Supporting Information

Radical Cyclization by *ipso* Substitution of Methoxy Group: Considerable Effect of HMPA on Samarium-Mediated Cyclization

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Experimental Section

General Methods. All reactions were carried out under a positive pressure of argon, and glassware and syringes were dried in an electric oven at 100 °C prior to use. Samarium (40 mesh) and 1,1-thiocarbonylimidazole were purchased from Across and Tokyo Kasei Kogyo, respectively. THF was distilled from sodium benzophenone ketyl under N₂. CH₂Cl₂ and HMPA were distilled from CaH₂ under N₂. Other solvents and reagents were used without further purification. Melting points are uncorrected. ¹H NMR spectra (300 or 500 MHz) were recorded in CDCl₃. Chemical shifts are reported in parts per million downfield from internal Me₄Si (s = singlet, d = doublet, dd = double doublet, ddd = doublet of double doublet, t = triplet, m = multiplet). Optical rotations were measured in CHCl₃ with a JASCO DIP-360 digital polarimeter. For flash chromatography, silica gel 60 (230–400 mesh, Merck) was employed.

Compound **32a**,¹ **S3**² and **S6**³ and was synthesized according to the following literature.

- 1 Tateiwa, J.; Horiuchi, H.; Hashimoto, K.; Yamauchi, T.; Uemura, S. *J. Org. Chem.* **1994**, *59*, 5901–5904.
- 2 Tanaka, T.; Mikamiyama, H.; Maeda, K.; Iwata, C. *J. Org. Chem.* **1998**, *63*, 9782–9793.
- 3 Adediran, S. A.; Cabaret, D.; Drouillat, B.; Pratt, R. F.; Wakselman, M. *Bioorg. Med. Chem.* **2001**, *9*, 1175–1183.

Scheme S1

Dimethyl 2,4,6-Trimethoxy-5-(3-oxobutyl)benzene-1,3-dicarboxylate (25). To a stirred mixture of dimethyl 5-bromomethyl-2,4,6-trimethoxybenzene-1,3-dicarboxylate **S1** (195 mg, 0.518 mmol), *O*-(*tert*-butyldimethylsilyl)propen-2-ol (357 mg, 2.07 mmol), and MS 4A (20 mg) in CH₂Cl₂ (10 mL) were added ZnCl₂ (70.5 mg, 0.518 mmol) at room temperature. After the mixture was stirred for 4 h at this temperature, the mixture was made basic with saturated NaHCO₃, and the whole was extracted with EtOAc. The extract was washed with water and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to leave an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (1:1) to give **25** (139 mg, 76% yield) as colorless crystals: mp 79–80 °C; IR (KBr) cm⁻¹: 1734 (C=O); ¹H NMR (300 MHz, CDCl₃) δ 2.14 (s, 3H, CMe), 2.62–2.70 (m, 2H), 2.78–2.84 (m, 2H), 3.79 (s, 6H, 2 × OMe), 3.82 (s, 3H, OMe), 3.92 (s, 6H, 2 × OMe); ¹³C NMR (75.5 MHz, CDCl₃) δ 18.1, 29.7, 43.3, 52.6 (2C), 62.4 (2C), 63.4, 118.6 (2C), 123.9, 154.5, 158.0 (2C), 166.1 (2C), 208.0; MS (EI) *m/z* (%) 355 (MH⁺, 67), 297 (100); HRMS (EI) calcd for C₁₇H₂₂O₈ (M⁺): 354.1311; found 354.1314.

Dimethyl 5-3-[(1*H*-Imidazol-1-ylcarbothioyl)oxy]butyl-2,4,6-trimethoxybenzene-1,3-dicarboxylate (8). To a stirred solution of the ketone **25** (95.3 mg, 0.269 mmol) in MeOH (10 mL) was added NaBH₄ (40.7 mg, 1.08 mmol) at 0 °C. The mixture was stirred for 1 h, and saturated NH₄Cl was added to the mixture. The whole was extracted with EtOAc, and the extract was washed with water and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to leave an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (1:1) to give the corresponding alcohol (93.8 mg, 98%) as a colorless oil: IR (KBr) cm⁻¹: 3547 (OH), 1732 (C=O); ¹H NMR (300 MHz, CDCl₃) δ 1.16 (d, *J* = 6.6 Hz, 3H, CMe), 1.59–1.68 (m, 2H, 2-CH₂), 2.11 (br s, 1H, OH), 2.59–2.77 (m, 2H, 1-CH₂), 3.61–3.69 (m, 1H, 3-H), 3.81 (s, 9H, OMe), 3.91 (s, 6H, 2 × OMe); ¹³C NMR (75.5 MHz, CDCl₃) δ 20.2, 23.1, 38.9, 52.7 (2C), 62.5 (2C), 63.4, 66.8, 118.6, 124.8, 154.3, 158.0 (3C), 166.2 (2C); MS (EI) *m/z* (%) 355 [(M–1)⁺, 0.1], 294 (100); HRMS (FAB) calcd for C₁₇H₂₅O₈ (MH⁺): 357.1550; found 357.1570.

A stirred mixture of the above alcohol (28.0 mg, 0.079 mmol), 1,1-thiocarbonylimidazole (77.8 mg, 0.39 mmol), and DMAP (48.0 mg, 0.39 mmol) in THF (3 mL) was heated under reflux for 12 h. The mixture was diluted with EtOAc, and the whole was washed with 5% HCl, saturated NaHCO₃, water and brine, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to leave an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (1:1) to give **8** (21.6 mg, 59%) as a colorless oil: IR (KBr) cm⁻¹: 1732 (C=O); ¹H NMR (300 MHz, CDCl₃) δ 1.48 (d, *J* = 6.0 Hz, 3H, CMe), 1.97–2.11 (m, 2H, 2'-CH₂), 2.64–2.72 (m, 2H, 1'-CH₂), 3.78 (s, 6H, 2 × OMe), 3.81 (s, 3H, OMe), 3.92 (s, 6H, 2 × OMe), 5.56–5.67 (m, 1H, 3'-H), 7.03 (s, 1H, Ar), 7.63 (s, 1H, Ar), 8.35 (s, 1H, Ar); ¹³C NMR (75.5 MHz, CDCl₃) δ 19.8, 20.0, 35.4, 52.6 (2C), 62.1 (2C), 63.4, 81.2, 117.7, 118.2, 123.5, 130.6, 136.6, 154.6, 157.6 (3C), 166.0 (2C), 183.6; MS (EI) *m/z* (%) 399 [(M–imid.)⁺, 6], 297 (100); HRMS (FAB) calcd for C₂₁H₂₇O₈N₂S (MH⁺): 467.1488; found 467.1476.

Scheme S2

Dimethyl 2,4,6-Trimethoxy-5-[(2-oxocyclopentyl)methyl]benzene-1,3-dicarboxylate (26). By a procedure similar to that described for the synthesis of **25**, dimethyl 5-bromomethyl-2,4,6-trimethoxybenzene-1,3-dicarboxylate (50 mg, 0.133 mmol) was converted into **26** (44.4 mg, 85% yield) by treatment with *O*-(*tert*-butyldimethylsilyl)cyclopenten-1-ol (39.4 mg, 0.199 mmol) and ZnCl₂ (4.0 mg, 0.027 mmol): colorless oil; IR (KBr) cm⁻¹: 1736 (C=O); ¹H NMR (300 MHz, CDCl₃) δ 1.40–1.46 (m, 1H), 1.58–1.65 (m, 1H), 1.82–1.95 (m, 2H), 2.05 (ddd, *J* = 18.6, 10.2, 8.4 Hz, 1H, 3'-CHH), 2.24 (dd, *J* = 18.6, 7.2 Hz, 1H, 3'-CHH), 2.42 (m, 1H, 1'-H), 2.45 (dd, *J* = 10.2, 10.2 Hz, 1H, 1-CHH), 2.97–3.02 (m, 1H, 1-CHH), 3.71 (s, 6H, 2 × OMe), 3.74 (s, 3H, OMe), 3.84 (s, 6H, 2 × OMe); ¹³C NMR (75.5 MHz, CDCl₃) δ 20.3, 23.7, 29.4, 37.8, 49.1, 52.6 (2C), 62.1 (2C),

63.3, 118.4, 123.0 (2C), 154.5, 158.2 (2C), 166.1 (2C), 220.2; MS (EI) m/z (%) 381 (MH^+ , 14), 297 (100); HRMS (FAB) calcd for $C_{19}H_{24}O_8Na$ (MNa^+): 403.1369; found 403.1359.

