

S,S-Dimethyl dithiocarbonate: A Novel Carbonyl Dication Synthron in the Synthesis of Ketones

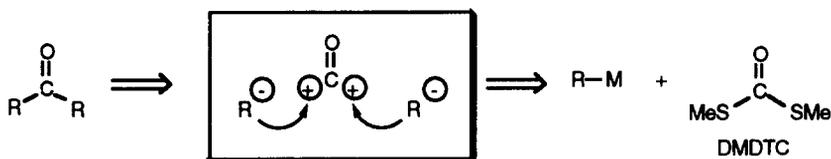
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Abstract: We report herein the use of DMDTC as an effective carbonyl dication equivalent in ketone synthesis. According to our strategy, we also successfully devised a synthetic pathway for *S*-methyl (trimethylsilyl)thioacetate which may be a potentially useful synthetic reagent in organic synthesis.
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Ketones are an important class of organic compounds whose synthesis and reactions have been actively studied during the last few decades.¹ In a retrosynthetic analysis for the formation of ketones, one can reasonably disconnect them into two carbanionic fragments as well as a carbonyl dication equivalent. Although this disconnection approach is simple and straightforward, known examples of this approach are rare.² In addition, almost all the known carbonyl dication synthons in ketone synthesis are indeed prepared from phosgene. As our continuing efforts in developing mild reagents that can be used to substitute phosgene or its derivatives in organic synthesis, we recently discovered that *S,S*-dimethyl dithiocarbonate (DMDTC) is a very useful reagent in urea synthesis.³ With regard to the facts that DMDTC is structurally similar to phosgene and could be prepared from methanol, carbon disulfide, and dimethyl sulfate through a two-step sequence, DMDTC is a potential candidate to substitute phosgene and its derivatives as an effective carbonyl dication synthron in ketone synthesis.



Our primary efforts are focused on developing an appropriate transition-metal catalyst that can effectively mediate the coupling reaction of DMDTC with Grignard or organolithium reagents. Since $\text{Fe}(\text{acac})_3$ and CuI are excellent promoters in the conversion of thioesters to ketones,^{2a, 4} they are potential candidates to investigate.

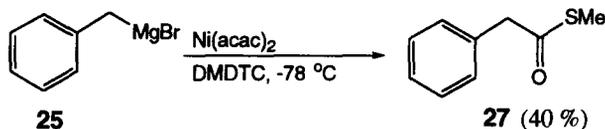
In an exploratory investigation carried out in the early stage of our study, we discovered that DMDTC does not react with hexylmagnesium bromide at -78°C . Gradually warming up the reaction mixture only lead to a complicated product mixture. In addition, our preliminary studies revealed that $\text{Fe}(\text{acac})_3$ is not an ideal catalyst. Reaction of hexylmagnesium bromide with DMDTC in the presence of catalytic amounts of $\text{Fe}(\text{acac})_3$ gives a product mixture of the corresponding thioester, ketone, and tertiary alcohol. Variation of the reaction

temperatures or the amounts of $\text{Fe}(\text{acac})_3$ do not significantly improve the product ratios. However, dihexylmagnesiocuprate reacts with DMDTC to afford ketone **2** exclusively in high yield (Table 1). The potential efficiency of this reagent attracted our attention and prompted further investigation.

In a typical run for the formation of **2**, $\text{CH}_3(\text{CH}_2)_5\text{MgBr}$ was treated with CuI at $-50\text{ }^\circ\text{C}$ in THF under argon for 2 hours, followed by addition of a solution of DMDTC. The reaction mixture was kept at $-50\text{ }^\circ\text{C}$ for 0.5 hour and then warmed up gradually to room-temperature for 4 hours. After typical workup and purification procedures, ketone **2** was obtained in pure form. The success of this process is highly dependent upon the extent of complete conversion of hexylbromide to the corresponding Grignard reagent in the previous step. The presence of any residual hexylbromide would destroy the cuprate reagent during the course of its formation and therefore retard the desired reaction. This procedure works well for most of the unhindered primary and secondary alkylmagnesium halides in our trials (Table 1) except in some cases, modifications of the reaction conditions are needed.

Perhaps due to intramolecular complexation,⁵ aryl and alkoxy substituted Grignard reagents are less reactive than hexylmagnesium bromide towards cuprate formation. As a consequence, formation of these kinds of cuprates at $-50\text{ }^\circ\text{C}$ is sluggish and incomplete. The presence of the unreacted Grignard reagents would consume the newly formed ketones, resulting tertiary alcohols as the final products (Table 2). For reasons of steric hindrance, unreacted cyclopentylmagnesium bromide (**5**) acts as a reducing agent rather than a nucleophile, transferring a hydride to **6** to provide **21** in moderate yield. In order to improve the yields of the desired ketones, higher reaction temperatures are usually required (entries 3-10 in Table 1) to ensure the cuprate formations

Unlike other aryl substituted cuprates, reaction of dibenzylmagnesiocuprate with DMDTC only afforded alcohol **26** as the product. Increasing the cuprate-formation temperature would not improve the results, only giving significant amounts of dibenzyl as the side product. Nevertheless, we discovered that thioester formation could be mediated by $\text{Ni}(\text{acac})_2$ at $-78\text{ }^\circ\text{C}$ to give **27** in moderate yield.



Although the reasons are not immediately obvious, ketone formation from **11** under typical reaction conditions is unsuccessful, giving a product mixture of **12a**, **12b**, and the corresponding tertiary alcohol. However, the reaction could be stopped at the stage of thioester formation by controlling the reaction temperature at $-50\text{ }^\circ\text{C}$ to give **12a** as the major product. In addition, the complication in the formation of **12b** could be subdued by employing one more equivalent of CuI in the reaction, affording **12b** in acceptable yield.

