Supporting Information

Metal Triflate-Catalyzed Cationic Benzylation and Allylation of 1,3-Dicarbonyl Compounds

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General Procedure

Warning: Nitromethane is hazardous because of the possibility of an explosion. ¹H NMR and ¹³C NMR spectra were measured with spectrometers operating at 300 or 400 MHz for proton nucleus in the solvents indicated. ¹H chemical shifts are reported in δ ppm with tetramethylsilane (TMS) as an internal standard. ¹³C chemical shifts are reported relative to the central peak of CDCl₃ (77 ppm). Infrared spectra were measured with a dispersive IR or FT-IR spectrometers. Melting points were measured on a hot-plate melting point apparatus and are uncorrected. Optical rotation was measured on a polarimeter. Preparative TLCs were performed on silica gel and were detected with UV light. Chromatographic purifications were performed on silica gel (40–50 μ m, spherical). GC analyses were performed with GC systems equipped with a glass capillary column (100% methylpolysiloxane, 30 m length, 0.25 mm inner diameter, 0.50 μ m film thickness) and flame ionization detection under a constant pressure of 1.25 kg/cm² nitrogen carrier gas or a constant velocity of 20 cm/sec nitrogen carrier gas. GC-MS analyses were performed with a GC system equipped with a glass capillary column (5%-phenyl, 95% methylpolysiloxane, 30 m length, 0.32 mm inner diameter, 0.25 μ m film thickness) and a mass selective detector with a constant velocity of 19 cm/sec helium carrier gas. The enantiomeric excess (ee) of the products was determined by chiral stationary phase HPLC.

Typical Procedure for Optimizing Reaction Conditions. A nitromethane solution (20 mL) of 1-(4-methoxyphenyl)ethanol (**1a**) (3.04 g, 20.0 mmol, 1 mol/L), acetylacetone (**2a**) (2.00 g, 20.0 mmol, 1 mol/L), and nitrocyclohexane (995 mg, 7.71 mmol, as an internal standard, 0.3–0.4 mol/L) was prepared. The solution was mixed with catalysts in 20 mL test tubes equipped with glass stoppers. At 20 °C: 2.97 mg of La(OTf)₃ and 1.01 mL of the solution; 4.50 mg of Yb(OTf)₃ and 1.45 mL of the solution; 2.70 mg of Sc(OTf)₃ and 1.10 mL of the solution; 4.60 mg of Hf(OTf)₄ and 1.19 mL of the solution. At 50 °C: 2.31 mg of La(OTf)₃ and 0.79 mL of the solution; 5.20 mg of Yb(OTf)₃ and 1.68 mL of the solution; 2.25 mg of Sc(OTf)₃ and 0.91 mL of the solution; 4.72 mg of Hf(OTf)₄ and 1.22 mL of the solution. At 80 °C: 3.14 mg of La(OTf)₃ and 1.07 mL of the solution; 4.46 mg of Yb(OTf)₃ and 1.44 mL of the solution; 2.70 mg of Sc(OTf)₃ and 1.10 mL of the solution; 3.89 mg of Hf(OTf)₄ and 1.00 mL of the solution. The mixtures in the test tubes were stirred at the corresponding temperatures. The reactions were followed by TLC. After the complete consumption of **1a** and the symmetrical ethers (*meso*- and *dl*-1-(4-methoxyphenyl)ethyl ethers), 65 µL of the reaction mixtures were taken and filtered through a short silica gel pad with 2 mL of ethyl acetate to remove insoluble materials. The filtrates were analyzed by GC and GC-MS. The programmed GC analysis temperature condition was 150 °C for 2 min, 10 °C/min, 260 °C for 17 min. The yields were determined using the calibration line prepared from nitrocyclohexane and **3a** using GC. For preparing the calibration line, three standard samples containing nitrocyclohexane (50, 50, 50 mg) and pure **3a** (50, 100, 150 mg) were analyzed by GC and [GC area (**3a**)]/[GC area (nitrocyclohexane)] was then plotted against [mol (**3a**)]/[mol (nitrocyclohexane)] to obtain the slope.

yield (%) CL*			
temp.(°C)	time (h)	La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
20	24	8	51	83	85
50	21.5	90	98	78	71
80	21.5	91	15	1	0

*CL (calibration line): The yield was calculated based on the calibration line prepared from nitrocyclohexane (internal) standard and **3a** (desired product).

Table 1 Entry 1. To a mixture of Yb(OTf)₃ (9.68 mg, 15.6 μmol) and **2a** (323.86 mg, 3.235 mmol) in CH₃NO₂ (3.12 mL), **1a** (487.53 mg, 3.203 mmol) was added at room temperature. The resulting mixture was stirred at 50 °C for 24 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 20/1 to 4/1) to afford **3a** (728.62 mg, 97%).

3-[1-(4-Methoxyphenyl)ethyl]pentane-2,4-dione (3a) CA registry Number: [727401-19-6]. Colorless prism: mp 52–53 °C; TLC R_f = 0.40 (hexane/ethyl acetate = 3/1); ¹H NMR (300 MHz, CDCl₃) δ: 7.11 (2 H, d, *J* = 8.8 Hz), 6.83 (2 H, d, *J* = 8.8 Hz), 3.98 (1 H, d, *J* = 11.3 Hz), 3.78 (3 H, s), 3.55 (1 H, dq, *J* = 11.3, 6.8 Hz), 2.26 (3 H, s), 1.84 (3 H, s), 1.19 (3 H, d, *J* = 6.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 203.0, 202.9, 158.0, 134.7, 127.9, 113.8, 76.6, 55.0, 39.6, 29.7, 29.6, 20.9; IR (KBr) cm⁻¹: 1723 (s), 1518 (s), 1365 (s), 1294 (m), 1251 (s), 1183 (s), 1147 (m), 1036 (m), 818 (m); EI-MS (70 eV) *m/z* (relative intensity): 234 (M⁺, 10), 191 (90), 173 (15), 135 (100), 43 (18); HRMS-EI (*m/z*): M⁺ calcd for C₁₄H₁₈O₃, 234.1256; found, 234.1259; Anal. Calcd for C₁₄H₁₈O₃: C, 71.77; H, 7.74. Found: C, 71.80; H, 7.87; GC analysis, 10.15 min (150 °C, 2 min, 10 °C/min, 260 °C, 17 min).

temp (°C)	time (h)	B yield (%) CL			
		La	Yb	Sc	Hf
20	36	1	0	1	3
50	36	79	81	71	64
80	36	68	42	3	2

temp (°C)	time (h)	C yield (%) CL			
		La	Yb	Sc	Hf
20		1	0	3	7
50		21	66	76	69
80		67	52	6	3

GC analysis for 3b

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
0	24	9	7	39	64
20	24	45	64	73	89
50	24	19	11	5	0

*IS (isolated yield): The yield was calculated based on the isolated yield of same reaction conditions.

Table 1 Entry 2. To a mixture of Hf(OTf)₄ (2.88 mg, 3.72 μmol) and **2b** (182.50 mg, 0.81381 mmol) in CH₃NO₂ (0.743 mL), **1a** (121.97 mg, 0.80143 mmol) was added at room temperature. And the resulting mixture was stirred at 20 °C for 7 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, hexane/ether = 7/3) to afford **3b** (254.83 mg, 89%).

2-[1-(4-Methoxyphenyl)ethyl]-1,3-diphenylpropane-1,3-dione (3b) Colorless prism: mp 109–113 °C; TLC R_f = 0.25 (hexane/ether = 7/3); ¹H NMR (300 MHz, CDCl₃) δ: 8.05-7.97 (2 H, m, with doublet character), 7.76-7.72 (2 H, m, with doublet character), 7.57-7.52 (1 H, m, with triplet character), 7.46-7.39 (3 H, m), 7.31-7.25 (3 H, m, with triplet character), 7.21-7.14 (2 H, m, with doublet character), 7.20-7.14 (2 H, m, with doublet character), 6.7-6.68 (2 H, m, with doublet character), 5.55 (1 H, d, *J* = 10.2 Hz), 4.04 (1 H, dq, *J* = 10.2, 7.1 Hz), 3.69 (1 H, s), 1.32 (3 H, d, *J* = 7.1 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 194.7, 194.4, 157.9, 137.0, 136.8, 135.6, 133.3, 132.8, 128.64, 128.63, 128.52, 128.33, 128.26, 113.7, 65.2, 55.2, 40.5, 20.5; IR (KBr) cm⁻¹: 1690 (s), 1520 (m), 1450 (m), 1260 (s), 1200 (m), 1180 (m), 980 (m), 820 (m), 760 (m), 690(m); EI-MS (70 eV) *m/z* (relative intensity): 358 (M⁺, 2), 253 (100), 135 (24), 105 (26), 77 (16); HRMS-EI (*m/z*): M⁺ calcd for C₂₄H₂₂O₃, 358.1569; found, 358.1570; Anal. Calcd for C₂₄H₂₂O₃: C, 80.42; H, 6.19. Found: C, 80.48; H, 6.34. GC analysis: 21.79 min (150 °C, 2 min, 10 °C/min, 300 °C, 13 min); HPLC: DAICEL CHIRALPAK AD, hexane/2-propanol = 9/1, 1 mL/min, 254 nm, 25.0 min, 31.0 min.

GC analysis for 3c

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
20	24	7	13	14	16
50	13	72(24 h)	75	70	73
80	13	61	59	60	61

Acetone was used for the sampling of GC analysis instead of ethyl acetate, because of the low solubility.

Table 1 Entry 3. To a mixture of Yb(OTf)₃ (1.51 mg, 2.43 μmol) and **2c** (48.93 mg, 0.4988 mmol) in CH₃NO₂ (0.0487 mL), **1a** (74.54 mg, 0.4898 mmol) was added at room temperature. And the resulting mixture was stirred at 50 °C for 13 h. After the reaction mixture was filtered through a short silica gel pad with acetone, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, ethyl acetate/acetone = 1/1) to afford **3c** (84.95 mg, 75%).

2-[1-(4-Methoxyphenyl)ethyl]cyclopentane-1,3-dione (3c), colorless needles: mp 176–178 °C; TLC R_f = 0.53 (ethyl acetate/acetone = 1/1); ¹H NMR (300 MHz, CDCl₃) δ: 7.30 (2 H, d, *J* = 8.4 Hz), 6.92 (2 H, d, *J* = 8.7 Hz), 3.94 (1 H, q, *J* = 6.9 Hz), 3.81 (3 H, s), 3.79 (1 H, d, *J* = 2.7 Hz), 2.44 (4H, s), 1.47 (3 H, d, *J* = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 194.9, 158.2, 135.2, 128.2, 121.8, 114.12, 55.3, 32.6, 30.3, 18.1; IR (KBr) cm⁻¹: 2900 (br), 2600 (br), 1580 (s), 1515 (m), 1380 (s), 1285 (s), 1250 (m), 1185 (m), 1120 (m), 830 (m); EI-MS (70 eV) *m/z* (relative intensity): 232 (M⁺, 52), 217 (100), 135 (27), 108 (17); HRMS-EI (*m/z*): M⁺ calcd for C₁₄H₁₆O₃, 232.1099; found, 232.1101; Anal. Calcd for C₁₄H₁₆O₃: C, 72.39; H, 6.94. Found: C, 72.38; H 7.04; GC analysis: 18.33 min (100 °C, 2 min, 10 °C/min, 300 °C, 8 min).

GC analysis for 3d

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
20	24	2	6	27	27
50	24	47	42	6	1

Table 1 Entry 4. To a mixture of La(OTf)₃ (3.49 mg, 5.95 μmol) and **2d** (138.55 mg, 1.2138 mmol) in CH₃NO₂ (2.476 mL), **1a** (199.95 mg, 1.3138 mmol) was added at room temperature. And the resulting mixture was stirred at 50 °C for 11 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 20/1 - 2/1) to afford **3d** (164.0 mg, 54%).

3-[1-(4-Methoxyphenyl)ethyl]-3-methylpentane-2,4-dione (3d) Colorless oil: TLC R_f = 0.47 (hexane/ethyl acetate = 7/3); ¹H NMR (300 MHz, CDCl₃) δ: 7.11 (2 H, d, *J* = 8.9 Hz), 6.80 (2 H, d, *J* = 8.9 Hz), 3.91 (1 H, q, *J* = 7.2 Hz), 3.78 (3 H, s), 2.17 (3 H, s), 1.83 (3 H, s), 1.37 (3 H, s), 1.18 (3 H, d, *J* = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 207.3, 206.3, 158.2, 133.3, 129.8, 113.4, 71.2, 55.2, 42.0, 28.1, 27.5, 16.9, 14.4; IR (neat) cm⁻¹: 1698 (s), 1516 (s), 1357 (m), 1249 (s), 1183 (m), 1035 (m), 837 (m); EI-MS (70 eV) *m/z* (relative intensity): 248(M⁺, 3), 135 (100), 43 (8); HRMS-EI (*m/z*): M⁺ calcd for C₁₅H₂₀O₃, 248.1412; found, 248.1407; Anal. Calcd for C₁₅H₂₀O₃: C, 72.55; H, 8.12. Found: C, 72.61; H, 8.27; GC analysis: 11.38 min (150 °C, 2 min, 10 °C/min, 300 °C, 13 min).

GC Analysis for 3e

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
50	24	3	19	38	43
70	22	24	78	83	82
90	22	0	78	74	71

Table 1 Entry 5. To a mixture of Sc(OTf)₃ (3.13 mg, 6.36 μmol) and **2a** (128.58 mg, 1.2843 mmol) in CH₃NO₂ (1.272 mL), **1b** (157.42 mg, 1.2886 mmol) was added at room temperature. And the resulting mixture was stirred at 70 °C for 21 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, hexane/ethyl acetate = 7/3) to afford **3e** (219.0 mg, 83%).

3-(1-Phenylethyl)pentane-2,4-dione (3e) CA registry Number: [5186-08-3]. Colorless prism: mp 41–44 °C; TLC R_f = 0.58 (hexane/ethyl acetate = 7/3); ¹H NMR (300 MHz, CDCl₃) δ: 7.32–7.17 (5 H, m), 4.03 (1 H, d, *J* = 11.4 Hz), 3.58 (1 H, dq, *J* = 11.1 Hz, 6.6 Hz), 2.27 (3 H, s), 1.83 (3 H, s), 1.21 (3 H, d, *J* = 6.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 203.1, 203.0, 142.8, 128.6, 127.1, 76.6, 40.5, 29.8, 9.7, 20.9; IR (neat) cm⁻¹: 1723 (m), 1698 (s), 1357 (s), 1156 (m), 760 (s), 701 (s); EI-MS (70 eV) *m/z* (relative intensity): 204 (M⁺, 1), 186 (10), 161 (100), 147 (33), 143 (14), 105 (33), 43 (26); HRMS-EI (*m/z*): M⁺ calcd for C₁₃H₁₆O₂, 204.1150; found, 204.1141; Anal. Calcd for C₁₃H₁₆O₂: C, 76.44; H, 7.90. Found: C, 76.84; H, 8.19; GC analysis: 7.01 min (150 °C, 2 min, 10 °C/min, 260 °C, 11 min).

GC Analysis for 3f

temp.(°C)	time (h)	yield (%) CL			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
20	6	1	3	4	5
60	6	78	92	97	93
100	6	78	44	6	3

Table 1 Entry 6. To a mixture of Hf(OTf)₄ (2.94 mg, 3.79 μ mol) and **2b** (171.10 mg, 0.76297 mmol) in CH₃NO₂ (0.759 mL), **1b** (93.50 mg, 0.7654 mmol) was added at room temperature. And the resulting mixture was stirred at 60 °C for 5 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 20/1-2/1) to afford **3f** (235.0 mg, 94%).

1,3-Diphenyl-2-(1-phenylethyl)propane-1,3-dione (3f) CA registry Number: [116140-58-0]. Colorless needles: mp 127–128 °C; TLC R_f = 0.61 (hexane/ethyl acetate = 3/1); ¹H NMR (300 MHz, CDCl₃) δ : 7.95 (2 H, d, J = 7.2 Hz), 7.66 (2 H, d, J = 7.2 Hz), 7.50–6.09 (11 H, m), 5.53 (1 H, d, J = 10.1 Hz), 4.00 (1 H, dq, J = 10.1, 6.9 Hz), 1.26 (3 H, d, J = 6.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ : 194.6, 194.2, 143.6, 137.0, 136.7, 133.3, 132.8, 128.7, 128.6, 128.31, 128.26, 128.2, 127.6, 126.4, 64.9, 41.2, 20.3; IR (KBr) cm⁻¹: 3050 (m), 3030 (m), 2950 (m), 1700 (s), 1595 (m), 1450 (m), 1280 (m), 1265 (s), 1220 (m), 1200 (m), 980 (m), 765 (m), 710 (m), 705 (m), 690 (m); EI-MS (70 eV) m/z (relative intensity): 328 (M⁺, 0.5), 223 (100), 105 (62), 77 (29); Anal. Calcd for C₂₃H₂₀O₂: C, 84.12; H, 6.14. Found: C, 84.22; H, 6.29; GC analysis: 18.73 min (150 °C, 2 min, 10 °C/min, 300 °C, 13 min).

GC Analysis for 3g

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
50	24	4	7	10	11
70	24	25	30	28	31
90	20	14	10	8	2

Table 1 Entry 7. To a mixture of Hf(OTf)₄ (1.84 mg, 2.37 μmol) and **2c** (48.11 mg, 0.490 mmol) in CH₃NO₂ (0.475 mL), **1b** (59.02 mg, 0.4831 mmol) was added at room temperature. And the resulting mixture was stirred at 70 °C for 24 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, ethyl acetate) to afford **3g** (30.75 mg, 31%).

