Allylcyanocuprates from Butylallyltellurides

Priscila Castelani and João V. Comasseto*

Instituto de Química, Universidade de São Paulo, Avenida Prof. Lineu Prestes, 748, Cx.P. 26077, 05599-970 São Paulo, Brazil

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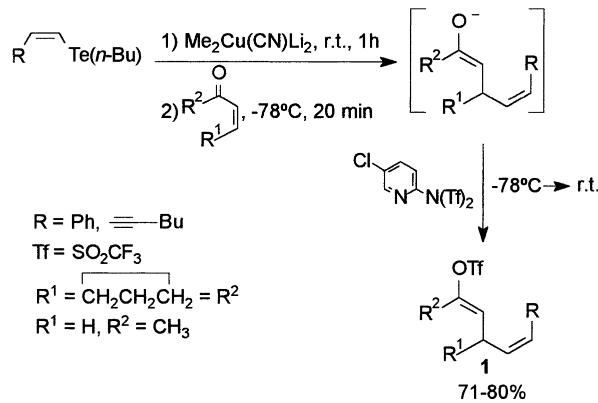
Lithium diallylcyanocuprates generated by reaction of allyl halides with lithium *n*-butyltellurolate followed by transmetalation with lithium dibutylcyanocuprate react with vinyl triflates leading to highly unsaturated hydrocarbons.

Introduction

The use of tellurium reagents and intermediates for synthetic purposes has been intensively studied in the course of the last two decades.[1] However, only recently it was reported the first application of a tellurium-based methodology in the synthesis of a complex natural product,[2] which consisted in the transformation of a *Z*-vinylic telluride into a *Z*-vinylic cuprate.[3] These Z-vinylic cuprates were also explored by us in the synthesis of vinyl triflates,[4] compounds widely used in coupling reactions due to the excellent leaving group properties of the trifluoromethanesulfonate group.[5] In view of the easy transformation of vinylic tellurides into vinylic cuprates, as well as the wide use of cuprates in organic synthesis,[6] we decided to extend the tellurium−copper exchange protocol to the preparation of allyl copper reagents. Allyl cuprates are difficult to prepare by classical routes in view of undesired side reactions,[7] only a few methods are available to access them, and in most of the cases, considerable quantities of Wurtz-type coupling products are formed.[8] Because of these aspects, this class of copper compounds was considered problematic and was little studied, but the reactivity of these cuprates is unique compared with alkyl or vinyl cyanocuprates, representing the most reactive organocopper reagents available.[8b] On the other hand, allylic tellurides are little studied species, since they react rapidly with oxygen to give tellurium-free oxygenated products.[9] Due to the instability of these reagents, they were prepared and used in a *one-pot* procedure, without isolation of tellurides.[10]

Scheme 1



Results and Discussion

In this paper we describe in detail for the first time the transformation of an allyltelluride into an allylcyanocuprate by transmetalation with dilithium dibutylcyanocuprate.[11] These intermediates were captured by reaction with vinyl triflates, leading to unsaturated systems. In the preparation of the vinyl triflates **1** some improvements were made in the methodology already established,[4] which consisted in the conjugated addition of Z-vinylic cyanocuprates, generated from Z-vinylic tellurides, to enones followed by O-functionalization obtaining vinyl triflates **1** with retention of the *Z* configuration. The use of 2-[*N*,*N*-bis(trifluoromethylsulfonyl)amino]-5-chloropyridine as the triflating agent increased the isolated yields of the reaction from 55 to 65% to 71−80%, without need of cosolvents such as HMPA (Scheme 1).

The method of choice to prepare the allylic tellurides **2** was through nucleophilic substitution by lithium

* Corresponding author. Tel: +55-11-30912176. Fax: +55-11-38155579. E-mail: jvcomass@iq.usp.br.

(1) (a) Petragnani, N. *Tellurium in Organic Synthesis: Best Synthetic Methods*; Academic Press: London, 1994. (b) Comasseto, J. V.; Barrientos-Astigarraga, R. E. *Aldrichim. Acta* **2000**, *33*, 66.

