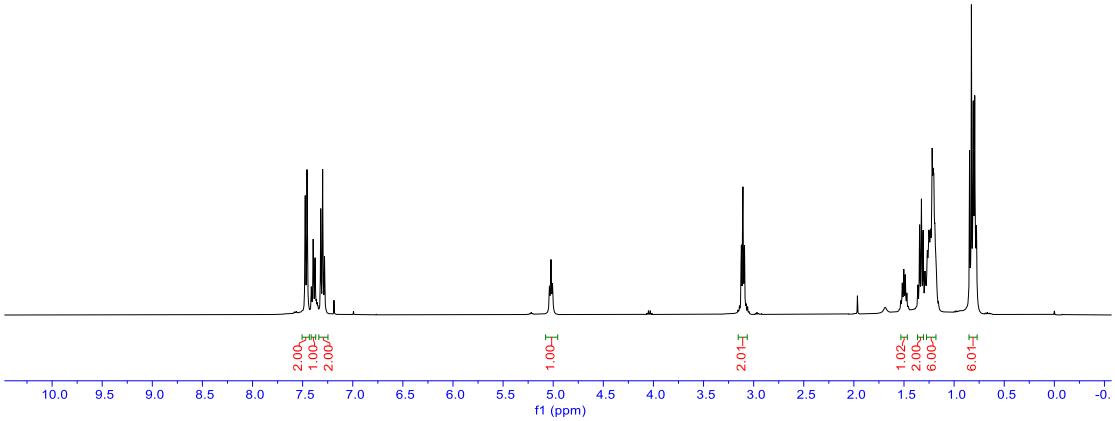


^{13}C NMR (101 MHz, $CDCl_3$)

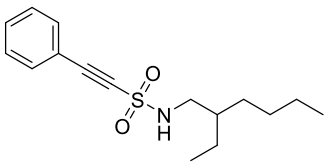
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S7



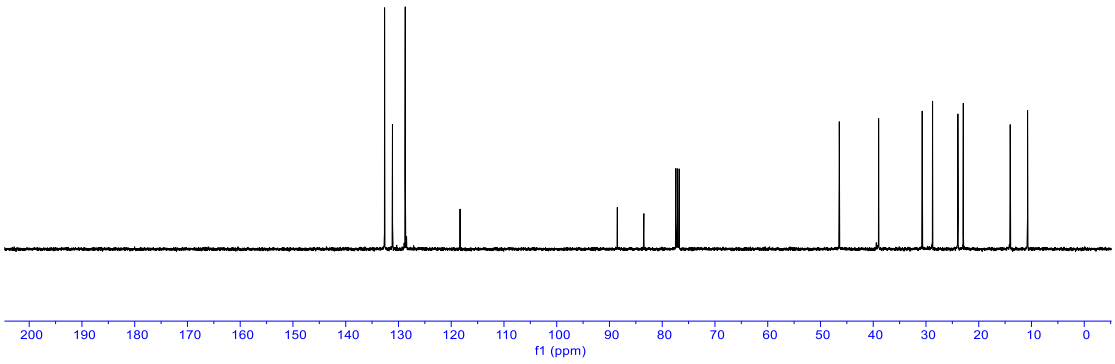
^{1}H NMR (400 MHz, $CDCl_3$)



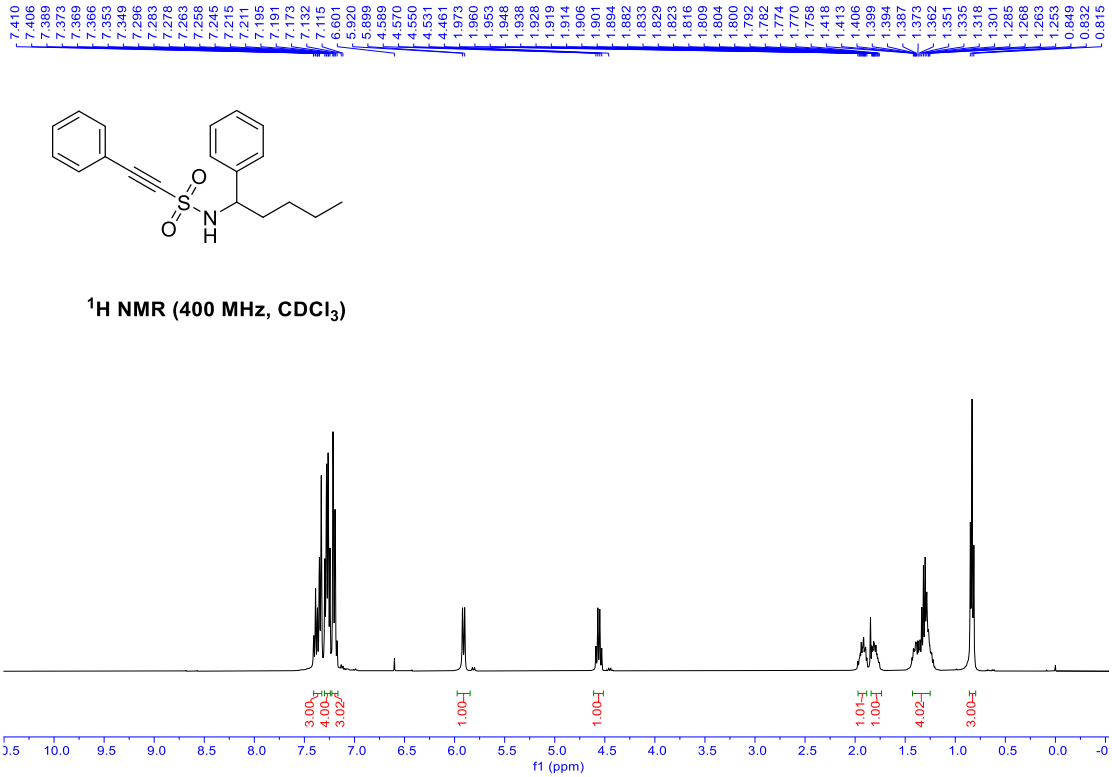
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S7



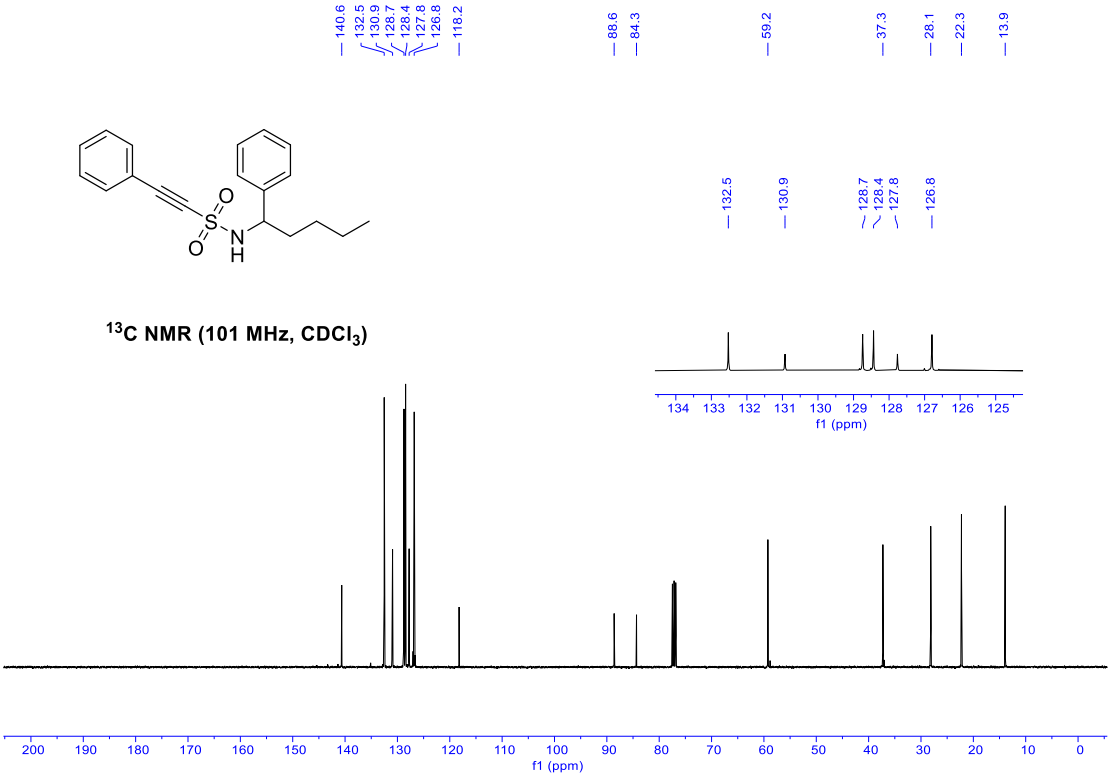
^{13}C NMR (101 MHz, $CDCl_3$)



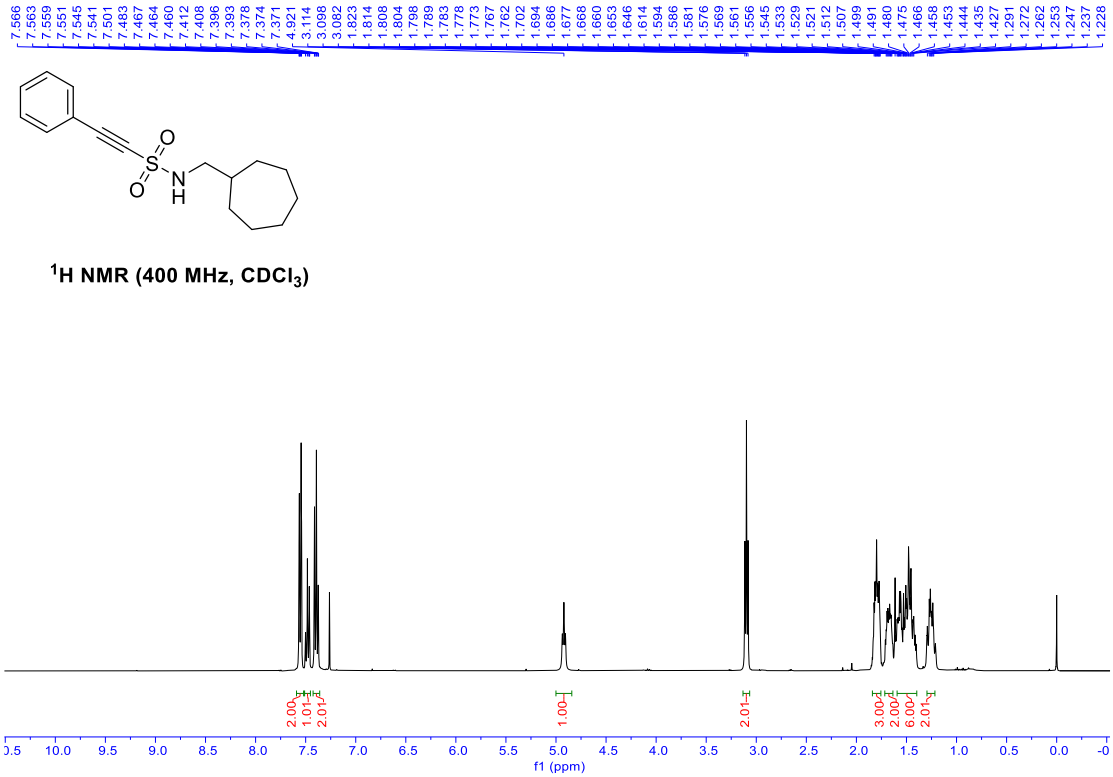
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S8



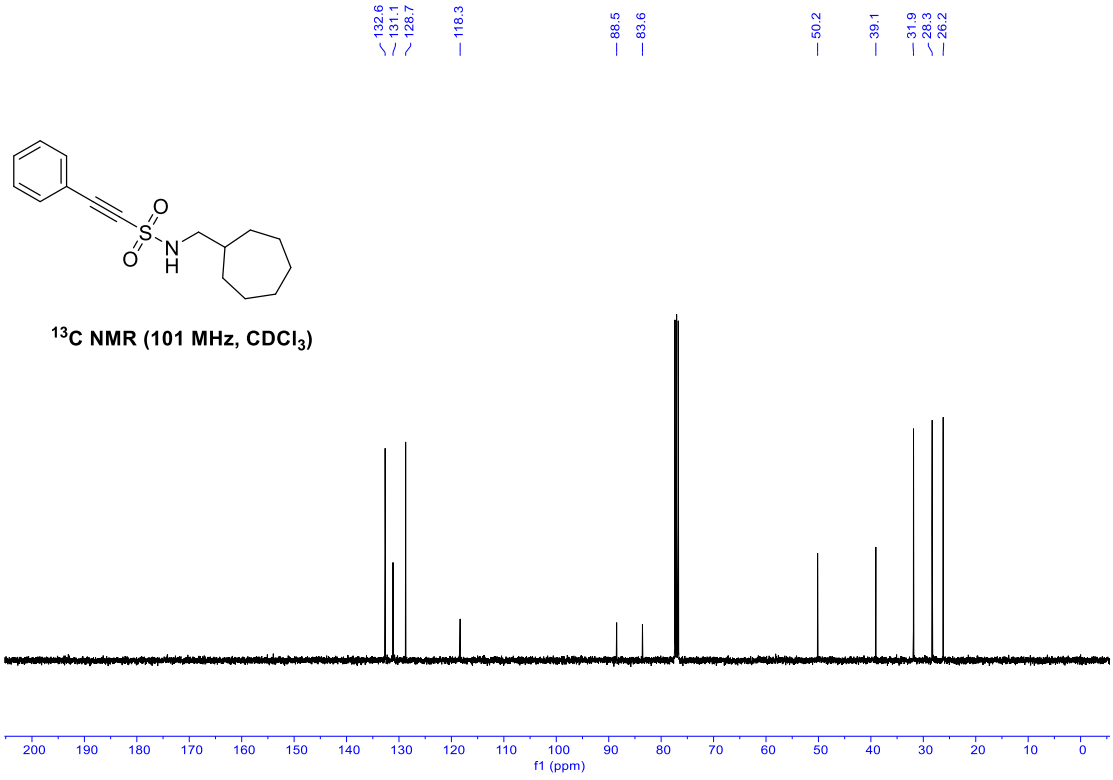
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S8



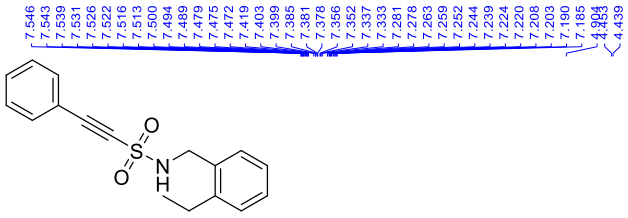
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S9

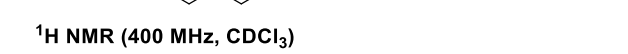


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S9

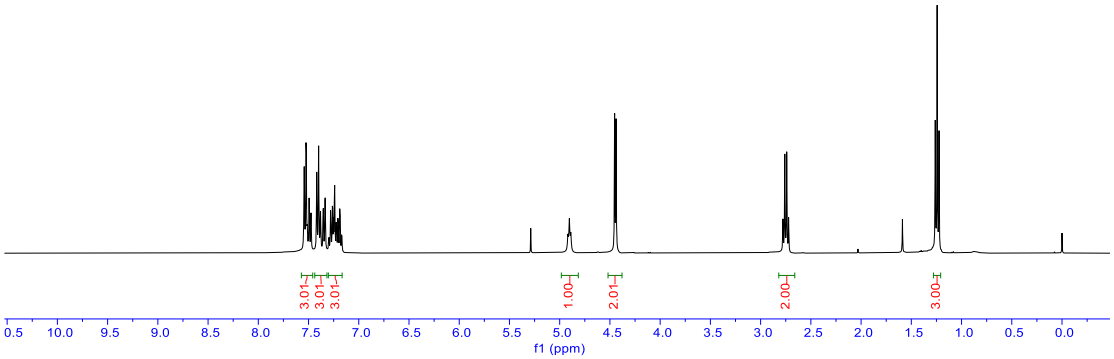


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S10

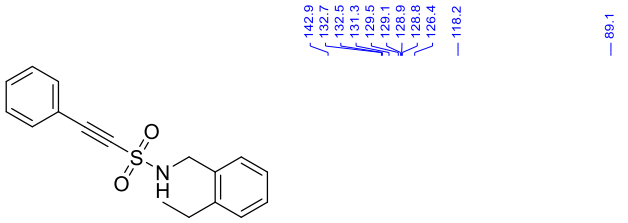


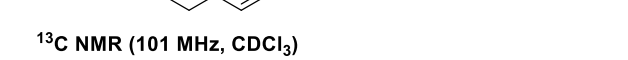


^{1}H NMR (400 MHz, $CDCl_3$)

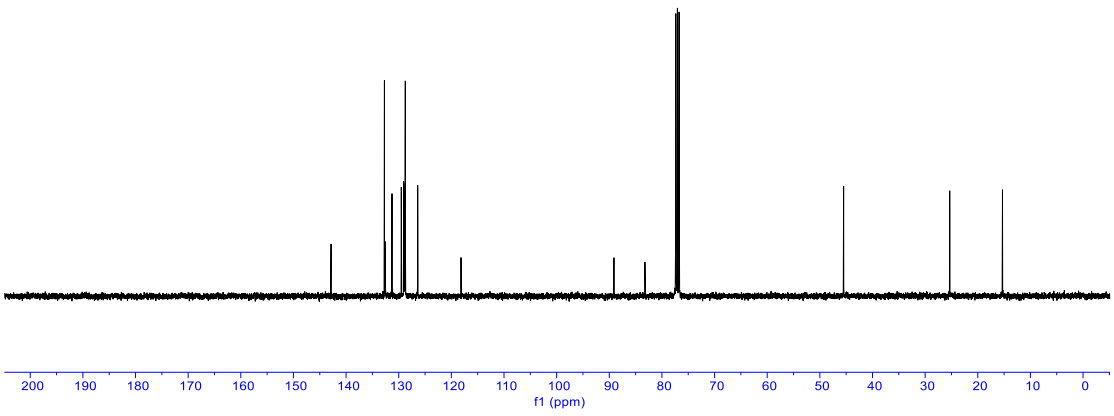


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S10

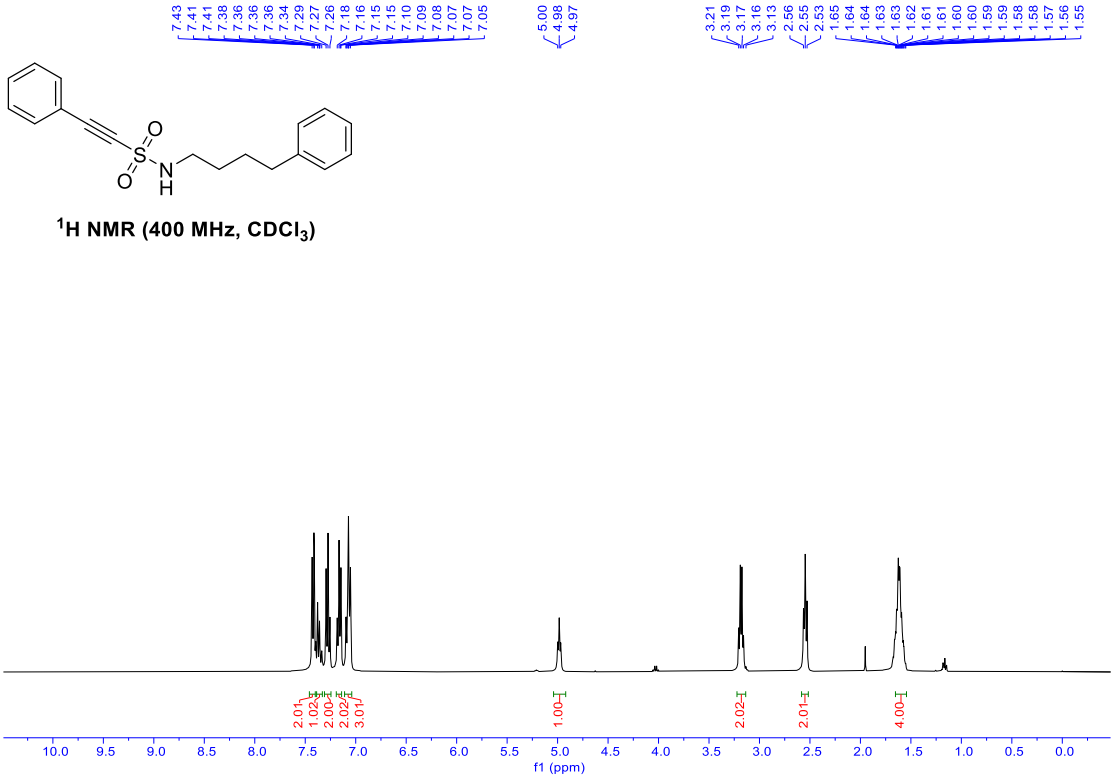




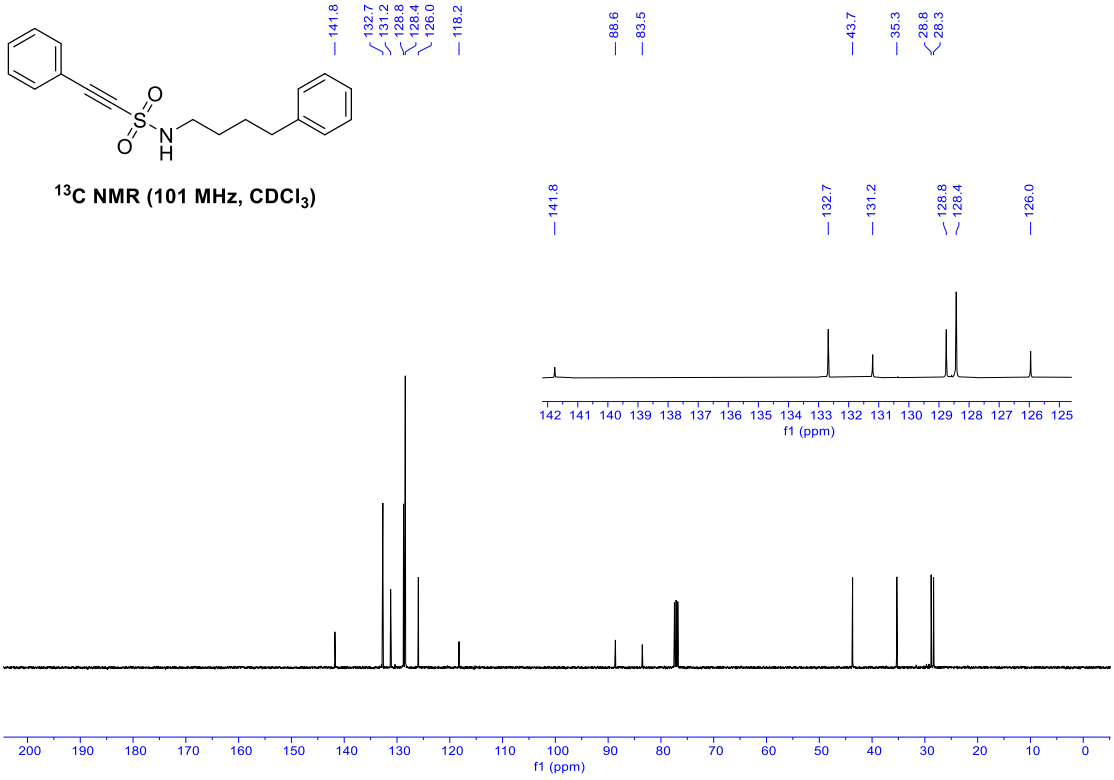
^{13}C NMR (101 MHz, $CDCl_3$)



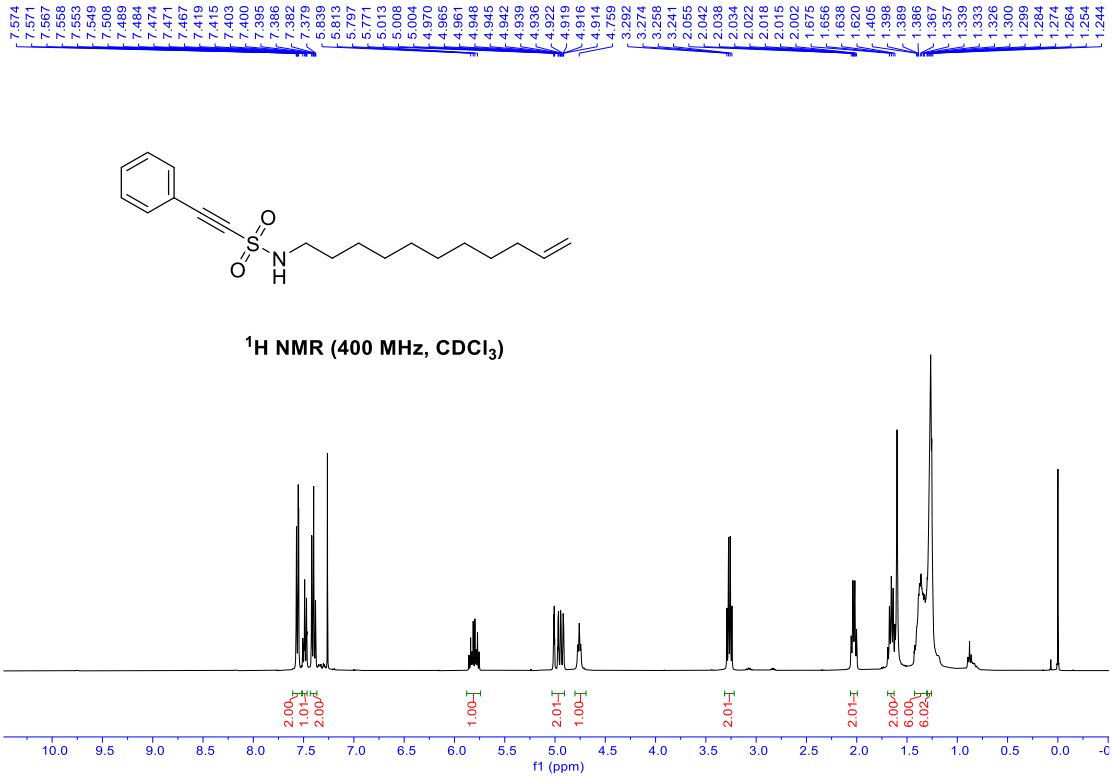
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S11



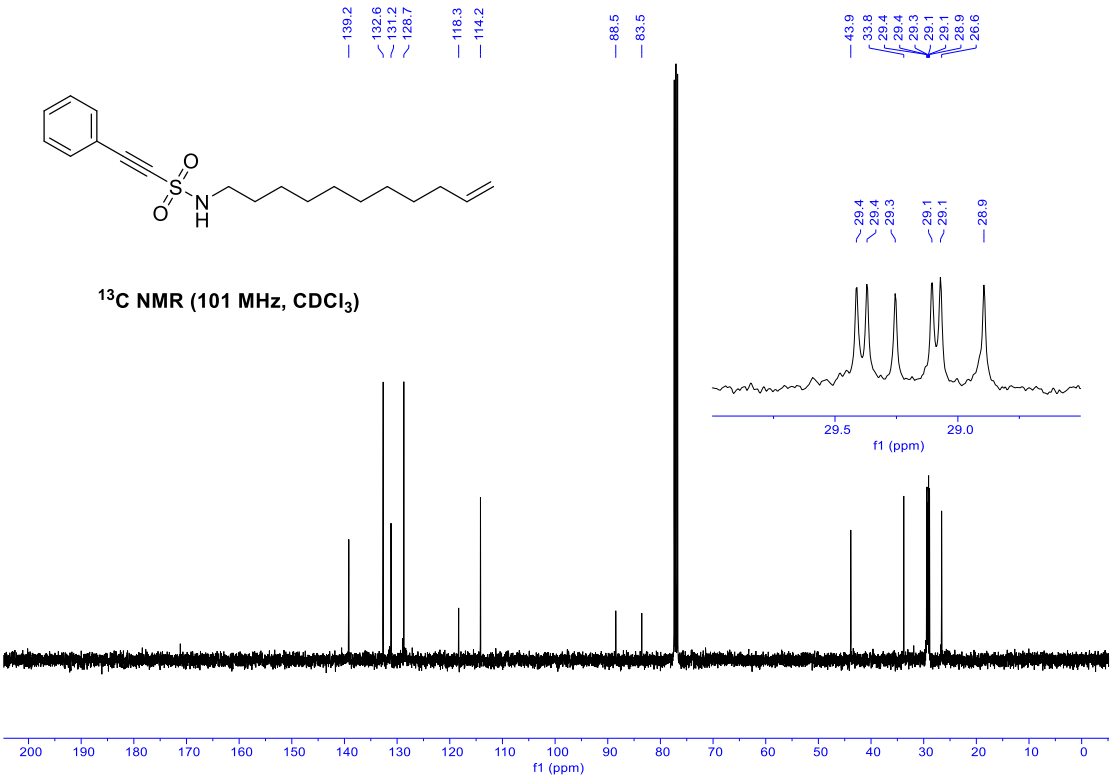
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S11



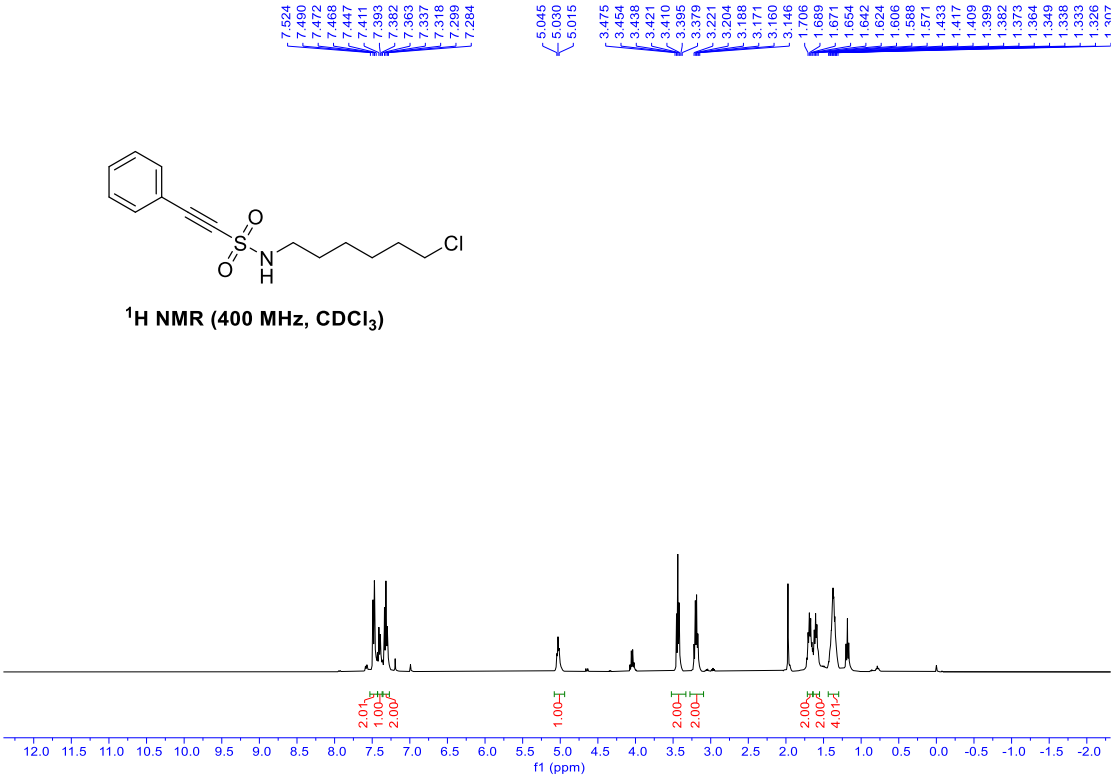
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S12



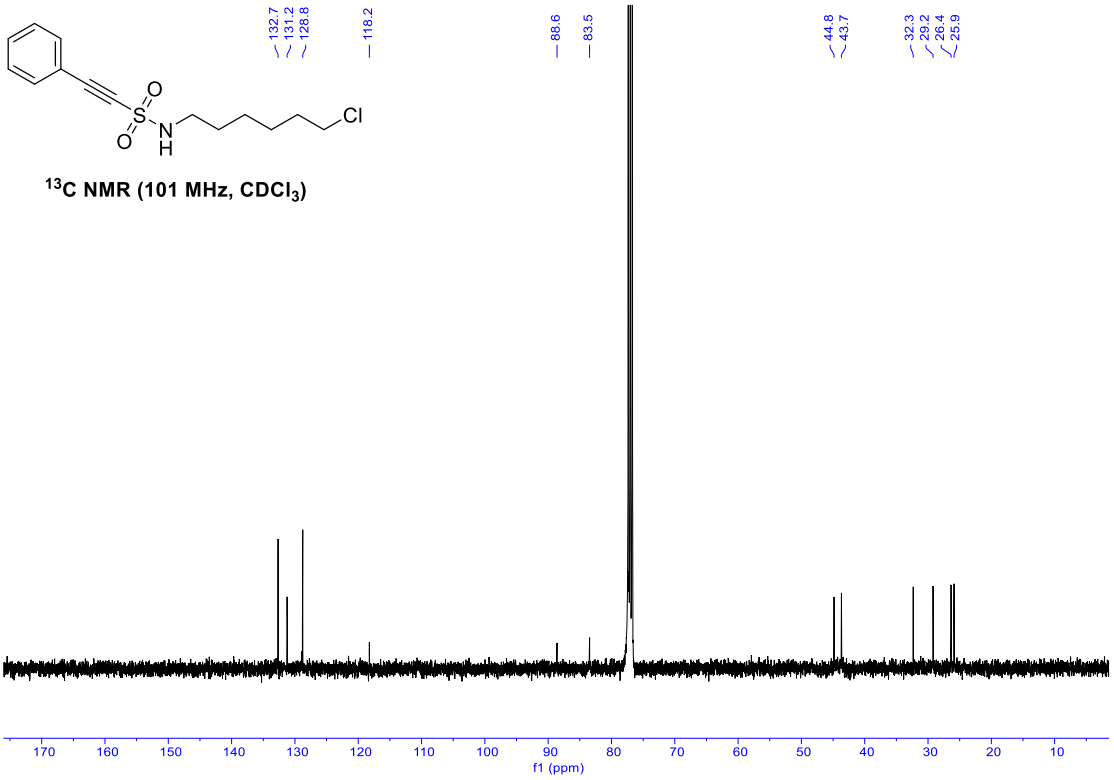
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S12



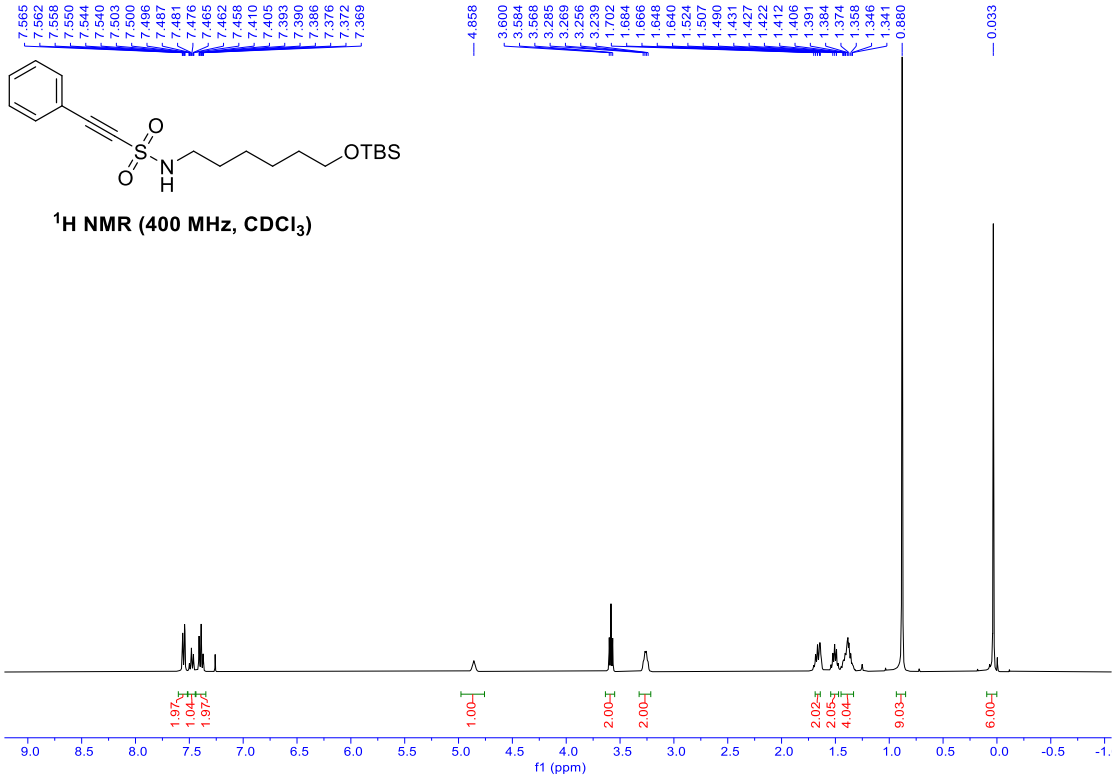
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S13



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S13

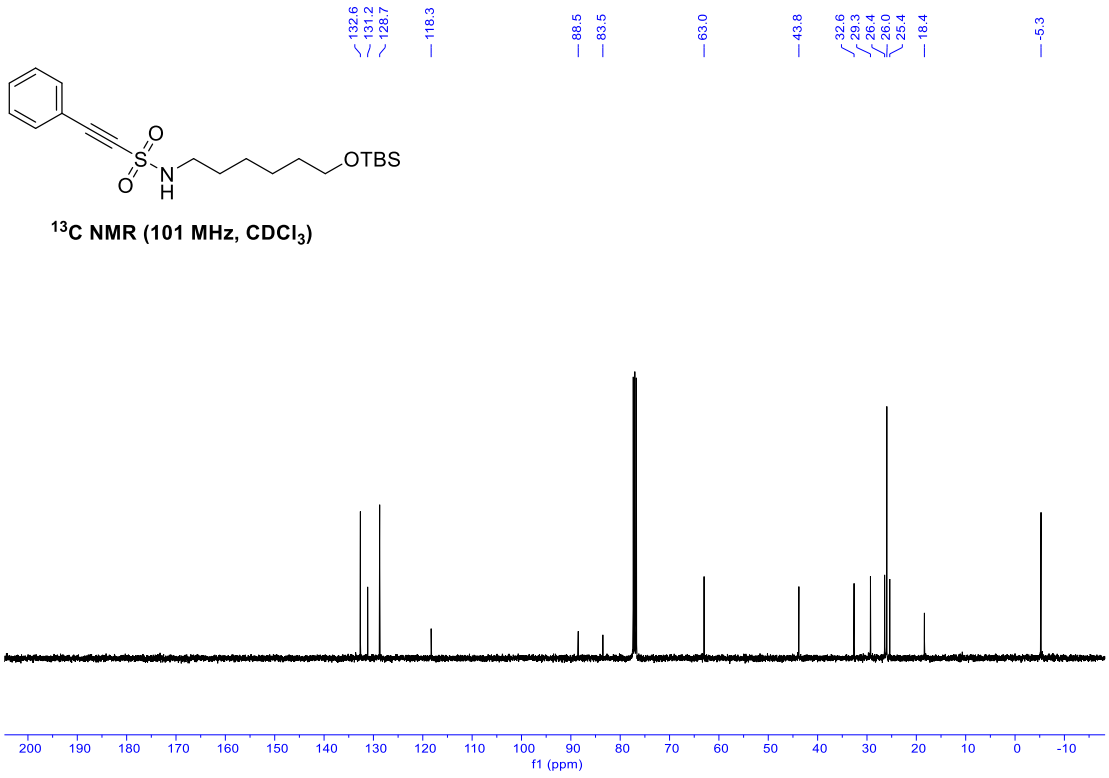


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S14



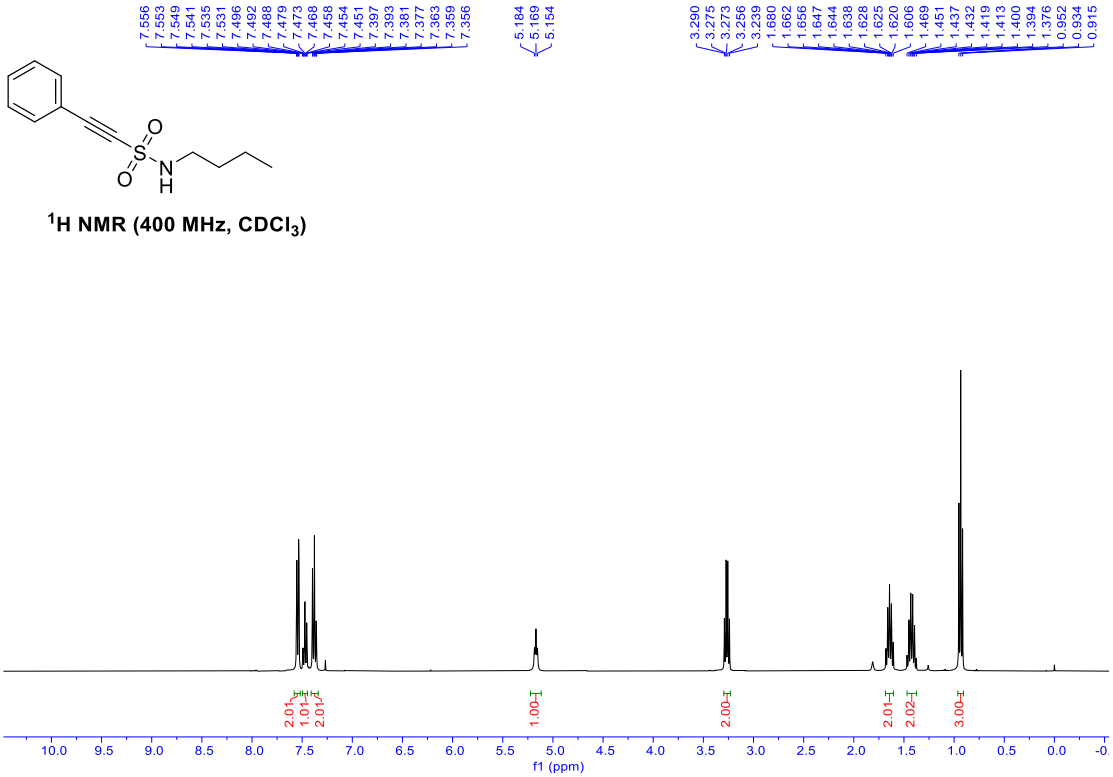
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S14



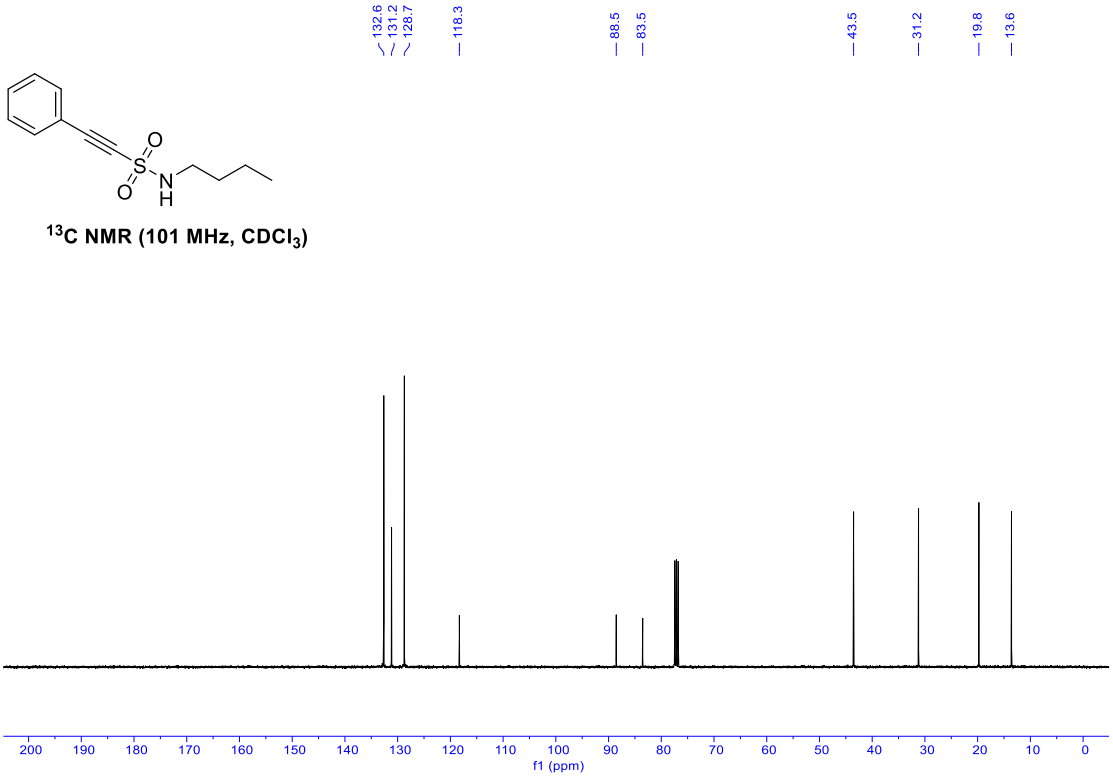
^{13}C NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S15



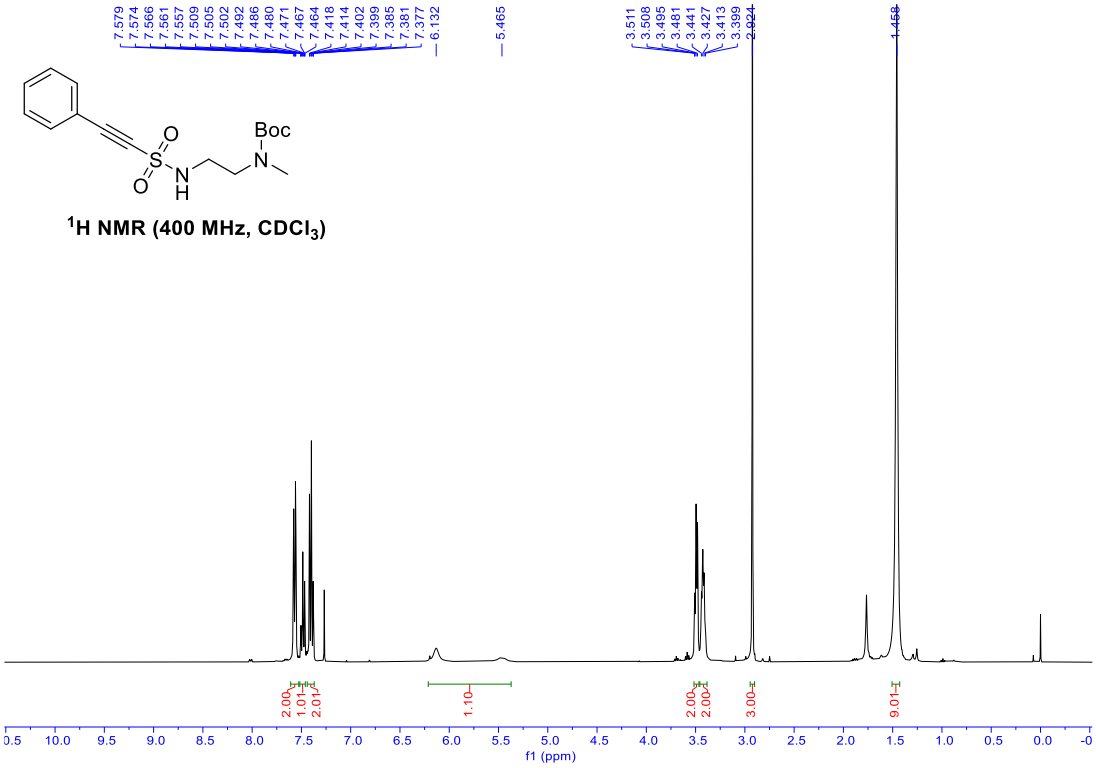
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S15

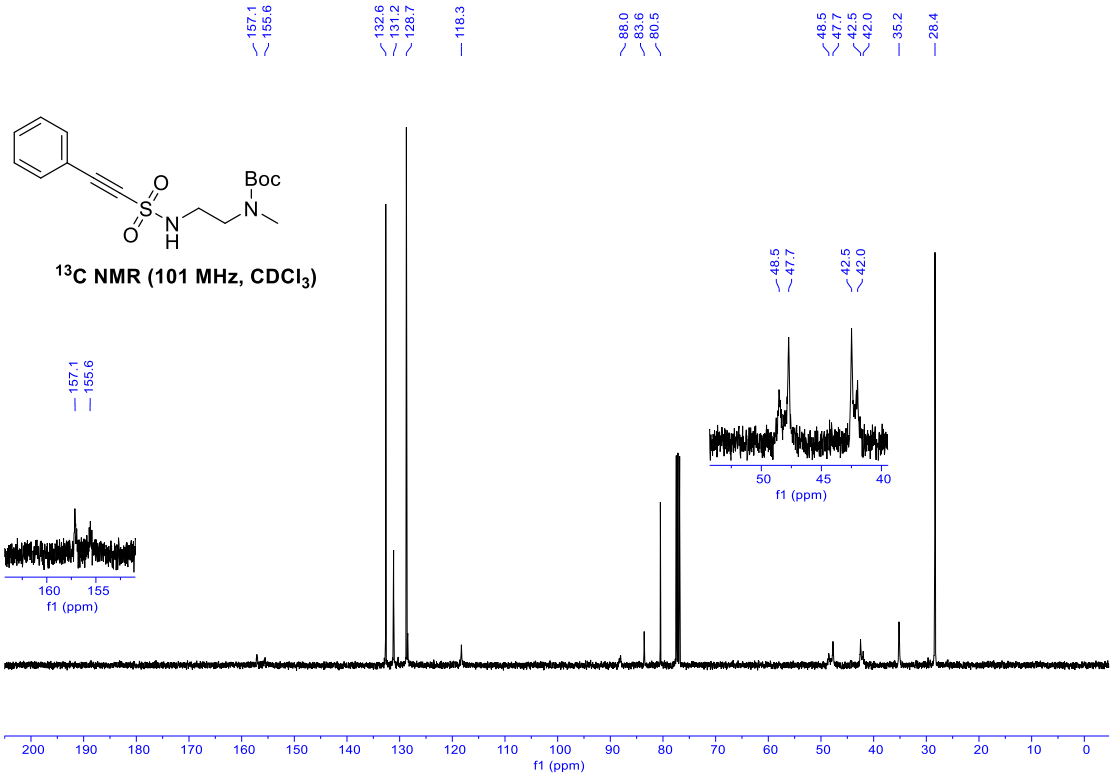


^{13}C NMR (101 MHz, $CDCl_3$)

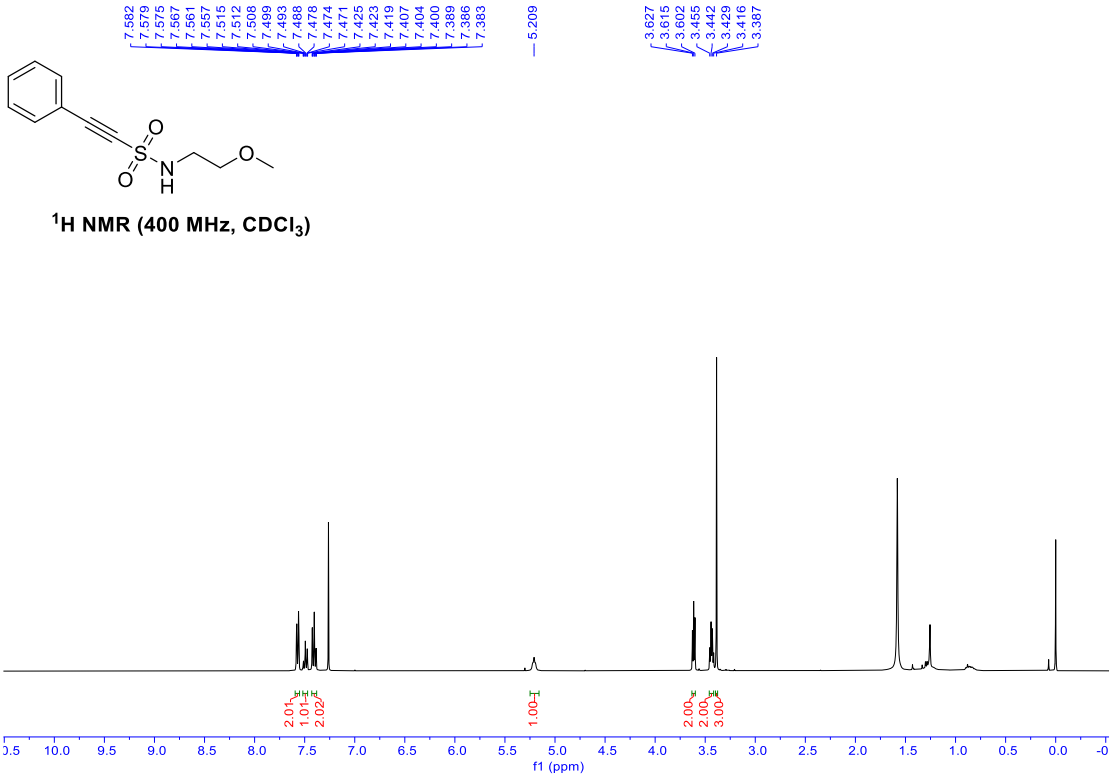
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S16



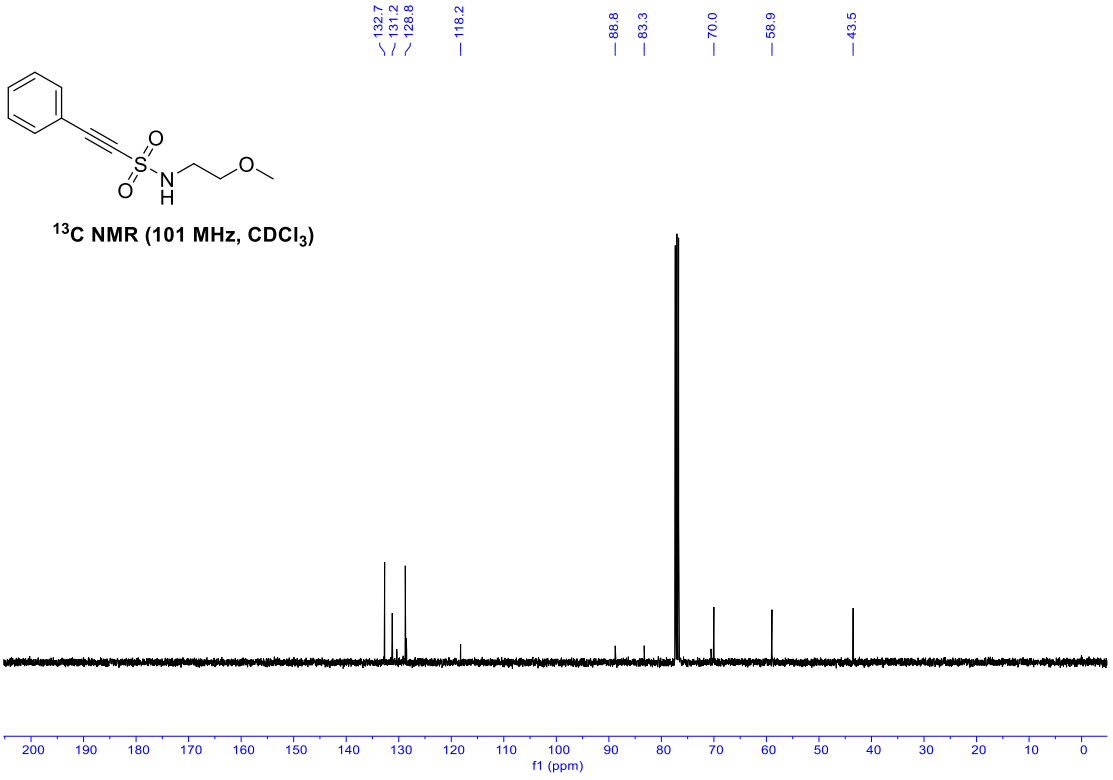
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S16



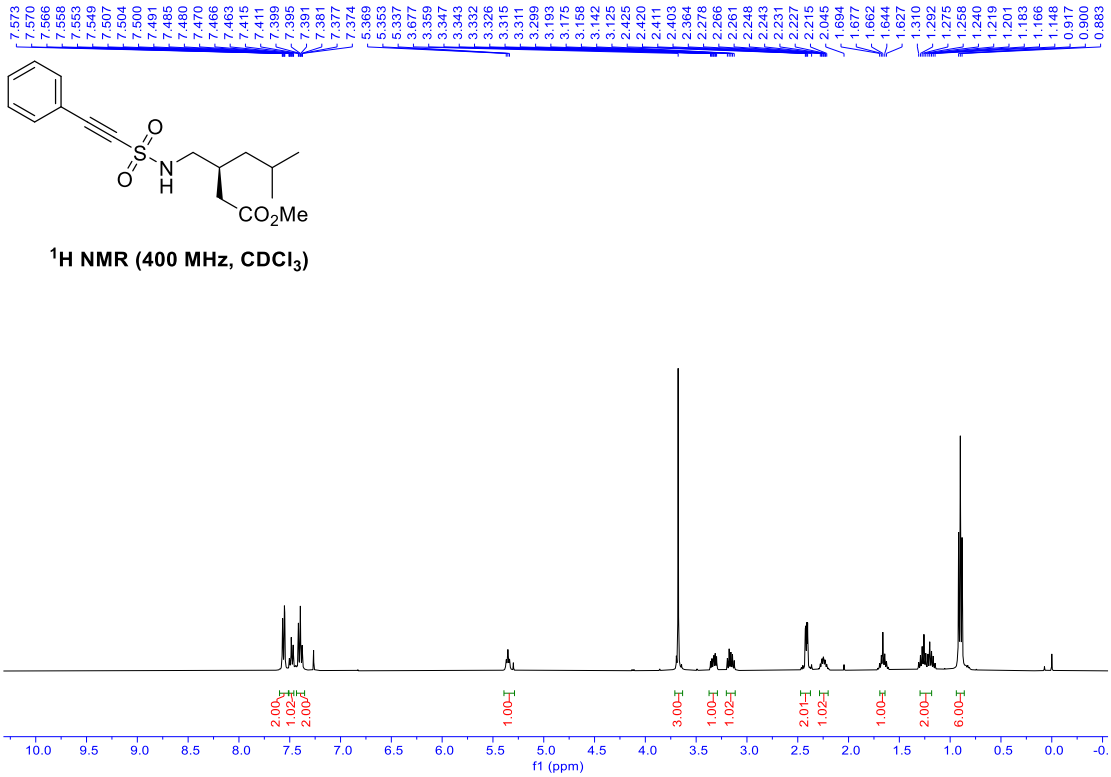
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S17



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S17

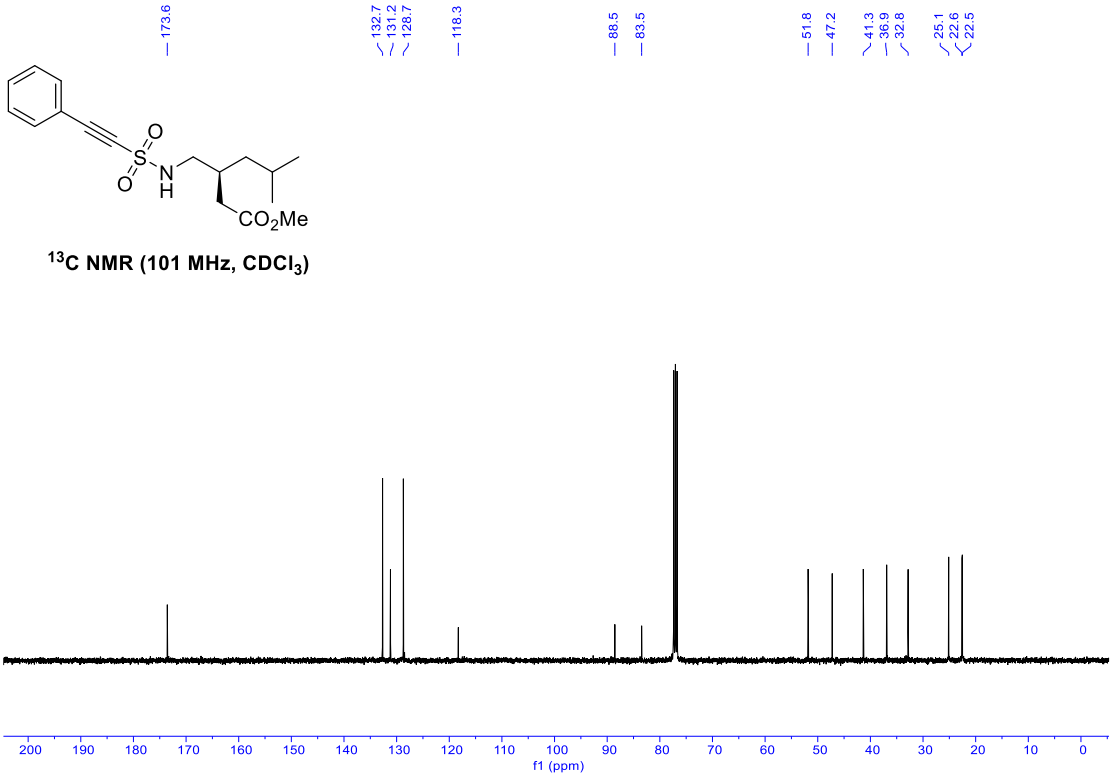


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S18



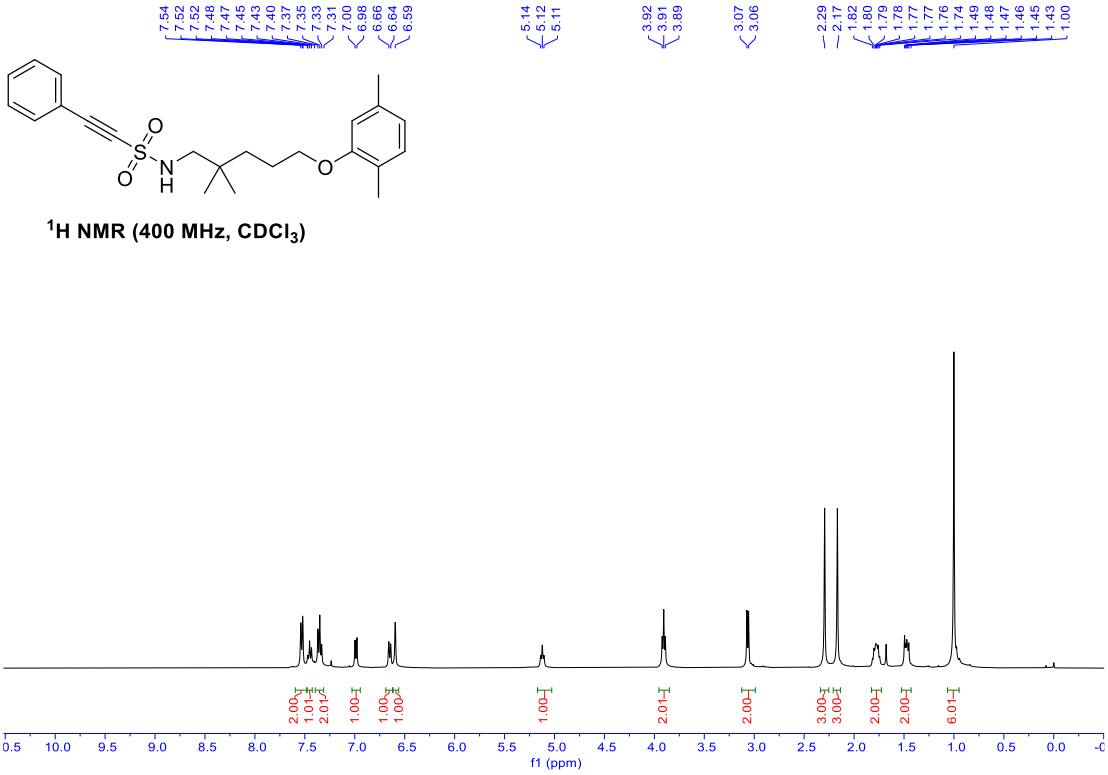
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S18



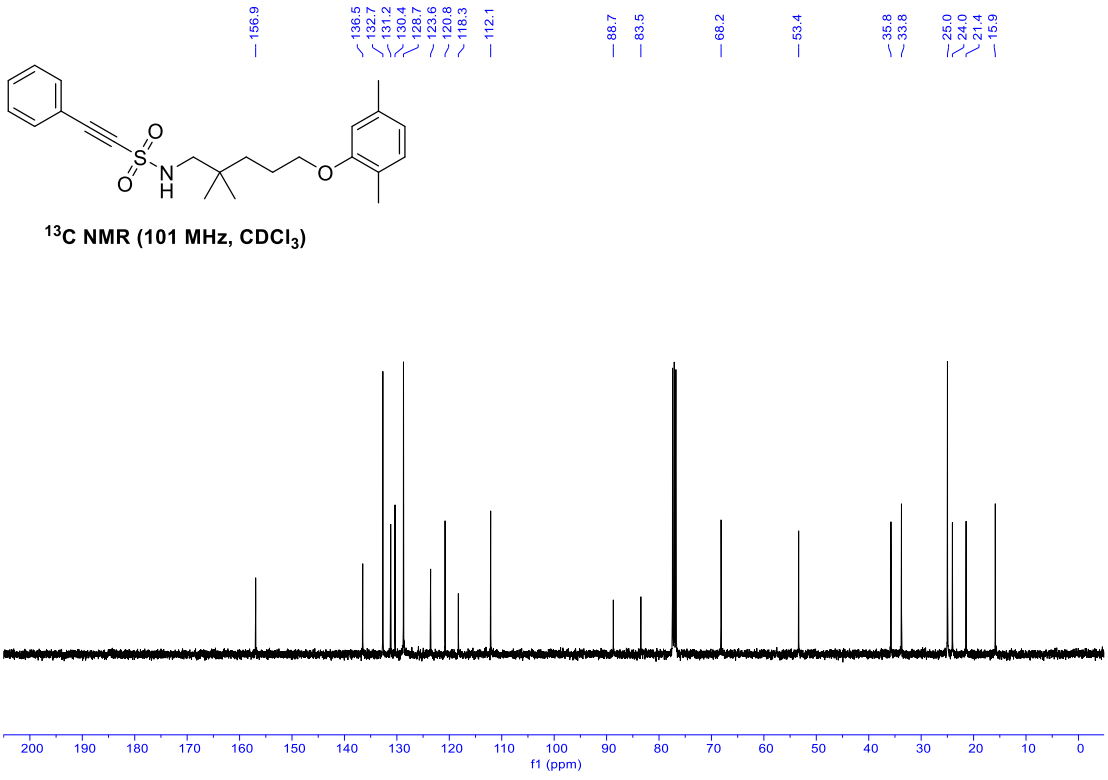
^{13}C NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S19



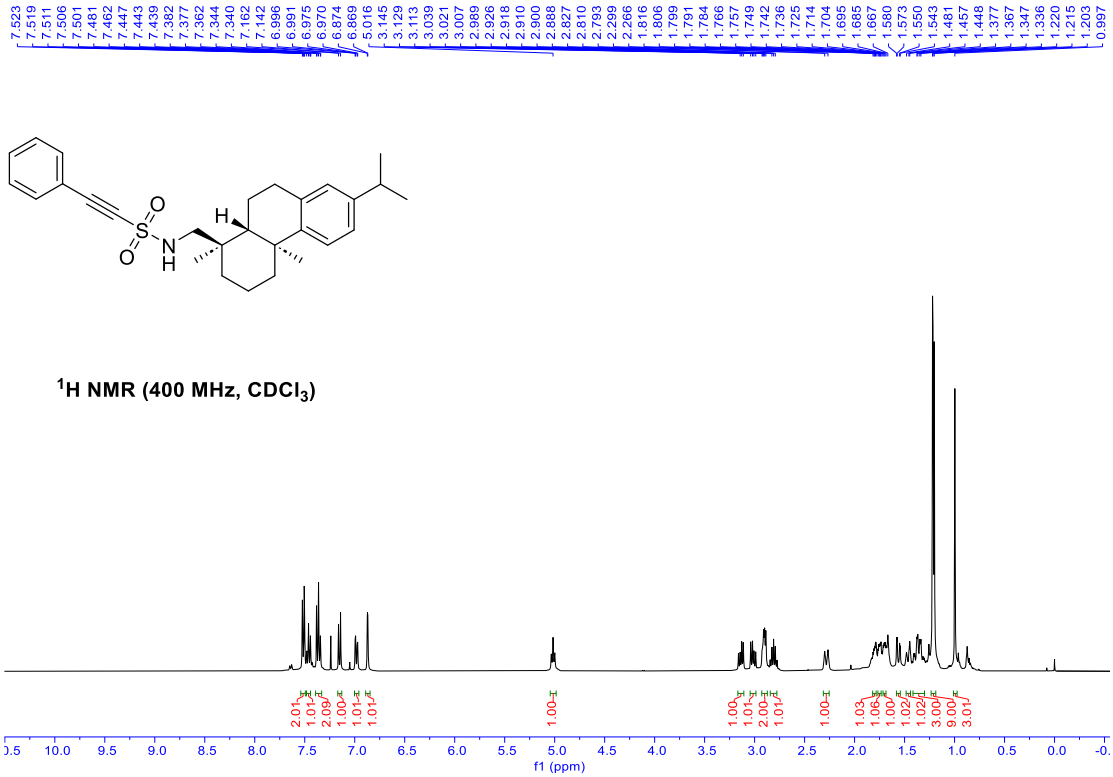
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S19

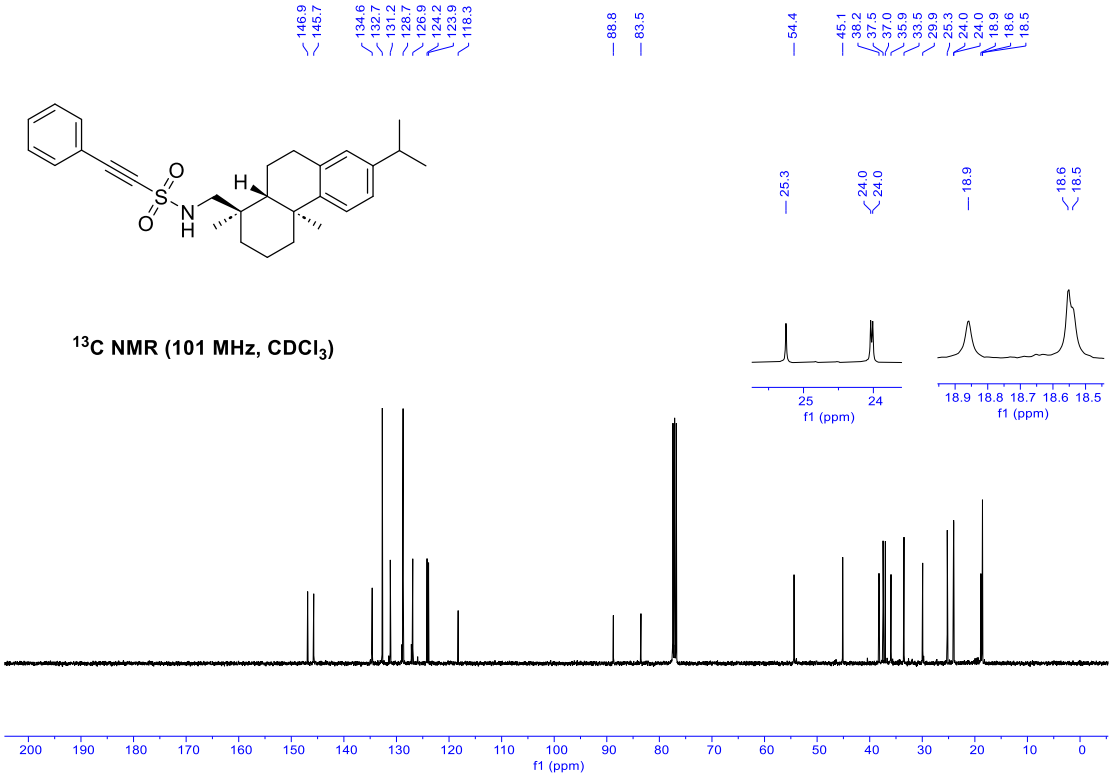


^{13}C NMR (101 MHz, $CDCl_3$)

