Supplementary Materials for

A Lewis Acid Activated Reaction of Zn with EtI to Promote Highly Enantioselective Alkyne Additions to Aldehydes

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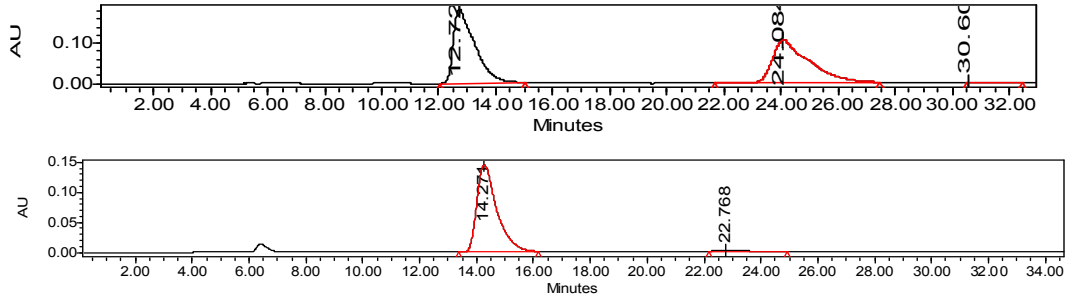
General Data. All reactions were carried out under nitrogen. Aldehydes were distilled before use. Zinc powder was activated with dilute HCl, dried at 120℃ for 3h under vacuum, and stored in a sealed flask.

HPLC analyses were carried out with the Waters 600 by using the Diacel Chiralcel OD column and eluting with 10% *i*-PrOH in hexane at 1.0 mL/min unless otherwise indicated, and were detected at 254 nm by the Waters 486. The optical rotations were measured on the JASCO DIP-1000 Polarimeter. The configuration of products were determined by comparison with the optical rotations reported literature or the previous HPLC results.

Experimental data:

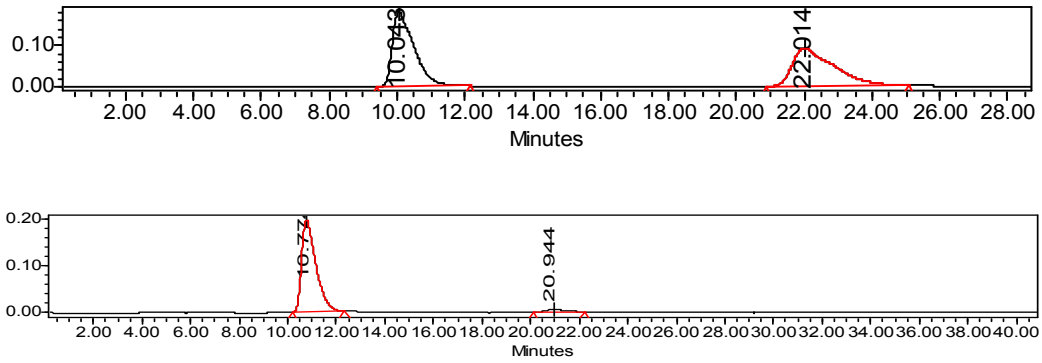
(*R*)-1,3-Diphenyl-prop-2-yn-1-ol:[1] 85% yield. 96% *ee* determined by HPLC analysis (OD column, 10% IPA in hexane, 1 mL/min, 254 nm). Retention time: t_{major} = 14.3 min, and t_{minor} = 22.8 min. Our previous HPLC result[1]: t_{major} = 13.6 min, and t_{minor} = 24.2 min.



Name codes	Retention Time	Area	% Area
1	14.271	6991860	97.97

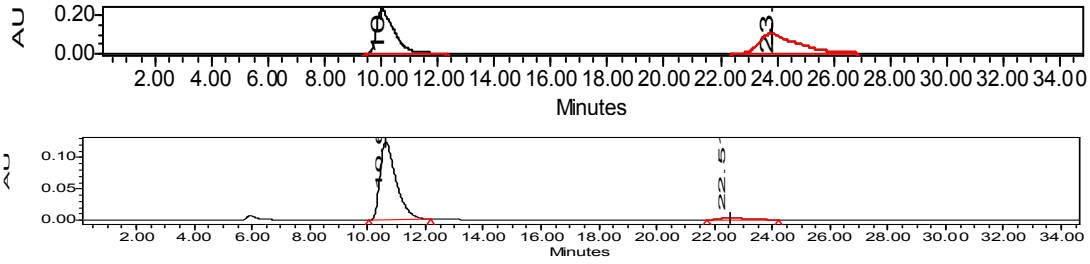
2	22.768	144933	2.03

(*R*)-3-Phenyl-1-p-tolyl-prop-2-yn-1-ol:[1] 90% yield. 91% *ee* determined by HPLC analysis (OD column, 10% IPA in hexane, 1 mL/min, 254 nm). Retention time: t_{major} = 10.8 min, and t_{minor} = 20.9 min. $[\alpha]^{22}_D$ = 5.8 (c = 1.2, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.45 (m, 4H), 7.37 – 7.28 (m, 3H), 7.22 (d, *J* = 8.2 Hz, 1H), 5.66 (s, 1H), 2.38 (s, 3H), 2.32 (br, 1H).



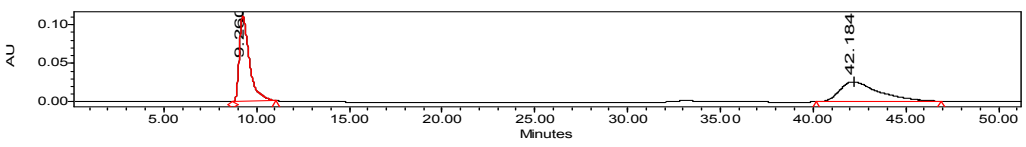
Name codes	Retention Time	Area	% Area
1	10.77	8003594	95.55
2	20.94	372976	4.45

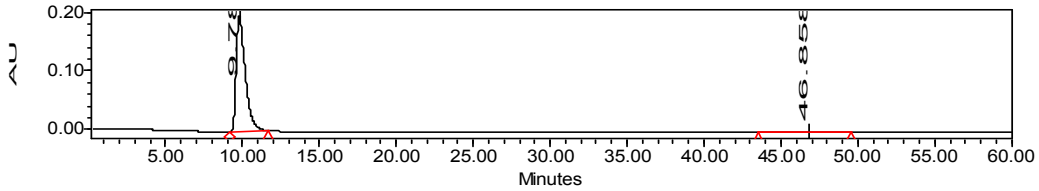
(*R*)-3-Phenyl-1-o-tolyl-prop-2-yn-1-ol:[2] 70% yield. 91% *ee* determined by HPLC analysis (OD column, 10% IPA in hexane, 1 mL/min, 254 nm). Retention time: t_{major} = 10.6 min, and t_{minor} = 22.5 min. $[\alpha]^{22}_D$ = -11.2 (c = 0.5, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 5.2, 3.7 Hz, 1H), 7.53 – 7.42 (m, 2H), 7.36 – 7.20 (m, 6H), 5.85 (d, *J* = 4.9 Hz, 1H), 2.51 (s, 3H), 2.17 (d, *J* = 5.2 Hz, 1H).



Name codes	Retention Time	Area	% Area
1	10.624	846306	95.59
2	22.518	223325	4.41

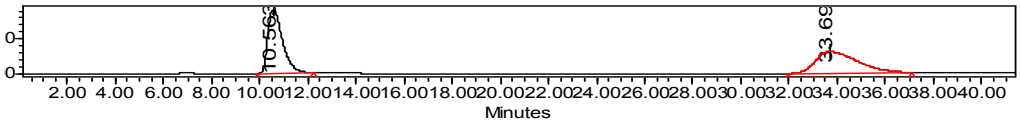
(*R*)-1-Phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol:[3] 95% yield. 96% *ee* determined by HPLC analysis (OD column, 10% IPA in hexane, 1 mL/min, 254 nm). $[\alpha]^{22}_D$ = 7.3 (c = 1.0, $CHCl_3$). lit[3] $[\alpha]^{20}_D$ = +10.9 (c = 1.0 in EtOH). Retention time: t_{major} = 9.5 min, and t_{minor} = 16.3 min. ^1H NMR (300 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 23.3, 8.3 Hz, 4H), 7.56 – 7.30 (m, 5H), 5.76 (s, 1H), 2.23 (s, 1H).

