Supporting information for

Ruthenium-catalysed selective synthesis of *mono*-deuterated terminal alkynes

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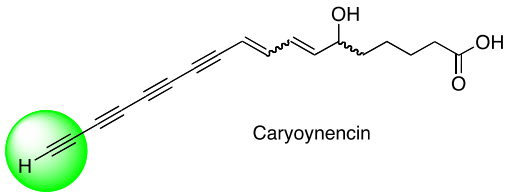
General experimental: All catalytic reactions were performed under nitrogen atmosphere. All stoichiometric reactions were performed in nitrogen atmosphere MBraun glove box. Chemicals were purchased from Acros, Sigma-Aldrich, Alfa-aesar, Spectrochem and used without further purification. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at Bruker AV-400 (^{1}H: 400 MHz, ^{13}C: 100.6 MHz, ^{31}P: 162 MHz). ^{1}H and $^{13}C\{1H\}$ NMR chemical shifts were reported in ppm downfield from tetramethyl silane. Multiplicity is abbreviated as: s, Singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplate. Assignment of spectra was done based on one dimensional (dept-135) NMR technique. IR Spectra were recorded in Perkin-Elmer FT-IR Spectrometer.

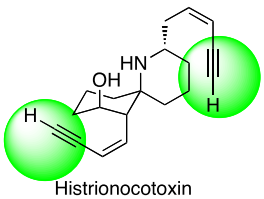
General procedure for the deuteration of terminal aromatic alkynes: To a screw cap scintillation vial terminal aromatic alkyne (0.5 mmol), catalyst (0.001 mmol), KO^{t}Bu (0.0025 mmol), 1,2-dimethoxyethane (0.5 ml) and degassed D_2O (0.2 ml) were added under nitrogen atmosphere. The reaction vial was wrapped with aluminium foil and immersed into a pre-heated oil bath. The reactions were stopped at the optimized time of deuterium incorporation and solvent was evaporated under reduced pressure. The resulted residue was extracted with dichloromethane and the combined organic phase is dried over sodium sulphate. Removal of solvent under reduced pressure provided pure products for further analysis.

General procedure for the deuteration of terminal aliphatic alkynes: To a screw cap scintillation vial terminal aliphatic alkyne (0.5 mmol), catalyst (0.0025 mmol), KO^{t}Bu (0.005 mmol), 1,2-dimethoxyethane (1 ml) and degassed D_2O (0.25 ml) were added under nitrogen atmosphere. Vial was covered with aluminium foil and immersed into a pre-heated oil bath. The reactions were stopped after 24 h and the solvent was evaporated under reduced pressure. The resulted residue was extracted with dichloromethane and combined organic phase is dried over sodium sulphate. Removal of solvent under reduced pressure provided pure products for further analysis.

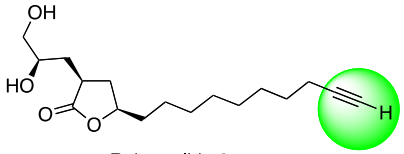
a)



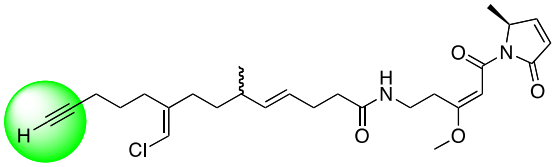
Caryoynencin



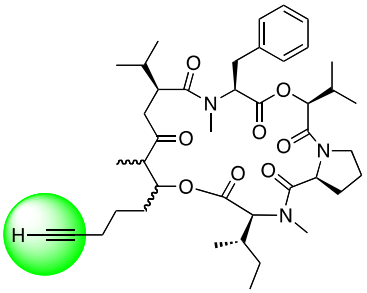
Histrionocotoxin



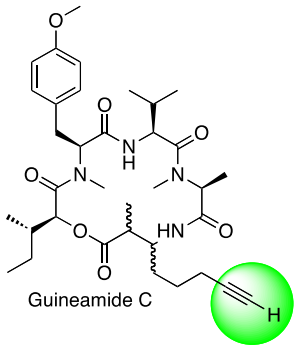
Rubrynolide 2



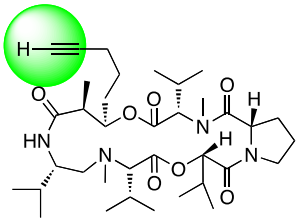
Jamicamide B



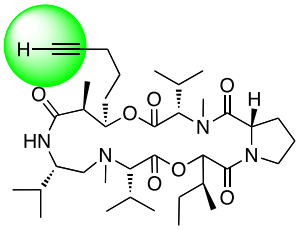
Antanapeptin A



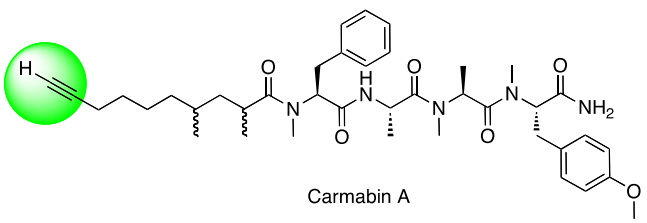
Guineamide C



Veragunamide H



Veragunamide C



Carmabin A

b)

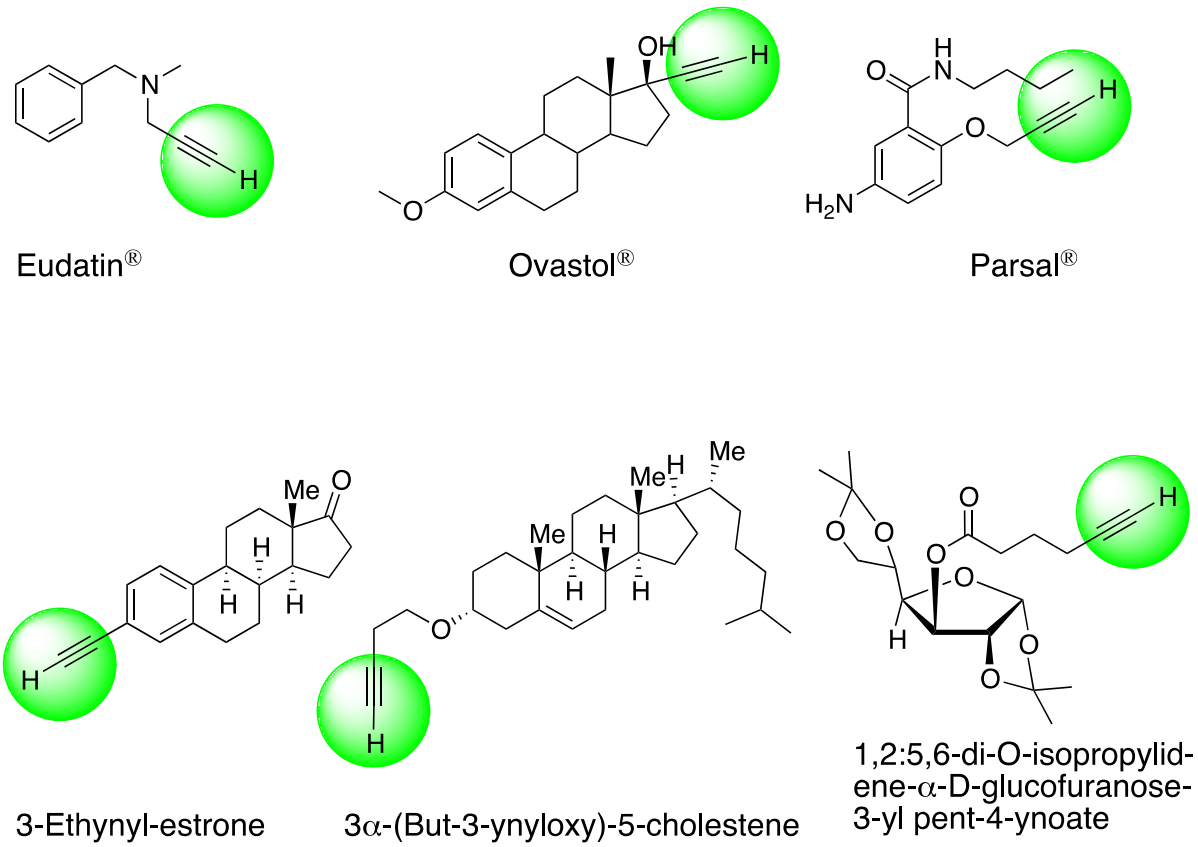
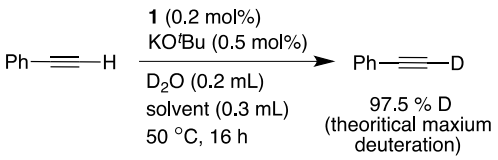


Fig. S1. Representative natural products (a)[1,2] drugs and bioactive molecules (b),[3] containing terminal alkyne functionality.

Table S1. Optimization of aryl terminal alkyne deuteration using phenyl acetylene.

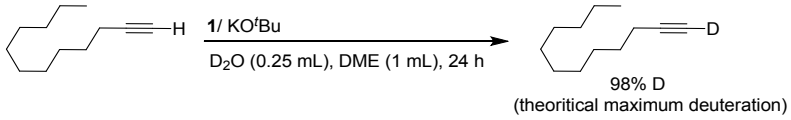


Entry	Solvent	% Deuteration
1	Acetone	43
2	THF	95
3	1,4-dioxane	92

4	**DME**	**97**
5[a,b,d]	DME	10
6[c,d]	DME	7

[a] Reaction performed without using catalyst under otherwise similar conditions.
[b] Reaction carried out in the absence catalyst.
[c] Reaction carried out in the absence of both catalyst and base.
[d] Data verified from two independent experiments.

Table S2. Optimization of aliphatic terminal alkyne deuteration using dodec-1-yne.

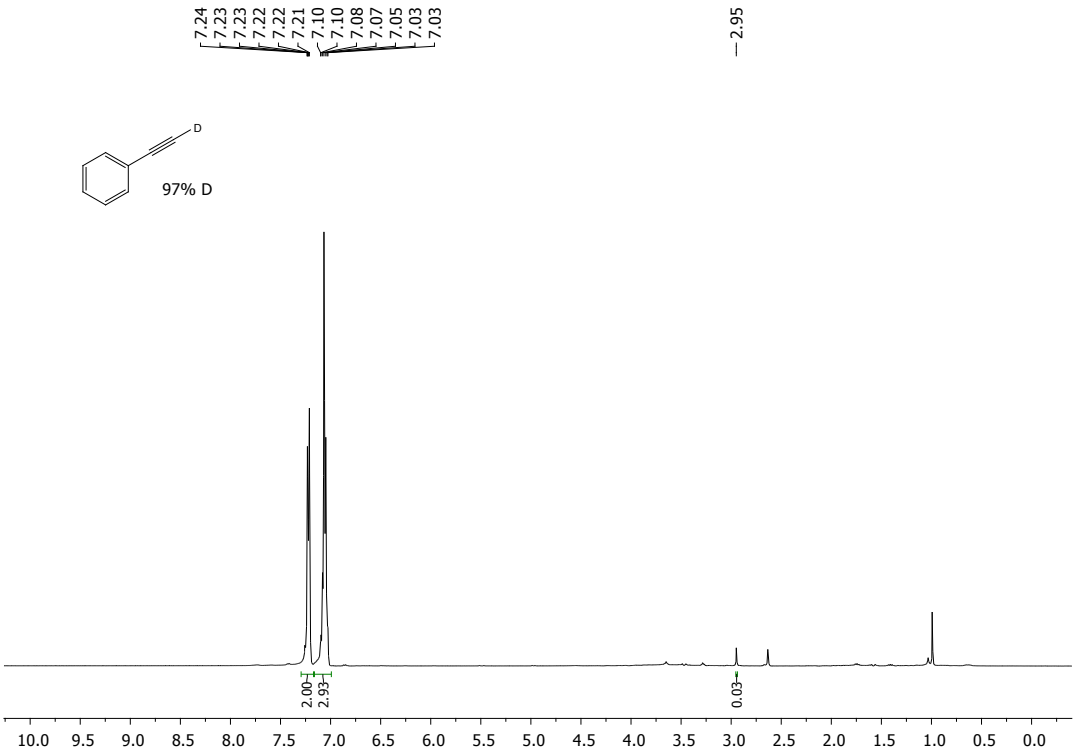


Entry	Catalyst **1** (mol%)	KO^{t}Bu (mol%)	Temp (°C)	% Deuteration
1	0.2	0.5	50	27
2	0.2	1	50	30
3	0.2	1	75	84
4	**0.5**	**1**	**90**	**96**
5[a,b,d]	-	1	90	19
6[c,d]	-	-	90	15

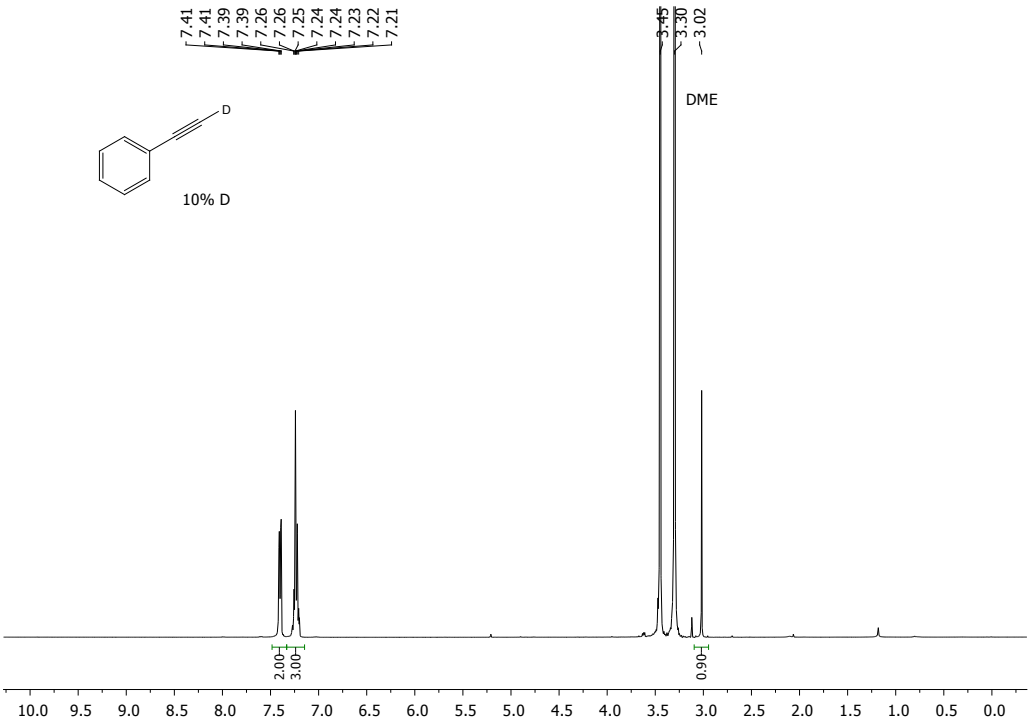
[a] Reaction performed without using catalyst under otherwise similar conditions.
[b] Reaction carried out in the absence catalyst.
[c] Reaction carried out in the absence of both catalyst and base.
[d] Data verified from two independent experiments.

Optimization studies: NMR spectra of deuterated alkynes:

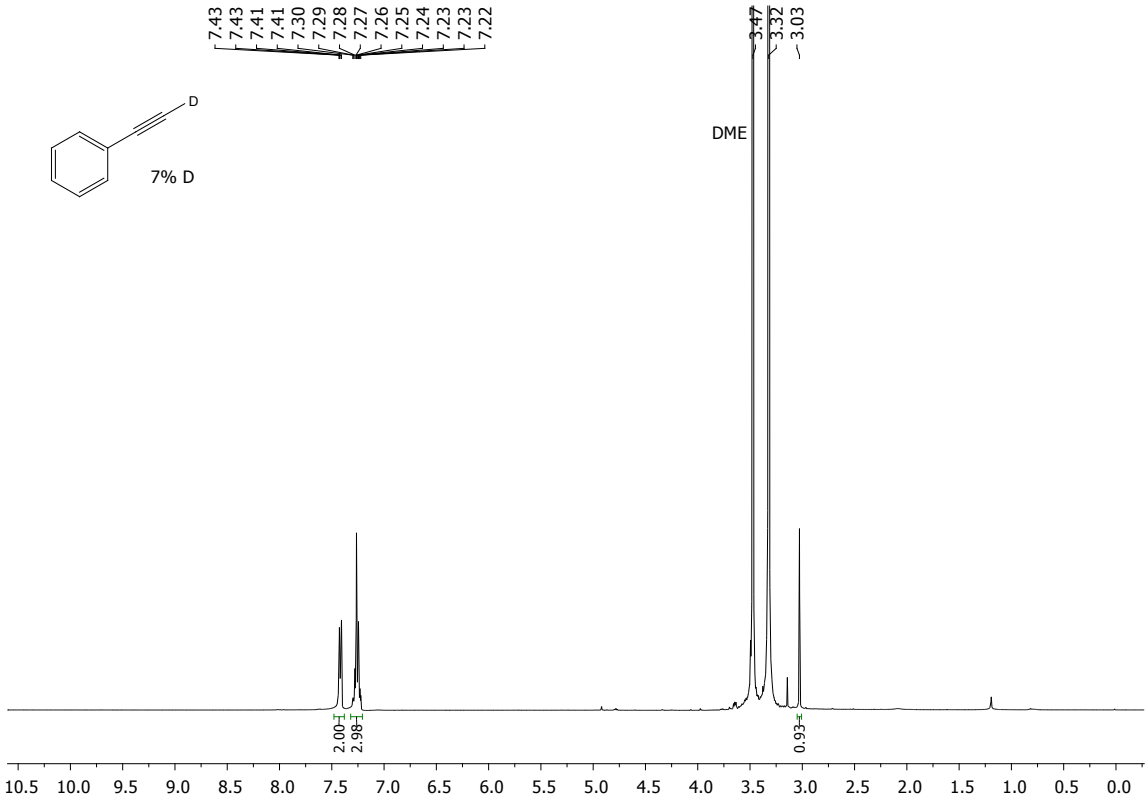
^{1}H NMR spectrum of optimization experiment with phenylacetylene-d1 (400 MHz, $CDCl_3$): (Table S1: Entry 4)



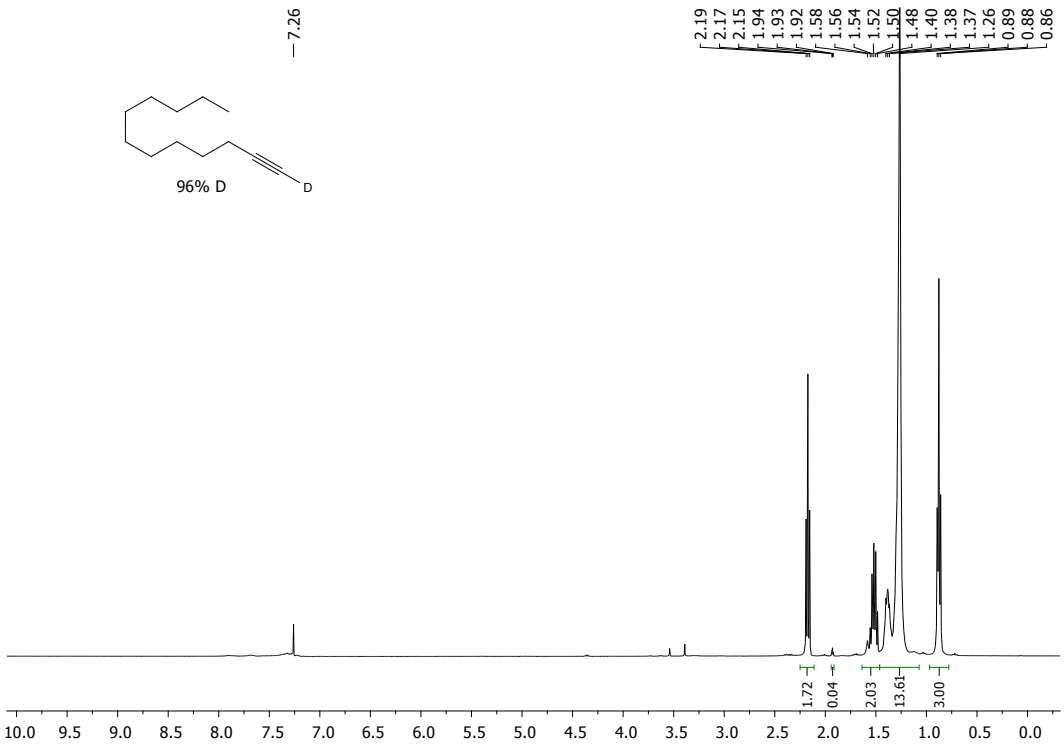
^{1}H NMR spectrum of controlled experiment (without catalyst) with phenylacetylene-d1 (400 MHz, $CDCl_3$): (Table S1: Entry 5)



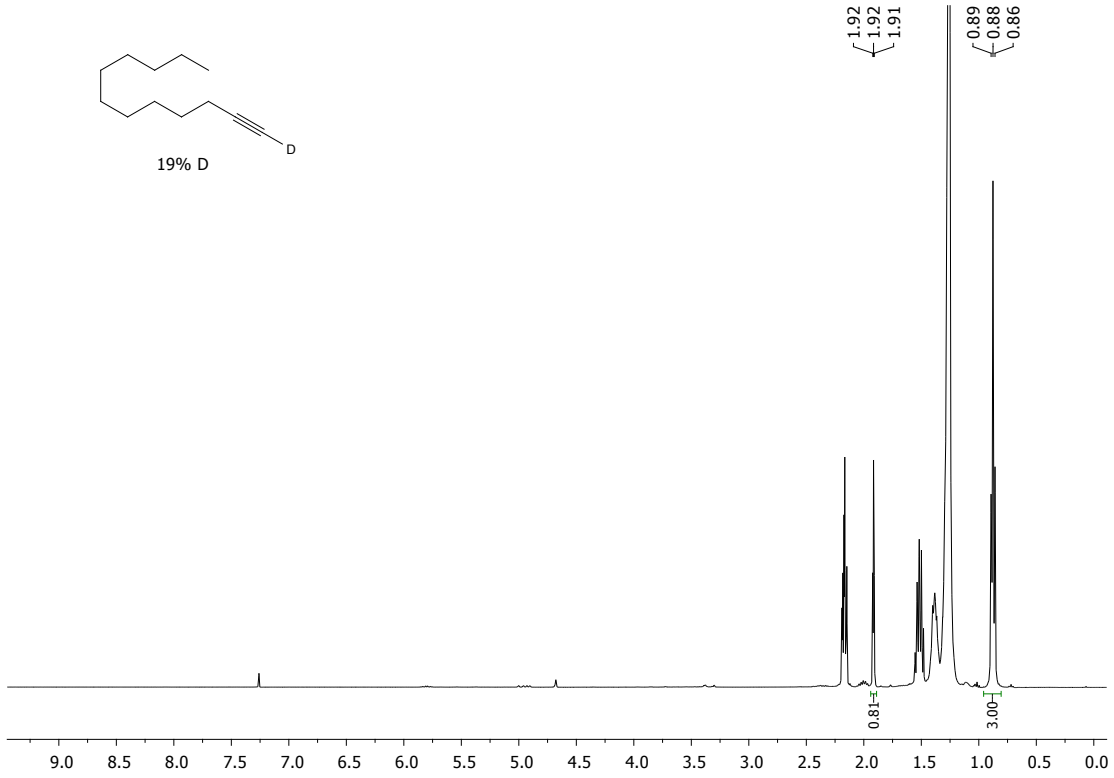
^{1}H NMR spectrum of controlled experiment (without catalyst and base) with phenylacetylene-d1 (400 MHz, $CDCl_3$): (Table S1: Entry 6)



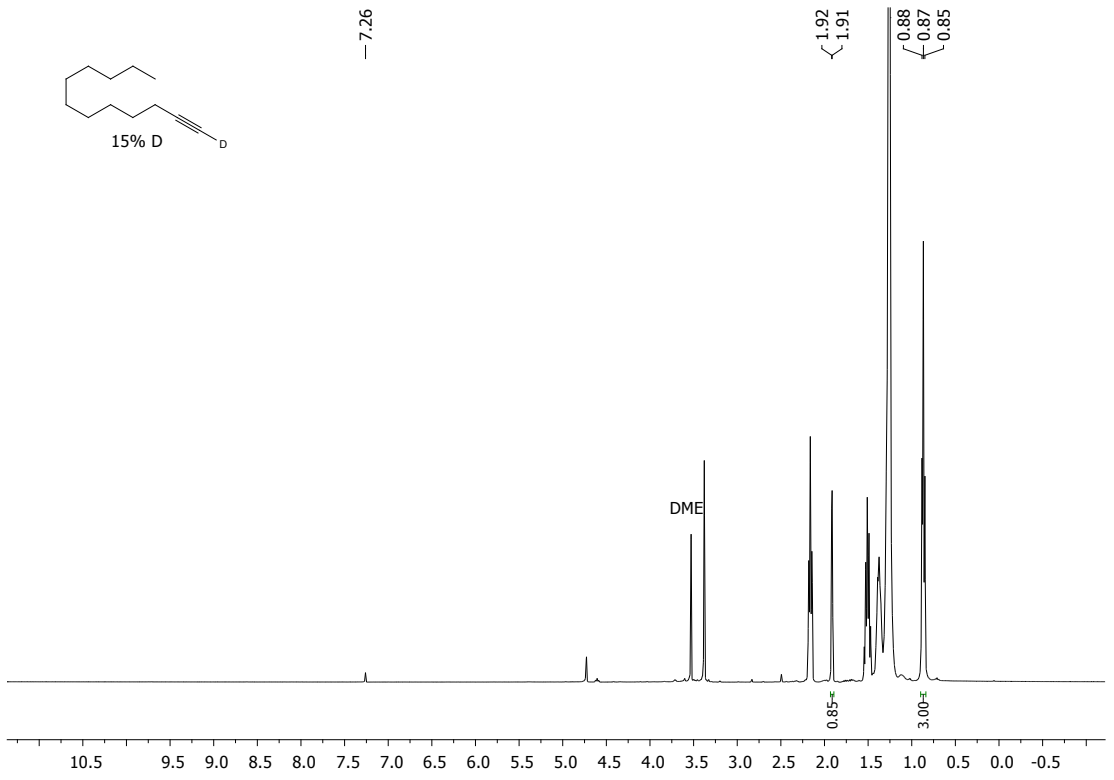
^{1}H NMR spectrum of optimization experiment (without catalyst) with dodec-1-yne-d1 (400 MHz, $CDCl_3$): (Table S2: Entry 4)



^{1}H NMR spectrum of optimization experiment (without catalyst) with dodec-1-yne-d1 (400 MHz, $CDCl_3$): (Table S2: Entry 5)

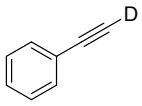


^{1}H NMR spectrum of optimization experiment (without catalyst) with dodec-1-yne-d1 (400 MHz, $CDCl_3$): (Table S2: Entry 6)

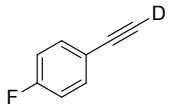


Spectral data of deuterated terminal alkynes:

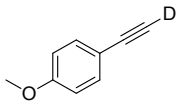
Ethynylbenzene-d1:[4] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24-7.21 (m, 2H, ArC*H*), 7.08-7.03 (m, 3H, ArC*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.29 (Ar*C*H), 127.96 (Ar*C*H), 127.58 (Ar*C*H), 121.63 (quat-*C*), 82.47-82.32 (t, quat-*C*), 76.97-76.20 (t).



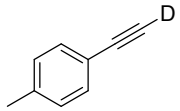
1-ethynyl-4-fluorobenzene-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50-7.45 (m, 2H, ArC*H*), 7.04-6.99 (m, 2H, ArC*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.69 (quat-*C*), 133.72 (Ar*C*H), 118.23 (quat-*C*), 115.10 (Ar*C*H), 83.24-83.05 (t, quat-*C*), 76.78-75.97 (t).



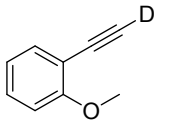
1-ethynyl-4-methoxybenzene-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 (d, *J* = 8 Hz, 2H, ArC*H*), 6.84 (d, *J* = 8 Hz, 2H, ArC*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.02 (quat-*C*), 133.67 (Ar*C*H), 114.25 (quat-*C*), 114.03 (Ar*C*H), 83.39-83.24 (t, quat-*C*), 76.05-75.29 (t), 55.33 (O*C*H_3).



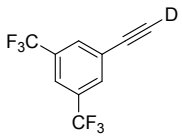
1-ethynyl-4-methylbenzene-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 (d, *J* = 8 Hz, 2H, ArC*H*), 7.15 (d, *J* = 8 Hz, 2H, ArC*H*), 2.38 (s, 3H, CH_3)^{13}C NMR (101 MHz, $CDCl_3$) δ 139.01 (quat-*C*), 132.11 (Ar*C*H), 129.16 (Ar*C*H), 119.15 (quat-*C*), 83.58-83.42 (t, quat-*C*), 76.74-76.97 (t), 21.55 (*C*H_3).



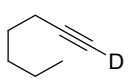
1-ethynyl-2-methoxybenzene-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48-7.45 (m, 1H, ArC*H*), 7.34-7.30 (m, 1H, ArC*H*), 6.93-6.88 (m, 2H, ArC*H*), 3.90 (s, 3H, OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.09 (quat-*C*), 134.35 (Ar*C*H), 129.43 (Ar*C*H), 124.10 (Ar*C*H), 111.90 (quat-*C*), 111.12 (Ar*C*H), 83.32-83.19 (t, quat-*C*), 76.15-75.36 (t), 55.20 (O*C*H_3).



1-ethynyl-3,5-bis(trifluoromethyl)benzene-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (s, 2H, ArC*H*), 7.84 (s, 1H, ArC*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.22 (Ar*C*H), 132.18 (quat-*C*, *J* = 33.03 Hz), 124.62 (Ar*C*H), 122.95 (*C*F_3, *J* = 273.71 Hz), 122.45 (quat-*C*), 81.05-80.25 (t, quat-*C*), 78.11-77.36 (t).

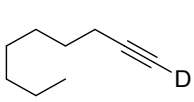


hept-1-yne-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.18 (t, *J* = 8 Hz, 2H, CH_2), 1.55-1.40 (m, 2H, CH_2), 1.39-1.27 (m, 4H, CH_2), 0.90 (t, *J* = 8 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ

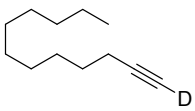


84.58-84.43 (t, quat-*C*), 68.29-67.54 (t), 31.08 (*C*H_2), 28.34 (*C*H_2), 22.31 (*C*H_2), 18.48 (*C*H_2), 14.08 (*C*H_3).

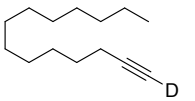
non-1-yne-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.17 (t, *J* = 8 Hz, 2H, C*H*$_2$), 1.52 (m, 2H, C*H*$_2$), 1.29-1.27 (m, 8H, C*H*$_2$), 0.88 (t, *J* = 8 Hz, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.50-84.35 (t, quat-*C*), 68.29-67.53 (t), 31.86 (*C*H_2), 28.92 (*C*H_2), 28.86 (*C*H_2), 28.65 (*C*H_2), 27.75 (*C*H_2), 18.50 (*C*H_2), 14.19 (*C*H_3).



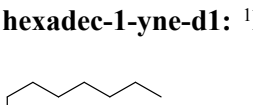
dodec-1-yne-d1:[4] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.17 (t, *J* = 8 Hz, 2H, C*H*$_2$), 1.58-1.50 (m, 2H, C*H*$_2$), 1.48-1.26 (m, 14H, C*H*$_2$), 0.88 (t, *J* = 8 Hz, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.46-84.31 (t, quat-*C*), 68.27-67.54 (t), 32.04 (*C*H_2), 29.78 (*C*H_2), 29.66 (*C*H_2), 29.46 (*C*H_2), 29.26 (*C*H_2), 28.91 (*C*H_2), 28.65 (*C*H_2), 22.82 (*C*H_2), 18.50 (*C*H_2), 14.22 (*C*H_3).