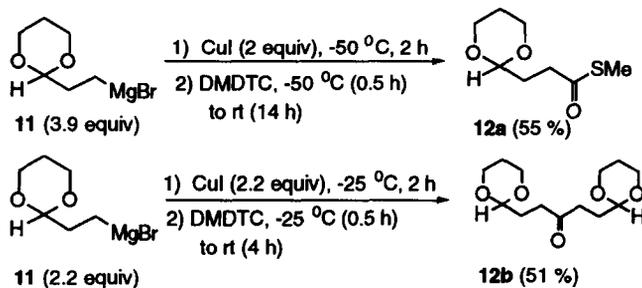
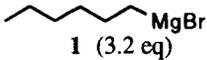
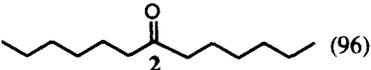
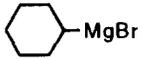
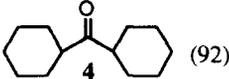
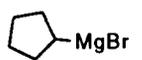
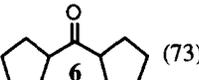
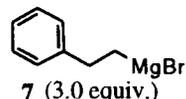
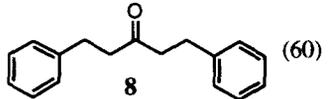
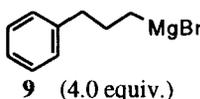
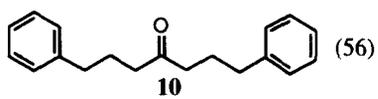
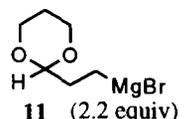
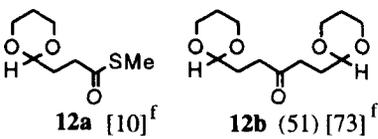
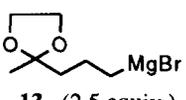
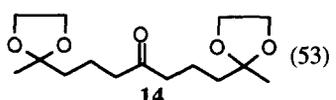
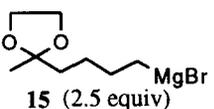
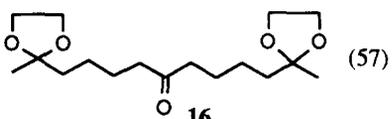
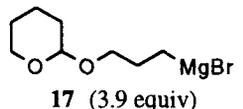
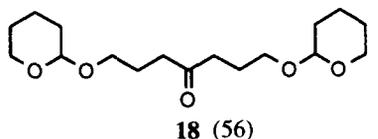
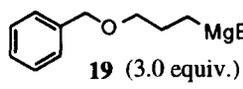
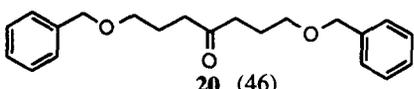


Table 1: Formation of Symmetrical Ketones by Reaction of DMDTC with various Cuprate Reagents

Entry	Grignard Reagent	Cuprate formation	Ketone formation	Major Product(s) (yield %) ^e
1	 1 (3.2 eq)	-50°C (2h) ^c	-50°C (0.5 h) to rt (4 h) ^a	 2 (96)
2	 3 (2.7 eq)	-50°C (2h) ^c	-50°C (0.5 h) to rt (4 h) ^b	 4 (92)
3	 5 (3.1 equiv.)	-25°C (2h) ^c	-25°C (0.5 h) to rt (4 h) ^b	 6 (73)
4	 7 (3.0 equiv.)	-15°C (6h) ^c	-15°C (0.5 h) to rt (16 h) ^b	 8 (60)
5	 9 (4.0 equiv.)	-25°C (6h)	-25°C (0.5 h) to rt (16 h) ^b	 10 (56)
6	 11 (2.2 equiv)	-25°C (2h) ^d	-25°C (0.5 h) to rt (3 h) ^b	 12a [10] ^f 12b (51) [73] ^f
7	 13 (2.5 equiv.)	-25°C (4h) ^c	-25°C (0.5 h) to rt (5.5 h) ^a	 14 (53)
8	 15 (2.5 equiv)	-25°C (4h) ^c	-25°C (0.5 h) to rt (3 h) ^a	 16 (57)
9	 17 (3.9 equiv)	-25°C (6 h) ^c	-25°C (0.5 h) to rt (16 h) ^a	 18 (56)
10	 19 (3.0 equiv.)	-15°C (6 h) ^c	-15°C (0.5 h) to rt (16 h) ^a	 20 (46)

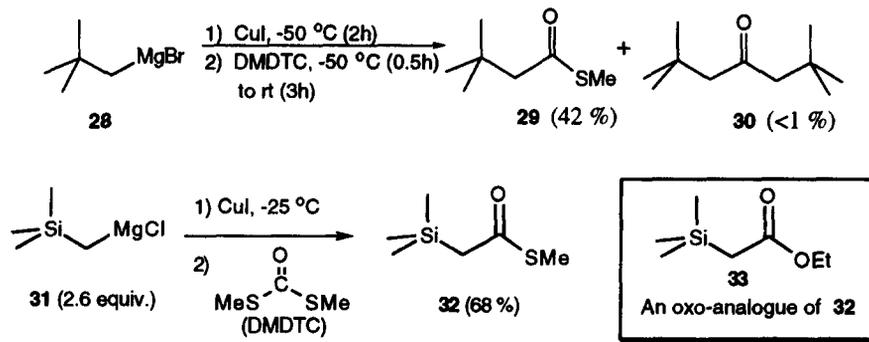
a, in THF; b, in ether; c, half an equivalent of CuI with respect to the Grignard reagent was used; d, one equivalent of CuI with respect to the Grignard reagent was used; e, isolated yield; f, GC yield.

Table 2: CuI Mediated Reaction of DMDTC with Aryl or Alkoxy Substituted Grignard Reagents at -50 °C

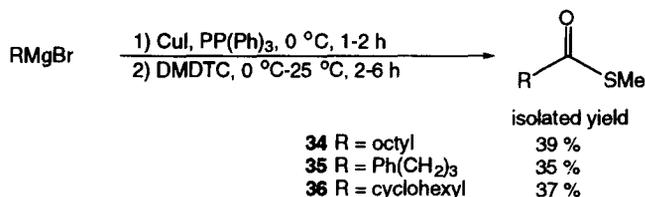
RMgBr (3-3.5 equiv.)	CuI, -50 °C 2 h	DMDTC -50 °C, 0.5 h and room temperature, 6-16 h	Major Product(s) (yield %) ^b
Grignard Reagent			
			 21 (52 %)
			 22 (41 %)
			 23 (34 %)
			 24 (47 %)
			 26 (53 %)

a. half an equivalent of CuI with respect to the Grignard reagents was used; b. isolated yield with respect to the amount of DMDTC.

