

**Palladium nanoparticles *in situ* synthesized on *Cyclea barbata* pectin as a heterogeneous catalyst for Heck coupling in water, reduction of nitrophenols and alkynes.**

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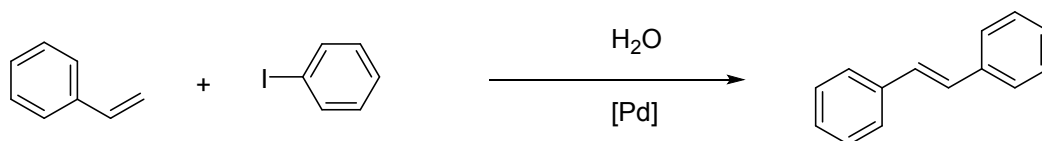
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## Supplementary Data

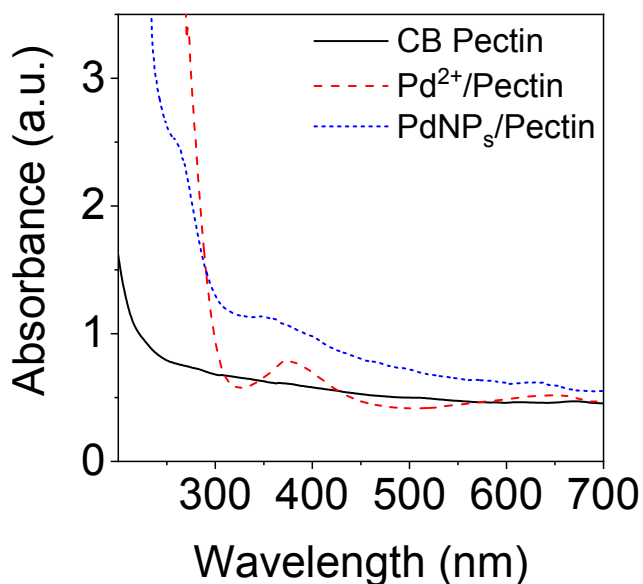
**Table S1.** Comparison of the results obtained from various palladium-based catalyst system for the Heck coupling reaction in water.



Catalyst	T (°C)	Time (h)	[Pd] (% mol)	Yield (%)	Ref.
PTFE-Pd NPs	90	15	1.0	91	[1]
Pd -TOTPS	150	6	0.03	60	[2]
PdNPs@PS- IL[Cl]	100	6	0.2	42	[3]
Pd@Cellulose	90	6	0.12	98	[4]
Pd@ PS-PEG	50	20	10	92	[5]
PdNPs@Pectin	90	6	0.5	90	This work

**Table S2.** Summary for catalytic performance of PdNPs@Pectin for reduction of nitrophenols.

Substrates	time (s)	k ( $10^{-3}, \text{s}^{-1}$ )	R <sup>2</sup>	TON	TOF ( $10^{-5}, \text{s}^{-1}$ )
<i>o</i> -nitrophenol	600	2.93	0.972	0.0289	4.82
<i>m</i> -nitrophenol	360	2.88	0.973	0.0289	8.03
<i>p</i> -nitrophenol	840	2.42	0.991	0.0289	3.44



**Figure S1.** UV-Vis spectra of *C. barbata* pectin, Pd<sup>2+</sup>@Pectin and PdNPs@Pectin

### Catalytic activity for Heck Coupling

*1,2-diphenylethene*. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ = 7.53 (m, 4H); 7.37 (m, 4H); 7.27 (m, 2H); 7.11 (s, 2H).

*1-methyl-4-styrylbenzene*.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta = 7.51$  (m, 2H); 7.42 (d,  $J$  8.5 Hz, 2H); 7.36 (m, 2H); 7.25 (m, 1H), 7.17 (d,  $J$  7.5 Hz, 2H), 7.07 (dd  $J$  16.5, 3.5 Hz, 2H), 2.36 (s, 3H).

*1-fluoro-4-styrylbenzene*.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta = 7.50$  (m, 4H); 7.37 (m, 2H); 7.28 (m, 1H); 7.09 (m, 4H).

