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Radical-Transfer Hydroamination of Olefins with N-Aminated Dihydropyridines

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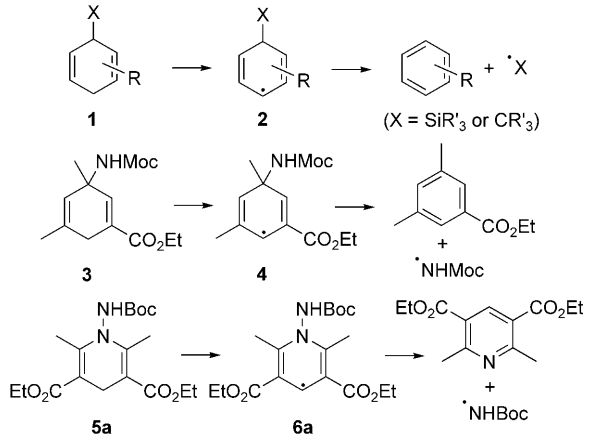
Abstract: An efficient synthesis of *N*-phthalimidyl, benzamidyl, acetamidyl, carbamoyl, and ureayl derivatives of dihydropyridines and the application of these reagents as precursors for N-centered radicals are presented. These aminated dihydropyridines could be used in radical-transfer hydroamination reactions of various electron-rich as well as nonactivated olefins in the presence of thiols as polarity-reversal catalysts. These reactions worked without the aid of any transition metal. Steric and electronic effects exerted by the N-substitutents of the N-centered radicals are discussed. In contrast to most metal-catalyzed processes, the radical hydroamination delivered the opposite regioisomer with excellent anti-Markovnikov selectivity. Hydroamination products were obtained as protected amines that are readily isolated.

Keywords: dihydropyridines · hydroamination · olefins · polarity-reversal catalysis · radical reactions

Introduction

Hydroamination of a nonactivated double bond is a very challenging task. Despite intensive research in that field, no general method has been reported for that very important reaction. Note that most of the pharmaceutical compounds and many natural products contain nitrogen and the development of novel methods for C–N bond formation is therefore important. Transition-metal and Brønsted acid-catalyzed hydroamination of olefins has been intensively studied. However, the reported methods still lack generality and most of the processes are limited to activated olefins.[1] In addition, most of the reported methods deliver Markovnikov addition products[2] and functional group tolerance is low. In contrast, radical reactions show high functional group tolerance, and addition of N-centered radicals to olefins delivers the anti-Markovnikov products. Therefore, we regard the radical approach[3] towards hydroamination of olefins as a highly promising complementary alternative to Brønsted acid and transition-metal-catalyzed hydroamination.

Walton and our group have shown that substituted 1,4-cyclohexadienes of type **1** can be used as precursors for C- and Si-centered radicals (Scheme 1). The cyclohexadienyl radicals **2** are readily generated by hydrogen-transfer reactions and this allows compounds **1** to be used in radical chain reactions.[4] The driving force for the generation of the Si- or C-centered radicals from cyclohexadienyls of type **2** is the arene resonance energy gained in the radical-fragmentation reaction.



Scheme 1. Proaromatic dienes as radical precursors.

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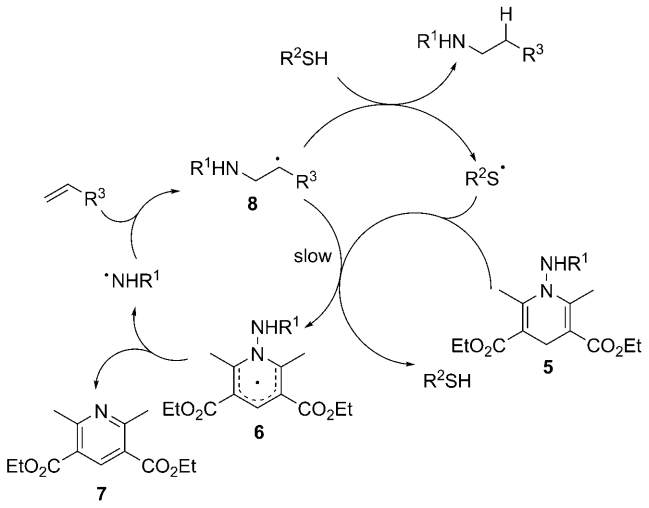
Based on these results, we further expanded the concept of using cyclohexadienyl radicals as proaromatic radical precursors for the generation of N-centered radicals.[5–7] For example, the aminated cyclohexadiene **3**, which upon hydrogen transfer provides cyclohexadienyl radical **4**, turned out to be an efficient precursor for the corresponding carbamoyl radical.[5] We successfully used reagent **3** in tin-free[8] radical-transfer hydroamination reactions of various nonactivated olefins. Unfortunately, large-scale synthesis of aminated cyclohexadiene **3** turned out to be tedious, and this radical precursor is unstable under acidic conditions. Moreover, hydroaminations with **3** had to be conducted at elevated temperatures. We were therefore looking for an alternative and found in the aminated dihydropyridine **5a** an improved reagent that can react through radical **6a** and subsequent fast fragmentation to a carbamoyl radical and the corresponding pyridine derivative. We communicated that the N-aminated dihydropyridine **5a** acts as a nontoxic radical-transfer hydroamination reagent.[9] Herein, we present in full detail that N-aminated dihydropyridines are readily prepared stable and efficient N-radical precursors, which can be used as reagents for the transition-metal-free hydroamination of unactivated olefins. An improved synthesis to compounds of type **5** was developed and this allowed the N-substituents at the amidyl radical to be systematically varied to study steric and electronic effects. Moreover, computational results on the fragmentation of radical **5** will be presented.

Results and Discussion

Concept

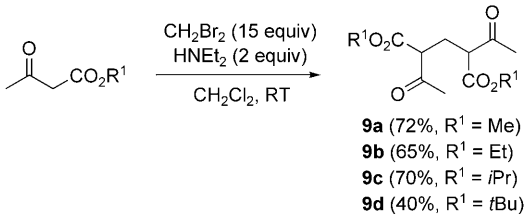
The mechanism of the radical-chain-transfer hydroamination of olefins with aminated dihydropyridines of type **5** is depicted in Scheme 2. An N-centered radical is allowed to add to an olefin to give adduct radical **8**, which can then be reduced with reagent **5** to the hydroamination product and dienyl radical **6**. Fragmentation of **6** will lead to pyridine **7** and the corresponding N-centered radical that sustains the chain. However, hydrogen-transfer reactions from C–H to C-centered radicals are generally inefficient processes, even if the C–H bond is activated by appropriate substituents as for the dihydropyridines studied herein (reaction of **8** with **5** is likely to be slow). This problem can be solved by adding a thiol as a catalyst, an application of the concept of polarity-reversal catalysis (PRC).[10] In the presence of a catalytic amount of a thiol, the slow reduction of a C-radical **8** with the N-aminated dihydropyridine **5** is replaced by an efficient hydrogen-transfer process from a thiol. The thiyl radical thus generated undergoes hydrogen abstraction from the N-aminated dihydropyridine due to polarity match to eventually regenerate the thiol catalyst and **6**, which should readily aromatize to generate the corresponding N-centered radical and pyridine **7**. The driving force for the aromatization is the resonance energy of the pyridine and the weak N–N bond.



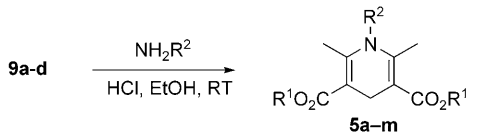
Scheme 2. Thiol-catalyzed radical-transfer hydroamination.

Synthesis of N-Aminated Dihydropyridines

The synthesis of the hydroamination reagents studied herein is shown in Scheme 3. We found that the protocol recently communicated by our group turned out to be not very general.[9] The reported procedure did not allow modification of the N-protecting group at the aminated dihydropyridine **5**. Therefore, an optimized sequence for preparation of **5** was developed. Ketoesters **9a–d** were readily prepared according to a literature procedure by α-methylenation of β-ke-



9a (72%, R^1 = Me)
9b (65%, R^1 = Et)
9c (70%, R^1 = *i*Pr)
9d (40%, R^1 = *t*Bu)



5a–m

5a (85%, R^1 = Et, R^2 = NHBoc)
5b (72%, R^1 = Me, R^2 = NHBoc)
5c (36%, R^1 = *i*Pr, R^2 = NHBoc)
5d (27%, R^1 = *t*Bu, R^2 =NHBoc)
5e (84%, R^1 = Et, R^2 = NHMoc)
5f (56%, R^1 = Et, R^2 = Phthalimidyl)
5g (38%, R^1 = Et, R^2 = NHAlloc)
5h (67%, R^1 = Et, R^2 = NHCOPh)
5i (61%, R^1 = Et, R^2 = NHCO(4-FC_6H_4))
5j (83%, R^1 = Et, R^2 = NHCO(2,6-$F_2C_6H_3$))
5k (78%, R^1 = Et, R^2 = NHCO(3,5-$F_2C_6H_3$))
5l (80%, R^1 = Et, R^2 = NHAc)
5m (78%, R^1 = Et, R^2 = NHCONHC$_2$H$_5$)

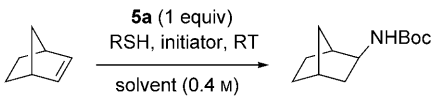
Scheme 3. Synthesis of the hydroamination reagents **5a–5m** (Boc = *tert*-butyloxycarbonyl; Moc = methyloxycarbonyl; Alloc = allyloxycarbonyl).

toesters with CH_2Br_2/$HNEt_2$.[11] Treatment of **9a–d** with various protected hydrazines in the presence of a catalytic amount of HCl afforded the targeted hydroamination reagents **5a–m** in moderate to good yields. We found that the *N*-aminophthalimidyl (**5f**), benzamidyl (**5h**), acetamidyl (**5l**), and ureayl (**5m**) derivatives are quite stable under air, whereas carbamate derivatives **5a–e** slowly decompose upon exposure to air.

Hydroamination of Norbornene with Reagent 5a: Variation of the PRC and Radical Initiator

We first studied radical hydroamination of norbornene as the acceptor with reagent **5a** by using various PRCs and radical initiators under different conditions. Treatment of norbornene (10 equiv) with **5a** (1 equiv) in benzene at 80 °C in the presence of 30 mol % α,α′-azobisisobutyronitrile (AIBN) and 15 mol % PhSH afforded *exo*-hydroamination product **10** in 54 % yield (Table 1, entry 1). It has previously been shown that radical additions onto norbornene occur with excellent *exo*-selectivity.[12] Hydroamination at room temperature with Et_3B/O_2 as an initiator (10 mol %) and 15 mol % PhSH afforded **10a** in 60 % yield (Table 1, entry 3), and a similar result was obtained in the absence of Et_3B with air as the initiator (entry 2). Thioacids as PRCs delivered lower yields under otherwise identical conditions (entries 4 and 5). Catalyst loading could be reduced to 5 mol % without diminishing the yield. Thus, 61 % yield was noted for the reaction with 2,2′-azobis(2,4-dimethyl-4-methoxyvaleronitrile) (V70) as the initiator (5 mol %) and PhSH (5 mol %) as PRC at room temperature in dichloromethane (entry 6). We thought that by using dioxygen as an initiator, some thiol catalyst was consumed through disulfide formation during the reaction. Therefore, the bulkier 2,6-dimethylthiophenol was tested to suppress disulfide formation. However, a similar result was obtained by replacing PhSH with the bulky 2,6-dimethylthiophenol as PRC (compare entries 6 and 9). Reactions in the absence of any PhSH or V70 resulted in lower yields (entries 7 and 8). Hydroamination by using 2-naphthylthiol or β-D-thioglucose-tetraacetate as PRCs were low yielding (entries 10 and 11). Ph_3SiSH (entry 12) and methyl thioglycolate (entry 13) provided slightly lower yields compared to the yield achieved with PhSH. A worse result was noted by using the electron-deficient pentafluorothiophenol as a PRC (15 %, entry 14). We next varied the amount of norbornene or the catalyst and initiator loading. However, all experiments conducted along this line showed a decrease in the yield (entries 15–18). From these initial optimization studies, we can conclude that the best result was achieved with the cheap and commercially available PhSH as the PRC. Therefore, the following experiments were performed by using either 0.05 or 0.15 equivalents of PhSH in combination with 1.5–10 equivalents of an olefin.

Table 1. Hydroamination of norbornene with **5a** under different conditions.



10a

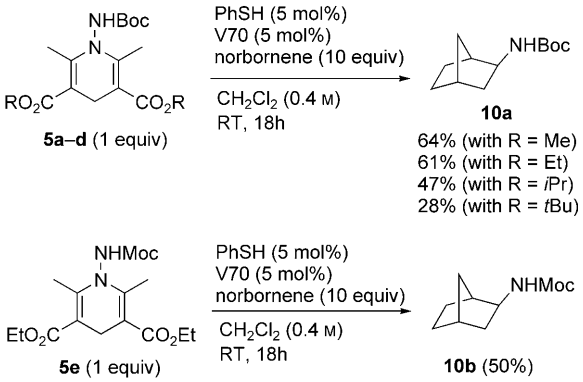
Entry	Solvent	Norbornene [equiv]	RSH [mol %]	Initiator [mol %][a]	Yield [%][b]
1	C_6H_6	10	PhSH (15)	AIBN[c]	54
2	C_6H_6	10	PhSH (15)	air	57
3	C_6H_6	10	PhSH (15)	Et_3B/O_2[d]	60
4	C_6H_6	10	PhCOSH (15)	Et_3B/O_2[d]	15
5	C_6H_6	10	1-Ad-thioacid (15)[e]	Et_3B/O_2[d]	7
6	CH_2Cl_2	10	PhSH (5)	V70(5)	61
7	CH_2Cl_2	10	–	V70(5)	40
8	CH_2Cl_2	10	PhSH (5)	–	35
9	CH_2Cl_2	10	2,6-Me_2-PhSH (5)	V70(5)	58
10	CH_2Cl_2	10	2-naphthyl-SH (5)	V70(5)	47
11	CH_2Cl_2	10	β-D-glucose-SH (5)	V70(5)	46
12	CH_2Cl_2	10	Ph_3SiSH (5)	V70(5)	33
13	CH_2Cl_2	10	MeO_2CCH_2SH (5)	V70(5)	37
14	CH_2Cl_2	10	C_6F_5SH (5)	V70(5)	15
15	CH_2Cl_2	4	PhSH (2)	V70(2)	20
16	CH_2Cl_2	4	PhSH (2)	V70(5)	37
17	CH_2Cl_2	4	PhSH (5)	V70(5)	47
18	CH_2Cl_2	2	PhSH (5)	V70(5)	45

[a] 10 mol % of Et_3B or 30 mol % of AIBN were used. [b] Isolated yields. [c] Conducted at 80 °C. [d] Air was used as an O_2 source and the reaction was conducted at RT. [e] Ad = adamantyl.

