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Supporting Information

69451 Weinheim, Germany

Brønsted Acid-Catalyzed Asymmetric Propargylation of Aldehydes**

Pankaj Jain, Hao Wang, Kendall N. Houk, and Jon C. Antilla**

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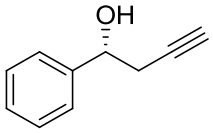
Supporting Information

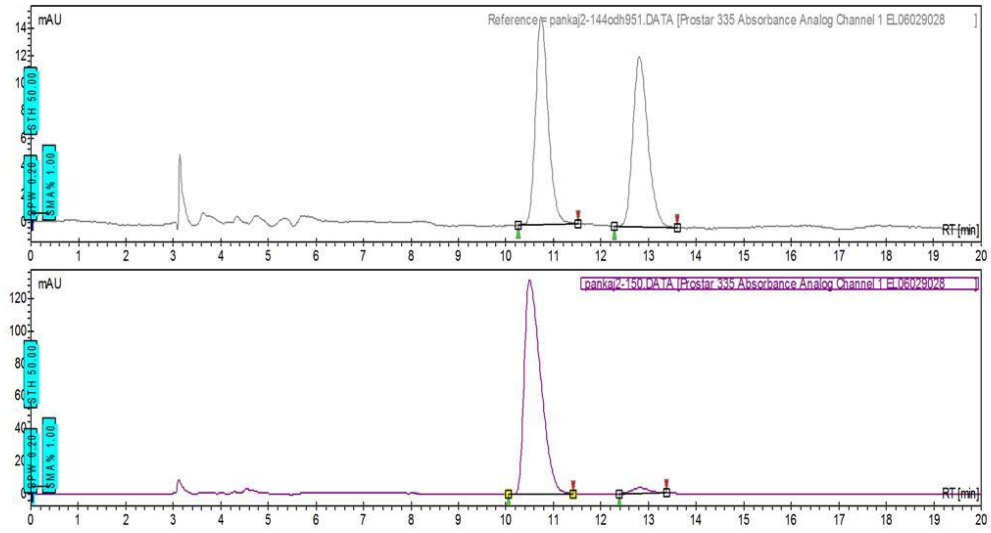
Contents:

General Considerations: All reactions were carried out in flame-dried screw-cap test tubes and were allowed to proceed under a dry argon atmosphere with magnetic stirring. Toluene was purified by passing through a column of activated alumina under a dry argon atmosphere. Aldehydes were purchased from commercial sources and were distilled prior to use. TRIP catalyst was prepared from chiral BINOL according to the known literature procedure. Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F_{254}). Visualization was accomplished UV light (256 nm), with the combination of ceric ammonium molybdate or potassium permanganate as indicator. Flash column chromatography was performed with Merck silica gel (230-400 mesh). Enantiomeric excess (ee) was determined using a Varian Prostar HPLC with a 210 binary pump and a 335 diode array detector. Optical rotations were performed on a Rudolph Research Analytical Autopol IV polarimeter (λ 589) using a 700-μL cell with a path length of 1-dm. ^{1}H NMR and ^{13}C NMR were recorded on a Varian Inova-400 spectrometer with chemical shifts reported relative to tetramethylsilane (TMS). All the compounds were known compounds and were characterized by comparing their ^{1}H NMR and ^{13}C NMR values to the reported values.

General procedure for the propargylation of aldehydes: A screw-cap reaction tube loaded with a stir bar and 4 Å MS (100 mg) was evacuated, flame-dried, and back-filled with argon. To this tube was added the (*R*)-TRIP-PA catalyst **PA5** (20 mol %), freshly distilled aldehyde (0.20 mmol) and 1.5 ml of dry toluene. The reaction mixture was then cooled to -20 °C followed by the addition of allenylboronic acid pinacol ester **2** (0.30 mmol), slowly over 30 seconds. The mixture was stirred for 96 hours at this temperature and then directly loaded on to a silica gel column and was purified by flash chromatography using ethyl acetate and hexanes (1 : 9).



(*R*)-1-Phenyl-but-3-yn-1-ol (3a): Following the general procedure for the propargylation of aldehydes in 2 mmol scale (benzaldhyde), the title compound was obtained in 95 % yield with spectral properties reported in literature.[1] (94% yield, 91% ee was obtained when the reaction was run at 0.2 mmol scale following the general procedure for propargylation). Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/iPrOH = 95/5, 1.0 mL/min), t_{major} = 10.49 min, t_{minor} 12.81 min; ee = 95%. $[\alpha]^{25}_{D}$ = +10.10 (c = 0.9, MeOH). The reported value[1] for the *R*-enantiomer (98% ee) is $[\alpha]^{24}_{D}$ = +12.9 (c = 1.55, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.21 (m, 5H), 4.86 (td, *J* = 6.5, 2.6 Hz, 1H), 2.69 – 2.55 (m, 2H), 2.36 (s, 1H), 2.06 (t, *J* = 2.8 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 142.39, 128.45, 127.96, 125.70, 80.62, 72.30, 70.94, 29.42.



Peak results :

pankaj2-144odh951.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

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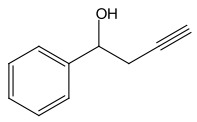
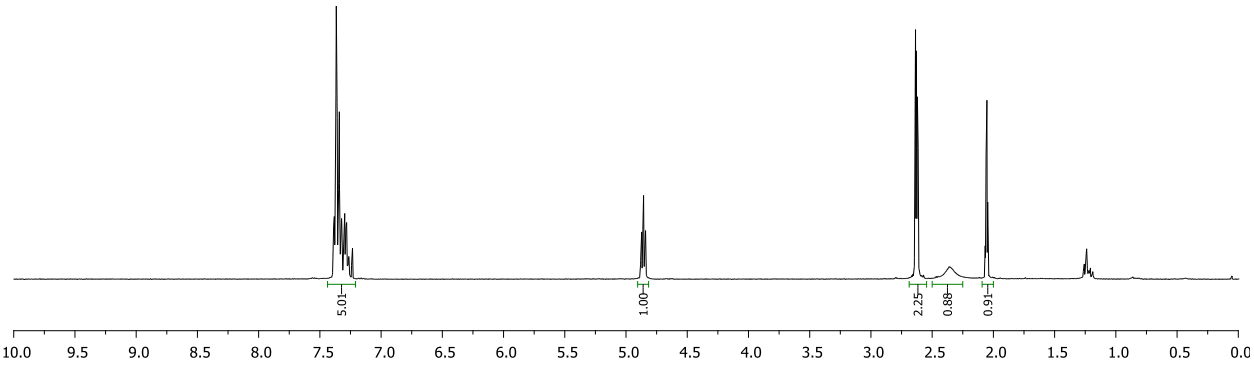
1	10.73	15.0	0.48	4.6	50.617
2	12.81	12.3	0.58	4.5	49.383
Total		27.3		9.2	100.000

pankaj2-150.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	10.49	131.1	0.65	52.6	97.538
2	12.81	3.3	0.65	1.3	2.462
Total		134.4		53.9	100.000


OH

3a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9.0
8.5
8.0
7.5
7.0
6.5
6.0
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2.0
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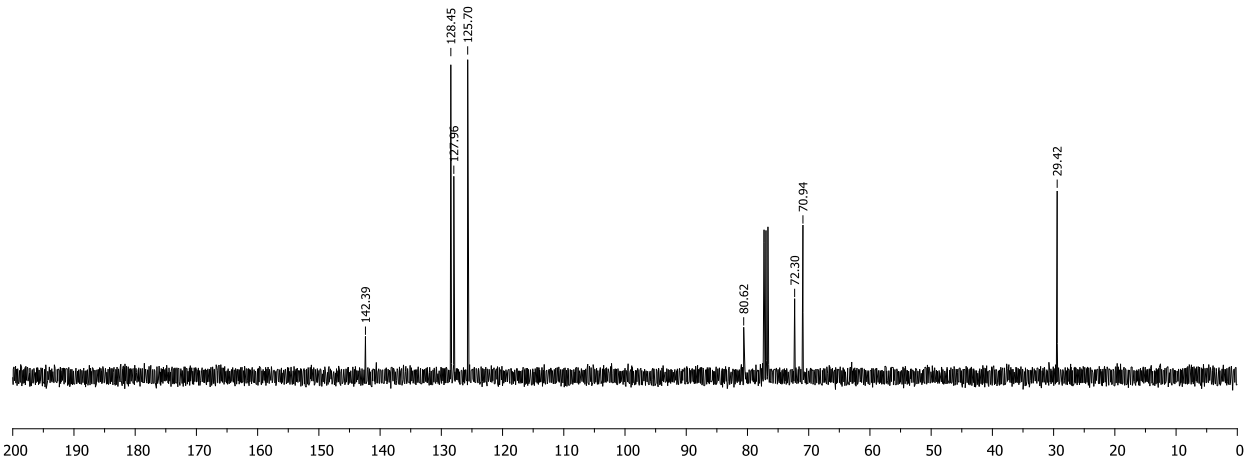
0.0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125.70
127.96
80.62
72.30
70.94
29.42
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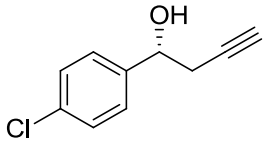
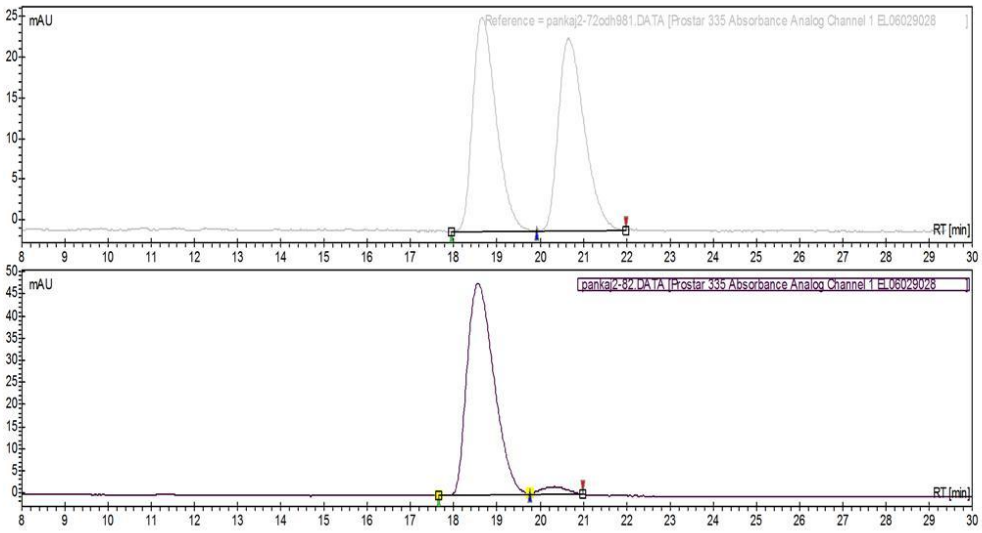


(*R*)-1-(4-Chloro-phenyl)-but-3-yn-1-ol (3b): Following the general procedure for the propargylation of aldehydes, the title compound was obtained in 95 % yield with spectral properties reported in literature.[2,3] Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/iPrOH = 98/2, 1.0 mL/min), t_{major} = 18.56 min, t_{minor} = 20.32 min; ee = 93%. $[\alpha]^{25}_{D}$ = +21.50 (c = 2.7, $CHCl_3$). The reported value[3] for the *S*-enantiomer (88% ee) is $[\alpha]^{20}_{D}$ = -35.9 (c = 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 4H), 4.83 (td, *J* = 6.5, 3.1 Hz, 1H), 2.69 – 2.51 (m, 2H), 2.40 (d, *J* = 3.3 Hz, 1H), 2.06 (t, *J* = 2.6 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 141.08, 133.91, 128.84, 127.38, 80.39, 71.85, 71.56, 29.70.



Peak results :

pankaj2-72odh981.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

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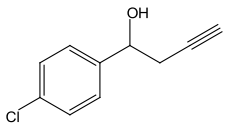
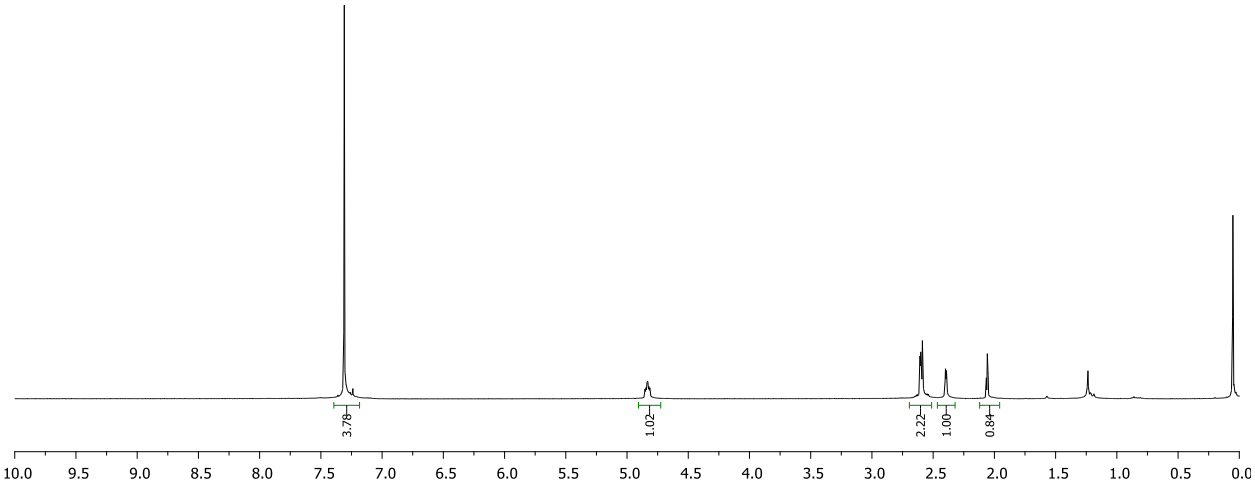
1	18.65	26.4	0.99	16.5	50.121
2	20.65	23.7	1.11	16.4	49.879
Total		50.0		33.0	100.000

pankaj2-82.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	18.56	47.9	1.17	34.8	96.283
2	20.32	1.9	1.12	1.3	3.717
Total		49.8		36.1	100.000


