154. Reduction of Indolin-2-ones and Desulfurization of Indoline-2-thiones to Indoline and Indole Derivatives

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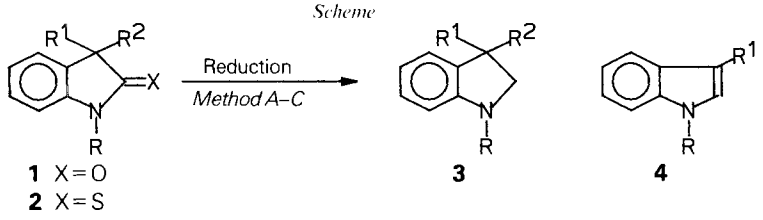
Reduction of indolin-2-ones with lithium aluminum hydride (LAH) or diisobutylaluminum hydride (DIBAL) and desulfurization of indoline-2-thiones with *Raney*-Ni were investigated. Treatment of indolin-2-ones **1** with LAH or DIBAL yielded indoles **4** and/or indolines **3** in moderate-to-high yields depending on the substituents at N and C(3) of **1**. Indoline-2-thiones **2** were desulfurized with *Raney*-Ni to give indoles **4** and/or indolines **3**.

1. Introduction. – Recently, we reported that, upon irradiation, indoline-2-thiones **2** gave the desulfurization products, indoles **4** [1] or indolines **3** [2] (*Scheme*). Reactions of indolin-2-ones **1** and indoline-2-thiones **2** with reducing agents have also been reported [3]. *Julian* and *Printy* [4] and *Hudson* and *Robertson* [5][1]) have reported that indolin-2-ones unsubstituted on the N-atom were inert to reduction by $LiAlH_4$; however, *N*-substituted indolin-2-ones were converted into the corresponding *N*-substituted indoles and indolines. On the other hand, *Smith* and *Yu* have reported that treatment of *N*-substituted

Scheme



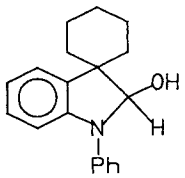
Method A: $LiAlH_4/Et_2O$; *B:* DIBAL/THF; *C: Raney*-Ni/MeOH

indolin-2-ones with $LiAlH_4$ yielded indolines [6]. Desulfurization of indoline-2-thiones to indoles with *Raney*-Ni has been reported by *Pleninger* and *Werst* [7]. However, conversion of indolin-2-ones **1** or indoline-2-thiones **2** to indolines **3** or indoles **4** has not been studied in details. Here, we report the reduction of **1** with $LiAlH_4$ or DIBAL (diisobutylaluminum hydride) [8] and the desulfurization of **2** with *Raney*-Ni to indolines **3** and/or indoles **4**.

2. Results and Discussion. – *Reduction of Indolin-2-ones* **1** *with* $LiAlH_4$ *or DIBAL.* *N*-Unsubstituted indolin-2-one (**1a**) was treated with $LiAlH_4$ in Et_2O under reflux or DIBAL in THF at room temperature to yield indole (**4a**) in low yields (19–30%), and

[1]) Under vigorous conditions, for example, refluxing in THF, indole was produced in low yield.

indoline (**3a**) was not obtained. The former result is incompatible with *Smith*'s results, in which indoline was produced; however, no experimental details were reported [6]. Treatment of *N*-unsubstituted indolin-2-one **1c**, which has two substituents at C(3), with $LiAlH_4$ gave indoline **3c** in high yield, while a transformation did not occur, when **1c** was treated with DIBAL even at higher temperature (reflux in THF). *N*-Substituted indolin-2-ones **1d,k** were reduced with both $LiAlH_4$ and DIBAL to yield indolines **3d,k** and indoles **4d,k**. The ratio **3k**/**4k** seems to depend on the reaction time. 1-Phenylindole (**4k**) thus obtained was not reduced further with $LiAlH_4$ under the same conditions. In case of 3-phenylindolin-2-ones **1e,h,n** possessing one H-atom at C(3), indoles **4e,h,n**, respectively, were produced as the sole products. However, 1-phenyl-3-methylindolin-2-one (**1l**) gave indoline **3l** and indole **4l**. Reduction of indolin-2-ones **1** to indolines **3** or indoles **4** was affected by the substituents at C(3) of **1**, in which bulky substituent such as Ph group did not easily reduce **1** to indolines. The relative yield of products **3l** and **4l** was reversed by use of reducing agents ($LiAlH_4$ and DIBAL). Indoline **3l** was obtained in higher yield than indole **4l** by use of $LiAlH_4$, while indole was predominantly produced by use of DIBAL. 1,3,3-Trisubstituted indolin-2-ones **1f,i,j,m,o,p,q,s** were reduced with $LiAlH_4$ and/or DIBAL to give indolines **3f,i,j,m,o,p,q,s**, respectively, in 22–98% yields, depending on the substituents at C(3) as well as at C(1). Indolin-2-one **1r** was not converted into the corresponding indoline; however, **1r** gave 2-hydroxyindoline derivative **5** in almost quantitative yield, probably due to steric factor at C(3). The results were summarized in the *Table*. The reaction mechanism almost certainly involves initial reduction to the reaction species **6** which then suffers elimination of H_3LiAlO^- or $(i\text{-}Bu)_2AlO^-$.



