Suzuki Cross-Coupling Reactions between Alkenylboronic Acids and Aryl Bromides Catalysed by a Tetraphosphane-Palladium Catalyst

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Keywords: Alkenes / Aryl halides / Catalysis / Cross-coupling / Palladium / Phosphanes

A range of alkenylboronic acids undergo Suzuki cross-coupling with aryl bromides in good yields in the presence of $[PdCl(C_3H_5)]_2$/*cis*,*cis*,*cis*-1,2,3,4-tetrakis[(diphenylphosphanyl)methyl]cyclopentane as a catalyst. A wide variety of 1-arylprop-1-enes, 2-arylprop-1-enes, 2-arylbut-1-enes and 1,1-diarylethylene or styrene derivatives have been prepared. Moreover, the reaction tolerates several functions, such as acetyl, formyl, nitrile or nitro. Furthermore, this catalyst can be used at low loading, even for reactions of sterically hindered substrates.

Introduction

The Suzuki cross-coupling reactions are among the most widely used palladium-catalysed methodologies in organic synthesis.[1−5] In recent years, the efficiencies of several thermally stable palladium catalysts in reactions between aryl halides and arylboronic acids have been studied in detail.[6−13] On the other hand, these reactions in the presence of alkenylboronic acids have attracted less attention,[14−33] although a few ligands have successfully been employed. The most popular of is triphenylphosphane, but the catalyst formed by association of this ligand with palladium complexes is not very efficient in terms of substrate/catalyst ratio.[15−29] Recently, more efficient palladium catalysts have also been successfully employed for Suzuki cross-coupling reactions with these alkenylboron derivatives.[30−33] Molander et al., for example, have reported that the $PdCl_2$(dppf) complex is an efficient catalyst for reactions between aryl bromides and alkenyltrifluoroborates.[31,32] Two palladium-supported catalyst have also been used successfully.[30,33] To the best of our knowledge, however, the efficiency of tetraphosphane ligands for the cross-coupling of alkenylboronic acids has not been reported.

Results and Discussion

In order to find stable and efficient palladium catalysts, we have prepared the tetrapodal[34] phosphane ligand *cis*,*cis*,*cis*-1,2,3,4-tetrakis[(diphenylphosphanyl)methyl]-cyclopentane, or Tedicyp (Scheme 1),[35] in which the four (diphenylphosphanyl)alkyl groups are stereospecifically bound to the same face of the cyclopentane ring. We have already reported the results obtained with Tedicyp as ligand in allylic substitution,[35] in Heck reactions,[36] in Suzuki cross-coupling[37−42] and in Sonogashira[43] reactions. As an example, a TON of 98 000 000 had been obtained for the coupling of 4-bromoacetophenone with benzeneboronic acid. We have also recently reported the cross-coupling of arylboronic acids with a range of vinyl bromides.[44] Here, in order to establish further the requirements for a successful Suzuki cross-coupling reaction, we wish to report on the reactions between alkenylboronic acids and a variety of aryl bromides in the presence of Tedicyp as the ligand.

Scheme 1

From previous results,[44] xylene was chosen as the solvent and potassium carbonate as the base for this study. The reactions were generally performed at 130 °C under argon in the presence of a 1:2 $[Pd(C_3H_5)Cl]_2$/Tedicyp ratio as catalyst.

We first tried to prepare styrene derivatives by the Suzuki reactions. Styrene derivatives have recently been prepared by Suzuki cross-coupling between arylboronic acids and vinyl bromide.[45] Here we describe the synthesis of these compounds by cross-coupling between vinylboronic acid and several aryl bromides (Scheme 2, Table 1). We have observed that it is indeed possible to cross-couple vinylboronic acid and aryl bromides efficiently, under conditions similar to those employed for the corresponding arylboronic acids. This reaction can be performed with as little as 0.01% cata-

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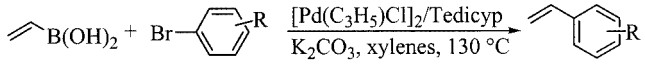
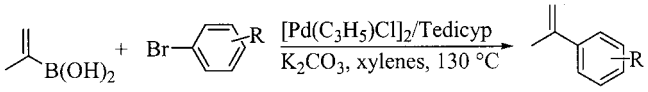
lyst. The $[Pd(C_3H_5)Cl]_2$/Tedicyp catalyst system is also tolerant of electronic variation in the aryl halide component. Vinylboronic acid reacts cleanly at 130 °C both with electron-poor and with electron-rich aryl bromides. A wide range of functions on the aryl bromide − such as methoxy, fluoro, trifluoromethyl, dimethylamino, nitro, nitrile, formyl or acetyl − was tolerated. A strong influence of these substituents on the reaction rate was observed. In the presence of *para*-substituted, electron-poor aryl bromides such as 4-bromoacetophenone or 4-bromobenzaldehyde, TONs of 1 000−2 400 were obtained (Entries 3−8, Table 1). In the presence of electron-rich aryl bromides, on the other hand, lower TONs of 89 and 250 were observed (Entries 1 and 2, Table 1). Lower TONs were also observed with *ortho*-substituted aryl bromides such as 2-bromobenzaldehyde or 2-bromobenzonitrile (Entries 11−15, Table 1).



Scheme 2

We next tried to evaluate the differences in reaction rate between mono- and di-*ortho*-substituted aryl bromides, and we observed that even very hindered aryl bromides could be coupled efficiently with vinylboronic acid. With 1-bromo-2,4,6-trimethylbenzene and 1-bromo-2,4,6-triisopropylbenzene, for example, high levels of conversion were obtained in the presence of 0.4 and 5% catalyst, respectively (Entries 16 and 17, Table 1). Moreover, the catalyst was also active for the heteroaryl bromide 3-bromoquinoline (Entries 18 and 19, Table 1).

