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First synthesis of both 1-aryl-4-[(*E*)-alk-1-enyl]-1*H*-1,2,3-triazoles and 1-aryl-4-[(*Z*)-1-(trimethylsilyl)alk-1-enyl]-1*H*-1,2,3-triazoles: assembly of π -extended 1,2,3-triazoles using a cross-coupling/click reaction sequence

Asuka Oikawa, Gan Kindaichi, Yasutaka Shimotori, Masayuki Hoshi

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cross-coupling/click reaction sequence

Asuka Oikawa, Gan Kindaichi, Yasutaka Shimotori, Masayuki Hoshi* Department of Biotechnology and Environmental Chemistry, Kitami Institute of Technology, 165 Koen-cho, Kitami, Hokkaido 090-8507, Japan Fax +81(157)247719; E-mail: <u>hoshi-m@chem.kitami-it.ac.jp</u>

Abstract: A practical and general synthetic approach to a series of π -extended 1,2,3-triazoles with both aryl and alkenyl moieties on the triazole ring is described. Synthesis of 1-aryl-4-[(E)-alk-1-enyl]-1H-1,2,3-triazoles can be achieved by the click reaction between terminal conjugated (E)-envnes, prepared by copper-mediated cross-coupling reaction of (E)-alk-1-enyldisiamylboranes with (trimethylsilyl)ethynyl bromide, and aryl azides, prepared from arylboronic acids and sodium azide in another flask and employed for the following click reaction without any purification. 1-Aryl-4-[(Z)-1-(trimethylsilyl)alk-1-enyl]-1H-1,2,3-triazoles can be also synthesized by a sequential three-step reaction, which involves copper-mediated cross-coupling reaction of (Z)-1-(trimethylsilyl)alk-1-enyldicyclohexylboranes with (trimethylsilyl)ethynyl bromide to form (Z)-1,3-bis(trimethylsilyl)alk-3-en-1-ynes, deprotection of the trimethylsilyl group on the alkynyl carbon atom to generate (Z)-3-(trimethylsilyl)alk-3-en-1-ynes and click reaction with aryl azides prepared in the same manner as described above. Both synthetic routes are tolerant of a wide range of functional groups with moderate to good yields.

Key words: 1,2,3-triazole, cross-coupling, click reaction, deprotection, alkenylborane, arylboronic acid, (trimethylsilyl)ethynyl bromide

1. Introduction

Since Sharpless and Meldal independently pioneered the copper(I)-catalyzed 1,3-dipolar cycloaddition reaction between organic azides and terminal alkynes to give 1,4-disubstituted 1,2,3-triazoles exclusively,¹ a wide variety of strategies have been developed for the cycloaddition reaction, the so-called click reaction.² As well as showing biological activities,³ compounds bearing 1,2,3-triazole moiety have found a large number of applications in different fields such as bioconjugation⁴ and materials science.⁵ The 1,2,3-triazole scaffold is stable not only under acidic and basic conditions but also under oxidative and reductive conditions. The chemically robust properties can be attributed to the heterocyclic aromatic system. Assembling further π -extended 1,2,3-triazoles can be performed by introduction of substituents such as aryl and alkenyl groups into 1-, 4-, and 5-positions of the triazole ring. The extension of conjugated system on 1,2,3-triazole ring, in fact, has been realized in the click reaction by making a choice from the substrates. Thus, use of arylethynes as terminal alkynes gives 4- or 5-aryl 1,2,3-triazoles upon choosing the reaction conditions^{2,6} and use of aryl and alkenyl azides furnishes 1-aryl⁷⁻⁹ and 1-alkenyl^{7a,h,8a,10} 1,2,3-triazoles, respectively. Although there are several reports on the formation of 4- or 5-alkenyl 1,2,3-triazoles,^{6a,h,7a,c,11} the precursor of the alkenyl group is limited to only a few conjugated enynes such as 1-ethynylcyclohexene. The click reaction using terminal conjugated (E)-envnes (2), to our knowledge, is the only our previous report, 12 in which the reaction with *in situ* generated various benzyl azides proceeded at room temperature to afford a wide range of 1-arylmethyl-4-[(E)-alk-1-enyl]-1H-1,2,3-triazoles in high yields. As our continued interest in assembling π -extended compounds utilizing in situ generated terminal conjugated envnes,¹³ we focused our attention on the copper(I)-catalyzed click reaction with any azides to extend π -conjugation at the 1-position as well as at the 4-position of 1,2,3-triazole. Herein, we report the first synthesis of both 1-aryl-4-[(E)-alk-1-enyl]-1H-1,2,3-triazoles (3) through a sequential two-step reaction and 1-aryl-4-[(Z)-1-(trimethylsilyl)alk-1-enyl]-1H-1,2,3-triazoles (6) through a sequential three-step reaction. The present protocol provides a practical and general way to access π -extended 1,2,3-triazoles 3 and 6, respectively, and is applicable to a wide range of starting materials.

2. Results and discussion

At first, our attention was turned to one-pot synthesis of 1-aryl-4-[(E)-alk-1-enyl]-1H-1,2,3-triazoles (**3**) through a sequence of copper-mediated cross-coupling reaction of (E)-alk-1-enyldisiamylborane (**1**) with (trimethylsilyl)ethynyl bromide followed by click reaction with *in situ* generated aryl azides. Although a lot of

methods have been reported for the synthesis of 1-aryl 1,2,3-triazoles employing in situ generation of aryl azides,⁷⁻⁹ most of these methods suffer from limitations such as prolonged heating, use of expensive ligand, substrate or solvent, use of modified copper catalyst or unstable substrate, troublesome preparation of substrate, and low yield. Accordingly, we chose a method where the preparation of aryl azides could be performed by the reaction of sodium azide with arylboronic acids, which are stable under air and commercially readily available, in the presence of a small amount of Cu(OAc)₂ in methanol under an air atmosphere at 55 °C for 1-3 h.^{8b} Thus, the cross-coupling reaction of (E)-oct-1-enyldisiamylborane (1a) (1.0 mmol) with (trimethylsilyl)ethynyl bromide (0.67 mmol) was carried out in the presence of Cu(acac)₂ (0.05 mmol) and NaOMe (1M, 0.75 mmol) at temperatures gradually rising from -15 °C to room temperature overnight to form (E)-dec-3-en-1-yne (2a). To the resulting solution of 2a, phenylboronic acid (1 mmol), NaN₃ (1.5 mmol), Cu(OAc)₂ (0.1 mmol), and MeOH (5 mL) were added, and the reaction mixture was stirred at 55 °C in open air for 1.5 h in order to generate phenyl azide. After cooled to ambient temperature, sodium ascorbate (0.1 mmol) for reduction of Cu(OAc)₂ was added to the resultant mixture, which was stirred at room temperature for 24 h (Scheme 1, eq 1). The desired product, 1-phenyl-4-[(E)-oct-1-enyl]-1H-1,2,3-triazole (3a), was isolated in 26% yield based on (trimethylsilyl)ethynyl bromide, indicating that the yield of the click reaction between 2a and phenyl azide was estimated to be less than 40%.¹⁴ It has been recognized that the click chemistry using copper(I)-catalyzed azide-alkyne cycloaddition furnishes 1,4-disubstituted 1,2,3-triazoles in very high yields.² We surmised that incomplete formation of phenyl azide may be responsible for the low yield of **3a**. This guess led us to prepare phenyl azide in another flask from phenylboronic acid in the same manner as described above. After phenyl azide, thus prepared, was transferred to the flask containing 2a, sodium ascorbate (0.1 mmol) was added to the mixture, which was stirred at room temperature for 24 h (Scheme 1, eq 2). To our delight, the click reaction could be improved to afford **3a** in 67% overall yield, indicating that the yield of the click reaction between 2a and phenyl azide increased up to 90%. This result ensured sufficient potential of our protocol. While all the steps could not be carried out in a one-pot manner, each step could be performed without operation such as exchange of solvent and filtration.



Scheme 1 Choice of the step for the preparation of phenylazide.

Having identified the separate preparation of aryl azides from arylboronic acids as the key step, we then explored the substrate scope of this semi-one-pot transformation using various combinations of terminal conjugated (*E*)-enynes (**2**) and aryl azides. The results are shown in Table 1. The semi-one-pot process mostly afforded products **3** in moderate to good yields with excellent regio- and stereoselectivities. It should be noted that aryl azides, prepared in another flask, could be directly used for the following click reaction without any purification. Different compounds **2** were suitable in this transformation. In particular, pre-chlorinated (*E*)-enyne, (*E*)-7-chlorohept-3-en-1-yne (**2b**), was tolerated well (entries 15-21). A variety of aryl azides, bearing electron-donating groups such as methoxy (entries 2, 10 and 16) and methyl (entries 3, 11, 12 and 17), and electron-withdrawing groups such as fluoro (entries 5 and 18), acetyl (entries 6 and 19), cyano (entriea 7 and 20) and nitro (entries 8, 14 and 21), worked well under the same reaction conditions. The electronic effect on the phenyl ring had little influence on the reactivity of aryl azide substrates. Unfortunately, a combination of substrates resulted in a complex mixture which could not be separated (entries 4 and 13).