It is worth mentioning that formation of ketone **30** from sterically hindered Grignard reagent **28** is ineffective, giving thioester **29** as the major product. By taking the advantages of this selectivity, we could efficiently synthesize *S*-methyl (trimethylsilyl)thioacetate **32** in one step. Thioester **32** is a potentially useful synthetic reagent whose higher *S*-alkyl or aryl homologs and oxo-analogue **33** proved to be a useful reagent in α,β -unsaturated thioester synthesis,⁶ silylation,⁷ nucleophilic addition,⁸ as well as 1,1-disubstituted ethylene formation.⁹



In an effort to develop a general synthetic route for unsymmetrical ketones, we examined the reaction of DMDTC with less reactive organocopper reagents. After exploring a number of reaction conditions, we eventually found that reaction of RCu-PPh_3 with DMDTC would result R(C=O)SMe selectively in moderate yields. Due to the low reactivity of the organocopper reagents, significant amounts of the starting DMDTC were recovered after reaction.



Our experiments first demonstrate that DMDTC can be an effective carbonyl dication equivalent in ketone synthesis. Oxygen-containing functional groups such as acetals and ethers can be tolerated. On the basis of our strategy, we could prepare **32** efficiently in good yield. The applications of **32** are under investigation.

ACKNOWLEDGMENT

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EXPERIMENTAL

General. THF and diethyl ether were distilled from sodium metal under N_2 with benzophenone as indicator. All the reactions were carried out under a N_2 or Ar atmosphere. DMDTC was prepared according to our recently published method.³ Reactions were typically monitored using either TLC on commercial silica gel plates or GC. IR spectra were recorded on a Bio-rad FTS 40 FT-IR spectrophotometer as neat film or KBr plate. ¹H NMR spectra were recorded on a Bruker AC300 (300 MHz) spectrometer. Chemical shifts (δ) are reported in ppm downfield from internal standard tetramethylsilane and coupling constants (J) are reported in Hertz (Hz). ¹³C spectra were either obtained on a Bruker AC300 (75 MHz) spectrometer. Mass spectra were determined using a HP-5989A mass spectrometer. Mps. were measured on a Melt-temp II melting-point apparatus, Laboratory Devices, USA.

A Representative Procedure for the Formation of Symmetrical Ketones from DMDTC: Dihexyl Ketone (2). To a vigorously stirred suspension of Mg (0.58 g, 24 mmol) in THF (1 mL) was added catalytic amounts of I_2 . A small portion of 1-bromohexane was added to initiate the reaction, followed by dropwise addition of a solution of 1-bromohexane (totally 3.3 g, 20 mmol) in 20 mL THF. After addition, the reaction mixture was further stirred for 30 min. The concentration of the hexylmagnesium bromide (1.07 M) was determined by titration, using HCl (1N) as standard and phenolphthalein as the indicator. The extent of conversion (92 %) was determined by GC analysis.

To prepare dihexyl ketone (**2**), the hexylmagnesium bromide (1.1 M, 3.6 mL, 3.9 mmol) was slowly added to a suspension of CuI (0.38 g, 2.0 mmol) in THF (2mL) at $-50\text{ }^{\circ}\text{C}$. The mixture was kept at $-50\text{ }^{\circ}\text{C}$ for 2 h, followed by addition of a solution of DMDTC (0.15 g, 1.2 mmol) in THF (1 mL). The reaction mixture was further reacted at $-50\text{ }^{\circ}\text{C}$ for 0.5 h and gradually warmed to room temperature (rt) for 4 h. The reaction was quenched by using saturated NH_4Cl solution. The crude product was extracted with CH_2Cl_2 , washed with saturated NaCl solution, concentrated and purified through liquid chromatography on silica gel, using a solvent gradient from hexanes to CH_2Cl_2 /hexanes (2:1) as eluent, to afford essentially pure **2** as colorless crystals (0.23 g, 1.16 mmol, 96 %): mp $30\text{--}32\text{ }^{\circ}\text{C}$ [*lit.*^{10a} $30\text{ }^{\circ}\text{C}$]; ^1H NMR (200 MHz, CDCl_3) δ 2.32 (t, $J = 7.2\text{ Hz}$, 4H), 1.53–1.42 (m, 4H), 1.21 (m, 12H), 0.84–0.78 (t, $J = 6.7\text{ Hz}$, 6H) [*lit.*^{10b} ^1H NMR δ 2.28 (t, 4H), 1.00–2.10 (m, 16H), 0.70–1.00 (m, 6H)]; ^{13}C NMR (75 MHz, CDCl_3) δ 211.5, 42.7, 31.5, 28.9, 23.8, 22.4, 13.9 [*lit.*^{XX} ^{13}C NMR 210.8, 42.3, 31.2, 28.5, 23.4, 22.1, 13.5]; IR ν 1713 cm^{-1} (C=O); MS m/z (rel. intensity, EI, 20 eV) 199 (M^{+1} , 35), 198 (M^+ , 100), 169 (5), 155 (5), 141 (10), 128 (15), 113 (30), 85 (8); HRMS (70 eV, M^+) calcd. for $\text{C}_{13}\text{H}_{26}\text{O}$: 198.1985, found 198.1982.

Dicyclohexyl Ketone (4). The cyclohexylmagnesium bromide solution (0.87 M) was prepared from bromocyclohexane (4.0 g, 25 mmol) and Mg (0.72 g, 30 mmol) in Et_2O (25mL) according to the representative procedure. The dicyclohexyl ketone (**4**) was obtained by reaction of DMDTC (0.31 g, 2.5 mmol) in Et_2O (2.5 mL) with a mixture of CuI (0.64 g, 3.4 mmol) and cyclohexylmagnesium bromide (0.87 M, 7.7 mL, 6.7 mmol) at $-50\text{ }^{\circ}\text{C}$ for 2h and at rt for 4 h. The reaction was worked up as usual and the crude product was purified through liquid chromatography on silica gel, using a solvent gradient from hexanes to CH_2Cl_2 /hexanes (2:1) as eluent, to afford essentially pure **4** as colorless crystals (0.45 g, 2.3 mmol, 92 %): ^1H NMR (300 MHz, CDCl_3) δ 2.46–2.36 (m, 2H), 1.73–1.62 (m, 10H), 1.36–1.14 (m, 10H) [*lit.*^{11a} ^1H NMR δ 2.20–2.60 (t, 2H), 1.00–2.00 (m, 20 H)]; ^{13}C NMR (75 MHz, CDCl_3) δ 217.0, 49.1, 28.5, 25.8, 25.7 [*lit.*^{11b} ^{13}C NMR δ 216.4, 48.9, 28.4, 25.7, 25.5]; IR ν 1704 cm^{-1} (C=O); MS m/z (rel. intensity, EI, 20 eV) 194 (M^+ , 15), 111 (50), 83 (100); HRMS (70 eV, M^{+1}) calcd. for $\text{C}_{13}\text{H}_{23}\text{O}$: 195.1750, found 195.1750.

