Supporting Information

Pd-catalyzed Synthesis of α,β-Unsaturated Ketones by Carbonylation of Vinyl Triflates and Nonaflates

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1. General comments

All reactions were carried out under an atmosphere of dry argon or nitrogen using standard Schlenk technique or 300 mL autoclave equipped with 10 mL vials. Solvents were dried and degassed and stored in ©Aldrich Sure/Stor flasks under argon. All of the ligands are commercial available or available in the ligand stock of our lab. Cyclohex-1-en-1-yl triflate was purchased from Aldrich and stored in the glovebox. The other triflates were synthesized during our last work for the formylation and alkoxy- and amino- carbonylation of vinyl triflates and stored in the fridge. TMEDA was purchased from ABCR and stored in a Schlenk. n-BuLi (2.5 M in hexane) was purchased from Aldrich and stored in a Schlenk in fridge. Benzeneboronic acid was bought from Aldrich and ABCR, and the one from ABCR need to be recrystallized with hot water. The other boronic acids, ketones, disopropylamine, and perfluorobutanesulfonfyl fluoride were purchased from Aldrich, TCI, Alfa, or ABCR, and used as received. Multiplets of NMR were assigned as s (singlet), d (doublet), t (triplet), q (quartet), br.s (broad singlet), dd (doublet of doublet), dt (doublet of triplet), td (triplet of doublet), tt (triplet of triplet), and m (multiplet).

2. Analytical methods

NMR spectra were recorded on Bruker AV 300, AV 400, or Fourier 300 spectrometers. 13C and 1H NMR spectra were referenced to signals of deutero solvents and residual protiated solvents, respectively. Gas chromatography analysis was performed on an Agilent HP-6890N network GC system with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 μm film thickness) using helium as carrier gas. High resolution mass spectra (HRMS) were recorded on Agilent 6210. Electron impact (EI) mass spectra were recorded on AMD 402 mass spectrometer (70 eV). The data are given as mass units per charge (m/z). The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, 70-230 mesh (Merck).

3. General procedures

Synthesis of nonaflates:
Nonaflates used in this work were synthesized by the following method according to a literature (Scheme S1).[1] In a representative procedure, To a cold solution (-78 °C) of i-Pr₂NH (1.1 eq., 5.5 mmol, 776 µL) in THF (30 mL) was added n-BuLi (1.1 eq., 2.2 mL, 2.5 M solution in hexane). After stirring 1 h, 8a (5 mmol, 518 µL) was added and stirring continued for 1 h. Then, neat NfF (2eq., 1796 µL) was added dropwise using a syringe pump under argon. After slowly warming up the solution to room temperature and stirring overnight, the mixture was concentrated by rotary evaporator and purified by chromatography (heptane elution for).


Synthesis of α,β-unsaturated ketones:
In a representative procedure, the reaction was carried out in a Parr Instruments 4560 series 300 mL autoclave containing an alloy plate with wells for five 10 mL glass vials. Under argon atmosphere, cyclohexenyl triflate 1 (0.5 mmol, 115.1 mg), TMEDA (0.75 eq., 56 µL, 43.6 mg), phenylboronic acid 4a (1.2 eq., 84.0 mg) and a magnetic stirring bar were placed in the vial, which were then capped with a septum equipped with an inlet needle and flushed with argon. A stock toluene solution (2 mL) containing Pd(OAc)₂ (0.5 mol%, 0.6 mg) and cataCXium® A (1.5 mol%, 3.3 mg) was then added to the vial with a syringe. The vial was placed in an alloy plate, which was then placed in the autoclave. Once sealed, the autoclave was purged three times with 15 bar nitrogen and three times with 5 bar CO, then pressurized to 5 bar CO at room temperature and heated at 60 °C for 16 h. It was then cooled to room temperature and vented to discharge the excess CO. The contents of the vial was purified by column chromatography with elution of ethyl acetate and heptane (0:100 to 15:100) to yield 83% of the pure product of 5a as a colorless oil. The other products were isolated by the same procedure with elution of ethyl acetate and heptane using a specified polarity according to the corresponding TLC.
Synthesis of 1-cyclohexenyl phenyl ketone in gram scale:
The reaction was carried out in a Parr Instruments 4560 series 50 mL autoclave with constant pressure equipment. Phenylboronic acid 2 (1.2 eq., 636.8 mg) and a magnetic stirring bar were placed in the autoclave. A stock toluene solution (8.7 mL) containing Pd(OAc)$_2$ (0.5 mol%, 5.2 mg) and cataCXium® A (1.5 mol%, 23.5 mg), and a stock toluene solution (8.7 mL) containing cyclohexenyl triflate 1 (4.3 mmol, 1 g, 760 µL), TMEDA (0.75 eq., 379.3 mg, 487 µL), were then added to the autoclave with a syringe. Once sealed, the autoclave was purged three times with 5 bar nitrogen and three times with 5 bar CO, then pressurized to 5 bar CO at room temperature and heated at 60 °C for 16 h. It was then cooled to room temperature and vented to discharge the excess CO. The contents of the autoclave were diluted by ethyl acetate and analyzed by GC.

