

Supporting Information

Catalytic Allylic Arylation of Cinnamyl Carbonates over Palladium

Nanoparticles Supported on a Thermoresponsive Polymer in Water

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Differential Scanning Calorimetry (DSC) curve of poly(NIPAM-co-4-VP)

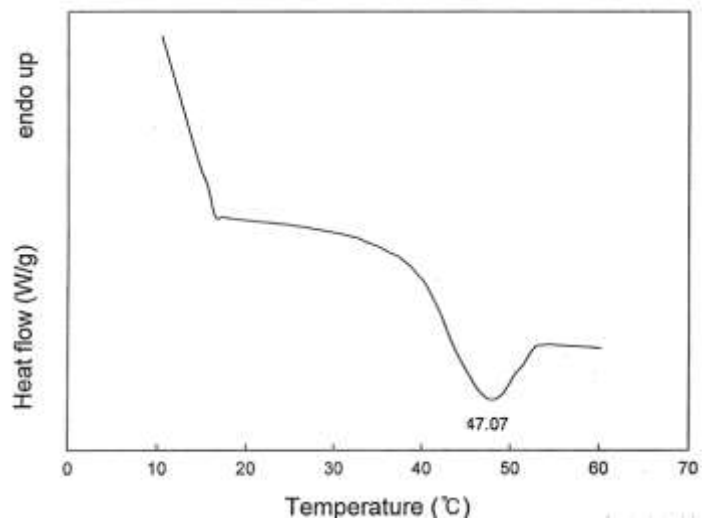


Figure S1. Differential Scanning Calorimetry (DSC) curve of poly(NIPAM-co-4-VP)

Energy Dispersive X-ray Analysis (EDXA) measurements

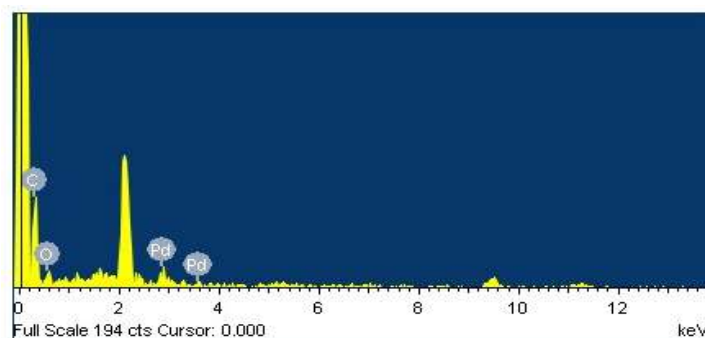


Figure S2. Energy Dispersive X-ray Analysis (EDXA) measurements of the catalyst

X-ray Photon Spectroscopy (XPS) Analysis

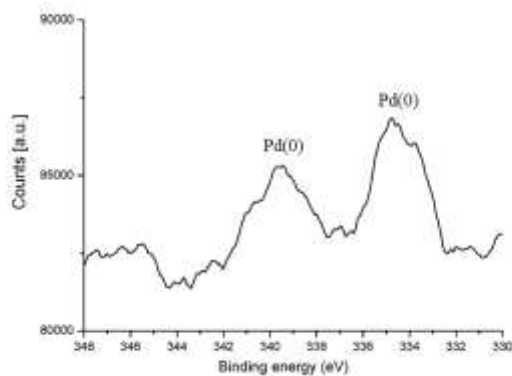


Figure S4. X-ray Photon Spectroscopy (XPS) spectrum of the fresh catalyst

Inductively Coupled Plasma (ICP) Report

Table S1. Inductively Coupled Plasma (ICP) quantitative measurements for Pd(0) in fresh catalyst and the reaction mixture.