(2) Marino, J. P.; McClure, M. S.; Holub, D. P.; Comasseto, J. V.; Tucci, F. C. *J. Am. Chem. Soc.* **2002**, *124*, 1664.

(3) (a) Comasseto, J. V.; Berriel, J. N. *Synth. Commun.* **1990**, *20*, 1681. (b) Tucci, F. C.; Chieffi, A.; Comasseto, J. V. *Tetrahedron Lett.* **1992**, *33*, 5721. (c) Tucci, F. C.; Chieffi, A.; Comasseto, J. V.; Marino, J. P. *J. Org. Chem.* **1996**, *61*, 4975.

(4) Moraes, D. N.; Barrientos-Astigarraga, R E.; Castelani, P.; Comasseto, J. V. *Tetrahedron* **2000**, *56*, 3327.

(5) McMurry, J. E. *Acc. Chem. Res.* **1988**, *21*, 47.

(6) Lipshutz, B. H.; Sengupta, S. *Org. React.* **1992**, *41*, 135.

(7) (a) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. (b) Lipshutz, B. H. *Synlett* **1990**, 119. (c) Lipshutz, B. H.; Hackmann, C. *J. Org. Chem.* **1994**, *59*, 7437.

(8) (a) Lipshutz, B. H.; Elworthy, T. R. *J. Org. Chem.* **1990**, *55*, 1695. (b) Lipshutz, B. H.; Crow, R.; Dimock, S. H.; Ellsworth, E. L. *J. Am. Chem. Soc.* **1990**, *112*, 4063. (c) Lipshutz, B. H.; Elworthy, T. R. *Tetrahedron Lett.* **1990**, *31*, 477. (d) Stack, D. E.; Klein, W. R.; Rieke, R. D. *Tetrahedron Lett.* **1993**, *34*, 3063. (e) Piers, E.; Kaller, A. M. *Synlett* **1996**, 549. (f) Wang, X.; Wu, Y.; Jiang, S.; Singh, G. *J. Org. Chem.* **2000**, *65*, 8146. (g) Sato, A.; Ito, H.; Yamaguchi, Y.; Taguchi, T. *Tetrahedron Lett.* **2000**, *41*, 10239.

(9) (a) Comasseto, J. V.; Ferreira, J. T. B.; Fontanillas, J. A. *J. Organomet. Chem.* **1984**, *277*, 261. (b) Uemura, S.; Fukuzawa, S. I.; Ohe, K. *Tetrahedron Lett.* **1985**, *26*, 921.

(10) Kanda, T.; Kato, S.; Sugino, T.; Kambe, N.; Sonoda, N. *J. Organomet. Chem.* **1994**, *473*, 71.

(11) A preliminary account of this reaction was published: Barrientos-Astigarraga, R. E.; Castelani, P.; Comasseto, J. V.; Formiga, H. B.; da Silva, N. C.; Sumida, C. Y.; Vieira, M. L. *J. Organomet. Chem.* **2001**, *623*, 43.

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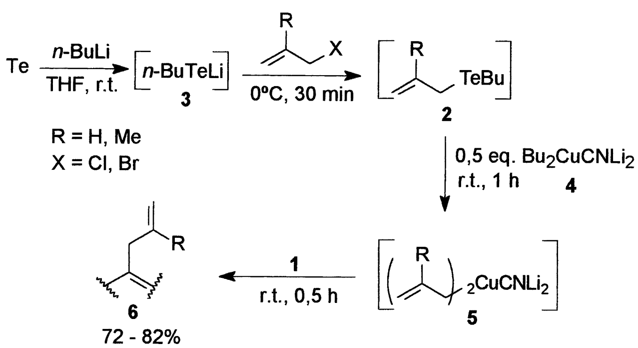
Scheme 2



n-butyltellurolate **3**, generated by reaction of *n*-butyllithium with elemental tellurium in THF at room temperature, on the allylic halides at 0 °C. The solution containing the allylic telluride **2** was then added at room temperature to a previously prepared solution of lithium dibutylcyanocuprate **4** in THF, leading presumably to the allylcyanocuprate **5**. The byproduct dibutyltelluride was formed in this step. Addition of vinyl triflates **1**[12] to the reaction mixture at room temperature resulted in the formation of the coupling products **7** in good yields (Scheme 2, Table 1).