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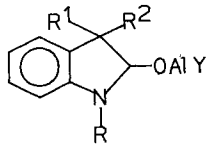

6a Y = H_3Li
b Y = $(i\text{-}Bu)_2$

Desulfurization of Indoline-2-thiones **2** *with* Raney-*Ni*. *Raney*-Ni is well known to be an excellent desulfurizing reagent. Thus, we investigated the transformation of indoline-2-thiones, which are readily prepared by the reaction of the corresponding indolin-2-ones with *Lawesson*'s reagent (2,4-bis(*p*-methoxyphenyl)-1,3-dithiaphosphetane-2,4-disulfide) [1] [2], to indolines or indoles by desulfurization with *Raney*-Ni. *N*-Unsubstituted indoline-2-thione (**2a**) was desulfurized with *Raney*-Ni to give indole (**4a**) in good yield, in agreement with results of *Pleninger* and *Werst* [7]. Indoline-2-thiones **2b,c** having two substituents at C(3) gave indoline **3b,c**, respectively, by treatment of **2b,c** with *Raney*-Ni. Desulfurization of 1-alkyl-3-monosubstituted indoline-2-thiones **2e,h** with *Raney*-Ni gave the corresponding indoles **4e,h** as the sole products. On the other hand, 1-phenylindoline-2-thiones **2k,l** gave both products, indolines **3k,l** and indoles **4k,l**. Product distribution of this reaction is in accord with that of $LiAlH_4$ reduction of indolin-2-ones **3**. 1,3,3-Trisubstituted indoline-2-thiones **2f,g,i,m,o,q,r,s** were treated with *Raney*-Ni to yield indoline derivatives **3f,g,i,m,o,q,r,s** in moderate-to-high yields depending on the

Table. *Yield of Indolines* **3** *and Indoles* **4**

	R	R^1	R^2	Yield [%][a])		
				Method	**3**	**4**
1a	H	H	H	*A*	–[b])	19
1a	H	H	H	*B*	–	36
2a	H	H	H	*C*	–	70
2b	H	Me	Me	*C*	60	
1c	H	Ph	Ph	*A*	97	
1c	H	Ph	Ph	*B*	0[c])	
2c	H	Ph	Ph	*C*	81	
1d	Me	H	H	*B*	7	22
1e	Me	Ph	H	*B*	–	46
2e	Me	Ph	H	*C*	–	68
2e	Me	Ph	H	*C*[d])	–	71
1f	Me	Me	Me	*A*	68	
2f	Me	Me	Me	*C*	92	
2g	Me	Ph	Me	*C*	69	
1h	Bu	Ph	H	*B*	–	69
1i	Bu	Me	Me	*A*	96	
2i	Bu	Me	Me	*C*	98	
1j	$PhCH_2$	Me	Me	*A*	95	
2j	$PhCH_2$	Me	Me	*C*	6[e])	
1k	Ph	H	H	*A*	49	18
1k	Ph	H	H	*B*[f])	14	42
1k	Ph	H	H	*B*[g])	24	44
2k	Ph	H	H	*C*	21	55
1l	Ph	Me	H	*A*	53	12
1l	Ph	Me	H	*B*	27	55
2l	Ph	Me	H	*C*	37	55
1m	Ph	Me	Me	*A*	27	
1m	Ph	Me	Me	*B*	32	
2m	Ph	Me	Me	*C*	44	
2m	Ph	Me	Me	*C*[d])	61	
1n	Ph	Ph	H	*B*	–	82
1o	Ph	Me	$EtOCH_2CH_2$	*A*	42	
2o	Ph	Me	$EtOCH_2CH_2$	*C*	69	
1p	Ph	Me	$EtSCH_2CH_2$	*A*	22	
2p	Ph	Me	$EtSCH_2CH_2$	*C*	0[h])	
1q	Ph	$-(CH_2)_4-$		*A*	67	
2q	Ph	$-(CH_2)_4-$		*C*	84	
1r	Ph	$-(CH_2)_5-$		*A*	0[i])	
2r	Ph	$-(CH_2)_5-$		*C*	77	
1s	Ph	$-(CH_2)_2-O-(CH_2)_2-$		*A*	83	
2s	Ph	$-(CH_2)_2-O-(CH_2)_2-$		*C*	53	