Having demonstrated that vinylboronic acid can be an efficient alkenylating agent for aryl bromides, we investigated the scope of the coupling reaction with substituted vinylboronic acids. We first studied the reactivity of isopropenylboronic acid (Scheme 3, Table 2). The results, presented in Table 2, also reveal a strong aryl bromide substituent effect on the reaction rate. Electron-withdrawing groups in the aryl bromides support the Suzuki reaction, while electron-donating groups are unfavourable. For example, turnover numbers of 3 100−8 600 can be achieved with this catalyst for activated substrates such as 4-bromoacetophenone, 4-bromobenzophenone, 4-bromobenzaldehyde and 4-bromobenzonitrile (Entries 3−10, Table 2). With deactivated 4-dimethylaminobromobenzene, on the other hand, we obtained a TON of 340 (Entries 11 and 12, Table 2). We next studied the influence of *ortho*-substituents on the aryl bromide, and the results observed were better than those seen in the couplings with vinylboronic acid (Table 1). 2-Bromoacetophenone and 2-bromobenzonitrile gave TONs similar to those for *para*-substituted aryl bromides (Entries 15, 16 and 20, Table 2), and satisfactory TONs were obtained even in the presence of highly congested substrates such as 9-bromoanthracene or 1-bromo-2,4,6-triisopropylbenzene (187 and 105; Entries 22−26, Table 2). In summary, isopropenylboronic acid proved to be a very efficient reagent for the introduction of an isopropenyl group into aryl derivatives.



Scheme 3

With but-1-en-2-ylboronic acid the coupling products were also obtained selectively and in good yields (Scheme 4,

Table 1. Suzuki reactions with $H_2C{=}CHB(OH)_2$ (see also Scheme 2)

Entry[a]	ArBr	Substrate/catalyst ratio	Product	Yield, %
1	4-*t*Bu-PhBr	250	**1**	87, 100[b][c]
2	4-NMe_2-PhBr	100	**2**	89
3	4-MeCO-C_6H_4Br	1000	**3**	85
4	4-MeCO-C_6H_4Br	10000	**3**	24[b]
5	4-HCO-C_6H_4Br	250	**4**	100[b]
6	4-HCO-C_6H_4Br	1000	**4**	78, 100[b]
7	4-CN-C_6H_4B	250	**5**	100[b]
8	4-CN-C_6H_4Br	1000	**5**	84, 100[b]
9	6-Methoxy-2-bromonaphthalene	250	**6**	80, 100[b]
10	6-Methoxy-2-bromonaphthalene	1000	**6**	64[b]
11	2-MeCO-C_6H_4Br	250	**7**	100[b]
12	2-MeCO-C_6H_4Br	1000	**7**	84, 100[b]
13	2-HCO-C_6H_4Br	100	**8**	85
14	2-CN-C_6H_4Br	250	**9**	87
15	2-CN-C_6H_4Br	1000	**9**	35[b]
16	2,4,6-Me_3−C_6H_2Br	250	**10**	88, 100[b]
17	2,4,6-*i*Pr_3−C_6H_2Br	20	**11**	22
18	3-Bromoquinoline	250	**12**	92
19	3-Bromoquinoline	1000	**12**	87[b]

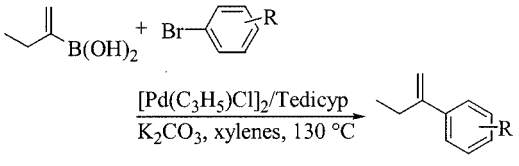
[a] Conditions: catalyst see ref.[35], aryl bromide (1 equiv.), $H_2C{=}CHB(OH)_2$ (3 equiv.), K_2CO_3 (2 equiv.), xylenes, 130 °C, 20 h. [b] Yield determined by GC and NMR. [c] Reaction time: 3 h.

Table 2. Suzuki reactions with $CH_3(C{=}CH_2)B(OH)_2$ (Scheme 3)

Entry[a]	ArBr	Substrate/catalyst ratio	Product	Yield, %
1	4-*t*Bu-PhBr	250	**13**	92, 100[b]
2	4-*t*Bu-PhBr	1000	**13**	54[b]
3	4-MeCO-C_6H_4Br	1000	**14**	96
4	4-MeCO-C_6H_4Br	10000	**14**	31[b]
5	4-PhCO-C_6H_4Br	1000	**15**	96
6	4-PhCO-C_6H_4Br	10000	**15**	66[b]
7	4-HCO-C_6H_4Br	1000	**16**	83
8	4-HCO-C_6H_4Br	10000	**16**	86[b]
9	4-CN-C_6H_4Br	1000	**17**	84, 100[b]
10	4-CN-C_6H_4Br	10000	**17**	36[b]
11	4-Me_2N-C_6H_4Br	100	**18**	86, 100[b]
12	4-Me_2N-C_6H_4Br	1000	**18**	34[b]
13	6-Methoxy-2-bromonaphthalene	10000	**19**	95
14	2-Ph-C_6H_4Br	250	**20**	87, 100[b]
15	2-MeO-C_6H_4Br	100	**21**	78, 100[b]
16	2-MeCO-C_6H_4Br	1000	**22**	79, 100[b]
17	2-MeCO-C_6H_4Br	10000	**22**	55[b]
18	2-HCO-C_6H_4Br	1000	**23**	56
19	2-NO_2-C_6H_4Br	250	**24**	89
20	2-NO_2-C_6H_4Br	1000	**24**	84[b]
21	2-CN-C_6H_4Br	1000	**25**	88
22	1-Bromonaphthalene	1000	**26**	95
23	9-Bromoanthracene	250	**27**	75
24	2,4,6-Me_3-C_6H_2Br	100	**28**	86
25	2,4,6-*i*Pr_3-C_6H_2Br	20	**29**	89, 100[b]
26	2,4,6-*i*Pr_3-C_6H_2Br	250	**29**	42[b]
27	3-Bromoquinoline	100	**30**	83

[a] Conditions: catalyst see ref.[35], aryl bromide (1 equiv.), $CH_3(C{=}CH_2)B(OH)_2$ (2 equiv.), K_2CO_3 (2 equiv.), xylenes, 130 °C, 20 h. [b] GC and NMR yield.

Table 3). The reaction rates were very similar to those observed in the presence of isopropenylboronic acid. The highest TONs were obtained in the presence of *ortho*- and *para*-substituted, electron-poor aryl bromides such as bromoacetophenone, bromobenzaldehyde or bromobenzonitrile (Entries 5−10 and 12−17, Table 3). Bromobenzene was also efficiently coupled, although lower TONs were observed (Entries 3 and 4, Table 3). No isomerisation of the double bond was generally detected.



