# A Convenient Synthesis of Some (1-Alkylethenyl)arenes and Bis(1-alkylethenyl)arenes

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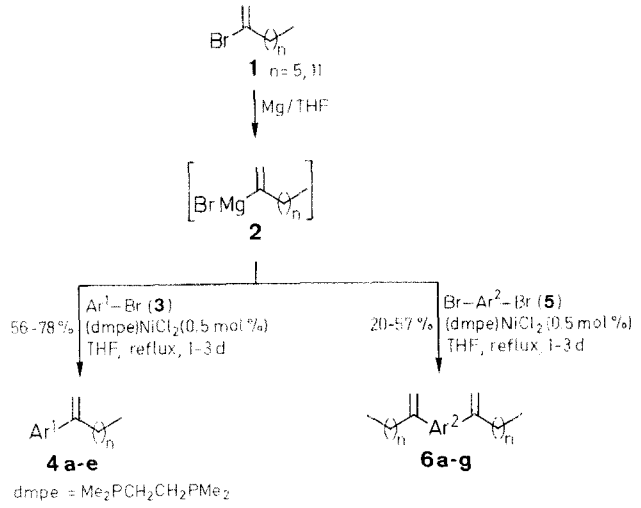
The title compounds may be prepared in good yields and high isomeric purities (98 + %) by reaction of 1-alkylethenylmagnesium bromides with bromo- or dibromoarenes, respectively. An improved synthesis of 2,6-dibromonaphthalene and the synthesis of 4,9-dibromopyrene are also described.

Aromatic compounds bearing two 1-alkylethenyl substituents are interesting monomers for the synthesis of novel polymers. They may be used as bifunctional dienes in repetitive Diels–Alder reactions with bifunctional dienophiles leading to ribbon-shaped polymers;[1-4] they also are potential candidates for the metathesis-polymerization of acyclic olefins to give new arylenevinylene polymers.[5,6] In both cases, rigid polymers would be obtained. The attachment of flexible alkyl chains to a rigid polymer backbone is a possible approach to increasing the solubility of such systems.[7-11] We present here a convenient and versatile synthesis of (1-alkylethenyl)arenes (2-aryl-1-alkenes) **4a–e** and bis(1-alkylethen)arenes **6a–g** carrying hexyl (n = 5) or dodecyl (n = 11) chains. The synthesis consists of the Ni-catalyzed coupling of bromoarenes **3** or dibromoarenes **5** with the Grignard reagents **2** derived from 2-bromo-1-octene (**1**, n = 5) or 2-bromo-1-tetradecene (**1**, n = 11). All compounds reported are new,[12] except for **4a**.[13]

It has been shown[14,15] that halogen atoms on aromatic rings can be replaced by vinylic groups via a one-step nickel- or palladium-catalyzed coupling reaction. Unfortunately, the only previously reported 1-alkene metalated (and then coupled) at C-2 was isopropenylmagnesium bromide.[16] It seemed to us that coupling reactions would satisfy the requirements for versatility in the synthesis of the desired bis-ene components. Other available methods, which often utilize Friedel–Crafts or Wittig reactions, may be competitive only in a few specific cases.[17-24]

It is presumed that solubilization of rigid species will require pendant alkyl groups larger than methyl; hence, we used 2-bromo-1-octene (**1**, n = 5) in coupling reactions with three bromoarenes **3** and six dibromoarenes **5** (2,6-dibromopyridine included), and 2-bromo-1-tetradecene (having the long dodecyl chain) in three coupling reactions. 2-Bromo-1-octene (**1**, n = 5) was synthesized following the procedure of Ref. 25, which was easily scaled up by a factor of 10. The previously unknown 2-bromo-1-tetradecene (**1**, n = 11) was prepared analogously in 65–80% yield. The regiochemical purity of both bromoalkenes was checked by high-field $^1$H-NMR spectroscopy. Comparison with the $^{13}$C satellites of the olefinic signals of **1** (n = 5) and **1** (n = 11) at $\delta$ = 5.35 and $\delta$ = 5.52, respectively, allowed the estimation of the amount of isomeric impurities to be less than 1%.




