Supplementary Material

Reactions of aliphatic terminal alkynes with Ti(O*i*Pr)$_4$/BuLi: selectivity, kinetic aspects, and a new tetramerisation process

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I. General information

Titanium(IV) isopropoxide was purchased from Sigma Aldrich, distilled under reduced pressure (≈ 70 °C at 2 mbar) and stored under argon for several months. *n*-Butyllithium (2.5 M solution in hexanes) and *sec*-butyllithium (1.4 M solution in cyclohexane) were purchased from Sigma-Aldrich and titrated once a month according to a literature method.[1] Three batches of *s*BuLi were employed: a bottle which had already been opened when the project started (bottle #1), the same bottle employed two years later ("old" bottle #1) and a freshly opened bottle, used over 10 weeks (bottle #2). Tetrahydrofuran and dichloromethane were purified using a MB SPS-800 solvent purification system (MBRAUN). Petroleum ether (40−60 °C fraction) was distilled at 450 mbar before use. Other solvents and commercial reagents were used as received, without purification.

All reactions were carried out under argon. The microwave-promoted experiments were run using a CEM Discover Microwave Synthesis System or an Anton Paar Monowave 300 Microwave Synthesis Reactor with the temperature and time parameters indicated. For other reactions, the temperatures mentioned are the temperatures of the cold baths or the oil baths used. For all experiments, the glassware, septa, syringes and needles were dried in a desiccator under vacuum (ca. 20 mbar), in the presence of $CaCl_2$ and silica gel with moisture indicator. The reaction vessels and the magnetic stirring bars were dried in an oven (120-130 °C) overnight or, alternatively, heated with a heat gun under a stream of argon just before the experiments. In either case, the flasks, fitted with a septum and a stirring bar, were allowed to cool down to room temperature under a gentle stream of argon before the introduction of the solvent and the reactants.

Thin-layer chromatography (TLC) plates were examined, after elution, under UV light and then developed using anisaldehyde, phosphomolybdic acid (PMA) or vanillin stains. Flash column chromatography was performed on VWR Chemicals or Merck silica gel 60 (40–63 μm). Concentration under reduced pressure was carried out using rotary evaporators at 40 °C.

Melting points were determined using a Stuart SMP40 apparatus. Infrared spectra were recorded with a Perkin-Elmer 2000 or a Perkin-Elmer Spectrum Two FT-IR spectrometer.

NMR spectra were recorded with an AVANCE 400 Bruker spectrometer (^{1}H at 400.2 MHz, ^{13}C at 100.6 MHz). Chemical shifts δ are given in parts per million (ppm), referenced to the peak of tetramethylsilane, defined at $\delta = 0.00$ for ^{1}H and ^{13}C NMR, or to the solvent peak [in $CDCl_3$: $\delta = 7.26$ (residual $CHCl_3$) for ^{1}H NMR and $\delta = 77.0$ for ^{13}C NMR]. Multiplicities are abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), br (broad). Coupling constants *J* are given in Hz and are rounded to the closest multiple of 0.5.

In the description of compounds, all the NMR chemical shifts indicated were measured from our spectra. When available, literature data were used for comparison/confirmation purposes. A number of products could not be isolated in pure form but were obtained in mixture with one or two other compounds; occasionally more. In such cases, assignment of the signals was done by combining several methods: careful analysis of 1D and 2D (COSY, HSQC and/or HMBC) NMR experiments, use of known data for some of the constituents of the mixture (if applicable), analogy with other products of similar structure, either obtained in this work or described in the literature, and use of the NMR spectra simulation tools available on the nmrshiftdb2 platform (http://www.nmrshiftdb.org; accessed in January 2024). Sometimes, all the signals of a given new product could be identified in

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[1] W. G. Kofron, L. M. Baclawski, *J. Org. Chem.* **1976**, *41*, 1879–1880.

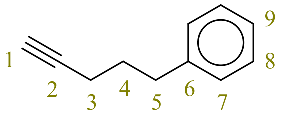
this way, notwithstanding the fact that it had not been perfectly isolated. Quite often however, only a few of the signals could be assigned with a sufficient degree of certainty. In such cases, only these selected characteristic signals are provided.

HRMS spectra were recorded using a tims-TOF mass spectrometer (Bruker) in the *Laboratoire de Chimie Moléculaire* (Ecole polytechnique, CNRS, Institut Polytechnique de Paris, Palaiseau, France). The electrospray source was used in positive mode. Samples were prepared in acetonitrile with 0.1% of formic acid, introduced at a 5 μL/min flow rate into the interface of the instrument. Capillary and end plate voltages were set at 4.5 kV and 0.7 kV. Nitrogen was used as the nebulizer and drying gas at 2.5 bar and 3 L/min, respectively, with a drying temperature of 180°C. Tuning mix (Agilent) was used for calibration. The elemental compositions of all ions were determined with the instrument software Data Analysis; the precision of mass measurement was better than 3 ppm.

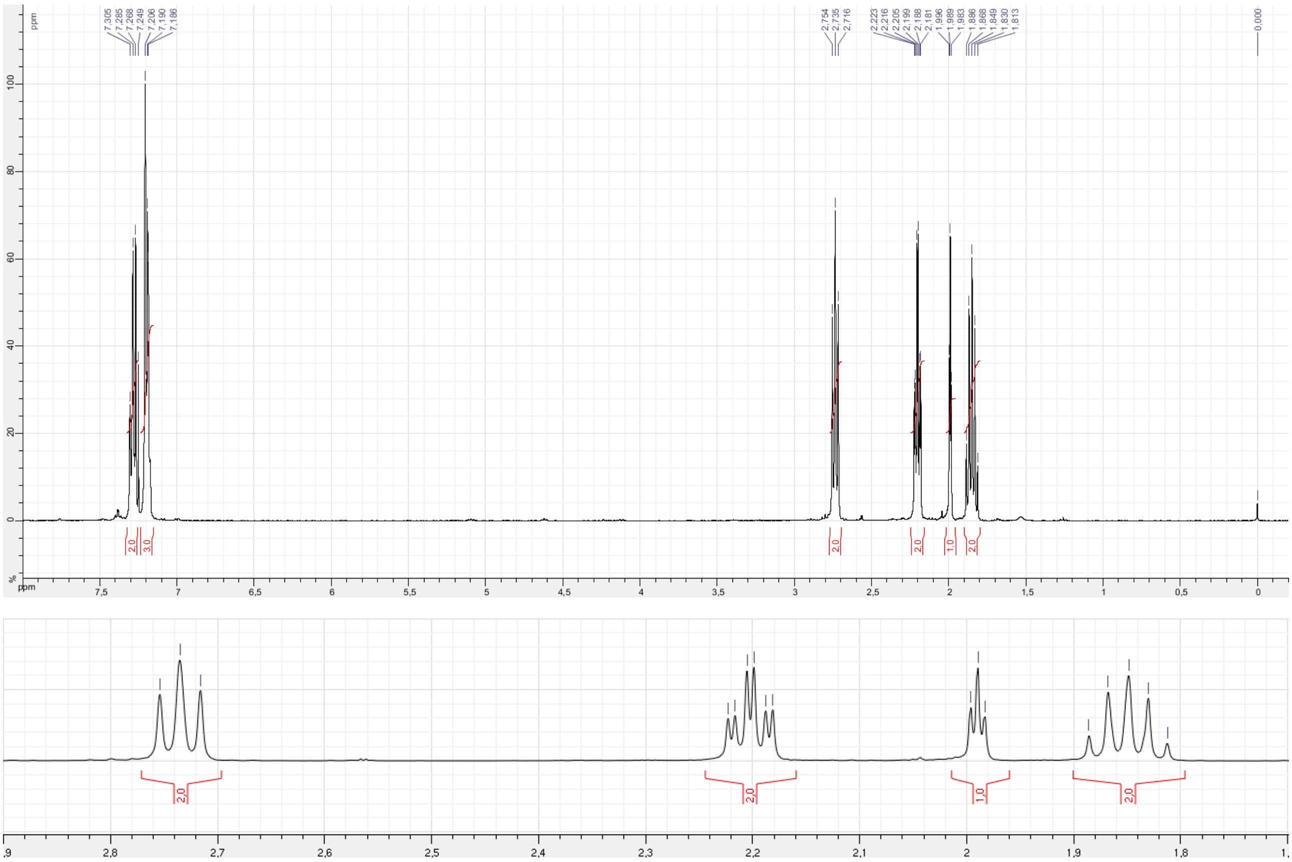
II. Preparation and characterisation of the starting alkynes

5-Phenylpent-1-yne **1a** and 3-phenylprop-1-yne **1b** were purchased from Alfa Aesar and used as received.

5-Phenylpent-1-yne **1a**[2]



Colourless liquid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.85 (2 H, tt, J 7.5, 7.0, H4), 1.99 (1 H, t, J 2.5, H1), 2.20 (2 H, td, J 7.0, 2.5, H3), 2.73 (2 H, t, J 7.5, H5), 7.19 (1 H, br t, J 7.0, H9), 7.20 (2 H, br d, J 8.0, H7), 7.29 (2 H, br dd, J 8.0, 7.0, H8). ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ 17.8 (C3), 30.0 (C4), 34.6 (C5), 68.7 (C1), 84.2 (C2), 125.9 (C9), 128.3, 128.5 (C7, C8), 141.5 (C6).



^{1}H NMR spectrum (CDCl$_3$, 400 MHz).
Note: spectrum recorded from a sample purchased from Alfa Aesar.

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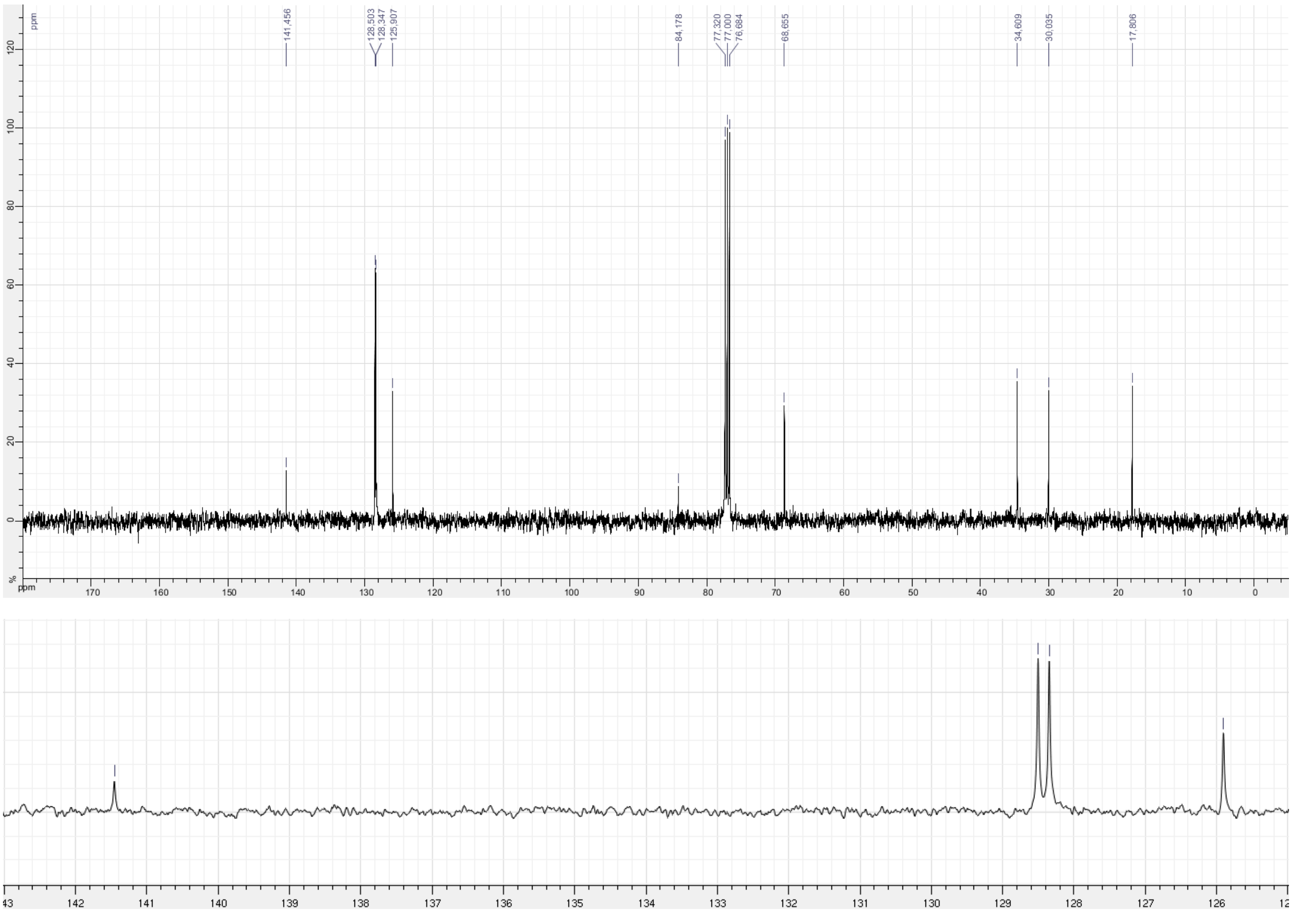
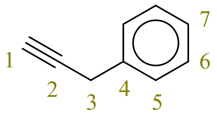
[2] Y. Kawasaki, Y. Ishikawa, K. Igawa, K. Tomooka, *J. Am. Chem. Soc.* **2011**, *133*, 20712−202715 (supporting information).

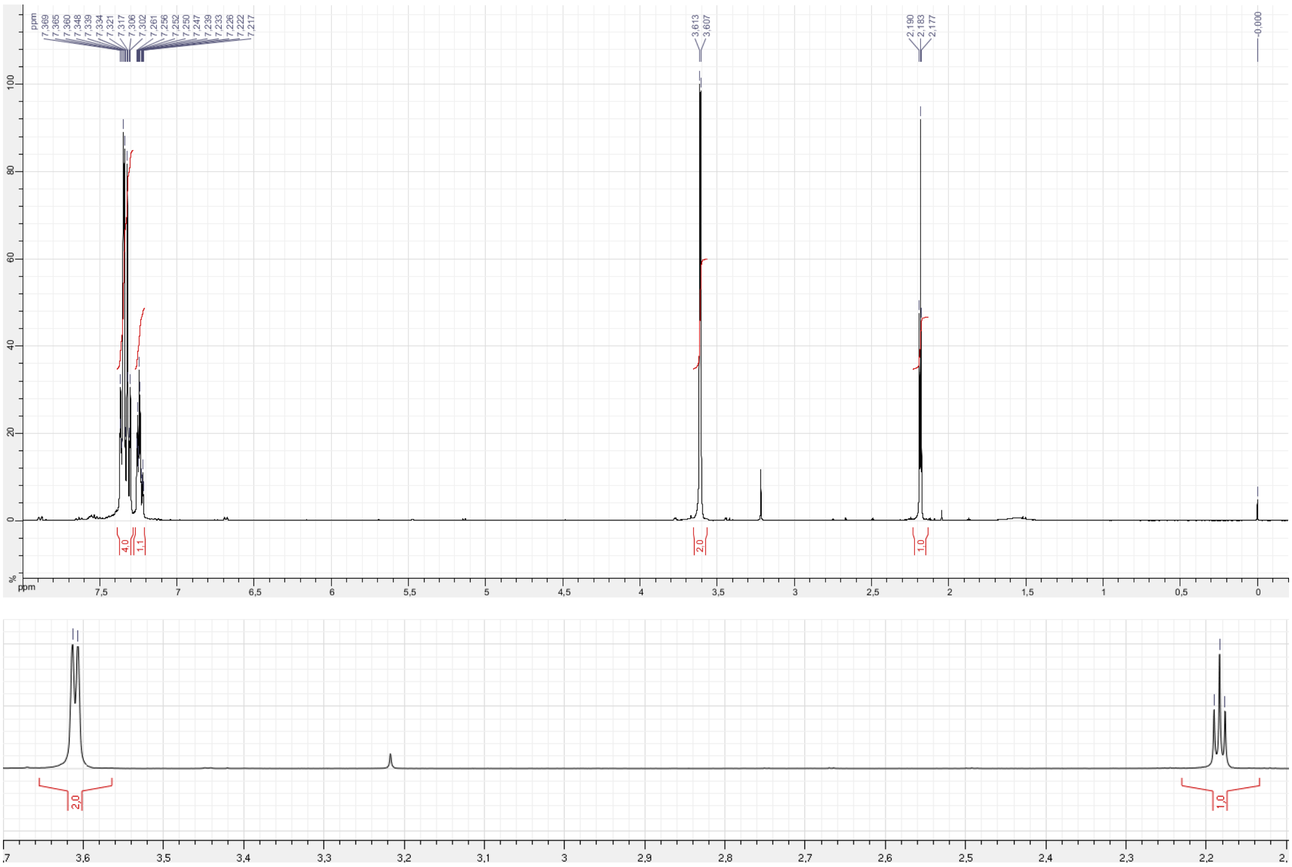


^{13}C NMR spectrum (CDCl$_3$, 100.6 MHz).
Note: spectrum recorded from a sample purchased from Alfa Aesar.

3-Phenylprop-1-yne **1b**[3]



Yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.18 (1 H, t, *J* 2.5, H1), 3.61 (2 H, d, *J* 2.5, H3), 7.24 (1 H, br t, *J* 7.0, H7), 7.29−7.38 (4 H, m, H5−H6). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 24.8 (C3), 70.4 (C1), 81.9 (C2), 126.7 (C7), 127.8, 128.5 (C5, C6), 136.1 (C4).



^{1}H NMR spectrum ($CDCl_3$, 400 MHz), recorded from a sample purchased from Alfa Aesar.

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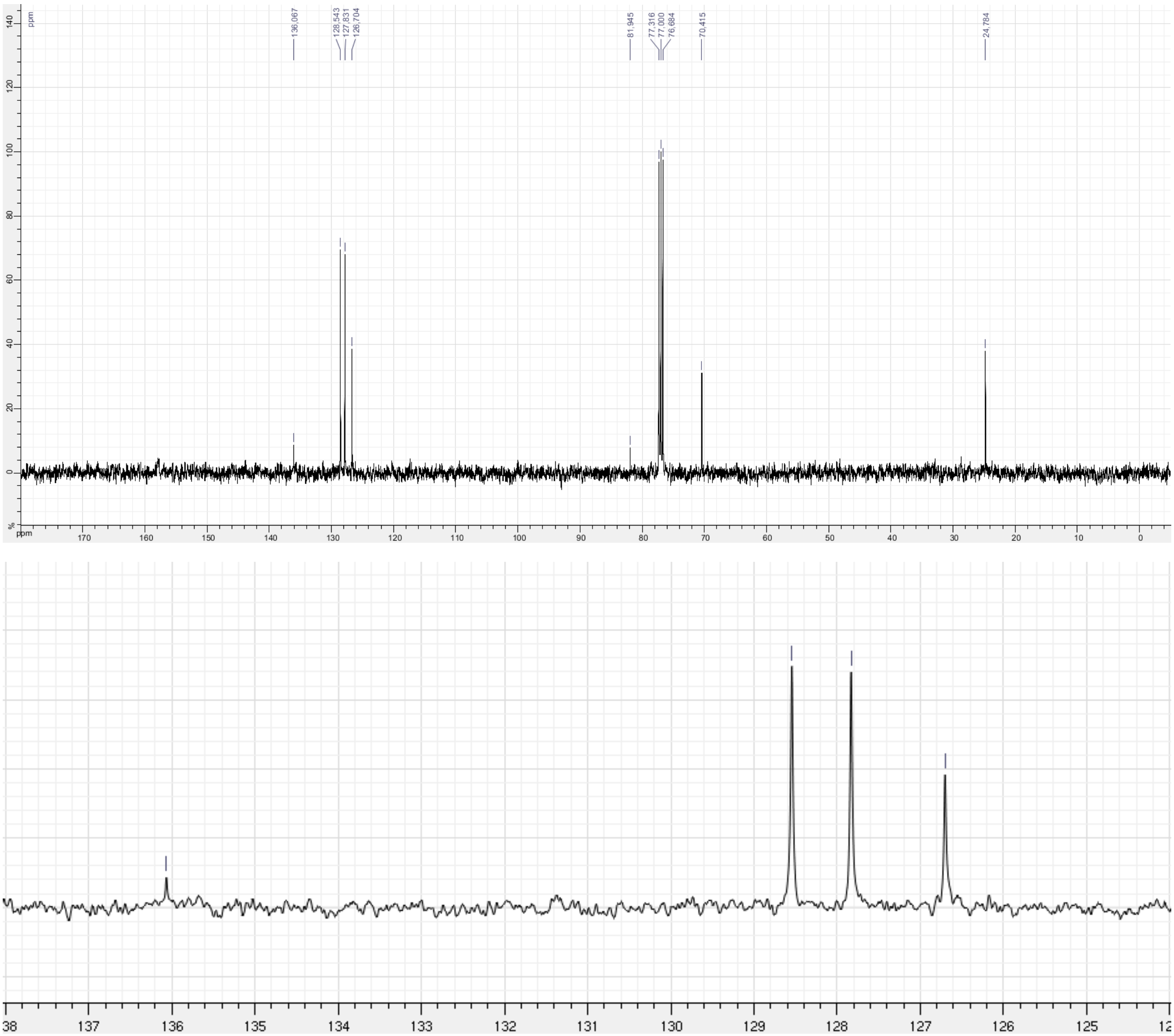
[3] A. Maercker, J. Fischenich, *Tetrahedron* **1990**, *51*, 10209−10218.



^{13}C NMR spectrum ($CDCl_3$, 100.6 MHz), recorded from a sample purchased from Alfa Aesar.

6-Benzyloxyhex-1-yne **1c** was made either by benzylation of commercially available 5-hexyn-1-ol (NaH, *n*Bu_4NI, BnBr, THF)[4] or, for the preparation of larger batches, by the Corey-Fuchs reaction, performed with 5-benzyloxypentanal:

a) Carbon tetrabromide (2.00 equiv, 57.4 mmol, 19.0 g) was added to a cold (0 °C) solution of triphenylphosphine (4.00 equiv, 115 mmol, 30.1 g) in CH_2Cl_2 (0.19 L). After 30 minutes of stirring at 0 °C, 5-benzyloxypentanal[5] (1.00 equiv, 28.7 mmol, 5.52 g) was added and the cold bath was removed. After 1 h of stirring at 20 °C, the solution was concentrated under reduced pressure. Flash column chromatography (silica gel, EtOAc/petroleum ether 10%) afforded pure 6,6-dibromohex-5-enoxymethylbenzene (8.16 g, 23.4 mmol, 82%).[6]

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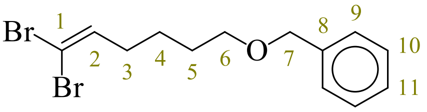
[4] M. Cloutier, M. Roudias, J.-F. Paquin, *Org. Lett.* **2019**, *21*, 3866–3870 (supporting information).

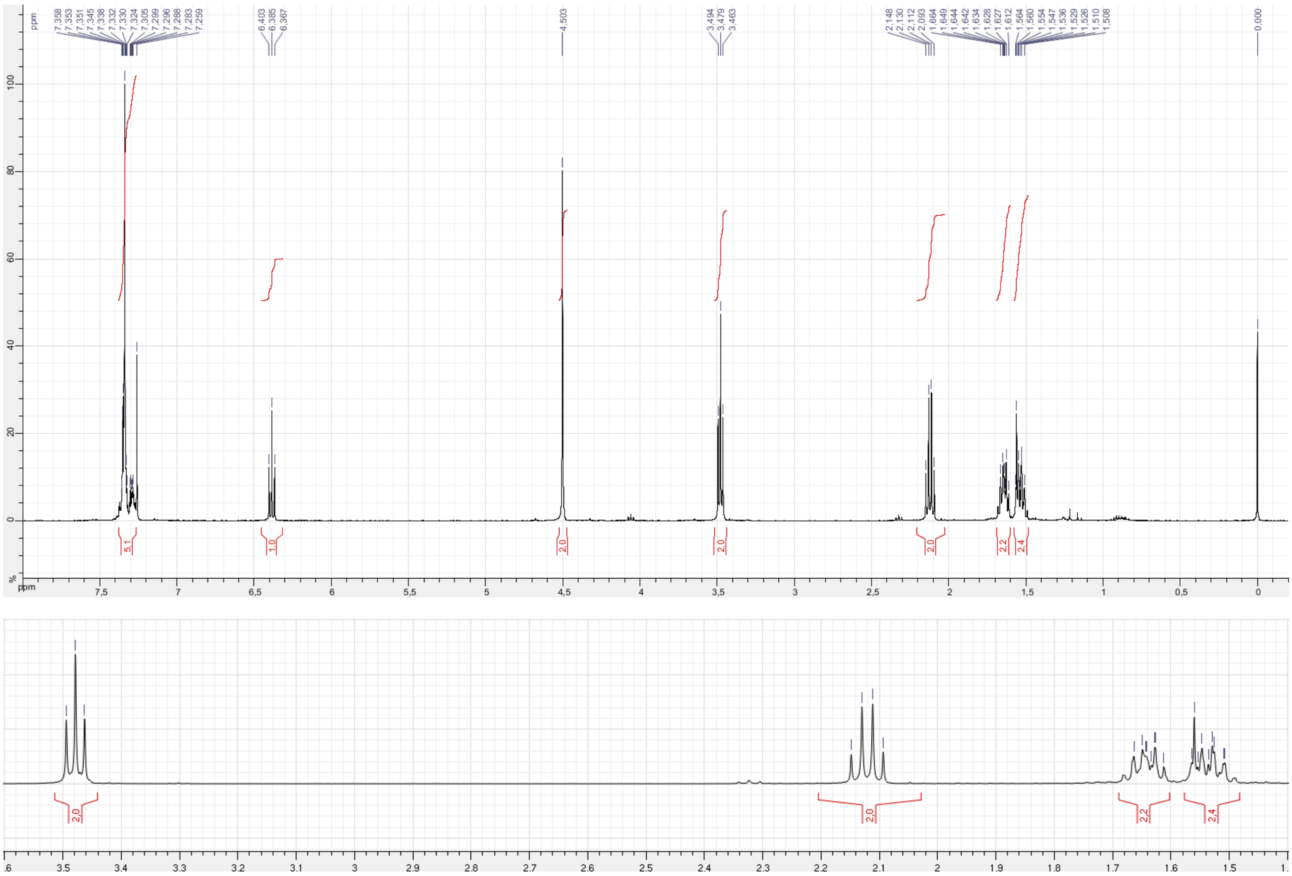
[5] D. B. Shinde, B. S. Kanth, M. Srilatha, B. Das, *Synthesis* **2012**, *44*, 469–473.

[6] Procedure adapted from D. Hack, P. Chauhan, K. Deckers, G. N. Hermann, L. Mertens, G. Raabe, D. Enders, *Org. Lett.* **2014**, *16*, 5188–5191 (supporting information).

6,6-Dibromohex-5-enoxymethylbenzene



Pale yellow oil. R_f 0.4 (EtOAc/Petroleum ether 10%, UV-active, anisaldehyde). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.53 (2 H, m, H4 or H5), 1.65 (2 H, m, H4 or H5), 2.12 (2 H, dt, J 7.5, 7.0, H3), 3.48 (2 H, t, J 6.5, H6), 4.50 (2 H, s, H7), 6.39 (1 H, t, J 7.5, H2), 7.27−7.38 (5 H, m, H9−H11).

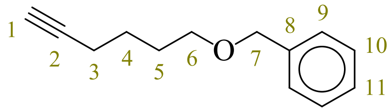


^{1}H NMR spectrum ($CDCl_3$, 400 MHz).

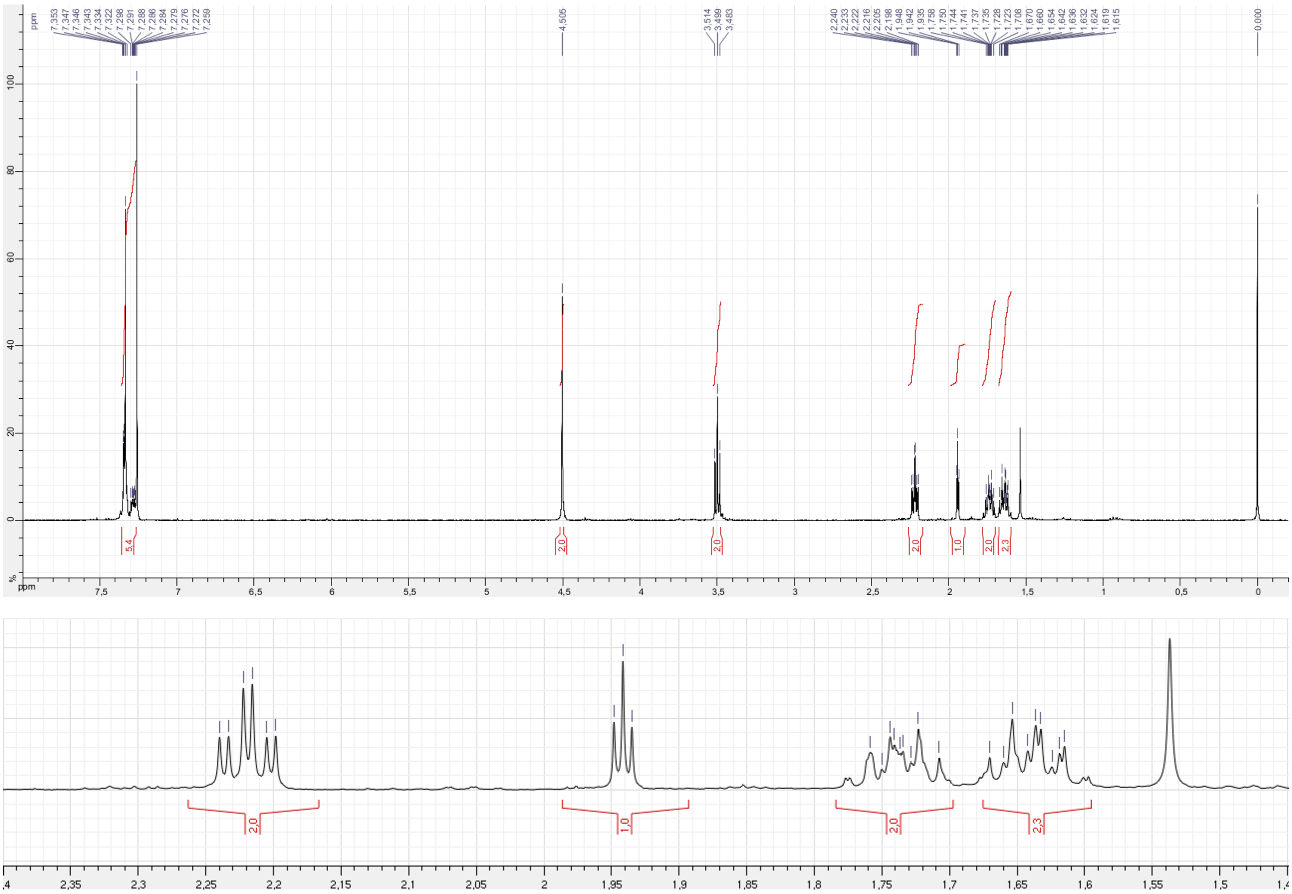
b) *n*-Butyllithium solution (1.60 M in hexanes, 1.50 equiv, 35.1 mmol, 21.9 mL) was added dropwise, over 30 minutes, at −70 °C, to a solution of 6,6-dibromohex-5-enoxymethylbenzene (1.00 equiv, 23.4 mmol, 8.16 g) in THF (67 mL). After two hours of stirring at the same temperature, saturated $NaHCO_3$ aqueous solution (15 mL) was added. The mixture was extracted with CH_2Cl_2 (3 × 90 mL). The combined organic layers were washed with brine (30 mL) and water (30 mL), then dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford essentially pure 6-benzyloxyhex-1-yne **1c** (4.41 g, 23.4 mmol, quantitative yield).[7]

7− Procedure adapted from J. S. Yadav, C. Chandravathi, N. Thrimurtulu, A. R. Prasad, A. A. Al Ghamdi, *Synthesis* **2013**, *45*, 1513–1518.

6-Benzyloxyhex-1-yne **1c**[8]



Colourless liquid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.64 (2 H, m, H4 or H5), 1.74 (2 H, m, H4 or H5), 1.94 (1 H, t, *J* 2.5, H1), 2.22 (2 H, td, *J* 7.0, 2.5, H3), 3.50 (2 H, t, *J* 6.5, H6), 4.50 (2 H, s, H7), 7.26−7.37 (5 H, m, H9−H11). ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ 18.2 (C3), 25.2 (C4), 28.7 (C5), 68.4 (C1), 69.7 (C6), 72.8 (C7), 84.3 (C2), 127.5 (C11), 127.6 (C9), 128.3 (C10), 138.5 (C8).



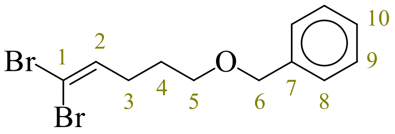
^{1}H NMR spectrum (CDCl$_3$, 400 MHz).

8− J.-C. Zhuo, J. Cai, A. H. Soloway, R. F. Barth, D. M. Adams, W. Ji, W. Tjarks, *J. Med. Chem.* **1999**, *42*, 1282−1292.

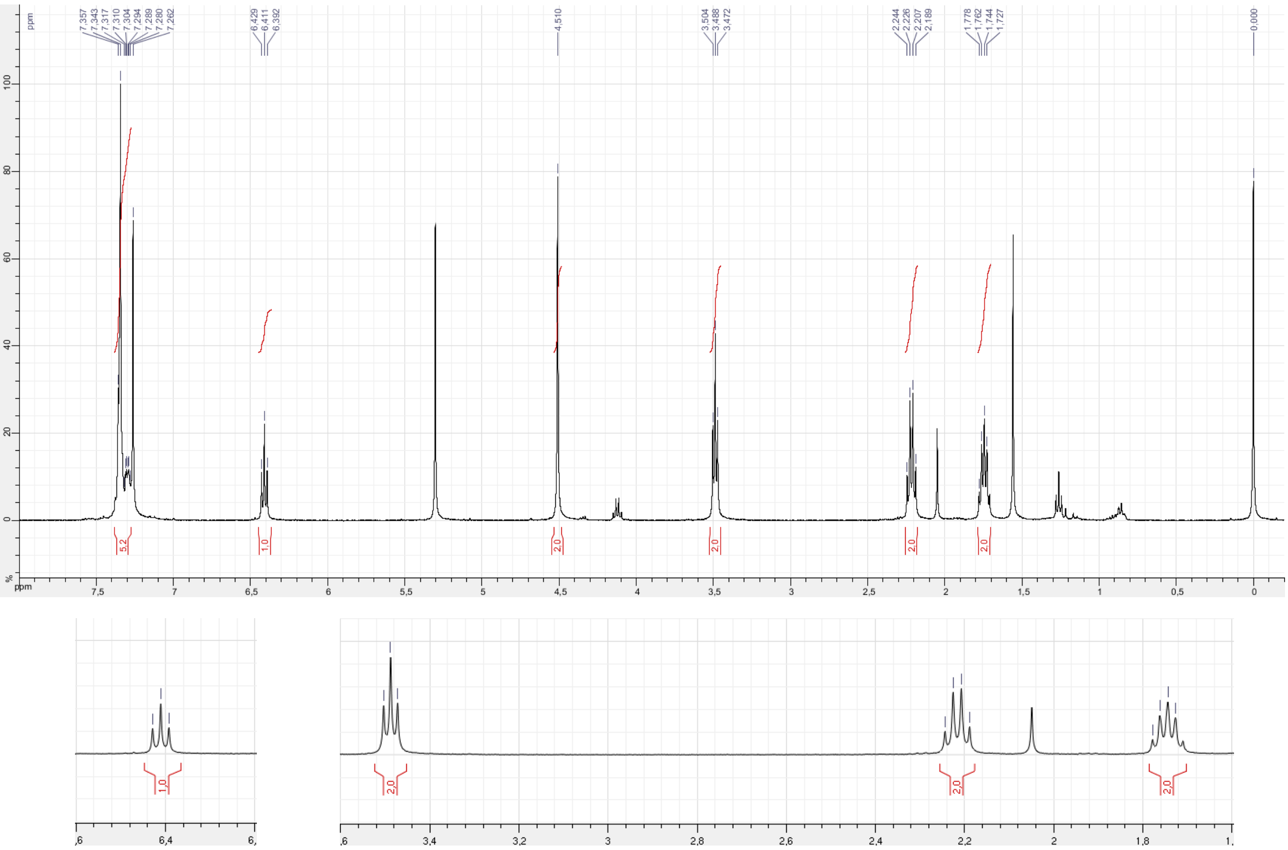
5-Benzyloxypent-1-yne **1d** was made by the Corey-Fuchs reaction, carried out with 4-benzyloxybutanal:[9]

a) Carbon tetrabromide (2.00 equiv, 80.0 mmol, 26.5 g) was added to a cold (0 °C) solution of triphenylphosphine (4.00 equiv, 160 mmol, 42.0 g) in CH_2Cl_2 (0.27 L). After 30 minutes of stirring at 0 °C, 4-benzyloxybutanal[10] (1.00 equiv, 40.0 mmol, 7.00 g) was added and the cold bath was removed. After 1 h of stirring at 20 °C, the solution was concentrated under reduced pressure. The crude product was filtered through a pad of silica gel to afford fairly pure 5,5-dibromopent-4-enoxymethylbenzene (9.97 g, 29.8 mmol, 75%), which was used in the next step without further purification.[6]

5,5-Dibromopent-4-enoxymethylbenzene[11]



Pale yellow oil. R_f 0.8 (EtOAc/Petroleum ether 10%, UV-active, vanillin).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.74 (2 H, tt, *J* 7.5, 6.5, H4), 2.22 (2 H, q, *J* 7.5, H3), 3.49 (2 H, t, *J* 6.5, H5), 4.51 (2 H, s, H6), 6.41 (1 H, t, *J* 7.5, H2), 7.28−7.38 (5 H, m, H8−H10).



^{1}H NMR spectrum ($CDCl_3$, 400 MHz).

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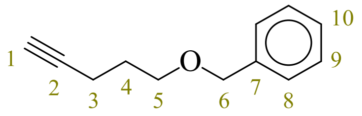
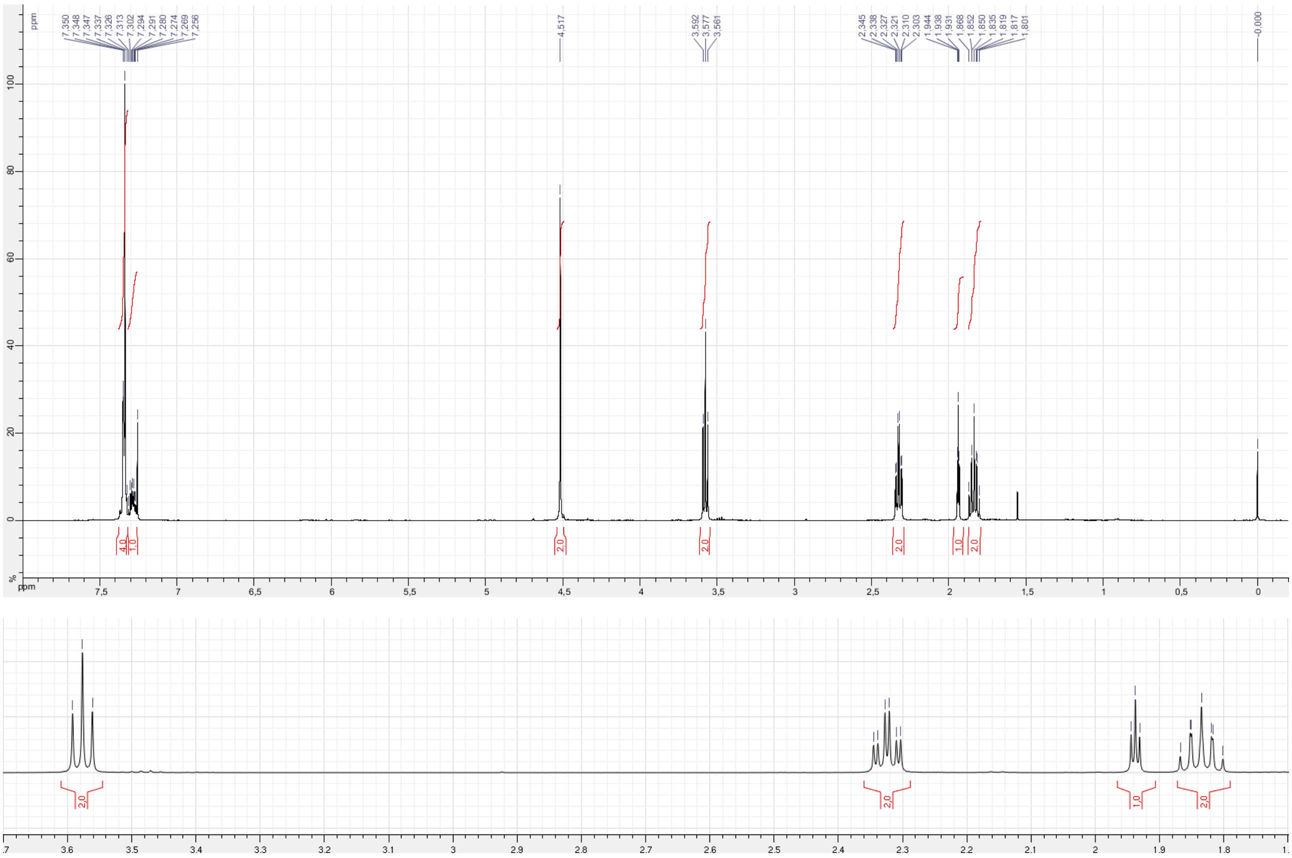
[9] H. Fuwa, K. Hirota, M. Sasaki, *Heterocycles* **2012**, *86*, 127–132.
[10] J. J. Kiddle, D. L. C. Green, C. M. Thompson, *Tetrahedron* **1995**, *51*, 2851–2864.
[11] M. L. N. Rao, D. N. Jadhav, P. Dasgupta, *Org. Lett.* **2010**, *12*, 2048–2051 (supporting information).

b) *n*-Butyllithium solution (1.60 M in hexanes, 1.50 equiv, 44.8 mmol, 28.0 mL) was added dropwise, over 30 minutes, at −70 °C, to a solution of 5,5-dibromopent-4-enoxymethylbenzene (1.00 equiv, 29.8 mmol, 9.97 g) in THF (85 mL). After two hours of stirring at the same temperature, saturated NaHCO$_3$ aqueous solution (30 mL) was added. The mixture was extracted with Et$_2$O (3 × 30 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure to afford essentially pure 5-benzyloxypent-1-yne **1d** (5.01 g, 28.8 mmol, 96%).[7]

5-Benzyloxypent-1-yne **1d**[12]

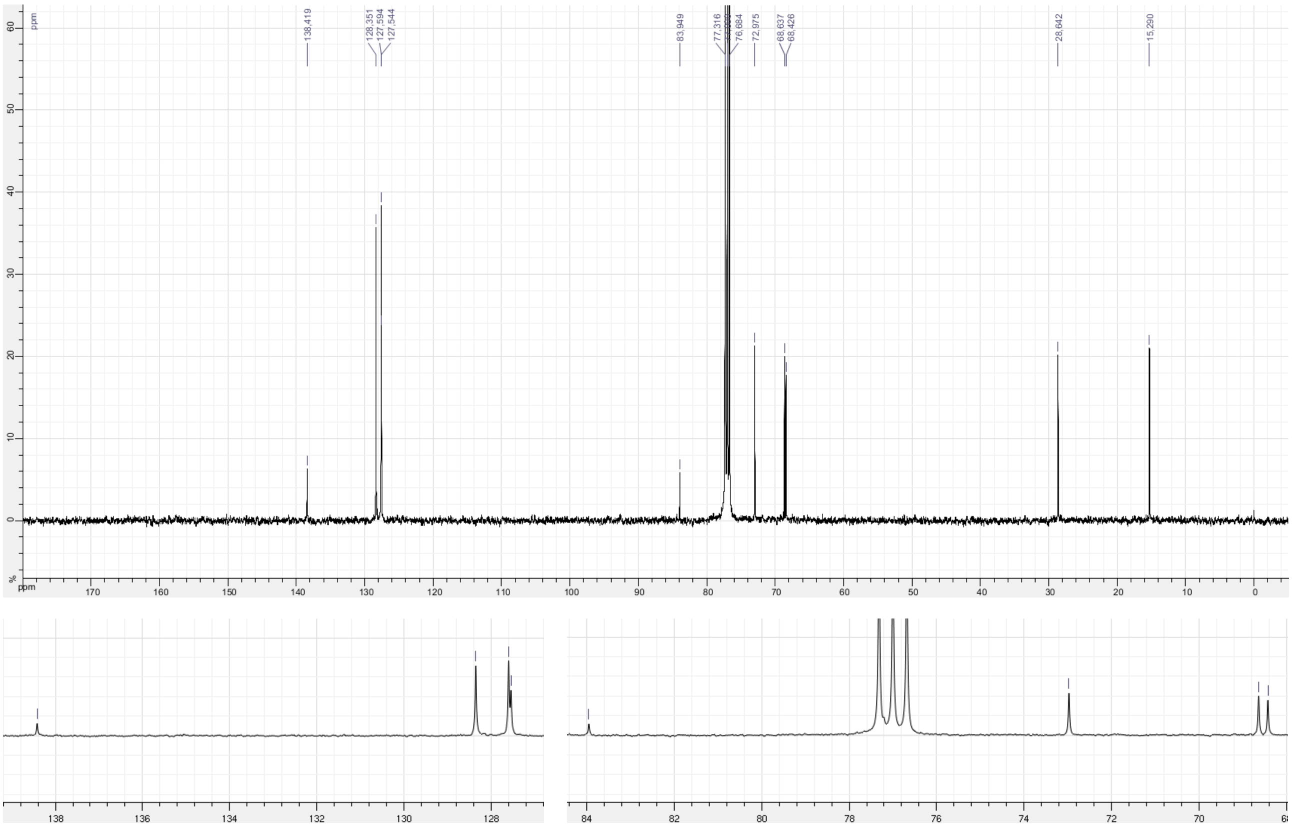


Colourless liquid. R_f 0.25 [EtOAc/Petroleum ether 5%, UV-active, anisaldehyde (dark orange colour)]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.83 (2 H, tt, J 7.0, 6.0, H4), 1.94 (1 H, t, J 2.5, H1), 2.32 (2 H, td, J 7.0, 2.5, H3), 3.58 (2 H, t, J 6.0, H5), 4.52 (2 H, s, H6), 7.29 (1 H, m, H10), 7.32−7.38 (4 H, m, H8−H9). ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ 15.3 (C4), 28.6 (C3), 68.4 (C1), 68.6 (C5), 73.0 (C6), 83.9 (C2), 127.5 (C10), 127.6 (C8), 128.4 (C9), 138.4 (C7).



^{1}H NMR spectrum (CDCl$_3$, 400 MHz).

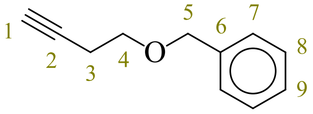
12− K. Miura, S. Okajima, T. Hondo, T. Nakagawa, T. Takahashi, A. Hosomi, *J. Am. Chem. Soc.* **2000**, *122*, 11348−11357 (supporting information).



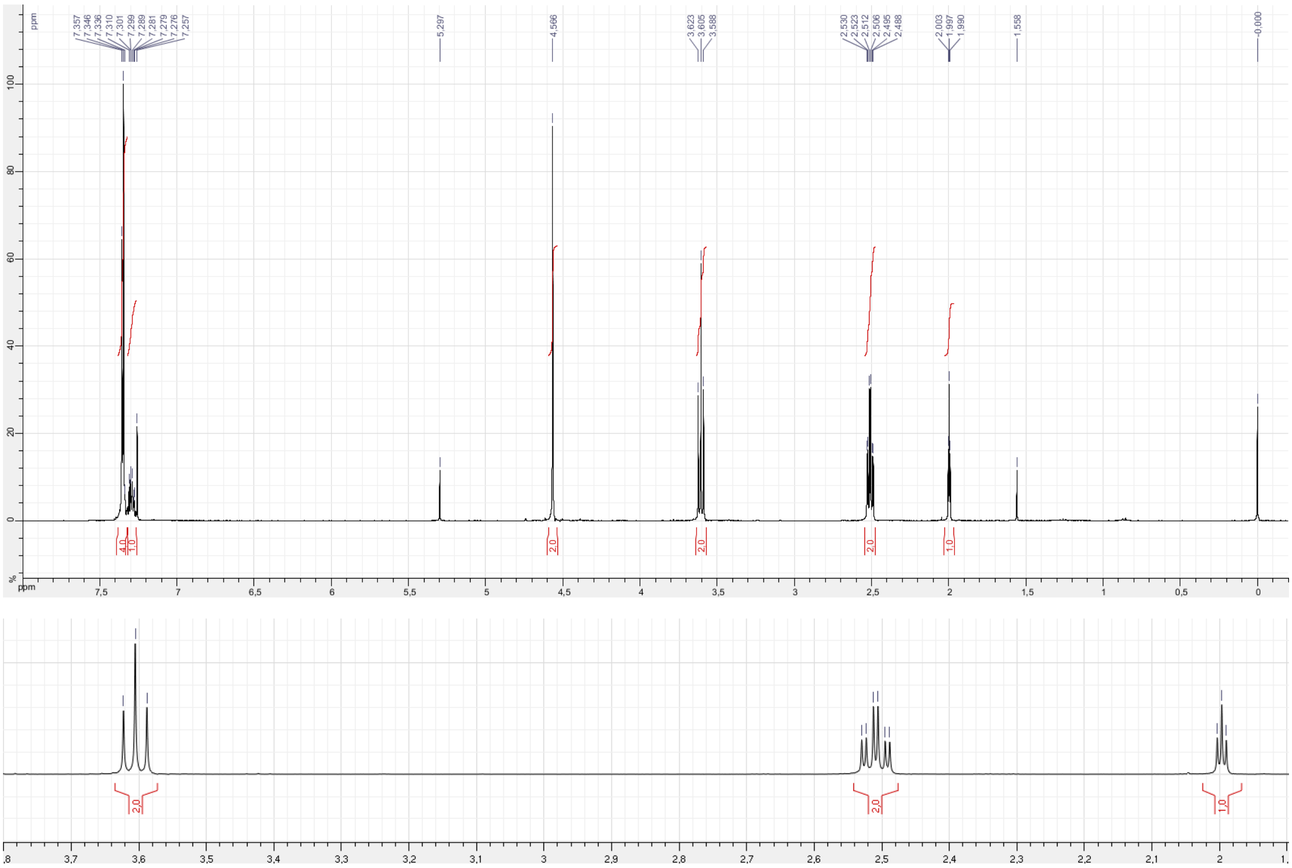
^{13}C NMR spectrum ($CDCl_3$, 100.6 MHz).

4-Benzyloxybut-1-yne **1e** was made by benzylation of commercially available but-3-yn-1-ol (NaH, nBu$_4$NI, BnBr, THF) and purified by flash column chromatography.[13]

4-Benzyloxybut-1-yne **1e**[14]



Colourless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.00 (1 H, t, *J* 2.5, H1), 2.51 (2 H, td, *J* 7.0, 2.5, H3), 3.61 (2 H, t, *J* 7.0, H4), 4.57 (2 H, s, H5), 7.29 (1 H, m, H9), 7.32−7.38 (4 H, m, H7−H8).



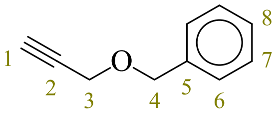
^{1}H NMR spectrum ($CDCl_3$, 400 MHz).

13− N. W. Boaz, B. Venepalli, *Org. Proc. Res. Dev.* **2001**, *5*, 127−131.

14− M. Takimoto, K. Shimizu, M. Mori, *Org. Lett.* **2001**, *3*, 3345−3347 (supporting information).

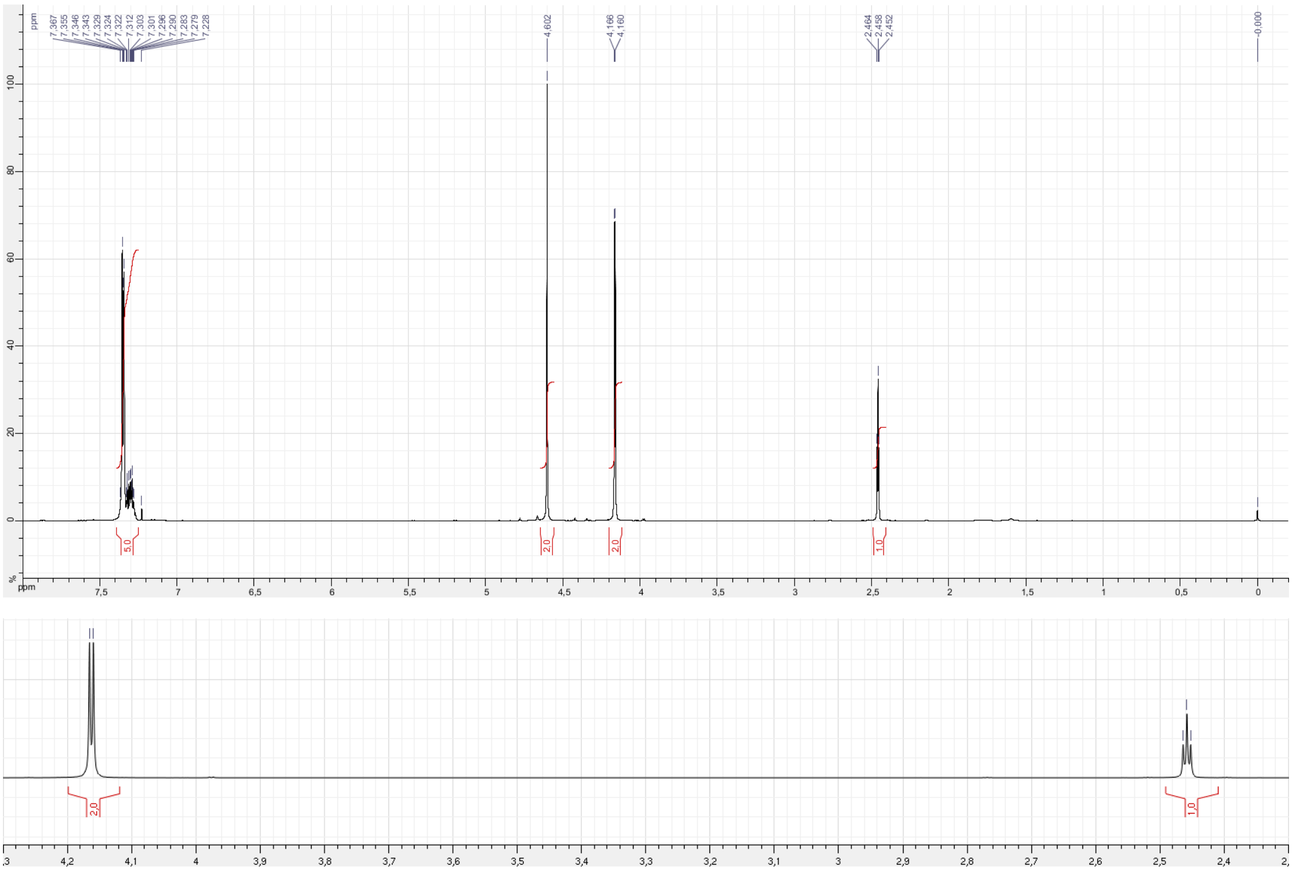
3-Benzyloxyprop-1-yne **1f** was made by alkylating benzyl alcohol with propargyl bromide (KOH, DMSO) and purified by distillation.[15]

3-Benzyloxyprop-1-yne **1f**[15]



Colourless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.46 (1 H, t, *J* 2.5, H1), 4.16 (2 H, d, *J* 2.5, H3), 4.60 (2 H, s, H4), 7.30 (1 H, m, H8), 7.33−7.38 (4 H, m, H6−H7).

^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 57.0 (C1), 71.5 (C3), 74.6 (C4), 79.6 (C2), 127.9 (C8), 128.1 (C6), 128.4 (C7), 137.2 (C5).



^{1}H NMR spectrum ($CDCl_3$, 400 MHz).

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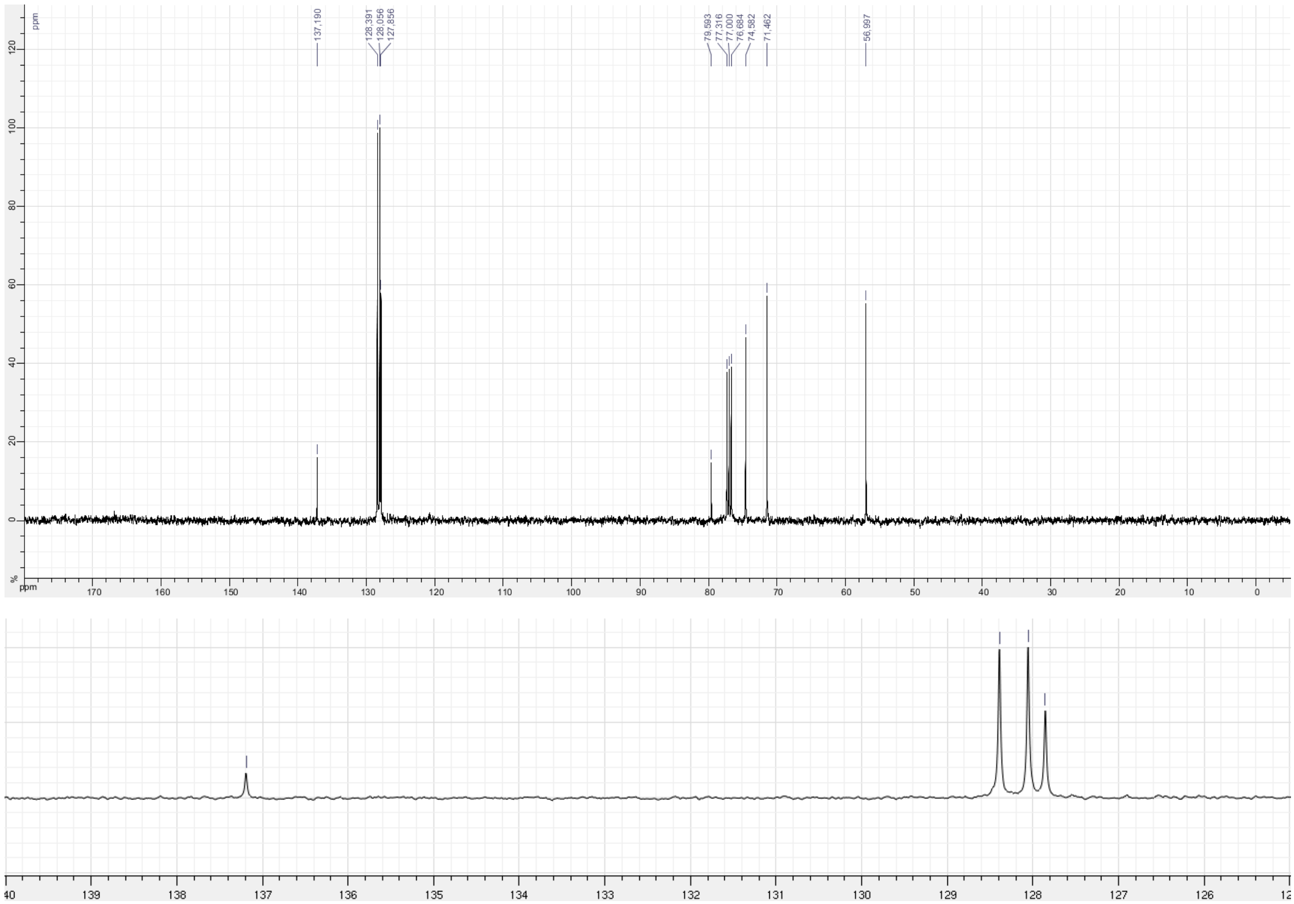
[15] D. L. Boger, M. S. S. Palanki, *J. Am. Chem. Soc.* **1992**, *114*, 9318−9327.



^{13}C NMR spectrum (CDCl$_3$, 100.6 MHz).

III. General procedures

■ **General procedure 1** (**GP1**): reaction at 0 °C of terminal alkynes with the organotitanium reagent generated by the reaction of *n*BuLi or *s*BuLi with Ti(O*i*Pr)$_4$.

n-Butyllithium or *s*-butyllithium solution (*p* equiv) was added dropwise, over 2−3 minutes, at 0 °C, to a solution of titanium(IV) isopropoxide (*n* equiv) in THF (5.0 mL).[16] The solution turned yellow, then orange and then dark brown. After 5 minutes of stirring at 0 °C, it had turned black and the terminal alkyne substrate **1** (1.00 equiv) was added dropwise, over 1−5 minutes.[16] The mixture was stirred at 0 °C for an additional *t* minutes. H_2O (0.5 mL) was then added. After 15 minutes of stirring, the septum was removed to expose the mixture to air and stirring was continued for 10 more minutes. The mixture was then filtered through a pad of sand, $MgSO_4$, celite and sand [from bottom to top; rinsing with Et_2O (20 mL)] and concentrated under reduced pressure (down to 50−100 mbar only) to afford the crude product.

■ **General procedure 2** (**GP2**): reaction at 0 °C of terminal alkynes with the organotitanium reagent generated from *n*BuLi and Ti(O*i*Pr)$_4$, with the preparation of crude products after 20 minutes, 30 minutes and 45 minutes of reaction.

n-Butyllithium solution (*p* equiv) was added dropwise, over 1−2 minutes, at 0 °C, to a solution of titanium(IV) isopropoxide (*n* equiv) in THF (5.0 mL).[16] The solution turned yellow, then orange and then brown. After 5 minutes of stirring at 0 °C, it had turned black and the terminal alkyne substrate **1** (1.00 equiv) was added dropwise, over 1−2 minutes.[16]

After 20 minutes of stirring at 0 °C, part of the solution (1.0 mL) was taken out using a syringe and introduced into another flask under Ar, at 0 °C. H_2O (0.1 mL) was then added to this flask. After 15 minutes of stirring, the septum was removed to expose it to air and stirring was continued for 10 more minutes. The white mixture was then filtered through a pad of sand, $MgSO_4$, celite and sand [from bottom to top; rinsing with Et_2O (6.0 mL)][17] and concentrated under reduced pressure (down to 50-60 mbar) to afford the crude product corresponding to t = 20 minutes.

The same operation was repeated after 30 minutes of reaction at 0 °C, to afford the crude product corresponding to t = 30 minutes.

After 45 minutes of reaction at 0 °C, the remaining solution was treated with H_2O (0.3 mL). After 15 minutes of stirring, the septum was removed to expose the mixture to air and stirring was continued for 10 more minutes. The mixture was then filtered through a pad of sand, celite, $MgSO_4$ and sand [from top to bottom; rinsing with Et_2O (12 mL)] and concentrated under reduced pressure (down to 50-60 mbar) to afford the crude product corresponding to t = 45 minutes.

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[16] Slow addition onto the cold inner walls of the flask.

[17] The funnel was connected to the reception flask by a vacuum adapter with a rubber conical sleeve. Mild vacuum was applied (water jet-pump).

■ **General procedure 3** (**GP3**): reaction at 0 °C of terminal alkynes with the organotitanium reagent generated from *n*BuLi and Ti(O*i*Pr)$_4$; the alkyne is added as a solution in THF.

n-Butyllithium solution (*p* equiv) was added dropwise, over 1−4 minutes, at 0 °C, to a solution of titanium(IV) isopropoxide (*n* equiv) in THF (V_1 mL).[16] The solution turned yellow, then orange and then dark brown. After 5 minutes of stirring at 0 °C, it had turned black and a solution of terminal alkyne substrate **1** (1.00 equiv) in THF (V_2 mL) was added dropwise, over 1−4 minutes.[16] The mixture was stirred at 0 °C for an additional *t* minutes. H_2O (0.5 mL) was then added. After 15 minutes of stirring, the septum was removed to expose the mixture to air and stirring was continued for 10 more minutes. The mixture was then filtered through a pad of sand, $MgSO_4$, celite and sand [from bottom to top; rinsing with Et_2O (20 mL)] and concentrated under reduced pressure (down to 50−100 mbar only) to afford the crude product.

■ **General procedure 4** (**GP4**): reaction at lower temperature of terminal alkynes with the organotitanium reagent generated from *n*BuLi and Ti(O*i*Pr)$_4$; the alkyne is added as a solution in THF.

n-Butyllithium solution (*p* equiv) was added dropwise, over 1−3 minutes, at 0 °C, to a solution of titanium(IV) isopropoxide (*n* equiv) in THF (3.5 mL).[16] The solution turned yellow, then orange and then dark brown. After 5 minutes of stirring at 0 °C, it had turned black. The mixture was cooled to *T* °C and a solution of terminal alkyne substrate **1** (1.00 equiv) in THF (0.5 mL) was added dropwise, over 1−3 minutes.[16] The mixture was stirred at *T* °C for an additional *t* minutes. H_2O (0.5 mL) was then added. After 15 minutes of stirring, the septum was removed to expose the mixture to air and stirring was continued for 10 more minutes. The mixture was then filtered through a pad of sand, $MgSO_4$, celite and sand [from bottom to top; rinsing with Et_2O (20 mL)] and concentrated under reduced pressure (down to 50 mbar only) to afford the crude product.

■ **General procedure 5** (**GP5**): reaction at 0 °C of terminal alkynes with the organotitanium reagent generated by the reaction of *n*BuLi with Ti(O*i*Pr)$_4$, conducted on a smaller scale.

n-Butyllithium solution (*p* equiv) was added dropwise, over 3−4 minutes, at 0 °C, to a solution of titanium(IV) isopropoxide (*n* equiv) in THF (2.0 mL).[16] The solution turned yellow, then orange and then dark brown. After 5 minutes of stirring at 0 °C, it had turned black and the terminal alkyne substrate **1** (1.00 equiv) was added dropwise, over 2−3 minutes.[16] The mixture was stirred at 0 °C for an additional *t* minutes. H_2O (0.5 mL) was then added. After 15 minutes of stirring, the septum was removed to expose the mixture to air and stirring was continued for 10 more minutes. The mixture was then filtered through a pad of sand, $MgSO_4$, celite and sand [from bottom to top; rinsing with Et_2O (20 mL)] and concentrated under reduced pressure (down to 50 mbar only) to afford the crude product.

■ **General procedure 6** (**GP6**): reaction at 0 °C of terminal alkynes with the organotitanium reagent generated by the reaction of *n*BuLi or *s*BuLi with Ti(O*i*Pr)$_4$, in the presence of an inorganic salt additive.

Before the experiment, the reaction vessel, containing the magnetic stirring bar and the ground inorganic salt (1.00 equiv, 2.00 mmol), was dried in an oven (120-130 °C) overnight, then cooled down to room temperature under a gentle stream of argon. THF (5.0 mL) and titanium(IV) isopropoxide (1.00 equiv, 2.00 mmol, 592 μL) were introduced into the flask. *n*-Butyllithium or *s*-butyllithium solution (1.65 equiv, 3.30 mmol) was then added dropwise, over 1.5 minutes, at 0 °C.[16] The solution turned yellow, then orange and then dark brown. After 5 minutes of stirring at 0 °C, it had turned black and 5-benzyloxypent-1-yne **1d** (1.00 equiv, 2.00 mmol, 348 mg, 350 μL) was added dropwise, over 30 s.[16] The mixture was stirred at 0 °C for an additional 45 minutes. H_2O (0.5 mL) was then added. After 15 minutes of stirring, the septum was removed to expose the mixture to air and stirring was continued for 10 more minutes. The mixture was then filtered through a pad of sand, $MgSO_4$, celite and sand [from bottom to top; rinsing with Et_2O (20 mL)] and concentrated under reduced pressure (down to 50 mbar only) to afford the crude product.

■ **General procedure 7** (**GP7**): reaction of terminal alkynes with the organotitanium reagent generated by the reaction of *n*BuLi with Ti(O*i*Pr)$_4$, with heating using a microwave reactor.

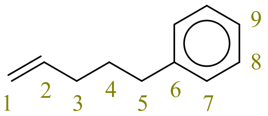
n-Butyllithium solution (0.900 equiv, 2.70 mmol) was added dropwise, over 1 minute, at 0 °C, to a solution of titanium(IV) isopropoxide (0.600 equiv, 1.80 mmol) in THF (4.0 mL), in a flame-dried 10 mL microwave vial.[16] After 5 minutes of stirring at 0 °C, the terminal alkyne substrate **1** (1.00 equiv, 3.00 mmol) was added dropwise to the dark solution. The septum on the vial was quickly replaced with the suitable sealed cap and the vial was immediately heated with the microwave synthesis reactor (*T* ° C, 15 min). After cooling, H_2O (0.5 mL) was added. After 30 minutes of stirring, the mixture was then filtered through a pad of sand, $MgSO_4$, celite and sand (from bottom to top; rinsing with Et_2O) and concentrated under reduced pressure (down to 50 mbar only) to afford the crude product.

IV. Experiments with 5-phenylpent-1-yne **1a**

IV.1. Characterisation of the products

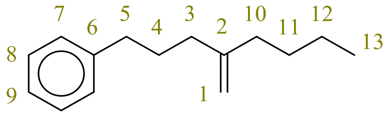
We were not able to isolate products **2a**, **2′a**, **3a** and **3′a**. They were obtained as components of more or less complex mixtures. The cyclotrimers **4a**/**4′a** were isolated as a mixture of the two regioisomers, contaminated with hydrocarbon impurities. In all cases, assignment of the signals was done as explained in the general information.

Pent-4-enylbenzene **2a**[18]



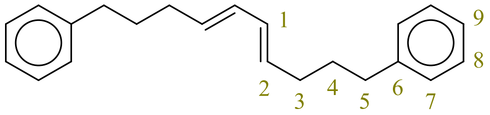
^{1}H NMR ($CDCl_3$, 400 MHz), characteristic signals: δ 4.97 (1 H, ddt, *J* 10.0, 2.0, 1.0, H1 *cis* to H2), 5.02 (1 H, ddt, *J* 17.0, 2.0, 1.5, H1 *trans* to H2), 5.83 (1 H, ddt, *J* 17.0, 10.0, 6.5, H2).

4-Methyleneoctylbenzene **2′a**[19]



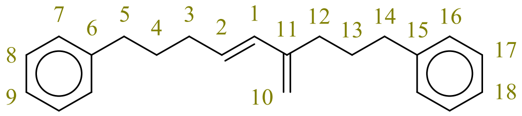
^{1}H NMR ($CDCl_3$, 400 MHz), characteristic signal: δ 4.72 (2 H, br s, H1).

[(4*E*,6*E*)-10-Phenyldeca-4,6-dienyl]benzene **3a**[20]



^{1}H NMR ($CDCl_3$, 400 MHz), characteristic signals: δ 5.59 (2 H, m, H2), 6.02 (2 H, m, *J* 14.5, H1).

[(*E*)-4-Methylene-9-phenyl-non-5-enyl]benzene **3′a**[21]



^{1}H NMR ($CDCl_3$, 400 MHz), characteristic signals: δ 4.87 (1 H, br s, H10a), 4.90 (1 H, br s, H10b), 5.65 (1 H, dt, *J* 16.0, 7.0, H2), 6.06 (1 H, br d, *J* 16.0, H1).

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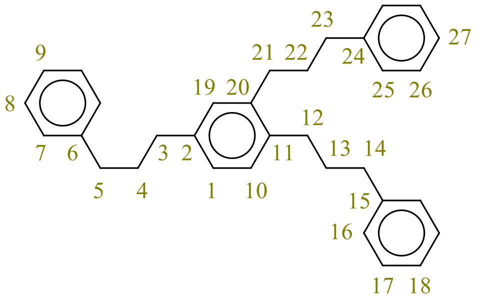
[18] J. C. Anderson, R. H. Munday, *J. Org. Chem.* **2004**, *69*, 8971−8974 (supporting information).

[19] We could not find literature NMR data for this compound but the signals we observed are in excellent agreement with the data previously obtained with the related molecule 5-methylenedecane: V. A. Rassadin, E. Nicolas, Y. Six, *Chem. Commun.* **2014**, *50*, 7666−7669 (supporting information).

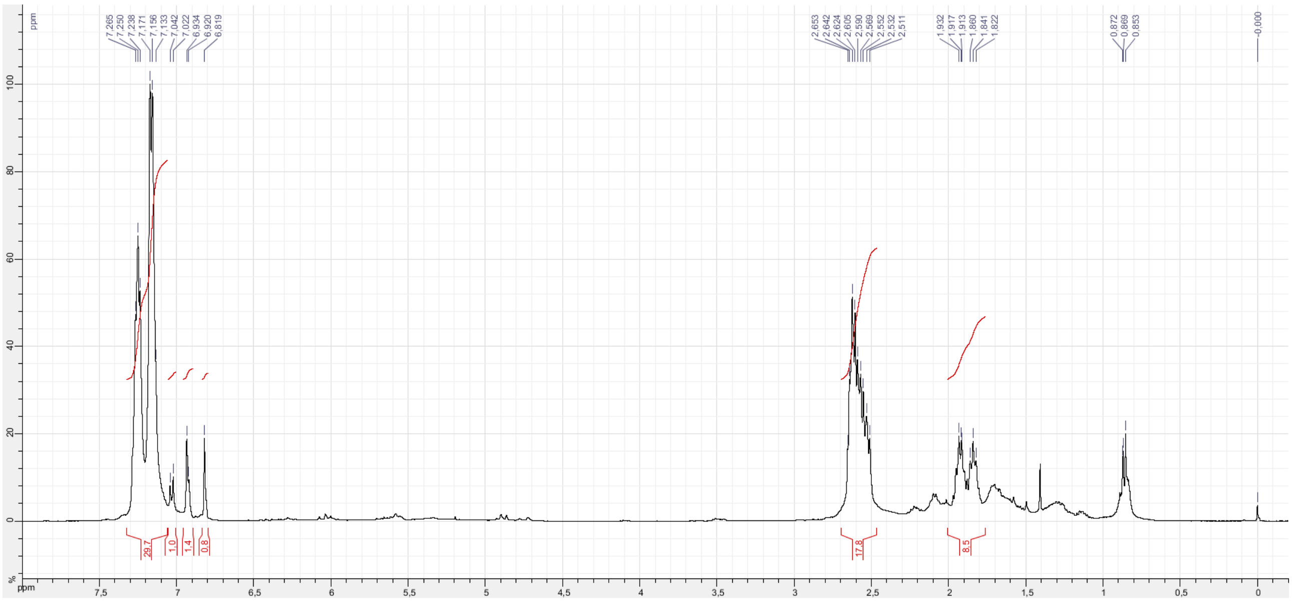
[20] J. R. Falck, S. Mohapatra, M. Bondlela, S. K. Venkataraman, *Tetrahedron. Lett.* **2002**, *43*, 8149−8151.

[21] We could not find literature NMR data for this compound but the signals we observed are in excellent agreement with the data previously obtained with the related molecule (*E*)-8-methylenetridec-6-ene: V. A. Rassadin, E. Nicolas, Y. Six, *Chem. Commun.* **2014**, *50*, 7666−7669 (supporting information).

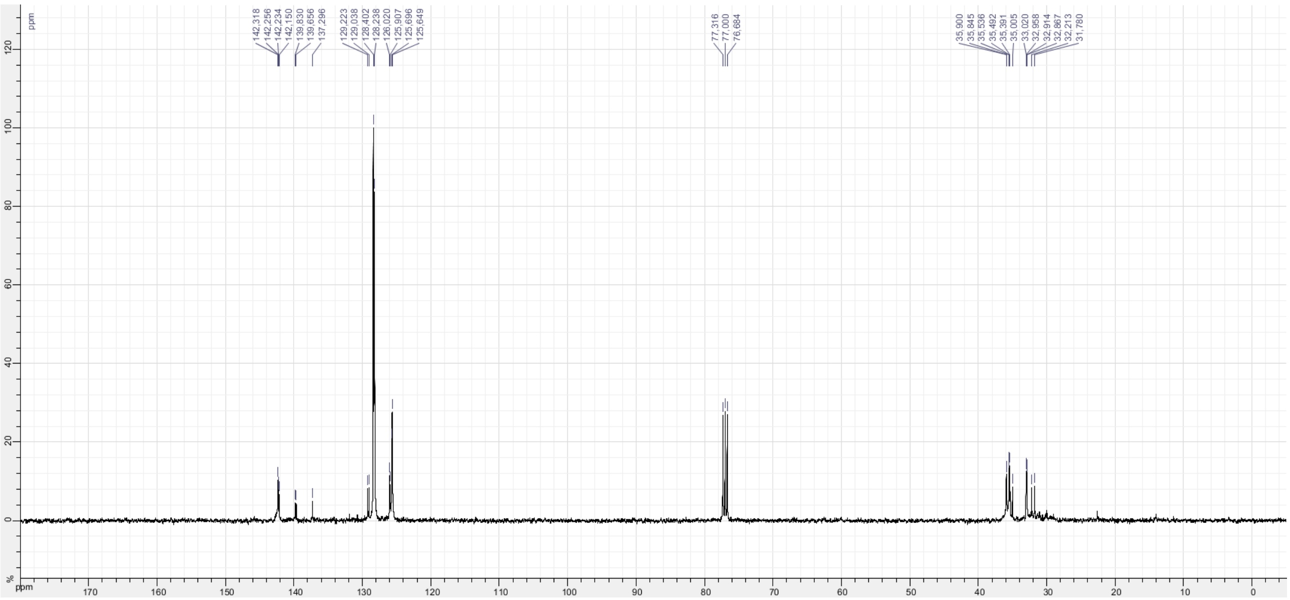
1,2,4-Tris(3-phenylpropyl)benzene **4a**



Yellow oil. R_f 0.25 [EtOAc/Petroleum ether 2%, UV-active, PMA].
^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.78−1.98 (6 H, m, H4, H13, H22), 2.48−2.68 (12 H, m, H3, H5, H12, H14, H21, H23), 6.94 (1 H, dd, *J* 8.5, 2.0, H1), 6.94 (1 H, d, *J* 2.0, H19), 7.04 (1 H, d, *J* 8.5, H10), 7.06−7.33 (15 H, m, H7−H9, H16−H18, H25−H27). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 31.8, 32.2 (C12, C21), 32.9, 32.9 (C13, C22), 33.0 (C4), 35.0 (C3), 35.5 (C5), 35.8, 35.9 (C14, C23), 125.6 (C9), 125.6, 125.7 (C18, C27), 125.9 (C1), 128.2, 128.2, 128.2 (C8, C17, C26), 128.4, 128.4, 128.4 (C7, C16, C25), 129.0 (C10), 129.2 (C19), 137.3 (C2), 139.7, 139.8 (C11, C20), 142.1, 142.2 (C15, C24), 142.3 (C6).

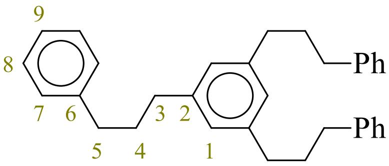


^{1}H NMR spectrum ($CDCl_3$, 400 MHz).
Note: this analysis was performed on a 72 : 28 mixture of **4a** and **4′a**, containing impurities.



^{13}C NMR spectrum (CDCl$_3$, 100.6 MHz).
Note: this analysis was performed on a 72 : 28 mixture of **4a** and **4′a**, containing impurities.

1,3,5-Tris(3-phenylpropyl)benzene **4′a**



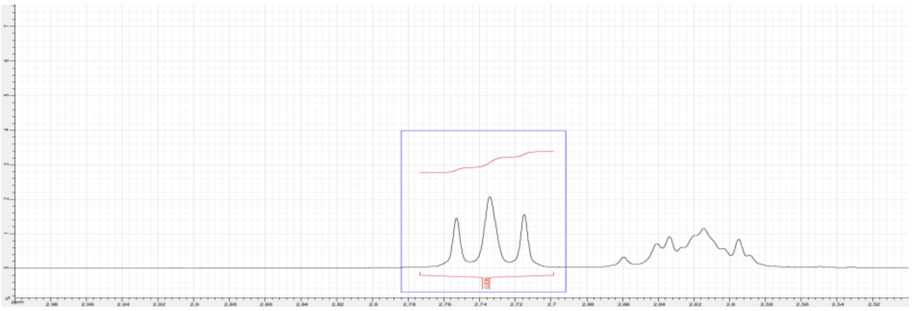
Yellow oil. R_f 0.25 [EtOAc/Petroleum ether 2%, UV-active, PMA]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.78−1.98 (6 H, m, H4), 2.48−2.68 (12 H, m, H3, H5), 6.82 (3 H, s, H1), 7.06−7.33 (15 H, m, H7−H9). ^{13}C NMR (CDCl$_3$, 100.6 Hz): δ 33.0 (C4), 35.4 (C3), 35.5 (C5), 125.6 (C9), 126.0 (C1), 128.2 (C8), 128.4 (C7), 142.2, 142.3 (C2, C6).

