33743) is gratefully acknowledged.

Registry No. **5**, 81542-94-1; **6**, 62820-13-7; **7**, 67707-87-3; **8**, 5949-05-3; **9** (isomer 1), 82507-56-0; **9** (isomer 2), 82507-57-1; **10**, 82507-58-2; **12**, 82507-44-6; **13**, 82507-45-7; **14**, 82507-46-8; **15**, 128471-61-4; **16**, 128571-81-3; **17**, 89-82-7; **18**, 2385-77-5; **19**, 128471-62-5; **20**, 128471-63-6; **21**, 128471-64-7; **22**, 128471-65-8; **23**, 128571-82-4; **24**, 128471-66-9; **25**, 128471-67-0; **26**, 128471-68-1; **27**, 4463-74-5; **28** (isomer 1), 128571-83-5; **28** (isomer 2), 128571-85-7; **29**, 80796-76-5; **30**, 128471-69-2; **31**, 128471-70-5; **32**, 128471-71-6; **33**, 128471-72-7; **34**, 128571-84-6; **35**, 128471-73-8; **36**, 128471-74-9; **37**, 128471-75-0; $CH_3CH{=}C(OMe)OTMS$, 34880-70-1.

Supplementary Material Available: ^1H and ^{13}C NMR spectra for compounds **9**, **13–16**, **22**, and **24** and crystal data for compound **32** (22 pages). Ordering information is given on any current masthead page.

Olefin Synthesis by Vanadium(V)-Induced Oxidative Decarboxylation–Deoxygenation of 3-Hydroxy Carboxylic Acids

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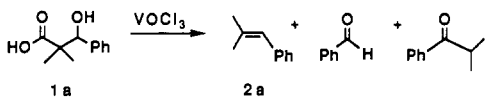
Oxidative decarboxylation of 3-hydroxy carboxylic acids can be effected with various V(V) complexes. This process likely yields an intermediate 1,4-metalla diradical. β-Elimination from this intermediate gives olefin and regenerates V(V), likely as VO_2Cl. Thus, although the overall process involves no net change in oxidation state for vanadium, the decarboxylation process is oxidatively induced. Intramolecular trapping of the intermediate yields glycolate and then C–C cleavage products, and skeletal rearrangement gives ketonic products. Qualitatively, rates for oxidative decarboxylation of the acids and the stereospecificity of formation of olefinic products depend on the electron-withdrawing ability of groups attached to vanadium. Methodology is described for the preparation of tri- and tetrasubstituted olefins in high yield from appropriate 3-hydroxy carboxylic acid precursors.

3-Hydroxy carboxylic acids are easily obtained products of "aldol" condensation processes. In concept, removing hydroxyl and carboxyl functionality from these "aldol" products enables the preparation of olefins from carbonyl precursors; in fact, several methods exist to realize this overall transformation.[1-3] One previously unexplored option for this transformation involves oxidatively removing the carboxylate unit and then β-elimination of the hydroxyl-derived fragment. Although oxidative decarboxylation of 2-hydroxy carboxylic acids is well known,[4] no investigation of 3-hydroxy carboxylic acids had been reported prior to our initial report.[5] At that time, we noted that readily available $VOCl_3$ or its simple derivatives could react with "aldol" acids to give olefins in a straightforward, synthetically useful way.

The Simple Reaction between $VOCl_3$ and 3-Hydroxy Carboxylic Acids. When $VOCl_3$ was added to a suspension of hydroxy acid **1a** (1 equiv) in anhydrous chlorobenzene at room temperature followed by heating to reflux, **2a** (61%) and benzaldehyde (37%) were obtained

Scheme I



(Scheme I). When solvents such as acetonitrile, dimethyl sulfoxide, or tetrahydrofuran (THF) were used, little olefin, but much isobutyrophenone, was produced.[6] When toluene was used, a major product observed by GC/MS (ca. 60%) showed solvent incorporation, though the structure of this product was not identified.[7] Unreactive, high-boiling chlorobenzene was the solvent of choice.

Several problems characterize the simple $VOCl_3$ system (Table I) including dehydration, double-bond migration, and E/Z isomerization. Dehydration, either proton (2 equiv of HCl are produced in the reaction) or Lewis acid catalyzed ($VOCl_3$ is a strong Lewis acid), can occur in 3-hydroxy carboxylic acids which are not disubstituted in the 2-position. For example, **1f** gave 3,3-diphenyl-2-propenoic acid (8) as the major product. When pure **2c*E*** was added to a reaction of $VOCl_3$ and 3-hydroxy carboxylic acid **1a** which was in progress, it rapidly E/Z isomerized; product olefins are thus unstable to these reaction conditions. However, when **2c** (E/Z = 0.74) was added to an ongoing reaction between $VOCl_3$ and **1a** to which 1 equiv of Proton Sponge (1,8-bis(dimethylamino)naphthalene)

(1) (a) Adam, W.; Baeza, J.; Liu, J.-C. *J. Am. Chem. Soc.* **1972**, *94*, 2000. (b) Noyce, D. S.; Banitt, E. H. *J. Org. Chem.* **1966**, *32*, 4043. (c) Krapcho, A. P.; Jahngen, E. G. E., Jr. *Ibid.* **1974**, *39*, 1650. (d) Schollkopf, U.; Hoppe, I. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 765. (e) Mageswaran, S.; Sultanbawa, M. U. S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 884. (f) Imai, T.; Nishida, S. *J. Org. Chem.* **1980**, *45*, 2354.

(2) Mulzer, J.; Lammer, O. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 628.

(3) Hara, S.; Taguchi, H.; Yamamoto, H.; Nozaki, H. *Tetrahedron Lett.* **1975**, 1545.

(4) For examples of oxidative decarboxylation of 2-hydroxy carboxylic acids with V(V), see: (a) Jones, J. R.; Waters, W. A.; Littler, J. S. *J. Chem. Soc., London* **1961**, 630. (b) Mehrotra, R. N. *J. Chem. Soc. B* **1968**, 642. (c) Paul, S. D.; Pradhan, D. G. *Indian J. Chem.* **1972**, *10*, 562. (d) Virtanen, P. O. I.; Karppinen, S. *Finn. Chem. Lett.* **1984**, 34. (e) Kalidoss, P.; Srinivasan, V. S. *J. Chem. Soc., Dalton, Trans.* **1984**, 2631. (f) Micera, G.: Deiana, S.; Dessi, A.; Pusino, A.; Gessa, C. *Inorg. Chim. Acta* **1986**, *120*, 49.