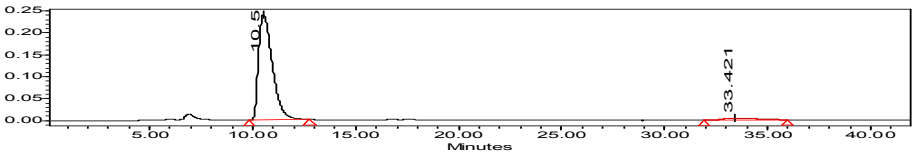




Name codes	Retention Time	Area	% Area
1	9.789	8091319	98.38
2	46.858	132885	1.62

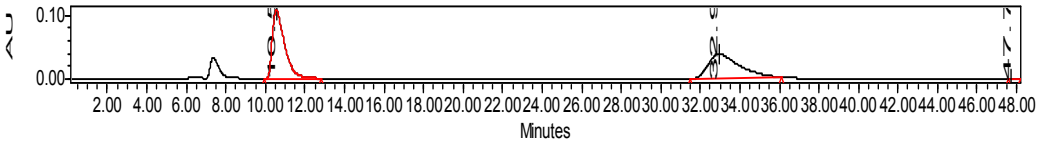
(*R*)-1-(4-Fluoro-phenyl)-3-phenyl-prop-2-yn-1-ol:[1] 90% yield. 91% *ee* determined by HPLC analysis (OD column, 10% IPA in hexane, 1 mL/min, 254 nm). Retention time: t_{major} = 10.5 min, and t_{minor} = 33.4 min. $[\alpha]^{22}_{D}$ = 6.2 (c = 1.10, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 – 7.55 (m, 2H), 7.52 – 7.42 (m, 2H), 7.41 – 7.29 (m, 3H), 7.16 – 7.02 (m, 2H), 5.68 (s, 1H), 2.37 (s, 1H).

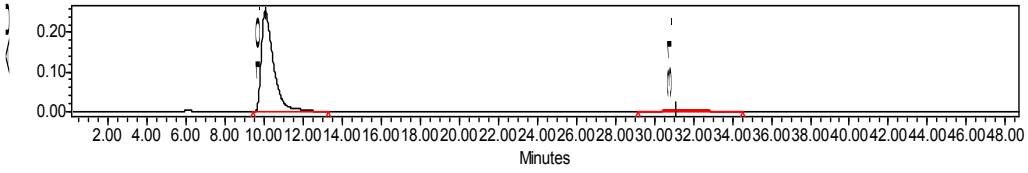




Name codes	Retention Time	Area	% Area
1	10.527	1127104	95.60
2	33.421	518164	4.40

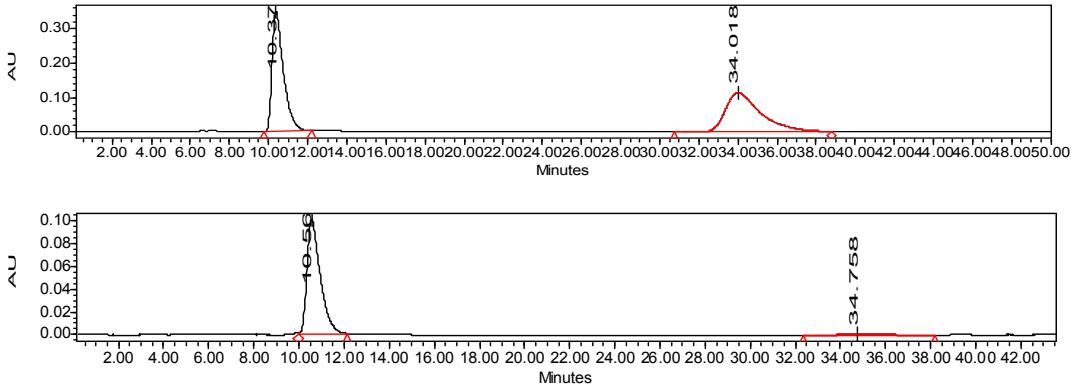
(*R*)-1-(4-Chloro-phenyl)-3-phenyl-prop-2-yn-1-ol:[1] 96% yield. 95% *ee* determined by HPLC analysis (OD column, 10% IPA in hexane, 1 mL/min, 254 nm). Retention time: t_{major} = 10.6 min, and t_{minor} = 31.1 min. $[\alpha]^{22}_{D}$ = 9.3 (c = 1.20, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.6 Hz, 2H), 7.52 – 7.44 (m, 2H), 7.35 (m, 5H), 5.67 (d, *J* = 3.7 Hz, 1H), 2.36 (d, *J* = 4.5 Hz, 1H).





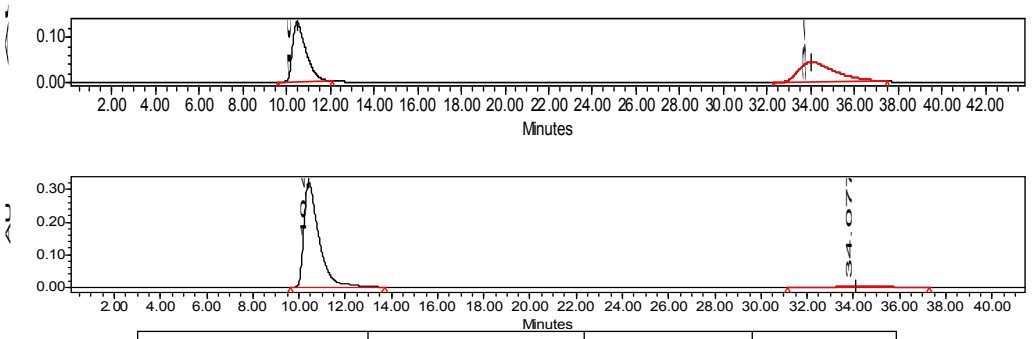
Name codes	Retention Time	Area	% Area
1	10.067	11021925	97.67
2	31.135	263141	2.33

(*R*)-1-(3-Chloro-phenyl)-3-phenyl-prop-2-yn-1-ol:[1] 93 % yield. 92% *ee* determined by HPLC analysis (OD column, 10% IPA in hexane, 1 mL/min, 254 nm). Retention time: t_{major} = 10.4 min, and t_{minor} = 34.1 min. $[\alpha]^{22}_D$ = 15.1 (c = 1.3, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.53 (d, *J* = 7.7 Hz, 3H), 7.39 (d, *J* = 6.9 Hz, 5H), 5.73 (s, 1H), 2.42 (s, 1H).



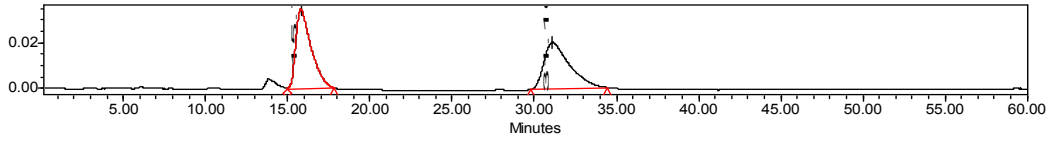
Name codes	Retention Time	Area	% Area
1	10.560	4148933	96.54
2	34.758	48570	3.46

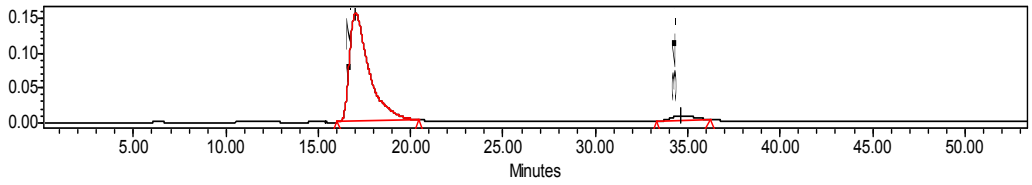
(*R*)-1-(4-Bromo-phenyl)-3-phenyl-prop-2-yn-1-ol:[1] 92% yield. 96 % *ee* determined by HPLC analysis (OD column, 10% IPA in hexane, 1 mL/min, 254 nm). Retention time: t_{major} = 10.4 min, and t_{minor} = 34.1 min. ^1H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.39 (m, 6H), 7.39 – 7.28 (m, 3H), 5.66 (d, *J* = 5.9 Hz, 1H), 2.29 (d, 1H).



Name codes	Retention Time	Area	% Area
1	10.424	14656914	97.80
2	34.077	329383	2.20

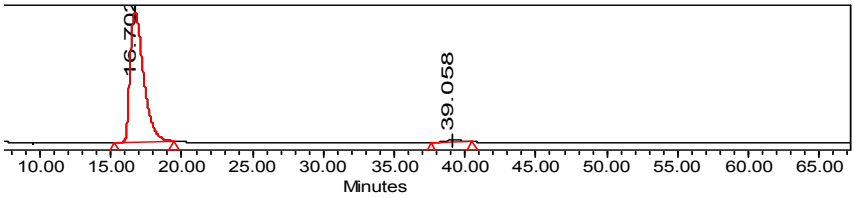
(*R*)-1-(4-Methoxy-phenyl)-3-phenyl-prop-2-yn-1-ol:[1] 92 % yield. 90 % *ee* determined by HPLC analysis (OD column, 10% IPA in hexane, 1 mL/min, 254 nm). Retention time: t_{major} = 15.5 min, and t_{minor} = 30.0 min. $[\alpha]^{22}_D$ = -10.1 (c = 1.1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.51 – 7.44 (m, 2H), 7.37 – 7.29 (m, 3H), 6.98 – 6.88 (m, 2H), 5.65 (d, *J* = 3.9 Hz, 1H), 3.82 (s, 4H), 2.38 (d, *J* = 4.8 Hz, 1H).