4. Characterization data of vinyl nonaflates

Note: For the $^{13}$C NMR (F coupled), peaks for the C of perfluorobutyl chain are too broad to be assigned (not shown in the following data).

8a: light yellow oil.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 5.70$ (td, $J = 4.1$, 2.0 Hz, 1H), 2.35 – 2.18 (m, 2H), 2.17 – 2.02 (m, 2H), 1.85 – 1.65 (m, 2H), 1.54 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 149.44$, 118.49, 27.63, 23.89, 22.66, 20.95.

$^{19}$F NMR (282 MHz, CDCl$_3$): $\delta = -80.83$ (tt, $J = 9.8$, 2.3 Hz, 3F), -109.67 – -111.61 (m, 2F), -121.09 (m, 2F), -124.84 – -127.15 (m, 2F).

MS (EI, 70 eV): m/z (%) = 380.0 (25) M+, 301.0 (10), 288.1 (11), 131.0 (16), 100.0 (12), 97.1 (20), 81.1 (36), 80.1 (27), 79.1 (24), 69.1 (100), 55.1 (37), 41.1 (63).

8b:

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 5.67$ (d, $J = 3.7$ Hz, 1H), 2.45 (t, $J = 3.7$ Hz, 1H), 1.93 (m, 1H), 1.72 – 1.56 (m, 1H), 1.34 (m, 1H), 1.16 (m, 1H), 1.03 (s, 3H), 0.93 (s, 3H), 0.79 (d, $J = 0.6$ Hz, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 155.46$, 117.57, 56.97, 53.95, 50.13, 30.83, 25.31, 19.66, 18.95, 9.43.

$^{19}$F NMR (282 MHz, CDCl$_3$): $\delta = -80.85$ (tt, $J = 10.0$, 2.5 Hz, 3F), -108.32 – -112.36 (m, 2F), -121.15 (m, 2F), -125.82 – -126.19 (m, 2F).

MS (EI, 70 eV): m/z (%) = 434.1 (16) M+, 151.1 (29), 123.1 (100), 95.1 (29), 81.1 (24), 69.0 (27).

8c:

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 6.72$ – 6.54 (m, 1H), 6.11 – 5.92 (m, 1H), 1.87 (dd, $J = 1.5$, 0.8 Hz, 3H), 1.21 (s, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 202.49$, 141.74, 141.74, 136.55, 133.15, 132.73, 46.69, 25.85, 15.49.

$^{19}$F NMR (282 MHz, CDCl$_3$): $\delta = -80.83$ (tt, $J = 9.8$, 2.1 Hz, 3F), -107.58 – -110.79 (m, 2F), -119.01 – -122.97 (m, 2F), -124.31 – -128.80 (m, 2F).

TLC (silica gel 60 F$_{254}$): Ethyl acetate:Heptane = 1:10, Rf = 0.3 (K MnO$_4$ stain).

MS (EI, 70 eV): m/z (%) = 434.1 (3) M+, 151.1 (100), 95.1 (82), 83.1 (23), 69.0 (24).
5. Characterization data of α,β-unsaturated ketones

\[ \begin{align*} 
3. & \quad \text{colorless oil.} \\
{^1}H \text{ NMR (300 MHz, CDCl}_3) & : \delta = 7.66 - 7.58 (\text{m, 2H}), 7.53 - 7.33 (\text{m, 3H}), 6.57 (\text{tt, } J = 3.9, \ 1.7 \ \text{Hz, 1H}), 2.48 - 2.36 (\text{m, 2H}), 2.25 (\text{m, 2H}), 1.76 - 1.59 (\text{m, 4H}). \\
{^{13}}C \text{ NMR (75 MHz, CDCl}_3) & : \delta = 198.19 (\text{C}=O), 144.24, 144.03, 138.67, 131.18, 129.07, 127.94, 26.07, 23.90, 21.97, 21.61. \\
\text{HRMS (EI)}: & \quad [M]+ \text{ calcd for } C_{13}H_{14}O, 186.10392; \text{ found, } 186.10388. \\
\text{MS (EI, 70 eV)}: & \quad m/z (\%) = 186.1 (100) \text{ M+}, 185.1 (69), 157.1 (30), 105.1 (85), 77.1 (56). \\
\end{align*} \]