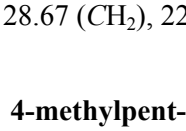
tetradec-1-yne-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.17 (t, *J* = 8 Hz, 2H, C*H*$_2$), 1.54-1.50 (m, 2H, C*H*$_2$), 1.48-1.26 (m, 18H, C*H*$_2$), 0.88 (t, *J* = 8 Hz, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.42-84.27 (t, quat-*C*), 68.28-67.53 (t), 32.09 (*C*H_2), 29.83 (*C*H_2), 29.81 (*C*H_2), 29.79 (*C*H_2), 29.69 (*C*H_2), 29.52 (*C*H_2), 29.29 (*C*H_2), 28.93 (*C*H_2), 28.68 (*C*H_2), 22.85 (*C*H_2), 18.51 (*C*H_2), 14.23 (*C*H_3).



hexadec-1-yne-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.17 (t, *J* = 8 Hz, 2H, C*H*$_2$), 1.56-1.50 (m, 2H, C*H*$_2$), 1.48-1.26 (m, 22H, C*H*$_2$), 0.88 (t, *J* = 8 Hz, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.51-84.37 (t, quat-*C*), 68.29-67.54 (t), 32.09 (*C*H_2), 29.85 (*C*H_2), 29.84 (*C*H_2), 29.82 (*C*H_2), 29.78 (*C*H_2), 29.67 (*C*H_2), 29.52 (*C*H_2), 29.28 (*C*H_2), 28.93 (*C*H_2), 28.67 (*C*H_2), 22.85 (*C*H_2), 18.52 (*C*H_2), 14.26 (*C*H_3).



4-methylpent-1-yne-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.08 (d, *J* = 8 Hz, 2H, C*H*$_2$), 1.82 (Sept, *J* = 6 Hz, 1H, ^{i}PrC*H*), 0.99 ((d, *J* = 4 Hz, 6H, ^{i}PrC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 83.91-83.17 (t, quat-*C*), 67.93-67.15 (t), 33.88 (*C*H_2), 28.17 (*C*H), 21.97 (*C*H_3).



5-methylhex-1-yne-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.18 (t, *J* = 8 Hz, 2H, C*H*$_2$), 1.73-1.66 (m, 1H, ^{i}PrC*H*), 1.46-1.39 (m, 2H, C*H*$_2$), 0.89 (d, J = 4 Hz, 6H, ^{i}PrC*H*$_3$). ^{13}C NMR (101

MHz, $CDCl_3$) δ 83.97-83.27 (t, quat-*C*), 67.23-66.55 (t), 42.77 (*C*H_2), 26.78 (*C*H), 22.33 (*C*H_3), 18.51(*C*H_3).

3-methylhex-1-yne-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.43 (m, 1H, C*H*), 1.49-1.39 (m, 4H, CH_2), 1.17 (d, *J* = 8 Hz, 3H, CH_3), 0.91 (t, J = 6 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.15-83.57 (t, quat-*C*), 67.33-66.85 (t), 38.12 (*C*H_2), 33.90 (*C*H), 20.54 (*C*H_3), 19.11 (*C*H_2), 13.45 (*C*H_3).

but-3-yn-1-ylbenzene-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30 (m, 2H, ArC*H*), 7.23 (m, 3H, ArC*H*), 2.86 (t, *J* = 8Hz, 2H, CH_2), 2.49 (t, *J* = 8Hz, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.57 (quat-*C*), 128.55 (Ar*C*H), 128.54 (Ar*C*H), 126.50 (Ar*C*H), 83.55-83.40 (t, quat-*C*), 69.18-68.78 (t), 34.99 (CH_2), 20.67 (CH_2).

3-(prop-2-yn-1-yloxy)prop-1-ene-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.94-5.84(m, 1H, Olefinic-C*H*), 5.32-5.22 (m, 2H, Olefinic-CH_2), 4.14 (s, 2H, CH_2), 4.06 (d, *J* = 8 Hz, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.95 (Olefinic-*C*H), 118.06 (Olefinic-*C*H_2), 79.37-79.22 (t, quat-*C*), 74.64-73.88 (t), 70.67 (*C*H_2), 57.14 (*C*H_2).

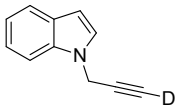
prop-2-yn-1-yl acrylate-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.43 (d, J = 20 Hz, 1H, Olefinic-C*H*), 6.12 (m, 1H, Olefinic-CH_2), 5.86 (d, J = 12 Hz, 1H, Olefinic-C*H*), 4.73 (s, 2H, OCH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.33 (Carbonyl-*C*), 131.97 (Olefinic-*C*H), 127.64 (Olefinic-*C*H_2), 77.61-77.08 (t, quat-*C*), 75.21-74.44 (t), 52.09 (*C*H_2).

prop-2-yn-1-yl benzoate-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.06 (d, J = 8 Hz, 2H, ArC*H*), 7.56 (t, J = 6 Hz, 1H, ArC*H*), 7.43 (t, J = 8 Hz, 2H, ArC*H*), 4.91 (s, 2H, OCH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.80 (Carbonyl-*C*), 133.37 (Ar*C*H), 129.84 (Ar*C*H), 129.45 (quat-*C*), 128.48 (Ar*C*H), 77.43-77.28 (t, quat-*C*), 75.26-74.49 (t), 52.47 (*C*H_2).

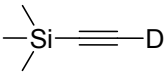
2-((prop-2-yn-1-yloxy)methyl)oxirane-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.20 (d, J = 4 Hz, 2H, CH_2), 3.80 (t, J = 8 Hz, 1H, C*H*), 3.47 (t, J = 8 Hz, 1H, C*H*), 3.15 (m, 1H, C*H*),

2.78 (t, J = 4 Hz, 1H, OCH_2), 2.61 (m, 1H, OCH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 79.06-78.91 (t, quat-*C*), 75.19-74.43 (t), 70.49 (O*C*H_2), 58.60 (O*C*H_2), 50.67 (*C*H), 44.45 (*C*H_2).

1-(prop-2-yn-1-yl)-1H-indole-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (d, *J* = 8 Hz, 1H, ArC*H*), 7.47

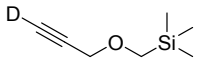


(d, *J* = 8 Hz, 1H, ArC*H*), 7.34 (t, *J* = 8 Hz, 1H, ArC*H*), 7.27-7.22 (m, 2H, ArC*H*), 6.63 (d, *J* = 4 Hz, 1H, ArC*H*), 4.89 (s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.86 (quat-*C*), 128.97 (quat-*C*), 127.33 (Ar*C*H), 121.97 (Ar*C*H), 121.21 (Ar*C*H), 119.97 (Ar*C*H), 109.42 (Ar*C*H), 102.16 (Ar*C*H), 77.33-76.84 (t, quat-*C*), 73.74-72.97 (t), 35.79 (*C*H_2).



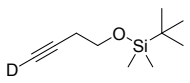
ethynyltrimethylsilane-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.06 (s, 9H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 89.11-88.67(t, quat-*C*), 73.55-76.94 (t), 3.09 (*C*H_3).

trimethyl((prop-2-yn-1-yloxy)methyl)silane-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ



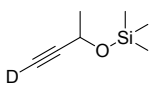
4.26 (s, 2H, OCH_2), 0.15 (s, 9H, CH_3), 0.06 (S, 2H, TMS-*C*H_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 81.75-81.60 (t, quat-*C*), 74.10-73.34 (t), 50.86 (O*C*H_2), 2.07(*C*H_3), 1.42 (TMS-*C*H_2).

(but-3-yn-1-yloxy)(tert-butyl)dimethylsilane-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.72 (t, J = 8 Hz,



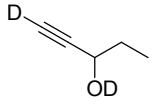
2H, OCH_2), 1.94 (t, J = 6 Hz, 2H, CH_2), 0.88 (s, 9H, CH_3), 0.06 (s, 6H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 81.21-81.06 (t, quat-*C*), 69.57-68.82 (t), 61.88 (O*C*H_2), 26.00 (*C*H_3), 22.94 (*C*H_2), 18.45 (quat-*C*), 5.18 (*C*H_3).

(but-3-yn-2-yloxy)trimethylsilane-d1: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.51 (q, J = 6 Hz, 1H, C*H*),



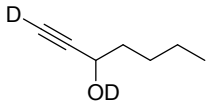
1.46 (d, J = 8 Hz, 3H, CH_3), 0.15 (s, 9H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 85.57-85.42 (t, quat-*C*), 72.31-71.93 (t), 58.12 (O*C*H), 24.26 (*C*H_3), 2.06 (*C*H_3).

pent-1-yn-3-ol-d2: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.29 (t, *J* = 8 Hz, 1H, OC*H*), 1.76-1.68 (m, 2H,

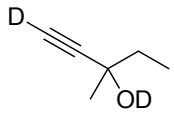


CH_2), 1.00 (t, *J* = 8 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.52-84.37 (t, quat-*C*), 73.09-72.33 (t), 63.43 (O*C*H), 30.73 (*C*H_2), 9.38 (*C*H_3).

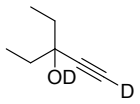
hept-1-yn-3-ol-d2: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.33 (t, *J* = 8 Hz, 1H, OC*H*), 1.74-1.67 (m, 2H, CH_2), 1.47-1.30 (m, 4H, CH_2), 0.91 (t, *J* = 8 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.83-84.68 (t, quat-*C*), 72.82-72.58 (t), 62.12 (O*C*H), 37.33 (*C*H_2), 27.25 (*C*H_2), 22.40 (*C*H_2), 14.03 (*C*H_3).



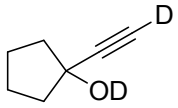
3-methylpent-1-yn-3-ol-d2: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.70-1.62 (m, 2H, CH_2), 1.44 (S, 3H, CH_3), 1.01 (t, *J* = 8 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 87.67-87.15 (t, quat-*C*), 71.50-70.74 (t), 68.49 (quat-*C*), 36.36 (*C*H_3), 29.15 (*C*H_2), 8.91 (*C*H_3).



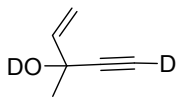
3-ethylpent-1-yn-3-ol-d2: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.68-1.61 (m, 4H, CH_2), 1.03-0.98 (m, 6H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ. 86.19-86.05 (t, quat-*C*), 72.51-71.05 (t), 71.94 (quat-*C*), 34.22 (*C*H_2), 8.48 (*C*H_3).



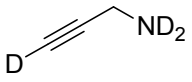
1-ethynylcyclopentanol-d2: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.94-1.91 (m, 4H, CH_2), 1.80-1.70 (m, 4H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 87.59-87.44 (t, quat-*C*), 74.15 (quat-*C*), 71.31-70.55 (t), 42.30 (*C*H_2), 23.44 (*C*H_2).



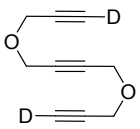
3-methylpent-1-en-4-yn-3-ol -d2: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.94 (m, 1H, Olefinic-C*H*), 5.51 (d, *J* = 16 Hz, 1H, Olefinic-CH_2), 5.12 (d, J = 12 Hz, 1H, Olefinic-C*H*), 1.54 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.62 (Olefinic-*C*H), 114.08 (Olefinic-*C*H_2), 85.90-85.38 (t, quat-*C*), 73.11-72.35, (t), 68.09 (quat-*C*), 29.96 (*C*H_3).



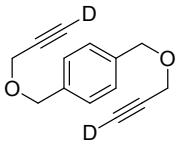
prop-2-yn-1-amine-d3: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.39 (s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 85.56-85.05 (t, quat-*C*), 71.58-70.63 (t), 31.18 (*C*H_2).



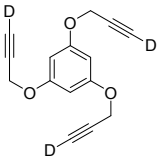
1,4-bis(prop-2-yn-1-yloxy)but-2-yne-d2: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.26 (s, 4H, OCH_2), 4.20 (s, 4H, OCH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.09 (quat-*C*), 78.44-78.29 (t, quat-*C*), 75.29-74.52 (t), 56.65 (O*C*H_2), 56.45 (O*C*H_2).



1,4-bis((prop-2-yn-1-yloxy)methyl)benzene-d2: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35 (s, 4H, ArC*H*), 4.60 (s, 4H, OCH_2), 4.16 (s, 4H, OCH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.06 (quat-*C*), 128.28 (ArC*H*), 79.31-79.16 (t, quat-*C*), 74.92-74.15 (t), 71.27 (O*C*H_2), 57.09 (O*C*H_2).

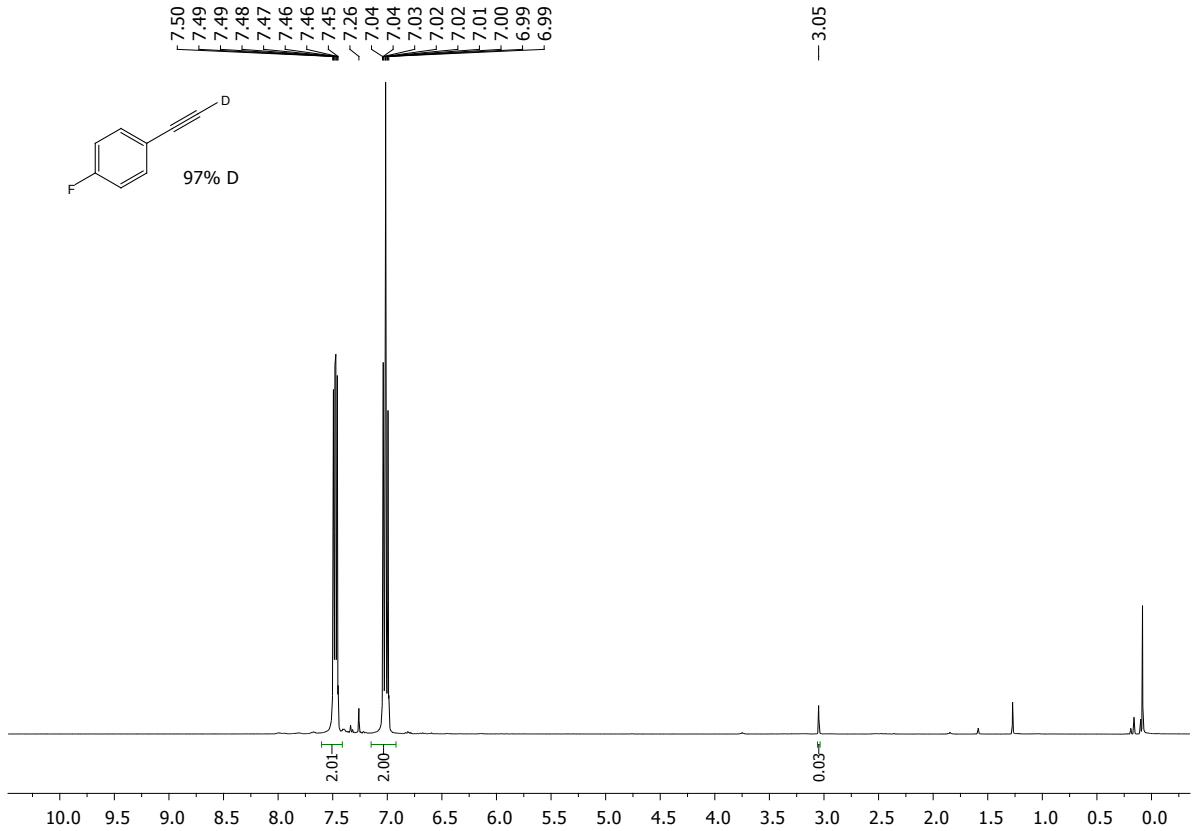


1,3,5-tris(prop-2-yn-1-yloxy)benzene-d3: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.26 (s, 3H, ArC*H*), 4.63 (s, 6H, OCH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.19 (quat-*C*), 92.77 (Ar*C*H), 84.27-83.15 (t, quat-*C*), 77.58-76.10 (t), 56.89 (O*C*H_2).

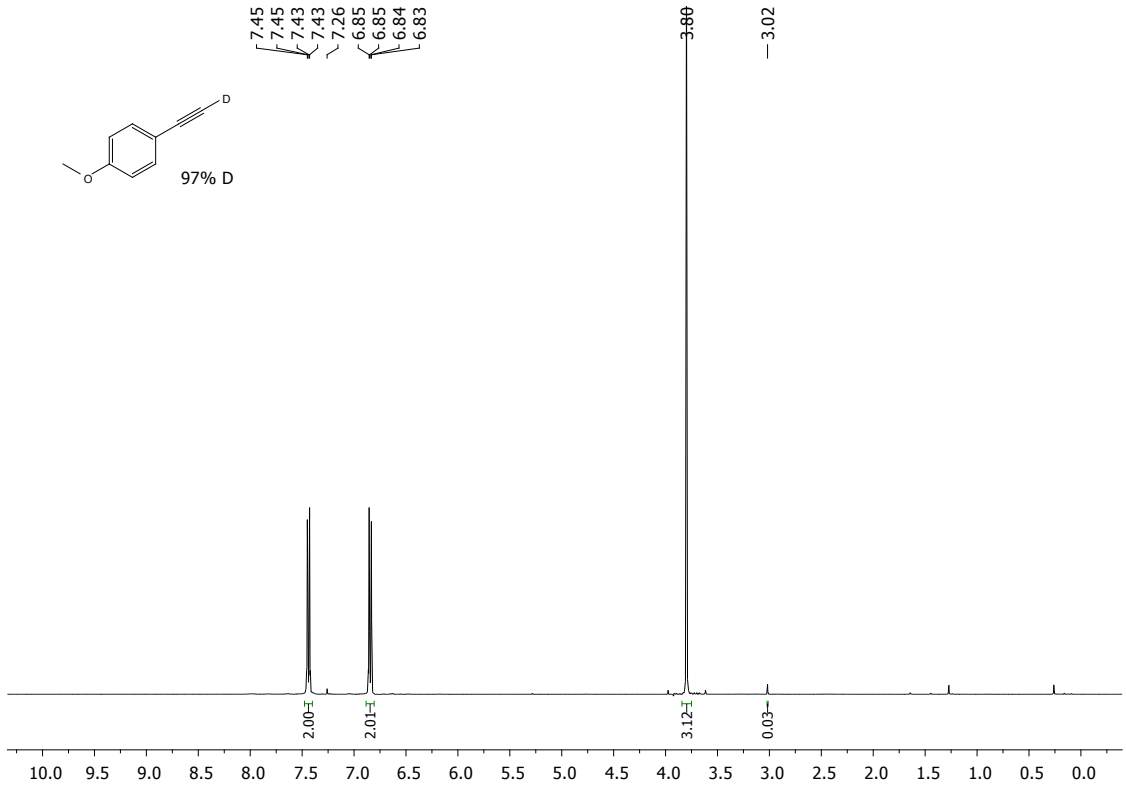


NMR spectra of deuterated terminal alkynes:

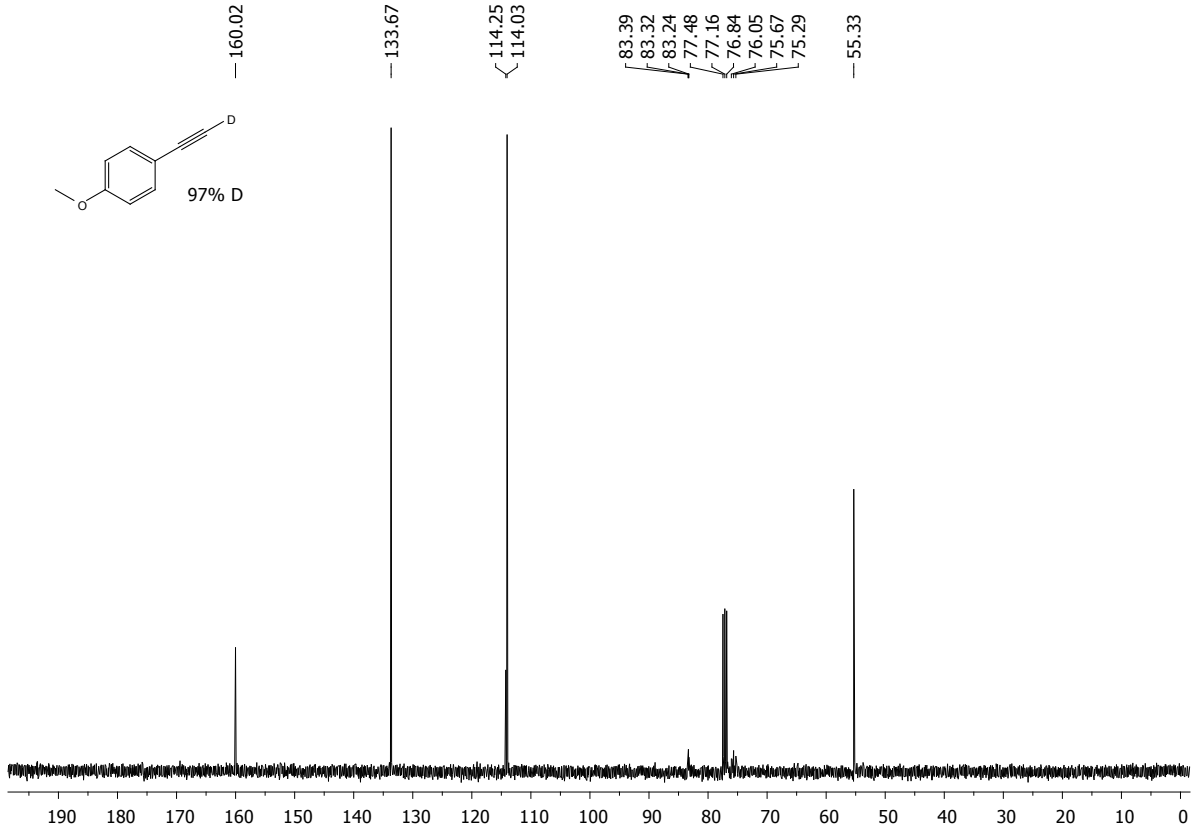
^{1}H NMR spectrum of 1-ethynyl-4-fluorobenzene-d1 (400 MHz, $CDCl_3$):



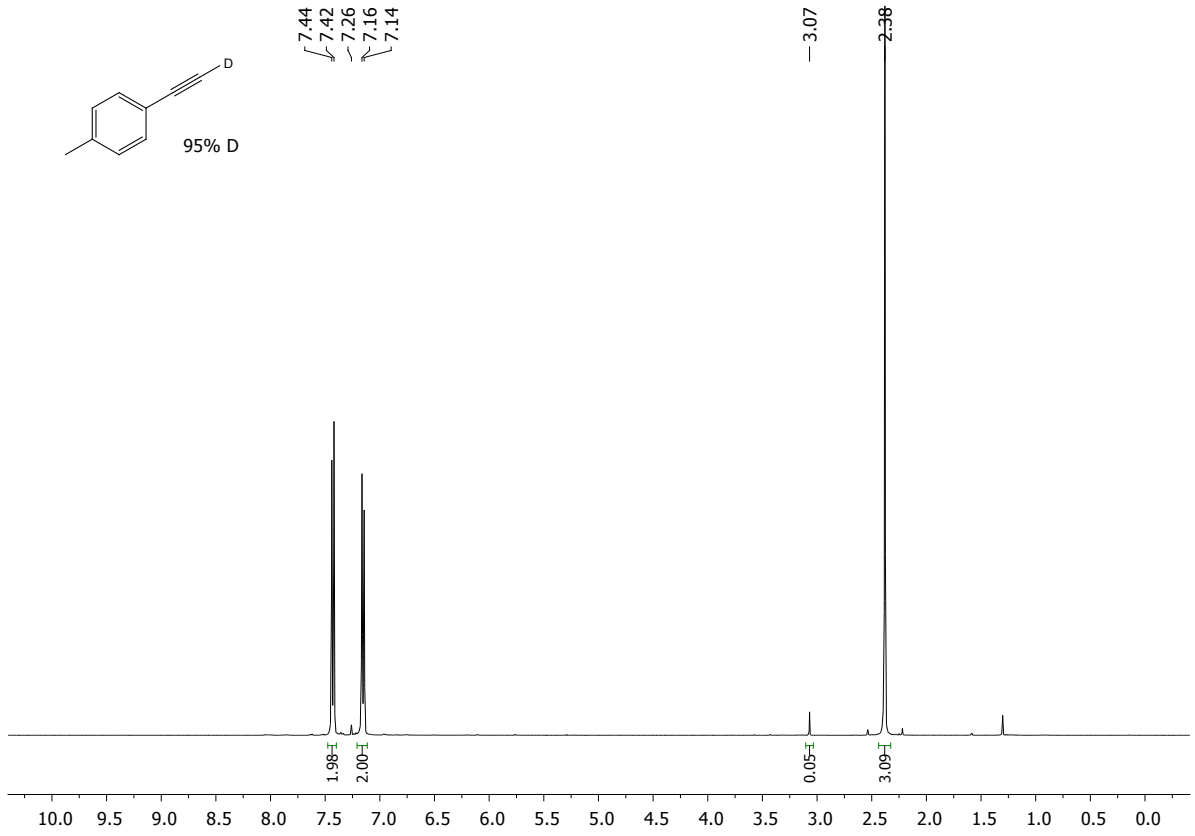
^{1}H NMR spectrum of 1-ethynyl-4-methoxybenzene-d1 (400 MHz, $CDCl_3$):



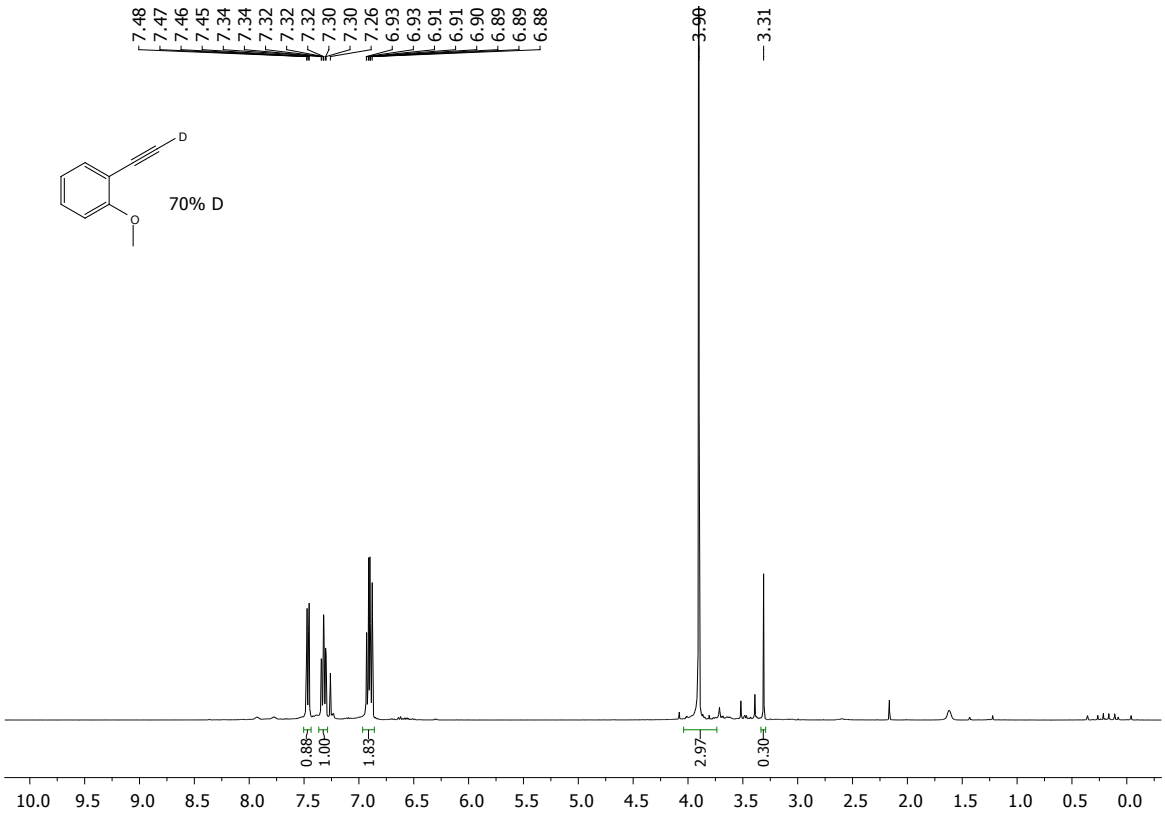
^{13}C NMR spectrum of 1-ethynyl-4-methoxybenzene-d1 (100.6 MHz, $CDCl_3$):



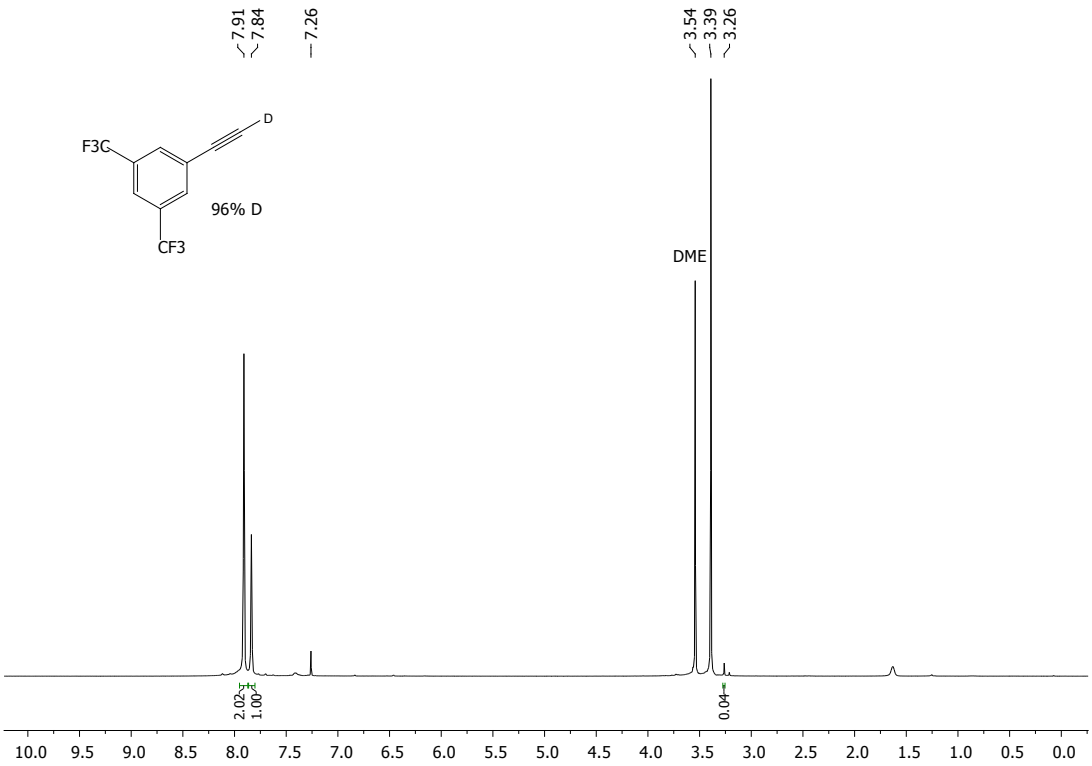
^{1}H NMR spectrum of 1-ethynyl-4-methylbenzene-d1 (400 MHz, $CDCl_3$):