IV.2. Analysis of the crude products by ^{1}H NMR spectroscopy

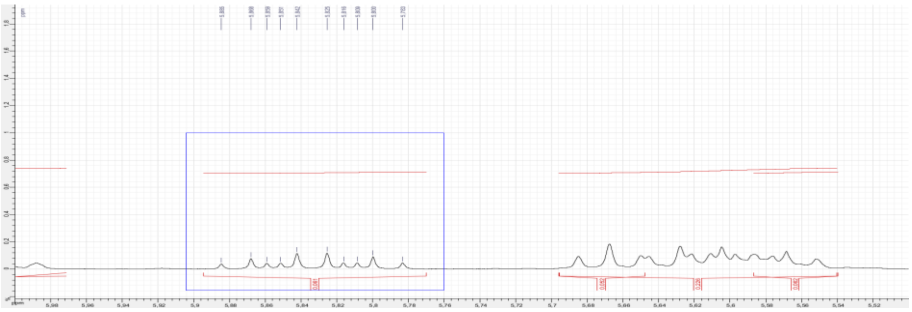
■ The phenyl groups were used as an internal standard: the integral of the signals in the interval 7.07−7.50 ppm was set to 5.00.

■ The following signals were used for the qualitative assessment of the product yields:

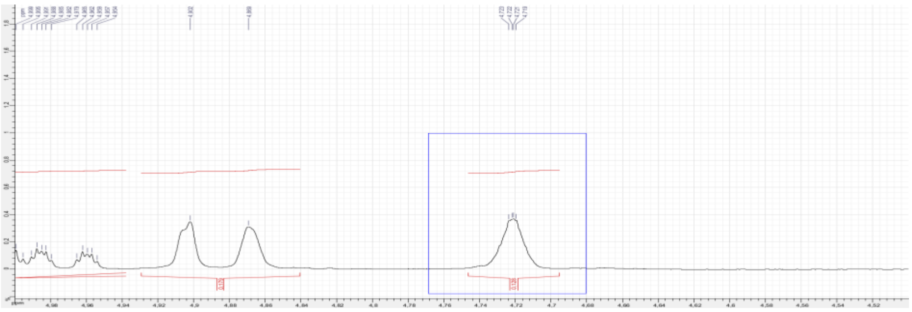
- Triplet (*J* 7.5 Hz) at 2.73 ppm: two protons of **1a**. Dividing the integral of this signal by two gave an estimation of the proportion of unconverted **1a**;



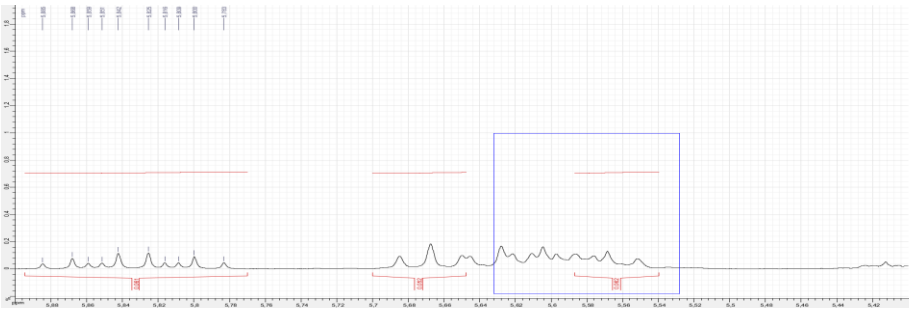
- Doublet of doublet of triplets (*J* 17.0, 10.0 and 6.5 Hz) at 5.83 ppm: one proton of **2a**.
  The integral of this signal gave an estimation of the yield of **2a**;



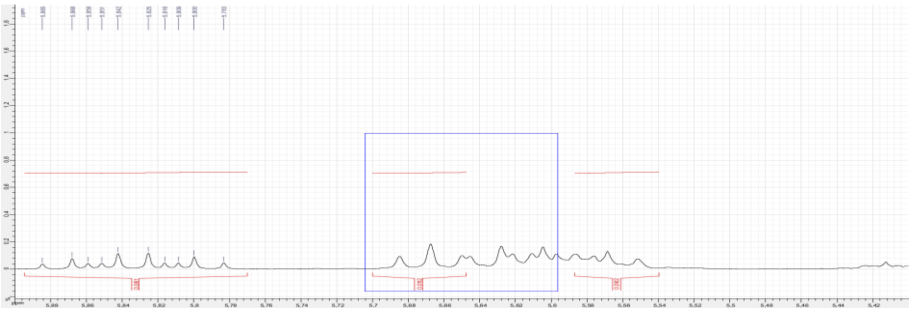
- Broad singlet at 4.72 ppm: two protons of **2′a**.
  Dividing the integral of this signal by two gave an estimation of the yield of **2′a**;



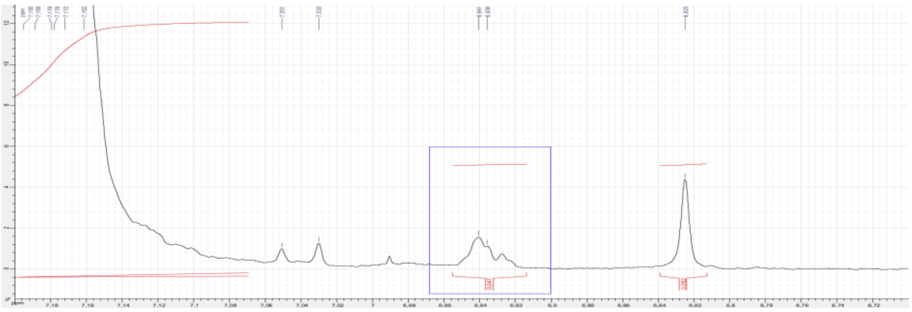
- Multiplet at 5.59 ppm: two protons of **3a**. The integral of the right half of this signal was measured, then multiplied by two to give an estimation of the yield of **3a**;



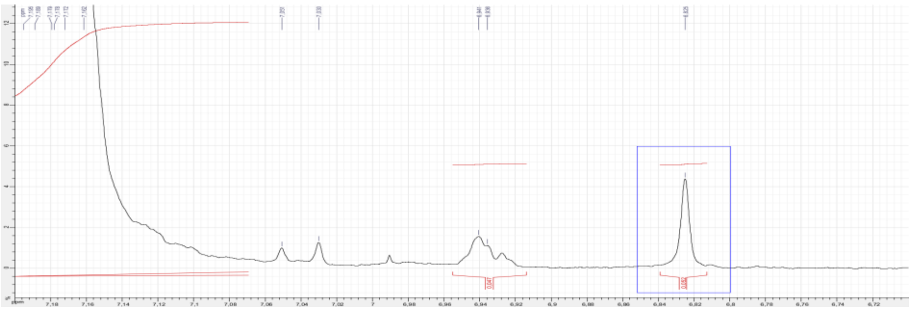
- Doublet of triplets at 5.65 ppm: one proton of **3′a**. The integral of the left half of this signal was measured, then multiplied by four to give an estimation of the yield of **3′a**;



- Multiplet in the range 6.91−6.96 ppm: two protons of **4a**.
  The integral of this signal was multiplied by 3/2 to give an estimation of the yield of **4a**;

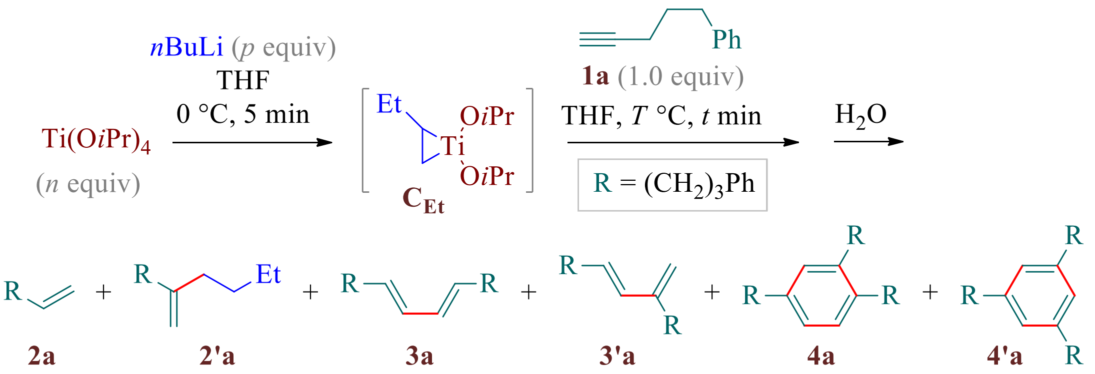


- Singlet at 6.82 ppm: three protons of **4′a**.
  The integral of this signal gave an estimation of the yield of **4′a**.



Note: this method of estimation is conservative. Indeed, the reference range of chemical shifts (7.07−7.50 ppm), assumed to correspond to the phenyl groups of all the compounds present in the solution, includes the signal of residual $CHCl_3$. To avoid excessive underestimation of the product yields, the samples were not diluted too much (typically, ca. 30 mg of crude product in 0.5 mL of $CDCl_3$).

IV.3. Summary of the experimental results obtained using **1a**



Subsection	*n*	*p*	*T*	*t*	S.m. **1a**	Alkene **2a**	Alkene **2′a**	Dienes **3a/3′a** (ratio)	Trimers **4a/4′a** (ratio)
IV.4.1.	4.4	6.6	0	20	2%	13%	13%	41 (46 : 54)	6% (50 : 50)
IV.4.1				30	2%	11%	14%	38% (47 : 53)	7% (57 : 43)
IV.4.1.				45	1%	9%	14%	37% (49 : 51)	8% (50 : 50)
IV.4.2.	2.2	3.3	0	20	3%	8%	11%	42 (48 : 52)	10% (60 : 40)
IV.4.2.				30	2%	7%	11%	38% (50 : 50)	12% (58 : 42)
IV.4.2.				45	2%	6%	11%	37% (51 : 49)	12% (58 : 42)
IV.4.3.	1.1	1.65	0	20	28%	3%	6%	34% (47 : 53)	12% (58 : 42)
IV.4.3.				30	13%	3%	7%	41% (49 : 51)	16% (62 : 38)
IV.4.3.				45	3%	5%	8%	44% (50 : 50)	20% (60 : 40)
IV.4.4.[a]	0.6	0.9	140	15	2%	4%	2%	9% (33 : 67)	38% (71 : 29)

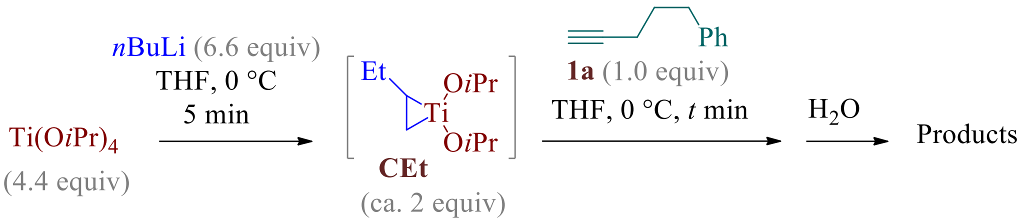
Colours for the starting material: ■ 0–10% ■ 11–20% ■ 21–30% ■ 31–40% ■ ≥41%

Colours for the product yields: ■ 0–10% ■ 11–20% ■ 21–30% ■ 31–40% ■ ≥41%

[a] Heating was applied using a microwave reactor.

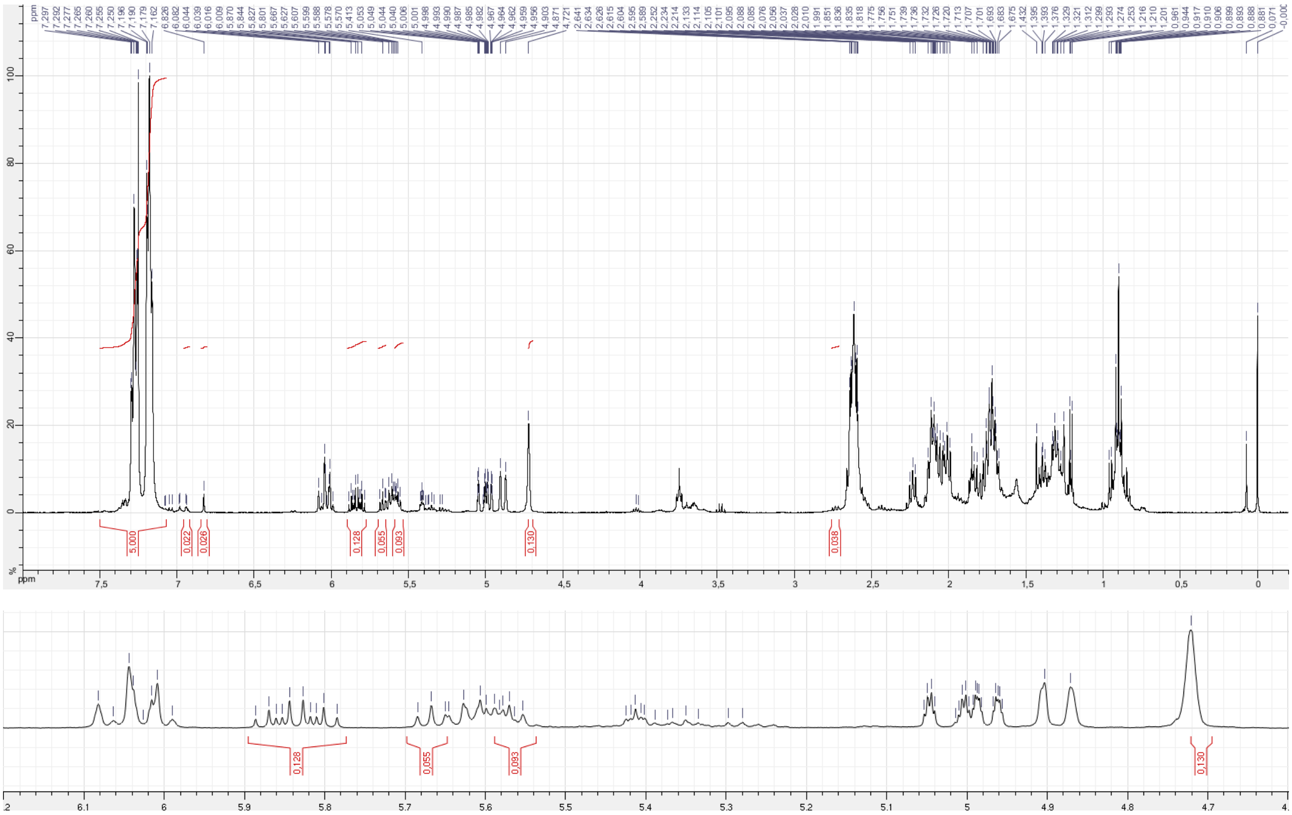
IV.4. Experimental detail

■ **IV.4.1.** With 4.4 equiv of Ti(O*i*Pr)$_4$, 6.6 equiv of *n*BuLi; reaction conducted at 0 °C for 20, 30 or 45 min.



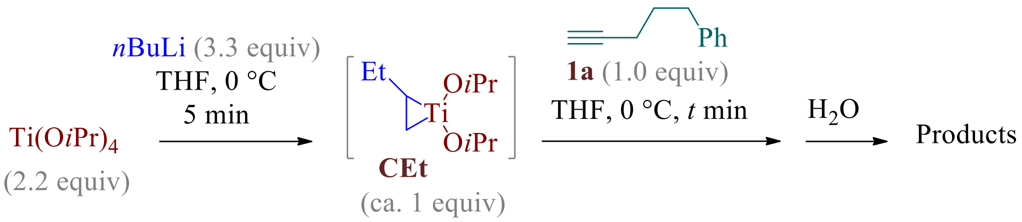
	S.m **1a**	Alkene **2a**	Alkene **2′a**	Diene **3a**	Diene **3′a**	Trimer **4a**	Trimer **4′a**	Total
t = 20	2%	13%	13%	19%	22%	3%	3%	75%
t = 30	2%	11%	14%	18%	20%	4%	3%	72%
t = 45	1%	9%	14%	18%	19%	4%	4%	69%

General procedure **GP2** was applied with *n* = 4.40 and *p* = 6.60.
n-Butyllithium solution (2.27 M in hexanes, 3.30 mmol, 1.45 mL) was added over 1 minute.
5-Phenylpent-1-yne **1a** (500 µmol, 75.9 µL) was added over 30 s.
Crude product after *t* = 20 minutes: colourless oil (10.0 mg).
Crude product after *t* = 30 minutes: colourless oil (12.8 mg).
Crude product after *t* = 45 minutes: colourless oil (68.5 mg).
Analysis of the three crude products, done as described in subsection IV.2., gave the qualitative estimation of the product yields shown in the table above.



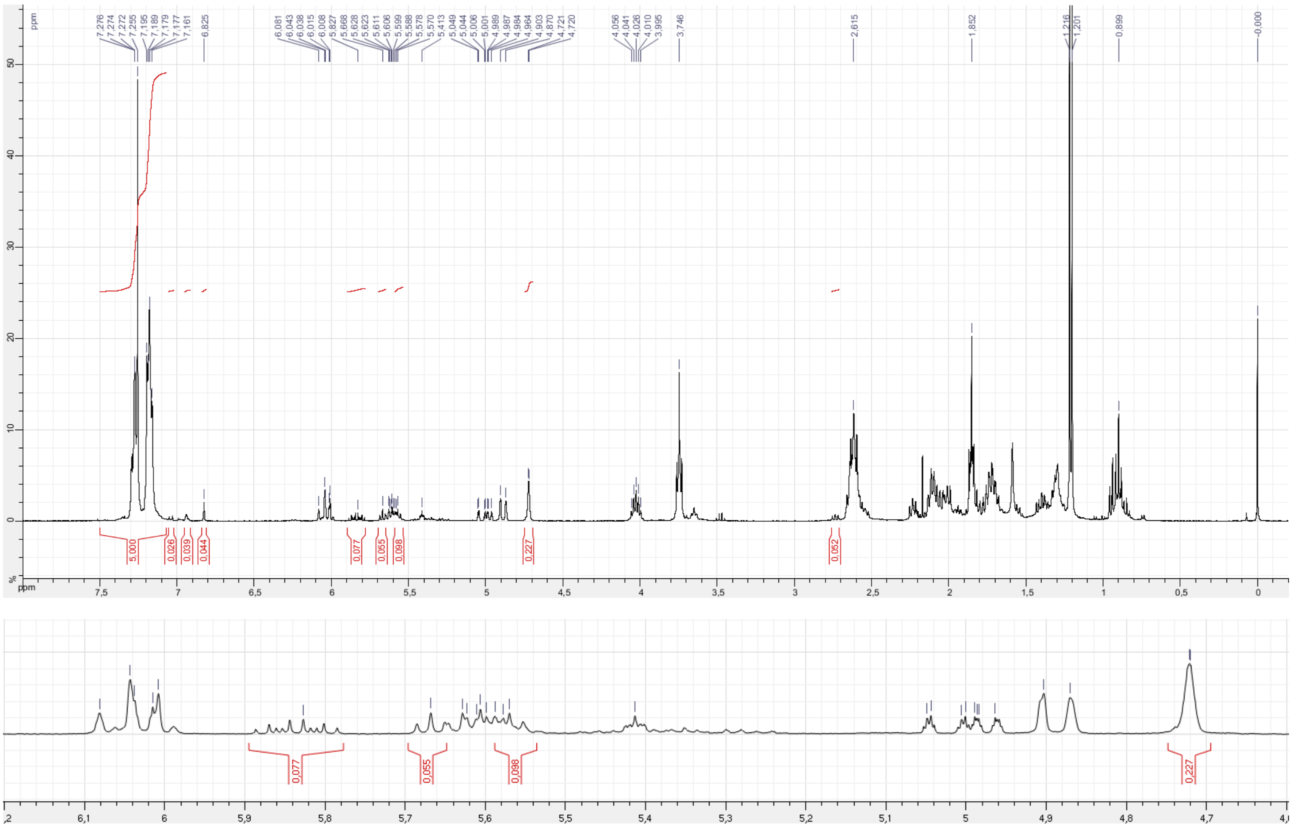
^{1}H NMR spectrum of the crude product after 20 min of reaction (CDCl$_3$, 400 MHz).

■ **IV.4.2.** With 2.2 equiv of Ti(O*i*Pr)$_4$, 3.3 equiv of *n*BuLi; reaction conducted at 0 °C for 20, 30 or 45 min.



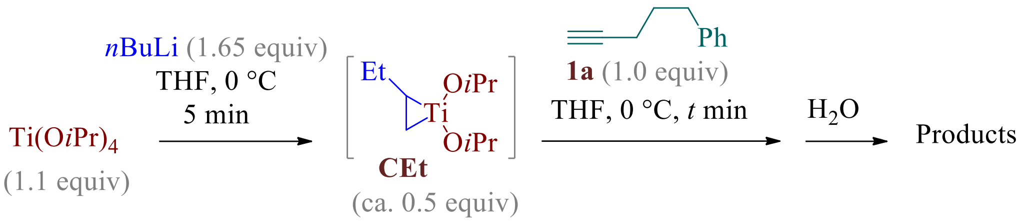
	S.m **1a**	Alkene **2a**	Alkene **2′a**	Diene **3a**	Diene **3′a**	Trimer **4a**	Trimer **4′a**	Total
t = 20	3%	8%	11%	20%	22%	6%	4%	74%
t = 30	2%	7%	11%	19%	19%	7%	5%	70%
t = 45	2%	6%	11%	19%	18%	7%	5%	68%

General procedure **GP2** was applied with *n* = 2.20 and *p* = 3.30.
n-Butyllithium solution (2.27 M in hexanes, 3.30 mmol, 1.45 mL) was added over 2 minutes.
5-Phenylpent-1-yne **1a** (1.00 mmol, 152 µL) was added over 1 minute.
Crude product after *t* = 20 minutes: pale yellow oil (27.7 mg).
Crude product after *t* = 30 minutes: pale yellow oil (26.4 mg).
Crude product after *t* = 45 minutes: pale yellow oil (116 mg).
Analysis of the three crude products, done as described in subsection IV.2., gave the qualitative estimation of the product yields shown in the table above.



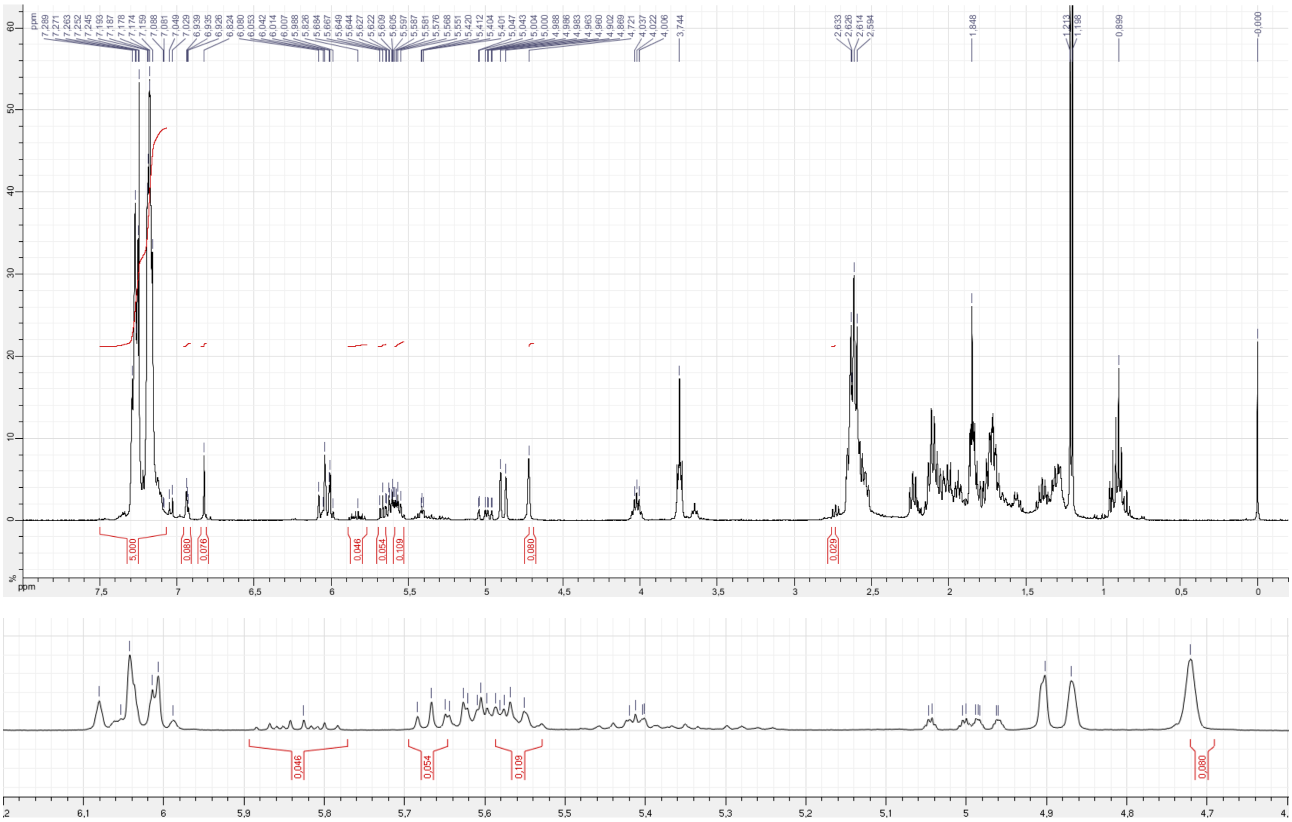
^{1}H NMR spectrum of the crude product after 20 min of reaction ($CDCl_3$, 400 MHz).

■ **IV.4.3.** With 1.1 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *n*BuLi; reaction conducted at 0 °C for 20, 30 or 45 min.



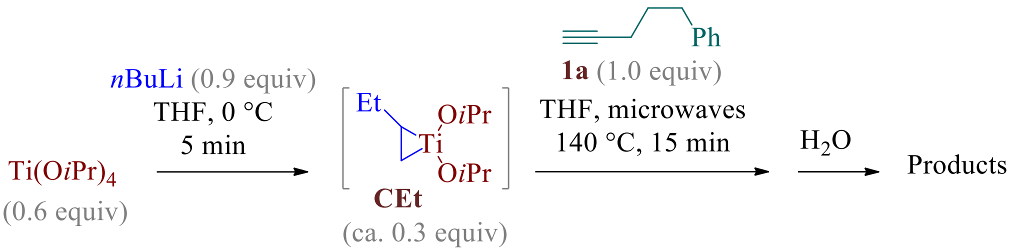
	S.m **1a**	Alkene **2a**	Alkene **2′a**	Diene **3a**	Diene **3′a**	Trimer **4a**	Trimer **4′a**	Total
t = 20	28%	3%	6%	16%	18%	7%	5%	83%
t = 30	13%	3%	7%	20%	21%	10%	6%	80%
t = 45	3%	5%	8%	22%	22%	12%	8%	80%

General procedure **GP2** was applied with *n* = 1.10 and *p* = 1.65.
n-Butyllithium solution (2.27 M in hexanes, 3.30 mmol, 1.45 mL) was added over 1.5 minute.
5-Phenylpent-1-yne **1a** (2.00 mmol, 304 µL) was added over 1.5 minute.
Crude product after *t* = 20 minutes: yellow oil (51.5 mg).
Crude product after *t* = 30 minutes: yellow oil (47.8 mg).
Crude product after *t* = 45 minutes: yellow oil (206 mg).
Analysis of the three crude products, done as described in subsection IV.2., gave the qualitative estimation of the product yields shown in the table above.



^{1}H NMR spectrum of the crude product after 45 min of reaction (CDCl$_3$, 400 MHz).

■ **IV.4.4.** With 0.6 equiv of Ti(O*i*Pr)$_4$, 0.9 equiv of *n*BuLi; reaction conducted at 140 °C for 15 min, under microwave conditions.

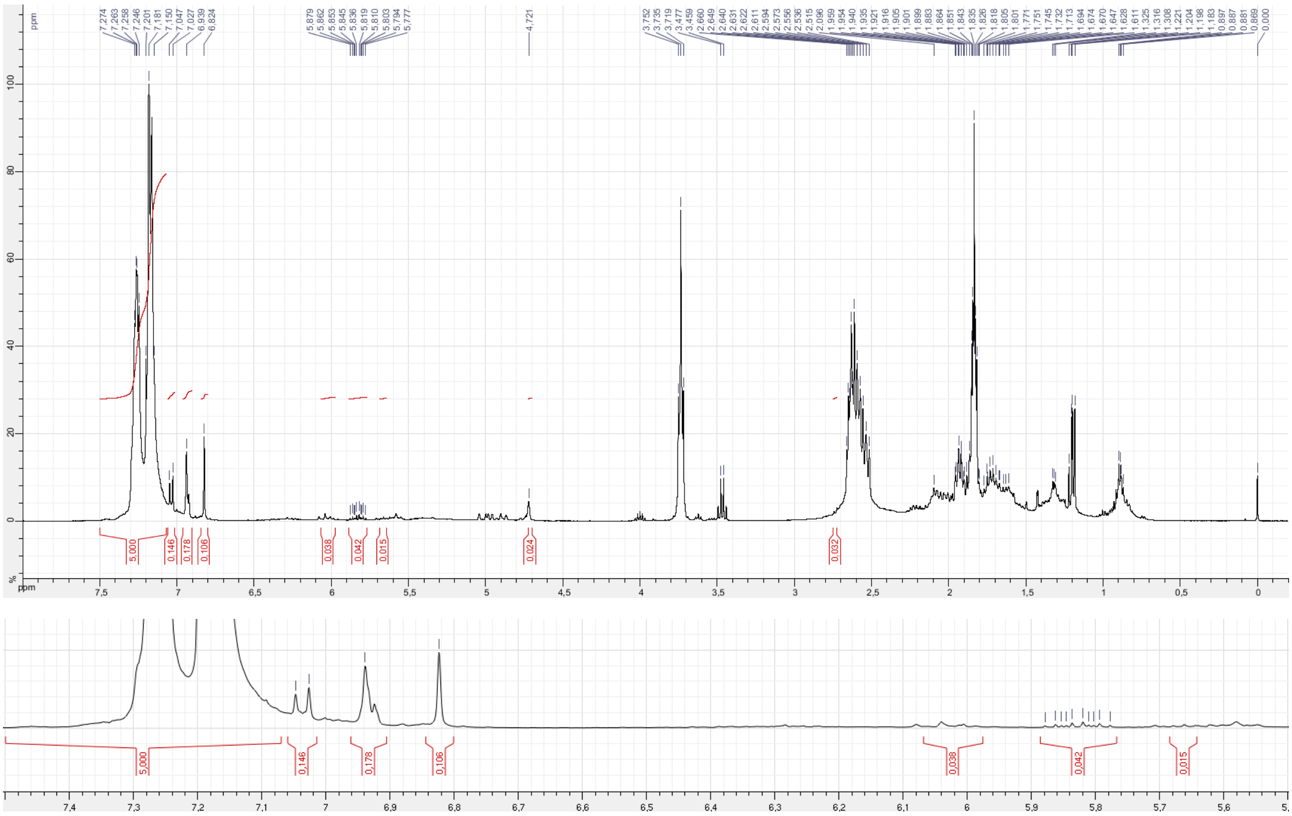


S.m **1a**	Alkene **2a**	Alkene **2′a**	Diene **3a**	Diene **3′a**	Trimer **4a**	Trimer **4′a**	Total
2%	4%	2%	3%	6%	27%	11%	55%

General procedure **GP7** was applied with *T* = 140 and with 5-phenylpent-1-yne **1a** (3.00 mmol, 455 µL) as the substrate.

Crude product: orange oil (524 mg). Analysis as described in subsection IV.2. gave the qualitative estimation of the product yields shown in the table above.

Flash column chromatography (silica gel, EtOAc/petroleum ether, gradient from 0% to 2%) afforded a 72 : 28 mixture of **4a** and **4′a**, contaminated with hydrocarbon impurities (302 mg).



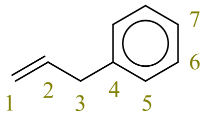
^{1}H NMR spectrum of the crude product (CDCl$_3$, 400 MHz).

V. Experiments with 3-phenylprop-1-yne **1b**

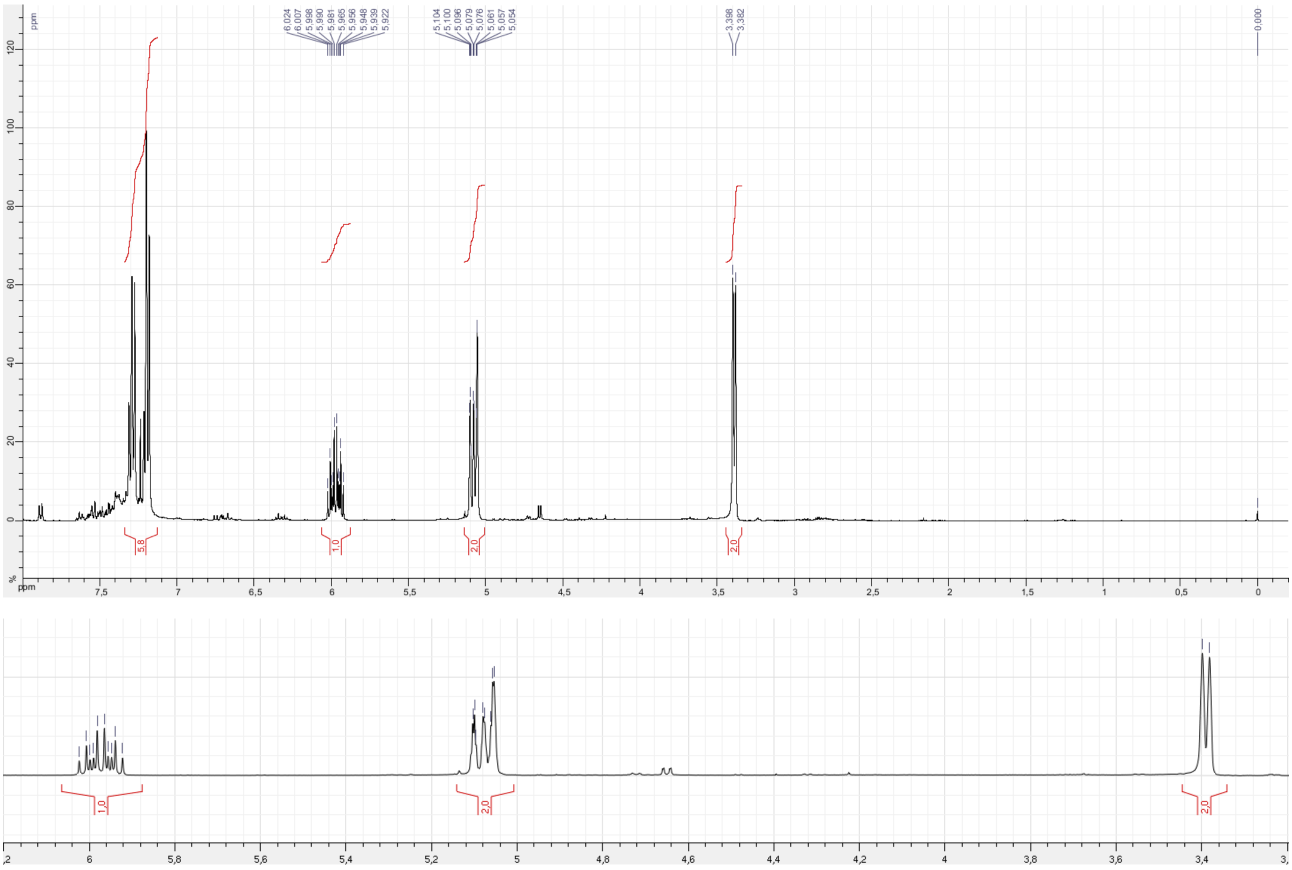
V.1. Characterisation of the products

Products **3b** and **5b** could be isolated in reasonably pure form. Conversely, **2b**, **2′b** and **3′b** were obtained as components of more or less complex mixtures. The cyclotrimers **4b**/**4′b** were isolated as a mixture of the two regioisomers. Assignment of the signals of mixtures of compounds was done as explained in the general information.

Allylbenzene **2b**[22]

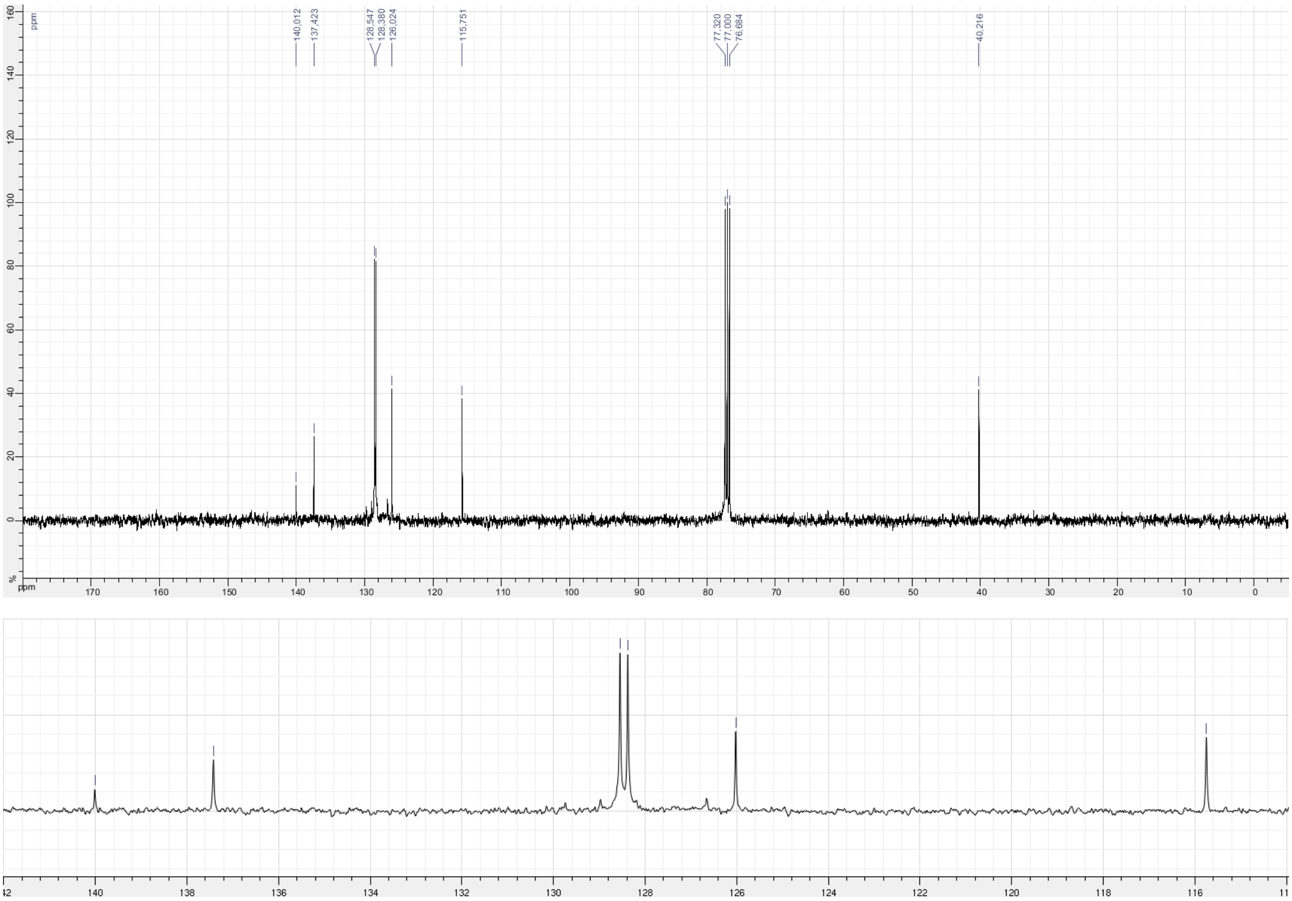


^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.39 (2 H, ddd, *J* 6.5, 1.5, 1.0, H3), 5.07 (1 H, ddt, *J* 10.0, 1.5, 1.0, H1 *cis* to H2), 5.08 (1 H, dq, *J* 17.0, 1.5, H1 *trans* to H2), 5.97 (1 H, ddt, *J* 17.0, 10.0, 6.5, H2), 7.19 (2 H, br d, *J* 8.0, H5), 7.20 (1 H, br t, *J* 7.5, H7), 7.29 (2 H, br dd *J* 8.0, 7.5, H6).
^{13}C NMR (CDCl$_3$, 100.6 MHz): δ 40.2 (C3), 115.8 (C1), 126.0 (C7), 128.4, 128.6 (C5, C6), 137.4 (C2), 140.0 (C4).



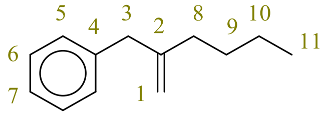
^{1}H NMR spectrum (CDCl$_3$, 400 MHz), recorded from a commercial sample (of rather poor quality).

22− Spectral Database for Organic Compounds, National Institute of Advanced Industrial Science and Technology (AIST), Japan: https://sdbs.db.aist.go.jp/sdbs/cgi-bin/landingpage?sdbsno=6325 (accessed in January 2024).



^{13}C NMR spectrum (CDCl$_3$, 100.6 MHz), recorded from the same commercial sample.

2-Methylenehexylbenzene **2’b**[23]



^{1}H NMR (CDCl$_3$, 400 MHz), characteristic signals: δ 0.88 (3 H, t, J 7.0, H11), 1.97 (2 H, br t, J 8.0, H8), 4.72 (1 H, br s, H1 *cis* to the Bn group), 4.81 (1 H, br s, H1 *trans* to the Bn group). ^{13}C NMR (CDCl$_3$, 100.6 MHz), characteristic signals: δ 13.8 (C11), 22.2 (C10), 29.6 (C9), 34.9 (C8), 42.8 (C3), 110.7 (C1), 149.0 (C2).

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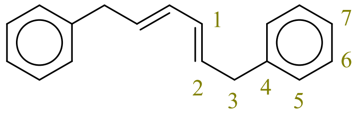
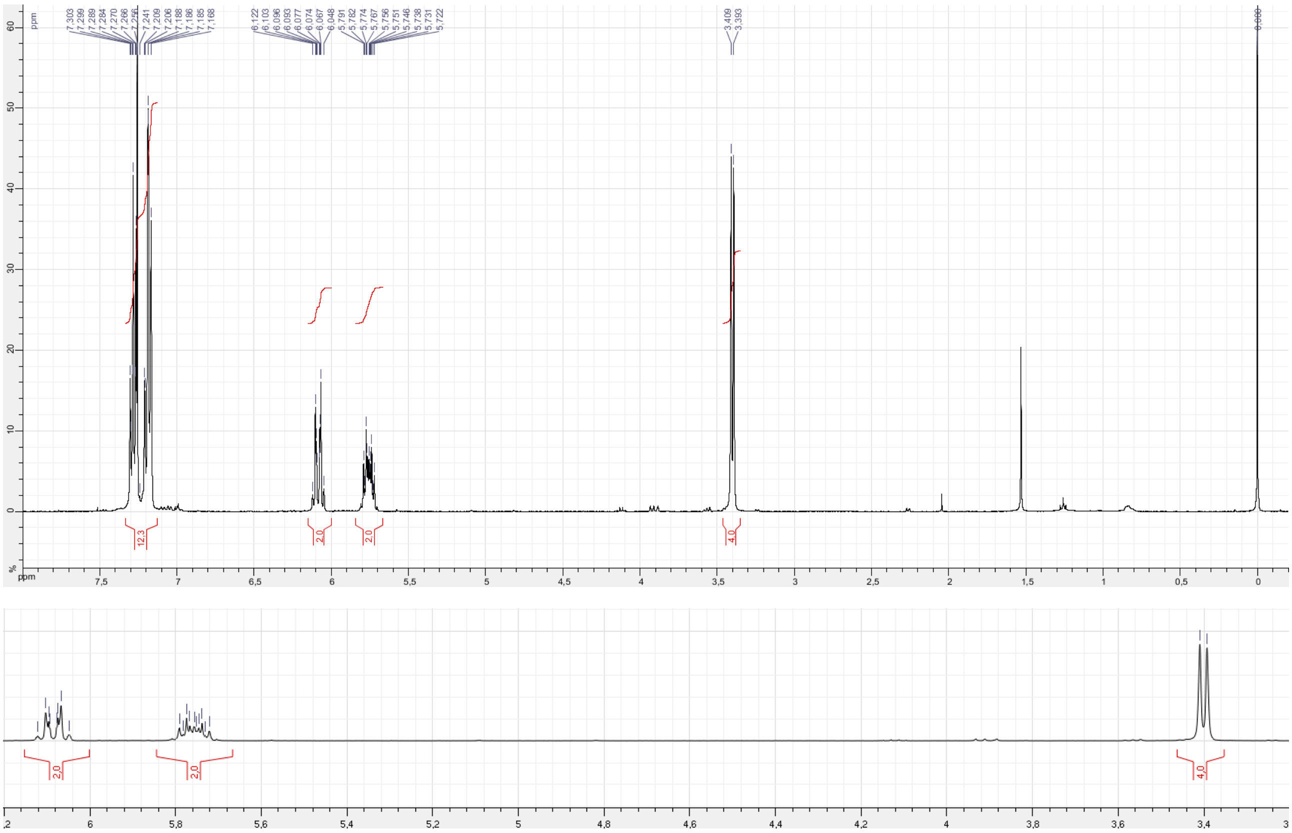
[23] We could not find literature NMR data for this compound but the signals we observed are in excellent agreement with the data previously obtained with the closely related molecule 2-methyleneheptylbenzene: N. A. Till, R. T. Smith, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2018**, *140*, 5701−5705 (supporting information).

[(2*E*,4*E*)-6-Phenylhexa-2,4-dienyl]benzene **3b**[24]



White solid. M.p. 74.0−75.1 °C (EtOAc); litt. 75 °C (MeOH).[25] R_f 0.35 [EtOAc/Petroleum ether 1%, UV-active, anisaldehyde (blue colour)].[26] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.40 (4 H, d, *J* 6.5, H3), 5.75 (2 H, m, distorted dt, *J* 14.5, 6.5, H2), 6.08 (2 H, m, *J* 14.5, H1), 7.18 (4 H, br d, *J* 7.5, H5), 7.19 (2 H, br t, *J* 7.5, H7), 7.28 (4 H, br t, *J* 7.5, H6). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 39.0 (C3), 126.0 (C7), 128.4, 128.6 (C5, C6), 131.2 (C1), 131.5 (C2), 140.3 (C4).

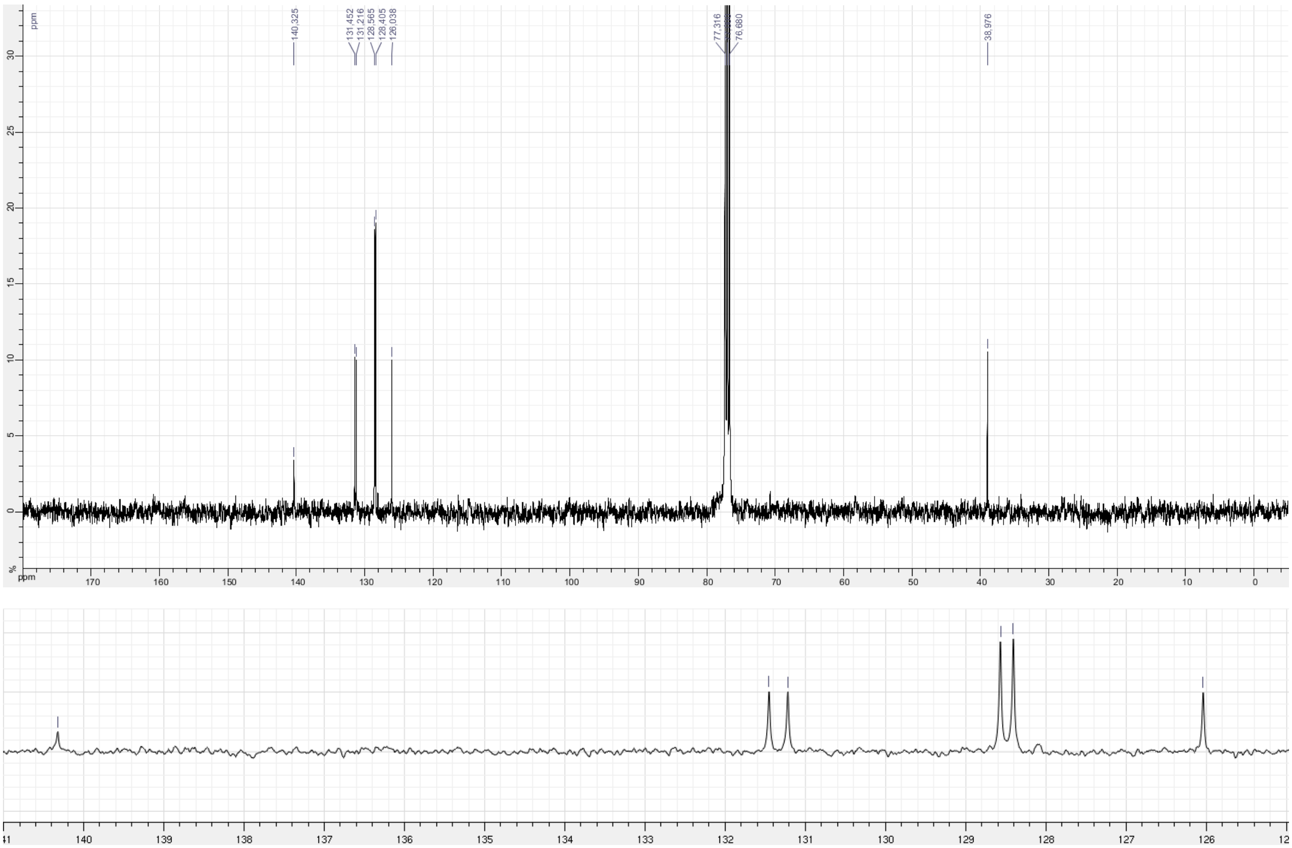


^{1}H NMR spectrum ($CDCl_3$, 400 MHz).

24− S. Yamada, H. Ohsawa, T. Suzuki, H. Takayama, *J. Org. Chem.* **1986**, *51*, 4934−4940.

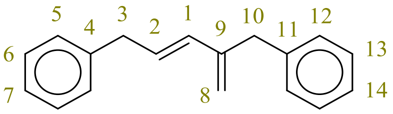
25− A. L. J. Beckwith, R. O. C. Norman, W. Waters, *J. Chem. Soc.* **1958**, 171−175.

26− During flash column chromatography on silica gel, [(2*E*,4*E*)-6-phenylhexa-2,4-dienyl]benzene comes out after [(2*E*)-4-benzylpenta-2,4-dienyl]benzene.

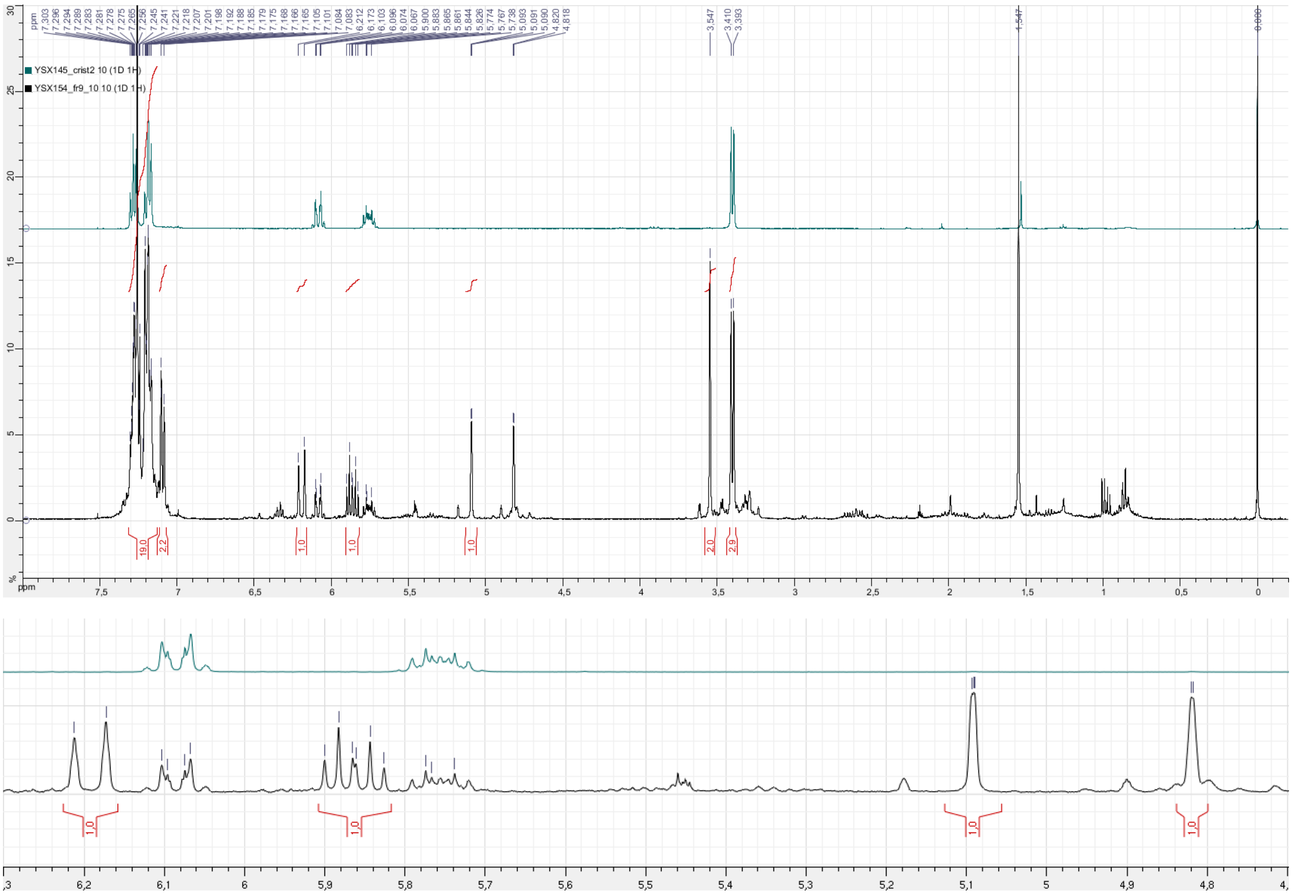


^{13}C NMR spectrum (CDCl$_3$, 100.6 MHz).

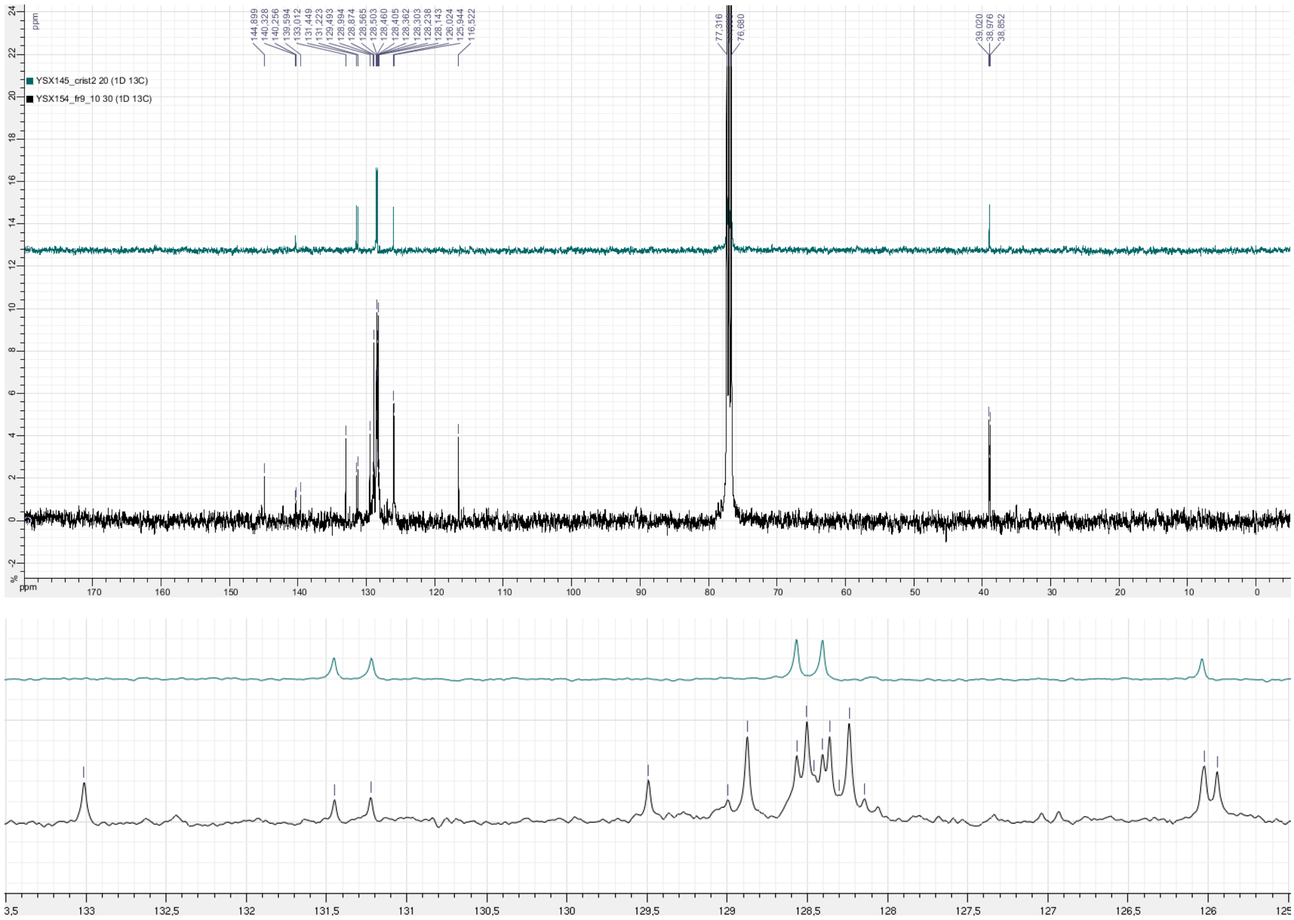
[(2*E*)-4-Benzylpenta-2,4-dienyl]benzene **3′b**



R$_f$ 0.35 [EtOAc/Petroleum ether 1%, UV-active, anisaldehyde (purple colour)].[26] ^{1}H NMR (CDCl$_3$, 400 MHz): *δ* 3.40 (2 H, d, *J* 7.0, H3), 3.55 (2 H, s, H10), 4.82 (1 H, br s, H8 *cis* to the Bn group), 5.09 (1 H, br s, H8 *trans* to the Bn group), 5.86 (1 H, dt, *J* 15.5, 7.0, H2), 6.19 (1 H, br d, *J* 15.5, H1), 7.09 (2 H, br d, *J* 7.5, H12), 7.13−7.31 (8 H, m, H5−H7, H13−H14). ^{13}C NMR (CDCl$_3$, 100.6 Hz): *δ* 38.9, 39.0 (C3, C10), 116.5 (C8), 125.9, 126.0 (C7, C14), 128.2, 128.4, 128.5, 128.9 (C5, C6, C12, C13), 129.5 (C2), 133.0 (C1), 139.6 (C11), 140.3 (C4), 144.9 (C9).

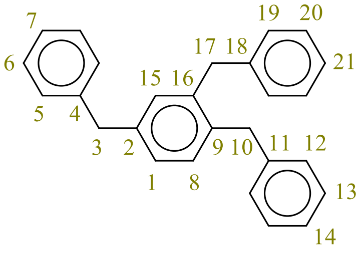


^{1}H NMR spectrum (CDCl$_3$, 400 MHz).
Note: this sample contained some impurities, including [(2*E*,4*E*)-6-phenylhexa-2,4-dienyl]benzene
(spectrum displayed in green, for comparison).



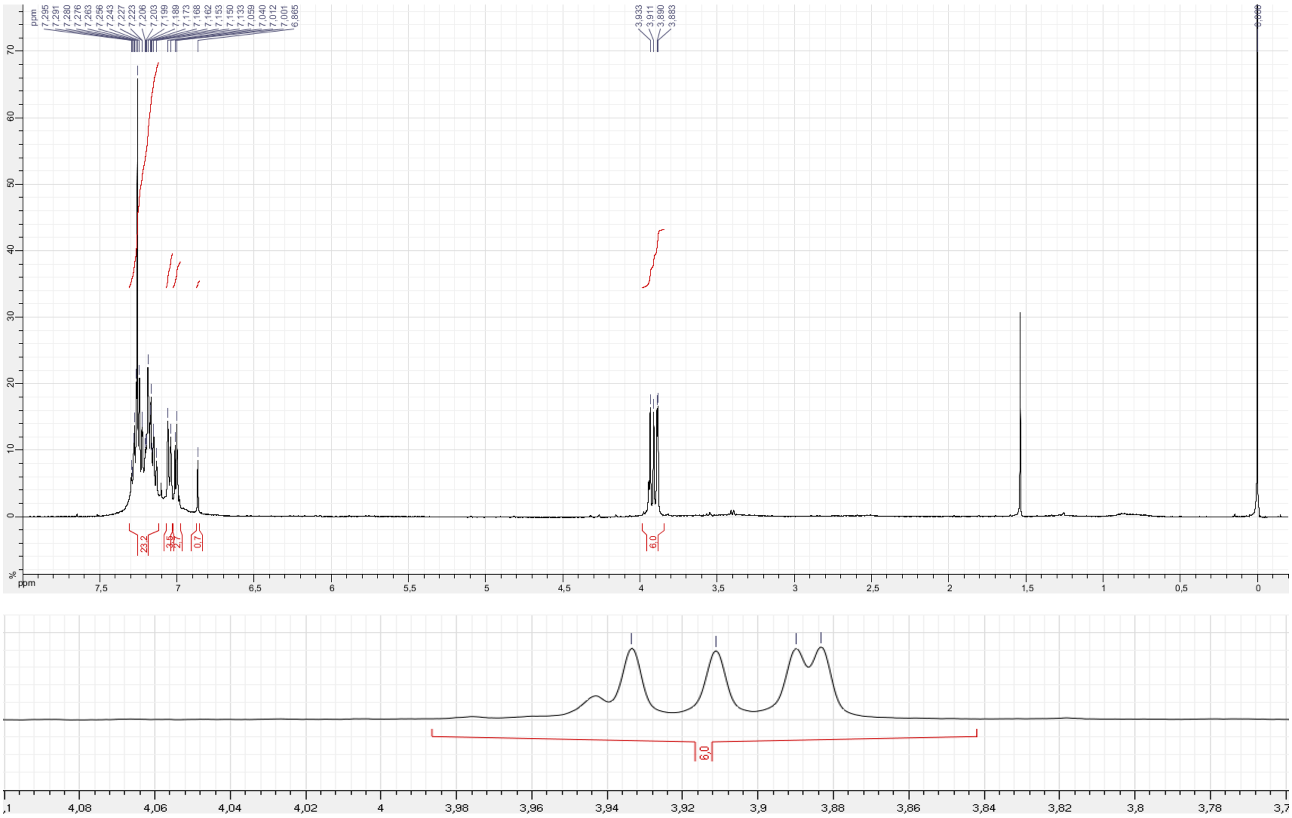
^{13}C NMR spectrum ($CDCl_3$, 100.6 MHz).
Note: this sample contained some impurities, including [(2*E*,4*E*)-6-phenylhexa-2,4-dienyl]benzene (spectrum displayed in green, for comparison).

1,2,4-Tribenzylbenzene **4b**[27]

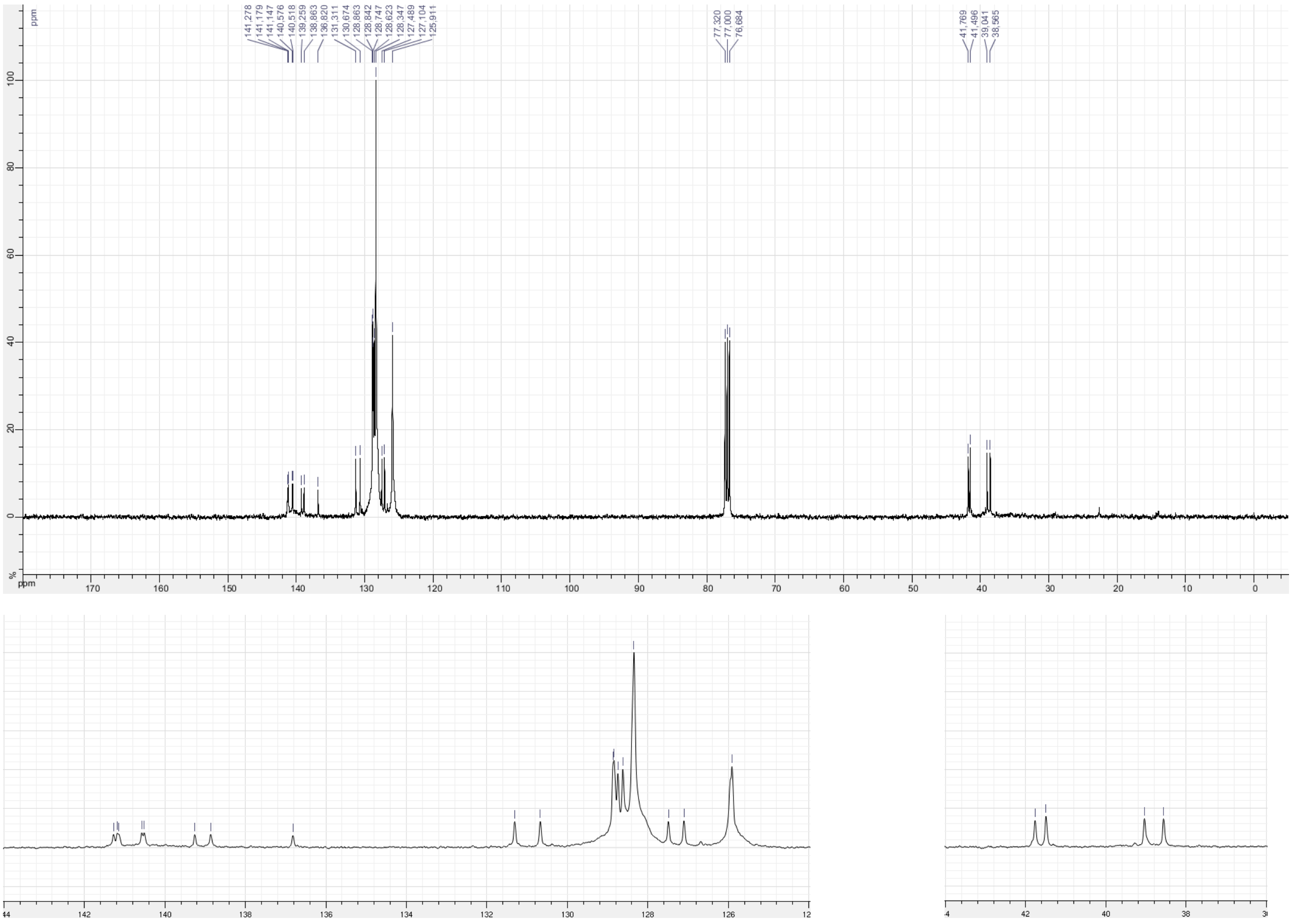


Orange oil. R_f 0.45 (EtOAc/Petroleum ether 2%, UV-active, PMA).
^{1}H NMR ($CDCl_3$, 400 MHz), characteristic signals: δ 3.88 (2 H, s, H3), 3.91 (2 H, s, H10 or H17), 3.93 (2 H, s, H10 or H17), 7.05 (4 H, br d, *J* 7.5, H12, H19), 7.12-7.30 (11 H, m, H5−H7, H13−H14, H20−H21). ^{13}C NMR ($CDCl_3$, 100.6 Hz): δ 38.6, 39.0 (C10, C17), 41.5 (C3), 125.9, 125.9, 125.9 (C7, C14, C21), 127.1 (C1), 128.3, 128.3, 128.3 (C6, C13, C20), 128.6, 128.7 (C12, C19), 128.8 (C5), 130.7 (C8), 131.3 (C15), 136.8 (C2), 138.9, 139.3 (C9, C16), 140.5, 140.6 (C11, C18), 141.2 (C4).

27− K. Tanaka, K. Toyoda, A. Wada, K. Shirasaka, M. Hirano, *Chem. Eur. J.* **2005**, *11*, 1145−1156.

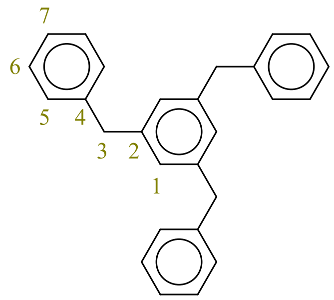


^{1}H NMR spectrum (CDCl$_3$, 400 MHz).
Note: this analysis was performed on a 78 : 22 mixture of **4b** and **4′b**.



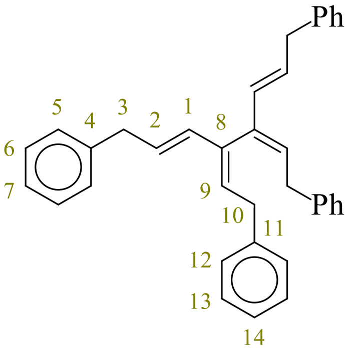
^{13}C NMR spectrum (CDCl$_3$, 100.6 MHz).
Note: this analysis was performed on a 78 : 22 mixture of **4b** and **4′b**.

1,3,5-Tribenzylbenzene **4′b**[27,28]



Orange oil. R_f 0.45 (EtOAc/Petroleum ether 2%, UV-active, PMA).
^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.89 (6 H, s, H3), 6.86 (3 H, s, H1), 7.12-7.30 (15 H, m, H5−H7).
^{13}C NMR (CDCl$_3$, 100.6 Hz): δ 41.8 (C3), 125.9 (C7), 127.5 (C1), 128.3 (C6), 128.9 (C5), 141.1 (C2), 141.3 (C4).

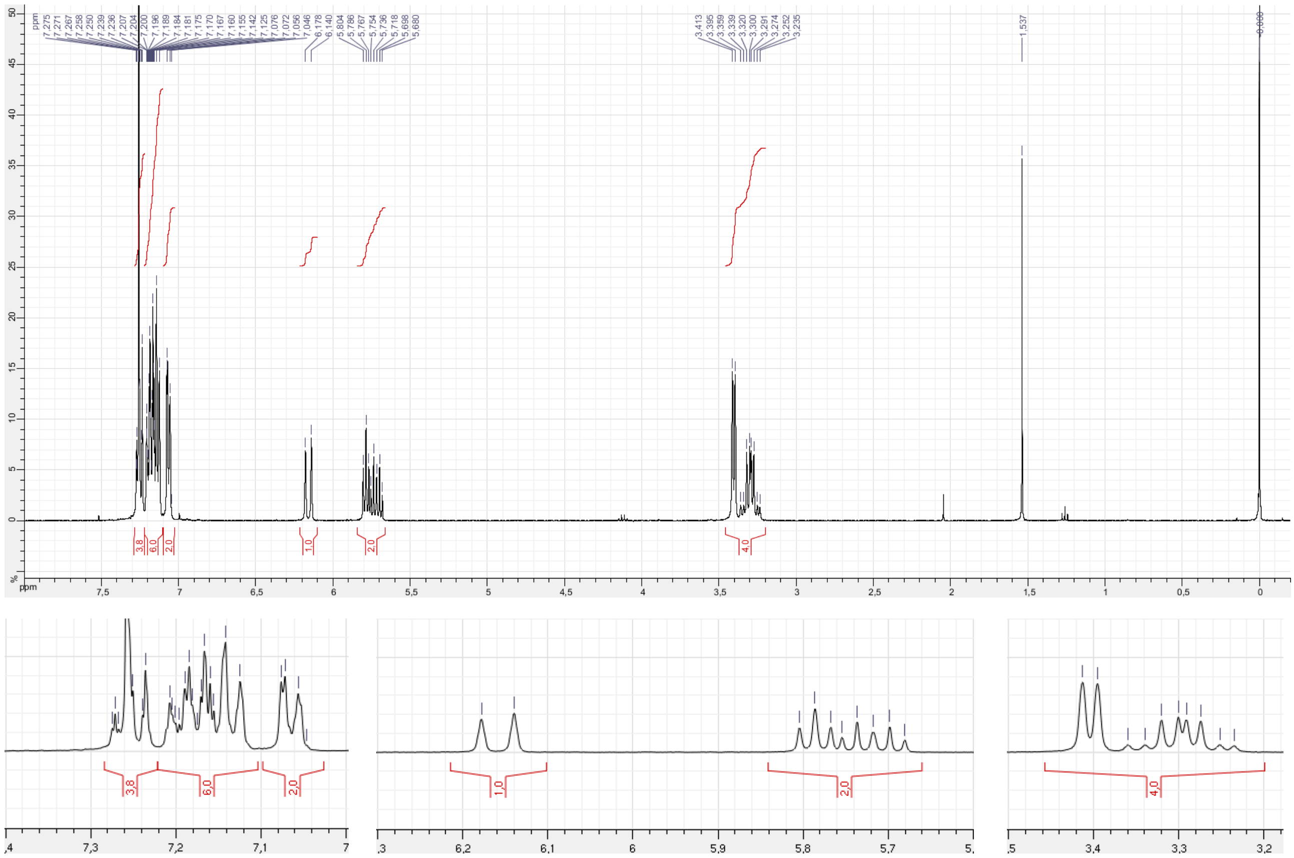
[(2*E*,4*Z*,5*Z*,6*E*)-8-Phenyl-4,5-bis(2-phenylethylidene) octa-2,6-dienyl]benzene **5b**



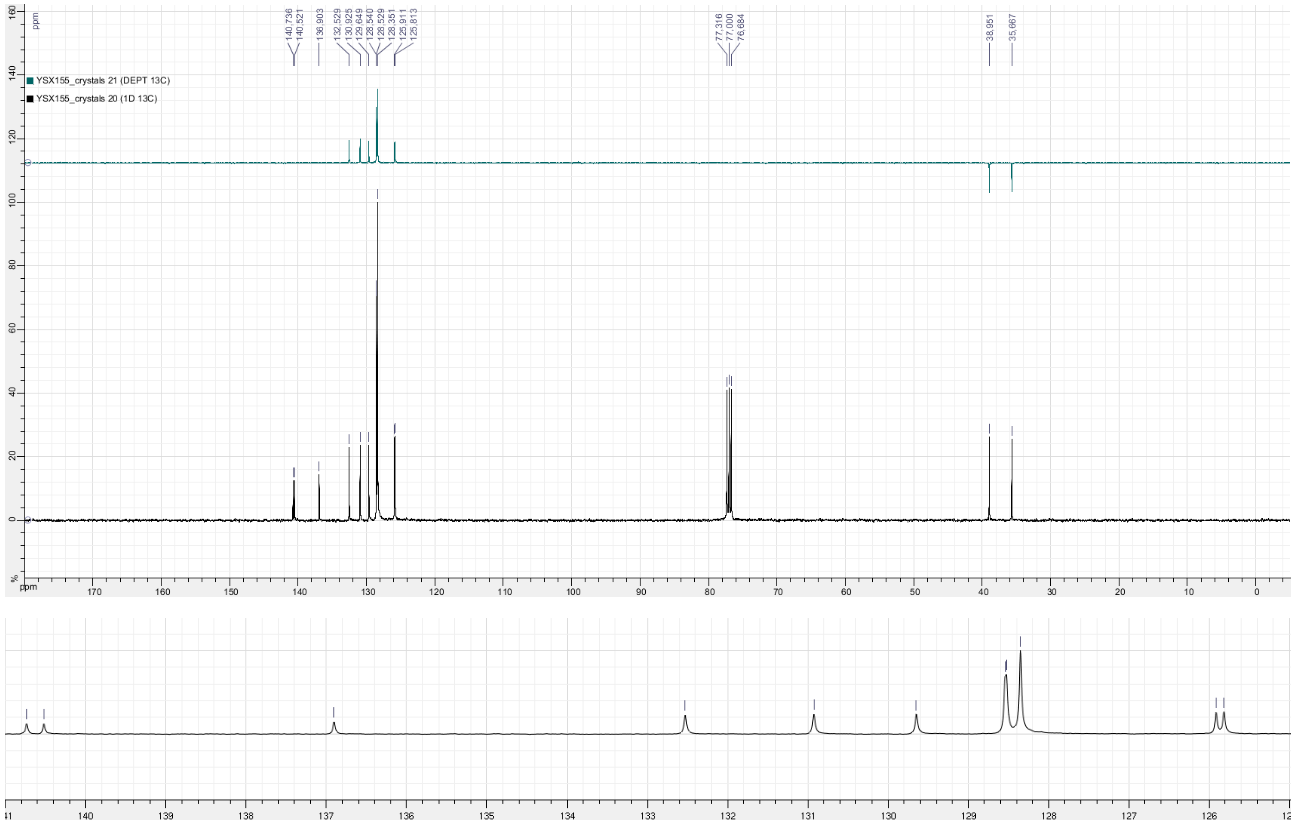
Colourless crystals. M.p. 74.9−77.0 °C (EtOAc); R_f 0.2 [EtOAc/Petroleum ether 1%, UV-active, anisaldehyde (blue-green colour)]. IR (neat): v 3061 (w), 3025 (w), 3010 (w), 2890 (w), 2836 (w), 1599 (w), 1492 (m), 1453 (m), 1432 (w), 1077 (w), 960 (s), 920 (w), 747 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.30 (4 H, AB part of an ABX system, δ_A 3.27, δ_B 3.32, J_{AB} 16.0, J_{AX} 6.5, J_{BX} 8.0, H10), 3.40 (4 H, dd, J 7.0, 1.5, H3), 5.72 (2 H, dt, J 15.5, 7.0, H2), 5.79 (2 H, dd, J 8.0, 6.5, H9), 6.16 (2 H, dt, J 15.5, 1.5, H1), 7.06 (4 H, br d, J 7.5, H12), 7.13 (4 H, br d, J 7.5, H5), 7.14−7.22 (8 H, m, H6 or H13, H7, H14), 7.25 (4 H, br dd, J 7.5, 7.0, H6 or H13). ^{13}C NMR (CDCl$_3$, 100.6 Hz): δ 35.7 (C10), 39.0 (C3), 125.8, 125.9 (C7, C14), 128.4, 128.4, 128.53, 128.54 (C5, C6, C12, C13), 129.6 (C2), 130.9 (C9), 132.5 (C1), 136.9 (C8), 140.5, 140.7 (C4, C11). HRMS (ES$^+$): *m/z* 467.2729 (MH$^+$ $C_{36}H_{35}^+$ requires 467.2733).

For the crystallographic data of **5b**, see section **XI** (p. 156).

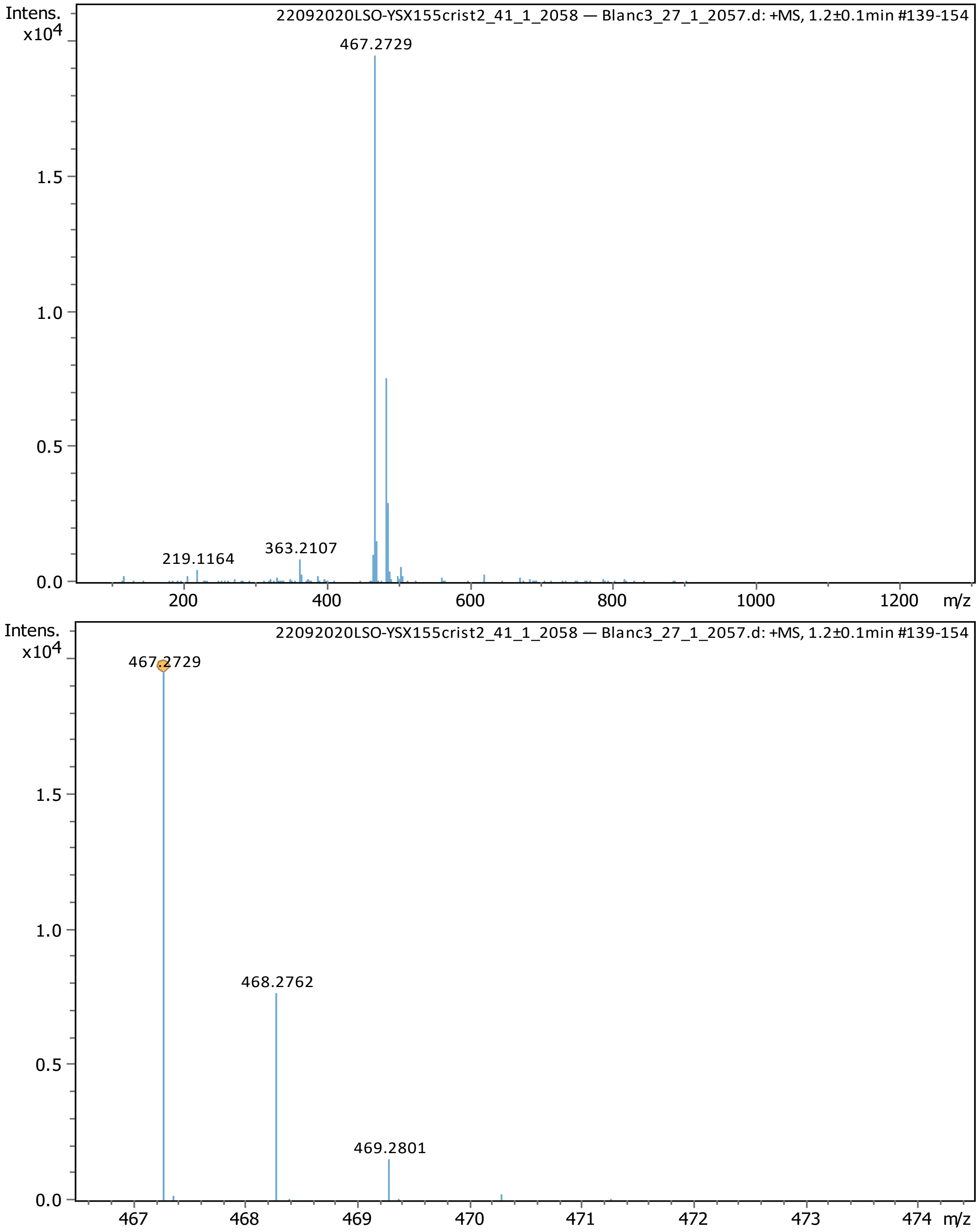
28− A. Rueda-Zubiaurre, N. Herrero-García, M. del Rosario Torres, I. Fernández, J. Osío Barcina, *Chem. Eur. J.* **2012**, *50*, 16884−16889.