Table 1

Synthesis of 1-aryl-4-[(E)-alk-1-enyl]-1*H*-1,2,3-triazoles via a sequence of cross-coupling^a followed by click reaction^b



2	$n-C_6H_{13}$	$4-CH_3OC_6H_4$	3ab	69
3	$n-C_6H_{13}$	$4-CH_3C_6H_4$	3ac	66
4	$n-C_6H_{13}$	$2-CH_3C_6H_4$	3ad	messy
5	$n-C_6H_{13}$	$4-FC_6H_4$	3ae	65
6	$n-C_{6}H_{13}$	$3-AcC_6H_4$	3af	64
7	$n-C_{6}H_{13}$	$3-NCC_6H_4$	3ag	58
8	$n-C_{6}H_{13}$	$3-NO_2C_6H_4$	3ah	65
9	C_6H_5	C_6H_5	3ba	74
10	C_6H_5	$4-CH_3OC_6H_4$	3bb	69
11	C_6H_5	$4-CH_3C_6H_4$	3bc	59
12	C_6H_5	$2-CH_3C_6H_4$	3bd	41
13	C_6H_5	$4-FC_6H_4$	3be	messy
14	C_6H_5	$3-NO_2C_6H_4$	3bh	46
15	$Cl(CH_2)_3$	C ₆ H ₅	3ca	73
16	$Cl(CH_2)_3$	$4-CH_3OC_6H_4$	3cb	65
17	$Cl(CH_2)_3$	$4-CH_3C_6H_4$	3cc	71
18	$Cl(CH_2)_3$	$4-FC_6H_4$	3ce	73
19	$Cl(CH_2)_3$	$3-AcC_6H_4$	3cf	68
20	$Cl(CH_2)_3$	$3-NCC_6H_4$	3cg	58
21	$Cl(CH_2)_3$	$3-NO_2C_6H_4$	3ch	63

^a Reaction conditions: **1** (1 mmol), Me₃SiC≡CBr (0.67 mmol), Cu(acac)₂ (0.05 mmol), 1M NaOMe (0.75 mmol), – 15 °C to room temperature overnight under argon.

^b Reaction conditions: ArN₃ prepared from arylboronic acid (1 mmol) and NaN₃ (1.5 mmol) in the presence of Cu(OAc)₂ (0.1 mmol) under air, Na ascorbate (0.1 mmol), room temperature for 24 h under argon.

^c Isolated yields after silica gel column chromatography.

We next focused on broadening the scope of enynes for the π -conjugated 1,2,3-triazole synthesis. In our previous report on the synthesis of conjugated envnes,¹⁵ it was demonstrated that not only terminal conjugated (E)-enynes (2) but also trimethysilyl-protected terminal conjugated enynes, (Z)-1,3-bis(trimethylsilyl)alk-3-en-1-ynes (5), could be prepared by copper-mediated cross-coupling reaction with (trimethylsilyl)ethynyl bromide under extremely mild conditions. Provided deprotection of the trimethylsilyl group attached to the alkyne of 5 is moiety performed, the deprotected compounds, (Z)-3-(trimethylsilyl)alk-3-en-1-ynes, can participate in click reaction. It has been reported that click reaction involving a deprotection step can be also carried out in a one-pot fashion,¹⁶ where tetrabutylammonium fluoride (TBAF) was frequently employed as the desilylating reagent. Alternatively, it was found that a solution of NaOMe in MeOH was an efficient reagent for the deprotection of the trimethylsilyl group from 5.¹⁵ Our previous results as well as literature reports prompted us to examine a two-step process involving the deprotection of 5 followed by click reaction with azide. cross-coupling reaction aryl Thus. the of (Z)-1-(trimethylsilyl)hex-1-enyldicyclhexylborane (4a)(1.0)mmol) with (trimethylsilyl)ethynyl bromide (0.67 mmol) was performed in the presence of CuI (0.1 mmol) and NaOH (1M, 0.75 mmol) at temperatures gradually rising from -15 °C to room temperature overnight to form (Z)-1,3-bis(trimethylsilyl)oct-3-en-1-yne (5a). To the resulting solution of 5a, phenyl azide, prepared from phenylboronic acid (1 mmol), NaN₃ (1.5 mmol), and Cu(OAc)₂ (0.1 mmol) in MeOH (5 mL) at 55 °C in open air for 1.5 h, was added, followed by addition of sodium ascorbate (0.1 mmol) and NaOMe (1 M, 1 mmol). The reaction mixture was stirred at room temperature for 24 h (Eq. 1). We were pleased to find that the two steps proceeded smothly at the same time to afford the desired product, 1-phenyl-4-[(Z)-1-(trimethylsilyl)hex-1-enyl]-1H-1,2,3-triazole (6a), in 60% isolated yield based on (trimethylsilyl)ethynyl bromide. The geometry of 6a was assigned by using desilylation of alkenylsilanes with retention of the double bond.¹⁷ Protodesilylation of **6a** with HI gave 1-phenyl-4-[(E)-hex-1-enyl]-1H-1,2,3-triazole¹⁸ as the sole product, thus demonstrating Z-configuration of 6a (Eq. 2).



To evaluate the scope of this semi-one-pot transformation, various combinations of (Z)-1,3-bis(trimethylsilyl)alk-3-en-1-ynes (**5**) and aryl azides were used. The reactions were conducted under the conditions described above, and the results are shown in Table 2. The semi-one-pot process afforded 1-aryl-4-[(Z)-1-(trimethylsilyl)alk-1-enyl]-1*H*-1,2,3-triazoles (**6**) exclusively in moderate to good yields. In this process, aryl azides, prepared in another flask, could be also used without any purification. It is noteworthy that such functional groups as acetyl,

cyano, and nitro on the phenyl ring of aryl azides were tolerated under basic conditions. However, the products bearing cyano group (entries 7 and 15) were obtained in lower yields compared with those bearing the other two functional groups (entries 6, 8, 14 and 16). The reaction with 2-methylphenyl azide resulted in low product yields (entries 4 and 12), probably due to steric hindrance. It is interesting to note that the use of NaOMe as the desilylating reagent afforded products **6** in higher yields than that of TBAF (entries 1, 8 and 9).

Table 2

) ₂ B	Cul, NaOH Me₃SiC≡CBr Ma	e3Si Ar	N ₃ [+ Cu(OAc) ₂] a a scorbate M NaO Me	Ar NNN
Me ₃ Si	R	Me ₃ Si R		6 Me ₃ Si R
Entry	R	Ar	Product	Yield (%) ^c
1	<i>n</i> -C ₄ H ₉	C ₆ H ₅	6aa	60 (45) ^d
2	$n-C_4H_9$	4-CH ₃ OC ₆ H ₄	6ab	63
3	$n-C_4H_9$	$4-CH_3C_6H_4$	6ac	68
4	$n-C_4H_9$	$2-CH_3C_6H_4$	6ad	32
5	n-C ₄ H ₉	$4-FC_6H_4$	6ae	65
6	<i>n</i> -C ₄ H ₉	3-AcC ₆ H ₄	6af	62
7	<i>n</i> -C ₄ H ₉	3-NCC ₆ H ₄	6ag	30
8	$n-C_4H_9$	$3-NO_2C_6H_4$	6ah	58 (42) ^d
9	C ₆ H ₅	C_6H_5	6ba	$54(44)^{d}$
10	C ₆ H ₅	4-CH ₃ OC ₆ H ₄	6bb	61
11	C ₆ H ₅	$4-CH_3C_6H_4$	6bc	53
12	C ₆ H ₅	$2-CH_3C_6H_4$	6bd	40
13	C_6H_5	$4-FC_6H_4$	6be	52
14	C_6H_5	$3-AcC_6H_4$	6bf	58
15	C ₆ H ₅	3-NCC ₆ H ₄	6bg	39
16	C_6H_5	$3-NO_2C_6H_4$	6bh	55

Synthesis of 1-aryl-4-[(Z)-1-(trimethylsilyl)alk-1-enyl]-1*H*-1,2,3-triazoles via a sequence of cross-coupling^a followed by desilylation/click reaction^b

^a Reaction conditions: 4 (1 mmol), Me₃SiC≡CBr (0.67 mmol), CuI (0.1 mmol), 1M or 2M NaOH (0.75 mmol), -15 °C to room temperature overnight under argon.

^b Reaction conditions: ArN₃ prepared from arylboronic acid (1 mmol) and NaN₃ (1.5 mmol) in the presence of Cu(OAc)₂ (0.1 mmol) under air, Na ascorbate (0.1 mmol),

1M NaOMe (1 mmol), room temperature for 24 h under argon.

