

**Carbonyl Ylide Cycloadditions of Dicobalt Carbonyl Complexes of
Propargylic Aldehydes**

by

Aaron J. Skaggs

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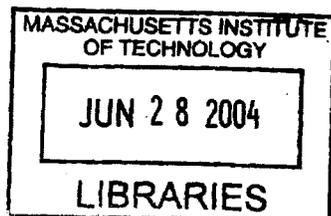
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Signature of Author _____
Department of Chemistry
May 20, 2004

Certified by _____
Timothy F. Jamison
Paul M. Cook Career Development Assistant Professor of Chemistry
Thesis Supervisor

Accepted by _____
Robert W. Field

Chairman, Departmental Committee of Graduate Students



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This thesis has been examined by a committee of the
Department of Chemistry as follows:

Jianshu Cao
Thesis Committee Chair

Bruce Tidor
Thesis Supervisor

Andrei Tokmakoff
y

For my Grandmothers

Carbonyl Ylide Cycloadditions of Dicobalt Carbonyl Complexes of Propargylic Aldehydes

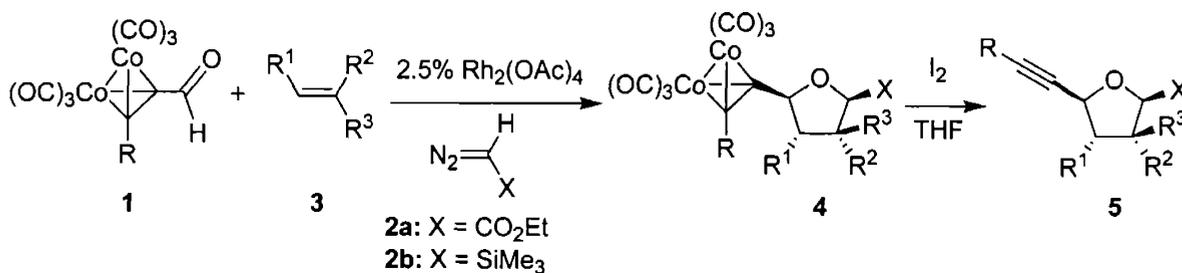
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Aaron J. Skaggs

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ABSTRACT

The intermolecular, three-component carbonyl ylide cycloaddition of a diazo compound, aldehyde, and carbon-carbon multiple bond is a powerful method to construct five-membered oxygen heterocycles. An adjacent dicobalt hexacarbonyl cluster permits the expansion of the scope of this process to include propargylic aldehydes (2-alkynals). The cluster not only increases the rate of reaction for this class of aldehydes, but also leads to a complete reversal in the diastereoselectivity compared to related methods and favors the exclusive formation of a 2,5-*cis* relationship in the products. Furthermore, the use of trimethylsilyldiazomethane (TMSD) as the carbene source allows coupling with a variety of dipolarophiles in moderate to high yields with good selectivity. Interaction of the $(\mu, \eta^2\text{-alkyne})\text{Co}_2(\text{CO})_6$ fragment with the neighboring positive charge of the 1,3-dipole is postulated to be a cause for the enhanced reactivity and selectivity. The choice of carbene transfer catalyst has no effect on either diastereocontrol or enantioselection, which suggests a mechanism involving a free ylide. While the $\text{Co}_2(\text{CO})_6$ fragment can be removed to give the free alkyne in high, a catalytic amount of cobalt in the cycloaddition is modestly effective. Exchange of one or two carbonyls of the cobalt cluster by achiral and chiral phosphorous ligands results in dramatically lowered reaction efficiency. X-ray crystal structures of two of these substituted cobalt clusters are presented.



Preface

Portions of this thesis have appeared in the following article that was co-written by the author:

Cobalt Cluster-Containing Carbonyl Ylides for Catalytic, Three-Component Assembly of Oxygen Heterocycles

Org. Lett. **2002**, *4*, 2277-2280.

Skaggs, A. J.; Lin, E. Y. Lin; Jamison, T. F.

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Abbreviations

ADC	acetylenedicarbaldehyde
Bn	benzyl
CAN	ammonium cerium(IV) nitrate
cap	ϵ -caprolactamate
$^{\circ}\text{C}$	degree (Celsius)
δ	chemical shift in parts per million
d.r.	diastereomeric ratio
DMAD	dimethyl acetylenedicarboxylate
EDA	ethyl diazoacetate
ee	enantiomeric excess
eq	equation
g	grams
h	hour
HRMS	high resolution mass spectroscopy
Hz	hertz
IR	infrared
M	molar
mg	milligram
MHz	megahertz
mmol	millimole
μL	microliter
min	minutes
mL	milliliter
MS	mass spectroscopy
NMR	nuclear magnetic resonance
OAc	acetate
oct	octanoate
OTf	trifluoromethanesulfonate
pfb	perfluorobutyrate
SiO_2	silica gel
TFA	trifluoroacetate
THF	tetrahydrofuran
TLC	thin layer chromatography
TMSD	trimethylsilyldiazomethane
TON	turnover number

A. Introduction

The efficient construction of five-membered oxygen heterocycles remains a relevant task due to their presence in a number of natural products.¹ Tetrahydrofurans, for example, found in monensin,² lonomycin,³ and in many amphidinolides,⁴ lignans⁵ and acetogenins,⁶ are representative examples, and their synthesis has attracted considerable attention because they display diverse biological functions.⁷

Many methods of dihydrofuran or tetrahydrofuran synthesis feature intramolecular C-O bond formation involving epoxide opening, displacement of a leaving group, or conjugate addition to unsaturated carbonyl compounds.^{1b,1c} Others make use of C-C bond formation and include ring-closing metathesis, intramolecular carbene insertions, and cyclizations of polar or radical intermediates. Two notable entries into this class of heterocycles make both one C-O and one C-C bond: annulation of allylic and allenic silanes with carbonyl compounds⁸ and Prins-Pinacol rearrangement of allylic acetals (Scheme 1).⁹ Each of these methods necessitates several steps to synthesize the required starting compounds. An intermolecular, multi-component

¹ (a) Furans and benzofurans: Greve, S.; Reck, S.; Friedrichsen, W. *Prog. Heterocycl. Chem.* **1998**, *10*, 129-152. Unsaturated furans: (b) Elliot, M. C. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1291-1318. (c) Elliot, M. C. *J. Chem. Soc., Perkin Trans. 1* **1998**, 4175-4200.

² (a) isolation: Haney, M. E., Jr.; Hoehn, M. M. *Antimicrob. Agents Chemother.* **1968**, 349-52. total synthesis: (b) Fukuyama, T.; Akasaka, K.; Karenewsky, D. S.; Schmid, G.; Kishi, Y. *J. Am. Chem. Soc.* **1979**, *101*, 259. (c) Collum, D. B.; McDonald, J. H., III; Still, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 2117.

³ (a) structure: Otake, N.; Keonuma, M.; Miyamae, H.; Sato, S.; Saito, Y. *Tetrahedron Lett.* **1975**, *47*, 4147-50. (b) synthesis of Lonomycin A: Evans, D. A.; Ratz, A. M.; Huff, B. E.; Sheppard, G. S. *J. Am. Chem. Soc.* **1995**, *117*, 3448-67.

⁴ Review on Amphidinolides: Ishibashi, M.; Kobayashi, J. *Heterocycles* **1997**, *44*, 543-572.

⁵ Review on Lignans: Ward, R. S. *Nat. Prod. Rep.* **1999**, *16*, 75-96.

⁶ Review on Acetogenins: Alali, F. Q.; Liu, X.-X.; McLaughlin, J. L. *J. Nat. Prod.* **1999**, *62*, 504-540.

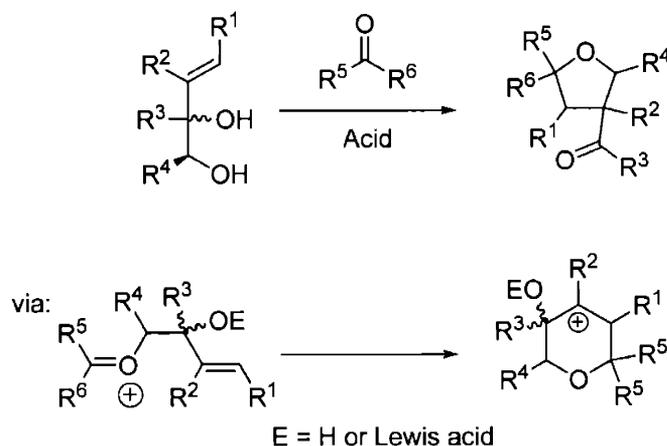
⁷ Boivin, T. L. B. *Tetrahedron* **1987**, *43*, 3309-3362.

⁸ (a) Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293. (b) Kwasigroch, C. A.; Tsai, Y.-M.; Danheiser, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 7233-7235. (c) Stoner, E. J.; Koyama, H.; Yamashita, D. S.; Klade, C. A.; Danheiser, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 4407-4413. (d) Yang, M.; Panek, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 9868. (e) Micalizio, G. C.; Roush, W. R. *Org. Lett.* **2000**, *2*, 461-464.

⁹ (a) Overman, L. E. *Acc. Chem. Res.* **1992**, *25*, 352-359. (b) Cohen, F.; MacMillan, D. W. C.; Overman, L. E.; Romero, A. *Org. Lett.* **2001**, *3*, 1225-1228.

processes that accomplishes this goal in one step would be advantageous over these longer routes.

Scheme 1. Prins-Pinacol reaction between an allylic diol and carbonyl compound can rapidly create tetrahydrofurans having many substituents (Overman, ref 9).



A convergent, three-component method of tetrahydrofuran synthesis involves 1,3-dipolar cycloaddition between a carbonyl ylide and an alkene, thus creating two C-C bonds in a single operation.¹⁰ The pioneering work of Huisgen demonstrated that a carbonyl ylide derived from a diazo compound and an aromatic aldehyde undergoes cycloaddition with an aldehyde molecule (to give a dioxolane) or an electron-deficient alkene (to give a tetrahydrofuran).¹¹ Maas¹² and Doyle¹³ later discovered more active catalysts for the latter process and expanded its scope to include two examples of carbonyl ylides generated from non-aromatic aldehydes. Scheme 2

¹⁰ (a) Carruthers, W. In *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press: Oxford, 1990. (b) McMills, M. C. and Wright, D. In *The Chemistry of Heterocyclic Compounds, Vol. 59: Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products*, Padwa, A. and Pearson, W. H., Eds.; John Wiley & Sons: New York, 2002; 253-314. (c) Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley-Interscience: New York, 1984; 1-176. (d) Padwa, A. *Acc. Chem. Res.* **1991**, *24*, 22-28. (e) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263-309. (f) Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223-269. (g) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; Wiley & Sons: New York, **1998**.

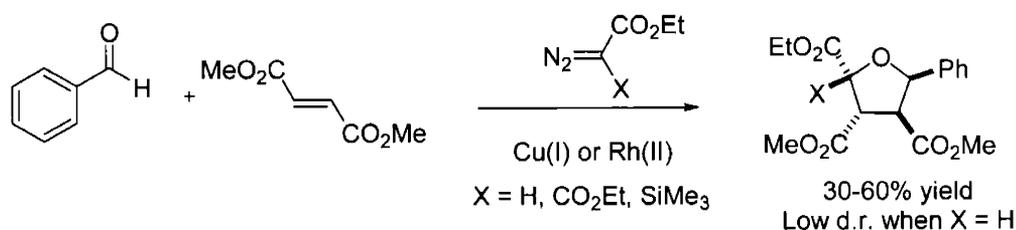
¹¹ de March, P.; Huisgen, R. *J. Am. Chem. Soc.* **1982**, *104*, 4953-4954.

¹² Alt, M.; Maas, G. *Tetrahedron* **1994**, *50*, 7435.

¹³ Doyle, M. P.; Forbers, D. C.; Protopopova, M. N.; Stanley, S. A.; Vasbinder, M. M.; Xavier, K. R. *J. Org. Chem.* **1997**, *62*, 7210-7215.

summarizes the results in this area. With most aldehydes and dipolarophiles, however, dioxolane formation was a significant competing pathway, limiting the range of tetrahydrofurans that could be prepared in this fashion.¹⁴

Scheme 2. Intermolecular carbonyl ylide cycloadditions are limited in scope, selectivity and yield.

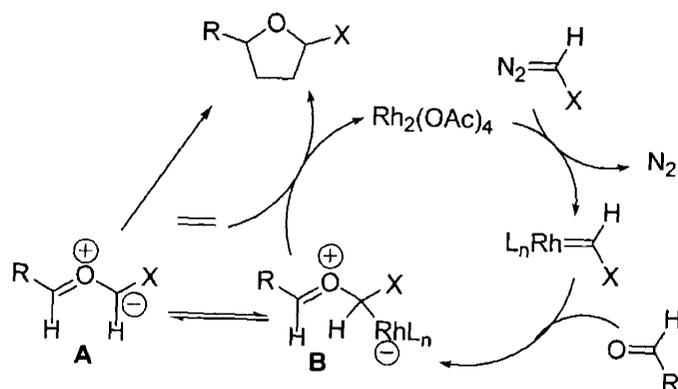


A possible catalytic cycle explaining how $\text{Rh}_2(\text{OAc})_4$ brings together a diazo compound, aldehyde, and alkene by way of a carbonyl ylide to form a tetrahydrofuran is presented in Scheme 3.¹⁵ First, the metal reacts with the diazo compound, extruding N_2 and generating a metal-bound carbene. Then this electrophilic carbenoid is intercepted by an aldehyde to produce the 1,3-dipole (Scheme 3, **A** or **B**). Trapping of either the free ylide (**A**) or the Rh-associated version (**B**) by an olefin accomplishes the tetrahydrofuran synthesis and regenerates the catalyst to continue the sequence.

¹⁴ Other methods of tetrahydrofuran synthesis involving carbonyl ylide cycloaddition: (a) Kagan, J.; Firth, B. E. *J. Org. Chem.* **1974**, *39*, 3145-3147. (b) Markowski, V.; Huisgen, R. *Tetrahedron Lett.* **1976**, *17*, 4643-4646. (c) Gill, H. S.; Landgrebe, J. A. *J. Org. Chem.* **1983**, *48*, 1051-1055. Namy, J. L.; Soupe, J.; Kagan, H. B. *Tetrahedron Lett.* **1983**, *24*, 765-766.

¹⁵ Doyle, M. P. *Chem. Rev.* **1986** *86*, 919-939.

Scheme 3. $\text{Rh}_2(\text{OAc})_4$ -mediated catalytic carbonyl ylide formation.



Generation of carbonyl ylides has been applied in a number of situations to produce oxygen heterocycles. Hamaguchi has reported a related three-component coupling reaction of vinylcarbenoids, aromatic aldehydes, and electron-deficient dipolarophiles.¹⁶ Stabilized carbonyl ylides can be produced *in situ* by electrocyclic ring opening of an epoxide¹⁷ or from the reaction of Seyferth's PhHgCX_3 reagents with aldehydes to produce 1,1,-dihalocarbonyl ylides.¹⁸ Independently, Hosomi and Takai have reported cycloadditions of carbonyl ylides lacking stabilizing groups with simple alkenes (and alkynes), but the symmetrical bis-(2-chloromethyl) ethers (or α -iodo alcohols) that function as 1,3-dipole precursors do not allow straightforward preparation of tetrahydrofurans with different substituents or functionality at the 2- and 5-positions (Scheme 4).¹⁹ The strongly reducing conditions can result in low functional group compatibility.

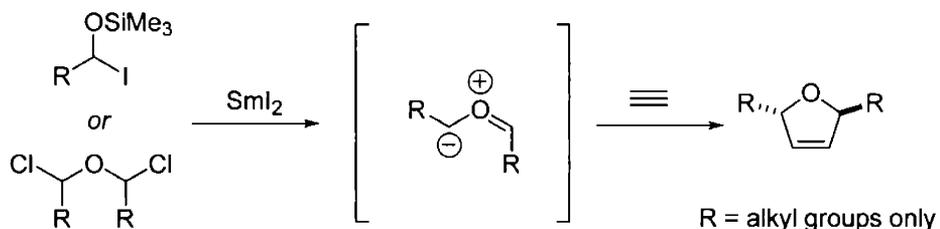
¹⁶ Hamaguchi, M.; Matsubara, H.; Nagai, T. *J. Org. Chem.* **2001**, *66*, 5395-5404.

¹⁷ (a) Markowski, V.; Huisgen, R. *Tetrahedron Lett.* **1976**, *50*, 4643-4646. (b) Kagan, J.; Firth, B. E. *J. Org. Chem.* **1974**, *39*, 3145-3147.

¹⁸ Seyferth, D. *Acc. Chem. Res.* **1972**, *5*, 65-74.

¹⁹ (a) Hojo, M.; Aihara, H.; Sugino, Y.; Sakata, K.; Nakamura, S.; Murakami, C.; Hosomi, A. *J. Org. Chem.* **1997**, *62*, 8610-8611. (b) Takai, K.; Kaihara, H.; Higashiura, K.-i.; Ikeda, N. *J. Org. Chem.* **1997**, *62*, 8612-8613. (c) Hojo, M.; Ohkuma, M.; Ishibashi, N.; Hosomi, A. *Tetrahedron Lett.* **1993**, *34*, 5943-5946. (d) Hojo, M.; Aihara, H.; Hosomi, A. *J. Am. Chem. Soc.* **1996**, *118*, 3533-3534. (e) Hojo, M.; Ishibashi, N.; Hosomi, A. *Synlett* **1996**, 234-237. (f) Hojo, M.; Aihara, H.; Ito, H.; Hosomi, A. *Tetrahedron Lett.* **1996**, *37*, 9241-9244.

Scheme 4. Dipolar cycloaddition of unstabilized carbonyl ylides (Hosomi and Takai, refs. 19).



The untapped potential of propargylic aldehydes in carbonyl ylide cycloaddition chemistry would increase the scope of this convergent reaction; an alkyne in the 2-position of a tetrahydrofuran could be a surrogate for alkyl, alkenyl, or alkynyl chains.²⁰ Furthermore, modification of this three-component reaction to accommodate dipolarophiles that were not only unsymmetrical, but also substantially less electron-deficient, such as enones, enoates, styrene derivatives, alkenylsilanes, and even simple olefins, would provide tetrahydrofurans in which all four positions of the ring are differentially substituted.

In this work, a metal-catalyzed, three-component coupling method is described that allows for differentiation of all four positions of the tetrahydrofuran ring. The 1,3-dipole generated *in situ* possesses an unusually broad range of reactivity, undergoing cycloaddition with highly electron-deficient alkynes and alkenes (*e.g.* DMAD and maleate esters) and even simple olefins (*e.g.* 1-heptene). Key to this approach is the use of a propargylic aldehyde protected by a dicobalt hexacarbonyl complex. To the best of our knowledge, these are the first dipolar cycloadditions of any type in the presence of alkyne-cobalt complexes,²¹ and the first use of trimethylsilyldiazomethane as the carbene source in such cycloaddition reactions. Furthermore, the exclusive 2,5-*cis* relationship observed in the products is complementary to the previous

²⁰ Larock, R. C. *Comprehensive Organic Transformations 2nd Ed.*; Wiley VCH; New York, 1997.

²¹ Tungsten-containing carbonyl ylide: Iwasawa, N.; Shido, M.; Kusama, H. *J. Am. Chem. Soc.* **2001**, *123*, 5814-5815.

reports in which a 2,5-*trans* relationship is favored.¹²⁻¹⁴ Electrocyclic ring closure of the cobalt cluster-containing 1,3-dipole to an epoxide is suggested as a possible reaction intermediate.²²

B. A Cobalt Cluster Effect

The initial experiments aimed at generating carbonyl ylides of propargylic aldehydes were unsatisfactory (Scheme 5). The slow addition of 300 mol% ethyl diazoacetate (EDA) and 100 mol% dimethyl acetylenedicarboxylate (DMAD) to 2-octynal and a catalytic amount of Rh₂(OAc)₄ led to a dihydrofuran product in 9% yield as a 3:1 mixture of diastereomers favoring the 2,5-*trans* relationship.²³ We surmised that the low yield arose from competing reactions of the 2-alkynal as a dipolarophile. Protection of the alkyne in 2-octynal by exposure to dicobalt octacarbonyl generated the (μ,η²-2-octynal)Co₂(CO)₆ complex in near quantitative yield.²⁴ When the dicobalt hexacarbonyl complex of 2-octynal (**1a**) reacted under analogous conditions, the dipolar cycloaddition product (**4a**) was produced in 68% yield. Most notably, the cluster remained intact during the reaction and provided a complete *reversal* of diastereoselectivity, giving the heterocycle *exclusively* as its 2,5-*cis* diastereomer (>20:1 d.r.).²⁵ An increase in the reaction yield in this case can be attributed to an increased nucleophilicity of the aldehyde through Nicholas cation stabilization of the carbonyl resonance structure.²⁶ A similar interaction with the positive charge of the 1,3-dipole by the cobalt cluster is proposed in Scheme 6.

²² Doyle, M. P.; Hu, W. H.; Timmons, D. J. *Org. Lett.* **2001**, 3, 933-935.

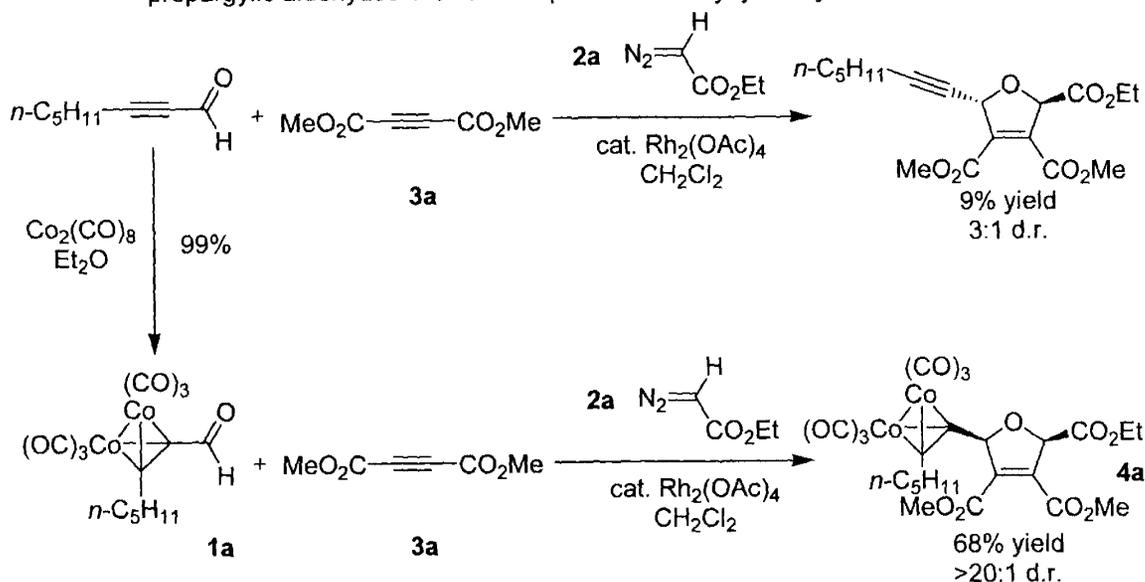
²³ Reactions conducted with E. Y. Lin.

²⁴ Seyferth, D.; Nestle, M. O.; Wehman, A. T. *J. Am. Chem. Soc.* **1970**, 92, 5520.

²⁵ See Section H for a discussion of the stereochemical origin.

²⁶ Reviews: (a) Nicholas, K. M. *Acc. Chem. Res.* **1987**, 20, 207. (b) Green, J. R. *Curr. Org. Chem.* **2001**, 5, 809-826. (c) Teobald, B. J. *Tetrahedron* **2002**, 58, 4133-4170.

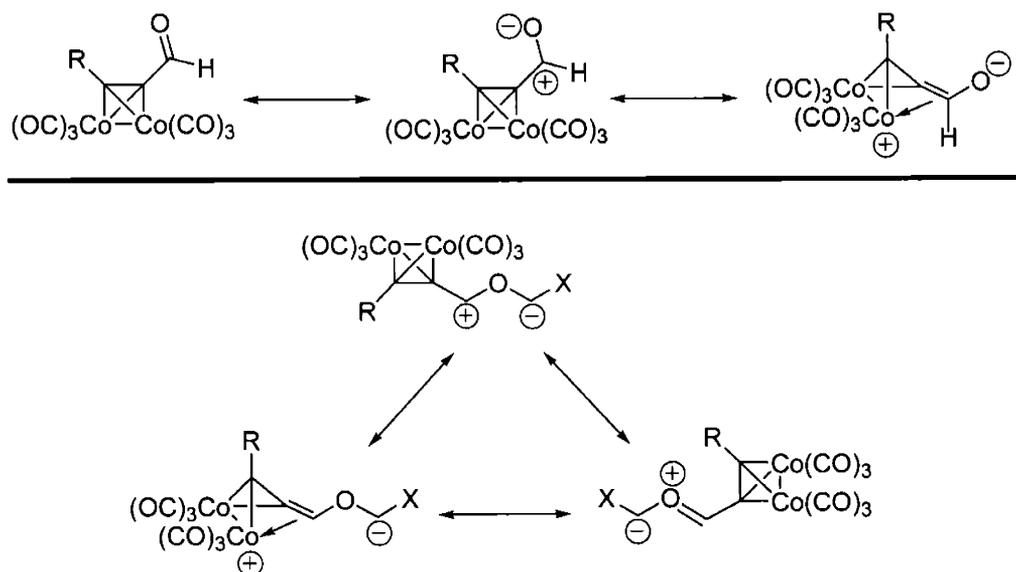
Scheme 5. A $\text{Co}_2(\text{CO})_8$ cluster reverses the stereochemistry and enhances the reactivity of propargylic aldehydes in three-component carbonyl ylide cycloadditions.



Enhanced selectivity in reactions of dicobalt hexacarbonyl alkyne complexes relative to their non-complexed alkynes has been detected previously in several types of transformations.²⁷ Undoubtedly, some of the increased selectivity can be attributed to the pronounced steric change that the large dicobalt hexacarbonyl fragment imparts to the linear alkyne. Clearly, the cobalt cluster has a beneficial effect in this case, providing the desired three-component coupling product in good yield and high selectivity.

²⁷ Reactions of ynals and ynones in which a $\text{Co}_2(\text{CO})_8$ cluster provides increased stereoselectivity. *Aldol reactions*: (a) Ju, J.; Reddy, B. R.; Khan, M.; Nicholas, K. M. *J. Org. Chem.* **1989**, *54*, 5426-5428. (b) Mukai, C.; Nagami, K.; Hanaoka, M. *Tetrahedron Lett.* **1989**, *30*, 5623-5626. (c) Mukai, C.; Nagami, K.; Hanaoka, M. *Tetrahedron Lett.* **1989**, *30*, 5627-5630. (d) Mukai, C.; Suzuki, K.; Nagami, K.; Hanaoka, M. *J. Chem. Soc., Perkin Trans. 1* **1992**, 141-145. (e) Mukai, C.; Kataoka, C.; Hanaoka, M. *J. Chem. Soc., Perkin Trans. 1* **1993**, 563-571. *Allylmetal and crotylmetal addition reactions*: (f) Roush, W. R.; Park, J. C. *J. Org. Chem.* **1990**, *55*, 1143-1144. (g) Ganesh, P.; Nicholas, K. M. *J. Org. Chem.* **1993**, *58*, 5587-5588. (h) Ganesh, P.; Nicholas, K. M. *J. Org. Chem.* **1997**, *62*, 1737-1747. *Lewis acid-mediated Nicholas reactions*: (i) Schreiber, S. L.; Sammakia, T.; Crowe, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 3128-3130. (j) Schreiber, S. L.; Klimas, M. T.; Sammakia, T. *J. Am. Chem. Soc.* **1987**, *109*, 5749-5759. (k) Sui, M.; Panek, J. S. *Org. Lett.* **2001**, *3*, 2439-2442. *Catalytic asymmetric reductions of 2-ynones ($\text{Co}_2(\text{CO})_8$ complex)*: (l) Corey, E. J.; Helal, C. J. *Tetrahedron Lett.* **1995**, *36*, 9153-9156. (m) Bach, J.; Berenguer, R.; Garcia, J.; Loscertales, T.; Vilarrasa, J. *J. Org. Chem.* **1996**, *61*, 9021-9025.

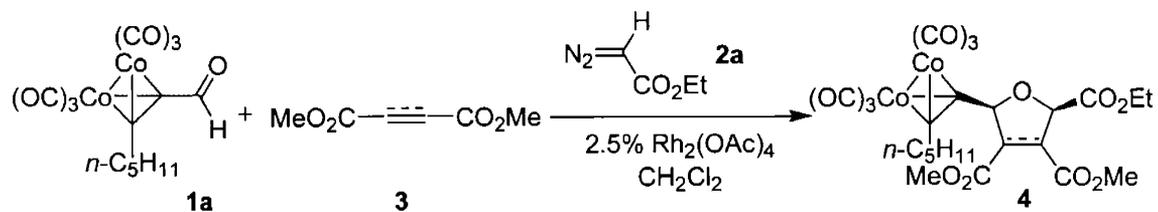
Scheme 6. Proposed involvement of a Nicholas cation in activation of the carbonyl and interaction with the adjacent carbonyl ylide.



C. Optimization of Stoichiometry and Reaction Parameters

Encouraged by this above result (Scheme 5), the reactivity of different dipolarophiles with the carbonyl ylide derived from **1a** and ethyl diazoacetate (EDA) was probed. Under otherwise identical reaction conditions, couplings with dimethyl maleate or dimethyl fumarate yielded the desired cycloadduct **4b** and **4c**, but considerable amounts of cycloaddition products of *diethyl* fumarate and *diethyl* maleate were also observed (entries 2 and 3, Table 1). Despite the slow addition of the diazo compound, dimerization of EDA and subsequent reaction with the 1,3-dipole occurred at a rate sufficient to be competitive with the externally included dipolarophile.

Table 1. Three component cycloaddition of **1a** and **2a** (EDA) with activated dipolarophiles.^[a]



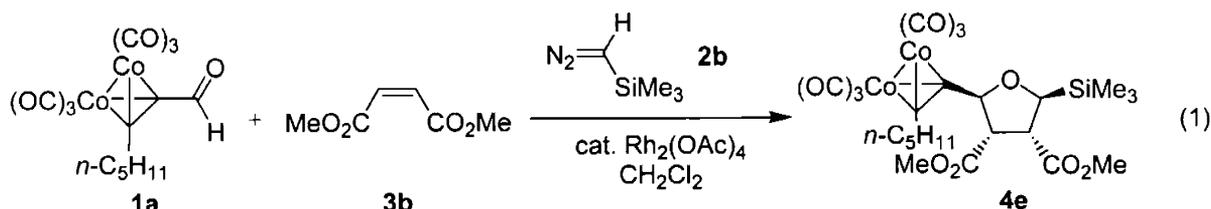
Entry	Dipolarophile	Product	Yield (%)
1 ^{[b],[c]}	 3a	 4a	68
2 ^[c]	 3b	 4b	<20
3 ^[d]	 3c	 4c	<20

[a] Reaction conditions: EDA (3 mmol) in CH₂Cl₂ (5 mL) was added via syringe pump over 6 h to a solution of the cobalt complex (1 mmol) and dipolarophile (1 mmol) in CH₂Cl₂ (5 mL). [b] DMAD (1 mmol) in CH₂Cl₂ (2.5 mL) and EDA (3 mmol) in CH₂Cl₂ (5 mL) were added via separate syringes over the 6 h. [c] Single diastereomer as determined by crude ¹H NMR. [d] Reaction was conducted at reflux. Product was a 6:1 mixture of regioisomers; major diastereomer shown.

It was thought that this competing reaction pathway could be minimized through the use of trimethylsilyldiazomethane (TMSD) as the carbene source. The carbenoid derived from TMSD, being less electrophilic than the carbenoid from EDA, does not readily dimerize under similar conditions.²⁸ Based on this idea, we chose to optimize the dipolar cycloaddition of **1a** and dimethyl maleate with TMSD (eq 1) by a systematic study of each of the reaction

²⁸ Carter, D. S.; Van Vranken, D. L. *Org. Lett.* **2000**, *2*, 1303-1305.

components. DMAD could not be used as the dipolarophile here, because it reacts slowly with the cobalt cluster and undergoes direct cycloaddition to TMSD.²⁹ Using the same proportions of reagents as in Table 1, dipolar cycloaddition of **1a**, and dimethyl maleate with TMSD (**2b**), gave the desired cobalt cluster-containing tetrahydrofuran (**4e**) as a single diastereomer, but in only 12% yield.

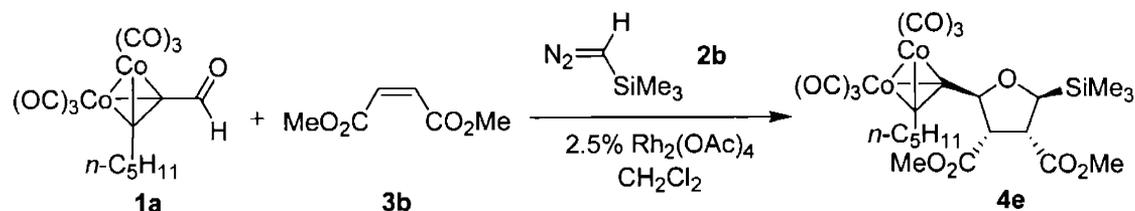


Efforts directed toward increasing the product yield by altering the stoichiometry of the coupling partners are shown in Table 2. Both an excess of the diazo compound and dipolarophile are required for complete consumption of the cobalt complex (entries 1, 2 and 4). By using 200 mol% of TMSD and 200 mol% of the dipolarophile (entry 5), the yield of the desired tetrahydrofuran (**4e**) was increased to 74%, still with no evidence of the formation of other diastereomers. Employment of a larger excess of diazo compound (300 mol%) is detrimental to the formation of the tetrahydrofuran (entries 3 and 6).³⁰

²⁹ Over time, the cobalt complex of DMAD becomes detectable in the reaction vessel when it is employed as a dipolarophile. DMAD reacts directly with **2b** (TMSD).

³⁰ Some of the decreased yield is due to the decomposition of the cobalt complex.

Table 2. Effect of stoichiometry on the three-component, carbonyl ylide cycloaddition.^[a]



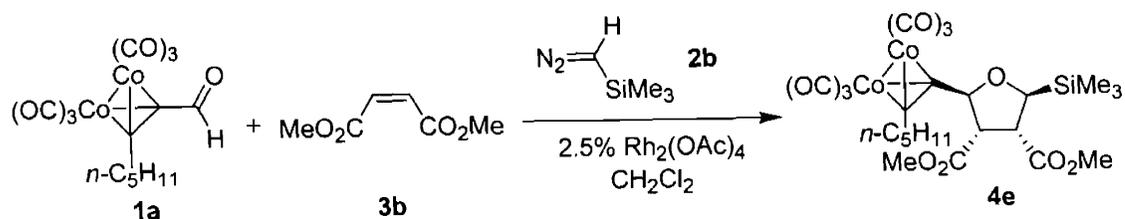
Entry	Dipolarophile (mol%)	TMSD (mol%)	Yield (%)	Recovered Aldehyde (%)
1	100	100	43	32
2	100	200	37	36
3	100	300	12	--[b]
4	200	100	47	30
5	200	200	74	--[b]
6	200	300	57	--[b]

[a] Reaction conditions: TMSD in CH₂Cl₂ (5 mL) was added via syringe pump over 6 h to the cobalt complex (1 mmol) and dipolarophile in CH₂Cl₂ (5 mL). [b] Not detected.

Using the optimum stoichiometry found from the studies summarized in Table 2, entry 5, the addition time of the TMSD next was studied (Table 3). Slow addition of the diazo compound was found to be required. Introducing **2b** directly to the reaction resulted in no isolation of **4e** and poor recovery of the starting cobalt complex **1a** (entry 1). When an excess of **2b** relative to the metal catalyst is present, it is possible that reactions of the diazo compound (and not its corresponding carbenoid) impede the desired transformation.³¹ Adding **2b** over six hours effectively addressed this problem but longer addition times resulted in slightly lower yield of **4e**.

³¹ Pyrazoline formation (direct dipolar cycloaddition of the diazo compound to an olefin) has been reported as a competing side reaction under similar conditions: Huisgen, R.; de March, P. *J. Am. Chem. Soc.* **1982**, *104*, 4953.

Table 3. Effect of addition time of TMSD (**2b**) on the yield of **4e**.^[a]

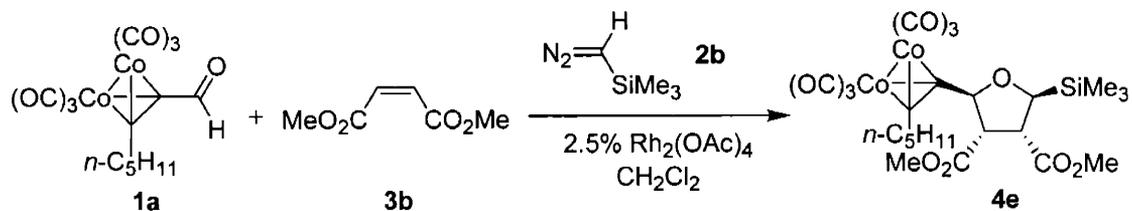


Entry	Addition Time (h)	Yield (%)	Diastereoselectivity
1	0	0 ^[b]	--
2	3	46	>20:1
3	6	74	>20:1
4	9	67	>20:1

[a] Reaction conditions: To the cobalt complex (1 mmol) and dipolarophile (2 mmol) in CH₂Cl₂ (5 mL), TMSD (2 mmol) in CH₂Cl₂ (5 mL) was added via syringe pump over time stated.
 [b] Recovered 57% starting aldehyde.

The data in Table 4 represent the effect of temperature on the overall reaction efficiency. Conducting the reaction below room temperature decreased the conversion, and substantial aldehyde **1a** was recovered (entry 1). As seen from entry 4, the thermal instability of dicobalt hexacarbonyl complexes precluded the use of temperatures above 40 °C. The free alkyne **5**, derived from the deprotection of the cobalt cluster after cycloaddition, was not identified in the reaction mixture.

Table 4. Effect of the reaction temperature on the yield of cycloaddition product **4e**.^[a]

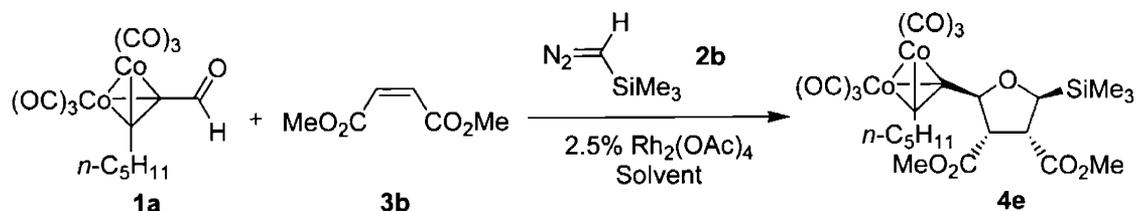


Entry	Temperature (°C)	Yield (%)	Diastereoselectivity
1 ^[b]	0	47	>20:1
2	25	74	>20:1
3	40	67	>20:1
4 ^[c]	85	0	--

[a] Reaction conditions: TMSD (2 mmol) in CH_2Cl_2 (5 mL) was added via syringe pump over 6 h to the cobalt complex (1 mmol) and dipolarophile (2 mmol) in CH_2Cl_2 (5 mL). [b] Recovered 33% starting aldehyde. [c] The solvent was 1,2-dichloroethane.

A solvent study found dichloromethane to be the superior solvent choice (Table 5). Among aromatic solvents, toluene was the best option and nearly as effective as methylene chloride (entries 2 and 3). The use of diethyl ether provided **4e** in 71% yield (entry 5). Acetonitrile and acetone were poor solvents; no new cobalt complexes were found upon analysis of the reaction mixture. It was hypothesized that these Lewis basic solvents bind to the Rh(II) catalyst and diminish the productive reaction with the diazo compound. The selectivity of the observed tetrahydrofuran **4e** is unchanged regardless of solvent.

Table 5. Effect of the solvent on the yield of cycloaddition product **4e**.^[a]



Entry	Solvent	Yield (%)	Diastereoselectivity
1	CH_2Cl_2	74	>20:1
2	Benzene	34	>20:1
3	Toluene	73	>20:1
4	Chlorobenzene	49	>20:1
5	Diethyl Ether	71	>20:1
6	THF	53	>20:1
7	<i>t</i> -BuOMe	33	>20:1
8	Acetone	0	--[b]
9	CH_3CN	0	--[b]

[a] Reaction conditions: To the cobalt complex (1 mmol) and dipolarophile (2 mmol) in solvent (5 mL) was added TMSD (2 mmol) in solvent (5 mL) via syringe pump over 6 h at room temperature. [b] Not available.

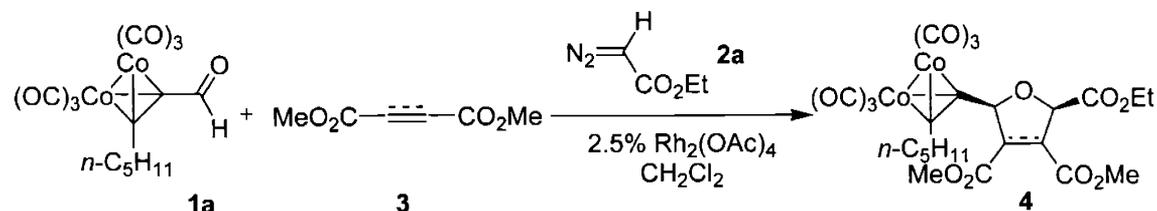
Even though a large number of metal salts react with the diazo compound, only complexes of Rh(II) and Cu(I) were effective to produce the three-component product.³² Evaluation of $\text{Rh}_2(\text{oct})_4$, $\text{Rh}_2(\text{TFA})_4$, $\text{Rh}_2(\text{pfb})_4$, $\text{Rh}_2(\text{cap})_4$, and $\text{Cu}(\text{OTf})$ found that only $\text{Rh}_2(\text{oct})_4$ was as effective as $\text{Rh}_2(\text{OAc})_4$.³³ The other catalysts required higher reaction

³² Use of the following catalysts failed to yield any cycloaddition products: $\text{Ag}(\text{OTf})$, $\text{Ag}(\text{OAc})$, AgSbF_6 , AuI , $\text{Ni}(\text{COD})_2$, NiCl_2 , $\text{Fe}(\text{DPPE})\text{Cl}_2$, $\text{Fe}(\text{TPP})$, $\text{FeCp}(\text{CO})_2\text{I}$, CoCp_2 , $\text{Co}(\text{acac})_3$, $\text{Ru}(\text{PPh}_3)_2\text{Cl}_2$, $\text{RuCl}_2(\text{COD})$, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$, $\text{Rh}(\text{CO})\text{PPh}_3\text{Cl}$, $\text{Rh}(\text{CO})_2(\text{acac})$, $[\text{RhCl}_2\text{Cp}^*]_2$, $\text{Pd}(\text{PPh}_3)_4$, PdCl_2 , $[\text{IrCl}(\text{COD})]_2$, IrCl_3 and $\text{Ir}(\text{acac})_3$.

³³ Employment of $\text{Rh}_2(\text{oct})_4$ in eq 1 provided **4e** in 73% yield

temperatures to be effective, produced the product in lower yields than $\text{Rh}_2(\text{OAc})_4$, but with no observable change in diastereoselectivity.³⁴

Table 6. Cycloaddition products of **1a** and **2a** using optimized stoichiometry.^[a]



Entry	Dipolarophile	Product	Yield
1 ^{[b],[c]}	 3a	 4a	68%
2 ^[c]	 3b	 4b	50%
3 ^[d]	 3c	 4c	50%

[a] Reaction conditions: EDA (3 mmol) in CH_2Cl_2 (5 mL) was added via syringe pump over 6 h to a solution of the cobalt complex (1 mmol) and dipolarophile (1 mmol) in CH_2Cl_2 (5 mL). [b] DMAD (1 mmol) in CH_2Cl_2 (2.5 mL) and EDA (3 mmol) in CH_2Cl_2 (5 mL) were added via separate syringes over the 6 h. [c] Single diastereomer as determined by crude ^1H NMR. [d] Reaction was conducted at reflux. Product was a 6:1 mixture of regioisomers; major diastereomer shown.

Application of the previously optimized stoichiometry (Table 2, entry 5) to the reactions of EDA (**2a**) and **1a** improved the yield with dimethyl maleate and dimethyl fumarate (Table 6,

³⁴ Yields with other catalysts ranged from 20-40%.

entries 2 and 3). Additionally, the products of carbonyl ylide cycloaddition to the carbene dimers of EDA were limited to under 5%. Reduction of the amount of EDA from 300 mol% resulted in less dimerization, allowing the carbonyl ylide to trap the desired dipolarophile. Less electron-poor olefins like methyl acrylate and styrene failed to provide the cycloaddition products even under these improved reaction conditions.³⁵ Once again, coupling of the carbonyl ylide with the by-products of EDA (diethyl fumarate and maleate) became the primary reaction pathway.

D. Scope of the Three Components

While holding the carbene source (TMSD, **2b**) and the cobalt cluster (**1a**) unchanged, a much broader dipolarophile scope was found to be possible than with EDA (Table 7). Dipolarophiles with at least one electron withdrawing group add to the 1,3-dipole in good yields. In the case of methyl acrylate (entry 4), cycloaddition (**4g**) was high yielding, but the regioselectivity was low. The isolated material was comprised of the compound shown along with a 3:1 mixture of *exo:endo* isomers of the other regioisomer.³⁶ The introduction of Lewis acids or different rhodium or copper catalysts had no noticeable effect on the distribution of the isomers of the tetrahydrofuran products.³⁷ Other unsymmetrical dipolarophiles (entries 5-7) exhibited good reactivity, but suffered from poor regioselectivity. Overall, the cycloaddition exhibited good stereoselectivity. Of the eight possible diastereomers that these reactions could produce, at most three could be detected. In all examples, the stereochemistry of the major

³⁵ Electron-rich olefins such as ethyl vinyl ether, phenyl vinyl sulfide, and 2,3-dihydrofuran were also unreactive.

³⁶ The diastereomers are completely inseparable and the material isolated is a single spot by TLC.

³⁷ Addition of Sn(OTf)₂, BF₃•OEt₂, AlMe₂Cl, La(OAc)₃, Sc(OTf)₃, Ga(acac)₃, or TiCl₄ produced no change in the integration of the regioisomers in the production of **4g**.

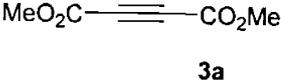
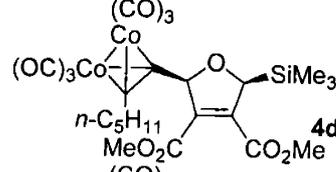
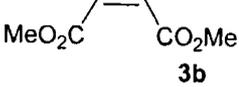
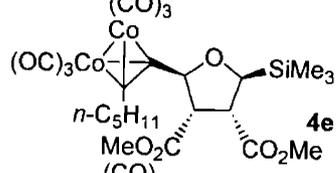
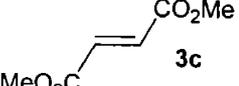
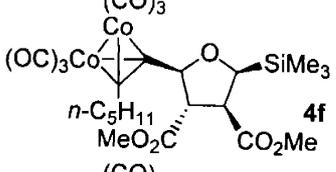
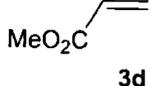
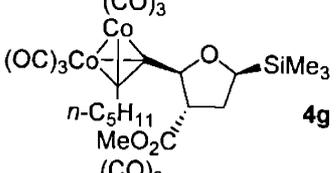
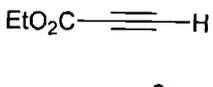
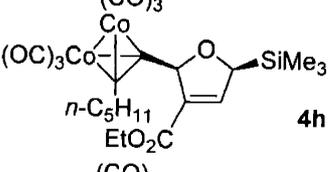
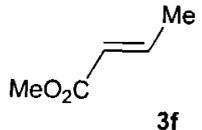
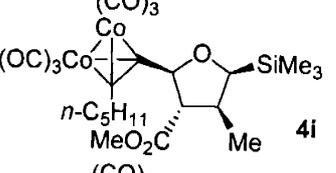
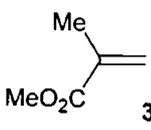
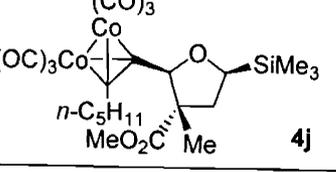
regioisomer had an exclusive 2,5-*cis* relationship and was the result of an *exo* mode of dipolarophile addition.³⁸

The carbonyl ylide generated from **1a** and **2b** can trap less activated, more challenging dipolarophiles (Table 8). The cycloaddition with styrene resulted in two tetrahydrofuran regioisomers in just greater than a 4:1 ratio with a combined yield of 46% (entry 1). The coupling and regioselectivity with 1-heptene was low, but highly *exo* selective. Norbornylene (entry 3) was nearly three-fold more efficient, and a single product from cycloaddition with this strained olefin was obtained in 29% yield.