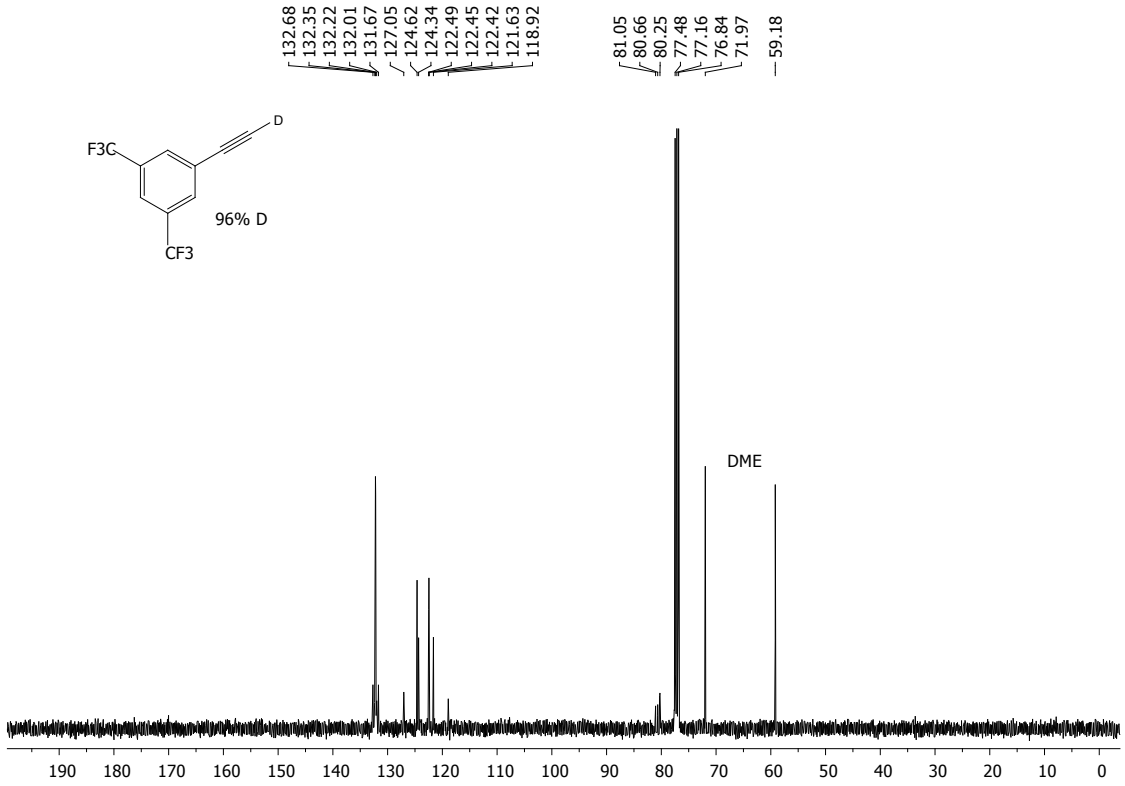
^{1}H NMR spectrum of 1-ethynyl-2-methoxybenzene-d1 (400 MHz, $CDCl_3$):



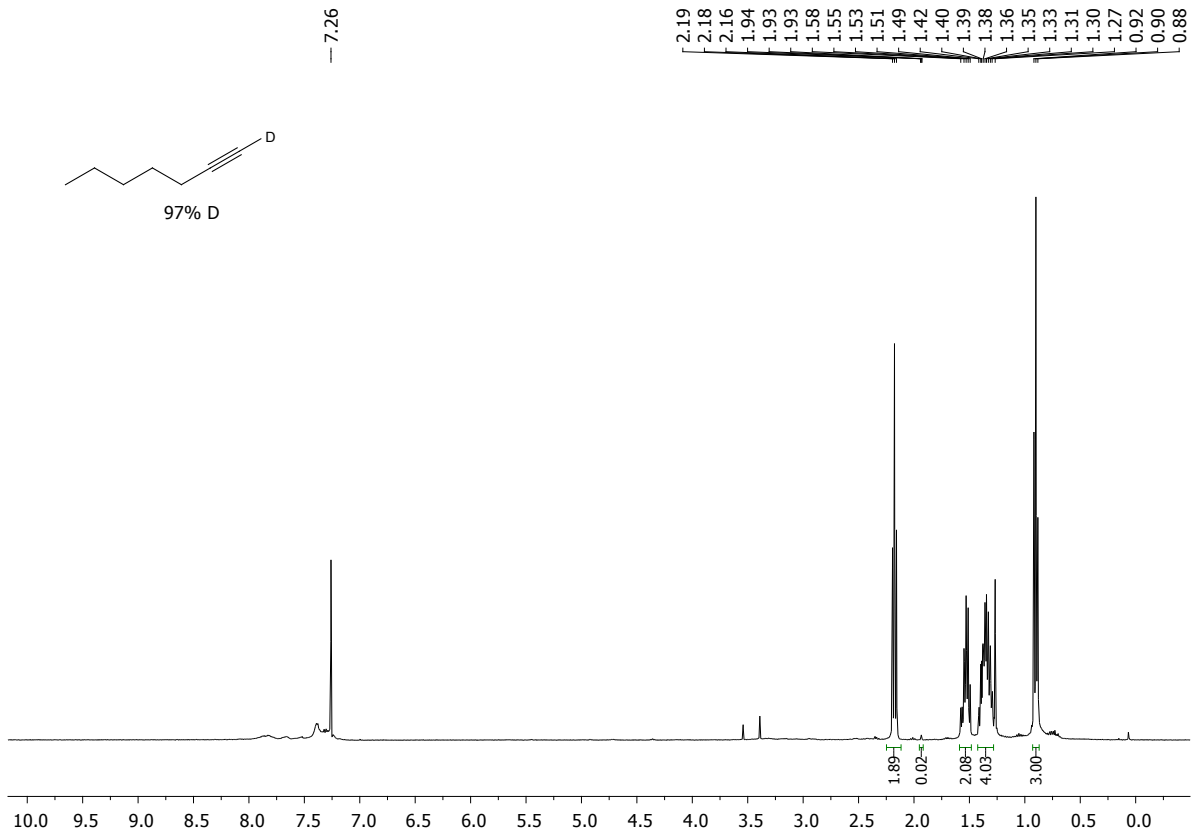
^{1}H NMR spectrum of 1-ethynyl-3,5-bis(trifluoromethyl)benzene-d1 (400 MHz, $CDCl_3$):



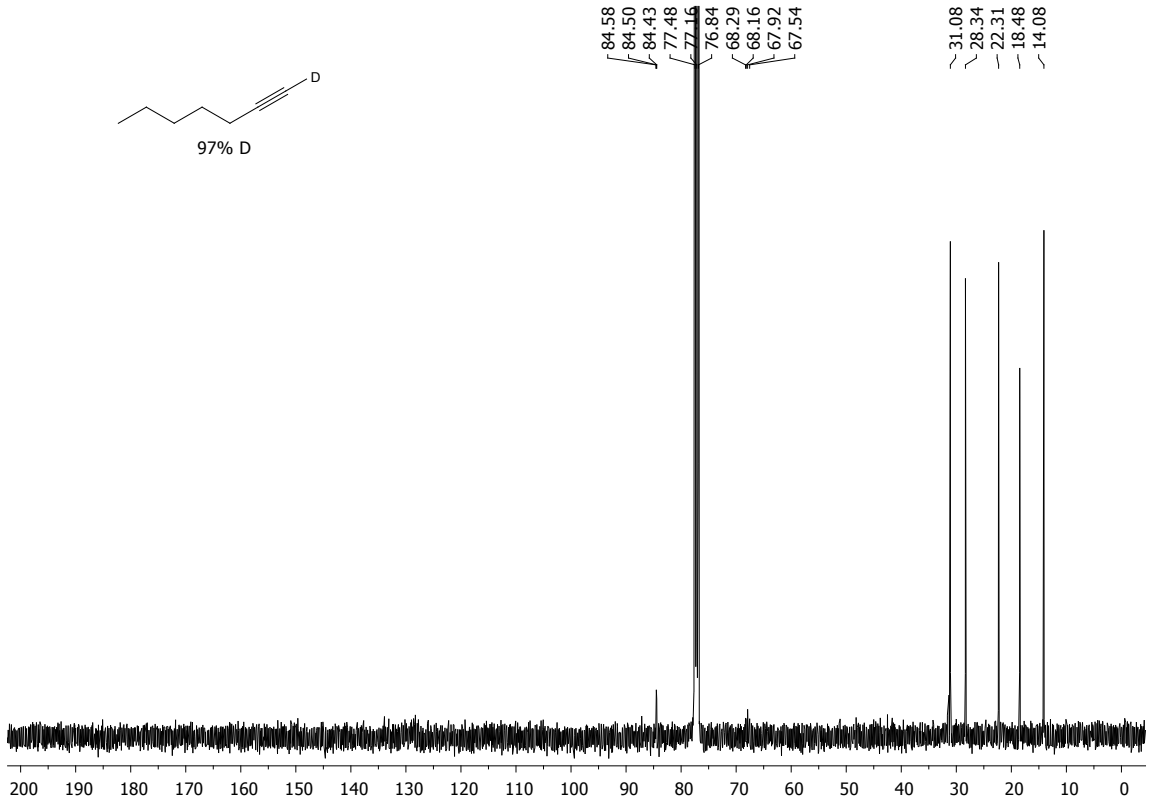
^{13}C NMR spectrum of 1-ethynyl-3,5-bis(trifluoromethyl)benzene -d1 (100.6 MHz, $CDCl_3$):



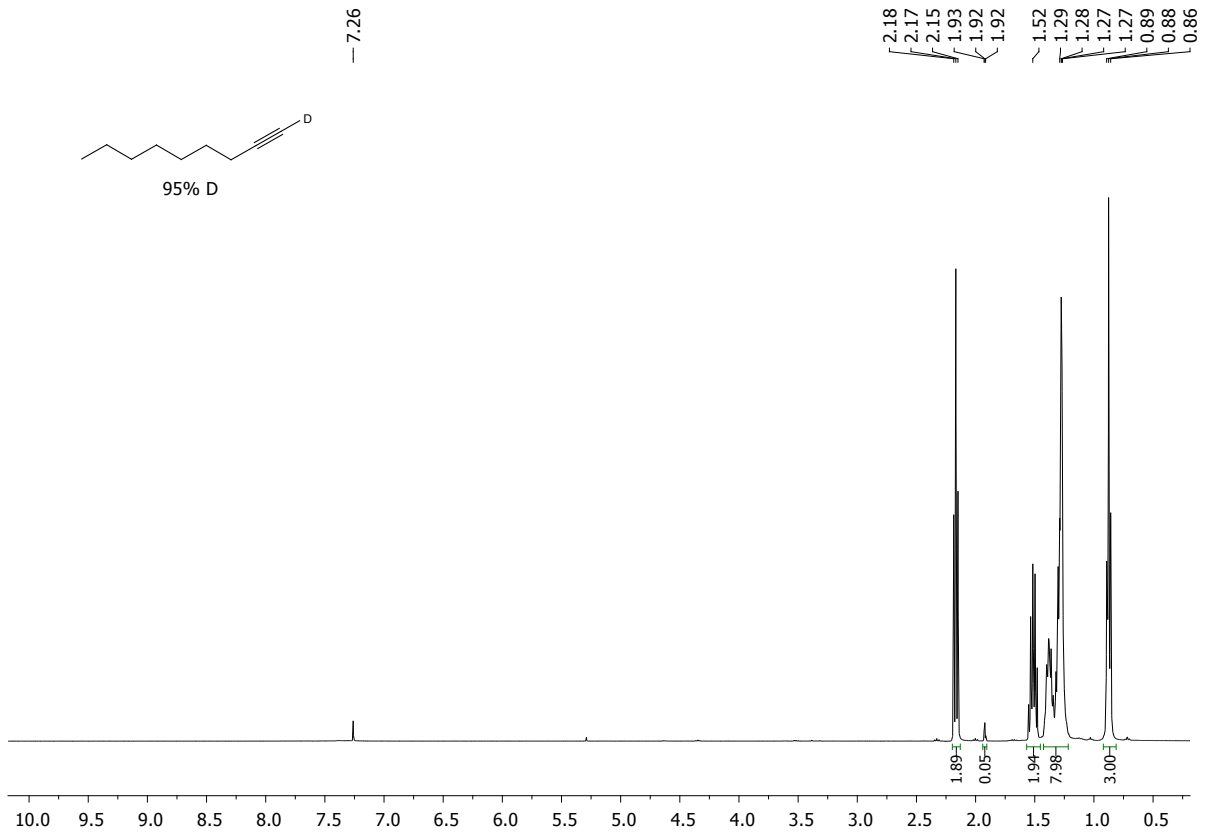
^{1}H NMR spectrum of hept-1-yne-d1 (400 MHz, $CDCl_3$):



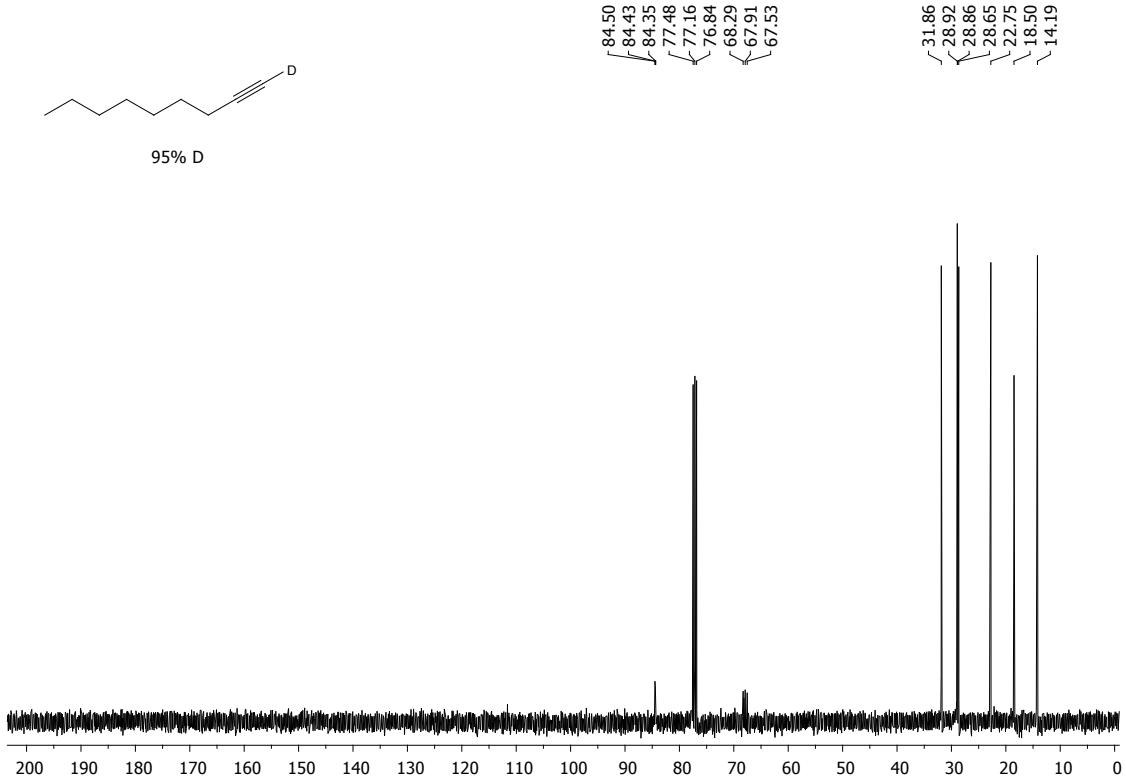
^{13}C NMR spectrum of hept-1-yne-d1 (100.6 MHz, $CDCl_3$):



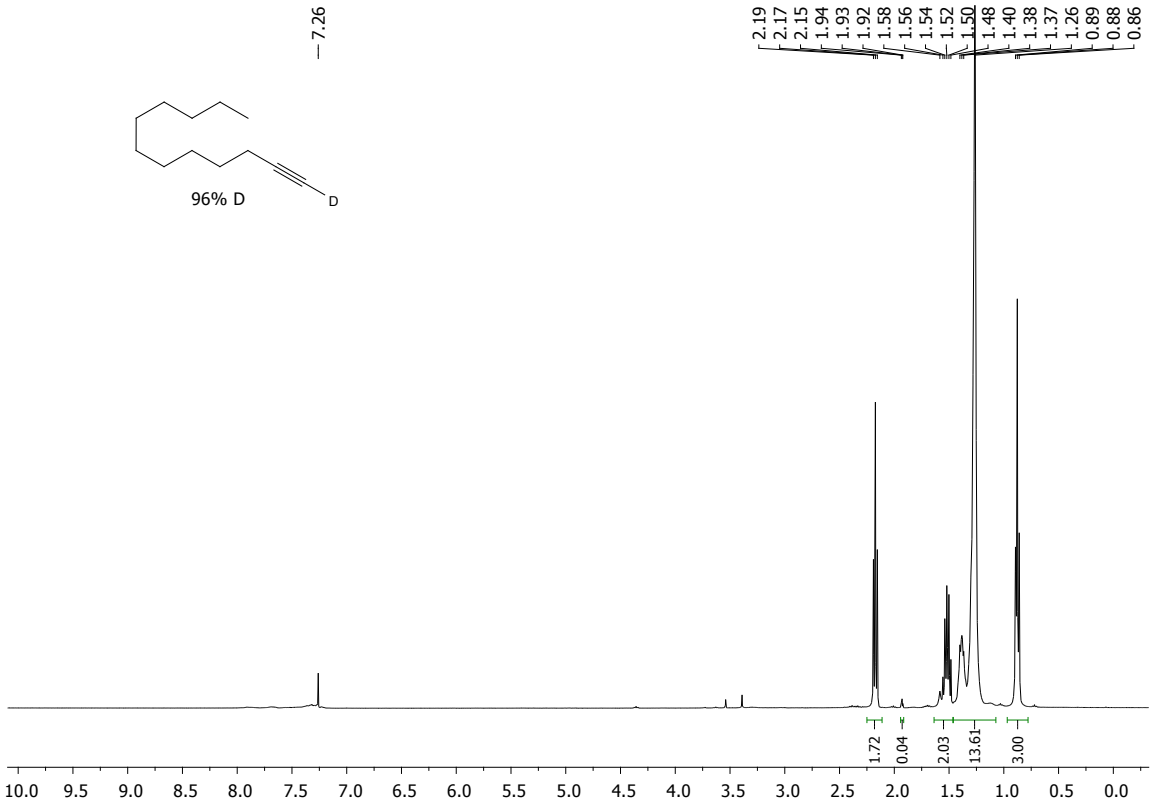
^{1}H NMR spectrum of non-1-yne-d1 (400 MHz, $CDCl_3$):



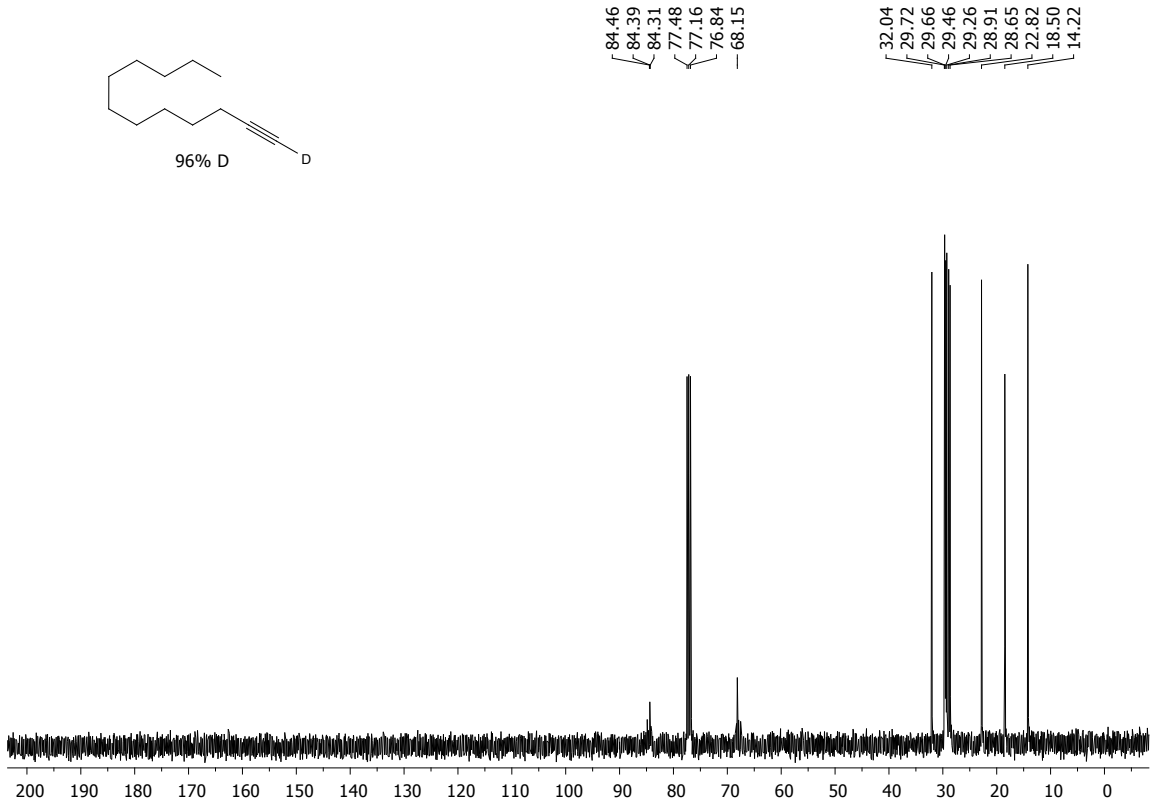
^{13}C NMR spectrum of non-1-yne-d1 (100.6 MHz, $CDCl_3$):



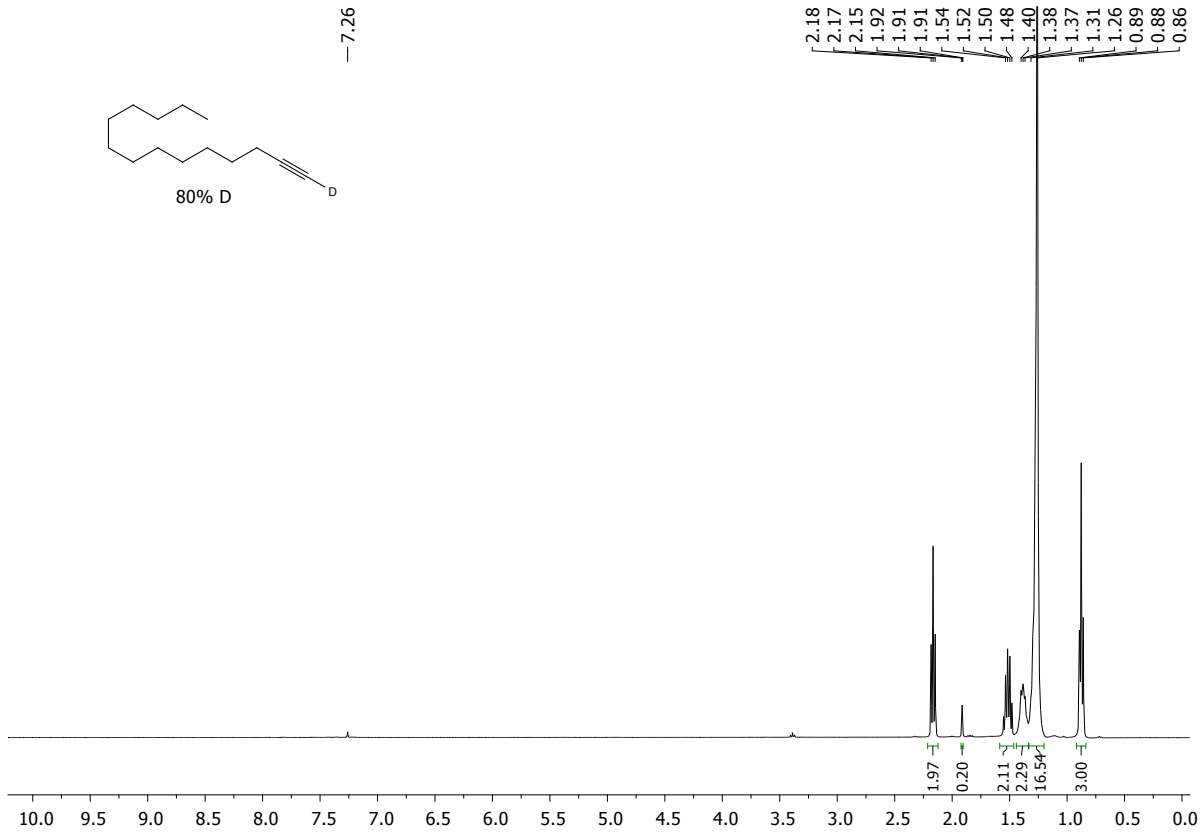
^{1}H NMR spectrum of dodec-1-yne-d1 (400 MHz, $CDCl_3$):



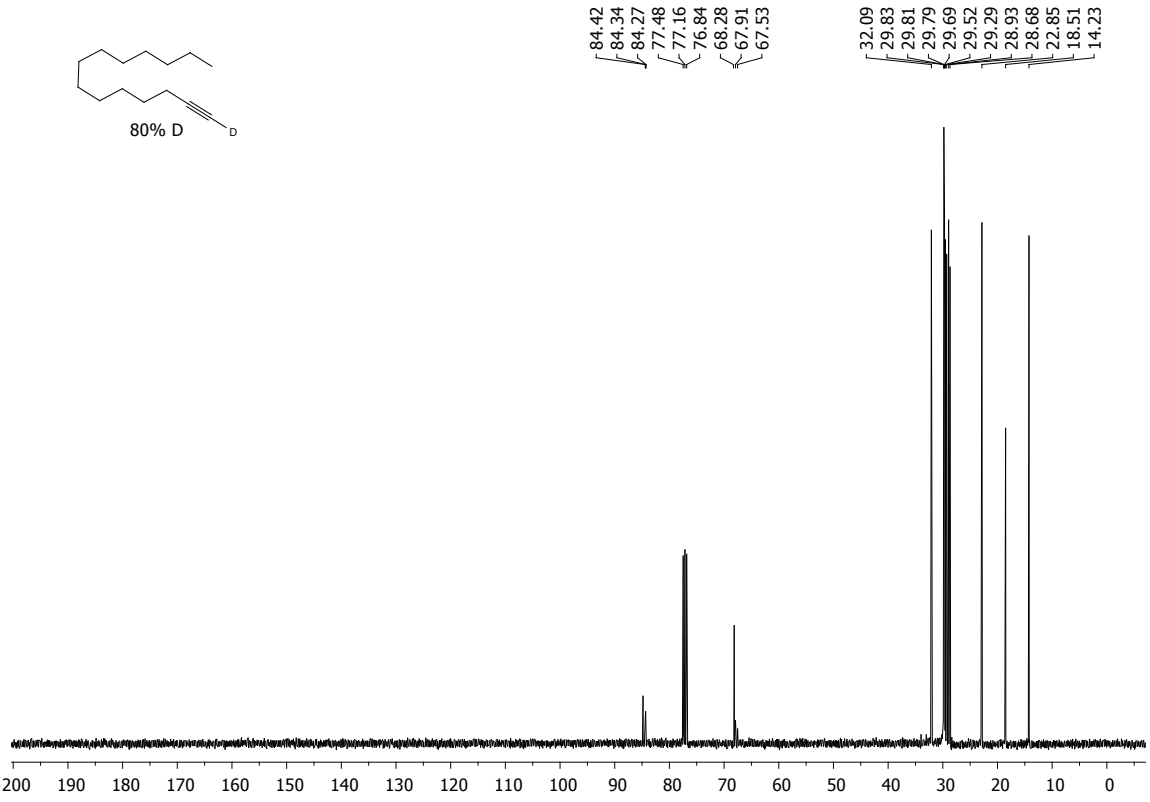
^{13}C NMR spectrum of dodec-1-yne-d1 (100.6 MHz, $CDCl_3$):



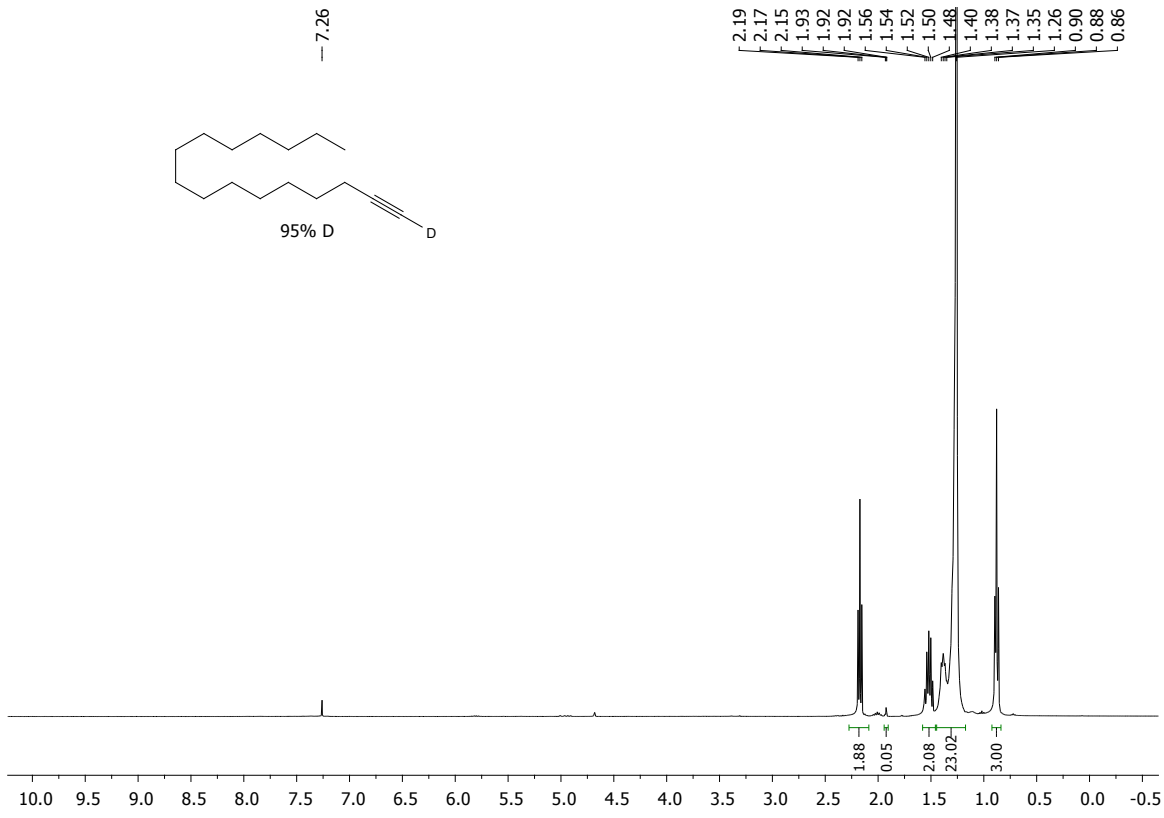
^{1}H NMR spectrum of tetradec-1-yne-d1 (400 MHz, $CDCl_3$):



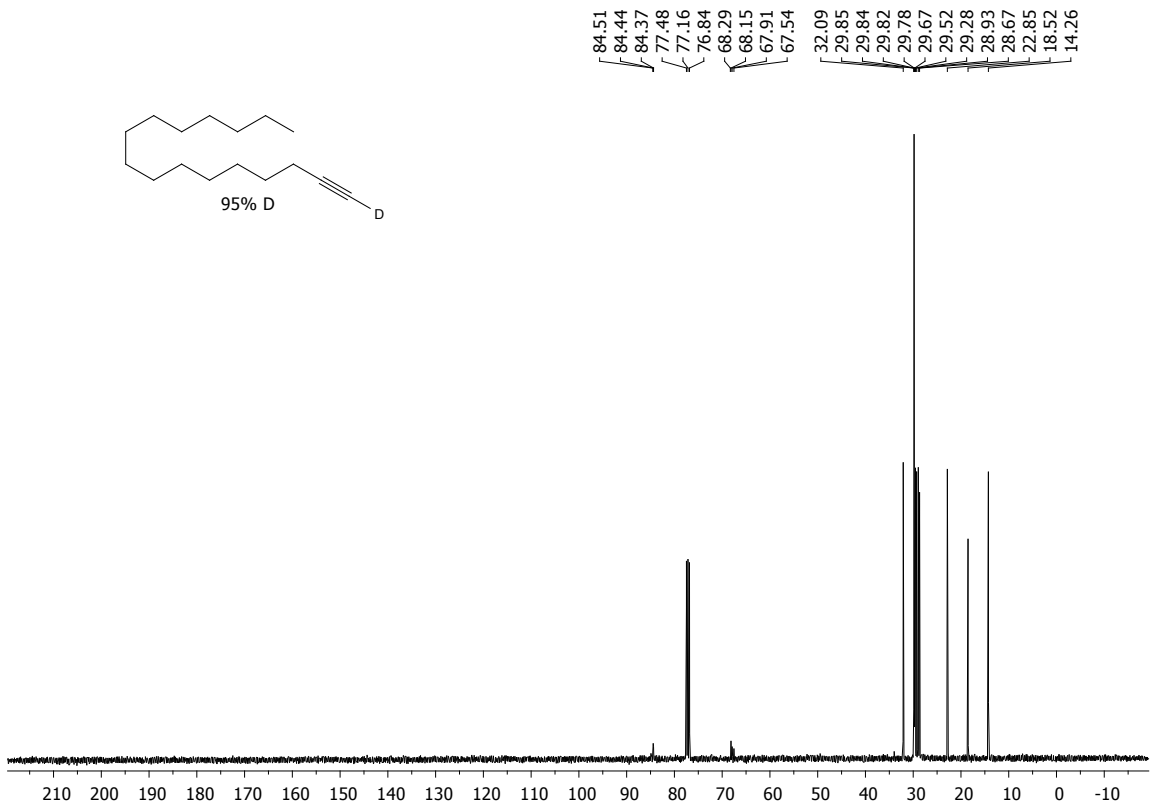
^{13}C NMR spectrum of tetradec-1-yne-d1 (100.6 MHz, $CDCl_3$):



