Supporting Information

Copper-Catalyzed Oxidative Alkenylation of C (sp^3)–H Bonds via Benzyl Radical Addition to β-Nitrostyrenes

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1. General information:
Column chromatography was generally performed on silica gel (100-200 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light (254 nm) to visualize the course of the reactions. The $^1$H (300 MHz) and $^{13}$C NMR (75 MHz) data were recorded on Bruker AV300 spectrometers using CDCl$_3$ as solvent. The chemical shifts ($\delta$) are reported in ppm and coupling constants ($J$) in Hz. $^1$H NMR spectra was recorded with tetramethylsilane ($\delta = 0.00$ ppm) as internal reference; $^{13}$C NMR spectra was recorded with CDCl$_3$ ($\delta = 77.500$ ppm) as internal reference.

2. Typical Experimental Procedure:
General procedure for the benzylarylation of $\beta$-nitrostyrenes with benzylic hydrocarbons: An oven-dried Schlenk tube (10 mL) was charged with $\beta$-nitrostyrenes (0.5 mmol, 1.0 equiv) and Cu (1.0 mol %). The tube was evacuated and backfilled with argon (three times). DTBP (1 mmol, 2.0 equiv) and the benzylic hydrocarbon (3.0 mL) were added by syringe. The tube was then sealed and the mixture was stirred for 8-12h at 110 $^\circ$C. Upon completion of the reaction, the mixture was diluted with EtOAc. The solvent was then removed under vacuum. The residue was purified with column chromatography on silica gel (eluent gradient of EtOAc/hexane, 1:40 to 1:5) to give the corresponding products 3 in the yields listed in Tables 2, 3, 4.

3. Study of possible mechanism
In order to explore the possible mechanism of the present transformation,

1. To investigate the details of the mechanism for this new reaction, we performed some additional experiments. Firstly, Radical scavengers such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and BHT (2,4-di-tert-butyl-4-methylphenol) completely inhibit the model reaction which indicate that the transformation may proceed via a radical course.

2. In the absence of toluene, only denitro-methylation product was obtained and the self-coupling of $\beta$-nitrostyrenes was not observed, which can suggest that styrene radical is not formed in the reaction system.
3. Competing Kinetic Isotope Effect (KIE) Experiment: an intermolecular competing kinetic isotope effect (KIE) experiment was carried out.
The mixture of 3ab and 3ab’

Note: The value of $k_H/k_D$ was calculated from the $^1$H NMR spectra above which should be the mixture of compound 3ab and 3ab’ (the KIE scheme). The sum of the integral of 3ab and 3ab’ at chemical shift 6.42-6.47 was integrated as 1.00 (both 3ab and 3ab’ keep the same double bond hydrogen). Compound 3ab has 2 hydrogen atoms at chemical shift 3.56-3.54, while 3ab’ has no H atoms. The amount of 3ab could be defined as 0.85 ($1.70/2=0.85$), on the other hand, the sum of 3ab and 3ab’ is 1.00, so the amount of 3ab’ is 0.07 (1.00-0.85=0.15). As a result, $k_H/k_D = 0.85/0.15 = 5.6$. 
(B) Spectra Analytical data for products

(E)-1-1, 3-diphenylpropene (3aa): Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.39 – 7.18 (m, 10H), 6.47 (d, $J = 15.9$ Hz, 1H), 6.37 (dt, $J = 15.7, 6.4$ Hz, 1H), 3.56 (d, $J = 6.3$ Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 140.23, 137.56, 131.14, 129.28, 128.71, 128.53, 127.14, 126.22, 126.17, 39.39. HRMS (TOF, EI$^+$) m/z calcd for C$_{15}$H$_{14}$ 194.1096 found 194.1094.

(E)-1-(4-Methyl)-3-phenylpropene (3ab): Colorless liquid. $^1$H NMR (300 MHz, DMSO) $\delta$ 7.37 – 7.22 (m, 7H), 7.11 (d, $J = 8.0$ Hz, 2H), 6.45 (d, $J = 15.9$ Hz, 1H), 6.34 (t, $J = 6.6$ Hz, 1H), 3.55 (d, $J = 6.5$ Hz, 2H), 2.34 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 140.40, 136.87, 134.78, 131.00, 129.23, 128.70, 128.50, 128.23, 126.16, 126.07, 39.38, 21.17. HRMS (TOF, EI$^+$) m/z calcd for C$_{16}$H$_{16}$ 208.1252 found 208.1248.

(E)-1-(4-Methoxyphenyl)-3-phenylpropene (3ac): Colorless liquid. $^1$H NMR (300 MHz, DMSO) $\delta$ 7.36 – 7.21 (m, 7H), 6.85 (d, $J = 8.7$ Hz, 2H), 6.42 (d, $J = 15.8$ Hz, 1H), 6.23 (dt, $J = 15.7, 6.8$ Hz, 1H), 3.81 (s, 3H), 3.54 (d, $J = 6.7$ Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 158.94, 140.52, 130.52, 128.69, 128.50, 127.28, 127.13, 126.92, 126.15, 113.98, 55.33, 39.38. HRMS (TOF, EI$^+$) m/z calcd for C$_{16}$H$_{16}$O 224.1201 found 224.1198.