Several features of this methodology are worthy of note. The attempted 1,4-addition of **5** (R = H) to cyclohexenone did not give the desired product in good yield. A complex mixture of products was formed instead, among them the expected 1,4-addition product. The use of additives ($BF_3{\cdot}Et_2O$, TMSCl) did not improve the yields.[13] In the reaction of **5a** with **1a**, the temperature of the coupling reaction influenced the reaction time. At −78 °C the time needed to consume **1a** was 12 h. By raising the temperature to 0 °C and to 25 °C, the reaction time was lowered to respectively 5 h and 30 min. The number of equivalents of cuprate used also influenced the course of the reaction. By using 1 equiv of the cuprate **5a** per equivalent of vinyltriflate **1a** the consumption of **1a** after 30 min was 50%; by using 2 and 3 equiv of **5a** per equivalent of **1a**, the consumption of **1a** was 80% and 100%, respectively, at the same reaction time. Another aspect of this reaction, which must be mentioned, is that the *n*-butyltellurolate anion can attack both α and γ sites of the allylhalide. In fact, cuprates generated from crotyl chloride led to a mixture of coupling products after reaction with vinyl triflates. In summary, the behavior of the allylcuprates generated by the telluride route parallels that of the allylcuprates generated by other methods,[5,6] but the present method presents the advantage of avoiding the prior generation of allyl Grignard or allyllithium intermediates and the isolation of organoelemental allylic precursors. The malodorous dibutyltelluride, often mentioned as a drawback of the tellurium-based synthetic methodologies, was easily transformed into odorless dibutyltellurium dichloride by treating the final reaction mixture with sodium hypochlorite. In addition, the transformation of the apolar dibutyltelluride into the polar dibutyltellurium dichloride facilitated the purification, since the difference in polarity between the hydrocarbon coupling product and the tellurium byproduct became considerable, a simple filtration through a short column of silica gel being enough to separate them.

Conclusion

In conclusion, the tellurium−copper exchange protocol constitutes a good method to prepare allylcyanocuprates, which, coupled with prior methodologies developed by us,[10] gives access to highly unsaturated hydrocarbons of defined stereochemistry. To the best of our knowledge, our work constitutes the first report concerning the generation of allylic cyanocuprates from the corresponding allylic tellurides.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on either a Bruker DPX-300, a Bruker DRX-500, or a Bruker AC-200 spectrometer using as internal standard tetramethylsilane and the central peak of $CDCl_3$ (77 ppm), respectively. Infrared spectra were recorded on a Perkin-Elmer 1600 spectrophotometer. Low-resolution mass spectra were obtained on a Finnigan 4021 spectrometer or on a GC/MS Hewlett-Packard 5988-8/5890 spectrometer, both operating at 70 eV. High-resolution mass spectra were obtained on a VG Autospec-Micromass operating at 70 eV. Elemental analysis was performed at the Microanalytical Laboratory of the Chemistry Institute, University of São Paulo. Column chromatography was carried out with Merck silica gel (230−400 mesh). Thin-layer chromatography (TLC) was performed on silica gel F-254 on aluminum. All solvents used were previously dried and distilled according to the usual methods.[14] THF and diethyl ether were distilled from sodium/benzophenone under N_2, immediately before use. Elemental tellurium (200 mesh) was purchased from Aldrich and dried overnight in an oven at 100 °C, and CuCN was dried under vacuum in an *Abderhalden* apparatus over P_2O_5, at 70 °C. Vinyl triflates were prepared according to the literature procedures.[4,12] The remaining chemicals were obtained from commercial sources. All operations were carried out in dried glassware, under an inert atmosphere of dry and deoxygenated N_2. The IUPAC names were obtained using the ACD/Lab web service, version 3.5, at http://www.acdlabs.com/ilab.