Dimethyl 5-[2-(1*H*-Imidazol-1-ylcarbothioyloxy)cyclopentylmethyl]-2,4,6-trimethoxybenzene-1,3-dicarboxylate (9). By a procedure similar to that described for the synthesis of **8** from **25**, **26** (150 mg, 0.394 mmol) was converted into **9** (108 mg, 55% yield for 2 steps) and a small amount (ca. 8% yield) of the minor isomer. Major isomer: colorless oil; IR (KBr) cm^{-1} : 1732 (C=O); 1H NMR (500 MHz, $CDCl_3$) δ 1.23-1.29 (m, 2H), 1.34-1.41 (m, 1H), 1.69-1.83 (m, 1H), 1.84-1.90 (m, 1H), 2.21-2.30 (m, 1H), 2.53-2.60 (m, 1H, 1'-H), 2.64 (dd, J = 13.5, 8.0 Hz, 1H, 1''-CHH), 2.74 (dd, J = 13.5, 7.0 Hz, 1H, 1''-CHH), 3.73 (s, 3H, OMe), 3.77 (s, 6H, 2 $\times$ OMe), 3.86 (s, 6H, 2 $\times$ OMe), 5.43-5.46 (m, 1H, 2''-H), 6.94 (s, 1H, Ar), 7.43 (s, 1H, Ar), 8.17 (s, 1H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.6, 27.1, 30.0, 31.0, 45.3, 52.6 (2C), 62.1 (2C), 63.4, 90.4, 117.6 (2C), 118.1, 122.7, 130.4, 136.7, 154.7, 158.1 (2C), 166.1 (2C), 183.6 (C=S); MS (FAB) m/z (%) 493 (MH^+ , 50), 333 (100); HRMS (FAB) calcd for $C_{23}H_{29}N_2O_8S$: 493.1645; found: 493.1655.

Scheme S3

Dimethyl (1'*R,1''*R**)-2,4,6-Trimethoxy-5-[3-methyl-1-(2-oxocyclopentyl)butyl]benzene-1,3-dicarboxylate (22) and Its (1'*R**,1''*S**)-Isomer (23).** By a procedure similar to that described for the synthesis of **25**, the chloride **S3** (600 mg, 1.54 mmol) was converted into **22** (257 mg, 38% yield) and **23** (218 mg, 32% yield) by treatment with *O*-(*tert*-butyldimethylsilyl)cyclopent-1-en-1-ol (367 mg, 2.31 mmol) and $ZnCl_2$ (37.4 mg, 0.31 mmol).

Compound **22**: colorless oil; IR (KBr) cm^{-1} : 1732 (C=O); 1H NMR (300 MHz, $CDCl_3$) δ 0.81 (d, J = 6.1 Hz, 3H, CMe), 0.86 (d, J = 6.1 Hz, 3H, CMe), 1.18-1.31 (m, 3H), 1.64-1.85 (m, 2H), 1.95-2.18 (m, 2H), 2.21-2.33 (m, 2H), 2.42-2.48 (m, 1H, 1''-H), 3.56-3.64 (m, 1H, 1'-H), 3.76 (s, 6H, 2 $\times$ OMe), 3.84 (s, 3H, OMe), 3.92 (s, 6H, 2 $\times$ OMe); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.5, 21.9, 23.7, 25.8, 28.6, 33.9, 38.7, 40.5, 52.6, 52.9 (3C), 63.7 (2C), 126.1 (4C), 154.8 (2C), 166.5 (2C), 219.2; MS (EI) m/z (%) 437 (MH^+ , 2), 297 (100); HRMS (EI) calcd for $C_{23}H_{32}O_8$ (M^+): 436.2098; found 436.2097.

Compound **23**: colorless oil; IR (KBr) cm^{-1} : 1731 (C=O); ^1H NMR (300 MHz, CDCl_3) δ 0.81 (d, J = 6.7 Hz, 3H, CMe), 0.93 (d, J = 6.7 Hz, 3H, CMe), 1.13-1.27 (m, 3H), 1.66-1.90 (m, 3H), 2.00 (td, J = 10.1, 3.7 Hz, 1H), 2.17 (ddd, J = 18.9, 9.7, 9.7 Hz, 1H, 3'-CHH), 2.31 (dd, J = 18.9, 7.3 Hz, 1H, 3'-CHH), 2.55-2.65 (m, 1H, 1''-H), 3.35 (ddd, J = 10.7, 10.1, 4.0 Hz, 1H, 1'-H), 3.78 (s, 6H, 2 $\times$ OMe), 3.85 (s, 3H, OMe), 3.93 (s, 6H, 2 $\times$ OMe); ^{13}C NMR (75.5 MHz, CDCl_3) δ 20.1, 21.8, 24.1, 26.3, 30.0, 34.4, 38.4, 42.3, 52.6, 52.9 (3C), 63.8 (2C), 116.9 (2C), 125.2 (2C), 155.1, 158.7, 166.5 (2C), 220.7; MS (EI) m/z (%) 437 (MH^+ , 2), 297 (100); HRMS (FAB) calcd for $\text{C}_{23}\text{H}_{32}\text{O}_8\text{Na}$ (MNa^+): 459.1995; found 459.1969.

Dimethyl (1'*R,1''*R**,2''*R**)- and (1'*R**,1''*R**,2''*S**)-5-{1-[2-(1*H*-Imidazol-1-ylcarbothioxyloxy)-cyclopentyl]-3-methylbutyl}-2,4,6-trimethoxybenzene-1,3-dicarboxylates (10a and 10b).** By a procedure similar to that described for the synthesis of **8** from **25**, **23** was converted into **10a** (50% yield for 2 steps) and **10b** (50% yield for 2 steps).

Compound **10a**: colorless oil; IR (KBr) cm^{-1} : 1732 (C=O); ^1H NMR (300 MHz, CDCl_3) δ 0.61 (d, J = 6.3 Hz, 3H, CMe), 0.68 (d, J = 6.6 Hz, 3H, CMe), 1.11-1.44 (m, 3H), 1.50-1.72 (m, 3H), 1.78 (ddd, J = 10.8, 10.8, 3.3 Hz, 1H), 1.97-2.02 (m, 2H), 2.47-2.60 (m, 1H, 1''-H), 3.40 (ddd, J = 11.4, 11.4, 5.1 Hz, 1H, 1'-H), 3.76 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.82 (s, 3H, OMe), 3.87 (s, 6H, 2 $\times$ OMe), 5.91 (m, 1H, 2''-H), 7.00 (s, 1H, Ar), 7.64 (s, 1H, Ar), 8.35 (s, 1H, Ar); ^{13}C NMR (75.5 MHz, CDCl_3) δ 21.5, 21.7, 23.9, 26.1, 29.5, 32.3, 33.3, 42.5, 48.9, 52.7, 52.8, 60.8, 62.0, 63.9, 87.7, 116.9, 117.0, 117.7, 125.3, 130.7, 136.7, 155.2, 158.0, 159.3, 166.5 (2C), 183.4; MS (EI) m/z (%) 549 (MH^+ , 0.2), 297 (100); HRMS (FAB) calcd for $\text{C}_{27}\text{H}_{37}\text{N}_2\text{O}_8\text{S}$ (MH^+): 549.2270; found 549.2277.

Compound **10b**: colorless oil; IR (KBr) cm^{-1} : 1732 (C=O); ^1H NMR (300 MHz, CDCl_3) δ 0.75 (d, J = 6.3 Hz, 3H, CMe), 0.84 (d, J = 6.6 Hz, 3H, CMe), 1.07-1.29 (m, 3H), 1.39 (ddd, J = 9.6, 9.6, 3.9 Hz, 1H), 1.63-1.65 (m, 2H), 1.80 (ddd, J = 12.2, 12.2, 3.9 Hz, 1H), 1.83-1.89 (m, 1H), 2.08-2.14 (m, 1H), 2.75-2.79 (m, 1H, 1''-H), 3.12 (td, J = 10.8, 10.8, 3.9 Hz, 1H, 1'-H), 3.76 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.82 (s, 3H, OMe), 3.89 (s, 3H, OMe), 3.90 (s, 3H, OMe), 5.63-5.68 (m, 1H, 2''-H), 7.02 (s, 1H, Ar), 7.62 (s, 1H, Ar), 8.32 (s, 1H, Ar); ^{13}C NMR (75.5 MHz, CDCl_3) δ 21.9, 23.3, 24.0, 26.2, 30.7, 32.6, 37.8, 42.4, 49.2, 52.7, 52.8, 60.8, 62.0, 63.8, 91.3, 116.8, 116.9, 125.1, 128.8, 130.6, 136.7, 155.2, 158.1, 159.0, 166.5 (2C), 183.5; MS (EI) m/z (%) 422 [(M-OCSIm) $^+$, 7], 297 (80), 68 (100); HRMS (FAB) calcd for $\text{C}_{27}\text{H}_{37}\text{N}_2\text{O}_8\text{S}$ (MH^+): 549.2270; found 549.2272.