| 4 | $Ar^1$ | n | 6 | $Ar^2$ | n |
|---|---|---|---|---|---|
| a | Ph | 5 | a | 1,2-$C_6H_4$ | 5 |
| b | Ph | 11 | b | 1,4-$C_6H_4$ | 5 |
| c | 1-naphthyl | 5 | c | 1,5-naphthalenediyl | 5 |
| d | 2-naphthyl | 5 | d | 2,6-naphthalenediyl | 5 |
| e | 2-naphthyl | 11 | e | 2,6-naphthalenediyl | 11 |
| | | | f | 4,9-pyrenediyl | 5 |
| | | | g | 2,6-pyridenediyl | 5 |

**Table 1.** Compounds **4** and **6** Prepared

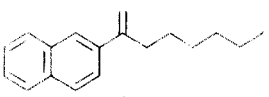
| Product | Yield (%) | mp (°C) and/or bp (°C)/mbar | Molecular Formula[a] or Lit. Data | IR (film) $\nu$ (cm$^{-1}$) | MS (70 eV) $m/z$, M$^+$ (%) |
|---|---|---|---|---|---|
| **4a** | 71 | 70/0.05 | 118/15[13] | 1625 (s) | 188 (5) |
| **4b** | 56 | 135/0.05 | $C_{20}H_{32}$ (272.5) | 1625 (w) | 272 (4) |
| **4c** | 76 | 97/0.02 | $C_{18}H_{22}$ (238.4) | 1632 (m), 1586 (m) | 238 (46) |
| **4d** | 78 | 119/0.02 | $C_{18}H_{22}$ (238.4) | 1635–1615 (m), 1585 (m) | 238 (23) |
| **4e** | 68 | 30 180/0.02 | $C_{24}H_{34}$ (322.5) | 1622 (w), 1595 (w) | 322 (11) |
| **6a** | 20 | 122/0.05 | $C_{22}H_{34}$ (298.5) | 1625 (w) | 298 (14) |
| **6b** | 51 | 122/0.05 | $C_{22}H_{34}$ (298.5) | 1635 (s), 1520 (s) | 298 (4) |
| **6c** | 54 | 140/0.05 | $C_{26}H_{36}$ (348.6) | 1635 (s), 1585 (s) | 348 (6) |
| **6d** | 55 | 35 165/0.05 | $C_{26}H_{36}$ (348.6) | 1620 (m), 1590 (w) | 348 (19) |
| **6e** | 57 | 62 | $C_{38}H_{60}$ (516.9) | 1622 (m), 1585 (w) | 516 (40) |
| **6f** | 57 | 190/0.05 | $C_{32}H_{38}$ (422.7) | 1645 (m), 1557 (m) | 422 (6) |
| **6g** | 55 | 121/0.2 | $C_{21}H_{33}N$ (299.5) | 1623 (m), 1562 (s) | 299 (90) |

[a] Satisfactory microanalyses obtained: C ±0.37, H ±0.35.

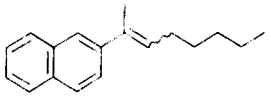
The published syntheses of 2,6-dibromonaphthalene[26-29] were improved in that the commercially available 6-bromo-2-naphthol was treated with triphenylphosphine dibromide.[30] Thus, pure 2,6-dibromonaphthalene was obtained in a one-step reaction on a 30 g scale in 28–35% yield. The hitherto unknown 4,9-dibromopyrene was obtained in 37% yield by dehydrogenation of 4,9-dibromo-1,2,3,6,7,8-hexahydropyrene with tetrachloro-1,2-benzoquinone.

