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Catalytic asymmetric alkylation in water in the presence of surfactants: influence of the nature of the nucleophile and the allylic acetate on the activity and enantioselectivity

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Abstract—Asymmetric palladium-catalyzed alkylation of 1,3-diphenyl-2-propenyl acetate with carbon and nitrogen nucleophiles occurs in water in the presence of a surfactant, a base, and Binap as the chiral ligand. Enantioselectivities up to 91% were obtained using carbon nucleophiles, and 93% using nitrogen nucleophiles, in the presence of $CTHASO_4$ as the surfactant. While the efficiency of the catalyst was higher in water in the presence of the surfactant in the case of carbon nucleophiles, no micellar effects were observed using the nitrogen nucleophiles. The alkylation was extended to other allylic acetates, but the efficiency as well the enantioselectivity of the coupling were lower.

1. Introduction

Organometallic homogeneous catalysis is now a well-used methodology in organic synthesis.[1,2] Since most chemical transformations of organic substrates are performed in organic solvents, in the laboratory as well in the industry, the substitution of organic solvents on both industrial and academic scales by water would be advantageous;[3] this is due to the fact that water is safe, benign, non toxic, environmentally friendly, and cheap compared to organic solvents. However one of the problems is the insolubility of organic products as well as organometallic catalysts in water.

One way to circumvent this problem is the use of a two-phase organic solvent–water system, the catalyst being located in water by the use of water-soluble ligands. However the main drawback of this system is the phase-transfer limitation giving generally very low reaction rates. In order to perform organometallic catalysis in water only, one possibility is the use of water-soluble ligands. Although many water-soluble ligands have been efficiently used in association with organometallic complexes, chiral water-soluble ligands are generally difficult to prepare. Moreover, the organic substrates have to show some significant water solubility. Surfactants have been used in order to solubilize both the organic reactants and products as well as the organometallic catalyst in water; this approach has been successfully applied in hydrogenation,[4–15] hydroformylation,[16] Suzuki coupling,[12,17–20] and aldol reactions.[21] It is also to be noted that in the asymmetric hydrogenation of α-amino acid precursors using rhodium complexes, higher enantioselectivities and activities have been obtained under these conditions than in normal organic solvents; this concept has been extended recently to the asymmetric hydrogenation in a membrane reactor equipped with an ultra filtration membrane.

Palladium-catalyzed alkylation of allylic substrates has recently been studied under such conditions. Uozumi et al. showed that an amphiphilic resin supported palladium complex was active in this alkylation reaction, the catalyst being recycled without loss of activity.[22] Asymmetric allylic alkylation was also performed using immobilized palladium complex of chiral ligands on amphiphilic resins,[23,24] as well as in water in the presence of surfactants,[25–27] with enantioselectivities of up to 98%. In continuation of our work on the asymmetric palladium-catalyzed alkylation of allylic acetates in water in the presence of micelles,[25,26] we present herein

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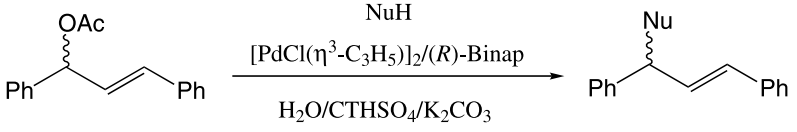
the extension of this reaction to other allylic acetates, as well as the use of carbon- and heteronucleophiles in this reaction.

2. Results and discussion

The palladium-catalyzed alkylation of *rac*-(*E*)-1,3-diphenyl-2-propenyl acetate **1** was extended to other carbon nucleophiles under the previously optimized conditions described for dimethyl malonate: (*R*)-Binap as the ligand, K_2CO_3 as the base, $CTAHSO_4$ as the surfactant, rt, 1 h reaction (Scheme 1). The results summarized in Table 1 showed a higher catalytic activity in water in the presence of the surfactant. After 1 h reaction, 95%, 85%, and 64% conversions were obtained in the alkylated product **2b**, **2c**, and **2d**, using, respectively, dimethyl methylmalonate, acetyl acetone, and diethyl acetamidomalonate as the nucleophiles, respectively, in the presence of $CTAHSO_4$ (Table 1, entries 4, 6, and 8). In neat water conversions of 62, 74, and 9% were obtained (Table 1, entries 3, 5, and 7). It is to be noted that the enantioselectivities obtained are very similar when the reaction was performed in neat water or in water in the presence of the surfactant.