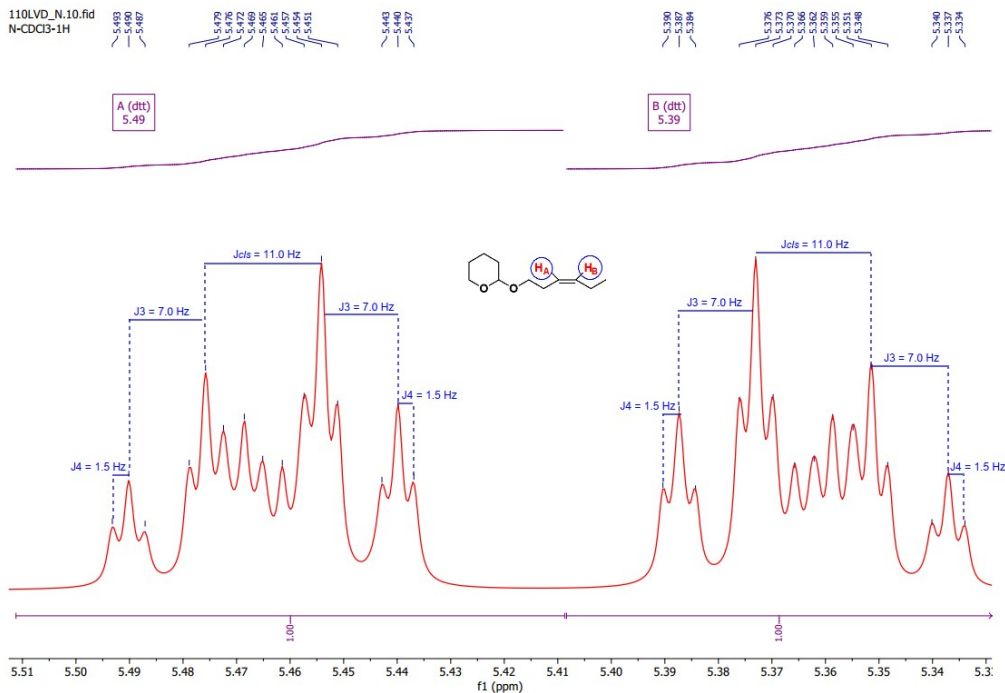
*1,2-di-*p*-tolylethene*.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta = 7.40$  (d,  $J$  8Hz, 4H); 7.16 (d,  $J$  8 Hz, 4H); 7.03 (s, 2H); 2.35 (s, 6H).

*1-fluoro-4-(4-methylstyryl)benzene*.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta = 7.47$  (m, 2H); 7.39 (d,  $J$  8.0 Hz, 2H); 7.17 (d,  $J$  7.5 Hz, 2H); 7.05 (m, 2H), 7.00 (m, 2H), 2.36 (s, 3H).

*1,2-bis(4-fluorophenyl)ethene*.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz, ppm):  $\delta = 7.47$  (m, 4H); 7.01 (m, 4H); 6.97 (s, 2H).

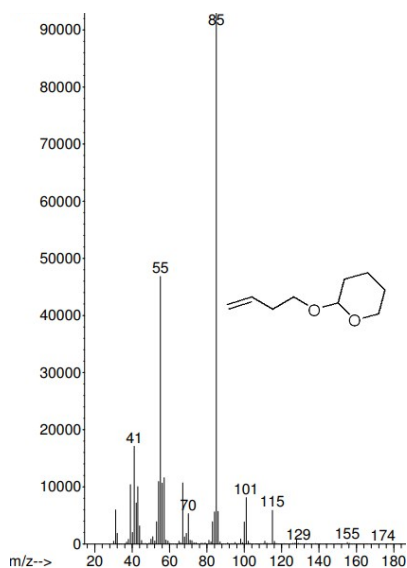
### **Catalytic activity for reduction of alkynes**

*(Z)-2-(hex-3-en-1-yloxy)tetrahydro-2H-pyran*.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz, ppm): 5.49-5.44 (dtt,  $J_1$  11Hz,  $J_2$  7Hz,  $J_3$  1.5 Hz 1H), 5.39-5.33 (dt,  $J_1$  10.5 Hz,  $J_2$  7.5 Hz,  $J_3$  1.5 Hz, 1H), 4.59 (m, 1H), 3.90-3.71 (m, 2H), 3.43-3.40 (m, 2H), 2.37-2.33 (m, 2H), 2.08-2.05 (m, 2H), 1.85-1.49 (m, 6H), 0.98-0.95 (t,  $J$  7.5 Hz, 3H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 125 MHz, ppm): 133.6, 125.0, 98.7, 67.1, 62.3, 30.7, 27.9, 25.5, 20.6, 19.6.

