Advanced Synthesis & Catalysis

Supporting Information

SUPPORTING INFORMATION

An Expedient Variant of Heck Reaction of Alkenyl Nonaflates: Homogeneous Ligand-free Pd-catalysis at Room Temperature

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General. NMR spectra were recorded on *Bruker 400 UltraShield* instrument in $CDCl_3$ as a solvent unless stated otherwise. ^1H and ^{13}C chemical shifts are expressed as ppm downfield from $SiMe_4$ ($\delta = 0$) used as an internal standard. Mass spectra were registered with *Varian* MAT 711 and with *Finnigan MAT 95XP* (HRMS) spectrometers. Microanalyses were performed with *Euro Elemental Analyser*. IR spectra were measured with spectrometer *FTIR-Bio Rad Excalibur*. TLC-analysis was performed using *Merck* silica gel *60 F_{254}* plates. Column chromatography was conducted on silica gel 60 (40–63 µm, *Fluka*). GC-analysis was performed on *Agilent Technologies 6890N* (FID-detector; HP-5 column, 30 m × 0.32 mm, 0.25 micron). DMF (*Riedel-de Haën*) and NEt_3 (*Riedel-de Haën*) were used as purchased without further purification. $Pd(OAc)_2$ was purchased from *Alfa Aesar*. Olefins were purchased from various suppliers and used without further purification. For the synthesis of alkenyl nonaflates, see ref.[15a]

Variation of the catalyst loading (see Figure 1)

To screw cap vials equipped with magnetic stirring bars, DMF (1 mL), *p*-xylene (6 drops; added *via* syringe) as an internal standard, Et_3N, cyclopentenyl nonaflate **1a**, methyl acrylate **2a** and $Pd(OAc)_2$ 10 mol.% (*a*), 5 mol.% (*b*) 1 mol.% (*c*) 0.5 mol.% (*d*) 0.1 mol.% (*e*) were subsequently added in the following amounts:

a: Et_3N (205.5 mg, 2.031 mmol), **1a** (372.0 mg, 1.016 mmol), **2a** (120.9 mg, 1.404 mmol), $Pd(OAc)_2$ (22.5 mg, 0.10 mmol);
b: Et_3N (203.2 mg, 2.008 mmol), **1a** (367.3 mg, 1.003 mmol), **2a** (114.3 mg, 1.327 mmol), $Pd(OAc)_2$ (11.721 mg, 0.052 mmol);
c: Et_3N (205.5 mg, 2.031 mmol), **1a** (366.5 mg, 1.001 mmol), **2a** (119.3 mg, 1.386 mmol), $Pd(OAc)_2$ (2.647 mg, 0.012 mmol);
d: Et_3N (204.4 mg, 2.020 mmol), **1a** (368.6 mg, 1.006 mmol), **2a** (115.3 mg, 1.339 mmol), $Pd(OAc)_2$ (1.104 mg, 0.005 mmol);
e: Et_3N (205.5 mg, 2.031 mmol), **1a** (367.3 mg, 1.003 mmol), **2a** (115.3 mg, 1.339 mmol), $Pd(OAc)_2$ (0.190 mg, 0.00085 mmol).

The mixtures were vigorously stirred at r.t., and the reaction progress was monitored after 0 h, 2 h, 5 h, 8 h and 11 h by GC (p = 15 psi; t = 100°C const.; the samples taken were diluted with *n*-hexane before injection); R_t = 1.66 min (*p*-xylene), 2.79 min (**1a**), 8.55 min (product **3a**).

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Poisoning Experiments

General. The methods described in detail in a review by Widegren and Finke[19] suggest that the poisoning reagent be added at a certain time *after the reaction had started, and a catalytically active system had formed*,[10b] the kinetic profile being recorded before and after the addition of the catalyst poison. When applying this rule to our system, we chose to add the poisoning reagents at the highest conversion rate (maximum slope of the curve) that is routinely attained at *ca.* 2.5 h after the beginning of the reaction.

With PPh_3 or thiophene: to screw cap vials equipped with magnetic stirring bars, DMF (1 mL), *p*-xylene (5 drops; added *via* syringe) as an internal standard, Et_3N, cyclopentenyl nonaflate **1a**, methyl acrylate **2a** and $Pd(OAc)_2$ were subsequently added. The mixtures were vigorously stirred at r.t., and the reaction progress was monitored as depicted in Figures 2 and 3 by GC as described above. After 2.5 h reaction time, the poisoning reagent was added by volume using *Hamilton* syringe (thiophene) or by weight (PPh_3) in the amounts designated below. The reaction progress was further monitored by GC.

Experiments with thiophene (see Figure 2):

a: Et_3N (206.5 mg, 2.041 mmol), **1a** (373.2 mg, 1.019 mmol), **2a** (117.1 mg, 1.360 mmol), $Pd(OAc)_2$ (11.2 mg, 0.049 mmol), thiophene (8 µl, 0.1 mmol);

b: Et_3N (207.5 mg, 2.050 mmol), **1a** (368.6 mg, 1.007 mmol), **2a** (117.0 mg, 1.360 mmol), $Pd(OAc)_2$ (11.2 mg, 0.049 mmol), thiophene (4 µl, 0.05 mmol);

c: Et_3N (207.5 mg, 2.050 mmol), **1a** (371.6 mg, 1.015 mmol), **2a** (118.5 mg, 1.376 mmol), $Pd(OAc)_2$ (11.2 mg, 0.049 mmol), thiophene (2 µl, 0.025 mmol);

d: Et_3N (204.5 mg, 2.021 mmol), **1a** (369.2 mg, 1.008 mmol), **2a** (113.1 mg, 1.314 mmol), $Pd(OAc)_2$ (11.2 mg, 0.049 mmol), thiophene (0.4 µl, 0.005 mmol);

e (reference run): Et_3N (207.5 mg, 2.050 mmol), **1a** (367.0 mg, 1.002 mmol), **2a** (118.0 mg, 1.370 mmol), $Pd(OAc)_2$ (11.2 mg, 0.049 mmol).