Next we used nitrogen nucleophiles in this alkylation reaction (Scheme 2). The results, summarized in Table 2, showed that there is practically no influence of the surfactant on either the activity or enantioselectivity of the coupling reaction. Benzylamine gave the allylated amine **3a** with 98% conversion and 93% and 92% ee, in neat water or in the presence of the surfactant, respectively (Table 2, entries 1 and 2). If the conversion was higher in the case of morpholine in the presence of the surfactant (98% versus 62% in neat water), the enantioselectivity of the reaction was lower (60% ee in the presence of $CTAHSO_4$, versus 84% ee in neat water) (Table 2, entries 3 and 4). The results conducted with potassium phthalimide (Table 2, entries 7 and 8) are quite similar with or without $CTAHSO_4$. Enantioselectivities up to 91 and 89% were obtained using (1-naphthylmethyl)amine as the nitrogen nucleophile in water alone or in water in the presence of $CTAHSO_4$ (Table 2, entries 5 and 6). Using potassium phthalimide as the nucleophile gave the corresponding amine **3d** in 92% and 87% ee in water alone or in water in the presence of $CTAHSO_4$ (Table 2, entries 7 and 8), but with lower conversion. However, when the reaction of potassium phtalimide with *rac*-1,3-diphenyl-2-propenyl acetate **1** was performed in water in the presence of $CTAHSO_4$ the formation of 54% of the hydrolyzed product **4** was detected, together with 41% of the alkylated product **3d**; this hydrolysis did not take place in neat water.

In order to increase the conversion into the alkylated product **3d**, we performed the reaction in the presence of other surfactants. The conversions in the presence of SDS or Tween 40 as the surfactants are low: 7 and 48% respectively, 91% ee being however obtained in the last example (Table 2, entries 9 and 11). Higher conversion (84%) was obtained in the presence of the zwitterionic



rac-**1** 1h/25°C **2 a-d**

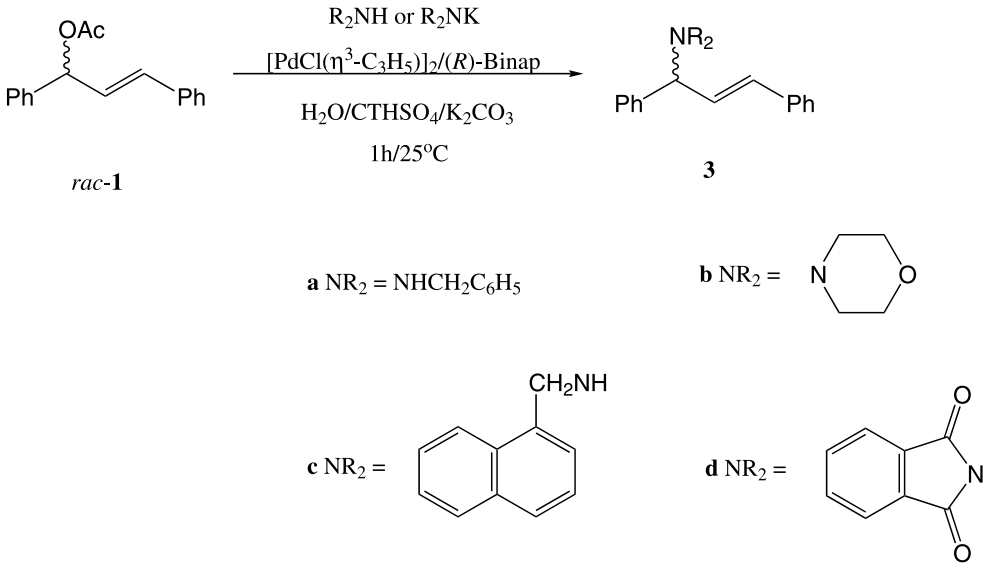
a Nu = $CH(CO_2Me)_2$
b Nu = $CH_3C(CO_2Me)_2$
c Nu = $CH(COMe)_2$
d Nu = $AcNHC(CO_2Et)_2$

Scheme 1.