2-(1-Phenylethyl)cyclopentane-1,3-dione (3g) Colorless oil: TLC *R_f* = 0.24 (hexane/ethyl acetate = 1/5); ¹H NMR (300 MHz, CDCl₃); δ: 7.39-7.30 (5 H, m), 5.19 (1 H, q, *J* = 6.6 Hz), 5.18 (1 H, d, *J* = 2.4 Hz), 2.73-2.55 (2 H, m), 2.47-2.30 (2 H, m), 1.65 (3 H, d, *J* = 6.6 Hz); ¹³C NMR (100 MHz, CDCl₃); δ: 202.6, 188.5, 140.6, 128.7, 128.2, 125.4, 106.4, 80.4, 33.9, 29.0, 23.5; IR (neat) cm⁻¹: 1705 (s), 1593 (s), 1355 (m), 1286 (m), 1247 (m), 1222 (m), 1183 (m), 1065 (m), 702 (m); EI-MS (70 eV) *m/z* (relative intensity): 202 (*M*⁺, 4), 105 (100), 77 (8). HRMS-EI (*m/z*): *M*⁺ calcd for C₁₃H₁₄O₂, 202.0994; found, 202.0997; Anal. Calcd for C₁₃H₁₄O₂: C, 77.20; H, 6.98. Found: C, 77.10; H, 6.95; GC analysis: 16.07 min (100 °C, 2 min, 10 °C/min, 300 °C, 8 min).

GC Analysis for 3h

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
50	24	-	-	-	26
70	24	10	28	61	57
90	20	56	52	27	24

Table 1 Entry 7. To a mixture of La(OTf)₃ (3.84 mg, 6.55 μmol) and **2d** (148.72 mg, 1.3029 mmol) in CH₃NO₂ (1.310 mL), **1b** (159.74 mg, 1.3076 mmol) was added at room temperature. And the resulting mixture was stirred at 90 °C for 13 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 20/1-2/1) to afford **3h** (160.0 mg, 56%).

3-(1-Phenylethyl)-3-methylpentane-2,4-dione (3h) Colorless oil: TLC R_f = 0.61 (hexane/ethyl acetate = 7/3); ¹H NMR (300 MHz, CDCl₃) δ: 7.29-7.17 (5 H, m), 3.95 (1 H, q, *J* = 7.2 Hz), 2.17 (3 H, s), 1.82 (3 H, s), 1.39 (3 H, s), 1.21 (3 H, d, *J* = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 207.1, 206.1, 141.23, 129.0 128.0, 126.8, 71.0, 42.7, 27.9, 27.5, 16.7, 14.5; IR (neat) cm⁻¹: 1719 (m), 1697 (s), 1453 (m), 1355 (m), 1198 (m), 765 (s), 704 (s); EI-MS (70 eV) *m/z* (relative intensity): 218 (M⁺, 1), 200 (22), 175 (31), 161 (64), 157 (24), 143 (12), 105 (100), 43 (30); HRMS-EI (*m/z*): M⁺ calcd for C₁₄H₁₈O₂, 218.1307; found, 218.1316; Anal. Calcd for C₁₄H₁₈O₂: C, 77.03; H, 8.31. Found: C, 76.83; H, 8.52; GC analysis: 8.55 min (150 °C, 2 min, 10 °C/min, 260 °C, 10 min).

GC Analysis for 5a

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
20	24	0	14	57	56
50	24	50	98	76	45
80	24	77	87	11	0

Table 2 Entry 1. To a mixture of Yb(OTf)₃ (17.66 mg, 28.47 μ mol) and **4a** (663.63 mg, 5.7153 mmol) in CH₃NO₂ (5.69 mL), **1a** (878.50 mg, 5.7724 mmol) was added at room temperature. And the resulting mixture was stirred at 50 °C for 24 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, cyclohexane/dichloromethane= 5/1 to 1/3) to afford **5a** (1.3950 g, 98%, 1% de).

Methyl 2-acetyl-3-(4-methoxyphenyl)butyrate (5a) diastereomixture, Colorless oil: TLC R_f = 0.43 (hexane/ethyl acetate = 7/3); ¹H NMR (300 MHz, CDCl₃) δ : 7.15-7.08 (2 H, m), 7.15-7.11 (2 H, m), 6.84-6.80 (2 H, m), 6.84-6.80 (2 H, m), 3.78 (3 H, s), 3.77 (3 H, s), 3.75 (3 H, s), 3.45 (3 H, s), 3.78-3.68 (1 H, m), 3.78-3.68 (1 H, m), 3.55-3.43 (1 H, m), 3.55-3.43 (1 H, m), 2.28 (3 H, s), 1.91 (3 H, s), 1.27 (3 H, d, J = 6.9 Hz), 1.22 (3 H, d, J = 6.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ : 202.14, 202.06, 168.8, 168.4, 158.2, 158.1, 135.1, 134.7, 128.2, 128.1, 114.0, 113.7, 67.7, 67.1, 55.23, 55.23, 52.5, 52.2, 39.5, 39.1, 30.1, 30.0, 20.9, 20.3; IR (neat) cm⁻¹: 2950 (m), 1740 (s), 1710 (s), 1610 (m), 1510 (s), 1460(m), 1440(m), 1360 (m), 1260 (s), 1190 (s), 1040 (m), 840 (m); EI-MS (70 eV) m/z (relative intensity): 250 (M⁺, 12), 232 (19), 175 (17), 161 (8), 135 (100); HRMS-EI (m/z): M⁺ calcd for C₁₄H₁₈O₄, 250.1205; found, 250.1208; Anal. Calcd for C₁₄H₁₈O₄: C, 67.18; H, 7.25. Found: C, 67.43; H, 7.42; GC analysis: 10.62 min, 10.95 min (major), (150 °C, 2 min, 10 °C/min, 260 °C, 17 min).

GC analysis for 5b

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
20	24	22	28	57	88
60	24	88	99	86	77
100	24	99	96	96	8

Table 2 Entry 2. To a mixture of Yb(OTf)₃ (6.36 mg, 10.25 μmol) and **4b** (416.16 mg, 2.1651 mmol) in CH₃NO₂ (2.05 mL), **1a** (328.02 mg, 2.1553 mmol) was added at room temperature. And the resulting mixture was stirred at 60 °C for 24 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 20/1 to 2/1) to afford **5b** (673.0 mg, 96% in 2% de).

Ethyl 2-benzoyl-3-(4-methoxyphenyl)butyrate (5b) diastereomixture, Colorless oil: TLC R_f = 0.33 (hexane/ethyl acetate = 4/1); ¹H NMR (300 MHz, CDCl₃) δ: 8.09 (2 H, d, J = 7.5 Hz), 7.84 (2 H, d, J = 7.5 Hz), 7.62-7.33 (3 H, m), 7.62-7.33 (3 H, m), 7.23 (2 H, d, J = 7.5 Hz), 6.84 (2 H, d, J = 7.5 Hz), 4.63 (1 H, d, J = 10.5 Hz), 4.58 (1 H, d, J = 10.8 Hz), 4.18 (2 H, q, J = 7.2 Hz), 3.93-3.76 (2 H, m, J = 7.2 Hz), 3.93-3.76 (1 H, m), 3.93-3.76 (1 H, m), 3.78 (3 H, s), 3.69 (3 H, s), 1.36 (3 H, d, J = 6.9 Hz), 1.22 (3 H, d, J = 6.9 Hz), 1.20 (3 H, t, J = 6.9 Hz), 0.91 (3 H, t, J = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 193.6, 193.5, 168.4, 167.8, 158.2, 157.9, 136.8, 136.6, 135.6, 135.3, 133.4, 133.0, 128.58, 128.58, 128.5, 128.3, 128.24, 128.24, 113.7, 62.0, 61.7, 61.5, 61.2, 55.3, 55.3, 39.6, 39.1, 20.9, 20.5, 14.2, 13.9; IR (neat) cm⁻¹: 2950 (m), 1740 (s), 1690 (s), 1520 (m), 1460 (m), 1260 (s), 1190 (m), 1040 (m), 840 (m), 700 (m); EI-MS (70 eV) m/z (relative intensity): 326 (M^+ , 13), 308 (31), 175 (30), 105 (32), 77 (17); HRMS-EI (m/z): M^+ calcd for C₂₀H₂₂O₄, 326.1518; found, 326.1518; Anal. Calcd for C₂₀H₂₂O₄: C, 73.60; H, 6.79. Found: C, 73.78; H, 7.06; GC analysis: 17.96 min, 18.41 min (major), (150 °C, 2 min, 10 °C/min, 260 °C, 17 min).

GC analysis for 5c

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
20	24	2	11	67	84
50	9	78	79	21	7
80	6.5	38	4	0	0

Table 2 Entry 3. To a mixture of Hf(OTf)₄ (2.36 mg, 3.05 μ mol) and **4c** (103.3 mg, 0.6069 mmol) in CH₃NO₂ (0.609 mL), **1a** (92.4 mg, 0.6071 mmol) was added at room temperature. And the resulting mixture was stirred at 20 °C for 24 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, cyclohexane/dichloromethane = 1/3) to afford **5c** (155.17 mg, 84% in 3% de by NMR). The diastereomixture was separated by silica gel column chromatography (hexane/ethyl acetate = 20/1).

Ethyl 1-[1-(4-methoxyphenyl)ethyl]-2-oxocyclohexanecarboxylate (5c**) Diastereomer A, major product,** Colorless needles: mp 100–102 °C; TLC R_f = 0.41 (hexane/ethyl acetate = 3/1); ¹H NMR (300 MHz, CDCl₃) δ : 7.09 (2 H, d, *J* = 8.7 Hz), 6.78 (2 H, d, *J* = 8.7 Hz), 4.01–3.89 (2 H, m), 3.77 (3 H, s), 3.67 (1 H, q, *J* = 7.1 Hz), 2.50–1.55 (8H, m), 1.29 (3 H, d, *J* = 7.2 Hz), 1.13 (3 H, t, *J* = 7.1 Hz); ¹³C NMR (100 MHz, CDCl₃) δ : 206.2, 170.3, 158.1, 134.0, 129.6, 113.2, 65.3, 61.1, 55.1, 41.9, 41.8, 30.1, 26.8, 22.5, 17.1, 14.0; IR (KBr) cm⁻¹: 1717 (s), 1516 (s), 1247 (s), 1210 (m), 1183 (m), 1137 (m), 1019 (m), 837 (m); EI-MS (70 eV) *m/z* (relative intensity): 304 (M⁺, 5), 286 (17), 213 (6), 135 (100); HRMS-EI (*m/z*): M⁺ calcd for C₁₈H₂₄O₄, 304.1675; found, 304.1678; Anal. Calcd for C₁₈H₂₄O₄: C, 71.03; H, 7.95. Found: C, 71.00; H 8.10; GC analysis: 16.12 min (150 °C, 2 min, 10 °C/min, 260 °C, 17 min).

Ethyl 1-[1-(4-methoxyphenyl)ethyl]-2-oxocyclohexanecarboxylate (5c) Diastereomer B, minor product, Colorless amorphous solid-viscous oil: TLC R_f = 0.48 (hexane/ethyl acetate = 3/1); ^1H NMR (300 MHz, CDCl_3) δ : 7.13 (2 H, d, J = 8.4 Hz), 6.79 (2 H, d, J = 8.7 Hz), 4.22 (2 H, q, J = 7.2 Hz), 3.78 (3 H, s), 3.48 (1 H, q, J = 7.2 Hz), 2.52-1.49 (8H, m), 1.28 (3 H, d, J = 7.2 Hz), 1.27 (3 H, t, J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ : 206.7, 170.5, 157.8, 133.8, 130.1, 112.7, 64.4, 60.8, 54.9, 41.7, 41.5, 35.5, 27.4, 22.6, 17.8, 14.0; IR (neat) cm^{-1} : 1713 (s), 1516 (s), 1245 (s), 1201 (m), 1137 (m), 1035 (m), 835 (m); EI-MS (70 eV) m/z (relative intensity): 304 (M^+ , 5), 286 (11), 213 (4), 135 (100), 105 (3); HRMS-EI (m/z): M^+ calcd for $\text{C}_{18}\text{H}_{24}\text{O}_4$, 304.1675; found, 304.1681; Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{O}_4$: C, 71.03; H, 7.95. Found: C, 70.90; H 8.11; GC analysis: 16.08 min (150 $^\circ\text{C}$, 2 min, 10 $^\circ\text{C}/\text{min}$, 260 $^\circ\text{C}$, 17 min).

GC analysis for 5d

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
60	24	0	3	29	40
80	24	4	43	77	61
100	24	56	69	65	48

Table 2 Entry 4. To a mixture of Sc(OTf)₃ (3.45 mg, 7.01 μmol) and **4a** (162.91 mg, 1.40300 mmol) in CH₃NO₂ (1.402 mL), **1b** (171.59 mg, 1.4046 mmol) was added at room temperature. And the resulting mixture was stirred at 80 °C for 12 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, cyclohexane/dichloromethane = 5/1 to 1/3) to afford **5d** (236.72 mg, 77% in 6% de).

Methyl 3-oxo-2-(1-phenylethyl)butyrate (5d), diastereomixture CA registry Number: [71686-93-6]. Colorless oil: TLC R_f = 0.68 (cyclohexane/dichloromethane = 1/6); ¹H NMR (300 MHz, CDCl₃) δ: 7.31-7.17 (5 H, m), 7.31-7.17 (5 H, m), 3.81 (1 H, d, *J* = 11.1 Hz), 3.76 (1 H, d, *J* = 10.8 Hz), 3.76 (1 H, s), 3.59-3.49 (1 H, m), 3.59-3.49 (1 H, m), 3.43 (1 H, s), 2.29 (3 H, s), 1.92 (3 H, s), 1.30 (3 H, d, *J* = 6.6 Hz), 1.24 (3 H, d, *J* = 6.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 201.78, 201.78, 168.7, 168.2, 142.9, 142.7, 128.5, 128.2, 127.11, 127.06, 126.7, 126.6, 67.3, 66.7, 52.4, 52.1, 40.1, 39.7, 30.0, 29.6, 20.6, 20.1; IR (neat) cm⁻¹: 2967 (m), 1747 (m), 1716 (m), 1494 (m), 1454 (m), 1433 (m), 1357 (m), 1288 (m), 1207 (m), 1163 (m), 765 (s), 701 (s); EI-MS (70 eV) *m/z* (relative intensity): 220 (M⁺, 1), 202 (100), 177 (41), 77 (145), 131 (33), 105 (82), 43 (23); HRMS-EI (*m/z*): M⁺ calcd for C₁₃H₁₆O₃, 220.1099, found, 220.1096; Anal. Calcd for C₁₃H₁₆O₃: C, 70.89; H, 7.32. Found: C 70.91; H 7.60; GC analysis: 7.43 min, 7.74 min (major) (150 °C, 2 min, 10 °C/min, 260 °C, 10 min).

GC analysis for 5e

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
60	24	0	3	8 ^a	38
80	6	0	7	47 ^b	59
100	-	9 (24 h)	41 (5 h)	59 (4 h) ^c	55 (1.25 h)

a: 7% de, b: 4%de, c: 3%de

Table 2 Entry 5. To a mixture of Sc(OTf)₃ (3.31 mg, 6.73 μmol) and **4b** (264.30 mg, 1.4833 mmol) in CH₃NO₂ (1.345 mL), **1b** (164.60 mg, 1.3474 mmol) was added at room temperature. And the resulting mixture was stirred at 85 °C for 8 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, cyclohexane/dichloromethane = 3/7) to afford **5e** (281.0 mg, 70% in 2%de).

Ethyl 2-benzoyl-3-phenylbutyrate (5e) diastereomixture, Colorless oil: TLC R_f = 0.53 (cyclohexane/dichloromethane = 1/5); ¹H NMR (300 MHz, CDCl₃) δ: 8.12-8.07 (2 H, m), 7.85-7.81 (2 H, m), 7.63-7.04 (8 H, m), 7.63-6.94 (8 H, m), 4.68 (1 H, d, J = 10.5 Hz), 4.63 (1 H, d, J = 10.8 Hz), 4.19 (2 H, q, J = 7.2 Hz), 3.88-3.76 (2 H, m), 3.88-3.76 (2 H, m), 3.88-3.76 (1 H, m), 3.88-3.76 (1 H, m), 1.38 (3 H, d, J = 7.2 Hz), 1.25 (3 H, d, J = 6.9 Hz), 1.22 (3 H, t, J = 7.2 Hz), 0.88 (3 H, t, J = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 193.4, 193.2, 168.3, 167.6, 143.5, 143.2, 136.6, 136.5, 133.4, 132.9, 128.50, 128.48, 128.2, 128.12, 128.12, 128.12, 127.5, 127.2, 126.5, 126.3, 61.6, 61.4, 61.2, 61.1, 40.3, 39.8, 20.7, 20.3, 14.1, 13.7; IR (KBr) cm⁻¹: 2970 (m), 1730 (s), 1690 (s), 1600 (m), 1460 (s), 1380 (m), 1300 (s), 1280 (s), 1230 (s), 1170 (s), 1040 (m), 1000 (m), 770 (m), 700 (m); EI-MS (70 eV) m/z (relative intensity): 296 (M⁺, 2), 278 (27), 223 (22), 191 (40), 145 (25), 105 (100), 77 (31); HRMS-EI (m/z): M⁺ calcd for C₁₉H₂₀O₃, 296.1412, found, 296.1412; Anal. Calcd for C₁₉H₂₀O₃: C, 77.00; H, 6.80. Found: C 77.24; H 7.03; GC analysis: 14.72 min, 14.93 min (major) (150 °C, 2 min, 10 °C/min, 260 °C, 10 min).

