

Improved Ethynylation of Nitrocarbonyl Derivatives by Cerium Trichloride Assisted Addition of Ethynyl Magnesium Bromide

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Abstract. The addition of the Grignard reagent ethynyl magnesium bromide to nitroarylcarbonyls in the presence of cerium chloride was investigated. Thus, 2- and 4-nitrobenzaldehyde, 2- and 4-nitroacetophenone, 2-nitrocinnamaldehyde and 1-aryl-3-aryl'-2-en-propanones (nitrochalcones **4a–g**), gave α -ethynyl-2- and 4-nitrophenylmethanol **2a–b**,

α -ethynyl-2- and 4-nitrophenyl ethanol **2c–d**, *trans*-1-(2-nitrophenyl)-1-penten-4-yn-3-ol (**5**) and *trans*-1-aryl-3-aryl'-1-penten-4-yn-3-ol **6a–g**, respectively. It was found that in the absence of the lanthanide, the ethynylation reaction was a low yielding process.

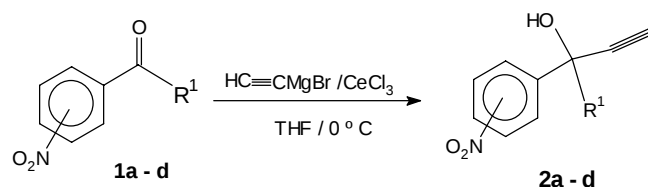
Addition of Grignard reagents to carbonyls or carbonyl equivalents is a fundamental reaction, which has been profusely investigated, and it remains as a very important synthetic tool [1]. The Grignard reaction has been significantly improved through the intermediary of organocerium reagents, which avoid Grignard abnormal reactions such as enolization, reduction, conjugate addition amongst others [2]. The chemistry of organocerium and organolanthanides reagents has been well exploited in organic synthesis as shown by a recent review [2b, 3]. The addition of Grignard reagents to carbonyls other than ketone carbonyls such as that of amides, esters, nitriles catalysed with cerium trichloride has been investigated as well [2a]. However, no reports of the Grignard reagent addition to nitrocarbonyls assisted with cerium trichloride were found. It has been acknowledged that Grignard addition to carbonyls is a difficult process if a nitro group is present [4]. Moreover it has been shown that reaction of the Grig-

nard reagent with the nitro group of nitrocarbonyls occurs more readily than with the ketone carbonyl [5], whilst the nitro and aldehyde carbonyl show a comparable reactivity towards the Grignard reagent [6]. However isolated examples of successful addition of Grignard reagents to nitro containing ketones have been reported [7, 8]. Organometallic compounds of titanium and zirconium have shown to be useful nucleophilic reagents which do not react with the nitro, iodo or cyano functional groups present in carbonyl derivatives [9]. On the other hand, addition of aromatic Grignard reagents to nitro arenes is well documented and, several studies involving the Grignard addition (benzyl and allyl Grignard reagents) to alkyl nitrocompounds and alkyl Grignard reagents to mononitroarenes have been reported [10]. The cerium chloride catalysed addition to nitroarenes has been investigated as well [11]. Then, it was interesting to study whether the presence of cerium trichloride had any effect on the Grignard addition of

ethynyl magnesium bromide to nitroarylcarbonyls thereby improving the synthesis of tertiary α -acetylenecarbinols, which are useful substrates for biological studies [12]. The results of this investigation are here presented.