(5) Meier, I. K.; Schwartz, J. *J. Am. Chem. Soc.* **1989**, *111*, 3069.

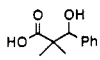
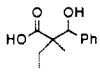
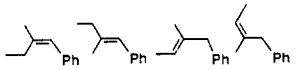
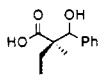
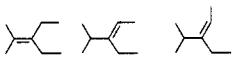
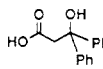
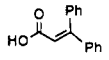
(6) Such solvents form adducts with $VOCl_3$. See: (a) Funk, V. H.; Weiss, W.; Zeising, M. *Z. Anorg. Allg. Chem.* **1958**, *296*, 36. (b) Baker, K. L.; Edwards, D. A.; Fowles, G. W. A.; Williams, R. G. *J. Inorg. Nucl. Chem.* **1967**, *29*, 1881. (c) Miles, S. J.; Wilkins, J. D. *Ibid.* **1975**, *37*, 2271.

(7) Such solvents form charge transfer complexes with $VOCl_3$. See: H.-L.; Krauss, H.-L.; Gnatz, G. *Chem. Ber.* **1962**, *95*, 1023. (b) Krauss, H.-L.; Deffner, U. *Z. Naturforsch.* **1964**, *19b*, 1.

(8) Cornforth, D. A.; Opara, A. E.; Read, G. *J. Chem. Soc. C* **1969**, 2799.

0022-3263/90/1955-5619$02.50/0

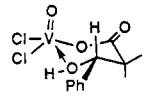
Table I. Reactions of 3-Hydroxy Carboxylic Acids with $VOCl_3$ in Refluxing Chlorobenzene

hydroxy acid	time, h	products[a] alkene	yield, %	other, yield, %
 1a[14]	0.5 70[b]		2a, 61 73	benzaldehyde, 37 0
 1b[11]	0.5		2a, 17	benzaldehyde, 5
 1c	0.5	 2cZ, 14 2cE, 26 6Z + E, 27		benzaldehyde, 20; 2-butanone, (confirmed by gc-ms)
 erythro-1c	0.5 40[b]	2cZ, 14 2cE, 26 20 27	6Z + E, 27 0	benzaldehyde, 20 0
 1d[6]	0.5		2d, 20	 51
 1e	0.5 44	 2e, 45[c] 34[c]	7Z + E, 55[c] 8[c]	
 1f[13]	3		2f, 18	 8, 80 (NMR)

[a] All yields by GC unless otherwise noted. [b] One equivalent of Proton Sponge was added. [c] In ethylene carbonate, 160 °C.

had been added, no change in this E/Z ratio was observed, even after 22 h. In this same way, double-bond migration was eliminated for products of **1c**. Thus, both double bond migration and E/Z isomerization of *product olefins* can be suppressed by addition of base. (Proton Sponge forms a pink complex with $VOCl_3$ [λ_{max} = 492 nm] which is only slightly soluble in chlorobenzene or in the other organic solvents investigated, and reactions between this complex and 3-hydroxy acids are slow.) Other bases (including urea, tetramethylurea, ammonia, potassium carbonate, pyridine, or 2,6-di-*tert*-butylpyridine) were less effective at suppressing byproducts. Unfortunately, the stereospecificity of the olefin forming step, itself, was not improved by adding base: reacting pure *erythro*-**1c** with $VOCl_3$ and 1 equiv of Proton Sponge gave the same products and yields as were obtained from a 1:1 mixture of diastereomers (Table I).

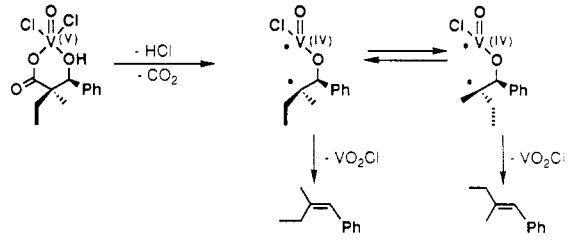
Coordination of the 3-Hydroxy Acid to Vanadium. Yellow $VOCl_3$ added to a suspension of **1a** in anhydrous chlorobenzene or benzene at room temperature gave a homogeneous orange-red solution. Data obtained by ^1H NMR and FTIR suggest this complex to be adduct A, shown below. The ^1H NMR spectrum of the $VOCl_3$/**1a**



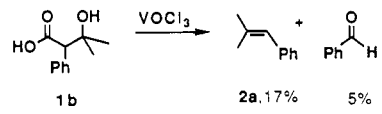
A

complex showed a downfield shift of the benzylic proton (from δ 4.68 in **1a** to δ 7.36 for the complex). Methyl and phenyl group peaks were shifted slightly upfield (from δ 0.93, 1.09, and 7.01–7.40 in **1a** to δ 0.77, 0.92, and 6.82–7.07 in the complex). A peak at δ 9.83 was observed for the complex, but not for free **1a**, suggesting that the hydroxyl group oxygen is coordinated to the vanadium center. With the exception of this last signal, all peaks were sharp.

Scheme II



Scheme III



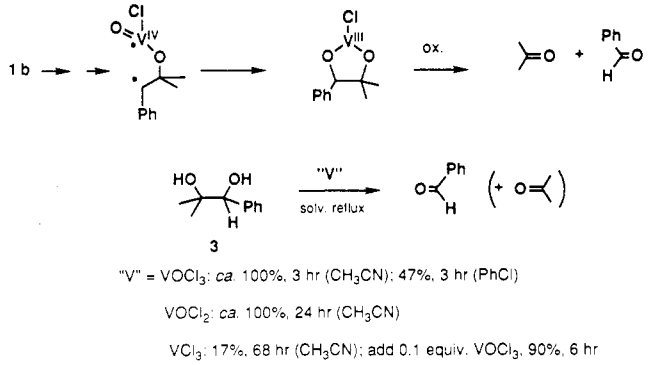
Integration of the ^1H NMR spectrum of the complex showed only one hydroxyl proton; the other was apparently lost as HCl. These properties are consistent with a V(V) carboxylate; V(IV) carboxylates are generally blue-green and paramagnetic.[9] Hydroxy acid **1a** has an IR spectrum (measured in benzene) showing ν_{CO} = 1704 cm^{-1} and ν_{OH} = 3582 cm^{-1}. For the $VOCl_3$/**1a** complex IR analysis (also in benzene) shows ν_{CO} = 1708 cm^{-1}, ν_{OH} = 3432 cm^{-1}, and a vanadyl group, $\nu_{V=O}$ = 990 cm^{-1}. The carbonyl stretch of the complex is found in the region of typical monomeric monooxo- and dioxovanadium(V) monocarboxylate carbonyl stretches (between 1720 and 1690 cm^{-1}).[10,11]