Table 1. Alkylation of allylic acetate *rac*-**1** by carbon nucleophiles[a]

Entry	Nu–H	Surfactant	Convn in **2** (%)[b]	E.e. (%)[b] (config.)
1	$CH_2(CO_2Me)_2$[c]	No	45	85 (*S*)
2	$CH_2(CO_2Me)_2$[c]	$CTHASO_4$	100	91 (*S*)
3	$CH_3CH(CO_2Me)_2$	No	62	90 (*R*)
4	$CH_3CH(CO_2Me)_2$	$CTHASO_4$	95	89 (*R*)
5	$CH_2(COMe)_2$	No	74	78 (*S*)
6	$CH_2(COMe)_2$	$CTHASO_4$	85	76 (*S*)
7	$AcNHCH(CO_2Et)_2$	No	9	–
8	$AcNHCH(CO_2Et)_2$	$CTHASO_4$	64	87 (*R*)

[a] [**1a**] = 75 mmol L^{-1}; [**1a**]:[NuH]:[$Pd(OAc)_2$]:[(*R*)-Binap]:[K_2CO_3]:[$CTAHSO_4$]:[Ph_2O] = 20:60:1:2:60:13.3:20; H_2O = 8 mL; 25°C; 1 h.
[b] Determined by GC and HPLC.
[c] Ref. 26.



Scheme 2.

Table 2. Alkylation of allylic acetate *rac*-**1** by nitrogen nucleophiles[a]

Entry	Nu–H	Surfactant	Convn in **3** (%)[b]	E.e. (%)[b] (config.)
1	Benzylamine	No	98	93 (*R*)
2	Benzylamine	$CTHASO_4$	98	92 (*R*)
3	Morpholine	No	62	84
4	Morpholine	$CTHASO_4$	98	60
5	(1-Naphthylmethyl)amine	No	100	91
6	(1-Naphthylmethyl)amine	$CTHASO_4$	97[d]	89
7	Potassium phthalimide[c]	No	44	92 (*R*)
8	Potassium phthalimide[c]	$CTHASO_4$	41[e]	87 (*R*)
9	Potassium phthalimide[c]	SDS	7	–
10	Potassium phthalimide[c]	DeDAPS	84	82 (*R*)
11	Potassium phthalimide[c]	Tween 40	48	91 (*R*)
12	Phenol	No	0	–
13	Phenol	$CTHASO_4$	13[f]	3

[a] [**1a**] = 75 mmol L^{-1}; [**1a**]:[NuH]:[$Pd(OAc)_2$]:[(*R*)-Binap]:[K_2CO_3]:[surfactant]:[Ph_2O] = 20:60:1:2:60:13.3:20; H_2O = 8 mL; 25°C; 1 h.
[b] Determined by GC and HPLC.
[c] No base was used.
[d] 3% alcohol formed.
[e] 54% alcohol formed.
[f] 49% alcohol formed.

surfactant DeDAPS, with enantioselectivities up to 82% ee (Table 2, entry 10).

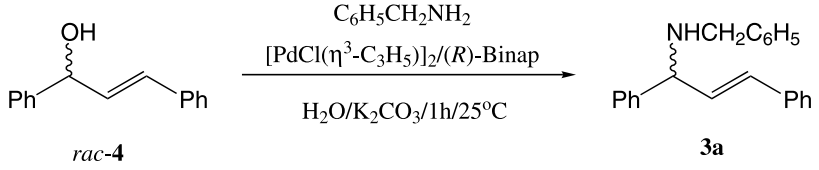
We also performed some experiments using phenol as the nucleophile. In neat water, no reaction occurred, while in the presence of $CTAHSO_4$, 13% of the allylic ether corresponding to the *O*-alkylated product was formed, together with 49% of alcohol **4** resulting from the hydrolysis of the allylic acetate.