[a]) Isolated yield. [b]) Not detected. [c]) No reaction (**1c** was recovered quantitatively, even when the reaction was carried out under reflux). [d]) Under a H_2 atmosphere. [e]) 3,3-Dimethylindoline (**3b**) was isolated in 60% yield as major product. [f]) Reaction time: 1 h. [g]) Longer reaction time (15 h). [h]) 57% Recovery of **2p**. [i]) 2-Hydroxyindoline derivative **5** was produced in almost quantitative yield.

substituent at C(1) and C(3). Generally, the formation of indolines from 1-phenylindoline-2-thiones seems to be slower than that of 1-methylindoline-2-thiones. Treatment of 1-benzyl-3,3-dimethylindoline-2-thione (**2j**) with *Raney*-Ni gave 3,3-dimethylindoline (**3b**) as major product, along with a small amount of 1-benzyl-3,3-dimethylindoline (**3j**)

(6%). The formation of **3b** is attributed to the C–N bond cleavage of (**3j**) under the reaction conditions. Indoline-2-thione **2p** having an additional thio in the same molecule did not give any desulfurization products, probably due to the S-atom acting as catalyst poison. Indoline-2-thiones **2e** and **2m** were treated with *Raney*-Ni under H_2 atmosphere also to yield indole **4e** and indoline **3m**, where yields increased slightly (*Table*).

In conclusion, depending on the substituent both on the N-atom and at C(3), indolines **3** and/or indoles **4** were produced by the reduction of indolin-2-ones **1** or by the desulfurization of indolin-2-thiones **2**.

Experimental Part

General. M.p. and b.p.: uncorrected. IR spectra: *Hitachi 260-30* spectrophotometer. ^{1}H- and ^{13}C-NMR spectra: on a *Jeol FX-100* (100 MHz) spectrometer, in $CDCl_3$ as solvent, using TMS as an internal standard.

Reduction of Indolin-2-ones **1** *with* $LiAlH_4$ (*Method A*). To a soln. of **1** (1 mmol) in Et_2O (30 ml), $LiAlH_4$ (1 mol-equiv.) was added in portions at r.t., and the mixture was refluxed for 2–3 h under Ar. The mixture was poured into dil. HCl soln., then extracted with Et_2O, and worked up. After evaporation, the residue was chromatographed on a silica-gel column with benzene/hexane 9:1–4:1 to yield indolines **3** and/or indoles **4**.

Reduction of **1** *with DIBAL* (*Method B*). To a soln. of **1** (1 mmol) in THF (30 ml), a soln. of DIBAL in toluene (3 mol-equiv.) was added dropwise at 0° (ice-bath), and the mixture was stirred for 1–2 h at r.t. under Ar. Usual workup gave **3** and/or **4**.

Desulfurization of Indoline-2-thiones **2** *with* Raney-*Ni* (*Method C*). A soln. of **2** (1 mmol) and a large excess of *Raney*-Ni in MeOH (30 ml) was heated to reflux for 1 h under Ar. *Raney*-Ni was removed by decantation, and the mixture was worked up in usual manner. Column chromatography of the residue yielded **3** and/or **4**. The structure of indolines **3d**,**k** and indoles **4a**,**e**,**h**,**k**,**l**,**n** was confirmed by direct comparison of their spectral data with those of authentic materials [1] [9].