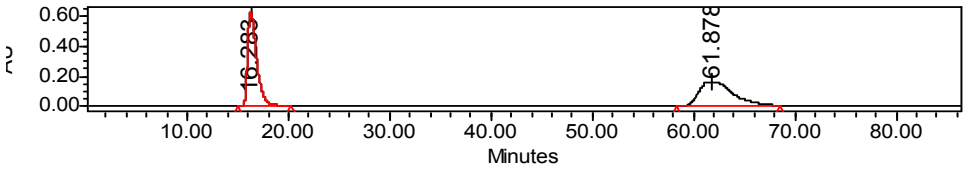
Name codes	Retention Time	Area	% Area
1	17.016	11664344	94.75
2	34.650	646931	5.25

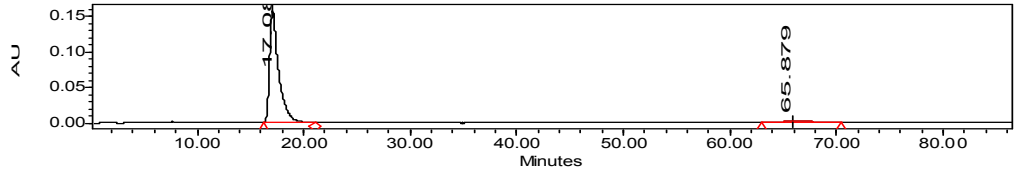
(*R*)-1-Naphthalen-1-yl-3-phenyl-prop-2-yn-1-ol:[2] 75% yield. 96% *ee* determined by HPLC analysis (OD column, 10% IPA in hexane, 1 mL/min, 254 nm). Retention time: t_{major} = 16.7 min, and t_{minor} = 39.1 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.3 Hz, 1H), 7.91 (dd, *J* = 19.2, 8.0 Hz, 3H), 7.63 – 7.45 (m, 5H), 7.36 – 7.29 (m, 3H), 6.36 (d, *J* = 3.7 Hz, 1H), 2.48 (d, *J* = 4.5 Hz, 1H). $[\alpha]^{22}_D$ = +30.2 (c = 1.1, $CHCl_3$). Our previous HPLC results[2]: (OD column, 10% IPA in hexane, 1 mL/min, 254 nm) t_{major} = 17.0 min, and t_{minor} = 37.3 min.



Name codes	Retention Time	Area	% Area
1	16.702	18319463	97.76
2	39.058	420233	2.24

(*R*)-1-(2-Naphthyl)-3-phenyl-prop-2-yn-1-ol:[2] 76% yield. 95% *ee* determined by HPLC analysis (OD column, 10% IPA in hexane, 1 mL/min, 254 nm). Retention time: t_{major} = 17.0 min, and t_{minor} = 65.9 min. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.95 – 7.85 (m, 3H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.56 – 7.51 (m, 4H), 7.38 – 7.34 (m, 3H), 5.89 (s, 1H), 2.42 (s, 1H). $[\alpha]^{22}_D$ = -10.0 (c 1.10, $CHCl_3$).

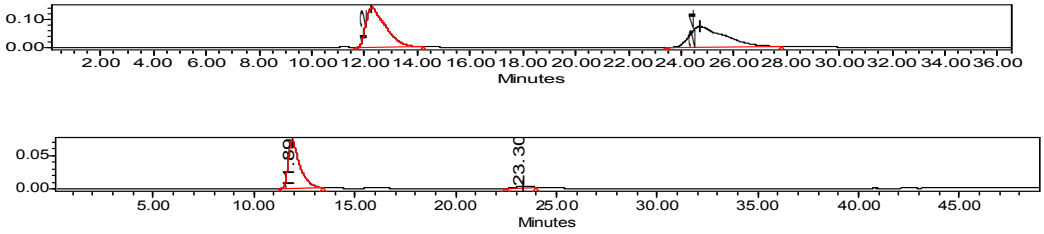




Name codes	Retention Time	Area	% Area
1	17.086	9467355	97.65
2	65.879	227630	2.35

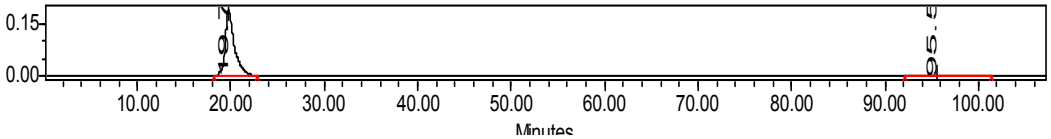
(*R*)-1-(Furan-2-yl)-3-phenylprop-2-yn-1-ol:[1] 60% yield. 91% *ee* determined by HPLC analysis (OD

column, 10% IPA in hexane, 1 mL/min, 254 nm). Retention time: t_{major} = 11.9 min, and t_{minor} = 23.4 min. Our previous HPLC result[1]: t_{major} = 12.8 min, and t_{minor} = 23.3 min. ^{1}H NMR (600 MHz, cdcl$_3$) δ 7.38 (d, *J* = 7.0 Hz, 2H), 7.34 (s, 1H), 7.26 – 7.18 (m, 3H), 6.42 (dd, *J* = 2.4, 0.7 Hz, 1H), 6.31 – 6.22 (m, 1H), 5.58 (s, 1H), 2.31 (s, 1H).



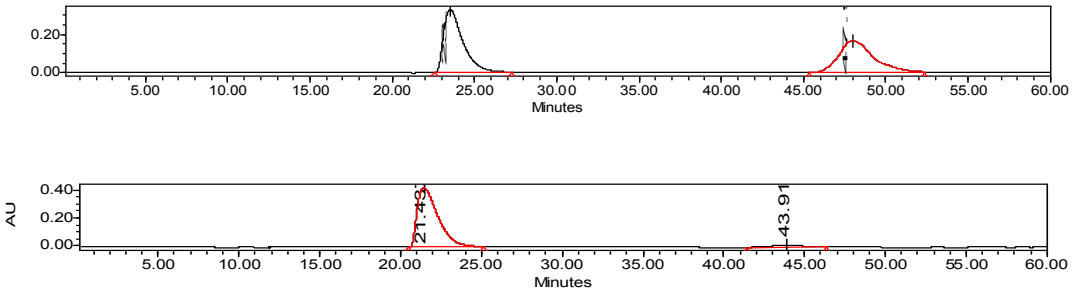
Name codes	Retention Time	Area	% Area
1	11.894	2837067	95.73
2	23.307	126414	4.27

(*R*)-1-(4-Nitrophenyl)-3-phenyl-prop-2-yn-1-ol:[7] 140 mg (containing 36 mg BINOL), 82% yield. 92% *ee* determined by HPLC analysis (OD column, 10% IPA in hexane, 1 mL/min, 254 nm). Retention time: t_{major} = 19.7min, and t_{minor} = 95.5 min. Our previous HPLC result[7]: t_{major} = 21.1 min, and t_{minor} = 97.52 min. ^{1}H NMR (600 MHz, cdcl$_3$) δ 8.24 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 7.3 Hz, 2H), 7.41 – 7.28 (m, *J* = 16.5, 8.3 Hz, 3H), 5.78 (s, 1H). It contains a small amount of (*S*)-BINOL not removed by column chromatography.



Name codes	Retention Time	Area	% Area
1	19.74	13063248	95.73
2	95.53	483901	3.57

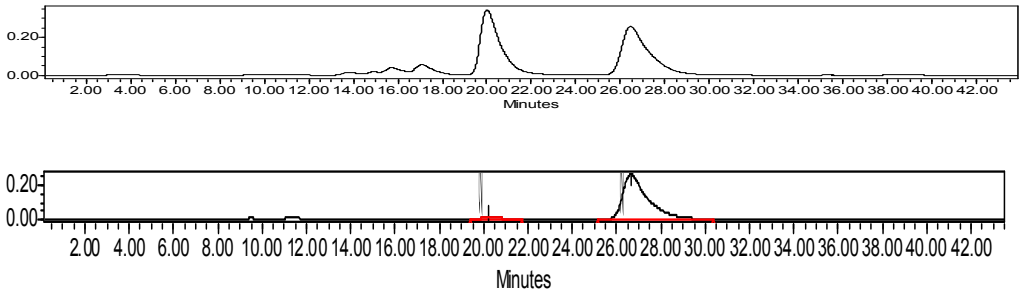
(*R*)-1,5-Diphenyl-2-pentyn-1-ol:[4] 78 % yield. 90 % *ee* determined by HPLC analysis (OD column, 5 % IPA in hexane, 1 mL/min, 220 nm). Retention time: t_{major} = 21.4 min, and t_{minor} = 43.9 min. $[\alpha]^{22}_D$ = +14.9 (c = 1.14, CHCl$_3$). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.52 (d, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.39 – 7.26 (m, 6H), 5.48 (s, 1H), 2.91 (t, *J* = 7.5 Hz, 2H), 2.64 (td, *J* = 15.0, 7.5 Hz, 2H), 2.11 (s, 1H).