Dimethyl (1'*R,1''*S**,2''*R**)- and (1'*R**,1''*S**,2''*S**)-5-{1-[2-(1*H*-Imidazol-1-ylcarbothioxyloxy)-cyclopentyl]-3-methylbutyl}-2,4,6-trimethoxybenzene-1,3-dicarboxylates (11a and 11b).** By a procedure similar to that described for the synthesis of **8** from **25**, **22** was converted into **11a** (50% yield for 2 steps) and **11b** (22% yield for 2 steps).

Compound **11a**: colorless oil; IR (KBr) cm^{-1} : 1732 (C=O); ^1H NMR (300 MHz, CDCl_3) δ 0.83 (d, J = 6.3 Hz, 3H, CMe), 0.88 (d, J = 6.6 Hz, 3H, CMe), 1.23-1.33 (m, 1H), 1.44 (ddd, J = 9.3, 9.3, 4.5 Hz, 1H), 1.54-1.64 (m, 1H), 1.71-1.92 (m, 5H), 2.14-2.19 (m, 1H), 2.57-2.61 (m, 1H, 1''-H), 3.36 (ddd, J = 10.5, 9.3, 4.8 Hz, 1H, 1'-H), 3.40 (s, 3H, OMe), 3.69 (s, 3H, OMe), 3.76 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.90 (s, 3H, OMe), 5.28 (m, 1H, 2'-H), 6.98 (s, 1H, Ar), 7.60 (s, 1H, Ar), 8.29 (s,

1H, Ar); ^{13}C NMR (75.5 MHz, CDCl_3) δ 21.5, 21.7, 23.9, 26.1, 29.5, 32.3, 33.3, 42.5, 48.9, 52.7, 52.8, 60.8, 62.0, 63.9, 87.7, 116.9, 117.0, 117.7, 125.3, 130.7, 136.7, 155.2, 158.0, 159.3, 166.5 (2C), 183.4; MS (FAB) m/z (%) 549 (MH^+ , 12), 389 (100); HRMS (FAB) calcd for $\text{C}_{27}\text{H}_{37}\text{N}_2\text{O}_8\text{S}$: 549.2271; found: 549.2280.

Compound **11b**: colorless oil; IR (KBr) cm^{-1} : 1734 (C=O); ^1H NMR (300 MHz, CDCl_3) δ 0.82 (d, $J = 6.3$ Hz, 3H, CMe), 0.84 (d, $J = 6.0$ Hz, 3H, CMe), 1.21-1.42 (m, 3H), 1.63-1.87 (m, 4H), 2.07-2.18 (m, 2H), 2.70-2.80 (m, 1H, 1''-H), 3.17 (ddd, $J = 11.1, 11.1, 4.5$ Hz, 1H, 1'-H), 3.61 (s, 3H, OMe), 3.73 (s, 6H, 2 $\times$ OMe), 3.80 (s, 3H, OMe), 3.85 (s, 3H, OMe), 5.32-5.36 (m, 1H, 2''-H), 6.90 (s, 1H, Ar), 7.40 (s, 1H, Ar), 8.12 (s, 1H, Ar); ^{13}C NMR (75.5 MHz, CDCl_3) δ 21.8, 23.5, 24.0, 26.1, 31.6, 32.3, 38.5, 42.0, 48.6, 52.6 (2C), 60.6, 61.8, 63.7, 89.8, 116.6 (2C), 118.1, 124.5, 130.0, 136.7, 155.4, 157.9, 158.7, 166.3, 166.3, 183.3; MS (FAB) m/z (%) 549 (MH^+ , 43), 389 (100); HRMS (FAB) calcd for $\text{C}_{27}\text{H}_{37}\text{N}_2\text{O}_8\text{S}$: 549.2271; found: 549.2272.

Dimethyl (1'R*,1''R*)-2,4,6-Trimethoxy-5-[3-methyl-1-(1-methyl-2-oxocyclopentyl)butyl]-benzene-1,3-dicarboxylate (24a) and Its (1'R*,1''S*)-Isomer (24b). By a procedure similar to that described for the synthesis of **25**, the chloride **S4** (620 mg, 1.59 mmol) was converted into a 1:1 mixture of **24a** and **24b** (690 mg, 96% yield) by treatment with *O*-(*tert*-butyldimethylsilyl)-2-methylcyclopent-1-en-1-ol (474 mg, 2.39 mmol) and ZnCl_2 (48.3 mg, 0.354 mmol).

Compound **24a**: colorless oil; IR (KBr) cm^{-1} : 1732 (C=O); ^1H NMR (300 MHz, CDCl_3) δ 0.79 (d, $J = 6.0$ Hz, 3H, CMe), 0.82 (s, 3H, CMe), 0.87 (d, $J = 6.0$ Hz, 3H, CMe), 1.10-1.16 (m, 2H), 1.68-1.74 (m, 2H), 1.76-1.99 (m, 2H), 2.10-2.18 (m, 2H), 2.30-2.36 (m, 1H), 3.72 (s, 3H, OMe), 3.72-3.80 (m, 1H, 1'-H), 3.838 (s, 3H, OMe), 3.842 (s, 3H, OMe), 3.91 (s, 3H, OMe), 3.92 (s, 3H, OMe); ^{13}C NMR (75.5 MHz, CDCl_3) δ 18.7, 21.8, 23.1, 24.0, 26.2, 33.9, 38.3, 39.1, 39.3, 52.1, 52.6, 52.7, 59.7, 62.1, 63.8, 116.4, 116.9, 124.1, 155.1, 158.9, 159.1, 166.5, 166.7, 222.9; MS (EI) m/z (%) 450 (M^+ , 2), 297 (100); HRMS (FAB) calcd for $\text{C}_{24}\text{H}_{34}\text{O}_8\text{Na}$ (MNa^+): 473.2151; found 473.2154.

Compound **24b**: colorless oil; IR (KBr) cm^{-1} : 1732 (C=O); ^1H NMR (300 MHz, CDCl_3) δ 0.76 (d, $J = 6.0$ Hz, 3H, CMe), 0.79 (d, $J = 6.0$ Hz, 3H, CMe), 1.06 (s, 3H, CMe), 1.10-1.24 (m, 3H), 1.60-1.74 (m, 2H), 1.76-1.99 (m, 2H), 2.10-2.18 (m, 2H), 3.43 (dd, $J = 11.4, 3.9$ Hz, 1H, 1'-H), 3.72 (s, 3H, OMe), 3.75 (s, 3H, OMe), 3.84 (s, 3H, OMe), 3.91 (s, 3H, OMe), 3.92 (s, 3H, OMe); ^{13}C NMR (75.5 MHz, CDCl_3) 18.3, 21.0, 21.7, 24.1, 26.2, 33.9, 35.7, 37.4, 37.7, 51.8, 52.6, 52.7, 60.1, 62.0,

63.9, 116.5, 116.6, 123.9, 155.1, 158.9, 159.1, 166.5, 166.7, 223.0; MS (EI) m/z (%) 450 (M^+ , 2), 297 (100); HRMS (FAB) calcd for $C_{24}H_{34}O_8Na$ (MNa^+): 473.2151; found 473.2154.

Dimethyl 5-{1-[2-(1*H*-Imidazol-1-ylcarbothioyloxy)-1-methylcyclopentyl]-3-methylbutyl}-2,4,6-trimethoxybenzene-1,3-dicarboxylates (12a, 12b, 13a and 13b). By a procedure similar to that described for the synthesis of **8** from **25**, the 1:1 diastereomixture **24** was converted into **12a** (25% yield for 2 steps), **12b** (22% yield for 2 steps), **13a** (20% yield for 2 steps), and **13b** (9% yield for 2 steps).