3,3-Dimethylindoline (**3b**). B.p. 60°/2 Torr. IR ($CHCl_3$): 3400, 1605. ^{1}H-NMR: 1.29 (*s*, 6 H); 3.28 (*s*, 2 H); 3.72 (*s*, 1 H); 6.57–6.80 (*m*, 2 H); 6.94–7.19 (*m*, 2 H). ^{13}C-NMR: 27.5 (*q*); 41.7 (*s*); 61.5 (*t*); 109.6 (*d*); 118.8 (*d*); 121.9 (*d*); 127.2 (*d*); 138.4 (*s*); 150.0 (*s*). Anal. calc. for $C_{10}H_{13}N$: C 81.58, H 8.90, N 9.51; found: C 81.49, H 8.89, N 9.51.

3,3-Diphenylindoline (**3c**). B.p. 190°/2 Torr. IR (film): 3380, 1590. ^{1}H-NMR: 3.54 (br. *s*, 1 H); 4.03 (*s*, 2 H); 6.60–6.81 (*m*, 2 H); 6.96–7.32 (*m*, 12 H). ^{13}C-NMR: 59.4 (*s*); 62.4 (*t*); 110.4 (*d*); 119.0 (*d*); 125.9 (*d*); 126.2 (*d*); 127.9 (*d*); 134.4 (*s*); 146.5 (*s*); 150.4 (*s*). Anal. calc. for $C_{20}H_{17}N$: C 88.53, H 6.62, N 5.16; found: C 88.37, H 6.30, N 5.16.

1,3,3-Trimethylindoline (**3f**). B.p. 45°/2 Torr. IR ($CHCl_3$): 1610, 1490. ^{1}H-NMR: 1.29 (*s*, 6 H); 2.74 (*s*, 3 H); 3.05 (*s*, 2 H); 6.43–6.77 (*m*, 2 H); 6.96–7.51 (*m*, 2 H). ^{13}C-NMR: 27.4 (*q*); 35.9 (*q*); 40.2 (*s*); 70.3 (*t*); 107.3 (*d*); 117.9 (*d*); 121.4 (*d*); 127.4 (*d*); 139.1 (*s*); 151.8 (*s*). Anal. calc. for $C_{11}H_{15}N$: C 81.93, H 9.37, N 8.68; found: C 81.91, H 9.47, N 8.68.

1,3-Dimethyl-3-phenylindoline (**3g**). B.p. 85°/2 Torr. IR ($CHCl_3$): 1600, 1490. ^{1}H-NMR: 1.70 (*s*, 3 H); 2.76 (*s*, 3 H); 3.30 (*A* of *ABq*, J = 8.8, 1 H); 3.52 (*B* of *ABq*, J = 8.8, 1 H); 6.53–7.38 (*m*, 9 H). ^{13}C-NMR: 26.3 (*q*); 36.1 (*q*); 48.3 (*s*); 72.1 (*t*); 107.8 (*d*); 118.3 (*d*); 123.7 (*d*); 126.1 (*d*); 126.5 (*d*); 127.8 (*d*); 128.1 (*d*); 137.7 (*s*); 147.4 (*s*); 152.5 (*s*). Anal. calc. for $C_{16}H_{17}N$: C 86.05, H 7.67, N 6.27; found: C 85.99, H 7.78, N 6.25.

1-Butyl-3,3-dimethylindoline (**3i**). B.p. 125°/2 Torr. IR (film): 1595, 1480. ^{1}H-NMR: 0.95 (*t*, J = 6.8, 3 H); 1.27 (*s*, 6 H); 1.12–1.65 (*m*, 4 H); 3.04 (*t*, J = 3.9, 2 H); 3.08 (*s*, 2 H); 6.39–6.70 (*m*, 2 H); 6.94–7.14 (*m*, 2 H). ^{13}C-NMR: 14.0 (*q*); 20.4 (*t*); 27.7 (*q*); 29.5 (*t*); 40.0 (*s*); 48.3 (*t*); 67.3 (*t*); 106.6 (*d*); 117.1 (*d*); 121.5 (*d*); 127.3 (*d*); 138.7 (*s*); 151.2 (*s*). Anal. calc. for $C_{14}H_{21}N$: C 82.70, H 10.41, N 6.83; found: C 82.77, H 10.46, N 6.84.