Experiments with PPh_3 (see Figure 3):

a: Et_3N (207.8 mg, 2.053 mmol), **1a** (370.0 mg, 1.010 mmol), **2a** (114.2 mg, 1.326 mmol), $Pd(OAc)_2$ (11.2 mg, 0.049 mmol), PPh_3 (13.2 mg, 0.05 mmol);

b: Et_3N (205.3 mg, 2.029 mmol), **1a** (369.5 mg, 1.009 mmol), **2a** (117.0 mg, 1.360 mmol), $Pd(OAc)_2$ (11.3 mg, 0.050 mmol), PPh_3 (6.6 mg 0.025 mmol);

c (reference run): Et_3N (209.2 mg, 2.067 mmol), **1a** (368.5 mg, 1.006 mmol), **2a** (119.5 mg, 1.388 mmol), $Pd(OAc)_2$ (11.2 mg, 0.049 mmol).

With metallic mercury: the reaction in DMF (1 ml) with *p*-xylene (5 drops; added *via* syringe) as an internal standard, Et_3N (205.0 mg, 2.026 mmol), **1a** (366.3 mg, 1.0 mmol), **2a** (117.0 mg, 1.36 mmol) and $Pd(OAc)_2$ (11.3 mg, 0.050 mmol) was carried out as described above. After 2.5 h, mercury 3.047g (15.19 mmol) was added, and the two-phase mixture was *vigorously* stirred for 1 h. The stirring was stopped, and the mercury phase was allowed to completely settle down to the bottom before the supernatant phase was transferred carefully into a new reaction vial equipped with magnetic stirring bar. The reaction progress was monitored further by GC as depicted in Figure 4 (curve *a*).

Centrifugation

The reaction in DMF (1 ml) with *p*-xylene (6 drops; added *via* syringe) as an internal standard, Et_3N (205.5 mg, 2.031 mmol), **1a** (372.6 mg, 1.017 mmol), **2a** (115.0 mg, 1.336 mmol), and $Pd(OAc)_2$ (11.3 mg, 0.050 mmol) was carried out and monitored as described above. After 2.5 h, the reaction solution was transferred into the centrifugation vial and centrifuged at 14.500 rpm

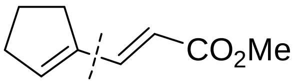
for 25 min to give a small amount of dark-brown residue and a clear yellowish supernatant solution. Approx. three quarter of the supernatant solution were carefully transferred into a new reaction vial and the reaction progress was monitored until the endpoint (see Figure 4, curve *b*).
Reference run (see Figure 4, curve *c*): DMF (1ml), Et_3N (205.8 mg, 2.034 mmol), **1a** (366.4 mg, 1.0 mmol), **2a** (117.0 mg, 1.36 mmol), $Pd(OAc)_2$ (11.2 mg, 0.049 mmol).

The solid residue was separated from the rest of the reaction solution, washed with DMF two times (2 × 1.5 ml) followed by a centrifugation with 14.500 rpm for 15 min each time. It was then added to a freshly prepared reaction solution comprising DMF (1 ml), Et_3N (207.0 mg, 2.045 mmol), **1a** (367.0 mg, 1.002 mmol), **2a** (114.7 mg, 1.332 mmol). The reaction mixture was monitored by GC after 6 h, 20 h and 24 h indicating no product **3a** formation.

Synthesis and Spectroscopic Data of the Coupling Products 3 and 4

General Procedure: DMF (1 mL), Et_3N, alkenyl nonaflate **1**, alkene **2**, and $Pd(OAc)_2$ (*ca*. 5 mol.%) were subsequently added to a screw-cap vial equipped with magnetic stirring bar. The reaction mixture was stirred for the designated amount of time (see Table 1) at ambient temperature. It was then subjected to aqueous workup (4 times extraction with in total 120 ml of pentane and 4 ml of water). The combined organic layers were washed with brine (20 ml) and dried with Na_2SO_4. The solvent was removed under reduced pressure and the residue purified by either column chromatography (silica gel, eluent: hexane : EtOAc = 20 : 1 unless stated otherwise) or Kugelrohr distillation, to give pure dienes **3** or **4**.

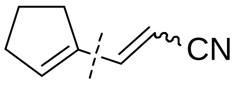
Synthesis of (*E*)-methyl 3-cyclopentenyl acrylate (*E*)-3a



(*E*)-**3a**

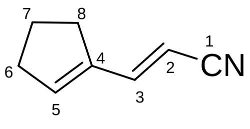
The synthesis was carried out according to the general procedure: NEt_3 (207.5 mg, 2.050 mmol), methyl acrylate **2a** (117.4 mg, 1.364 mmol), cyclopentenyl nonaflate **1a** (368.8 mg, 1.006 mmol), $Pd(OAc)_2$ (11.2 mg, 0.049 mmol). After column chromatography, the pure product (*E*)-**3a** was obtained as a white solid (144.4 mg, 94% yield). Analytical data match well those described in literature.[14f]

Synthesis of 3-cyclopentenyl-acrylonitrile (*E/Z*)-3b



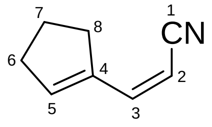
(*E/Z*)-**3b**, *E/Z* = 79:21

The synthesis was carried out according to the general procedure: NEt_3 (207.8 mg, 2.053 mmol), acrylonitrile **2b** (73.0 mg, 1.376 mmol), cyclopentenyl nonaflate **1a** (372.7 mg, 1.017 mmol), $Pd(OAc)_2$ (11.5 mg, 0.051 mmol). Kugelrohr distillation at 65°C (1.0 mbar) furnished the product **3b** (111.5 mg, 92% yield, *E/Z* ratio 79:21) as a colourless oil.