These results are in sharp contrast to other reports of this type of cycloaddition where dioxolane formation becomes the major reaction pathway when less electron-poor dipolarophiles are used.¹¹⁻¹³ In all cases, dioxolane products comprise less than 10% of the reaction yield. However, attempts to employ electron-rich dipolarophiles, e.g. ethyl vinyl ether, phenyl vinyl sulfide, or vinyl acetate, fail to produce detectable amounts of the desired cycloaddition product. Addition of *trans*- or *cis*-stilbene produced no cycloaddition. Even when using dipolarophiles that do not effectively trap the nascent carbonyl ylide, dioxolane by-products are not increased, and the starting cobalt complex is typically recovered unchanged.

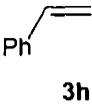
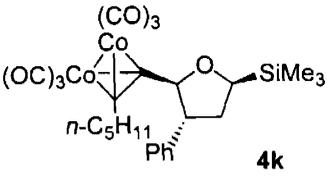
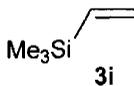
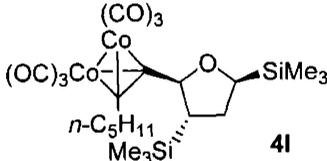
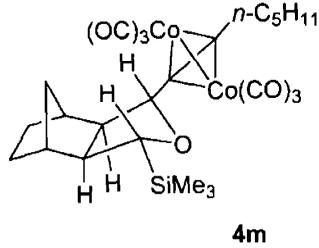
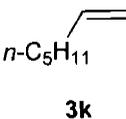
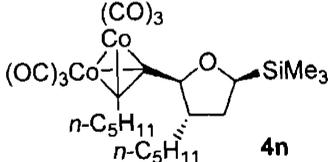
³⁸ The stereochemistry was assigned using 1D nOe experiments.

Table 7. Cycloaddition of **1a** and **2b** with activated dipolarophiles (eq 2).^[a]

Entry	Dipolarophile	Product	Yield ^[b]	d.r. ^[c]
1 ^[d]	 3a	 4d	32%	>20:1
2	 3b	 4e	74%	>20:1
3 ^[e]	 3c	 4f	66%	>6:1
4	 3d	 4g	73% (53:47)	>20:1 ^[f]
5	 3e	 4h	60% (75:25)	>20:1 ^[g]
6	 3f	 4i	55% (50:50)	>20:1 ^[h]
7 ^[e]	 3g	 4j	64% (71:29)	>20:1 ^[h]

[a] Standard conditions: TMSD (**2b**, 2 mmol) in CH₂Cl₂/hexanes (5 mL/1 mL) was added over 6 h to **1a** (1 mmol), dipolarophile (2 mmol), and Rh₂(OAc)₄ (0.025 mmol) in CH₂Cl₂ (5 mL). Structural assignment of **4f** by nOe measurements; **4e** was based on analogy to the X-ray structure of **6**. Assignments of other products were based on analogy. [b] Major isomer shown; regioselectivity in parentheses. [c] Diastereomeric ratios (d.r.) are from ¹H NMR and given for the major regioisomer. [d] DMAD (1 mmol) in 2.5 mL of CH₂Cl₂ was added via a separate syringe over 6 h. [e] Reaction conducted at reflux. [f] For the minor regioisomer, d.r. 3:1. [g] For the minor regioisomer, d.r. >20:1. [h] For the minor regioisomer, d.r. 1:1.

Table 8. Cycloaddition of **1a** and **2b** with various dipolarophiles (eq 2).^[a]

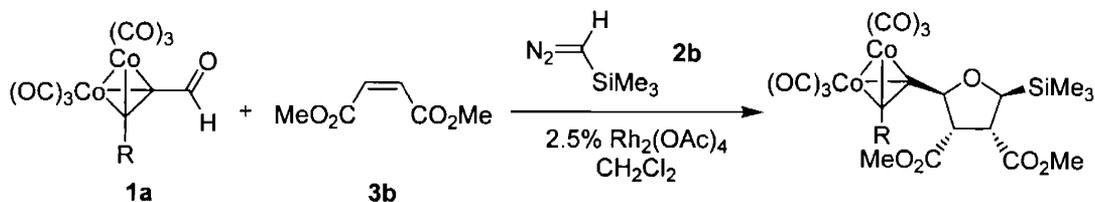
Entry	Dipolarophile	Product	Yield (%) ^[b]
1			46 (82:18)
2			37 (70:30)
3			29
4 ^[c]			11 (60:40)

[a] Standard conditions: TMSD (**2b**, 2 mmol) in CH₂Cl₂/hexanes (5 mL/1 mL) was added over 6 h to **1a** (1 mmol), dipolarophile (2 mmol), and Rh₂(OAc)₄ (0.025 mmol) in CH₂Cl₂ (5 mL). Structural assignments of **4k** and **4m** were based on nOe measurements. Structural assignments of other products were based on analogy. [b] Major product shown; regioselectivity given in parentheses. [c] The d.r. >20:1 for both regioisomers.

Table 9 includes examples of the three-component cycloaddition of TMSD and dimethyl maleate with dicobalt hexacarbonyl complexes of different alkynals. Substrates containing alkyl groups of different lengths react to generate products in similar yields (Table 9, entries 1 and 2). Both aryl substituents and branching are tolerated, affording tetrahydrofurans in good yields and high diastereoselectivity (Table 9, entries 3 and 4). The dialdehyde cobalt complex (**1e**)

produces tetrahydrofuran **9** in 29% yield.³⁹ The cobalt complex of 2-ynones, 2-ynoates and propargylic esters proved unreactive toward cycloaddition.

Table 9. Varying the cobalt cluster substituents in the three-component cycloaddition with **2b** and **3b**.^[a]



Entry	Cluster	R =	Yield (%)	Product	Diastereoselectivity
1	1a	<i>n</i> -C ₅ H ₁₁	74	5	>20:1
2	1b	Me	73	6	>20:1
3	1c	Ph	57	7	>20:1
4	1d	CH(OEt) ₂	69	8	>20:1
5	1e	CHO	29	9	>20:1

[a] Reaction conditions: To the cobalt complex (1 mmol) and dipolarophile in CH₂Cl₂ (5 mL) was added TMSD in CH₂Cl₂ (5 mL) via syringe pump over 6 h.

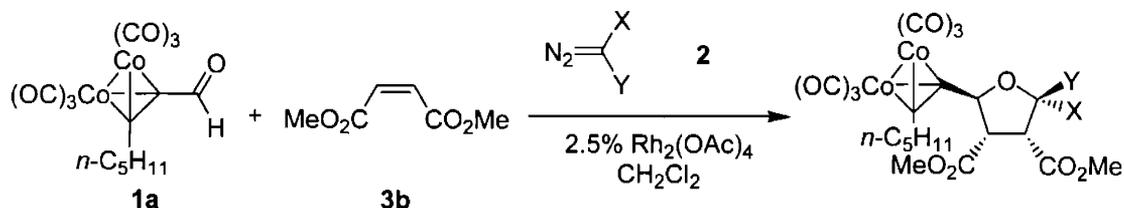
Other carbene sources were inferior in reactivity to TMSD (Table 10). For the silyl-substituted diazo compounds (entries 1, 3, and 4), cycloaddition products were produced in decreasing yields as the size of the substitution increased.⁴⁰ Diazo compounds that generated disubstituted carbenes were not successful in providing cycloaddition (entries 4 and 5.) It is likely that the steric constraints from the cobalt complex adjacent to the aldehyde began to

³⁹ Successive dipolar cycloaddition of the pendant aldehyde of **9** gives two bis(cycloaddition) isomers in a combined yield of 20% as a 1:1 ratio of diastereomers.

⁴⁰ Aoyama, T.; Shiori, T. *Chem. Pharm. Bull.* **1981**, *29*, 3249.

impede the reaction with more hindered carbenes. Nevertheless, in each case where dipolar cycloaddition takes place, only a single tetrahydrofuran diastereomer could be detected.

Table 10. Dipolar cycloaddition of diazo compounds (**2**) with **1a** and **3b**.^[a]



Entry	X =, Y =, 2	Yield (%)	Diastereoselectivity
1	H, SiMe ₃ , 2a	74	>20:1
2	H, CO ₂ Et, 2b	50	>20:1
3	H, SiMe ₂ Bn, 2c	63	>20:1 ^[c]
4	SiMe ₃ , SiMe ₃ , 2d	0	.. ^[b]
5	CO ₂ Et, CO ₂ Et, 2e	0	.. ^[b]

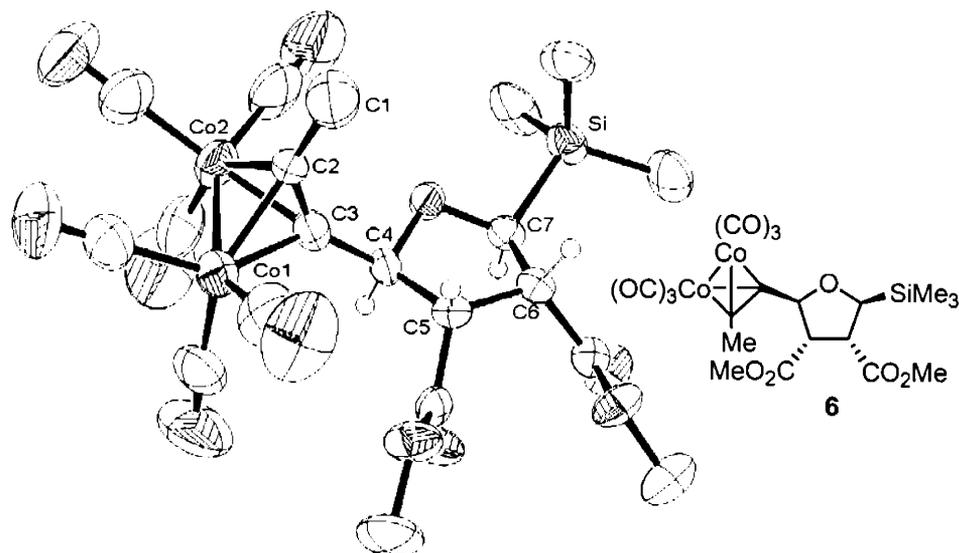
[a] Reaction conditions: To the cobalt complex (1 mmol) and dipolarophile (2 mmol) in CH₂Cl₂ (5 mL) was added the diazo compound (2 mmol) in CH₂Cl₂ (5 mL) over 6 h via syringe pump. [b] Not available. Recovered **1a**. [c] Compound **4e'**.

E. Proof of Stereochemistry and Cobalt Removal

The product of the cycloaddition of (μ,η^2 -2-butyne)Co₂(CO)₆, TMSD, and dimethyl maleate was isolated as a solid (**6**). Recrystallization from hexanes afforded material suitable for analysis by single-crystal X-ray diffraction.⁴¹ The structure (Figure 1) confirmed that a 2,5-*cis* relationship existed between the propynyl cobalt carbonyl complex and the trimethylsilyl group and that the stereochemistry of the dipolarophile was retained in the course of the reaction.

⁴¹ See Section L of the Supporting Information for full crystal structure details.

Figure 1. Molecular structure of **6**. Hydrogen atoms of the ring are depicted to highlight stereochemistry. Thermal ellipsoids of the ORTEP are set at the 50% probability level.



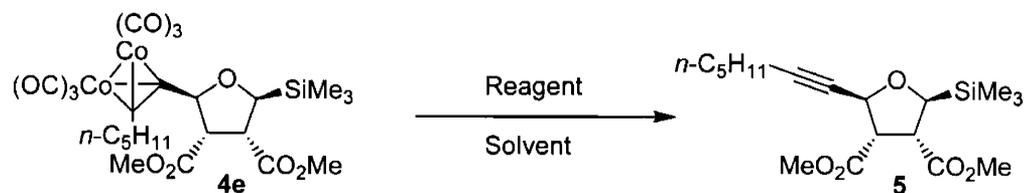
The cobalt cluster enables elaboration of the heterocycle via Pauson-Khand⁴² or Nicholas reactions. Attempts at removal of the cobalt cluster are described in Table 11. Ceric ammonium nitrate (CAN) fails to give the free alkyne **5** in high yield. Other commonly used methods of demetallation are also disappointing.⁴³ Liberation of the alkyne occurs in excellent yield upon exposure to molecular iodine (entry Table 11).⁴⁴

⁴² (a) Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855-5860. (b) Schore, N. E. *Org. React.* **1991**, *40*, 1-90. (c) Geis, O.; Schmalz, H.-G. *Angew. Chem., Int. Ed.* **1998**, *37*, 911-914. (d) Brummond, K. M.; Kent, J. L. *Tetrahedron* **2000**, *56*, 3263-3283.

⁴³ Jones, G. B.; Wright, J. M.; Rush, T. M.; Plourde, G. W., II; Kelton, T. F.; Mathews, J. E.; Huber, R. S.; Davidson, J. P. *J. Org. Chem.* **1997**, *62*, 9379-9381.

⁴⁴ Tanaka, S.; Tsukiyama, T.; Isobe, M. *Tetrahedron Lett.* **1993**, *34*, 5757-5760.

Table 11. Protocols for cobalt cluster removal.^[a]



Entry	Reagent	Solvent	Yield (%)
1	NMO	CH ₂ Cl ₂	56
2	CAN	Acetone	68
3	Fe(NO ₃) ₃	Acetone	72
4	NaSMe	DMSO	41
5	TBAF	THF	<10
6	I ₂	THF	97

[a] Reaction conditions: 500 mol% reagent was added to a solution of the cobalt complex at 0 °C.

F. Cobalt Catalysis

Although the cobalt cluster can be put onto and taken off of the alkyne in excellent yield, conditions employing a catalytic amount of a cobalt cluster would eliminate the protection and reprotection step of the alkyne.⁴⁵ Our attempts at realizing this goal were inspired by accounts of transfer of a cobalt cluster from one alkyne to another (Scheme 7).⁴⁶ The fact that this equilibrium favors electron-poor acetylenes pointed to the feasibility of modifying the reaction sequence to be catalytic in cobalt.⁴⁷ The electronic difference between product **4** and a 2-alkynal should favor production of **1**.

⁴⁵ The catalytic amount of cobalt cluster still needs to be removed from the product, but a substoichiometric amount of oxidizing agent is effective.

⁴⁶ Housecroft, C. E.; *Metal-Metal Bonded Carbonyl Dimers and Clusters*; Oxford University Press: Oxford, U.K., 1996, 63.

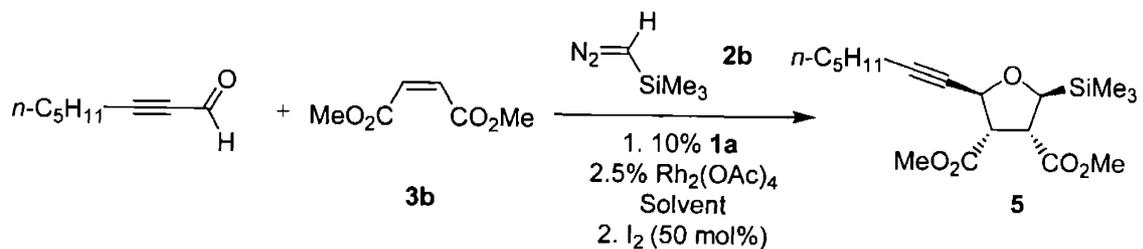
⁴⁷ The better backbonding ability of electron-poor alkynes is thought to be responsible for the equilibrium.

Scheme 7. Cobalt transfer between a cycloaddition product (**4**) and a propargylic aldehyde regenerates **1**.



When using only a catalytic amount of a cobalt cluster, a noticeable increase in the yield and diastereoselectivity occurs from changing the solvent from methylene chloride to toluene (Table 12). Diethyl ether was even more effective (entry 3). An increase in both yield and selectivity was attributed to the achievement of cobalt transfer, and choice of solvent was important in controlling this equilibrium. The yield of the catalytic cobalt process was at best 20% lower than in the stoichiometric case (Table 13). Changing temperature and reagent stoichiometry did not result in an improved yield, but for all reactions conducted in diethyl ether, the selectivity of the dipolar cycloaddition was >20:1.

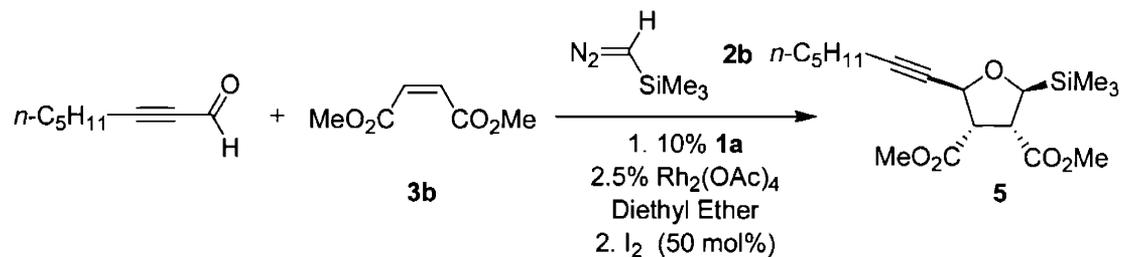
Table 12. Effects of solvent on a cobalt-cluster catalyzed dipolar cycloaddition.^[a]



Entry	Solvent	Yield (%)	Diastereoselectivity	[Co] TON
1	CH ₂ Cl ₂	11	3:1	1
2	THF	15	5:1	1.5
3	Toluene	23	10:1	2
4	Ether	55	>20:1	5.5

[a] Reaction conditions: To the alkyne (1 mmol) and **3b** (2 mmol) in the stated solvent (5 mL) was added the TMSD (2 mmol) in solvent (5 ml) via syringe pump over 9 h. TON is turnover number.

Table 13. Changing stoichiometry and temperature in cobalt-cluster catalyzed dipolar cycloadditions have an effect on the production of **5**.^[a]

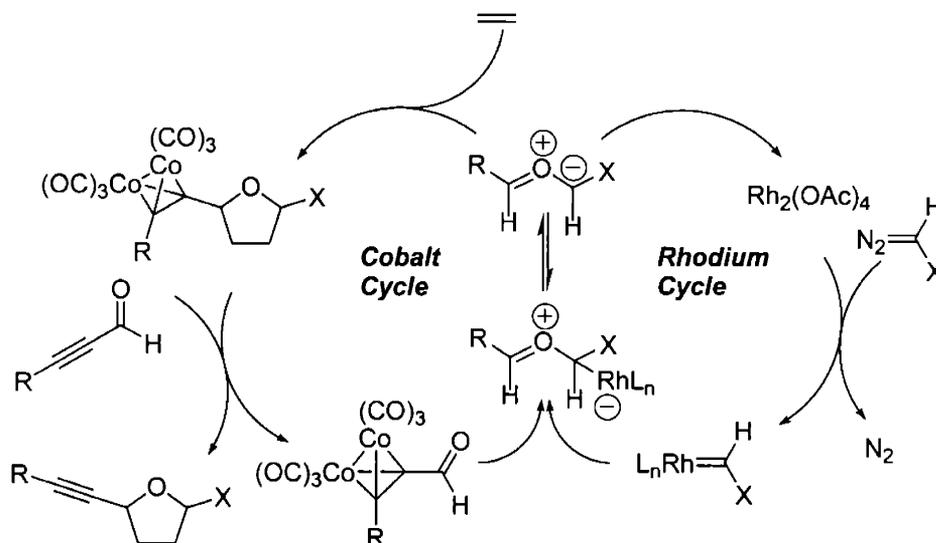


Entry	Aldehyde (mol%)	TMSD (mol%)	Dipolarophile (mol%)	Yield (%) ^[b]
1	90	100	100	11 (45)
2	190	100	200	41 (55)
3	290	100	300	12 (0)
4	90	200	200	30 (31)
5	90	100	200	22 (41)
6	190	200	100	13 (20)

[a] Reaction conditions: The cobalt complex, 2-alkynal and dipolarophile were dissolved in 5 mL Et₂O. TMSD (2 mmol) in 5 mL Et₂O was added via syringe pump over 9 h. [b] Yield at ambient temperature listed first. Yield of the identical reaction conducted at reflux shown in parentheses. Product in each reaction >20:1 d.r. by ¹H NMR. Yields are based on limiting reagent.

Scheme 8 presents how this catalytic cycle might work in tandem with the rhodium-mediated carbonyl ylide assembly. The small electronic difference in the starting alkyne and the product complex **4** might result in slow cobalt turnover and can be an explanation of the lower yield under the catalytic conditions.

Scheme 8. Cooperation of the two catalytic cycles is necessary for efficacious dipolar cycloaddition.



G. Attempts at Enantioselective, Catalytic Three-Component Dipolar Cycloadditions

With a highly diastereoselective three-component carbonyl ylide cycloaddition reaction in hand, investigations aimed at rendering the process enantioselective were conducted. We considered two strategies for controlling the handedness in the cycloaddition:

- 1) Exploration of asymmetric carbene catalysts;
- 2) Modification of the cobalt cluster with chiral ligands.

It is well-documented from a number of reactions that chiral Rh(II) and Cu(I) complexes can produce non-racemic compounds by carbene transfer. Asymmetric cyclopropanation of various olefins and C-H insertions have been reported.^{10g,11} Only recently have examples of enantioselective carbonyl ylide cycloadditions have been reported.^{48,49} In all of these cases, the

⁴⁸ Intramolecular: (a) Hodgson, D. M.; Stupple, P. A.; Johnstone, C. *Tetrahedron Lett.* **1997**, *38*, 6471-6472. (b) Hodgson, D. M.; Stupple, P. A.; Johnstone, C. *Chem. Commun.* **1999**, 2185-2186. (c) Hodgson, D. M.; Stupple, P. A.; Pierard, F. Y. T. M.; Labande, A. H.; Johnstone, C. *Chem. Eur. J.* **2001**, *7*, 4465-4476.

⁴⁹ Two-component couplings (diazo and carbonyl groups in the same molecule): (a) Kitagaki, S.; Anada, M.; Kataoka, O.; Matsuno, K.; Umeda, C.; Watanabe, N.; Hashimoto, S.-i. *J. Am. Chem. Soc.* **1999**, *121*, 1417-1418. (b) Kitagaki, S.; Yasugahira, M.; Anada, M.; Nakajima, M.; Hashimoto, S.-i. *Tetrahedron Lett.* **2000**, *41*, 5931-5935.

1,3-dipole is cyclic, formed through an intramolecular reaction of a carbene and a tethered carbonyl moiety.

We were initially drawn to the report by Doyle and co-workers describing low levels of enantioselection (up to 30% ee) in the trapping reaction of a carbonyl ylide by an aldehyde.^{13,50} The major diastereomer of the enantioenriched dioxolane has a 2,5-*cis* arrangement. Since the intermediate 1,3-dipole having an adjacent $\text{Co}_2(\text{CO})_6(\text{alkyne})$ fragment produces the same 2,5-*cis* arrangement in cycloadditions with alkenes, we examined several chiral Rh(II) complexes with the hope that some enantioselection could be achieved by a similar mechanism. The cobalt containing carbonyl ylides were unreactive toward aldehydes, so a direct comparison to this work of Doyle is not possible.⁵¹

Scheme 9 details the chiral catalysts that were examined. Application of chiral Rh(II) catalysts to the reaction of **1b**, **2b**, **3b** produced the cycloadduct in lower yield compared to $\text{Rh}_2(\text{OAc})_4$.⁵² In all cases, enantioselectivity could not be detected, and changing the solvent, temperature, or catalyst loading did not affect this outcome.⁵³ A simple explanation for the production of completely racemic products from these trials is that the metal catalyst is not associated with the 1,3-dipole when it reacts with a dipolarophile.

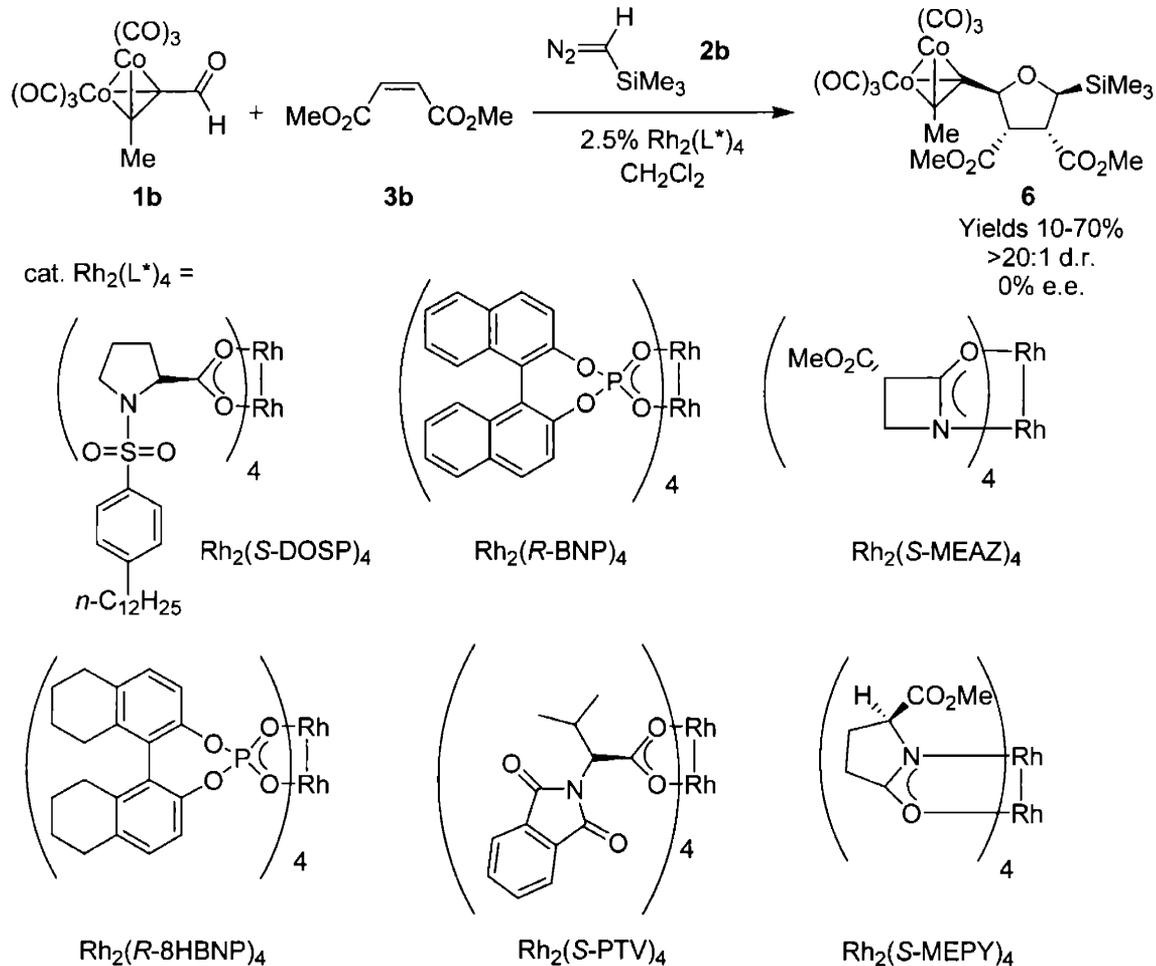
⁵⁰ Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, 98, 911-935.

⁵¹ Use of benzaldehyde, 4-methoxybenzaldehyde, or 4-nitrobenzaldehyde as dipolarophiles in eq 1, gave no new cobalt complex and **1a** could be recovered in good yield.

⁵² Yields ranged from 20-60%.

⁵³ Chiral GC analysis of the demetallated alkyne from **6** (G-TA column)

Scheme 9. Chiral Rh(II) catalysts do not provide enantioselectivity in carbonyl ylide cycloadditions.

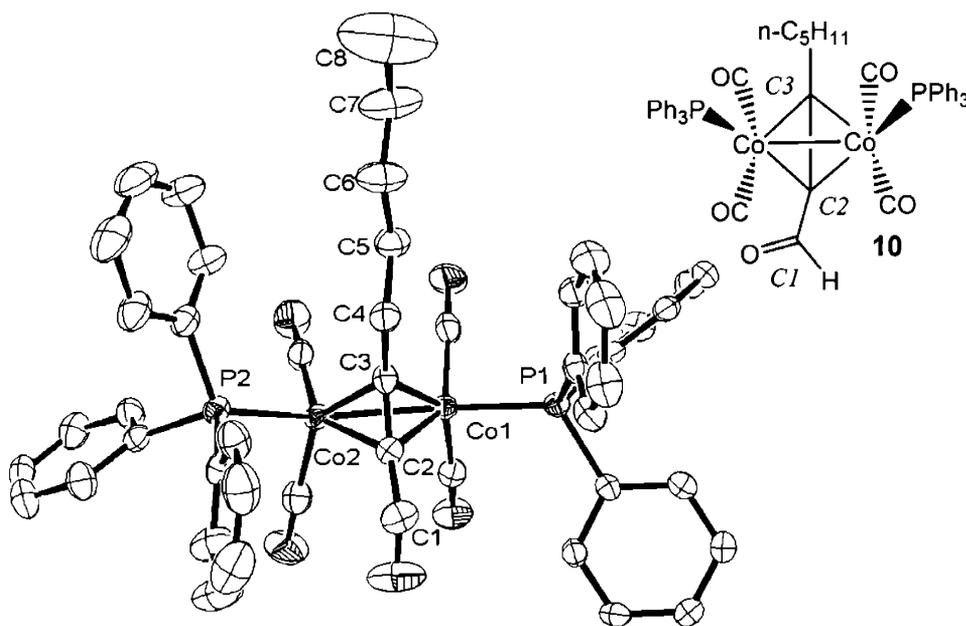


We next turned our efforts toward studying the effect of altering the ligand field of the cobalt cluster. Phosphine ligands readily displace as many as four carbonyls of dicobalt hexacarbonyl alkyne complexes.⁵⁴ Conducting the reaction depicted in eq 1 in the presence of both one and two equivalents of PPh_3 and $P(OEt)_3$ had a deleterious effect on the formation of cycloaddition products. Only under conditions with a cobalt cluster to triethylphosphite ratio of 1:1 resulted in the desired three-component cycloaddition. Removal of the cluster with CAN gave 43% of free alkyne **5** as a single diastereomer.

⁵⁴ Chia, L. S.; Cullen, W. R.; Franklin, M.; Manning, A. R. *Inorg. Chem.* **1975**, *14*, 2521-2526.

In the reaction employing an excess of PPh₃, the only product isolated was the 2:1 adduct of PPh₃ and **1a** (compound **10**).⁵⁵ An X-ray structure was obtained from crystals of **10** grown in ethyl acetate and hexane (Figure 2).⁵⁶ The Co-P bond distances of 2.22 Å and Co-Co bond length of 2.48 Å were typical of previously reported phosphine-substituted cobalt complexes of alkynes.⁵⁷ Examination of the structure suggested a simple steric reason for the low reactivity of **10**, that an aryl group from each of the PPh₃ ligands extends out beyond the aldehyde and shields it from reacting with the carbenoid.

Figure 2. The X-ray structure of (μ,η²-2-octynal)Co₂(CO)₄(PPh₃)₂. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms omitted for clarity.



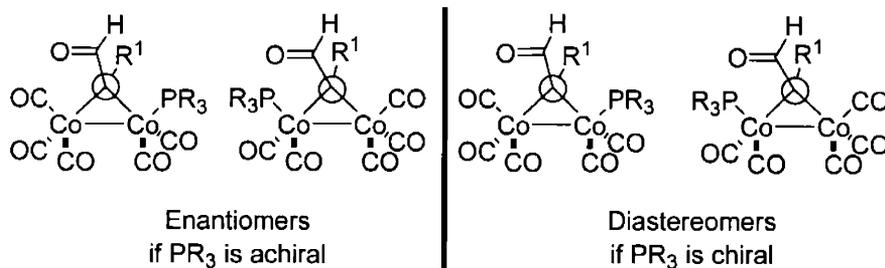
⁵⁵ Isolated in 34% yield.

⁵⁶ See Section L of the Supporting Information for full crystal structure details.

⁵⁷ Derdau, V.; Laschat, S.; Dix, I.; Jones, P. G. *Organometallics* **1999**, *18*, 3859.

The consequence of substitution of one of the cobalt atoms in an alkyne $\text{Co}_2(\text{CO})_6$ complex by a generic phosphorous ligand (PR_3) is represented in Scheme 10.⁵⁸ For unsymmetrical alkynes, modification of the cluster by a chiral ligand leads to two diastereomers.⁵⁹ In an attempt to determine if a chiral ligand on the cobalt cluster could direct the diastereoselectivity in the course of the cycloaddition reaction, the (-)-trimenthyl phosphite complex of **1e** was prepared. For **1e**, the symmetrical alkyne makes the formation of diastereomers is not possible (Scheme 10, where R^1 =aldehyde). Red blocks of this paramagnetic material were grown from diethyl ether, and the X-ray analysis is depicted in (Figure 3).⁶⁰ No crystal structures of cobalt alkyne carbonyl complexes containing a single phosphite ligand (either chiral or achiral) have been previously obtained, but the Co-P bond length of 2.18 Å, is only slightly shorter than in the structure of **7** (*vide supra*). At 2.49 Å, the Co-Co bond distance is basically identical to that in $(\mu, \eta^2\text{-2-octynal})\text{Co}_2(\text{CO})_4(\text{PPh}_3)_2$. The replacement of **1a** by chiral cobalt complex **11** under the conditions in eq 1 gives back **11** unchanged in greater than 80% mass recovery.⁶¹

Scheme 10. Substituting an alkynal-cobalt complex by a phosphorous ligand (PR_3) can lead to either enantiomers or diastereomers.



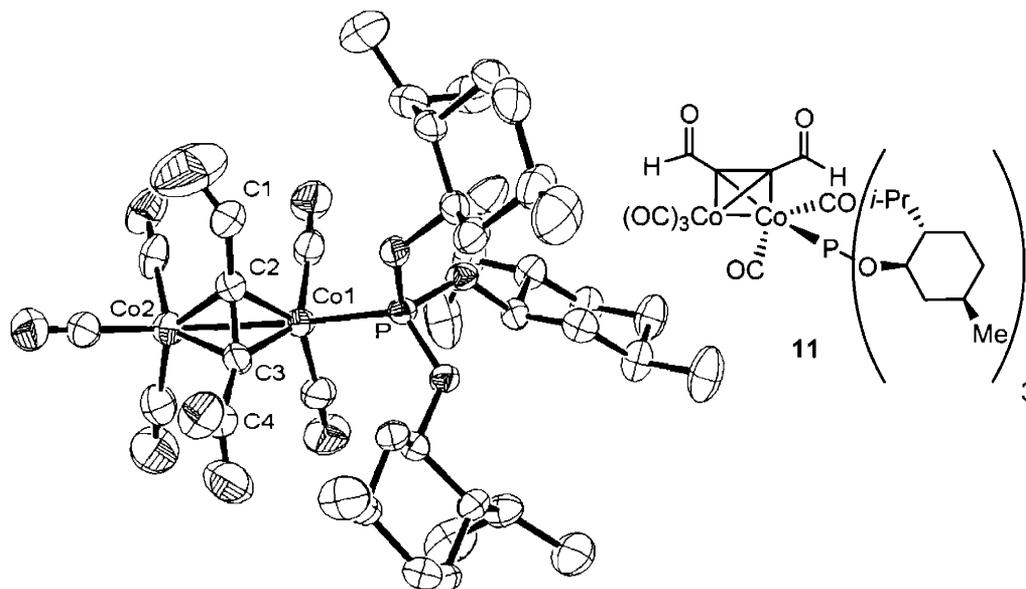
⁵⁸ Carbery, D. R.; Kerr, W. J.; Lindsay, D. M.; Scott, J. S.; Watson, S. P. *Tetrahedron Lett.* **41**, 3235-3239.

⁵⁹ Verdaguer, X.; Pericàs, M. A.; Riera, A.; Maestro, M. A.; Mahía, J. *Organometallics* **2003**, *22*, 1868-1877.

⁶⁰ See Section L of the Supporting Information for full crystal structure details.

⁶¹ Even under forcing conditions (refluxing toluene) **11** is recovered in good yield. Four new aldehyde resonances in a ratio of 2:1.5:3:1 are detectable in the ^1H NMR of the crude reaction mixture. If these products correspond to the four possible diastereomers from a dipolar cycloaddition on one of the aldehydes of **11**, then the diastereoselectivity imparted by this chiral ligand is low.

Figure 3. ORTEP representation of $(\mu, \eta^2\text{-ADC})\text{Co}_2(\text{CO})_5[(-)\text{-trimenthyl phosphite}]$. Thermal ellipsoids drawn at 50% probability. The solid state structure is composed of equal *syn* and *anti* aldehyde conformations, which are represented at C4 in the figure. Hydrogen atoms omitted for clarity.



H. Stereochemical Model and Mechanistic Discussion

The results from the exploration of each of the reaction parameters allow us to comment on the mechanism of this transformation. As shown in Scheme 3, the first issue to address is whether the catalyst that transfers the carbene to the aldehyde remains coordinated during cycloaddition (**A** versus **B**).

The evidence supporting the involvement of a metal-free ylide (**A**), is that the cycloaddition of **1a**, TMSD, and methyl acrylate using several Rh(II) dimers and a Cu(I) catalyst provides identical distributions of isomers. It is highly unlikely that Rh(II) dimers of various steric and electronic properties and the copper source could each give the *exact* selectivity if bound to the dipole during reaction with the alkene. The only reasonable explanation for the

unaltered diastereoselectivity is if the cycloaddition proceeds via a common intermediate. Free ylide **A** satisfies this condition.

Scheme 11 follows the mechanistic pathways available for the production of free ylide **A**. Direct dissociation of the metal catalyst from **B** would generate the highly reactive, unstable ylide intermediate **A**. A more energetically favorable pathway to produce **A** might instead be from epoxide **C**.⁶² Ring closure of **B** to **C** returns the catalysts to the reaction medium.⁶³ Reversible interconversion of **A** and **C** by electrocyclic ring closing and opening would eliminate any enantioselectivity produced in the reaction of **1** in the presence of chiral metal catalysts.⁶⁴

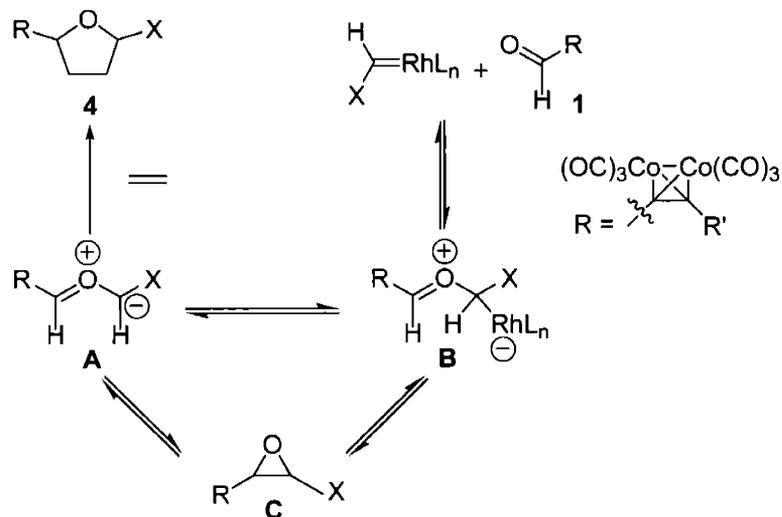
The fact that no **C** has been identified from the reaction mixture does not preclude it as an intermediate in the formation of **4**. In many cases, unproductive reactions permitted recovery of **1**, but no **C** was ever observed. Epoxides with a proximal (alkyne)Co₂(CO)₆ fragment might be especially prone to decomposition through a Nicholas cation intermediate.²⁴ If **A** and **C** interconvert, then reassociation of the metal to free ylide **A** could serve to regenerate **1** and the metal bound carbene. It is at present impossible to distinguish whether free ylide **A** is formed from **B** or **C**; however, the dipolar cycloaddition of cobalt cluster-containing carbonyl ylides does not likely happen by way of **B**, the metal-bound ylide. Further studies are required to fully elucidate the mechanism and determine whether epoxide **C** is an intermediate in this process.

⁶² See reference 18 for the generation of epoxides from stabilized carbenes and aromatic aldehydes.

⁶³ Cyclic 1,3-dipoles have so far been required for the observation of enantioselectivity (refs 32 and 33). Rate of electrocyclic ring-closure is probably much slower with these 1,3-dipoles because of strain. Harsh conditions are frequently necessary to generate carbonyl ylides from epoxides (reference 12).

⁶⁴ Carbonyl ylides are planar.

Scheme 11. A metal-free carbonyl ylide (**A**) can originate from epoxide **C**.



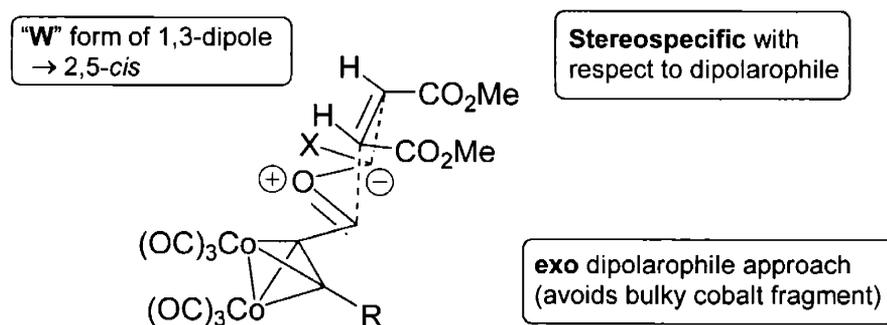
Incorporating the results from the crystal structure of **6** and the evidence for cycloaddition through a free ylide, a stereochemical model can be constructed to account for the high selectivity observed in the cycloaddition (Figure 4). The dipolarophile reacts stereospecifically, so a true, concerted cycloaddition mechanism is operative.⁶⁵ The invariability of the 2,5-*cis* arrangement of the cycloaddition products means the dipolarophile only reacts with the cobalt cluster-containing carbonyl ylide in a “**W**” conformation.⁶⁶ The presence of the adjacent cobalt cluster encourages an *exo* dipolarophile trajectory to avoid a steric interaction of the approaching group and the cobalt cluster. The same model also accounts for the selectivity in reactions of unsymmetrical dipolarophiles. Again, the carbonyl ylide reacts only through a “**W**” conformation. The stabilization of the positive charge of the dipole by the cobalt cluster (Scheme 6) makes the distal end of the carbonyl ylide more nucleophilic. Alignment of that carbon of the dipole with the more electrophilic carbon of the dipolarophile

⁶⁵ Maleate esters (*cis*) lead to only *cis* cycloaddition products; Fumarate esters (*trans*), lead only to *trans* cycloaddition products.

⁶⁶ Houk, K. N.; Rondan, N. G.; Santiago, C.; Gallo, C. J.; Gandour, R. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1980**, *102*, 1504-1512, and references therein. The Woodward-Hoffman rules dictate that both the dipole and dipolarophile react suprafacially in a thermal, six electron cycloaddition.

accounts for the observed sense of regioselectivity. The size of the cobalt cluster forces an *exo* olefin trajectory and leads to the prediction of the same major product that is detected from the reaction sequence.

Figure 4. A model consistent with the stereochemical outcome obtained in the dipolar cycloaddition of cobalt cluster-containing carbonyl ylides.



I. Conclusion

The incorporation of an alkynyl dicobalt hexacarbonyl complex adjacent to a carbonyl ylide confers increased reactivity, selectivity and scope in reactions with a wide variety of unsaturated carbon-carbon bonds. In a single step, highly substituted tetrahydrofuran products are constructed in moderate to good yields with high selectivity from three separate starting materials. The stabilizing effect of a dicobalt hexacarbonyl cluster and exploitation of TMSD as the carbene source both prove critical to allow expansion of the process to include dipolarophiles like methyl acrylate and styrene. Subsequent removal of the cobalt fragment with iodine is demonstrated in near quantitative yield. While the use of a catalytic amount of cobalt benefits the reaction, the stoichiometric variant is ultimately higher yielding. Evidence suggests the reaction proceeds by way of a free ylide (**A**), arising directly from **B** or by a cobalt-assisted reversible formation from epoxide **C**.

J. Experimental Section

Unless stated otherwise, all compounds were purchased from commercial suppliers (Acros, Aldrich, Alfa Aesar, or Strem) and used without further purification. THF, Et₂O and toluene were distilled from sodium/benzophenone ketyl. All other anhydrous grade solvents were purchased from Aldrich Chemical Co. Dicobalt octacarbonyl (Co₂(CO)₈) was purchased exclusively from Strem Chemicals, Inc. Trimethylsilyldiazomethane (2.0 M solution in hexanes or ether) was purchased from Aldrich Chemical Co.

Analytical thin layer chromatography (TLC) was performed on silica gel 60 F₂₅₄ aluminum plates precoated with a fluorescent indicator. Flash chromatography was performed using silica gel 60 (40-63 μm) from Silicycle. All ¹H and ¹³C NMR spectra were recorded using Varian 300 MHz or 500 MHz spectrometers at ambient temperature. IR spectra were recorded as a thin film between NaCl plates on a Perkin-Elmer Model 2000 FT-IR instrument. Regioselectivity in the dipolar cycloaddition reaction was determined by ¹H NMR integrations of the signals corresponding to the hydrogen atom of the heterocycle also adjacent to the cobalt cluster.

Preparation of dicobalt hexacarbonyl alkyne clusters. All dicobalt hexacarbonyl alkyne complexes were synthesized from the commercially available aldehyde (procedure 1) or the corresponding diethyl acetal (procedure 2). Any example of each follows:

Procedure 1)

Dicobalt hexacarbonyl complex of 2-octynal (1a). A 1 L round bottom flask was charged with 7.70 mL (54.0 mmol) of 2-octynal. Dry ether (500 mL) was added followed by dicobalt octacarbonyl (20.3 g, 59.3 mmol) in one portion. Evolution of gas was observed almost immediately and a needle was inserted through the rubber septum to facilitate pressure

equilibrium. After gas evolution had ceased and the solution had been stirred for three hours the ether was removed using a rotary evaporator. The residue was purified by silica gel chromatography using 20:1 hexanes:ethyl acetate. Evaporation of the eluent provided the title compound as a thick, dark red oil (21.5 g, 52.4 mmol, 97%.) This compound, although moderately sensitive to air and heat, could be used over several weeks with no noticeable change in reactivity if stored in a freezer ($-30\text{ }^{\circ}\text{C}$) under an inert atmosphere. IR (NaCl): 2933, 2028, 1669, 1581, 1125 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 10.30 (s, 1H), 2.91 (br s, 2H), 0.90-1.90 (br m, 9H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 199 (br), 190.9, 34.7, 32.1, 31.8, 22.7, 14.3, resonances from the alkyne carbons not observed; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{12}\text{Co}_2\text{O}_7$ [$M+\text{Na}$] 432.9139, found 432.9148.

Procedure 2)

Dicobalt hexacarbonyl complex of 2-butyne (1b). To a 1 L round bottom flask was added 2-butyne diethyl acetal (5.6 mL, 35.4 mmol) followed by THF (300 mL). To this solution was added dicobalt octacarbonyl (12.7 g, 37.1 mmol) in one portion. Evolution of gas was observed almost immediately and a needle was inserted through the rubber septum to facilitate pressure equilibrium. After gas evolution had ceased and the solution had been stirred for three hours, the solution was cooled in a water/ice bath. A 1 N solution of HCl (300 mL) was then added, and acetal hydrolysis was monitored by TLC analysis (approximately 6 hours). After removal of the THF using a rotary evaporator, the crude reaction mixture was transferred to a separatory funnel with ether. The ether layer was washed with water (2 X 150 mL), and then with brine (150 mL). The ether layer was dried over MgSO_4 , filtered, and concentrated using a rotary evaporator to yield a dark red solid. The residue was purified by silica gel chromatography using 20:1 hexanes:ethyl acetate, and evaporation of the eluent provided the title compound as a dark red

solid (11.9 g, 33.6 mmol, 95% over the two steps.) This compound, although moderately sensitive to air and heat, could be used over several weeks with no noticeable change in reactivity if stored in a freezer (-30°C) under an inert atmosphere. CAUTION: Special care should be taken to avoid prolonged contact with air, as this solid has been found to be pyrophoric. IR (NaCl, CDCl_3): 2906, 2101, 2033, 1663, 1583, 1126 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 10.30 (s, 1H), 2.74 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 198.7 (br), 191.6, 21.4, resonances from the alkyne carbons not observed; HRMS: (ESI) m/z calcd for $\text{C}_{10}\text{H}_4\text{Co}_2\text{O}_7$ [$M+\text{Na}$] 376.8513, found 376.8521.

