Supporting Information

for

Dynamic kinetic resolution of benzoins by enzyme-metal combo catalysis.

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1. ***Materials***

Lipase TL® from *Pseudomonas stutzeri* was a generous gift from Meito & Sangyo Co, Ltd®. Shvo's catalyst (1-Hydroxytetraphenylcyclopentadienyl(tetraphenyl-2,4-cyclopentadien-1-one)-μ-hydrotetracarbonyldiruthenium (II), 98%) was obtained from Strem Chemicals Inc. (Newburyport, MA, USA).

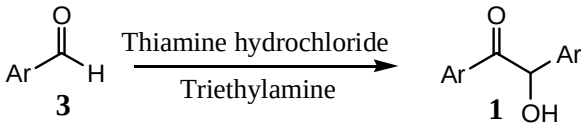
2. ***Analytical methods***

HPLC analysis were performed with a chiral column Chiracel OD (cellulose carbamate, 25 cm x 0.46 cm i. d) at room temperature, using HPLC (mobile phase of n-hexane/ 2-propanol, 90/10 at a flow rate of 0.8 mL/min).

NMR spectra were recorded on a Bruker AC-250. Chemical shifts (δ) are reported in parts per million (ppm) relative to $CHCl_3$ (^1H: δ 7.27 ppm) and $CDCl_3$ (^{13}C: δ 77.0 ppm).

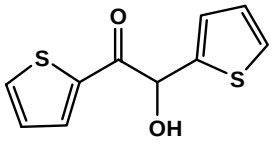
Column chromatography purifications were conducted on silica gel 60 (40-63 μm). TLC was carried out on aluminium sheets precoated with silica gel; the spots were visualized under UV light (λ=254 nm).

3. ***Synthesis of 2,2´-Thenoin (R,S-1d) and 3,3´-Thenoin (R,S-1e)***



3	**Ar**	1
3a: 2-Thiophenecarboxaldehyde	Ar = **2-Thienyl-**	**1d**: 2-Thenoin
3b**: 3-Thiophenecarboxaldehyde**	**Ar** = 3-Thienyl-	**1e**: 3-Thenoin

3. 1. Synthesis of 2-thenoin [2-hydroxy-1,2-di(thiophen-2-yl)ethanone], (R,S)-1d.

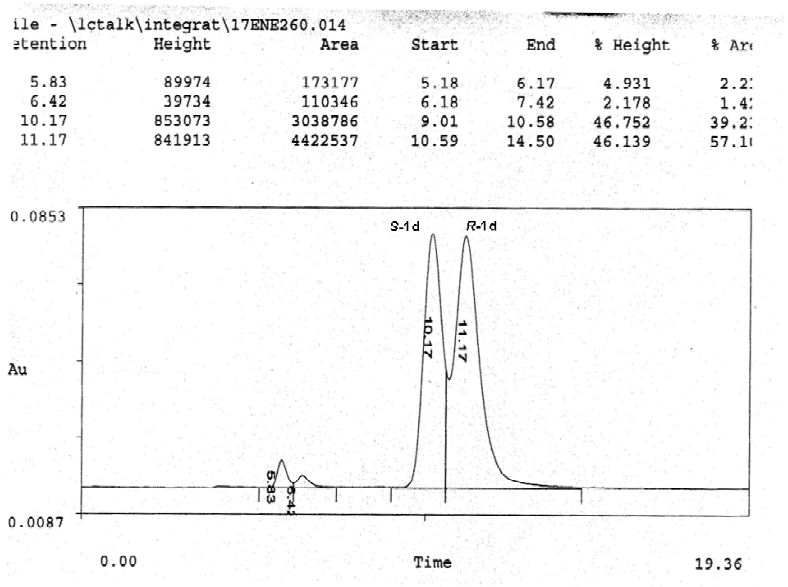


Thiamine hydrochloride (1.686 g, 5 mmol) was dissolved in absolute ethanol (30 mL) in a round bottom flask and triethylamine (4.2 mL, 30mmol) and 2-thiophenecarboxaldehyde were added (8.9 mL, 100mmol). The mixture was stirred at room temperature, under argon atmosphere. The solution presented a dark green color, turning to red in 15 minutes. The reaction progress was followed by TLC (n-hexane/ 2-propanol, 7/2 (v/v); **3a**, R_f = 0.25; **1d**, R_f = 0.09). After 24 hours the product started to precipitate. The mixture was filtered and the white solid collected (10.75 g, 48 mmol) was washed with cold ethanol (48% yield).