Dicyclopentyl Ketone (6). The cyclopentylmagnesium bromide solution (0.82 M) was prepared from 1-bromocyclopentane (7.5 g, 50 mmol) and Mg (1.2 g, 50 mmol) in Et_2O (50 mL) according to the representative procedure. The corresponding cuprate reagent was prepared from CuI (1.6 g, 8.2 mmol) and cyclopentylmagnesium bromide (0.82 M, 20 mL, 16 mmol) at $-25\text{ }^{\circ}\text{C}$ for 2 h. To the cuprate solution, a solution of DMDTC (0.62 g, 5.1 mmol) in Et_2O (5 mL) was added at $-25\text{ }^{\circ}\text{C}$. After reaction at $-25\text{ }^{\circ}\text{C}$ for 0.5 h and at rt for 4 h, the mixture was worked up according to the representative procedure to provide a crude oil which was purified through liquid chromatography on silica gel, using a solvent gradient from hexanes to CH_2Cl_2 /hexane = 1/2 as eluent to obtain **6** (0.61 g, 3.7 mmol, 72 %) as a colorless solid: ^1H NMR (300 MHz, CDCl_3) δ 2.95–2.79 (m, 2H), 1.71–1.39 (m, 16H) [*lit.*¹² ^1H NMR δ 2.98 (2H), 1.30–2.00 (16H)]; ^{13}C NMR (75 MHz, CDCl_3) : δ 216.0, 50.5, 29.2, 25.9 [*lit.*^{11b} ^{13}C NMR δ 215.0, 50.0, 28.6, 25.5]; IR ν 1706 cm^{-1} (C=O); MS m/z (rel. intensity, EI, 20 eV) 166 (M^+ , 10), 97 (50), 69 (100); HRMS (70 eV, M^+) calcd. for $\text{C}_{11}\text{H}_{18}\text{O}$: 166.1359, found 166.1355.

1,5-Diphenyl-3-pentanone (8). The 2-phenylethylmagnesium bromide solution (0.87 M) was prepared from 2-bromoethylbenzene (2.5 g, 14 mmol) and Mg (0.4 g, 17 mmol) in Et_2O (15 mL) according to the representative procedure. The corresponding cuprate reagent was prepared from CuI (0.83 g, 4.4 mmol) in Et_2O

(4 mL) and 2-phenylethylmagnesium bromide (0.87 M, 8 mL, 7.2 mmol) at -15 °C for 6 h. To the cuprate solution, a solution of DMDTC (0.27 g, 2.2 mmol) in Et₂O (2 mL) was added. After reaction at -15 °C for 0.5 h and at rt for 16 h, the mixture was worked up according to the representative procedure to provide a crude oil which was purified through liquid chromatography on silica gel, using a solvent gradient from hexanes to CH₂Cl₂ /hexane = 1/2 as eluent to obtain **8** (0.31 g, 1.3 mmol, 60 %) as a colorless solid: ¹H NMR (300 MHz, CDCl₃) δ 7.30-7.25 (m, 4H), 7.21-7.14 (m, 6H), 2.89 (t, *J* = 7.5 Hz, 4H), 2.70 (t, *J* = 7.5 Hz, 4H) [lit.¹³ ¹H NMR δ 7.20 (2, 10H), 2.70 (m, 8H)]; ¹³C NMR (75 MHz, CDCl₃) δ 209.1, 141.0, 128.5, 128.3, 126.1, 44.5, 29.7; IR ν 1713 cm⁻¹ (C=O); MS *m/z* (rel. intensity, EI, 20 eV) 238 (M⁺, 30), 220 (5), 133 (55), 105 (85), 91 (100), 77 (20); HRMS (70 eV, M⁺) calcd. for C₁₇H₁₈O: 238.1359, found 238.1361.

1,7-Diphenyl-4-heptanone (10). The 3-phenylpropylmagnesium bromide solution (1.3 M) was prepared from 1-bromopropylbenzene (6.0 g, 30 mmol) and Mg (0.79 g, 33 mmol) in Et₂O (30 mL) according to the representative procedure. The corresponding cuprate reagent was prepared from CuI (2.7 g, 14 mmol) and 3-phenylpropylmagnesium bromide (1.3 M, 20 mL, 26 mmol) at -25 °C for 6 h. To the cuprate solution, a solution of DMDTC (0.79 g, 6.5 mmol) in Et₂O (6 mL) was added at -25 °C. After reaction at -25 °C for 0.5 h and at rt for 16 h, the mixture was worked up according to the representative procedure to provide a crude oil which was purified through liquid chromatography on silica gel, using a solvent gradient from hexanes to CH₂Cl₂ /hexane = 1/2 as eluent to obtain **10** (0.97 g, 3.7 mmol, 56 %) as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 7.35-7.30 (m, 4H), 7.25-7.19 (m, 6H), 2.65 (t, *J* = 7.5 Hz, 4H), 2.41 (t, *J* = 7.3 Hz, 4H), 1.99-1.89 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 210.3, 141.5, 128.3, 128.2, 125.8, 41.8, 34.9, 25.0; IR ν 1711 cm⁻¹ (C=O); MS *m/z* (rel. intensity, EI, 20 eV) 266 (M⁺, 8), 175 (20), 162 (8), 147 (6), 104 (100), 91 (45); HRMS (70 eV, M⁺) calcd. for C₁₉H₂₂O: 266.1672, found 266.1669.