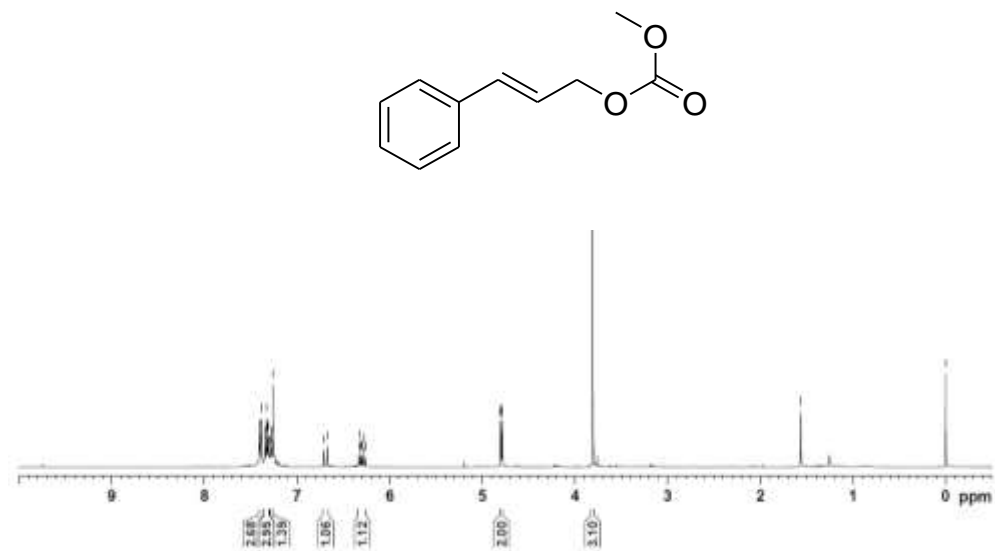
Entry	Sample Name	Sample	Element investigated	Result (ppm)	Observation
1	Pd@PNIPAM	Fresh catalyst	Pd	19600	0.184mmol Pd/g of polymer
2	water	Filtrate	Pd	20	Insignificant leaching out of Pd after the 1 st recycle

Spectroscopic data of the products

NMR Spectroscopic data of Cinnamyl methyl carbonates (1a-c) and the coupling products of allylic arylation (3a-l)

Cinnamyl methyl carbonate (1a):¹ Colorless oil, 3.229 g (84%); $R_f = 0.37$ (hexanes/EtOAc, 20/1, v/v) ¹H

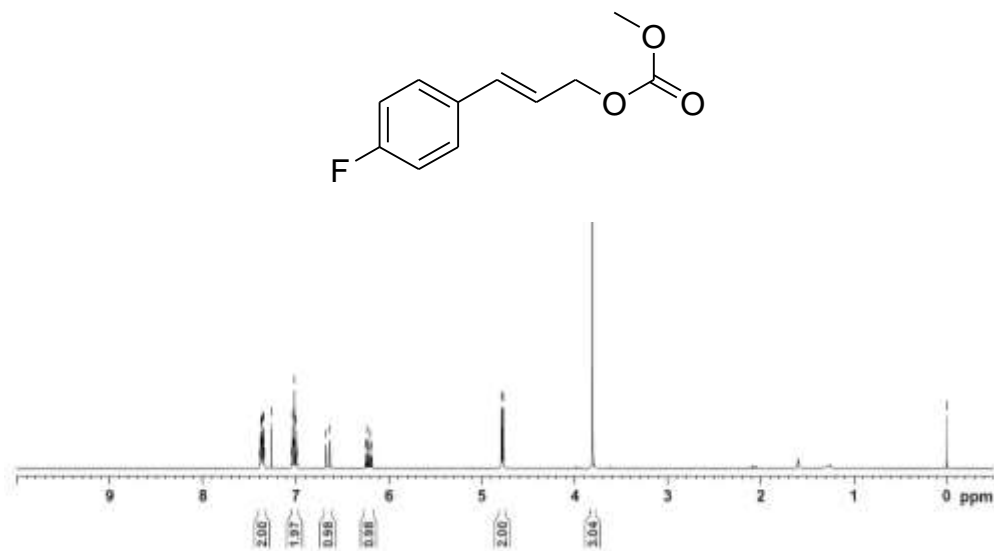
NMR (400 MHz, CDCl₃, TMS): δ 7.26-7.41 (m, 5H, ArH), 6.69 (d, $J = 16.0$ Hz, 1H, CH=), 6.30 (dt, $J = 15.6, 6.4$ Hz, 1H, CH=), 4.79 (d, $J = 6.4$ Hz, 2H, CH₂), 3.81 (s, 3H, OCH₃).