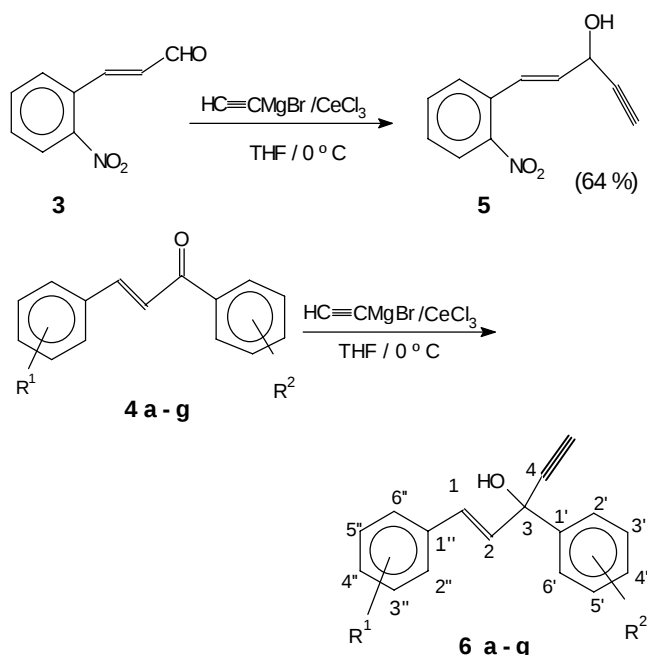
Ethynylcerium chloride was prepared *in situ* from ethynylmagnesium bromide (0.5M THF solution) and cerium trichloride following the Imamoto protocol [2a]. Then it was treated with *p*-nitrobenzaldehyde **1a** in dry THF. The reaction proceeded smoothly at 0 °C to give the desired ethynyl carbinol **2a** in nearly quantitative yield. Compound **2a** had been previously prepared *via* *p*-nitrobenzaldehyde ethynylation with ethynyl lithium in 86% yield [12] and with ethynylmagnesium bromide (prepared from acetylene and methylmagnesium bromide.) in an unspecified yield [13]. Similarly, the reaction of ethynyl magnesium bromide/CeCl₃ with *o*-nitrobenzaldehyde gave the addition product **2b** in good yield, whereas the yield decreased sharply (more than 50% of starting nitroaldehyde being recovered), if the reaction was performed in the absence of the lanthanide. The ethynylated carbinol **2c** has been prepared from *p*-nitroacetophenone **1c** and ethynyl magnesium bromide [14], however several attempts to reproduce the experimental reported yield, were unsuccessful. Variations in the number of molar equivalents were made, and both types of additions were tried, *i.e.* addition of the nitrocarbonyl to the Grignard reagent/CeCl₃ suspension, and addition of ethynyl magnesium bromide to a nitrocarbonyl/CeCl₃ suspension, with the latter procedure giving slightly better results, and compound **2c** was isolated in only 10% yield. The reaction most probably is a reversible process, although no addition to the nitro group was observed. In sharp contrast, the *ortho* isomer **1d** gave an excellent yield of the ethynylated product **2d**. The latter result may be explained by consideration of the nitro group itself, which might have forced the carbonyl out of the conjugation plane, thus favouring the addition reaction.

Then it seemed interesting to investigate whether a conjugated nitro group might affect the ethynylation



1	-NO ₂	-R ¹	2	Yield (%)
a	4-	H	a	98
b	2-	H	b	68
c	4-	Me	c	10
d	2-	Me	d	86

Scheme 1 Ethynylated Nitrocarbinols from Nitrophenyl Carbonyls and Ethynylcerium Chloride



4	R ¹	R ²	6	(Yield %)
a	4'-NO ₂	H	a	68.0
b	4'-CH ₃	4''-NO ₂	b	91.3
c	2'-NO ₂	4''-CH ₃	c	60.8
d	2'-NO ₂	H	d	33.0
e	2'-NO ₂	4''-NO ₂	e	57.5
f	2'-NO ₂	2''-NO ₂	f	50.0
g	4'-CH ₃	2''-NO ₂	g	30.4