3-(1,3-Dioxane-2-yl)thiopropionic Acid S-Methyl Ester (12a). The 2-(1,3-Dioxane-2-yl)ethylmagnesium bromide solution (0.96 M) was prepared from 2-(2-bromoethyl)-1,3-dioxane (2.0 g, 10 mmol) and Mg (0.25 g, 10.5 mmol) in THF (10 mL) according to the representative procedure. The corresponding cuprate reagent was prepared from CuI (0.81 g, 4.3 mmol) in THF (4.5 mL) and 2-(1,3-dioxane-2-yl)ethylmagnesium bromide (0.96 M, 9.0 mL, 8.6 mmol) at -50 °C for 2 h. To the cuprate solution, a solution of DMDTC (0.27 g, 2.2 mmol) in THF (2.2 mL) was added. After reaction at -50 °C for 0.5 h and at rt for 14 h, the mixture was worked up according to the representative procedure to provide a crude oil which was purified through liquid chromatography on silica gel, using a solvent gradient from hexanes/CH₂Cl₂ = 1/1 to 1/2 as eluent to obtain **12a** (0.23 g, 1.2 mmol, 55 %) as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 4.52 (t, *J* = 5.0 Hz, 1H), 4.03 (dd, *J* = 12 Hz, 5 Hz, 2H), 3.70 (dt, *J* = 12 Hz, 2.2 Hz, 2H), 2.64 (t, *J* = 8.1 Hz, 2H), 2.24 (s, 3H), 2.04-1.96 (m, 1H), 1.93-1.86 (m, 2H), 1.30-1.26 (d, *J* = 12 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 199.3, 100.5, 66.7, 37.9, 30.4, 25.6, 11.5; IR (neat) ν 1692 cm⁻¹ (C=O); MS *m/z* (rel. intensity, EI, 20 eV) 189 (M⁺-1, 10), 175 (13), 143 (100), 85 (95), 100 (20); HRMS (70 eV, M⁺) calcd. for C₈H₁₄O₃S: 190.0664, found 190.0662.

1,5-Bis(1,3-dioxane-2-yl)-3-pentanone (12b). The Grignard solution (0.96 M) was prepared according to the previous procedure. The corresponding cuprate reagent was prepared from CuI (0.98 g, 4.7 mmol) in THF (4 mL) and 2-(1,3-dioxane-2-yl)ethylmagnesium bromide (0.96 M, 5.0 mL, 4.7 mmol) at -25 °C for 4 h. To the cuprate solution, a solution of DMDTC (0.25 g, 2.0 mmol) in THF (2.0 mL) was added. After

reaction at $-25\text{ }^{\circ}\text{C}$ for 0.5 h and at rt for 15 h, the mixture was worked up according to the representative procedure to provide a crude oil which was purified through liquid chromatography on silica gel, using hexanes/ethyl acetate = 1/3 as eluent to obtain **12b** (0.26 g, 1.0 mmol, 51 %) as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 4.47 (t, $J = 5.0$ Hz, 2H), 4.01–2.96 (dd, $J = 12$ Hz, 5 Hz, 4H), 3.65 (dt, $J = 12$ Hz, 3.3 Hz, 4H), 2.45 (t, $J = 7.2$ Hz, 4H), 2.04–1.96 (m, 2H), 1.78 (dt, $J = 7.2$ Hz, 5 Hz, 4H), 1.27–1.22 (d, $J = 12.3$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 209.6, 100.8, 66.7, 36.5, 28.9, 25.6; IR ν 1714 cm^{-1} (C=O); MS m/z (rel. intensity, EI, 20 eV) 258 (M^+ , 5), 257 (M^+-1 , 10), 156 (23), 143 (24), 100 (100), 87 (60); HRMS (70 eV, M^+-1) calcd. for $\text{C}_{12}\text{H}_{21}\text{O}_4$: 258.1468, found 258.1458.

1,7-Bis(2-methyl-1,3-dioxolane-2-yl)-4-heptanone (14). To a vigorously stirred mixture of Mg (0.60 g, 25 mmol) and 2-(3-chloropropyl)-2-methyl-1,3-dioxolane (2.0 g, 12 mmol) in THF (15 mL) was added catalytic amounts of I_2 and two drops of dibromoethane. The mixture was warmed at $80\text{ }^{\circ}\text{C}$ and two drops of methylmagnesium bromide (1.0 M) was added to initiate the reaction. After addition, the reaction mixture was kept at reflux for 2 h to obtain 3-(2-methyl-1,3-dioxolane-2-yl)propylmagnesium chloride (0.90 M). The corresponding cuprate reagent was prepared from CuI (1.0 g, 5.4 mmol) in THF (5 mL) and 3-(2-methyl-1,3-dioxolane-2-yl)propylmagnesium chloride (0.90 M, 12.0 mL, 10.8 mmol) at $-25\text{ }^{\circ}\text{C}$ for 4 h. To the cuprate solution, a solution of DMDTC (0.54 g, 4.4 mmol) in THF (4.0 mL) was added. After reaction at $-25\text{ }^{\circ}\text{C}$ for 0.5 h and at rt for 5.5 h, the mixture was worked up according to the representative procedure to provide a crude oil which was purified through liquid chromatography on silica gel, using a gradient eluent from hexanes/ethyl acetate = 1/6 to hexanes/ethyl acetate = 1/3 to obtain **14** (0.66 g, 2.31 mmol, 53 %) as a colorless oil: ^1H NMR (300 MHz, CD_3CN) δ 3.79–3.75 (m, 8H), 2.27 (t, $J = 6.8$ Hz, 4H), 1.55–1.44 (m, 8H), 1.15 (s, 6H); ^{13}C NMR (75 MHz, CD_3CN) δ 210.2, 109.5, 64.3, 42.2, 38.0, 23.4, 18.0; IR ν 1711 cm^{-1} (C=O); MS m/z (rel. intensity, EI, 20 eV) 287 (M^++1 , 20), 271 (8), 99 (20), 87 (100); HRMS (70 eV, M^+) calcd. for $\text{C}_{15}\text{H}_{26}\text{O}_5$: 286.1781, found 286.1788.

