Fucoidan-mediated green synthesis of palladium nanoparticles as a recyclable catalyst for Heck coupling and alkyne reduction in pheromone synthesis

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1. Experimental procedures and characterization data (GC–MS and NMR spectra) for the Heck coupling reaction, alkyne reduction, and the synthesis of insect pheromone.

The Heck coupling and Alkyne reduction reactions were carried out under nitrogen (N_2) atmosphere to ensure reduction and stabilization of the Pd^0 catalyst.

1.1. Catalytic activity for Heck reaction

The mixture of aryl halides **(1)** (1 mmol), olefines **(2)** (1.1 mmol), K_2CO_3 (2.6 mmol), and PdNPs@Fu catalyst (2.0 mg), anhydrous DMF (2.0 mL) was placed in a 25 mL ground-neck flask. Nitrogen gas was bubbled through the mixture for approximately 20 min to remove oxygen. The reaction mixture was stirred with a magnetic stirrer at a temperature of 100 ℃ for 6 hours in oil bath. Upon completion of the reaction, the conversion was monitored by thin layer chromatography (TLC) using *n*-hexane and ethyl acetate as the solvent system. Subsequently, the mixture was extracted with *n*-hexane, and the organic layer was washed successively with distilled water and saturated brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude product. The resulting product was isolated through silica gel column chromatography with an *n*-hexane/ethyl acetate mixture as the eluting solvent, and its purity was verified by GCMS analysis. **(Table 2)**. The catalyst recycling procedure was carried out as follows: after the completion of the reaction, *n*-hexane was added to the reaction medium to extract the organic components (with a volume ratio of *n*-hexane:DMF = 2:1). The mixture was centrifuged at 4 °C and 10,000 rpm for 5 min, and the hexane layer was carefully separated. The DMF phase was subsequently extracted twice with *n*-hexane. The remaining DMF layer containing the catalyst was reused by adding a fresh mixture of iodobenzene and styrene, followed by continuous stirring for 6 hours to perform the next catalytic run.

***(E)*-stiben *(1a)*:** H = 94%. Mp = 122-114 °C. R_f = . GC-MS (*m/z)*: 27, 39, 51, 63, 75, 76, 89, 102, 115, 126, 139, 152, 165, 166, 180 (100).

***(E)*-1-methoxy-4-(4-methylstyryl)benzene (1b):** H = 95%. Mp = 167-168. R_f = 0.85. GC-MS (*m/z)*: 15, 28, 42, 51, 63, 76, 89, 104, 127, 139, 152, 164, 181, 193, 209, 224 (100), 226.

***(E)*-4-(4-methoxystyryl)benzonitrile (1c):** H = 96%. Mp = 135-137. R_f = 0.52. GC-MS (*m/z)*: 15, 39, 51, 63, 75, 88, 102, 114, 126, 140, 152, 165, 177, 190, 204, 219, 235 (100).

***(E)*-1-fluoro-4-(4-methylstyryl)benzene (1d):** H = 80%. Mp = 159-161. R_f = 0.92. GC-MS (*m/z)*: 63, 79, 92, 105, 115, 126 137, 152, 165, 178, 197, 208, 212 (100).

***(E)*-4-(4-fluorostyryl)benzonitrile (1e):** H = 83%. Mp = 135-137. R_f = 0.63. GC-MS (*m/z)*: 27, 39, 51, 63, 75, 85, 98, 111, 120, 131, 145, 157, 169, 183, 196, 208, 223 (100).

***(E)*-1-chloro-4-(4-methylstyryl)benzene (1f):** H = 76%. Mp = 200-202. R_f = 0.85. GC-MS (*m/z)*: 27, 36, 51, 63, 76, 89, 99, 115, 128, 139, 152, 163, 178, 193 (100), 228.

***(E)*-4-(4-chlorostyryl)benzonitrile (1g):** H = 85. Mp = 173-175. R_f = 0.73. GC-MS (*m/z)*: 39, 51, 63, 75, 88, 99, 113, 126, 151, 164, 176, 204 (100), 224, 239.

1.2. Catalytic activity for reduction of alkynes

Alkynes (1 mmol) were reacted with KOH (1.1 mmol) along with PdNPs@Fu (2.0 mg) catalyst in 6 mL of DMF. The mixture was placed in a 25 mL ground-neck flask. Nitrogen gas was bubbled through the mixture for approximately 20 min to remove oxygen. The reaction mixture was stirred with a magnetic stirrer at 110 °C for 6 hours in an oil bath. The completion of the reaction was confirmed by TLC, employing *n*-hexane and ethyl acetate as the mobile phase. After completion of the reaction, the mixture was extracted with ethyl acetate, and the organic layer was successively washed with distilled water and saturated brine, then dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to afford the crude product. The pure compound was subsequently isolated by silica gel column chromatography using an *n*-hexane/ethyl acetate mixture as the eluent, and its purity was verified by GC–MS and ^{1}H NMR analyses (Table 3). For the catalyst recycling procedure, after the reaction had been completed, ethyl acetate was added to the reaction medium to extract the organic components (volume ratio of ethyl acetate to DMF = 2:1). The resulting mixture was centrifuged at 4 °C and 10.000 rpm for 5 min, and the ethyl acetate layer was carefully removed. The DMF phase was then extracted twice more with ethyl acetate. The residual DMF layer containing the catalyst was reused by adding a fresh portion of 2-(but-2-yn-1-yloxy)tetrahydro-2*H*-pyran, followed by continuous stirring for 6 h to perform the next catalytic cycle.

Styrene (2a): H = 95%. GC-MS (*m/z)*: 27, 38, 51, 54, 63, 73, 78, 79, 87, 98, 103, 104 (100).

4-chlorostyrene (2b): H = 94%. GC-MS (*m/z)*: 27, 37, 51, 52, 63, 77, 85, 98, 103 (100), 112, 123, 138.

***Cis*-stilbene (2c):** H = 94%. GC-MS (*m/z)*: 15, 27, 39, 51, 63, 76, 89, 98, 115, 126, 139, 152, 154, 165, 180 (100), 181.

***(Z)*-1-methoxy-3-styrylbenzene (2d)**: H = 93%.^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54 – 7. 52 (*m,* 1H), 7.34 (*d, J* = 7.8 Hz, 1H), 7.35 – 7.32 (*m,* 1H), 7.26 – 2.24 (*m,* 2H), 7.23 – 7.17 (*m,* 2H), 7.13 (*t, J* = 8.4 Hz, 7.8 Hz 1H), 6.83 (*d, J* = 7.2 Hz, 1H), 6.74 (*dd, J* = 2.4 Hz, 8.4 Hz, 1H), 6.62 – 6.56 (*m,* 1H), 3.64 (*s,* 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.4; 138.6; 131.7; 130.5; 130.2; 128.9; 128.4; 128.2; 127.1; 116.4; 113.8; 55.0. GC-MS: 51.0, 63.0, 76.0, 89.0, 105.0, 115.0, 139.0, 152.0, 155.0, 165.0, 179.0, 194.0, 210.0.

***(Z)*-2-(but-2-en-1-yloxy)tetrahydro-2*H*-pyran (2e)**: H = 94%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.69 – 5.64 (*m,* 1H), 5.61 – 5.56 (*m,* 1H), 4.65 – 4.63 (*m,* 1H), 4.29 – 4.25 (*m,* 1H), 3.97 – 3.82 (*m,* 1H), 3.54 – 3.50 (m, 2H), 1.87 – 1.64 (*m,* 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 127.9; 126.7; 98.0; 62.3; 62.0; 54.7; 30.3; 22.7; 19.6.

1.3. Synthesis of insect pheromone

Synthesis of 2-(dodec-3-yn-1-yloxy)tetrahydro-2*H*-pyran (3): 1-decyne (**1**, 1.38 g, 10.0 mmol) was dissolved in THF (5 mL) and transferred to a three-neck round-bottom flask (50 mL). The reaction mixture was stirred with a magnetic stirrer at -78 °C under N_2 atmosphere. Then, 4 mL *n*-BuLi 2.5 M in cyclohexane was added dropwise, followed by a solution of KI (127 mg, 0.77 mmol) was added. After stirring for 1 hour at –78 °C, 2-(2-bromoethoxy)tetrahydro-2*H*-pyran (**2,** 1.68 mg, 8 mmol) was introduced. After 30 minutes at -78 °C, the reaction was progressively heated to 0 °C and agitated for two hours at room temperature. The mixture was then refluxed for 16 h, and the reaction progress was monitored by thin-layer chromatography (TLC). To obtain the crude product, upon completion, the reaction was quenched, washed with saturated $NaHCO_3$ solution, extracted with *n*-Hexane, saturated NaCl, and dried over anhydrous $MgSO_4$. The crude product **(3)** was used in the subsequent reaction without further purification.

