Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron Letters 47 (2006) 3549–3552

Tetrahedron Letters

A simple method for the conversion of propargyl alcohols to symmetrical 1,5-diynes using low valent titanium reagents

Galla V. Karunakar and Mariappan Periasamy*

School of Chemistry, University of Hyderabad, Central University P.O., Hyderabad 500 046, India

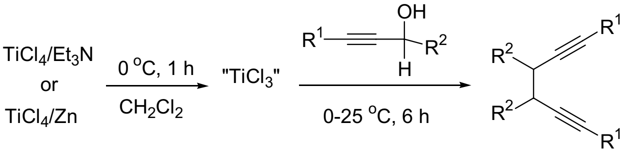
Received 1 January 2006; revised 3 March 2006; accepted 15 March 2006
Available online 5 April 2006

Abstract—Reaction of propargyl alcohols with low valent titanium species, prepared using the $TiCl_4/Et_3N$ and $TiCl_4/Zn$ reagent systems, gives the corresponding symmetrical 1,5-diynes in 56–74% yields.

1,5-Diynes are an important class of compounds useful for the synthesis of enediynes,[1] 1,5-enynes,[2] 1,5-dienes,[3] alkylidenecyclopentenones, butenolides,[4] pyrroles,[5] unsaturated macrocyclic compounds[6] and several pharmaceutically important compounds.[7] Hence, the development of methods for the synthesis of 1,5-diynes is important. During the course of our research efforts towards the development of organotitanium reagents,[8,9] we have developed a one-pot method for the synthesis of 1,5-diynes from the corresponding propargyl alcohols using low valent titanium species. The results are reported herein.

We observed that the reaction of undec-5-yn-4-ol **1a** ($R^1 = C_5H_{11}$, $R^2 = C_3H_7$) with the low valent titanium species, produced in situ using the $TiCl_4/Et_3N$ or $TiCl_4/Zn$ reagent system, gave the corresponding 1,5-diyne **2a** in a 71% yield (Scheme 1).[10] We also examined the reaction of propargyl alcohol **1a** using the titanium reagent prepared with various amines including Bu_3N, $^iPr_2NEt$ and Et_3N (Table 1, entries 1–3).

Optimum results were obtained using the readily accessible triethylamine (Table 1, entry 1). Several other propargyl alcohol derivatives were converted to the corresponding symmetrical 1,5-diynes under these conditions (Table 1). The yields were in the range of 58–74%. The 1,5-diynes were obtained as diastereomeric mixtures in some cases (Table 1). The major isomer obtained in the case of the 1,5-diyne **2h** was found to be *dl* as revealed by single crystal X-ray analysis.[11] The ORTEP diagram of the crystal structure of the 1,5-diyne **2h** is shown in Figure 1.



Scheme 1.

The reaction in the case of the propargyl alcohol **1k** gave the corresponding allenyne **3a** in 51–61% yields using different amines (Scheme 2).[12]

The structure of the allenyne **3a** was confirmed by single crystal X-ray analysis.[13] The ORTEP diagram of **3a** is shown in Figure 2.

A tentative mechanism involving reaction of the Ti(III) species,[8h] produced in situ with the propargyl alcohol followed by homolysis of the carbon oxygen bond, to give a Ti(IV) and propargyl radical species may be considered. The propargyl radicals could then couple to give the 1,5-diyne and allenyne depending upon the steric requirements (Scheme 3).

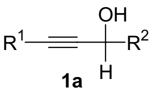
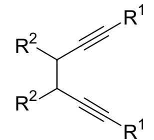
We also examined this transformation using the titanium reagent prepared by reducing $TiCl_4$ with Zn, since this system also gives $TiCl_3$ as the major species (Scheme 1).[14] The results are summarized in Table 2.

Keywords: Symmetrical 1,5-diynes; Low valent titanium species; Propargyl alcohols.