Scheme 4

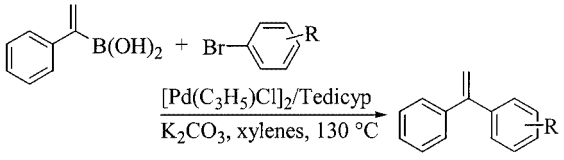
We also studied the synthesis of 1,1-biarylethylene derivatives by Suzuki cross-coupling. We have already reported the synthesis of these compounds through Suzuki cross-coupling between α-bromostyrene and arylboronic acids.[44] Here we report the synthesis of these compounds by cross-coupling between 1-phenylvinylboronic acid and aryl bromides. The Suzuki reaction between this vinylboronic acid and functionalized aryl bromides should be a powerful procedure for the preparation of functionalized 1,1-biarylethylene derivatives (Scheme 5, Table 4). We observed that this reaction can be performed with as little as 0.01% catalyst and tolerates a wide range of functions − such as methoxy,

Table 3. Suzuki reactions with $CH_3CH_2(C{=}CH_2)B(OH)_2$ (see also Scheme 4)

Entry[a]	ArBr	Substrate/catalyst ratio	Product	Yield, %
1	PhI	100	**31**	78, 100[b]
2	PhI	1000	**31**	33[b]
3	PhBr	100	**31**	91[c]
4	PhBr	250	**31**	86[b]
5	4-MeCO-C_6H_4Br	1000	**32**	93
6	4-MeCO-C_6H_4Br	10000	**32**	98[b] [d]
7	4-HCO-C_6H_4Br	1000	**33**	90
8	4-HCO-C_6H_4Br	10000	**33**	34[b]
9	4-CN-C_6H_4Br	1000	**34**	94
10	4-CN-C_6H_4Br	10000	**34**	65[b]
11	2-Me-C_6H_4Br	250	**35**	93
12	2-MeCO-C_6H_4Br	1000	**36**	86, 100[b]
13	2-MeCO-C_6H_4Br	10000	**36**	84[b]
14	2-HCO-C_6H_4Br	1000	**37**	89, 100[b]
15	2-HCO-C_6H_4Br	10000	**37**	75[b]
16	2-CN-C_6H_4Br	1000	**38**	84, 100[b]
17	2-CN-C_6H_4Br	10000	**38**	80[b]

[a] Conditions: catalyst see ref.[35], aryl bromide (1 equiv.), $CH_3CH_2(C{=}CH_2)B(OH)_2$ (2 equiv.), K_2CO_3 (2 equiv.), xylenes, 130 °C, 20 h. [b] Yield determined by GC and NMR. [c] 80 °C. [d] The formation of 7% of 2-arylbut-2-ene was observed.

fluoro, acetyl, formyl, nitrile or benzoyl − on the aryl bromide. Higher reaction rates were observed in the presence of *para*-substituted aryl bromides (Entries 1−7, Table 4) than with *ortho*-substituted aryl bromides (Entries 8−10, Table 4). No evidence of stilbene derivatives from a competing Heck reaction was observed in any case.



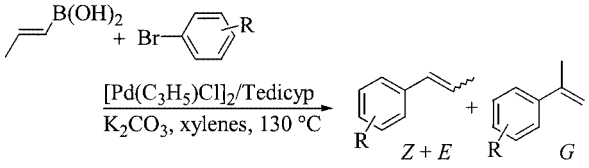
Scheme 5

Table 4. Suzuki reactions with $Ph(C{=}CH_2)B(OH)_2$ (see also Scheme 5)

Entry[a]	ArBr	Substrate/catalyst ratio	Product	Yield, %
1	4-MeO-C_6H_4Br	11000	**39**	88, 100[b]
12	4-F-C_6H_4Br	11250	**40**	91
13	4-F-C_6H_4Br	11000	**40**	100[b]
14	4-MeCO-C_6H_4Br	15000	**41**	80
15	4-HCO-C_6H_4Br	11000	**42**	80, 100[b]
16	4-CN-C_6H_4Br	15000	**43**	78
17	4-PhCO-C_6H_4Br	10000	**44**	83, 99[b]
18	2-MeCO-C_6H_4Br	11000	**45**	51
19	2-CN-C_6H_4Br	11250	**46**	81, 100[b]
10	2-CN-C_6H_4Br	11000	**46**	100[b]

[a] Conditions: catalyst see ref.[35], aryl bromide (1 equiv.), $Ph(C{=}CH_2)B(OH)_2$ (2 equiv.), K_2CO_3 (2 equiv.), xylenes, 130 °C, 20 h. [b] GC and NMR yield.

We lastly studied the synthesis of (*E*)-1-arylprop-1-enes by cross-coupling between (*E*)-prop-1-en-1-ylboronic acid and aryl bromides. We have already reported the preparation of similar compounds with $[Pd(C_3H_5)Cl]_2$/Tedicyp as catalyst in Heck reactions between aryl bromides and alk-1-enes. In all cases, we had obtained mixtures of regio- and stereoisomers and the best selectivity in favour of (*E*)-1-arylalk-1-enes was 70%.[46] Here, to determine the most efficient procedure for the preparation of such compounds, we also prepared them by the Suzuki reaction (Scheme 6, Table 5). Quite similar reaction rates were observed for both Heck and Suzuki reactions, and the reaction performed in the presence of (*E*)-prop-1-en-1-ylboronic acid also gave mixtures of regio- and stereoisomers. This substrate seems to react both through a Heck reaction and subsequent deboronation (isomer geminal *G*) and through a Suzuki reaction [isomers (*Z*) and (*E*)].[47] In the presence of 4-bromobenzophenone, 4-bromobenzaldehyde and 4-bromobenzonitrile, mixtures of the three isomers were obtained and the best selectivity in favour of (*E*)-1-arylprop-1-enes was 83% (Entries 1−6, Table 5). A reaction performed at a lower temperature gave higher selectivity in favour of the (*E*) isomer (Entry 7, Table 5). In the presence of *ortho*-substituted aryl bromides the selectivity in favour of the linear isomers was also higher, up to 95% of the (*E*) isomer being obtained (Entries 8 and 9, Table 5). These results indicate that the Heck reaction seems to be the most economical procedure for the preparation of these vinylarenes. However, the Suzuki cross-coupling procedure reported here is very simple and overcomes the inconvenience of using gas under pressure.