We found that the Grignard reagents **2** derived from the 2-bromo-1-alkenes **1** (n = 5,11) react with bromoarenes **3** and dibromoarenes **5** in the presence of 0.5 mol % of (dmpe)$Cl_2$Ni in boiling tetrahydrofuran to give the vinylic compounds **4a–e** and **6b–g** in good yields whereas **6a** was obtained in only 20% yield (Table 1). The $^1$H-NMR spectra of the raw materials indicated that the reaction proceeds cleanly to give only one product. However, some material is lost during work-up of the products. In the preparation of compounds **6** it was found to be advantageous to use the Grignard reagent in 30% excess; the reported formation of a significant amount of mono-substituted material is thereby completely suppressed.[16] Occasionally, the formation of a small amount of the substituted butadiene derived from homo-coupling of **2** was observed. The reactions were performed on a 10–20 g scale; e.g., 15 g of 2,6-dibromonaphthalene were converted into 10 g (54%) of **6d**. The catalyst was completely removed by filtration through silica gel and the product was purified by distillation or recrystallization. All spectroscopic and analytical data are in full agreement with the proposed structures (Tables 1, 2). The two distinct $^1$H-NMR signals of the two geminal olefinic protons are particularly interesting: they appear as slightly broadened doublets at $\delta$ = 5.15 (± 0.10) and $\delta$ = 5.45 (± 0.35), showing a geminal coupling constant of 1.65 Hz (± 0.35 Hz). The $^{13}$C-NMR spectrum showed the olefinic triplets at $\delta$ = 113.3 ± 1.7, as expected.

The possible formation of isomers during the course of the coupling reaction was investigated in some detail using the synthesis of 2-(1-hexylethenyl)naphthalene (**4d**) as a representative example. 2-Bromo-1-octene (**1**, n = 5) was prepared with high regiospecificity (99%). The extension of the olefinic region of the $^1$H-NMR spectrum of the crude reaction mixture containing **4d** revealed signals of its isomer **7** (1–2%) but of none of other isomers. Hence, the degree of isomerization is estimated to be less than 2%. No evidence of increased formation of isomerized material was detected in any of the other cases, if acidic impurities were avoided.