^c Isolated yields after silica gel column chromatography.

^d 1M TBAF (2 mmol) was used instead of 1M NaOMe (1 mmol).

3. Conclusion

In conclusion, we have reported a practical and general method for the synthesis of 1-aryl-4-[(E)-alk-1-enyl]-1H-1,2,3-triazolesbut not only also 1-aryl-4-[(Z)-1-(trimethylsilyl)alk-1-enyl]-1H-1,2,3-triazoles through a cross-coupling/click reaction sequence. To the best of our knowledge, the present protocol represents the first example of constructing a series of π -extended 1,2,3-triazoles with both an aryl moiety at the 1-position and a geometrical defined alkenyl moiety at the 4-positin on the triazole ring. This approach uses simple and readily available starting materials and shows good functional compatibility. The procedure can be successfully performed without isolation and purification of any compounds during the process, albeit in a semi-one-pot manner. These features make this protocol potentially attractive for the synthesis of the π -extended 1,2,3-triazoles.

4. Experimental

4.1. General information

NMR spectra were recorded on JEOL JNM-A-500 or JEOL JNM-ECA-600 spectrometer. Chemical shifts are quoted in parts per million (ppm) downfield of TMS. Coupling constants *J* are quoted in Hz. IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer, and only the strongest/structurally most important absorption peaks are listed. Electrospray ionization (ESI) HRMS analyses were measured on a Thermo Scientific Exactive instrument. Melting points were determined on a Yamato MP-21 and are uncorrected. TLC analyses were carried out using aluminium sheets pre-coated with silica gel 60 F₂₅₄ purchased from Merck. Product purification was performed by column chromatography using silica gel 60 (Kanto Chemical, 63-210 μ m). Unless otherwise noted, commercially available materials were used after distillation over CaH₂ under argon. 1-(Trimethylsilyl)alk-1-ynes were used after distillation under argon. THF was distilled from Na-benzophenone ketyl under argon before use. Borane dimethyl sulfide complex (BH₃·SMe₂) was purchased from Aldrich. (Trimethylsilyl)ethynyl bromide was prepared according to the literature procedure.¹⁹

4.2. General procedure for the synthesis of 1-aryl-4-[(*E*)-alk-1-enyl]-1*H*-1,2,3-triazoles

A 25 mL round-bottomed flask was charged with a solution of BH₃·SMe₂ (1 mmol) in THF (3 mL) under an argon atmosphere. To the solution was added 2-methylbut-2-ene (0.14 g, 2 mmol) dropwise at -15 °C, and the reaction mixture was stirred for 2 h at room temperature to form a solution of disiamylborane in THF.²⁰ To this solution was added alk-1-yne (1 mmol) dropwise at -15 °C, and the mixture was stirred for 2 h at 0 °C. A solution of (E)-alk-1-enyldisiamylborane 1 (1 mmol) in THF, thus prepared, was cooled to -15 °C, and Cu(acac)₂ (0.013 g, 0.05 mmol) was added to the solution under a flow of argon, followed by dropwise addition of (trimethylsilyl)ethynyl bromide (0.119 g, 0.67 mmol) and NaOMe (1M, 0.75 mL, 0.75 mmol). The resulting mixture was allowed to warm gradually to room temperature and stirred overnight to form (E)-alk-3-en-1-yne 2. In another 25 mL round-bottomed flask, aryl azide was prepared by using arylboronic acid (1 mmol), NaN₃ (0.098 g, 1.5 mmol), Cu(OAc)₂ (0.018 g, 0.1 mmol) and MeOH (5 mL). Thus, the mixture was stirred at 55 °C for 1.5-3.0 h under aerobic condition.^{8b} To the flask containing (E)-alk-3-en-1-yne 2 was transferred a dark brown suspension of aryl azide in MeOH, and (+)-sodium L-ascorbate (0.02 g, 0.1 mmol) was added to the mixture under a flow of argon. The resulting mixture was stirred at room temperature for 24 h and then treated by bubbling air through the solution with tube pump at room temperature for 2 h to oxidize the residual organoboron compound. The mixture was extracted with EtOAc (3×10 mL), washed with brine (10 mL), dried (Na₂SO₄), and filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel to give product 3.

4.3. General procedure for the synthesis of 1-aryl-4-[(Z)-1-(trimethylsilyl)alk-1-enyl]-1*H*-1,2,3-triazoles

A 25 mL round-bottomed flask was charged with a solution of $BH_3 \cdot SMe_2$ (1 mmol) in THF (3 mL) under an argon atmosphere. To the solution was added cyclohexene (0.164 g, 2 mmol) dropwise at 0 °C, and the reaction mixture was stirred for 2 h at this temperature to form a white suspension of dicyclohexylborane in THF.²⁰ To this suspension was added 1-(trimethylsilyl)alk-1-yne (1 mmol) dropwise at 0 °C, and the mixture was stirred for 2 h at this temperature to produce a clear solution of (Z)-1-(trimethylsilyl)alk-1-enyldicyclohexylborane 4 in THF. This solution was cooled to - 15 °C, and CuI (0.019 g, 0.1 mmol) was added to the solution under a flow of argon, followed by dropwise addition of (trimethylsilyl)ethynyl bromide (0.119 g, 0.67 mmol) and NaOH (1M, 0.75 mL for 4a or 2M, 0.375 mL for 4b, 0.75 mmol). The resulting mixture was allowed to warm gradually to room temperature and stirred overnight to form (Z)-1,3-bis(trimethylsilyl)alk-3-en-1-yne 5. In another 25 mL round-bottomed flask, aryl azide was prepared as described in general procedure for the synthesis of 1-aryl-4-[(*E*)-alk-1-enyl]-1*H*-1,2,3-triazoles. То the flask containing (Z)-1,3-bis(trimethylsilyl)alk-3-en-1-yne 5 was transferred a dark brown suspension of aryl azide in MeOH, and (+)-sodium L-ascorbate (0.02 g, 0.1 mmol) was added to the mixture under a flow of argon, followed by addition of NaOMe (1M, 1.0 mL, 1.0 mmol). The resulting mixture was stirred at room temperature for 24 h and worked up as experimental procedure for the described а typical synthesis in of 1-aryl-4-[(E)-alk-1-enyl]-1H-1,2,3-triazoles. Product 6 was isolated by column chromatography on silica gel.

4.4. Characterization of the products

4.4.1. 4-[(E)-Oct-1-enyl]-1-phenyl-1H-1,2,3-triazole (**3aa**). Light-brown solid, hexane-EtOAc (7:3) as eluent, mp. 58-59 °C. ¹H NMR (500 MHz, CDCl₃): $\delta = 0.89$ (t, J = 6.8 Hz, 3H), 1.26-1.40 (m, 6H), 1.45-1.53 (m, 2H), 2.21-2.27 (m, 2H), 6.45 (d, J = 16.1 Hz, 1H), 6.52 (dt, J = 16.1 and 6.8 Hz, 1H), 7.40-7.45 (m, 1H), 7.49-7.54 (m, 2H), 7.70-7.75 (m, 2H), 7.86 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 14.1$ (CH₃), 22.6 (CH₂), 28.8 (CH₂), 28.9 (CH₂), 31.7 (CH₂), 32.9 (CH₂), 117.4 (=CH), 117.8 (=CH), 120.4 (2 × CH_{arom}), 128.5 (CH_{arom}), 129.7 (2 × CH_{arom}), 134.6 (=CH), 137.0 (C_{arom}), 147.1 (=C). IR (KBr): v = 3132, 2923, 2854, 1598, 1504, 1465, 1234, 1217, 1045, 977, 756, 684 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₆H₂₁N₃Na: 278.1626; found 278.1630.

4.4.2. 1-(4-Methoxyphenyl)-4-[(E)-oct-1-enyl]-1H-1,2,3-triazole (**3ab**). Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 57-58 °C. ¹H NMR (600 MHz, CDCl₃): $\delta = 0.89$ (t, J = 6.8 Hz, 3H), 1.26-1.39 (m, 6H), 1.45-1.51 (m, 2H), 2.20-2.25 (m, 2H), 6.43 (d, J = 16.1 Hz, 1H), 6.48 (dt, J = 16.1 and 6.8 Hz, 1H), 6.97-7.02 (m, 2H), 7.58-7.63 (m, 2H), 7.77 (s, 1H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 14.1$ (CH₃), 22.6 (CH₂), 28.8 (CH₂), 29.0 (CH₂), 31.7 (CH₂), 32.9 (CH₂), 55.6 (CH₃), 114.7 (2 × CH_{arom}), 117.5 (=CH), 118.0 (=CH), 122.0 (2 × CH_{arom}), 130.5 (C_{arom}), 134.2 (=CH), 146.9 (=C), 159.6 (C_{arom}). IR

(KBr): $v = 3122, 2923, 2856, 1519, 1251, 1232, 1043, 970, 833 \text{ cm}^{-1}$. HRMS (ESI): m/z[M + Na]⁺ calcd for C₁₇H₂₃ON₃Na: 308.1731; found 308.1732.