(E)-1-(4-Methylthiophenyl)-3-phenylpropene (3ad): Colorless liquid. $^1$H NMR (300 MHz, DMSO) $\delta$ 7.35 – 7.16 (m, 9H), 6.50 – 6.25 (m, 2H), 3.54 (d, $J = 6.2$ Hz, 2H), 2.48 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 140.19, 137.09, 134.69, 130.48, 128.86, 128.69, 128.53, 126.97, 126.59, 126.22, 39.38, 16.10. HRMS (TOF, EI$^+$) m/z calcd for C$_{16}$H$_{18}$S 240.0973 found 240.0970.

(E)-1-(3,4-Dimethylphenyl)-3-phenylpropene (3ae): Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.35 – 7.19 (m, 6H), 7.17 – 7.03 (m, 3H), 6.42 (d, $J = 15.9$ Hz, 1H), 6.30 (dt, $J = 15.7, 6.5$ Hz, 1H), 3.54 (d, $J = 6.4$ Hz, 2H), 2.24 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 140.48, 136.57, 135.56, 135.23, 131.08, 129.82, 128.70, 128.48, 128.06, 127.45, 126.14, 123.65, 39.39, 19.76, 19.46. HRMS (TOF, EI$^+$) m/z calcd for C$_{17}$H$_{18}$ 222.1409 found 222.1405.
(E)-1-(3,4-Dimethoxyphenyl)-3-phenylpropene (3af): 1 Colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.37 – 7.17 (m, 5H), 6.95 – 6.87 (m, 2H), 6.82 (dd, J = 10.1, 6.3 Hz, 2H), 6.40 (d, J = 15.7 Hz, 1H), 6.23 (dt, J = 15.7, 6.8 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.54 (d, J = 6.7 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 149.12, 148.57, 140.42, 133.00, 130.74, 128.73, 128.52, 127.43, 126.20, 119.20, 111.30, 108.79, 56.00, 55.87, 39.36. HRMS (TOF, EI⁺) m/z calcd for C₁₇H₁₉O₂ 254.1307 found 254.1304.

(E)-1-(1-Naphthyl)-3-phenylpropene (3ag): 2 Colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ 8.21 – 8.09 (m, 1H), 7.94 – 7.82 (m, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 7.1 Hz, 2H), 7.57 – 7.49 (m, 1H), 7.48 – 7.41 (m, 2H), 7.41 – 7.31 (m, 2H), 7.30 – 7.17 (m, 1H), 6.42 (dt, J = 15.4, 6.9 Hz, 1H), 3.71 (dd, J = 6.9, 1.2 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 140.23, 135.36, 133.71, 132.52, 131.25, 128.77, 128.61, 128.55, 128.44, 127.58, 126.29, 125.95, 125.73, 125.69, 123.94, 123.78, 39.79. HRMS (TOF, EI⁺) m/z calcd for C₁₉H₁₆ 244.1252 found 244.1250.

(E)-1-(4-Chlorophenyl)-3-phenylpropene (3ah): 1 Colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.33 (dd, J = 8.8, 5.7 Hz, 2H), 7.29 – 7.20 (m, 7H), 6.45 – 6.29 (m, 2H), 3.55 (d, J = 6.5 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 139.92, 136.06, 132.73, 130.09, 129.91, 128.71, 128.68, 128.59, 127.38, 126.33, 39.35. HRMS (TOF, EI⁺) m/z calcd for C₁₅H₁₃Cl 228.0706 found 228.0708.

(E)-1-(4-Fluorophenyl)-3-phenylpropene (3ai): 1 Colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.38 – 7.19 (m, 7H), 7.03 – 6.93 (m, 2H), 6.42 (d, J = 15.8 Hz, 1H), 6.28 (dt, J = 15.8, 6.7 Hz, 1H), 3.55 (d, J = 6.5 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 162.11 (d, J = 246.0 Hz), 140.11, 133.71 (d, J = 3.4 Hz), 129.92 (d, J = 0.6 Hz), 129.08 (d, J = 2.2 Hz), 128.68, 128.56, 127.59 (d, J = 7.9 Hz), 126.27, 115.38 (d, J = 21.5 Hz), 39.32. HRMS (TOF, EI⁺) m/z calcd for C₁₅H₁₃F 212.1002 found 212.1005.

(E)-1-(4-trifluoromethylphenyl)-3-phenylpropene (3aj): 1 Colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.55 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 7.38 – 7.30 (m, 2H), 7.28 – 7.21 (m,
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.34-7.19 (m, 5H), 7.10 (d, $J = 5.0$ Hz, 1H), 6.93 (dt, $J = 9.4$, 3.2 Hz, 2H), 6.56 (d, $J = 15.6$ Hz, 1H), 6.21 (dt, $J = 15.6$, 6.9 Hz, 1H), 3.52 (d, $J = 6.9$ Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 142.70, 139.87, 129.20, 128.74, 128.56, 127.26, 126.29, 124.77, 124.33, 123.52, 39.14. HRMS (TOF, EI$^+$) m/z calcd for C$_{13}$H$_{12}$S 200.0660 found 200.0656.