GC analysis for **5f**

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
20	24	0	0	1	1
60	9	8	26	55	57
100	6.5	53	49	38	31

Table 2 Entry 6. To a mixture of Hf(OTf)₄ (7.67 mg, 9.90 μmol) and **4c** (340.35 mg, 1.9996 mmol) in CH₃NO₂ (1.98 mL), **1b** (247.37 mg, 2.0244 mmol) was added at room temperature. And the resulting mixture was stirred at 60 °C for 21 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, cyclohexane/dichloromethane = 5/1 to 1/3) to afford **5f** (311.6 mg, 57%). For diastereomer separation, the mixture was separated by column chromatography (silica gel, hexane/ethyl acetate = 20/1 to 5/1).

Ethyl 2-2xo-1-(1-phenylethyl)cyclohexanecarboxylate (5f), diastereomer A Colorless oil; TLC R_f = 0.30 (hexane/ethyl acetate = 10/1, 2 times); ^1H NMR (400 MHz, CDCl_3) δ : 7.27-7.15 (5 H, m), 4.16 (2 H, q, J = 7.2 Hz), 3.44 (1 H, q, J = 7.0 Hz), 2.42-2.35 (2 H, m), 2.00 (1 H, ddd, J = 14.0, 8.0, 2.8 Hz), 1.92-1.82 (1H, m), 1.62-1.40 (4H, m), 1.24 (3 H, d, J = 7.0 Hz), 1.20 (3 H, t, J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ : 207.1, 170.8, 142.0, 129.5, 127.6, 126.5, 64.6, 61.1, 42.8, 41.8, 35.9, 27.7, 22.9, 18.0, 13.9.

Ethyl 2-2xo-1-(1-phenylethyl)cyclohexanecarboxylate (5f), diastereomer B, Colorless oil; TLC R_f = 0.26 (hexane/ethyl acetate = 10/1, 2 times); ^1H NMR (400 MHz, CDCl_3) δ : 7.27-6.95 (5 H, m), 3.92-3.80 (2 H, m), 3.65 (1 H, q, J = 7.0 Hz), 2.45-2.34 (2 H, m), 2.28-2.20 (1 H, m), 1.88-1.83 (1H, m), 1.68-1.56 (4H, m), 1.23 (3 H, d, J = 7.0 Hz), 1.02 (3 H, t, J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ : 206.1, 170.3, 142.0, 128.7, 127.8, 126.7, 65.3, 61.1, 42.6, 41.9, 30.1, 26.8, 22.6, 16.9, 14.0.

Ethyl 2-2xo-1-(1-phenylethyl)cyclohexanecarboxylate (5f), diastereomixture: IR (neat) cm^{-1} : 1715 (s), 1454 (m), 1450 (m), 1241 (s), 1199 (s), 1139 (m), 702 (m); EI-MS (70 eV) m/z (relative intensity): 274 (M^+ , 1), 256 (49), 229 (8), 183 (40), 170 (17), 105 (100); HRMS-EI (m/z): M^+ calcd for $\text{C}_{17}\text{H}_{22}\text{O}_3$, 274.1569, found, 274.1568; Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{O}_3$: C, 74.42; H, 8.08. Found: C, 74.33; H, 8.45; GC analysis: 12.72 min (Diastereomers were not separated. 150 °C, 2 min, 10 °C/min, 260 °C, 17 min).

Table 3 GC analysis for 7a

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
60	14	2	5	99	98
80	14	3	8	89	74
100	21.5	1	6	79	78

Table 3 Entry 1. To a mixture of Hf(OTf)₄ (3.51 mg, 4.53 μmol) and **6a** (117.78 mg, 0.9119 mmol) in CH₃NO₂ (0.906 mL), **1a** (136.27 mg, 0.89539 mmol) was added at room temperature. And the resulting mixture was stirred at 60 °C for 12 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, hexane/ethyl acetate = 1/4) to afford **7a** (232.0 mg, 98% in 2% de by NMR).

2-[1-(4-Methoxyphenyl)-ethyl]-N,N-dimethyl-3-oxobut-2-enamide (7a) diastereomixture, Colorless oil: TLC R_f = 0.48 (hexane/ethyl acetate = 1/4); ¹H NMR (300 MHz, CDCl₃) δ: 7.17-7.12 (2 H, m), 7.17-7.12 (2 H, m), 6.84-6.79 (2 H, m), 6.84-6.79 (2 H, m), 3.93 (1 H, d, J = 10.8 Hz), 3.79 (1 H, d, J = 10.5 Hz), 3.78 (3 H, s), 3.77 (3 H, s), 3.74-3.60 (1 H, m), 3.74-3.60 (1 H, m), 3.13 (3 H, s), 3.02 (3 H, s), 2.78 (3 H, s), 2.72 (3 H, s), 2.28 (3 H, s), 1.97 (3 H, s), 1.23 (3 H, d, J = 6.9 Hz), 1.20 (3 H, d, J = 6.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 204.8, 204.4, 167.4, 167.4, 158.1, 158.0, 135.5, 135.1, 128.3, 128.1, 114.0, 113.6, 66.4, 65.6, 55.6, 55.2, 40.0, 39.4, 37.8, 37.5, 36.3, 35.9, 27.2, 27.0, 22.1, 19.7; IR (neat) cm⁻¹: 2950 (m), 1715 (m), 1650 (s), 1520 (m), 1475 (m), 1410 (m), 1370 (m), 1260 (s), 1195 (m), 1155 (m), 1130 (m), 1050 (m), 845 (m); EI-MS (70 eV) m/z (relative intensity): 263 (M⁺, 11), 220 (100), 175 (22), 135 (32), 72 (17); HRMS-EI (m/z): M⁺ calcd for C₁₅H₂₁NO₃, 263.1521; found, 263.1525; Anal. Calcd for C₁₅H₂₁NO₃: C, 68.42; H, 8.04; N, 5.32. Found: C, 68.39; H, 8.21; N, 5.04; GC analysis: 12.72 min, 13.29 min (major) (150 °C, 2 min, 10 °C/min, 300 °C, 13 min).

GC analysis for 7b

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
60	12	7	46	50	80
80	12	0	70	72	73
100	12	61	59	68	77

Table 3 Entry 2. To a mixture of $\text{Hf}(\text{OTf})_4$ (2.98 mg, 3.85 μmol) and **7b** (95.99 mg, 833.8 μmol) in CH_3NO_2 (0.770 mL), **1a** (122.06 mg, 0.8033 mmol) was added at room temperature. And the resulting mixture was stirred at 60 °C for 12 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, hexane/ethyl acetate = 1/5) to afford **7b** (158.87 mg, 80% in 13% de by GC, 14% de by NMR).

temp.(°C)	time (h)	yield (%) IS			
		Yb(OTf) ₃ (0.5 mol%)	Yb(OTf) ₃ (5 mol%)	Hf(OTf) ₃ (0.5 mol%)	Hf(OTf) ₄ (5 mol%)
20	24	3	1	1	50
		La(OTf) ₃ (0.5 mol%)	Yb(OTf) ₃ (0.5 mol%)	Sc(OTf) ₃ (0.5 mol%)	Hf(OTf) ₄ (0.5 mol%)
60	24	3	18	61	76
100	24	7	44	60	65

Table 3 Entry 2, the data in parenthesis. To a mixture of Hf(OTf)₄ (3.71 mg, 4.79 μ mol) and **7b** (159.69 mg, 70% in H₂O, 970.925 μ mol) in CH₃NO₂ (0.958 mL), **1a** (147.77 mg, 0.97095 mmol) was added at room temperature. And the resulting mixture was stirred at 60 °C for 13.5 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, hexane/ethyl acetate = 1/5) to afford **7b** (182.81 mg, 76% in 28% de by GC, 24% de by NMR).

2-[1-(4-Methoxyphenyl)ethyl]-N-methyl-3-oxobutyramide (7b), diastereomixture, Colorless prism: mp 105–109 °C; TLC R_f = 0.25 (hexane/ethyl acetate = 1/5); ¹H NMR (300 MHz, CDCl₃) δ : 7.07-7.00 (2 H, m), 7.07-7.00 (2 H, m), 6.78-6.74 (2 H, m), 6.78-6.74 (2 H, m), 6.39 (1H, br), 5.89 (1 H, br), 3.70 (3 H, s), 3.70 (3 H, s), 3.55 (1 H, d, *J* = 11.4 Hz), 3.48 (1 H, d, *J* = 9.9 Hz), 3.42-3.33 (1 H, m), 3.26-3.15 (1 H, m), 2.76 (3 H, d, *J* = 5.1 Hz), 2.52 (3 H, d, *J* = 4.8 Hz), 2.15 (3 H, s), 1.76 (3 H, s), 1.21 (3 H, d, *J* = 6.9 Hz), 1.17 (3 H, d, *J* = 6.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ : 207.9, 206.9, 167.8, 167.5, 158.2, 158.1, 134.8, 134.6, 127.94, 127.94, 114.0, 113.8, 69.3, 69.1, 55.19, 55.16, 42.4, 40.7, 31.2, 30.5, 26.6, 26.3, 20.6, 19.6; IR (KBr) cm⁻¹: 3304 (s), 1717 (s), 1651 (s), 1545 (m), 1518 (s), 1249 (s), 1183 (m), 1158 (m), 1033 (s), 830 (m), 812 (m); EI-MS (70 eV) *m/z* (relative intensity): 249 (M⁺, 9), 206 (100), 175 (32), 135 (44); HRMS-EI (*m/z*): M⁺ calcd for C₁₄H₁₉NO₃, 249.1365; found, 249.1364; Anal. Calcd for C₁₄H₁₉NO₃: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.37; H, 7.77; N, 5.56; GC analysis: 12.15 min, 12.25 min (major) (150 °C, 2 min, 10 °C/min, 300 °C, 3 min).

GC analysis for 7c

cat.(mol%)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
0.5	24	-	-	0	3
1	24	0	0	0	1
2.5	24	0	0	2	6
5	24	0	0	9	31
10	24	-	-	19	22
20	24	-	-	31	5

Table 3 Entry 3. To a mixture of Hf(OTf)₄ (15.30 mg, 19.75 μ mol) and **6a** (57.32 mg, 0.4438 mmol) in CH₃NO₂ (0.395 mL), **1b** (48.85 mg, 0.3999 mmol) was added at room temperature. And the resulting mixture was stirred at 100 °C for 24 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, ethyl acetate) to afford **7c** (32.90 mg, 35% in 4% de).

N,N-Dimethyl-3-oxo-2-(1-phenylethyl)butyramide (7c) diastereomixture, Colorless prism: mp 60–63 °C; TLC R_f = 0.59 (ethyl acetate); ¹H NMR (300 MHz, CDCl₃) δ : 7.32–7.15 (5 H, m), 7.32–7.15 (5 H, m), 3.99 (1 H, d, *J* = 10.8 Hz), 3.84 (1 H, d, *J* = 11.1 Hz), 3.79–3.63 (1 H, m), 3.79–3.63 (1 H, m), 3.13 (3 H, s), 3.02 (3 H, s), 2.77 (3 H, s), 2.70 (3 H, s), 2.29 (3 H, s), 1.97 (3 H, s), 1.25 (3 H, d), 1.23 (3 H, d, *J* = 6.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ : 204.4, 204.0, 167.22, 167.18, 143.3, 143.0, 128.5, 128.1, 127.2, 127.0, 126.6, 126.5, 65.9, 65.1, 40.7, 40.1, 37.7, 37.4, 36.2, 35.7, 27.1, 27.0, 21.8, 19.5; IR (KBr) cm⁻¹ 2940 (m), 2900 (m), 1710 (m), 1690 (m), 1620 (s), 1590 (m), 1400 (m), 1350 (m), 1140 (m), 760 (m), 700 (m); EI-MS (70 eV) *m/z* (relative intensity): 233 (M⁺, 4), 190 (100), 176 (13), 145 (12), 105 (18), 72 (15); HRMS-EI (*m/z*): M⁺ calcd for C₁₄H₁₉NO₂, 233.1416; found, 233.1409; Anal. Calcd for C₁₄H₁₉NO₂: C, 72.07; H, 8.21, N, 6.00. Found: C, 72.11; H, 8.45, N, 6.17; GC analysis: 14.80 min, 15.32 min (major) (100 °C, 2 min, 10 °C/min, 300 °C, 13 min).

GC analysis for 7d

temp (°C)	cat.(mol%)	time (h)	yield (%) IS	
			Sc(OTf) ₃	Hf(OTf) ₄
100	2.5	24	8	14
100	5	24	17	11
100	10	24	18	13
100	20	24	16	0

Table 3 Entry 4. To a mixture of Hf(OTf)₄ (34.26 mg, 44.22 μmol) and **6b** (106.91 mg, 0.9286 mmol) in CH₃NO₂ (0.885 mL), **1b** (109.95 mg, 0.9001 mmol) was added at room temperature. And the resulting mixture was stirred at 100 °C for 24 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, hexane/ethyl acetate = 1/5) to afford **7d** (21.76 mg, 11%, 25% de by GC, 23% de by NMR).

temp (°C)	cat.(mol%)	time (h)	yield (%) IS			
			La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
60	2.5	24	0	0	0	0
80	2.5	24	0	0	1	1
100	2.5	24	0	0	2	2
100	5	24	-	-	9	6
100	10	24	-	-	21	16
100	20	24	-	-	15	0

Table 3 Entry 4, the data in parenthesis. To a mixture of $\text{Hf}(\text{OTf})_4$ (25.48 mg, 32.89 μmol) and **6b** (70% solution in H_2O , 109.34 mg, 0.6648 mmol) in CH_3NO_2 (0.665 mL), **1b** (81.18 mg, 0.6645 mmol) was added at room temperature. And the resulting mixture was stirred at 100 °C for 24 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, ethyl acetate) to afford **7d** (9.22 mg, 6%, 20% de).

***N*-Methyl-3-oxo-2-(1-phenylethyl)butyramide (7d) Diastereomixture**, Colorless needles: mp 104–107 °C; TLC R_f = 0.56 (ethyl acetate); ^1H NMR (300 MHz, CDCl_3) δ : 7.38–7.16 (5 H, m), 7.38–7.16 (5 H, m), 6.45 (1H, br), 5.91 (1 H, br), 3.67 (1 H, d, J = 11.1 Hz), 3.59 (1 H, d, J = 10.2 Hz), 3.50 (1 H, dq, J = 10.2, 6.9 Hz), 3.32 (1 H, dq, J = 11.1 Hz, 6.9 Hz), 2.84 (3 H, d, J = 5.1 Hz), 2.57 (3 H, d, J = 4.5 Hz), 2.23 (3 H, s), 1.81 (3 H, s), 1.31 (3 H, d, J = 6.9 Hz), 1.27 (3 H, d, J = 6.9 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ : 207.9, 206.9, 167.7, 167.4, 142.8, 142.6, 128.7, 128.4, 127.0, 127.0, 126.93, 126.86, 69.1, 69.0, 43.3, 41.5, 31.3, 30.6, 26.6, 26.4, 20.4, 219.4; IR (KBr) cm^{-1} 3267 (br), 1723 (s), 1643 (s), 1568 (s), 1493 (m), 1454 (m), 1411 (m), 1353 (m), 1163 (s), 761 (s), 703 (s); EI-MS (70 eV) m/z (relative intensity): 219 (M^+ , 4), 176 (100), 162 (16), 145 (13), 105 (20); HRMS-EI (m/z): M^+ calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2$, 219.1259; found, 219.1257; Anal. Calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2$: C, 71.21; H, 7.81, N, 6.39. Found: C, 71.11; H, 8.07, N, 6.16; GC analysis: 16.24 min, 16.28 min (major) (50 °C, 2 min, 15 °C/min, 300 °C, 6 min).

Synthesis of Alcohols for Table 4

1-(2,6-dimethylphenyl)ethanol¹ CA registry Number: [19447-06-4]. In a 300 mL three necked round bottom flask equipped with a condenser, magnesium turnings (875 mg, 36 mmol) were stirred for 15 min under argon atmosphere. Dry tetrahydrofuran (50 mL) was added, then I_2 (5 mg) was added at room temperature, and the resulting mixture was stirred for 10 min. Tetrahydrofuran solution of 2-bromo-*m*-xylene (5.13 g, 27.7 mmol) was added dropwise over 30 min at room temperature. The mixture was stirred at 40 °C for 20 min, then cooled to 0 °C. Acetaldehyde (2.3 mL, 42 mmol) was added dropwise over 3 min at 0 °C. The mixture was stirred at 0 °C for 4 h, then at reflux for 1 h. After cooled to room

temperature, 1 mol/L hydrochloric acid was slowly added. The mixture was extracted with dichloromethane (50 mL three times). The combined organic layer was washed with brine (100 mL), and dried over MgSO_4 , filtered, and the filtrate was concentrated to afford colorless oil. The solid was purified by column chromatography (silica gel, hexane/ethyl acetate = 20/1 to 2/1) to afford 1-(2,6-dimethylphenyl)ethanol (3.237 g, 78%) as colorless amorphous solid. TLC R_f = 0.42 (hexane/ethyl acetate = 3/1); ^1H NMR (300 MHz, CDCl_3) δ : 7.71-6.97 (3 H, m, Ar-H), 5.39 (1 H, qd, J = 6.7, 2.2 Hz), 2.44 (6 H, s), 1.71 (1 H, d, J = 1.7 Hz), 1.54 (3 H, d, J = 6.7 Hz); IR (KBr) cm^{-1} : 3313 (br), 1471 (m), 1447 (m), 1416 (m), 1336 (m), 1299 (m), 1192 (m), 1106 (m), 1073 (s), 893 (m), 773 (s); EI-MS (70 eV) m/z (relative intensity): 150 (M^+ , 31), 135 (100), 132 (89), 107 (57), 91 (43); HRMS-EI (m/z): M^+ calcd for $\text{C}_{10}\text{H}_{14}\text{O}$, 150.1045; found, 150.1048.