Activation of the 3-Hydroxy Acid. Reduction of V(V) to V(IV) followed by rapid CO_2 loss to give the radical, RHĊ(OH), is rate-determining in oxidative decarboxylation of lactic, malic, and mandelic acids.[4a] If a similar process occurred for the 3-hydroxy carboxylic acid, a 1,4-metalla diradical intermediate would be formed. (Similar diradical intermediates have been proposed in epoxide deoxygenation by low-valent vanadium and molybdenum complexes[12] and in epoxidation of olefins by oxomanganase(V) porphyrins.[13]) β-Elimination from this intermediate gives olefin and regenerates V(V), likely as VO_2Cl. Thus, although the overall process involves no net change in oxidation state for vanadium, the decarboxylation process is oxidatively induced. Competitive rotation about the C–C single bond in the intermediate could give an E and Z product mixture (Scheme II).

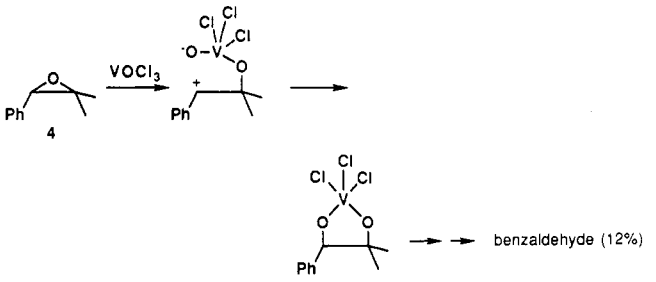
Origin of Byproducts of Olefin Synthesis. When **1a** was treated with $VOCl_3$ in refluxing chlorobenzene, olefin **2a** (61%) and benzaldehyde (37%) were produced. If **1a** underwent a "retro-aldol" reaction, benzaldehyde and isobutyric acid would be produced, but no isobutyric acid could be detected in the reaction mixture. When **1b** was allowed to react with $VOCl_3$, both olefin **2a** (17%) and benzaldehyde (5%) were found after 30 min (the predominant pathway for this acid is dehydration) (Scheme III). For benzaldehyde to be produced in this latter case not only must decarboxylation occur, but also *a new carbon–oxygen bond must be formed.* Carbon–carbon bond cleavage could then occur to give benzaldehyde. A similar postulate explains how **1c** yields benzaldehyde and 2-butanone as byproducts of olefin synthesis.

(9) Paul, R. C.; Kumar, A. *J. Inorg. Nucl. Chem.* **1965**, *27*, 2537.
(10) (a) Miller, F. A.; Cousins, L. R. *J. Chem. Phys.* **1957**, *26*, 329. (b) Preuss, F.; Woitschach, J.; Schug, H. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3723. (c) Preuss, F.; Woitschach, J. *Z. Naturforsch.* **1979**, *34B*, 163.
(11) (a) Kalinnikov, V. T.; Zelentsov, V. V.; Ubozhenko, O. D.: Aminov, T. G. *Dokl. Chem.* **1972**, *206*, 753. (b) Walter, J. P.; Dartiguenave, M.; Dartiguenave, Y. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3207.
(12) Hayasi, Y.; Schwartz, J. *Inorg. Chem.* **1981**, *20*, 3473.
(13) Groves, J. T.; Kruper, W. J.; Haushalter, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 6375.

Scheme IV



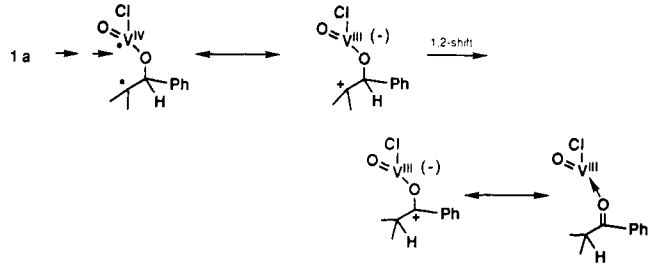
Scheme V



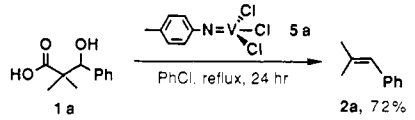
A possible route to benzaldehyde from **1a**, **1b**, or **1c** involves the 1,4-metalla diradical shown in Scheme IV. Cyclization of this intermediate to vanadyl oxygen would give a glycolate which could cleave oxidatively to give benzaldehyde. In this mechanism vanadium undergoes an overall reduction by two units of formal charge. To test if an oxidized glycolate intermediate were the source of the carbonyl-containing byproducts, **3**[14] was treated with $VOCl_3$, $VOCl_2$, and VCl_3 in acetonitrile, chlorobenzene, or benzene solvent systems. With 1 equiv of $VOCl_3$, **3** was quantitatively converted to benzaldehyde after 3 h in acetonitrile at reflux, or in 47% after 3 h in chlorobenzene at reflux. No olefin **2a** was formed in either reaction. When **3** and $VOCl_2$ were heated to reflux in acetonitrile, total conversion to benzaldehyde was achieved in 24 h. In benzene and chlorobenzene, less benzaldehyde was produced (33% in 72 h and 3% in 16 h, respectively). Here, too, no olefin **2a** could be detected in the reactions in acetonitrile and benzene and only trace amounts could be found in the reaction in chlorobenzene. In acetonitrile, VCl_3 reacted with **3** to give only 17% benzaldehyde after 68 h at reflux (ca. 66% unreacted **3** can be detected); however, addition of 0.2 equiv of $VOCl_3$ to this reaction mixture resulted in almost quantitative conversion of **3** to benzaldehyde after only 6 additional h at reflux. Therefore, high-valent vanadium is necessary in order for large amounts of benzaldehyde to be formed, and polar solvents such as acetonitrile result in higher benzaldehyde yields than do nonpolar solvents such as benzene or chlorobenzene. Benzaldehyde (73% in 90 min) and little else was obtained when VOF_3 was reacted with 3-hydroxy carboxylic acid **1a** in refluxing chlorobenzene. Because fluorine is more electron-withdrawing than is chlorine, a pathway in which the metal is reduced (glycol formation) would be favored by electrophilic VOF_3. Interestingly, adding 1 equiv of Proton Sponge to the reaction of **1a** and $VOCl_3$ suppressed benzaldehyde formation.