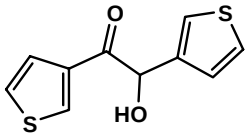
^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.79 (1H, dd, *J*=3.8 Hz, *J*=1.0 Hz), 7.75 (1H, dd, *J*=4.9 Hz, *J*=1.1 Hz), 7.34 (1H, dd, *J*=5.9 Hz, *J*=1.1 Hz), 7.15 (1H, dd, *J*=4.9 Hz), 7.13 (1H, dddd, *J*=3.5 Hz, *J*=1.2 Hz, *J*=0.6Hz), 7.01 (1H, dd, *J*=5.1 Hz, *J*=3.5 Hz), 6.07 (1H, s), 4.41 (1H, 2d, *J*=1.4 Hz, *J*=0.8 Hz). **^{13}C NMR** (63 MHz, $CDCl_3$) δ (ppm): 190.3,

142.4, 139.6, 135.8, 134. , 128.8, 127.6 , 127.3, 127.2, 71.3. Anal. Calcd. for $C_{10}H_8O_2S_2$: C, 53.53; H, 3.59; S, 28.59. Found: C, 53.58; H, 3.62; S, 28.56.

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8 mL/min): retention time **(*R*)-1d**= 11.17 min, **(*S*)-1d**= 10.17 min.



3. 2. ***Synthesis of 3-thenoin [(2-hydroxy-1,2-di(thiophen-3-yl)ethanone]*** **(R,S)-*1e.***



3-thenoin was synthesized by the same method as for 2-thenoin, using 3-thiophenecarboxaldehyde (**3b**) as substrate. The evolution of the reaction was followed by TLC (n-hexane/2-propanol, 7/2 (v/v); **3b**, R_f = 0.45; **1e** R_f = 0.25). The reaction time was 24 hours, and 9.18 g of **1e** (41 mmol) were collected (41% yield).

^{1}**H NMR** (250 MHz, $CDCl_3$) δ: 4.34 (1H, d, *J*= 6,0 Hz), 5.84 (1H, d, *J*= 6.0 Hz), 6.99 (1H, dd, *J*= 4.9 Hz, *J*= 1.2 Hz), 7.28 (1H, d, *J*= 2.8 Hz), 7.3 (1H, dd, *J*= 2.9 Hz, *J*= 0.7 Hz), 7.33 (1H, dd, *J*= 2.7 Hz, *J*= 1.1 Hz), 7.51 (1H, dd, *J*= 5.3 Hz, *J*= 1.1 Hz), 8.04 (1H,

dd, *J*= 2.8 Hz, *J*= 1.2 Hz). **^{13}C RMN** (63 MHz, $CDCl_3$) δ: 72.4, 124.2, 124.2, 126.5, 127.0, 127.2, 134.2, 192.3. Anal. Calcd. for $C_{10}H_8O_2S_2$: C, 53.55; H, 3.59; S, 28.59. Found: C, 53.52; H, 3.92; S, 27.36.

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8 mL/min): retention time **(*R*)-1e**= 12.64 min, **(*S*)-1e**= 10.72 min.

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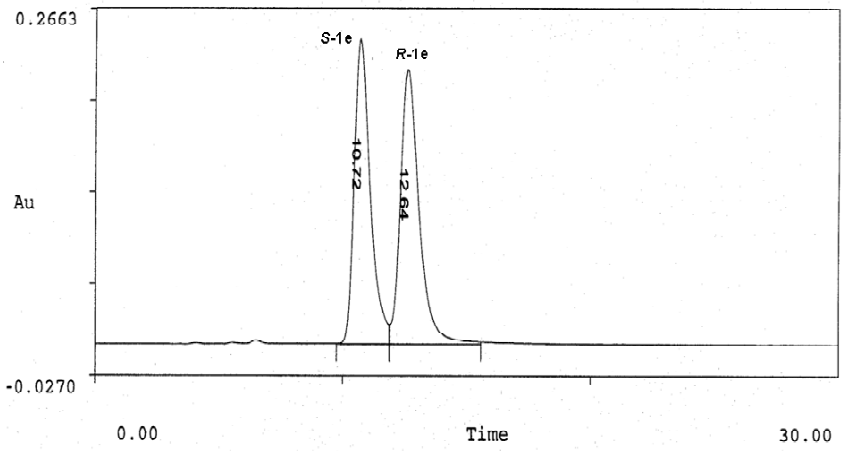
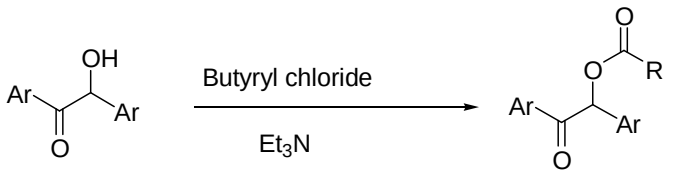
Retention	Height	Area	Start	End	% Height	% Ar
10.72	2662420	11987064	9.76	11.89	52.632	48.6
12.64	2396114	12669785	11.90	15.60	47.368	51.3



