Phosphine-Free Palladium Catalyzed Heck reaction with using natural compounds

Stanisława Tarnowicz-Ligus, Anna M. Trzeciak*

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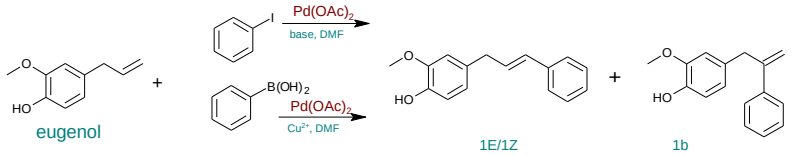
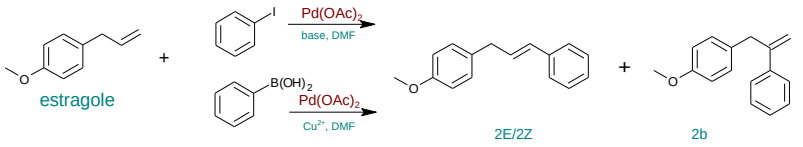
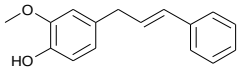
General Remarks: Products have been characterized by the GC-MS (HP II 5890 + Mass Selective Detector HP 5971A) and by ^{1}H NMR and ^{13}C NMR. NMR spectra have been measured for the post-reaction mixtures. Unless noted, ^{1}H NMR spectra were recorded on Bruker 500 MHz in $CDCl_3$, ^{13}C NMR spectra were recorded on 125 MHz in $CDCl_3$.

Control experiment 1:







1E/1Z (2-methoxy-4-(3-phenyl-2-propen-1-yl)-phenol)
(**1E/1Z**) MS: m/z (%) = 91 (30), 115 (37), 131 (16), 165 (12), 179 (17), 207 (23), 240 (100) [M^+]
^{1}H–NMR (500 MHz, $CDCl_3$): δ = 7.37–7.33 (m, 2,6H, H_{Ar}), 7.31–7.27 (m, 2,4H, H_{Ar}), 6.91 (d, *J* = 12.4Hz, 3H, H_{Ar}), 6.42 (d, *J* = 15.8Hz, 1H, CH), 6.28–6.22 (m, 1H, CH), 3.86 (s, 3H, CH_3), 3.56 (d, *J* = 7.1Hz, 2H,CH_2) ppm.
^{13}C–NMR (125 MHz, $CDCl_3$): δ = 146.82, 145.28, 140.50, 130.89, 130.12, 128.75, 128.54, 126.97, 126.20, 119.82, 114.59, 108.27, 55.90, 39.36 ppm.

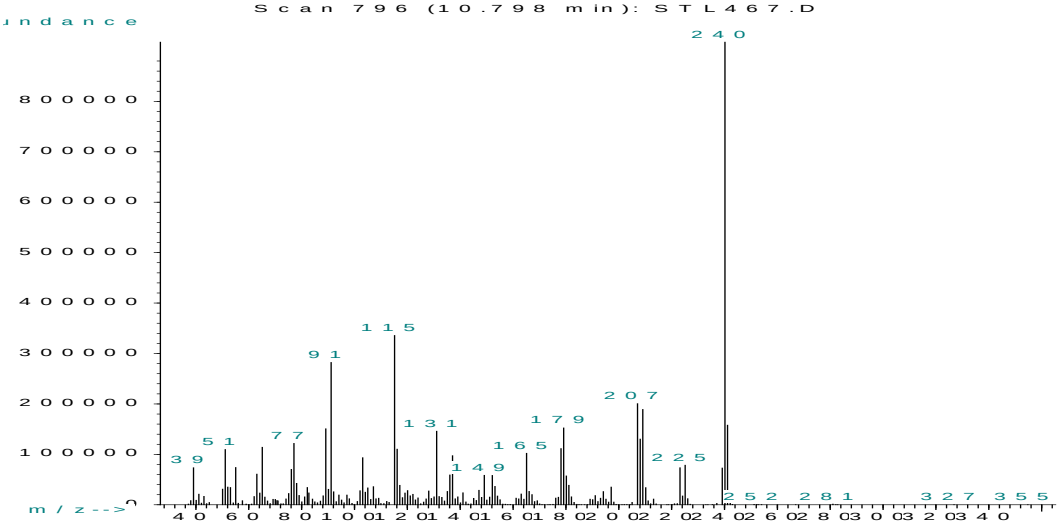
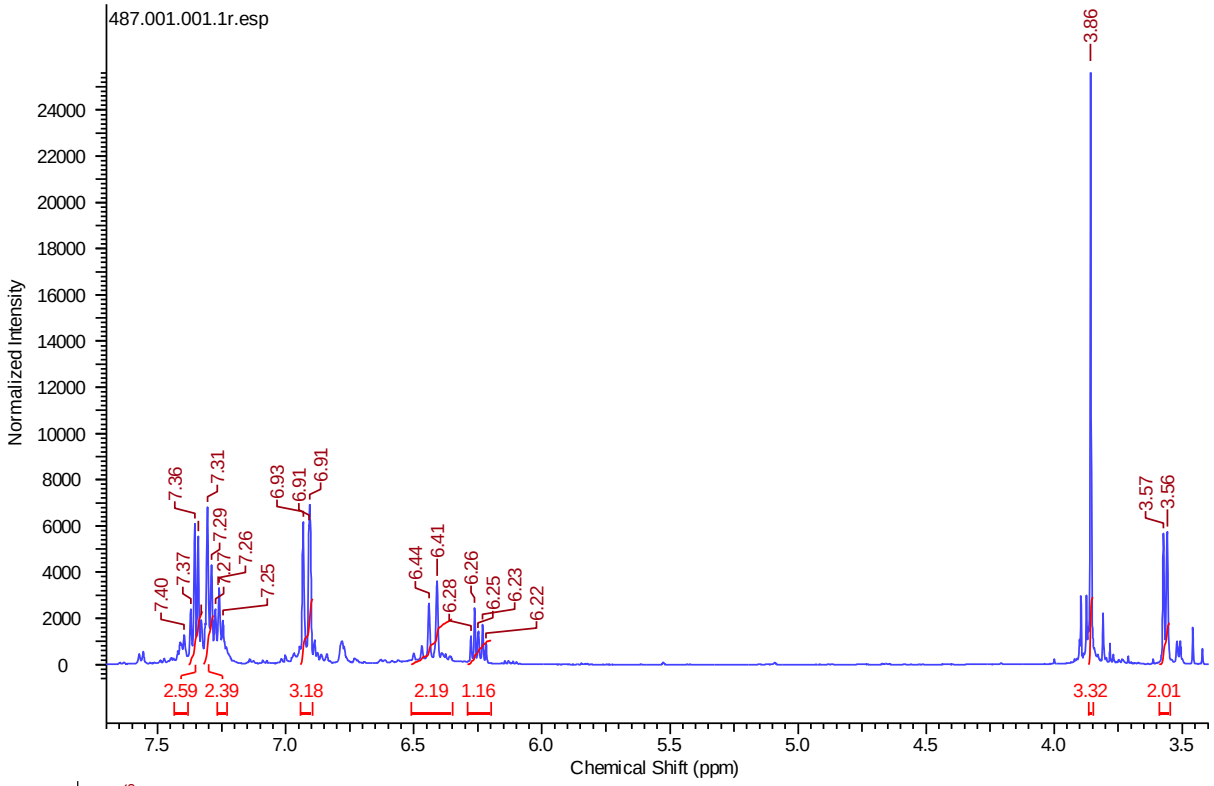


Figure S1. Mass spectrum of (2-methoxy-4-(3-phenyl-2-propen-1-yl)-phenol) (**1E)** and **(1Z**).


487.001.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
3.86
3.57
3.56
7.36
7.31
7.40
7.37
7.29
7.27
7.26
7.25
6.93
6.91
6.91
6.44
6.41
6.28
6.26
6.25
6.23
6.22
2.59
2.39
3.18
2.19
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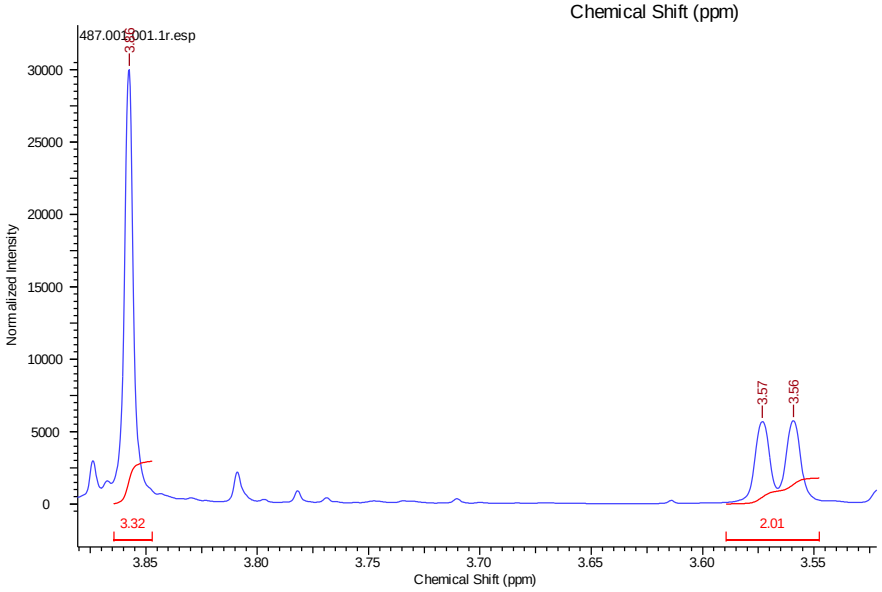
2.01


487.001.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
3.86
3.57
3.56
3.32
2.01