\[ \begin{align*} 
5a. & \quad \text{colorless oil.} \\
{^1}H \text{ NMR (300 MHz, CDCl}_3) & : \delta = 7.53 - 7.25 (\text{m, 2H}), 7.21 - 6.92 (\text{m, 2H}), 6.59 (\text{m, 1H}), 2.39 (\text{m, 2H}), 2.28 - 2.12 (\text{m, 2H}), 1.86 - 1.49 (\text{m, 4H}). \\
{^{13}}C \text{ NMR (75 MHz, CDCl}_3) & : \delta = 194.61 (\text{C}=O), 159.25 (\text{d, } J = 249.5 \text{ Hz, C-F}), 146.44 (\text{d, } J = 1.4 \text{ Hz}), 139.72, 131.55 (\text{d, } J = 8.1 \text{ Hz}), 129.75 (\text{d, } J = 3.5 \text{ Hz}), 127.81 (\text{d, } J = 16.5 \text{ Hz}), 123.81 (\text{d, } J = 3.6 \text{ Hz}), 115.81 (\text{d, } J = 21.9 \text{ Hz}), 26.31, 22.91, 21.74, 21.47. \\
\text{19F NMR (282 MHz, CDCl}_3) & : \delta = -114.03. \\
\text{MS (EI, 70 eV)}: & \quad m/z (\%) = 204.1 (46) \text{ M+}, 203.1 (29), 123.0 (100), 95.1 (22). \\
\end{align*} \]

\[ \begin{align*} 
5b. & \quad \text{colorless oil.} \\
{^1}H \text{ NMR (300 MHz, CDCl}_3) & : \delta = 7.93 (\text{m, 1H, -aryl-}), 7.61 - 7.39 (\text{m, 2H, -aryl-}), 7.28 (\text{m, 1H, -aryl-}), 6.22 (\text{td, } J = 4.0, \ 2.0 \text{ Hz, -vinyl-}), 3.78 (\text{s, 3H}), 2.42 (\text{m, -C}_2\text{H}_5), 2.12 (\text{m, -C}_2\text{H}_5), 1.82 - 1.45 (\text{m, -C}_2\text{H}_5). \\
{^{13}}C \text{ NMR (75 MHz, CDCl}_3) & : \delta = 198.47, 166.60, 143.88, 142.09, 140.56, 132.02, 129.87, 129.12, 129.03, 127.76, 52.32, 26.09, 23.18, 21.90, 21.64. \\
\text{MS (EI, 70 eV)}: & \quad m/z (\%) = 244.2 (51) \text{ M+}, 243.2 (46), 213.1 (23), 212.1 (100), 211.1 (40), 197.1 (66), 185.1 (48), 163.1 (70), 77.1 (30). \\
\text{TLC (silica gel 60 F}_{254}: & \quad \text{Ethyl acetate:Heptane = 1:2, } \ R_f = 0.52. \\
\end{align*} \]

\[ \begin{align*} 
5c. & \quad \text{colorless oil.} \\
{^1}H \text{ NMR (300 MHz, CDCl}_3) & : \delta = 8.41 (\text{m, 1H, -aryl-}), 8.32 (\text{m, 1H, -aryl-}), 7.93 (\text{m, 1H, -aryl-}), 7.61 (\text{m, 1H, -aryl-}), 6.58 (\text{td, } J = 4.0, \ 2.0 \text{ Hz, -vinyl-}), 3.78 (\text{s, 3H, -COCH}_3), 2.61 (\text{s, 3H, -COCH}_3), 2.39 (\text{m, -CH}_3), 2.26 (\text{tt, } J = 5.9, \ 3.3 \text{ Hz, 2H, -CH}_2), 1.89 - 1.50 (\text{m, 4H, -CH}_2). \\
{^{13}}C \text{ NMR (75 MHz, CDCl}_3) & : \delta = 195.35, 147.81, 145.94, 140.20, 138.52, 134.73, 129.36, 125.64, 123.84, 26.32, 23.72, 21.80, 21.47. \\
\text{MS (EI, 70 eV)}: & \quad m/z (\%) = 231.1 (18) \text{ M+}, 214.1 (100), 184.1 (25), 150.1 (55), 81.1 (32). \\
\text{TLC (silica gel 60 F}_{254}: & \quad \text{Ethyl acetate:Heptane = 1:2, } \ R_f = 0.52. \\
\end{align*} \]