(*E*)-**3b**

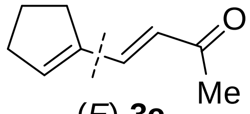
^1H NMR (C_6D_6, 400 MHz): δ = 1.47 (quint, ^3J = 7.5 Hz, 2 H, 7-CH_2), 1.71–1.77 (m, 2 H) and 1.94–2.01 (m, 2 H) (6-CH_2 and 8-CH_2), 4.47 (d, ^3J = 16.3 Hz, 1 H, 2-CH), 5.41 (br.s, 1 H, 5-CH), 6.55 (d, ^3J = 16.3 Hz, 1 H, 3-CH). ^{13}C ($CDCl_3$, 100.65 MHz): δ = 22.9 (7-CH$_2$), 30.2 and 33.6 (6-CH$_2$ and 8-CH$_2$), 95.7 (2-CH), 118.6 (CN), 140.9 (4-C), 141.8 (5-CH), 146.7 (3-CH). IR (film): $\tilde{\nu}$ = 2925, 2855 cm^{-1} (=C–H, C–H), 1665 cm^{-1} (C=C). MS (EI, 80 eV): m/z (%) = 119 (M$^+$, 100), 91 ([M$^+$ – 28], 43). HRMS: calcd. for C_8H_9N (M$^+$) 119.0735, found 119.073499. C,H,N-analysis (%): calcd. for C_8H_9N (119.164): C, 80.63; H, 7.61; N, 11.75; found C, 80.20; H, 7.43; N, 11.67.



(*Z*)-**3b**

^{1}H NMR (C_6D_6, 400 MHz): δ = 1.55 (quint, ^3J = 7.6 Hz, 2 H, 7-CH$_2$), 1.92–1.98 (m, 2 H) and 2.74 (m$_c$, 2 H) (6-CH$_2$ and 8-CH$_2$), 4.41 (d, ^3J = 11.7 Hz, 1 H, 2-CH), 5.58 (br.s, 1 H, 5-CH), 6.06 (d, ^3J = 11.7 Hz, 1 H, 3-CH). ^{13}C ($CDCl_3$, 100.65 MHz): δ = 23.7 (7-CH$_2$), 31.5 and 32.6 (6-CH$_2$ and 8-CH$_2$), 93.4 (2-CH), 117.9 (CN), 141.4 (4-C), 143.6 and 145.2 (5-CH and 3-CH). IR (film): $\tilde{\nu}$ = 2925, 2855 cm^{-1} (=C–H, C–H), 1665 cm^{-1} (C=C). MS (EI, 80 eV): m/z (%) = 119 (M$^+$, 100), 91 ([M$^+$ – 28], 43). HRMS: calcd. for C_8H_9N (M$^+$) 119.0735, found 119.073499. C,H,N-analysis (%): calcd. for C_8H_9N (119.164): C, 80.63; H, 7.61; N, 11.75; found C, 80.20; H, 7.43; N, 11.67.

Synthesis of (*E*)-4-cyclopentenyl but-3-en-2-one (*E*)-3c

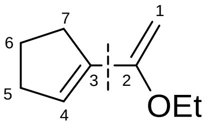


(*E*)-**3c**

The synthesis was carried out according to the general procedure: NEt$_3$ (202.7 mg, 2.003 mmol), methyl vinyl ketone **2c** (91.4 mg, 1.304 mmol), cyclopentenyl nonaflate **1a** (369.0 mg, 1.007 mmol), Pd(OAc)$_2$ (11.2 mg, 0.049 mmol). Kugelrohr distillation at 63–66°C (0.44 mbar) furnished the product (*E*)-**3c** as a colourless oil (122.8 mg, 90% yield). Analytical data match well those described in literature.[25]

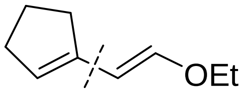
Synthesis of 1-(1-ethoxyethenyl)cyclopentene 4d and (*E*)-1-(2-ethoxyethenyl)cyclopentene (*E*)-3d

The synthesis was carried out according to the general procedure: NEt$_3$ (204.0 mg, 2.016 mmol), ethyl vinyl ether **2d** (102.0 mg, 1.414 mmol), cyclopentenyl nonaflate **1a** (374.5 mg, 1.022 mmol), Pd(OAc)$_2$ (11.2 mg, 0.049 mmol). Kugelrohr distillation at 62°C (4.0 mbar) furnished the product as a mixture of regioisomers (*E*)-**3d** and **4d** (6:94 ratio) as a colourless oil (121.3 mg, 86% yield).