Hydroamination of Norbornene with Various Aminated Dihydropyridines

We first investigated the substituent effect at the ester moiety of the N-aminated dihydropyridine. Reactions with reagents **5a–d** were conducted under optimized conditions in the presence of PhSH (5 mol %) and V70 (5 mol %) in dichloromethane at room temperature for 18 hours to afford **10a** (Scheme 4). We found that the reaction yield steadily decreased by increasing the size of the alkyl substituent at the ester moiety in going from the methyl (64 %), ethyl (61 %), and isopropyl (47 %) to the *tert*-butyl ester (28 %). It seems that hydrogen abstraction by the thiyl radical from the dihydropyridine is strongly affected by the ester moiety for steric reasons.

By replacing the bulky Boc group in the reagent by a smaller Moc (methyloxycarbonyl) group, a slight decrease in the yield was observed and **10b** was isolated in 50 % yield. Disappointingly, the benzoyl- and the acetyl-protected dihydropyridines **5h** and **5l** did not deliver any hydroamination product under optimized conditions. Therefore, the fluorinated benzamides were not tested with this particular substrate. The



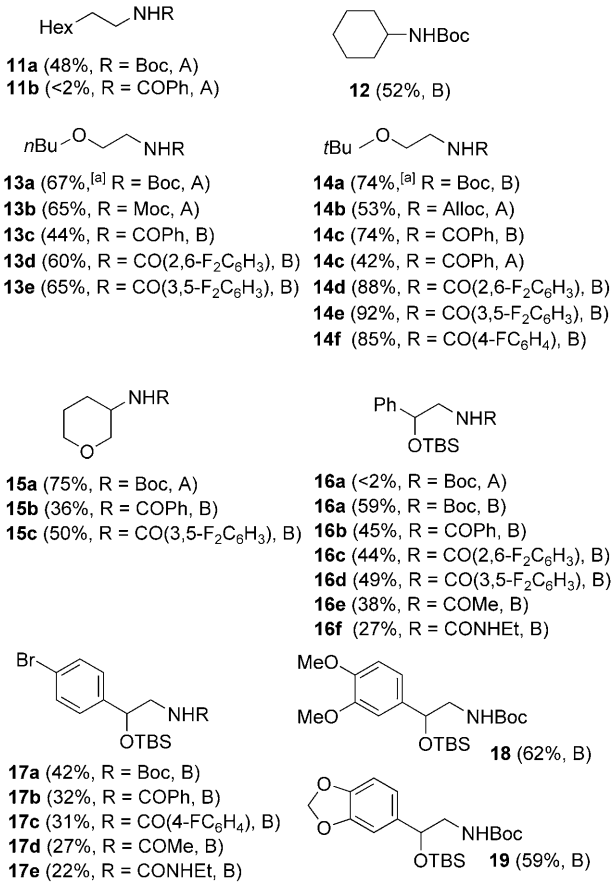
Scheme 4. Hydroamination of norbornene with various reagents.

phthalimidyl and ureayl reagents **5f** and **5m** did not work as well under these conditions. With **5m** we faced solubility problems. At least for norbornene as a radical acceptor, the carbamoyl-protected dihydropyridines delivered the highest yields. Moreover, the ester moiety at the reagent should be charged with a linear alkyl group.

Hydroamination of Various Alkenes with Various Reagents under Optimized Conditions

To study the scope and limitations of our method, various olefins were treated with various reagents under different conditions. Reagents that failed in the hydroamination of norbornene were also included in these studies. Hydroaminations were conducted at room temperature with V70 as an initiator in dichloromethane (method A), and with AIBN in benzene at 80 °C as an initiator (method B). All yields reported are based on isolated material. In Scheme 5, hydroamination products **11**–**19** successfully prepared by hydroamination of 1-octene, cyclohexene, and various enol ethers are depicted; yields and method used are given in brackets.

We found that hydroamination of 1-octene did not proceed with perfect regiochemistry. Reaction of **5a** with 1-octene using method A delivered **11a** in 48% yield along with its regioisomeric Markovnikov product (6%, not shown in the figure). Cyclohexene was successfully hydroaminated with reagent **5a** (→**12**: 52%). As for the norbornene system, the benzoylated hydroamination reagent **5h** was not efficient for hydroamination of 1-octene. As the amidyl radicals have an electrophilic character, higher yields should be obtained in the hydroamination of electron-rich enol ethers. Indeed, products **13**–**19** were isolated in 22–92% yield with perfect anti-Markovnikov selectivity. Butyl vinyl ether reacted at room temperature efficiently with carbamoyl-protected aminated dihydropyridines **5a** and **5e**, and the protected amino alcohols **13a** and **13b** were isolated in 67 and 65% yield, respectively. Pleasingly, for this electron-rich substrate we found that the benzoylated reagent **5h** provided adduct **13c** in a satisfactory yield (44%) using method B. Increasing the electrophilicity of the amidyl radicals by introducing F-substituents (see reagents **5j** and **5k**) led to a further increase in the yield (→**13d**: 60%; →**13e**: 65%). Even higher yields (up to 92%) were achieved with *tert*-butyl vinyl ether as a radical acceptor. Again, for the benzamidyl radical series, the introduction of F-substituents led to improved yields: two F-substituents are better than one F-substituent, probably for electronic reasons, and the 2,6-isomer afforded slightly lower yields than the 3,5-difluoro-substituted benzamidyl radical, probably for steric reasons.



Scheme 5. Hydroamination of 1-octene, cyclohexene, and enol ethers with various reagents Method A: with 2 to 10 equivalents of olefin; 5 mol% V70, 5 mol% PhSH, RT, CH_2Cl_2. Method B: with 1.5 to 10 equivalents of olefin; 30 mol% AIBN, 15 mol% PhSH, reflux, benzene. [a] Isolated as a mixture with pyridine **7**.

Protected secondary alkyl-substituted amines can readily be prepared regioselectively starting with dihydropyrane. As for most substrates tested so far, the Boc-protected reagent **5a** turned out to be more reactive than the benzoylated amination reagent **5h** (→**15a**: 75%; →**15b**: 36%). Again, increasing electrophilicity of the benzamidyl radical provided an improved yield (→**15c**: 50%). Similar reactivity trends were observed in the reaction of silyl enol ethers derived from acetophenone derivatives (see **16a**–**d**). For this compound class, we also tested the acetyl- and ureayl-protected aminodihydropyridine **5l** and **5m** and found that both compounds were not efficient hydroamination reagents. As expected, decreasing the nucleophilicity of the silyl enol ether by introducing a bromine substituent at the arene moiety

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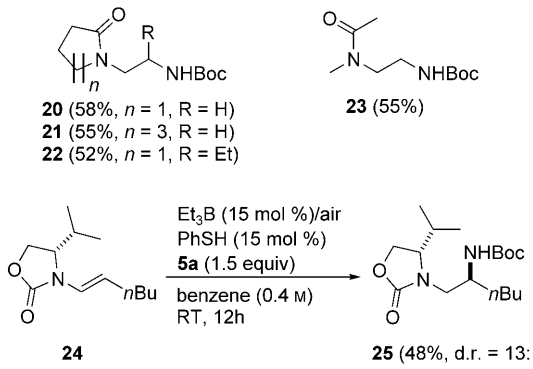
led to a decrease in the yields (see **17a–e**) and increasing nucleophilicity afforded higher yields (→**18**: 62%; →**19**: 59%). It is important to note that these amino alcohols are biologically interesting compounds.

Enamides could also be regioselectively hydroaminated with reagent **5a**. For this substrate class we found that the Et_3B/O_2 initiation method was best suited to run the transfer hydroaminations (Scheme 6). Reactions were conducted at



Scheme 6. Hydroamination of enamides with reagent **5a** and Et_3B (15 mol%)/O_2 as an initiator at RT in benzene.

room temperature and protected vicinal diamines **20–23** were isolated in 52 to 58% yield (Scheme 4). Under these conditions, the acylated dihydropyridines did not show any reactivity. We could also show that the chiral enecarbamate **24** was hydroaminated with high diastereoselectivity (diastereomeric ratio (d.r.) = 13:1) to give **25** in 48% yield, thereby showing the potential of our method for the preparation of enantiomerically pure diamines.[13]

Analysis of Radical Fragmentation by DFT Calculations

Finally, we used DFT methods to evaluate the dissociation energy of three dienyl radicals **6′** (methyl esters) that bore different N-substitutents -NHR[1] as leaving radicals. The geometries of the intermediates were optimized with the generalized gradient approximation functional proposed by Perdew, Burke, and Ernzerhof (PBE),[14] using a triple-zeta basis set (def2-TZVP)[15] and an atom pair-wise dispersion correction.[16] Only the most stable conformers were considered in the reactions. Single-point energies of these conformers were also obtained with the double-hybrid functional B2-PLYP[17] and a quadruple-zeta basis set (def2-QZVP),[15] also adding a dispersion correction.[18] All calculations were performed with Turbomole 6.0.[19]

Figure 1 shows the spin density of the NH-Moc-substituted intermediate **6′e**. The nitrogen of the dihydropyridine is already involved in the delocalization of the radical, which facilitates the N–N bond scission in the fragmentation.

As Table 2 reveals, the dissociation is an endoenergetic process. We have shown this before for similar, unsymetrically substituted cyclohexadienyl radicals.[5b] For those systems, dissociation energies were found to be very similar to

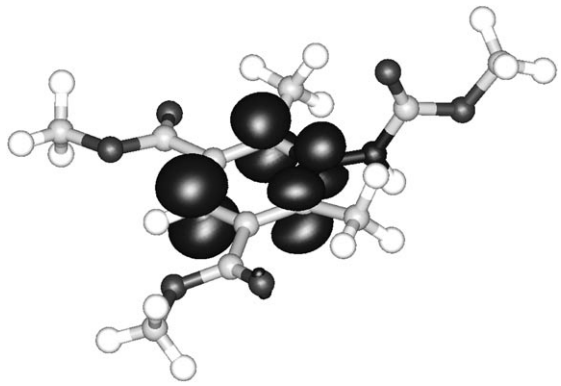


Figure 1. Structure and spin density of the N-NH-Moc-substituted radical **6′e**. The isosurface represents a value of $(\rho_\alpha - \rho_\beta) = +0.004$ a.u.

Table 2. DFT reaction energies for the aromatization reaction of **6′e**, **6b**, and **6′j**.

	Leaving radical	ΔE_{diss} [kcal mol^{-1}]	
		PBE-D/def2-TZVP	B2PLYP-D/def2-QZVP[a]
6′e	NH-Moc	+11.3	+9.6
6b	NH-Boc	+11.5	+10.2
6′j	NH-CO-2,4-$F_2C_6H_3$	+7.2	+4.2

[a] PBE-D/def2-TZVP geometries.

those with NH-Moc as a leaving radical. Hence, the additional nitrogen atom in the ring does not influence reaction energies to a large extent. Dissociation barriers were only slightly higher (1–5 kcal mol^{-1}) than the reaction energies. It is therefore fair to regard the dissociation also here as a facile process within the reaction cycle. The pyridine as a product has no considerable impact on the energy of the dissociation step.

Notably, the dissociation of **6b** (NH-Boc) and **6′e** (NH-Moc) is more endoenergetic than the dissociation of the 2,4-difluorophenylcarbonyl intermediate **6′j**, even more so with the more reliable B2PLYP-D double-hybrid functional, which gives an energy of only 4.2 kcal mol^{-1} for the step.

Conclusion

An efficient synthesis of benzamidyl, acetamidyl, and urea derivatives of N-aminated dihydropyridines and the application of these reagents as precursors for N-centered radicals have been presented. The novel synthesis allowed us to prepare N-aminated dihydropyridines that were not accessible by using known procedures. These dihydropyridines have successfully been used in the radical-transfer hydroamination of various electron-rich as well as nonactivated olefins in the presence of a polarity-reversal catalyst. Thiophenol turned out to be best suited as a PRC among the tested thiols. The size of the alkyl group at the ester moiety of the reagents strongly influenced the hydroamination reaction. The best yields have been obtained with primary alkyl esters. The N-protecting group at the N-centered radical,

which influences the electrophilicity of the radical, showed a strong electronic effect on the reaction outcome. In general, the best yields were achieved with carbamate derivatives as hydroamination reagents. The carbamate derivatives worked on aliphatic alkenes, on enol ethers, on enamides, and on enecarbamates. However, the benzamidyl-protected aminated dihydropyridines reacted efficiently only with enol ethers as substrates. We found that increasing the electrophilicity of the N-centered radical by introducing F-substituents at the arene of the benzamidyl group led to higher yields in the hydroamination of enol ethers. Reactions with the carbamate-protected reagents could be performed at room temperature, whereas higher reaction temperatures were necessary when applying benzamidyl, acetamidyl, and urea derivatives as hydroamination reagents. In contrast to metal-catalyzed processes, the radical hydroamination delivered products with excellent anti-Markovnikov selectivities. Moreover, the radical hydroaminations described herein are environmentally benign tin-free processes.

Experimental Section

*General Procedure **I** (α-Methylenation of Ketones)*[11]

A mixture of dibromomethane (15 equiv) and diethylamine (2 equiv) was stirred at 55 °C for 1.5 h and was then cooled to room temperature. A preheated mixture of dibromomethane/diethylamine was added at room temperature to a solution of alkyl acetoacetate (1 equiv) in CH_2Cl_2. The resulting mixture was then stirred for 1 h. The reaction mixture was concentrated under reduced pressure. Diethyl ether was added, and most of the ammonium salt was precipitated. After filtration of the precipitation, the solid was thoroughly washed with diethyl ether. The combined diethyl ether layers were concentrated and then purified by flash column chromatography (silica gel) to give the corresponding 2,4-diacetylpentanedioic acid dialkyl ester.