* Corresponding author. Tel.: +91 40 23134814; fax: +91 40 23012460; e-mail: mpsc@uohyd.ernet.in

0040-4039/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2006.03.097

Table 1. Conversion of propargyl alcohols into 1,5-diynes using the $TiCl_4/R_3N$ reagent system[a]

Entry	Substrate	Reducing agent	Product[b]	Diastereomeric ratio[c]	Yield[d] (%)
1	 **1a** $R^1 = C_5H_{11}$ $R^2 = C_3H_7$	Et_3N	 $R^1 = C_5H_{11}$ $R^2 = C_3H_7$ **2a**	100:0	71
2	**1a**	Bu_3N	**2a**	100:0	66
3	**1a**	$^{i}Pr_2NEt$	**2a**	100:0	61
4	$R^1 = C_5H_{11}$, $R^2 = {}^{i}Bu$ **1b**	Et_3N	$R^1 = C_5H_{11}$, $R^2 = {}^{i}Bu$ **2b**	86:14	68
5	$R^1 = C_5H_{11}$, $R^2 = C_7H_{15}$ **1c**	Et_3N	$R^1 = C_5H_{11}$, $R^2 = C_7H_{15}$ **2c**	100:0	69
6	$R^1 = C_5H_{11}$, $R^2 = C_9H_{19}$ **1d**	Et_3N	$R^1 = C_5H_{11}$, $R^2 = C_9H_{19}$ **2d**	100:0	74
7	$R^1 = Ph$, $R^2 = C_4H_9$ **1e**	Et_3N	$R^1 = Ph$, $R^2 = C_4H_9$ **2e**	100:0	68
8	$R^1 = Ph$, $R^2 = C_7H_{15}$ **1f**	Et_3N	$R^1 = Ph$, $R^2 = C_7H_{15}$ **2f**	100:0	58
9	$R^1 = Ph$, $R^2 = C_9H_{19}$ **1g**	Et_3N	$R^1 = Ph$, $R^2 = C_9H_{19}$ **2g**	100:0	63
10	$R^1 = Ph$, $R^2 =$ 1-Naphth **1h**	Et_3N	$R^1 = Ph$, $R^2 =$ 1-Naphth **2h**	87:13	61

[a] The reactions were carried out using $TiCl_4$ (2 mmol), R_3N (4 mmol) and propargyl alcohol (2 mmol).

[b] All the products (**2a**–**h**) were identified by IR, ^1H NMR, ^{13}C NMR and mass spectral data and the products **2a**–**f** and **2h** were also characterized by elemental analysis.

[c] Diastereomeric ratios were estimated from ^1H NMR (400 MHz) spectral signals.

[d] Yields of isolated products.

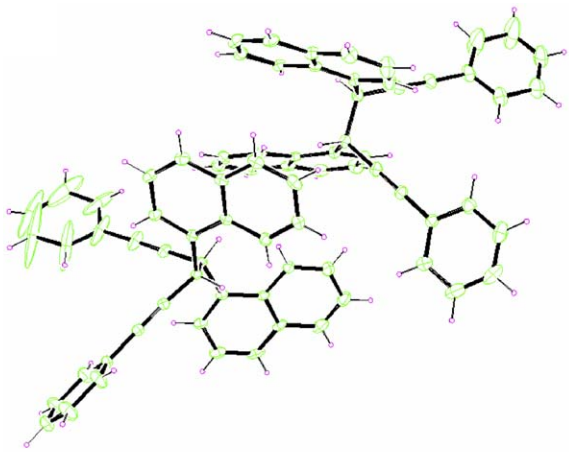


Figure 1. An ORTEP representation of the crystal structure of 1,5-diyne **2h**. (Thermal ellipsoids are drawn at 15% probability.)

