

NHC Pd^{II} complexes for the solvent-free telomerization of isoprene with methanol

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Experimental procedures

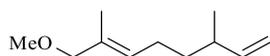
General information

Chemicals and solvents were obtained from commercial sources. Palladium complexes were synthesized according to published procedures.^{S1-S6} Methanol was used instantly after drying, dry glove box-stored sodium methoxide was used. Freshly distilled isoprene was used. GC analysis was performed using Agilent 7820A instrument equipped PID analyzer. NMR spectra were obtained on a Bruker “Ascend™ 400” (400 MHz ¹H, 101 MHz ¹³C). The chemical shifts are frequency referenced relative to the residual undeuterated solvent peaks. Coupling constants J are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as “s”, “d”, “t” or “m” for singlet, doublet, triplet or multiplet, respectively. The abbreviation “br” is given for broadened signals.

General procedure:

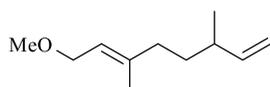
Into a 7 ml oven-dried argon-filled vial equipped with a screw cap with a septum, methanol (1 equiv.), sodium methoxide (2 mol%), catalyst (0.1 mol%) and isoprene (2 equiv.) were placed. The mixture was stirred at room temperature for 72 h, and then filtered. The filtrate was analyzed by GC using nonane as the standard, which confirmed the presence telomers **1a-c** and dimers **2a,b**. The mixture then was additionally analyzed by ¹H NMR using standard (BHT).

¹H NMR analysis of selected isomers (analyzed in mixture)



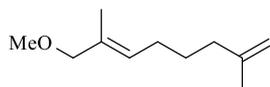
1-Methoxy-2,6-dimethyl-2,7-octadiene, **1a**

¹H NMR (400 MHz, CDCl₃) 5.72-5.66 (m, 1H), 5.41-5.39 (m, 1H), 4.98-4.93 (m, 2H), 3.79 (s, 2H), 3.28 (s, 3H), 2.12-2.08 (m, 1H), 2.05-2.0 (m, 2H), 1.63 (s, 3H), 1.41 (m, 2H), 1.00 (m, 3H). NMR data are in agreement with those previously reported.^{S7}



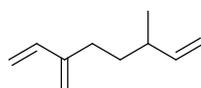
1-Methoxyocta-3,6-dimethyl-2,7-diene, **1b**

^1H NMR (400 MHz, CDCl_3) δ 5.72-5.66 (m, 1H), 5.35-5.33 (m, 1H), 4.98-4.93 (m, 2H), 3.93 (d, $J = 6.8$ Hz, 2H), 3.32 (s, 3H), 2.12-2.08 (m, 1H), 2.05-2.0 (m, 2H), 1.67 (s, 3H), 1.44-1.40 (m, 2H), 1.00 (m, 3H). NMR data are in agreement with those previously reported.^{S7}



1-Methoxy-2,7-dimethyl-2,7-octadiene, **1c**

^1H NMR (400 MHz, CDCl_3) δ 5.41-5.39 (m, 1H), 4.73-4.67 (m, 2H), 3.81-3.80 (m, 2H), 3.14 (s, 3H), 2.05-2.0 (m, 4H), 1.83 (s, 3H), 1.21 (s, 3H). NMR data are in agreement with those previously reported.^{S7}



3-Methyl-6-methylideneocta-1,7-diene, **2a**

^1H NMR (400 MHz, CDCl_3) δ 6.37 (dd, $J = 17.6, 10.8$ Hz, 1H), 5.75-5.66 (m, 1H), 5.2-5.0 (m, 6H), 2.24-2.0 (m, 3H), 1.68-1.41 (m, 2H), 1.03 (d, $J = 6.7$ Hz, 3H). NMR data are in agreement with those previously reported.^{S8}