*General Procedure **II** (Preparation of N-Aminodihydropyridines)*

HCl (1 N, 0.5 equiv) and the corresponding hydrazide (1.0–1.2 equiv) were added to a stirred solution of 2,4-diacetylpentanedioic acid dialkyl ester (1.0 equiv) in ethanol (same volume as HCl solution) at room temperature, and the resulting solution was stirred for 18 h under argon. The reaction mixture was then extracted with CH_2Cl_2 and washed with $NaHCO_3$ (aq.), then dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude material was purified by flash column chromatography (silica gel) or precipitated by adding diethyl ether to afford the corresponding N-aminated dihydropyridines.

*General Procedure **IIIA** (Hydroamination of Olefins at Room Temperature)*

A mixture of the hydroamination reagent (1 equiv), the olefin (2 to 10 equiv), the initiator V70 (0.05 equiv), and thiophenol (0.05 equiv) in dry CH_2Cl_2 was placed in a sealed tube under argon. The reaction mixture was stirred in the sealed tube under argon at room temperature for 18 h. Solvent was removed under reduced pressure and the resulting residue was purified by flash column chromatography (silica gel) to afford the desired hydroamination product.

*General Procedure **IIIB** (Hydroamination of Olefins at 80 °C)*

A mixture of the hydroamination reagent (1 equiv), the olefin (1.5 to 10 equiv), the initiator AIBN (0.30 equiv) and thiophenol (0.15 equiv) in dry benzene was placed in a sealed tube under argon. The reaction mixture was heated in the sealed tube under argon at 80 °C (oil bath temperature) for 18 h. The reaction mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. The crude mixture was purified by flash column chromatography (silica gel) to afford the desired hydroamination product.

*General Procedure **IIIC** (Hydroamination of Olefins at Room Temperature)*

A solution of the appropriate olefin (2.5 to 10 equiv) and Et_3B (0.10 to 0.15 equiv, 1 M solution in *n*-hexane) in dry benzene was stirred in a screw-cap Schlenk tube under argon. A solution of the hydroamination reagent (1.0 equiv) and thiophenol (0.15 equiv) in dry benzene was added slowly to the reaction mixture over 10 to 12 h at room temperature using a syringe pump. The argon supply was then removed from the reaction mixture. The reaction was initiated by addition of a small amount of air through a syringe into the Schlenk tube and immediately adding the reagent by using a syringe pump. After complete addition of the reagent, the solvent was removed under reduced pressure. Purification by flash column chromatography (silica gel) afforded the desired hydroamination product.

*2,4-Diacetylpentanedioic Acid Dimethyl Ester (**9a**)*

Prepared according to general procedure **I** using CH_2Br_2 (26.0 mL, 372.0 mmol), $HNEt_2$ (5.1 mL, 49.5 mmol), and methyl acetoaccetate (2.7 mL, 24.8 mmol) in CH_2Cl_2 (50 mL). Purification by flash column chromatography (methyl *tert*-butyl ether (MTBE)/pentane, 1:2) provided **9a** as a yellow liquid (2.20 g, 72 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.22–2.45 (m, 8H; $COCH_3$ and CH), 3.53–3.59 (m, 2H; CH_2), 3.74 ppm (s, 6H; CO_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.5 (CH_2), 29.3 (CH_3), 52.6 (CH_3), 56.4 (CH), 169.5 (C), 202.1 ppm (C); IR (neat): $\tilde{\nu}$ = 3005, 2957, 1743, 1717, 1437, 1361, 1248, 1151 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{11}H_{16}O_6Na$ $[M+Na]^+$: 267.0839; found: 267.0835.

*2,4-Diacetylpentanedioic Acid Diethyl Ester (**9b**)*

Prepared according to general procedure **I** using CH_2Br_2 (52.0 mL, 742.5 mmol), $HNEt_2$ (10.28 mL, 99.1 mmol), and methyl acetoaccetate (6.44 mL, 49.5 mmol) in CH_2Cl_2 (100 mL). Purification by flash column chromatography (ethyl acetate (EtOAc)/pentane, 1:3) provided **9b** as a yellow liquid (4.37 g, 65 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21–1.33 (m, 6H; CH_2CH_3), 2.05–2.65 (m, 8H; $COCH_3$ and CH), 3.53–3.65 (m, 2H; CH_2), 4.21–4.55 ppm (m, 4H; CH_2CH_3). Physical data are in agreement with those reported in the literature.[11]

*2,4-Diacetylpentanedioic Acid Diisopropyl Ester (**9c**)*

Prepared according to general procedure **I** using CH_2Br_2 (26.0 mL, 372.0 mmol), $HNEt_2$ (5.1 mL, 49.5 mmol), and methyl acetoaccetate (3.6 mL, 24.8 mmol) in CH_2Cl_2 (50 mL). Purification by flash column chromatography (MTBE/pentane, 1:3) provided **9c** as a yellow liquid (2.60 g, 70 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.19–1.30 (m, 12H; $CH(CH_3)_2$), 2.21–2.31 (m, 8H; $COCH_3$ and CH), 3.47 (t, J = 6.0 Hz, 2H; CH_2), 4.98–5.12 ppm (m, 1H; $CH(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (CH_3), 25.4 (CH_2), 29.2 (CH_3), 56.9 (CH), 69.4 (CH), 168.5 (C), 202.2 ppm (C); IR (neat): $\tilde{\nu}$ = 2983, 2940, 1731, 1714, 1375, 1359, 1248, 1182, 1148, 1104 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{15}H_{24}O_6Na$ $[M+Na]^+$: 323.1465; found: 323.1460.

*2,4-Diacetylpentanedioic Acid Di-tert-butyl Ester (**9d**)*

Prepared according to general procedure **I** using CH_2Br_2 (21.0 mL, 300.0 mmol), $HNEt_2$ (4.2 mL, 40.0 mmol), and methyl acetoaccetate (3.3 mL, 20.0 mmol) in CH_2Cl_2 (50 mL). Purification by flash column chromatography (MTBE/pentane, 1:3) provided **9d** as a yellow liquid (1.3 g, 40 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.45 (s, 27H; $(CH_3)_3$), 2.16–2.36 (m, 8H; $COCH_3$ and CH), 3.41 ppm (t, J = 7.5 Hz, 2H; CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.6 (CH_2), 27.9 (CH_3), 29.2 (CH_3), 57.8 (CH), 82.4 (CH), 168.1 (C), 202.6 ppm (C); IR (neat): $\tilde{\nu}$ = 2979, 2934, 1737, 1714, 1369, 1252, 1122, 845 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{17}H_{28}O_6Na$ $[M+Na]^+$: 351.1778; found: 351.1787.

*1-tert-Butoxycarbonylamino-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylic Acid Diethyl Ester (**5a**)*

Prepared according to general procedure **II** using **9b** (272 mg, 1.0 mmol), *N*-Boc-hydrazide (132 mg, 1.0 mmol), and HCl (1 N, 0.5 mL, 0.5 mmol) in EtOH (0.5 mL). Purification by flash column chromatography (MTBE/pentane, 1:3) provided **5a** as a light yellow solid (313 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.97$ (t, $J = 7.1$ Hz, 6H; CH_2CH_3), 1.28 (s, 9H; $C(CH_3)_3$), 2.34 (s, 6H; CH_3-vinylic), 3.61 (s, 2H; CH_2-vinylic), 4.01 (q, $J = 7.1$ Hz, 4H; CH_2CH_3), 6.31–5.86 ppm (br, 1H; N*H*). Physical data are in agreement with those reported in the literature.[9]

*1-tert-Butoxycarbonylamino-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylic Acid Dimethyl Ester (**5b**)*

Prepared according to general procedure **II** using **9a** (2.0 g, 8.2 mmol), *N*-Boc-hydrazide (1.1 g, 8.5 mmol), and HCl (1 N, 4.1 mL, 4.1 mmol) in EtOH (4.1 mL). Purified by precipitation provided **5b** as a light yellow solid (2.0 g, 72%). M.p. 108–109 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 1.47 (s, 9H; $C(CH_3)_3$), 2.25 (s, 6H; CH_3-vinylic), 3.25 (s, CH_2-vinylic), 3.70 (s, 6H; OCH_3), 6.57–6.81 ppm (m, 1H; N*H*); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.7$ (CH_3), 24.6 (CH_2), 28.1 (CH_3), 51.3 (CH_3), 82.3 (C), 102.2 (C), 149.6 (C), 154.4 (C), 168.1 ppm (C); IR (neat): $\tilde{\nu} =$ 3294, 2982, 2951, 1703, 1604, 1504, 1434, 1390, 1201, 1159, 1083, 1019 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{16}H_{24}N_2O_6Na$ $[M+Na]^+$: 363.1527; found: 363.1534; elemental analysis calcd (%) for $C_{16}H_{24}N_2O_6$: C 56.46, H 7.11, N 8.23; found: C 56.53, H 7.16, N 8.22.

*1-tert-Butoxycarbonylamino-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylic Acid Diisopropyl Ester (**5c**)*

Prepared according to general procedure **II** using **9c** (2.4 g, 8.0 mmol), *N*-Boc-hydrazide (1.06 g, 8.0 mmol), and HCl (1 N, 4.0 mL, 4.0 mmol) in EtOH (4.0 mL). Purification by flash column chromatography (MTBE/pentane, 1:4) provided **5c** as a light green solid (1.15 g, 36%). M.p. 135–136 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.24$ (d, $J = 8$ Hz, 12H; CH-$(CH_3)_2$), 1.47 (s, 9H; $C(CH_3)_3$), 2.22 (s; CH_3-vinylic), 3.18–3.23 (m, 2H; CH_2-vinylic), 4.98–5.06 (m; $CH(CH_3)_2$), 6.68–6.83 ppm (br, 1H; N*H*); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.7$ (CH_3), 22.0 (CH_3), 24.7 (CH_2), 28.2 (CH_3), 68.2 (CH), 82.1 (C), 102.8 (C), 148.8 (C), 154.6 (C), 167.4 ppm (C); IR (neat): $\tilde{\nu} =$ 3300, 2980, 1697, 1604, 1387, 1371, 1245, 1201, 1160, 1109 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{20}H_{32}N_2O_6Na$ $[M+Na]^+$: 419.1789; found: 419.2154; elemental analysis calcd (%) for $C_{20}H_{32}N_2O_6$: C 60.59, H 8.14, N 7.07; found: C 60.26, H 8.15, N 7.00.

*(2,3,5,6-Tetramethyl-4H-pyridin-1-yl)carbamic Acid tert-Butyl Ester (**5d**)*

Prepared according to general procedure **II** using **9d** (0.91 g, 2.77 mmol), *N*-Boc-hydrazide (0.37 g, 2.80 mmol), and HCl (1 N, 1.4 mL, 1.4 mmol) in EtOH (1.4 mL). Purification by flash column chromatography (MTBE/pentane, 1:4) provided **5d** as a light green solid (0.32 g, 27%). M.p. 126–127 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.47$ (s, 27H; $C(CH_3)_3$), 2.19 (s, 6H; CH_3-vinylic), 3.15 (s; CH_2-vinylic), 6.57–6.61 ppm (m, 1H; N*H*); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.6$ (CH_3), 25.3 (CH_2), 28.2 (CH_3), 28.3 (CH_3), 79.8 (C), 82.0 (C), 104.0 (C), 147.9 (C), 154.6 (C), 167.3 ppm (C); IR (neat): $\tilde{\nu} =$ 3307, 2977, 1684, 1606, 1367, 1243, 1158, 1005 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{22}H_{36}N_2O_6Na$ $[M+Na]^+$: 447.2466; found: 447.2458; elemental analysis calcd (%) for $C_{22}H_{36}N_2O_6$: C 62.24, H 8.55, N 6.60; found: C 62.14, H 8.51, N 6.50.

*1-Methoxycarbonylamino-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylic Acid Diethyl Ester (**5e**)*

Prepared according to general procedure **II** using **9b** (1.09 g, 4.0 mmol), *N*-Moc-hydrazide (360 mg, 4.0 mmol), and HCl (1 N, 2.0 mL, 2.0 mmol) in EtOH (2.0 mL). Purification by flash column chromatography (MTBE/pentane, 1:1) provided **5e** as a light green solid (1.1 g, 84%). M.p. 133–134 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.28$ (t, $J = 7.5$ Hz, 6H; CH_2CH_3), 2.25 (s, 6H; CH_3-vinylic), 3.25 (s, 2H; CH_2-vinylic), 3.79 (s, 3H; OCH_3), 4.18 (q, $J = 7.5$ Hz, 4H; CH_2CH_3), 6.65–6.79 ppm (br, 1H; N*H*); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.3$ (CH_3), 14.6 (CH_3), 24.5 (CH_2), 53.3 (CH_3), 60.0 (CH_2), 96.5 (C), 102.5 (C), 149.0 (C), 167.8 ppm (C); IR (neat): $\tilde{\nu} =$ 3260, 2988, 1714, 1700, 1606, 1528, 1383, 1274, 1197, 1087, 1049 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{15}H_{22}N_2O_6Na$ $[M+Na]^+$: 349.1370; found: 349.1377; elemental analysis calcd (%) for $C_{15}H_{22}N_2O_6$: C 55.21, H 6.79, N 8.58; found: C 55.20, H 6.84, N 8.53.

*1-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylic Acid Diethyl Ester (**5f**)*

Prepared according to general procedure **II** using **9b** (136 mg, 0.5 mmol), *N*-aminophthalimide (81 mg, 0.5 mmol), and HCl (4 N, 0.2 mL, 0.8 mmol) in EtOH (1.0 mL). Purification by flash column chromatography (MTBE/pentane, 1:2) provided **5f** as a light yellow solid (111 mg, 56%). M.p. 135–136 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.29$ (t, $J = 7.5$ Hz, 6H; CH_2CH_3), 2.10 (s, 6H; CH_3-vinylic), 3.38 (s, 2H; CH_2-vinylic), 4.19 (q, $J = 7.5$ Hz, 4H; CH_2CH_3), 7.85–7.88 (m, 2H; C*H*-aromatic), 7.96–7.98 ppm (m, 2H; C*H*-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.2$ (CH_3), 14.3 (CH_3), 24.9 (CH_2), 60.0 (CH_2), 104.1 (C), 124.5 (C), 129.0 (CH), 135.4 (C), 146.6 (CH), 165.5 (C), 167.4 ppm (C); IR (neat): $\tilde{\nu} =$ 2981, 1739, 1701, 1616, 1388, 1285, 1199, 1107, 879, 718 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{21}H_{22}N_2O_6Na$ $[M+Na]^+$: 421.1370; found: 421.1375.

