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Formation of Vinylic Dipyrroles by the Deprotonation of *meso*-Alkyl and *meso*-Benzyl Dipyrrin HCl Salts

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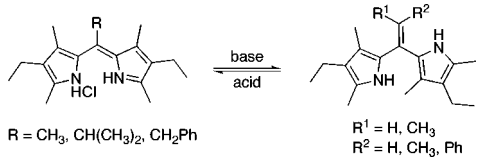

Under basic conditions, dipyrrin salts bearing alkyl and benzyl groups at the *meso*-position undergo deprotonation to give vinylic dipyrroles, rather than the corresponding free-base dipyrrins. The deprotonation is reversible and quantitatively returns the dipyrrinato framework under acidic conditions.

Dipyrrins (dipyrromethenes, **1**)[1] are fully conjugated, planar, 12-π-electron molecules that formally consist of a pyrrole attached to an azafulvene (Figure 1). Conversion into monoanionic species upon deprotonation of the pyrrolic N-*H* gives dipyrrinato units that can serve as bidentate ligands for the synthesis of supramolecular assemblies,[2,3] helicates,[4−7] metal-organic frameworks,[8] boron difluoride (BODIPY) dyes,[9,10] and other complexes.[11−13]

For convenience, the 5-position is termed the *meso*-position. Dipyrrins bearing aryl substituents at the *meso*-position display enhanced stability,[14] cf. their *meso*-H counterparts,[1] and free-bases of *meso*-aryl dipyrrins may be isolated and stored in air.[1] As part of ongoing investigations to identify the scope and limitations of dipyrrinato ligands we herein report the synthesis and reactivity of *meso*-alkyl and *meso*-benzyl dipyrrins, classes of compounds that until now have been known largely as their BODIPY complexes.[15−20]

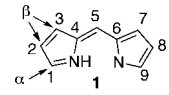

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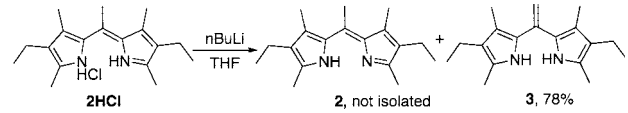
FIGURE 1. Dipyrrin skeleton.

SCHEME 1. Deprotonation of *meso*-Methyl Dipyrrin 2



2HCl **2**, not isolated **3**, 78%

Free-base dipyrrins are typically prepared by treating the corresponding hydrobromide or hydrochloride salts with bases such as LiH or ammonium hydroxide.[21] In an attempt to obtain a *meso*-alkyl dipyrrin free-base, **2HCl** was reacted with LiH. In this instance, the use of LiH did not provide access to the desired free-base, with an intractable mixture resulting. The slow addition of 1.1 equiv of *n*BuLi to an anhydrous THF solution of **2HCl** under an inert atmosphere afforded a product that was purified via extraction (Scheme 1). Surprisingly, the ^{1}H NMR spectrum of the isolated compound dissolved in CD_3OD showed that the *meso*-methyl signal, previously at δ 2.75 ppm for the **2HCl** salt, was no longer present and instead a signal at δ 5.10 ppm had appeared: such a chemical shift is more in line with an sp^2 hybridized carbon atom, rather than an sp^3 hybridized carbon atom.

Further NMR data (DEPTQ-135) collected on the isolated material revealed only three types of methyl group to be present whereas four would be expected for the free-base **2**. Moreover, the absence of signals for the fourth methyl group in the aliphatic region was accompanied by the presence of a vinylic resonance at δ 107.5 ppm, correlating with the signal at δ 5.10 ppm in the ^{1}H NMR spectrum. Together, these data are consistent with a formulation such as **3**, in which deprotonation at the *meso*-methyl group had occurred. Moreover, ^{15}N NMR spectroscopic analysis revealed a signal at δ −233.5 ppm after treatment with BuLi, compared to δ −213.7 ppm for **2HCl**: δ −233.5 ppm is consistent with typical ^{15}N chemical shifts for pyrrolic compounds.[22] A crystal of the isolated compound suitable for X-ray

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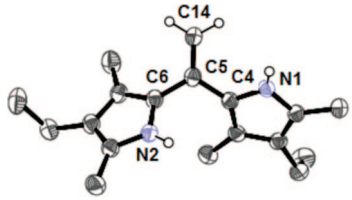

FIGURE 2. ORTEP representation of dipyrrole **3**, shown with probability ellipsoids of 50%.