Scheme 2 Ethynylated Nitrocarbinols from Nitro-substituted Chalcones and Ethynylcerium Chloride

process. Thus, *trans*-2-nitrocinnamaldehyde (**3**) and the nitro-substituted chalcones **4** (prepared by using standard procedures) were treated with the mixture ethynyl magnesium bromide/CeCl₃. In this and in previous cases an excess of the ethynyl cerium reagent was employed. In the first case, the reaction proceeded at 0 °C, and the ethynylated product **5** was isolated in 64% yield as the mixture of enantiomers. Similarly, nitro-chalcones **4** were ethynylated to the corresponding ethynyl carbinols **6**. In general, the reaction went to completion, however purification of the crude product through a chromatographic column caused a reversible process to varying degree for each compound, leading to the recovery of starting material (as has been previously observed [15]). Thus, the yields reflect a certain degree of stability, except for nitrochalcone **4g**, which showed a poor conversion to the corresponding ethynylated product. NMR spectroscopic measurements clearly showed that in all cases the 1,2-addition product had been isolated as anticipated in Grignard reagent conjugated additions involving cerium chloride catalysis [16], the 1,4-addition compound was not detected. From Scheme 2, it is interesting to note that even dinitrosubstituted chalcones **4e** and **4f** underwent the ethynylation process,

Table 1 ^{13}C NMR spectroscopic data of compounds **6a–g**

	6a	6b ^{a)}	6c ^{b)}	6d	6e	6f	6g ^{c)}
C-1	127.40	128.39	129.23	128.55	128.04	129.26	129.35
C-2	125.60	125.80	125.62	125.69	124.37	127.39	126.93
C-3	72.49	70.60	72.50	72.49	72.49	71.08	71.23
C-4	83.97	83.91	84.20	84.06	84.92	82.21	82.75
C-5	76.31	75.32	76.12	76.28	78.00	76.49	75.91
Ar'							
C-1'	142.56	136.95	132.18	132.12	132.07	131.96	132.84
C-2'	128.57	130.60	147.95	147.92	149.45	147.78	131.27
C-3'	123.87	128.28	124.61	124.61	125.31	124.78	129.98
C-4'	147.04	132.05	128.43	125.07	129.95	133.44	138.33
C-5'	123.87	128.28	137.33	137.20	138.30	133.44	128.98
C-6'	128.57	130.60	133.14	129.04	134.25	129.49	131.27
Ar''							
C-1''	141.04	146.14	139.30	142.13	148.52	135.16	135.79
C-2''	126.94	125.98	124.61	128.26	129.72	149.32	149.47
C-3''	136.73	122.41	129.01	133.19	125.36	124.70	124.75
C-4''	128.37	150.70	138.11	128.19	151.81	129.00	128.66
C-5''	136.73	122.41	129.01	133.19	125.36	135.02	132.12
C-6''	126.94	125.98	124.61	128.26	129.72	132.35	129.22

a) $4'\text{-CH}_3$ δ 20.24 b) $4''\text{-CH}_3$ δ 21.08 c) 4-CH_3 δ 21.23

although the nitro group at the 2-aromatic ring position caused a lower yield.

^1H NMR and ^{13}C NMR spectroscopic data of ethynylated products are given in the experimental section. An assignment supported by chemical shifts tables [17] for all carbons in products **6a–g** is given in Table 1.

We concluded that addition of the Grignard reagent, ethynylmagnesium bromide to nitro containing carbonyls (ketone or aldehyde) is a feasible process. In this investigation it was clear that cerium chloride does participate in the ethynylation process, since in its absence, the reaction was not selective or even failed.

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Experimental

Melting points were determined on a electrothermal melting point apparatus and are uncorrected. IR spectra were recorded on a double beam Perkin-Elmer Model 1600-FTIR. ^1H NMR spectra at 300 MHz and ^{13}C NMR spectra at 75.46 were obtained with a Bruker DPX-300 Fourier transform spectrometer. Chemical shifts are reported as parts per million, relative to Me_4Si as internal standard. Mass spectra were recorded on a double beam Jeol JMS AX505HA spectrometer, using the electron impact technique. All experiments were carried out under an inert atmosphere. The purification of crude reaction mixtures was carried out by column chromatography using silica gel (Merck 70–230 Mesh) as solid support.