Synthesis of (*Z*)-2-(dodec-3-en-1-yloxy)tetrahydro-2*H*-pyran (4): A mixture of 2-(dodec-3-yn-1-yloxy)tetrahydro-2*H*-pyran (2 g), KOH (0.5 g), NPsPd@Fu catalyst (2.0 mg), and solvent DMF (6 mL) was placed in a thick-walled Pyrex seal tube. The reaction was carried out at 145 °C for 6 hours under a nitrogen atmosphere to maintain inert conditions. Upon completion, the

reaction mixture was monitored by thin-layer chromatography (TLC) and extracted with *n*-hexane (2 × 30 mL). The organic layer was washed several times with distilled water and dried over anhydrous $MgSO_4$. The crude product was then purified by column chromatography (EtOAc: *n*-Hexane) to afford the pure compound **(4)**. H = 92%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.45–5.44 (*m,* 1H), 5.41–5.36 (*m*, 1H), 4.61 – 5.59 (*m*, 1H), 3.90–3.86 (*m*, 1H), 3.75–3.71 (*m*, 1H), 3.52–3.48 (*m*, 1H), 3.43–3.39 (*m*, 1H), 2.37–2.33 (*m*, 1H), 2.06–2.03 (*m*, 1H), 1.86–1.81 (*m*, 1H), 1.73–1.69 (*m*, 1H), 1.60–1.58 (*m*, 1H), 1.55–1.50 (*m*, 1H), 1.36–1.32 (*m*, 2H), 1.31–1.26 (*m*, 14H), 0.88 (*t*, *J* = 7.2, 13.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 132.1; 125.5; 98.8; 67.1; 62.3; 31.9; 30.7; 29.7; 29.5; 29.3; 29.3; 28.0; 27.4; 25.5; 22.7; 19.6; 14.1.

Synthesis of *(Z)*-dodec-3-en-1-ol (5): Dissolve (*Z*)-2-(dec-3-en-1-yloxy)tetrahydro -2*H*-pyran (0.4 g) and *p*-toluenesulfonic acid monohydrate (0.03 g) in CH_3OH (4 mL), and add to 50 mL two-neck round-bottom flask. The reaction mixture was sonicated at room temperature for 2 hours. Monitor the reaction by TLC. After completion, the mixture was washed with saturated $NaHCO_3$ (30 mL), extracted with diethyl ether, washed with brine, and dried over anhydrous $MgSO_4$. Concentrate under reduced pressure and purify the crude product by column chromatography (EtOAc: *n*-Hexane) to afford the pure compound. Finally, the yield was calculated, and the product was labeled accordingly. H = 91%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.58 – 5.57 (m, 1H), 5.38 – 5. 35 (m, 1H), 3.64 (*t, J* = 6.0, 6.6, 2H), 2.35 – 2.31 (*m*, 2H), 2.08 – 2.03 (*m*, 2H), 1.40 (*s*, 1H), 1.36 – 1.34 (*m*, 2H), 1, 33 – 1.24 (*m*, 10H), 0.88 (*t*, *J* = 6.6, 7.2, 3H). GC-MS: 15.0, 27.0, 41.0, 54.0, 57.0, 67.0, 81.0, 82.0, 95.0, 108.0, 109.0, 123.0, 138.0, 151.0, 166.0, 184.0). ^{13}C NMR (150 MHz, $CDCl_3$): δ 133.6; 124.9; 62.4; 31.9; 30.8; 29.7; 29.5; 29.3, 29.3; 27.4; 22.7; 14.0.

Synthesis of *(Z)*-dodec-3-en-1-yl (*E*)-but-2-enoate (6): Add crotonyl chloride (1.3 g) after dissolving (*Z*)-dec-3-en-1-ol (1.56 g) in pyridine at 0 °C. After that, the mixture was agitated for two hours at room temperature using an induction stirrer, and thin-layer chromatography (TLC) was used to track the reaction process. The mixture was allowed to cool naturally once the reaction was finished, neutralized with 10% HCl, and then extracted using diethyl ether. The organic layer was dried with $MgSO_4$ after being sequentially cleaned with saturated $CuSO_4$ solution, $NaHCO_3$, distilled water, and saturated NaCl. To get the pure product, purify the crude product using column chromatography (EtOAc: *n*-Hexane). H = 94%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.00 – 6.94 (*m*,

1H), 5.85 – 5.82 (*m*, 1H), 5.52 – 5.48 (*m*, 1H), 5.38 – 5.35 (*m*, 1H), 4.12 (*t*, *J* = 6.0 Hz, 7.2 Hz, 2H), 2.42 – 2.38 (*m*, 2H), 2.05 – 2.02 (*m*, 2H), 1.87 (*dd*, *J* = 7.2 Hz, 1.8 Hz, 3H), 1.35 – 1.33 (*m*, 2H), 1.32 – 1.27 (*m*, 12H), 0.88 (*t*, *J* = 6.6 Hz, 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.6; 144.5; 133.0; 124.4; 122.8; 63.7; 31.9; 29.7; 29.6; 29.5; 29.3; 27.3; 26.9; 22.7; 17.9; 14.8.

2. Calculation of TON and TOF

Calculation of %wt Pd in PdNPs@Fu catalyst

Parameter	**Value**	**Remarks**
C_{Pd} = ICP-MS Pd concentration (ppb = µg/L; ICP-MS analysis on final solution)	5.197 ppb	Average of 2 measurements
f = Dilution factor	200 x 100 = 20000	Provided by the analyst
V_{sample} (L) = Sample solution volume	10 mL = 0.010 L	
m = Sample weight in mg	10 mg	

Pd concentration in solution: $C_{solution} = \frac{C_{Pd} f}{1000}$ (Unit: mg/L)

Pd mass in catalyst: $m_{Pd} = \frac{C_{Pd} f V_{sample}}{10^6}$ (Unit: mg)

Pd content: $wt\% = \frac{C_{Pd} f V_{sample}}{10^4 m}$ (Unit: %)

a) Pd concentration in solution and Pd mass in catalyst:

$$C_{solution}\ (mg/L) = \frac{5.197\ pbb}{1000} \times 20000 \approx 103.94\ mg/L\ (or\ 103.94\ ppm)$$

(with f = 20000)

m_{Pd} = 103.94 mg/L x 0.010 L = 1.0394 mg

b) %wt Pd

$$\%wt\ Pd = \frac{1.0394\ mg}{10\ mg} \times 100\% = 10.394\%$$

Result: Palladium (Pd) content in PdNPs@Fu catalyst is 10.394 %wt.

Moles of Pd catalyst = $\frac{Mass\ of\ PdNPs@Fu}{Molecular\ mass\ of\ Pd} \times Pd\ mass\ in\ cat. \approx$

$\approx$ 0.001953 mmol

Moles of product formed = $Moles\ of\ PdNPs@Fu \times Yield\ of\ reaction$ (%)

= 1 mmol x 0.93 $\approx$ 0.93 mmol

(Example: 93% yield # 0.93, with Entry 2 – Table 2 of Heck coupling)

Calculation formula of TON and TOF

Turnover Number (TON): TON = $\frac{Moles\ of\ product\ formed}{Moles\ of\ Pd\ catalyst}$

Where:

- *Moles of product* = amount of desired product formed (often determined by GC, NMR, or isolation).
- *Moles of Pd catalyst* = total moles of Pd present in the catalyst used (calculated from Pd loading wt% or ICP-MS).

Turnover Frequency (TOF): TOF = $\frac{TON}{time}$;

or directly: TOF = $\frac{Moles\ of\ product}{Moles\ of\ Pd\ catalyst \times time\ (h)}$;

Units: TOF is typically given in h^{-1}.

Calculation of TON and TOF (Time t = 6 h)

We used the optimum catalyst mass of 2.0 mg for the sample reaction (Heck coupling, Entry 6 and Alkyne Reduction, Entry 7).