Scheme 6

Conclusion

In summary, we have established that the Tedicyp/palladium system is not limited to Suzuki reactions of arylboronic acids; alkenylboronic acids are also efficiently coupled. In the presence of this catalyst, Suzuki cross-couplings of vinylboronic acid, isopropenylboronic acid, but-1-en-2-ylboronic acid, 1-phenylvinylboronic acid or (*E*)-prop-1-en-1-ylboronic acid can be performed with as little as 0.01% catalyst. In view of the high price of palladium, the practi-

Table 5. Suzuki reactions with (*E*)-$MeCH{=}CHB(OH)_2$ (Scheme 6)

Entry[a]	ArBr	Substrate/catalyst ratio	Product	Ratio *G*/*Z*/*E*	Yield
1	4-MeCO-C_6H_4Br	250	**47**	6:11:83	90
2	4-MeCO-C_6H_4Br	1000	**47**	6:12:82	63[b]
3	4-HCO-C_6H_4Br	250	**48**	17:11:72	89, 100[b]
4	4-HCO-C_6H_4Br	1000	**48**	18:18:64	80[b]
5	4-CN-C_6H_4Br	250	**49**	17:6:77	100[b]
6	4-CN-C_6H_4Br	1000	**49**	15:8:77	74
7	4-CN-C_6H_4Br	250	**49**	7:12:81	100[b] [c]
8	2-MeCO-C_6H_4Br	250	**50**	0:5:95	79
9	2-CN-C_6H_4Br	250	**51**	2:5:93	74

[a] Conditions: catalyst see ref.[35], aryl bromide (1 equiv.), (*E*)-$MeCH{=}CHB(OH)_2$ (2 equiv.), K_2CO_3 (2 equiv.), xylenes, 130 °C, 20 h. [b] Yield determined by GC and NMR. [c] 70 °C.

cal advantage of such low catalyst loading reactions may become increasingly important for industrial processes. This efficiency probably comes from the presence of the four (diphenylphosphanyl)alkyl groups stereospecifically bound to the same face of the cyclopentane ring, which probably increases the coordination of the ligand to the metal and prevent precipitation of the catalyst. The cross-coupling of alkenylboronic acids with aryl bromides is generally slower than the cross-coupling of alkenyl bromides with arylboronic acids,[44] but the functional group tolerance is remarkable, substituents such as fluoro, methyl, methoxy, acetyl, formyl, benzoyl, nitro and nitrile on the aryl bromide having been used successfully. As would be expected, both the steric hindrance and the electronic properties of the aryl bromide have an effect on the reaction rates, but even the *o*,*o*-disubstituted aryl bromide partners provide the desired products.

Experimental Section

General Remarks: All reactions were run under argon in Schlenk tubes with the use of vacuum lines. Analytical grade xylene was not distilled before use. Some of the aryl halides were distilled before use. Potassium carbonate (99+) was used without drying. Alkenylboronic acid were prepared by a reported procedure,[48] by addition of 2 equiv. of $B(OMe)_3$ to alkenylmagnesium bromide solutions in THF at −90 °C, the solution then being warmed to room temperature, poured onto ice, extracted with diethyl ether and dried ($MgSO_4$), and the solvents being evaporated. Vinylboronic acid is not very stable and was prepared just before use. Isopropenylboronic acid, but-1-en-2-ylboronic acid, 1-phenylvinylboronic acid and (*E*)-prop-1-en-1-ylboronic acid were stored at −20 °C. The reactions were followed by GC and NMR for high boiling point substrates and by GC for low boiling point substrates. GC/MS were recorded with a Varian Saturn 2100T spectrometer. ^1H and ^{13}C NMR spectrum were recorded with a Bruker 300 MHz spectrometer in $CDCl_3$ solutions. Chemical shifts are reported in ppm relative to $CDCl_3$ (7.25). Flash chromatography was performed on silica gel (230−400 mesh) GC and NMR yields in the tables are conversions of the aryl halides into the products calculated from GC and ^1H NMR spectra of the crude mixtures.

General Procedure for the Coupling of Alkenylboronic Acids with Aryl Bromides: Treatment of the aryl bromide (10 mmol), K_2CO_3 (2.76 g, 20 mmol) and the alkenylboronic acid (20 or 30 mmol, see Tables 1−5) at the appropriate temperature (see Tables 1−5) under argon in xylene (10 mL) in the presence of the Tedicyp/palladium complex for 20 h afforded the corresponding coupling product after addition of water, extraction with dichloromethane or diethyl ether, separation, drying ($MgSO_4$), evaporation and filtration through silica gel.

4-*tert*-Butylstyrene (1): ^1H NMR: δ = 1.31 (s, 9 H, Me), 5.18 (d, *J* = 10.9 Hz, 1 H, =CH*H*), 5.70 (d, *J* = 17.6 Hz, 1 H, =CH*H*), 6.69 (dd, *J* = 17.6, 10.9 Hz, 1 H, =C*H*), 7.34 (m, 4 H, Ar) ppm.

***N*,*N*-dimethyl-4-vinylaniline (2):** ^1H NMR: δ = 2.95 (s, 6 H, Me), 5.01 (d, *J* = 10.8 Hz, 1 H, =CH*H*), 5.53 (d, *J* = 17.5 Hz, 1 H, =CH*H*), 6.60 (dd, *J* = 17.5, 10.8 Hz, 1 H, =C*H*), 6.69 (d, *J* = 9.0 Hz, 2 H, Ar), 7.30 (d, *J* = 9.0 Hz, 2 H, Ar) ppm.

4-Vinylacetophenone (3): ^1H NMR: δ = 2.58 (s, 3 H, Me), 5.39 (d, *J* = 11.7 Hz, 1 H, =CH*H*), 5.86 (d, *J* = 17.6 Hz, 1 H, =CH*H*), 6.75 (dd, *J* = 17.6, 11.7 Hz, 1 H, =C*H*), 7.46 (d, *J* = 8.3 Hz, 2 H, Ar), 7.90 (d, *J* = 8.3 Hz, 2 H, Ar) ppm.

4-Vinylbenzaldehyde (4): ^1H NMR: δ = 5.42 (d, *J* = 11.9 Hz, 1 H, =CH*H*), 5.90 (d, *J* = 17.6 Hz, 1 H, =CH*H*), 6.76 (dd, *J* = 17.6, 11.9 Hz, 1 H, =C*H*), 7.53 (d, *J* = 8.3 Hz, 2 H, Ar), 7.83 (d, *J* = 8.3 Hz, 2 H, Ar), 9.97 (s, 1 H, CHO) ppm.

4-Vinylbenzonitrile (5): ^1H NMR: δ = 5.43 (d, *J* = 11.9 Hz, 1 H, = CH*H*), 5.86 (d, *J* = 17.6 Hz, 1 H, =CH*H*), 6.72 (dd, *J* = 17.6, 11.9 Hz, 1 H, =C*H*), 7.47 (d, *J* = 8.5 Hz, 2 H, Ar), 7.60 (d, *J* = 8.5 Hz, 2 H, Ar) ppm.