Dicobalt hexacarbonyl complex of phenylpropargyl aldehyde (1c). According to procedure 2, reaction of phenylpropargyl aldehyde diethyl acetal (5.2 mL, 25 mmol) with dicobalt octacarbonyl (9 g, 26 mmol) afforded 9.6 g (23 mmol, 92% yield) of title compound. IR (NaCl): 2956, 2101, 2033, 1667, 691 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz): δ 10.54 (s, 1H), 7.60 (m, 2H), 7.39 (m, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 198.4 (br), 191.8, 137.0, 130.5, 129.9, 129.7, 92.8, 86.2.

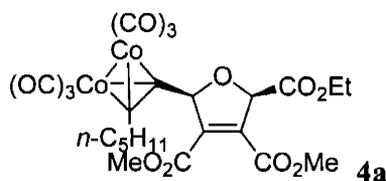
Dicobalt hexacarbonyl complex of 4,4-diethoxy-2-butyne-1-al (1d). According to procedure 1, reaction of 4,4-diethoxy-2-butyne-1-al (1.0 g, 6.5 mmol) with dicobalt octacarbonyl (2.3 g, 6.7 mmol) afforded 2.8 g (6.3 mmol, 97% yield) of title compound. IR (NaCl): 2982, 2934, 2879, 2062, 1668, 1583, 1066 cm^{-1} . ^1H NMR (CDCl_3 , 500 MHz): δ 10.28 (s, 1H), 5.50 (s, 1H), 3.73 (m, 4H), 2.45 (m, 6H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 198 (br), 191.4, 102.1, 95.7, 85.0, 64.3, 15.7.

Dicobalt hexacarbonyl complex of acetylene dicarbaldehyde (1e). Using procedure 2, reaction of 1,1,4,4-tetraethoxy-2-butyne (5.0 mL, 21 mmol) with dicobalt octacarbonyl (7.5 g, 22

mmol) afforded 5.2 g (14 mmol, 67% yield) of the title compound. IR (NaCl,): 2087, 2039, 1663 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz): δ 10.30 (s, 1H).

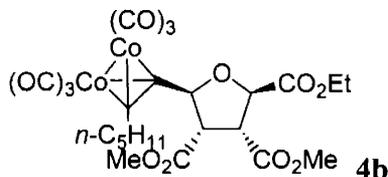
Standard experimental procedure used for the intermolecular carbonyl ylide cycloadditions with diazo compounds, cobalt alkyne complexes of 2-alkynals, and dipolarophiles.

For the exact proportion of reagents please refer to appropriate table in the text. All reactions were performed on a 1 mmol scale. An over-dried 50mL flask with teflon coated stir bar was sealed with a rubber septum and cooled under an Ar atmosphere. The aldehyde (1 mmol), 5mL solvent, dipolarophile (2 mmol) and carbene transfer reagent (e.g. $\text{Rh}_2(\text{OAc})_4$) were added to the flask. The diazo compound was diluted to a volume of 6 mL with addition reaction solvent and allowed to add to the reaction vessel containing the other components over 6h via syringe pump (1 mL/min). When the diazo compound had added, the reaction was filtered through a 4 cm plug of silica gel, eluting with CH_2Cl_2 . Concentration in vacuo and silica gel chromatography (hexanes:dichloromethane) yielded tetrahydrofurans listed. Yields refer to combined cycloaddition isomers. Diastereoselectivity of the reaction determined by ^1H NMR.

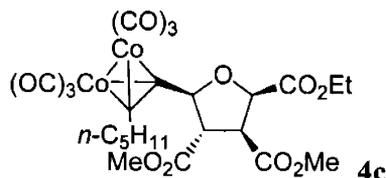


The standard procedure was used with **1a** (0.420 g, 1.02 mmol), except for the following modifications. The dipolarophile, dimethyl acetylenedicarboxylate (**3a**, 125 μL , 1.02 mmol), was not added to the reaction vessel, but instead taken up into an air-tight syringe and diluted to 2.5 mL with CH_2Cl_2 . The diazo compound, **2a** (315 μL , 3.00 mmol), was diluted to a volume of 2.5 mL with CH_2Cl_2 . These two solutions were introduced to the reaction mixture over 6 hours. Silica gel chromatography (20:1 hexanes:ethyl acetate) provided **4a** as a dark red oil (0.443 g,

0.69 mmol, 68% yield). IR (NaCl): 2958, 2091, 2050, 2021, 1734 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 6.51 (d, $J=6.0$ Hz, 1H), 5.55 (d, $J=5.7$ Hz, 1H), 4.23-4.29 (m, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 2.72-2.79 (m, 2H), 1.46-1.67 (m, 2H), 1.35-1.48 (m, 4H), 1.29 (t, $J=7.2$ Hz, 3H), 0.93 (t, $J=7.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 200.1 (br), 168.9, 162.8, 162.3, 138.1, 136.9, 100.8, 93.6, 88.8, 85.3, 62.8, 53.4, 53.3, 34.3, 32.4, 32.2, 23.1, 14.8, 14.6; HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{24}\text{Co}_2\text{O}_{13}$ [$M+\text{Na}$] 660.9773, found 660.9760.

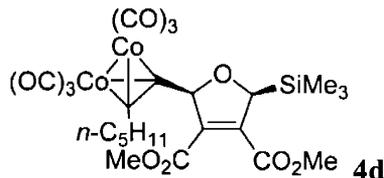


The standard procedure was followed with **1a** (0.411 g, 1.00 mmol), **3b** (250 μL , 2.00 mmol), and **2a** (210 μL , 2.00 mmol). Silica gel chromatography (3:1 hexanes:dichloromethane) provided **4b** as a dark red oil (0.322 g, 0.50 mmol, 50% yield). IR (NaCl): 2956, 2091, 2051, 1738 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 5.83 (d, $J=8.5$ Hz, 1H), 4.74 (d, $J=6.5$ Hz, 1H), 4.17-4.25 (m, 2H), 3.84 (dd, $J=6.5$ Hz, 6.0 Hz, 1H), 3.71 (s, 3H), 3.68 (s, 3H), 3.20 (t, $J=8.3$ Hz, 1H), 2.78-2.83 (m, 2H), 1.60-1.72 (m, 2H), 1.33-1.49 (m, 4H), 1.15-1.31 (m, 5H), 0.90 (t, $J=7.3$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz): δ 199.5 (br), 169.9, 169.5, 168.9, 101.9, 95.1, 80.7, 78.6, 61.9, 54.8, 52.8, 52.7, 51.4, 34.0, 32.1, 31.9, 22.8, 14.5, 14.4; HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{26}\text{Co}_2\text{O}_{13}$ [$M+\text{Na}$] 662.9930, found 662.9910.

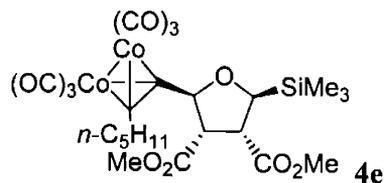


Except that the reaction was conducted at reflux, the standard procedure was followed with **1a** (0.411 g, 1.00 mmol), **3c** (0.288 g, 2.00 mmol), and **2a** (250 μL , 2.00 mmol). Silica gel chromatography (3:1 hexanes:dichloromethane) provided **4c** as a dark red oil (0.321 g, 0.50 mmol, 50% yield). IR (NaCl): 2956, 2014, 1741 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ 5.52 (d, $J=7.5$ Hz, 1H), 4.95 (d, $J=4.0$ Hz, 1H), 4.25 (q, $J=7.5$ Hz, 2H), 3.86 (t, $J=5.2$ Hz, 1H partially obscured by methyl ester resonances), 3.79 (s, 3H), 3.77 (s, 3H), 3.41 (t, $J=7.5$ Hz, 1H), 2.81 (t, $J=8.3$ Hz, 2H), 1.60-1.65 (m, 2H), 1.20-1.49 (m, 7H), 0.93 (t, $J=7.0$ Hz, 3H). Selected resonances for minor isomer: 5.22 (d, $J=8.5$ Hz, 1 H minor), 4.81 (d, $J=8.5$ Hz, 1H minor), 3.73 (s, 3H minor), 3.70 (s, 3H minor), all other resonances are nearly isochronous with major isomer;

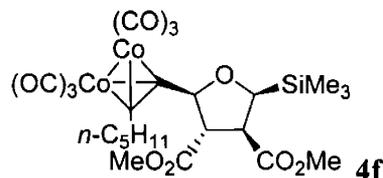
^{13}C NMR (CDCl_3 , 125 MHz): δ 199.5 (br), 171.2, 171.1, 170.8, 101.0, 93.8, 83.0, 79.3, 66.2, 62.1, 54.9, 53.2, 52.7, 34.1, 32.1, 31.7, 22.8, 14.5, 14.4 resonances from major isomer only; HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{26}\text{Co}_2\text{O}_{13}$ [$M+\text{Na}$] 662.9930, found 662.9946.



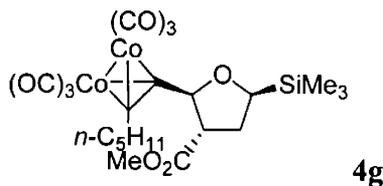
The standard procedure was used with **1a** (0.410 g, 1.00 mmol), except for the following modifications. The dipolarophile, dimethyl acetylenedicarboxylate (**3a**, 125 μL , 1.02 mmol), was not added to the reaction vessel, but instead taken up into an air-tight syringe and diluted to 2.5 mL with CH_2Cl_2 . The diazo compound, **2b** (1.0 mL, 2.0 mmol), was diluted to a volume of 2.5 mL with CH_2Cl_2 . These two solutions were introduced to the reaction mixture over 6 hours. Silica gel chromatography (3:1 hexanes:dichloromethane) provided **4d** as a dark red oil (0.205 g, 0.32 mmol, 32% yield). IR (NaCl): 2956, 2861, 2111, 2047, 1720, 1250 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 6.24 (d, $J=8.1$ Hz, 1H), 4.78 (d, $J=7.8$ Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 2.92 (dd, $J=8.1$ Hz, 7.8 Hz, 2H), 1.62-1.71 (m, 2H), 1.2-1.47 (m, 4H), 0.92 (t, $J=7.2$ Hz, 3H), 0.15 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 200.6 (br), 164.7, 163.7, 146.1, 133.3, 101.5, 93.6, 88.1, 82.0, 52.9, 52.7, 34.6, 32.5, 32.1, 23.1, 14.7, -2.7; HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{24}\text{Co}_2\text{O}_{11}\text{Si}$ [$M+\text{Na}$] 660.9957, 660.9931 found.



The standard procedure was followed with **1a** (0.411 g, 1.00 mmol), **3b** (250 μL , 2.00 mmol), and **2b** (1.0 mL, 2.0 mmol). Silica gel chromatography (3:1 hexanes:dichloromethane) provided **4e** as a dark red oil (0.476 g, 0.74 mmol, 74% yield). IR (NaCl): 2956, 2005, 2016, 1744 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 5.18 (d, $J=8.7$ Hz, 1 H), 3.87 (d, $J=9.9$ Hz, 1 H), 3.70 (s, 3 H), 3.68 (s, 3 H), 3.35 (dd, $J=9.9$, 9.9 Hz, 1 H), 2.95 (dd, $J=9.0$, 9.0 Hz, 1 H), 2.78 (dd, $J=6.9$, 6.3 Hz, 2 H), 1.25-1.67 (m, 6 H), 0.92 (t, $J=7.2$ Hz, 3 H), 0.07 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 199.9 (br), 172.6, 171.2, 100.4, 94.0, 82.6, 75.1, 56.3, 52.3 (2 resonances), 50.3, 33.9, 32.0, 31.7, 22.7, 14.2, -3.8; HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{30}\text{Co}_2\text{O}_{11}\text{Si}$ [$M+\text{Na}$] 663.0114, found 663.0109.

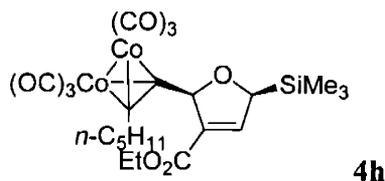


Except that the reaction was conducted at reflux, the standard procedure was followed with **1a** (0.411 g, 1.00 mmol), **3c** (0.288 g, 2.00 mmol), and **2b** (1.0 mL, 2.0 mmol). Silica gel chromatography (3:1 hexanes:dichloromethane) provided **4f** as a dark red oil (0.421 g, 0.66 mmol, 66% yield). IR (NaCl): 2956, 2021, 1742, 1618, 1173 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 5.08 (d, $J=7.8$ Hz, 1H minor), 4.91 (d, $J=8.1$ Hz, 1H, major), 3.75 (s, 3H major), 3.71 (s, 3H major), 3.62-3.72 (m, 1H major + 1H minor + 6H minor from ester protons), 3.59 (two overlapping doublet of doublets, $J_{\text{major}}=7.8$ Hz, 3.9 Hz, 1H major + 1H minor), 3.46 (two overlapping doublet of doublets, $J_{\text{major}}=7.8$ Hz, 3.8 Hz, 1H major + 1H minor), 2.81 (two overlapping doublet of doublets, $J_{\text{major}}=8.1$ Hz, 7.2 Hz, 2H major + 2H minor) 1.59-1.71 (m, 2H major + 2H minor), 1.21-1.49 (m, 4H major + 4H minor), 0.93 (two overlapping triplets, $J_{\text{major}}=6.9$ Hz, 3H major + 3H minor), 0.13 (s, 9H minor), 0.09 (s, 9H major). ^{13}C NMR (CDCl_3 , 125 MHz): δ 199.9 (br), 173.2, 173.1, 100.2, 94.0, 85.2, 76.8, 55.5, 52.6, 52.3, 51.9, 34.2, 32.2, 31.9, 22.9, 14.4, -2.8, resonances from major isomer only; HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{30}\text{Co}_2\text{O}_{11}\text{Si}$ [$M+\text{Na}$] 662.9930, found 662.9920.

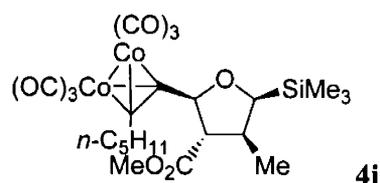


The standard procedure was followed with **1a** (0.411 g, 1.00 mmol), **3d** (180 μL , 2.00 mmol), and **2b** (1.0 mL, 2.0 mmol). Silica gel chromatography (3:1 hexanes:dichloromethane) provided **4g** as a dark red oil (0.423 g, 0.73 mmol, 73% yield). IR (NaCl): 2957, 2090, 2020, 1739, 1615 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ 4.96 (d, $J=7.5$ Hz, 1H major), 4.94 (t, $J=8.0$ Hz, 1H minor), 3.73 (s, 3H major), 3.71 (s, 3H minor), 3.65 (t, $J=7.2$ Hz, 1H major, partially obscured by methyl ester resonances), 3.62 (d, $J=9.0$ Hz, 1H minor), 3.03 (br m, 1H minor), 2.79-2.81 (m, 2H all isomers + 1H major), 2.61 (br m, 1H minor), 2.35 (br m, 1H major), 2.11 (br q, $J=11.5$ Hz, 1H major), 1.83 (br q, $J=10.5$ Hz, 1H minor), 1.63-1.66 (m, 2H all isomers), 1.26-1.44 (m, 4H all isomers), 0.93 (overlapping triplets, $J=6.7$ Hz, 3H all isomers), 0.08 (s, 9H minor), 0.6 (s, 9H major), selected resonances for endo isomer of minor product: 4.78, (t, $J=7.8$ Hz), 3.55 (d,

$J=8.0$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz): δ 200.0 (br), 174.3, 100.0, 99.2, 84.3, 73.0, 53.1, 52.3, 34.2, 33.7, 32.1, 31.9, 22.9, 14.4, -3.6, resonances from major isomer only; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{28}\text{Co}_2\text{O}_9\text{Si}$ [$M+\text{Na}$] 605.0059, found 605.0032.

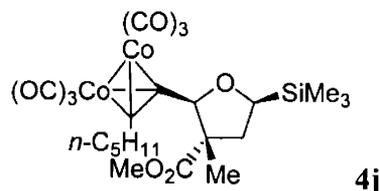


The standard procedure was followed with **1a** (0.412 g, 1.00 mmol), **3e** (205 μL , 2.02 mmol), and **2b** (1.0 mL, 2.0 mmol). Silica gel chromatography (3:1 hexanes:dichloromethane) provided **4h** as a dark red oil (0.355 g, 0.60 mmol, 60% yield). IR (NaCl): 2960, 2875, 2091, 2050, 1721, 1248 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 7.02 (s, 1H minor), 6.56 (s, 1H, major), 6.17 (d, $J=3.6$ Hz, 1H minor), 6.10 (d, $J=4.5$ Hz, 1H major), 4.77 (d, $J=3.3$ Hz, 1H major), 4.64 (d, $J=4.5$ Hz, 1H minor), 4.17-4.36 (2 overlapping quartets, $J_{\text{major}}=4.5$ Hz, $J_{\text{minor}}=4.2$ Hz, 2H major + 2H minor), 2.81-2.98 (m, 2H major + 2H minor), 1.64-1.78 (m, 2H major + 2H minor), 1.26-1.51 (m, 7H major + 7H minor), 0.89-0.98 (m, 3H major + 3H minor), 0.38 (s, 9H minor), 0.15 (s, 9H major); ^{13}C NMR (CDCl_3 , 125 MHz): δ 200.0 (br), 169.5, 137.4, 110.5, 87.6, 80.5, 61.2, 34.7, 32.4, 32.2, 23.2, 15.1, 14.7, -1.2, resonances from the alkyne carbons not observed, resonances from major isomer only; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{27}\text{Co}_2\text{O}_9\text{Si}$ [$M-\text{H}$] 593.0083, found 593.0077.

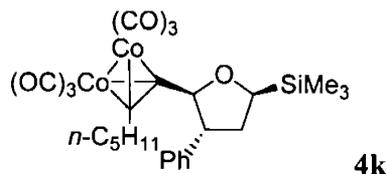


The standard procedure was followed with **1a** (0.411 g, 1.00 mmol), **3f** (215 μL , 2.03 mmol), and **2b** (1.0 mL, 2.0 mmol). Silica gel chromatography (3:1 hexanes:dichloromethane) provided **4i** as a dark red oil (0.327 g, 0.55 mmol, 55% yield). IR (NaCl): 2959, 2875, 2090, 2006, 1736 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 4.95 (d, $J=7.8$ Hz, 1H major), 4.90 (d, $J=6.0$ Hz, 1H minor), 3.72 (s, 3H major), 3.71 (s, 3H minor), 3.63 (d, $J=4.2$ Hz, 1H minor), 3.58 (d, $J=6.3$ Hz, 1H major), 2.76-2.88 (overlapping doublet of doublets, 2H all isomers), 2.61 (dd, $J=9.6$ Hz, 3.4 Hz, 1H minor), 2.41 (dd, $J=7.5$, 3.3, 1H major), 1.58-1.66 (m, 2H all isomers), 1.32-1.49 (m, 4H all isomers), 1.2-1.5 (m, obscured, 1H all isomers), 1.22 (d, $J=7.2$ Hz, 3H minor), 1.16 (d, $J=7.2$ Hz, 3H major), 0.92 (overlapping triplets, $J=6.9$ Hz, 3H all isomers), 0.09 (s, 9H major), 0.05 (s,

9H minor), selected resonance for *endo* isomer of minor product: 4.30 (d, $J=8.1$ Hz), all other resonances obscured by major isomers; ^{13}C NMR (CDCl_3 , 125 MHz): δ 200.8 (br), 175.0, 100.5, 96.3, 84.9, 78.7, 62.0, 52.7, 43.7, 34.6, 32.4, 32.2, 23.2, 21.0, 14.7, -1.7, resonances from major isomer only; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{30}\text{Co}_2\text{O}_9\text{Si}$ [$M+\text{Na}$] 619.0215, found 619.0214.

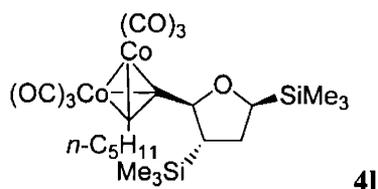


The standard procedure was followed with **1a** (0.411 g, 1.00 mmol), **3g** (215 μL , 2.01 mmol), and **2b** (1.0 mL, 2.0 mmol). Silica gel chromatography (3:1 hexanes:dichloromethane) provided **4j** as a dark red oil (0.382 g, 0.64 mmol, 64% yield). IR (NaCl): 2957, 2875, 2049, 2089 (s), 1732, 1250 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 5.04 (s, 1H major), 4.84 (t, $J=8.2$ Hz, 1H minor), 3.73 (s, 3H major), 3.68 (s, 3H minor), 3.64 (t, $J=9.3$ Hz, 1H major), 3.16 (s, 1H minor), 2.73-2.85 (m, 2H major + 2H minor), 2.68 (dd, $J=12.3$ Hz, 9.3 Hz, 1H major), 2.55 (dd, $J=12.6$ Hz, 9.0 Hz, 1H minor), 2.08 (dd, $J=12.6$ Hz, 7.5 Hz, 1H minor), 1.78 (dd, $J=12.3$ Hz, 10.5 Hz, 1H major), 1.59-1.71 (m, 2H major + 2H minor), 1.33-1.47 (m, 4H major + 4H minor), 1.39 (s, overlapping with previous multiplet, 3H minor), 1.23 (s, 3H major), 0.92 (two overlapping triplets, $J_{\text{major}}=7.0$ Hz, 3H major + 3H minor), 0.06 (s, 9H minor), 0.04 (s, 9H major), selected resonances for *endo* isomer of minor product: 4.85 (t, $J=8.7$ Hz), 4.52 (s); ^{13}C NMR (CDCl_3 , 75 MHz): δ 200.1 (br), 176.4, 100.1, 96.1, 89.1, 71.5, 54.1, 52.3, 43.5, 34.3, 32.0, 31.7, 24.8, 22.9, 14.2, -3.9, resonances from major isomer only; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{30}\text{Co}_2\text{O}_9\text{Si}$ [$M+\text{Na}$] 619.0215, found 619.0207.

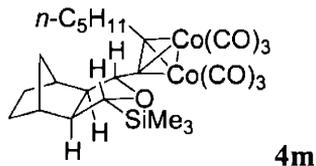


The standard procedure was followed with **1a** (0.412 g, 1.00 mmol), **3h** (230 μL , 2.01 mmol), and **2b** (1.0 mL, 2.0 mmol). Silica gel chromatography (20:1 hexanes:dichloromethane) provided **4k** as a dark red oil (0.276 g, 0.46 mmol, 46% yield). IR (NaCl): 2957, 2860, 2089, 1996, 1250, 841 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 7.31 (br s, 5H major, 5H minor, partially obscured by residual CHCl_3), 5.18 (t, $J=7.7$ Hz, 1H minor), 4.88 (d, $J=9.0$ Hz, 1H major), 3.89

(t, $J=9.2$ Hz, 1H major), 3.56 (d, $J=11.1$ Hz, 1H minor), 3.29 (q, $J=9.9$ Hz, 1H minor), 3.44 (q, $J=9.3$ Hz, 1H major), 2.83 (t, $J=8.1$ Hz, 2H minor), 2.16-2.50 (m, 4H major, 2H minor), 1.66 (q, $J=7.2$ Hz, 2H minor), 1.12-1.43 (m, 4H major, 2H minor), 0.92 (t, $J=6.7$ Hz, 3H minor), 0.83 (t, $J=6.7$ Hz, 3H major), 0.08 (s, 9H major), -0.08 (s, 9H minor); ^{13}C NMR (CDCl_3 , 75 MHz): δ 200.3 (br), 142.3, 128.8, 128.1, 127.0, 99.5, 95.8, 88.4, 72.4, 54.8, 39.6, 34.1, 31.8, 31.5, 22.5, 14.1, -3.9, resonances from major isomer only; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{30}\text{Co}_2\text{O}_7\text{Si}$ [M^+] 600.0417, found 600.0418.

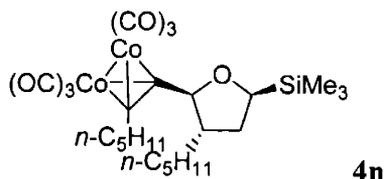


The standard procedure was followed with **1a** (0.411 g, 1.00 mmol), **3i** (295 μL , 2.01 mmol), and **2b** (1.0 mL, 2.0 mmol). Silica gel chromatography (20:1 hexanes:dichloromethane) provided **4l** as a dark red oil (0.219 g, 0.37 mmol, 37% yield). IR (NaCl): 2957, 2088, 2006, 1616, 1250 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 4.80 (d, $J=7.2$ Hz, 1H major), 4.70 (t, $J=7.4$ Hz, 1H minor), 3.46 (d, $J=10.2$ Hz, 1H minor), 3.22 (dd, $J=12.6$ Hz, 5.4 Hz, 1H major), 2.78 (t, $J=8.1$ Hz, 2H major + 2H minor), 2.13-2.20 (m, 1H minor), 2.07 (q, $J=12.3$ Hz, 1H major), 1.84-1.93 (m, 1H major + 1H minor), 1.52-1.75 (m, 2H major + 2H minor), 1.25-1.51 (m, 4H major + 4H minor), 1.20-1.30 (m, 1H major, 1H minor), 0.94 (t, $J=6.9$ Hz, 3H major + 3H minor), 0.060-0.113 (two overlapping, broad singlets, 18H major + 18H minor). ^{13}C NMR (CDCl_3 , 125 MHz): δ 201.2 (br), 101.0, 99.4, 83.3, 73.6, 36.0, 34.7, 32.8, 32.5, 32.4, 23.2, 14.7, -2.3, -3.3, resonances from major isomer only; HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{33}\text{Co}_2\text{O}_7\text{Si}_2$ [$M\text{-H}$] 595.0423, found 595.0414.

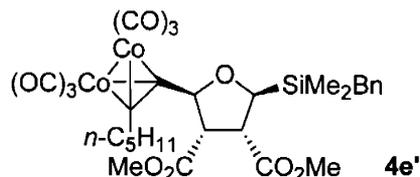


The standard procedure was followed with **1a** (0.411 g, 1.00 mmol), **3j** (0.188 g, 2.00 mmol), and **2b** (1.0 mL, 2.0 mmol). Silica gel chromatography (15:1 hexanes:dichloromethane) provided **4m** as a dark red oil (0.169 g, 0.29 mmol, 29% yield). IR (NaCl): 2956, 2088, 2047, 1248, 840 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 4.33 (d, $J=7.8$ Hz, 1H), 3.01 (d, $J=9.6$ Hz, 1H), 2.81 (t, $J=8.0$ Hz, 2H), 2.20 (s, 1H), 2.09 (t, $J=9.5$ Hz, 1H), 1.97 (s, 1H), 1.84 (t, $J=8.4$ Hz, 1H),

1.75 (d, $J=10.8$ Hz, 1H), 1.66 (t, $J=7.7$ Hz, 2H), 1.51-1.61 (m, 2H), 1.30-1.50 (m, 4H), 1.09-1.15 (m, 3H), 0.93 (t, 6.9 Hz), 0.05 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 200.9 (br), 100.3, 97.9, 85.9, 77.75, 59.8, 40.2, 39.6, 34.7, 33.4, 32.4, 32.3, 29.1, 28.9, 23.2, 14.7, -3.2; HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{32}\text{Co}_2\text{O}_7\text{Si}$ [$M+\text{Na}$] 613.0475, found 613.0486.



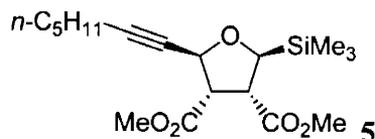
The standard procedure was followed with **1a** (0.411 g, 1.00 mmol), **3k** (280 μL , 1.99 mmol), and **2b** (1.0 mL, 2.0 mmol). Silica gel chromatography (25:1 hexanes:dichloromethane) provided **4n** as a dark red oil (0.063 g, 0.11 mmol, 11% yield). IR (NaCl): 2931, 2859, 2089, 2046, 1249 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ 4.82 (t, $J=7.5$ Hz, 1H minor), 4.36 (d, $J=7.0$ Hz, 1H major), 3.49 (dd, $J=8.0, 7.5$, 1H major), 3.12 (d, $J=9.0$ Hz, 1H minor), 2.81 (overlapping t, $J=8.0$ Hz, 2H major + 2H minor), 1.21-2.19 (m, 17H major + 17H minor), 0.88-1.19 (two sets of overlapping t, 6H major + 6H minor), 0.05 (s, 9H minor), 0.03 (s, 9H major); ^{13}C NMR (CDCl_3 , 125 MHz): δ 200.9 (br), 87.3, 71.9, 49.8, 42.5, 35.5, 34.7, 34.3, 32.8, 32.4, 32.3, 28.8, 23.3, 14.6 (2), -3.3, resonances from the alkyne carbons not observed, resonances from major isomer only; HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{35}\text{Co}_2\text{O}_7\text{Si}$ [$M-\text{H}$] 593.0811, found 593.0821.



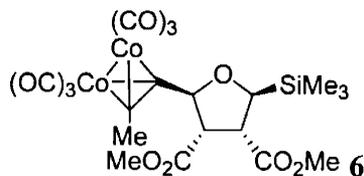
Standard three-component dipolar cycloaddition was followed using diazo **2c** to yield 451 mg (0.63 mmol, 63%) of **4e'**.

IR (NaCl): 2956, 2091, 2028, 2052, 1741 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 7.2 (m, 2H), 7.0-7.19 (m, 3H), 5.19 (d, $J=9.0$ Hz, 1H), 3.92 (d, $J=10$ Hz, 1H), 3.70 (s, 3H), 3.68 (s, 3H), 3.39 (dd, $J=10.5$ Hz, $J=9.5$ Hz, 1H), 2.97 (dd, $J=10.5$ Hz, $J=9.0$ Hz, 1H), 2.78-2.83 (m, 2H), 2.21 (q, $J=14$ Hz, 2H), 1.60-1.77 (m, 2H), 1.38-1.54 (m, 4H), 0.93 (t, $J=7\text{H}$, 3H), 0.06 (s, 3H), 0.02 (s,

3H). ^{13}C NMR (125 MHz, CDCl_3): δ 200.5, 172.9, 171.6, 139.7, 129.0, 125.0, 100.9, 94.3, 83.0, 74.3, 56.8, 52.9, 52.8, 50.7, 34.4, 32.5, 32.2, 23.5, 23.2, 14.7, -5.3, -5.7.

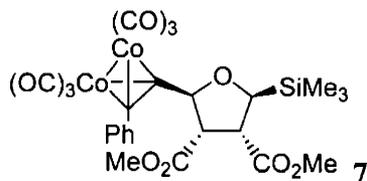


To a 25 mL round bottom was added **4e** (0.961 g, 1.50 mmol) and THF (2.0 mL). The vessel was placed in an ice bath, and I_2 (2.92 g, 11.5 mmol) in THF (11.0 mL) was added dropwise over a few minutes. After three hours, the ice bath was removed and the reaction mixture was warmed to room temperature. The contents of the reaction vessel were poured into a separatory funnel containing 50 mL ether and 25 mL saturated aqueous $\text{Na}_2\text{S}_2\text{O}_8$. Upon shaking, a clear ether layer and a light pink aqueous layer were obtained. The aqueous layer was removed and washed once with ether (25 mL). The combined organic layers were washed with water (25 mL), brine (25 mL), and then dried over MgSO_4 . Filtration and evaporation afforded a light yellow residue that was filtered through a small amount of silica gel with (10:1 hexanes:ethyl acetate) to provide **5** as a colorless oil (0.515 g, 1.45 mmol, 97% yield). IR (NaCl): 2955, 2244, 1792, 1745, 1250, 843 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 4.78 (dt, $J_d=6.6$ Hz, $J_f=1.9$ Hz, 1H), 3.76 (d, $J=9.6$ Hz, 1H), 3.70 (s, 3H), 3.67 (s, 3H), 3.19-3.34 (m, 2H), 2.20 (td, $J_f=6.9$ Hz, $J_i=1.9$ Hz, 2H), 1.50 (quintet, $J=6.9$ Hz, 2H), 1.31-1.35 (m, 4H), 0.89 (t, $J=7.1$ Hz, 3H), 0.09 (s, 9H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 172.1, 170.8, 87.4, 77.9, 75.0, 72.3, 55.8, 52.5, 52.4, 49.2, 31.4, 28.5, 22.6, 19.2, 14.4, -3.4; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{30}\text{O}_5\text{Si}$ [$M+\text{Na}$] 377.1755, found 377.1762.



The standard procedure was followed with **2a** (0.354 g, 1.00 mmol), **3b** (250 μL , 2.00 mmol), and **2b** (1.0 mL, 2.0 mmol). Silica gel chromatography (3:1 hexanes:dichloromethane) provided **6** as a dark red solid (0.429 g, 0.73 mmol, 73% yield). IR (NaCl, CCl_4): 2954, 2091, 2050, 1750, 760 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 5.16 (d, $J=9.0$ Hz, 1H), 3.86 (d, $J=9.5$, 1H), 3.70 (s, 3H), 3.68 (s, 3H), 3.37 (t, $J=10.0$ Hz, 1H), 2.89 (dd, $J=10.5$ Hz, 9.3 Hz, 1H), 2.64 (s, 3H), 0.07 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 200.4 (br), 173.3, 171.5, 82.6, 75.5, 66.6, 56.7, 52.8 (2

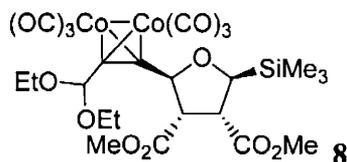
resonances), 50.6, 21.4, 16.0, -3.5; HRMS (ESI) m/z calcd for $C_{20}H_{22}Co_2O_{11}Si$ [$M+Na$] 606.9488, found 606.9486.



According to standard procedure (**1c**) 416 mg (1.00 mmol) yielded 368 mg (0.57 mmol, 57% yield) of the above compound.

IR (NaCl): 3650, 2093, 2055, 2026, 1734, 1700, 1436 cm^{-1} .

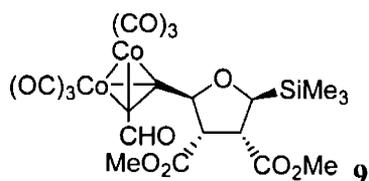
1H NMR (500 MHz, $CDCl_3$): δ 7.59 (m, 2H), 7.33 (m, 3H), 5.46 (d, $J=9$ Hz, 1H), 4.02 (d, $J=10.5$ Hz, 1H), 3.70 (s, 3H), 3.58 (s, 3H), 3.41 (q, $J=10.5$ Hz, 1H), 3.41 (t, $J=10.5$ Hz, 1H), 3.14 (dd, $J=10.5, 9$ Hz, 1H), 0.10 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 200 (br), 172.7, 171.9, 138.3, 130.5, 129.4, 128.6, 93.8, 92.3, 83.6, 76.2, 60.0, 52.8, 52.7, 51.2, -3.3.



According to standard procedure (**1d**) yielded 464 mg (0.69 mmol) of compound shown.

IR (NaCl): 2956, 2096, 2057, 2030, 1747, 1209 cm^{-1} .

1H NMR (300 MHz, $CDCl_3$): δ 5.43 (s, 1H), 5.23 (d, $J=8.4$ Hz, 1H), 3.7-3.88 (m, 4H), 3.69 (s, 3H), 3.68 (s, 3H), 3.45 (q, $J=7.2$ Hz, 1H), 3.33 (t, $J=10.5$ Hz, 1H), 3.10 (dd, $J=11$ Hz, 8.4 Hz, 1H), 1.22 (m, 6H), 0.05 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 200 (br), 172.9, 171.9, 102.3, 83.1, 76.1, 64.4, 63.9, 56.6, 52.8, 52.7, 50.9, 16.8, 15.7, -3.4.



According to standard procedure **1e** provided above compound isolated in 174 mg (0.29 mmol).

IR (NaCl): 2956, 2104, 2067, 2040, 1733, 1669, 1438, 1164 cm^{-1} .

^1H NMR (300 MHz, CDCl_3): δ 10.3 (1H), 5.19 (d, $J=9.3$ Hz, 1H), 3.87 (d, $J=9$ Hz, 1H), 3.70 (s, 3H), 3.68 (s, 3H) 3.41 (t, $J=9$ Hz, 1H), 2.86 (t, $J=9$ Hz), 0.08 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3): δ 200 (br), 172.7, 171.9, 138.3, 130.5, 129.4, 128.6, 93.8, 92.3, 83.6, 76.2, 60.0, 52.8, 52.7, 51.2, -3.3.

Dicobalt tetracarbonyl bis(triphenylphosphine) complex of 2-octynal (10).

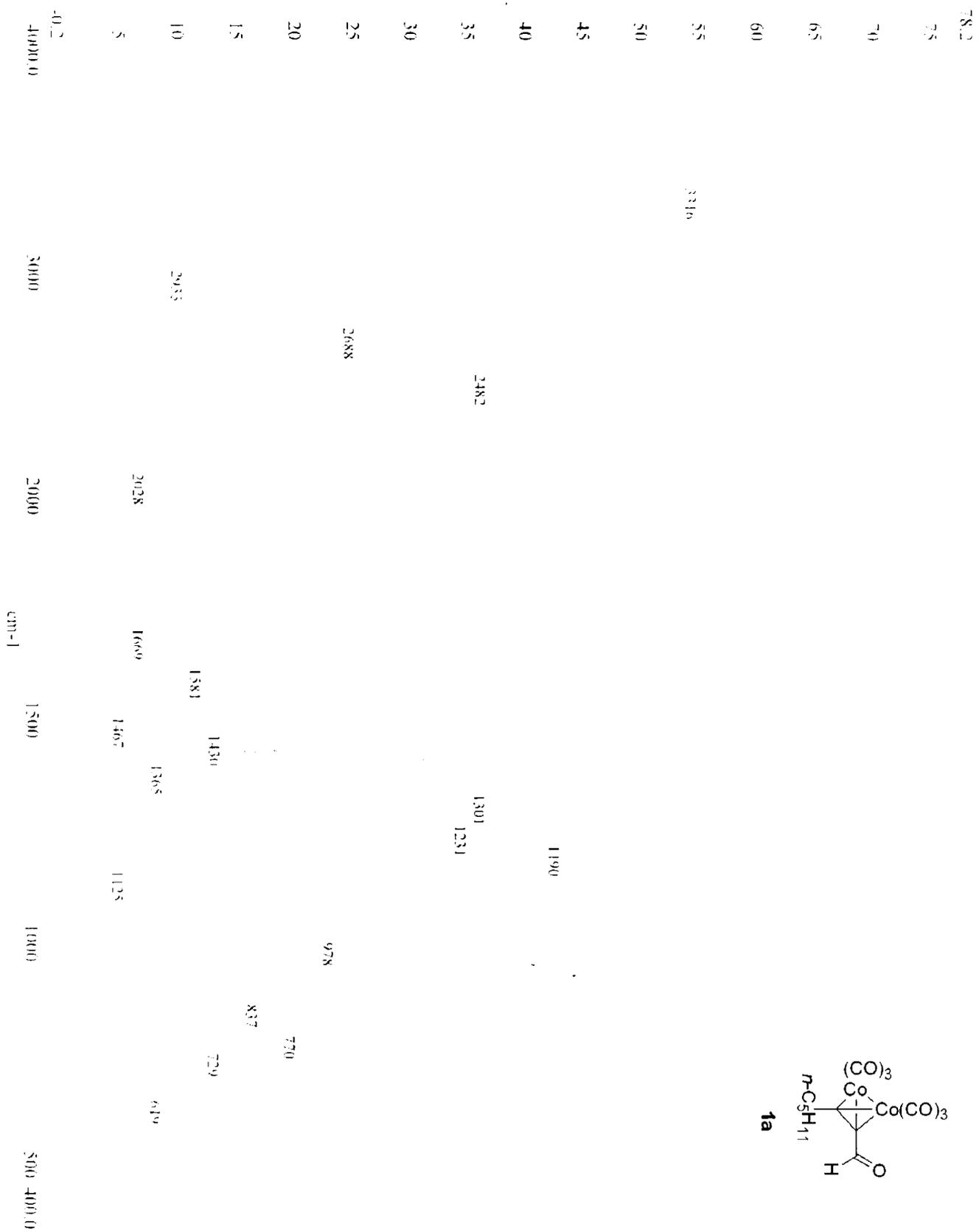
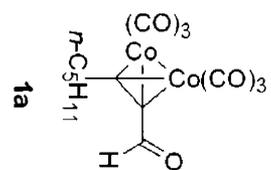
The standard three-component dipolar cycloaddition was followed with **1a**, **2b**, and **3c**, but triphenylphosphine 525 mg (2.0 mmol) was added at the beginning of the reaction. Isolated 299 mg (0.34 mmol, 34%). A portion was recrystallized from ethyl acetate:hexane and the crystal structure was determined by X-ray diffraction.

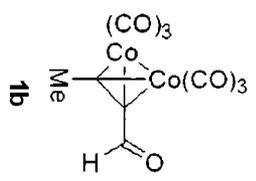
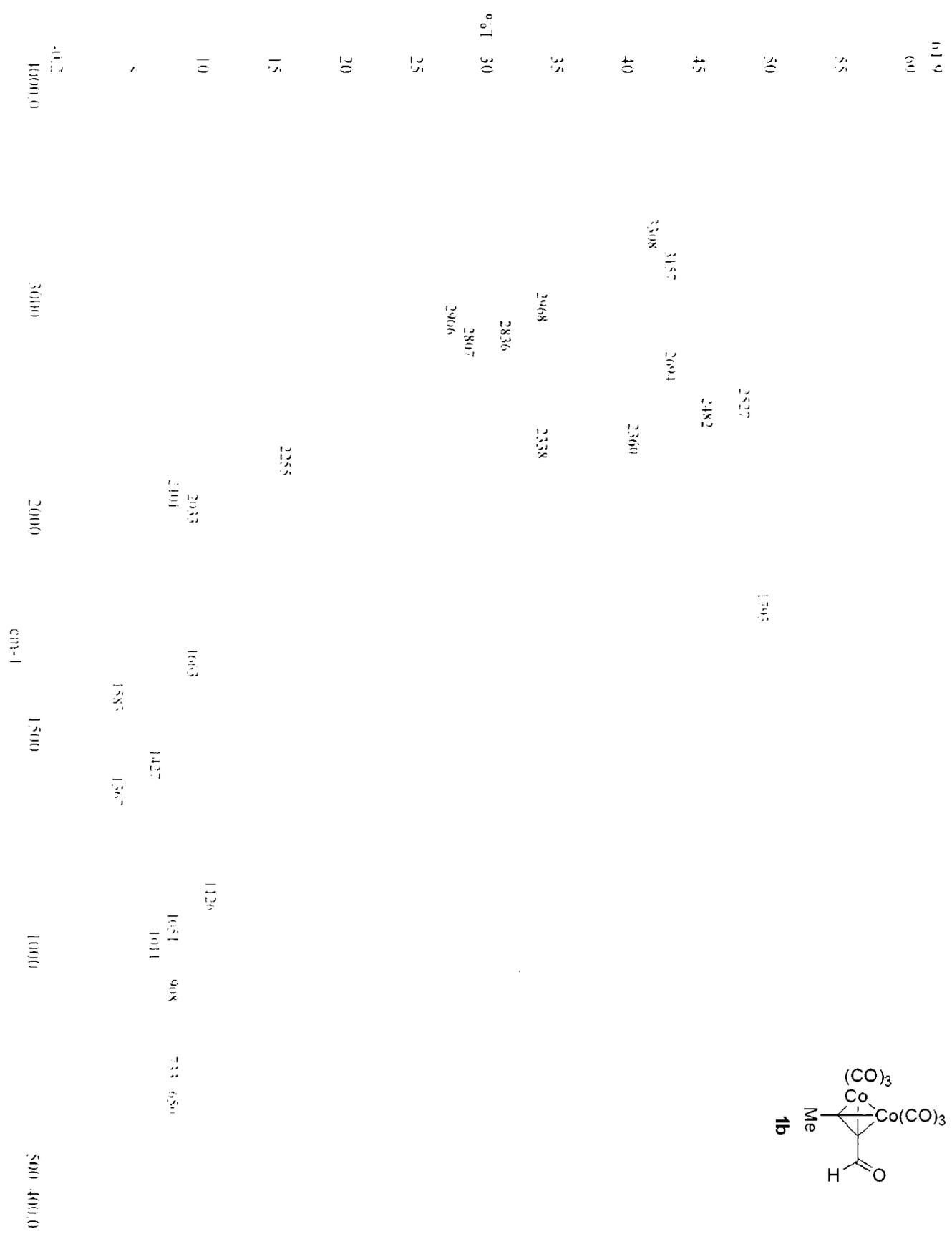
^1H NMR (300 MHz, CDCl_3): δ 9.36 (s, 1H), 7.41-7.50 (m, 12H), 7.30 (m, 18H), 1.64 (m, 2H), 0.87-1.01 (m, 4H), 0.72 (t, $J=7.2$ Hz, 3H), 0.52-0.62 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 194 (br), 175.8, 135.9 (t, $J=19$ Hz), 133.8 (t, $J=5$ Hz), 130.6, 129 (t, $J=4.6$ Hz), 125.4, 109.1, 32.5, 32.3, 31.3, 23.3, 14.8

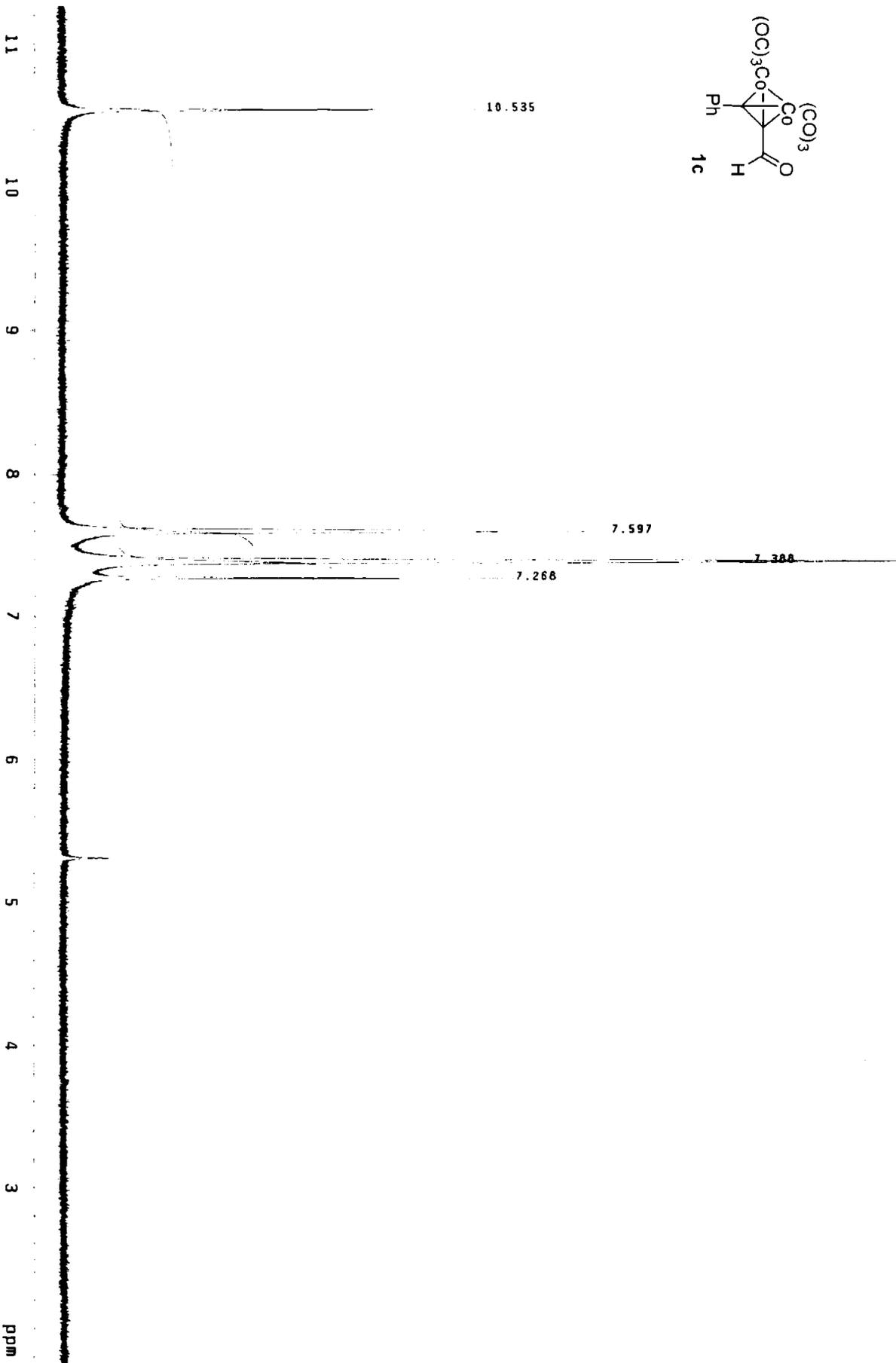
Dicobalt pentacarbonyl (-)-trimenthyl phosphite complex of acetylenedicarbaldehyde (11).