4.4.3. 1-(4-Methylphenyl)-4-[(E)-oct-1-enyl]-1H-1,2,3-triazole (**3ac**). White solid, hexane-EtOAc (7:3) as eluent, mp. 77-78 °C. ¹H NMR (500 MHz, CDCl₃): $\delta = 0.89$ (t, J = 6.8 Hz, 3H), 1.25-1.40 (m, 6H), 1.45-1.53 (m, 2H), 2.19-2.27 (m, 2H), 2.41 (s, 3H), 6.44 (d, J = 16.1 Hz, 1H), 6.50 (dt, J = 16.1 and 6.3 Hz, 1H), 7.27-7.32 (m, 2H), 7.57-7.62 (m, 2H), 7.82 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 14.1$ (CH₃), 21.0 (CH₃), 22.6 (CH₂), 28.8 (CH₂), 28.9 (CH₂), 31.7 (CH₂), 32.9 (CH₂), 117.3 (=CH), 117.8 (=CH), 120.2 (2 × CH_{arom}), 130.1 (2 × CH_{arom}), 134.4 (=CH), 134.7 (C_{arom}), 138.6 (C_{arom}), 146.9 (=C). IR (KBr): v = 3122, 2923, 2854, 1519, 1232, 1217, 1041, 975, 817, 738 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₇H₂₃N₃Na: 292.1782; found 292.1781.

4.4.4. 1-(4-Fluorophenyl)-4-[(E)-oct-1-enyl]-1H-1,2,3-triazole (**3ae**). Light-brown solid, hexane-EtOAc (7:3) as eluent, mp. 71-73 °C. ¹H NMR (500 MHz, CDCl₃): $\delta = 0.89$ (t, J = 6.8 Hz, 3H), 1.23-1.42 (m, 6H), 1.44-1.53 (m, 2H), 2.18-2.28 (m, 2H), 6.43 (d, J = 16.1 Hz, 1H), 6.51 (dt, J = 16.1 and 6.3 Hz, 1H), 7.15-7.25 (m, 2H), 7.65-7.75 (m, 2H), 7.82 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 14.1$ (CH₃), 22.6 (CH₂), 28.9 (CH₂), 28.9 (CH₂), 31.7 (CH₂), 32.9 (CH₂), 116.6 (d, J = 23.7 Hz, 2 × CH_{arom}), 117.5 (=CH), 117.7 (=CH), 122.3 (d, J = 8.2 Hz, 2 × CH_{arom}), 133.3 (CH_{arom}), 134.6 (=CH), 147.2 (=C), 162.2 (d, J = 248.3 Hz, C_{arom}). IR (KBr): v = 3124, 2925, 2856, 1519, 1224, 1041, 977, 839, 742 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₆H₂₀N₃FNa: 296.1532; found 296.1531.

4.4.5. 1-(3-Acetoxyphenyl)-4-[(E)-oct-1-enyl]-1H-1,2,3-triazole (**3af**). Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 56-57 °C. ¹H NMR (500 MHz, CDCl₃): $\delta = 0.89$ (t, J = 6.8 Hz, 3H), 1.25-1.40 (m, 6H), 1.44-1.53 (m, 2H), 2.20-2.27 (m, 2H), 2.66 (s, 3H), 6.44 (d, J = 16.1 Hz, 1H), 6.53 (dt, J = 16.1 and 8.3 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.96-8.02 (m, 2H), 8.01 (s, 1H), 8.25-8.28 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 13.9$ (CH₃), 22.4 (CH₂), 26.5 (CH₃), 28.6 (CH₂), 28.7 (CH₂), 31.5 (CH₂), 32.7 (CH₂), 117.1 (=CH), 117.4 (=CH), 119.1 (CH_{arom}), 124.2 (CH_{arom}), 128.0 (CH_{arom}), 129.9 (CH_{arom}), 134.8 (=CH), 137.1 (C_{arom}), 138.1 (C_{arom}), 147.1 (=C), 196.5 (C=O). IR (KBr): v = 3134, 2925, 2854, 1674, 1593, 1504, 1454, 1267, 1215, 1043, 968, 893, 806, 682 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₈H₂₃ON₃Na: 320.1731; found 320.1730.

4.4.6. 1-(3-Cyanophenyl)-4-[(E)-oct-1-enyl]-1H-1,2,3-triazole (**3ag**). White solid, hexane-EtOAc (7:3) as eluent, mp. 52-53 °C. ¹H NMR (500 MHz, CDCl₃): $\delta = 0.89$ (t, J = 6.8 Hz, 3H), 1.26-1.40 (m, 6H), 1.46-1.53 (m, 2H), 2.22-2.28 (m, 2H), 6.44 (dt, J = 16.1 and 1.4 Hz, 1H), 6.56 (dt, J = 16.1 and 6.8 Hz, 1H), 7.64-7.74 (m, 2H), 7.89 (s, 1H), 8.01-8.07 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 14.0$ (CH₃), 22.5 (CH₂), 28.8 (CH₂), 31.6 (CH₂), 32.9 (CH₂), 114.0 (C_{arom}), 116.8 (=CH), 117.2 (=CH), 117.4 (=C), 123.2 (CH_{arom}), 124.1 (CH_{arom}), 130.8 (CH_{arom}), 131.7 (CH_{arom}), 135.5 (=CH), 137.5 (C_{arom}), 147.6 (=C). IR (KBr): v = 3130, 2925, 2854, 2235, 1587, 1487, 1217, 1043, 972, 893, 804, 680, 667 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₇H₂₀N₄Na: 303.1580; found 303.1579.

4.4.7. 1-(3-Nitrophenyl)-4-[(E)-oct-1-enyl]-1H-1,2,3-triazole (**3ah**). Light-yellow solid, hexane-EtOAc (7:3) as eluent, mp. 80-81 °C. ¹H NMR (600 MHz, CDCl₃): $\delta = 0.89$ (t, J = 6.8 Hz, 3H), 1.27-1.44 (m, 6H), 1.46-1.53 (m, 2H), 2.22-2.28 (m, 2H), 6.45 (d, J = 15.8 Hz, 1H), 6.57 (dt, J = 15.8 and 6.8 Hz, 1H), 7.74 (t, J = 8.2 Hz, 1H), 7.98 (s, 1H), 8.17-8.21 (m, 1H), 8.26-8.30 (m, 1H), 8.57 (t, J = 2.0 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 14.1$ (CH₃), 22.6 (CH₂), 28.8 (CH₂), 28.9 (CH₂), 31.7 (CH₂), 33.0 (CH₂), 114.9 (CH_{arom}), 117.0 (=CH), 117.3 (=CH), 122.9 (CH_{arom}), 125.7 (CH_{arom}), 130.9 (CH_{arom}), 135.6 (=CH), 137.8 (C_{arom}), 147.8 (=C), 148.9 (C_{arom}). IR (KBr): $\nu = 3143$, 2920, 2852, 1541, 1348, 1265, 1043, 966, 885, 800, 734, 704 cm⁻¹. HRMS (ESI): *m/z* [M + Na]⁺ calcd for C₁₆H₂₀O₂N₄Na: 323.1478; found 323.1479.

4.4.8. *1-Phenyl-4-[(E)-2-phenylethenyl]-1H-1,2,3-triazole* (**3ba**). Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 149-150 °C. ¹H NMR (600 MHz, CDCl₃): δ = 7.15 (d, *J* = 16.5 Hz, 1H), 7.26-7.31 (m, 1H), 7.34-7.40 (m, 2H), 7.42 (d, *J* = 16.5 Hz, 1H), 7.42-7.47 (m, 1H), 7.50-7.56 (m, 4H), 7.73-7.78 (m, 2H), 8.01 (s, 1H). ¹³C NMR (150 MHz, CDCl₃): δ = 116.2 (=CH), 118.2 (=CH), 120.4 (2 × CH_{arom}), 126.5 (2 × CH_{arom}), 128.1 (CH_{arom}), 128.7 (2 × CH_{arom}), 129.7 (2 × CH_{arom}), 131.3 (=CH), 136.6 (C_{arom}), 136.9 (C_{arom}), 146.8 (=C). IR (KBr): v = 3130, 1504, 1232, 1043, 964, 756, 688 cm⁻¹. HRMS (ESI): *m/z* [M + Na]⁺ calcd for C₁₆H₁₃N₃Na: 270.1001; found 270.1001.