Ethynylation Reaction (General Procedure)

The nitroarylaldehydes, nitroarylketones, *trans*-nitrocinnam-

aldehyde and ethynyl magnesium bromide (0.5M solution) were purchased from Aldrich Chemical Co.

Cerium trichloride was dried as described in the literature [2a]. The reaction flask containing the lanthanide was placed in an iced cold water bath (0 °C), and then dry THF was added. The suspension was agitated for two hours, and then ethynylmagnesium bromide added, stirring was continued for two hours at the same temperature. Then the nitroarylcarbonyl dissolved in THF was gradually added and stirring continued until ambient temperature was reached. Progress of the reaction was monitored by thin layer chromatography (hexane/ethyl acetate 8:2). When reaction ended, a 5% ammonium chloride aqueous solution was added, stirring continued for 30 min., and the mixture filtered through Celite. THF was removed, ethyl acetate added and the organic phase separated, washed and dried (Na_2SO_4). Solvent was removed under reduced pressure and the residue purified through a chromatographic column. Alternatively the nitroaryl carbonyl was first added to the CeCl_3/THF suspension kept at 0 °C followed by addition of the Grignard reagent.

α -Ethynyl-4-nitrophenylmethanol (**2a**)

Cerium chloride (1.22 g, 4.95 mmol), ethynylmagnesium bromide (0.64 g, 4.96 mmol), and 4-nitrobenzaldehyde (0.15 g, 0.99 mmol) in THF (5 mL) were combined following the general procedure, to give the title compound as a light yellow oil [12] (0.174 g, 98%).

α -Ethynyl-2-nitrophenylmethanol (**2b**)

Cerium chloride (1.22 g, 4.95 mmol), ethynylmagnesium bromide (0.64 g, 4.96 mmol), and 2-nitrobenzaldehyde (0.15 g, 0.99 mmol) in THF (5 mL) were combined following the general procedure, to give the title compound as a coloured oil (0.12 g, 68%). – IR (film): ν/cm^{-1} = 3492, 2116, 1526, 1348. – ^1H NMR (CDCl_3): δ/ppm = 2.64 (d, 1H; H-3; J = 4.8 Hz); 3.43 (1H; OH); 6.03 (d, 1H; CH, J = 4.8 Hz); 7.52 (t, 1H; H-4', J_o = 8.0 Hz); 7.68 (td, 1H; H-5', J_o = 8.0 Hz); 7.97

(d, 2H; H-3', H-6'; $J_0 = 8$ Hz). – ^{13}C NMR (CDCl_3): $\delta/\text{ppm} = 60.84$ (C-3); 75.04 (C-1); 81.43 (C-2); 125.00 (C-3'); 129.19 (C-6'); 129.39 (C-4); 133.87 (C-5); 134.83 (C-1); 147.72 (C-2). – MS (m/z) 177, 160 (M-17), 115 (100%), 77, 51.

$\text{C}_9\text{H}_7\text{NO}_3$ Calcd.: C 61.01 H 3.95
(177.2) Found: C 60.59 H 4.14.

α -Ethynyl-4-nitrophenylethanol (2c)

Similarly, CeCl_3 (1.20 g, 4.87 mmol), ethynylmagnesium bromide, (0.63 g, 4.87 mmol), and 4-nitroacetophenone (0.15 g, 0.91 mmol) were combined following the general procedure to give the title compound as an oil [13] (0.18 g, 10%).

α -Ethynyl-2-nitrophenylethanol (2d)