An alternate mechanism for benzaldehyde formation from **1a** involves intermediate epoxide **4**[15] opening by

Scheme VI



Scheme VII



Lewis acid attack on oxygen followed by collapse to the glycol and cleavage (Scheme V).[4a,16] Epoxide **4** was synthesized and treated with $VOCl_3$ in benzene. After 23 h of reflux, benzaldehyde (12%), but no olefin **2a**, was found, and byproducts not observed in the reaction of $VOCl_3$ with **1a** were also produced.

Ketonic byproducts were also observed in polar solvents; for **1d**, pinacolone was the major product observed (51%), even in chlorobenzene. These skeletally rearranged ketones might have glycolate precursors; formation of a cationic center followed by a 1,2-shift would yield the ketone, or these same carbonium ions might derive directly from decarboxylation of the 3-hydroxy acid (Scheme VI). Carbonium ion intermediates have been invoked in oxidations effected by oxometalloporphyrins[17] or in chromium(VI)-based epoxidation procedures[18] in which skeletal isomerization has been observed. 2-Chloro-2-methyl-1-phenyl-1-propanone was also a (minor) byproduct of **1a**, which likely derives from chlorine atom abstraction (for which an analogue is seen in CrO_2Cl_2 oxidation of olefins[18]).

Trichloro(*p*-tolylimino)vanadium(V): An Improved Oxidation System. If the oxo unit of $VOCl_3$ were involved in byproduct formation by intercepting a carbon-centered radical, replacing the oxo unit with an inert group should suppress or eliminate byproduct formation. (Arylimino)vanadium trichlorides are easily prepared from $VOCl_3$ and trichloro(*p*-tolylimino)vanadium(V) (**5a**)[19] reacts with **1a** in refluxing chlorobenzene to give **2a** (72% in 24 h) with minimal formation of benzaldehyde (0–3%) (Scheme VII). No analogue of the glycol (the amino alcohol) was observed before or after hydrolysis.

X-ray crystallographic data for $[V(NC_6H_4CH_3)Cl(O\text{-}2,6\text{-}C_6H_3Me_2)_2]_2$ show the V–N–C skeleton to be nearly linear (175.8 (3)°); the V–N unit is a formal triple bond (1.644 (3)Å) with π-donation from N to V.[19,20] This imido

(14) Huffman, J. W.; Browder, L. E. *J. Org. Chem.* **1962**, *27*, 3208.

(15) Hevesi, L.; Nagy, J. B.; Krief, A.; Derovane, E. G. *Org. Magn. Reson.* **1977**, *10*, 14. For 2,2-dimethyl-3-phenyloxirane, ^1H NMR ($CDCl_3$): δ 1.07 (s, CH_3), 1.47 (s, CH_3), 3.86 (s, *CH*Ph), 7.60 (m, Ph).

(16) (a) Littler, J. S.; Mallet, A. I.; Waters, W. A. *J. Chem. Soc.* **1960**, 2761. (b) Littler, J. S.; Waters, W. A. *Ibid.* **1960**, 2767. (c) Waters, W. A.; Littler, J. S. Oxidation by Vanadium(V), Cobalt(III), and Manganese(III). In *Oxidation in Organic Chemistry*; Wiberg, K. B., Ed.; Academic Press: New York, 1965; Part A, pp 185–241.

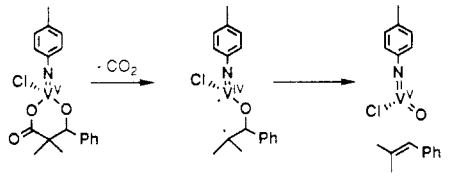
(17) For example, see: Traylor, T. G.; Nakano, T.; Dunlap, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 2782.

(18) (a) Sharpless, K. B.; Teranishi, A. Y.; Backvall, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 3120. (b) Miyaura, N.; Kochi, J. K. *Ibid.* **1983**, *105*, 2368. (c) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981; pp 169–171.

(19) Devore, D. D.; Lichtenhan, J. D.; Takusagawa, F.; Maatta, E. A. *J. Am. Chem. Soc.* **1987**, *109*, 7408.

(20) A linear V–N unit need not indicate π-bonding, however. See, for example: Anhaus, J. T.; Kee, T. P.; Schofield, M. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 1642.

Scheme VIII

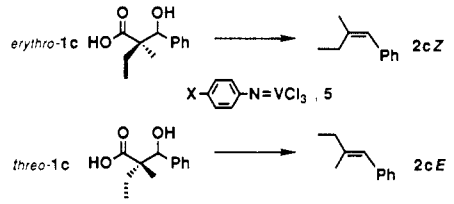


species should be a weaker Lewis acid than $VOCl_3$ in which π-donation occurs from oxygen to V ($\nu_{V=O}$ = 1035 cm^{-1}). Ring-substituted (arylimino)vanadium trichlorides provide the possibility of systematic reactivity manipulation of V(V) systems: π-donation from the aryl ring to V(V) should be sensitive to donor or acceptor substituent groups. ^{51}V NMR spectra have been measured for a series of para-substituted (arylimino)vanadium(V) complexes:[19] ^{51}V chemical shifts for $Cl_3V{=}NC_6H_4X$ correlate well with σ_{para} values for X (σ_{para} values are the sum of resonance and inductive contributions, σ_R and σ_I). The relative ordering of ^{51}V chemical shifts in these (arylimino)vanadium(V) complexes follows an "inverse" χ dependence,[21] in which an increase in shielding of the metal is observed with increasing electronegativity, χ, of the ligands attached to it: $VOBr_3$ (δ +432) < $V(NC_6H_4OCH_3)Cl_3$ (δ +403) < $V(NC_6H_4CH_3)Cl_3$ (δ +305) < $VOCl_3$ (δ 0) < VOF_3 (δ −632).[19,21a]