Typical Procedure for the Preparation of Vinylic Triflates from Ketones. To a cold (−78 °C) solution of lithium diisopropylamide (4.4 mmol) in THF (10 mL) was added slowly the corresponding ketone (4 mmol). After 1.5 h at this temperature, a solution of *N*-(2-pyridyl)triflimide (1.57 g, 4.4 mmol) in THF (5 mL) was introduced, and the reaction mixture was allowed to warm to room temperature and stirred for 5 h. The resulting mixture was extracted with ethyl acetate (30 mL) and washed with brine (3 × 30 mL). The organic phase was dried with magnesium sulfate, and the solvents were evaporated. The residue was purified by silica gel column chromatography eluting with hexane.

Cyclohex-1-enyl Trifluoromethanesulfonate (1a). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 5.77−5.75 (m, 1H); 2.34−2.30 (m, 2H); 2.20−2.16 (m, 2H); 1.81−1.76 (m, 2H); 1.63−1.58 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 149.4; 118.6 (quart., J_{C-F} = 445 Hz); 118.5; 27.6; 23.9; 22.7; 21.0. LR-MS *m/z* (rel int): 230 (15) (M^+), 79 (40), 69 (100).

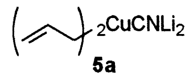
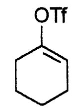
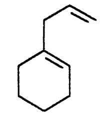
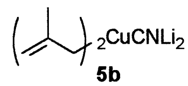
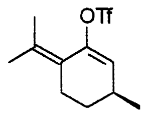
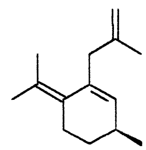
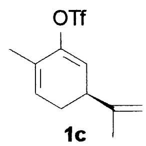
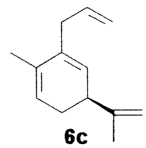
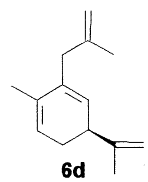
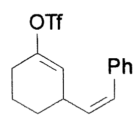
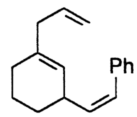
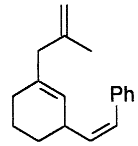
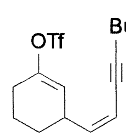
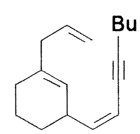
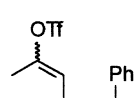
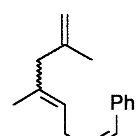
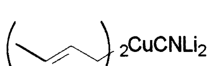
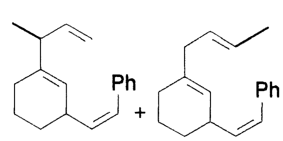
6-Isopropylidene-3-methylcyclohex-1-enyl Trifluoromethanesulfonate (1b). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 5.57 (d, J = 3.5 Hz, 1H); 2.55−2.51 (m, 2H); 2.26−2.20 (m, 1H); 1.93 (s, 3H); 1.89−1.83 (m, 1H); 1.78 (s, 3H); 1.32−1.25 (m, 1H); 1.08 (d, J = 7.1 Hz, 3H). ^{13}C NMR (125

(12) Other vinyl triflates were prepared using *N*-(2-pyridil)triflimide as the triflating agent, according to: Ritter, K. *Synthesis* **1993**, 735.

(13) Lipshutz, B. H.; Ellsworth, E. L.; Dimock, S. H.; Smith, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 4404.

(14) Perrin, D. D.; Amarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: London, 1980.

Table 1. Generation of the Allylcyanocuprates and Their Coupling Reaction with Vinylic Triflates

Entry	Allylcuprate 5	Vinyltriflate 1	Product 6	Yields (%)
1	 **5a**	 **1a**	 **6a**	72
2	 **5b**	 **1b**	 **6b**	78
3	**5a**	 **1c**	 **6c**	75
4	**5b**	**1c**	 **6d**	80
5	**5a**	 **1d**	 **6e**	82
6	**5b**	**1d**	 **6f**	80
7	**5a**	 **1e**	 **6g**	77
8	**5b**	 **1f**	 **6h**	73
9	 **5c**	**1d**		67