Similarly, CeCl_3 (1.19 g, 4.83 mmol), ethynylmagnesium bromide, (0.63 g, 4.83 mmol), and 2-nitroacetophenone (0.10 g, 0.60 mmol) were combined following the general procedure to give the title compound as an oil (0.10 g, 86%). – IR (film): $\nu/\text{cm}^{-1} = 3512$, 2116, 1532, 1368. – ^1H NMR (CDCl_3): $\delta/\text{ppm} = 1.98$ (s, 3H; CH_3); 2.62 (s, 1H; CH); 3.84 (s, 1H; OH); 7.44 (t, 1H; H-4' $J_0 = 8.0$ Hz); 7.53 (t, 2H; H-5' $J_0 = 9.0$ Hz); 7.59 (d, 1H; H-6' $J_0 = 8.0$ Hz); 7.81 (d, 1H; H-3' $J_0 = 8$ Hz). – ^{13}C NMR (CDCl_3): $\delta/\text{ppm} = 30.98$ (CH_3); 67.93 (C-1); 73.16 (C-3); 84.92 (C-2); 124.46 (C-3); 127.46 (C-4); 128.91 (C-6); 131.98 (C-5); 136.85 (C-1); 149.36 (C-2). – MS (m/z) 191, 174 (M-17), 176 (100%), 104, 77.

$\text{C}_{10}\text{H}_9\text{NO}_3$ Calcd.: C 62.82 H 4.71
(191.3) Found: C 62.68 H 4.82.

trans-1-(2-Nitrophenyl)-1-penten-4-yn-3-ol (5)

Similarly, CeCl_3 (1.04 g, 4.23 mmol), ethynylmagnesium bromide, (0.55 g, 4.25 mmol), and *trans*-2-nitrocinnamaldehyde (0.15 g, 0.60 mmol) were combined following the general procedure, to give the title compound as an oil (0.11 g, 64%). – IR (film): $\nu/\text{cm}^{-1} = 3400$, 2118, 1606, 1522. – ^1H NMR (CDCl_3): $\delta/\text{ppm} = 2.67$ (d, 1H; H-5); 3.15 (s, 1H; OH); 5.13 (m, 1H; H-3); 6.28 (dd, 1H; H-2, $J_{\text{trans}} = 15.7$ Hz, $J_{\text{allyl}} = 5.6$ Hz); 7.27 (dd, 1H; H-1, $J_{\text{trans}} = 15.7$ Hz, $J = 5.6$ Hz); 7.43 (t, 1H; H-4', $J_0 = 8.0$ Hz); 7.58 (q, 2H; H-5', H-6', $J_0 = 8$ Hz); 7.92 (d, 1H; H-2', $J_0 = 9$ Hz). – ^{13}C NMR (CDCl_3): $\delta/\text{ppm} = 62.25$ (C-3); 75.10 (C-5); 82.17 (C-4); 124.60 (C-2); 127.42 (C-3'); 128.65 (C-1); 128.98 (C-4'); 131.87 (C-1'); 133.30 (C-5'); 132.76 (C-6'); 147.82 (C-2'). – MS (m/z) 203, 186 (M-17), 148 (100%), 77, 51.

$\text{C}_{11}\text{H}_9\text{NO}_3$ Calcd.: C 65.02 H 4.43
(203.4) Found: C 65.12 H 4.61.

trans-1-(4-Nitrophenyl-3-phenyl-1-penten-4-yn-3-ol (6a)

Similarly, CeCl_3 (1.16 g, 4.70 mmol), ethynylmagnesium bromide (0.61 g, 4.70 mmol), and 3-(4-nitrophenyl)-1-phenyl-2-en-propanone (0.20 g, 0.79 mmol) were combined following the general procedure, to give the title compound as an oil (0.15 g, 68%). – IR (film): $\nu/\text{cm}^{-1} = 3424$, 2114, 1596. – ^1H NMR (CDCl_3): $\delta/\text{ppm} = 2.91$ (s, 1H; H-5); 3.06 (s, 1H; OH); 6.50 (d, 1H; H-2, $J = 17.6$ Hz); 7.00 (d, 1H; H-1, $J = 17.6$ Hz); 7.30–7.45 (m, 3H; H-3", H-4", H-5"); 7.50 (d, 2H; H-2', H-6', $\text{BB}' J = 8.8$ Hz); 7.68 (d, 2H; H-2", H-6" $J = 7.0$ Hz) 8.15 (d, 2H; H-3', H-5' $\text{AA}' J = 8.8$ Hz). – MS (m/z) 279, 263 (M-17), 145, 77, 53.