According to Scheme VIII, V(V) must be reduced to V(IV) and then reoxidized to V(V). An electron-donating group on vanadium should stabilize the higher oxidation state, and the opposite behavior should be observed for an electron-withdrawing group. In order to examine whether ^{51}V NMR measured effects of ligand π-donor ability correlate with reactivity of the V(V) species, reactions of **1a** with trichloro(arylimino)-V(V) complexes, $Cl_3V{=}NC_6H_4X$ (X = CH_3 (**5a**), OCH_3 (**5b**), CF_3 (**5c**)), were carried out. Qualitative relative rates for olefin synthesis were X = $CF_3 \geq CH_3 > OCH_3$; reactions using $VOCl_3$ were fastest.

The pathway shown in Scheme VIII suggests that the stereochemistry of the olefinic product should be determined by relative rates for isomerization of the diradical versus its β-elimination of VO_2Cl (with concomittant reoxidation of V(IV) to V(V)). Donor groups, X, should give rise to olefin with favored retention of configuration (Table II). *erythro*-**1c** forms a diastereomerically pure complex with **5a** which is different from that one formed from *threo*-**1c**. *erythro*-**1c** should give **2c*Z*** if retention of stereochemistry occurs in the reaction. On heating the *erythro*-**1c**/**5a** complex (75 °C), more *Z* olefin was formed initially; however, **2c*E*** was detected, even at short reaction times. On heating the *threo*-**1c**/**5a** complex (75 °C), the *E* olefin was formed at first; but, over longer reaction time, **2c*Z*** was also produced. Only in the case of X = OCH_3 (**5b**), the most electron-donating substituent, was **2c*Z*** the major isomer, and this was true only after short reaction times (E/Z = 0.41 after 0.5 h). Unfortunately, over longer reaction times this ratio increased until E/Z = 1.0 after 48 h. For X = CH_3 (**5a**) or NO_2 (**5d**), **2c*E*** was the major isomer and no change in the E/Z ratio (~1.4) was observed over time. *threo*-**1c** should give **2c*E*** if retention of stereochemistry occurs in the reaction. In the case of **5b** (X = OCH_3), good stereospecificity was again seen at short reaction times (E/Z = 7.0 after 0.5 h) and, over longer times, the E/Z ratio decreased until it was 4.0 after 24 h. With **5a** (X = CH_3), a lesser degree of stereospecificity was observed (E/Z = 4.5 after 0.5 h) and the E/Z ratio decreased to 3.2 over the course of 24 h. Using **5d** (X = NO_2; the most electron-withdrawing substituent used), the E/Z ratio remained ca. 2.6 from 0.5 to 24 h. Thus the stereospecificity of the reactions at short times increased in the order $NO_2 < CH_3 < OCH_3$.

Table II. Reactions of Pure Diastereomers of 3-Hydroxy Carboxylic Acid 1c and Trichloro(arylimino)vanadium(V) Compounds (in Refluxing Chlorobenzene)



X	acid	time, h	E/Z	other, %	total,[a] %
OCH_3	*erythro*	0.5	0.41	–	27
		1	0.52	–	35
		2	0.63	–	44
		24	0.86	~1	66
		48	1.0	~1	74
CH_3	*erythro*	0.5	1.3	–	68
		1	1.4	–	75
		2	1.4	–	79
		96	1.4	~1	94
NO_2	*erythro*	0.5	1.5	–	64
		1	1.4	–	59
		2	1.5	–	64
		24	1.5	~2	71
OCH_3	*threo*	0.5	7.0	–	30
		1	5.6	–	37
		2	5.2	–	42
		24	4.0	–	60
CH_3	*threo*	0.5	4.5	–	61
		1	4.2	–	63
		2	3.7	–	75
		24	3.2	~4	93
NO_2	*threo*	0.5	2.6	~3	61
		1	2.7	~2	61
		2	2.8	~2	62
		24	2.6	~2	66

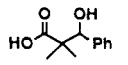
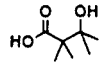
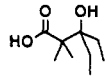
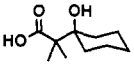
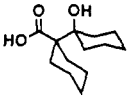
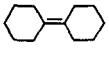
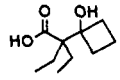
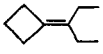
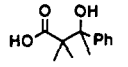
[a] Yields were determined by gas chromatography.

Olefins **2c*E*** and **2c*Z*** (E/Z = 0.74) were added to a mixture of **5a** and **1a** which had been heated together for 30 min in refluxing chlorobenzene. Over 24 h, the E/Z ratio for **2** increased to 0.82; therefore, it appears that *product* olefins can isomerize under the synthesis reaction conditions. Addition of 1 equiv of Proton Sponge, which quenched secondary isomerization processes with $VOCl_3$, did not suppress E/Z isomerization of products of the reaction of *erythro*-**1c** and **5b**; metallic residues from this latter reaction may be responsible for such secondary isomerization.

Tetrasubstituted olefins can be formed in excellent yields using trichloro(*p*-tolylimino)vanadium(V) (**5a**). These targets are the best thus far examined for V-induced olefin synthesis when Proton Sponge was added to reactions in which double-bond migration was possible in the product (Table III). Yields obtained are comparable and, in several cases, superior to those reported for preparation via the β-lactone.[1] For example, in the case of olefin **2i**, thermolysis of the β-lactone gave a mixture of products containing only approximately 20% of the derived olefin, the V(V) route gave only **2i**. In the case of olefin **2h**, a lower yield is probably the result of extreme steric hindrance which may make the formation of the initial vanadium(V) carboxylate complex more difficult. In no case (cf. **1d** with $VOCl_3$) were skeletally isomerized ketonic byproducts observed.

(21) (a) Rehder, D. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 771. (b) Priebsch, W.; Rehder, D. *Inorg. Chem.* **1985**, *24*, 3058–62.