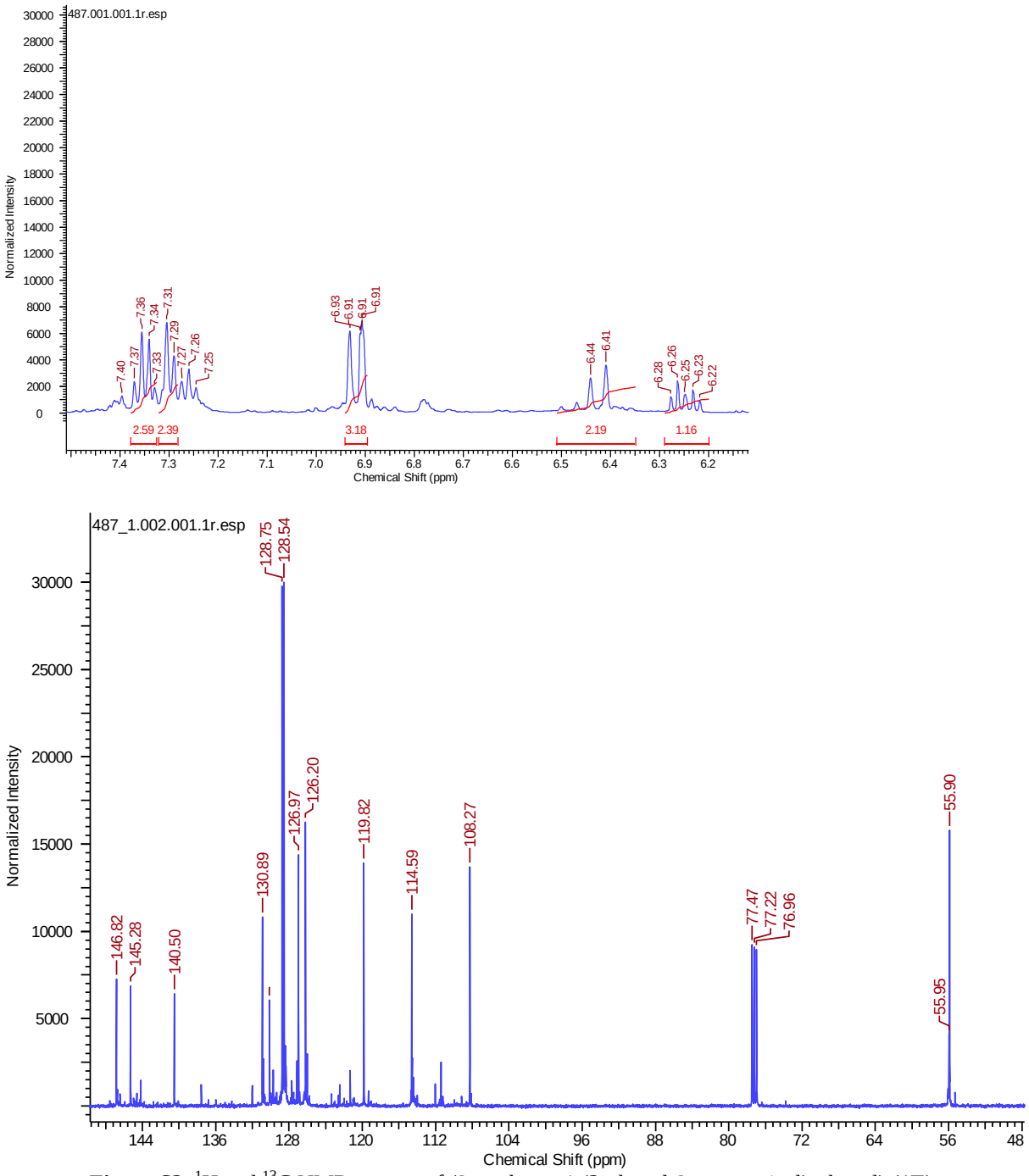
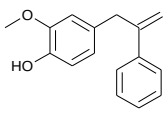


Figure S2. ^{1}H and ^{13}C NMR spectra of (2-methoxy-4-(3-phenyl-2-propen-1-yl)-phenol) (**1E**). Reaction conditions (method A): PhI (1 mmol), eugenol (1 mmol), K_2CO_3 (2 mmol), $Pd(OAc)_2$ (1×10^{-5}mol), DMF:H_2O (4:1), 3h, 100°C



1b (2-methoxy-4-(2-phenylprop-2-en-1-yl)-phenol)
MS: m/z (%) = 77 (24), 103 (24), 137 (100), 225 (17), 240 (85) [M^+]

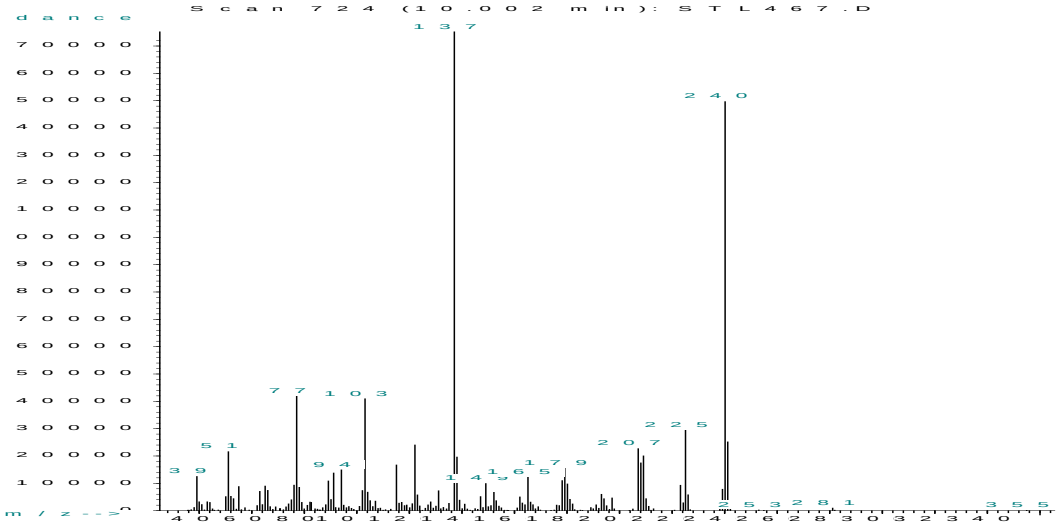
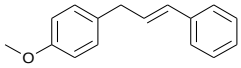


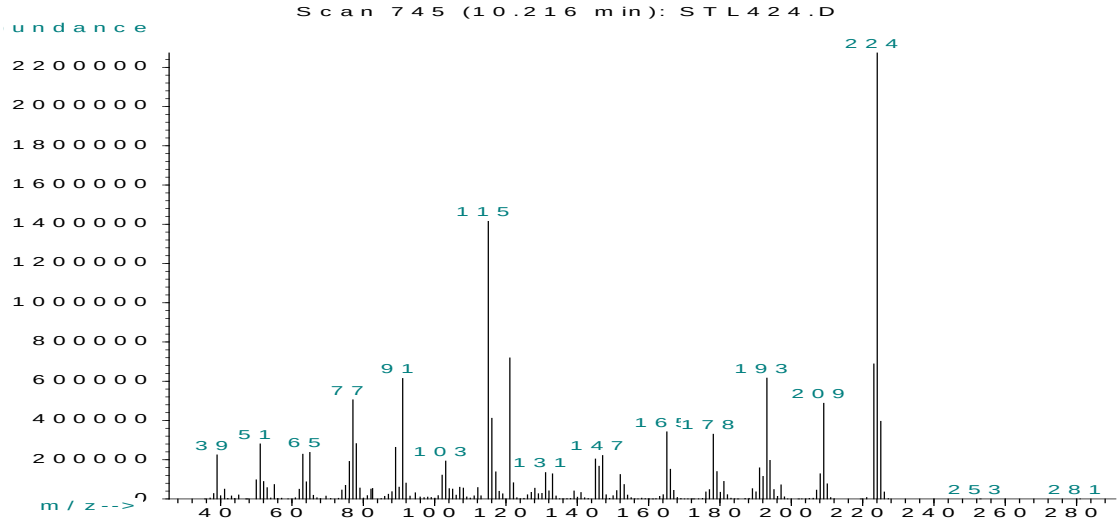
Figure S3. Mass spectrum of 1b (2-methoxy-4-(2-phenylprop-2-en-1-yl)-phenol) (**1b**).



2E/2Z (1-Phenyl-3-(4-methoxyphenyl)-1-propene)
MS: m/z (%) = 77 (21), 91 (25), 115 (61), 121 (31), 165 (14), 178 (14), 193 (27), 209 (21), 224 (100) [M^+] [1]
^{1}H–NMR (500 MHz, $CDCl_3$): δ = 7.49–7.32 (m, 12H, H_{Ar}), 7. 29 (d, *J* = 8.8, 2H, H_{Ar}), 6.99 (d, 8.8 Hz, 2H, H_{Ar}), 6.96 (d, 8.8 Hz, 2H, H_{Ar}), 6.55 (m, 2H, CH, CH), 6.47 (td, *J* = 15.6, 6.7 Hz, 1H, CH), 6.35 (td, *J* = 15.6, 6.7 Hz, 1H, CH), 3.89 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 3.65 (d, *J* = 6.9, 2H, CH_2), 3.62 (d, *J* = 6.7, 2H, CH_2) ppm [2].

2E ((E)-1-Phenyl-3-(4-methoxyphenyl)-1-propene)
^{13}C–NMR (125 MHz, $CDCl_3$): δ = 158.29, 137.73, 130.93, 130.65, 130.03, 129.78, 128.67, 127.42, 126.30, 113.95, 55.36, 38.62 ppm [2].

2Z ((Z)- 1-Phenyl-3-(4-methoxyphenyl)-1-propene)
^{13}C–NMR (125 MHz, $CDCl_3$): δ = 159.06, 140.63, 132.32, 130.49, 129.85, 128.84, 128.64, 127.22, 127.20, 114.11, 55.28, 39.51 ppm.



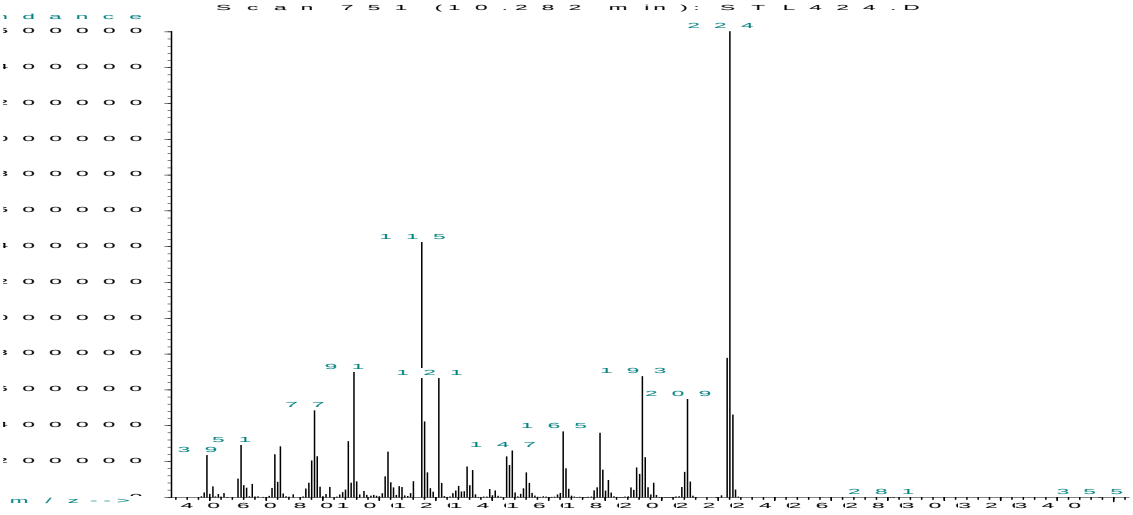
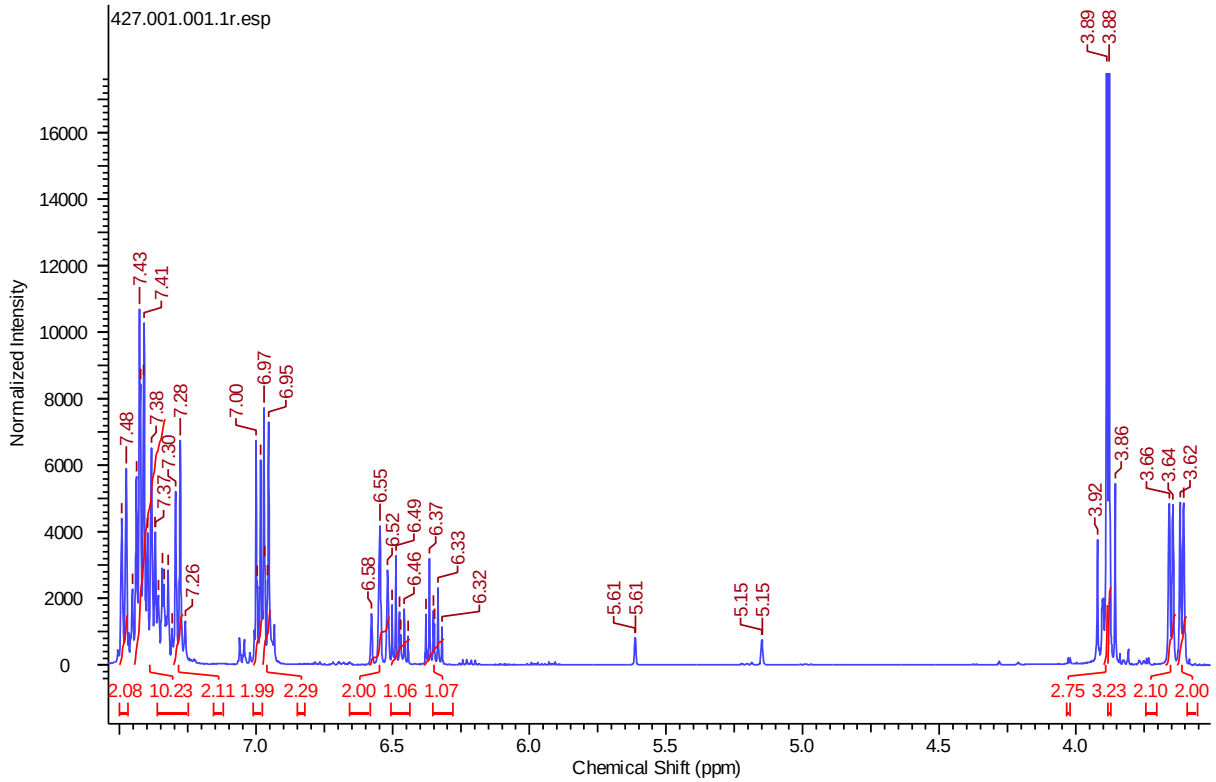
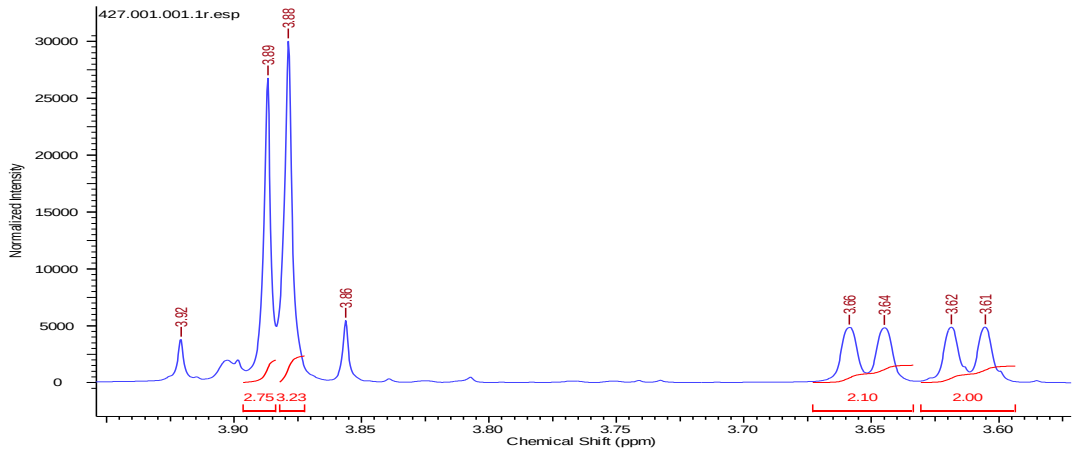