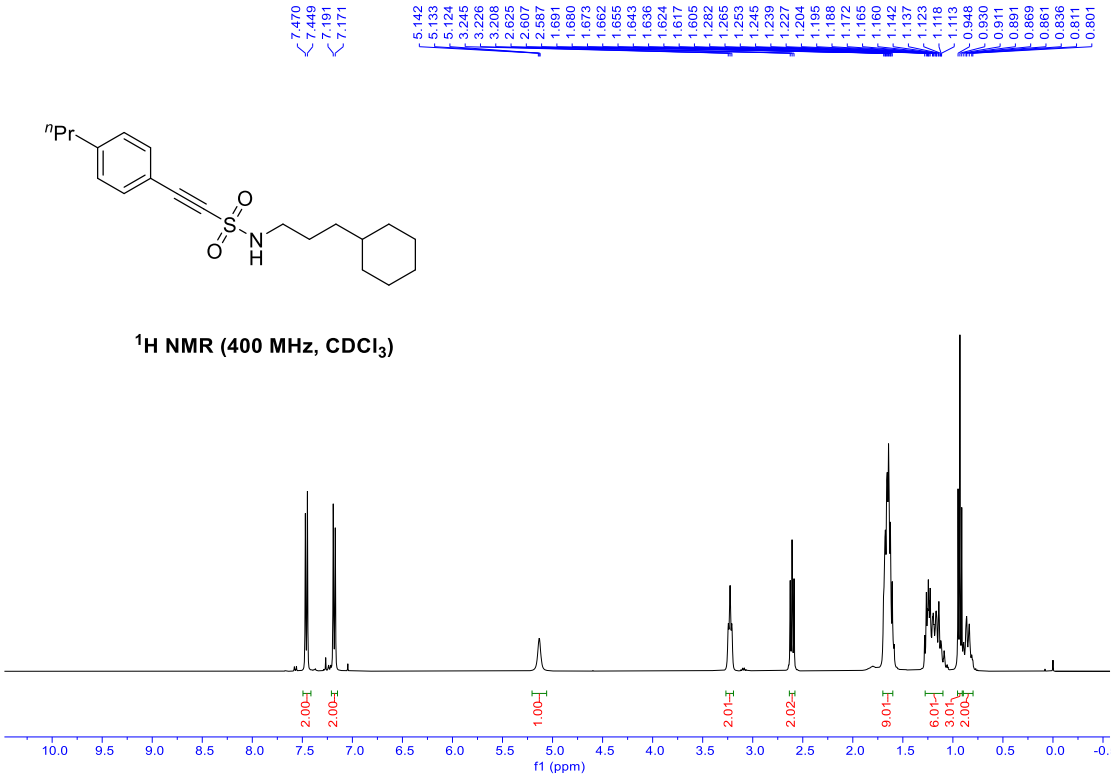
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S20



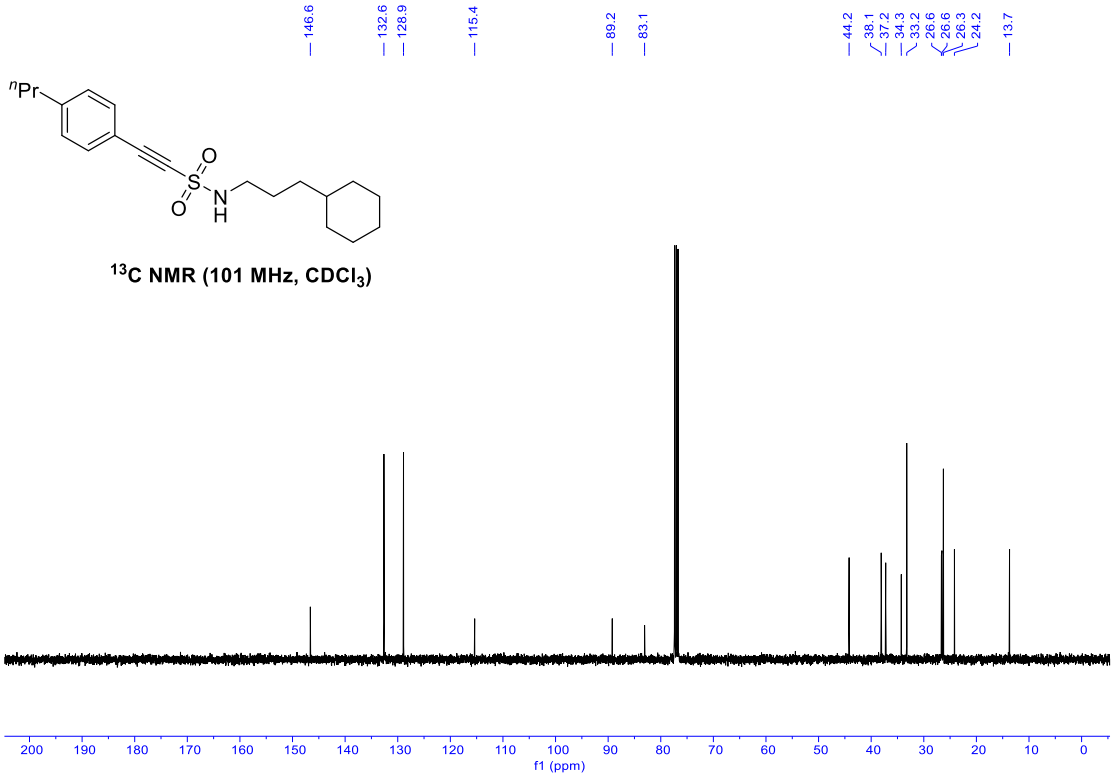
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S20



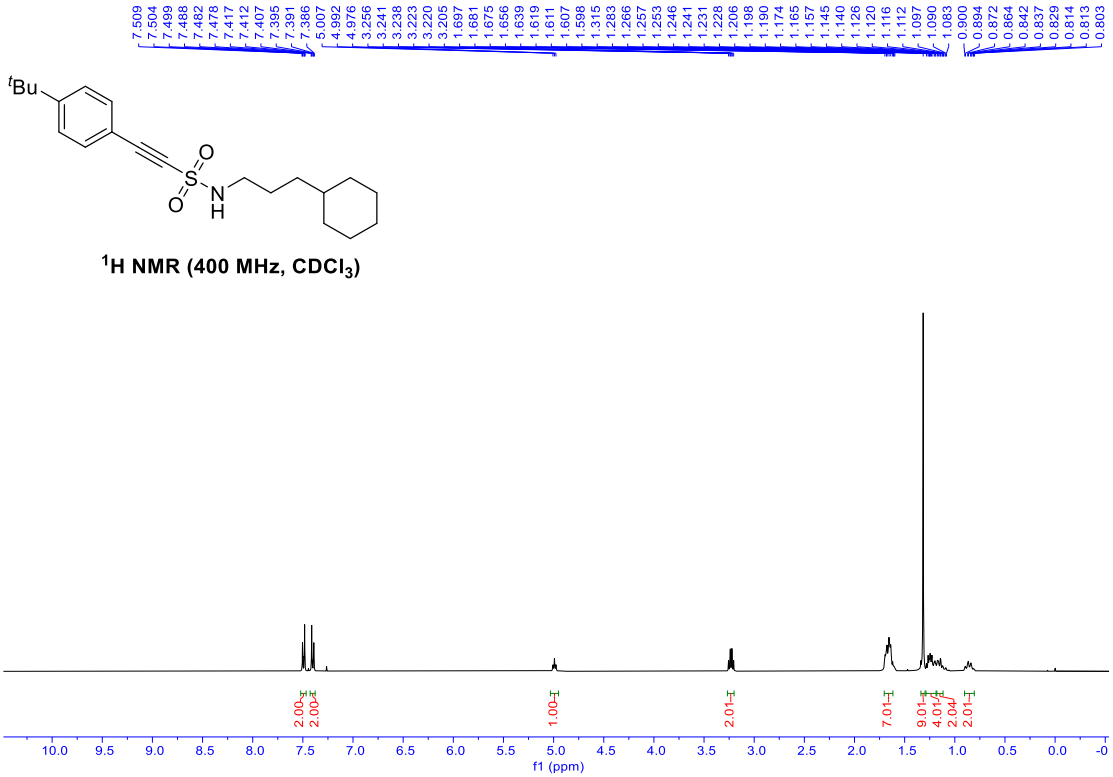
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S21



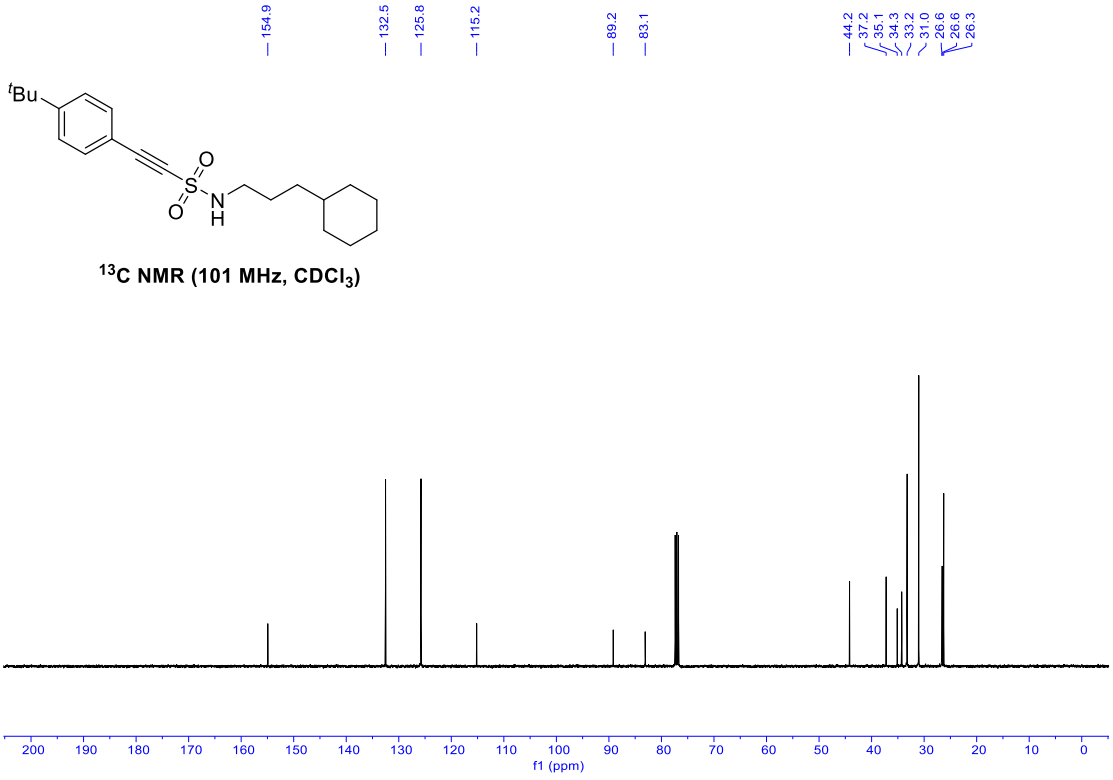
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S21



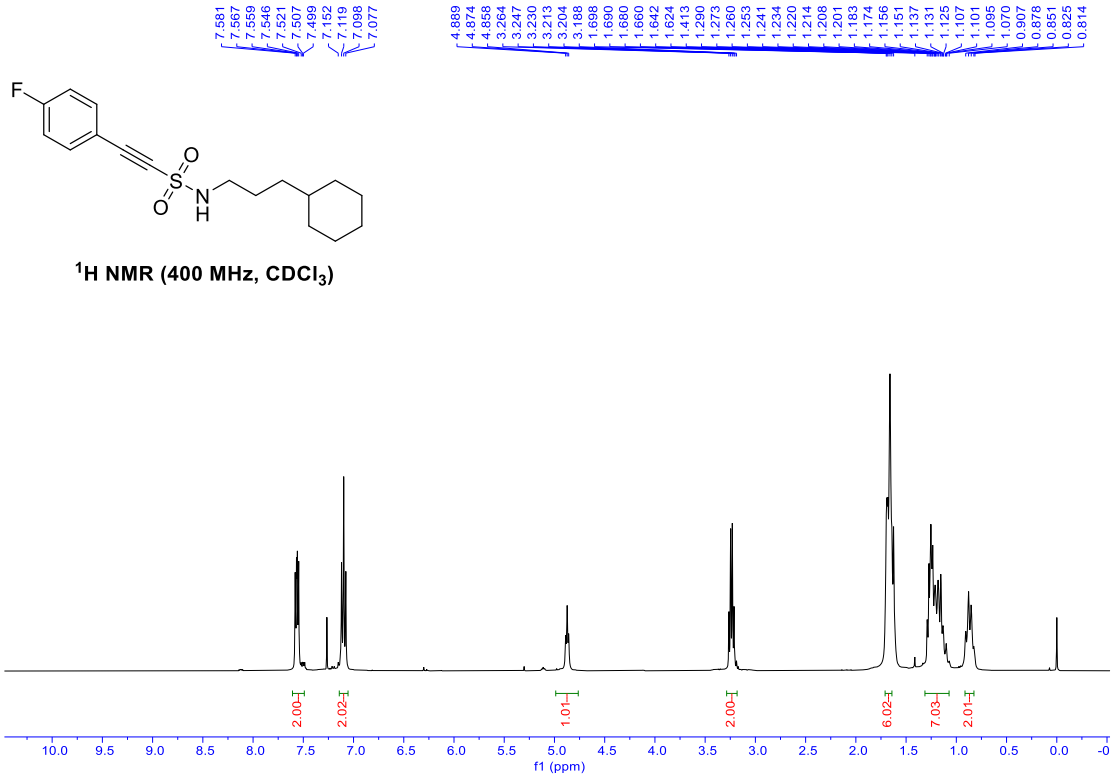
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S22



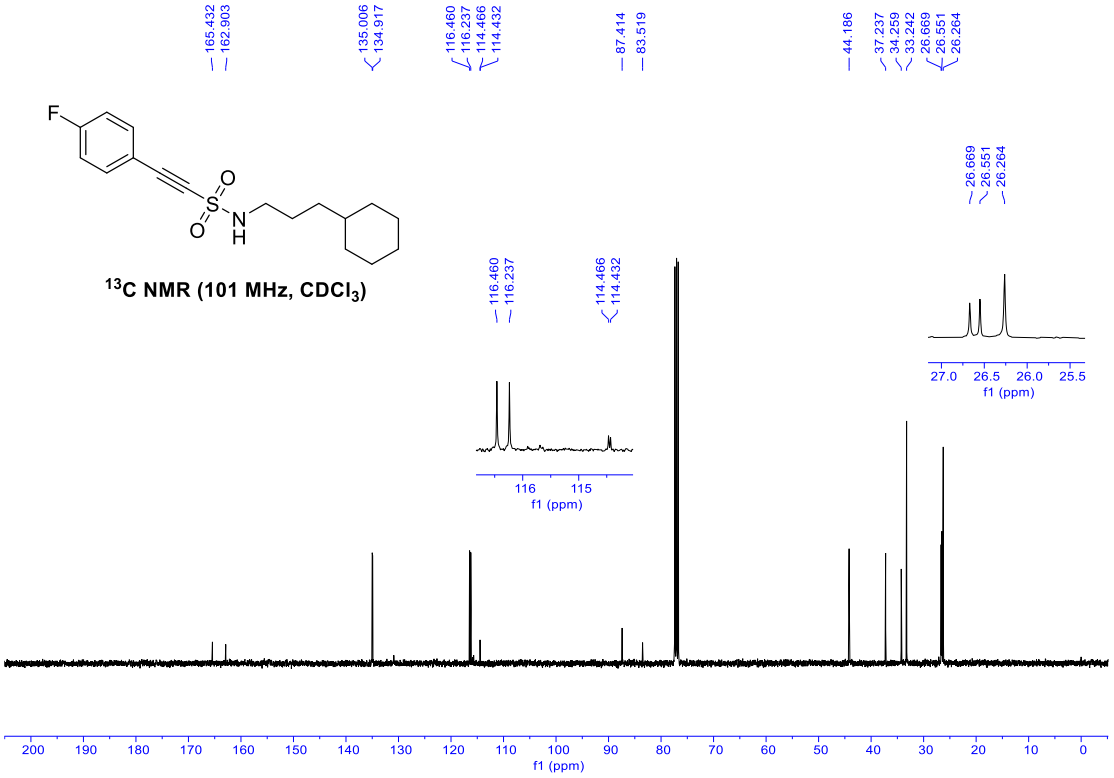
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S22



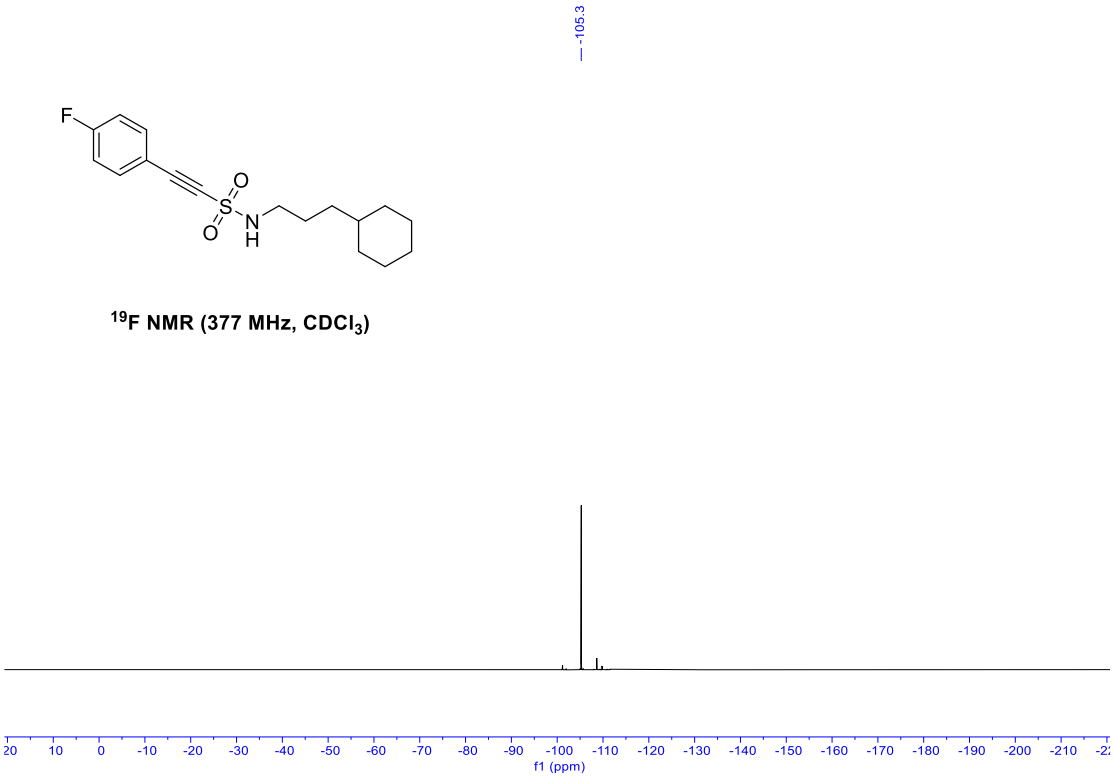
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S23



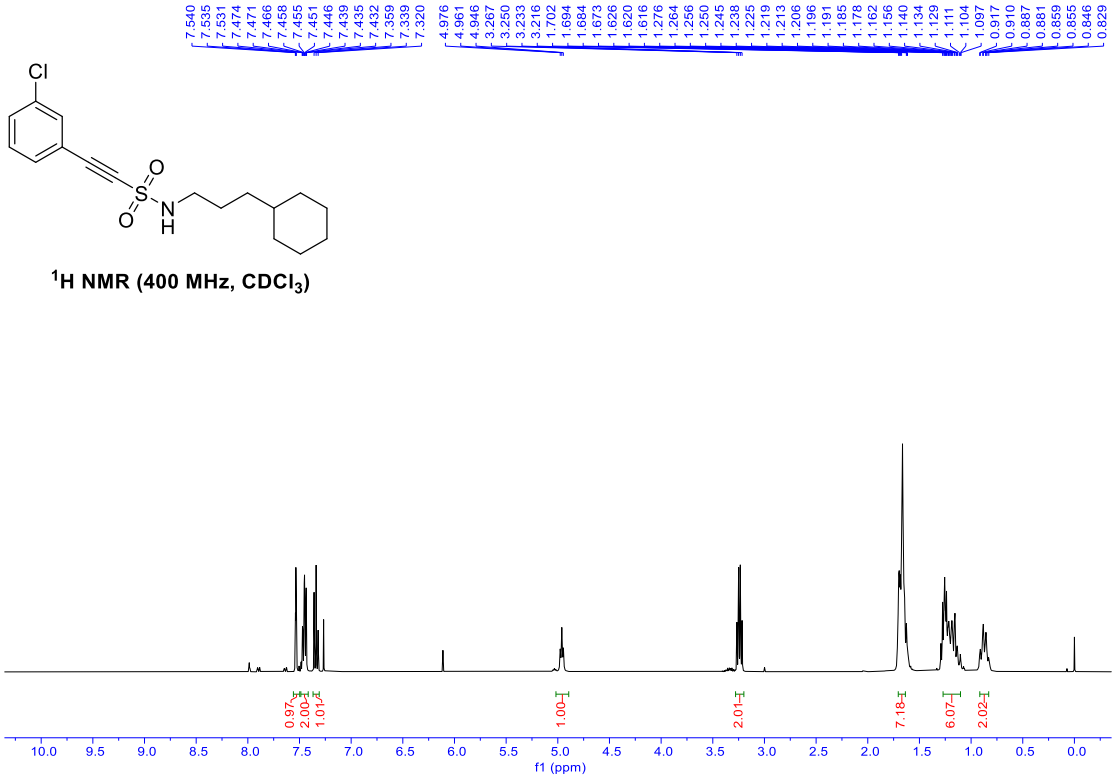
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S23



^{19}F NMR (377 MHz, $CDCl_3$) spectrum of S23

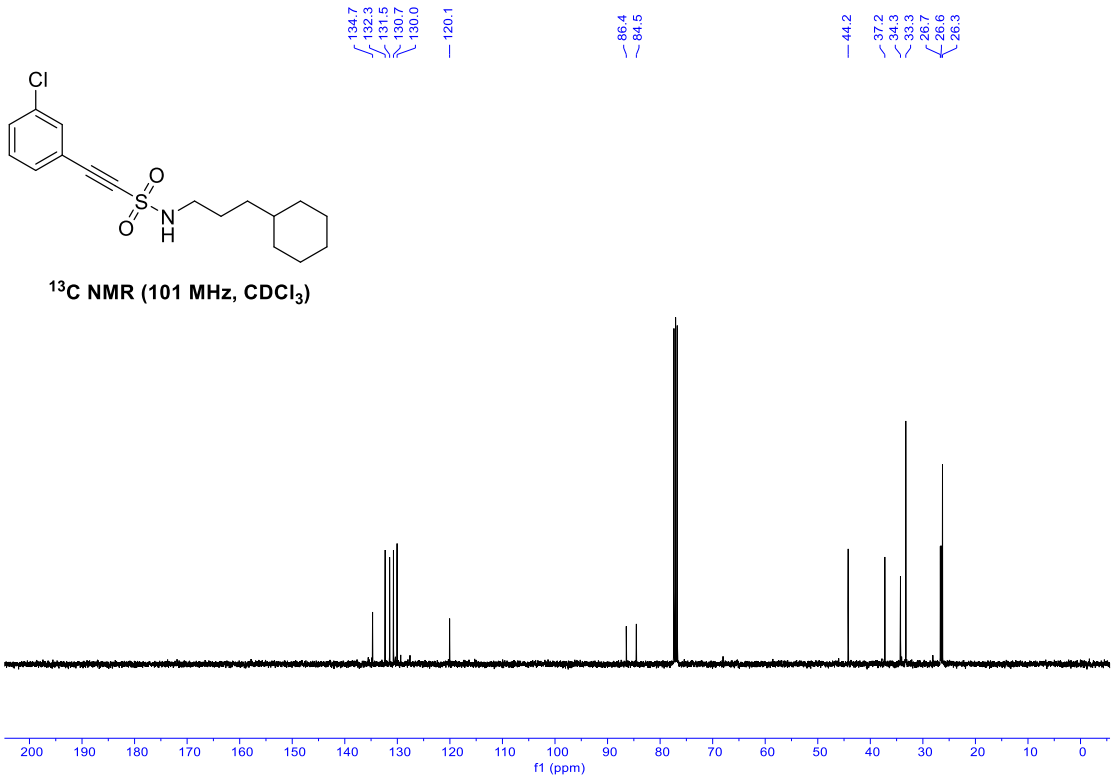


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S24



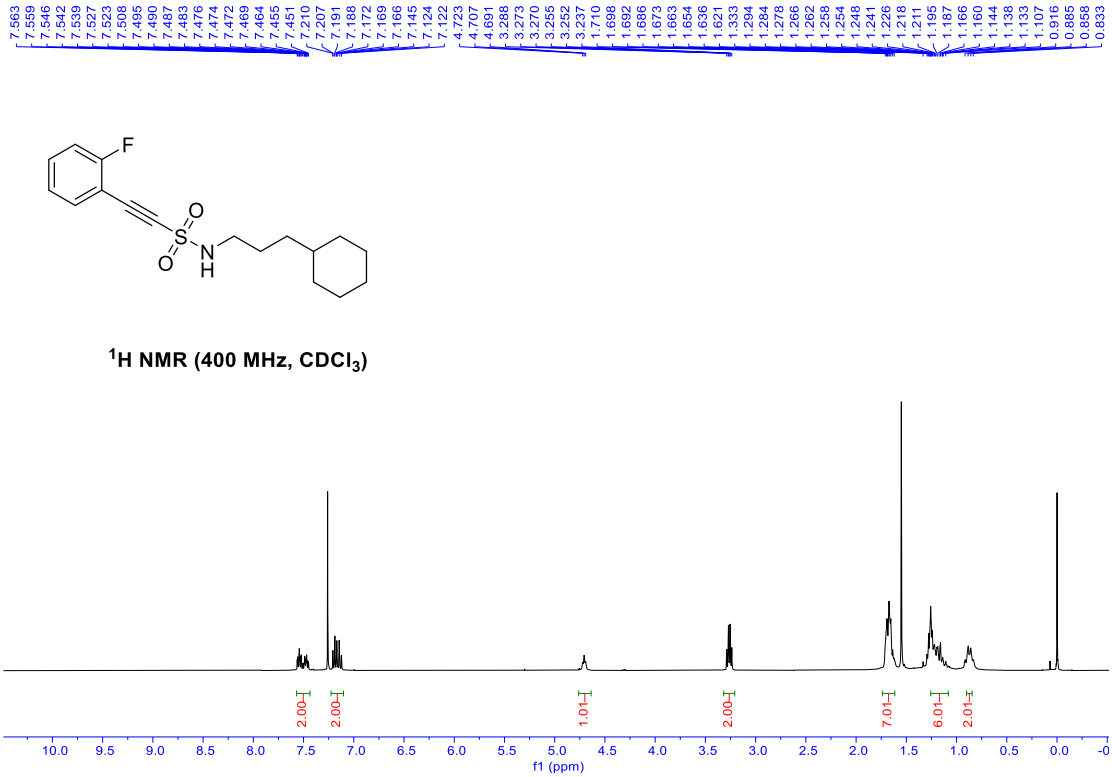
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S24

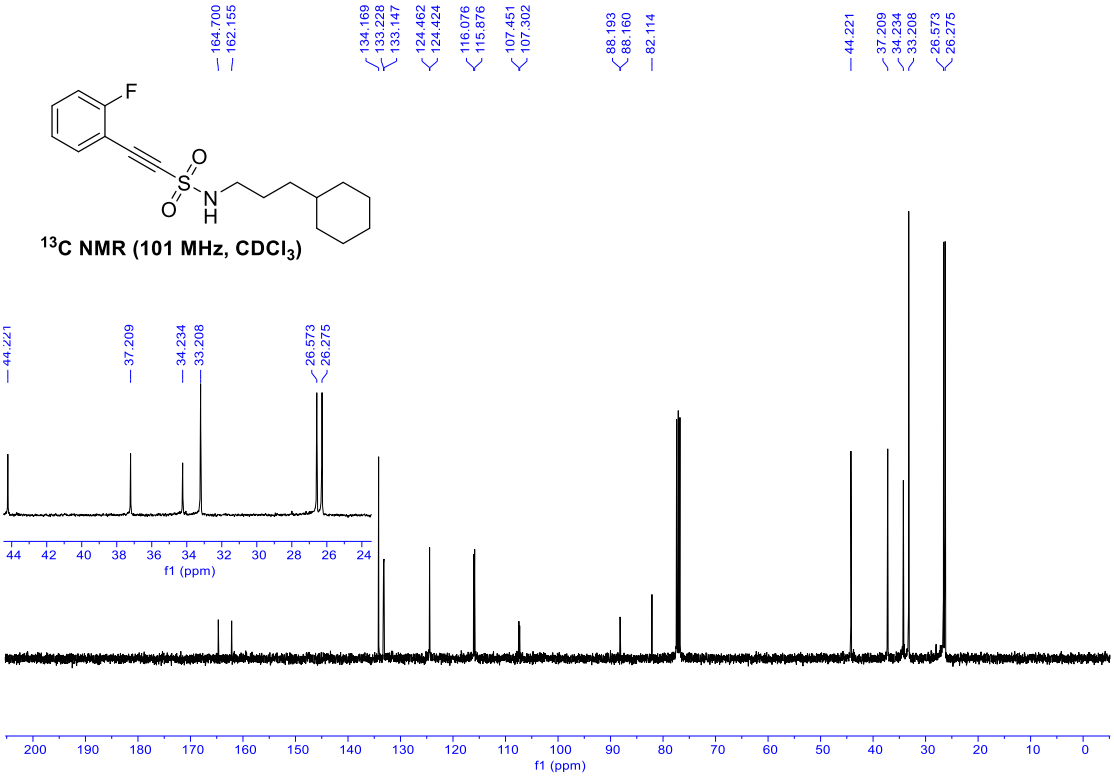


^{13}C NMR (101 MHz, $CDCl_3$)

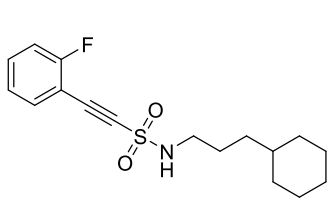
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S25



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S25

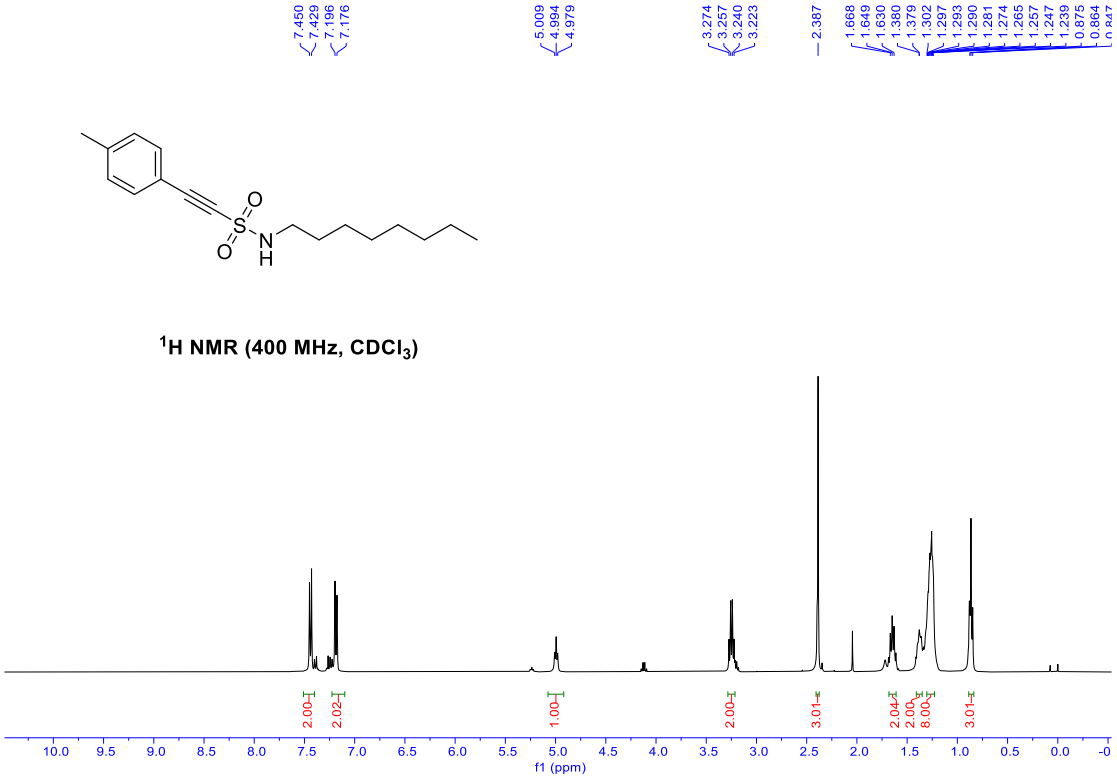


^{19}F NMR (377 MHz, $CDCl_3$) spectrum of S25

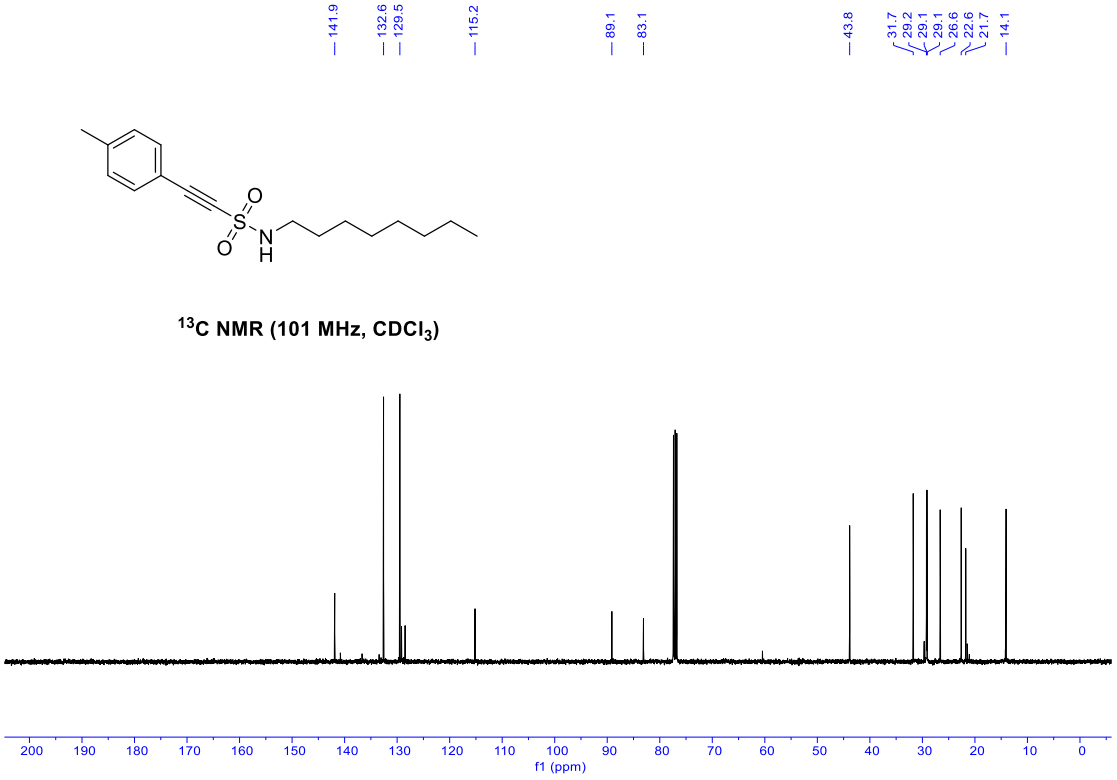


^{19}F NMR (377 MHz, $CDCl_3$)

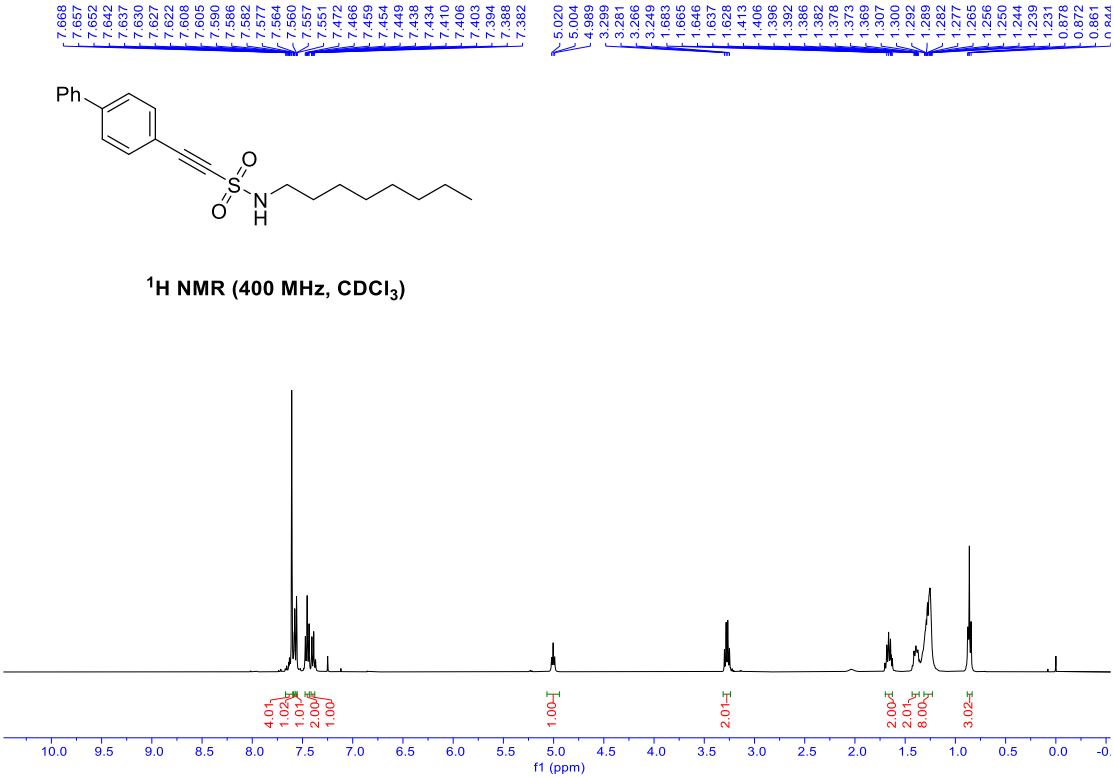
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S26



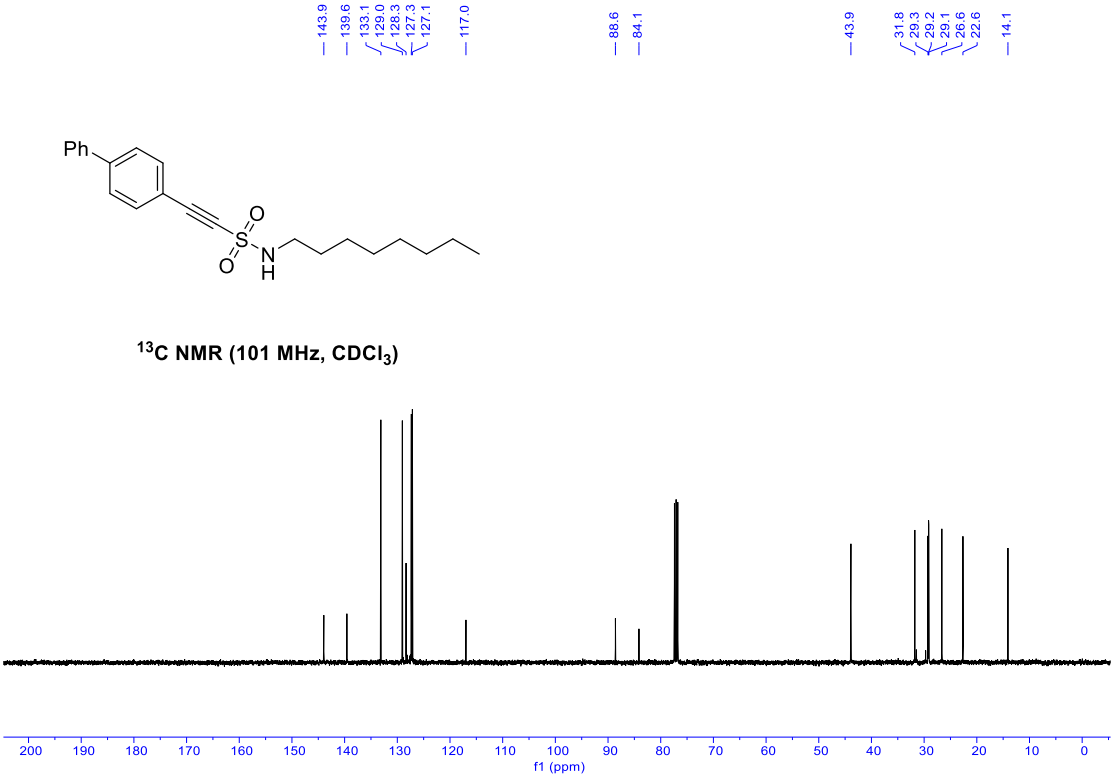
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S26



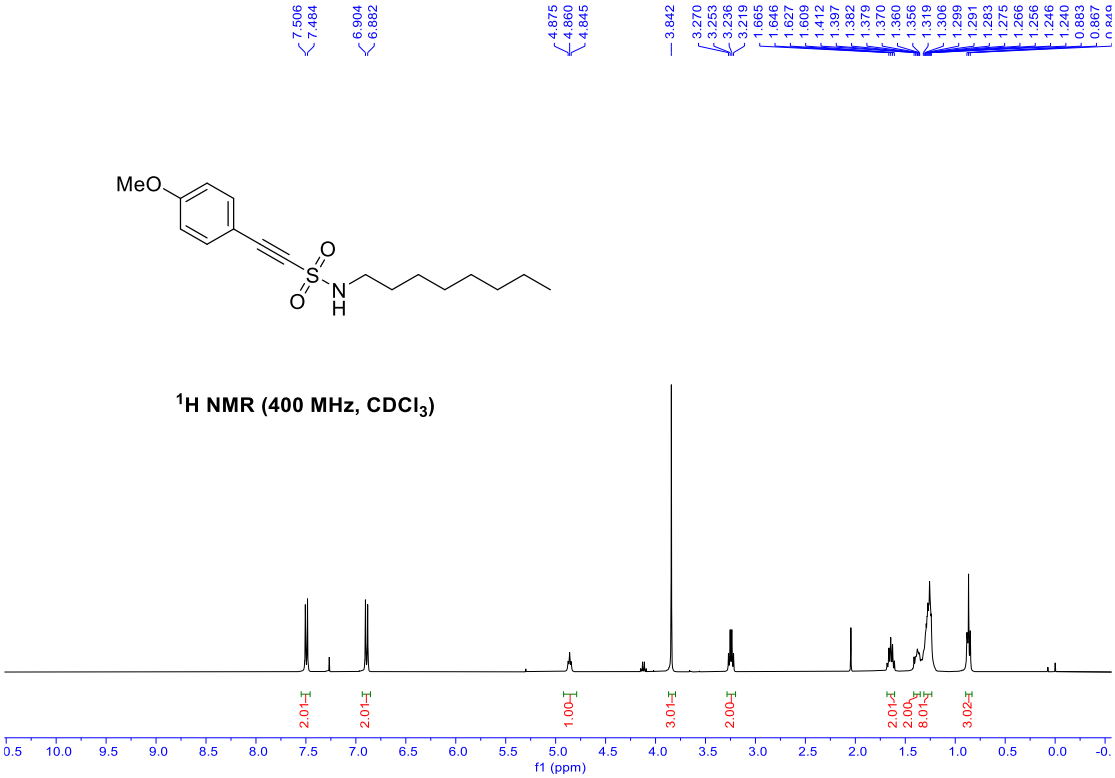
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S27



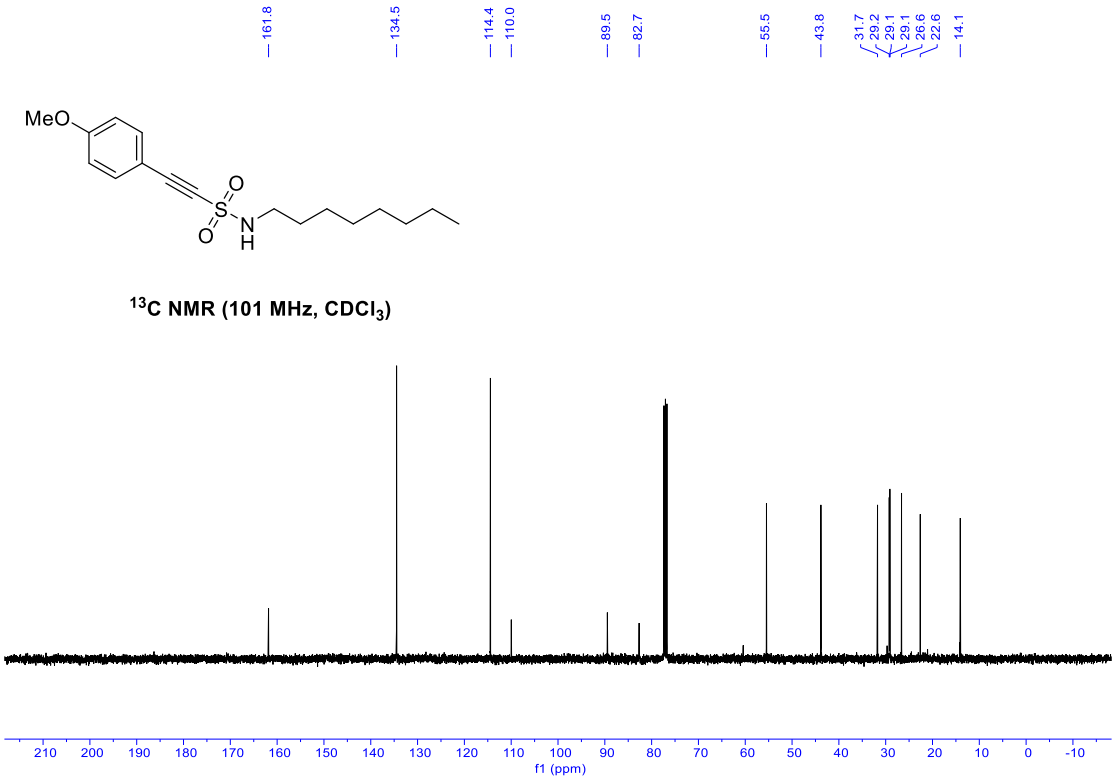
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S27



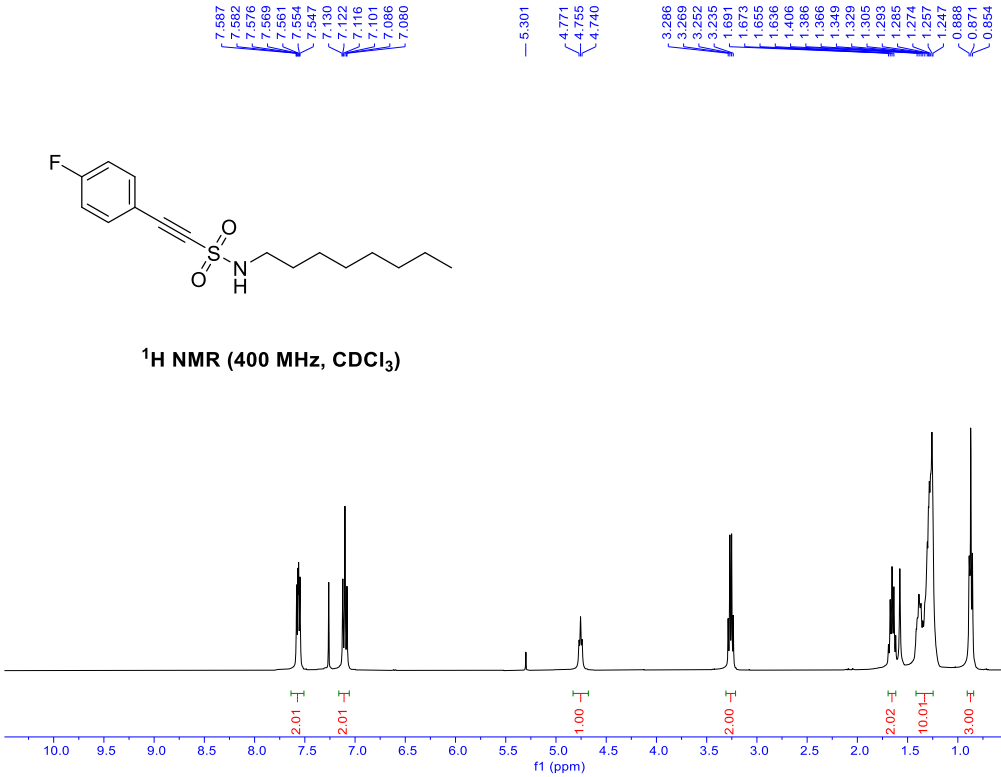
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S28



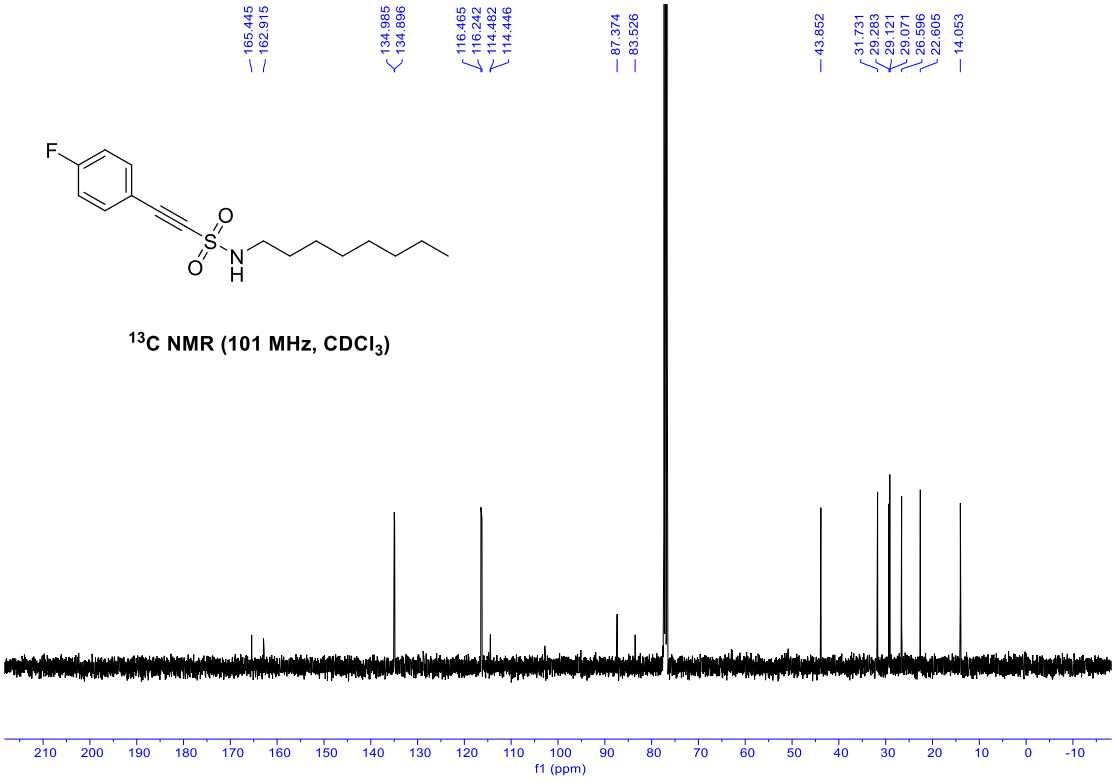
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S28



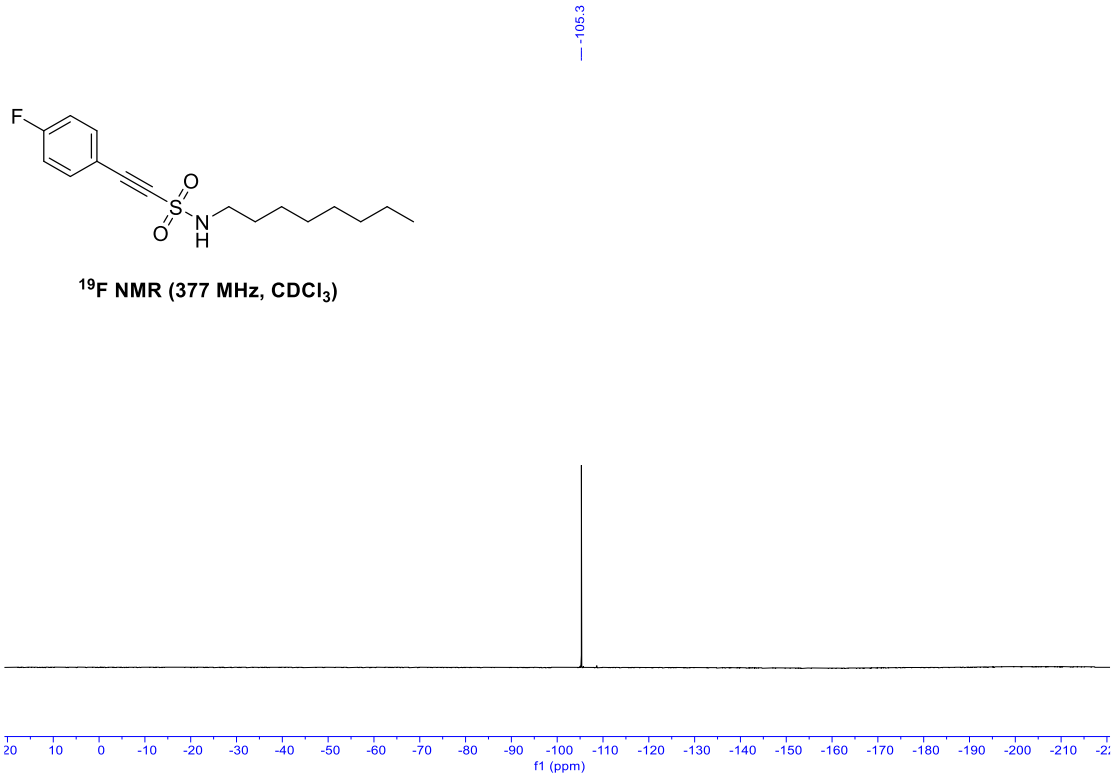
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S29



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S29

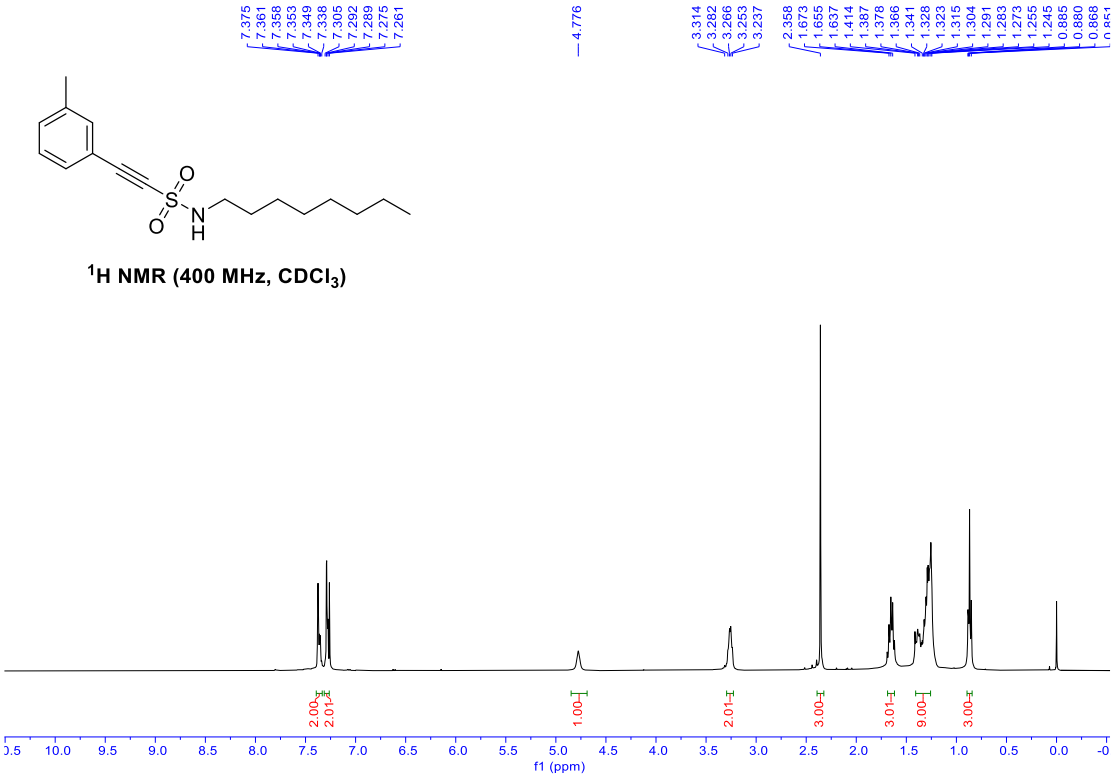


^{19}F NMR (377 MHz, $CDCl_3$) spectrum of S29

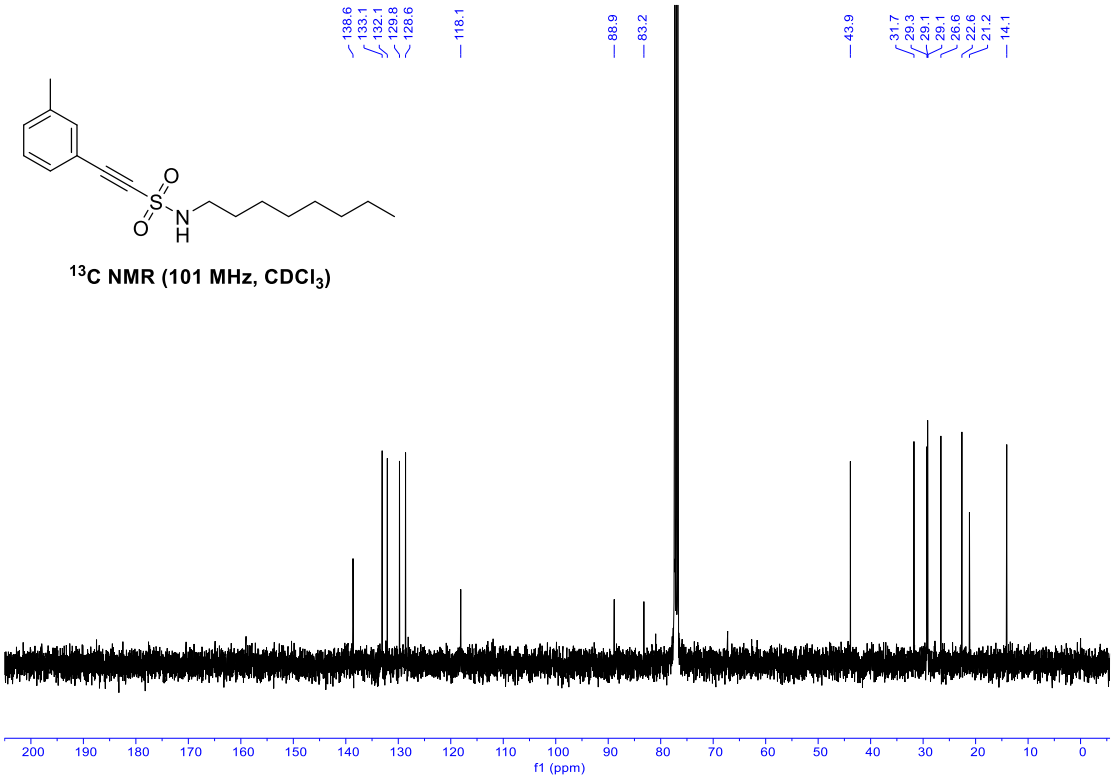


^{19}F NMR (377 MHz, $CDCl_3$)

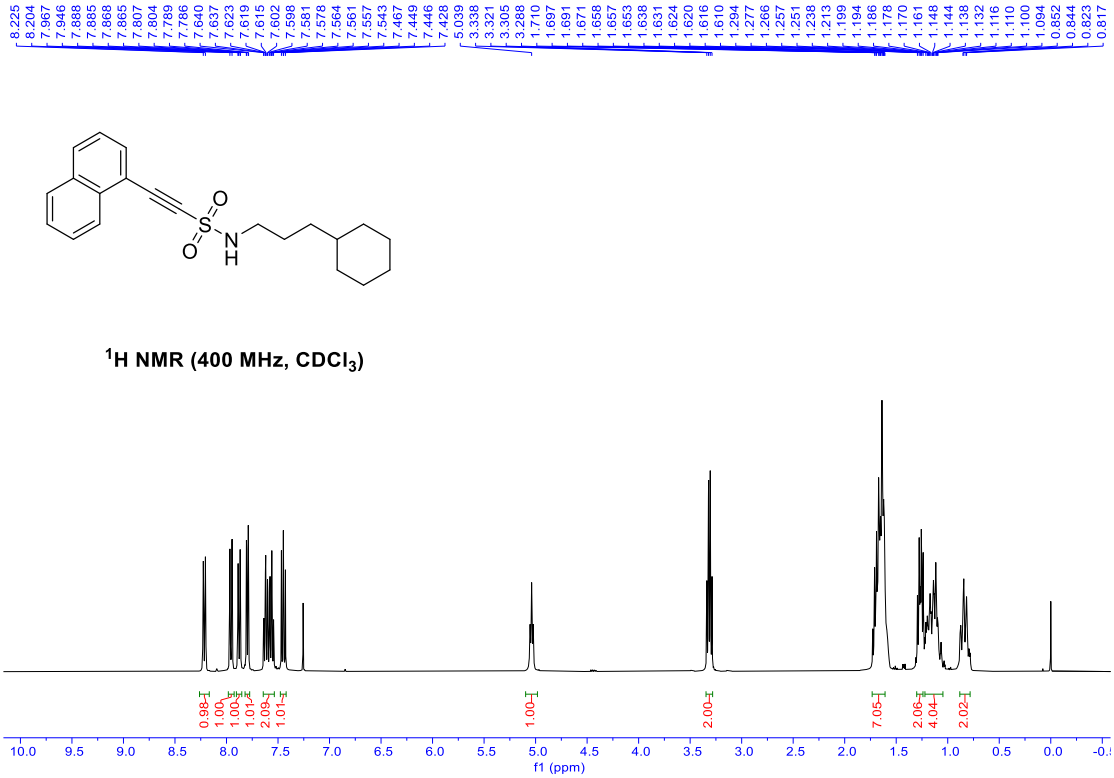
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S30



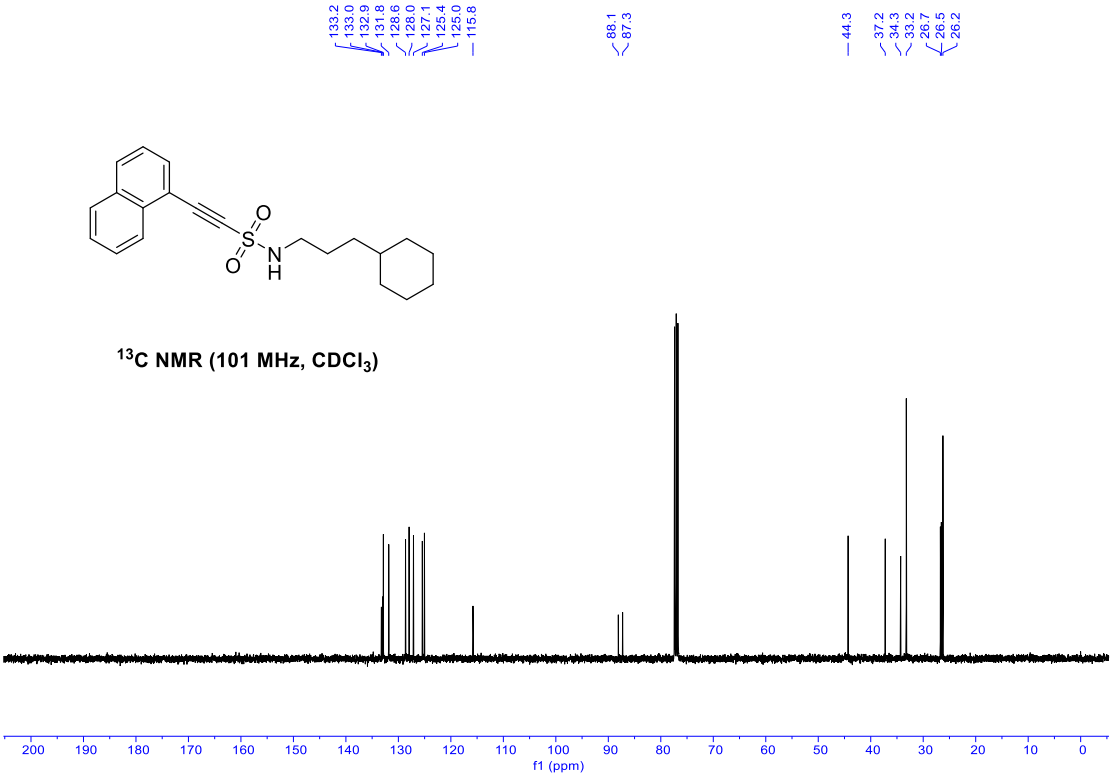
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S30



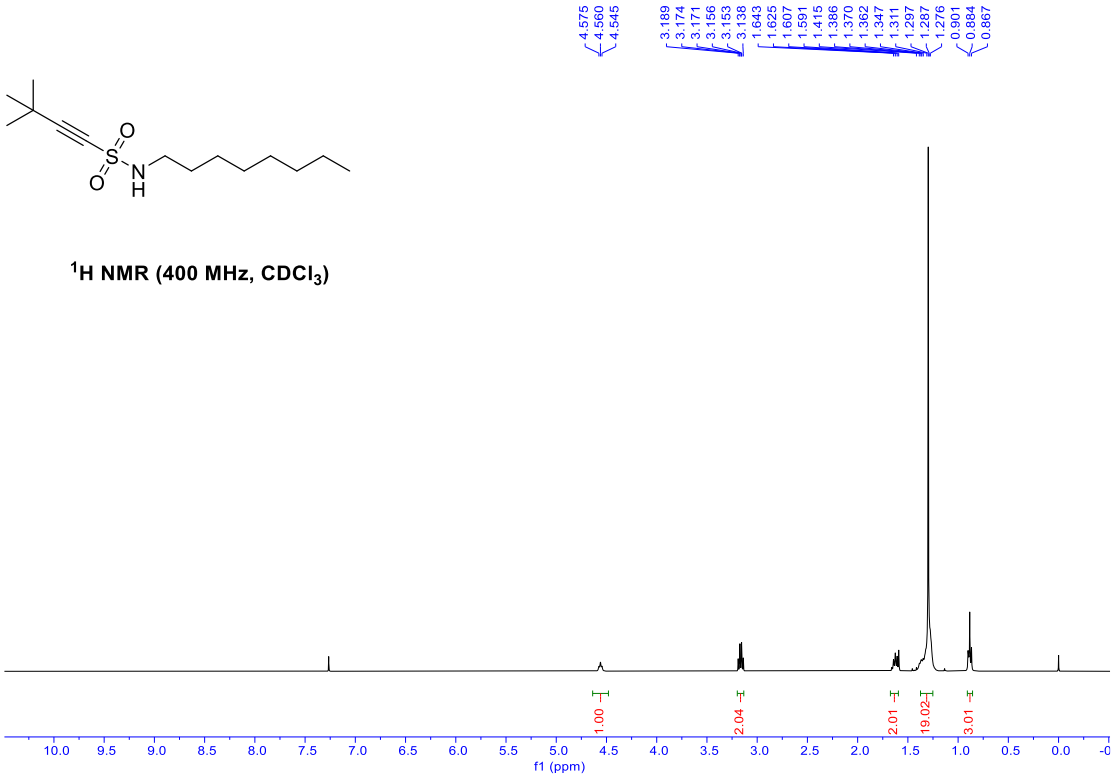
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S31



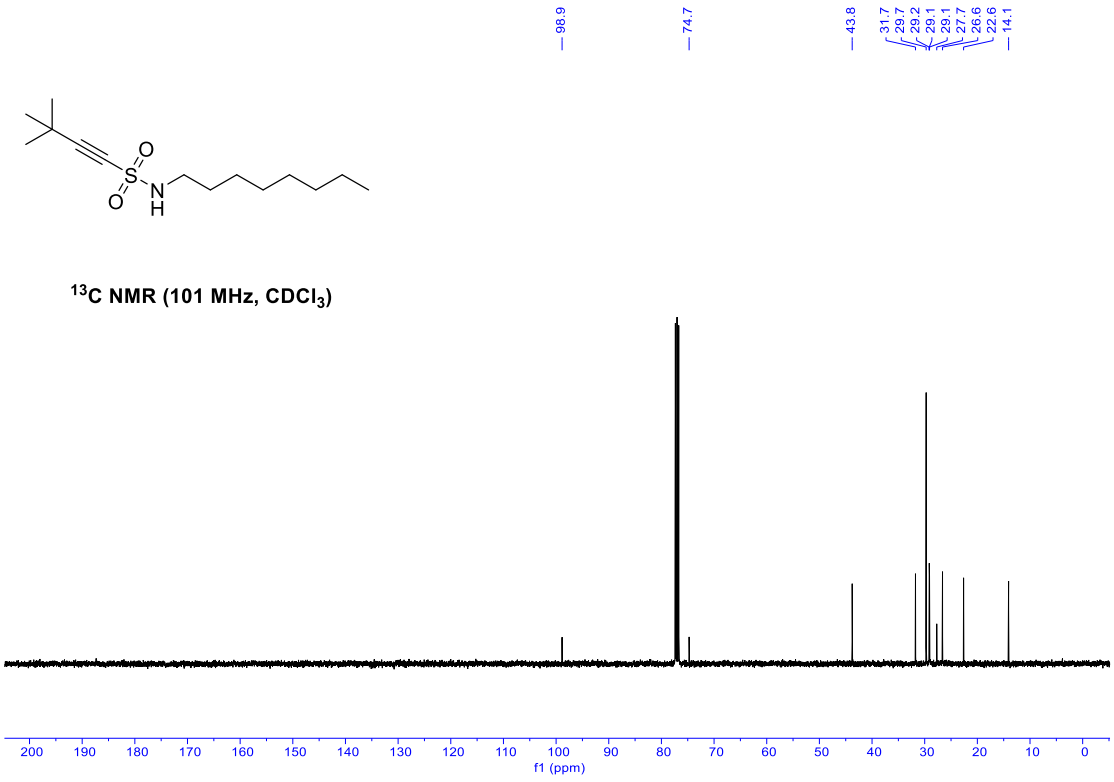
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S31