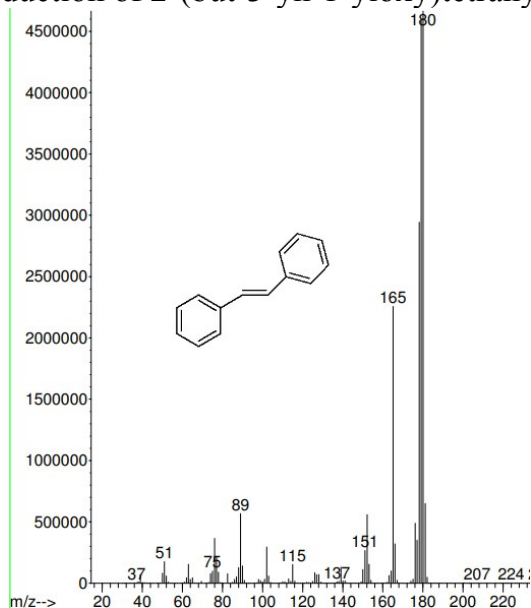


**Figure S2.** The two protons (*Z*) configuration of (*Z*)-2-(hex-3-en-1-yloxy)tetrahydro-2H-pyran.

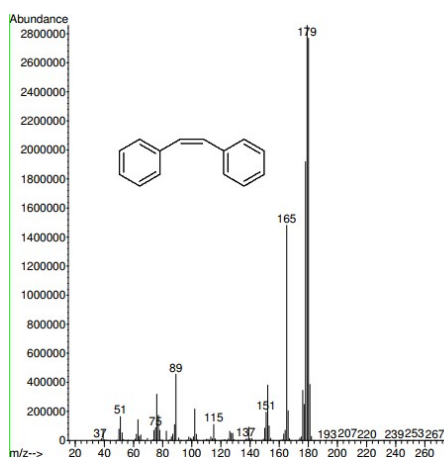
2-(*but-3-en-1-yloxy*)tetrahydro-2H-pyran. Bp: 85°C/10 mmHg.  $n_D^{29} = 1.449$ . GC-MS,  $m/z$ : 41, 55, 70, 85 (100), 101, 115, 129, 155.



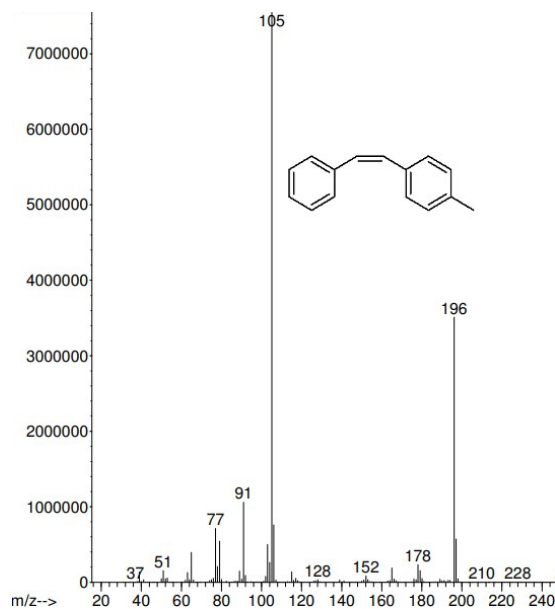
**Figure S3.** GC-MS spectrum of 2-(but-3-en-1-yloxy)tetrahydro-2H-pyran from reduction of 2-(but-3-yn-1-yloxy)tetrahydro-2H-pyran



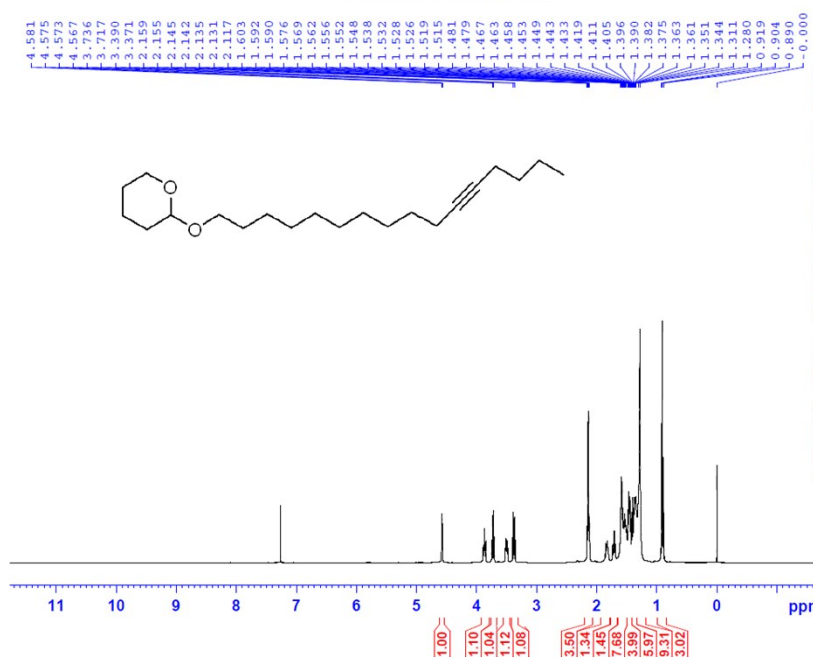
**Figure S4.** GC-MS spectrum *trans*-1,2-diphenylethene from Sonogashira coupling