Figure S4. Mass spectrum of 1-Phenyl-3-(4-methoxyphenyl)-1-propene (**2E**) and (**2Z**).





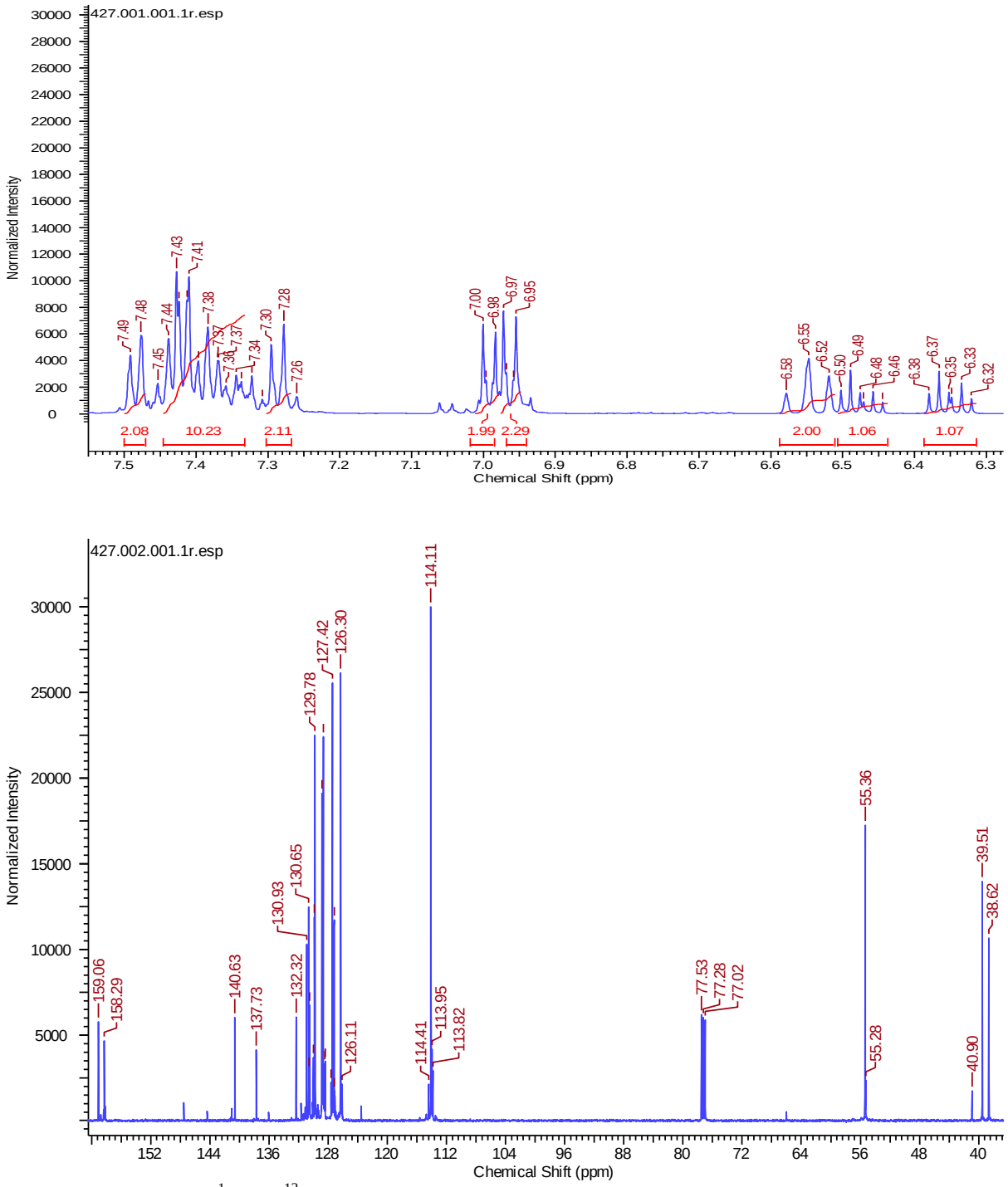
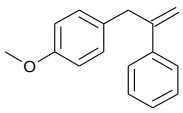


Figure S5. ^{1}H and ^{13}C NMR spectra of 1-Phenyl-3-(4-methoxyphenyl)-1-propene (**2E**).
Reaction conditions (method A): PhI (1 mmol), estragole (1 mmol), K_2CO_3 (2 mmol), $Pd(OAc)_2$ (1×10^{-5}mol), DMF ($5cm^3$), 3h, 100^oC



2b (1-methoxy-4-(2-phenyl-2-propen-1-yl)-benzene)
MS: m/z (%) = 77 (23), 103 (13), 121 (100), 193 (10), 209 (10), 224 (45) [M^+]

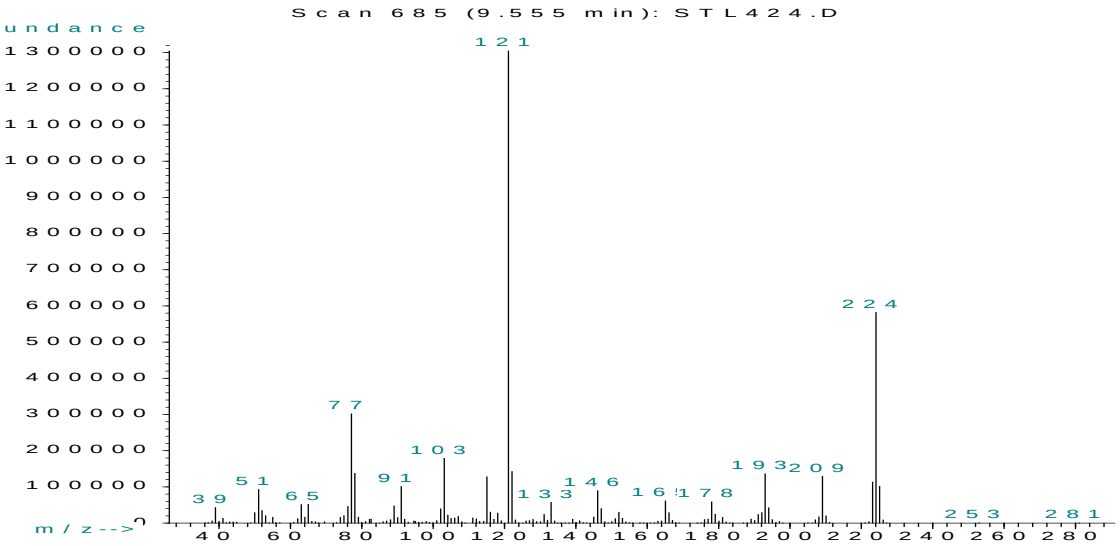
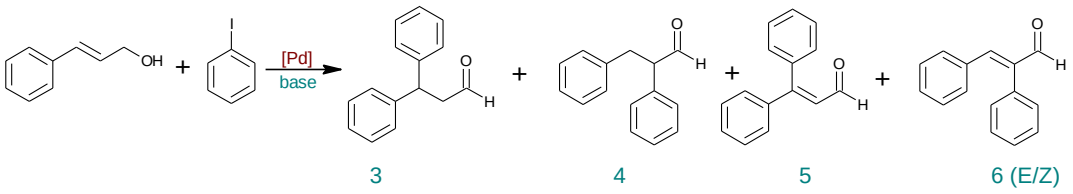
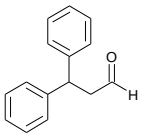


Figure S6. Mass spectrum of (1-methoxy-4-(2-phenyl-2-propen-1-yl)-benzene) (**2b**).

Control experiment 2:





3 (3,3-diphenylpropanal)
MS: m/z (%) = 77 (20), 105 (23), 167 (100), 192 (20), 210 (56) [M^+] [3].
^{1}H–NMR (500 MHz, $CDCl_3$): δ = 9.74 (t, *J* = 1.91, 1H, CHO), 7.25–7.17 (m, 10H, H_{Ar}), 4.63 (t, *J* = 7.82 Hz, 1H, CH), 3.17 (dd, *J* = 7.82, 1.91 Hz, 2H, CH_2) ppm [3,5].
^{13}C–NMR (125 MHz, $CDCl_3$): δ = 198.33, 142.20, 128.26, 127.24, 126.42, 46.95, 42.91 [3].