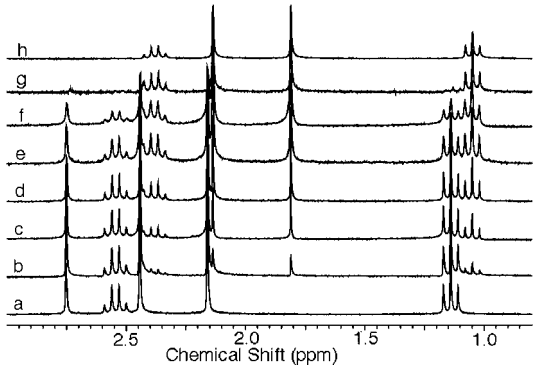

FIGURE 3. ^{1}H NMR titration of **2HCl** with NaOD in CD_3OD. Spectra b−h were recorded upon the addition of aliquots containing NaOD, as per Table 1.

diffraction analysis was grown via the evaporation of solvent from a pentane solution, and the structure was thus confirmed to be that of **3**, a vinylic dipyrrole (Figure 2).

The X-ray structure of **3** shows the loss of the planarity of the molecule (cf. a dipyrrin) where the two nitrogen atoms adopt an almost anti conformation to presumably minimize the polarity of the molecule and steric interactions. The bond angles of C4−C5−C6 117.6(2)°, C4−C5−C14 120.8(2)°, and C6−C5−C14 121.6°(2) support the formation of a trigonal planar-sp^2 carbon atom at the *meso*-position. Importantly, the C5−C14 bond was found to be 1.338(3) Å, the shortest C−C bond within the molecule, again supporting the formation of a double bond between C5 and C14.

In response to these interesting observations, dipyrrin salt **2HCl** was titrated with a solution of deuterated sodium hydroxide NaOD (in CD_3OD) (Figure 3). As expected, the deprotonation could be monitored by the disappearance of the *meso*-methyl resonance at δ 2.75 ppm in the ^{1}H NMR spectrum. Additionally, the ^{1}H NMR spectra showed a change in the chemical shift of all other alkyl substituents. Taking advantage of these changes, the ratio of the product dipyrrole to the reactant dipyrrin was calculated based on the integration of the triplet methyl groups below δ 1.25 ppm. Determining the pH of the reaction mixture during the titration gave enough data to calculate the apparent acidity constant, pK_a, of **2HCl** by using the Henderson−HasselBalch equation (Table 1). After the addition of each aliquot of NaOD solution, the pH was measured using a stainless steel probe inserted into the NMR tube.

To investigate the reversibility of the process, a solution containing **3** was back-titrated with a solution of DCl in CD_3OD (Figure 4). The ^{1}H NMR spectra for the acidic titration reveals the reversibility of the deprotonation, and the complete recovery of the dipyrrin **2HCl**.

The deprotonation of the *meso*-methyl dipyrrin salt **2HCl** was also studied using absorption spectroscopic analysis: a solution of **2HCl** in methanol was titrated with 0.01 M aliquots of NaOH. During the course of the titration, the absorption spectra (Figure 5) showed the disappearance of the band at 496 nm, corresponding to the fully conjugated dipyrrinato unit, concomitant with the appearance of a new band at 295 nm, corresponding to the cross-conjugated dipyrrolic ethene **3**. Furthermore, back-titration of the solution of **3** with 0.01 M HCl (Figure S1, Supporting Information) resulted in total recovery of the dipyrrin salt **2HCl**, also supporting the reversibility of the deprotonation.

TABLE 1. pH and pK_a for the Titration of 2HCl with NaOD in CD_3OD

spectrum	equiv of NaOD	ratio of **2HCl**:**3** triplet integrals below δ 1.25 ppm	pH	pK_a
a	0.00	1:0	5.5	
b	0.18	1:0.41	6.6	7.22
c	0.36	1:0.48	6.8	7.11
d	0.54	1:0.72	7.0	7.14
e	0.72	1:1.24	7.2	7.11
f	0.90	1:1.96	7.4	7.11
g	1.26	1:4.37	7.8	7.16
h	1.44	0:1	10.4	