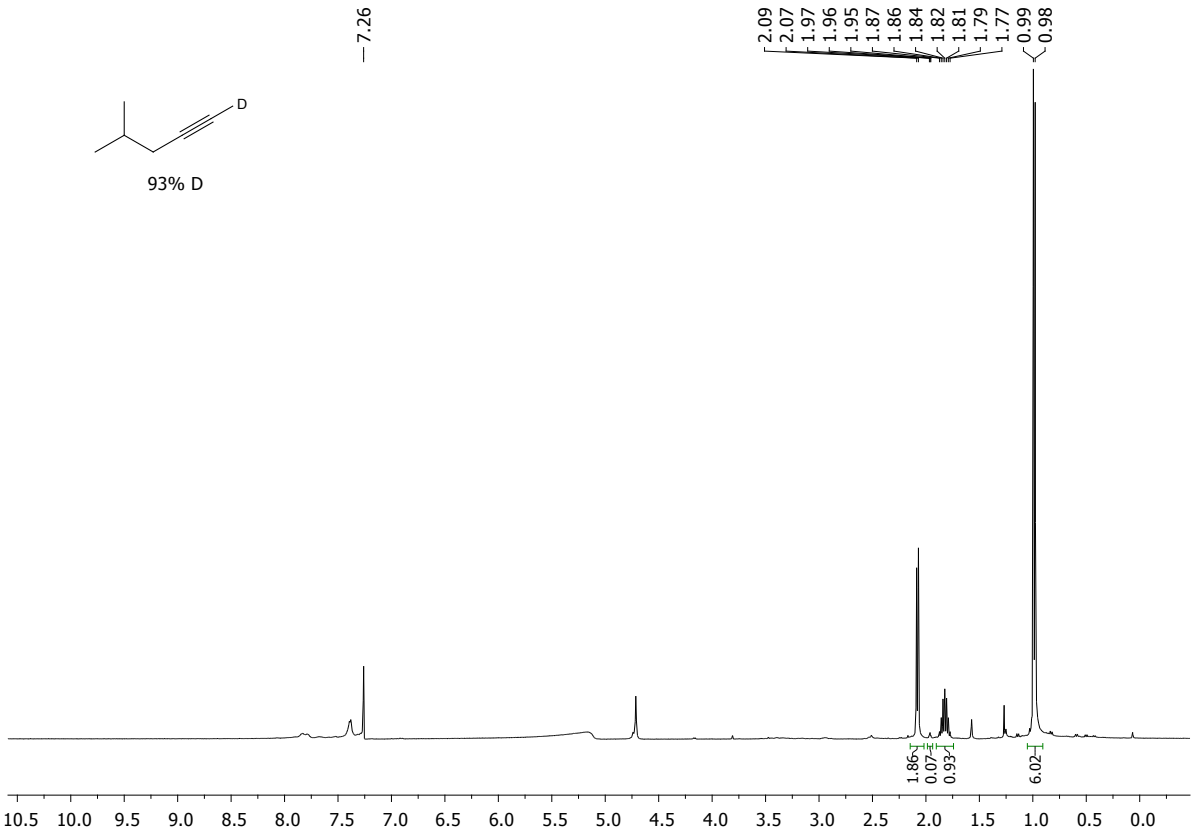
^{1}H NMR spectrum of hexadec-1-yne-d1 (400 MHz, $CDCl_3$):



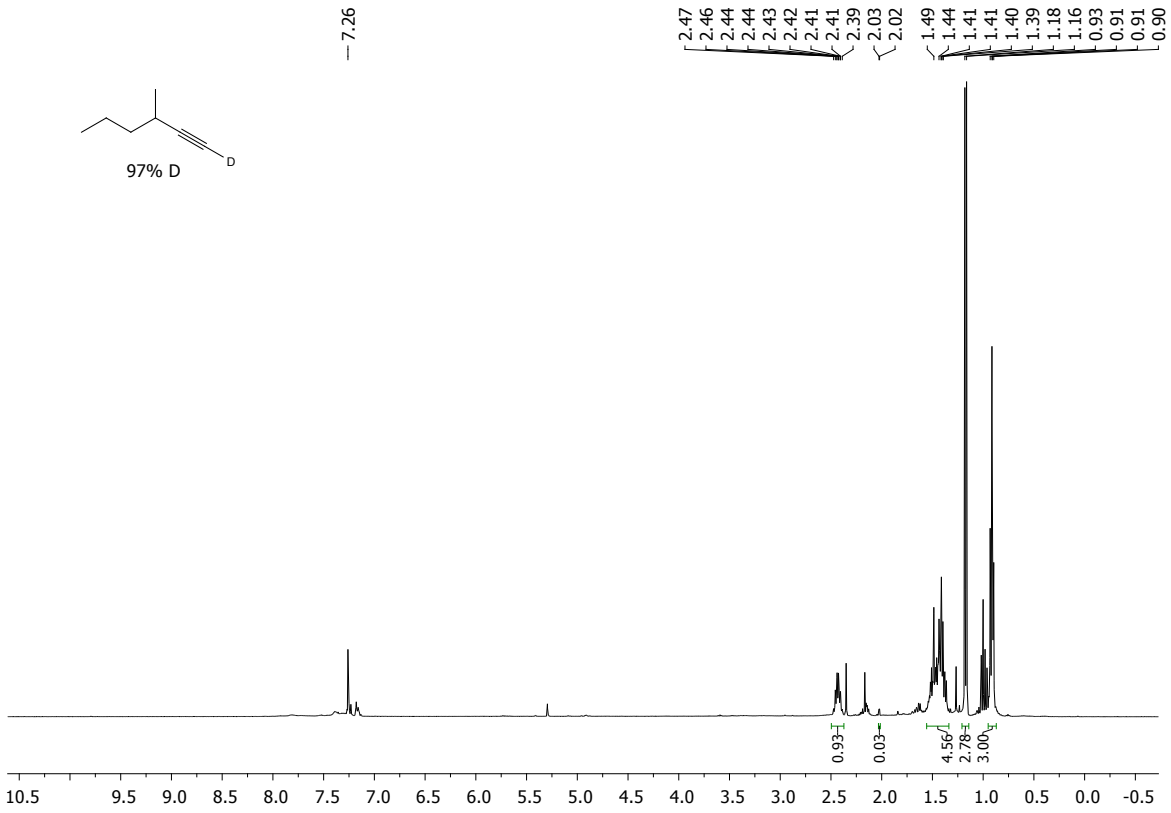
^{13}C NMR spectrum of hexadec-1-yne-d1 (100.6 MHz, $CDCl_3$):



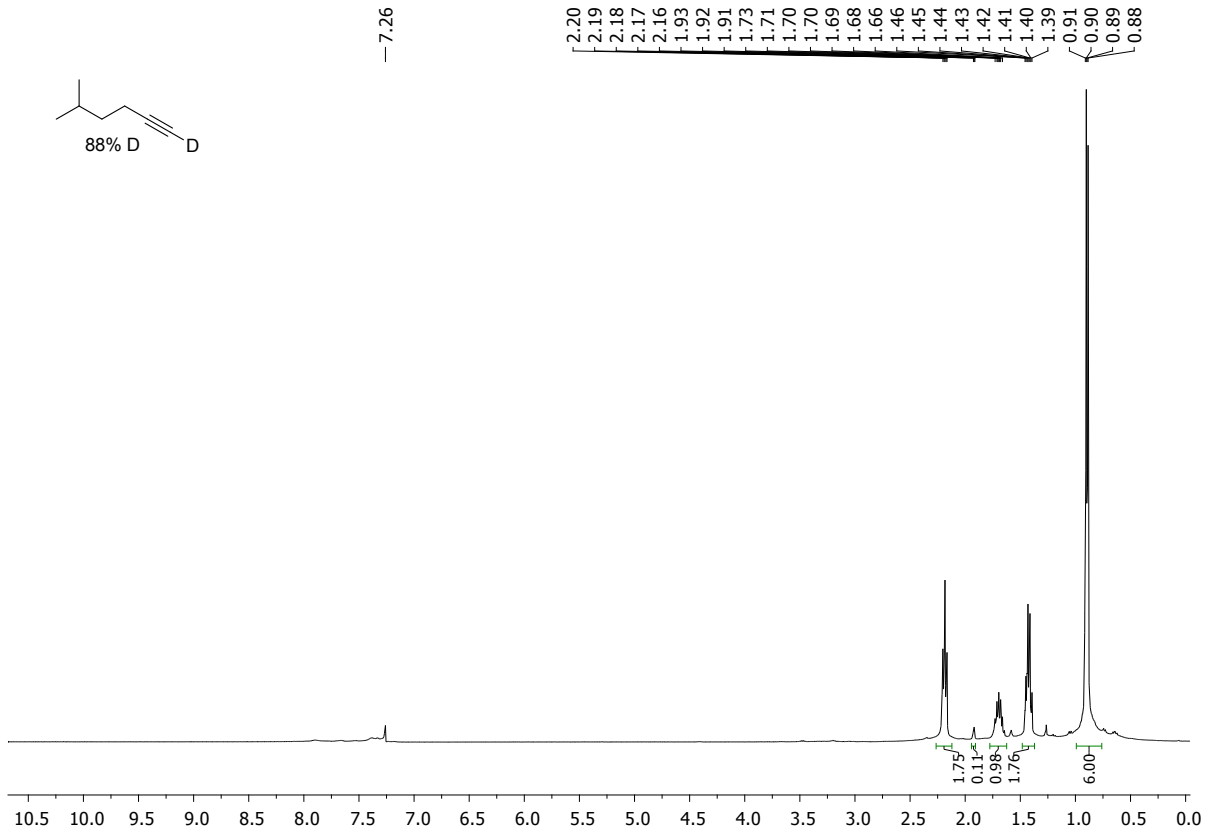
^{1}H NMR spectrum of 4-methylpent-1-yne-d1 (400 MHz, $CDCl_3$):



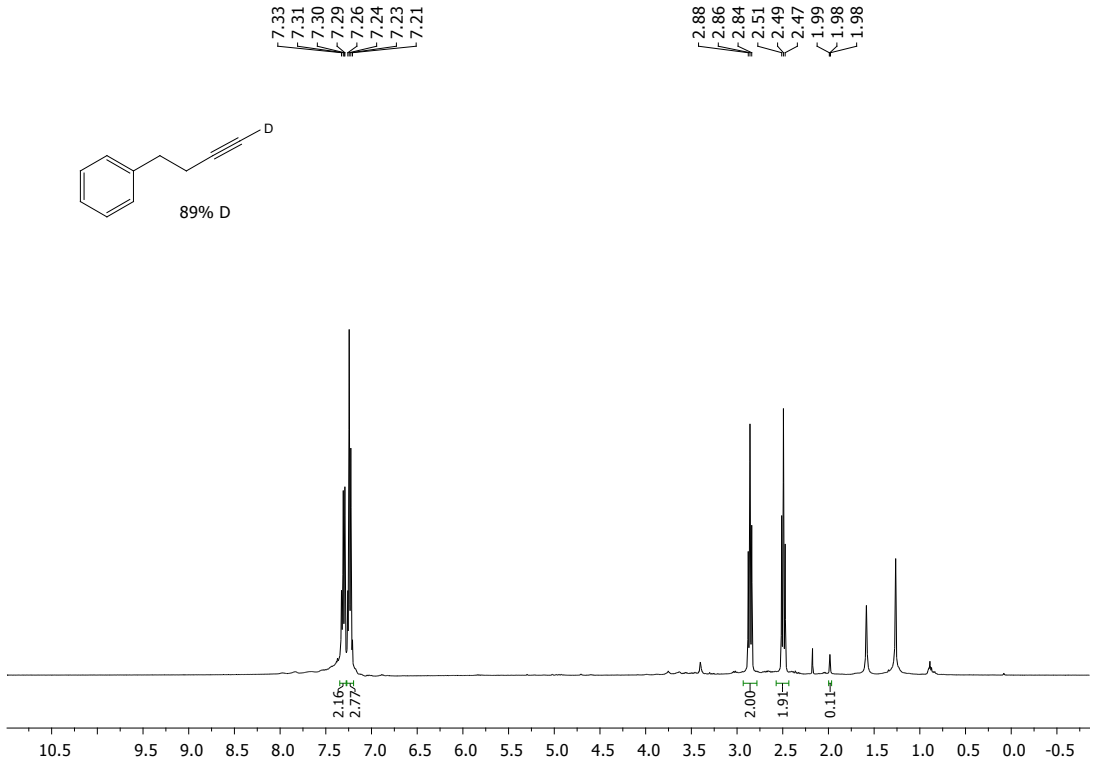
^{1}H NMR spectrum of 3-methylhex-1-yne-d1 (400 MHz, $CDCl_3$):



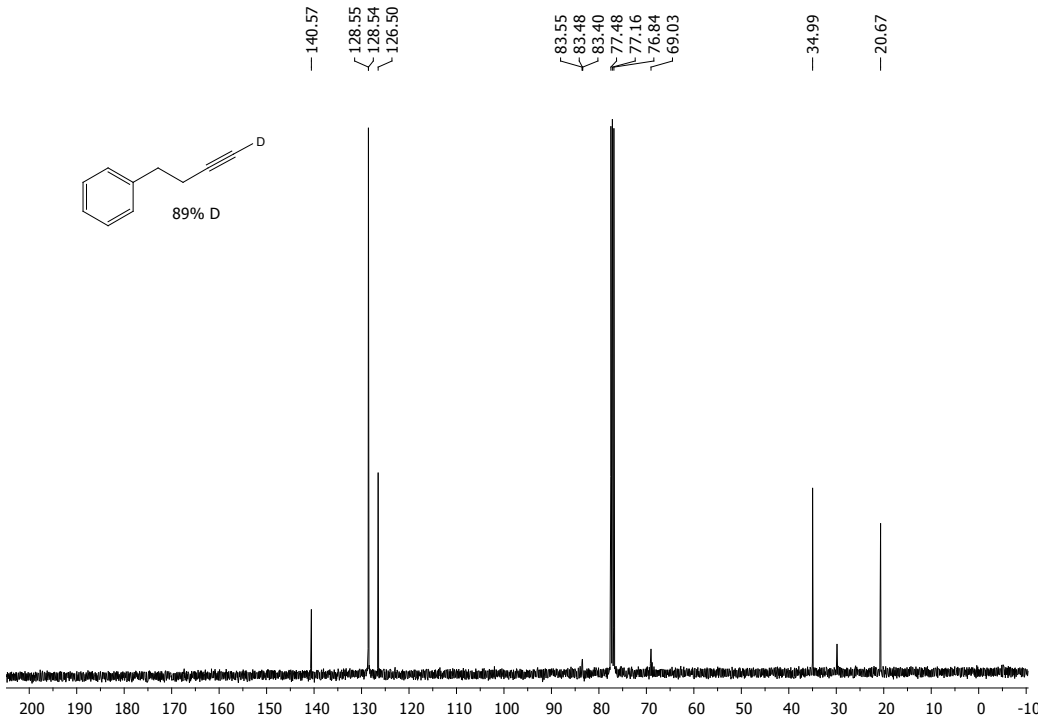
^{1}H NMR spectrum of 5-methylhex-1-yne-d1 (400 MHz, $CDCl_3$):



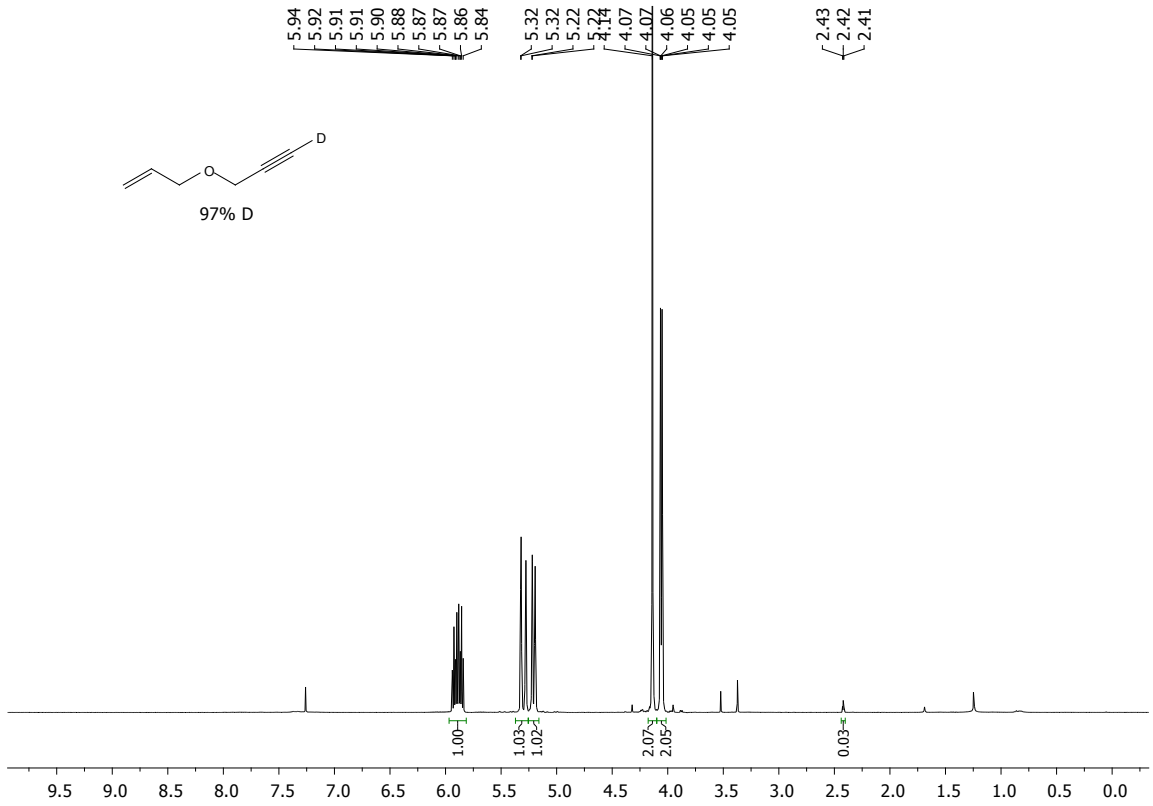
^{1}H NMR spectrum of but-3-yn-1-ylbenzene-d1 (400 MHz, $CDCl_3$):



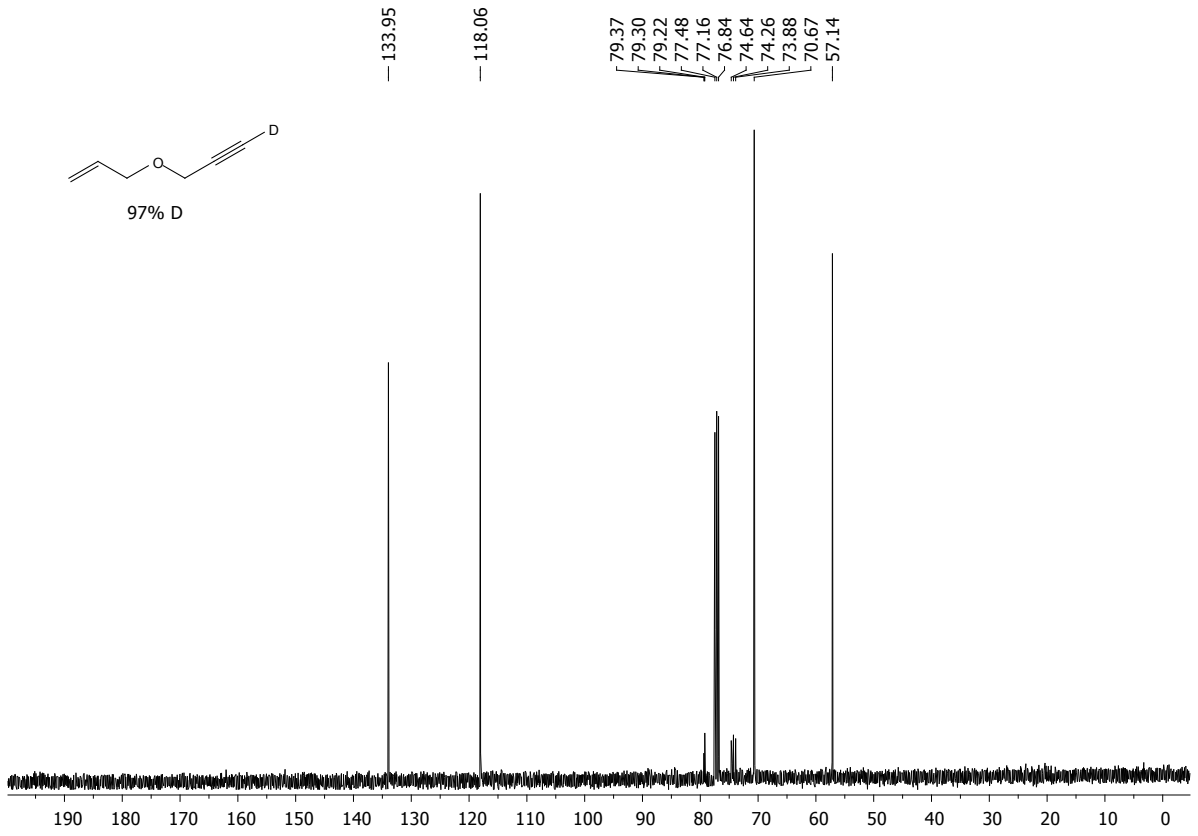
^{13}C NMR spectrum of but-3-yn-1-ylbenzene-d1 (100.6 MHz, $CDCl_3$):



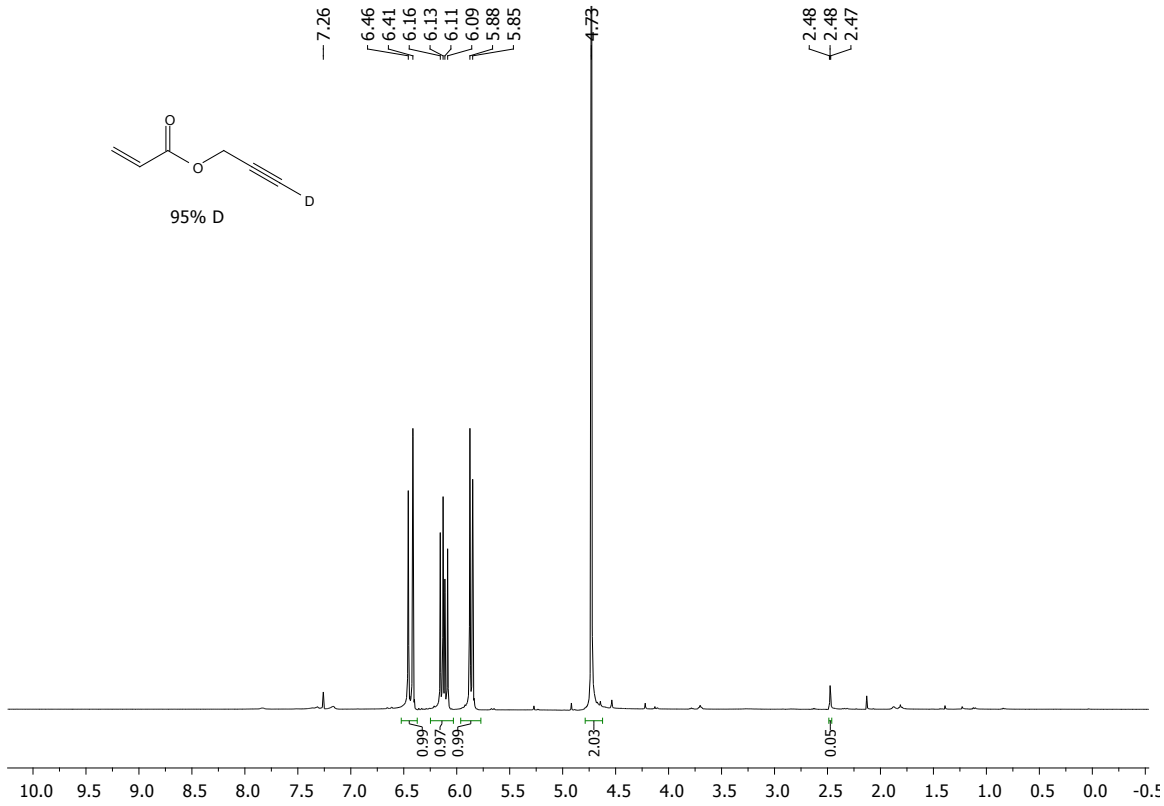
^{1}H NMR spectrum of 3-(prop-2-yn-1-yloxy)prop-1-ene-d1 (400 MHz, $CDCl_3$):



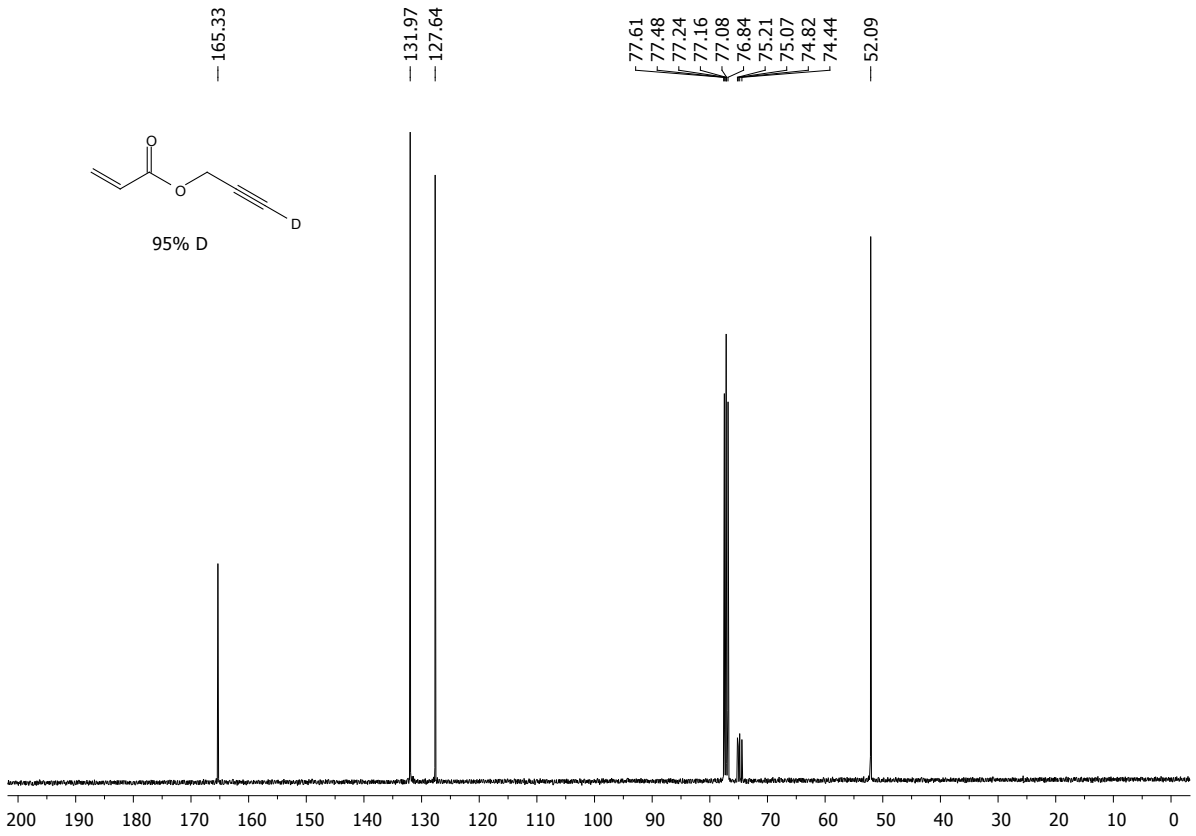
^{13}C NMR spectrum of 3-(prop-2-yn-1-yloxy)prop-1-ene-d1 (100.6 MHz, $CDCl_3$):



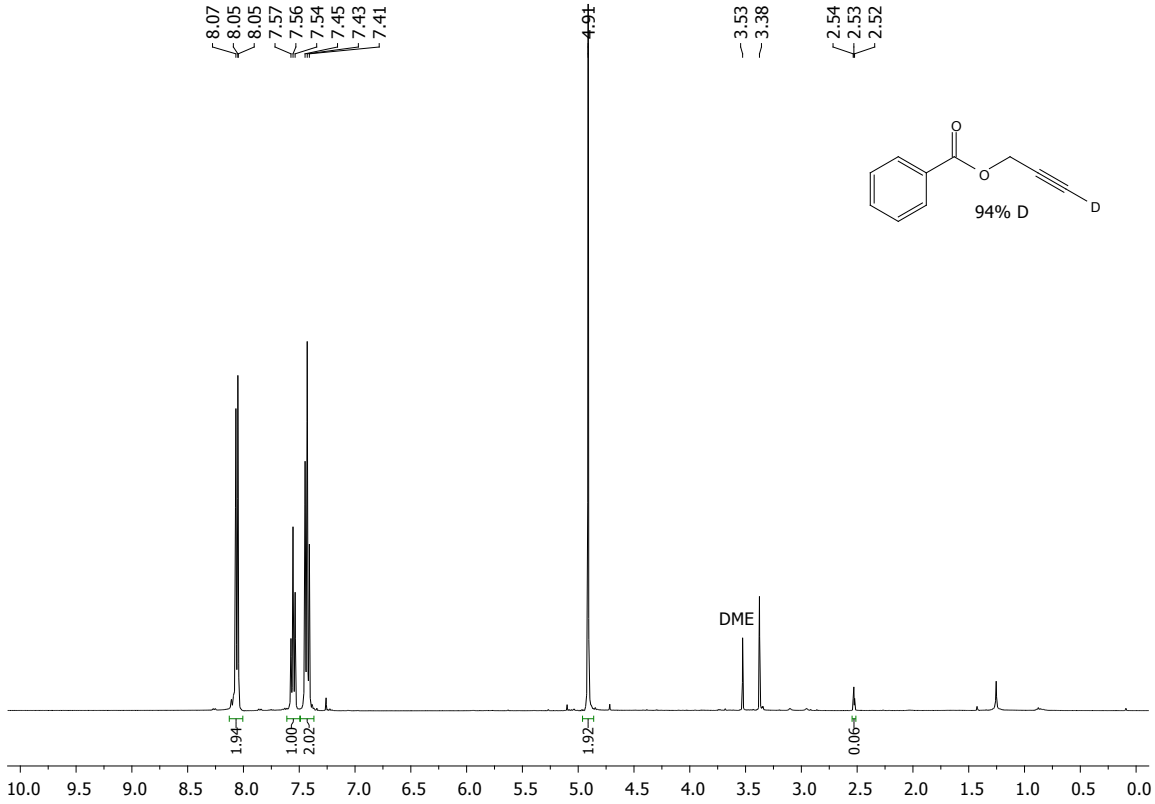
^{1}H NMR spectrum of prop-2-yn-1-yl acrylate-d1 (400 MHz, $CDCl_3$):