1-(4-nitrophenyl)ethanol² CA registry Number: [6531-13-1]. To a hexane (307 mL) solution of 4-nitroacetophenone (5.804 g, 30.785 mmol), moist alumina (15.4 g) and NaBH_4 (291 mg, 7.696 mmol) was added, and the mixture was stirred at 40°C for 6.5 h. After cooled to room temperature, the mixture was filtered, and the filtrate was concentrated to afford yellow oil. The oil was purified by column chromatography (silica gel, hexane/ethyl acetate = 20/1 to 1/1) to afford 1-(4-nitrophenyl)ethanol (3.889 g, 76%) as yellow amorphous solid: TLC R_f = 0.30 (hexane/ethyl acetate = 1/1); ^1H NMR (300 MHz, CDCl_3) δ : 8.19 (2 H, d, J = 9.0 Hz), 7.55 (2 H, d, J = 9.0 Hz), 5.03 (1 H, qd, J = 6.0, 3.0 Hz), 2.21 (1 H, d, J = 3.0 Hz), 1.52 (3 H, d, J = 6.0 Hz); IR (neat) cm^{-1} : 3374 (br), 1604 (m), 1519 (s), 1348 (s), 1089 (s), 1012 (m), 855 (s), 700 (s); EI-MS (70 eV) m/z (relative intensity): 167 (M^+ , 2), 166 ($\text{M}-1$, 2), 152 ($\text{M}-\text{CH}_3$, 100), 107 (34), 77 (25); HRMS-EI (m/z): M^+ calcd for $\text{C}_8\text{H}_9\text{NO}_3$, 152.0348; found, 152.0351.

1-(ferrocenyl)ethanol CA registry Number: [1277-49-2]. To a ethanol (22 mL) solution of acetylferrocene (5.0064 g, 21.95 mmol), NaBH_4 (840.0 mg, 21.95 mmol) was added, and the mixture was stirred at 70°C for 0.5 h. The reaction was followed by GC. After the acetylferrocene was disappeared, the reaction mixture was cooled to room temperature and H_2O (100 mL) was added. The mixture was extracted with ethyl acetate (100 mL three times). The combined organic layer was washed with brine (100 mL), and dried over MgSO_4 , filtered, and the filtrate was concentrated to afford orange amorphous solid (4.8771 g, 96%). The solid was recrystallized from cyclohexane to give orange needles: mp: 63–67 °C TLC R_f = 0.43 (hexane/ethyl acetate = 2/1); ^1H NMR (300 MHz, CDCl_3) δ : 4.55 (1 H, qd, J = 6.4, 4.7 Hz), 4.24-3.99 (9 H, m), 1.83 (1 H, d, J = 4.7 Hz), 1.44 (3 H, d, J = 6.4 Hz); IR (KBr) cm^{-1} : 3214 (br), 1410 (m), 1306 (m), 1238 (m), 1069 (m), 999 (s), 869 (s), 808 (m); EI-MS (70 eV) m/z (relative intensity): 231 ($\text{M}+1$, 15), 230 (M^+ , 100), 212 (77), 138 (60); HRMS-EI (m/z): M^+ calcd for $\text{C}_{12}\text{H}_{14}\text{OFe}$, 230.0394; found, 230.0397. Bis 1,1'-ferrocenylethyl ether was formed during NMR measurement by a trace amount of acid in CDCl_3 : ^1H NMR (300 MHz, CDCl_3) δ : 4.43 (2 H, q, J = 6.3 Hz), 4.40 (2 H, q, J = 6.6 Hz), 4.24-4.07 (18 H, m), 4.24-4.07 (18 H, m), 1.49 (6 H, d, J = 6.3 Hz), 1.43 (6 H, d, J = 6.6 Hz); EI-MS (70 eV) m/z (relative intensity): 443 ($\text{M}+1$, 30), 442 (M^+ , 100), 214 (15), 213 (79).

GC analysis for **3i**

	temp (°C)				
	20	40	60	80	100
yield (%) IS	8	48	86	7	4
time (h)	21	21	18.5	18.5	18.5

Table 4 Entry 2. To a mixture of $\text{Hf}(\text{OTf})_4$ (3.53 mg, 4.56 μmol) and **2b** (204.53 mg, 0.91204 mmol) in CH_3NO_2 (0.911 mL), 1-(2,6-dimethylphenyl)ethanol (135.73 mg, 903.56 mmol) was added at room temperature. And the resulting mixture was stirred at 60 °C for 13 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, toluene/dichloromethane = 2/1) to afford **3i** (268.64 mg, 86%).

2-[1-(2,6-Dimethylphenyl)ethyl]-1,3-diphenylpropane-1,3-dione (3i**)**, Colorless oil: TLC R_f = 0.58 (hexane/ethyl acetate = 7/3); ^1H NMR (300 MHz, CDCl_3) δ : 8.06 (2 H, d, J = 7.2 Hz), 7.60-7.15 (8 H, m), 6.82-6.70 (3 H, m), 6.02 (1 H, d, J = 11.4 Hz), 4.50 (1 H, dq, J = 11.4 Hz, 7.2 Hz), 2.48 (3 H, s), 2.34 (3 H, s), 1.25 (3 H, d, J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.1, 194.2, 139.3, 137.2, 137.0, 135.2, 133.4, 132.6, 130.0, 128.8, 128.7, 128.2, 127.9, 127.2, 62.1, 36.5, 22.2, 21.6, 17.6; IR (neat) cm^{-1} : 1669 (s), 1599 (m), 1580 (m), 1450 (m), 1274 (s), 1212 (s), 992 (s), 768 (m), 690 (m); EI-MS (70 eV) m/z (relative intensity): 356 (M^+ , 0.3), 338 (28), 251 (20), 233 (46), 132 (100), 105 (77), 77 (35); HRMS-EI (m/z): M^+ calcd for $\text{C}_{25}\text{H}_{24}\text{O}_2$, 356.1776; found, 356.1779; Anal. Calcd for $\text{C}_{25}\text{H}_{24}\text{O}_2$: C, 84.24; H, 6.79. Found: C, 84.33; H, 6.93; GC analysis: 19.80 min (150 °C, 2 min, 10 °C/min, 300 °C, 13 min)

Synthesis of **3j**

Table 4 Entry 3. To a mixture of $\text{Hf}(\text{OTf})_4$ (3.65 mg, 4.71 μmol) and **2b** (220.60 mg, 0.98370 mmol) in CH_3NO_2 (0.942 mL), 1-(4-methylphenyl)ethanol (132.65 mg, 0.97400 mmol) was added at room temperature. And the resulting mixture was stirred at $40\text{ }^\circ\text{C}$ for 12 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, hexane/ethyl acetate = 3/1) to afford **3j** (310.81 mg, 93%).

1,3-Diphenyl-2-(1-*p*-tolylethyl)propane-1,3-dione (3j**)**, Colorless prism: mp $122\text{--}124\text{ }^\circ\text{C}$; TLC R_f = 0.59 (hexane/ethyl acetate = 7/3); ^1H NMR (300 MHz, CDCl_3) δ : 8.06 (2 H, d, J = 7.8 Hz), 7.75 (2 H, d, J = 6.9 Hz), 7.59-6.96 (10 H, m), 5.58 (1 H, d, J = 10.2 Hz), 4.05 (1 H, dq, J = 10.2 Hz, 6.9 Hz), 2.21 (3 H, s), 1.32 (3 H, d, J = 6.9 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ : 194.7, 194.2, 140.6, 137.0, 136.7, 135.8, 133.3, 132.7, 128.9, 128.6, 128.5, 128.3, 128.2, 127.3, 64.9, 40.8, 21.0, 20.5; IR (KBr) cm^{-1} : 1696 (s), 1661 (s), 1448 (m), 1290 (m), 1199 (m), 996 (m), 706 (s), 692 (s); EI-MS (70 eV) m/z (relative intensity): 342 (M^+ , 1), 237 (100), 119 (10), 105 (31), 77 (16); HRMS-EI (m/z): M^+ calcd for $\text{C}_{24}\text{H}_{22}\text{O}_2$, 342.1620; found, 342.1616; Anal. Calcd for $\text{C}_{24}\text{H}_{22}\text{O}_2$: C, 84.18; H, 6.48 Found: C, 84.35; H, 6.44; GC analysis: 25.08 min ($100\text{ }^\circ\text{C}$, 2 min, $10\text{ }^\circ\text{C}/\text{min}$, $300\text{ }^\circ\text{C}$, 8 min); GC analysis: 20.10 min ($150\text{ }^\circ\text{C}$, 2 min, $10\text{ }^\circ\text{C}/\text{min}$, $300\text{ }^\circ\text{C}$, 8 min).

GC analysis for 3k

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
20	24	3	7	10	16
60	24	91	88	84	76
100	18.5	48	47	0	0

Table 4 Entry 4. To a mixture of La(OTf)₃ (4.53 mg, 7.73 μ mol) and **2b** (348.15 mg, 1.5525 mmol) in CH₃NO₂ (1.546 mL), 1-(2-methylphenyl)ethanol (211.50 mg, 1.5530 mmol) was added at room temperature. And the resulting mixture was stirred at 60 °C for 24 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 20/1 to 2/1) to afford **3k** (485.0 mg, 91%).

Table 4 Entry 4. To a mixture of Hf(OTf)₄ (2.80 mg, 3.61 μ mol) and **2b** (162.14 mg, 0.72302 mmol) in CH₃NO₂ (0.723 mL), 1-(2-methylphenyl)ethanol (102.58 mg, 0.75321 mmol) was added at room temperature. And the resulting mixture was stirred at 45 °C for 13 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, hexane/ethyl acetate = 7/3) to afford **3k** (238.6 mg, 96%).

1,3-Diphenyl-2-(1-*o*-tolylethyl)propane-1,3-dione (3k), Colorless prism: mp 112–114 °C; TLC R_f = 0.40 (hexane/ethyl acetate = 3/1); ¹H NMR (300 MHz, CDCl₃) δ : 8.10–8.06 (2 H, m), 7.76–7.73 (2 H, m), 7.60–7.22 (7 H, m), 7.06–6.94 (3 H, m), 5.74 (1 H, d, *J* = 10.5 Hz), 4.33 (1 H, dq, *J* = 10.5 Hz, 6.9 Hz), 2.41 (3 H, s), 1.24 (3 H, d, *J* = 6.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ : 195.0, 194.2, 142.2, 137.1, 136.8, 135.8, 133.4, 132.8, 130.4, 128.71, 128.71, 128.24, 128.23, 126.1, 125.8, 125.6, 64.1, 36.1, 20.7, 19.8; IR (KBr) cm⁻¹: 2950 (m), 1695 (s), 1660 (m), 1600 (m), 1580 (m), 1450 (m), 1330 (m), 1290 (m), 1270 (m), 1220 (m), 1205 (m), 1185 (m), 990 (m), 770 (m), 700 (m); EI-MS (70 eV) *m/z* (relative intensity): 342 (M⁺, 0.5), 237 (78), 219 (26), 118 (63), 105 (100), 77 (45); HRMS-EI (*m/z*): M⁺ calcd for C₂₄H₂₂O₂, 342.1620; found, 342.1620; Anal. Calcd for C₂₄H₂₂O₂: C, 84.18; H, 6.48. Found: C, 84.39; H, 6.72; GC analysis: 25.20 min (150 °C, 2 min, 10 °C/min, 260 °C, 17 min).

GC analysis for 3l

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
20	24	1	2	5	4
60	24	38	53	68	79
100	9	56	49	59	42

Table 4 Entry 6. To a mixture of Hf(OTf)₄ (9.67 mg, 12.48 μmol) and **2b** (570.69 mg, 2.5445 mmol) in CH₃NO₂ (2.496 mL), 1-(4-chlorophenyl)ethanol (398.78 mg, 2.5463 mmol) was added at room temperature. And the resulting mixture was stirred at 60 °C for 6 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, cyclohexane/dichloromethane = 5/1 to 1/2) to afford **3l** (733.5 mg, 79%).

2-[1-(4-Chlorophenyl)ethyl]-1,3-diphenylpropane-1,3-dione (3l) CA registry Number: [727401-27-6]. Colorless prism: mp 111–112 °C; TLC R_f = 0.46 (hexane/ethyl acetate = 3/1); ¹H NMR (300 MHz, CDCl₃) δ: 8.05–8.00 (2 H, m), 7.76–7.73 (2 H, m), 7.57–7.12 (10 H, m), 5.55 (1 H, d, *J* = 9.9 Hz), 4.06 (1 H, dq, *J* = 9.9 Hz, 6.9 Hz), 1.31 (3 H, d, *J* = 6.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 194.3, 194.0, 142.2, 136.8, 136.5, 133.5, 133.1, 132.1, 128.9, 128.7, 128.6, 128.4, 128.3, 64.8, 40.6, 20.4; IR (KBr) cm⁻¹: 1685 (s), 1590 (m), 1445 (m), 1280 (m), 1265 (m), 1220 (m), 1200 (m), 975 (m), 760 (m), 705 (m), 680 (m); EI-MS (70 eV) *m/z* (relative intensity): 362 (M⁺, 1), 257 (100), 105 (52), 77 (25); HRMS-EI (*m/z*): M⁺ calcd for C₂₃H₁₉O₂Cl, 362.1074, found, 362.1071; Anal. Calcd for C₂₃H₁₉ClO₂: C, 76.13; H, 5.28. Found: C, 76.18; H, 5.51; GC analysis: 21.72 min (150 °C, 2 min, 10 °C/min, 300 °C, 13 min).

GC analysis for 3m

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
60	20	6	14	21	23
100	20	51	67	65	65

Table 4 Entry 7. To a mixture of Hf(OTf)₄ (3.53 mg, 4.5562 μmol) and **2b** (205.54 mg, 0.91654 mmol) in CH₃NO₂ (0.911 mL), methyl 4-(1-hydroxyethyl)benzoate (165.00 mg, 0.91565 mmol) was added at room temperature. And the resulting mixture was stirred at 90 °C for 18.5 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, hexane/ethyl acetate = 7/3) to afford **3m** (231.6 mg, 65%).

Methyl 4-(3-benzoyl-4-oxo-4-phenyl-2-butyl)benzoate (3m), Colorless needles: mp 142–144 °C; TLC R_f = 0.54 (hexane/ethyl acetate = 7/3); ¹H NMR (300 MHz, CDCl₃) δ: 8.07–8.03 (2 H, m), 7.88–7.85 (2 H, m), 7.76–7.73 (2 H, m), 7.60–7.26 (8 H, m), 5.62 (1 H, d, *J* = 10.2 Hz), 4.14 (1 H, dq, *J* = 10.2 Hz, 6.9 Hz), 3.85 (3 H, s), 1.34 (3 H, d, *J* = 6.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 194.2, 193.9, 166.6, 149.1, 136.8, 136.5, 133.5, 133.1, 129.6, 128.8, 128.7, 128.4, 128.4, 127.6, 64.6, 52.0, 41.2, 20.3; IR (KBr) cm⁻¹: 2950 (m), 1720 (s), 1690 (s), 1600 (m), 1450 (m), 1440 (m), 1320 (m), 1295 (s), 1260 (s), 1230 (m), 1200 (m), 1120 (m), 970 (m), 760 (m), 710 (m), 685 (m); EI-MS (70 eV) *m/z* (relative intensity): 386 (M⁺, 0.4), 282 (20), 281 (100), 105 (61), 77 (21).; HRMS-EI (*m/z*): M⁺ calcd for C₂₅H₂₂O₄, 386.1518; found, 386.1514; Anal. Calcd for C₂₅H₂₂O₄: C, 77.70; H, 5.74. Found: C, 77.59; H, 5.69; GC analysis: 25.20 min (150 °C, 2 min, 10 °C/min, 300 °C, 13 min).

GC analysis for 3n

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
100	20	8	16	23	25
100	60	-	-	-	31
100	20	-	-	-	60 (2.5 mol% cat.)

Table 4 Entry 8. To a mixture of Hf(OTf)₄ (26.76 mg, 34.54 μ mol) and **2b** (319.60 mg, 1.4252 mmol) in CH₃NO₂ (1.382 mL), 1-(4-nitrophenyl)ethanol (239.5 mg, 1.4327 mmol) was added at room temperature. And the resulting mixture was stirred at 100 °C for 24 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 20/1 to 2/1) to afford **3n** (327.0 mg, 61%).