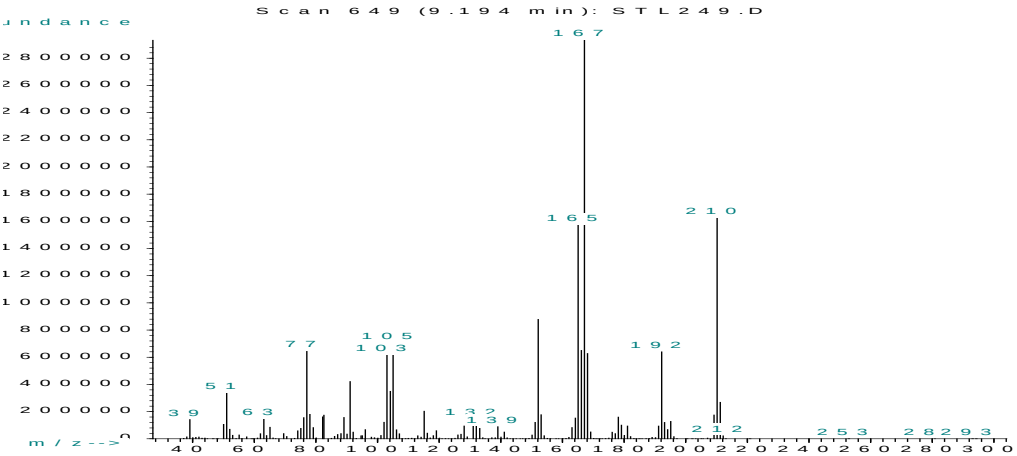


Figure S7. Mass spectrum of 3,3-diphenylpropanal (**3**).

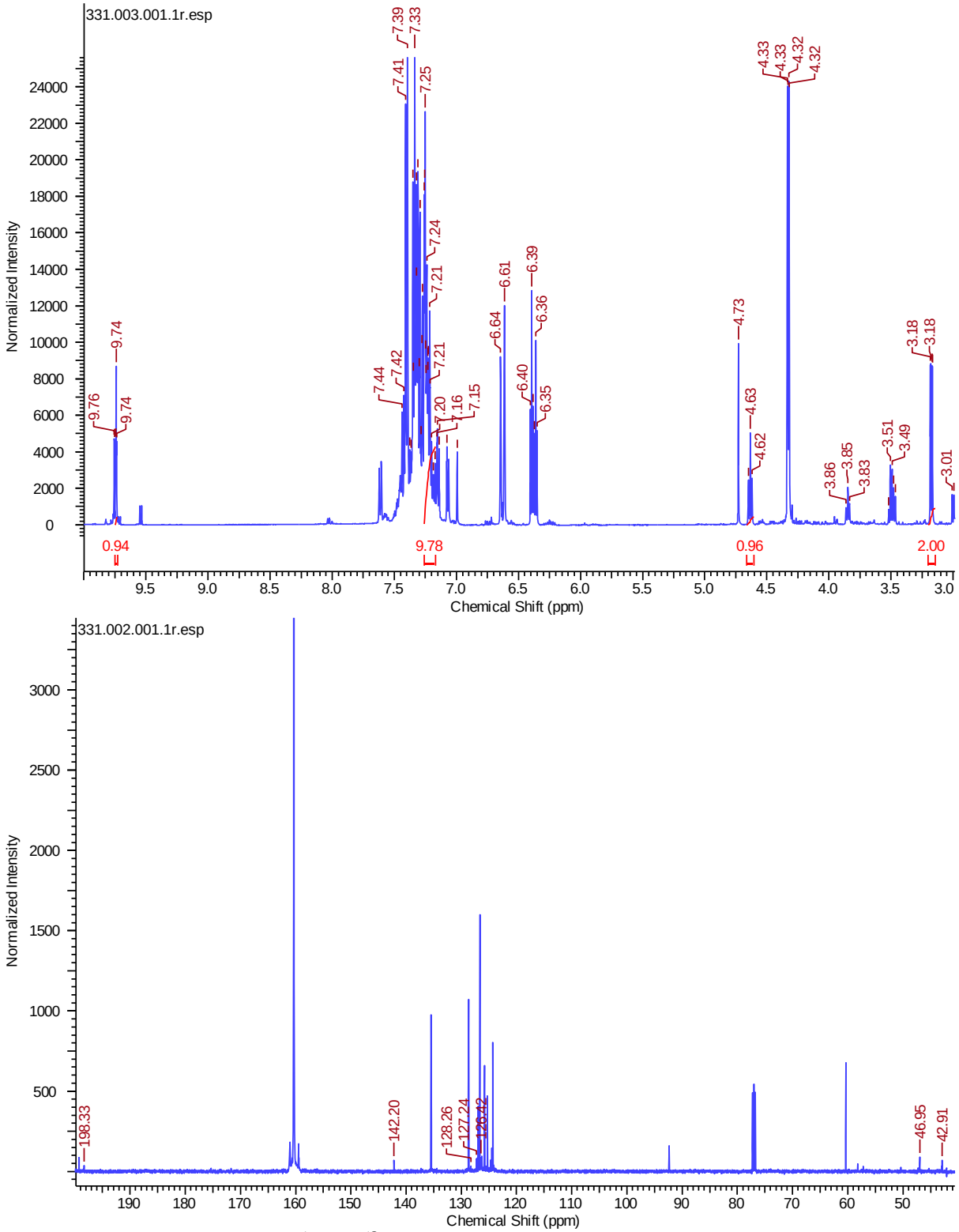
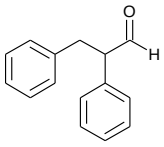


Figure S8. ^{1}H and ^{13}C NMR spectra of 3,3-diphenylpropanal (**3**).
Reaction conditions (method C): PhI (1 mmol), cinnamyl alcohol (1 mmol), K_2HPO_4 (2 mmol), $Pd(OAc)_2$ (1×10^{-5}mol), DMF, 6h, 100°C



4 (2,3-diphenylpropanal)
MS: m/z (%) = 77 (12), 91 (100), 103 (9), 165 (9), 181 (18), 210 (32) [M^+] [4]

^{1}H–NMR (500 MHz, $CDCl_3$): δ = 9.76 (d, *J* = 1.53, 1H, CHO), 7.31–7.26 (m, 10H, H_{Ar}), 3.85 (t, *J* = 6.68 Hz, 1H, CH), 3.48 (dd, *J* = 13.44, 6.68 Hz, 1H, CH_2), 2.98 (dd, *J* = 14.11, 7.82 Hz, 1H, CH_2) [5] ppm.
^{13}C–NMR (125 MHz, $CDCl_3$): δ = 199.24, 135.47, 128.67, 126.96, 126.63, 125.85, 125.79, 125.26, 124.29, 33.83, 28.68

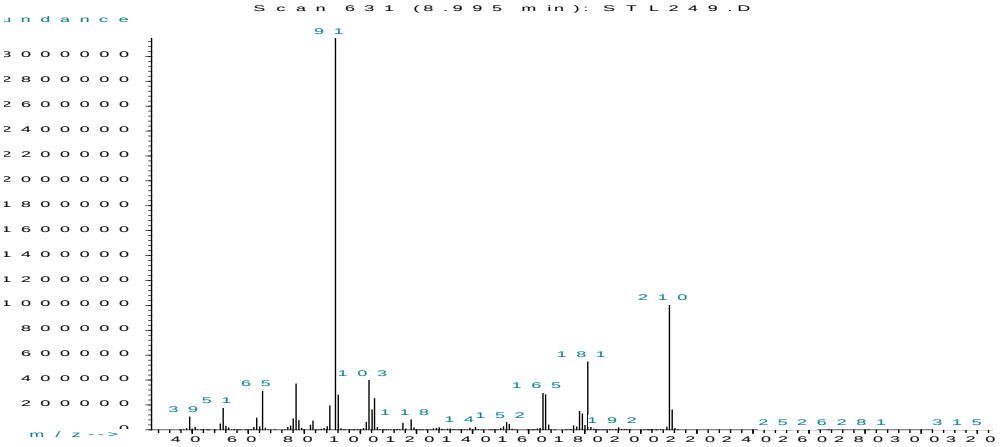
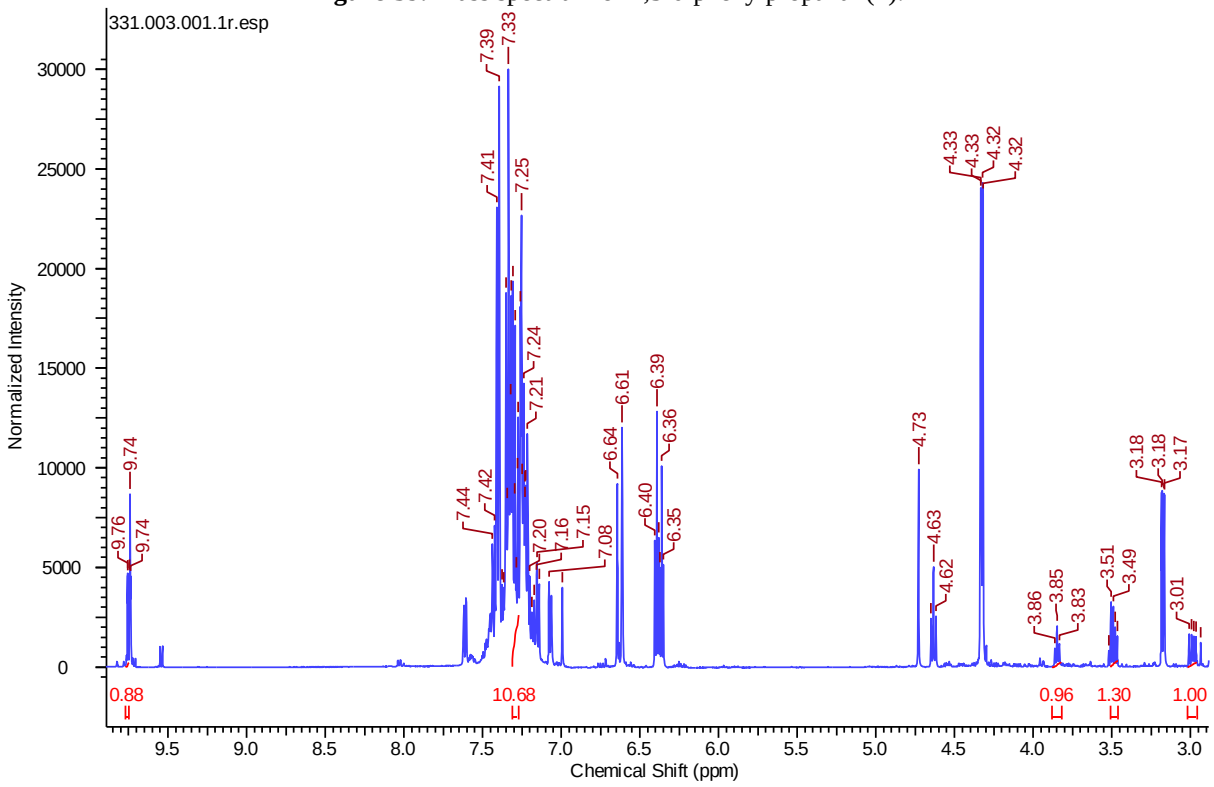


Figure S9. Mass spectrum of 2,3-diphenylpropanal (**4**).



