Supporting Information

Room Temperature, Solventless Telomerization of Isoprene with Alcohols Using (*N*-Heterocyclic Carbene)-Palladium Catalysts

Irene Maluenda,[a] Ming-Tsz Chen, [b] Daniel Guest, [a] S. Mark Roe,[a]
Michael L. Turner [b] and Oscar Navarro[a]*

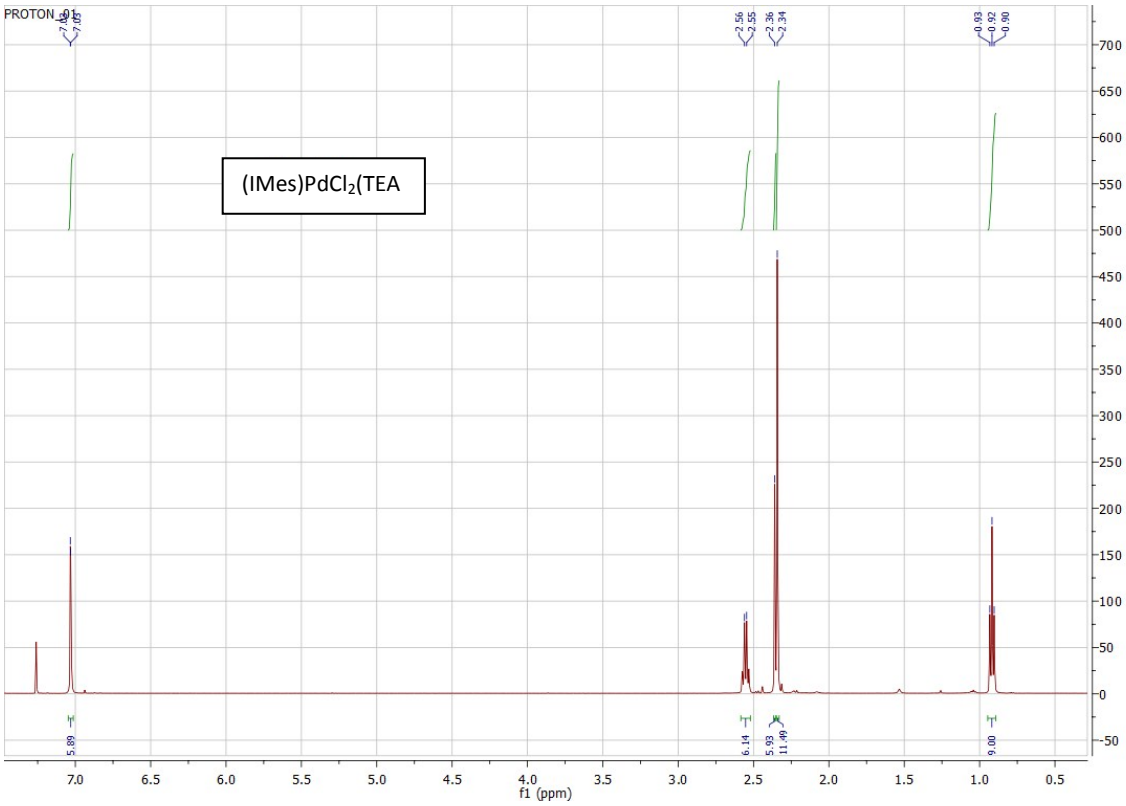
[a]Department of Chemistry, University of Sussex, Brighton, BN1 9QJ, United Kingdom
[b]School of Chemistry, The University of Manchester, Manchester, M13 9PL, United Kingdom.

General procedure for the synthesis of complexes

In a glovebox, a microwave vial equipped with a magnetic stir bar was charged with 0.5 mmol of $Pd(acac)_2$, and 0.55 mmol of the corresponding NHC·HCl salt under nitrogen. Then 5 mL of dry THF were injected and the mixture was reacted for 0.5 h at 110 ºC in a microwave reactor to obtain (IMes)PdCl(acac). After completion, THF was evaporated and the solid redisolved in CH_2Cl_2 and filtered through a silica plug. This solid was reacted with HCl in dioxane under nitrogen for 2h, with vigorous stirring. A change in colour from yellow to orange was immediately detected after addition of HCl to obtain the dimer. 0.12 mmol of $[Pd(\mu Cl)Cl(IMes)]_2$, or 0.29 mmol of $[Pd(\mu Cl)Cl(SIMes)]_2$ were suspended in dichloromethane and an excess of triethylamine (0.5 mL) was added, stirring this mixture at room temperature for 1 hour. Finally, the solvent was removed under vacuum, resulting in a pale yellow solid that was washed several times with cold pentane.