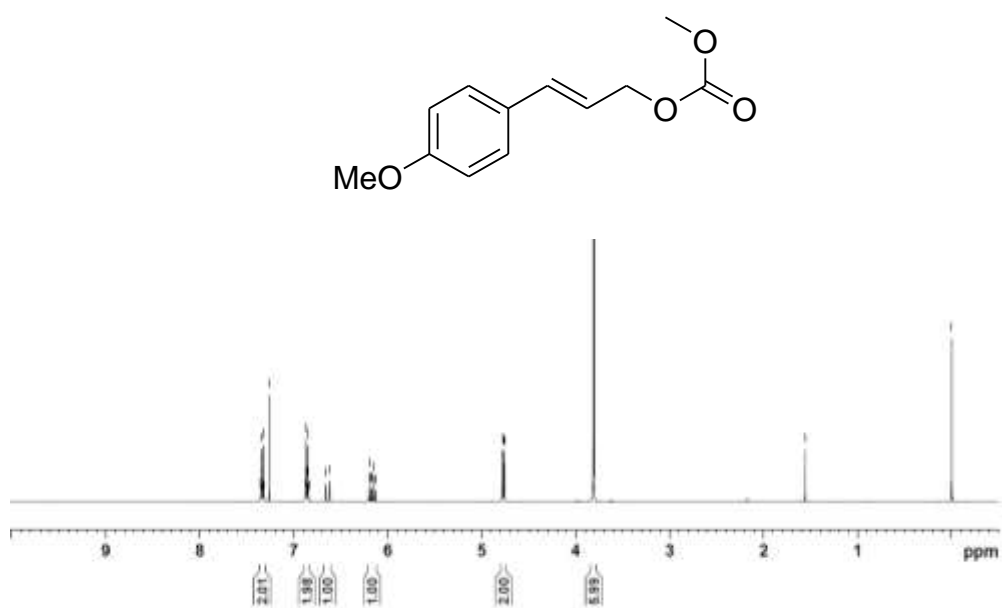
(E)-3-(4-Fluorophenyl)allyl methyl carbonate (1b):¹ Colorless oil, 3.447 g (82%); $R_f = 0.52$

(hexanes/EtOAc, 20/1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.36 (dd, $J = 8.8, 5.6$ Hz, 2H, ArH), 7.02 (t, $J =$

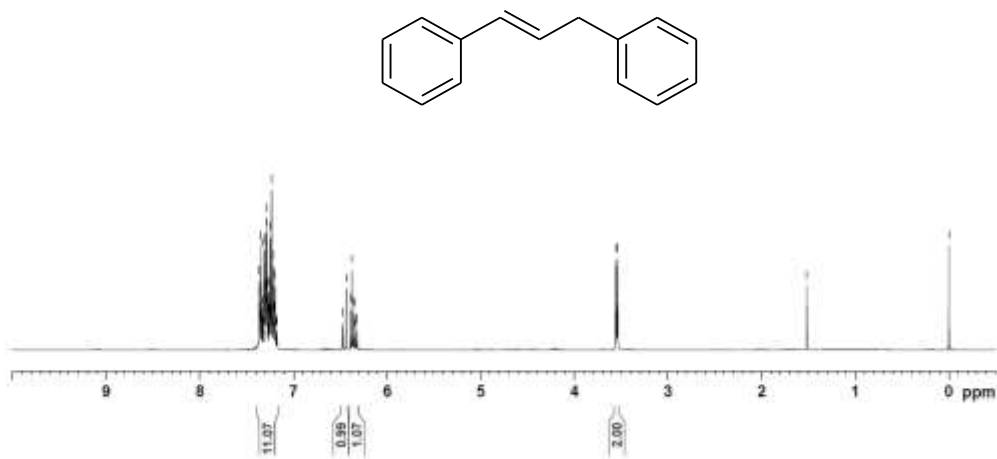
8.8 Hz, 1H, ArH, CH=), 6.65 (d, $J = 15.6$ Hz, 1H, CH=), 6.22 (dt, $J = 15.6, 6.4$ Hz, 2H, ArH), 4.78 (dd, $J = 6.8,$
1.6 Hz, 2H, CH₂), 3.81 (s, 3H, OCH₃).



(E)-3-(4-Methoxyphenyl)allyl methyl carbonate (1c):¹ Yellowish gummy solid, 3.911 g (88%); $R_f = 0.24$
(hexanes/EtOAc, 20/1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.33 (d, $J = 8.4$ Hz, 2H, ArH), 6.86 (d, $J = 8.8$
Hz, 2H, ArH), 6.64 (d, $J = 16.0$ Hz, 1H, CH=), 6.16 (dt, $J = 15.6, 6.8$ Hz, 1H, CH=), 4.77 (dd, $J = 6.4, 1.2$ Hz, 2H,
CH₂), 3.81 (s, 3H, OCH₃).



