Supplementary Materials for

Highly Enantioselective Phenylacetylene Additions to Ketones Catalyzed by (S)-BINOL-Ti Complex

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Analysis of the optically Active Tertiary Propargylic Alcohols.

2-(4-Chloro-phenyl)-4-phenyl-but-3-yn-2-ol: 73% yield isolated after 48 h reaction in Step 3. 89% ee determined by HPLC analysis (Chiralcel OD column, 5% IPA in hexane, 241.5nm). Retention time: $t_{\text{major}}=8.78$ and $t_{\text{minor}}=10.54$ min. ^1H NMR (200 MHz, CDCl_3) δ 7.68-7.31 (m, 2H), 7.49-7.44 (m, 2H), 7.35-7.31 (m, 5H), 2.60 (brs, 1H), 1.84 (s, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 144.2, 133.5, 131.7, 128.6, 128.4, 128.3, 126.5, 122.3, 91.9, 85.2, 69.9, 33.

4-Phenyl-2-m-tolyl-but-3-yn-2-ol: 66% yield isolated after 48 h reaction in Step 3. 90% ee determined by HPLC analysis (Chiralcel OD column, 5% IPA in hexane, 241.5nm). Retention time: $t_{\text{major}}=9.19$ and $t_{\text{minor}}=10.91$ min. ^1H NMR (200 MHz, CDCl_3) δ 7.54-7.45 (m, 4H), 7.32-7.23 (m, 4H), 7.12 (d, 1H), 2.38 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 145.6, 138.0, 131.7, 128.4, 128.2, 125.6, 122.6, 122.1, 119.8, 92.7, 84.7, 70.3, 33.2, 21.5.

2,4-Diphenyl-but-3-yn-2-ol: 67% yield isolated after 48 h reaction in Step 3. 85% ee determined by HPLC analysis (Chiralcel OD column, 5% IPA in hexane, 241.5nm). Retention time: $t_{\text{major}}=9.15$ and $t_{\text{minor}}=11.02$ min. ^1H NMR (200 MHz, CDCl_3) δ 7.74 (d, 2H), 7.47-7.26 (m, 8H), 2.5 (s, 1H), 1.87 (s, 3H).

2-(3-Bromo-phenyl)-4-phenyl-but-3-yn-2-ol: 68% yield isolated after 48 h reaction in Step 3. 86% ee determined by HPLC analysis (Chiralcel OD column, 5% IPA in hexane, 241.5nm). Retention time: $t_{\text{major}}=9.59$ and $t_{\text{minor}}=12.08$ min. ^1H NMR (200 MHz, CDCl_3) δ 7.88 (m, 3H), 7.66-7.20 (m, 8H), 2.55 (brs, 1H), 1.85 (s, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 147.9, 131.7, 130.8, 129.9, 128.6, 128.3, 123.7, 122.4, 122.2, 92.3, 85.0, 69.9, 33.4.

2-(3-Methoxy-phenyl)-4-phenyl-but-3-yn-2-ol: 81% yield isolated after 48 h reaction in Step 3. 92% ee determined by HPLC analysis (Chiralcel OD column, 5% IPA in hexane, 241.5nm). Retention time: $t_{\text{major}}=12.67$ and $t_{\text{minor}}=15.69$ min.

3-Methyl-1,5-diphenyl-pent-1-en-4-yn-3-ol: 88% yield isolated after 18 h reaction in Step 3. 73% ee determined by HPLC analysis (Chiralcel OD column, 5% IPA in hexane, 254nm). Retention time: $t_{\text{major}}=14.42$ and $t_{\text{minor}}=28.25$ min.

2-Naphthalen-2-yl-4-phenyl-but-3-yn-2-ol: 72% yield isolated after 48 h reaction in Step 3. 85% ee determined by HPLC analysis (Chiralcel OD column, 5% IPA in hexane, 225 nm). Retention time: $t_{\text{major}}=13.59$ and $t_{\text{minor}}=18.30$ min. ^1H NMR (200 MHz, CDCl_3) δ 8.18 (s, 1H), 7.87-7.77 (m, 4H), 7.52-7.45 (m, 4H), 7.34-7.30 (m, 3H), 2.68 (brs, 1H), 1.95 (s, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 142.9, 133.0, 132.9, 131.8, 128.5, 128.3, 128.2, 126.2, 126.1, 122.6, 92.5, 85.1, 70.5, 33.1.

2-(2-Fluoro-phenyl)-4-phenyl-but-3-yn-2-ol: 80% yield isolated after 48 h reaction in Step 3. 66% ee determined by HPLC analysis (Chiralcel OD column, 5% IPA in hexane, 241.5 nm). Retention time: $t_{\text{major}}=9.80$ and $t_{\text{minor}}=12.18$ min. ^1H NMR (200 MHz, CDCl_3) δ 7.78-7.70 (m, 1H), 7.48-7.44 (m, 2H), 7.32-7.25 (m, 4H), 7.19-7.04 (m, 2H), 2.79 (brs, 1H), 1.98 (s, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 131.7, 129.7, 129.5, 128.5, 128.2, 124.0, 123.9, 116.6, 116.1, 92.6, 84.1, 68.1, 30.6.