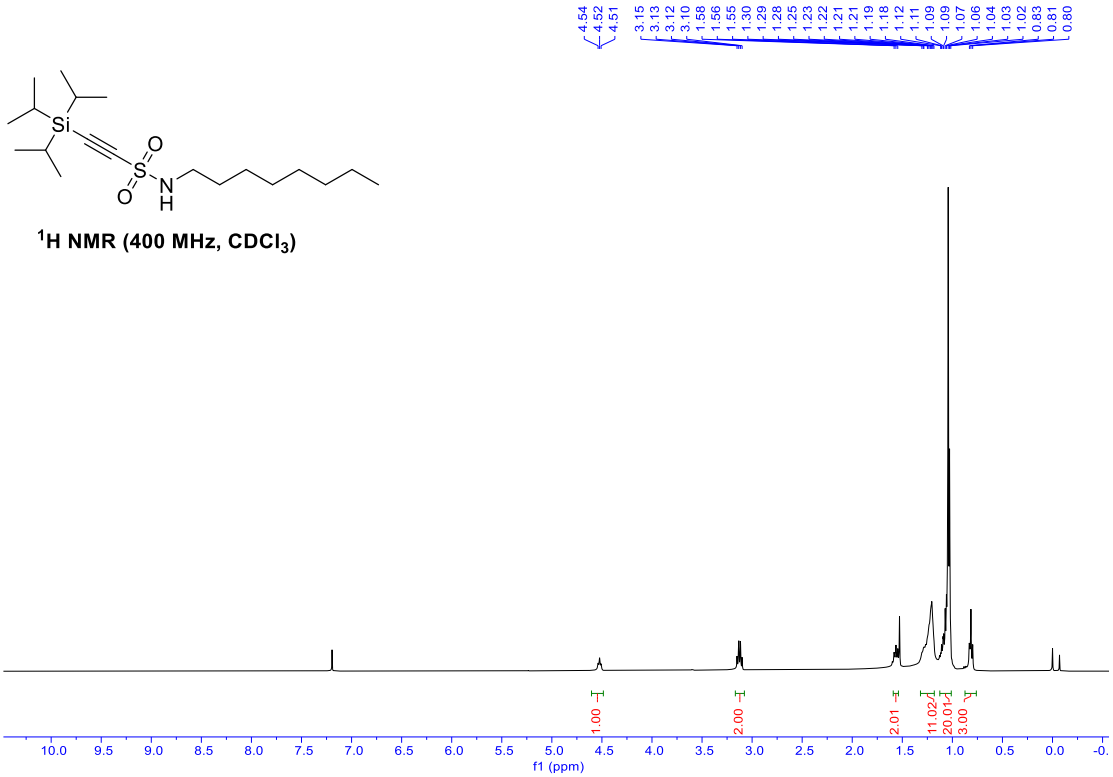
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S32



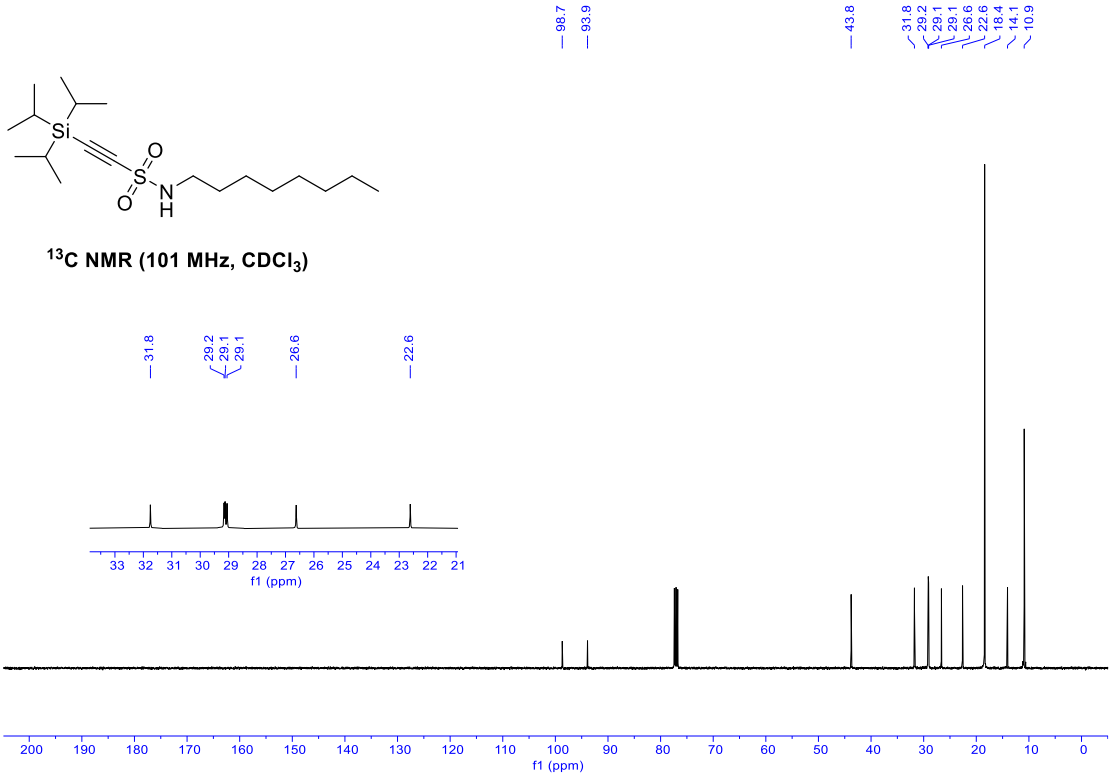
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S32



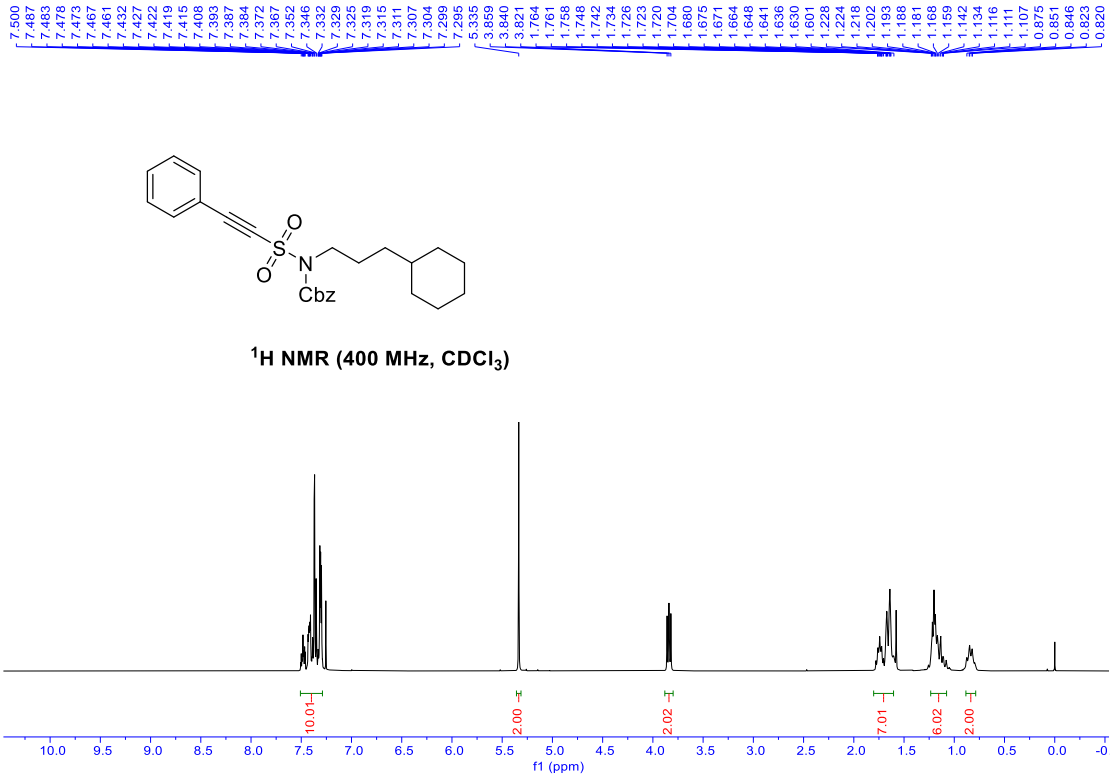
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of S33



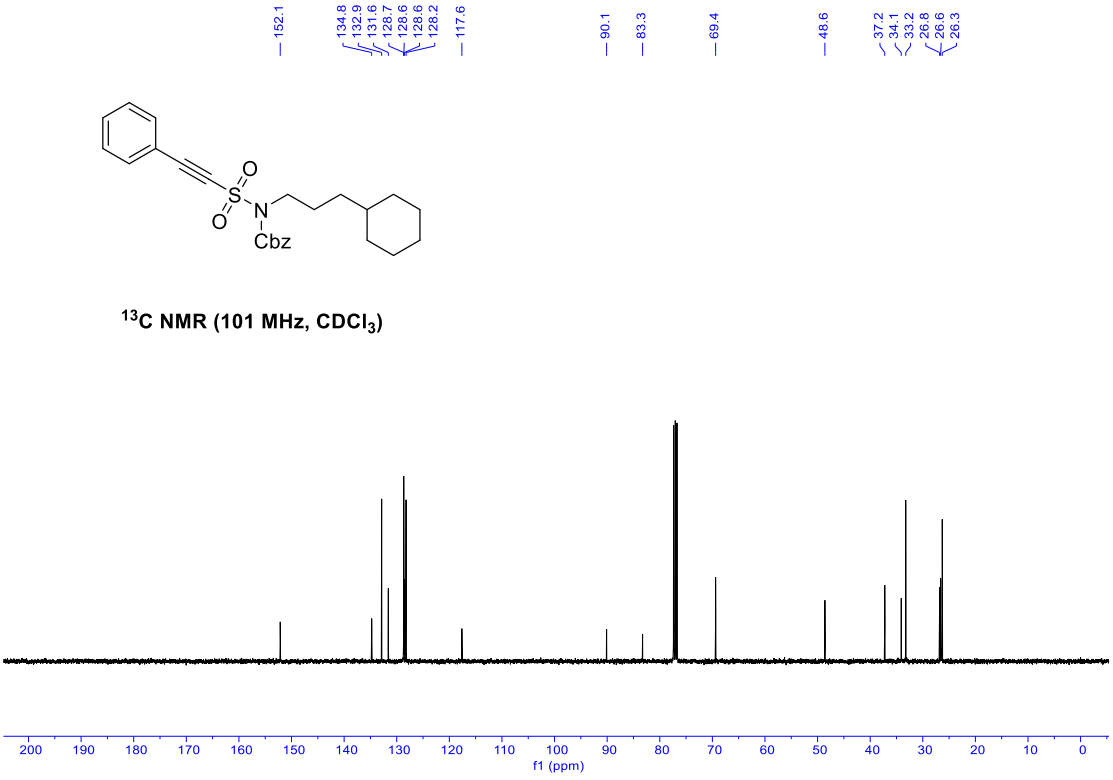
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of S33



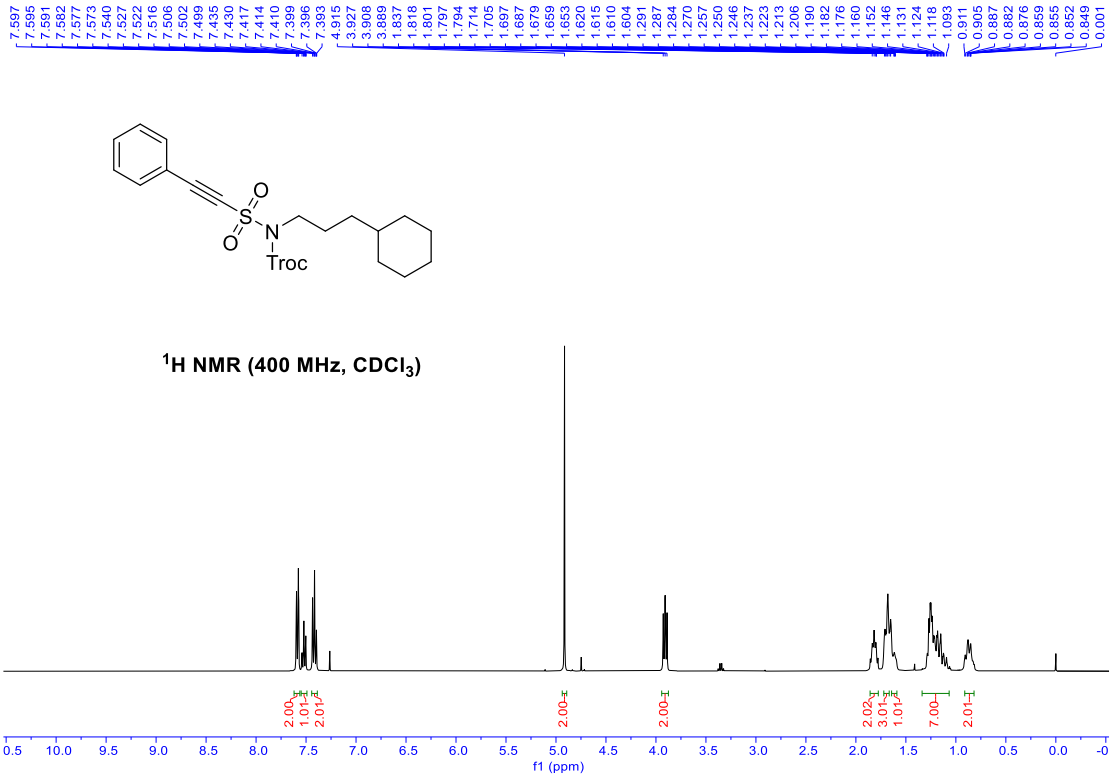
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1a



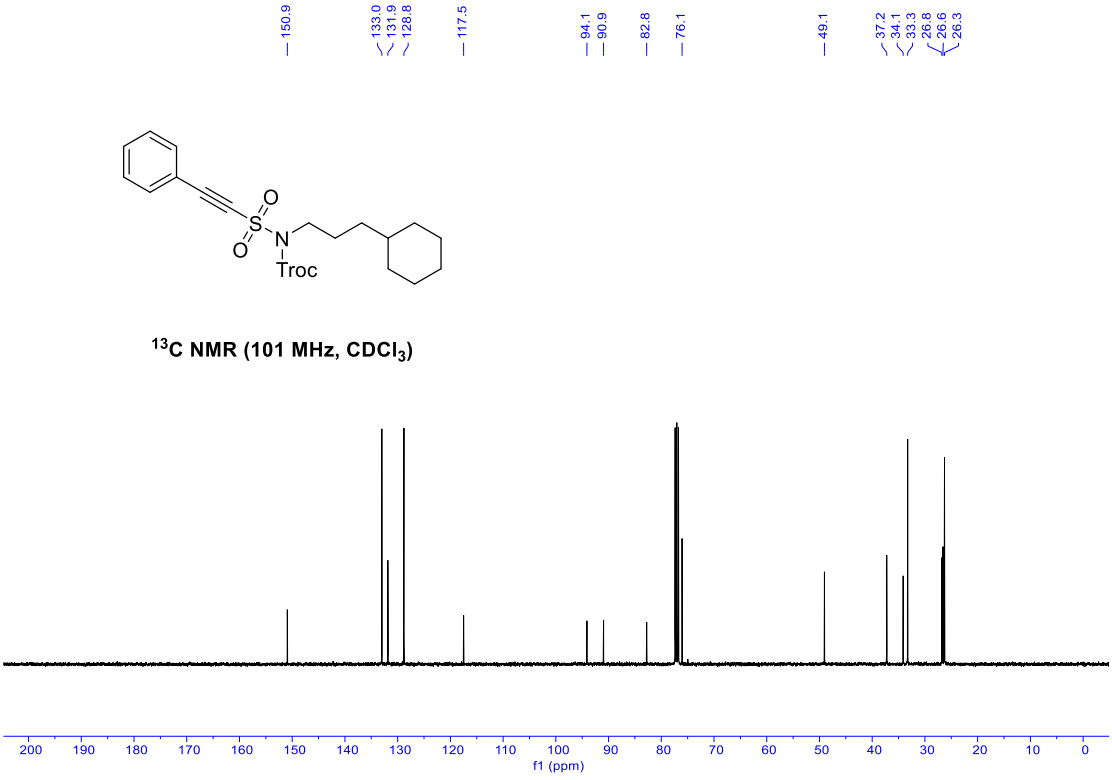
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1a



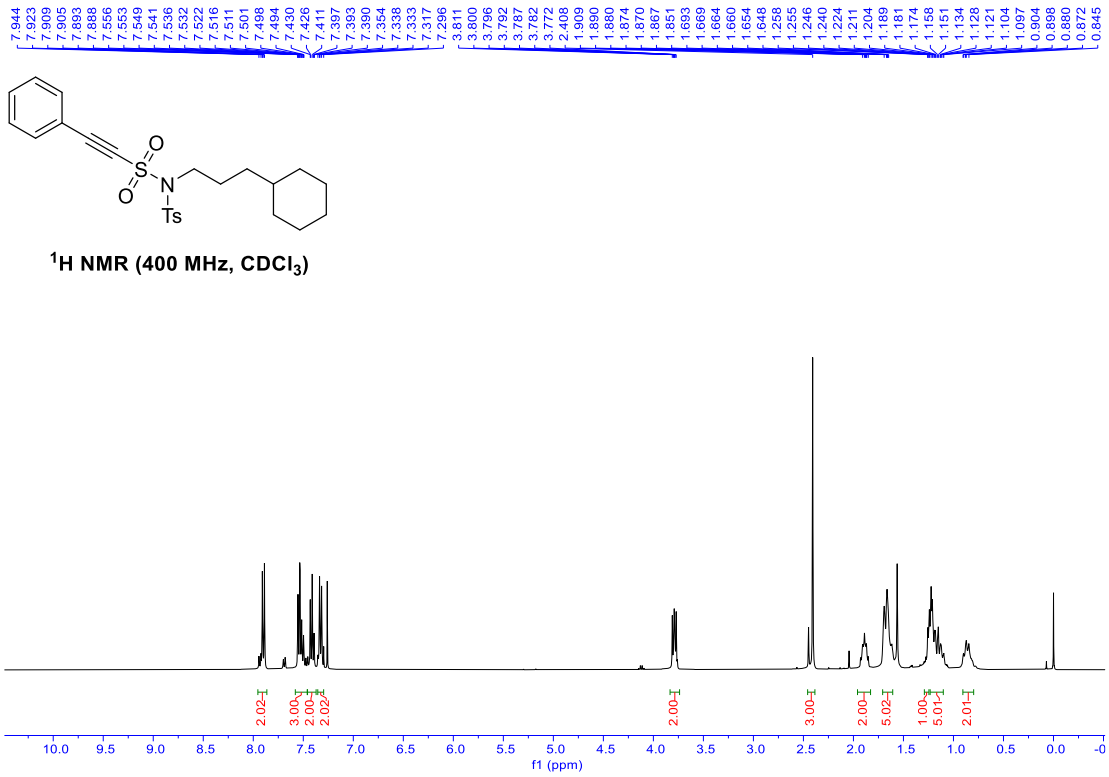
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1b



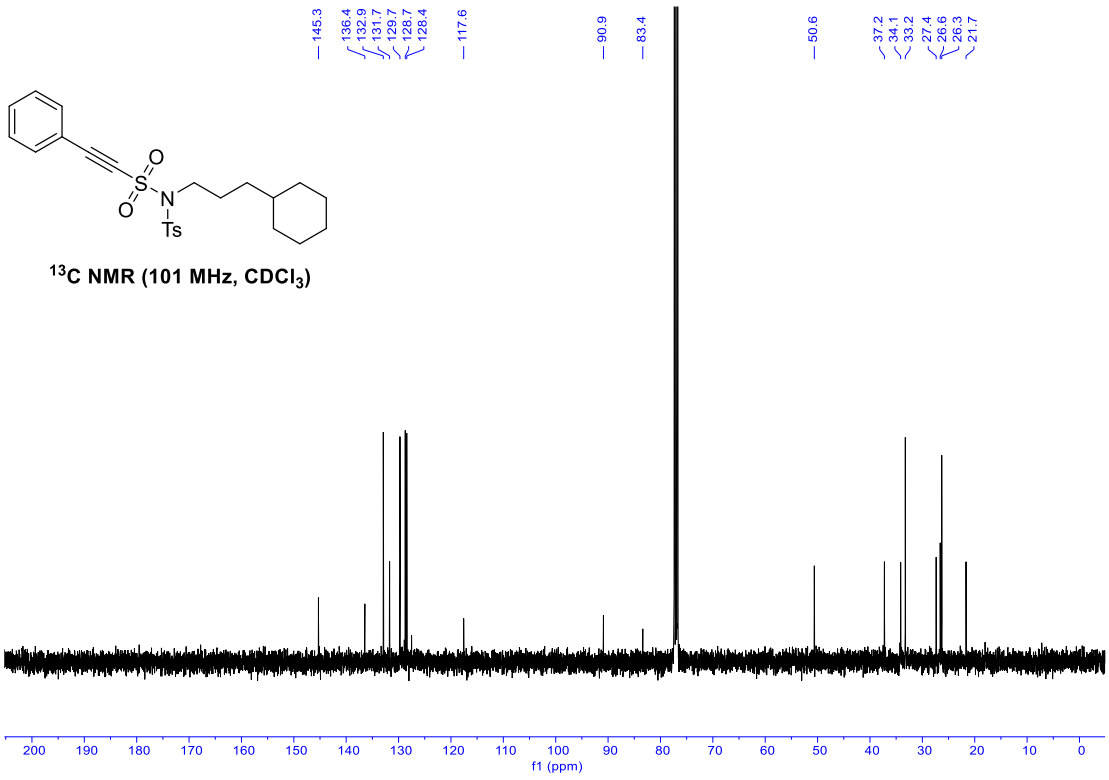
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1b



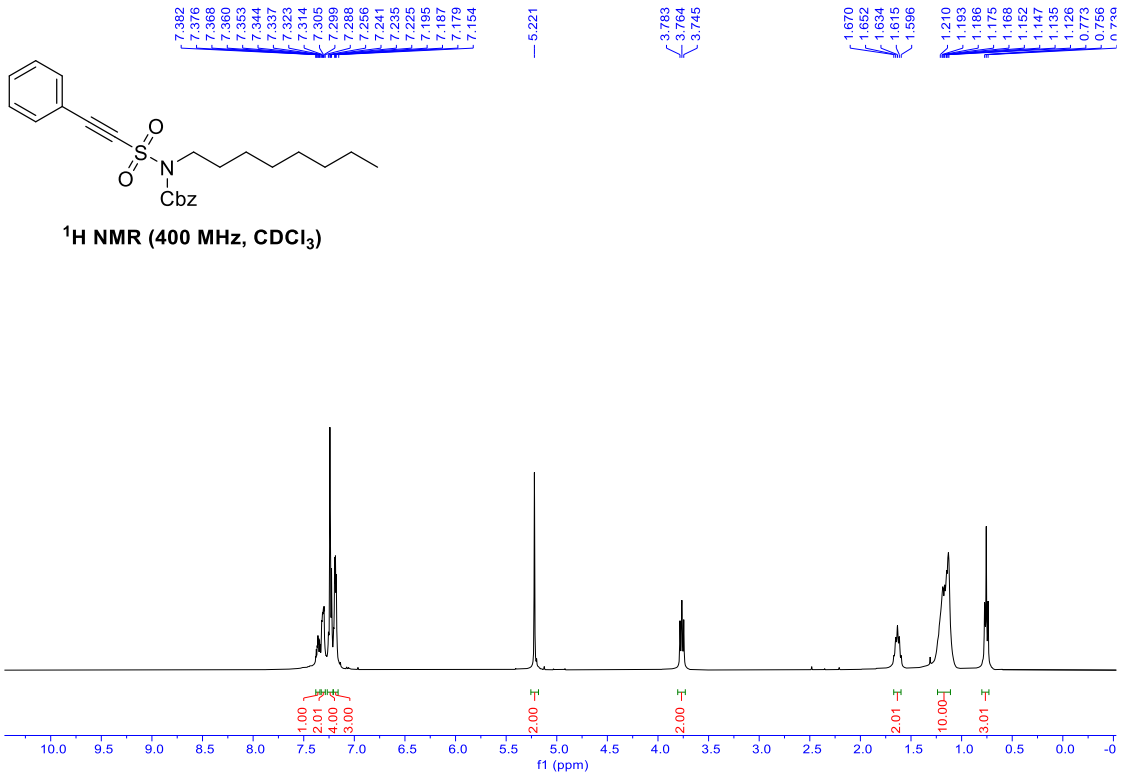
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1c



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1c

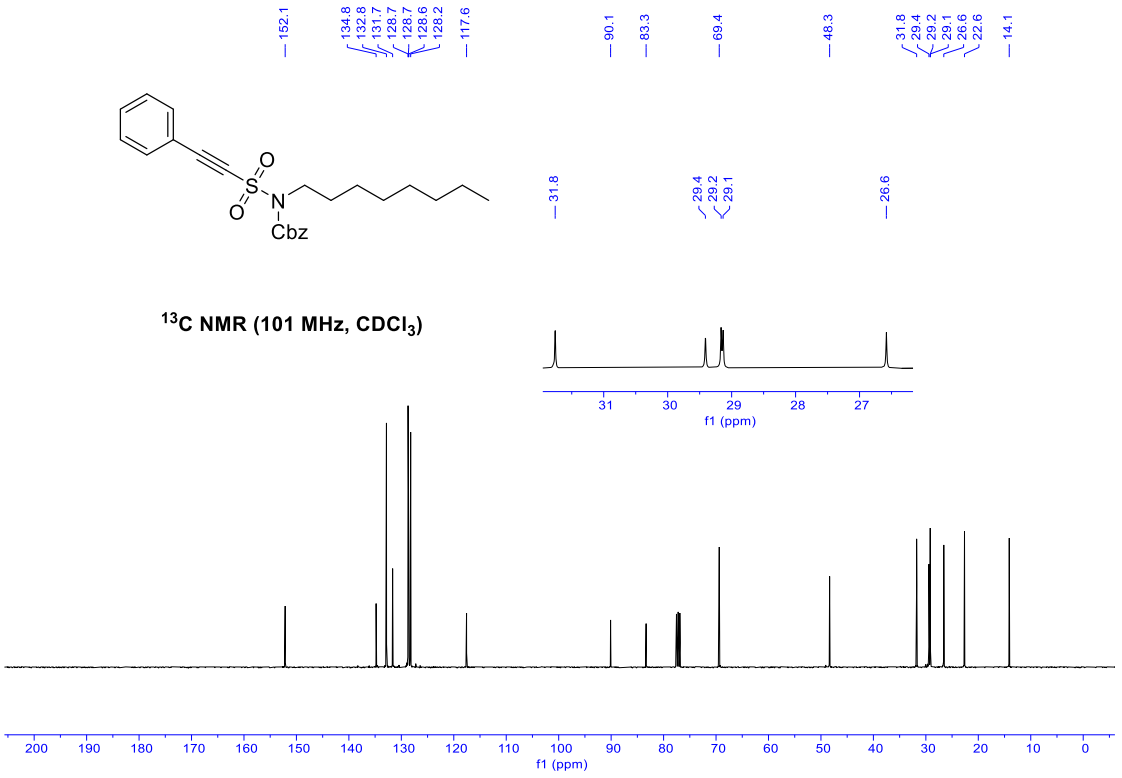


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1d



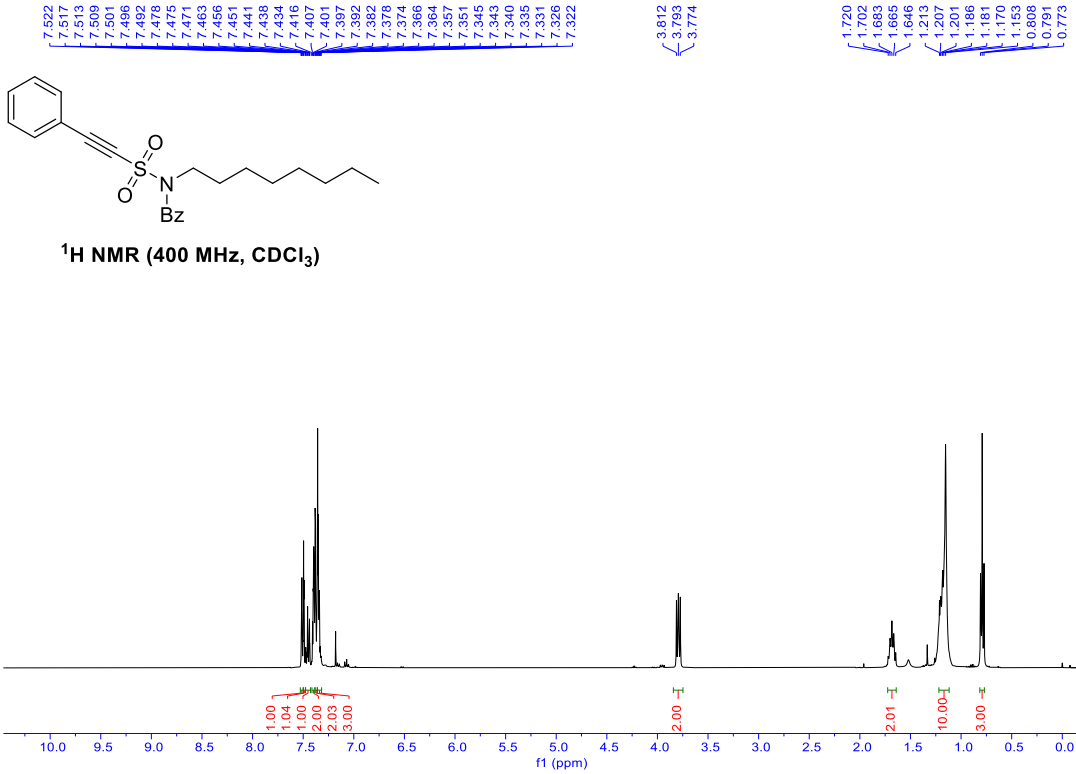
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1d

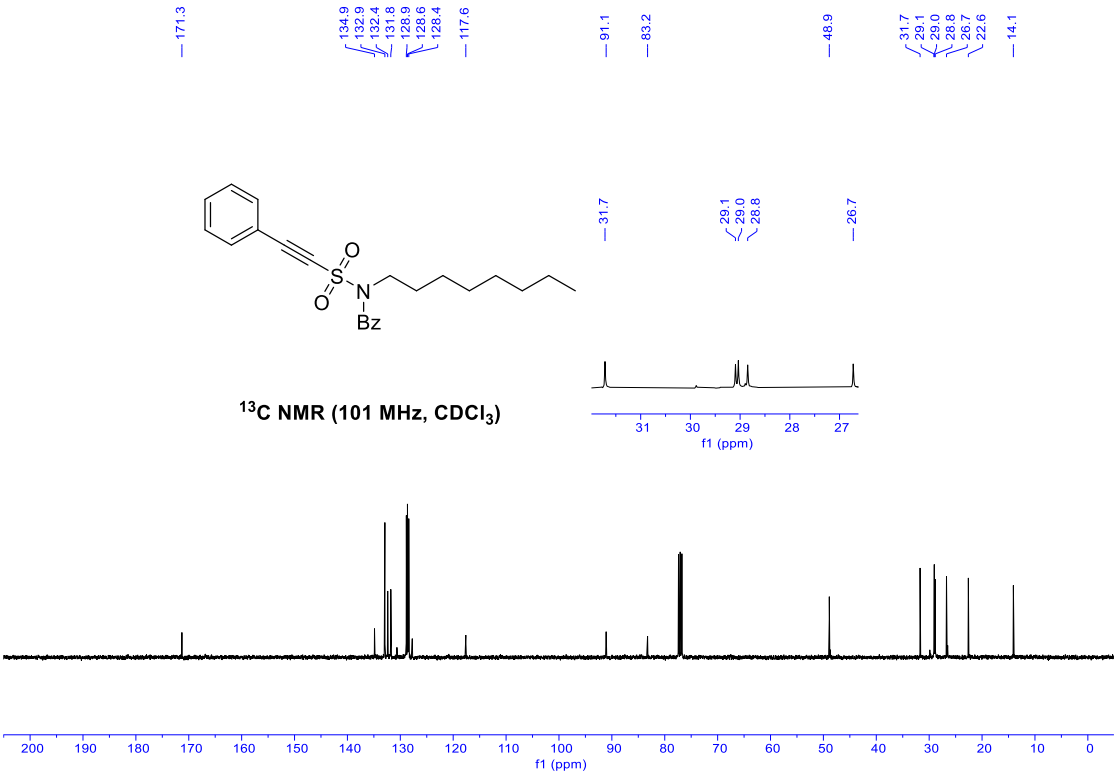


^{13}C NMR (101 MHz, $CDCl_3$)

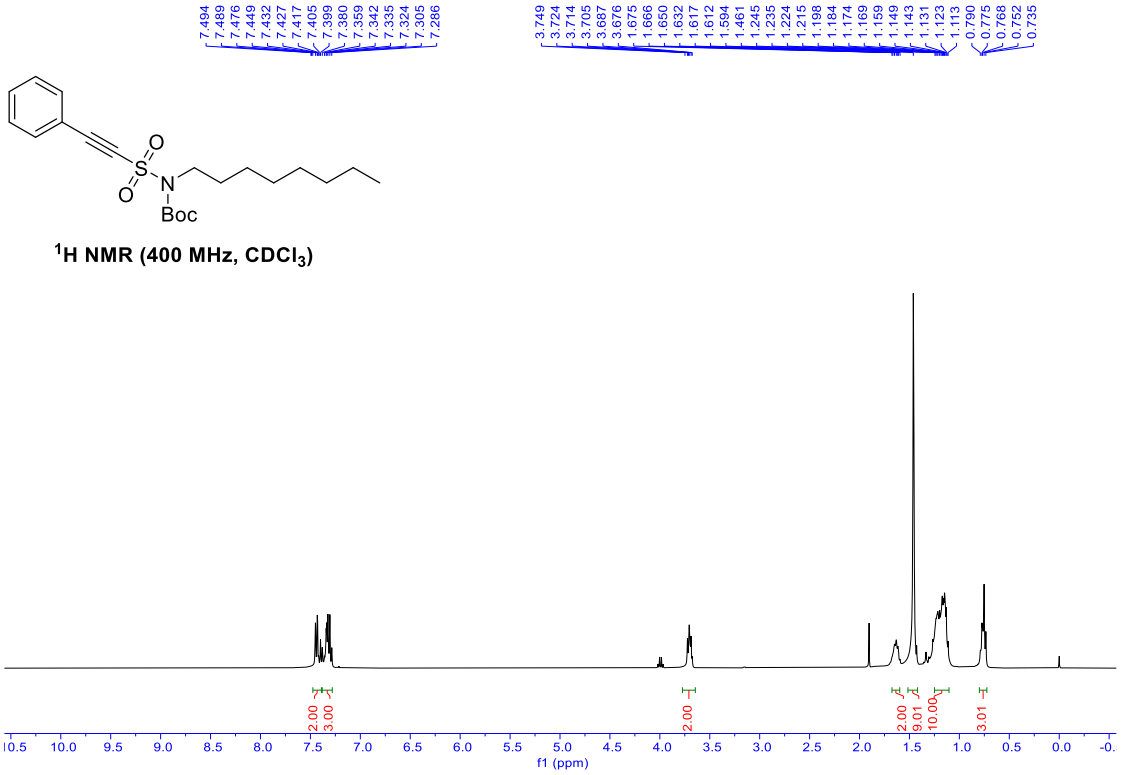
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1e



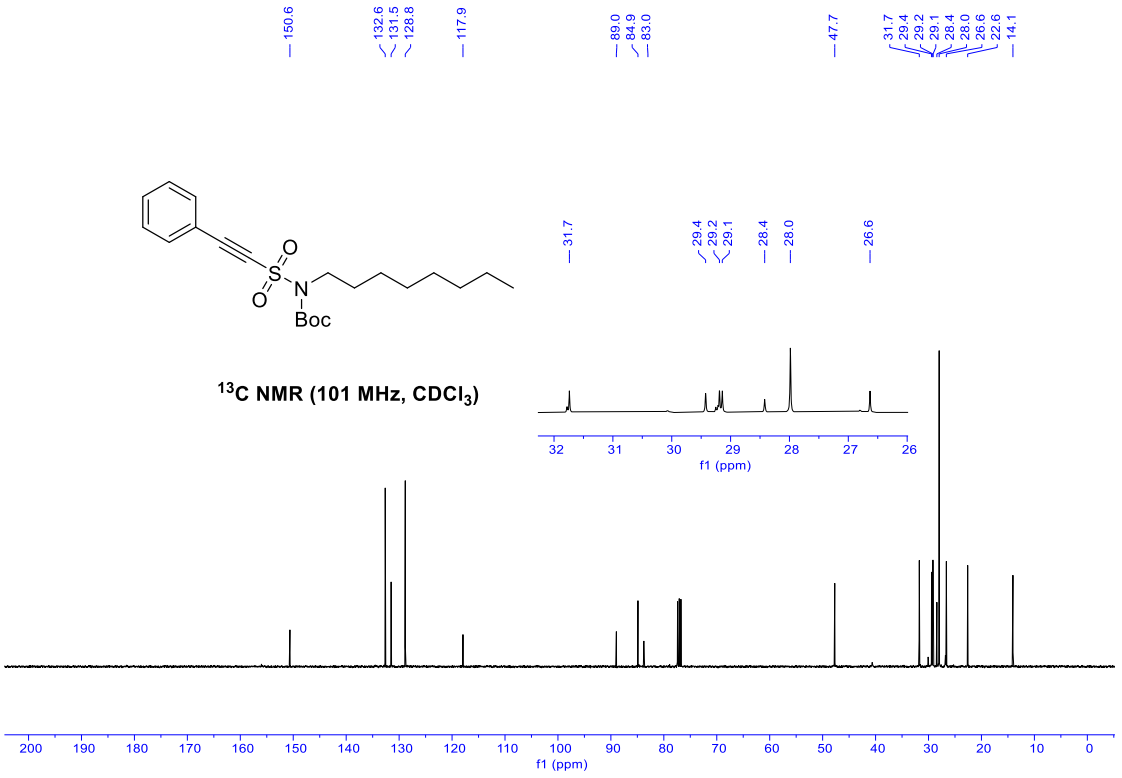
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1e



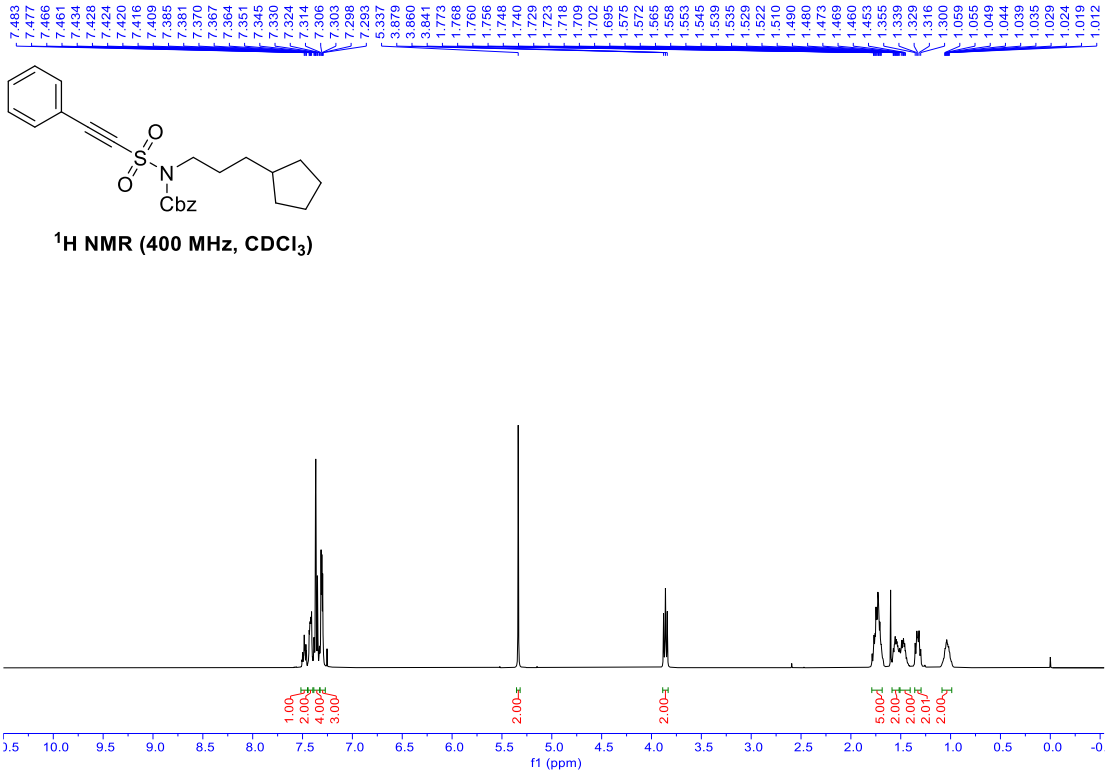
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1f



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1f

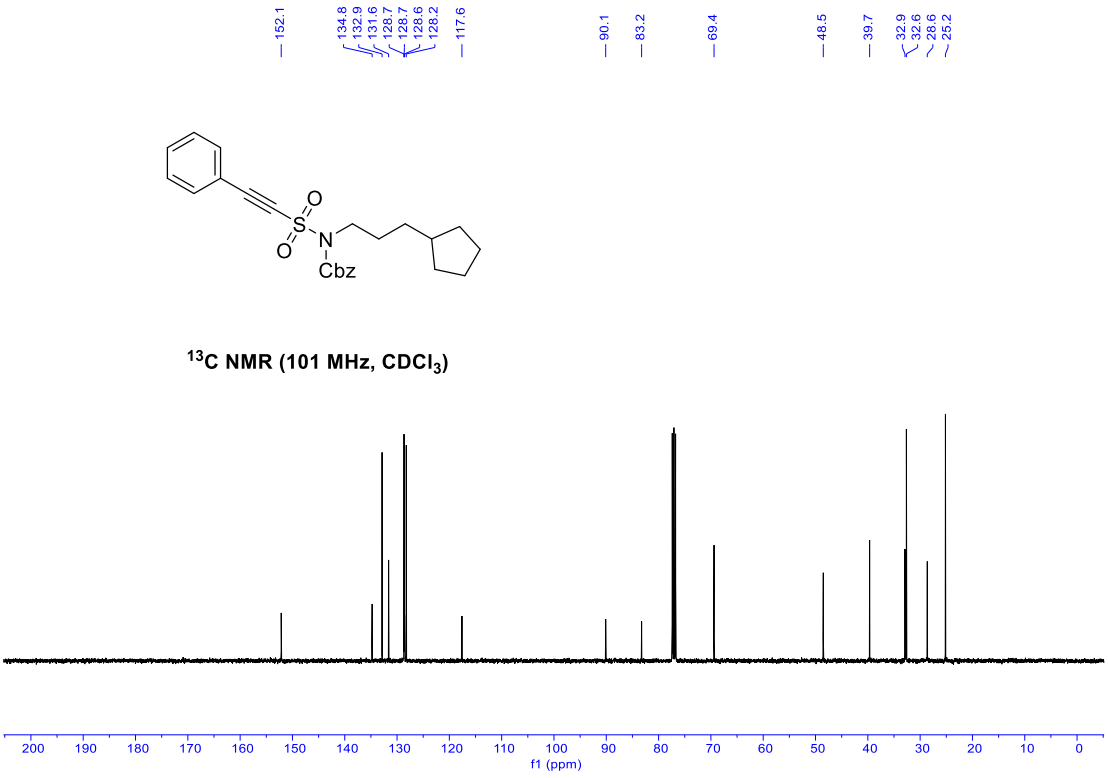


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1g



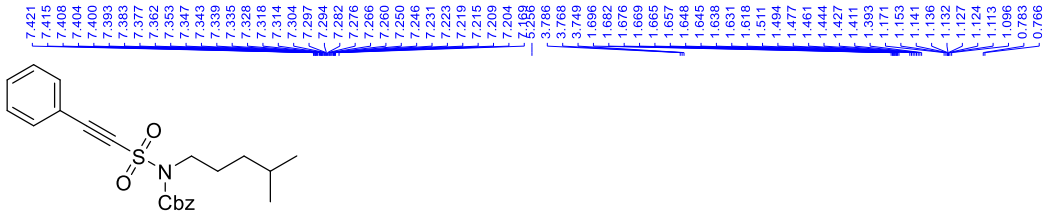
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1g

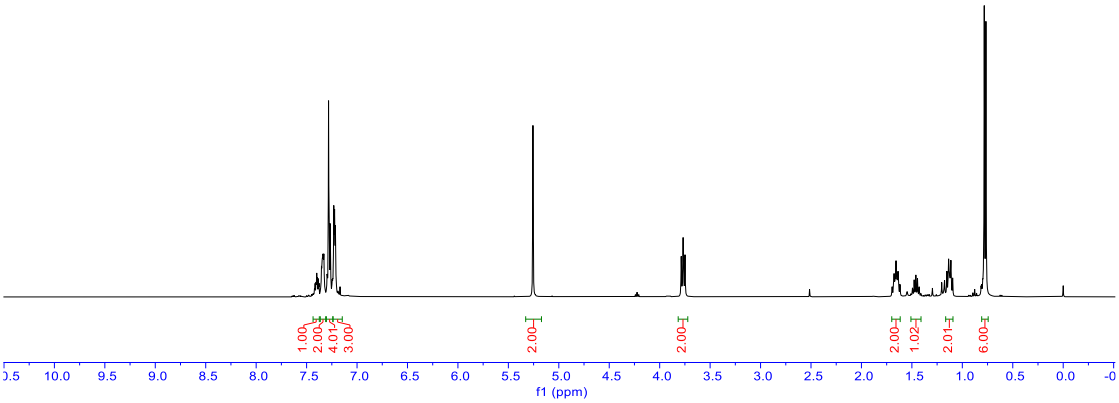


^{13}C NMR (101 MHz, $CDCl_3$)

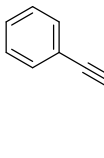
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1h



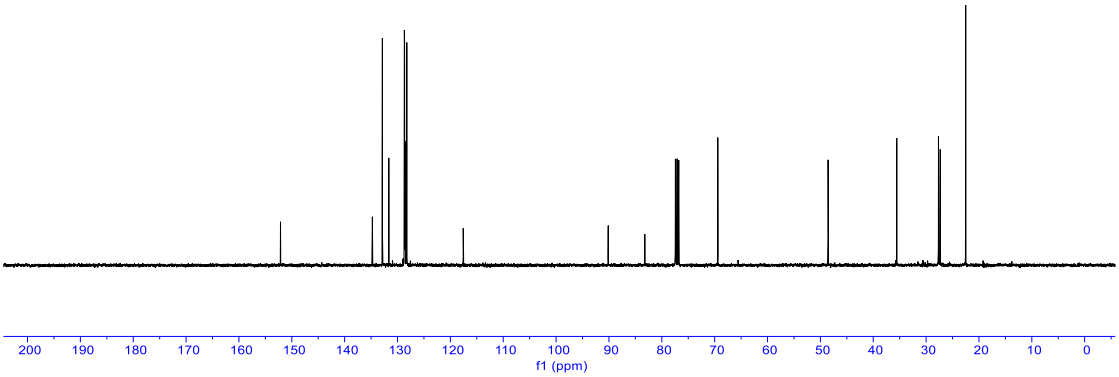
^{1}H NMR (400 MHz, $CDCl_3$)



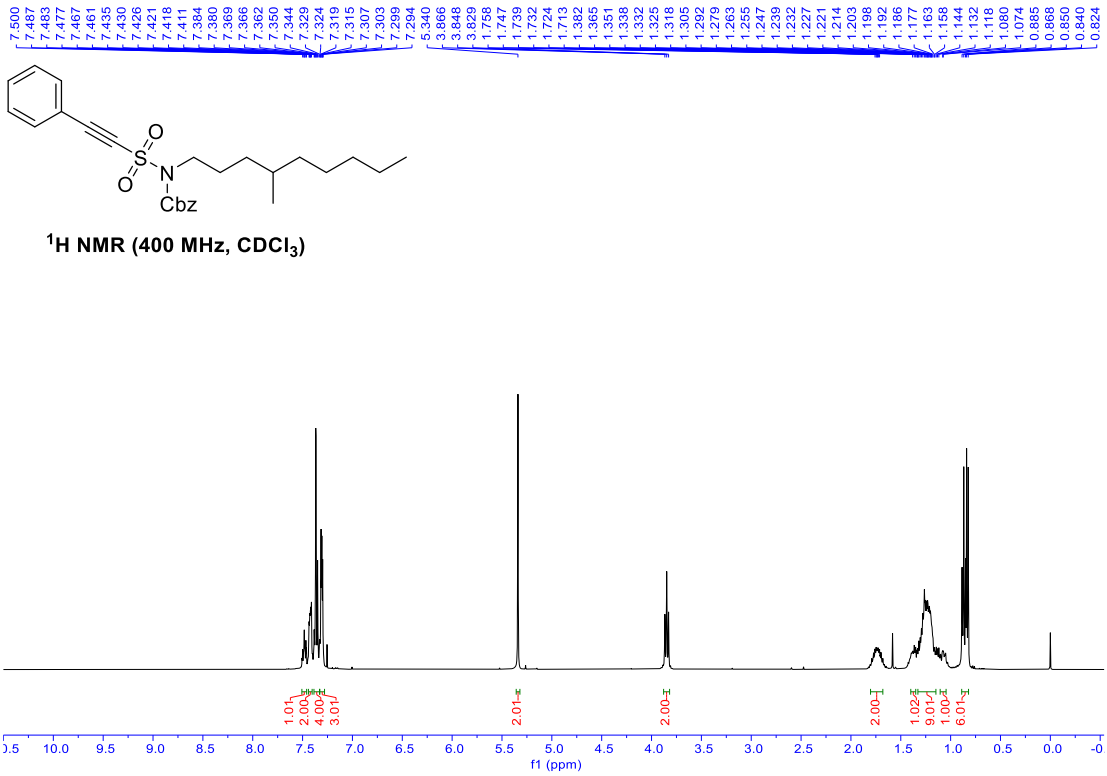
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1h



^{13}C NMR (101 MHz, $CDCl_3$)

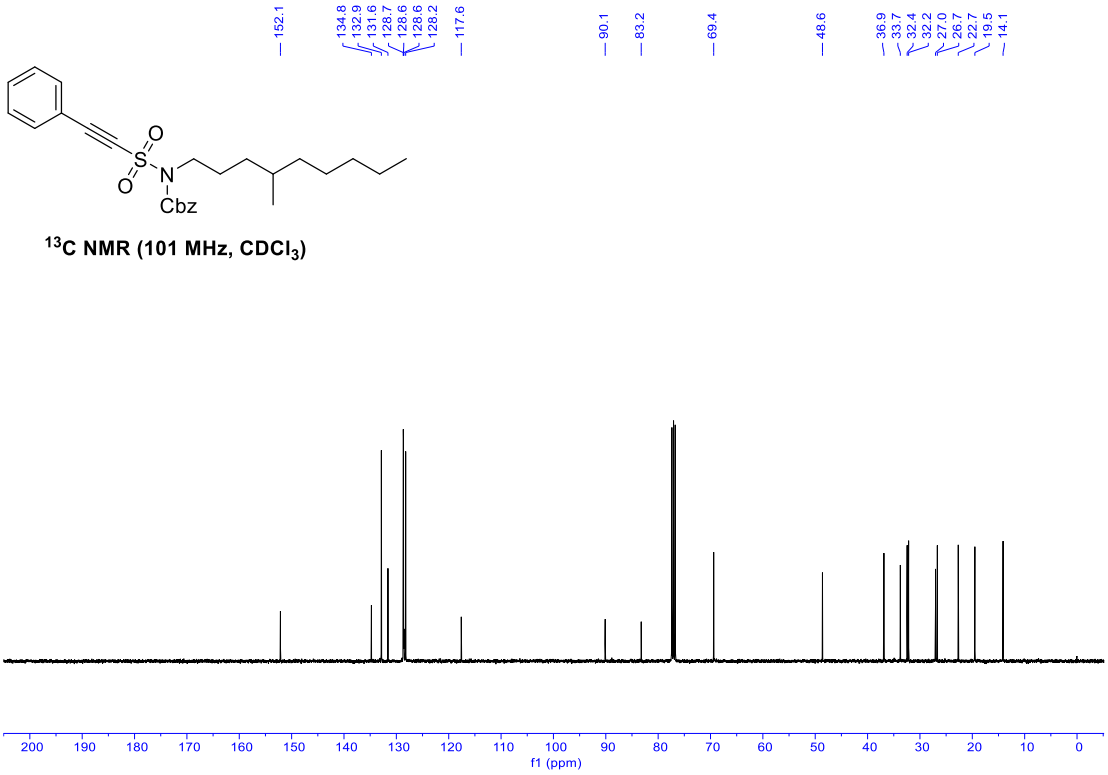


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1i



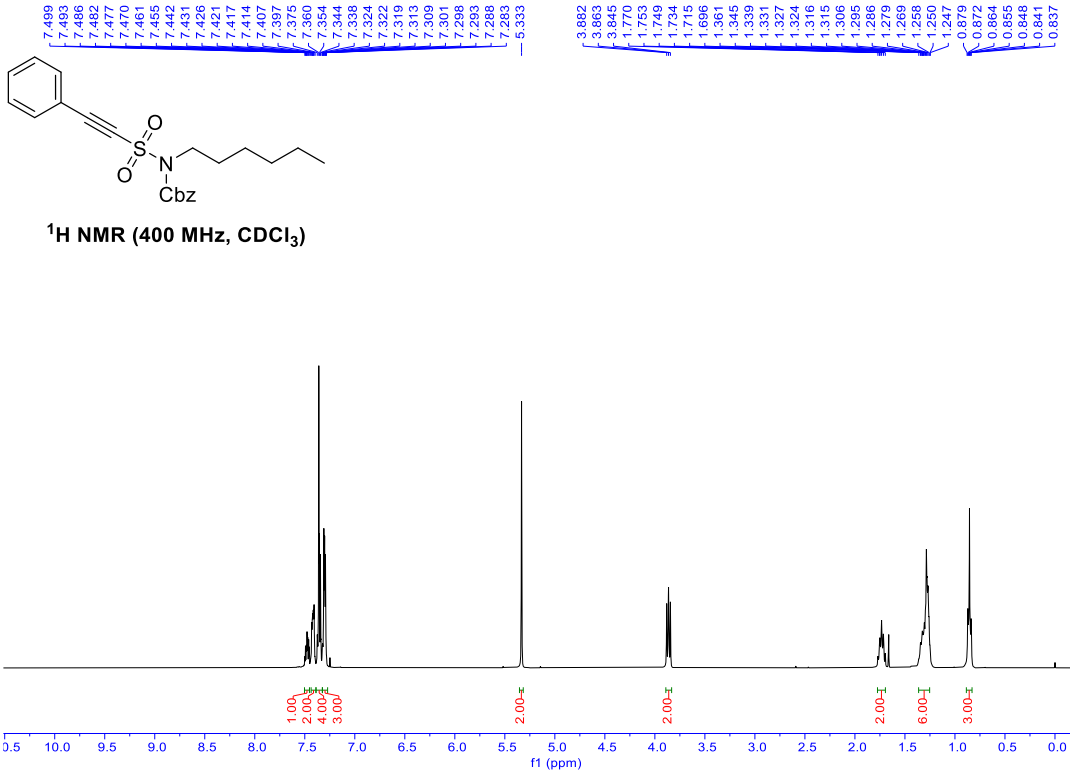
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1i



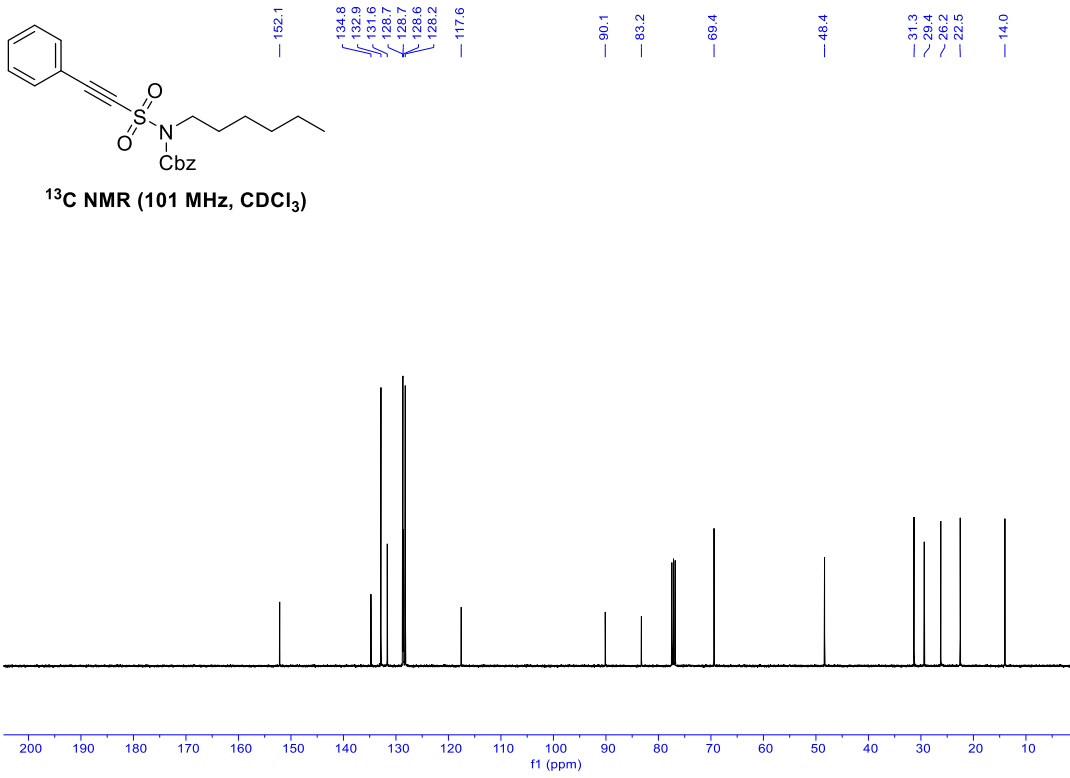
^{13}C NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1j



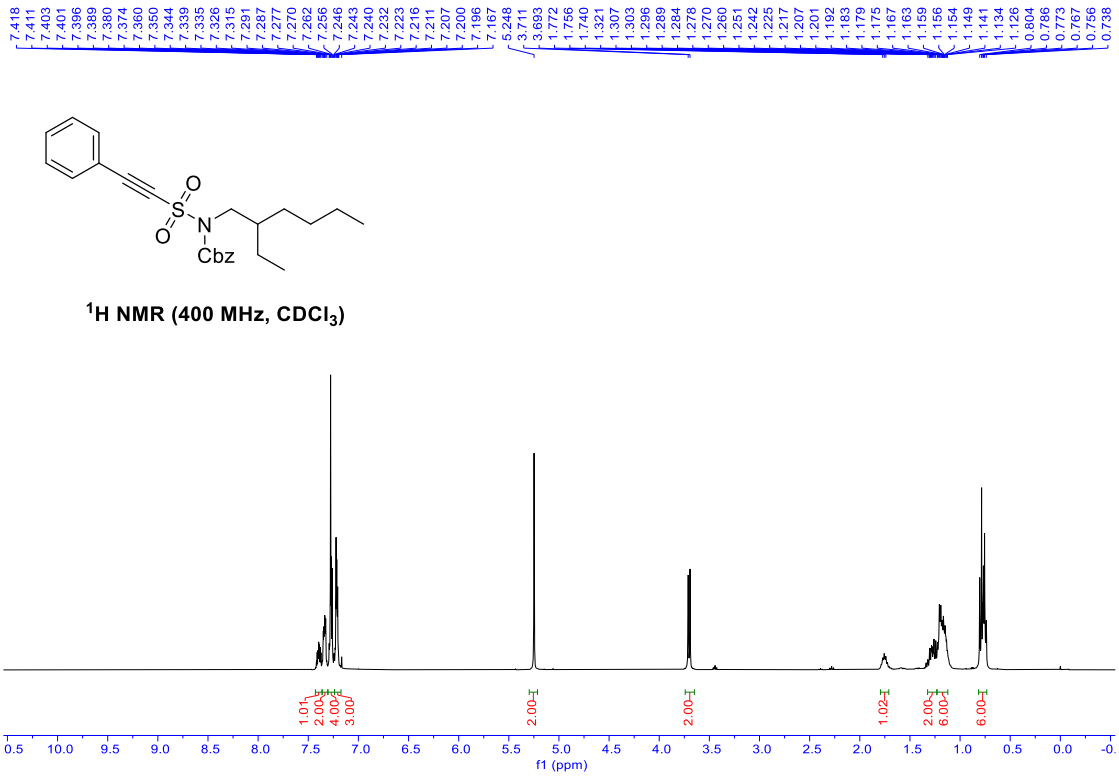
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1j

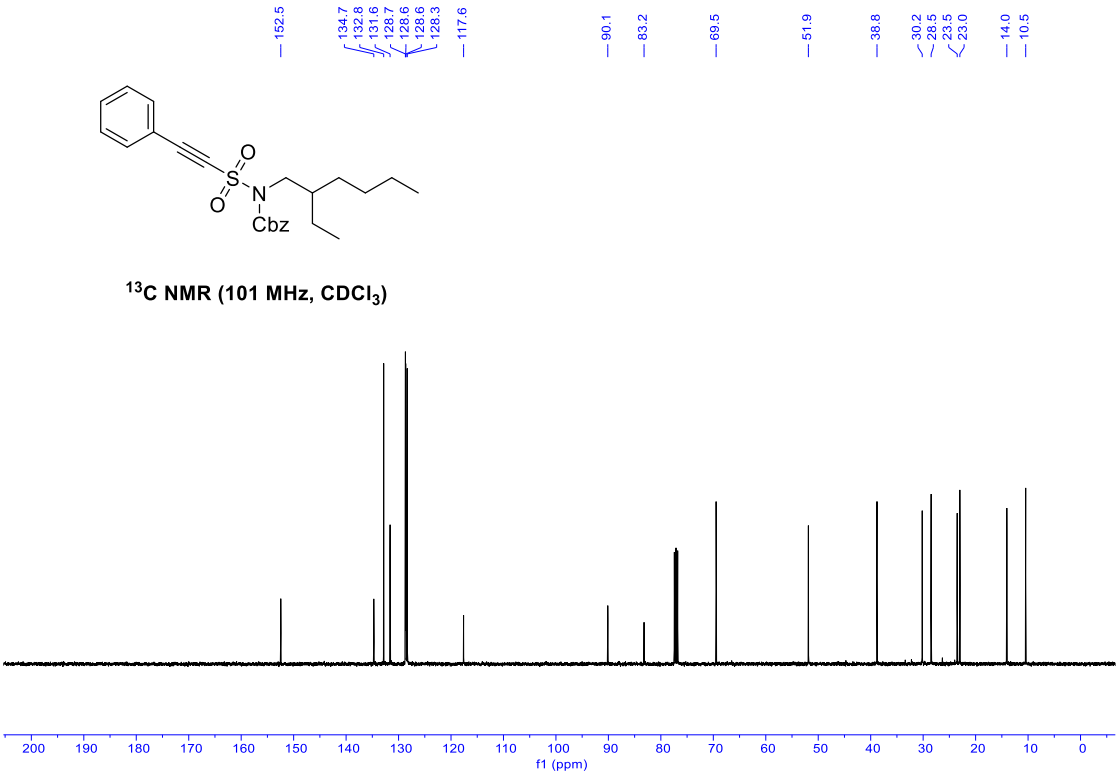


^{13}C NMR (101 MHz, $CDCl_3$)

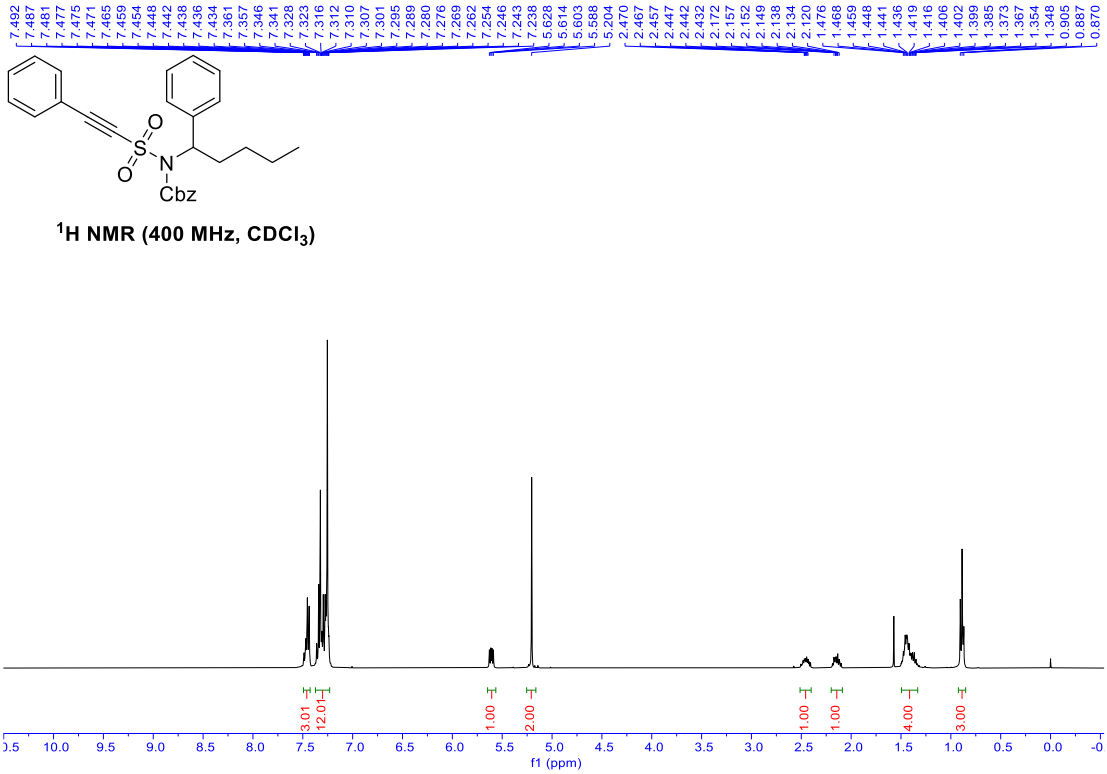
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1k



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1k

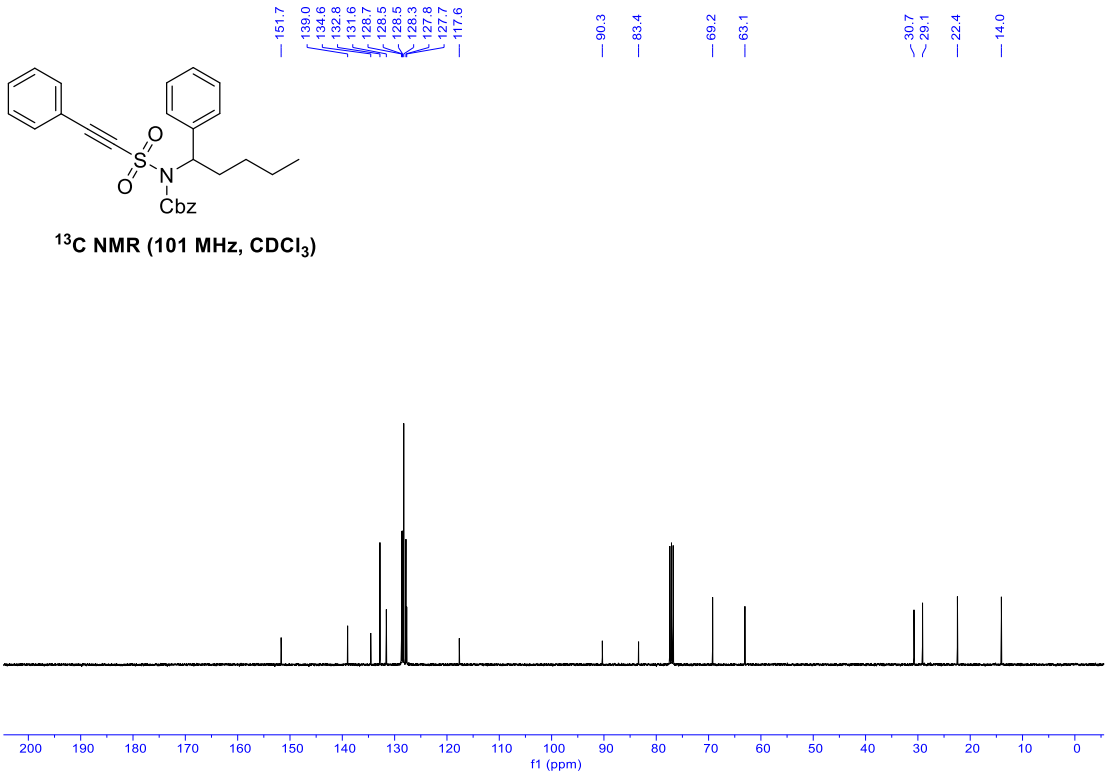


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1l



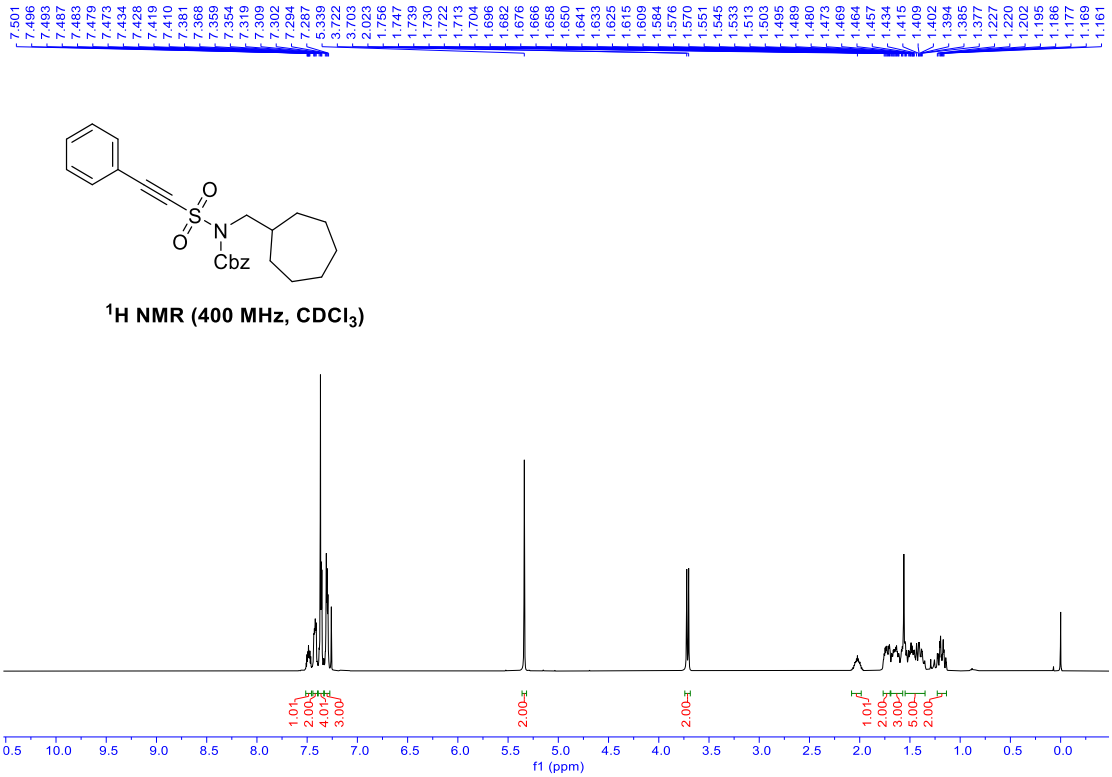
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1l