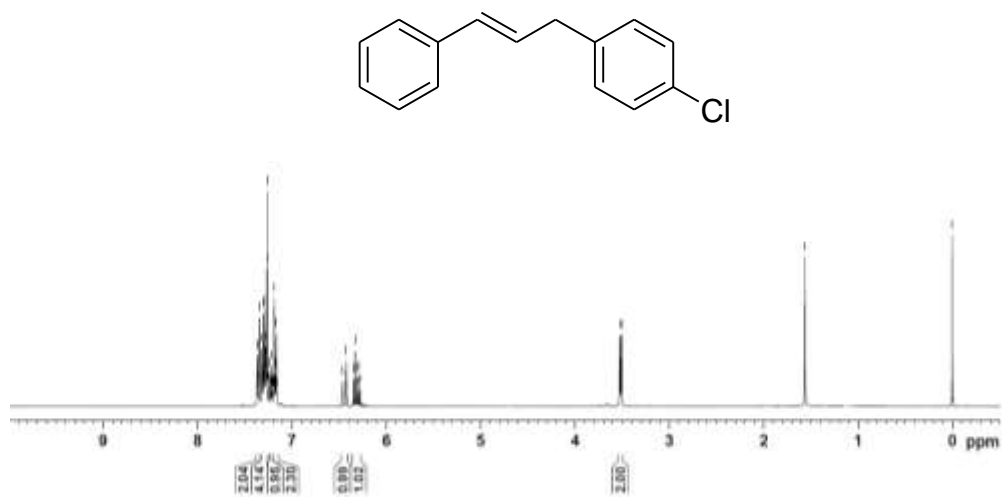
(1E)-1,3-Diphenylpropene (3a):² Colorless oil, 0.184 g (95%); $R_f = 0.71$ (hexanes/EtOAc, 10/1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.18-7.37 (m, 10H, ArH), 6.46 (d, $J = 16.0$ Hz, 1H, CH=), 6.36 (dt, $J = 16.0, 6.4$ Hz, 1H, CH=), 3.55 (d, $J = 6.4$ Hz, 2H, CH_2).



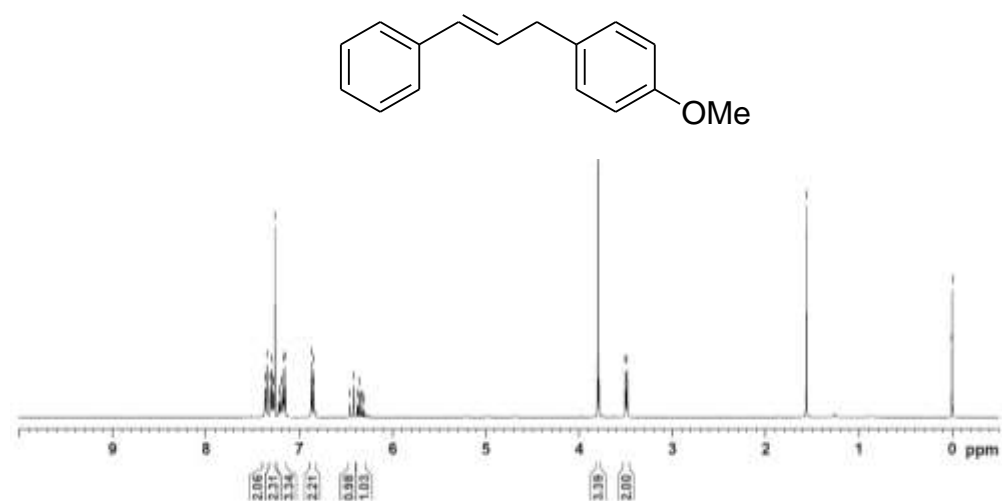
(1E)-3-(4-Methylphenyl)-1-phenylpropene (3b):² Colorless oil, 0.195 g (94%); $R_f = 0.75$ (hexanes/EtOAc, 10/1, v/v); ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.36 (d, $J = 7.6$ Hz, 2H, ArH), 7.29 (t, $J = 7.2$ Hz, 2H, ArH), 7.20 (t, $J = 7.2$ Hz, 1H, ArH), 7.13 (m, 4H, ArH), 6.45 (d, $J = 15.6$ Hz, 1H, CH=), 6.35 (dt, $J = 16.0, 6.4$ Hz, 1H, CH=), 3.52 (d, $J = 6.8$ Hz, 2H, CH_2), 2.34 (s, 3H, CH_3).