(E)-1-(3-methylphenyl)-3-phenylpropene (3am): Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.37–7.22 (m, 6H), 7.22–7.13 (m, 3H), 7.04 (d, $J = 4.6$ Hz, 1H), 6.45 (d, $J = 16.0$ Hz, 1H), 6.41–6.28 (m, 1H), 3.56 (d, $J = 6.1$ Hz, 2H), 2.34 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 140.30, 139.87, 129.20, 128.74, 128.56, 127.26, 126.29, 124.77, 124.33, 123.34, 39.40, 21.41. HRMS (TOF, EI$^+$) m/z calcd for C$_{16}$H$_{16}$ 208.1252 found 208.1255.

(E)-1-(3-bromophenyl)-3-phenylpropene (3an): Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.51 (t, $J = 1.7$ Hz, 1H), 7.35–7.31 (m, 3H), 7.28–7.23 (m, 4H), 7.16 (t, $J = 7.8$ Hz, 1H), 6.38 (t, $J = 3.7$ Hz, 2H), 3.56 (d, $J = 3.4$ Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 139.76, 139.74, 131.05, 130.03, 130.00, 129.72, 129.08, 128.72, 128.61, 126.37, 124.83, 122.78, 39.32. HRMS (TOF, EI$^+$) m/z calcd for C$_{15}$H$_{13}$Br 272.0201 found 272.0197.

(E)-1-(2-chlorophenyl)-3-phenylpropene (3ao): Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.51 (dd, $J = 7.4$, 2.1 Hz, 1H), 7.37–7.21 (m, 6H), 7.17 (td, $J = 6.9$, 1.7 Hz, 2H), 6.88 (d, $J = 15.7$ Hz, 1H), 6.51–6.45 (m, 2H), 3.59 (d, $J = 2.9$ Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 141.02 (q, $J = 0.8$Hz), 139.58, 132.18, 129.87, 128.73, 128.64, 126.43, 126.30, 125.50 (q, $J = 3.8$Hz), 122.51, 118.91, 39.38. HRMS (TOF, EI$^+$) m/z calcd for C$_{16}$H$_{13}$F$_3$ 262.0969 found 262.0964.
(E)-1-(2-methylphenyl)-3-phenylpropene (3ap): Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.46 – 7.41 (m, 1H), 7.37 – 7.20 (m, 5H), 7.14 (d, $J = 2.6$ Hz, 3H), 6.68 (d, $J = 15.6$ Hz, 1H), 6.25 (dt, $J = 15.6$, 7.0 Hz, 1H), 3.59 (d, $J = 6.6$ Hz, 2H), 2.36 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 140.37, 136.70, 135.14, 130.57, 130.22, 129.11, 128.67, 128.53, 127.09, 126.19, 126.07, 125.67, 39.69, 19.85. HRMS (TOF, EI$^+$) m/z calcd for C$_{16}$H$_{16}$ 208.1252 found 208.1255.

(E)-1-(phenyl)-3-(4-methylphenyl)-propene (4ba): Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.39 – 7.25 (m, 4H), 7.21 (dt, $J = 4.8$, 1.9 Hz, 1H), 7.14 (s, 4H), 6.46 (d, $J = 15.9$ Hz, 1H), 6.35 (dt, $J = 15.7$, 6.4 Hz, 1H), 3.52 (d, $J = 6.3$ Hz, 2H), 2.34 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 137.63, 137.13, 135.71, 130.91, 129.59, 129.21, 128.59, 128.52, 127.07, 126.16, 38.96, 21.04. HRMS (TOF, EI$^+$) m/z calcd for C$_{16}$H$_{16}$ 208.1252 found 208.1248.

(E)-1-(4-methylphenyl)-3-(4-methylphenyl)-propene (3bb): Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.26 (d, $J = 8.0$ Hz, 2H), 7.17 – 7.07 (m, 6H), 6.43 (d, $J = 15.9$ Hz, 1H), 6.29 (dt, $J = 15.8$, 6.6 Hz, 1H), 3.51 (d, $J = 6.5$ Hz, 2H), 2.34 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 137.31, 136.79, 135.64, 134.86, 130.77, 129.21, 129.19, 128.58, 128.53, 126.06, 38.96, 21.16, 21.04. HRMS (TOF, EI$^+$) m/z calcd for C$_{17}$H$_{18}$ 222.1409 found 222.1412.

(E)-1-(4-trifloromethylphenyl)-3-(4-methylphenyl)-propene (3bc): Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.54 (d, $J = 8.1$ Hz, 1H), 7.44 (d, $J = 8.4$ Hz, 1H), 7.14 (s, 2H), 6.46 (t, $J = 3.7$ Hz, 1H), 3.54 (d, $J = 3.7$ Hz, 1H), 2.35 (s, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 141.08, 136.48, 135.97, 132.49, 129.63, 129.32, 128.61, 126.27, 125.48 (q, $J = 3.8$ Hz, CF$_3$), 122.51, 38.96, 21.04. HRMS (TOF, EI$^+$) m/z calcd for C$_{17}$H$_{15}$F$_3$ 276.1126 found 276.1122.

(E)-1-(thiopheneyl)-3-(4-methylphenyl)-propene (3bd): Colorless liquid. $^1$H NMR (300 MHz,
CDCl$_3$ δ 7.17 – 7.10 (m, 5H), 6.94 (dt, $J = 10.1$, 3.3 Hz, 2H), 6.57 (ddd, $J = 15.6$, 1.3, 0.7 Hz, 1H), 6.22 (dt, $J = 15.6$, 6.9 Hz, 1H), 3.49 (dd, $J = 6.9$, 1.2 Hz, 2H), 2.36 (s, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 142.81, 136.78, 135.80, 129.54, 129.26, 128.64, 127.25, 124.70, 124.12, 123.47, 38.74, 21.06. HRMS (TOF, EI$^+$) m/z calcd for C$_{14}$H$_{14}$S 214.0816 found 214.0812.

