Nickel(II) Compounds Derived from *tripod* Ligands: Efficient Catalysts for the Stereoselective Heterodimerization of Styrene and Propene

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Dedicated to Professor Günter Helmchen[‡]

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The *tripod* ligands $RCH_2C(CH_2X)(CH_2Y)(CH_2Z)$ form tetracoordinate compounds with $NiHal_2$. If two of the donor functions X, Y, Z are phosphanes, square-planar coordination is observed. In contrast, donor sets X,Y,Z = P,N,N or N,N,N form tetrahedral compounds, by *P*,*N* or *N*,*N* coordination, that are active in the catalysis of olefin oligomerization with MAO as a co-catalyst. These catalyst systems are also active in the stereoselective heterodimerization of olefins. The co-dimerization of styrene and propene by these systems leads to 4-phenyl-2-pentene almost exclusively, with regioselectivities up to 98% and (*E*)/(*Z*) ratios of up to 95:5, surpassing other reported catalysts for this process. The products of these catalytic transformations have been fully characterized by GC/MS techniques as well by isolation, NMR and MS characterization of the pure compounds.

Introduction

Transition metal catalysed heterodimerization of olefins is a versatile method of carbon−carbon bond formation.[1,2] The co-dimerization of styrene and ethene has been much studied since its first report in 1965.[3] Many transition metals are active in this process[4,5] but catalysts containing nickel are the most active ones.[2,6,7] They could even be developed into systems that allow the enantioselective hydrovinylation of styrene.[7] Conversely, the long-standing problem of co-dimerizing styrene with propene[4a,5b,8] has only been partially solved.[7d,7e] The major prerequisite for an effective catalyst in this process appears to be a hemilabile co-ligand.[9]

Nickel(II) compounds containing P,N- or N,N-bonded chelate ligands are promising candidates as precatalysts in this type of reaction. The recent synthesis[10] of $(R'CH_2)(CH_2Z)C(CH_2\text{-}\kappa^1\text{-}X)(CH_2\text{-}\kappa^1\text{-}Y)NiHal_2$ compounds derived from potential *tripod* ligands $R'CH_2C(CH_2X)(CH_2Y)(CH_2Z)$ (R′ = H, OMe; X, Y, Z = PR_2, NR_2) has prompted the study of their catalytic properties as co-dimerization catalysts. The results of such a study are reported here.

Results and Discussion

The propensity of *tripod*-derived nickel(II) chelate compounds to act as precatalysts in styrene olefin co-dimerization was tested for compounds **1**−**5** (Scheme 1).

An initial check as to whether the compounds − when activated with MAO − lead to catalysts for ethene oligomerization[11] found that none of the compounds containing two phosphane donors in the chelate cycle (**5a**−**5d**) was active. However, compounds containing a P,N or an N,N donor set in the chelate cycle (**1**−**4**) are active as oligomerization catalysts. The ethene oligomers formed were soluble in toluene. GC/MS analysis of the toluene solution and of the gaseous phase revealed a broad distribution of oligomers up to an oligomerization degree around $n = 12$ with the expected decay of the respective yields with increasing degree of oligomerization (Scheme 2).

The oligomerization process is not stereoregular: instead of one single GC/MS peak at each oligomerization degree n, a pattern of overlapping peaks is observed, all of which correspond to the same mass number.

This first test with ethene as a substrate showed that compounds **1**−**4** − containing hemilabile P,N- and N,N-bonded chelates − are candidates as potential precatalysts of olefin co-dimerization. The next test therefore probed the activity of these compounds in the presence of MAO for propene dimerization.[12] The test was limited to **1a**, which was found to promote the dimerization of propene with more than 90% of the product being 2-methyl-1-pentene (Scheme 3). This product was isolated by distillation and

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[‡] As a late contribution to his 60th birthday.