Name codes	Retention Time	Area	% Area
1	21.437	37925919	94.96

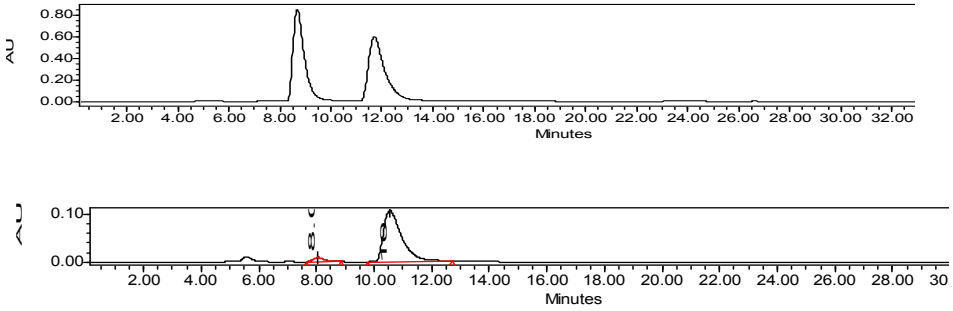
2	43.911	2010955	5.04

(*R*)-1-Cyclohexenyl-3-phenylprop-2-yn-1-ol:[4] 58.5% yield. 92 % *ee* determined by HPLC analysis (OD column, 5% IPA in hexane, 0.5 mL/min, 254 nm). Retention time: t_{major} = 20.2 min, and t_{minor} = 26.6 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 – 7.51 (m, 2H), 7.51 – 7.28 (m, 3H), 6.26 – 6.11 (m, 1H), 5.57 (d, *J* = 4.2 Hz, 1H), 2.31 (d, *J* = 5.1 Hz, 1H), 2.26 – 2.02 (m, 4H), 1.70 – 1.56 (m, 4H).



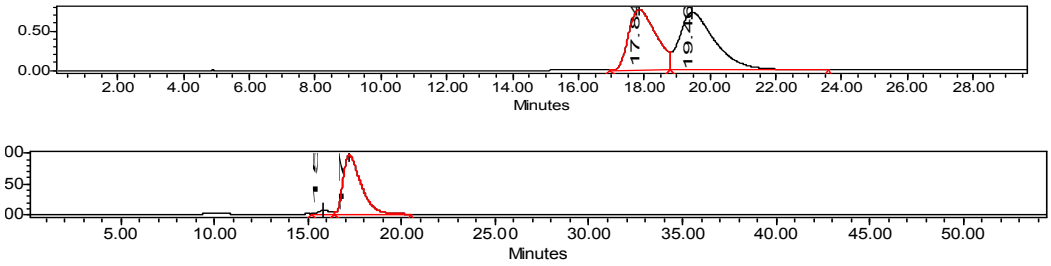
Name codes	Retention Time	Area	% Area
1	20.23	829333	3.85
2	26.642	20702064	96.15

(*R*)-1-Phenyl-hept-2-yn-1-ol:[5] 80 % yield. 91 % *ee* determined by HPLC analysis (OD column, 5% IPA in hexane, 0.5 mL/min, 254 nm). Retention time: t_{major} = 10.5 min, and t_{minor} = 8 min. ^{1}H NMR (600 MHz, cdcl$_3$) δ 7.55 (t, *J* = 8.6 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 5.46 (s, 1H), 2.28 (td, *J* = 7.1, 1.9 Hz, 2H), 2.08 (s, 1H), 1.62 – 1.48 (m, 3H), 1.48 – 1.37 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). $[\alpha]^{22}_D$ = + 18.44 (c = 0.50, $CHCl_3$)



Name codes	Retention Time	Area	% Area
1	8.043	231947	4.67
2	10.551	4737600	95.33

(*R*)-1-(3-Chlorophenyl)-non-2-yn-1-ol:[6] 72 % yield. 91 % *ee* determined by HPLC analysis (OD column, 5% IPA in hexane, 0.5 mL/min, 254 nm). Retention time: t_{major} = 17.8 min, and t_{minor} = 16.4 min. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.39 (d, *J* = 5.5 Hz, 1H), 7.31 – 7.22 (m, 2H), 5.40 (s, 1H), 2.25 (t, *J* = 7.1 Hz, 2H), 2.15 (s, 1H), 1.60 – 1.49 (m, 2H), 1.42 – 1.22 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H). $[\alpha]^{22}_D$ = 30.4 (c 1.50, $CHCl_3$). lit [6]for *S* configuration:$[\alpha]^{20}_D$ = -73.6 (c 1.50, $CHCl_3$)



Name codes	Retention Time	Area	% Area
1	15.827	2922575	4.34
2	17.199	64465979	95.66

Reference：

1. Gao, G.; Xie, R. –G.; Pu, L. *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5417.
2. Li, Z.-B.; Pu, L. *Org. Lett.* **2004**, *6*, 1065.
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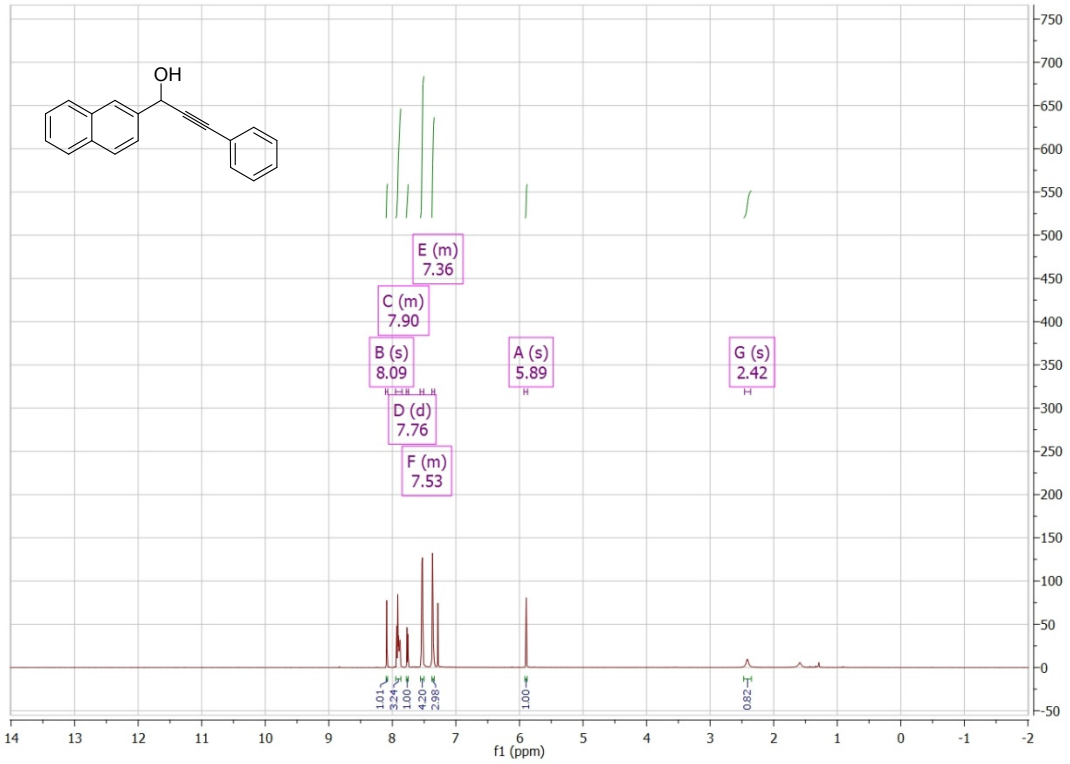
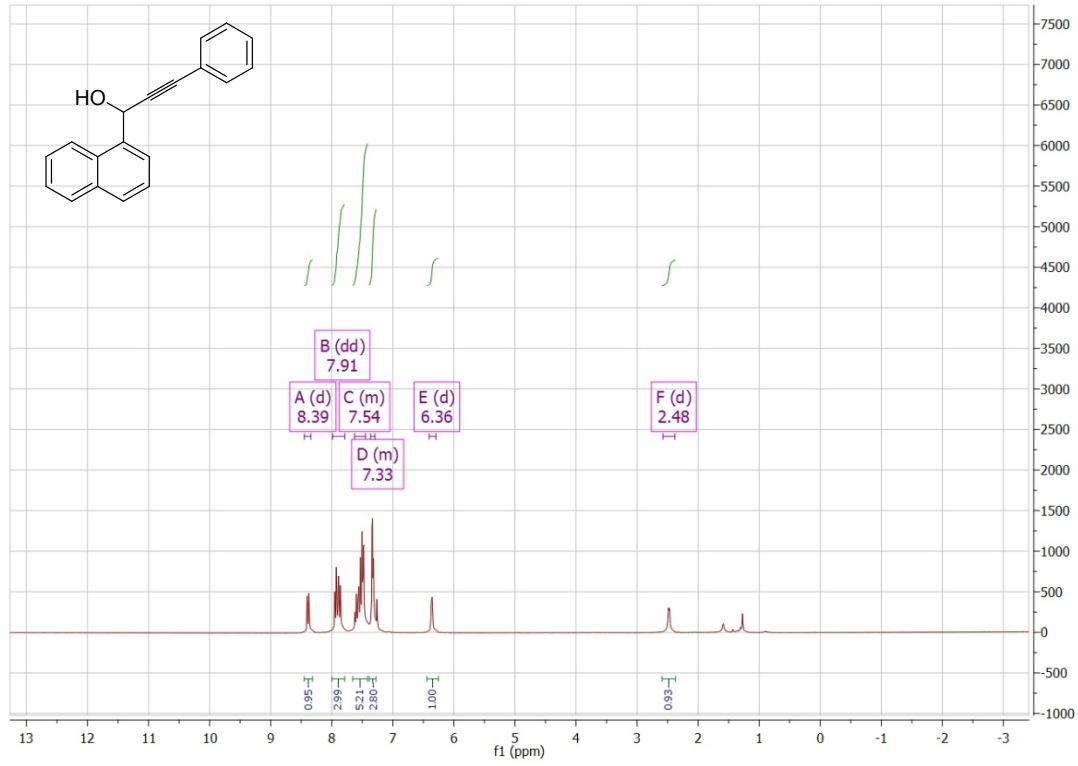
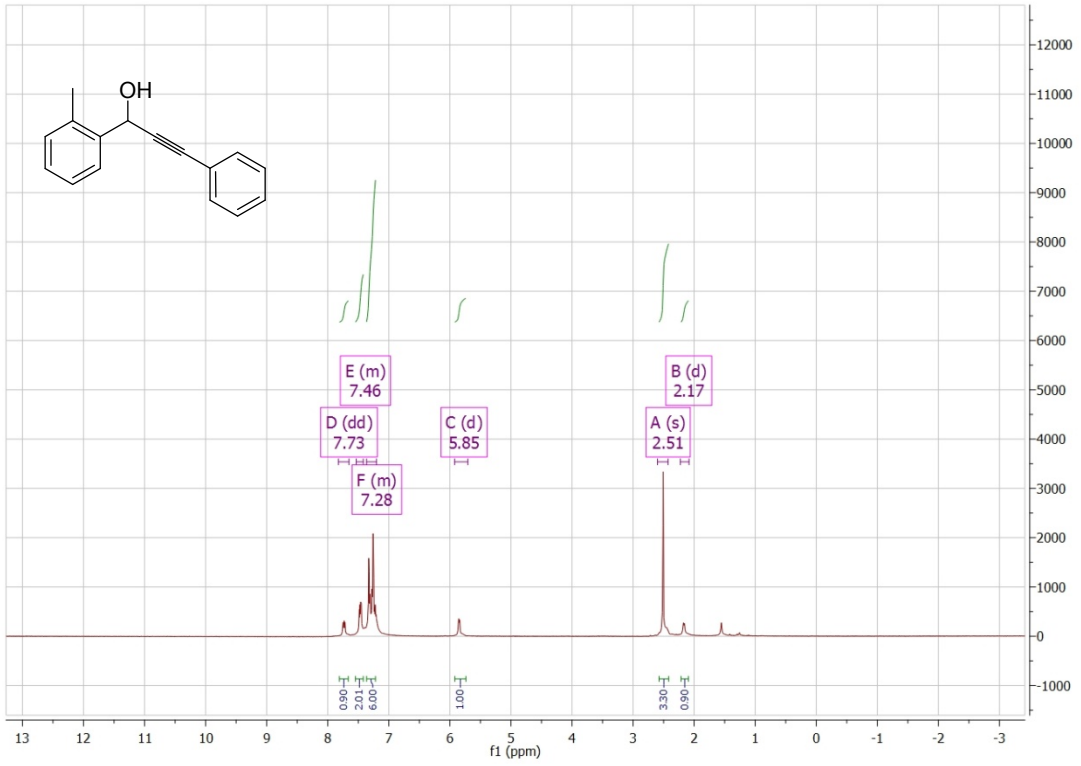
7. Moore, D.; Pu, L. *Org. Lett*. **2002**, *4*, 1855.