4.4.9. 1-(4-Methoxyphenyl)-4-[(E)-2-phenylethenyl]-1H-1,2,3-triazole (**3bb** $). White solid, hexane-EtOAc (7:3) as eluent, mp. 153-154 °C. ¹H NMR (600 MHz, DMSO-d₆): <math>\delta = 3.84$ (s, 3H), 7.14-7.18 (m, 2H), 7.26 (d, J = 16.5 Hz, 1H), 7.28-7.32 (m, 1H), 7.37 (d, J = 16.5 Hz, 1H), 7.38-7.42 (m, 2H), 7.60-7.64 (m, 2H), 7.81-7.85 (m, 2H), 8.87 (s, 1H). ¹³C NMR (150 MHz, DMSO-d₆): $\delta = 55.5$ (CH₃), 114.8 (2 × CH_{arom}), 117.0 (=CH),

119.9 (=CH), 121.5 (2 × CH_{arom}), 126.3 (2 × CH_{arom}), 127.8 (CH_{arom}), 128.7 (2 × CH_{arom}), 129.9 (C_{arom}), 130.0 (=CH), 136.4 (C_{arom}), 145.9 (=C), 159.2 (C_{arom}). IR (KBr): v = 3118, 1515, 1245, 1232, 1035, 1026, 962, 833, 815, 750, 704, 692 cm⁻¹. HRMS (ESI): <math>m/z [M + Na]⁺ calcd for C₁₇H₁₅ON₃Na: 300.1107; found 300.1106.

4.4.10. 1-(4-Methylphenyl)-4-[(E)-2-phenylethenyl]-1H-1,2,3-triazole (**3bc**). Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 156-157 °C. ¹H NMR (500 MHz, CDCl₃): δ = 2.42 (s, 3H), 7.14 (d, *J* = 16.6 Hz, 1H), 7.25-7.40 (m, 5H), 7.41 (d, *J* = 16.6 Hz, 1H), 7.49-7.54 (m, 2H), 7.60-7.65 (m, 2H), 7.98 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 21.1 (CH₃), 116.2 (=CH), 118.3 (=CH), 120.3 (2 × CH_{arom}), 126.5 (2 × CH_{arom}), 128.0 (CH_{arom}), 128.7 (2 × CH_{arom}), 130.2 (2 × CH_{arom}), 131.3 (=CH), 134.6 (C_{arom}), 136.6 (C_{arom}), 138.9 (C_{arom}), 146.5 (=C). IR (KBr): v = 3120, 1517, 1215, 962, 839, 767, 750, 694 cm⁻¹. HRMS (ESI): *m*/*z* [M + Na]⁺ calcd for C₁₇H₁₅N₃Na: 284.1158; found 284.1157.

4.4.11. 1-(2-Methylphenyl)-4-[(E)-2-phenylethenyl]-1H-1,2,3-triazole (**3bd**). Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 106-107 °C. ¹H NMR (600 MHz, CDCl₃): δ = 2.25 (s, 3H), 7.17 (d. *J* = 16.1 Hz, 1H), 7.26-7.31 (m, 1H), 7.32-7.48 (m, 7H), 7.51-7.55 (m, 2H), 7.76 (s, 1H). ¹³C NMR (150 MHz, CDCl₃): δ = 17.9 (CH₃), 116.3 (=CH), 121.9 (=CH), 125.9 (CH_{arom}), 126.5 (2 × CH_{arom}), 126.8 (CH_{arom}), 128.0 (CH_{arom}), 128.7 (2 × CH_{arom}), 129.8 (CH_{arom}), 131.0 (CH_{arom}), 131.5 (=CH), 133.6 (C_{arom}), 136.4 (C_{arom}), 136.7 (C_{arom}), 145.9 (=C). IR (KBr): v = 3134, 1504, 1041, 966, 761, 707, 692 cm⁻¹. HRMS (ESI): *m*/*z* [M + Na]⁺ calcd for C₁₇H₁₅N₃Na: 284.1158; found 284.1158.

4.4.12. 1-(3-Nitrophenyl)-4-[(E)-2-phenylethenyl]-1H-1,2,3-triazole (**3bh**). Yellow solid, hexane-EtOAc (7:3) as eluent, mp. 124-125 °C. ¹H NMR (600 MHz, CDCl₃): δ = 7.16 (d, *J* = 16.5 Hz, 1H), 7.30-7.34 (m, 1H), 7.37-7.42 (m, 2H), 7.48 (d, *J* = 16.5 Hz, 1H), 7.53-7.57 (m, 2H), 7.77 (t, *J* = 8.2 Hz, 1H), 8.12 (s, 1H), 8.22-8.25 (m, 1H), 8.30-8.33 (m, 1H), 8.62 (t, *J* = 2.0 Hz, 1H). ¹³C NMR (150 MHz, DMSO-d₆): δ = 114.4 (CH_{arom}), 116.5 (=CH), 120.3 (=CH), 122.9 (CH_{arom}), 125.8 (CH_{arom}), 126.4 (2 × CH_{arom}), 128.0 (CH_{arom}), 128.7 (2 × CH_{arom}), 130.7 (=CH), 131.5 (CH_{arom}), 136.1 (C_{arom}), 137.0 (C_{arom}), 146.4 (=C), 148.4 (C_{arom}). IR (KBr): v = 3139, 3085, 1537, 1494, 1346, 1217, 1045, 968, 883, 871, 798, 748, 734, 702, 686, 669 cm⁻¹. HRMS (ESI): *m*/*z* [M + Na]⁺ calcd for C₁₆H₁₂O₂N₄Na: 315.0854; found 315.0855.

4.4.13. 4-[(E)-5-Chloropent-1-enyl]-1-phenyl-1H-1,2,3-triazole (3ca). Off-white solid,

hexane-EtOAc (7:3) as eluent, mp. 69-70 °C. ¹H NMR (500 MHz, CDCl₃): δ = 1.92-2.00 (m, 2H), 2.37-2.44 (m, 2H), 3.59 (t, J = 6.8 Hz, 2H), 6.84-6.51 (m, 2H), 7.40-7.44 (m, 1H), 7.48-7.53 (m, 2H), 7.70-7.74 (m, 2H), 7.88 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 29.9 (CH₂), 31.6 (CH₂), 44.2 (CH₂), 117.7 (=CH), 119.2 (=CH), 120.3 (2 × CH_{arom}), 128.6 (CH_{arom}), 129.7 (2 × CH_{arom}), 131.8 (=CH), 136.9 (C_{arom}), 146.5 (=C). IR (KBr): v = 3122, 2956, 1598, 1504, 1230, 1045, 970, 759, 688 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₃H₁₄N₃CINa: 270.0768; found 270.0768.

4.4.14. 4-[(*E*)-5-Chloropent-1-enyl]-1-(4-methoxyphenyl)-1H-1,2,3-triazole (**3***c***b**). Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 76-77 °C. ¹H NMR (600 MHz, CDCl₃): $\delta = 1.94$ -2.00 (m, 2H), 2.38-2.44 (m, 2H), 3.59 (t, *J* = 6.8 Hz, 2H), 3.86 (s, 3H), 6.44-6.52 (m, 2H), 6.99-7.03 (m, 2H), 7.59-7.63 (m, 2H), 7.78 (s, 1H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 29.9$ (CH₂), 31.7 (CH₂), 44.2 (CH₂), 55.6 (CH₃), 114.7 (2 × CH_{arom}), 117.9 (=CH), 119.3 (=CH), 122.0 (2 × CH_{arom}), 130.4 (C_{arom}), 131.7 (=CH), 146.3 (=C), 159.7 (C_{arom}). IR (KBr): $\nu = 3132$, 2958, 2839, 1519, 1257, 1218, 1110, 1028, 970, 837, 815 cm⁻¹. HRMS (ESI): *m*/*z* [M + Na]⁺ calcd for C₁₄H₁₆ON₃ClNa: 300.0874; found 300.0872.

4.4.15. 4-[(E)-5-Chloropent-1-enyl]-1-(4-methylphenyl)-1H-1,2,3-triazole (3cc). Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 80-81 °C. ¹H NMR (500 MHz, CDCl₃): $\delta = 1.92$ -1.99 (m, 2H), 2.36-2.43 (m, 2H), 2.40 (s, 3H), 3.58 (t, J = 6.8 Hz, 2H), 6.47-6.50 (m, 2H), 7.26-7.31 (m, 2H), 7.56-7.61 (m, 2H), 7.86 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 20.9$ (CH₃), 29.8 (CH₂), 31.5 (CH₂), 44.1 (CH₂), 117.6 (=CH), 119.0 (=CH), 120.1 (2 × CH_{arom}), 130.0 (2 × CH_{arom}), 131.7 (=CH), 134.5 (C_{arom}), 138.6 (C_{arom}), 146.1 (=C). IR (KBr): $\nu = 3149$, 3049, 2925, 1515, 1444, 1265, 1230, 1045, 968, 817, 746 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₄H₁₆N₃ClNa: 284.0924; found 284.0923.