(1E)-3-(4-Chlorophenyl)-1-phenylpropene (3c):² Colorless oil, 0.192 g (96%); $R_f = 0.59$ (hexanes/EtOAc, 10/1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3 , TMS): δ 7.36 (d, $J = 7.6$ Hz, 2H, ArH), 7.26-7.32 (m, 4H, ArH), 7.16-7.24 (m, 3H, ArH), 6.44 (d, $J = 16.0$ Hz, 1H, CH=), 6.31 (dt, $J = 16.0, 6.4$ Hz, 1H, CH=), 3.52 (d, $J = 6.8$ Hz, 2H, CH_2).

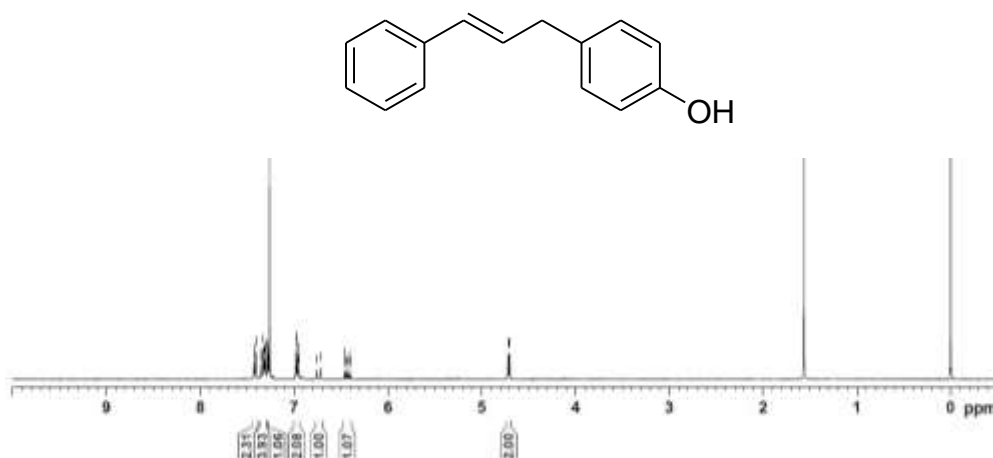


(1E)-3-(4-Methoxyphenyl)-1-phenylpropene (3d):² Colorless oil, 0.203 g (91%); $R_f = 0.60$ (hexanes/EtOAc, 10/1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3 , TMS): δ 7.36 (d, $J = 7.6$ Hz, 2H), 7.29 (t, $J = 7.2$ Hz, 2H, ArH), 7.19 (t, $J = 7.6$ Hz, 1H, ArH), 7.16 (d, $J = 8.4$ Hz, 2H, ArH), 6.86 (d, $J = 8.0$ Hz, 2H, ArH), 6.43 (d, $J = 15.6$ Hz, 1H, CH=), 6.34 (dt, $J = 16.0, 6.4$ Hz, 1H, CH=), 3.80 (s, 3H, OCH_3), 3.49 (d, $J = 6.4$ Hz, 2H, CH_2).

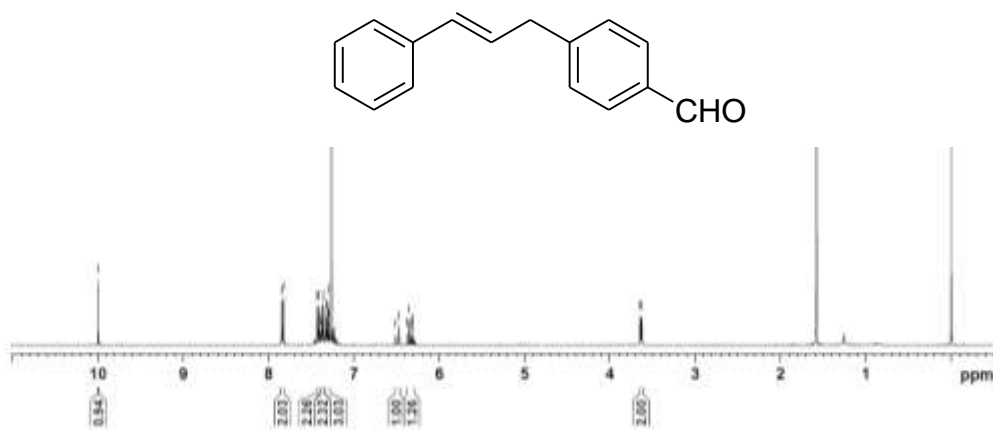


(1E)-3-(4-Hydroxyphenyl)-1-phenylpropene (3e):³ White solid, 0.193 g (92%), mp. 64-65 $^\circ\text{C}$; $R_f = 0.32$ (hexanes/EtOAc, 10/1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3 , TMS): δ 7.42 (d, $J = 7.2$ Hz, 2H, ArH), 7.27-7.35 (m, 4H,