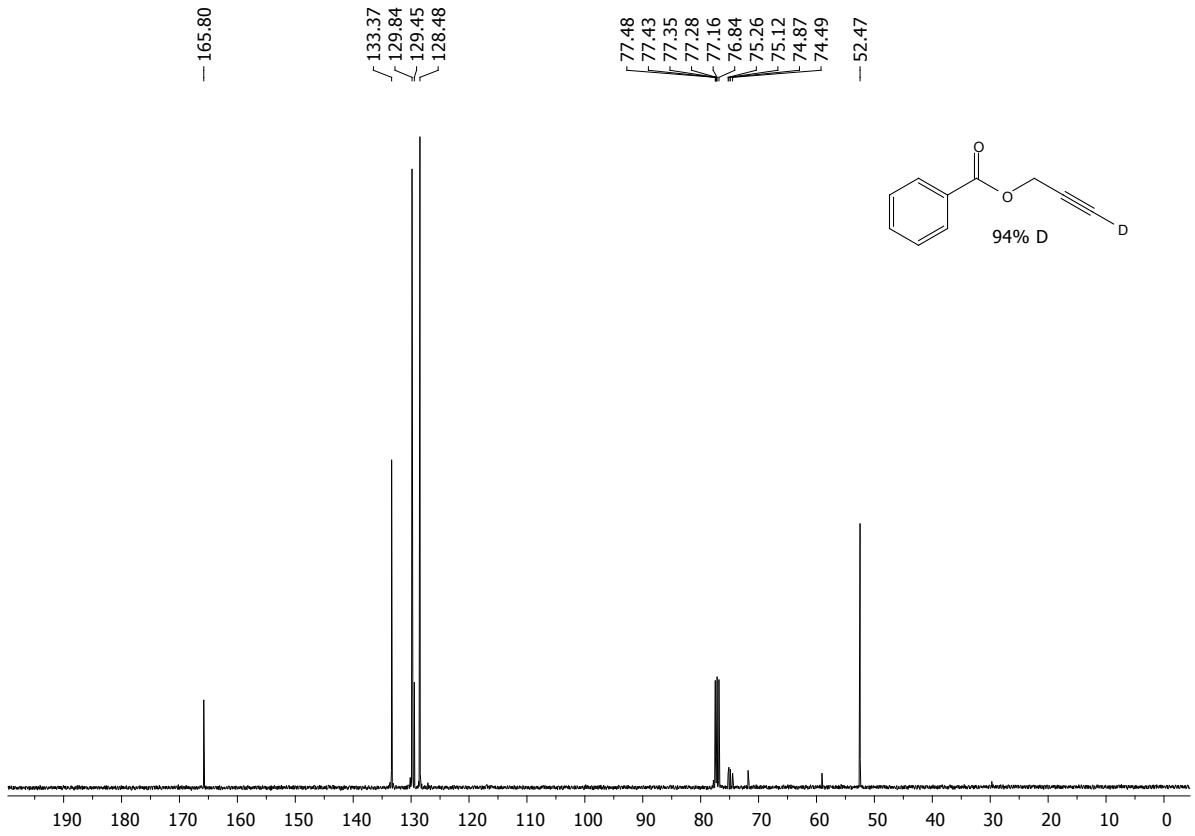
^{13}C NMR spectrum of prop-2-yn-1-yl acrylate-d1 (100.6 MHz, $CDCl_3$):



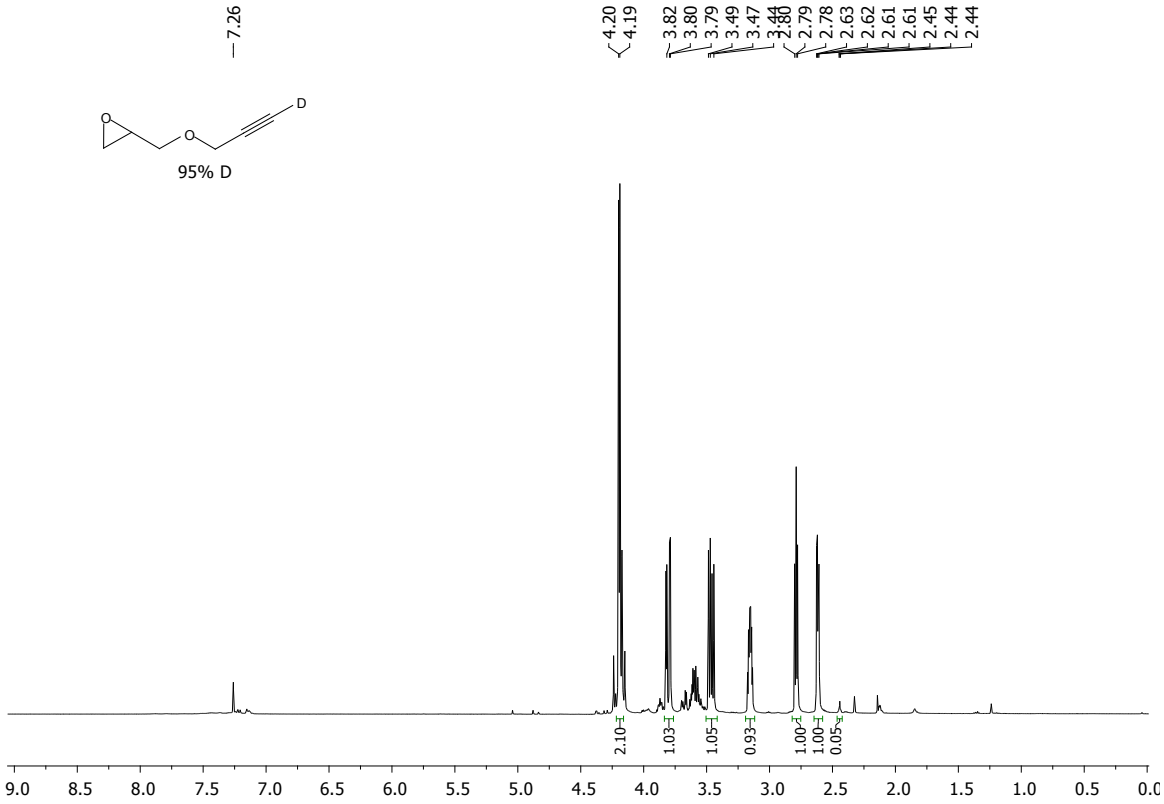
^{1}H NMR spectrum of prop-2-yn-1-yl benzoate-d1 (400 MHz, $CDCl_3$):



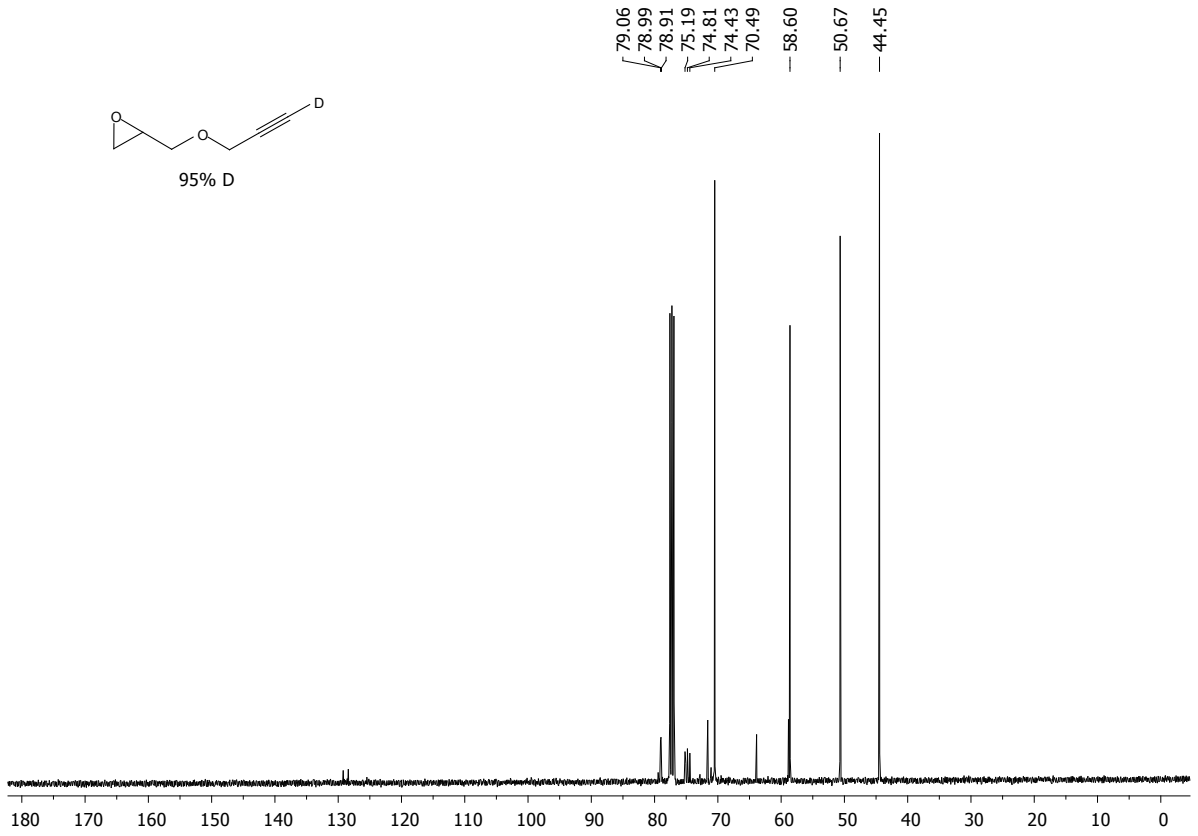
^{13}C NMR spectrum of prop-2-yn-1-yl benzoate-d1 (100.6 MHz, $CDCl_3$):



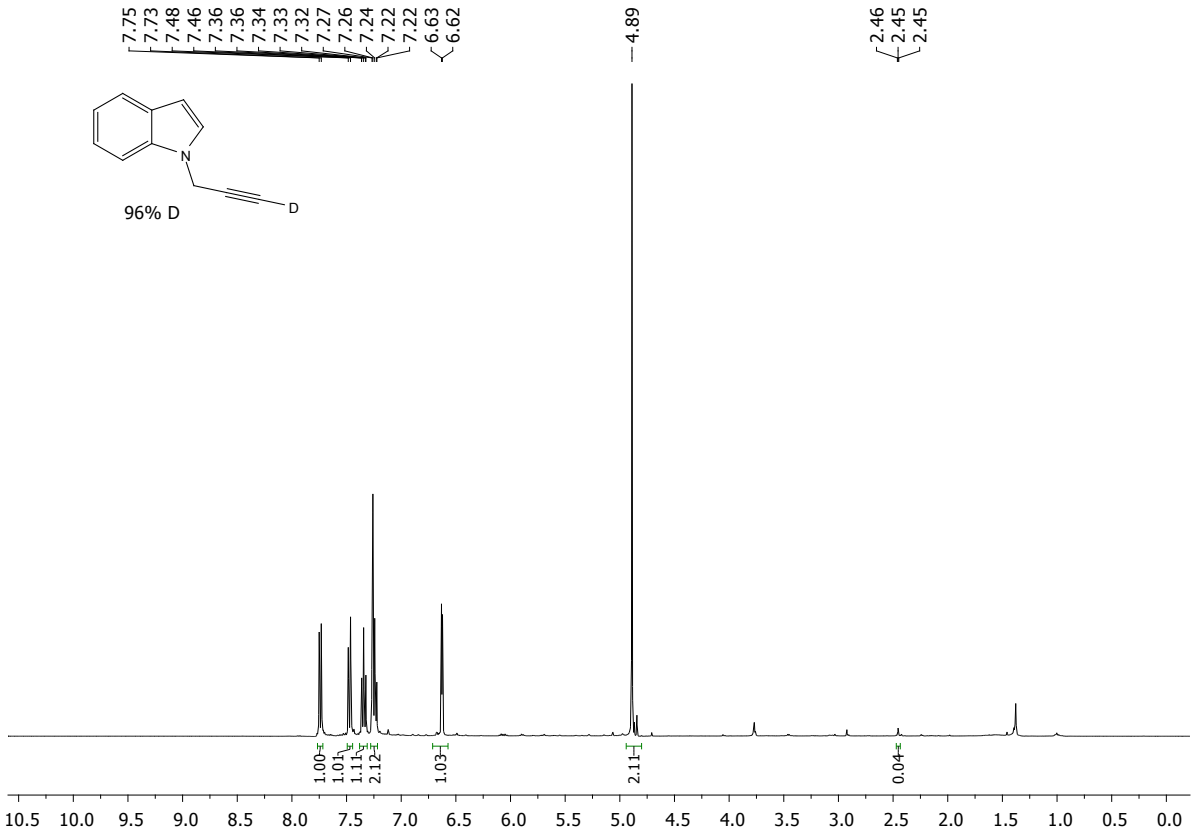
^{1}H NMR spectrum of 2-((prop-2-yn-1-yloxy)methyl)oxirane-d1 (400 MHz, $CDCl_3$):



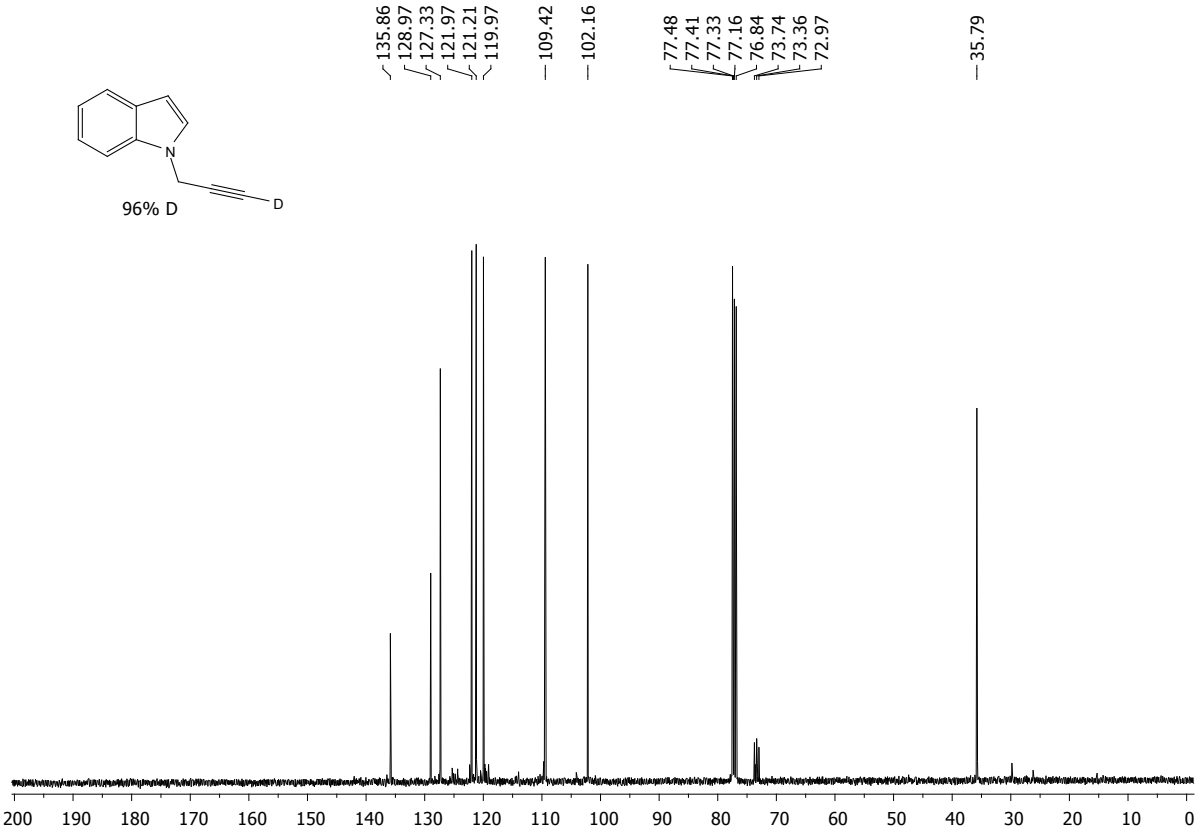
^{13}C NMR spectrum of 2-((prop-2-yn-1-yloxy)methyl)oxirane-d1 (100.6 MHz, $CDCl_3$):



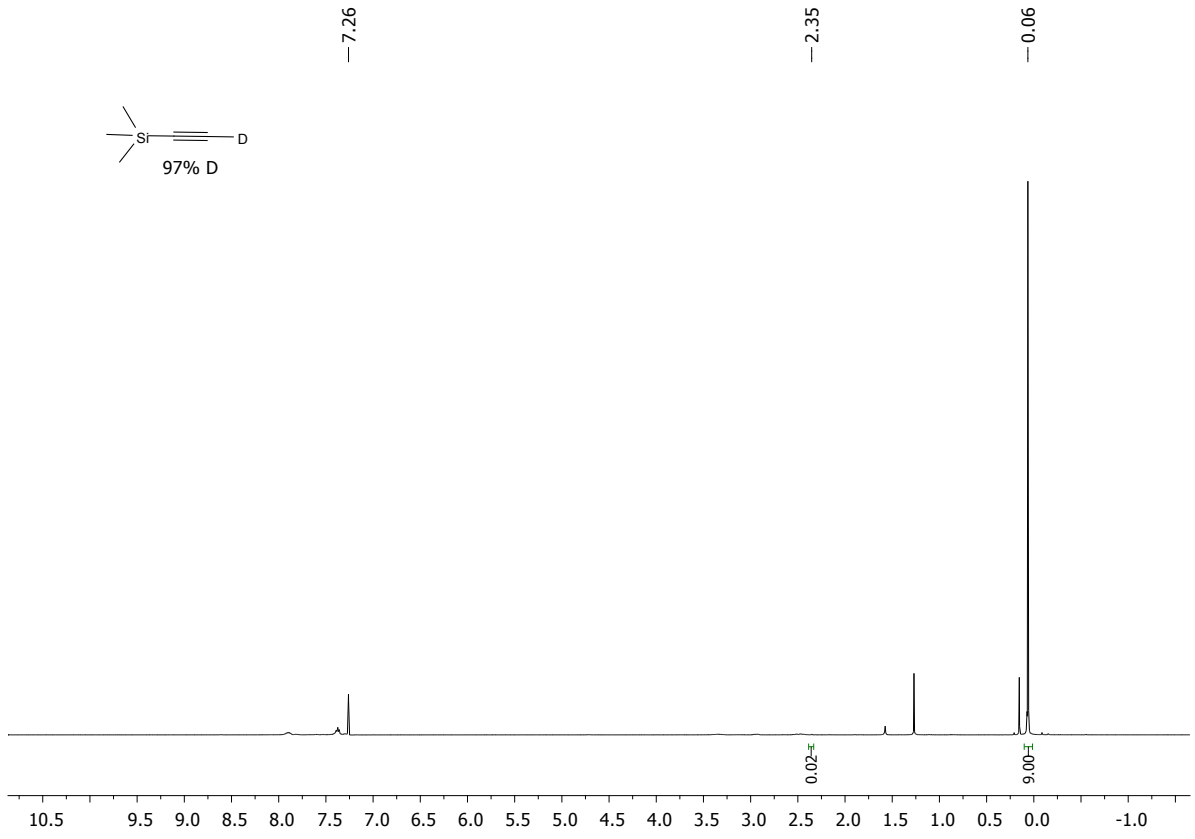
^{1}H NMR spectrum of 1-(prop-2-yn-1-yl)-1H-indole-d1 (400 MHz, $CDCl_3$):



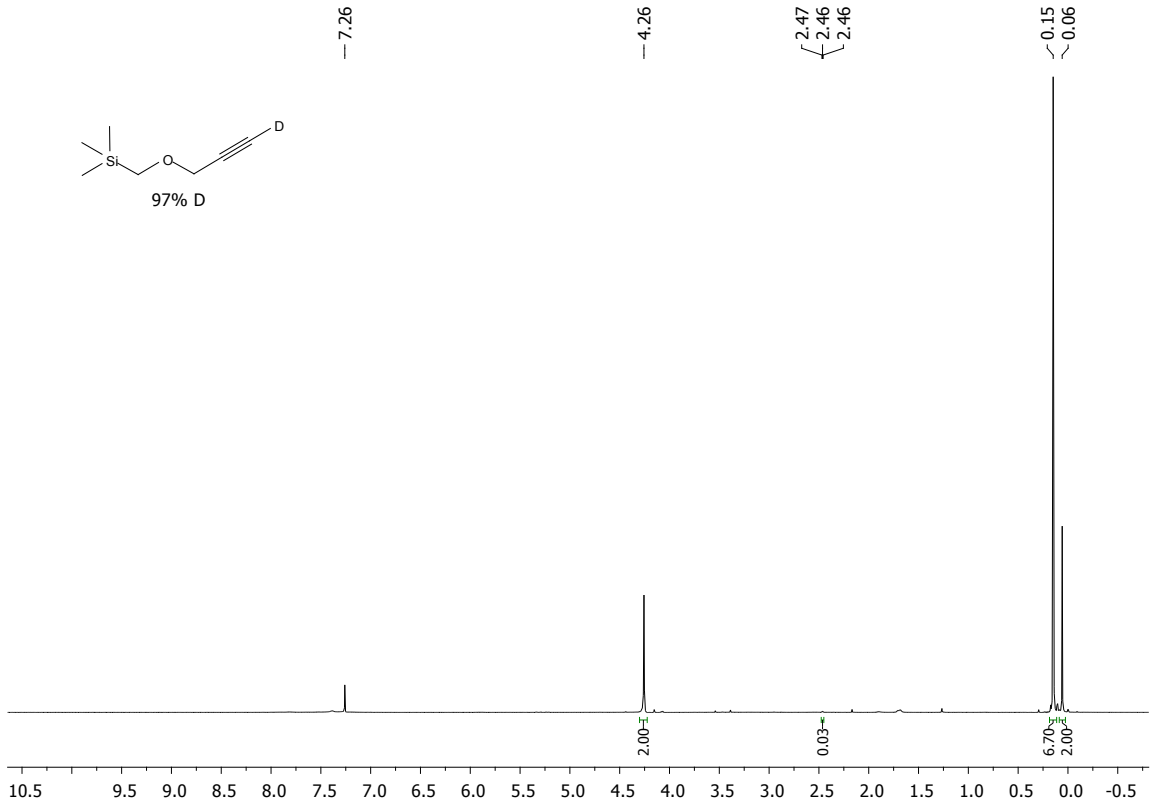
^{13}C NMR spectrum of 1-(prop-2-yn-1-yl)-1H-indole-d1 (100.6 MHz, $CDCl_3$):



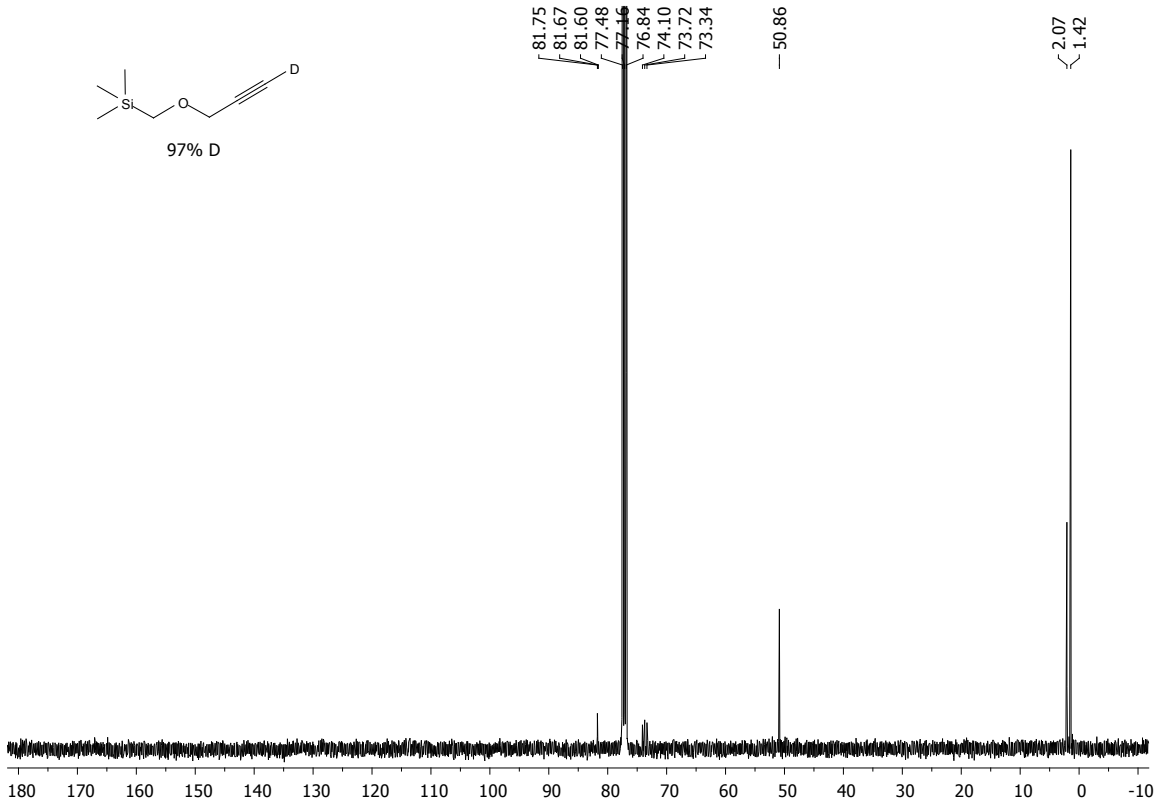
^{1}H NMR spectrum of ethynyltrimethylsilane-d1 (400 MHz, $CDCl_3$):



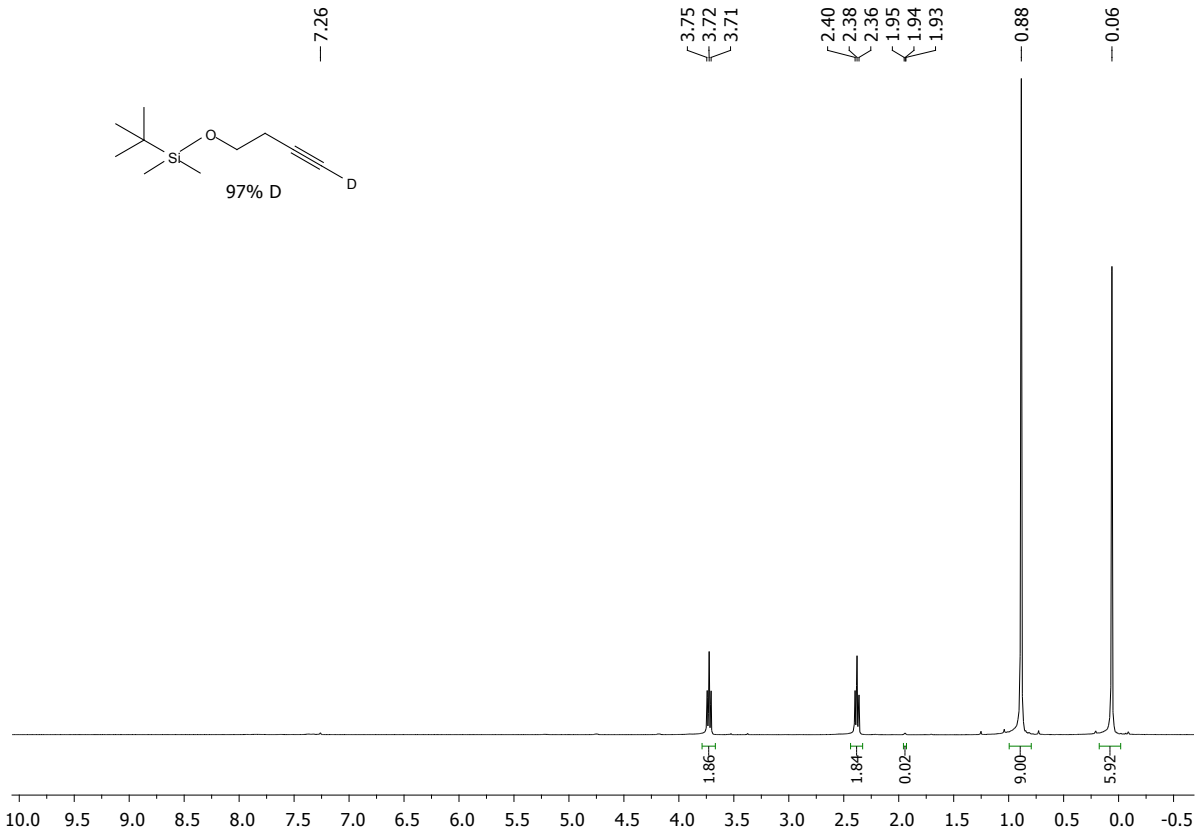
^{1}H NMR spectrum of trimethyl((prop-2-yn-1-yloxy)methyl)silane-d1 (400 MHz, $CDCl_3$):



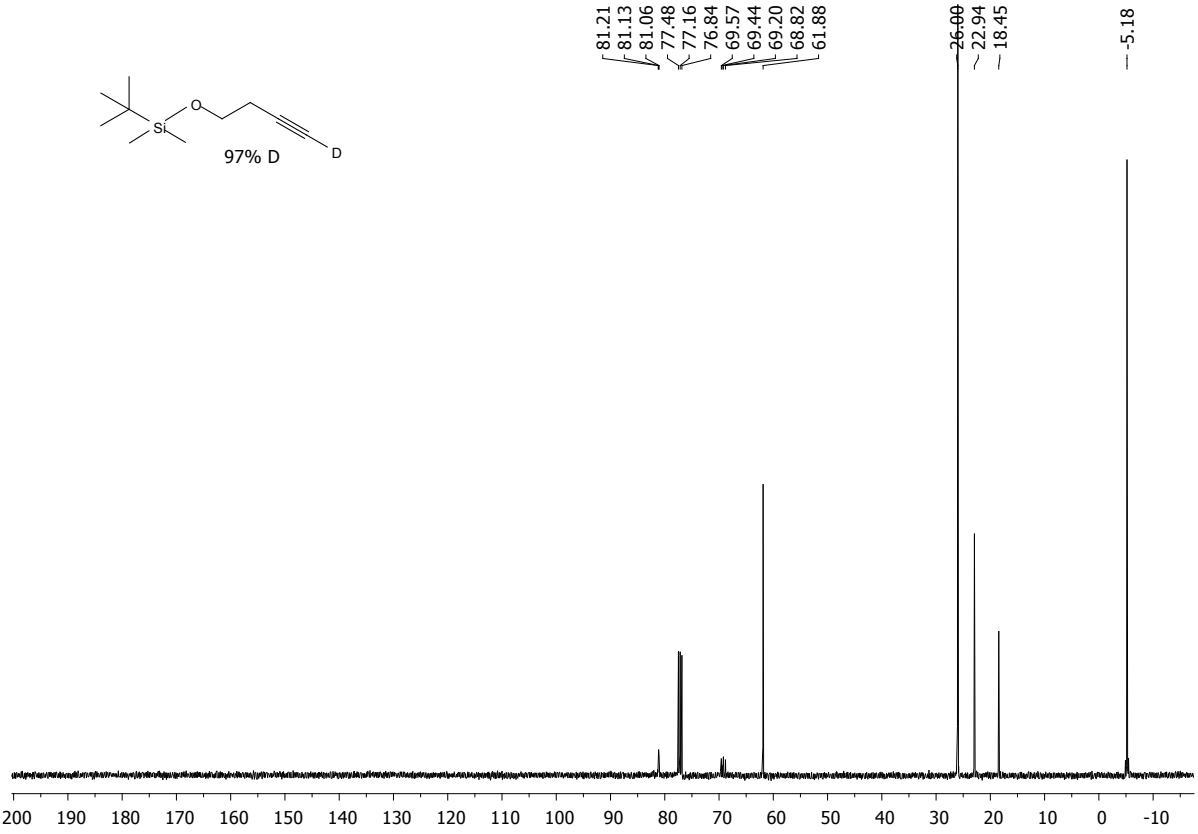
^{13}C NMR spectrum of (but-3-yn-2-yloxy)trimethylsilane -d1 (100.6 MHz, $CDCl_3$):