**4d**



**7**

**Table 2.** NMR-Spectral Data of Compounds **4** and **6**

| Compound | $^1$H-NMR ($CDCl_3$/TMS)[a] $\delta$, $J$(Hz) | $^{13}$C-NMR ($CDCl_3$/TMS)[a] $\delta$ |
|---|---|---|
| **4a** | 2.45 (t, 2H, $J$ = 7.4); 5.05, 5.25 (2d, 1H each, $J$ = 1.8); 7.15–7.45 (m, 5H) | 35.4 (t); 111.9 (t); 126.1; 127.2; 128.2 (3d); 141.6; 148.9 (2s) |
| **4b** | 2.48 (t, 2H, $J$ = 7.4); 5.05; 5.26 (2d, 1H each, $J$ = 1.8); 7.20–7.40 (m, 5H) | [b] |
| **4c** | 2.52 (t, 2H, $J$ = 7.4); 5.10, 5.40 (2d, 1H each, $J$ = 1.8); 7.30–8.15 (m, 7H) | 38.6 (t); 114.9 (t); 124.9; 125.2; 125.5; 125.6; 125.9; 127.0; 128.2 (7d); 131.4; 133.7; 141.7; 149.2 (4s) |
| **4d** | 2.75 (t, 2H, $J$ = 6.7); 5.20, 5.55 (2d, 1H each, $J$ = 1.3); 7.45–7.95 (m, 7H) | 35.4 (t); 112.5 (t); 124.6; 124.7; 125.6; 126.0; 127.5; 127.7; 128.1 (7d); 132.8; 133.4; 138.8; 148.6 (4s) |
| **4e** | 2.60 (t, 2H, $J$ = 7.8); 5.14, 5.40 (2d, 1H each, $J$ = 1.3); 7.42–7.80 (m, 7H) | [b] |
| **6a** | 2.43 (t, 4H, $J$ = 6.5); 5.05, 5.15 (2d, 2H each, $J$ = 2.0); 7.15–7.40 (m, 4H) | 36.8 (t); 113.7 (t); 126.6; 129.2 (2d); 141.1, 151.3 (2s) |
| **6b** | 2.48 (t, 4H, $J$ = 6.8); 5.05, 5.25 (2d, 2H each, $J$ = 1.4); 7.38 (s, 4H) | 35.2 (t); 111.6 (t); 125.9 (d); 140.3; 148.3 (2s) |
| **6c** | 2.50 (t, 4H, $J$ = 7.0); 5.10, 5.45 (2d, 2H each, $J$ = 1.3); 7.26 (d, 4H, $J$ = 7.0); 7.45 (dd, 2H, $J$ = 7.0 (both)); 7.97 (d, 2H, $J$ = 7.0) | 38.7 (t); 114.8 (t); 124.8; 124.9; 125.0 (3d); 131.5; 141.9; 149.6 (3s) |
| **6d** | 2.65 (t, 4H, $J$ = 6.7); 5.18, 5.45 (2d, 2H each, $J$ = 1.5); 7.60 (dd, 2H, $J$ = 8.2, 1.8); 7.75–7.92 (m, 4H) | 35.3 (t); 112.4 (t); 124.3; 124.9; 127.9 (3d); 132.7; 138.6; 148.6 (3s) |
| **6e** | 2.62 (t, 4H, $J$ = 7.2); 5.17, 5.43 (2s, 2H each); 7.55 (d, 2H, $J$ = 8.5); 7.78 (d, 2H, $J$ = 8.5); 7.81 (s, 2H) | [b] |
| **6f** | 2.65 (t, 4H, $J$ = 7.4); 5.25, 5.50 (2d, 2H each, $J$ = 1.8); 7.87 (s, 2H); 7.98 (dd, 2H, $J$ = 7.8, 7.6); 8.15 (d, 2H, $J$ = 7.6); 8.40 (d, 2H, $J$ = 7.8) | 38.4 (t); 115.1 (t); 123.1 (d); 124.3 (s); 124.9; 125.7; 125.8; 129.9; 131.0; 146.0; 149.5 (7s) |
| **6g** | 2.63 (t, 4H, $J$ = 6.9); 5.23, 5.75 (2d, 2H each, $J$ = 1.5); 7.32 (d, 2H, $J$ = 7.8); 7.55 (t, 1H, $J$ = 7.8) | 33.8 (t); 114.1 (t); 118.3; 136.3 (2d); 149.0; 157.3 (2s) |

[a] The signals for the alkyl chains are omitted except for those of the methylene group attached to the olefinic group.
[b] The $^{13}$C-NMR signals of compounds **4b**, **4e**, and **6e** (n = 11) are identical with those of the corresponding compounds with n = 5.

All reagents were purchased from Aldrich Chemical Co. and used without further purification. 1,5-Dibromonaphthalene,[31] (dmpe)-$Cl_2$Ni,[32,33] 1-tetradecyne,[34] and 4,9-dibromo-1,2,3,6,7,8-hexahydropyrene[35] were prepared according to literature procedures. THF was freshly distilled from Na. All reactions with Grignard reagents were carried out under $N_2$. 2-Bromo-1-tetradecene (**1**, n = 11) was purified using a "Spaltrohr-Kolonne" (Fischer HMS 500) with 90 th. plates.

Melting points were recorded on a Reichert Thermovar melting point microscope and are uncorrected. Mass spectra were obtained using a Varian MAT 7A with EI ionisation. IR spectra were recorded on a Perkin-Elmer 1430 spectrophotometer, NMR spectra on a Bruker AC 300 spectrometer ($^1$H: 300 MHz; $^{13}$C: 75.5 MHz).