***4. Synthesis of butyric esters of benzoins: 2-oxo-1,2-diphenylethyl butyrate (R,S-2b), 1,2-di(furan-2-yl)-2-oxoethyl butyrate (R,S-2d), 2-oxo-1,2-di(thiophen-2-yl)ethyl butyrate (R,S-2g), 2-oxo-1,2-di(thiophen-3-yl)ethyl butyrate (R,S-2h), 1,2-bis(4-methoxyphenyl)-2-oxoethyl butyrate (R,S-2i), 1,2-bis(4-ethoxyphenyl)-2-oxoethyl butyrate (R,S-2j)*:**

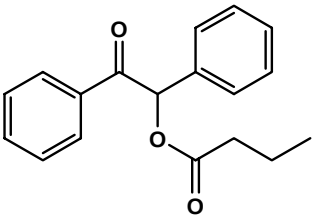
General procedure:



(*R*,*S*)-1 **(*R*,*S*)-2**

1 was dissolved in dichloromethane and triethylamine (1.1 equiv.) and butyryl chloride (1.5 equiv.) were added. The mixture was stirred at room temperature. After 15 hours the product was purified by silica-gel column chromatography (n-hexane/ethyl acetate 5/1 (v/v))

4. 1: 2-oxo-1,2-diphenylethyl butyrate (*R*,*S*-2b) (44% yield)



^{1}H NMR (250 MHz, $CDCl_3$): 7.97 (2H, dd, *J*=8.3, *J*=2.0 Hz), 7.96 (2H, dd, *J*=8.3, *J*=1.5 Hz), 7.57 (1H, t, *J*=1.3 Hz), 7.54 (1H, t, *J*=2.4 Hz), 7.51 (1H, m), 7.48 (1H, d, *J*=1.9 Hz), 7.45 (1H, dd, *J*=1.4, *J*=2.0 Hz), 7.42 (1H, m), 7.39 (1H, dd, *J*=1.9, *J*=2.0 Hz), 7.37 (1H, d, *J*=1.9 Hz), 6.89(1H, s), 2.54 (1H, c, *J*=7.6 Hz), 2.42 (1H, c, *J*=7.6 Hz), 1.74 (2H, sex, *J*=7.4 Hz), 1.0 (3H, t, *J*=7.4 Hz). **^{13}C NMR** (63 MHz, $CDCl_3$) δ (ppm): 194.37, 173.62, 135.10, 134.10, 133.86, 129.67, 129.51, 129.51, 112.80, 76.92, 36.27, 18.80, 14.03. Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.59; H, 6.43. Found: C, 75.44; H, 6.23.

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8 mL/min): retention time **(*R*)-2b**= 5.04 min, **(*S*)-2b**= 5.55 min.

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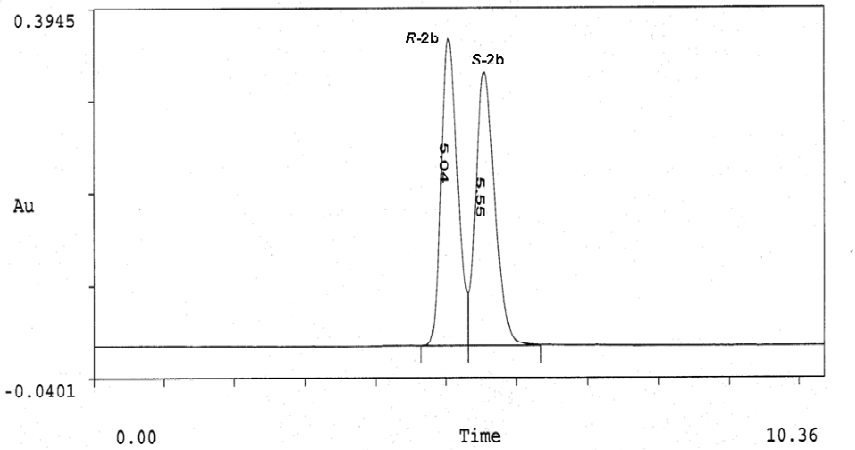
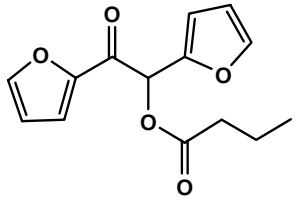
Retention	Height	Area	Start	End	% Height	% Ar
5.04	3944607	6314216	4.64	5.31	52.940	48.8
5.55	3506420	6598577	5.32	6.34	47.060	51.1