\[ \begin{align*} 
5d. & \quad \text{colorless oil.} \\
{^1}H \text{ NMR (300 MHz, CDCl}_3) & : \delta = 8.04 - 7.82 (\text{m, 2H, -aryl-}), 7.75 - 7.54 (\text{m, 2H, -aryl-}), 6.55 (\text{td, } J = 4.0, \ 2.0 \text{ Hz, 1H, -vinyl-}), 2.61 (\text{s, 3H, -COCH}_3), 2.39 (\text{m, -CH}_3), 2.26 (\text{tt, } J = 5.9, \ 3.3 \text{ Hz, 2H, -CH}_2), 1.89 - 1.50 (\text{m, 4H, -CH}_2). \\
{^{13}}C \text{ NMR (75 MHz, CDCl}_3) & : \delta = 197.52, 197.23, 145.93, 142.75, 138.72, 138.60, 129.00, 127.88, 26.73, 26.18, 23.59, 21.80, 21.47. \\
\text{MS (EI, 70 eV)}: & \quad m/z (\%) = 228.2 (100) \text{ M+}, 185.1 (57), 157.1 (20), 147.1 (52). \\
\text{TLC (silica gel 60 F}_{254}: & \quad \text{Ethyl acetate:Heptane = 1:5, } \ R_f = 0.24. \\
\end{align*} \]
SUPPORTING INFORMATION

5e, colorless oil.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.66 – 7.54$ (m, 2H, -aryl-), 7.50 – 7.35 (m, 2H, -aryl-), 6.73 (dd, J = 17.6, 10.9 Hz, 1H, -CH=CH$_2$), 6.55 (td, J = 3.9, 1.9 Hz, 1H, -vinyl-), 5.82 (m, 1H, -CH=CCH$_2$), 5.33 (dd, J = 10.9, 0.8 Hz, 1H, -CH=CH$_2$), 2.40 (m, 2H, -CH$_2$), 2.24 (m, -CH$_2$), 1.82 – 1.52 (m, 4H, -CH$_2$).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 197.52, 143.35, 140.35, 138.60, 137.69, 135.99, 129.49, 125.67, 115.72, 25.96, 23.92, 21.92, 21.56.

MS (EI, 70 eV): m/z (%) = 212.2 (100) M+, 211.2 (44), 185.2 (37), 184.1 (22), 183.1 (27), 131.1 (76), 103.1 (37), 77.1 (36).

5f, colorless oil.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.72 – 7.62$ (m, 2H, -aryl-), 7.23 (m, 2H, -aryl-), 6.56 (td, J = 4.0, 2.0 Hz, 1H, -vinyl-), 2.40 (m, 2H, -CH$_2$), 2.26 (m, 2H, -CH$_2$), 1.80 – 1.54 (m, 4H, -CH$_2$).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 196.52, 151.28 – 151.21$ (q, J = 2.3 Hz, C=OCF$_3$), 144.38, 144.21, 138.60, 137.01, 130.90, 125.43 – 115.17 (q, J = 342 Hz, COCFC$_3$), 120.09 – 120.08 (d, J = 1.1 Hz, CHCOCF$_3$), 26.10, 23.85, 21.88, 21.53.

$^{3.42}$MS (EI, 70 eV): m/z (%) = 270.1 (36) M+, 269.1 (22), 189.0 (100), 185.1 (67).

5g, colorless oil.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 8.01$ (dd, J = 7.7, 1.3 Hz, 1H, -aryl-), 7.93 (m, 1H, -aryl-), 7.62 – 7.28 (m, 5H, -aryl-), 6.68 (td, J = 4.0, 2.0 Hz, 1H, -vinyl-), 2.54 (tt, J = 6.3, 3.2 Hz, 2H, -CH$_2$), 2.30 – 2.16 (m, 2H, -CH$_2$), 1.85 – 1.56 (m, 4H, -CH$_2$).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 195.24, 156.31, 153.33, 146.29, 139.55, 127.61, 127.50, 125.15, 124.18, 123.49, 123.02, 122.77, 122.23, 120.65, 112.00, 26.42, 23.37, 21.98, 21.67.