OH
Cl

3b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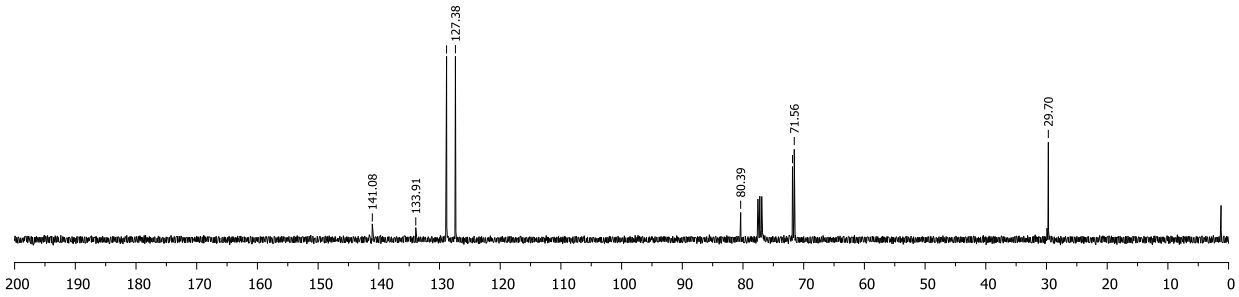
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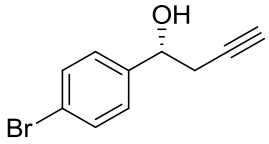
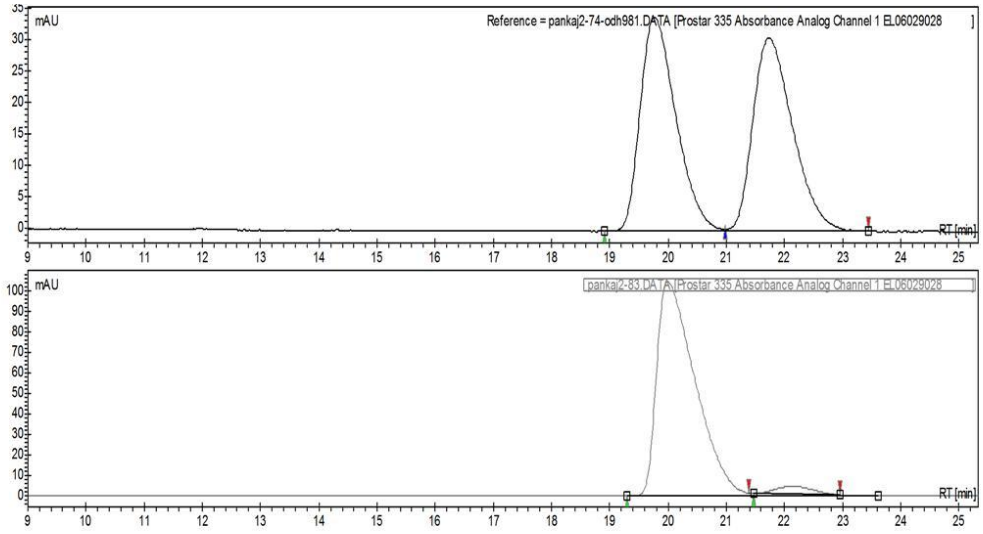


(*R*)-1-(4-Bromo-phenyl)-but-3-yn-1-ol (3c): Following the general procedure for the propargylation of aldehydes, the title compound was obtained in 93 % yield with spectral properties reported in literature.[4] Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/iPrOH = 98/2, 1.0 mL/min), t_{major} = 20.00 min, t_{minor} = 22.15 min; ee = 93%. $[\alpha]^{25}_{D}$ = +19.52 (c = 2.15, $CHCl_3$). The reported value[4] for the *S*-enantiomer (81% ee) is $[\alpha]_D$ = -28.4 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.36 (m, 2H), 7.29-7.15 (m, 2H), 4.85-4.72 (m, 1H), 2.66-2.50 (m, 2H), 2.37 (br s, 1H), 2.07-1.97 (m, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 141.59, 131.78, 127.71, 122.03, 80.34, 71.87, 71.58, 29.64.



Peak results :

pankaj2-74-odh981.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

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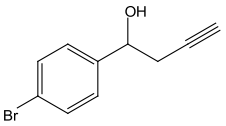
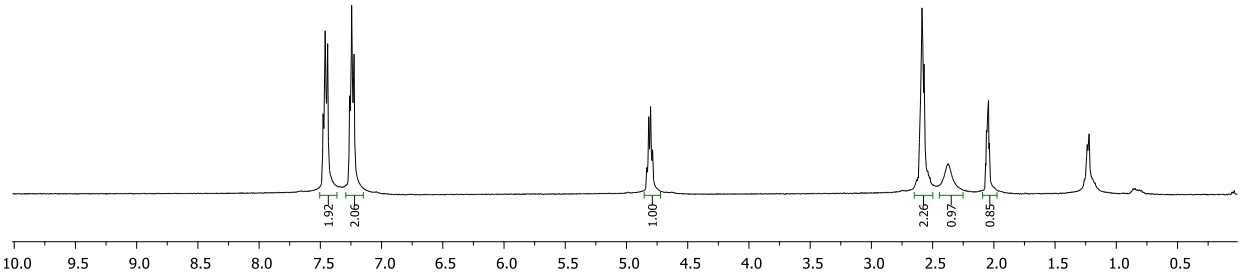
1	19.77	34.0	1.13	24.1	49.766
2	21.73	30.7	1.26	24.4	50.234
Total		64.7		48.5	100.000

pankaj2-83.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	20.00	104.5	1.25	79.5	96.440
2	22.15	3.9	1.19	2.9	3.560
Total		108.4		82.5	100.000


OH
Br

3c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2.26
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6.5
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2.5
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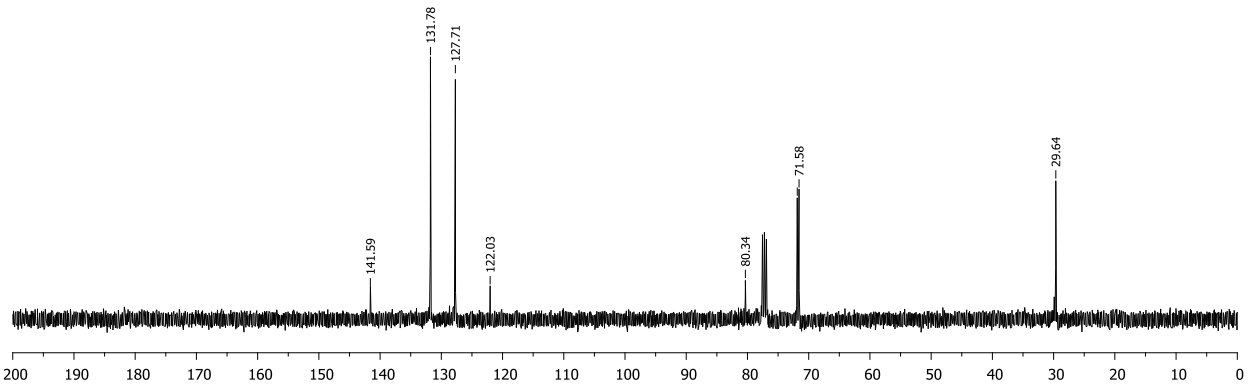
1.0
0.5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71.58
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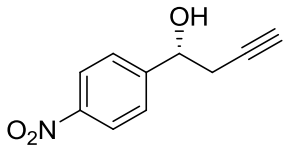
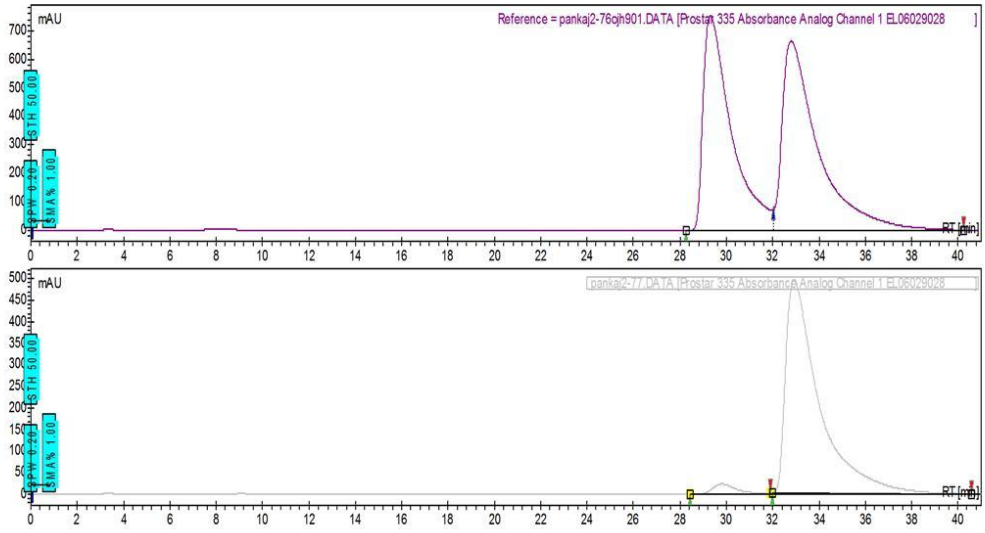


(*R*)-1-(4-Nitro-phenyl)-but-3-yn-1-ol (3d): Following the general procedure for the propargylation of aldehydes, the title compound was obtained in 96 % yield with spectral properties reported in literature.[5] Enantiomeric excess was determined by HPLC with a chiralcel OJ-H column (hexane/iPrOH = 90/10, 1.0 mL/min), t_{minor} = 29.81 min, t_{major} = 32.92 min; ee = 93%. $[\alpha]^{25}_{D}$ = +3.48 (c = 0.37, $CHCl_3$). The absolute configuration was determined by analogy. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.09 (m, 2H), 7.68 – 7.45 (m, 2H), 5.02-4.95 (m, 1H), 2.75-2.56 (m, 3H), 2.10 (td, *J* = 2.6, 0.6 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 149.64, 147.79, 126.87, 123.88, 79.57, 72.18, 71.50, 29.70.



Peak results :

pankaj2-76ojh901.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

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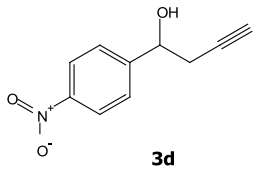
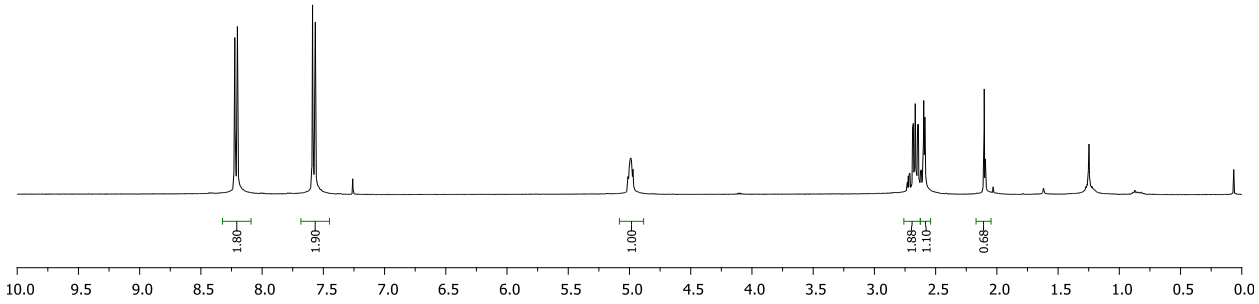
1	29.32	752.4	2.02	1056.8	47.010
2	32.80	663.0	2.44	1191.3	52.990
Total		1415.4		2248.1	100.000

pankaj2-77.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	29.81	24.1	1.85	30.8	3.579
2	32.92	496.6	2.26	829.6	96.421
Total		520.6		860.4	100.000


OH
O
N+
O-

3d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6.5
6.0
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2.0
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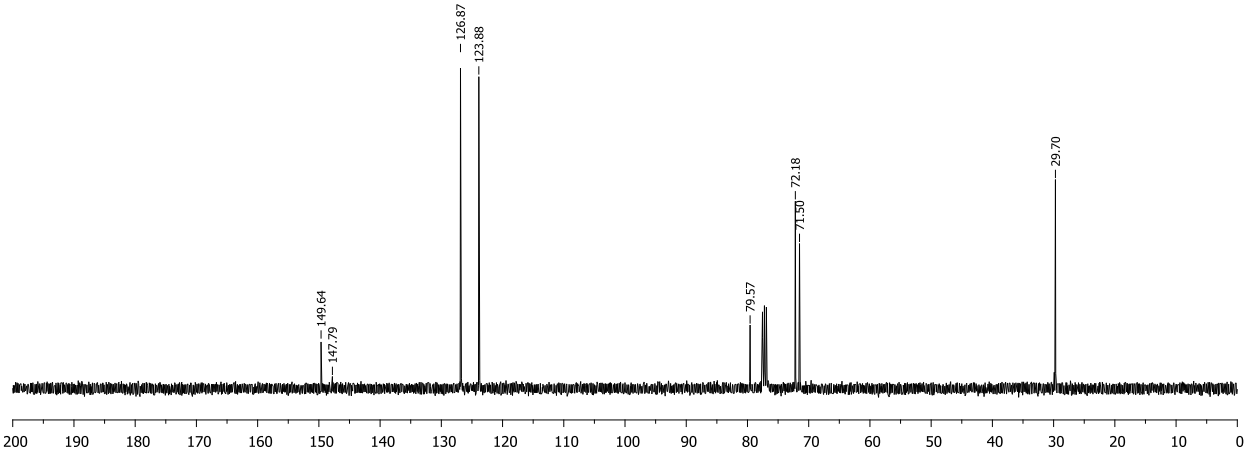
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79.57
72.18
71.50
29.70
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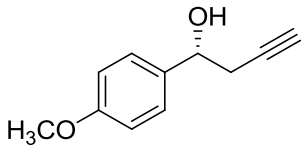
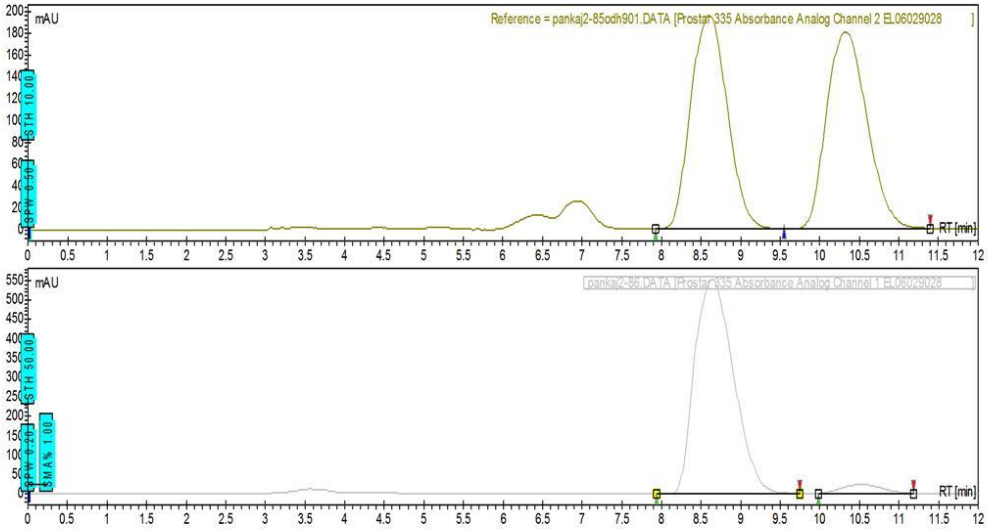


(*R*)-1-(4-Methoxy-phenyl)-but-3-yn-1-ol (3e): Following the general procedure for the propargylation of aldehydes, the title compound was obtained in 87 % yield with spectral properties reported in literature.[3,4] Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/iPrOH = 90/10, 1.0 mL/min), t_{major} = 8.64 min, t_{minor} = 10.53 min; ee = 92%. $[\alpha]^{25}_{D}$ = +33.60 (c = 1.45, $CHCl_3$). The reported value[3] for the *S*-enantiomer (89 % ee) is $[\alpha]^{28}_{D}$ = -36.2 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 6.92 – 6.86 (m, 2H), 4.84 (t, *J* = 6.4 Hz, 1H), 3.81 (s, 3H), 2.66-2.60 (m, 2H), 2.30 (br s, 1H), 2.07 (t, *J* = 2.6 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 159.56, 134.87, 127.23, 114.08, 81.03, 72.21, 71.08, 55.51, 29.61.