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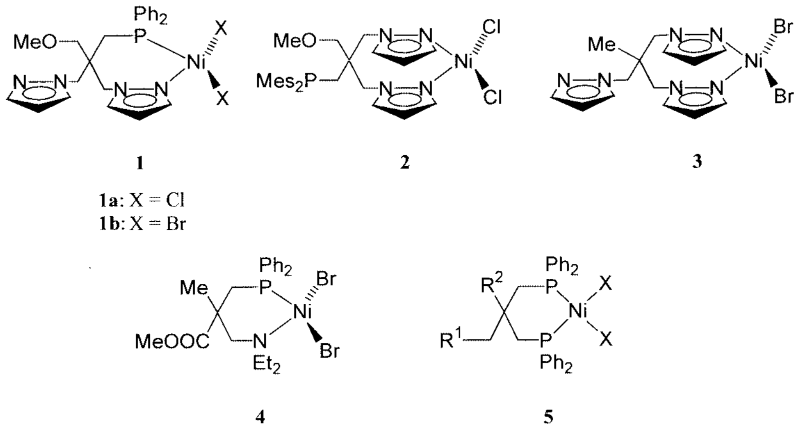


1 **2** **3**

1a: X = Cl
1b: X = Br

4 **5**

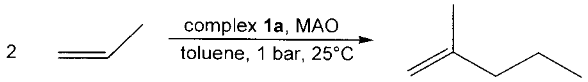
5a: R^1 = H R^2 = Me X = Cl
5b: R^1 = NEt_2 R^2 = Me X = Cl
5c: R^1 = pz R^2 = CH_2OMe X = Cl
5d: R^1 = pz R^2 = CH_2OMe X = Br

Scheme 1

$$n\ H_2C{=}CH_2 \xrightarrow[\text{toluene, 1 bar, 25°C}]{\text{precatalyst, MAO}} (C_2H_4)_n \qquad n = 2 - 12$$

precatalyst = any of the compounds **1-4**

Scheme 2



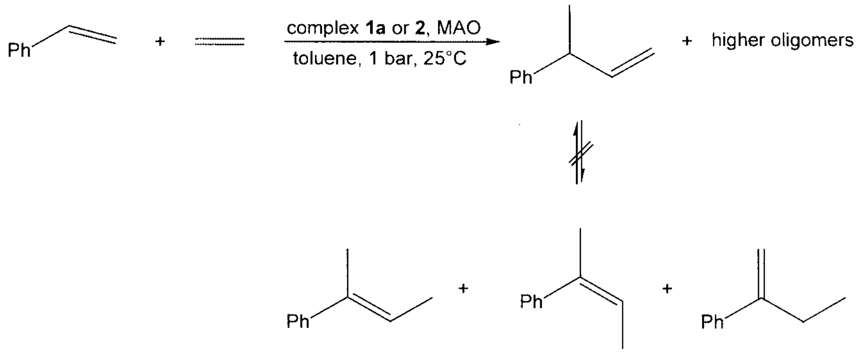
Scheme 3

identified unequivocally by 1D- and 2D-NMR spectroscopy (see Exp. Sect.).

This test shows that the catalytic process of dimerization is completely regioselective in this case.[13] Regioselectivity is an essential prerequisite for an effective heterodimerization catalyst. The next test was to analyse the potential catalytic dimerization of styrene and ethane with **1a** and **2** as precatalysts. The formation of heterodimers was observed in each case. From the many conceivable kinds of isomeric heterodimers only 3-phenyl-1-butene was formed (Scheme 4). The catalytic process was run until all styrene had been consumed (18 h, 0.1 mol % precatalyst). GC/MS analysis of the products showed that only around 30% of the products consisted of the dimer, while the rest were trimers or tetramers with all combinations of constituting olefins being present. However, no styrene dimer was observed.

These findings show that regioselective hydrovinylation of styrene is catalysed by the systems tested. They also demonstrate that the catalyst systems are too active since they activate the heterodimer for further C−C bond formation.