$\text{C}_{17}\text{H}_{13}\text{NO}_3$ Calcd.: C 73.11 H 4.65
(279.6) Found: C 73.00 H 4.70.

trans-1-(4-Methylphenyl)-3-(4'-nitrophenyl)-1-penten-4-yn-3-ol (6b)

Similarly, CeCl_3 (0.83 g, 3.36 mmol), ethynylmagnesium bromide, (0.44 g, 3.40 mmol), and 1-(4-nitrophenyl)-3-(4-tolyl)-2-en-propanone (0.15 g, 0.56 mmol) were combined following the general procedure to give the title compound as an oil (0.15 g, 91.3%). – IR (film): $\nu/\text{cm}^{-1} = 3416$, 2116, 1606, 1518. – ^1H NMR ($\text{CDCl}_3/\text{DMSO}-d_6$): $\delta/\text{ppm} = 2.30$ (s, 3H; CH_3); 3.09 (s, 1H; H-5); 3.16 (s, 1H; OH); 6.24 (d, 1H; H-2, $J = 15.0$ Hz); 6.92 (d, 1H; H-1, $J = 15.0$ Hz); 7.10 (d, 2H; H-3', H-5', $\text{BB}' J = 8.0$ Hz); 7.27 (d, 2H; H-2', H-6', $\text{AA}' J = 8.0$ Hz); 7.86 (d, 2H; H-2", H-6", $\text{BB}' J = 9.0$ Hz); 8.17 (d, 2H; H-3", H-5", $\text{AA}' J = 9.0$ Hz). – M/S (m/z) 293, 276 (M-17), 171, 105 (100%), 91.

$\text{C}_{18}\text{H}_{15}\text{NO}_3$ Calcd.: C 73.72 H 5.12
(293.5) Found: C 73.52 H 5.23.

trans-1-(2-Nitrophenyl)-3-(4'-tolyl)-1-penten-4-yn-3-ol (6c)

Similarly, CeCl_3 (0.83 g, 3.36 mmol), ethynylmagnesium bromide, (0.44 g, 3.40 mmol), and 1-(4-tolyl)-3-(2-nitrophenyl)-2-en-propanone (0.15 g, 0.56 mmol) were combined following the general procedure, to give the title compound as an oil (0.10 g, 60.8%). – IR (film): $\nu/\text{cm}^{-1} = 3400$, 2116, 1606, 1522. – ^1H NMR (CDCl_3): $\delta/\text{ppm} = 2.37$ (s, 3H; CH_3); 2.91 (s, 1H; H-5); 2.95 (s, 1H; OH); 6.32 (d, 1H; H-2 $J = 16.1$ Hz); 7.22 (d, 2H; H-3", H-5" $\text{BB}' J = 8.0$ Hz); 7.45–7.50 (m, 1H; H-4'); 7.55–7.65 (t, 4H; H-5", H-6", H-2', H-6' AA'); 7.97 (d, 1H; H-3', $J = 7.8$ Hz). – MS (m/z) 293, 276 (M-17), 105, 91, 65, 53 (100%).

$\text{C}_{18}\text{H}_{15}\text{NO}_3$ Calcd.: C 73.72 H 5.12
(293.5) Found: C 73.60 H 5.09.

trans-1-(2-Nitrophenyl)-3-phenyl-1-penten-4-yn-3-ol (6d)