4d

^{1}H NMR (C_6D_6, 400 MHz): δ = 1.13 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$*Me*), 1.75 (m$_c$, 2 H, 6-CH$_2$), 2.31 (m$_c$, 2 H) and 2.45 (m$_c$, 2 H) (5-CH$_2$ and 7-CH$_2$), 3.55 (q, ^3J = 7.0 Hz, 2 H, OC*H$_2$*Me), 4.07 (d, ^2J = 1.5 Hz, 1 H, 1-CH$_2$), 4.19 (d, ^2J = 1.5 Hz, 1 H, 1-CH$_2$), 5.07 (br.s, 1 H, =CH$_2$), 6.29 (quint, J = 2.2 Hz, 1 H, 4-CH).^{13}C NMR (C_6D_6, 100.65 MHz): δ = 14.6 (OCH$_2$*Me*), 23.6 (6-CH$_2$), 32.7 and 33.3 (5-CH$_2$ and 7-CH$_2$), 62.6 (O*C*H$_2$Me), 83.4 (1-CH$_2$), 127.98 (4-CH), 139.9 (3-C), 158.4 (2-C). IR (film): $\tilde{\nu}$ = 2975, 2940, 2895 cm^{-1} (=C–H, C–H), 1680 cm^{-1} (C=C). MS (EI, 80 eV): m/z (%) = 138 (M$^+$, 18), 123 ([M$^+$ – Me], 100), 110 ([M$^+$ – C$_2$H$_4$], 71). HRMS: calcd. for $C_9H_{14}O$ (M$^+$) 136.0888, found 136.088819. C,H-analysis (%): calcd. for $C_9H_{14}O$ (138.207): C, 78.21; H, 10.21; O, 11.58; found C, 77.85; H, 9.96.

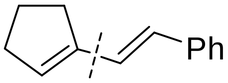


(*E*)-**3d**

NMR (selected signals): ^{1}H NMR (C_6D_6, 400 MHz), δ = 1.02 (t, ^{3}J = 7.0 Hz, 3 H, OCH$_2$*Me*), 3.43 (q, ^{3}J = 7.0 Hz, 2 H, OC*H*$_2$Me), 5.50 (m$_c$, 1 H, C*H*=C), 5.89 (d, ^{3}J = 12.8 Hz, 1 H, C*H*=CHOEt), 6.49 (d, ^{3}J = 12.8 Hz, 1 H, CH=C*H*OEt). ^{13}C (C_6D_6, 100.65 MHz), δ = 14.8 (OCH$_2$*Me*), 23.7, 31.9 and 32.8 (all CH$_2$), 64.9 (O*C*H$_2$Me), 104.2, 125.0 and 148.5 (all CH). IR (film): $\tilde{\nu}$ = 2975, 2940, 2895 cm^{-1} (=C–H, C–H), 1680 cm^{-1} (C=C). MS (EI, 80 eV): m/z (%) = 138 (M^{+}, 18), 123 ([M^{+} – Me], 100), 110 ([M^{+} – C_2H_4], 71). HRMS: calcd. for $C_9H_{14}O$ (M^{+}) 136.0888, found 136.088819. C,H-analysis (%): calcd. for $C_9H_{14}O$ (138.207): C, 78.21; H, 10.21; O, 11.58; found C, 77.85; H, 9.96.

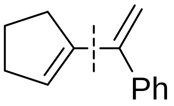
Synthesis of (*E*)-(2-cyclopent-1-enyl-ethenyl)benzene 3e and (1-cyclopent-1-enyl-ethenyl)benzene 4e

The synthesis was carried out according to the general procedure. NEt$_3$ (205.1 mg, 2.027 mmol), styrene **2e** (141.5 mg, 1.358 mmol), cyclopentenyl nonaflate **1a** (366.9 mg, 1.002 mmol), Pd(OAc)$_2$ (11.4 mg, 0.051 mmol). The pure product was furnished as a mixture of regioisomers (*E*)-**3e** and **4e** in the ratio of (93:7) as a colourless solid (146.5 mg, 86% yield).



(*E*)-**3e**

Analytical data match well those described in literature.[14f]

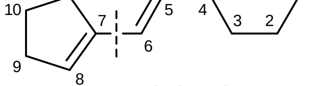


4e

NMR (selected signals): ^{1}H (CDCl$_3$, 400 MHz), δ = 5.07 (br.s, 1 H, =CH$_2$), 5.07 (br.s, 1 H, =CH$_2$), 5.58 (m$_c$, 1 H, C*H*=C). ^{13}C (CDCl$_3$, 100.65 MHz), δ = 113.6 (=CH$_2$).

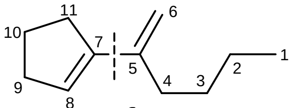
Synthesis of (*E*)-1-hex-1-enyl-cyclopentene (*E*)-3f, 1-hex-1-en-2-yl-cyclopentene 4f and 1-hex-2-enyl-cyclopentene

The synthesis was carried out according to the general procedure. NEt$_3$ (207.5 mg, 2.050 mmol), 1-hexene **2f** (113 mg, 1.343 mmol), cyclopentenyl nonaflate **1a** (367.8 mg, 1.004 mmol), Pd(OAc)$_2$ (11.2 mg, 0.049 mmol). Flash chromatography with n-pentane furnished the product as a mixture of regioisomers (*E*)-**3f**,[26] **4f** and 1-hex-2-enyl-cyclopentene (ratio: 56:31:13) (127.0 mg, 84% yield) as a slightly yellowish oil.



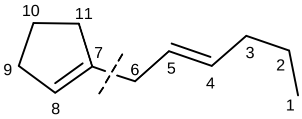
(*E*)-**3f**

^{13}C (CDCl$_3$, 100.65 MHz): δ = 13.96 (1-Me), 22.28 and 23.13 (2- and 10-CH$_2$), 31.40, 31.70, 32.55 and 32.69 (3-, 4-, 9- and 11-CH$_2$), 126.91, 128.06 and 131.31 (5-, 6- and 8-CH), 142.71 (7-C).