Compound **12a**: colorless oil; IR (KBr) cm^{-1} : 1732 (C=O); 1H NMR (300 MHz, $CDCl_3$) δ 0.76 (d, $J = 6.6$ Hz, 3H, CMe), 0.82 (d, $J = 6.3$ Hz, 3H, CMe), 0.91 (s, 3H, CMe), 1.18-1.31 (m, 2H), 1.78-2.10 (m, 6H), 2.03 (ddd, $J = 13.3, 13.3, 3.0$ Hz, 1H, 2'-H), 3.41 (s, 3H, OMe), 3.67 (dd, $J = 9.9, 1.8$ Hz, 1H, 1'-H), 3.73 (s, 3H, OMe), 3.76 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.89 (s, 3H, OMe), 5.17 (d, $J = 4.2$ Hz, 1H, 2''-H), 7.01 (s, 1H, Ar), 7.64 (s, 1H, Ar), 8.33 (s, 1H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.3, 20.8, 21.6, 24.0, 26.1, 30.2, 36.5, 37.7, 39.1, 51.3, 52.4, 52.7, 60.2, 61.3, 64.0, 93.2, 116.1, 116.4, 118.0, 123.5, 130.1, 136.7, 155.3, 158.6, 159.4, 166.3, 166.7, 183.1; MS (FAB) m/z (%) 563 (MH^+ , 51), 353 (100); HRMS (FAB) calcd for $C_{28}H_{39}N_2O_8S$: 563.2427; found: 563.2445.

Compound **12b**: colorless oil; IR (KBr) cm^{-1} : 1734 (C=O); 1H NMR (300 MHz, $CDCl_3$) δ 0.78 (d, $J = 5.7$ Hz, 3H, CMe), 0.81 (d, $J = 5.7$ Hz, 3H, CMe), 1.05 (s, 3H, CMe), 1.12-1.26 (m, 3H), 1.48-1.78 (m, 4H), 2.07 (ddd, $J = 12.0, 12.0, 2.4$ Hz, 1H), 2.41-2.51 (m, 1H), 3.37 (dd, $J = 11.7, 3.6$ Hz, 1H, 1'-H), 3.61 (s, 3H, OMe), 3.69 (s, 3H, OMe), 3.71 (s, 3H, OMe), 3.80 (s, 3H, OMe), 3.86 (s, 3H, OMe), 5.48 (t, $J = 8.1$ Hz, 1H, 2''-H), 6.88 (s, 1H, Ar), 7.32 (s, 1H, Ar), 8.12 (s, 1H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 18.3, 18.9, 21.6, 24.1, 26.0, 27.6, 36.3, 37.6, 41.9, 49.1, 52.5, 52.6, 59.9, 61.4, 63.6, 89.7, 116.0, 116.1, 117.5, 122.8, 130.2, 136.8, 155.2, 158.5, 159.0, 166.3, 166.5, 183.4; MS (FAB) m/z (%) 563 (MH^+ , 53), 297 (100); HRMS (FAB) calcd for $C_{28}H_{39}N_2O_8S$: 563.2427; found: 563.2424.

Compound **13a**: colorless prisms; mp 135–136 °C; IR (KBr) cm^{-1} : 1732 (C=O); 1H NMR (300 MHz, $CDCl_3$) δ 0.51 (d, $J = 6.0$ Hz, 3H, CMe), 0.74 (d, $J = 6.0$ Hz, 3H, CMe), 0.91 (s, 3H, CMe), 0.95-1.12 (m, 2H), 1.19-1.24 (m, 1H), 1.59-1.68 (m, 2H), 1.76-1.90 (m, 2H), 2.18-2.22 (m, 1H), 2.22 (ddd, $J = 12.6, 12.6, 2.7$ Hz, 1H), 3.68 (s, 3H, OMe), 3.71-3.74 (m, 1H, 1'-H), 3.73 (s, 3H, OMe), 3.80 (s, 3H, OMe), 3.85 (s, 3H, OMe), 3.87 (s, 3H, OMe), 5.55 (d, $J = 5.1$ Hz, 1H, 2''-H), 6.99 (s, 1H, Ar), 7.69 (s, 1H, Ar), 8.39 (s, 1H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 18.8, 19.9, 21.2, 24.1, 30.6, 31.6, 35.4, 37.1, 37.4, 51.3, 52.8 (2C), 60.4, 62.1, 64.0, 91.8, 116.7, 117.1, 117.8, 122.9, 130.7, 136.6, 155.2, 159.2, 160.0, 166.5, 166.7, 183.0; MS (FAB) m/z (%) 563 (MH^+ , 52), 297 (100); HRMS (FAB) calcd for $C_{28}H_{39}N_2O_8S$: 563.2427; found: 563.2444..

Compound **13b**: colorless oil; IR (KBr) cm^{-1} : 1732 (C=O); 1H NMR (300 MHz, $CDCl_3$) δ 0.77 (d, $J = 5.7$ Hz, 3H, CMe), 0.79 (d, $J = 5.7$ Hz, 3H, CMe), 1.03 (s, 3H, CMe), 1.11-1.30 (m, 2H), 1.40-1.46 (m, 1H), 1.52-1.81 (m, 4H), 1.97 (ddd, $J = 13.2, 13.2, 3.0$ Hz, 1H), 2.34-2.49 (m, 1H), 3.36 (dd, $J = 11.4, 2.4$ Hz, 1H, 1'-H), 3.62 (s, 3H, OMe), 3.64 (s, 3H, OMe), 3.67 (s, 3H, OMe), 3.73 (s, 3H, OMe), 3.80 (s, 3H, OMe), 5.37 (dd, 1H, $J = 8.1, 6.3$ Hz, 2''-H), 6.92 (s, 1H, Ar), 7.43 (s, 1H, Ar), 8.16 (s, 1H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 19.8, 21.2, 21.6, 24.1, 26.5, 29.5, 36.4, 37.3, 41.0,

48.7, 52.6 (2C), 60.4, 61.4, 64.1, 88.5, 116.1, 116.2, 117.9, 122.7, 130.2, 136.8, 155.5, 158.7, 159.2, 166.4, 166.5, 184.1; MS (FAB) m/z (%) 563 (MH^+ , 50), 353 (100); HRMS (FAB) calcd for $C_{28}H_{39}N_2O_8S$: 563.2427; found: 563.2418.

2-[3-Methyl-1-(2,4,6-trimethoxyphenyl)butyl]cyclopentanones (31a and 31b). To a stirred solution of 2,4,6-trimethoxybenzaldehyde **S5** (10.0 g, 51.0 mmol) and cyclopentanone (4.51 mL, 51.0 mmol) in Et_2O was added 1N NaOH (20 mL). After the mixture was stirred at room temperature for 11.5 h, water was added to the mixture. The whole was extracted with CH_2Cl_2 , and the extract was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to leave a crystalline mass, which was recrystallized from $EtOH$ to give 2-[(2,4,6-trimethoxyphenyl)methylene]cyclopentan-1-one (10.3 g, 77% yield) as colorless crystals. CuI (726 mg, 3.81 mmol) was added to a solution of $i-BuMgBr$ (1.0 M in Et_2O ; 3.81 mL, 3.81 mmol) at $-20\text{ }^\circ C$ and the mixture was stirred at room temperature until the solution showed a blue color. $BF_3 \cdot OEt_2$ (0.48 mL, 3.81 mmol) was added to the mixture at $-78\text{ }^\circ C$ and the mixture was stirred for 5 min at this temperature. The above crystals (200 mg, 0.762 mmol) were added to this reagent at $-78\text{ }^\circ C$, and the mixture was stirred at $-20\text{ }^\circ C$ until the starting material was disappeared on TLC. Saturated NH_4Cl was added to the mixture and the whole was extracted with $EtOAc$. The extract was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to leave an oily residue, which was purified by column chromatography over silica gel with n -hexane– $EtOAc$ (5:1) to give **31a** (47.3 mg, 19% yield) and **31b** (58.8 mg, 24% yield).

Compound 31a: colorless crystals; mp $88\text{--}89\text{ }^\circ C$; IR (KBr) cm^{-1} : 1736 ($C=O$); 1H NMR (300 MHz, $CDCl_3$) δ 1.90 (d, $J = 6.6$ Hz, 3H, CMe), 1.96 (d, $J = 6.6$ Hz, 3H, CMe), 2.20–2.27 (m, 1H), 2.39–2.45 (m, 1H), 2.76–3.11 (m, 5H), 3.32–3.38 (m, 2H), 3.73–3.83 (m, 1H, 2-H), 4.56 (ddd, $J = 10.2, 10.2, 3.9$ Hz, 1H, 1'-H), 4.90 (s, 6H, $2 \times OMe$), 4.94 (s, 3H, OMe), 5.81 (d, $J = 2.1$ Hz, 1H, Ar), 6.05 (d, $J = 2.1$ Hz, 1H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.1, 21.4, 24.2, 26.4, 29.5, 32.7, 38.4 (2C), 40.7, 51.8, 55.1 (2C), 90.5, 111.7 (2C), 159.2 (3C), 222.2; MS (EI) m/z (%) 320 (M^+ , 1), 181 (100). Anal. Calcd for $C_{19}H_{28}O_4$: C, 71.22; H, 8.81. Found: C, 71.16; H, 8.73.