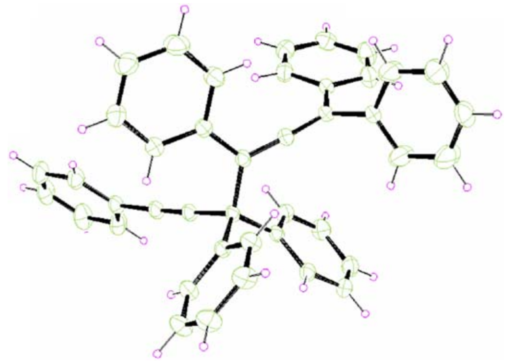
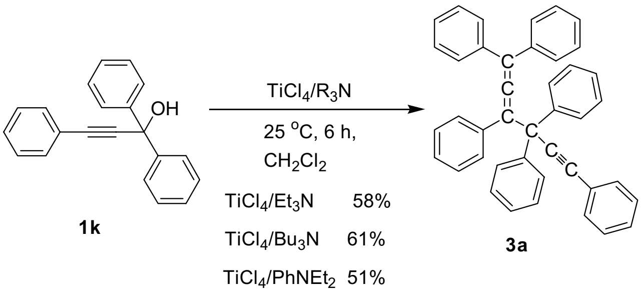
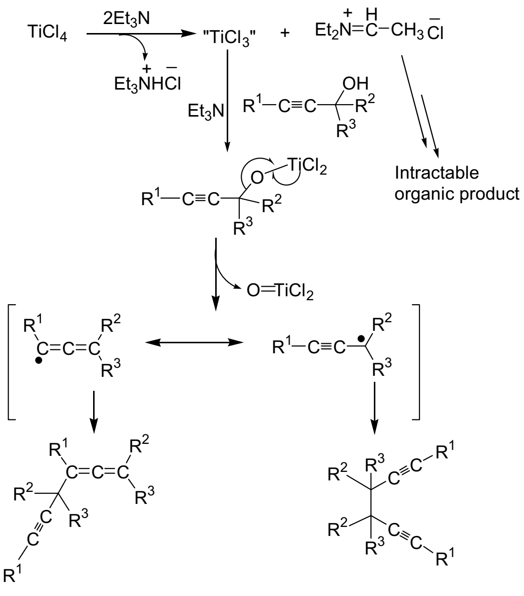


Figure 2. An ORTEP representation of the crystal structure of allenyne **3a**. (Thermal ellipsoids are drawn at 20% probability.)



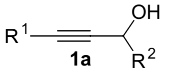
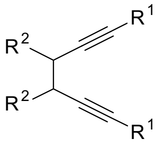
Scheme 2.



Scheme 3.

Previously, 1,5-diynes had been prepared via the reaction of 1,3-dilithiopropyne and propargyl chloride,[15a] or 3-silylpropargyl carbonates using a palladium catalyst,[15b] and via the reaction of propargyl carbonates

Table 2. Conversion of propargyl alcohols into 1,5-diynes using the $TiCl_4$/Zn reagent system[a]

Entry	Substrate	Product[b]	Diastereomeric ratio[c]	Yield[d] (%)
1		 $R^1 = C_5H_{11}$ $R^2 = C_3H_7$ **2a**	100:0	63
2	$R^1 = C_5H_{11}$, $R^2 = C_9H_{19}$ **1d**	$R^1 = C_5H_{11}$, $R^2 = C_9H_{19}$ **2d**	100:0	58
3	R^1 = Ph, $R^2 = C_4H_9$ **1e**	R^1 = Ph, $R^2 = C_4H_9$ **2e**	100:0	68
4	R^1 = Ph, R^2 = 1-Naphth **1h**	R^1 = Ph, R^2 = 1-Naphth **2h**	84:16	71
5	$R^1 = C_5H_{11}$, R^2 = 1-Naphth **1i**	$R^1 = C_5H_{11}$, R^2 = 1-Naphth **2i**	83:17	66
6	$R^1 = C_5H_{11}$, R^2 = Ph **1j**	$R^1 = C_5H_{11}$, R^2 = Ph **2j**	87:13	56

[a] The reactions were carried out using $TiCl_4$ (2 mmol), Zn (4 mmol) and propargyl alcohol (2 mmol).

[b] All the products (**2a**–**j**) were identified by IR, ^1H NMR, ^{13}C NMR and mass spectral data and the products **2a**–**h** were also characterized by elemental analysis.

[c] Diastereomeric ratios were estimated from ^1H NMR (400 MHz) spectral signals.

[d] Yields are of isolated products.

mediated by $Ti(O^iPr)_2Cl_2$/Mg.[15c] Since 1,5-diynes can now be readily accessed via simple one-pot procedures, the methods described here have considerable potential for further synthetic exploitation.