Similarly, CeCl_3 (0.87 g, 3.53 mmol) in THF (30 mL), ethynylmagnesium bromide, (0.45 g, 3.55 mmol) and 1-phenyl-3-(2-nitrophenyl)-2-en-propanone (0.15 g, 0.59 mmol) were combined following the general procedure, to give the title compound as an oil (0.055 g, 33%). – IR (film): $\nu/\text{cm}^{-1} = 3416$, 2116, 1606, 1522. – ^1H NMR (CDCl_3): $\delta/\text{ppm} = 2.92$ (s, 1H; H-5); 3.01 (s, 1H; OH); 6.32 (d, 1H; H-2, $J = 17.6$ Hz); 7.37–7.42 (m, 4H; H-4', H-3", H-4", H-5"); 7.49 (d, 1H; H-1, $J = 17.6$ Hz). 7.55 (d, 2H; HH-5', H-6', $J_0 = 8.0$ Hz); 7.73 (d, 2H; H-2", H-6", $J_0 = 7.0$ Hz); 7.97 (d, 1H; H-3', $J_0 = 8.0$ Hz). – MS (m/z) 279, 263 (M-17), 131, 120 (100%), 77.

$\text{C}_{17}\text{H}_{13}\text{NO}_3$ Calcd.: C 73.11 H 4.65
(279.1) Found: C 73.25 H 4.81.

trans-1-(2-Nitrophenyl)-3-(4'-nitrophenyl)-1-penten-4-yn-3-ol (6e)

Similarly, CeCl_3 (0.59 g, 2.40 mmol), ethynylmagnesium bromide, (0.31 g, 2.40 mmol), and 4-(nitrophenyl)-3-(2-nitrophenyl)-2-en-propanone (0.12 g, 0.40 mmol) were combined following the general procedure, to give the title compound as an oil (0.075 g, 57.5%). – IR (film): $\nu/\text{cm}^{-1} = 3522$, 2114, 1606, 1510. – ^1H NMR ($(\text{CD}_3)_2\text{CO}$): $\delta/\text{ppm} = 2.88$ (s, 1H; H-5); 3.52 (s, 1H; OH); 6.49 (d, 1H; H-2 $J = 16.0$ Hz); 7.46 (d, 1H; H-1 $J = 16.0$ Hz); 7.55 (t, 1H; H-4' $J_0 = 7.0$ Hz); 7.68 (t, 2H; H-5' $J_0 = 7.0$ Hz); 7.77 (d, 1H; H-6' $J_0 = 7.0$ Hz); 7.98 (d, 2H; H-2", H-6" $\text{BB}' J = 9.0$ Hz); 8.26 (d, 1H; H-3', $J_0 = 8.0$ Hz); 8.28 (d, 2H; H-3", H-5", $\text{AA}' J = 9.0$ Hz). – MS (m/z) 324, 307 (M-17), 202, 148 (100%), 132.

$C_{17}H_{12}N_2O_5$ Calcd.: C 62.96 H 3.70
(324.2) Found: C 63.01 H 3.59.

trans-1-(2-Nitrophenyl-3-(2'-nitrophenyl)-1-penten-4-yn-3-ol (6f)

Similarly, $CeCl_3$ (0.55 g, 2.23 mmol), ethynylmagnesium bromide (0.29 g, 2.24 mmol), and 1-(2-nitrophenyl)-3-(2-nitrophenyl)-2-en-propanone (0.11 g, 0.368 mmol) were combined following the general procedure, to give the title compound as an oil (0.06 g, 50%). – IR (film): ν/cm^{-1} = 3518, 2116, 1606, 1524, 1346. – 1H NMR ($CDCl_3$): δ/ppm = 2.89 (s, 1H; H-5); 3.88 (s, 1H; OH); 6.56 (d, 1H; H-2 J = 16.4 Hz); 7.45–7.50 (m, 2H; H-4, H-4''); 7.48 (d, 1H; H-1, J = 16.4 Hz); 7.61–7.67 (m, 4H; H-6'', H-5', H-5'', H-6'); 7.94 (c, 2H; H-3', H-3'', J_o = 8.0 Hz). – MS (m/z) 324, 307 (M-17), 176, 132 (100%), 121.