Compound 31b: colorless oil; IR (KBr) cm^{-1} : 1732 ($C=O$); 1H NMR (300 MHz, $CDCl_3$) δ 1.92 (d, $J = 6.0$ Hz, 3H, CMe), 1.93 (d, $J = 6.0$ Hz, 3H, CMe), 2.20–2.33 (m, 2H), 2.77–3.07 (m, 3H), 3.13–3.28 (m, 4H), 3.54–3.62 (m, 1H, 2-H), 4.81 (ddd, $J = 11.4, 7.5, 4.2$ Hz, 1H, 1'-H), 4.88 (s, 6H, $2 \times OMe$), 4.93 (s, 3H, OMe), 5.81 (d, $J = 2.1$ Hz, 1H, Ar), 6.05 (d, $J = 2.1$ Hz, 1H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.5, 21.4, 24.1, 26.0, 28.1, 32.6, 38.5 (2C), 39.0, 52.5, 55.0 (2C), 90.5, 111.7

(2C), 159.1 (3C), 220.1; MS (EI) m/z (%) 320 (M^+ , 3), 181 (100); HRMS (EI) calcd for $C_{19}H_{28}O_4$ (M^+): 320.1990; found 320.1987.

2-[3-Methyl-1-(2,4,6-trimethoxyphenyl)butyl]cyclopentyl-1H-imidazole-1-carbothioate

(14a–d). By a procedure similar to that described for the synthesis of **8** from **25**, **31a** was converted into **14a** (50% yield for 2 steps) and **14b** (50% yield for 2 steps). Similarly, **31b** was converted into **14c** (43% yield for 2 steps) and **14d** (25% yield for 2 steps).

Compound **14a**: colorless oil; IR (KBr) cm^{-1} : 1716; 1H NMR (300 MHz, $CDCl_3$) δ 0.53 (d, J = 6.3 Hz, 3H, CMe), 0.67 (d, J = 6.3 Hz, 3H, CMe), 1.00–1.06 (m, 2H), 1.35 (ddd, J = 8.1, 8.1, 3.9 Hz, 1H), 1.45–1.62 (m, 3H), 1.90–2.04 (m, 3H), 2.53–2.58 (m, 1H, 2-H), 3.49 (ddd, J = 10.8, 10.8, 3.3 Hz, 1H, 1'-H), 3.71 (s, 3H, OMe), 3.74 (s, 3H, OMe), 3.75 (s, 3H, OMe), 5.80–5.83 (m, 1H, 1-H), 6.03–6.07 (m, 2H, Ar), 6.99 (s, 1H, Ar), 7.69 (s, 1H, Ar), 8.38 (s, 1H, Ar); MS (EI) m/z (%) 433 (MH^+ , 2), 181 (100).

Compound **14b**: colorless oil; IR (KBr) cm^{-1} : 1608; 1H NMR (300 MHz, $CDCl_3$) δ 0.72 (d, J = 6.3 Hz, 3H, CMe), 0.77 (d, J = 6.3 Hz, 3H, CMe), 1.08–1.24 (m, 4H), 1.56–1.70 (m, 2H), 1.79–1.85 (m, 1H), 1.99 (ddd, J = 12.9, 12.9, 3.3 Hz, 1H), 2.13–2.23 (m, 1H, 3-H), 2.69–2.78 (m, 1H), 3.21 (ddd, J = 10.5, 10.5, 3.3 Hz, 1H, 1'-H), 3.72 (s, 3H, OMe), 3.75 (s, 3H, OMe), 3.78 (s, 3H, OMe), 5.59–5.64 (m, 1H, 1-H), 6.07–6.10 (m, 2H, Ar), 7.02 (s, 1H, Ar), 7.63 (s, 1H, Ar), 8.32 (s, 1H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.5, 23.1, 24.1, 26.4, 29.8, 32.3, 35.4, 41.4, 49.2, 55.2, 55.3, 55.7, 90.3, 91.1, 91.6, 111.7, 118.0, 130.5, 136.7, 159.2, 159.3, 160.0, 183.7; MS (FAB) m/z (%) 455 (MNa^+ , 20), 181 (100); HRMS (FAB) calcd for $C_{23}H_{32}NaN_2O_4S$: 455.1980; found: 455.1987.

Compound **14c**: colorless oil; IR (KBr) cm^{-1} : 1606; 1H NMR (300 MHz, $CDCl_3$) δ 0.74 (d, J = 6.3 Hz, 3H, CMe), 0.77 (d, J = 6.6 Hz, 3H, CMe), 1.07–1.14 (m, 1H), 1.20 (ddd, J = 10.5, 10.5, 4.2 Hz, 1H), 1.51–1.62 (m, 1H), 1.74–1.83 (m, 4H), 1.93 (ddd, J = 12.3, 12.3, 3.0 Hz, 1H), 2.08–2.14 (m, 1H), 2.67–2.73 (m, 1H, 2-H), 3.12 (s, 3H, OMe), 3.33 (ddd, J = 11.2, 11.2, 3.9 Hz, 1H, 1'-H), 3.72 (s, 3H, OMe), 3.74 (s, 3H, OMe), 5.28 (dd, J = 3.0, 3.0 Hz, 1H, 1-H), 5.86 (d, J = 2.1 Hz, 1H, Ar), 6.05 (d, J = 2.1 Hz, 1H, Ar), 7.01 (s, 1H, Ar), 7.63 (s, 1H, Ar), 8.33 (s, 1H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.4, 22.8, 24.2, 26.1, 30.5, 31.5, 36.8, 41.0, 48.1, 55.1, 55.2, 55.6, 90.5, 90.8, 91.0, 111.1, 118.0, 129.8, 136.2, 158.6, 159.2, 159.7, 183.4; MS (FAB) m/z (%) 455 (MNa^+ , 12), 181 (100); HRMS (FAB) calcd for $C_{23}H_{32}NaN_2O_4S$: 455.1980; found: 455.1994.

Compound **14d**: colorless oil; IR (KBr) cm^{-1} : 1699; 1H NMR (300 MHz, $CDCl_3$) δ 0.73 (d, J = 6.0 Hz, 3H, CMe), 0.76 (d, J = 6.6 Hz, 3H, CMe), 1.12–1.37 (m, 2H), 1.56–1.76 (m, 4H), 1.98–2.18 (m, 3H), 2.71–2.77 (m, 1H, 2-H), 3.19 (ddd, J = 11.1, 11.1, 4.2 Hz, 1H, 1'-H), 3.57 (s, 3H, OMe), 3.69 (s, 3H, OMe), 3.72 (s, 3H, OMe), 5.31 (ddd, J = 7.8, 6.6, 4.2 Hz, 1H, 1-H), 5.81 (d, J = 2.4 Hz, 1H, Ar), 5.91 (d, J = 2.4 Hz, 1H, Ar), 6.89 (s, 1H, Ar), 7.33 (s, 1H, Ar), 7.93 (s, 1H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.4, 22.8, 24.2, 26.1, 30.5, 31.5, 36.8, 41.0, 48.1, 55.1, 55.2, 55.6, 90.5, 90.8, 91.0, 111.1, 118.0, 129.8, 136.2, 158.6, 159.2, 159.7, 183.4; MS (FAB) m/z (%) 455 (MNa^+ , 12), 181 (100); HRMS (FAB) calcd for $C_{23}H_{32}NaN_2O_4S$: 455.1980; found: 455.1994.

Dimethyl 5-Butyl-2,4,6-trimethoxybenzene-1,3-dicarboxylate (15). By a procedure identical with that described for the synthesis of **18**, the thiocarbamate **8** (53.2 mg, 0.114 mmol) was converted into **15** (32.9 mg, 85% yield): colorless oil; IR (KBr) cm^{-1} : 1732 (C=O); ^1H NMR (300 MHz, CDCl_3) δ 0.92 (t, $J = 7.5$ Hz, 3H, CMe), 1.39 (q, $J = 7.5$ Hz, 2H, 2'- CH_2), 1.49-1.55 (m, 2H, 3'- CH_2), 2.53-2.59 (m, 2H, 1'- CH_2), 3.80 (s, 6H, $2 \times \text{OMe}$), 3.82 (s, 3H, OMe), 3.91 (s, 6H, $2 \times \text{OMe}$); ^{13}C NMR (75.5 MHz, CDCl_3) δ 13.8, 23.1, 23.9, 32.2, 52.6 (2C), 62.4 (2C), 63.4, 118.6 (2C), 126.1 (2C), 158.1 (2C), 166.3 (2C); MS (EI) m/z (%) 340 (M^+ , 27), 297 (100); HRMS (EI) calcd for $\text{C}_{17}\text{H}_{24}\text{O}_7$ (M^+): 340.1524; found 340.1522.