*1-Allyloxycarbonylamino-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylic Acid Diethyl Ester (**5g**)*

Prepared according to general procedure **II** using **9b** (1.45 g, 5.34 mmol), but-3-enoic acid hydrazide[20] (620 mg, 5.34 mmol), and HCl (1 N, 2.7 mL, 2.7 mmol) in EtOH (2.7 mL). Purification by flash column chromatography (MTBE/pentane, 1:3) provided **5g** as a light green solid (714 mg, 38%). M.p. 105–106 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.25$–1.30 (m, 6H; CH_2CH_3), 2.23 (s, 6H; CH_3-vinylic), 3.24 (s; CH_2-vinylic), 4.13–4.17 (m, 4H; CH_2CH_3), 4.65 (d, $J = 4$ Hz, 2H; OCH_2-vinylic), 5.27 (d, $J =$ 12 Hz, 1H; CH*H*-vinylic), 5.33 (d, $J = 16$ Hz, 1H; C*H*H-vinylic), 5.86–5.96 (m, 1H; C*H*-vinylic), 7.00–7.21 ppm (br, 1H; N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.3$ (CH_3), 14.6 (CH_3), 24.6 (CH_2), 66.1 (CH_2), 66.8 (CH_2), 102.7 (CH), 118.9 (CH_2), 131.7 (C), 148.8 (C), 155.3 (C), 167.8 ppm (C); IR (neat): $\tilde{\nu} =$ 3264, 2982, 1698, 1607, 1521, 1390, 1259, 1195, 1051 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{17}H_{24}N_2O_6Na$ $[M+Na]^+$: 375.1527; found: 375.1530.

*1-Benzoylamino-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylic Acid Diethyl Ester (**5h**)*

Prepared according to general procedure **II** using **9b** (140 mg, 0.51 mmol), benzoic acid hydrazide (68 mg, 0.5 mmol), and HCl (1 N, 0.25 mL, 0.25 mmol) in EtOH (0.25 mL). Purification by flash column chromatography (MTBE/pentane, 1:1) provided **5h** as a light green solid (500 mg, 67%). M.p. 130–131 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.26$ (t, $J = 7.5$ Hz, 6H; CH_2CH_3), 2.25 (s, 6H; CH_3-vinylic), 3.24 (d, $J =$ 19.5 Hz, 1H; C*H*H), 3.34 (d, $J = 19.5$ Hz, 1H; CH*H*), 4.07–4.20 (m, 4H; CH_3CH_2), 7.45–7.50 (m, 2H; C*H*-aromatic), 7.55–7.61 (m, 1H; C*H*-aromatic), 7.83–7.86 (m, 2H; C*H*-aromatic), 8.74 ppm (s, 1H; N*H*); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.3$ (CH_3), 14.8 (CH_3), 24.8 (CH_2), 60.2 (CH_2), 102.4 (C), 127.3 (CH), 129.0 (CH), 131.2 (C), 132.8 (CH), 148.7 (C), 167.0 (C), 168.1 ppm (C); IR (neat): $\tilde{\nu} =$ 3274, 2981, 1695, 1603, 1517, 1388, 1292, 1267, 1195, 1100, 1053 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{20}H_{24}N_2O_5Na$ $[M+Na]^+$: 395.1577; found: 395.1576; elemental analysis calcd (%) for $C_{20}H_{24}N_2O_5$: C 64.50, H 6.50, N 7.52; found: C 64.02, H 6.43, N 7.42.

*1-(4-Fluorobenzoylamino)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylic Acid Diethyl Ester (**5i**)*

Prepared according to general procedure **II** using **9b** (1.63 g, 6.0 mmol), 4-fluorobenzoic acid hydrazide (0.92 g, 6.0 mmol), and HCl (1 N, 3.0 mL, 3.0 mmol) in EtOH (3.0 mL). Purification by flash column chromatography (MTBE/pentane, 2:1) provided **5i** as a light green solid (1.43 g, 61%). M.p. 137–138 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.26$ (t, $J =$ 7.5 Hz, 6H; CH_2CH_3), 2.22 (s, 6H; CH_3-vinylic), 3.22 (d, $J = 18$ Hz, 1H; C*H*H), 3.32 (d, $J = 18$ Hz, 1H; CH*H*), 4.11–4.20 (m, 4H; CH_3CH_2), 7.12–7.18 (m, 2H; C*H*-aromatic), 7.87–7.92 (m, 2H; C*H*-aromatic), 8.89 ppm (s, 1H; N*H*); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.3$ (CH_3), 14.8 (CH_3), 24.9 (CH_2), 60.2 (CH_2), 102.5 (C), 116.15 (d, $J = 22.5$ Hz, CH), 127.3 (C),

129.86 (d, $J=9.0$ Hz, CH), 148.5 (C), 165.5 (d, $J=252.8$ Hz, C), 166.0 (C), 168.1 ppm (C); IR (neat): $\tilde{\nu}=3300$, 2984, 1695, 1604, 1498, 1388, 1292, 1237, 1193, 1096, 1053, 852, 766 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{20}H_{23}FN_2O_5Na$ $[M+Na]^+$: 413.1483; found: 413.1478; elemental analysis calcd (%) for $C_{20}H_{23}FN_2O_5$: C 61.53, H 5.94, N 7.18; found: C 61.60, H 5.93, N 6.97.

*1-(2,6-Difluorobenzoylamino)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylic Acid Diethyl Ester (**5j**)*

Prepared according to general procedure **II** using **9b** (1.63 g, 6 mmol), 2,6-difluorobenzoic acid hydrazide (1.50 g, 8.7 mmol), and HCl (1 N, 3.0 mL, 3.0 mmol) in EtOH (3.0 mL). Purification by precipitation provided **5j** as a white solid (2.04 g, 83%). M.p. 157–158 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.27$ (t, $J=7.5$ Hz, 6H; CH_2CH_3), 2.28 (s, 6H; CH_3-vinylic), 3.24 (s, 2H; CH_2-vinylic), 4.08–4.20 (m, 4H; CH_3CH_2), 6.95–7.01 (m, 2H; C*H*-aromatic), 7.39–7.49 (m, 1H; C*H*-aromatic), 8.56 ppm (s, 1H; N*H*); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=14.3$ (CH_3), 14.7 (CH_3), 24.7 (CH_2), 60.1 (CH_2), 102.8 (C), 111.5 (t, $J=21.8$ Hz; C), 112.2 (d, $J=21.8$ Hz; CH), 132.9 (t, $J=9.0$ Hz; CH), 148.2 (C), 160.5 (C), 160.1 (dd, $J^1=6.8$ Hz and $J^2=251.3$ Hz; C), 168.0 ppm (C); IR (neat): $\tilde{\nu}=3232$, 2986, 1699, 1667, 1611, 1470, 1392, 1291, 1192, 1118, 1060, 1007, 789, 759 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{20}H_{22}F_2N_2O_5Na$ $[M+Na]^+$: 431.1389; found: 431.1388; elemental analysis calcd (%) for $C_{20}H_{22}F_2N_2O_5$: C 58.82, H 5.43, N 6.86; found: C 58.61, H 5.39, N 6.79.

*1-(3,5-Difluorobenzoylamino)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylic Acid Diethyl Ester (**5k**)*

Prepared according to general procedure **II** using **9b** (1.63 g, 6 mmol), 3,5-difluorobenzoic acid hydrazide (1.20 g, 7.0 mmol), and HCl (1 N, 3.0 mL, 3.0 mmol) in EtOH (3.0 mL). Purification by precipitation provided **5k** as a white solid (1.92 g, 78%). M.p. 168–169 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.27$ (t, $J=7.5$ Hz, 6H; CH_2CH_3), 2.20 (s, 6H; CH_3-vinylic), 3.22 (d, $J=18$ Hz, 1H; C*H*H), 3.31 (d, $J=18$ Hz, 1H; CH*H*), 4.10–4.24 (m, 4H; CH_3CH_2), 7.01–7.07 (m, 1H; C*H*-aromatic), 7.40–7.43 (m, 2H; C*H*-aromatic), 9.03 ppm (s, 1H; N*H*); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=14.3$ (CH_3), 14.7 (CH_3), 24.8 (CH_2), 60.1 (CH_2), 102.5 (C), 108.1 (t, $J=25.1$ Hz; CH), 110.8 (dd, $J^1=9.0$ Hz and $J^2=17.3$ Hz; CH), 134.4 (t, $J=8.3$ Hz; C), 148.3 (C), 163.1 (dd, $J^1=12.0$ Hz and $J^2=250.5$ Hz; C), 164.8 (C), 168.3 ppm (C); IR (neat): $\tilde{\nu}=3233$, 2984, 1698, 1666, 1597, 1518, 1441, 1390, 1338, 1285, 1177, 1125, 1059, 990, 873, 759 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{20}H_{22}F_2N_2O_5Na$ $[M+Na]^+$: 431.1389; found: 431.1386; elemental analysis calcd (%) for $C_{20}H_{22}F_2N_2O_5$: C 58.82, H 5.43, N 6.86; found: C 58.74, H 5.29, N 6.70.

*1-Acetylamino-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylic Acid Diethyl Ester (**5l**)*

Prepared according to general procedure **II** using **9b** (1.09 g, 4.0 mmol), acetic acid hydrazide (296 mg, 4.0 mmol), and HCl (1 N, 2.0 mL, 2.0 mmol) in EtOH (2.0 mL). Purification by flash column chromatography (100% MTBE) provided **5l** as a white solid (990 mg, 80%). M.p. 146–147 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.25$–1.32 (m, 6H; CH_2CH_3), 2.01 (s, 3H; CH_3-vinylic, rotamer-1), 2.07 (s, 3H; CCH_3, rotamer-1), 2.19 (s, 3H; CCH_3, rotamer-2), 2.25 (s, 3H; CH_3-vinylic, rotamer-2), (s, 6H; CH_3-vinylic), 2.95 (d, $J=18$ Hz, 1H; C*H*H, rotamer-1), 3.20 (d, $J=18$ Hz, 1H; C*H*H, rotamer-2), 3.30 (d, $J=18$ Hz, 1H; CH*H*, rotamer-2), 3.54 (d, $J=19.5$ Hz, 1H; CH*H*, rotamer-1), 4.11–4.23 (m, 4H; CH_3CH_2), 7.68 (s, 1H; N*H*, rotamer-1), 7.94 ppm (s, 1H; N*H*, rotamer-2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=14.3$ (CH_3), 14.7 (CH_3), 15.1 (CH_3), 19.0 (CH_3), 19.3 (CH_3), 20.3 (CH_3), 24.4 (CH_2), 24.7 (CH_2), 60.1 (CH_2), 60.4 (CH_2), 102.3 (C), 103.4 (C), 148.4 (C), 148.5 (C), 167.4 (C), 168.0 (C), 169.4 (C), 174.8 ppm (C); IR (neat): $\tilde{\nu}=3238$, 2990, 1696, 1673, 1601, 1380, 1294, 1186, 1063 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{15}H_{22}N_2O_5Na$ $[M+Na]^+$: 333.1421; found: 333.1413; elemental analysis calcd (%) for $C_{15}H_{22}N_2O_5$: C 58.05, H 7.15, N 9.03; found: C 57.78, H 6.94, N 8.99.

*1-(3-Ethylureido)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylic Acid Diethyl Ester (**5m**)*

Prepared according to general procedure **II** using **9b** (2.72 g, 10.0 mmol), ethylurea hydrazide[21] (1.30 g, 12.6 mmol), and HCl (1 N, 5.0 mL, 5.0 mmol) in EtOH (5.0 mL). Purification by precipitation provided **5m** as a light yellow solid (2.64 g, 78%). M.p. 164–165 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta=1.01$ (t, $J=7.5$ Hz, 3H; NCH_2CH_3), 1.22 (t, $J=7.5$ Hz, 6H; CH_2CH_3), 2.16 (s, 6H; CH_3-vinylic), 3.02–3.25 (m, 4H; CH_2-vinylic and NCH_2CH_3), 4.08–4.15 (m, 4H; CH_2CH_3), 6.65–6.75 (br, 1H; N*H*), 8.57 ppm (s, 1H; N*H*); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta=14.8$ (CH_3), 15.4 (CH_3), 16.0 (CH_3), 25.0 (CH_2), 34.6 (CH_2), 59.9 (CH_2), 100.4 (C), 151.3 (C), 157.4 (C), 167.4 ppm (C); IR (neat): $\tilde{\nu}=3306$, 2979, 1696, 1641, 1598, 1387, 1289, 1198, 1077, 1060, 760 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{16}H_{25}N_3O_5Na$ $[M+Na]^+$: 362.1686; found: 362.1687.