1-Benzyl-3,3-dimethylindoline (**3j**). B.p. 165°/2 Torr. IR (film): 1600, 1585. ^{1}H-NMR: 1.27 (*s*, 6 H); 3.03 (*s*, 2 H); 4.21 (*s*, 2 H); 6.40–6.75 (*m*, 2 H); 6.95–7.35 (*m*, 7 H). ^{13}C-NMR: 27.5 (*q*); 40.0 (*s*); 53.0 (*t*); 67.7 (*t*); 106.9 (*d*); 117.7 (*d*); 121.6 (*d*); 126.9 (*d*); 127.3 (*d*); 127.6 (*d*); 128.2 (*d*); 128.3 (*d*); 138.4 (*s*); 128.7 (*s*); 150.9 (*s*). Anal. calc. for $C_{17}H_{19}N$: C 86.02, H 8.06, N 5.90; found: C 85.67, H 8.05, N 5.90.

1-Phenylindoline (**3k**). M.p. 49–50°. IR (KBr): 1590, 1495. ^{1}H-NMR: 3.10 (*t*, J = 8.3, 2 H); 3.93 (*t*, J = 8.3, 2 H); 6.64–7.53 (*m*, 9 H). ^{13}C-NMR: 28.2 (*t*); 52.1 (*t*); 108.1 (*d*); 117.6 (*d*); 118.8 (*d*); 120.9 (*d*); 125.0 (*d*); 127.1 (*d*); 129.1 (*d*); 131.2 (*s*); 144.2 (*s*); 147.1 (*s*). Anal. calc. for $C_{14}H_{13}N$: C 86.11, H 6.71, N 7.17; found: C 86.10, H 6.66, N 7.17.

3-Methyl-1-phenylindoline (**3l**). IR (film): 1590, 1495. ^{1}H-NMR: 1.35 (*d*, *J* = 6.8, 3 H); 3.29–3.61 (*m*, 2 H); 3.87–4.50 (*m*, 1 H); 6.67–7.76 (*m*, 9 H). ^{13}C-NMR: 19.8 (*q*); 34.7 (*d*); 60.0 (*t*); 108.1 (*d*); 117.5 (*d*); 118.9 (*d*); 120.7 (*d*); 123.7 (*d*); 127.1 (*d*); 129.1 (*d*); 136.3 (*s*); 144.0 (*s*); 146.5 (*s*). Anal. calc. for $C_{15}H_{15}N$: C 86.08, H 7.22, N 7.22; found: C 86.31, H 7.04, N 6.74.

3,3-Dimethyl-1-phenylindoline (**3m**). B.p. 135°/2 Torr. M.p. 59–60°. IR (KBr): 1595, 1500. ^{1}H-NMR: 1.34 (*s*, 6 H); 3.66 (*s*, 2 H); 6.68–7.41 (*m*, 9 H). ^{13}C-NMR: 27.8 (*q*); 39.8 (*s*); 66.3 (*t*); 108.1 (*d*); 117.4 (*d*); 119.0 (*d*); 120.7 (*d*); 122.2 (*d*); 127.1 (*d*); 129.1 (*d*); 140.2 (*s*); 144.1 (*s*); 145.5 (*s*). Anal. calc. for $C_{16}H_{17}N$: C 86.05, H 7.67, N 6.27; found: C 85.74, H 7.73, N 6.24.

3-(2-Ethoxyethyl)-3-methyl-1-phenylindoline (**3o**). B.p. 170°/2 Torr. IR (film): 1585, 1500. ^{1}H-NMR: 1.09 (*t*, *J* = 6.8, 3 H); 1.37 (*s*, 3 H); 1.95 (*t*, *J* = 6.3, 2 H); 3.35 (*q*, *J* = 6.8, 2 H); 3.42 (*t*, *J* = 6.3, 2 H); 3.63 (*d*, *J* = 9.3, 1 H); 3.87 (*d*, *J* = 9.3, 1 H); 6.67–7.40 (*m*, 9 H). ^{13}C-NMR: 15.1 (*q*); 26.3 (*q*); 40.2 (*t*); 42.0 (*s*); 64.5 (*t*); 66.2 (*t*); 67.5 (*t*); 108.2 (*d*); 117.4 (*d*); 118.9 (*d*); 120.7 (*d*); 122.8 (*d*); 129.0 (*d*); 138.6 (*s*); 143.9 (*s*); 145.8 (*s*). Anal. calc. for $C_{19}H_{23}NO$: C 81.09, H 8.23, N 4.97; found: C 80.89, H 8.21, N 4.98.