Table III. Syntheses of Tetrasubstituted Olefins (and 1a) via the Reaction of Trichloro(*p*-tolylimino)vanadium(V) with 3-Hydroxy Carboxylic Acids

hydroxy acid		product[a] structure		yield, %	conditions
	1a[1a]		2a	72	24h, PhCl, reflux
	1d[8]		2d	89	19 h, PhCl, reflux
	1e		2e	80	48 h, 1,2,4-$C_6H_3Cl_3$,[b] 132°
	1g[1a]		2g[1a]	77	70 h, 1,2,4-$C_6H_3Cl_3$,[b] 160°
	1h[1c]		2h[1c]	48	68 h, PhCl,[b] reflux
	1i		2i	88	53 h, PhCl,[b] reflux
	1j[1a]		2j[1a]	>95	49 h, PhCl,[b] reflux

[a] All yields by GC. [b] 1 equiv of Proton Sponge was added.

Experimental Section

General. All reactions which involved organometallic reagents were performed under an atmosphere of nitrogen or argon which had been deoxygenated by passing through a column of reduced BTS catalyst and dried by passing through a column of 4-Å molecular sieves. Reactions were carried out in standard Schlenk glassware. Liquid transfers were performed by syringe or cannula and solid transfers were performed under a stream of inert gas or in a Vacuum Atmospheres drybox. Melting points were obtained in open tubes and are uncorrected.

Nuclear magnetic resonance data were obtained with Brucker WM250, JEOL GSX270, General Electric QE300, or JEOL GSX500 instruments. Air- and moisture-sensitive samples were prepared in 5-mm screw-cap tubes in the drybox. Mass spectral data are reported for the four highest peaks (relative intensities).

Analytical gas chromatography was performed on a gas chromatograph equipped with a flame ionization detector. Yields were determined by comparison of peak areas of products versus the peak area of an internal standard. Preparative gas chromatography was performed on a gas chromatograph equipped with a thermal conductivity detector. Thin-layer chromatography (TLC) was performed on Analtech silica gel GF plates (250 micron) using UV and iodine visualization. Column chromatography was performed on Merck silica gel (60 grade, 60 Å).

Tetrahydrofuran (THF), ether, and hydrocarbon solvents were freshly distilled under nitrogen from sodium benzophenone ketyl. Approximately 5% tetraglyme was added to hydrocarbon solvents to ensure solubility of the ketyl. Chlorobenzene was distilled under nitrogen from P_2O_5. All other solvents and organic compounds were distilled under nitrogen from the appropriate drying agents. Commercially obtained vanadium compounds were used as received.

2,2-Dimethyl-3-hydroxy-3-phenylpropionic Acid (1a). A modification of the literature procedure[1a] was used. Unless otherwise indicated, 3-hydroxy acids and olefins were synthesized according to this route, and identities of compounds were confirmed by comparison of spectral and melting point data with that reported in the literature. Typically a 500-mL Schlenk flask was charged with THF and diisopropylamine to make a 0.29 M solution. The flask was cooled to −78 °C (dry ice/ethanol), and a stoichiometric amount of *n*-butyllithium (1.6 M in hexane) was added. The solution was stirred at −78 °C for several minutes and then was allowed to warm to room temperature. The lithium diisopropylamide (LDA) solution was titrated[22] (43.2 mmol). A solution of isobutyric acid (21.6 mmol, 0.5 equiv) in 20 mL of THF was added slowly into the LDA solution at room temperature. The reaction mixture was stirred for an hour at room temperature, and then neat benzaldehyde (21.6 mmol, 0.5 equiv) was added. The mixture was stirred for an additional 16 h and then quenched by being poured over ice. This solution was extracted five times with ~200-mL portions of diethyl ether, and then the aqueous layer was acidified with 6 N HCl. White crystals precipitated from solution, and these were filtered, washed with water and pentane, and dried under vacuum. In the case of 3-hydroxy carboxylic acids which oiled out upon acidification of the aqueous solution, the products were extracted into diethyl ether (3 × 150 mL), the ether was dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo.

1a: yield 2.801 g (14.4 mmol, 67%; lit.[1a] 31%); mp 132.5–134.0 °C (lit.[1a] mp 134.5–135.5 °C); ^{1}H NMR[23] (acetone-d_6) δ 1.04 (s, 3), 1.13 (s, 3), 4.99 (s, 1), 7.2–7.4 (m, 5); ^{1}H NMR (benzene-d_6) δ 0.93 (s, 3), 1.09 (s, 3), 4.68 (s, 1), 7.01–7.40 (m, 5).

2-Ethyl-3-hydroxy-2-methyl-3-phenylpropionic Acid (1c). The procedure described above for the preparation of **1a** was followed using 2-methylbutyric acid and benzaldehyde as starting materials. The 3-hydroxy carboxylic acid (a 1:1 mixture of diastereomers) was obtained in 43% yield: mp 106.5–108.5 °C; mass spectrum 208.1 (2.5), 107.0 (99.8), 102.0 (100.0), 87.0 (74.9), 79.0 (48.0); HRMS calcd for $C_{12}H_{16}O_3$ 208.1099, found 208.1106.

The *erythro* diastereomer (2*R**,3*S**) was separated from the *threo* (2*R**,3*R**) by column chromatography (50:50:1 ether/hexane/acetic acid). The *erythro* (2*R**,3*S**) diastereomer was eluted first: mp 128.0–129.5 °C; ^{1}H NMR (acetone-d_6) δ 0.88 (t, J = 7.5 Hz, 3), 0.97 (s, 3), 1.68 (m, 1), 1.92 (m, 1), 4.99 (s, 1), 7.19–7.38 (m, 5); ^{1}H NMR (benzene-d_6) δ 0.81 (t, J = 7.3 Hz, 3), 1.00 (s, 3), 0.9–2.0 (m, 2), 2.2 (br s, 2, OH's), 4.66 (s, 1), 6.83–7.35 (m, 5); ^{13}C NMR (DMSO-d_6) δ 9.74, 14.64, 29.77, 52.74, 77.05, 127.36, 127.83 (this peak appears to be two unresolved peaks), 143.31, 177.00. The *threo* diastereomer (2*R**,3*R**) eluted next: mp 129.0–131.0 °C; ^{1}H NMR (acetone-d_6) δ 0.80 (t, J = 7.4 Hz, 3), 0.99 (s, 3), 1.08 (m, 1), 1.79 (m, 1), 4.96 (s, 1), 7.23–7.37 (m, 5); ^{1}H NMR (benzene-d_6) δ 0.71 (t, J = 7.27 Hz, 3), 1.03 (s, 3), 0.99–1.9 (m, 4, CH_2CH_3, OH's), 4.72 (s, 1), 6.83–7.39 (m, 5); ^{13}C NMR (DMSO-d_6) δ 9.25, 14.44, 29.55, 52.15, 77.99, 127.59, 127.8, 128.39, 142.63, 177.53. For the *erythro* diastereomer. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.28; H, 7.90. For the *threo* diastereomer. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.11; H, 7.85.