Acknowledgements

We thank the ILS-UOH, for a senior research fellowship to G.V.K. and a research Grant to M.P. Support of the DST, for the 400 MHz NMR facility under the FIST program and also for the National Single Crystal XRD facility is gratefully acknowledged. We are also grateful to the UGC, for support under the 'University of Potential for Excellence (UPE)' and the Centre for Advance Study (CAS) programs.

References and notes

1. (a) Dai, W. M.; Fong, K. C. *Tetrahedron Lett.* **1996**, *37*, 8413–8416; (b) Dai, W.; Fong, K. C.; Danjo, H.; Nishimoto, S. *Angew. Chem., Int. Ed. Engl.* **1961**, *35*, 779–781; (c) Jones, G. B.; Wright, J. M.; Plourde, G. W., II; Hynd, G.; Huber, R. S.; Mathews, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 1937–1944; (d) Nuss, J. M.; Murphy, M. M. *Tetrahedron Lett.* **1994**, *35*, 37–40; (e) Negishi, E.; Rand, C. L.; Jadhav, K. P. *J. Org. Chem.* **1981**, *46*, 5041–5044; (f) Myers, A. G.; Dragovich, P. S. *J. Am. Chem. Soc.* **1992**, *114*, 5859–5860; (g) Zein, N.; Schroeder, D. R. In *Advances in DNA Sequence Specific Agents*; Jones, G. B., Ed.; Jai Press: Greenwich, CT, 1998; Vol. 3.
2. (a) Keinan, E.; Bosch, E. *J. Org. Chem.* **1986**, *51*, 4006–4016; (b) Henrick, C. A. *Tetrahedron* **1977**, *33*, 1845–1889; (c) Taber, D. F.; He, Y.; Xu, M. *J. Am. Chem. Soc.* **2004**, *126*, 13900–13901; (d) Uenishi, J.; Matsui, K. *Tetrahedron Lett.* **2001**, *42*, 4353–4355.
3. Dumond, Y.; Negishi, E. *J. Am. Chem. Soc.* **1999**, *121*, 11223–11224.
4. Sugamwara, S.; Uemura, K.; Tsukada, N.; Inoue, Y. *J. Mol. Cat. A: Chem.* **2003**, *195*, 55–61.
5. Balasubramanian, R.; Keith, A. J.; Armstrong, D.; Odom, A. L. *Org. Lett.* **2004**, *6*, 2957–2960.
6. (a) Sondheimer, F.; Ben-Efraim, D. A.; Gaoni, Y. *J. Am. Chem. Soc.* **1961**, *83*, 1682–1685; (b) Sondheimer, F.; Ben-Efraim, D. A.; Wolousky, R. *J. Am. Chem. Soc.* **1961**, *83*, 1675–1681.
7. (a) Gilchrist, T. L. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2849–2866; (b) *Pyrroles, Chemistry of Heterocyclic Compounds*; Jones, R. A., Ed.; Wiley: New York, 1990; Vol. 48, (c) Faills, A. G.; Forgione, P. *Tetrahedron* **2001**, *57*, 5899–5913.
8. (a) Periasamy, M.; Jayakumar, K. N.; Bharathi, P. *J. Org. Chem.* **2005**, *70*, 5420–5425; (b) Periasamy, M.; Suresh, S.; Ganesan, S. S. *Tetrahedron Lett.* **2005**, *46*, 5521–5524; (c) Suresh, S.; Periasamy, M. *Tetrahedron Lett.* **2004**, *45*, 6291–6294; (d) Periasamy, M.; Kishorebabu, N.; Jayakumar, K. N. *Tetrahedron Lett.* **2003**, *44*, 8939–8941; (e) Periasamy, M. *ARKIVOC* **2002**, *VII*, 151–166; (f) Periasamy, M.; Jayakumar, K. N.; Bharathi, P. *Chem. Commun.* **2001**, 1728–1729; (g) Bharathi, P.; Periasamy, M. *Org. Lett.* **1999**, *1*, 857–859; (h) Periasamy, M.; Srinivas, G.; Karunakar, G. V.; Bharathi, P. *Tetrahedron Lett.* **1999**, *40*, 7577–7580.
9. Bharathi, P.; Periasamy, M. *Organometallics* **2000**, *19*, 5511–5513.
10. *Typical procedure for the preparation of 1,5-diynes using the $TiCl_4$/Et_3N reagent system*: In dichloromethane (35 mL), $TiCl_4$ (0.38 g, 0.2 mL, 2 mmol) and Et_3N (0.4 g, 0.56 mL, 4 mmol) were taken at 0 °C under N_2. The reaction mixture was stirred for 1 h at 0 °C. To this, undec-5-yn-4-ol **1a** (0.34 g, 2 mmol) was added and the reaction mixture stirred for another 6 h at 25 °C. Saturated NH_4Cl solution (10 mL) was added and the reaction mixture stirred for 10 min. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic extract was washed with brine solution (5 mL) and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was chromatographed on a silica gel column using hexane as eluent to afford the 1,5-diyne **2a** (0.214 g, 71%). A similar procedure was followed for experiments using propargyl alcohol (2 mmol), $TiCl_4$ (2 mmol), Zn (4 mmol) in DCM (35 mL) and THF (2 mL). *Spectral data for products* **2a**–**j**. Compound **2a**: IR (neat) 2961, 2235, 1460 cm^{-1}; (diastereomeric ratio) dr 100:0; ^1H NMR (400 MHz, $CDCl_3$, δ ppm) 0.89–0.97 (m, 12H), 1.21–1.36 (8H), 1.50–1.57 (8H), 1.88–1.92 (4H), 2.21–2.24 (4H), 4.54–4.58 (m, 2H); ^{13}C