A. Mol_{Pd} catalyst

Mol_{Pd} = (2.0 mg x 0.10394)/106.42 g/mol $\approx$ 0.001953 mmol

B. Heck Coupling reaction (Yield = 93%)

$Mol_{product}$ = 1 mmol x 0.93 = 0.93 mmol

$\Rightarrow TON_{Heck}$ = 0.93 mmol/0.001953 mmol $\approx$ 476

$\Rightarrow TOF_{Heck}$ = 476/6 h $\approx$ 79.3 h^{-1}

C. Alkyne reduction reaction (Yield = 94%)

$Mol_{product}$ = 1 mmol x 0.94 = 0.94 mmol

$\Rightarrow TON_{Alkyne}$ = 0.94 mmol/0.001953 mmol ≈ 481

$\Rightarrow TOF_{Alkyne}$ = 481/6 h ≈ 80.2 h^{-1}

3. GC–MS spectra of the Heck coupling reaction products (1a–1g)

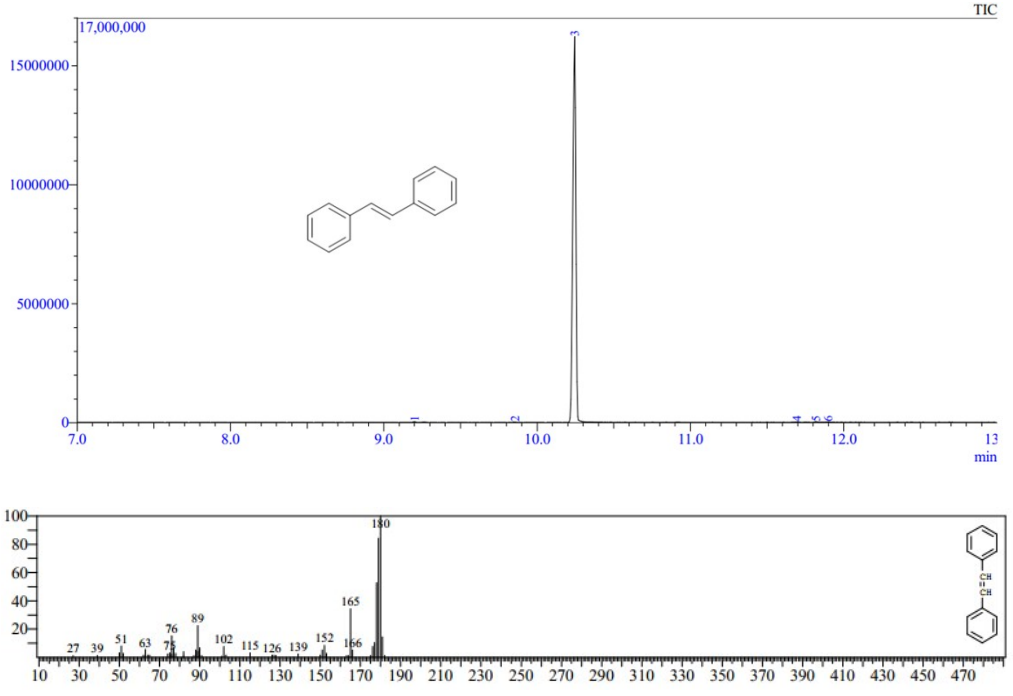


Figure S1. GC-MS spectrum of **1a**

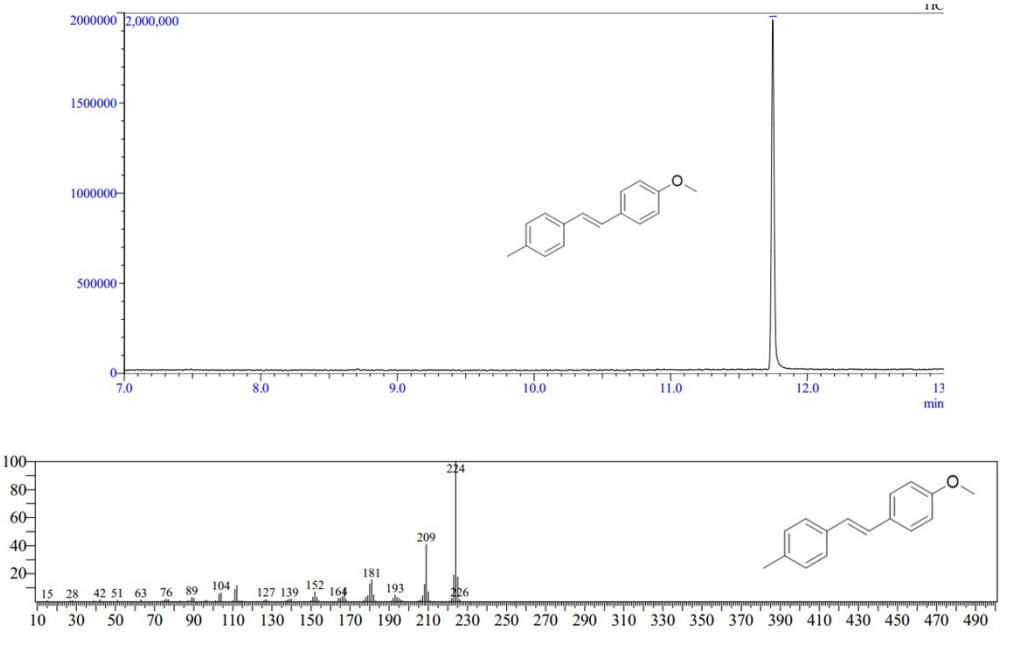


Figure S2. GC-MS spectrum of **1b**

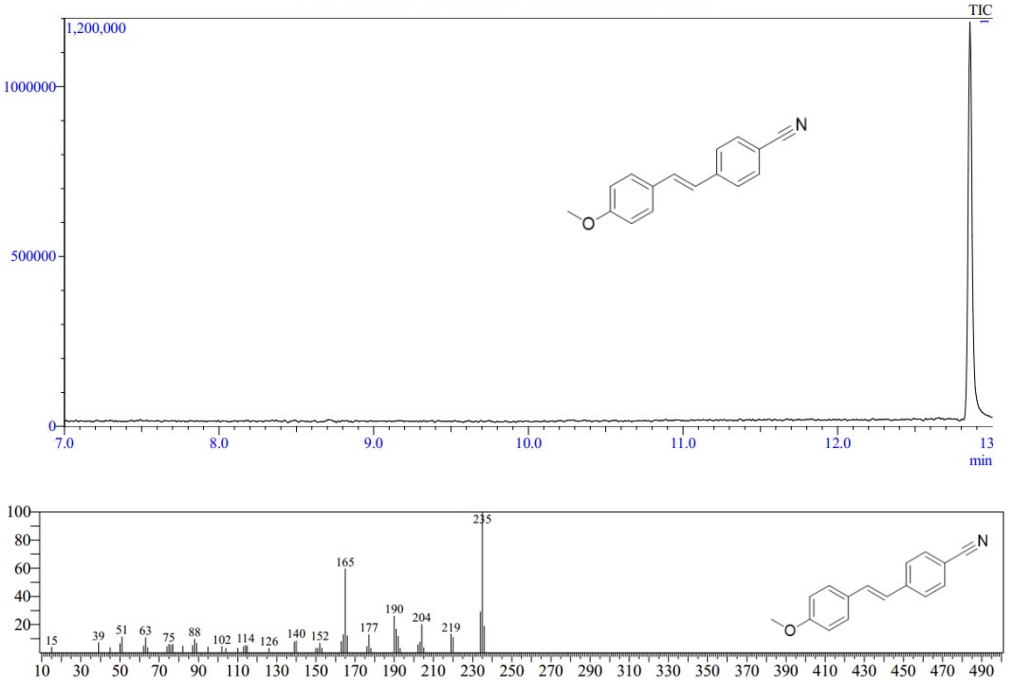


Figure S3. GC-MS spectrum of **1c**

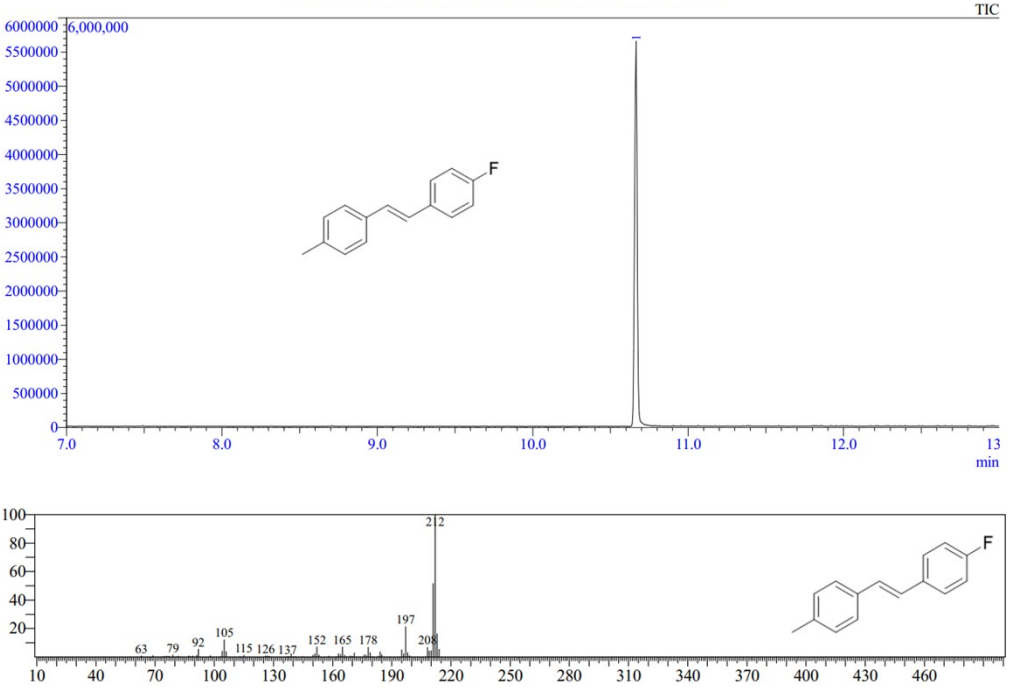


Figure S4. GC-MS spectrum of **1d**

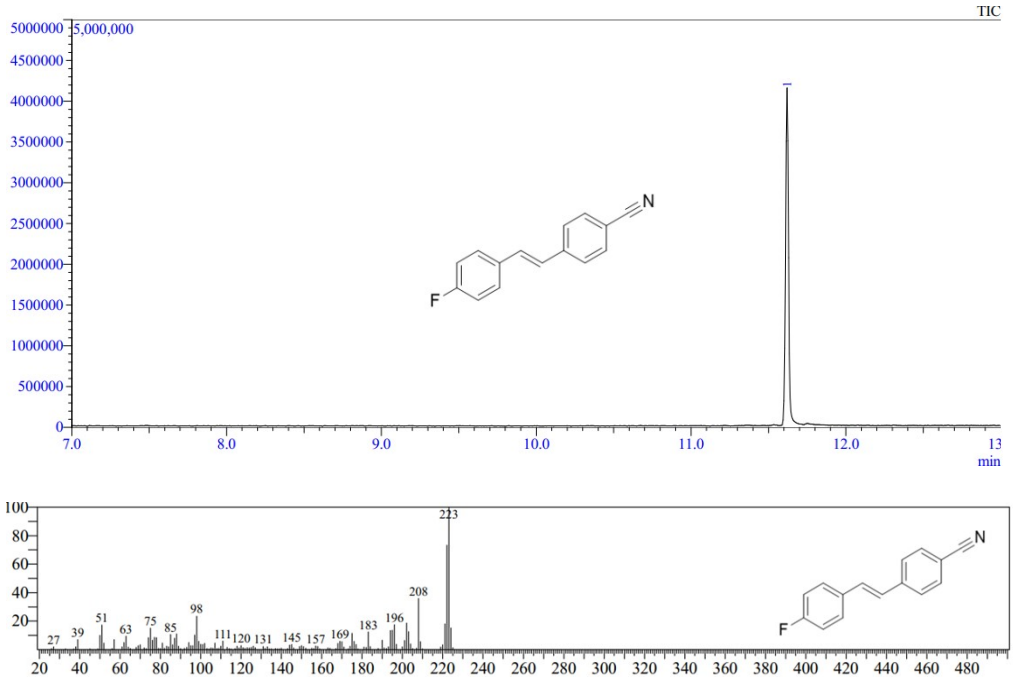


Figure S5. GC-MS spectrum of **1e**

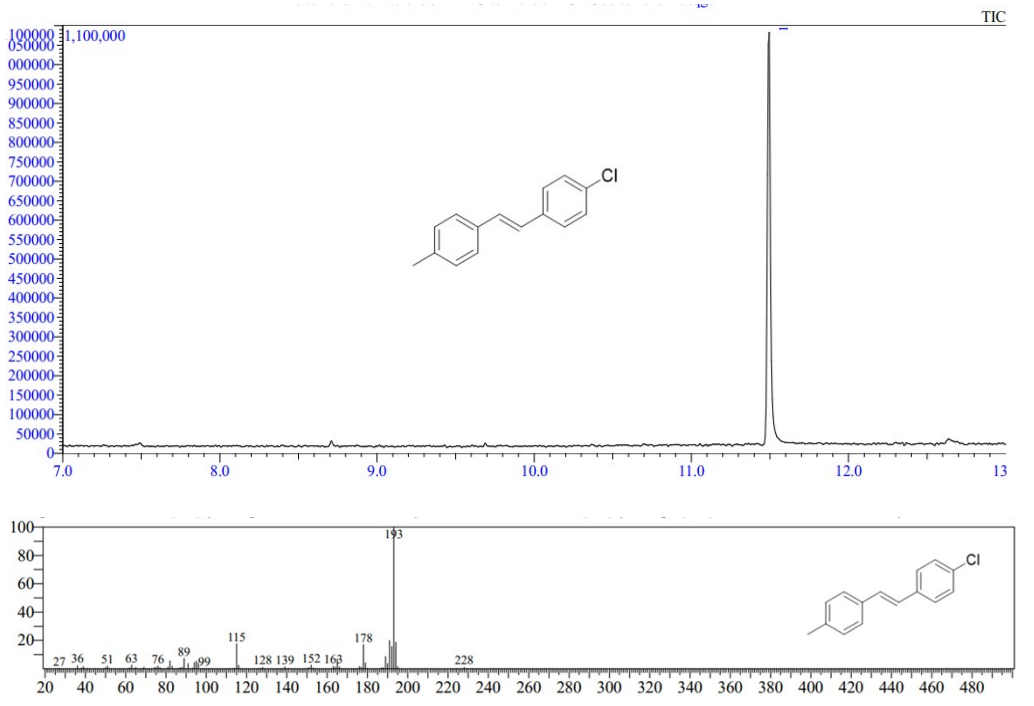


Figure S6. GC-MS spectrum of **1f**

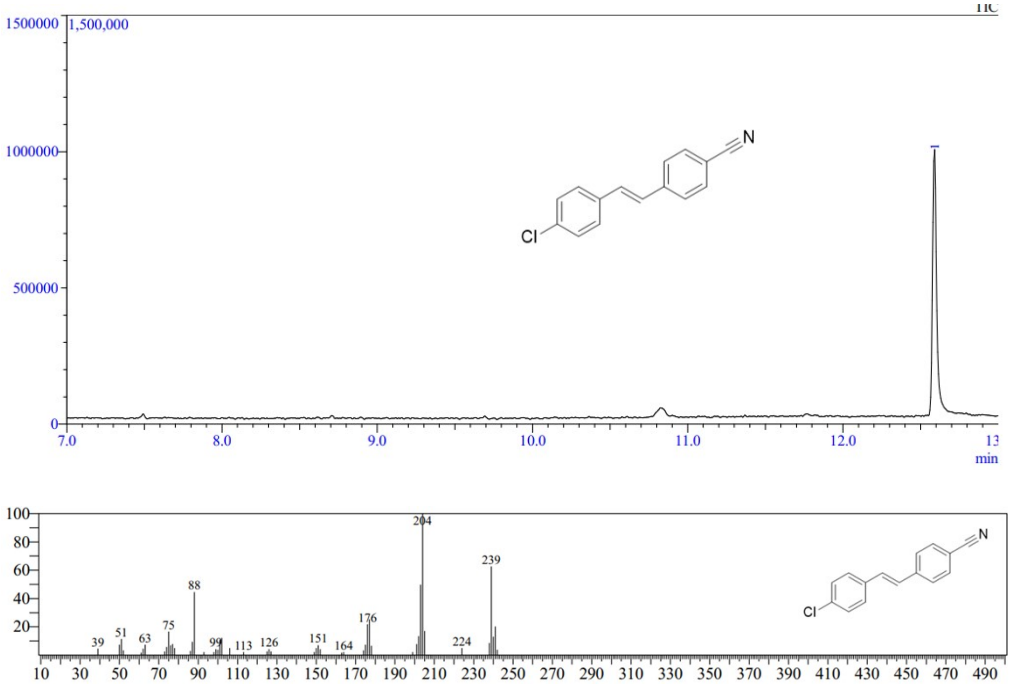