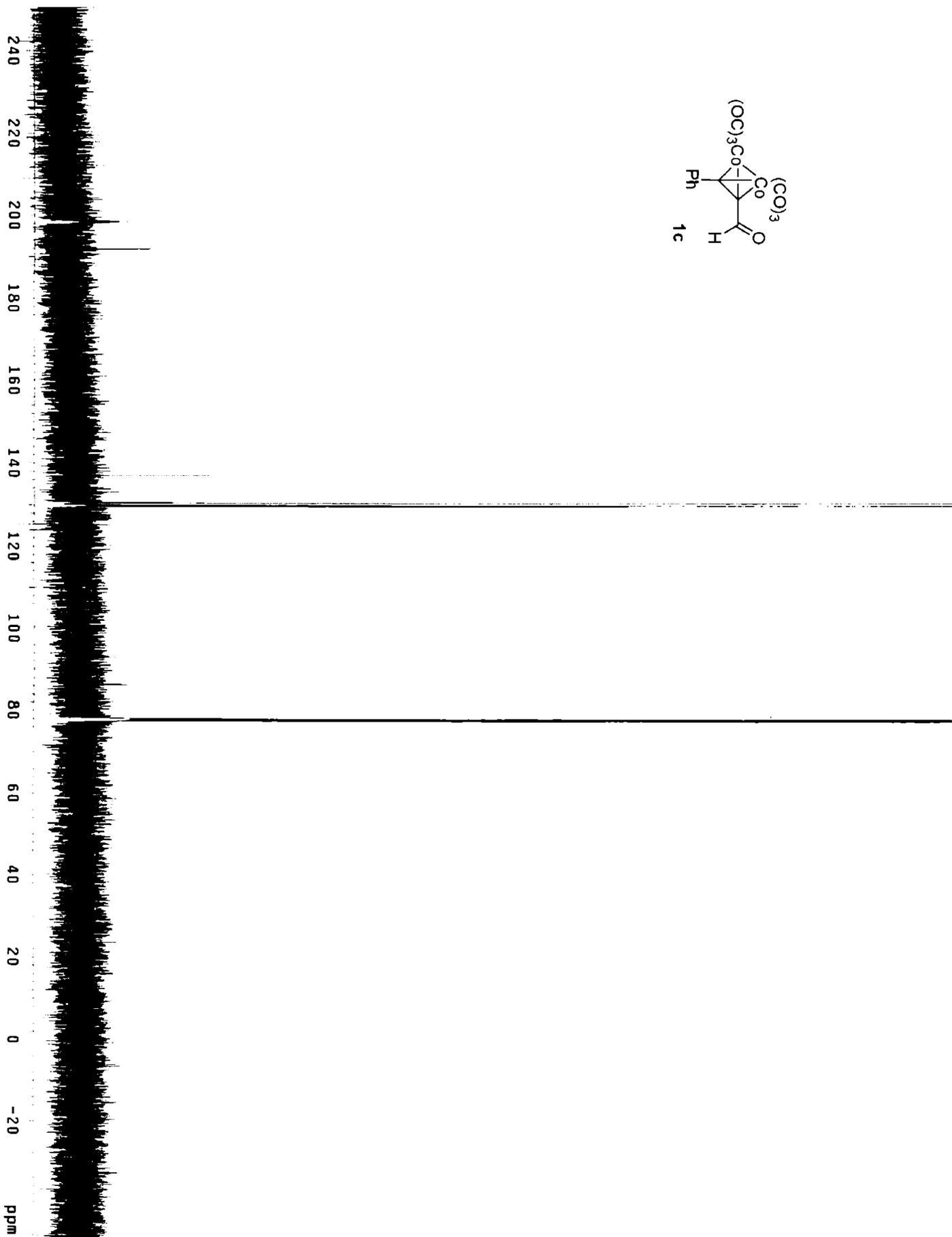
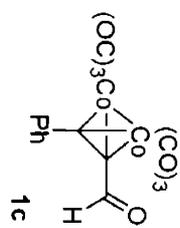
To a THF solution of freshly prepared (-)-trimenthyl phosphite (5 mmol) was added cobalt complex **1e** (1.6 g, 4.3 mmol). The progress was monitored by TLC until no **1e** remained (3-6 h). Concentration *en vacuo* and silica gel chromatography (1:9 ethyl acetate:hexane) provided **8** as an orange solid (2.0 g, 2.4 mmol, 56% yield). Recrystallization of a portion from ether gave red-orange blocks.

^1H NMR (300 MHz, CDCl_3): δ 10.22 (s, 1H), 10.14 (s, 1H), 4.15 (br s, 3H), 2.06 (m, 7H), 1.65 (m, 10H), 1.31 (m, 6H), 0.82-0.91 (br m ~30H). ^{31}P NMR (CDCl_3 , 121 MHz): δ 143 (s).



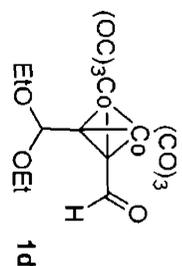
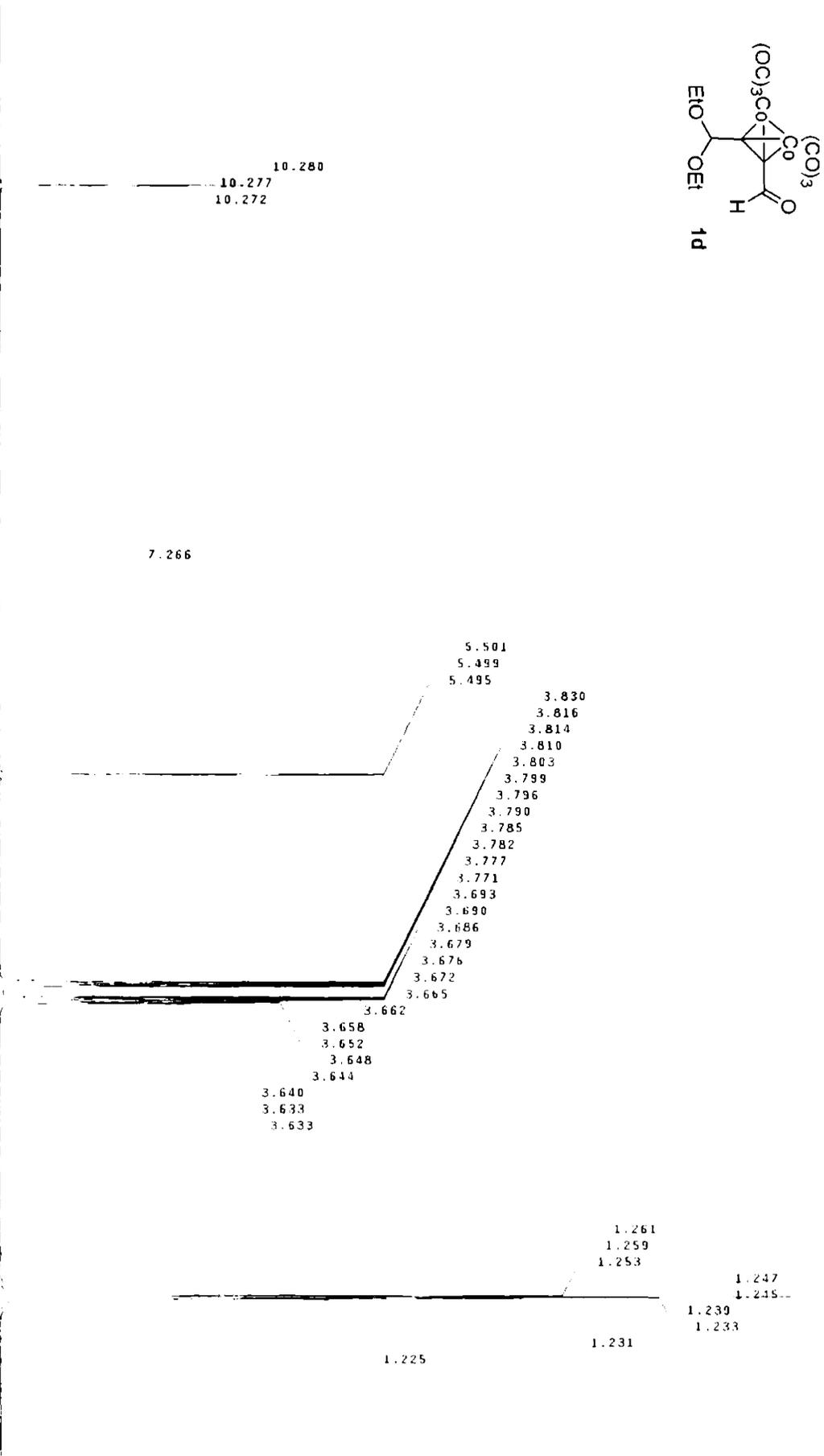


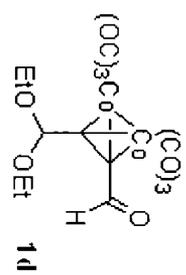
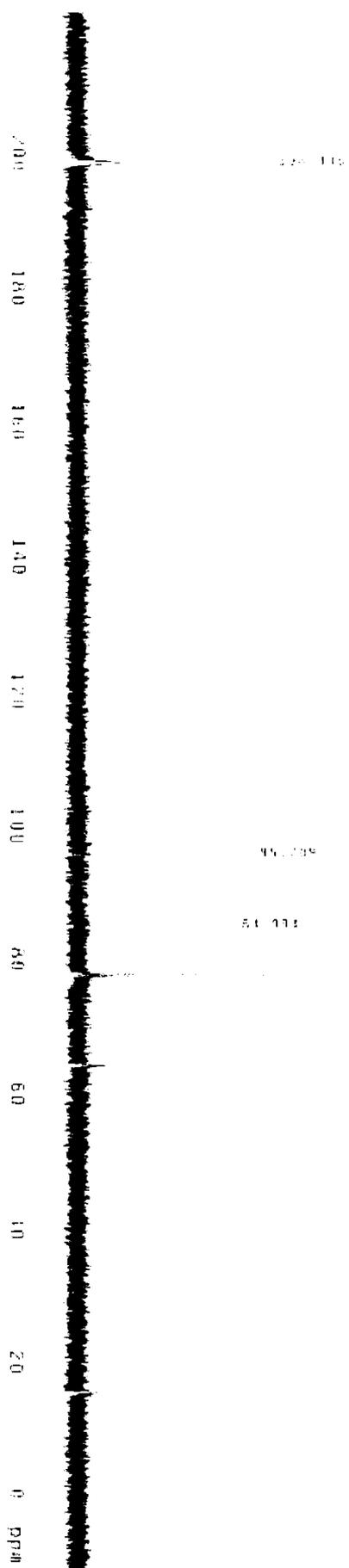


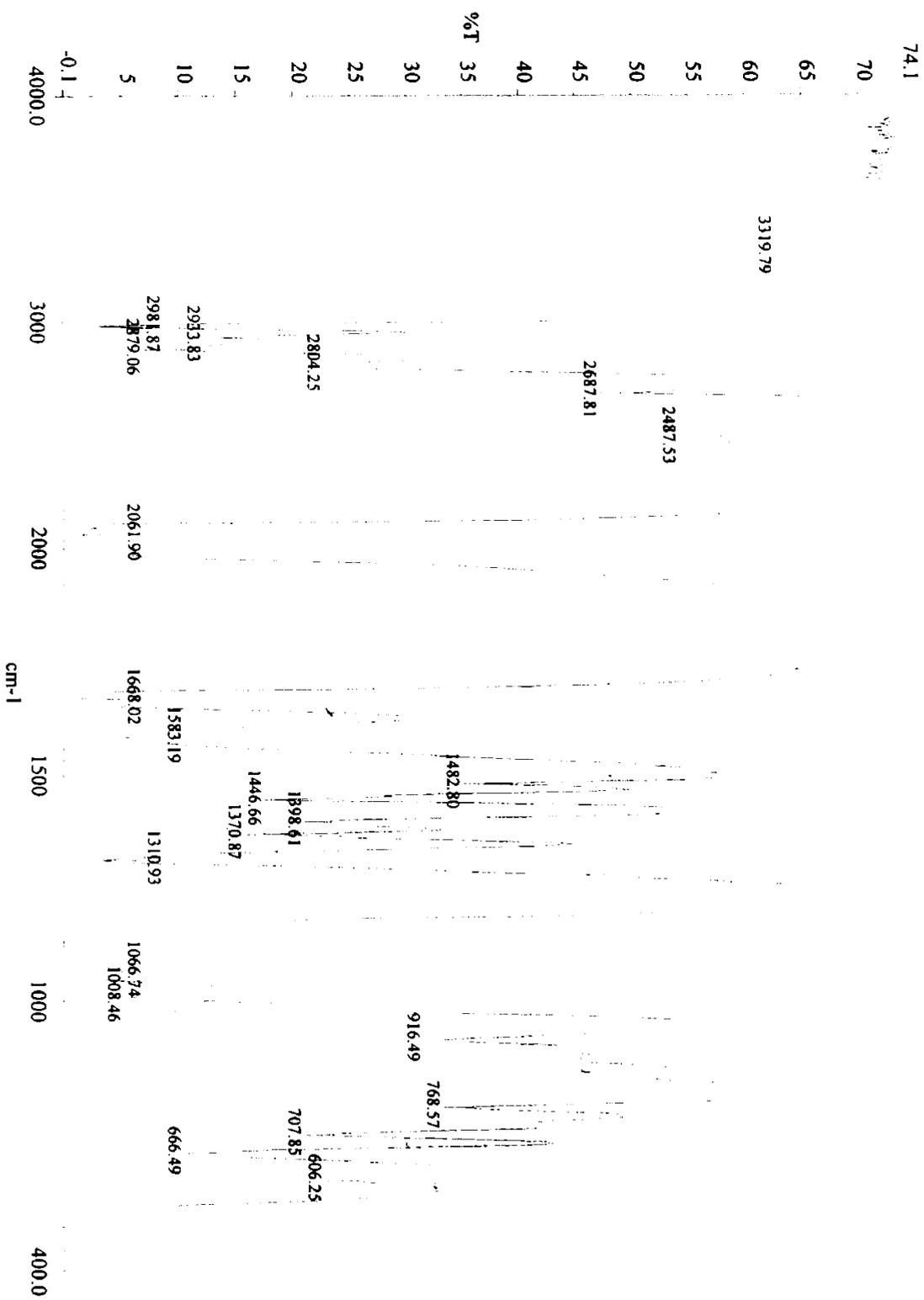
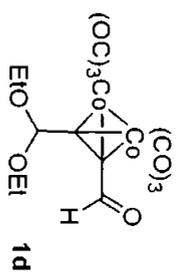


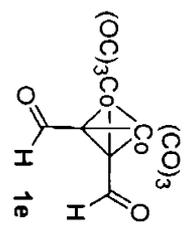


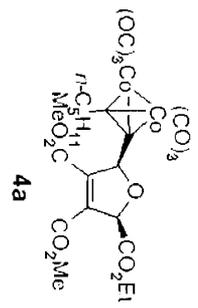
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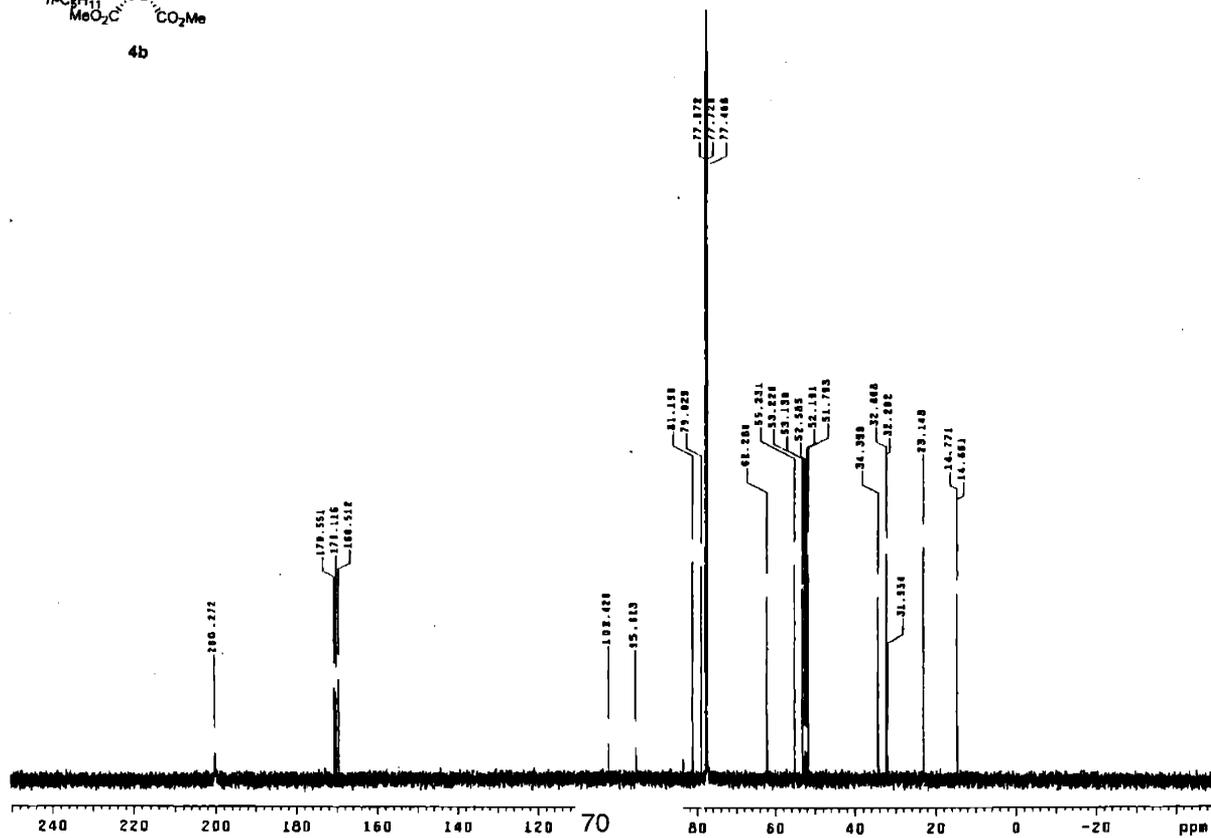
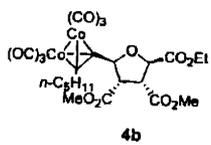
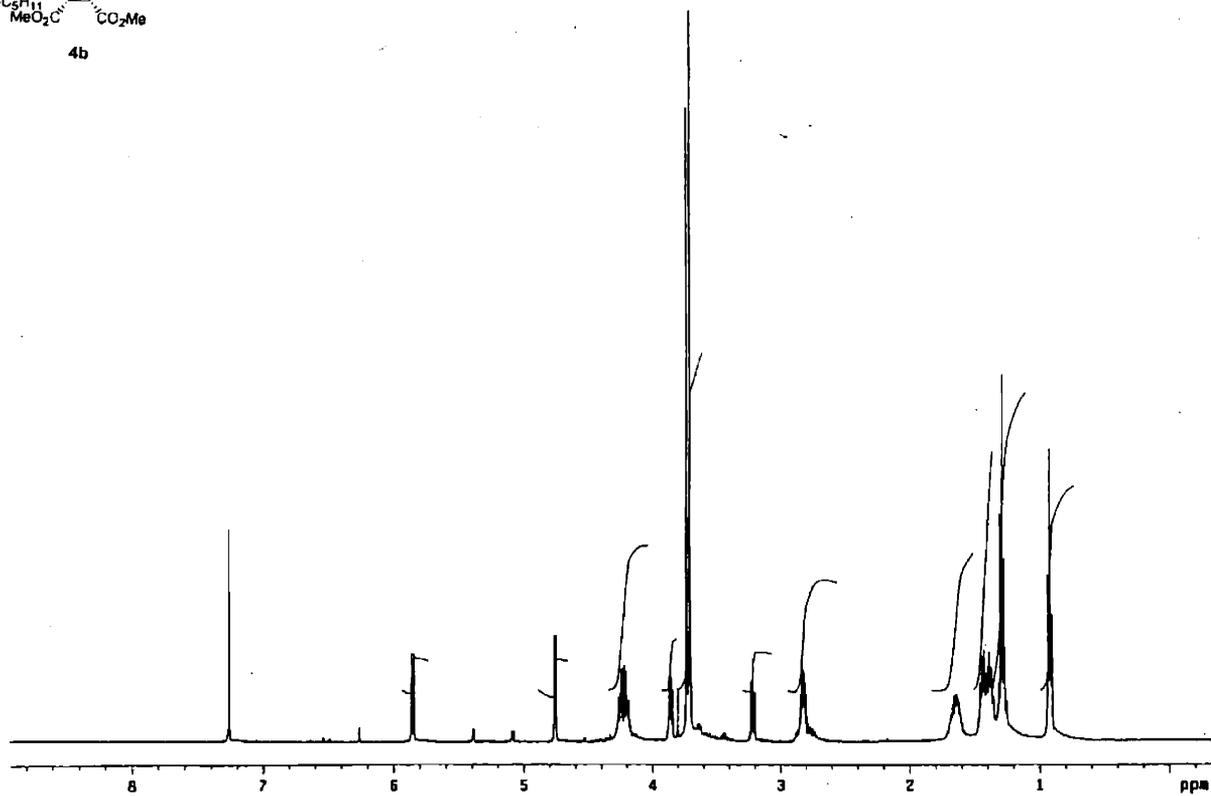
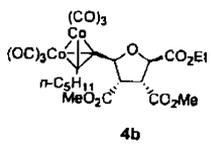


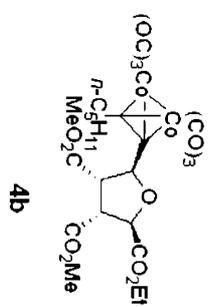
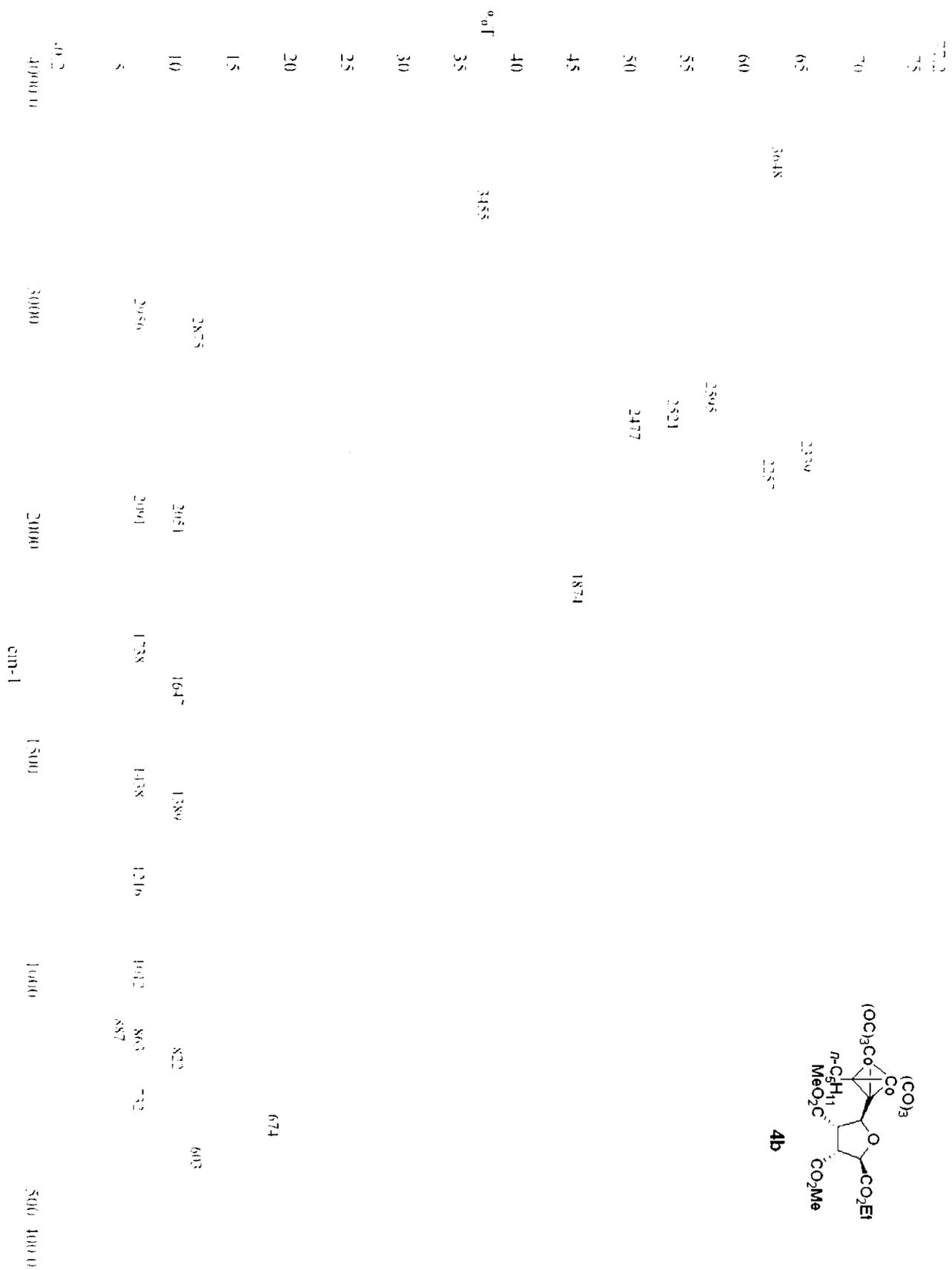


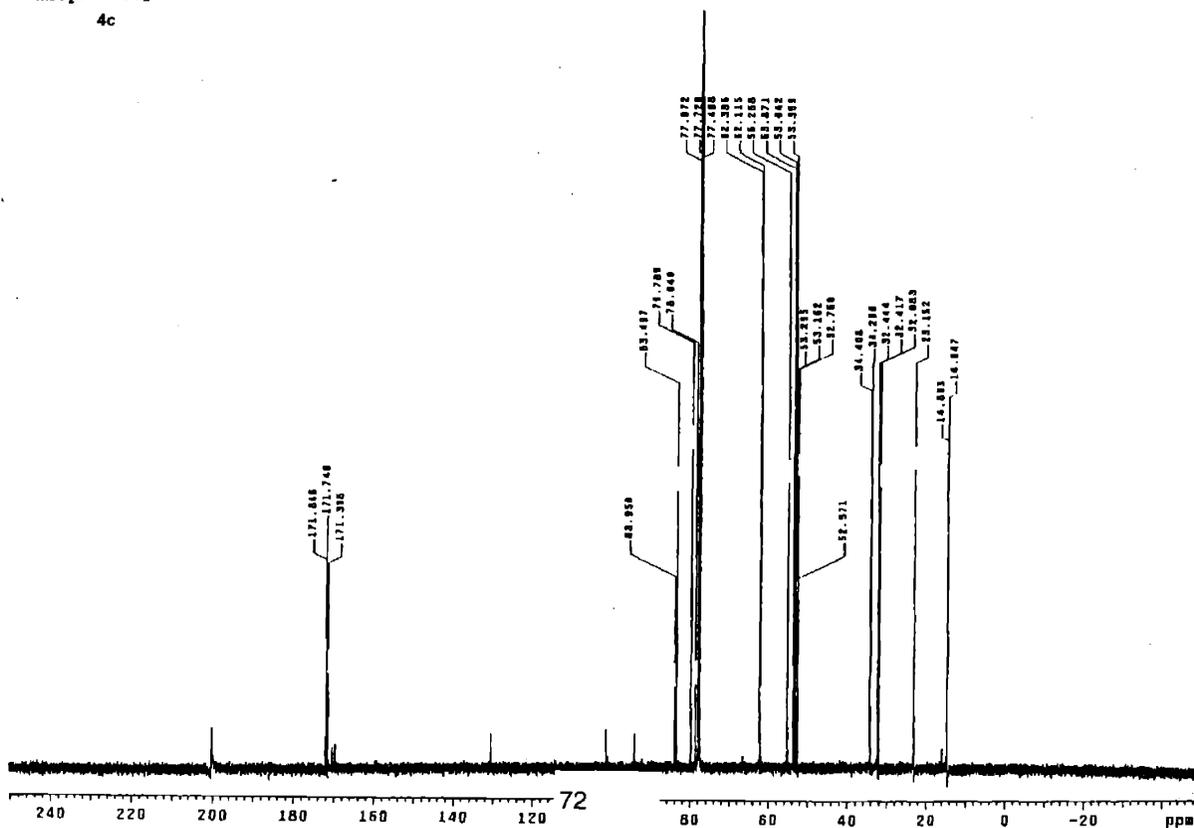
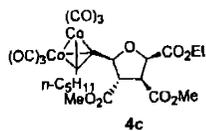
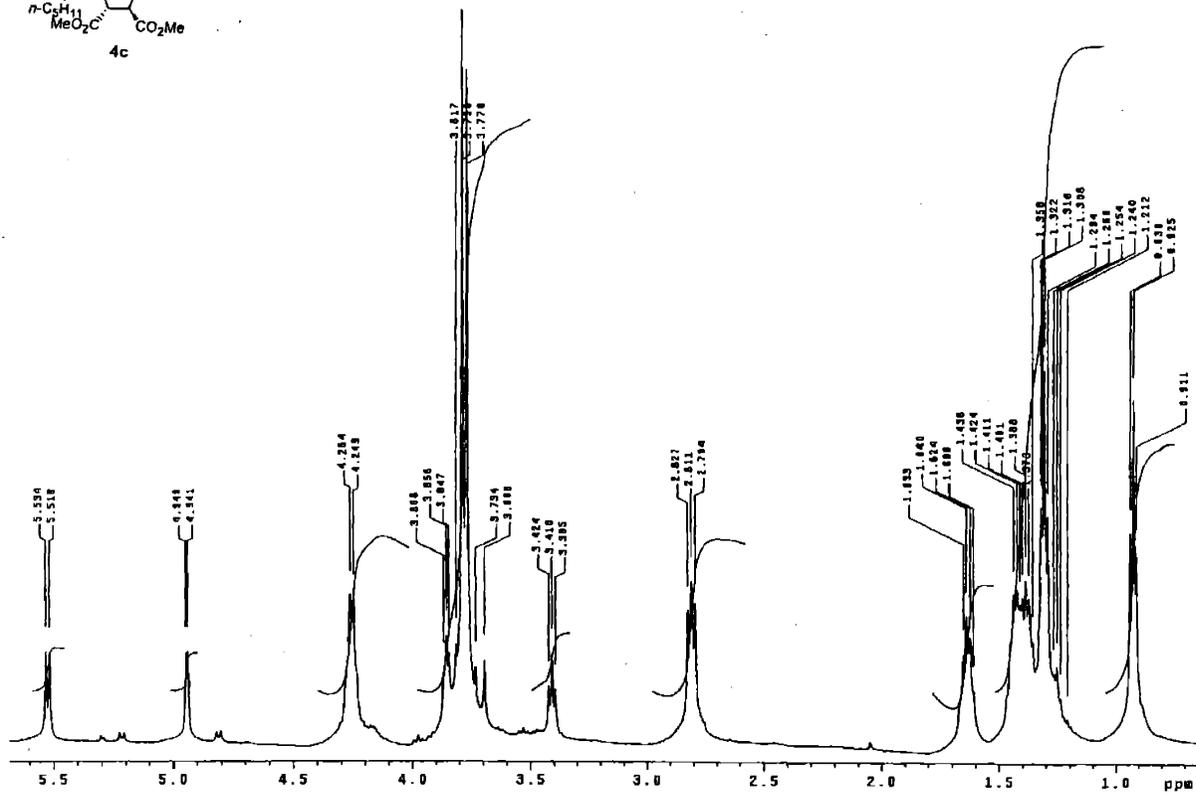
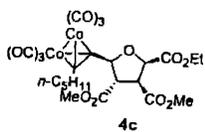


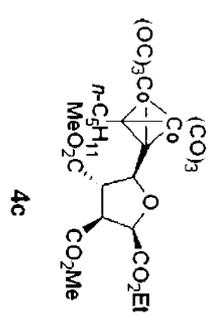
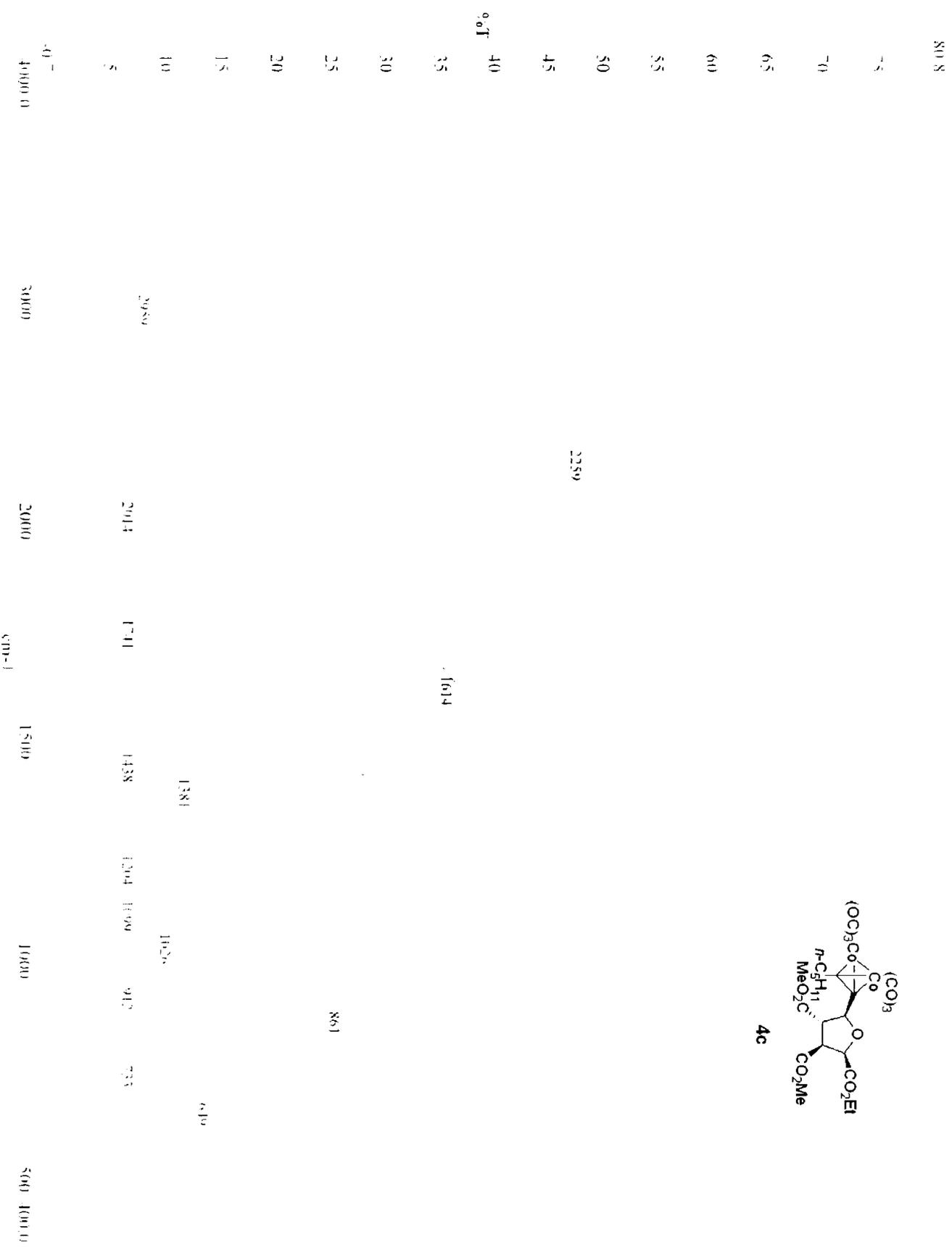


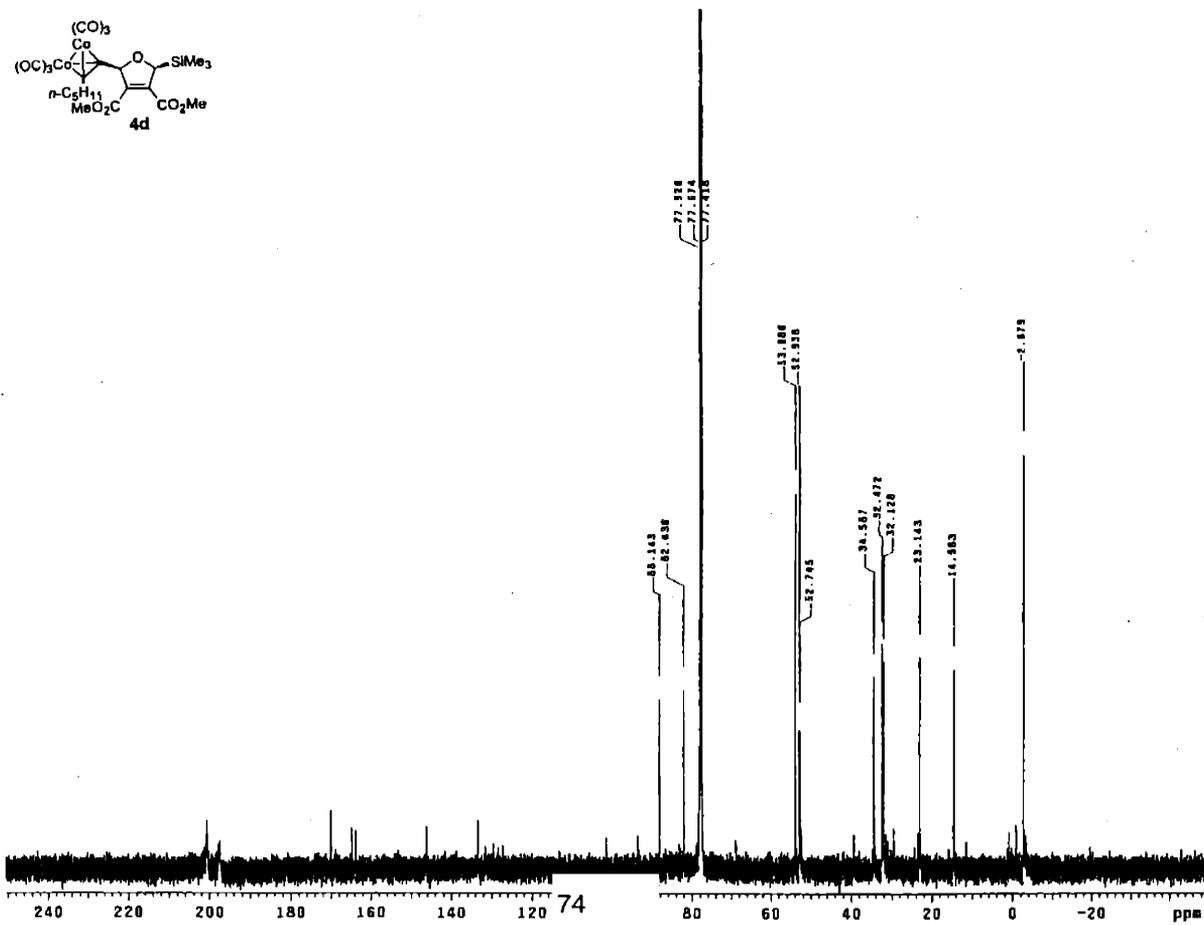
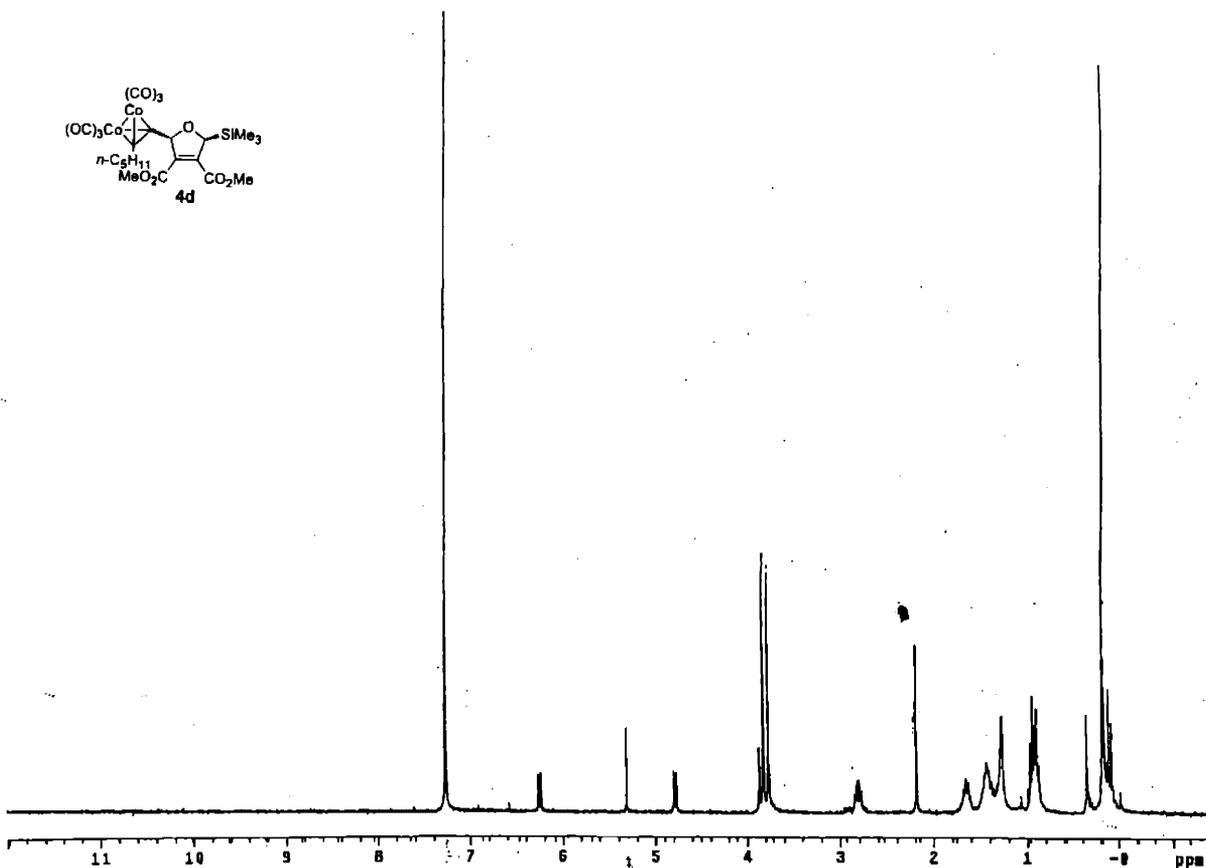


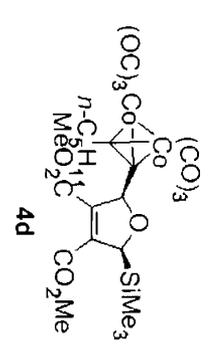
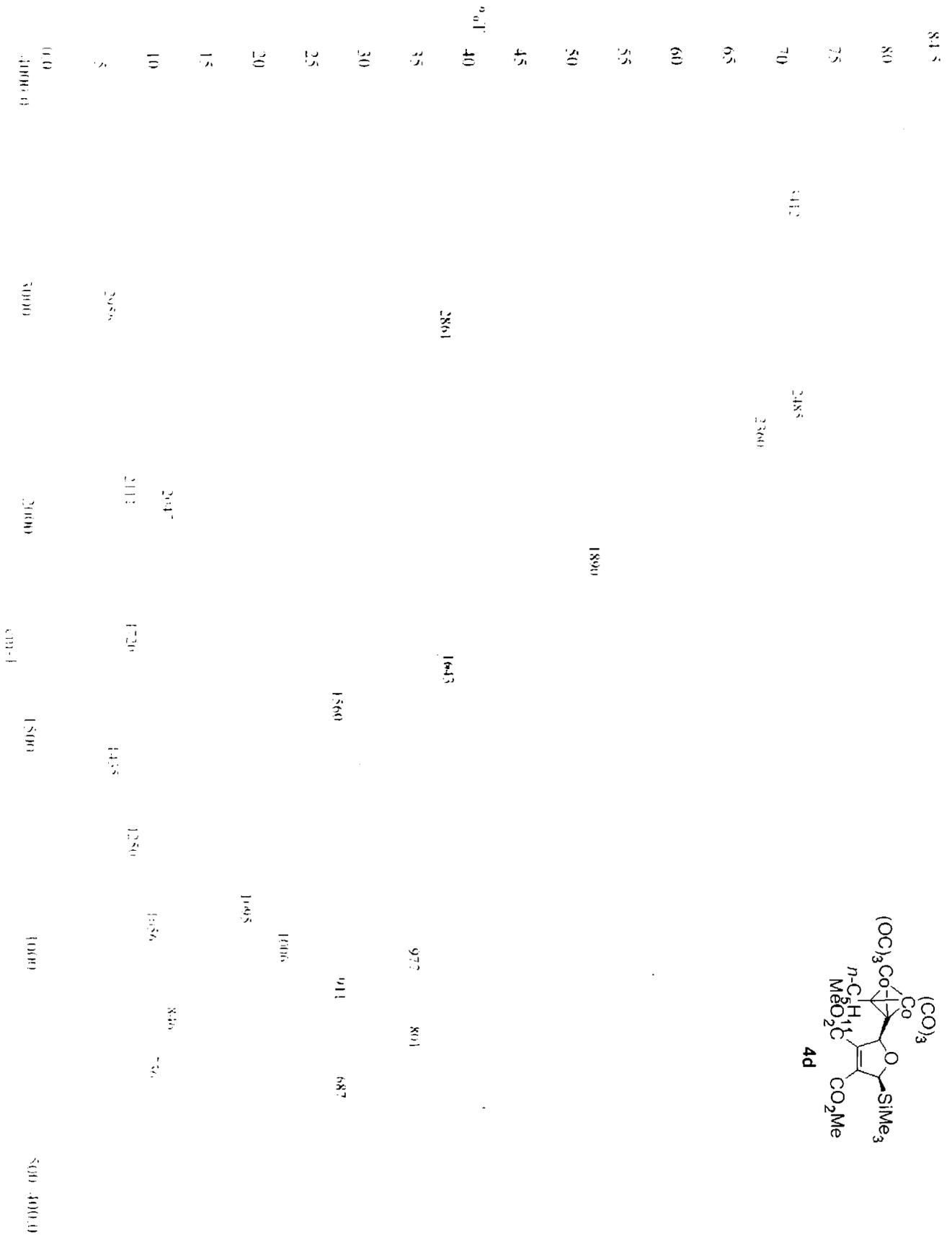