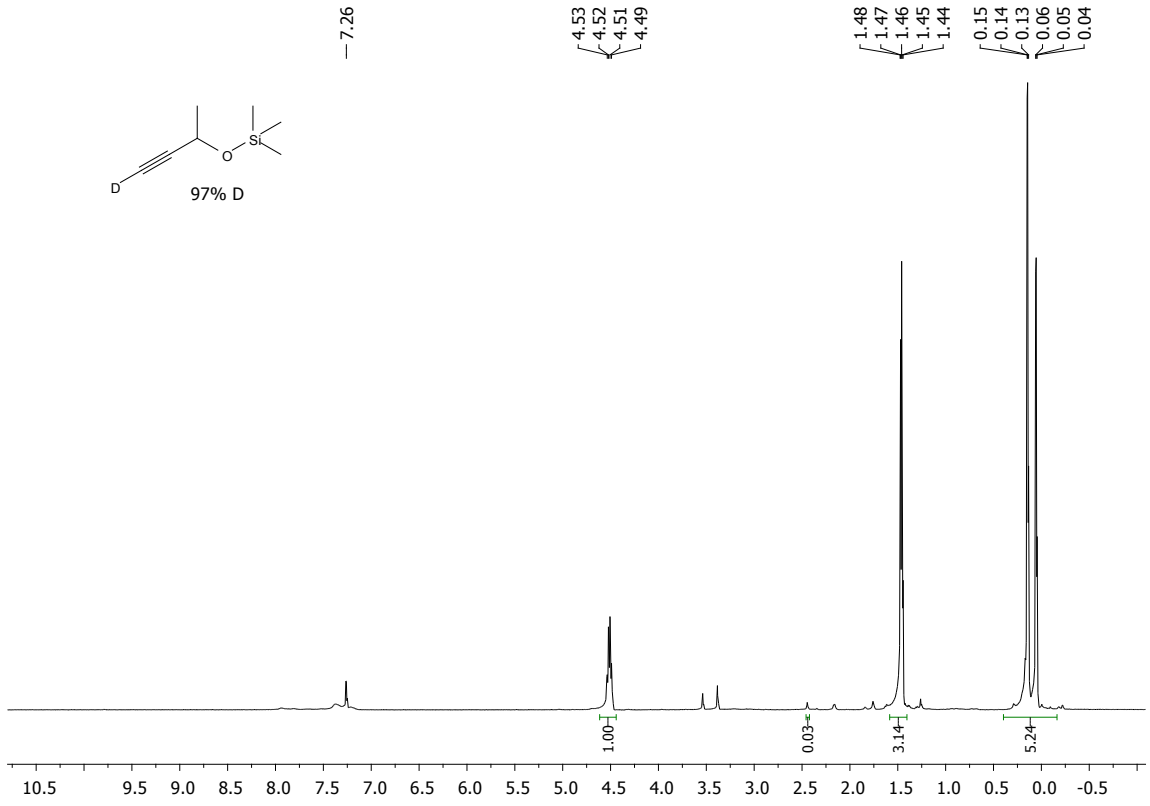
^{1}H NMR spectrum of (but-3-yn-1-yloxy)(tert-butyl)dimethylsilane-d1 (400 MHz, $CDCl_3$):



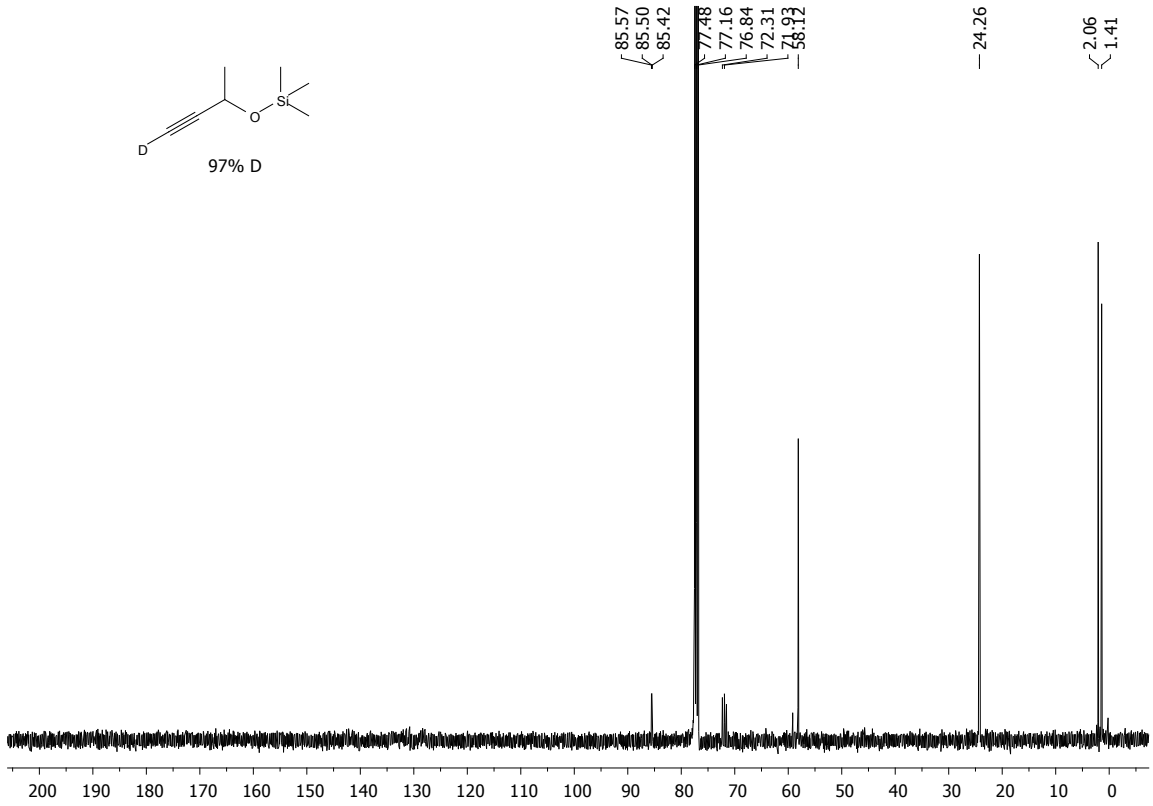
^{13}C NMR spectrum of (but-3-yn-1-yloxy)(tert-butyl)dimethylsilane-d1 (100.6 MHz, $CDCl_3$):



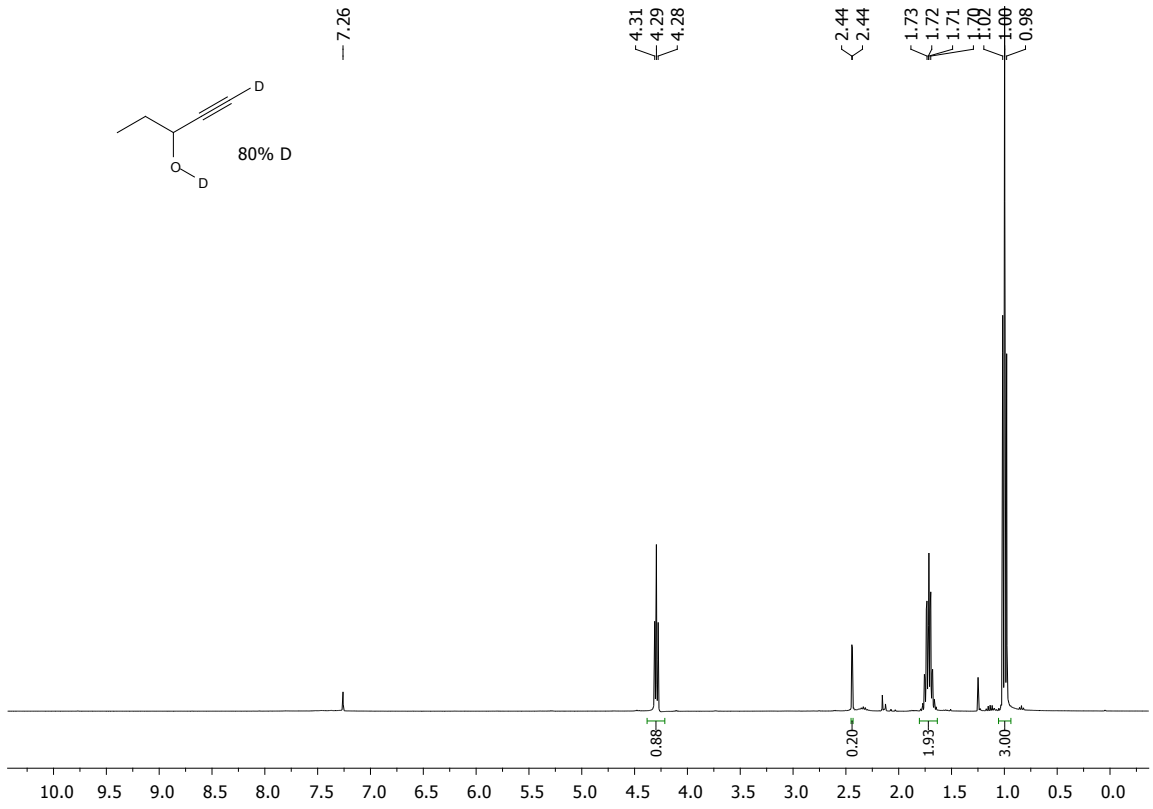
^{1}H NMR spectrum of (but-3-yn-2-yloxy)trimethylsilane-d1 (400 MHz, $CDCl_3$):



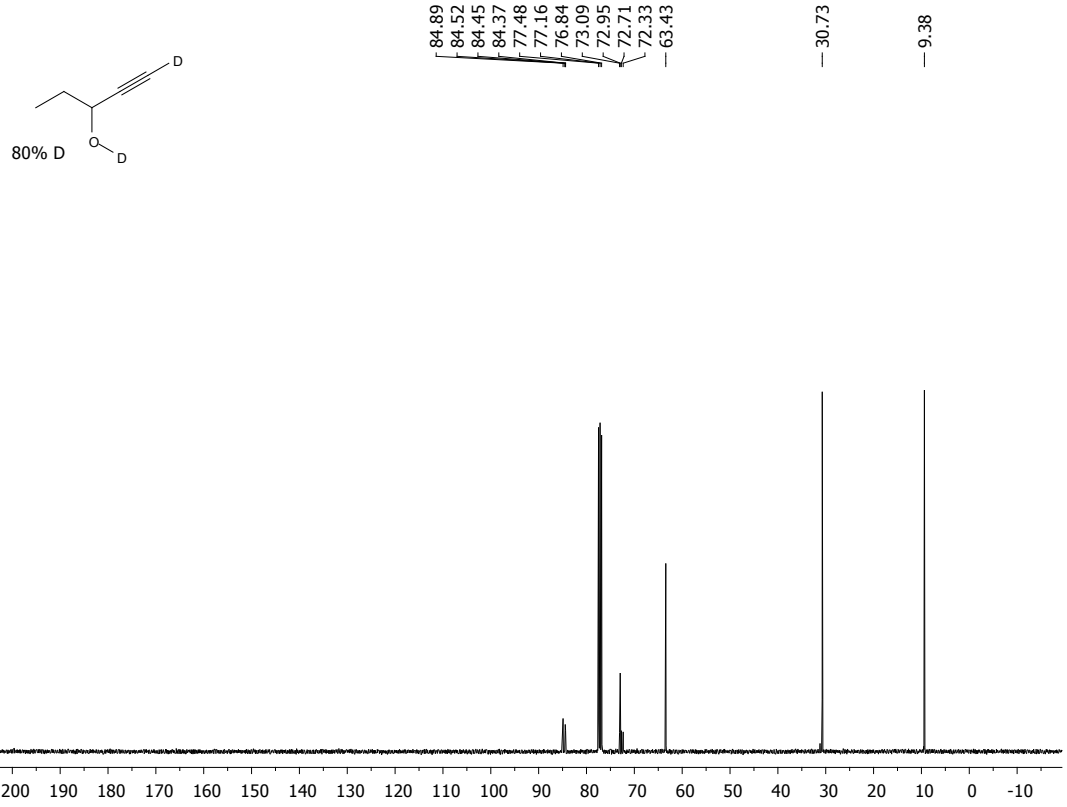
^{13}C NMR spectrum of (but-3-yn-2-yloxy)trimethylsilane-d1 (100.6 MHz, $CDCl_3$):



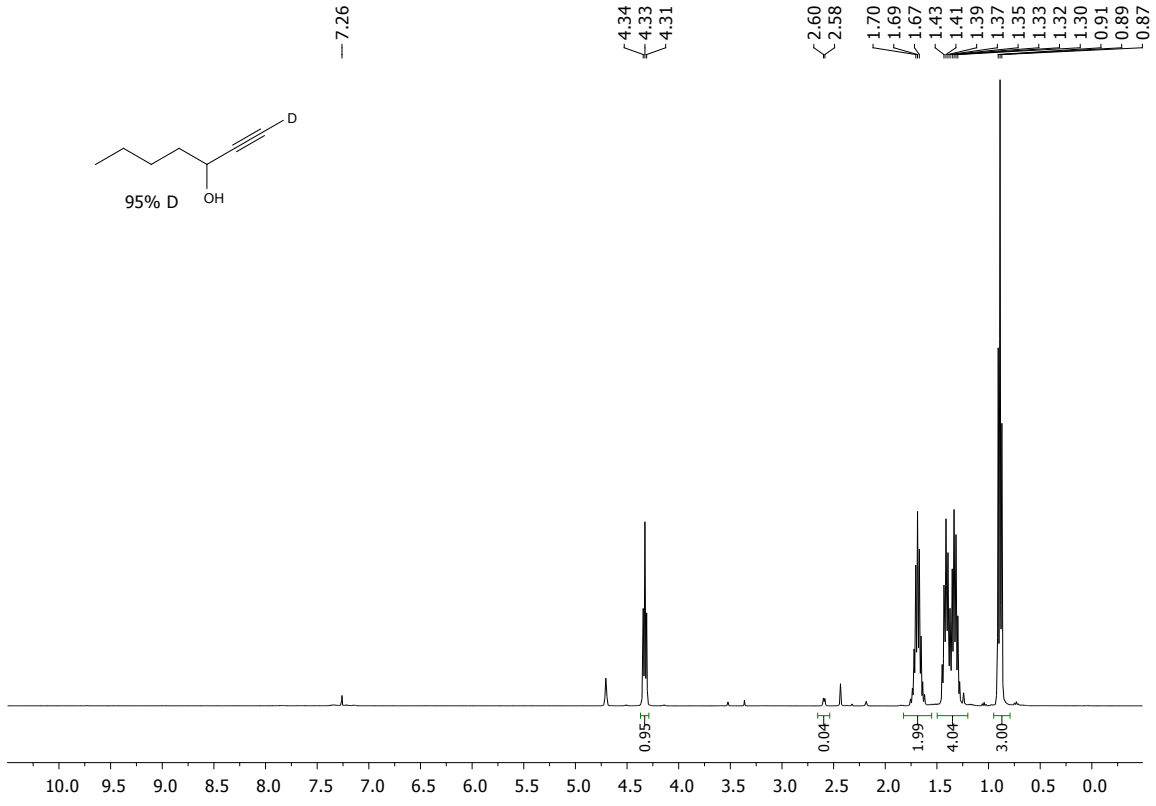
^{1}H NMR spectrum of pent-1-yn-3-ol-d2 (400 MHz, $CDCl_3$):



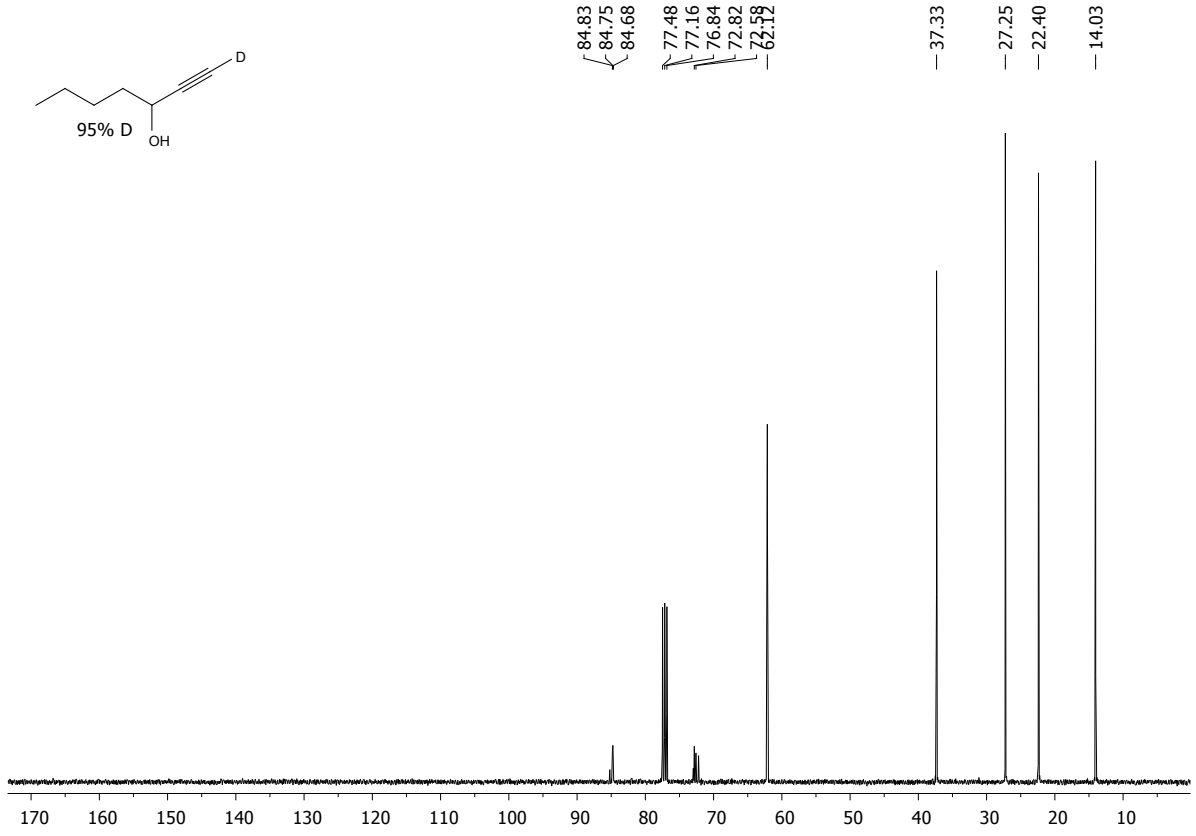
^{13}C NMR spectrum of pent-1-yn-3-ol-d2: (100.6 MHz, $CDCl_3$):



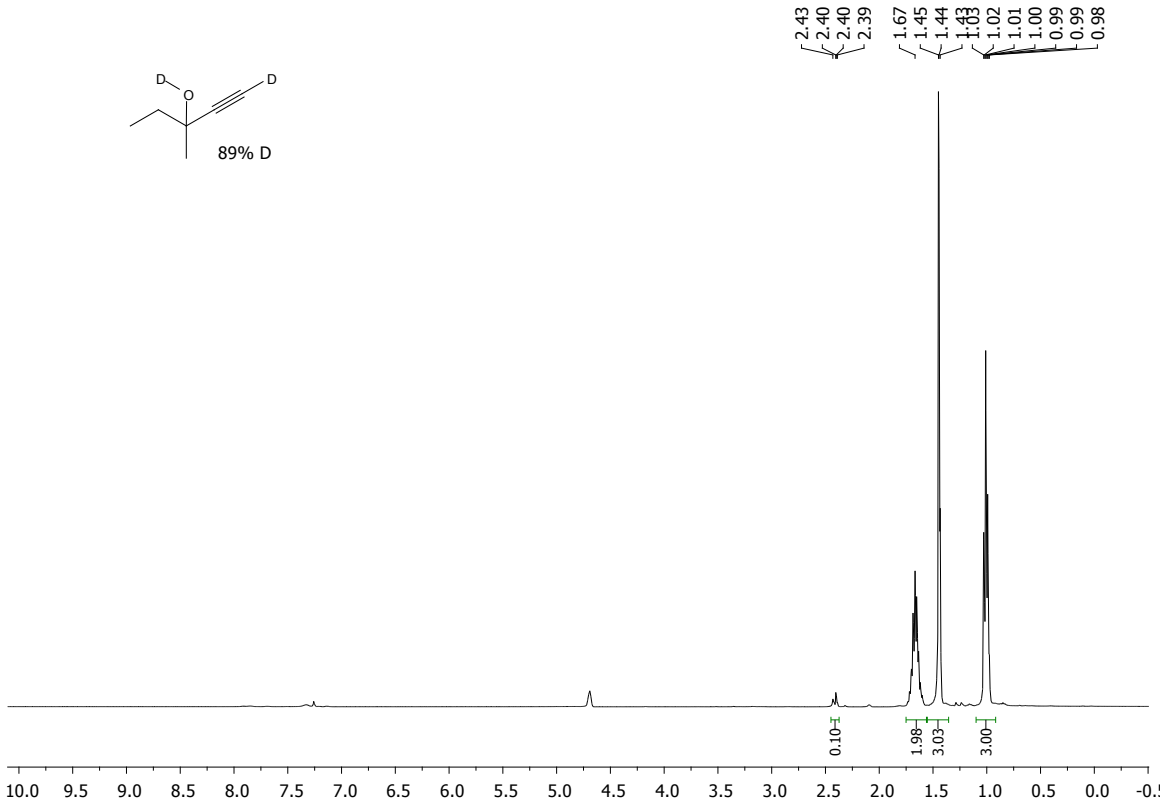
^{1}H NMR spectrum of hept-1-yn-3-ol-d2 (400 MHz, $CDCl_3$):



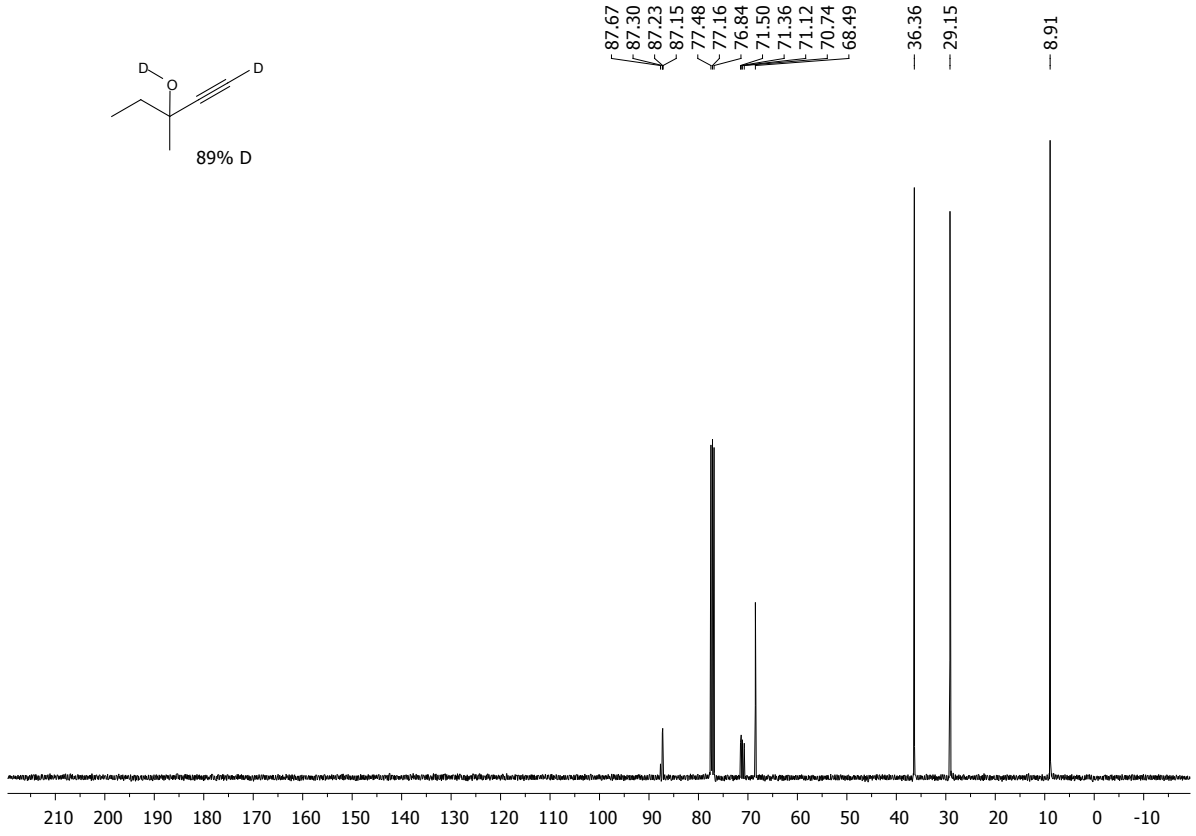
^{13}C NMR spectrum of hept-1-yn-3-ol-d2 (100.6 MHz, $CDCl_3$):



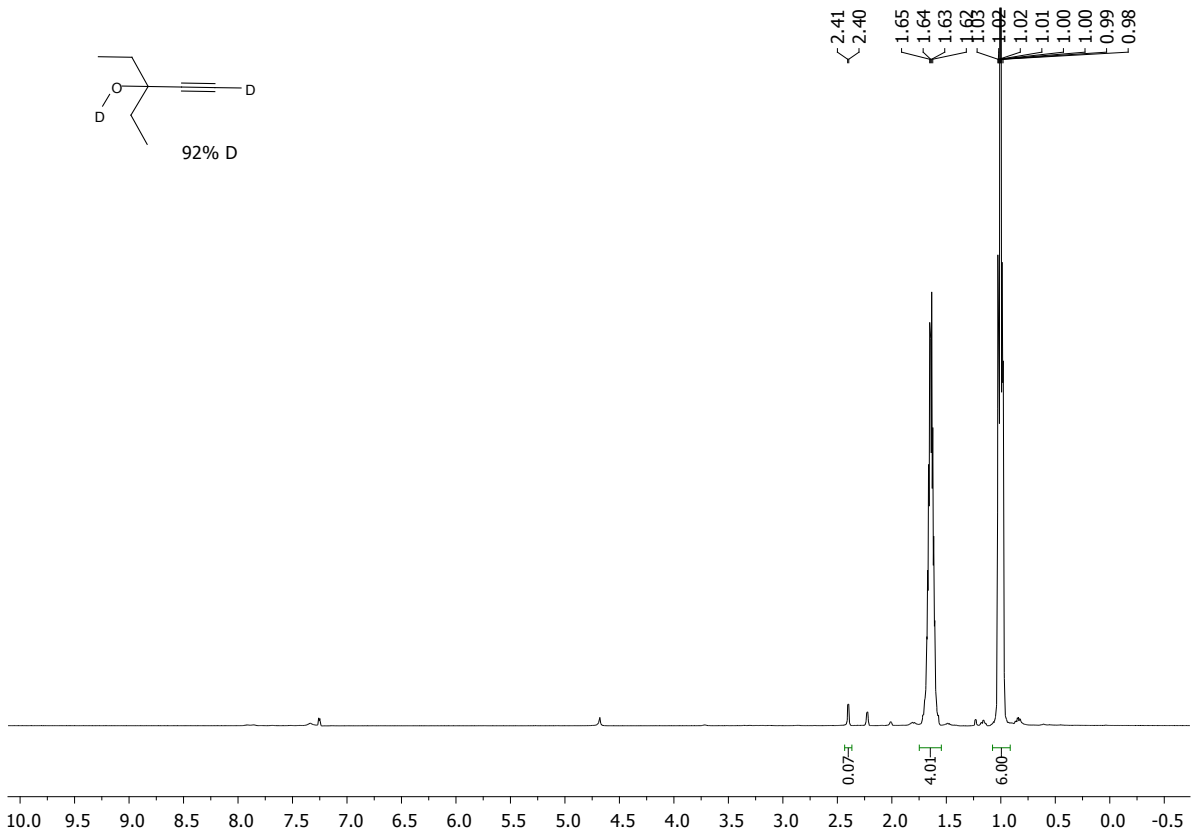
^{1}H NMR spectrum of 3-methylpent-1-yn-3-ol-d2 (400 MHz, $CDCl_3$):



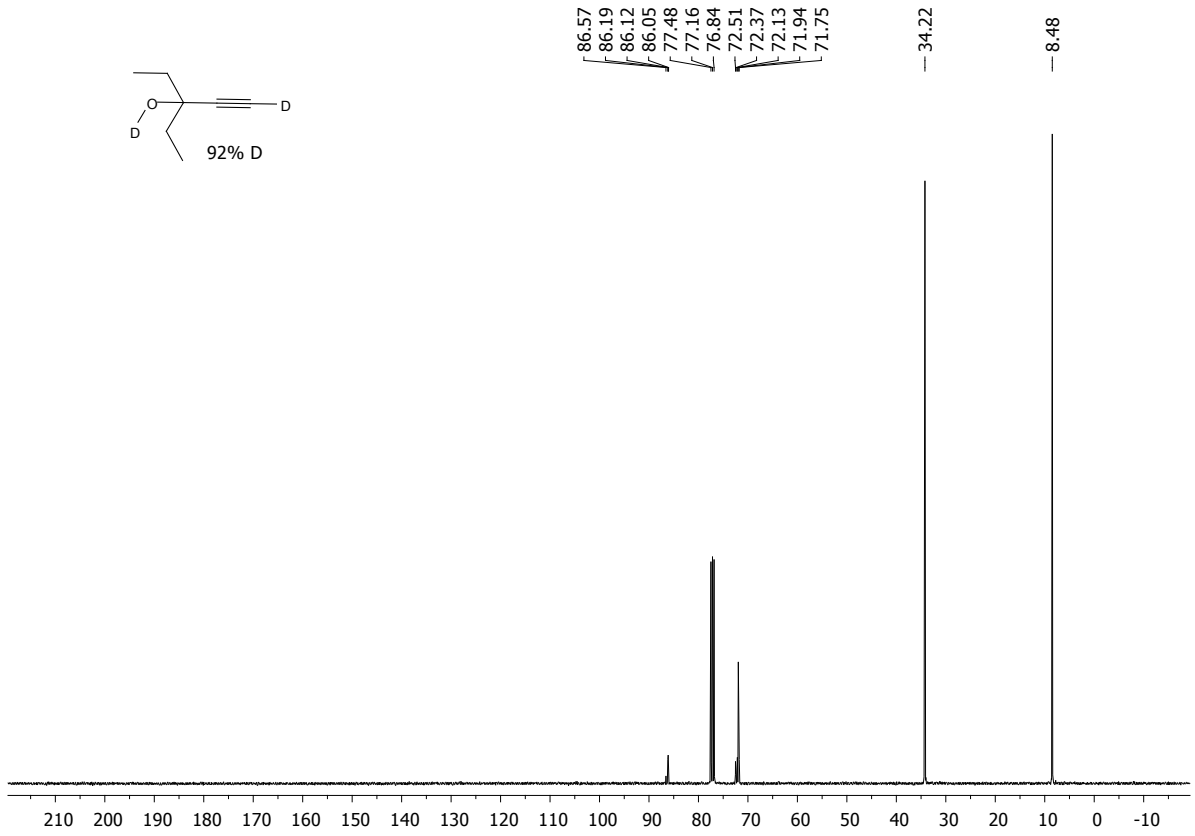
^{13}C NMR spectrum of 3-methylpent-1-yn-3-ol-d2 (100.6 MHz, $CDCl_3$):