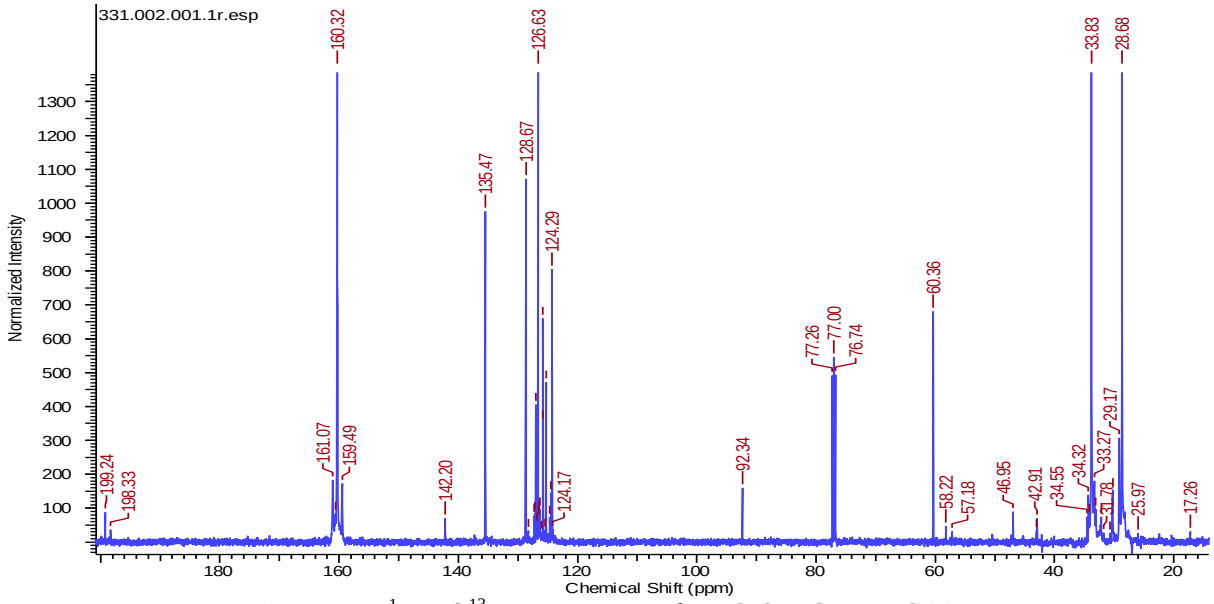
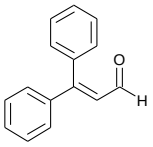


Figure S10. ^{1}H and ^{13}C NMR spectra of 2,3-diphenylpropanal (**4**).



5 (3,3-diphenylprop-2-enal)

MS: m/z (%) = 77 (18), 89 (14), 102 (44), 152 (12), 165 (15), 178 (50), 207 (100), 208 (73) [M^{+}] [6]

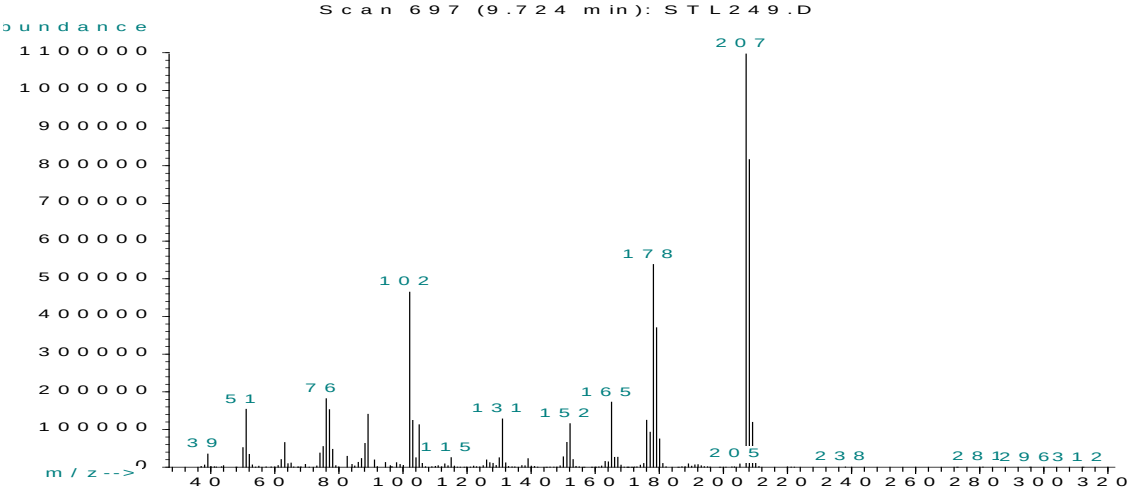
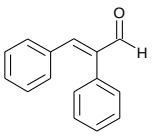


Figure S11. Mass spectrum of 3,3-diphenylprop-2-enal (**5**).



6 ((2*E*)-2,3-diphenylprop-2-enal)

MS: m/z (%) = 77 (18), 89 (18), 102 (44), 152 (20), 165 (26), 178 (79), 207 (56), 208 (100) [M^{+}] [4]

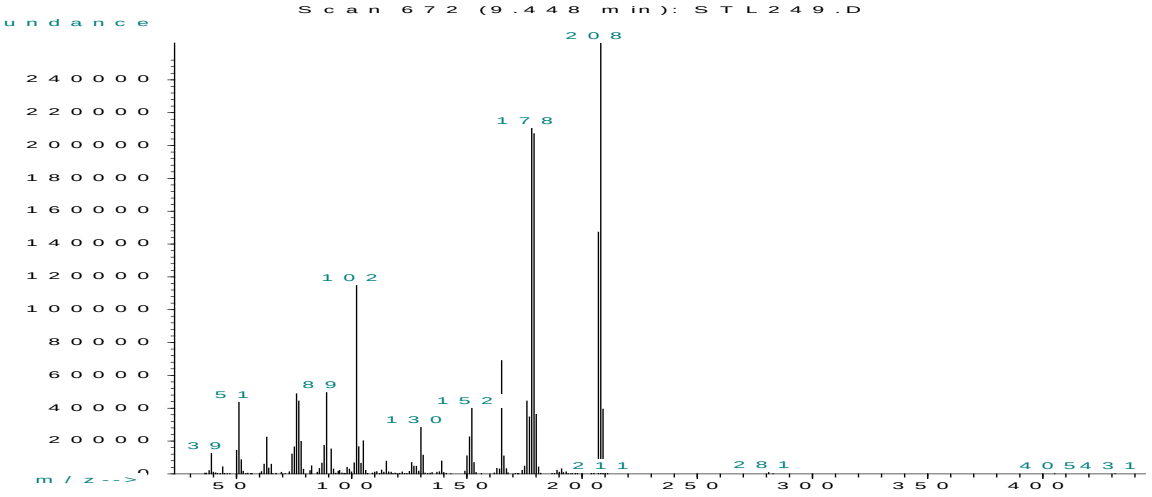
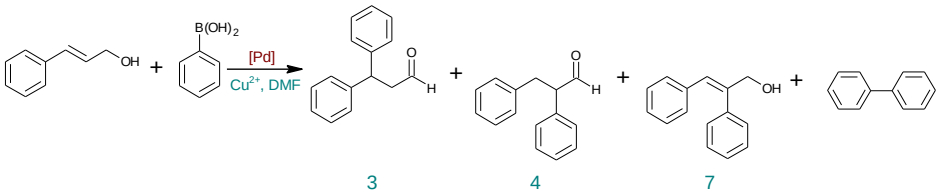
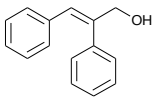


Figure S12. Mass spectrum of (2E)-2,3-diphenylprop-2-enal (**6**).

Control experiment 3:





7 (2,3-diphenyl-2-propen-1-ol)
MS: m/z (%) = 77 (18), 91 (54), 105 (100), 165 (114), 178 (25), 210 (46).
^{1}H–NMR (500 MHz, $CDCl_3$): δ = 7.45–7.42 (m, 5H, H_{Ar}), 7.33–7.10 (m, 5H, H_{Ar}), 7.02 (s, 1H, CH), 4.73 (s, 2H, CH_2), 1.86 (s, 1H, OH) ppm.
^{13}C–NMR (125 MHz, $CDCl_3$): δ = 140.59, 138.71, 136.86, 128.89, 128.58, 128.32, 127.62, 127.29, 126.54, 126.23, 68.30 ppm.

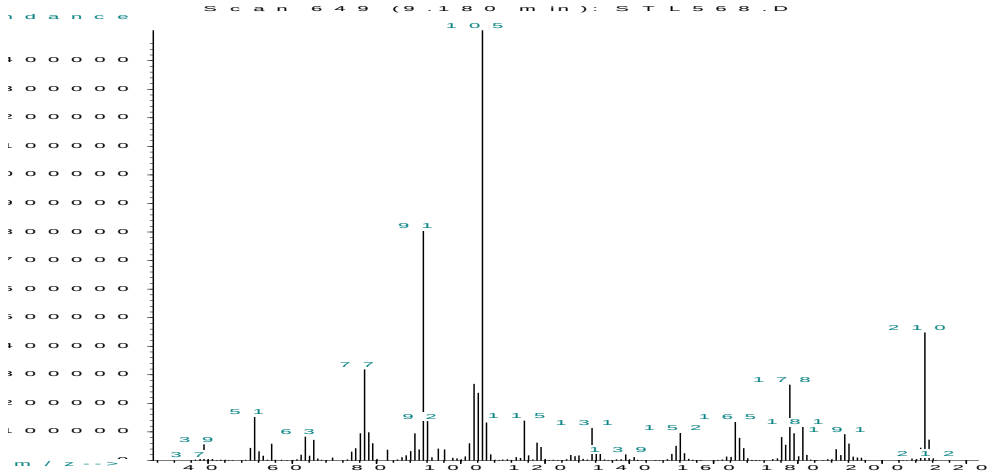


Figure S13. Mass spectrum of 2,3-diphenyl-2-propen-1-ol (**7**).

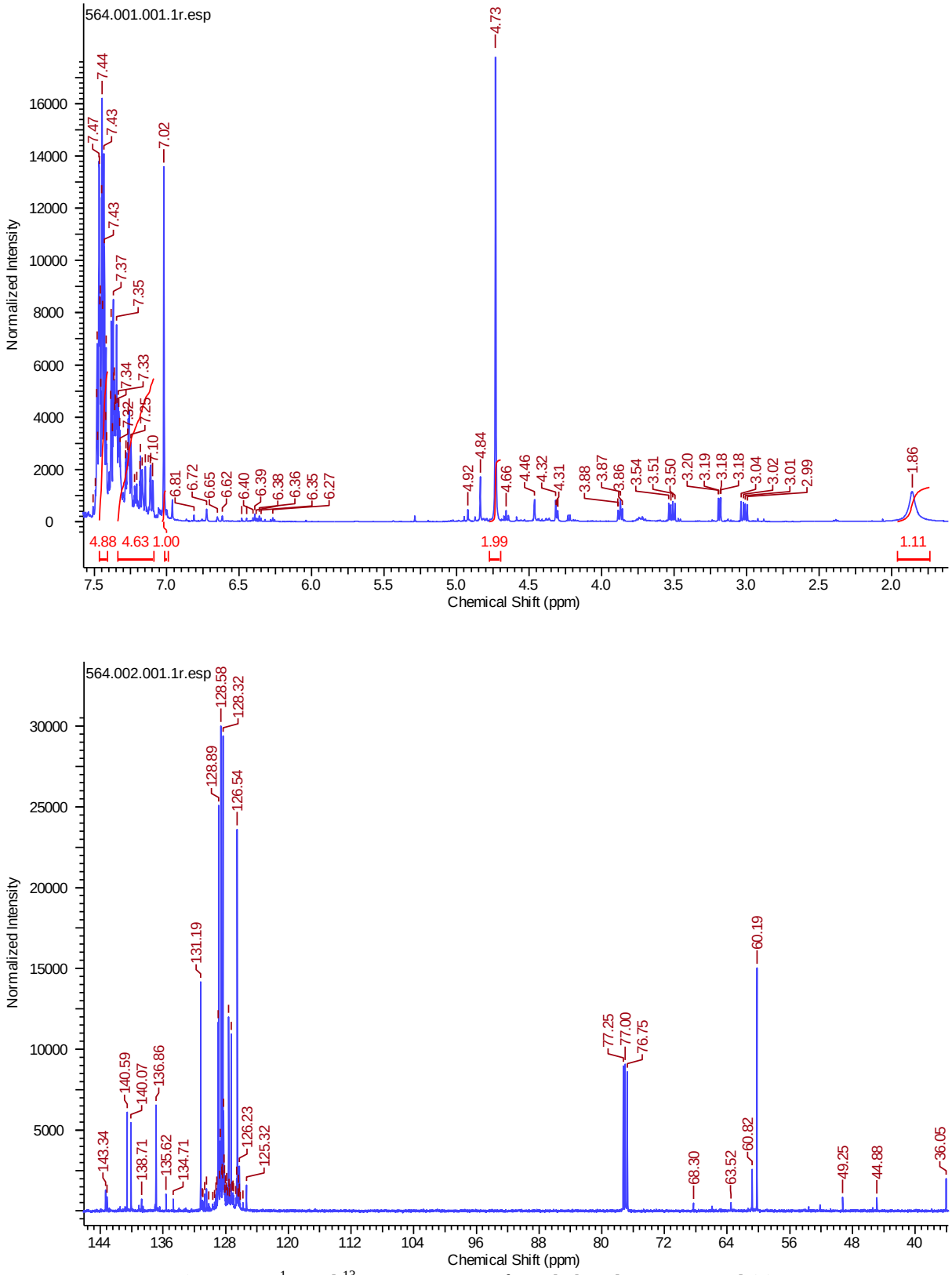
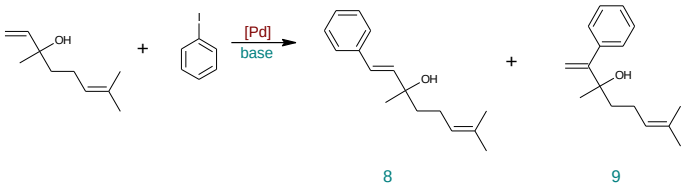
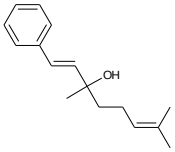