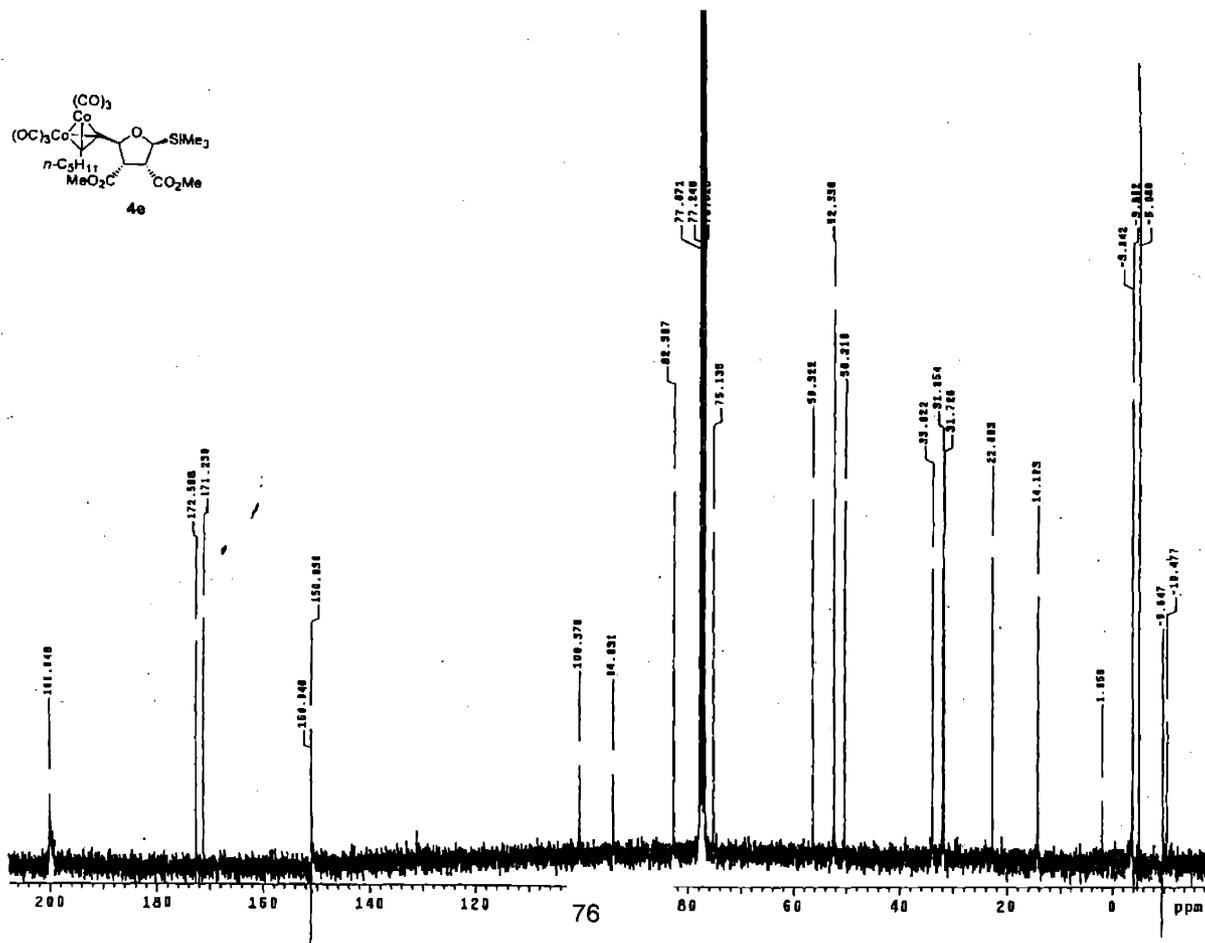
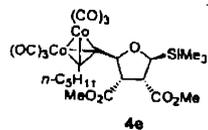
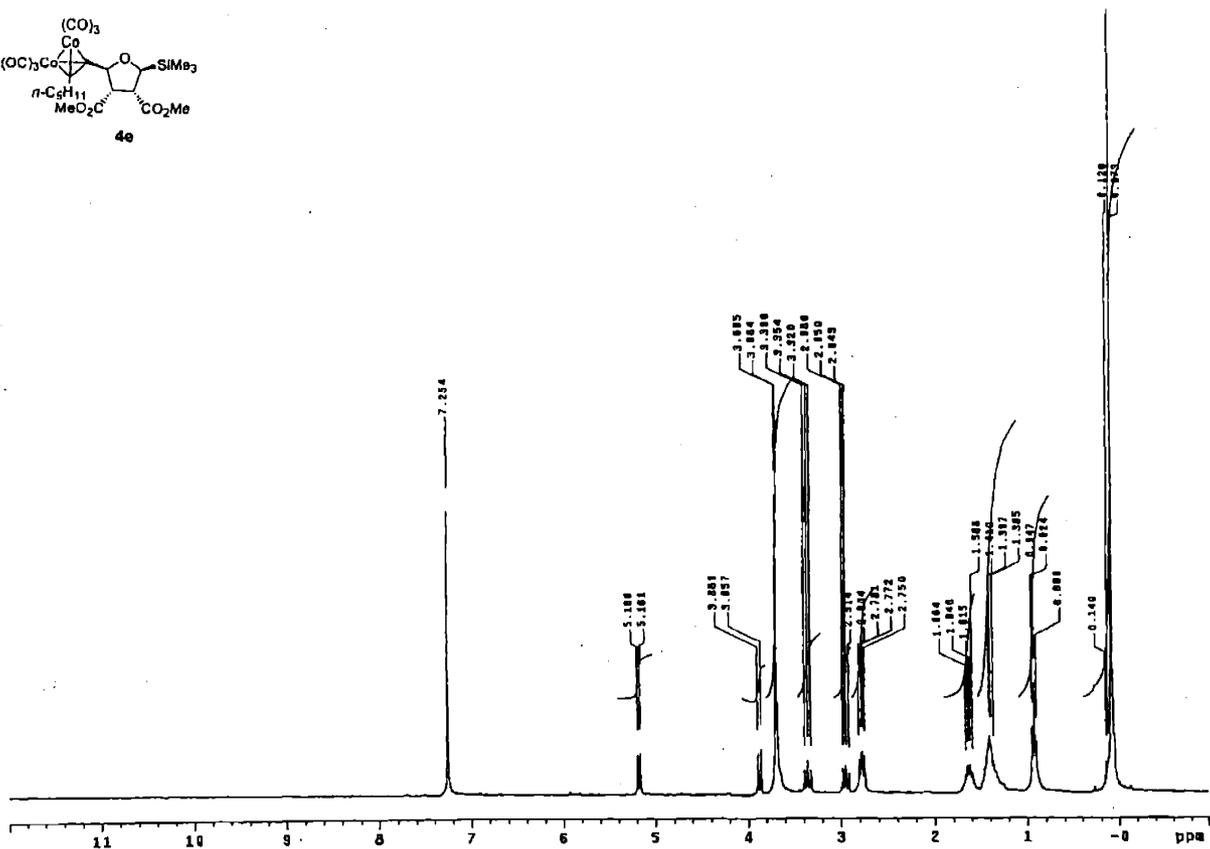
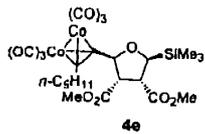


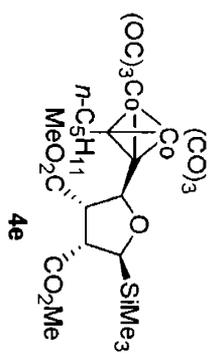
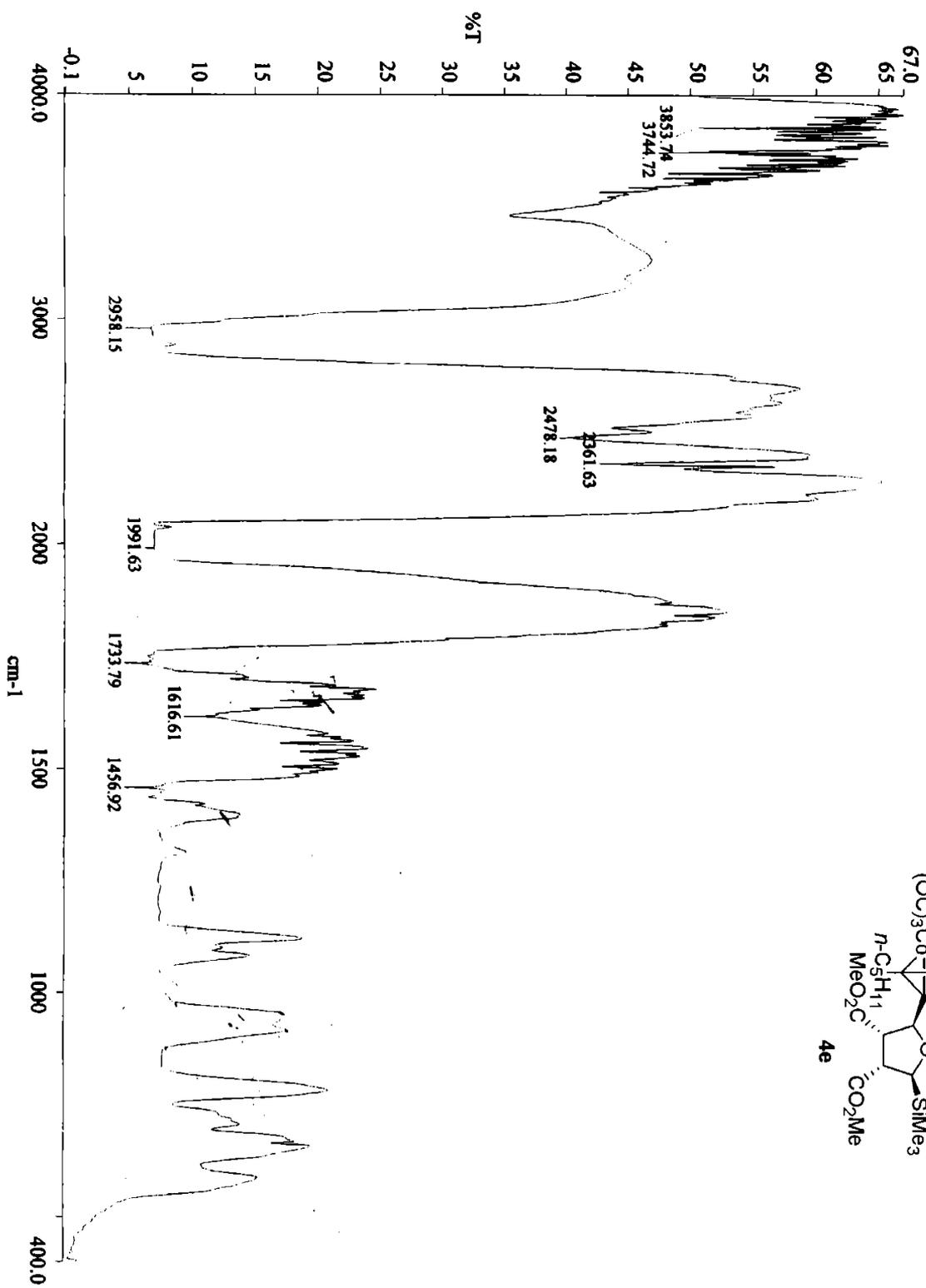


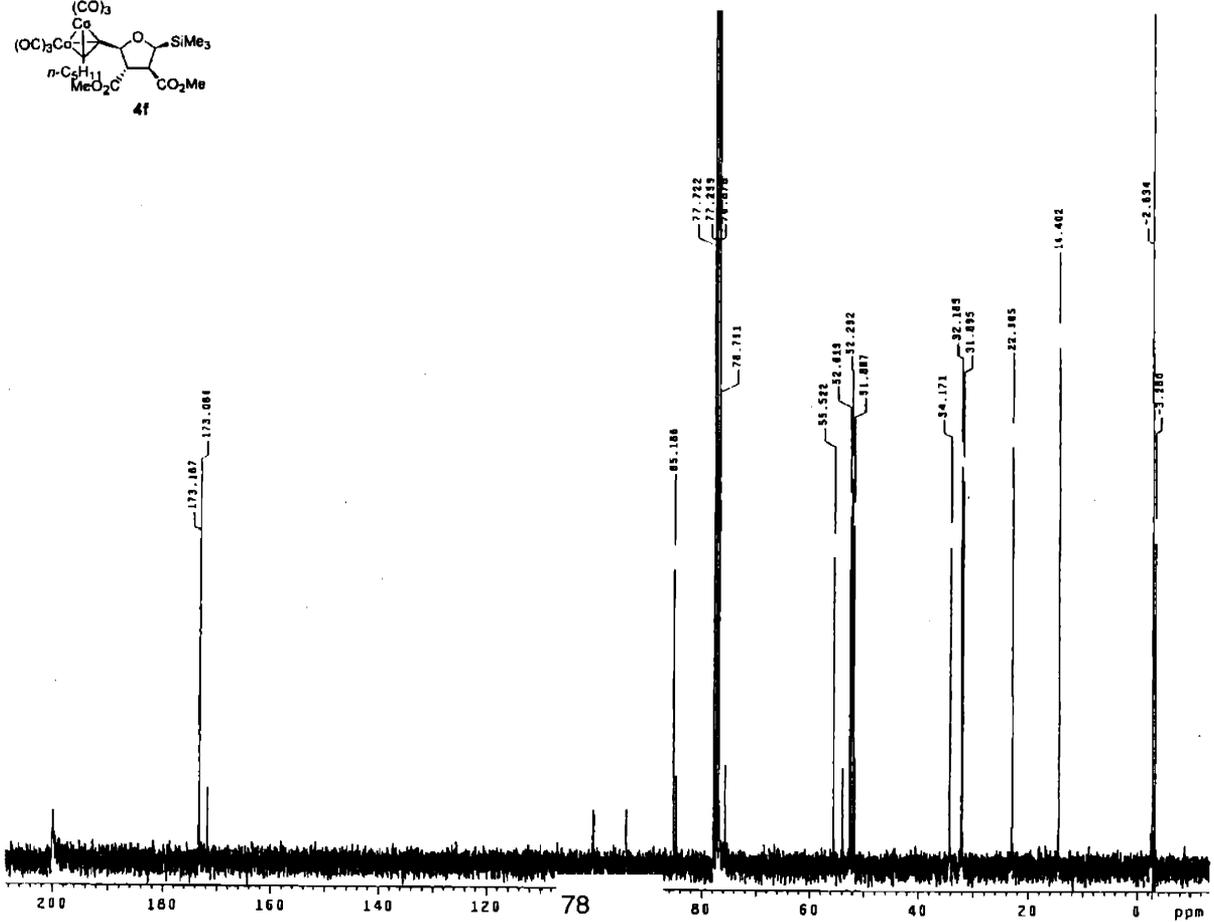
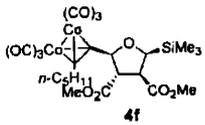
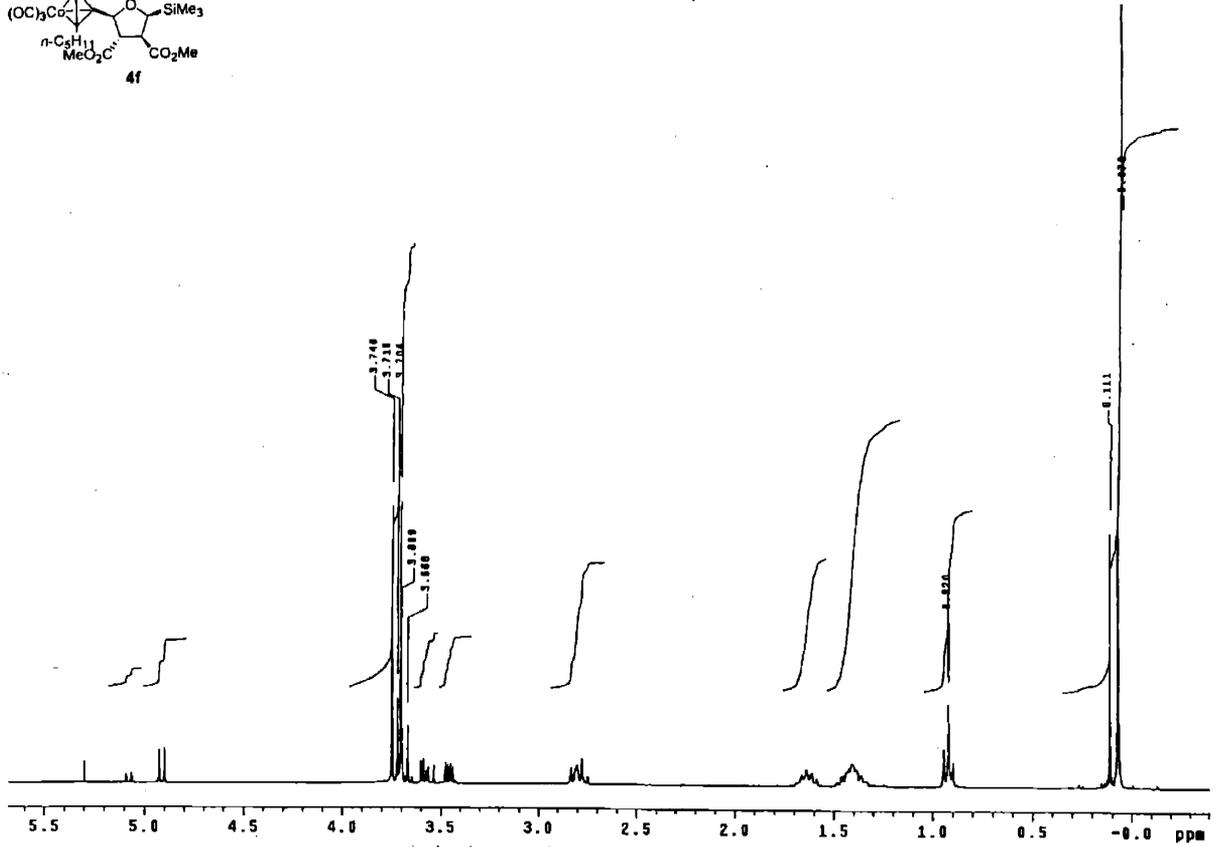
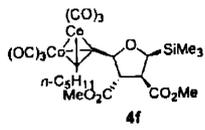


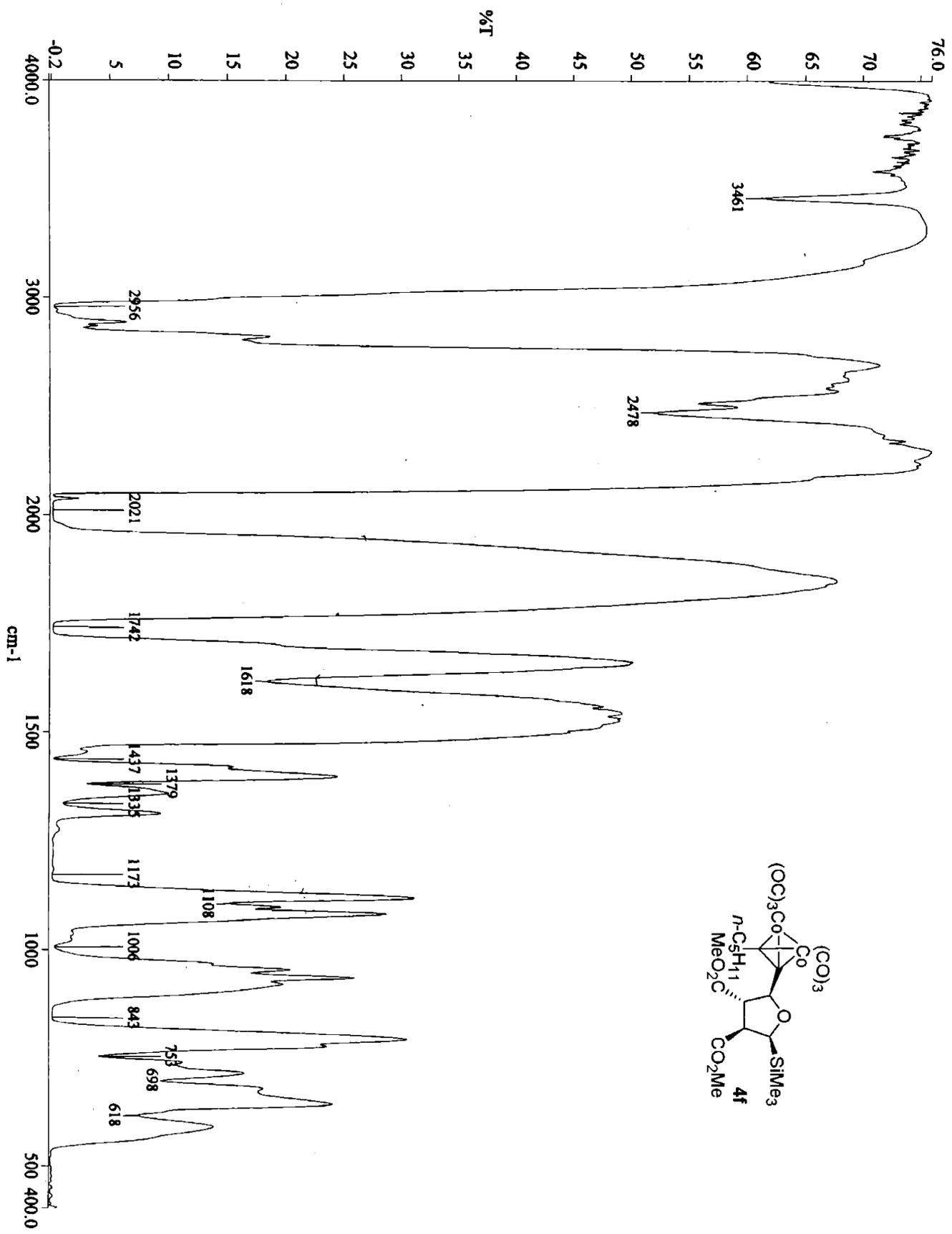


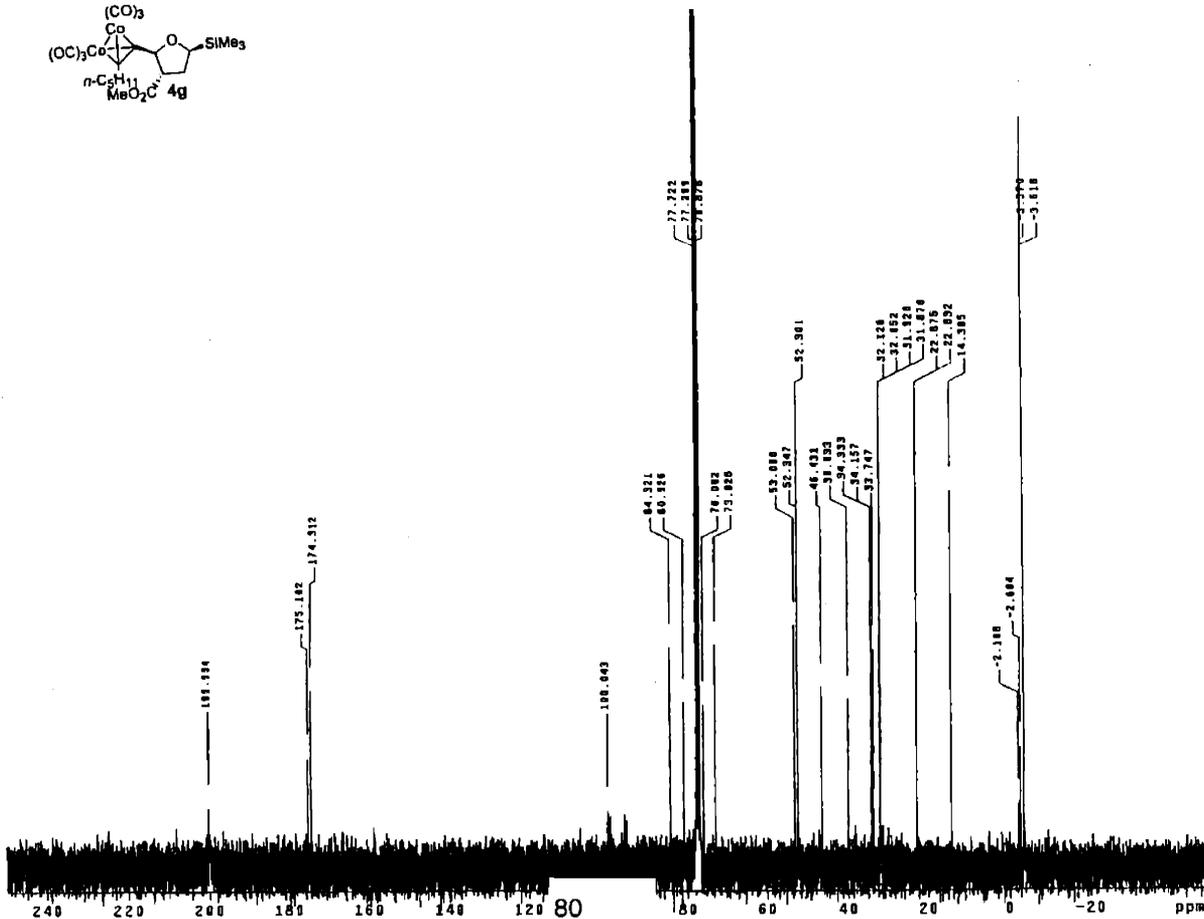
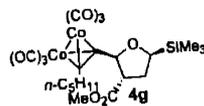
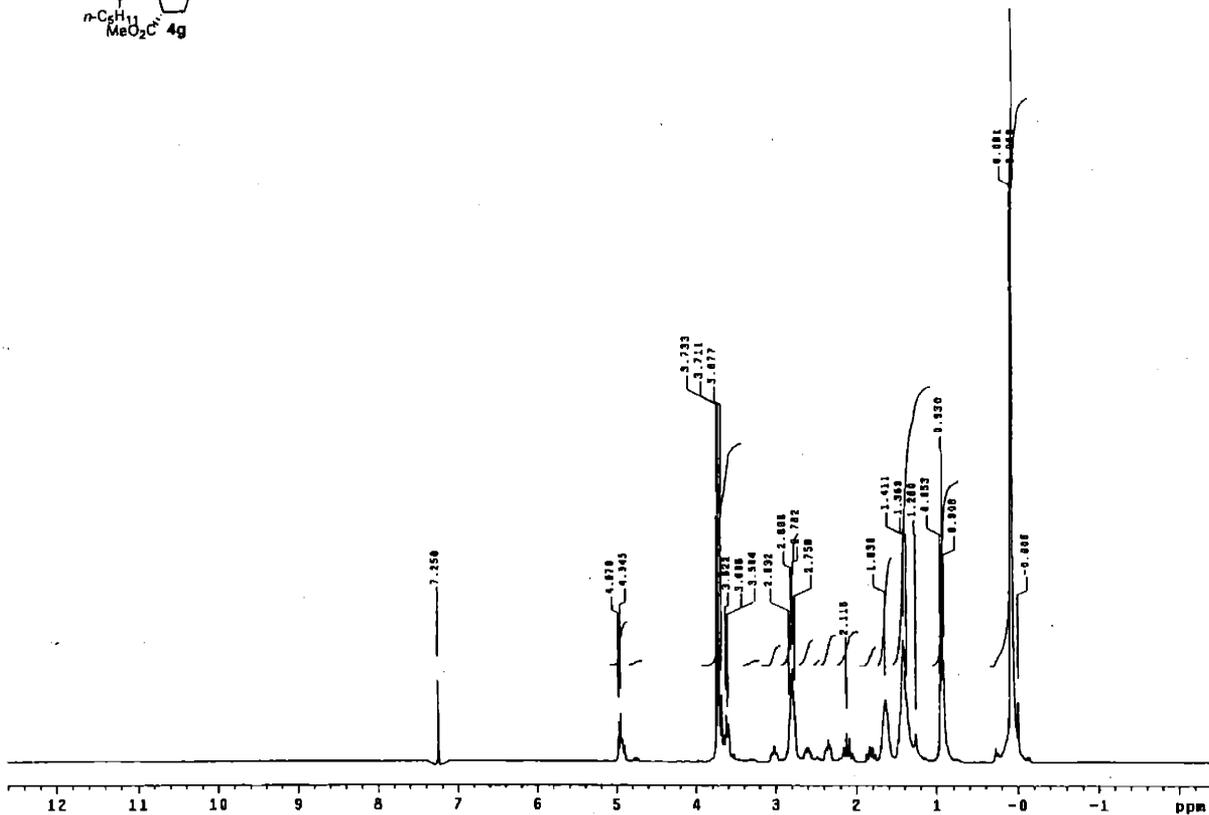
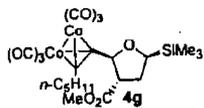


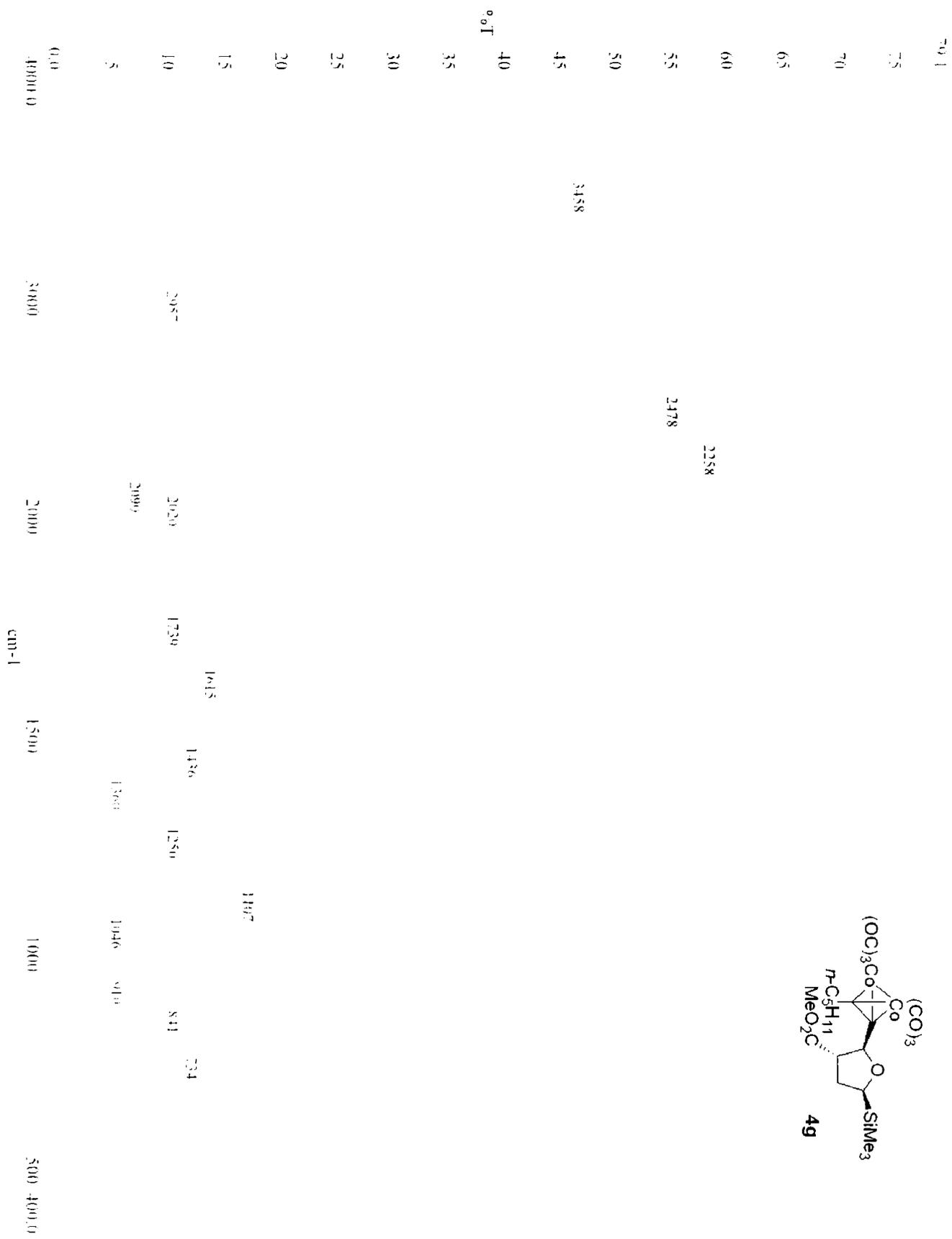
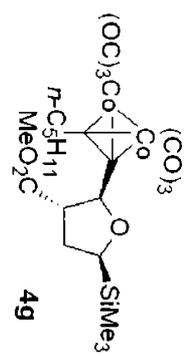


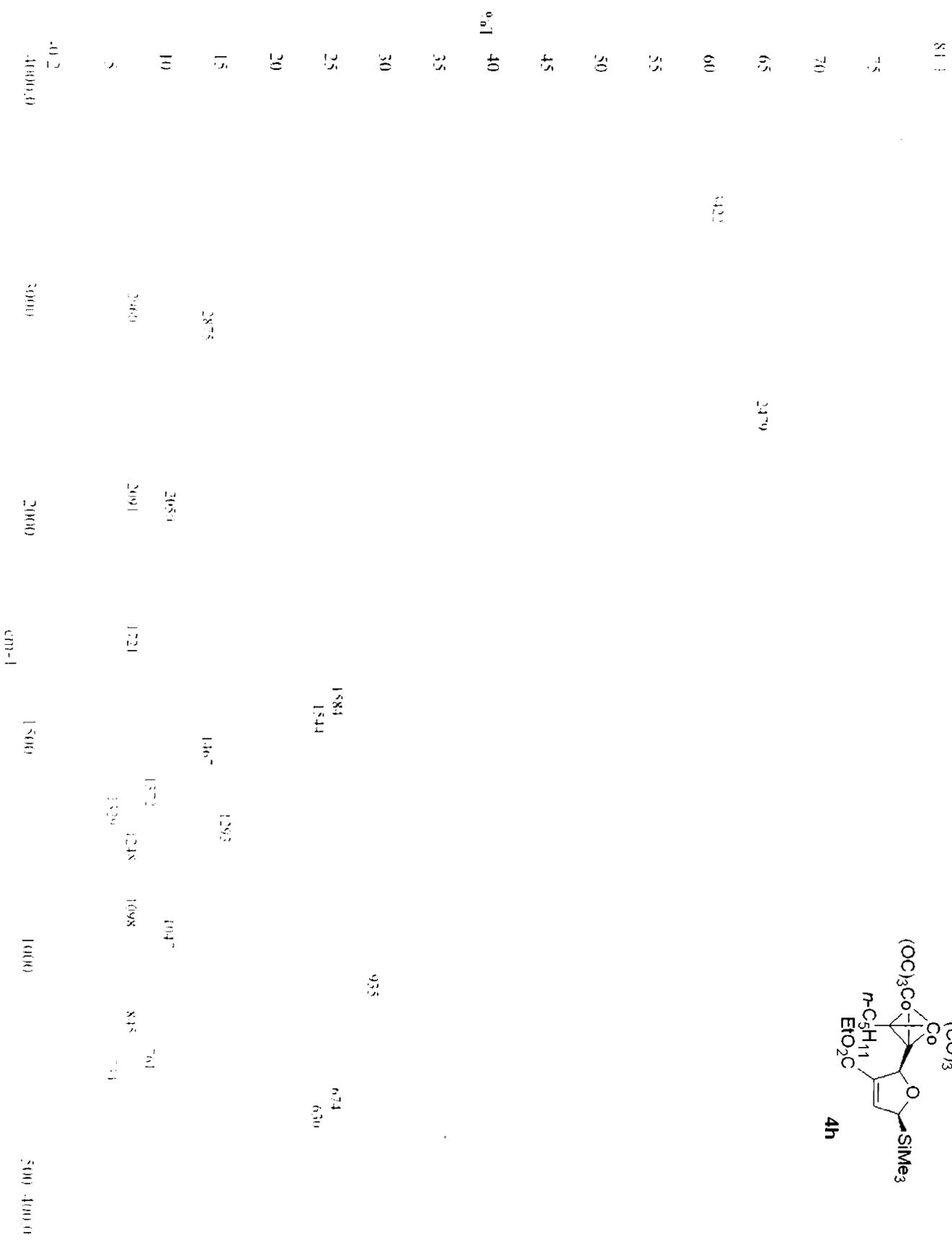
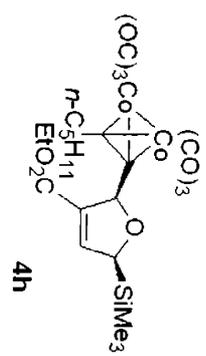


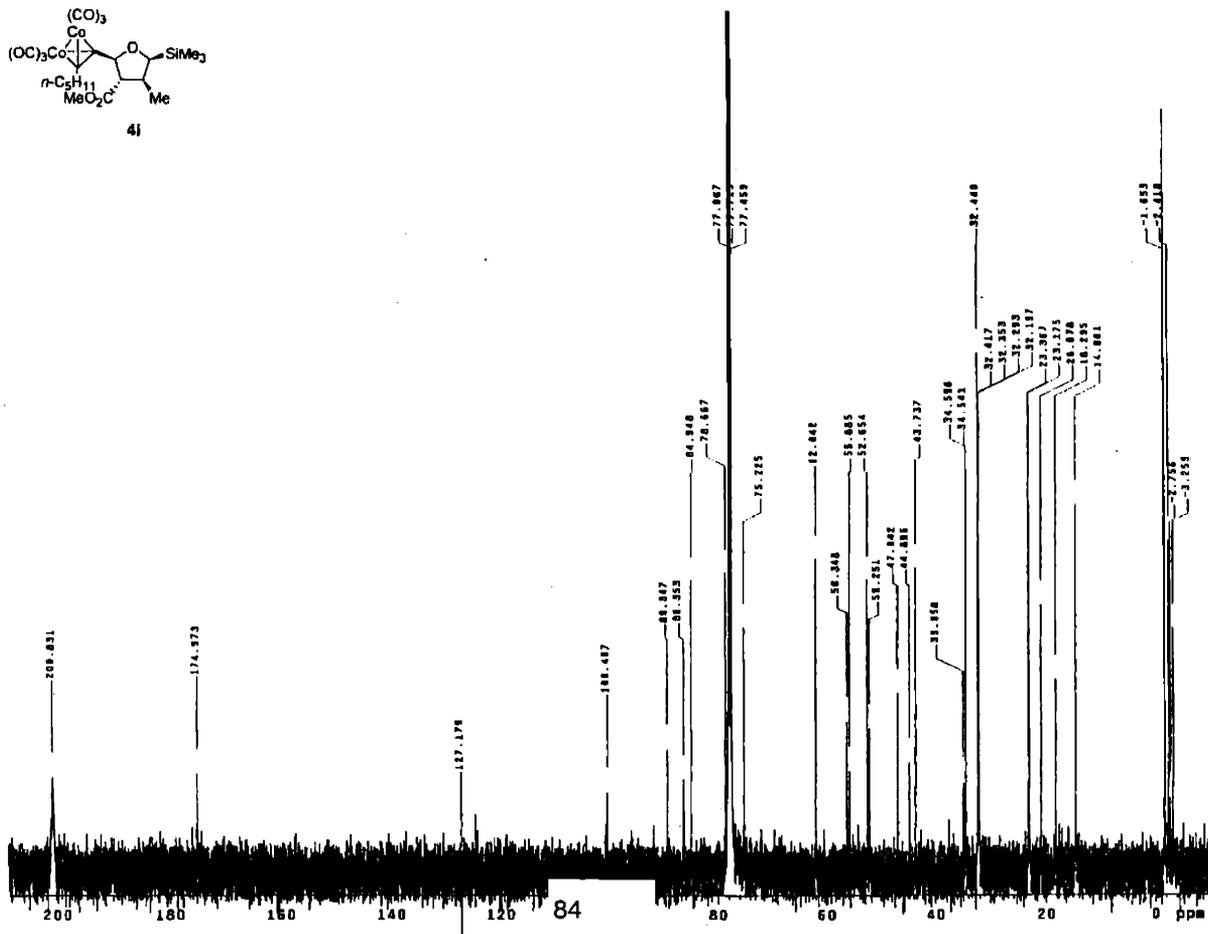
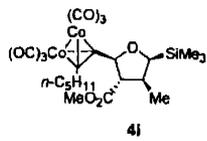
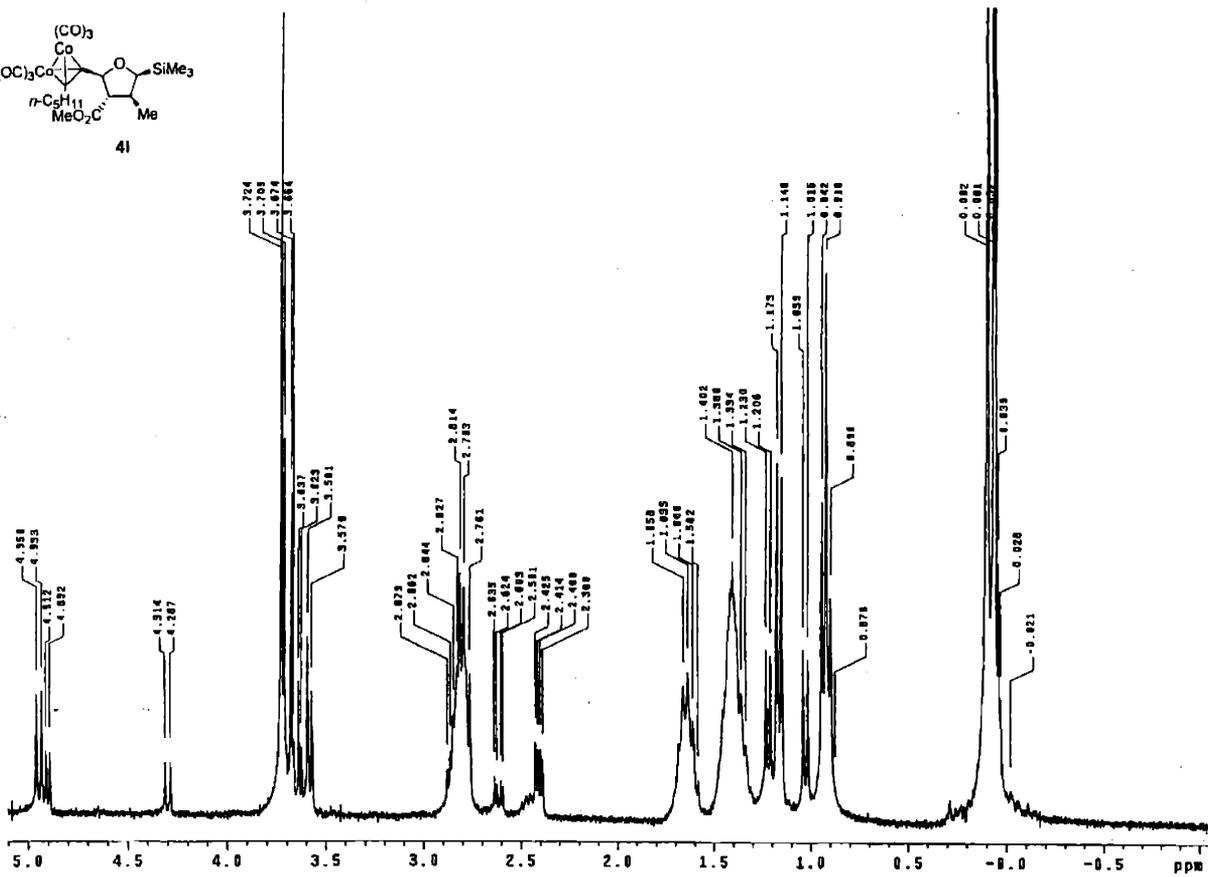
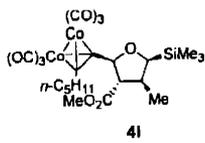


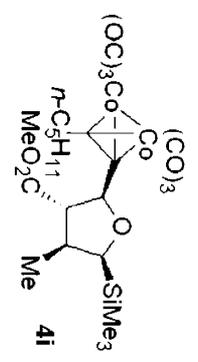


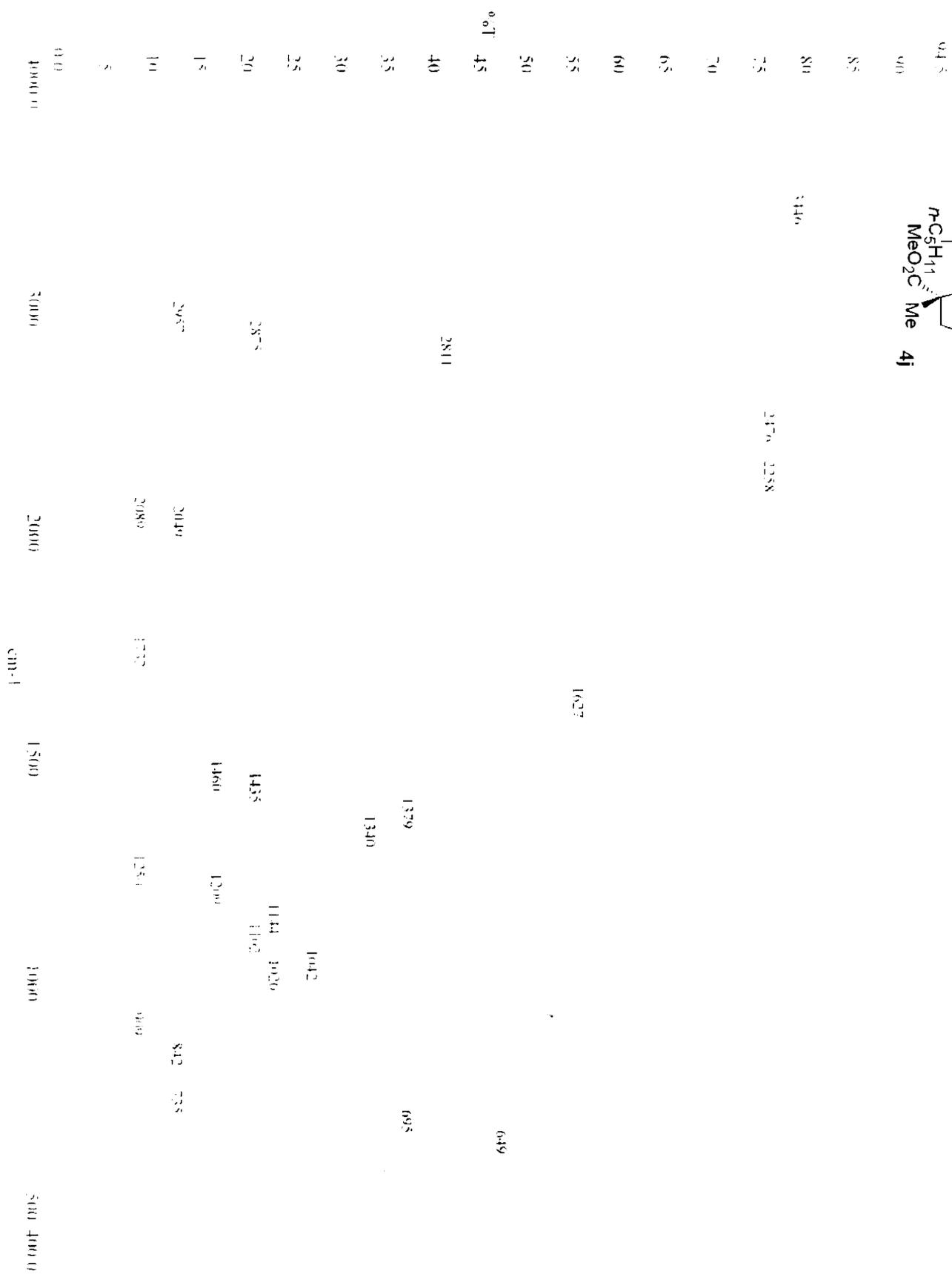
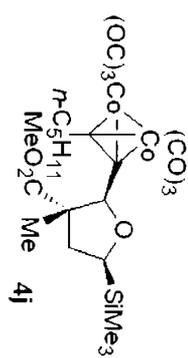




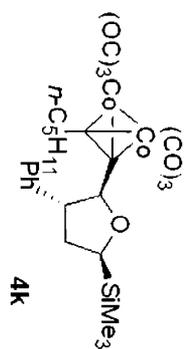
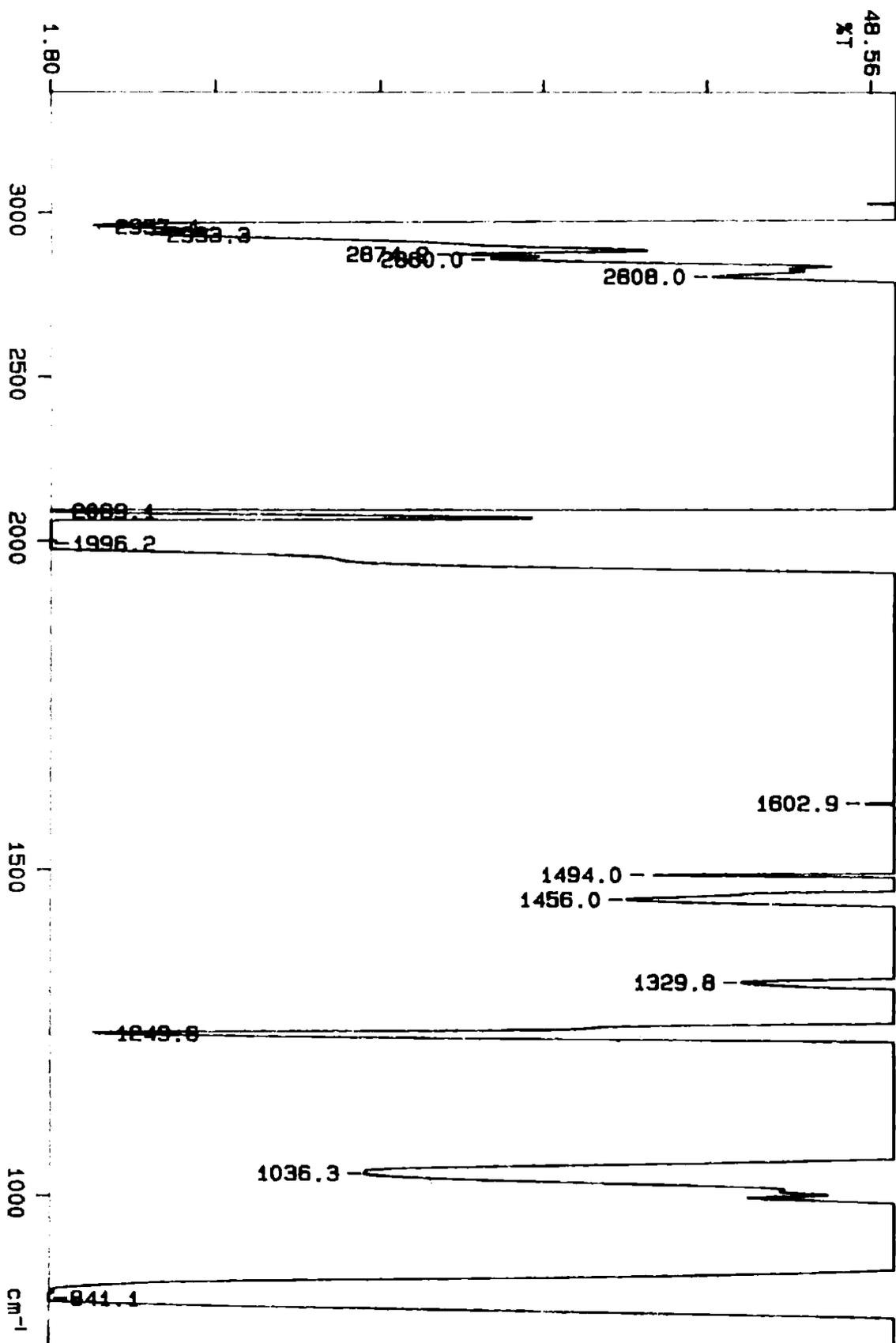