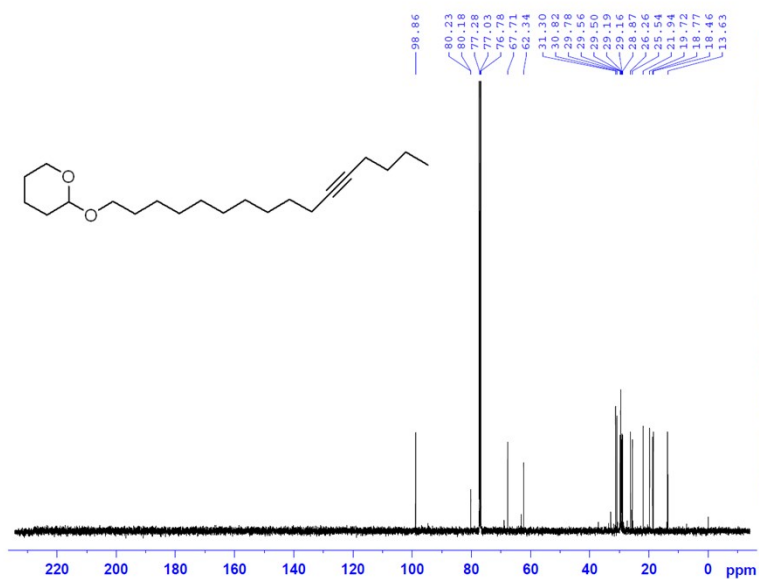
**Figure S5.** GC-MS spectrum of *cis*-1,2-diphenylethene from reduction of 1,2-diphenylethyne



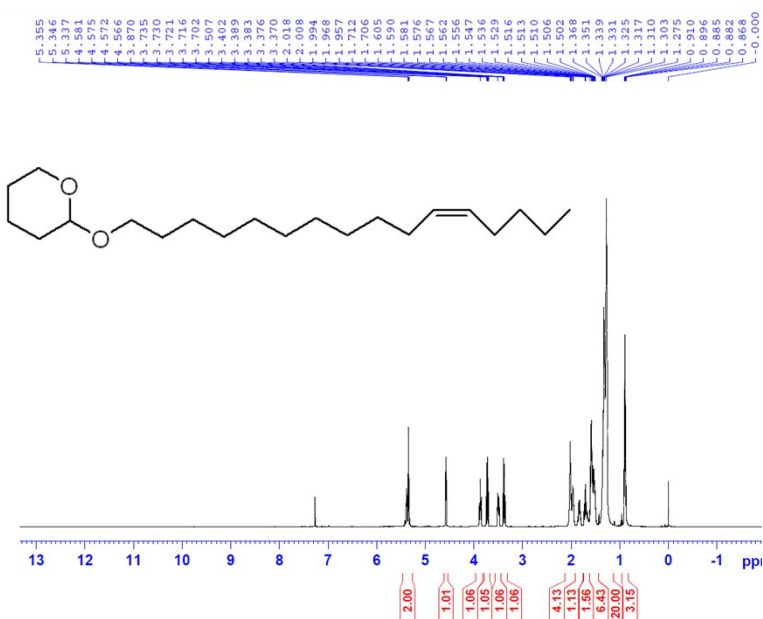
**Figure S6.** GC-MS spectrum *cis*-1-methyl-4-styrylbenzene from reduction of 1-methyl-4-(phenylethynyl)benzene