$^E$-1-(2-methylphenyl)-3-(4-methylphenyl)-propene (3be): Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.55 – 7.40 (m, 1H), 7.24 – 7.05 (m, 7H), 6.68 (d, $J = 15.6$ Hz, 1H), 6.35 – 6.10 (m, 1H), 3.56 (d, $J = 6.9$ Hz, 2H), 2.37 (s, 3H), 2.36 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 137.29, 136.78, 135.68, 135.13, 130.88, 130.22, 129.22, 128.89, 128.55, 127.04, 126.06, 125.69, 39.29, 21.06, 19.87. HRMS (TOF, EI$^+$) m/z calcd for C$_{17}$H$_{18}$ 222.1409 found 222.1407.

$^E$-1-(phenyl)-3-(3-methylphenyl)-propene (3bf): Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.39 (dd, $J = 5.3$, 3.3 Hz, 2H), 7.36 – 7.28 (m, 2H), 7.29 – 7.18 (m, 5H), 7.11 – 7.01 (m, 3H), 6.47 – 6.27 (m, 2H), 2.35 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 158.93, 140.46, 138.10, 130.48, 130.39, 129.46, 128.40, 127.28, 126.90, 125.71, 114.01, 55.34, 39.34, 21.43. HRMS (TOF, EI$^+$) m/z calcd for C$_{17}$H$_{18}$O 238.1358 found 238.1361.

$^E$-1-(4-methoxyphenyl)-3-(3-methylphenyl)-propene (3bg): Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.36 – 7.28 (m, 2H), 7.21 (t, $J = 7.5$ Hz, 1H), 7.07-7.04 (m, 3H), 6.88 – 6.81 (m, 2H), 6.42 (d, $J = 15.7$ Hz, 1H), 6.22 (dt, $J = 15.7$, 6.9 Hz, 1H), 3.81 (s, 3H), 3.51 (d, $J = 6.7$ Hz, 2H), 2.35 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 158.93, 140.46, 138.10, 130.48, 130.39, 129.46, 128.40, 127.28, 126.90, 125.71, 114.01, 55.34, 39.34, 21.43. HRMS (TOF, EI$^+$) m/z calcd for C$_{17}$H$_{18}$O 238.1358 found 238.1361.

$^E$-1-(4-chlorophenyl)-3-(3-methylphenyl)-propene (3bh): Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.35 – 7.18 (m, 5H), 7.11 – 7.01 (m, 3H), 6.47 – 6.27 (m, 2H), 2.36 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 139.86, 138.10, 130.24, 129.48, 129.46, 128.40, 127.28, 126.90, 125.71, 114.01, 55.34, 39.34, 21.43. HRMS (TOF, EI$^+$) m/z calcd for C$_{16}$H$_{15}$Cl 242.0862 found 242.0863.
(E)-1-(2-Furyl)-3-(3-methylphenyl)-propene (3bi): Colorless liquid. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.31 (d, \(J = 1.4\) Hz, 1H), 7.24 – 7.16 (m, 1H), 7.10 – 7.00 (m, 3H), 6.37 – 6.19 (m, 3H), 6.16 (d, \(J = 3.2\) Hz, 1H), 3.48 (d, \(J = 6.2\) Hz, 2H), 2.34 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 153.12, 141.45, 139.84, 138.14, 129.49, 128.48, 128.42, 126.98, 125.74, 119.61, 111.13, 106.58, 39.04, 21.40. HRMS (TOF, EI\(^+\)) \(m/z\) calcd for C\(_{14}\)H\(_{14}\)O 198.1045 found 198.1048.

(\(E\))-1-(1-Naphthyl)-3-(3-methylphenyl)-propene (3bj): Colorless liquid. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.16 – 8.10 (m, 1H), 7.85 (dd, \(J = 6.8, 2.8\) Hz, 1H), 7.76 (d, \(J = 8.2\) Hz, 1H), 7.59 (d, \(J = 7.0\) Hz, 1H), 7.48 (dd, \(J = 23.0, 11.1, 6.3\) Hz, 3H), 7.31 – 7.02 (m, 5H), 6.39 (dt, \(J = 15.4, 7.0\) Hz, 1H), 3.65 (d, \(J = 6.8\) Hz, 2H), 2.36 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 140.14, 138.18, 135.36, 133.69, 132.61, 131.23, 129.51, 128.52, 128.48, 128.26, 127.52, 126.99, 125.90, 125.74, 125.69, 125.66, 123.93, 123.74, 39.72, 21.44. HRMS (TOF, EI\(^+\)) \(m/z\) calcd for C\(_{20}\)H\(_{18}\) 258.1409 found 258.1412.