We followed the conversion and the enantioselectivity of the alkylated product versus reaction time when benzylamine or (1-naphthylmethyl)amine were used as the nucleophile, in neat water or in the presence of $CTAHSO_4$ (Table 3). For benzylamine in neat water, the conversion increased with the reaction time, the obtained enantioselectivities being 98%, 99%, and 93% ee, after 15, 30, and 60 min, respectively. No formation of hydrolyzed product **4** was detected. In the presence of $CTAHSO_4$ as the surfactant, the conversion into **3a** was only 59% after 15 min, and increased to 100% after 30 min; the observed enantioselectivities being 96%, 97%, and 92% ee, respectively. However, we also noticed under these conditions the formation of 41% of alcohol **4** after 15 min, that was further transformed into the alkylated compound **3a** in the presence of the palladium catalyst. Indeed, when the allylic alcohol *rac*-**4** and benzylamine were stirred under the above mentioned conditions of alkylation, 32% conversion to **3a** was observed in neat water and 18% in the presence of $CTAHSO_4$ (Scheme 3). Moreover, the observed ee's for product **3a** were 95% ee in neat water and 80% ee in the presence of the surfactant, that are in agreement with the formation of a η^3-allyl-palladium complex and

Table 3. Alkylation of allylic acetate *rac*-**1** by benzylamine and (1-naphthylmethyl)amine[a]

Entry	Nucleophile	Time (min)	$CTAHSO_4$	Convn in **2** (%)[b]	Ee (%)[b] (*R*)
1	Benzylamine	15	No	82	98
2	Benzylamine	15	Yes	59 (41% **4**)	96
3	Benzylamine	30	No	94	99
4	Benzylamine	30	Yes	100	97
5	Benzylamine	60	No	98	93
6	Benzylamine	60	Yes	98	92
7	(1-Naphthylmethyl)amine	5	No	100	70
8	(1-Naphthylmethyl)amine	5	Yes	100	74
9	(1-Naphthylmethyl)amine	10	No	100	96
10	(1-Naphthylmethyl)amine	10	Yes	100	82
11	(1-Naphthylmethyl)amine	60	No	100	91
12	(1-Naphthylmethyl)amine	60	Yes	97	89

[a] [**1a**] = 75 mmol L^{-1}; [**1a**]:[NuH]:[$Pd(OAc)_2$]:[(*R*)-Binap]:[K_2CO_3]:[$CTHSO_4$]:[Ph_2O] = 20:60:1:2:60:13.3:20; H_2O = 8 mL; 25°C; 1 h.
[b] Determined by GC and HPLC.



rac-**4** **3a**

H_2O Convn = 32% ee = 95% (*R*)

H_2O + $CTAHSO_4$ Convn = 18% ee = 80% (*R*)

Scheme 3.

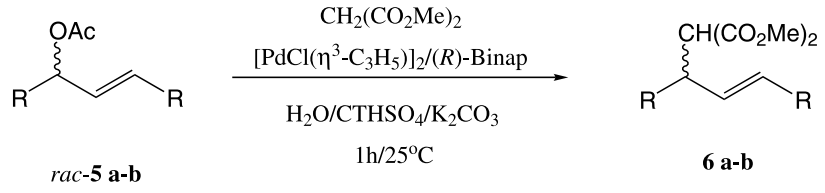
excluded the pathway via a carbocationic intermediate. The palladium-catalyzed allylation of amines using allylic alcohols as the η^3-allyl precursors has already been mentioned by Yang et al.,[28–31] although an allylic non-activated hydroxyl is not a good leaving group in this catalytic process.