**Figure S7.** <sup>1</sup>H NMR spectrum of 2-(dodec-11-yn-1-yloxy)tetrahydro-2H-pyran (**3**)

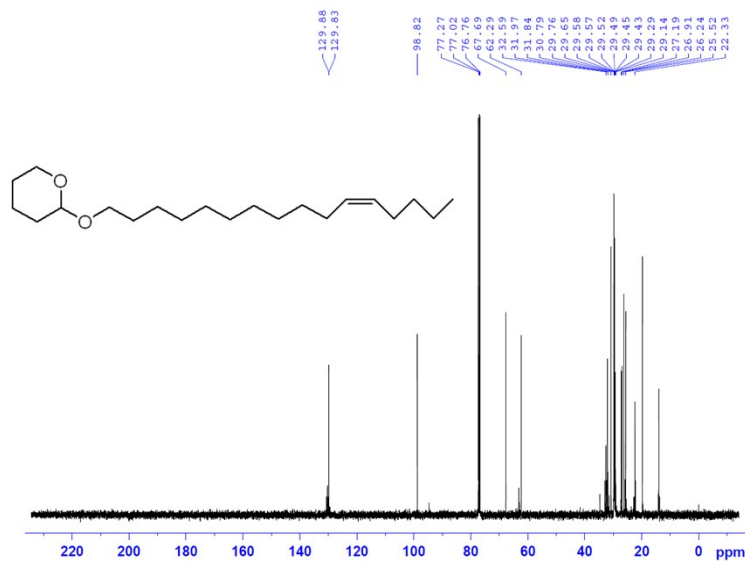


**Figure S8.** <sup>13</sup>C NMR spectrum of 2-(dodec-11-yn-1-yloxy)tetrahydro-2H-pyran (3)

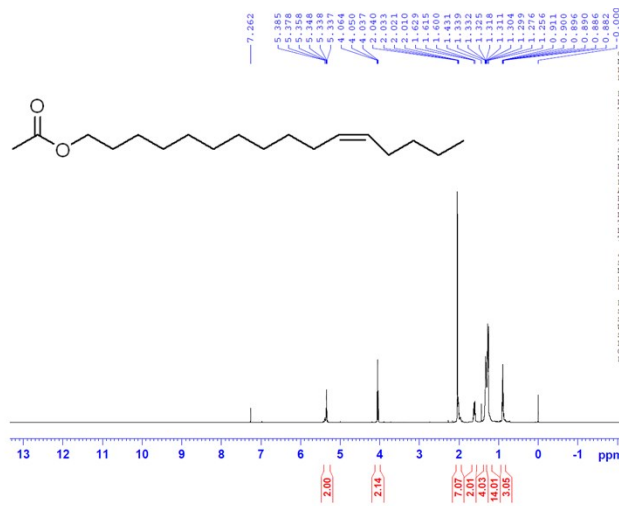


**Figure S9.** <sup>1</sup>H NMR spectrum of 2-(dodec-11-en-1-yloxy)tetrahydro-2H-pyran (4)

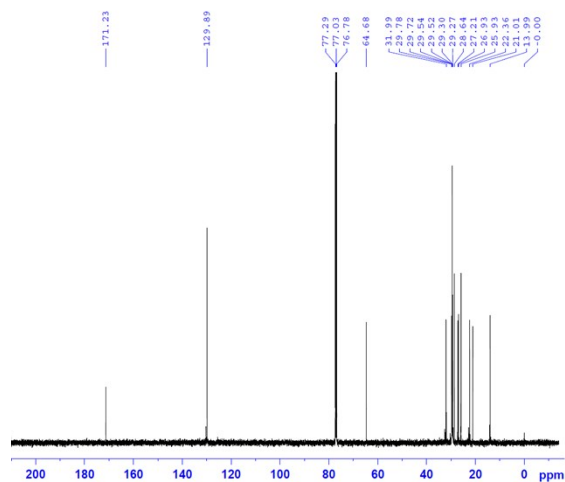




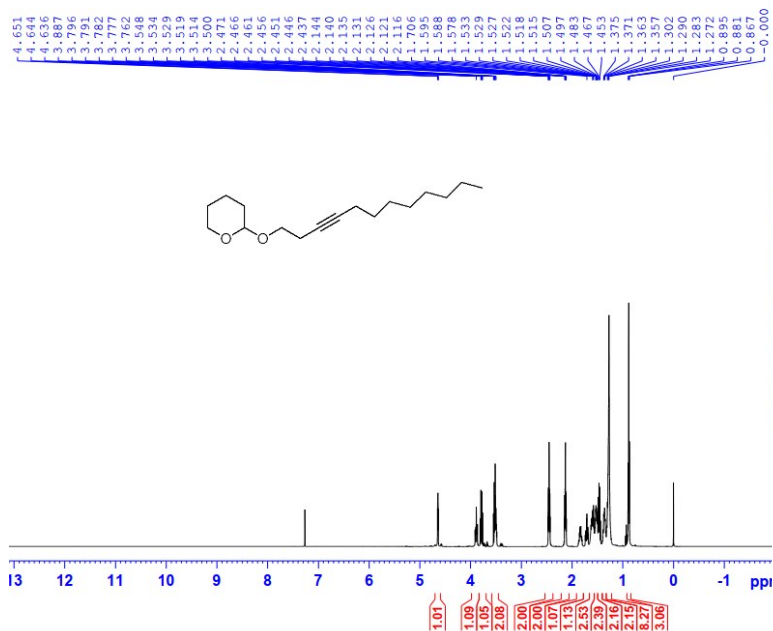
**Figure S10.** <sup>13</sup>C NMR spectrum of 2-(dodec-11-en-1-yloxy)tetrahydro-2H-pyran (**4**)



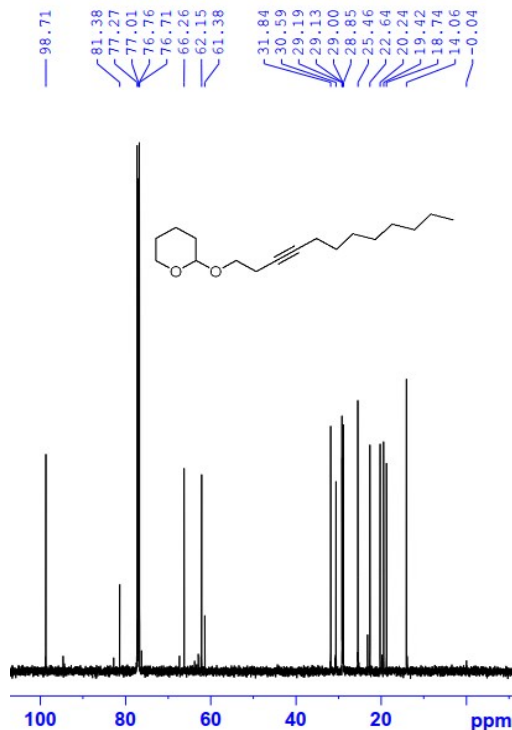
**Figure S11.** <sup>1</sup>H NMR spectrum of (Z)-11-hexadecenyl acetate (**5**)