(\(E\))-1-(phenyl)-3-(2-methylphenyl)-propene (3bk): Colorless liquid. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.39 – 7.26 (m, 4H), 7.25 – 7.15 (m, 5H), 6.45 – 6.29 (m, 2H), 3.55 (d, \(J = 4.9\) Hz, 2H), 2.36 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 138.30, 137.64, 136.45, 130.98, 130.28, 129.28, 128.63, 128.53, 127.09, 126.46, 126.15, 126.13, 36.91, 19.47. HRMS (TOF, EI\(^+\)) \(m/z\) calcd for C\(_{16}\)H\(_{16}\) 208.1252 found 208.1255.

(\(E\))-1-(1-Naphthyl)-3-(2-methylphenyl)-propene (3bl): Colorless liquid. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.11 – 8.02 (m, 1H), 7.88 – 7.80 (m, 1H), 7.75 (d, \(J = 8.1\) Hz, 1H), 7.58 (d, \(J = 7.1\) Hz, 1H), 7.54 – 7.39 (m, 3H), 7.32 – 7.07 (m, 5H), 6.37 (dt, \(J = 15.5, 6.6\) Hz, 1H), 3.67 (dd, \(J = 6.5, 1.4\) Hz, 2H), 2.41 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 138.30, 136.46, 135.45, 133.68, 131.86, 131.21, 130.33, 129.29, 128.51, 128.30, 127.50, 126.51, 126.21, 125.91, 125.69, 125.66, 123.88, 123.70, 37.35, 19.52. HRMS (TOF, EI\(^+\)) \(m/z\) calcd for C\(_{20}\)H\(_{18}\) 258.1409 found 258.1410.

(\(E\))-1-(4-trifloromethylphenyl)-3-(2-methylphenyl)-propene (3bm): Colorless liquid. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.50 (dd, \(J = 7.5, 1.9\) Hz, 1H), 7.34 (dd, \(J = 7.6, 1.6\) Hz, 1H), 7.32 – 7.14 (m,
6H), 6.81 (d, J = 15.8 Hz, 1H), 6.32 – 6.25 (m, 1H), 3.59 (dd, J = 6.7, 1.4 Hz, 2H), 2.37 (s, 3H); 
\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) δ 141.06, (q, J = 6.06 Hz, 141.09, 141.07, 141.05, 141.03), 137.67, 
136.43, 131.54, 130.38, 130.24, 129.69, 129.33, 128.83 (dd, J = 31.0, 18.5 Hz, 129.17, 128.91, 
128.74, 128.51), 126.67, 126.24, 126.14, 125.47 (q, J = 3.8 Hz, 125.55, 125.50, 125.45, 125.40), 
36.90, 19.44. \(\text{HRMS (TOF, E}^+\) m/z calcd for C\(_{17}\)H\(_{15}\)F\(_2\) 276.1126 found 276.1128.

\(\text{C}_{3}H_{3}C_{3}H_{3}\) 
\(\text{(E)}\)-1-(2-methylphenyl)-3-(2-methylphenyl)-propene (3bn): \(^9\) Colorless liquid. \(^1\)H NMR (300 
MHz, CDCl\(_3\)) δ 7.47 – 7.38 (m, 2H), 7.25 – 7.20 (m, 1H), 7.16 – 7.10 (m, 3H), 6.61 (d, J = 15.7 Hz, 1H), 6.21 (dt, J = 15.6, 6.6 Hz, 1H), 3.57 (dd, J = 6.6, 1.5 Hz, 2H), 2.34 
(d, J = 13.9 Hz, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) δ 138.43, 136.81, 136.40, 135.07, 130.25, 
130.19, 129.94, 129.16, 129.02, 127.04, 126.42, 126.14, 126.05, 125.65, 37.24, 19.80, 19.45. 
\(\text{HRMS (TOF, E}^+\) m/z calcd for C\(_{17}\)H\(_{18}\) 222.1409 found 222.1411.

\(\text{C}_{3}H_{3}C_{3}H_{3}\) 
\(\text{(E)}\)-1-(phenyl)-3-(3,5-dimethylphenyl)-propene (3ca): \(^6\) Colorless liquid. \(^1\)H NMR (300 MHz, 
CDCl\(_3\)) δ 7.39 (dd, J = 5.3, 3.3 Hz, 2H), 7.35 – 7.28 (m, 2H), 7.25 – 7.20 (m, 1H), 6.88 (s, 3H), 
6.48 (d, J = 15.8 Hz, 1H), 6.37 (dd, J = 14.4, 7.8 Hz, 1H), 3.50 (d, J = 6.5 Hz, 2H), 2.32 (s, 3H), 
2.31 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) δ 140.13, 138.06, 137.66, 130.90, 129.55, 128.53, 127.86, 
127.08, 126.52, 126.19, 39.31, 21.30. \(\text{HRMS (TOF, E}^+\) m/z calcd for C\(_{17}\)H\(_{18}\) 222.1409 found 222.1413.

\(\text{C}_{3}H_{3}C_{3}H_{3}\) 
\(\text{(E)}\)-1-(4-methylphenyl)-3-(3,5-dimethylphenyl)-propene (3cb): Colorless oil, \(^1\)H NMR (300 
MHz, CDCl\(_3\)) δ 7.33 – 7.26 (m, 3H), 7.12 (d, J = 7.9 Hz, 3H), 6.88 (s, 3H), 6.45 (d, J = 15.8 Hz, 
1H), 6.30 (dt, J = 15.7, 6.8 Hz, 1H), 3.48 (d, J = 6.7 Hz, 2H), 2.34 (s, 3H), 2.31 (s, 6H); \(^{13}\)C NMR (75 
MHz, CDCl\(_3\)) δ 140.31, 138.02, 136.81, 134.88, 130.75, 129.23, 128.50, 127.81, 126.51, 
126.09, 39.30, 21.29, 21.17. \(\text{HRMS (TOF, E}^+\) m/z calcd for C\(_{18}\)H\(_{20}\) 236.1565 found 236.1568.