NMR (100 MHz, $CDCl_3$, δ ppm): 13.2, 13.9, 18.7, 19.5, 22.1, 28.1, 30.9, 41.6, 49.3, 78.6, 87.2; MS (EI) $m/z = 302$. Elemental analysis for $C_{22}H_{38}$, calculated C = 87.34%, H = 12.66%, observed C = 87.37%, H = 12.63%. Compound **2b**: IR (neat) 2959, 2237, 1467 cm^{-1}; dr 86:14; ^1H NMR (400 MHz, $CDCl_3$, δ ppm) 0.82–1.00 (m, 18H), 1.29–1.42 (m, 10H), 1.48–1.61 (4H), 1.78–1.85 (4H), 2.17–2.24 (4H), 4.54–4.57 (2H). Additional signals for the minor isomer 1.86–1.91 (4H), 1.94–2.01 (4H), 2.37–2.45 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 13.4, 18.7, 21.9, 22.3, 25.7, 28.1, 30.8, 48.2, 48.6, 87.2, 98.5; MS (EI) $m/z = 330$. Elemental analysis for $C_{24}H_{42}$, calculated C = 87.19%, H = 12.81%, observed C = 87.17%, H = 12.83%. Compound **2c**: IR (neat) 2928, 2233, 1458 cm^{-1}; dr 100:0; ^1H NMR (400 MHz, $CDCl_3$, δ ppm) 1.88–1.67 (m, 12H), 1.23–1.32 (m, 24H), 1.43–1.49 (8H), 1.81–1.86 (4H), 2.14–1.18 (4H), 4.45–4.49 (2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.1, 18.7, 22.6, 26.2, 28.1, 28.8, 29.1, 29.4, 31.0, 31.6, 31.9, 39.7, 49.7, 78.7,87.3; MS (EI) $m/z = 414$. Elemental analysis for $C_{30}H_{54}$, calculated C = 86.88%, H = 13.12%, observed C = 86.81%, H = 13.19%. Compound **2d**: IR (neat) 2959, 2231, 1462 cm^{-1}; dr 100:0; ^1H NMR (400 MHz, $CDCl_3$, δ ppm) 1.67–1.88 (m, 12H), 1.23–1.32 (m, 24H), 1.43–1.49 (m, 8H), 1.81–1.86 (8H, m), 2.14–2.18 (m, 8H), 4.45–4.49 (2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.1, 18.7, 22.2, 22.6, 24.5, 25.7, 26.2, 28.1, 28.8, 29.1, 31.0, 31.6, 31.9, 39.7, 49.7, 78.7, 87.3; MS (EI) $m/z = 470$. Elemental analysis calculated for $C_{34}H_{62}$, calculated C = 86.73%, H = 13.27%, observed C = 86.71%, H = 13.29%. Compound **2e**: IR (neat) 2992, 2234, 1486 cm^{-1}; dr 100:0; ^1H NMR (400 MHz, $CDCl_3$, δ ppm) 1.02 (t, 6H, $J = 7$ Hz), 1.40–1.47 (m, 4H), 1.59–1.66 (m, 4H), 2.06–2.12 (m, 4H), 4.82 (t, 2H, $J = 6.4$ Hz), 7.34–7.50 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 13.9, 22.0, 28.4, 39.1, 49.3, 86.0, 87.5, 122.2, 128.3, 128,7, 131.8; MS (EI) $m/z = 342$. Elemental analysis for $C_{26}H_{30}$, calculated C = 91.17%, H = 