References

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NMR spectra and GC profiles

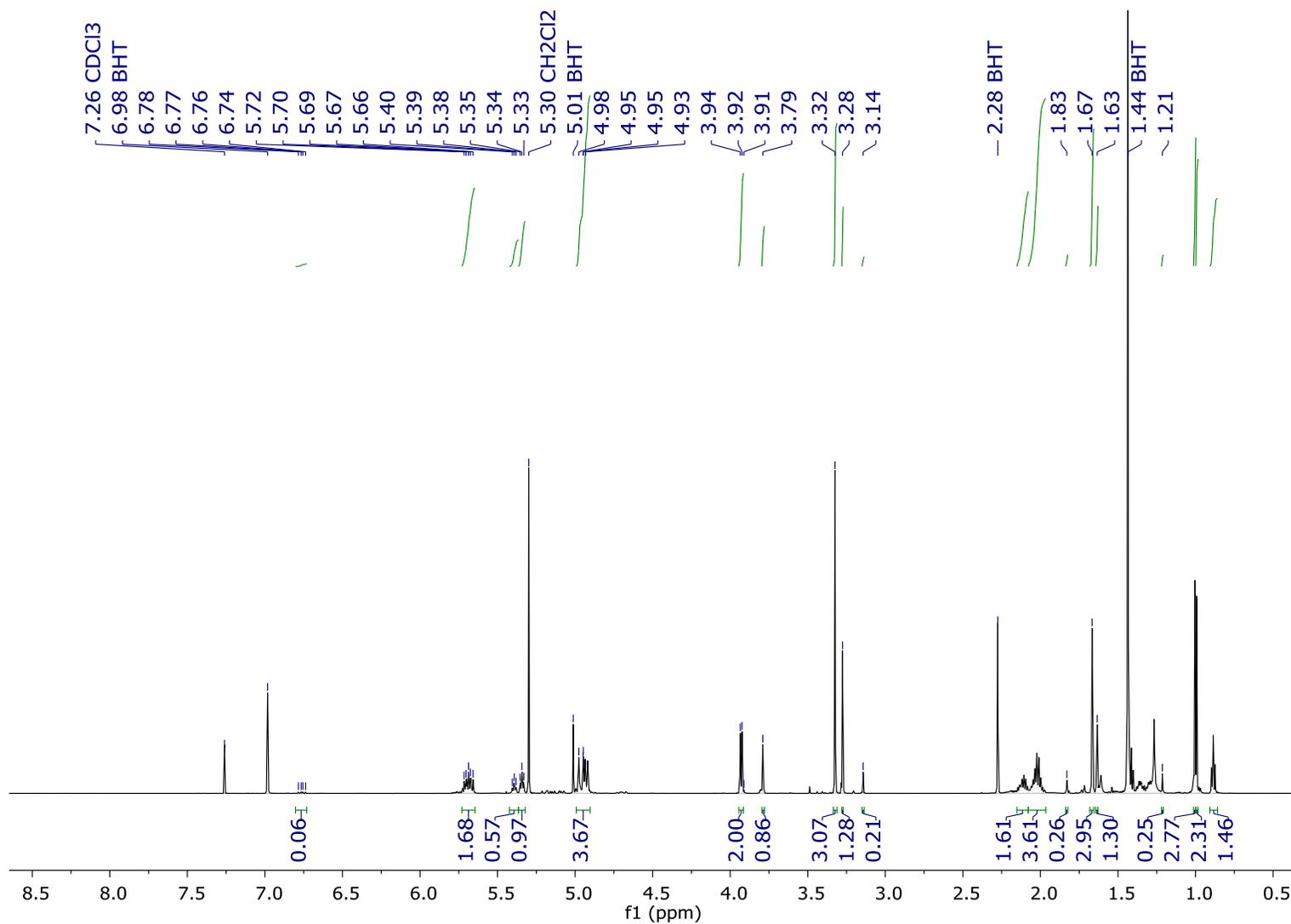


Figure S1. ¹H NMR (400 MHz, Chloroform-*d*) spectra of isomers mixture for Table 2 Entry 2.