Consequently, the codimerization of *p*-chlorostyrene and ethene was analysed using **1a** and MAO as precatalyst system. This substituted styrene should be a less active olefin than styrene, such that the formation of oligomers containing more than one *p*-chlorostyrene moiety should be suppressed. It was observed that the catalyst system is still active with these components. The reaction is, however, much slower than with styrene, such that after 18 h (0.4 mol % precatalyst) only 45% of *p*-chlorostyrene had reacted. The almost exclusive product of this reaction is the heterodimeric compound 3-(*p*-chlorophenyl)-1-butene (Scheme 5). A very minor amount of a trimer composed of one *p*-chlorostyrene and two ethene moieties is formed. Thus, the



Scheme 4

selectivity of the catalyst system for the formation of heterodimers increases with decreasing activity of the olefinic partners.

All the above tests give credit to the idea that styrene and propene might be the proper choice of olefins to be codimerized by the above catalyst systems.

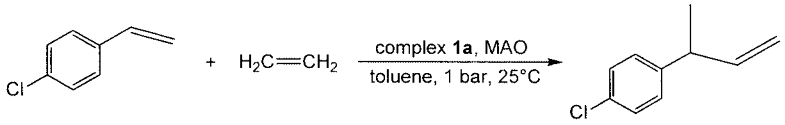
As a precatalyst for the heterodimerization of styrene and propene the system $[(\eta^3\text{-allyl})\text{NiBr}]_2/\text{PPh}_3/\text{AgOTf}$ has been described recently.[7e] This reaction was run in CH_2Cl_2 at −20 °C to give the co-dimerization products in more than 90% yield based on styrene.

A catalyst system composed of P,N or N,N chelate compounds **1−4** and MAO in toluene gives good yields of the desired dimers even at room temperature (see Scheme 6). The identity of the heterodimers was proved beyond doubt by their isolation, by distillation, and a combination of mass spectra, 1D- and 2D-NMR experiments (see Exp. Sect.).

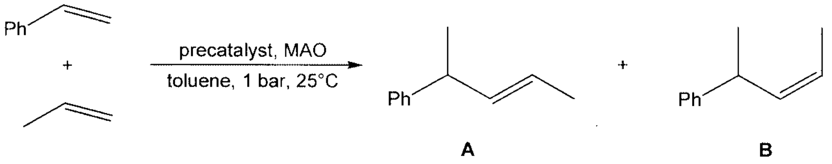
The regioselectivity of this process − depending on the reaction conditions − is up to 98%, corresponding to the almost exclusive formation of 4-phenyl-2-pentene[14] (**A**, **B**) as the dimerization products. The (*E*) isomer is the predominant compound in each case, with (*E*)/(*Z*) ratios (**A/B**) between 89:11 and 95:5 depending on the catalyst and the reaction conditions. The observed regioselectivity (up to 98%) and stereoselectivities (up to 95:5) are higher than those reported for the $[(\eta^3\text{-allyl})\text{NiBr}]_2$ system (regioselectivity: 80%; stereoselectivity: 88:12).[7e]

The results of this analysis (Table 1) show that compounds that contain at least one nitrogen donor in the chelate cycle (Runs 1−10) are active as precatalysts, while none of the compounds that contain two phosphorus donors in their chelate cycle (Runs 11−14) show any activity.

The selectivity of the systems containing hemilabile P,N and N,N chelates (**1−4**) with respect to the formation of 4-phenyl-2-pentene (**A**, **B**) depends on the catalyst/substrate ratio (see Table 1). With 1.5 mol % of the catalyst (relative to styrene) up to 80% dimeric products are obtained. With lower catalyst/styrene ratios the yield of dimeric products decreases and is only around 20% for a ratio of 0.1 mol % (Table 1). The activities of the individual catalyst systems based on **1−4** are not too different in this process (Table 1).