MHz, $CDCl_3$) δ (ppm): 147.0; 131.6; 125.8; 123.3; 118.5 (quart., J_{C-F} = 445 Hz); 31.0; 30.9; 27.6; 23.0; 22.4; 20.8. LR-MS *m/z* (rel int): 284 (47) (M^+), 151 (99), 119 (35), 109 (42), 91 (47), 81 (100), 69 (50), 55 (63). IR ν (cm^{-1}) (neat): 3083, 2973, 1658, 1421, 1212, 1143, 902, 609. Anal. Calcd for $C_{11}H_{15}F_3O_3S$: C, 46.47; H, 5.32. Found: C, 46.75; H, 5.25.

3-Isopropenyl-6-methylcyclohexa-1,5-dienyl Trifluoromethanesulfonate (1c). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 5.70–5.69 (m, 1H); 5.65 (d, J = 4.2 Hz, 1H); 4.82 (s, 2H); 3.17 (dq, J = 4.2 Hz, 8.8 Hz, 12.1 Hz, 1H); 2.37–2.32 (m, 1H); 2.29–2.25 (m, 1H); 1.82 (d, J = 1.8 Hz, 3H), 1.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 147.8; 145.3; 127.2;

126.2; 118.2 (quart., $J_{C-F} = 446$ Hz); 111.8; 41.4; 27.6; 20.5; 16.6. LR-MS *m*/*z* (rel int): 282 (30) (M^+), 149 (34), 121 (34), 107 (64), 93 (70), 91 (100), 77 (40). IR ν (cm^{-1}) (neat): 2963, 2931, 1654, 1417, 1208, 1144, 995, 886, 617. Anal. Calcd for $C_{11}H_{13}F_3O_3S$: C, 46.81; H, 4.64. Found: C, 46.67; H, 4.58.

Typical Procedure for the Coupling Reaction between Allylic Cuprates and Vinylic Triflates. To a suspension of elemental tellurium (0.838 g, 6.6 mmol) in THF (10 mL) under nitrogen was added dropwise *n*-butyllithium (from a 1.5 M solution in hexane, 4.4 mL, 6.6 mmol) at room temperature. A limpid yellow solution was formed. Then the appropriate allylic halide (6.6 mmol) was added at 0 °C, and the mixture was stirred at that temperature for 30 min. The resulting mixture was transferred, via cannula, at room temperature, to a two-necked rounded-bottomed flask containing a solution of $Bu_2CuCNLi_2$, prepared previously by the addition of *n*-butyllithium (from a 1.5 M solution in hexane, 4 mL, 6 mmol) at −75 °C to a THF (15 mL) suspension of CuCN (0.27 g, 3 mmol), and stirred at that temperature for 1 h. Then the corresponding vinylic triflate was added, and the mixture was stirred for 20 min, until the consumption of the triflate, monitored by TLC. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with a 1:1 solution of saturated aqueous NH_4Cl and NH_4OH (4 × 50 mL) and then with a 5% solution of NaClO, until the organic phase became colorless. The organic phase was dried with magnesium sulfate, and the solvents were evaporated. The residue was purified by silica gel column chromatography eluting with hexane.

1-Allylcyclohexene (6a). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 6.05 (ddt, J = 16.8 Hz, 10.1 Hz, 6.9 Hz, 1H); 5.70−5.67 (m, 1H); 5.32−5.24 (m, 2H); 2.92 (d, J = 6.6 Hz, 1H); 2.27−2.22 (m, 2H); 2.21−2.15 (m, 2H); 1.91−1.81 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 137.2, 136.5, 122.1, 115.6, 42.8, 28.6, 25.5, 23.2, 22.7. LR-MS *m*/*z* (rel int): 122(20) (M^+), 93 (17), 81 (100), 67 (14), 53 (20). IR ν (cm^{-1}) (neat): 2957, 2929, 2864, 1710, 1639, 1461, 1376, 1075, 1028, 994, 912.