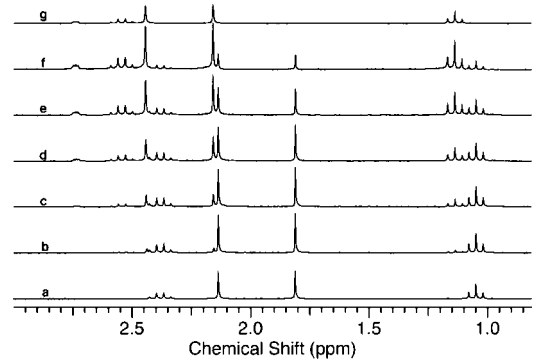

FIGURE 4. ^{1}H NMR titration of **3** with DCl in CD_3OD. Spectra b−g were recorded upon subsequent additions of aliquots each containing 0.18 equiv of DCl.

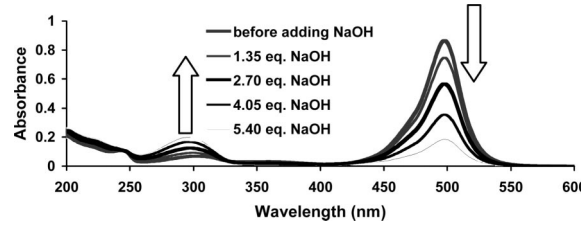

FIGURE 5. Absorption spectra of **2HCl** titrated with 0.01 M NaOH.

Michael addition to the *meso*-position of dipyrrins gives *meso*-substituted dipyrromethanes;[23−27] however, the chemistry of *meso*-alkyl dipyrrins is under investigated. A *meso*-methyl BODIPY complex underwent hydroxide addition at the *meso*-position, followed by the elimination of water to give a vinylic dipyrrole BF_2^- potassium salt.[28] Vinylic dipyrroles were isolated as minor products upon reacting 2-unsubstituted pyrroles with 1-acyl-2-bromoacetylenes.[29,30] Furthermore, a 2,2′-dicarboxylate analogue of **3** was isolated in quantitative yield from the reaction

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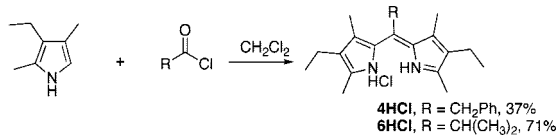
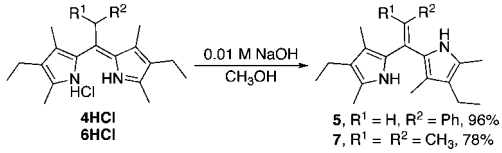
SCHEME 2. Synthesis of *meso*-Benzyl and *meso*-Isopropyl Dipyrrins salts 4HCl and 6HCl



SCHEME 3. Deprotonation of *meso*-Benzyl and *meso*-Isopropyl Dipyrrins Salts 4HCl and 6HCl



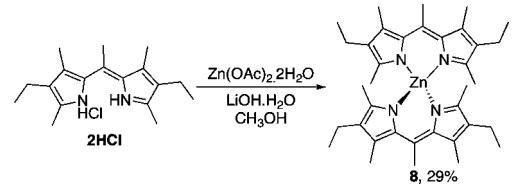
of ethyl 2,3-dimethyl-4-pyrrolecarboxylate with acetyl chloride.[31] The latter report related the tautomerization of *meso*-methyl dipyrrin free-bases to the corresponding vinylic dipyrroles, but did not directly acknowledge that the deprotonation of dipyrrin HX salts would directly give the vinylic dipyrrole if the pK_a of a *meso*-methyl proton were lower than that of the azafulvenium N-*H* atom. Two related reports[32,33] describe and characterize a series of 1,1′-dicarboxylate analogues of **3**, the first of which was isolated as a minor product upon the reaction of benzyl 3,4-dimethylpyrrole-2-carboxylate with acetic anhydride and tin(IV) chloride. Subsequently, good yields of a vinylic dipyrrole were obtained upon treatment of a 5-(chloromethyl) dipyrromethane with base. The vinyl group of such dipyrroles was found to undergo electrophilic attack and hydrogenation, and to be susceptible to photo-oxidative cleavage in the case of a 3,3′-unsubstituted derivative.

Given the interesting properties of *meso*-methyl dipyrrin salt **2HCl**, we explored the deprotonation of the *meso*-benzyl and the *meso*-isopropyl dipyrrin salts **4HCl** and **6HCl**, respectively. These were prepared by using the corresponding acetyl chloride and 2 equiv of 3-ethyl-2,4-dimethylpyrrole, according to Scheme 2.