6-Methoxy-2-vinylnaphthalene (6): ^1H NMR: δ = 3.92 (s, 3 H, OMe), 5.29 (d, *J* = 11.0 Hz, 1 H, =CH*H*), 5.83 (d, *J* = 17.5 Hz, 1 H, =CH*H*), 6.86 (dd, *J* = 17.5, 11.0 Hz, 1 H, =C*H*), 7.10−7.20 (m, 2 H, Ar), 7.58−7.72 (m, 4 H, Ar) ppm.

2-Vinylacetophenone (7): ^1H NMR: δ = 2.57 (s, 3 H, Me), 5.33 (d, *J* = 10.9 Hz, 1 H, =CH*H*), 5.63 (d, *J* = 17.6 Hz, 1 H, =CH*H*), 7.19 (dd, *J* = 17.6, 10.9 Hz, 1 H, =C*H*), 7.32 (t, *J* = 7.5 Hz, 1 H, Ar), 7.44 (t, *J* = 7.5 Hz, 1 H, Ar),), 7.55 (d, *J* = 7.5 Hz, 1 H, Ar). 7.62 (d, *J* = 7.5 Hz, 1 H, Ar) ppm.

2-Vinylbenzaldehyde (8): ^1H NMR: δ = 5.51 (d, *J* = 10.9 Hz, 1 H, =CH*H*), 5.69 (d, *J* = 17.4 Hz, 1 H, =CH*H*), 7.39−7.59 (m, 4 H, =C*H* and Ar*)*, 7.82 (d, *J* = 7.6 Hz, 1 H, Ar), 10.29 (s, 1 H, CHO) ppm.

2-Vinylbenzonitrile (9): ^1H NMR: δ = 5.53 (d, *J* = 10.9 Hz, 1 H, = CH*H*), 5.94 (d, *J* = 17.6 Hz, 1 H, =CH*H*), 7.07 (dd, *J* = 17.6, 10.9 Hz, 1 H, =C*H*), 7.33 (t, *J* = 7.5 Hz, 1 H, Ar), 7.54 (t, *J* = 7.5 Hz, 1 H, Ar),), 7.62 (d, *J* = 7.5 Hz, 1 H, Ar). 7.66 (d, *J* = 7.5 Hz, 1 H, Ar) ppm.

2,4,6-Trimethylstyrene (10): ^1H NMR: δ = 2.26 (s, 9 H, Me), 5.22 (dd, *J* = 18.0, 2.0 Hz, 1 H, =CH*H*), 5.49 (dd, *J* = 11.3, 2.0 Hz, 1 H, =CH*H*), 6.66 (dd, *J* = 18.0, 11.3 Hz,1 H, =C*H*), 6.85 (s, 2 H, Ar) ppm.

2,4,6-Triisopropylstyrene (11): ^1H NMR: δ = 1.18 (d, *J* = 6.8 Hz, 6 H, Me), 1.25 (d, *J* = 6.8 Hz, 12 H, Me), 2.85 (sept., *J* = 6.8 Hz, 1 H, CH), 3.24 (sept., *J* = 6.8 Hz, 2 H, CH), 5.17 (dd, *J* = 17.8, 2.3 Hz, 1 H, =CH*H*), 5.50 (dd, *J* = 11.3, 2.3 Hz, 1 H, =CH*H*), 6.76 (dd, *J* = 17.8, 11.3 Hz, 1 H, =C*H*), 6.99 (s, 2 H, Ar) ppm.

3-Vinylquinoline (12): ^1H NMR: δ = 5.44 (d, *J* = 11.1 Hz, 1 H, = CH*H*), 5.96 (d, *J* = 17.8 Hz, 1 H, =CH*H*), 6.85 (dd, *J* = 17.8, 11.1 Hz, 1 H, =C*H*), 7.51 (t, *J* = 7.2 Hz, 1 H, Ar), 7.66 (t, *J* = 7.2 Hz, 1 H, Ar), 7.78 (d, *J* = 8.1 Hz, 1 H, Ar), 8.02−8.10 (m, 2 H, Ar), 9.01 (d, *J* = 1.9 Hz, 1 H, Ar) ppm.

2-(4-*tert*-Butylphenyl)propene (13): ^1H NMR: δ = 1.30 (s, 9 H, *t*Bu), 2.14 (s, 3 H, Me), 5.03 (s, 1 H, =CH*H*), 5.35 (s, 1 H, =CH*H*), 7.35 (d, *J* = 8.7 Hz, 2 H, Ar), 7.42 (d, *J* = 8.7 Hz, 2 H, Ar) ppm.

2-(4-Acetylphenyl)propene (14): ^1H NMR: δ = 2.07 (s, 3 H, Me), 2.56 (s, 3 H, COMe), 5.17 (s, 1 H, =CH*H*), 5.47 (s, 1 H, =CH*H*), 7.49 (d, *J* = 7.5 Hz, 2 H, Ar), 7.91 (d, *J* = 7.5 Hz, 2 H, Ar) ppm.

2-(4-Benzoylphenyl)propene (15): ^1H NMR: δ = 2.07 (s, 3 H, Me), 5.07 (s, 1 H, =CH*H*), 5.43 (s, 1 H, =CH*H*), 7.30−7.50 (m, 5 H, Ar), 7.30−7.50 (m, 4 H, Ar) ppm.

2-(4-Formylphenyl)propene (16): ^1H NMR: δ = 2.11 (s, 3 H, Me), 5.20 (s, 1 H, =CH*H*), 5.48 (s, 1 H, =CH*H*), 7.54 (d, *J* = 8.5 Hz, 2 H, Ar), 7.86 (d, *J* = 8.5 Hz, 2 H, Ar), 9.96 (s, 1 H, CHO) ppm.

2-(4-Cyanophenyl)propene (17): ^{1}H NMR: δ = 2.08 (s, 3 H, Me), 5.20 (s, 1 H, =CH*H*), 5.46 (s, 1 H, =CH*H*), 7.50 (d, *J* = 8.7 Hz, 2 H, Ar), 7.59 (d, *J* = 8.7 Hz, 2 H, Ar) ppm.

2-(4-Dimethylaminophenyl)propene (18): ^{1}H NMR: δ = 2.14 (s, 3 H, Me), 2.97 (s, 6 H, Me), 4.93 (s, 1 H, =CH*H*), 5.28 (s, 1 H, =CH*H*), 6.71 (d, *J* = 9.0 Hz, 2 H, Ar), 7.41 (d, *J* = 9.0 Hz, 2 H, Ar) ppm.