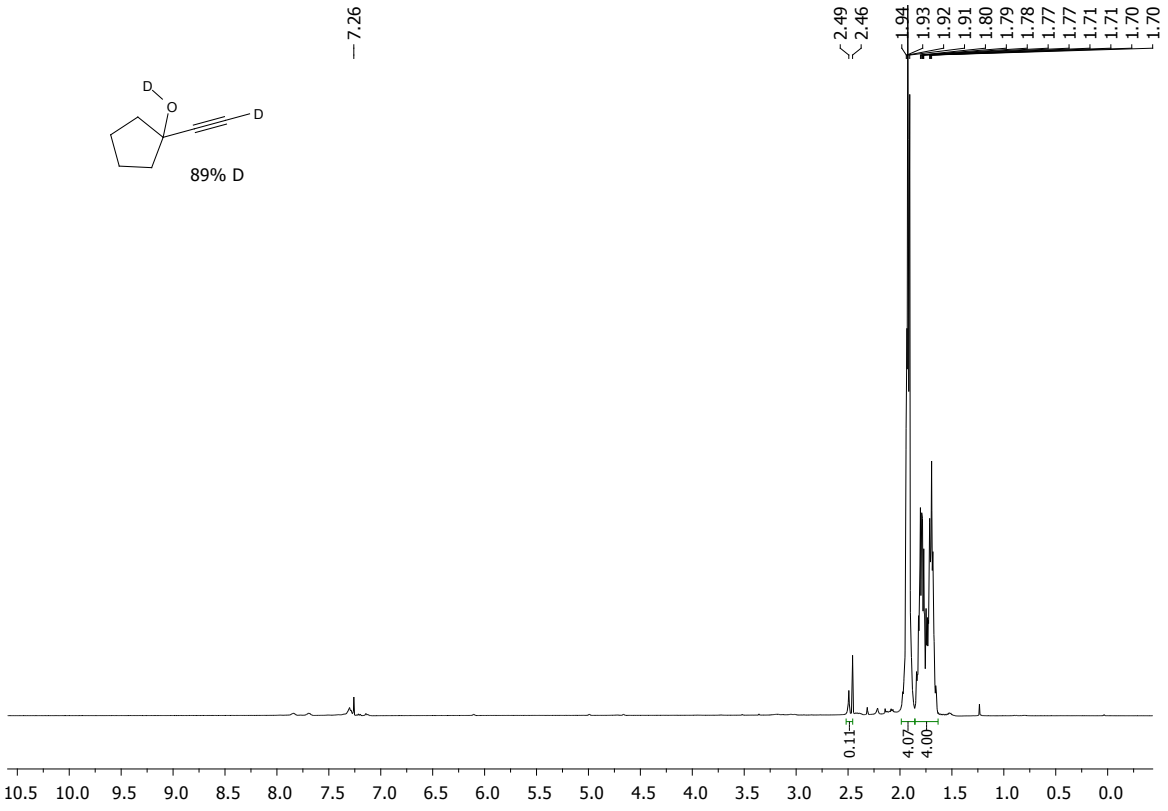
^{1}H NMR spectrum of 3-ethylpent-1-yn-3-ol-d2 (400 MHz, $CDCl_3$):



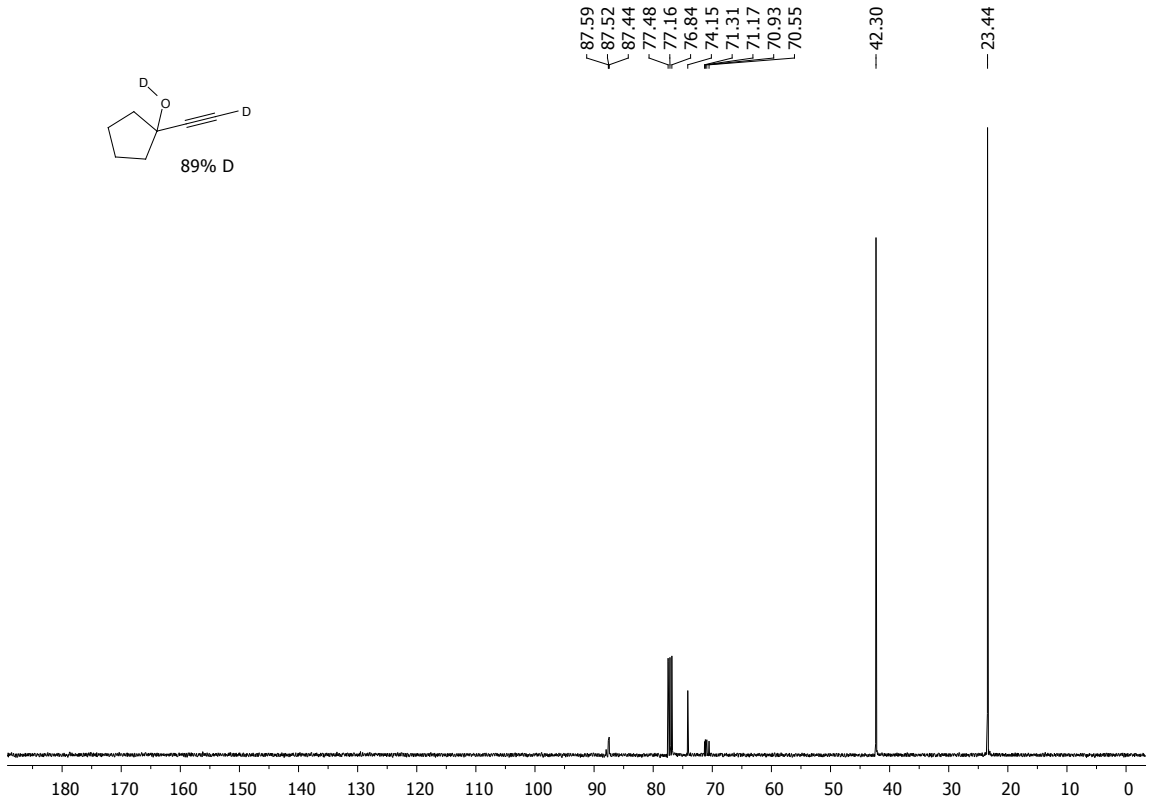
^{13}C NMR spectrum of 3-ethylpent-1-yn-3-ol-d2 (100.6 MHz, $CDCl_3$):



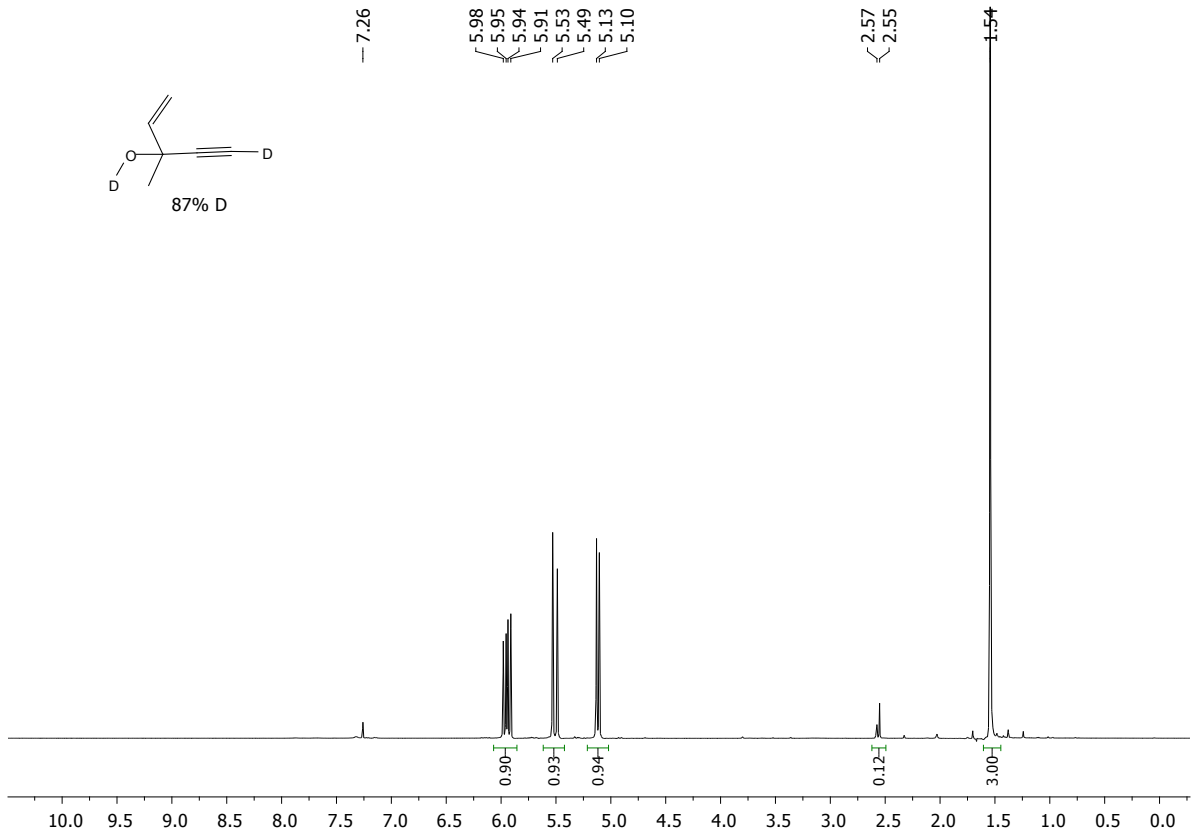
^{1}H NMR spectrum of 1-ethynylcyclopentanol-d2 (400 MHz, $CDCl_3$):



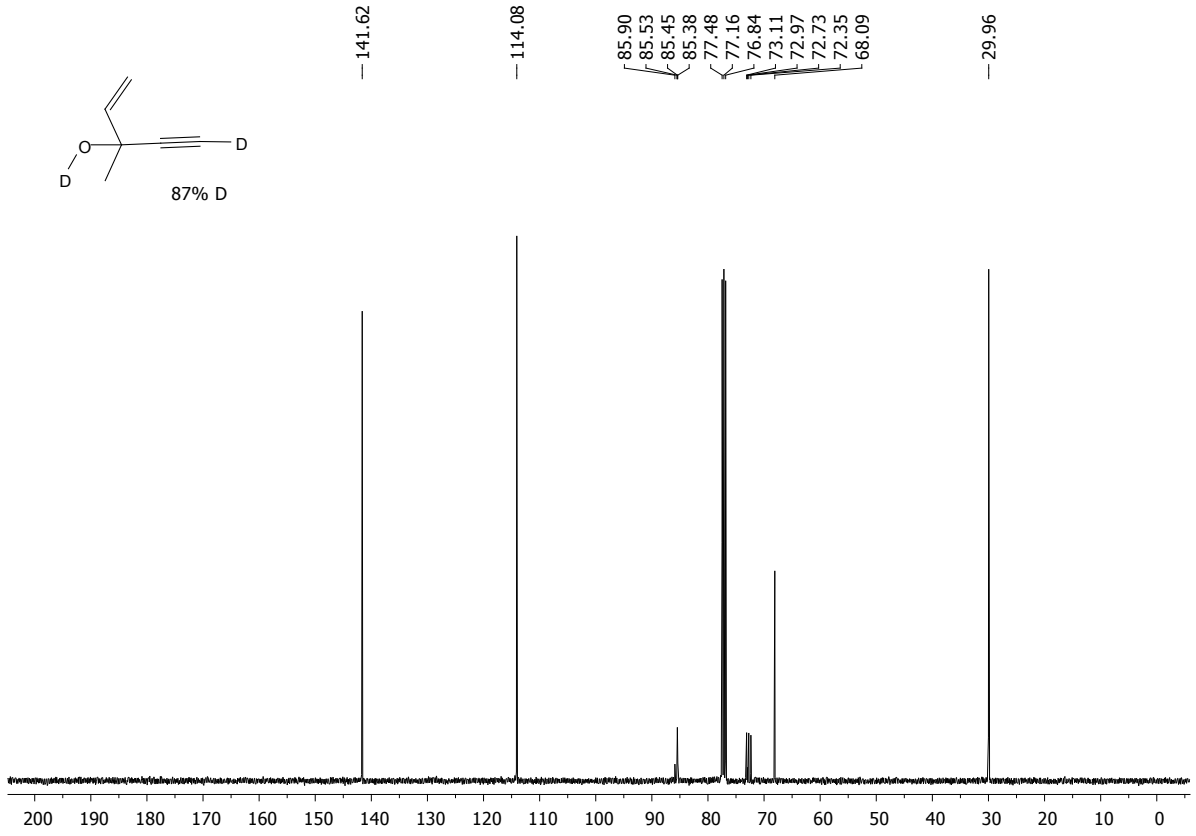
^{13}C NMR spectrum of 1-ethynylcyclopentanol-d2 (100.6 MHz, $CDCl_3$):



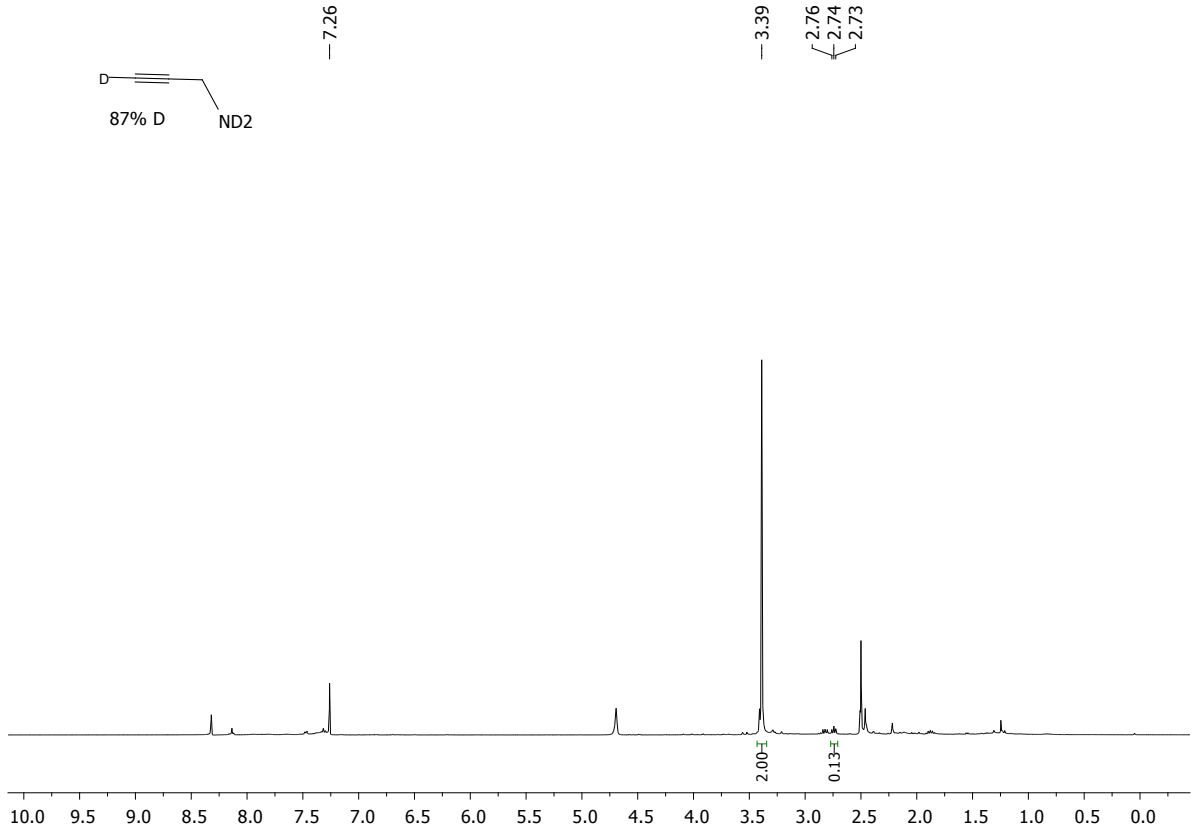
^{1}H NMR spectrum of 3-methylpent-1-en-4-yn-3-ol -d2 (400 MHz, $CDCl_3$):



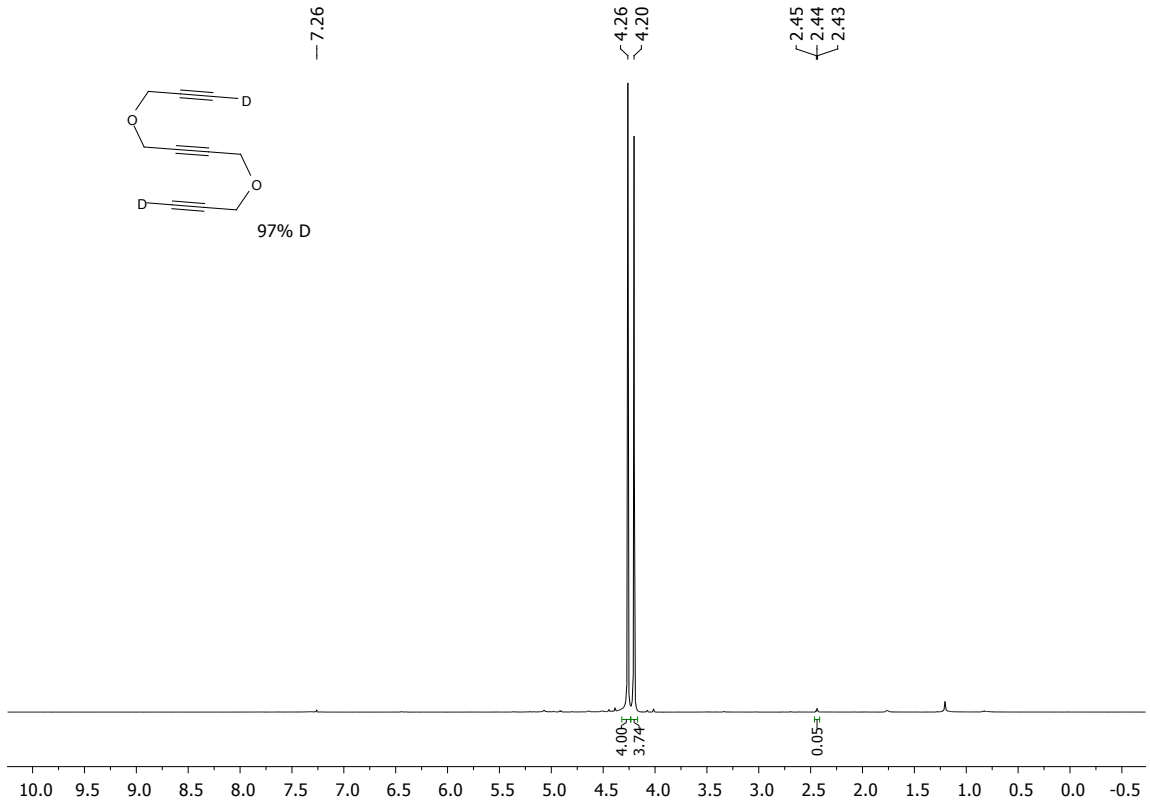
^{13}C NMR spectrum of 3-methylpent-1-en-4-yn-3-ol -d2 (100.6 MHz, $CDCl_3$):



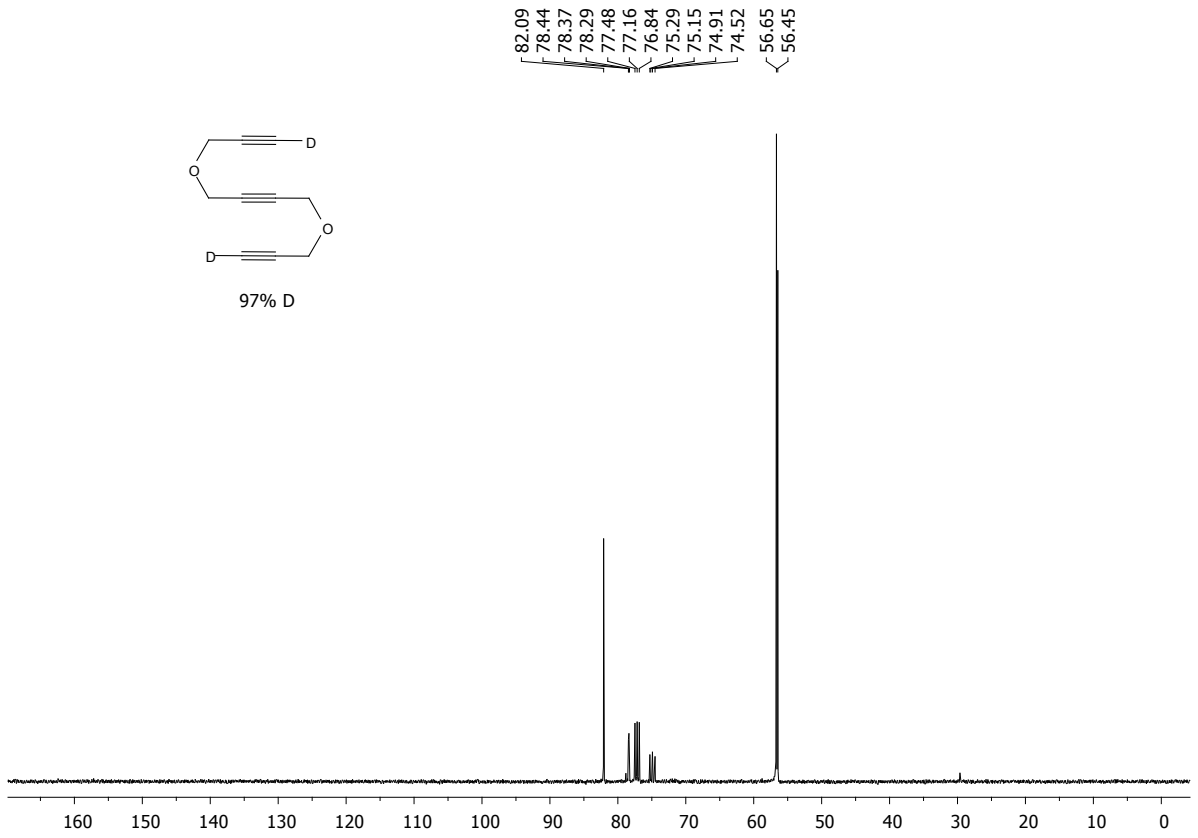
^{1}H NMR spectrum of prop-2-yn-1-amine-d3 (400 MHz, $CDCl_3$):



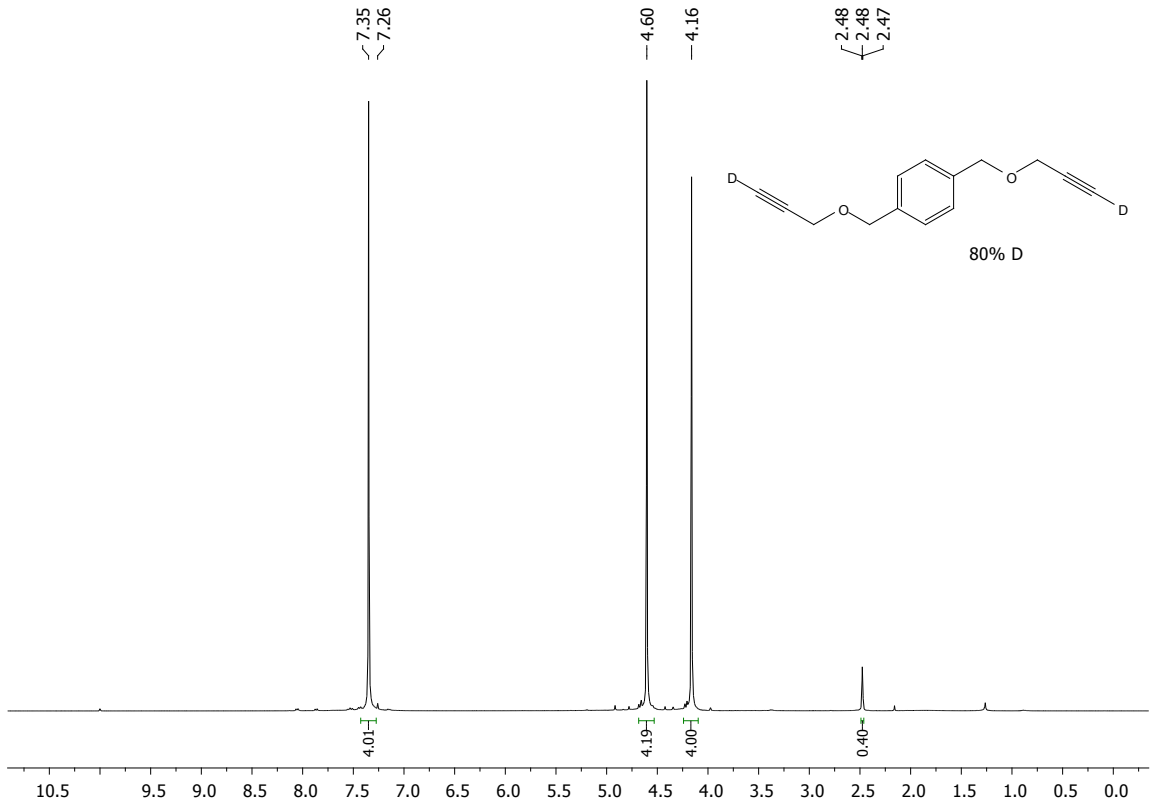
^{1}H NMR spectrum of 1,4-bis(prop-2-yn-1-yloxy)but-2-yne-d2 (400 MHz, $CDCl_3$):



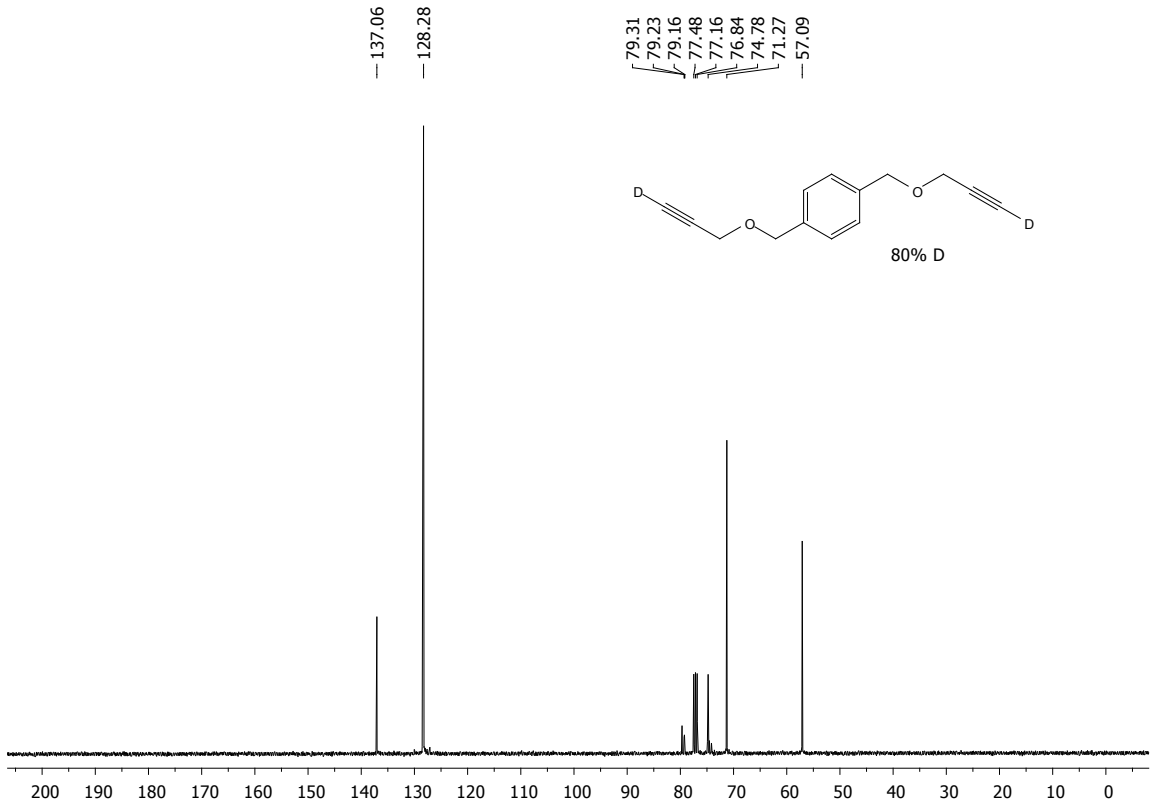
^{13}C NMR spectrum of 1,4-bis(prop-2-yn-1-yloxy)but-2-yne-d2 (100.6 MHz, $CDCl_3$):



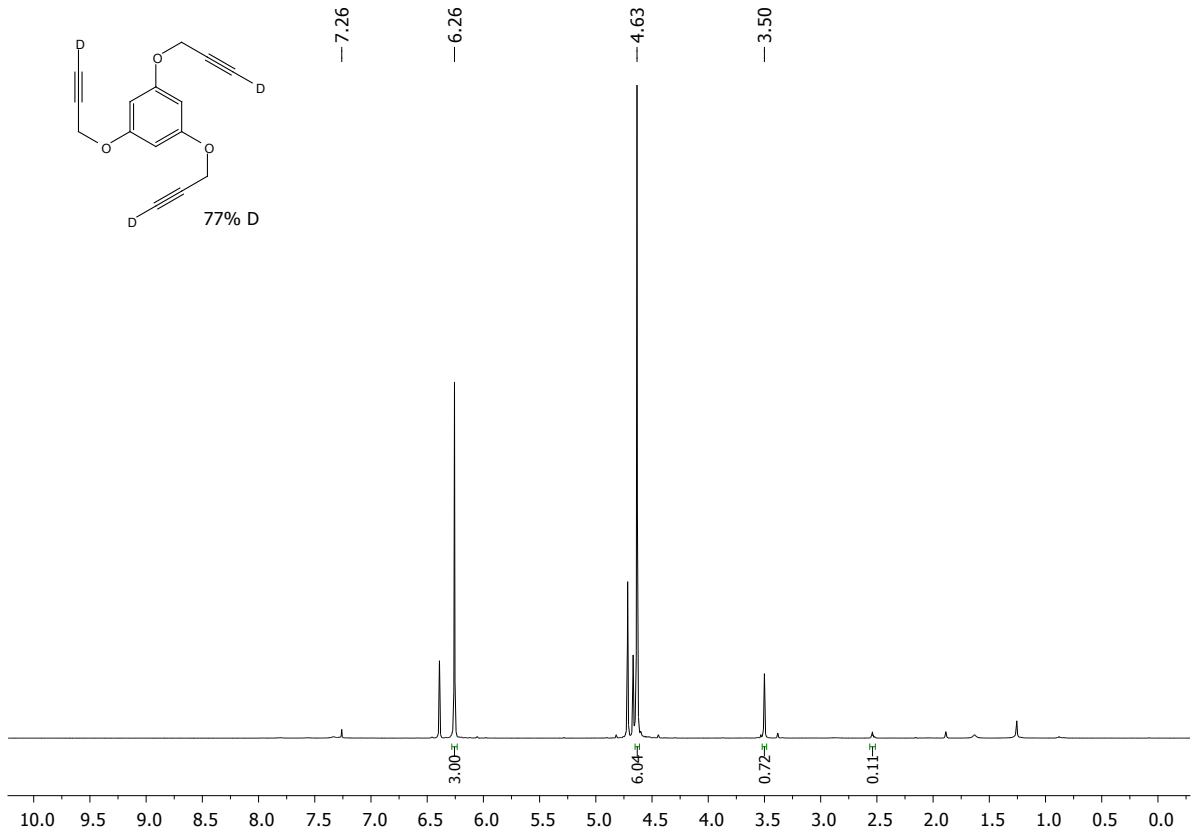
^{1}H NMR spectrum of 1,4-bis((prop-2-yn-1-yloxy)methyl)benzene-d2 (400 MHz, $CDCl_3$):



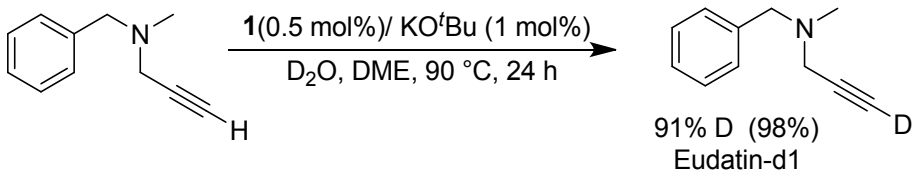
^{13}C NMR spectrum of 1,4-bis((prop-2-yn-1-yloxy)methyl)benzene-d2 (100.6 MHz, $CDCl_3$):



^{1}H NMR spectrum of 1,3,5-tris(prop-2-yn-1-yloxy)benzene-d3 (400 MHz, $CDCl_3$):