Scheme 5



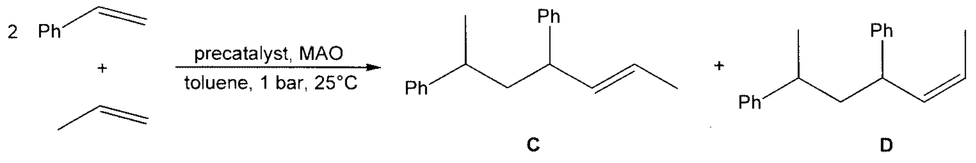
precatalyst = any of the compounds **1-4**

Scheme 6

Table 1. Catalytic activity of tripod compounds **1−5** in the heterodimerization of styrene and propene

Run[a]	Total yield[b] of dimers	Regioselectivity[c]	(*E*)/(Z) ratio of 3-phenyl-1-butene	Molar ratio catalyst/styrene	Coordinating donors of precatalyst		Precatalyst[d]
1	81%	85%	89:11	1.50 mol %	P,N	Br_2	**1b**
2	75%	88%	89:11	1.50 mol %	P,N	Cl_2	**1a**
3	56%	92%	90:10	0.75 mol %	P,N	Cl_2	**1a**
4	55%	97%	90:10	0.30 mol %	N,N	Cl_2	**2**
5	54%	89%	89:11	0.50 mol %	P,N	Br_2	**1b**
6	52%	95%	90:10	0.75 mol %	N,N	Br_2	**3**
7	29%	98%	95:5	0.10 mol %	N,N	Cl_2	**2**
8	22%	89%	89:11	0.10 mol %	P,N	Cl_2	**1**
9	21%	61%	90:10	0.75 mol %	P,N	Cl_2	**4**
10	19%	83%	89:11	0.10 mol %	P,N	Br_2	**1b**
11	−	−	−	0.75 mol %	P,P	Cl_2	**5a**
12	−	−	−	0.75 mol %	P,P	Cl_2	**5b**
13	−	−	−	0.75 mol %	P,P	Cl_2	**5c**
14	−	−	−	0.75 mol %	P,P	Br_2	**5d**

[a] Reaction time: 18 h; solvent: toluene; temperature: 25 °C; pressure: 1 bar. [b] Determined by GC/MS. [c] Regioselectivity towards 3-phenyl-1-butene (3-phenyl-1-butene/other dimers). [d] Co-catalyst: MAO.