2-[1-(4-Nitrophenyl)ethyl]-1,3-diphenylpropane-1,3-dione (3n), Pale yellow prism: mp 100–103 °C; TLC R_f = 0.44 (hexane/ethyl acetate = 7/3); ¹H NMR (300 MHz, CDCl₃) δ : 8.08–8.04 (4 H, m), 7.77–7.74 (2 H, m), 7.63–7.26 (8 H, m), 5.61 (1 H, d, J = 10.2 Hz), 4.20 (1 H, dq, J = 10.2 Hz, 6.9 Hz), 1.36 (3 H, d, J = 6.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ : 193.9, 193.6, 151.5, 146.7, 136.6, 136.2, 133.7, 133.4, 128.9, 128.7, 128.6, 128.5, 128.3, 123.5, 64.5, 41.0, 20.3; IR (KBr) cm⁻¹: 1694 (s), 1599 (m), 1518 (s), 1448 (m), 1346 (s), 1270 (m), 1224 (m), 1201 (m), 978 (m), 859 (m), 712 (m), 688 (m); EI-MS (70 eV) m/z (relative intensity): 373 (M^+ , 0.2), 269 (10), 268 (58), 252 (14), 251 (39), 105 (100), 77 (53); HRMS-EI (m/z): M^+ calcd for C₂₃H₁₉NO₄, 373.1314; found, 373.1312; Anal. Calcd for C₂₃H₁₉NO₄: C, 73.98; H, 5.13; N, 3.75. Found: C, 74.22; H, 5.40; N, 3.51; GC analysis: 25.86 min (150 °C, 2 min, 10 °C/min, 300 °C, 17 min).

Ferrocenyl ethanol

Table 4 Entry 9. To a mixture of $\text{Hf}(\text{OTf})_4$ (1.95 mg, 2.52 μmol) and **2b** (112.88 mg, 0.5034 mmol) in CH_3NO_2 (0.503 mL), 1-ferrocenylethanol (115.81 mg, 0.5034 mmol) was added at $20\text{ }^\circ\text{C}$. And the resulting mixture was stirred at $20\text{ }^\circ\text{C}$ for 0.5 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 10/1 - 4/3) to afford **3o** (218.34 mg, 99%).

2-(1-ferrocenylethyl)-1,3-diphenylpropane-1,3-dione (3o**)**, Orange needles: $150\text{--}151\text{ }^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ : 7.86–7.81 (2 H, m), 7.72–7.66 (2 H, m), 7.54–7.41 (2 H, m), 7.40–7.26 (4 H, m), 5.28 (1 H, d, $J = 8.7\text{ Hz}$), 4.11 (5 H, s), 4.43–4.22 (1 H, m), 3.95 (2 H, t, $J = 2.1\text{ Hz}$), 3.85–3.80 (2 H, m) 1.44 (3 H, d, $J = 6.9\text{ Hz}$); ^{13}C NMR (100 MHz, CDCl_3) δ : 195.2, 194.1, 136.9, 136.8, 133.1, 132.8, 128.50, 128.50, 128.4, 28.3, 92.1, 69.2, 68.6, 67.4, 67.3, 65.8, 65.1, 35.3, 18.6; IR (KBr) cm^{-1} : 1695 (s), 1670 (m), 1600 (m), 1450 (m), 1290 (s), 1270 (m), 1230 (m), 1200 (m), 1190 (m), 1100 (m), 1000 (m), 830 (m), 770 (s), 710 (m), 695 (m); EI-MS (70 eV) m/z (relative intensity): 436 (M^+ , 9), 344 (100), 279 (15), 223 (32), 212 (76), 147 (16), 121 (13), 105 (23), 77 (15); HRMS-EI (m/z): M^+ calcd for $\text{C}_{27}\text{H}_{24}\text{O}_2\text{Fe}$, 436.1126; found, 436.1128; Anal. Calcd for $\text{C}_{27}\text{H}_{24}\text{O}_2\text{Fe}$: C, 74.32; H, 5.54. Found: C, 74.19; H, 5.71; GC analysis: The product **3o** decomposed at GC condition ($100\text{ }^\circ\text{C}$, 2 min, $10\text{ }^\circ\text{C}/\text{min}$, $300\text{ }^\circ\text{C}$, 13 min or $150\text{ }^\circ\text{C}$, 2 min, $10\text{ }^\circ\text{C}/\text{min}$, $300\text{ }^\circ\text{C}$, 8 min); HPLC: DAICEL CHIRALCEL OD-H, hexane/2-propanol = 9/1, 1 mL/min, 254 nm, 15.0 min, 17.9 min.

GC analysis for 3p

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
20	12.5	-	-	-	89
70	4	74	55	18	23
100	4	56	9	0	0

Table 4 Entry 10. To a mixture of Hf(OTf)₄ (3.62 mg, 4.67 μmol) and **2b** (209.47 mg, 0.9341 mmol) in CH₃NO₂ (0.934 mL), 4-methoxybenzylalcohol (130.52 mg, 0.9447 mmol) was added at room temperature. And the resulting mixture was stirred at 20 °C for 7 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, cyclohexane/dichloromethane = 1/1) to afford **3p** (286.0 mg, 89%).

2-(4-Methoxybenzyl)-1,3-diphenylpropane-1,3-dione (3p) CA registry Number: [29045-01-0]. Colorless prism: mp 96–97 °C; TLC R_f = 0.38 (hexane/ethyl acetate = 3/1); ¹H NMR (300 MHz, CDCl₃) δ: 7.91-7.87 (4 H, m), 7.56-7.38 (6 H, m), 7.16 (2 H, d, *J* = 8.1 Hz), 6.76 (2 H, d, *J* = 8.7 Hz), 5.48 (1 H, t, *J* = 6.8 Hz), 3.73 (1 H, s), 3.39 (2 H, d, *J* = 6.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 195.1, 158.1, 135.9, 133.2, 130.9, 129.8, 128.6, 128.4, 113.9, 59.4, 55.2, 34.5; IR (KBr) cm⁻¹: 1660 (s), 1580 (m), 1510 (m), 1440 (m), 1300 (m), 1240 (s), 1170 (m), 1030 (m), 820 (m), 760 (m), 740 (m), 680 (m); EI-MS (70 eV) *m/z* (relative intensity): 344 (M⁺, 2), 239 (100), 105 (21), 77 (15); HRMS-EI (*m/z*): M⁺ calcd for C₂₃H₂₀O₃, 344.1412, found, 344.1416; Anal. Calcd for C₂₃H₂₀O₃: C, 80.21; H, 5.85. Found: C, 80.21; H, 6.11; GC analysis: 22.05 min (150 °C, 2 min, 10 °C/min, 300 °C, 13 min).

GC analysis for 3q

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
100	5	22	33	37	34
100	24	27	36	38	33

Table 4 Entry 11. To a mixture of Hf(OTf)₄ (26.43 mg, 34.11 μmol) and **2b** (1.5300 g, 6.8137 mmol) in CH₃NO₂ (6.62 mL), benzylalcohol (737.11 mg, 6.8153 mmol) was added at room temperature. And the resulting mixture was stirred at 100 °C for 5 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, hexane/dichloromethane = 1/5) to afford a mixture of **3q** and impurity (1.3129 g). The mixture was purified by bulb-to-bulb distillation (240-250 °C/0.25 Torr) to give colorless liquid (732.3 mg, 34%) and viscous residue (580 mg). The distilled liquid solidified on standing, and the solid was recrystallized from cyclohexane to afford colorless prisms. (499.7 mg, 23%)

2-Benzyl-1,3-diphenylpropane-1,3-dione (3q) CA registry Number: [28918-09-4]. Colorless prisms: mp: 102–103 °C TLC R_f = 0.25 (cyclohexane/dichloromethane = 3/1); ¹H NMR (300 MHz, CDCl₃) δ: 7.90-7.85 (4 H, m), 7.64-7.02 (11 H, m), 5.52 (1 H, t, *J* = 6.6 Hz), 3.45 (2 H, d, *J* = 6.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 195.1, 138.9, 135.9, 133.3, 128.8, 128.7, 128.44, 128.44, 126.5, 59.1, 35.3; IR (KBr) cm⁻¹: 1696 (s), 1666 (s), 1593 (m), 1446 (m), 1350 (m), 1213 (s), 948 (m), 759 (m), 696 (m), 607 (m); EI-MS (70 eV) *m/z* (relative intensity): 314 (M⁺, 1), 209 (100), 131 (6), 105 (46), 77 (27); HRMS-EI (*m/z*): M⁺ calcd for C₂₂H₁₈O₂, 314.1307; found, 314.1309; GC analysis: 18.87 min (150 °C, 2 min, 10 °C/min, 300 °C, 13 min).

Scheme 2.

(*S*)-1-(4-methoxyphenyl)ethanol (**1a**) was prepared by the (*R*)-oxazaborolidine-catalyzed asymmetric borane reduction³ of 4'-methoxyacetophenone.

HPLC: DAICEL CHIRALPAK AD, hexane/2-propanol = 95/5, 1 mL/min, 254 nm

DL-1-(4methoxyphenyl)ethanol

11.7 min, 49.9%, 12.3 min 50.1%.

(*S*)-1-(4-methoxyphenyl)ethanol

11.9 min, 1.4%, 12.6 min 98.6%.

Scheme 2. 3b After a mixture of $\text{Hf}(\text{OTf})_4$ (2.68 mg, 3.46 μmol) and **2b** (155.14 mg, 0.6918 mmol) in CH_3NO_2 (0.692 mL) was stirred at 20 °C for 10 min, (*S*)-**1a** (101.33 mg, 0.6658 mmol) was added at room temperature (22 °C). And the resulting mixture was stirred at 20 °C for 7 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, hexane/ether = 7/3) to afford **3b** (236.05 mg, 99%). HPLC: DAICEL CHIRALPAK AD, hexane/2-propanol = 9/1, 0.5 mL/min, 254 nm

Table 4 entry 1. DL-3b

25.0 min, 49.9%, 31.0 min 50.1%.

Scheme 2. 3b

25.0 min, 49.5%, 31.0 min 50.5%.

Scheme 2

(*R*)-1-(4-nitrophenylethanol) was prepared by the (*S*)-oxazaborolidine-catalyzed asymmetric borane reduction³ of 4'-nitroacetophenone. HPLC: DAICEL CHIRALPAK AD, hexane/ethanol = 9/1, 0.5 mL/min, 254 nm

DL-1-(4-nitrophenyl)ethanol

18.9 min, 49.3%, 20.0 min 50.7%.

(*R*)-1-(4-nitrophenyl)ethanol

18.9 min, 98.5%, 21.1 min 1.5%.

Scheme 2. 3n To a mixture of $\text{Hf}(\text{OTf})_4$ (5.25 mg, 6.78 μmol) and **2b** (61.82 mg, 0.2757 mmol) in CH_3NO_2 (0.271 mL), (*R*)-1-(4-nitrophenyl)ethanol (45.99 mg, 0.2751 mmol) was added at room temperature. And the resulting mixture was stirred at 100 °C for 24 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, hexane/ethyl acetate = 1/1 then, hexane/diethyl ether = 1/1) to afford **3n** (60.0 mg, 58%). HPLC: DAICEL CHIRALCEL OD-H, hexane/2-propanol = 9/1, 1 mL/min, 254 nm

Table 4 entry 8. DL-3n

15.0 min, 49.5%, 20.5 min 50.5%.

Scheme 2. 3n

14.7 min, 49.3%, 20.0 min 50.7%.

Scheme 2

(*S*)-1-(ferrocenyl)ethanol was prepared by the (*R*)-oxazaborolidine-catalyzed asymmetric borane reduction³ of acetylferrocene. HPLC: DAICEL CHIRALPAK AD, hexane/ethanol = 10/1, 1 mL/min, 254 nm

DL-1-(ferrocenyl)ethanol

15.5 min, 50.0%, 16.6 min 50.0%.

(*S*)-1-(ferrocenyl)ethanol

15.5 min, 1.4%, 16.5 min 98.6%.

Scheme 2. 3o To a mixture of $\text{Hf}(\text{OTf})_4$ (0.77 mg, 0.99 μmol) and **2b** (44.97 mg, 0.2005 mmol) in CH_3NO_2 (0.199 mL), 1-ferrocenylethanol (46.21 mg, 0.2008 mmol) was added at 20 °C. And the resulting mixture was stirred at 20 °C for 0.5 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, hexane/ethyl acetate = 7/3) to afford **3o** (84.52 mg, 97%). $[\alpha]_D^{25.5} -25.9^\circ$ (c 1.690, CHCl_3); HPLC: DAICEL CHIRALCEL OD-H, hexane/2-propanol = 9/1, 0.5 mL/min, 254 nm

Table 4 Entry 9. DL-3o

15.0 min, 50.0%, 17.9 min 50.0%.

Scheme 2. 3o

15.0 min, 2.5%, 17.9 min 97.5%.

Scheme 3. Reaction of Allylic Alcohols

GC analysis for **9**

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
40	6	22	28	33	35
70	6	40	44	39	36
100	6	51	36	35	16

Scheme 3. To a mixture of La(OTf)₃ (2.08 mg, 3.55 μmol) and **2b** (155.20 mg, 0.6921 mmol) in CH₃NO₂ (0.710 mL), cinnamyl alcohol (**8**) (93.06 mg, 0.6935 mmol) was added at room temperature. And the resulting mixture was stirred at 100 °C for 8.5 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, hexane/ethyl acetate = 3/1) to afford **9** (122.0 mg, 52%).

(E)-1,3-Diphenyl-2-(3-phenyl-2-propenyl)propane-1,3-dione (9**)** CA registry Number: [329327-83-5]. Pale yellow prism: mp: 74–76; TLC R_f = 0.52 (hexane/ethyl acetate = 3/1); ¹H NMR (300 MHz, CDCl₃) δ: 8.00-7.80 (4 H, m), 7.60-7.09 (11 H, m), 6.47 (1 H, dt, *J* = 15.6, 1.2 Hz), 6.24 (1 H, dt, *J* = 15.6, 7.2 Hz), 5.35 (1 H, t, *J* = 6.9 Hz), 3.03 (2 H, td, *J* = 6.9, 1.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 195.2, 136.81, 135.81, 133.4, 132.3, 128.8, 128.4, 128.3, 127.2, 126.6, 126.0, 57.2, 33.1; IR (KBr) cm⁻¹: 3020 (m), 2920 (m), 1670 (s), 1600 (s), 1580 (s), 1500 (m), 1450 (m), 1320 (m), 1200 (m), 1080 (m), 970 (s), 940 (m), 790 (m), 750 (s), 700 (s); EI-MS (70 eV) *m/z* (relative intensity): 340 (M⁺, 3), 235 (100), 105 (33), 91 (22), 77 (21); HRMS-EI (*m/z*): M⁺ calcd for C₂₄H₂₀O₂, 340.1463; found, 340.1465; Anal. Calcd for C₂₄H₂₀O₂: C, 84.68; H, 5.92. Found: C, 84.57; H, 6.26; GC analysis: 28.48 min (100 °C, 2 min, 10 °C/min, 300 °C, 8 min); GC analysis: 23.53 min (150 °C, 2 min, 10 °C/min, 300 °C, 13 min).

GC analysis for 11

temp.(°C)	time (h)	yield (%) IS			
		La(OTf) ₃	Yb(OTf) ₃	Sc(OTf) ₃	Hf(OTf) ₄
40	6	46	75	84	84
70	6	82	73	53	36
100	6	45	29	11	0

Scheme 3. To a mixture of Sc(OTf)₃ (0.82 mg, 1.67 μ mol) and **2b** (72.73 mg, 0.333 mmol) in CH₃NO₂ (0.333 mL), 2-cyclohexenol (32.70 mg, 0.333 mmol) was added at room temperature. And the resulting mixture was stirred at 40 °C for 6 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, hexane/ethyl acetate = 5/1) to afford **11** (85.52 mg, 84%).

2-(2-Cyclohexenyl)-1,3-diphenylpropane-1,3-dione (11) CA registry Number: [173492-56-3]. Colorless needles: mp 109–110 °C; TLC R_f = 0.42 (hexane/ethyl acetate = 5/1); ¹H NMR (300 MHz, CDCl₃) δ : 8.01-7.96 (4 H, m), 7.58-7.39 (6 H, m), 5.78-5.39 (1 H, m), 5.54-5.48 (1 H, m), 5.27 (1 H, d, *J* = 10.2 Hz), 3.51-3.47 (1 H, m), 2.04-2.00 (2 H, m), 1.80-1.33 (4 H, m); ¹³C NMR (100 MHz, CDCl₃) δ : 194.9, 194.5, 137.0, 136.8, 133.3, 133.2, 129.2, 128.64, 128.64, 128.61, 128.57, 128.4, 62.6, 37.3, 27.5, 25.2, 21.3; IR (KBr) cm⁻¹: 2900 (m), 1680 (s), 1590 (m), 1580 (m), 1445 (m), 1270 (s), 1190 (m), 980 (m), 710 (m), 680 (m); EI-MS (70 eV) *m/z* (relative intensity): 304 (M⁺, 1), 199 (100), 105 (32), 77 (19); HRMS-EI (*m/z*): M⁺ calcd for C₂₁H₂₀O₂, 304.1463; found, 304.1457; Anal. Calcd for C₂₁H₂₀O₂: C, 82.86; H, 6.62. Found: C, 82.67; H, 6.88; GC analysis: 22.90 min (150 °C, 2 min, 10 °C/min, 260 °C, 17 min); GC analysis: 23.38 min (100 °C, 2 min, 10 °C/min, 300 °C, 1137 min).

Synthesis of symmetrical ether **12** for Equation 2.