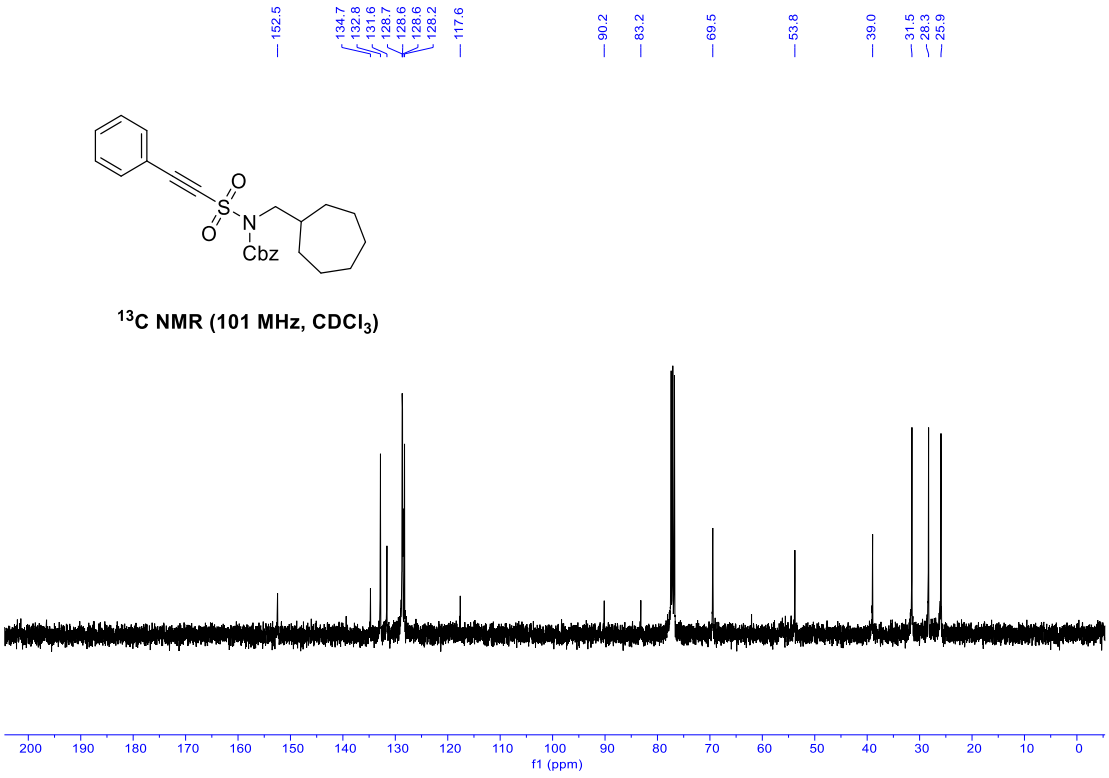
^{13}C NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1m



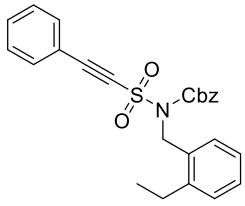
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1m

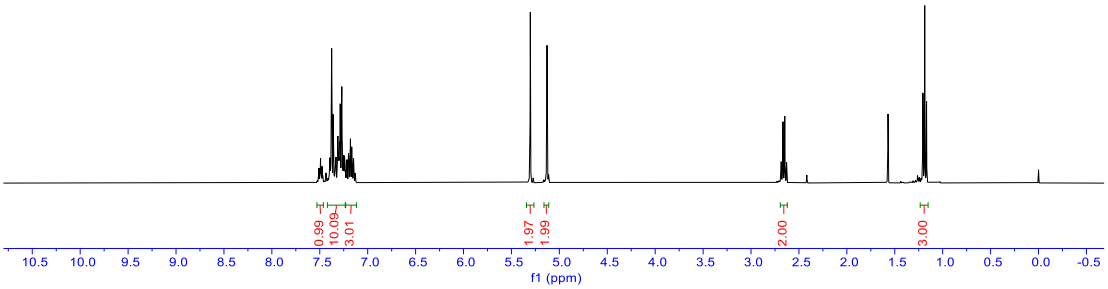


^{13}C NMR (101 MHz, $CDCl_3$)

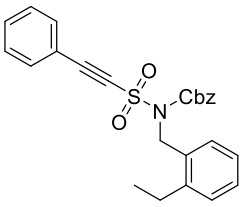
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1n



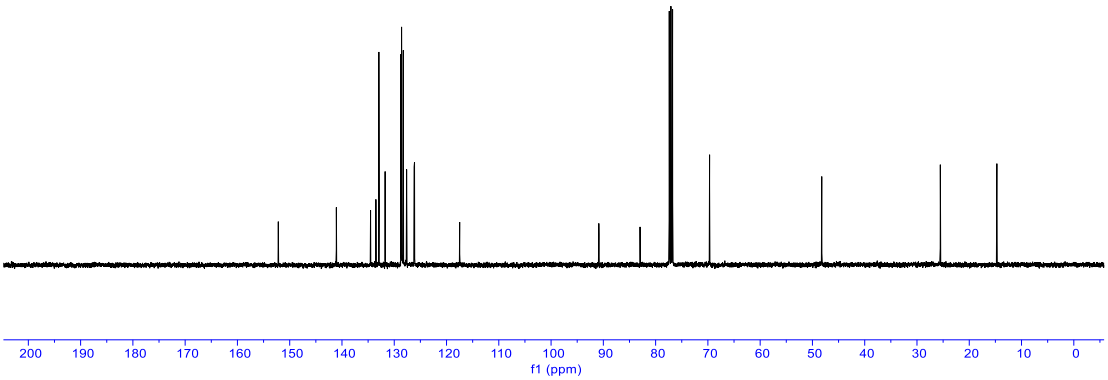
^{1}H NMR (400 MHz, $CDCl_3$)



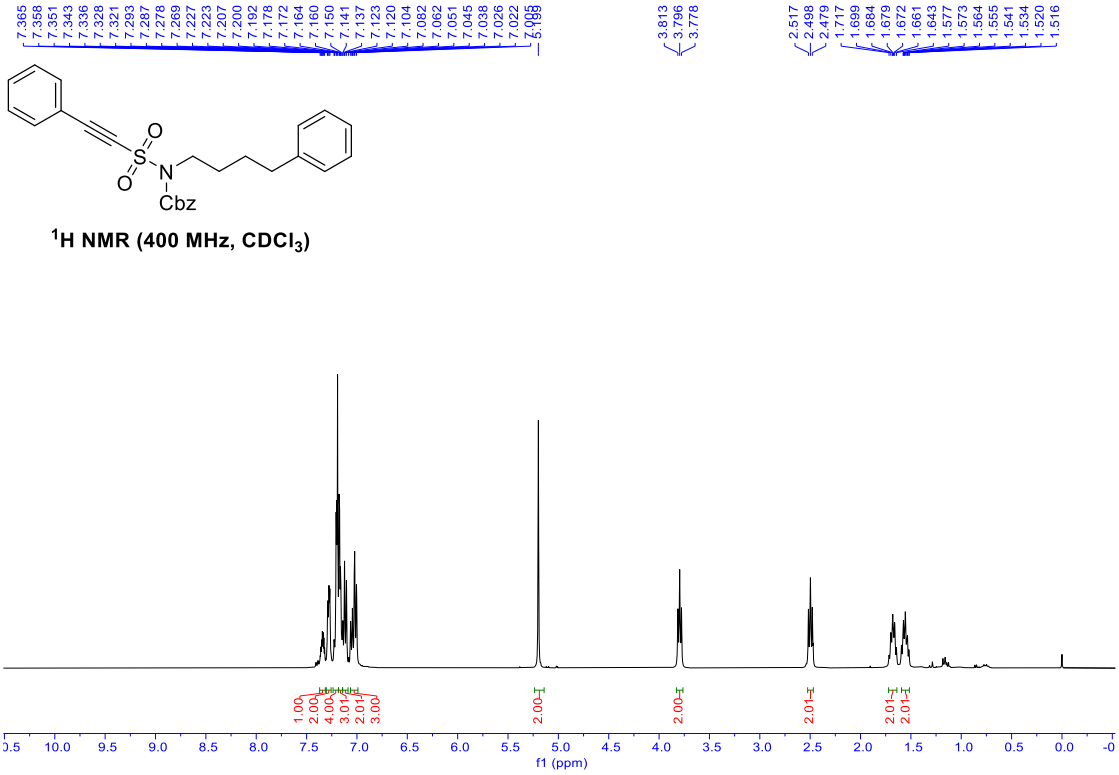
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1n



^{13}C NMR (101 MHz, $CDCl_3$)

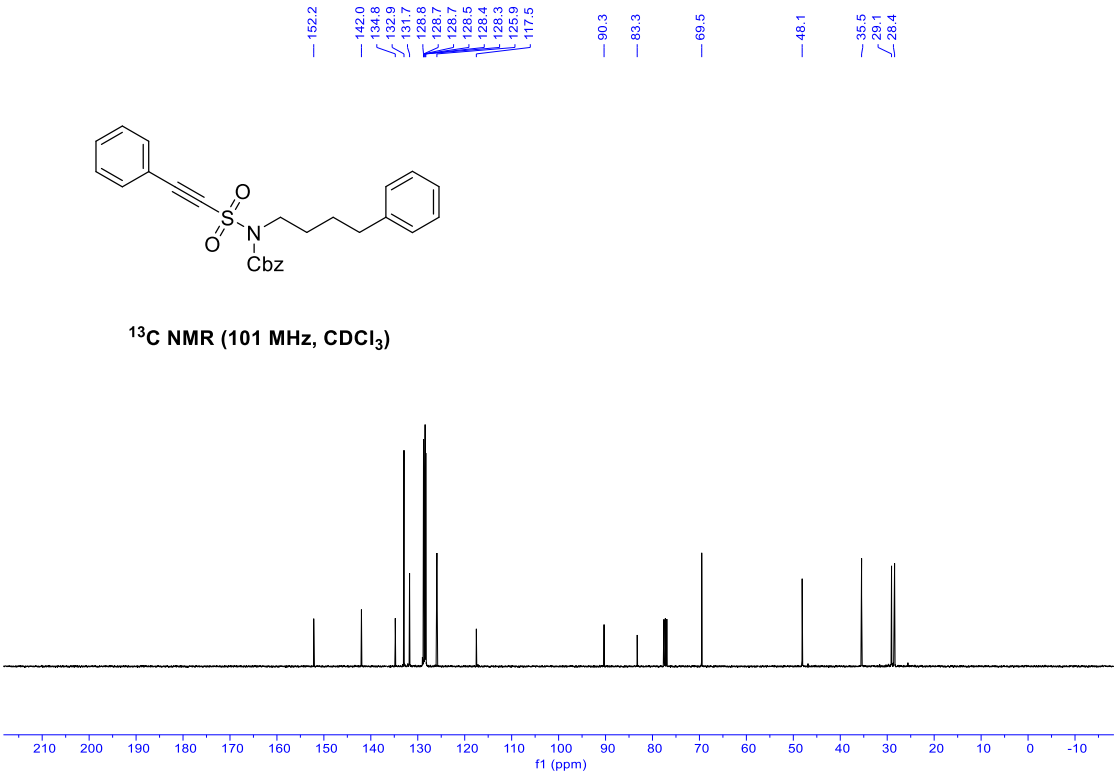


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1o



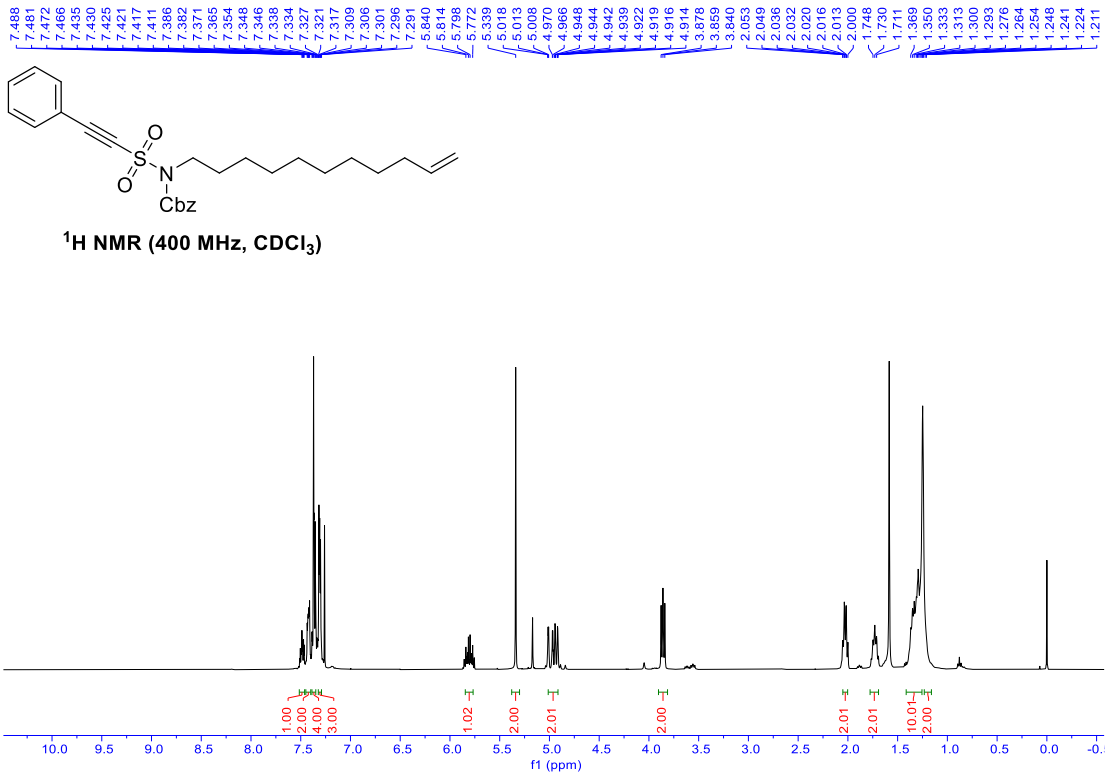
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1o



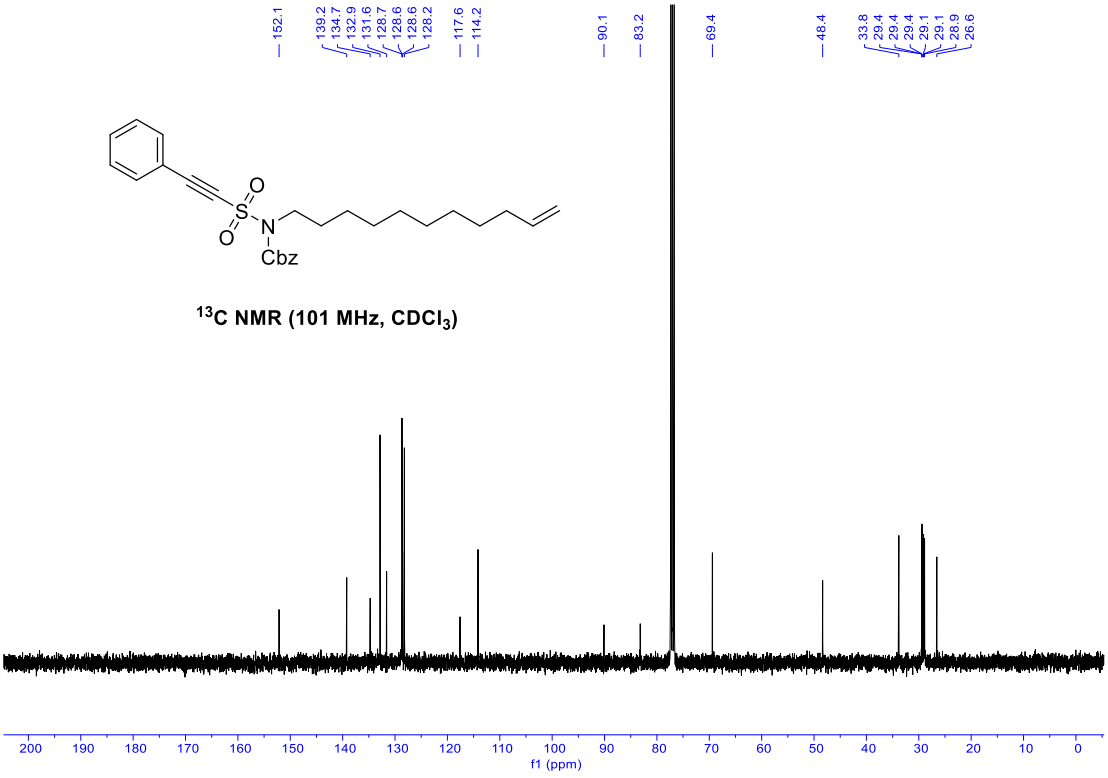
^{13}C NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1p



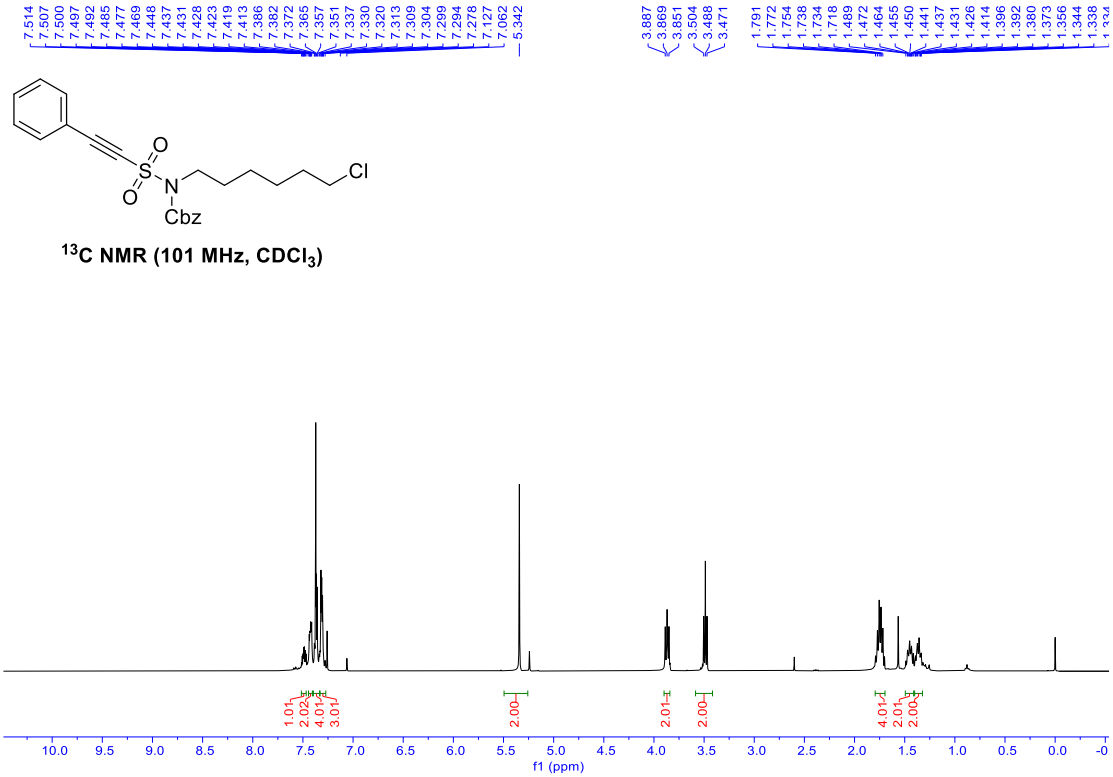
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1p

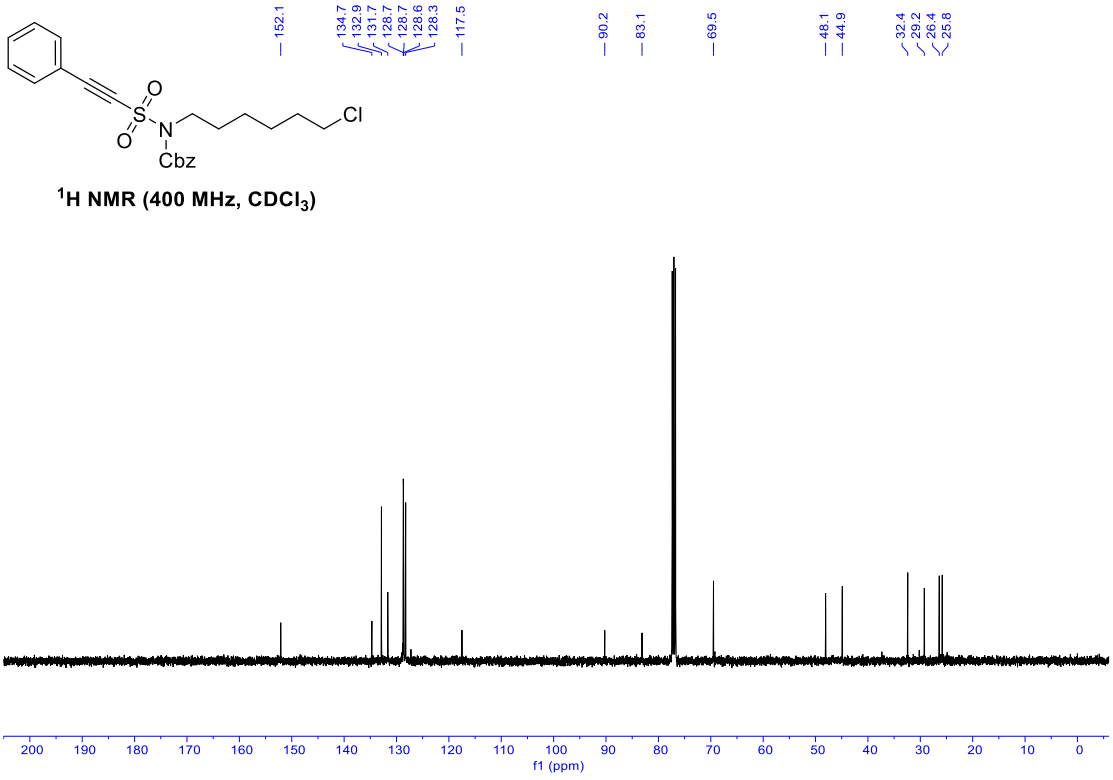


^{13}C NMR (101 MHz, $CDCl_3$)

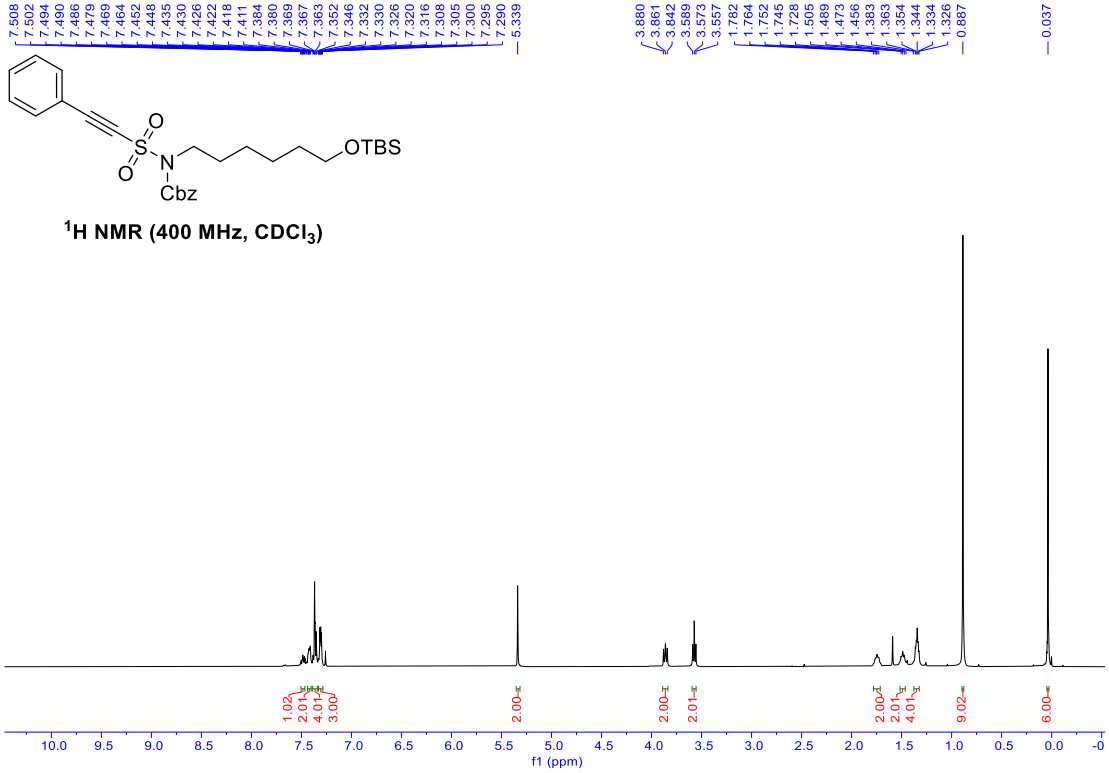
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1q



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1q

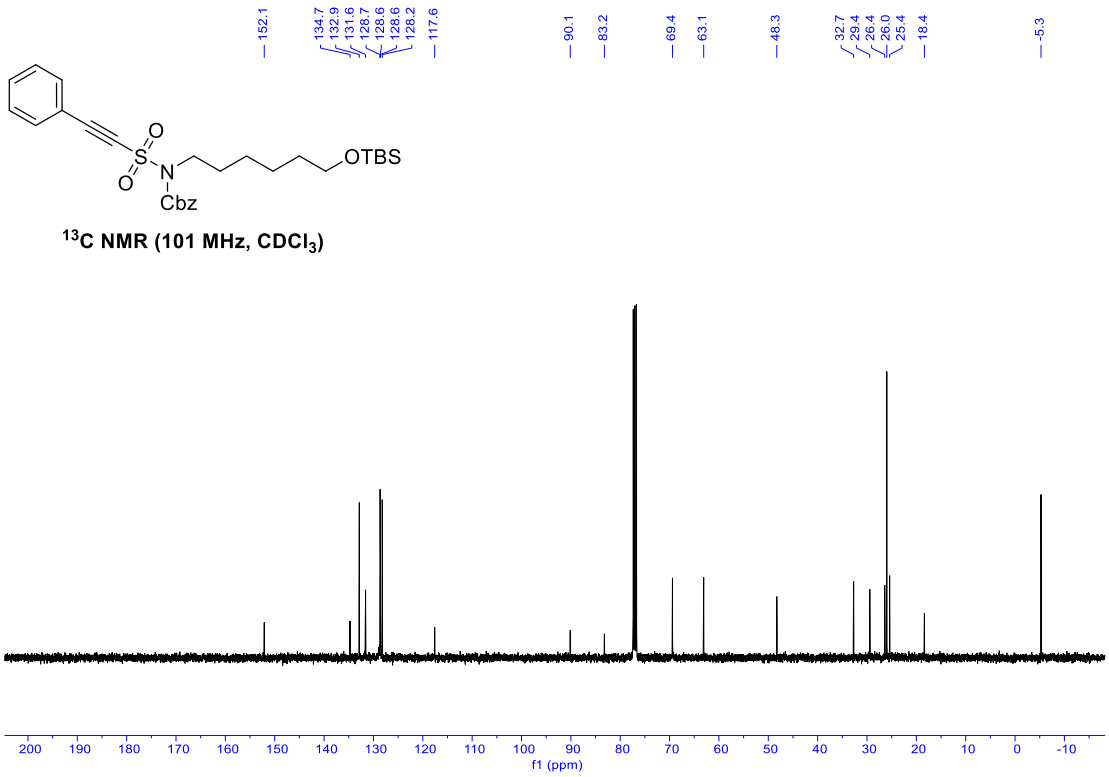


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1r



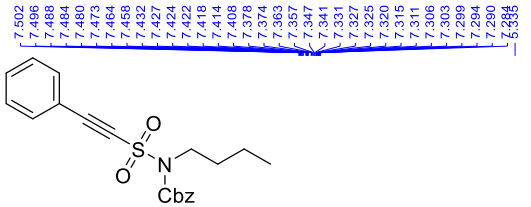
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1r



^{13}C NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1s



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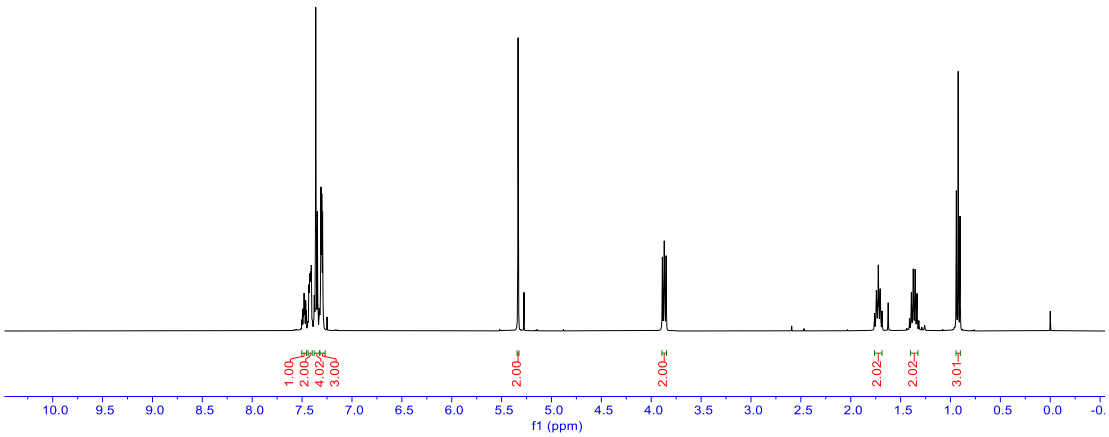
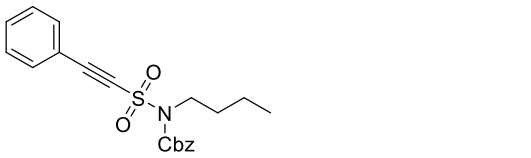
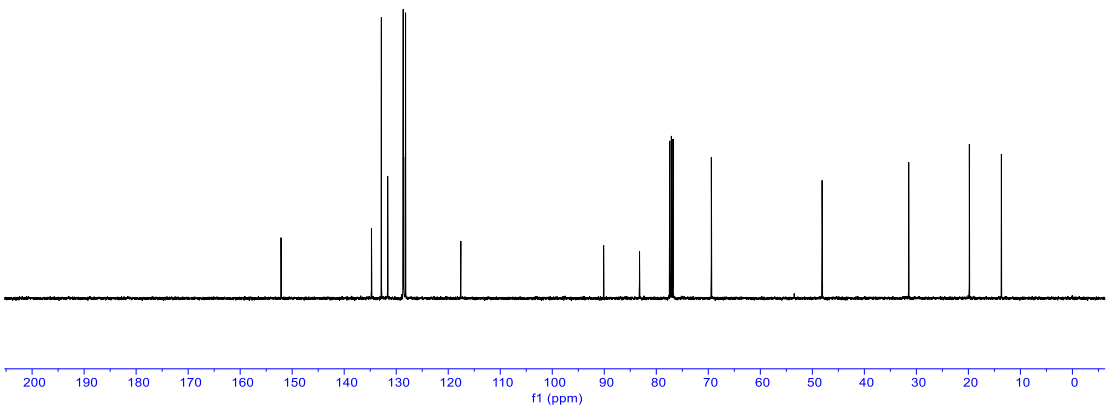


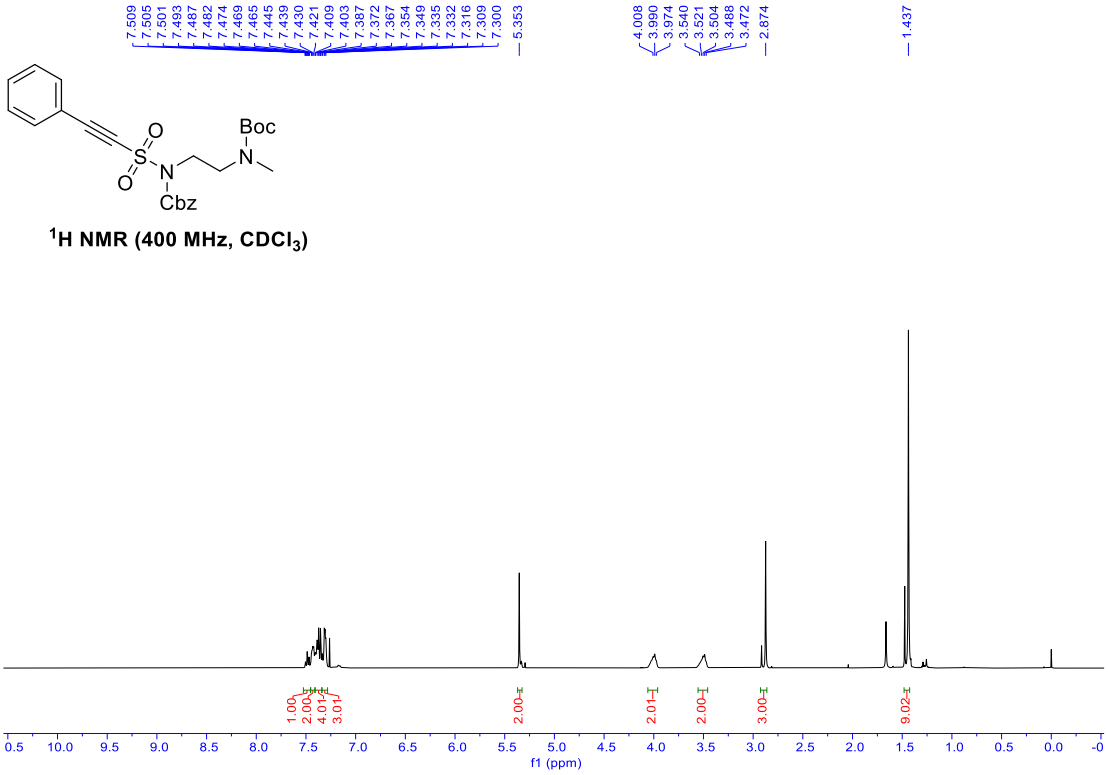
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1s



^{13}C NMR (101 MHz, $CDCl_3$)

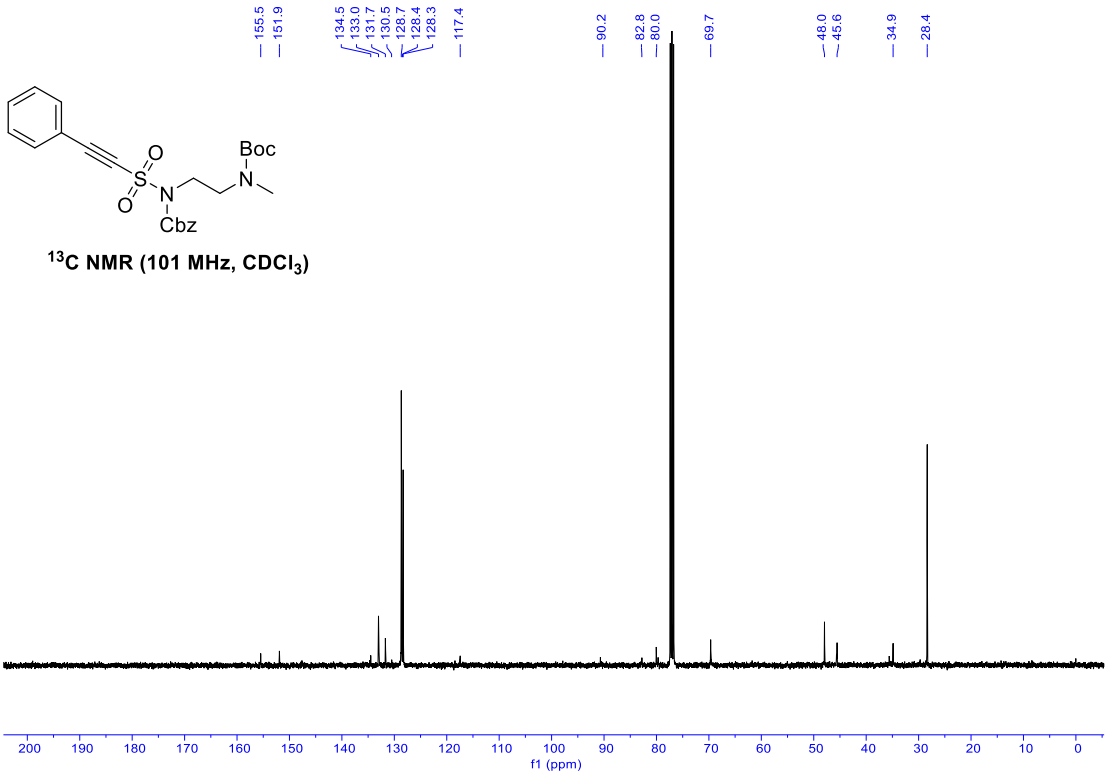


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1t



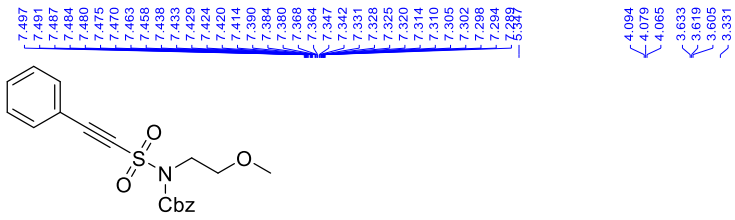
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1t

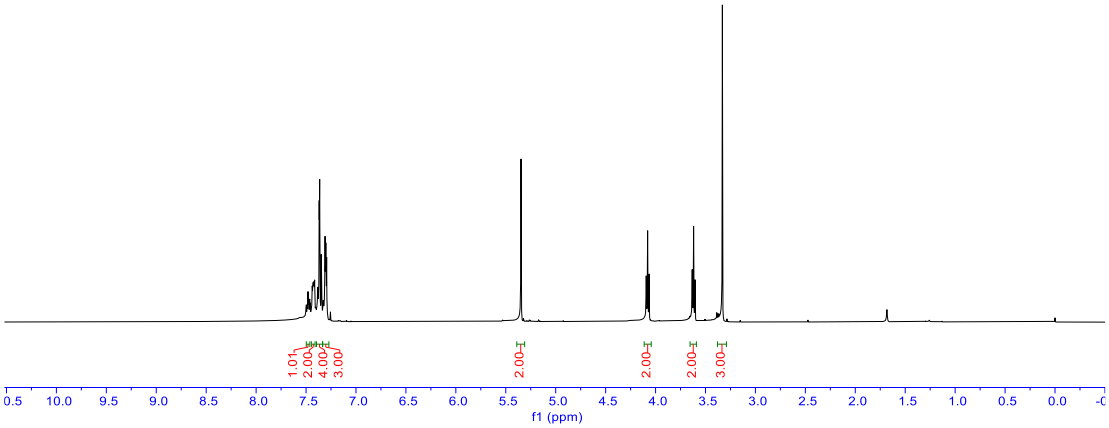


^{13}C NMR (101 MHz, $CDCl_3$)

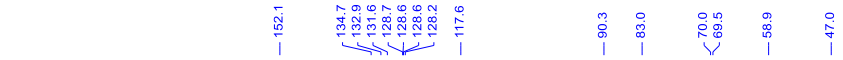
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1u

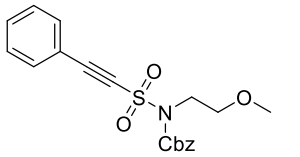


^{1}H NMR (400 MHz, $CDCl_3$)

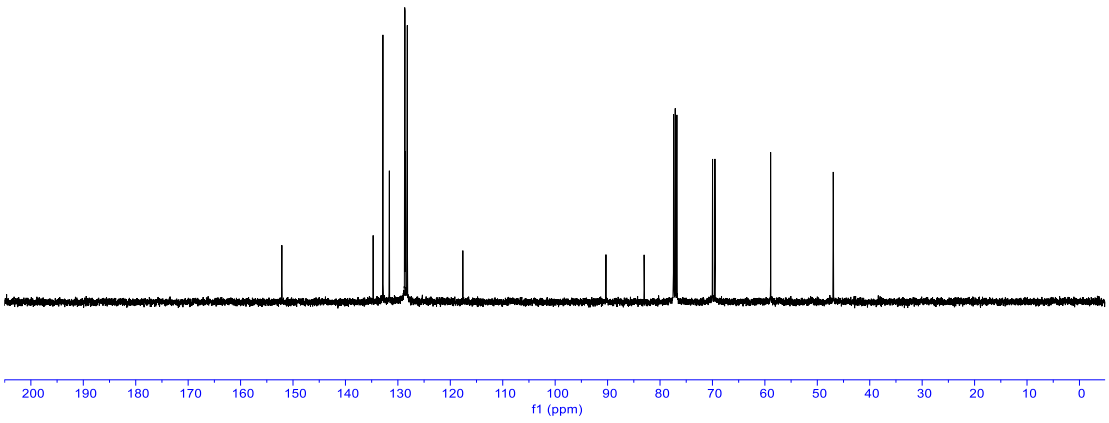


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1u

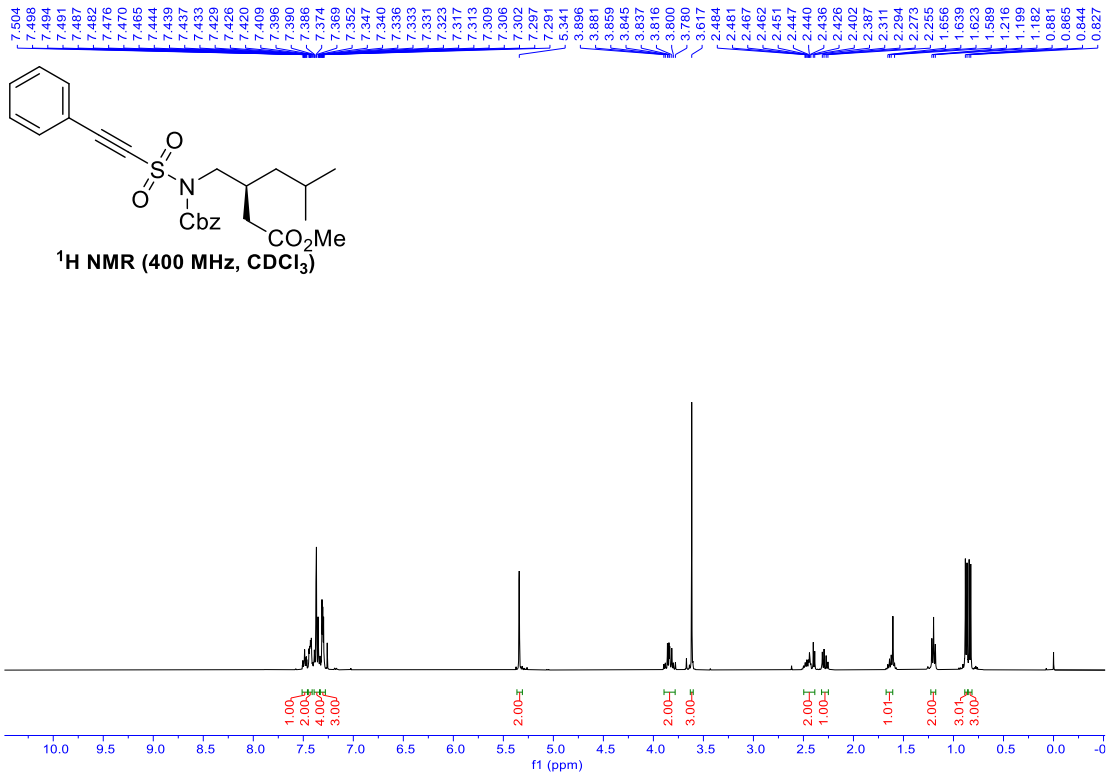




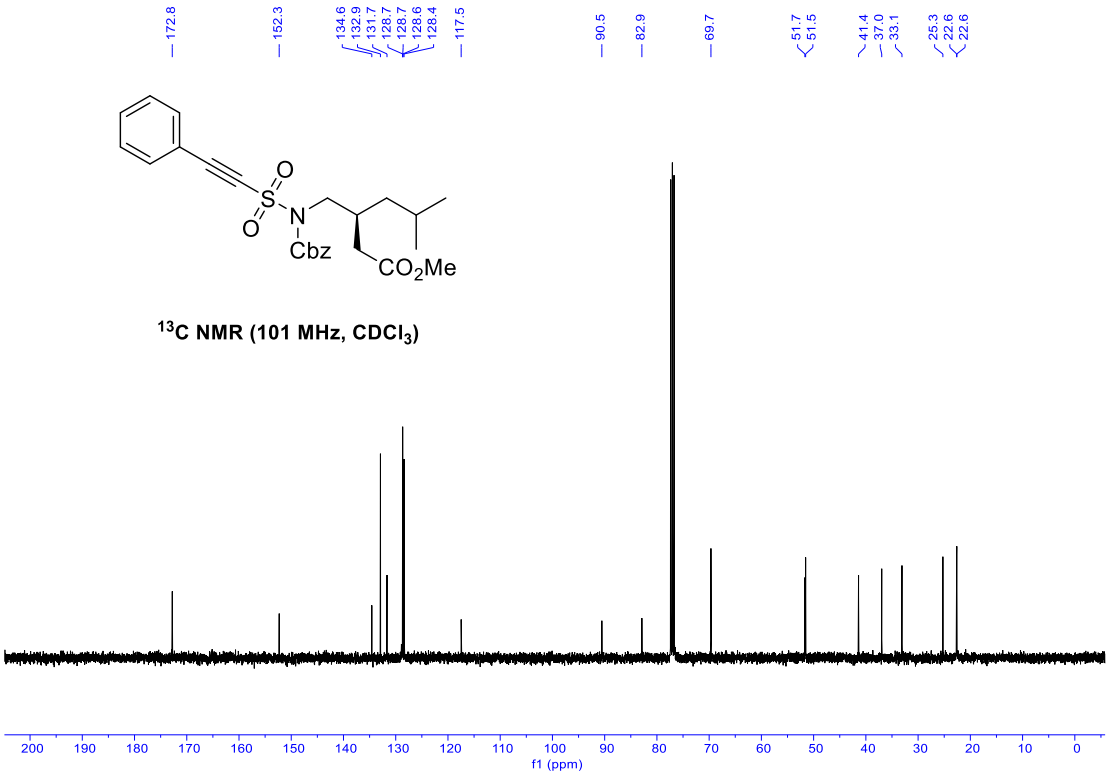
^{13}C NMR (101 MHz, $CDCl_3$)



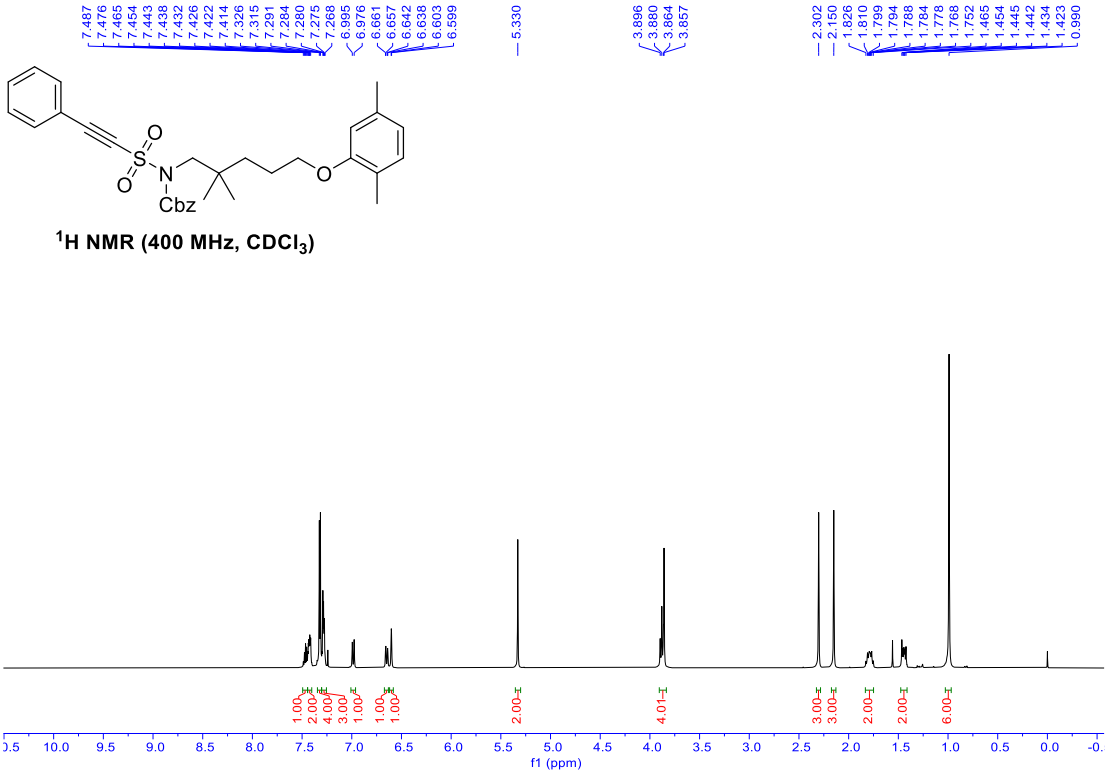
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1v



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1v

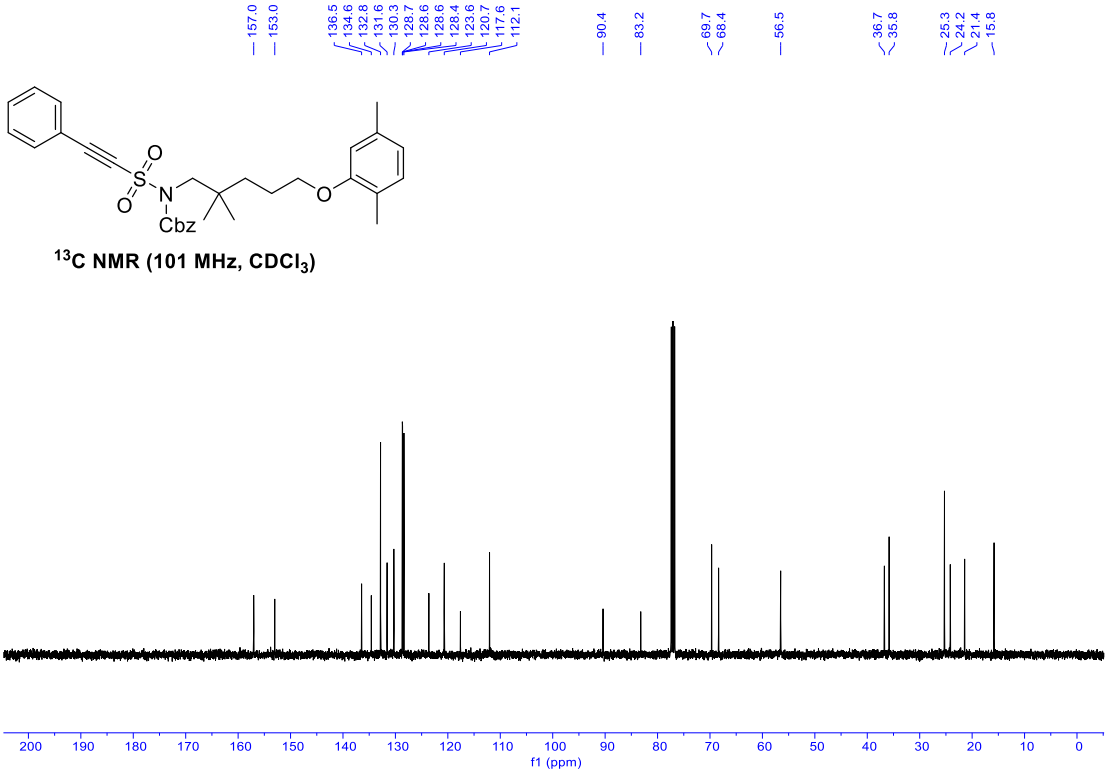


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1w



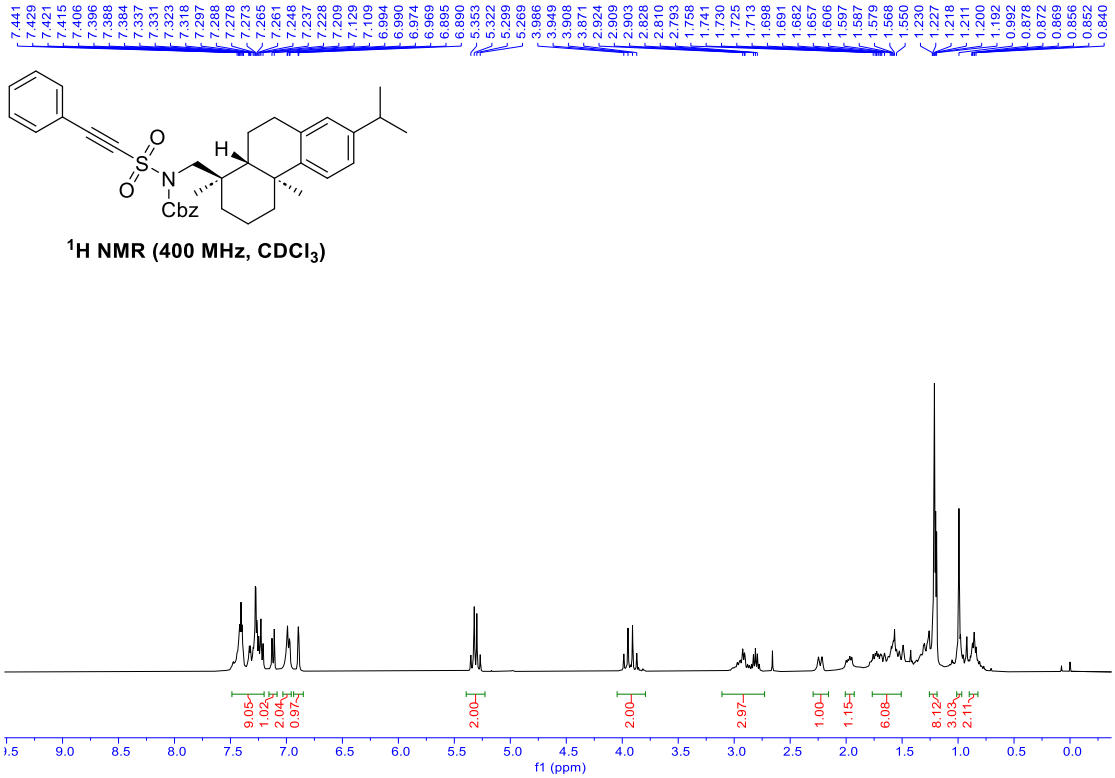
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1w



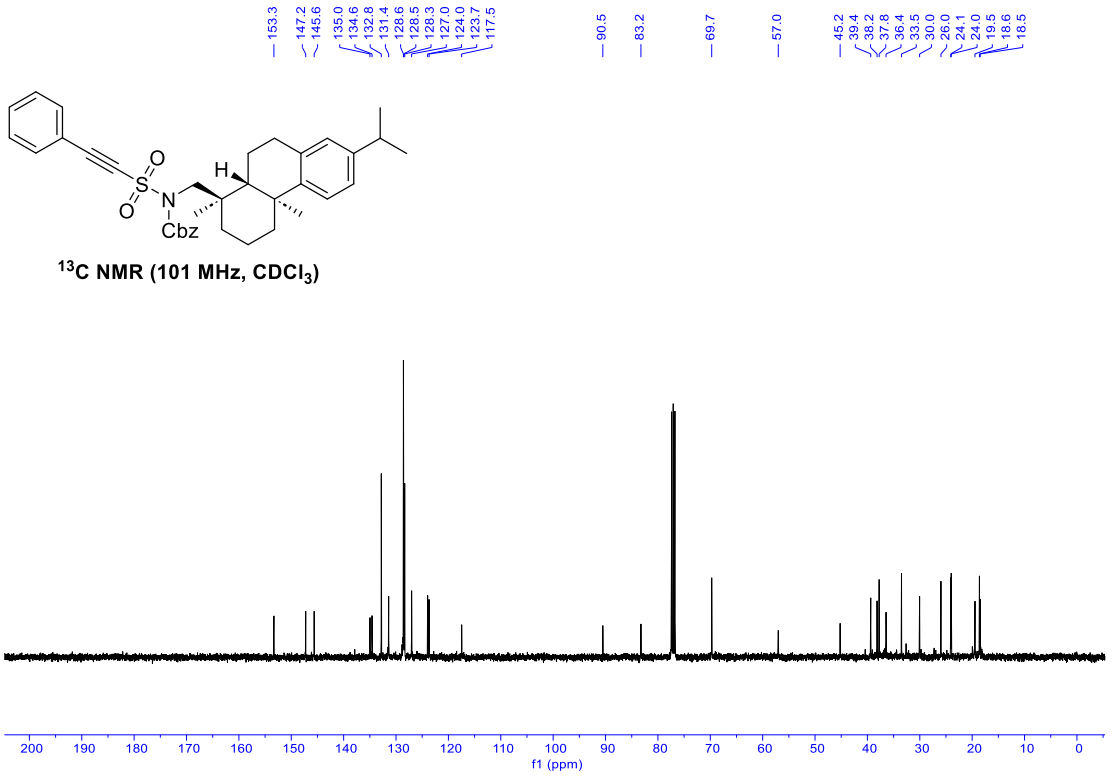
^{13}C NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1x



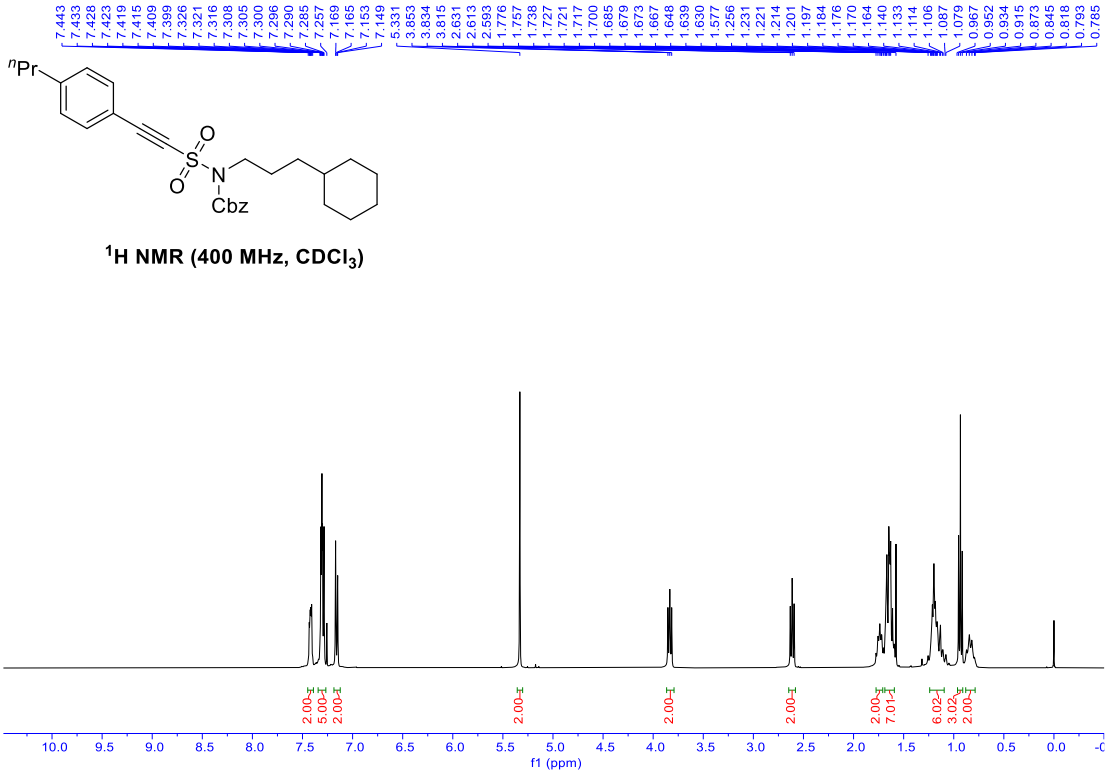
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1x



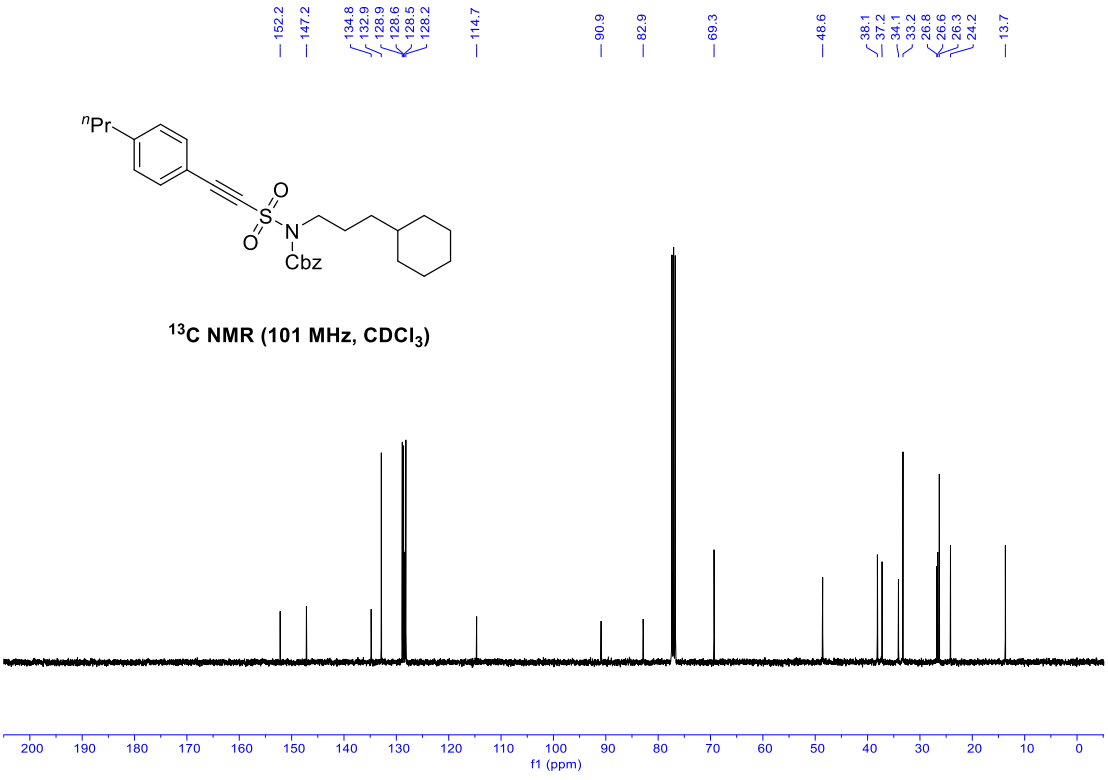
^{13}C NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1aa



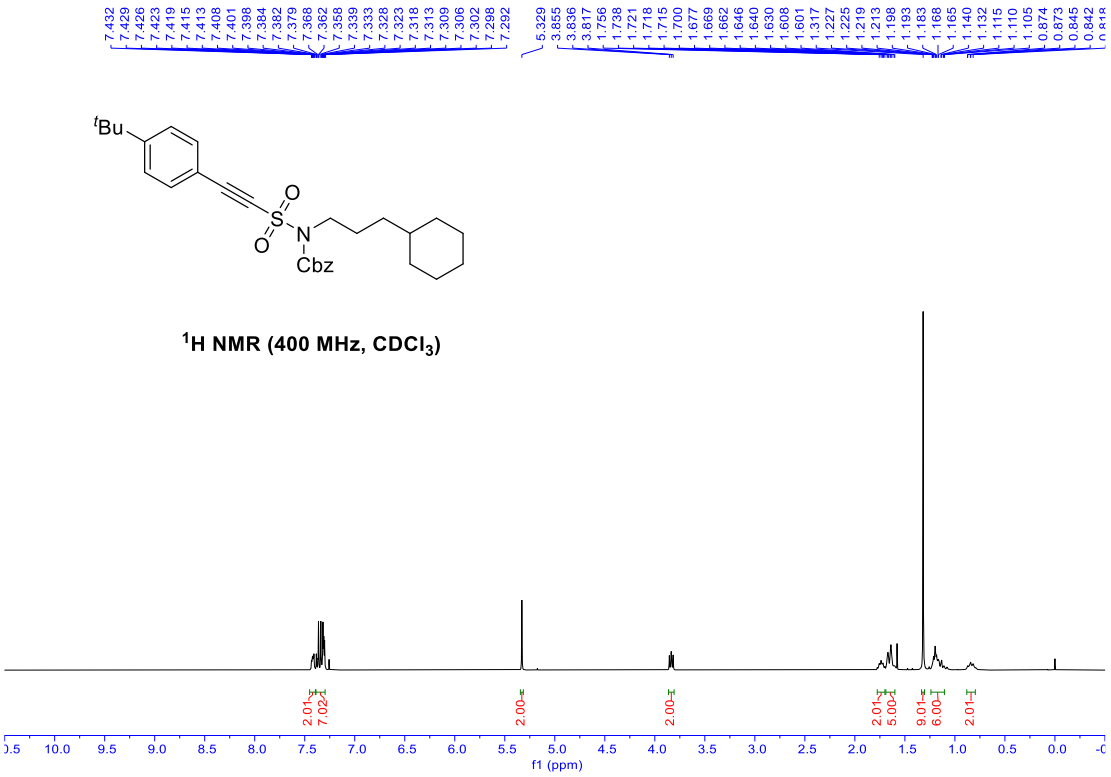
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1aa

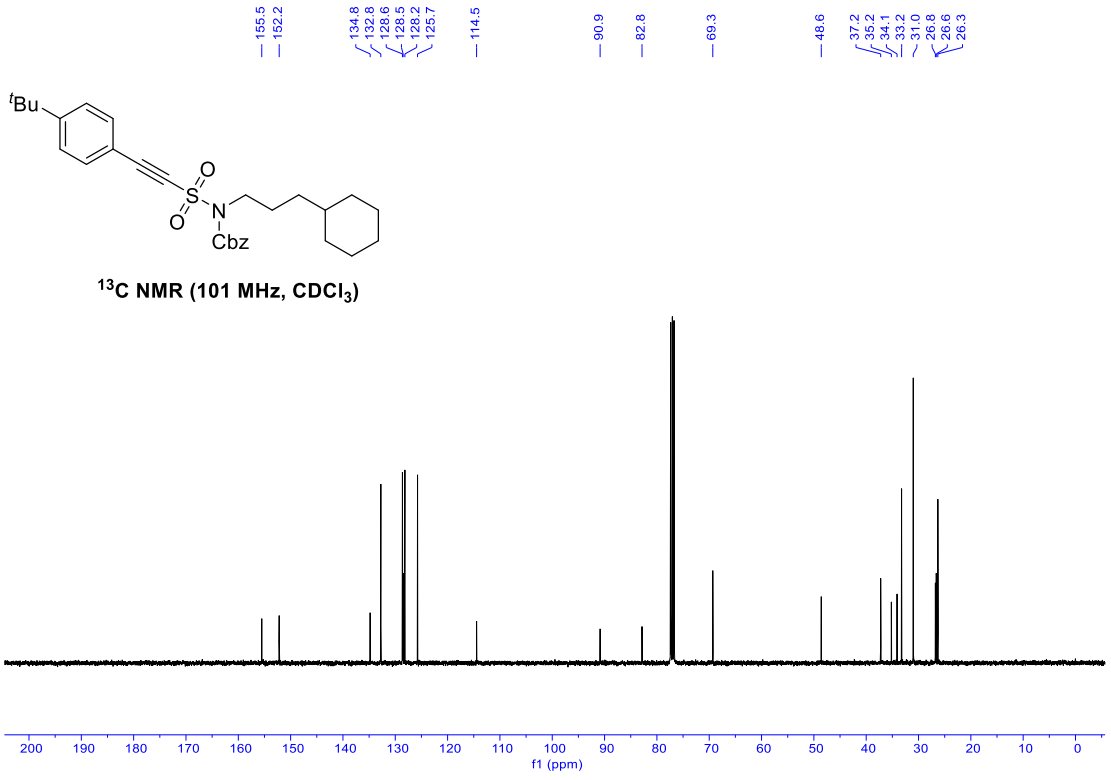


^{13}C NMR (101 MHz, $CDCl_3$)

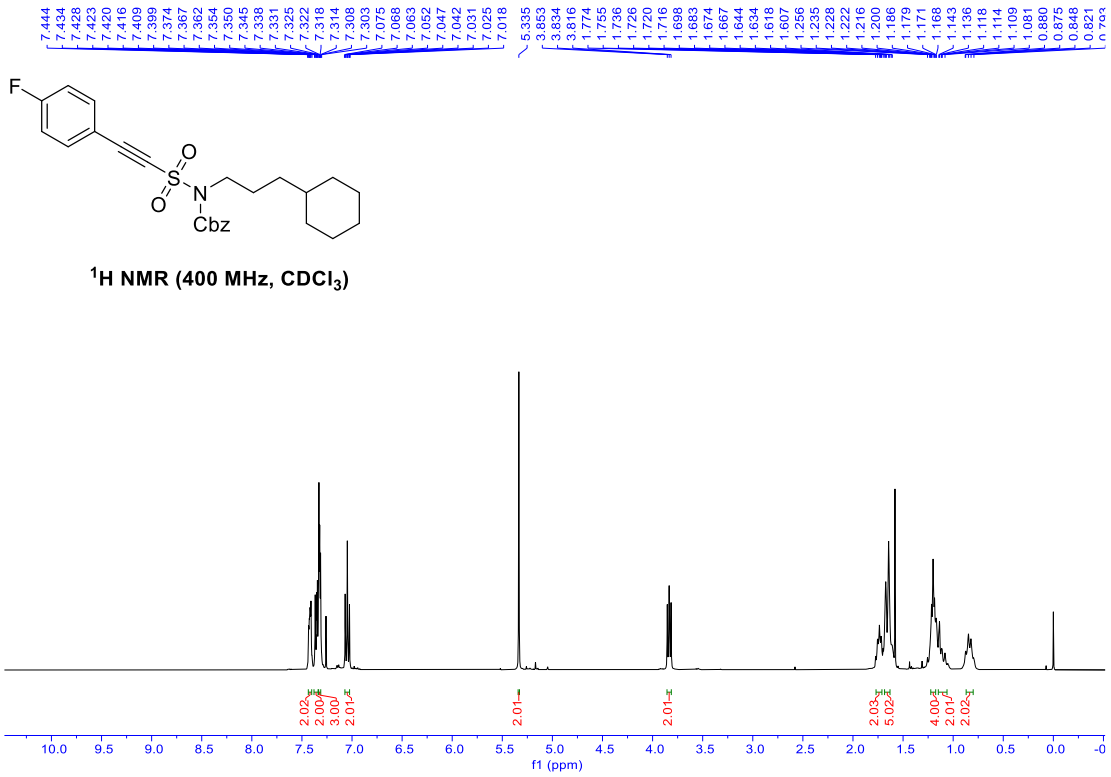
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1ab