2-(6-Methoxy-2-naphthyl)propene (19): ^{1}H NMR: δ = 2.24 (s, 3 H, Me), 3.92 (s, 3 H, OMe), 5.12 (s, 1 H, =CH*H*), 5.49 (s, 1 H, =CH*H*), 7.15 (m, 2 H, Ar), 7.65−7.80 (m, 3 H, Ar), 7.82 (s, 1 H, Ar) ppm.

2-(2-Phenylphenyl)propene (20): ^{1}H NMR: δ = 2.00 (s, 3 H, Me), 5.34 (s, 1 H, =CH*H*), 5.42 (s, 1 H, =CH*H*), 7.50−7.80 (m, 9 H, Ar) ppm.

2-(2-Methoxyphenyl)propene (21): ^{1}H NMR: δ = 2.11 (s, 3 H, Me), 3.83 (s, 3 H, OMe), 5.04 (s, 1 H, =CH*H*), 5.16 (s, 1 H, =CH*H*), 6.85−7.35 (m, 4 H, Ar) ppm.

2-(2-Acetylphenyl)propene (22): ^{1}H NMR: δ = 2.10 (s, 3 H, Me), 2.48 (s, 3 H, Me), 4.87 (s, 1 H, =CH*H*), 5.19 (s, 1 H, =CH*H*), 7.26 (d, *J* = 7.5 Hz, 1 H, Ar), 7.31 (td, *J* = 7.5, 1.5 Hz, 1 H, Ar), 7.41 (td, *J* = 7.5, 1.5 Hz, 1 H, Ar), 7.47 (dd, *J* = 7.5, 1.5 Hz, 1 H, Ar) ppm. $C_{11}H_{12}O$ (160.2): calcd. C 82.46, H 7.55; found C 82.68, H 7.38. MS (EI, 70 eV): *m*/*z* (%) = 160 (21) [M^+].

2-(2-Formylphenyl)propene (23): ^{1}H NMR: δ = 2.15 (s, 3 H, Me), 4.87 (s, 1 H, =CH*H*), 5.43 (s, 1 H, =CH*H*), 7.32 (d, *J* = 7.5 Hz, 1 H, Ar), 7.37 (t, *J* = 7.5 Hz, 1 H, Ar), 7.52 (td, *J* = 7.5, 1.3 Hz, 1 H, Ar), 7.88 (dd, *J* = 7.5, 1.3 Hz, 1 H, Ar), 10.19 (s, 1 H, CHO) ppm.

2-(2-Nitrophenyl)propene (24): ^{1}H NMR: δ = 2.07 (s, 3 H, Me), 4.92 (s, 1 H, =CH*H*), 5.15 (s, 1 H, =CH*H*), 7.31 (d, *J* = 7.5 Hz, 1 H, Ar), 7.38 (t, *J* = 7.5 Hz, 1 H, Ar), 7.53 (t, *J* = 7.5 Hz, 1 H, Ar), 7.83 (d, *J* = 7.5 Hz, 1 H, Ar) ppm.

2-(2-Cyanophenyl)propene (25): ^{1}H NMR: δ = 2.20 (s, 3 H, Me), 5.23 (s, 1 H, =CH*H*), 5.35 (s, 1 H, =CH*H*), 7.34 (m, 2 H, Ar), 7.51 (td, *J* = 8.0, 1.3 Hz, 1 H, Ar), 7.63 (dd, *J* = 8.0, 1.3 Hz, 1 H, Ar) ppm.

2-(1-Naphthyl)propene (26): ^{1}H NMR: δ = 2.16 (s, 3 H, Me), 5.05 (s, 1 H, =CH*H*), 5.40 (s, 1 H, =CH*H*), 7.10−8.00 (m, 7 H, Ar) ppm.

9-Isopropenylanthracene (27): ^{1}H NMR: δ = 2.27 (s, 3 H, Me), 5.16 (s, 1 H, =CH*H*), 5.77 (s, 1 H, =CH*H*), 7.47 (m, 4 H, Ar), 8.00 (m, 2 H, Ar), 8.17 (m, 2 H, Ar), 8.40 (m, 1 H, Ar) ppm.

2-(2,4,6-Trimethylphenyl)propene (28): ^{1}H NMR: δ = 1.93 (s, 3 H, Me), 2.21 (s, 6 H, Me), 2.26 (s, 3 H, Me), 4.73 (s, 1 H, =CH*H*), 5.23 (s, 1 H, =CH*H*), 6.85 (s, 2 H, Ar) ppm.

2-(2,4,6-Triisopropylphenyl)propene (29): ^{1}H NMR: δ = 1.18 (d, *J* = 6.8 Hz, 6 H, Me), 1.28 (d, *J* = 6.8 Hz, 12 H, Me), 1.95 (s, 3 H, Me), 2.85 (sept., *J* = 6.8 Hz, 1 H, CH), 3.05 (sept., *J* = 6.8 Hz, 2 H, CH), 4.76 (s, 1 H, =CH*H*), 5.24 (s, 1 H, =CH*H*), 6.96 (s, 2 H, Ar) ppm. $C_{18}H_{28}$ (244.4): calcd. C 88.45, H 11.55; found C 88.18, H 11.29. MS (EI, 70 eV): *m*/*z* (%) = 244 (51) [M^+].

3-Isopropenylquinoline (30): ^{1}H NMR: δ = 2.20 (s, 3 H, Me), 5.25 (s, 1 H, =CH*H*), 5.54 (s, 1 H, =CH*H*), 7.51 (td, *J* = 8.1, 1.2 Hz, 1 H, Ar), 7.63 (td, *J* = 8.1, 1.2 Hz, 1 H, Ar), 7.77 (dd, *J* = 8.1, 1.2 Hz, 1 H, Ar), 8.06 (m, 2 H, Ar), 9.09 (d, *J* = 1.9 Hz, 1 H, Ar) ppm.

2-Phenylbut-1-ene (31): ^{1}H NMR: δ = 1.08 (t, *J* = 7.4 Hz, 3 H, Me), 2.48 (q, *J* = 7.4 Hz, 2 H, CH_2), 5.05 (s, 1 H, =CH*H*), 5.26 (s, 1 H, =CH*H*), 7.20−7.45 (m, 5 H, Ph) ppm.