Bis 1-(4-methoxyphenyl)ethyl ether (12**), diastereomixture** CA registry Number: [88288-58-8]. To a suspension of $\text{La}(\text{OTf})_3$ (30.10 mg, 51.36 μmol) in CH_3NO_2 (41 mL), 1-(4-methoxyphenyl)ethanol (1.5062 g, 9.8968 mmol) was added at room temperature. And the resulting mixture was stirred at $20\text{ }^\circ\text{C}$ for 3.5 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, toluene/ethyl acetate = 20/1) to afford **12** (1.262 g, 89% in 27% de).

Colorless oil: TLC R_f = 0.22 (hexane/ethyl acetate = 20/1); ^1H NMR (300 MHz, CDCl_3) δ : 7.25-7.17 (2 H, m), 7.25-7.17 (2 H, m), 6.91-6.79 (2 H, m), 6.91-6.79 (2 H, m), 4.46 (2 H, q, J = 6.6 Hz), 4.18 (2 H, q, J = 6.6 Hz), 3.80 (3 H, s), 3.77 (3 H, s), 1.43 (6 H, d, J = 6.6 Hz), 1.35 (6 H, d, J = 6.6 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ : 158.7, 158.5, 136.3, 136.0, 127.3, 127.3, 113.7, 113.5, 73.73, 73.69, 55.24, 55.24, 24.8, 22.9; IR (neat) cm^{-1} : 1611 (m), 1512 (s), 1246 (s), 1092 (s), 1038 (s), 831 (s); EI-MS (70 eV) m/z (relative intensity): 286 (M^+ , 13), 121 (9), 135 (100), 121 (9); HRMS-EI (m/z): M^+ calcd for $\text{C}_{18}\text{H}_{22}\text{O}_3$, 286.1569; found, 286.1565; Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_3$: C, 75.50; H, 7.74. Found: C, 75.53; H, 7.84; GC analysis: 19.12 min, 19.25 min (major) ($100\text{ }^\circ\text{C}$, 2 min, $10\text{ }^\circ\text{C}/\text{min}$, $300\text{ }^\circ\text{C}$, 13 min).

Equation 2

To a mixture of $\text{Yb}(\text{OTf})_3$ (3.59 mg, 5.79 μmol) and **2a** (119.28 mg, 1.1914 mmol) in CH_3NO_2 (1.158 mL), **12** (170.58 mg, 0.59567 mmol) was added at room temperature. And the resulting mixture was stirred at $50\text{ }^\circ\text{C}$ for 23 h. After the reaction mixture was filtered through a short silica gel pad with ethyl acetate, the filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC (silica gel, hexane/ethyl acetate = 7/3) to afford **3a** (243.0 mg, 87%).

NMR study for Enol Ratio of Dicarboxyl Compounds in Nitromethane- d_3

Appropriate amounts of dicarboxyl compounds were dissolved in nitromethane- d_3 (total volume, 0.60 mL). The NMR spectra were measured at 25 °C.

dicarboxyl compounds	mg	conc. mol/L	enol %	NMR signal* (δ)	
				keto	enol
2a	10.59	0.176	55	2.17	2.03
2b	8.85	0.0658	95	4.76	7.10
2c	2.68	0.0455	6	6.70	5.24
2d	10.25	0.149	34	1.25	1.85
4a	11.12	0.160	4	3.51	5.05
4b	11.79	0.102	13	1.24	1.33
4c	12.60	0.123	72	3.42	1.25
6a	10.34	0.133	11	2.18	1.91
6b	10.23	0.148	5	2.90-2.73	6.14
6b (70% in H ₂ O)	10.59	0.107	4	3.41	1.85

* Selected NMR signals for integration.

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DATIM MENUF OBNUC
 NON 300.40 MHz
 1H 130.00 KHz
 1150.00 Hz
 5.30 usec
 97.30 usec
 0.20000 msec
 1.0000 msec
 32768
 32768
 16
 1
 6006.01 Hz
 66.70 usec
 5.4559 sec
 1.5440 sec
 ACQTM
 PD
 ADBIT 16
 RGAIN 12
 BF 0.09 Hz
 T1 0.00
 T2 0.00
 T3 90.00
 T4 100.00
 EXMOD
 EXPCM
 IRNUC 1H
 IFR 300.40 MHz
 IRSET 130.00 KHz
 IRFIN 1150.00 Hz
 IRRPW 50 usec
 511
 CR409.als
 TH5
 SF 25.60 KHz
 LKSET 52.0 Hz
 LKFIN 200
 LKLEV 25
 LGAIN 135
 LKPHS 1475
 LKSIG 14 Hz
 CSPED
 FILDC
 FILDF

Wed Apr 25 12:52:03 2007
 NON
 1H
 300.40 MHz
 130.00 KHz
 1150.00 Hz
 5.30 usec
 97.30 usec
 0.20000 msec
 1.0000 msec
 32768
 32768
 16
 1
 6006.01 Hz
 66.70 usec
 5.4559 sec
 1.5440 sec
 ACQTM
 PD
 ADBIT 16
 RGAIN 12
 BF 0.09 Hz
 T1 0.00
 T2 0.00
 T3 90.00
 T4 100.00
 EXMOD
 EXPCM
 IRNUC 1H
 IFR 300.40 MHz
 IRSET 130.00 KHz
 IRFIN 1150.00 Hz
 IRRPW 50 usec
 511
 CR409.als
 TH5
 SF 25.60 KHz
 LKSET 52.0 Hz
 LKFIN 200
 LKLEV 25
 LGAIN 135
 LKPHS 1475
 LKSIG 14 Hz
 CSPED
 FILDC
 FILDF

3a

D:\Dicarbonyl\3a-DEPTT.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Sat Sep 24 18:11:51 2005
BCM
13C

100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
256
1
27322.40 Hz

14.65 usec
1.1993 sec
1.7940 sec

16
23
1.20 Hz
0.00
0.00
90.00
100.00

BCM
Bilevel.complete.decoupling.Set_IRRPW
1H

399.65 MHz
124.00 KHz
10500.00 Hz
45 usec

511
3a-DEPTT.als
TH5FG2

61.60 KHz
79.0 Hz
180
27
311
370
12 Hz

3a

KY336A

KY336A

S46

3a-C-KY336A

3b-H400-KY258B

D:\Dicarbonyl\3b-H400-KY258B.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Thu Nov 10 11:03:33 2005
NON
1H

399.65 MHz
124.00 KHz
10500.00 Hz
5.70 usec
72.15 usec
0.20000 msec
1.0000 msec
32768
32768
4
1
8000.00 Hz

50.00 usec
4.0960 sec
2.9010 sec

16
12
0.12 Hz
0.00
0.00
90.00
100.00

NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H

399.65 MHz
124.00 KHz
10500.00 Hz
45 usec

511
3b-H400-KY258B.als
TH5FG2

61.60 KHz
79.0 Hz
180
26
311
617
15 Hz

3b

D:\Dicarbonyl\3b-DEPTT-KY258B.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Thu Nov 10 11:23:58 2005
BCM
13C
100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
400
1
27322.40 Hz
14.65 usec
1.1993 sec
1.7940 sec

KY258B

PPM

KY258B

S48

BCM
Bilevel.complete.decoupling.Set_IRRPW
1H
399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511
3b-DEPTT-KY258B.als
TH5FG2
61.60 KHz
79.0 Hz
180
26
311
581
14 Hz

PPM

3b-DEPT-KY258B

3b

3c-H-KY274A

D:\Dicarbonyl\3c-H-KY274A.als

Mon Feb 28 16:21:27 2005
NON
1H

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6006.01 Hz
66.70 usec
5.4559 sec
1.5440 sec
16
25
0.09 Hz
0.00
0.00
90.00
100.00

NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H
300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
3c-H-KY274A.als
TH5
25.60 KHz
52.0 Hz
200
19
179
675
14 Hz

3c

Fri Sep 08 19:29:02 2006
BCM
13C

100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
1600
1

27322.40 Hz
14.65 usec
1.1993 sec
1.7940 sec

BCM
Bilevel,complete,decoupling:Set_JRRPW
1H

399.65 MHz
124.00 KHz
10500.00 Hz
45 usec

511
3c-DEPT.als
TH5FG2

61.60 KHz
79.0 Hz
180
27
293
755
13 Hz

3c

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

PPM

25

50

100

150

175

200

S50

3c

PPM

50

100

150

175

200

3c

18.13

30.25

32.60

55.33

76.68

77.08

77.32

114.18

121.75

128.24

135.14

158.16

194.92

3d-H-KY283A

D:\NMR-Data\NMR-KONNO\KY200-299\Ky283a.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Sat Feb 19 18:42:08 2005
NON
1H

300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6013.20 Hz

66.70 usec
5.4493 sec
1.5510 sec
16
19
0.09 Hz
0.00
0.00
90.00
100.00

NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H

300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
Ky283a.als
TH5

25.60 KHz
52.0 Hz
200
19
179
697
14 Hz

3d

D:\Dicarbonyl\3d-DEPT.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Thu Jan 12 17:27:23 2006
BCM
13C
100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
800
1
27322.40 Hz

KY283A

KY283A

S52

207.28
206.26
133.29
129.83
113.41
77.32
77.06
76.68
71.23
55.23
42.04
28.05
27.48
16.87
14.42

KY283A-2

3d

3a

D-#Dicarbonyl#3e-H.als

Tue Sep 12 19:35:43 2006
NON
1H
300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6006.01 Hz
66.70 usec
5.4559 sec
1.5440 sec
16
13
0.12 Hz
0.00
0.00
90.00
100.00
NON
NON: Single coupled: PW1_ACQTM_PD:1H,13C,1
1H
300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
3e-H.als
TH5
25.60 KHz
52.0 Hz
200
23
135
946
13 Hz

Wed Sep 13 13:19:55 2006
BCM
13C

100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
800
1
27322.40 Hz

14.65 usec
1.1993 sec
1.7940 sec

16
24
1.20 Hz
0.00
0.00
90.00
100.00

BCM
Bilevel,complete,decoupling:Set_JRRPW
1H

399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511

3e-DEPTT.als
TH5FG2

61.60 KHz
79.0 Hz
180
29
293
1450
11 Hz

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

3a

3a

S54

3e

3e

3f-H-KY-130B

D:\Dicarbonyl\3f-H-KY-130B.als

S55

Fri Mar 10 11:08:34 2006
BCM
13C

100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
400
1
27322.40 Hz

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU

FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4

EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

BCM
Bilevel.complete.decoupling.Set_IRRPW
1H
399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511
3f-DEPTT.als
TH5FG2
61.60 KHz
79.0 Hz
180
30
293
2148
11 Hz

3f

KY-181B

D:\Dicarbonyl\3g-H-KY-181B.als

Mon Sep 13 18:23:39 2004
NON
1H

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6013.20 Hz
66.70 usec
5.4493 sec
1.5510 sec
16
19
0.09 Hz
0.00
0.00
90.00
100.00

NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H

300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
3g-H-KY-181B.als
TH5
25.60 KHz
52.0 Hz
200
22
179
1267
14 Hz

3g

Thu Feb 24 01:12:55 2005
 BCM
 13C

100.40 MHz
 125.00 KHz
 10500.00 Hz
 6.20 usec
 18.88 usec
 0.20000 msec
 1.0000 msec
 32768
 32768
 400
 1
 27322.40 Hz

14.65 usec
 1.1993 sec
 1.7940 sec

BCM
 Bilevel.complete.decoupling.Set_IRRPW
 1H

399.65 MHz
 124.00 KHz
 10500.00 Hz
 45 usec
 511

3g-DEPTT.als
 TH5FG2

61.60 KHz
 79.0 Hz
 180
 25
 311
 711
 13 Hz

3g

DATIM
 MENUF
 OBNUC
 OFR
 OBSET
 OFBIN
 PW1
 DEADT
 PREDL
 IWT
 POINT
 SPO
 TIMES
 DUMMY
 FREQU
 FLT
 DELAY
 ACQTM
 PD
 ADBIT
 RGAIN
 BF
 T1
 T2
 T3
 T4
 EXMOD
 EXPCM
 IRNUC
 IFR
 IRSET
 IRFIN
 IRRPW
 IRATN
 DFILE
 SF
 LKSET
 LKFIN
 LKLEV
 LGAIN
 LKPHS
 LKSIG
 CSPED
 FILDC
 FILDF

KY276A

KY276A

S58

3d-DEPT-KY276A

3h-H-KY273A

D:\Dicarbonyl\3h-H-KY273A.als

Fri Feb 18 10:42:30 2005
NON
1H

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRSET
IRFIN
IRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6013.20 Hz
66.70 usec
5.4493 sec
1.5510 sec
16
19
0.12 Hz
0.00
0.00
90.00
100.00
NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H
300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
3h-H-KY273A.als
TH5
25.60 KHz
52.0 Hz
200
18
170
518
13 Hz

D:\Dicarbonyl\3h-DEPTT.als

Wed Mar 08 14:25:14 2006
BCM
13C
100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
512
1
27322.40 Hz
14.65 usec
1.1993 sec
1.7940 sec
16
24
1.20 Hz
0.00
0.00
90.00
100.00
BCM
Bilevel,complete,decoupling,Set_IRRPW
1H
399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511
3h-DEPTT.als
TH5FG2
61.60 KHz
79.0 Hz
180
27
293
698
13 Hz

S60

KY702A

3h-DEPT-KY702A

3h

3i-H-KY354A

D:\Dicarbonyl\3i-H-KY354A.als

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

C:\WINNMR98\TEMPDATA\Auto3DEPT_1
KY354A2
Tue Apr 19 19:35:51 2005
13C
DEPT

100.40 MHz
125.00 KHz
10500.0 Hz
32768
27322.4 Hz
128
1.199 sec
1.794 sec
12.2 us
24.3 C
CDCL3
77.00 ppm
1.20 Hz
24

3j-H-KY351A

D:\NMR-Data\NMR-KONNO\KY300-399\KY351A.als

Mon Apr 18 10:17:45 2005
NON
1H
300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6006.01 Hz
66.70 usec
5.4559 sec
1.5440 sec
16
16
0.09 Hz
0.00
0.00
90.00
100.00
NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H
300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
KY351A.als
TH5
25.60 KHz
52.0 Hz
200
19
179
731
14 Hz
DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRSET
IRFIN
IRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

3j
with small amount of EtOAc

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

C:\WINNMR98\TEMPDATA\Auto3DEPT_135_E1_FT.als
KY354A-2
Tue Apr 19 18:51:06 2005
13C
DEPT
100.40 MHz
125.00 KHz
10500.0 Hz
32768
27322.4 Hz
128
1.199 sec
1.794 sec
12.2 us
1H
24.5 c
CDCl3
77.00 ppm
1.20 Hz
24

3k-H-KY280A

D:\Dicarbonyl\3k-H-KY280A.als

3k

DFILE C:\WINNMR98\TEMPDATA\Aut
COMNT ortho-Me+DBM
DATIM Fri Jun 24 17:13:59 2005
OBNUC 13C
EXMOD DEPT
OBFREQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 27322.4 Hz
SCANS 128
ACQTM 1.199 sec
PD 1.794 sec
PWL 12.2 us
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 24

3k

3I-H-KY307A

D:\NMR-Data\NMR-KONNO\KY300-399\KY307A.als

DATIM 0.00
MNUF 1.26
OBNUC 1.28
OFR 1.51
OBSET 3.95
OBFIN 3.98
PW1 3.98
DEADT 4.00
PREDL 4.01
IWT 4.02
POINT 4.03
SPO 4.06
TIMES 5.51
DUMMY 5.54
FREQU 6.97
FLT 6.98
DELAY 6.98
ACQTM 6.99
PD 7.00
ADBIT 7.01
RGAIN 7.02
BF 7.03
T1 7.07
T2 7.08
T3 7.09
T4 7.10
EXMOD 7.12
EXPCM 7.13
IRNUC 7.16
IFR 7.17
IRSET 7.18
IRFIN 7.19
IRPW 7.20
IRATN 7.20
DFILE 7.21
SF 7.22
LKSET 7.23
LKFIN 7.24
LKLEV 7.31
LGAIN 7.32
LKPHS 7.32
LKSIG 7.34
CSPED 7.35
FILDC 7.37
FILDF 7.37

Wed Mar 09 17:46:04 2005
NON
1H

300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
8
1
6006.01 Hz
66.70 usec
5.4559 sec
1.5440 sec
16
16
0.09 Hz
0.00
0.00
90.00
100.00

NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H

300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
KY307A.als
TH5
25.60 KHz
52.0 Hz
200
20
179
920
14 Hz

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Thu Feb 09 11:01:22 2006
BCM
13C
100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
512
1
27322.40 Hz
14.65 usec
1.1993 sec
1.7940 sec

BCM
Bilevel,complete,decoupling:Set_IRRPW
1H
399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511
31-DEPTT.als
TH5FG2
61.60 KHz
79.0 Hz
180
27
293
271
11 Hz

KY242A

KY242A

S68

KY242A

3m-H400-KY339A-2

D:\Dicarbonyl\3m-H400-KY339A-2.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Thu Apr 07 12:38:30 2005
NON
1H

399.65 MHz
124.00 KHz
10500.00 Hz
72.15 usec
5.70 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
8000.00 Hz

50.00 usec
4.0960 sec
2.9010 sec
16
14
0.12 Hz
0.00
0.00
90.00
100.00

NON
NON: Single coupled: PW1_ACQTM_PD:1H,13C,1
1H

399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511
3m-H400-KY339A-2.als
TH5FG2
61.60 KHz
79.0 Hz
180
26
311
939
12 Hz