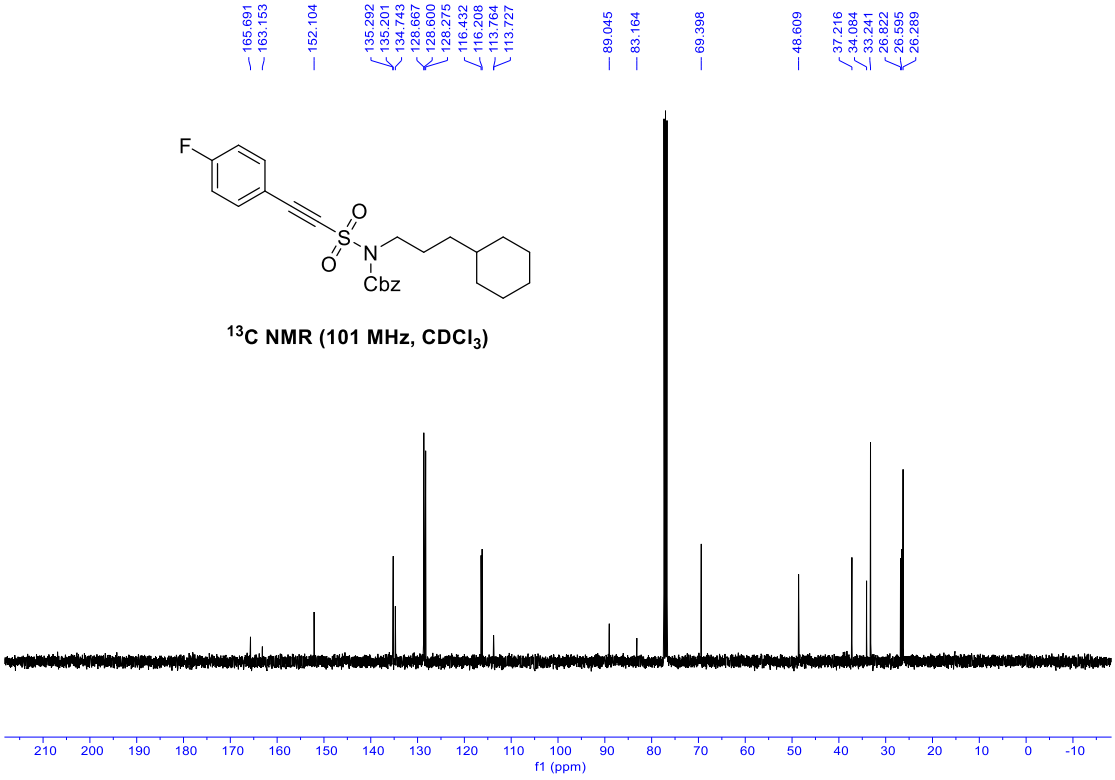
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1ab



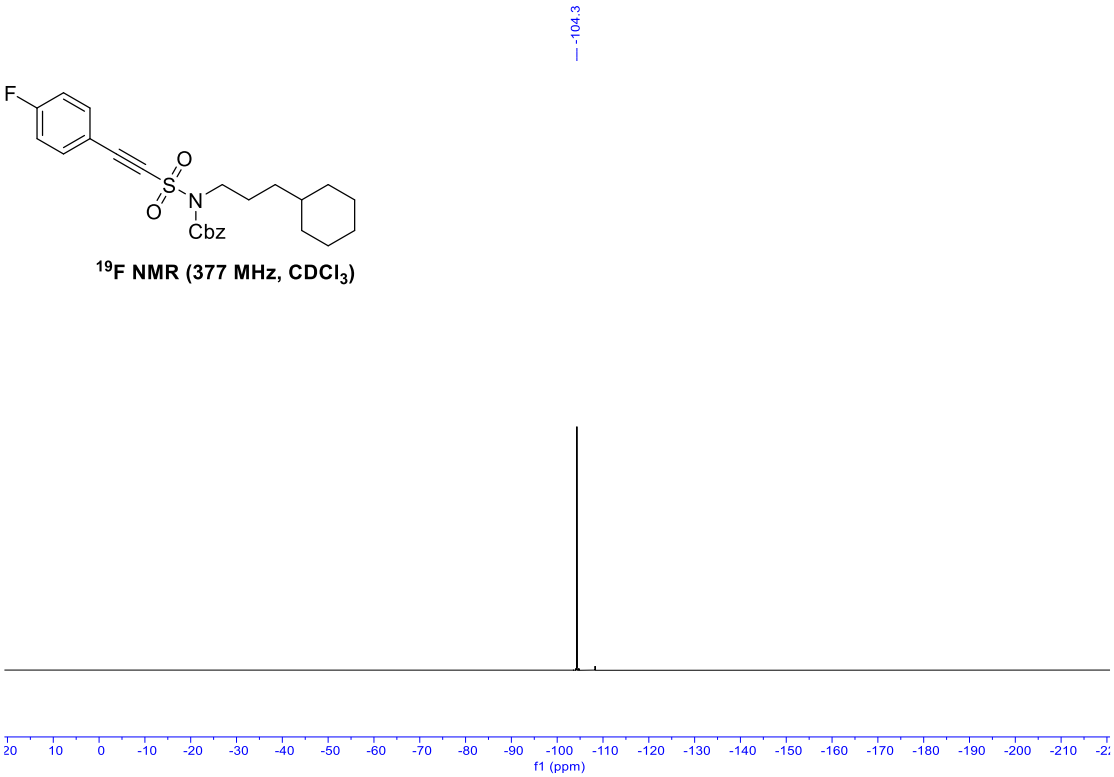
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1ac



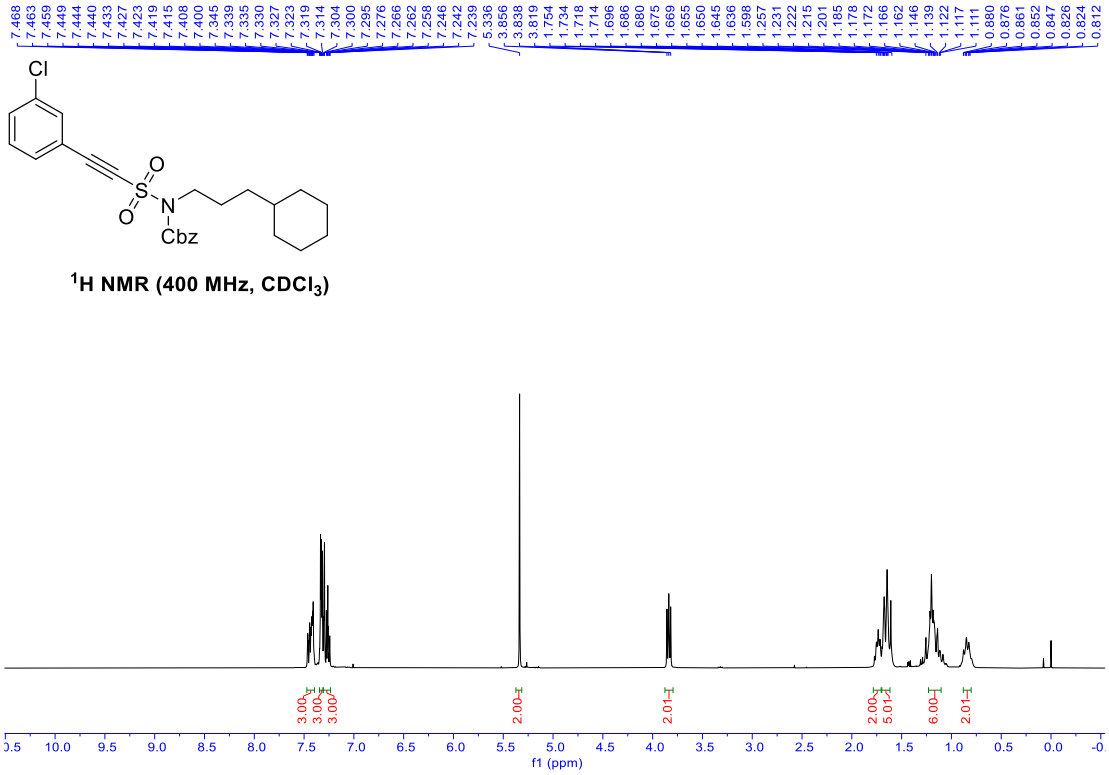
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1ac



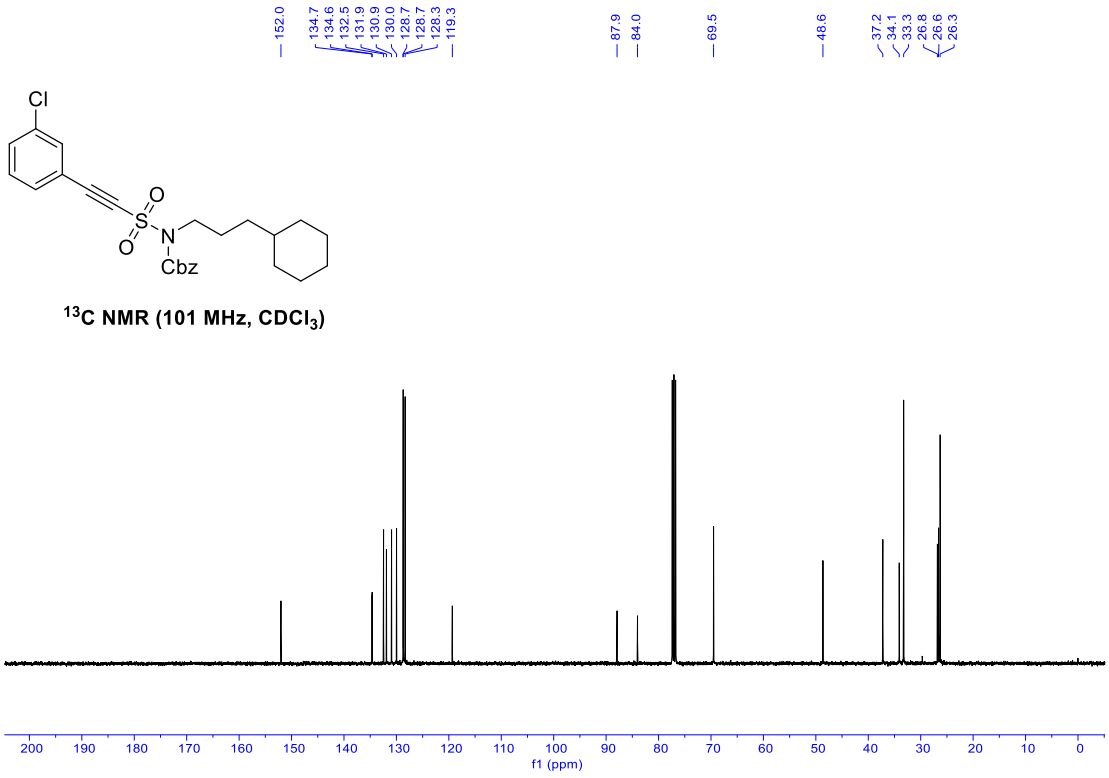
^{19}F NMR (377 MHz, $CDCl_3$) spectrum of 1ac



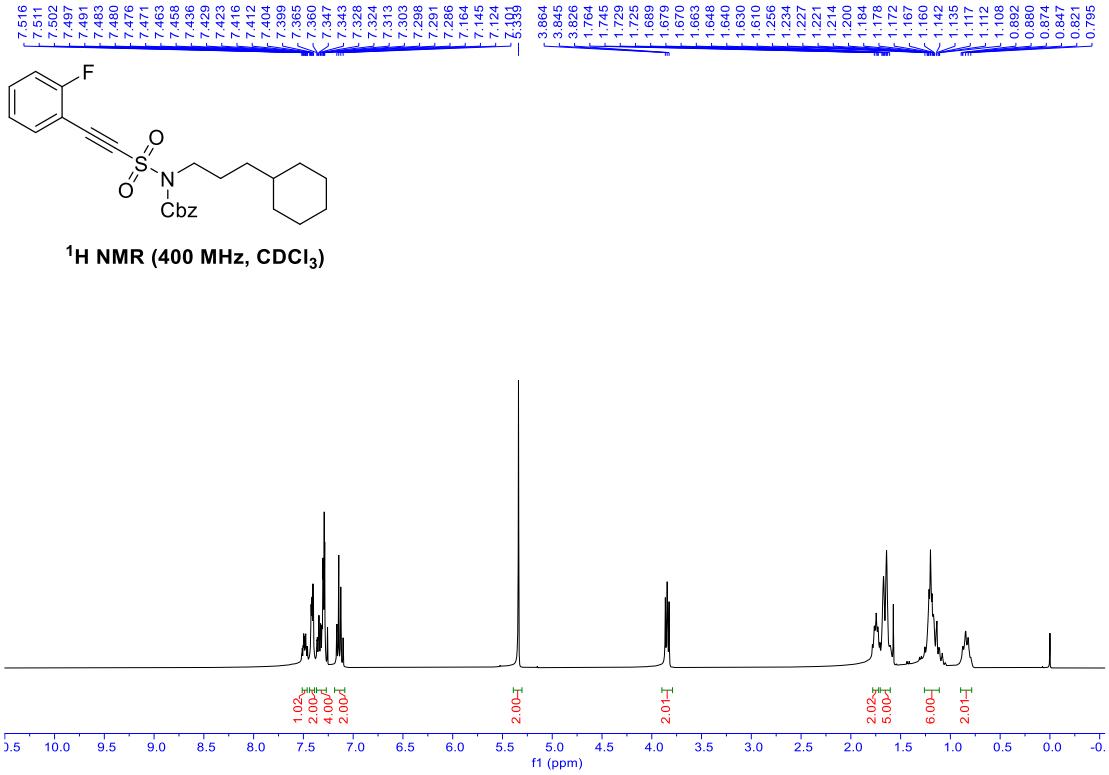
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1ad



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1ad

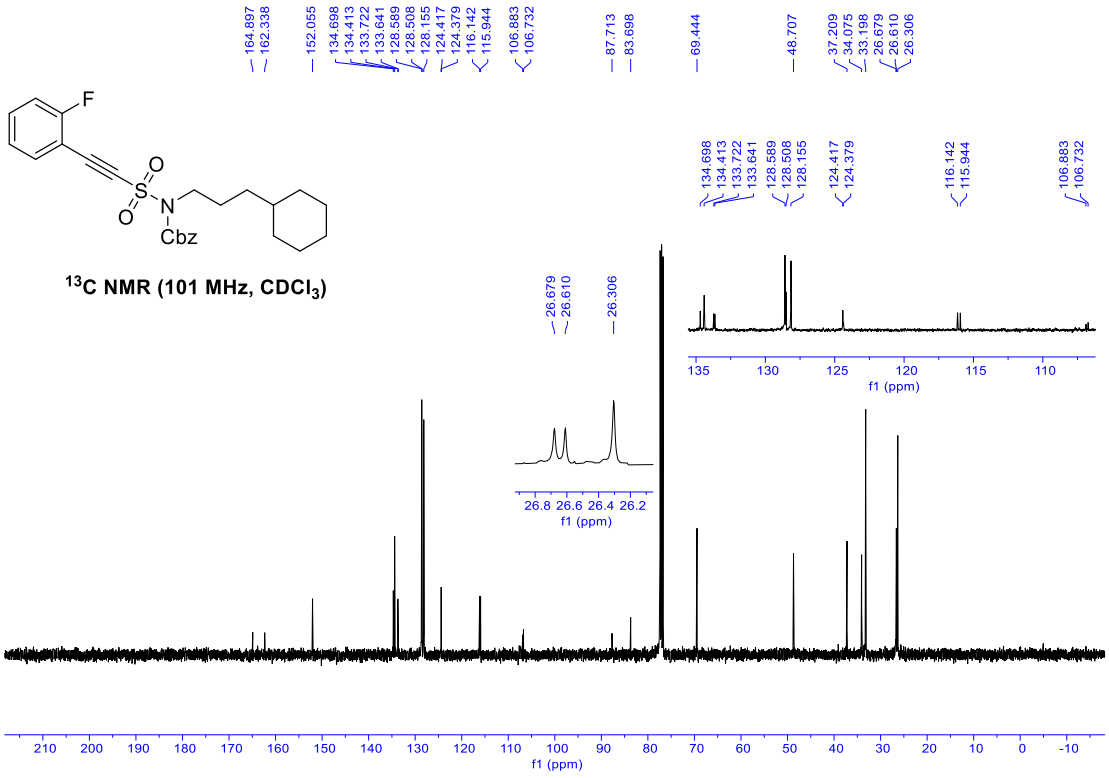


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1ae



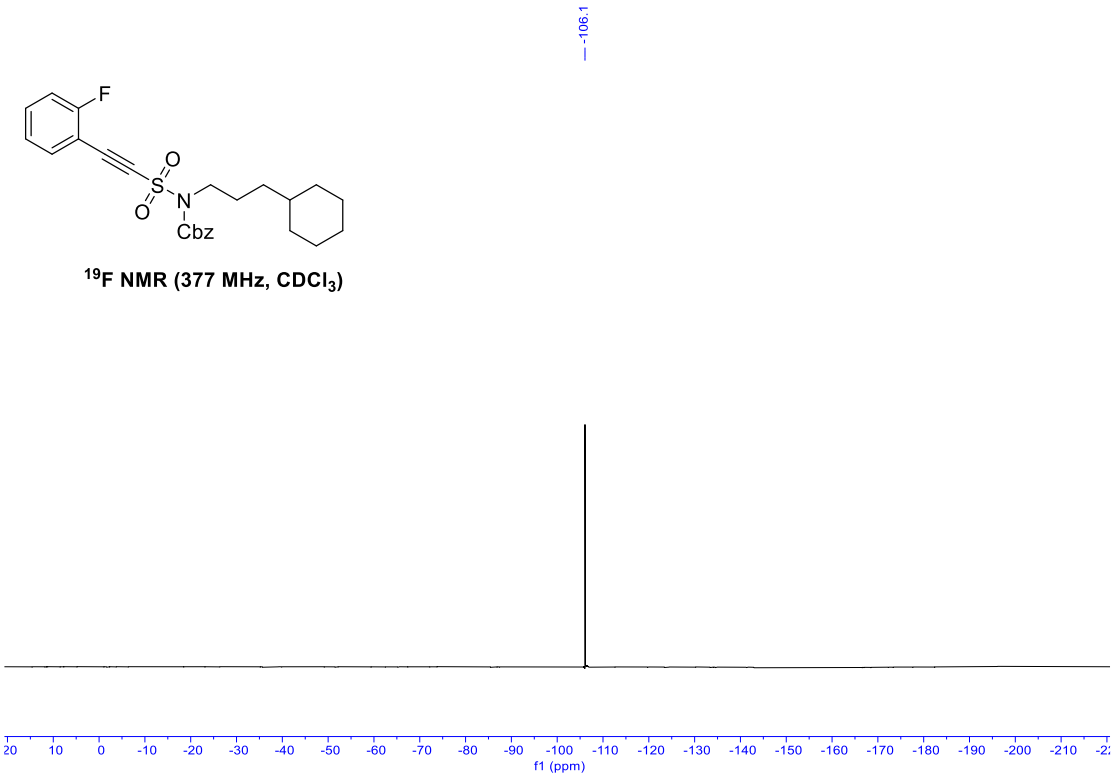
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1ae

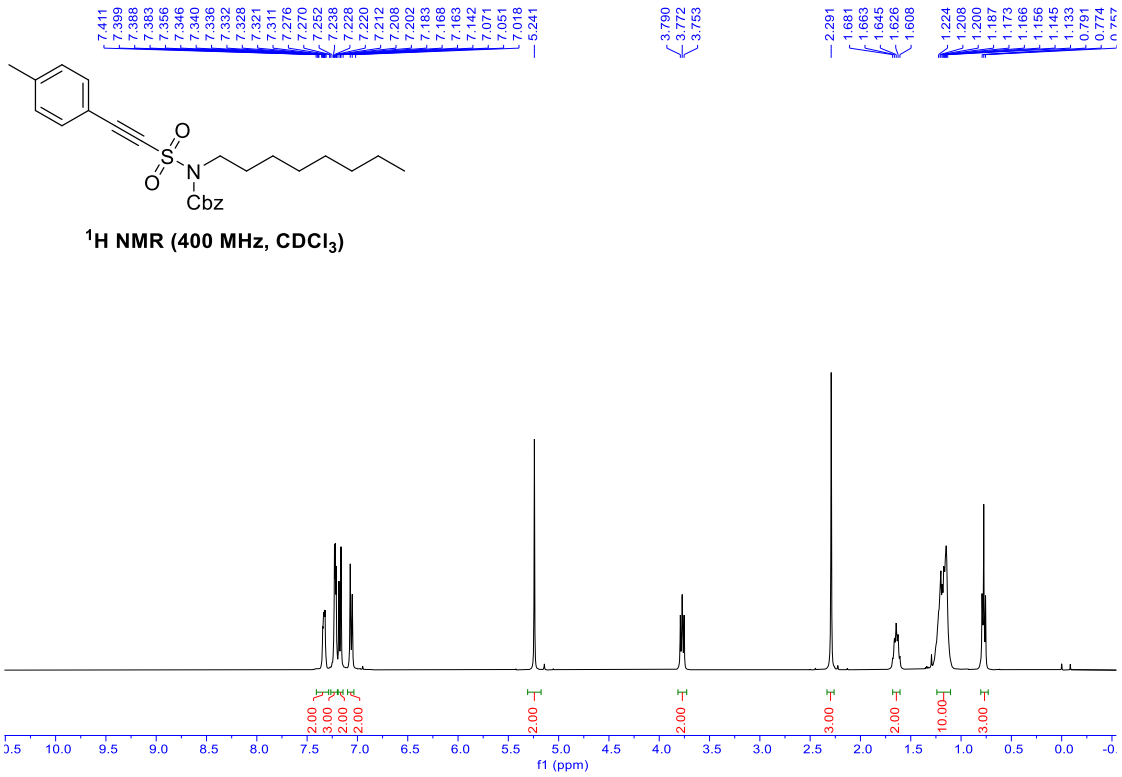


^{13}C NMR (101 MHz, $CDCl_3$)

^{19}F NMR (377 MHz, $CDCl_3$) spectrum of 1ae

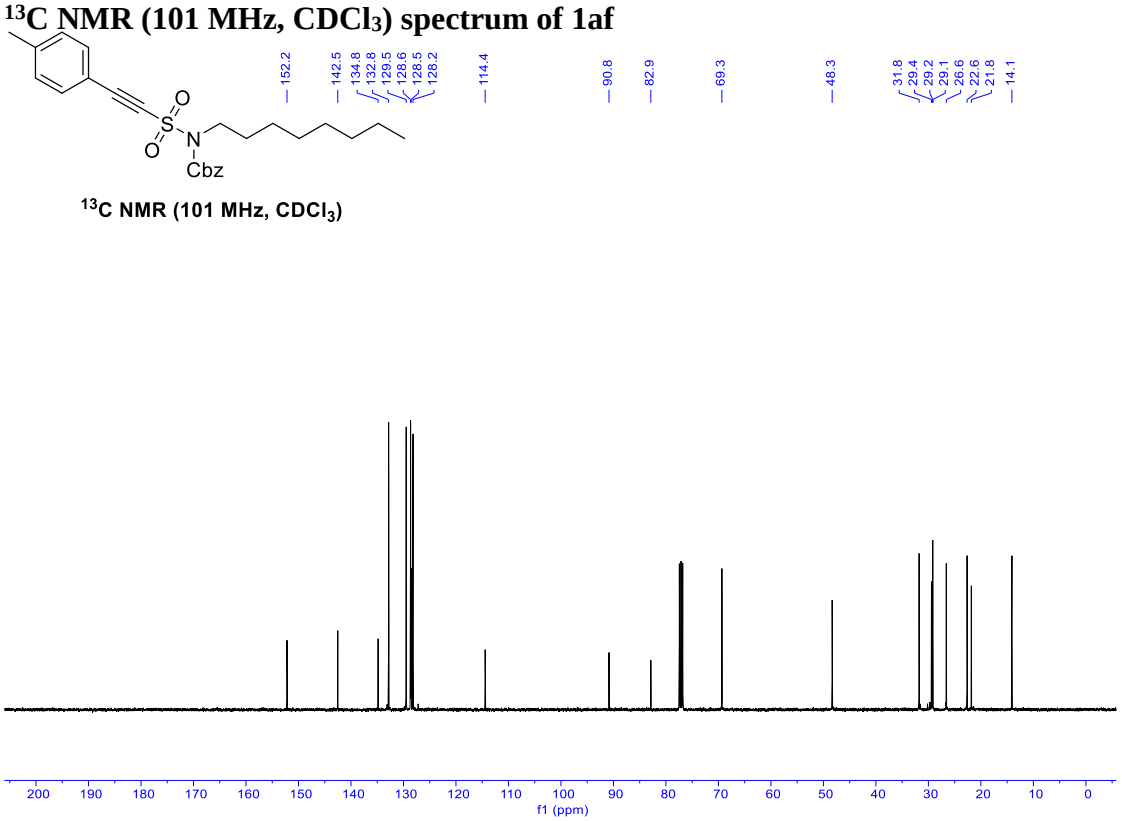


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1af



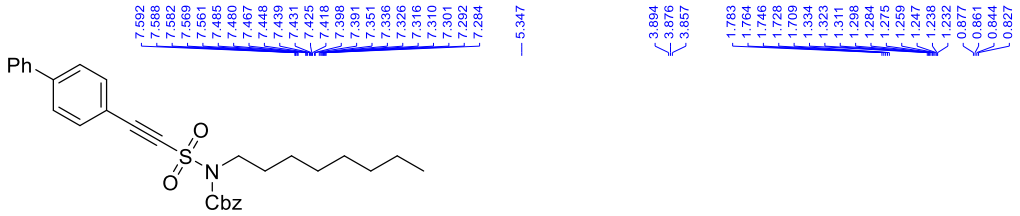
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1af

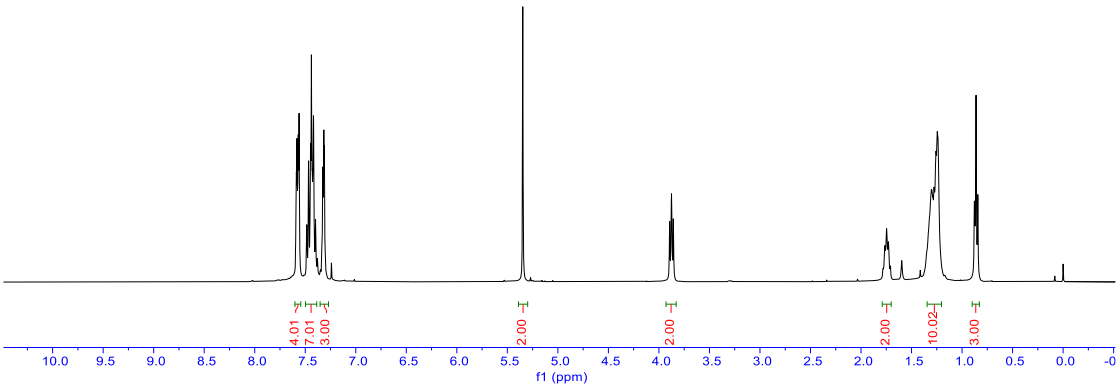


^{13}C NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1ag

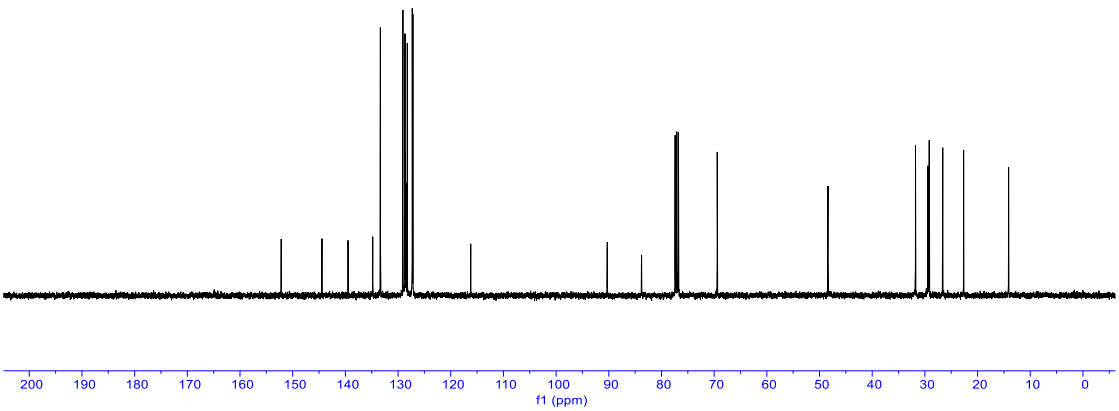


^{1}H NMR (400 MHz, $CDCl_3$)

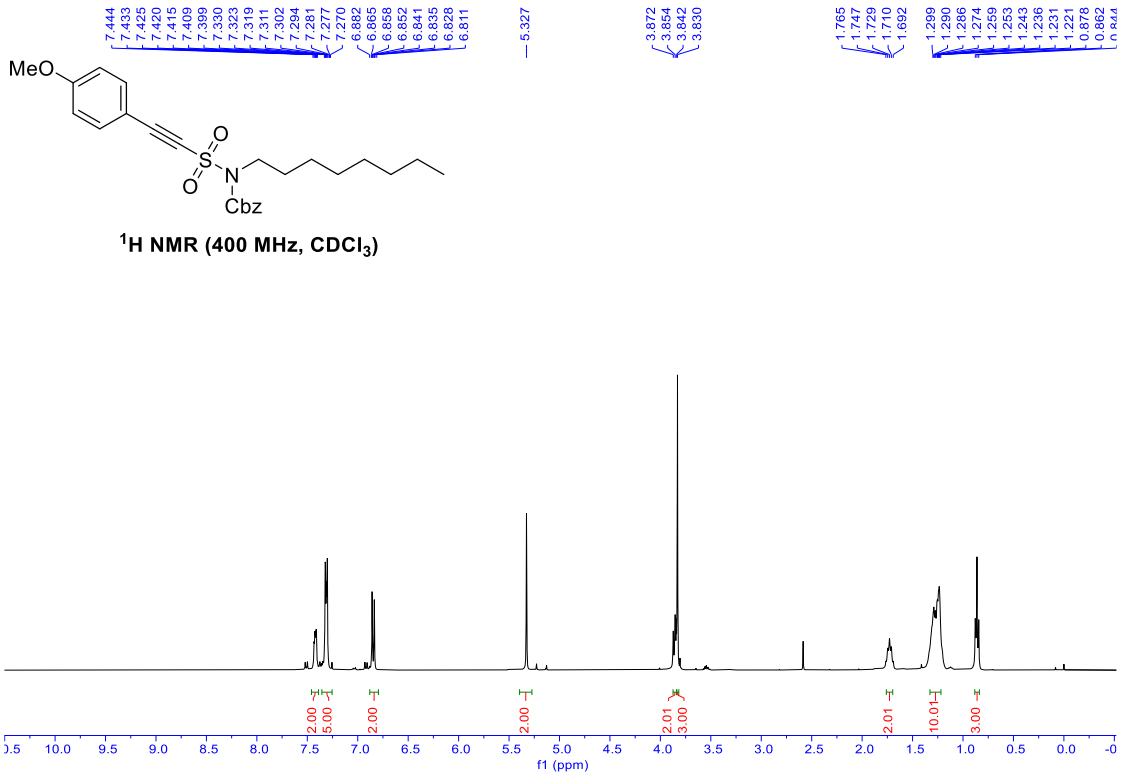


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1ag

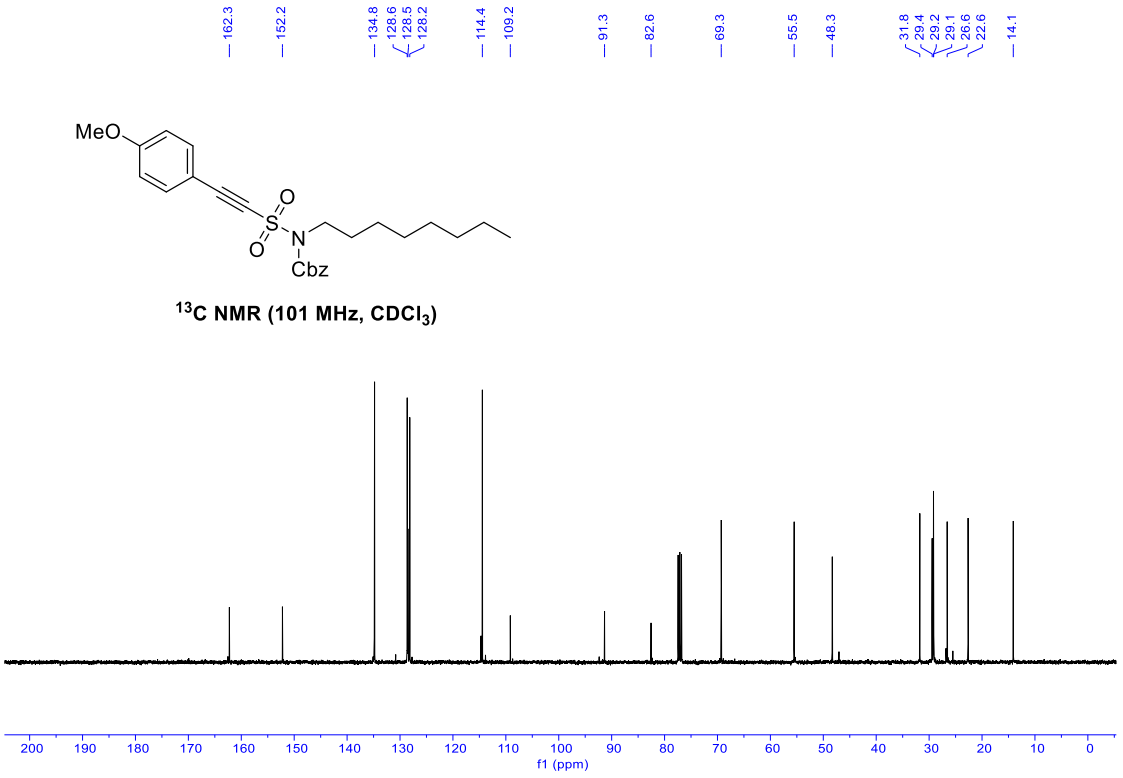
^{13}C NMR (101 MHz, $CDCl_3$)



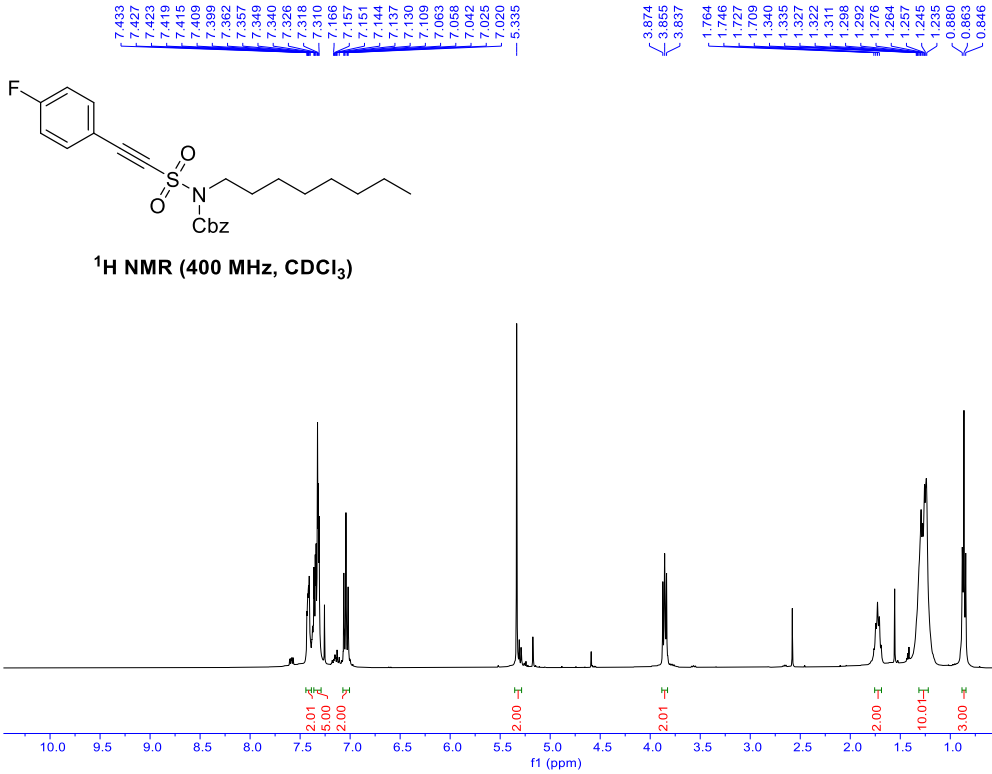
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1ah



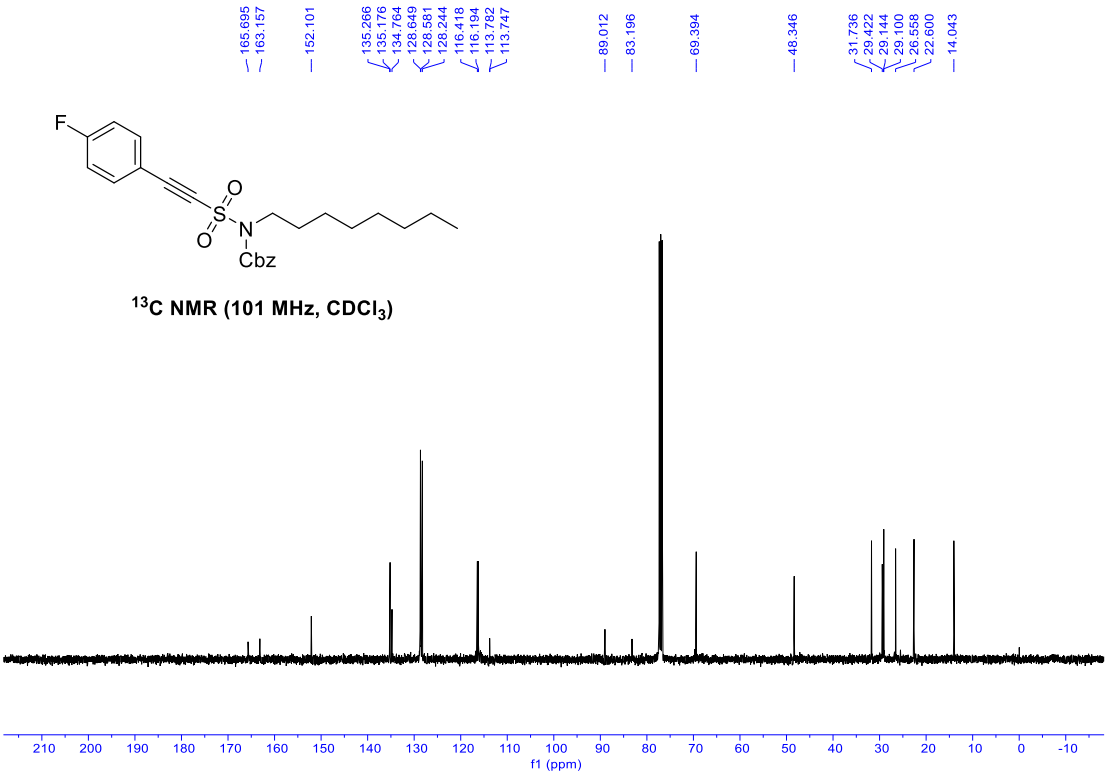
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1ah



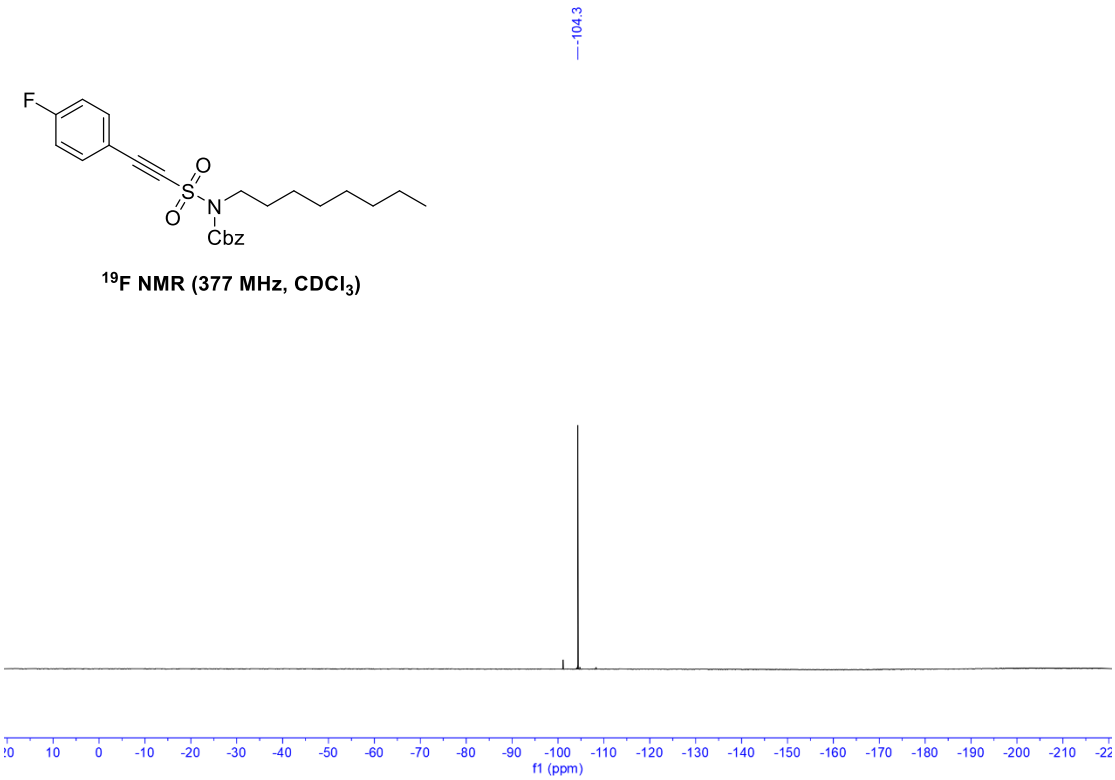
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1ai



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1ai

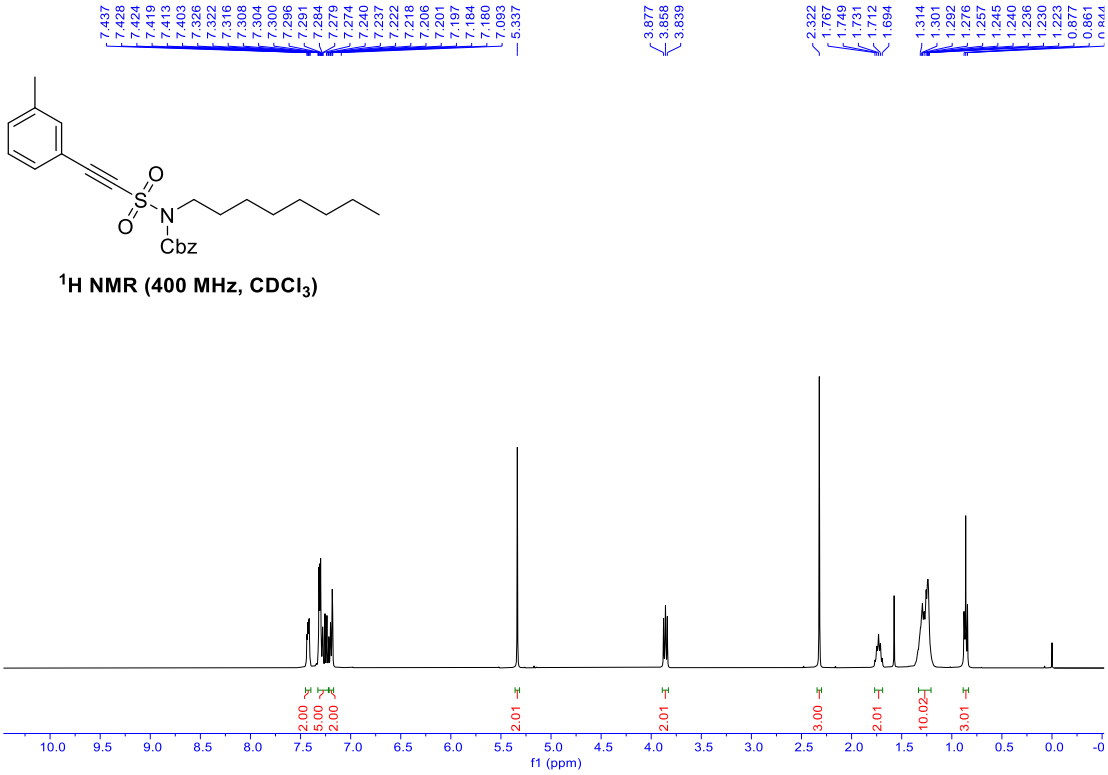


^{19}F NMR (377 MHz, $CDCl_3$) spectrum of 1ai

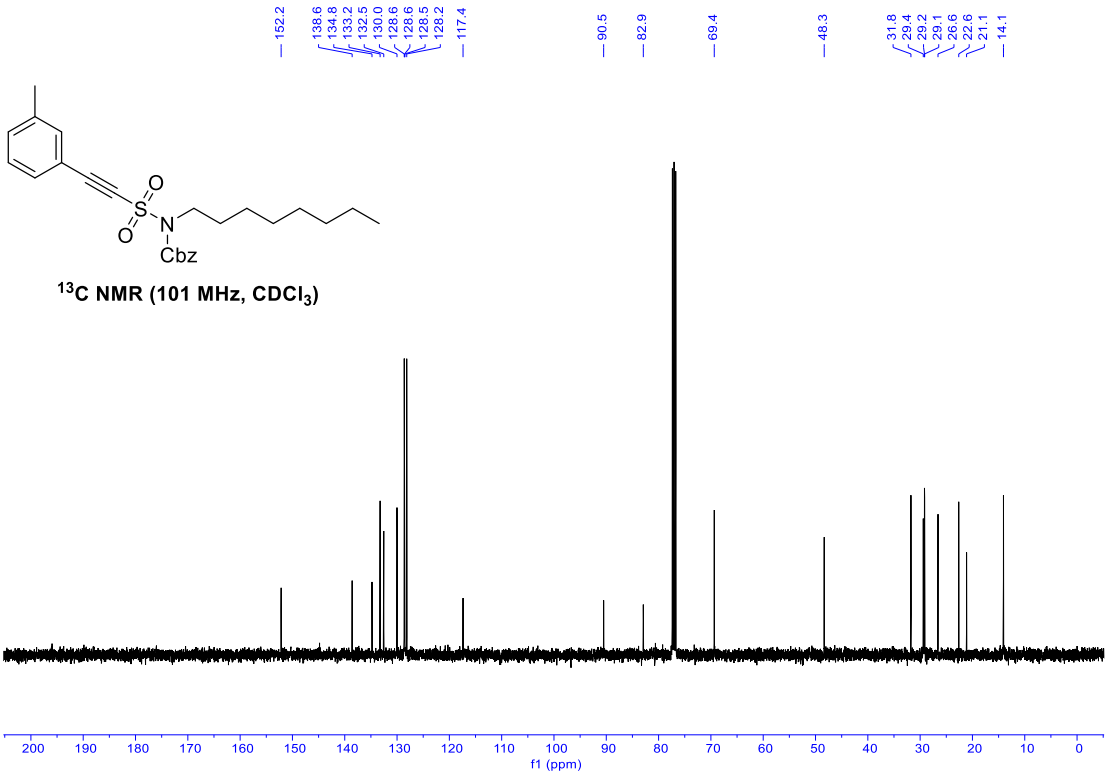


^{19}F NMR (377 MHz, $CDCl_3$)

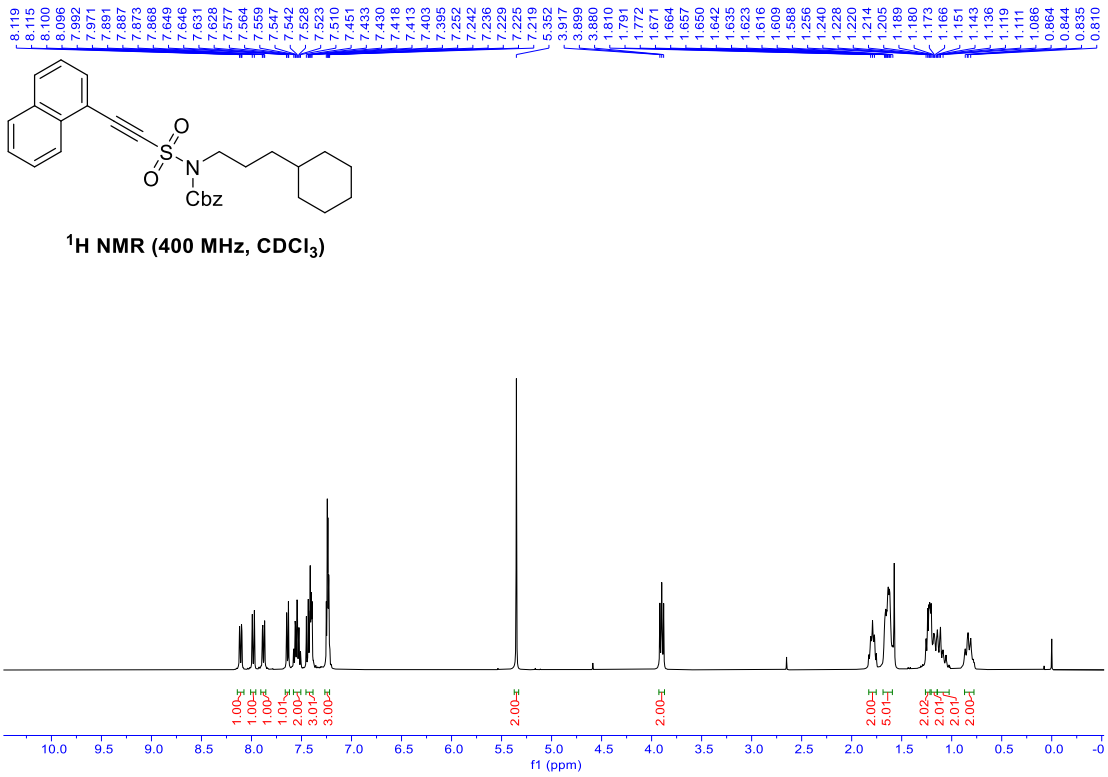
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1aj



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1aj

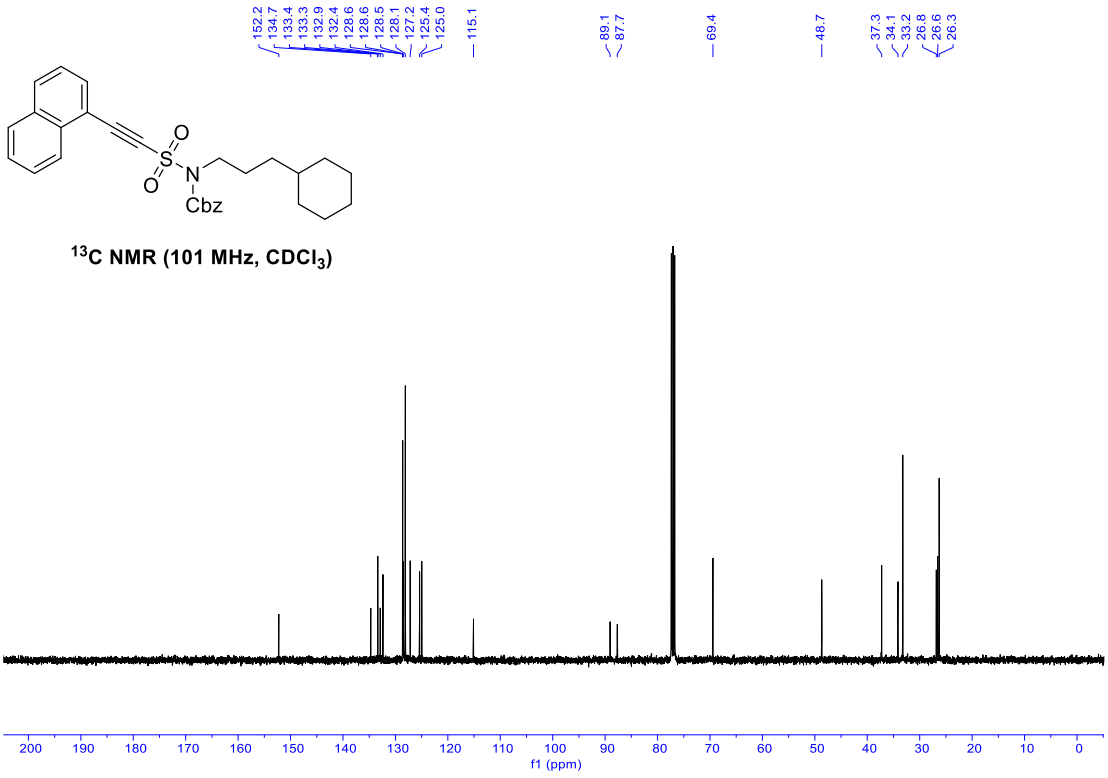


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1ak



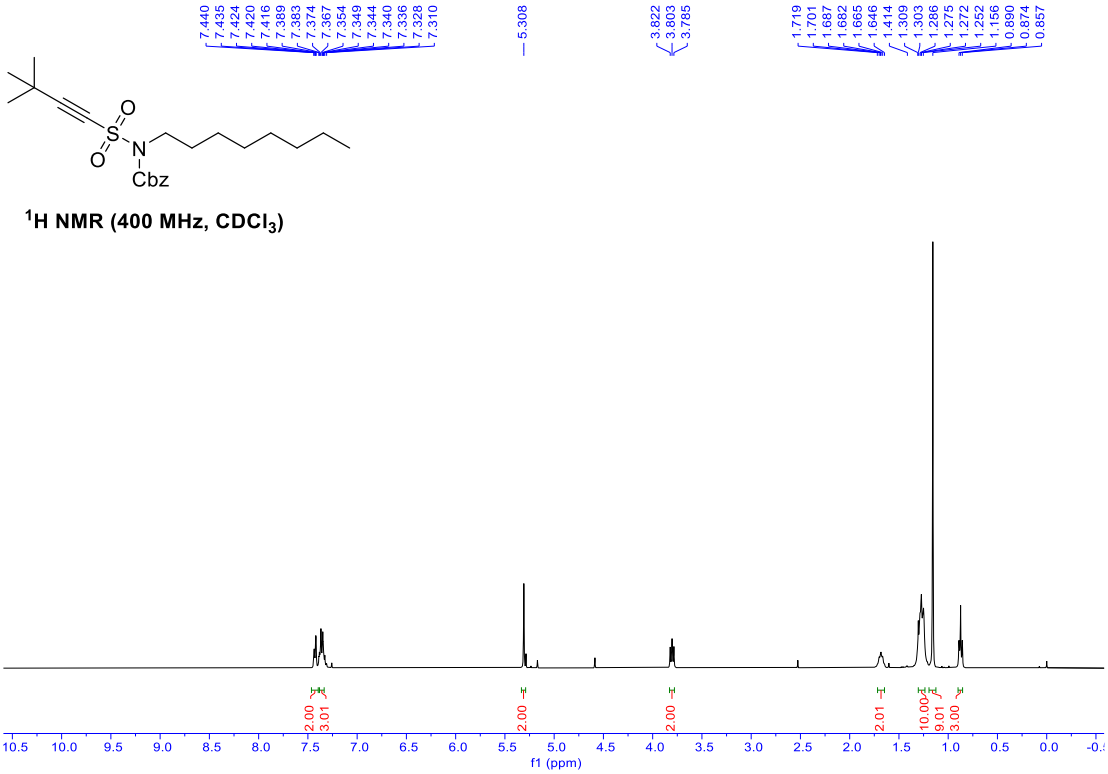
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1ak



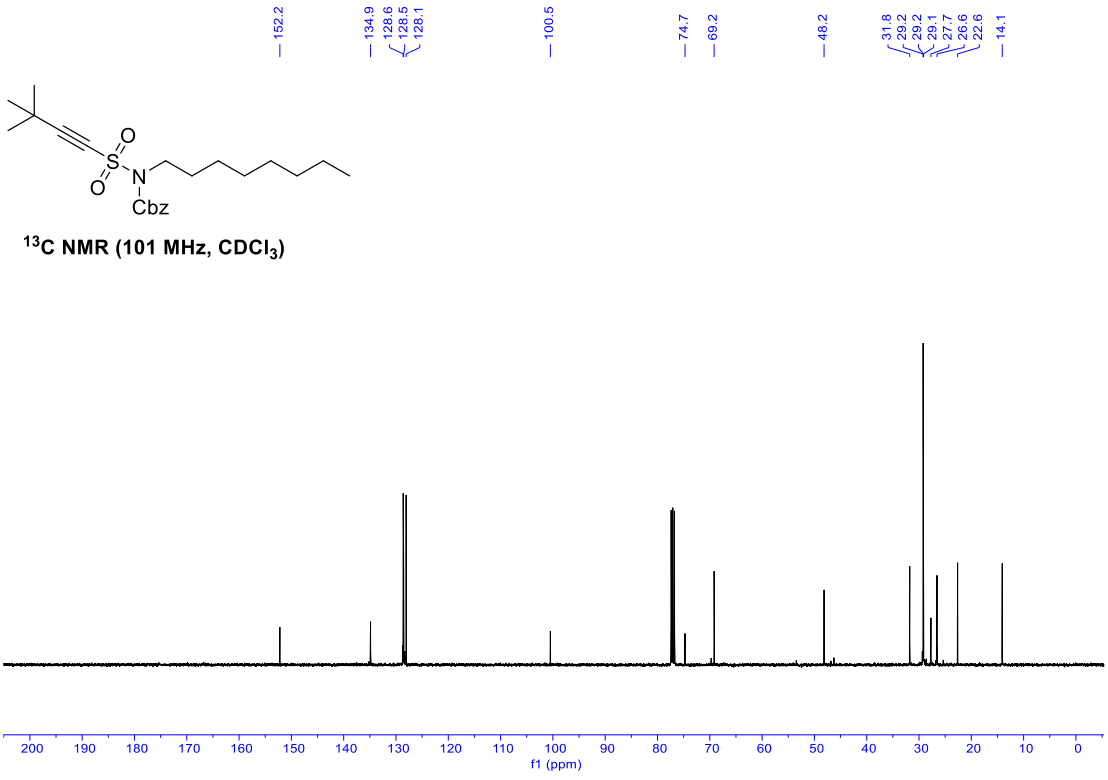
^{13}C NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1al



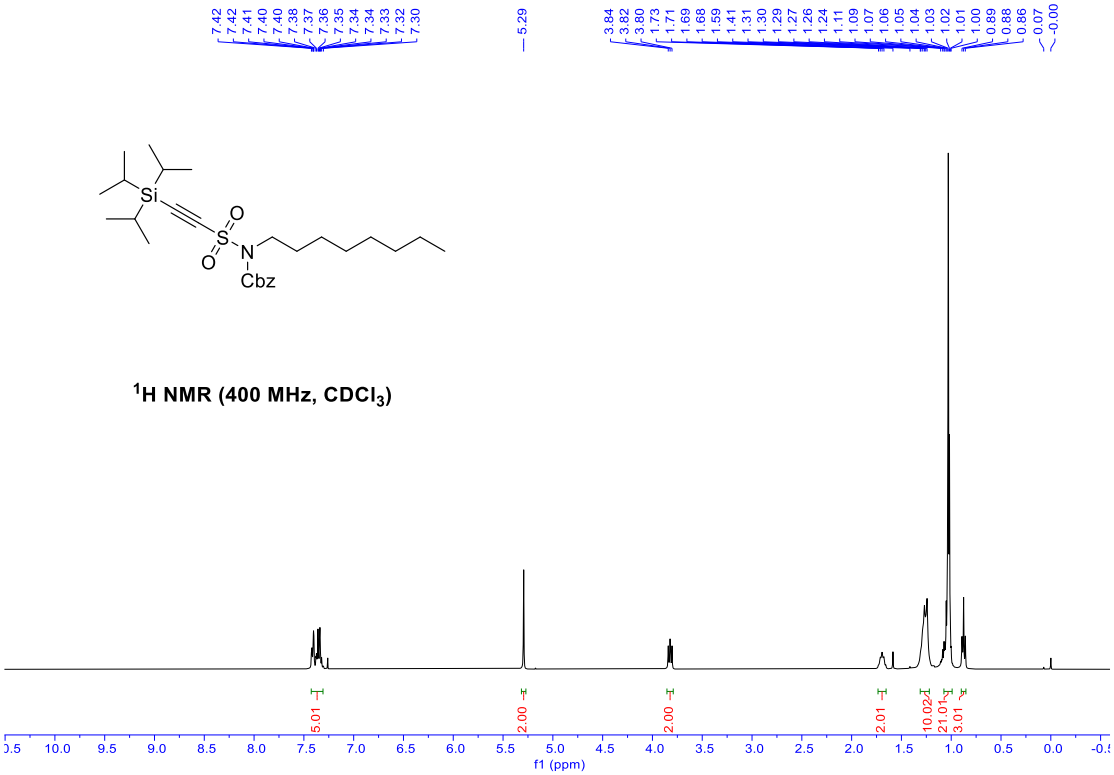
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1al

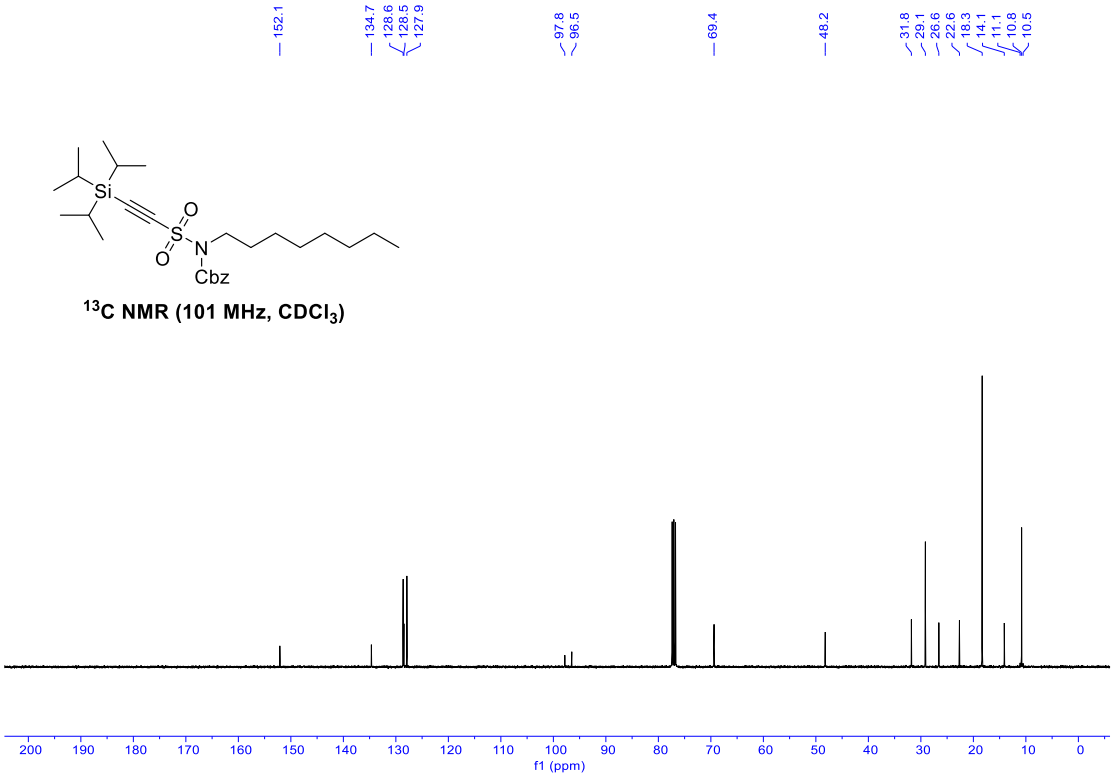


^{13}C NMR (101 MHz, $CDCl_3$)

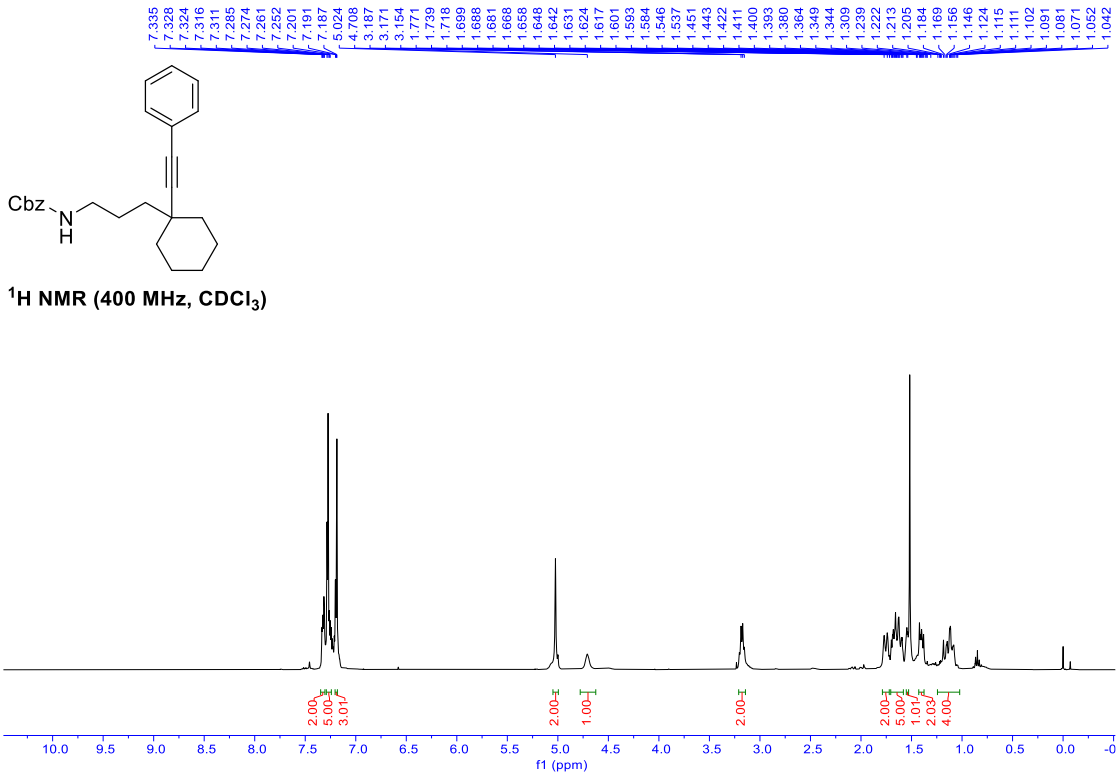
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1am



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1am

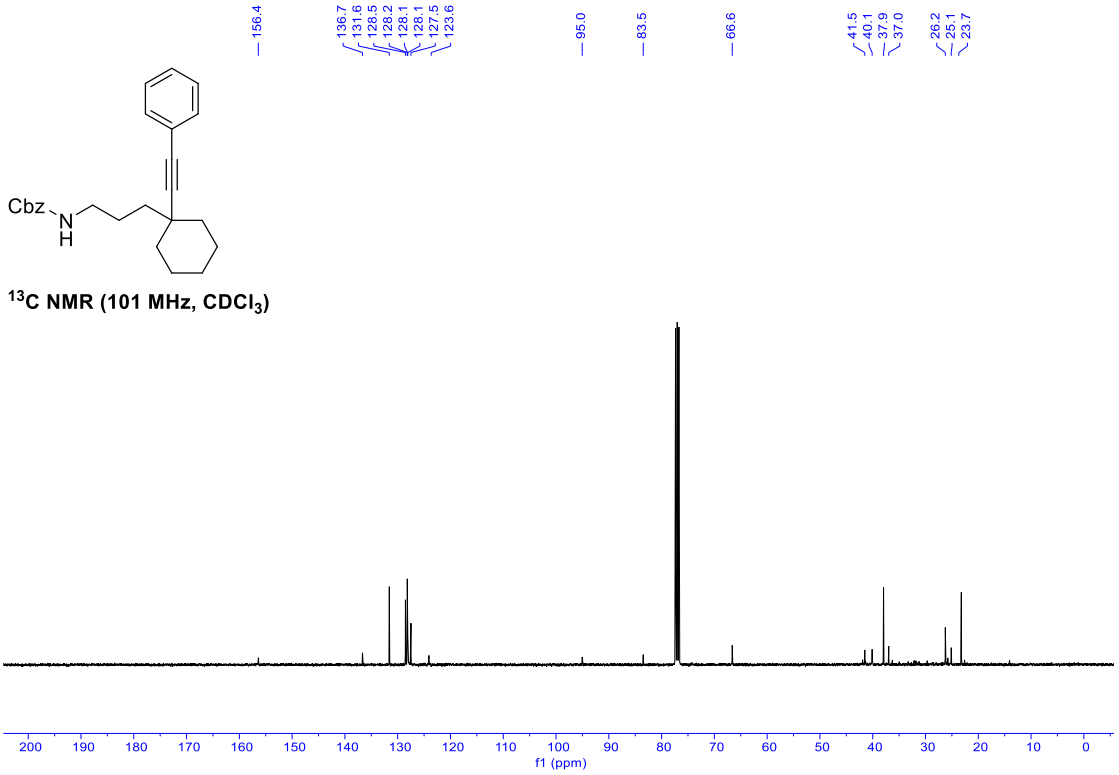


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2a



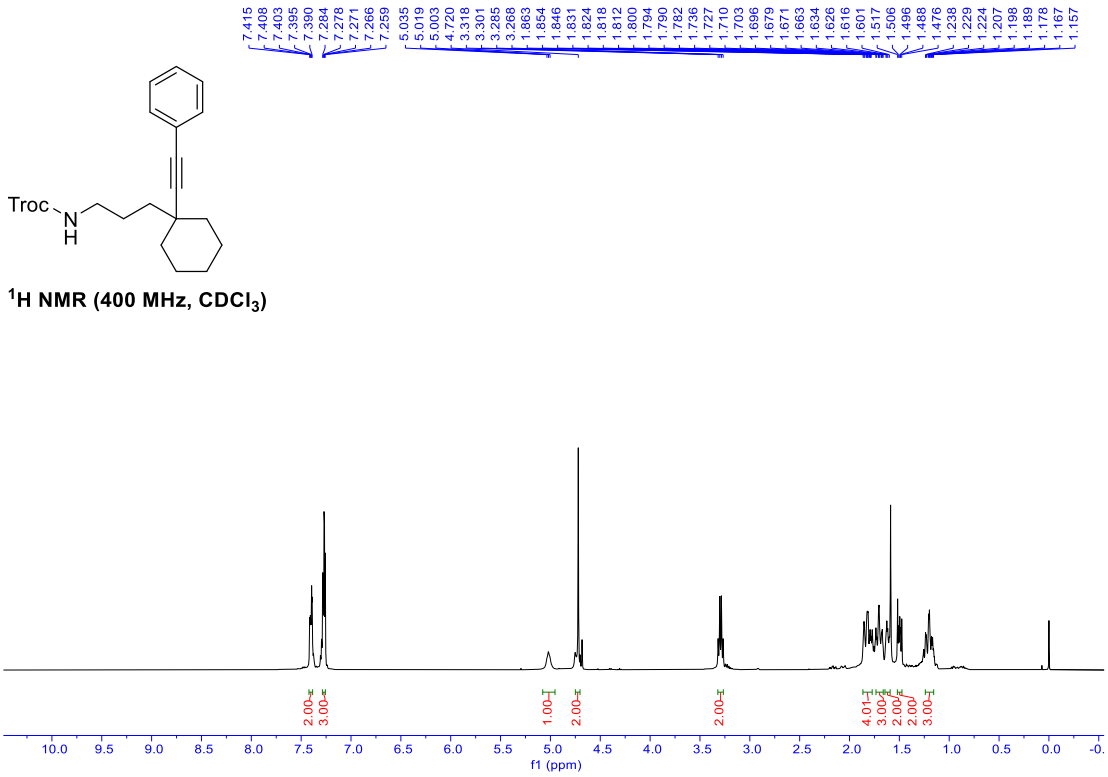
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2a