^{1}H NMR spectrum (CDCl$_3$, 400 MHz).



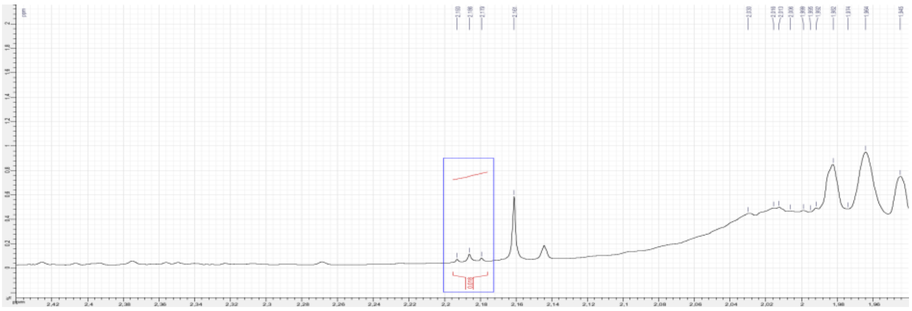
^{13}C NMR and DEPT135 spectra (CDCl$_3$, 100.6 MHz).


Intens.
x10^4
22092020LSO-YSX155crist2_41_1_2058 — Blanc3_27_1_2057.d: +MS, 1.2±0.1min #139-154
467.2729
363.2107
219.1164
1.5
1.0
0.5
0.0
200
400
600
800
1000
1200
m/z
Intens.
x10^4
22092020LSO-YSX155crist2_41_1_2058 — Blanc3_27_1_2057.d: +MS, 1.2±0.1min #139-154
467.2729
468.2762
469.2801
1.5
1.0
0.5
0.0
467
468
469
470
471
472
473
474
m/z

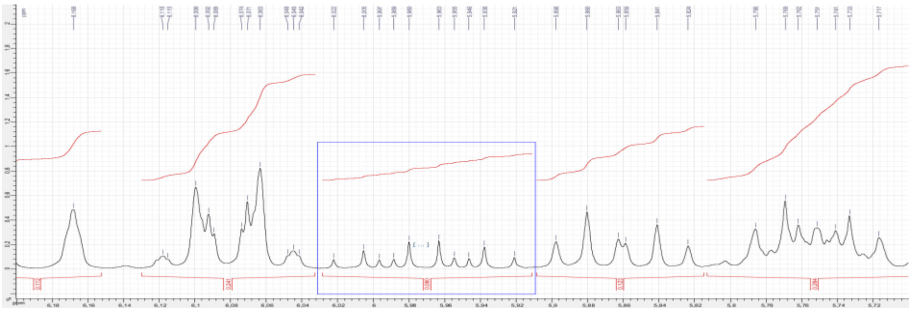
HRMS (ES$^+$).

V.2. Analysis of the crude products by ^{1}H NMR spectroscopy

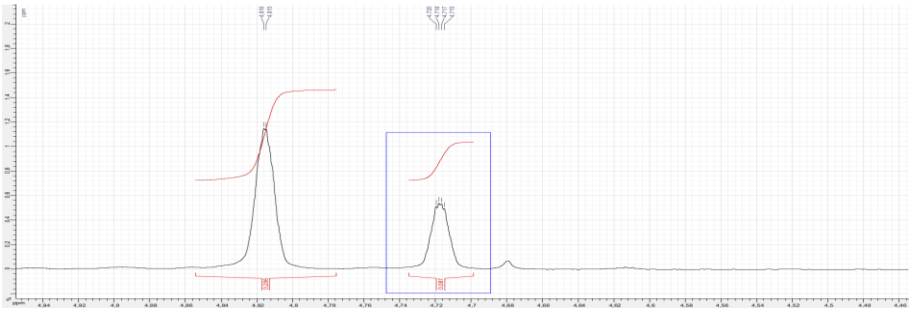
- The phenyl groups were used as an internal standard: the integral of the signals in the interval 7.06–7.40 ppm was set to 5.00.
- The following signals were used for the qualitative assessment of the product yields:
  - Triplet (*J* 2.5 Hz) at 2.18 ppm: one proton of **1b**.
    The integral of this signal gave an estimation of the proportion of unconverted **1b**;



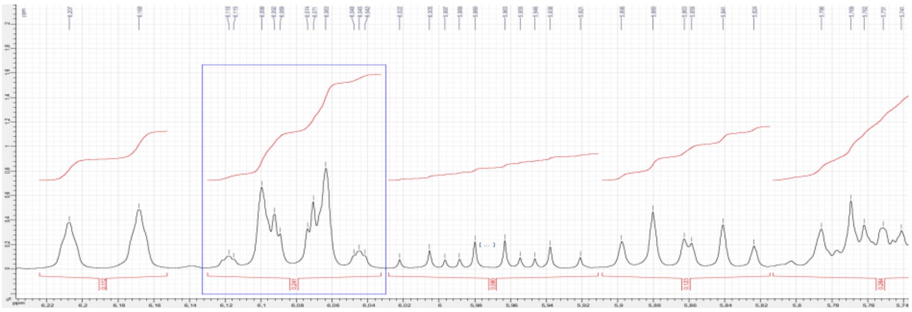
  - Doublet of doublet of triplets (*J* 17.0, 10.0 and 6.5 Hz) at 5.97 ppm: one proton of **2b**.
    The integral of this signal gave an estimation of the yield of **2b**;



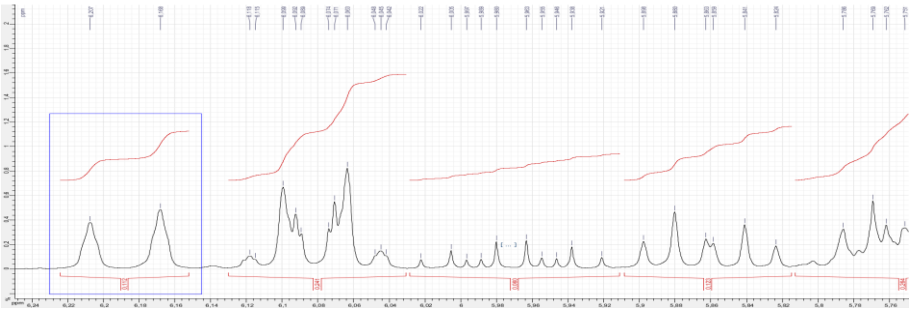
  - Broad singlet at 4.72 ppm: one proton of **2′b**.
    The integral of this signal gave an estimation of the yield of **2′b**;



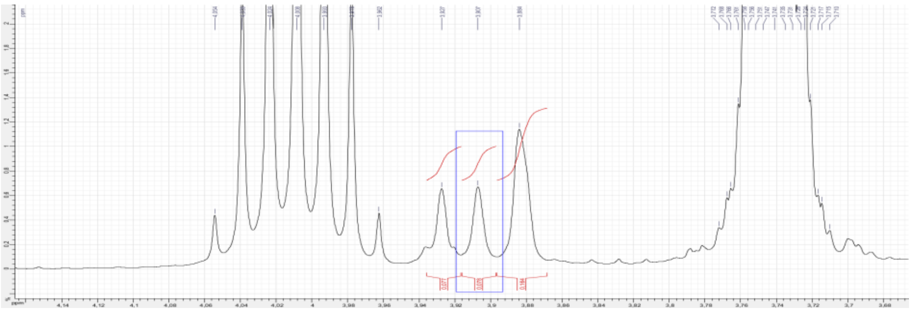
  - Multiplet at 6.08 ppm: two protons of **3b**.
    The integral of this signal gave an estimation of the yield of **3b**;



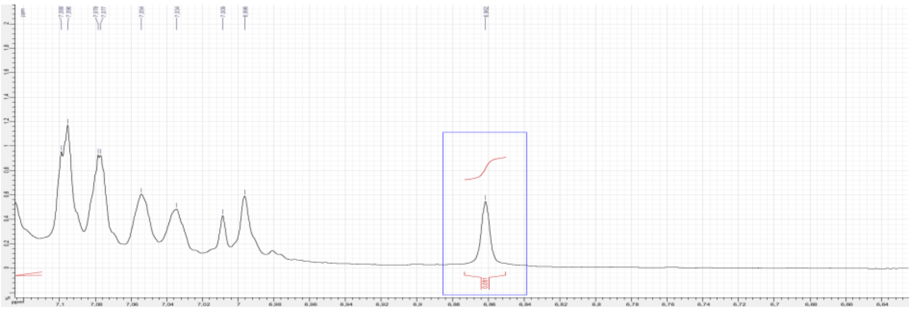
- Broad doublet (*J* 15.5 Hz) at 6.19 ppm: one proton of **3′b**. The integral of this signal was measured, then multiplied by two to give an estimation of the yield of **3′b**;



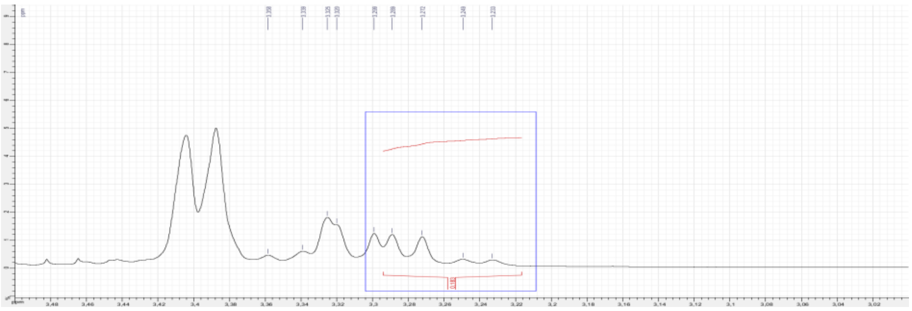
- Singlet at 3.91 ppm: two protons of **4b**.
  The integral of this signal was multiplied by 3/2 to give an estimation of the yield of **4b**;



- Singlet at 6.86 ppm: three protons of **4′b**.
  The integral of this signal gave an estimation of the yield of **4′b**.



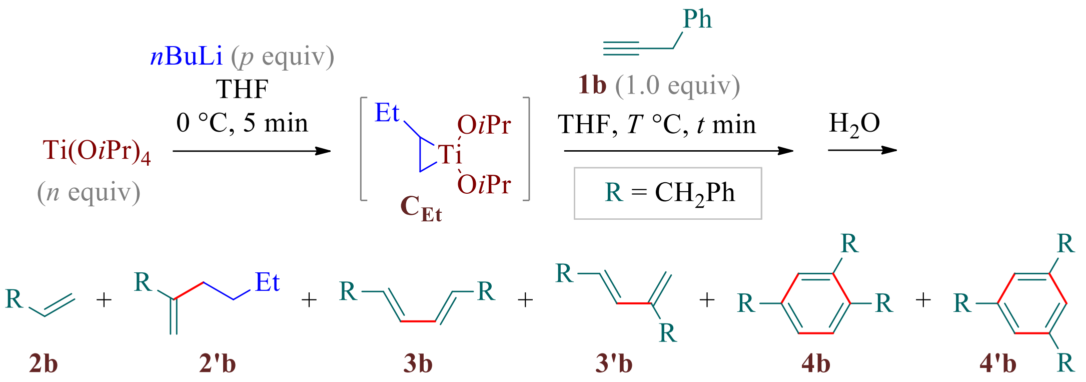
- AB part of an ABX system at 3.30 ppm: four protons of **5b**. The integral of the right half of this signal was measured, then multiplied by two to give an estimation of the yield of **5b**.



Note: this method of estimation is conservative, as in the case of the reactions of **1a**. Accordingly, to avoid excessive underestimation of the product yields, the samples were not diluted too much (typically, ca. 30 mg of crude product in 0.5 mL of $CDCl_3$).

V.3. Summary of the experimental results obtained using **1b**

■ With *n*BuLi, in THF.



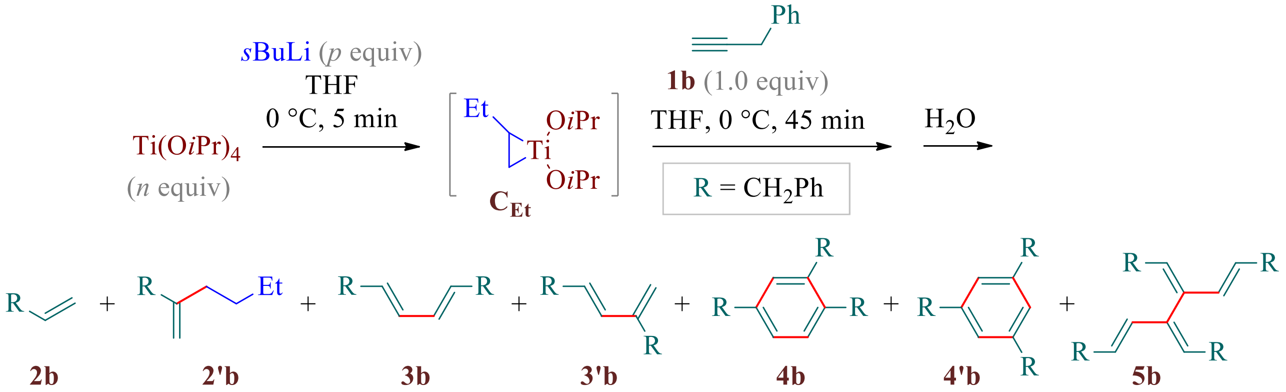
Subsection	*n*	*p*	*T*	*t*	S.m. **1b**	Alkene **2b**	Alkene **2′b**	Dienes **3b/3′b** (ratio)	Trimers **4b/4′b** (ratio)
V.4.1.	3.4	5.1	0	45	Traces	11%	10%	49% (49 : 51)	7% (71 : 29)
V.4.2.	2.2	3.3	0	45	2%	6%	8%	44% (52 : 48)	16% (69 : 31)
V.4.4.		then	0 24	45 120	0%	3%	7%	8% (75 : 25)	24% (67 : 33)
V.4.5.	1.1	1.65	0	45	3%	5%	5%	31% (55 : 45)	31% (71 : 29)
V.4.6.[a]	0.6	0.9	140	15	0%	3%	Traces%	7% (43 : 57)	42% (71 : 29)

Colours for the starting material: ■ 0−10% ■ 11−20% ■ 21−30% ■ 31−40% ■ ≥41%

Colours for the products: ■ 0−10% ■ 11−20% ■ 21−30% ■ 31−40% ■ ≥41%

[a] Heating was applied using a microwave reactor.

■ With *s*BuLi,[a] in THF.



Subsection	*n*	*p*	s.m. **1b**	Alkene **2b**	Alkene **2′b**	Dienes **3b/3′b** (ratio)	Trimers **4b/4′b** (ratio)	Tetramer **5b**
V.4.7.	2.2	3.3	1%	18%	7%	39% (49 : 51)	6% (67 : 33)	0%
V.4.8.[b]	1.1	1.65	12%	5%	3%	29% (41 : 59)	5% (64 : 36)	30%

Colours for the starting material: 🟥 0−10% 🟥 11−20% 🟥 21−30% 🟥 31−40% 🟥 ≥41%

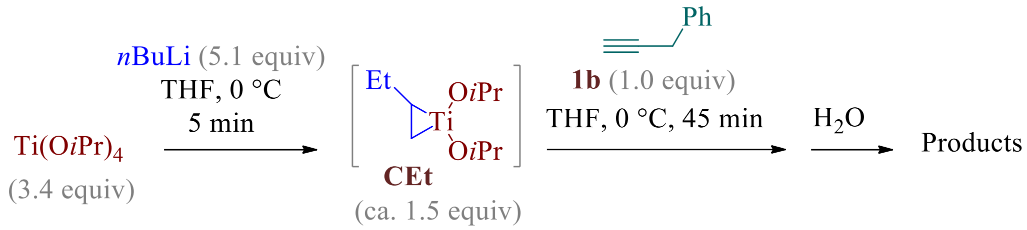
Colours for the products: 🟩 0−10% 🟩 11−20% 🟩 21−30% 🟩 31−40% 🟩 ≥41%

[a] Bottle #1 was used in these experiments.

[b] Mean values are given for the yields, calculated from the similar results of two runs carried out under the same conditions.

V.4. Experimental detail

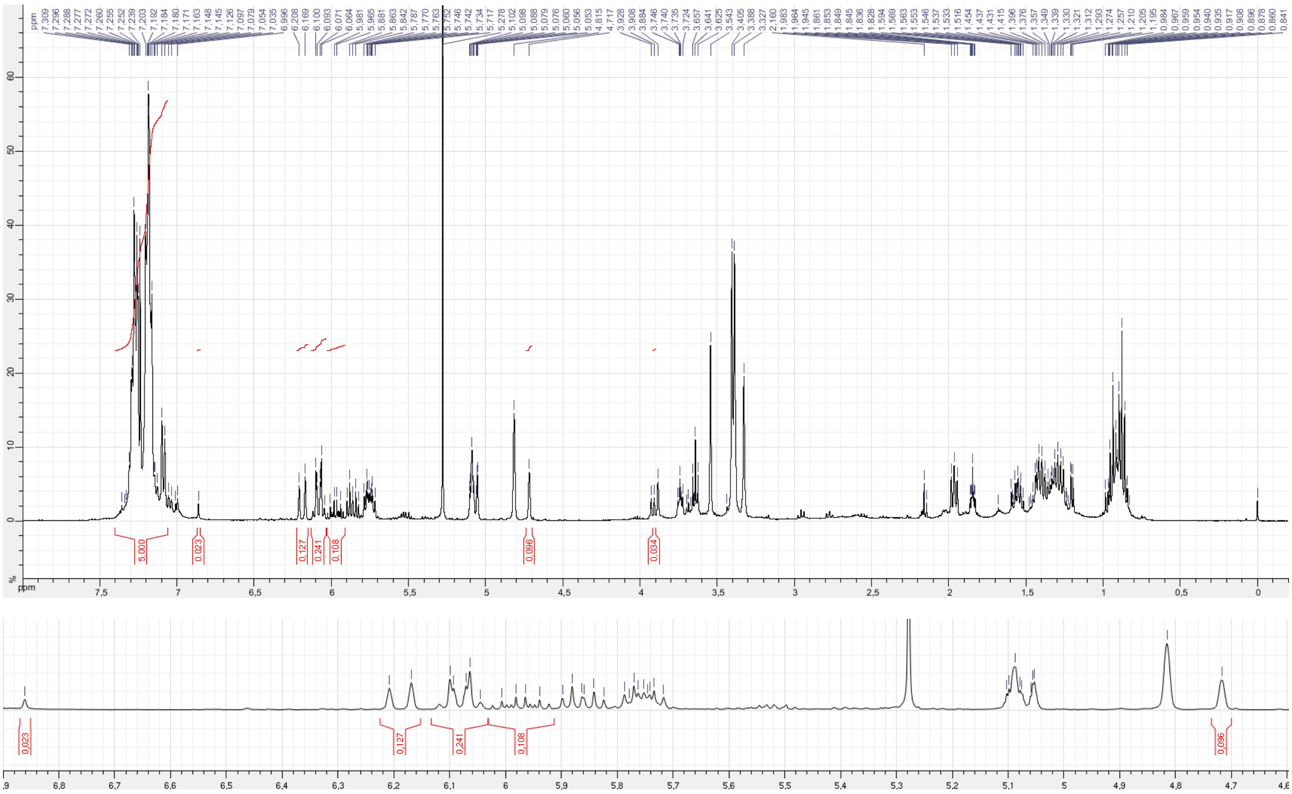
■ **V.4.1.** With 3.4 equiv of Ti(O*i*Pr)$_4$, 5.1 equiv of *n*BuLi; reaction conducted at 0 °C for 45 min.



S.m **1b**	Alkene **2b**	Alkene **2′b**	Diene **3b**	Diene **3′b**	Trimer **4b**	Trimer **4′b**	Total
Traces	11%	10%	24%	25%	5%	2%	77%

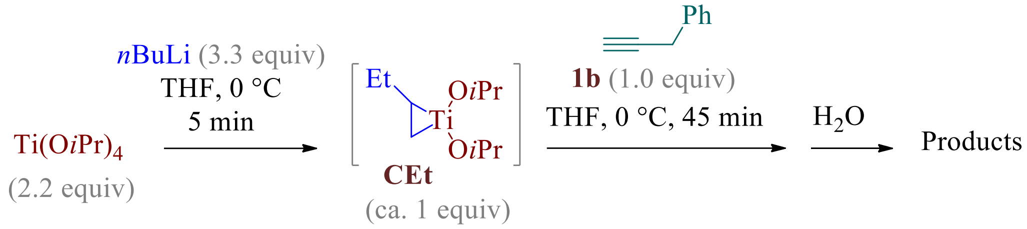
General procedure **GP3** was applied with $n = 3.38$, $p = 5.08$, $V_1 = 5.0$, $V_2 = 2.0$ and $t = 45$.
n-Butyllithium solution (2.34 M in hexanes, 3.30 mmol, 1.41 mL) was added over 2 minutes. The THF solution of 3-phenylprop-1-yne **1b** (650 µmol, 81 µL) was added over 1 minute.

Crude product: dark yellow oil (104 mg). Analysis as described in subsection V.2. gave the qualitative estimation of the product yields shown in the table above.



^{1}H NMR spectrum of the crude product ($CDCl_3$, 400 MHz).

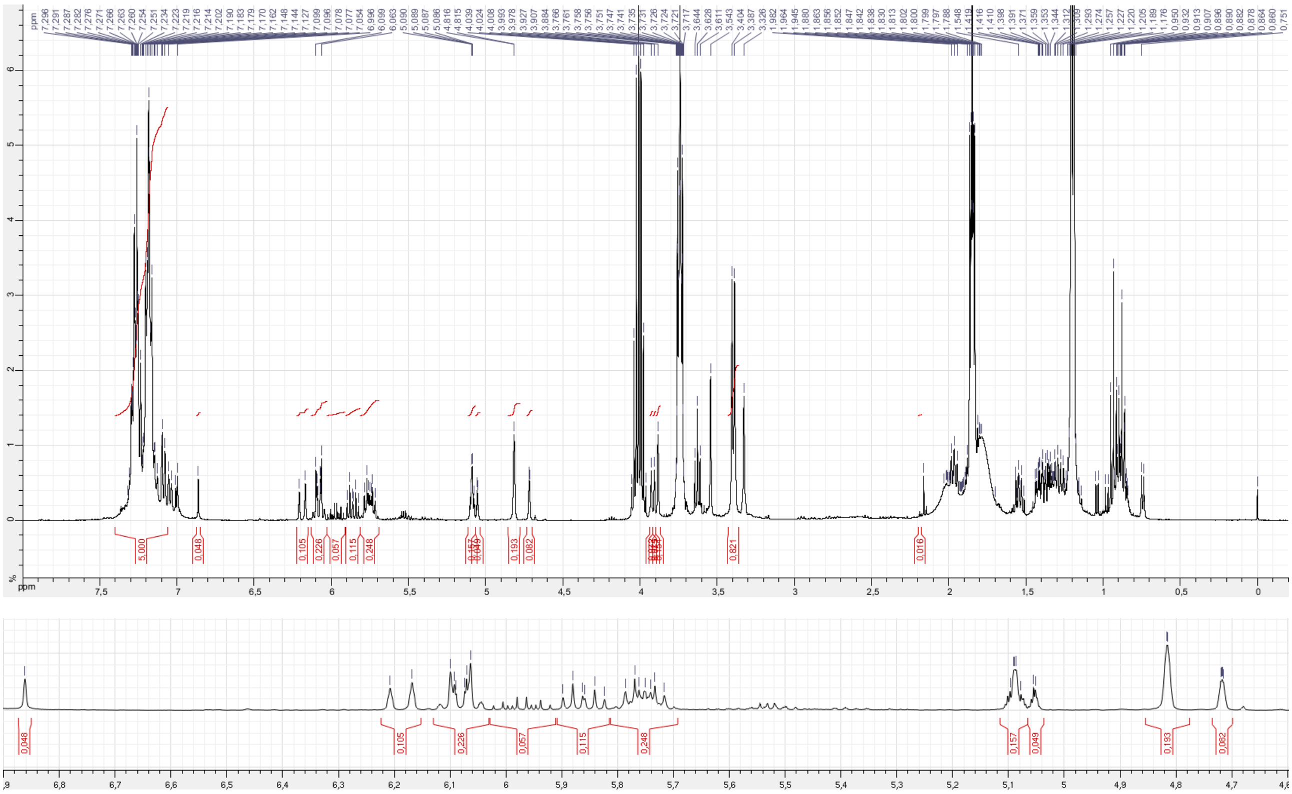
■ **V.4.2.** With 2.2 equiv of Ti(O*i*Pr)$_4$, 3.3 equiv of *n*BuLi; reaction conducted at 0 °C for 45 min.



S.m **1b**	Alkene **2b**	Alkene **2′b**	Diene **3b**	Diene **3′b**	Trimer **4b**	Trimer **4′b**	Total
2%	6%	8%	23%	21%	11%	5%	76%

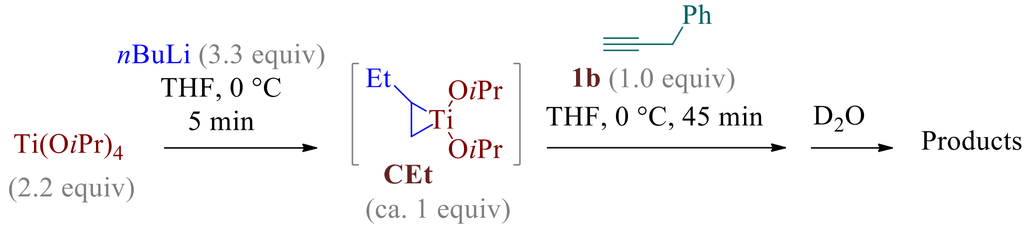
General procedure **GP1** was applied with $n = 2.20$, $p = 3.30$ and $t = 45$. *n*-Butyllithium solution (2.34 M in hexanes, 3.30 mmol, 1.41 mL) was added over 2 minutes. 3-Phenylprop-1-yne **1b** (1.00 mmol, 124 µL) was added over 1 minute.

Crude product: dark yellow oil (237 mg). Analysis as described in subsection V.2. gave the qualitative estimation of the product yields shown in the table above.



^{1}H NMR spectrum of the crude product ($CDCl_3$, 400 MHz).

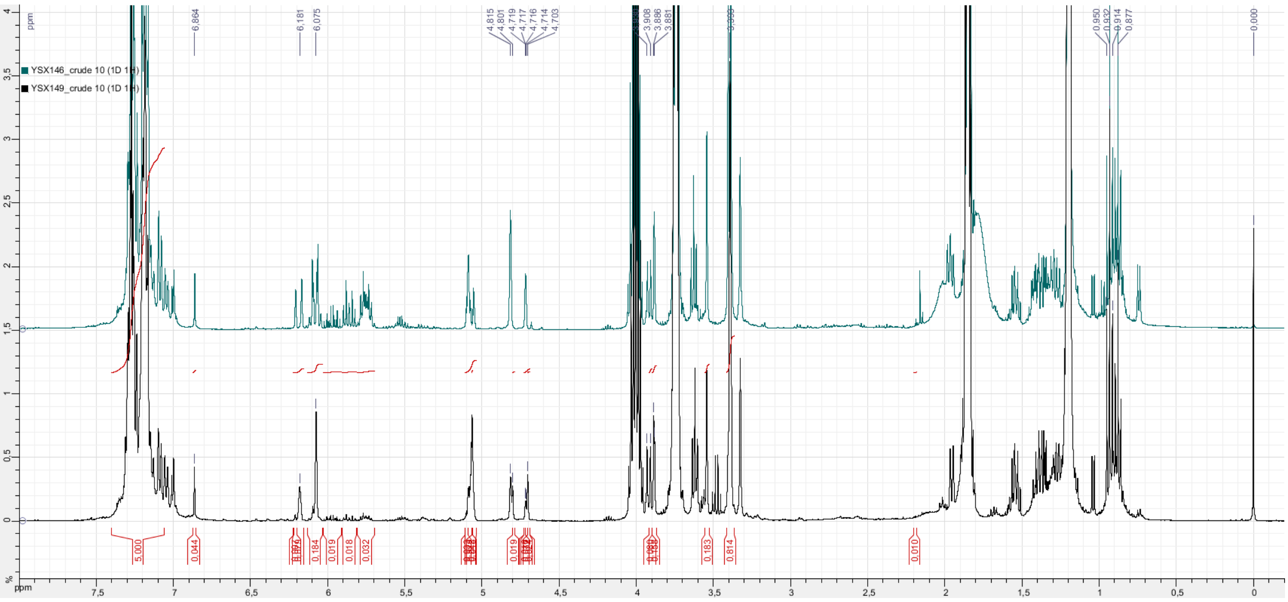
■ **V.4.3.** With 2.2 equiv of Ti(O*i*Pr)$_4$, 3.3 equiv of *n*BuLi; reaction conducted at 0 °C for 45 min and then quenched with D_2O.



S.m **1b**	Alkene **2b**	Alkene **2′b**	Diene **3b**	Diene **3′b**	Trimer **4b**	Trimer **4′b**	Total
1%	12% (~83% -*d*)	8% (~60% -*d*; n.d.)[a]	18% (~83% -*d*$_2$)	16% (~82% -*d*; ~32% -*d*)[a]	12%	4%	71%

[a] Deuterium was incorporated at two different positions (see further below for detail).

n-Butyllithium solution (2.34 M in hexanes, 3.30 equiv, 3.30 mmol, 1.41 mL) was added dropwise, over 2 minutes, at 0 °C, to a solution of titanium(IV) isopropoxide (2.20 equiv, 2.20 mmol, 651 µL) in THF (5.0 mL).[16] The solution turned yellow, orange, then dark brown. After 5 minutes of stirring at 0 °C, 3-phenylprop-1-yne **1b** (1.00 equiv, 1.00 mmol, 124 µL) was added dropwise, over 4 minutes, to the black solution. The mixture was stirred at 0 °C for an additional 45 minutes. D_2O (0.5 mL) was then added. After 15 minutes of stirring, the septum was removed to expose the mixture to air and stirring was continued for 10 more minutes. The mixture was then filtered through a pad of sand, celite, $MgSO_4$ and sand [from top to bottom; rinsing with Et_2O (20 mL)] and concentrated under reduced pressure (down to 100 mbar only) to afford a yellow oil (319 mg). Analogous analysis as described in subsection V.2., detailed further below for the compounds containing deuterium atoms, gave the qualitative estimation of the product yields shown in the table above.

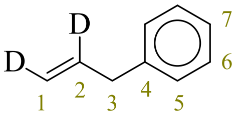


^{1}H NMR spectrum of the crude product ($CDCl_3$, 400 MHz).
The spectrum of the crude product of the same reaction, quenched with H_2O, is displayed in green (top).

^{1}H NMR spectrum of the crude product ($CDCl_3$, 400 MHz) (detail).
The spectrum of the crude product of the same reaction, quenched with H_2O, is displayed in green (top).

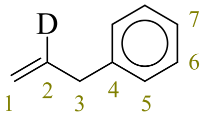
NMR analysis of the incorporation of deuterium into the products:

[(*E*)-2,3-Dideuterioallyl]benzene **2b**-d_2



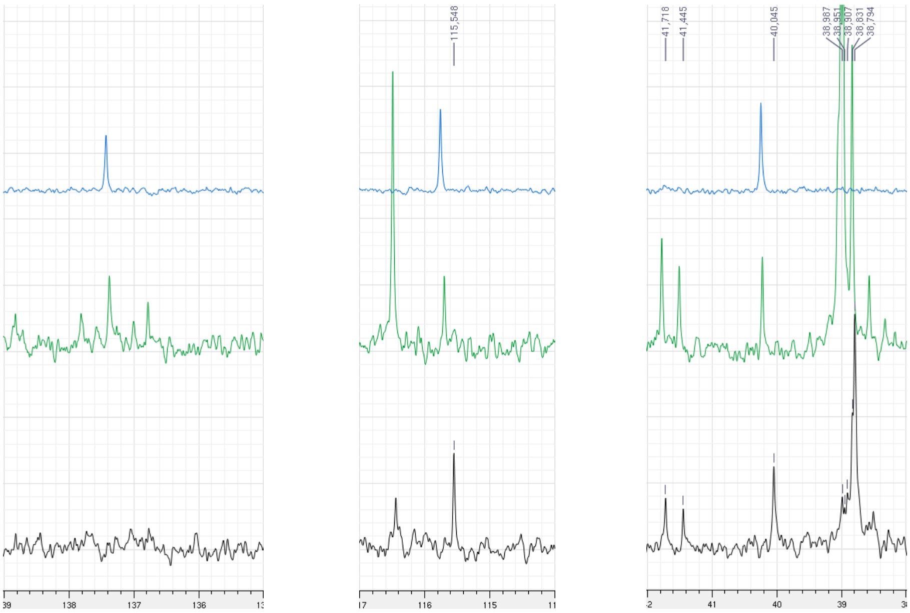
There is no evidence that this compound was produced in any significant amount (see below).

2-Deuterioallylbenzene **2b**-*d*



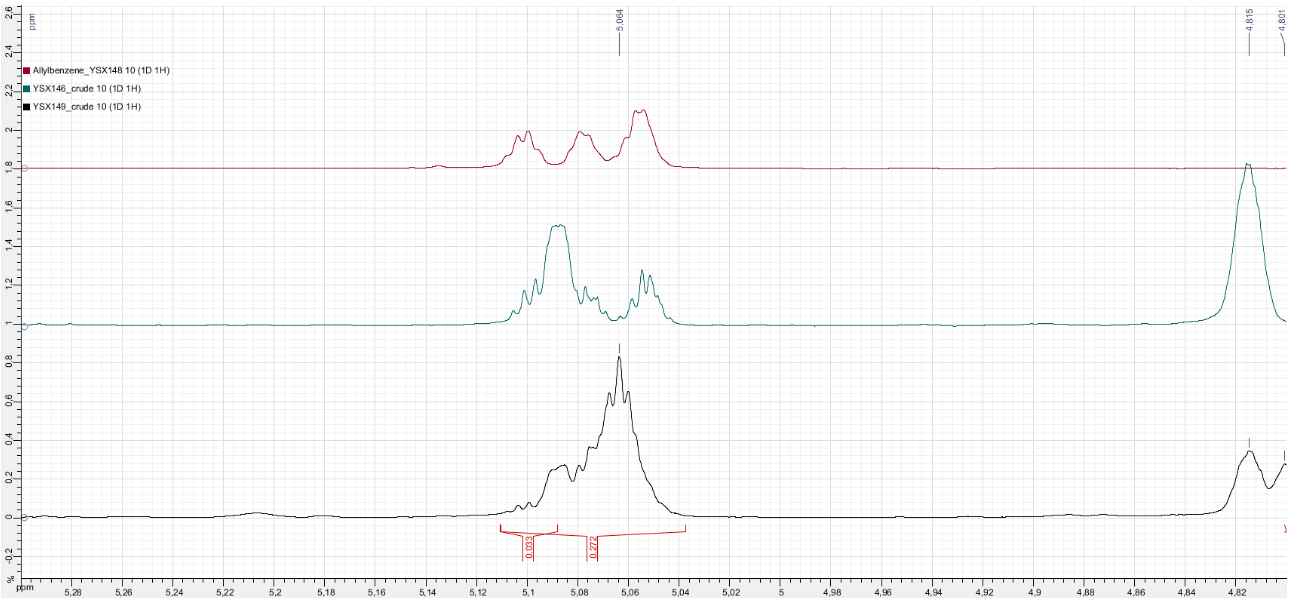
^{1}H NMR ($CDCl_3$, 400 MHz), characteristic signal: δ 5.04-5.08 (2 H, m, H1). ^{13}C NMR ($CDCl_3$, 100.6 MHz), characteristic signals: δ 40.0 (C3), 115.5 (C1).

^{13}C NMR: The peaks of C1 and C3 of **2b** were somewhat displaced, lying at 115.5 and 40.0 ppm respectively in **2b**-*d*, *vs* 115.8 and 40.2 in **2b**. The relative intensity of the C1 peak was unchanged compared to C3 and no new signal looking like a triplet appeared in this region, showing that no or very little deuterium incorporation had taken place at C1. In contrast, the signal at 137.4 ppm (C2 of **2b**) disappeared completely, suggesting a high incorporation of deuterium at this position. No triplet was unambiguously observed in this region, because of insufficient signal-to-noise ratio.



^{13}C NMR spectrum of the crude product ($CDCl_3$, 100.6 MHz) (details).
The spectrum of the crude product of the same reaction, quenched with H_2O, is displayed in green (middle).
The spectrum of an authentic sample of allylbenzene is displayed in blue (top).

^1H NMR: The signals of H3 could not be observed because of overlap with signals belonging to other compounds. Residual H2 signal of **2b** was observed at 5.97 ppm, with much lower intensity than in the crude product of the same reaction having been quenched with H_2O, suggesting high deuterium incorporation at this position. The signals of H1 changed dramatically, because of the absence of ^3J coupling due to the replacement of H2 with a deuterium atom. The yields of **2b**-*d* and **2b** were estimated to be 10% and 2% respectively (see further below), corresponding to a deuterium incorporation of 83% at C2.



^1H NMR spectrum of the crude product ($CDCl_3$, 400 MHz) (detail).
The spectrum of the crude product of the same reaction, quenched with H_2O, is displayed in green (middle).
The spectrum of an authentic sample of allylbenzene is displayed in red (top).

■ Comments on the apparently selective formation of 2-deuterioallylbenzene **2b**-*d*, at the expense of the expected product, [(*E*)-2,3-dideuterioallyl]benzene **2b**-d_2:

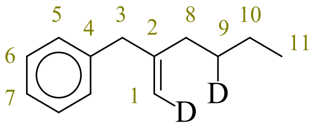
This observation can be interpreted in several ways.

- One possibility is that only the thermodynamically more basic C−Ti bond of **Db** had time to undergo deuteriolysis under the reaction conditions applied (15 minutes with warming from 0 °C to room temperature). The deuteriolysis of the second, less substituted C−Ti bond could then be much slower. When the contents of the flask are later exposed to air and the solution eventually passed through a pad of celite and $MgSO_4$, comparatively faster protonolysis with H_2O would gradually take place, delivering the monodeuteriated product detected, **2b**-*d*.
- Alternatively, a side reaction might take place before the addition of D_2O, transforming **Db** into a vinyltitanium species having only one C−Ti bond at C2.
- A combination of both hypotheses can be envisaged as well, if the side reaction mentioned converts only a part of **Db** and the remaining complex then behaves as proposed in the first hypothesis, when D_2O is added.

Knowing which is correct is important because the construction of our kinetic model is based on the assumption that the amounts of compound **2** observed in the crude products reflect the quantity of complex **D** present in the solution just before the hydrolytic work-up. If the second hypothesis is correct, at least in part, then our kinetic model and rate constants will need to be adjusted to take this more complex situation into account.

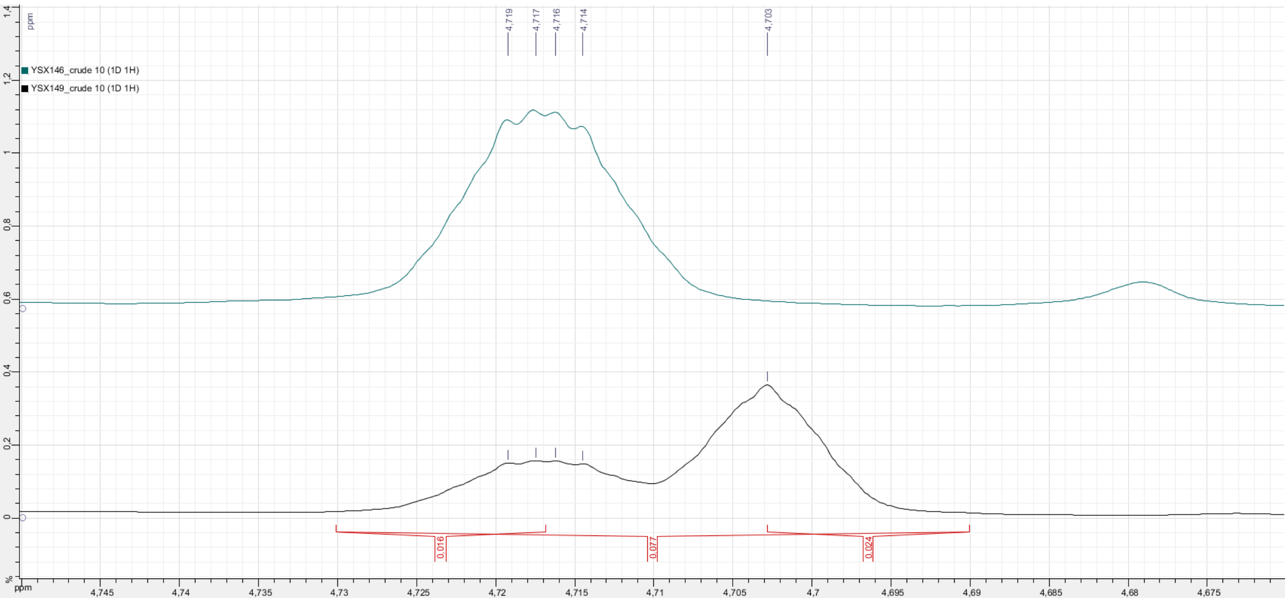
Using DCl instead of D_2O and open the flask after a longer time would help probe the first hypothesis and get insight into this problem.

[(2*E*)-4-Deuterio-2-(deuteriomethylene)hexyl]benzene **2′b**-d_2



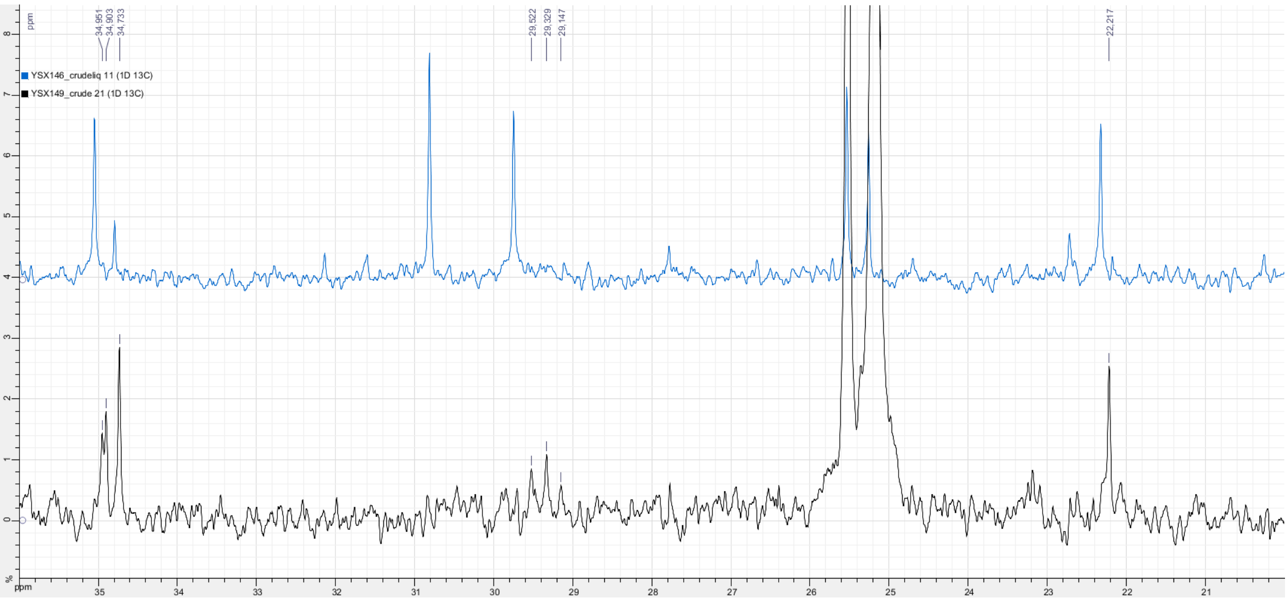
^1H NMR ($CDCl_3$, 400 MHz), characteristic signal: δ 4.70 (1 H, br s, H1 cis to the benzyl group).
^{13}C NMR ($CDCl_3$, 100.6 MHz), characteristic signals: δ 13.9 (C11), 22.2 (C10), 29.3 (t, *J* 18.5, C9), 34.9 (C8), 42.9 (C3), 149.1 (C2).

^1H NMR: next to the residual broad singlet at 4.72 ppm of **2′b** (H1 *cis* to the benzyl group), a new broad singlet appeared at 4.70 ppm, with a simpler coupling pattern, corresponding to **2′b**-d_2. Integration of the signals allowed to estimate a ~60% incorporation of deuterium at carbon C1, with the configuration shown.



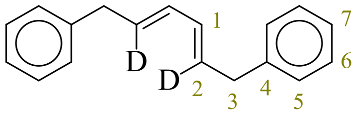
^{1}H NMR spectrum of the crude product ($CDCl_3$, 400 MHz) (detail).
The spectrum of the crude product of the same reaction, quenched with H_2O, is displayed in green (top).

^{13}C NMR: compared to the peak at 22.2 ppm (C10), the signal at 29.6 ppm (C9 of **2′b**) virtually disappeared, suggesting a high incorporation of deuterium at this position. A triplet was perhaps dimly visible, at 29.3 ppm. The signal at 34.9 ppm (C8 of **2′b**) was split into two new signals: at 34.95 ppm (assigned to **2′b**-*d*, having deuterium at C9 only) and at 34.90 pm, more intense, assigned to **2′b**-d_2.



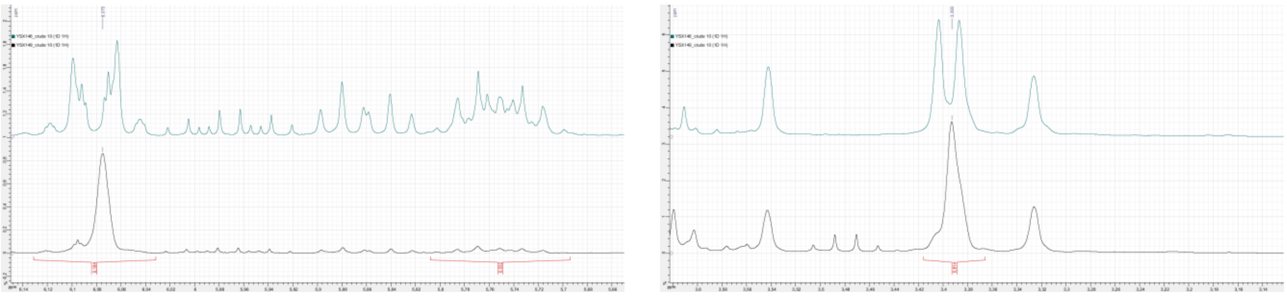
^{13}C NMR spectrum of the crude product ($CDCl_3$, 100.6 MHz) (detail).
The spectrum of the crude product of the same reaction, quenched with H_2O, is displayed in blue (top).

[(2*E*,4*E*)-2,5-Dideuterio-6-phenyl-hexa-2,4-dienyl]benzene **3b**-*d*$_2$



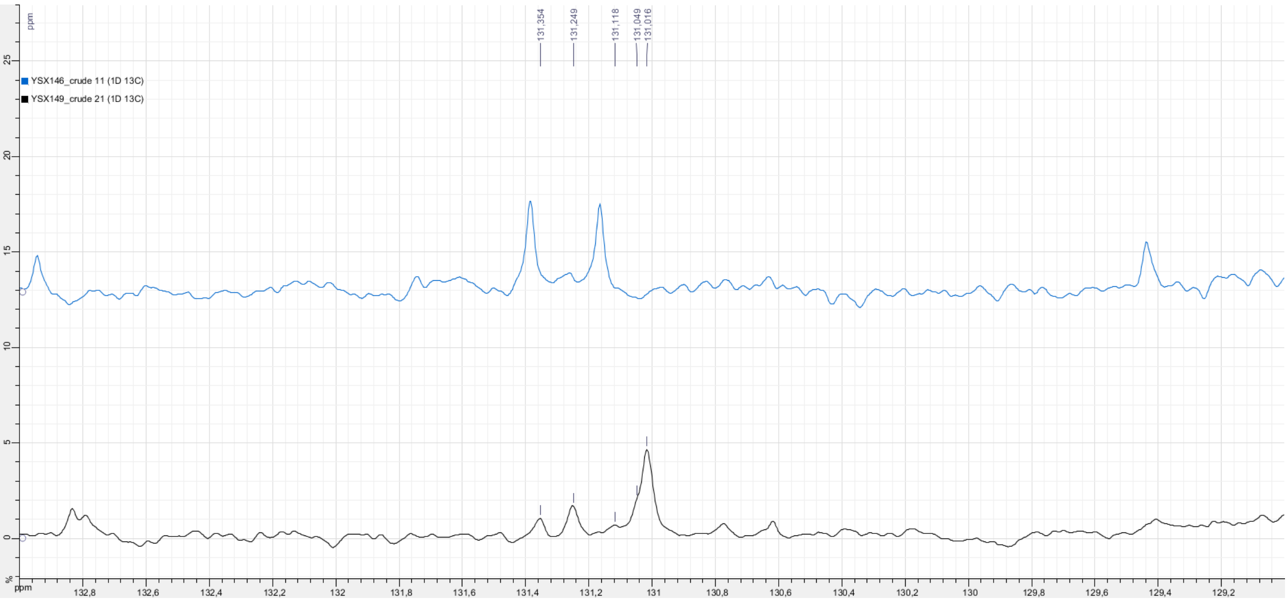
^{1}H NMR (CDCl$_3$, 400 MHz), characteristic signals: δ 3.39 (4 H, br s, H3), 6.07 (2 H, br s, H1).
^{13}C NMR (CDCl$_3$, 100.6 MHz), characteristic signals: δ 38.8 (C3), 126.0 (C7), 128.3, 128.5 (C5, C6), 131.0 (C1), 140.3 (C4).

^{1}H NMR: the identifiable multiplets at 5.75 ppm and at 6.08 ppm (H2 and H1 of **3b**) essentially disappeared. A new intense broad singlet was visible at 6.07 ppm, corresponding to H1 of **3b**-*d*$_2$. The doublet at 3.40 ppm (H3 of **3b**) became a broad singlet (H3 of **3b**-*d*$_2$). Integration of the 6.03-6.13 ppm interval and of the residual signal at 5.75 ppm allowed to estimate a ~83% incorporation of deuterium at C2.



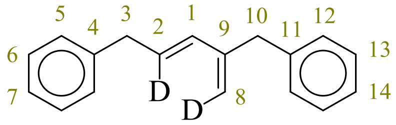
^{1}H NMR spectrum of the crude product (CDCl$_3$, 400 MHz) (detail).
The spectrum of the crude product of the same reaction, quenched with H$_2$O, is displayed in green (top).

^{13}C NMR: the non-deuteriated compound **3b** displayed two peaks at 131.2 and 131.5 ppm, corresponding to carbons C1 and C2 respectively. Essentially one major peak is now visible for **3b**-*d*$_2$ in this region, which is assigned to C1. C2 is expected to have become a triplet, at around 131.5 ppm, but the presence of other peaks, probably belonging to minor amounts of **4b**, **3b** and partially deuteriated **3b**-*d*, makes the precise location of this triplet uncertain.



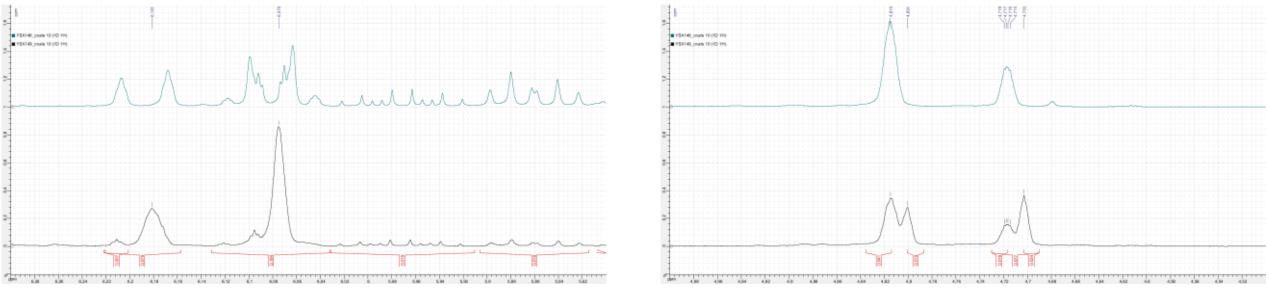
^{13}C NMR spectrum of the crude product (CDCl$_3$, 100.6 MHz) (detail).
The spectrum of the crude product of the same reaction, quenched with H$_2$O, is displayed in blue (top).

[(2E,4Z)-4-benzyl-2,5-dideuterio-penta-2,4-dienyl]benzene
3′b-d_2



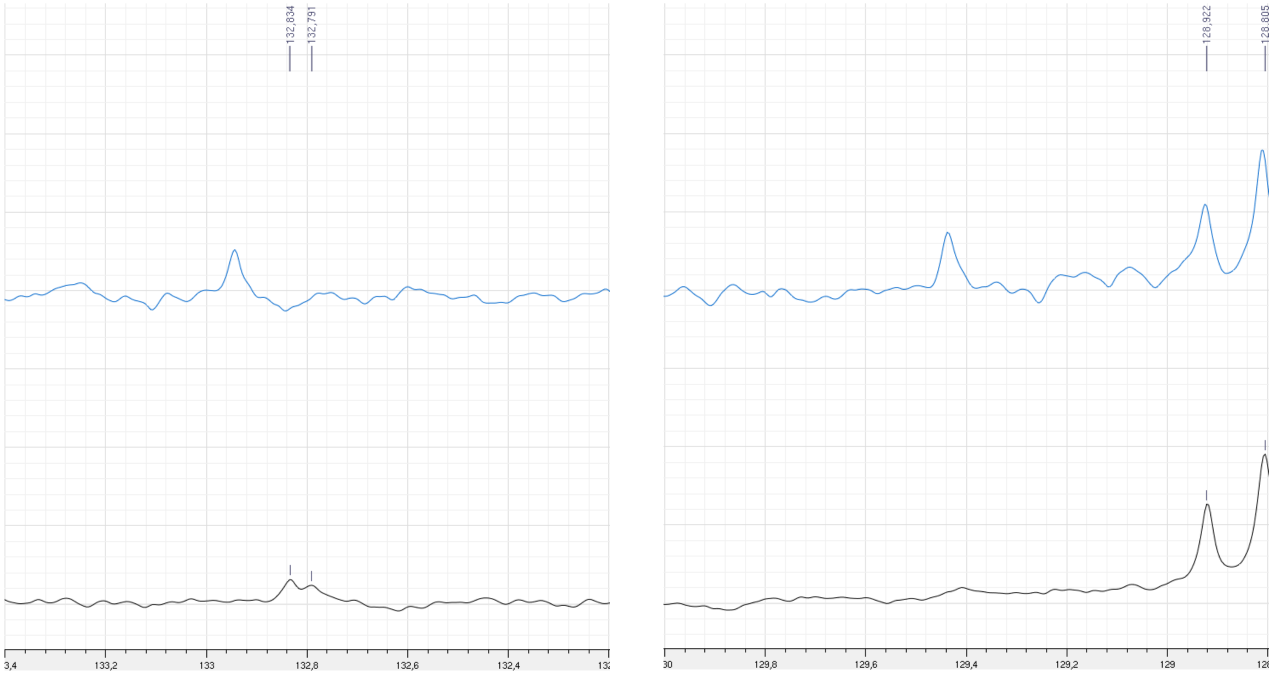
^{1}H NMR (CDCl$_3$, 400 MHz), characteristic signals: δ 3.54 (2 H, s, H10), 4.80 (1 H, br s, H8 *cis* to the Bn group), 6.18 (1 H, br s, H1). ^{13}C NMR (CDCl$_3$, 100.6 MHz), characteristic signals: δ 132.8 (C1), 144.8 (C9).

^{1}H NMR: the identifiable broad doublet at 6.19 ppm (H1 of **3′b**) essentially disappeared. A new broad singlet was visible at 6.18 ppm, corresponding to H1 of **3′b**-d_2. Integration of the 6.16-6.22 ppm interval and of the left half part of the signal at 6.19 ppm of residual **3′b** led to an estimated ~82% deuterium incorporation at C2. This is confirmed by the signal of H2 at 5.86 ppm (residual **3′b**), the intensity of which was dramatically reduced, as compared with the reaction having been hydrolysed with H_2O. The intensity of the broad singlet at 4.82 ppm (H8 *cis* to the Bn group of **3b**) was reduced and a new broad singlet appeared at 4.80 ppm, with a simpler coupling pattern (H8 *cis* to the Bn group of **3′b**). Integration of the half parts of these signals that were not overlapping allowed to estimate the incorporation of deuterium at carbon C8 to be ~32%.



^{1}H NMR spectrum of the crude product (CDCl$_3$, 400 MHz) (detail).
The spectrum of the crude product of the same reaction, quenched with H_2O, is displayed in green (top).

^{13}C NMR: the intensity of the peak at 116.5 ppm (C8 of residual **3′b**) was somewhat diminished. The peak at 129.5 ppm (C2) had disappeared, confirming high deuterium incorporation at this position. The expected triplet was not observed, due to insufficient signal-to-noise ratio. The peak at 133.0 ppm (C1) was split into two new smaller signals, at 132.79 (less intense) and 132.83 ppm (more intense). They are respectively assigned as the C1 signal of **3′b**-d_2 and **3′b**-*d*, the latter having deuterium at C2 only.

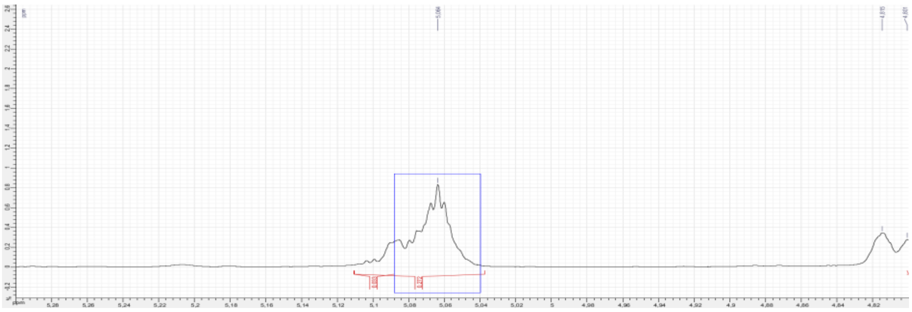


^{13}C NMR spectrum of the crude product ($CDCl_3$, 100.6 MHz) (details).
The spectrum of the crude product of the same reaction, quenched with H_2O, is displayed in blue (top).

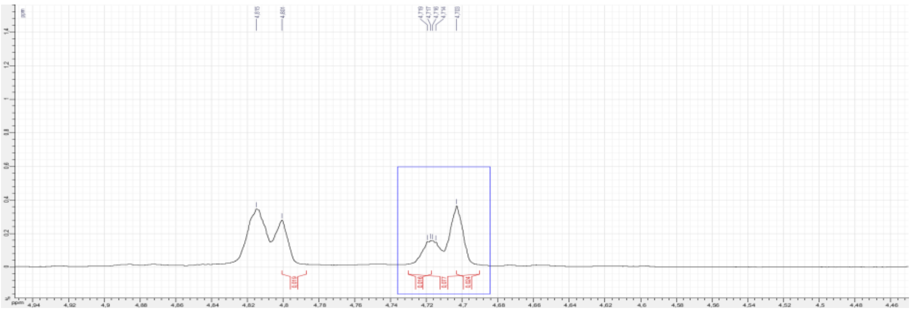
No evidence of incorporation of deuterium in compounds **4b** or **4′b** was found.

Estimation of the product yields by NMR:

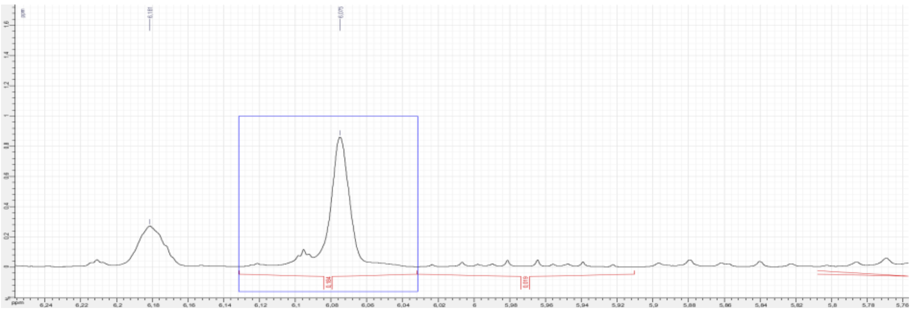
- The phenyl groups were used as an internal standard: the integral of the signals in the interval 7.06–7.40 ppm was set to 5.00.
- The same signals were used for the qualitative assessment of the product yields as in the previous experiment, except for the following:
  - Multiplet around 5.06 ppm, accounting for two protons of **2b**-*d*. The integral of the pattern in the range 5.04-5.11 ppm was taken: 0.272. From this value was substracted the integral of the signals of residual **2b** and **3′b**. The left half part of the latter (5.088-5.110 ppm) did not overlap with other signals; it was measured and multiplied by two: 2 × 0.033 = 0.066. Result for two protons of **2b**-*d*: 0.272 – 0.066 = 0.204. The estimated yield of **2b**-*d* is thus 10%.



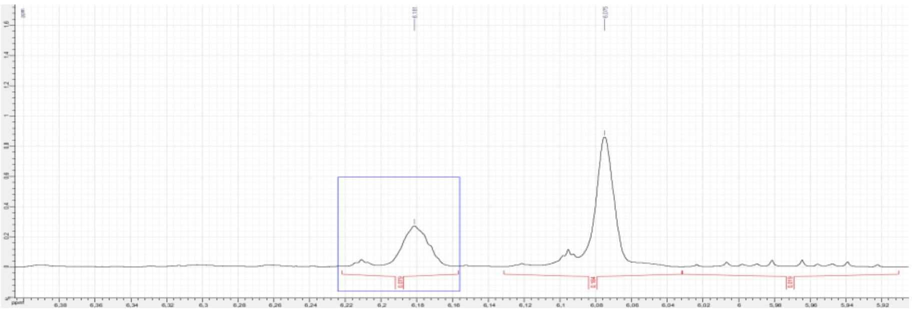
  - Broad singlet at 4.70 ppm and broad singlet at 4.72 ppm: one proton of **2′b**-d_2 and **2′b**, respectively. The integral of these signals gave an estimation of the combined yields of **2′b** and **2′b**-d_2: 7.7%.



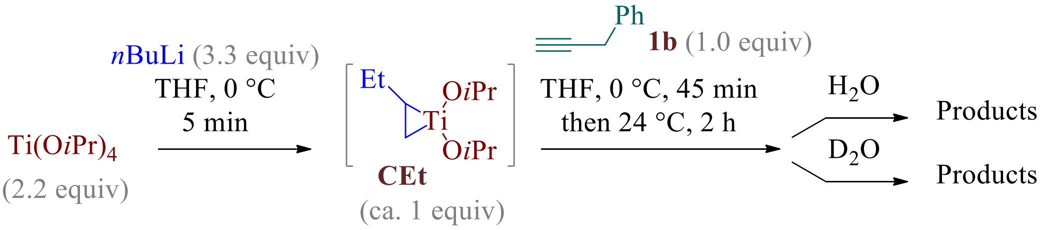
- Broad singlet at 6.07 ppm and multiplet at 6.08 ppm: two protons of **3b**-d_2 and two protons of **3b**, respectively. The integral of these signals gave an estimation of the combined yields of **3b** and **3b**-d_2: 18%.



- Broad singlet at 6.18 ppm and broad doublet (*J* 15.5 Hz) at 6.19 ppm: one proton of **3′b**-d_2 and one proton of **3′b**, respectively. The integral of these signals was measured, then multiplied by two to give an estimation of the combined yields of **3′b** and **3′b**-d_2: 16%.



■ **V.4.4.** With 2.2 equiv of Ti(O*i*Pr)$_4$, 3.3 equiv of *n*BuLi; reaction conducted at 0 °C for 45 min and then at 24 °C for 2 h (stability test for the intermediate organometallic species).

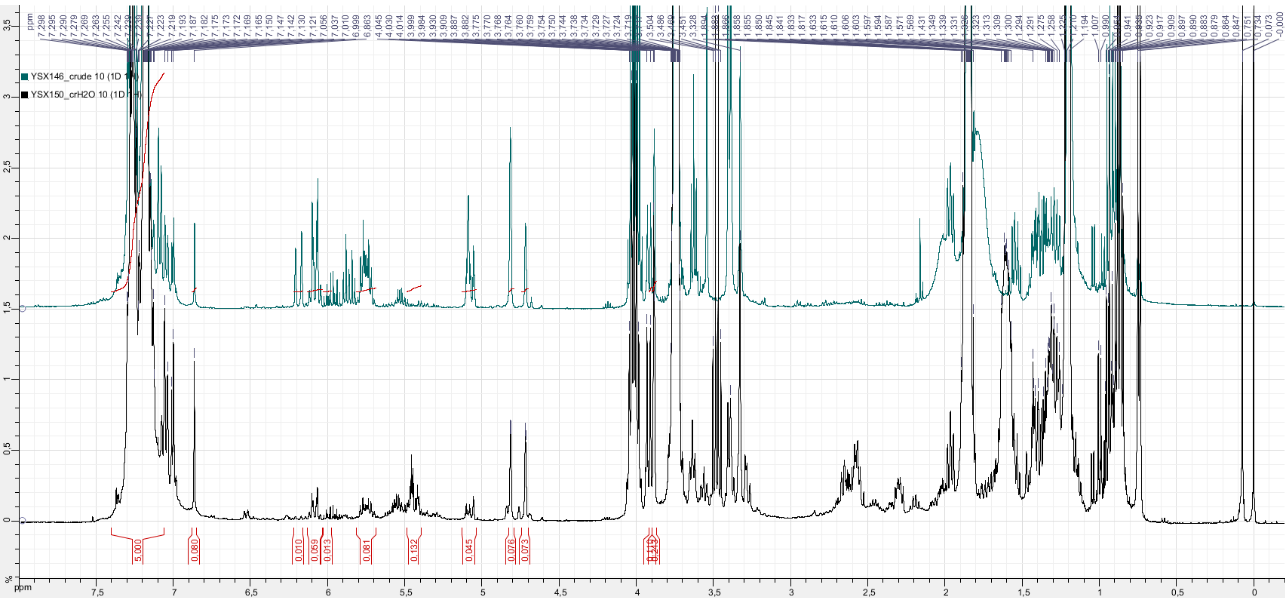


S.m **1b**	Alkene **2b**	Alkene **2′b**	Diene **3b**	Diene **3′b**	Trimer **4b**	Trimer **4′b**	Total
0%	3%	7%	6%	2%	16%	8%	42%

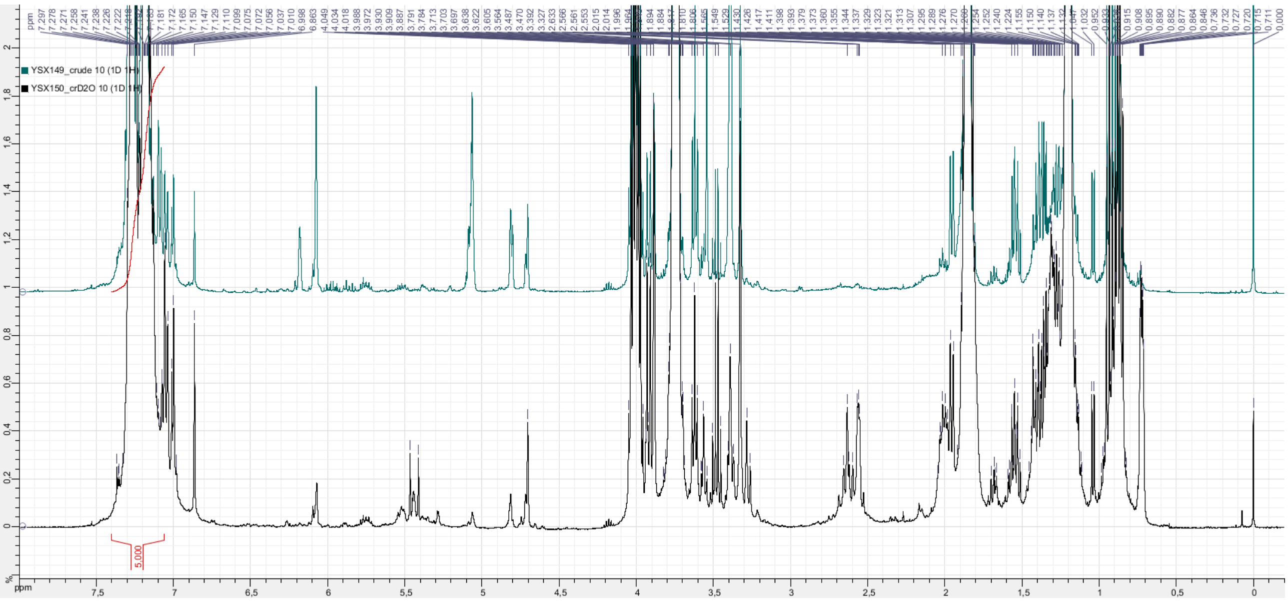
n-Butyllithium solution (2.34 M in hexanes, 3.30 equiv, 3.30 mmol, 1.41 mL) was added dropwise, over 2 minutes, at 0 °C, to a solution of titanium(IV) isopropoxide (2.20 equiv, 2.20 mmol, 651 µL) in THF (5.0 mL).[16] The solution turned yellow, orange, dark brown, then black. After 5 minutes of stirring at 0 °C, 3-phenylprop-1-yne **1b** (1.00 equiv, 1.00 mmol, 124 µL) was added dropwise, over 4 minutes. The mixture was stirred at 0 °C for an additional 45 minutes, then for 2 h at 24 °C.

A part of the solution (3.5 mL) was taken and put into another flask. To this flask, H_2O (0.25 mL) was added. After 15 minutes of stirring, the septum was removed to expose the mixture to air and stirring was continued for 10 more minutes. The mixture was then filtered through a pad of sand, celite, $MgSO_4$ and sand [from top to bottom; rinsing with Et_2O (20 mL)] and concentrated under reduced pressure (down to 100 mbar only) to afford a pale-yellow oil (127 mg). Analysis of this crude product as described in subsection V.2. gave the qualitative estimation of the yields shown in the table above. Additional signals were detected, revealing the presence of other products, which we were not able to identify.

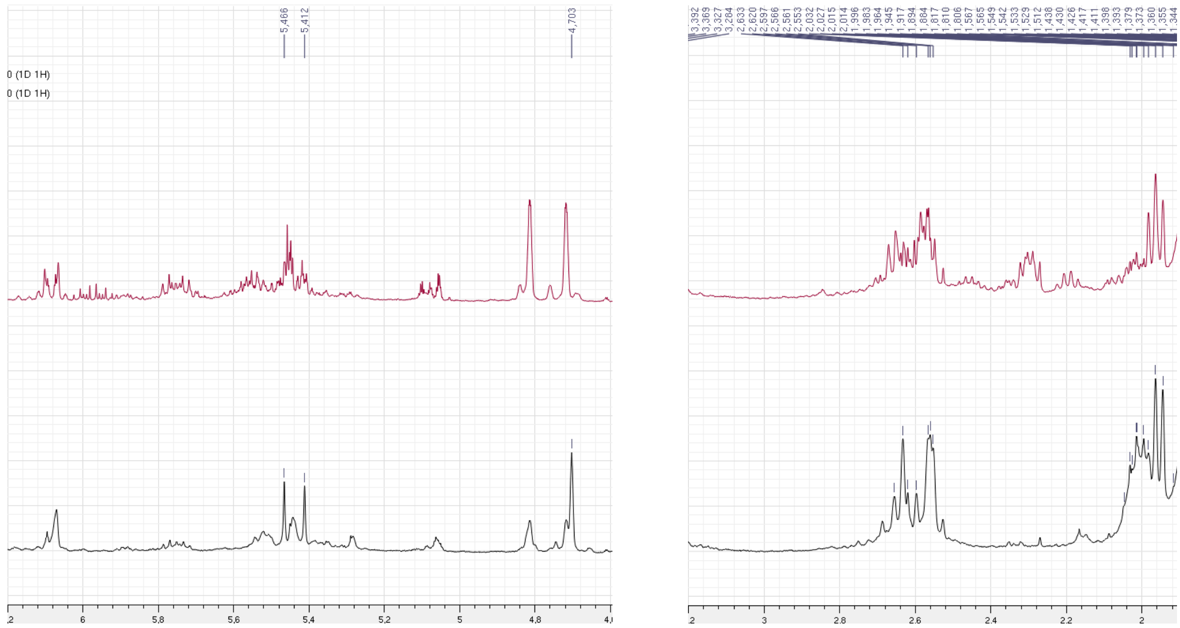
The remainder of the reaction mixture was worked-up similarly, with D_2O (0.25 mL) instead of H_2O. A pale-yellow oil was obtained (187 mg). Comparison of the ^{1}H NMR signals of this mixture with those of the crude product obtained after work-up with H_2O showed that the new unidentified products still possessed carbon-titanium bonds.



^{1}H NMR spectrum of the crude product, after work-up with H_2O ($CDCl_3$, 400 MHz).
The spectrum of the crude product of the same reaction, run for 45 minutes, is displayed in green (top).

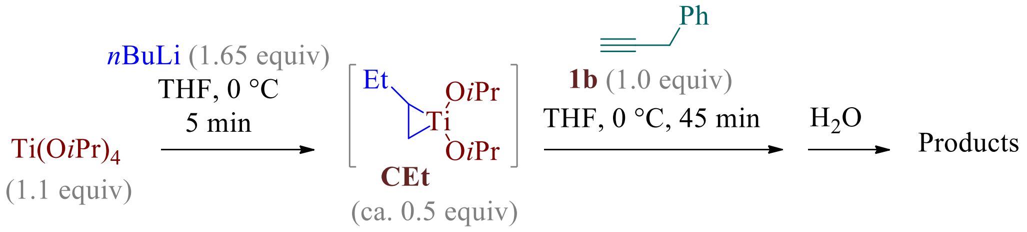


^{1}H NMR spectrum of the crude product, after work-up with D_2O ($CDCl_3$, 400 MHz).
The spectrum of the crude product of the same reaction, run for 45 minutes, is displayed in green (top).



^{1}H NMR spectrum of the crude product (details) ($CDCl_3$, 400 MHz).
Top (in red): reaction quenched with H_2O. Bottom: reaction quenched with D_2O.

■ **V.4.5.** With 1.1 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *n*BuLi; reaction conducted at 0 °C for 45 min.

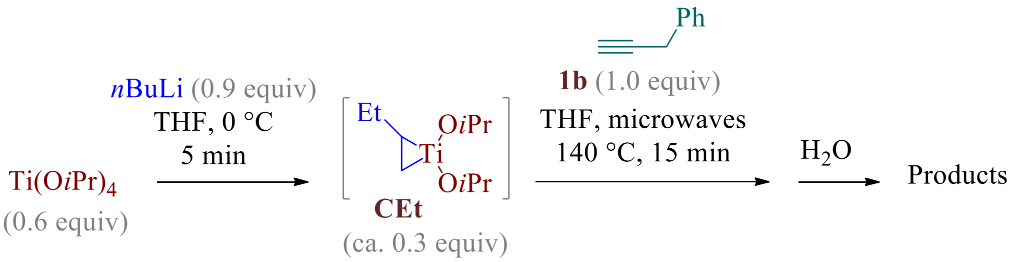


S.m **1b**	Alkene **2b**	Alkene **2′b**	Diene **3b**	Diene **3′b**	Trimer **4b**	Trimer **4′b**	Total
3%	5%	5%	17%	14%	22%	9%	75%

General procedure **GP1** was applied with $n = 1.10$, $p = 1.65$ and $t = 45$. *n*-Butyllithium solution (2.34 M in hexanes, 3.30 mmol, 1.41 mL) was added over 2.5 minutes. 3-Phenylprop-1-yne **1b** (2.00 mmol, 249 µL) was added over 4.5 minutes.

Crude product: dark yellow oil (347 mg). Analysis as described in subsection V.2. gave the qualitative estimation of the product yields shown in the table above.

■ **V.4.6.** With 0.6 equiv of Ti(O*i*Pr)$_4$, 0.9 equiv of *n*BuLi; reaction conducted at 140 °C for 15 min, under microwave conditions.



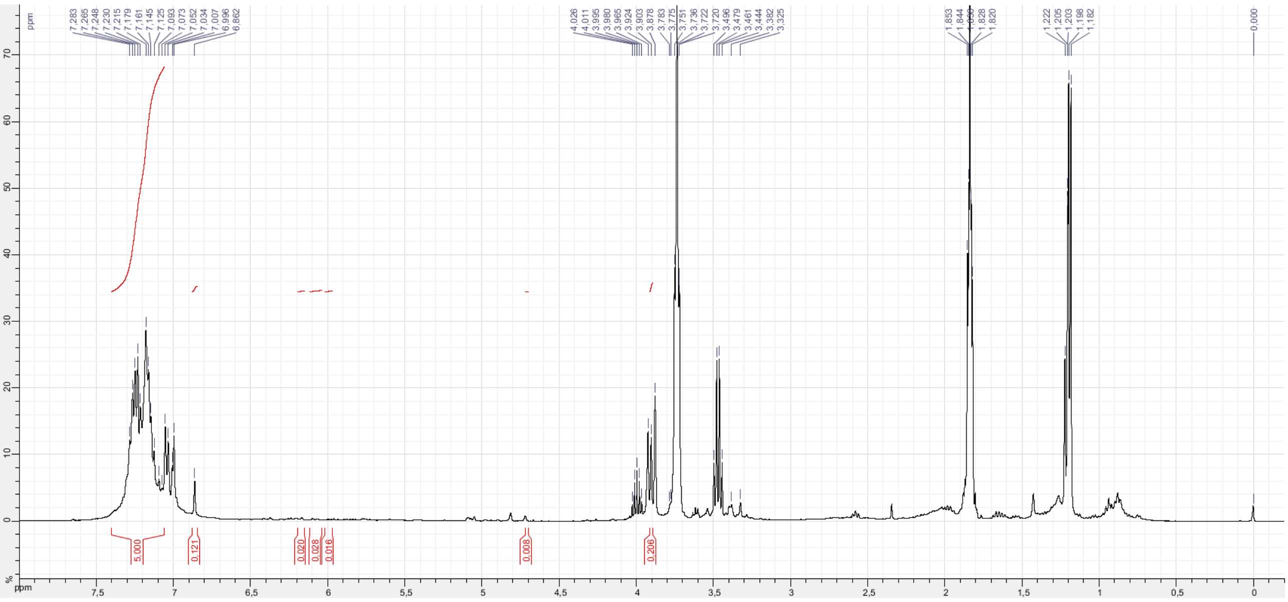
S.m **1b**	Alkene **2b**	Alkene **2′b**	Diene **3b**	Diene **3′b**	Trimer **4b**	Trimer **4′b**	Total
0%	3%	Traces	3%	4%	31% (49%)	12% (14%)	53%

Yields in parentheses correspond to isolated products.

General procedure **GP7** was applied with *T* = 140 and with 3-phenylprop-1-yne **1b** (3.00 mmol, 373 µL) as the substrate.

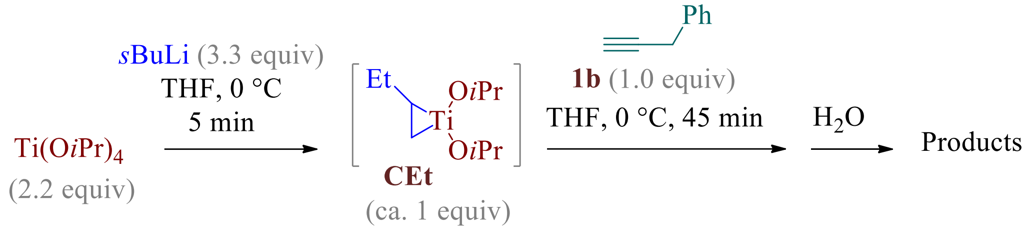
Crude product: orange oil (372 mg). Analysis as described in subsection V.2. gave the qualitative estimation of the product yields shown in the table above.

Flash column chromatography (silica gel, EtOAc/petroleum ether, gradient from 0% to 2%) afforded a 78 : 22 mixture of **4b** and **4’b** (219 mg, 628 µmol, 63%).



^{1}H NMR spectrum of the crude product ($CDCl_3$, 400 MHz).