4f

^{13}C ($CDCl_3$, 100.65 MHz): δ = 14.02 (1-Me), 22.75 and 23.12 (2- and 10-CH_2), 31.24, 32.72, 33.32 and 33.89 (3-, 4-, 9- and 11-CH_2), 111.01 (6-CH_2), 126.77 (8-CH), 143.60 and 144.74 (5- and 7-C).

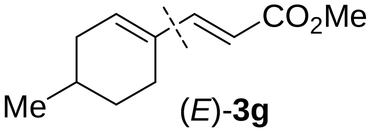


1-hex-2-enyl-cyclopentene

^{13}C ($CDCl_3$, 100.65 MHz): δ = 13.68 (1-Me), 22.66 and 23.42 (2- and 10-CH_2), 32.49, 34.62 (double int.) and 35.10 (3-, 6-, 9- and 11-CH_2), 123.70, 127.74 and 131.42 (4-, 5- and 8-CH), 144.03 (7-C).

A mixture of all three isomers (56:31:13). ^{1}H NMR (C_6D_6, 400 MHz): δ = 0.86 (t, ^3J = 7.1 Hz, 3 H, Me, L), 0.87 (t, ^3J = 7.4 Hz, 3 H, Me, S), 0.89 (t, ^3J = 7.4 Hz, 3 H, Me, M), 1.22–1.37 (m), 1.52 (m_c, 2 H, CH_2, M), 1.73–1.85 (m), 1.96 (m_c, 2 H, 3-CH_2, S), 2.06 (m_c, 2 H, 4-CH_2, L), 2.22 (m_c, 2 H, CH_2, S), 2.28–2.36 (m), 2.38–2.48 (m), 2.78 (br. d, ^3J = 6.4 Hz, 2 H, 6-CH_2, S), 4.97 and 5.00 (both br. s, 1 H, 6-CH_2, M) 5.40–5.61 (m), 5.71 (m_c, 1 H, 8-CH, M), 6.36 (d, *J* = 15.6 Hz, 1 H, C*H*=CH).

Synthesis of (*E*)-methyl 3-(4-methylcyclohex-1-enyl) acrylate (*E*)-3g

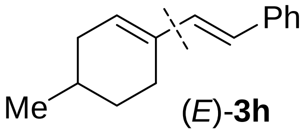


(*E*)-**3g**

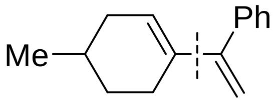
The synthesis was carried out according to the general procedure: NEt_3 (206.5 mg, 2.040 mmol), methyl acrylate **2a** (114.0 mg, 1.324 mmol), 4-methylcyclohex-1-enyl nonafluorobutanesulfonate **1b** (396.5 mg, 1.005 mmol), $Pd(OAc)_2$ (11.2 mg, 0.049 mmol). After column chromatography, the pure product (*E*)-**3g** was obtained as a white solid (179.5 mg, 98% yield). M_p = (34-35)°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.98 (d, ^3J = 6.6 Hz, 3 H, Me), 1.27 (dtd, ^2J = 13.0 Hz, ^3J = 10.8, 5.8 Hz, 1 H, CH_{ax} of CH_2), 1.69 (m_c, 1 H, C*H*), 1.77–1.87 (m, 2 H, CH_2), 2.07–2.18 (m, 1 H, C*H* of CH_2), 2.20–2.34 (m, 2 H, CH_2), 3.74 (s, 3 H, OMe), 5.76 (d, ^3J = 15.8 Hz, 1 H, CH=C*H*CO_2Me), 6.14 (m_c, 1 H, C*H*=C), 7.30 (d, ^3J = 15.8 Hz, 1 H, C*H*=CHCO_2Me). ^{13}C ($CDCl_3$, 100.65 MHz): δ = 21.5 (Me), 24.1 (CH_2), 28.2 (CH), 30.3 and 34.9 (both CH_2), 51.4 (OMe), 114.3, (CH), 134.6 (CH=*C*), 138.5 and 148.0 (both CH), 168.1 (C=O). IR (KBr): $\tilde{\nu}$ = 3010 cm^{-1} (=C–H), 2950, 2865 cm^{-1} (C–H), 1715 cm^{-1} (C=O), 1635 cm^{-1} (C=C). MS (EI, 80 eV): m/z (%) = 180 (M^+, 14), 165 ([M^+ – CH_3], 61), 121 ([M^+ – CO_2CH_3], 100). HRMS: calcd. for $C_{11}H_{16}O_2$ (M^+) 180.1150, found 180.115039. C,H-analysis (%): calcd. for $C_{11}H_{16}O_2$ (180.224): C, 73.30; H, 8.95; O, 17.75; found C, 72.88; H, 8.84.

Synthesis of (*E*)-1-[2-(4-methylcyclohex-1-enyl)ethenyl]benzene (*E*)-3h and 1-[1-(4-methylcyclohex-1-enyl)ethenyl]benzene 4h

The synthesis was carried out according to the general procedure. NEt_3 (205.0 mg, 2.026 mmol), styrene (139.8 mg, 1.342 mmol), nonaflate **1b** (401.0 mg, 1.017 mmol), $Pd(OAc)_2$ (11.2 mg, 0.049 mmol). Flash chromatography with n-pentane furnished the product as a mixture of the regioisomers (*E*)-**3h** and **4h** (84:16 ratio, 198.6 mg, 98% yield) as a colorless oil.