When (1-naphthylmethyl)amine was used as the nucleophile, the reaction was very fast, the conversion being quantitative after 5 min, in neat water or in the presence of $CTAHSO_4$. No formation of alcohol **4** was detected in this case. However we noticed a change in the enantiomeric excess of the obtained allylic amine **3c**. In neat water, the ee was 70% after 5 min, and then 96% and 91% after 15 and 60 min, respectively. When the reaction was performed in the presence of $CTAHSO_4$, the ee of **3c** increased with the reaction time, the obtained ees being 74%, 82%, and 89% ee, after 5, 15, and 60 min, respectively. This change in enantioselectivity, although not very important, implied that the formed allylic amine **3c** could be also a precursor for the formation of the η^3-allyl-palladium intermediate, the reaction being in this case reversible. Effectively, when *rac*-**3c** was stirred under the conditions used for the alkylation reaction in the presence of (*R*)-Binap, $CTAHSO_4$ or Tween 40 being used as the surfactant, enantioselectivities up to 7% and 5% ee were obtained; these values, although not very high, showed effectively that one of the reasons of the change in enantioselectivity during the process could be the reversibility of the alkylation reaction under these conditions. Such a reversibility has already been mentioned by Bäckwall et al. in the *C*-alkylation of allylic acetates.[32]

We also extended this palladium-catalyzed alkylation reaction in water in the presence of $CTAHSO_4$ using dimethyl malonate as the nucleophile to other aliphatic allylic acetates, having quite different hydrophobicities (Scheme 4). Allylic acetates *rac*-**5a** and *rac*-**5b** gave the expected alkylated products, but with low conversion after 1 h whatever the conditions used: 51 and 37% in neat water, and 20 and 14% in the presence of $CTAHSO_4$, respectively (Table 4). This could be due to the higher hydrophilicity of these unsaturated acetates in water, compared to **1**. It is also to be noted that the observed enantioselectivities are quite similar in water only and in the presence of the surfactant: 41% and 45% ee for **5a**, and 18% and 27% ee for **5b**. No micellar effect was observed using these two allylic acetates.

The condensation of cyclohexenyl acetate with dimethyl malonate occured quantitatively under the standard conditions after 1 h, with or without $CTAHSO_4$ (Scheme 5); however, the enantioselectivity was exactly the same, 19%. Again no micellar effects were observed in this case.

Finally we performed the condensation reaction between racemic ketoester **9** and allyl acetate in the presence of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ associated with (*R*)-Binap, $CTAHSO_4$ being the surfactant (Scheme 6). The



rac-**5 a-b** **6 a-b**

a R = CH_3; **b** R = n-C_3H_7

Scheme 4.

Table 4. Alkylation of allylic acetates *rac*-**5** by dimethyl malonate[a]

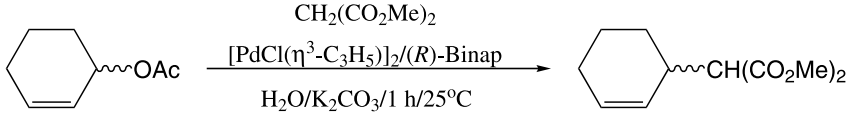
Entry	Allylic substrate	Surfactant	Convn in **6** (%)[b]	Ee (%)[b]
1	**5a**	No	51	41 (*S*)
2	**5a**	$CTAHSO_4$	20	45 (*S*)
3	**5b**	No	37	18
4	**5b**	$CTAHSO_4$	14	27

[a] [**5**] = 75 mmol L^{-1}; [**5**]:[NuH]:[$Pd(OAc)_2$]:[(*R*)-Binap]:[K_2CO_3]:[$CTHSO_4$]:[Ph_2O] = 20:60:1:2:60:13.3:20; H_2O = 8 mL; 25°C; 1 h.
[b] Determined by GC and HPLC.

reaction occurred readily, with or without surfactant, the conversion being quantitative after 15 min. Unfortunately the enantioselectivities are low, 14% ee without surfactant and 10% ee with surfactant.