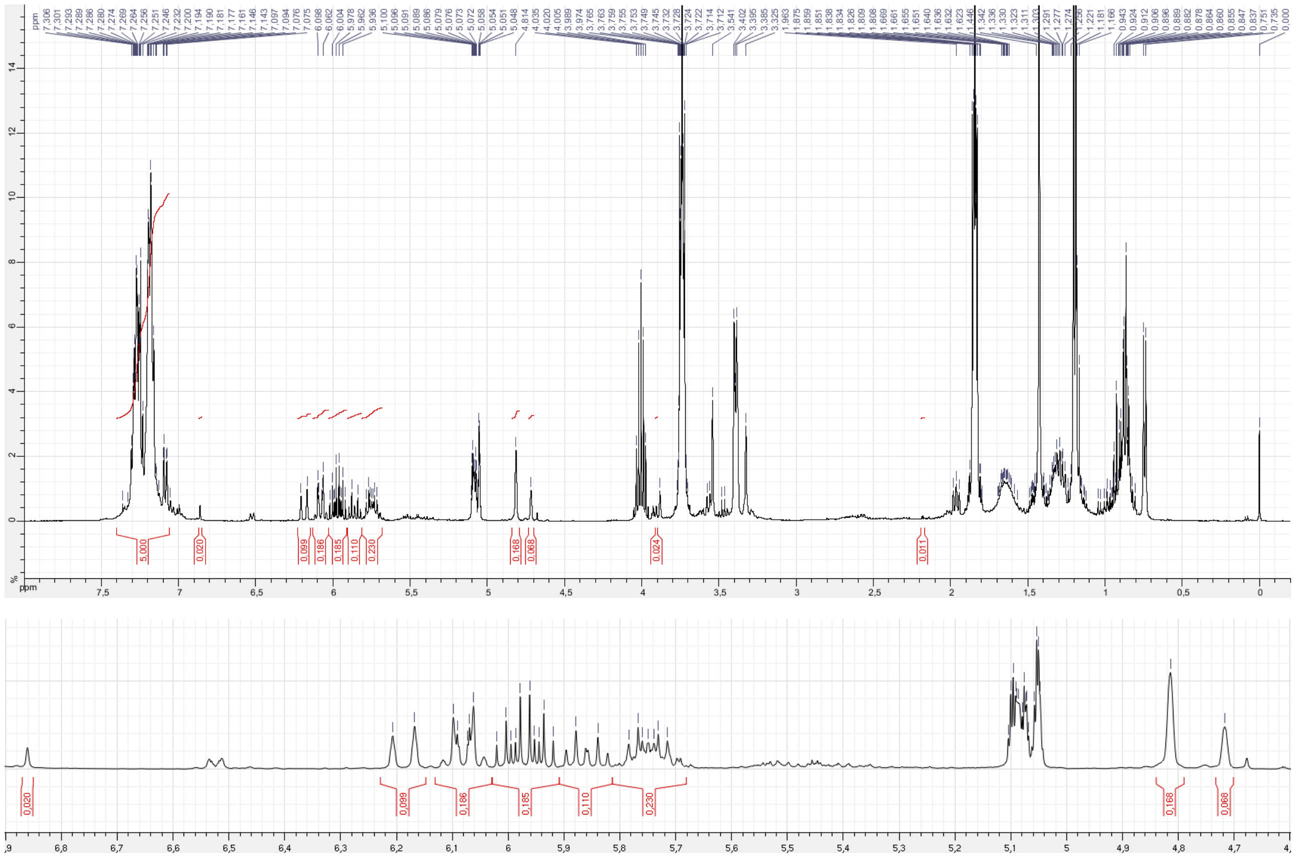
■ **V.4.7.** With 2.2 equiv of Ti(O*i*Pr)$_4$, 3.3 equiv of *s*BuLi (bottle #1); reaction conducted at 0 °C for 45 min.



S.m **1b**	Alkene **2b**	Alkene **2′b**	Diene **3b**	Diene **3′b**	Trimer **4b**	Trimer **4′b**	Total
1%	18%	7%	19%	20%	4%	2%	71%

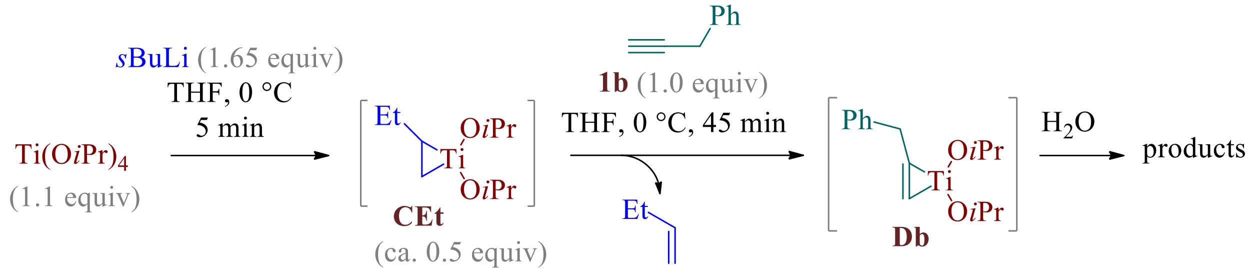
General procedure **GP1** was applied with *n* = 2.20, *p* = 3.30 and *t* = 45. *s*-Butyllithium solution (1.14 M in cyclohexane, 3.30 mmol, 2.89 mL) was added over 2 minutes. 3-Phenylprop-1-yne **1b** (1.00 mmol, 124 μL) was added over 4 minutes.

Crude product: yellow oil (229 mg). Analysis as described in subsection V.2. gave the qualitative estimation of the product yields shown in the table above.



^{1}H NMR spectrum of the crude product (CDCl$_3$, 400 MHz).

■ **V.4.8.** With 1.1 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *s*BuLi (bottle #1); reaction conducted at 0 °C for 45 min.

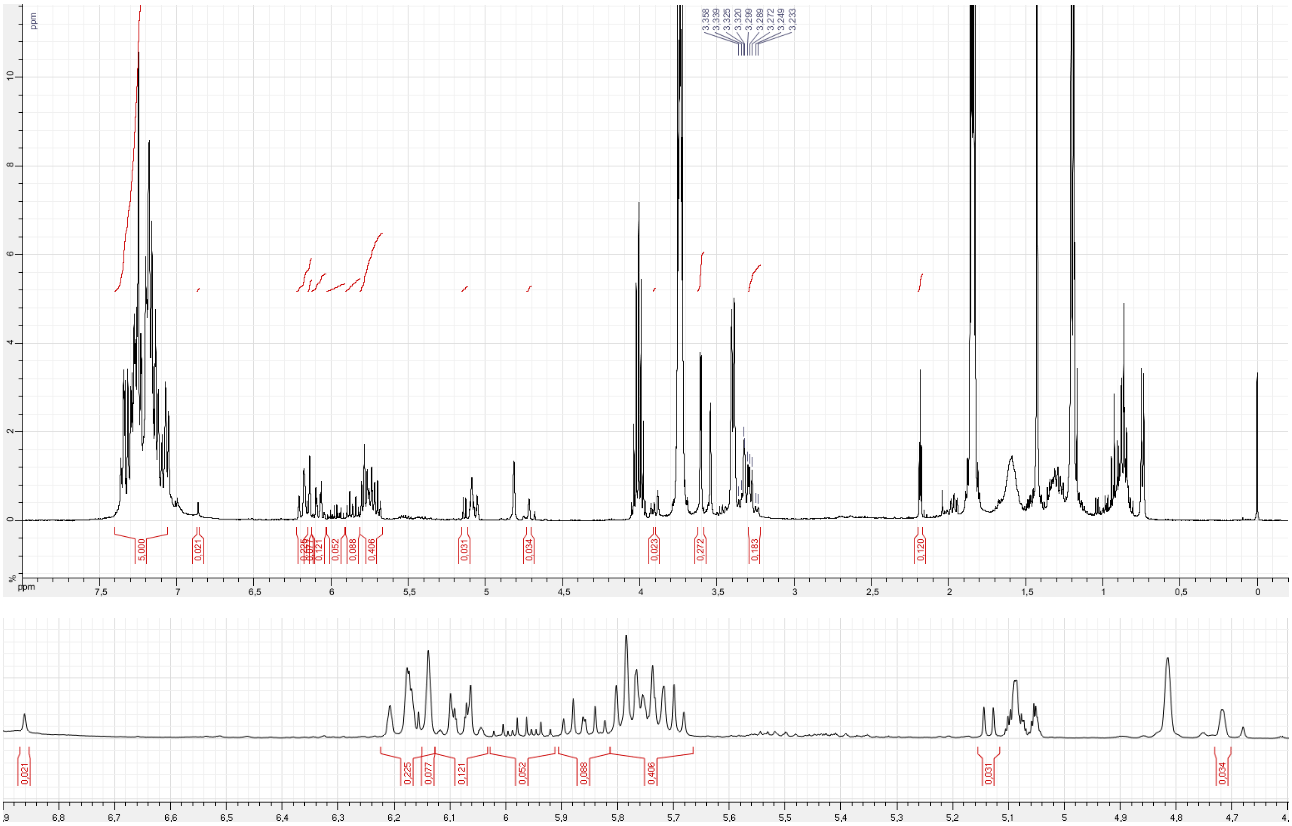


	S.m **1b**	Alkene **2b**	Alkene **2′b**	Diene **3b**	Diene **3′b**	Trimer **4b**	Trimer **4′b**	Tetramer **5b**	Total
Run 1	12%	5%	3%	12%	18%	3%	2%	32%	87%
Run 2	12%	5%	3%	12%	17%	4%	2%	28%	83%

- Run 1: General procedure **GP1** was applied with *n* = 1.10, *p* = 1.65 and *t* = 45. *s*-Butyllithium solution (1.14 M in cyclohexane, 3.30 mmol, 2.89 mL) was added over 2 minutes. 3-Phenylprop-1-yne **1b** (2.00 mmol, 249 µL) was added over 4 minutes.

Crude product: yellow oil (401 mg). Analysis as described in subsection V.2. gave the qualitative estimation of the product yields shown in the table above.

After thorough concentration under reduced pressure, the residue (yellow oil, 221 mg) was purified by flash column chromatography (silica gel, EtOAc/petroleum ether, gradient from 0% to 2%), to afford a neat 21 : 21 : 4 : 3 : 51 mixture of diene **3b**, diene **3′b**, trimer **4b**, trimer **4′b** and tetramer **5b** (127 mg, corresponding to 73.9, 73.9, 14.1, 10.6 and 180 µmol respectively), as well as a small sample of pure **5b** (1.1 mg, 2.4 µmol, 0.5%). These correspond to 7%, 7%, 2%, 2% and 36% yields for diene **3b**, diene **3′b**, trimer **4b**, trimer **4′b** and tetramer **5b**, respectively.



^{1}H NMR spectrum of the crude product ($CDCl_3$, 400 MHz).

• Run 2: an identical procedure was applied as in run 1. A yellow oil (390 mg) was obtained and analysed as described in subsection V.2., to give qualitative estimation of the product yields shown in the table above.

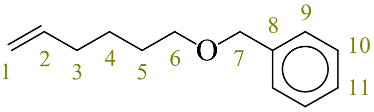
After thorough concentration under reduced pressure, the residue (yellow oil, 212 mg) was triturated with MeOH (1.0 mL). In the freezer, a solid separated from the MeOH solution. The liquid was removed when still cold. The solid residue was allowed to warm to 20 °C and dried under reduced pressure. A yellow gum was obtained (116 mg). The process was repeated with 0.5 mL of MeOH, to afford yellow crystals (94.9 mg). Recrystallisation from EtOAc (0.5 mL) gave pure tetramer **5b** (35.1 mg). A second batch (35.2 mg) was obtained by another recrystallisation from the mother liquor. Total for **5b**: 70.3 mg, 151 µmol, 30%.

VI. Experiments with 6-benzyloxyhex-1-yne **1c**

VI.1. Characterisation of the products

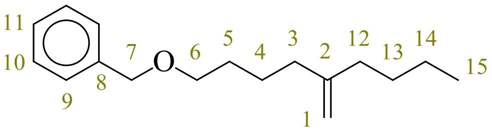
Products **2c**, **2′c** and **5c** were obtained as components of more or less complex mixtures. Dienes **3c**/**3′c** and cyclotrimers **4c**/**4′c** were obtained as mixtures of the two regioisomers. Assignment of the signals of mixtures of compounds was done as explained in the general information.

6-Benzyloxyhex-1-ene **2c**[29]

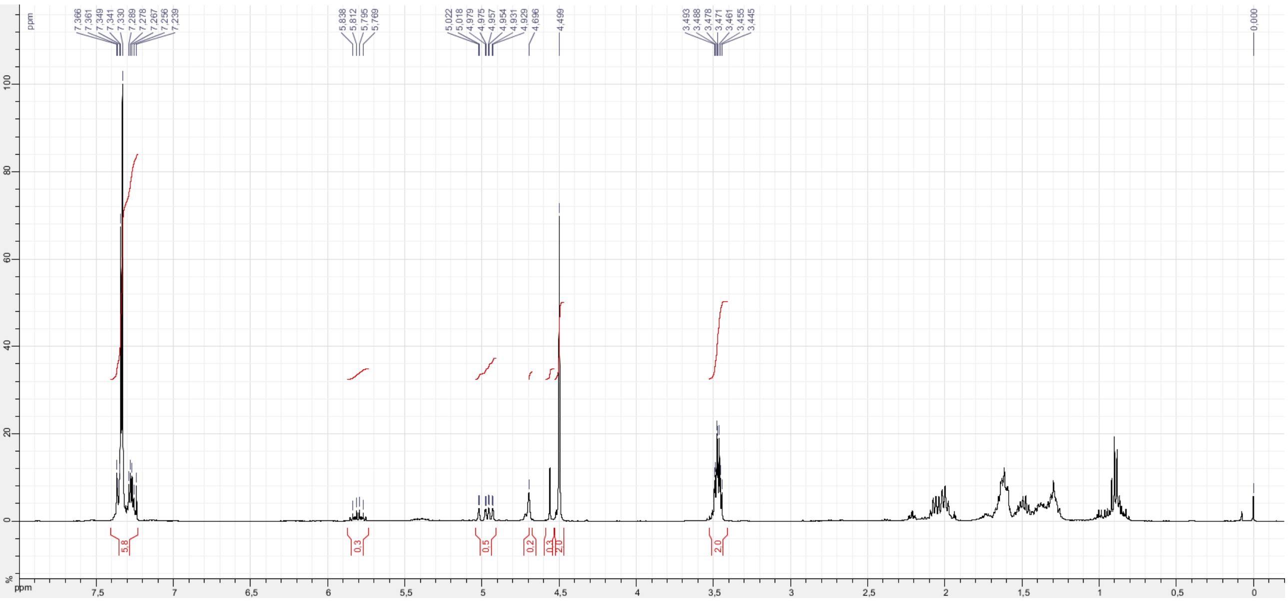


Colourless oil. ^{1}H NMR (CDCl$_3$, 400 MHz), characteristic signals: δ 3.48 (2 H, t, *J* 6.0, H6), 4.94 (1 H, ddt, *J* 10.0, 2.0, 1.0, H1 *cis* to H2), 5.00 (1 H, ddt, *J* 17.0, 2.0, 1.5, H1 *trans* to H2), 5.81 (1 H, ddt, *J* 17.0, 10.0, 6.5, H2), 7.24−7.39 (5 H, m, H9−H11).

5-Methylenenonoxymethylbenzene **2′c**



Colourless oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.90 (3 H, t, *J* 7.0, H15), 1.23−1.78 (8 H, m, H4−H5, H13−H14), 1.96−2.11 (4 H, m, H3, H12), 3.46 (2 H, t, *J* 6.5, H6), 4.70 (2 H, br s, H1), 7.24−7.39 (5 H, m, H9−H11).



^{1}H NMR spectrum (CDCl$_3$, 400 MHz).

Note: this sample contained a 60 : 40 mixture of alkenes **2c** and **2′c**, together with an unidentified other product.

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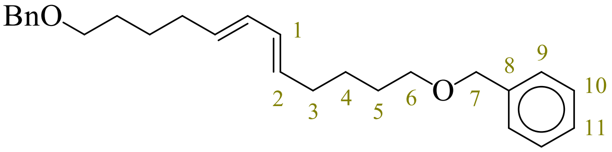
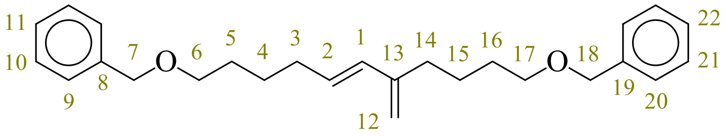
[29] H. Lebel, V. Paquet, *J. Am. Chem. Soc.* **2004**, *126*, 320−328 (supporting information).

[(*E*,*E*)-12-Benzyloxydodeca-5,7-dienoxy]methylbenzene **3c**

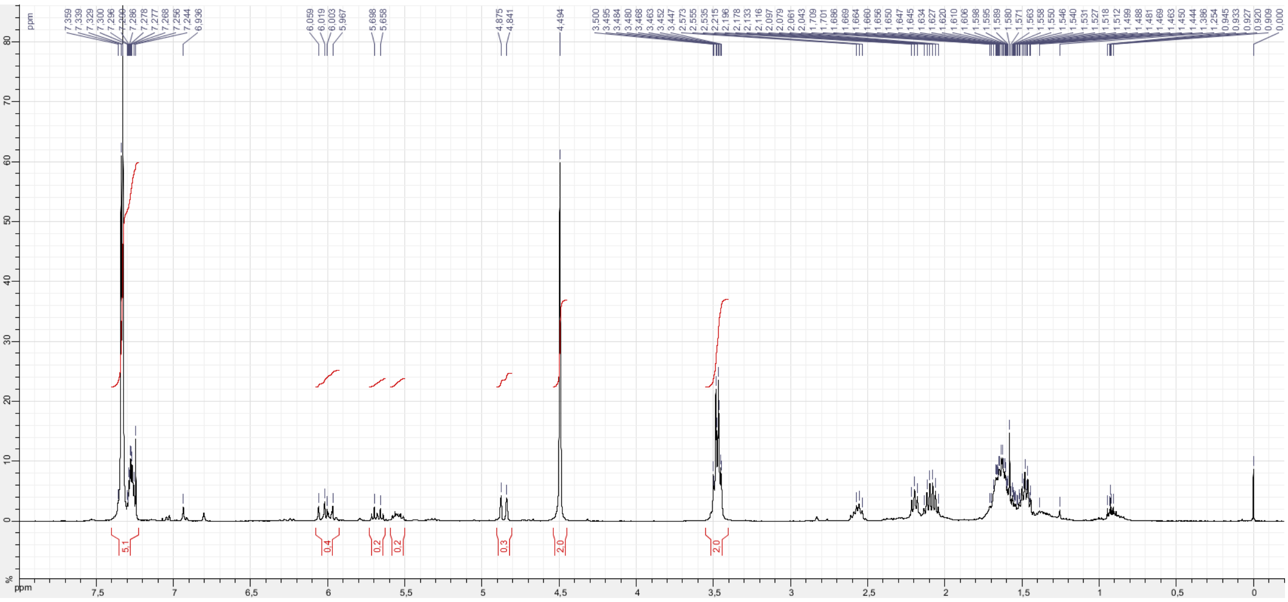


Colourless oil. ^{1}H NMR (CDCl$_3$, 400 MHz), characteristic signals: δ 5.55 (2 H, m, H2), 5.98 (2 H, m, H1).

[(*E*)-11-Benzyloxy-5-methylene-undec-6-enoxy]methylbenzene **3′c**

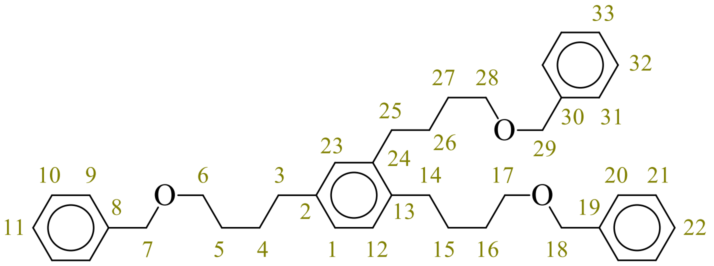


Colourless oil. ^{1}H NMR (CDCl$_3$, 400 MHz), characteristic signals: δ 4.84 (1 H, br s, H12a), 4.88 (1 H, br s, H12b), 5.68 (1 H, dt, J 16.0, 7.0, H2), 6.04 (1 H, br d, J 16.0, H1).



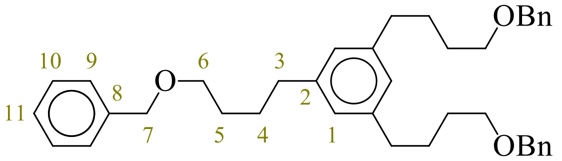
^{1}H NMR spectrum (CDCl$_3$, 400 MHz).
Note: this analysis was performed on a 36 : 64 mixture of **3c** and **3′c**.

1,2,4-Tris(4-benzyloxybutyl)benzene **4c**

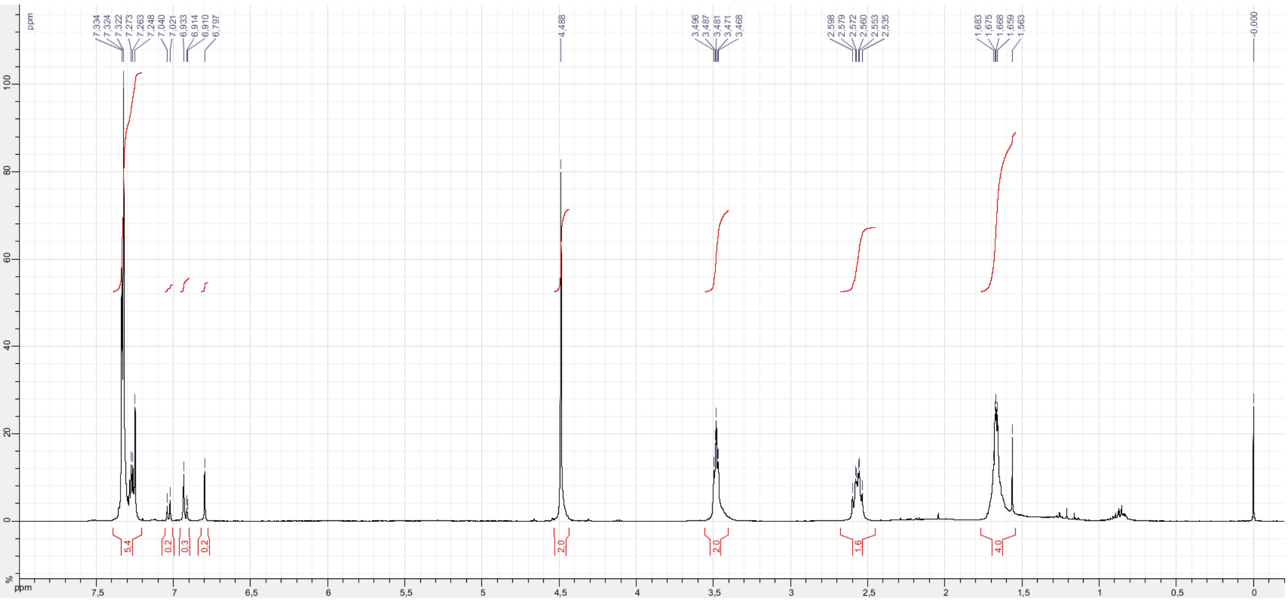


Pale yellow oil. R_f 0.5 (EtOAc/Petroleum ether 10%, UV-active, PMA). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.60−1.73 (12 H, m, H4−H5, H15−H16, H26−H27), 2.51−2.61 (6 H, m, H3, H14, H25), 3.43−3.53 (6 H, m, H6, H17, H28), 4.49 (6 H, br s, H7, H18, H29), 6.92 (1 H, dd, *J* 7.5, 2.0, H1), 6.93 (1 H, d, *J* 2.0, H23), 7.03 (1 H, d, *J* 7.5, H12), 7.22−7.38 (15 H, m, H9−H11, H20−H22, H31−H33). ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ 27.7, 27.8 (C15, C26), 28.0 (C4), 29.3 (C5), 29.6, 29.7 (C16, C27), 31.9, 32.3 (C14, C25), 35.2 (C3), 70.1, 70.1, 70.1 (C6, C17, C28), 72.7, 72.7, 72.7 (C7, C18, C29), 125.8 (C1), 127.3, 127.3, 127.3 (C11, C22, C33), 127.4, 127.4, 127.4 (C9, C20, C31), 128.2, 128.2, 128.2 (C10, C21, C32), 128.9 (C12), 129.1 (C23), 137.2 (C2), 138.5, 138.5, 138.5 (C8, C19, C30), 139.7, 139.8 (C13, C24).

1,3,5-Tris(4-benzyloxybutyl)benzene **4′c**

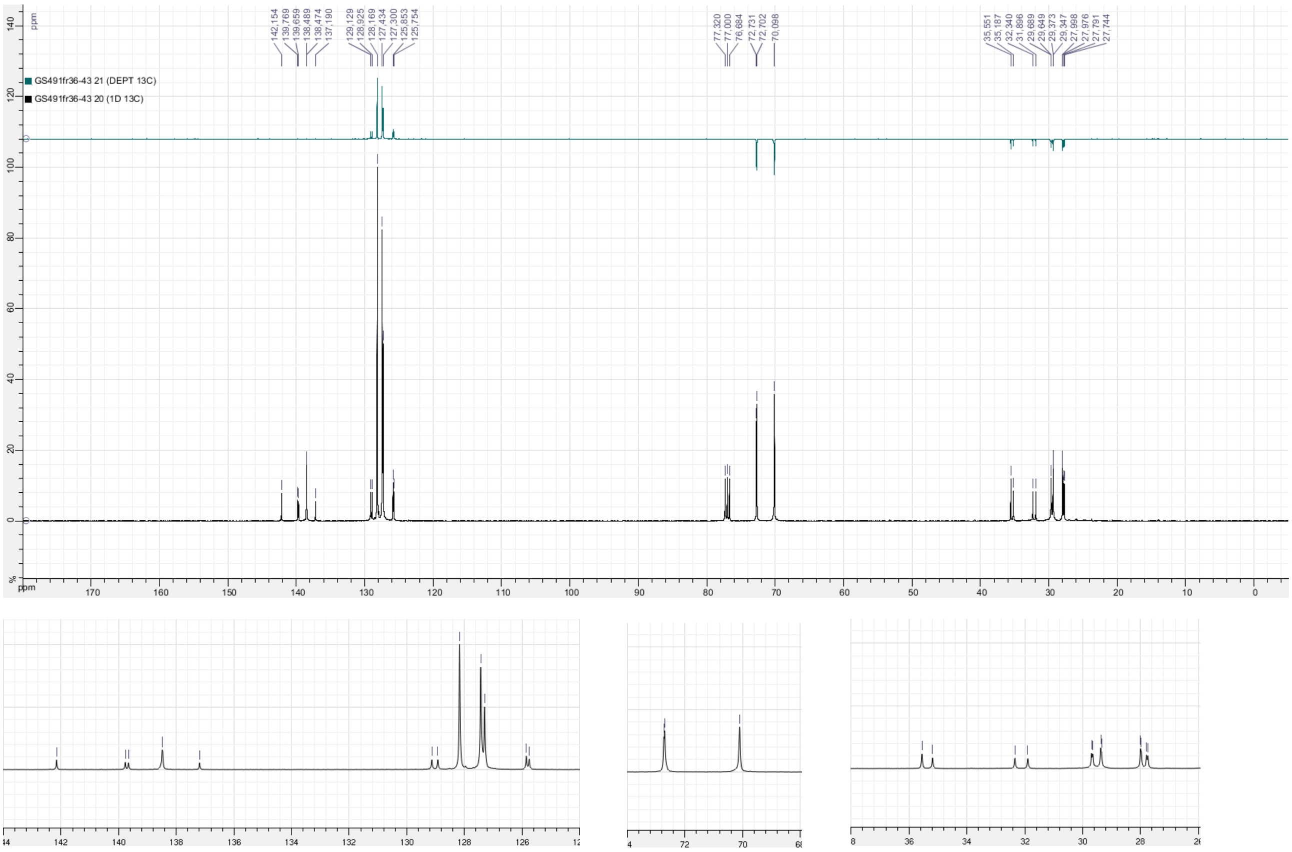


Pale yellow oil. R_f 0.5 (EtOAc/Petroleum ether 10%, UV-active, PMA).^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.60−1.73 (12 H, m, H4−H5), 2.51−2.61 (6 H, m, H3), 3.43−3.53 (6 H, m, H6), 4.49 (6 H, s, H7), 6.80 (3 H, s, H1), 7.22−7.38 (15 H, m, H9−H11). ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ 28.0 (C4), 29.4 (C5), 35.6 (C3), 70.1 (C6), 72.7 (C7), 125.9 (C1), 127.3 (C11), 127.4 (C9), 128.2 (C10), 138.5 (C8), 142.2 (C2).



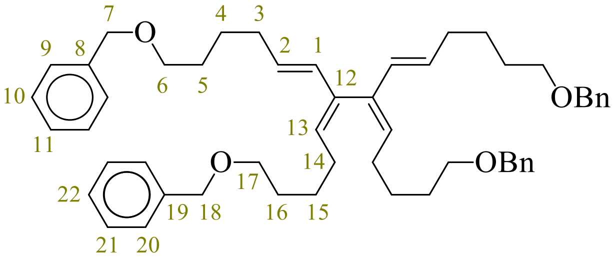
^{1}H NMR spectrum (CDCl$_3$, 400 MHz).

Note: this analysis was performed on a 70 : 30 mixture of **4c** and **4′c**.



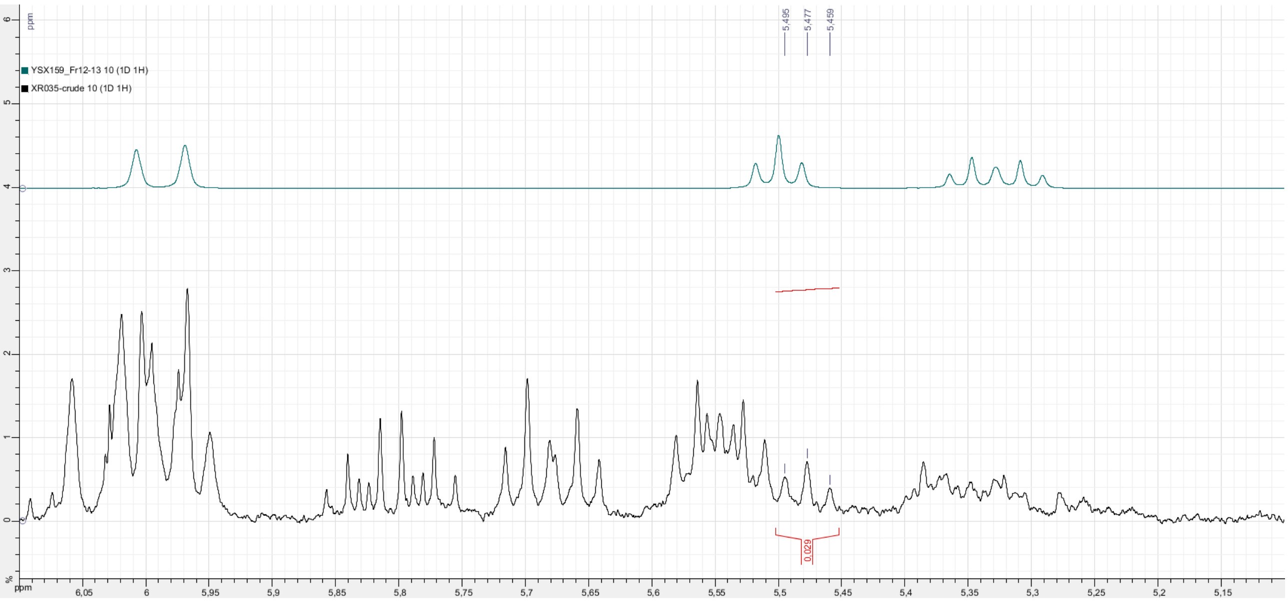
^{13}C and DEPT135 NMR spectra ($CDCl_3$, 100.6 MHz).
Note: this analysis was performed on a 68 : 32 mixture of **4c** and **4′c**.

[(5*Z*,7*Z*,8*E*)-13-Benzyloxy-6-[(*E*)-6-benzyloxyhex-1-enyl]-7-(5-benzyloxypentylidene)trideca-5,8-dienoxy]methylbenzene **5c**



^{1}H NMR (CDCl$_3$, 400 MHz), characteristic signals: δ 5.48 (2 H, dd, *J* 8.0, 6.5, H13).

This compound was produced in very small relative amounts and we were not able to isolate it. Nonetheless, the characteristic signal observed at 5.48 ppm is assigned to the structure **5c**, by analogy with the closely related compound **5d**. Moreover, this signal was only observed when *s*BuLi was used, which is also consistent with the results concerning the other tetramers **5b**, **5d** and **5e**.



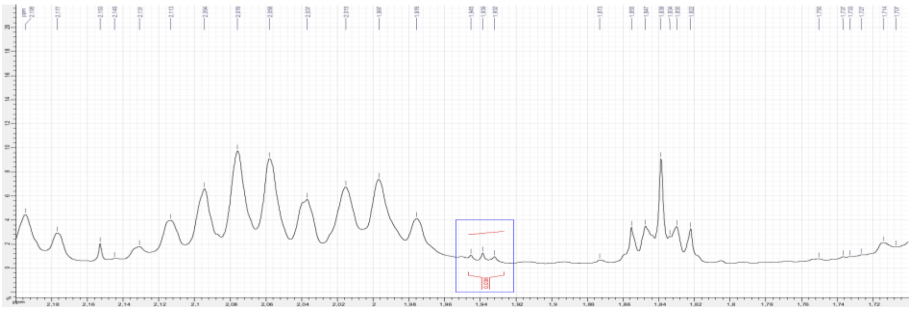
^{1}H NMR spectrum of a crude product (CDCl$_3$, 400 MHz) (detail).
Note: the characteristic signal at 5.48 ppm (with the integral) is to be compared with a spectrum of pure **5d** (shown on top, in green colour).

VI.2. Analysis of the crude products by ^{1}H NMR spectroscopy

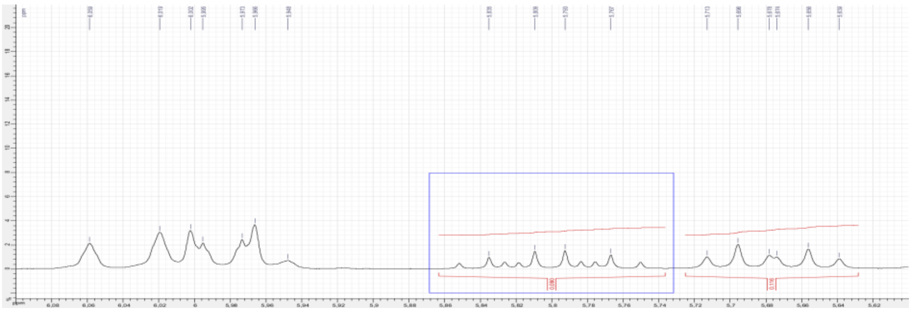
■ The benzyl CH_2 protons were used as an internal standard: the integral of the signals in the interval 4.35−4.60 ppm was set to 2.00.

■ The following signals were used for the qualitative assessment of the product yields:

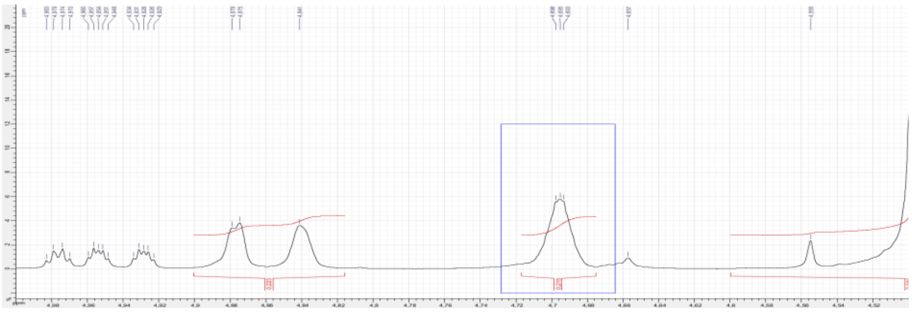
- Triplet (*J* 2.5 Hz) at 1.94 ppm: one proton of **1c**.
  The integral of this signal gave an estimation of the proportion of unconverted **1c**;



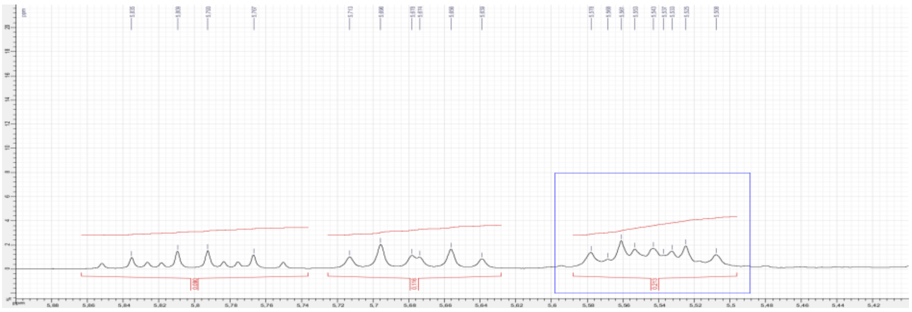
- Doublet of doublet of triplets (*J* 17.0, 10.0 and 6.5 Hz) at 5.81 ppm: one proton of **2c**.
  The integral of this signal gave an estimation of the yield of **2c**;



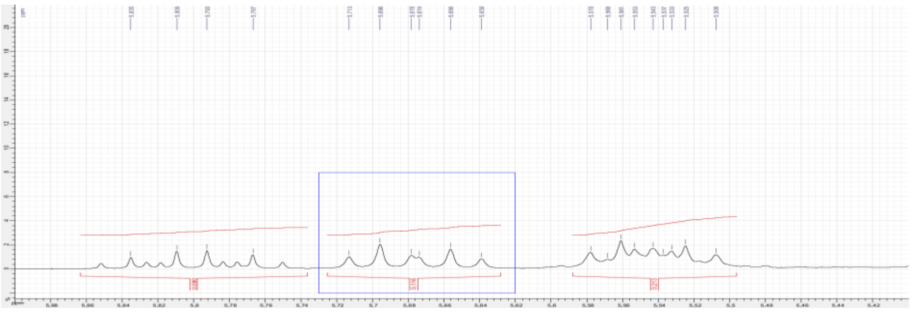
- Broad singlet at 4.70 ppm: two protons of **2′c**.
  Dividing the integral of this signal by two gave an estimation of the yield of **2′c**;



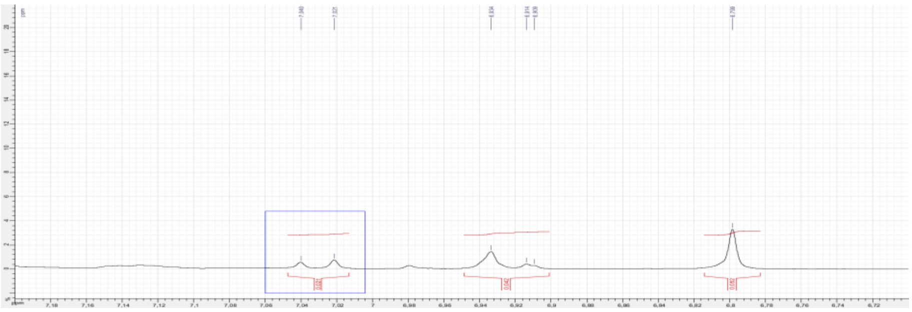
- Multiplet at 5.55 ppm: two protons of **3c**.
  The integral of this signal gave an estimation of the yield of **3c**;



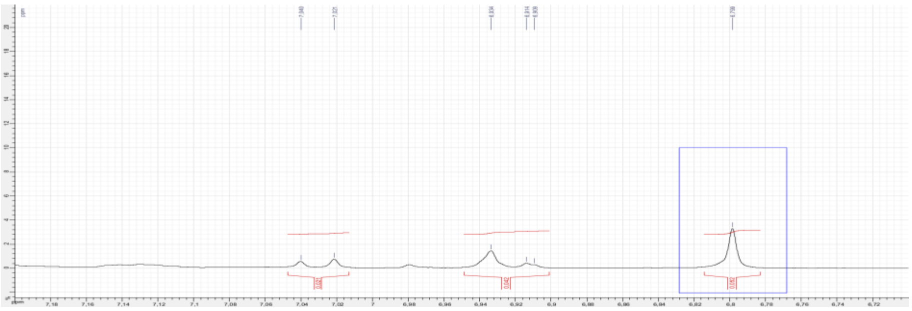
- Doublet of triplets (*J* 16.0 and 7.0 Hz) at 5.68 ppm: one proton of **3′c**. The integral of this signal was measured, then multiplied by two to give an estimation of the yield of **3′c**;



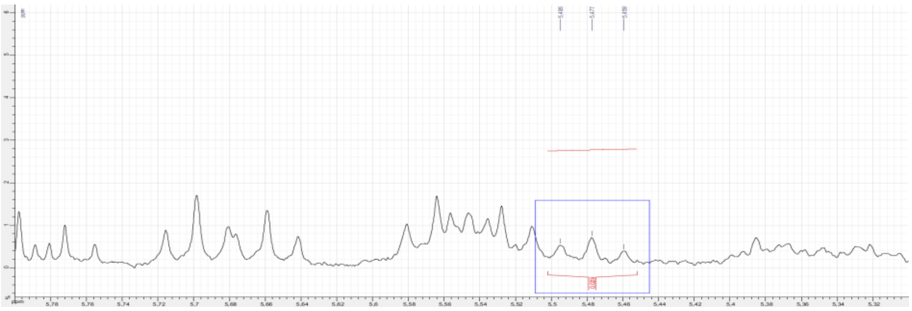
- Doublet (*J* 7.5 Hz) at 7.03 ppm: one proton of **4c**.
  The integral of this signal was multiplied by 3 to give an estimation of the yield of **4c**;



- Singlet at 6.80 ppm: three protons of **4′c**.
  The integral of this signal gave an estimation of the yield of **4′c**.

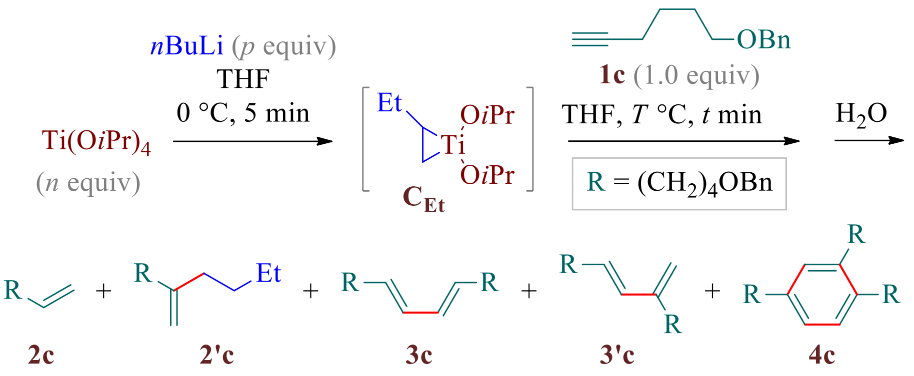


- Doublet of doublets (*J* 8.0 and 6.5 Hz) at 5.48 ppm: two protons of **5c**.
  The integral of this signal was multiplied by two to give an estimation of the yield of **5c**.



VI.3. Summary of the experimental results obtained using **1c**

■ With *n*BuLi, in THF.



Subsection	*n*	*p*	*T*	*t*	S.m. **1c**	Alkene **2c**	Alkene **2′c**	Dienes **3c/3′c** (ratio)	Trimers **4c/4′c** (ratio)
VI.4.1.	4.4	6.6	0	20	7%	18%	13%	10% (80 : 20)	6% (50 : 50)
VI.4.2.	2.2	3.3	0	30	4%	9%	11%	44% (48 : 52)	11% (55 : 45)
VI.4.3.			20		0%	8%	13%	24% (67 : 33)	16% (56 : 44)
VI.4.4.	1.1	1.65	0	45	7%	5%	7%	37% (47:53)	14% (66:34)
VI.4.5.	0.6	0.9	20	30	0%	3%	6%%	32% (50 : 50)	25% (64 : 36)
VI.4.6.[a,b]	0.6	0.9	140	15	0%	5%	1%	9% (42 : 58)	30% (69 : 31)

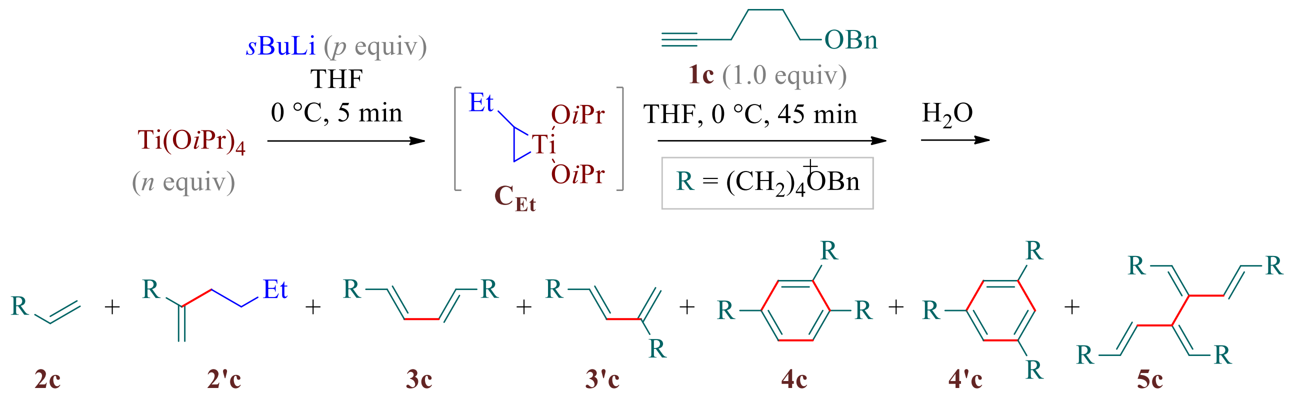
Colours for the starting material: ☐ 0−10% ☐ 11−20% ☐ 21−30% ■ 31−40% ■ ≥41%

Colours for the products: ☐ 0−10% ☐ 11−20% ☐ 21−30% ■ 31−40% ■ ≥41%

[a] Mean values are given for the yields, calculated from the similar results of two runs carried out under the same conditions.

[b] Heating was applied using a microwave reactor.

■ With *s*BuLi, in THF.



Subsection	*n*	*p*	s.m. **1c**	Alkene **2c**	Alkene **2′c**	Dienes **3c**/**3′c** (ratio)	Trimers **4c**/**4′c** (ratio)	Tetramer **5c**
VI.4.7.[a]	2.2	3.3	4%	20%	10%	34% (47 : 53)	1% (n.d.)	traces
VI.4.8.[b]	1.1	1.65	11%	7%	8%	33% (44 : 56)	4% (56:44)	6%

Colours for the starting material: ■ 0−10% ■ 11−20% ■ 21−30% ■ 31−40% ■ ≥41%

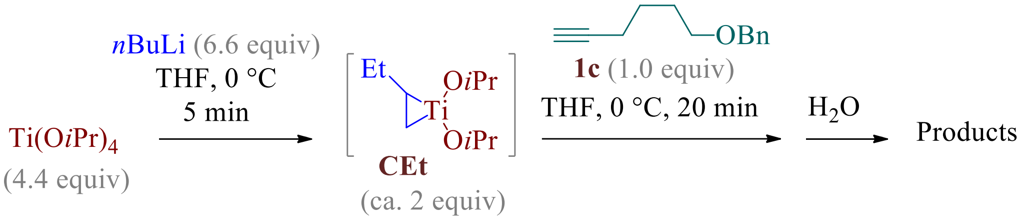
Colours for the products: ■ 0−10% ■ 11−20% ■ 21−30% ■ 31−40% ■ ≥41%

[a] Bottle #1 was used.

[b] “Old” bottle #1 was used.

VI.4. Experimental detail

■ **VI.4.1.** With 4.4 equiv of Ti(O*i*Pr)$_4$, 6.6 equiv of *n*BuLi;
reaction conducted at 0 °C for 20 min.

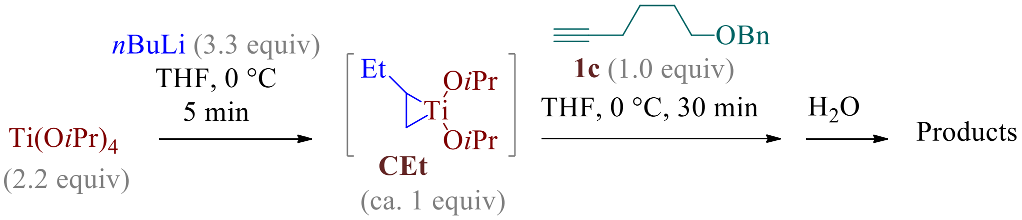


S.m **1c**	Alkene **2c**	Alkene **2′c**	Diene **3c**	Diene **3′c**	Trimer **4c**	Trimer **4′c**	Total
7%	18%	13%	8%	2%	3%	3%	54%

General procedure **GP3** was applied with *n* = 4.40, *p* = 6.60, V_1 = 3.5, V_2= 0.5 and *t* = 20.
n-Butyllithium solution (2.38 M in hexanes, 6.60 mmol, 2.77 mL) was added over 3 minutes. The THF solution of 6-benzyloxyhex-1-yne **1c** (1.00 mmol, 188 mg) was added over 3 minutes.

Crude product: pale yellow oil (181 mg). Analysis as described in subsection VI.2. gave the qualitative estimation of the product yields shown in the table above.

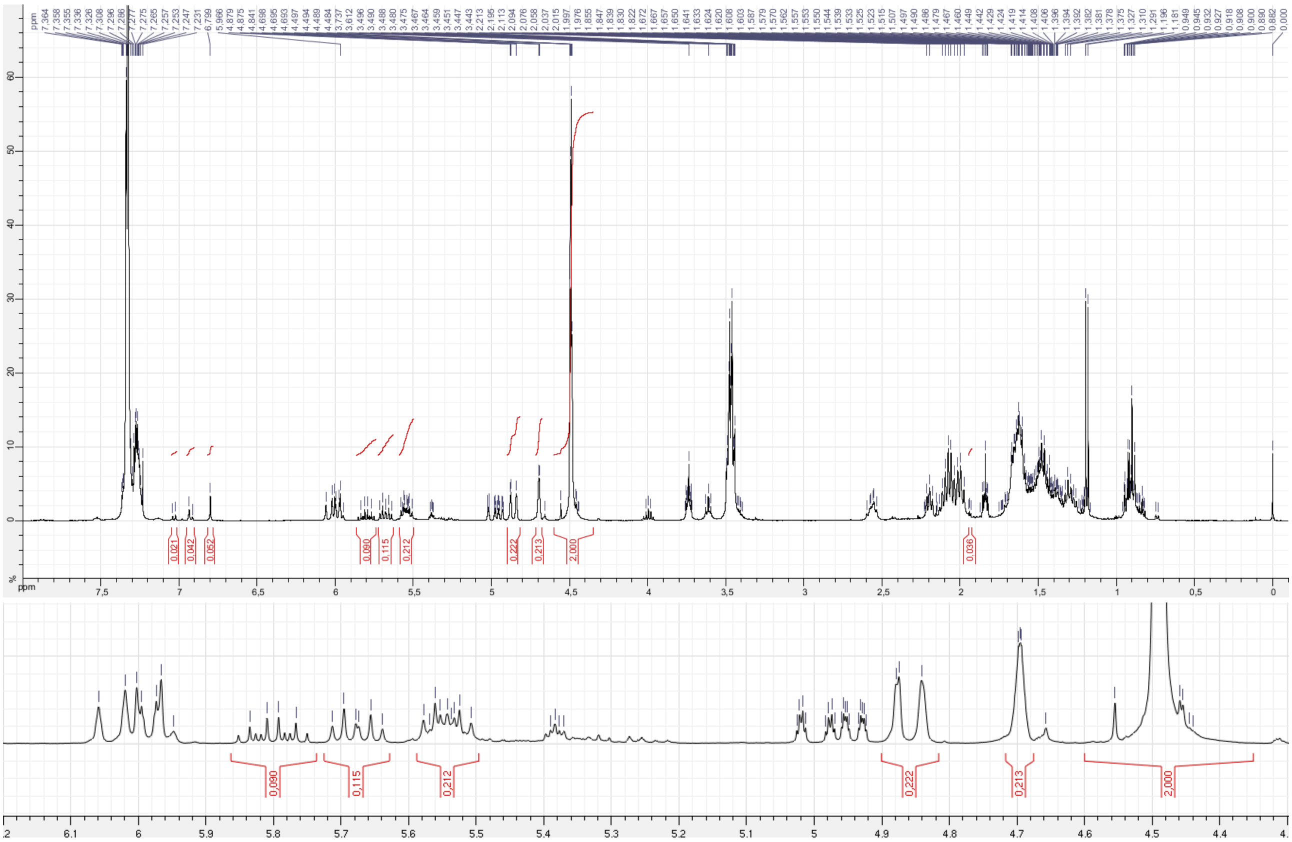
■ **VI.4.2.** With 2.2 equiv of Ti(O*i*Pr)$_4$, 3.3 equiv of *n*BuLi;
reaction conducted at 0 °C for 30 min.



S.m **1c**	Alkene **2c**	Alkene **2′c**	Diene **3c**	Diene **3′c**	Trimer **4c**	Trimer **4′c**	Total
4%	9%	11%	21%	23%	6%	5%	79%

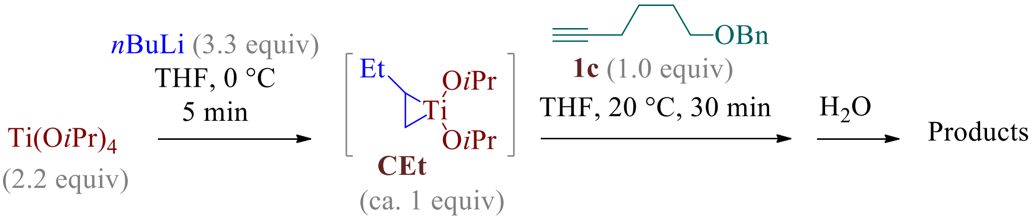
General procedure **GP3** was applied with *n* = 2.20, *p* = 3.30, V_1 = 3.5, V_2= 0.5 and *t* = 30.
n-Butyllithium solution (2.34 M in hexanes, 3.30 mmol, 1.41 mL) was added over 1 minute. The THF solution of 6-benzyloxyhex-1-yne **1c** (1.00 mmol, 188 mg) was added over 1 minute.

Crude product: yellow oil (208 mg). Analysis as described in subsection VI.2. gave the qualitative estimation of the product yields shown in the table above.



^1H NMR spectrum of the crude product ($CDCl_3$, 400 MHz).

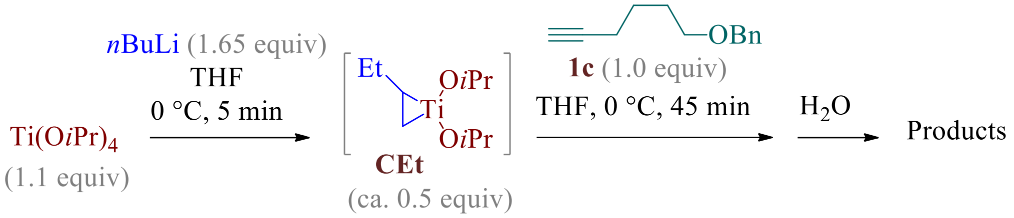
■ VI.4.3. With 2.2 equiv of $Ti(OiPr)_4$, 3.3 equiv of *n*BuLi; reaction conducted at 20 °C for 30 min.



S.m **1c**	Alkene **2c**	Alkene **2′c**	Diene **3c**	Diene **3′c**	Trimer **4c**	Trimer **4′c**	Total
≈ 0%	8%	13%	16%	8%	9%	7%	61%

n-Butyllithium solution (2.34 M in hexanes, 3.30 equiv, 3.30 mmol, 1.41 mL) was added dropwise, at 0 °C, to a solution of titanium(IV) isopropoxide (2.20 equiv, 2.20 mmol, 651 µL) in THF (3.5 mL). After 5 minutes of stirring at 0 °C, a solution of 6-benzyloxyhex-1-yne **1c** (1.00 equiv, 1.00 mmol, 188 mg) in THF (0.5 mL) was added dropwise. The cold bath was removed and the mixture was stirred for an additional 30 minutes. H_2O (0.5 mL) was then added and the septum was removed. After 15 minutes of stirring, the mixture was filtered through a pad of sand, celite, $MgSO_4$ and sand [from top to bottom; rinsing with Et_2O (20 mL)] and concentrated under reduced pressure (down to 50 mbar) to afford a yellowish oil (248 mg). Analysis of this crude product as described in subsection VI.2. gave the qualitative estimation of the product yields shown in the table above.

■ **VI.4.4.** With 1.1 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *n*BuLi; reaction conducted at 0 °C for 45 min.



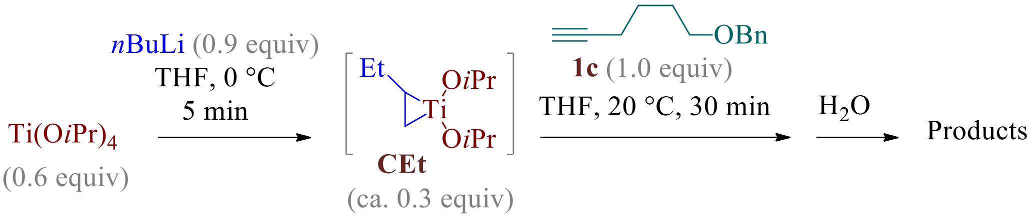
S.m **1c**	Alkene **2c**	Alkene **2′c**	Diene **3c**	Diene **3′c**	Trimer **4c**	Trimer **4′c**	Total
8%	5%	7%	17%	20%	9%	5%	71%[a]
7%	5%	7%	15%	17%	8%	4%	63%[b]

[a] Yields estimated as depicted in VI.2. (benzyl CH_2 protons used as an internal standard).

[b] Yields estimated using (*E*)-cinnamic acid (500 µmol, 74.1 mg) as an internal standard.

General procedure **GP1** was applied with $n = 1.10$, $p = 1.65$ and $t = 45$. *n*-Butyllithium solution (2.31 M in hexanes, 3.30 mmol, 1.43 mL) was added over 2 minutes. 6-Benzyloxyhex-1-yne **1c** (2.00 mmol, 377 mg) was added over 1 min 40 s. Crude product: yellow oil (371 mg). Analysis as described in subsection VI.2. gave the qualitative estimation of the product yields shown in the table above.

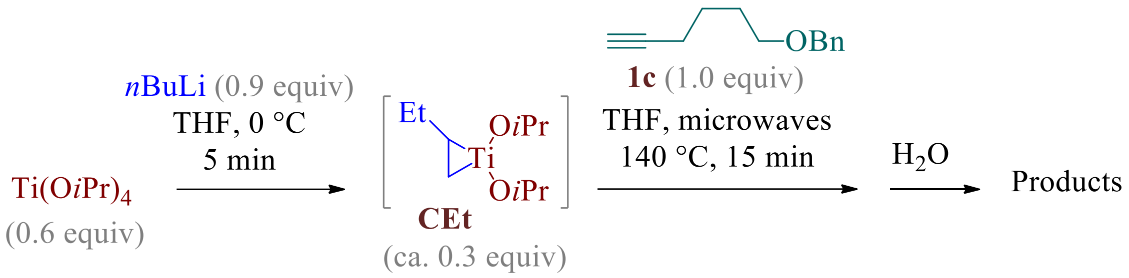
■ **VI.4.5.** With 0.6 equiv of Ti(O*i*Pr)$_4$, 0.9 equiv of *n*BuLi; reaction conducted at 20 °C for 30 min.



S.m **1c**	Alkene **2c**	Alkene **2′c**	Diene **3c**	Diene **3′c**	Trimer **4c**	Trimer **4′c**	Total
0%	3%	6%%	16%	16%	16%	9%	66%

n-Butyllithium solution (2.34 M in hexanes, 0.900 equiv, 2.70 mmol, 1.15 mL) was added dropwise, at 0 °C, to a solution of titanium(IV) isopropoxide (0.600 equiv, 1.80 mmol, 534 µL) in THF (3.5 mL). After 5 minutes of stirring at 0 °C, a solution of 6-benzyloxyhex-1-yne **1c** (1.00 equiv, 3.00 mmol, 565 mg) in THF (0.5 mL) was added dropwise. The cold bath was removed and the mixture was stirred for an additional 30 minutes. H_2O (0.5 mL) was then added and the septum was removed. After 15 minutes of stirring, the mixture was filtered through a pad of sand, celite, $MgSO_4$ and sand [from top to bottom; rinsing with Et_2O (20 mL)] and concentrated under reduced pressure (down to 50 mbar) to afford a yellow oil (545 mg). Analysis of this crude product as described in subsection VI.2. gave the qualitative estimation of the product yields shown in the table above.

■ **VI.4.6.** With 0.6 equiv of Ti(O*i*Pr)$_4$, 0.9 equiv of *n*BuLi;
reaction conducted at 140 °C for 15 min, under microwave conditions.



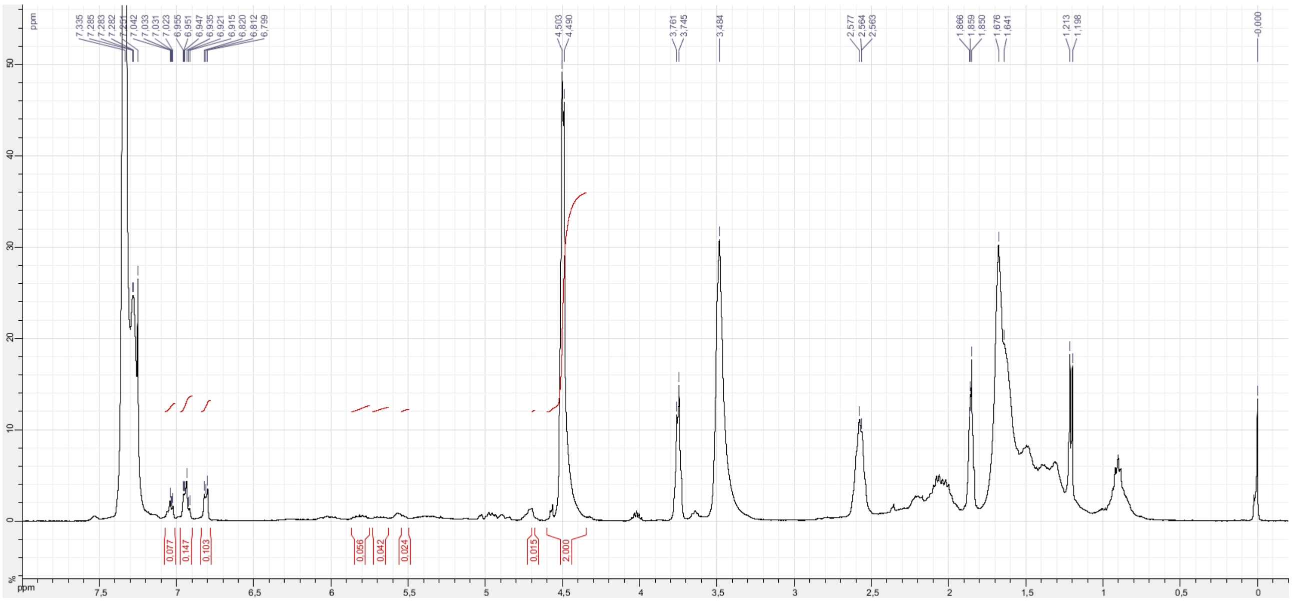
	S.m **1c**	Alkene **2c**	Alkene **2′c**	Diene **3c**	Diene **3′c**	Trimer **4c**	Trimer **4′c**	Total
Run 1	0%	6%	1%	4% (2%)	8% (4%)	22% (20%)	10% (10%)	51%
Run 2	0%	4%	2%	4%	3%	20% (20%)	9% (8%)	42%

In parentheses: yields of isolated products.

- Run 1: General procedure **GP7** was applied with *T* = 140 and with 6-benzyloxyhex-1-yne **1c** (3.00 mmol, 565 mg) as the substrate.

Crude product: orange oil (563 mg). Analysis as described in subsection VI.2. gave the qualitative estimation of the product yields shown in the table above.

Flash column chromatography (silica gel, EtOAc/petroleum ether, gradient from 1% to 10%) afforded a 60 : 40 mixture of alkenes **2c** and **2′c**, contaminated by an unidentified compound, (57.5 mg), a 36 : 64 mixture of fairly pure dienes **3c** and **3′c** (23.9 mg, 63.1 µmol, 6%) and a 68 : 32 mixture of pure **4c** and **4′c** (169 mg, 299 µmol, 30%).

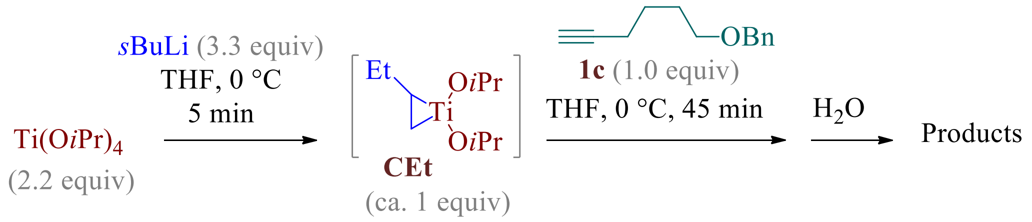


^{1}H NMR spectrum of the crude product (CDCl$_3$, 400 MHz).

- Run 2: the reaction was repeated under the same conditions, to afford a yellow oil (528 mg). Analysis of this crude product as described in subsection VI.2. gave the qualitative estimation of the product yields shown in the table above.

Flash column chromatography (silica gel, EtOAc/petroleum ether, gradient from 2% to 10%) afforded a 70 : 30 mixture of pure **4c** and **4’c** (159 mg, 282 µmol, 28%).

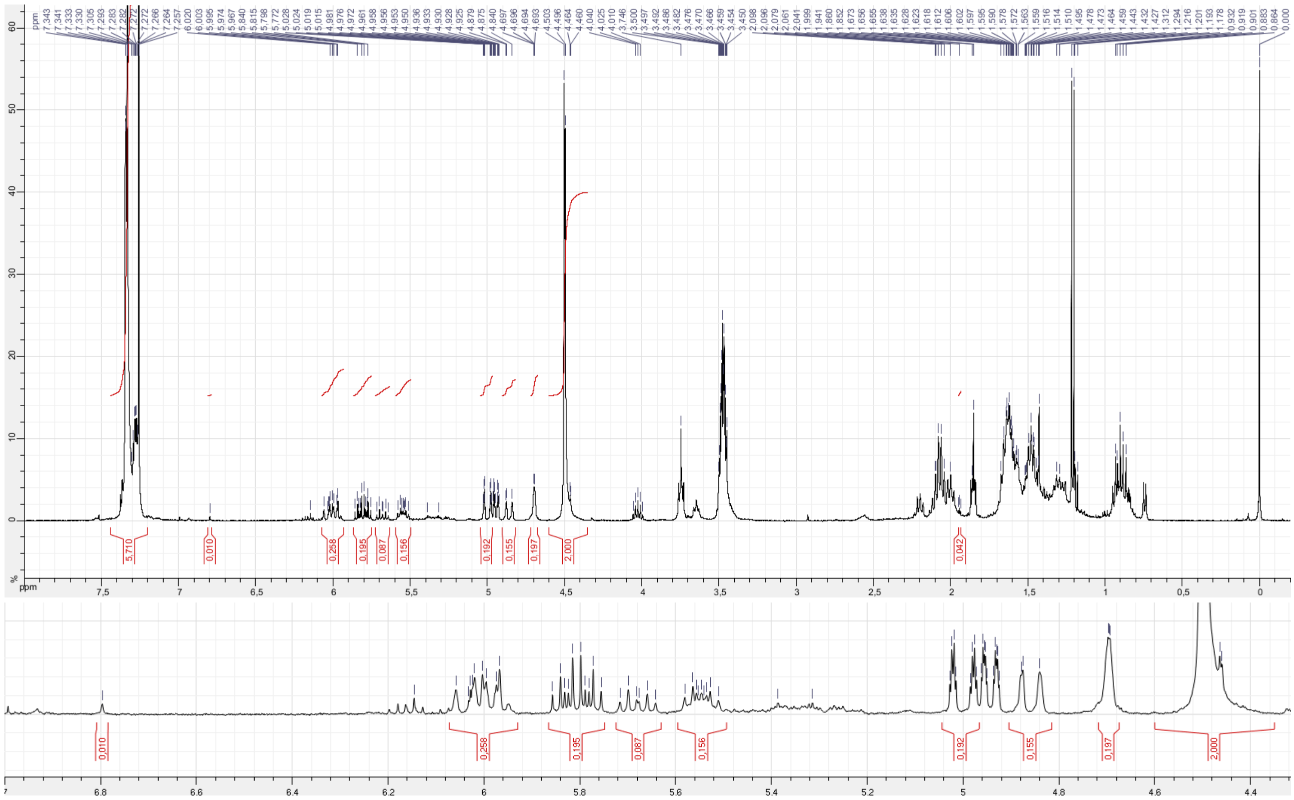
VI.4.7. With 2.2 equiv of Ti(O*i*Pr)$_4$, 3.3 equiv of *s*BuLi (bottle #1); reaction conducted at 0 °C for 45 min.



S.m **1c**	Alkene **2c**	Alkene **2′c**	Diene **3c**	Diene **3′c**	Trimer **4c**	Trimer **4′c**	Tetramer **5c**	Total
4%	20%	10%	16%	18%	≈ 0%	1%	traces	69%

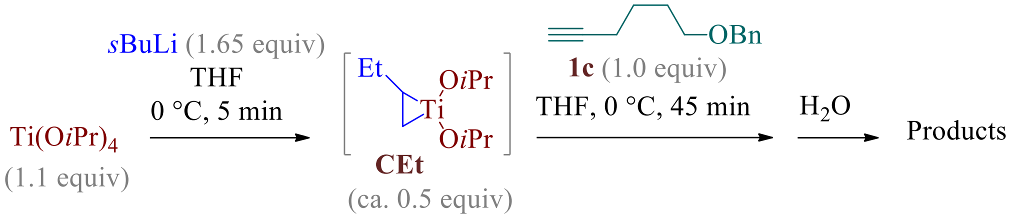
General procedure **GP1** was applied with *n* = 2.20, *p* = 3.30 and *t* = 45. *s*-Butyllithium solution (1.14 M in cyclohexane, 3.30 mmol, 2.89 mL) was added over 2 minutes. 6-Benzyloxyhex-1-yne **1c** (1.00 mmol, 188 mg) was added over 4 minutes.

Crude product: pale yellow oil (213 mg). Analysis as described in subsection VI.2. gave the qualitative estimation of the product yields shown in the table above.



^{1}H NMR spectrum of the crude product (CDCl$_3$, 400 MHz).

■ **VI.4.8.** With 1.1 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *s*BuLi (“old” bottle #1); reaction conducted at 0 °C for 45 min.



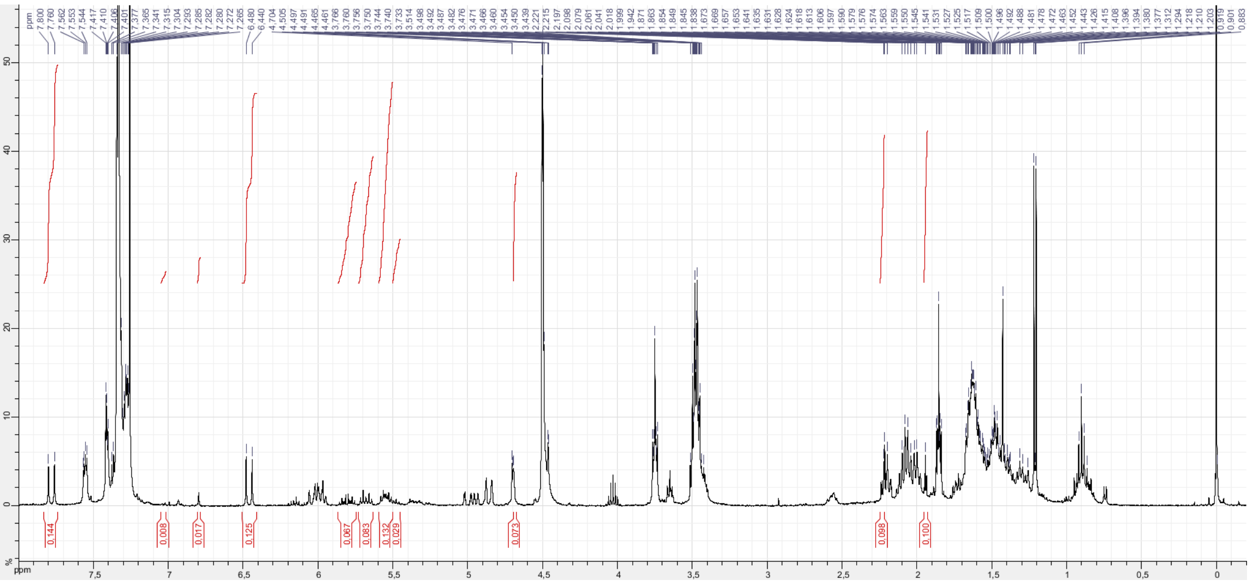
S.m **1c**	Alkene **2c**	Alkene **2′c**	Diene **3c**	Diene **3′c**	Trimer **4c**	Trimer **4′c**	Tetramer **5c**	Total
11%	7%	8%	14%	18%	2%	2%	6%	68%[a]
10%	7%	7%	13%	17%	2%	2%	6%	64%[b]

[a] Yields estimated as depicted in VI.2. (benzyl CH_2 protons used as an internal standard).

[b] Yields estimated using (*E*)-cinnamic acid (250 µmol, 37.05 mg) as an internal standard.

General procedure **GP1** was applied with *n* = 1.10, *p* = 1.65 and *t* = 45. *s*-Butyllithium solution (1.23 M in cyclohexane, 3.30 mmol, 2.68 mL) was added over 1 minute. 6-Benzyloxyhex-1-yne **1c** (2.00 mmol, 377 mg) was added over 2 min 45s. Crude product: yellow oil (425 mg).

Analysis as described in subsection VI.2. gave the qualitative estimation of the product yields shown in the table above.



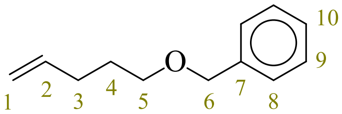
^{1}H NMR spectrum of the crude product ($CDCl_3$, 400 MHz).

VII. Experiments with 5-benzyloxypent-1-yne **1d**

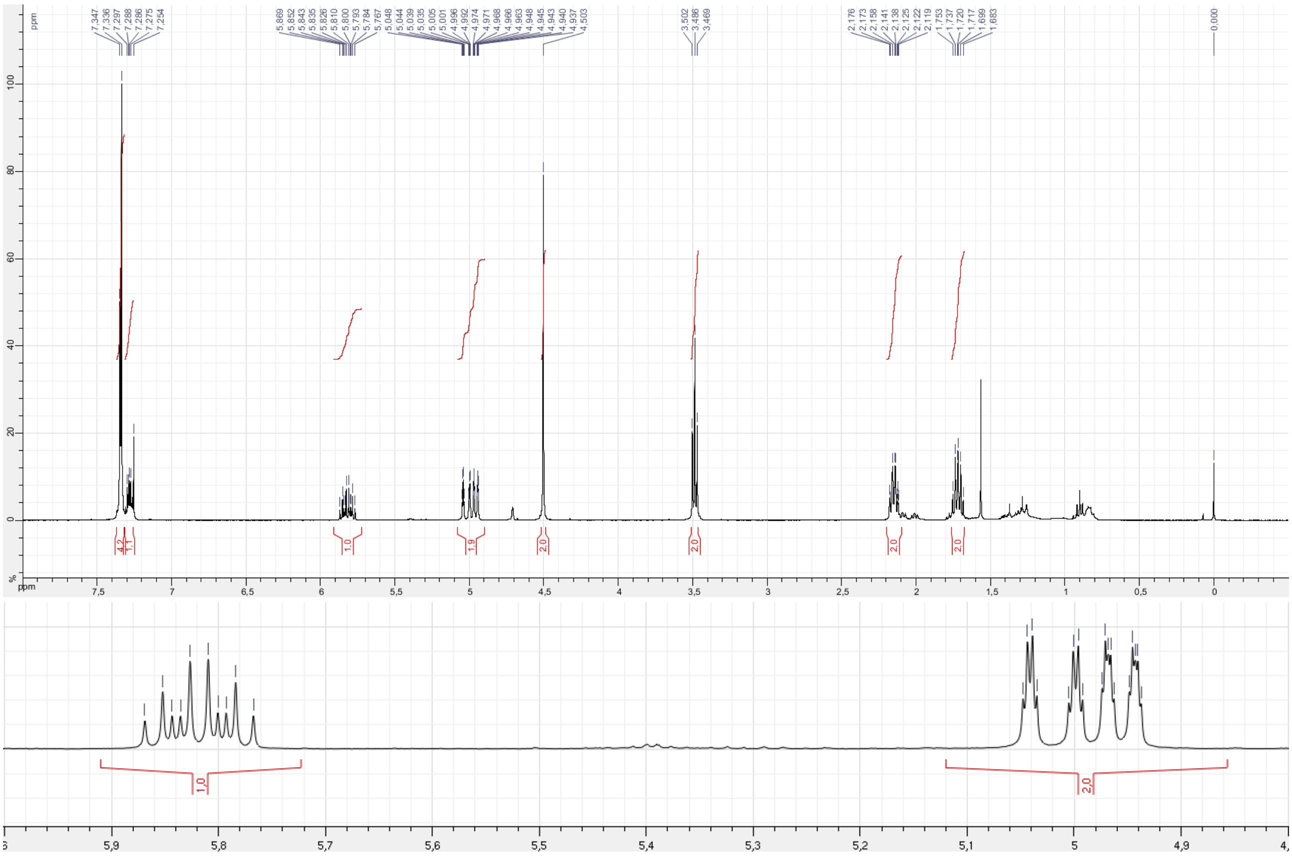
VII.1. Characterisation of the products

Products **2d**, **2′d** and **5d** could be isolated in reasonably pure form. Conversely, dienes **3d**/**3′d** and cyclotrimers **4d**/**4′d** were only obtained as mixtures of the two regioisomers. In these cases, assignment of the signals was done as explained in the general information.

5-Benzyloxypent-1-ene **2d**[30]

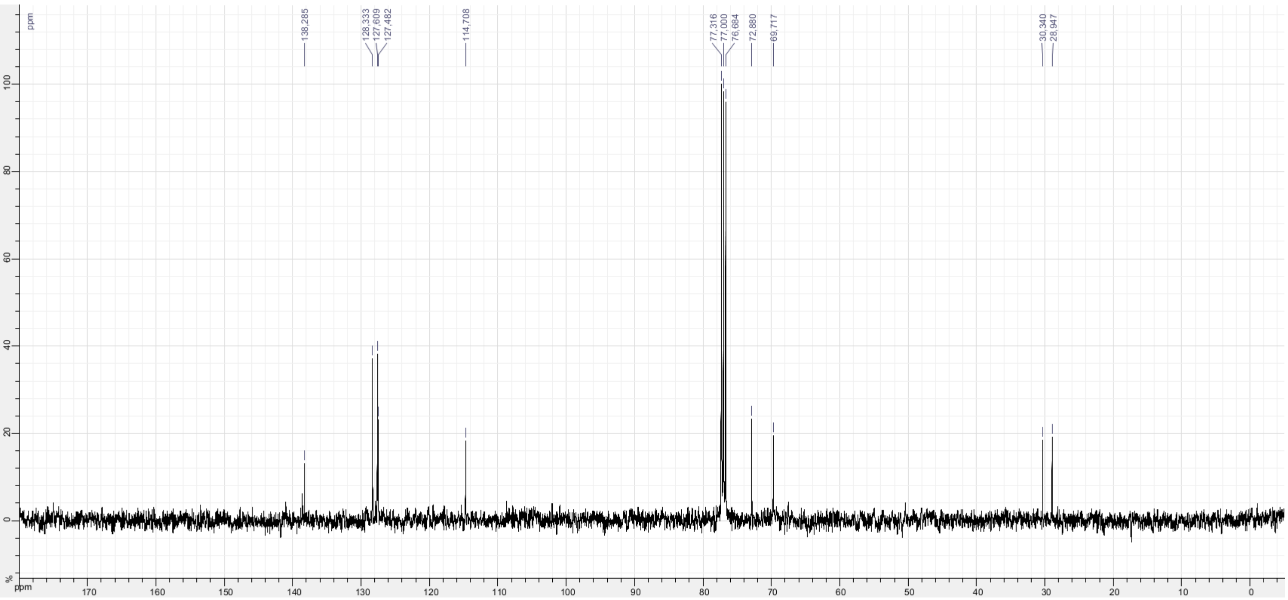


^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.72 (2 H, tt, *J* 7.5, 6.5, H4), 2.15 (2 H, tddd, *J* 7.5, 6.5, 1.5, 1.0, H3), 3.49 (2 H, t, *J* 6.5, H5), 4.50 (2 H, s, H6), 4.96 (1 H, ddt, *J* 10.0, 2.0, 1.0, H1 *cis* to H2), 5.02 (1 H, ddt, *J* 17.0, 2.0, 1.5, H1 *trans* to H2), 5.82 (1 H, ddt, *J* 17.0, 10.0, 6.5, H2), 7.29 (1 H, m, H10), 7.32−7.37 (4 H, m, H8−H9). ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ 28.9 (C4), 30.3 (C3), 69.7 (C5), 72.9 (C6), 114.7 (C1), 127.5 (C10), 127.6 (C8), 128.3 (C9), 138.3 (C2).