precatalyst = any of the compounds **1**-**4**

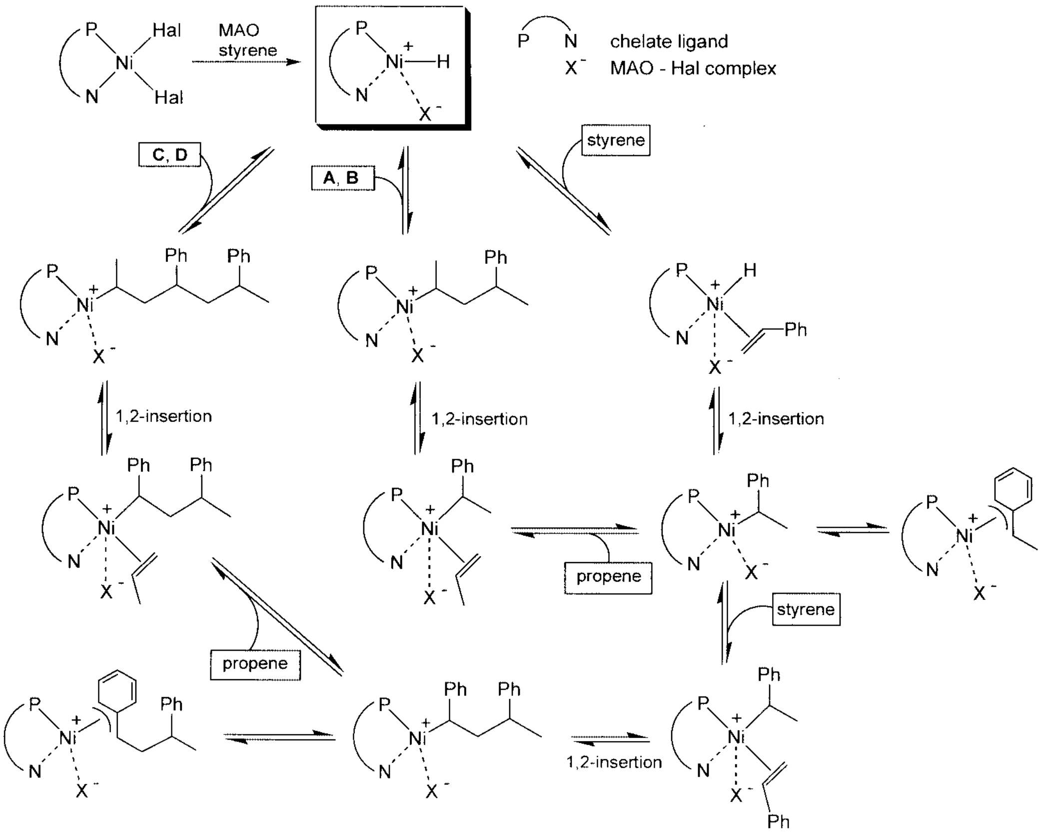
Scheme 7

Only **4**, which bears an Et_2N donor instead of a pyrazole donor (**1**−**3**), appears to be somewhat less reactive and less selective (Table 1). The reactivity of all systems is such that within 18 h styrene is quantitatively consumed, even if the molar ratio of catalyst/styrene is only 0.1 mol %.

In all experiments that lead to the catalytic formation of styrene/propene heterodimers (see Table 1), 4,6-diphenyl-2-heptene[15] is a by-product. This heterotrimer is composed of one propene and two styrene entities (**C**, **D**) (Scheme 7). The formation of **C** and **D** is completely regioselective. The (*E*)/(*Z*) ratio (**C**/**D**) is between 80:20 and 85:15 throughout, such that the reaction is also stereoselective in this respect. Both **C** and **D** were identified unequivocally by their isolation by distillation, and a combination of MS, 1D- and 2D-NMR experiments (see Exp. Sect.).

With "high" molar ratios of precatalyst/styrene (1.5 mol %), in addition to the trimer 4,6-diphenyl-2-heptene (**C**, **D**) other trimers composed of one styrene and two propene units are also formed, while with lower ratios (0.1−0.75 mol %) 4,6-diphenyl-2-heptene (**C**, **D**) is by far the predominant trimer (90−99%). The lowest percentage (65%) of **C** and **D** amongst these trimers was found with 1.5 mol % of **1b** as the precatalyst.

All the precatalysts **1**−**4** are paramagnetic nickel(II) compounds with a tetrahedral coordination around the metal atom. When the toluene solutions of these precatalysts are treated with MAO, these blue to violet tetrahedrally coordinated compounds turn red, which is characteristic of such diamagnetic square-planar nickel(II) compounds. This indicates that the substitution of the halide function by a methyl group occurs since the replacement of an Ni−Hal bond by an Ni−C bond in this type of compound leads to a transformation of tetrahedral into square-planar coordination due to the increased ligand field.[10b]



Scheme 8

All of the above observations may be rationalized by the mechanistic scheme shown in Scheme 8. In principle the scheme is similar to the accepted hypothesis concerning olefin oligomerization by nickel catalysts.[7a,7e] Activation of the precatalyst by MAO and its reaction with styrene leads to a coordinatively unsaturated cationic Ni−H species, which is able to add styrene. (The individual steps, which result in the activated Ni−H species, are shown in refs.[2,7a,7e]) Coordinative reactivity results from X^- being trapped by MAO and by the hemilability of the Ni−N coordination (dashed lines in Scheme 8). The usual sequence of insertion steps leads to 4-phenyl-2-pentene (**A**, **B**) when propene is added as the second olefin (inner circle of Scheme 8). When styrene is also added as the second olefin the sequence shown in the outer circle of Scheme 8 leads to the formation of 4,6-diphenyl-2-heptene (**C**, **D**) provided that propene is the third olefinic constituent taken up by the catalyst. The observed regioselectivity is in complete agreement with this scheme. All routes incorporate 1,2-insertions as crucial steps, from which the observed regioselectivity follows as a natural consequence.