$C_{17}H_{12}N_2O_5$ Calcd.: C 62.96 H 3.70
(324.2) Found: C 62.78 H 3.80.

trans 1-(4-Methylphenyl)-3-(2'-nitrophenyl)-1-penten-4-yn-3-ol (6g)

Similarly, $CeCl_3$ (0.83 g, 3.36 mmol), ethynylmagnesium bromide (0.44 g, 3.4 mmol), and 1-(2-nitrophenyl)-3-(4-tolyl)-2-en-propanone (0.15 g, 0.56 mmol) were combined following the general procedure, to give the title compound as pale yellow microcrystals, *m.p.* 134–136 °C (0.05 g, 30.4%). – IR (KBr): ν/cm^{-1} = 3518, 2116, 1606, 1534, 1368. – 1H NMR ($CDCl_3$): δ/ppm = 2.37 (s, 3H; CH_3); 2.86 (s, 1H; H-5); 3.87 (s, 1H; OH); 6.53 (d, 1H; H-2 J = 17.0 Hz); 7.02 (d, 1H; H-1 J = 17.0 Hz); 7.17 (d, 2H; H-3', H-5' BB' J = 8.0 Hz); 7.37 (d, 2H; H-2', H-6 AA' J = 8.0 Hz); 7.47 (t, 1H; H-4' J_o = 7.0 Hz); 7.57 (t, 1H; H-5'' J_o = 7 Hz); 7.65 (d, 1H; H-6'' J_o = 7.0 Hz); 7.9 (d, 1H; H-3'' J_o = 7.0 Hz). – MS (m/z) 293, 276 (M-17), 119 (100%), 105, 95, 65.

$C_{18}H_{15}NO_3$ Calcd.: C 73.72 H 5.12
(293.5) Found: C 73.70 H 5.09.

References

- [1] J. S. Thayer, Adv. Organomet. Chem., **1975**, 13, 1., B. J. Wakefield, in Comprehensive Organometallic Chemistry, G. Wilkinson, F. G. A. Stone, E. W. Abel (Eds), Pergamon Press, **1982**, Vol. 7, Chapter 44.
- [2] (a) T. Imamoto, N. Takeyama, K. Nakamura, T. Hatajima, Y. Kamiya, J. Am. Chem. Soc. **1989**, 111, 4692; (b) G. A. Molander, Chem. Rev. **1992**, 92, 29
- [3] T. Imamoto, Lanthanides in Organic Synthesis, Academic Press, London 1994
- [4] J. March. Advanced Organic Chemistry, 3a Ed., John Wiley & Sons, New York, 1985, p. 820
- [5] G. Bartoli, M. Bosco, R. Dalpozzo, Tetrahedron Lett. **1985**, 26, 115
- [6] G. Bartoli, E. Marcantoni, M. Petrini, J. Org. Chem. **1992**, 57, 5834
- [7] K. Eichinger, Monatsh. Chem. **1978**, 109, 461
- [8] E. A. Adegohe, T. A. Emokpue, H. Ephraim-Bassey, C. A. Oyelola, J. Heterocycl. Chem. **1987**, 24, 1705
- [9] B. Weidmann, D. Seebach, Angew. Chem. Int. Ed. Engl. **1983**, 22, 31
- [10] G. Bartoli, Acc. Chem. Res. **1984**, 17, 109
- [11] G. Bartoli, E. Marcantoni, M. Petrini, J. Chem. Soc., Chem. Comm. **1993**, 1373
- [12] J. W. Ricigliano, T. M. Penning, Biochem. J. **1989**, 262, 139
- [13] B. M. Nilsson, U. Hacksell, J. Heterocycl. Chem. **1989**, 26, 269
- [14] D. O' Hagan, N. A. Zaidi, Tetrahedron Asymm. **1994**, 5, 1111
- [15] G. Bartoli, M. Bosco, R. Dalpozzo, M. Petrini, Tetrahedron **1987**, 43, 4221
- [16] T. Imamoto, Y. Sugiura, J. Phys. Org. Chem. **1989**, 2, 93
- [17] T. Hase, Tables for Organic Spectrometry Chemistry, **1992**, Helsinki Otatiesto editions

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