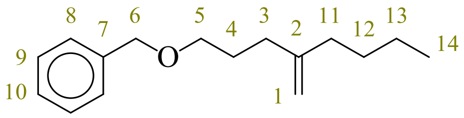
^{1}H NMR spectrum (CDCl$_3$, 400 MHz).

30− D. W. P. M. Lowik, R. M. J. Liskamp, *Eur. J. Org. Chem.* **2000**, 1219−1228.

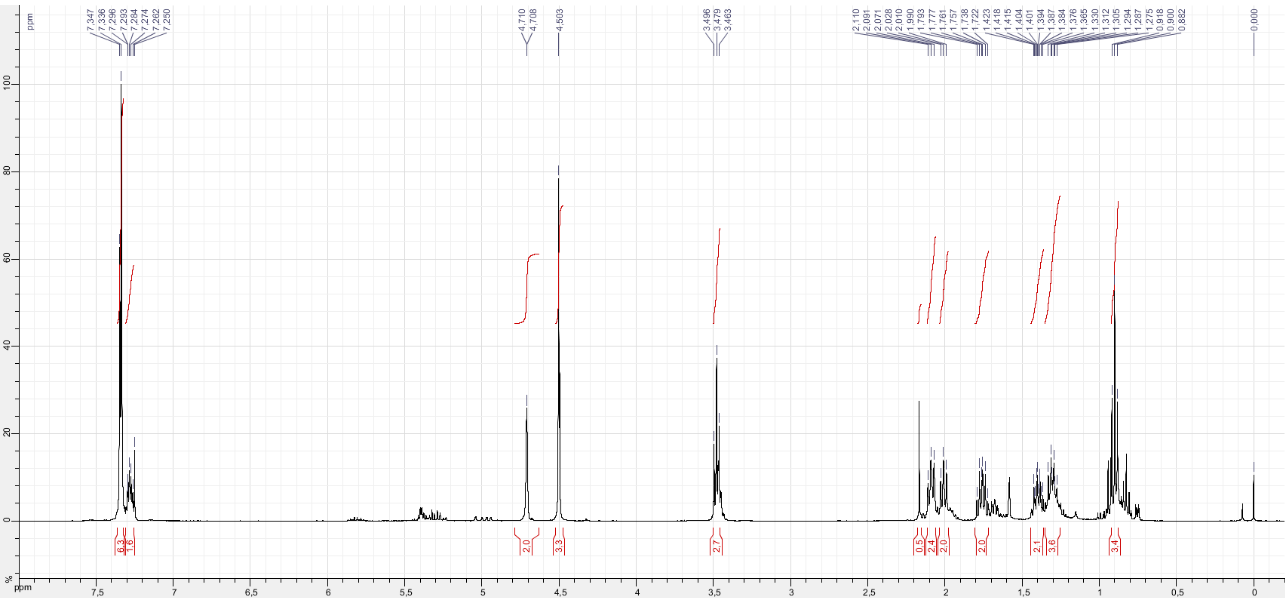


^{13}C NMR spectrum (CDCl$_3$, 100.6 MHz).

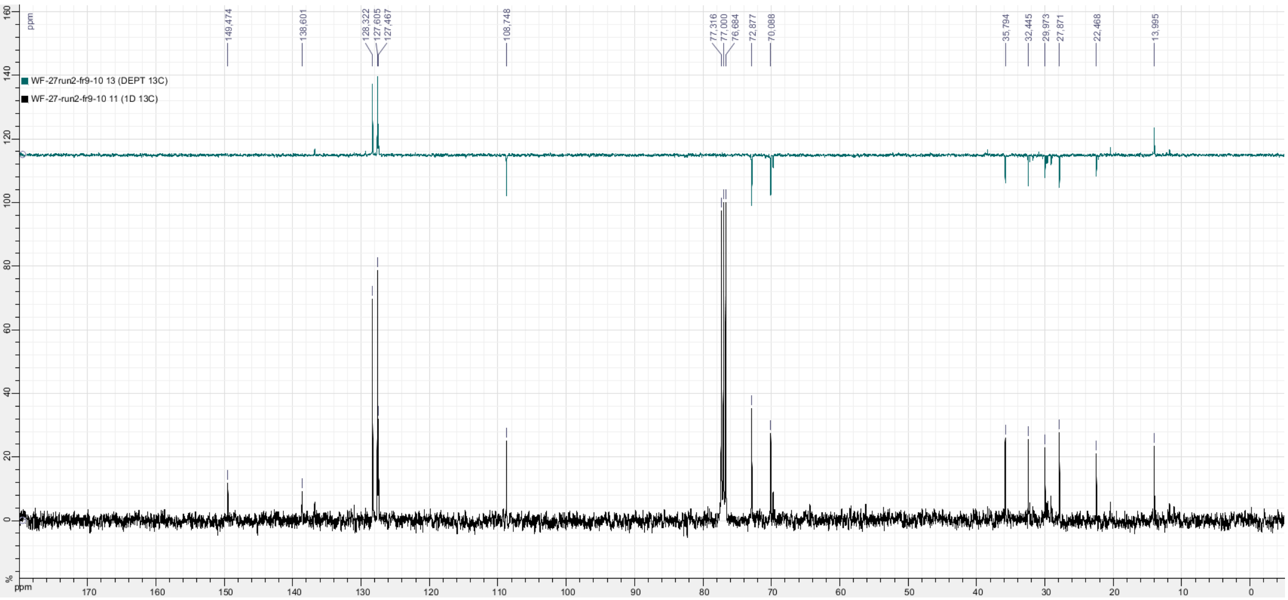
4-Methyleneoctoxymethylbenzene **2′d**



^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.90 (3 H, t, *J* 7.5, H14), 1.30 (2 H, qt, *J* 7.5, 7.0, H13), 1.40 (2 H, tt, *J* 7.5, 7.0, H12), 1.76 (2 H, tt, *J* 7.5, 6.5, H4), 2.01 (2 H, br t, *J* 7.5, H11), 2.09 (2 H, br t, *J* 7.5, H3), 3.48 (2 H, t, *J* 6.5, H5), 4.50 (2 H, s, H6), 4.71 (2 H, br s, H1), 7.28 (1 H, m, H10), 7.31−7.37 (4 H, m, H8−H9). ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ 14.0 (C14), 22.5 (C13), 27.9 (C4), 30.0 (C12), 32.4 (C3), 35.8 (C11), 70.1 (C5), 72.9 (C6), 108.7 (C1), 127.5 (C10), 127.6 (C8), 128.3 (C9), 138.6 (C7), 149.5 (C2).

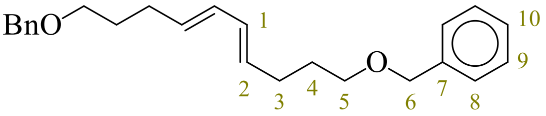


^{1}H NMR spectrum (CDCl$_3$, 400 MHz).



^{13}C and DEPT135 NMR spectra (CDCl$_3$, 100.6 MHz).

[(*E*,*E*)-10-Benzyloxydeca-4,6-dienoxy]methylbenzene **3d**



Viscous colourless oil. R_f 0.3 [EtOAc/Petroleum ether 10%, UV-active, anisaldehyde (dark purple colour)]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.71 (4 H, tt, *J* 7.5, 6.5, H4), 2.16 (4 H, br td, *J* 7.5, 7.0, H3), 3.48 (4 H, t, *J* 6.5, H5), 4.50 (4 H, s, H6), 5.55 (2 H, m, H2), 6.00 (2 H, m, H1), 7.25−7.31 (2 H, m, H10), 7.31−7.37 (8 H, m, H8−H9). ^{13}C NMR (CDCl$_3$, 100.6 Hz): δ 29.2 (C4), 29.4 (C3), 69.7 (C5), 72.9 (C6), 127.5 (C10), 127.6 (C8), 128.3 (C9), 130.7 (C2), 131.7 (C1), 138.6 (C7). HRMS (EI): *m/z* 259.1701 ([M−Bn]$^+$ $C_{17}H_{23}O_2^+$ requires 259.1693).[31]

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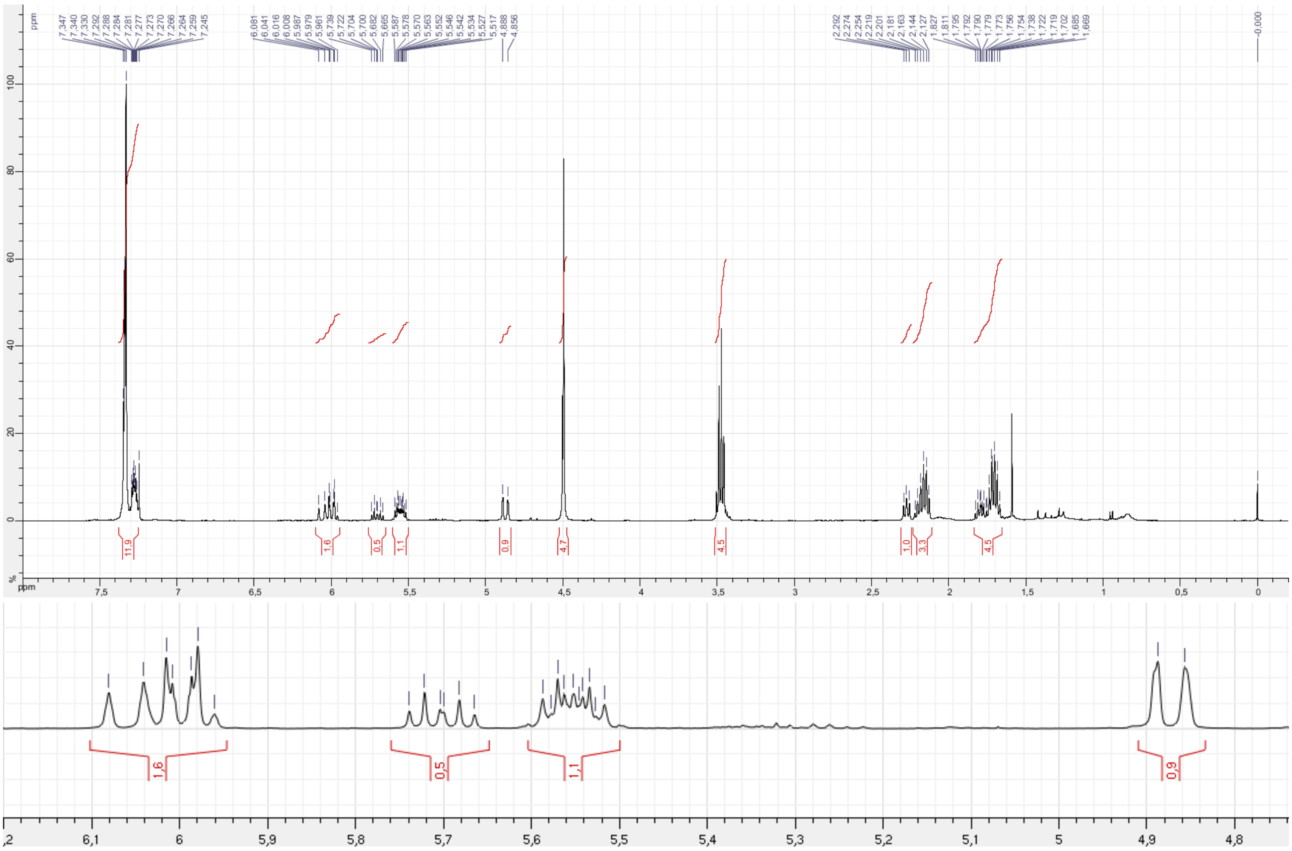
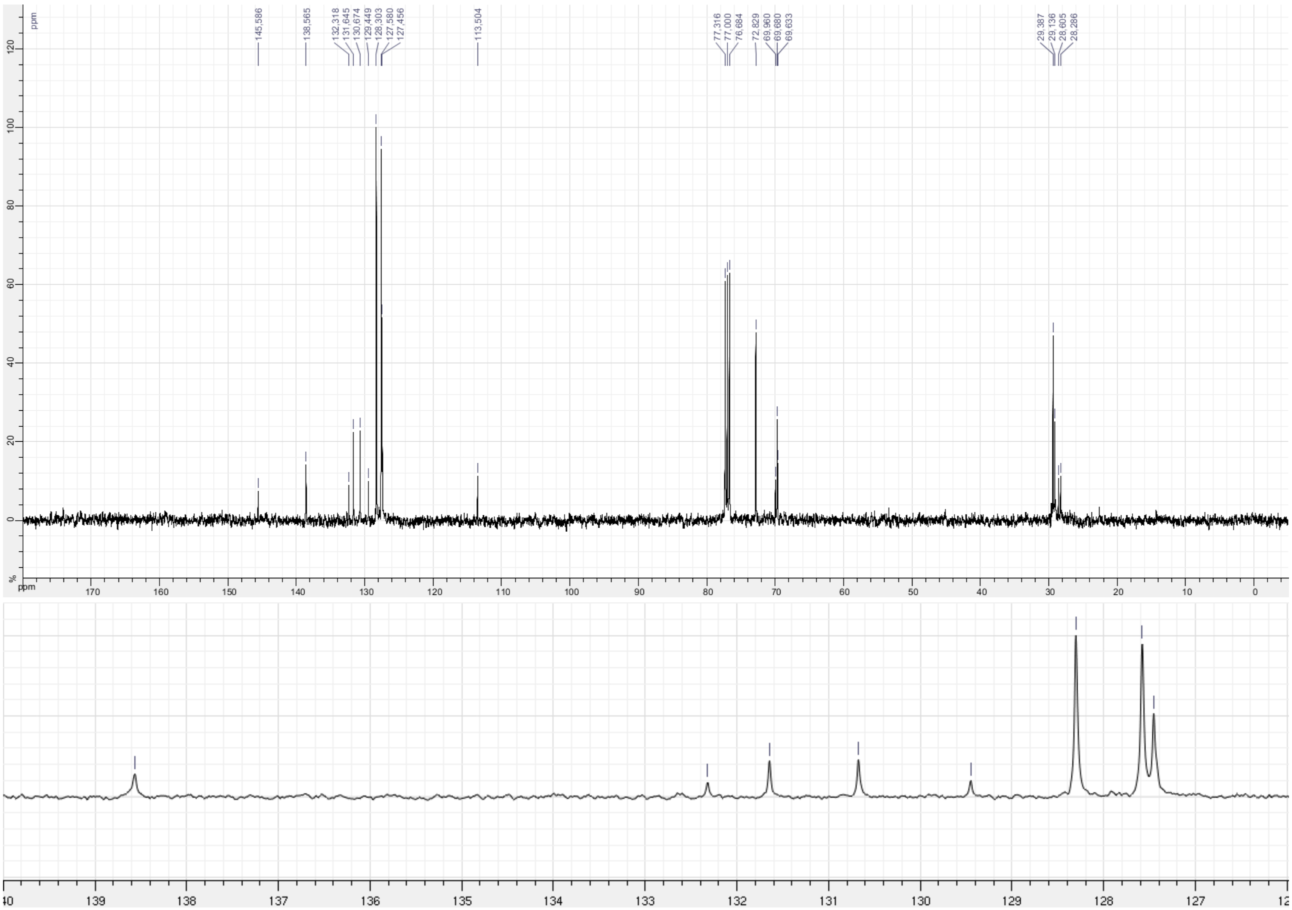
[31] Analysis performed on a 43 : 57 mixture of **3d** and **3′d**.



^{1}H NMR spectrum ($CDCl_3$, 400 MHz).

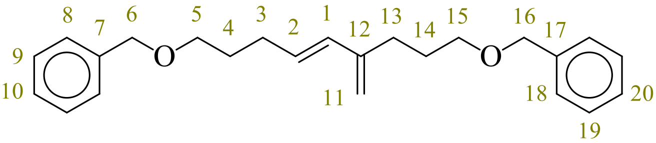
Note: this analysis was performed on a 53 : 47 mixture of **3d** and **3′d**.



^{13}C NMR spectrum ($CDCl_3$, 100.6 MHz).

Note: this analysis was performed on a 53 : 47 mixture of **3d** and **3′d**.

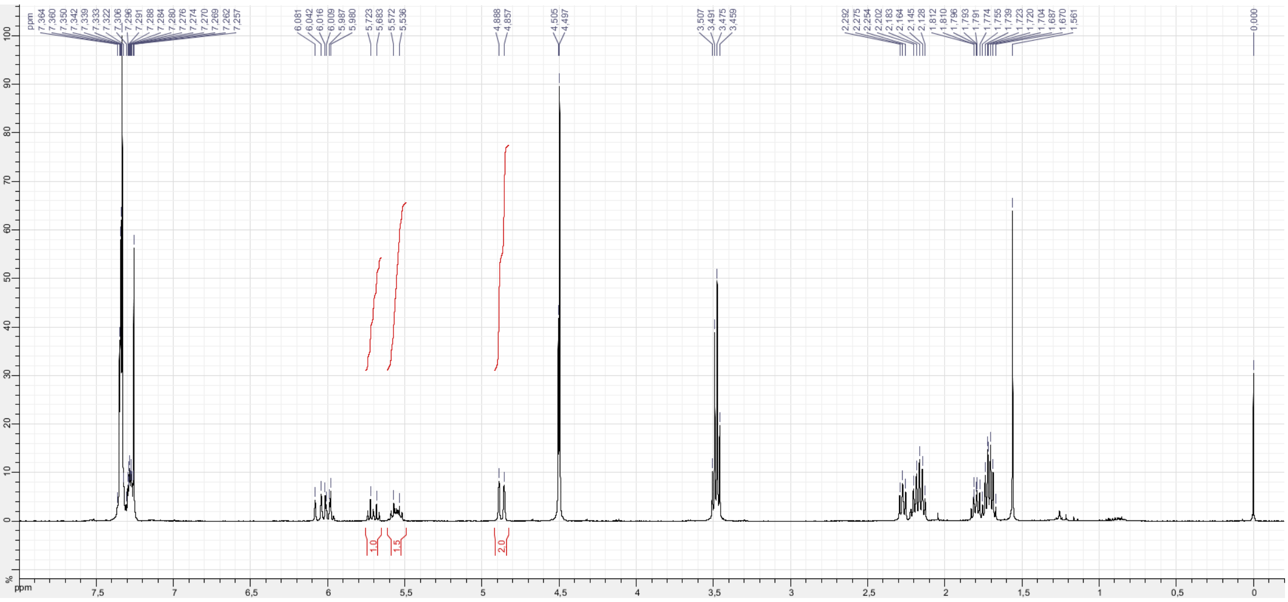
[(*E*)-9-benzyloxy-4-methylene-non-5-enoxy]methylbenzene **3′d**



Viscous colourless oil. R_f 0.3 [EtOAc/Petroleum ether 10%, UV-active, anisaldehyde (dark purple colour)]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.72 (2 H, tt, *J* 7.5, 6.5, H4), 1.79 (2 H, tt, *J* 7.5, 6.5, H14), 2.19 (2 H, tdd, *J* 7.5, 7.0, 1.5, H3), 2.27 (2 H, td, *J* 7.5, 1.0, H13), 3.48 (2 H, t, *J* 6.5, H5), 3.49 (2 H, t, *J* 6.5, H15), 4.50 (2 H, s, H6), 4.51 (2 H, s, H16), 4.86 (1 H, br s, H11a), 4.89 (1 H, br s, H11b), 5.70 (1 H, dt, *J* 16.0, 7.0, H2), 6.06 (1 H, dt, *J* 16.0, 1.5, H1), 7.25-7.31 (2 H, m, H10, H20), 7.31−7.37 (8 H, m, H8−H9, H18−H19).

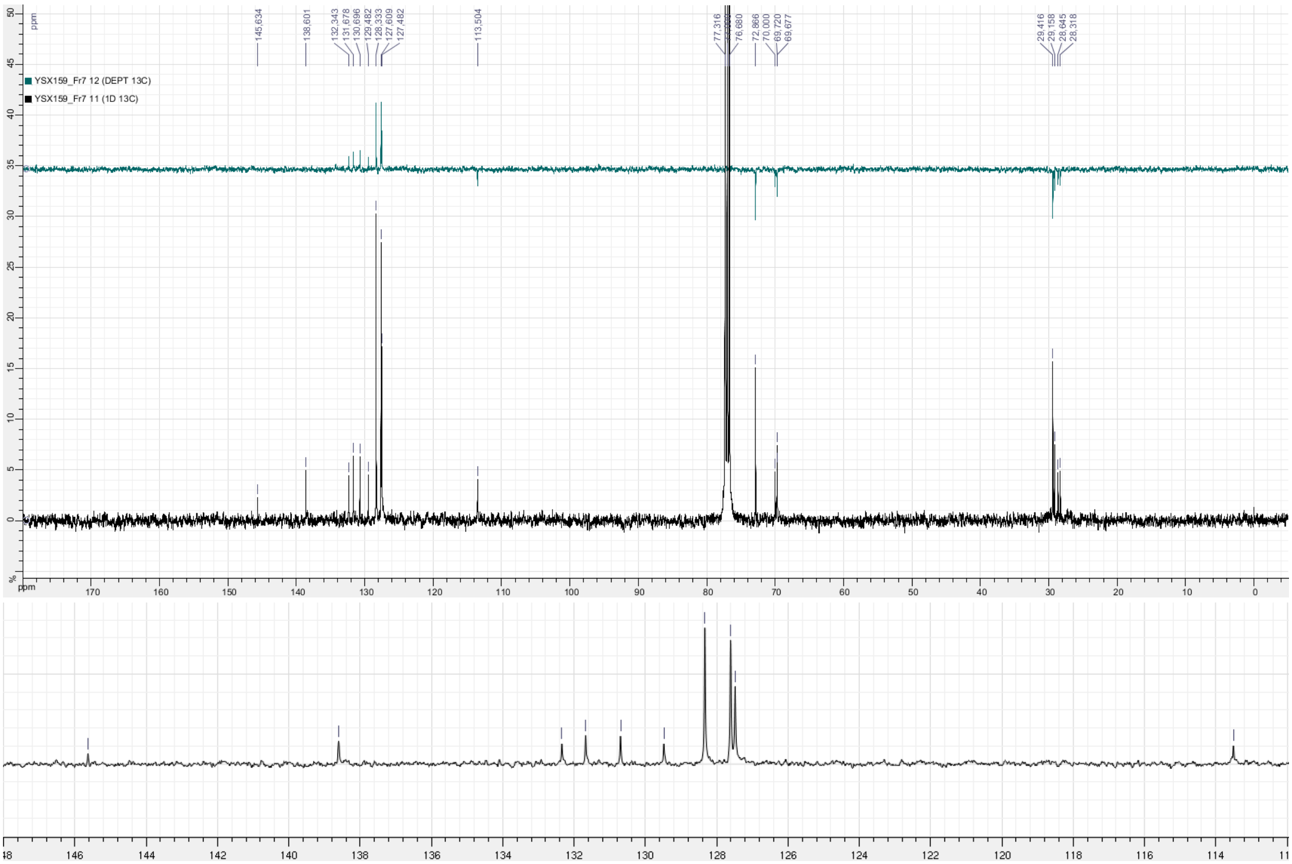
^{13}C NMR (CDCl$_3$, 100.6 Hz): δ 28.3, 28.6 (C4, C13), 29.4, 29.4 (C3, C14), 69.7 (C5), 70.0 (C15), 72.9, 72.9 (C6, C16), 113.5 (C11), 127.5, 127.5 (C10, C20), 127.6, 127.6 (C8, C18), 128.3, 128.3 (C9, C19), 129.5 (C2), 132.3 (C1), 138.6, 138.6 (C7, C17), 145.6 (C12).

HRMS (EI): *m/z* 259.1701 ([M−Bn]$^+$ $C_{17}H_{23}O_2^+$ requires 259.1693).[31]



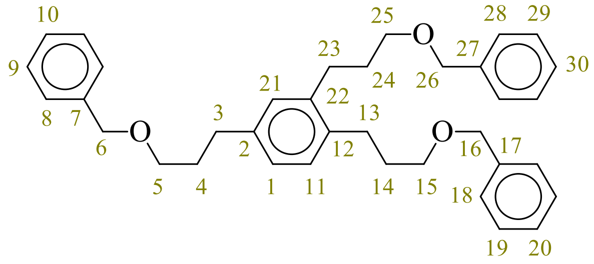
^{1}H NMR spectrum (CDCl$_3$, 400 MHz).

Note: this analysis was performed on a 43 : 57 mixture of **3d** and **3′d**.



^{13}C NMR and DEPT135 spectra ($CDCl_3$, 100.6 MHz).
Note: this analysis was performed on a 43 : 57 mixture of **3d** and **3′d**.

1,2,4-Tris(3-benzyloxyproyl)benzene **4d**



Colourless liquid. R_f 0.2 (EtOAc/Petroleum ether 10%, UV-active, PMA). IR (neat): ν 2927 (m), 2854 (m), 1495 (w), 1452 (m), 1352 (m), 1204 (w), 1099 (s), 1075 (m), 1027 (m), 734 (s) cm^{-1}.[32] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.84−1.95 (6 H, m, H4, H14, H24), 2.64 (2 H, br t, *J* 7.5, H3), 2.68 (4 H, br t, *J* 8.0, H13, H23), 3.46−3.52 (6 H, m, H5, H15, H25), 4.50 (6 H, br s, H6, H16, H26), 6.94 (1 H, dd, *J* 7.5, 2.0, H1), 6.96 (1 H, d, *J* 2.0, H21), 7.04 (1 H, d, *J* 7.5, H11), 7.24−7.37 (15 H, m, H8−H10, H18−H20, H28−H30). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 28.6, 29.0 (C13, C23), 31.07, 31.14 (C14, C24), 31.4 (C4), 31.9 (C3), 69.6 (C5), 69.80, 69.81 (C15, C25), 72.8, 72.9, 72.9 (C6, C16, C26), 126.0 (C1), 127.5, 127.5, 127.5 (C10, C20, C30), 127.6, 127.6, 127.6 (C8, C18, C28), 128.3, 128.3, 128.3 (C9, C19, C29), 129.2 (C11), 129.4 (C21), 137.1 (C2), 138.6, 138.6, 138.6 (C7, C17, C27), 139.5, 139.7 (C12, C22).

HRMS (ESI): *m/z* 523.3223 ([MH]$^+$ $C_{36}H_{43}O_3^+$ requires 523.3207), 545.3043 ([MNa]$^+$ $C_{36}H_{42}NaO_3^+$ requires 545.3026), 561.2784 ([MK]$^+$ $C_{36}H_{42}KO_3^+$ requires 561.2766).[32]

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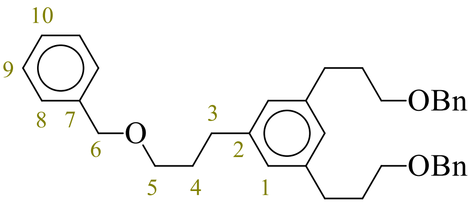
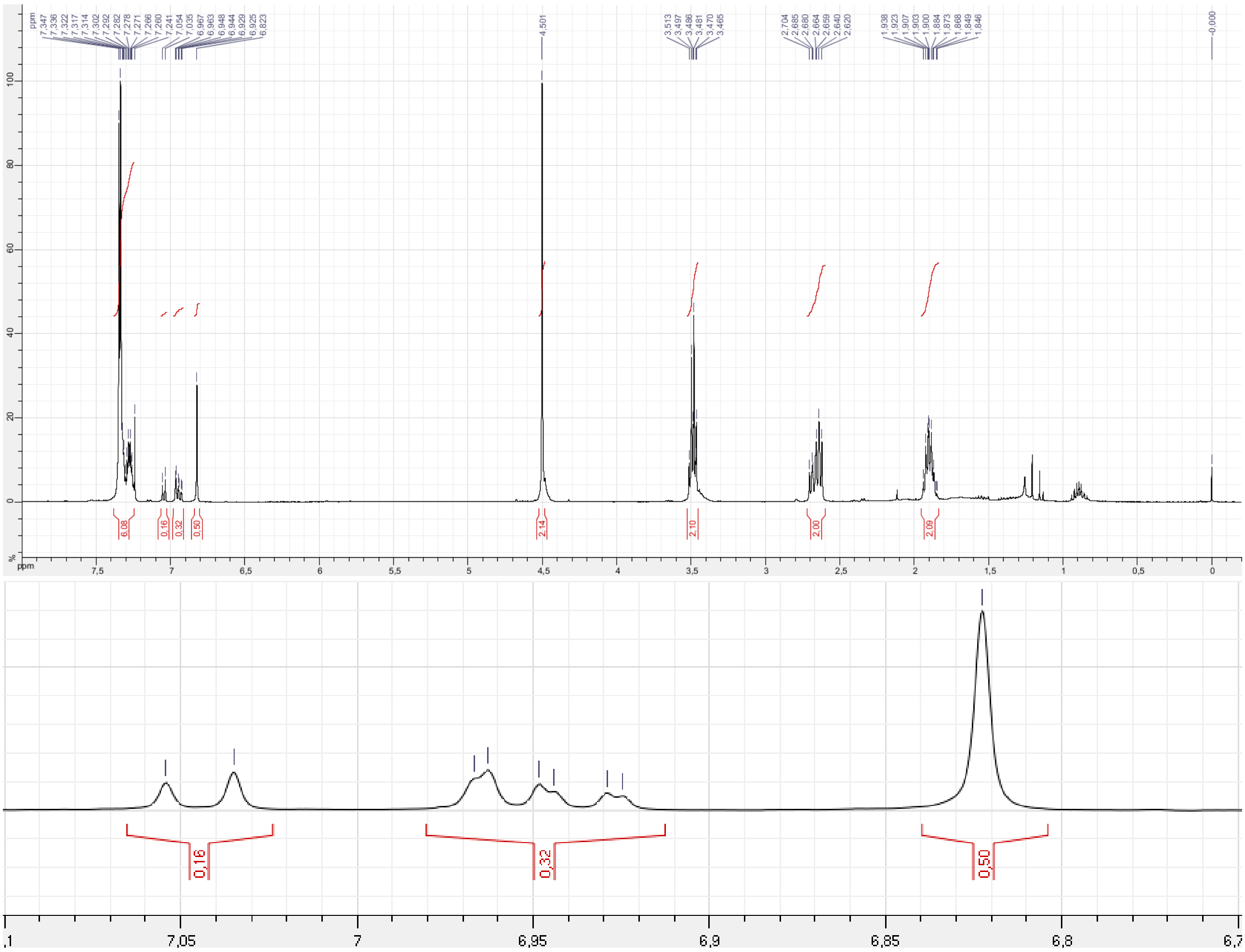
[32] − Analysis performed on a 49 : 51 mixture of **4d** and **4′d**.

1,3,5-Tris(3-benzyloxyproyl)benzene **4′d**

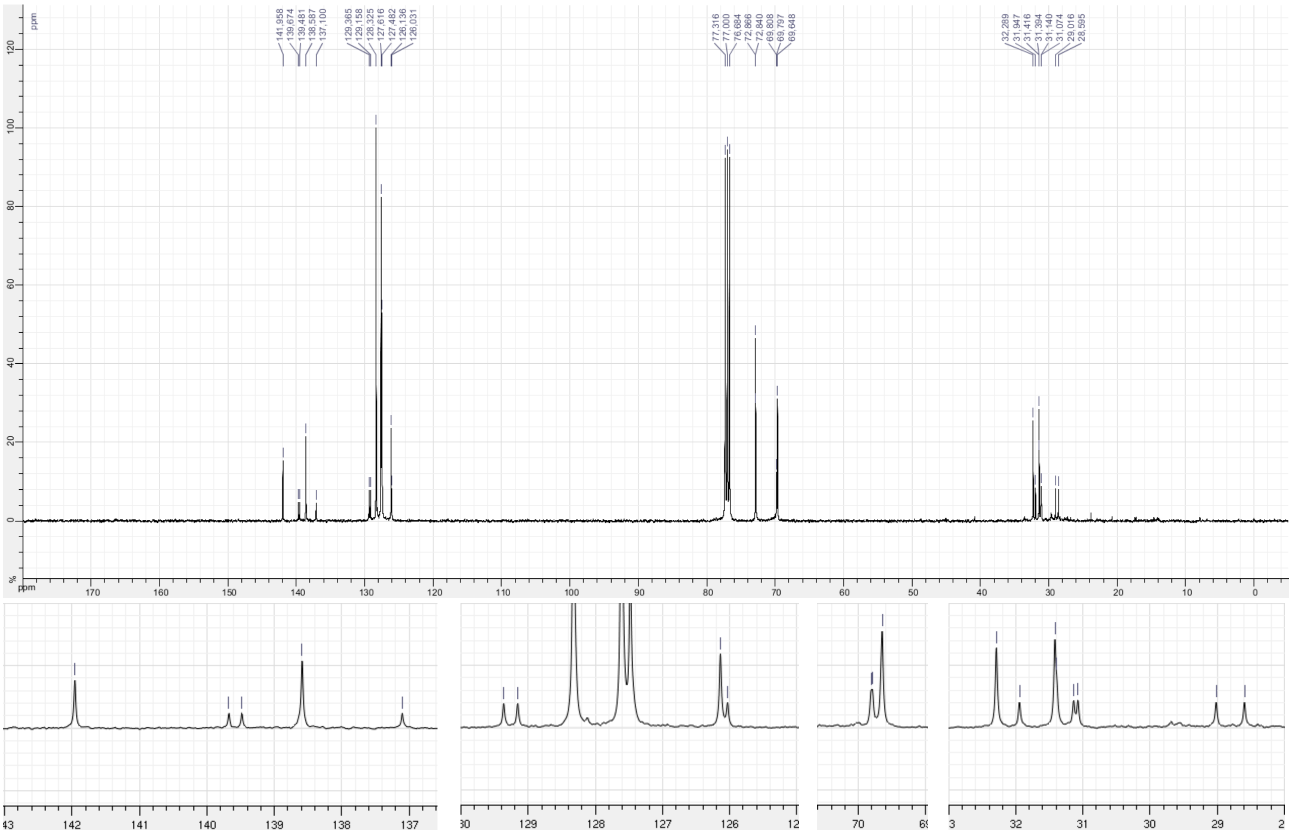


Colourless liquid. R_f 0.2 (EtOAc/Petroleum ether 10%, UV-active, PMA). IR: see 1,2,4-tris(3-benzyloxyproyl)benzene **4d**. ^{1}H NMR (CDCl$_3$, 400 MHz): *δ* 1.84−1.95 (6 H, m, H4), 2.64 (6 H, br t, *J* 7.5, H3), 3.48 (6 H, t, *J* 6.5, H5), 4.50 (6 H, s, H6), 6.82 (3 H, s, H1), 7.24−7.37 (15 H, m, H8−H10). ^{13}C NMR (CDCl$_3$, 100.6 MHz): *δ* 31.4 (C4), 32.3 (C3), 69.6 (C5), 72.9 (C6), 126.1 (C1), 127.5 (C10), 127.6 (C8), 128.3 (C9), 138.6 (C7), 142.0 (C2). HRMS: see 1,2,4-tris(3-benzyloxyproyl)benzene **4d**.



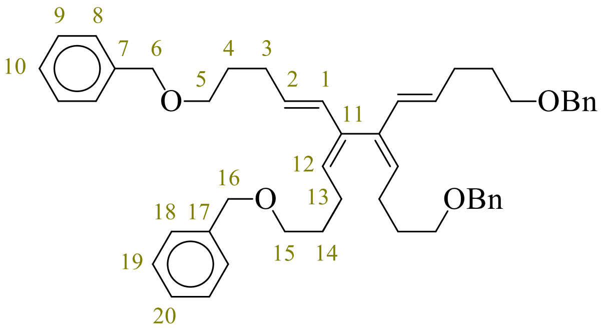
^{1}H NMR spectrum (CDCl$_3$, 400 MHz).

Note: this analysis was performed on a 49 : 51 mixture of **4d** and **4′d**.

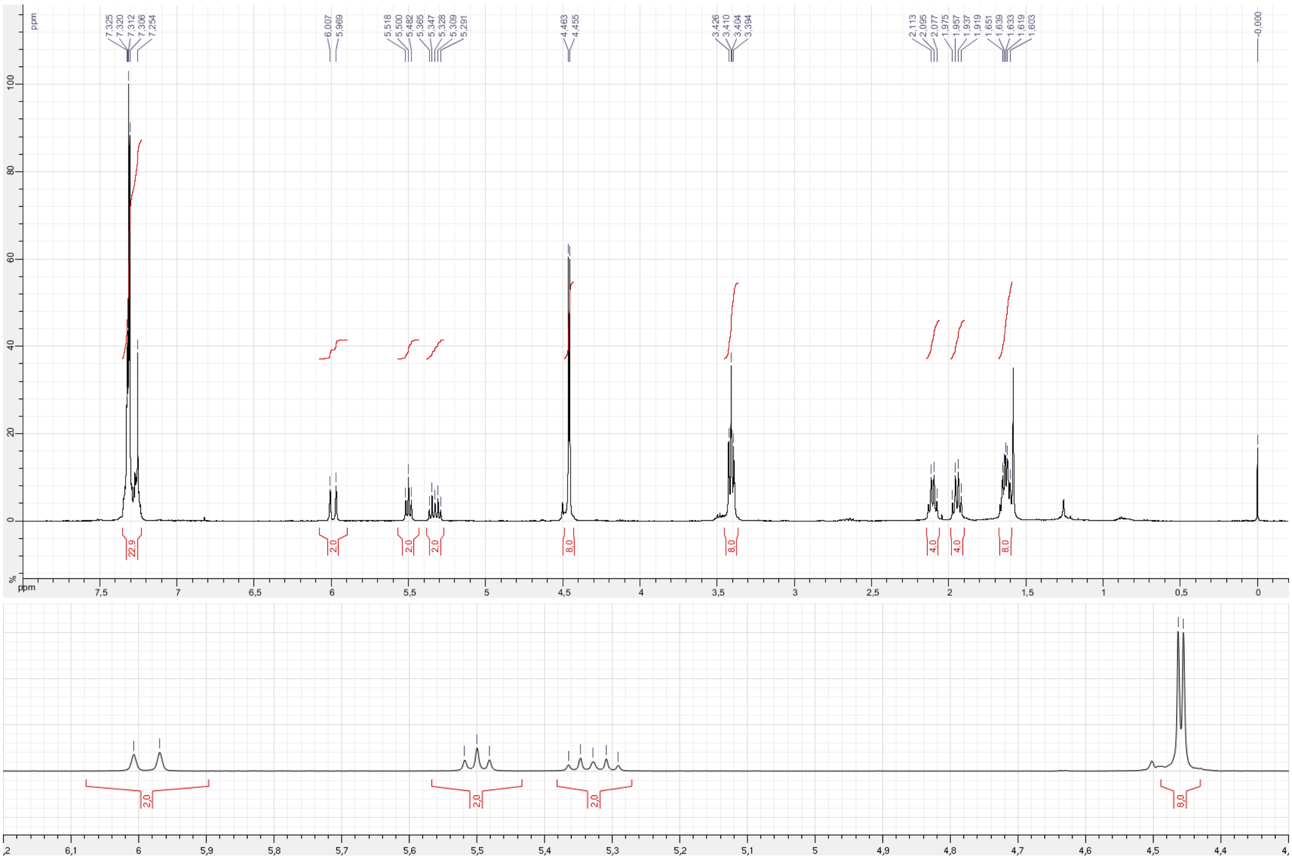


^{13}C NMR spectrum (CDCl$_3$, 100.6 MHz).
Note: this analysis was performed on a 49 : 51 mixture of **4d** and **4′d**.

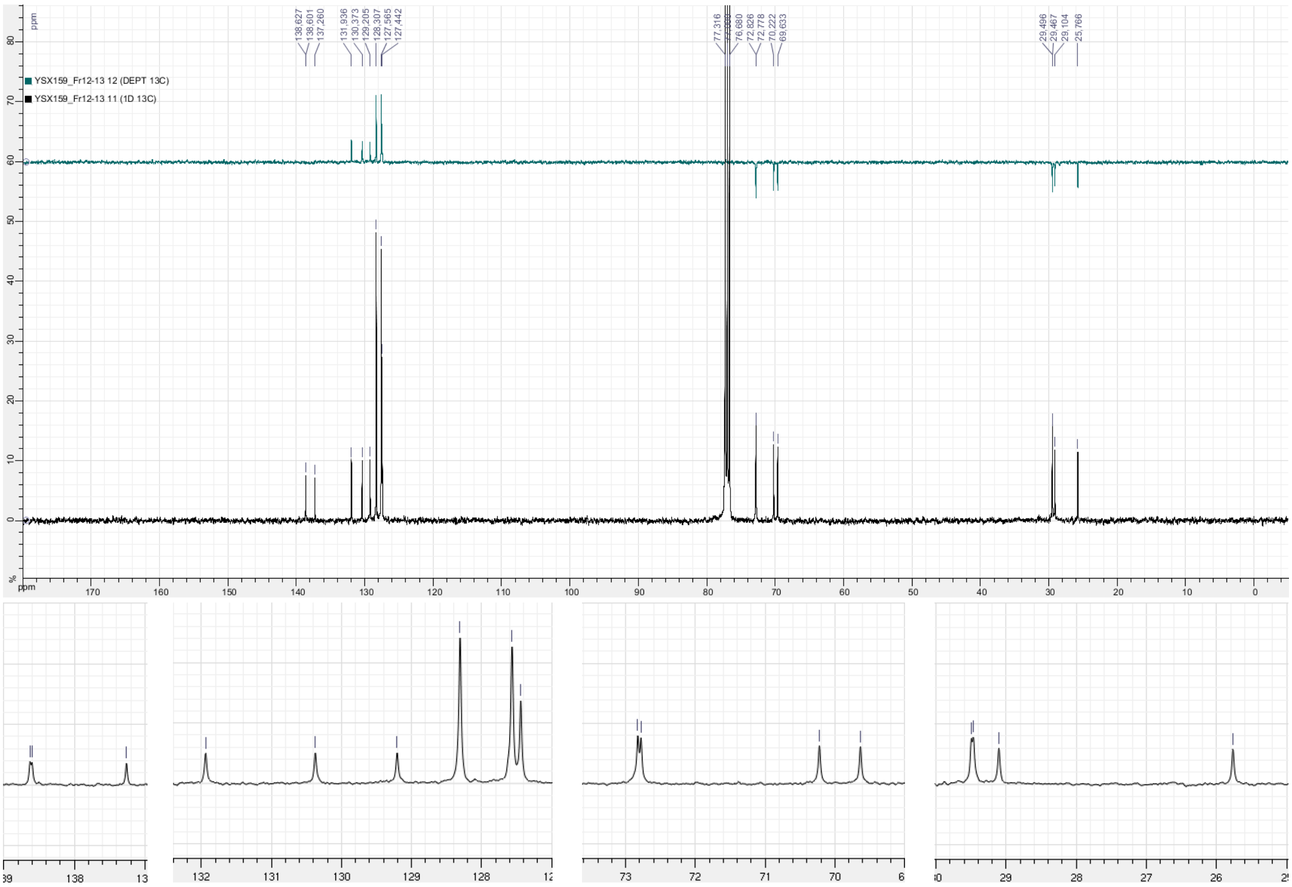
[(4*E*,6*Z*,7*Z*,8*E*)-12-Benzyloxy-6-(4-benzyloxybutylidene)-7-(4-benzyloxy-3-methyl-butylidene)dodeca-4,8-dienoxy]methylbenzene **5d**



Viscous colourless oil. R_f 0.2 [EtOAc/Petroleum ether 10%, UV-active, anisaldehyde (dark blue colour)]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.58−1.68 (8 H, m, H4, H14), 1.95 (4 H, q, J 7.5, H13), 2.10 (4 H, tdd, J 7.5, 7.0, 1.5, H3), 3.40 (4 H, t, J 6.5, H5 or H15), 3.41 (4 H, t, J 6.5, H5 or H15), 4.45 (4 H, s, H6 or H16), 4.46 (4 H, s, H6 or H16), 5.33 (2 H, dt, J 15.5, 7.0, H2), 5.50 (2 H, dd, J 8.0, 6.5, H12), 5.99 (2 H, dt, J 15.5, 1.5, H1), 7.23−7.36 (20 H, m, H8−H10, H18−H20). ^{13}C NMR (CDCl$_3$, 100.6 Hz): δ 25.8 (C13), 29.1 (C3), 29.467, 29.496 (C4, C14), 69.6, 70.2 (C5, C15), 72.778, 72.826 (C6, C16), 127.4, 127.4 (C10, C20), 127.6, 127.6 (C8, C18), 128.3, 128.3 (C9, C19), 129.2 (C2), 130.4 (C12), 131.9 (C1), 137.3 (C11), 138.601, 138.627 (C7, C17). HRMS: no signal (the molecule may not be volatile enough).



^{1}H NMR spectrum ($CDCl_3$, 400 MHz).



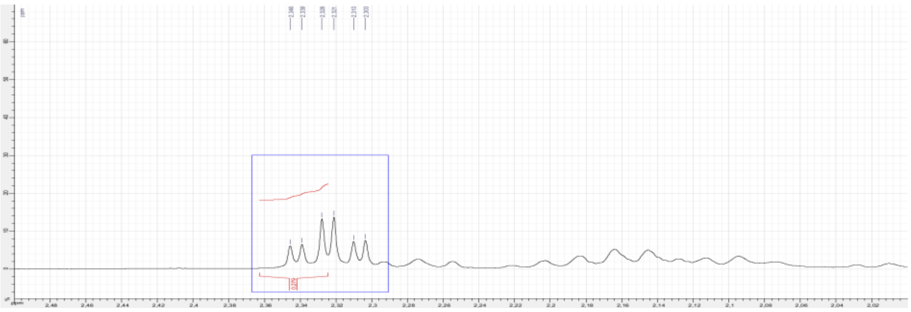
^{13}C NMR and DEPT135 spectra ($CDCl_3$, 100.6 MHz).

VII.2. Analysis of the crude products by ^{1}H NMR spectroscopy

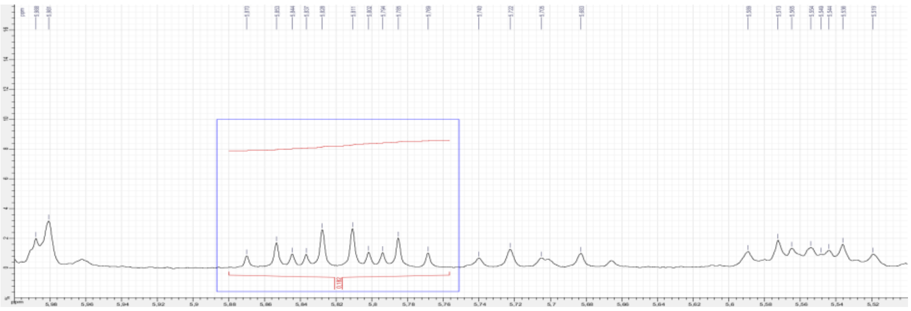
■ In the ^{1}H NMR spectrum of the crude products, the integral of the signals in the interval 4.36−4.60 ppm was set to 2.00: the benzyl CH_2 protons were used as an internal standard. Alternatively, (*E*)-cinnamic acid (250 µmol, 37.05 mg) was added to the crude products and the doublet at 6.46 ppm was used as an internal standard (the integral was set to 0.125).

■ The following signals were used for the qualitative assessment of the product yields:

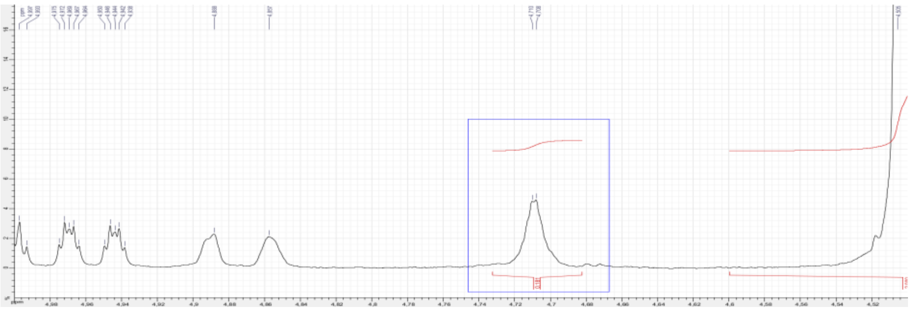
- Triplet of doublets (*J* 7.0 and 2.5 Hz) at 2.32 ppm: two protons of **1d**. The integral of the left half of this signal gave an estimation of the proportion of unconverted **1d**;



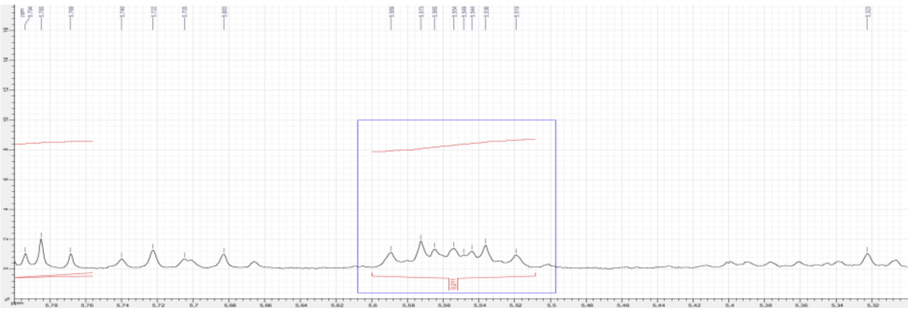
- Doublet of doublet of triplets (*J* 17.0, 10.0 and 6.5 Hz) at 5.82 ppm: one proton of **2d**.
  The integral of this signal gave an estimation of the yield of **2d**;



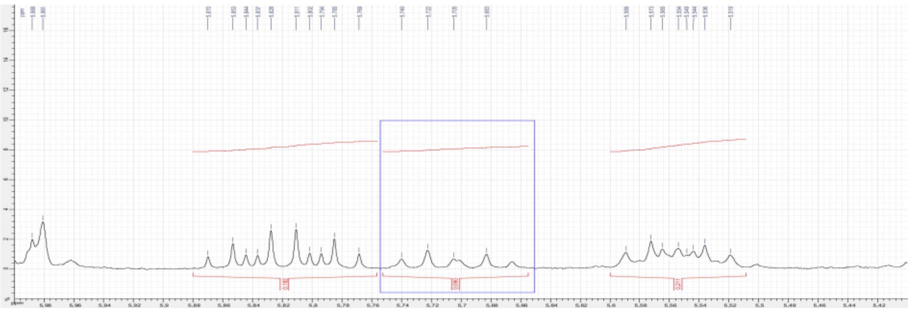
- Broad singlet at 4.71 ppm: two protons of **2′d**.
  Dividing the integral of this signal by two gave an estimation of the yield of **2′d**;



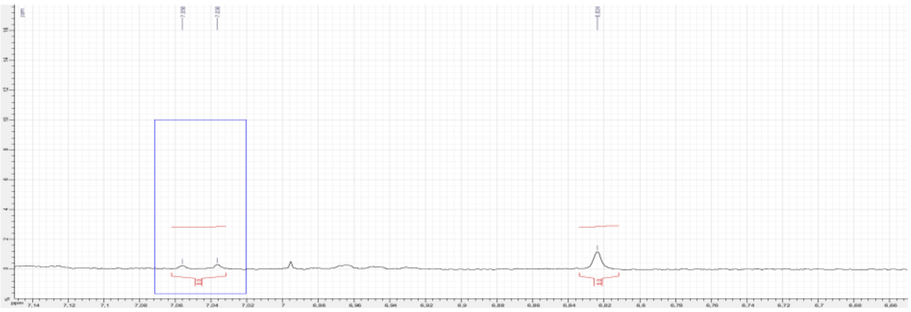
- Multiplet at 5.55 ppm: two protons of **3d**.
  The integral of this signal gave an estimation of the yield of **3d**;



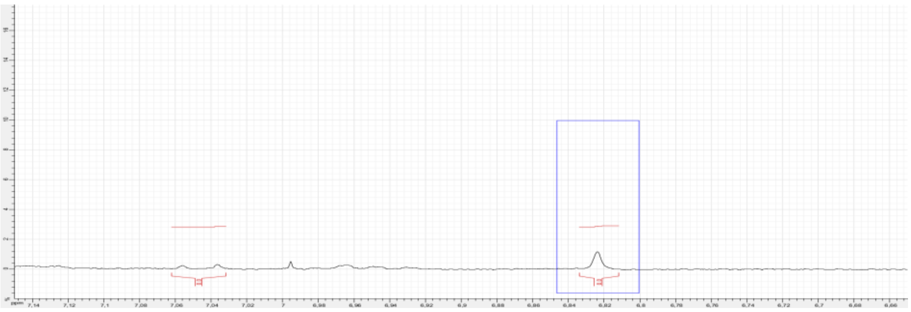
- Doublet of triplets (*J* 16.0 and 7.0 Hz) at 5.70 ppm: one proton of **3′d**. The integral of this signal was measured, then multiplied by two to give an estimation of the yield of **3′d**;



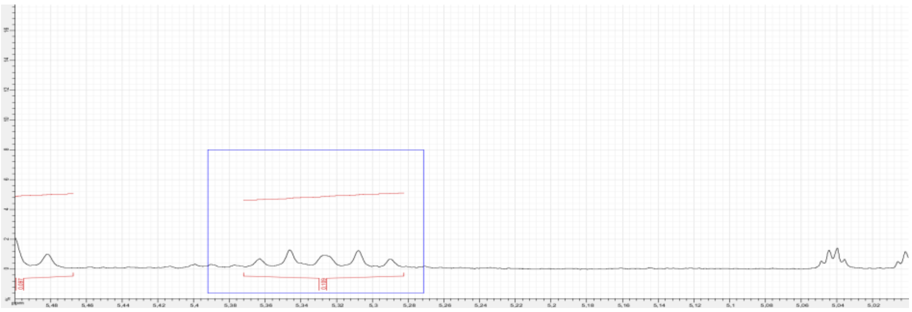
- Doublet (*J* 7.5 Hz) at 7.05 ppm: one proton of **4d**.
  The integral of this signal was multiplied by 3 to give an estimation of the yield of **4d**;



- Singlet at 6.82 ppm: three protons of **4′d**.
  The integral of this signal gave an estimation of the yield of **4′d**.

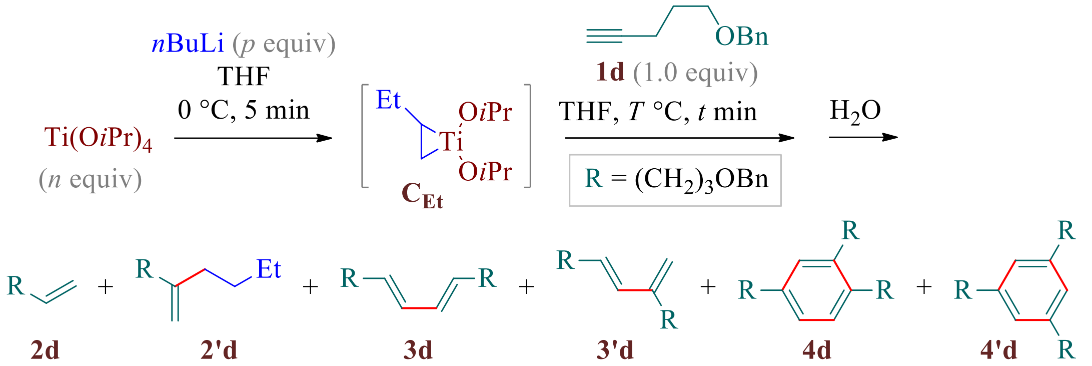


- Doublet of triplets (*J* 15.5 and 7.0 Hz) at 5.33 ppm: two protons of **5d**.
  The integral of this signal was multiplied by two to give an estimation of the yield of **5d**.



VII.3. Summary of the experimental results obtained using **1d**

■ With *n*BuLi, in THF.



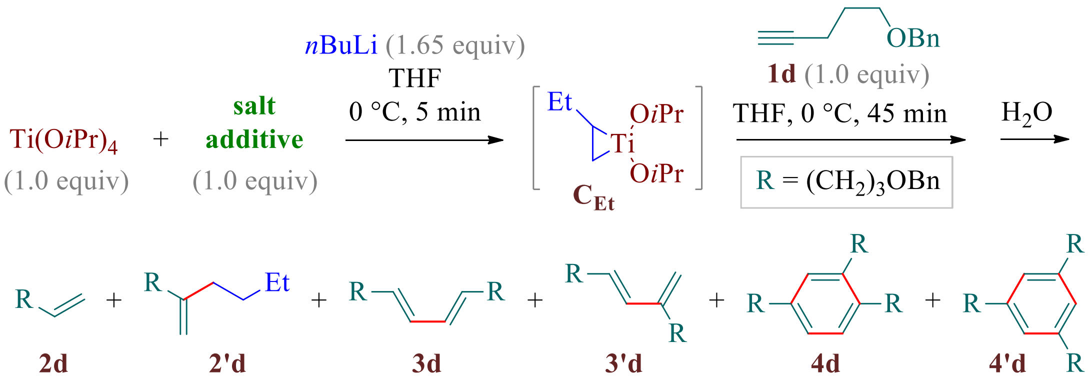
Subsection	*n*	*p*	*T*	*t*	S.m. **1d**	Alkene **2d**	Alkene **2′d**	Dienes **3d/3′d** (ratio)	Trimers **4d/4′d** (ratio)
VII.4.1.[a]	4.4	6.6	0	20	2%	24%	12%	33% (49 : 51)	4% (75 : 25)
VII.4.2.[a]				**120**	1%	8%	11%	21% (69 : 31)	6% (67 : 33)
VII.4.3.[a]	2.2	3.3	0	30	3%	14%	9%	42% (52 : 48)	12% (67 : 33)
VII.4.4.			**−40**		57%	11%	5%	20% (40 : 60)	0%
VII.4.5.			**−78**		75%	11%	5%	2% (50 : 50)	0%
VII.4.7.	1.1	1.65	0	20	28%	2%	6%	33% (48 : 52)	13% (69 : 31)
VII.4.7.				30	14%	3%	7%	39% (49 : 51)	18% (67 : 33)
VII.4.7.				45	3%	4%	7%	42% (50 : 50)	20% (70 : 30)

Colours for the starting material: ■ 0−10% ■ 11−20% ■ 21−30% ■ 31−40% ■ ≥41%

Colours for the products: ■ 0−10% ■ 11−20% ■ 21−30% ■ 31−40% ■ ≥41%

[a] Mean values are given for the yields, calculated from the similar results of two runs carried out under the same conditions.

■ With *n*BuLi, in THF, with salt additives.[a]



Subsection	Salt additive	S.m. **1d**	Alkene **2d**	Alkene **2′d**	Dienes **3d/3′d** (ratio)	Trimers **4d/4′d** (ratio)
VII.4.8.	None	3%	4%	7%	24% (58 : 42)	26% (64 : 36)
VII.4.9.	NaCl	6%	4%	8%	22% (61 : 39)	24% (62 : 38)
VII.4.10.	LiCl	3%	4%	8%	16% (65 : 35)	20% (62 : 38)
VII.4.11.[b]	LiBr	3%	4%	8%	19% (58 : 42)	20% (58 : 42)
VII.4.12.	LiOMe	4%	4%	7%	27% (56 : 44)	22% (63 : 37)
VII.4.13.	LiOH	2%	4%	8%	24% (63 : 37)	20% (67 : 33)
VII.4.14.	Li_2SO_4	3%	4%	6%	24% (61 : 39)	17% (65 : 35)
VII.4.15.	Li_2SO_4[c]	2%	5%	7%	25% (64 : 36)	24% (66 : 34)

Colours for the starting material: ■ 0–10% ■ 11–20% ■ 21–30% ■ 31–40% ■ ≥41%

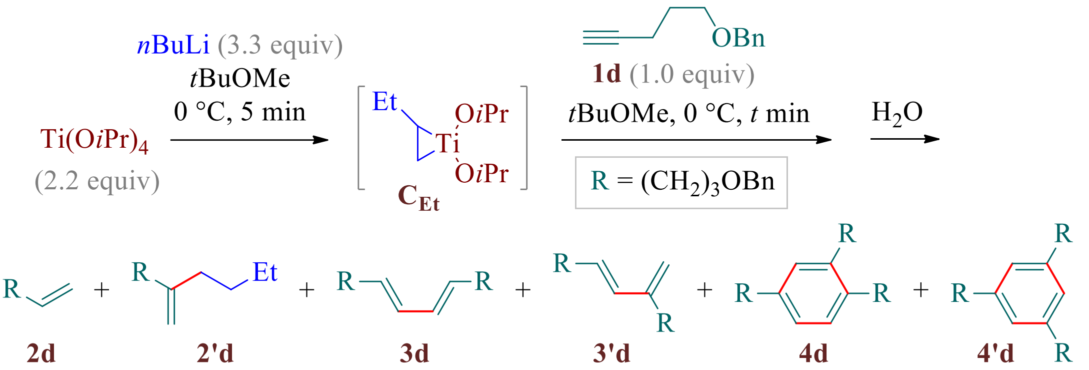
Colours for the products: ■ 0–10% ■ 11–20% ■ 21–30% ■ 31–40% ■ ≥41%

[a] Yields estimated using (*E*)-cinnamic acid as an internal standard, unless otherwise stated.

[b] Yields estimated using the benzyl CH_2 protons as an internal standard.

[c] 0.50 equiv of Li_2SO_4.

■ With *n*BuLi, in *t*BuOMe.

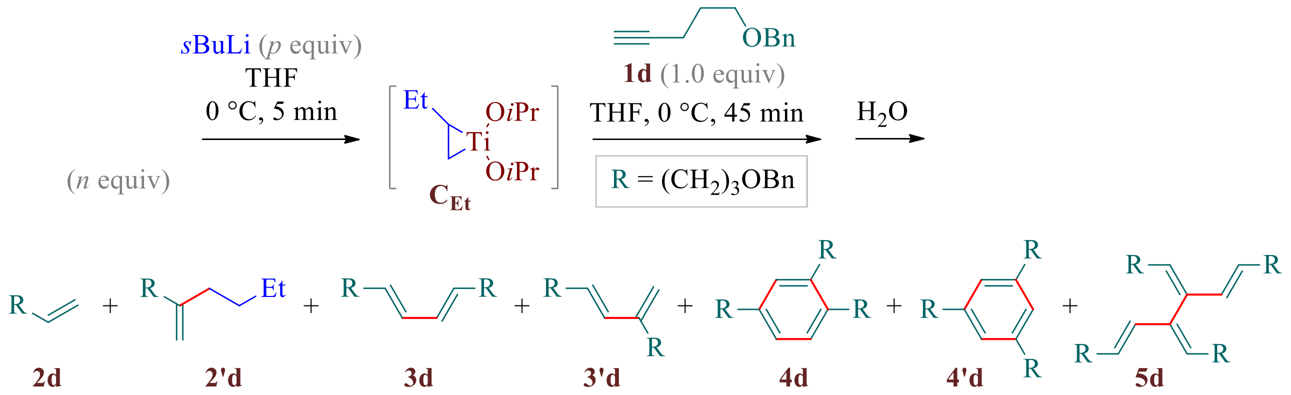


Subsection	*t*	s.m. **1d**	Alkene **2d**	Alkene **2′d**	Dienes **3d/3′d** (ratio)	Trimers **4d/4′d** (ratio)
VII.4.6.	20	0%	20%	9%	Traces	16% (50 : 50)
VII.4.6.	30	0%	20%	9%	Traces	16% (50 : 50)
VII.4.6.	45	0%	18%	8%	Traces	16% (50 : 50)

Colours for the starting material: □ 0–10% □ 11–20% □ 21–30% ■ 31–40% ■ ≥41%

Colours for the products: □ 0–10% □ 11–20% □ 21–30% ■ 31–40% ■ ≥41%

■ With *s*BuLi, in THF.[a]



Subsection	*n*	*p*	s.m. **1d**	Alkene **2d**	Alkene **2′d**	Dienes **3d/3′d** (ratio)	Trimers **4d/4′d** (ratio)	Tetramer **5d**
VII.4.16.[b,c]	2.2	3.3	1%	18%	9%	39% (54 : 46)	5% (60 : 40)	0%
VII.4.17.[b,c]	1.1	1.65	28%	7%	4%	28% (43 : 57)	3% (67 : 33)	21%
VII.4.18.[d,e]			16%	4%	3%	30% (41 : 59)	5% (61 : 39)	6%
VII.4.19.[d,f]			15%	7%	5%	30% (49 : 51)	4% (59 : 41)	8%
VII.4.20.[d,f]	1.2	1.65	20%	10%	4%	25% (48 : 52)	4% (64 : 36)	12%
VII.4.21.[d,g]	1.0	1.65	11%	11%	6%	28% (49 : 51)	5% (60 : 40)	12%
VII.4.22.[d,f]	1.0	1.65	2%	9%	7%	30% (50 : 50)	7% (62 : 38)	11%
VII.4.23.[d,f]	0.90	1.65	2%	7%	7%	21% (54 : 46)	8% (64 : 36)	6%
VII.4.24.[d,f]	1.0	1.8	2%	10%	7%	28% (54 : 46)	7% (60 : 40)	10%
VII.4.25.[d,f]	1.0	1.50	24%	8%	4%	24% (47 : 53)	4% (67 : 33)	11%

Colours for the starting material: 🟥 0−10% 🟥 11−20% 🟥 21−30% 🟥 31−40% 🟥 ≥41%

Colours for the products: 🟩 0−10% 🟩 11−20% 🟩 21−30% 🟩 31−40% 🟩 ≥41%

[a] Yields estimated using (*E*)-cinnamic acid as an internal standard, unless otherwise stated.

[b] Yields estimated using the benzyl CH_2 protons as an internal standard.

[c] Bottle #1 was used.

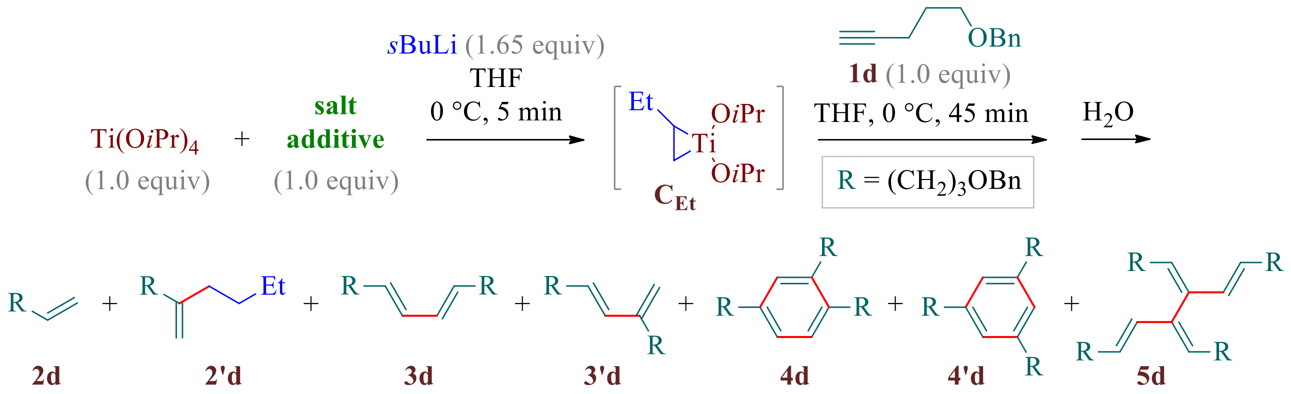
[d] Bottle #2 was used.

[e] Slow addition of the substrate **1d** (8 minutes).

[f] Fast addition of the substrate **1d** (30 s).

[g] The reaction was stopped after 25 minutes.

■ With *s*BuLi, in THF, with salt additives.[a,b]



Subsection	Salt additive	S.m. **1d**	Alkene **2d**	Alkene **2′d**	Dienes **3d/3′d** (ratio)	Trimers **4d/4′d** (ratio)	Tetramer **5d**
VII.4.22.	None	2%	9%	7%	30% (50 : 50)	7% (62 : 38)	11%
VII.4.26.	NaCl	3%	11%	8%	32% (57 : 43)	12% (54 : 46)	7%
VII.4.27.	LiCl	3%	3%	4%	25% (58 : 42)	26% (58 : 42)	3%
VII.4.28.[c]	LiBr	10%	3%	4%	24% (52 : 48)	19% (59 : 41)	3%
VII.4.29.	LiBr[d]	2%	3%	6%	18% (65 : 35)	26% (54 : 46)	1%
VII.4.30.	LiOMe	4%	10%	7%	30% (56 : 44)	12% (58 : 42)	4%
VII.4.31.	LiOH	4%	8%	7%	34% (33 : 47)	10% (62 : 38)	8%
VII.4.32.	Li$_2$SO$_4$[e]	2%	9%	7%	31% (57 : 43)	10% (58 : 42)	5%

Colours for the starting material: 🟥 0−10% 🟥 11−20% 🟥 21−30% 🟥 31−40% 🟥 ≥41%

Colours for the products: 🟩 0−10% 🟩 11−20% 🟩 21−30% 🟩 31−40% 🟩 ≥41%

[a] Yields estimated using (*E*)-cinnamic acid as an internal standard, unless otherwise stated.

[b] Bottle #2 was used.

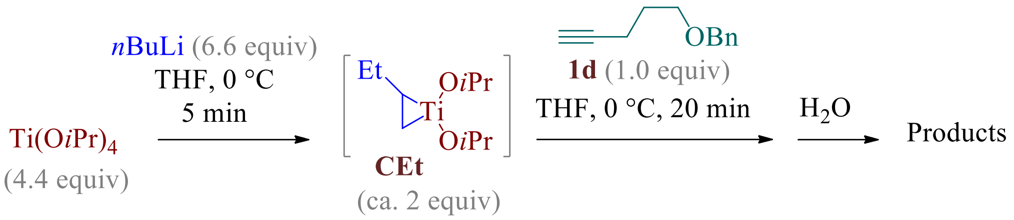
[c] Yields estimated using the benzyl CH$_2$ protons as an internal standard.

[d] 2.0 equiv of LiBr.

[e] 0.50 equiv of Li$_2$SO$_4$.

VII.4. Experimental detail

■ **VII.4.1.** With 4.4 equiv of Ti(O*i*Pr)$_4$, 6.6 equiv of *n*BuLi; reaction conducted at 0 °C for 20 min.



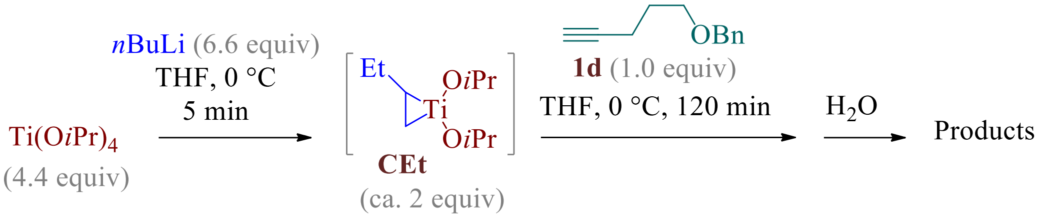
	S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Total
Run 1	2%	26%	13% (13%)	15% (10%)	15% (8%)	3%	1%	75%
Run 2	2%	22%	12% (6%)	18% (13%)	19% (13%)	3%	1%	77%

In parentheses: yields of isolated products.

- Run 1: General procedure **GP3** was applied with $n = 4.40$, $p = 6.60$, $V_1 = 3.5$, $V_2 = 0.5$ and $t = 20$. *n*-Butyllithium solution (2.38 M in hexanes, 6.60 mmol, 2.77 mL) was added over 2 minutes. The THF solution of 5-benzyloxypent-1-yne **1d** (1.00 mmol, 174 mg) was added over 3 minutes. Crude product: pale yellow oil (128 mg). Analysis as described in subsection VII.2. (benzyl CH_2 protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above. Flash column chromatography (silica gel, CH_2Cl_2/petroleum ether, gradient from 10% to 100%) afforded relatively pure 4-methyleneoctoxymethylbenzene **2′d** (29.6 mg, 127 µmol, 13%) and a 53 : 47 mixture of pure [(*E*,*E*)-10-benzyloxydeca-4,6-dienoxy]methylbenzene **3d** and [(*E*)-9-benzyloxy-4-methylene-non-5-enoxy]methylbenzene **3′d** (32.2 mg, 91.9 µmol, 18%).

- Run 2: General procedure **GP3** was applied with $n = 4.40$, $p = 6.60$, $V_1 = 3.5$, $V_2 = 0.5$ and $t = 20$. *n*-Butyllithium solution (2.38 M in hexanes, 6.60 mmol, 2.77 mL) was added over 4 minutes. The THF solution of 5-benzyloxypent-1-yne **1d** (1.00 mmol, 174 mg) was added over 3 minutes. Crude product: pale yellow oil (136 mg). Analysis as described in subsection VII.2. (benzyl CH_2 protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above. Flash column chromatography (silica gel, CH_2Cl_2/petroleum ether, gradient from 10% to 100%) afforded relatively pure 4-methyleneoctoxymethylbenzene **2′d** (29.6 mg, 58.1 µmol, 6%) and a 51 : 49 mixture of pure [(*E*,*E*)-10-benzyloxydeca-4,6-dienoxy]methylbenzene **3d** and [(*E*)-9-benzyloxy-4-methylene-non-5-enoxy]methylbenzene **3′d** (45.6 mg, 130 µmol, 26%).

■ **VII.4.2.** With 4.4 equiv of Ti(O*i*Pr)$_4$, 6.6 equiv of *n*BuLi; reaction conducted at 0 °C for 120 min.

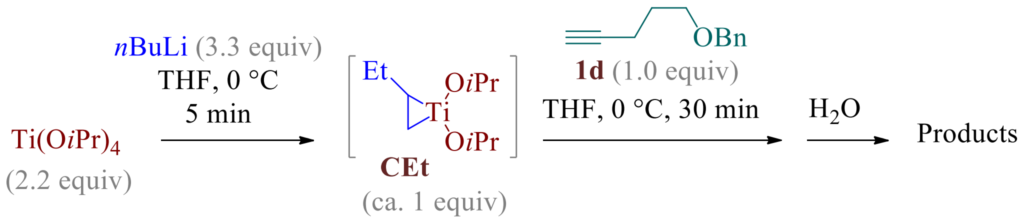


	S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Total
Run 1	Traces	7%	12%	10%	3%	4%	2%	38%
Run 2	1%	10%	11%	19%	10%	5%	2%	58%

- Run 1: General procedure **GP3** was applied with n = 4.40, p = 6.60, V_1 = 3.5, V_2= 0.5 and t = 120. *n*-Butyllithium solution (2.38 M in hexanes, 6.60 mmol, 2.77 mL) was added over 2 minutes. The THF solution of 5-benzyloxypent-1-yne **1d** (1.00 mmol, 174 mg) was added over 2 minutes. Crude product: colourless oil (143 mg). Analysis as described in subsection VII.2. (benzyl CH$_2$ protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

- Run 2: General procedure **GP3** was applied with n = 4.40, p = 6.60, V_1 = 3.5, V_2= 0.5 and t = 120. *n*-Butyllithium solution (2.38 M in hexanes, 6.60 mmol, 2.77 mL) was added over 3 minutes. The THF solution of 5-benzyloxypent-1-yne **1d** (1.00 mmol, 174 mg) was added over 3 minutes. Crude product: colourless oil (131 mg). Analysis as described in subsection VII.2. (benzyl CH$_2$ protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

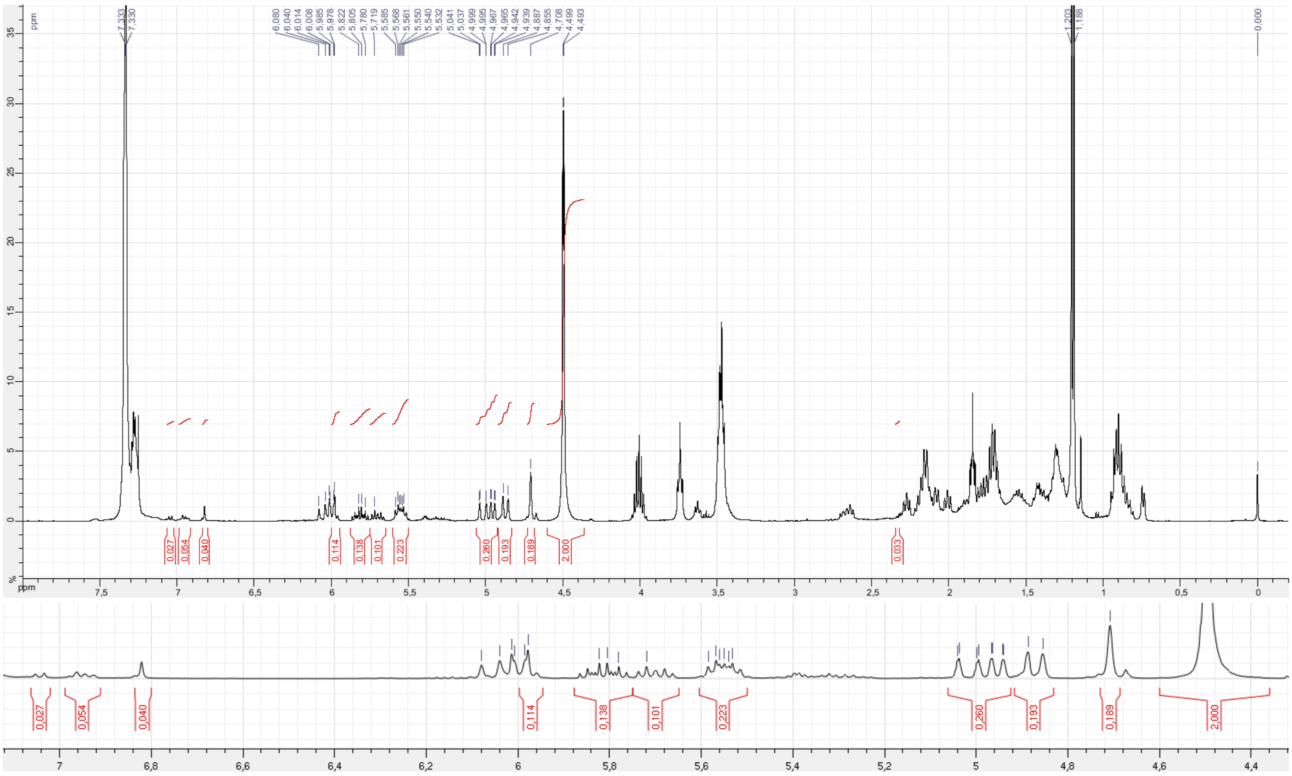
■ **VII.4.3.** With 2.2 equiv of Ti(O*i*Pr)$_4$, 3.3 equiv of *n*BuLi; reaction conducted at 0 °C for 30 min.



	S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Total
Run 1	3%	14%	9%	22%	20%	8%	4%	80%
Run 2	3%	14%	10%	22%	20%	8%	4%	81%

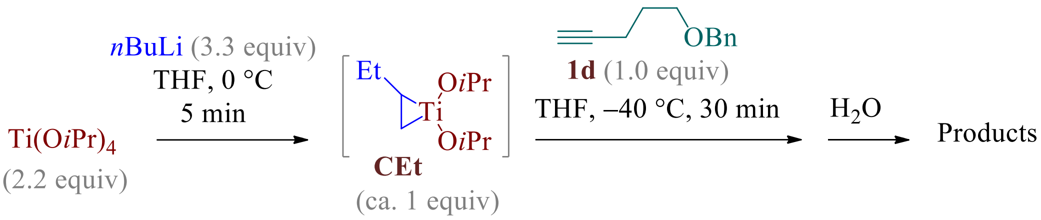
- Run 1: General procedure **GP3** was applied with n = 2.20, p = 3.30, V_1 = 3.5, V_2= 0.5 and t = 30. *n*-Butyllithium solution (2.20 M in hexanes, 3.30 mmol, 1.50 mL) was added over 3 minutes. The THF solution of 5-benzyloxypent-1-yne **1d** (1.00 mmol, 174 mg) was added over 3 minutes. Crude product: yellow oil (194 mg). Analysis as described in subsection VII.2. (benzyl CH_2 protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

- Run 2: this reaction was repeated with another bottle of *n*-butyllithium solution (2.38 M in hexanes), giving a nearly identical result.



^{1}H NMR spectrum of the crude product of run 1 ($CDCl_3$, 400 MHz).