Dimethyl 5-(Cyclopentylmethyl)-2,4,6-trimethoxybenzene-1,3-dicarboxylate (16). By a procedure identical with that described for the synthesis of **18**, the thiocarbamate **9** (40.5 mg, 0.0822 mmol) was converted into **16** (26.5 mg, 88% yield): colorless oil; IR (KBr) cm^{-1} : 1736 (C=O); ^1H NMR (300 MHz, CDCl_3) δ 1.11-1.24 (m, 2H), 1.44-1.47 (m, 2H), 1.58-1.60 (m, 4H), 2.00-2.15 (m, 1H, 2'-H), 2.56 (d, $J = 7.2$ Hz, 2H, 1'- CH_2), 3.77 (s, 6H, $2 \times \text{OMe}$), 3.80 (s, 3H, OMe), 3.89 (s, 6H, $2 \times \text{OMe}$); ^{13}C NMR (75.5 MHz, CDCl_3) δ 24.8 (2C), 29.6, 32.6 (2C), 40.4, 52.6 (2C), 62.1 (2C), 63.4, 118.4, 125.3 (2C), 154.0, 158.3 (2C), 166.4 (2C); MS (EI) m/z (%) 366 (M^+ , 16.8), 297 (100); HRMS (EI) calcd for $\text{C}_{19}\text{H}_{26}\text{O}_7$ (M^+): 366.1670; found 366.1678.

2-(1-Cyclopentyl-3-methylbutyl)-1,3,5-trimethoxybenzene (21). By a procedure identical with that described for the synthesis of **18**, the thiocarbamate **14a** (17.6 mg, 0.0407 mmol) was converted into **21** (12.3 mg, 99% yield): colorless prisms; IR (KBr) cm^{-1} : 1606 (C=C); ^1H NMR (300 MHz, CDCl_3) δ 0.74 (d, $J = 6.3$ Hz, 3H, CMe), 0.77 (d, $J = 6.3$ Hz, 3H, CMe), 0.88-0.95 (m, 1H, 3-H), 1.10-1.29 (m, 4H), 1.29-1.88 (m, 4H), 1.80-1.96 (m, 2H), 2.21-2.36 (m, 1H), 3.01 (ddd, $J = 10.8, 10.8, 3.6$ Hz, 1H, 1'-H), 3.73 (s, 3H, OMe), 3.74 (s, 3H, OMe), 3.78 (s, 3H, OMe), 6.03-6.15 (m, 2H, Ar); ^{13}C NMR (75.5 MHz, CDCl_3) δ 21.6, 24.4, 24.9, 25.4, 26.4, 31.7, 32.4, 39.0, 42.1, 43.9, 55.1,

55.3, 55.8, 90.5, 91.3, 114.6, 158.7, 159.2, 160.1; MS (EI) m/z (%) 307 (MH^+ , 10), 181 (100); HRMS (EI) calcd for $C_{19}H_{30}O_3$ (M^+): 306.2198; found 306.2195.

Scheme S9

Methyl 2-Methoxy-3-(3-oxobutyl)benzoate (32c). A mixture of methyl 3-formyl-2-methoxybenzoate **S6** (76.9 mg, 0.396 mmol) and $Ph_3P=CHC(O)Me$ (164 mg, 0.515 mmol) in benzene (3 mL) was heated under reflux for 2 h. The mixture was concentrated under reduced pressure to leave an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (2:1) to give methyl (*E*)-2-methoxy-3-(3-oxo-1-butenyl)benzoate (79.7 mg, 86% yield). This enoate (79.7 mg, 0.340 mmol) was then subjected to the catalytic hydrogenation in EtOAc (6.5 mL) using Pd/C (36.2 mg) under atmospheric pressure of hydrogen at room temperature for 30 min. The mixture was filtered and the filtrate was concentrated under reduced pressure to an oil, which was purified by short pad of silica gel with *n*-hexane–EtOAc (2:1) to give **32c** (74.1 mg, 92% yield, 79% yield for 2 steps) as a colorless oil: IR (KBr) cm^{-1} : 1716 (C=O); 1H NMR (300 MHz, $CDCl_3$) δ 2.08 (s, 3H, CMe), 2.72 (t, $J = 7.6$ Hz, 2H), 2.87 (t, $J = 7.6$ Hz, 2H), 3.79 (s, 3H, OMe), 3.86 (s, 3H, OMe), 7.02 (dd, $J = 7.6, 7.6$ Hz, 1H, Ar), 7.29 (dd, $J = 7.6, 1.8$ Hz, 1H, Ar), 7.62 (dd, $J = 7.6, 1.8$ Hz, 1H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 24.3, 29.8, 43.9, 52.1, 62.1, 123.6, 124.4, 129.8, 134.3, 135.5, 158.3, 166.6, 207.7; MS (EI) m/z (%) 236 (M^+ , 17), 161 (100). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.05; H, 6.73.

[2-Methoxy-3-(3-oxobutyl)phenyl]methyl acetate (32b). A stirred mixture of **32c** (170 mg, 0.717 mmol), ethylene glycol (0.40 mL, 7.17 mmol), and *p*-TsOH (1.4 mg, 0.00717 mmol) in dry benzene (5 mL) was heated under reflux for 1 h. After cooling, the mixture was washed with saturated $NaHCO_3$ and water, and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to leave an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (2:1) to give the corresponding ethylene acetal (200 mg, 99% yield) as a colorless oil. To a stirred suspension of $LiAlH_4$ (27.1 mg, 0.713 mmol) in Et_2O (5 mL) was added a solution of the above ethylene acetal (200 mg, 0.713 mmol) in Et_2O (3 mL) at 0 °C, and the mixture was stirred for 30 min. Water was added to the mixture, and the whole was filtered through a plug of Celite. The filtrate was concentrated and purified by column chromatography over silica gel with *n*-hexane–EtOAc (2:1) to give the corresponding alcohol (171 mg, 95% yield) as a colorless oil. This alcohol (170 mg, 0.674 mmol) was acetylated by treatment with Ac_2O (0.127 mL, 1.35 mmol) and DMAP (247 mg, 2.02 mmol) in $CHCl_3$ (5 mL) to afford the corresponding acetate (192 mg, 97% yield) after purification by column chromatography over silica gel with *n*-hexane–EtOAc (2:1). IR (KBr) cm^{-1} : 1740 (C=O), 1716 (C=O); 1H NMR (300 MHz, $CDCl_3$) δ 2.07 (s, 3H, CMe), 2.12 (s, 3H, CMe), 2.73 (t, $J = 7.9$ Hz, 2H), 2.89 (t, $J = 7.9$ Hz, 2H), 3.75 (s, 3H, OMe), 5.13 (s, 2H, OCH_2),

7.02 (dd, $J = 7.6, 7.6$ Hz, 1H, Ar), 7.13 (dd, $J = 7.6, 1.8$ Hz, 1H, Ar), 7.20 (dd, $J = 7.6, 1.8$ Hz, 1H, Ar); ^{13}C NMR (75.5 MHz, CDCl_3) δ 21.0, 24.0, 29.9, 44.0, 61.6, 61.8, 124.4, 128.6, 129.3, 130.5, 134.3, 156.9, 170.8, 207.8; MS (EI) m/z (%) 250 (M^+ , 1), 147 (100). Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4$: C, 67.18; H, 7.25. Found: C, 67.44; H, 7.31.