2-(4-Acetylphenyl)but-1-ene (32): ^{1}H NMR: δ = 1.10 (t, *J* = 7.4 Hz, 3 H, Me), 2.58 (s, 3 H, Me), 2.49 (q, *J* = 7.4 Hz, 2 H, CH_2), 5.14 (s, 1 H, =CH*H*), 5.37 (s, 1 H, =CH*H*), 7.46 (d, *J* = 8.2 Hz, 2 H, Ar), 7.91 (d, *J* = 8.2 Hz, 2 H, Ar) ppm.

2-(4-Formylphenyl)but-1-ene (33): ^{1}H NMR: δ = 1.05 (t, *J* = 7.4 Hz, 3 H, Me), 2.49 (q, *J* = 7.4 Hz, 2 H, CH_2), 5.18 (s, 1 H, =CH*H*), 5.37 (s, 1 H, =CH*H*), 7.54 (d, *J* = 7.5 Hz, 2 H, Ar), 7.82 (d, *J* = 7.5 Hz, 2 H, Ar), 9.95 (s, 1 H, CHO) ppm. $C_{11}H_{12}O$ (160.2): calcd. C 82.46, H 7.55; found C 82.25, H 7.27. MS (EI, 70 eV): *m*/*z* (%) = 160 (100) [M^+].

2-(4-Cyanophenyl)but-1-ene (34): ^{1}H NMR: δ = 1.10 (t, *J* = 7.4 Hz, 3 H, Me), 2.47 (q, *J* = 7.4 Hz, 2 H, CH_2), 5.19 (s, 1 H, =CH*H*), 5.35 (s, 1 H, =CH*H*), 7.47 (d, *J* = 8.3 Hz, 2 H, Ar), 7.60 (d, *J* = 8.3 Hz, 2 H, Ar) ppm. $C_{11}H_{11}N$ (157.2): calcd. C 84.04, H 7.05; found C 83.87, H 7.00. MS (EI, 70 eV): *m*/*z* (%) = 157 (81) [M^+].

2-(2-Methylphenyl)but-1-ene (35): ^{1}H NMR: δ = ^{1}H NMR: δ = 1.02 (t, *J* = 7.4 Hz, 3 H, Me), 2.31 (q, *J* = 7.4 Hz, 2 H, CH_2), 2.27 (s, 3 H, Me), 4.83 (s, 1 H, =C*H*H), 5.15 (s, 1 H, =CH*H*), 7.00−7.30 (m, 4 H, Ar) ppm.

2-(2-Acetylphenyl)but-1-ene (36): ^{1}H NMR: δ = 1.05 (t, *J* = 7.4 Hz, 3 H, Me), 2.42 (q, *J* = 7.4 Hz, 2 H, CH_2), 2.48 (s, 3 H, Me), 4.91 (s, 1 H, =CH*H*), 5.18 (s, 1 H, =CH*H*), 7.22 (d, *J* = 7.8 Hz, 1 H, Ar), 7.30 (t, *J* = 7.8 Hz, 1 H, Ar), 7.38 (t, *J* = 7.8 Hz, 1 H, Ar), 7.48 (d, *J* = 7.8 Hz, 1 H, Ar) ppm. $C_{12}H_{14}O$ (174.2): calcd. C 82.72, H 8.10; found C 82.48, H 7.91. MS (EI, 70 eV): *m*/*z* (%) = 174 (45) [M^+].

2-(2-Formylphenyl)but-1-ene (37): ^{1}H NMR: δ = 1.00 (t, *J* = 7.4 Hz, 3 H, Me), 2.45 (q, *J* = 7.4 Hz, 2 H, CH_2), 4.91 (s, 1 H, =CH*H*), 5.37 (s, 1 H, =CH*H*), 7.27 (d, *J* = 7.8 Hz, 1 H, Ar), 7.37 (t, *J* = 7.8 Hz, 1 H, Ar), 7.52 (t, *J* = 7.8 Hz, 1 H, Ar), 7.92 (d, *J* = 7.8 Hz, 1 H, Ar), 10.15 (s, 1 H, CHO) ppm. $C_{11}H_{12}O$ (160.2): calcd. C 82.46, H 7.55; found C 82.29, H 7.24. MS (EI, 70 eV): *m*/*z* (%) = 160 (13) [M^+].

2-(2-Cyanophenyl)but-1-ene (38): ^{1}H NMR: δ = 1.05 (t, *J* = 7.4 Hz, 3 H, Me), 2.49 (q, *J* = 7.4 Hz, 2 H, CH_2), 5.15 (s, 1 H, =CH*H*), 5.34 (s, 1 H, =CH*H*), 7.32 (d, *J* = 7.5 Hz, 1 H, Ar), 7.34 (t, *J* = 7.5 Hz, 1 H, Ar), 7.52 (t, *J* = 7.5 Hz, 1 H, Ar), 7.64 (d, *J* = 7.5 Hz, 1 H, Ar) ppm. $C_{11}H_{11}N$ (157.2): calcd. C 84.04, H 7.05; found C 83.75, H 6.97. MS (EI, 70 eV): *m*/*z* (%) = 157 (55) [M^+].

1-(4-Methoxyphenyl)-1-phenylethylene (39): ^{1}H NMR: δ = 3.82 (s, 3 H, Me), 5.35 (d, *J* = 1.3 Hz, 1 H, =CH*H*), 5.39 (d, *J* = 1.3 Hz, 1 H, =C*H*H), 6.86 (d, *J* = 9.0 Hz, 2 H, Ar), 7.27 (d, *J* = 9.0 Hz, 2 H, Ar), 7.33 (m, 5 H, Ph) ppm.

1-(4-Fluorophenyl)-1-phenylethylene (40): ^{1}H NMR: δ = 5.34 (d, *J* = 1.1 Hz, 1 H, =CH*H*), 5.36 (d, *J* = 1.1 Hz, 1 H, =C*H*H), 6.93 (t, *J* = 8.8 Hz, 2 H, Ar), 7.23 (dd, *J* = 5.4, 8.8 Hz, 2 H, Ar), 7.26 (m, 5 H, Ph) ppm.

1-(4-Acetylphenyl)-1-phenylethylene (41): ^{1}H NMR: δ = 2.50 (s, 3 H, COMe), 5.43 (s, 1 H, =CH*H*), 5.44 (s, 1 H, =C*H*H), 7.25 (m, 5 H, Ph), 7.32 (d, *J* = 7.9 Hz, 2 H, Ar), 7.26 (d, *J* = 7.9 Hz, 2 H, Ar) ppm.