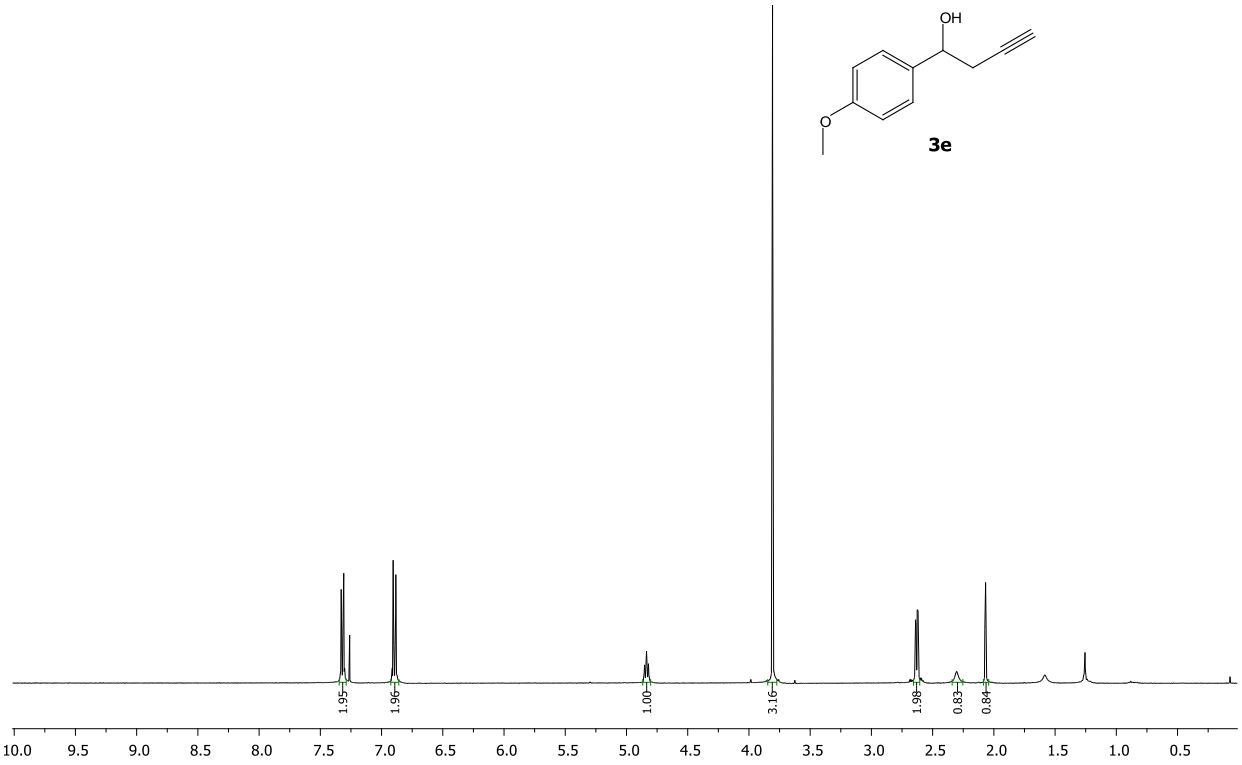
Peak results :

pankaj2-85odh901.DATA [Prostar 335 Absorbance Analog Channel 2 EL06029028]

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	8.60	49.57	195.4	104.4	49.567
2	UNKNOWN	10.32	50.43	180.7	106.2	50.433
Total			100.00	376.0	210.7	100.000

pankaj2-86.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	8.64	552.8	0.90	313.2	95.840
2	10.53	23.3	0.94	13.6	4.160
Total		576.1		326.8	100.000


OH
O
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1.96
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1.98
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0.84
10.0
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8.5
8.0
7.5
7.0
6.5
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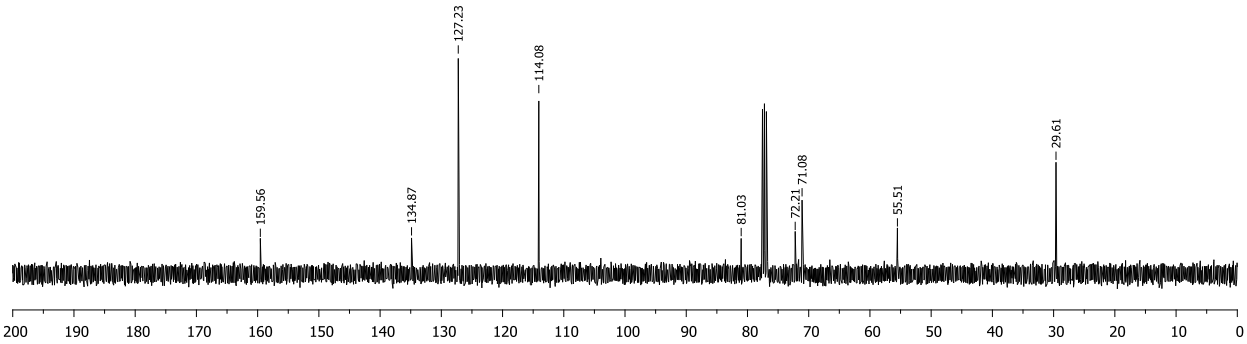
159.56
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127.23
114.08
81.03
72.21
71.08
55.51
29.61
200
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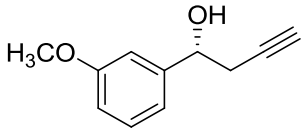
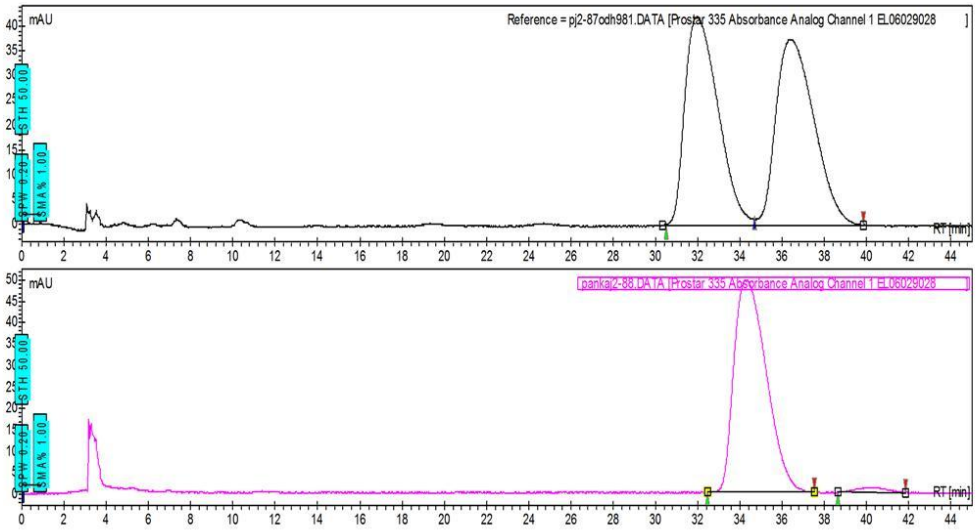


(*R*)-1-(3-Methoxy-phenyl)-but-3-yn-1-ol (3f): Following the general procedure for the propargylation of aldehydes, the title compound was obtained in 92 % yield with spectral properties reported in literature.[6] Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/iPrOH = 98/2, 1.0 mL/min), t_{major} = 34.28 min, t_{minor} = 39.96 min; ee = 96%. $[\alpha]^{25}_{D}$ = +7.09 (c = 0.34, $CHCl_3$). The absolute configuration was determined by analogy. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 1H), 6.97 – 6.90 (m, 2H), 6.82 (ddd, *J* = 8.2, 2.4, 1.1 Hz, 1H), 4.83 (td, *J* = 6.4, 3.4 Hz, 1H), 3.80 (s, 3H), 2.64 – 2.59 (m, 2H), 2.38 (d, *J* = 3.5 Hz, 1H), 2.06 (t, *J* = 2.6 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 159.95, 144.35, 129.74, 118.22, 113.68, 111.49, 80.86, 72.46, 71.21, 55.45, 29.65.



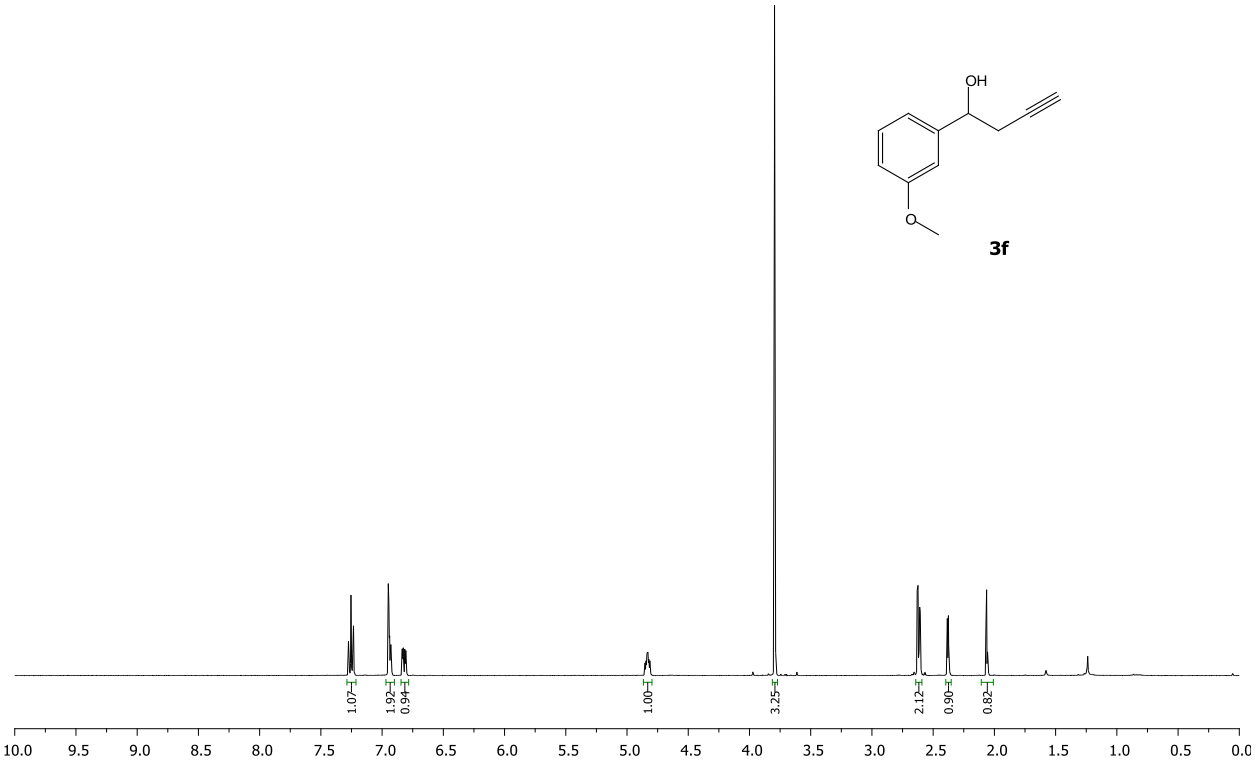
Peak results :

pj2-87odh981.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	31.96	42.2	2.87	77.0	49.355
2	36.39	37.6	3.28	79.0	50.645
Total		79.8		156.0	100.000

pankaj2-88.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	34.28	49.5	2.79	87.9	97.997
2	39.96	1.1	1.82	1.8	2.003
Total		50.6		89.7	100.000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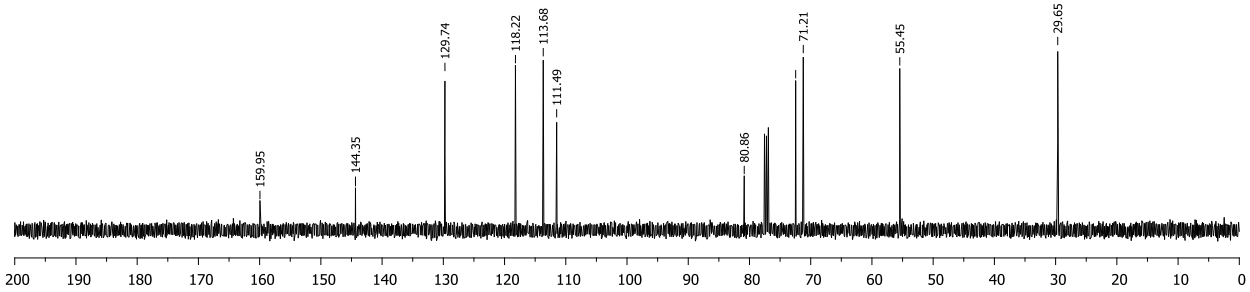
1.92
0.94
1.00
3.25
2.12
0.90
0.82
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

3f


159.95
144.35
129.74
118.22
113.68
111.49
80.86
71.21
55.45
29.65
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190
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90
80
70
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40
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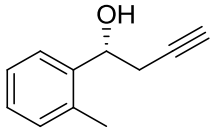
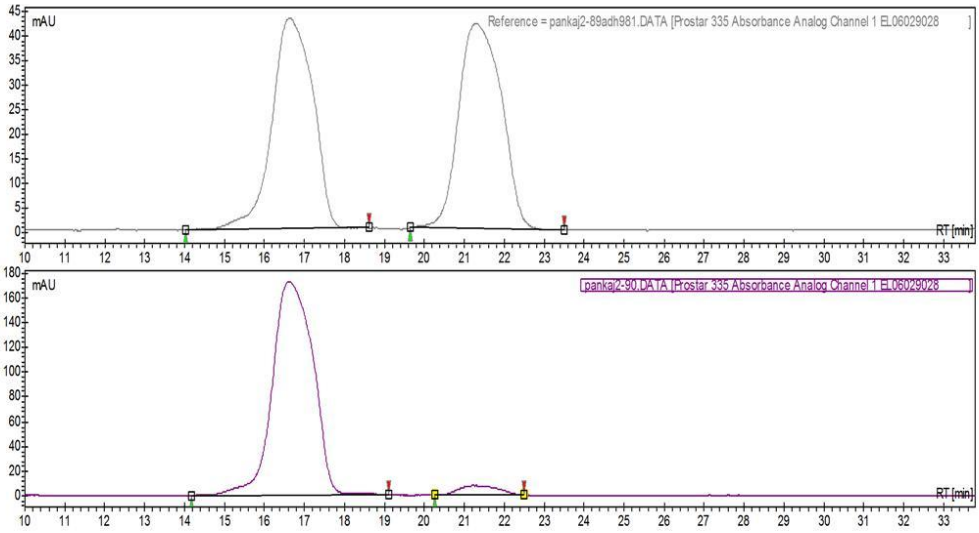


(*R*)-1-*o*-Tolyl-but-3-yn-1-ol (3g): Following the general procedure for the propargylation of aldehydes, the title compound was obtained in 91 % yield with spectral properties reported in literature.[4] Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/iPrOH = 98/2, 1.0 mL/min), t_{major} = 16.61 min, t_{minor} = 21.21 min; ee = 92%. $[\alpha]^{25}_{D}$ = +35.57 (c = 1.96, $CHCl_3$). The reported value[4] for the *S*-enantiomer (89 % ee) is $[\alpha]^{25}_{D}$ = -63.2 (c = 0.58, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.4 Hz, 1H), 7.26-7.20 (m, 3H), 5.10 (dd, *J* = 7.3, 5.4 Hz, 1H), 2.62 – 2.57 (m, 2H), 2.35 (s, 3H), 2.32 (br s, 1H), 2.07 (td, *J* = 2.6, 0.8 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 140.69, 134.80, 130.66, 127.96, 126.55, 125.27, 81.13, 70.97, 69.10, 28.48, 19.27.