**2-Bromo-1-tetradecene (1, n = 11):**
A slow stream of dry HBr (Linde AG) is passed through a column filled with $CaBr_2$ and then introduced into a stirred, ice-cooled suspension of $Et_4NBr$ (117 g, 0.55 mol) in $CH_2Cl_2$ (200 mL). The desired amount of HBr (45.0 g, 0.55 mol) is determined by weighing the whole flask. 1-Tetradecyne (98.0 g, 0.50 mol) is added, the flask is stoppered tightly, and the stirred mixture is heated to 35–38 °C for 4.5 h. When the temperature of the mixture has reached 20 °C, $Et_2O$ (500 mL) is added, the precipitated salt is filtered off, the solvent is removed under reduced pressure, and the remaining oil is distilled under high vacuum through a 20 cm Vigreux column to give: (1) 1-tetradecyne (10.1 g, bp 75–90 °C/0.05 mbar), (2) 2-bromo-1-tetradecene (**1**, n = 11; 110 g, 80.5%; bp 95–110 °C/0.05 mbar) containing ≈ 5% of impurities (determined by $^1$H-NMR-spectrometry) which were not investigated further. Pure 2-bromo-1-tetradecene (impurities < 0.5%) is obtained by distillation through a Fischer-Spaltrohr column at 74 °C/0.05 mbar; yield: 89 g (65%).

$C_{14}H_{27}Br$ (275.3) calc. C 61.08 H 9.88
found 60.95 9.77

MS (EI): *m/z* (%) = 276, 274 ($M^+$, 3.25).

IR (film): $\nu$ = 2920 (s), 2850 (s), 1625 (m), 1465 (m), 880 (s) $cm^{-1}$.

$^1$H-NMR ($CDCl_3$/TMS): $\delta$ = 0.85 (t, 3 H, $J$ = 6.9 Hz, $CH_3$); 1.15–1.60 (m, 20 H, $CH_{2alkyl}$); 2.40 (t, 2 H, $J$ = 7.2 Hz, $CH_{2allyl}$); 5.35, 5.55 (2 d, 1 H, each, $J$ = 1.5 Hz, $=CH_2$).

$^{13}$C-NMR ($CDCl_3$/TMS): $\delta$ = 14.0 (q); 22.6, 27.9, 28.4, 29.3, 29.5, 29.6, 31.9 (7 t); 41.4 (t); 116.0 (d); 134.9 (s).

**2,6-Dibromonaphthalene:**[30]

A 1000 mL three-necked flask, fitted with thermometer, pressure-equalizing dropping funnel, and reflux condenser, is charged with $Ph_3P$ (130 g, 0.5 mol) and MeCN (250 mL). The stirred suspension is cooled in an ice bath, and $Br_2$ (80 g, 0.5 mol) is added dropwise, keeping the temperature below 25 °C. Then, 6-bromo-2-naphthol (100 g, 0.44 mol) is added and the mixture is heated at 60–70 °C for 2 h. All volatile material is then removed under vacuum up to 110 °C (bath). The condenser is replaced by a wide glass tube, connected to a 250 mL two-necked flask which is half-filled with $H_2O$. The stirred mixture is then heated at 320 °C using a heating mantle until the evolution of HBr ceases ($\approx$ 1 h). The residual black oil is cooled to 150 °C and poured into a large crystallizing dish. By cooling with liquid $N_2$, crystallization of the oil is completed. The resultant black solid is powdered and extracted with petroleum ether (bp 60–80 °C) (600 mL) in a soxhlet apparatus for 20 h. On cooling the extract to −18 °C, crude 2,6-dibromonaphthalene (45 g, 35%) precipitates. The product is isolated by suction, washed with hot EtOH (2 × 150 mL), and dried in high vacuum to give a light yellow solid; yield (average of three independent runs): 36 g (0.125 mol, 28%); mp 155 °C (Lit.[26] mp 159 °C). All analytical data are in full agreement with those given in Refs. 26–29.