*Bicyclo[2.2.1]hept-2-yl-carbamic Acid tert-Butyl Ester (**10a**)*

Prepared according to general procedure **III A** using **5a** (74 mg, 0.20 mmol), norbornene (188 mg, 2.0 mmol), V70 (3.08 mg, 0.01 mmol), and thiophenol (1.1 mg, 0.01 mmol) in dry CH_2Cl_2 (1.0 mL). Purification by flash column chromatography (MTBE/pentane, 1:9) provided **10a** as a white solid (26 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.09$–1.50 (m, 7H; CH_2), 1.48 (s, 9H; $C(CH_3)_3$), 1.60–1.74 (m, 1H; CH_2), 2.16–19 (br, 1H; C*H*), 2.22–2.24 (br, 1H; C*H*), 3.43–3.46 (br, 1H; NHC*H*), 4.38–4.44 ppm (br, 1H; N*H*). Physical data are in agreement with those reported in the literature.[9]

*Bicyclo[2.2.1]hept-2-yl-carbamic Acid Methyl Ester (**10b**)*

Prepared according to general procedure **III A** using **5e** (65 mg, 0.20 mmol), norbornene (188 mg, 2.0 mmol), V70 (3.08 mg, 0.01 mmol), and thiophenol (1.1 mg, 0.01 mmol) in dry CH_2Cl_2 (0.5 mL). Purification by flash column chromatography (MTBE/pentane, 1:6) provided **10b** as a white solid (26 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.07$–1.52 (m, 7H; CH_2), 1.74–1.81 (m, 1H; CH_2), 2.16–19 (br, 1H; C*H*), 2.23–2.26 (br, 1H; C*H*), 3.48–3.53 (br, 1H; NHC*H*), 3.64 (s, 9H; OCH_3), 4.48–4.54 ppm (br, 1H; N*H*). Physical data are in agreement with those reported in the literature.[5b]

*Octylcarbamic Acid tert-Butyl Ester (**11a**)*

Prepared according to general procedure **III A** using **5a** (110 mg, 0.30 mmol), 1-octene (168 mg, 1.5 mmol), V70 (4.62 mg, 0.015 mmol), and thiophenol (1.65 mg, 0.015 mmol) in dry CH_2Cl_2 (1.0 mL). Purification by flash column chromatography (MTBE/pentane, 1:9) provided **11a** as a colorless oil that contained the other regioisomer in a 1:6 ratio (determined by ^{1}H NMR spectroscopic analysis; 33 mg, 48%, combined yield of both isomers). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.87$ (t, $J=6$ Hz, 3H; CH_3), 1.20–1.35 (m, 12H; CH_2), 1.44 (s, 9H; $C(CH_3)_3$), 3.06–3.13 (m, 2H; NCH_2), 4.45–4.53 ppm (br, 1H; N*H*). Physical data are in agreement with those reported in the literature.[9]

*Cyclohexylcarbamic Acid tert-Butyl Ester (**12**)*

Prepared according to general procedure **III B** using **5a** (100 mg, 0.27 mmol), cyclohexene (110 mg, 1.4 mmol), AIBN (13 mg, 0.08 mmol), and thiophenol (4.36 mg, 0.04 mmol) in dry benzene (0.7 mL). Purification by flash column chromatography (pentane/Et_2O, 10:1) provided **12** as a white solid (28 mg, 52%). M.p. 76–68 °C; ^{1}H NMR (300 MHz, C_6D_6): $\delta=0.71$–0.92 (m, 3H; CH_2, C*H*H), 0.98–1.12 (m, 2H; CH_2), 1.26–1.41 (m, 3H; CH_2, CH*H*), 1.48 (s, 9H; $C(CH_3)_3$), 1.74–1.78 (m, 2H; CH_2), 3.52–3.55 (m, 1H; C*H*NH), 4.08–4.10 ppm (br, 1H; N*H*); ^{13}C NMR (75 MHz, C_6D_6): $\delta=25.1$ (CH_2), 25.8 (CH_2), 28.6 (CH_3), 33.4 (CH_2), 49.5 (CH), 78.4 (C), 155.0 ppm (C); IR (neat): $\tilde{\nu}=3364$, 2933, 2853, 1681, 1523, 1448, 1388, 1365, 1316, 1278, 1251, 1233, 1168, 1047, 1026, 902 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{11}H_{21}NO_2Na$ $[M+Na]^+$: 222.1465; found: 222.1472.

*(2-Butoxyethyl)carbamic Acid Methyl Ester (**13b**)*

Prepared according to general procedure **III A** using **5e** (65 mg, 0.20 mmol), *tert*-butyl vinyl ether (200 mg, 2.0 mmol), V70 (3.08 mg,

0.01 mmol), and thiophenol (1.1 mg, 0.01 mmol) in dry CH_2Cl_2 (0.75 mL). Purification by flash column chromatography (MTBE/pentane, 1:3) provided **13b** as a colorless oil (22.7 mg, 65%): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.92$ (t, $J = 7.5$ Hz, 3H; CH_3), 1.25–1.42 (m, 2H; CH_2), 1.50–1.59 (m, 2H; CH_2), 3.27–3.50 (m, 6H; OCH_2CH_2, NCH_2 and OCH_2), 3.61 (s, 3H; OCH_3), 5.02–5.12 ppm (br, 1H; NH). Physical data are in agreement with those reported in the literature.[5b]

*N-(2-Butoxyethyl)benzamide (**13c**)*

Prepared according to general procedure **IIIB** using **5h** (111.6 mg, 0.30 mmol), *n*-butyl vinyl ether (300 mg, 3 mmol), AIBN (14.8 mg, 0.09 mmol), and thiophenol (4.9 mg, 0.045 mmol) in dry benzene (0.75 mL). Purification by flash column chromatography (MTBE/pentane, 1:2) provided **13c** as a light yellow oil (29.2 mg, 44%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.92$ (t, $J = 7.5$ Hz, 3H; CH_2CH_3), 1.30–1.40 (m, 2H; CH_2CH_3), 1.51–1.59 (m, 2H; CH_2), 3.47 (t, $J = 7.5$ Hz, 2H; OCH_2), 3.57–3.60 (m, 2H; NCH_2), 3.60–3.67 (m, 2H; OCH_2), 6.54–6.62 (br, 1H; NH), 7.39–7.52 (m, 3H; CH-aromatic), 7.76–7.79 ppm (m, 2H; CH-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.9$ (CH_3), 19.3 (CH_2), 31.6 (CH_2), 39.8 (CH_2), 69.2 (CH_2), 70.1 (CH_2), 126.9 (CH), 128.5 (CH), 131.4 (CH), 134.6 (C), 167.4 ppm (C); IR (neat): $\tilde{\nu} = 3332$, 2958, 2933, 2870, 1640, 1540, 1489, 1305, 1117, 712, 694 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{13}H_{19}NO_2Na$ $[M+Na]^+$: 244.1308; found: 244.1300.

*N-(2-Butoxyethyl)-2,6-difluorobenzamide (**13d**)*

Prepared according to general procedure **IIIB** using **5j** (122.4 mg, 0.30 mmol), *n*-butyl vinyl ether (300 mg, 3 mmol), AIBN (14.8 mg, 0.09 mmol), and thiophenol (4.9 mg, 0.045 mmol) in dry benzene (0.75 mL). Purification by flash column chromatography (MTBE/pentane, 2:3) provided **13d** as a colorless oil (46 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.90$ (t, $J = 7.5$ Hz, 9H; CH_2CH_3), 1.28–1.41 (m, 2H; $CH_2CH_2CH_3$), 1.49–1.58 (m, 2H; $CH_2CH_2CH_3$), 3.45 (t, $J = 6.0$ Hz, 2H; OCH_2CH_2), 3.55–3.66 (m, 4H; NCH_2 and OCH_2), 6.34–6.44 (br, 1H; NH), 6.90–6.95 (m, 2H; CH-aromatic), 7.29–7.39 ppm (m, 1H; CH-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.8$ (CH_3), 19.2 (CH_2), 31.6 (CH_2), 39.8 (CH_2), 68.9 (CH_2), 71.0 (CH_2), 111.9 (dd, $J^1 = 3.0$ Hz and $J^2 = 23.3$ Hz; CH), 114.4 (t, $J = 19.9$ Hz; C), 131.5 (t, $J = 10.1$ Hz; CH), 160.0 (d, $J^1 = 7.5$ Hz and $J^2 = 251.3$ Hz; C), 160.3 ppm (C); IR (neat) $\tilde{\nu} = 3288$, 3078, 2959, 2934, 2870, 1653, 1625, 1546, 1466, 1301, 1235, 1117, 1006, 792 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{13}H_{17}F_2NO_2Na$ $[M+Na]^+$: 280.1120; found: 280.1104.

*N-(2-Butoxyethyl)-3,5-difluorobenzamide (**13e**)*

Prepared according to general procedure **IIIB** using **5k**(122.4 mg, 0.30 mmol), *n*-butyl vinyl ether (300 mg, 3 mmol), AIBN (14.8 mg, 0.09 mmol), and thiophenol (4.9 mg, 0.045 mmol) in dry benzene (0.75 mL). Purification by flash column chromatography (MTBE/pentane, 2:3) provided **13e** as a white solid (50 mg, 65%). M.p. 49–50 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.95$ (t, $J = 7.5$ Hz, 9H; CH_2CH_3), 1.36–1.44 (m, 2H; $CH_2CH_2CH_3$), 1.55–1.65 (m, 2H; $CH_2CH_2CH_3$), 3.50 (t, $J = 6.0$ Hz, 2H; OCH_2CH_2), 3.59–3.68 (m, 4H; NCH_2 and OCH_2), 6.52–6.62 (br, 1H; NH), 6.92–7.92 (m, 1H; CH-aromatic), 7.28–7.35 ppm (m, 2H; CH-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.8$ (CH_3), 19.3 (CH_2), 31.6 (CH_2), 40.0 (CH_2), 68.9 (CH_2), 71.0 (CH_2), 106.7 (t, $J = 25.1$ Hz; CH), 110.2 (dd, $J^1 = 8.3$ Hz and $J^2 = 18.3$ Hz; CH), 138.0 (t, $J = 8.3$ Hz; C), 162.9 (d, $J^1 = 12.0$ Hz and $J^2 = 249$ Hz; C), 165.0 ppm (C); IR (neat): $\tilde{\nu} = 3315$, 3088, 2959, 2935, 2868, 1644, 1593, 1545, 1438, 1326, 1122, 988, 854, 766, 671 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{13}H_{17}F_2NO_2Na$ $[M+Na]^+$: 280.1120; found: 280.1117.

*(2-tert-Butoxyethyl)carbamic Acid Allyl Ester (**14b**)*

Prepared according to general procedure **IIIA** using **5g** (106 mg, 0.30 mmol), *tert*-butyl vinyl ether (300 mg, 3 mmol), V70 (4.62 mg, 0.015 mmol), and thiophenol (1.65 mg, 0.015 mmol) in dry CH_2Cl_2 (0.75 mL). Purification by flash column chromatography (MTBE/pentane, 1:5) provided **14b** as a light yellow oil (32 mg, 53%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.17$ (s, 9H; $C(CH_3)_3$), 3.30–3.34 (m, 2H; NCH_2), 3.40–3.43 (m, 2H; OCH_2), 4.56 (d, $J = 6.0$ Hz, 2H; OCH_2-vinylic), 5.12–5.18 (br, 1H; NH), 5.20 (dd, $J^1 = 3.0$ Hz and $J^2 = 18.0$ Hz, 1H; CHH-vinylic), 5.30 (dd, $J^1 = 3.0$ Hz and $J^2 = 18.0$ Hz, 1H; CHH-vinylic), 5.85–5.98 ppm (m, 1H; CH-vinylic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 27.5$ (CH_3), 41.6 (CH_2), 60.5 (CH_2), 65.4 (CH_2), 73.1 (C), 117.5 (CH_2), 133.0 (CH), 156.3 ppm (C); IR (neat): $\tilde{\nu} = 3340$, 2975, 2937, 2874, 1724, 1522, 1364, 1252, 1196, 1091, 995, 931 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{10}H_{19}NO_3Na$ $[M+Na]^+$: 224.1527; found: 224.1263.

*N-(2-tert-Butoxyethyl)benzamide (**14c**)*

Prepared according to general procedure **IIIB** using **5h** (111.6 mg, 0.30 mmol), *tert*-butyl vinyl ether (300 mg, 3 mmol), AIBN (14.8 mg, 0.09 mmol), and thiophenol (4.9 mg, 0.045 mmol) in dry benzene (0.75 mL). Purification by flash column chromatography (MTBE/pentane, 1:1) provided **14c** as a light yellow oil (48.9 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.20$ (s, 9H; $C(CH_3)_3$), 3.51–3.54 (m, 2H; NCH_2), 3.57–3.62 (m, 2H; OCH_2), 6.58–6.62 (br, 1H; NH), 7.39–7.51 (m, 3H; CH-aromatic), 7.74–7.78 ppm (m, 2H; CH-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 27.5$ (CH_3), 40.4 (CH_2), 60.4 (CH_2), 73.2 (C), 126.8 (CH), 128.5 (CH), 131.3 (CH), 134.8 (C), 167.4 ppm (C); IR (neat): $\tilde{\nu} = 3323$, 2974, 1638, 1539, 1489, 1363, 1305, 1195, 1087, 866, 694 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{13}H_{19}NO_2Na$ $[M+Na]^+$: 244.1308; found: 244.1302.

*N-(2-tert-Butoxyethyl)-2,6-difluorobenzamide (**14d**)*

Prepared according to general procedure **IIIB** using **5j** (122.4 mg, 0.30 mmol), *tert*-butyl vinyl ether (300 mg, 3 mmol), AIBN (14.8 mg, 0.09 mmol), and thiophenol (4.9 mg, 0.045 mmol) in dry benzene (0.75 mL). Purification by flash column chromatography (MTBE/pentane, 2:3) provided **14d** as a colorless oil (68 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.19$ (s, 9H; $C(CH_3)_3$), 3.51–3.55 (m, 2H; NCH_2), 3.59–3.64 (m, 2H; OCH_2), 6.36–6.44 (br, 1H; NH), 6.91–6.97 (m, 2H; CH-aromatic), 7.30–7.40 ppm (m, 2H; CH-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 27.5$ (CH_3), 40.3 (CH_2), 60.2 (CH_2), 73.2 (C), 112.0 (dd, $J^1 = 2.3$ Hz and $J^2 = 23.3$ Hz; CH), 114.5 (t, $J = 21.4$ Hz; C), 131.5 (t, $J = 9.8$ Hz; CH), 160.0 (dd, $J^1 = 7.5$ Hz and $J^2 = 262.5$ Hz; C), 160.2 ppm (C); IR (neat): $\tilde{\nu} = 3295$, 3079, 2976, 2937, 1656, 1626, 1548, 1467, 1364, 1302, 1236, 1196, 1092, 1007, 793 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{13}H_{17}F_2NO_2Na$ $[M+Na]^+$: 280.1120; found: 280.1119.

*N-(2-tert-Butoxyethyl)-3,5-difluorobenzamide (**14e**)*

Prepared according to general procedure **IIIB** using **5k** (122.4 mg, 0.30 mmol), *tert*-butyl vinyl ether (300 mg, 3 mmol), AIBN (14.8 mg, 0.09 mmol), and thiophenol (4.9 mg, 0.045 mmol) in dry benzene (0.75 mL). Purification by flash column chromatography (MTBE/pentane, 2:3) provided **14e** as a white solid (71 mg, 92%). M.p. 55–56 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.13$ (s, 9H; $C(CH_3)_3$), 3.44–3.54 (m, 4H; NCH_2 and OCH_2), 6.52–6.58 (br, 1H; NH), 6.80–6.91 (m, 1H; CH-aromatic), 7.18–7.24 ppm (m, 2H; CH-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 27.5$ (CH_3), 40.6 (CH_2), 60.1 (CH_2), 73.3 (C), 106.6 (t, $J = 25.1$ Hz; CH), 110.1 (dd, $J^1 = 8.3$ Hz and $J^2 = 17.3$ Hz; CH), 138.1 (t, $J = 8.3$ Hz; C), 162.9 (dd, $J^1 = 12.0$ Hz and $J^2 = 249.0$ Hz; C), 164.9 ppm (C); IR (neat): $\tilde{\nu} = 3322$, 3091, 2975, 2938, 2874, 1644, 1593, 1545, 1438, 1363, 1328, 1194, 1123, 1090, 987, 867, 763, 671 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{13}H_{17}F_2NO_2Na$ $[M+Na]^+$: 280.1120; found: 280.1119.