1,9-Bis(2-methyl-1,3-dioxolane-2-yl)-5-nonanone (16) To a vigorously stirred mixture of Mg (0.80 g, 33 mmol) and 2-(4-chlorobutyl)-2-methyl-1,3-dioxolane (1.8 g, 9.9 mmol) in THF (13 mL) was added catalytic amounts of I_2 and four drops of dibromoethane. After addition, the reaction mixture was kept at reflux for 20 h to obtain 4-(2-methyl-1,3-dioxolane-2-yl)butylmagnesium chloride (0.90 M). The corresponding cuprate reagent was prepared from CuI (0.84 g, 4.4 mmol) in THF (4 mL) and 4-(2-methyl-1,3-dioxolane-2-yl)butylmagnesium chloride (0.90 M, 1.0 mL, 8.8 mmol) at $-25\text{ }^{\circ}\text{C}$ for 4 h. To the cuprate solution, a solution of DMDTC (0.43 g, 3.5 mmol) in THF (3.0 mL) was added. After reaction at $-25\text{ }^{\circ}\text{C}$ for 0.5 h and at rt for 3 h, the mixture was worked up according to the representative procedure to provide a crude oil which was purified through liquid chromatography on silica gel, using a gradient eluent from hexanes/ethyl acetate = 1/7 to hexanes/ethyl acetate = 1/3 to obtain **16** (0.62 g, 2.0 mmol, 57 %) as a colorless oil: ^1H NMR (300 MHz, CD_3CN) δ 3.92–3.82 (m, 8H), 2.41 (t, $J = 7.2$ Hz, 4H), 1.63–1.46 (m, 8H), 1.39–1.28 (m, 4H), 1.25 (s, 6H); ^{13}C NMR (75 MHz, CD_3CN) δ 212.1, 110.8, 65.6, 43.4, 40.0, 25.1, 24.8, 24.4; IR ν 1711 cm^{-1} (C=O); MS m/z (rel. intensity, EI, 20 eV) 314 (M^+ , 0.6), 299 (M^+-15 , 12), 128 (6), 87 (100); HRMS (70 eV, M^+) calcd. for $\text{C}_{17}\text{H}_{30}\text{O}_5$: 314.2095, found 314.2101.

1,7-Bis(tetrahydropyran-2-yloxy)-4-heptanone (18). The 3-(tetrahydropyran-2-yloxy)propylmagnesium bromide solution (0.88 M) was prepared from 2-(3-bromopropoxy)tetrahydrofuran (3.0 g, 14

mmol) and Mg (0.97 g, 40 mmol) in THF (13 mL) according to the representative procedure. The corresponding cuprate reagent was prepared from CuI (1.1 g, 5.9 mmol) in THF (5 mL) and 3-(tetrahydropyran-2-yloxy)propylmagnesium bromide (0.88 M, 13.0 mL, 11 mmol) at -25 °C for 6 h. To the cuprate solution, a solution of DMDTC (0.36 g, 2.9 mmol) in THF (2.0 mL) was added. After reaction at -25 °C for 0.5 h and at rt for 16 h, the mixture was worked up according to the representative procedure to provide a crude oil which was purified through liquid chromatography on silica gel, using hexanes/ethyl acetate = 1/2 as eluent to obtain **18** (0.51 g, 1.6 mmol, 56 %) as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 4.45 (t, *J* = 3.3 Hz, 2H), 3.74-3.59 (m, 4H), 3.41-3.29 (m, 4H), 2.45 (t, *J* = 7.1 Hz, 4H), 1.82-1.42 (m, 16H); ¹³C NMR (75 MHz, CDCl₃) δ 210.2, 98.7, 66.4, 62.2, 39.4, 30.5, 25.3, 23.8, 19.5; IR ν 1713 cm⁻¹ (C=O); MS *m/z* (rel. intensity, EI, 20 eV) 315 (M⁺+1, 0.1), 314 (M⁺, 0.09), 213 (M⁺-101, 7), 129 (50), 111 (10), 85 (100); HRMS (70 eV, M⁺) calcd. for C₁₇H₃₀O₅: 314.2095, found 314.2087.

1,7-Bis(benzyloxy)heptan-4-one (20). The 3-(benzyloxy)propylmagnesium bromide solution (0.90 M) was prepared from 1-benzyloxy-3-bromopropane (2.0 g, 8.7 mmol) and Mg (0.42 g, 18 mmol) in THF (8.5 mL) according to the representative procedure. The corresponding cuprate reagent was prepared from CuI (0.70 g, 3.7 mmol) in THF (3 mL) and 3-(benzyloxy)propylmagnesium bromide (0.97 M, 7.5 mL, 7.3 mmol). To the cuprate solution, a solution of DMDTC (0.30 g, 2.5 mmol) in THF (2.0 mL) was added. After reaction at -15 °C for 6 h and at rt for 16 h, the mixture was worked up according to the representative procedure to provide a crude oil which was purified through liquid chromatography on silica gel, using hexanes/ethyl acetate = 1/2 as eluent to obtain **20** (0.37 g, 1.1 mmol, 46 %) as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 7.37-7.25 (m, 10H), 4.47 (s, 4H), 3.47 (t, *J* = 6.2 Hz, 4H), 2.52 (t, *J* = 7.2 Hz, 4H), 1.93-1.84 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 210.1, 138.3, 128.1, 127.4, 127.3, 72.6, 69.1, 39.2, 23.7; IR ν 1713 cm⁻¹ (C=O); MS *m/z* (rel. intensity, EI, 20 eV) 327 (M⁺+1, 10), 219 (15), 129 (95), 111 (42), 106 (13), 91 (100); HRMS (70 eV, M⁺) calcd. for C₂₁H₂₆O₃: 326.1883, found 326.1880.

Di(cyclopentyl)methanol (21) To a suspension of CuI (1.6 g, 8.2 mmol) in Et₂O (8 mL) was added cyclopentylmagnesium bromide (0.82 M, 20 mL, 16 mmol) at -50 °C. After addition, the mixture was stirred at -50 °C for 2 h and a solution of DMDTC (0.62 g, 5.1 mmol) in Et₂O (5 mL) was added. The mixture was further reacted at -50 °C for 6 h and quenched by addition of saturated NH₄Cl solution. The crude product was extracted with CH₂Cl₂, washed with brine, dried over anhydrous MgSO₄, concentrated under reduced pressure, and purified through liquid chromatography on silica gel, using a solvent gradient from hexanes to CH₂Cl₂/hexanes = 1/1 as eluent to obtain **21** as colorless crystals (0.45 g, 2.7 mmol, 52 %): mp 46-48 °C [*lit.*¹⁴ 45 °C]; ¹H NMR (300 MHz, CDCl₃) δ 3.33-3.27 (t, *J* = 9 Hz, 1H), 1.90-1.87 (m, 2H), 1.72-1.28 (m, 16H) [*lit.*¹² ¹H NMR δ 3.35 (1H), 1.10-2.50 (18 H)]; ¹³C NMR (75 MHz, CDCl₃) δ 78.2, 44.7, 29.3, 27.4, 25.6, 25.5; MS *m/z* (rel. intensity, EI, 20 eV) 168 (M⁺, 1), 150 (2), 99 (60), 81 (100); HRMS (70 eV, M⁺) calcd. for C₁₁H₂₀O: 168.1515, found: 168.1522. Anal. calcd. for C₁₁H₂₀O: C, 78.51%, H, 11.98 %. found C, 78.31%, H, 11.92 %; IR ν 3396 cm⁻¹ (C-OH).