Deprotonation of **4HCl** upon treatment with base occurred at the *meso*-substituent to give the dipyrrole **5** in excellent yield (Scheme 3). The deprotonation was monitored through the disappearance of the signal at δ 4.69 ppm (corresponding to the benzylic CH_2 protons of **4HCl**) and the appearance of a new signal at δ 6.40 ppm (corresponding to the vinylic proton of **5**, Figure S6 in the Supporting Information). Moreover, ^{15}N NMR spectroscopic analysis showed a shift from δ −212.0 for **4HCl** to δ −232.5 ppm for dipyrrole **5**, again consistent with chemical shifts for pyrrolic, rather than dipyrrinato, compounds.[22]

Titrating a solution of the *meso*-benzyl dipyrrin salt **4HCl** in methanol with 0.01 M NaOH also resulted in the production of dipyrrole **5**, as monitored using absorption spectroscopy (Figure S2, Supporting Information). The deprotonation was confirmed through the decreasing absorbance band at 506 nm, concomitant with the increasing absorbance band at 370 nm. This transformation corresponds to the loss of the dipyrrin to give the dipyrrolic styrene cross-conjugated system. The back-titration of the dipyrrole **5** with dilute HCl (0.01 M) did not recover **4HCl**, in contrast to the *meso*-methyl case whereby **2HCl** was recovered easily. However, a concentrated solution of HCl converted **5** to its salt **4HCl** as confirmed by using both ^{1}H NMR and absorption spectroscopy (Figures S4 and S6, Supporting Information). This result is in contrast to the case where only 13.5 equiv of 0.01 M HCl were needed to protonate **3** to produce the *meso*-methyl dipyrrin **2HCl**. The requirement to use concentrated HCl indicates the enhanced stability of **5**, cf. **3**, and this may be attributed to the formation of the cross-conjugated dipyrrolic styrene.

SCHEME 4. Synthesis of *meso*-Methyl Dipyrrinato Zinc Complex 8



A similar set of titration experiments were conducted with the *meso*-isopropyl substituted dipyrrin salt **6HCl** (Scheme 3). A methanolic solution of **6HCl** was thus titrated with 0.01 M NaOH and the deprotonation was monitored with absorption spectroscopy (Figure S4, Supporting Information). The formation of the dipyrrole **7** was confirmed through the decreasing absorbance of the band at 503 nm and the increasing absorbance of the band at 268 nm. ^{1}H NMR spectroscopic analysis confirmed the deprotonation of dipyrrin **6HCl** to dipyrrole **7** through monitoring the disappearance of the doublet at δ 1.37 ppm (corresponding to the secondary isopropyl proton) and the appearance of a new signal at δ 1.06 ppm (corresponding to the allylic methyl protons). Additionally, ^{15}N NMR spectroscopic analysis showed a shift in the chemical shift of **6HCl** from δ −211.0 to −231.0 ppm for the corresponding dipyrrole **7**.[22] Back-titration returned the salt (Figure S5, Supporting Information).

As a result of the interesting acid/base behavior of these *meso*-substituted dipyrrins, we sought to investigate the ability of *meso*-alkyl dipyrrins to form metal complexes with $Zn(OAc)_2$ in the presence of NaOAc; this general procedure usually gives excellent yields of Zn(II) complexes (Scheme 4).[22] Surprisingly, the homoleptic Zn(II) dipyrrinato complex of **2** was not isolated after treatment under these standard conditions, although use of lithium hydroxide in combination with $Zn(OAc)_2$ led to the isolation of the Zn(II) complex **8** in low yield (Scheme 4), cf. high yields (83%) for the *meso*-H analogue.[22] The low complexation yield was attributed to the formation of **3** under the basic conditions. In the absence of base with either $ZnCl_2$ or $Zn(OAc)_2$, no reaction occurred. These experiments shed light upon the potential mechanism of complexation for HBr and HCl salts of dipyrrins, i.e. initial (reversible) formation of the dipyrrin free-base is essential, and then complexation involves a series of equilibria. If the free-base is removed by way of dipyrrole formation, then complexation yields for the dipyrrinato ligand will be low although tautomerization to the free-base is obviously under equilibrium. It is curious that treatment of *meso*-methyl dipyrrinato BF_2 complexes with Grignard or organolithium reagents does not effect deprotonation at the *meso*-alkyl

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substituent, and substitution at boron occurs instead:[10,16−18,34] presumably the nature of the N−B bonds within a dipyrrinato BF_2 complex (formally monoanionic dipyrrinato ligand) is much more favored than that in the corresponding vinylic dipyrrole (dianionic), and thus the *meso*-methyl protons are not particularly acidic once complexation to boron has occurred.