*N-(2-tert-Butoxyethyl)-4-fluorobenzamide (**14f**)*

Prepared according to general procedure **IIIB** using **5i** (117 mg, 0.30 mmol), *tert*-butyl vinyl ether (300 mg, 3 mmol), AIBN (14.8 mg, 0.09 mmol), and thiophenol (4.9 mg, 0.045 mmol) in dry benzene (0.75 mL). Purification by flash column chromatography (MTBE/pentane, 1:1) provided **14f** as a light yellow solid (61 mg, 85%). M.p. 53–54 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.20$ (s, 9H; $C(CH_3)_3$), 3.51–3.62 (m, 4H; NCH_2 and OCH_2), 6.48–6.54 (br, 1H; NH), 7.07–7.13 (m, 2H; CH-aromatic), 7.74–7.80 ppm (m, 2H; CH-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 27.6$ (CH_3), 40.5 (CH_2), 60.4 (CH_2), 73.3 (C), 115.5 (d, $J = 21.8$ Hz; CH), 129.2 (d, $J = 9.0$ Hz; CH), 130.9 (d, $J = 3.0$ Hz; C), 163.0 (C), 166.3 ppm (C); IR (neat): $\tilde{\nu} = 3332$, 2975, 1639, 1603, 1545,

1501, 1363, 1231, 1194, 1160, 1088, 850, 765 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{13}H_{18}FNO_2Na$ $[M+Na]^+$: 262.1214; found: 262.1209.

*(Tetrahydropyran-3-yl)carbamic Acid tert-Butyl Ester (**15a**)*

Prepared according to general procedure **IIIA** using **5a** (110 mg, 0.30 mmol), 3,4-dihydro-2*H*-pyran (126 mg, 1.5 mmol), V70 (4.62 mg, 0.015 mmol), and thiophenol (1.65 mg, 0.015 mmol) in dry CH_2Cl_2 (1.0 mL). Purification by flash column chromatography (MTBE/pentane, 1:3) provided **15a** as a light yellow solid containing the other regioisomer in a 1:8 ratio (determined by ^1H NMR spectroscopic analysis; 45 mg, 75%, combined yield of both isomers). M.p. 66–67°C; ^1H NMR (300 MHz, $CDCl_3$): $\delta=1.43$–1.89 (m, 4H; CH_2), 1.43 (s, 9H; C(CH_3)$_3$), 3.36–3.39 (m, 1H; C*H*NH), 3.3.58–3.66 (m, 3H; OCH_2 and OC*H*H), 3.74–3.79 (m, 1H; OCH*H*), 4.75–4.84 ppm (br, 1H; N*H*); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=23.3$ (CH_2), 28.4 (CH_3), 29.1 (CH_2), 46.0 (CH), 68.1 (CH_2), 71.7 (CH_2), 79.3 (C), 155.2 ppm (C); IR (neat): $\tilde{\nu}=3330$, 2975, 2940, 2851, 1712, 1695, 1522, 1366, 1308, 1244, 1172, 1094, 1023 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{10}H_{19}F_2NO_3Na$ $[M+Na]^+$: 224.1257; found: 224.1242.

*N-(Tetrahydropyran-3-yl)benzamide (**15b**)*

Prepared according to general procedure **IIIB** using **5h** (111.6 mg, 0.30 mmol), 3,4-dihydro-2*H*-pyran (126 mg, 1.5 mmol), AIBN (14.8 mg, 0.09 mmol), and thiophenol (4.9 mg, 0.045 mmol) in dry benzene (0.75 mL). Purification by flash column chromatography (MTBE/pentane, 3:1) provided **15b** as a colorless oil containing the other regioisomer in a 1:6 ratio (determined by ^1H NMR spectroscopic analysis; 22 mg, 36%, combined yield of both isomers). ^1H NMR (300 MHz, $CDCl_3$): $\delta=$ 1.57–1.93 (m, 4H; CH_2), 3.60–3.64 (m, 2H; OCH_2), 3.67–3.74 (m, 1H; OC*H*H), 3.81–3.86 (m, 1H; OCH*H*), 4.18–4.23 (m, 1H; C*H*NH), 6.47–6.55 (br, 1H; N*H*), 7.40–7.53 (m, 3H; C*H*-aromatic), 7.77–7.81 ppm (m, 2H; C*H*-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=22.8$ (CH_2), 28.4 (CH_2), 45.3 (CH), 68.4 (CH_2), 71.4 (CH_2), 126.9 (CH), 128.6 (CH), 131.5 (CH), 134.6 (C), 166.8 ppm (C); IR (neat): $\tilde{\nu}=3307$, 3062, 2944, 2854, 1637, 1539, 1490, 1324, 1094, 1031 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{12}H_{15}NO_2Na$ $[M+Na]^+$: 228.0995; found: 228.0990.

*3,5-Difluoro-N-(tetrahydropyran-3-yl)benzamide (**15c**)*

Prepared according to general procedure **IIIB** using **5k** (122.4 mg, 0.30 mmol), 3,4-dihydro-2*H*-pyran (126 mg, 1.5 mmol), AIBN (14.8 mg, 0.09 mmol), and thiophenol (4.9 mg, 0.045 mmol) in dry benzene (0.75 mL). Purification by flash column chromatography (MTBE/pentane, 3:2) provided **15c** as a colorless oil containing the other regioisomer in a 1:6 ratio (determined by ^1H NMR spectroscopic analysis; 36 mg, 50%, combined yield of both isomers). ^1H NMR (300 MHz, $CDCl_3$): $\delta=$ 1.57–1.96 (m, 4H; CH_2), 3.62–3.66 (m, 2H; OCH_2), 3.78–3.83 (m, 2H; OC*H*H and OCH*H*), 4.12–4.20 (m, 1H; C*H*NH), 6.48–6.57 (br, 1H; N*H*), 6.93–6.97 (m, 1H; C*H*-aromatic), 7.25–7.33 ppm (m, 2H; C*H*-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=22.7$ (CH_2), 28.1 (CH_2), 45.6 (CH), 68.3 (CH_2), 71.1 (CH_2), 106.8 (t, $J=25.1$ Hz; CH), 110.3 (dd, $J^1=$ 9.0 Hz and $J^2=17.3$ Hz; CH), 138.0 (t, $J=7.9$ Hz; C), 163.0 (d, $J^1=$ 12.0 Hz and $J^2=249$ Hz; C), 164.4 ppm (C); IR (neat): $\tilde{\nu}=3287$, 3081, 2944, 2848, 1637, 1594, 1540, 1435, 1342, 1120, 1096, 1094, 984 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{12}H_{13}F_2NO_2Na$ $[M+Na]^+$: 264.0807; found: 264.0805.

*[2-(tert-Butyldimethylsilanyloxy)-2-phenylethyl]carbamic Acid tert-Butyl Ester (**16a**)*

Prepared according to general procedure **IIIB** using **5a** (100 mg, 0.27 mmol), *tert*-butyldimethyl(1-phenylvinyloxy)silane (160 mg, 0.68 mmol), AIBN (13 mg, 0.08 mmol), and thiophenol (4.4 mg, 0.04 mmol) in dry benzene (0.7 mL). Purification by flash column chromatography (Et_2O/pentane, 1:12) provided **16a** as a colorless oil (56 mg, 59%). ^1H NMR (300 MHz, C_6D_6): $\delta=0.10$ (s, 3H; Si–CH_3), 0.05 (s, 3H; Si–CH_3), 0.93 (s, 9H; SiC(CH_3)$_3$), 1.44 (s, 9H; C(CH_3)$_3$), 3.06 (ddd, $J^1=$ 13.4 Hz, $J^2=7.6$ Hz and $J^3=5.3$ Hz, 1H; C*H*HNH), 3.39–3.47 (m, 1H; CH*H*NH), 4.50–4.60 (br, 1H; N*H*), 4.82 (dd, $J^1=7.6$ and $J^2=4.1$ Hz, 1H; OC*H*), 7.01–7.05 (m, 1H; C*H*-aromatic), 7.10 (d, $J=7.4$ Hz, 2H; C*H*-aromatic), 7.25 ppm (d, $J=7.4$ Hz, 2H; C*H*-aromatic); ^{13}C NMR (75 MHz, C_6D_6): $\delta=4.9$ (CH_3), −4.6 (CH_3), 18.4 (C), 26.0 (CH_3), 28.5 (CH_3), 49.6 (CH_2), 74.3 (CH), 78.7 (C), 126.3 (CH), 128.5 (CH), 143.0 (C), 155.8 ppm (C); IR (neat): $\tilde{\nu}=3374$, 2956, 2930, 2857, 1718, 1503, 1472, 1454, 1390, 1254, 1171, 1098, 1066, 977, 940, 830, 778, 753, 700 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{19}H_{33}NSiO_3Na$ $[M+Na]^+$: 374.2122; found: 374.2126.

*N-[2-(tert-Butyldimethylsilanyloxy)-2-phenylethyl]benzamide (**16b**)*

Prepared according to general procedure **IIIB** using **5h** (111.6 mg, 0.30 mmol), *tert*-butyldimethyl(1-phenylvinyloxy)silane (140 mg, 0.6 mmol), AIBN (14.8 mg, 0.09 mmol), and thiophenol (4.9 mg, 0.045 mmol) in dry benzene (0.75 mL). Purification by flash column chromatography (MTBE/pentane, 1:6) provided **16b** as a light yellow oil (48 mg, 45%). ^1H NMR (300 MHz, $CDCl_3$): $\delta=-0.11$ (s, 3H; Si–CH_3), 0.02 (s, 3H; Si–CH_3), 0.90 (s, 9H; SiC(CH_3)$_3$), 3.38–3.47 (m, 1H; C*H*HNH), 3.78–3.84 (m, 1H; CH*H*NH), 4.90–4.94 (m, 1H; OC*H*), 6.38–6.47 (br, 1H; N*H*), 7.26–7.52 (m, 8H; C*H*-aromatic), 7.73 ppm (d, $J=$ 9.0 Hz, 2H; C*H*-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=-4.9$ (CH_3), −4.6 (CH_3), 18.2 (C), 25.8 (CH_3), 48.2 (CH_2), 73.6 (CH), 126.0 (CH), 126.8 (CH), 127.7 (CH), 128.4 (CH), 128.6 (CH), 131.4 (CH), 134.6 (C), 142.3 (C), 167.2 ppm (C); IR (neat): $\tilde{\nu}=3309$, 3064, 3031, 2955, 2929, 2886, 2857, 1641, 1540, 1490, 1293, 1253, 1100, 959, 864, 836, 778, 700 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{21}H_{29}NO_2SiNa$ $[M+Na]^+$: 378.1860; found: 378.1854.

*N-[2-(tert-Butyldimethylsilanyloxy)-2-phenylethyl]-2,6-difluorobenzamide (**16c**)*

Prepared according to general procedure **IIIB** using **5j** (122.4 mg, 0.30 mmol), *tert*-butyldimethyl(1-phenyl-vinyloxy)silane (140 mg, 0.6 mmol), AIBN (14.8 mg, 0.09 mmol), and thiophenol (4.9 mg, 0.045 mmol) in dry benzene (0.75 mL). Purification by flash column chromatography (MTBE/pentane, 1:6) provided **16c** as a colorless oil (52 mg, 44%). ^1H NMR (300 MHz, $CDCl_3$): $\delta=-0.12$ (s, 3H; Si–CH_3), 0.05 (s, 3H; Si–CH_3), 0.88 (s, 9H; SiC(CH_3)$_3$), 3.43–3.51 (m, 1H; C*H*HNH), 3.77–3.85 (m, 1H; CH*H*NH), 4.90–4.94 (m, 1H; OC*H*), 6.18–6.27 (br, 1H; N*H*), 6.90–6.97 (m, 2H; C*H*-aromatic), 7.27–7.40 ppm (m, 6H; C*H*-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=-5.2$ (CH_3), −4.7 (CH_3), 18.1 (C), 25.7 (CH_3), 48.1 (CH_2), 73.4 (CH), 111.9 (dd, $J^1=2.3$ Hz and $J^2=$ 23.3 Hz; CH), 114.2 (t, $J=18.8$ Hz; C), 126.1 (CH), 126.8 (CH), 127.8 (CH), 128.3 (CH), 131.6 (t, $J=10.1$ Hz; CH), 142.0 (C), 160.1 (d, $J^1=$ 6.8 Hz and $J^2=251.3$ Hz; C), 160.2 ppm (C); IR (neat): $\tilde{\nu}=3289$, 3067, 3034, 2960, 2930, 2886, 2858, 1656, 1621, 1547, 1467, 1292, 1255, 1098, 1006, 837, 778, 700 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{21}H_{27}F_2NO_2SiNa$ $[M+Na]^+$: 414.1671; found: 414.1668.

*N-[2-(tert-Butyldimethylsilanyloxy)-2-phenylethyl]-3,5-difluorobenzamide (**16d**)*

Prepared according to general procedure **IIIB** using **5k** (122.4 mg, 0.30 mmol), *tert*-butyldimethyl(1-phenylvinyloxy)silane (140 mg, 0.6 mmol), AIBN (14.8 mg, 0.09 mmol), and thiophenol (4.9 mg, 0.045 mmol) in dry benzene (0.75 mL). Purification by flash column chromatography (MTBE/pentane, 1:6) provided **16d** as a colorless oil (58 mg, 49%). ^1H NMR (300 MHz, $CDCl_3$): $\delta=-0.11$ (s, 3H; Si–CH_3), 0.02 (s, 3H; Si–CH_3), 0.90 (s, 9H; SiC(CH_3)$_3$), 3.37–3.46 (m, 1H; C*H*HNH), 3.73–3.82 (m, 1H; CH*H*NH), 4.89–4.96 (m, 1H; OC*H*), 6.38–6.47 (br, 1H; N*H*), 6.94–6.97 (m, 1H; C*H*-aromatic), 7.22–7.44 ppm (m, 7H; C*H*-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=-5.1$ (CH_3), −4.7 (CH_3), 18.1 (C), 25.6 (CH_3), 48.3 (CH_2), 73.3 (CH), 106.8 (t, $J=25.1$ Hz; CH), 110.1 (dd, $J^1=9.0$ Hz and $J^2=17.3$ Hz; CH), 125.9 (CH), 127.8 (CH), 128.4 (CH), 138.0 (t, $J=8.3$ Hz; C), 141.9 (C), 163.4 (d, $J^1=12.0$ Hz and $J^2=$ 249 Hz; C), 164.8 ppm (C); IR (neat): $\tilde{\nu}=3347$, 2930, 2858, 1645, 1594, 1542, 1438, 1333, 1251, 1123, 1095, 988, 835, 776, 700 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{21}H_{27}F_2NO_2SiNa$ $[M+Na]^+$: 414.1671; found: 414.1663.