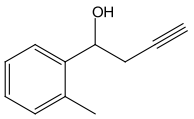
Peak results :

pankaj2-89adh981.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

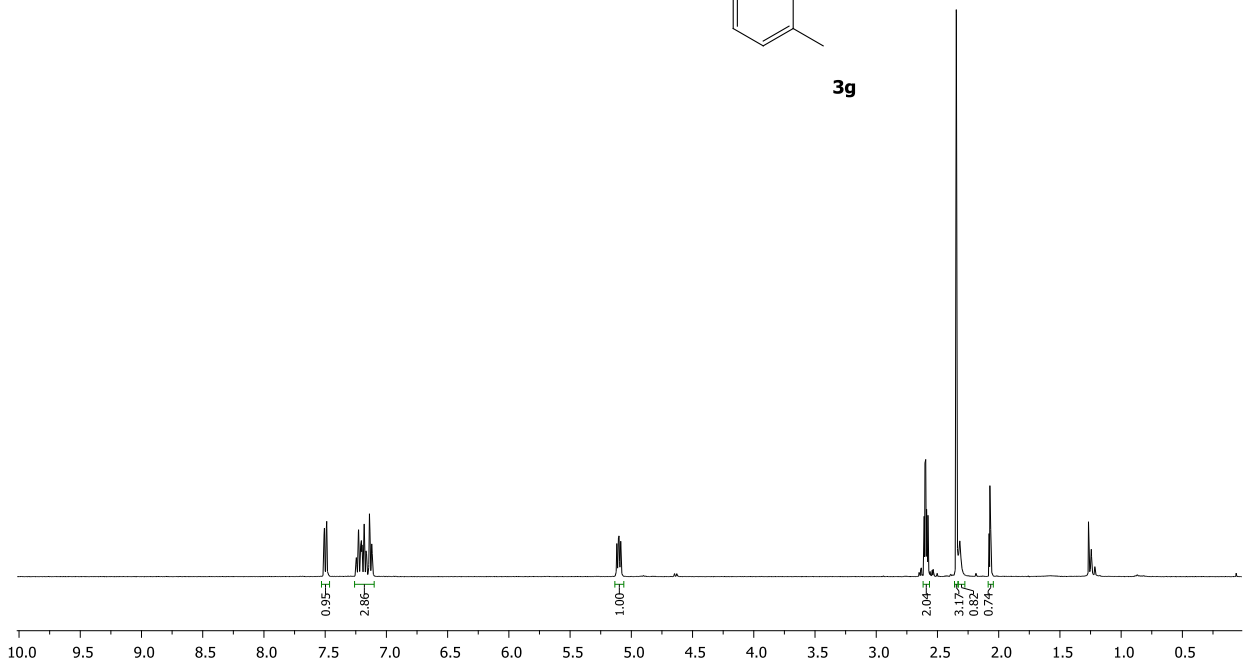
Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	16.63	42.8	1.78	51.2	49.591
2	21.28	41.8	1.86	52.0	50.409
Total		84.6		103.2	100.000

pankaj2-90.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
2	16.61	172.5	1.74	203.0	95.766
1	21.21	7.6	1.73	9.0	4.234
Total		180.1		212.0	100.000


OH

3g


0.95
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1.00
2.04
3.17
0.82
0.74
10.0
9.5
9.0
8.5
8.0
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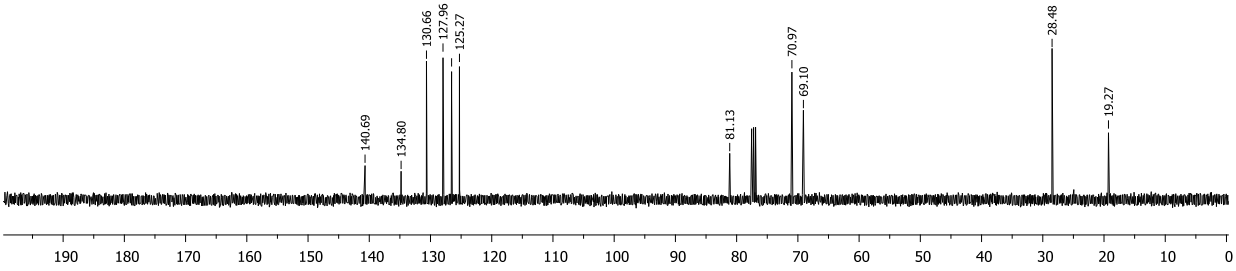
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


140.69
134.80
130.66
127.96
125.27
81.13
70.97
69.10
28.48
19.27
190
180
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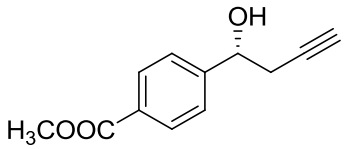
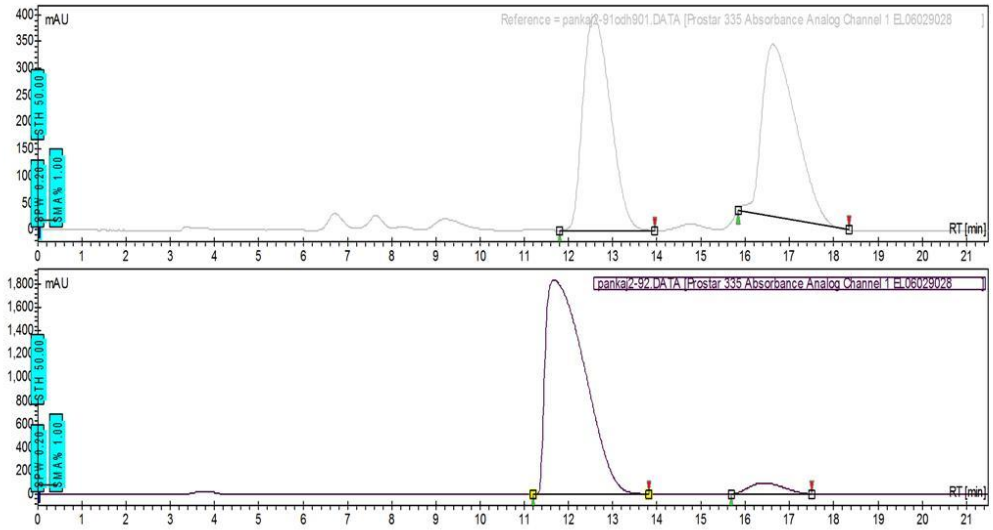
90
80
70
60
50
40
30
20
10
0



(*R*)-Methyl 4-(1-hydroxybut-3ynyl)benzoate (3h): Following the general procedure for the propargylation of aldehydes, the title compound was obtained in 94 % yield with spectral properties reported in literature.[7] Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/iPrOH = 90/10, 1.0 mL/min), t_{major} = 11.67 min, t_{minor} = 16.43 min; ee = 91%. $[\alpha]^{25}_{D}$ = +33.33 (c = 2.04, $CHCl_3$). The absolute configuration was determined by analogy. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 4.97 – 4.86 (m, 1H), 3.90 (d, *J* = 0.7 Hz, 3H), 2.76 – 2.50 (m, 3H), 2.07 (td, *J* = 2.6, 0.7 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 167.06, 147.63, 129.96, 129.88, 125.94, 80.24, 72.03, 71.60, 52.34, 29.60.



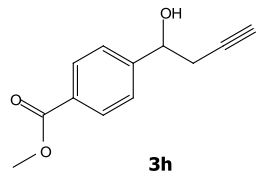
Peak results :

pankaj2-91odh901.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

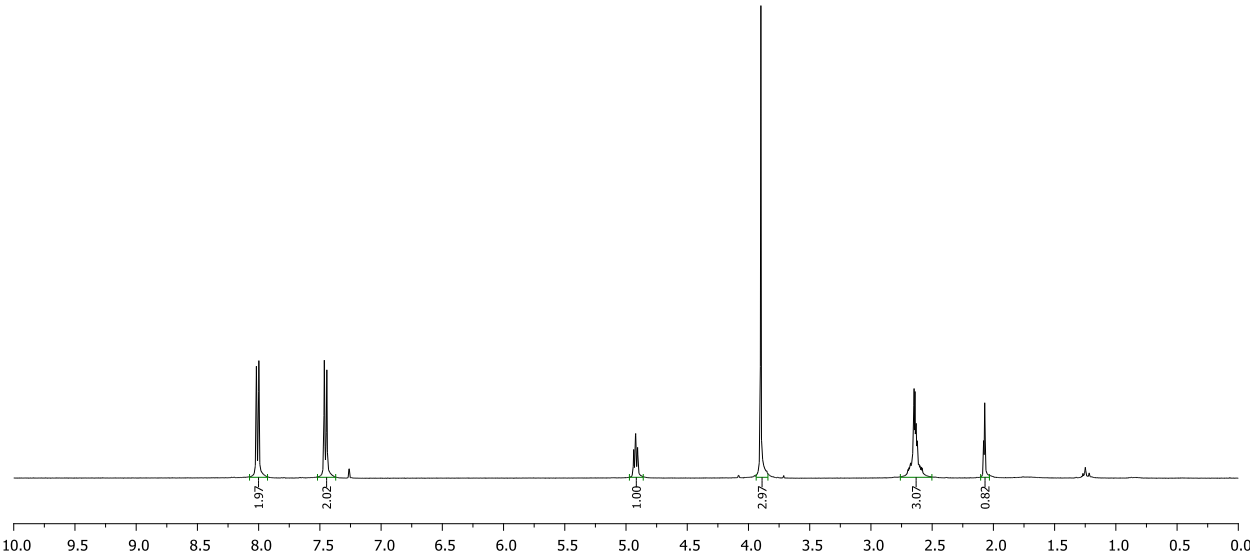
Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	12.57	398.0	1.16	286.6	49.826
2	16.63	320.7	1.47	288.6	50.174
Total		718.7		575.3	100.000

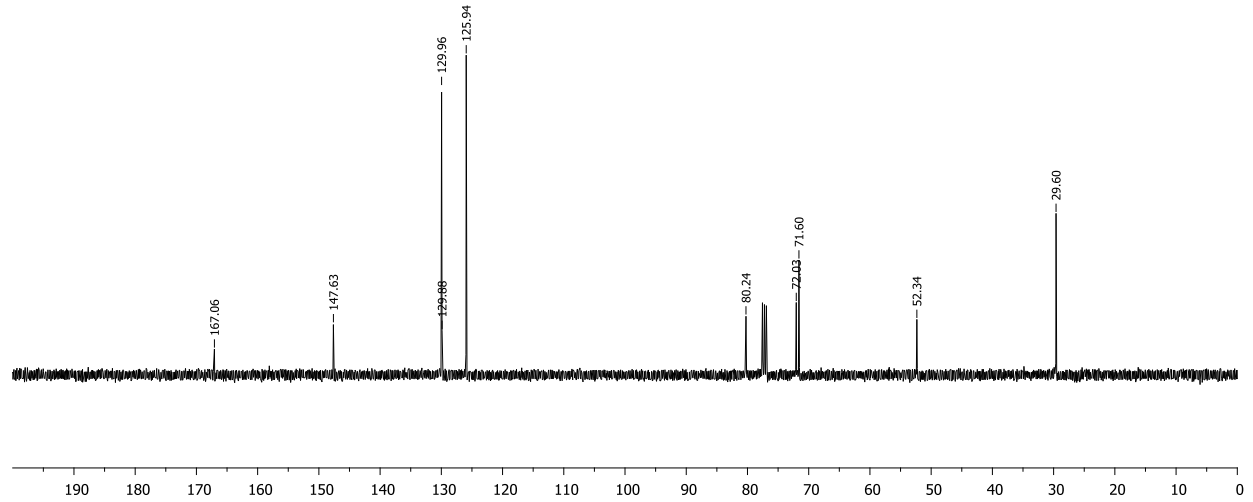
pankaj2-92.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	11.67	1834.5	1.61	1872.0	95.568
2	16.43	94.4	1.47	86.8	4.432
Total		1928.9		1958.8	100.000


OH
O
O

3h


1.97
2.02
1.00
2.97
3.07
0.82
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


167.06
147.63
129.88
129.96
125.94
80.24
72.03
71.60
52.34
29.60
190
180
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70
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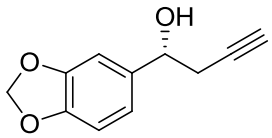
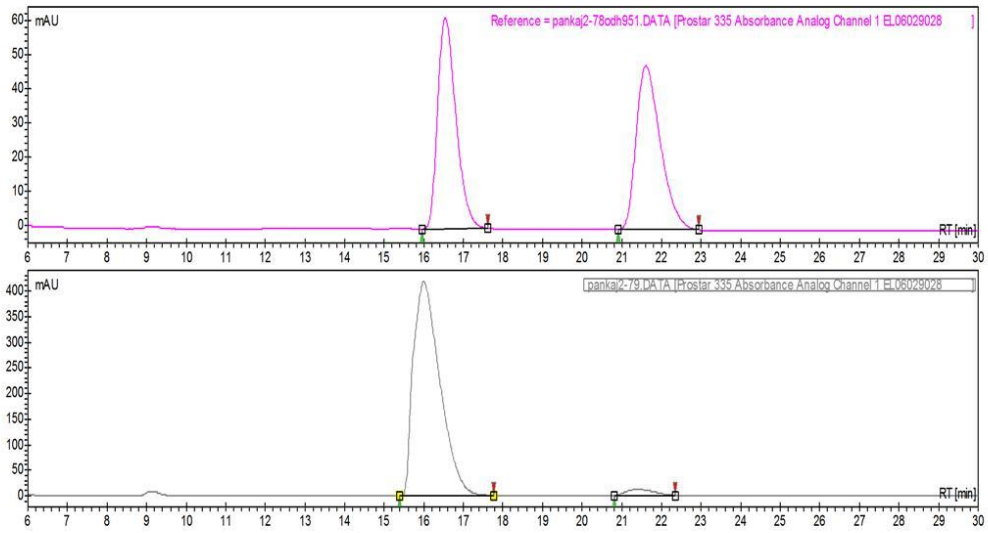
20
10
0



(*R*)-1-(Benzo[d][1,3]dioxol-5-yl)but-3-yn-1-ol (3i): Following the general procedure for the propargylation of aldehydes, the title compound was obtained in 92 % yield with spectral properties reported in literature.[8] Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/iPrOH = 95/5, 1.0 mL/min), t_{major} = 15.99 min, t_{minor} = 21.40 min; ee = 94%. $[\alpha]^{25}_{D}$ = +3.91 (c = 1.70, $CHCl_3$). The absolute configuration was determined by analogy. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 – 6.72 (m, 3H), 5.95 (s, 2H), 4.79 (td, *J* = 6.4, 3.0 Hz, 1H), 2.60 (dd, *J* = 6.6, 2.6 Hz, 2H), 2.33 (d, *J* = 3.2 Hz, 1H), 2.08 (t, *J* = 2.6 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 148.07, 147.56, 136.82, 119.54, 108.40, 106.58, 101.36, 80.90, 72.50, 71.30, 29.79.