Conclusion

The *tripod* ligands $RC(CH_2X)(CH_2Y)(CH_2Z)$ (X,Y,Z = P,N,N or N,N,N) coordinate to $NiHal_2$ in a bidentate mode, resulting in tetrahedral nickel(II) compounds that are active as precatalysts (co-catalyst: MAO) in the heterodimerization of styrene and propene. The current results indicate that the yield of dimeric products and the selectivity of the catalysts may be further increased by optimising the reaction conditions (i.e. styrene/precatalyst ratio, reaction temperature, solvent). The yield of dimeric products reached so far is up to 80% with regioselectivities of up to 98% and stereoselectivities of up to 95%.

Pyrazole as a nitrogen donor in *tripod* ligands has been found to promote this selectivity, while the third non-coordinated donor function, serving as a dangling arm, has no major influence on the catalytic activities. This finding should stimulate further experiments in which different groups at the dangling arm are introduced to either change the solubility of the precatalysts or to fix them on a support.

Experimental Section

General Remarks: All (hetero)dimerization reactions were carried out under moisture- and oxygen-free conditions by means of standard Schlenk techniques. The Schlenk flasks were equipped with a gas balloon. All solvents were dried by standard methods[16] and distilled under argon. Complexes **1**−**5** were prepared according to literature procedures.[10] Ethene, propene, styrene, *p*-chlorostyrene, MAO (10% solution in toluene), and dodecane were purchased from Aldrich and were used without further purification. NMR: Bruker Avance DPX 200 at 200.12 MHz (^1H); 50.323 MHz ($^{13}C\{^1H\}$); $T = 303$ K; chemical shifts (δ) in ppm with respect to $CDCl_3$ (^1H: δ = 7.27 ppm; ^{13}C: δ = 77.0 ppm) as internal standard. GC/MS: Agilent 6890 (GC) interfaced to an Agilent 5973N (MS) equipped with an HP-5MS capillary column (30 m long, 0.25 mm inner diameter) with helium as carrier gas. Yields of the products (Table 1) refer to dodecane as internal standard.

Typical Procedure for the (Hetero)dimerization Reaction: Styrene (500−2000 mg), precatalyst **1**−**4** (5.0−20.0 mg; 0.1−1.5 mol %), and dodecane (200 mg) as internal standard were dissolved in toluene (25 mL) at 25 °C. MAO (3.0 mL of a 10% solution in toluene) was then added to the reaction mixture, and the solution immediately turned from violet to red. Ethene or propene (1 bar), respectively, was then introduced into the catalyst solution and the resultant reaction mixture was stirred at 25 °C for 18 h under ethene or propene (1 bar), respectively. For GC/MS analysis the reaction mixture (0.5 mL) was quenched with a solution of half-concentrated HCl (20 mL) and diethyl ether (20 mL). The aqueous phase was extracted with diethyl ether (20 mL). The combined organic layers were washed with brine and dried with $MgSO_4$. For preparative isolation of the oligomerization products the same type of workup procedure was applied in an appropriately scaled-up version. After removing the solvent, the following products were isolated by Kugelrohr distillation:

2-Methyl-1-pentene: ^1H NMR ($CDCl_3$): δ = 1.04 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3), 1.51−1.62 (m, 2 H, CH_2CH_3), 1.75 (s, 3 H, $=CCH_3$), 2.10 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, $=CCH_2$), 4.80 (br. s, 2 H, $=CH_2$) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.2 (s, CH_2CH_3), 20.5 (s, CH_2CH_3), 23.1 (s, $=CCH_3$), 40.4 (s, $=CCH_2$), 110.2 (s, $=CH_2$), 137.8 (s, $=C_q$) ppm. MS (EI): *m/z* (%) = 84 (34) [M^+], 69 (100) [$M^+ - CH_3$], 55 (13) [$M^+ - CH_2CH_3$]. B.p. 60 °C (1013 mbar).