To summarize, the *meso*-methyl dipyrrin **2HCl**, the *meso*-isopropyl **6HCl**, and the *meso*-benzyl dipyrrin **4HCl** exhibit deprotonation at the *meso*-substituent when treated with base. The resulting dipyrridyl ethenes were fully characterized, including crystallographic data for **3**. The reaction of the dipyrrin **2HCl** with $Zn(OAc)_2$ gave an unexpected low yield for Zn(II) complexation involving dipyrrinato ligands, presumably as a consequence of the formation of the dipyrrole under the reaction conditions. Caution should be taken when working with *meso*-alkyl and *meso*-benzyl dipyrrins under basic conditions such that the dipyrrinato skeleton is maintained, as needed for efficient and high-yielding complexation. This study demonstrates that *meso*-alkyl and *meso*-benzyl dipyrrins have very different acid−base properties compared to the *meso*-H and *meso*-aryl analogues, and that very different reactivity profiles are exhibited.

Experimental Section

1,1′-Di-κ-(3-ethyl-2,4-dimethyl)pyrrolylethene (3). Within a glovebox, *n*BuLi (0.292 mL of a 1.6 M hexanes solution, 0.47 mmol) was added dropwise to a magnetically stirring solution of **2HCl**[19] (130 mg, 0.424 mmol) in THF (3 mL). Upon the addition, the color of the solution changed from dark red to yellow-brown. After 1 h, the solvent was removed *in vacuo* and the product was extracted with pentane. The resulting dark yellow solution was filtered through Celite to remove any insoluble material. The solvent was removed from the filtrate *in vacuo* to yield the title compound (89 mg, 78%). $\lambda_{max/nm}$ 295 (ε 15 000); δ_H (500 MHz, CD_3OD) 5.10 (2H, s), 2.44 (4H, q, J = 7.50), 2.15 (6H, s), 1.79 (6H, s), 1.14 (6H, t, J = 7.50); δ_C (125 MHz, CD_3OD) 133.0, 125.9, 122.2, 122.1, 116.7, 107.5, 17.8, 15.8, 10.5, 10.3; δ_N (50.7 MHz, CD_3OD) δ −233.5; *m*/*z* (ESI$^+$) 271.2122 (MH^+), calcd $C_{18}H_{26}N_2$ 270.2096. Crystals suitable for X-ray diffraction analysis were grown via the evaporation of a pentane solution of **3** under reduced pressure.

κ²-(4,4′-Diethyl-3,3′,5,5′-tetramethyl-*meso*-benzyldipyrrin) Hydrochloride (4HCl). Phenylacetyl chloride (5.41 g, 33 mmol) was added to a solution of 3-ethyl-2,4-dimethylpyrrole (1.85 g, 15 mmol) in CH_2Cl_2 (15 mL), and the mixture was heated at reflux temperature for 1 h. The pink mixture was extracted with water (2 × 30 mL), and the organic fraction was dried over Na_2SO_4. Removal of the organic solvent *in vacuo* gave the crude product that was triturated with petroleum ether to give the title compound as a dark orange solid (2.10 g, 37%). $\lambda_{max/nm}$ 506 (ε 75 000); δ_H (500 MHz, $CDCl_3$) 12.2 (2H, s), 7.20 (2H, d, J = 7.5), 7.11 (2H, t, J = 7.5), 7.04 (1H, t, J = 7.5), 2.39 (6H, s), 2.33 (4H, q, J = 7.5), 2.00 (6H, s), 1.02 (6H, t, J = 7.5); δ_C (125 MHz, CD_3OD) 151.8, 148.3, 139.4, 139.1, 134.7, 132.9, 130.8, 130.0, 129.1, 128.0, 18.4, 14.9, 12.5, 12.4; δ_N (50.7 MHz, $CDCl_3$) −212.0; *m*/*z* (ESI$^+$) 347.2456 $(MH - HCl)^+$, calcd $C_{24}H_{31}N_2$ 347.2487.