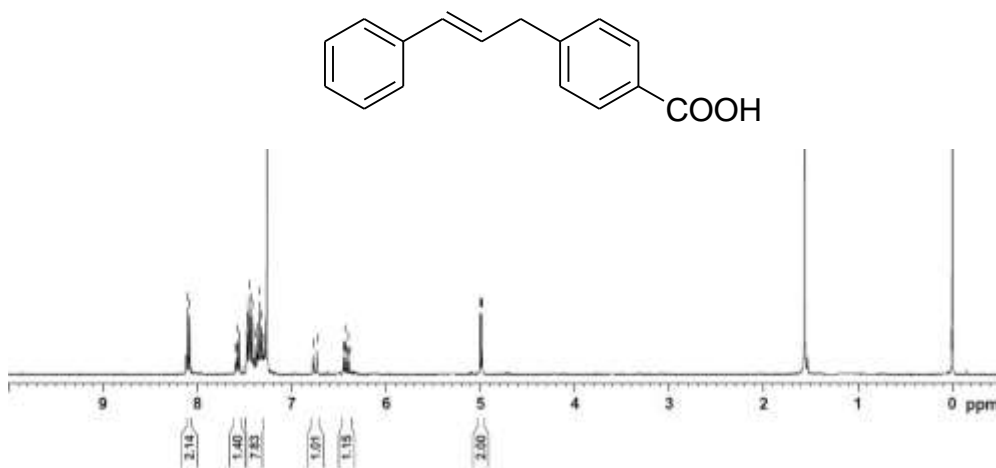
ArH), 6.97 (d, $J = 7.2$ Hz, 2H, ArH), 6.74 (d, $J = 16.0$ Hz, 1H, CH=), 6.52 (dt, $J = 15.6, 6.0$ Hz, 1H, CH=), 4.71 (d, $J = 5.8$ Hz, 2H, CH₂).



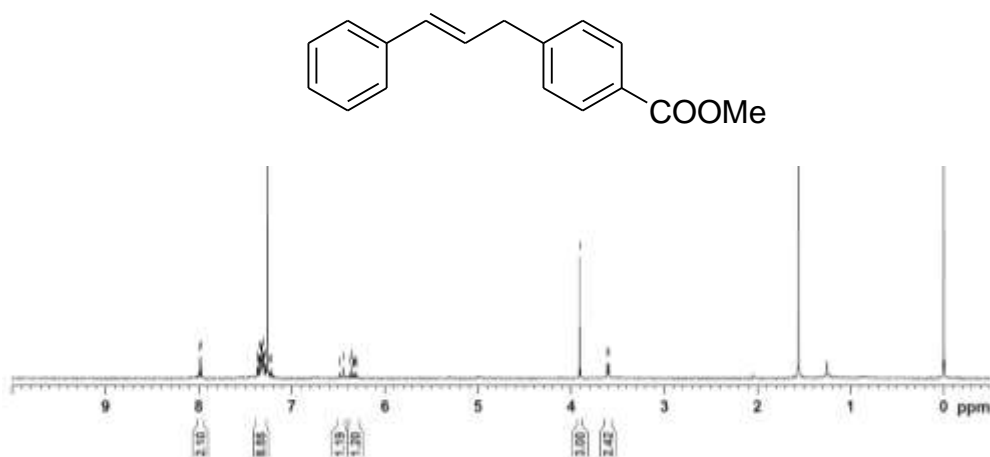
(1E)-3-(4-Formylphenyl)-1-phenylpropene (3f):⁴ Colorless oil, 0.199 g (90%); $R_f = 0.37$ (hexanes/EtOAc, 10/1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ 9.99 (s, 1H, CHO), 7.84 (d, $J = 8.0$ Hz, 2H, ArH), 7.29-7.43 (m, 7H, ArH), 6.49 (d, $J = 15.6$ Hz, 1H, CH=), 6.34 (dt, $J = 15.6, 6.8$ Hz, 1H, CH=), 3.64 (d, $J = 6.8$ Hz, 2H, CH₂).