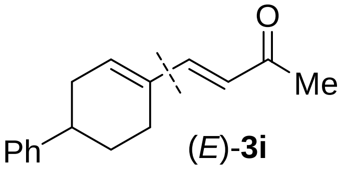

(E)-**3h**

^{1}H NMR (CDCl$_3$, 400 MHz): δ = 0.98 (d, ^3J = 6.7 Hz, 3 H, Me), 1.24–1.35 (m, 1 H), 1.64–1.85 (m, 3 H), 2.15–2.32 (m, 2 H), and 2.32–2.42 (m, 1 H) (3 CH$_2$ and MeCH), 5.85 (m$_c$, 1 H, CH=C), 6.42 (d, ^3J = 16.2 Hz, CH=CH), 6.77 (d, ^3J = 16.2 Hz, CH=CH), 7.14–7.19 (m, 1 H, CH_p, Ph), 7.26–7.31 (m, 2 H, CH_m, Ph), 7.37–7.40 (m, 2 H, CH_o, Ph). ^{13}C (CDCl$_3$, 100.65 MHz): δ = 21.71 (Me), 24.5 (CH$_2$), 28.6 (MeCH), 30.7 (CH$_2$), 34.6 (CH$_2$), 124.8 (CH), 126.1 and 128.5 (CH$_m$ and CH$_o$), 126.8 (CH), 130.3 (CH), 132.3 (CH), 135.4 (C), 138.0 (C). IR (film): $\tilde{\nu}$ = 3025, 2950, 2920, 2870 cm^{-1} (=C–H, C–H), 1635, 1600 cm^{-1} (C=C). MS (EI, 80 eV): m/z (%) = 198 (M$^+$, 100), 183 ([M$^+$ – CH$_3$], 25), 91 (53). HRMS: calcd. for C_{15}H18 (M$^+$) 198.1409, found 198.140850. C,H-analysis (%): calcd. for C_{15}H18 (198.303): C, 90.85; H, 9.15; found C, 90.71; H, 9.06.


4h

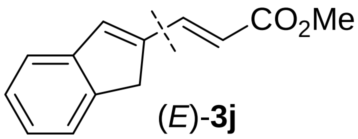
NMR (selected signals): ^{1}H NMR (CDCl$_3$, 400 MHz), δ = 0.97 (d, ^3J = 7 Hz, 3 H, Me), 4.98 (1 H) and 5.18 (1 H) (both br.s, CH_2=C), 5.58 (m$_c$, 1 H, CH=C). ^{13}C (CDCl$_3$, 100.65 MHz), δ = 21.70 (Me), 26.4 (CH$_2$), 28.2 (MeCH), 31.1 (CH$_2$), 34.0 (CH$_2$), 111.1 (CH$_2$=C), 126.9 (CH), 127.8 and 128.7 (CH$_m$ and CH$_o$), 128.6 (CH), 136.7 (C), 142.1 (C), 151.4 (C=CH$_2$). IR (film): $\tilde{\nu}$ = 3025, 2950, 2920, 2870 cm^{-1} (=C–H, C–H), 1635, 1600 cm^{-1} (C=C). MS (EI, 80 eV): m/z (%) = 198 (M$^+$, 100), 183 ([M$^+$ – CH$_3$], 25), 91 (53). HRMS: calcd. for C_{15}H18 (M$^+$) 198.1409, found 198.140850. C,H-analysis (%): calcd. for C_{15}H18 (198.303): C, 90.85; H, 9.15; found C, 90.71; H, 9.06.

Synthesis of (*E*)-4-(4-phenylcyclohex-1-enyl) but-3-en-2-one (*E*)-3i


(E)-**3i**

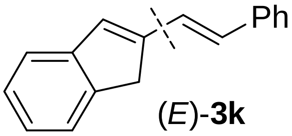
The synthesis was carried out according to the general procedure: NEt$_3$ (205.3 mg, 2.029 mmol), methyl vinyl ketone **2c** (95.5 mg, 1.362 mmol), 4-phenylcyclohex-1-enyl nonafluorobutanesulfonate **1c** (458.7 mg, 1.005 mmol), Pd(OAc)$_2$ (11.3 mg, 0.050 mmol). After column chromatography (hexane : EtOAc = 5 : 1), the pure product (E)-**3i**[27] was obtained as a slightly yellowish solid (222.8 mg, 98% yield). ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.76–1.87 (m, 1 H), 2.04–2.11 (m, 1 H), 2.25–2.42 (m, 3 H), and 2.50–2.59 (m, 1 H) (all CH$_2$), 2.30 (s, 3 H, Me), 2.80–2.88 (m, 1 H, PhCH), 6.09 (d, ^3J = 16.1 Hz, 1 H, C(O)CH=CH), 6.29–6.32 (m, 1 H, CH=C), 7.16–7.24 (m, 4 H, C(O)CH=CH and 3CH_{Ph}), 7.29–7.34 (m, 2 H, 2CH_{Ph}). ^{13}C (CDCl$_3$, 100.65 MHz): 24.7 (CH$_2$), 27.3 (Me), 29.2 (CH$_2$), 34.5 (CH$_2$), 39.7 (PhCH), 124.7 (CH), 126.3 (CH), 126.7 and 128.5 (CH$_m$ and CH$_o$), 135.0 (C), 138.9 (CH), 145.9 (C), 146.2 (CH), 198.9 (C=O).