*N-[2-(tert-Butyldimethylsilanyloxy)-2-phenylethyl]acetamide (**16e**)*

Prepared according to general procedure **IIIB** using **5l** (93 mg, 0.30 mmol), *tert*-butyldimethyl(1-phenylvinyloxy)silane (140 mg, 0.6 mmol), AIBN (14.8 mg, 0.09 mmol), and thiophenol (4.9 mg,

0.045 mmol) in dry benzene (0.75 mL). Purification by flash column chromatography (MTBE/pentane, 1:1) provided **16e** as a colorless oil (33 mg, 38%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.16$ (s, 3H; Si–CH_3), −0.02 (s, 3H; Si–CH_3), 0.84 (s, 9H; SiC(CH_3)$_3$), 1.91(s, 3H; CCH_3), 3.08–3.17 (m, 1H; C*H*HNH), 3.51–3.60 (m, 1H; CH*H*NH), 4.71–4.75 (m, 1H; OC*H*), 5.65–5.74 (br, 1H; N*H*), 7.20–7.27 ppm (m, 5H; C*H*-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -5.0$ (CH_3), −4.7 (CH_3), 18.2 (C), 23.3 (CH_3), 25.8 (CH_3), 47.8 (CH_2), 73.6 (CH), 126.0 (CH), 127.6 (CH), 128.3 (CH), 142.2 (C), 169.8 ppm (C); IR (neat): $\tilde{\nu} = 3289$, 3067, 3031, 2955, 2929, 2857, 1651, 1552, 1453, 1373, 1255, 1096, 964, 835, 777, 700 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{16}H_{27}NO_2SiNa$ [*M*+Na]$^+$: 316.1703; found: 316.1706.

*1-[2-(tert-Butyldimethylsilanyloxy)-2-phenylethyl]-3-ethylurea (**16f**)*

Prepared according to general procedure **IIIB** using **5m** (101.7 mg, 0.30 mmol), *tert*-butyldimethyl(1-phenylvinyloxy)silane (140 mg, 0.6 mmol), AIBN (14.8 mg, 0.09 mmol), and thiophenol (4.9 mg, 0.045 mmol) in dry benzene (2 mL). Purification by flash column chromatography (MTBE/pentane, 1:1) provided **16f** as a colorless oil (26 mg, 27%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.16$ (s, 3H; Si–CH_3), −0.01 (s, 3H; Si–CH_3), 0.84 (s, 9H; SiC(CH_3)$_3$), 1.06 (t, $J = 7.5$ Hz, 3H; CH_2CH_3), 3.07–3.16 (m, 3H; C*H*HNH and CH_2CH_3), 3.34–3.43 (m, 1H; CH*H*NH), 4.40–4.49 (br, 1H; N*H*), 4.52–4.61 (br, 1H; N*H*), 4.72–4.76 (m, 1H; OC*H*), 7.18–7.27 ppm (m, 5H; C*H*-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -5.0$ (CH_3), −4.7 (CH_3), 15.5 (CH_3), 18.2 (C), 25.8 (CH_3), 35.4 (CH_2), 49.2 (CH_2), 74.4 (CH), 126.1 (CH), 127.5 (CH), 128.2 (CH), 142.5 (C), 158.2 ppm (C); IR (neat): $\tilde{\nu} = 3322$, 2956, 2929, 2885, 2857, 1631, 1571, 1472, 1362, 1252, 1096, 1068, 938, 835, 777, 700 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{17}H_{30}N_2O_2SiNa$ [*M*+Na]$^+$: 345.1969; found: 345.1968.

*[2-(4-Bromophenyl)-2-(tert-butyldimethylsilanyloxy)ethyl]carbamic Acid tert-Butyl Ester (**17a**)*

Prepared according to general procedure **IIIB** using **5a** (100 mg, 0.27 mmol), [1-(4-bromophenyl)vinyloxy]-*tert*-butyldimethylsilane (210 mg, 0.68 mmol), AIBN (13 mg, 0.08 mmol), and thiophenol (4.4 mg, 0.04 mmol) in dry benzene (0.7 mL). Purification by flash column chromatography (Et_2O/pentane, 1:12) provided **17a** as a colorless oil (49 mg, 42%). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.15$ (s, 3H; Si–CH_3), 0.01 (s, 3H; Si–CH_3), 0.89 (s, 9H; Si–C(CH_3)$_3$), 1.43 (s, 9H; C(CH_3)$_3$), 2.87–2.97 (m, 1H; C*H*HNH), 3.28 (ddd, $J^1 = 11.5$ Hz, $J^2 = 7.1$ Hz and $J^3 = 4.3$ Hz, 1H; CH*H*NH), 4.44–4.52 (br, 1H; N*H*), 4.67 (dd, $J^1 = 7.1$ Hz and $J^2 = 4.1$ Hz, 1H; OC*H*), 6.90 (d, $J = 8.3$ Hz, 2H; C*H*-aromatic), 7.21 ppm (d, $J = 8.3$ Hz, 2H; C*H*-aromatic); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 4.9$ (CH_3), −4.7 (CH_3), 18.4 (C), 25.9 (CH_3), 28.5 (CH_3), 49.4 (CH_2), 73.6 (CH), 78.9 (C), 121.7 (CH), 131.7 (CH), 131.1 (C), 141.9 (C), 155.7 ppm (C); IR (neat): $\tilde{\nu} = 3372$, 2930, 2857, 1718, 1501, 1391, 1365, 1254, 1169, 1091, 1010, 939, 836, 778 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{19}H_{32}Br^{79}NO_3Na$ [*M*+Na]$^+$: 454.1209; found: 454.1212.

*N-[2-(4-Bromophenyl)-2-(tert-butyldimethylsilanyloxy)ethyl]benzamide (**17b**)*

Prepared according to general procedure **IIIB** using **5h** (111.6 mg, 0.30 mmol), [1-(4-bromophenyl)vinyloxy]-*tert*-butyldimethylsilane (187 mg, 0.6 mmol), AIBN (14.8 mg, 0.09 mmol), and thiophenol (4.9 mg, 0.045 mmol) in dry benzene (0.75 mL). Purification by flash column chromatography (MTBE/pentane, 1:6) provided **17b** as a light yellow oil (41 mg, 32%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.12$ (s, 3H; Si–CH_3), 0.00 (s, 3H; Si–CH_3), 0.89 (s, 9H; SiC(CH_3)$_3$), 3.32–3.41 (m, 1H; C*H*HNH), 3.71–3.79 (m, 1H; CH*H*NH), 4.86–4.90 (m, 1H; OC*H*), 6.39–6.47 (br, 1H; N*H*), 7.25 (d, $J = 9.0$ Hz, 2H; C*H*-aromatic), 7.39–7.52 (m, 5H; C*H*-aromatic), 7.72 ppm (d, $J = 9.0$ Hz, 2H; C*H*-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -5.0$ (CH_3), −4.7 (CH_3), 18.1 (C), 25.8 (CH_3), 48.1 (CH_2), 73.0 (CH), 121.6 (C), 126.8 (CH) , 127.7 (CH), 128.6 (CH), 131.5 (CH), 134.4 (C), 141.4 (C), 167.3 ppm (C); IR (neat): $\tilde{\nu} = 3316$, 3064, 2955, 2928, 2886, 2856, 1639, 1538, 1486, 1362, 1295, 1251, 1088, 1010, 958, 835, 776, 693 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{21}H_{28}Br^{79}NO_2SiNa$ [*M*+Na]$^+$: 456.0965; found: 456.0996.

*N-[2-(4-Bromophenyl)-2-(tert-butyldimethylsilanyloxy)ethyl]-4-fluorobenzamide (**17c**)*

Prepared according to general procedure **IIIB** using **5i** (117 mg, 0.30 mmol), [1-(4-bromophenyl)vinyloxy]-*tert*-butyldimethylsilane (187 mg, 0.6 mmol), AIBN (14.8 mg, 0.09 mmol), and thiophenol (4.9 mg, 0.045 mmol) in dry benzene (1.5 mL). Purification by flash column chromatography (MTBE/pentane, 1:6) provided **17c** as a colorless oil (42 mg, 31%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.11$ (s, 3H; Si–CH_3), 0.00 (s, 3H; Si–CH_3), 0.89 (s, 9H; SiC(CH_3)$_3$), 3.32–3.40 (m, 1H; C*H*HNH), 3.70–3.78 (m, 1H; C*H*HNH), 4.86–4.90 (m, 1H; OC*H*), 6.35–6.44 (br, 1H; N*H*), 7.07–7.14 (m, 2H; C*H*-aromatic), 7.25 (d, $J = 9.0$ Hz, 2H; C*H*-aromatic), 7.45–7.49 (m, 2H; C*H*-aromatic), 7.71–7.77 ppm (m, 2H; C*H*-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 5.0$ (CH_3), −4.7 (CH_3), 18.1 (C), 25.8 (CH_3), 48.2 (CH_2), 72.9 (CH), 115.6 (d, $J = 21.8$ Hz; CH), 121.6 (C) , 127.7 (CH), 129.1 (d, $J = 9.0$ Hz, CH), 131.6 (CH), 133.4 (C), 141.4 (C), 145.4 (C), 166.2 ppm (C); IR (neat): $\tilde{\nu} = 3317$, 2954, 2929, 2886, 2857, 1640, 1603, 1542, 1501, 1286, 1235, 1160, 1090, 958, 835, 776 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $(C_{21}H_{27}Br^{79}FNO_2Si)_2Na$ [*M*+Na]$^+$: 925.1849; found: 925.1844.

*N-[2-(4-Bromophenyl)-2-(tert-butyldimethylsilanyloxy)ethyl]acetamide (**17d**)*

Prepared according to general procedure **IIIB** using **5l** (93 mg, 0.30 mmol), [1-(4-bromophenyl)vinyloxy]-*tert*-butyldimethylsilane (187 mg, 0.6 mmol), AIBN (14.8 mg, 0.09 mmol), and thiophenol (4.9 mg, 0.045 mmol) in dry benzene (0.75 mL). Purification by flash column chromatography (MTBE/pentane, 1:1) provided **17d** as a light yellow oil (30 mg, 27%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.11$ (s, 3H; Si–CH_3), 0.03 (s, 3H; Si–CH_3), 0.90 (s, 9H; SiC(CH_3)$_3$), 1.95 (s, 3H; CCH_3), 3.09–3.17 (m, 1H; C*H*HNH), 3.51–3.59 (m, 1H; CH*H*NH), 4.73–4.77 (m, 1H; OC*H*), 5.68–5.76 (br, 1H; N*H*), 7.19 (d, $J = 9.0$ Hz, 2H; C*H*-aromatic), 7.45 ppm (d, $J = 9.0$ Hz, 2H; C*H*-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -5.0$ (CH_3), −4.7 (CH_3), 18.2 (C), 23.3 (CH_3), 25.8 (CH_3), 47.7 (CH_2), 73.0 (CH), 121.5 (C), 127.7 (CH), 131.5 (CH), 141.4 (C), 169.8 ppm (C); IR (neat): $\tilde{\nu} = 3290$, 3082, 2955, 2929, 2886, 2857, 1652, 1553, 1487, 1362, 1252, 1110, 1088, 1010, 966, 836, 777 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{16}H_{26}Br^{79}NO_2SiNa$ [*M*+Na]$^+$: 394.0808; found: 384.0807.

*1-[2-(4-Bromophenyl)-2-(tert-butyldimethylsilanyloxy)ethyl]-3-ethylurea (**17e**)*

Prepared according to general procedure **IIIB** using **5m** (101.7 mg, 0.30 mmol), [1-(4-bromophenyl)vinyloxy]-*tert*-butyldimethylsilane (187 mg, 0.6 mmol), AIBN (14.8 mg, 0.09 mmol), and thiophenol (4.9 mg, 0.045 mmol) in dry benzene (0.75 mL). Purification by flash column chromatography (MTBE/pentane, 1:1) provided **17e** as a colorless oil (26 mg, 22%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.10$ (s, 3H; Si–CH_3), 0.03 (s, 3H; Si–CH_3), 0.88 (s, 9H; SiC(CH_3)$_3$), 1.11 (t, $J = 6.0$ Hz, 3H; CH_2CH_3), 3.09–3.20 (m, 3H; C*H*HNH and CH_2CH_3), 3.34–3.43 (m, 1H; CH*H*NH), 4.42–4.49 (br, 1H; N*H*), 4.56–4.64 (br, 1H; N*H*), 4.74–4.78 (m, 1H; OC*H*), 7.19 (d, $J = 9.0$ Hz, 2H; C*H*-aromatic), 7.44 ppm (d, $J = 9.0$ Hz, 2H; C*H*-aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -5.0$ (CH_3), −4.7 (CH_3), 15.5 (CH_3), 18.2 (C), 25.8 (CH_3), 35.4 (CH_2), 49.0 (CH_2), 73.7 (CH), 121.3 (C), 127.8 (CH), 131.4 (CH), 141.7 (C), 158.0 ppm (C); IR (neat): $\tilde{\nu} = 3318$, 2956, 2929, 2886, 2857, 1633, 1572, 1486, 1258, 1089, 1011, 937, 835, 779 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{17}H_{29}Br^{79}N_2O_2SiNa$ [*M*+Na]$^+$: 423.1074; found: 423.1068.