3-[2-(Ethylthio)ethyl]-3-methyl-1-phenylindoline (**3p**). B.p. 180°/2 Torr. IR (film): 1595, 1500. ^{1}H-NMR: 1.17 (*t*, 3 H); 1.37 (*s*, 3 H); 1.81–2.05 (*m*, 2 H); 2.28–2.69 (*m*, 4 H); 3.71 (*dd*, *J* = 9.8, 10.7, 2 H); 6.68–7.41 (*m*, 9 H). ^{13}C-NMR: 14.7 (*q*); 26.0 (*q*); 26.8 (*t*); 29.5 (*t*); 41.1 (*t*); 43.2 (*s*); 64.1 (*t*); 108.3 (*d*); 117.5 (*d*); 119.0 (*d*); 120.9 (*d*); 122.8 (*d*); 127.4 (*d*); 129.1 (*d*); 137.7 (*s*); 143.7 (*s*); 146.0 (*s*). Anal. calc. for $C_{19}H_{23}NS$: C 76.71, H 7.79, N 4.70; found: C 76.76, H 7.85, N 4.55.

1'-Phenylspiro[cyclopentane-1,3'-indoline] (**3q**). B.p. 165°/2 Torr. IR (film): 1590, 1500. ^{1}H-NMR: 1.49–1.95 (*m*, 8 H); 3.68 (*s*, 2 H); 6.66–7.40 (*m*, 9 H). ^{13}C-NMR: 24.8 (*t*); 39.9 (*t*); 51.1 (*s*); 65.9 (*t*); 107.9 (*d*); 117.5 (*d*); 119.1 (*d*); 120.6 (*d*); 122.4 (*d*); 127.0 (*d*); 129.0 (*d*); 139.0 (*s*); 144.0 (*s*); 146.2 (*s*). Anal. calc. for $C_{18}H_{19}N$: C 86.70, H 7.68, N 5.61; found: C 86.40, H 7.62, N 5.88.

1'-Phenylspiro[cyclohexane-1,3'-indoline] (**3r**). B.p. 185°/2 Torr. IR (film): 1590, 1500. ^{1}H-NMR: 1.04–1.90 (*m*, 10 H); 3.76 (*s*, 2 H); 6.66–7.40 (*m*, 9 H). ^{13}C-NMR: 28.1 (*t*); 25.6 (*t*); 36.6 (*t*); 44.0 (*s*); 61.9 (*t*); 108.2 (*d*); 117.3 (*d*); 118.8 (*d*); 120.5 (*d*); 122.6 (*d*); 127.2 (*d*); 129.0 (*d*); 140.2 (*s*); 144.1 (*s*); 145.6 (*s*). Anal. calc. for $C_{19}H_{21}N$: C 86.64, H 8.03, N 5.31; found: C 86.47, H 8.04, N 5.29.

1-Phenylspiro[indoline-3,1'-oxane] (**3s**). M.p. 112–113°. IR (KBr): 1590, 1500. ^{1}H-NMR: 1.53–2.27 (*m*, 4 H); 3.36–4.07 (*m*, 6 H); 6.67–7.45 (*m*, 9 H). ^{13}C-NMR: 35.6 (*t*); 41.6 (*s*); 61.5 (*t*); 64.8 (*t*); 108.3 (*d*); 117.5 (*d*); 118.1 (*d*); 122.7 (*d*); 127.6 (*d*); 128.2 (*d*); 129.0 (*d*); 138.3 (*s*); 143.7 (*s*); 145.7 (*s*). Anal. calc. for $C_{18}H_{19}NO$: C 81.47, H 7.21, N 5.27; found: C 81.78, H 7.13, N 5.20.

Spiro[cyclohexane-1,3'-indolin]-2'-ol (**5**). IR (KBr): 3270, 1595, 1500. ^{1}H-NMR: 1.00–2.02 (*m*, 10 H); 2.24 (*d*, *J* = 9.8, 1 H); 5.23 (*d*, *J* = 9.8, 1 H); 6.68–7.54 (*m*, 9 H). ^{13}C-NMR: 23.1 (*t*); 23.8 (*t*); 25.6 (*t*); 29.1 (*t*); 36.8 (*t*); 49.0 (*s*); 93.4 (*d*); 109.5 (*d*); 118.8 (*d*); 119.9 (*d*); 122.4 (*d*); 123.3 (*d*); 127.5 (*d*); 129.3 (*d*); 138.1 (*d*); 142.9 (*s*); 143.3 (*s*). Anal. calc. for $C_{19}H_{21}NO$: C 81.68, H 7.57, N 5.01; found: C 82.04, H 7.58, N 4.98.

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