Scheme S10

Methyl 4-Methoxy-3-(3-oxobutyl)benzoate (33). By a procedure identical with that described for the synthesis of **32c**, methyl 3-formyl-4-methoxybenzoate **S7** was converted into **33** (70% yield, 2 steps): colorless prisms; mp 60–61°C; IR (KBr) cm^{-1} : 1740 ($\text{C}=\text{O}$), 1716 ($\text{C}=\text{O}$); ^1H NMR (300 MHz, CDCl_3) δ 2.14 (s, 3H, CMe), 2.71 (t, $J = 8.1$ Hz, 2H), 2.88 (t, $J = 8.1$ Hz, 2H), 3.86 (s, 6H, 2 $\times$ OMe), 6.84 (d, $J = 8.8$ Hz, 1H, Ar), 7.80 (d, $J = 2.2$ Hz, 1H, Ar), 7.89 (dd, $J = 8.8, 2.2$ Hz, 1H, Ar); MS (EI) m/z (%) 236 (M^+ , 60), 161 (100). Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_4$: C, 66.09; H, 6.83. Found: C, 66.08; H, 6.77.

Scheme S11

Methyl 3-(3-Oxobutyl)benzoate (34). By a procedure identical with that described for the synthesis of **32c**, methyl 3-formylbenzoate **S8** was converted into **34** (80% yield, 2 steps): colorless oil; IR (KBr) cm^{-1} : 1720 ($\text{C}=\text{O}$); ^1H NMR (300 MHz, CDCl_3) δ 1.99 (s, 3H, CMe), 2.63 (t, $J = 7.8$ Hz, 2H), 2.78 (t, $J = 7.8$ Hz, 2H), 3.75 (s, 3H, OMe), 7.25–7.17 (m, 2H, Ar), 7.72–7.70 (m, 2H, Ar); ^{13}C NMR (75.5 MHz, CDCl_3) δ 29.2, 29.8, 44.5, 51.9, 127.2, 128.3, 129.1, 130.1, 132.9, 141.2, 166.8, 207.2; MS (EI) m/z (%) 206 (M^+ , 22), 174 (100). Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3$: C, 69.89; H, 6.84. Found: C, 69.81; H, 6.86.

Scheme S12

Methyl 2-Methoxy-3-(4-oxopentyl)benzoate (35). By a procedure similar to that described for the synthesis of **32c**, methyl 3-formyl-2-methoxybenzoate **S6** was converted into **35** (46% yield, 2 steps) by Wittig reaction with $\text{Ph}_3\text{P}(\text{CH}_2)_2\text{C}(\text{OCH}_2\text{CH}_2\text{O})\text{CH}_3\text{-I}$ and NaH, hydrogenation, and cleavage of the ethylene acetal with 1N HCl: colorless oil; IR (KBr) cm^{-1} : 1730 ($\text{C}=\text{O}$); ^1H NMR (300 MHz, CDCl_3) δ 1.84 (tt, $J = 7.2$ Hz, 2H, 2'- CH_2), 2.07 (s, 3H, CMe), 2.40 (t, $J = 7.2$ Hz, 2H), 2.62 (t, $J = 7.2$ Hz, 2H), 3.77 (s, 3H, OMe), 3.86 (s, 3H, OMe), 7.03 (dd, $J = 7.2, 7.2$ Hz, 1H, Ar),

7.29 (dd, $J = 7.2, 1.8$ Hz, 1H, Ar), 7.60 (dd, $J = 7.2, 1.8$ Hz, 1H, Ar); ^{13}C NMR (75.5 MHz, CDCl_3) δ 24.3, 28.7, 29.8, 42.7, 52.0, 62.2, 123.5, 124.4, 129.5, 134.2, 136.1, 158.2, 166.7, 208.5; MS (EI) m/z (%) 250 (M^+ , 13), 132 (100); HRMS (FAB) calcd for $\text{C}_{14}\text{H}_{19}\text{O}_4$ (MH^+): 251.1283; found 251.1290.

Methyl 2-Methoxy-3-[(2-oxopropyl)oxy]methylbenzoate (38). To a stirred solution of methyl 2-methoxy-3-(bromomethyl)benzoate (100 mg, 0.39 mmol) and 1-hydroxypropan-2-one **S9** (1.0 mL, 1.37 mmol) in CH_2Cl_2 (2 mL) was added CaSO_4 (300 mg) at room temperature, and the mixture was stirred for 30 min. Silver(I) oxide (178.1 mg, 0.78 mmol) was added to the mixture in three portions and the mixture was stirred for 10 h at room temperature. The mixture was filtered, and the filtrate was concentrated and purified by column chromatography over silica gel with n -hexane–EtOAc (1:1) to give **38** (37.0 mg, 43%) as a colorless oil: IR (KBr) cm^{-1} : 1728 (C=O); ^1H NMR (300 MHz, CDCl_3) δ 2.11 (s, 3H, CMe), 3.79 (s, 3H, OMe), 3.86 (s, 3H, OMe), 4.07 (s, 2H), 4.61 (s, 2H), 7.12 (dd, $J = 7.5$ Hz, 1H, Ar), 7.56 (dd, $J = 7.5, 1.8$ Hz, 1H, Ar), 7.73 (dd, $J = 7.5, 1.8$ Hz, 1H, Ar); ^{13}C NMR (75.5 MHz, CDCl_3) δ 26.4, 52.3, 62.9, 67.8, 75.4, 123.9, 124.3, 131.5, 132.1, 133.7, 158.2, 166.4, 206.4; MS (EI) m/z (%) 252 (M^+ , 5), 221 (100); HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{16}\text{O}_5\text{Na}$ (MNa^+): 275.0895; found 275.0874.

Methyl 2-Methoxy-3-(5-oxohexyl)benzoate (39). By a procedure similar to that described for the synthesis of **32c**, methyl 3-formyl-2-methoxybenzoate **S6** was converted into **39** (48% yield, 3 steps) by the first Wittig reaction with $\text{Ph}_3\text{P=CHCHO}$, the second Wittig reaction with $\text{Ph}_3\text{P=CHCOMe}$, and the catalytic hydrogenation: colorless oil; IR (KBr) cm^{-1} : 1713 (C=O); ^1H NMR (500 MHz, CDCl_3) δ 1.57–1.67 (m, 4H, 2'- CH_2 and 3'- CH_2), 2.13 (s, 3H, CMe), 2.46 (t, $J = 6.7$ Hz, 2H), 2.67 (t, $J = 6.7$ Hz, 2H), 3.83 (s, 3H, OMe), 3.92 (s, 3H, OMe), 7.07 (dd, $J = 7.9$ Hz, 1H, Ar), 7.34 (dd, $J = 7.9, 1.8$ Hz, 1H, Ar), 7.65 (dd, $J = 7.9, 1.8$ Hz, 1H, Ar); ^{13}C NMR (75.5 MHz, CDCl_3) δ 23.4, 29.4, 29.7, 29.8, 43.2, 52.0, 62.1, 123.4, 124.2, 129.2, 134.0, 136.5, 158.0, 166.6, 208.7; MS (EI) m/z (%) 265 (MH^+ , 1), 232 (100); HRMS (FAB) calcd for $\text{C}_{15}\text{H}_{21}\text{O}_4$ (MH^+): 265.1440; found 265.1440.

Scheme S15

Methyl 2-Methoxy-3-[(1-methoxycarbonyl-2-oxocyclopentyl)methyl]benzoate (40). A stirring mixture of sodium (44.3 mg, 1.93 mmol) and toluene (10 mL) was heated under reflux to give a suspension of minute particles of sodium in toluene. After cooling, a solution of methyl 2-oxocyclopentanecarboxylate (0.24 mL, 1.93 mmol) in benzene (10 mL) was added dropwise to the mixture over 30 min, and the mixture was heated under reflux for 2.5 h. Methyl 2-methoxy-3-(bromomethyl)benzoate **S9** (500 mg, 1.93 mmol) in benzene (5 mL) was added to the mixture, and the stirring was continued for 14 h under reflux. The mixture was concentrated to give a residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (4:1) to afford **40** (230 mg, 37% yield) as a colorless oil: IR (KBr) cm^{-1} : 1755 (C=O), 1728 (C=O); ^1H NMR (300 MHz, CDCl_3) δ 1.62–1.66 (m, 1H), 1.81–1.93 (m, 2H), 2.00–2.09 (m, 1H), 2.12–2.40 (m, 2H), 3.09 (d, $J = 14.0$ Hz, 1H, 1'-CHH), 3.37 (d, $J = 14.0$ Hz, 1H, 1'-CHH), 3.71 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.89 (s, 3H, OMe), 7.03 (dd, $J = 7.6, 7.6$ Hz, 1H, Ar), 7.29 (dd, $J = 7.6, 1.8$ Hz, 1H, Ar), 7.68 (dd, $J = 7.6, 1.8$ Hz, 1H, Ar); ^{13}C NMR (75.5 MHz, CDCl_3) δ 19.5, 31.7, 32.4, 38.1, 52.2, 52.6, 61.3, 62.1, 123.6, 124.4, 130.7, 131.5, 135.6, 159.0, 166.5, 171.5, 214.9; MS (EI) m/z (%) 320 (M^+ , 10), 180 (100); HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{21}\text{O}_6$ (MH^+): 321.1338; found 321.1324.