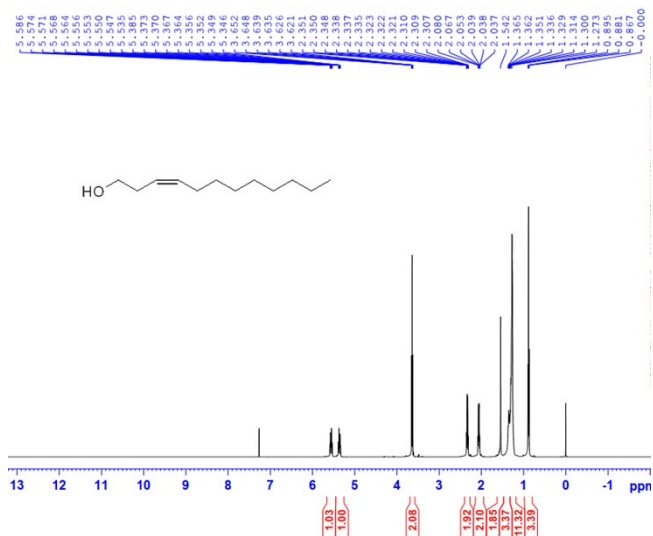
**Figure S12.**  $^{13}\text{C}$  NMR spectrum of (*Z*)-11-hexadecenyl acetate (**5**)



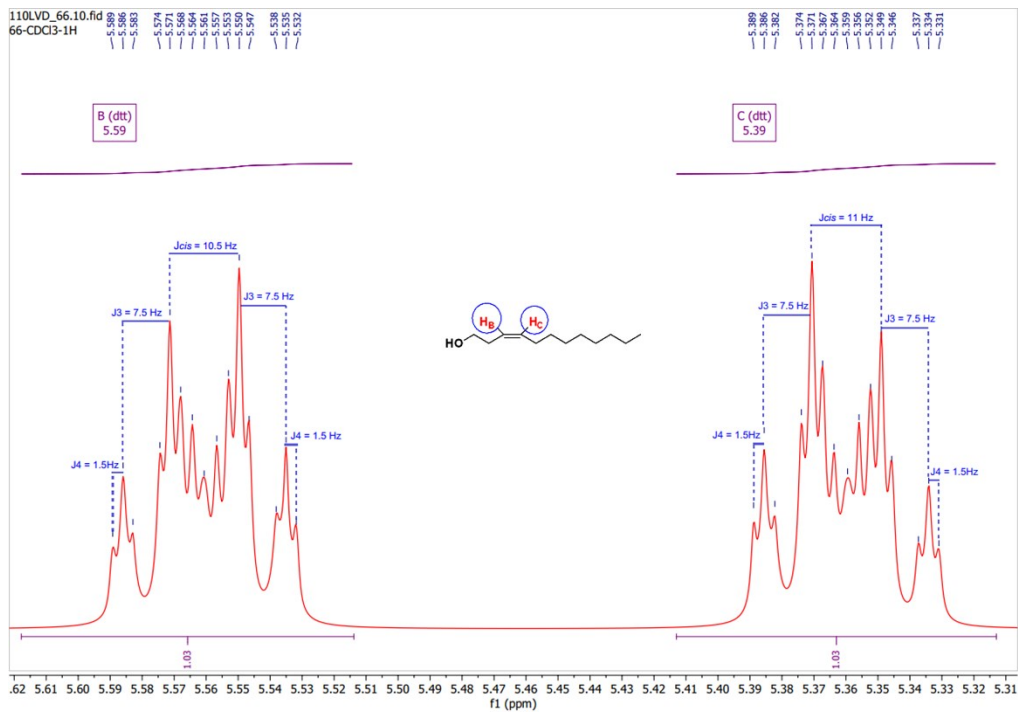
**Figure S13.**  $^1\text{H}$  NMR spectrum of 2-(dodec-3-yn-1-yloxy)tetrahydro-2H-pyran (**8**)