8.83%, observed C = 91.21%, H = 8.79%. Compound **2f**: IR (neat) 2932, 2231, 1478 cm^{-1}; dr 100:0; ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 0.85 (t, $J = 7.1$ Hz, 6H), 1.22–1.51 (m, 10H), 1.62–1.73 (m, 4H), 1.18–1.46 (m, 6H), 2.06–2.15 (m, 4H), 4.84 (s, 2H), 7.10–7.21 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.1, 22.7, 26.3, 28.8, 29.1, 31.4, 39.4, 49.4, 86.1, 87.6, 122.3, 128.4, 128.7, 131.8; MS (EI) $m/z = 426$. Elemental analysis for $C_{32}H_{42}$, calculated C = 90.08%, H = 9.92%, observed C = 90.11%, H = 9.89%. Compound **2g**: IR (neat) 2926, 2231, 1491 cm^{-1}; dr 100:0; ^1H NMR (400 MHz, $CDCl_3$, δ ppm) 0.92 (t, 6H, $J = 6.8$ Hz), 1.25–1.42 (m, 24 H), 1.59–1.68 (m, 4H), 2.04–2.10 (m, 4H), 4.80 (s, 2H), 7.33–7.48 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.1, 22.7, 26.3, 29.3, 29.5, 29.6, 29.7, 31.9, 39.4, 49.4, 86.0, 87.5, 122.3, 127.8, 127.9, 131.8; MS (EI) $m/z = 482$. Compound **2h**: IR (KBr) 2930, 2223, 1461 cm^{-1}; dr 87:13; ^1H NMR (400 MHz, $CDCl_3$, δ ppm) 5.21 (1H, *dl*), 5.92 (1H, *meso*), 7.18–7.90 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 63.6, 68.4, 69.7, 87.0, 88.7, 124.2, 125.1, 125.2, 125.5, 126.2, 126.7, 127.9, 128.3, 128.9, 129.4, 130.5, 131.8, 132.9, 133.8; MS (EI) $m/z = 482$. Elemental analysis for $C_{38}H_{26}$, calculated C = 94.57%, H = 5.43%, observed C = 94.62%, H = 5.38%. Compound **2i**: IR (KBr) 2928, 2231, 1456 cm^{-1}; dr 83:17; ^1H NMR (400 MHz, $CDCl_3$, δ ppm) 0.85–0.96 (t, 6H, $J = 8.4$ Hz), 1.19–1.57 (m, 12H), 1.57–2.26 (4H), 4.87 (s, 1H), 5.05 (s, 1H), 7.31–8.19 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.0, 18.2, 22.2, 28.3, 28.7, 31.0, 40.9, 80.5, 85.0, 123.3, 125.3, 125.4, 125.8, 127.1, 127.6, 129.1, 133.7, 136.0; MS (EI) $m/z = 470$. Compound **2j**: IR (KBr) 2930, 2232, 1462 cm^{-1}; dr 87:13; ^1H NMR (400 MHz, $CDCl_3$, δ ppm) 0.91 (t, 6H, $J = 7$ Hz), 1.22–1.46 (m, 8H), 1.60–1.74 (m, 4H), 2.30–2.34 (m, 4H), 5.23 (s, 1H), 5.64 (s, 1H), 7.26–7.37 (m, 6H), 7.37–7.58 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 13.9, 18.9, 22.1, 28.3, 31.1, 69.5, 78.1, 88.7, 127.6, 127.8, 128.2, 139.3.; MS (EI) $m/z = 370$.