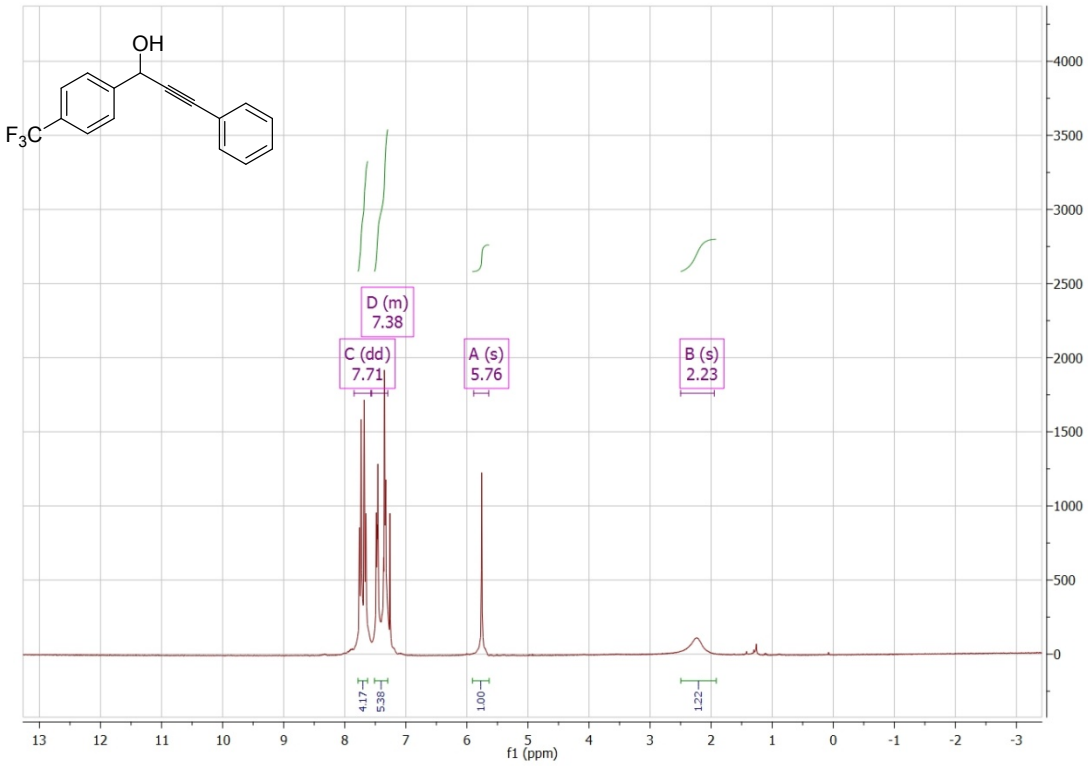
^{1}H NMR Spectra: NMR Data

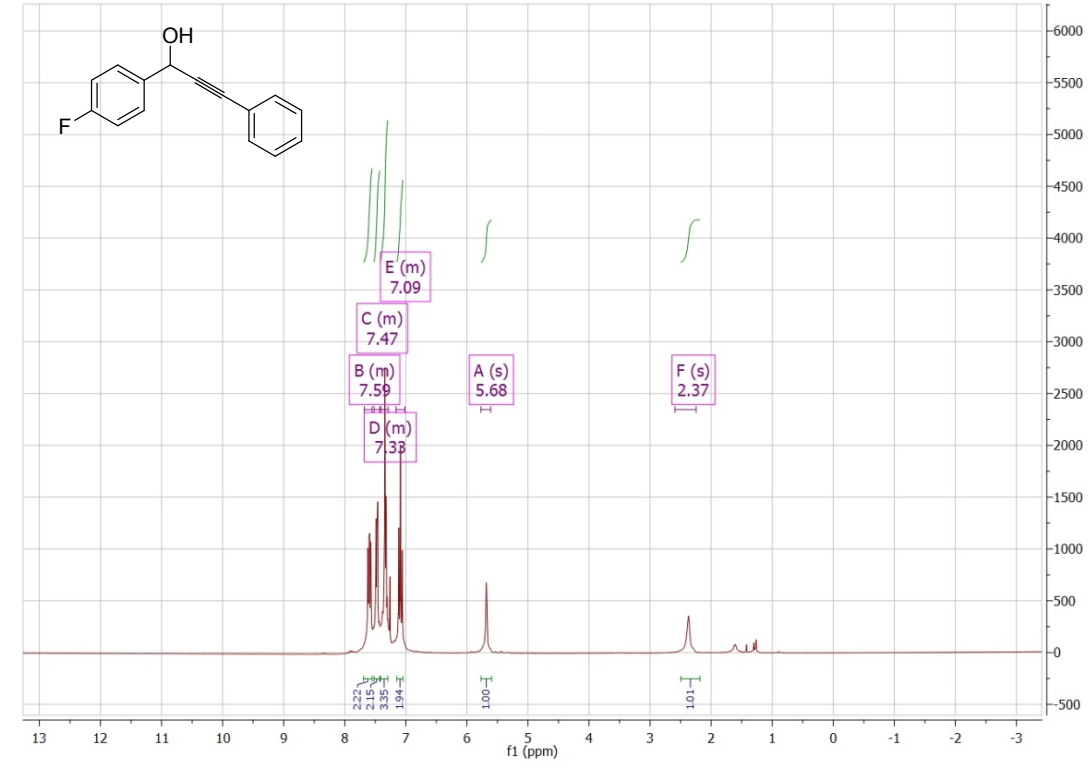


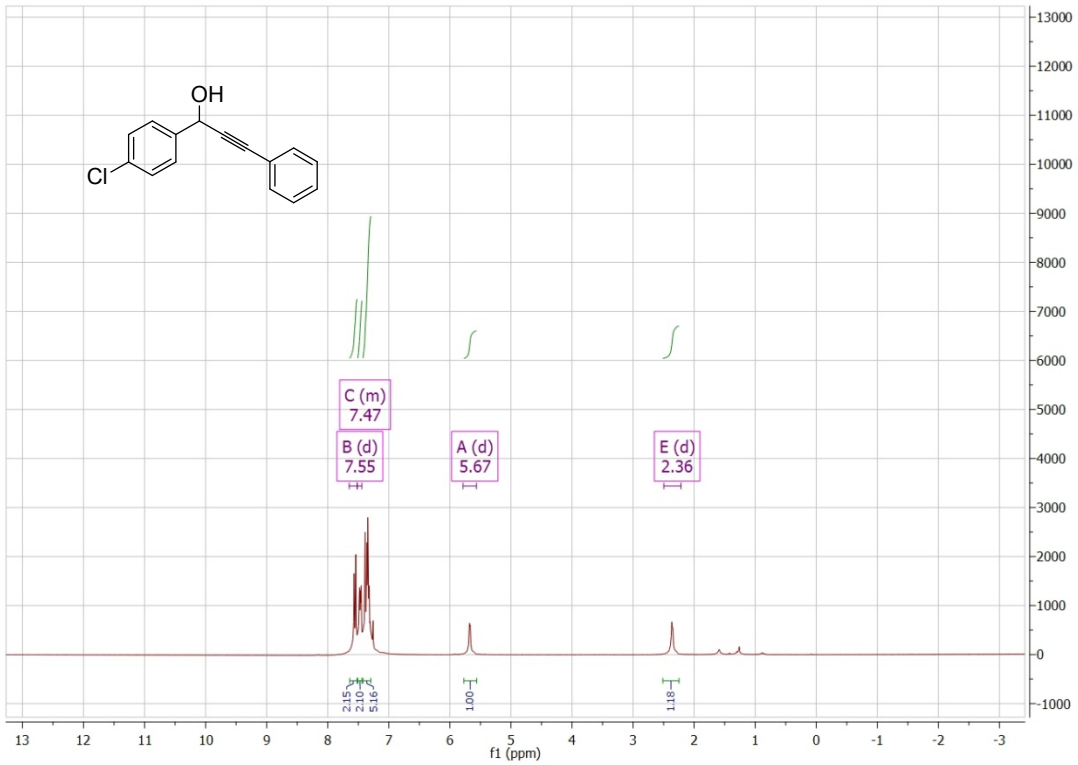


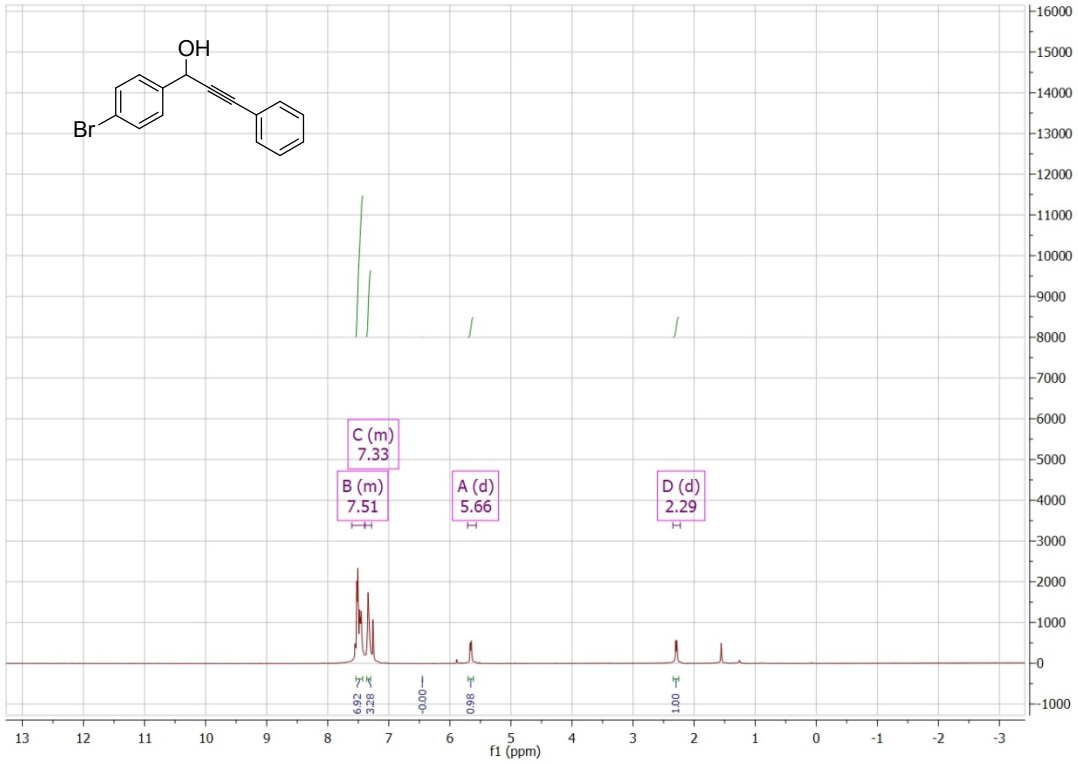

OH
E (m)
7.32
D (m)
7.49
F (d)