Synthesis of (*E*)-methyl 3-(1*H*-inden-2-yl) acrylate (*E*)-3j


(E)-**3j**

The synthesis was carried out according to the general procedure: NEt$_3$ (204.2 mg, 2.018 mmol), methyl acrylate **2a** (118.0 mg, 1.370 mmol), 1H-inden-2-yl nonafluorobutanesulfonate **1d** (422.8 mg, 1.020 mmol), Pd(OAc)$_2$ (11.1 mg, 0.049 mmol). The pure product (*E*)-**3j** was obtained as an ochre coloured solid (189.6 mg, 93% yield), mp 103–104°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.57 (br.s, 2 H, CH_2), 3.79 (s, 3 H, OMe), 6.08 (d, ^3J = 15.6 Hz, 1 H, CH=C*H*CO_2Me), 7.11 (br.s, 1 H, C*H*=C), 7.23–7.30 (m, 2 H, 2 CH_{Ar}), 7.39–7.42 (m, 1 H, CH_{Ar}), 7.43–7.46 (m, 1 H, CH_{Ar}), 7.70 (d, ^3J = 15.6 Hz, 1 H, C*H*=$CHCO_2$Me). ^{13}C ($CDCl_3$, 100.65 MHz): δ = 37.1 (CH_2), 51.6 (OMe), 117.8, 122.1, 124.0, 126.7, 126.9, 138.4, and 140.1 (*C*H=*C*H and all *C*H_{Ar}), 143.50, 143.52, and 144.0 (all C), 167.6 (C=O). IR (KBr): $\tilde{\nu}$ = 3025, 2950, 2920, 2870 cm^{-1} (=C–H, C–H), 1635, 1600 cm^{-1} (C=C). MS (EI, 80 eV): m/z (%) = 198 (M^+, 100), 183 ([M^+ – CH_3], 25), 91 (53). HRMS: calcd. for $C_{13}H_{12}O_2$ (M^+) 200.0837, found 200.083740. C,H-analysis (%): calcd. for $C_{13}H_{12}O_2$ (200.233): C, 77.98; H, 6.04; O, 15.98; found C, 90.71; H, 9.06

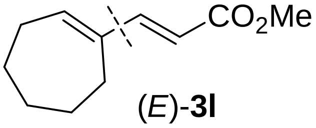
Synthesis of 2-(2-phenylethenyl)-1*H*-indene (*E*)-3k



(*E*)-**3k**

The synthesis was carried out according to the general procedure: NEt_3 (206.8 mg, 2.043 mmol), styrene **2e** (140.0 mg, 1.344 mmol), 1*H*-inden-2-yl nonafluorobutanesulfonate **1d** (421.0 mg, 1.016 mmol), $Pd(OAc)_2$ (11.2 mg, 0.049 mmol). The pure product (*E*)-**3k**[28] was obtained as a yellowish solid (208.4 mg, 94% yield). H NMR ($CDCl_3$, 400 MHz): δ = 3.65 (s, 2 H, CH_2), 6.77 (d, ^3J = 16.2 Hz, 1 H, CH=C*H*), 6.83 (br.s, 1 H, C*H*=C), 7.14–7.26 (m, 4 H), 7.31–7.36 (m, 3 H), 7.40–7.43 (m, 1 H), and 7.45–7.49 (m, 2 H) (all CH_{Ar}, CH_{Ph} and CH=C*H*). ^{13}C ($CDCl_3$, 100.65 MHz): δ = 37.4 (CH_2), 120.9, 123.6, 124.9, and 125.0 (all CH), 126.4 and 128.7 (*C*H_m and *C*H_o), 126.6, 127.5, 129.4, and 131.4 (all CH), 137.3, 142.8, 145.2, and 146.3 (all C).

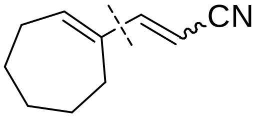
Synthesis of (*E*)-methyl 3-cyclohept-1-enyl acrylate (*E*)-3l



(*E*)-**3l**

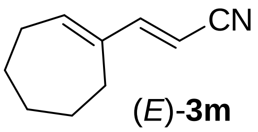
The synthesis was carried out according to the general procedure: NEt_3 (203.5 mg, 2.011 mmol), methyl acrylate **2a** (118.9 mg, 1.381 mmol), cyclohept-1-enyl nonafluorobutanesulfonate **1e** (394.3 mg, 1.0 mmol), $Pd(OAc)_2$ (11.1 mg, 0.049 mmol). Column chromatography furnished the product (*E*)-**3l** (179.0 mg, 92% yield) as a colourless oil. Analytical data match well those described in literature.[14f]

Synthesis of 3-cyclohept-1-enyl-acrylonitrile (*E/Z*)-3m



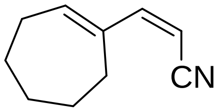
(*E/Z*)-**3m**, *E/Z* = 67:33

The synthesis was carried out according to the general procedure: NEt_3 (204.6 mg, 2.022 mmol), acrylonitrile **2b** (76.0 mg, 1.432 mmol), cyclohept-1-enyl nonafluorobutanesulfonate **1e** (395.7 mg, 1.003 mmol), $Pd(OAc)_2$ (11.3 mg, 0.050 mmol). Kugelrohr distillation at 100°C (5.0 mbar) furnished the product **3m**[14e] (127.8 mg, 87% yield, *E/Z*-ratio 67:33) as a colorless oil.