\(\text{C}_{3}H_{3}C_{3}H_{3}\) 
\(\text{(E)}\)-1-(2-methylphenyl)-3-(3,5-dimethylphenyl)-propene (3cc): Colorless oil, \(^1\)H NMR (300 
MHz, CDCl\(_3\)) δ 7.47 – 7.44 (m, 1H), 7.18 – 7.15 (m, 3H), 6.89 (s, 3H), 6.69 (d, J = 15.6 Hz, 1H), 
6.24 (dt, J = 15.5, 7.0 Hz, 1H), 3.53 (d, J = 6.9 Hz, 2H), 2.38 (s, 3H), 2.32 (s, 6H); \(^{13}\)C NMR (75 
MHz, CDCl\(_3\)) δ 140.27, 138.04, 136.75, 135.13, 130.79, 130.23, 128.82, 127.82, 127.04, 126.47, 
126.06, 125.65, 39.60, 21.30, 19.88. \(\text{HRMS (TOF, E}^+\) m/z calcd for C\(_{18}\)H\(_{20}\) 236.1565 found
(E)-1-(3,4-dimethylphenyl)-3-(3,5-dimethylphenyl)-propene (3cd): Colorless oil, \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.17 – 7.01 (m, 4H), 6.87 (s, 2H), 6.42 (d, \(J = 15.8\) Hz, 1H), 6.29 (dt, \(J = 15.7, 6.7\) Hz, 1H), 3.47 (d, \(J = 6.6\) Hz, 2H), 2.31 (s, 6H), 2.25 (s, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 140.37, 138.00, 136.56, 135.50, 135.31, 130.82, 129.81, 128.32, 127.78, 127.46, 126.50, 123.65, 39.30, 21.29, 19.77, 19.47. HRMS (TOF, EI\(^+\)) \(m/z\) calcd for C\(_{19}\)H\(_{22}\) 250.1722 found 250.1718.

(E)-1-(4-methylphenyl)-3-phenylbutene (3da): \(^{10}\) Colorless oil, \(^1\)H NMR (300 MHz, DMSO) \(\delta\) 7.35 – 7.19 (m, 7H), 7.10 (d, \(J = 8.0\) Hz, 2H), 6.44 – 6.28 (m, 2H), 3.69 – 3.58 (m, 1H), 2.33 (s, 3H), 1.47 (d, \(J = 7.0\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 145.87, 136.80, 134.87, 134.29, 129.22, 128.50, 128.43, 127.35, 126.19, 126.09, 42.59, 21.32, 21.16. HRMS (TOF, EI\(^+\)) \(m/z\) calcd for C\(_{17}\)H\(_{18}\) 222.1409 found 222.1408.

(E)-1-(4-trifluoromethylphenyl)-3-phenylbutene (3db): \(^{11}\) Colorless oil, \(^1\)H NMR (300 MHz, DMSO) \(\delta\) 7.54 (d, \(J = 8.3\) Hz, 2H), 7.44 (d, \(J = 8.3\) Hz, 2H), 7.28 (qt, \(J = 7.0, 5.9\) Hz, 5H), 6.56 – 6.39 (m, 2H), 3.73 – 3.62 (m, 1H), 1.49 (d, \(J = 7.0\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 145.08, 141.15 (d, \(J = 1.4\) Hz), 138.09, 128.64, 128.47 (d, \(J = 2.4\) Hz), 127.43, 127.33, 126.47, 126.33, 126.13 (d, \(J = 2.5\) Hz), 125.47 (q, \(J = 3.9\) Hz), 42.68, 21.06. HRMS (TOF, EI\(^+\)) \(m/z\) calcd for C\(_{17}\)H\(_{15}\)F\(_3\) 276.1126 found 276.1123.

(E)-1-(3,4-dimethylphenyl)-3-phenylbutene (3dc): Colorless oil, \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.37 – 7.03 (m, 8H), 6.43 – 6.28 (m, 2H), 3.69 – 3.58 (m, 1H), 2.24 (s, 6H), 1.47 (d, \(J = 7.0\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 145.93, 136.56, 135.49, 135.31, 134.13, 129.80, 128.50, 128.48, 127.44, 127.36, 126.17, 123.68, 42.58, 21.32, 19.76, 19.46. HRMS (TOF, EI\(^+\)) \(m/z\) calcd for C\(_{18}\)H\(_{20}\) 236.1565 found 236.1568.