7.22
A (s)
5.66
C (s)
2.32
B (s)
2.38
4.36
3.20
2.11
1.00
3.32
1.06
f1 (ppm)

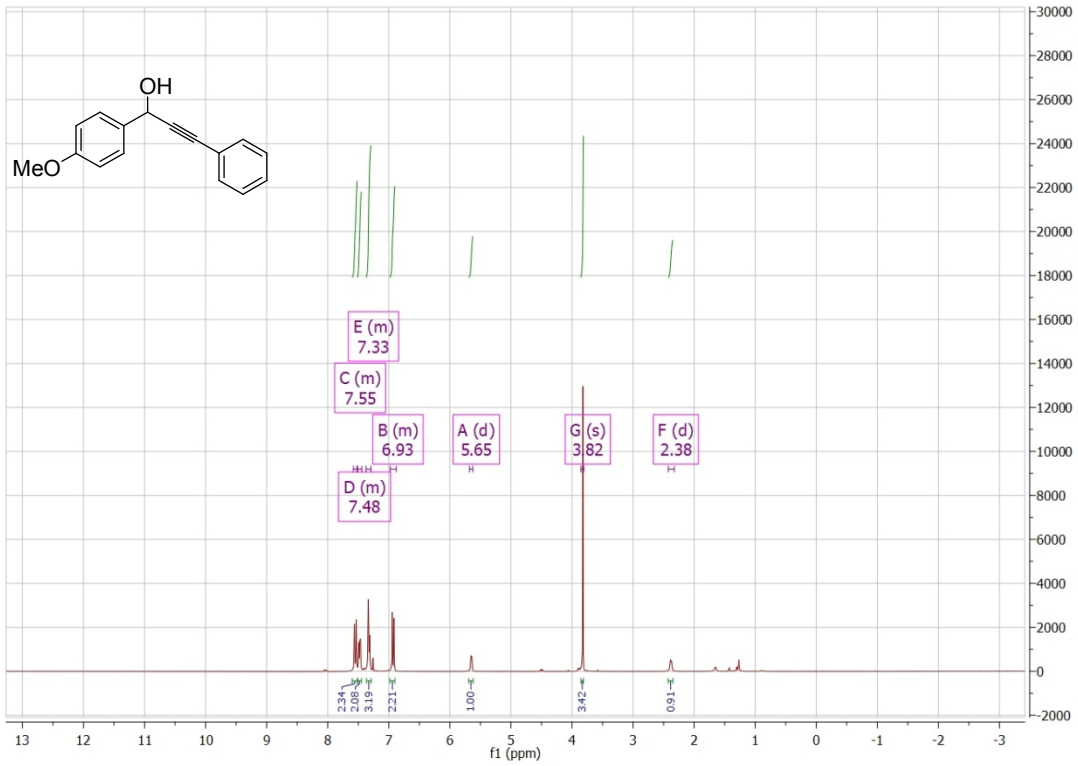

OH
E (m)
7.46
D (dd)
7.73
F (m)
7.28
C (d)
5.85
B (d)
2.17
A (s)
2.51
0.90
2.01
6.00
1.00
3.30
0.90
f1 (ppm)