MS (EI): m/z (%) = 276.1 (100) M+, 275.1 (51), 195.1 (63).

5h, colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.44$ (dd, J = 2.4, 0.7 Hz, 1H, -aryl-), 7.88 (dd, J = 8.6, 2.4 Hz, 1H, -aryl-), 6.72 (dd, J = 8.6, 0.7 Hz, 1H, -aryl-), 6.52 (tt, J = 3.9, 1.7 Hz, 1H, -vinyl-), 3.93 (s, 3H, -OC$_3$H$_3$), 2.40 – 2.31 (m, 2H, -CH$_2$), 2.27 – 2.17 (m, 2H, -CH$_2$), 1.74 – 1.56 (m, 4H, -CH$_2$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 195.35, 165.85, 149.21, 142.84, 139.63, 138.74, 127.56, 110.69, 53.85, 26.00, 24.05, 21.93, 21.59.


MS (EI, 70 eV): m/z (%) = 217.2 (80) M+, 216.1 (74), 202.1 (24), 188.1 (37), 164.1 (100).

TLC (silica gel 60 F$_{254}$): Ethyl acetate:Heptane = 1:2, RF = 0.52.

5i, colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.89 – 7.75$ (m, 3H, -aryl-), 7.47 – 7.33 (m, 2H, -aryl-), 6.87 (tt, J = 3.9, 1.7 Hz, 1H, -vinyl-), 2.51 – 2.16 (m, 4H, -CH$_2$), 1.82 – 1.50 (m, 4H, -CH$_2$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 190.40, 144.20, 142.96, 142.00, 141.13, 138.81, 138.61, 129.76, 126.73, 125.56, 124.69, 122.62, 25.91, 24.24, 21.88, 21.53.

MS (EI, 70 eV): m/z (%) = 242.1 (100) M+, 241.1 (30), 223.1 (21), 214.1 (22), 213.1 (25), 161.0 (91), 133.0 (35), 89.0 (58).

TLC (silica gel 60 F$_{254}$): Ethyl acetate:Heptane = 1:2, RF = 0.63.
SUPPORTING INFORMATION

7a, O
H NMR (300 MHz, CDCl$_3$): $\delta = 7.70 – 7.71$ (m, 2H, -aryl-H), 7.62 – 7.28 (m, 8H, -aryl-H), 7.19 (q, $J = 1.4$ Hz, 1H, -vinyl-H), 2.28 (d, $J = 1.4$ Hz, 3H, -C$_3$H$_3$).
$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 199.48, 142.24, 138.52, 136.88, 135.81, 131.67, 129.71, 129.51, 128.61, 128.49, 128.22, 14.46.$
MS (EI, 70 eV): m/z (%) = 222.2 (100) M+, 221.2 (86), 207.1 (35), 115.1 (44), 105.1 (64), 77.1 (53).

TLC (silica gel 60 F$_{254}$): Ethyl acetate:Heptane = 1:5, RF = 0.17.

7b, , colorless oil.
H NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 7.70 – 7.75$ (m, 2H, -aryl-H), 7.55 – 7.47 (m, 1H, -aryl-H), 7.46 – 7.32 (m, 2H, -aryl-H), 6.51 (t, $J = 8.4$ Hz, 1H, -vinyl-H), 2.70 – 2.52 (m, 2H, -CH$_2$), 2.46 – 2.24 (m, 2H, -CH$_2$), 1.83 – 1.39 (m, 8H, -C$_2$H$_4$).
MS (EI, 70 eV): m/z (%) = 214.2 (73) M+, 213.2 (35), 145.1 (25), 105.1 (100), 77.1 (64).

TLC (silica gel 60 F$_{254}$): Ethyl acetate:Heptane = 1:5, RF = 0.5.

7c, , colorless oil.
H NMR (300 MHz, CDCl$_3$): $\delta = 7.74 – 7.58$ (m, 2H, -aryl-H), 7.56 – 7.30 (m, 3H, -aryl-H), 6.43 (t, $J = 3.9$, 1.6 Hz, 1H, -vinyl-H), 4.00 (s, 4H, -OCH$_2$CH$_2$O), 2.67 (m, -CH$_2$), 2.57 – 2.41 (m, 2H, -CH$_2$), 1.86 (t, $J = 6.6$ Hz, 2H, -CH$_2$).
$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 197.18, 140.17, 138.38, 138.04, 131.46, 129.11, 128.07, 107.28, 64.56, 36.51, 30.68, 23.42.$
MS (EI, 70 eV): m/z (%) = 243.1 (28) M+, 172.1 (20), 105.1 (36), 86.1 (100), 77.1 (35).