(IMes)PdCl$_2$(TEA) (1b): Yield: 134 mg (96 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.92 (t, *J* = 7.2 Hz, $N(CH_2CH_3)_3$), 9H), 2.34 (s, o-Ar-C*H*$_3$, 12H), 2.36 (s, p-Ar-C*H*$_3$, 6H), 2.55 (q, *J* = 7.2 Hz, $N(CH_2CH_3)_3$, 6H), 7.03 (s, C*H*, 2H), 7.03 (s, Ar*H*, 4*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 9.2 (s, $N(CH_2CH_3)_3$), 19.3 (s, CH_3-ArH), 21.1 (s, CH_3-ArH), 46.2 (s, $N(CH_2CH_3)_3$), 124.0 (s, *C*H aromatic), 128.9 (s, *C*H aromatic), 135.1 (s, *C* aromatic), 136.4 (s, *C* aromatic), 138.9 (s, *C* aromatic), 151.8 (s, *C* carbene). Anal. Calcd. For $C_{27}H_{39}Cl_2N_3Pd$: C, 55.63; H, 6.74; N, 7.21. Found: C, 55.49; H, 6.47; N, 7.06.

(SIMes)PdCl$_2$(TEA) (2b): Yield: 321 mg (94%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.82 (t, *J* = 7.0 Hz, $N(CH_2CH_3)_3$, 9H), 2.31 (s, *p*-Ar-C*H*$_3$, 6H), 2.49 (q, *J* = 7.0 Hz, $N(CH_2CH_3)$, 6H), 2.55 (s, *o*-Ar-C*H*$_3$, 12H), 4.00 (s, C*H*$_2$, 4H), 6.99 (s, Ar*H*, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 9.0 (s, $N(CH_2CH_3)_3$), 19.5 (s, CH_3-Ph), 21.0 (s, CH_3-Ph), 46.4 (s, $N(CH_2CH_3)_3$), 50.9 (s, CH_2), 129.2 (s, *C*H aromatic), 134.9 (s, *C* aromatic), 137.4 (s, *C* aromatic), 138.2 (s, *C* aromatic), 