1-(4-Formylphenyl)-1-phenylethylene (42): ^{1}H NMR: δ = 5.53 (s, 1 H, =CH*H*), 5.54 (s, 1 H, =C*H*H), 7.27 (m, 5 H, Ph), 7.47 (d, *J* = 8.2 Hz, 2 H, Ar), 7.83 (d, *J* = 8.2 Hz, 2 H, Ar), 10.00 (s, 1 H, CHO) ppm.

1-(4-Cyanophenyl)-1-phenylethylene (43): ^{1}H NMR: δ = 5.51 (s, 1 H, =CH*H*), 5.56 (s, 1 H, =C*H*H), 7.27 (m, 2 H, Ph), 7.54 (m, 3 H, Ph), 7.42 (d, *J* = 8.5 Hz, 2 H, Ar), 7.62 (d, *J* = 8.5 Hz, 2 H, Ar) ppm.

1-(4-Benzoylphenyl)-1-phenylethylene (44): ^{1}H NMR: δ = 5.61 (s, 2 H, =C*HH*), 7.34 (m, 5 H, Ar), 7.42 (d, *J* = 8.2 Hz, 2 H, Ar), 7.46 (t, *J* = 7.7 Hz, 2 H, Ar), 7.58 (t, *J* = 7.5 Hz, 1 H, Ar), 7.77 (d, *J* = 8.3 Hz, 2 H, Ar), 7.82 (d, *J* = 7.5 Hz, 2 H, Ar) ppm. $C_{21}H_{16}O$ (284.3): calcd. C 88.70, H 5.67; found C 88.54, H 5.47. MS (EI, 70 eV): *m*/*z* (%) = 284 (100) [M^+].

1-(2-Acetylphenyl)-1-phenylethylene (45): ^{1}H NMR: δ = 2.62 (s, 3 H, Me), 5.25 (d, *J* = 1.3 Hz, 1 H, =CH*H*), 5.75 (d, *J* = 1.3 Hz, 1 H, =C*H*H), 7.25−7.62 (m, 7 H, Ar), 8.02 (d, *J* = 8.5 Hz, 2 H, Ar) ppm.

1-(2-Cyanophenyl)-1-phenylethylene (46): ^{1}H NMR: δ = 5.46 (s, 1 H, =CH*H*), 5.84 (s, 1 H, =C*H*H), 7.22−7.34 (m, 6 H, Ar), 7.40 (t, *J* = 7.5 Hz, 1 H, Ar), 7.54 (d, *J* = 7.5 Hz, 1 H, Ar), 7.68 (d, *J* = 7.5 Hz, 1 H, Ar) ppm.

(*E*)-1-(4-Acetylphenyl)prop-1-ene (47): ^{1}H NMR: δ = 1.90 (d, *J* = 5.3 Hz, 3 H, Me), 2.59 (s, 3 H, COMe), 6.40 (m, 1 H, =CH), 6.43 (d, *J* = 15.9 Hz, 1 H, =CH), 7.36 (d, *J* = 8.0 Hz, 2 H, Ar), 7.86 (d, *J* = 8.0 Hz, 2 H, Ar) ppm.

(*E*)-1-(4-Formylphenyl)prop-1-ene (48): ^{1}H NMR: δ = 1.91 (d, *J* = 5.1 Hz,, 3 H, Me), 6.43 (m, 1 H, =CH), 6.45 (d, *J* = 15.3 Hz, 1 H, =CH), 7.45 (d, *J* = 8.3 Hz, 2 H, Ar), 7.81 (d, *J* = 8.3 Hz, 2 H, Ar), 9.95 (s, 1 H, CHO) ppm.

(*E*)-1-(4-Cyanophenyl)prop-1-ene (49): ^{1}H NMR: δ = 1.90 (d, *J* = 5.3 Hz, 3 H, Me), 6.39 (m, 2 H, CH=CH), 7.36 (d, *J* = 7.8 Hz, 2 H, Ar), 7.55 (d, *J* = 7.8 Hz, 2 H, Ar) ppm.

(*E*)-1-(2-Acetylphenyl)prop-1-ene (50): ^{1}H NMR: δ = 1.88 (d, *J* = 5.3 Hz, 3 H, Me), 2.54 (s, 3 H, OMe), 6.10 (dq, *J* = 15.5, 5.3 Hz, 1 H, =CH), 6.85 (d, *J* = 15.5 Hz, 1 H, =CH), 7.20−7.50 (m, 3 H, Ar), 7.55 (d, *J* = 7.7 Hz, 1 H, Ar) ppm.

(*E*)-1-(2-Cyanophenyl)prop-1-ene (51): ^{1}H NMR: δ = 1.97 (dd, *J* = 6.6, 1.7 Hz, 3 H, Me), 6.44 (dq, *J* = 15.7, 6.6 Hz, 1 H, =CH), 6.74 (dd, *J* = 15.7, 1.7 Hz, 1 H, =CH), 7.20−7.70 (m, 4 H, Ar) ppm. $C_{10}H_9N$ (143.2): calcd. C 83.88, H 6.34; found C 83.60, H 6.15. MS (EI, 70 eV): *m*/*z* (%) = 143 (100) [M^+].

Chemical Abstract Registry No.: 1, 1746−23−2; **2**, 2039−80−7; **3**, 10537−63−0; **4**, 1791−26−0; **5**, 3435−51−6; **6**, 63444−51−9; **7**, 52095−40−6; **8**, 28272−96−0; **9**, 34560−28−6; **10**, 769−25−5; **11**, 2039−92−1; **12**, 67752−31−2; **13**, 25163−88−6; **14**, 5359−04−6; **15**, 103384−71−0; **16**, 10133−50−3; **17**, 19956−03−7; **18**, 25108−56−9; **19**, 34352−92−6; **20**, 22364−43−8; **21**, 10278−02−1; **23**, 23417−79−0; **24**, 60249−97−0; **25**, 23877−63−6; **26**, 1855−47−6; **27**, 58873−48−6; **28**, 14679−13−1; **30**, 104967−60−4; **31**, 2039−93−2; **32**, 42427−52−1; **35**, 82902−62−3; **39**, 4333−75−9; **40**, 395−21−1; **41**, 87324−13−8; **42**, 389582−37−0; **43**, 81329−28−4; **45**, 50431−52−2; **46**, 92757−92−1; **47**, 109586−46−1; **48**, 169030−21−1; **49**, 74254−13−0; **50**, 91388−33−9.

Acknowledgments

We thank the CNRS and the "Conseil Général des Bouches-du-Rhône, Fr" for providing financial support.

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Received October 6, 2003