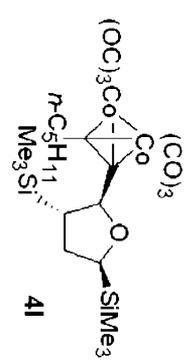


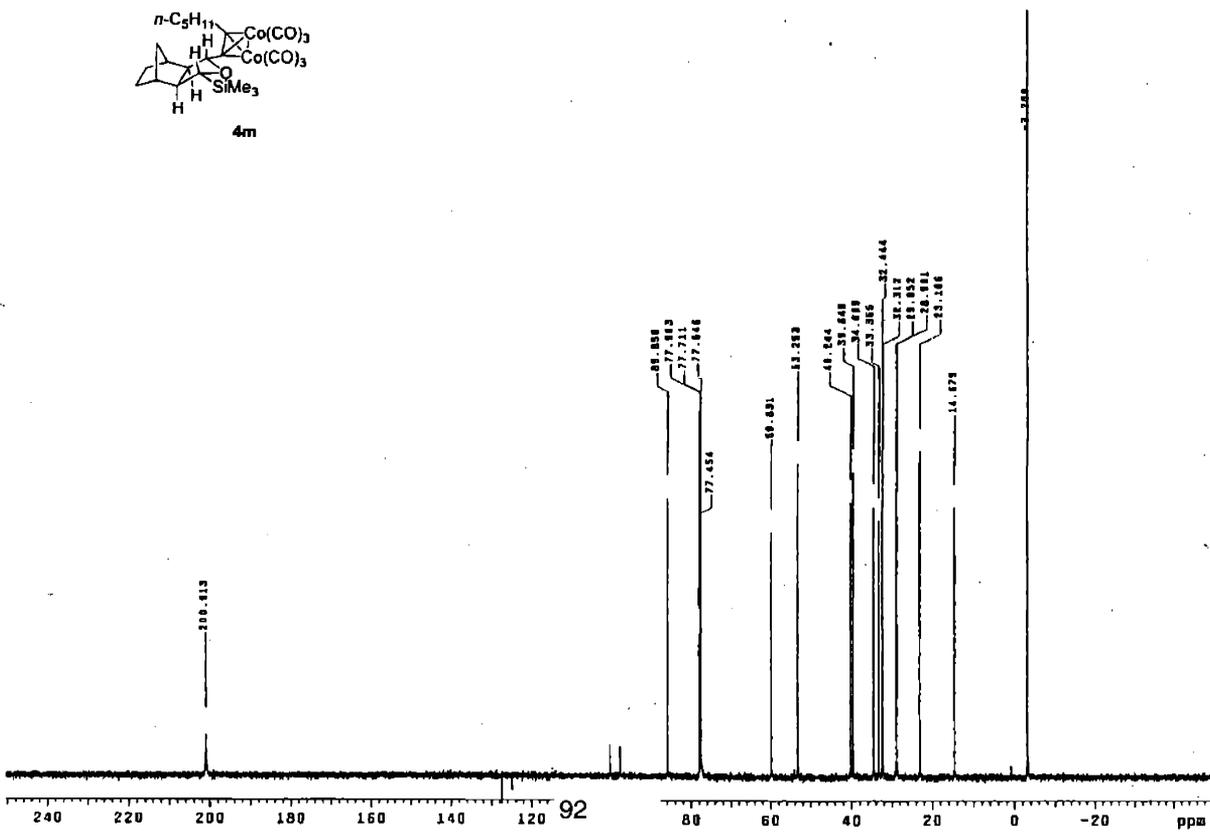
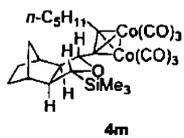
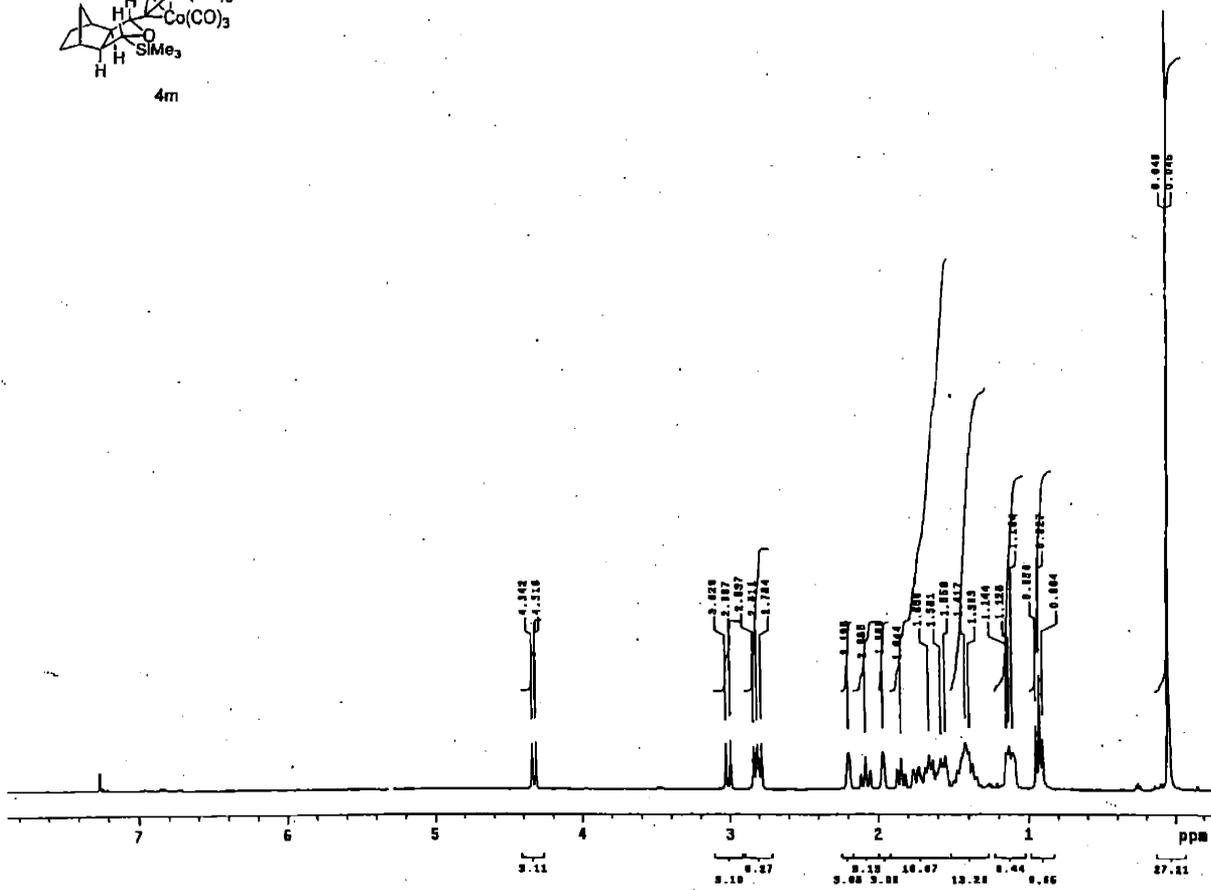
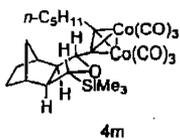


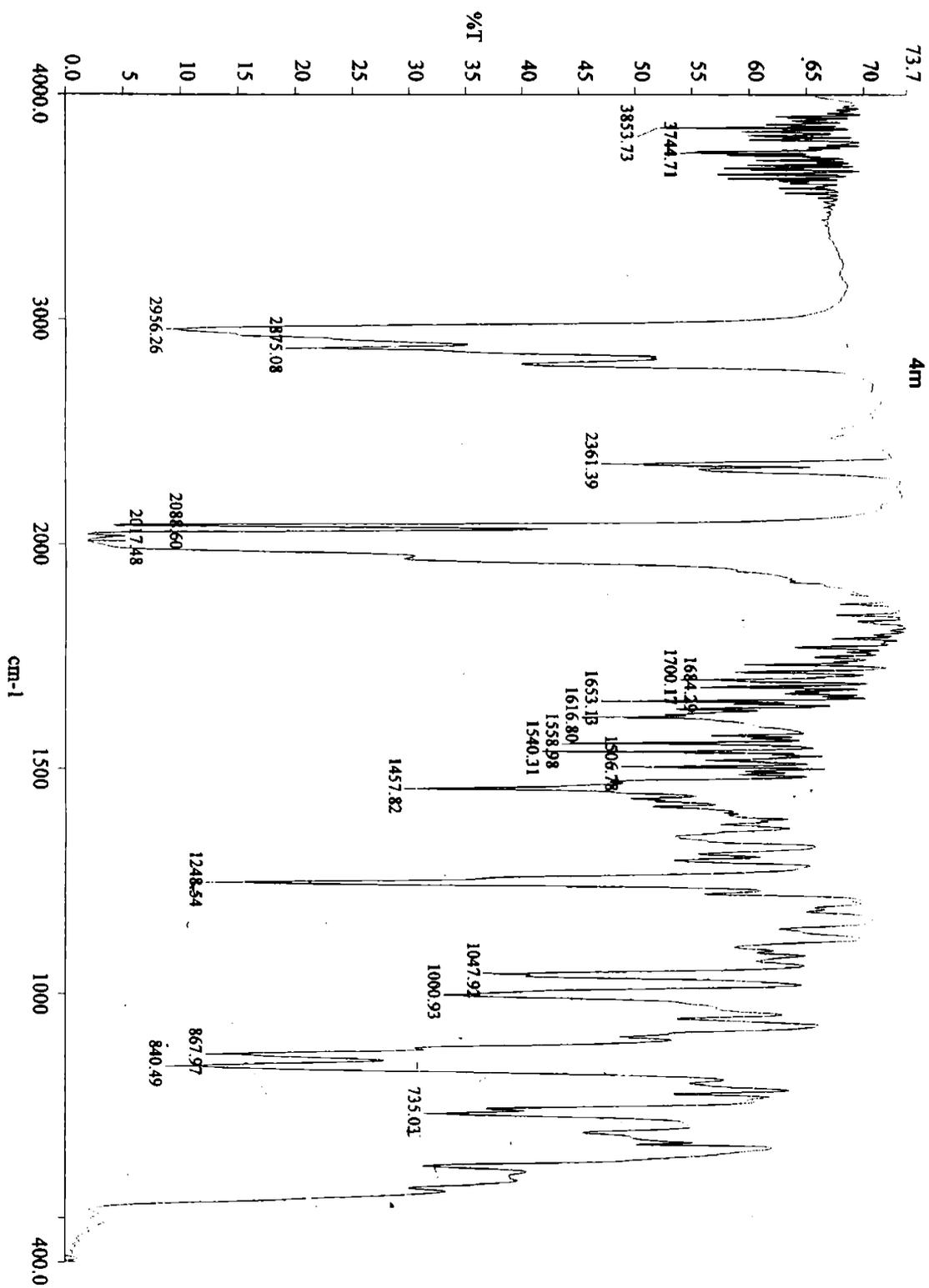
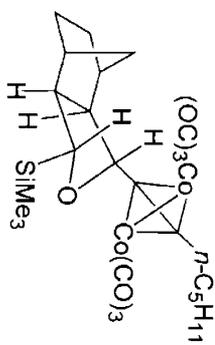


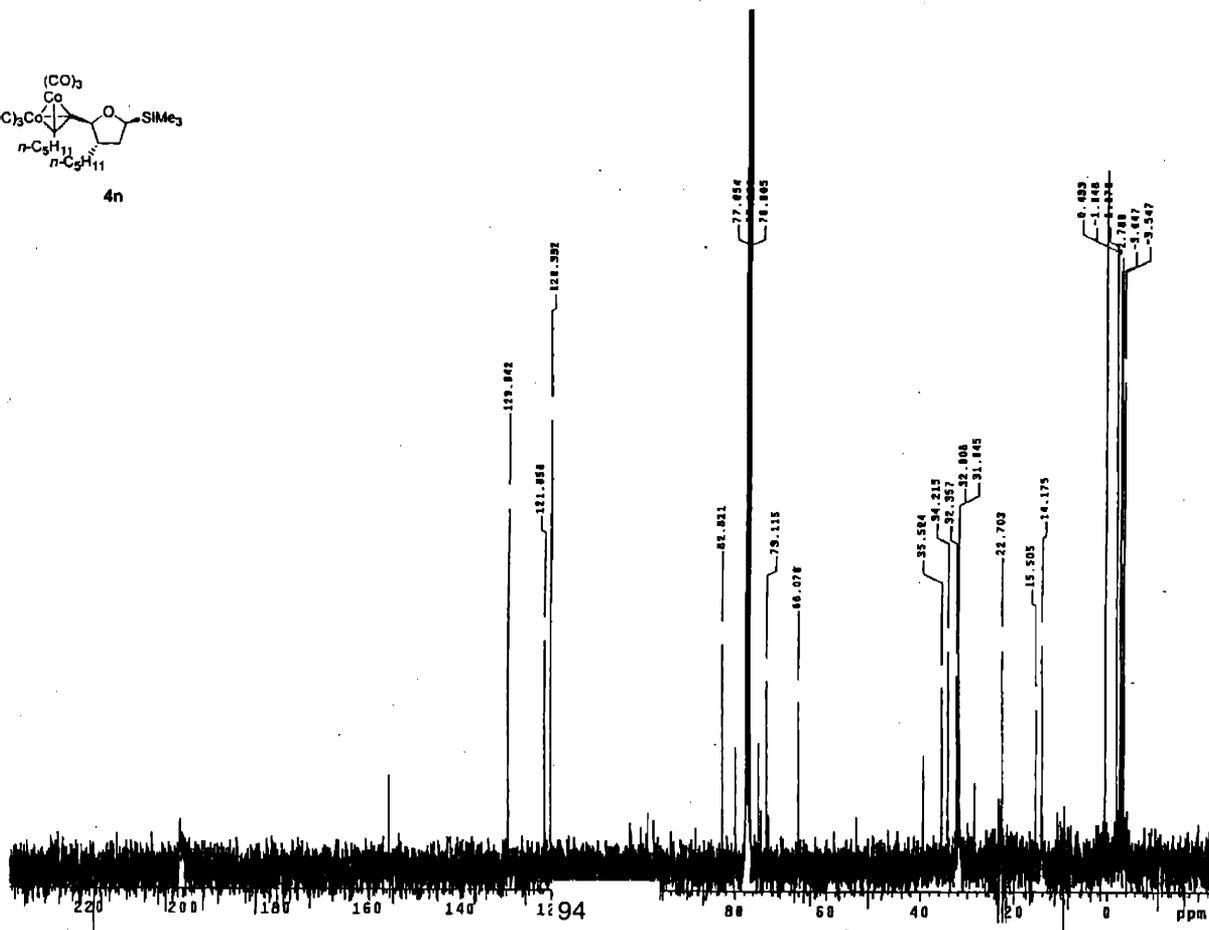
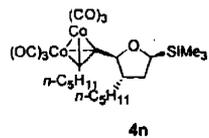
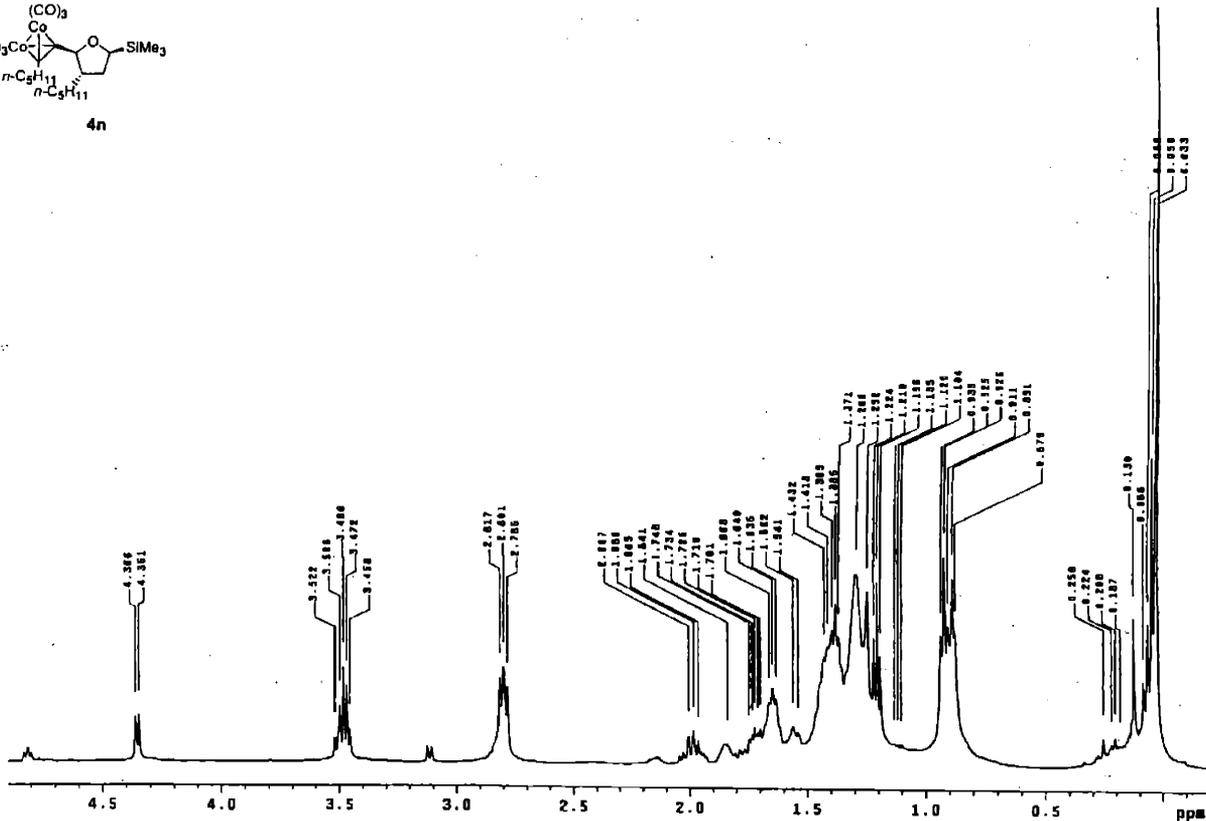
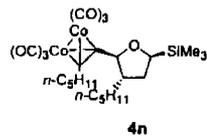
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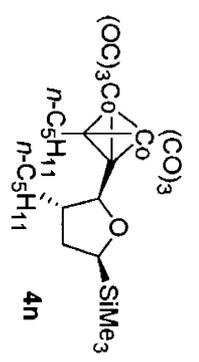
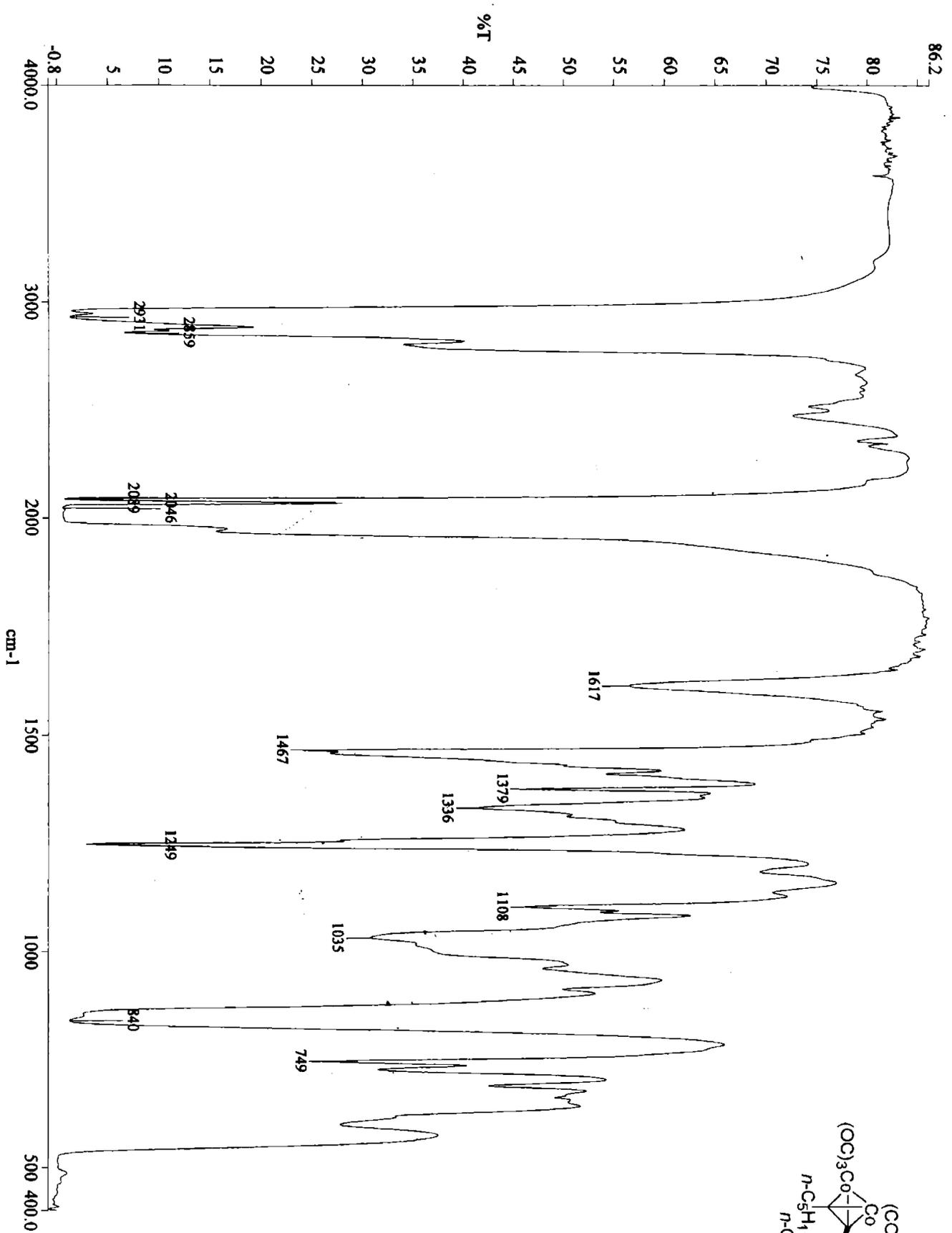




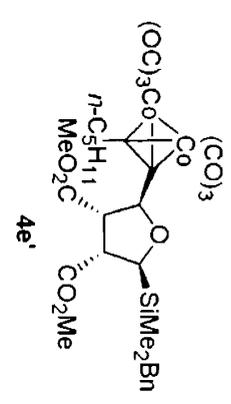








10
9
8
7
6
5
4
3
2
1
-0
ppm

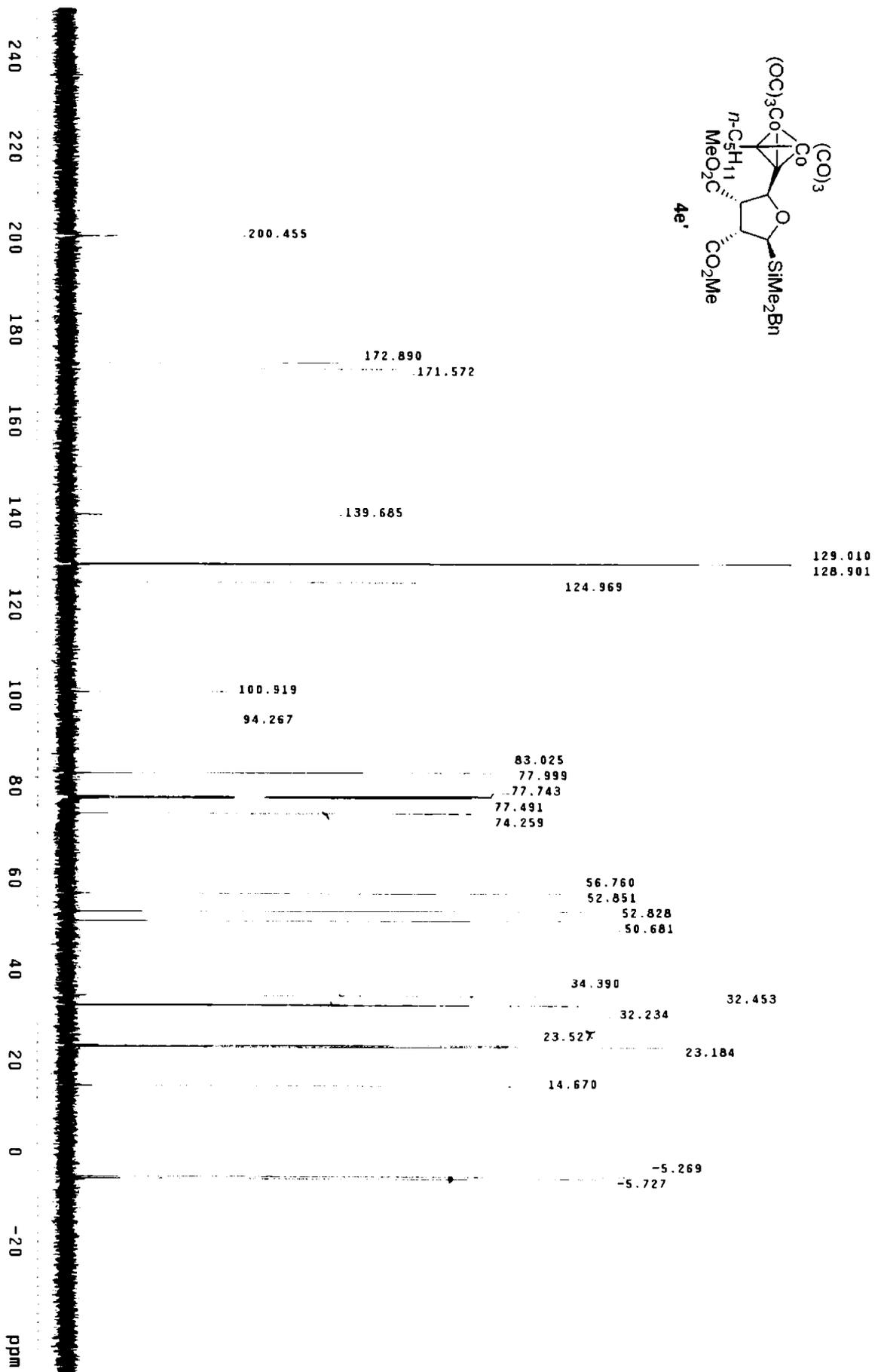


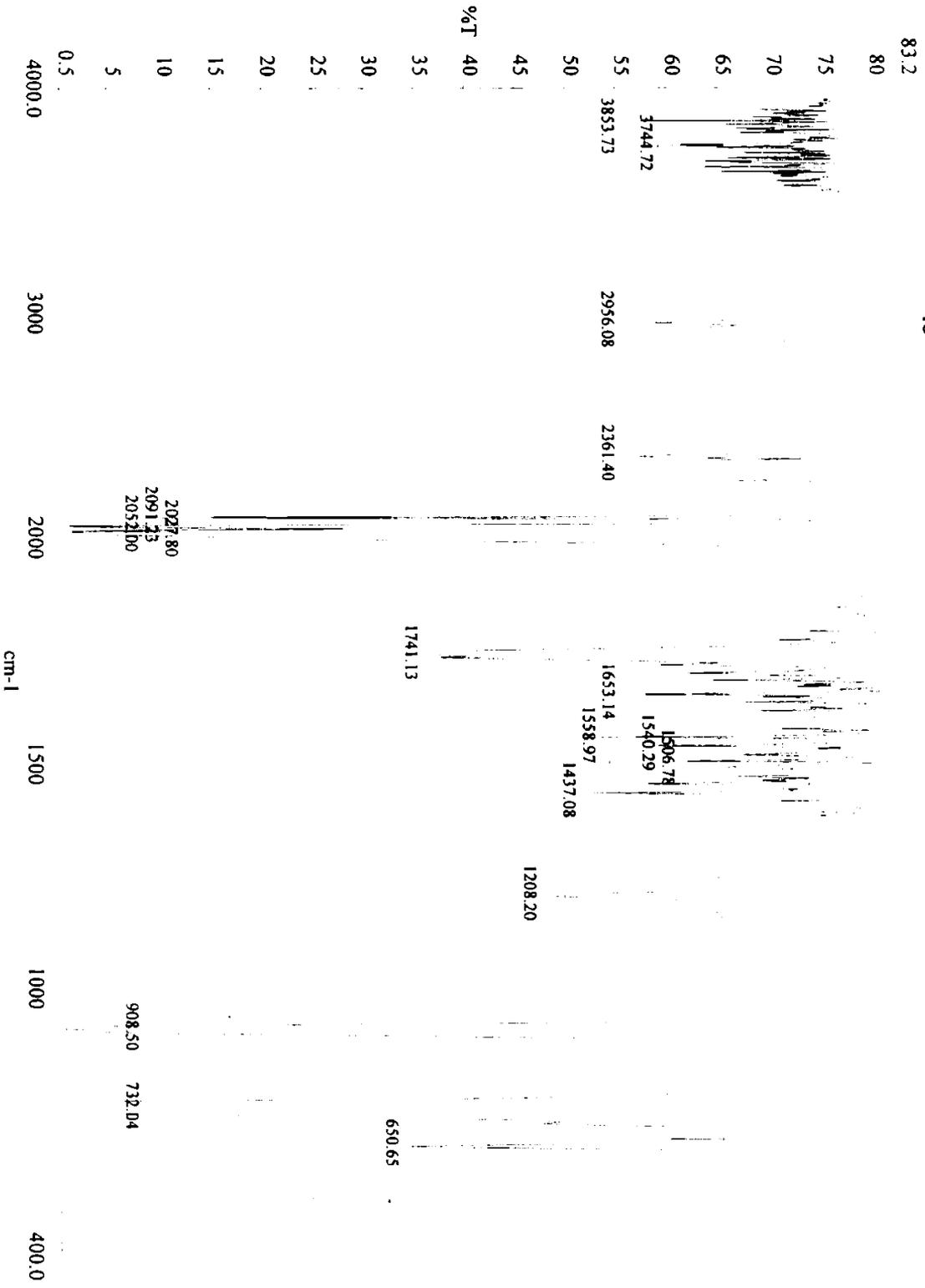
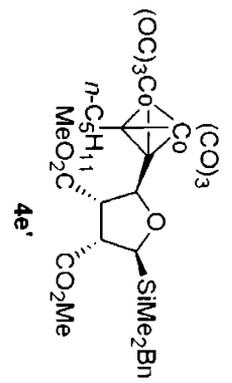
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7.211
7.199
7.196
7.098
7.083
7.024
7.009
7.008

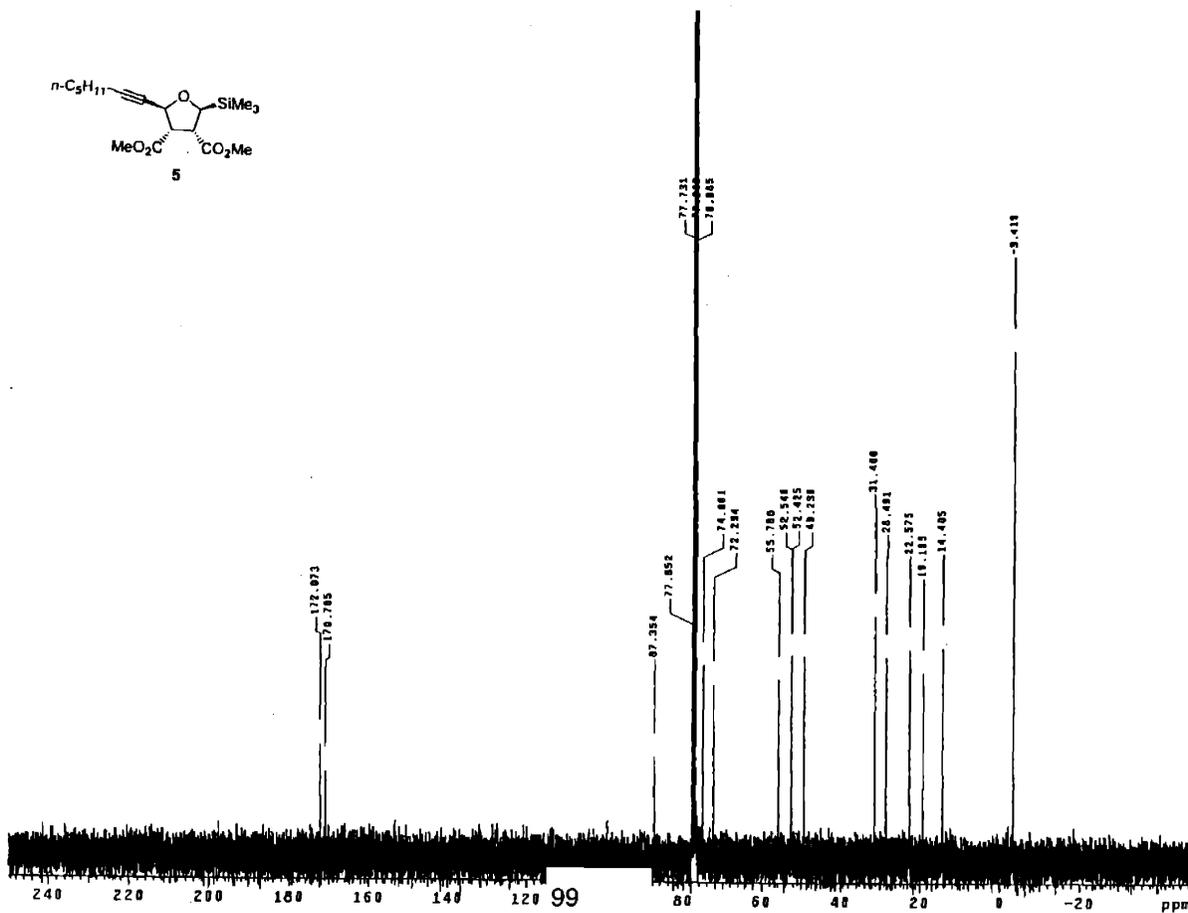
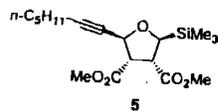
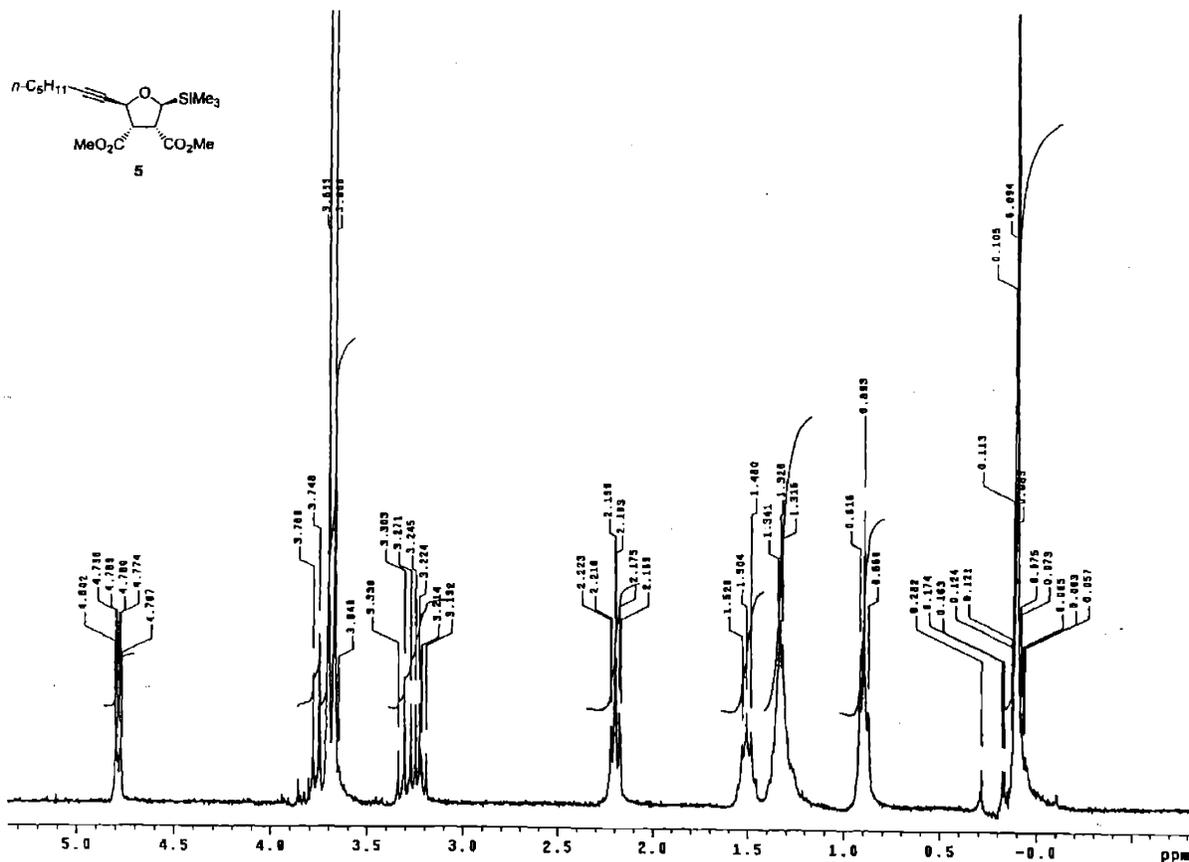
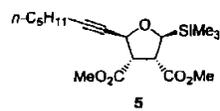
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5.187

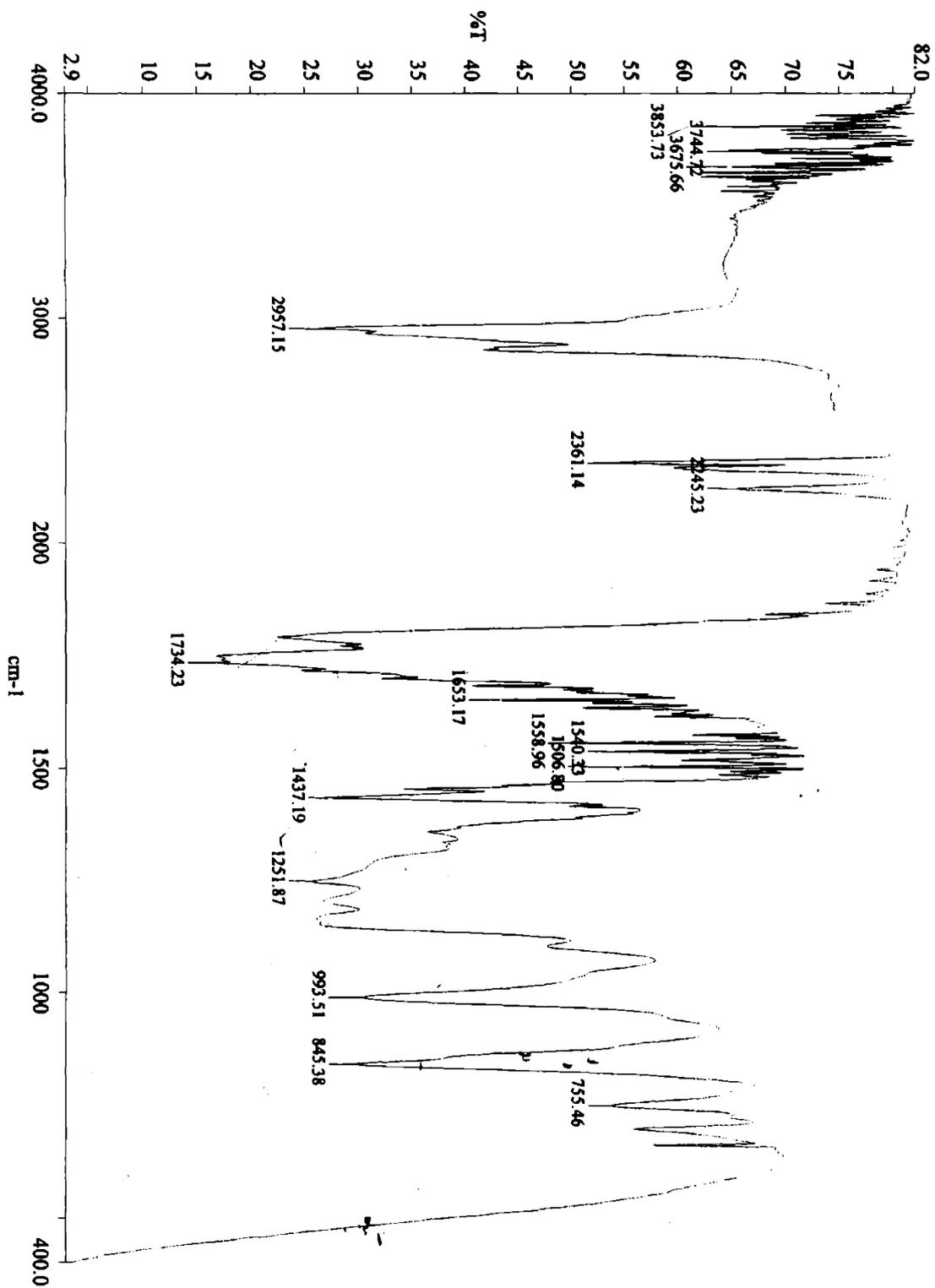
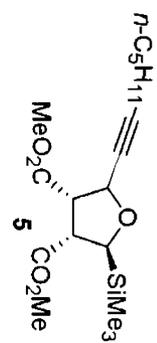
3.937
3.917

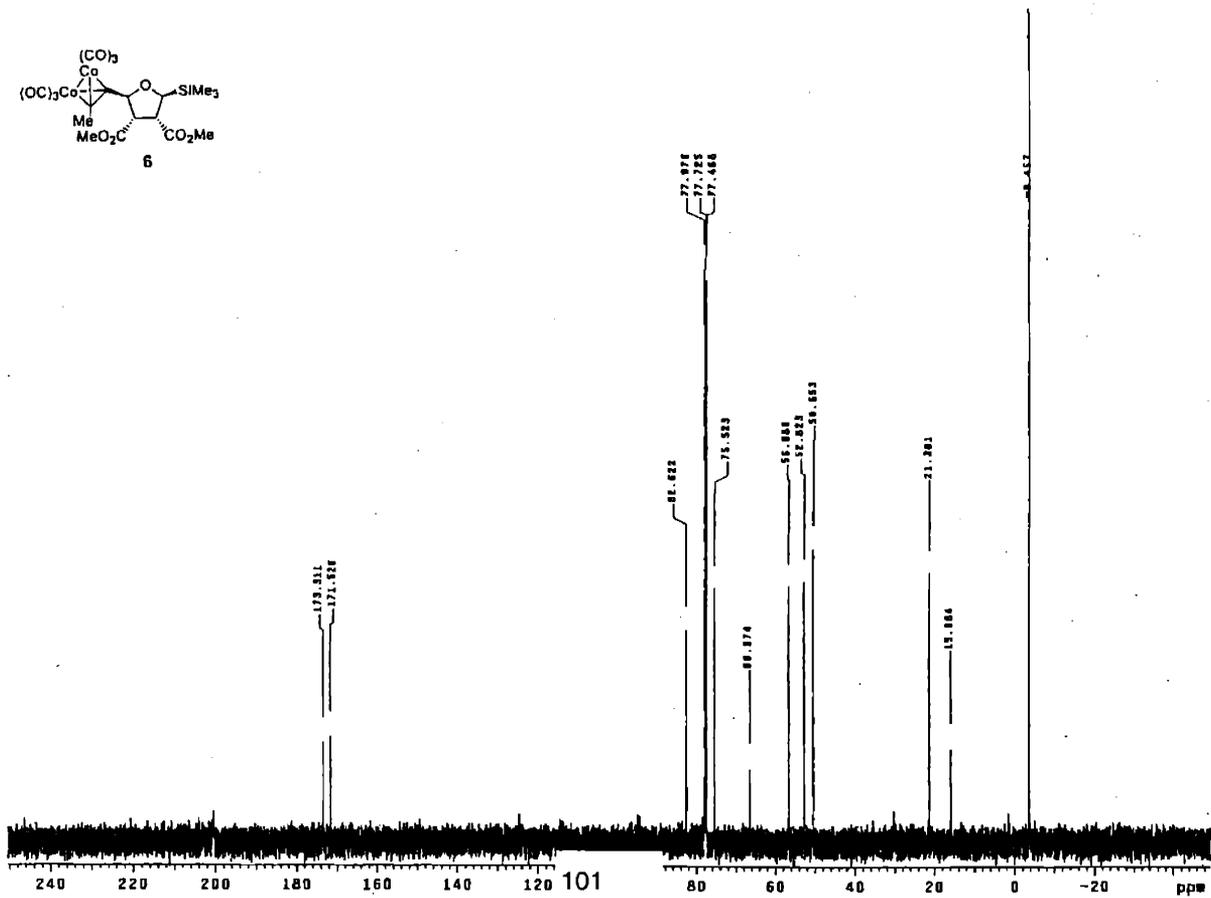
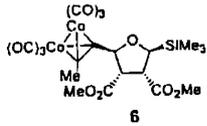
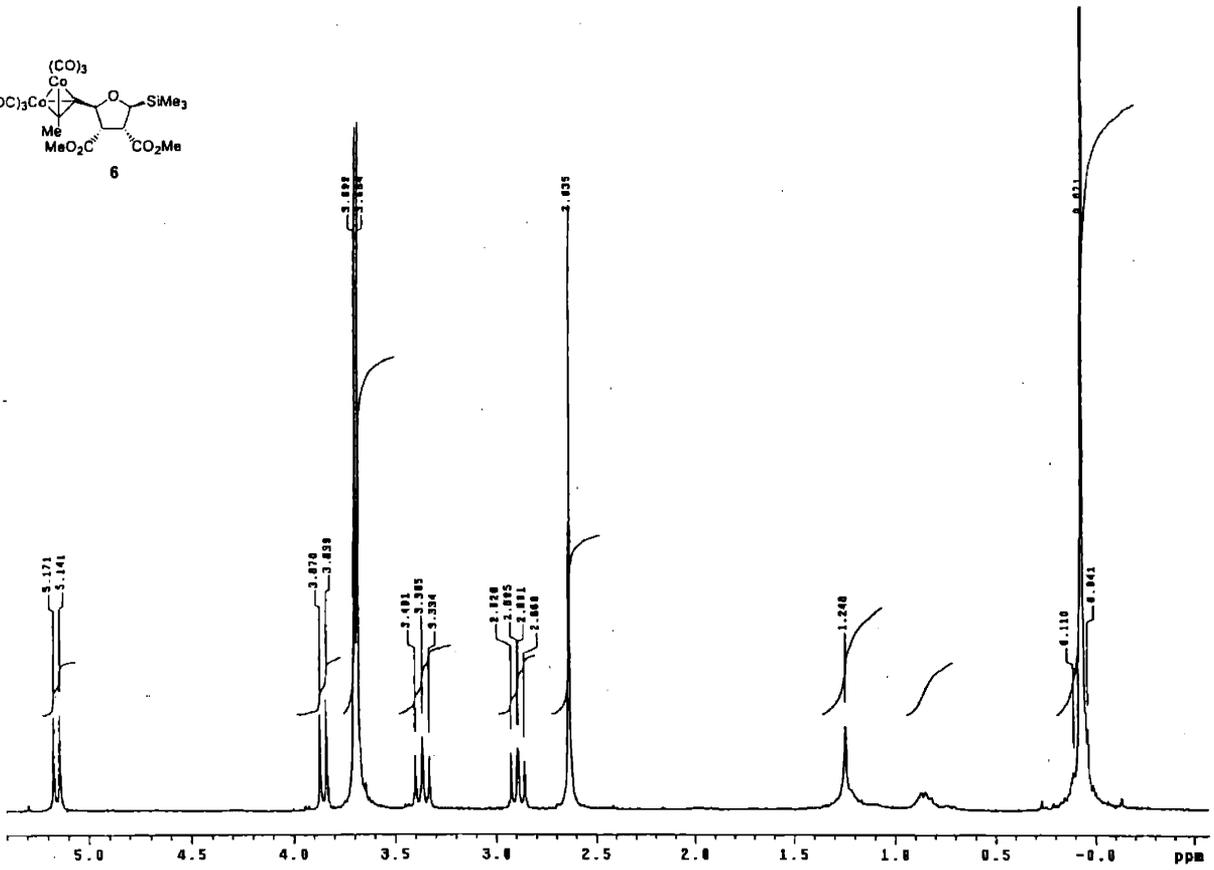
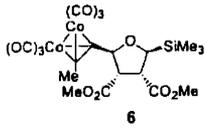
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3.675
3.406
3.387
3.385
3.365
2.988
2.970
2.967
2.949
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2.817
2.810
2.804
2.798
2.791
2.785
2.263
2.235
2.190
2.162
1.656
1.468
1.461
1.451
1.446
1.436
1.423
1.410
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1.380
1.366
0.947
0.933
0.919
0.059
0.052
0.017
0.010