(*E*)-**3m**

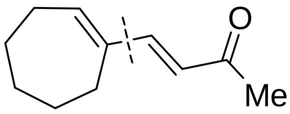
^{1}H NMR (C_6D_6, 400 MHz): δ = 1.10–1.25 (m, 4 H, 2 CH_2), 1.36–1.47 (m, 2 H, CH_2), 1.67 (m_c, 2 H, CH_2), 1.81 (m_c, 2 H, CH_2), 4.56 (d, ^3J = 16.4 Hz, 1 H, CH=C*H*CN), 5.55 (t, ^3J = 6.8 Hz, 1 H, C*H*=C), 6.44 (d, ^3J = 16.4 Hz, 1 H, C*H*=CHCN). ^{13}C ($CDCl_3$, 100.65 MHz): δ = . 25.6, 25.93, 26.4, 29.0, and 31.5 (all CH_2), 92.3 (=*C*HCN), 119.1 (CN), 141.5 (*C*=CH), 144.7 (CH), 154.5 (CH).



(*Z*)-**3m**

^{1}H NMR (C_6D_6, 400 MHz): δ = 1.10–1.25 (m, 2 H, CH_2), 1.36–1.47 (m, 4 H, 2 CH_2), 1.86 (m_c, 2 H, CH_2), 2.57 (m_c, 2 H, CH_2), 4.42 (d, ^3J = 12.1 Hz, 1 H, CH=C*H*CN), 5.85 (t, ^3J = 6.8 Hz, 1 H, C*H*=C), 5.90 (d, ^3J = 12.1 Hz, 1 H, C*H*=CHCN). ^{13}C ($CDCl_3$, 100.65 MHz): δ = 25.8, 25.96, 28.5, 28.8, and 31.6 (all CH_2), 90.9 (=*C*HCN), 117.5 (CN), 142.1 (*C*=CH), 144.6 (CH), 152.8 (CH).

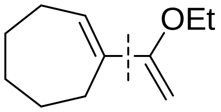
Synthesis of (*E*)-3-cyclohept-1-enyl but-3-en-2-one (*E*)-3n



(*E*)-**3n**

The synthesis was carried out according to the general procedure. NEt_3 (204.0 mg, 2.016 mmol), methyl vinyl ketone **2c** (91.9 mg, 1.311 mmol), cyclohept-1-enyl nonafluorobutanesulfonate **1e** (395.0 mg, 1.002 mmol), $Pd(OAc)_2$ (11.2 mg, 0.049 mmol). Kugelrohr distillation at 80°C (0.026 mbar) furnished the product (*E*)-**3n**[29] (154.8 mg, 94% yield) as a colourless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.50–1.57 (m, 4 H, 2CH_2), 1.76–1.82 (m, 2 H, CH_2), 2.28 (s, 3 H, Me), 2.29–2.36 (m, 4 H, 2CH_2), 6.10 (d, ^3J = 16.0 Hz, 1 H, C(O)C*H*=CH), 6.36 (t, ^3J = 6.8 Hz, 1 H, C*H*=C), 7.12 (d, ^3J = 16.0 Hz, 1 H, C(O)CH=C*H*). ^{13}C ($CDCl_3$, 100.65 MHz): δ = 25.9, 26.2 and 27.1 (all CH_2), 27.4 (Me), 29.3 and 31.9 (both CH_2), 124.2 (CH), 142.3 (*C*=CH), 144.9 and 148.1 (both CH), 199.0 (C=O).

Synthesis of 1-(1-ethoxyethenyl)cycloheptene 4o



4o

The synthesis was carried out according to the general procedure: NEt_3 (207.1 mg, 2.046 mmol), ethyl vinyl ether **2d** (102.5 mg, 1.421 mmol), cyclohept-1-enyl nonafluorobutanesulfonate **1e** (396.8 mg, 1.006 mmol), $Pd(OAc)_2$ (11.2 mg, 0.049 mmol). Kugelrohr distillation at 70°C (1.1 mbar) furnished the product **4o** (152.2 mg, 91% yield) as a slightly yellowish oil. ^{1}H NMR (C_6D_6, 400 MHz): δ = 1.11 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$*Me*), 1.37–1.43 (m), 1.48–1.53 (m), 1.60–1.66 (m), 2.12 (m_c) and 2.41 (m_c) (all CH_2), 3.53 (q, ^3J = 7.0 Hz, 2 H, OC*H*$_2$Me), 4.00 (d, ^2J = 2.2 Hz, 1 H, =CH_2), 4.36 (d, ^2J = 2.2 Hz, 1 H, =CH_2), 6.67 (t, ^3J = 7.0 Hz, 1 H, C*H*=C). ^{13}C NMR (C_6D_6, 100.65 MHz): δ = 14.7 (OCH$_2$*Me*), 26.86, 26.88, 28.5, 29.5 and 32.7 (all CH_2), 63.0 (O*C*H$_2$Me), 81.2 (=CH_2), 129.9 (C=*C*H), 140.6 (*C*=CH), 162.6 (*C*=CH_2). IR (film): $\tilde{\nu}$ = 2930, 2860 cm^{-1} (=C–H, C–H), 1665 cm^{-}

^{1} (C=C). MS (EI, 80 eV): m/z (%) = 166 (M^+, 5), 151 ([M^+ – Me], 100), 138 ([$M^+ – C_2H_4$], 30) 123 (56). HRMS: calcd. for $C_{11}H_{18}O$ (M^+) 166.1358, found 166.135770. C,H-analysis (%): calcd. for $C_{11}H_{18}O$ (166.26): C, 79.46; H, 10.91; O, 9.62; found C, 79.06; H, 10.84.