4.4.16. 4-[(E)-5-Chloropent-1-enyl]-1-(4-fluorophenyl)-1H-1,2,3-triazole (3ce). Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 80-82 °C. ¹H NMR (500 MHz, CDCl₃): $\delta = 1.91-2.00$ (m, 2H), 2.36-2.44 (m, 2H), 3.59 (t, J = 6.3 Hz, 2H), 6.46-6.50 (m, 2H), 7.16-7.23 (m, 2H), 7.66-7.73 (m, 2H), 7.87 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 29.9$ (CH₂), 31.6 (CH₂), 44.3 (CH₂), 116.6 (d, J = 22.7 Hz, 2 × CH_{arom}), 117.9 (=CH), 119.1 (=CH), 122.3 (d, J = 9.3 Hz, 2 × CH_{arom}), 132.0 (=CH), 133.2 (d, J = 2.0 Hz, C_{arom}), 146.6 (=C), 162.2 (d, J = 249.3 Hz, C_{arom}). IR (KBr): v = 3126, 1504, 1444, 1230, 1197, 1047, 972, 833, 744 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for

C₁₃H₁₃N₃FClNa: 288.0674; found 288.0673.

4.4.17. $1-(3\text{-}Acetoxyphenyl)-4-[(E)-5\text{-}chloropent-1\text{-}enyl]-1H-1,2,3\text{-}triazole}$ (3cf). Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 90-91 °C. ¹H NMR (600 MHz, CDCl₃): $\delta = 1.95$ -2.02 (m, 2H), 2.40-2.47 (m, 2H), 2.68 (s, 3H), 3.61 (t, J = 6.8 Hz, 2H), 6.52 (d, J = 16.5 Hz, 1H), 6.54 (dt, J = 16.5 and 6.2 Hz, 1H), 7.65 (t, J = 7.8 Hz, 1H), 7.97 (s, 1H), 7.99-8.04 (m, 2H), 8.27 (br s, 1H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 26.7$ (CH₃), 29.9 (CH₂), 31.6 (CH₂), 44.2 (CH₂), 117.6 (=CH), 118.9 (=CH), 119.4 (CH_{arom}), 124.6 (CH_{arom}), 128.3 (CH_{arom}), 130.2 (CH_{arom}), 132.5 (=CH), 137.3 (C_{arom}), 138.4 (C_{arom}), 146.8 (=C), 196.7 (C=O). IR (KBr): v = 3128, 2937, 1681, 1591, 1494, 1450, 1359, 1265, 1045, 999, 966, 792, 686 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₅H₁₆ON₃ClNa: 312.0874; found 312.0875.

4.4.18. 4-[(E)-5-Chloropent-1-enyl]-1-(3-cyanophenyl)-1H-1,2,3-triazole (3cg). Light-brown solid, hexane-EtOAc (7:3) as eluent, mp. 62-63 °C. ¹H NMR (600 MHz, CDCl₃): $\delta = 1.95$ -2.02 (m, 2H), 2.41-2.47 (m, 2H), 3.61 (t, J = 6.8 Hz, 2H), 6.50 (d, J = 16.5 Hz, 1H), 6.55 (dt, J = 16.5 and 6.8 Hz, 1H), 7.67 (t, J = 7.3 Hz, 1H), 7.71-7.75 (m, 1H), 7.90 (s, 1H), 8.01-8.05 (m, 1H), 8.05-8.07 (m, 1H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 29.9$ (CH₂), 31.5 (CH₂), 44.2 (CH₂), 114.1 (C_{arom}), 117.2 (=CH), 117.4 (=C), 118.7 (=CH), 123.3 (CH_{arom}), 124.2 (CH_{arom}), 130.9 (CH_{arom}), 131.9 (CH_{arom}), 132.9 (=CH), 137.5 (C_{arom}), 147.1 (=C). IR (KBr): v = 3134, 2233, 1587, 1487, 1444, 1043, 999, 966, 794, 680 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₄H₁₃N₄ClNa: 295.0722; found 295.0723.

4.4.19. 4-[(*E*)-5-Chloropent-1-enyl]-1-(3-nitrophenyl)-1H-1,2,3-triazole (3ch). Light-yellow solid, hexane-EtOAc (7:3) as eluent, mp. 100-101 °C. ¹H NMR (600 MHz, CDCl₃): $\delta = 1.96$ -2.02 (m, 2H), 2.42-2.48 (m, 2H), 3.61 (t, *J* = 6.8 Hz, 2H), 6.51 (d, *J* = 16.4 Hz, 1H), 6.57 (dt, *J* = 16.4 and 6.8 Hz, 1H), 7.75 (t, *J* = 8.2 Hz, 1H), 8.00 (s, 1H), 8.18-8.21 (m, 1H), 8.28-8.31 (m, 1H), 8.58 (t, *J* = 2.0 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 29.9$ (CH₂), 31.6 (CH₂), 44.2 (CH₂), 114.9 (CH_{arom}), 117.3 (=CH), 118.6 (=CH), 123.0 (CH_{arom}), 125.7 (CH_{arom}), 131.0 (=CH), 133.0 (CH_{arom}), 137.6 (C_{arom}), 147.2 (=C), 148.9 (C_{arom}). IR (KBr): v = 3151, 3093, 1537, 1494, 1346, 1224, 1047, 964, 883, 871, 798, 734, 669 cm⁻¹. HRMS (ESI): *m*/*z* [M + Na]⁺ calcd for C₁₃H₁₃O₂N₄ClNa: 315.0620; found 315.0621.

4.4.20. 1-Phenyl-4-[(Z)-1-(trimethylsilyl)hex-1-enyl]-1H-1,2,3-triazole (6aa). Yellow

liquid, hexane-EtOAc (95:5) as eluent. ¹H NMR (600 MHz, CDCl₃): $\delta = 0.27$ (s, 9H), 0.93 (t, J = 6.8 Hz, 3H), 1.36-1.51 (m, 4H), 2.31-2.37 (m, 2H), 6.63 (t, J = 7.4 Hz, 1H), 7.39-7.43 (m, 1H), 7.48-7.54 (m, 2H), 7.71 (s, 1H), 7.72-7.77 (m, 2H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 0.7$ (Me₃Si), 13.9 (CH₃), 22.3 (CH₂), 31.7 (CH₂), 31.8 (CH₂), 117.1 (=CH), 120.0 (2 × CH_{arom}), 128.2 (CH_{arom}), 129.5 (2 × CH_{arom}), 137.0 (C_{arom}), 149.3 (=CH), 152.4 (=C). IR (KBr): v = 2954, 2925, 2856, 1514, 1247, 1222, 1045, 877, 839 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₇H₂₅N₃NaSi: 322.1707; found 322.1706.

4.4.21. 1-(4-Methoxyphenyl)-4-[(Z)-1-(trimethylsilyl)hex-1-enyl]-1H-1,2,3-triazole (**6ab**). Yellow liquid, hexane-EtOAc (9:1) as eluent. ¹H NMR (600 MHz, CDCl₃): $\delta = 0.27$ (s, 9H), 0.93 (t, J = 6.8 Hz, 3H), 1.36-1.50 (m, 4H), 2.30-2.37 (m, 2H), 3.84 (s, 3H), 6.62 (br s, 1H), 6.97-7.02 (m, 2H), 7.58-7.70 (m, 3H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 0.9$ (Me₃Si), 14.0 (CH₃), 22.4 (CH₂), 31.9 (2 × CH₂), 55.5 (CH₃), 114.6 (2 × CH_{arom}), 117.5 (=CH), 121.8 (2 × CH_{arom}), 129.8 (=C), 130.7 (C_{arom}), 149.1 (=CH), 152.4 (=C), 159.5 (C_{arom}). IR (KBr): v = 2956, 2929, 2856, 1595, 1514, 1463, 1253, 1222, 1039, 987, 877, 833, 759 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₈H₂₇ON₃NaSi: 352.1810; found 352.1811.

4.4.22. *1*-(*4*-*Methylphenyl*)-4-[(*Z*)-1-(*trimethylsilyl*)*hex*-1-*enyl*]-1*H*-1,2,3-*triazole* (*6ac*). Yellowish liquid, hexane-EtOAc (95:5) as eluent. ¹H NMR (600 MHz, CDCl₃): $\delta = 0.28$ (s, 9H), 0.93 (t, *J* = 6.8 Hz, 3H), 1.35-1.49 (m, 4H), 2.30-2.36 (m, 2H), 2.37 (s, 3H), 6.61 (t, *J* = 7.6 Hz, 1H), 7.24-7.28 (m, 2H), 7.58-7.62 (m, 2H), 7.70 (s, 1H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 0.7$ (Me₃Si), 13.8 (CH₃), 20.8 (CH₃), 22.2 (CH₂), 31.7 (CH₂), 31.7 (CH₂), 117.0 (=CH), 119.8 (2 × CH_{arom}), 129.6 (=C), 129.9 (2 × CH_{arom}), 134.7 (C_{arom}), 138.0 (C_{arom}), 148.9 (=CH), 152.3 (=C). IR (KBr): v = 2954, 2925, 2856, 1515, 1247, 1222, 1045, 1028, 987, 877, 839, 758 cm⁻¹. HRMS (ESI): *m*/*z* [M + Na]⁺ calcd for C₁₈H₂₇N₃NaSi: 336.1861; found 336.1862.