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 EXREF 0.00 ppm
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 RGAIN 16

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RGAIN 16

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 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 14

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EXMOD
OBFREQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

Tue Dec 21 13:36:35 1999

1H
NON

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32768
10000.0 Hz
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3.723 sec
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CDCL3
0.00 ppm
0.12 Hz
16

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 CTEMP 25.2 C
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 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 24

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BF 1.20 Hz
RGAIN 25

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 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 16

C:\WINNMR95\TEMPDATA\AUTOINC

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 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 13

D:\wakayama\396\non.als

DFILE
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EXMOD
OBFREQ
OBSET
OBFIN
POINT
FREQ
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

Tue Nov 16 13:20:02 1999

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32768
10000.0 Hz
16
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3.723 sec
5.3 us
1H
24.5 c
CDCL3
0.00 ppm
0.12 Hz
13

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 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
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IRNUC
CTEMP 22.1 C
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BF 1.20 Hz
RGAIN 24

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CTEMP 21.7 C
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EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 15

D:\wakayama\398\non.als

DFILE
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FW1
IRNUC
CTEMP
SILVNT
EXREF
BF
RGAIN

Fri Nov 19 23:58:24 1999

1H

NON

300.40 MHz

130.00 KHz

1150.0 Hz

32768

10000.0 Hz

16

3.277 sec

3.723 sec

5.3 us

1H

23.9 c

CDCL3

7.24 ppm

0.12 Hz

14

C:\WINMR95\TEMPDATA\AUTO2BCM_ET

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 RGAIN 25

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 SLVNT CDCL3
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 BF 0.12 Hz
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C:\WINNMR95\COMMON\DEFAULT.

DFILE
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EXMOD
OBFREQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

Fri Mar 19 23:32:06 1999

13C
BCM
75.45 MHz
124.00 KHz
1840.0 Hz
32768
20408.1 Hz
100
1.606 sec
1.394 sec
4.0 us
1H
24.3 C
CDCL3
77.00 ppm
1.20 Hz
24

C:\WINNR95\COMMON\DEFAULT.ALS

DFILE COMMT
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PD 3.723 sec
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CTEMP 22.5 c
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BF 0.12 Hz
RGAIN 14

4.1264

2.8543

1.9535

3.0000

37

(300 MHz, CDCl₃)

PPM

0

1

2

3

4

5

6

7

8

C:\WINNMR95\COMMON_DEFAULT.ALS

DFILE
COMNT
DATIM
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EXMOD
OBFRQ
OBSET
OBFIN
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FREQU
SCANS
ACQTM
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IRNUC
CTEMP
SLVNT
EXREF
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RGAIN

Fri May 21 22:35:47 1999
13C
BCM

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100
1.606 sec
1.394 sec
4.0 us

1H

22.3 C

CDCL3

77.00 ppm

1.20 Hz

25

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 ACQTM 3.723 sec
 PD 5.3 us
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 IIRNUC 20.7 c
 CTMP CDCL3
 SLVNT 0.00 ppm
 EXREF 0.12 Hz
 BF 16
 RGAIN

C:\WINNR95\COMMON_DEFAULT.ALS

DEFILE
COMNT
DATIM
OBNUC
EXMOD
OBFREQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
FW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

Fri Apr 09 23:46:30 1999

1H
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32768
10000.0 Hz
16
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3.723 sec
5.3 us
1H
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0.12 Hz
12

(300 MHz, CDCl₃)

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DUMMY : 1 times

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RESOL : 0.61 Hz

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OBNUC : 1H

OBPRO : 500.00 MHz

OBSET : 162167.63 Hz

RGAIN : 20

SCANS : 32 times

SLVNT : CDCL3

SPINNT : 12 Hz

TEMP : 27.7 C

C:\WINNMR95\COMMON_DEFAULT.

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 POINT 32768
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 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 25

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	PRE0 : 0.0100 msec	0.0100 msec
	INT0 : 1000.0000 msec	1000.0000 msec
	RES0 : 0.61 Hz	0.61 Hz
	PM1 : 2.053 usec	2.053 usec
	ORNGC : IH	IH
	ORFHQ : 500.00 MHz	500.00 MHz
	ORSET : 162167.63 Hz	162167.63 Hz
	ORAIN : 25	25
	SCANS : 32 times	32 times
	SWNT : CDCL3	CDCL3
	SPINNING : 7 Hz	7 Hz
	TEMP : 26.8 C	26.8 C

DFILE E:\W
 COMNT
 DATIM Wed 1
 OBNUC 13C
 EXMOD BCM
 OBFRQ
 OBSET
 OBFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 PW1
 IRNUC 1H
 CTEMP
 SLVNT CDCL
 EXREF
 BF
 RGAIN

¹H Line

Date : Wed Nov 7 10:24:58 2001

Filename : se1701.mdata
 Comment : ¹H Line
 SliceHistory : non

POINT : 16384 points
 SAMPD : 16384 points
 FREQ : 10000.0 Hz
 FILTR : 5000 Hz
 DELAY : 40.0 usec
 DEADT : 58.7 usec
 INVL : 100.0 usec
 TIMES : 32 times
 DUMMY : 4 times
 PD : 5.3616 sec
 ACQTM : 1638.3999 msec
 PREDL : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.61 Hz
 PW1 : 2.63 usec
 OBNJC : 1H
 OBFRQ : 500.00 MHz
 OBSET : 162167.63 Hz
 RGAIN : 22
 SCANS : 32 times
 SLVNT : CDCL3
 SPINNT : 12 Hz
 SPINNT : 28.3 C
 TEMP :

DFILE E:\WAKAYAMA\328\SHITA\NON_ALS
 COMNT 328polar
 DATIM Thu Jul 22 23:54:31 1999
 OBRUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 10000.0 Hz
 SCANS 32
 ACQTM 3.277 sec
 PD 3.723 sec
 PWL 5.3 us
 IIRUC 1H
 CTEMP 20.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 15

C:\WINNER95\TEMPDATA\AUTO1BCM_E1

DFILE 328polar
 DATIM Fri Jul 23 03:35:18 1999
 OBNUC 13C
 EXMOD BCM
 OBFRQ 75.45 MHz
 OBSET 124.00 KHz
 OBFIN 1840.0 Hz
 POINT 32768
 FREQU 20408.1 Hz
 SCANS 4300
 ACQTM 1.606 sec
 PD 1.394 sec
 PW1 4.0 us
 IRNUC 1H
 CTEMP 20.3 c
 SLVNT CDCl3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 24

C:\WINNR95\COMMON_DEFAULT.ALS

DFILE
COMET
DATIM
OBNUC
EXMOD
OBFREQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
FWI
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

Fri May 07 10:29:43 1999

1H
NON
300.40 MHz
130.00 KHz
1150.0 Hz
32768
10000.0 Hz
16
3.277 sec
3.723 sec
5.3 us
1H
24.1 C
CDCL3
7.26 ppm
0.12 Hz
16

E:\WAKAYAMA\980296\7RINGBCM

sevenring
Sat May 08 09:01:02 1999

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRO
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

13C
BCM
75.45 MHz
124.00 KHz
1840.0 Hz
32768
20408.1 Hz
11000
1.606 sec
1.394 sec
4.0 us
1H
23.9 c
CDCL3
77.00 ppm
1.20 Hz
24

C:\WINNMR95\COMMON_DEFAULT.ALS

DFILE COMNT
 DATIM Thu Jan 20 22:33:00 2000
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.0 Hz
 POINT 32768
 FREQU 10000.0 Hz
 SCANS 44
 ACQTM 3.277 sec
 PD 3.723 sec
 PW1 5.3 us
 TRNUC 1H
 CTEMP 21.3 c
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 0.12 Hz
 RGAIN 15

C:\WINNMR95\COMMON\DEFAULT.ALS

DEFILE
COMMT
DATIM
OBNUC
EXMOD
OBFREQ
OBFSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
FW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

Tue Apr 13 11:04:38 1999

13C
BCM
75.45 MHz
124.00 KHz
1840.0 Hz
32768
20408.1 Hz
125
1.606 sec
1.394 sec
4.0 us
1H
23.4 C
CDCL3
77.00 ppm
1.20 Hz
24