Tris(2-phenylethyl)methanol (22) Compound **22** was prepared according to the preparative procedure for compound **21** in 41 % yield: mp 70-72 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.33-7.28 (m, 6H), 7.24-7.17 (m, 9H), 2.74-2.68 (m, 6H), 1.93-1.88 (m, 6H) [*lit.*¹⁵ ¹H NMR δ 7.20 (s, 15 H), 2.67 (m, 6H), 1.86 (m, 6H), 1.33 (s, 1H)]; ¹³C NMR (75 MHz, CDCl₃) δ 142.2, 128.5, 128.3, 125.9, 74.2, 41.2, 30.1; MS *m/z* (rel.

intensity, EI, 20 eV) 326 ($M^+ - 18$, 8), 239 (12), 117 (15), 105 (10), 91 (100); HRMS (70 eV, $M^+ - 18$) calcd. for $C_{25}H_{26}$: 326.2036, found 326.2031. Anal. calcd. for $C_{25}H_{28}O$: C, 87.16%, H, 8.19%, found C, 87.15%, H, 8.19%; IR ν 3485 cm^{-1} (C-OH).

Tris(3-phenylpropyl)methanol (23) Compound **23** was prepared according to the preparative procedure for compound **21** in 34 % yield: 1H NMR (300 MHz, $CDCl_3$) δ 7.35-7.30 (m, 6H), 7.25-7.19 (m, 9H), 2.61 (t, $J = 7.3$ Hz, 6H), 1.64-1.57 (m, 6H), 1.55-1.44 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3, 128.4, 128.3, 125.7, 74.2, 38.6, 36.2, 25.2; MS m/z (rel. intensity, EI, 20 eV) 368 ($M^+ - 18$, 45), 291 (10), 267 (25), 171 (22), 160 (20), 145 (23), 131 (21), 104 (95), 91 (100); HRMS (70 eV, $M^+ - 18$) calcd. for $C_{28}H_{32}$: 368.2496, found 368.2506; IR ν 3549 cm^{-1} (C-OH).

Tris(3-(benzyloxy)propyl)methanol (24) Compound **24** was prepared according to the preparative procedure for compound **21** in 47 % yield: 1H NMR (300 MHz, $CDCl_3$) δ 7.35-7.24 (m, 15H), 4.51 (s, 6H), 3.50-3.47 (t, $J = 5.9$ Hz, 6H), 1.72-1.64 (m, 6H), 1.58-1.53 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 128.2, 127.5, 127.4, 73.0, 72.8, 70.8, 35.8, 23.9; MS m/z (rel. intensity, EI, 20 eV) 327 ($M^+ + 1$, 10), 219 (15), 129 (95), 111 (42), 106 (13), 91 (100); HRMS (70 eV, M^+) calcd. for $C_{31}H_{40}O_4$: 476.2928, found 476.2930; IR ν 3445 cm^{-1} (C-OH).

Tris(phenylmethyl)methanol (26) Compound **26** was prepared according to the preparative procedure for compound **21** in 53 % yield: mp 112-114 °C [*lit.*¹⁶ 110-114 °C]; 1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.25 (m, 15H), 2.83 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.3, 130.8, 128.1, 126.4, 73.9, 45.8; MS m/z (rel. intensity, EI, 20 eV) 284 ($M^+ - 18$, 1), 211 (45), 193 (30), 91 (100); HRMS (70 eV, $M^+ - 18$) calcd. for $C_{22}H_{20}$: 284.1566, found 284.1565; IR ν 3569 cm^{-1} (OH).

(2-Phenyl)thioacetic Acid S-Methyl Ester (27). To a flask with $Ni(acac)_2$ (0.77 g, 3.0 mmol) was added benzylmagnesium chloride (1.16 M, 13 mL, 15 mmol) at -78 °C under argon. The mixture was stirred at -78 °C for 1 h, and a solution of DMDTC (0.61 g, 5.0 mmol) in THF (5 mL) was added. The reaction was allowed to proceed at -78 °C for 3 h and quenched by addition of a saturated NH_4Cl solution. The crude product was extracted with CH_2Cl_2 , dried over anhydrous Na_2SO_4 , concentrated under reduced pressure and purified through liquid chromatography on silica gel, using a solvent gradient from hexanes to CH_2Cl_2 /hexanes = 1.5 as eluent to obtain **27** (0.34 g, 2.0 mmol, 40 %) as a slightly yellowish oil: 1H NMR (300 MHz, $CDCl_3$) δ 7.36-7.24 (m, 5H), 3.82 (s, 2H), 2.27 (s, 3H) [*lit.*¹⁷ 1H NMR 7.20 (s, 5H), 3.65 (s, 2H), 2.10 (s, 3H)]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.7, 133.6, 129.5, 128.6, 127.3, 50.3, 11.8; IR ν 1691 cm^{-1} (C=O for thioesters); MS m/z (rel. intensity, EI, 20 eV) 167 ($M^+ + 1$, 60), 166 (M^+ , 78), 139 (40), 91 (100); HRMS (70 eV, M^+) calcd. for $C_9H_{10}OS$ 166.0453, found 166.0425.

(3,3-Dimethyl)thiobutanoic Acid S-Methyl Ester (29) The neopentylmagnesium chloride solution (0.40 M) was prepared from neopentylchloride (2.5 g, 23 mmol) and Mg (1.5 g, 62 mmol) in Et_2O (15.0 mL) according to the representative procedure. The corresponding cuprate reagent was prepared from CuI (1.2 g, 6.0 mmol) in Et_2O (6 mL) and neopentylmagnesium chloride (0.4 M, 30 mL, 12 mmol) at -50 °C for 2 h. To the cuprate solution, a solution of DMDTC (0.51 g, 4.2 mmol) in Et_2O (4.0 mL) was added. After reaction at -50 °C for 0.5 h and at rt for 2 h, the mixture was worked up according to the representative procedure to

provide a crude oil which was purified through liquid chromatography on silica gel, using a eluent gradient from hexanes to $\text{CH}_2\text{Cl}_2/\text{hexanes} = 1/2$ to obtain **29** (0.26 g, 1.8 mmol, 42 %) as a colorless oil: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 2.43 (s, 2H), 2.26 (s, 3H), 1.01 (s, 9H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 198.2, 56.6, 31.4, 29.6, 11.7; IR ν 1713 cm^{-1} (C=O); MS m/z (rel. intensity, EI, 20 eV) 146 (M^+ , 5), 131 (3), 99 (75), 89 (10), 57 (100); HRMS (M^+) calcd. for $\text{C}_7\text{H}_{14}\text{OS}$: 146.0766, found 146.0770.