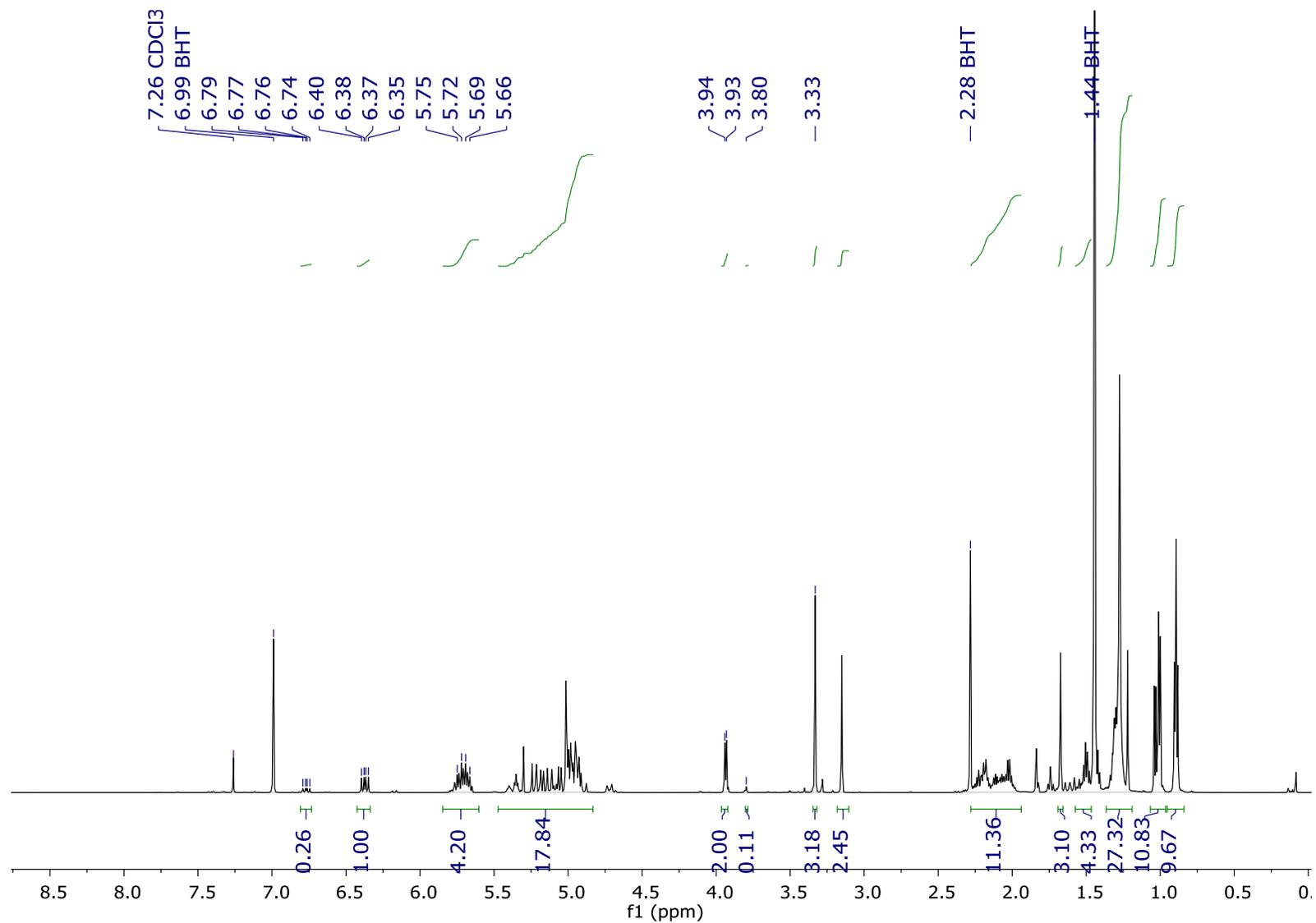


Figure S2. ¹H NMR (400 MHz, Chloroform-*d*) spectra of isomers mixture for Table 1 Entry 6.