3-Phenyl-1-butene: ^1H NMR ($CDCl_3$): δ = 1.37 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 3.45−3.61 (m, 1 H, PhC*H*), 5.01−5.09 (m, 2 H, $=CH_2$), 5.98−6.07 (m, 1 H, $=CH$), 7.19−7.30 (m, 5 H, aromat. *H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.1 (s, CH_3), 43.7 (s, PhCH), 113.3 (s, $=CH_2$), 125.9−145.5 (m, aromat. *C*), 143.8 (s, $=CH$) ppm. MS (EI): *m/z* (%) = 132 (25) [M^+], 117 (100) [$M^+ - CH_3$], 91 (25) [$C_7H_7^+$], 77 (18) [$C_6H_5^+$], 65 (10) [$C_5H_5^+$], 51 (22) [$C_4H_3^+$]. B.p. 30 °C (0.1 mbar).

(*E*)-4-Phenyl-2-pentene (A): ^1H NMR ($CDCl_3$): δ = 1.46 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, $PhCHCH_3$), 1.80 (d, $^3J_{H,H}$ = 6.2 Hz, 3 H, $=CHCH_3$), 3.54 (quint, $^3J_{H,H}$ = 6.9 Hz, 1 H, PhC*H*), 5.51−5.68 (m, 1 H, $CH_3CH=$), 5.76 (dd, $^3J_{H,H}$ = 6.8, $^3J_{H,H}$ = 15.2 Hz, 1 H, $CHCH=$), 7.24−7.44 (m, 5 H, aromat. *H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.1 (s, $=CHCH_3$), 21.8 (s, $PhCHCH_3$), 42.9 (s, PhCH), 124.0 (s, $CH_3CH=$), 126.3−128.7 (m, aromat. *C*), 136.8 (s, $CHCH=$) ppm. MS (EI): *m/z* (%) = 146 (22) [M^+], 131 (100) [$M^+ - CH_3$], 116 (14) [$M^+ - 2CH_3$], 91 (31) [$C_7H_7^+$], 77 (10) [$C_6H_5^+$]. B.p. 35−40 °C (0.1 mbar).

(*E*)-4,6-Diphenyl-2-heptene (C): ^1H NMR ($CDCl_3$): δ = 1.39 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, $PhCHCH_3$), 1.83 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H, $=CHCH_3$), 2.01−2.21 (m, 2 H, CH_2), 2.87 (sext, 1 H, $^3J_{H,H}$ = 7.2 Hz, $PhCHCH_3$), 3.25 (q, $^3J_{H,H}$ = 7.6 Hz, 1 H, $PhCHCH=$), 5.55−5.61 (m, 1 H, $CH_3CH=$), 5.76 (dd, $^3J_{H,H}$ = 7.9, $^3J_{H,H}$ = 15.0 Hz, 1 H, $PhCHCH=$), 7.25−7.47 (m, 10 H, aromat. *H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.2 (s, $=CHCH_3$), 23.0 (s, $PhCHCH_3$), 37.8 (s, $PhCHCH_3$), 45.1 (s, CH_2), 47.1 (s, $PhCHCH=$), 125.6 (s, $CH_3CH=$), 126.4−146.0 (m, aromat. *C*), 135.4 (s, $PhCHCH=$) ppm. MS (EI): *m/z* (%) = 250 (12) [M^+], 145 (10) [$M^+ - PhCHCH_3$], 131 (100) [$M^+ - PhCH(CH_3)CH_2$], 105 (35) [$PhCHCH_3^+$], 91 (38) [$C_7H_7^+$], 77 (10) [$C_6H_5^+$]. B.p. 215−220 °C (0.1 mbar).

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