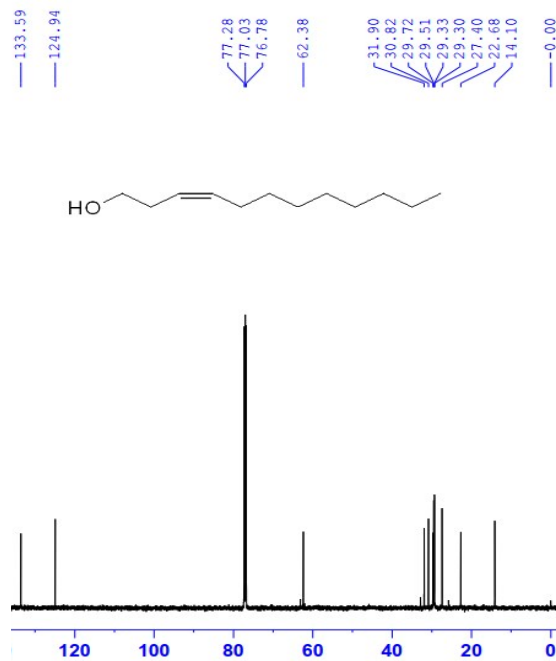
**Figure S14.** <sup>13</sup>C NMR spectrum of 2-(dodec-3-yn-1-yloxy)tetrahydro-2H-pyran (**8**)



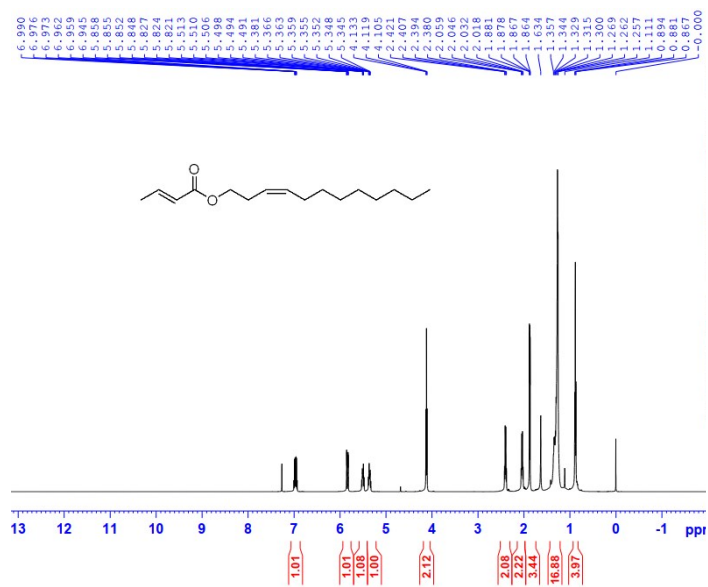
**Figure S15.** <sup>1</sup>H NMR spectrum of (Z)-dodec-3-en-1-ol (**9**)



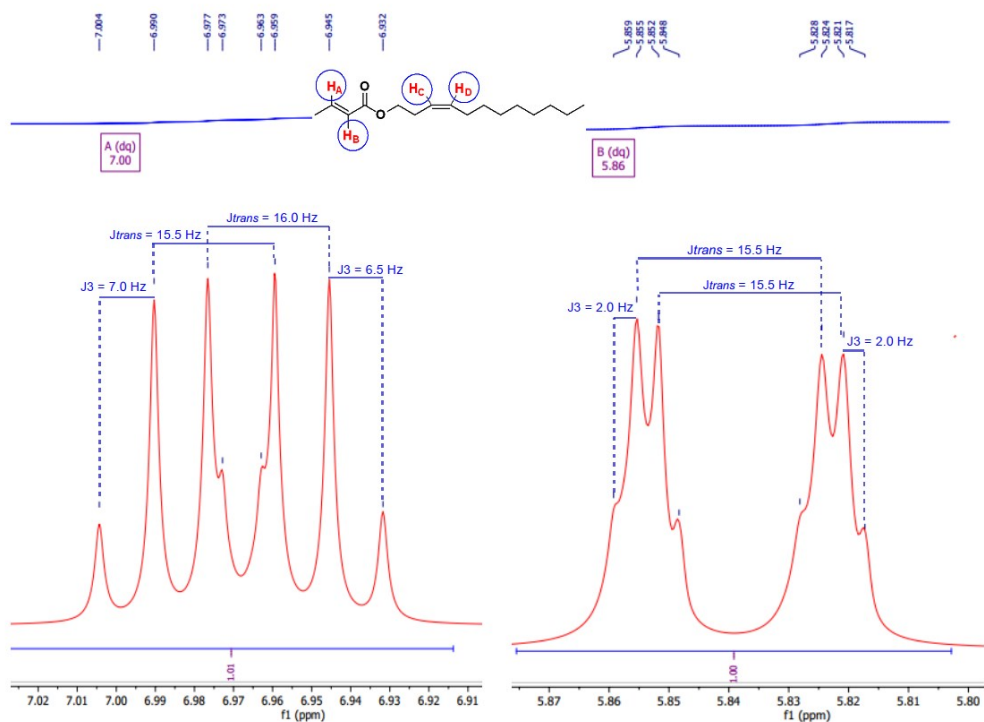
**Figure S16.** The two protons (Z) configuration of (Z)-dodec-3-en-1-ol (9)