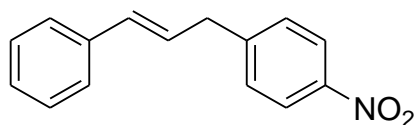
(1E)-3-(4-Carboxyphenyl)-1-phenylpropene (3g):⁵ Colorless oil, 0.205 g (86%); $R_f = 0.36$ (hexanes/EtOAc, 20/1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.09 (d, $J = 6.8$ Hz, 2H, ArH), 7.57 (t, $J = 7.6$ Hz, 1H, ArH), 7.26-7.48 (m, 6H, ArH), 6.75 (d, $J = 16.0$ Hz, 1H, CH=), 6.42 (dt, $J = 16.0, 6.4$ Hz, 1H, CH=), 4.99 (d, $J = 6.4$ Hz, 2H, CH₂).

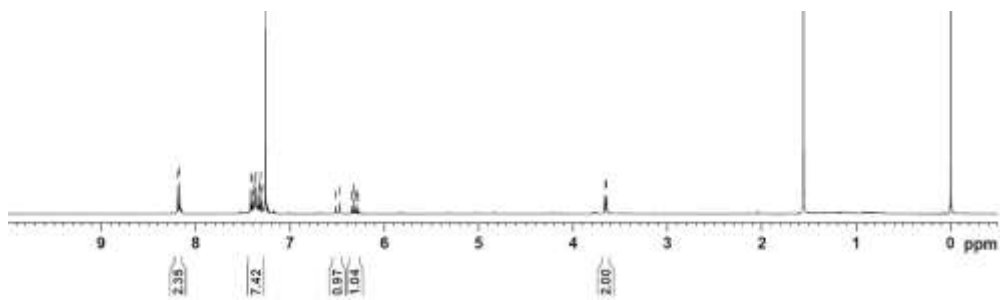


(1E)-3-(4-Methoxycarbonylphenyl)-1-phenylpropene (3h):⁶ Colorless oil, 0.216 g (86%); $R_f = 0.38$ (hexanes/EtOAc, 20/1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3 , TMS): δ 7.98 (d, $J = 8.4$ Hz, 2H, ArH), 7.21-7.37 (m, 7H, ArH), 6.47 (d, $J = 15.6$ Hz, 1H, CH=), 6.33 (dt, $J = 16.0, 6.8$ Hz, 1H, CH=), 3.91 (s, 3H, COOCH_3), 3.60 (d, $J = 6.8$ Hz, 2H, CH_2).



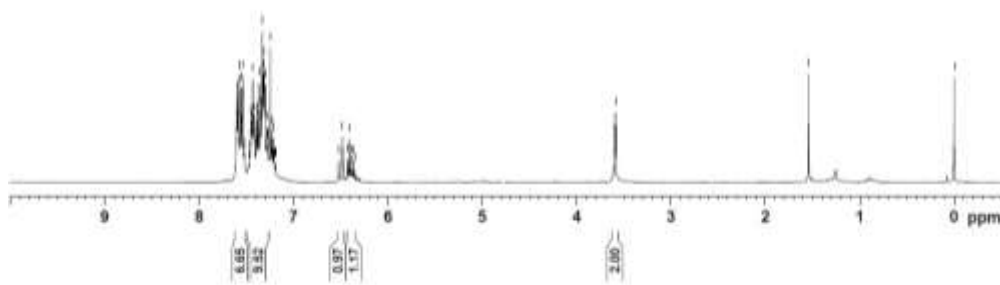
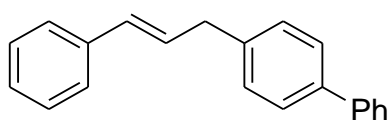
(1E)-3-(4-Nitrophenyl)-1-phenylpropene (3i):⁷ Colorless oil, 0.201 g (84%); $R_f = 0.40$ (hexanes/EtOAc, 20/1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3 , TMS): δ 8.18 (d, $J = 8.8$ Hz, 2H, ArH), 7.30-7.42 (m, 7H, ArH), 6.49 (d, $J = 15.6$ Hz, 1H, CH=), 6.31 (dt, 15.6, 6.8 Hz, 1H, CH=), 3.65 (d, $J = 6.4$ Hz, 2H, CH_2).