6-Isopropylidene-3-methyl-1-(2-methallyl)cyclohexene (6b). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 5.38 (d, J = 3.1 Hz, 1H); 4.75−4.74 (m, 1H); 4.69−4.68 (m, 1H); 3.01−2.95 (m, 2H); 2.39−2.35 (m, 1H); 2.28−2.26 (m, 1H); 2.12−2.07 (m, 1H); 1.87−1.81 (m, 1H); 1.78 (s, 3H); 1.72 (s, 3H); 1.66 (s, 3H); 1.27−1.18 (m, 1H); 0.99 (d, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 145.6, 135.5, 135.2, 131.0, 124.8, 110.9, 45.3, 32.3, 31.4, 28.4, 23.1, 22.5, 22.3, 21.7. LR-MS *m*/*z* (rel int): 190 (39) (M^+), 175 (83), 147 (52), 119 (100), 105 (68), 91 (69), 77 (30). IR ν (cm^{-1}) (neat): 2966, 2931, 2873, 1721, 1649, 1455, 1158, 1053, 1016, 891, 756. HRMS calc for $C_{14}H_{22}$, 190.17215; found, 190.17215.

3-Allyl-5-isopropenyl-2-methylcyclohexa-1,3-diene (6c). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 5.85 (ddt, J = 16.5 Hz, 10.5 Hz, 6.3 Hz, 1H); 5.57−5.55 (m, 1H); 5.45−5.44 (m, 1H); 5.06−5.02 (m, 2H); 4.77−4.73 (m 2H); 2.88−2.86 (m, 3H); 2.16−2.10 (m, 2H); 1.77−1.76 (m, 3H); 1.75−1.73 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 148.5, 137.5, 136.4, 133.1, 126.5, 122.6, 116.0, 110.5, 42.4, 37.7, 28.7, 21.2, 19.6. LR-MS *m*/*z* (rel int): 174 (29) (M^+), 133 (73), 117 (34), 105 (100), 91 (61), 77 (25). IR ν (cm^{-1}) (neat): 2971, 2928, 2867, 1641, 1438, 1375, 1051, 996, 912, 892. HRMS: calc for $C_{13}H_{18}$, 174.14085; found, 174.14128.

5-Isopropenyl-2-methyl-3-(2-methylallyl)cyclohexa-1,3-diene (6d). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 5.56−5.54 (m, 1H); 5.45 (d, J = 3.5 Hz, 1H); 4.79−4.77 (m, 2H); 4.74−4.73 (m, 1H); 4.70−4.69 (m, 1H); 2.92−2.88 (m, 1H); 2.84 (d, J = 16.0 Hz, 1H); 2.77 (d, J = 16.0 Hz, 1H); 2.16−2.10 (m, 2H); 1.75−1.73 (m, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 148.2; 144.5; 135.5; 133.1; 127.2; 122.0; 111.1; 110.0; 42.1; 41.7; 28.4; 22.6; 20.8; 19.0. LR-MS *m*/*z* (rel int): 188 (26) (M^+), 173 (16), 133 (67), 117 (24), 105 (100), 91 (50), 77 (25). IR ν (cm^{-1}) (neat): 2969, 2931, 2868, 1721, 1647, 1445, 1375, 1096, 1050, 891. HRMS calc for $C_{14}H_{20}$, 188.15650; found, 188.15648.

[2-(3-Allylcyclohexen-2-enyl)vinyl]benzene (6e). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 7.32−7.18 (m, 5H); 6.39 (d, J = 11.5 Hz, 1H); 5.79 (ddt, J = 17.0 Hz, 10.1 Hz, 6.9 Hz, 1H); 5.49 (dd, J = 10.6 Hz, 11.4 Hz, 1H); 5.33−5.32 (m, 1H); 5.08−4.99 (m, 2H); 3.41−3.35 (m, 1H); 2.69 (d, J = 6.6 Hz, 2H); 1.98−1.89 (m, 2H); 1.81−1.74 (m, 2H); 1.57−1.50 (m, 1H); 1.39−1.33 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 137.7, 137.4, 137.2, 136.6, 128.2, 127.9, 126.6, 124.7, 115.7, 42.5, 34.7, 29.6, 28.1, 21.3. LR-MS *m*/*z* (rel int): 224 (16) (M^+), 183 (100), 155 (18), 141 (57), 91 (90), 77 (29). IR ν (cm^{-1}) (neat): 3078, 3005, 2929, 2863, 1725, 1638, 1601, 1494, 1446, 995, 914, 767, 699. Anal. Calcd for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 90.81; H, 8.82.