3. Conclusion

In conclusion we have extended the asymmetric palladium-catalyzed alkylation reaction of *rac*-1,3-diphenyl-2-propenyl acetate in water in the presence or not of surfactants to carbon as well as nitrogen and oxygen nucleophiles. In the case of carbon nucleophiles, increasing activity was observed due to micellar effect, the enantioselectivities in neat water or in the presence of surfactants being quite close. When amines were used as nucleophiles, similar results were generally obtained in the presence or not of surfactants; this is probably due to the high solubility of amines in water. No micellar effect was observed when the reaction was extended to other allylic carbonates, probably due again to the higher solubility of these acetates in water compared to 1,3-diphenyl-2-propenyl acetate.

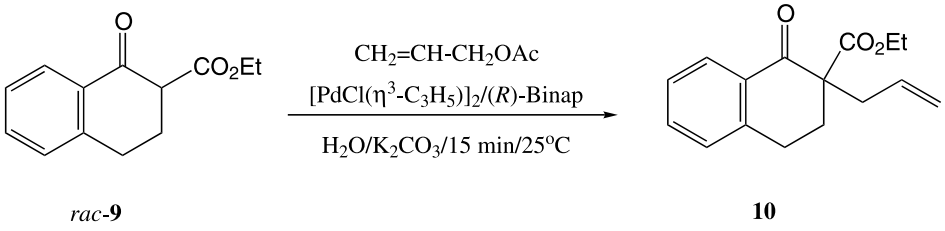


rac-**7** **8**

H_2O Convn = 99% ee = 19% (*R*)

H_2O + $CTAHSO_4$ Convn = 99% ee = 19% (*R*)

Scheme 5.



rac-**9** **10**

H_2O Convn = 100% ee = 14%

H_2O + $CTAHSO_4$ Convn = 95% ee = 10%

Scheme 6.

4. Experimental

4.1. General

All reactions were conducted in Schlenk tubes under nitrogen. NMR spectra were recorded on a Brucker 300 MHz instrument and referenced to Me_4Si as internal standard. Conversion was determined by GC using a Quadrex OV1 column (30 m×0.25 mm), enantiomeric excess was determined by HPLC with Chiralpak^{AD} column (25 cm×4.6 mm) using hexane/2-PrOH as the eluent, the flow rate being 0.5 mL/min, the detection being done by UV at 225 nm.

All detergents and most of the ligands were purchased from commercial sources and used as obtained. $C_{16}H_{33}NMe_3HSO_4$ ($CTAHSO_4$ or cetyltrimethylammonium hydrogen sulfate), $C_{12}H_{25}OSO_3Na$ (SDS or sodium dodecyl sulfate), Tween 40 (polyoxyethylene sorbitan monopalmitate), DeDAPS (*N*-decyl-*N*,*N*-dimethyl-3-ammonio-1-propanesulfonate), were obtained from Aldrich, $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and (*R*)-Binap from Strem. Unsaturated acetates **1**,[33] **5a**–**b**,[34] **7**,[35] and ketoester **9**[36] were prepared in accordance with the literature.

4.2. Standard alkylation reaction

A mixture of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (5.5 mg, 15 μmol), the appropriate ligand (60 mmol), and then the surfactant (0.2 mmol) in water (4 mL) was stirred in a Schlenk tube for 15 min. This solution was added to a Schlenk tube containing the allylic acetate (0.6 mmol) and diphenyl ether (102.1 mg, 0.6 mmol), as the internal standard. After 10 min, this solution was transferred to another Schlenk tube containing K_2CO_3 (249 mg, 1.8 mmol), the nucleophile (1.8 mmol), and eventually the surfactant (0.2 mmol) in water (4 mL). After being stirred for the indicated time, THF (2 mL) was added to the mixture and the solution was filtered. Evaporation of the solvents gave a residue that was subjected to column chromatography on silica gel. The conversion was determined by GC and the enantioselectivity by HPLC.