**4,9-Dibromopyrene:**

4,9-Dibromo-1,2,3,6,7,8-hexahydropyrene (12.0 g, 32 mmol) and tetrachloro-*o*-benzoquinone (27.6 g, 110 mmol) are heated in boiling dry toluene (300 mL) for 60 h under $N_2$. The resultant redbrown solution is columnchromatographed through neutral aluminia (activity I; eluent toluene). The first fraction gives the product as pale yellow crystals (6.0 g) which are recrystallized from hot $CHCl_3$ (250 mL) to give the pure product as colorless crystals; yield: 4.5 g (39%); mp 247 °C.

| | | | |
|---|---|---|---|
| $C_{18}H_8Br_2$ | calc. | C 53.35 | H 2.23 |
| (384.1) | found | 53.68 | 2.40 |

MS (EI): *m/z* (%) = 362 (49), 360 (100), 358 (57).

IR (KBr): $\nu$ = 3030 (w), 1585 (s), 1436 (s), 1418 (m), 1213 (m), 988 (m), 872 (s), 783 (s), 715 (s) $cm^{-1}$.

$^1$H-NMR ($CDCl_3$/TMS): $\delta$ = 8.00–8.28 [m, 4 H, H-1 (H-6), H-2 (H-7)]; 8.40 [s, 2 H, H-5 (H-10)]; 8.57 [d, 2 H, $J$ = 7.7 Hz, H-3 (H-8)].

$^{13}$C-NMR ($CDCl_3$/TMS): $\delta$ = 122.5 (s); 124.5 (s); 125.7, 125.8, 127.0 (3 d); 129.8 (s); 130.8 (s); 131.4 (d).

**2,6-Bis(1-hexylethenyl)naphthalene (6d); Typical Coupling Procedure:**

A 500 mL two-necked flask equipped with a pressure-equalizing dropping funnel and a reflux condenser attached to an $N_2$ line is dried under reduced pressure and filled with $N_2$. The flask is charged with 2,6-dibromonaphthalene (15 g, 0.052 mol), (dmpe)$NiCl_2$ (105 mg, 0.5 mol %, based on Grignard reagent), and THF (100 mL). A warm Grignard solution prepared from Mg turnings (3.75 g, 0.15 mol) and 2-bromo-1-octene (**1**, n = 5; 26.0 g, 0.13 mol) in THF (75 mL), is filtered into the dropping funnel through glass wool. Addition of the first drops of the Grignard solution, changes the color of the clear mixture to red, then to brown. After an induction period of $\approx$ 2 min, the solution begins to boil, and the Grignard reagent is added so that gentle boiling of the mixture is maintained. After 60 h, the mixture is cooled to 20 °C and carefully hydrolyzed with ice water (150 mL). The layers are separated, and the aqueous layer is extracted with $Et_2O$ (2 × 50 mL). The combined organic layers are dried ($MgSO_4$) and the solvent is evaporated. The remaining yellow-brown oil (20 g) is dissolved in petroleum ether (bp 30–40 °C; 30 mL) and this solution is filtered through silica gel (300 g). The solvent is removed, and the remaining pale yellow oil (17.5 g) is distilled under high vacuum to give (1) *7,8-bis(methylene)tetradecane* (0.5 g, bp 69 °C/0.02 mbar) and (2) product **6d** as a colorless oil which crystallizes spontaneously; yield: 10.0 g (55%).

All other coupling reactions are carried out in the same manner and on the same scale. Reaction times and exceptions from the typical procedure are given below; for other data, see Tables 1 and 2.

*(1-Hexylethenyl)benzene (2-Phenyl-1-octene,* **4a***)*; reaction time: 36 h; colorless oil.