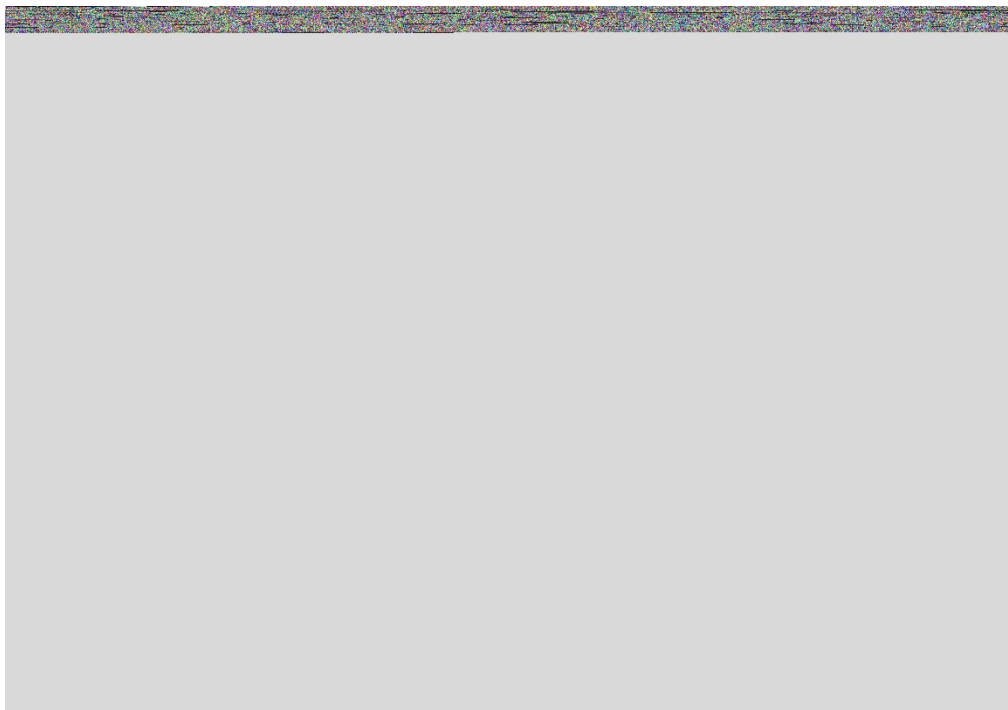
**Figure S17.** <sup>13</sup>C NMR spectrum of (Z)-dodec-3-en-1-ol (9)



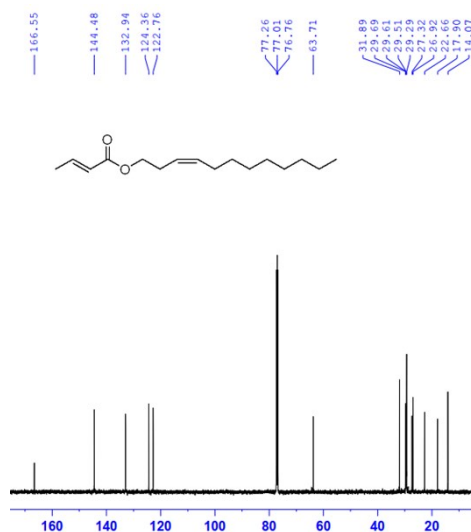
**Figure S18.**  $^1\text{H}$  NMR spectrum of (*Z*)-Dodec-3-en-1-yl (*E*)-2-butenate (**10**)



**Figure S19.** The two protons (*E*)-configuration of (*Z*)-Dodec-3-en-1-yl (*E*)-2-butenate (**10**)



**Figure S20.** The two protons (*Z*) configuration of (*Z*)-Dodec-3-en-1-yl (*E*)-2-butenate (**10**)



**Figure S21.** <sup>13</sup>C NMR spectrum of (*Z*)-Dodec-3-en-1-yl (*E*)-2-butenate (**10**)

## References

- [1] A. Ohtaka, M. Kawase, S. Aihara, Y. Miyamoto, A. Terada, K. Nakamura, G. Hamasaka, Y. Uozumi, T. Shinagawa, O. Shimomura, R. Nomura, *ACS Omega*, 2018, 3 (8), 10066–10073.
- [2] S. Jagtap, R. Deshpande, *Tetrahedron Letters*, 2013, 54, 2733–2736.
- [3] K. Qiao, R. Sugimura, Q. Bao, D. Tomida, C. Yokoyama, *Catalysis Communications*, 2008, 9, 2470–2474.
- [4] Y. Xu, L. Zhang, Y. Cui, *Journal of Applied Polymer Science*, 2008, 110, 2996–3000.
- [5] Y. Uozumi, T. Kimura, *Synlett* 2002, 12, 2045–2048.