Figure S7. GC-MS spectrum of **1g**

4. GC–MS, ^{1}H NMR, and ^{13}C NMR spectra of the reduced alkyne products (2a–2e).

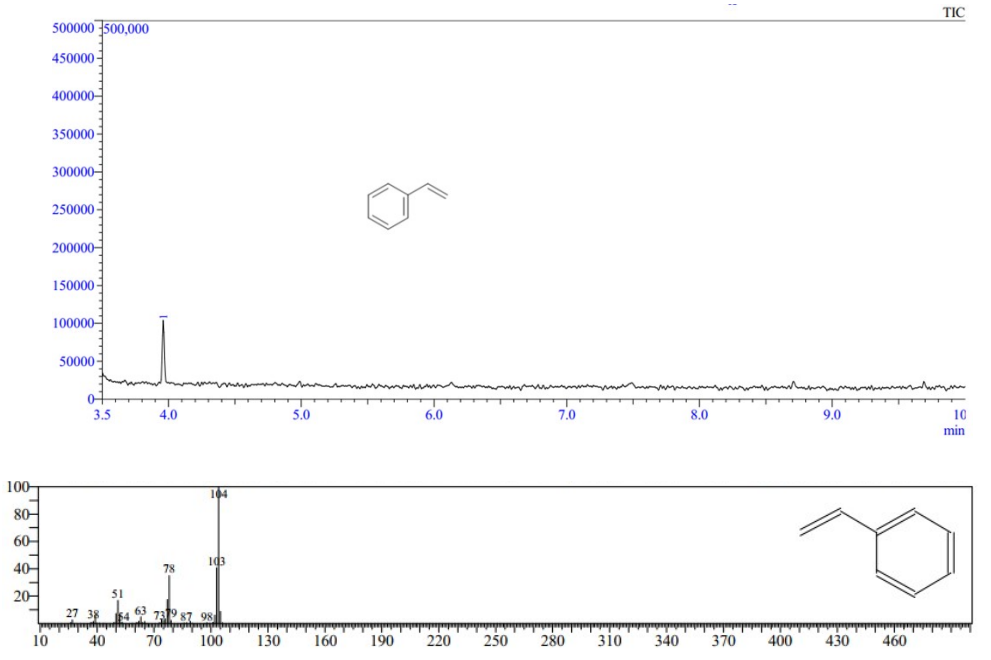


Figure S8. GC-MS spectrum of **2a**

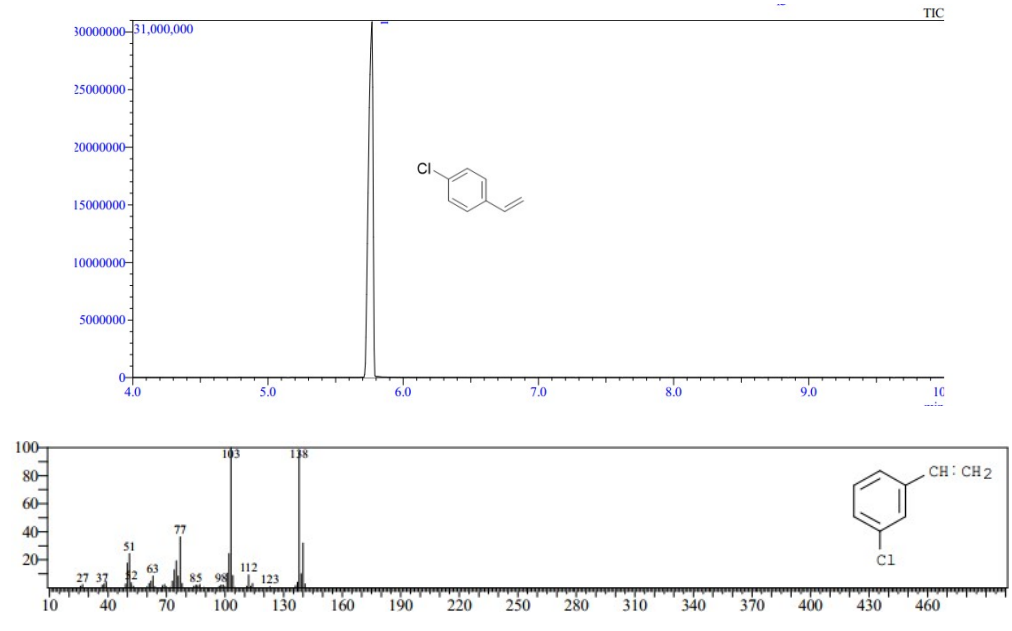


Figure S9. GC-MS spectrum of **2b**

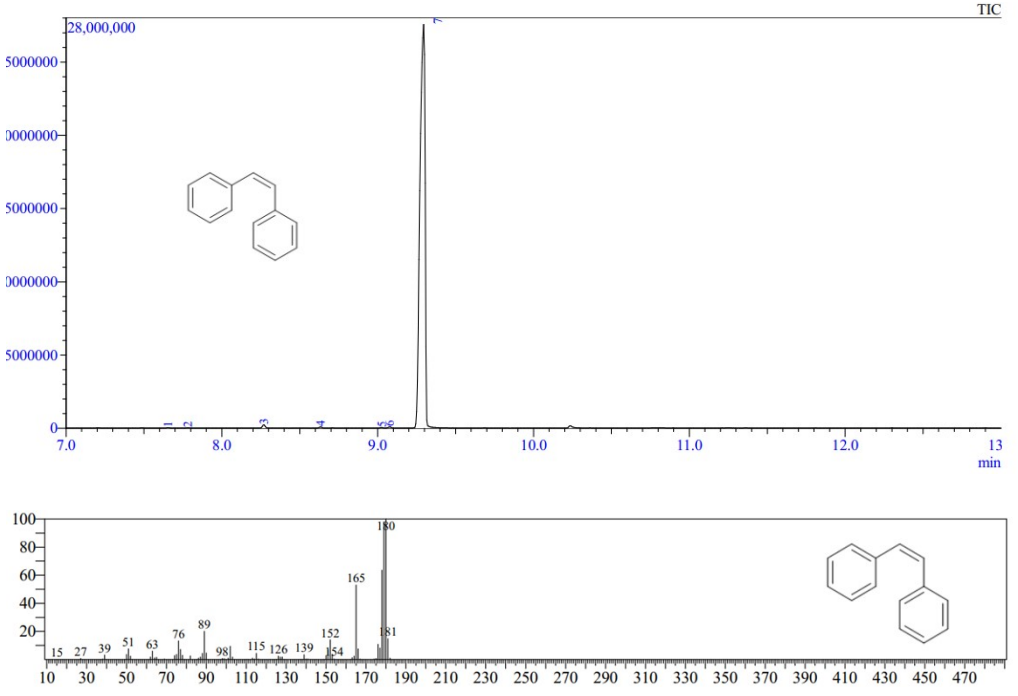


Figure S10. GC-MS spectrum of **2c**

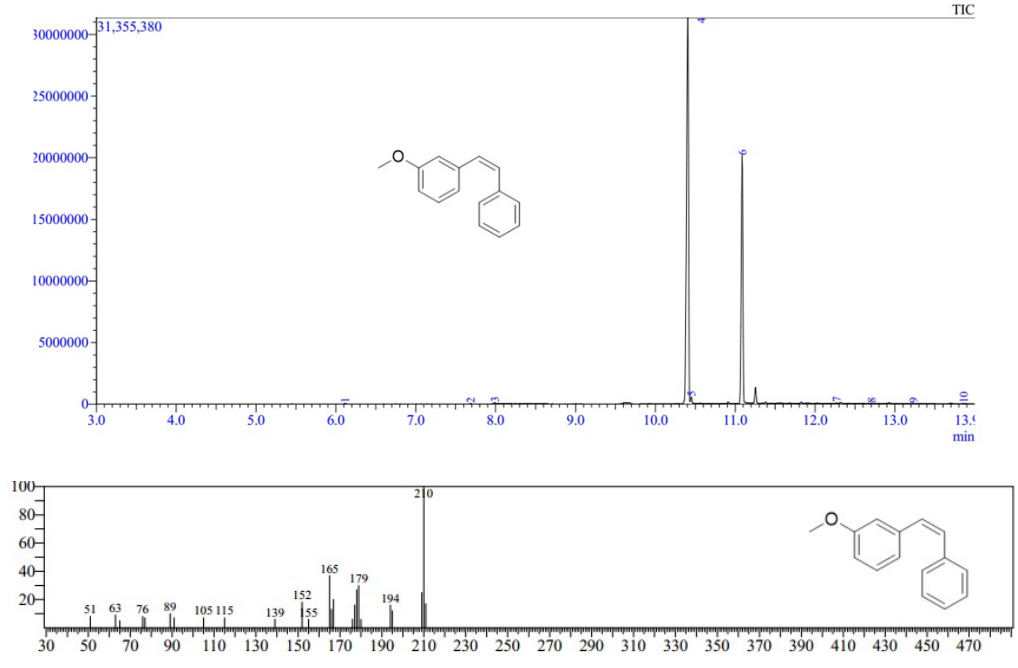


Figure S11. GC-MS spectrum of **2d**

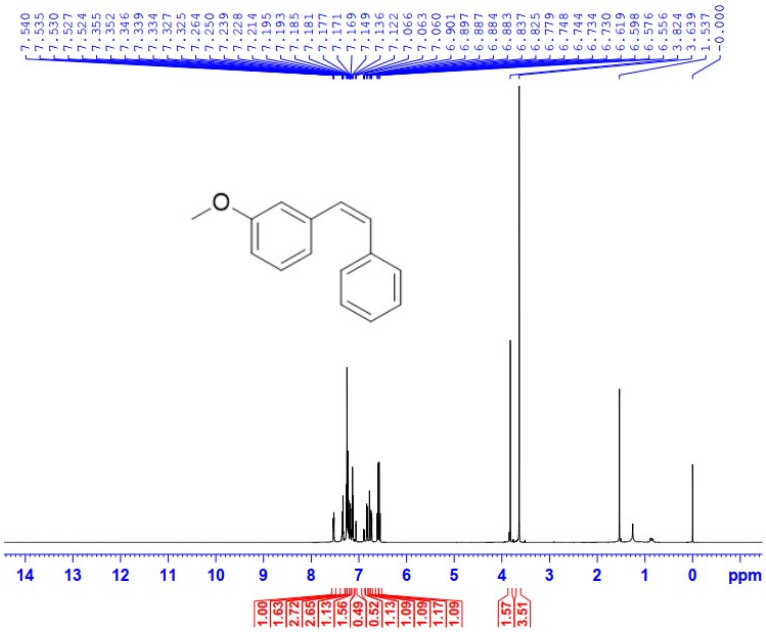


Figure S12. ^{1}H NMR spectrum of **2d** (600 Hz, $CDCl_3$)