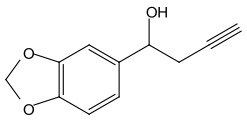
Peak results :

pankaj2-78odh951.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

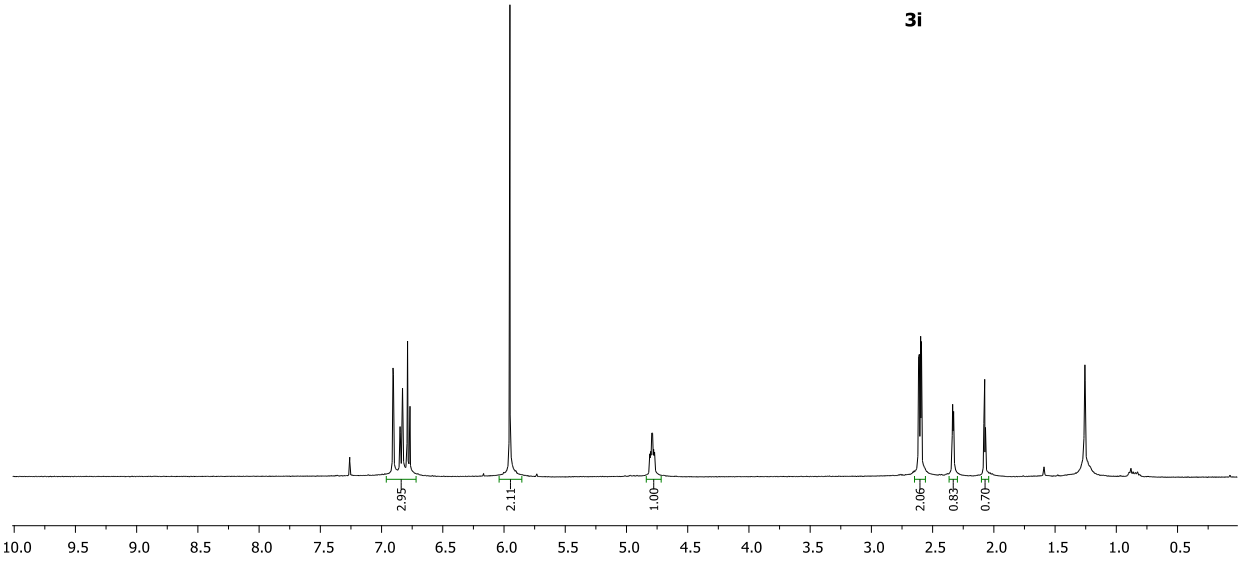
Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	16.53	61.8	0.85	33.0	49.412
2	21.61	47.9	1.11	33.8	50.588
Total		109.7		66.8	100.000

pankaj2-79.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	15.99	418.9	1.23	324.8	97.100
2	21.40	12.0	1.30	9.7	2.900
Total		430.8		334.5	100.000


OH
O
O

3i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2.06
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9.0
8.5
8.0
7.5
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6.5
6.0
5.5
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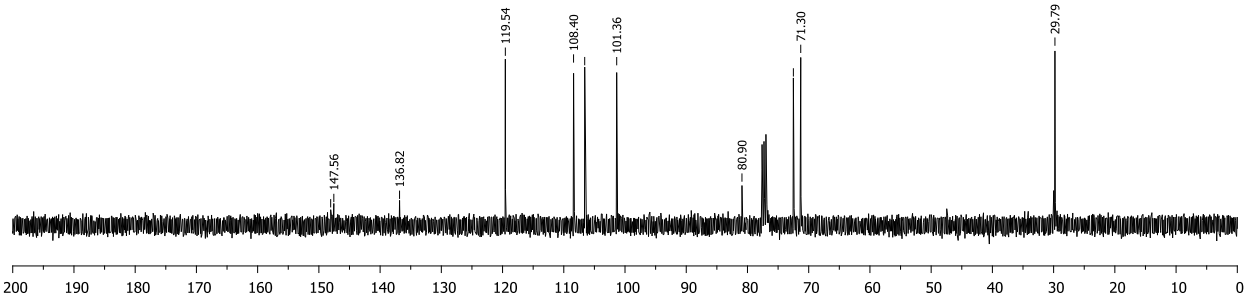
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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80.90
71.30
29.79
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70
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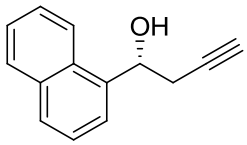
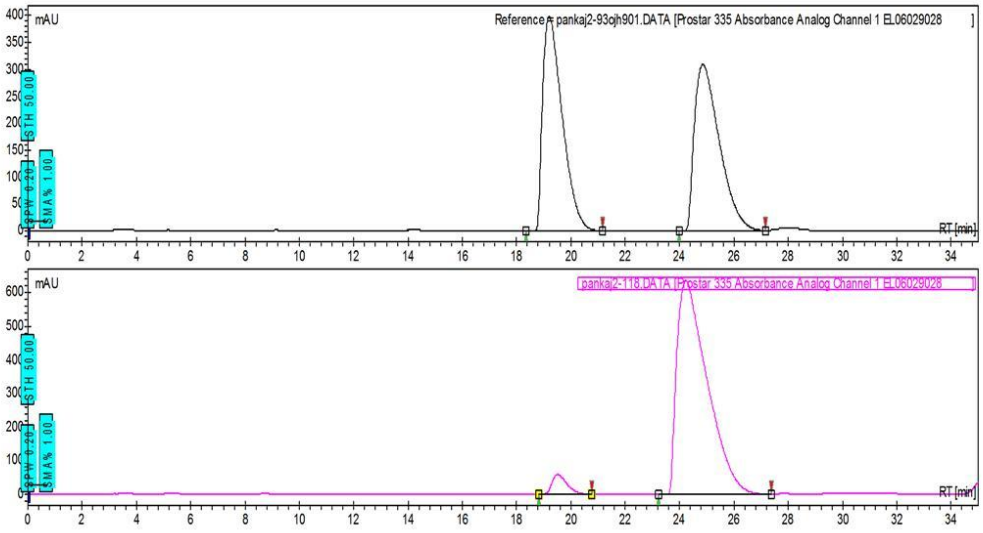


(*R*)-1-(Naphthalen-1-yl)but-3-yn-1-ol (3j): Following the general procedure for the propargylation of aldehydes, the title compound was obtained in 93 % yield with spectral properties reported in literature.[3,9] Enantiomeric excess was determined by HPLC with a chiralcel OJ-H column (hexane/iPrOH = 90/10, 1.0 mL/min), t_{minor} = 19.52 min, t_{major} = 24.85 min; ee = 91%. $[\alpha]^{25}_{D}$ = +60.64 (c = 1.96, PhH). The reported value[3] for the *S*-enantiomer (84 % ee) is $[\alpha]^{28}_{D}$ = -53.2 (c = 1, PhH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 1H), 7.92 – 7.78 (m, 2H), 7.72 (d, *J* = 7.1 Hz, 1H), 7.58 – 7.45 (m, 3H), 5.67 (dd, *J* = 8.1, 4.0 Hz, 1H), 2.95-2.85 (m, 1H), 2.81-2.71 (m, 1H), 2.56 (br s, 1H), 2.15 (t, *J* = 2.4 Hz, 1H).^{13}C NMR (100.6 MHz, $CDCl_3$) δ 138.00, 133.99, 130.39, 129.25, 128.70, 126.50, 125.85, 125.61, 123.17, 122.97, 81.17, 71.46, 69.51, 28.90.



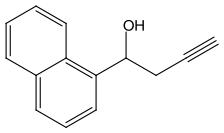
Peak results :

pankaj2-93ojh901.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

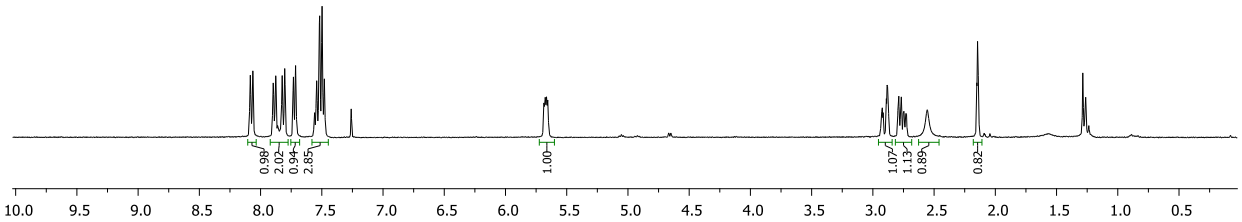
Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	19.20	398.5	1.34	333.1	50.236
2	24.85	308.8	1.69	330.0	49.764
Total		707.3		663.0	100.000

pankaj2-118.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	19.52	59.0	1.00	37.5	4.387
2	24.23	637.3	2.11	818.4	95.613
Total		696.3		855.9	100.000


OH

3j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0.89
0.82
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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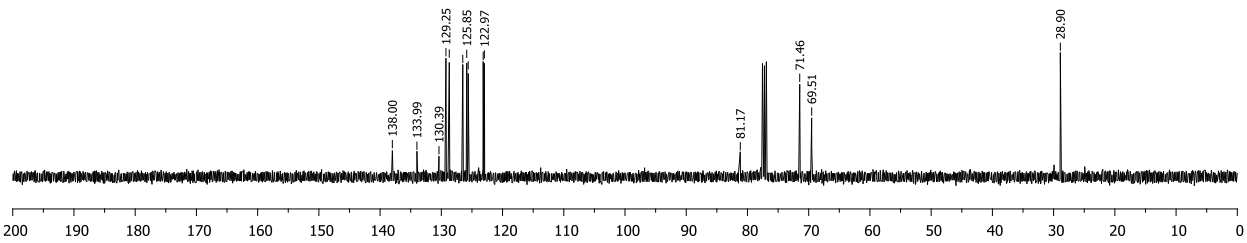
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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129.25
125.85
122.97
81.17
71.46
69.51
28.90
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90
80
70
60
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20
10
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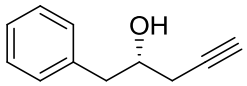
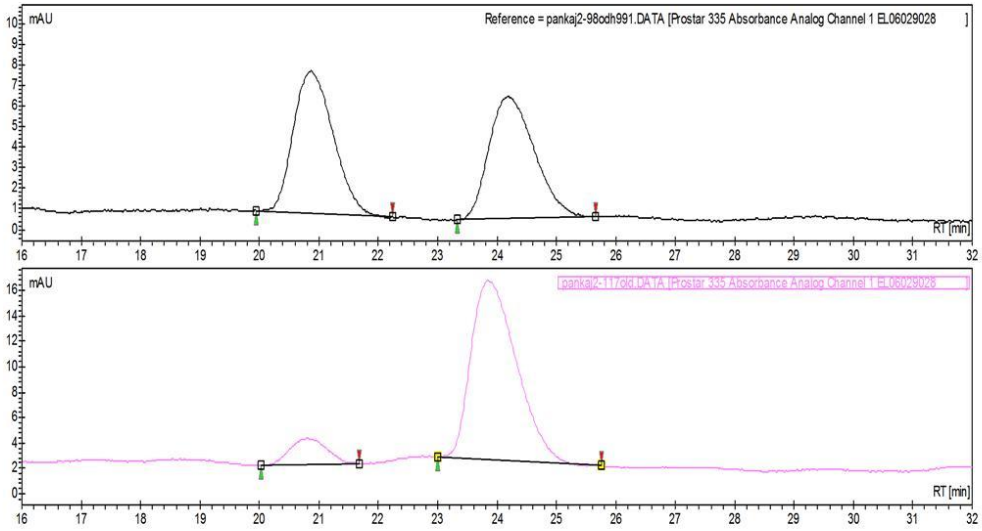


(*R*)-1-Phenylpent-4-yn-2-ol (3k): Following the general procedure for the propargylation of aldehydes, the title compound was obtained in 90 % yield with spectral properties reported in literature.[8] Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/iPrOH = 99/1, 1.0 mL/min), t_{minor} = 20.80 min, t_{major} = 23.85 min; ee = 79%. $[\alpha]^{25}_{D}$ = +0.53 (c = 0.55, $CHCl_3$). The absolute configuration was determined by analogy. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.13 (m, 5H), 4.06 – 3.88 (m, 1H), 2.95-2.78 (m, 2H), 2.49 – 2.30 (m, 2H), 2.09 (t, *J* = 2.7 Hz, 1H), 1.95 (d, *J* = 4.4 Hz, 1H).^{13}C NMR (100.6 MHz, $CDCl_3$) δ 137.87, 129.61, 128.83, 126.90, 80.82, 71.33, 71.03, 42.70, 26.64.