The separation of the racemic mixture under HPLC conditions is as follows: dimethyl [(*E*)-1,3-diphenylprop-2-en-1-yl]malonate **2a**, Daicel Chiralpak AD, hexane/2-PrOH 6:4, t_R 16 min (*R*)-isomer and 20 min (*S*)-isomer; dimethyl [(*E*)-1,3-diphenylprop-2-en-1-yl](methyl)malonate **2b**, Daicel Chiralpak AD, hexane/2-PrOH 98:2, t_R 37 min (*R*)-isomer and 40 min (*S*)-isomer; 3-[(*E*)-1,3-diphenylprop-2-en-1-yl]pentane-2,4-dione **2c**, Daicel Chiralpak AD, hexane/2-PrOH 7:3, t_R 15 min (*R*)-isomer and 16 min (*S*)-isomer; diethyl (acetylamino)[(*E*)-1,3-diphenylprop-2-en-1-yl]malonate **2d**, Daicel Chiralpak AD, hexane/2-PrOH 97:3, t_R 21 min (*R*)-isomer and 27 min (*S*)-isomer; (*E*)-*N*-benzyl-1,3-diphenylprop-2-en-1-amine **3a**, Daicel Chiralpak AD, hexane/2-PrOH 98:2, t_R 47 min (*R*)-isomer and 54 min (*S*)-isomer; 4-[(*E*)-1,3-diphenylprop-2-en-1-yl]morpholine **3b**, Daicel Chiralpak AD, hexane/2-PrOH 97:3, t_R 16 min (+)-isomer and 17 min (−)-isomer; 2-[(*E*)-1,3-diphenylprop-2-en-1-yl]-1*H*-isoindole-1,3-(2*H*)-dione **3d**, Daicel Chiralpak AD, hexane/2-PrOH 97:3, t_R 36 min (*S*)-isomer and 42 min (*R*)-isomer; dimethyl [(*E*)-1-*n*-propylhex-2-en-1-yl]malonate **6b**, Daicel Chiralpak AD, hexane/2-PrOH 150:1, t_R 36 min (*S*)-isomer and 42 min (*R*)-isomer; ethyl 2-allyl-1-oxo-1,2,3,4-tetrahydronaphtalene-2-carboxylate **10**, $[\alpha]_D^{20} = -2.5$ (*c* 0.8, $CHCl_3$) (ee = 10%), Daicel Chiralpak AD, hexane/2-PrOH 200:1, t_R 44 min (+)-isomer and 46 min (−)-isomer.

The separation of the racemic mixture of dimethyl [(*E*)-1-methylbut-2-en-1-yl]malonate **6a**[37] and dimethyl cyclohex-2-en-1-ylmalonate **8**[38] was performed by ^1H NMR using $Eu(hfc)_3$ in C_6D_6.

The absolute configuration of **2a**,[39] **2b**,[40] **2c**,[39] **2d**,[41] **3a**,[42] **3d**,[43] and **6b**[39] were determined by correlation with their specific rotations.

4.3. [(*E*)-1,3-diphenylprop-2-en-1-yl](1-naphthylmethyl)-amine, 3c

$R_f = 0.5$ (petroleum ether-ethyl acetate 20:3); $[\alpha]_D^{20} = -11.2$ (*c* 2.5, $CHCl_3$) (ee = 91%); HPLC, Daicel Chiralpak AD, 0.5 mL/min, hexane/2-PrOH 95:5, 225 nm, t_R 18 min (−)-isomer and 20 min (+)-isomer; ^1H NMR (300 MHz, $CDCl_3$): δ 1.76 (bs, 1H, NH), 4.20 (d, $J = 5.1$ Hz, 2H, CH_2), 4.49 (d, $J = 7.5$ Hz, 1H, C*H*NH), 6.36 (dd, $J = 15.8$, 7.5 Hz, 1H, =CH-), 6.61 (d, $J = 15.8$ Hz, 1H, =CH-), 7.16–8.10 (m, 17H, H_{arom}); ^{13}C NMR (75 MHz, $CDCl_3$): δ 49.7, 65.9, 124.3, 125.8, 126.1, 126.5, 126.6, 126.9, 127.8, 127.9, 128.2, 128.9, 129.1, 130.9, 133.1, 136.4, 137.4, 143.4. Anal. calcd for $C_{26}H_{23}N$ (349.48): C, 89.36; H, 6.63; found: C, 89.57; H, 6.77.

Acknowledgements

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