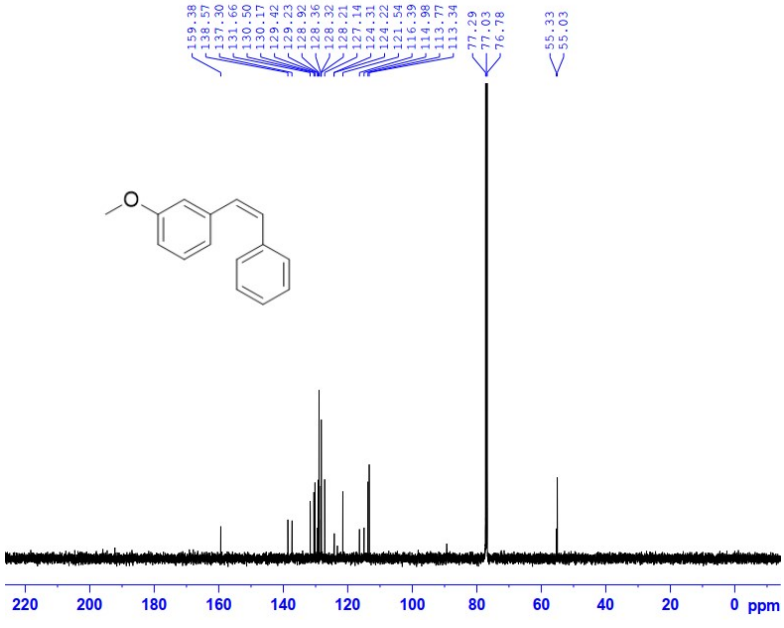


Figure S13. ^{13}C NMR spectrum of **2d** (150 Hz, $CDCl_3$)

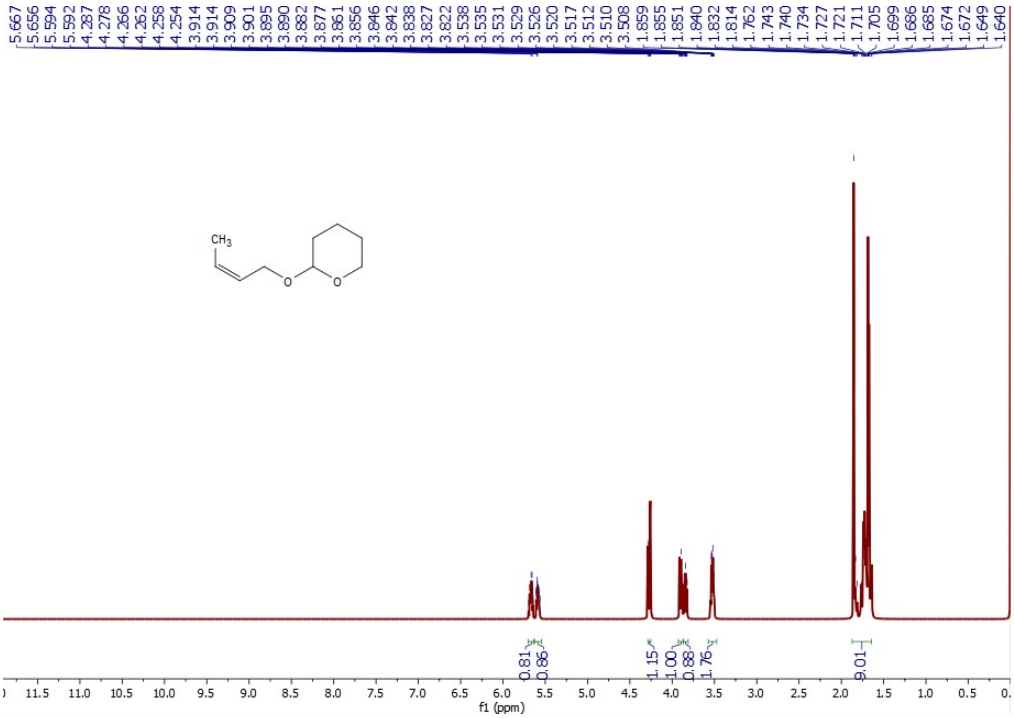


Figure S14. ^{1}H NMR spectrum of **2e** (600 Hz, $CDCl_3$)

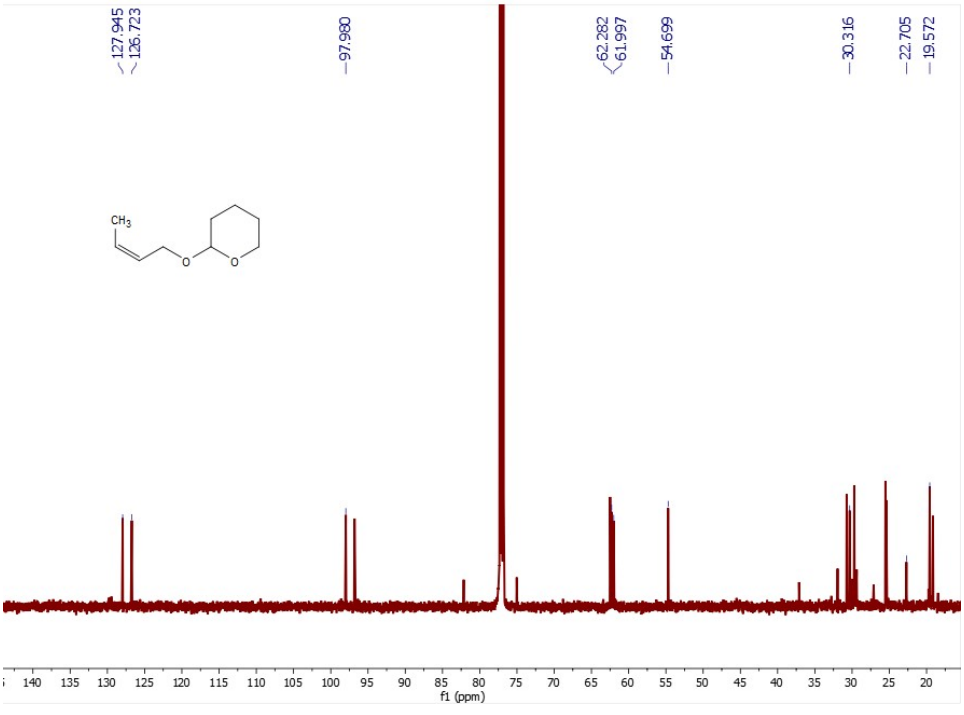


Figure S13. ^{13}C NMR spectrum of **2e** (150 Hz, $CDCl_3$)

5. GC–MS, ^{1}H NMR, and ^{13}C NMR spectra of the synthesized insect pheromone compounds (4–6)

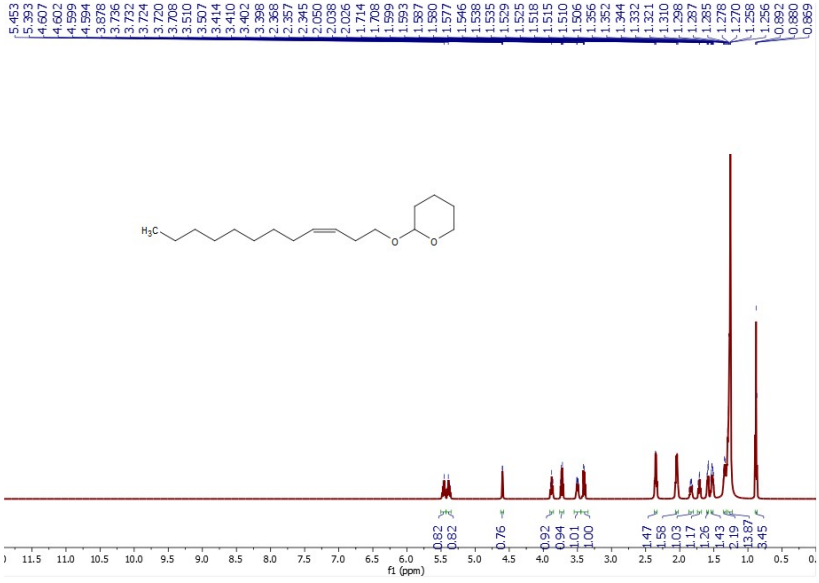


Figure S14. ^{1}H NMR spectrum of **(4)** (600 Hz, $CDCl_3$)