D:\Dicarbonyl\3m-DEPT-KY339A-2.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Thu Apr 07 12:51:44 2005
BCM
13C

100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
256
1
27322.40 Hz

14.65 usec
1.1993 sec
1.7940 sec

16
24
1.20 Hz
0.00
0.00
90.00
100.00

BCM
Bilevel.complete.decoupling.Set_IRRPW
1H

399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511

3m-DEPT-KY339A-2.als
TH5FG2

61.60 KHz
79.0 Hz
180
26
311
887
11 Hz

3m-DEPT-KY339A-2

KY339A-2

KY339A-2

S70

3n-H-KY299B

D:\Dicarbonyl\3m-H-Ky299b.als

DATIM 0.00
MNUF
OBNUC
OFR
OBSET
OBFN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Thu Mar 03 10:50:59 2005
NON
1H
300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6006.01 Hz
66.70 usec
5.4559 sec
1.5440 sec
16
15
0.12 Hz
0.00
0.00
90.00
100.00
NON
NON: Single coupled: PW1_ACQTM_PD:1H,13C,1
1H
300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
3m-H-Ky299b.als
TH5
25.60 KHz
52.0 Hz
200
20
179
915
14 Hz

with small amount of EtOAc

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Thu Feb 09 11:56:58 2006
BCM
13C

100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
512
1
27322.40 Hz

14.65 usec
1.1993 sec
1.7940 sec

PPM

KY299B

KY299B

S72

KY299B

3o-ferro+DBM

D:\NMR-Data\NMR-NOI\#Compound\3o-ferro+DBM\#Auto1NON_E1_FT.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Fri Sep 08 13:05:25 2006
NON
1H

399.65 MHz
124.00 KHz
10500.00 Hz
5.70 usec
72.15 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
8000.00 Hz

50.00 usec
4.0960 sec
2.9010 sec

16
14
0.12 Hz
0.00
0.00
90.00
100.00

NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H

399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511

Auto1NON_E1_FT.als
TH5FG2

61.60 KHz
79.0 Hz
180
27
293
711
12 Hz

D:\Dicarbonyl\30-DEPT.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Fri Sep 08 13:45:47 2006
BCM
13C
100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
800
1
27322.40 Hz

14.65 usec
1.1993 sec
1.7940 sec
16
24
1.20 Hz
0.00
0.00
90.00
100.00

BCM
Bilevel,complete,decoupling:Set_IRRPW
1H
399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511

30-DEPT.als
TH5FG2
61.60 KHz
79.0 Hz
180
27
293
697
12 Hz

30-ferro+DBM

30-ferro+DBM

S74

30-ferro+DBM

3p-H-KY331AA

D:\Dicarbonyl\3p-H-KY331AA.als

DATIM
MNUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Tue Mar 15 12:16:47 2005
NON
1H

300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
8
1
6006.01 Hz

66.70 usec
5.4559 sec
1.5440 sec
16
15
0.12 Hz
0.00
0.00
90.00
100.00

NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H

S75

3p-H-KY331AA.als
TH5

300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511

3p

with small amount of EtOAc

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

C:\WINNMR98\TEMPDATA\Auto3DEPT_135_E1_FT.als
KY331A-2
Thu Apr 14 13:30:34 2005
13C
DEPT
100.40 MHz
125.00 KHz
10500.0 Hz
32768
27322.4 Hz
128
1.199 sec
1.794 sec
12.2 us
1H
24.9 C
CDCL3
77.00 ppm
1.20 Hz
24

S76

3q

D:\Dicarbonyl\3q-1H.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IFR
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Tue Feb 13 14:06:27 2007
NON
1H

399.65 MHz
124.00 KHz
10500.00 Hz
5.70 usec
72.15 usec
0.20000 msec
1.0000 msec
32768
32768
16
1

8000.00 Hz
50.00 usec
4.0960 sec
2.9010 sec
16
15
0.12 Hz
0.00
0.00
90.00
100.00

NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H

399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511
3q-1H.als
TH5FG2

61.60 KHz
79.0 Hz
180
27
293
669
12 Hz

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Tue Feb 13 14:46:48 2007
BCM
13C
100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
800
1
27322.40 Hz

14.65 usec
1.1993 sec
1.7940 sec
16
24
1.20 Hz
0.00
0.00
90.00
100.00

BCM
Bilevel,complete.decoupling:Set_IRRPW
1H
399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511
Auto2BCM_E1_FT.als
TH5FG2
61.60 KHz
79.0 Hz
180
27
293
631
11 Hz

3q

3q

S78

3q

5a-H-KY234A

D:\Dicarbonyl\5a-H-KY234A.als

Sat Jan 08 17:28:15 2005
NON
1H
300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6013.20 Hz
66.70 usec
5.4493 sec
1.5510 sec
16
14
0.12 Hz
0.00
0.00
90.00
100.00
NON
NON: Single coupled: PW1_ACQTM_PD:1H,13C,1
1H
300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
5a-H-KY234A.als
TH5
25.60 KHz
52.0 Hz
200
19
179
774
13 Hz

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Diastereo mixture

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

C:\WINNMR98\TEMPDATA\Auto3DEPT_1
KY234A-2
Thu Apr 14 14:43:57 2005
13C
DEPT
100.40 MHz
125.00 KHz
10500.0 Hz
32768
27322.4 Hz
256
1.199 sec
1.794 sec
12.2 us
1H
24.8 C
CDCL3
77.00 ppm
1.20 Hz
24

Diastereomixture

5b-H-TO2-column

D:\Dicarbonyl\5b-H-TO2-COLUMN.als

Partially separated diastereomixture.

KY266

D:\Dicarbonyl\5b-H-KY266.als

Tue Feb 08 17:34:52 2005
NON
1H

300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
8
1
6013.20 Hz
66.70 usec
5.4493 sec
1.5510 sec
16
15
0.12 Hz
0.00
0.00
90.00
100.00

NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H

582

DATM
MENUC
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IFR
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

0.0000
0.0761
1.3672
1.3440
1.2347
1.2121
0.9349
0.9110
0.8878

4.6431
4.6083
4.5967
4.5607
4.2163
4.1925
4.1693
4.1465
3.8646
3.8505
3.8420
3.8267
3.8188
3.8029
3.7822
3.7559
3.6924

8.1017
8.0766
8.0495
7.8244
7.6150
7.5918
7.5674
7.5087
7.4831
7.3854
7.3598
7.3347
7.2560
7.2431
7.2150
7.1418
7.1137
6.8273
6.8260
6.7198
6.6917

PPM
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5

D:\Dicarbonyl\5b-DEPT-KY266.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Fri Jan 13 14:29:57 2006
BCM
13C
100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
600
1
27322.40 Hz
14.65 usec
1.1993 sec
1.7940 sec

PPM

KY266

S83

BCM
Bileval.complete.decoupling.Set_IRRPW
1H
399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511
5b-DEPT-KY266.als
TH5FG2
61.60 KHz
79.0 Hz
180
27
300
741
10 Hz

KY266

Diastereomixture

5c-diastereomixture-H-KY529-1A

D:\Dicarbonyl\5c-diastereomixture-H-KY529-1A.als

DATIM 300.40 MHz
 MENUF 130.00 KHz
 OBNUC 1150.00 Hz
 OFR 5.30 usec
 OBIN 97.30 usec
 PW1 0.20000 msec
 DEADT 1.0000 msec
 PREDL 32768
 IWT 16
 POINT 1
 SPO 6006.01 Hz
 TIMES 1
 DUMMY 66.70 usec
 FREQU 5.4559 sec
 DELAY 1.5440 sec
 ACQTM 16
 PD 12
 ADBIT 0.12 Hz
 RGAIN 0.00
 BF 0.00
 T1 90.00
 T2 100.00
 T3
 T4
 EXMOD
 EXPCM
 IRNUC
 IFR 300.40 MHz
 IRSET 130.00 KHz
 IRFIN 1150.00 Hz
 IRRPW 50 usec
 IRATN 511
 DFILE 5c-diastereomixture-H-KY529-1A.als
 SF TH5
 LKSET 25.60 KHz
 LKFIN 52.0 Hz
 LKLEV 200
 LGAIN 22
 LKPHS 179
 LKSIG 1246
 CSPED 14 Hz
 FILDC
 FILDF

5c-diastereomer-A-H-KY223AA2

D:\NMR-Data\NMR-KONNO\KY200-299\Ky223aa2.als

DATIM 0.00
MENUF 0.07
OBNUC
OFR
OBSET 300.40 MHz
OBFIN 130.00 KHz
PW1 1150.00 Hz
DEADT 97.30 usec
PREDL 0.20000 msec
IWT 1.0000 msec
POINT 32768
SPO 32768
TIMES 16
DUMMY 1
FREQU 6013.20 Hz
FLT
DELAY 66.70 usec
ACQTM 5.4493 sec
PD 1.5510 sec
ADBIT 16
RGAIN 24
BF 0.09 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD
EXPCM
IRNUC
IRF 300.40 MHz
IRSET 130.00 KHz
IRFIN 1150.00 Hz
IRPW 50 usec
IRATN 511
DFILE Ky223aa2.als
SF TH5
LKSET 25.60 KHz
LKFIN 52.0 Hz
LKLEV 200
LGAIN 21
LKPHS 179
LKSIG 1024
CSPED 12 Hz
FILDC
FILDF

Mon Dec 13 11:27:59 2004
NON
1H

Diastereomer A

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDG
FILDG

Wed Jan 11 15:44:41 2006
BCM
13C
100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
400
1
27322.40 Hz
14.65 usec
1.1993 sec
1.7940 sec
16
23
1.20 Hz
0.00
0.00
90.00
100.00
BCM
Bileval.complete.decoupling.Set_IRRPW
1H
399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511
5c-diastereomer-A-DEPT-KY223AA.als
TH5FG2
61.60 KHz
79.0 Hz
180
29
300
1474
12 Hz

PPM

KY223AA

S86

PPM

KY223AA

Diastereomer A

5c-diastereomer-B-H-KY223AB

D:\Dicarbonyl\5c-diastereomer-B-H-KY223AB.als

D:\Dicarbonyl\5c-diastereomer-B-DEPT-KY223AB.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Thu Jan 12 14:24:02 2006
BCM
13C
100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
400
1
27322.40 Hz
14.65 usec
1.1993 sec
1.7940 sec

PPM

KY223AB

885

BCM
Bileval.complete.decoupling.Set_IRRPW
1H
399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511
5c-diastereomer-B-DEPT-KY223AB.als
TH5FG2
61.60 KHz
79.0 Hz
180
26
300
324
11 Hz

PPM

206.65
157.82
170.54
133.77
130.07
112.69
77.32
77.00
76.68
64.42
60.78
54.85
41.67
41.53
35.47
27.39
22.60
17.83
14.00

5c-diastereomer-B-DEPT-KY223AB

5c

Diastereomer B

PPM

5d-H-KY241B

D:\Dicarbonyl\5d-H-KY241B.als

DATIM MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Tue Jan 18 15:40:18 2005
NON
1H

300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6013.20 Hz
66.70 usec
5.4493 sec
1.5510 sec
16
19
0.09 Hz
0.00
0.00
90.00
100.00

NON
NON: Single coupled: PW1_ACQTM_PD: 1H, 13C, 1
1H

300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
5d-H-KY241B.als
TH5
25.60 KHz
52.0 Hz
200
20
179
822
13 Hz

5d

Diastereomixture

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Thu Mar 09 18:28:26 2006
BCM
13C

100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
512
1
27322.40 Hz

14.65 usec
1.1993 sec
1.7940 sec

16
23
1.20 Hz
0.00
0.00
90.00
100.00

BCM
Bilevel.complete.decoupling.Set_IRRPW
1H

399.65 MHz
124.00 KHz
10500.00 Hz
45 usec

511
5d-DEPT-KY738.als
TH5FG2

61.60 KHz
79.0 Hz
180
27
293
629
14 Hz

5d

Diastereomixture

KY738

KY738

065

KY738

5e-H-KY238-1A2

D:\Dicarbonyl\5e-H-KY238-1A2.als

Sat Jan 22 12:52:28 2005
NON
1H
300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
8
1
6013.20 Hz
66.70 usec
5.4493 sec
1.5510 sec
16
24
0.09 Hz
0.00
0.00
90.00
100.00
NON
NON: Single coupled: PW1_ACQTM_PD:1H,13C:1
1H
300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
5e-H-KY238-1A2.als
TH5
25.60 KHz
52.0 Hz
200
22
179
1665
14 Hz
DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

D:\Dicarbonyl\5e-DEPT.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Wed Mar 08 13:28:17 2006
BCM
13C
100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
400
1
27322.40 Hz
14.65 usec
1.1993 sec
1.7940 sec

BCM
Bilevel,complete,decoupling:Set_IRRPW
1H
399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511
5e-DEPT.als
TH5FG2
61.60 KHz
79.0 Hz
180
26
293
504
10 Hz

5bb

5bb

S92

5e-DEPT

5f-H-diastereomixture

D:\Dicarbonyl\5f-H-diastereomixture.als

Diastereomixture

5f-diastereomer-A-H-TS34-23-TLC-ue

D:\NMR-Data\NMR-NOI\Compound\TS34-23-TLC-ue\1H.als

Mon May 22 17:16:26 2006
NON
1H

399.65 MHz
124.00 KHz
10500.00 Hz
5.70 usec

72.15 usec
0.20000 msec
1.0000 msec
32768
32768

16
1
8000.00 Hz

50.00 usec
4.0960 sec
2.9010 sec

16
17
0.12 Hz
0.00
0.00
90.00
100.00

NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H

399.65 MHz
124.00 KHz
10500.00 Hz
45 usec

511
1H.als
TH5FG2

61.60 KHz
79.0 Hz
180
27
293
1176
12 Hz

5f
Diastereomer A

D:\NMR-Data\NMR-NOI\Compound\TS34-23-TLC-ue\DEPT.als

DATIM
MENUF
OBNUC

OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
PW1 6.20 usec
DEADT 18.88 usec
PREDL 0.20000 msec
IWT 1.0000 msec
POINT 32768
SPO 32768
TIMES 512
DUMMY 1
FREQU 27322.40 Hz
FLT
DELAY 14.65 usec
ACQTM 1.1993 sec
PD 1.7940 sec

TS34-23-TLC-ue

TS34-23-TLC-ue

965

EXMOD
EXPCM
IRNUC

IRF 399.65 MHz
IRSET 124.00 KHz
IRFIN 10500.00 Hz
IRPW 45 usec
IRATN 511
DFILE
SF TH5FG2
LKSET 61.60 KHz
LKFIN 79.0 Hz
LKLEV 180
LGAIN 27
LKPHS 293
LKSIG 832
CSPED 11 Hz
FILDC
FILDF

126.66
127.81
128.70
141.97
170.31
206.08

TS34-29-TLC-sita

13.96
16.90
22.55
26.83
30.09
41.86
42.56
61.12
65.30
76.68
77.00
77.32

Diastereomer A

5f-diastereomer-B-H-TS34-29-TLC-sita

D:\NMR-Data\NMR-NOUI\Compound\TS34-29-TLC_sita\1H.als

S97

Diastereomer B

D:\Dicarbonyl\5f-DEPT-TS34-29-TLV-sita.als

5f-diastereomer-B-DEPT-TS34-29-TLC-sita

5f

Diastereomer B

7a-H-KY239A

D:\Dicarbonyl\7a-H-KY239A.als

DATIM MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDf

Tue Jan 18 19:41:34 2005
NON
1H

300.40 MHz
130.00 KHz
1150.00 Hz
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6013.20 Hz
66.70 usec
5.4493 sec
1.5510 sec
16
24
0.12 Hz
0.00
0.00
90.00
100.00

NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H

695

300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
7a-H-KY239A.als
TH5
25.60 KHz
52.0 Hz
200
18
179
543
14 Hz

7a

Diastereomixture

D:\Dicarbonyl\7a-DEPT-KY472-A.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Thu Jan 12 16:27:54 2006
BCM
13C
100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
400
1
27322.40 Hz

14.65 usec
1.1993 sec
1.7940 sec

PPM

200 175 150 125 100 75 50 25

KY472A

KY472A

S100

EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

BCM
Bilevel.complete.decoupling.Set_IRRPW
1H
399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511
7a-DEPT-KY472-A.als
TH5FG2
61.60 KHz
79.0 Hz
180
27
300
918
8 Hz

200 175 150 125 100 75 50 25

167.39
158.11
135.52
135.05
128.29
128.09
113.99
113.59
77.32
77.09
76.68
65.56
55.21
40.02
39.43
37.82
37.51
36.31
35.89
27.16
27.03
22.12
19.74

KY472A

7a

Diastereomixture

7b-H-KY323C

D:\Dicarbonyl\7b-H-KY323C.als

Mon Mar 14 12:49:19 2005
NON
1H
300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
8
1
6006.01 Hz
66.70 usec
5.4559 sec
1.5440 sec
16
17
0.31 Hz
0.00
0.00
90.00
100.00
NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H
300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
7b-H-KY323C.als
TH5
25.60 KHz
52.0 Hz
200
19
179
766
14 Hz

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

7b
Diastereomixture

D:\Dicarbonyl\7b-DEPT-KY323C.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELTA
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRFR
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Wed Jan 11 14:34:53 2006
BCM
13C
100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
400
1
27322.40 Hz