*[2-(tert-Butyldimethylsilanyloxy)-2-(3,4-dimethoxyphenyl)ethyl]carbamic Acid tert-Butyl Ester (**18**)*

Prepared according to general procedure **IIIB** using **5a** (100 mg, 0.27 mmol), *tert*-butyl[1-(3,4-dimethoxyphenyl)vinyloxy]dimethylsilane (120 mg, 0.41 mmol), AIBN (13 mg, 0.08 mmol), and thiophenol (4.4 mg, 0.04 mmol) in dry benzene (0.7 mL). Purification by flash column chromatography (MTBE/pentane, 7:1) provided **18** as a colorless oil (68 mg, 62%). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.03$ (s, 3H; Si–CH_3), −0.10 (s, 3H; Si–CH_3), 0.97 (s, 9H; Si–C(CH_3)$_3$), 1.46 (s, 9H; C(CH_3)$_3$) 3.14 (ddd, $J^1 = 13.5$ Hz, $J^2 = 7.8$ Hz and $J^3 = 5.3$ Hz, 1H; C*H*HNH), 3.37 (s, 3H; OCH_3), 3.44 (s, 3H; OCH_3), 3.49–3.57 (m, 1H; CH*H*NH), 4.63–4.66 (br,

1H; N*H*), 4.86 (dd, $J^1=7.8$ Hz and $J^2=4.1$ Hz, 1H; OC*H*), 6.54 (d, $J=8.2$ Hz, 1H; C*H*-aromatic), 6.84 (dd, $J^1=8.2$ Hz and $J^2=1.6$ Hz, 1H; C*H*-aromatic), 6.89 ppm (d, $J=1.6$ Hz, 1H; C*H*-aromatic); ^{13}C NMR (75 MHz, C_6D_6): $\delta=4.8$ (CH_3), −4.5 (CH_3), 18.5 (C), 26.1 (CH_3), 28.5 (CH_3), 49.8 (CH_2), 55.6 (CH_3), 55.5 (CH3), 74.2 (CH), 78.8 (C), 110.2 (CH), 112.2 (CH), 118.5 (CH), 135.6 (C), 149.7 (C), 150.3 (C), 155.9 ppm (C); IR (neat): $\tilde{\nu}=3386$, 2931, 2856, 1711, 1594, 1515, 1464, 1365, 1260, 1158, 1092, 1030, 834, 777 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{21}H_{37}SiNO_5Na$ $[M+Na]^+$: 434.2333; found: 434.2361.

*[2-(1,3-Benzodioxol-5-yl)-2-(tert-butyldimethylsilanyloxy)ethyl]carbamic Acid tert-Butyl Ester (**19**)*

Prepared according to general procedure **IIIB** using **5a** (100 mg, 0.27 mmol), 1-(1,3-benzodioxol-5-yl)vinyloxy-*tert*-butyldimethylsilane (190 mg, 0.68 mmol), AIBN (13 mg, 0.08 mmol), and thiophenol (4.4 mg, 0.04 mmol) in dry benzene (0.7 mL). Purification by flash column chromatography (Et_2O/pentane, 7:1) provided **19** as a colorless oil (63 mg, 59%). ^{1}H NMR (300 MHz, C_6D_6): $\delta=0.09$ (s, 3H; Si−CH_3), 0.04 (s, 3H; Si−CH_3), 0.90 (s, 9H; Si−C(CH_3)$_3$), 1.43 (s, 9H; C(CH_3)$_3$), 2.98–3.07 (m, 1H; C*H*HNH), 3.35–3.40 (m, 1H; CH*H*NH), 4.54–4.62 (br, 1H; N*H*), 4.71 (dd, $J^1=7.0$ Hz and $J^2=3.96$ Hz, 1H; OC*H*), 5.29 (s, 2H; OCH_2), 6.54–6.65 (m, 2H; C*H*-aromatic), 6.83–6.90 ppm (br, 1H; C*H*-aromatic); ^{13}C NMR (75 MHz, C_6D_6): $\delta=4.9$ (CH_3), −4.6 (CH_3), 18.4 (C), 26.0 (CH_3), 28.5 (CH_3), 49.7 (CH_2), 74.1 (CH), 78.7 (C), 100.9 (CH_2), 106.8 (CH), 108.2 (CH), 119.7 (CH), 137.1 (C), 147.5 (C), 148.2 (C), 155.8 ppm (C); IR (neat): $\tilde{\nu}=3377$, 2930, 2857, 1716, 1504, 1488, 1442, 1390, 1365, 1248, 1172, 1089, 1041, 938, 870, 778 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{20}H_{33}NSiO_5Na$ $[M+Na]^+$: 418.2020; found: 418.2032.

*[2-(2-Oxo-pyrrolidin-1-yl)ethyl]carbamic Acid tert-Butyl Ester (**20**)*

Prepared according to general procedure **IIIC** using **5a** (100 mg, 0.27 mmol), 1-vinylpyrrolidin-2-one (90 mg, 0.82 mmol), Et_3B (30 μL, 0.03 mmol), and thiophenol (4.4 mg, 0.04 mmol) in dry benzene (0.7 mL). Purification by flash column chromatography (acetone/pentane, 1:2) provided **20** as a colorless oil (35 mg, 58%). ^{1}H NMR (300 MHz, C_6D_6): $\delta=$ 1.31–1.21 (m, 2H; CH_2), 1.43 (s, 9H; C(CH_3)$_3$), 1.94 (t, $J=8.1$ Hz, 2H; CH_2CO), 2.71 (t, $J=7.0$ Hz, 2H; CH_2N), 3.05–3.08 (m, 4H; NCH_2CH_2NH), 5.32–5.39 ppm (br, 1H; N*H*); ^{13}C NMR (75 MHz, C_6D_6): $\delta=17.9$ (CH_2), 28.5 (CH_3), 30.7 (CH_2), 38.9 (CH_2), 42.6 (CH_2), 46.8 (CH_2), 78.6 (C), 156.3 (C), 174.9 ppm (C); IR (neat): $\tilde{\nu}=3331$, 2926, 1674, 1523, 1463, 1391, 1365, 1271, 1170, 856 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{11}H_{20}N_2O_3Na$ $[M+Na]^+$: 251.1366; found: 251.1385.

*[2-(2-Oxo-perhydroazepin-1-yl)ethyl]carbamic Acid tert-Butyl Ester (**21**)*

Prepared according to general procedure **IIIC** using **5a** (100 mg, 0.27 mmol), 1-vinylperhydroazepin-2-one (110 mg, 0.82 mmol), Et_3B (30 μL, 0.03 mmol), and thiophenol (4.4 mg, 0.04 mmol) in dry benzene (0.7 mL). Purification by flash column chromatography (acetone/pentane, 1:4) provided **21** as a colorless oil (38 mg, 55%). ^{1}H NMR (300 MHz, C_6D_6): $\delta=$1.08–1.18 (m, 4H; CH_2), 1.26–1.28 (m, 2H; CH_2), 1.44 (s, 9H; C(CH_3)$_3$), 2.21–2.25 (m, 2H; CH_2CO), 2.67–2.69 (m, 2H; CH_2N), 3.15–3.25 (m, 4H; NCH_2CH_2NH), 5.46–5.53 ppm (br, 1H; N*H*); ^{13}C NMR (75 MHz, C_6D_6): $\delta=23.5$ (CH_2), 28.5 (CH_3), 28.7 (CH_2), 29.9 (CH_2), 37.2 (CH_2), 40.1 (CH_2), 47.9 (CH_2), 49.6 (CH_2), 78.4 (C), 156.4 (C), 175.9 ppm (C); IR (neat): $\tilde{\nu}=3330$, 2930s, 1710, 1633, 1520, 1446, 1391, 1250, 1172, 857 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{13}H_{24}N_2O_3Na$ $[M+Na]^+$: 279.1679; found: 279.1670.

*[1-(2-Oxo-pyrrolidin-1-ylmethyl)propyl]carbamic Acid tert-Butyl Ester (**22**)*

Prepared according to general procedure **IIIC** using **5a** (100 mg, 0.27 mmol), ((*E*)-1-but-1-enyl)pyrrolidin-2-one (110 mg, 0.82 mmol), Et_3B (30 μL, 0.03 mmol), and thiophenol (4.4 mg, 0.04 mmol) in dry benzene (0.7 mL). Purification by flash column chromatography (acetone/pentane, 1:3) provided **22** as a white solid (27 mg, 52%). M.p. 98–100 °C; ^{1}H NMR (300 MHz, C_6D_6): $\delta=$0.87–0.94 (m, 3H; CH_3), 1.16–1.47 (m, 4H; CH_2), 1.56 (s, 9H; C(CH_3)$_3$), 2.04–2.23 (m, 2H; CH_2CO), 2.70–2.78 (m, 2H; CH_2N), 3.21–3.30 (m, 1H; C*H*HN), 3.48–3.58 (m, 1H; CH*H*N), 3.76–3.88 (m, 1H; C*H*NH), 4.94 ppm (d, $J=8.4$ Hz, 1H; N*H*); ^{13}C NMR (75 MHz, C_6D_6): $\delta=10.4$ (CH_3), 18.1 (CH_2), 26.1 (CH_2), 28.5 (CH_3), 30.8 (CH_2), 46.7 (CH_2), 47.1 (CH_2), 50.6 (CH), 78.3 (C), 156.2 (C), 174.8 ppm (C); IR (neat): $\tilde{\nu}=3285$, 2927, 1702, 1677, 1538, 1388, 1316, 1373, 1242, 1164, 1076, 990, 751 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{13}H_{24}N_2O_3Na$ $[M+Na]^+$: 279.1679; found: 279.1678.

*[2-(Acetylmethylamino)ethyl]carbamic Acid tert-Butyl Ester (**23**)*

Prepared according to general procedure **IIIC** using **5a** (100 mg, 0.27 mmol), *N*-methyl-*N*-vinylacetamide (67 mg, 0.68 mmol), Et_3B (30 μL, 0.03 mmol), and thiophenol (4.4 mg, 0.04 mmol) in dry benzene (0.7 mL). Purification by flash column chromatography (acetone/pentane, 1:2) provided **23** as a white solid (32 mg, 55%). M.p. 105–107 °C; ^{1}H NMR (300 MHz, C_6D_6): $\delta=1.41$ (s, 9H; C(CH_3)$_3$, rotamer-1), 1.43 (s, 9H; C(CH_3)$_3$, rotamer-2), 1.48 (s, 3H; CH_3CO, rotamer-1), 1.58 (s, 3H; CH_3CO, rotamer-2), 1.89 (s, 3H; NCH_3, rotamer-1), 2.18 (s, 3H; NCH_3, rotamer-2), 2.65 (br, 2H; NCH_2, rotamer-1), 2.81 (br, 2H; CH_2NH, rotamer-1), 3.13 (br, 4H; NCH_2CH_2NH, rotamer-2), 5.25 (br, 1H; N*H*, rotamer-1), 5.36 ppm (br, 1H; N*H*, rotamer-2); ^{13}C NMR (75 MHz, C_6D_6): $\delta=20.9$ (CH_3, rotamer-1), 21.4 (CH_3, rotamer-2), 28.5 (CH_3, rotamer-1), 28.5 (CH_3, rotamer-2), 32.9 (CH_3, rotamer-1), 35.7 (CH_3, rotamer-2), 38.8 (CH_2, rotamer-1), 39.3 (CH_2, rotamer-2), 47.1 (CH_2, rotamer-2), 49.8 (CH_2, rotamer-1), 78.4 (C, rotamer-2), 78.8 (C, rotamer-1), 156.0 (C, rotamer-1), 156.3 (C, rotamer-2), 169.9 (C, rotamer-1), 170.7 ppm (C, rotamer-2); IR (neat): $\tilde{\nu}=3285$, 2927, 1702, 1677, 1538, 1388, 1316, 1373, 1242, 1164, 1076, 990, 751 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{10}H_{20}N_2O_3Na$ $[M+Na]^+$: 239.1366; found: 239.1371.

*{(S)-1-[(S)-4-Isopropyl-2-oxooxazolidin-3-ylmethyl]pentyl}carbamic Acid tert-Butyl Ester (**25**)*

Prepared according to general procedure **IIIC** using **5a** (160 mg, 0.43 mmol), **24**[9] (60 mg, 0.28 mmol), Et_3B (43 μL, 0.04 mmol), and thiophenol (4.4 mg, 0.04 mmol) in dry benzene (0.6 mL). Purification by flash column chromatography (MTBE/pentane, 1:2) provided **25** as a white solid that contained the other diastereoisomer in a 1:13 ratio (diastereomeric ratio was determined by GC analysis of the crude reaction mixture; 45 mg, 48%, combined yield of both diastereoisomers). Physical data of the major diastereoisomer are given. M.p. 90–92 °C; $[\alpha]_D=-36.0$ ($c=1.0$ in C_6H_6). ^{1}H NMR (400 MHz, C_6D_6): $\delta=0.44$ (d, $J=7.0$ Hz, 3H; CH(CH_3)$_2$), 0.55 (d, $J=6.9$ Hz, 3H; CH(CH_3)$_2$), 0.78 (t, $J=6.5$ Hz, 3H; CH_3), 1.19–0.94 (m, 6H; CH_2), 1.46 (s, 9H; C(CH_3)$_3$), 1.63–1.56 (m, 1H; C*H*(CH$_3$)$_2$), 2.64 (dd, $J^1=14.3$ Hz and $J^2=3.3$ Hz, 1H; NC*H*H), 3.44 (dd, $J_1=14.3$ Hz and $J_2=11.0$ Hz, 1H; NCH*H*), 3.60 (dd, $J^1=7.7$ Hz and $J^2=$ 4.5 Hz, 1H; OC*H*H), 3.75–3.91 (m, 3H; NHC*H*, OCH*H*, NC*H*), 4.62 ppm (d, $J=9.4$ Hz, 1H; N*H*); ^{13}C NMR (100 MHz, C_6D_6): $\delta=14.1$ (CH_3), 14.3 (CH_3), 17.3 (CH_3), 22.9 (CH_2), 27.5 (CH_2), 28.3 (CH), 28.4 (CH_3), 32.7 (CH_2), 46.4 (CH_2), 48.2 (CH), 58.1 (CH), 62.7 (CH_2), 78.7 (C), 156.4 (C), 159.1 ppm (C); IR (neat): $\tilde{\nu}=3331$, 2961, 2932, 1745, 1703, 1523, 1440, 1391, 1365, 1252, 1172, 1050, 767 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{17}H_{32}N_2O_4Na$ $[M+Na]^+$: 351.2254; found: 351.2260.

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