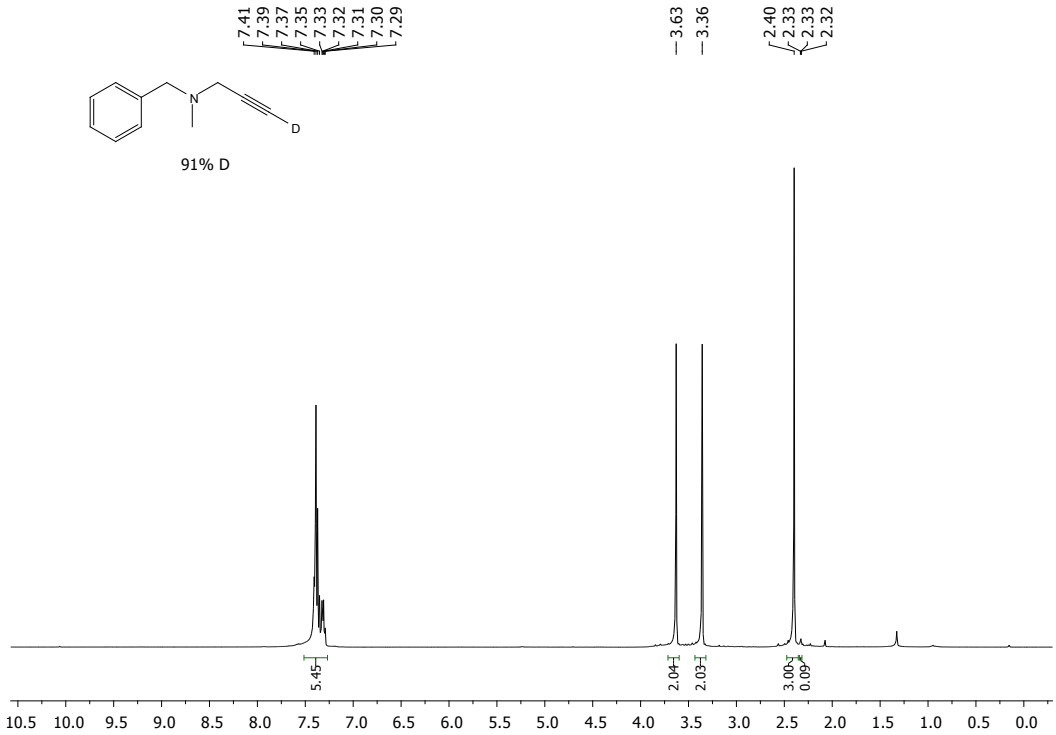
Synthesis of Eudatin-d1:



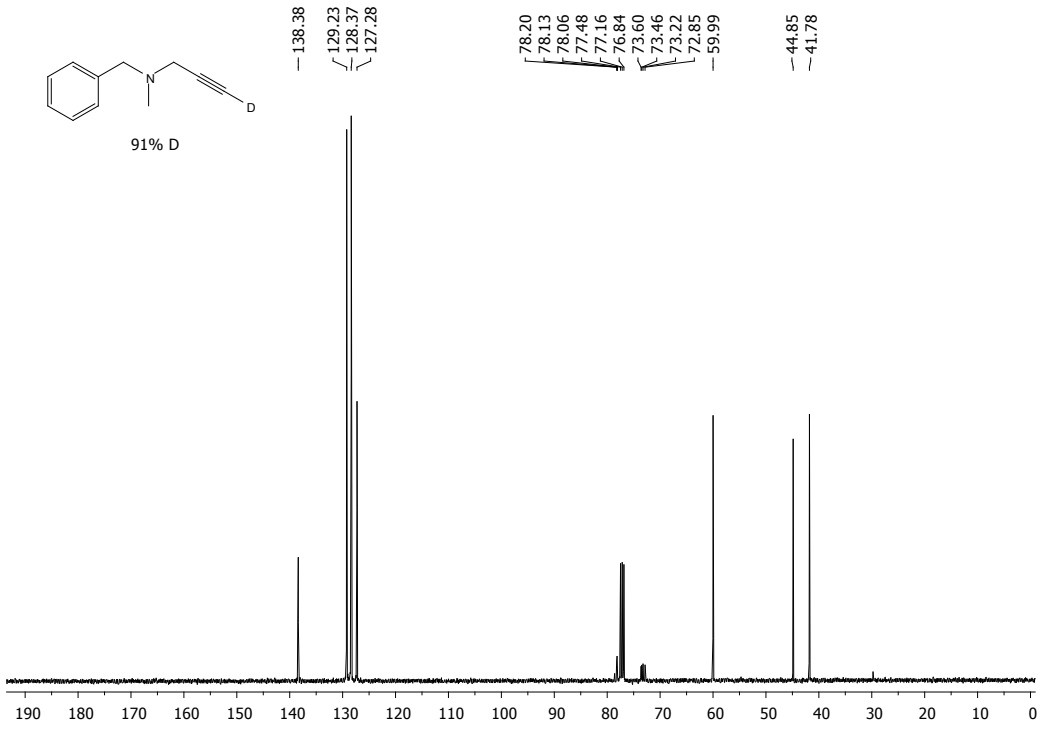
In a srew-cap scintillation vial *N*-benzyl-*N*-methylprop-2-yn-1-amine (0.5 mmol, 80 mg), **1** (0.0025 mmol, 1.5 mg), KO^{t}Bu (0.005 mmol, 0.6 mg) and 1,2-dimethoxyethane (1 ml) were added under nitrogen atmosphere. Degassed D_2O (0.25 ml, 12.5 mmol) was added under nitrogen atmosphere and the reaction vial immersed into a preheated oil bath of 90 °C. After 24 h the solvent is evaporated and the product is extracted with dichloromethane. The combined organic layers then dried over sodium sulphate and after removal of solvent under vaccum provided 91% deuterium incorporated Eudatin-d1. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41-7.29 (m, 5H, ArC*H*), 3.63 (CH_2), 3.36 (CH_2), 2.40 (CH_3). ^{13}C

NMR (101 MHz, $CDCl_3$) δ 138.38 (quat-*C*), 129.23 (Ar*C*H), 128.37 (Ar*C*H), 127.28 (Ar*C*H), 78.20-78.06 (t, quat-*C*), 73.60-72.85 (t), 59.99 (*C*H_2), 44.85 (*C*H_2), 41.78 (*C*H_3).

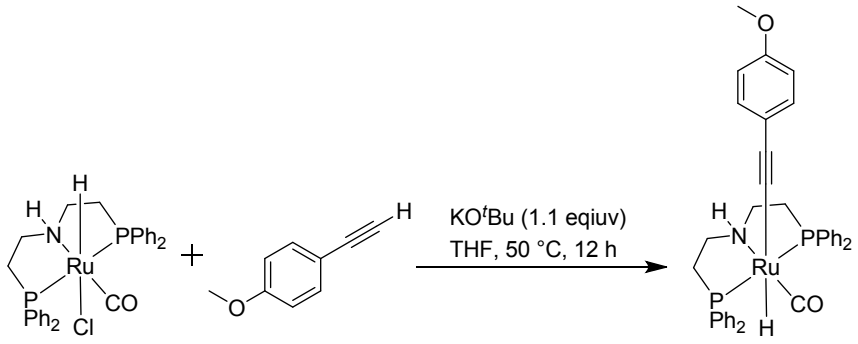
^{1}H NMR spectrum of N-benzyl-N-methylprop-2-yn-1-amine-d1 (400 MHz, $CDCl_3$):



^{13}C NMR spectrum of N-benzyl-N-methylprop-2-yn-1-amine-d1 (100.6 MHz, $CDCl_3$):

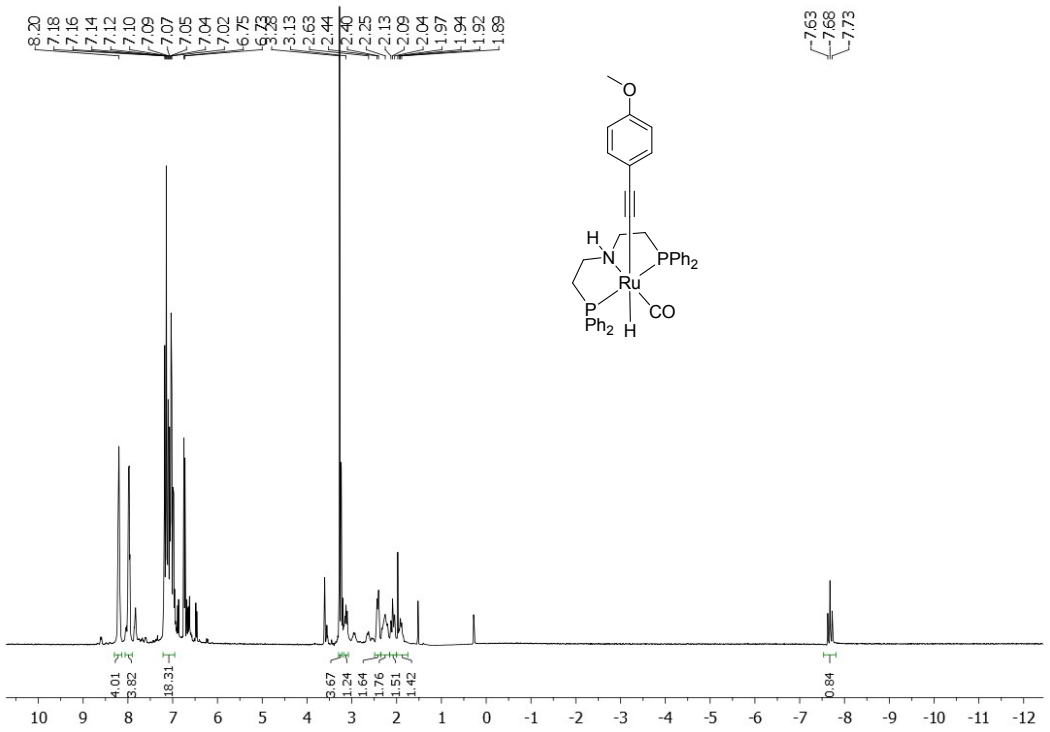


Synthesis and characterization of Ru-acetylide complex 2a:

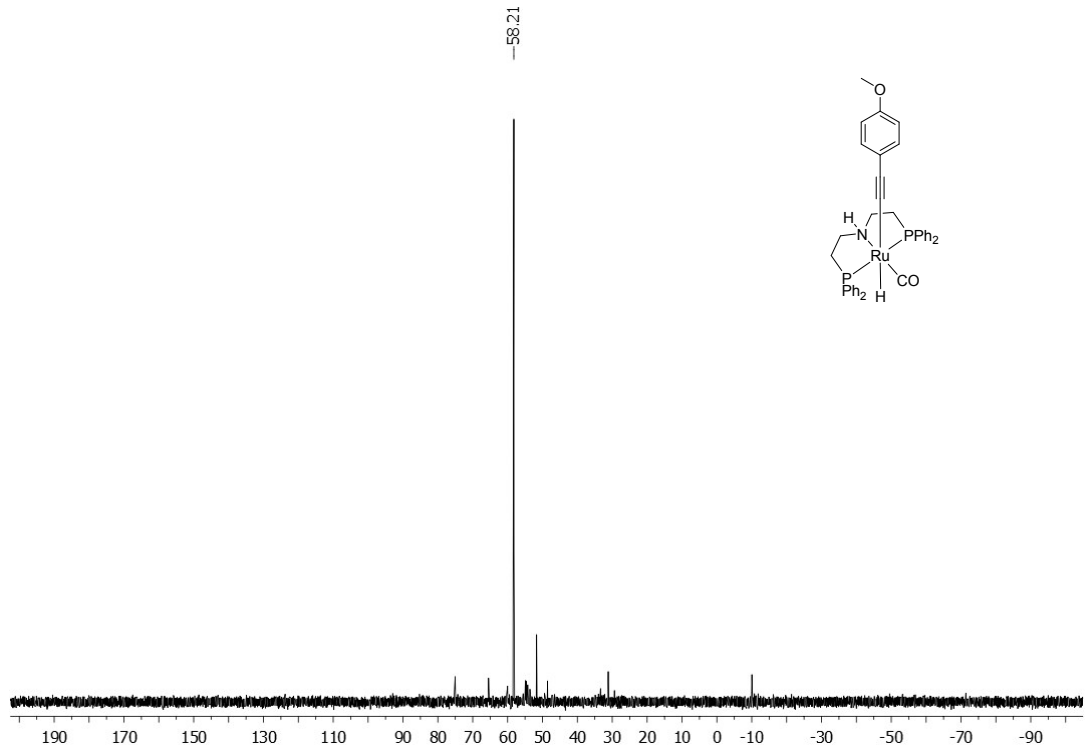


In a screw cap scintillation vial Ru-macho **1** (0.032 mmol, 20 mg), KO^{t}Bu (1.1 equiv, 0.035 mmol, 4 mg) and THF (1 ml) were added and the resulting mixture was allowed to stir at room temperature for 30 min. To the reddish-brown solution 4-ethynyl-anisole (1.1 equiv. 0.035 mmol, 4 µl) was added dropwise. The resulting solution then stirred for another 12 h at 50 °C. The volume of light yellow solution was reduced under vaccum and slow addition of cold hexane (2 ml) provided light yellow precipitate. The solution was decanted and the precipitate was washed with hexane (1 ml) three times. The precipitate was dried under vacuum for overnight to afford **2a** as light yellow solid in 77% yield (17.30 mg). IR (C_6H_6): 3428, 2092 (Ru-*H*), 1915, 1610, 1384, 1266, 1176, 1100, 962, 896, 741 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.21 (m, 4H, ArC*H*), 7.98 (m, 4H, ArC*H*), 7.09 (m, 16H, ArC*H*), 3.28 (s, 3H, OCH_3), 3.13 (br s, 1H, N*H*), 2.42 (br, 2H, CH_2), 2.25 (br, 2H, CH_2), 2.09 (t, *J* = 16 Hz, 2H, CH_2), 1.92 (t, *J* = 12 Hz, 2H, CH_2), -7.68 (t, *J* = 20 Hz, 1H, Ru–*H*). ^{31}P{^{1}H} NMR (CDCl3): δ 58.21 (s).

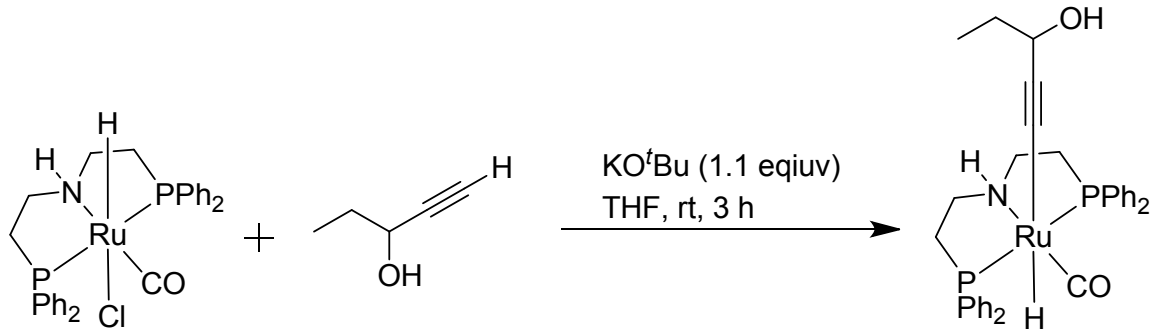
^{1}H NMR spectrum of Ru-acetylide complex **2a**:



^{31}P NMR spectrum of Ru-acetylide complex **2a**:

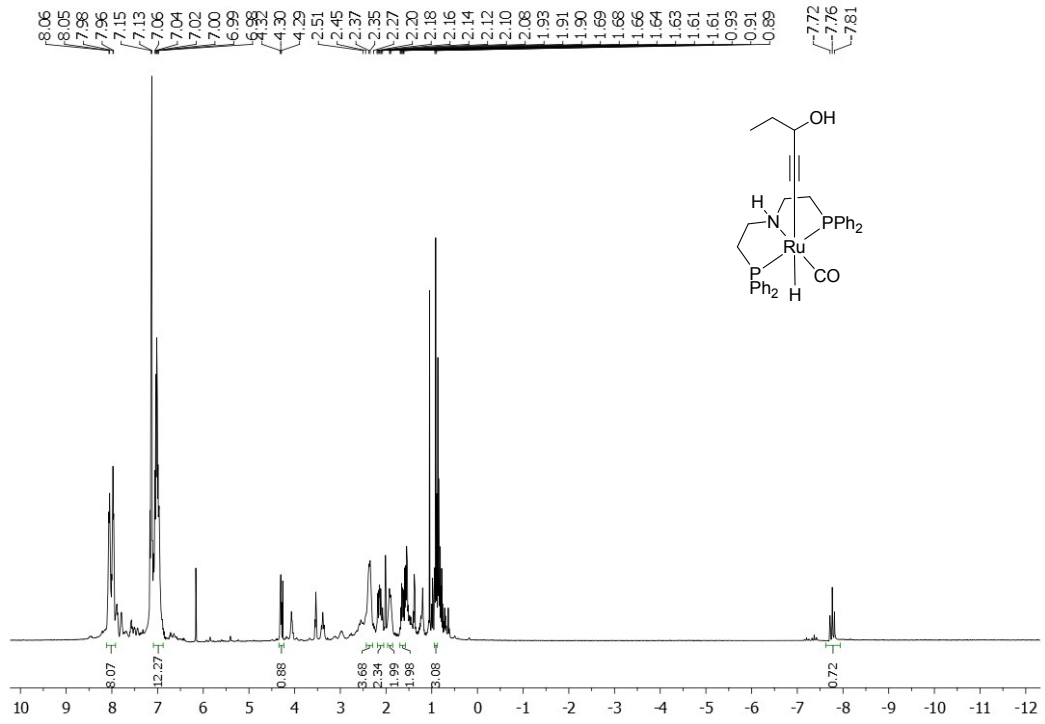


Synthesis and characterization of Ru-acetylide complex 2b:

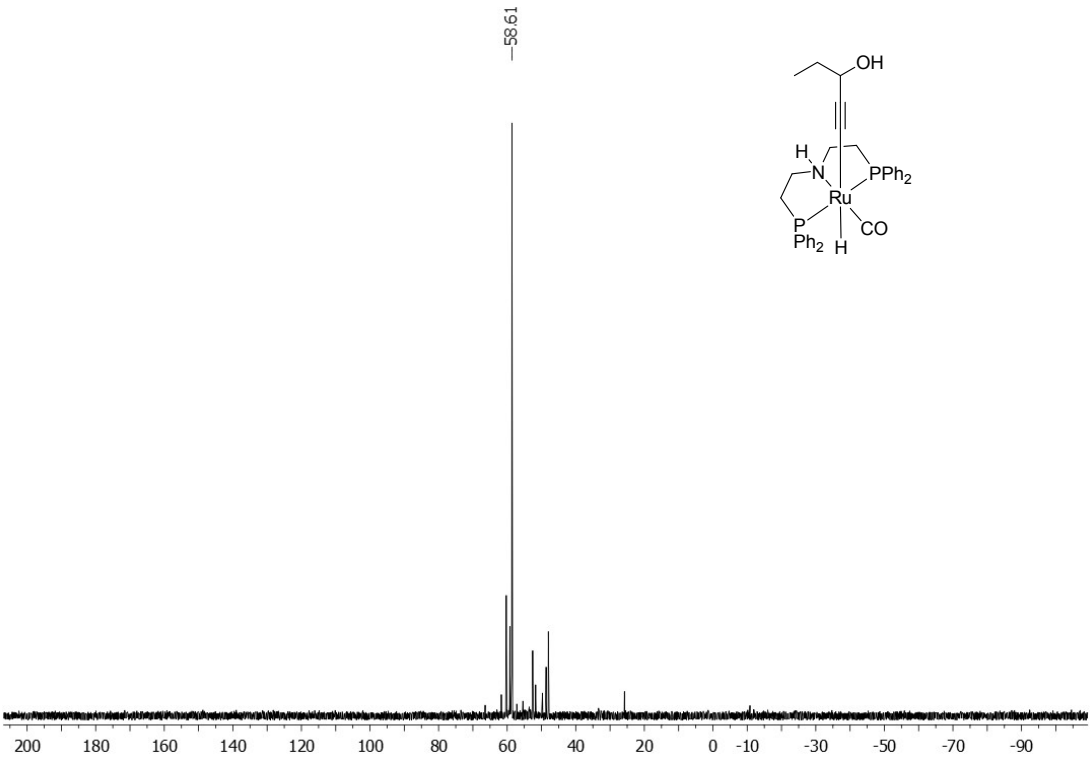


In a screw cap scintillation vial Ru-macho **1** (0.032 mmol, 20 mg), KO^{t}Bu (1.1 equiv, 0.035 mmol, 4 mg) and THF (1 ml) was added and the resulting mixture was allowed to stir at room temperature for 30 min. To the light yellow solution pent-1-yn-3-ol (1.1 equiv. 0.035 mmol, 3 µl) was added dropwise. The resulting solution then stirred for another 3 h. The volume of light yellow solution was then reduced under vaccum and slow addition of cold hexane (2 ml) provided light yellow precipitate. The solution was decanted and the precipitate was washed with hexane (1 ml) three times. The resulted yellow complex was dried under vacuum for overnight (17 mg, 80%). IR (C_6H_6): 3431, 2923, 2038 (Ru-*H*), 1924, 1734, 1603, 1495, 1177, 1100, 835, 729 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.05 (m, 4H, ArC*H*), 7.99 (m, 4H, ArC*H*), 7.00 (m, 12H, ArC*H*), 4.30 (t, *J* = 8 Hz, 1H, OC*H*), 3.38 (br s, 1H, N*H*), 2.37 (br, 4H, CH_2), 2.14 (br, 2H, CH_2), 1.91 (br, 2H, CH_2), 1.64 (m, 2H, CH_2), 0.91(t, J = 8Hz, 3H, CH_3), -7.76 (t, *J* = 20 Hz, 1H, Ru–*H*). ^{31}P{^{1}H} NMR (CDCl3): δ 58.61 (s).

^{1}H NMR spectrum of Ru-acetylide complex **2b**:



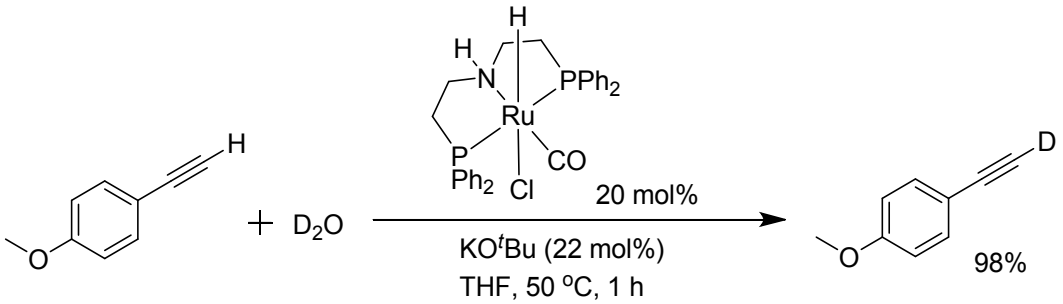
^{31}P NMR spectrum of Ru-acetylide complex **2b**:



Determination of the molecular structure of 2b in the solid state by X-ray single crystal diffraction: Single crystals of complex **2b** suitable for X-ray analysis were obtained from a solution of benzene and hexane. A crystal suited for single crystal x-ray diffraction measurements was mounted on a glass fibre. Geometry and intensity data were collected with a Bruker SMART D8 goniometer equipped with an APEX CCD detector and with an Incoatec microsource (Mo-Kα radiation, λ = 0.71073 Å, multilayer optics). Temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT+[4] and corrected for absorption with SADABS.[5] The structure was solved by direct methods and refined on F^2 with SHELXL-97.[6,7]

Crystal data of Ru-acetylide complex 2b: $C_{40}H_{43}NO_2P_2Ru$, crystal dimensions: 0.1 × 0.1 × 0.09, monoclinic with space group P121/c, a = 13.3813 (7)Å, b = 13.5583 (7) Å, c = 20.6709 (11) Å, α = 90°, β = 104.397 (3)°, γ = 90°, V = 3632.5 (3)Å^3, Z = 4, T = 100 K, $2\theta_{max}$ = 29.587, ρ_{calcd} = 1.340 g/cm^3, μ (MoKα) = 0.554 mm^{-1}. min/max transmission factors = 0.6087/0.7459, 10155 Reflections collected, 8833 unique ($R1$ = 0.0574), $WR2$ = 0.1611 (all data). The structure has been deposited at the CCDC data center and can be retrieved by using the number CCDC 1445337.

Catalytic experiment to observe the intermediacy of 2a:



In a screw cap NMR tube Ru-Macho **1** (0.024 mmol, 15 mg), KO^{t}Bu (0.026 mmol, 3 mg) and THF (0.4 ml) were added under nitrogen atmosphere and the resulting reaction mixture shaken for 10 minutes. 4-Ethynyl anisole (0.12 mmol, 16 μl) was added slowly and then deuterium oxide (0.1 ml)

was added under nitrogen atmosphere. The NMR tube then heated to 50 °C and monitored by ^{1}H and ^{31}P NMR spectroscopy.

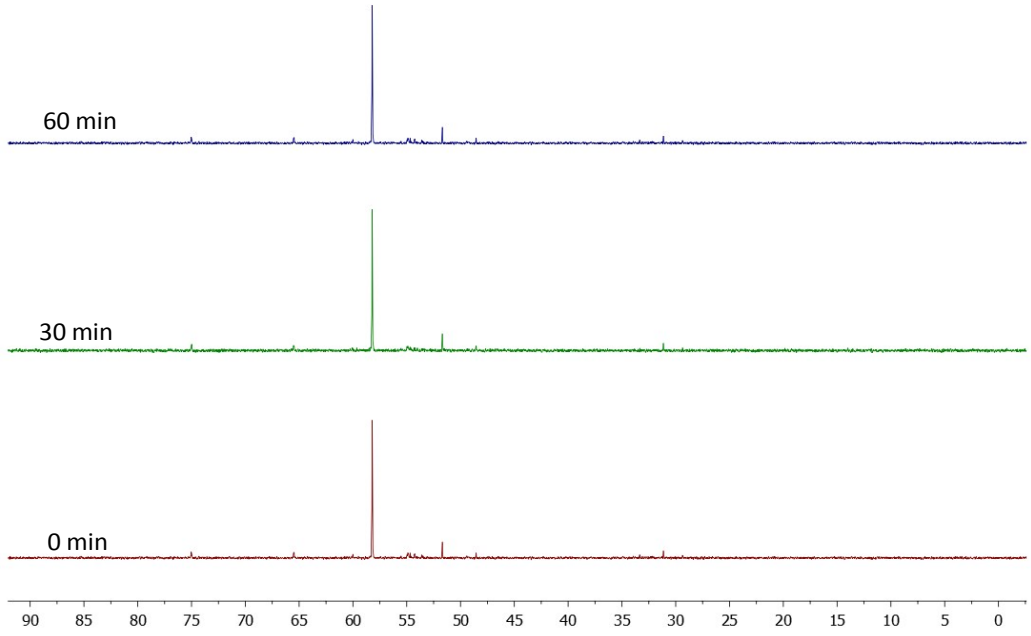


Fig. S3: Stacked ^{31}P NMR spectra of the catalytic reaction for the deuteration of 4-ethynyl anisole catalyzed by **2a**.

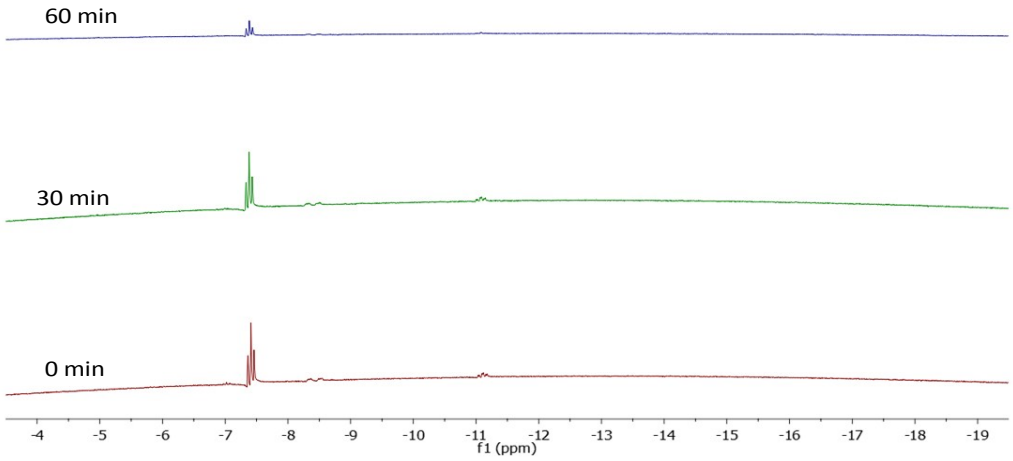
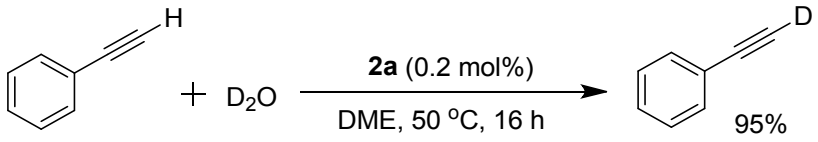


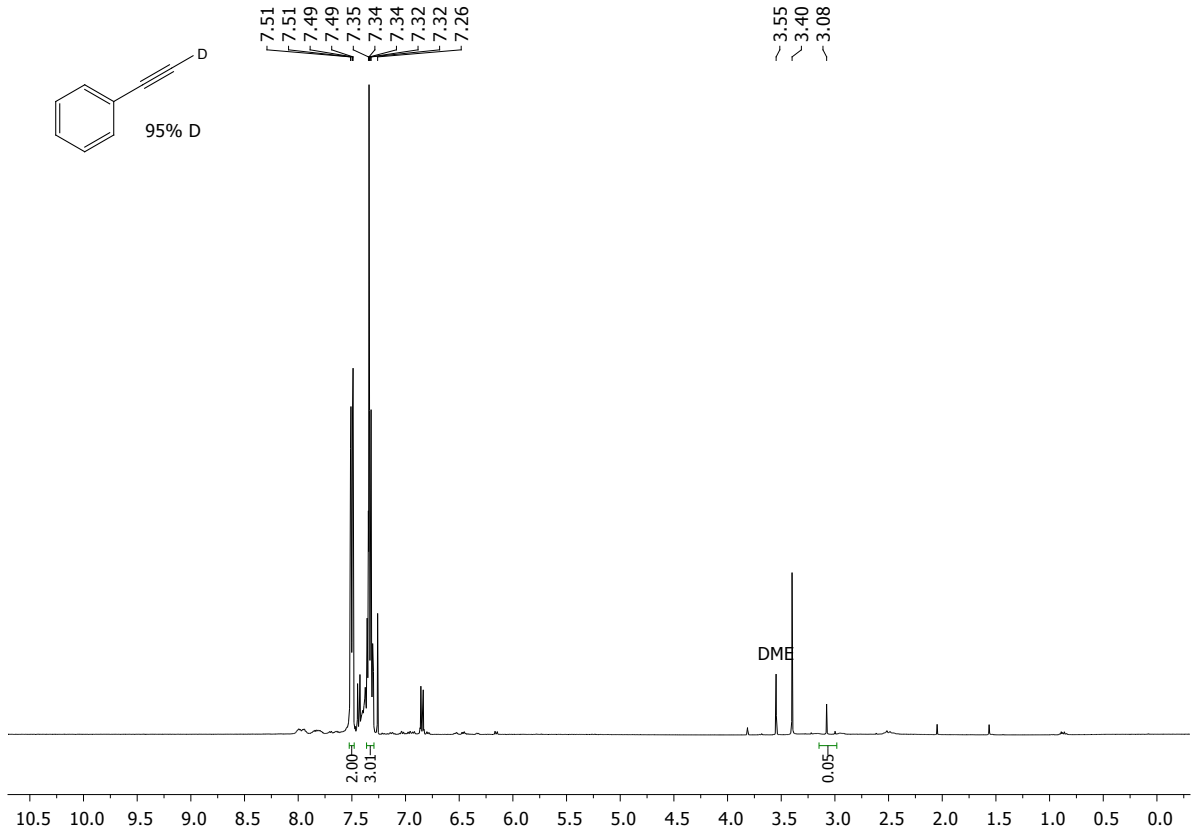
Fig. S4: Stacked ^{1}H NMR spectra of the catalytic reaction for the deuteration of 4-ethynyl anisole catalyzed by **2a**.

Catalytic experiment in absence of base using 2a as catalyst:



In a screw cap scintillation vial phenylacetylene (0.5 mmol, 55 µl), **2a** (0.00099 mmol, 0.7 mg), DME (0.3 ml) and D_2O (0.2 ml) were added under nitrogen atmosphere. The reaction vial then heated to 50 °C. After 16 h the resulted residue was extracted with dichloromethane and the combined organic phase is dried over sodium sulphate. Solvent was removed under reduced pressure and the product was analysed by ^{1}H and ^{13}C NMR spectroscopy.

^{1}H NMR spectrum of experiment in Scheme 2d (without base and using **2a** as catalyst) with phenylacetylene (400 MHz, $CDCl_3$):



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