183.7 (s, *C* carbene) Anal. Calcd. For $C_{27}H_{41}Cl_2N_3Pd$: C, 55.44; H, 7.06; N, 7.18. Found: C, 55.09; H, 7.15; N, 7.13.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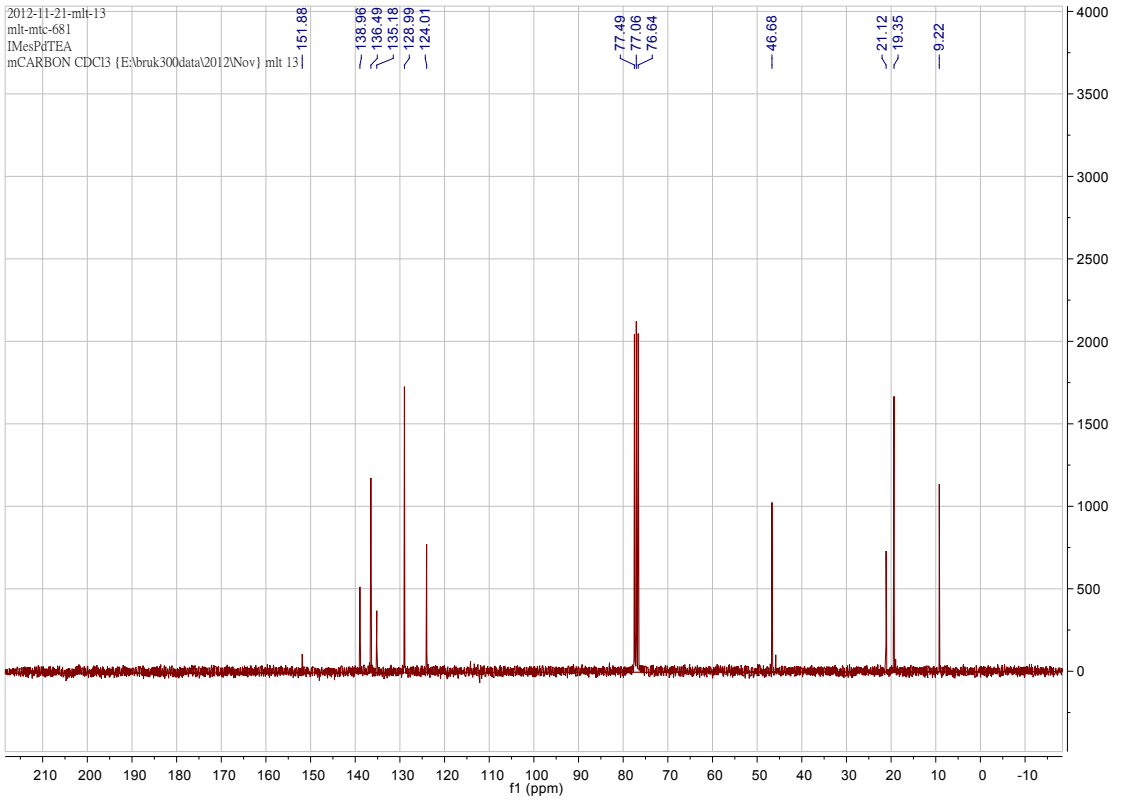
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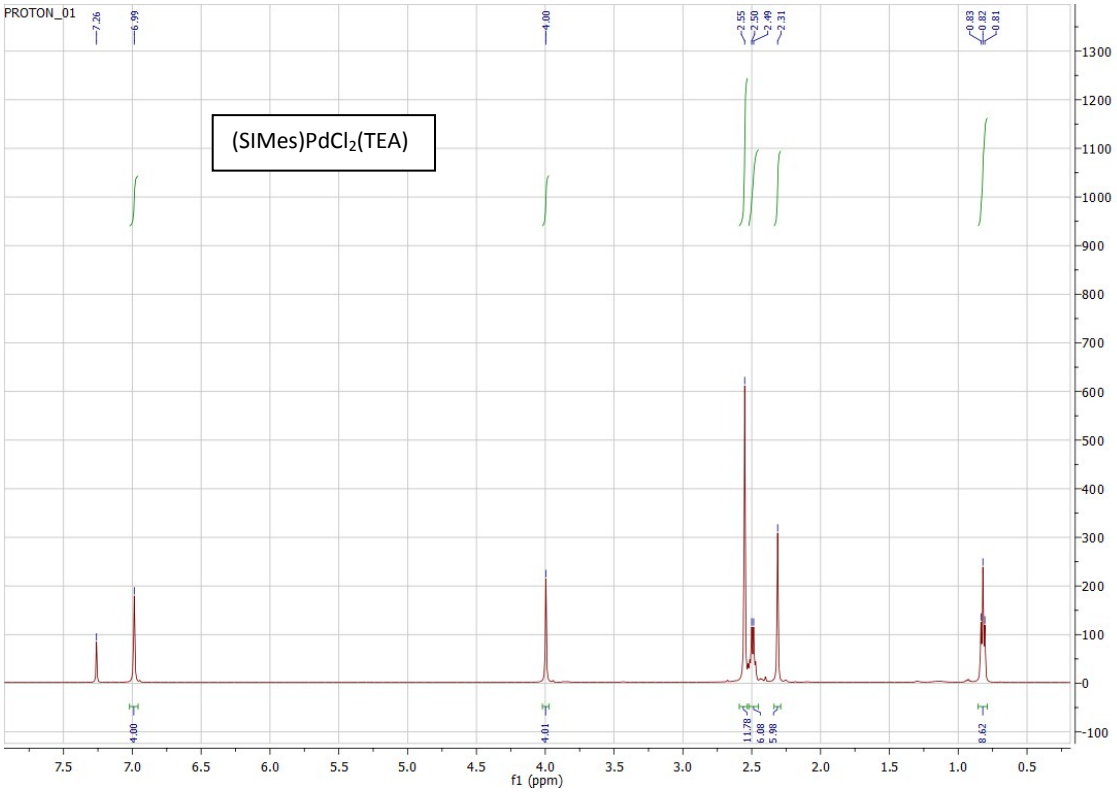
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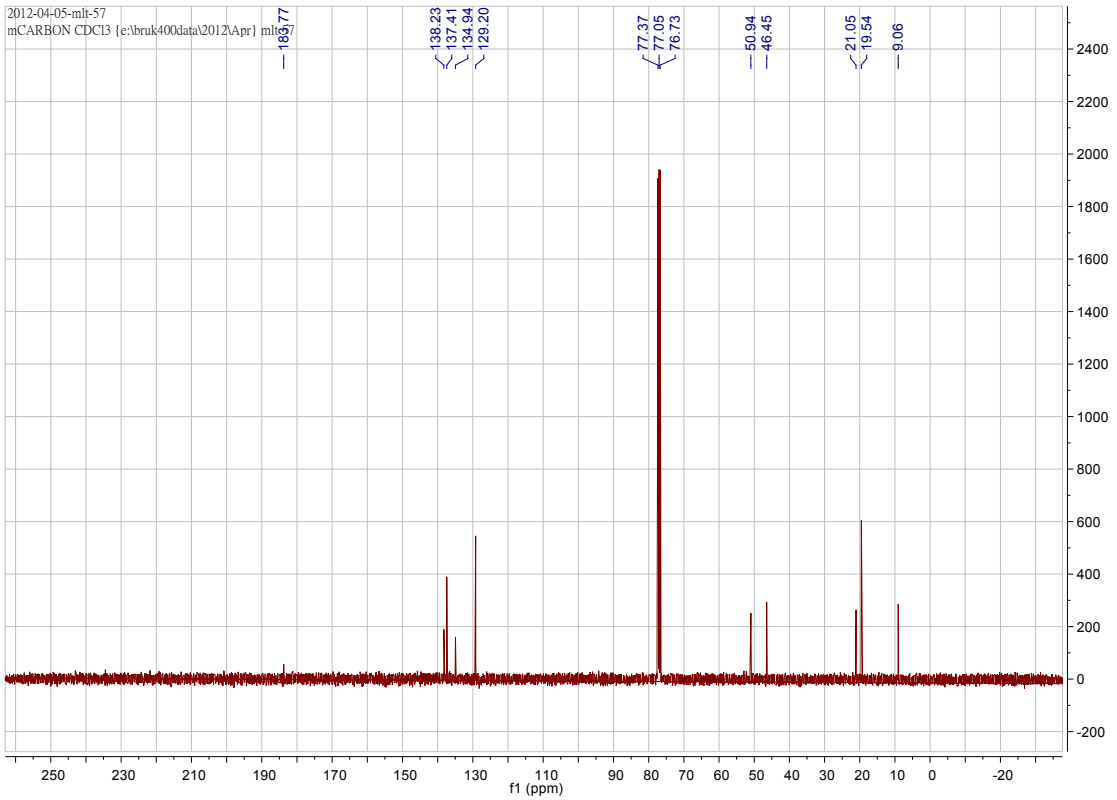
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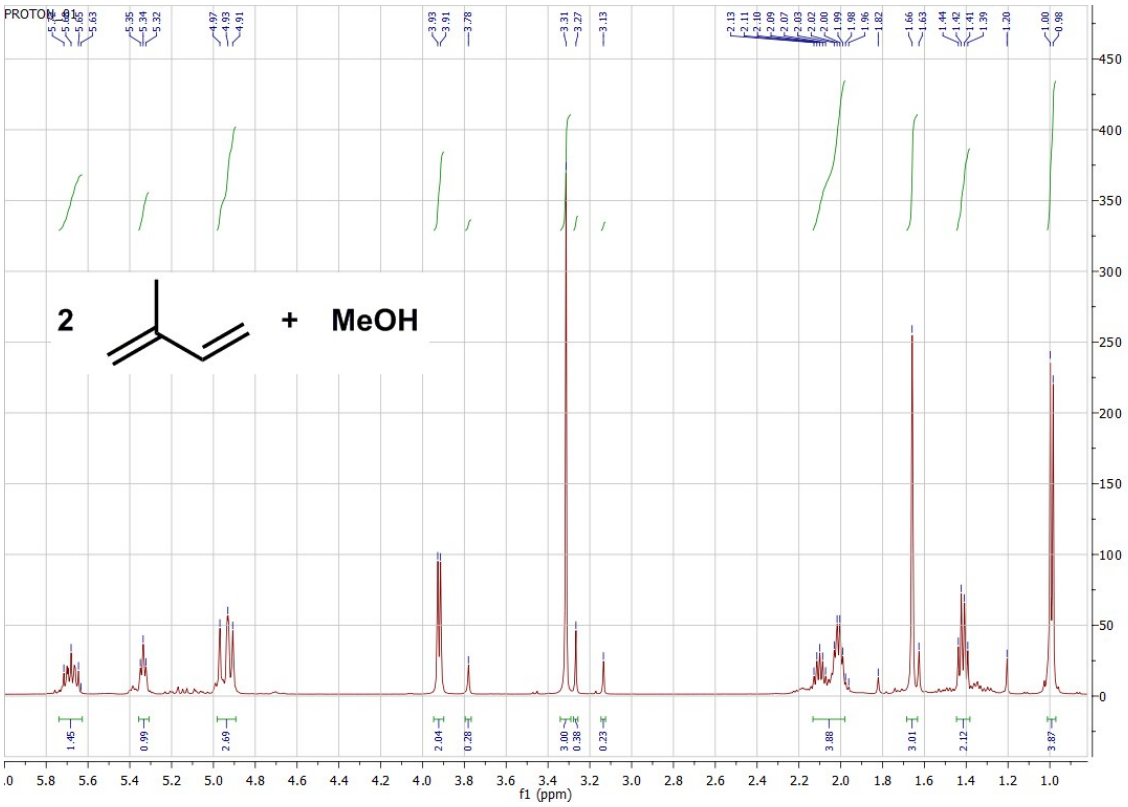
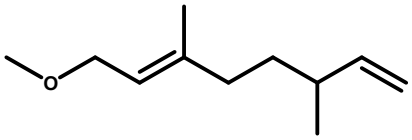
General procedure for the telomerization of isoprene with alcohols