(E)-(2-cyclopentylvinyl)benzene (3ea): \(^{3}\) Colorless oil, \(^1\)H NMR (300 MHz, DMSO) \(\delta\) 7.38 –
7.26 (m, 4H), 7.18 (t, J = 7.1 Hz, 1H), 6.38 (d, J = 15.9 Hz, 1H), 6.21 (dd, J = 15.8, 7.6 Hz, 1H), 2.68 – 2.52 (m, 1H), 1.80 (dt, J = 10.6, 4.7 Hz, 2H), 1.77 – 1.57 (m, 4H), 1.40 (ddd, J = 15.6, 12.8, 7.0 Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 138.03, 135.75, 128.48, 127.91, 126.73, 125.97, 43.81, 33.25, 25.28. HRMS (TOF, EI$^+$) m/z calcd for C$_{13}$H$_{16}$ 172.1252 found 172.1254.

(E)-(2-cyclohexylvinyl)benzene(3eb): Colorless oil, $^1$H NMR (300 MHz, DMSO) $\delta$ 7.41 – 7.17 (m, 5H), 6.38 (d, J = 16.1 Hz, 1H), 6.21 (dd, J = 16.0, 6.8 Hz, 1H), 2.16 (tdd, J = 10.2, 6.9, 3.5 Hz, 1H), 1.88 – 1.68 (m, 4H), 1.44 – 1.14 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 138.18, 136.90, 128.50, 127.35, 126.77, 126.02, 41.21, 33.05, 26.27, 26.13. HRMS (TOF, EI$^+$) m/z calcd for C$_{14}$H$_{18}$ 186.1409 found 186.1412.

(E)-styrylcyclooctane (3ec): Colorless oil, $^1$H NMR (300 MHz, DMSO) $\delta$ 7.38 – 7.26 (m, 4H), 7.22 – 7.16 (m, 1H), 6.34 (d, J = 16.0 Hz, 1H), 6.22 (dd, J = 15.9, 7.1 Hz, 1H), 2.40 (s, 1H), 1.84 – 1.68 (m, 4H), 1.60-1.54 (m, 10H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 138.24, 137.90, 128.48, 126.91, 126.69, 125.99, 41.37, 31.96, 27.51, 26.10, 25.16. HRMS (TOF, EI$^+$) m/z calcd for C$_{16}$H$_{22}$ 214.1722 found 214.1723.

1-((E)-4-methylstyryl)bicyclo[2.2.1]heptane (3ed): Colorless oil, $^1$H NMR (300 MHz, DMSO) $\delta$ 7.23 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 6.27 (d, J = 15.9 Hz, 1H), 6.07 (dd, J = 15.8, 8.0 Hz, 1H), 2.32 (s, 3H), 2.28-2.24 (m, 2H), 2.13 (s, 1H), 1.63 – 1.12 (m, 8H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 136.38, 135.56, 135.30, 129.17, 127.16, 125.87, 45.45, 42.80, 38.02, 36.70, 35.86, 29.83, 29.09, 21.12. HRMS (TOF, EI$^+$) m/z calcd for C$_{16}$H$_{20}$ 212.1565 found 212.1564.

1-((E)-4-methylstyryl)adamantine (3ee): White solid, m.p. 116 °C, $^1$H NMR (300 MHz, DMSO) $\delta$ 7.27 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 6.22 (d, J = 16.3 Hz, 1H), 6.06 (d, J = 16.2 Hz, 1H), 2.33 (s, 1H), 2.03 (s, 3H), 1.81 – 1.64 (m,12H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 141.19, 136.37, 135.52, 129.18, 125.92, 124.40, 77.48, 77.06, 76.64, 42.39, 37.00, 35.14, 28.61, 21.14. HRMS (TOF, EI$^+$) m/z calcd for C$_{19}$H$_{24}$ 252.1878 found 252.1875.
(E)-2-4-chlorostyryl-tetrahydrofuran (3ef): Colorless oil, $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.33 – 7.24 (m, 4H), 6.54 (d, $J = 15.9$ Hz, 1H), 6.18 (dd, $J = 15.8$, 6.5 Hz, 1H), 4.46 (q, $J = 7.0$ Hz, 1H), 4.01 – 3.93 (m, 1H), 3.85 (dt, $J = 14.5$, 7.2 Hz, 1H), 2.19 – 2.07 (m, 1H), 2.04 – 1.91 (m, 2H), 1.70 (dd, $J = 15.5$, 11.8, 7.3 Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 135.48, 133.14, 131.35, 129.18, 128.70, 127.70, 79.49, 68.25, 32.40, 25.94. HRMS (TOF, EI$^+$) m/z calcd for C$_{12}$H$_{13}$ClO$_2$ 208.0655 found 208.0658.

(E)-2-(4-chlorostyryl)-1,4-dioxane (3eg): Colorless oil, $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.29 (s, 4H), 6.64 (dd, $J = 16.1$, 1.1 Hz, 1H), 6.06 (dd, $J = 16.1$, 6.1 Hz, 1H), 4.25 (t, $J = 7.4$ Hz, 1H), 3.93 – 3.59 (m, 5H), 3.41 (dd, $J = 11.5$, 10.1 Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 135.00, 133.64, 131.39, 128.80, 127.75, 125.90, 75.91, 70.92, 66.65, 66.36. HRMS (TOF, EI$^+$) m/z calcd for C$_{12}$H$_{13}$ClO$_2$ 224.0604 found 224.0608.