{2-[3-(2-Methylallyl)cyclohex-2-enyl]vinyl}benzene (6f). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 7.33−7.19 (m, 5H); 6.40 (d, J = 11.5 Hz, 1H); 5.50 (dd, J = 10.5 Hz, 11.4 Hz, 1H); 5.34 (m, 1H); 4.76−4.71 (m, 2H); 3.38−3.33 (m, 1H); 2.66 (s, 2H); 1.90−1.88 (m, 2H); 1.81−1.75 (m, 3H); 1.66 (s, 3H); 1.39−1.33 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 143.9, 137.8, 137.3, 136.7, 128.7, 128.2, 127.8, 126.6, 125.8, 111.6, 47.1, 34.8, 29.6, 27.6, 21.8, 21.4. LR-MS *m*/*z* (rel int): 238 (18) (M^+), 223 (2), 183 (100), 155 (15), 141 (44), 91 (45), 77 (16). IR ν (cm^{-1}) (neat): 3069, 3016, 2927, 1646, 1601, 1494, 1445, 1374, 1073, 1028, 890, 794, 767, 699. Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.48; H, 9.04.

1-Allyl-3-oct-1-en-3-ynylcyclohexene (6g). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 5.79 (ddt, J = 17.0 Hz, 10.0 Hz, 7.0 Hz, 1H); 5.65 (d, J = 10.0 Hz, 1H); 5.40 (dtd, J = 10.6 Hz, 2.3 Hz, 1.0 Hz, 1H); 5.28−5.27 (m, 1H); 5.01−4.98 (m, 2H); 3.39−3.36 (m, 1H); 2.69 (dd, J = 6.8 Hz, 0.8 Hz, 2H); 2.33 (td, J = 7.0 Hz, 2.2 Hz, 2H); 1.82−1.71 (m, 2H); 1.56−1.49 (m, 3H); 1.47−1.39 (m, 2H); 1.34−1.23 (m, 3H); 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 146.3, 136.6, 124.1, 115.6, 108.3, 94.5, 94.4, 77.2, 42.4, 36.9, 30.9, 28.5, 28.0, 21.9, 21.3, 19.2, 13.6. LR-MS *m*/*z* (rel int): 228 (2) (M^+), 187 (43), 171 (48), 157 (23), 143 (31), 131 (78), 117 (52), 105 (35), 91 (100), 79 (48), 67 (42). IR ν (cm^{-1}) (neat): 2958, 2930, 2859, 1638, 1460, 1431, 994, 913, 749. HRMS: calc for $C_{17}H_{24}$, 228.18780; found, 228.18751.

(5,7-Dimethylocta-1,4,7-trienyl)benzene (6h). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 7.37−7.26 (m, 5H); 6.43 (d, J = 11.5 Hz, 1H); 5.68−5.61 (m, 1H); 5.33 (tquart., J = 7.2 Hz, 1.5 Hz, 1H); 4.74−4.73 (m, 1H); 4.69−4.68 (m, 1H); 3.04−3.01 (m, 2H); 2.69 (s, 2H); 1.66 (quart., J = 1.5 Hz, 3H); 1.62−1.61 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 143.2, 137.4, 134.0, 131.3, 128.8, 128.7, 128.1, 126.5, 124.5, 111.1, 40.4, 27.6, 23.4, 22.2. LR-MS *m*/*z* (rel int): 212 (8) (M^+), 157 (98), 142 (26), 129 (88), 115 (57), 91 (100), 77 (35). IR ν (cm^{-1}) (neat): 2970, 2932, 1719, 1646, 1447, 1076, 1029, 891, 769, 698. HRMS: calc for $C_{16}H_{20}$, 212.15650; found, 212.15660.

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