In a 5 mL vial equipped with a screw cap and a septum, 0.015 mmol of the corresponding [(NHC)$PdCl_2$(TEA)] catalyst and 0.2 mmol of sodium methoxide were dissolved in 15 mmol of alcohol with vigorous stirring for 10 minutes. Then nitrogen was injected through the septum in order to flush the air, and finally 3 mL of isoprene (30 mmol) were injected. The mixture was stirred at room temperature for 72 hours to obtain a pale yellow, turbid solution. The catalyst was removed by filtration, and the oily mixture of products was analyzed by GC-MS. Telomers and dimers were identified when possible by comparison with available data from the literature. [1,2] The reaction mixture was distilled under reduced pressure and the fraction containing the telomers was analyzed by ^{1}HNMR.



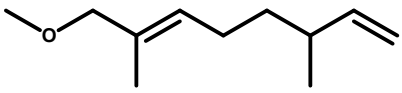


1-methoxy-3,6-dimethyl-2,7-octadiene (H2H)

^{1}H NMR ($CDCl_3$, 500 MHz)

δ (ppm) 5.72 -5.63 (m, 1H), 5.35 -5.32 (m, 1H), 4.97-4.91 (m, 2H), 3.92 (d, 2H), 3.31 (s, 3H), 2.13-2.17 (m, 1H), 2.03-1.96 (m, 2H), 1.66 (s, 3H), 1.44-1.39 (m, 2H), 0.99 (d, 3H).

MS (m/z): 153, 136 [M^+ - MeOH], 85, 68, 55.

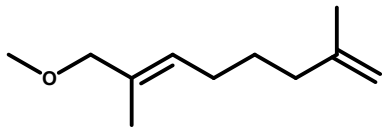


1-methoxy-2,6-dimethyl-2,7-octadiene (T2H)

Selected signals in ^{1}H NMR ($CDCl_3$, 500 MHz)

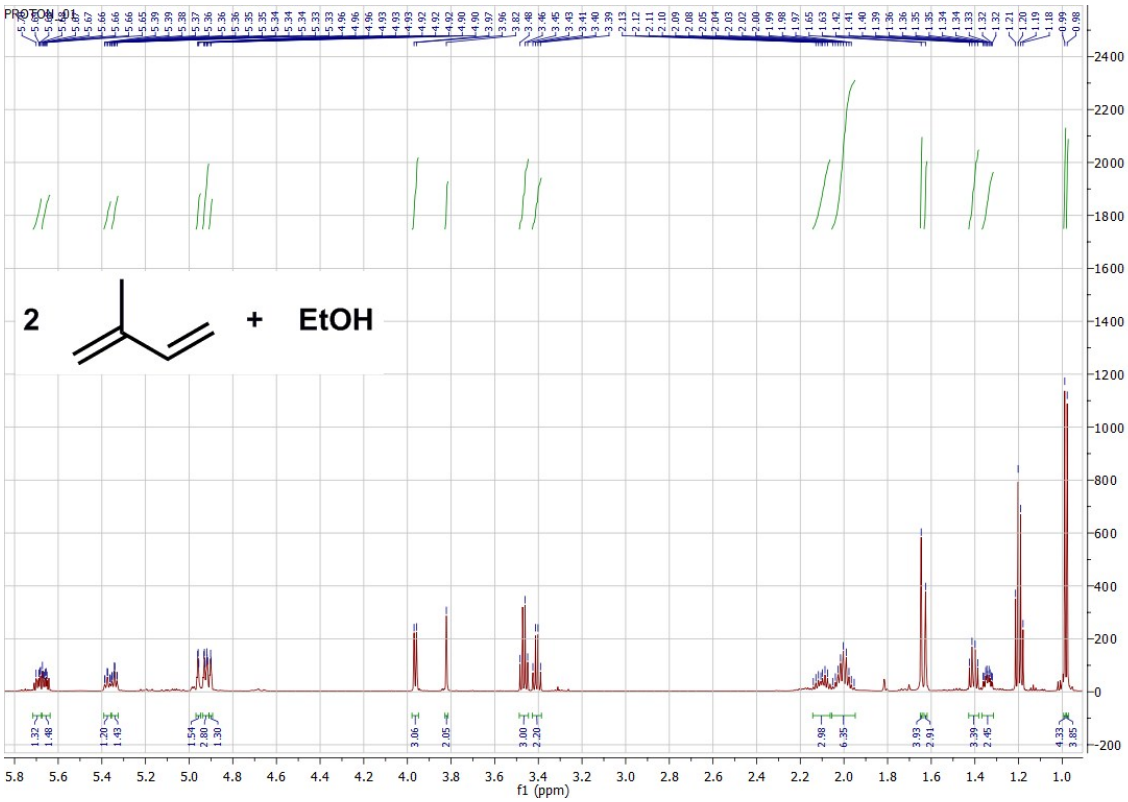
δ (ppm) 3.78 (s, 2H), 3.27 (s, 3H), 1.63 (s, 3H).