2,2′-Di-κ-(3-ethyl-2,4-dimethyl)pyrrolylstyrene (5). Sodium hydroxide (1 M, 25 mL) was added to a magnetically stirring solution of **4HCl** (55.5 mg, 0.145 mmol) in CH_2Cl_2 (25 mL), and the solution color changed from dark red to yellow-brown. After 5 min, the CH_2Cl_2 solution was separated and dried over Na_2SO_4. The solvent was removed *in vacuo* to yield the title compound (48 mg, 96%). $\lambda_{max/nm}$ 370 (ε 23 600); δ_H (500 MHz, CD_3OD) 6.90−7.03 (5H, m), 6.35 (1H, s), 2.31 (4H, q, J = 7.5), 2.10 (3H, s), 2.01 (3H, s), 1.65 (3H, s), 1.50 (3H, s), 0.98 (3H, t, J = 7.50), 0.97 (3H, t, J = 7.50); δ_C (125 MHz, CD_3OD) 140.8, 129.6, 128.9, 128.9, 128.0, 126.2, 125.1, 124.9, 124.6, 123.3, 123.2, 122.3, 118.5, 117.1, 18.8, 18.6, 16.6, 16.4, 11.1, 11.0, 10.2, 10.1; δ_N (50.7 MHz, CD_3OD) δ −232.5; *m*/*z* (ESI+) 369.2274 (M+Na)+, calcd $C_{24}H_{30}N_2Na$ 369.2307.

κ²-(4,4′-Diethyl-3,3′,5,5′-tetramethyl-*meso*-isopropyldipyrrin) Hydrochloride (6HCl). Isobutyryl chloride (3.68 g, 35 mmol) was added to a solution of 3-ethyl-2,4-dimethylpyrrole (1.85 g, 15 mmol) in CH_2Cl_2 (15 mL), and the mixture was heated at reflux temperature for 1 h. The pink mixture was extracted with water (2 × 30 mL), and the organic solution was dried over Na_2SO_4. Removal of the organic solvent *in vacuo* gave the crude product that was triturated with petroleum ether to give the title compound as a dark orange solid (1.97 g, 71%). $\lambda_{max/nm}$ 503 (ε 40 000); δ_H (500 MHz, $CDCl_3$) 11.9 (2H, s) 4.04 (1H, m, J = 7.0), 2.51 (6H, s), 2.34 (4H, q, J = 7.5), 1.79 (6H, s), 1.37 (6H, d, J = 7.0), 0.99 (6H, t, J = 7.5); δ_C (125 MHz, CD_3OD) 158.3, 149.6, 138.5, 132.4, 131.7, 35.8, 22.7, 18.1, 15.1, 13.1, 12.1; δ_N (50.7 MHz, $CDCl_3$) −211.0; *m*/*z* (ESI$^+$) 299.2453 $(MH - HCl)^+$, calcd $C_{20}H_{31}N_2$ 299.2487.

1,1-Di-κ-(3-ethyl-2,4-dimethyl)pyrrolyl-2-methylpropene (7). Sodium hydroxide (1 M, 25 mL) was added to a magnetically stirring solution of **6HCl** (50 mg, 0.145 mmol) in CH_2Cl_2 (25 mL). Upon the addition, the color of the solution changed from dark red to yellow-brown. After 5 min, the CH_2Cl_2 fraction was isolated and then dried over Na_2SO_4. The solvent was removed *in vacuo* to yield the title compound (41 mg, 92%). $\lambda_{max/nm}$ 268 (ε 14 000); δ_H (500 MHz, CD_3OD) 2.31 (4H, q, J = 7.5), 2.05 (3H, s), 1.91 (3H, s), 1.73 (6H, s), 1.66 (6H, s), 0.97 (3H, t, J = 7.5), 0.96 (3H, t, J = 7.5); δ_C (125 MHz, CD_3OD) 131.9, 128.2, 122.8, 120.8, 120.7, 115.9, 22.8, 18.8, 18.6, 16.5, 16.4, 11.2, 11.0, 10.7, 10.5; δ_N (50.7 MHz, CD_3OD) δ −231.0; *m*/*z* (ESI$^+$) 299.2469, calcd $C_{20}H_{30}N_2$ 298.2409.

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Supporting Information Available: Experimental procedures, spectra, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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