*(1-Dodecylethenyl)benzene (2-Phenyl-1-tetradecene,* **4b***)*; reaction time: 48 h, colorless oil.

*1-(1-Hexylethenyl)naphthalene [2-(1-Naphthyl)-1-octene,* **4c***]*; reaction time: 36 h; colorless oil.

*2-(1-Hexylethenyl)naphthalene [2-(2-Naphthyl)-1-octene,* **4d***]*: reaction time: 36 h, colorless oil.

*2-(1-Dodecylethenyl)naphthalene [2-(2-Naphthyl)-1-tetradecene,* **4e***]*; reaction time: 36 h; colorless oil which crystallizes spontaneously and is recrystallized from hot MeOH.

*1,2-Bis(1-hexylethenyl)benzene* **(6a)**; reaction time: 48 h; colorless oil.

*1,4-Bis(1-hexylethenyl)benzene* **(6b)**; reaction time: 60 h; colorless oil.

*1,5-Bis(1-hexylethenyl)naphthalene* **(6c)**; reaction time: 60 h; light yellow oil.

*2,6-Bis(1-dodecylethenyl)naphthalene* **(6e)**; reaction time: 48 h. After filtration of the crude product solution through silica gel, and evaporation, the crude product is washed with hot MeOH and dried in vacuum. The purity of the crystalline pale yellow product **6e** is sufficient for most applications. Recrystallization from a large amount of methanol gives colorless crystals.

*4,9-Bis(1-hexylethenyl)pyrene* **(6f)**; prepared on a smaller scale (4 g, 11.1 mmol); reaction time: 60 h. The crude product is chromatographed through silica gel with petroleum ether as eluent and dried in high vacuum. After distillation, product **6f** is obtained as a light yellow oil.

*2,6-Bis(1-hexylethenyl)pyridine* **(6g)**; reaction time: 48 h; colorless oil.

**2-(2-Hexylethenyl)naphthalene (7):**

A solution of 2-(1-hexylethenyl)naphthalene (**4d**; 1.5 g, 6.3 mmol) in $CHCl_3$ (5 mL) containing trifluoroacetic acid (a few drops) is heated to reflux for 3 h. The solvent is then evaporated and the remaining pale-yellow oil is distilled under high vacuum to give product **7** as a colorless oil; yield: 1.3 g (86%); bp 110 °C/0.002 mbar.

$C_{18}H_{22}$ (238.4); microanalysis not performed.

MS (EI): *m/z* (%) = 238 ($M^+$, 44).

IR (film): $\nu$ = 3050 (m), 2970–2840 (s), 1628 (m), 1502 (m), 1465 (m), 850 (s), 812 (s), 745 (s), 485 (s) $cm^{-1}$.

The NMR-spectral data are given for the *E*-isomer; the chemical shifts obtained with the *Z*-isomer are virtually the same exept for the olefinic proton in the $^1$H-NMR spectrum ($\delta$ = 5.55); *E*/*Z* = 9:1.

$^1$H-NMR ($CDCl_3$/TMS): $\delta$ = 0.90 (t, 3 H, $J$ = 6.9 Hz, $CH_{3alkyl}$); 1.15–1.55 (m, 6 H, $CH_{2alkyl}$); 2.13 (d, 3 H, $J$ = 1.3 Hz, $CH_{3allyl}$); 2.25 (m, 2 H, $CH_{2allyl}$); 5.95 (dt, 1 H, $J$ = 7.2, 1.3 Hz); $H_{olefin}$); 7.45–7.85 (m, 7 $H_{arom}$).

$^{13}$C-NMR ($CDCl_3$/TMS): $\delta$ = 14.0 (q); 15.7 (q); 22.6, 28.9, 29.3 (3 t); 31.7 (t); 123.8 (d); 124.4, 125.3, 125.9, 127.4, 127.5, 128.0, 129.5 (7 d); 132.4, 133.6 (2 s); 134.3 (s); 141.2 (q).

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