(E)-4-(4-methylphenyl)-but-3-en-2-ol (3eh): Colorless oil, $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.31 – 7.25 (m, 2H), 7.13 (d, $J = 7.9$ Hz, 2H), 6.54 (d, $J = 15.8$ Hz, 1H), 6.21 (dd, $J = 15.9$, 6.5 Hz, 1H), 4.54 – 4.42 (m, 1H), 2.34 (s, 3H), 1.60 (s, 1H), 1.37 (d, $J = 6.4$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 137.52, 133.97, 132.62, 129.43, 129.31, 126.41, 69.07, 23.47, 21.19. HRMS (TOF, EI$^+$) m/z calcd for C$_{11}$H$_{14}$O 162.1045 found 162.1041.

(E)-2-methyl-4-(4-methylphenyl)-but-3-en-2-ol (3ei): Colorless oil, $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.28 (d, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 7.9$ Hz, 2H), 6.56 (d, $J = 16.1$ Hz, 1H), 6.31 (d, $J = 16.1$ Hz, 1H), 2.34 (s, 3H), 1.58 (s, 1H), 1.43 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 137.26, 133.97, 132.62, 129.43, 129.31, 126.41, 69.07, 23.47, 21.19. HRMS (TOF, EI$^+$) m/z calcd for C$_{12}$H$_{16}$O 176.1201 found 176.1204.

References

(C) Original Spectra

(E)-1, 3-diphenylpropene (3aa):
(E)-1-(4-Methyl)-3-phenylpropene (3ab):
(E)-1-(4-Methoxyphenyl)-3-phenylpropene (3ac):
(E)-1-(4-methylthiophenyl)-3-phenylpropene (3ad):

\[ \text{H}_3\text{CS}^- \]

\[ \text{Ph} \]
(E)-1-(3,4-Dimethylphenyl)-3-phenylpropene (3ae):
(E)-1-(3,4-Dimethoxyphenyl)-3-phenylpropene (3af):
(E)-1-(1-Naphthyl)-3-phenylpropene (3ag):
(E)-1-(4-Chlorophenyl)-3-phenylpropene (3ah):
(E)-1-(4-Fluorophenyl)-3-phenylpropene (3ai):
(E)-1-(4-trifluoromethylphenyl)-3-phenylpropene(3aj):
(E)-1-(2-furyl)-3-phenyl propene(3ak):
(E)-1-(2-Thiophene)-3-phenylpropene (3a1):
(E)-1-(3-methylphenyl)-3-phenylpropene(3am):
(E)-1-(3-bromophenyl)-3-phenylpropene(3an):
(E)-1-(2-chlorophenyl)-3-phenylpropene(3ao):
(E)-1-(2-methylphenyl)-3-phenylpropene (3ap):
(E)-1-(phenyl)-3-(4-methylphenyl)-propene (4ba):
(E)-1-(4-methylphenyl)-3-(4-methylphenyl)-propene (3bb):
(E)-1-(4-trifloromethylphenyl)-3-(4-methylphenyl)-propene (3bc):
(E)-1-(thiophen-2-yl)-3-(4-methylphenyl)-propene (3bd):
(E)-1-(2-methylphenyl)-3-(4-methylphenyl)-propene (3be):
(E)-1-(phenyl)-3-(3-methylphenyl)-propene (3bf):
(E)-1-(4-methoxyphenyl)-3-(3-methylphenyl)-propene (3bg):
(E)-1-(4-chlorophenyl)-3-(3-methylphenyl)-propene (3bh):
(E)-1-(2-Furyl)-3-(3-methylphenyl)-propene (3bi):
(E)-1-(1-Naphthyl)-3-(3-methylphenyl)-propene (3bj):
(E)-1-(phenyl)-3-(2-methylphenyl)-propene (3bk):
(E)-1-(1-Naphthyl)-3-(2-methylphenyl)-propene (3bl):
(E)-1-(4-trifloromethylphenyl)-3-(2-methylphenyl)-propene (3bm):
(E)-1-(2-methylphenyl)-3-(2-methylphenyl)-propene (3bn):
(E)-1-(phenyl)-3-(3,5-dimethylphenyl)-propene (3ca):
(E)-1-(4-methylphenyl)-3-(3,5-dimethylphenyl)-propene (3cb):
(E)-1-(2-methylphenyl)-3-(3,5-dimethylphenyl)-propene (3cc):
\((E)-1-(3,4\text{-dimethylphenyl})-3-(3,5\text{-dimethylphenyl})\text{-propene (3cd):}\)
(E)-1-(4-methylphenyl)-3-phenylbutene (3da):
(E)-1-(4-trifloromethylphenyl)-3-phenylbutene (3db):

\[ (E)-1-(3,4\text{-dimethylphenyl})-3\text{-phenylbutene (3dc)}: \]
(E)-(2-cyclopentylvinyl)benzene (3a):
(E)-(2-cyclohexylvinyl)benzene (3eb):
(E)-styrylcyclooctane (3ee):
1-((E)-4-methylstyrlyl)bicyclo[2.2.1]heptane (3ed):
1-((E)-4-methylstyryl)adamantine (3ee):
(E)-2-4-chlorostyryl-tetrahydrofuran (3ef):
(E)-2-(4-chlorostyryl)-1,4-dioxane (3eg):
(E)-4-(4-methylphenyl)-but-3-en-2-ol (3eh):
(E)-2-methyl-4-(4-methylphenyl)-but-3-en-2-ol (3ei):