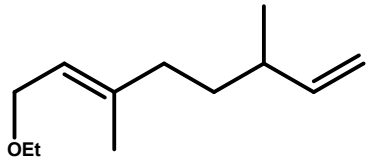
MS (m/z): 136 [M^+ - MeOH], 121, 85, 68, 55.



1-methoxy-2,7-dimethyl-2,7-octadiene (T2T)

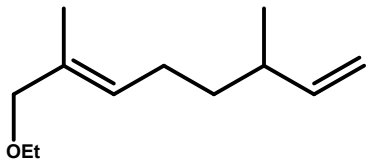
Selected signals in ^{1}H NMR ($CDCl_3$, 500 MHz)
δ (ppm) 3.13 (s, 3H), 1.82 (s, 3H), 1.20 (s, 3H).
MS (m/z): 153 (M^+ - CH_3), 85, 68, 55.





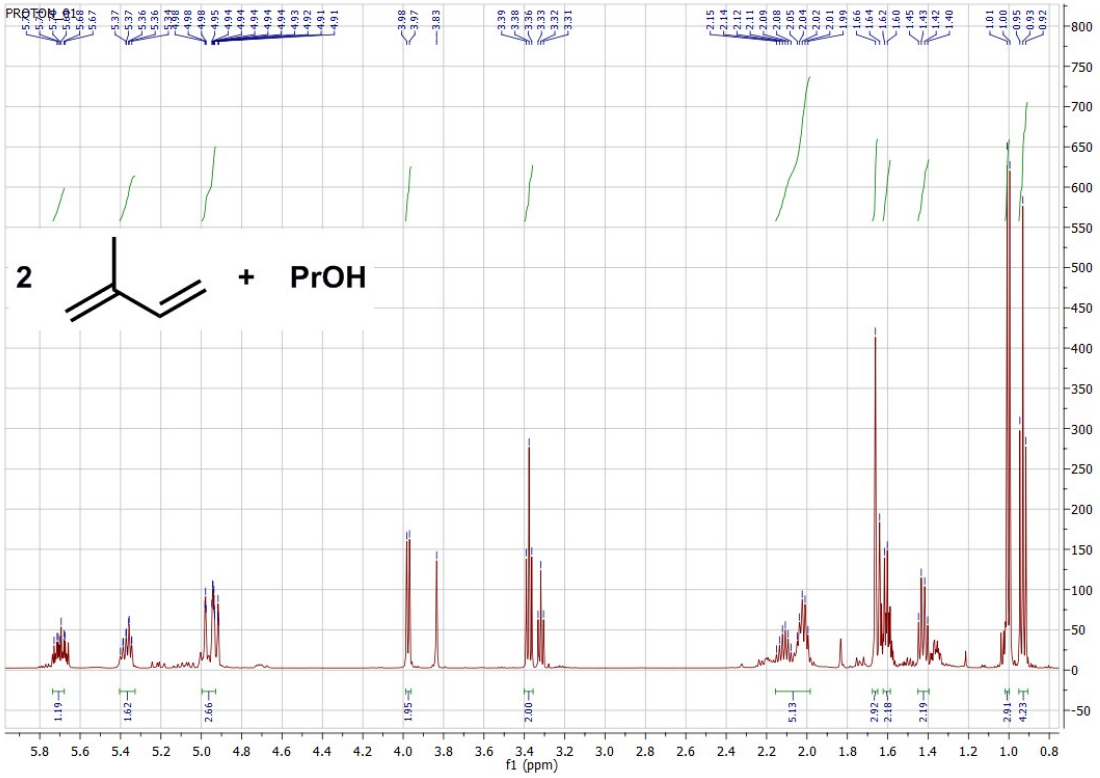
1-ethoxy-3,6-dimethyl-2,7-octadiene (H2H)

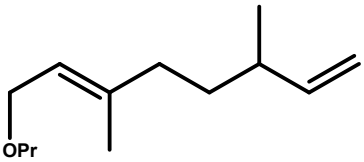
^{1}H NMR ($CDCl_3$, 500 MHz)
δ (ppm) 5.70-5.65 (m, 1H), 5.35-5.33 (t, 1H), 4.96-4.90 (m, 2H), 3.97-3.96 (d, 2H), 3.48-3.45 (q, 2H), 2.15-2.08 (m, 1H), 2.04-1.99 (m, 2H) 1.65 (s, 3H), 1.42-1.39 (m, 2H), 1.21-1.19 (t, 3H), 0.99-0.98 (d, 3H).