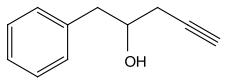
Peak results :

pankaj2-98odh991.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

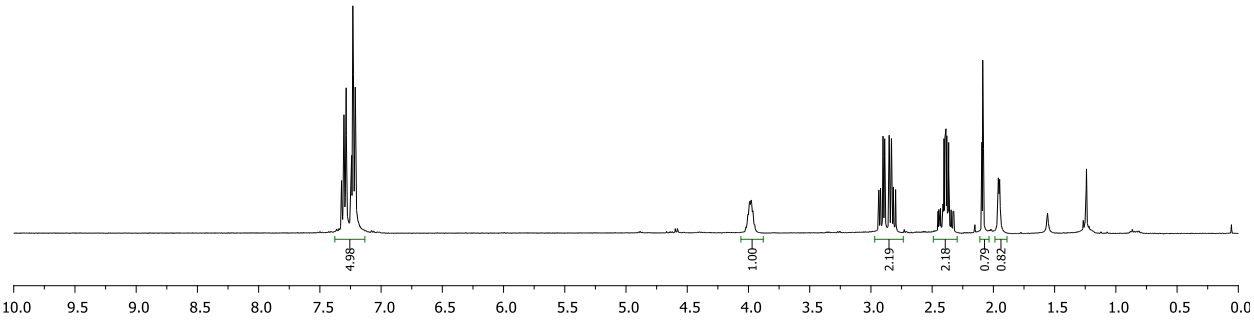
Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	20.87	6.9	1.23	5.3	50.579
2	24.19	5.9	1.39	5.2	49.421
Total		12.8		10.6	100.000

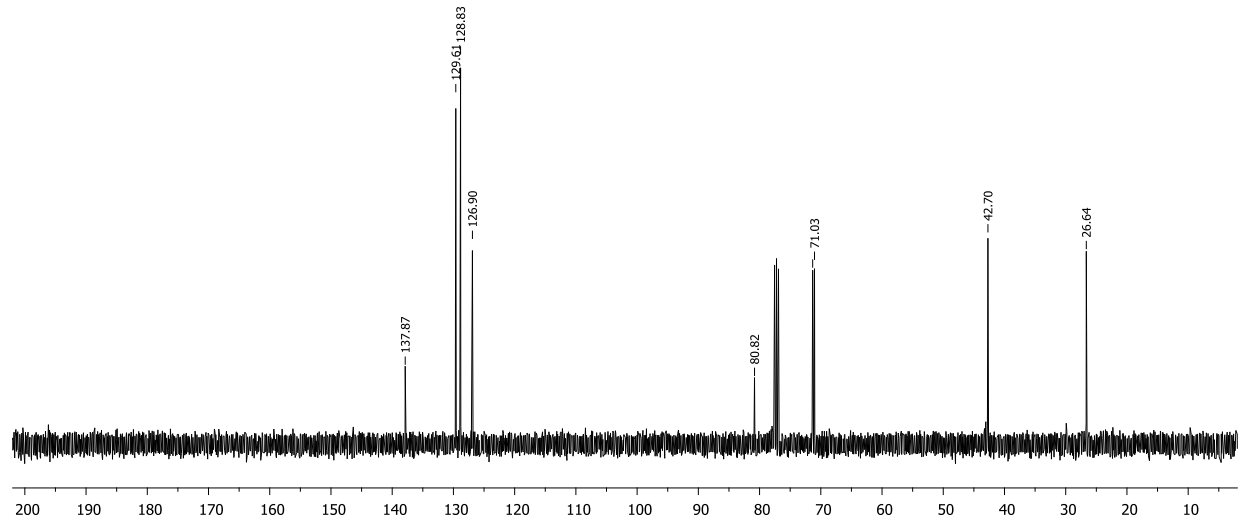
pankaj2-117old.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

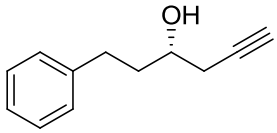
Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	20.80	2.1	1.23	1.5	10.640
2	23.85	14.1	1.42	12.5	89.360
Total		16.1		13.9	100.000


OH

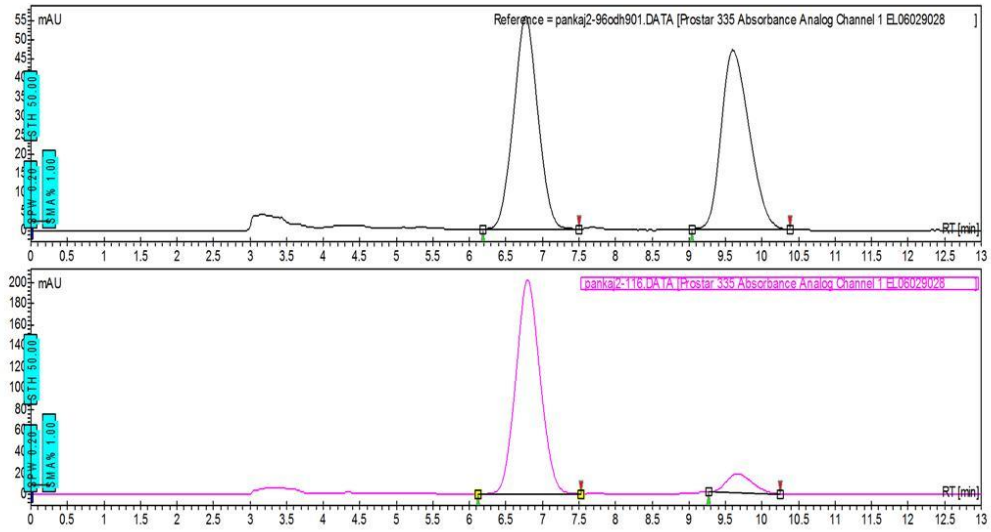
3k


4.98
1.00
2.19
2.18
0.79
0.82
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


137.87
129.61
128.83
126.90
80.82
71.03
42.70
26.64
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



(*S*)-1-Phenylhex-5-yn-3-ol (3l): Following the general procedure for the propargylation of aldehydes, the title compound was obtained in 92 % yield with spectral properties reported in literature.[10] Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/iPrOH = 90/10, 1.0 mL/min), t_{major} = 6.97 min, t_{minor} = 9.67 min; ee = 82 %. $[\alpha]^{25}_{D}$ = -13.51 (c = 1.38, $CHCl_3$). The reported value[3] for the *R*-enantiomer (42 % ee) is $[\alpha]^{28}_{D}$ = +8.70 (c = 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.08 (m, 5H), 3.83-3.70 (m, 1H), 2.86-2.63 (m, 2H), 2.50 – 2.24 (m, 2H), 2.05 (t, *J* = 2.6 Hz, 1H), 1.96 (d, *J* = 5.2 Hz, 1H), 1.90-1.82 (m, 2H).^{13}C NMR (100.6 MHz, $CDCl_3$) δ 141.84, 128.65, 128.63, 126.14, 80.85, 71.22, 69.32, 37.99, 32.10, 27.72.



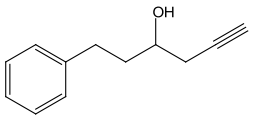
Peak results :

pankaj2-96odh901.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

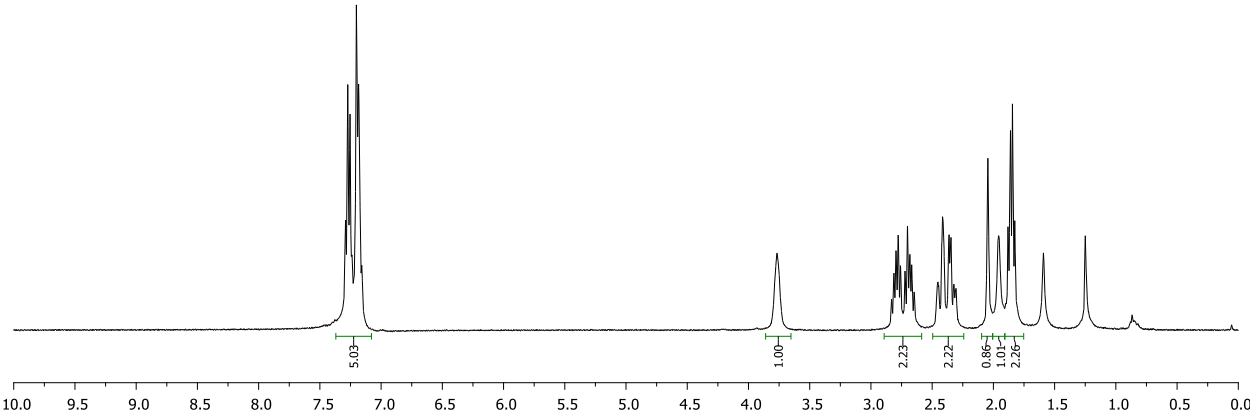
Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	6.76	55.7	0.62	21.3	49.950
2	9.60	46.9	0.73	21.3	50.050
Total		102.6		42.6	100.000

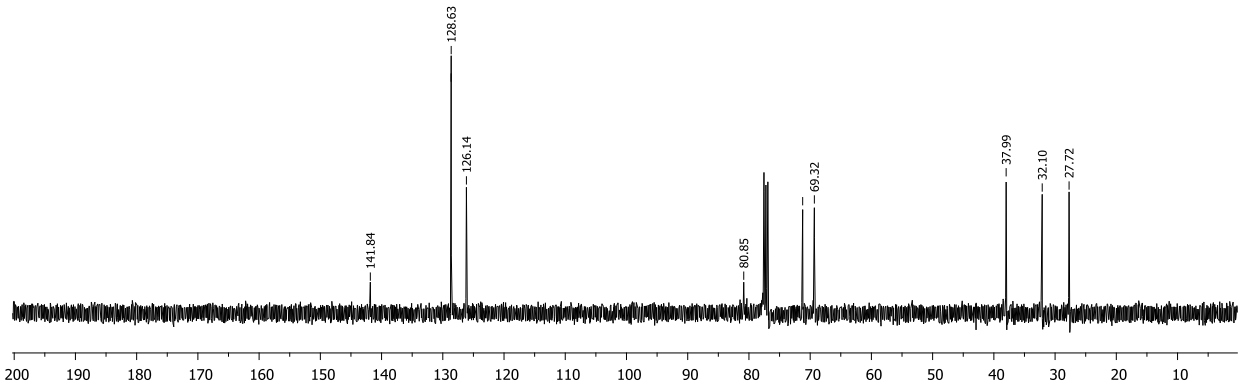
pankaj2-116.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

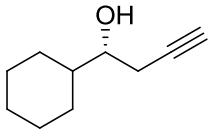
Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	6.79	201.7	0.62	76.8	90.981
2	9.67	18.1	0.68	7.6	9.019
Total		219.8		84.4	100.000


OH

3l

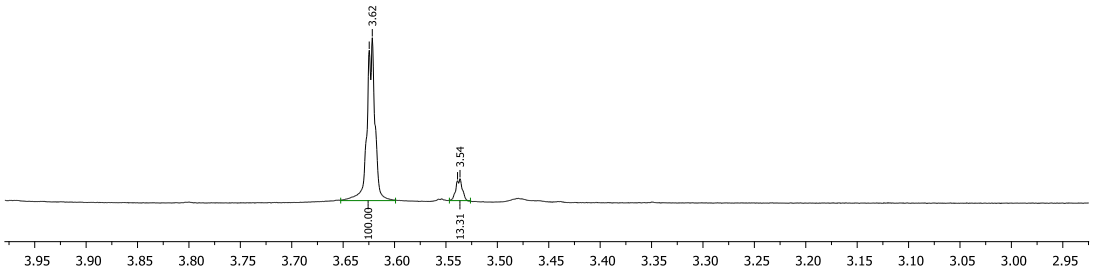

5.03
1.00
2.23
2.22
0.86
1.01
2.26
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

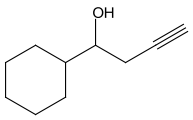

128.63
126.14
141.84
80.85
69.32
37.99
32.10
27.72
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



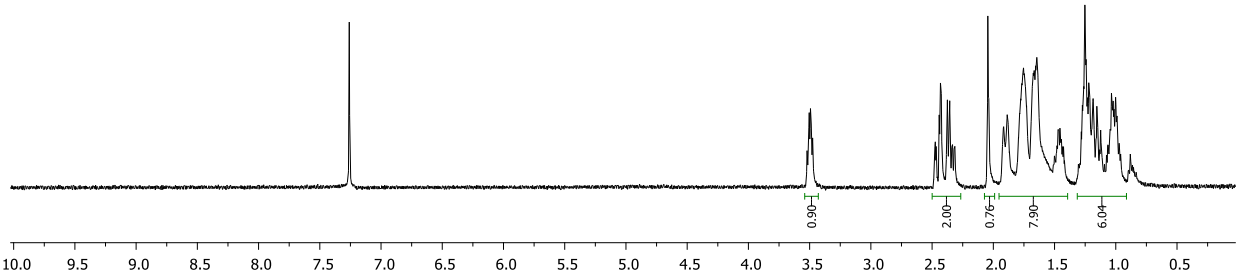
(*R*)-1-Cyclohexyl-but-3-en-1-ol (3m): Following the general procedure for the propargylation of aldehydes, the title compound was obtained in 89 % yield with spectral properties reported in literature.[3,10,11] Enantiomeric excess was determined to be 77 % by ^{1}H NMR of the crude material after esterification with (*R*)-MTPACl by comparing the singlets at δ 3.62 (major) and 3.54 (minor).[3] $[\alpha]^{25}_D$ = +7.70 (c = 0.35, $CHCl_3$). The reported value[11] for the *R*-enantiomer (59% ee) is $[\alpha]^{20}_D$ = +7 (c = 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.54-3.45 (m, 1H), 2.50 – 2.27 (m, 2H), 2.05 (t, *J* = 2.6 Hz, 1H), 1.95 – 1.39 (m, 7H), 1.31 – 0.91 (m, 5H).^{13}C NMR (100.6 MHz, $CDCl_3$) δ 84.92, 74.23, 70.90, 42.72, 29.24, 28.39, 26.59, 26.33, 26.17, 24.85.

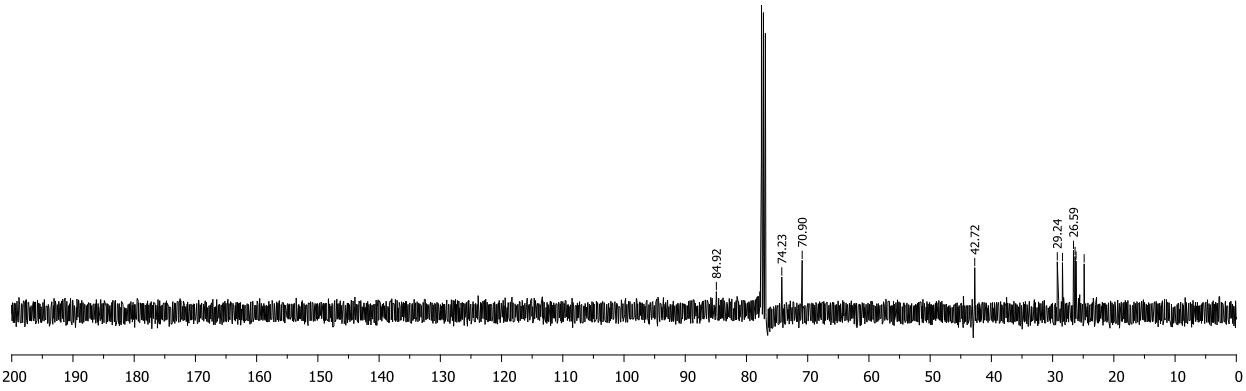
^{1}H NMR of the crude**3m** after esterefication with (R)-MTPACl




OH

3m


0.90
2.00
0.76
7.90
6.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


84.92
74.23
70.90
42.72
29.24
26.59
200
190
180
170
160
150
140
130
120
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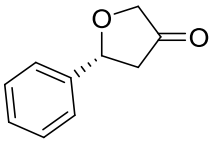
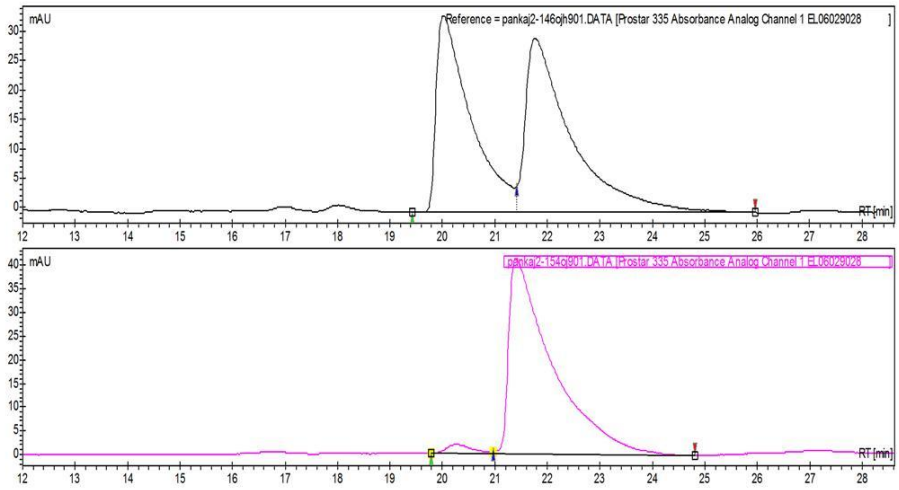
100
90
80
70
60
50
40
30
20
10
0



(*R*)-5-phenyldihydrofuran-3-one (4): Following Zhang's gold catalysis procedure,[7] while using 3,5-dichloropyridine *N*-oxide as the oxidant, the title compound was obtained in 54 % yield with spectral properties reported in literature.[7] Enantiomeric excess was determined by HPLC with a chiralcel OJ-H column (hexane/iPrOH = 90/10, 1.0 mL/min), t_{minor} = 20.27 min, t_{major} = 21.41 min; ee = 95 %. $[\alpha]^{25}_{D}$ = +67.61 (c = 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.32 (m, 5H), 5.29 (dd, *J* = 9.5, 6.3 Hz, 1H), 4.25 (d, *J* = 17.0 Hz, 1H), 4.02 (d, *J* = 17.0 Hz, 1H), 2.87 (dd, *J* = 17.9, 6.3 Hz, 1H), 2.55 (dd, *J* = 17.9, 9.5 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 214.38, 140.18, 128.94, 128.54, 126.07, 79.57, 71.95, 44.94.