4.4.23. 1-(2-Methylphenyl)-4-[(Z)-1-(trimethylsilyl)hex-1-enyl]-1H-1,2,3-triazole (**6ad** $). Yellowish liquid, hexane-EtOAc (95:5) as eluent. ¹H NMR (600 MHz, CDCl₃): <math>\delta = 0.27$ (s, 9H), 0.93 (t, J = 7.2 Hz, 3H), 1.36-1.51 (m, 4H), 2.23 (s, 3H), 2.32-2.37 (m, 2H), 6.68 (t, J = 7.6 Hz, 1H), 7.29-7.41 (m, 4H), 7.46 (s, 1H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 0.8$ (Me₃Si), 14.0 (CH₃), 17.9 (CH₃), 22.5 (CH₂), 31.9 (CH₂), 31.9 (CH₂), 120.9 (=CH), 125.9 (CH_{arom}), 126.7 (CH_{arom}), 129.4 (=C), 129.5 (CH_{arom}), 131.3 (CH_{arom}), 133.6 (C_{arom}), 136.7 (C_{arom}), 149.3 (=CH), 151.4 (=C). IR (KBr): v = 2954, 2927, 2856, 1500, 1463, 1247, 1043, 877, 840, 761 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for

C₁₈H₂₇N₃NaSi: 336.1861; found 336.1861.

4.4.24. 1-(4-Fluorophenyl)-4-[(Z)-1-(trimethylsilyl)hex-1-enyl]-1H-1,2,3-triazole (**6ae**). Yellowish liquid, hexane-EtOAc (9:1) as eluent. ¹H NMR (600 MHz, CDCl₃): δ = 0.27 (s, 9H), 0.93 (t, *J* = 6.8 Hz, 3H), 1.35-1.49 (m, 4H), 2.30-2.36 (m, 2H), 6.61 (t, *J* = 7.6 Hz, 1H), 7.15-7.21 (m, 2H), 7.69-7.74 (m, 3H). ¹³C NMR (150 MHz, CDCl₃): δ = 0.7 (Me₃Si), 13.8 (CH₃), 22.3 (CH₂), 31.7 (2 × CH₂), 116.4 (d, *J* = 23.1 Hz, 2 × CH_{arom}), 117.2 (=CH), 122.0 (d, *J* = 8.7 Hz, 2 × CH_{arom}), 129.5 (=C), 133.3 (C_{arom}), 149.3 (=CH), 152.7 (=C), 161.9 (d, *J* = 248.5 Hz, C_{arom}). IR (KBr): v = 2956, 2927, 2856, 1514, 1245, 1222, 1045, 877, 839 cm⁻¹. HRMS (ESI): *m*/*z* [M + Na]⁺ calcd for C₁₇H₂₄N₃FNaSi: 340.1611; found 340.1612.

4.4.25. 1-(3-Acetoxyphenyl)-4-[(Z)-1-(trimethylsilyl)hex-1-enyl]-1H-1,2,3-triazole (**6af**). Yellowish liquid, hexane-EtOAc (8:2) as eluent. ¹H NMR (600 MHz, CDCl₃): $\delta = 0.29$ (s, 9H), 0.93 (t, J = 6.8 Hz, 3H), 1.36-1.50 (m, 4H), 2.31-2.38 (m, 2H), 2.66 (s, 3H), 6.62 (t, J = 7.5 Hz, 1H), 7.58-7.65 (m, 1H), 7.89 (s, 1H), 7.94-7.99 (m, 1H), 8.00-8.05 (m, 1H), 8.29 (s, 1H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 0.8$ (Me₃Si), 14.0 (CH₃), 22.4 (CH₃), 26.7 (CH₂), 31.8 (CH₂), 31.8 (CH₂), 117.2 (=CH), 119.3 (CH_{arom}), 124.3 (CH_{arom}), 127.9 (CH_{arom}), 129.6 (=C), 130.1 (CH_{arom}), 137.5 (C_{arom}), 138.3 (C_{arom}), 149.6 (=CH), 153.1 (=C), 196.7 (C=O). IR (KBr): v = 2956, 2927, 2858, 1693, 1591, 1448, 1357, 1259, 1224, 1045, 877, 840, 792, 686 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₉H₂₇ON₃NaSi: 364.1810; found 364.1811.

4.4.26. 1-(3-Cyanophenyl)-4-[(Z)-1-(trimethylsilyl)hex-1-enyl]-1H-1,2,3-triazole (**6ag**). White solid, hexane-EtOAc (9:1) as eluent, mp. 98-99 °C. ¹H NMR (600 MHz, CDCl₃): $\delta = 0.27$ (s, 9H), 0.94 (t, J = 6.8 Hz, 3H), 1.35-1.51 (m, 4H), 2.31-2.38 (m, 2H), 6.62 (t, J = 7.5 Hz, 1H), 7.63-7.72 (m, 2H), 7.75 (s, 1H), 8.03-8.08 (m, 2H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 0.8$ (Me₃Si), 14.0 (CH₃), 22.4 (CH₃), 31.8 (CH₂), 31.9 (CH₂), 114.0 (CH_{arom}), 116.8 (=CH), 117.5 (=C), 123.1 (CH_{arom}), 124.1 (CH_{arom}), 129.4 (=C), 130.8 (CH_{arom}), 131.5 (CH_{arom}), 137.7 (C_{arom}), 150.1 (=CH), 153.4 (=C). IR (KBr): v = 3149, 2954, 2929, 2233, 1732, 1589, 1487, 1247, 1226, 1051, 1004, 883, 839, 758, 682 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₈H₂₄N₄NaSi: 347.1662; found 347.1661.

4.4.27. 1-(3-Nitrophenyl)-4-[(Z)-1-(trimethylsilyl)hex-1-enyl]-1H-1,2,3-triazole (**6ah**). Yellow solid, hexane-EtOAc (9:1) as eluent, mp. 100-101 °C. ¹H NMR (600 MHz, CDCl₃): $\delta = 0.28$ (s, 9H), 0.94 (t, J = 6.8 Hz, 3H), 1.36-1.51 (m, 4H), 2.32-2.38 (m, 2H), 6.62 (t, J = 7.6 Hz, 1H), 7.72-7.76 (m, 1H), 7.84 (s, 1H), 8.19-8.23 (m, 1H), 8.25-8.29 (m, 1H), 8.57-8.59 (m, 1H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 0.8$ (Me₃Si), 14.0 (CH₃), 22.4 (CH₃), 31.8 (CH₂), 31.9 (CH₂), 114.8 (CH_{arom}), 116.9 (=CH), 122.7 (CH_{arom}), 125.7 (CH_{arom}), 129.4 (=C), 130.8 (CH_{arom}), 137.9 (C_{arom}), 148.9 (C_{arom}), 150.1 (=CH), 153.6 (=C). IR (KBr): v = 3139, 3101, 2952, 2925, 2860, 1539, 1350, 1244, 1228, 1043, 879, 839, 808, 736, 669 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₇H₂₄O₂N₄NaSi: 367.1560; found 367.1560.

4.4.28. 1-Phenyl-4-[(Z)- 2-phenyl-1-(trimethylsilyl)ethenyl]-1H-1,2,3-triazole (**6ba**). Off-white solid, hexane-EtOAc (9:1) as eluent, mp. 111-112 °C. ¹H NMR (600 MHz, CDCl₃): $\delta = 0.07$ (s, 9H), 7.28-7.37 (m, 5H), 7.40-7.45 (m, 1H), 7.50-7.55 (m, 2H), 7.76-7.80 (m, 2H), 7.84 (s, 1H), 7.90 (s, 1H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 0.7$ (Me₃Si), 117.5 (=CH), 120.3 (2 × CH_{arom}), 127.4 (CH_{arom}), 127.9 (2 × CH_{arom}), 128.4 (CH_{arom}), 128.5 (2 × CH_{arom}), 129.7 (2 × CH_{arom}), 133.8 (C_{arom}), 137.1 (C_{arom}), 139.4 (=C), 146.1 (=CH), 152.4 (=C). IR (KBr): v = 2952, 1598, 1500, 1417, 1247, 1224, 1047, 1035, 840, 756, 690 cm⁻¹. HRMS (ESI): *m*/*z* [M + Na]⁺ calcd for C₁₉H₂₁N₃NaSi: 342.1393; found 342.1394.