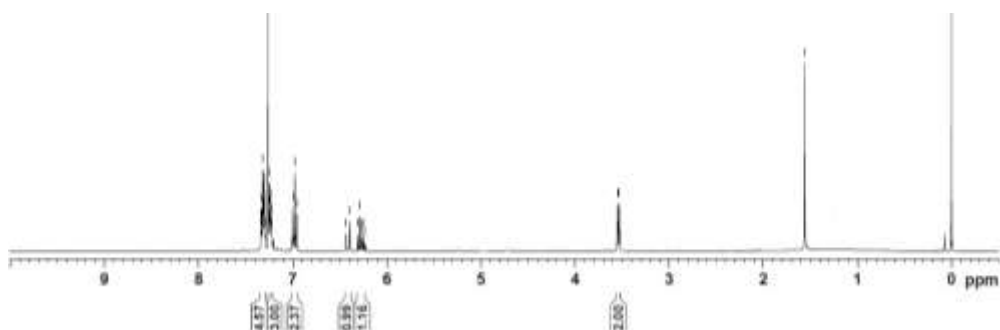
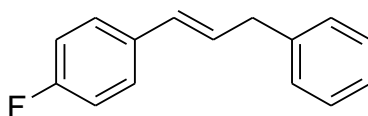
(1E)-3-Biphenyl-1-phenylpropene (3j):⁸ Colorless oil, 0.256 g (95%); $R_f = 0.75$ (hexanes/EtOAc, 20/1, v/v);

¹H NMR (400 MHz, CDCl₃, TMS): δ 7.19-7.61 (m, 14H, ArH), 6.50 (d, $J = 16.0$ Hz, 1H, CH=), 6.39 (dt, $J = 16.0$, 6.4 Hz, 1H, CH=), 3.59 (d, $J = 6.8$ Hz, 2H, CH₂).

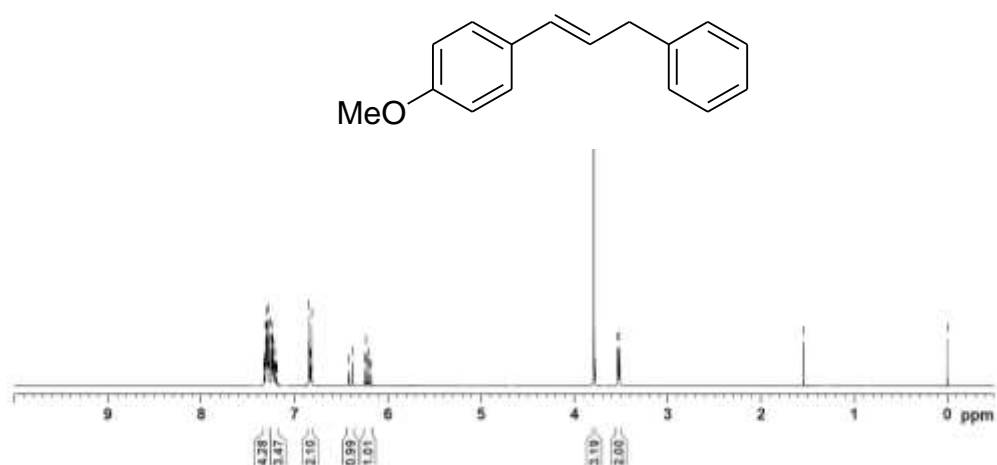


(1E)-1-(4-Fluorophenyl)-3-phenylpropene (3k):² Colorless oil, 0.197 g (93%); $R_f = 0.74$ (hexanes/EtOAc,

4/1, v/v); ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.29-7.34 (m, 4H, ArH), 7.23-7.25 (m, 3H, ArH), 6.98 (t, $J = 8.8$ Hz, 2H, ArH), 6.41 (d, $J = 16.0$ Hz, 1H, CH=), 6.27 (dt, $J = 15.6$, 6.8 Hz, 1H, CH=), 3.54 (d, $J = 6.4$ Hz, 2H, CH₂).



(1E)-1-(4-Methoxyphenyl)-3-phenylpropene (3I):² White solid, 0.206 g (92%), mp. 29-30 °C; $R_f = 0.40$ (hexanes/EtOAc, 20/1, v/v), $^1\text{H NMR}$ (400 MHz, CDCl_3 , TMS): δ 7.19-7.33 (m, 7H, ArH), 6.83 (d, $J = 8.8$ Hz, 2H, ArH), 6.40 (d, $J = 15.6$ Hz, 1H, CH=), 6.21 (dt, $J = 15.6, 6.8$ Hz, 1H, CH=), 3.79 (s, 3H, OCH_3), 3.53 (d, $J = 6.8$ Hz, 2H, CH_2).



References

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