TLC (silica gel 60 F$_{254}$): Ethyl acetate:Heptane = 1:5, RF = 0.17.
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**MS (EI, 70 eV):** m/z (%) = 240.2 (56) M+, 225.2 (69), 197.1 (51), 135.1 (21), 105.1 (100), 77.1 (37).

**TLC (silica gel 60 F_{254}):** Ethyl acetate:Heptane = 1:5, Rf = 0.54.

7f, orange oil.

**1H NMR (400 MHz, CDCl$_3$):** $\delta$ = 7.73 – 7.67 (m, 2H, -aryl-H), 7.58 – 7.52 (m, 1H, -aryl-H), 7.49 – 7.41 (m, 2H, -aryl-H), 7.39 (m, 1H, -vinyl-H), 6.74 (dd, $J$ = 2.4, 0.6 Hz, 1H, -vinyl-H), 1.95 (dd, $J$ = 1.5, 0.6 Hz, 3H, -CH$_3$), 1.25 (s, 6H, -CH$_3$).

**13C NMR (101 MHz, CDCl$_3$):** $\delta$ = 204.06, 194.44, 154.61, 136.81, 135.62, 133.77, 132.56, 130.33, 129.48, 128.45, 46.41, 25.38, 15.63.

**MS (EI, 70 eV):** m/z (%) = 240.2 (73) M+, 225.1 (100), 197.1 (77), 169.1 (27), 105.1 (76), 91.1 (23), 77.1 (58).

7g, colorless oil.

**1H NMR (300 MHz, CDCl$_3$):** $\delta$ = 7.76 – 7.66 (m, 2H, -aryl-H), 7.57 – 7.50 (m, 1H, -aryl-H), 7.49 – 7.40 (m, 2H, -aryl-H), 6.65 (tt, $J$ = 1.5, 0.7 Hz, 1H, -vinyl-H), 5.07 (dd, $J$ = 12.6, 1.7 Hz, 2H, -C=CH$_2$), 3.11 (td, $J$ = 5.8, 1.6 Hz, 1H, -CH), 2.84 – 2.50 (m, 2H, -CH$_2$), 1.50 (d, $J$ = 8.8 Hz, 1H, -CH$_3$), 1.46 (s, 3H, -CH$_3$), 0.85 (s, 3H, -CH$_3$).

**13C NMR (75 MHz, CDCl$_3$):** $\delta$ = 195.74, 149.16, 147.37, 137.95, 137.82, 131.71, 129.17, 128.15, 115.39, 50.92, 42.93, 42.41, 34.87, 25.80, 21.89.

**MS (EI, 70 eV):** m/z (%) = 238.2 (18) M+, 223.2 (42), 196.1 (23), 105.1 (100), 77.1 (44).

7h, colorless oil.

**1H NMR (300 MHz, CDCl$_3$):** $\delta$ = 7.94 – 7.73 (m, 2H, -aryl-H), 7.58 – 7.47 (m, 1H, -aryl-H), 7.46 – 7.34 (m, 2H, -aryl-H), 5.97 (d, $J$ = 3.3 Hz, 1H, -vinyl-H), 2.56 (dd, $J$ = 18.4, 6.0 Hz, 1H), 2.52 – 2.36 (m, 1H), 2.33 – 2.25 (m, 1H), 2.04 – 1.84 (m, 1H), 1.77 – 1.61 (m, 4H), 1.72 (s, 3H, -C=CH$_3$), 1.51 – 1.32 (m, 1H), 1.43 (s, 3H, -C=CH$_3$), 1.09 (d, $J$ = 7.2 Hz, 3H, -CH-CH$_3$).

**13C NMR (75 MHz, CDCl$_3$):** $\delta$ = 198.09, 142.59, 140.31, 137.62, 132.44, 129.81, 128.97, 128.12, 127.22, 31.80, 31.54, 27.01, 23.94, 21.17, 20.79.

**MS (EI, 70 eV):** m/z (%) = 240.2 (66) M+, 225.2 (100).

**TLC (silica gel 60 F$_{254}$):** Ethyl acetate:Heptane = 1:10, Rf = 0.27.

**TLC (silica gel 60 F$_{254}$):** Ether:Pentane = 1:10, Rf = 0.37.
6. Spectra of vinyl nonaflates
7. Spectra of α,β-unsaturated ketones
8. References