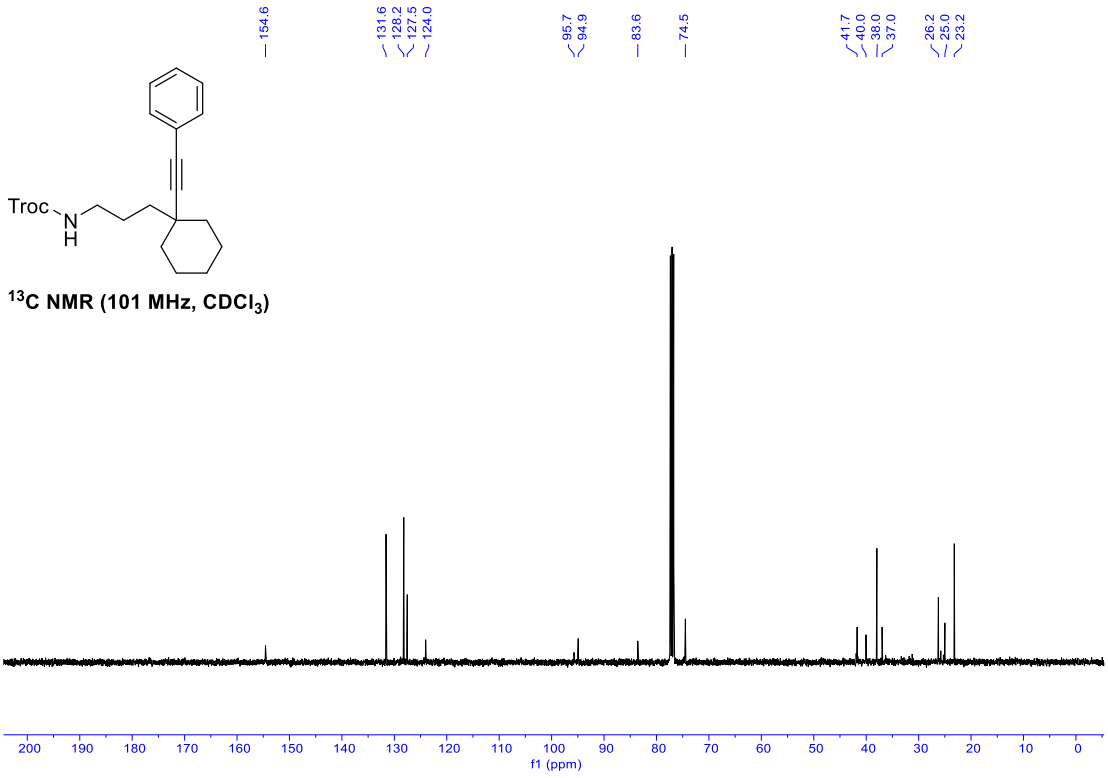
^{13}C NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2b



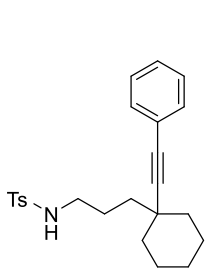
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2b



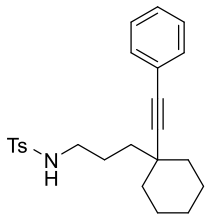
^{13}C NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2c



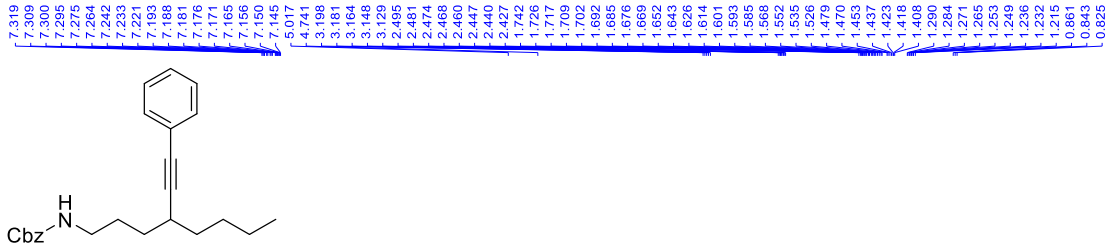
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2c

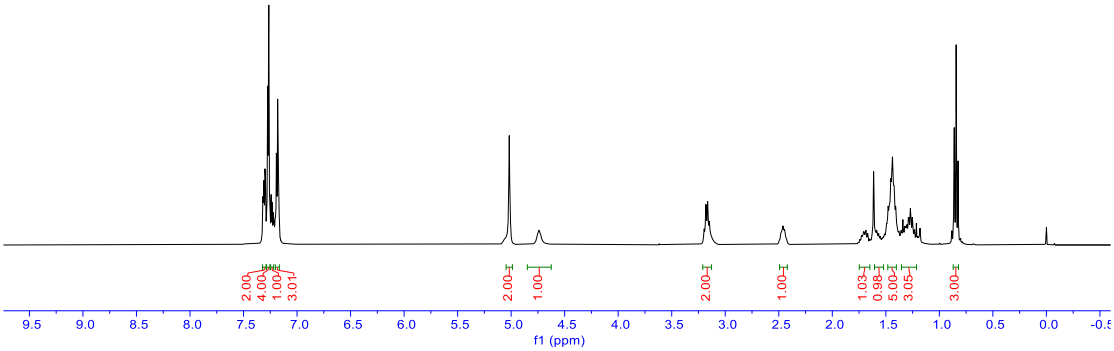


^{13}C NMR (101 MHz, $CDCl_3$)

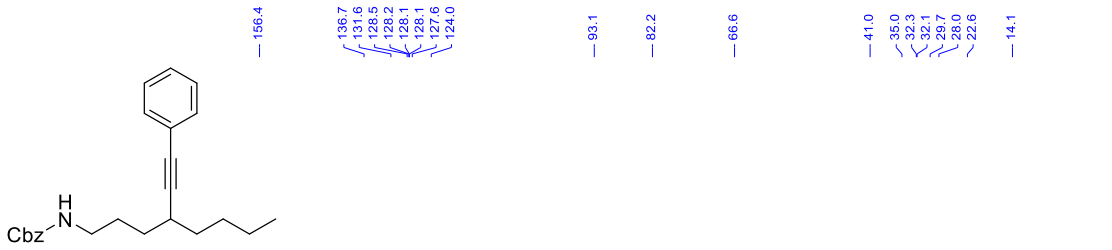
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2d



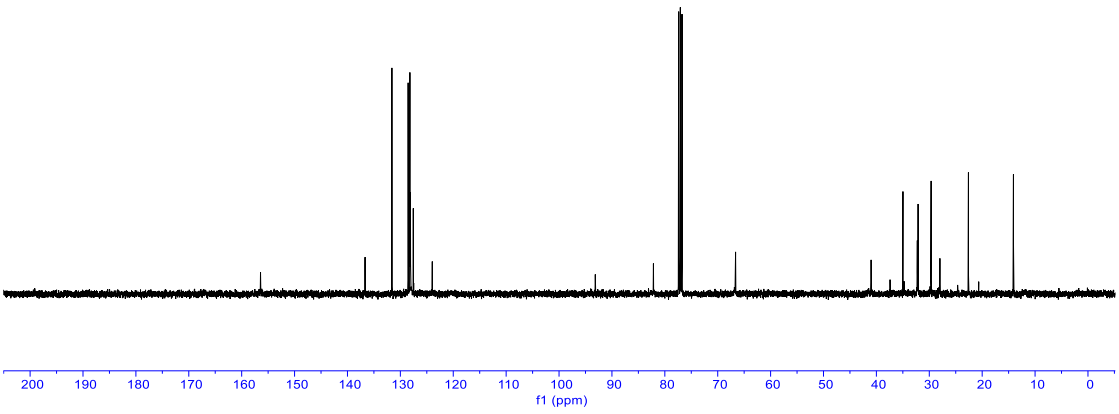
^{1}H NMR (400 MHz, $CDCl_3$)



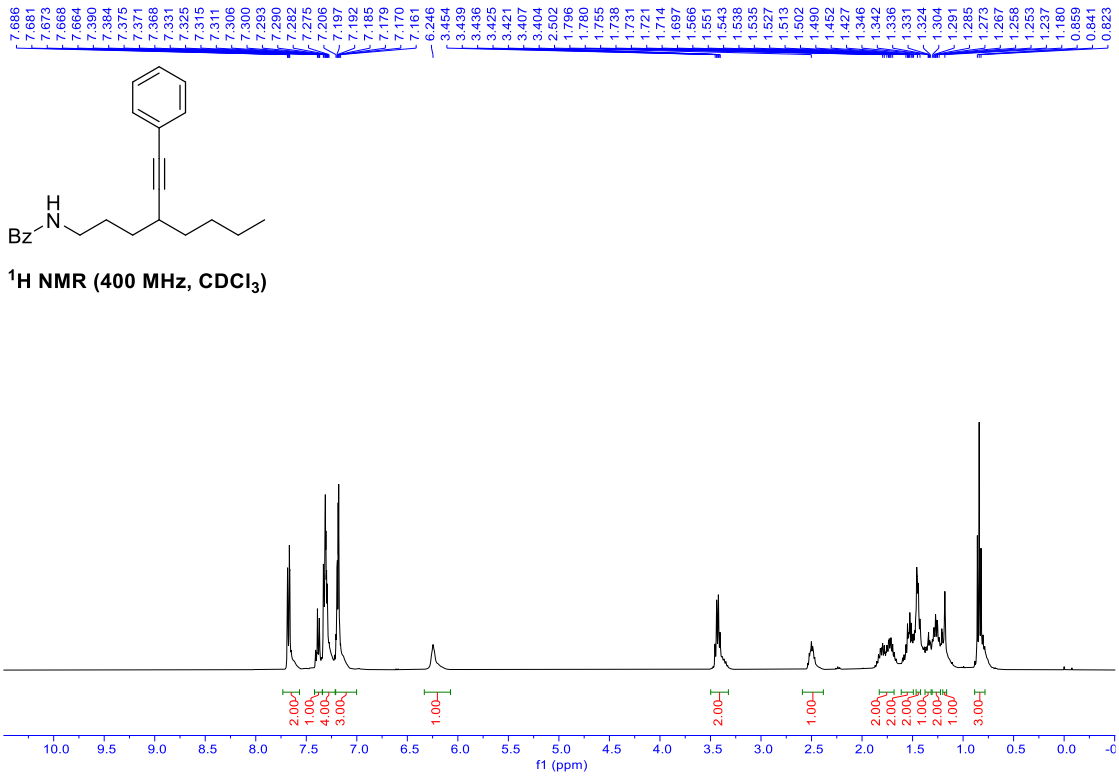
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2d



^{13}C NMR (101 MHz, $CDCl_3$)

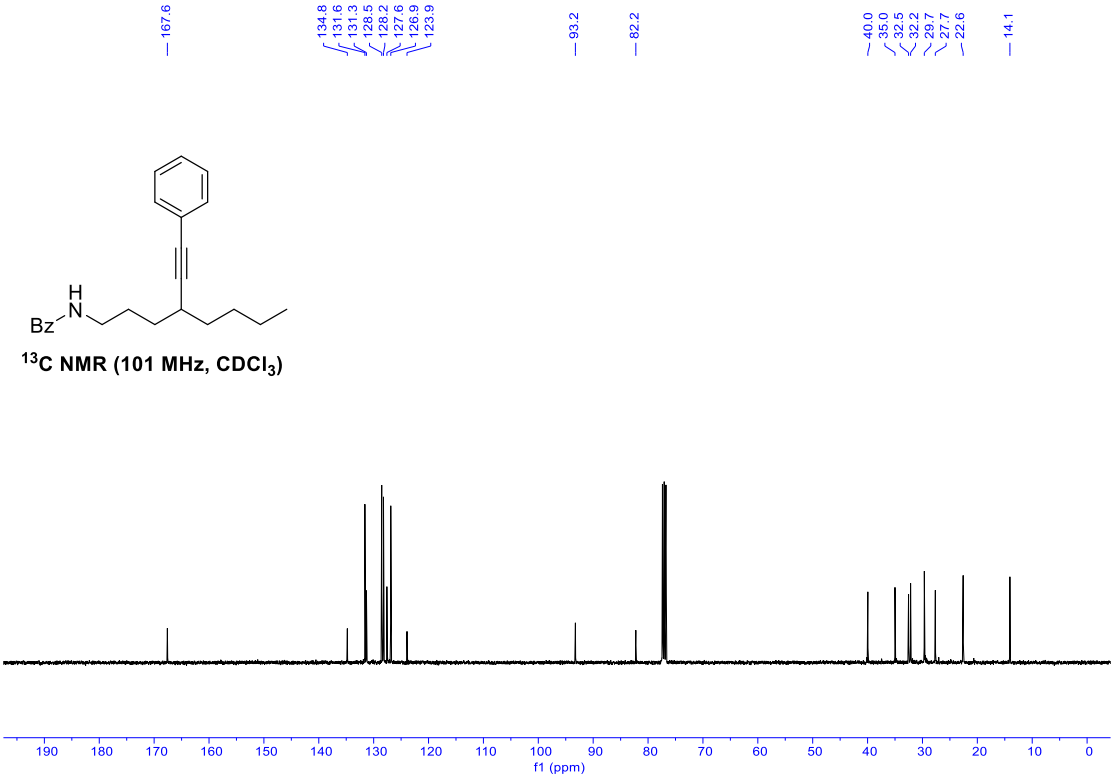


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2e



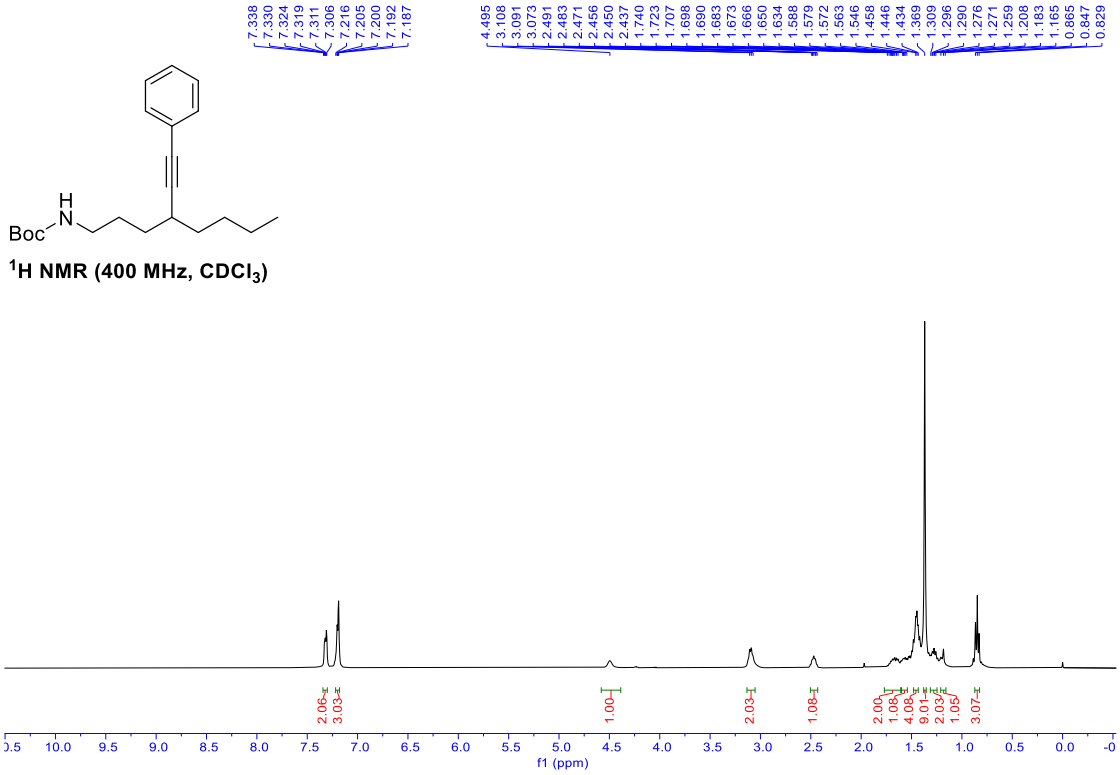
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2e

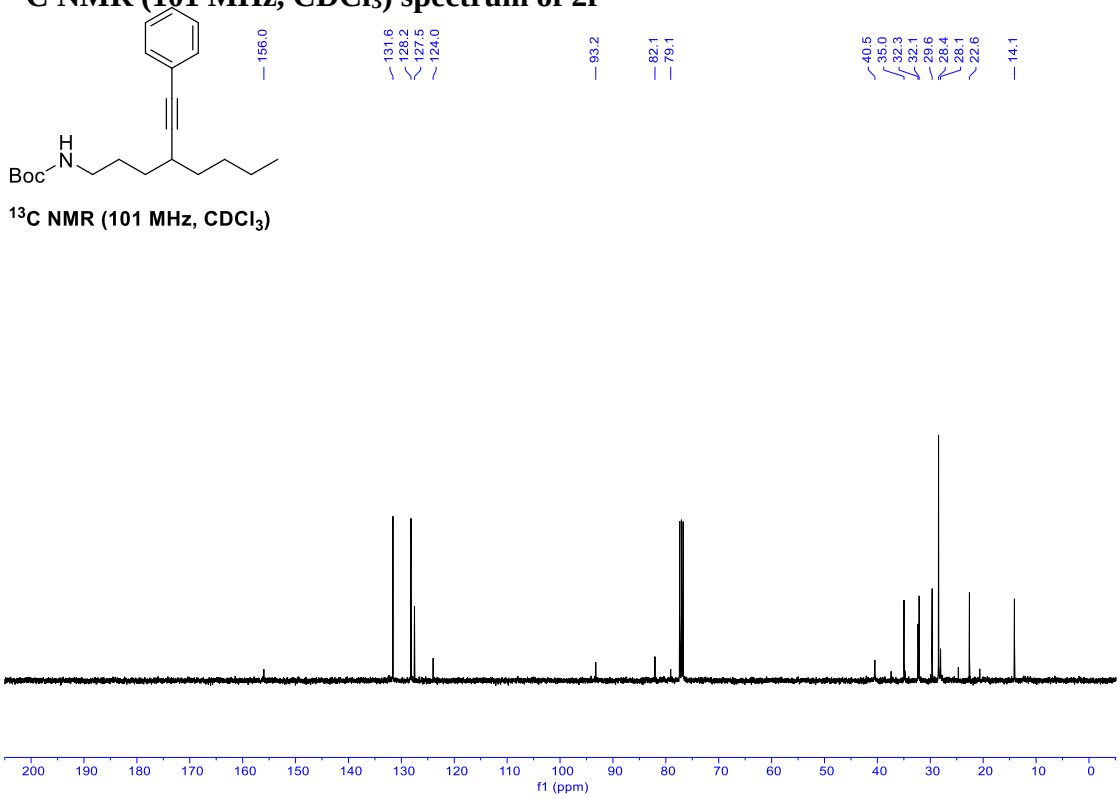


^{13}C NMR (101 MHz, $CDCl_3$)

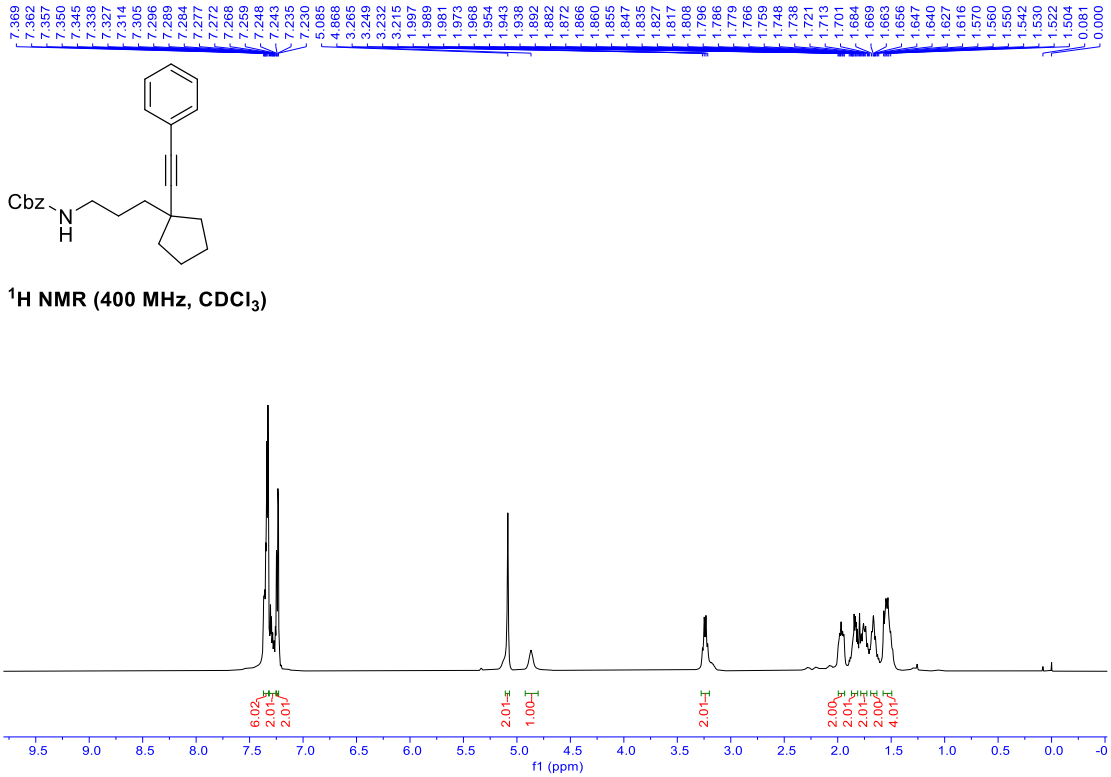
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2f



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2f

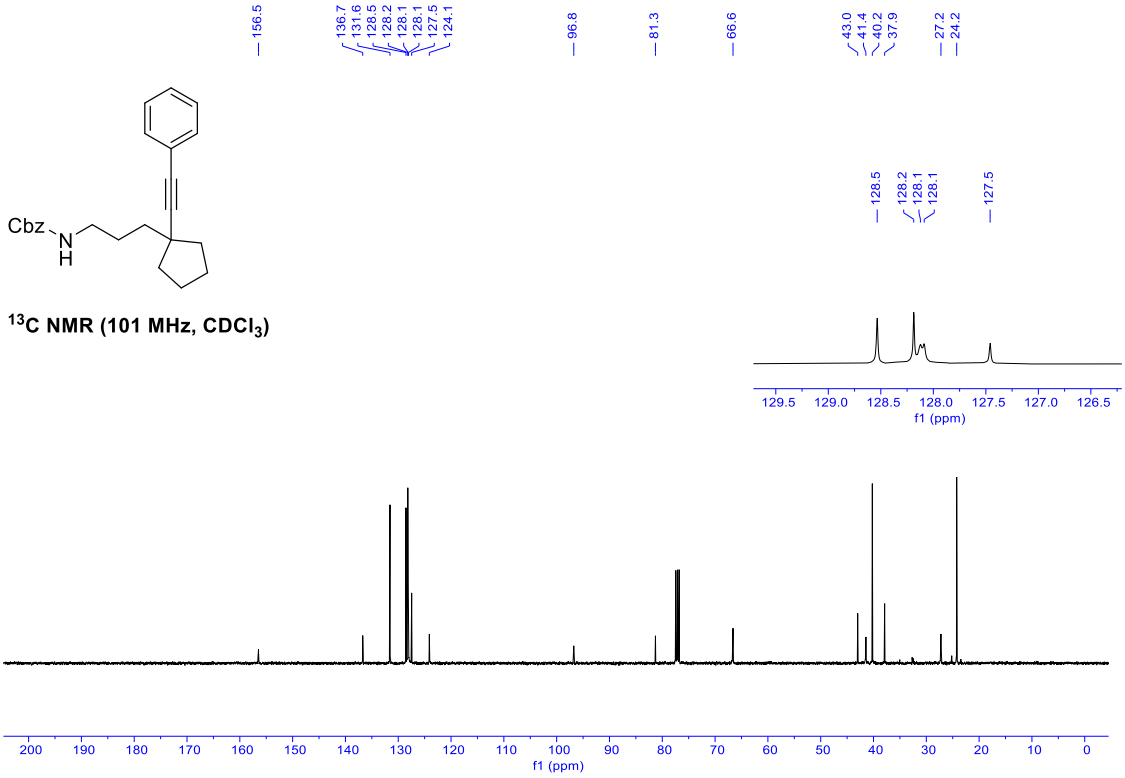


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2g



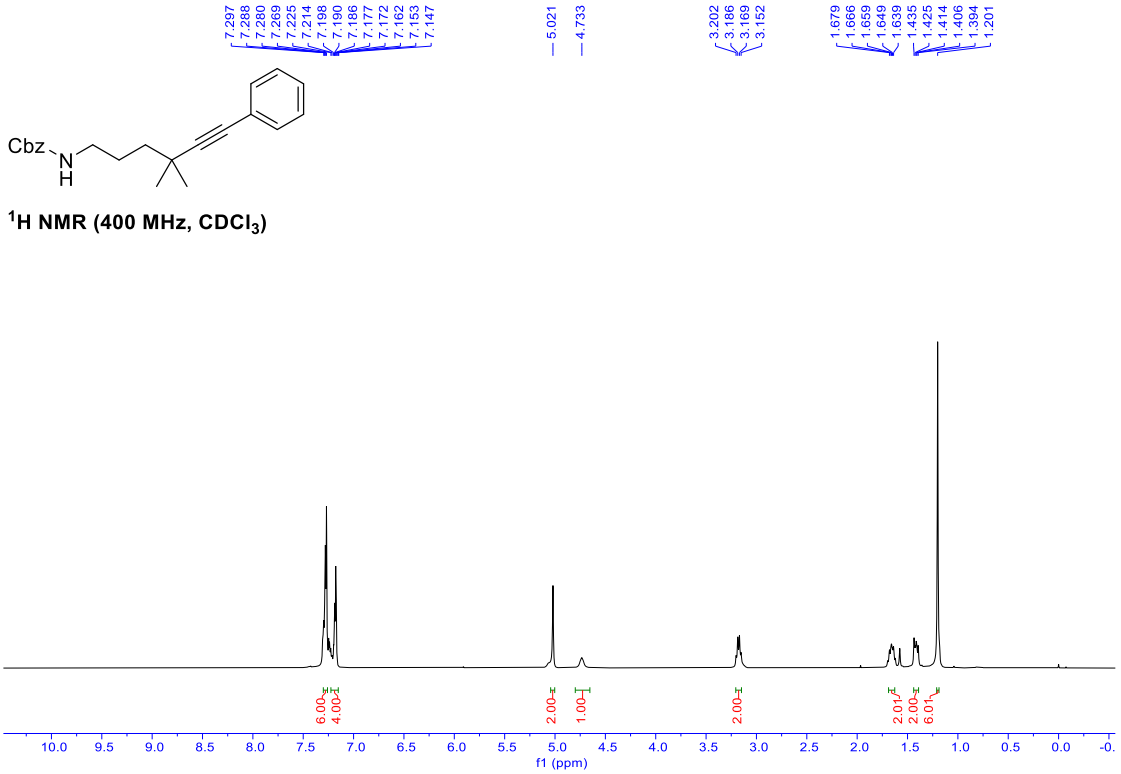
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2g



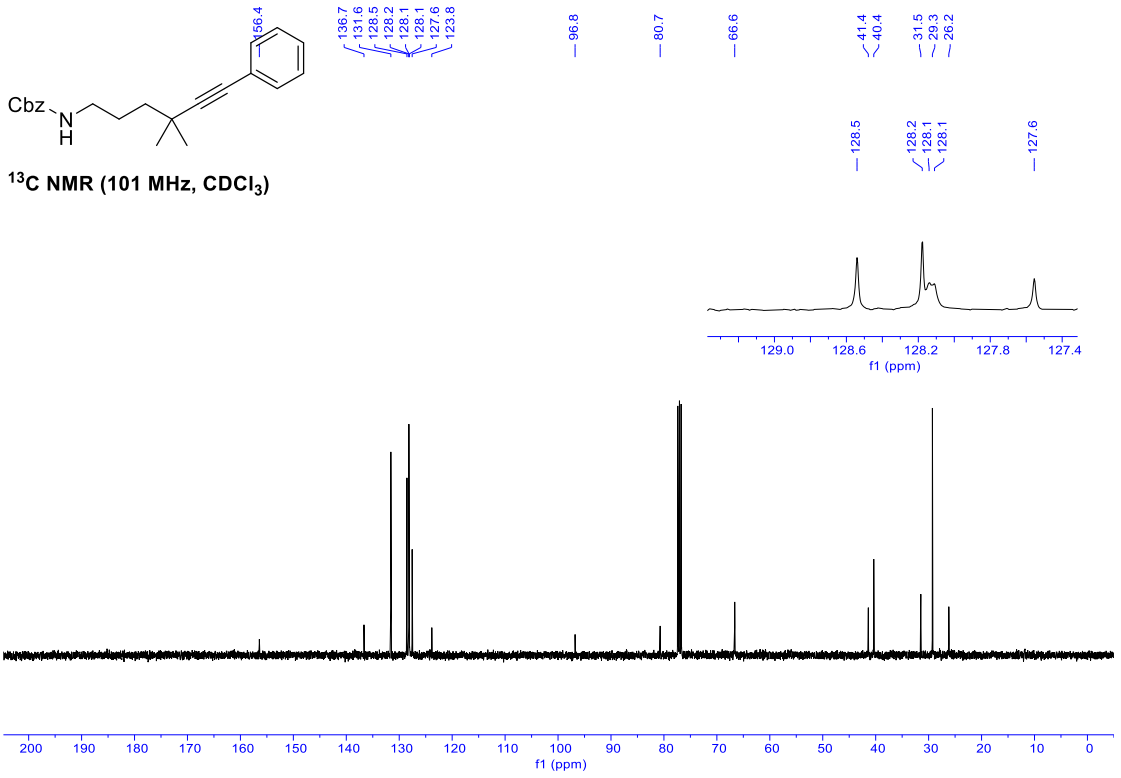
^{13}C NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2h



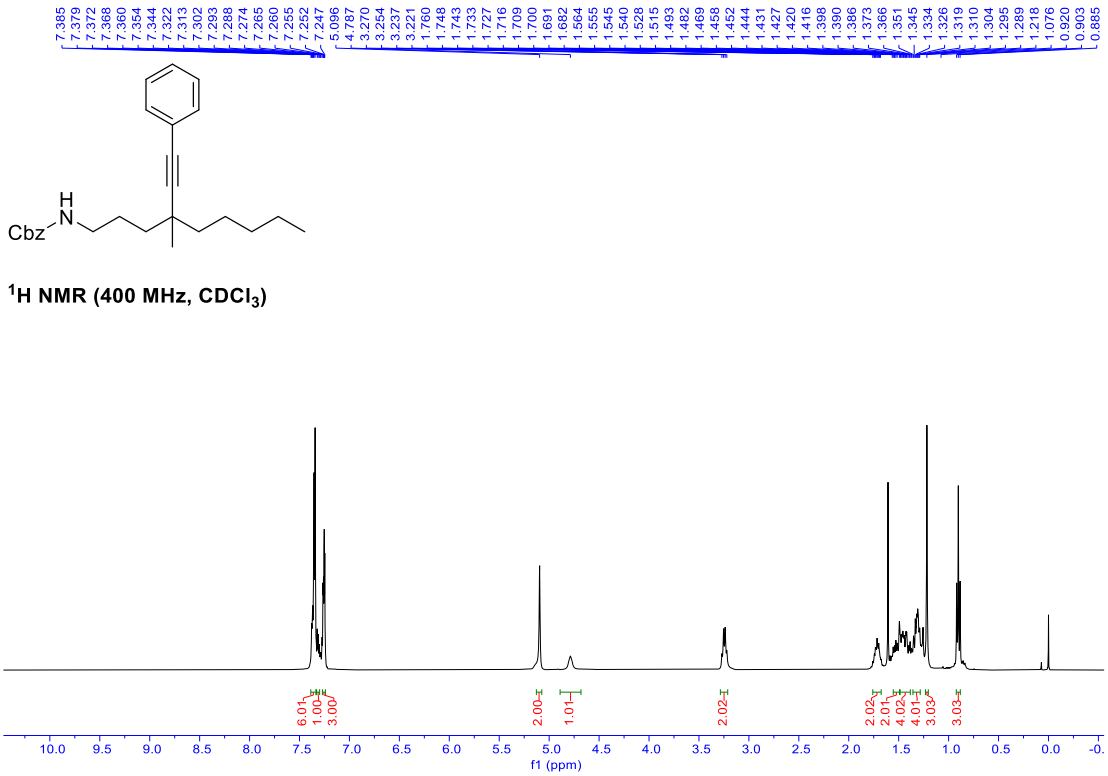
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2h



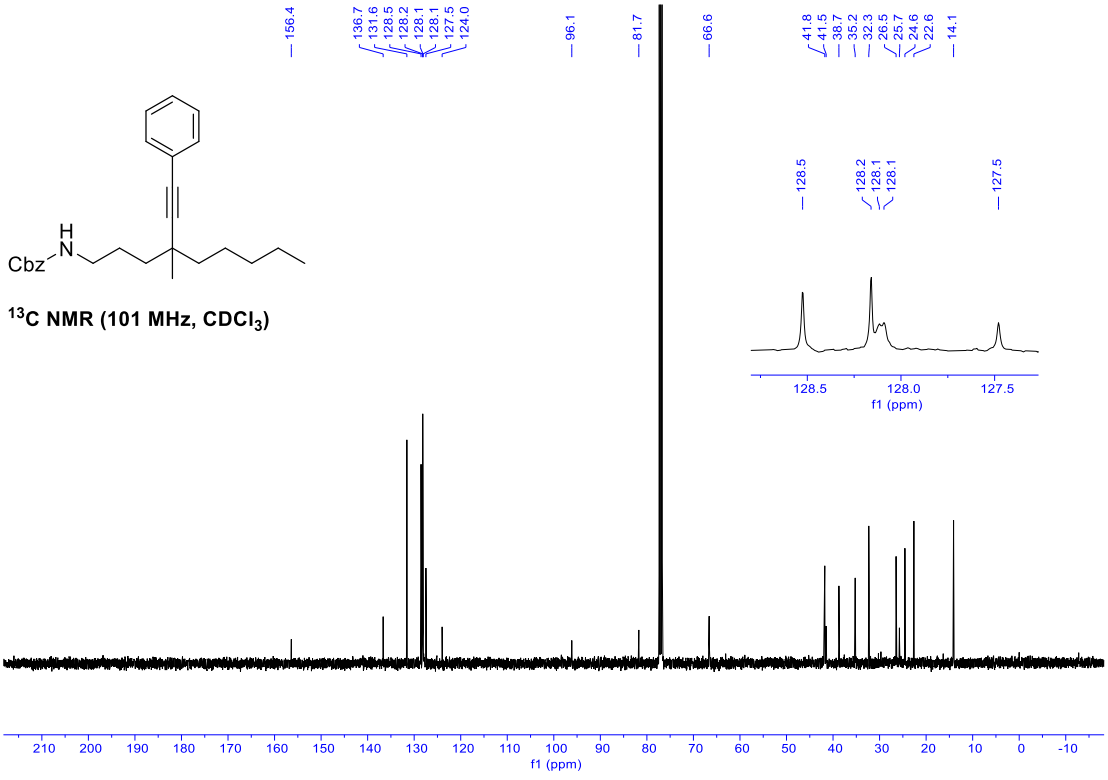
^{13}C NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2i



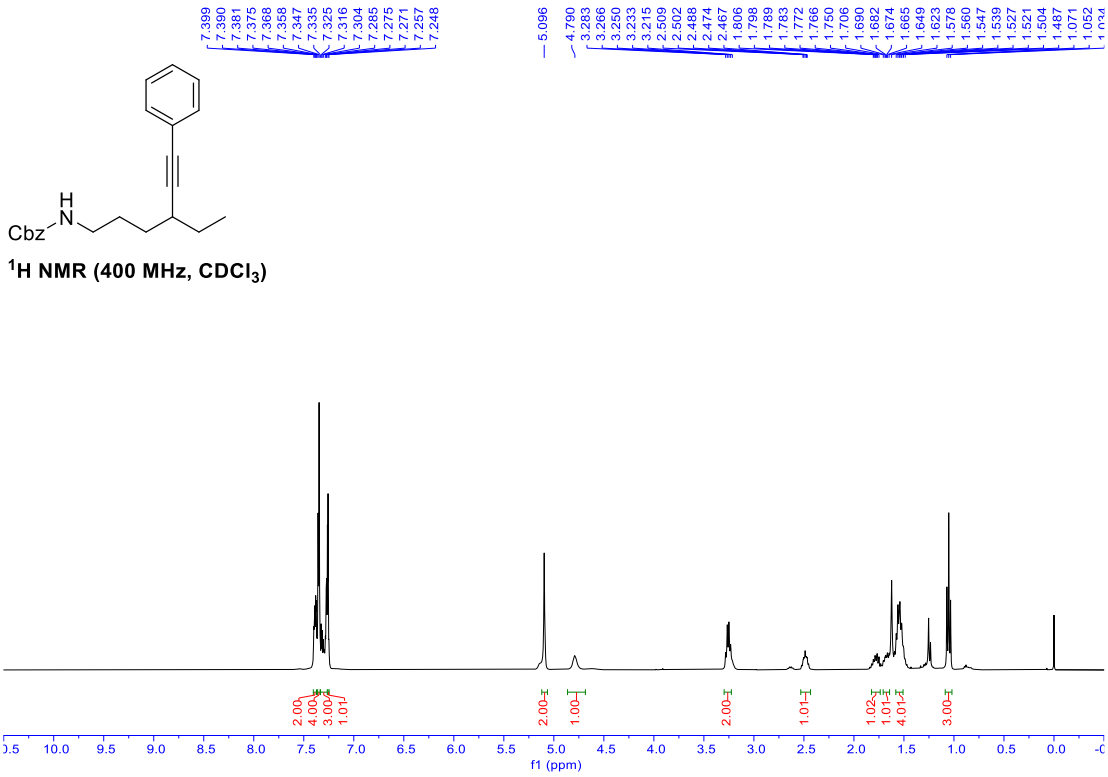
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2i

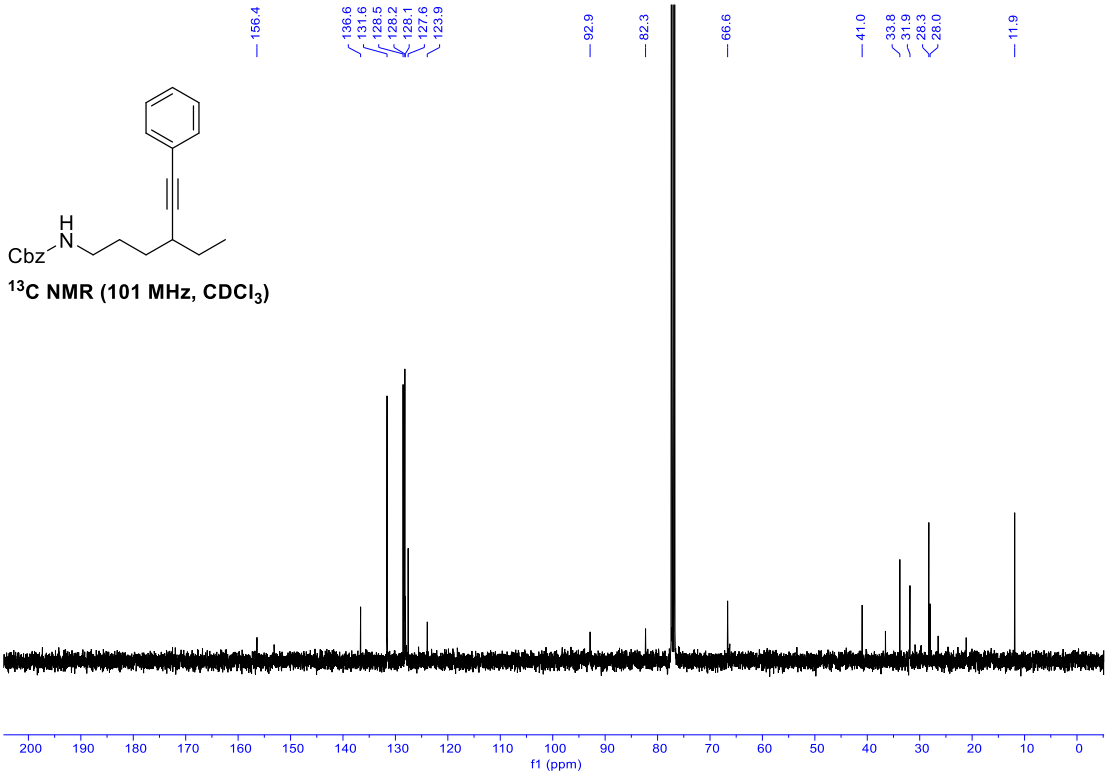


^{13}C NMR (101 MHz, $CDCl_3$)

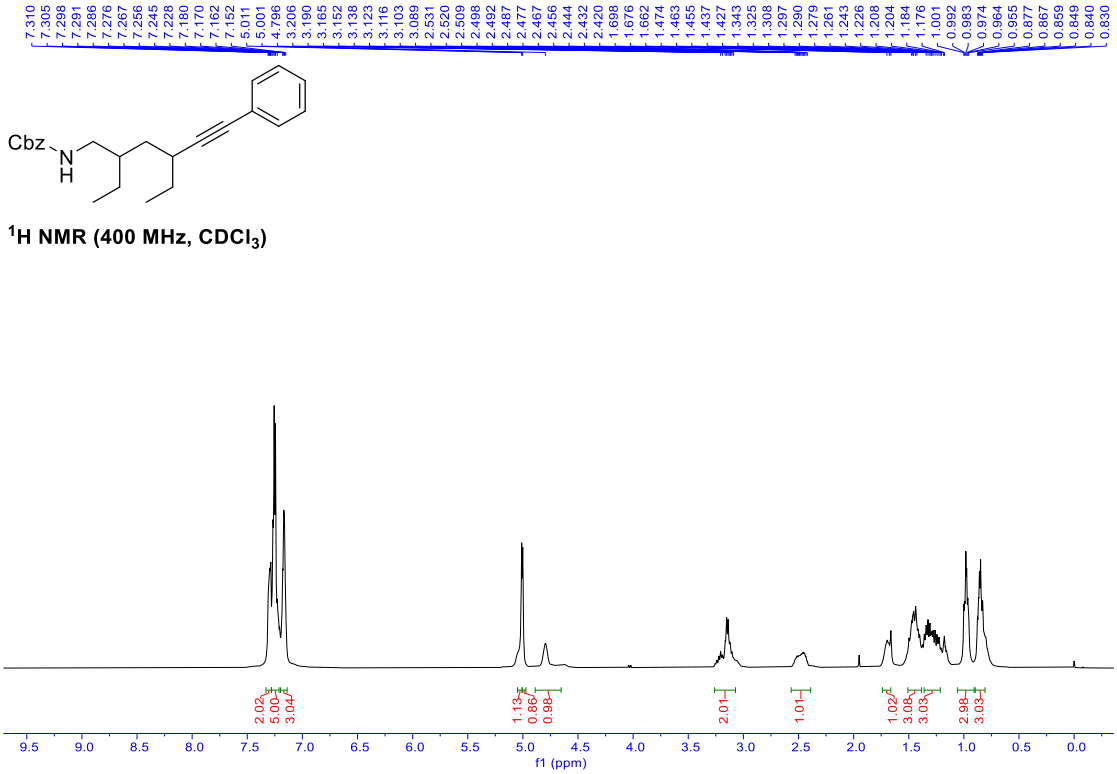
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2j



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2j

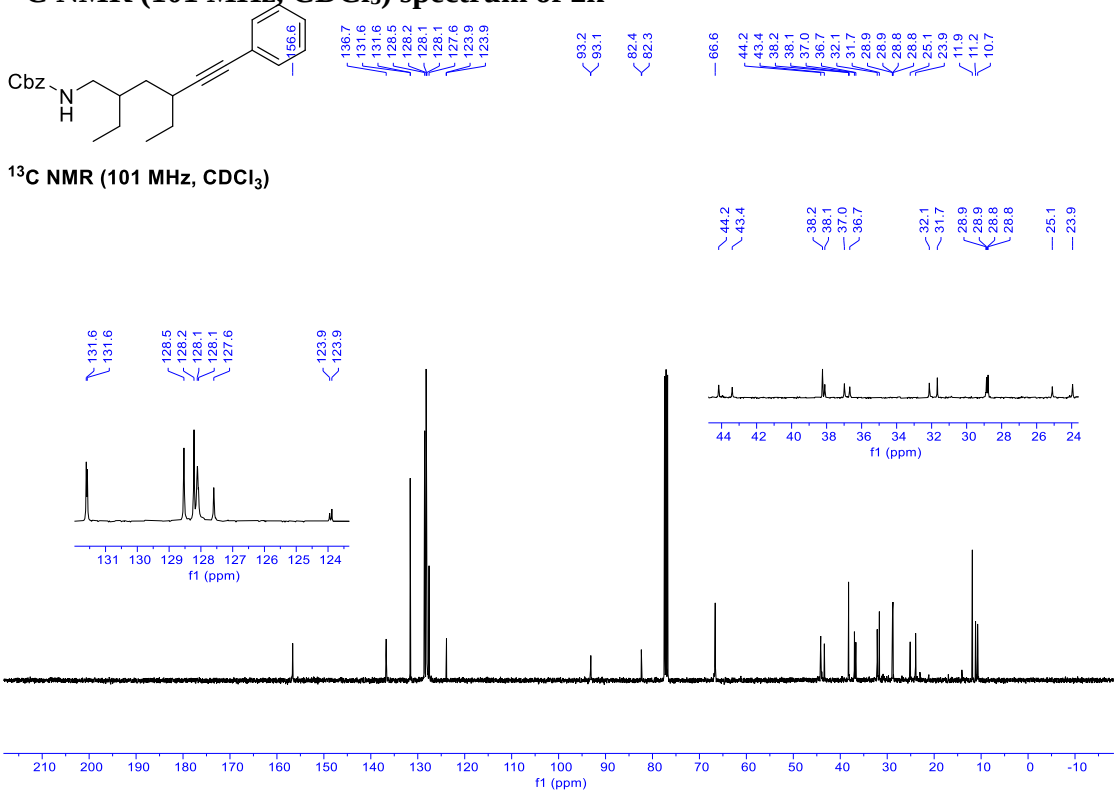


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2k

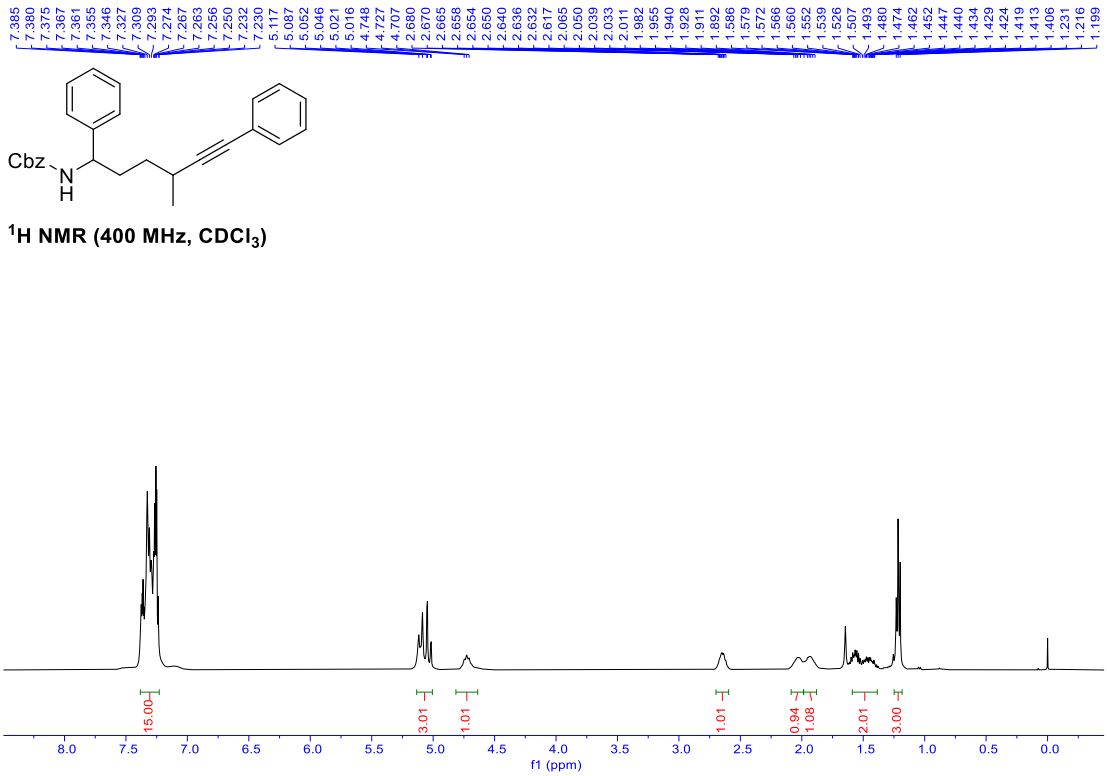


^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2k

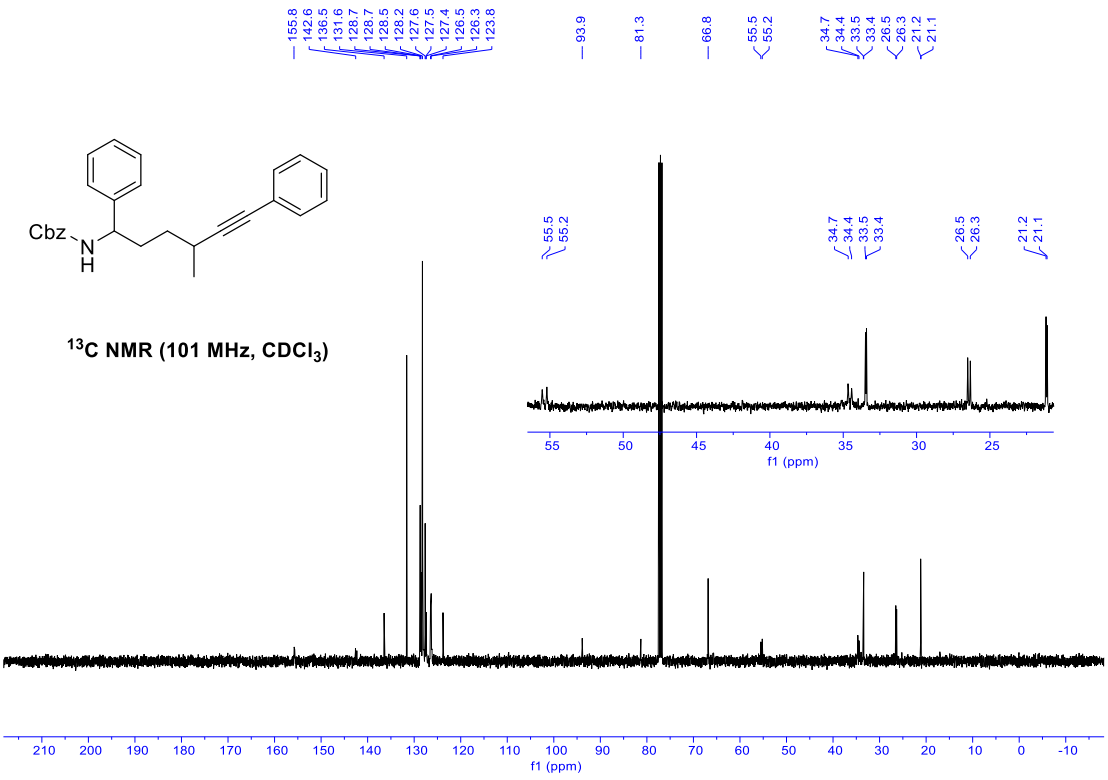


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2l



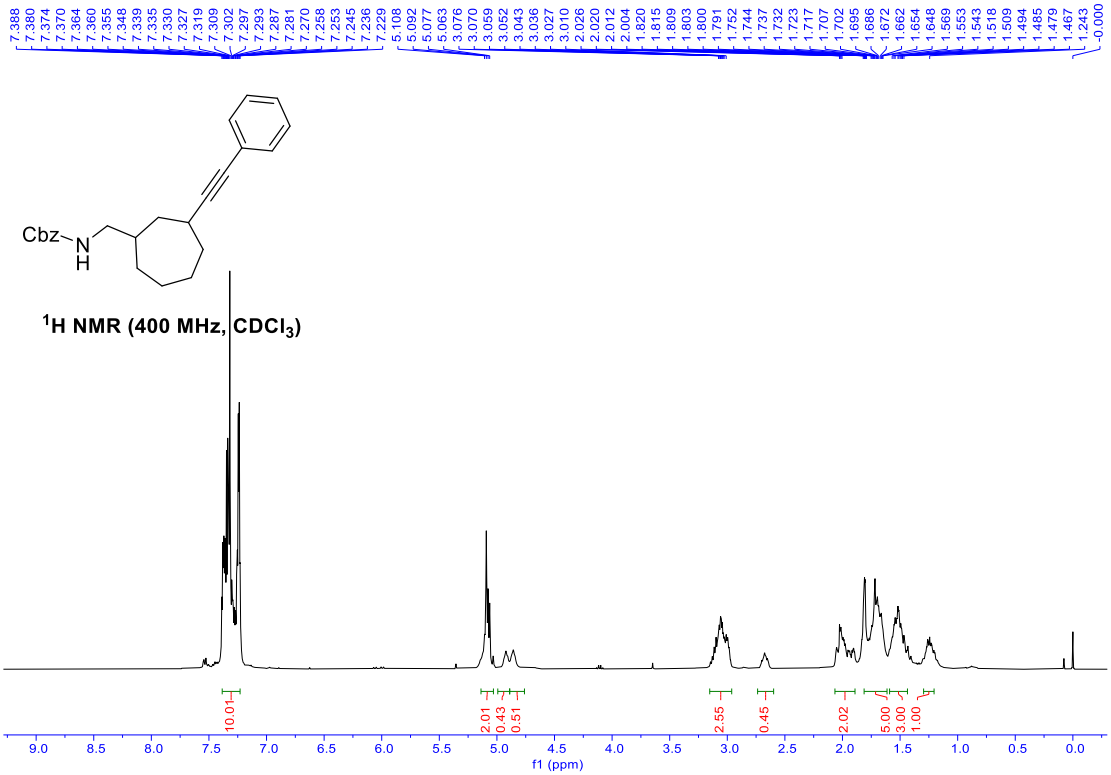
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2l

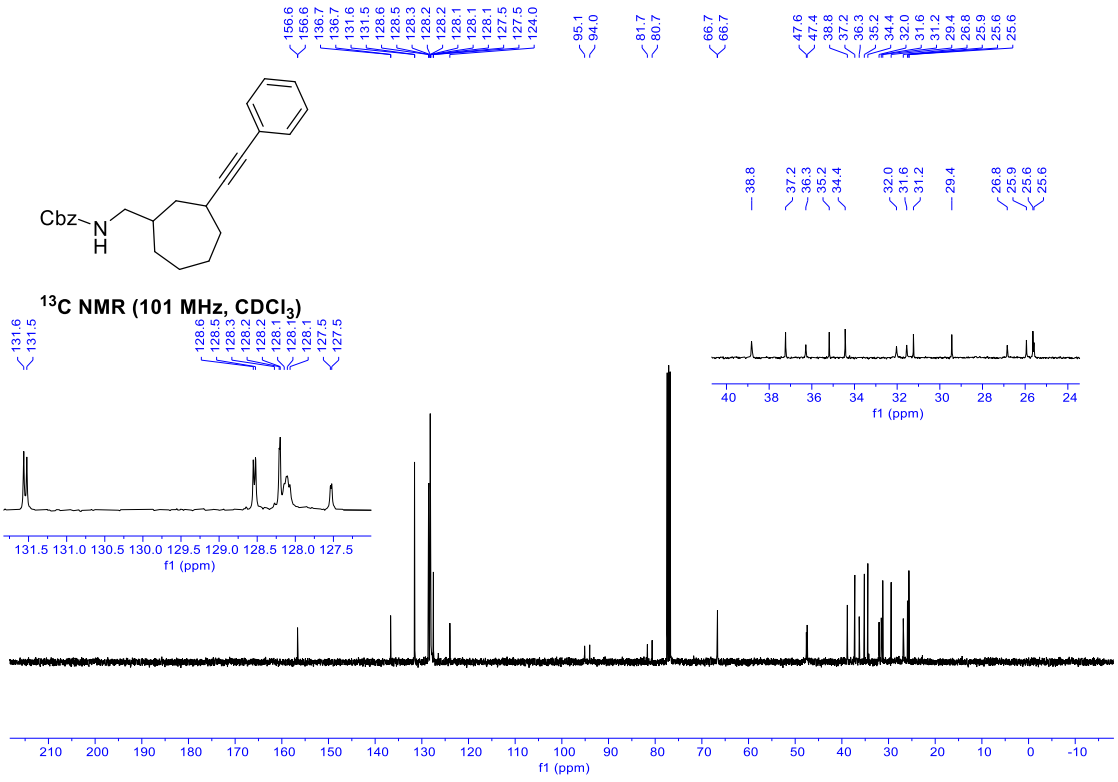


^{13}C NMR (101 MHz, $CDCl_3$)

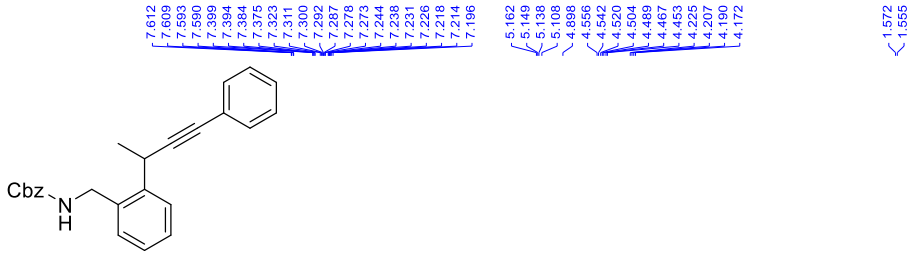
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2m



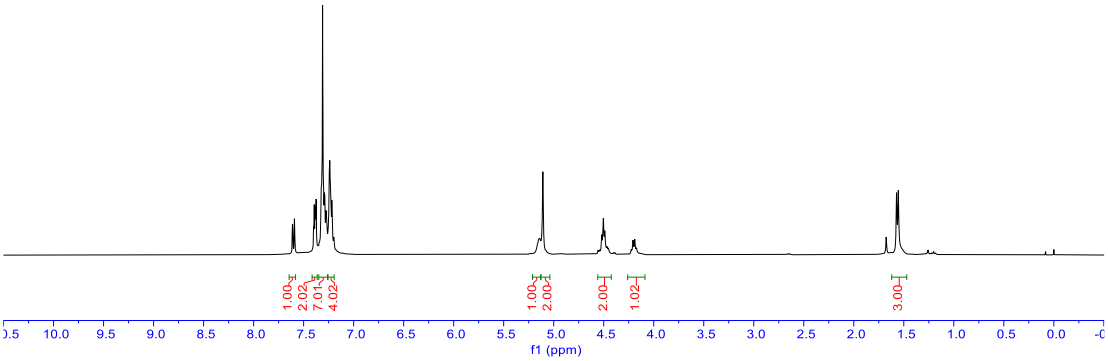
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2m



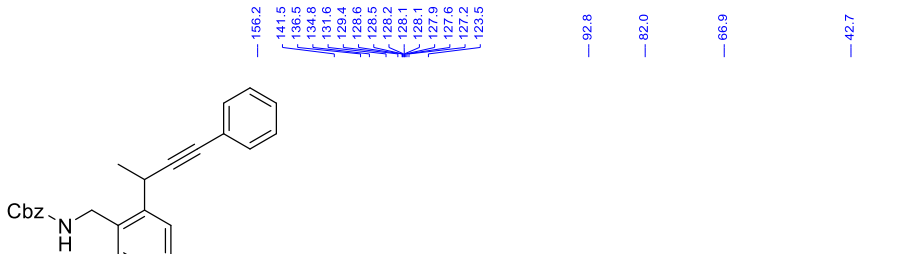
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2n



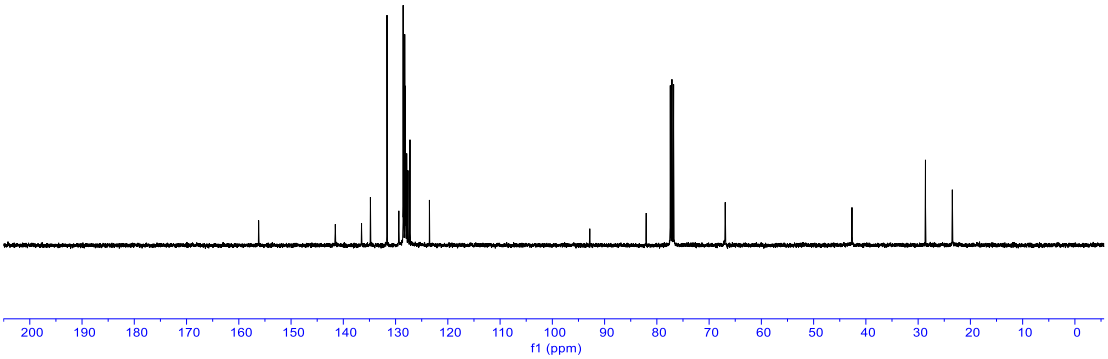
^{1}H NMR (400 MHz, $CDCl_3$)



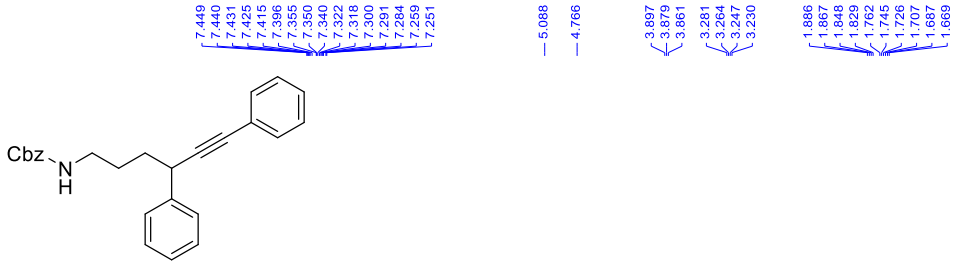
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2n



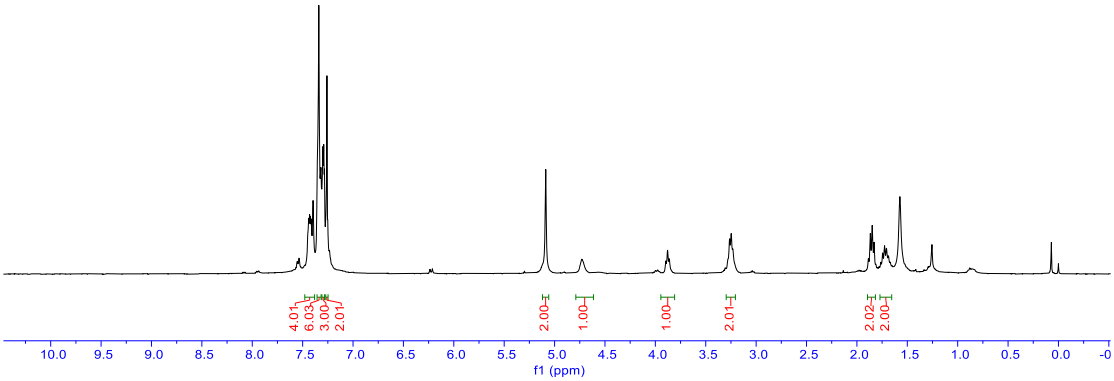
^{13}C NMR (101 MHz, $CDCl_3$)



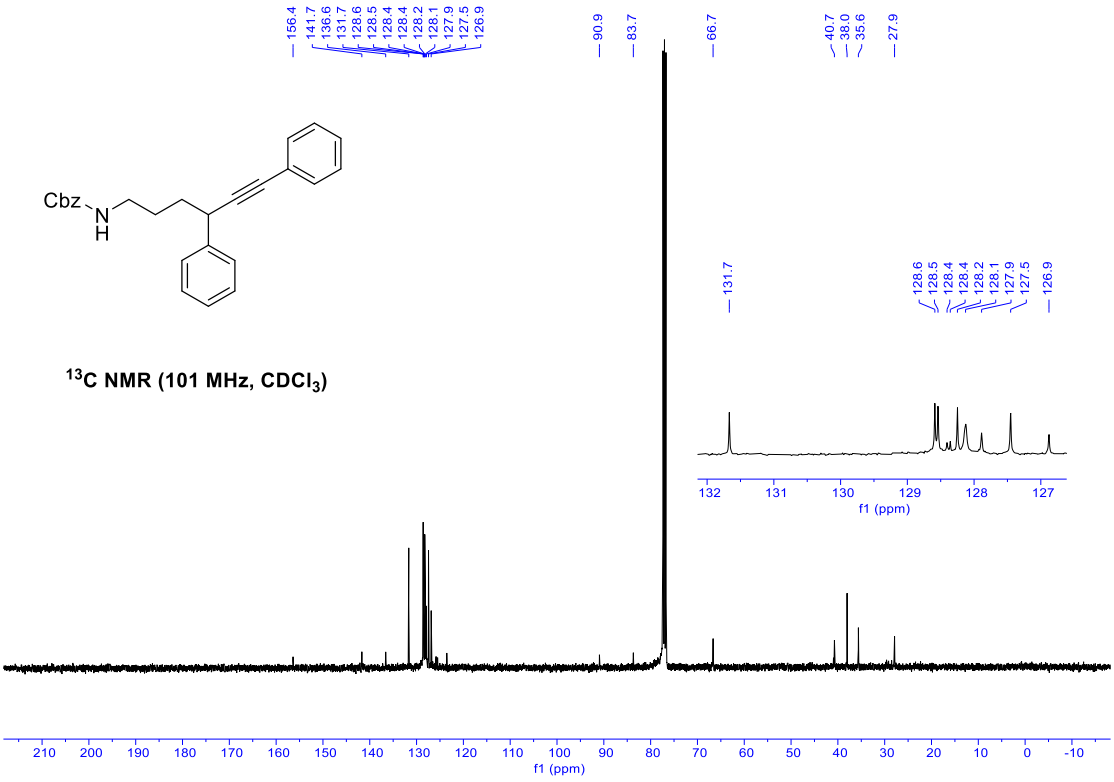
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2o



^{1}H NMR (400 MHz, $CDCl_3$)