1-ethoxy-2,6-dimethyl-2,7-octadiene (T2H)

Selected signals in ^{1}H NMR ($CDCl_3$, 500 MHz)
δ (ppm) 3.82 (s, 2H), 3.43-3.39 (q, 2H), 2.14-2.08 (m, 1H), 1.63 (s, 3H).

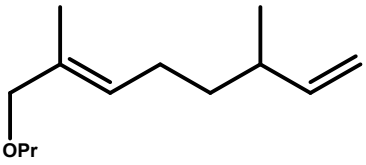




1-propoxy-3,6-dimethyl-2,7-octadiene (H2H)

^{1}H NMR ($CDCl_3$, 500 MHz)

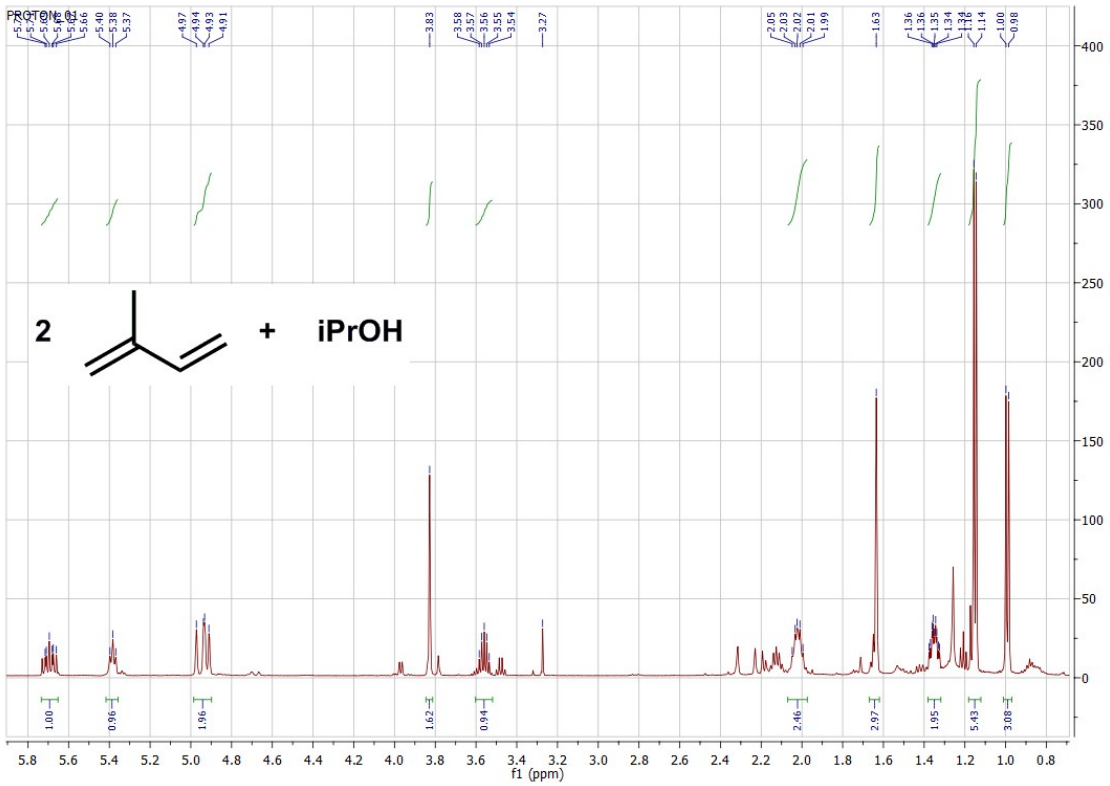
δ (ppm) 5.74-5.66 (m, 1H), 5.37-5.36 (m, 1H), 4.98-4.94 (m, 2H), 3.98-3.97 (d, 2H), 3.39-3.36 (t, 2H), 2.15-2.08 (m, 1H) 2.04-1.99 (m, 2H), 1.66 (s, 3H), 1.62-1.60 (m, 2H), 1.45-1.40 (m, 2H), 1.01 (d, 3H), 0.94 (t, 3H)

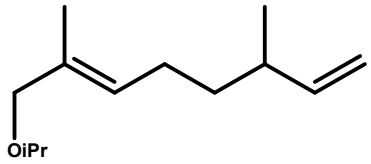


1-propoxy-2,6-dimethyl-2,7-octadiene (T2H)

Selected signals ^{1}H NMR ($CDCl_3$, 500 MHz)

δ (ppm) 3.83 (s, 2H), 3.33-3.31 (t, 2H), 1.64 (s, 3H).