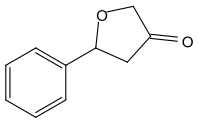
Peak results :

pankaj2-146ojh901.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

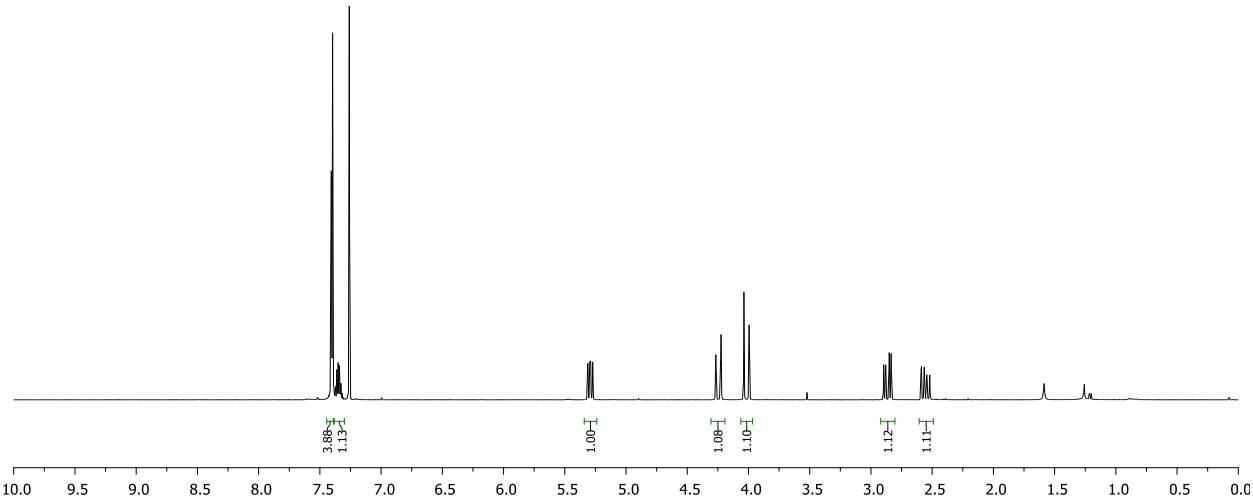
Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	20.01	33.4	1.13	25.3	45.822
2	21.77	29.6	1.32	29.9	54.178
Total		63.0		55.1	100.000

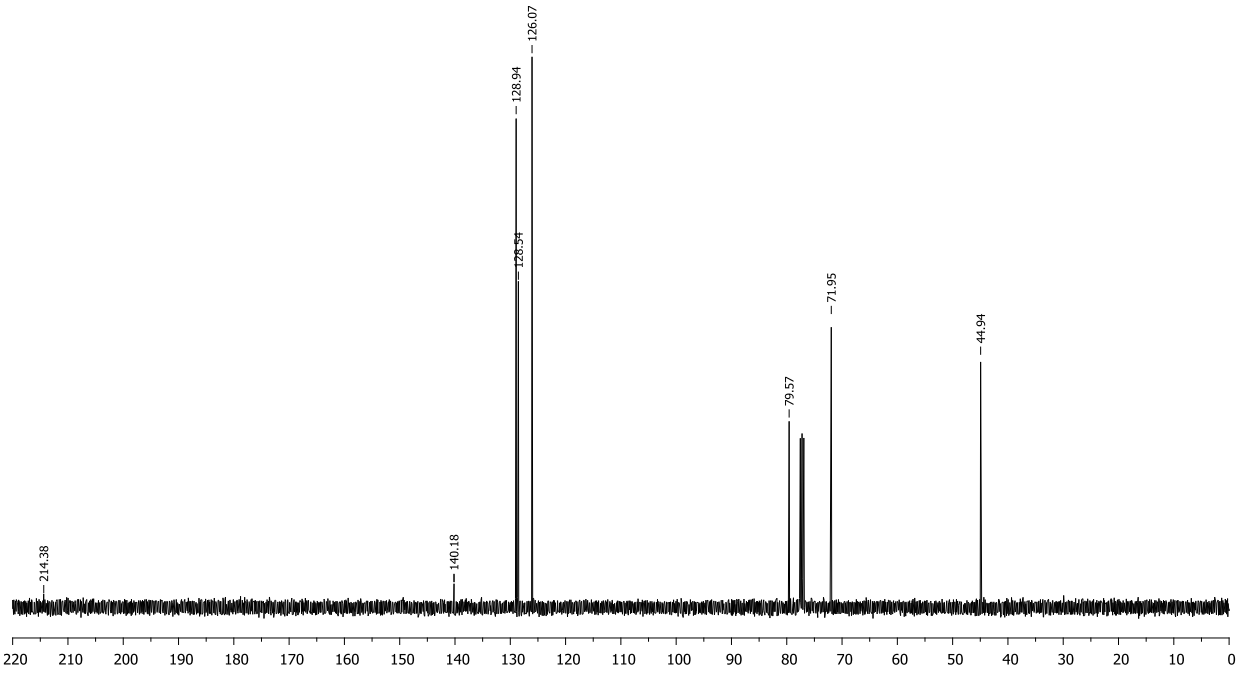
pankaj2-154oj901.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

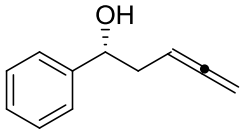
Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	20.27	1.9	0.85	1.1	2.639
2	21.41	41.1	1.31	39.4	97.361
Total		43.0		40.5	100.000



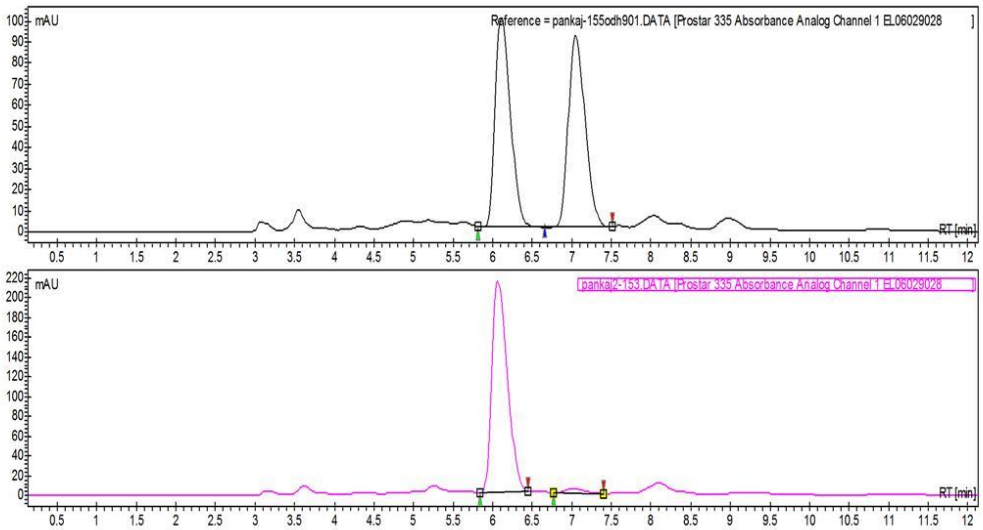
4


3.88
1.13
1.00
1.08
1.10
1.12
1.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


214.38
140.18
128.94
128.54
126.07
79.57
71.95
44.94
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



(*R*)-1-phenylpenta-3,4-dien-1-ol (5): Following the reported procedure[12] the title compound was obtained in 34 % yield with spectral properties reported in literature.[12,13] Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/iPrOH = 90/10, 1.0 mL/min), t_{major} = 6.07 min, t_{minor} = 7.01 min; ee = 95 %. $[\alpha]^{25}_{D}$ = +45.88 (c = 0.60, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 4H), 7.31 – 7.27 (m, 1H), 5.12 (p, *J* = 7.0 Hz, 1H), 4.77 (t, *J* = 6.5 Hz, 1H), 4.72 (dt, *J* = 6.7, 2.8 Hz, 2H), 2.52 – 2.40 (m, 2H), 2.17 (br s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 209.70, 143.83, 128.63, 127.82, 126.06, 86.32, 75.28, 73.84, 38.70.



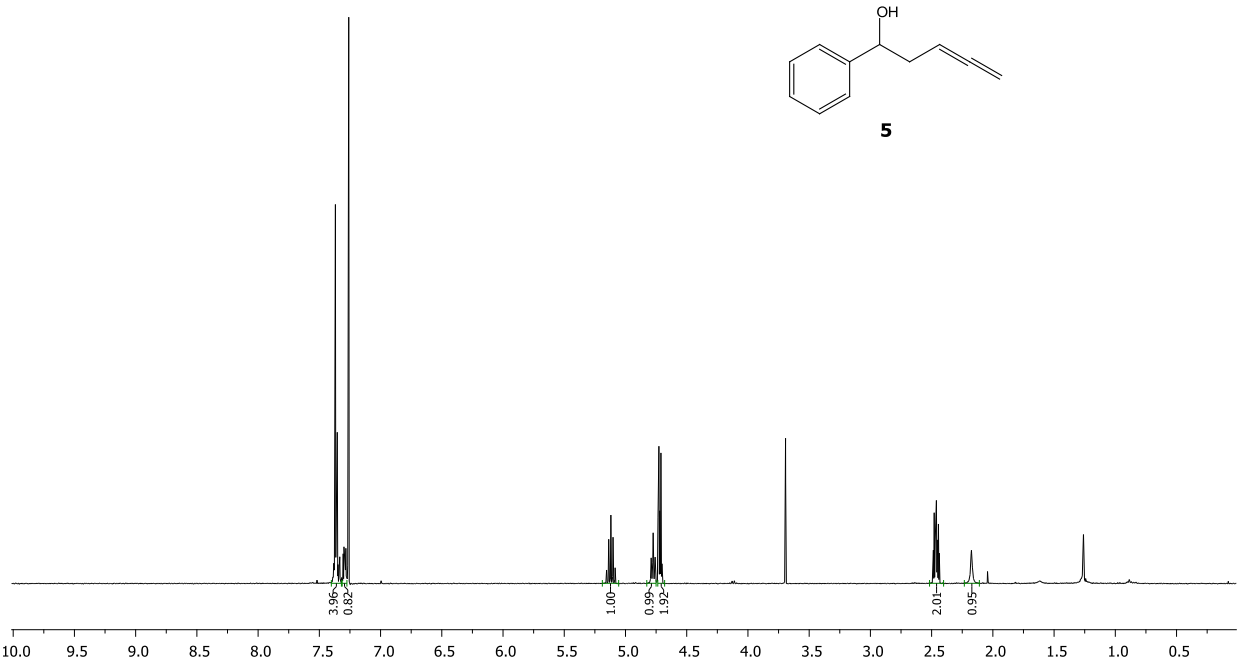
Peak results :

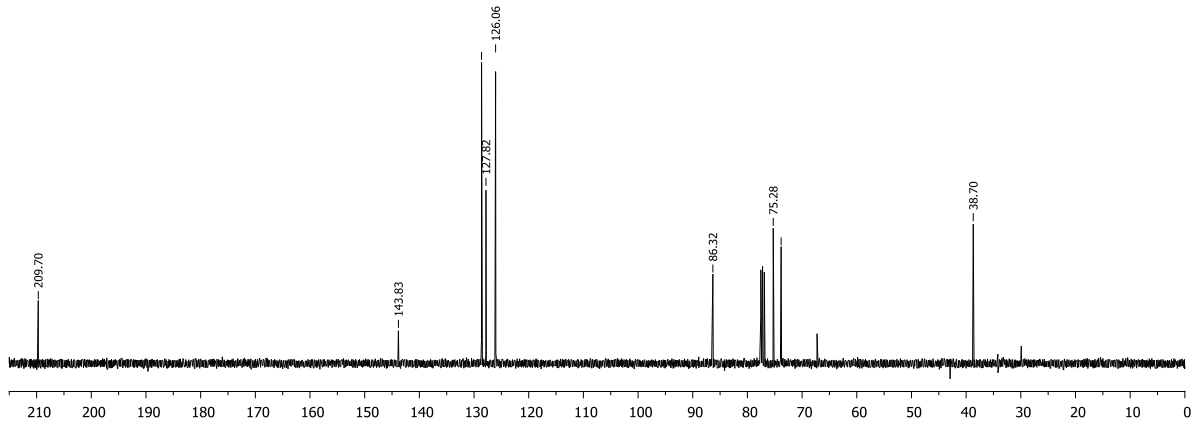
pankaj-155odh901.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	6.11	99.2	0.36	22.1	49.846
2	7.04	90.4	0.40	22.3	50.154
Total		189.7		44.4	100.000

pankaj2-153.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
2	6.07	213.7	0.37	48.7	97.559
1	7.01	4.8	0.40	1.2	2.441
Total		218.5		49.9	100.000


OH
5
3.96
0.82
1.00
0.99
1.92
2.01
0.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


209.70
143.83
126.06
127.82
86.32
75.28
38.70
210
200
190
180
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160
150
140
130
120
110
100
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70
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40
30
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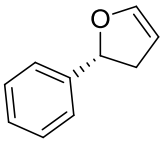
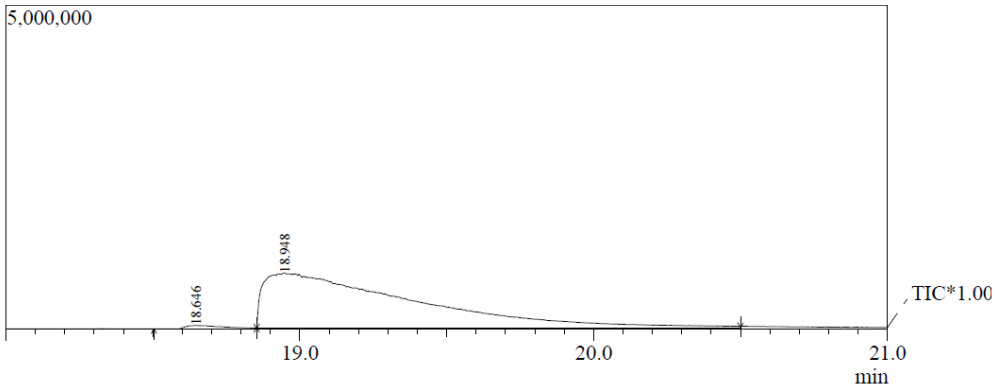
10
0



(*R*)-2-phenyl-2,3dihydrofuran (4): Following the literature procedure,[14] the title compound was obtained in 61 % yield with spectral properties reported in literature.[15] Enantiomeric excess was determined to be >94 % by chiral GC (80 °C for 2 min, increase 1 °C/min for 38 min, cyclodex-B column), t_{minor} = 18.65 min, t_{major} = 18.95 min; $[\alpha]^{25}_{D}$ = -28.10 (c = 0.23, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.24 (m, 5H), 6.49 – 6.43 (m, 1H), 5.53 (dd, *J* = 10.7, 8.4 Hz, 1H), 5.01 – 4.94 (m, 1H), 3.14 – 3.05 (m, 1H), 2.67 – 2.58 (m, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 145.54, 143.26, 128.73, 127.84, 125.81, 99.24, 82.57, 38.07.