2,2-Dimethyl-3-ethyl-3-hydroxypentanoic Acid (1e). The procedure described above for the preparation of **1a** was followed using isobutyric acid and 2-pentanone as starting materials. The 3-hydroxy carboxylic acid was obtained as white crystals: mp 44.0–45.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.96 (t, J = 7.51 Hz, 6), 1.26 (s, 6), 1.65 (m, J = 7.14, 7.46, 7.84 Hz, 4); ^{13}C NMR ($CDCl_3$) δ 9.30, 22.16, 28.81, 51.02, 77.87, 182.41. Anal. Calcd for $C_9H_{18}O_3$: C, 62.04; H, 10.41. Found: C, 62.10; H, 10.09.

2-(1-Hydroxycyclobutyl)-2-ethylbutyric Acid (1i). The procedure described for the preparation of **1a** was followed using 2-ethylbutyric acid and cyclobutanone as starting materials. The product (36%) was obtained as white crystals after column chromatography using 50:25:1 hexane/ether/acetic acid as eluent: mp 68–9 °C; ^{1}H NMR (acetone-d_6) δ 0.86 (t, 6, J = 8 Hz), 1.56–2.04 (m, 8), 2.58 (m, 2); ^{13}C NMR (acetone-d_6) δ 9.72, 14.67, 24.28, 34.07, 55.65, 80.89, 176.59. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.78; H, 9.45.

Separation of (*E*)- and (*Z*)-2-Methyl-1-phenyl-1-butene (2c). A mixture of (*E*)- and (*Z*)-2-methyl-1-phenyl-1-butene

(22) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

(23) Berner, D.; Dahn, H.; Vogel, P. *Helv. Chim. Acta* **1980**, *63*, 2538. For $HO_2CC(CH_3)_2{}^{13}C(OH)HPh$: ^{1}H NMR (acetone d_6) δ 1.05 (d, $^3J_{CH}$ = 6.4 Hz, 3), 1.13 (d, $^3J_{CH}$ = 5.8 Hz, 3), 4.97 (d, $^1J_{CH}$ = 145 Hz, 1), 7.30 (s, 5).

(24) The first diastereomer to elute from the column was identified as the *erythro* by converting it to (*E*)-2-methyl-1-phenyl-1-butene via the triphenylphosphine–diethyl azodicarboxylate adduct (anti elimination).[2]

(Wiley Organics) was separated by preparative GC on 10% OV-17. The *Z* isomer was eluted first: ^{1}H NMR ($CDCl_3$) δ 1.12 (t, J = 7.6 Hz, 3), 1.90 (d, J = 1.2 Hz, 3), 2.28 (q, J = 7.6 Hz, 2), 6.28 (s, 1), 7.21–7.33 (m, 5); ^{1}H NMR (benzene-d_6) δ 0.87 (t, J = 7.6 Hz, 3), 1.65 (s, 3), 2.10 (q, J = 7.6 Hz, 2), 6.22 (s, 1), 7.00–7.18 (m, 5). This olefin was identified as the *Z* isomer by irradiating the doublet at δ 1.90 and observing NOE of the singlet at δ 6.28. The *E* isomer was eluted next: ^{1}H NMR ($CDCl_3$) δ 1.14 (t, J = 7.4 Hz, 3), 1.89 (d, J = 1.1 Hz, 3), 2.22 (q, J = 7.4 Hz, 2), 6.29 (s, 1), 7.20–7.34 (m, 5); ^{1}H NMR (benzene-d_6) δ 0.93 (t, J = 7.5 Hz, 3), 1.65 (s, 3), 1.96 (q, J = 7.4 Hz, 2), 6.25 (s, 1), 7.00–7.18 (m, 5). This olefin was identified as the *E* isomer by irradiating the quartet at δ 2.22 and observing NOE of the singlet at δ 6.29.

(1-Ethylpropylidene)cyclobutane (2i). This compound was prepared using the procedure of Adam.[1a] The olefin was isolated by preparative gas chromatography (0.1% SP-1000 on Carbopack B): ^{1}H NMR (benzene-d_6) δ 0.89 (t, J = 7.44 Hz, 6), 1.74 (quint, J = 8 Hz, 2), 1.85 (m, 4), 2.54 (t, J = 8 Hz, 4); ^{13}C NMR (benzene-d_6) δ 13.32, 16.92, 23.28, 29.74, 132.22, 134.01; HRMS calcd for C_9H_{16} 124.1252, found 124.1258.

Trichloro((*p*-nitrophenyl)imino)vanadium(V) (5d). The procedure described[19] for the preparation of trichloro(*p*-tolylimino)vanadium(V) was followed using *p*-nitrophenylisocyanate (5.067 g, 30.9 mmole) and vanadium oxytrichloride (2.92 ml, 31.0 mmol) in 83 mL of octane. The yellow, insoluble isocyanate darkened to a brown color and dissolved upon addition of the $VOCl_3$. The reaction was heated to reflux for 18 h, after which time it had become dark purple. The solvent was removed under vacuum to leave a dark brown solid which was washed with pentane and dried under vacuum (7.08 g, 78% yield): ^{1}H NMR ($CDCl_3$) δ 7.75, 8.34 (AA'BB'); IR (KBr) 3090 (m, br), 1729 (w, br), 1599 (w), 1582 (m), 1520 (s), 1346 (s), 1326 (s), 1309 (s), 1108 (m, V=N), 851 (m), 558 (w), 494 (w), 490 (m), 482 (m), 471 (s), 461 (s) cm^{-1}; HRMS calcd for $C_6H_4Cl_3N_2O_2V$ 291.8778, found 291.8782.