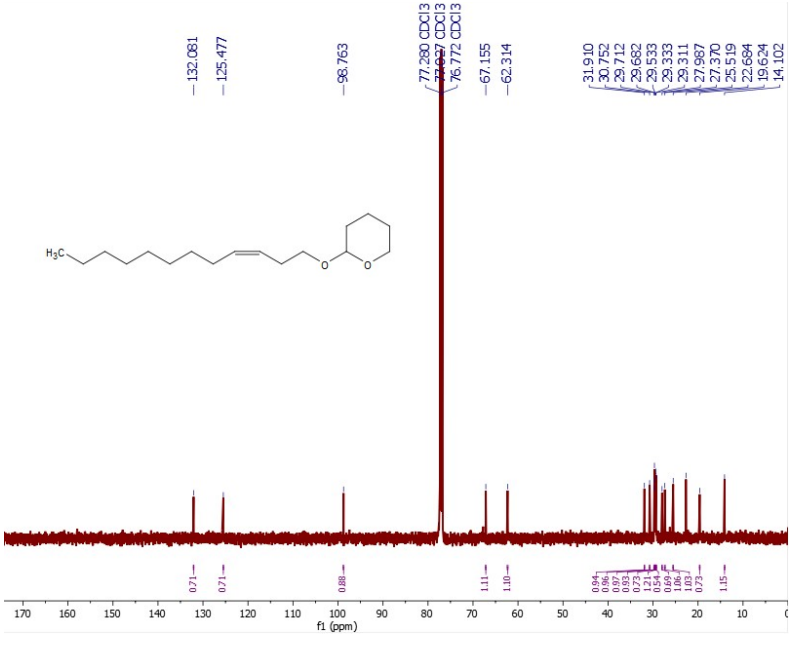


Figure S15. ^{13}C NMR spectrum of **(4)** (150 Hz, $CDCl_3$)

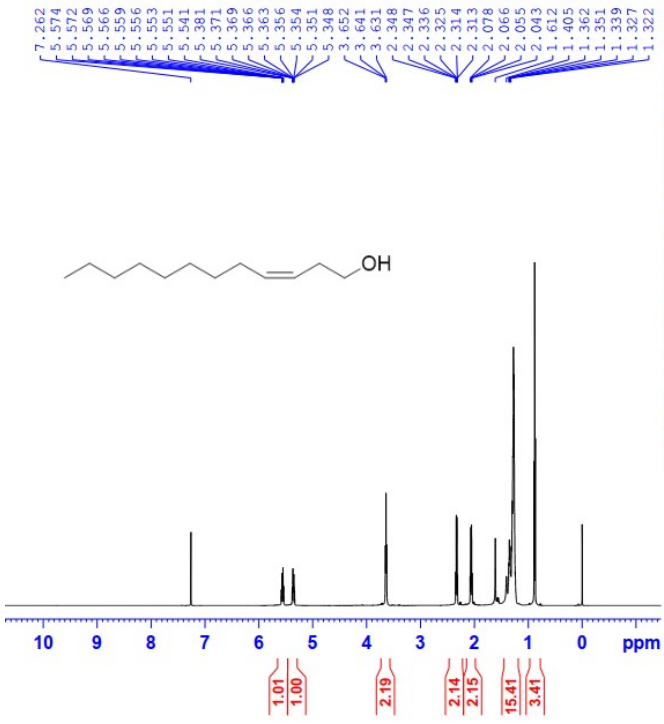


Figure S16. ^{1}H NMR spectrum of **(5)** (600 Hz, $CDCl_3$)

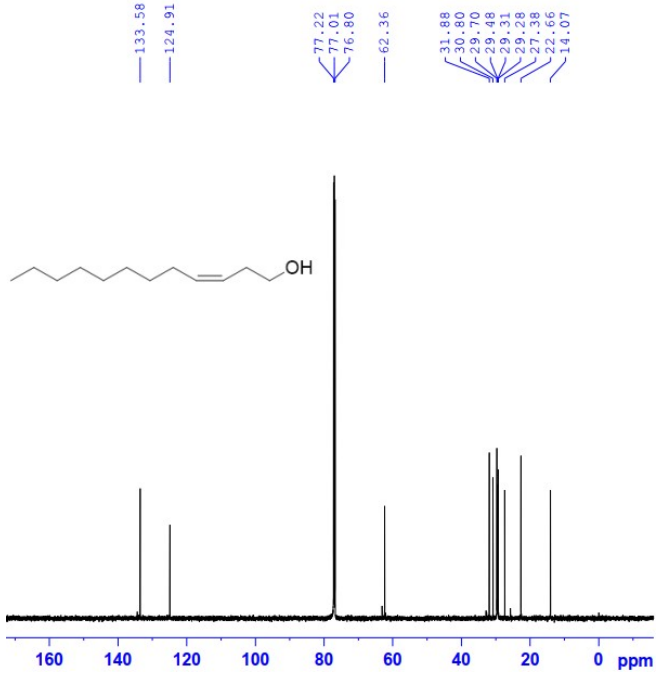


Figure S17. ^{13}C NMR spectrum of **(5)** (150 Hz, $CDCl_3$)

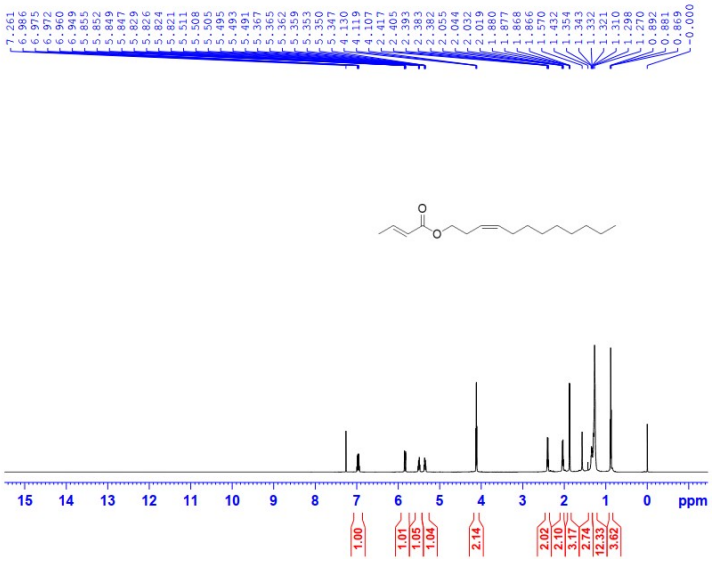


Figure S18. ^{1}H NMR spectrum of **(6)** (600 Hz, $CDCl_3$)