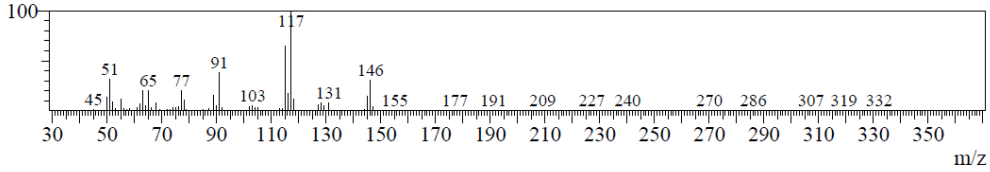


Peak Report TIC

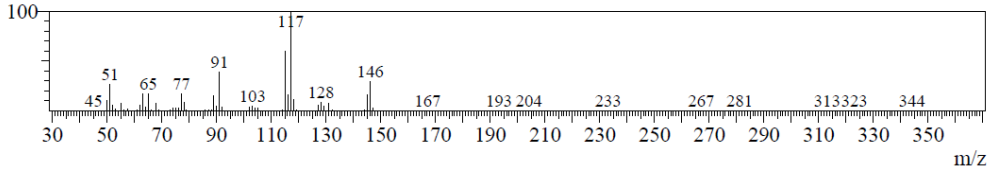
Peak#	R.Time	Area%	Name	Base m/z
1	18.646	1.57		117.15
2	18.948	98.43		117.10
		100.00		

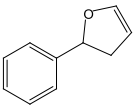
Spectrum

Peak#:1 R.Time:18.6(Scan#:4095)
MassPeaks:86

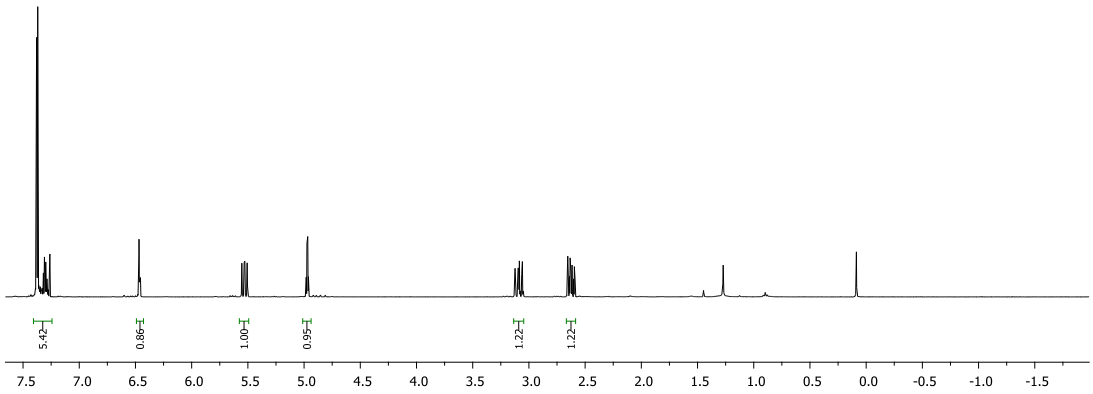


Peak#:2 R.Time:18.9(Scan#:4185)
MassPeaks:99





6


5.42
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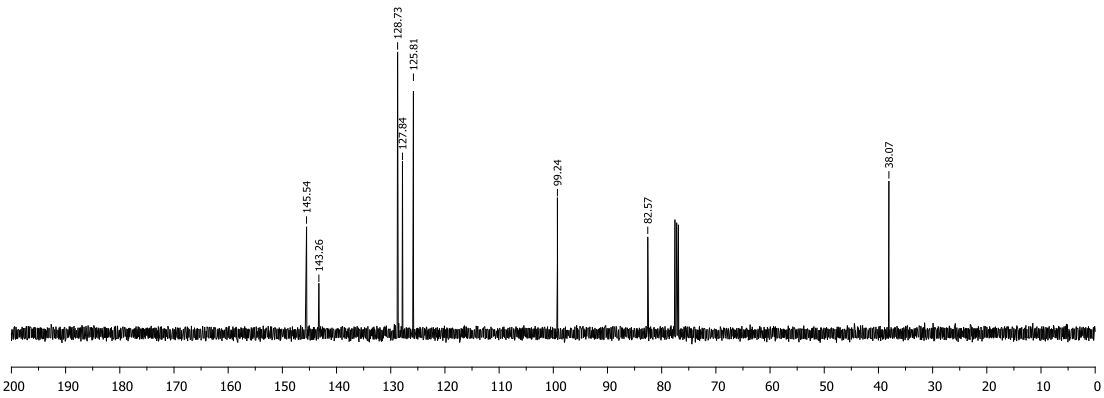
0.99
1.22
1.22
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5


145.54
143.26
128.73
127.84
125.81
99.24
82.57
38.07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Full reference 17:

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TSr1

B	0.30191459	0.92047127	0.00000000
C	1.89522159	0.31233727	0.43231500
C	2.20439059	0.78524427	1.56587000
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H	2.35492359	2.35323227	2.99862100
H	1.78930059	0.72553527	3.62759200
O	0.47330559	2.14798427	-0.71072600
C	-0.44184941	2.13853827	-1.82233700
O	-0.40132141	-0.00186773	-0.86570600
C	-0.52048141	0.60817827	-2.17939900
C	-1.79028341	2.70511827	-1.34373900
H	-2.22307841	2.08319427	-0.55459200
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H	0.16610659	4.06346527	-2.58408600
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H	-1.80275041	-0.90433273	-3.04713200
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C	-1.42520041	2.87403227	5.55636500
C	-1.90597441	0.52868227	5.19655300
C	-1.99588741	1.67621427	5.99142200
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H	-1.16324241	-0.31701773	3.34812800
H	-1.49693041	3.76846827	6.16917500
H	-2.34751641	-0.40435773	5.53562800
H	-2.50967241	1.63624827	6.94831000
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O	-1.24637741	-2.44184773	-0.30714400
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O	-0.17909841	-2.25910673	2.08228800
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C	1.69383659	-7.52204173	2.53986700
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C	-2.40890841	-5.22648073	1.06069900
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C	-2.14442941	-7.57028573	0.59549400
C	-4.29375241	-6.52078473	0.32249100
C	-3.48824741	-7.65545273	0.25140800
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C	3.06265259	-4.25555173	1.15757200
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C	3.50696659	-4.08437173	-0.17599800
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C	5.03864159	-2.31648173	0.55470800
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H	-6.26267641	-1.93773273	-1.36842400
C	3.14979459	-3.55467373	3.64474100
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C	4.29828259	-4.04991173	4.54601200
H	2.34951759	-4.29734473	3.69937100
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H	3.31024759	-1.43163073	4.17814800
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C	6.15201659	-1.31968773	0.25483000
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H	4.86175059	0.30387127	-0.44882200
H	6.55592359	0.45474427	-0.94804000
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H	7.76181259	-2.76937973	0.57225900
H	7.29650559	-2.57853473	-1.12458200
H	8.25836359	-1.32152073	-0.32837400
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H	4.59121259	-6.44214073	-1.16400700
H	3.72960359	-6.46602273	-2.71513300
H	4.91283059	-5.19363373	-2.37648800
H	1.46384659	-3.54341673	-1.99453200
H	2.99461359	-3.39998073	-2.88502700
H	1.90794959	-4.75865073	-3.20734800
C	-4.72164441	-4.06838873	-1.84226800
C	-3.96716641	-3.03674673	-2.70011300
C	-5.95136441	-4.61937273	-2.59009000
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C	-4.66277241	-4.09896573	3.32455400
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C	-3.90520241	-3.09425173	4.21323800
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H	-5.59430641	-5.14708673	4.99731100
H	-6.61897841	-3.88238973	4.29871200
H	-3.00601641	-2.72922473	3.70835500
H	-4.53133241	-2.23132173	4.47103000
H	-3.60052441	-3.57440273	5.15144900
C	-7.19166341	-0.53150473	0.80081600
C	-8.55022141	-0.74470073	0.10806600
C	-6.44951241	0.67953427	0.20244700
H	-7.39376341	-0.30350673	1.85648700
H	-9.09396241	-1.58577573	0.55217000
H	-9.17491741	0.15216127	0.19868300
H	-8.42631441	-0.95475573	-0.96100500
H	-2.51702541	2.78847327	-2.15823800
H	-6.21982041	0.51792227	-0.85758400
H	-7.05882841	1.58859827	0.27736000

Sum of electronic and zero-point Energies= -3146.510009
Sum of electronic and thermal Energies= -3146.441101
Sum of electronic and thermal Enthalpies= -3146.440156
Sum of electronic and thermal Free Energies= -3146.617796
Imaginary frequency: -365.06 cm^{-1}

TSs1

B	-1.11729300	3.26467100	-1.01100600
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C	-3.37098900	3.09539800	0.02050700
C	-3.39167600	3.47921200	1.32939200
H	-3.17200100	2.34024300	-1.98042500
H	-3.85606500	4.42338700	1.61108600
H	-3.44543300	2.70009100	2.08856900
O	-0.96357500	4.52917700	-1.65233400
C	0.25270900	4.47670100	-2.42585200
O	-0.28312000	2.30873600	-1.70893900
C	0.31722300	2.96241900	-2.85844600
C	1.42489400	4.88378900	-1.51581700
H	1.54894400	4.18095000	-0.68707500
H	1.21350000	5.87217400	-1.09473200
H	2.36924100	4.94302500	-2.06829700
C	0.12467400	5.46733300	-3.58345800
H	0.06941400	6.48647300	-3.18669200
H	-0.78090700	5.28549000	-4.16684100
H	0.99195300	5.41185800	-4.25208700
C	1.72492200	2.40010600	-3.05234200
H	2.31843100	2.48039000	-2.13922800
H	1.67089300	1.34129100	-3.32765700
H	2.24663900	2.92942900	-3.85821300
C	-0.54924500	2.65235800	-4.08762300
H	-1.55369000	3.07307300	-3.98189700
H	-0.63989200	1.56700200	-4.20044500
H	-0.10376200	3.05222100	-5.00487100
O	-0.78881200	3.21835200	0.43827000
C	-1.41334700	3.99652700	1.28412600
H	-1.62567900	5.01108300	0.93274200

C	-1.05623300	3.85272600	2.71436900
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C	-1.03296200	4.77604600	4.95523800
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C	-0.37882000	3.62991200	5.41509400
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H	-0.13370800	1.91224600	2.47672700
H	-1.27324200	5.58211900	5.64305400
H	0.45750500	1.71410400	4.87795800
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H	-0.22440500	0.75601900	-1.35521700
O	-0.25802200	-0.24980800	-1.23156200
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C	3.90765400	-3.66569800	1.57184900
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C	4.18344300	-1.44630600	0.41239500
C	4.46706800	-0.42778200	1.35068100
C	4.73038800	-1.37593200	-0.89229200
C	5.29439300	0.63349800	0.96197100
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C	8.15781000	1.44888600	-1.07060400
H	6.81648500	2.54428600	0.19133800
H	5.11586500	3.10962100	-1.54207000
H	6.74058700	3.62565500	-2.03980800
H	6.01342300	2.17428700	-2.74783900
H	8.61681600	0.87551500	-0.25777300
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H	8.79761300	2.31418400	-1.28240700
C	3.91388600	-0.43891800	2.77602700
C	3.13574800	0.84875900	3.10687100

C	5.03227000	-0.68755000	3.80722400
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H	2.32088600	0.99736000	2.39406000
H	2.70752900	0.77628100	4.11493700
H	3.78267200	1.73398300	3.09084400
H	5.55337700	-1.63329900	3.61893000
H	5.78081500	0.11346700	3.78077000
H	4.61871600	-0.72496100	4.82250400
C	4.49199600	-2.46010800	-1.94354600
C	5.80256200	-3.18389000	-2.31181700
C	3.79366800	-1.90350500	-3.19879000
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H	5.60582200	-3.99384300	-3.02478900
H	6.52430200	-2.50065900	-2.77493400
H	2.84190700	-1.43166100	-2.93651300
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H	-6.58814800	1.57404100	-2.05134800
H	-7.69148900	2.34754800	-0.90849500
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C	-2.89751000	-0.78420200	-3.56816900
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H	-2.38849100	-1.06876700	-4.49722300
H	-3.74487100	-0.14350300	-3.84254300
H	-4.59133300	-3.81920800	-3.16775000
H	-5.22425800	-2.34369300	-3.90927700
H	-3.82284400	-3.15921200	-4.62311300
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C	-4.72110100	-3.22602500	3.01671400
C	-3.14517900	-1.24586400	3.26956600
H	-2.77243100	-3.03573900	2.17049100
H	-5.03173200	-4.05713700	2.37353800
H	-4.35117100	-3.64631300	3.95982300
H	-5.61303200	-2.63042100	3.24500500
H	-2.33073000	-0.67997800	2.80729400
H	-3.95642200	-0.54821200	3.51129900
H	-2.77648200	-1.66230300	4.21487400

Sum of electronic and zero-point Energies= -3146.508455
Sum of electronic and thermal Energies= -3146.439604
Sum of electronic and thermal Enthalpies= -3146.438660
Sum of electronic and thermal Free Energies= -3146.615719
Imaginary frequency: -356.96 cm^{-1}

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