11. *Crystal data*: For the 1,5-diyne **2h**: molecular formula: $C_{76}H_{52}$, MW = 965.18, triclinic, space group: *P1*, $a = 10.1221(8)$ Å, $b = 14.9303(12)$ Å, $c = 18.7341(15)$ Å, $\alpha = 90.8400(10)°$, $\beta = 103.840(2)°$, $\gamma = 90.520(2)°$, $V = 2748.5(4)$ Å^3, $Z = 2$, $\rho_c = 1.166$ mg m^{-3}, $\mu = 0.066$ mm^{-1}, $T = 298$ K, of the 21,406 reflections collected, 7174 were unique [$R_{int} = 0.0563$]. Refinement on all data converged at $R_1 = 0.0734$, $wR_2 = 0.2016$. (Deposition number CCDC 293657.)
12. *Procedure for the preparation of allenyne* **3a** *using the $TiCl_4/Et_3N$ reagent system*: In dichloromethane (35 mL), $TiCl_4$ (0.38 g, 0.2 mL, 2 mmol) and Et_3N (0.3 g, 0.42 mL, 3 mmol) were taken at 0 °C under N_2. The reaction mixture was stirred for 1 h at 0 °C. To this, 1,1,3-triphenyl-2-propyne-1-ol **1k**, (0.568 g, 2 mmol), was added and the reaction allowed to stir for another 12 h at 25 °C. Saturated NH_4Cl solution (10 mL) was added and stirring was continued for 10 min. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic extract was washed with brine solution (5 mL) and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was chromatographed on a silica gel column with hexane to give allenyne **3a** (0.34 g, 64%). *Spectral data*: **3a**: IR (KBr) 2926, 2230, 1948, 1489 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, δ ppm) 7.11–7.63 (m, 30H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 54.8, 87.2, 93.5, 115.8, 123.5, 126.9, 127.0, 127.4, 127.8, 128.0, 128.1, 128.2, 128.3, 128.7, 128.8, 131.6, 135.0, 136.2, 143.8, 209.3; MS (EI) $m/z = 534$. Elemental analysis for $C_{42}H_{30}$, calculated C = 94.34%, H = 5.66%; observed C = 94.43%, H = 5.55%.
13. *Crystal data*: For the allenyne **3a**: $C_{42}H_{30}$, MW = 534.66, triclinic, space group: *P1*, $a = 9.3743(6)$ Å, $b = 10.2376(7)$ Å, $c = 16.0252(10)$ Å, $\alpha = 86.6500(10)°$, $\beta = 89.4930(10)°$; $\gamma = 78.4450(10)°$, $V = 1504.19(17)$ Å^3, $Z = 2$, $\rho_c = 1.180$ mg m^{-3}, $\mu = 0.067$ mm^{-1}, $T = 298$ K, of the 17,711 reflections collected, 7064 were unique [$R_{int} = 0.0485$]. Refinement on all data converged at $R_1 = 0.0564$, $wR_2 = 0.1612$. (Deposition number CCDC 293656.)
14. Periasamy, M.; Srinivas, G.; Suresh, S. *Tetrahedron Lett.* **2001**, *42*, 7123–7125.
15. (a) Pereira, A. R.; Cabezas, J. A. *J. Org. Chem.* **2005**, *70*, 2594–2597; (b) Ogoshi, S.; Nishigushi, S.; Tsutsumi, K.; Kurosawa, H. *J. Org. Chem.* **1995**, *60*, 4650–4652; (c) Yang, F.; Zhao, G.; Ding, Y.; Zhao, Z.; Zheng, Y. *Tetrahedron Lett.* **2002**, *43*, 1289–1293.