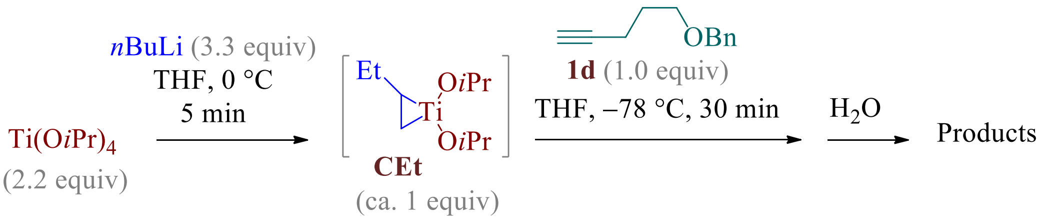
■ **VII.4.4.** With 2.2 equiv of Ti(O*i*Pr)₄, 3.3 equiv of *n*BuLi;
reaction conducted at −40 °C for 30 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Total
57%	11%	5%	8%	12%	0%	0%	93%

General procedure **GP4** was applied with $n = 2.20$, $p = 3.30$, $T = -40$ and $t = 30$.
n-Butyllithium solution (2.20 M in hexanes, 3.30 mmol, 1.50 mL) was added over 3 minutes. The THF solution of 5-benzyloxypent-1-yne **1d** (1.00 mmol, 174 mg) was added over 2 minutes. Crude product: oil (158 mg). Analysis as described in subsection VII.2. (benzyl CH_2 protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

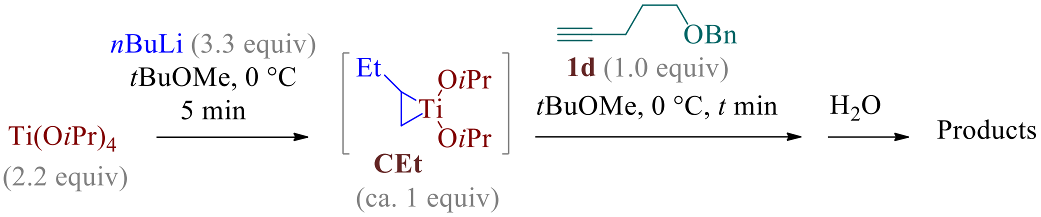
■ **VII.4.5.** With 2.2 equiv of Ti(O*i*Pr)₄, 3.3 equiv of *n*BuLi;
reaction conducted at −78 °C for 30 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Total
75%	11%	5%	1%	1%	0%	0%	93%

General procedure **GP4** was applied with $n = 2.20$, $p = 3.30$, $T = -78$ and $t = 30$.
n-Butyllithium solution (2.20 M in hexanes, 3.30 mmol, 1.50 mL) was added over 2 minutes. The THF solution of 5-benzyloxypent-1-yne **1d** (1.00 mmol, 174 mg) was added over 1 minute. Crude product: oil. Analysis as described in subsection VII.2. (benzyl CH_2 protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

■ VII.4.6. With 2.2 equiv of Ti(O*i*Pr)$_4$, 3.3 equiv of *n*BuLi; reaction conducted at 0 °C for 20, 30 or 45 min in *t*BuOMe.



	S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Total
t = 20	0%	20%	9%	Traces	Traces	8%	8%	45%
t = 30	0%	20%	9%	Traces	Traces	8%	8%	45%
t = 45	0%	18%	8%	Traces	Traces	8%	8%	42%
		(4%)	(7%)			(5%)	(6%)	

In parentheses: yields of isolated products.

n-Butyllithium solution (2.27 M in hexanes, 3.30 equiv, 3.30 mmol, 1.45 mL) was added dropwise, over 2 minutes, at 0 °C, to a solution of titanium(IV) isopropoxide (2.20 equiv, 2.20 mmol, 651 µL) in *t*BuOMe (5.0 mL). After 5 minutes of stirring at 0 °C, 5-benzyloxypent-1-yne **1d** (1.00 equiv, 1.00 mmol, 174 mg) was added dropwise, over 45 s.

After 20 minutes of stirring at 0 °C, part of the solution (1.0 mL) was taken and put into another flask under Ar, at 0 °C. H_2O (0.1 mL) was then added to this flask. After 15 minutes of stirring, the septum was removed to expose it to air and stirring was continued for 10 more minutes. The white mixture was then filtered through a pad of sand, celite, $MgSO_4$ and sand [from top to bottom; rinsing with Et_2O (6.0 mL)] and concentrated under reduced pressure (down to 50 mbar) to afford a dark yellow oil (28.1 mg).

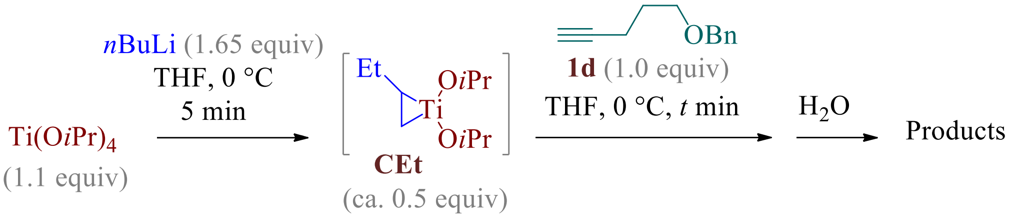
The same operation was repeated after 30 minutes of reaction at 0 °C, to afford a dark yellow oil (30.4 mg).

After 45 minutes of reaction at 0 °C, the remaining solution was treated with H_2O (0.3 mL). After 15 minutes of stirring, the septum was removed to expose the mixture to air and stirring was continued for 10 more minutes. The mixture was then filtered through a pad of sand, celite, $MgSO_4$ and sand [from top to bottom; rinsing with Et_2O (12 mL)] and concentrated under reduced pressure (down to 50 mbar) to afford a dark yellow oil (178 mg).

Analysis of the three crude products, done as described in subsection VII.2. (benzyl CH_2 protons as an internal standard), gave the qualitative estimation of the product yields shown in the table above.

Flash column chromatography (silica gel, EtOAc/petroleum ether, gradient from 2% to 50%) of the combined thoroughly concentrated crude products (163 mg) afforded a 65 : 35 mixture of 4-methyleneoctoxymethylbenzene **2’d** and 5-benzyloxypent-1-ene **2d**, somewhat contaminated with unidentified impurities (23.8 mg, 72.7 µmol, 7% and 39.2 µmol, 4% respectively) and a 49 : 51 mixture of pure **4d** and **4’d** (19.2 mg, 36.7 µmol, 11%).

■ **VII.4.7.** With 1.1 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *n*BuLi; reaction conducted at 0 °C for 20, 30 or 45 min.



	S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Total
t = 20	28%	2%	6%	16%	17%	9%	4%	82%
t = 30	14%	3%	7%	19%	20%	12%	6%	81%
t = 45	3%	4%	7%	21%	21%	14%	6%	76%

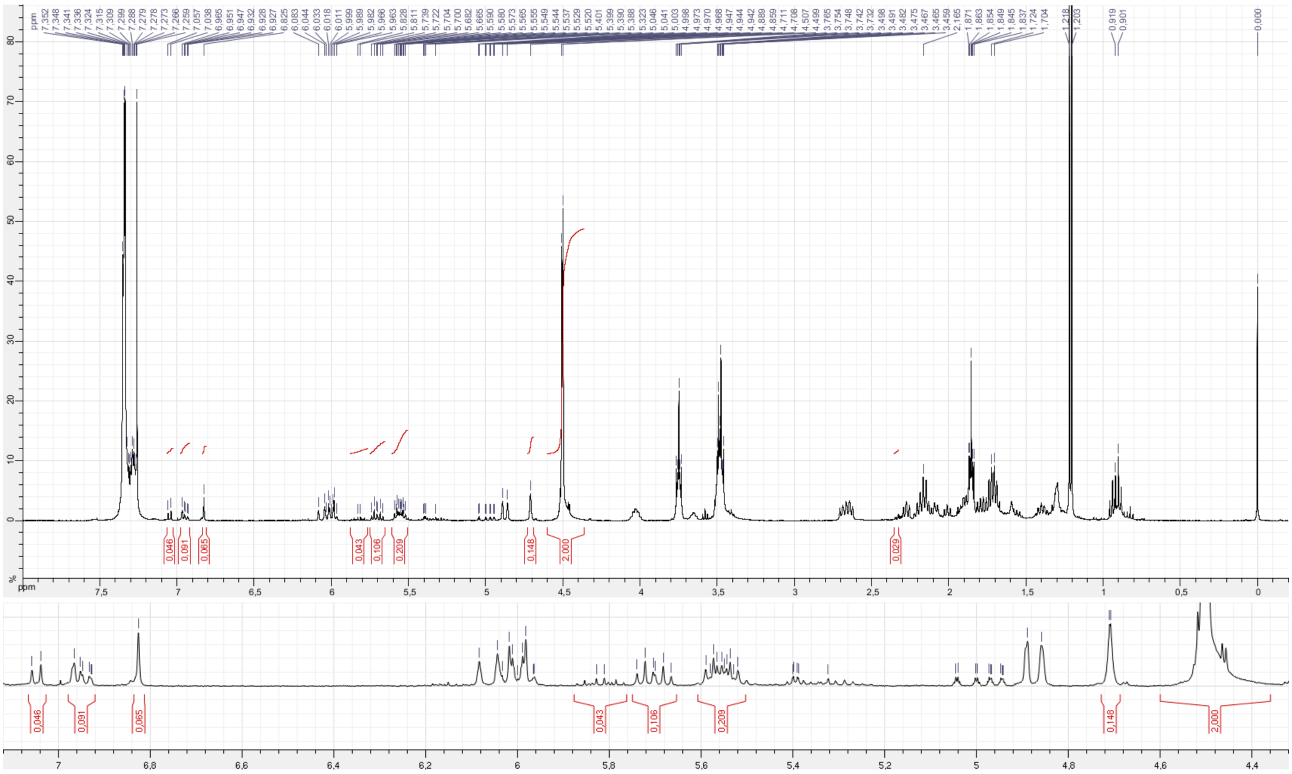
General procedure **GP2** was applied with *n* = 1.10 and *p* = 1.65. *n*-Butyllithium solution (2.27 M in hexanes, 3.30 mmol, 1.45 mL) was added over 1 min 15 s. 5-Benzyloxypent-1-yne **1d** (2.00 mmol, 348 mg) was added over 1 min 20 s.

Crude product after *t* = 20 minutes: yellow oil (33.4 mg).

Crude product after *t* = 30 minutes: yellow oil (62.1 mg).

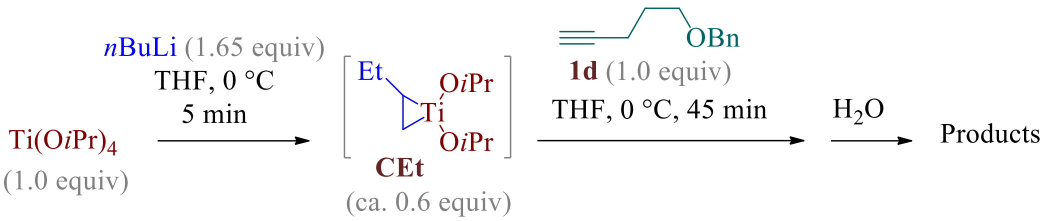
Crude product after *t* = 45 minutes: yellow oil (293 mg).

Analysis of the three crude products, done as described in subsection VII.2. (benzyl CH$_2$ protons as an internal standard), gave the qualitative estimation of the product yields shown in the table above.



^{1}H NMR spectrum of the crude product after 45 min of reaction (CDCl$_3$, 400 MHz).

■ **VII.4.8.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *n*BuLi; reaction conducted at 0 °C for 45 min.



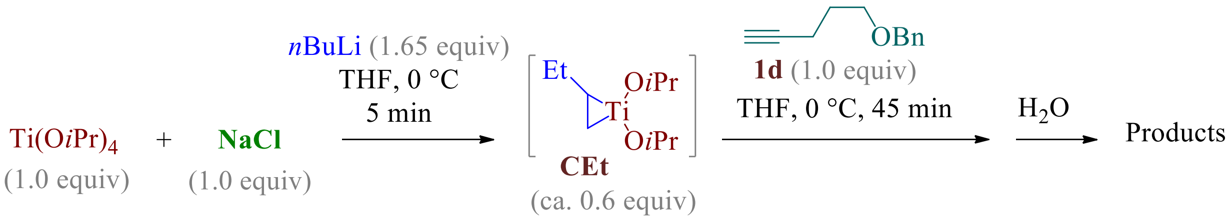
S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Total
3.8%	4.1%	8.2%	15.2%	11.0%	18.0%	10.0%	70%[a]
3.4%	3.7%	7.4%	13.9%	10.0%	16.5%	9.1%	64%[b]

[a] Yields estimated as depicted in VII.2. (benzyl CH$_2$ protons used as an internal standard).

[b] Yields estimated using (*E*)-cinnamic acid (250 µmol, 37.05 mg) as an internal standard.

General procedure **GP1** was applied with $n = 1.00$, $p = 1.65$, $T = 0$ and $t = 45$. *n*-Butyllithium solution (2.17 M in hexanes, 3.30 mmol, 1.52 mL) was added over 1.5 minutes. 5-Benzyloxypent-1-yne **1d** (2.00 mmol, 348 mg) was added over 30 s. Crude product: yellow oil (384 mg). Analysis as described in subsection VII.2. (benzyl CH$_2$ protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

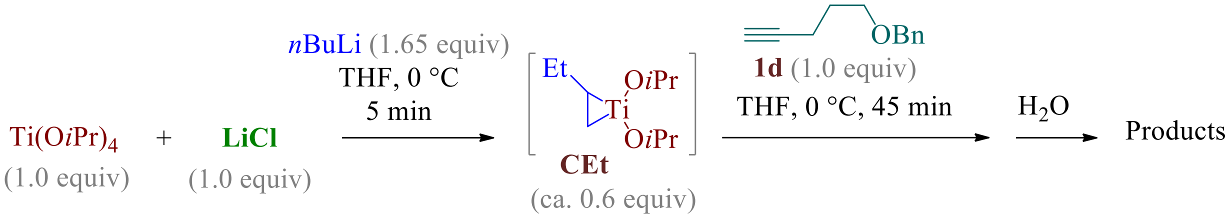
■ **VII.4.9.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *n*BuLi; with **NaCl** (1.0 equiv); reaction conducted at 0 °C for 45 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Total
6.0%	4.2%	7.9%	13.3%	8.4%	15.0%	9.3%	64%

General procedure **GP6** was applied with *n*-butyllithium solution (2.17 M in hexanes) and NaCl as the salt additive. Crude product: yellow oil (361 mg). Analysis as described in subsection VII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.

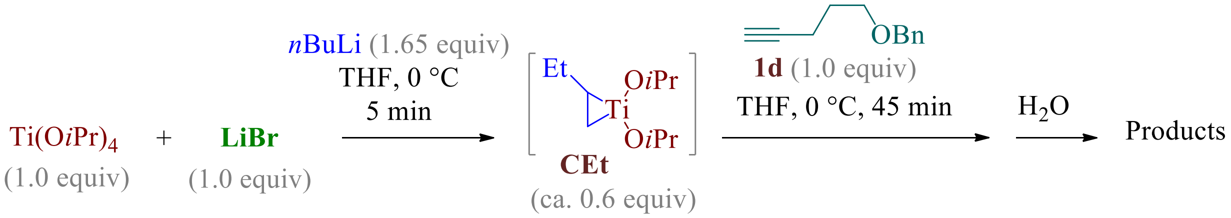
■ **VII.4.10.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *n*BuLi; with **LiCl** (1.0 equiv); reaction conducted at 0 °C for 45 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Total
2.8%	4.1%	8.4%	10.2%	5.6%	12.6%	7.6%	51%

General procedure **GP6** was applied with *n*-butyllithium solution (2.24 M in hexanes) and LiCl as the salt additive. Crude product: yellow oil (327 mg). Analysis as described in subsection VII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.

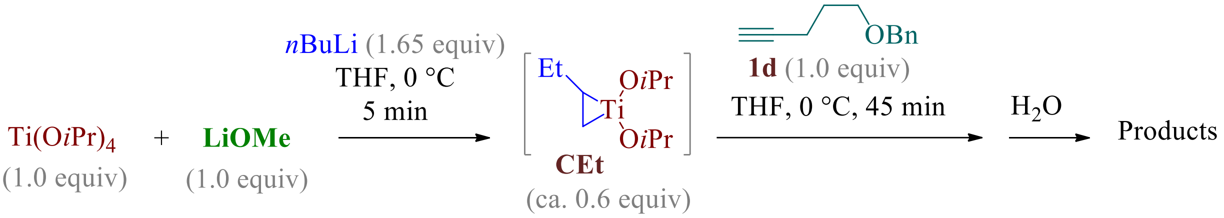
■ **VII.4.11.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *n*BuLi; with **LiBr** (1.0 equiv); reaction conducted at 0 °C for 45 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Total
3.4%	4.3%	8.5%	11.0%	8.0%	11.7%	8.4%	55%

General procedure **GP6** was applied with *n*-butyllithium solution (2.17 M in hexanes) and LiBr as the salt additive. Crude product: yellow oil (271 mg). Analysis as described in subsection VII.2. (benzyl CH$_2$ protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

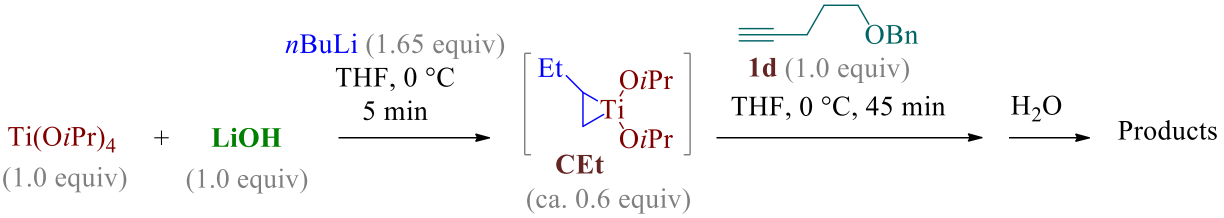
■ **VII.4.12.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *n*BuLi; with **LiOMe** (1.0 equiv); reaction conducted at 0 °C for 45 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Total
4.3%	3.8%	7.3%	15.0%	11.6%	13.8%	8.2%	64%

General procedure **GP6** was applied with *n*-butyllithium solution (2.17 M in hexanes) and LiOMe as the salt additive. Crude product: yellow oil (365 mg). Analysis as described in subsection VII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.

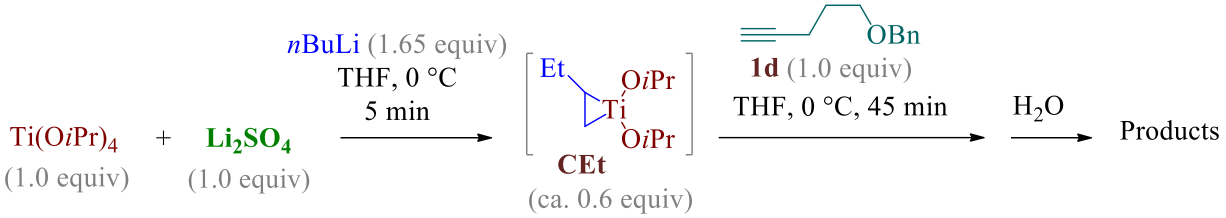
■ **VII.4.13.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *n*BuLi; with **LiOH** (1.0 equiv); reaction conducted at 0 °C for 45 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Total
2.0%	4.3%	7.9%	15.2%	9.0%	13.5%	6.5%	58%

General procedure **GP6** was applied with *n*-butyllithium solution (2.17 M in hexanes) and LiOMe as the salt additive. Crude product: yellow oil (339 mg). Analysis as described in subsection VII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.

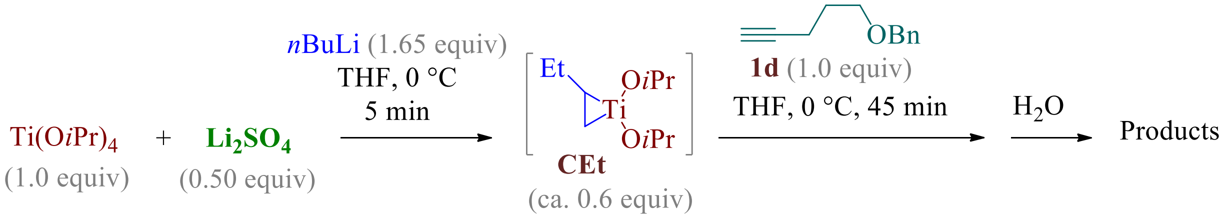
■ **VII.4.14.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *n*BuLi; with **Li$_2$SO$_4$** (1.0 equiv); reaction conducted at 0 °C for 45 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Total
3.1%	3.8%	6.4%	14.8%	9.6%	11.1%	6.1%	55%

General procedure **GP6** was applied with *n*-butyllithium solution (2.31 M in hexanes) and Li$_2$SO$_4$ as the salt additive. Crude product: yellow oil (453 mg). Analysis as described in subsection VII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.

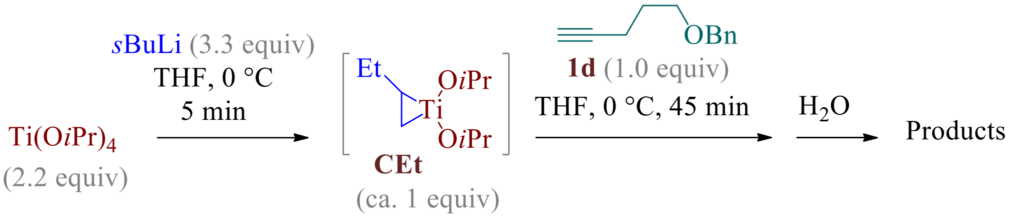
■ **VII.4.15.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *n*BuLi; with **Li$_2$SO$_4$** (0.50 equiv); reaction conducted at 0 °C for 45 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Total
2.5%	5.4%	6.8%	16.3%	9.0%	16.2%	8.2%	64%

General procedure **GP6** was applied with *n*-butyllithium solution (2.17 M in hexanes) and Li$_2$SO$_4$ as the salt additive, except 0.50 equiv of the latter were used. Crude product: yellow oil (354 mg). Analysis as described in subsection VII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.

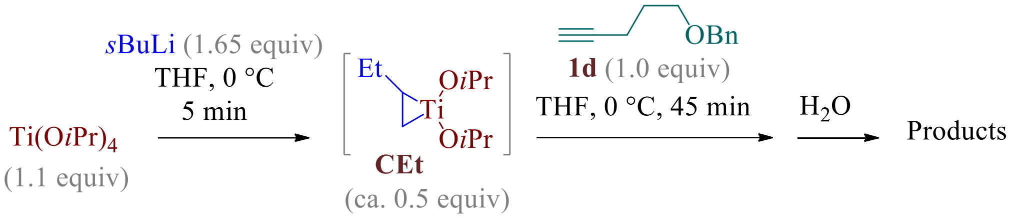
■ **VII.4.16.** With 2.2 equiv of Ti(O*i*Pr)$_4$, 3.3 equiv of *s*BuLi (bottle #1); reaction conducted at 0 °C for 45 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Total
1%	18%	9%	21%	18%	3%	2%	72%

General procedure **GP1** was applied with *n* = 2.20, *p* = 3.30 and *t* = 45. *s*-Butyllithium solution (1.14 M in cyclohexane, 3.30 mmol, 2.89 mL) was added over 2 minutes. 5-Benzyloxypent-1-yne **1d** (1.00 equiv, 1.00 mmol, 174 mg) was added over 4 minutes. Crude product: pale yellow oil (216 mg). Analysis as described in subsection VII.2. (benzyl CH_2 protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

■ **VII.4.17.** With 1.1 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *s*BuLi (bottle #1); reaction conducted at 0 °C for 45 min.



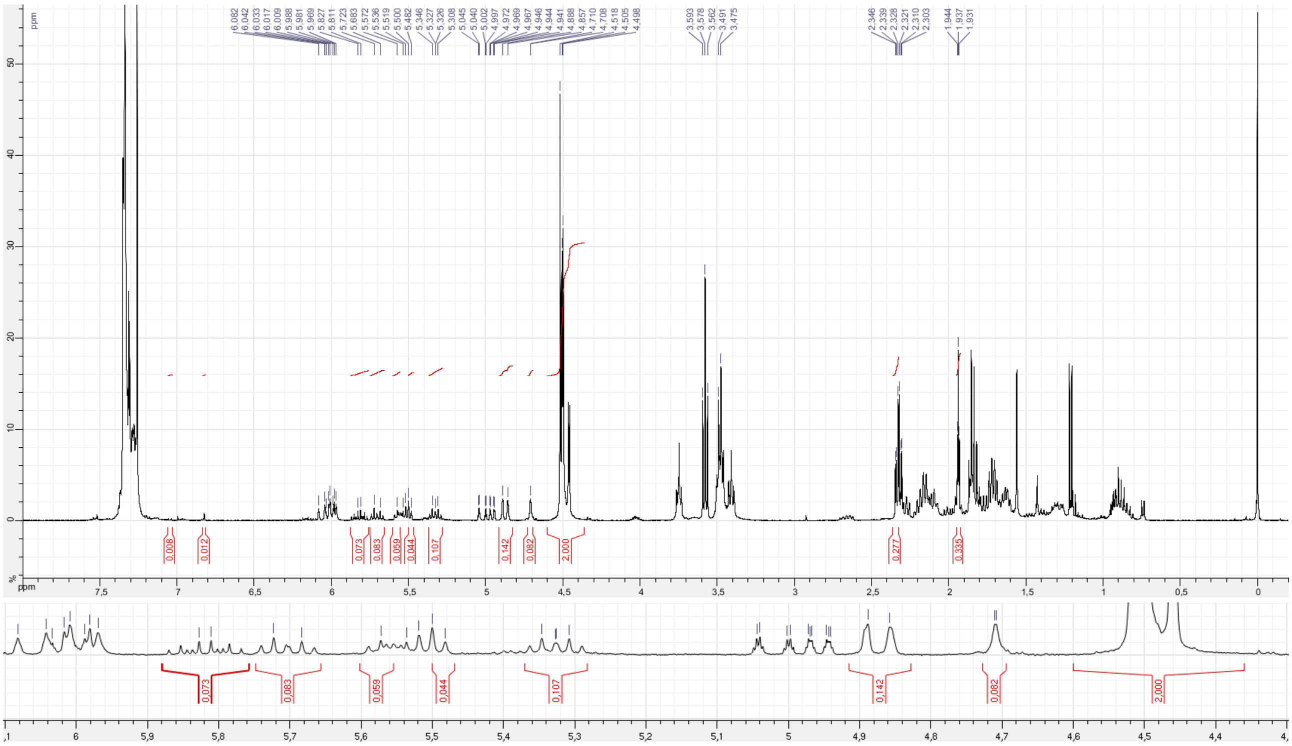
S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Tetramer **5d**	Total
28%	7%	4%	12% (1%)	16% (2%)	2%	1%	21% (5%)	91%

In parentheses: yields of isolated products.

General procedure **GP1** was applied with *n* = 1.10, *p* = 1.65 and *t* = 45. *s*-Butyllithium solution (1.14 M in cyclohexane, 3.30 mmol, 2.89 mL) was added over 2 minutes. 5-Benzyloxypent-1-yne **1d** (2.00 mmol, 348 mg) was added over 1 minute. Crude product: yellow oil (343 mg).

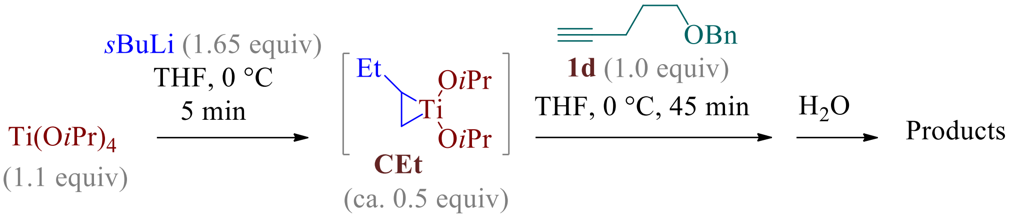
Analysis as described in subsection VII.2. (benzyl CH$_2$ protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

The crude product was more thoroughly concentrated (20 mbar), then triturated several times with MeOH (0.5 mL fractions). In the first three fractions (206 mg), the major components were starting alkyne **1d** and monoalkene products **2d** and **2′d**. The fourth fraction (49.6 mg) contained mostly the two diene regioisomers **3d** and **3′d** and the tetramer **5d**. The residue (62.3 mg) contained impure **5d**. Flash column chromatography of the fourth MeOH fraction (silica gel, EtOAc / petroleum ether, gradient from 2% to 20%) afforded a clean 43 : 57 mixture of **3d** and **3′d** (5.9 mg, 16.8 µmol, 3%), as well as pure tetramer **5d** (8.9 mg, 12.7 µmol, 5%).



^{1}H NMR spectrum of the crude product (CDCl$_3$, 400 MHz).

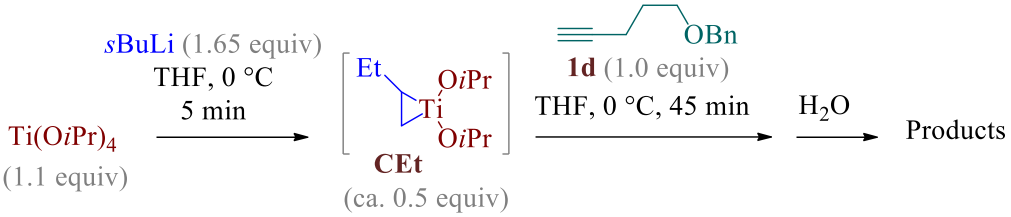
■ **VII.4.18.** With 1.1 equiv of Ti(O*i*Pr)4, 1.65 equiv of *s*BuLi (bottle #2); reaction conducted at 0 °C for 45 min. Substrate **1d** added over 8 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Tetramer **5d**	Total
16.1%	4.4%	3.5%	12.2%	17.6%	3.0%	1.9%	6.4%	65%

General procedure **GP1** was applied with $n = 1.10$, $p = 1.65$ and $t = 45$. *s*-Butyllithium solution (1.36 M in cyclohexane, 3.30 mmol, 2.43 mL) was added over 1.5 minutes. 5-Benzyloxypent-1-yne **1d** (2.00 mmol, 348 mg) was added over **8 minutes**. Crude product: yellow oil (370 mg). Analysis as described in subsection VII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.

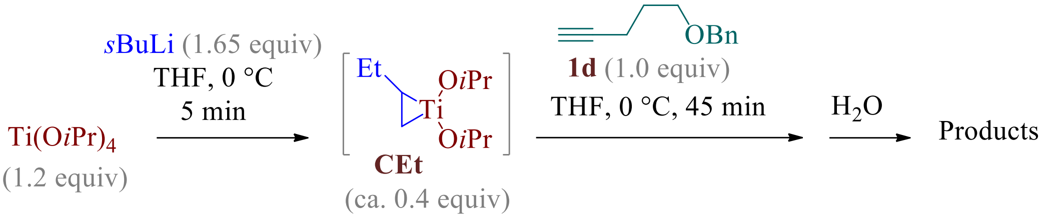
■ **VII.4.19.** With 1.1 equiv of Ti(O*i*Pr)4, 1.65 equiv of *s*BuLi (bottle #2); reaction conducted at 0 °C for 45 min. Substrate **1d** added over 30 s.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Tetramer **5d**	Total
14.7%	7.4%	5.3%	14.8%	15.6%	2.4%	1.7%	8.0%	70%

General procedure **GP1** was applied with $n = 1.10$, $p = 1.65$ and $t = 45$. *s*-Butyllithium solution (1.36 M in cyclohexane, 3.30 mmol, 2.43 mL) was added over 1.5 minutes. 5-Benzyloxypent-1-yne **1d** (2.00 mmol, 348 mg) was added over **30 s**. Crude product: yellow oil (325 mg). Analysis as described in subsection VII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.

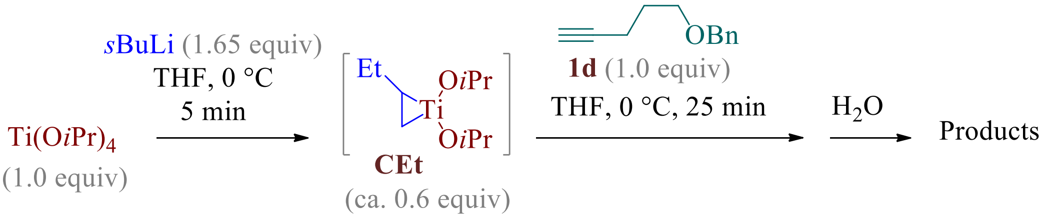
■ **VII.4.20.** With 1.2 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *s*BuLi (bottle #2);
reaction conducted at 0 °C for 45 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Tetramer **5d**	Total
20.0%	9.8%	4.4%	12.0%	13.2%	2.5%	1.4%	11.6%	75%

General procedure **GP1** was applied with *n* = 1.20, *p* = 1.65 and *t* = 45. *s*-Butyllithium solution (1.36 M in cyclohexane, 3.30 mmol, 2.43 mL) was added over 1.5 minutes. 5-Benzyloxypent-1-yne **1d** (2.00 mmol, 348 mg) was added over 30 s. Crude product: yellow oil (350 mg). Analysis as described in subsection VII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.

■ **VII.4.21.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *s*BuLi (bottle #2);
reaction conducted at 0 °C for 25 min.



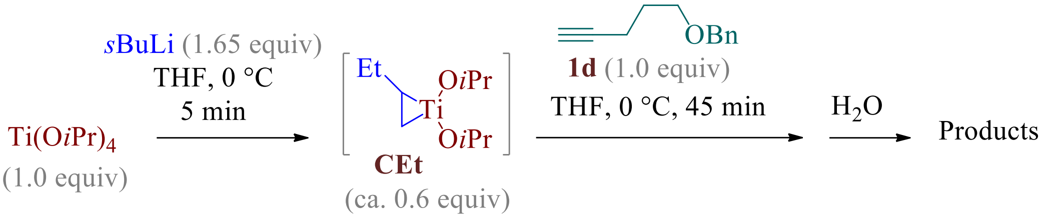
S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Tetramer **5d**	Total
12.0%	12.4%	6.5%	15.0%	16.0%	3.0%	2.2%	13.2%	80%[a]
10.9%	11.1%	5.9%	13.6%	14.4%	3.0%	2.0%	12.0%	73%[b]

[a] Yields estimated using benzyl CH_2 protons used as an internal standard.

[b] Yields estimated using (*E*)-cinnamic acid as an internal standard.

General procedure **GP1** was applied with *n* = 1.00, *p* = 1.65, *T* = 0 and *t* = 25.
s-Butyllithium solution (1.36 M in cyclohexane, 3.30 mmol, 2.43 mL) was added over 1.5 minutes. 5-Benzyloxypent-1-yne **1d** (2.00 mmol, 348 mg) was added over 30 s. Crude product: yellow oil (351 mg). Analysis as described in subsection VII.2. gave the qualitative estimation of the product yields shown in the table above.

■ **VII.4.22.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *s*BuLi (bottle #2); reaction conducted at 0 °C for 45 min.



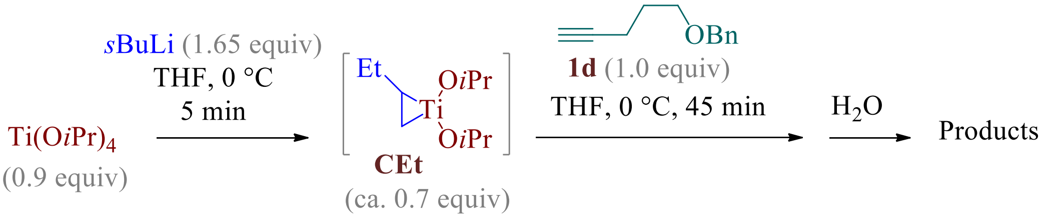
S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Tetramer **5d**	Total
2.2%	10.5%	7.8%	17.4%	17.2%	4.8%	2.9%	12.4%	75%[a]
2.0%	9.2%	6.8%	15.2%	15.2%	4.2%	2.6%	10.8%	66%[b]

[a] Yields estimated using benzyl CH_2 protons used as an internal standard.

[b] Yields estimated using (*E*)-cinnamic acid as an internal standard.

General procedure **GP1** was applied with n = 1.00, p = 1.65, T = 0 and t = 45.
s-Butyllithium solution (1.36 M in cyclohexane, 3.30 mmol, 2.43 mL) was added over 1.5 minutes. 5-Benzyloxypent-1-yne **1d** (2.00 mmol, 348 mg) was added over 30 s. Crude product: yellow oil (353 mg). Analysis as described in subsection VII.2. gave the qualitative estimation of the product yields shown in the table above.

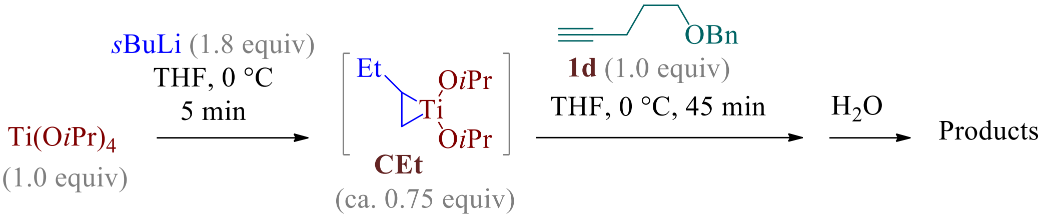
■ **VII.4.23.** With 0.9 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *s*BuLi (bottle #2); reaction conducted at 0 °C for 45 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Tetramer **5d**	Total
1.7%	7.4%	7.4%	11.2%	9.6%	5.4%	3.0%	5.6%	51%

General procedure **GP1** was applied with n = 0.90, p = 1.65, T = 0 and t = 45.
s-Butyllithium solution (1.36 M in cyclohexane, 3.30 mmol, 2.43 mL) was added over 1.5 minutes. 5-Benzyloxypent-1-yne **1d** (2.00 mmol, 348 mg) was added over 30 s. Crude product: yellow oil (303 mg). Analysis as described in subsection VII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.

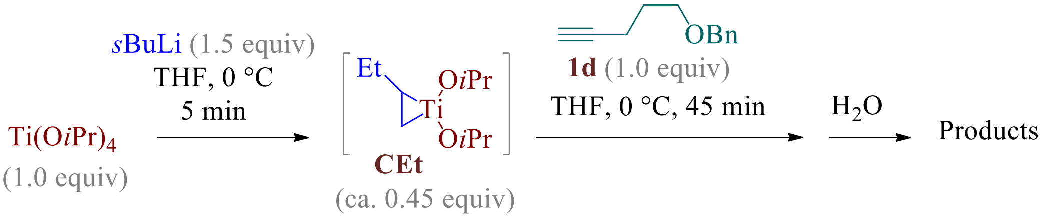
■ **VII.4.24.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.8 equiv of *s*BuLi (bottle #2);
reaction conducted at 0 °C for 45 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Tetramer **5d**	Total
2.0%	10.5%	7.2%	15.2%	13.2%	4.2%	2.8%	9.6%	65%

General procedure **GP1** was applied with *n* = 1.00, *p* = 1.80, *T* = 0 and *t* = 45.
s-Butyllithium solution (1.36 M in cyclohexane, 3.60 mmol, 2.65 mL) was added over 1.5 minutes. 5-Benzyloxypent-1-yne **1d** (2.00 mmol, 348 mg) was added over 30 s. Crude product: yellow oil (352 mg). Analysis as described in subsection VII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.

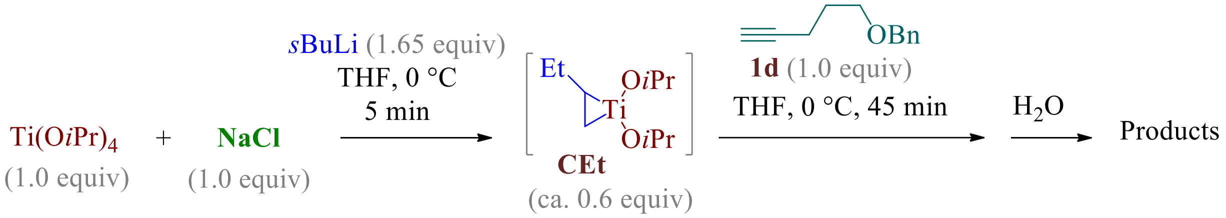
■ **VII.4.25.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.5 equiv of *s*BuLi (bottle #2);
reaction conducted at 0 °C for 45 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Tetramer **5d**	Total
24.0%	7.7%	4.5%	11.4%	12.8%	2.4%	1.2%	10.8%	75%

General procedure **GP1** was applied with *n* = 1.00, *p* = 1.50, *T* = 0 and *t* = 45.
s-Butyllithium solution (1.36 M in cyclohexane, 3.00 mmol, 2.21 mL) was added over 1.5 minutes. 5-Benzyloxypent-1-yne **1d** (2.00 mmol, 348 mg) was added over 30 s. Crude product: yellow oil (369 mg). Analysis as described in subsection VII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.

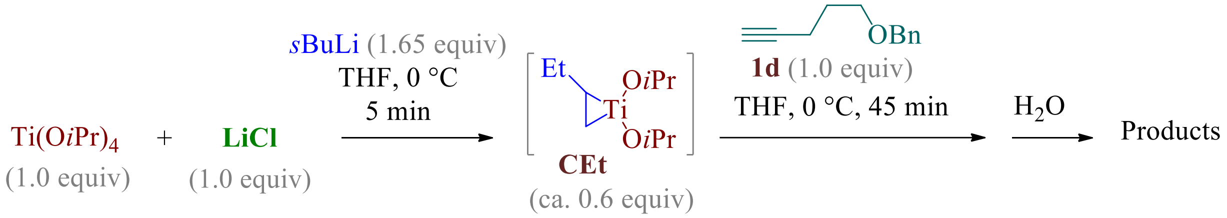
■ **VII.4.26.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *s*BuLi (bottle #2); with **NaCl** (1.0 equiv); reaction conducted at 0 °C for 45 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Tetramer **5d**	Total
3.2%	10.7%	8.0%	18.0%	13.6%	6.3%	5.3%	6.8%	72%

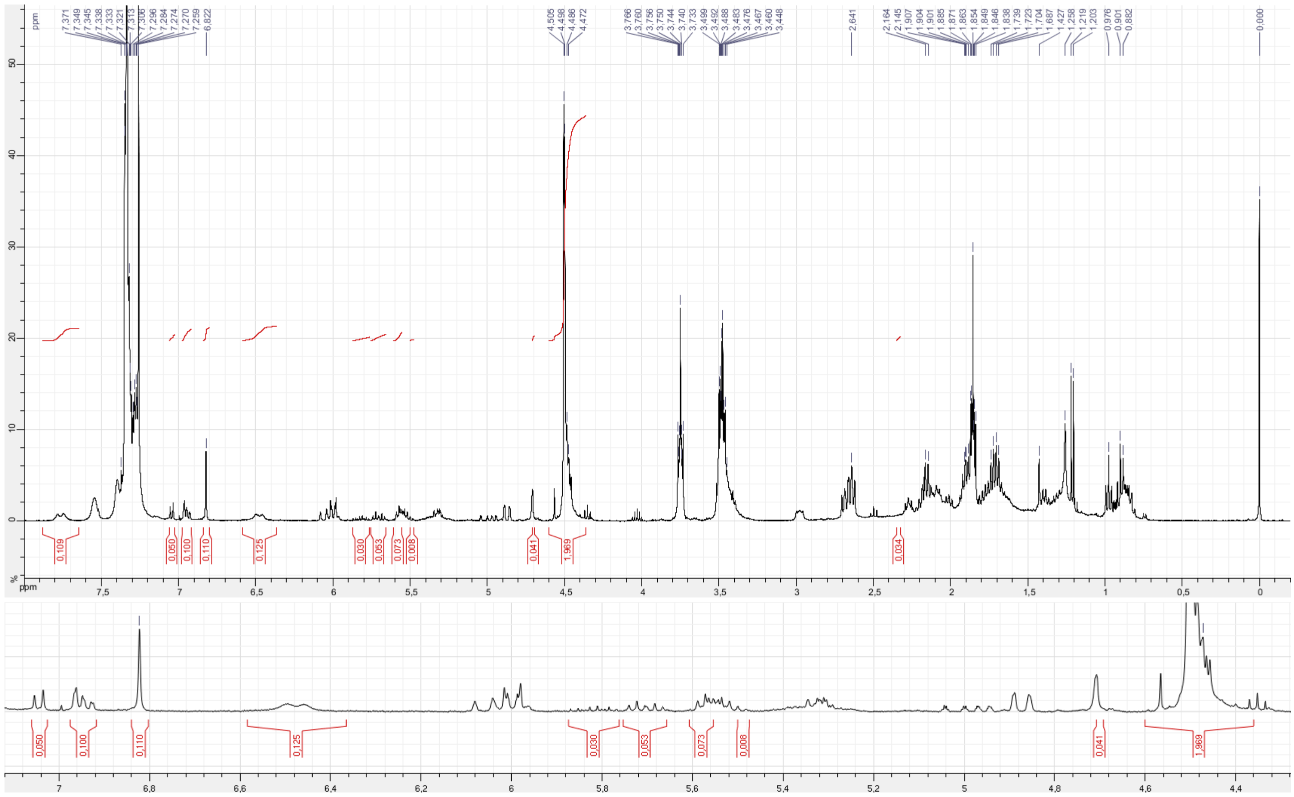
General procedure **GP6** was applied with *s*-butyllithium solution (1.36 M in cyclohexane, 3.30 mmol, 2.43 mL) and NaCl as the salt additive. Crude product: yellow-orange oil (382 mg). Analysis as described in subsection VII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.

■ **VII.4.27.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *s*BuLi (bottle #2); with **LiCl** (1.0 equiv); reaction conducted at 0 °C for 45 min.



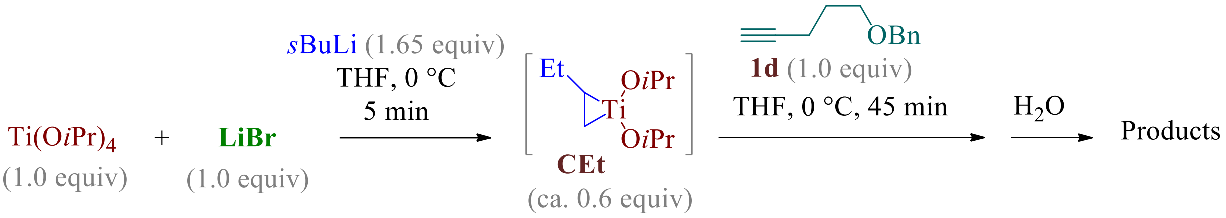
S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Tetramer **5d**	Total
3.4%	3.0%	4.1%	14.6%	10.6%	15.0%	11.0%	3.2%	65%

General procedure **GP6** was applied with *s*-butyllithium solution (1.36 M in cyclohexane, 3.30 mmol, 2.43 mL) and LiCl as the salt additive. Crude product: yellow oil (386 mg). Analysis as described in subsection VII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.



^{1}H NMR spectrum of the crude product (CDCl$_3$, 400 MHz).

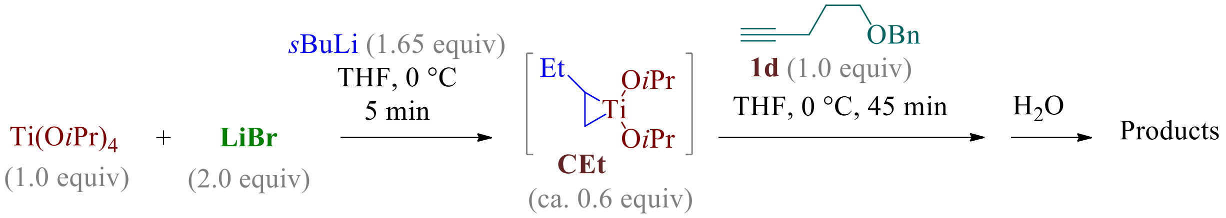
■ **VII.4.28.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *s*BuLi (bottle #2); with **LiBr** (1.0 equiv); reaction conducted at 0 °C for 45 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Tetramer **5d**	Total
9.6%	2.8%	4.3%	12.2%	11.4%	7.8%	11.5%	3.2%	63%

General procedure **GP6** was applied with *s*-butyllithium solution (1.36 M in cyclohexane, 3.30 mmol, 2.43 mL) and LiBr as the salt additive. Crude product: yellow oil (362 mg). Analysis as described in subsection VII.2. (benzyl CH_2 protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

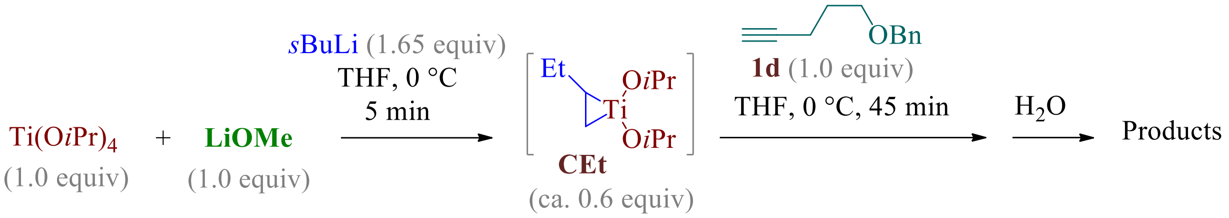
■ **VII.4.29.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *s*BuLi (bottle #2); with **LiBr** (2.0 equiv); reaction conducted at 0 °C for 45 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Tetramer **5d**	Total
0.0%	2.8%	5.9%	11.7%	6.4%	14.2%	12.2%	1.2%	54%

General procedure **GP6** was applied with *s*-butyllithium solution (1.25 M in cyclohexane, 3.30 mmol, 2.64 mL) and LiBr (2.00 equiv) as the salt additive. Crude product: yellow oil (379 mg). Analysis as described in subsection VII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.

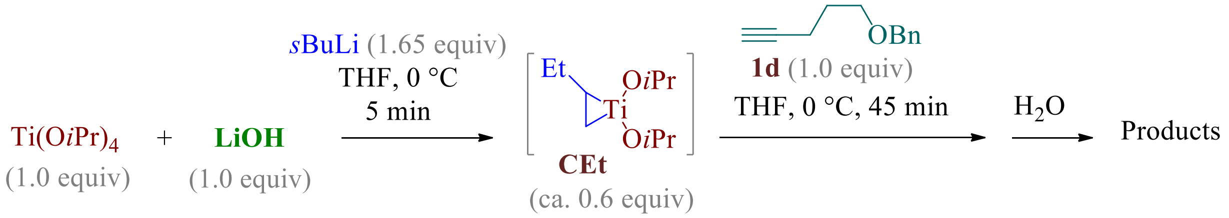
■ **VII.4.30.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *s*BuLi (bottle #2); with **LiOMe** (1.0 equiv); reaction conducted at 0 °C for 45 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Tetramer **5d**	Total
4.0%	10.5%	7.4%	17.0%	13.4%	7.2%	5.2%	4.4%	69%

General procedure **GP6** was applied with *s*-butyllithium solution (1.36 M in cyclohexane, 3.30 mmol, 2.43 mL) and LiOMe as the salt additive. Crude product: yellow oil (365 mg). Analysis as described in subsection VII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.

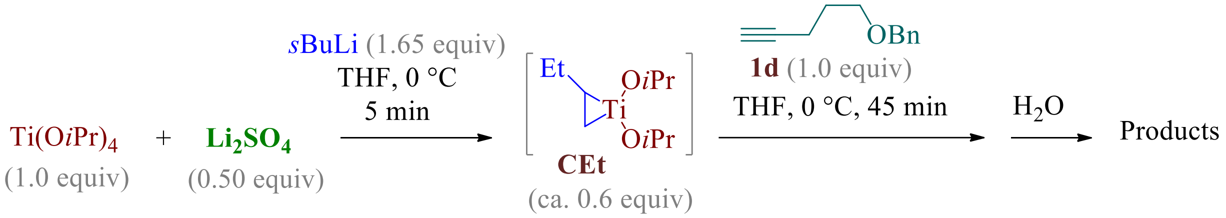
■ **VII.4.31.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *s*BuLi (bottle #2); with **LiOH** (1.0 equiv); reaction conducted at 0 °C for 45 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Tetramer **5d**	Total
3.6%	8.5%	7.1%	18.2%	16.0%	6.0%	3.6%	7.6%	71%

General procedure **GP6** was applied with *s*-butyllithium solution (1.36 M in cyclohexane, 3.30 mmol, 2.43 mL) and LiOH as the salt additive. Crude product: yellow oil (374 mg). Analysis as described in subsection VII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.

■ **VII.4.32.** With 1.0 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *s*BuLi (bottle #2);
with **Li$_2$SO$_4$** (0.5 equiv); reaction conducted at 0 °C for 45 min.



S.m **1d**	Alkene **2d**	Alkene **2′d**	Diene **3d**	Diene **3′d**	Trimer **4d**	Trimer **4′d**	Tetramer **5d**	Total
2.1%	8.6%	6.7%	17.4%	13.2%	6.0%	4.4%	4.8%	63%

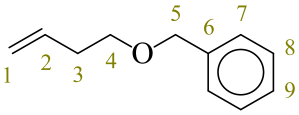
General procedure **GP6** was applied with *s*-butyllithium solution (1.36 M in cyclohexane, 3.30 mmol, 2.43 mL) and Li$_2$SO$_4$ as the salt additive. Crude product: yellow oil (346 mg). Analysis as described in subsection VII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.

VIII. Experiments with 4-benzyloxybut-1-yne **1e**

VIII.1. Characterisation of the products

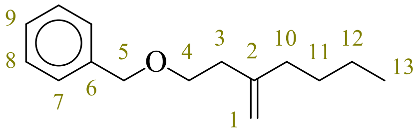
Product **3′e** was isolated in imperfectly pure form. Compounds **2e**, **2′e**, **3e**, **4′e** and **5e** were obtained as components of more or less complex mixtures. The cyclotrimer **4e** was obtained in fairly pure form, the only minor contaminent detected being the other regioisomer **4′e**. Assignment of the signals of mixtures of compounds was done as explained in the general information.

4-Benzyloxybut-1-ene **2e**[33]



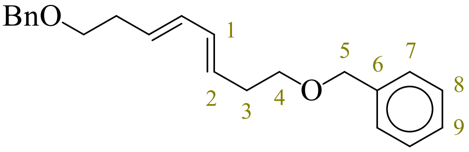
^{1}H NMR (CDCl$_3$, 400 MHz), characteristic signals: δ 5.03 (1 H, ddt, *J* 10.0, 2.0, 1.0, H1 *cis* to H2), 5.09 (1 H, ddt, *J* 17.0, 2.0, 1.5, H1 *trans* to H2), 5.82 (1 H, ddt, *J* 17.0, 10.0, 6.5, H2). ^{13}C NMR (CDCl$_3$, 100.6 MHz), characteristic signal: δ 116.3 (C1).

3-Methyleneheptoxymethylbenzene **2′e**



^{1}H NMR (CDCl$_3$, 400 MHz), characteristic signals: δ 4.76 (1 H, br s, H1a), 4.78 (1 H, br s, H1b). ^{13}C NMR (CDCl$_3$, 100.6 MHz), characteristic signal: δ 110.1 (C1).

[(3*E*,5*E*)-8-Benzyloxyocta-3,5-dienoxy]methylbenzene **3e**[34]



^{1}H NMR (CDCl$_3$, 400 MHz), characteristic signals: δ 5.58 (2 H, m, H2), 6.06 (2 H, m, H1).

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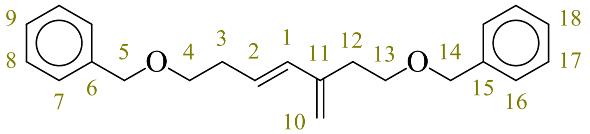
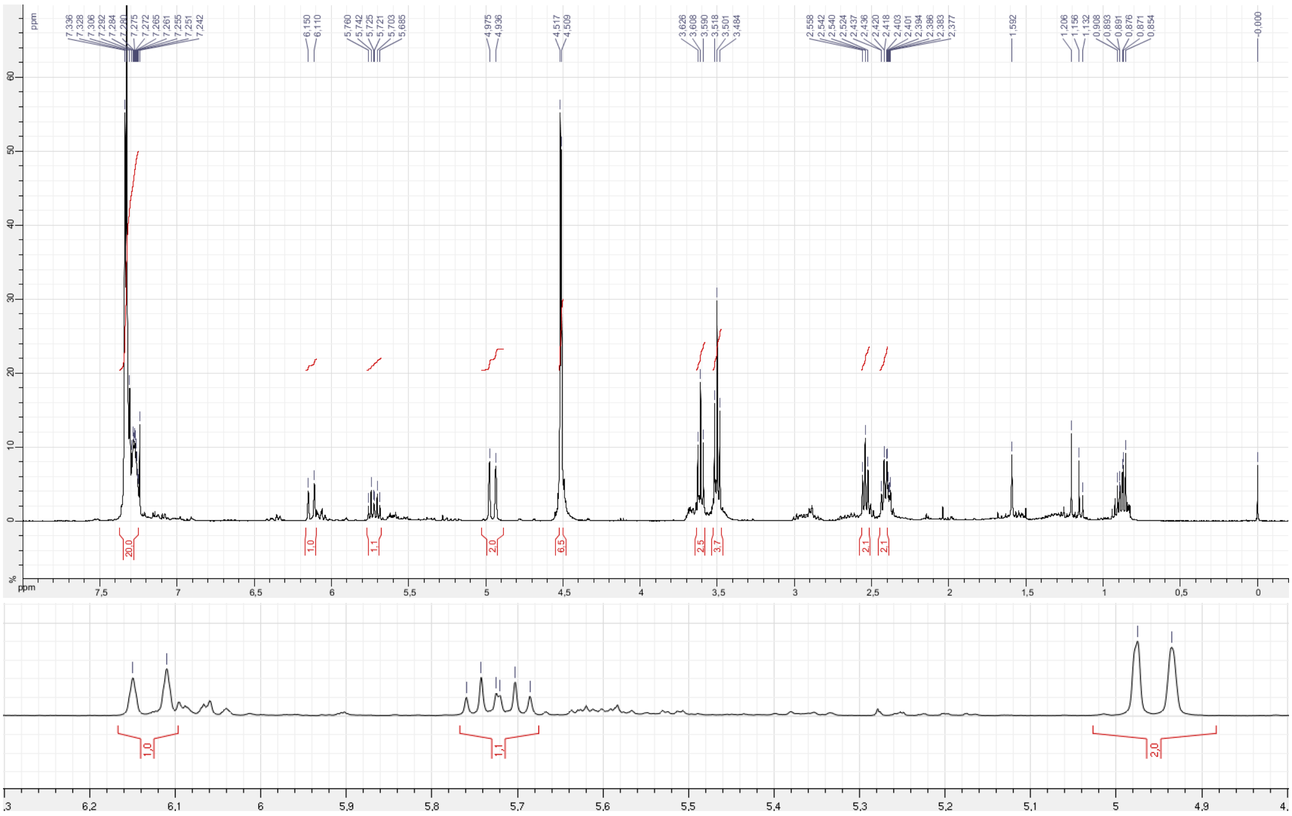
[33] J. Ćirakovic´, T. G. Driver, K. A. Woerpel, *J. Am. Chem. Soc.* **2002**, *124*, 9370−9371 (supporting information).

[34] S. Kanemoto, S. Matsubara, K. Oshima, K. Utimoto, H. Nozaki, *Chem. Lett.* **1987**, 5−6.

[(*E*)-7-Benzyloxy-3-methylene-hept-4-enoxy]methylbenzene **3′e**



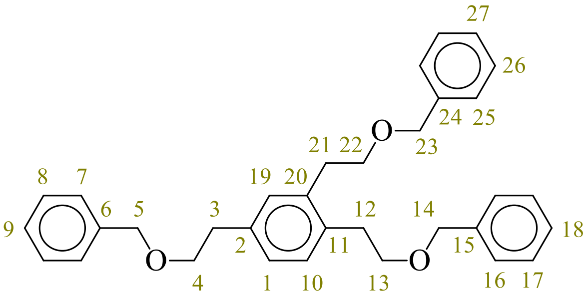
R_f 0.45 [EtOAc/Petroleum ether 10%, UV-active, PMA]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.42 (2 H, td, *J* 7.0, 1.0, H3), 2.54 (2 H, td, *J* 7.0, 1.0, H12), 3.50 (2 H, t, *J* 7.0, H4), 3.61 (2 H, t, *J* 7.0, H13), 4.51 (2 H, s, H5 or H14), 4.52 (2 H, s, H5 or H14), 4.94 (1 H, br s, H10a), 4.97 (1 H, br s, H10b), 5.72 (1 H, dt, *J* 16.0, 7.0, H2), 6.13 (1 H, br d, *J* 16.0, H1), 7.24−7.36 (10 H, m, H7−H9, H16−H18).



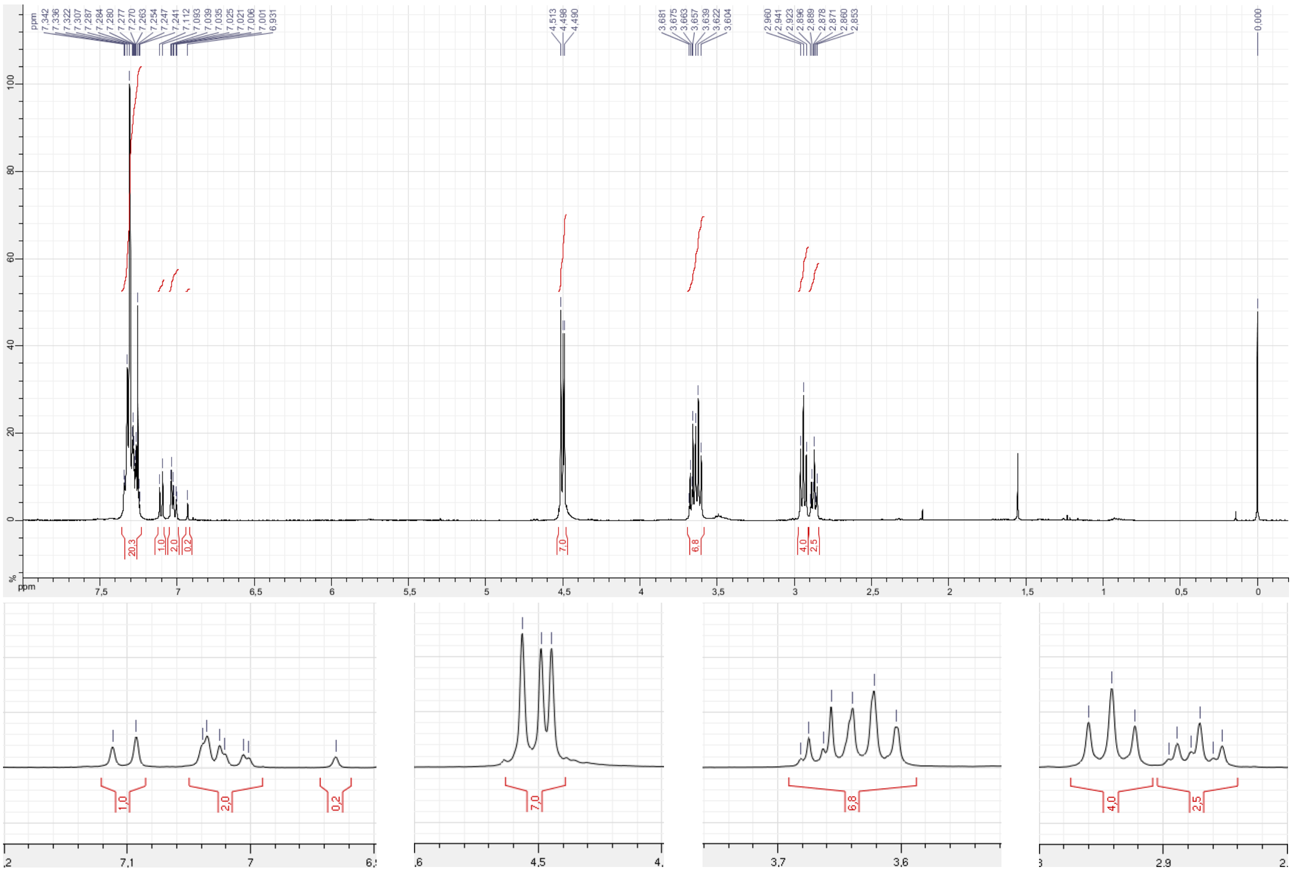
^{1}H NMR spectrum (CDCl$_3$, 400 MHz).

Note: this sample contained significant amounts of impurities.

1,2,4-Tris(2-benzyloxyethyl)benzene **4e**



Colourless oil. R_f 0.3 (EtOAc/Petroleum ether 10%, UV-active, PMA). IR (neat): ν 2929 (w), 2855 (m), 1495 (w), 1453 (m), 1360 (m), 1204 (w), 1092 (s), 1074 (s), 1027 (m), 733 (s) cm^{-1}.[35] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.87 (2 H, t, J 7.0, H3), 2.94 (4 H, t, J 7.5, H12, H21), 3.62 (2 H, t, J 7.5, H13 or H22), 3.62 (2 H, t, J 7.5, H13 or H22), 4.49 (2 H, s, H14 or H23), 4.50 (2 H, s, H14 or H23), 4.51 (2 H, s, H5), 3.66 (2 H, t, J 7.0, H4), 7.01 (1 H, dd, J 7.5, 1.5, H1), 7.04 (1 H, d, J 1.5, H19), 7.10 (1 H, d, J 7.5, H10), 7.24−7.35 (15 H, H7−H9, H16−H18, H25−H27). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 32.7, 33.1 (C12, C21), 35.9 (C3), 71.0, 71.0 (C13, C22), 71.3 (C4), 72.91 (C5), 72.95, 72.95 (C14, C23), 127.0 (C1), 127.5, 127.5, 127.5 (C9, C18, C27), 127.6, 127.6, 127.6 (C7, C16, C25), 128.3, 128.3, 128.3 (C8, C17, C26), 129.8 (C10), 130.4 (C19), 134.7 (C2), 136.8, 136.9 (C11, C20), 138.35, 138.35 (C15, C24), 138.38 (C6). MS (ESI): m/z 355.1, 373.2 ([M−OBn]$^+$), 445.3, 463.1, <u>503.3</u> ([MNa]$^+$), 539.2.[35]



^{1}H NMR spectrum ($CDCl_3$, 400 MHz).

Note: this analysis was performed on a 93 : 7 mixture of **4e** and **4′e**.

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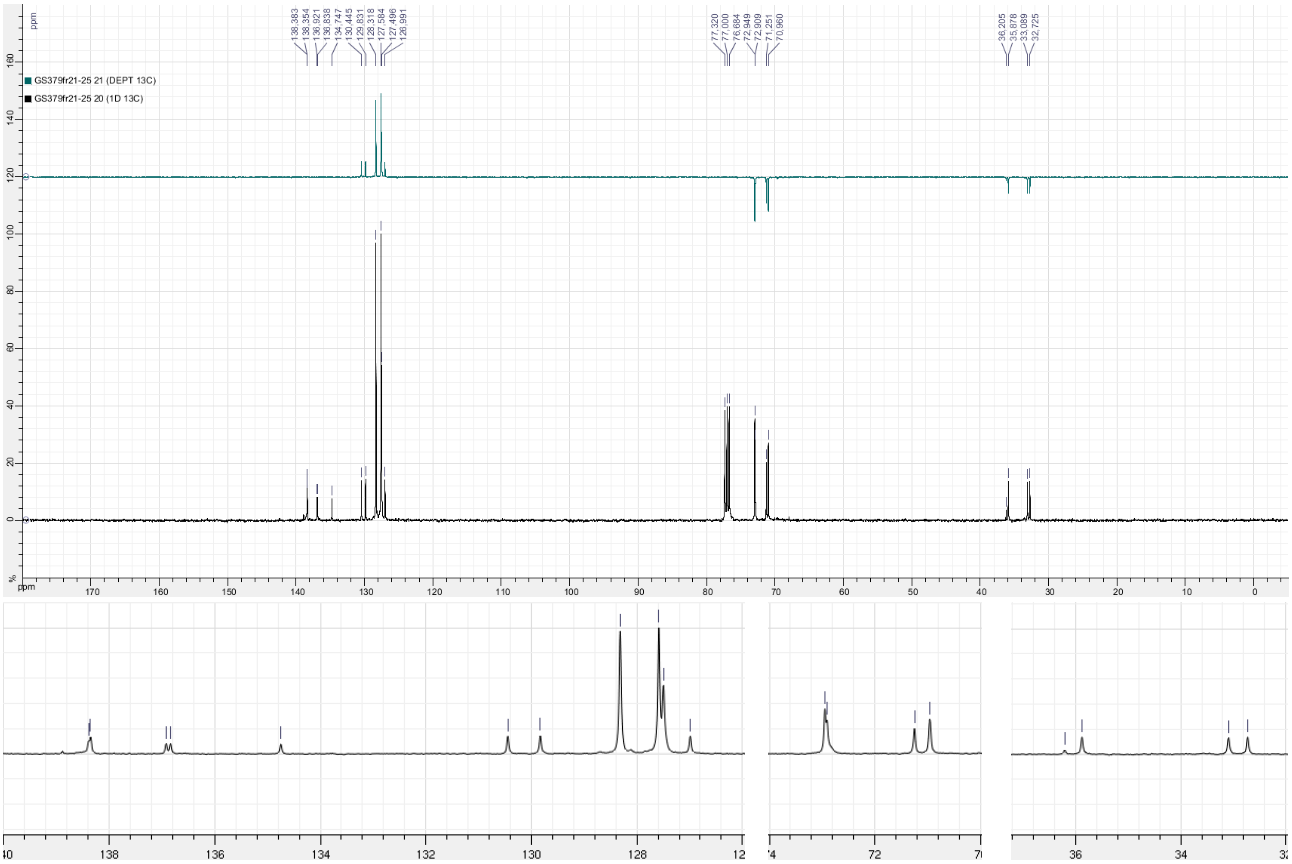
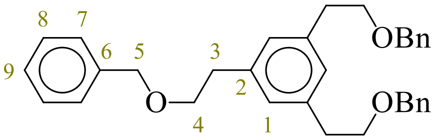
[35] Analysis performed on a 93 : 7 mixture of **4e** and **4′e**.



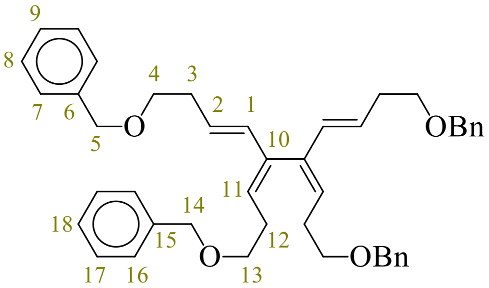
^{13}C and DEPT135 NMR spectra (CDCl$_3$, 100.6 MHz).
Note: this analysis was performed on a 93 : 7 mixture of **4e** and **4′e**.

1,3,5-Tris(2-benzyloxyethyl)benzene **4′e**



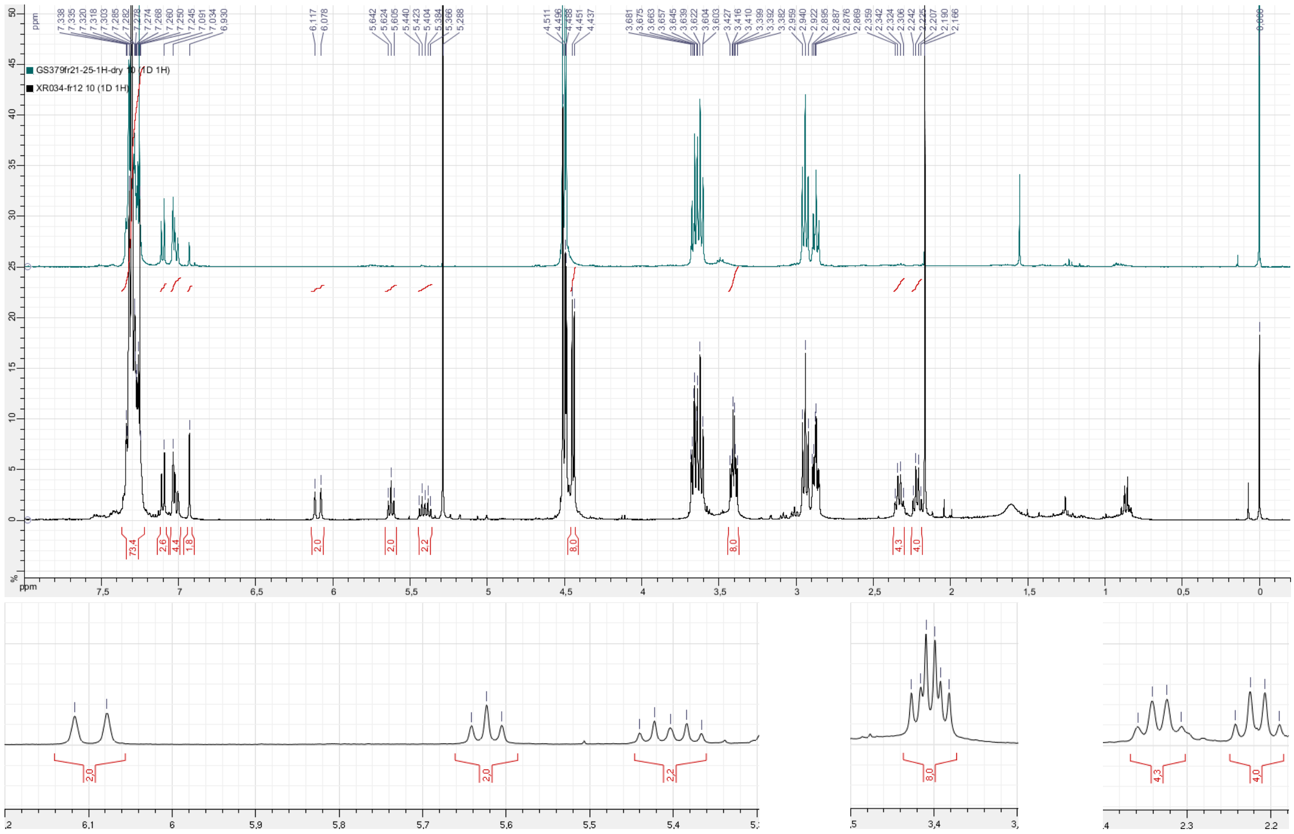
R$_f$ 0.3 (EtOAc/Petroleum ether 10%, UV-active, PMA). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.88 (6 H, t, *J* 7.0, H3), 3.66 (6 H, t, *J* 7.0, H4), 4.51 (6 H, s, H5), 6.93 (3 H, s, H1), 7.24−7.35 (15 H, H7−H9). ^{13}C NMR (CDCl$_3$, 100.6 MHz), characteristic signals: δ 36.2 (C3), 72.9 (C5), 127.5 (C1).

[(3*Z*,5*Z*,6*E*)-9-Benzyloxy-4-[(*E*)-4-benzyloxybut-1-enyl]-5-(3-benzyloxypropylidene)nona-3,6-dienoxy]methylbenzene **5e**



R$_f$ 0.4 [EtOAc/Petroleum ether 20%, UV-active, anisaldehyde (blue-grey colour)]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.22 (4 H, dt, *J* 7.5, 7.0, H12), 2.33 (4 H, qd, *J* 7.0, 1.5, H3), 3.40 (4 H, t, *J* 7.0, H4 or H13), 3.41 (4 H, t, *J* 7.0, H4 or H13), 4.44 (4 H, s, H5 or H14), 4.45 (4 H, s, H5 or H14), 5.40 (2 H, dt, *J* 15.5, 7.0, H2), 5.62 (2 H, t, *J* 7.5, H11), 6.10 (2 H, dt, *J* 15.5, 1.5, H1), 7.23−7.36 (20 H, m, H7−H9, H16−H18).

This compound was produced in small relative amounts and we were not able to isolate it. Nonetheless, the characteristic signals observed at 5.40; 5.62 and 6.10 ppm are assigned to the structure **5e**, by analogy with the closely related compound **5d**. Moreover, these signals were only observed when *s*BuLi was used, which is also consistent with the results concerning the other tetramers **5b**, **5c** and **5d**.



^{1}H NMR spectrum (CDCl$_3$, 400 MHz).

Note: this analysis was performed on a 59 : 15 : 26 mixture of **4e**, **4′e** and **5e**.

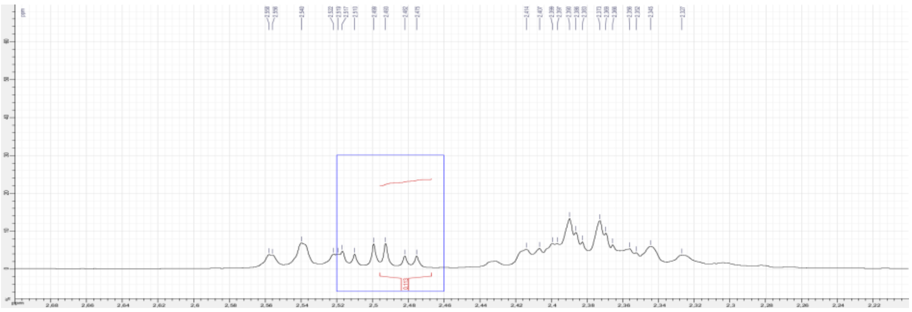
(the spectrum of a 93 : 7 mixture of **4e** and **4′e** is displayed in green, on top, for comparison).

VIII.2. Analysis of the crude products by ^{1}H NMR spectroscopy

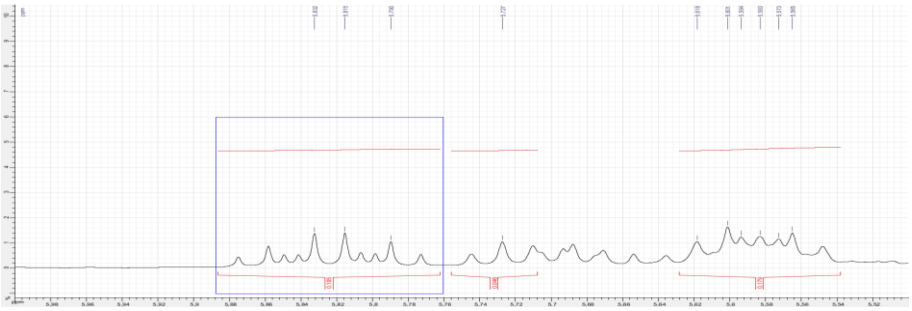
■ In the ^{1}H NMR spectrum of the crude products, the integral of the signals in the interval 4.30−4.60 ppm was set to 2.00: the benzyl CH$_2$ protons were used as an internal standard. Alternatively, (*E*)-cinnamic acid (500 μmol, 74.1 mg) was added to the crude products and the doublet at 6.46 ppm (vinylic CH proton) was used as an internal standard (the integral was set to 0.250).