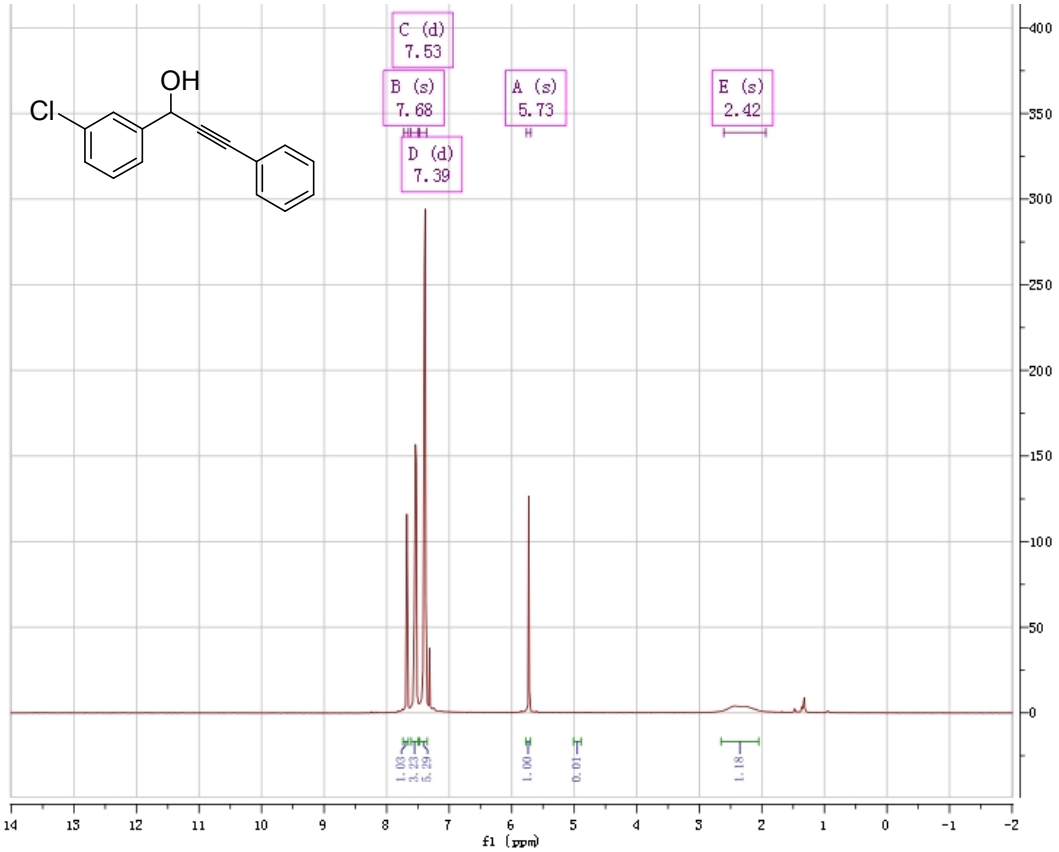

OH
F3C
D (m)
7.38
C (dd)
7.71
A (s)
5.76
B (s)
2.23
4.17
5.38
1.00
1.22
f1 (ppm)

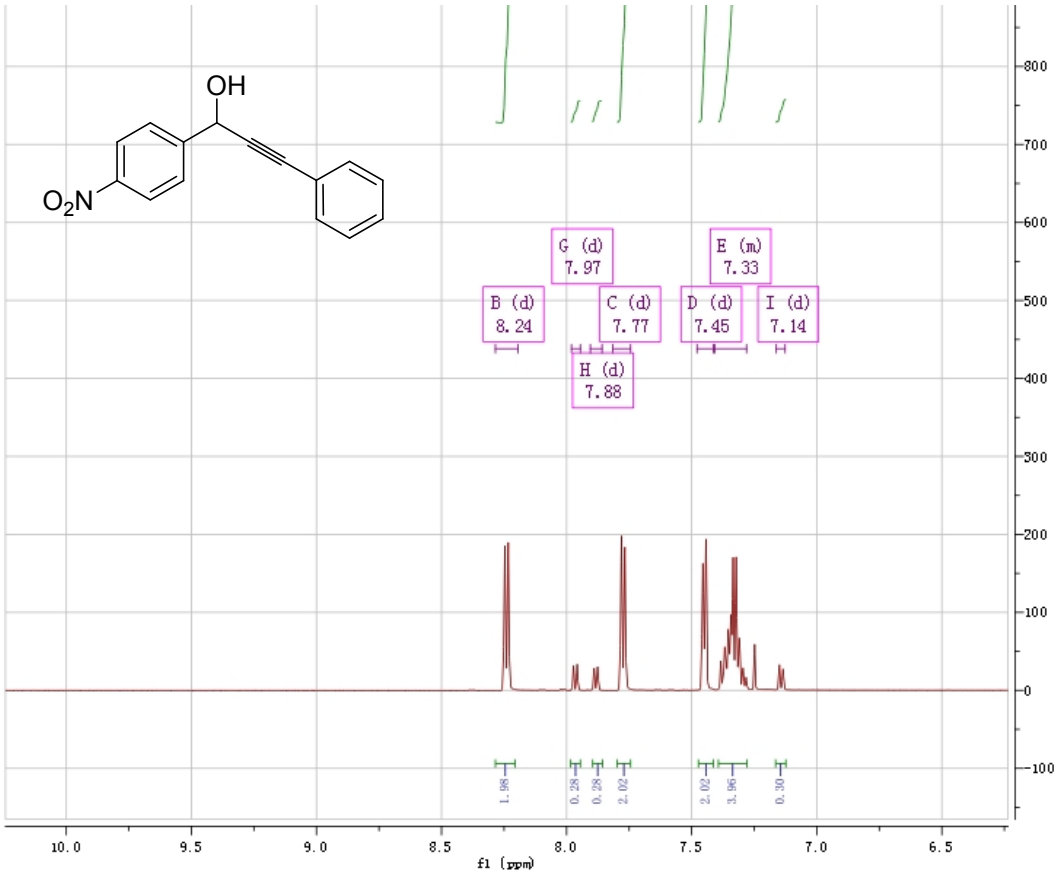

OH
F
E (m)
7.09
C (m)
7.47
B (m)
7.59
A (s)
5.68
F (s)
2.37
D (m)
7.33
2.22
2.15
3.35
1.94
1.00
1.01
f1 (ppm)


OH
Cl
C (m)
7.47
B (d)
7.55
A (d)
5.67
E (d)
2.36
2.15
2.10
5.16
1.00
1.18
f1 (ppm)

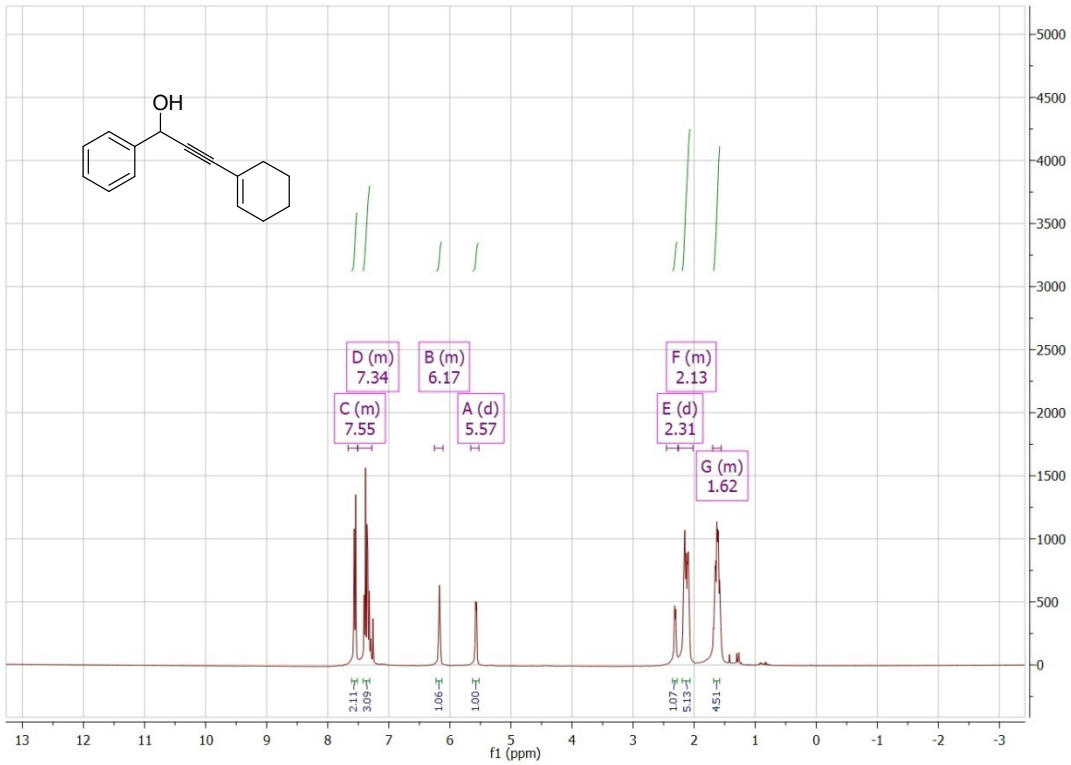

OH
Br
C (m)
7.33
B (m)
7.51
A (d)
5.66
D (d)
2.29
6.92
3.28
0.00
0.98
1.00
f1 (ppm)