2-Methyl-1-phenyl-2-butene (6). Ethylidenetriphenylphosphorane (0.372 g, 1.28 mmol) was weighed into a small Schlenk flask, and 10 mL of THF was added. The flask was topped with a condenser and airless adapter and was attached to a nitrogen line. Phenylacetone (169 μl, 1.28 mmol) was added by syringe, and the reaction mixture was stirred at room temperature for 3.5 h and then at reflux for 4 days. The reaction mixture was then cooled, 10 drops of water was added, and the solution was evaporatively distilled to separate products from unreacted ylide and triphenylphosphine oxide. Solvent was removed in vacuo to leave an oil: ^{1}H NMR[25] ($CDCl_3$) δ 1.57 (d, J = 3 Hz), 1.63 (m), 1.74 (d, J = 6.6 Hz) [combined areas 6], 3.30, 3.39 (2 s, 2, CH_2), 5.35, 5.41 (2, q, J = 6.4, 6.4 Hz, 1 H, =C*H*CH_3), 7.2–7.4 (m, 5).

3-Ethyl-4-methyl-2-pentene (7). Byproducts of the reaction between $VOCl_3$ and **1e** were compared with known materials (Wiley Organics). For **7** prepared from **1e**: major isomer (Wiley "low bp"), *E*[26] 112.2 (M$^+$, 12.3), 83.2 (47.1), 55.1 (100.0), 41.2 (48.4), 39.2 (30.7); minor isomer (Wiley "high bp"), *Z*[26] 112.2 (M$^+$, 17.6), 83.2 (74.4), 55.2 (100.0), 41.2 (44.7), 39.2 (29.5).

A Typical Procedure for the Reaction of a 3-Hydroxy Carboxylic Acid with Vanadium Oxytrichloride. Vanadium oxytrichloride (47.1 μL, 0.500 mmol) was added to a suspension of **1a** (0.0971 g, 0.500 mmol) in 5 mL of chlorobenzene. The reaction was stirred at room temperature for 15 min (the mixture became a homogeneous, orange-red solution) and was then heated to reflux (the mixture became dark greenish-brown). Aliquots were removed periodically and were hydrolyzed with a few drops of water and were either evaporatively distilled or filtered through a Florisil/cotton plug to remove the metals before analysing by gas chromatography.

Detection of 3,3-Diphenyl-2-propenoic Acid (8) as a Product in the Reaction of $VOCl_3$ and 3,3-Diphenyl-3-hydroxypropanoic Acid (1f). Vanadium oxytrichloride was added to a mixture of chlorobenzene and **1f** at room temperature. After being stirred at room temperature for 15 min, the reaction was heated to reflux. An aliquot taken after 24 h was hydrolyzed with 6 N HCl, and volatiles obtained by reduced-pressure distillation showed **8**[27] (80% by NMR).

A Typical Procedure for the Reaction of a 3-Hydroxy Carboxylic Acid with a Trichloro(arylimino)vanadium(V) Compound. Acid **1a** (0.0588 g, 0.303 mmol) and trichloro(*p*-tolylimino)vanadium(V) (**5a**) (0.080 g, 0.30 mmol) were weighed into a Schlenk flask, and 1.75 mL of chlorobenzene was added. The reaction was stirred at room temperature for 15 min (the mixture was a greenish-brown color) and was then heated to reflux (the mixture became dark brown). Aliquots were removed periodically and were hydrolyzed with a few drops of water and were either evaporatively distilled or filtered through a Florisil/cotton plug to remove the metals before analyzing by gas chromatography.

^{1}H NMR Data for the Complexes of 5a with Pure *erythro*-1c and Pure *threo*-1c. The reactions were performed in an analogous manner to the procedure described above except that reactions were run in NMR tubes. The designation *erythro* corresponds to (2*R**,3*S**) and the designation *threo* corresponds to (2*R**,3*R**): ^{1}H NMR of the **5a**/*erythro*-**1c** complex (benzene-d_6, room temperature) δ 0.81 (m, 3), 0.99 (br s, 3), 1.2–2.1 (2 br m, 2), 1.75 (s, 3), 4.75 (br s, 1), 6.32 (m, 1), 6.99–7.31 (m, 5); ^{1}H NMR of the **5a**/*erythro*-**1c** complex (benzene-d_6, 105 min, 75 °C) δ 0.46–2.12 (m, 8) [1.56 (s, $H_2NC_6H_4CH_3$), 1.65 (s, $C_6H_4CH_3$), 2], [4.67 (s), 5.2 (m), 6.25 (m), 1], 6.99–7.31 (m 5); ^{1}H NMR of the **5a**/*erythro*-**1c** complex (benzene-d_6, 24 h, 75 °C) δ 0.46–2.12 (m, 8) [1.56 (s, $H_2NC_6H_4CH_3$), 1.66 (s, $C_6H_4CH_3$), 2], [4.67 (s), 5.2 (m), 6.25 m), 1], 6.99–7.31 (m, 5); ^{1}H NMR of the **5a**/*threo*-**1c** complex (benzene-d_6, room temperature) δ 0.75 (m, 3), 0.8–2.2 (2 br m, 2), 1.05 (br s, 3), 1.77 (s, 3), 4.88 (br s, 1), 6.36 (m, 1), 6.98–7.23 (m, 5); ^{1}H NMR of the **5a**/*threo*-**1c** complex (benzene-d_6, 105 min, 75 °C) δ 0.51–1.97 (m, 8) [1.56 (s, $H_2NC_6H_4CH_3$), 1.65 (s, $C_6H_4CH_3$), 2], [4.77 (s), 5.3 (m), 6.26 (m), 1], 6.98–7.23 (m, 5); ^{1}H NMR of the **5a**/*threo*-**1c** complex (benzene-d_6, 24 h, 75 °C) δ 0.51–2.07 (m, 8), [1.56 (s, $H_2NC_6H_4CH_3$), 1.65 (s, $C_6H_4CH_3$), 2], [4.77 (s), 5.3 (m), 6.26 (m), 1 H], 6.98–7.23 (m, 5).

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