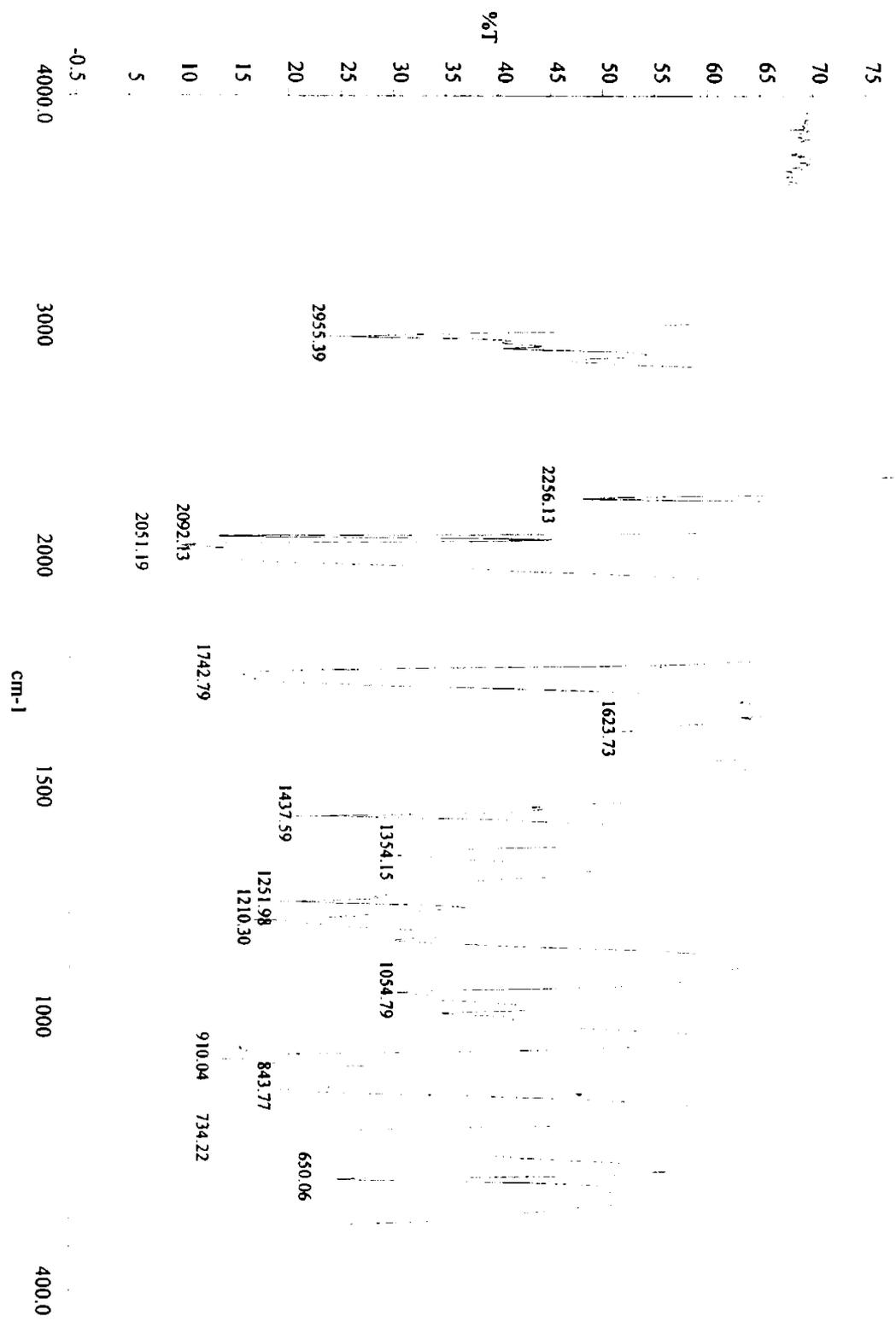
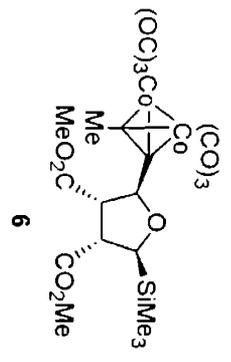


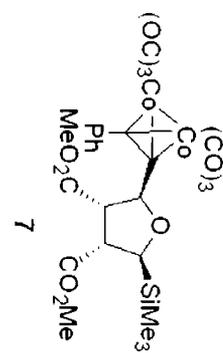






81.2





7.592
7.581
7.574
7.518
7.515
7.500
7.264
7.262
7.262

5.169
5.151
5.150
5.102
5.100

4.028
4.007

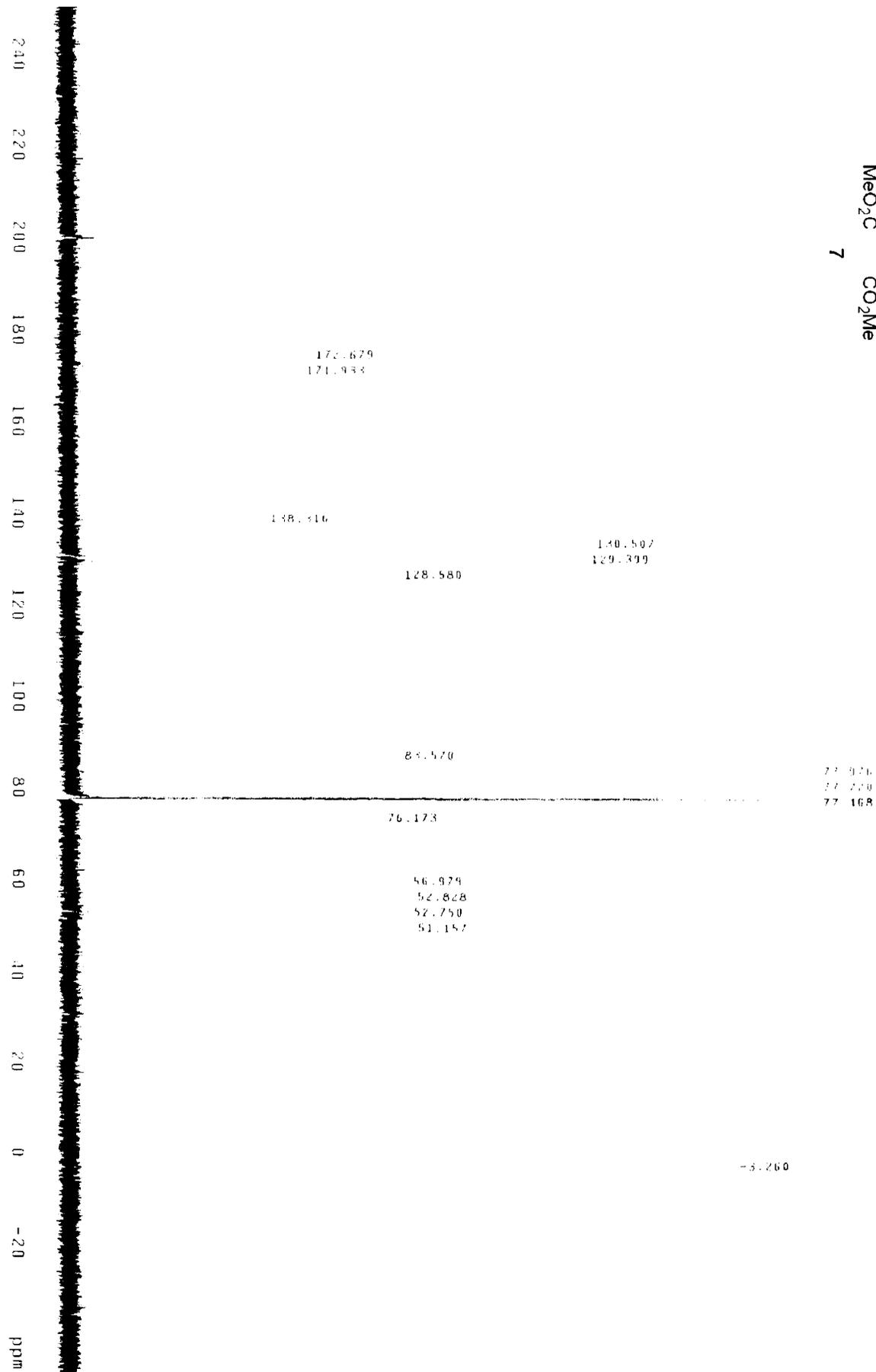
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3.086
3.100
3.111

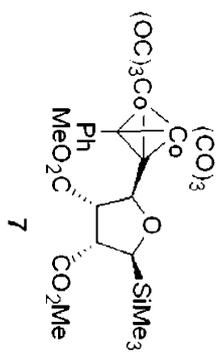
1.156

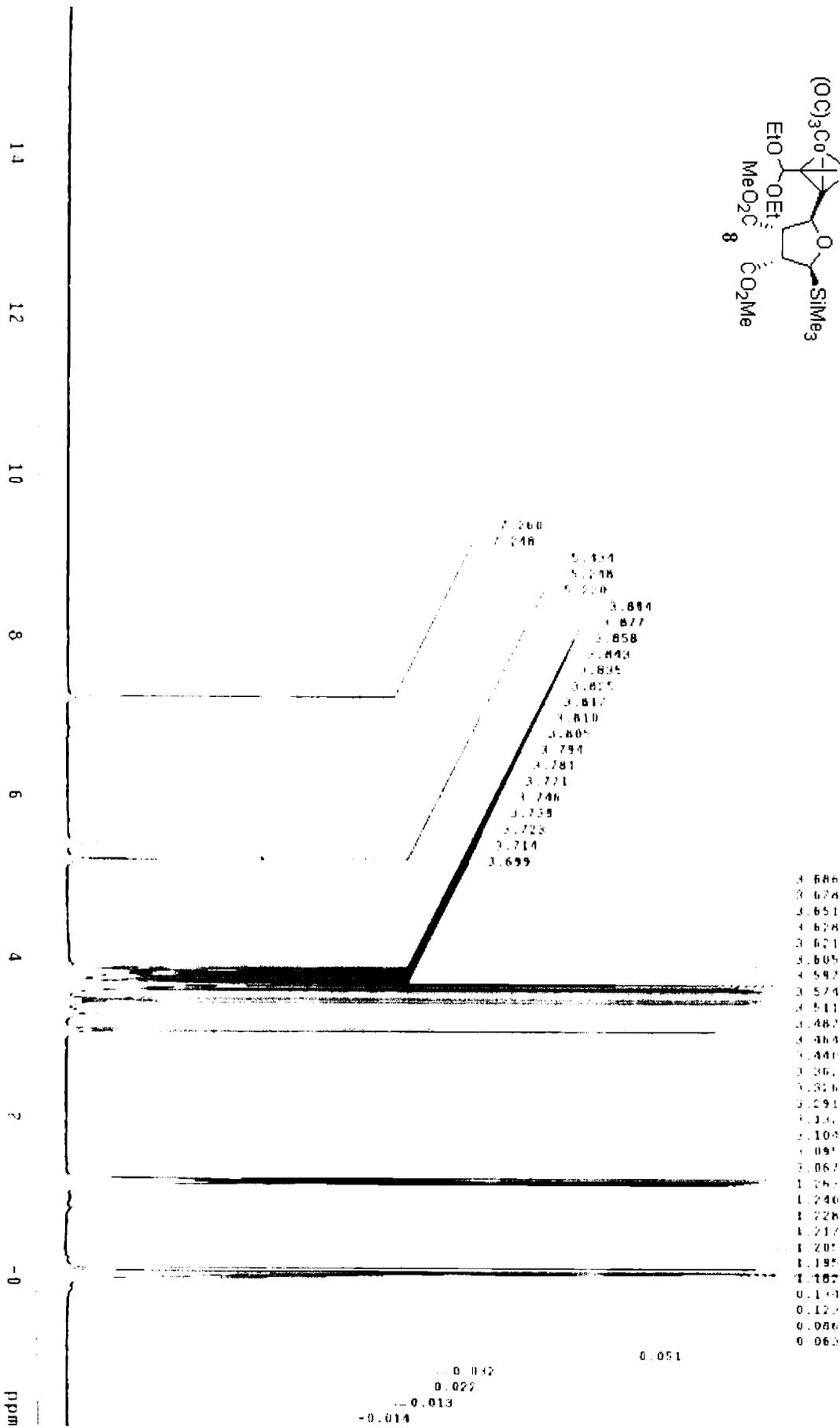
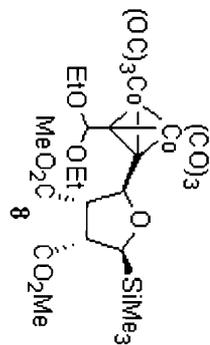
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3.576

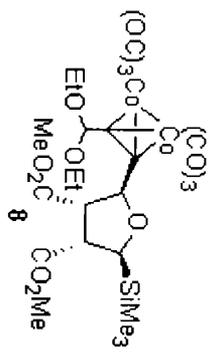
0.105
0.104
0.103

8 7 6 5 4 3 2 1 0 ppm









195.979
172.885
171.874

16.186

8.117

77.577
77.770
77.168

66.578

76.054

64.586

63.912
60.558
57.277

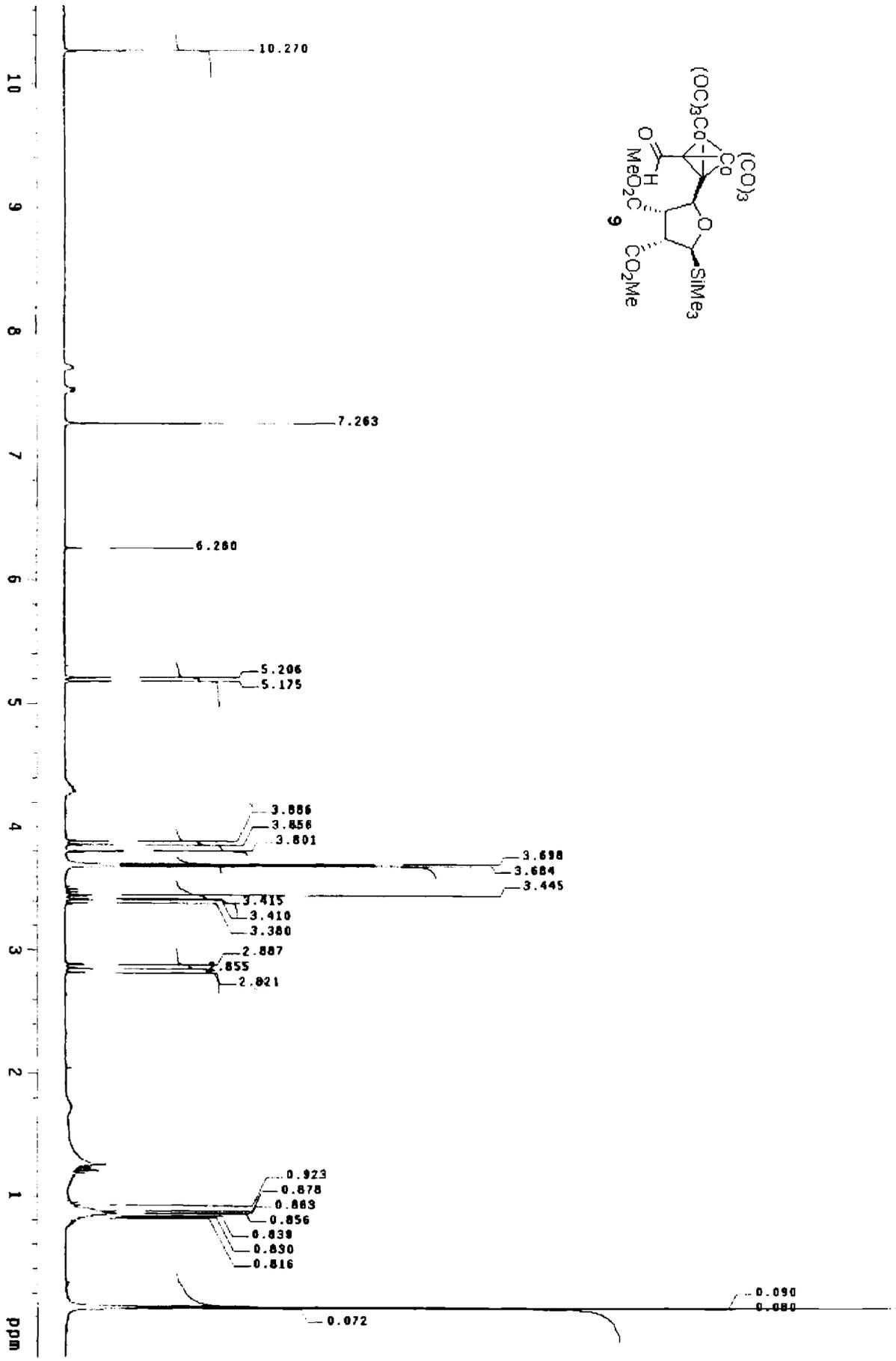
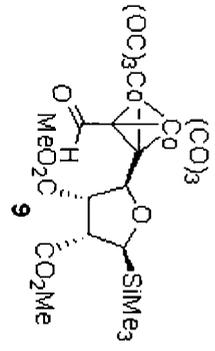
52.717
50.877

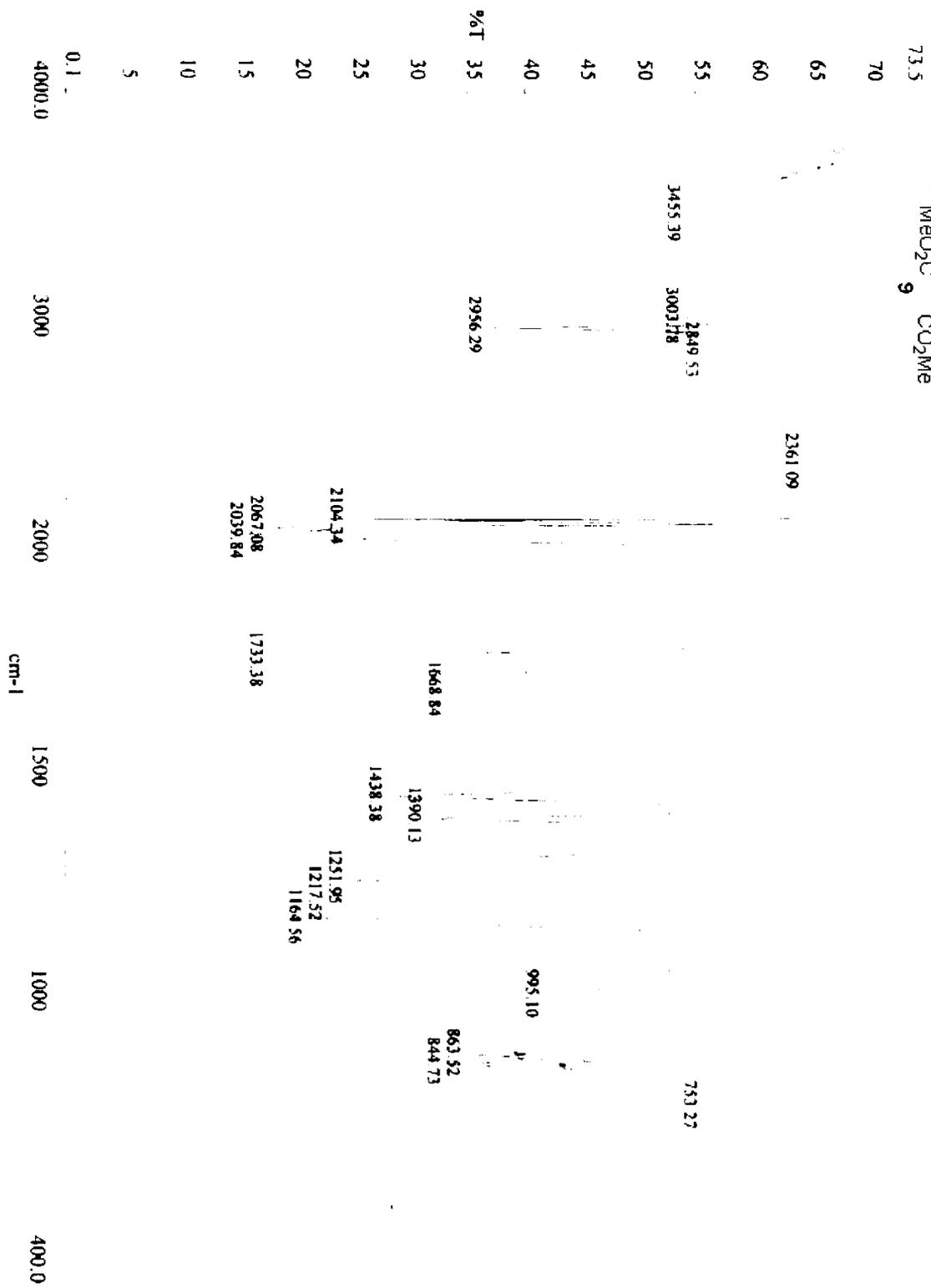
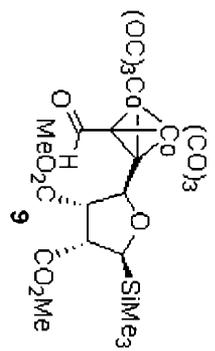
15.988

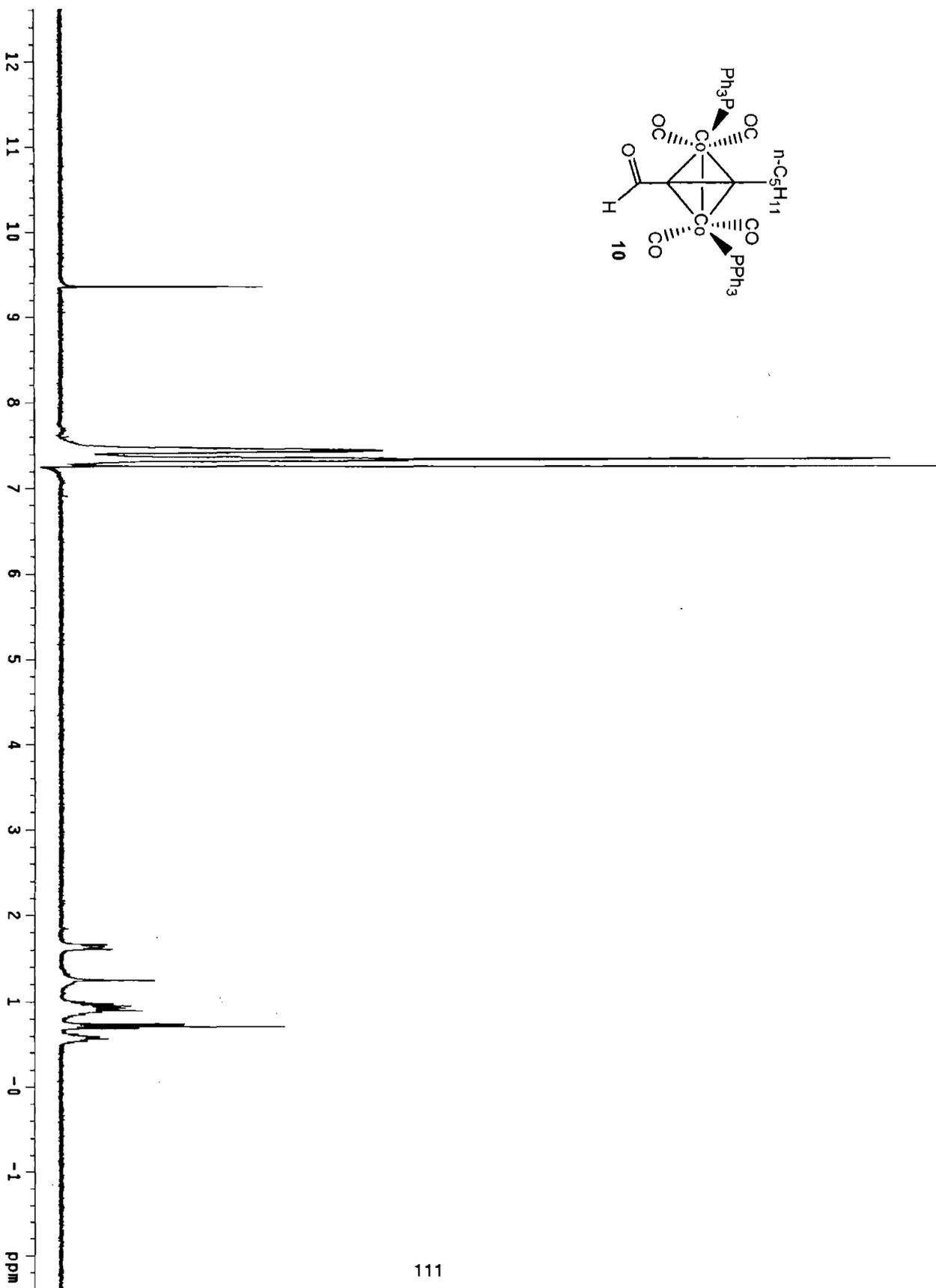
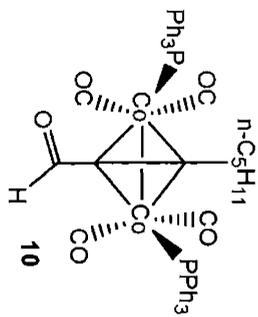
15.273
15.668

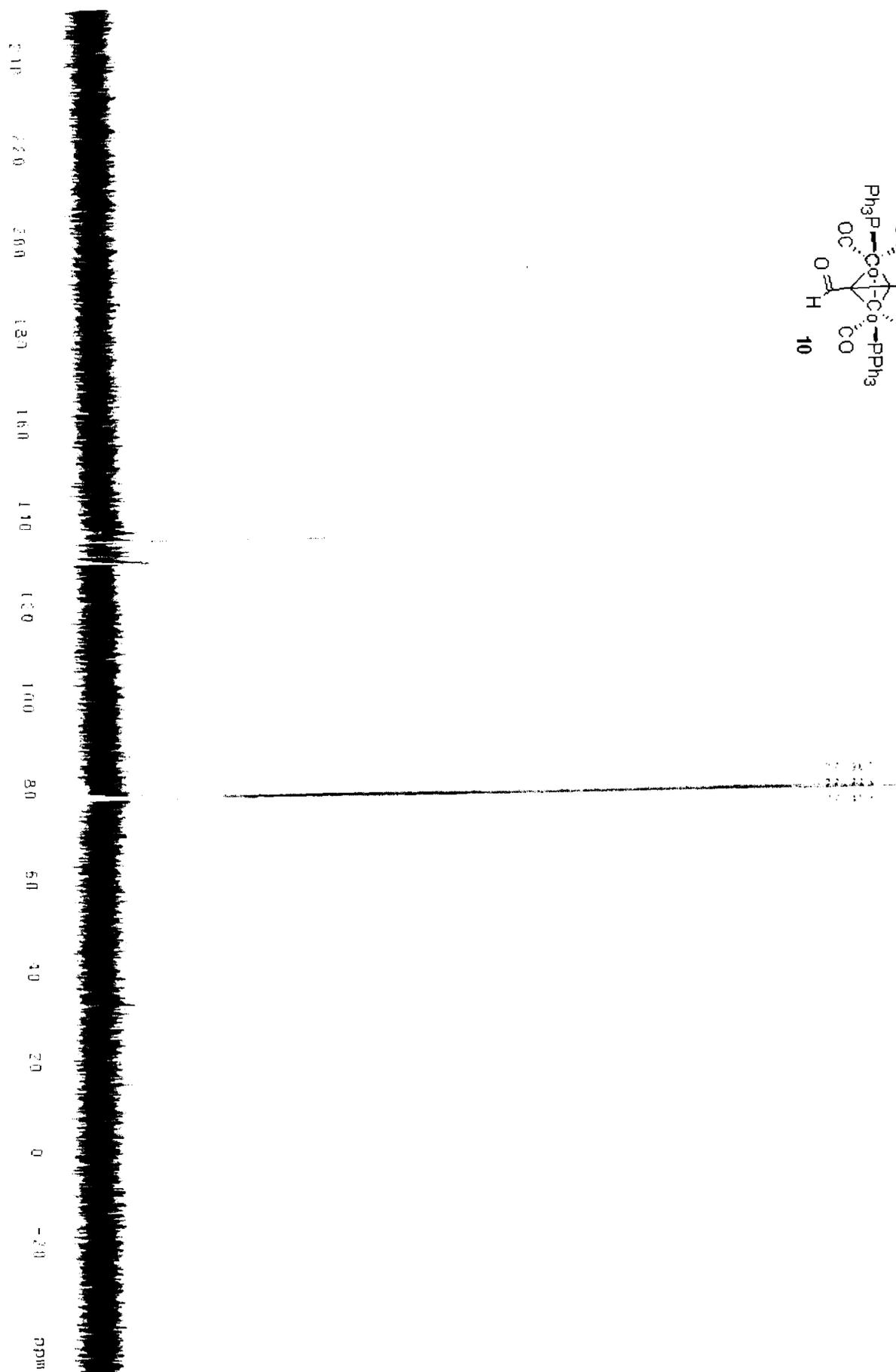
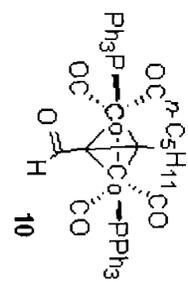
-8.570

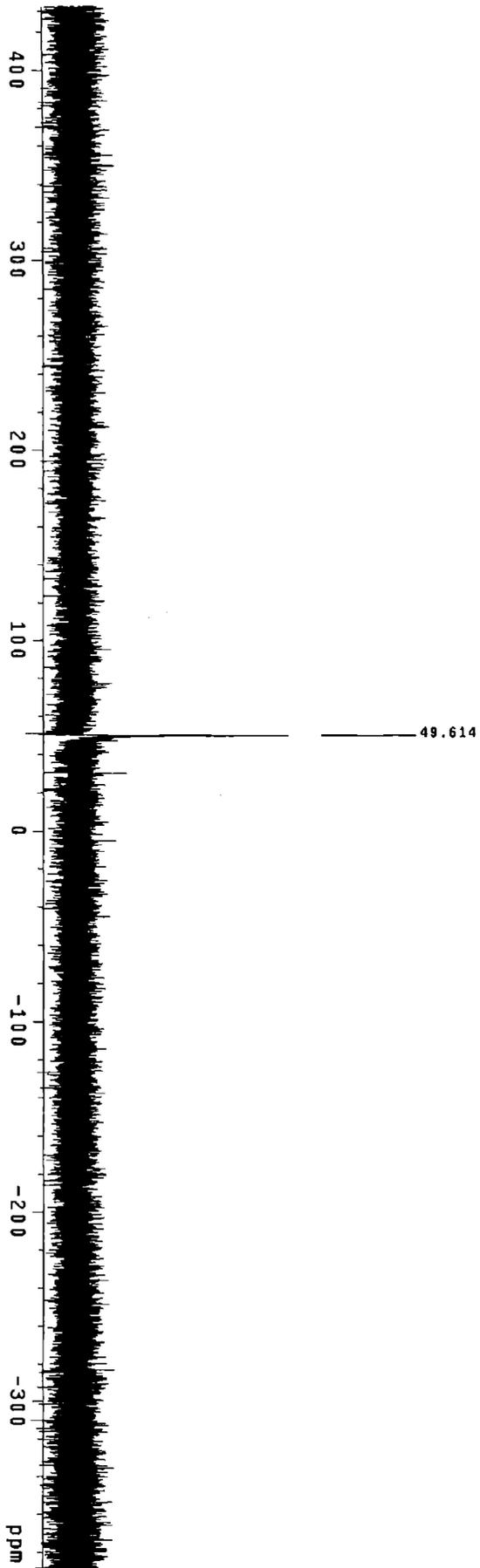
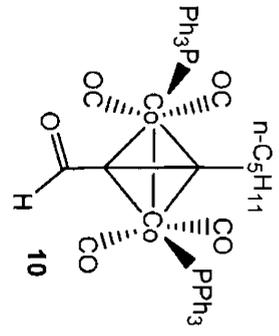


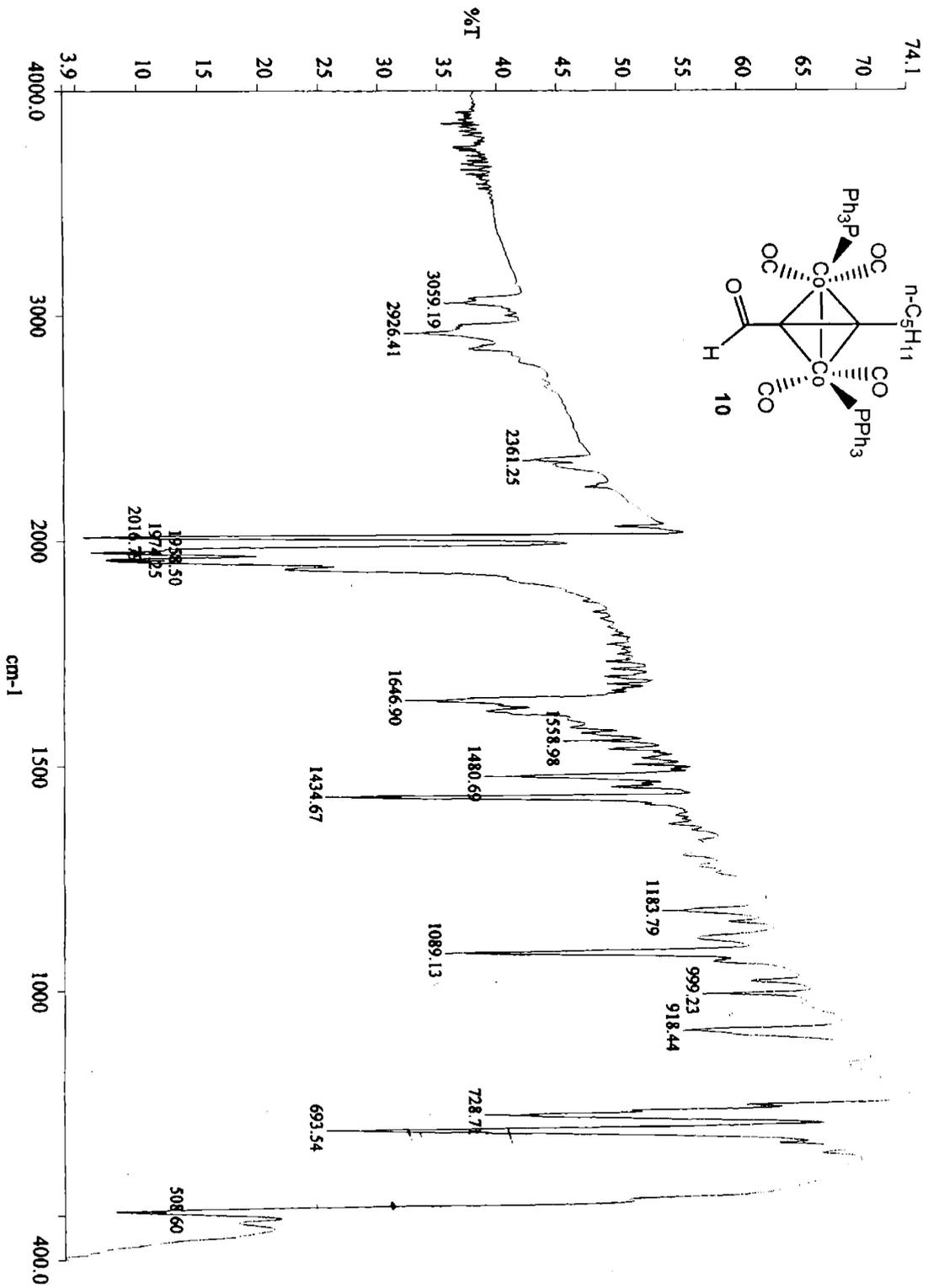


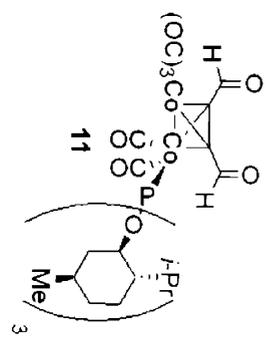
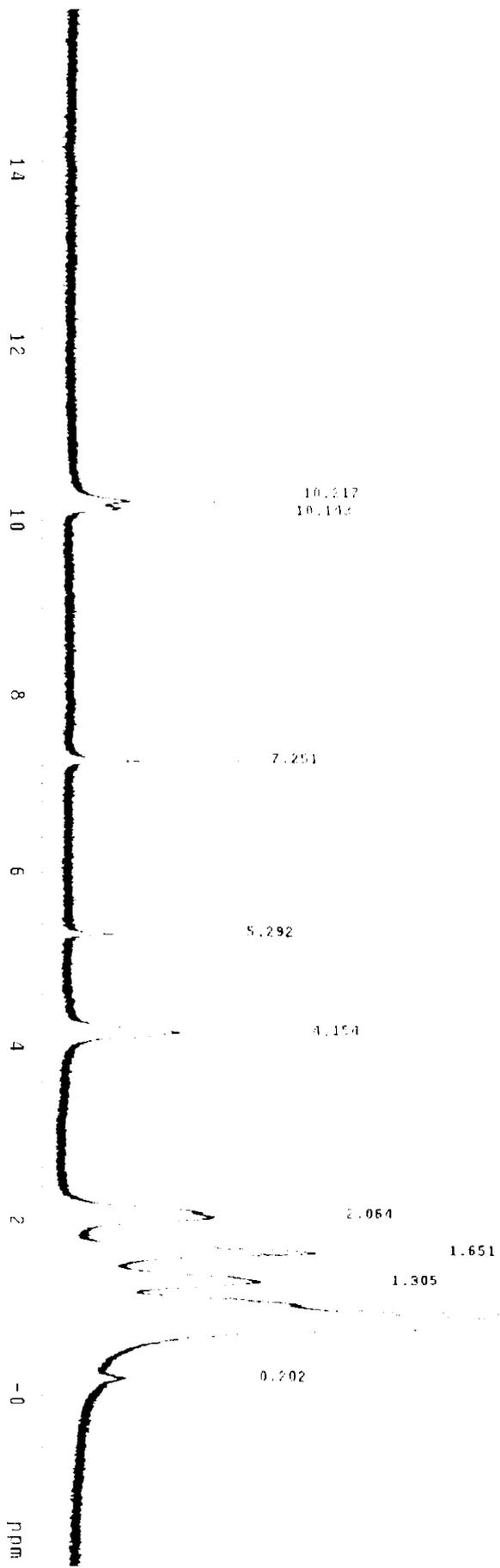


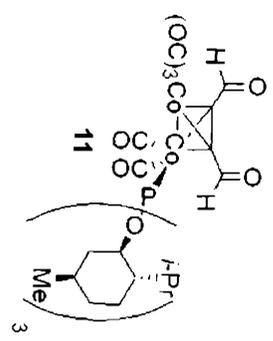
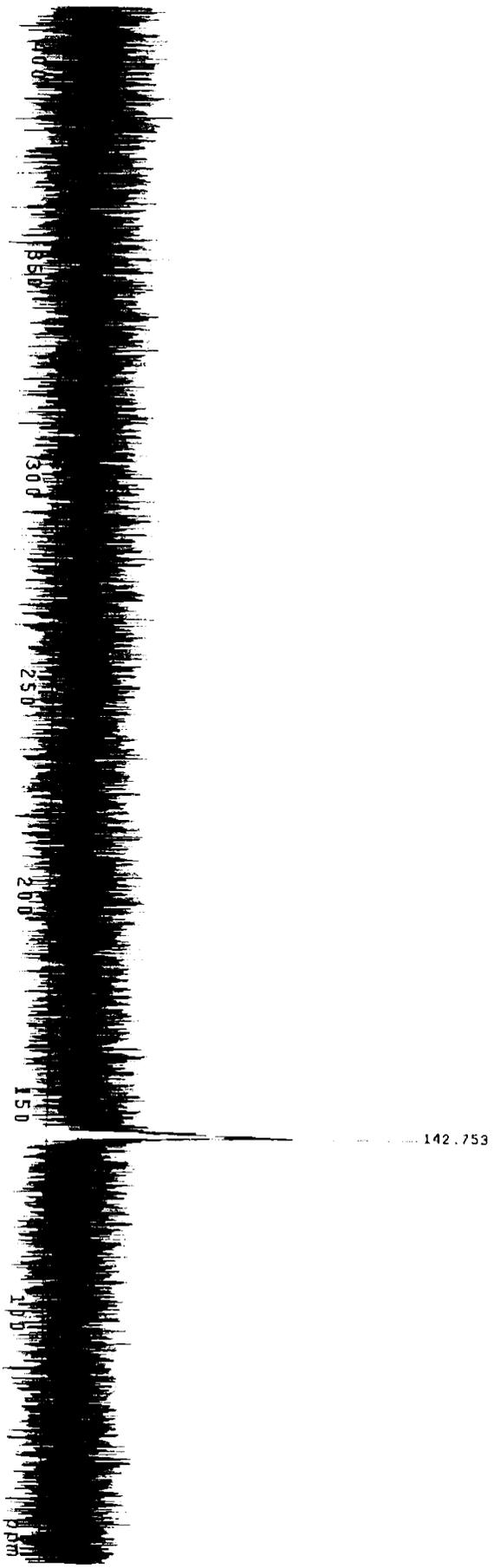












L. X-ray Crystal Structure Data

Table 1. Crystal data and structure refinement for 00274t (Compound 6)

Identification code	00274t	
Empirical formula	C ₂₀ H ₂₂ Co ₂ O ₁₁ Si	
Formula weight	584.33	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.678(6) Å	α = 90°.
	b = 9.253(5) Å	β = 94.235(9)°.
	c = 24.678(13) Å	γ = 90°.
Volume	2659(2) Å ³	
Z	4	
Density (calculated)	1.460 Mg/m ³	
Absorption coefficient	1.343 mm ⁻¹	
F(000)	1192	
Crystal size	0.36 x 0.24 x 0.24 mm ³	
Theta range for data collection	2.32 to 20.00°.	
Index ranges	-11 ≤ h ≤ 10, -8 ≤ k ≤ 8, -23 ≤ l ≤ 23	
Reflections collected	7421	
Independent reflections	2472 [R(int) = 0.0411]	
Completeness to theta = 20.00°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2472 / 0 / 314	
Goodness-of-fit on F ²	1.050	
Final R indices [I > 2σ(I)]	R1 = 0.0606, wR2 = 0.1287	
R indices (all data)	R1 = 0.0698, wR2 = 0.1250	
Largest diff. peak and hole	1.294 and -0.528 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 02189t. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Co1Co	0.12349(8)	0.20443(12)	0.09988(4)	0.0538(4)
Co2 Co	0.24908(9)	0.31122(12)	0.03410(4)	0.0571(4)
Si Si	0.70967(17)	0.2354(2)	0.15418(9)	0.0501(6)
O1 O	0.4843(4)	0.2815(5)	0.13192(17)	0.0427(12)
O2 O	0.6029(5)	0.3260(6)	0.2939(2)	0.0593(15)
O3 O	0.4922(4)	0.1386(5)	0.31259(19)	0.0506(14)
O4 O	0.3229(4)	0.3692(6)	0.2653(2)	0.0623(16)
O5 O	0.2180(4)	0.1689(6)	0.2545(2)	0.0603(15)
O6 O	0.0814(7)	-0.0446(9)	0.1681(3)	0.120(3)
O7 O	0.0629(6)	0.4584(9)	0.1644(4)	0.130(3)
O8 O	-0.0666(6)	0.1428(9)	0.0185(3)	0.115(3)
O9 O	0.1996(9)	0.6171(9)	0.0547(4)	0.155(4)
O10 O	0.1215(7)	0.2321(10)	-0.0690(3)	0.121(3)
O11 O	0.4820(7)	0.3192(12)	-0.0008(3)	0.146(4)
C1 C	0.3093(7)	-0.0189(9)	0.0602(4)	0.073(3)
H1A H	0.3906	-0.0116	0.0531	0.110
H1B H	0.2657	-0.0584	0.0281	0.110
H1C H	0.3012	-0.0830	0.0913	0.110
C2 C	0.2652(6)	0.1251(8)	0.0724(3)	0.0439(19)
C3 C	0.2882(6)	0.2381(8)	0.1079(3)	0.0416(19)
C4 C	0.3737(5)	0.2868(7)	0.1522(3)	0.0354(18)
H4 H	0.3560	0.3882	0.1629	0.042
C5 C	0.3797(5)	0.1887(7)	0.2029(3)	0.0340(17)
H5 H	0.3522	0.0893	0.1927	0.041
C6 C	0.5108(5)	0.1853(7)	0.2207(3)	0.0339(17)
H6 H	0.5391	0.0846	0.2155	0.041
C7 C	0.5651(5)	0.2833(7)	0.1794(3)	0.0369(18)
H7 H	0.5692	0.3839	0.1942	0.044
C8 C	0.7476(7)	0.3855(10)	0.1085(4)	0.081(3)
H8A H	0.7623	0.4736	0.1299	0.122
H8B H	0.6838	0.4024	0.0811	0.122
H8C H	0.8165	0.3595	0.0903	0.122
C9 C	0.6930(7)	0.0653(9)	0.1152(3)	0.071(3)
H9A H	0.6440	0.0823	0.0818	0.106
H9B H	0.6577	-0.0081	0.1372	0.106
H9C H	0.7686	0.0314	0.1058	0.106
C10 C	0.8174(6)	0.2165(10)	0.2128(4)	
H10A H	0.8925	0.1937	0.1996	0.110
H10B H	0.7942	0.1384	0.2365	0.110
H10C H	0.8226	0.3073	0.2333	0.110
C11 C	0.3056(6)	0.2527(9)	0.2445(3)	

C12 C 0.1396(7) 0.2271(11) 0.2922(4)
 H12A H 0.1833 0.2585 0.3255 0.132
 H12B H 0.0846 0.1521 0.3010 0.132
 H12C H 0.0981 0.3097 0.2755 0.132 Uiso 1 1 calc R . .
 C13 C 0.5420(6) 0.2282(8) 0.2793(3) 0.0384(18) Uani 1 1 d . . .
 C14 C 0.5105(8) 0.1693(9) 0.3700(3) 0.070(3) Uani 1 1 d . . .
 H14A H 0.5930 0.1794 0.3798 0.105 Uiso 1 1 calc R . .
 H14B H 0.4798 0.0899 0.3908 0.105 Uiso 1 1 calc R . .
 H14C H 0.4712 0.2594 0.3782 0.105 Uiso 1 1 calc R . .
 C15 C 0.0978(8) 0.0559(12) 0.1437(4) 0.081(3) Uani 1 1 d . . .
 C16 C 0.0812(7) 0.3573(12) 0.1382(4) 0.075(3) Uani 1 1 d . . .
 C17 C 0.0063(8) 0.1660(11) 0.0502(4) 0.078(3) Uani 1 1 d . . .
 C18 C 0.2199(9) 0.4979(13) 0.0455(4) 0.092(3) Uani 1 1 d . . .
 C19 C 0.1705(9) 0.2615(11) -0.0299(4) 0.081(3) Uani 1 1 d . . .
 C20 C 0.3899(10) 0.3181(13) 0.0128(4) 0.099(4) Uani 1 1 d . . .
 Co1 0.0407(7) 0.0648(8) 0.0553(7) -0.0001(6) -0.0003(5) 0.0006(5)
 Co2 0.0634(8) 0.0646(8) 0.0427(7) 0.0123(6) -0.0012(5) -0.0001(6)
 Si 0.0385(13) 0.0542(14) 0.0589(15) 0.0086(12) 0.0134(11) 0.0027(11)
 O1 0.032(3) 0.061(3) 0.036(3) 0.005(3) 0.003(2) -0.001(2)
 O2 0.067(4) 0.052(4) 0.058(4) 0.001(3) -0.005(3) -0.023(3)
 O3 0.075(4) 0.043(3) 0.034(3) -0.003(3) 0.002(3) -0.014(3)
 O4 0.063(4) 0.053(4) 0.074(4) -0.022(3) 0.026(3) -0.002(3)
 O5 0.051(3) 0.078(4) 0.054(4) -0.008(3) 0.023(3) -0.020(3)
 O6 0.123(6) 0.117(6) 0.119(7) 0.042(5) -0.004(5) -0.055(5)
 O7 0.107(6) 0.128(7) 0.158(8) -0.066(6) 0.029(5) 0.027(5)
 O8 0.065(5) 0.169(8) 0.105(6) -0.009(5) -0.032(4) -0.002(5)
 O9 0.214(10) 0.067(5) 0.178(9) 0.012(6) -0.026(7) 0.016(6)
 O10 0.130(7) 0.176(8) 0.055(5) -0.008(5) -0.017(4) -0.003(6)
 O11 0.091(6) 0.273(12) 0.077(5) 0.037(6) 0.028(4) -0.026(7)
 C1 0.076(6) 0.064(6) 0.078(7) -0.010(5) -0.008(5) 0.004(5)
 C2 0.046(5) 0.050(5) 0.035(4) -0.007(4) 0.000(4) 0.018(4)
 C3 0.035(4) 0.047(5) 0.045(5) 0.015(4) 0.009(4) 0.005(4)
 C4 0.029(4) 0.037(4) 0.040(4) 0.000(4) -0.002(4) 0.004(3)
 C5 0.035(4) 0.034(4) 0.034(4) -0.004(4) 0.007(3) -0.004(3)
 C6 0.037(4) 0.024(4) 0.041(5) -0.003(4) 0.005(3) -0.001(3)
 C7 0.035(4) 0.035(4) 0.041(5) 0.003(4) 0.009(4) -0.001(3)
 C8 0.051(6) 0.088(7) 0.111(8) 0.036(6) 0.044(5) 0.009(5)
 C9 0.068(6) 0.082(6) 0.065(6) 0.000(5) 0.029(5) 0.013(5)
 C10 0.041(5) 0.091(7) 0.089(7) 0.011(6) 0.009(4) 0.003(5)
 C11 0.041(5) 0.040(5) 0.035(5) 0.010(4) 0.003(4) -0.001(4)
 C12 0.056(6) 0.137(9) 0.077(7) -0.010(7) 0.039(5) -0.013(6)
 C13 0.043(5) 0.028(4) 0.044(5) -0.002(4) 0.000(4) -0.002(4)
 C14 0.100(7) 0.067(6) 0.040(6) 0.000(5) -0.003(5) -0.012(5)
 C15 0.065(7) 0.100(8) 0.076(7) -0.006(6) -0.006(5) -0.026(6)
 C16 0.045(5) 0.092(8) 0.088(7) -0.013(6) 0.013(5) 0.002(5)
 C17 0.050(6) 0.112(8) 0.072(7) 0.006(6) 0.007(5) 0.004(6)