■ The following signals were used for the qualitative assessment of the product yields:

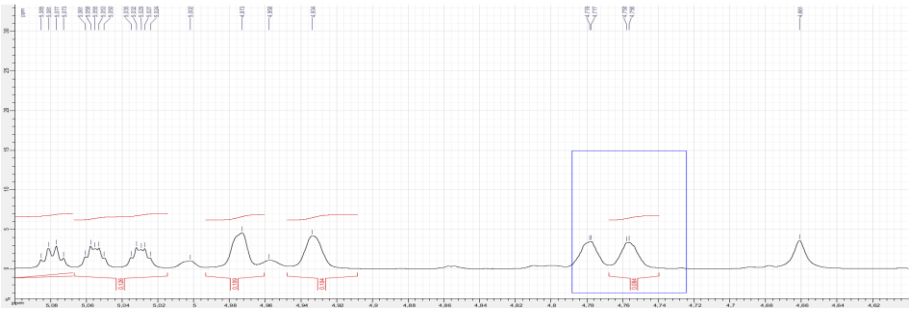
- Triplet of doublets at 2.51 ppm (*J* 7.0 and 2.5 Hz): two protons of **1e**. The integral of the right half of this signal gave an estimation of the proportion of unconverted **1e**;



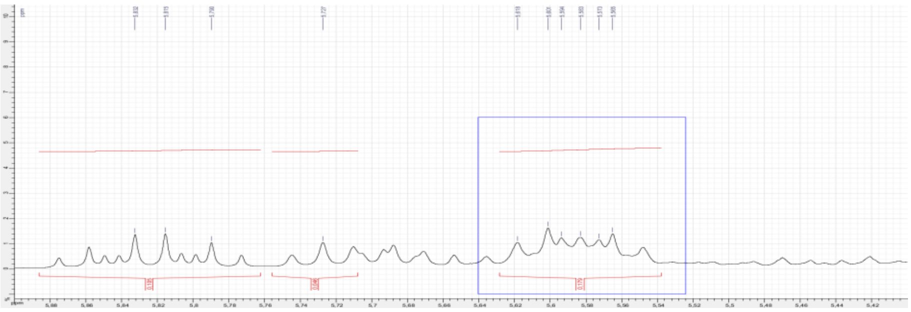
- Doublet of doublet of triplets (*J* 17.0, 10.0 and 6.5 Hz) at 5.82 ppm: one proton of **2e**. The integral of this signal gave an estimation of the yield of **2e**;



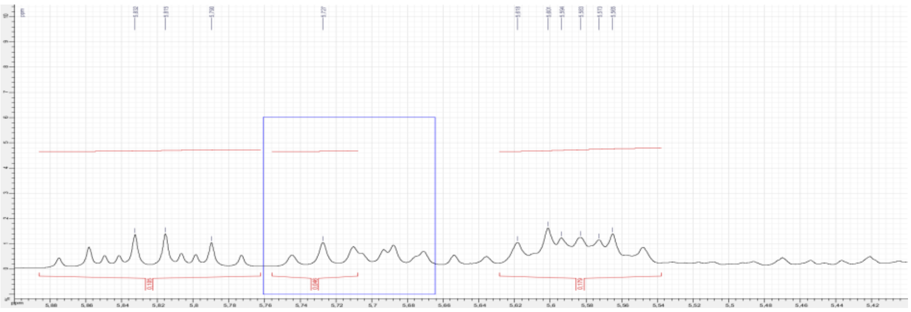
- Broad singlet at 4.76 ppm: one proton of **2′e**. The integral of this signal gave an estimation of the yield of **2′e**;



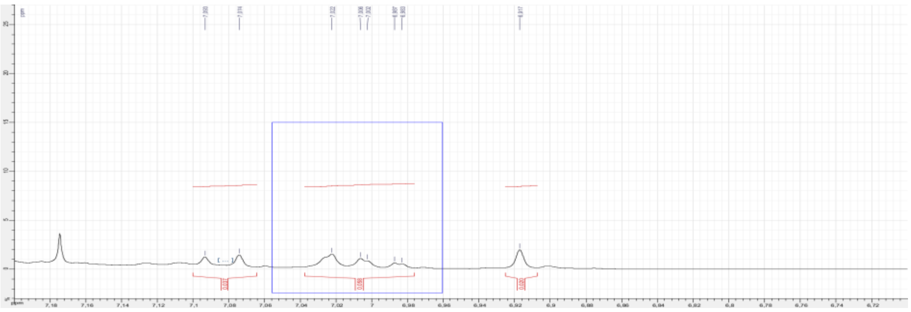
- Multiplet at 5.58 ppm: two protons of **3e**.
  The integral of this signal gave an estimation of the yield of **3e**;



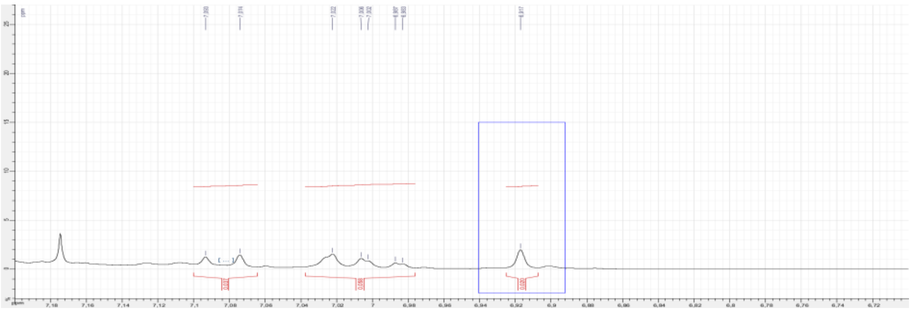
- Doublet of triplets (*J* 16.0 and 7.0 Hz) at 5.72 ppm: one proton of **3′e**.
  The integral of the left half of this signal was measured, then multiplied by four to give an estimation of the yield of **3′e**;



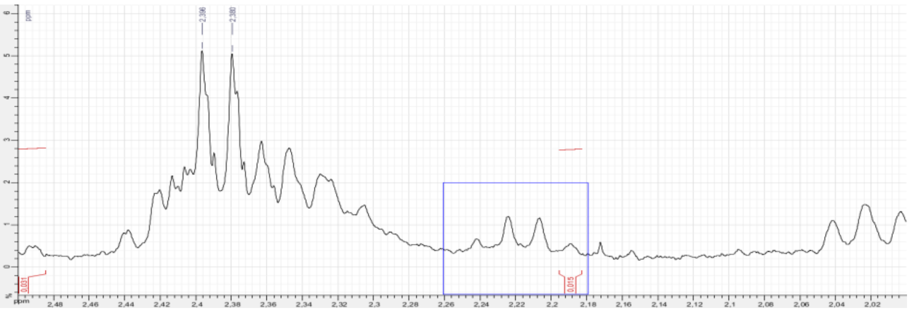
- Signals in the range 6.98−7.04 ppm: two protons of **4e**.
  The integral of these signals was multiplied by 3/2 to give an estimation of the yield of **4e**;



- Singlet at 6.93 ppm: three protons of **4′e**.
  The integral of this signal gave an estimation of the yield of **4′e**.

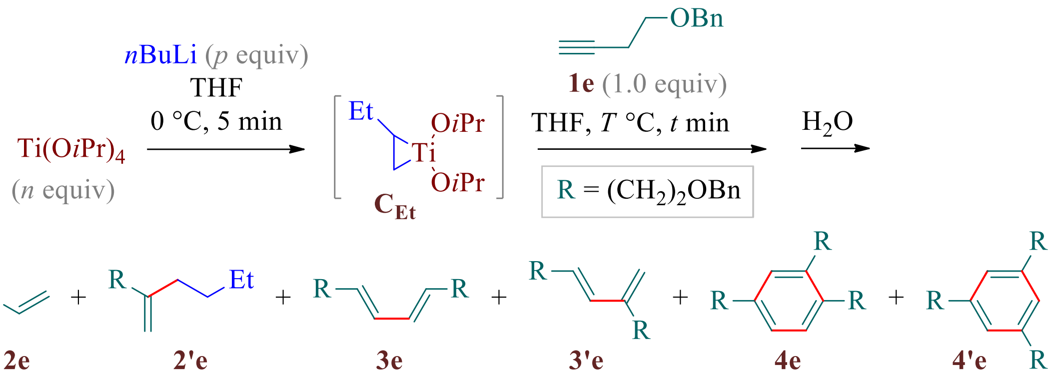


- Doublet of triplets at 2.22 ppm: four protons of **5e**. The integral of the right peak of this signal was measured, then multiplied by six to give an estimation of the yield of **5e**.



VIII.3. Summary of the experimental results obtained using **1e**

■ With *n*BuLi, in THF.



Subsection	*n*	*p*	*T*	*t*	S.m. **1e**	Alkene **2e**	Alkene **2′e**	Dienes **3e/3′e** (ratio)	Trimers **4e/4′e** (ratio)
VIII.4.1.	3.3	4.5	0	20	46%	4%	4%	24% (50 : 50)	10% (90 : 10)
VIII.4.2.	2.2	3.3	0	15	17%	7%	7%	35% (49 : 51)	17% (94 : 6)
VIII.4.3.				20	4%	11%	8%	37% (49 : 51)	18% (94 : 6)
VIII.4.4.[a]				30	2%	11%	8%	25% (61 : 39)	20% (90 : 10)
VIII.4.5.				90	2%	5%	9%	21% (62 : 38)	27% (93 : 7)
VIII.4.6.			−20	30	61%	5%	4%	16% (44 : 56)	0%
VIII.4.7.			−40		75%	5%	3%	7% (43 : 57)	0%
VIII.4.8.			−78	120	72%	14%	4%	Traces	0%
VIII.4.9.	1.1	1.65	0	45	2%	2%	5%	25% (57 : 43)	36% (95 : 5)
VIII.4.10.[b]	0.6	0.9	100	15	0%	3%	3%	8% (38 : 62)	50% (92 : 8)
VIII.4.11.[a,b]	0.6	0.9	140	15	0%	5%	2%	8% (25 : 75)	47% (89 : 11)

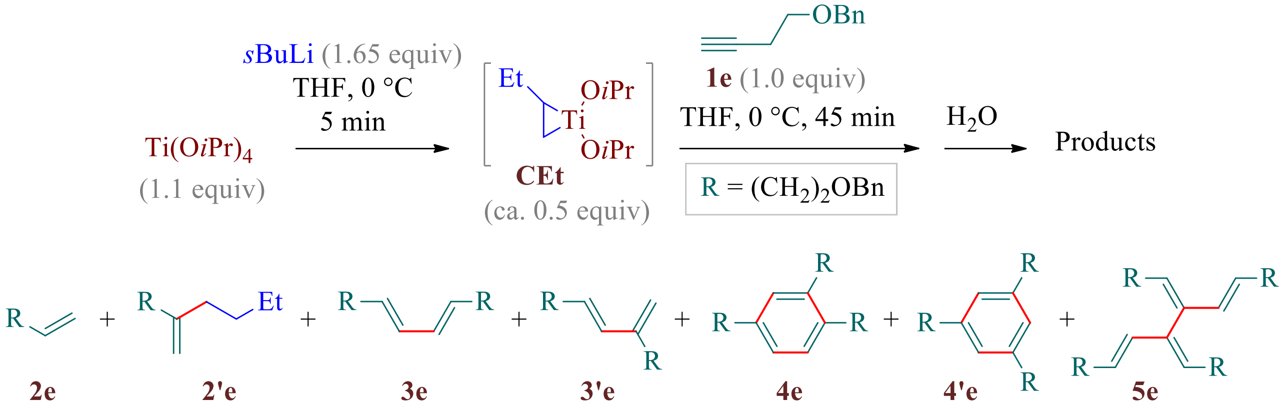
Colours for the starting material: 🟥 0−10% 🟥 11−20% 🟥 21−30% 🟥 31−40% 🟥 ≥41%

Colours for the products: 🟩 0−10% 🟩 11−20% 🟩 21−30% 🟩 31−40% 🟩 ≥41%

[a] Mean values are given for the yields, calculated from the similar results of two-three runs carried out under the same conditions.

[b] Heating was applied using a microwave reactor.

■ With *s*BuLi,[a] in THF.



Subsection	s.m. **1e**	Alkene **2e**	Alkene **2′e**	Dienes **3e**/**3′e** (ratio)	Trimers **4e**/**4′e** (ratio)	Tetramer **5e**
VIII.4.12.	3%	6%	4%	22% (44 : 56)	16% (91 : 9)	9%

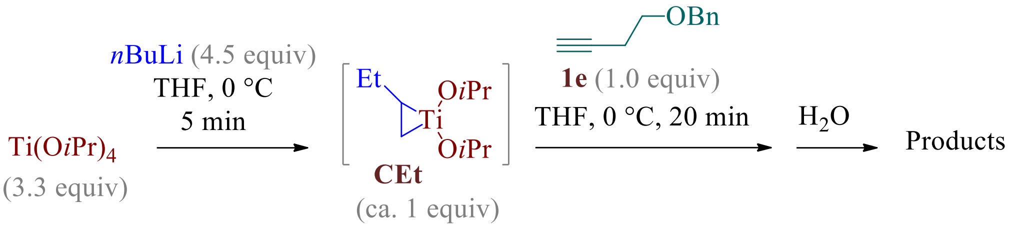
Colours for the starting material: ▢ 0–10% ▢ 11–20% ▢ 21–30% ▢ 31–40% ▢ ≥41%

Colours for the products: ▢ 0–10% ▢ 11–20% ▢ 21–30% ▢ 31–40% ▢ ≥41%

[a] "Old" bottle #1 was used.

VIII.4. Experimental detail

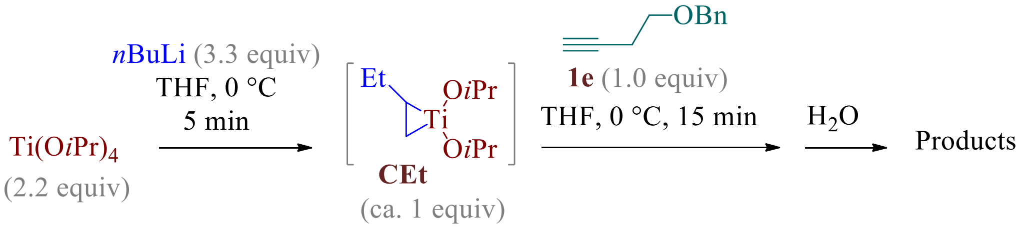
■ VIII.4.1. With 3.3 equiv of Ti(O*i*Pr)₄, 4.5 equiv of *n*BuLi; reaction conducted at 0 °C for 20 min.



S.m **1e**	Alkene **2e**	Alkene **2′e**	Diene **3e**	Diene **3′e**	Trimer **4e**	Trimer **4′e**	Total
46%	4%	4%	12%	12%	9%	1%	88%

General procedure **GP3** was applied with $n = 3.30$, $p = 4.50$, $V_1 = 3.5$, $V_2 = 0.5$ and $t = 20$. *n*-Butyllithium solution (2.38 M in hexanes, 4.50 mmol, 1.89 mL) was added over 3 minutes. The THF solution of 4-benzyloxybut-1-yne **1e** (1.00 mmol, 160 mg) was added over 3 minutes. Crude product: yellow oil (256 mg). Analysis as described in subsection VIII.2. (benzyl CH_2 protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

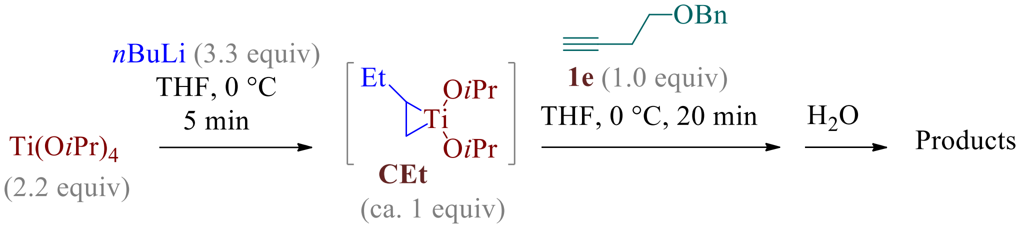
■ VIII.4.2. With 2.2 equiv of Ti(O*i*Pr)₄, 3.3 equiv of *n*BuLi; reaction conducted at 0 °C for 15 min.



S.m **1e**	Alkene **2e**	Alkene **2′e**	Diene **3e**	Diene **3′e**	Trimer **4e**	Trimer **4′e**	Total
17%	7%	7%	17%	18%	16%	1%	83%

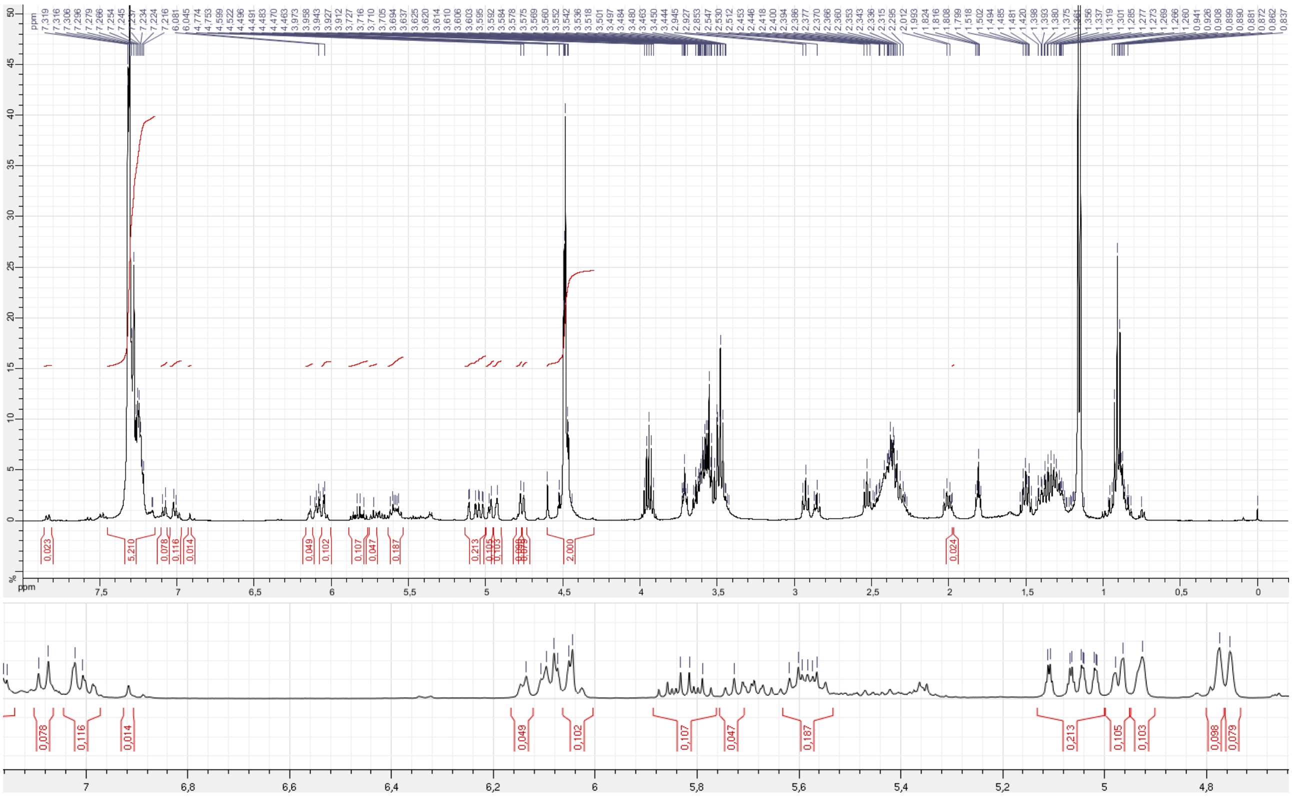
General procedure **GP3** was applied with $n = 2.20$, $p = 3.30$, $V_1 = 3.5$, $V_2 = 0.5$ and $t = 15$. *n*-Butyllithium solution (2.38 M in hexanes, 3.30 mmol, 1.38 mL) was added over 3 minutes. The THF solution of 4-benzyloxybut-1-yne **1e** (1.00 mmol, 160 mg) was added over 2 minutes. Crude product: yellow oil (164 mg). Analysis as described in subsection VIII.2. (benzyl CH_2 protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

■ **VIII.4.3.** With 2.2 equiv of Ti(O*i*Pr)$_4$, 3.3 equiv of *n*BuLi; reaction conducted at 0 °C for 20 min.



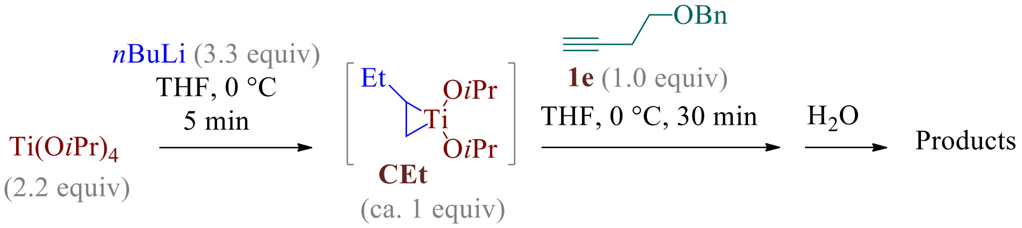
S.m **1e**	Alkene **2e**	Alkene **2′e**	Diene **3e**	Diene **3′e**	Trimer **4e**	Trimer **4′e**	Total
4%	11%	8%	18%	19%	17%	1%	78%

General procedure **GP3** was applied with n = 2.20, p = 3.30, V_1 = 3.5, V_2= 0.5 and t = 20. *n*-Butyllithium solution (2.38 M in hexanes, 3.30 mmol, 1.38 mL) was added over 3 minutes. The THF solution of 4-benzyloxybut-1-yne **1e** (1.00 mmol, 160 mg) was added over 2 minutes. Crude product: yellow oil (164 mg). Analysis as described in subsection VIII.2. (benzyl CH$_2$ protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.



^{1}H NMR spectrum of the crude product (CDCl$_3$, 400 MHz).

■ **VIII.4.4.** With 2.2 equiv of Ti(O*i*Pr)$_4$, 3.3 equiv of *n*BuLi; reaction conducted at 0 °C for 30 min.

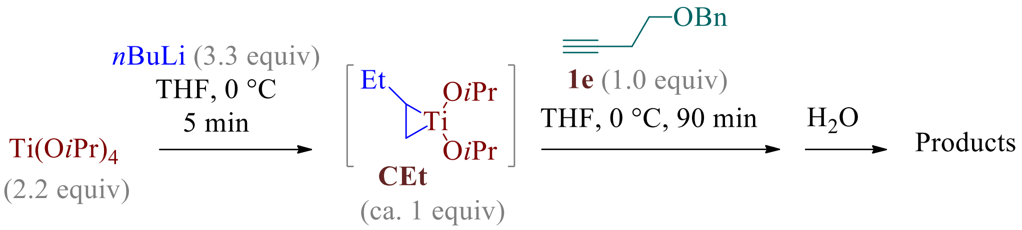


	S.m **1e**	Alkene **2e**	Alkene **2′e**	Diene **3e**	Diene **3′e**	Trimer **4e**	Trimer **4′e**	Total
Run 1	2%	13%	8%	17%	12%	15%	2%	69%
Run 2	3%	9%	8%	14%	8%	22%	2%	66%

- Run 1: General procedure **GP3** was applied with n = 2.20, p = 3.30, V_1 = 3.5, V_2= 0.5 and t = 30. *n*-Butyllithium solution (2.20 M in hexanes, 3.30 mmol, 1.50 mL) was added over 3 minutes. The THF solution of 4-benzyloxybut-1-yne **1e** (1.00 mmol, 160 mg) was added over 2 minutes. Crude product: yellow oil (158 mg). Analysis as described in subsection VIII.2. (benzyl CH_2 protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

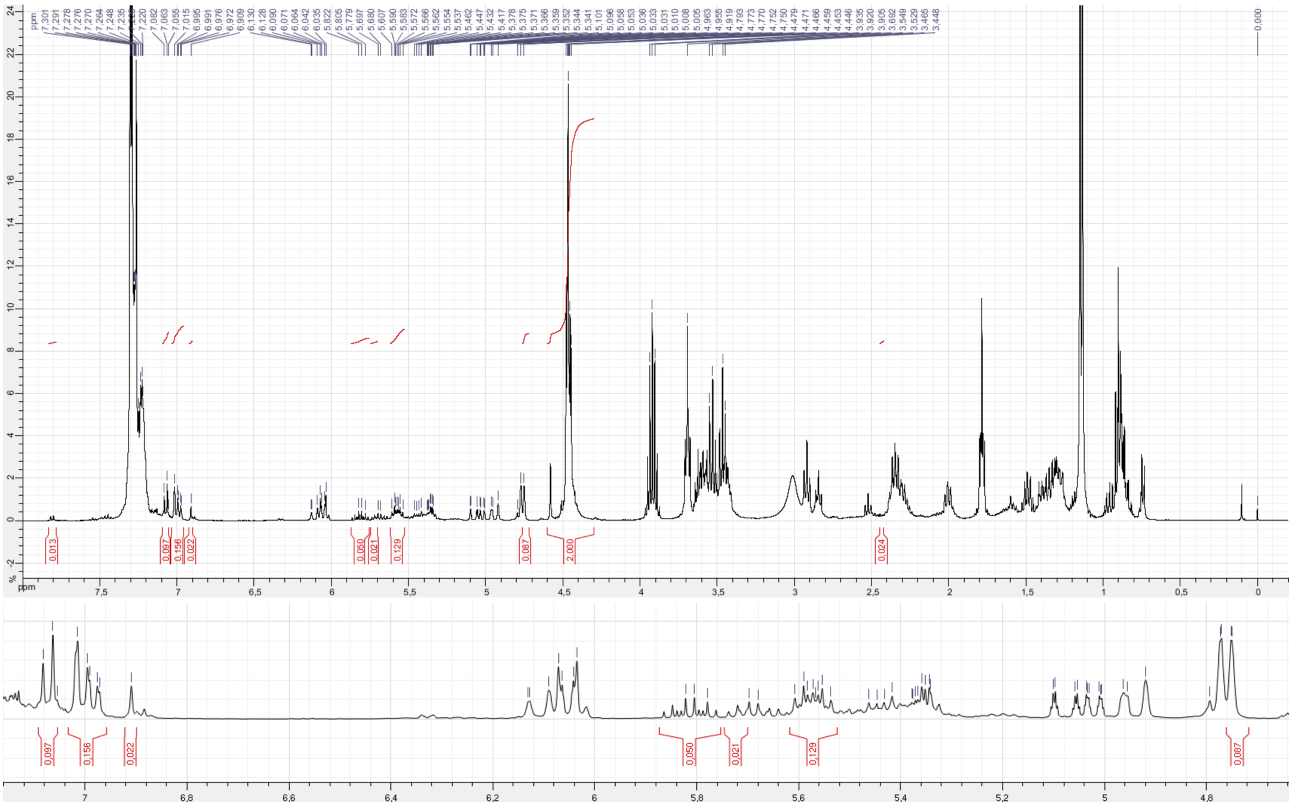
- Run 2: this reaction was repeated with another bottle of *n*-butyllithium solution (2.38 M in hexanes), to afford a yellow oil (158 mg). Analysis of this crude product as described in subsection VIII.2. (benzyl CH_2 protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

■ **VIII.4.5.** With 2.2 equiv of Ti(O*i*Pr)$_4$, 3.3 equiv of *n*BuLi; reaction conducted at 0 °C for 90 min.



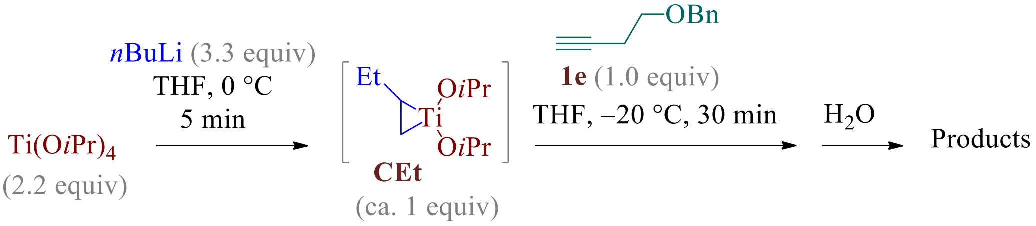
S.m **1e**	Alkene **2e**	Alkene **2′e**	Diene **3e**	Diene **3′e**	Trimer **4e**	Trimer **4′e**	Total
2%	5%	9%	13%	8%	25%	2%	64%

General procedure **GP3** was applied with n = 2.20, p = 3.30, V_1 = 3.5, V_2= 0.5 and t = 90. *n*-Butyllithium solution (2.38 M in hexanes, 3.30 mmol, 1.38 mL) was added over 3 minutes. The THF solution of 4-benzyloxybut-1-yne **1e** (1.00 mmol, 160 mg) was added over 3 minutes. Crude product: yellow oil. Analysis as described in subsection VIII.2. (benzyl CH$_2$ protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.



^{1}H NMR spectrum of the crude product (CDCl$_3$, 400 MHz).

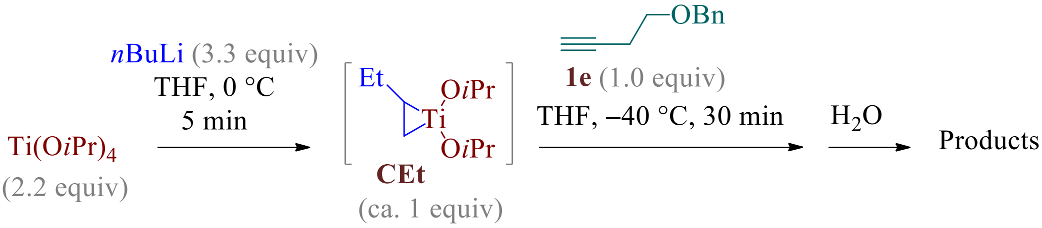
■ **VIII.4.6.** With 2.2 equiv of Ti(O*i*Pr)$_4$, 3.3 equiv of *n*BuLi;
reaction conducted at −20 °C for 30 min.



S.m **1e**	Alkene **2e**	Alkene **2′e**	Diene **3e**	Diene **3′e**	Trimer **4e**	Trimer **4′e**	Total
61%	5%	4%	7%	9%	0%	0%	86%

General procedure **GP4** was applied with $n = 2.20$, $p = 3.30$, $T = -20$ and $t = 30$.
n-Butyllithium solution (2.38 M in hexanes, 3.30 mmol, 1.38 mL) was added over 3 minutes. The THF solution of 4-benzyloxybut-1-yne **1e** (1.00 mmol, 160 mg) was added over 2 minutes. Crude product: yellow oil (158 mg). Analysis as described in subsection VIII.2. (benzyl CH_2 protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

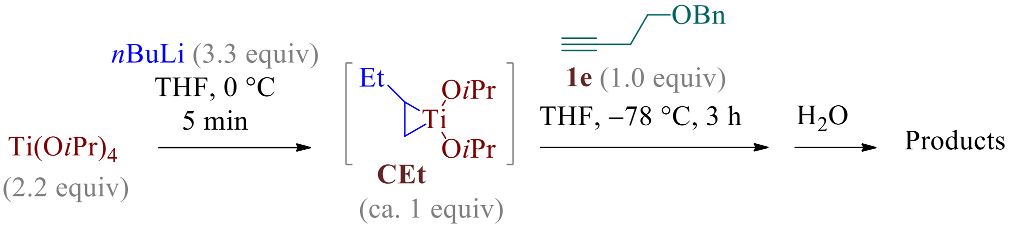
■ **VIII.4.7.** With 2.2 equiv of Ti(O*i*Pr)$_4$, 3.3 equiv of *n*BuLi;
reaction conducted at −40 °C for 30 min.



S.m **1e**	Alkene **2e**	Alkene **2′e**	Diene **3e**	Diene **3′e**	Trimer **4e**	Trimer **4′e**	Total
75%	5%	3%	3%	4%	0%	0%	90%

General procedure **GP4** was applied with $n = 2.20$, $p = 3.30$, $T = -40$ and $t = 30$.
n-Butyllithium solution (2.38 M in hexanes, 3.30 mmol, 1.38 mL) was added over 3 minutes. The THF solution of 4-benzyloxybut-1-yne **1e** (1.00 mmol, 160 mg) was added over 3 minutes. Crude product: pale yellow oil (121 mg). Analysis as described in subsection VIII.2. (benzyl CH_2 protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

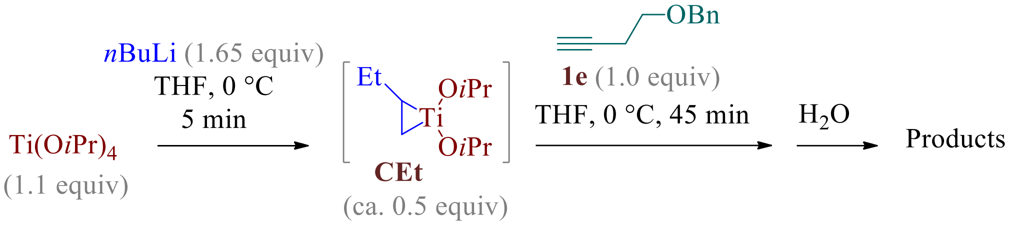
■ **VIII.4.8.** With 2.2 equiv of Ti(O*i*Pr)$_4$, 3.3 equiv of *n*BuLi;
reaction conducted at −78 °C for 120 min.



S.m **1e**	Alkene **2e**	Alkene **2′e**	Diene **3e**	Diene **3′e**	Trimer **4e**	Trimer **4′e**	Total
72%	14%	4%	Traces	Traces	0%	0%	90%

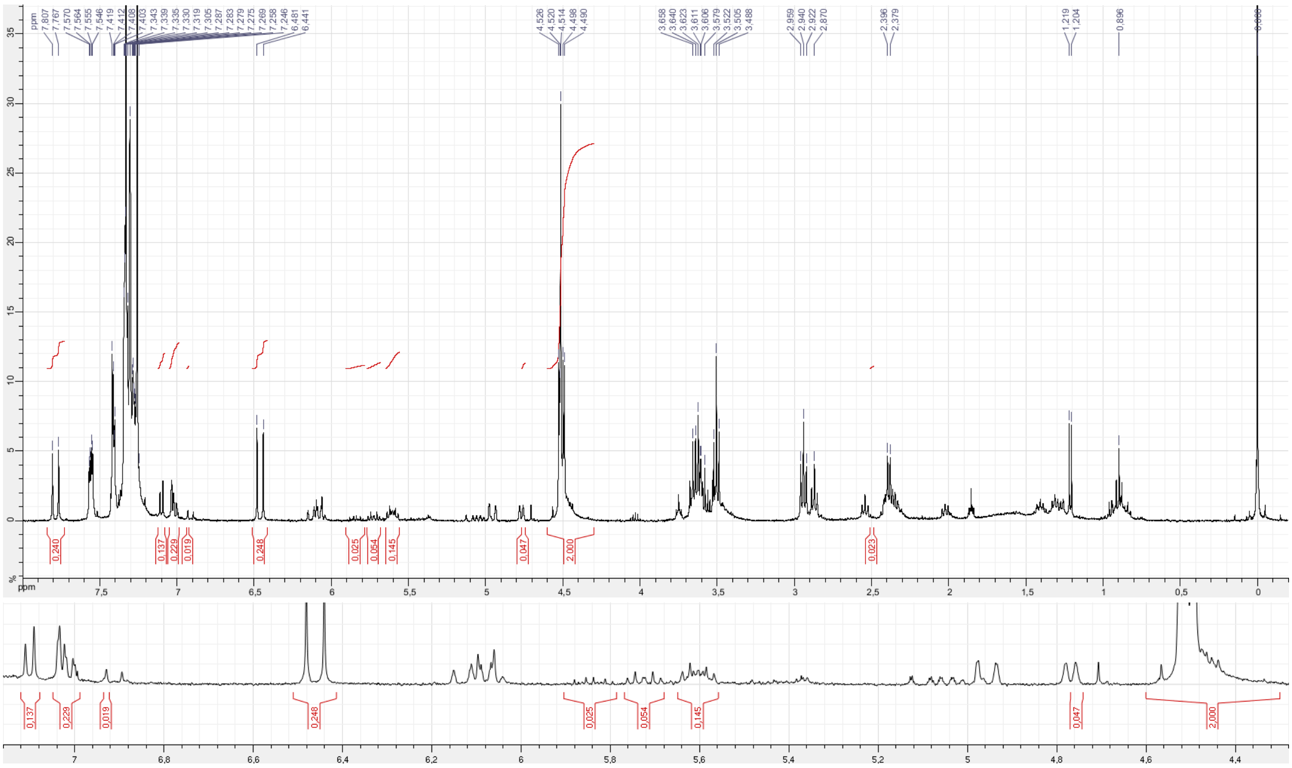
General procedure **GP4** was applied with n = 2.20, p = 3.30, T = −78 and t = 180.
n-Butyllithium solution (2.20 M in hexanes, 3.30 mmol, 1.50 mL) was added over 2 minutes. The THF solution of 4-benzyloxybut-1-yne **1e** (1.00 mmol, 160 mg) was added over 2 minutes. Crude product: colourless oil (119 mg). Analysis as described in subsection VIII.2. (benzyl CH_2 protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

■ **VIII.4.9.** With 1.1 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *n*BuLi; reaction conducted at 0 °C for 45 min.



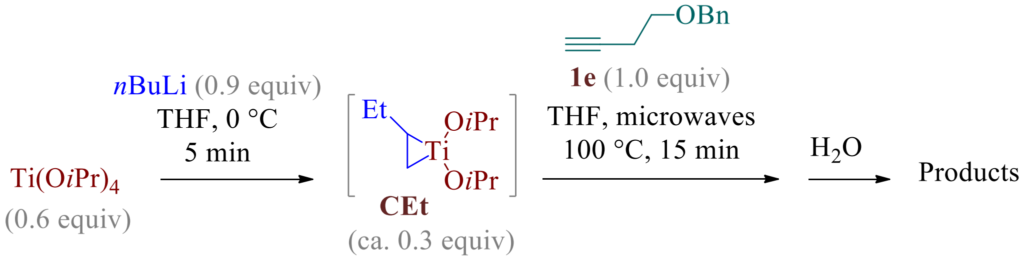
S.m **1e**	Alkene **2e**	Alkene **2′e**	Diene **3e**	Diene **3′e**	Trimer **4e**	Trimer **4′e**	Total
2.3%	2.5%	4.7%	14.5%	10.8%	34.3%	1.9%	71%

General procedure **GP1** was applied with $n = 1.10$, $p = 1.65$, $T = 0$ and $t = 45$.
n-Butyllithium solution (2.31 M in hexanes, 3.30 mmol, 1.43 mL) was added over 3 min. 4-Benzyloxybut-1-yne **1e** (2.00 mmol, 320 mg) was added over 2 min. Crude product: yellow oil (254 mg). Analysis as described in subsection VIII.2. (benzyl CH$_2$ protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.



^{1}H NMR spectrum of the crude product (CDCl$_3$, 400 MHz).

■ **VIII.4.10.** With 0.6 equiv of Ti(O*i*Pr)$_4$, 0.9 equiv of *n*BuLi; reaction conducted at 100 °C for 15 min, under microwave conditions.



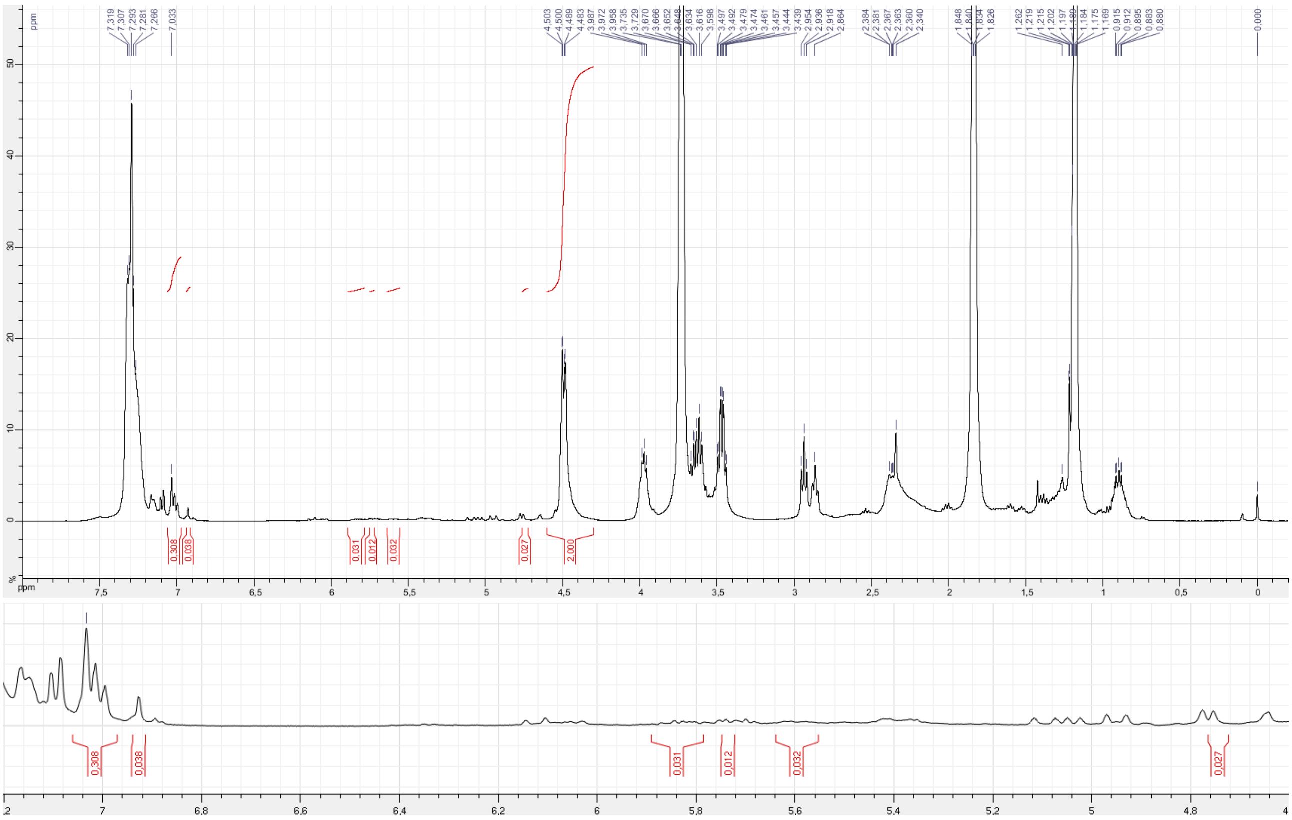
S.m **1e**	Alkene **2e**	Alkene **2′e**	Diene **3e**	Diene **3′e**	Trimer **4e**	Trimer **4′e**	Total
0%	3%	3%	3%	5% (5%)	46% (37%)	4% (3%)	64%

In parentheses: yields of isolated products.

General procedure **GP7** was applied with *T* = 100 and with 4-benzyloxybut-1-yne **1e** (3.00 mmol, 481 mg) as the substrate.

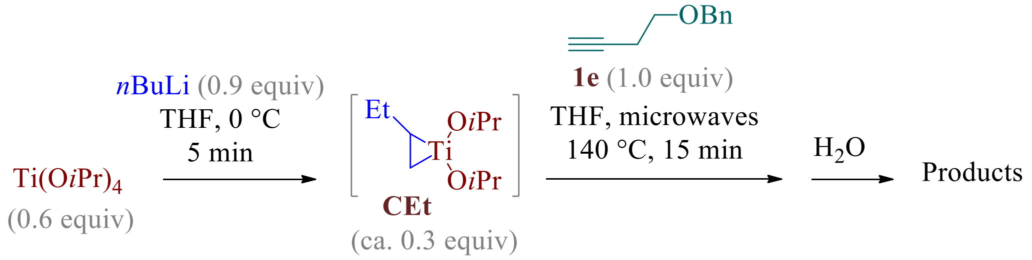
Crude product: yellow oil (390 mg). Analysis as described in subsection VIII.2. (benzyl CH$_2$ protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

Flash column chromatography (silica gel, EtOAc/petroleum ether, gradient from 2% to 20%) afforded relatively pure diene **3′e** (23.9 mg, 74.1 µmol, 5%) and a 92 : 8 mixture of pure **4e** and **4′e** (192 mg, 399 µmol, 40%).



^{1}H NMR spectrum of the crude product (CDCl$_3$, 400 MHz).

■ **VIII.4.11.** With 0.6 equiv of Ti(O*i*Pr)$_4$, 0.9 equiv of *n*BuLi; reaction conducted at 140 °C for 15 min, under microwave conditions.



	S.m **1e**	Alkene **2e**	Alkene **2′e**	Diene **3e**	Diene **3′e**	Trimer **4e**	Trimer **4′e**	Total
Run 1	0%	6%	1%	Not determined[a]		38% (13%)	8% (1%)	53%
Run 2	0%	5%	2%	2%	8%	44%	4%	65%
Run 3	0%	4%	2%	2%	4%	44% (31%)	4% (3%)	60%

In parentheses: yields of isolated products.

[a] The characteristic signals of these compounds overlapped with those of unidentified products.

- Run 1: General procedure **GP7** was applied with $T = 140$ and with 4-benzyloxybut-1-yne **1e** (3.00 mmol, 481 mg) as the substrate.

Crude product: brown oil (447 mg). Analysis as described in subsection VIII.2. (benzyl CH$_2$ protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

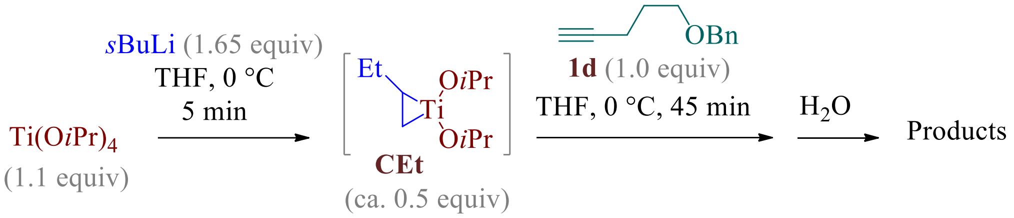
Flash column chromatography (silica gel, EtOAc/petroleum ether, gradient from 2% to 20%) afforded a 91 : 9 mixture of pure **4e** and **4′e** (67.2 mg, 140 µmol, 14%).

- Run 2: this reaction was repeated under the same conditions, to afford a brown oil (499 mg). Analysis of this crude product as described in subsection VIII.2. (benzyl CH$_2$ protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

- Run 3: the reaction was repeated under the same conditions, to afford an orange oil (413 mg). Analysis of this crude product as described in subsection VIII.2. (benzyl CH$_2$ protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

Flash column chromatography (silica gel, EtOAc/petroleum ether, gradient from 2% to 20%) afforded a 92 : 8 mixture of pure **4e** and **4′e** (163 mg, 338 µmol, 34%).

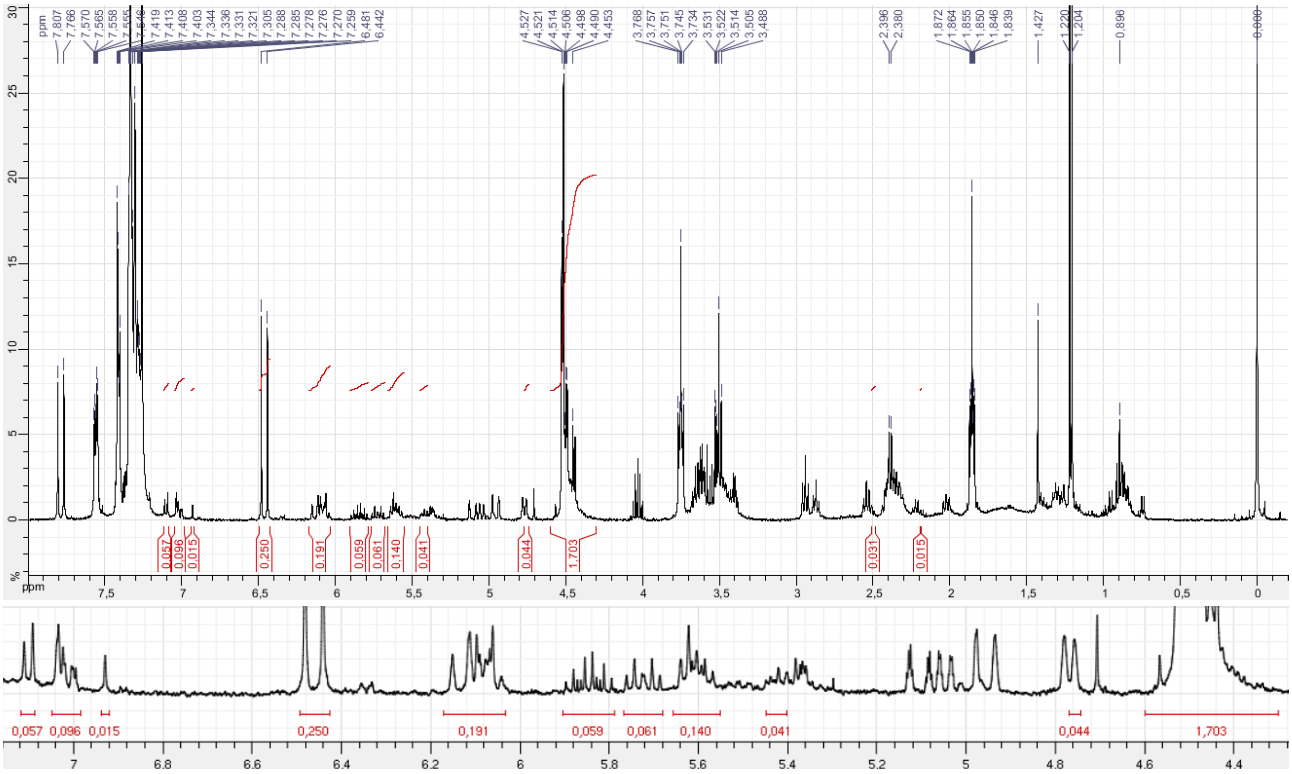
■ **VIII.4.12.** With 1.1 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *s*BuLi (“old” bottle #1); reaction conducted at 0 °C for 45 min.



S.m **1e**	Alkene **2e**	Alkene **2′e**	Diene **3e**	Diene **3′e**	Trimer **4e**	Trimer **4′e**	Tetramer **5e**	Total
3.1%	5.9%	4.4%	9.5%	12.2%	14.4%	1.5%	9.0%	60%

General procedure **GP1** was applied with *n* = 1.10, *p* = 1.65 and *t* = 45. *s*-Butyllithium solution (1.23 M in cyclohexane, 3.30 mmol, 2.68 mL) was added over 3.5 min. 4-Benzyloxybut-1-yne **1e** (2.00 mmol, 320 mg) was added over 1.5 min. Crude product: yellow oil (304 mg). Analysis as described in subsection VIII.2. [(*E*)-cinnamic acid as an internal standard] gave the qualitative estimation of the product yields shown in the table above.

Flash column chromatography (silica gel, EtOAc/petroleum ether, gradient from 5% to 50%) afforded a 59 : 15 : 26 mixture of **4e**, **4′e** and **5e** (26.4 mg) and other fractions containing more complex mixtures.



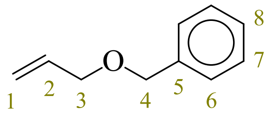
^{1}H NMR spectrum of the crude product ($CDCl_3$, 400 MHz).

IX. Experiments with 3-benzyloxyprop-1-yne **1f**

IX.1. Characterisation of the products

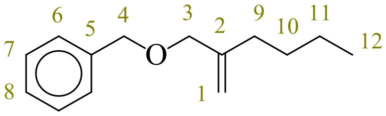
Products **2′f**, **3f** and **4f** could be isolated in reasonably pure form. Conversely, **2f** and the minor isomers of the diene and cyclotrimer products, **3′f** and **4′f**, were obtained as components of more or less complex mixtures. In these cases, assignment of the signals was done as explained in the general information.

3-Benzyloxyprop-1-ene **2f**[36]

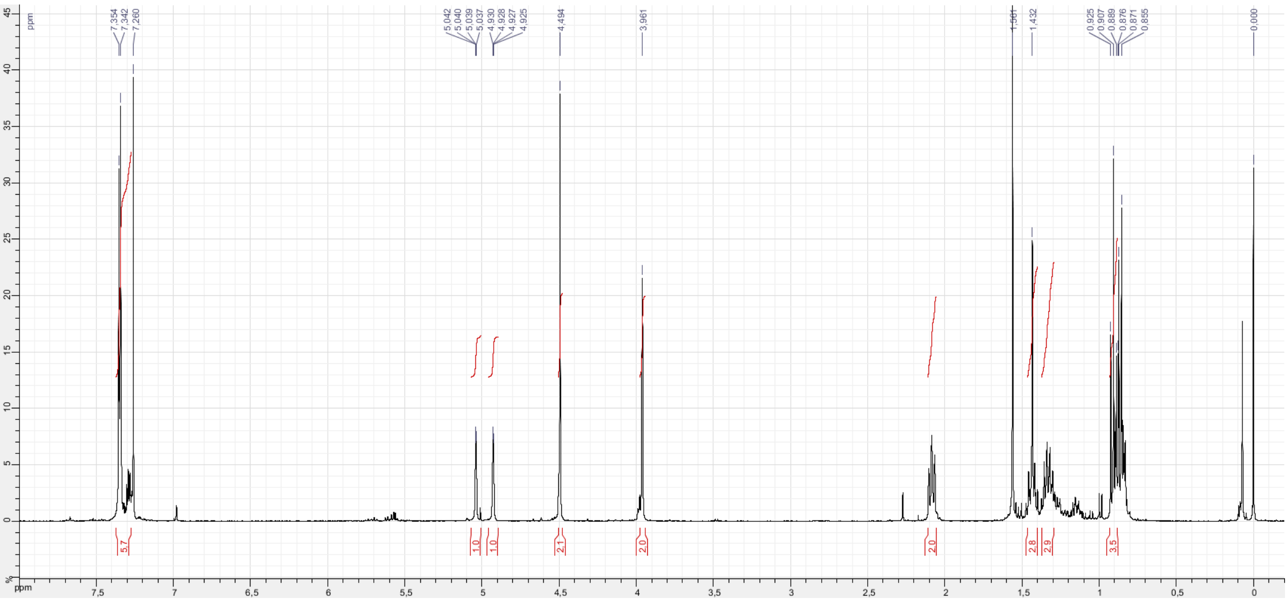


^{1}H NMR (CDCl$_3$, 400 MHz), characteristic signal: δ 5.95 (1 H, ddt, *J* 17.5, 10.5, 5.5, H2).

2-Methylenehexoxymethylbenzene **2′f**



^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.91 (3 H, t, *J* 7.5, H12), 1.34 (2 H, quint, *J* 7.5, H11), 1.44 (2 H, quint, *J* 7.5, H10), 2.08 (2 H, t, *J* 7.5, H9), 3.96 (2 H, br s, H3), 4.49 (2 H, s, H4), 4.93 (1 H, br s, H1a), 5.04 (1 H, br s, H1b), 7.29 (1 H, m, H8), 7.32−7.38 (4 H, m, H6−H7).
^{13}C NMR (CDCl$_3$, 100.6 MHz), characteristic signals: δ 14.0 (C12), 22.5 (C11), 71.9 (C3), 73.1 (C4), 111.4 (C1), 127.5 (C8), 127.7 (C6), 128.3 (C7), 138.5 (C5), 146.3 (C2).



^{1}H NMR spectrum (CDCl$_3$, 400 MHz).

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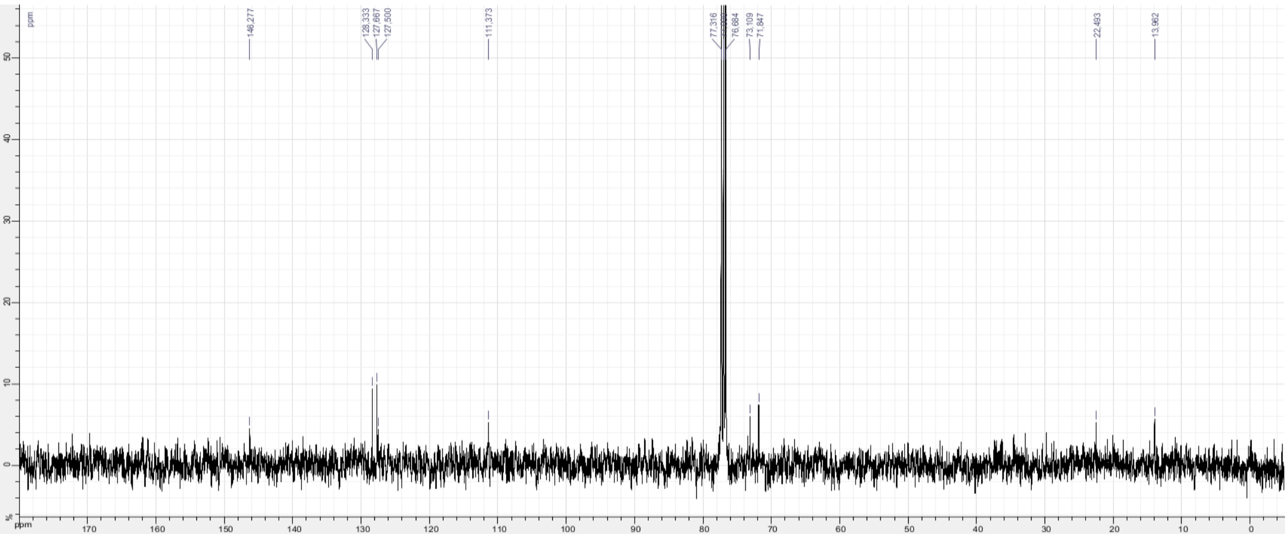
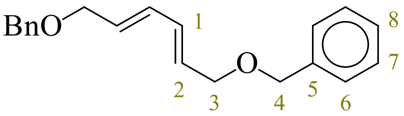
[36] K. C. Nicolaou, A. P. Patron, K. Ajito, P. K. Richter, H. Khatuya, P. Bertinato, R. A. Miller, M. J. Tomaszewski, *Chem. Eur. J.* **1996**, *2*, 847−868.

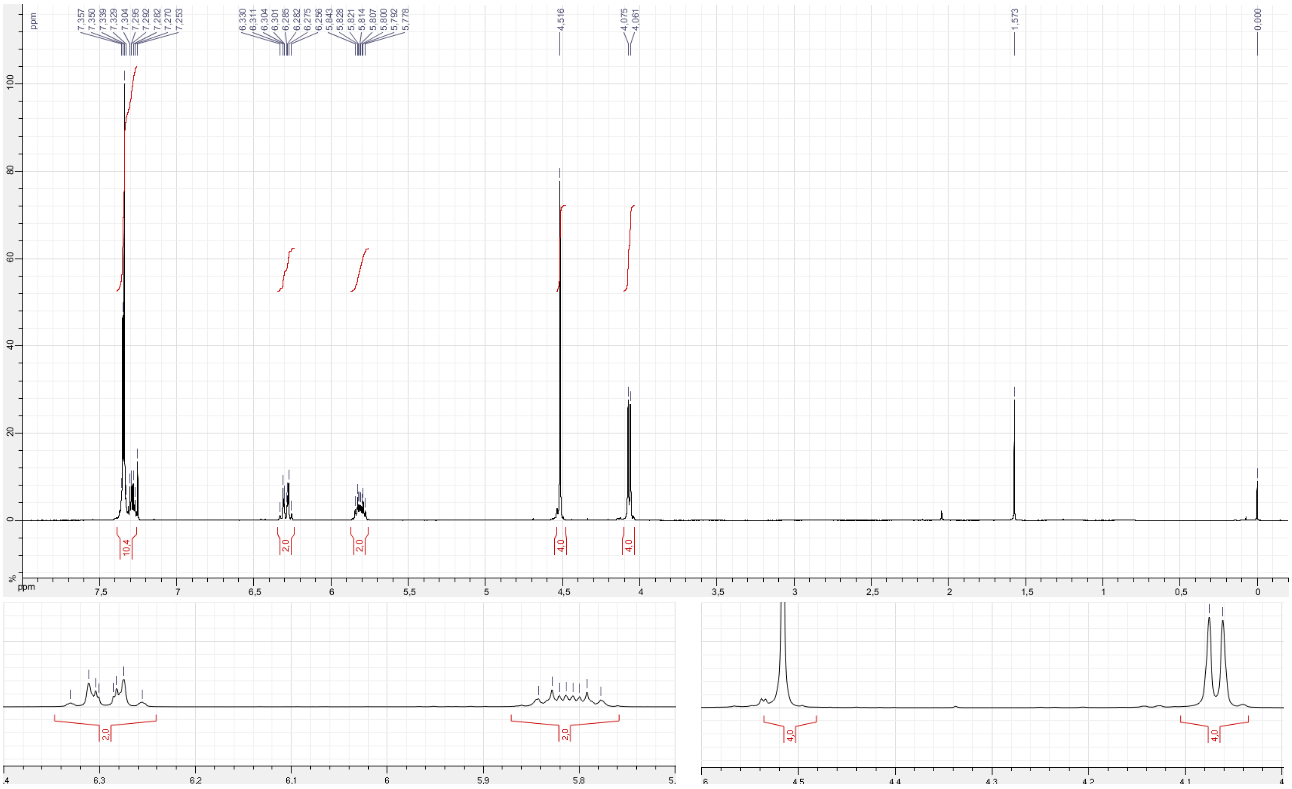


^{13}C NMR spectrum ($CDCl_3$, 100.6 MHz).

[(2*E*,4*E*)-6-Benzyloxyhexa-2,4-dienoxy]methylbenzene **3f**[37]



R_f 0.25 (EtOAc/Petroleum ether 5%, UV-active, phosphomolybdic acid). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 4.07 (4 H, d, *J* 5.5, H3), 4.52 (4 H, s, H4), 5.81 (2 H, m, H2), 6.29 (2 H, m, H1), 7.29 (2 H, m, H8), 7.31−7.38 (8 H, m, H6−H7). ^{13}C NMR ($CDCl_3$, 100.6 MHz): *δ* 70.2 (C3), 72.1 (C4), 127.6 (C8), 127.7 (C6), 128.4 (C7), 129.9 (C2), 132.0 (C1), 138.2 (C5).



^{1}H NMR spectrum ($CDCl_3$, 400 MHz).

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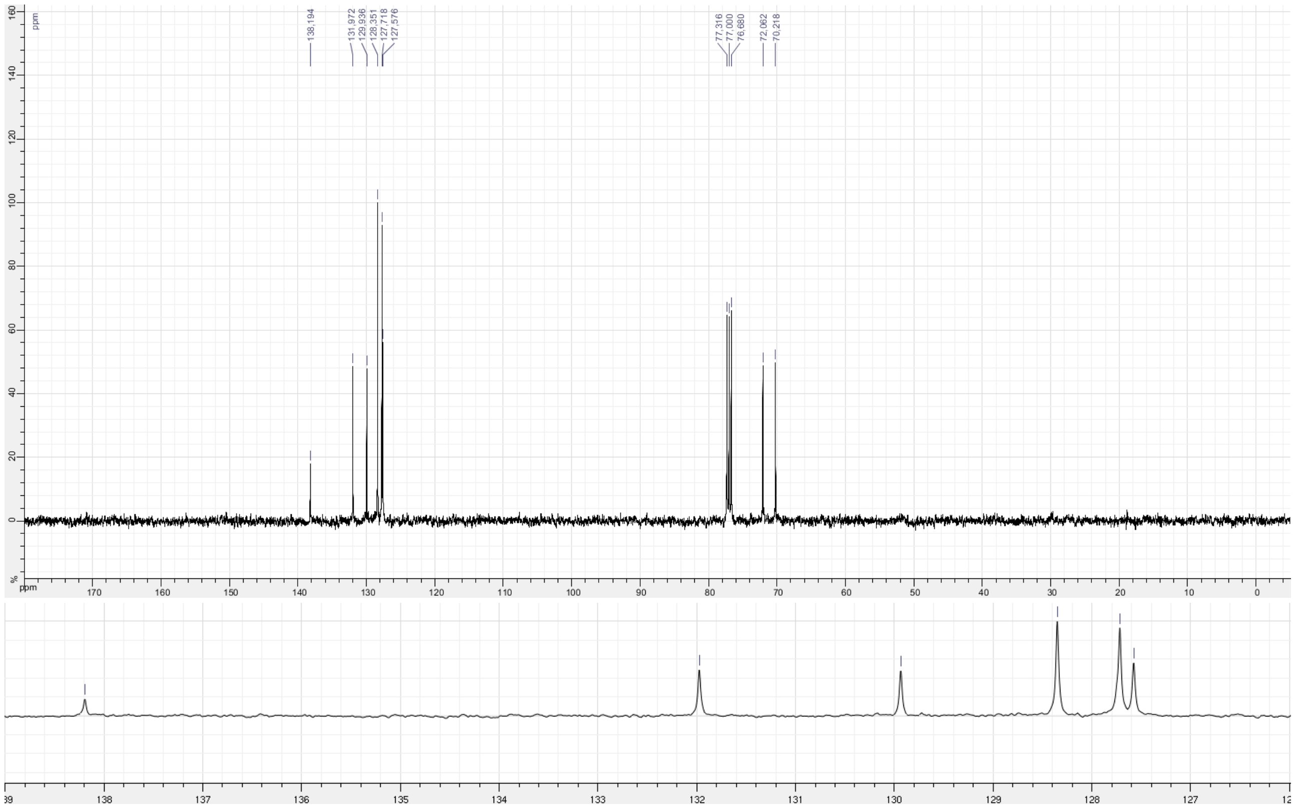
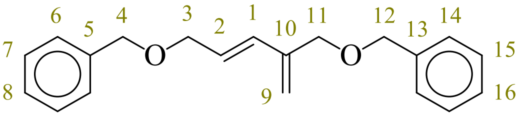
[37] T. Ishikawa, A. Ogawa, T. Hirao, *J. Organomet. Chem.* **1999**, *575*, 76−79.



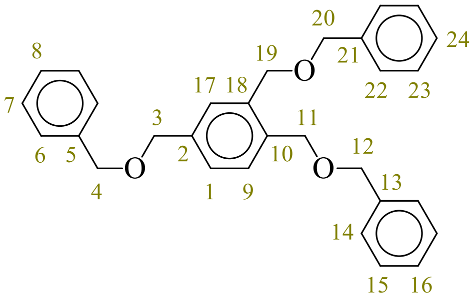
^{13}C NMR spectrum ($CDCl_3$, 100.6 MHz).

[(*E*)-5-Benzyloxy-2-methylene-pent-3-enoxy]methylbenzene **3′f**

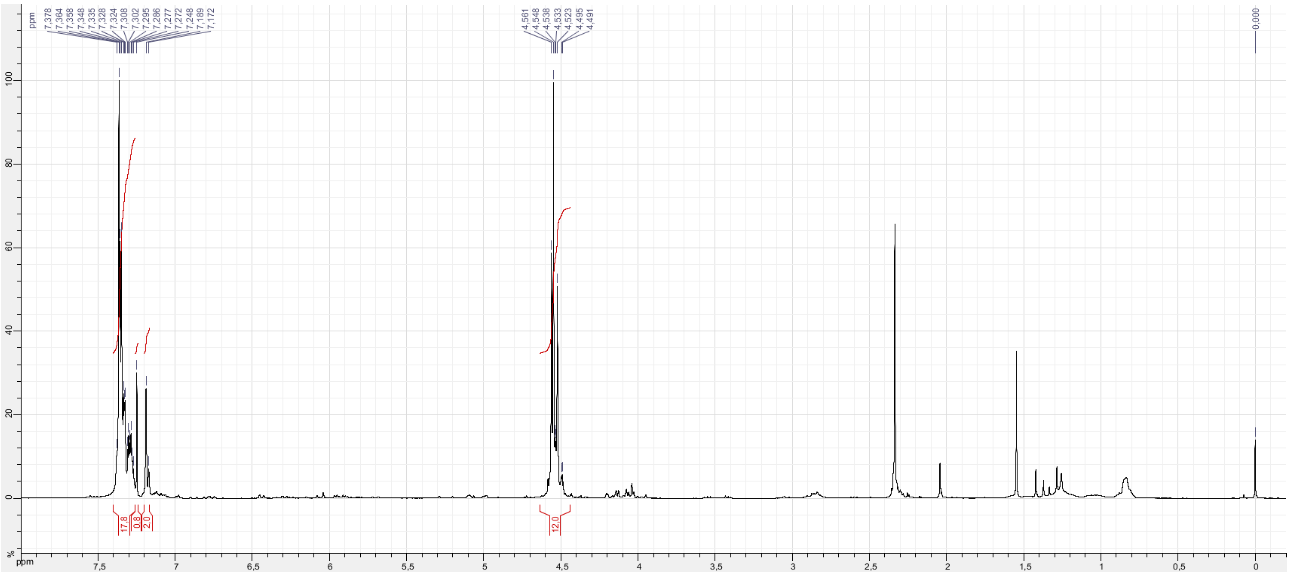


^{1}H NMR ($CDCl_3$, 400 MHz), characteristic signal: δ 5.91 (1 H, dt, *J* 16.0, 6.0, H2).

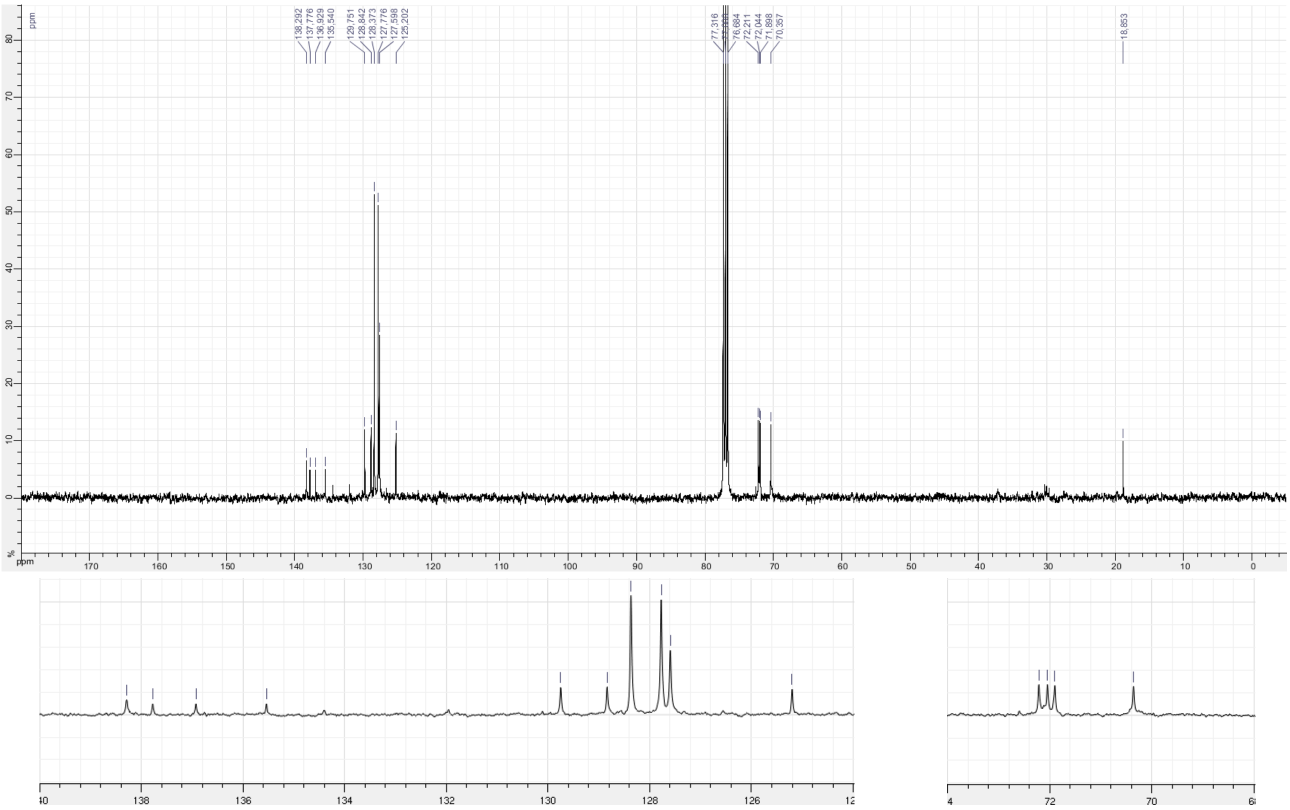
1,2,4-Tris(benzyloxymethyl)benzene **4f**



R$_f$ 0.2 [CH_2Cl_2/Petroleum ether 50% (two successive migrations were performed), UV-active, phosphomolybdic acid]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.52 (4 H, br s, H11, H19), 4.55 (6 H, br s, H4, H12, H20), 4.56 (2 H, s, H3), 7.18 (1 H, d, J 7.5, H9), 7.19 (1 H, br s, H17), 7.26−7.39 (16 H, m, H1, H6−H8, H14−H16, H22−H24). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 70.4, 70.4 (C11, C19), 71.9, 72.0 (C3, C4), 72.2, 72.2 (C12, C20), 125.2 (C1), 127.6, 127.6, 127.6 (C8, C16, C24), 127.8, 127.8, 127.8 (C6, C14, C22), 128.4, 128.4, 128.4 (C7, C15, C23), 128.8 (C9), 129.8 (C17), 135.5 (C2), 138.3, 138.3, 138.3 (C5, C13, C21), 136.9, 137.8 (C10, C18).

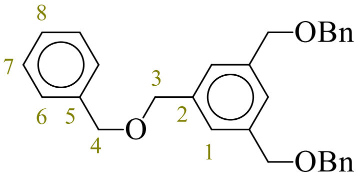


^{1}H NMR spectrum (CDCl$_3$, 400 MHz).
Note: this sample contained significant amounts of impurities.



^{13}C NMR spectrum (CDCl$_3$, 100.6 MHz).
Note: this sample contained significant amounts of impurities.

1,3,5-Tris(benzyloxymethyl)benzene **4′f**



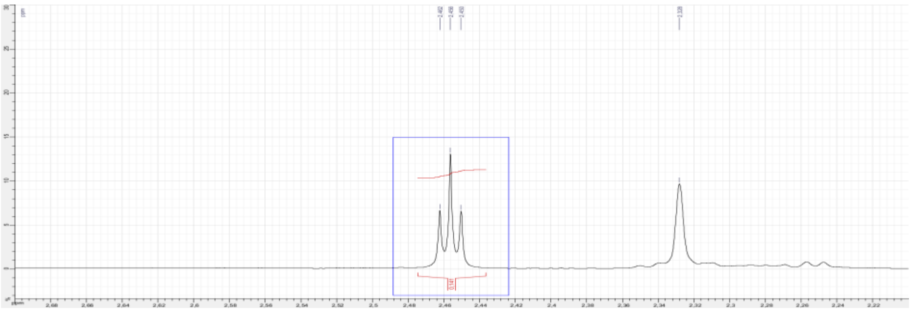
^{1}H NMR (CDCl$_3$, 400 MHz), characteristic signal: δ 7.22 (3 H, s, H1).

IX.2. Analysis of the crude products by NMR spectroscopy

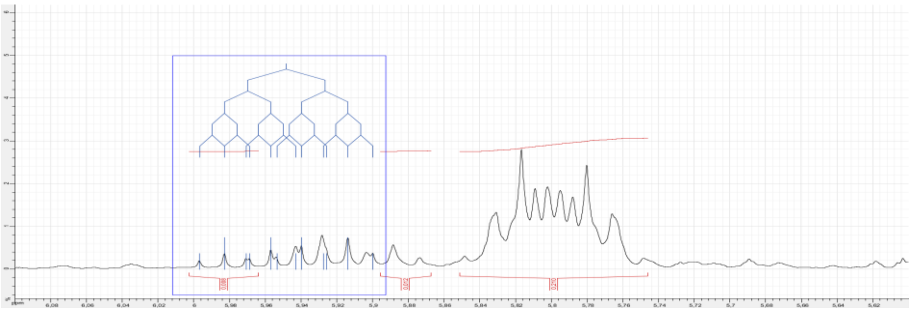
■ In the ^{1}H NMR spectrum of the crude products, the integral of the signals in the interval 4.36−4.63 ppm was set to 2.00: the benzyl CH$_2$ protons were used as an internal standard. Alternatively, (*E*)-cinnamic acid (250 µmol, 37.05 mg) was added to the crude products and the doublet at 6.46 ppm (vinylic CH proton) was used as an internal standard (the integral was set to 0.125).

■ The following signals were used for the qualitative assessment of the product yields:

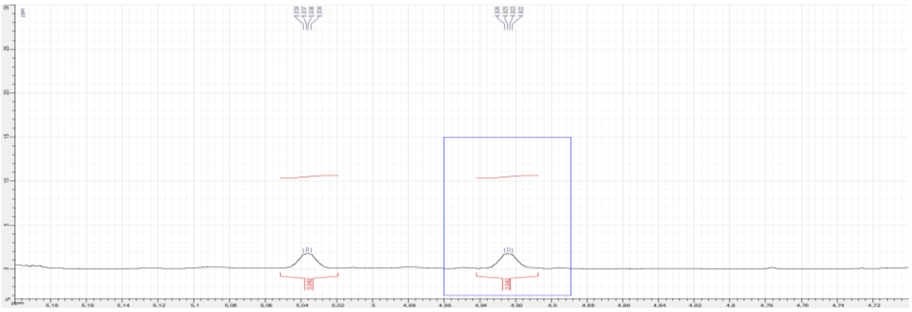
- Triplet (*J* 2.5 Hz) at 2.46 ppm: one proton of **1f**.
  The integral of this signal gave an estimation of the proportion of unconverted **1f**;



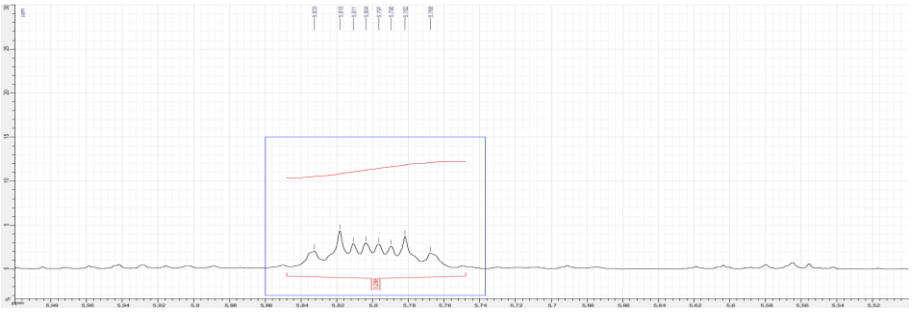
- Doublet of doublet of triplets (*J* 17.5, 10.5 and 5.5 Hz) at 5.95 ppm: one proton of **2f**.
  The integral of the four far-left peaks of this signal was measured, then multiplied by 16/5 to give an estimation of the yield of **2f**;



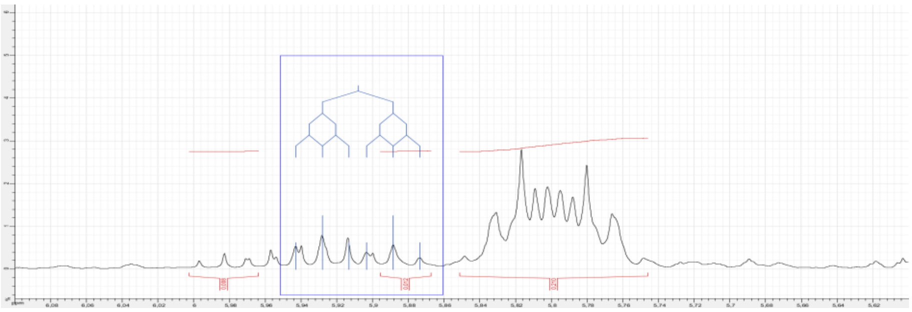
- Broad singlet at 4.93 ppm: one proton of **2′f**.
  The integral of this signal gave an estimation of the yield of **2′f**;



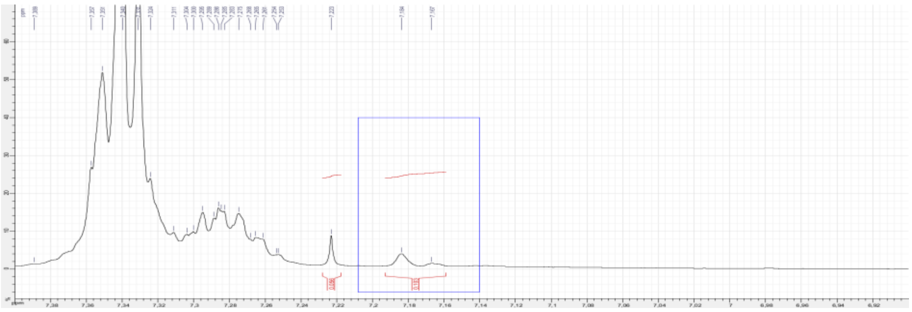
- Multiplet at 5.80 ppm: two protons of **3f**.
  The integral of this signal gave an estimation of the yield of **3f**;



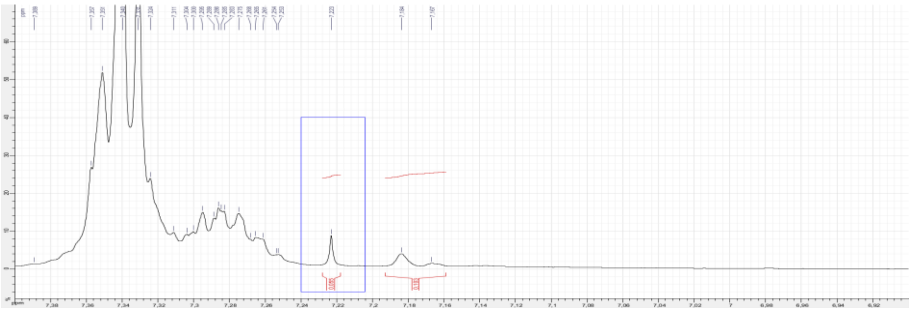
- Doublet of triplets (*J* 16.0 and 6.0 Hz) at 5.91 ppm: one proton of **3′f**.
  The integral of the two far-right peaks of this signal was measured, then multiplied by 8/3 to give an estimation of the yield of **3′f**;



- Multiplet in the range 7.16−7.20 ppm: two protons of **4f**.
  The integral of this signal was multiplied by 3/2 to give an estimation of the yield of **4f**;

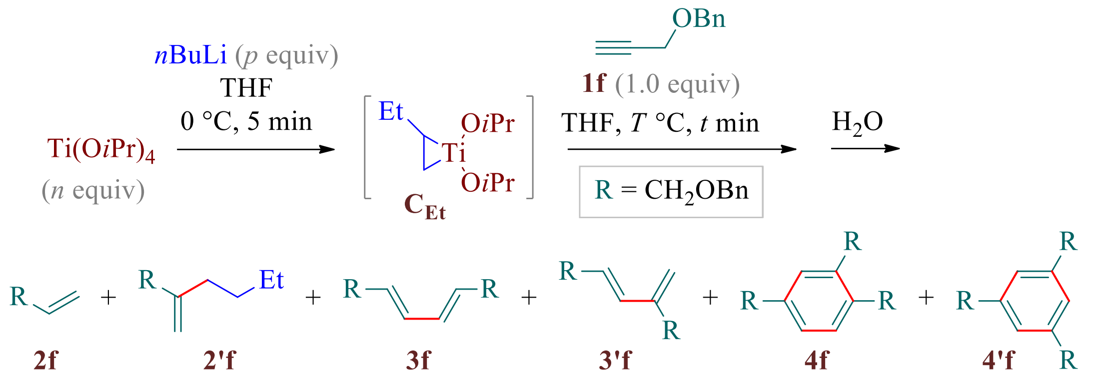


- Singlet at 7.22 ppm: three protons of **4′f**.
  The integral of this signal gave an estimation of the yield of **4′f**.