4.4.29. 1-(4-Methoxyphenyl)-4-[(Z)-2-phenyl-1-(trimethylsilyl)ethenyl]-1H-1,2,3-

triazole (6bb). White solid, hexane-EtOAc (9:1) as eluent, mp. 100-102 °C. ¹H NMR (600 MHz, CDCl₃): $\delta = 0.07$ (s, 9H), 3.86 (s, 3H), 7.00-7.04 (m, 2H), 7.28-7.37 (m, 5H), 7.65-7.69 (m, 2H), 7.81 (s, 1H), 7.83 (s, 1H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 0.8$ (Me₃Si), 55.6 (CH₃), 114.7 (2 × CH_{arom}), 117.7 (=CH), 121.9 (2 × CH_{arom}), 127.4 (CH_{arom}), 127.9 (2 × CH_{arom}), 128.5 (2 × CH_{arom}), 130.6 (C_{arom}), 133.9 (C_{arom}), 139.5 (=C), 145.9 (=CH), 152.2 (=C), 159.6 (C_{arom}). IR (KBr): v = 2956, 1515, 1255, 1226, 1043, 839, 754, 698 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₂₀H₂₀ON₃NaSi: 369.1264; found 369.1265.

4.4.30. 1-(4-Methylphenyl)-4-[(Z)-2-phenyl-1-(trimethylsilyl)ethenyl]-1H-1,2,3-

triazole (*6bc*). White solid, hexane-EtOAc (9:1) as eluent, mp. 112-113 °C. ¹H NMR (600 MHz, CDCl₃): $\delta = 0.07$ (s, 9H), 2.46 (s, 3H), 7.27-7.37 (m, 7H), 7.62-7.67 (m, 2H), 7.81-7.87 (m, 2H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 0.8$ (Me₃Si), 21.1 (CH₃), 117.5 (=CH), 120.2 (2 × CH_{arom}), 127.4 (CH_{arom}), 127.9 (2 × CH_{arom}), 128.5 (2 × CH_{arom}), 130.2 (2 × CH_{arom}), 133.9 (C_{arom}), 134.9 (C_{arom}), 138.5 (C_{arom}), 139.5 (=C), 145.9 (=CH), 152.3 (=C). IR (KBr): v = 2954, 1519, 1247, 1224, 1031, 989, 840, 817, 754, 698, 667 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₂₀H₂₀N₃NaSi: 353.1315;

found 353.1316.

4.4.31. 1-(2-Methylphenyl)-4-[(Z)-2-phenyl-1-(trimethylsilyl)ethenyl]-1H-1,2,3-triazole (6bd). Yellowish liquid, hexane-EtOAc (95:5) as eluent. ¹H NMR (600 MHz, CDCl₃): $\delta = 0.07$ (s, 9H), 2.24 (s, 3H), 7.25-7.41 (m, 9H), 7.65 (s, 1H), 7.89 (s, 1H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 0.6$ (Me₃Si), 17.7 (CH₃), 121.1 (=CH), 125.7 (CH_{arom}), 126.6 (CH_{arom}), 127.3 (CH_{arom}), 127.7 (2 × CH_{arom}), 128.3 (2 × CH_{arom}), 129.5 (CH_{arom}), 131.2 (CH_{arom}), 133.5 (C_{arom}), 136.4 (C_{arom}), 139.3 (=C), 145.8 (=CH), 151.1 (=C). IR (KBr): v = 2952, 1498, 1247, 1045, 840, 761, 698 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₂₀H₂₀N₃NaSi: 353.1315; found 353.1314.

4.4.32. 1-(4-Fluorophenyl)-4-[(Z)-2-phenyl-1-(trimethylsilyl)ethenyl]-1H-1,2,3-triazole (**6be**). White solid, hexane-EtOAc (9:1) as eluent, mp. 123-124 °C. ¹H NMR (600 MHz, CDCl₃): $\delta = 0.07$ (s, 9H), 7.18-7.24 (m, 2H), 7.28-7.37 (m, 5H), 7.72-7.77 (m, 2H), 7.82 (s, 1H), 7.86 (s, 1H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 0.7$ (Me₃Si), 116.6 (d, J = 23.1 Hz, $2 \times CH_{arom}$), 117.6 (=CH), 122.2 (d, J = 8.6 Hz, $2 \times CH_{arom}$), 127.5 (CH_{arom}), 127.9 ($2 \times CH_{arom}$), 128.5 ($2 \times CH_{arom}$), 133.4 (C_{arom}), 133.7 (C_{arom}), 139.3 (=C), 146.2 (=CH), 152.6 (=C), 162.2 (d, J = 248.5 Hz, C_{arom}). IR (KBr): v = 3112, 1514, 1228, 1053, 835, 761 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₉H₂₀N₃FNaSi: 360.1299; found 360.1300.

4.4.33. 1-(3-Acetoxyphenyl)-4-[(Z)-2-phenyl-1-(trimethylsilyl)ethenyl]-1H-1,2,3-triazole (**6bf**). White solid, hexane-EtOAc (8:2) as eluent, mp. 112-113 °C. ¹H NMR (600 MHz, CDCl₃): $\delta = 0.08$ (s, 9H), 2.69 (s, 3H), 7.29-7.38 (m, 5H), 7.66 (t, J = 7.6 Hz, 1H), 7.83 (s, 1H), 7.99 (s, 1H), 7.99-8.03 (m, 1H), 8.06-8.09 (m, 1H), 8.32 (br s, 1H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 0.7$ (Me₃Si), 26.7 (CH₃), 117.3 (=CH), 119.3 (CH_{arom}), 124.5 (CH_{arom}), 127.5 (CH_{arom}), 127.9 (2 × CH_{arom}), 128.1 (CH_{arom}), 128.5 (2 × CH_{arom}), 130.1 (CH_{arom}), 133.7 (C_{arom}), 137.5 (C_{arom}), 138.4 (C_{arom}), 139.3 (=C), 146.3 (=CH), 152.9 (=C), 196.7 (C=O). IR (KBr): $\nu = 2954$, 1693, 1591, 1488, 1448, 1357, 1259, 1226, 1047, 842, 792, 756, 698 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₂₁H₂₃ON₃NaSi: 384.1498; found 384.1499.

4.4.34. 1-(3-Cyanophenyl)-4-[(Z)-2-phenyl-1-(trimethylsilyl)ethenyl]-1H-1,2,3-triazole (*bbg*). White solid, hexane-EtOAc (9:1) as eluent, mp. 182-184 °C. ¹H NMR (600 MHz, CDCl₃): $\delta = 0.07$ (s, 9H), 7.29-7.39 (m, 5H), 7.66-7.74 (m, 2H), 7.82 (s, 1H), 7.94 (s, 1H), 8.07-8.12 (m, 2H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 0.7$ (Me₃Si), 114.1 (C_{arom}),

117.0 (=CH), 117.5 (=C), 123.3 (CH_{arom}), 124.2 (CH_{arom}), 127.6 (CH_{arom}), 127.9 (2 × CH_{arom}), 128.5 (2 × CH_{arom}), 130.8 (CH_{arom}), 131.7 (CH_{arom}), 133.5 (C_{arom}), 137.6 (C_{arom}), 139.1 (=C), 146.7 (=CH), 153.3 (=C). IR (KBr): v = 3138, 2235, 1589, 1498, 1444, 1245, 1228, 1047, 842, 802, 754, 696, 677 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₂₀H₂₀N₄NaSi: 367.1350; found 367.1349.

4.4.35. $1-(3-Nitrophenyl)-4-[(Z)-2-phenyl-1-(trimethylsilyl)ethenyl]-1H-1,2,3-triazole (6bh). Light-brown solid, hexane-EtOAc (8:2) as eluent, mp. 200 °C (dec). ¹H NMR (600 MHz, CDCl₃): <math>\delta = 0.08$ (s, 9H), 7.30-7.39 (m, 5H), 7.74-7.79 (m, 1H), 7.83 (s, 1H), 8.01 (s, 1H), 8.22-8.27 (m, 1H), 8.29-8.34 (m, 1H), 8.61-8.64 (m, 1H). ¹³C NMR (150 MHz, CDCl₃): $\delta = 0.7$ (Me₃Si), 114.9 (CH_{arom}), 117.1 (=CH), 122.8 (CH_{arom}), 125.7 (CH_{arom}), 127.7 (CH_{arom}), 127.9 (2 × CH_{arom}), 128.5 (2 × CH_{arom}), 130.9 (CH_{arom}), 133.5 (C_{arom}), 137.8 (C_{arom}), 139.1 (C_{arom}), 146.8 (=CH), 148.9 (C_{arom}), 153.4 (=C). IR (KBr): $\nu = 3138$, 1535, 1488, 1350, 1245, 1226, 1043, 889, 844, 806, 756, 734, 711, 696 cm⁻¹. HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₉H₂₀O₂N₄NaSi: 387.1248; found 387.1247.

Supplementary data

Supplementary data associated with this article can be found in the online version, at

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