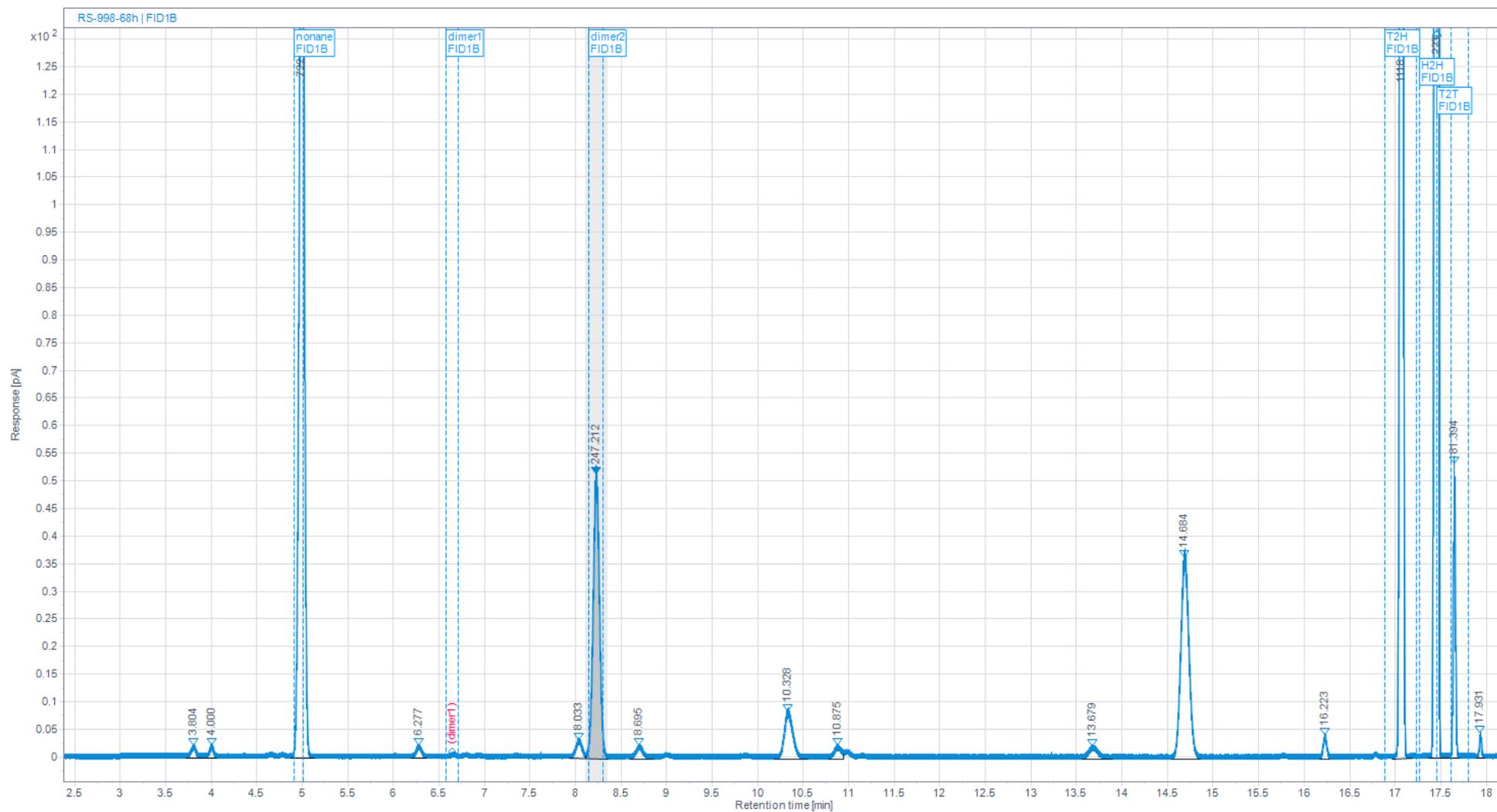


Figure S3. PID/GC Chromatogram of product mixture for Table 2 Entry 2.