Figure S14. ^{1}H and ^{13}C NMR spectra of 2,3-diphenyl-2-propen-1-ol (**7**).

Control experiment 4:





8 ((1*E*)-3,7-dimethyl-1-phenylocta-1,6-dien-3-ol)
MS: m/z (%) = 43 (81), 69 (24), 77 (15), 91 (20), 105 (11), 129 (46), 147 (100), 172 (46), 197 (4), 230 (2) [M^+]
^{1}H–NMR (500 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 7.82 Hz, 2H, H_{Ar}), 7.32 (t, *J* = 7.44 Hz, 2H, H_{Ar}), 7.24 (t, *J* = 7.44 Hz, 1H, H_{Ar}), 6.61 (d, *J* = 16.21 Hz, 1H, CH), 6.29 (d, *J* = 16.02 Hz, 1H, CH), 5.09 (t, *J* = 7.25, 1H, CH), 5.16 (t, *J* = 7.15 Hz, 1H, CH), 2.17–2.03 (m, 2H, CH_2), 1.81 (s, 1H, OH), 1.70 (s, 3H, CH_3), 1.68–1.66 (m, 2H, CH_2), 1.61 (s, 3H, CH_3), 1.40 (s, 3H, CH_3) ppm.
^{13}C–NMR (125 MHz, $CDCl_3$): δ = 137.05, 136.61, 123.02, 128.50, 127.26, 127.09, 126.33, 124.30, 73.43, 42.51, 28.24, 25.66, 22.93, 17.70.

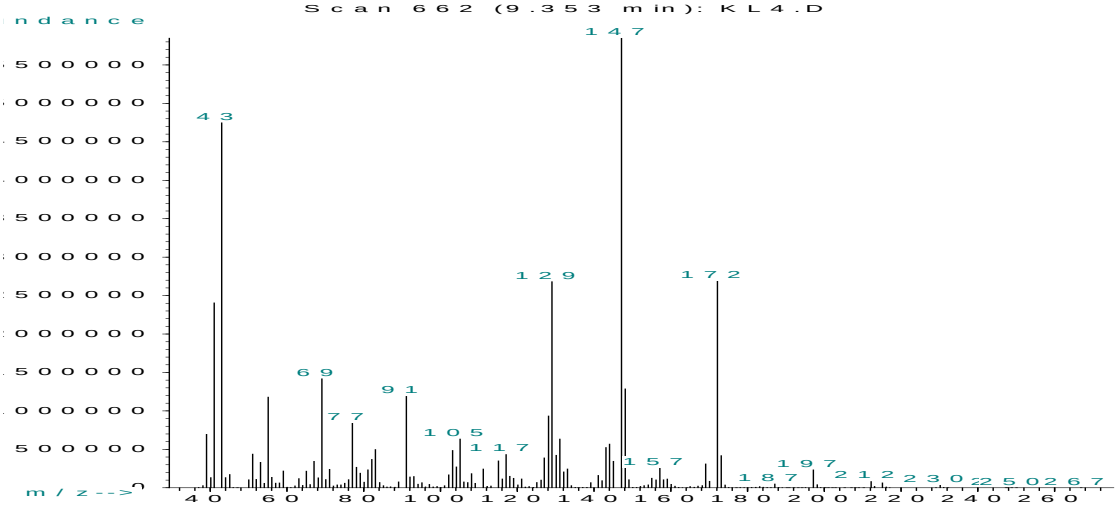


Figure S15. Mass spectrum of (1E)-3,7-dimethyl-1-phenylocta-1,6-dien-3-ol) (**8**).

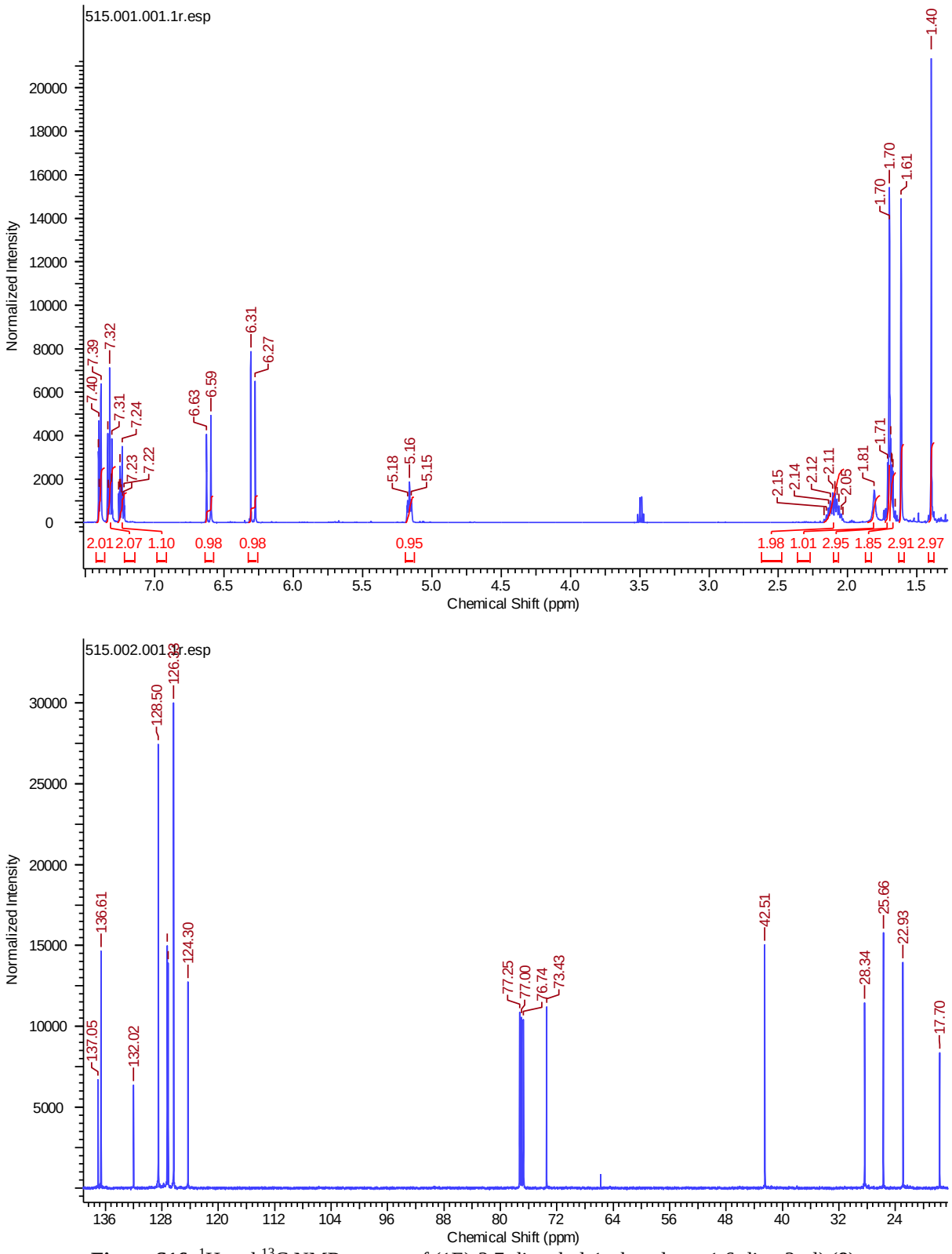
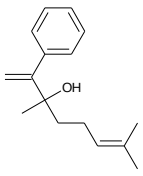


Figure S16. ^{1}H and ^{13}C NMR spectra of (1E)-3,7-dimethyl-1-phenylocta-1,6-dien-3-ol) (**8**). Reaction conditions (method C): PhI (1 mmol), linalool (1 mmol), Et_3N (2 mmol), $Pd(OAc)_2$ (1×10^{-5}mol), DMF, 5h, 100°C



9 (3,7-dimethyl-2-phenylocta-1,6-dien-3-ol)
MS: m/z (%) = 43 (33), 77 (6), 91 (8), 105 (5), 129 (24), 147 (100), 172 (6), 212 (5), 230 (2) [M^+]