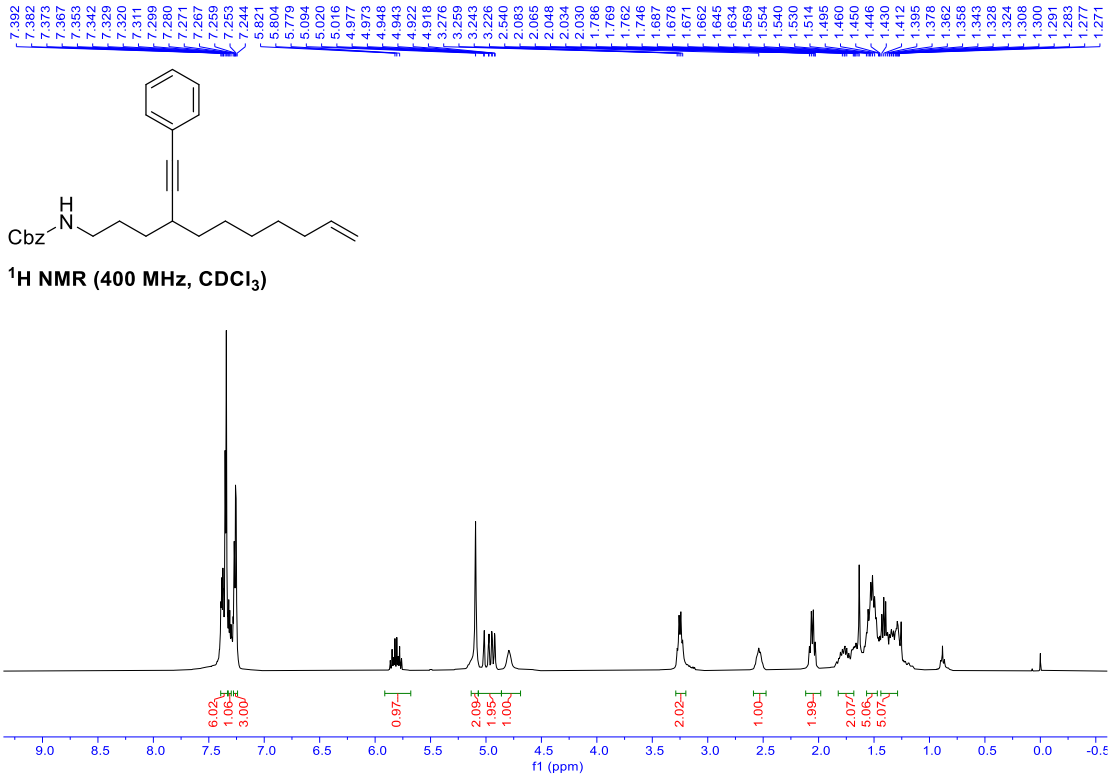


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2o

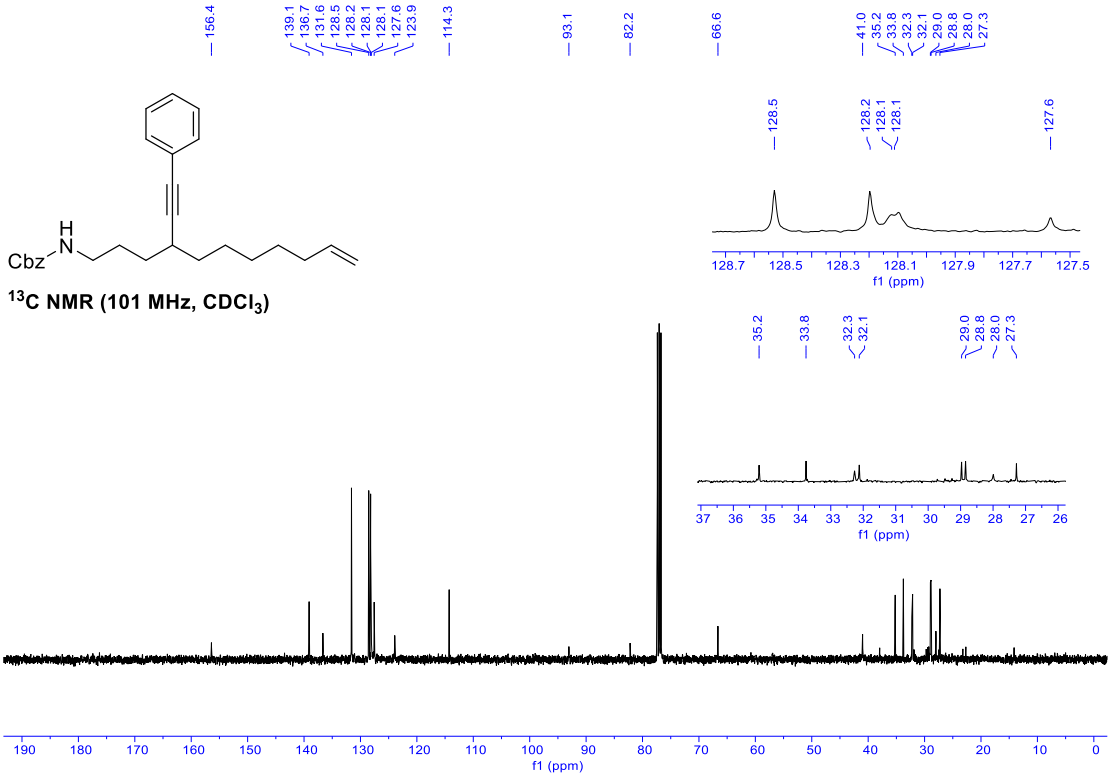


^{13}C NMR (101 MHz, $CDCl_3$)

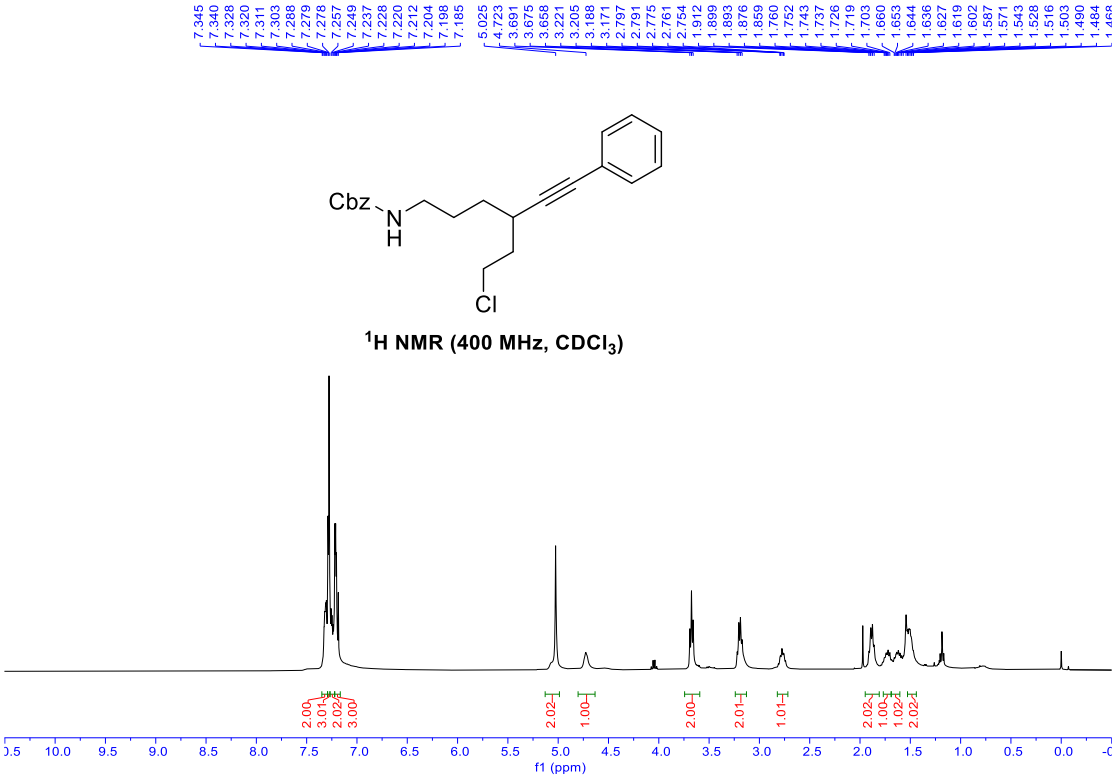
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2p



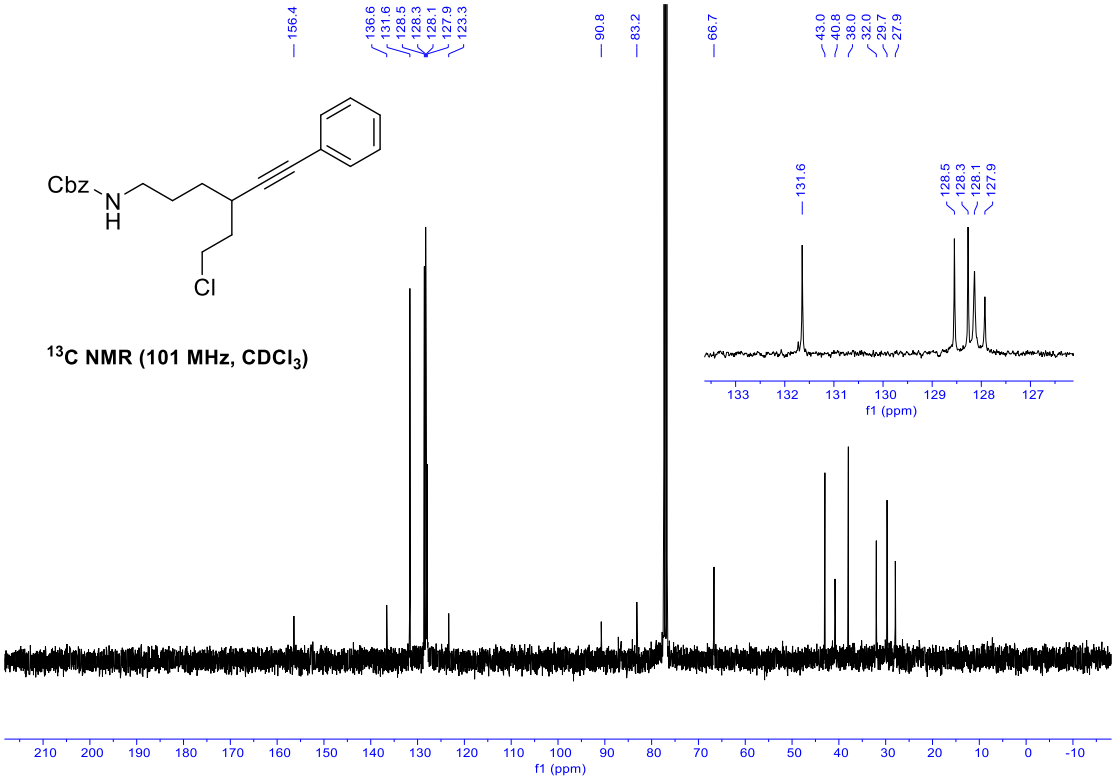
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2p



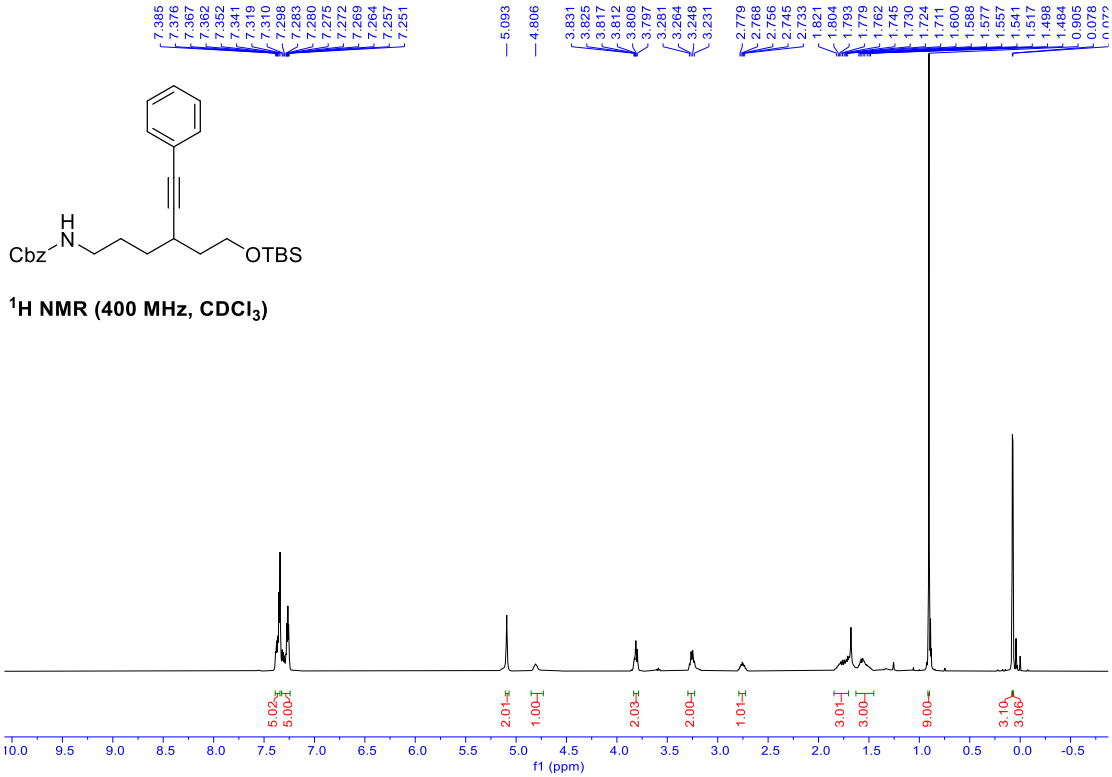
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2q



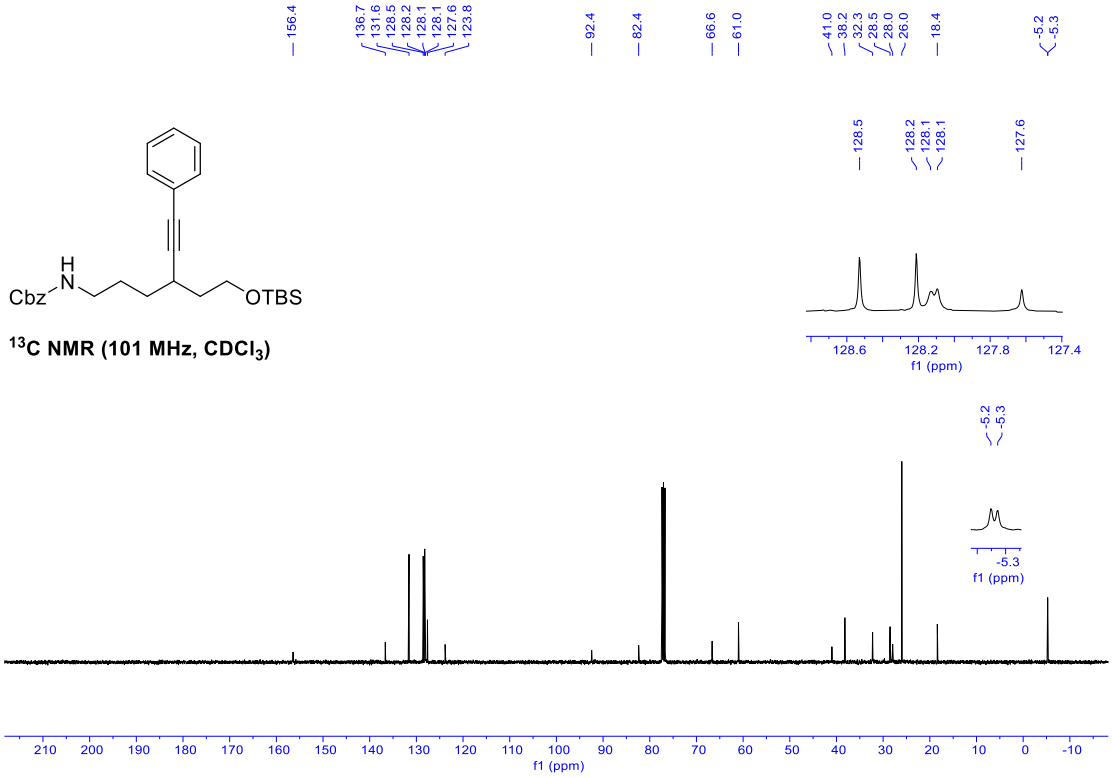
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2q



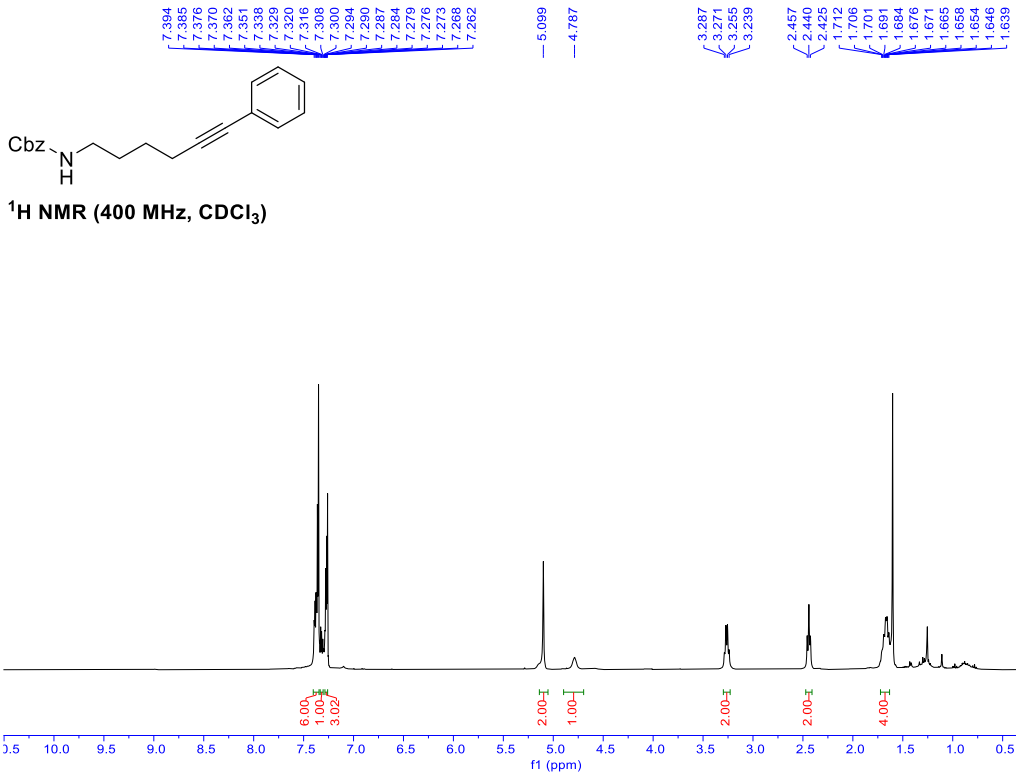
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2r



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2r

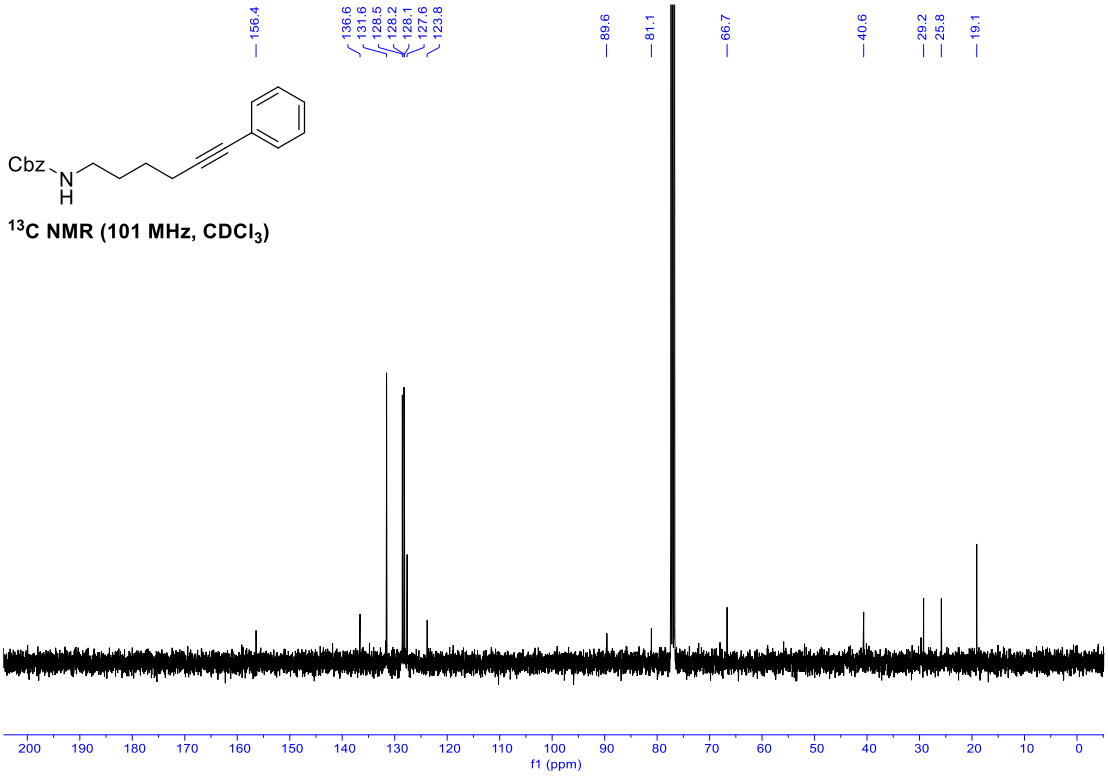


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2s



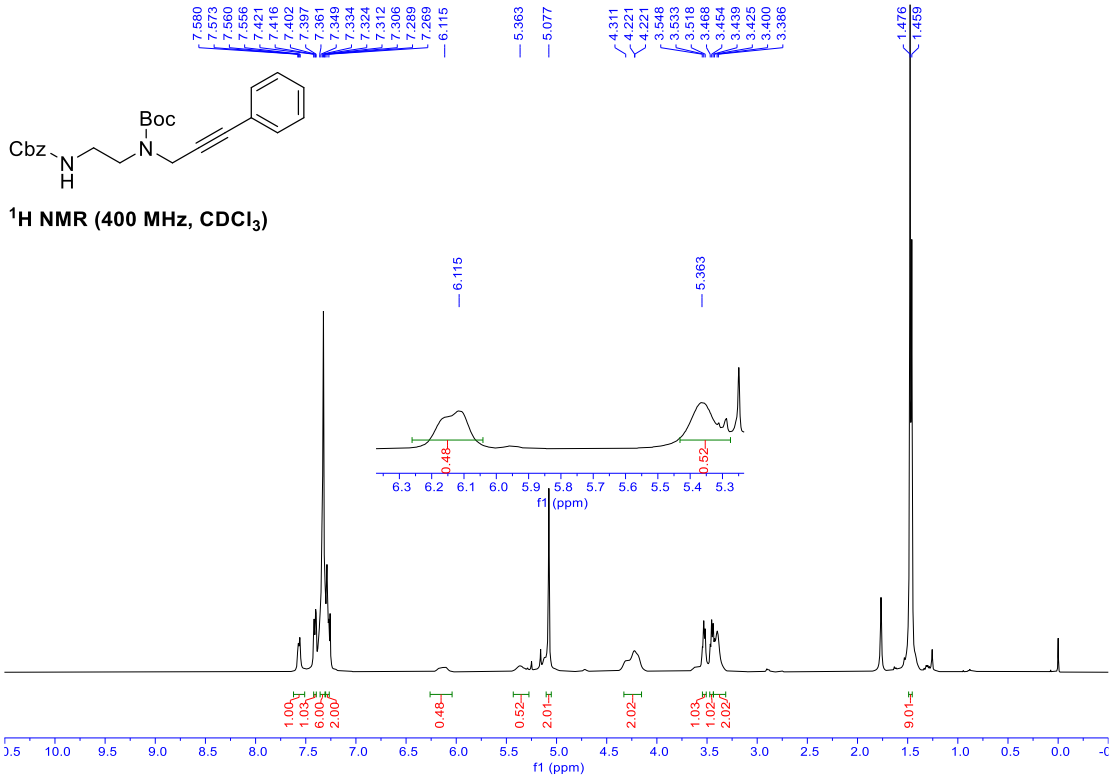
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2s

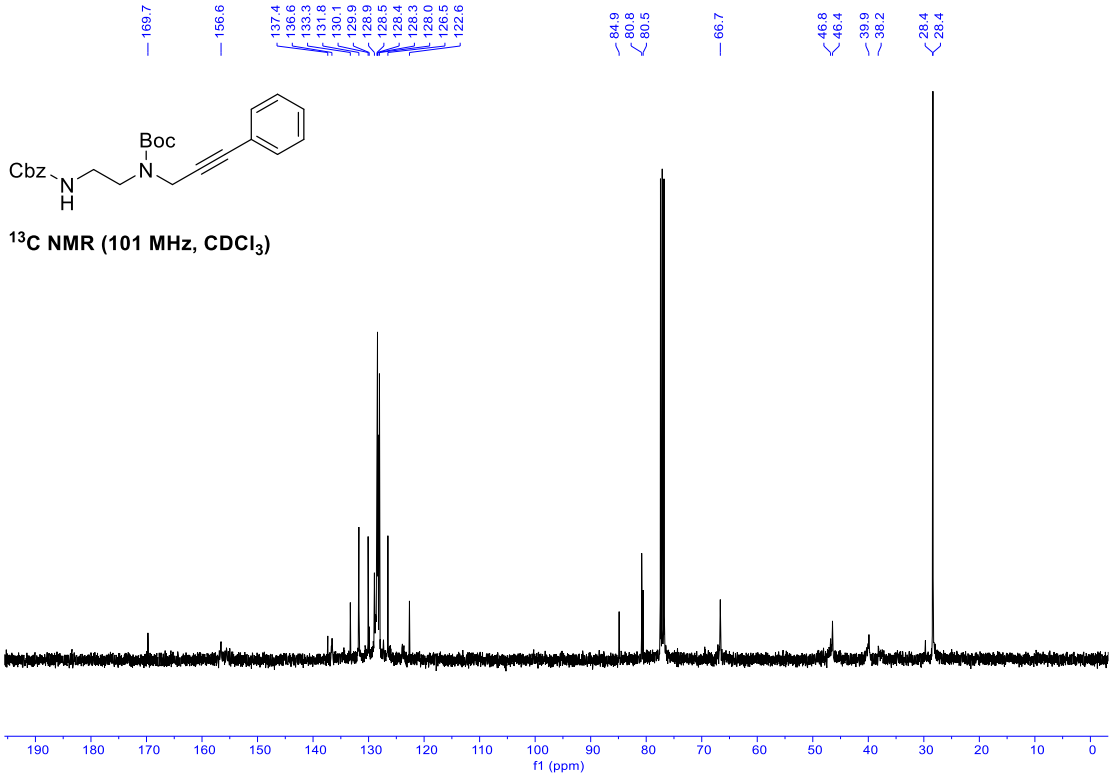


^{13}C NMR (101 MHz, $CDCl_3$)

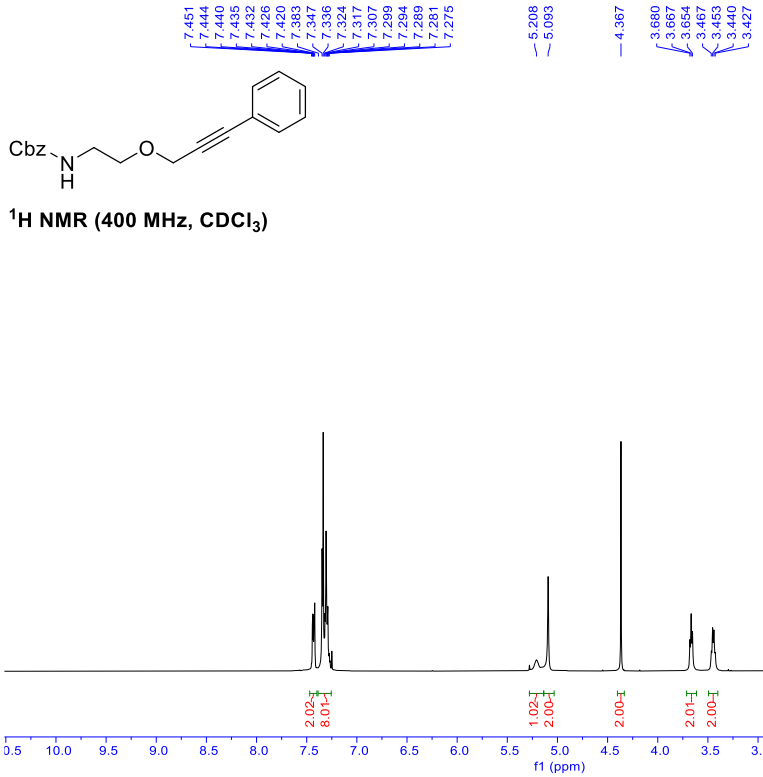
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2t



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2t

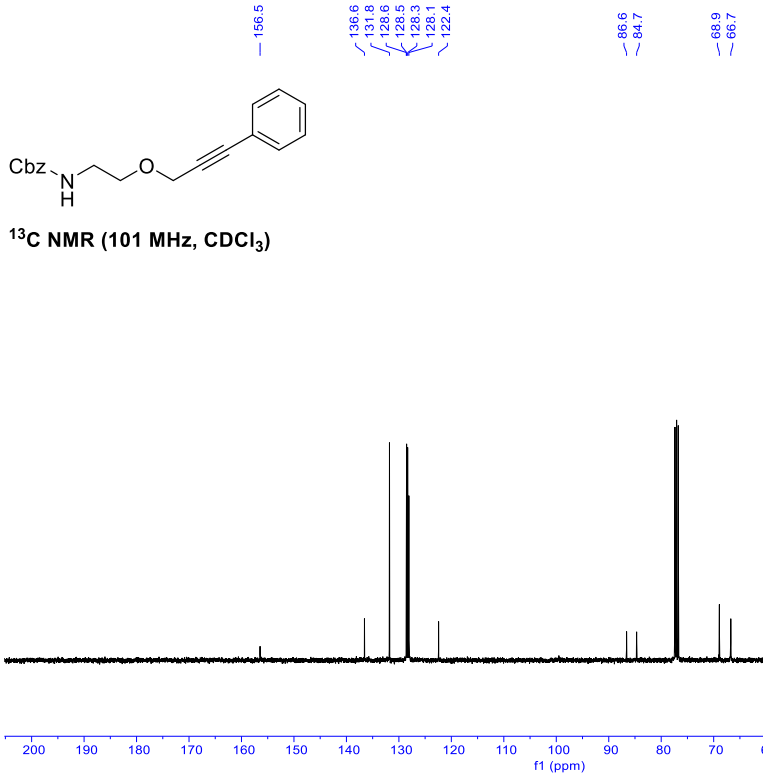


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2u



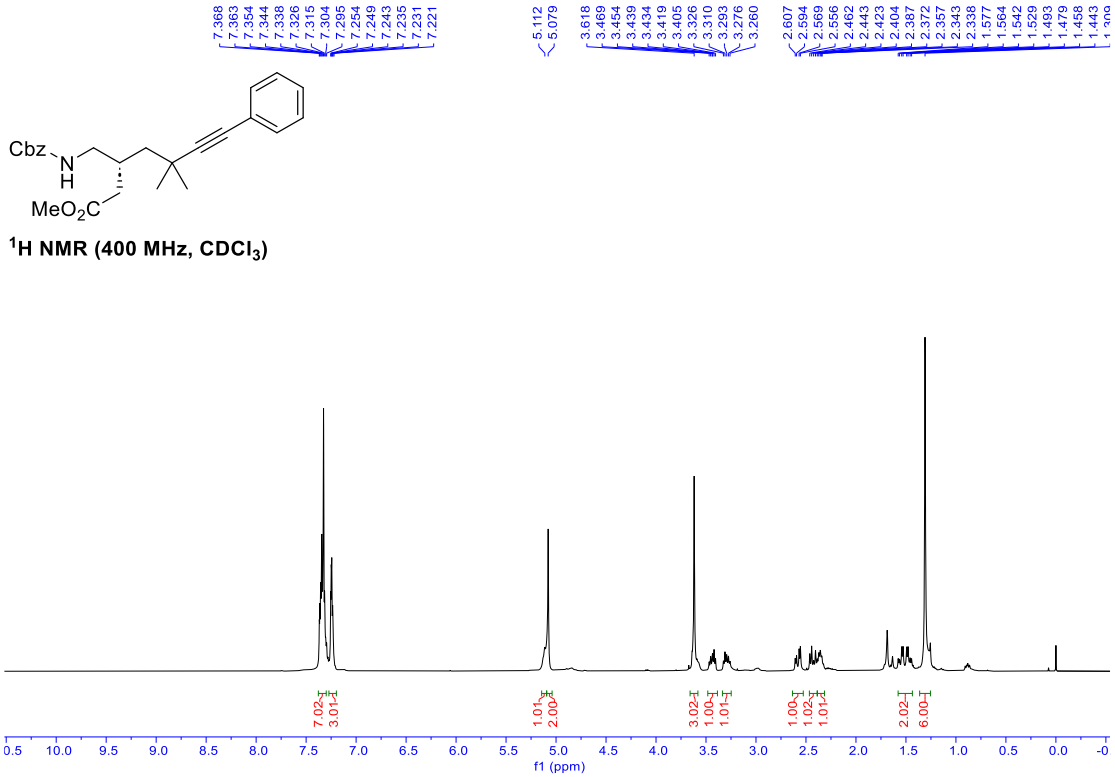
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2u



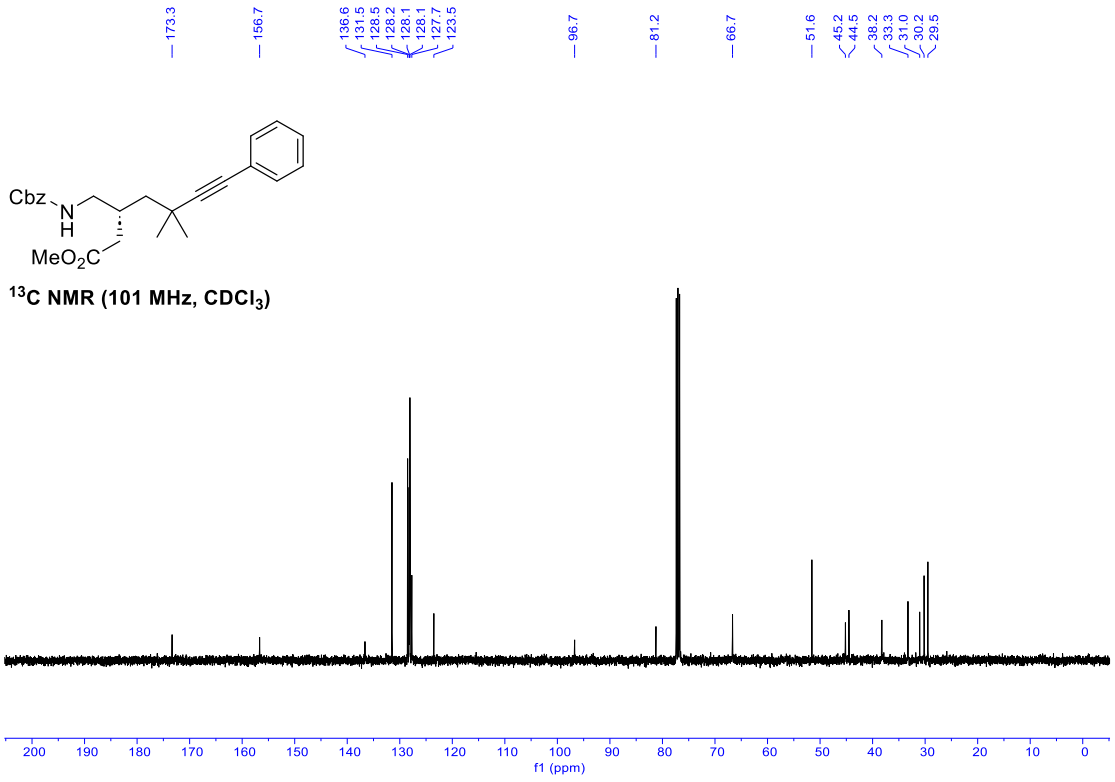
^{13}C NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2v



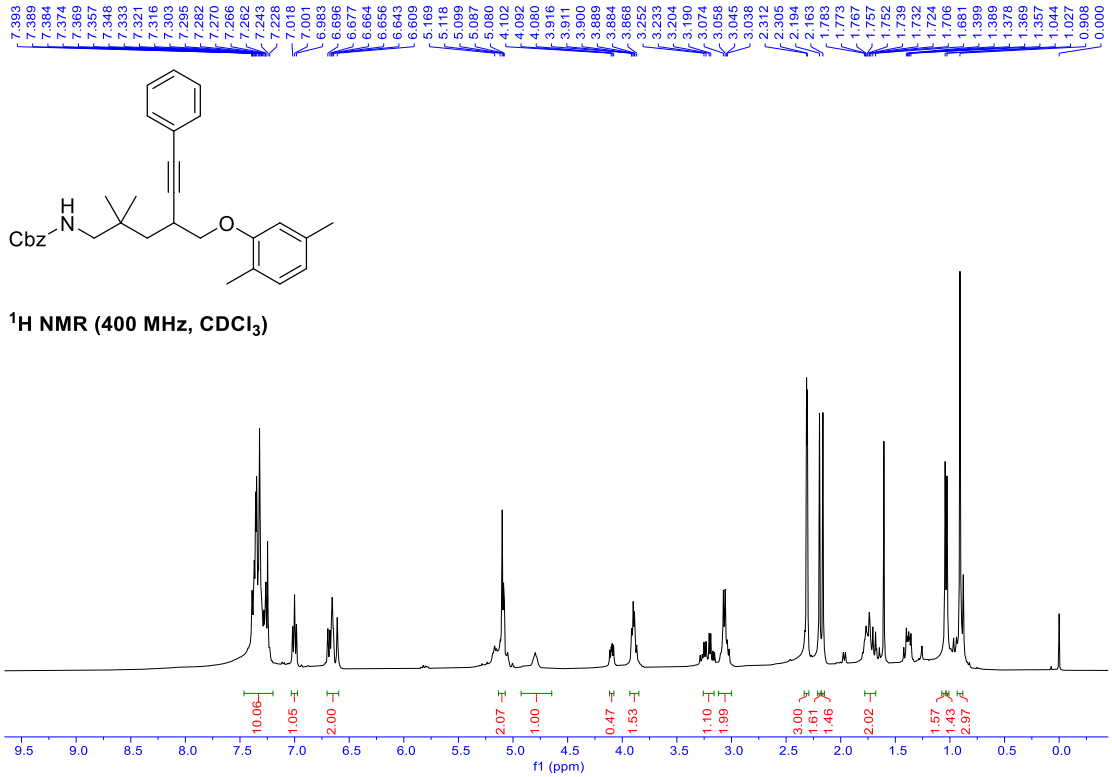
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2v

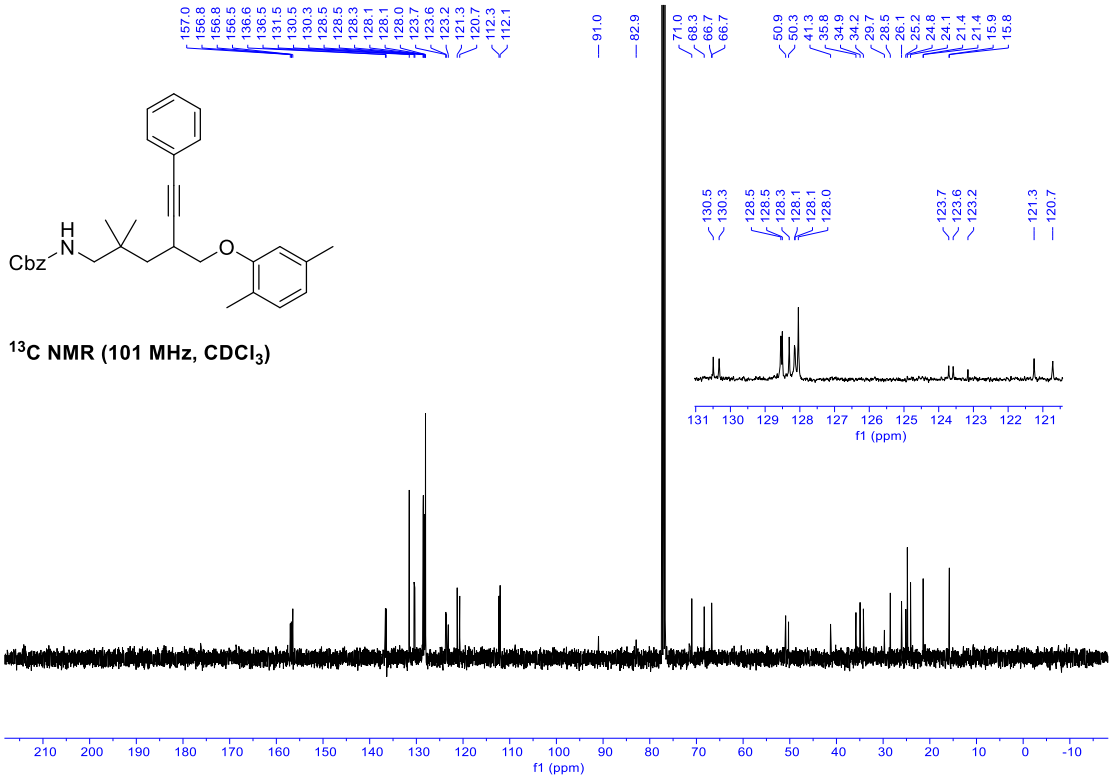


^{13}C NMR (101 MHz, $CDCl_3$)

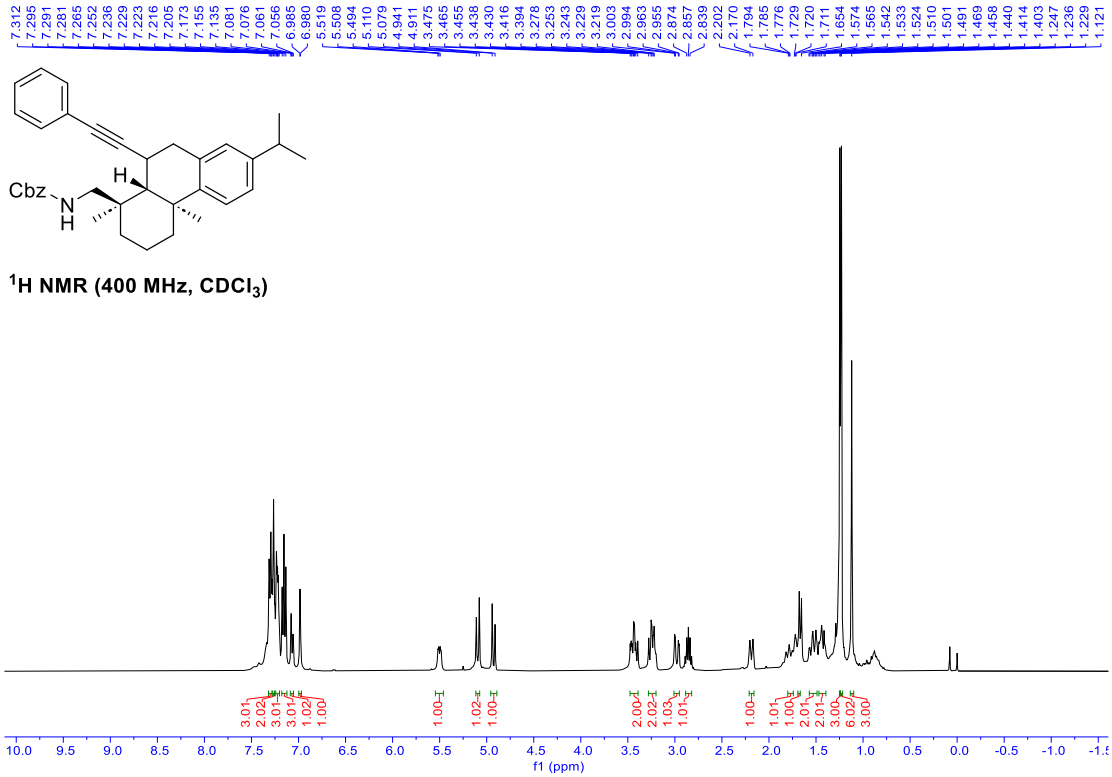
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2w



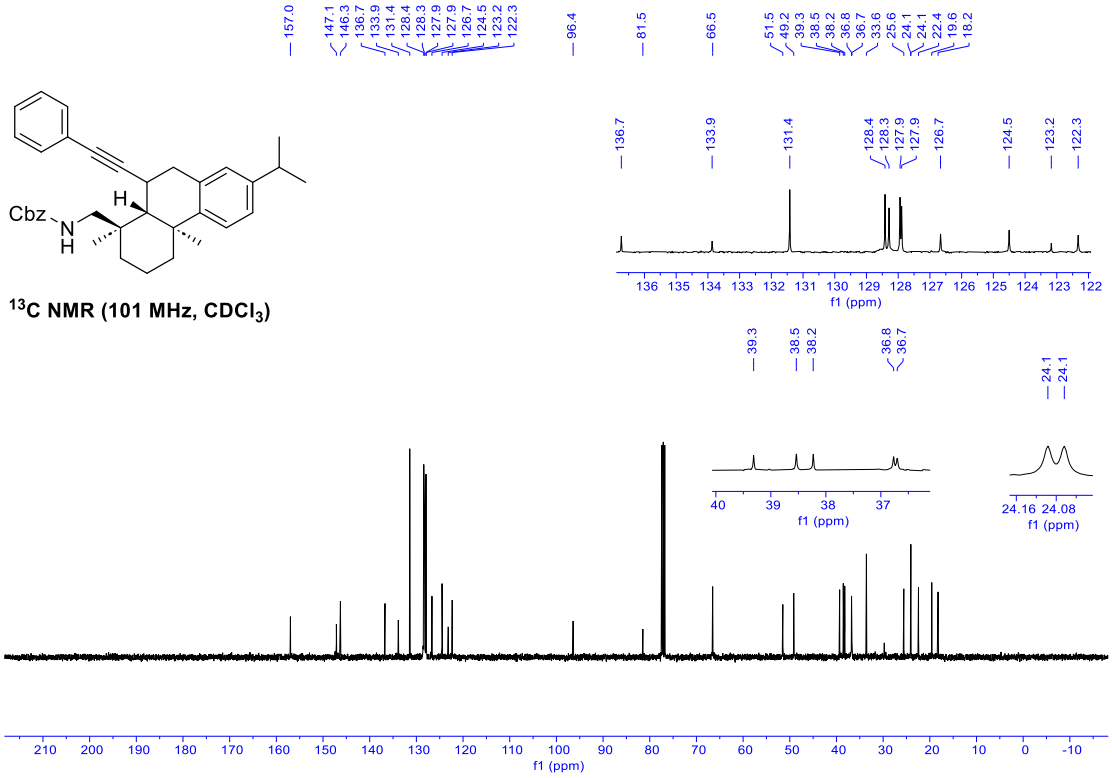
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2w



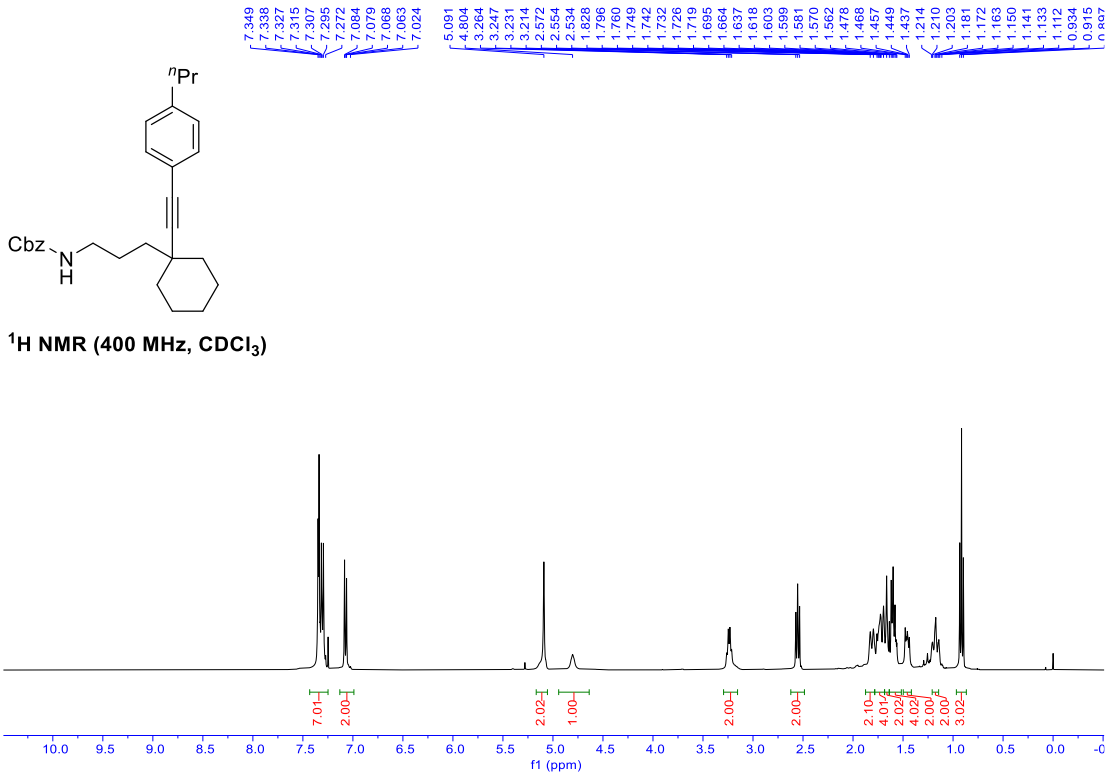
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2x



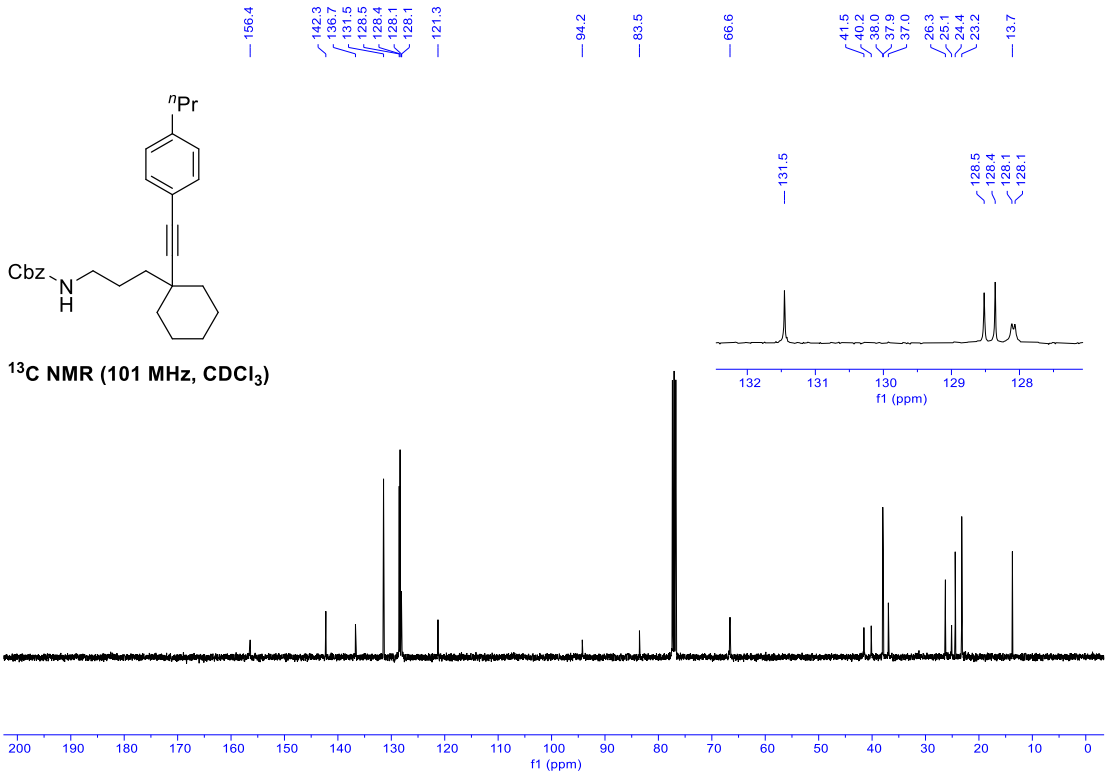
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2x



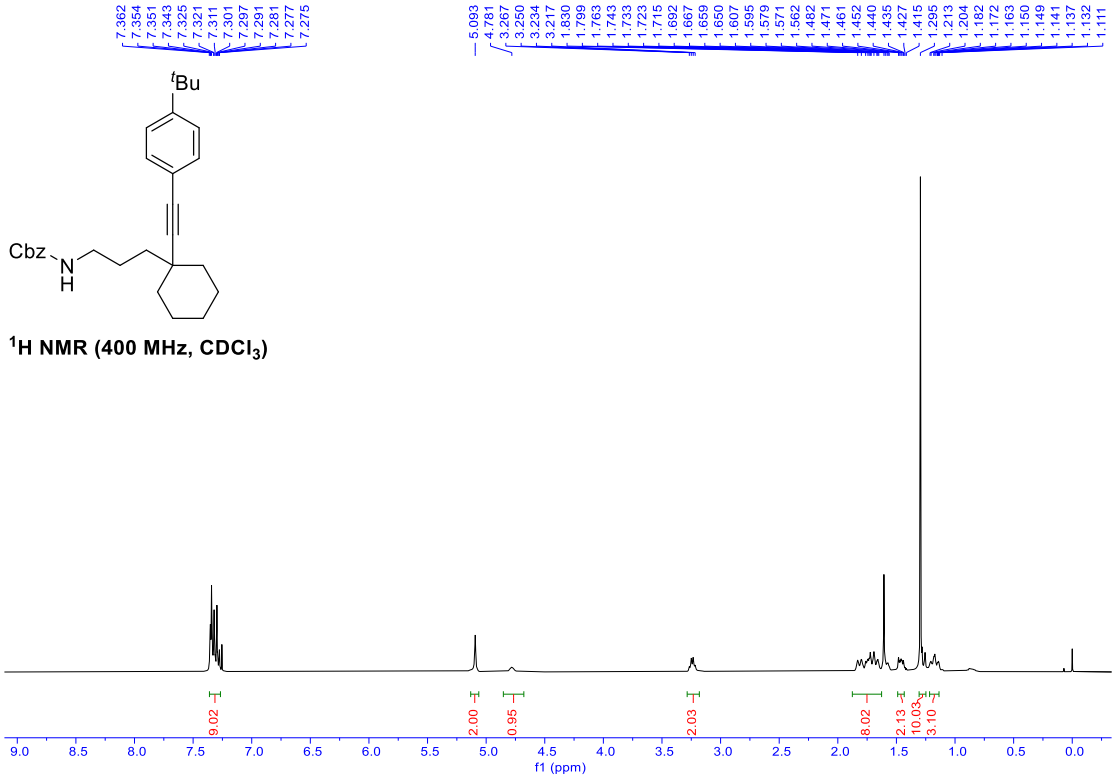
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2aa



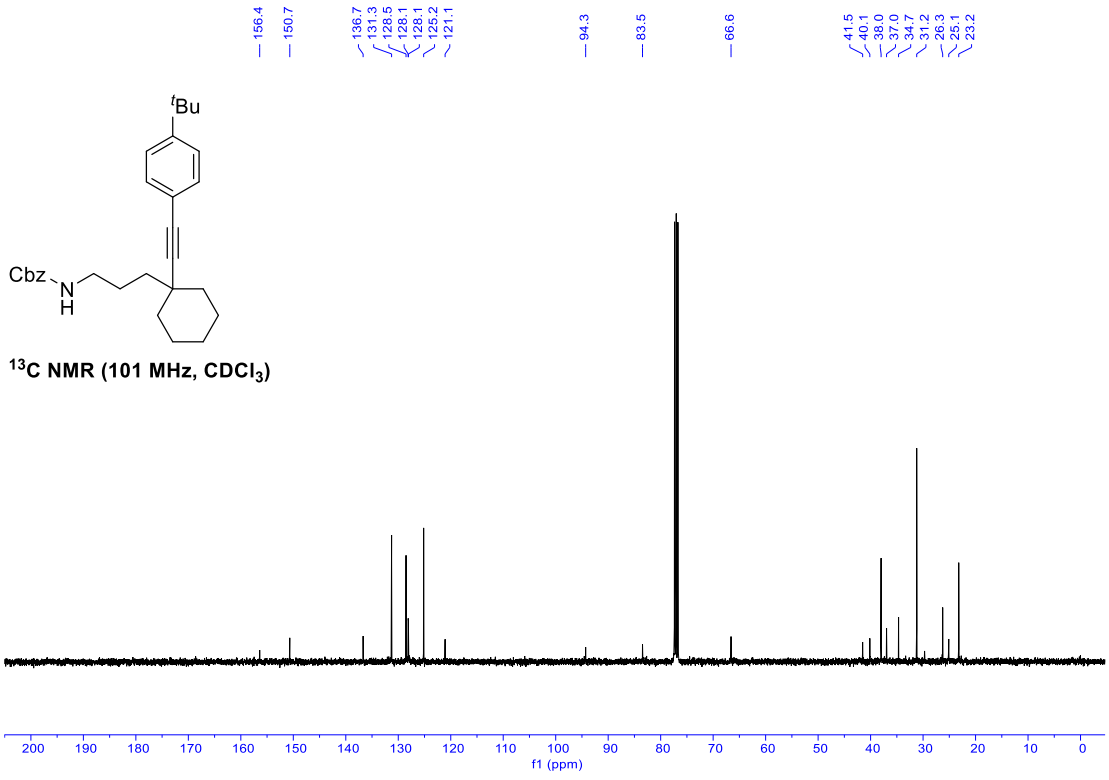
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2aa



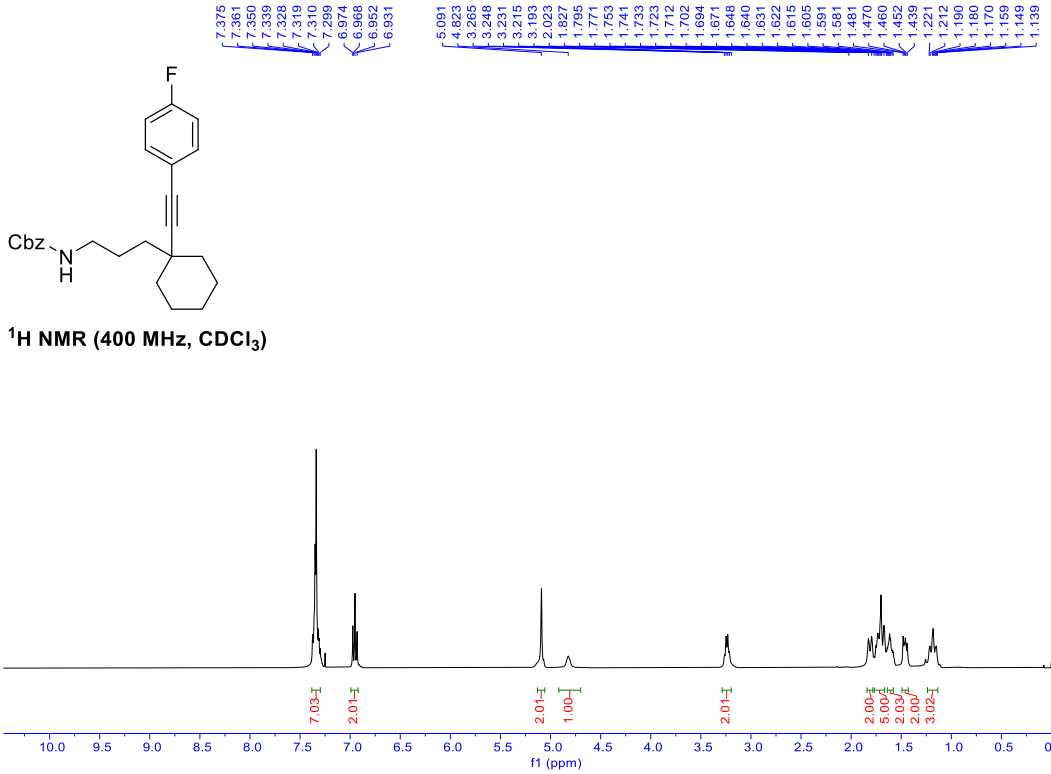
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2ab



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2ab

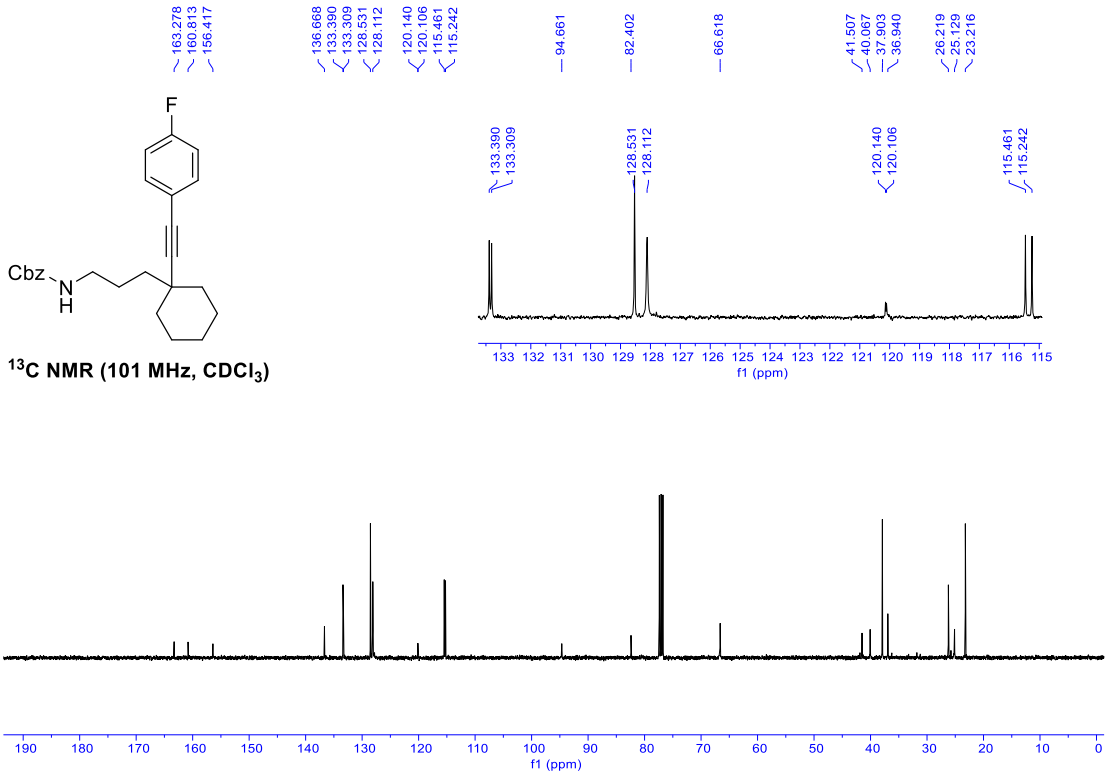


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2ac



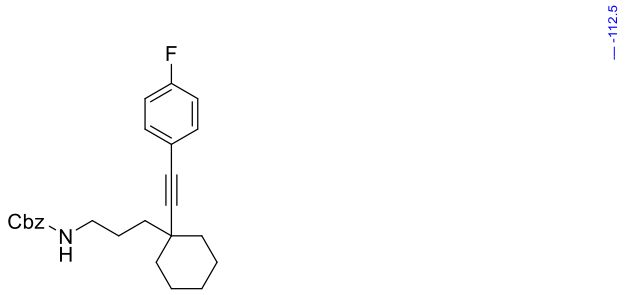
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2ac



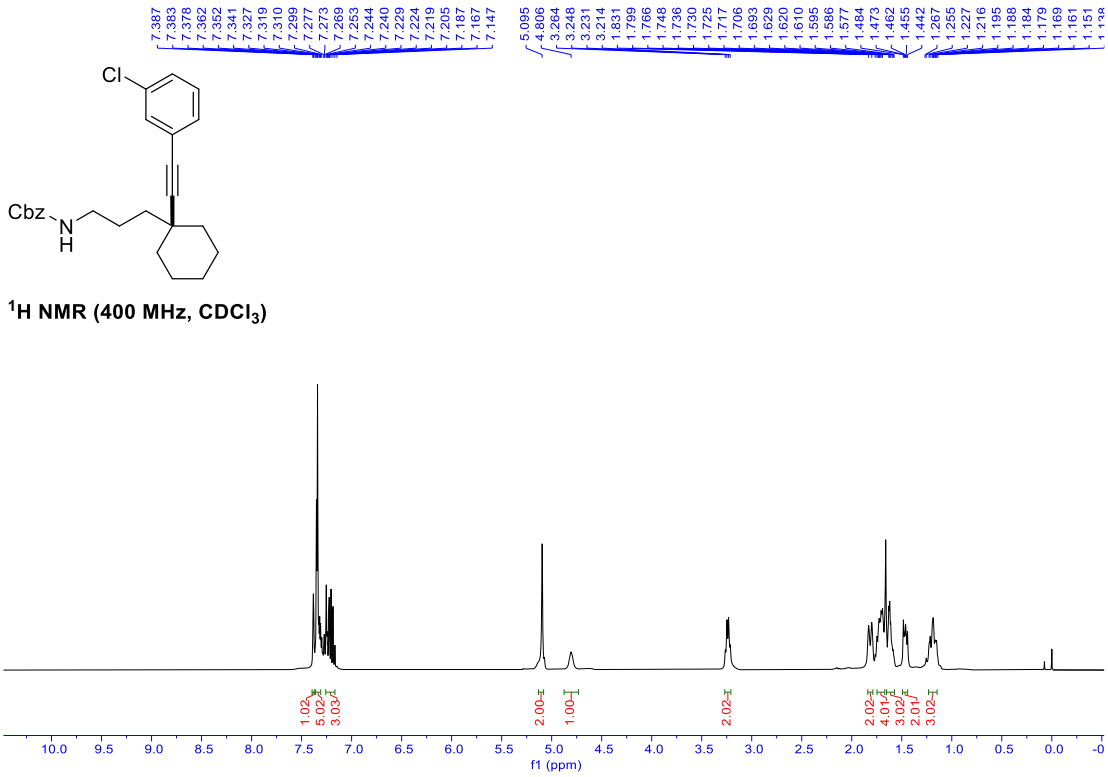
^{13}C NMR (101 MHz, $CDCl_3$)

^{19}F NMR (377 MHz, $CDCl_3$) spectrum of 2ac

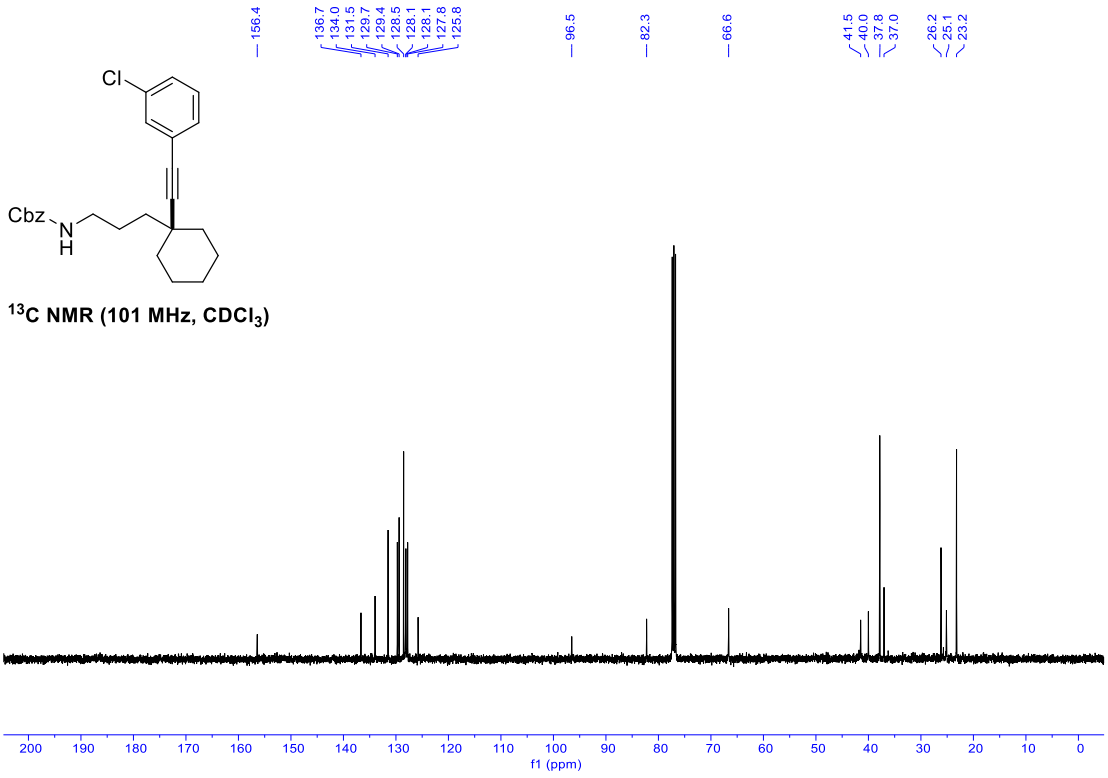


^{19}F NMR (377 MHz, $CDCl_3$)

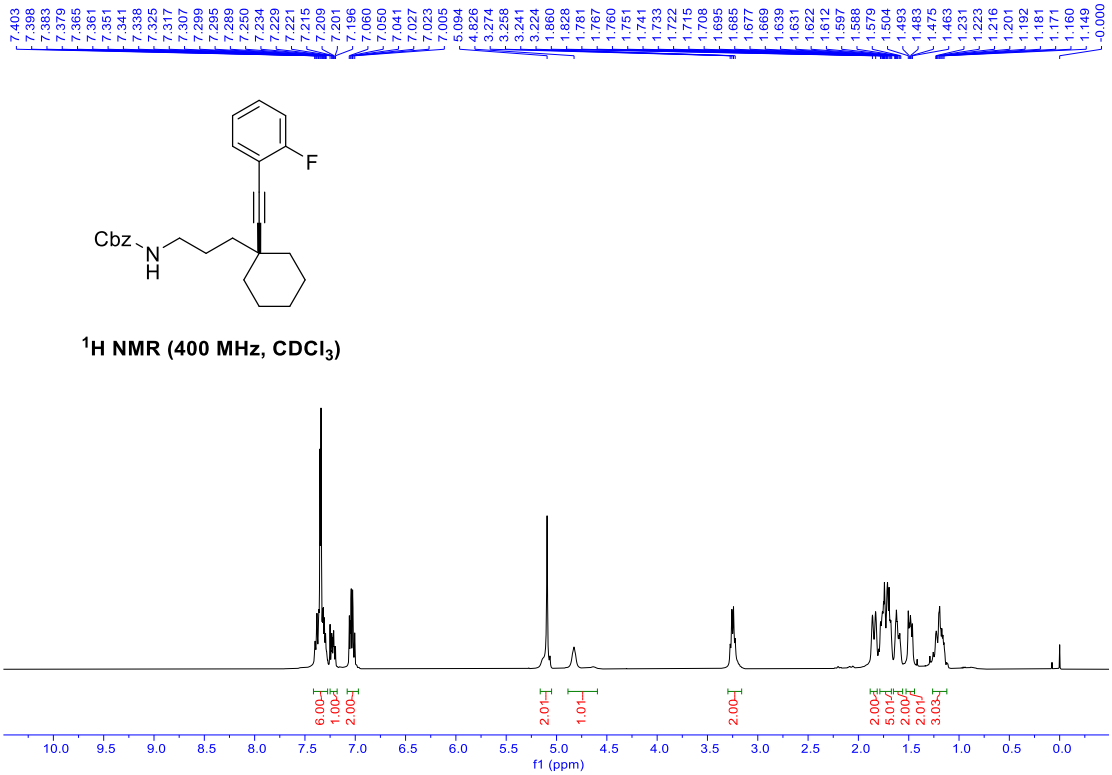
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2ad



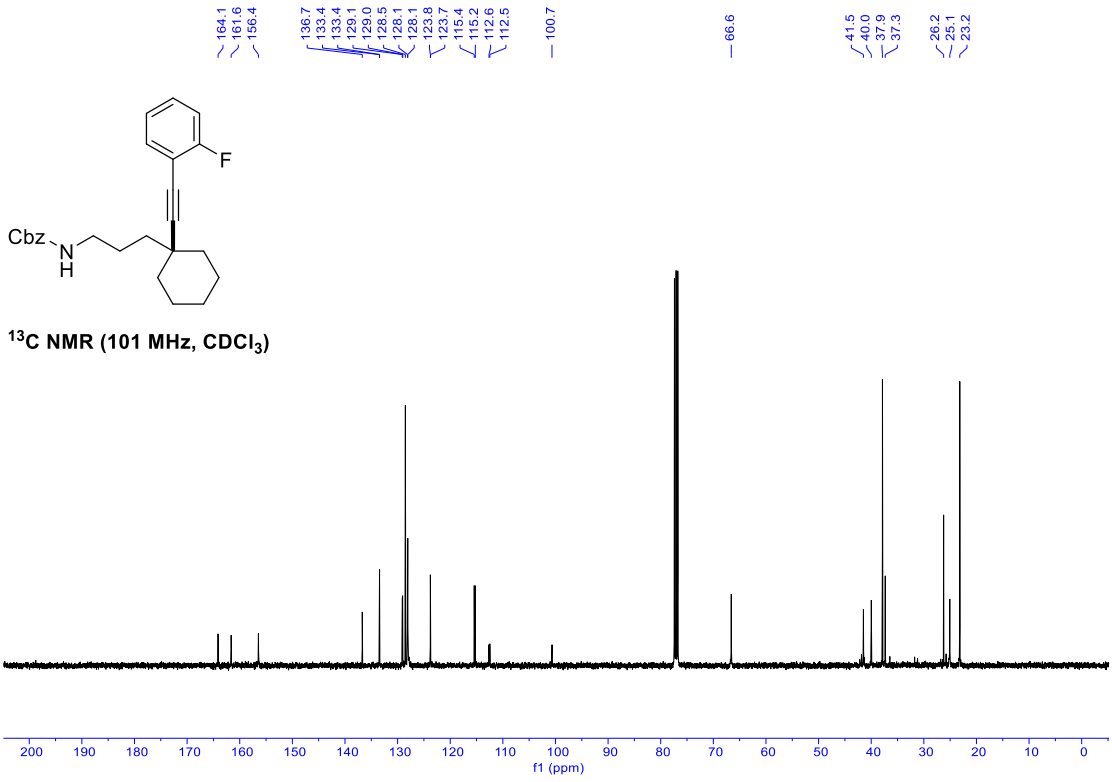
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2ad