C18 0.109(9) 0.088(8) 0.075(7) 0.022(7) -0.023(6) 0.007(7)
C19 0.086(7) 0.100(8) 0.057(7) 0.012(6) 0.007(6) -0.004(6)
C20 0.099(9) 0.153(11) 0.045(6) 0.031(7) 0.010(6) -0.003(8)

Table 3. Bond lengths [Å] and angles [°] for 02189t

Co1 C15 1.787(12)
Co1 C16 1.792(11)
Co1 C17 1.803(11)
Co1 C3 1.944(7)
Co1 C2 1.975(7)
Co1 Co2 2.4727(17)
Co2 C20 1.764(12)
Co2 C18 1.786(13)
Co2 C19 1.826(11)
Co2 C3 1.965(7)
Co2 C2 1.967(7)
Si C9 1.848(8)
Si C10 1.854(8)
Si C8 1.863(8)
Si C7 1.895(7)
O1 C4 1.420(7)
O1 C7 1.449(8)
O2 C13 1.190(8)
O3 C13 1.332(8)
O3 C14 1.444(9)
O4 C11 1.205(8)
O5 C11 1.320(8)
O5 C12 1.456(9)
O6 C15 1.132(11)
O7 C16 1.165(10)
O8 C17 1.134(10)
O9 C18 1.154(12)
O10 C19 1.117(10)
O11 C20 1.151(11)
C1 C2 1.468(11)
C2 C3 1.378(10)
C3 C4 1.495(9)
C4 C5 1.543(9)
C5 C11 1.511(9)
C5 C6 1.563(9)
C6 C13 1.516(9)
C6 C7 1.536(9)
C15 Co1 C16 102.9(4)
C15 Co1 C17 96.1(4)

C16 Co1 C17 106.9(4)
C15 Co1 C3 105.7(4)
C16 Co1 C3 97.4(4)
C17 Co1 C3 142.7(4)
C15 Co1 C2 96.0(4)
C16 Co1 C2 138.2(4)
C17 Co1 C2 107.8(4)
C3 Co1 C2 41.2(3)
C15 Co1 Co2 147.0(3)
C16 Co1 Co2 103.4(3)
C17 Co1 Co2 95.1(3)
C3 Co1 Co2 51.1(2)
C2 Co1 Co2 51.0(2)
C20 Co2 C18 101.8(5)
C20 Co2 C19 99.8(4)
C18 Co2 C19 106.8(4)
C20 Co2 C3 97.6(4)
C18 Co2 C3 102.8(4)
C19 Co2 C3 141.5(4)
C20 Co2 C2 96.7(4)
C18 Co2 C2 141.6(4)
C19 Co2 C2 102.7(4)
C3 Co2 C2 41.0(3)
C20 Co2 Co1 145.2(3)
C18 Co2 Co1 98.9(4)
C19 Co2 Co1 100.5(3)
C3 Co2 Co1 50.37(19)
C2 Co2 Co1 51.3(2)
C9 Si C10 111.4(4)
C9 Si C8 109.9(4)
C10 Si C8 111.4(4)
C9 Si C7 108.0(3)
C10 Si C7 109.6(3)
C8 Si C7 106.4(3)
C4 O1 C7 105.6(5)
C13 O3 C14 116.3(6)
C11 O5 C12 115.8(6)
C3 C2 C1 139.8(7)
C3 C2 Co2 69.4(4)
C1 C2 Co2 136.0(6)
C3 C2 Co1 68.2(4)
C1 C2 Co1 136.3(6)
Co2 C2 Co1 77.7(3)
C2 C3 C4 141.5(6)
C2 C3 Co1 70.7(4)
C4 C3 Co1 136.5(5)

C2 C3 Co2 69.5(4)
C4 C3 Co2 132.2(5)
Co1 C3 Co2 78.5(3)
O1 C4 C3 107.9(5)
O1 C4 C5 106.1(5)
C3 C4 C5 113.8(5)
C11 C5 C4 109.0(5)
C11 C5 C6 114.5(5)
C4 C5 C6 103.0(5)
C13 C6 C7 113.4(6)
C13 C6 C5 115.1(5)
C7 C6 C5 104.2(5)
O1 C7 C6 104.7(5)
O1 C7 Si 105.9(4)
C6 C7 Si 120.1(5)
O4 C11 O5 123.6(7)
O4 C11 C5 123.6(7)
O5 C11 C5 112.8(7)
O2 C13 O3 124.3(6)
O2 C13 C6 125.8(7)
O3 C13 C6 109.9(6)
O6 C15 Co1 174.9(10)
O7 C16 Co1 174.6(8)
O8 C17 Co1 179.1(9)
O9 C18 Co2 177.4(11)
O10 C19 Co2 179.2(11)
O11 C20 Co2 178.4(12)

Table 1. Crystal data and structure refinement for 02189t. (Compound 7)

Identification code	02189t	
Empirical formula	C ₄₈ H ₄₂ Co ₂ O ₅ P ₂	
Formula weight	878.62	
Temperature	192(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.1746(6) Å	α = 90°.
	b = 28.274(2) Å	β = 99.7310(10)°.
	c = 16.2897(11) Å	γ = 90°.
Volume	4164.9(5) Å ³	
Z	4	
Density (calculated)	1.401 Mg/m ³	
Absorption coefficient	0.920 mm ⁻¹	
F(000)	1816	
Crystal size	0.52 x 0.44 x 0.22 mm ³	
Theta range for data collection	2.51 to 22.00°.	
Index ranges	-8 ≤ h ≤ 9, -29 ≤ k ≤ 29, -17 ≤ l ≤ 12	
Reflections collected	13651	
Independent reflections	5045 [R(int) = 0.0376]	
Completeness to theta = 22.00°	98.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5045 / 0 / 515	
Goodness-of-fit on F ²	1.050	
Final R indices [I > 2σ(I)]	R1 = 0.0542, wR2 = 0.1448	
R indices (all data)	R1 = 0.0563, wR2 = 0.1466	
Largest diff. peak and hole	1.572 and -0.483 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 02189t. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Co(1)	6437(1)	1582(1)	8199(1)	24(1)
Co(2)	6676(1)	786(1)	7603(1)	26(1)
P(1)	6958(1)	2347(1)	8389(1)	24(1)
P(2)	8005(1)	274(1)	7006(1)	28(1)
O(1)	6945(4)	1314(1)	9963(2)	56(1)
O(2)	3221(4)	1619(1)	7649(2)	47(1)
O(3)	3847(4)	637(1)	6476(2)	62(1)
O(4)	6273(4)	282(1)	9121(2)	58(1)
O(5)	5961(4)	1643(2)	5856(2)	74(1)
C(1)	6990(5)	1612(2)	6370(3)	40(1)
C(2)	7201(4)	1405(1)	7180(2)	27(1)
C(3)	8199(4)	1291(1)	7860(2)	28(1)
C(4)	9824(4)	1299(2)	8184(3)	32(1)
C(5)	10265(5)	1198(2)	9107(3)	41(1)
C(6)	11928(5)	1146(2)	9380(3)	58(1)
C(7)	12375(6)	1053(3)	10325(4)	86(2)
C(8)	13890(12)	1045(6)	10617(6)	186(6)
C(9)	6740(5)	1426(2)	9281(3)	34(1)
C(10)	4478(5)	1621(1)	7873(3)	32(1)
C(11)	4938(5)	689(2)	6915(3)	38(1)
C(12)	6478(5)	474(2)	8531(3)	37(1)
C(13)	5877(4)	2782(1)	7704(2)	24(1)
C(14)	5967(5)	3258(2)	7917(3)	34(1)
C(15)	5185(5)	3594(2)	7411(3)	40(1)
C(16)	4285(5)	3458(2)	6686(3)	40(1)
C(17)	4184(5)	2989(2)	6466(3)	37(1)
C(18)	4976(4)	2650(1)	6963(2)	28(1)
C(19)	6678(4)	2567(1)	9412(2)	26(1)
C(20)	5417(4)	2414(2)	9716(3)	33(1)
C(21)	5105(5)	2578(2)	10465(3)	38(1)
C(22)	6050(5)	2898(2)	10934(3)	38(1)
C(23)	7300(5)	3051(1)	10644(2)	31(1)
C(24)	7611(4)	2891(1)	9889(2)	28(1)
C(25)	8860(4)	2523(1)	8327(3)	28(1)
C(26)	10008(5)	2439(2)	8986(3)	36(1)
C(27)	11432(5)	2571(2)	8937(3)	46(1)
C(28)	11760(5)	2780(2)	8233(4)	52(1)
C(29)	10655(5)	2857(2)	7558(3)	45(1)
C(30)	9198(5)	2731(2)	7615(3)	37(1)
C(31)	9735(5)	41(1)	7604(3)	34(1)
C(32)	9913(5)	19(2)	8465(3)	47(1)

C(33)	11182(6)	-163(2)	8940(4)	62(2)
C(34)	12300(6)	-324(2)	8552(4)	61(2)
C(35)	12135(6)	-316(2)	7712(4)	62(2)
C(36)	10855(5)	-144(2)	7224(3)	48(1)
C(37)	8543(5)	522(1)	6069(3)	32(1)
C(38)	7493(5)	564(2)	5347(3)	48(1)
C(39)	7864(7)	775(2)	4643(3)	66(2)
C(40)	9256(7)	958(2)	4661(4)	65(2)
C(41)	10285(7)	926(2)	5371(4)	59(2)
C(42)	9931(5)	715(2)	6065(3)	41(1)
C(43)	7051(4)	-284(1)	6665(2)	30(1)
C(44)	6287(5)	-509(2)	7212(3)	39(1)
C(45)	5581(5)	-936(2)	7007(3)	45(1)
C(46)	5612(5)	-1141(2)	6243(3)	41(1)
C(47)	6357(5)	-919(2)	5692(3)	45(1)
C(48)	7093(5)	-499(2)	5903(3)	43(1)

Table 3. Bond lengths [Å] and angles [°] for 02189t.

Co(1)-C(10)	1.789(5)	C(5)-C(6)	1.523(7)
Co(1)-C(9)	1.793(5)	C(6)-C(7)	1.547(8)
Co(1)-C(2)	1.972(4)	C(7)-C(8)	1.392(11)
Co(1)-C(3)	1.974(4)	C(13)-C(14)	1.387(6)
Co(1)-P(1)	2.2251(11)	C(13)-C(18)	1.393(6)
Co(1)-Co(2)	2.4748(7)	C(14)-C(15)	1.377(6)
Co(2)-C(12)	1.786(5)	C(15)-C(16)	1.376(6)
Co(2)-C(11)	1.808(5)	C(16)-C(17)	1.373(6)
Co(2)-C(2)	1.970(4)	C(17)-C(18)	1.380(6)
Co(2)-C(3)	1.992(4)	C(19)-C(24)	1.397(6)
Co(2)-P(2)	2.2211(11)	C(19)-C(20)	1.401(6)
P(1)-C(25)	1.834(4)	C(20)-C(21)	1.379(6)
P(1)-C(19)	1.837(4)	C(21)-C(22)	1.389(6)
P(1)-C(13)	1.837(4)	C(22)-C(23)	1.382(6)
P(2)-C(37)	1.823(4)	C(23)-C(24)	1.383(6)
P(2)-C(31)	1.838(4)	C(25)-C(30)	1.381(6)
P(2)-C(43)	1.844(4)	C(25)-C(26)	1.392(6)
O(1)-C(9)	1.140(5)	C(26)-C(27)	1.373(6)
O(2)-C(10)	1.149(5)	C(27)-C(28)	1.369(8)
O(3)-C(11)	1.137(5)	C(28)-C(29)	1.382(7)
O(4)-C(12)	1.146(5)	C(29)-C(30)	1.401(6)
O(5)-C(1)	1.154(6)	C(31)-C(32)	1.386(7)
C(1)-C(2)	1.428(6)	C(31)-C(36)	1.388(7)
C(2)-C(3)	1.351(6)	C(32)-C(33)	1.384(7)
C(3)-C(4)	1.495(6)	C(33)-C(34)	1.370(9)
C(4)-C(5)	1.517(6)	C(34)-C(35)	1.351(8)

C(35)-C(36)	1.390(7)	C(25)-P(1)-Co(1)	116.12(13)
C(37)-C(42)	1.386(6)	C(19)-P(1)-Co(1)	113.31(13)
C(37)-C(38)	1.393(6)	C(13)-P(1)-Co(1)	119.05(12)
C(38)-C(39)	1.386(7)	C(37)-P(2)-C(31)	104.49(19)
C(39)-C(40)	1.374(9)	C(37)-P(2)-C(43)	105.09(19)
C(40)-C(41)	1.366(8)	C(31)-P(2)-C(43)	100.16(18)
C(41)-C(42)	1.366(7)	C(37)-P(2)-Co(2)	111.18(13)
C(43)-C(44)	1.379(6)	C(31)-P(2)-Co(2)	119.36(15)
C(43)-C(48)	1.388(6)	C(43)-P(2)-Co(2)	114.97(13)
C(44)-C(45)	1.384(7)	O(5)-C(1)-C(2)	131.9(5)
C(45)-C(46)	1.377(7)	C(3)-C(2)-C(1)	145.4(4)
C(46)-C(47)	1.368(7)	C(3)-C(2)-Co(2)	71.0(2)
C(47)-C(48)	1.381(7)	C(1)-C(2)-Co(2)	133.2(3)
C(10)-Co(1)-C(9)	106.74(19)	C(3)-C(2)-Co(1)	70.1(2)
C(10)-Co(1)-C(2)	104.40(17)	C(1)-C(2)-Co(1)	131.5(3)
C(9)-Co(1)-C(2)	138.29(18)	Co(2)-C(2)-Co(1)	77.79(14)
C(10)-Co(1)-C(3)	140.54(18)	C(2)-C(3)-C(4)	141.5(4)
C(9)-Co(1)-C(3)	100.00(18)	C(2)-C(3)-Co(1)	69.9(2)
C(2)-Co(1)-C(3)	40.05(16)	C(4)-C(3)-Co(1)	135.3(3)
C(10)-Co(1)-P(1)	99.38(13)	C(2)-C(3)-Co(2)	69.2(2)
C(9)-Co(1)-P(1)	96.21(13)	C(4)-C(3)-Co(2)	135.0(3)
C(2)-Co(1)-P(1)	105.37(12)	Co(1)-C(3)-Co(2)	77.21(14)
C(3)-Co(1)-P(1)	106.07(12)	C(3)-C(4)-C(5)	115.5(4)
C(10)-Co(1)-Co(2)	95.22(13)	C(4)-C(5)-C(6)	113.2(4)
C(9)-Co(1)-Co(2)	98.77(13)	C(5)-C(6)-C(7)	113.0(4)
C(2)-Co(1)-Co(2)	51.07(11)	C(8)-C(7)-C(6)	115.1(6)
C(3)-Co(1)-Co(2)	51.72(11)	O(1)-C(9)-Co(1)	178.0(4)
P(1)-Co(1)-Co(2)	155.09(4)	O(2)-C(10)-Co(1)	176.1(4)
C(12)-Co(2)-C(11)	104.2(2)	O(3)-C(11)-Co(2)	178.6(4)
C(12)-Co(2)-C(2)	143.13(18)	O(4)-C(12)-Co(2)	176.3(4)
C(11)-Co(2)-C(2)	99.25(18)	C(14)-C(13)-C(18)	118.6(4)
C(12)-Co(2)-C(3)	110.08(18)	C(14)-C(13)-P(1)	119.6(3)
C(11)-Co(2)-C(3)	138.85(18)	C(18)-C(13)-P(1)	121.8(3)
C(2)-Co(2)-C(3)	39.87(16)	C(15)-C(14)-C(13)	121.0(4)
C(12)-Co(2)-P(2)	100.99(14)	C(14)-C(15)-C(16)	119.9(4)
C(11)-Co(2)-P(2)	96.98(14)	C(17)-C(16)-C(15)	119.7(4)
C(2)-Co(2)-P(2)	103.99(12)	C(16)-C(17)-C(18)	120.9(4)
C(3)-Co(2)-P(2)	98.17(12)	C(17)-C(18)-C(13)	119.9(4)
C(12)-Co(2)-Co(1)	95.05(13)	C(24)-C(19)-C(20)	118.1(4)
C(11)-Co(2)-Co(1)	104.70(14)	C(24)-C(19)-P(1)	124.1(3)
C(2)-Co(2)-Co(1)	51.14(11)	C(20)-C(19)-P(1)	117.8(3)
C(3)-Co(2)-Co(1)	51.06(11)	C(21)-C(20)-C(19)	121.0(4)
P(2)-Co(2)-Co(1)	148.93(4)	C(20)-C(21)-C(22)	120.1(4)
C(25)-P(1)-C(19)	103.81(18)	C(23)-C(22)-C(21)	119.5(4)
C(25)-P(1)-C(13)	101.85(18)	C(22)-C(23)-C(24)	120.6(4)
C(19)-P(1)-C(13)	100.40(16)	C(23)-C(24)-C(19)	120.6(4)

C(30)-C(25)-C(26)	118.2(4)
C(30)-C(25)-P(1)	120.9(3)
C(26)-C(25)-P(1)	120.9(3)
C(27)-C(26)-C(25)	120.8(4)
C(28)-C(27)-C(26)	120.8(4)
C(27)-C(28)-C(29)	119.9(4)
C(28)-C(29)-C(30)	119.2(5)
C(25)-C(30)-C(29)	121.1(4)
C(32)-C(31)-C(36)	117.7(4)
C(32)-C(31)-P(2)	119.7(3)
C(36)-C(31)-P(2)	122.5(4)
C(33)-C(32)-C(31)	121.7(5)
C(34)-C(33)-C(32)	119.4(5)
C(35)-C(34)-C(33)	119.8(5)
C(34)-C(35)-C(36)	121.6(5)
C(31)-C(36)-C(35)	119.6(5)
C(42)-C(37)-C(38)	117.9(4)
C(42)-C(37)-P(2)	122.3(3)
C(38)-C(37)-P(2)	119.5(3)
C(39)-C(38)-C(37)	120.2(5)
C(40)-C(39)-C(38)	120.1(5)
C(41)-C(40)-C(39)	120.0(5)
C(42)-C(41)-C(40)	120.1(5)
C(41)-C(42)-C(37)	121.5(5)
C(44)-C(43)-C(48)	118.0(4)
C(44)-C(43)-P(2)	117.9(3)
C(48)-C(43)-P(2)	124.0(3)
C(43)-C(44)-C(45)	121.0(4)
C(46)-C(45)-C(44)	120.3(5)
C(47)-C(46)-C(45)	119.3(4)
C(46)-C(47)-C(48)	120.5(4)
C(47)-C(48)-C(43)	120.8(4)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 02189t. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Co(1)	21(1)	24(1)	25(1)	0(1)	3(1)	0(1)
Co(2)	23(1)	24(1)	30(1)	0(1)	3(1)	2(1)
P(1)	19(1)	26(1)	26(1)	-1(1)	3(1)	1(1)
P(2)	25(1)	26(1)	32(1)	1(1)	5(1)	2(1)
O(1)	86(3)	57(2)	24(2)	9(2)	0(2)	-2(2)
O(2)	24(2)	66(2)	51(2)	6(2)	5(2)	1(2)
O(3)	32(2)	82(3)	65(2)	-8(2)	-13(2)	-9(2)
O(4)	85(3)	51(2)	43(2)	11(2)	22(2)	-2(2)
O(5)	53(2)	126(4)	40(2)	23(2)	2(2)	17(2)
C(1)	34(3)	44(3)	42(3)	9(2)	8(2)	-1(2)
C(2)	26(2)	28(2)	27(2)	1(2)	7(2)	0(2)
C(3)	25(2)	25(2)	33(2)	-4(2)	9(2)	-2(2)
C(4)	20(2)	34(2)	41(2)	-2(2)	4(2)	1(2)
C(5)	33(3)	45(3)	43(3)	3(2)	0(2)	0(2)
C(6)	35(3)	81(4)	52(3)	17(3)	-6(2)	-8(3)
C(7)	42(3)	129(6)	79(4)	41(4)	-10(3)	0(4)
C(8)	128(9)	307(18)	109(7)	70(10)	-19(6)	-80(10)
C(9)	34(3)	28(2)	41(3)	-7(2)	6(2)	-4(2)
C(10)	37(3)	31(2)	29(2)	2(2)	12(2)	0(2)
C(11)	35(3)	36(2)	45(3)	-2(2)	13(2)	1(2)
C(12)	37(3)	28(2)	44(3)	-5(2)	4(2)	3(2)
C(13)	19(2)	26(2)	26(2)	-4(2)	6(2)	-3(2)
C(14)	33(2)	33(2)	33(2)	-4(2)	-4(2)	-3(2)
C(15)	51(3)	25(2)	42(3)	-2(2)	-3(2)	0(2)
C(16)	49(3)	29(2)	38(3)	4(2)	-6(2)	5(2)
C(17)	44(3)	37(3)	25(2)	2(2)	-8(2)	-2(2)
C(18)	28(2)	26(2)	31(2)	-4(2)	4(2)	-1(2)
C(19)	23(2)	28(2)	25(2)	4(2)	3(2)	5(2)
C(20)	26(2)	38(2)	35(2)	-4(2)	2(2)	0(2)
C(21)	29(2)	53(3)	33(2)	-1(2)	12(2)	1(2)
C(22)	44(3)	41(2)	28(2)	-3(2)	6(2)	7(2)
C(23)	36(2)	29(2)	27(2)	-4(2)	-1(2)	0(2)
C(24)	26(2)	26(2)	31(2)	4(2)	2(2)	1(2)
C(25)	25(2)	25(2)	37(2)	-8(2)	9(2)	0(2)
C(26)	27(2)	38(2)	42(3)	-2(2)	3(2)	4(2)
C(27)	20(2)	54(3)	63(3)	-11(3)	1(2)	2(2)
C(28)	26(3)	57(3)	78(4)	-23(3)	19(3)	-7(2)
C(29)	39(3)	46(3)	57(3)	-10(2)	28(2)	-7(2)
C(30)	28(2)	42(3)	41(3)	-11(2)	10(2)	-1(2)
C(31)	27(2)	26(2)	48(3)	0(2)	2(2)	-1(2)
C(32)	38(3)	51(3)	49(3)	9(2)	0(2)	11(2)

C(33)	56(4)	63(3)	60(3)	14(3)	-11(3)	17(3)
C(34)	36(3)	50(3)	87(5)	14(3)	-12(3)	6(2)
C(35)	33(3)	55(3)	99(5)	3(3)	16(3)	14(3)
C(36)	38(3)	43(3)	64(3)	-2(2)	11(2)	12(2)
C(37)	33(2)	24(2)	40(2)	-2(2)	13(2)	8(2)
C(38)	34(3)	64(3)	48(3)	11(3)	12(2)	14(2)
C(39)	65(4)	94(5)	39(3)	18(3)	12(3)	39(3)
C(40)	82(5)	55(3)	70(4)	17(3)	47(4)	16(3)
C(41)	72(4)	44(3)	67(4)	-6(3)	32(3)	-11(3)
C(42)	49(3)	34(2)	43(3)	-4(2)	15(2)	-9(2)
C(43)	25(2)	29(2)	34(2)	0(2)	3(2)	6(2)
C(44)	45(3)	31(2)	40(3)	-3(2)	7(2)	-4(2)
C(45)	41(3)	33(3)	62(3)	2(2)	14(2)	0(2)
C(46)	32(3)	29(2)	61(3)	-11(2)	3(2)	0(2)
C(47)	46(3)	38(3)	54(3)	-17(2)	13(2)	-4(2)
C(48)	43(3)	41(3)	47(3)	-8(2)	17(2)	-1(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for 02189t.

	x	y	z	U(eq)
H(1)	7858	1750	6226	48
H(4A)	10212	1614	8067	38
H(4B)	10308	1063	7870	38
H(5A)	9775	903	9242	49
H(5B)	9906	1458	9427	49
H(6A)	12421	1438	9235	69
H(6B)	12285	881	9069	69
H(7A)	11924	1301	10631	103
H(7B)	11952	745	10457	103
H(8A)	14378	847	10250	279
H(8B)	14078	915	11183	279
H(8C)	14283	1367	10623	279
H(14)	6578	3353	8420	41
H(15)	5267	3918	7563	48
H(16)	3735	3689	6338	48
H(17)	3562	2897	5965	45
H(18)	4906	2327	6801	34
H(20)	4766	2194	9400	40
H(21)	4242	2472	10660	45
H(22)	5839	3010	11450	45
H(23)	7952	3268	10965	37

H(24)	8467	3003	9694	34
H(26)	9805	2289	9476	43
H(27)	12198	2516	9398	56
H(28)	12748	2872	8208	63
H(29)	10879	2993	7061	54
H(30)	8430	2791	7158	44
H(32)	9143	133	8737	56
H(33)	11278	-176	9529	74
H(34)	13188	-441	8873	73
H(35)	12912	-431	7448	74
H(36)	10748	-152	6634	58
H(38)	6520	446	5338	58
H(39)	7153	794	4147	79
H(40)	9503	1107	4180	78
H(41)	11250	1051	5381	70
H(42)	10653	700	6557	50
H(44)	6246	-370	7738	46
H(45)	5072	-1089	7395	54
H(46)	5122	-1433	6100	49
H(47)	6368	-1056	5160	55
H(48)	7636	-356	5522	51

Table 1. Crystal data and structure refinement for 031600 (Compound **8**)

Identification code	031600	
Empirical formula	C ₃₉ H ₅₉ Co ₂ O ₁₀ P	
Formula weight	836.69	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P4(2)2(1)2	
Unit cell dimensions	a = 20.4055(18) Å	α = 90°.
	b = 20.4055(18) Å	β = 90°.
	c = 21.052(3) Å	γ = 90°.
Volume	8765.5(16) Å ³	
Z	8	
Density (calculated)	1.268 Mg/m ³	
Absorption coefficient	0.843 mm ⁻¹	
F(000)	3536	
Crystal size	0.50 x 0.36 x 0.08 mm ³	
Theta range for data collection	2.00 to 23.28°.	
Index ranges	-10 ≤ h ≤ 22, -18 ≤ k ≤ 21, -21 ≤ l ≤ 22	
Reflections collected	16954	
Independent reflections	6274 [R(int) = 0.0726]	
Completeness to theta = 23.28°	98.8 %	
Absorption correction	Integration	
Max. and min. transmission	0.8772 and 0.5431	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6274 / 0 / 488	
Goodness-of-fit on F ²	1.086	
Final R indices [I > 2σ(I)]	R1 = 0.0470, wR2 = 0.0979	
R indices (all data)	R1 = 0.0567, wR2 = 0.1012	
Absolute structure parameter	-0.013(18)	
Extinction coefficient	0.00044(5)	
Largest diff. peak and hole	0.555 and -0.262 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 031600. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Co(1)	3615(1)	7242(1)	1908(1)	35(1)
Co(2)	4336(1)	7797(1)	1122(1)	44(1)
P	2759(1)	7231(1)	2530(1)	30(1)
O(1)	2812(1)	6788(1)	3151(1)	36(1)
O(2)	2061(1)	7010(1)	2272(1)	33(1)
O(3)	2685(1)	7940(1)	2828(1)	36(1)
O(11)	4247(3)	9015(3)	2272(3)	153(3)
O(41)	2675(4)	8588(4)	676(4)	67(2)
O(51)	4602(2)	7091(2)	2916(2)	73(1)
O(61)	3535(2)	5947(2)	1309(2)	79(1)
O(71)	5551(2)	7786(2)	1876(2)	75(1)
O(81)	4542(2)	8974(2)	336(2)	72(1)
O(91)	4440(2)	6737(2)	178(2)	102(2)
C(1)	3743(3)	8753(3)	2140(2)	57(2)
C(2)	3727(2)	8176(2)	1732(2)	39(1)
C(3)	3377(2)	7880(2)	1274(2)	37(1)
C(4)	2947(3)	8022(3)	747(3)	61(2)
C(5)	4209(2)	7127(2)	2535(3)	49(1)
C(6)	3547(2)	6446(3)	1545(2)	51(1)
C(7)	5089(3)	7781(3)	1573(3)	55(1)
C(8)	4472(3)	8514(3)	632(3)	52(2)
C(9)	4398(3)	7154(4)	531(3)	69(2)
C(11)	2548(2)	6124(2)	3234(2)	34(1)
C(12)	2984(2)	5764(2)	3706(2)	41(1)
C(13)	2686(2)	5090(2)	3842(3)	49(1)
C(14)	1982(2)	5134(2)	4074(3)	56(2)
C(15)	1555(2)	5494(2)	3590(3)	47(1)
C(16)	1849(2)	6169(2)	3466(2)	41(1)
C(21)	1789(2)	7089(2)	1632(2)	33(1)
C(22)	1236(2)	6592(2)	1554(2)	36(1)
C(23)	939(2)	6678(2)	891(2)	41(1)
C(24)	678(2)	7366(2)	797(2)	42(1)
C(25)	1205(2)	7884(2)	901(2)	39(1)
C(26)	1540(2)	7778(2)	1544(2)	37(1)
C(31)	2324(2)	8121(2)	3405(2)	39(1)
C(32)	2774(2)	8545(2)	3810(2)	41(1)
C(33)	2390(3)	8784(3)	4392(2)	58(2)
C(34)	1756(3)	9129(3)	4209(3)	63(2)
C(35)	1316(2)	8701(3)	3798(3)	58(1)
C(36)	1701(2)	8468(2)	3216(2)	45(1)
C(121)	3703(2)	5734(3)	3502(3)	65(2)

C(122)	3848(3)	5282(4)	2949(3)	102(3)
C(123)	4155(3)	5573(3)	4069(4)	104(3)
C(151)	847(2)	5539(3)	3813(3)	72(2)
C(221)	1426(3)	5878(2)	1713(2)	50(1)
C(222)	1875(3)	5564(3)	1221(3)	79(2)
C(223)	807(3)	5448(3)	1803(3)	74(2)
C(251)	927(3)	8574(2)	859(3)	62(2)
C(321)	3429(3)	8225(2)	3972(2)	51(1)
C(322)	3389(3)	7669(3)	4449(3)	77(2)
C(323)	3938(3)	8730(3)	4193(3)	72(2)
C(351)	688(3)	9054(3)	3607(3)	87(2)
O(41')	2780(5)	7588(6)	383(4)	110(4)

Table 3. Bond lengths [Å] and angles [°] for 031600.

Co(1)-C(6)	1.800(6)	C(11)-C(12)	1.524(6)
Co(1)-C(5)	1.807(6)	C(12)-C(13)	1.530(6)
Co(1)-C(3)	1.927(4)	C(12)-C(121)	1.532(7)
Co(1)-C(2)	1.955(5)	C(13)-C(14)	1.518(6)
Co(1)-P	2.1835(13)	C(14)-C(15)	1.530(7)
Co(1)-Co(2)	2.4872(9)	C(15)-C(151)	1.522(7)
Co(2)-C(7)	1.808(6)	C(15)-C(16)	1.524(6)
Co(2)-C(9)	1.813(7)	C(21)-C(26)	1.506(6)
Co(2)-C(8)	1.811(6)	C(21)-C(22)	1.526(6)
Co(2)-C(2)	1.947(4)	C(22)-C(23)	1.532(6)
Co(2)-C(3)	1.989(4)	C(22)-C(221)	1.543(6)
P-O(3)	1.585(3)	C(23)-C(24)	1.514(6)
P-O(2)	1.590(3)	C(24)-C(25)	1.524(6)
P-O(1)	1.593(3)	C(25)-C(251)	1.520(7)
O(1)-C(11)	1.468(5)	C(25)-C(26)	1.532(6)
O(2)-C(21)	1.466(5)	C(31)-C(36)	1.509(6)
O(3)-C(31)	1.467(5)	C(31)-C(32)	1.522(6)
O(11)-C(1)	1.192(7)	C(32)-C(321)	1.527(7)
O(41)-C(4)	1.292(7)	C(32)-C(33)	1.534(6)
O(41')-C(4)	1.220(7)	C(33)-C(34)	1.521(8)
O(51)-C(5)	1.136(6)	C(34)-C(35)	1.523(8)
O(61)-C(6)	1.133(6)	C(35)-C(351)	1.525(8)
O(71)-C(7)	1.137(6)	C(35)-C(36)	1.530(6)
O(81)-C(8)	1.136(6)	C(121)-C(122)	1.513(9)
O(91)-C(9)	1.132(7)	C(121)-C(123)	1.545(8)
C(1)-C(2)	1.459(7)	C(221)-C(222)	1.524(8)
C(2)-C(3)	1.341(6)	C(221)-C(223)	1.551(7)
C(3)-C(4)	1.444(7)	C(321)-C(322)	1.517(7)
C(11)-C(16)	1.510(6)	C(321)-C(323)	1.535(7)

C(6)-Co(1)-C(5)	104.1(2)	C(2)-C(3)-C(4)	141.7(5)
C(6)-Co(1)-C(3)	107.3(2)	C(2)-C(3)-Co(1)	70.9(3)
C(5)-Co(1)-C(3)	139.7(2)	C(4)-C(3)-Co(1)	145.2(4)
C(6)-Co(1)-C(2)	143.9(2)	C(2)-C(3)-Co(2)	68.4(3)
C(5)-Co(1)-C(2)	100.8(2)	C(4)-C(3)-Co(2)	119.4(3)
C(3)-Co(1)-C(2)	40.41(18)	Co(1)-C(3)-Co(2)	78.84(17)
C(6)-Co(1)-P	100.58(16)	O(41)-C(4)-C(3)	122.1(6)
C(5)-Co(1)-P	95.57(16)	O(41')-C(4)-C(3)	120.6(6)
C(3)-Co(1)-P	102.73(13)	O(51)-C(5)-Co(1)	175.4(5)
C(2)-Co(1)-P	102.52(14)	O(61)-C(6)-Co(1)	176.7(5)
C(6)-Co(1)-Co(2)	100.05(16)	O(71)-C(7)-Co(2)	177.1(5)
C(5)-Co(1)-Co(2)	98.59(15)	O(81)-C(8)-Co(2)	177.6(5)
C(3)-Co(1)-Co(2)	51.69(13)	O(91)-C(9)-Co(2)	177.6(6)
C(2)-Co(1)-Co(2)	50.25(13)	O(1)-C(11)-C(16)	109.2(3)
P-Co(1)-Co(2)	151.25(4)	O(1)-C(11)-C(12)	108.0(3)
C(7)-Co(2)-C(9)	106.7(3)	C(16)-C(11)-C(12)	111.7(4)
C(7)-Co(2)-C(8)	100.6(2)	C(11)-C(12)-C(13)	108.9(4)
C(9)-Co(2)-C(8)	100.5(3)	C(11)-C(12)-C(121)	113.3(4)
C(7)-Co(2)-C(2)	101.8(2)	C(13)-C(12)-C(121)	113.5(4)
C(9)-Co(2)-C(2)	141.7(2)	C(14)-C(13)-C(12)	112.5(4)
C(8)-Co(2)-C(2)	98.8(2)	C(13)-C(14)-C(15)	110.7(4)
C(7)-Co(2)-C(3)	138.9(2)	C(151)-C(15)-C(16)	111.8(4)
C(9)-Co(2)-C(3)	103.9(2)	C(151)-C(15)-C(14)	111.3(4)
C(8)-Co(2)-C(3)	100.0(2)	C(16)-C(15)-C(14)	108.9(4)
C(2)-Co(2)-C(3)	39.82(17)	C(11)-C(16)-C(15)	111.8(4)
C(7)-Co(2)-Co(1)	98.32(16)	O(2)-C(21)-C(26)	110.1(3)
C(9)-Co(2)-Co(1)	99.68(19)	O(2)-C(21)-C(22)	107.8(3)
C(8)-Co(2)-Co(1)	146.92(17)	C(26)-C(21)-C(22)	111.0(4)
C(2)-Co(2)-Co(1)	50.54(13)	C(21)-C(22)-C(23)	108.3(4)
C(3)-Co(2)-Co(1)	49.47(13)	C(21)-C(22)-C(221)	114.7(4)
O(3)-P-O(2)	107.97(16)	C(23)-C(22)-C(221)	113.9(4)
O(3)-P-O(1)	101.51(15)	C(24)-C(23)-C(22)	111.4(4)
O(2)-P-O(1)	100.38(15)	C(23)-C(24)-C(25)	112.1(4)
O(3)-P-Co(1)	107.76(12)	C(251)-C(25)-C(24)	111.9(4)
O(2)-P-Co(1)	121.00(11)	C(251)-C(25)-C(26)	110.3(4)
O(1)-P-Co(1)	116.33(12)	C(24)-C(25)-C(26)	110.2(4)
C(11)-O(1)-P	126.6(3)	C(21)-C(26)-C(25)	113.0(4)
C(21)-O(2)-P	128.5(3)	O(3)-C(31)-C(36)	108.8(4)
C(31)-O(3)-P	127.3(3)	O(3)-C(31)-C(32)	107.7(4)
O(11)-C(1)-C(2)	121.3(6)	C(36)-C(31)-C(32)	112.9(4)
C(3)-C(2)-C(1)	143.0(5)	C(31)-C(32)-C(321)	114.2(4)
C(3)-C(2)-Co(2)	71.8(3)	C(31)-C(32)-C(33)	108.7(4)
C(1)-C(2)-Co(2)	134.0(4)	C(321)-C(32)-C(33)	113.9(4)
C(3)-C(2)-Co(1)	68.7(3)	C(34)-C(33)-C(32)	112.3(4)
C(1)-C(2)-Co(1)	132.7(3)	C(35)-C(34)-C(33)	112.3(4)
Co(2)-C(2)-Co(1)	79.21(17)	C(34)-C(35)-C(351)	112.1(5)

C(34)-C(35)-C(36)	109.3(4)
C(351)-C(35)-C(36)	111.5(5)
C(31)-C(36)-C(35)	111.6(4)
C(122)-C(121)-C(12)	115.3(5)
C(122)-C(121)-C(123)	110.5(5)
C(12)-C(121)-C(123)	111.3(5)
C(222)-C(221)-C(22)	113.6(4)
C(222)-C(221)-C(223)	109.6(4)
C(22)-C(221)-C(223)	110.8(4)
C(322)-C(321)-C(32)	114.9(5)
C(322)-C(321)-C(323)	109.7(4)
C(32)-C(321)-C(323)	111.9(4)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 031600. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
Co(1)	33(1)	37(1)	34(1)	-5(1)	-1(1)	-1(1)
Co(2)	37(1)	55(1)	41(1)	-4(1)	5(1)	-5(1)
P	34(1)	29(1)	29(1)	-2(1)	-2(1)	-3(1)
O(1)	42(2)	29(2)	36(2)	0(1)	-6(2)	-3(1)
O(2)	35(2)	34(2)	31(2)	4(1)	-5(1)	-6(1)
O(3)	41(2)	31(2)	34(2)	-5(1)	7(2)	-7(1)
O(11)	134(5)	118(5)	208(7)	-82(5)	-2(5)	-17(4)
O(41)	58(5)	62(5)	81(6)	31(4)	-26(4)	-3(4)
O(51)	53(2)	96(3)	70(3)	21(2)	-27(2)	-14(2)
O(61)	91(3)	54(3)	90(3)	-35(2)	13(3)	-5(2)
O(71)	41(2)	75(3)	110(3)	21(3)	-18(2)	-10(2)
O(81)	74(3)	84(3)	56(2)	18(2)	-7(2)	-23(2)
O(91)	112(4)	105(4)	88(4)	-45(3)	37(3)	-13(3)
C(1)	67(4)	49(3)	53(3)	3(3)	-1(3)	-21(3)
C(2)	39(3)	42(3)	34(3)	-2(2)	4(2)	-5(2)
C(3)	32(2)	50(3)	29(3)	3(2)	2(2)	-3(2)
C(4)	56(4)	85(5)	42(3)	5(3)	-6(3)	-27(3)
C(5)	43(3)	50(3)	53(3)	5(3)	5(3)	-8(3)
C(6)	39(3)	64(4)	49(3)	-12(3)	3(3)	-5(3)
C(7)	33(3)	56(3)	75(4)	12(3)	12(3)	-5(3)
C(8)	41(3)	72(4)	44(3)	-1(3)	3(2)	-13(3)
C(9)	66(4)	85(5)	57(4)	-8(4)	21(3)	-13(4)
C(11)	41(3)	25(2)	35(3)	0(2)	6(2)	1(2)
C(12)	40(3)	34(3)	49(3)	11(2)	-5(2)	3(2)
C(13)	41(3)	46(3)	59(3)	11(3)	1(3)	8(2)
C(14)	53(3)	38(3)	77(4)	21(3)	8(3)	-2(2)
C(15)	36(3)	42(3)	63(3)	15(3)	5(2)	4(2)
C(16)	43(3)	37(3)	42(3)	4(2)	-5(2)	9(2)
C(21)	34(3)	35(3)	30(2)	-3(2)	1(2)	-1(2)
C(22)	33(3)	32(3)	42(3)	-4(2)	-1(2)	-4(2)
C(23)	34(3)	49(3)	40(3)	-9(2)	-5(2)	-5(2)
C(24)	47(3)	44(3)	34(3)	-4(2)	-6(2)	2(2)
C(25)	44(3)	40(3)	33(3)	2(2)	-8(2)	-3(2)
C(26)	43(3)	30(2)	37(3)	-7(2)	1(2)	-7(2)
C(31)	50(3)	32(3)	34(3)	-1(2)	9(2)	-7(2)
C(32)	59(3)	31(2)	33(2)	-6(2)	7(3)	-7(2)
C(33)	80(4)	52(3)	42(3)	-13(3)	12(3)	-14(3)
C(34)	80(4)	43(3)	65(4)	-19(3)	36(3)	-6(3)
C(35)	48(3)	49(3)	76(4)	-15(3)	16(3)	-7(3)
C(36)	41(3)	40(3)	53(3)	-9(2)	7(2)	-6(2)
C(121)	38(3)	60(4)	97(5)	36(4)	2(3)	6(3)

C(122)	63(4)	130(7)	112(6)	50(5)	36(4)	46(4)
C(123)	56(4)	80(5)	177(8)	37(5)	-50(5)	-8(3)
C(151)	47(3)	65(4)	103(5)	44(4)	7(3)	1(3)
C(221)	58(3)	34(3)	57(3)	-7(2)	-11(3)	-4(2)
C(222)	77(4)	43(3)	117(5)	-10(4)	-13(4)	9(3)
C(223)	92(5)	51(4)	79(4)	4(3)	-4(4)	-24(3)
C(251)	78(4)	41(3)	67(4)	12(3)	-22(3)	2(3)
C(321)	65(4)	45(3)	42(3)	-2(2)	-8(3)	1(3)
C(322)	113(5)	57(4)	62(4)	14(3)	-31(4)	-13(4)
C(323)	67(4)	60(4)	88(4)	1(3)	-24(4)	-9(3)
C(351)	63(4)	86(5)	112(6)	-27(4)	31(4)	1(4)
O(41')	76(6)	201(12)	52(5)	-8(7)	-1(5)	-26(7)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 031600.

	x	y	z	U(eq)
H(1)	3344	8924	2303	68
H(4A)	2842	8463	646	73
H(4B)	2770	7674	502	73
H(11)	2557	5890	2817	41
H(12)	2968	6017	4113	49
H(13A)	2700	4823	3450	58
H(13B)	2954	4865	4168	58
H(14A)	1970	5369	4485	67
H(14B)	1807	4687	4142	67
H(15)	1564	5242	3183	56
H(16A)	1581	6400	3144	49
H(16B)	1837	6429	3863	49
H(21)	2138	6998	1311	40
H(22)	887	6719	1864	43
H(23A)	1278	6586	566	49
H(23B)	579	6359	833	49
H(24A)	313	7443	1097	50
H(24B)	503	7407	360	50
H(25)	1542	7833	560	47
H(26A)	1913	8087	1582	44
H(26B)	1225	7880	1887	44
H(31)	2210	7714	3646	47
H(32)	2877	8943	3552	50
H(33A)	2286	8405	4668	69
H(33B)	2667	9089	4639	69

H(34A)	1517	9253	4600	75
H(34B)	1863	9536	3976	75
H(35)	1192	8306	4052	69
H(36A)	1424	8166	2964	54
H(36B)	1810	8849	2946	54
H(121)	3823	6185	3359	78
H(12A)	3785	4826	3082	152
H(12B)	4302	5346	2810	152
H(12C)	3550	5382	2597	152
H(12D)	4051	5134	4231	156
H(12E)	4087	5896	4407	156
H(12F)	4613	5585	3931	156
H(15A)	826	5800	4204	108
H(15B)	679	5098	3897	108
H(15C)	581	5749	3483	108
H(221)	1667	5884	2127	59
H(22A)	1629	5484	829	118
H(22B)	2043	5148	1386	118
H(22C)	2243	5859	1132	118
H(22D)	577	5406	1397	111
H(22E)	516	5654	2116	111
H(22F)	936	5013	1955	111
H(25A)	683	8623	461	93
H(25B)	1287	8892	870	93
H(25C)	633	8652	1220	93
H(321)	3600	8031	3569	61
H(32A)	3277	7846	4868	116
H(32B)	3814	7446	4472	116
H(32C)	3052	7357	4315	116
H(32D)	3778	8952	4575	108
H(32E)	4010	9053	3856	108
H(32F)	4352	8506	4288	108
H(35A)	464	9214	3988	130
H(35B)	400	8750	3379	130
H(35C)	795	9425	3330	130

Curriculum Vitae

EDUCATION:

Massachusetts Institute of Technology, Cambridge, MA, 1999-present
Ph.D. Candidate: Organic Chemistry
University of Kentucky, Lexington, KY, 1995-1999
B.S. Chemistry, Cum Laude

AWARDS and HONORS:

- National Science Foundation Predoctoral Fellowship, 2000-2003
- Phi Beta Kappa, University of Kentucky, 1998
- First Place, Southeast Regional ACS, Organic Division Undergraduate Research Presentation Competition, 1998
- Stephen Harris Cook Undergraduate Summer Research Fellowship, Department of Chemistry, University of Kentucky, 1998
- University of Kentucky Chancellor's Scholarship, 1995-1999
- Thomas B. Nantz Memorial Scholarship, Department of Chemistry, University of Kentucky, 1997-1999

EXPERIENCE:

Massachusetts Institute of Technology, 1999-present

Research Assistant, Professor Timothy F. Jamison

Reactivity and selectivity of (μ, η^2 -propargylic aldehyde) $\text{Co}_2(\text{CO})_6$ complexes.

- Three component carbonyl ylide cycloadditions employing these complexes, a carbene source, and an olefin produce tetrahydrofurans with good selectivity.
- Catalytic, asymmetric aldol reactions of propargylic aldehydes mediated by chiral cobalt clusters.

Massachusetts Institute of Technology, Fall 1999, 2002, Spring 2000

Laboratory Teaching Assistant, Beginning and Intermediate Chemistry Courses, MA

Guided approximately 20 students per semester through an integrated lab sequence designed for chemistry majors.

University of Kentucky, 1997-1999

Undergraduate Researcher, Professor Robert B. Grossman

Sequential double Michael reactions of tethered diacids to alkynones construct highly functionalized carbocycles. Extension of this work to internal alkynones produced compounds with three contiguous, all carbon, quaternary centers with high diastereoselection.

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