(2-Trimethylsilyl)thioacetic Acid S-Methyl Ester (32). The trimethylsilylmethylmagnesium chloride solution (0.97 M) was prepared from chloromethyltrimethylsilane (3.0 g, 24 mmol) and Mg (0.6 g, 25 mmol) in Et_2O (24 mL) according to the representative procedure. The corresponding cuprate reagent was prepared from CuI (1.5 g, 7.8 mmol) in Et_2O (8 mL) and trimethylsilylmethylmagnesium chloride (16 mL, 16 mmol) at $-50\text{ }^\circ\text{C}$ for 2 h. To the cuprate solution, a solution of DMDTC (0.73 g, 6.0 mmol) in Et_2O (6 mL) was added. After reaction at $-50\text{ }^\circ\text{C}$ for 0.5 h, $0\text{ }^\circ\text{C}$ for 1.5 h and at rt for 2 h, the mixture was worked up according to the representative procedure to provide a crude oil which was purified through liquid chromatography on silica gel, using a solvent gradient from hexanes to $\text{CH}_2\text{Cl}_2/\text{hexanes} = 1/3$ as eluent to obtain **32** (0.67 g, 4.1 mmol, 68 %) as a colorless oil: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 2.30 (s, 2H), 2.24 (s, 3H), 0.10 (s, 9H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 196.9, 38.2, 11.9, -1.5; IR ν 1681 cm^{-1} (C=O); MS m/z (rel. intensity, EI, 20 eV) 147 (M^+-15 , 5), 115 (95), 73 (100); HRMS (70 eV, M^+-15) calcd. for $\text{C}_5\text{H}_{11}\text{OSSi}$: 147.0294, found 147.0298.

A Representative Procedure for the Formation of Thioesters from DMDTC and Alkylcopper Reagents: Thiononanoic Acid S-Methyl Ester (34). To a slurry of CuI (1.8 g, 9.1 mmol) and PPh_3 (2.4 g, 9.1 mmol) in Et_2O (5 mL) was added an ethereal solution of $\text{CH}_3(\text{CH}_2)_7\text{MgBr}$ (0.91 M, 10 mL) at $0\text{ }^\circ\text{C}$ under argon. The mixture was allowed to react at $0\text{ }^\circ\text{C}$ for 40 min, followed by addition of an ethereal solution (4 mL) of DMDTC (0.5 g, 4.1 mmol). The reaction mixture was kept at $0\text{ }^\circ\text{C}$ for 6 h and quenched by addition of saturated aqueous NH_4Cl solution. The crude product was extracted with CH_2Cl_2 and purified through liquid chromatography on silica gel, using a solvent gradient from hexanes to $\text{CH}_2\text{Cl}_2/\text{hexanes}$ (1/4) as eluent, to provide essentially pure **23** (0.3 g, 1.6 mmol, 39 %) as a colorless oil: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 2.53 (t, $J = 7.5$ Hz, 2H), 2.57 (s, 3H), 1.63 (m, 2H), 1.24 (m, 10 H), 0.85 (t, $J = 6.6$ Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 200.1, 44.0, 31.8, 29.2, 29.1, 29.0, 25.7, 22.6, 14.1, 11.5; IR ν 1696 cm^{-1} (C=O for thioesters); MS m/z (rel. intensity, EI, 70 eV) 189 (M^++1 , 72), 188 (M^+ , 20), 141 (M^+-SCH_3 , 100); HRMS (70 eV, M^+) calcd. for $\text{C}_{10}\text{H}_{20}\text{OS}$: 188.1236, found 188.1233.

(4-Phenyl)thiobutanoic Acid S-Methyl Ester (35). Compound **35** was obtained according to the representative procedure as a colorless oil (35 %): $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.26-7.31 (m, 2H), 7.16-7.22 (m, 3H), 2.65 (t, $J = 7.5$ Hz, 2H), 2.57 (t, $J = 7.5$ Hz, 2H), 2.29 (s, 3H), 1.95-2.05 (m, 2H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 199.5, 141.1, 128.4, 128.3, 126.0, 43.1, 34.8, 27.1, 11.5 [*lit.*¹⁸ 199.0, 140.9, 128.2, 128.1, 125.8, 42.8, 34.6, 26.9, 11.2]; IR ν 1688 cm^{-1} (C=O for thioesters); MS m/z (rel. intensity, EI, 70 eV) 195 (M^++1 , 20), 194 (M^+ , 5), 147 (M^+-SCH_3 , 100), 91 (25); HRMS (70 eV, M^+) calcd. for $\text{C}_{11}\text{H}_{14}\text{OS}$: 194.0766, found 194.0766.

(Cyclohexane)thiocarboxylic Acid S-Methyl Ester (36) Compound **36** was obtained according to the representative procedures as a colorless oil (37 %): $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 2.42-2.51 (m, 1H), 2.24 (s, 3H), 1.89 (d, $J = 12.3$ Hz, 2H), 1.78-1.79 (m, 2H), 1.75-1.75 (m, 1H), 1.39-1.50 (m, 2H), 1.15-

1.35 (m, 3H) [lit.¹⁷ 1.1–2.8 (m, 11H), 2.2 (s, 3H)]; ¹³C NMR (75 MHz, CDCl₃) 203.5, 52.5, 29.5, 25.6, 25.5, 11.1; IR ν 1692 cm⁻¹ (C=O for thioesters); MS m/z (rel. intensity, EI, 70 eV) 158 (M⁺, 6), 143 (M⁺-CH₃, 10), 111 (M⁺-SCH₃, 58); 83 (C₆H₁₁⁺, 100), 55 (53); HRMS (70 eV, M⁺) calcd. for C₈H₁₄OS: 158.0767, found 158.0770

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