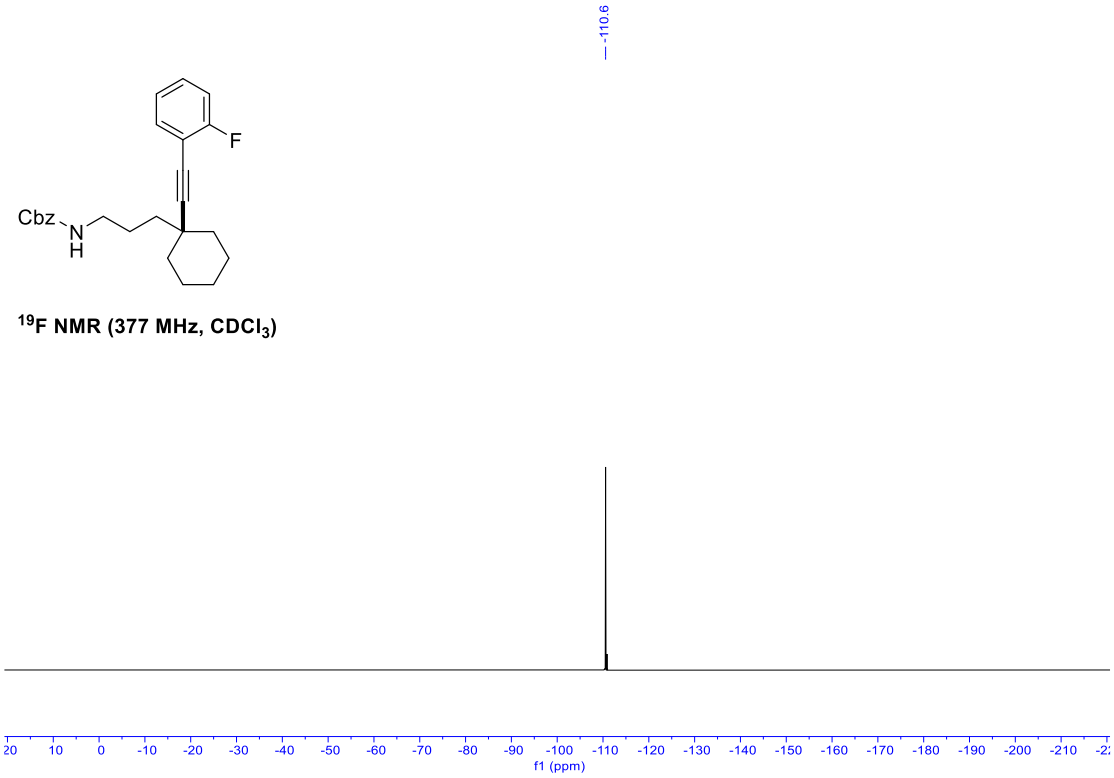
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2ae



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2ae

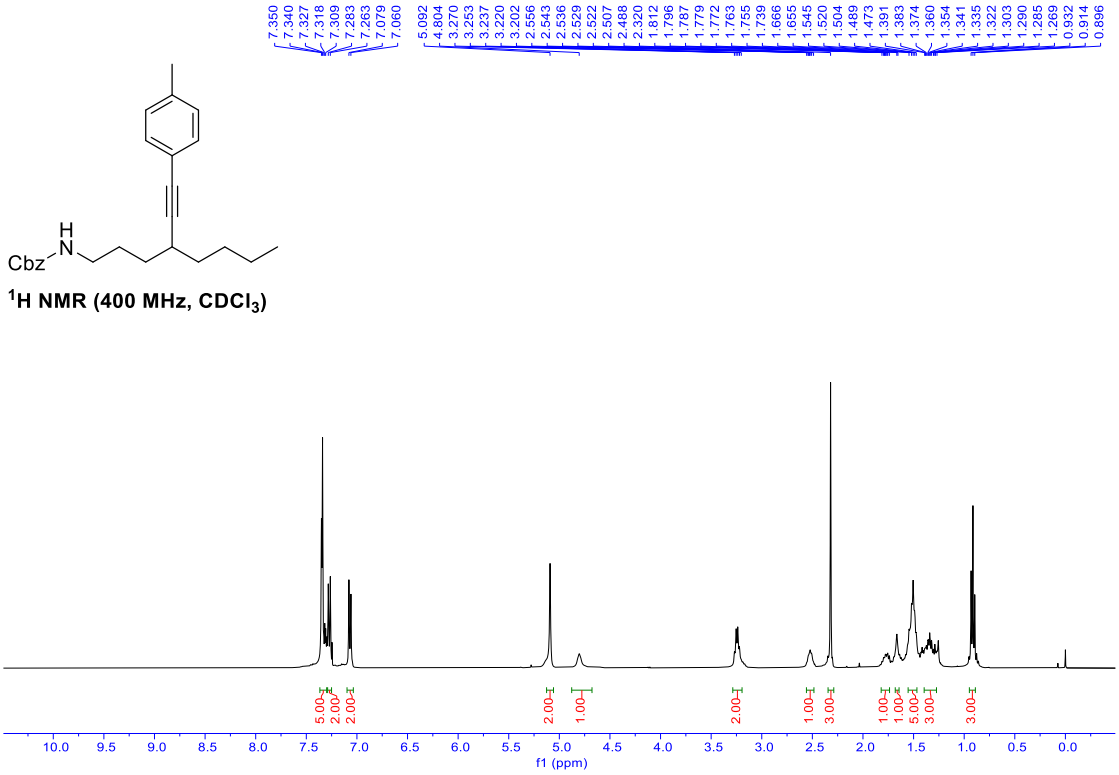


^{19}F NMR (377 MHz, $CDCl_3$) spectrum of 2ae

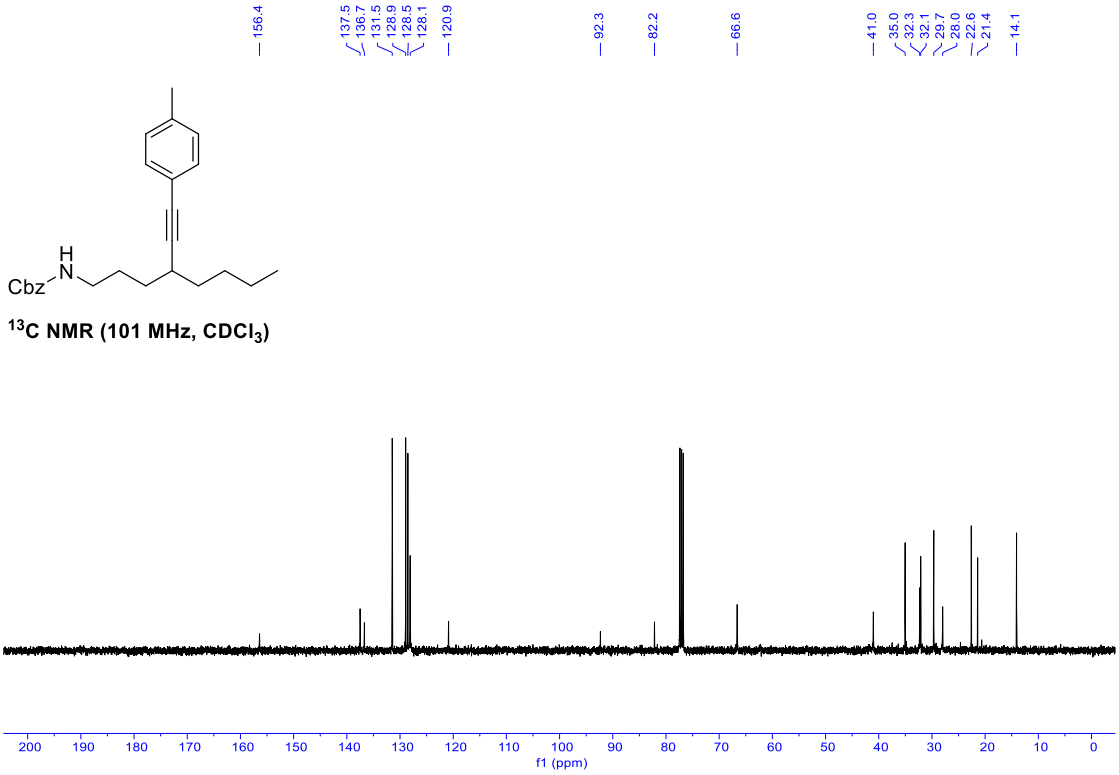


^{19}F NMR (377 MHz, $CDCl_3$)

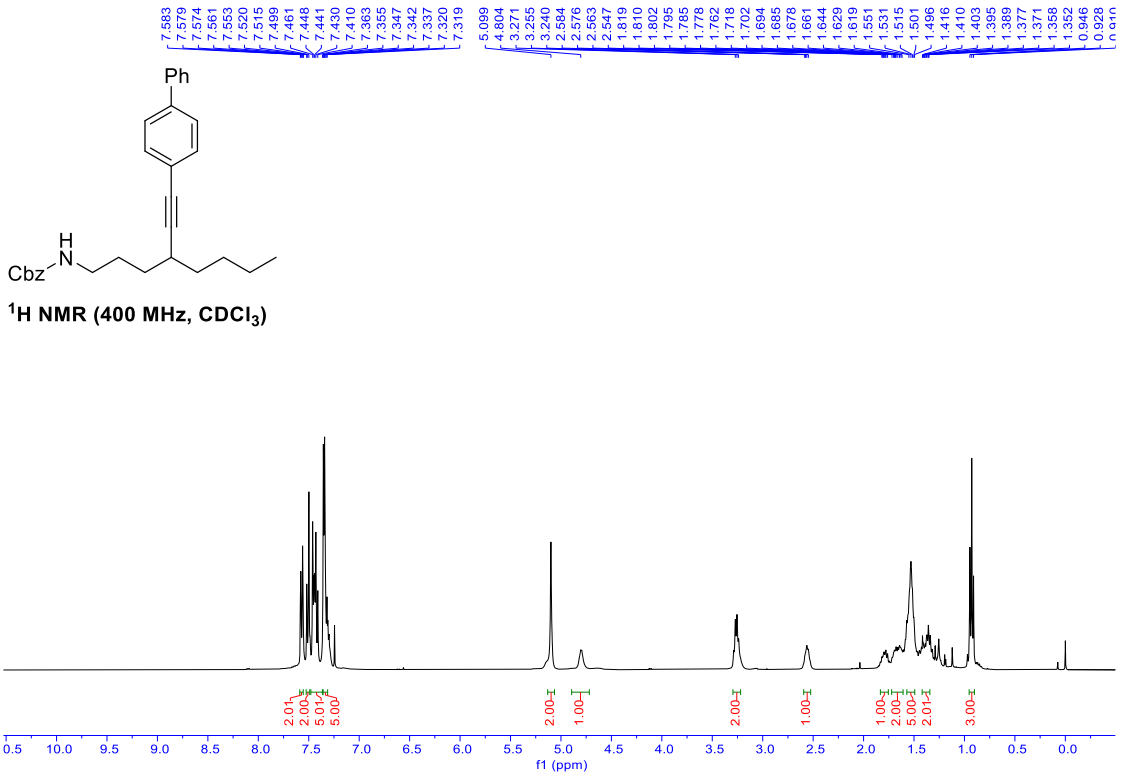
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2af



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2af

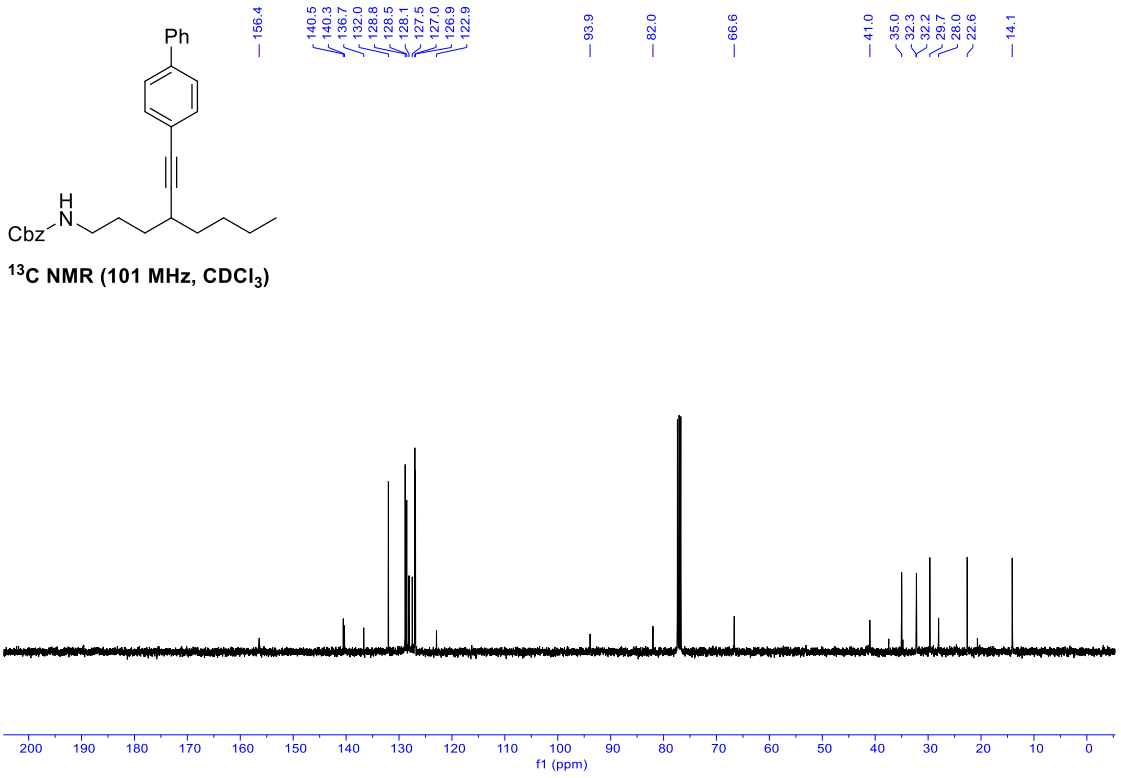


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2ag



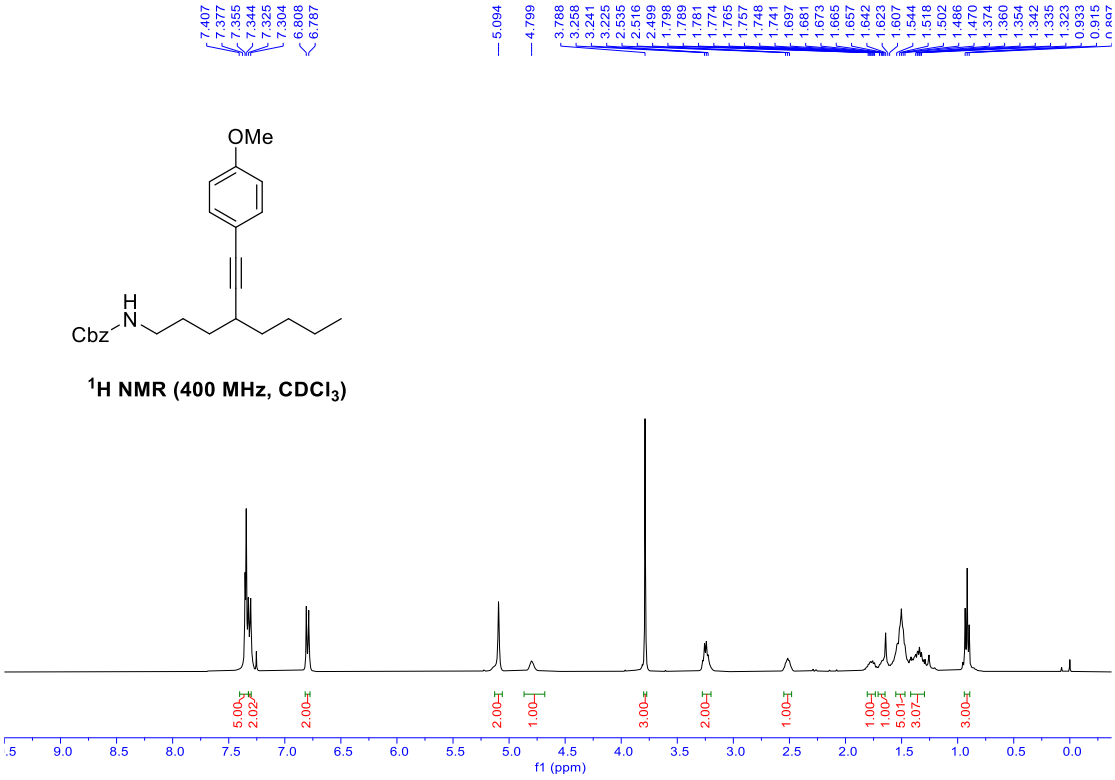
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2ag

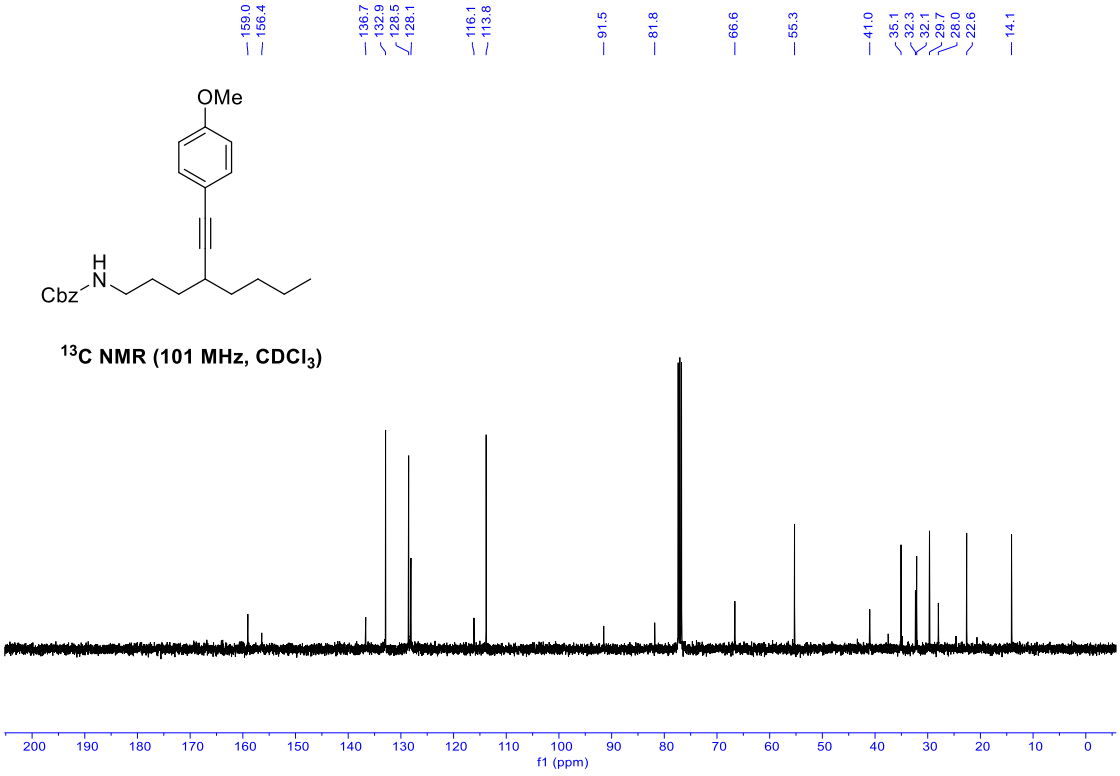


^{13}C NMR (101 MHz, $CDCl_3$)

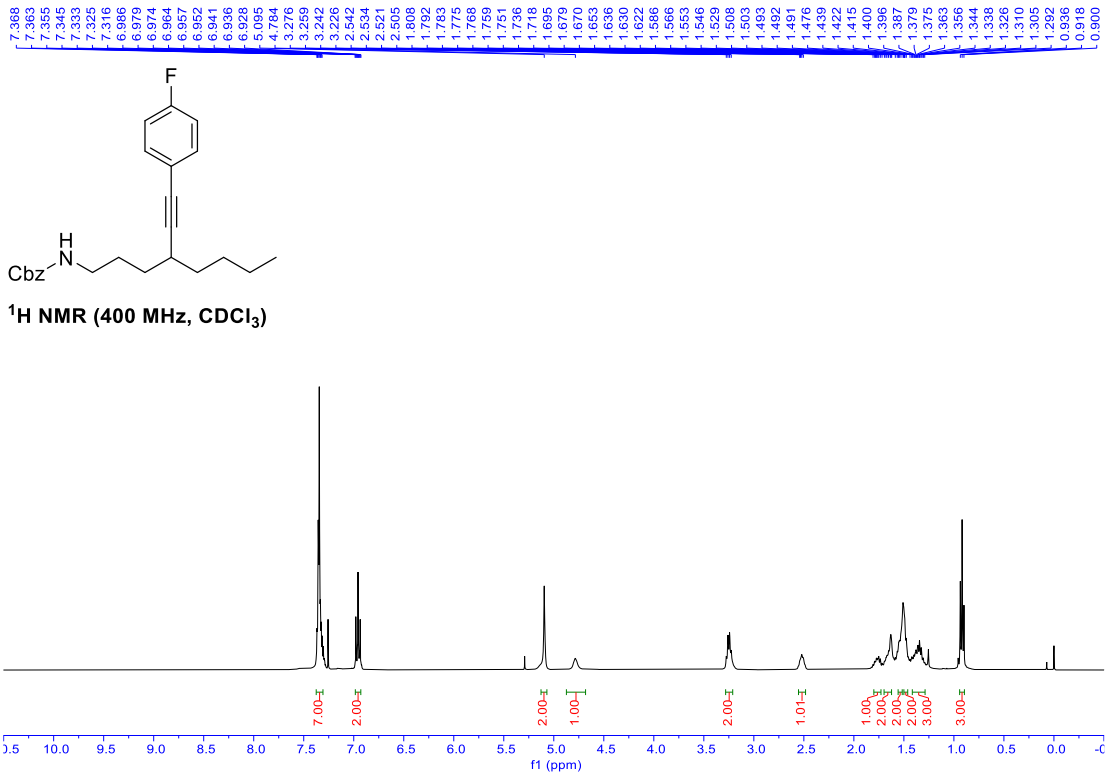
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2ah



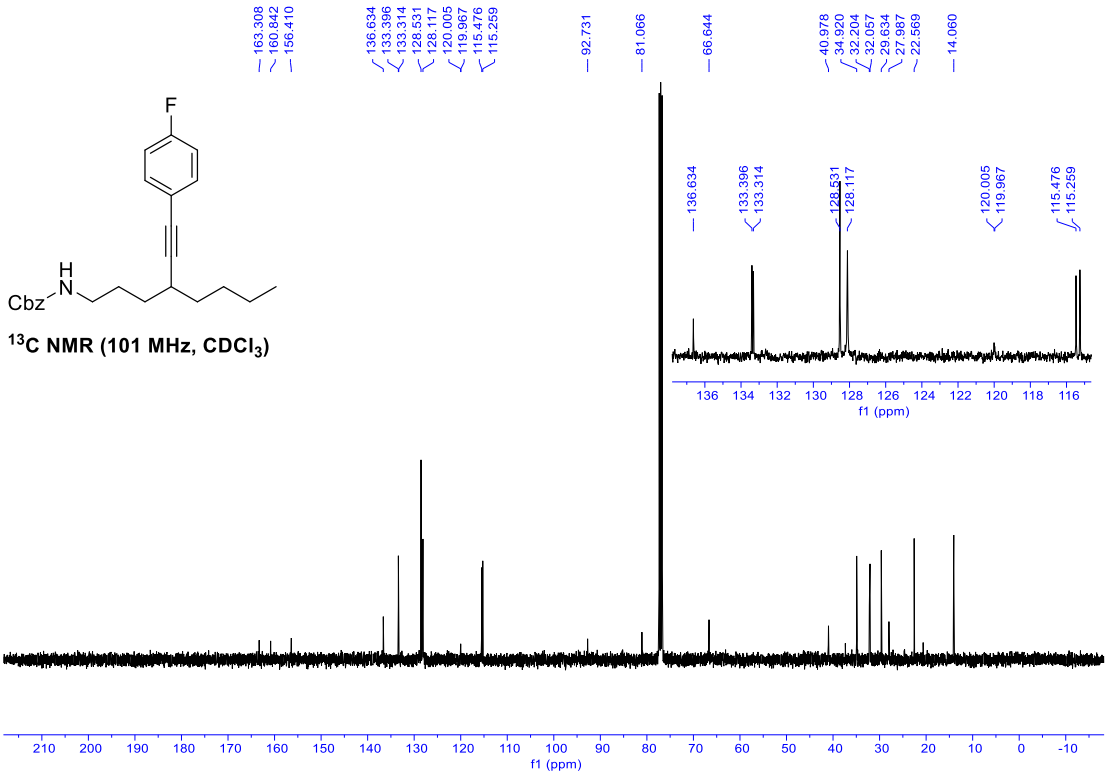
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2ah



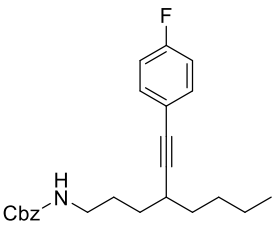
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2ai



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2ai

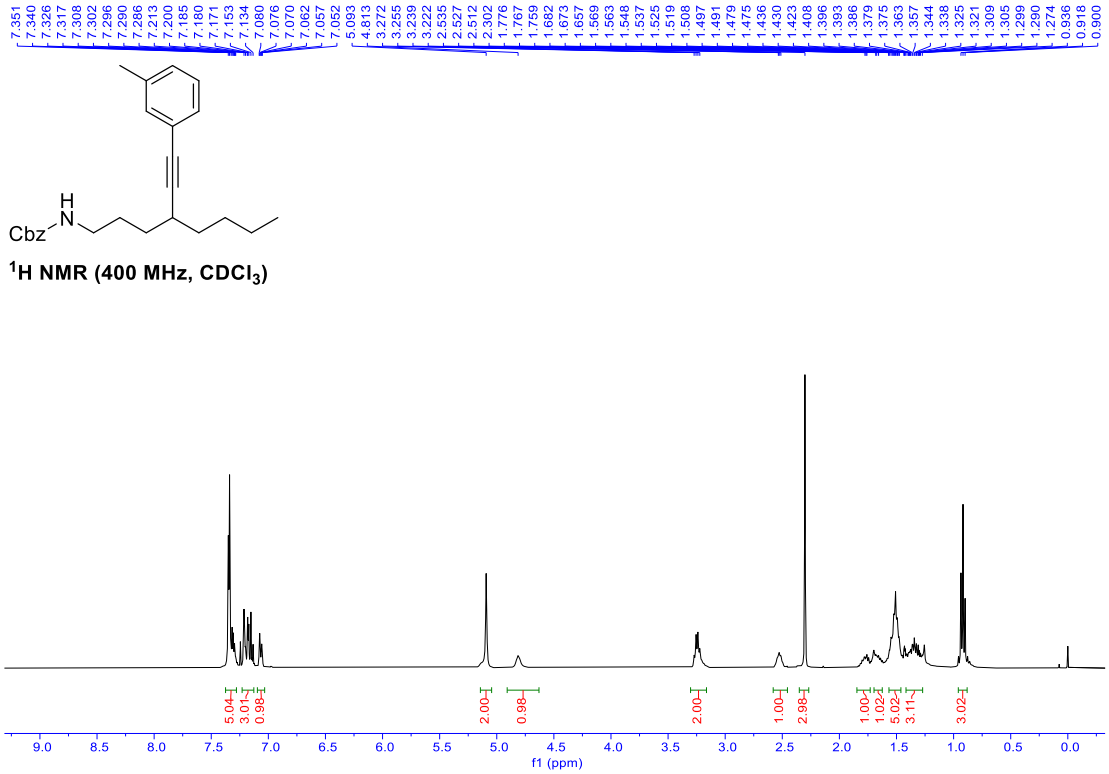


^{19}F NMR (377 MHz, $CDCl_3$) spectrum of 2ai

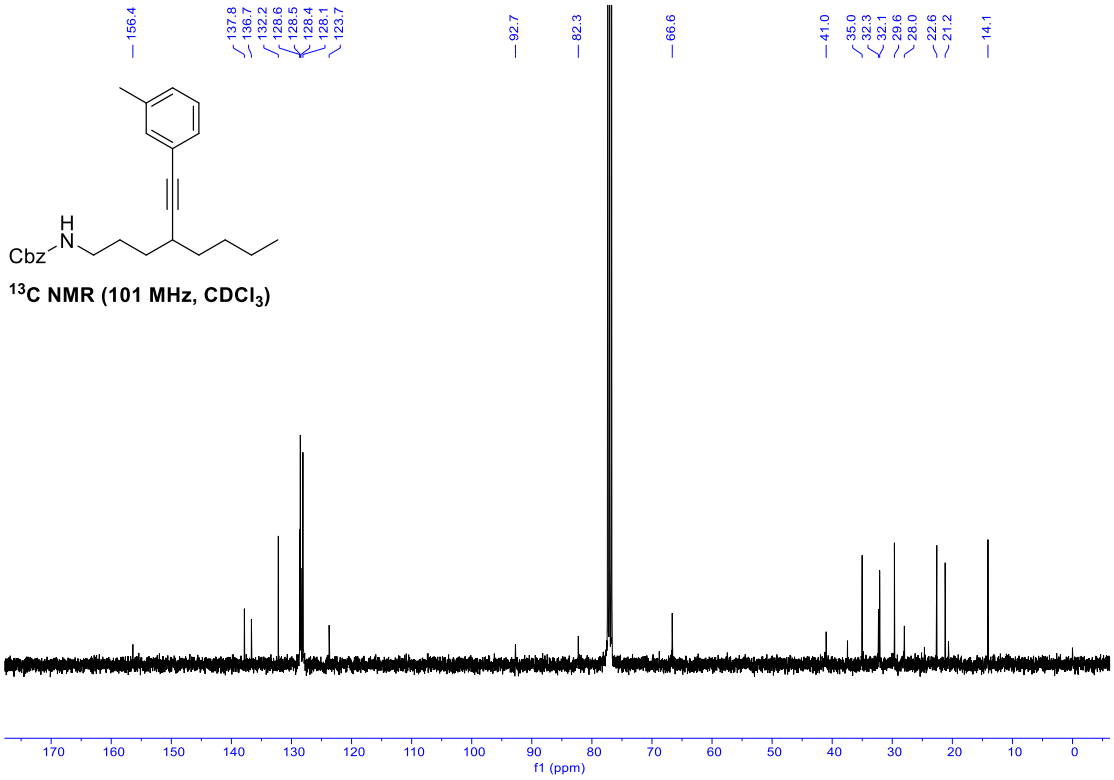


^{19}F NMR (377 MHz, $CDCl_3$)

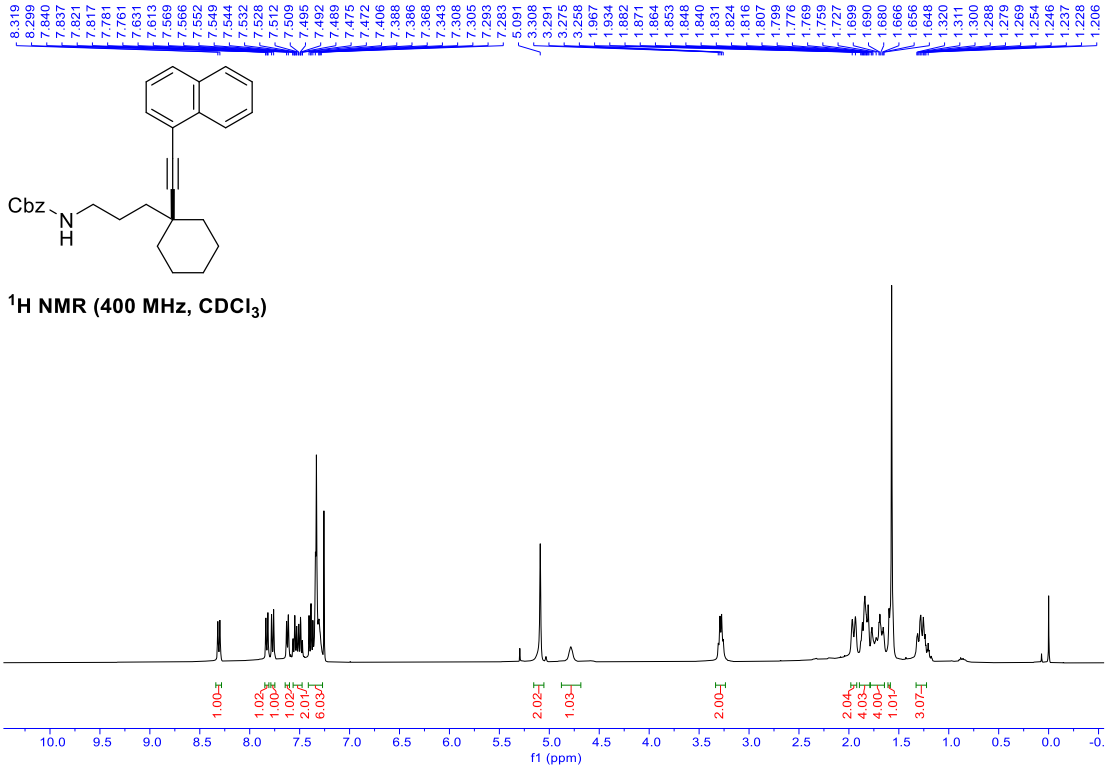
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2aj



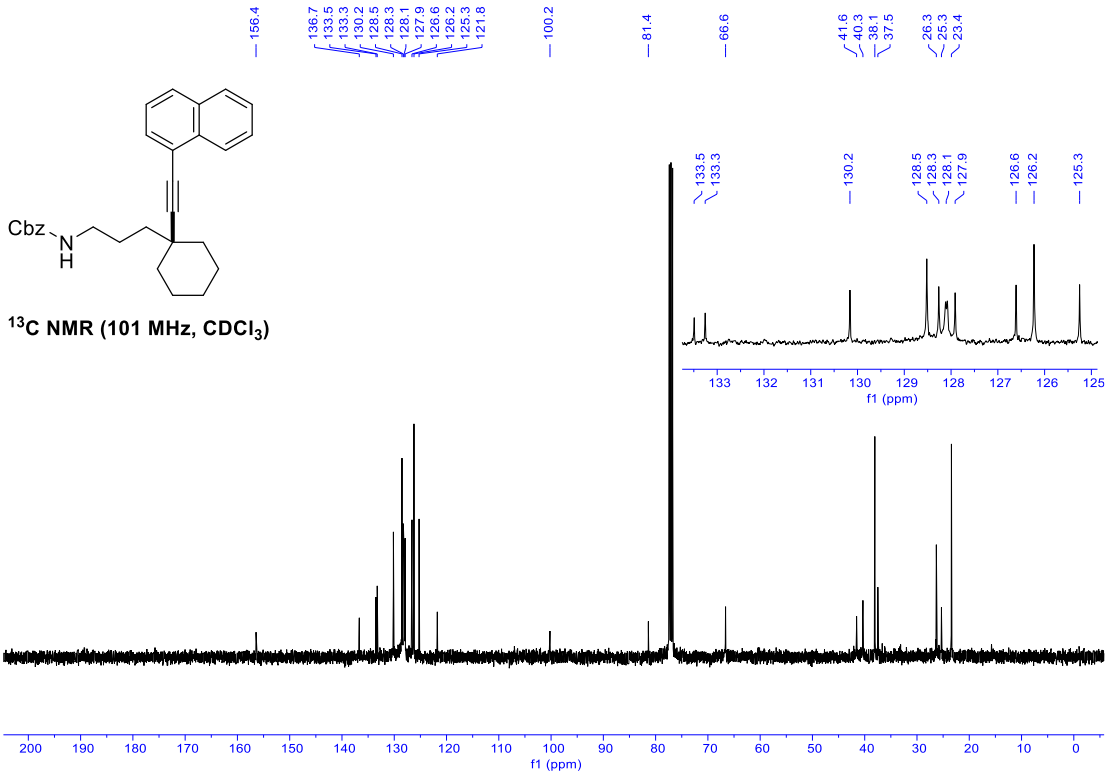
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2aj



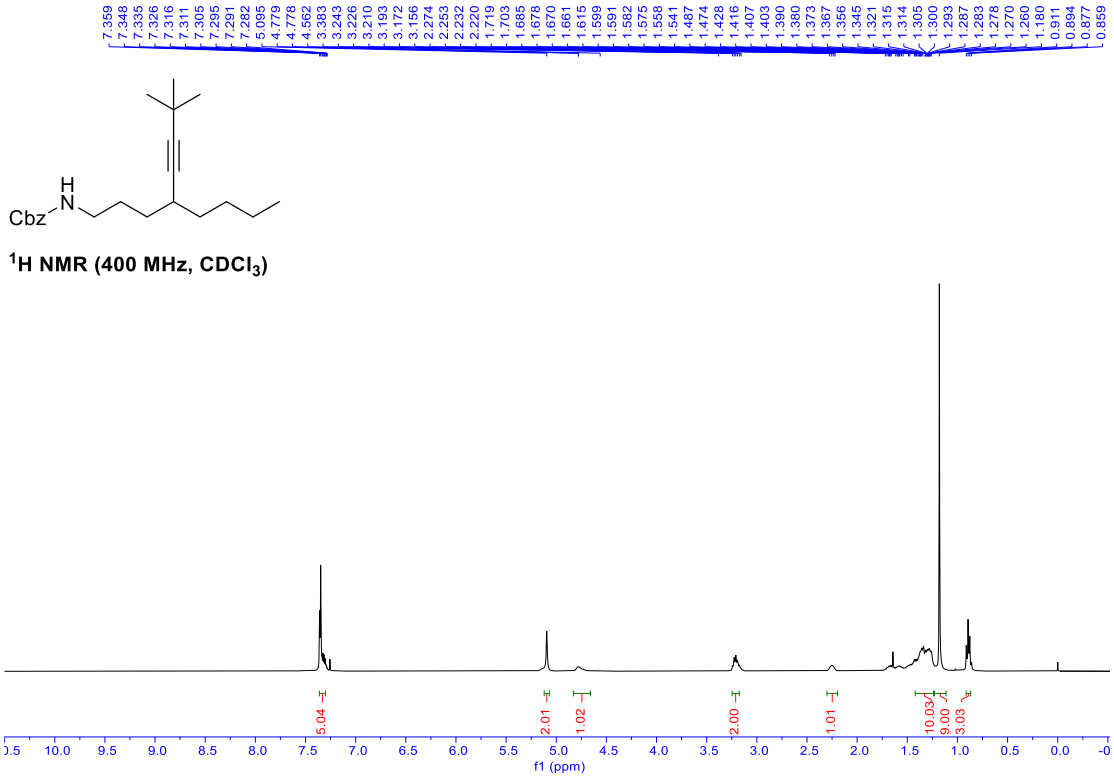
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2ak



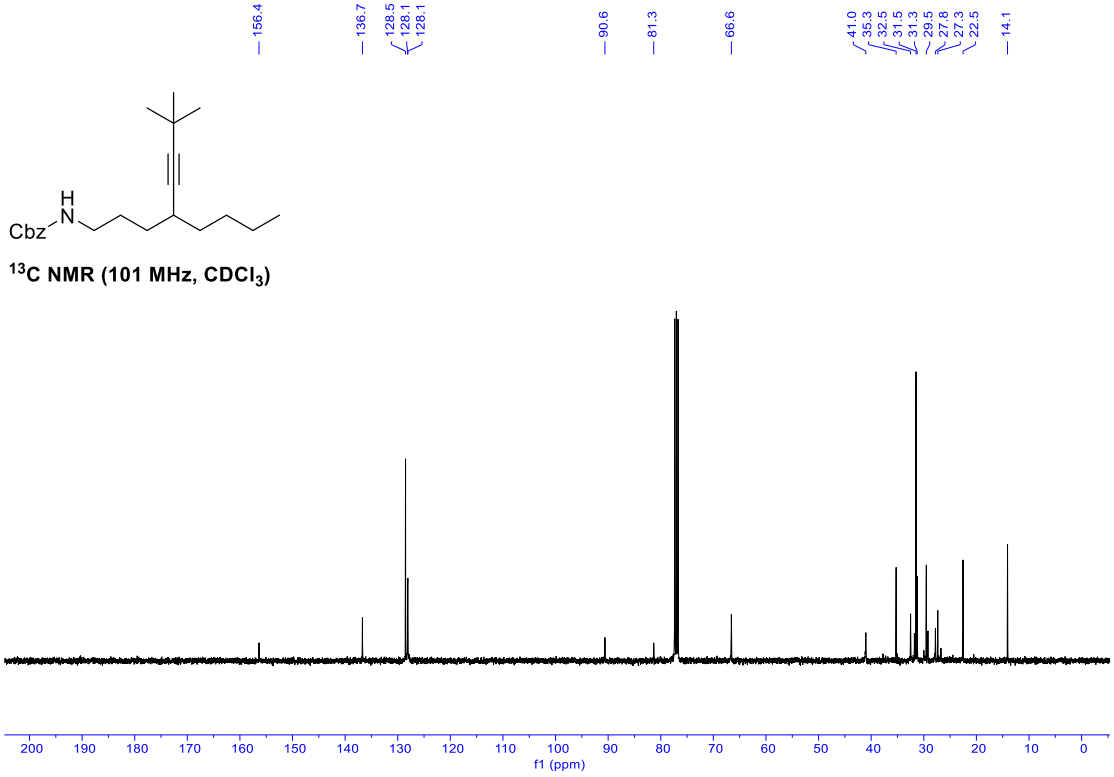
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2ak



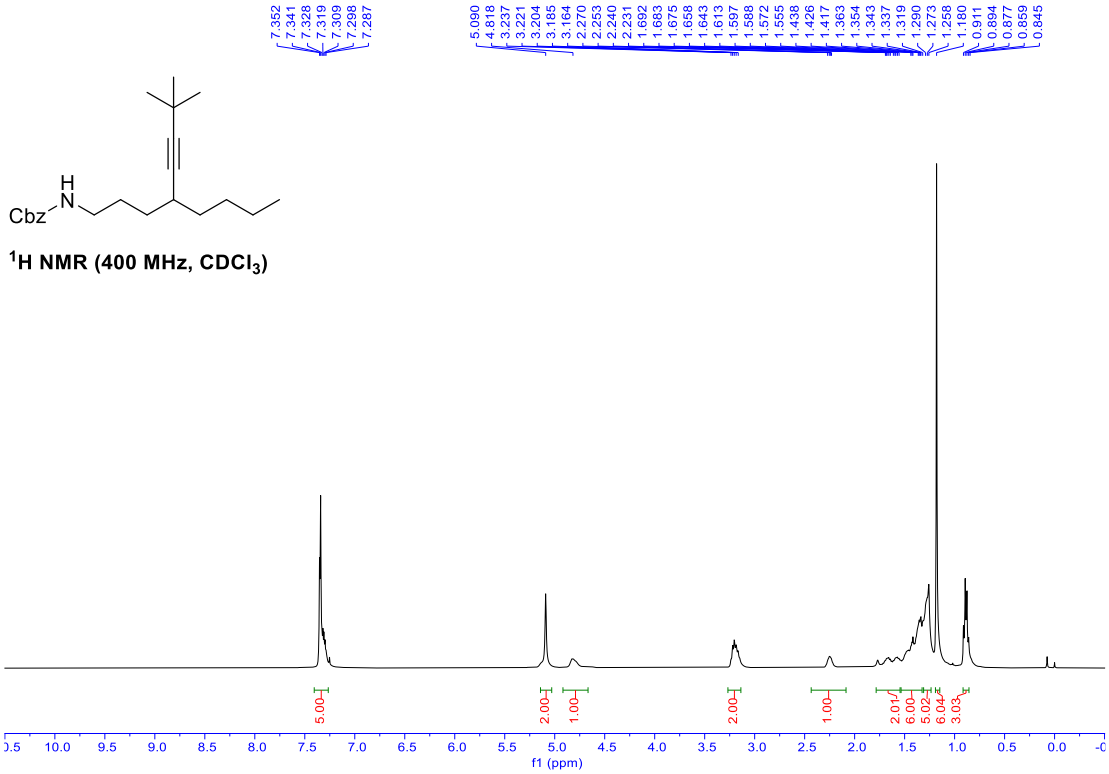
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2al



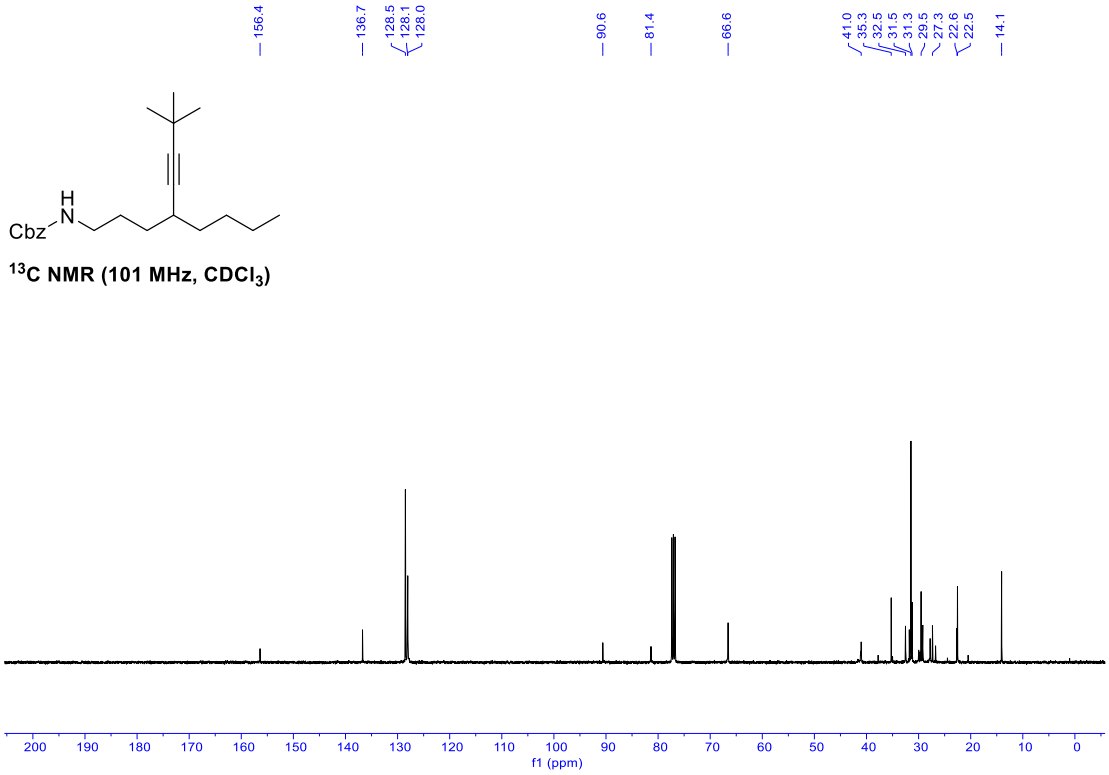
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2al



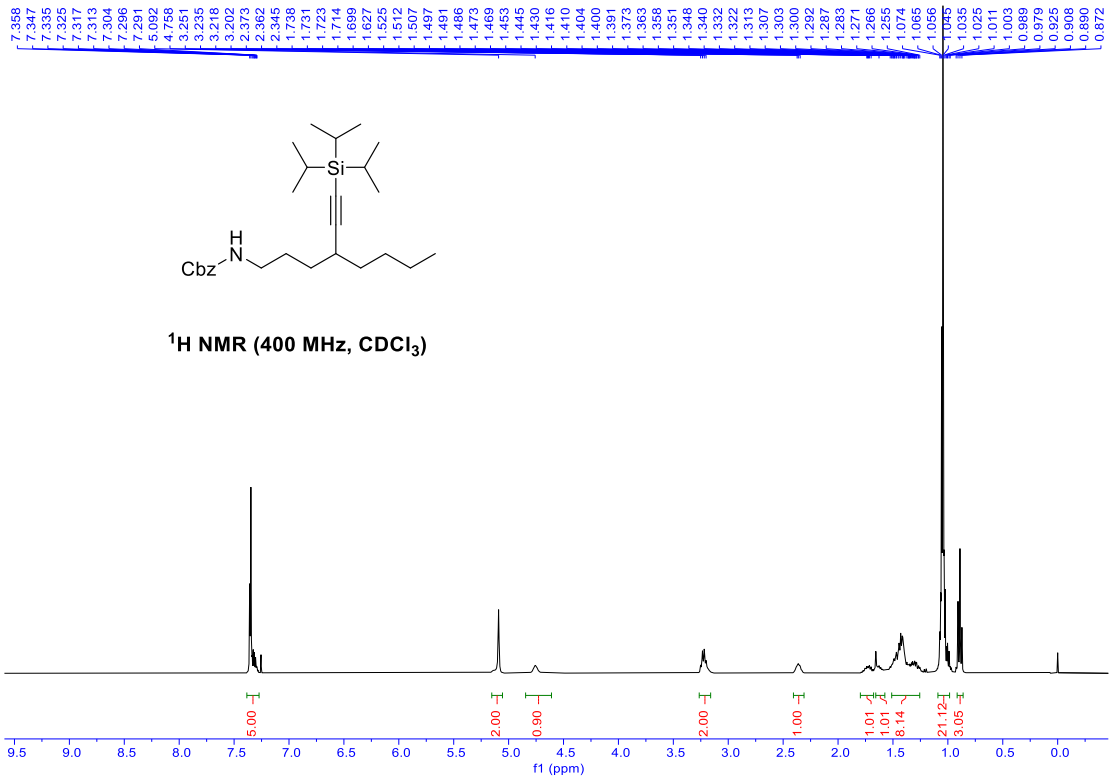
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2



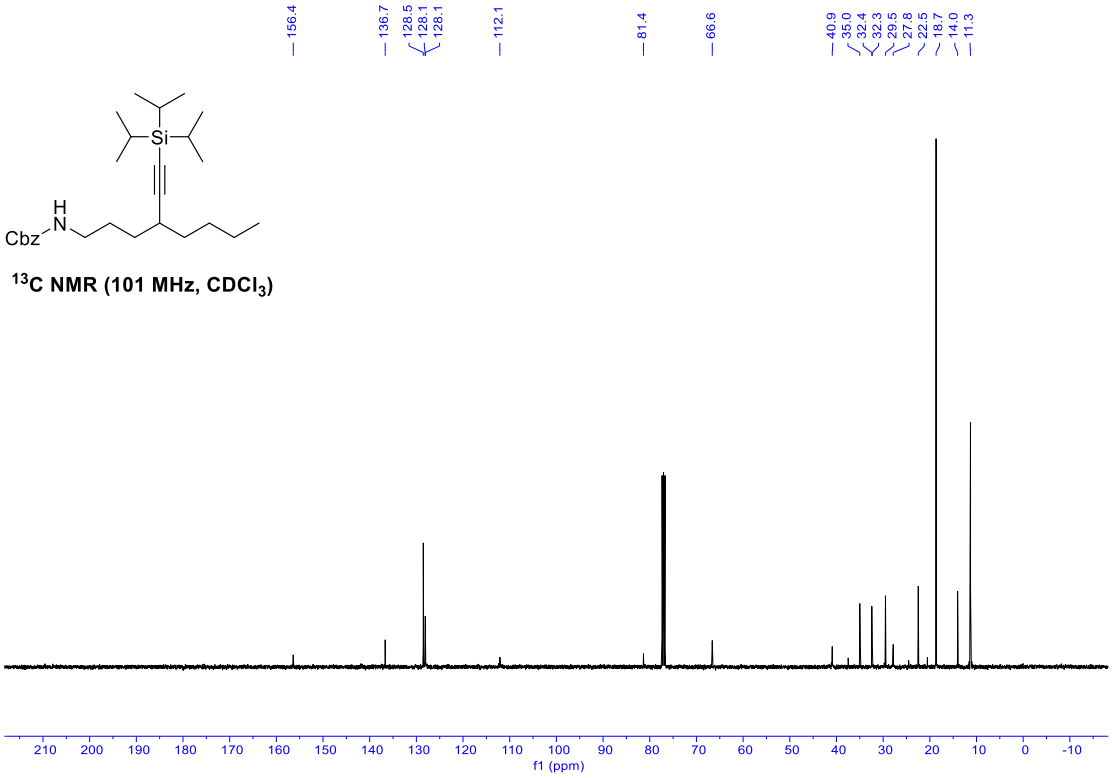
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of



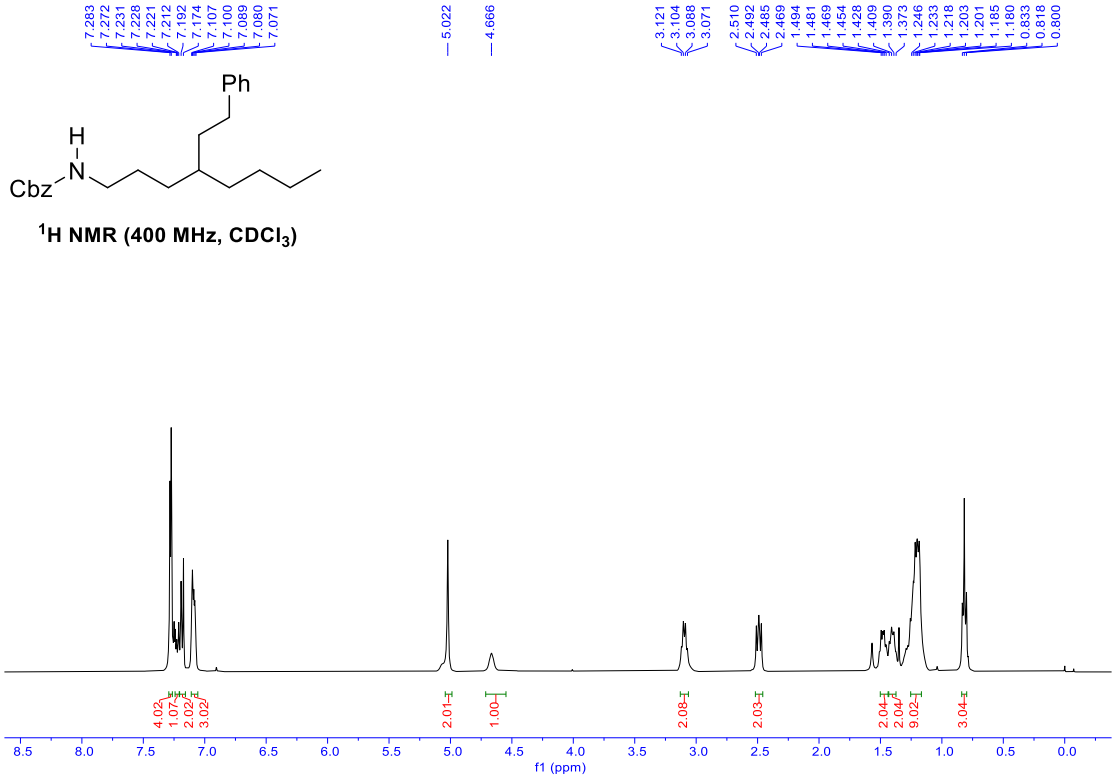
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2am



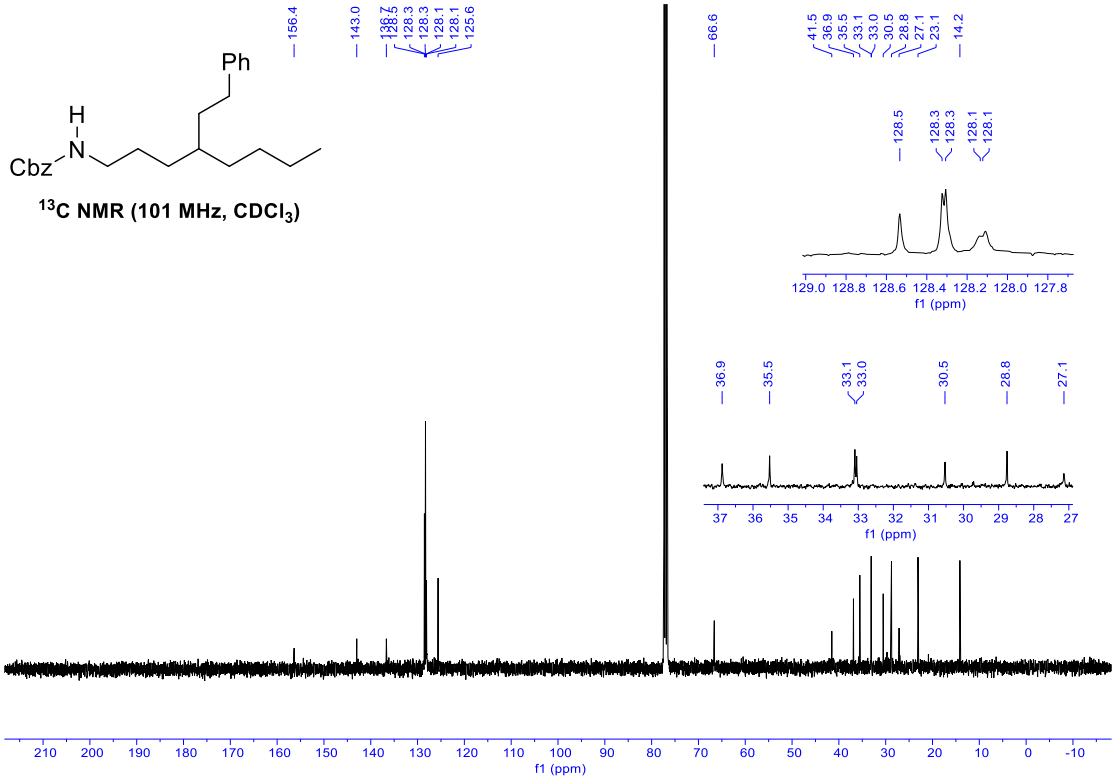
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2am



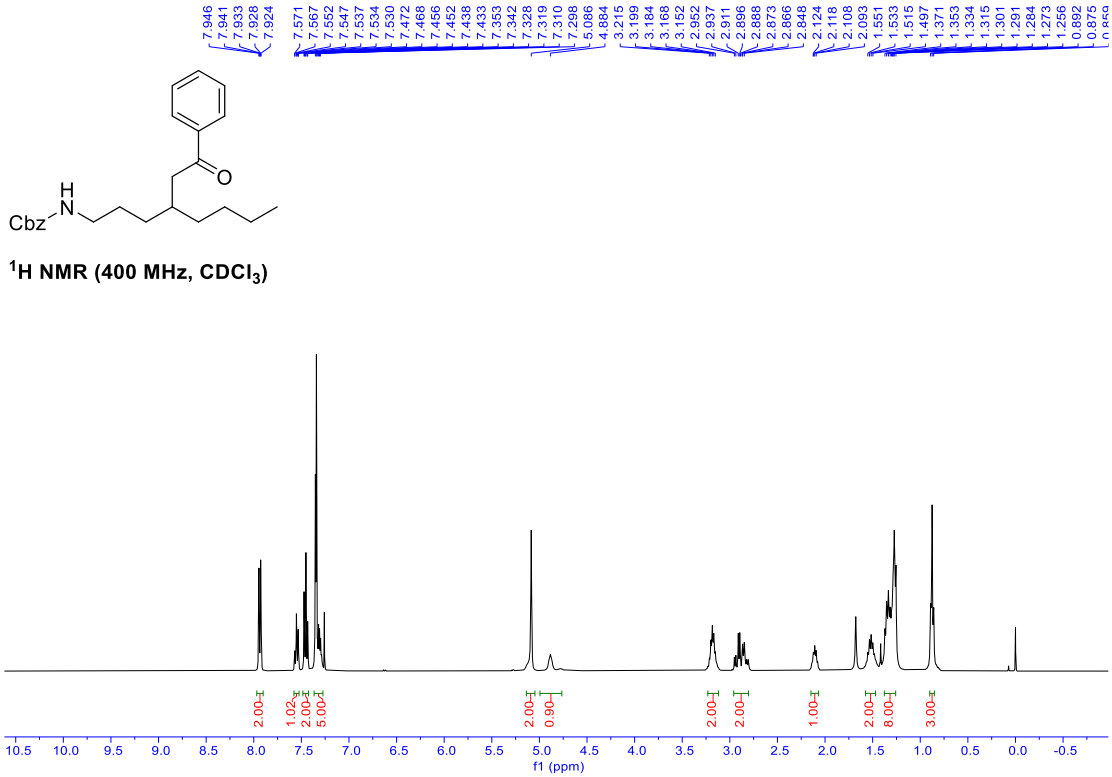
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3



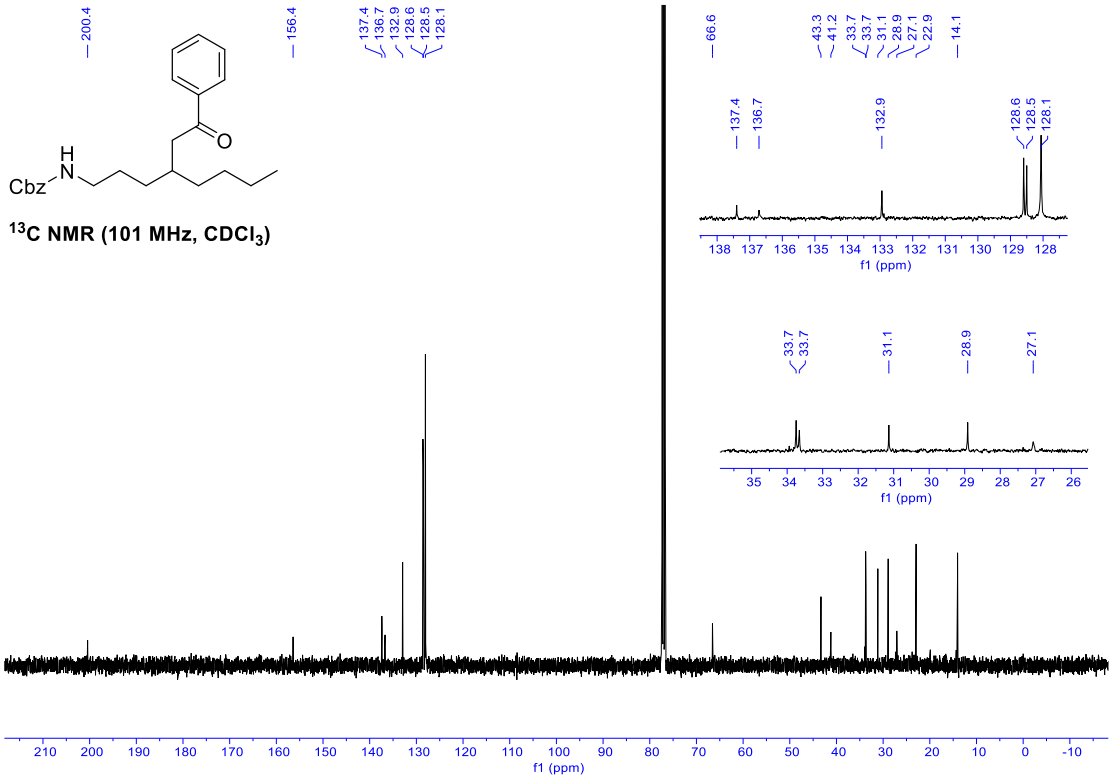
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3



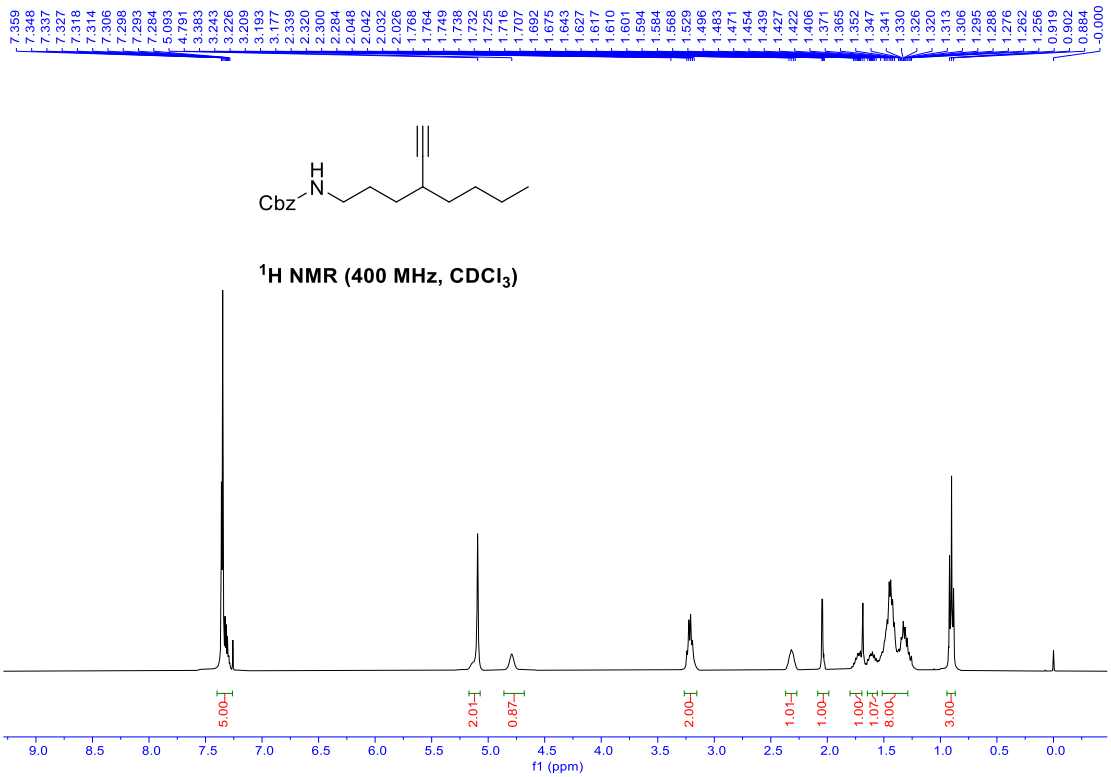
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4



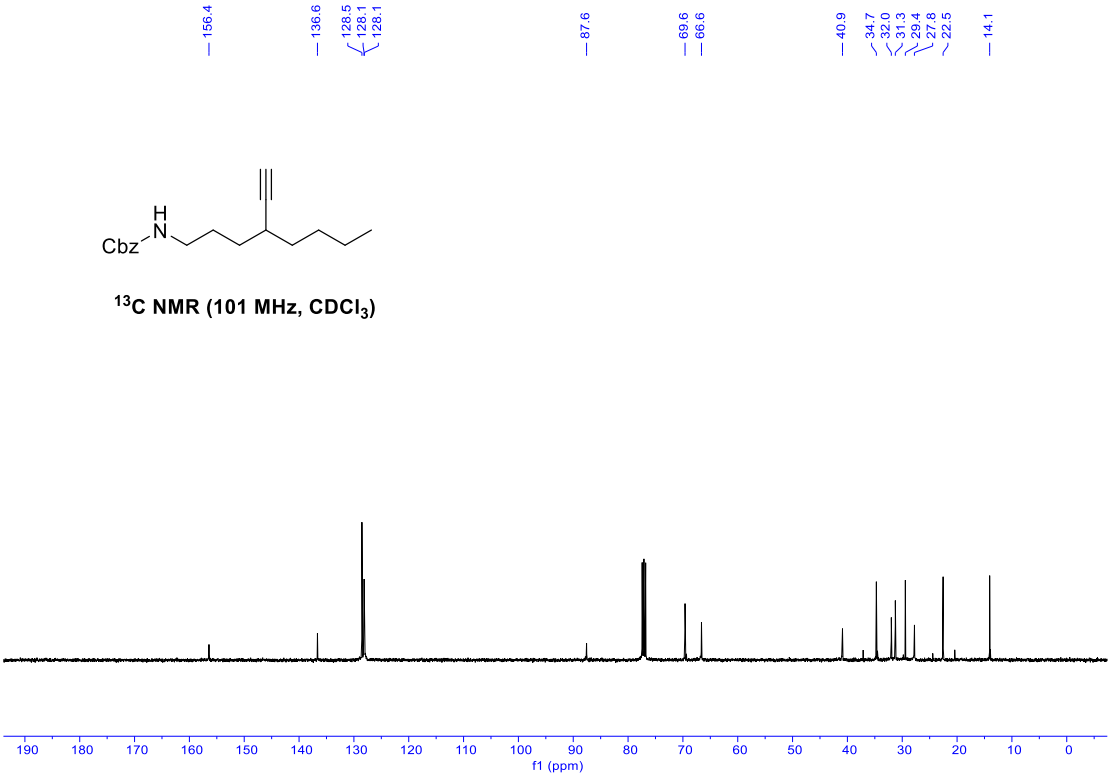
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4



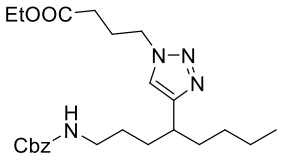
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5



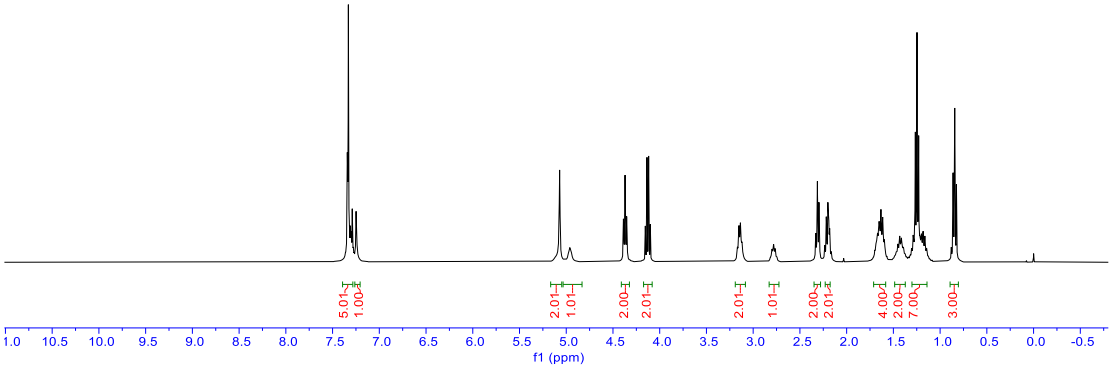
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5



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



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 6