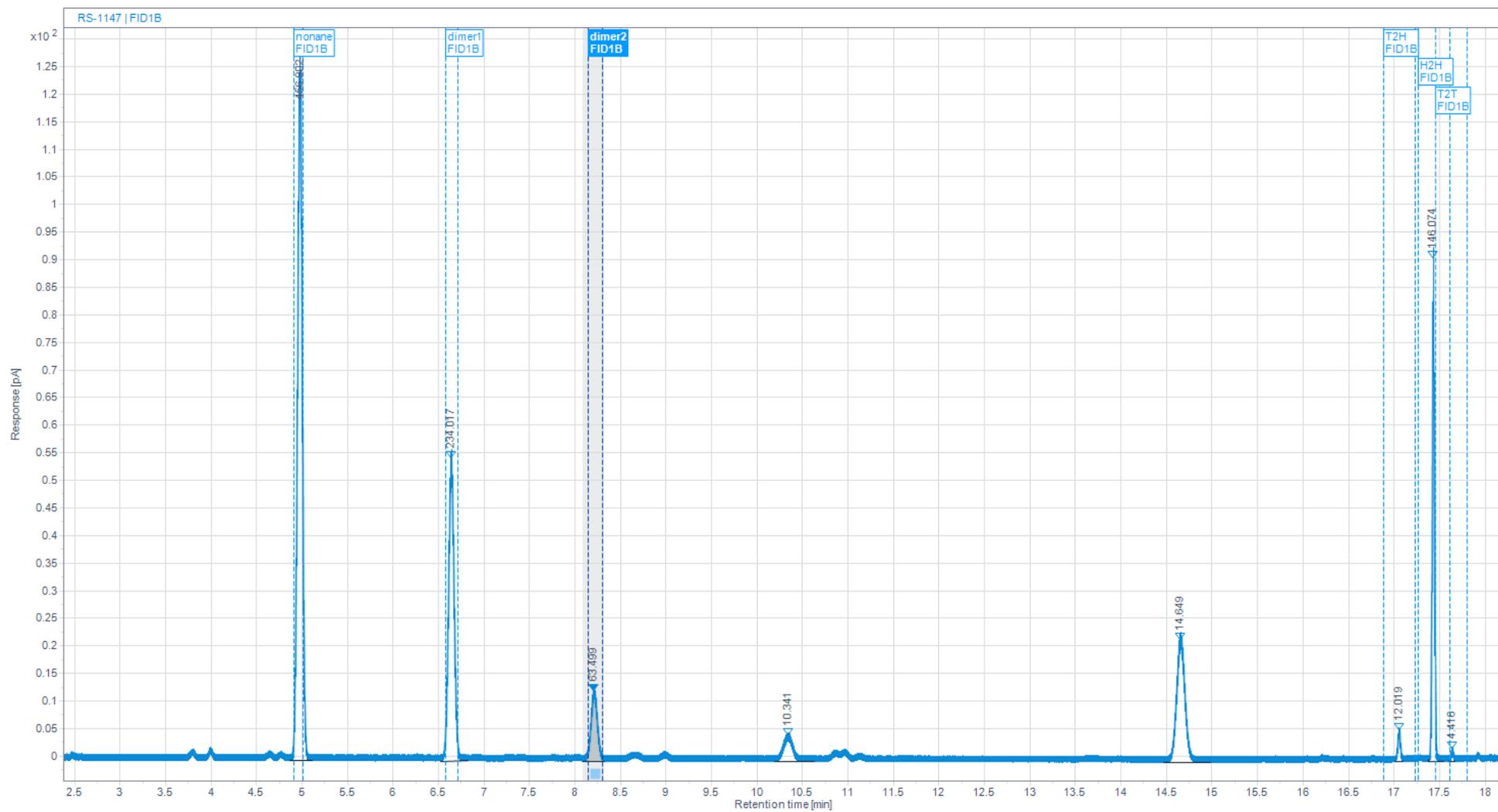


Figure S4. PID/GC Chromatogram of product mixture for Table 1 Entry 6.