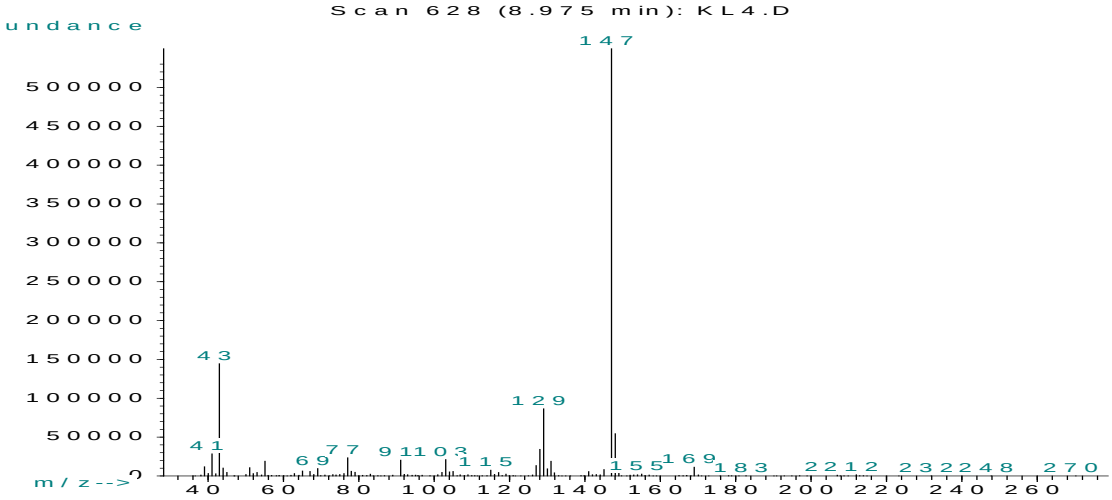
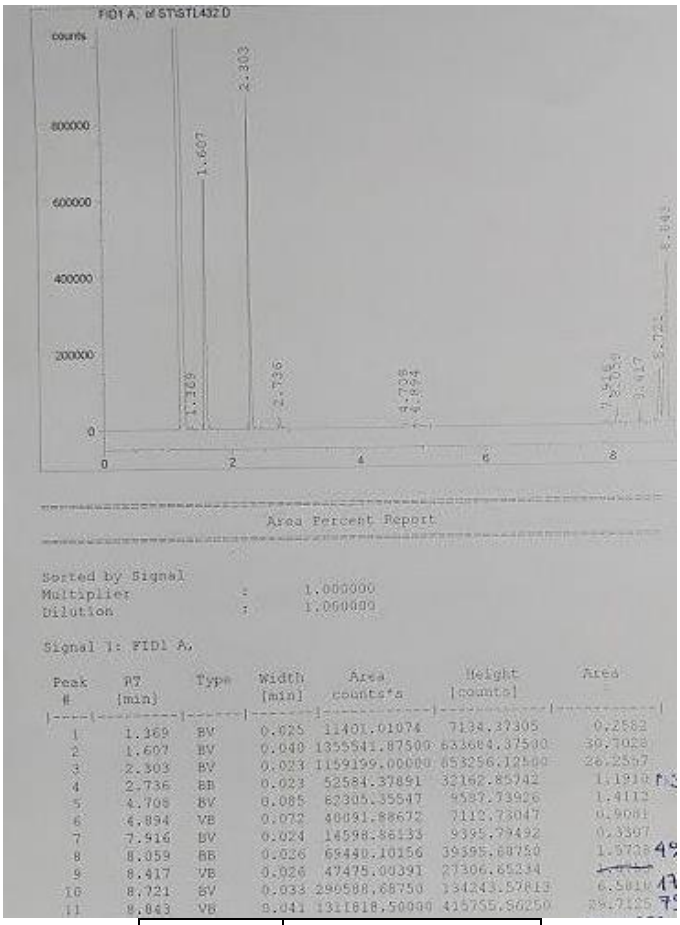


Figure S17. Mass spectrum of (3,7-dimethyl-2-phenylocta-1,6-dien-3-ol) (**9**).

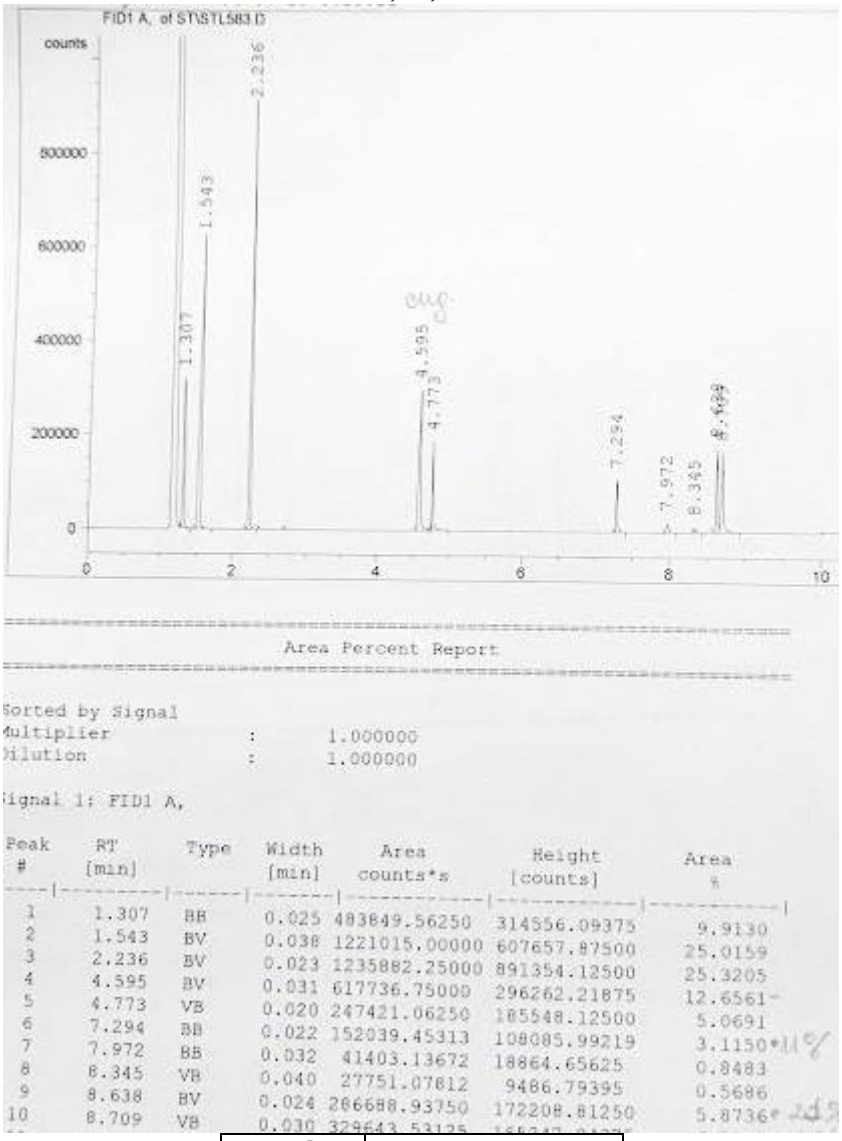
GC examples (preparation of samples for GC was described in the Experimental part)



Peak [min]	Compound
1.607	DMF
2.303	mesitylene
2.736	PhI

4.708	eugenol
4.894	biphenyl
8.059	1b
8.721	1Z
8.843	1E

Figure S18. GC profile for the Heck reaction of PhI with eugenol.
Reaction conditions (method A): PhI (1 mmol), eugenol (1 mmol), K_2CO_3 (2 mmol), $Pd(OAc)_2$ (1×10^{-5}mol), DMF, 1h, 100°C



Area Percent Report

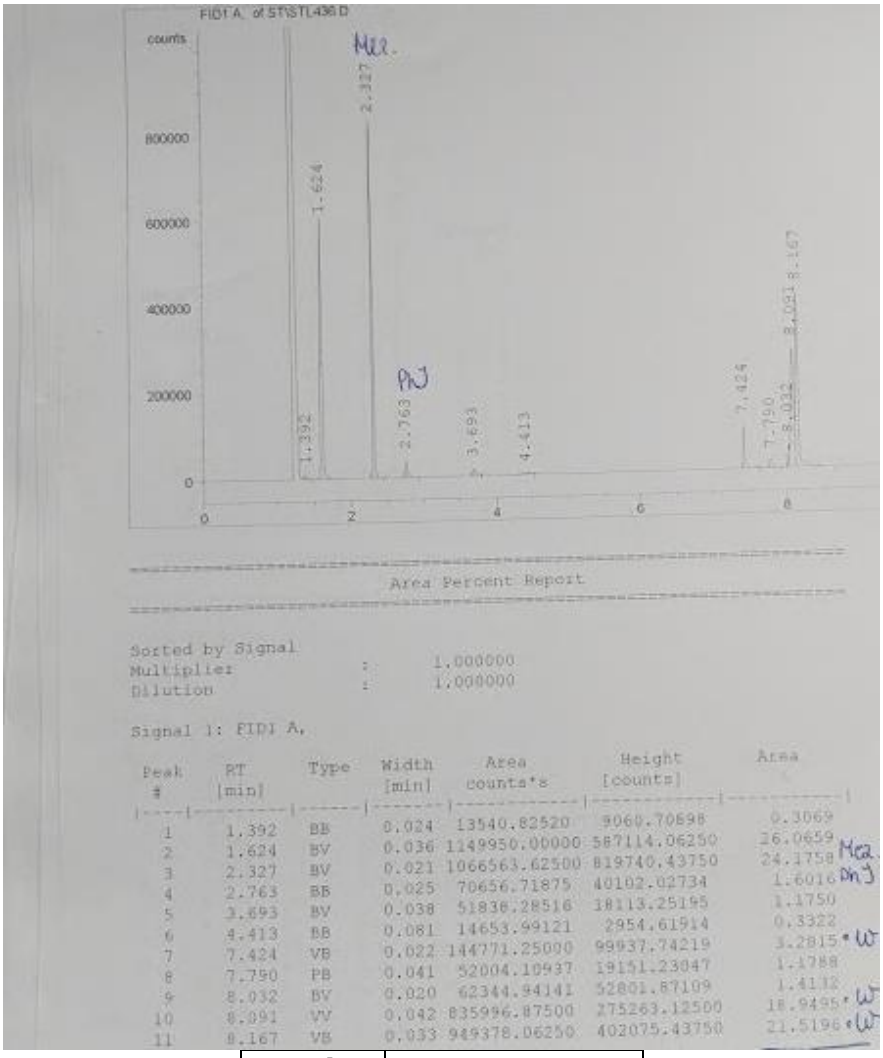
Sorted by Signal
Multiplier : 1.000000
Dilution : 1.000000

Signal 1: FID1 A,

Peak #	RT [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	1.307	BB	0.025	483849.56250	314556.09375	9.9130
2	1.543	BV	0.038	1221015.00000	607657.87500	25.0159
3	2.236	BV	0.023	1235882.25000	891354.12500	25.3205
4	4.595	BV	0.031	617736.75000	296262.21875	12.6561
5	4.773	VB	0.020	247421.06250	185548.12500	5.0691
6	7.294	BB	0.022	152039.45313	108085.99219	3.1150
7	7.972	BB	0.032	41403.13672	18864.65625	0.8483
8	8.345	VB	0.040	27751.07812	9486.79395	0.5686
9	8.638	BV	0.024	286688.93750	172208.81250	5.8736
10	8.709	VB	0.030	329643.53125		

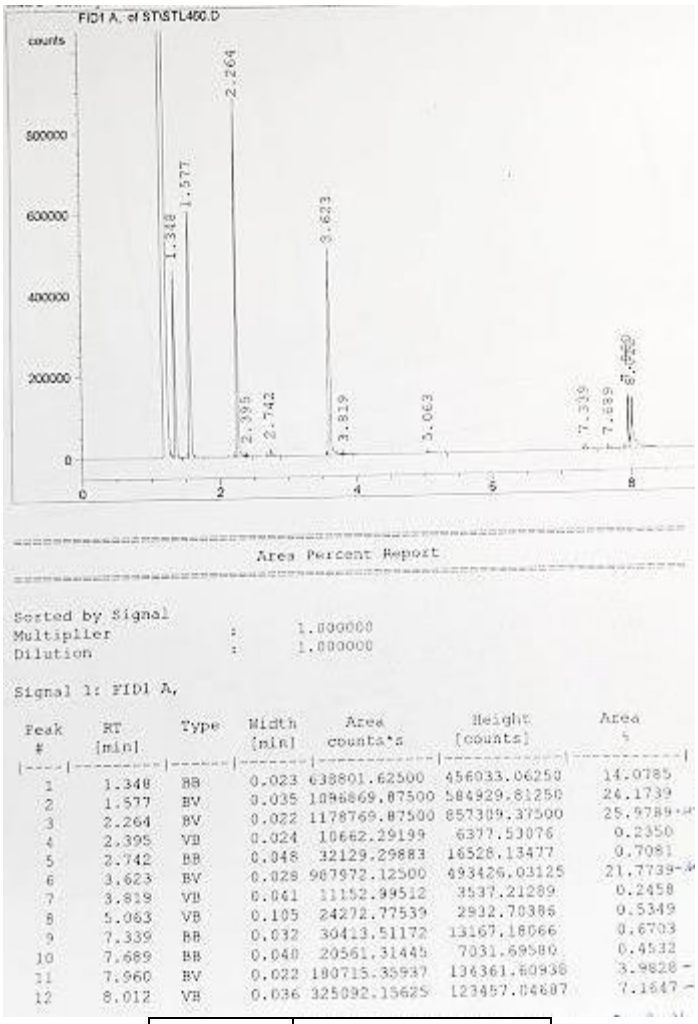
Peak [min]	**Compound**
1.543	DMF
2.236	mesitylene
4.595	eugenol
4.773	biphenyl
7.294	1b
8.638	1Z
8.709	1E