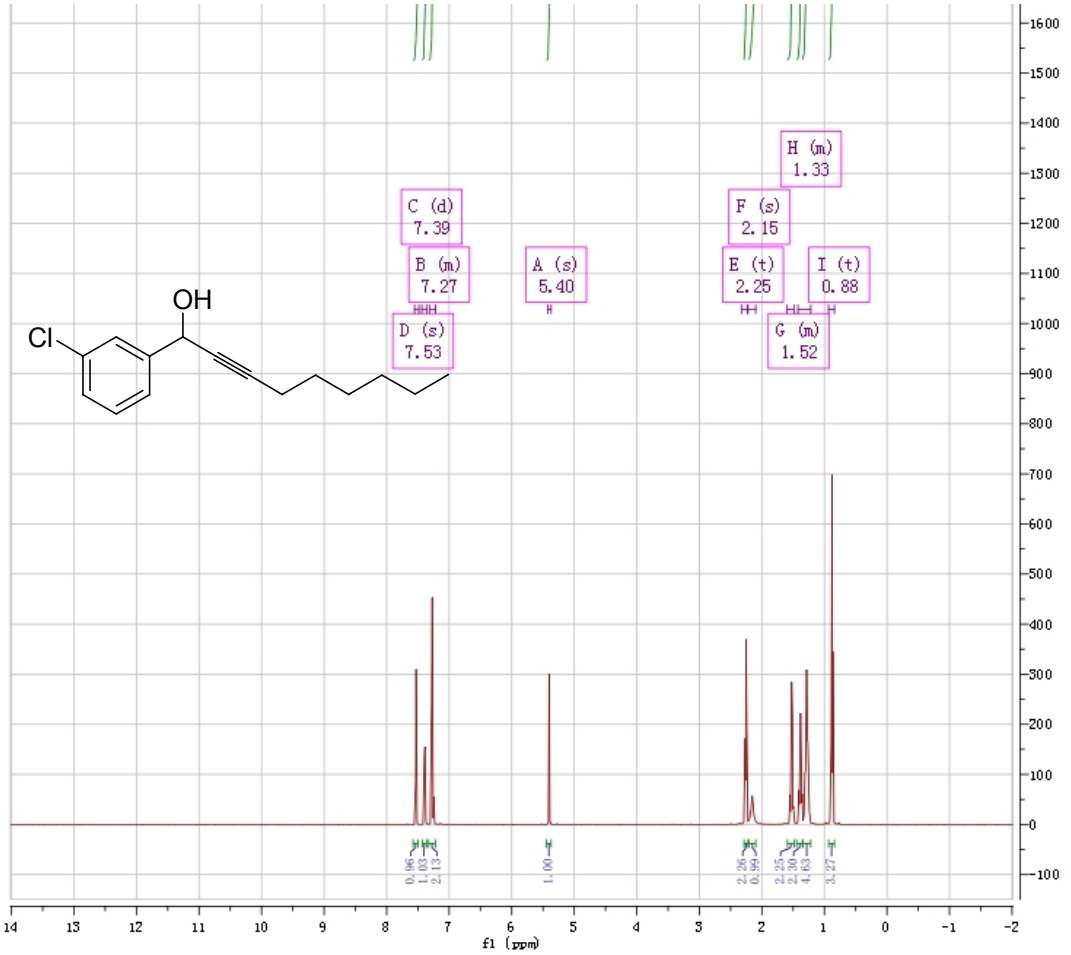

OH
MeO
E (m)
7.33
C (m)
7.55
B (m)
6.93
A (d)
5.65
G (s)
3.82
F (d)
2.38
D (m)
7.48
f1 (ppm)

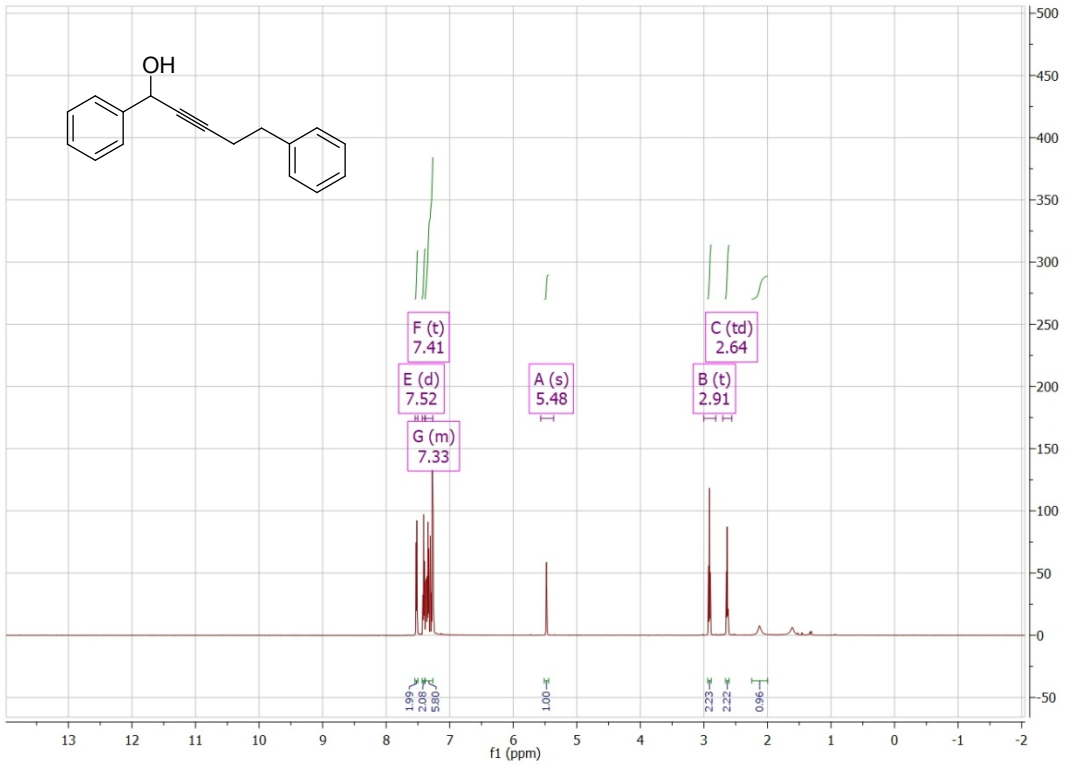

OH
Cl
C (d)
7.53
B (s)
7.68
A (s)
5.73
E (s)
2.42
D (d)
7.39
f1 (ppm)

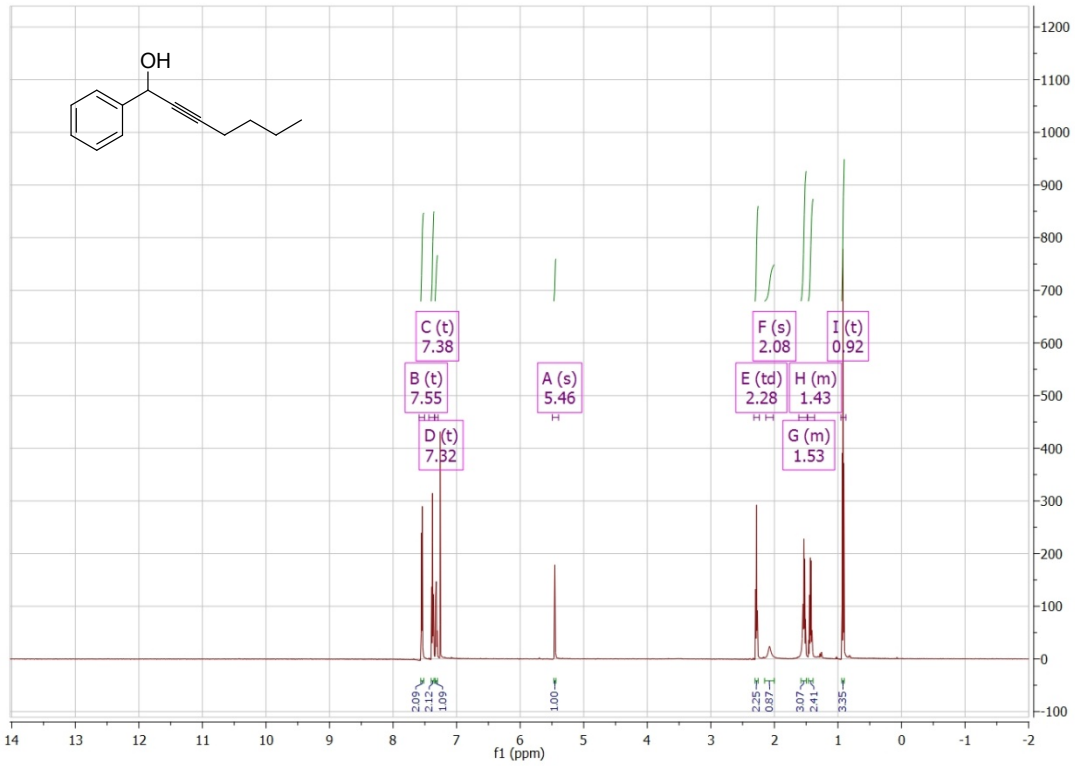

OH
O2N
G (d) 7.97
E (m) 7.33
B (d) 8.24
C (d) 7.77
D (d) 7.45
I (d) 7.14
H (d) 7.88
f1 (ppm)


OH
O
G (m) 7.22
F (s) 7.34
B (m) 6.27
E (d) 7.38
A (s) 5.58
D (s) 2.31
C (dd) 6.42
f1 (ppm)


OH
D (m)
7.34
B (m)
6.17
F (m)
2.13
C (m)
7.55
A (d)
5.57
E (d)
2.31
G (m)
1.62
f1 (ppm)


OH
Cl
H (m)
1.33
C (d)
7.39
F (s)
2.15
B (m)
7.27
A (s)
5.40
E (t)
2.25
I (t)
0.88
D (s)
7.53
G (m)
1.52
f1 (ppm)


OH
F (t)
7.41
E (d)
7.52
G (m)
7.33
A (s)
5.48
C (td)
2.64
B (t)
2.91
f1 (ppm)


OH
C (t)
7.38
B (t)
7.55
D (t)
7.32
A (s)
5.46
F (s)
2.08
I (t)
0.92
E (td)
2.28
H (m)
1.43
G (m)
1.53
f1 (ppm)