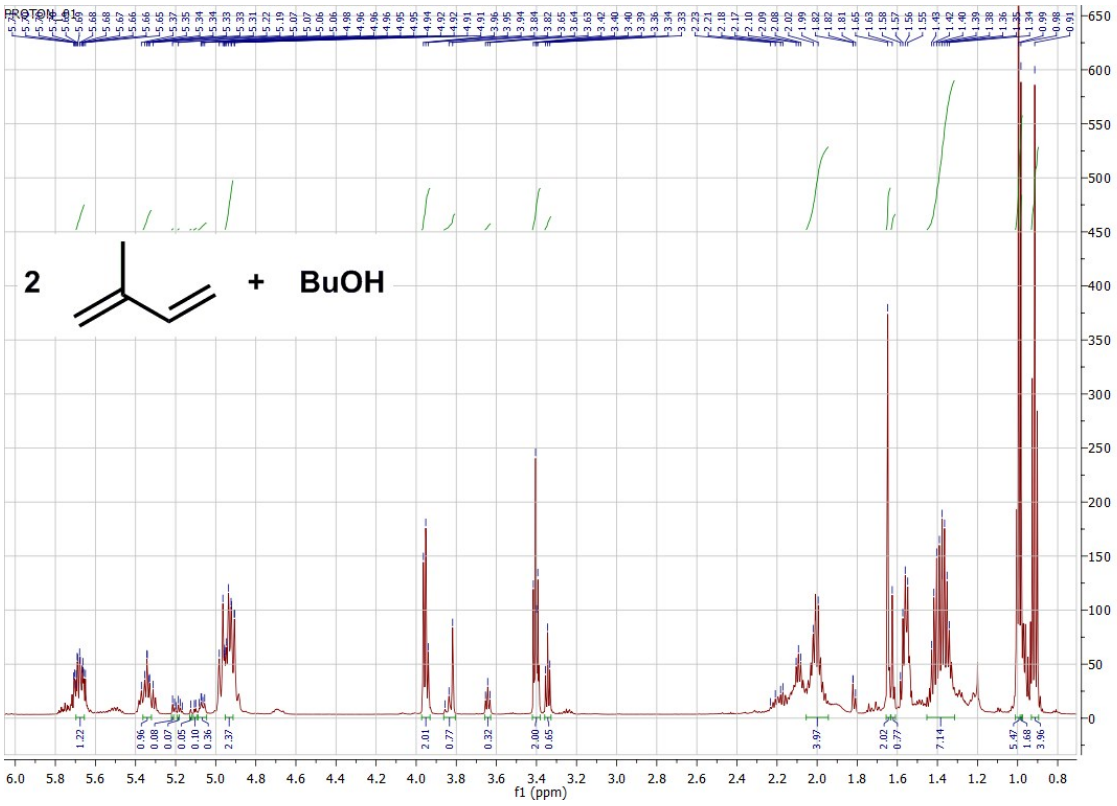


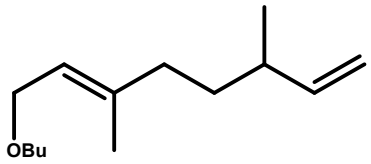


1-isopropoxy-2,6-dimethyl-2,7-octadiene (T2H)

^{1}H NMR ($CDCl_3$, 500 MHz)

δ (ppm) 5.71-5.66 (m, 1H), 5.40-5.37 (m, 1H), 4.97-4.91 (m, 2H), 3.83 (s, 2H), 3.58-3.55 (sept, 1H), 2.14-2.11 (m, 1H), 2.05-1.99 (m, 2H), 1.63 (s, 3H), 1.16-1.14 (d, 6H), 1.00-0.98 (d, 3H).

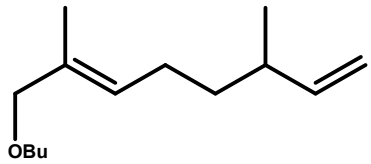




1-butoxy-3,6-dimethyl-2,7-octadiene (H2H)

^{1}H NMR ($CDCl_3$, 500 MHz)

δ (ppm) 5.72-5.65 (m, 1H), 5.37-5.33 (m, 1H), 4.96-4.94 (m, 2H), 3.96-3.95 (d, 2H), 3.42-3.39 (t, 2H), 2.04-1.99 (m, 4H), 1.65 (s, 3H), 0.99 (t, 3H).



1-butoxy-2,6-dimethyl-2,7-octadiene (T2H)

Selected signals in ^{1}H NMR ($CDCl_3$, 500 MHz)

δ (ppm) 3.95 (s, 2H), 3.36-3.33 (t, 2H), 1.63 (s, 3H), 0.91 (t, 3H).

1. R. C. Nunes, M. H. Araujo, E. N. dos Santos, *Catal. Commun.*, 2007, **8**, 1798.

2. R. Jackstell, A. Grotevendt, D. Michalik, L. El Firdoussi, M. Beller, *J. Organomet. Chem*., 2007, **692**, 4737.