■ The amount of benzyl alcohol was determined by ^{13}C NMR spectroscopy, by comparing the intensities of the peaks of the PhCH_2O carbons for benzyl alcohol (*δ* 64.6 ppm) and for starting 3-benzyloxyprop-1-yne (*δ* 74.6 ppm).

IX.3. Summary of the experimental results obtained using **1f**



Subsection	*n*	*p*	*T*	*t*	S.m. **1f**	Alkene **2f**	Alkene **2′f**	Dienes **3f/3′f** (ratio)	Trimers **4f/4′f** (ratio)
IX.4.1.[a]	4.4	6.6	0	20	2%	4%	6%	13% (85 : 15)	0%
IX.4.2.[a]	2.2	3.3	0	20	4%	3%	5%	19% (95 : 5)	Not detected
IX.4.3.	1.2	1.8	0	30	11%	1%	4%	30% (93 : 7)	21% (86 : 14)
IX.4.4.			−20		67%	2%	2%	11% (91 : 9)	8% (75 : 25)
IX.4.5.	1.1	1.65	0	20	43%	3%	3%	24% (87 : 13)	10% (90 : 10)
IX.4.6.[b]				30	16%	2%	4%	29% (93 : 7)	17% (86 : 14)
IX.4.7.[a]				45	7%	3%	4%	26% (92 : 8)	18% (>95 : 5)

Colours for the starting material: 🟥 0−10% 🟥 11−20% 🟥 21−30% 🟥 31−40% 🟥 ≥41%

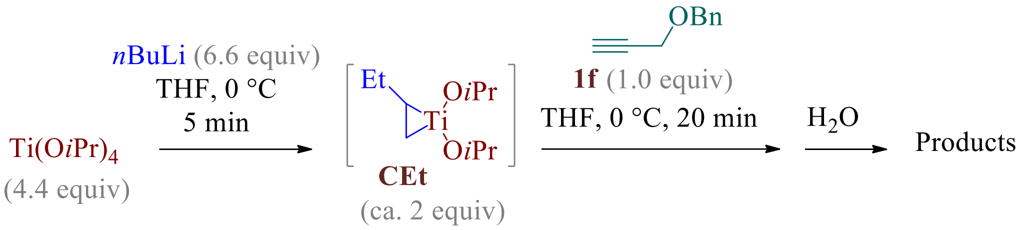
Colours for the products: 🟩 0−10% 🟩 11−20% 🟩 21−30% 🟩 31−40% 🟩 ≥41%

[a] Benzyl alcohol was the major product observed.

[b] Mean values are given for the yields, calculated from the similar results of two runs carried out under the same conditions.

IX.4. Experimental detail

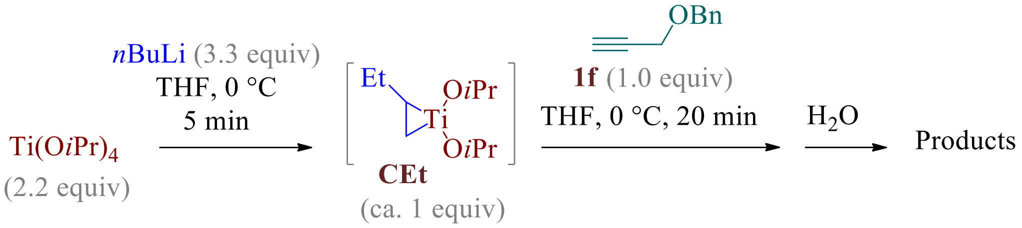
■ **IX.4.1.** With 4.4 equiv of Ti(O*i*Pr)$_4$, 6.6 equiv of *n*BuLi; reaction conducted at 0 °C for 20 min.



S.m **1f**	Alkene **2f**	Alkene **2′f**	Diene **3f**	Diene **3′f**	Trimer **4f**	Trimer **4′f**	Benzyl alcohol	Total
2%	4%	6%	11%	2%	0%	0%	Major product	>25%

General procedure **GP3** was applied with *n* = 4.40, *p* = 6.60, V_1 = 3.5, V_2= 0.5 and *t* = 20. *n*-Butyllithium solution (2.38 M in hexanes, 6.60 mmol, 2.77 mL) was added over 4 minutes. The THF solution of 3-benzyloxyprop-1-yne **1f** (1.00 mmol, 146 mg) was added over 4 minutes. Crude product: dark yellow oil (143 mg). Analysis as described in subsection IX.2. (benzyl CH_2 protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

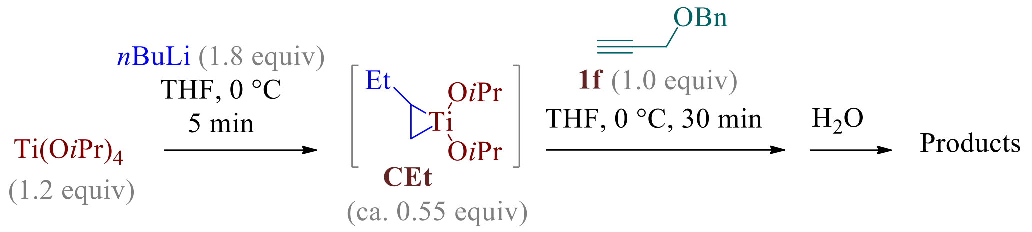
■ **IX.4.2.** With 2.2 equiv of Ti(O*i*Pr)$_4$, 3.3 equiv of *n*BuLi; reaction conducted at 0 °C for 20 min.



S.m **1f**	Alkene **2f**	Alkene **2′f**	Diene **3f**	Diene **3′f**	Trimer **4f**	Trimer **4′f**	Benzyl alcohol	Total
4%	3%	5%	18%	1%	Not detected	Not detected	58%	89%

General procedure **GP3** was applied with *n* = 2.20, *p* = 3.30, V_1 = 3.5, V_2= 0.5 and *t* = 20. *n*-Butyllithium solution (2.38 M in hexanes, 3.30 mmol, 1.38 mL) was added over 3 minutes. The THF solution of 3-benzyloxyprop-1-yne **1f** (1.00 mmol, 146 mg) was added over 3 minutes. Crude product: dark yellow oil (108 mg). Analysis as described in subsection IX.2. (benzyl CH_2 protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

■ **IX.4.3.** With 1.2 equiv of Ti(O*i*Pr)$_4$, 1.8 equiv of *n*BuLi; reaction conducted at 0 °C for 30 min.

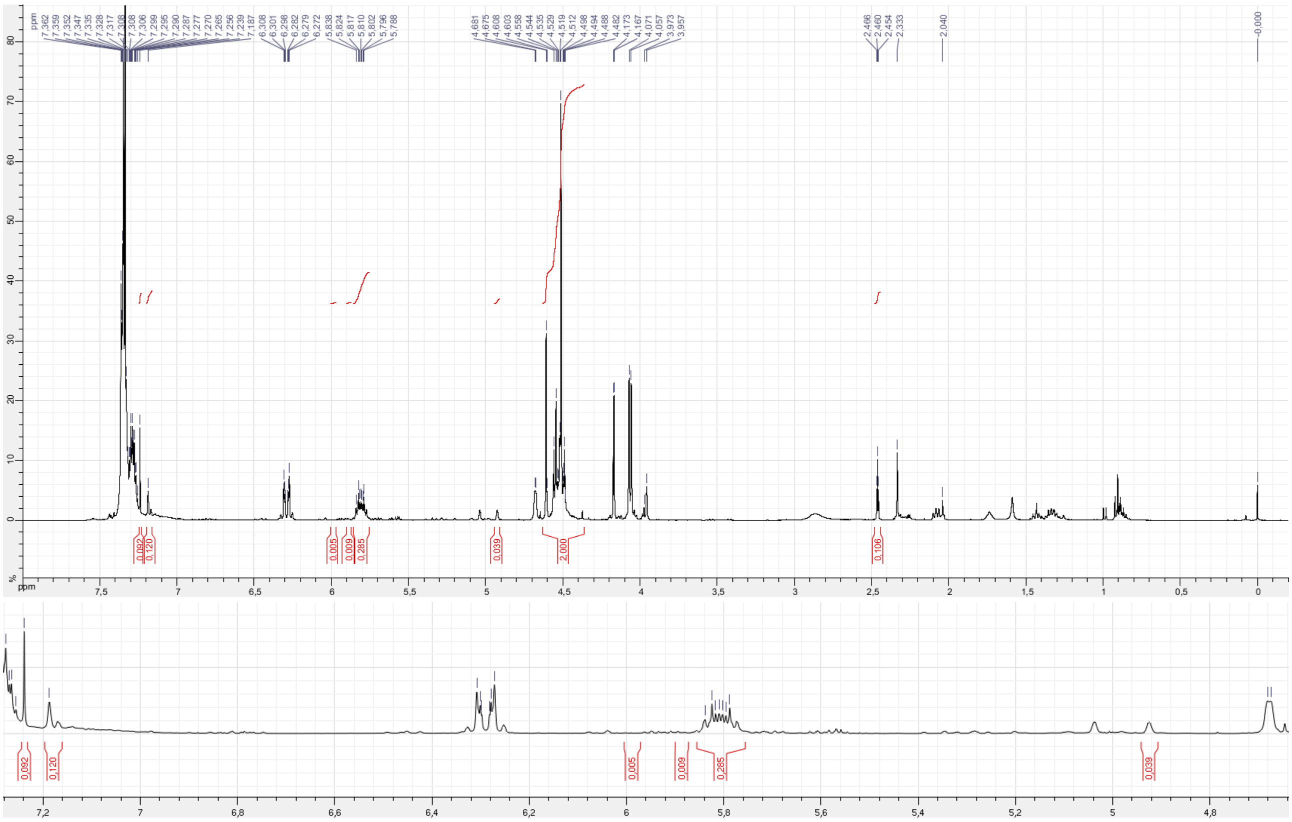


S.m **1f**	Alkene **2f**	Alkene **2′f**	Diene **3f**	Diene **3′f**	Trimer **4f**	Trimer **4′f**	Benzyl alcohol	Total
11%	1%	4%	28% (21%)	2%	18% (5%)	3%	7%	91%

In parentheses: yields of isolated products.

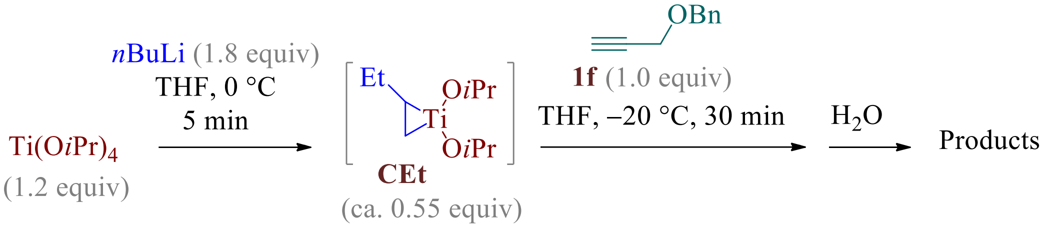
General procedure **GP5** was applied with *n* = 1.20, *p* = 1.80 and *t* = 30. *n*-Butyllithium solution (2.38 M in hexanes, 1.80 mmol, 756 µL) was added over 4 minutes. 3-Benzyloxyprop-1-yne **1f** (1.00 mmol, 146 mg) was added over 3 minutes. Crude product: dark yellow oil (86.7 mg).
Analysis as described in subsection IX.2. (benzyl CH$_2$ protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

Flash column chromatography (silica gel, CH$_2$Cl$_2$/petroleum ether, gradient from 10% to 100%) afforded fairly pure 1,2,4-tris(benzyloxymethyl)benzene **4f** (7.3 mg, 17 µmol, 5%) and pure [(2*E*,4*E*)-6-benzyloxyhexa-2,4-dienoxy]methylbenzene **3f** (31.1 mg, 106 µmol, 21%).



^{1}H NMR spectrum of the crude product (CDCl$_3$, 400 MHz).

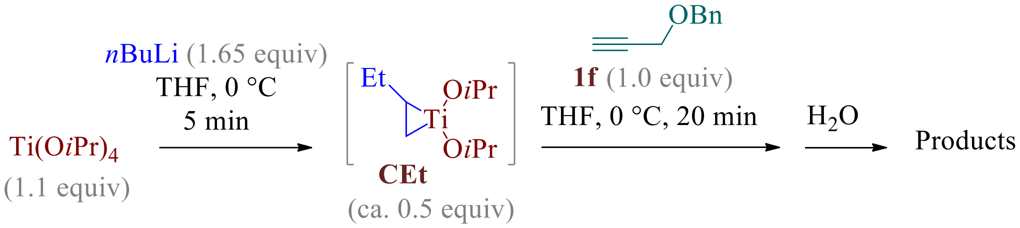
■ **IX.4.4.** With 1.2 equiv of $\mathrm{Ti(O\mathit{i}Pr)_4}$, 1.8 equiv of *n*BuLi; reaction conducted at −20 °C for 30 min.



S.m **1f**	Alkene **2f**	Alkene **2′f**	Diene **3f**	Diene **3′f**	Trimer **4f**	Trimer **4′f**	Benzyl alcohol	Total
67%	2%	2%	10%	1%	6%	2%	0%	90%

n-Butyllithium solution (2.38 M in hexanes, 1.80 equiv, 1.80 mmol, 756 µL) was added dropwise, over 3 minutes, at 0 °C, to a solution of titanium(IV) isopropoxide (1.20 equiv, 1.20 mmol, 355 µL) in THF (2.0 mL).[16] After 5 minutes of stirring at 0 °C, the mixture was cooled to −20 °C and 3-benzyloxyprop-1-yne (1.00 equiv, 1.00 mmol, 146 mg) was added dropwise, over 3 minutes.[16] The mixture was stirred at −20 °C for an additional 30 minutes. H_2O (0.25 mL) was then added and the septum was removed to expose the mixture to air. After 15 minutes of stirring, the dark colour had disappeared. The mixture was then filtered through a pad of sand, celite, $MgSO_4$ and sand [from top to bottom; rinsing with Et_2O (20 mL)] and concentrated under reduced pressure to afford a pale yellow oil (112 mg). Analysis of this crude product as described in subsection IX.2. (benzyl CH_2 protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

■ **IX.4.5.** With 1.1 equiv of $\mathrm{Ti(O\mathit{i}Pr)_4}$, 1.65 equiv of *n*BuLi; reaction conducted at 0 °C for 20 min.

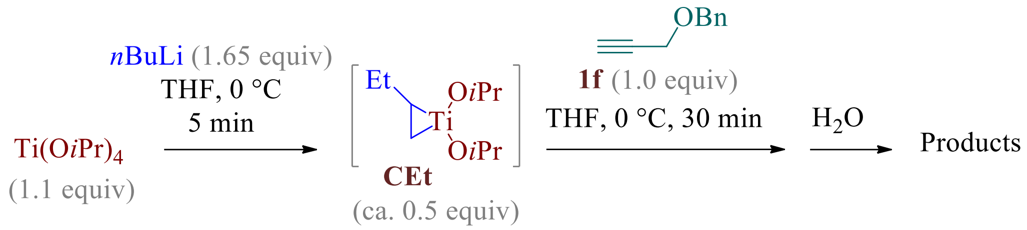


S.m **1f**	Alkene **2f**	Alkene **2′f**	Diene **3f**	Diene **3′f**	Trimer **4f**	Trimer **4′f**	Benzyl alcohol	Total
43%	3%	3%	21%	3%	9%	1%	8%	91%

General procedure **GP5** was applied with $n = 1.10$, $p = 1.65$ and $t = 20$. *n*-Butyllithium solution (2.38 M in hexanes, 1.65 mmol, 693 µL) was added over 3 minutes. 3-Benzyloxyprop-1-yne **1f** (1.00 mmol, 146 mg) was added over 3 minutes. Crude product: yellow oil (102 mg).

Analysis as described in subsection IX.2. (benzyl CH_2 protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

■ **IX.4.6.** With 1.1 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *n*BuLi; reaction conducted at 0 °C for 30 min.



	S.m **1f**	Alkene **2f**	Alkene **2′f**	Diene **3f**	Diene **3′f**	Trimer **4f**	Trimer **4′f**	Benzyl alcohol	Total
Run 1	14%	2%	4% (2%)	29% (26%)	2%	15% (11%)	2%	16%	84%
Run 2	18%	3%	4%	24% (19%)	2%	15% (5%)	3%	27%	97%

In parentheses: yields of isolated products.

- Run 1: General procedure **GP5** was applied with *n* = 1.10, *p* = 1.65 and *t* = 30. *n*-Butyllithium solution (2.38 M in hexanes, 1.65 mmol, 693 µL) was added over 3 minutes. 3-Benzyloxyprop-1-yne **1f** (1.00 mmol, 146 mg) was added over 3 minutes. Crude product: yellow oil (108 mg).

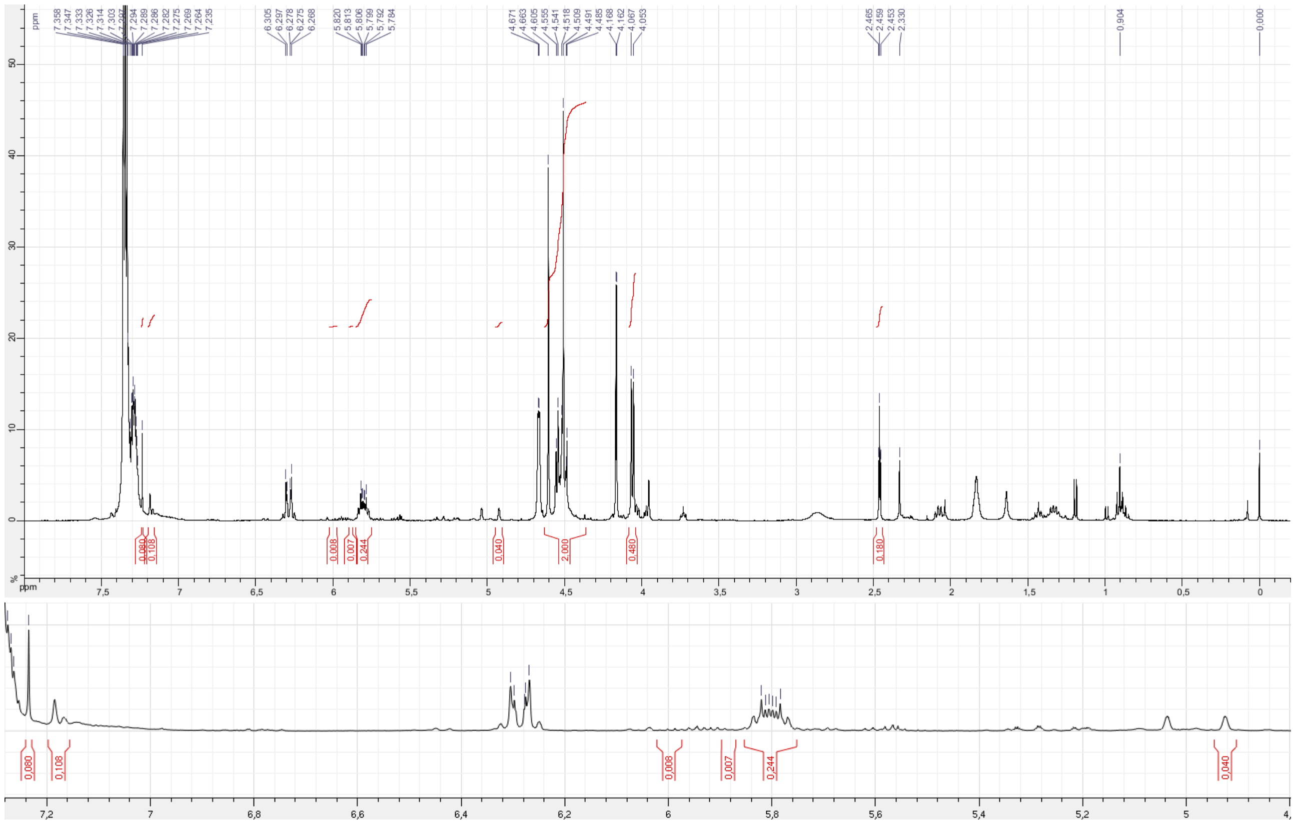
Analysis as described in subsection IX.2. (benzyl CH$_2$ protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

Flash column chromatography (silica gel, EtOAc/petroleum ether, gradient from 1% to 5%) afforded relatively pure 1,2,4-tris(benzyloxymethyl)benzene **4f** (16 mg, 36 µmol, 11%), fairly pure 2-methylenehexoxymethylbenzene **2′f** (5 mg, 24 µmol, 2%) and pure [(2*E*,4*E*)-6-benzyloxyhexa-2,4-dienoxy]methylbenzene **3f** (39 mg, 132 µmol, 26%).

- Run 2: General procedure **GP5** was applied with *n* = 1.10, *p* = 1.65 and *t* = 20. *n*-Butyllithium solution (2.38 M in hexanes, 1.65 mmol, 693 µL) was added over 3 minutes. 3-Benzyloxyprop-1-yne **1f** (1.00 mmol, 146 mg) was added over 2 minutes. Crude product: yellow oil (140 mg).

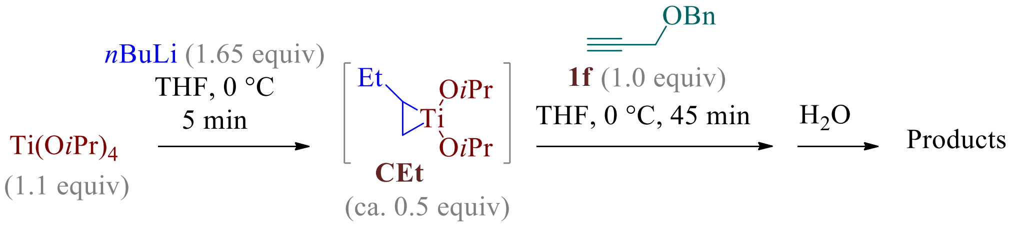
Analysis as described in subsection IX.2. (benzyl CH$_2$ protons as an internal standard) gave the qualitative estimation of the product yields shown in the table above.

After further concentration at lower pressure, flash column chromatography (silica gel, CH$_2$Cl$_2$/petroleum ether, gradient from 5% to 100%) afforded relatively pure 1,2,4-tris(benzyloxymethyl)benzene **4f** (7.5 mg, 17 µmol, 5%) and pure [(2*E*,4*E*)-6-benzyloxyhexa-2,4-dienoxy]methylbenzene **3f** (27.8 mg, 94.4 µmol, 19%).



^{1}H NMR spectrum of the crude product ($CDCl_3$, 400 MHz).

■ **IX.4.7.** With 1.1 equiv of Ti(O*i*Pr)$_4$, 1.65 equiv of *n*BuLi; reaction conducted at 0 °C for 45 min.



S.m **1f**	Alkene **2f**	Alkene **2′f**	Diene **3f**	Diene **3′f**	Trimer **4f**	Trimer **4′f**	Benzyl alcohol	Total
7.0%	2.6%	4.4%	24.2%	2.1%	17.8%	0%	27%	85%[a]
5.5%	2.2%	3.4%	19.0%	1.6%	13.8%	0%	21%	66%[b]

[a] Yields estimated as depicted in VII.2. (benzyl CH_2 protons used as an internal standard).

[b] Yields estimated using (*E*)-cinnamic acid (250 µmol, 37.05 mg) as an internal standard.

General procedure **GP1** was applied with $n = 1.10$, $p = 1.65$ and $t = 45$.
n-Butyllithium solution (2.31 M in hexanes, 3.30 mmol, 1.43 mL) was added over 1.5 minutes. 3-Benzyloxyprop-1-yne **1f** (2.00 mmol, 292 mg, 289 µL) was added over 2 minutes. Crude product: yellow oil (261 mg). Analysis as described in subsection IX.2. gave the qualitative estimation of the product yields shown in the table above.

X. Kinetic study

■ An online kinetic simulator tool developed by Bob Hanson was used,[38] that can be accessed at the following address on the St. Olaf College web site (January 2024):

https://www.stolaf.edu/depts/chemistry/courses/toolkits/126/js/kinetics/

■ The study was conducted on the transformation of 5-benzyloxypent-1-yne **1d**. The goal was to estimate the rate constants of all the elementary steps in such a way as to obtain a good agreement with the product distributions and yields observed experimentally.

The molecule names were abbreviated as follows:

Alkyne: 5-benzyloxypent-1-yne **1d**;

TCPane: titanacyclopropane species **C_{Et}**;

TCPene: titanacyclopropene complex **Dd**, giving 5-benzyloxypent-1-ene **2d** after hydrolysis;

TCPentene: titanacyclopentene complex **Fd**, giving 4-methyleneoctoxymethylbenzene **2′d** after hydrolysis;

TCPdienes: used as a non-differentiating abbreviation for titanacyclopentadiene complexes **Ed** and **E′d**, which give the two dienes [(*E*,*E*)-10-benzyloxydeca-4,6-dienoxy]methylbenzene **3d** and [(*E*)-9-benzyloxy-4-methylene-non-5-enoxy]methylbenzene **3′d** after hydrolysis.

Trims: used as a non-differentiating abbreviation for the two cyclotrimerized products 1,2,4-tris(3-benzyloxyproyl)benzene **4d** and 1,3,5-tris(3-benzyloxyproyl)benzene **4′d**.

BP: a generic name for the by-products formed.

■ The reactions chosen for the simulations were the following:

- With 4.4 equiv of $Ti(OiPr)_4$ and 6.6 equiv of *n*BuLi; reaction time of 20 min at 0 °C (subsection **VII.4.1.**). Average values for the two runs were calculated for the product yields estimated by NMR.

- With 2.2 equiv of $Ti(OiPr)_4$ and 3.3 equiv of *n*BuLi; reaction time of 30 min at 0 °C (subsection **VII.4.3.**). Both runs gave nearly identical results. Average values were calculated for the product yields estimated by NMR.

- With 1.1 equiv of $Ti(OiPr)_4$ and 1.65 equiv of *n*BuLi, for which the product distribution had been determined after 20, 30 and 45 min at 0 °C (subsection **VII.4.7.**).

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[38] R. M. Hanson, *J. Chem. Educ.* **2002**, *79*, 1379–1379.

The experimental yields evaluated by NMR spectroiscopy after running these experiments are shown below:

Experiment	Alkyne	TCPene	TCPentene	TCPdienes	Trims	BP
VII.4.1. (20 min)	2%	24%	12.5%	33.5%	4%	24%
VII.4.3. (30 min)	3%	14%	9.5%	42%	12%	19.5%
VII.4.7. (20 min)	28%	2%	6%	33%	13%	18%
VII.4.7. (30 min)	14%	3%	7%	39%	18%	19%
VII.4.7. (45 min)	3%	4%	7%	42%	20%	24%

The following parameters were applied for the simulations:

Experiment	Starting concentrations		end (sec)	dt (sec)
	[TCPane]	[Alkyne]		
VII.4.1. (20 min)	0.295[a]	0.148[a]	1200	1
VII.4.3. (30 min)	0.182[b]	0.182[b]	1800	1
VII.4.7. (20 min)	0.155[c]	0.31[c]	1200	1
VII.4.7. (30 min)			1800	1
VII.4.7. (45 min)			2700	1

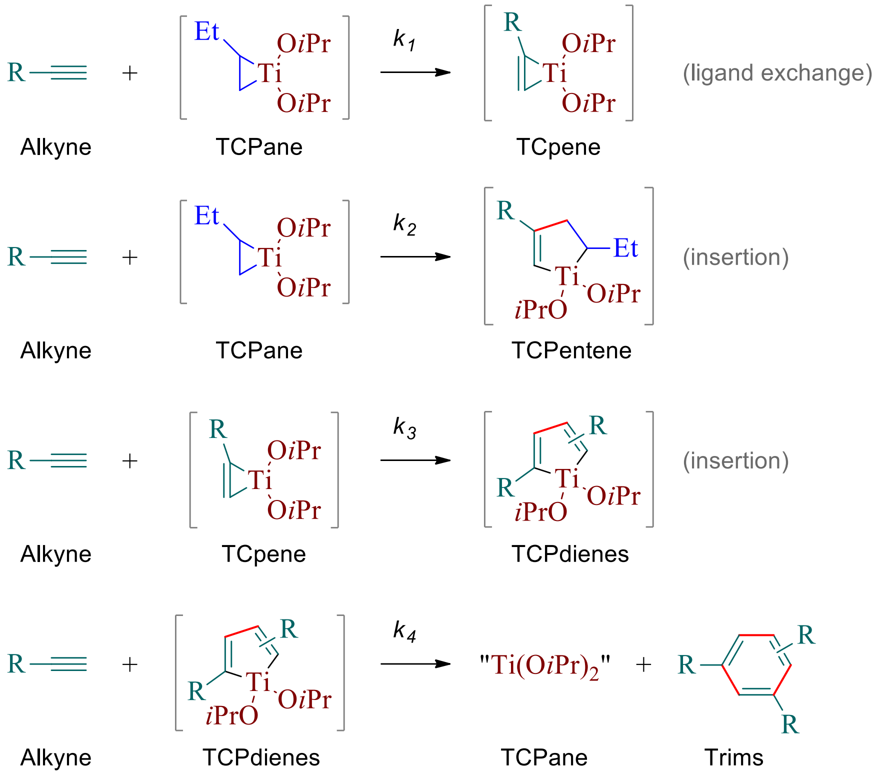
[a] The volume of the solution was assumed to be 6.77 mL and the initial amount of titanacyclopropane **C$_{\mathrm{Et}}$** was estimated to be 2.00 mmol. [b] The volume of the solution was assumed to be 5.50 mL and the initial amount of titanacyclopropane **C$_{\mathrm{Et}}$** was estimated to be 1.00 mmol. [c] The volume of the solution was assumed to be 6.45 mL and the initial amount of titanacyclopropane **C$_{\mathrm{Et}}$** was estimated to be 1.00 mmol.

The end concentrations were calculated on the basis of the experimental yields and are displayed below:

Experiment	Alkyne	TCPene	TCPentene	TCPdienes	Trims	BP
VII.4.1. (20 min)	0.002960	0.03552	0.01850	0.02479	0.00197	0.03552
VII.4.3. (30 min)	0.00546	0.02548	0.01729	0.03822	0.007280	0.03549
VII.4.7. (20 min)	0.08680	0.00620	0.01860	0.05115	0.01343	0.05580
VII.4.7. (30 min)	0.04340	0.00930	0.02170	0.06045	0.01860	0.005890
VII.4.7. (45 min)	0.00930	0.01240	0.02170	0.06510	0.02067	0.07440

X.1. First stage: very simplified model

Most of the elementary steps leading to the observed products were known and are shown below.

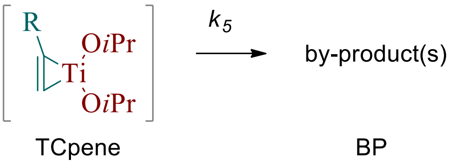


In this simple model, the active titanium(II) species liberated during the elementary step leading to the cyclotrimersied products Trims are identified as TCPane. It is necessary to account for the production of by-products as well. Indeed, the total yields of identified products starting from the alkyne **1d** for all experiments was markedly under 100%. Examination of the results of experiments conducted for extended time (e.g. 2 hours) indicate that species TCPentene and Tdienes are relatively stable complexes. In contrast, important yield erosion is observed for the alkene product **2d**, suggesting significant decomposition of the titanacyclopropene complex **Dd** (TCPene). Although multiple decomposition pathways of all the organometallic species involved must operate, more information would be needed to take them into account. For this reason and on the basis of the observations mentioned above, only decomposition of TCPene was considered, giving a by-product BP. This important simplification made the kinetic modelling practicable.

For each of the five sets of experimental data, the kinetic constants were optimised empirically (trial and error method) in order to achieve a perfect fit with the end concentrations.

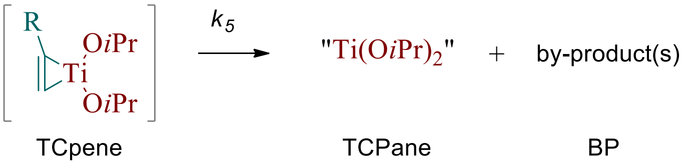
Two hypotheses were envisaged in the simulations:

■ First hypothesis: complex TCPene simply decomposes to give BP. The titanium atom originally present in TCPane is "lost" and no longer participates in the mechanism.

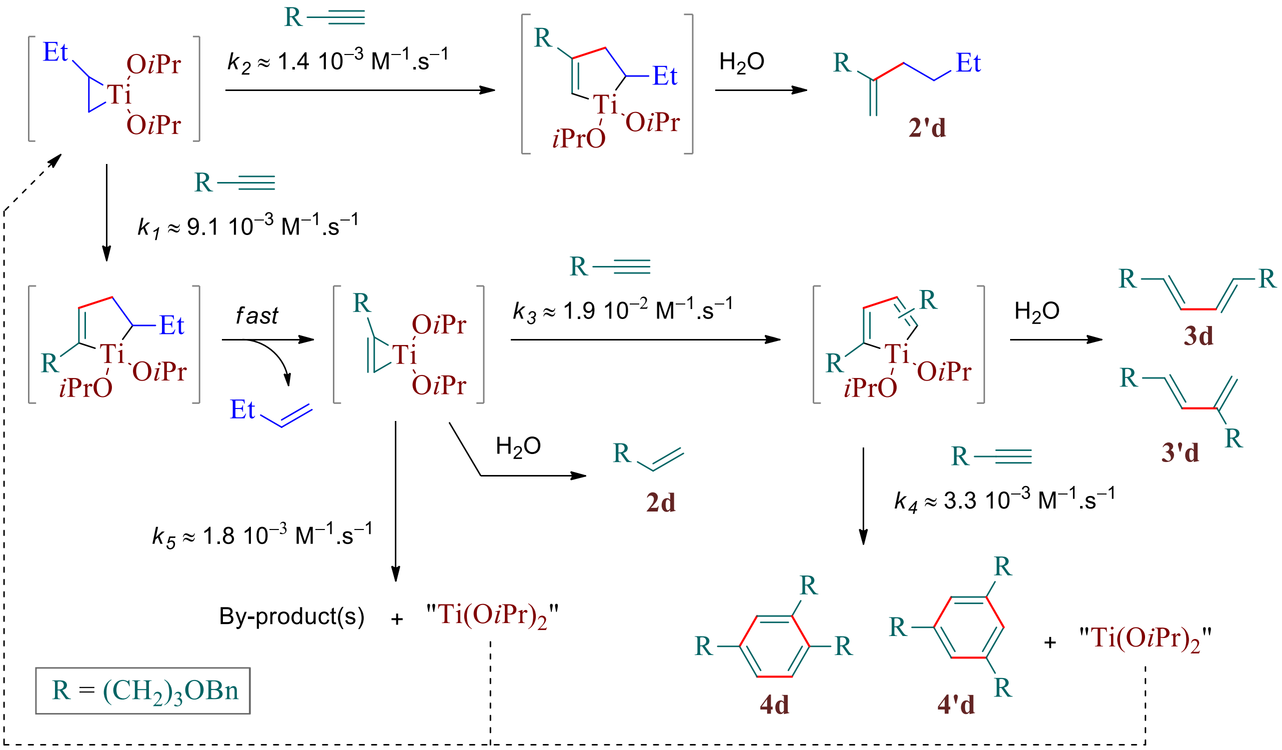


This led to two important problems: first, for experiment **VII.4.7.** (45 min), it was found that there was not enough starting complex TCPane to account for the product yields observed: the theoretical amount of remaining TCPane after 45 min was found to be negative; secondly, optimisation could be conducted successfully for the reaction after 20 min and after 30 min but the optimised kinetic constants were found to be very different for each of these reaction times, varying by a factor of up to three.

■ In the second hypothesis, decomposition of TCPene gives a by-product BP and liberates active titanium(II) species, which is again identified as TCPane, in this simplified model.



The kinetic constants k_1 to k_5 could be optimised for each reaction and much more consistent results were obtained. For each kinetic constant, an average value was then calculated, which led to the following simplified mechanistic picture:



To test this model, all the experiments were simulated again, using the calculated average values for the kinetic constants. For example, for experiment **VII.4.7**, the following data was submitted to the simulator (with a dt of 1 second and 1200 calculation steps, for *t* = 20 min):

```
  Alkyne + TCPane --> TCPene          k1=0.009138
  Alkyne + TCPane --> TCPentene       k2=0.001402
  Alkyne + TCPene --> TCPdienes       k3=0.019356
  Alkyne + TCPdienes --> TCPane + Trims       k4=0.003334
  TCPene --> TCPane + BP      k5=0.0018
//------------------------------------
[Alkyne]=0.31
[TCPane]=0.155
```

The results are shown in the Table below. The average deviation for the product yields is about 3%, with a maximal deviation of 13%.

Experiment	Alkyne	TCPene	TCPentene	TCPdienes	Trims
VII.4.1. (20 min)	**2%**	**24%**	**12%**	**33%**	**4%**
	2%	**11%**	**11%**	**31%**	**3%**
VII.4.3. (30 min)	**3%**	**14%**	**9%**	**42%**	**12%**
	4%	**5%**	**9%**	**38%**	**9%**
VII.4.7. (20 min)	**28%**	**2%**	**6%**	**33%**	**13%**
	19%	**5%**	**7%**	**37%**	**18%**
VII.4.7. (30 min)	**14%**	**3%**	**7%**	**39%**	**18%**
	10%	**3%**	**7%**	**38%**	**22%**
VII.4.7. (45 min)	**3%**	**4%**	**7%**	**42%**	**20%**
	4%	**2%**	**8%**	**37%**	**26%**

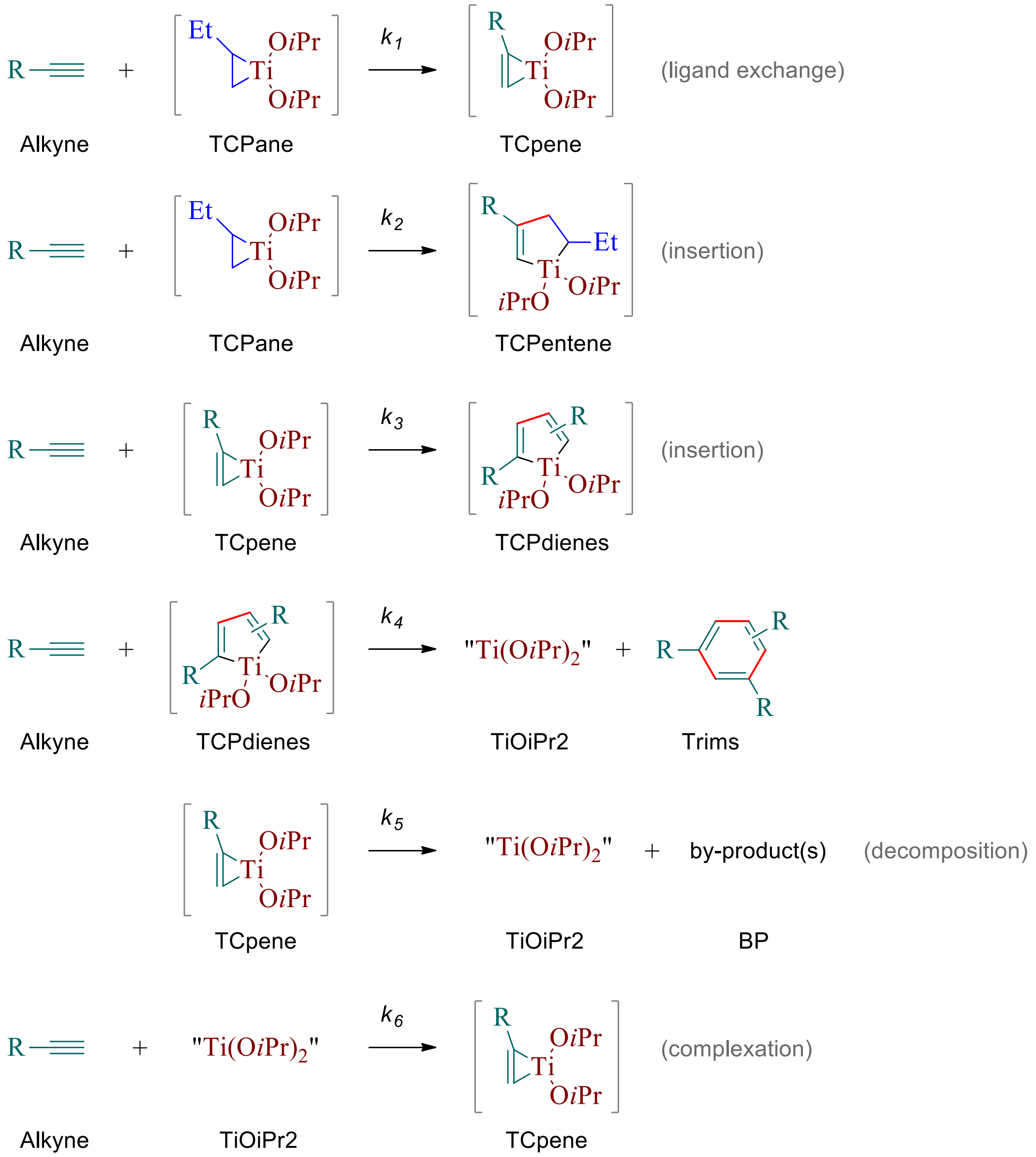
Experimental yields. Calculated yields.

Less than 2% difference. Less than 5% difference. More than 5% difference.

X.2. Second stage: more advanced model

■ A shortcoming of the first model was the identification of the titanium(II) species, regenerated after the formation of the cyclotrimerised products, with the titanacyclopropane TCPane, which is not realistic. Indeed, these titanium(II) species should coordinate to the starting terminal alkyne more rapidly than to any 1-butene remaining in the solution. Therefore, they should be converted into the titanacyclopropene intermediate TCPene but should not lead to any significant regeneration of the starting titanacyclopropane complex TCPane.

To account for this, these titanium(II) species were incorporated in the model as a distinct chemical entity, under the name TiOiPr2:



A difficulty associated with this modification was the introduction of an additional kinetic constant k_6. As a result, several sets of optimised kinetic constants could lead to a perfect fit for any given experiment. Several k_6/k_1 ratios had therefore to be tested.

Better results were obtained with $k_6/k_1 = 2$, compared with $k_6/k_1 = 1$.

■ At this stage, a new problem was spotted with the kinetic constant k_5 of the TCPene decomposition process. We found that the latter could vary by a factor of up to 8.8 depending on the experiments. Judging that this was due to the assumption that the decomposition of TCPene quantitatively regenerated titanium(II) species, which is perhaps not realistic, we tried to consider two distinct decomposition pathways, one proceeding with loss of active titanium species, the other with regeneration of Ti^{II}:

TCPene → BP1 + TiOiPr2 k5
TCPene → BP2 k5'

Since the exact natures of the byproducts BP1 and BP2 were not important for calculations, they were given the same common generic name BP as before:

TCPene → BP + TiOiPr2 k5
TCPene → BP k5'

Calculations were carried out with $k_{5'} = 0.5\ k_5$, $k_{5'} = k_5$, $k_{5'} = 2\ k_5$ and $k_{5'} = 3\ k_5$ (with $k_6 = 2\ k_1$ in each case). The results proved to be disappointing: simulation could not be achieved at all for some experiments (e.g. with $k_{5'} = 3\ k_5$); in one case, variation of k_5 could be somewhat reduced to a factor of 6.9 ($k_{5'} = 2\ k_5$) but then, variation of all the other kinetic constants increased significantly. Moreover, none of these experiments led to a better fit, as compared to the previous simpler model.

■ Therefore, we came back to the simpler model and continued trying other k_6/k_1 ratios.

The best result was obtained with $k_6 = 5\ k_1$. Applying the kinetic constants found for experiment **VII.4.7** resulting in average deviation for the product yields of 2.2% and a maximal deviation of 5.9% (Table below).

k_6/k_1 ratio	Average deviation for the product yields	Maximal deviation
1	2.9%	11.6%
2	2.4%	9.1%
3	2.3%	7.7%
4	2.2%	6.7%
5	2.2%	5.9%
6	2.2%	6.0%
7	2.1%	6.3%
8	2.1%	6.4%

The simulation results with this new model are summarised in the following table.

Experiment	Alkyne	TCPene	TCPentene	TCPdienes	Trims
VII.4.1. (20 min)	**2%**	**24%**	**12%**	**33%**	**4%**
	4%	**18%**	**12%**	**31%**	**3%**
VII.4.3. (30 min)	**3%**	**14%**	**9%**	**42%**	**12%**
	5%	**10%**	**9%**	**38%**	**7%**
VII.4.7. (20 min)	**28%**	**2%**	**6%**	**33%**	**13%**
	22%	**8%**	**6%**	**38%**	**13%**
VII.4.7. (30 min)	**14%**	**3%**	**7%**	**39%**	**18%**
	10%	**6%**	**7%**	**41%**	**17%**
VII.4.7. (45 min)	**3%**	**4%**	**7%**	**42%**	**20%**
	3%	**4%**	**7%**	**42%**	**20%**

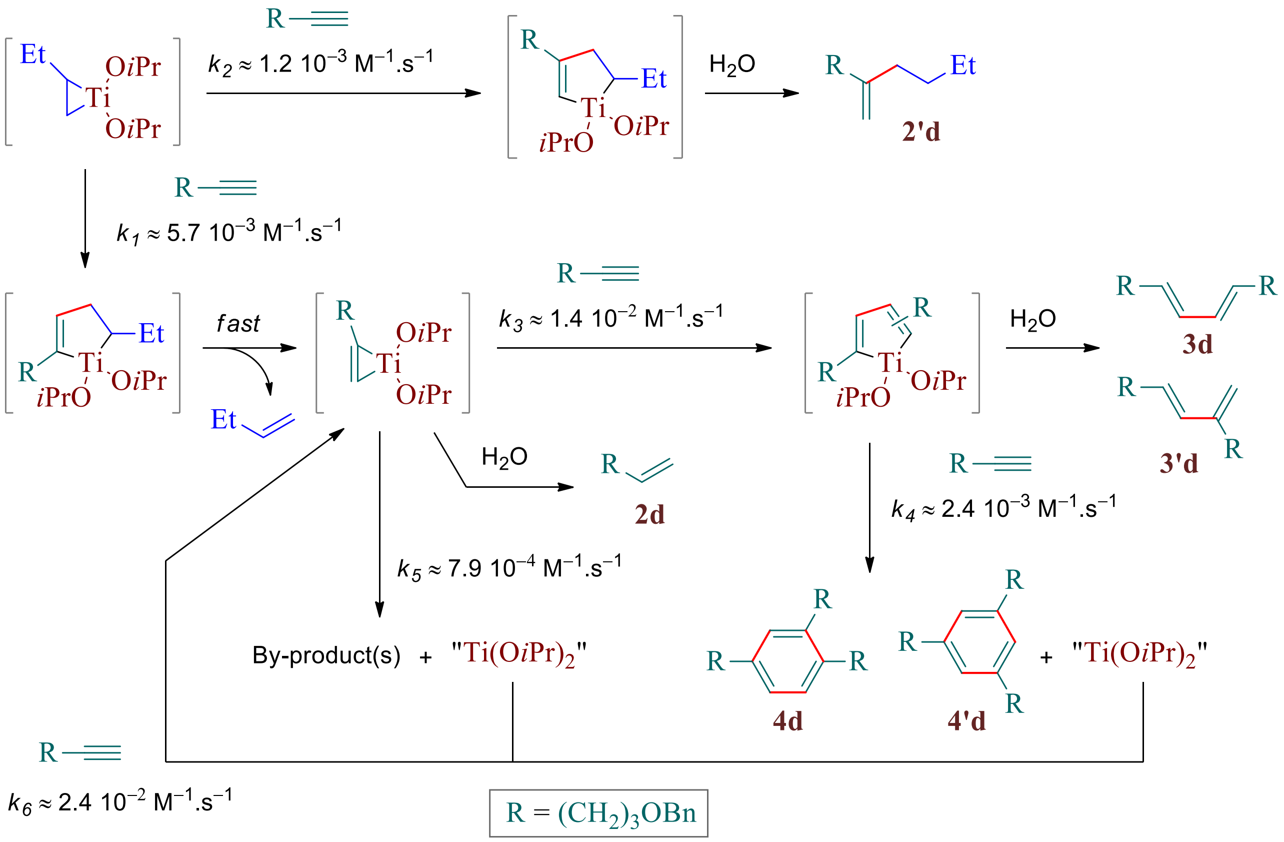
Experimental yields. Calculated yields.

Less than 2% difference. Less than 5% difference. More than 5% difference.

■ Finally, an optimisation of all the kinetic constants k_1 to k_5 was carried out by slightly modifying them, one at a time, so as to further reduce the average deviation, in an iterative fine-tuning process. This process resulted in an average deviation for the product yields of 1.85% and a maximal deviation of 6.36%, with the following optimised kinetic constants:

Alkyne + TCPane --> TCPene k1=0.00566
Alkyne + TCPane --> TCPentene k2=0.00119
Alkyne + TCPene --> TCPdienes k3=0.0136
Alkyne + TCPdienes --> TiOiPr2 + Trims k4=0.00236
TCPene --> TiOiPr2 + BP k5=0.000788
Alkyne + TiOiPr2 --> TCPene k6=0.0245

This new model can thus be displayed as the following mechanistic scheme:



Its performance in the simulations, illustrated in the following table, can be compared with the table previously obtained, which clearly reveals significant improvement.

Experiment	Alkyne	TCPene	TCPentene	TCPdienes	Trims
VII.4.1. (20 min)	**2%**	**24%**	**12%**	**33%**	**4%**
	6%	**24%**	**12%**	**32%**	**3%**
VII.4.3. (30 min)	**3%**	**14%**	**9%**	**42%**	**12%**
	8%	**13%**	**10%**	**40%**	**8%**
VII.4.7. (20 min)	**28%**	**2%**	**6%**	**33%**	**13%**
	26%	**8%**	**7%**	**37%**	**13%**
VII.4.7. (30 min)	**14%**	**3%**	**7%**	**39%**	**18%**
	14%	**7%**	**7%**	**42%**	**18%**
VII.4.7. (45 min)	**3%**	**4%**	**7%**	**42%**	**20%**
	5%	**5%**	**7%**	**44%**	**22%**

Experimental yields. Calculated yields.

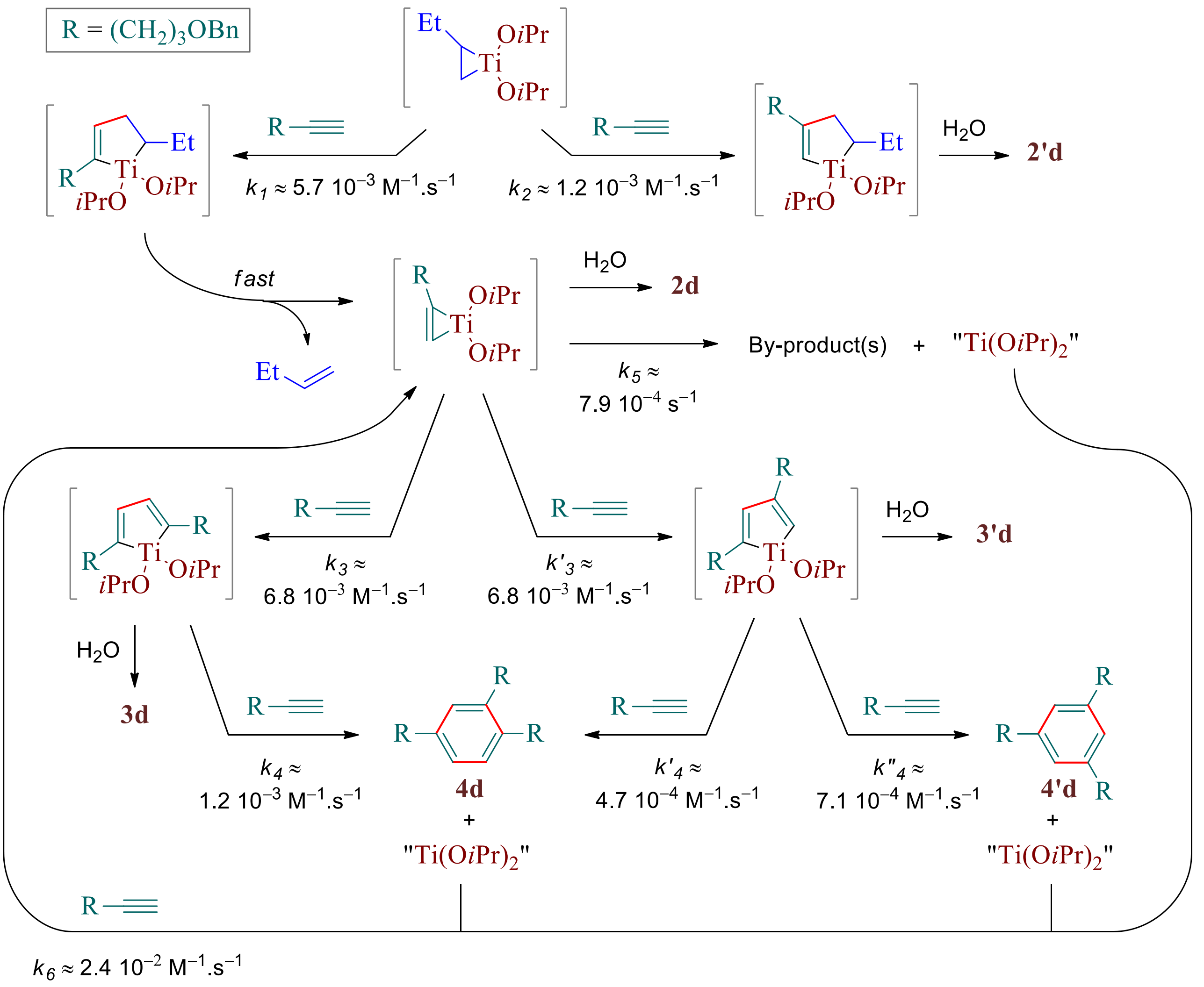
Less than 2% difference. Less than 5% difference. More than 5% difference.

■ Finally, the kinetic model could be refined further by taking selectivity aspects into account.

For the production of the titanacyclopentadiene isomers TCPdienes, the selectivity can be assumed to be close to 50 : 50, as estimated by considering the experiments **VII.4.1.**, where significant amounts of dienes had been produced but little trimers. The rates of formation of each isomer of TCPdienes can therefore be considered to be identical, with values equal to half the overall kinetic constant k_4 evaluated in the previous part.

The selectivity of the cyclotrimerised products formation was estimated to be 70 : 30 in favour of the 1,2,4 isomer, based on the experiment giving the highest amount of these products: 20% (experiment **VII.4.7.**, 45 min). In that case, the ratio of the dienes was still close to 50 : 50, which suggests that the two TCPdienes isomers react with the starting alkyne at about the same rate. Moreover, the 1,4 isomer of TCPdienes can only produce the 1,2,4 trimer. A simple calculation then leads to the conclusion that the 1,3 isomer of TCPdienes reacts with the starting alkyne with 40 : 60 selectivity in favour of the 1,3,5 trimer.

These considerations lead to the following refined mechanistic scheme:



XI. X-Ray diffraction analysis of compound **5b**

CCDC-2311234 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

A suitable crystal of **5b** ($C_{36}H_{34}$; M = 466.63 g/mol) for X-Ray diffraction single crystal experiment was selected and mounted on the goniometer head of a D8 VENTURE (Bruker AXS) diffractometer equipped with a (CMOS) PHOTON 100 detector, using Mo-$K\alpha$ radiation (λ = 0.71073 Å, multilayer monochromator), at T = 150 K. The crystal structure was described in monoclinic symmetry and $C\ 2/c$ (I.T.#15) space group. Cell parameters have been refined as follows: a = 30.102(7), b = 7.9549(17), c = 11.215(2) Å, β = 93.791(8), V = 2679.6(10) Å^3. Number of formula unit Z = 4, calculated density d = 1.157 g.cm^{-3}, absorption coefficient μ = 0.065 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[39] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[40] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 3055 unique intensities and 163 parameters converged at ωR_F^2 = 0.1216 (R_F = 0.0478) for 2467 observed reflections with $I > 2\sigma(I)$.

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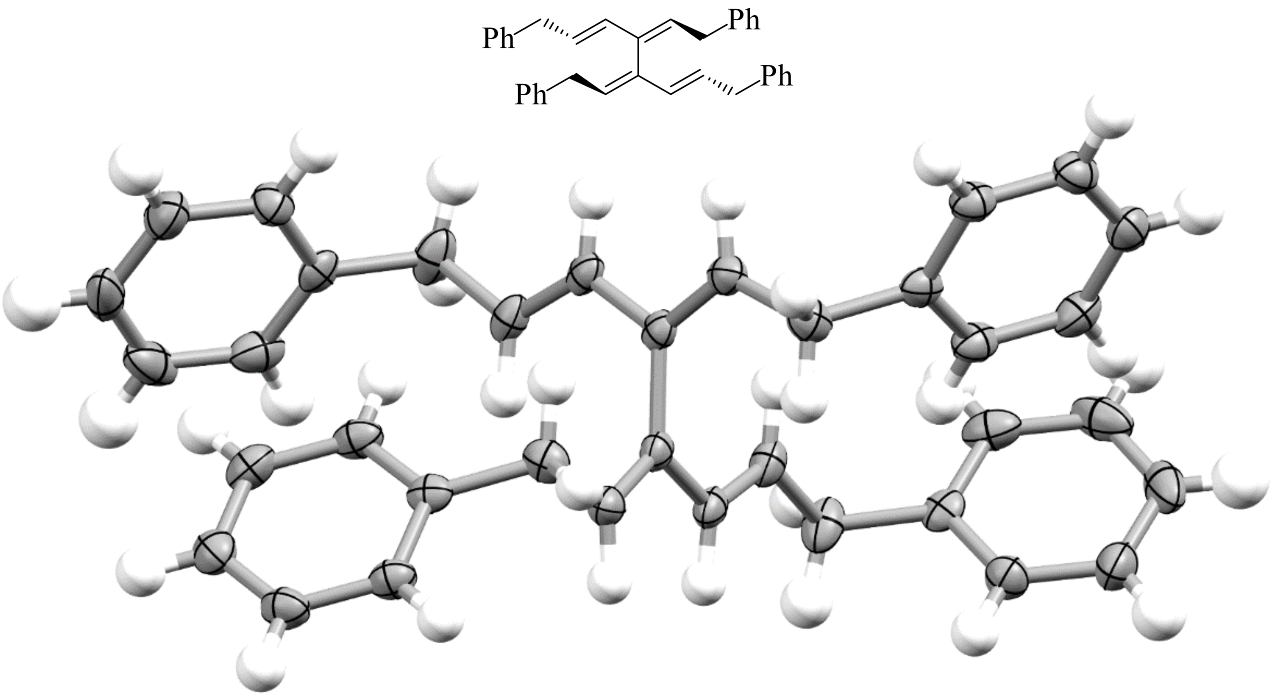
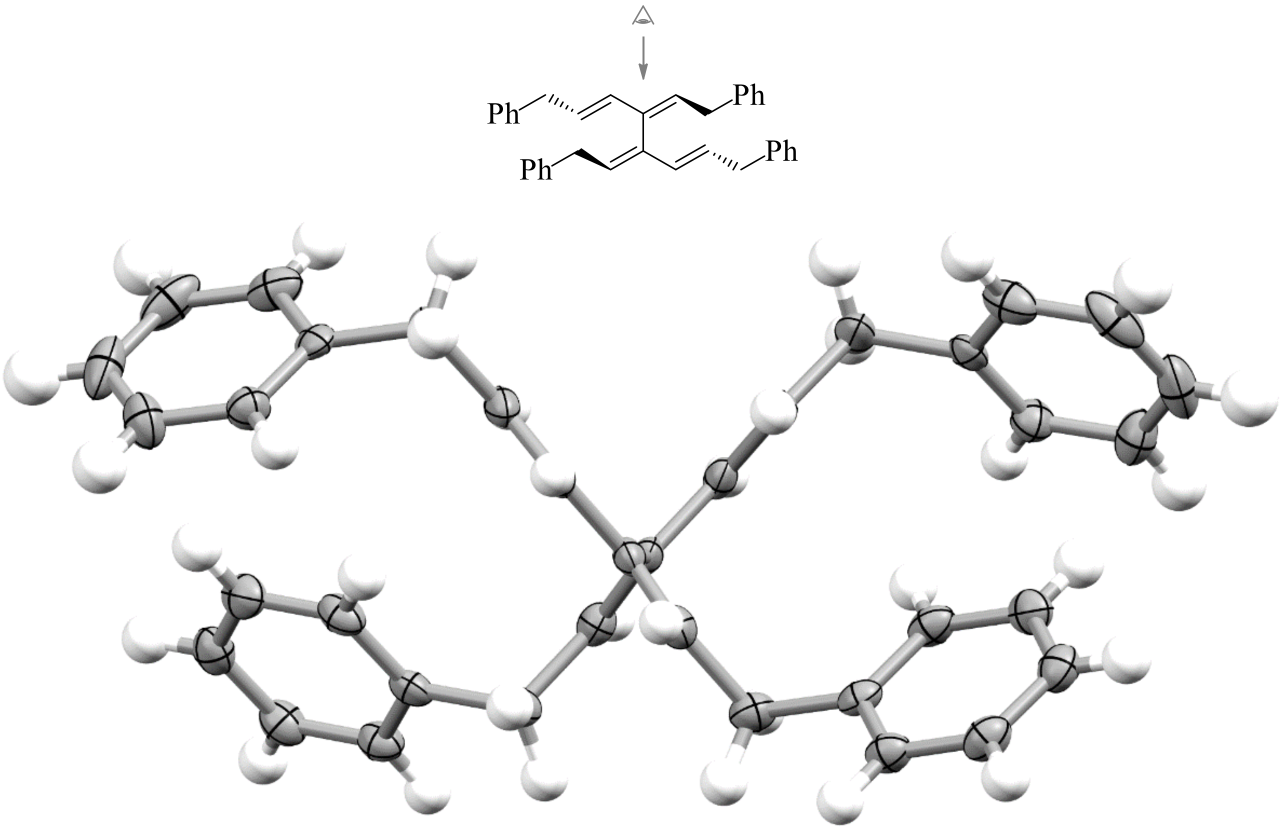
[39] G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3−8.
[40] G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3−8.



X-ray structure of **5b** (view 1). Ellipsoids are drawn at the 50% probability level.



X-ray structure of **5b** (view 2). Ellipsoids are drawn at the 50% probability level.

Table 1. Crystal data and structure refinement for 5b.

Empirical formula	$C_{36}H_{34}$
Formula weight	466.63 g/mol
Temperature	150 K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, C 2/c
Unit cell dimensions	a = 30.102(7) Å, b = 7.9549(17) Å, c = 11.215(2) Å, alpha = 90 °, beta = 93.791(8) °, gamma = 90 °
Volume	2679.6(10) $Å^3$
Z, Calculated density	4, 1.157 $g.cm^{-3}$
Absorption coefficient	0.065 mm^{-1}
F(000)	1000
Crystal size	0.500 × 0.400 × 0.250 mm
Crystal color	colourless
Θ range for data collection	1.356 to 27.522 °
h_min, h_max	−38, 38
k_min, k_max	−10, 9
l_min, l_max	−14, 13
Reflections collected / unique	12834 / 3055 [R(int) = 0.0500]
Reflections [I>2σ(I)]	2467
Completeness to theta_max	0.988
Absorption correction type	multi-scan
Max. and min. transmission	0.984 , 0.798
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3055 / 0 / 163
Goodness-of-fit	1.042
Final R indices [I>2 σ (I)]	R_1 = 0.0478, wR_2 = 0.1216
R indices (all data)	R_1 = 0.0611, wR_2 = 0.1341
Largest diff. peak and hole	0.172 and −0.243 $e.Å^{-3}$

Table 2. Fractional coordinates, site occupancy (%) and equivalent isotropic displacement parameters (Å^2) for 5b.

U(eq) is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	occ.	U(eq)	adp
C1	-0.09954(4)	0.54137(16)	0.09667(11)	1	0.0270(3)	Uani
C2	-0.11546(5)	0.45501(17)	-0.00516(12)	1	0.0308(3)	Uani
H2	-0.096678	0.377164	-0.041779	1	0.037	Uiso
C3	-0.15841(5)	0.48123(19)	-0.05382(12)	1	0.0345(3)	Uani
H3	-0.168871	0.421237	-0.123347	1	0.041	Uiso
C4	-0.18610(5)	0.59421(19)	-0.00168(13)	1	0.0350(3)	Uani
H4	-0.215646	0.611323	-0.034592	1	0.042	Uiso
C5	-0.17042(5)	0.68222(19)	0.09886(13)	1	0.0358(3)	Uani
H5	-0.189215	0.760658	0.134837	1	0.043	Uiso
C6	-0.12756(5)	0.65654(17)	0.14716(12)	1	0.0324(3)	Uani
H6	-0.117074	0.718385	0.215821	1	0.039	Uiso
C7	-0.05277(5)	0.51465(17)	0.15113(12)	1	0.0321(3)	Uani
H7A	-0.053160	0.515515	0.239328	1	0.038	Uiso
H7B	-0.041891	0.403192	0.126738	1	0.038	Uiso
C8	-0.02161(4)	0.64812(17)	0.11282(11)	1	0.0276(3)	Uani
H8	-0.017742	0.655733	0.029609	1	0.033	Uiso
C9	0.00136(4)	0.75779(16)	0.18334(11)	1	0.0245(3)	Uani
C10	0.02998(4)	0.88372(17)	0.13104(12)	1	0.0272(3)	Uani
H10	0.029627	0.887382	0.046315	1	0.033	Uiso
C11	0.05626(4)	0.99279(17)	0.19079(13)	1	0.0301(3)	Uani
H11	0.056579	0.992138	0.275545	1	0.036	Uiso
C12	0.08565(5)	1.11772(19)	0.13275(15)	1	0.0375(4)	Uani
H12A	0.077151	1.232842	0.155867	1	0.045	Uiso
H12B	0.080771	1.108332	0.044839	1	0.045	Uiso
C13	0.13449(4)	1.09044(16)	0.16807(12)	1	0.0271(3)	Uani
C14	0.15515(6)	1.17250(19)	0.26566(13)	1	0.0393(4)	Uani
H14	0.138407	1.245784	0.312308	1	0.047	Uiso
C15	0.20008(6)	1.1483(2)	0.29558(14)	1	0.0492(5)	Uani
H15	0.213922	1.204817	0.362789	1	0.059	Uiso
C16	0.22481(5)	1.0429(2)	0.22865(15)	1	0.0474(4)	Uani
H16	0.255680	1.027333	0.248845	1	0.057	Uiso
C17	0.20440(5)	0.9607(2)	0.13251(14)	1	0.0420(4)	Uani
H17	0.221228	0.887357	0.086113	1	0.050	Uiso
C18	0.15967(5)	0.98367(18)	0.10272(12)	1	0.0320(3)	Uani
H18	0.145945	0.925174	0.036223	1	0.038	Uiso

Table 3. Anisotropic displacement parameters (Å^2) for 5b.

The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$.

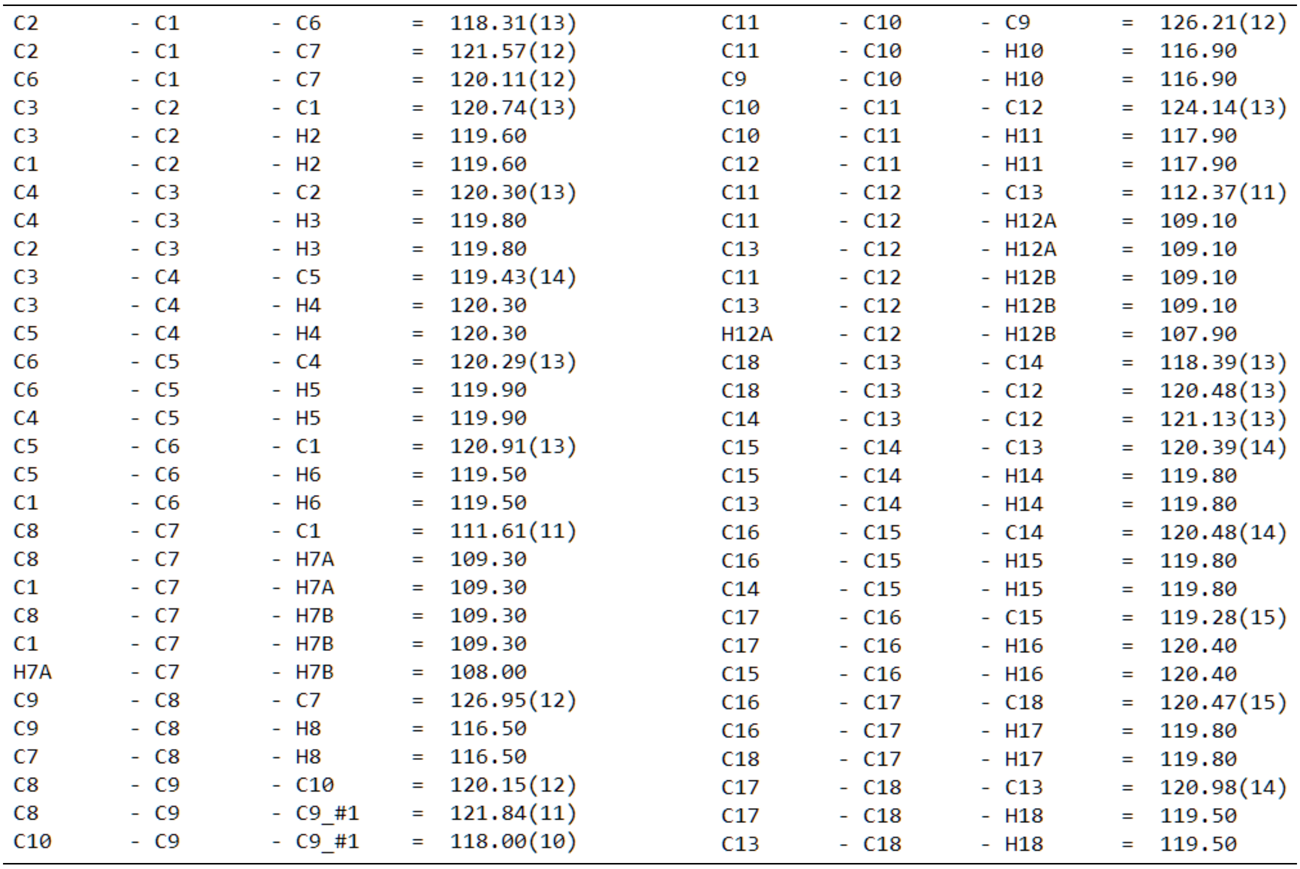
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0324(7)	0.0230(6)	0.0259(6)	0.0008(5)	0.0048(5)	-0.0079(5)
C2	0.0364(7)	0.0282(7)	0.0284(7)	-0.0041(5)	0.0056(5)	-0.0035(6)
C3	0.0385(8)	0.0369(8)	0.0279(7)	-0.0038(6)	0.0009(6)	-0.0086(6)
C4	0.0311(7)	0.0387(8)	0.0353(7)	0.0052(6)	0.0042(6)	-0.0060(6)
C5	0.0372(8)	0.0337(7)	0.0383(8)	-0.0025(6)	0.0150(6)	-0.0009(6)
C6	0.0389(8)	0.0303(7)	0.0286(7)	-0.0065(5)	0.0076(5)	-0.0087(6)
C7	0.0364(8)	0.0281(7)	0.0314(7)	-0.0008(5)	-0.0001(6)	-0.0039(6)
C8	0.0255(6)	0.0317(7)	0.0259(6)	0.0008(5)	0.0028(5)	0.0048(5)
C9	0.0188(6)	0.0265(6)	0.0285(6)	0.0023(5)	0.0040(5)	0.0050(5)
C10	0.0202(6)	0.0312(7)	0.0308(6)	0.0073(5)	0.0059(5)	0.0067(5)
C11	0.0224(6)	0.0279(7)	0.0407(7)	0.0068(6)	0.0083(5)	0.0030(5)
C12	0.0297(7)	0.0291(7)	0.0545(9)	0.0150(6)	0.0103(6)	0.0012(6)
C13	0.0287(6)	0.0208(6)	0.0327(7)	0.0054(5)	0.0091(5)	-0.0057(5)
C14	0.0541(10)	0.0332(8)	0.0319(7)	-0.0035(6)	0.0133(6)	-0.0101(7)
C15	0.0589(10)	0.0564(10)	0.0311(8)	0.0027(7)	-0.0071(7)	-0.0301(9)
C16	0.0272(7)	0.0699(12)	0.0444(9)	0.0214(8)	-0.0031(6)	-0.0138(7)
C17	0.0311(8)	0.0536(10)	0.0422(8)	0.0043(7)	0.0087(6)	0.0072(7)
C18	0.0315(7)	0.0317(7)	0.0327(7)	-0.0040(5)	0.0012(5)	-0.0022(6)

Table 4. Bond lengths [Å] for 5b.

C1 - C2 = 1.3905(18)
C1 - C6 = 1.3910(19)
C1 - C7 = 1.5120(19)
C2 - C3 = 1.385(2)
C2 - H2 = 0.9500
C3 - C4 = 1.382(2)
C3 - H3 = 0.9500
C4 - C5 = 1.384(2)
C4 - H4 = 0.9500
C5 - C6 = 1.381(2)
C5 - H5 = 0.9500
C6 - H6 = 0.9500
C7 - C8 = 1.4983(19)
C7 - H7A = 0.9900
C7 - H7B = 0.9900
C8 - C9 = 1.3389(18)
C8 - H8 = 0.9500
C9 - C10 = 1.4685(18)
C9 - C9_#1 = 1.503(2)
C10 - C11 = 1.326(2)
C10 - H10 = 0.9500
C11 - C12 = 1.5068(18)
C11 - H11 = 0.9500
C12 - C13 = 1.5126(19)
C12 - H12A = 0.9900
C12 - H12B = 0.9900
C13 - C18 = 1.3808(19)
C13 - C14 = 1.386(2)
C14 - C15 = 1.385(2)
C14 - H14 = 0.9500
C15 - C16 = 1.376(3)
C15 - H15 = 0.9500
C16 - C17 = 1.371(2)
C16 - H16 = 0.9500
C17 - C18 = 1.378(2)
C17 - H17 = 0.9500
C18 - H18 = 0.9500

Symmetry transformations used to generate equivalent atoms:
#1 −x, y, −z+1/2 T = [0, 0, 0]

Table 5. Angles [°] for 5b.

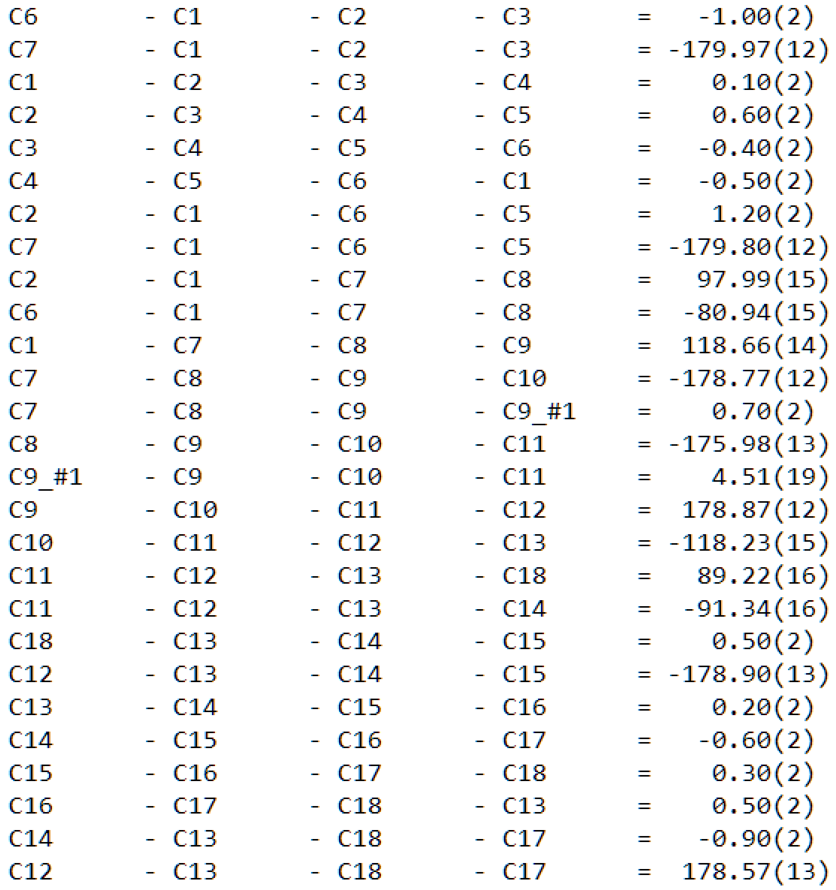


C2	- C1	- C6	=	118.31(13)	C11	- C10	- C9	=	126.21(12)
C2	- C1	- C7	=	121.57(12)	C11	- C10	- H10	=	116.90
C6	- C1	- C7	=	120.11(12)	C9	- C10	- H10	=	116.90
C3	- C2	- C1	=	120.74(13)	C10	- C11	- C12	=	124.14(13)
C3	- C2	- H2	=	119.60	C10	- C11	- H11	=	117.90
C1	- C2	- H2	=	119.60	C12	- C11	- H11	=	117.90
C4	- C3	- C2	=	120.30(13)	C11	- C12	- C13	=	112.37(11)
C4	- C3	- H3	=	119.80	C11	- C12	- H12A	=	109.10
C2	- C3	- H3	=	119.80	C13	- C12	- H12A	=	109.10
C3	- C4	- C5	=	119.43(14)	C11	- C12	- H12B	=	109.10
C3	- C4	- H4	=	120.30	C13	- C12	- H12B	=	109.10
C5	- C4	- H4	=	120.30	H12A	- C12	- H12B	=	107.90
C6	- C5	- C4	=	120.29(13)	C18	- C13	- C14	=	118.39(13)
C6	- C5	- H5	=	119.90	C18	- C13	- C12	=	120.48(13)
C4	- C5	- H5	=	119.90	C14	- C13	- C12	=	121.13(13)
C5	- C6	- C1	=	120.91(13)	C15	- C14	- C13	=	120.39(14)
C5	- C6	- H6	=	119.50	C15	- C14	- H14	=	119.80
C1	- C6	- H6	=	119.50	C13	- C14	- H14	=	119.80
C8	- C7	- C1	=	111.61(11)	C16	- C15	- C14	=	120.48(14)
C8	- C7	- H7A	=	109.30	C16	- C15	- H15	=	119.80
C1	- C7	- H7A	=	109.30	C14	- C15	- H15	=	119.80
C8	- C7	- H7B	=	109.30	C17	- C16	- C15	=	119.28(15)
C1	- C7	- H7B	=	109.30	C17	- C16	- H16	=	120.40
H7A	- C7	- H7B	=	108.00	C15	- C16	- H16	=	120.40
C9	- C8	- C7	=	126.95(12)	C16	- C17	- C18	=	120.47(15)
C9	- C8	- H8	=	116.50	C16	- C17	- H17	=	119.80
C7	- C8	- H8	=	116.50	C18	- C17	- H17	=	119.80
C8	- C9	- C10	=	120.15(12)	C17	- C18	- C13	=	120.98(14)
C8	- C9	- C9_#1	=	121.84(11)	C17	- C18	- H18	=	119.50
C10	- C9	- C9_#1	=	118.00(10)	C13	- C18	- H18	=	119.50

Symmetry transformations used to generate equivalent atoms:

#1 −x, y, −z+1/2 T = [0, 0, 0]

Table 6. Torsion angles [°] for 5b.



C6	- C1	- C2	- C3	= -1.00(2)
C7	- C1	- C2	- C3	= -179.97(12)
C1	- C2	- C3	- C4	= 0.10(2)
C2	- C3	- C4	- C5	= 0.60(2)
C3	- C4	- C5	- C6	= -0.40(2)
C4	- C5	- C6	- C1	= -0.50(2)
C2	- C1	- C6	- C5	= 1.20(2)
C7	- C1	- C6	- C5	= -179.80(12)
C2	- C1	- C7	- C8	= 97.99(15)
C6	- C1	- C7	- C8	= -80.94(15)
C1	- C7	- C8	- C9	= 118.66(14)
C7	- C8	- C9	- C10	= -178.77(12)
C7	- C8	- C9	- C9_#1	= 0.70(2)
C8	- C9	- C10	- C11	= -175.98(13)
C9_#1	- C9	- C10	- C11	= 4.51(19)
C9	- C10	- C11	- C12	= 178.87(12)
C10	- C11	- C12	- C13	= -118.23(15)
C11	- C12	- C13	- C18	= 89.22(16)
C11	- C12	- C13	- C14	= -91.34(16)
C18	- C13	- C14	- C15	= 0.50(2)
C12	- C13	- C14	- C15	= -178.90(13)
C13	- C14	- C15	- C16	= 0.20(2)
C14	- C15	- C16	- C17	= -0.60(2)
C15	- C16	- C17	- C18	= 0.30(2)
C16	- C17	- C18	- C13	= 0.50(2)
C14	- C13	- C18	- C17	= -0.90(2)
C12	- C13	- C18	- C17	= 178.57(13)

Symmetry transformations used to generate equivalent atoms:

#1 −x, y, −z+1/2 T = [0, 0, 0]