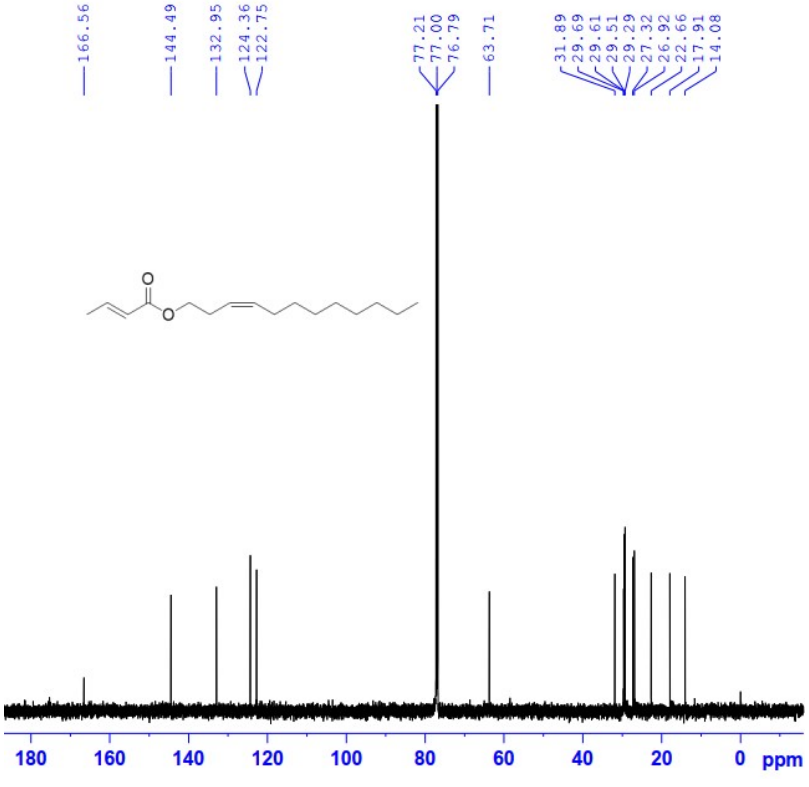
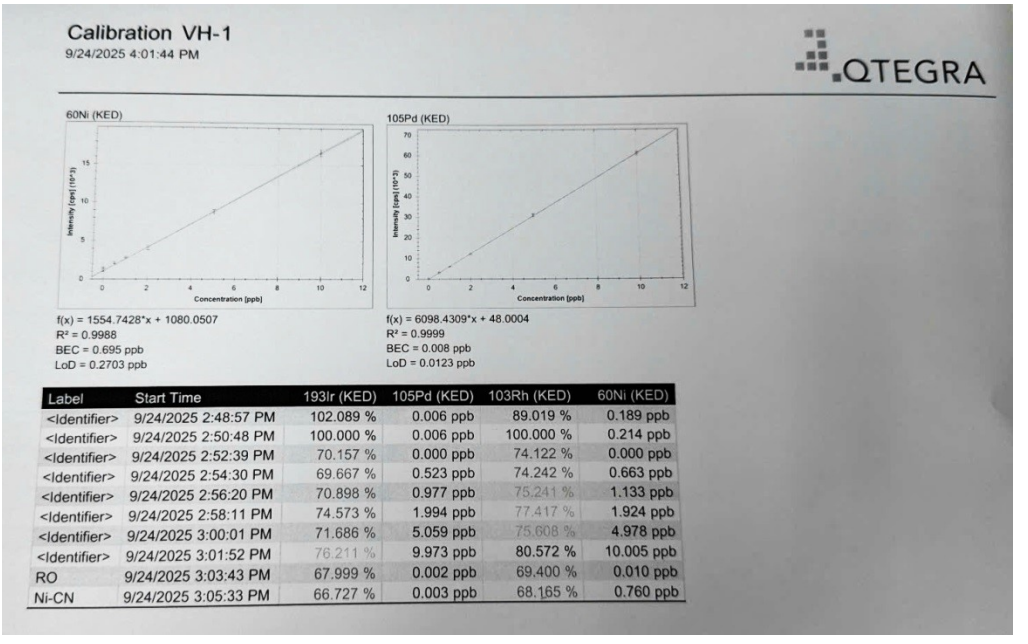


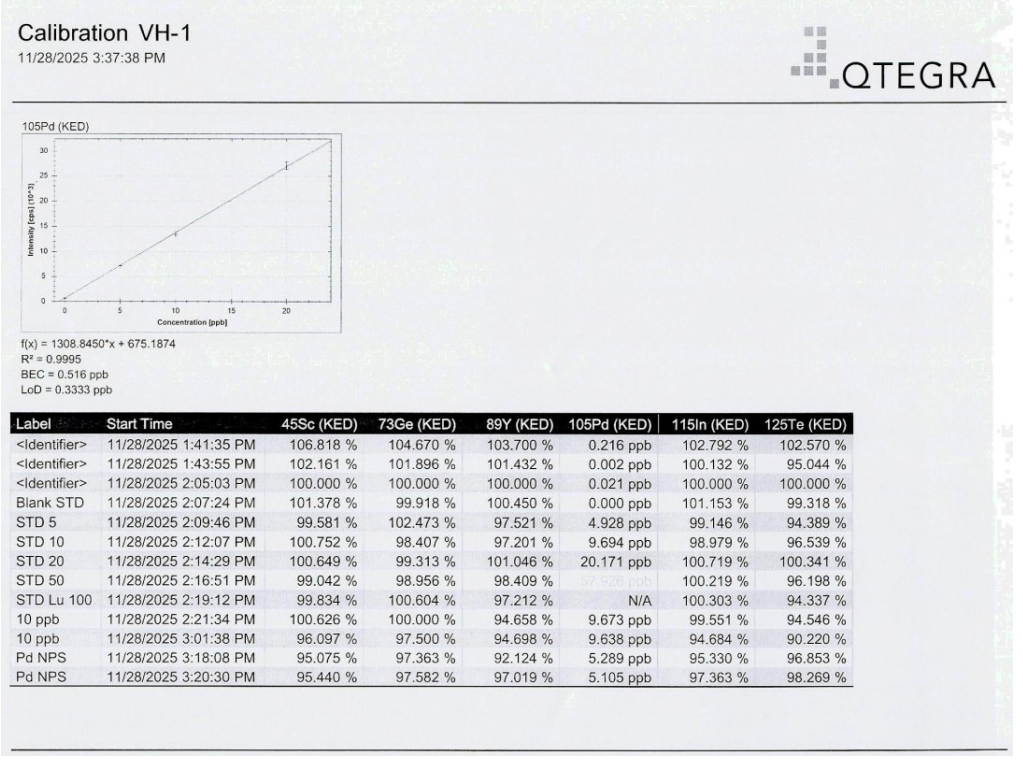
Figure S19. ^{13}C NMR spectrum of **(6)** (150 Hz, $CDCl_3$)

6. ICP-MS and XRD:



Label	Start Time	193Ir (KED)	105Pd (KED)	103Rh (KED)	60Ni (KED)
<Identifier>	9/24/2025 2:48:57 PM	102.089 %	0.006 ppb	89.019 %	0.189 ppb
<Identifier>	9/24/2025 2:50:48 PM	100.000 %	0.006 ppb	100.000 %	0.214 ppb
<Identifier>	9/24/2025 2:52:39 PM	70.157 %	0.000 ppb	74.122 %	0.000 ppb
<Identifier>	9/24/2025 2:54:30 PM	69.667 %	0.523 ppb	74.242 %	0.663 ppb
<Identifier>	9/24/2025 2:56:20 PM	70.898 %	0.977 ppb	75.241 %	1.133 ppb
<Identifier>	9/24/2025 2:58:11 PM	74.573 %	1.994 ppb	77.417 %	1.924 ppb
<Identifier>	9/24/2025 3:00:01 PM	71.686 %	5.059 ppb	75.608 %	4.978 ppb
<Identifier>	9/24/2025 3:01:52 PM	76.211 %	9.973 ppb	80.572 %	10.005 ppb
RO	9/24/2025 3:03:43 PM	67.999 %	0.002 ppb	69.400 %	0.010 ppb
Ni-CN	9/24/2025 3:05:33 PM	66.727 %	0.003 ppb	68.165 %	0.760 ppb

Figure S19. Sample 1 - dissolved PdNPs@Fu in distilled water (H_2O)



Label	Start Time	45Sc (KED)	73Ge (KED)	89Y (KED)	105Pd (KED)	115In (KED)	125Te (KED)
<Identifier>	11/28/2025 1:41:35 PM	106.818 %	104.670 %	103.700 %	0.216 ppb	102.792 %	102.570 %
<Identifier>	11/28/2025 1:43:55 PM	102.161 %	101.896 %	101.432 %	0.002 ppb	100.132 %	95.044 %
<Identifier>	11/28/2025 2:05:03 PM	100.000 %	100.000 %	100.000 %	0.021 ppb	100.000 %	100.000 %
Blank STD	11/28/2025 2:07:24 PM	101.378 %	99.918 %	100.450 %	0.000 ppb	101.153 %	99.318 %
STD 5	11/28/2025 2:09:46 PM	99.581 %	102.473 %	97.521 %	4.928 ppb	99.146 %	94.389 %
STD 10	11/28/2025 2:12:07 PM	100.752 %	98.407 %	97.201 %	9.694 ppb	98.979 %	96.539 %
STD 20	11/28/2025 2:14:29 PM	100.649 %	99.313 %	101.046 %	20.171 ppb	100.719 %	100.341 %
STD 50	11/28/2025 2:16:51 PM	99.042 %	98.956 %	98.409 %	57.926 ppb	100.219 %	96.198 %
STD Lu 100	11/28/2025 2:19:12 PM	99.834 %	100.604 %	97.212 %	N/A	100.303 %	94.337 %
10 ppb	11/28/2025 2:21:34 PM	100.626 %	100.000 %	94.658 %	9.673 ppb	99.551 %	94.546 %
10 ppb	11/28/2025 3:01:38 PM	96.097 %	97.500 %	94.698 %	9.638 ppb	94.684 %	90.220 %
Pd NPS	11/28/2025 3:18:08 PM	95.075 %	97.363 %	92.124 %	5.289 ppb	95.330 %	96.853 %
Pd NPS	11/28/2025 3:20:30 PM	95.440 %	97.582 %	97.019 %	5.105 ppb	97.363 %	98.269 %

Figure S20. Sample 2 - dissolved in HNO_3