Figure S19. GC profile for the Heck-type reaction of eugenol with $PhB(OH)_2$.
Reaction conditions (method B): eugenol (1 mmol), phenylboronic acid (1.5 mmol), Cu^{2+} salt (2 mmol), $Pd(OAc)_2$ (1×10^{-6} mol), DMF (5 cm^3), 6h, 100°C



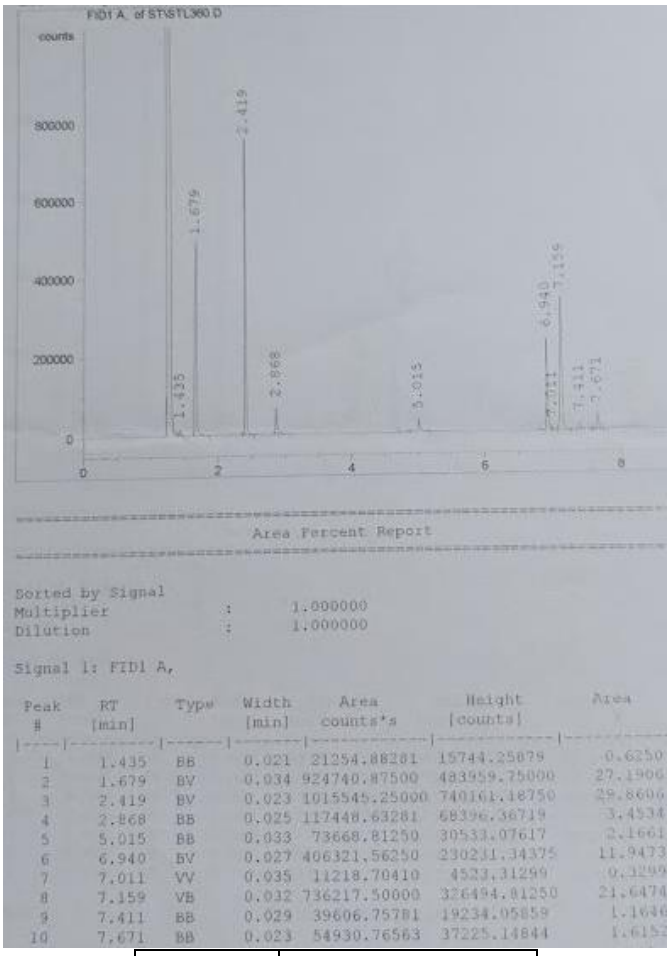
Peak [min]	Coumpound
1.624	DMF
2.327	mesitylene
2.763	PhI
3.693	estragole
7.424	2b
8.091	2Z
8.167	2E

Figure S20. GC profile for the Heck reaction of PhI with estragole.
Reaction conditions (method A): PhI (1 mmol), estragole (1 mmol), K_2CO_3 (2 mmol), $Pd(OAc)_2$ (1×10^{-5}mol), DMF (5 cm^3), 3h, 100^{o}C



Peak [min]	Compound
1.577	DMF
2.264	mesitylene
3.623	estragole
7.339	2b
7.960	2Z
8.012	2E

Figure S21. GC profile for the Heck-type reaction of estragole with $PhB(OH)_2$.
Reaction conditions (method B): estragole (1 mmol), phenylboronic acid (1.5 mmol), Cu^{2+} salt (2 mmol), $PdCl_2cod$ (1×10^{-5} mol), DMF (5 cm^3), 4h, 100°C



Area Percent Report

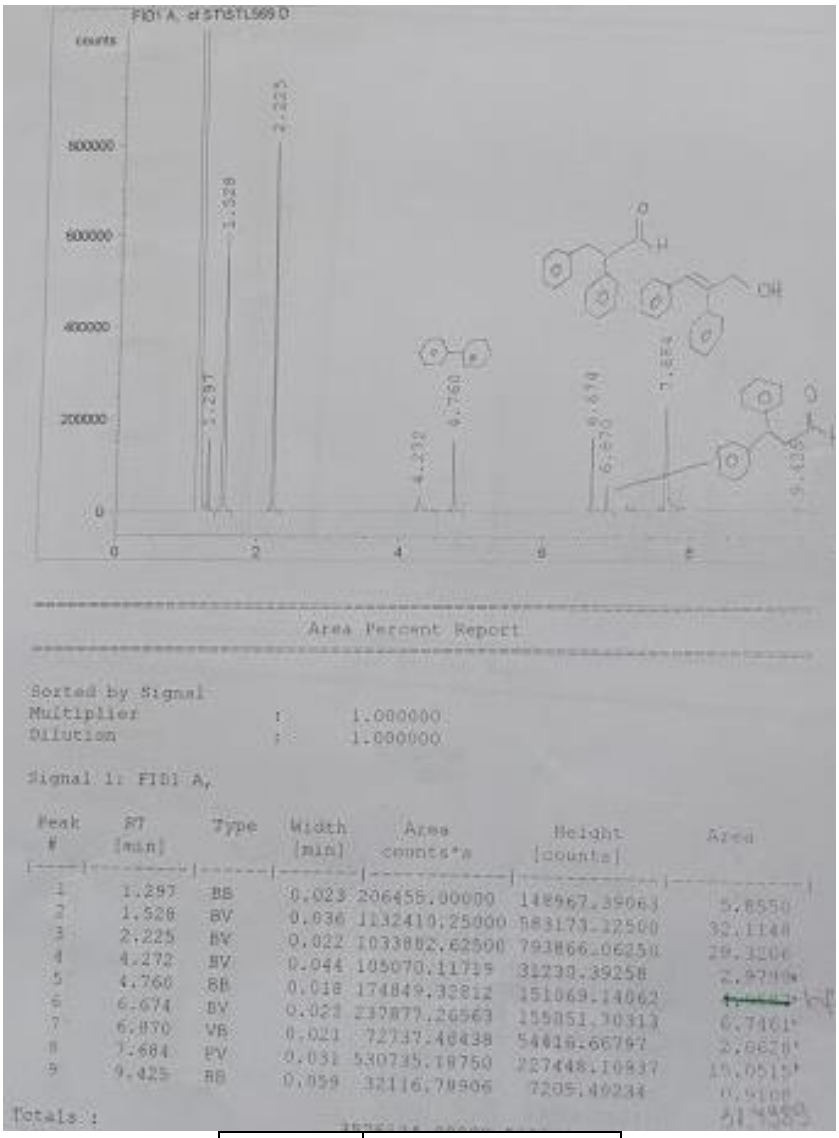
Sorted by Signal
Multiplier : 1.000000
Dilution : 1.000000

Signal 1: FID1 A,

Peak #	RT [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	1.435	BB	0.021	21254.88281	15744.25879	0.6250
2	1.679	BV	0.034	924740.87500	483959.75000	27.1906
3	2.419	BV	0.023	1015545.25000	740161.18750	29.8600
4	2.868	BB	0.025	117448.63281	68396.36719	3.4534
5	5.015	BB	0.033	73668.81250	30533.07617	2.1661
6	6.940	BV	0.027	406321.56250	230231.34375	11.9473
7	7.011	VV	0.035	11218.70410	4523.31299	0.3299
8	7.159	VB	0.032	736217.50000	326494.81250	21.6474
9	7.411	BB	0.029	39606.75781	19234.05859	1.1646
10	7.671	BB	0.023	54930.76563	37225.14844	1.6152

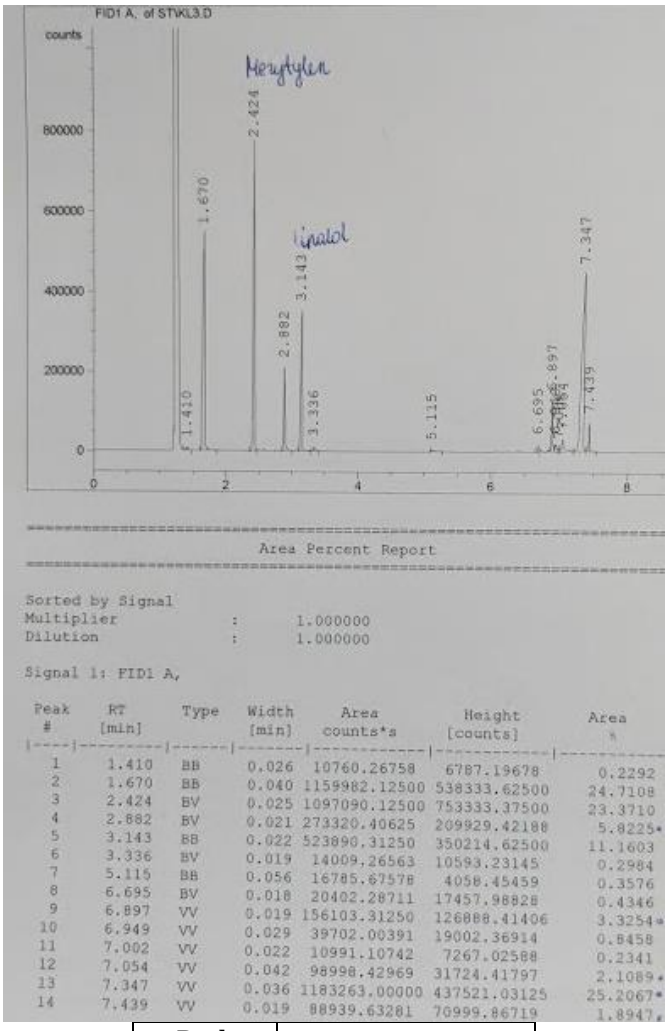
Peak [min]	**Compound**
1.679	DMF
2.419	mesitylene
2.868	PhI
5.015	biphenyl
6.940	3
7.159	4
7.411	6
7.671	5

Figure S22. GC profile for the Heck reaction of cinnamyl alcohol with PhI.
Reaction conditions (method C): PhI (1 mmol), cinnamyl alcohol (1 mmol), NaOAc (2 mmol), $PdCl_2$cod (1×10^{-5} mol), DMF (5 cm^3), TBAB (1g), 6h, 100 °C



Peak [min]	Compound
1.528	DMF
2.225	mesitylene
4.272	cinnamyl alcohol
4.760	biphenyl
6.674	4
6.870	3
7.784	7

Figure S23. GC profile for the Heck-type reaction of cinnamyl alcohol with $PhB(OH)_2$. Reaction conditions (method B): cinnamyl alcohol (1 mmol), phenylboronic acid (1.5 mmol), Cu^{2+} salt (2 mmol), Pd_2dba_3 (1×10^{-5} mol), DMF (5 cm^3), 0.5h, 50°C



Peak [min]	Compound
1.670	DMF
2.424	mesitylene
3.143	linalool
3.336	linalool
5.115	biphenyl
6.897	9
7.054	8
7.347	8

Figure S24. GC profile for the Heck reaction of linalool with PhI.
Reaction conditions (method C): PhI (1 mmol), linalool (1 mmol), NaOAc (2 mmol), $PdCl_2cod$ (1×10^{-5} mol), DMF (5 cm^3), 3h, 140^oC

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