14.65 usec
1.1993 sec
1.7940 sec
16
24
1.20 Hz
0.00
0.00
90.00
100.00

BCM
Bileval.complete.decoupling.Set_IRRPW
1H
399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511

7b-DEPT-KY323C.als
TH5FG2

61.60 KHz
79.0 Hz
180
27
300
385
13 Hz

7b-DEPT-KY323C

207.89
206.92
167.81
167.48
158.19
158.13
134.77
134.60
127.94
113.97
113.74
77.32
77.00
76.68
69.29
69.13
55.19
55.16
42.40
40.64
31.22
30.48
26.55
26.33
20.58
19.58

S102

KY323C

7b

Diastereomixture

D:\Dicarbonyl\7c-DEPT-KY240C.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Wed Jan 11 15:05:21 2006
BCM
13C
100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
400
1
27322.40 Hz
14.65 usec
1.1993 sec
1.7940 sec

PPM

KY240C

S104

BCM
Bileval.complete.decoupling.Set_IRRPW
1H
399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511
7c-DEPT-KY240C.als
TH5FG2
61.60 KHz
79.0 Hz
180
26
300
388
7 Hz

KY240C

7c

Diastereomixture

7d-H-(CR383B)

D:\Dicarbonyl\7d-H-CR383.als

Tue Sep 12 10:37:25 2006
NON
1H

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

0.00

1.26
1.28
1.30
1.32
1.82
2.23
2.57
2.58
2.83
2.85
3.28
3.30
3.31
3.32
3.33
3.33
3.35
3.36
3.46
3.48
3.48
3.49
3.50
3.51
3.52
3.54
3.58
3.59
3.60
3.65
3.68

5.91

6.45
7.17
7.18
7.19
7.19
7.20
7.21
7.21
7.22
7.23
7.27
7.28
7.30
7.31

16.50

0.98

1.49

3.70
4.09

4.78

3.24

3.00

4.80

1.64

0.95

1.94

NON
1H

EXMOD
EXPCM
IRNUC

0.00

0.12 Hz

0.00

0.00

90.00

100.00

NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1

399.65 MHz

124.00 KHz

10500.00 Hz

45 usec

511

7d-H-CR383.als

TH5FG2

61.60 KHz

79.0 Hz

180

26

293

720

11 Hz

7d

Diastereomixture

D:\Dicarbonyl\7d-DEPT-CR383B.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDG
FILDG

Tue Sep 12 11:57:37 2006
BCM
13C
100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
1600
1
27322.40 Hz
14.65 usec
1.1993 sec
1.7940 sec

PPM

7d(CR383B)

S106

BCM
Bileval.complete.decoupling.Set_IRRPW
1H
399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511
7d-DEPT-CR383B.als
TH5FG2
61.60 KHz
79.0 Hz
180
26
293
701
11 Hz

7d(CR383B)

7d

Diastereomixture

9-H-KY265A-2-2

D:\Dicarbonyl\9-H-KY265A-2-2.als

D:\Dicarbonyl\9-DEPT-471.als

Wed Dec 27 12:17:55 2006
BCM
13C

100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
800
1
27322.40 Hz

14.65 usec
1.1993 sec
1.7940 sec
16
24
1.20 Hz
0.00
0.00
90.00
100.00

BCM
Bileval,complete,decoupling:Set_IRRPW
1H

399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511
9-DEPT-471.als
TH5FG2
61.60 KHz
79.0 Hz
180
29
293
1454
13 Hz

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

471-9

PPM

471-9

S108

PPM

471-9

KY226B-A2

D:\Dicarbonyl\11-H-KY226-B-A2.als

DATIM 1.36
 MENUF 1.37
 OBNUC 1.39
 OFR 1.39
 OBFIN 1.40
 PW1 1.40
 DEADT 1.42
 PREDL 1.42
 IWT 1.57
 POINT 1.59
 SPO 1.60
 TIMES 1.61
 DUMMY 1.62
 FREQU 1.70
 FLT 1.71
 DELAY 1.71
 ACQTM 1.72
 PD 1.73
 ADBIT 1.73
 RGAIN 1.75
 BF 1.76
 T1 1.77
 T2 1.78
 T3 1.79
 T4 2.00
 EXMOD 2.01
 EXPCM 2.01
 IRNUC 2.02
 IFR 2.03
 IRSET 2.17
 IRFIN 3.46
 IRRPW 3.47
 IRATN 3.48
 DFILE 3.48
 SF 3.49
 LKSET 3.50
 LKFIN 3.50
 LKLEV 5.27
 LGAIN 5.29
 LKPHS 5.49
 LKSIG 5.50
 CSPED 5.52
 FILDC 5.52
 FILDf 5.71
 5.71
 5.72
 5.73
 5.74
 5.75
 7.26
 7.41
 7.43
 7.45
 7.52
 7.52
 7.53
 7.53
 7.54
 7.54
 7.55
 7.56
 7.56
 7.57
 7.98
 7.98
 7.99
 8.00
 8.00

399.65 MHz
 124.00 KHz
 10500.00 Hz
 5.70 usec
 72.15 usec
 0.20000 msec
 1.0000 msec
 32768
 32768
 8
 1
 8000.00 Hz
 50.00 usec
 4.0960 sec
 2.9010 sec
 16
 16
 0.12 Hz
 0.00
 0.00
 90.00
 100.00
 NON-Single coupled:PW1_ACQTM_PD:1H,13C,1
 1H
 399.65 MHz
 124.00 KHz
 10500.00 Hz
 45 usec
 511
 11-H-KY226-B-A2.als
 TH5FG2
 61.60 KHz
 79.0 Hz
 180
 27
 311
 1306
 12 Hz

11

D:\Dicarbonyl\11-DEPT-KY226-B-A2.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
256
1
27322.40 Hz
14.65 usec
1.1993 sec
1.7940 sec
16
24
1.20 Hz
0.00
0.00
90.00
100.00
100.00

BCM
Bilevel.complete.decoupling.Set_IRRPW
1H
399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511
11-DEPT-KY226-B-A2.als
TH5FG2
61.60 KHz
79.0 Hz
180
27
311
1271
11 Hz

11

S110

12-H

D:\Dicarbonyl\12-1H(300).als

S111

Tue Sep 12 19:40:26 2006
NON
1H
300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
16
6006.01 Hz
1
66.70 usec
5.4559 sec
1.5440 sec
16
12
0.12 Hz
0.00
0.00
90.00
100.00
NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H
300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
12-1H(300).als
TH5
25.60 KHz
52.0 Hz
200
23
135
1246
13 Hz

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRSET
IRFIN
IRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

0.00
0.00

1.33
1.36
1.42
1.44

3.19

3.77
3.80
4.15
4.17
4.19
4.21
4.43
4.45
4.47
4.49

6.80
6.81
6.81
6.83
6.84
6.85
6.87
6.88
6.89
6.90
6.91
7.18
7.18
7.20
7.21
7.23
7.24

3.00
1.45

2.42
3.82

1.52

0.99

5.29

5.32

Diastereomixture

Thu Sep 14 11:48:21 2006
BCM
13C
100.40 MHz
125.00 KHz
10500.00 Hz
6.20 usec
18.88 usec
0.20000 msec
1.0000 msec
32768
32768
800
1
27322.40 Hz
14.65 usec
1.1993 sec
1.7940 sec
16
24
1.20 Hz
0.00
0.00
90.00
100.00
BCM
Bilevel,complete,decoupling:Set_IRRPW
1H
399.65 MHz
124.00 KHz
10500.00 Hz
45 usec
511
12-DEPT.als
TH5FG2
61.60 KHz
79.0 Hz
180
26
293
538
11 Hz

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

12(MO14)

12(MO14)

S112

12(MO14)

12

Diastereomixture

2,6-dimethylphenylethanol

D:\NMR-Data\NMR-NOJI\Compound\2,6-dimethylphenylethanol.als

Fri Jan 12 16:45:17 2007
NON
1H
300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6006.01 Hz
66.70 usec
5.4559 sec
1.5440 sec
16
20
0.12 Hz
0.00
0.00
90.00
100.00
NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H
300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
2,6-dimethylphenylethanol.als
TH5
25.60 KHz
52.0 Hz
200
24
191
1119
13 Hz

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IFR
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

KY287

D:\NMR-Data\NMR-KONNO\KY200-299\KY287.als

Mon Feb 21 12:12:45 2005
NON
1H

300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6013.20 Hz
66.70 usec
5.4493 sec
1.5510 sec
16
15
0.09 Hz
0.00
0.00
90.00
100.00

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
NON:1H

300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511

KY287.als
TH5

25.60 KHz
52.0 Hz
200
19
179
653
14 Hz

S114

ferrocenylethanol

D:\NMR-Data\NMR-NOJI\Compound\199\ferrocenylethanol.als

Fri Jan 12 16:50:37 2007
NON
1H

300.40 MHz
130.00 KHz
1150.00 Hz
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6006.01 Hz
66.70 usec
5.4559 sec
1.5440 sec
16
20
0.12 Hz
0.00
0.00
90.00
100.00

NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1

300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511

ferrocenylethanol.als
TH5
25.60 KHz
52.0 Hz
200
24
191
1163
14 Hz

with small amount of dimeric ether
See next page.

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

HT24-C

D-#Dicarbonyl#Fc-ether (264)Ht24-C.als

Wed Apr 24 17:38:44 2002
NON
1H

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IFR
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKPIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

0.0000

1.5003
1.4789
1.4447
1.4233

4.4581
4.4361
4.4312
4.4148
4.4105
4.3885
4.3659
4.2297
4.2261
4.2218
4.2096
4.1925
4.1528
4.1308
4.0960

7.2517

2.003
3.000

1.634

(2a) 2,4-pentanedione (25.1C)-2

D:\Dicarbonyl\EnolRatio\2a) 2,4-pentanedione (25.1C)-2.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Thu May 25 12:54:30 2006
NON
1H

300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6006.01 Hz

66.70 usec
5.4559 sec
1.5440 sec
16
15
1.20 Hz
0.00
0.00
90.00
100.00

NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H

300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
(2a) 2,4-pentanedione (25.1C)-2.als
TH5

25.50 KHz
17.0 Hz
200
20
141
1262
14 Hz

2a

-4.45

0.00

2.24
2.17
2.03
1.96
1.81

3.64

4.34
4.34
4.33

5.62

S117

6.00

4.93

1.30

0.86

0.37

PPM

-4.00

-3.00

-2.00

-1.00

0.00

1.00

2.00

3.00

4.00

5.00

6.00

(2) dibenzoylmethane (26.1C)

D:\Dicarbonyl\EnolRatio\2b) dibenzoylmethane (26.1C).als

DATIM 300.40 MHz
MENUF 130.00 KHz
OBNUC 1150.00 Hz
OFR 5.30 usec
OBFIN 97.30 usec
PW1 0.20000 msec
DEADT 1.0000 msec
PREDL 32768
IWT 16
POINT 1
SPO 6006.01 Hz
TIMES 1
DUMMY 16
FREQU 66.70 usec
FLT 5.4559 sec
ACQTM 1.5440 sec
PD 16
ADBIT 16
RGAIN 1.20 Hz
BF 0.00
T1 0.00
T2 90.00
T3 100.00
T4
EXMOD NON
EXPCM NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
IRNUC 1H
IFR 300.40 MHz
IRSET 130.00 KHz
IRFIN 1150.00 Hz
IRRPW 50 usec
IRATN 511
DFILE (2b) dibenzoylmethane (26.1C).als
SF th5
LKSET 25.50 KHz
LKFIN 17.0 Hz
LKLEV 180
LGAIN 15
LKPHS 139
LKSIG 1560
CSPED 14 Hz
FILDC
FILDF

(03) 1,3-cyclopentanedione (25.1C)

D-#Dicarbonyl#EnolRatio#(2c) 1,3-cyclopentanedione (25.1C)-2.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IFR
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Thu May 25 12:47:49 2006
NON
1H

300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1

6006.01 Hz
66.70 usec
5.4559 sec
1.5440 sec
16
18
1.20 Hz
0.00
0.00
90.00
100.00

NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H

300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511

(2c) 1,3-cyclopentanedione (25.1C)-2.als
TH5

25.50 KHz
17.0 Hz
200
20
141
939
14 Hz

2c

(4) 3-methyl-2,4-pentanedione (25.5C)

D:\Dicarbonyl\EnolRatio\2d) 3-methyl-2,4-pentanedione (25.5C).als

DATIM
MNUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Thu May 25 11:00:12 2006
NON
1H

300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6006.01 Hz
66.70 usec
5.4559 sec
1.5440 sec
16
15
1.20 Hz
0.00
0.00
90.00
100.00

NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1

300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511

(2d) 3-methyl-2,4-pentanedione (25.5C).als
th5

25.50 KHz
17.0 Hz
180
15
139
1339
14 Hz

-3.54

0.00

4.34
4.34
4.33
3.89
3.86
3.83
3.81
3.78
3.61
2.38
2.26
2.19
2.17
2.14
2.11
2.02
2.00
1.96
1.85
1.49
1.38
1.37
1.32
1.26
1.23

PPM

(5) methyl acetoacetate(25.1C)-2

D:\Dicarbonyl\EnolRatio\4a) methyl acetoacetate(25.1C)-2.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Thu May 25 19:07:42 2006
NON
1H

300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6006.01 Hz
66.70 usec
5.4559 sec
1.5440 sec
16
15
1.20 Hz
0.00
0.00
90.00
100.00

NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H
300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
(4a) methyl acetoacetate(25.1C)-2.als
TH5
25.50 KHz
17.0 Hz
200
20
141
1380
13 Hz

4a

(4b) ethyl benzoylacetate (25.0C)

D-#Dicarbonyl#EnolRatio#(4b) ethyl benzoylacetate (25.0C).als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Thu May 25 11:19:04 2006
NON
1H

300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6006.01 Hz
66.70 usec
5.4559 sec
1.5440 sec
16
17
1.20 Hz
0.00
0.00
90.00
100.00

NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H

300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511

(4b) ethyl benzoylacetate (25.0C).als
th5

25.50 KHz
17.0 Hz
180
15
139
1320
13 Hz

D:¥Dicarbonyl¥EnolRatio¥(4c) ethyl 2-oxocyclohexanecarboxylate (25.1°C).als

DATIM MENUF OBNUC
OFR OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSGI
CSPED
FILDC
FILDF

NON: Single.coupled:PW1_ACQTM_PD:1H,13C,1

EXMOD
EXPCM
IRNUC
IFR
IRSET
IRFIN
IRRPW

TH5
(4c) ethyl 2-oxocyclohexanecarboxylate (25.1C).

DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

4C

(6a) N,N-dimethylacetamide (25.2C)-4

D:\Dicarbonyl\EnolRatio\6a) N,N-dimethylacetamide (25.2C)-4.als

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

Fri May 26 14:01:30 2006
NON
1H

300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6006.01 Hz

66.70 usec
5.4559 sec
1.5440 sec
16
15
0.12 Hz
0.00
0.00
90.00
100.00

NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H

300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511

(6a) N,N-dimethylacetamide (25.2C)-4.als
TH5

25.50 KHz
17.0 Hz
200
20
141
945
13 Hz

(6b)-N-methylacetamide dry (25.3C)

D:\NMR-Data\NMR-NOUI\Compound\6b)-N-methylacetamide dry.als

Sat Jan 13 17:27:12 2007
NON
1H
300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
8
1
6006.01 Hz
66.70 usec
5.4559 sec
1.5440 sec
16
15
0.12 Hz
0.00
0.00
90.00
100.00
NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H
300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
(6b)-N-methylacetamide dry.als
TH5
25.50 KHz
17.0 Hz
200
20
135
1886
12 Hz

DATIM
MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
POINT
SPO
TIMES
DUMMY
FREQU
FLT
DELAY
ACQTM
PD
ADBIT
RGAIN
BF
T1
T2
T3
T4
EXMOD
EXPCM
IRNUC
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

anhydrous

dimethyl malonate CD3NO2 25.2C

D:\NMR-Data\NMR-NOUI\Compound\dimethyl malonate CD3NO2 25.2C.als

Sat Jan 13 17:49:53 2007

DATIM MENUF
OBNUC
OFR
OBSET
OBFIN
PW1
DEADT
PREDL
IWT
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SPO
TIMES
DUMMY
FREQU
FLT
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ACQTM
PD
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RGAIN
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T1
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EXMOD
EXPCM
IRNUC
IRF
IRSET
IRFIN
IRRPW
IRATN
DFILE
SF
LKSET
LKFIN
LKLEV
LGAIN
LKPHS
LKSIG
CSPED
FILDC
FILDF

NON
1H
300.40 MHz
130.00 KHz
1150.00 Hz
5.30 usec
97.30 usec
0.20000 msec
1.0000 msec
32768
32768
16
1
6006.01 Hz
66.70 usec
5.4559 sec
1.5440 sec
16
14
0.12 Hz
0.00
0.00
90.00
100.00
NON
NON:Single.coupled:PW1_ACQTM_PD:1H,13C,1
1H
300.40 MHz
130.00 KHz
1150.00 Hz
50 usec
511
dimethyl malonate CD3NO2 25.2C.als
TH5
25.50 KHz
17.0 Hz
200
20
135
1562
13 Hz

0.0104
-0.0006
-0.0116

2.0925

3.3440
3.4044
3.4471
3.4703
3.6733
3.6990
3.7185
3.7380
3.7416
3.7630
3.9618
4.3247
4.3314
4.3375
4.3442
4.3509
4.3582
4.3662

S127

PPM