4-Phenyl-2-p-tolyl-but-3-yn-2-ol: 64% yield isolated after 48 h reaction in Step 3. 87% ee determined by HPLC analysis (Chiralcel OD column, 5% IPA in hexane, 241.5 nm). Retention time: $t_{\text{major}}=8.86$ and $t_{\text{minor}}=11.71$ min. ^1H NMR (200 MHz, CDCl_3) δ 7.60 (d, 2H), 7.50-7.45 (m, 2H), 7.33-7.29 (m, 3H), 7.18 (d, 2H), 2.50 (s, 1H), 2.34 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 142.8, 137.4, 131.7, 129.0, 128.4, 128.3, 124.9, 119.2, 92.1, 85.4, 70.2, 33.2, 21.0.

File : C:\HPCHEM\1\DATA\61604.D
Operator : HP5988A MS, Lanzhou University
Acquired : 16 Jun 2004 8:36 using AcqMethod DIP550
Instrument : HP 5988
Sample Name: Zhou Yi-feng, 1#
Misc Info : State Key Lab of Applied Organic Chemistry
Vial Number: 1

P-d

Abundance

Average of 0.682 to 0.704 min.: 61604.D

Abundance

Average of 0.682 to 0.704 min.: 61604.D

Zhou Yi-feng, 1#

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
35.00	371	46.00	15	57.10	257	68.05	72
36.10	23	47.00	632	58.10	62	69.05	251
37.00	213	48.00	10	59.10	80	70.05	102
38.10	174	49.00	572	60.05	60	71.05	143
39.15	826	50.10	1357	61.05	342	72.05	63
40.10	88	51.10	1829	62.05	514	73.05	481
41.10	363	52.10	304	63.05	1102	74.05	1223
42.10	154	53.10	219	64.05	164	75.05	3457
43.10	5327	54.00	40	65.05	249	76.05	1308
44.10	210	55.10	332	66.05	50	77.05	1953
45.10	529	56.10	77	67.05	130	78.05	230

Average of 0.682 to 0.704 min.: 61604.D

Zhou Yi-feng, 1#

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
79.05	100	89.95	111	102.00	1416	112.95	1256
80.10	45	91.00	351	103.00	458	113.95	240
81.10	181	92.00	67	104.00	149	114.95	935
81.90	188	93.50	95	104.95	283	115.95	172
83.00	128	94.50	320	105.95	83	117.05	96
83.90	2920	96.00	68	106.95	99	118.00	49
85.00	326	97.00	145	107.95	54	118.95	185
85.90	2195	98.00	345	108.95	114	119.55	43
87.00	575	99.00	360	110.05	217	120.50	490
88.00	1202	100.00	380	110.95	3647	121.55	75
89.00	644	101.00	2387	111.95	636	121.90	150

Average of 0.682 to 0.704 min.: 61604.D

Zhou Yi-feng, 1#

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
122.95	148	134.90	72	146.95	27	159.05	19
124.05	25	135.90	80	149.00	286	159.95	47
124.95	288	136.95	212	150.00	424	160.95	87
125.90	447	138.90	5452	151.00	543	161.95	87
127.00	693	139.95	446	152.00	391	162.95	280
128.90	7876	140.90	1728	153.00	78	163.95	79
129.95	764	141.90	137	154.00	215	164.95	222
130.95	107	143.00	137	155.00	54	166.05	52
132.00	28	144.00	101	156.00	62	166.95	28
133.00	29	145.00	562	156.95	26	167.95	11
133.90	42	146.00	70	157.95	9	168.95	17

Average of 0.682 to 0.704 min.: 61604.D

Zhou Yi-feng, 1#

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
171.20	8	183.90	10	196.95	25	208.05	17
172.95	42	184.90	28	198.00	19	210.00	19
173.95	114	185.90	56	198.95	71	211.95	204
175.05	172	186.90	243	200.00	236	212.95	5181
175.95	1238	188.05	155	201.00	244	213.95	984
177.00	777	188.95	381	202.00	1041	214.95	1710
178.00	3733	189.90	109	203.00	680	215.95	270
178.95	802	191.00	204	204.00	183	216.95	32
179.95	109	192.00	121	205.00	97	218.05	35
180.90	62	193.00	67	206.00	99	218.95	87
183.05	23	193.95	28	207.00	49	220.10	57

Average of 0.682 to 0.704 min.: 61604.D

Zhou Yi-feng, 1#

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
220.95	1873	236.05	24	256.00	3226		
221.95	335	237.10	21	257.00	2059		
222.95	80	237.90	83	258.00	1039		
224.00	28	239.05	481	259.00	134		
224.95	55	240.90	10000	260.05	20		
225.95	10	242.05	1596				
226.95	23	242.90	3108				
227.95	30	243.95	511				

229.00	23	244.95	61
231.00	65	248.90	9
231.80	13	255.00	5063