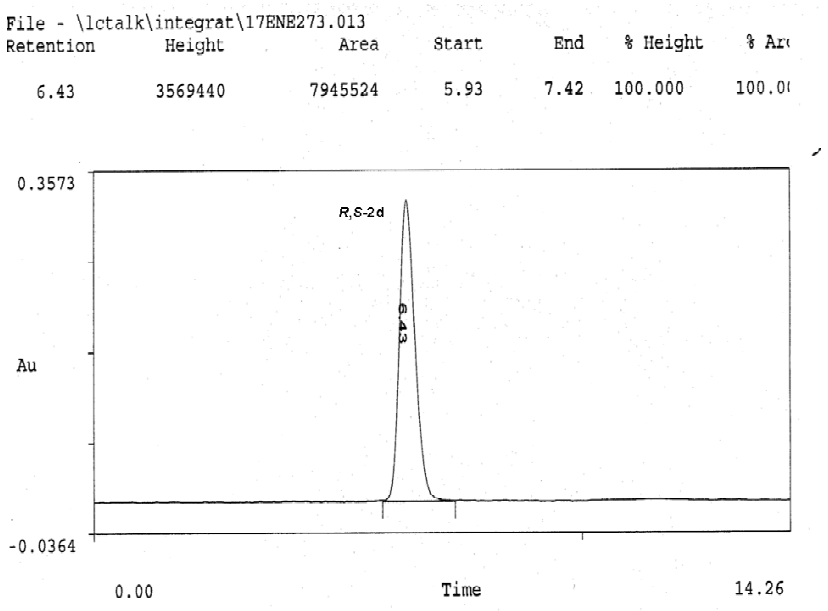


4. 2: 1,2-di(furan-2-yl)-2-oxoethyl butyrate (*R,S*-2d) (67% yield)

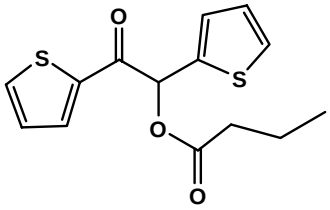


^{1}H NMR (250 MHz, $CDCl_3$): 7.50 (1H, dd, *J*=1.7 Hz, *J*=0.7 Hz), 7.38 (1H, dd, *J*=1.8 Hz, *J*=0.8 Hz), 7.20 (1H, dd, *J*=3.5 Hz, *J*=0.7 Hz), 6.9 (1H, s), 6.45 (1H, dd, *J*=3.6 Hz, *J*=1.7 Hz), 6.43 (1H, dd, *J*=3.3, *J*=0.4 Hz), 2.39 (1H, t, *J*=7.4 Hz), 2.37 (1H, t, *J*=7.5 Hz), 1.73 (2H, sex, *J*=7.4 Hz), 0.99 (3H, t, *J*=7.4 Hz). **^{13}C NMR** (63 MHz, $CDCl_3$) δ (ppm): 178.8, 171.8, 149.2, 146.1, 145.5, 143.1, 118.1, 111.4 , 110.6, 110.0, 69.1, 34.5, 17.3, 12.5. Anal. Calcd. for $C_{14}H_{14}O_5$: C, 64.12; H, 5.38. Found: C, 62.83; H, 5.29.

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8 mL/min): retention time: **(*R,S*)-2d**= 6.43 min.



4. 3: 2-oxo-1,2-di(thiophen-2-yl)ethyl butyrate (*R*,*S*-2g) (86% yield).



^{1}H NMR (250 MHz, $CDCl_3$): 7.84 (1H, dd, *J*=3.8 Hz, *J*=1.0 Hz), 7.70 (1H, dd, *J*=4.9 Hz, *J*=1.1 Hz), 7.4 (1H, dd, *J*=5.1 Hz, *J*=1.2 Hz), 7.40 (1H, dd, *J*=5.1 Hz, *J*=1.2 Hz), 7.21 (1H, ddd, *J*=3.6, *J*=1.1, *J*=0.5, Hz), 7.13 (1H, dd, *J*=4.93 Hz, *J*=3.9 Hz), 7.03 (1H, dd, *J*=5.2 Hz, *J*=3.5 Hz), 6.9 (1H, s), 2.49 (1H, t, *J*=7.7 Hz), 2.47 (1H, t, *J*=7.3 Hz), 1.73 (2H, sex, *J*=7.4 Hz), 0.99 (3H, t, *J*=7.4 Hz). **^{13}C NMR** (63 MHz, $CDCl_3$) δ (ppm): 185.9, 173.3, 140.7, 135.9, 135.2, 133.8, 129.2, 128.7, 128.4, 127.7, 73.2, 36.2, 18.7, 14.0. Anal. Calcd. for $C_{14}H_{14}O_3S_2$: C, 57.12; H, 4.79; S, 21.78. Found: C, 56.26; H, 4.64; S, 21.30.

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8 mL/min): retention time: **(*R*)-2g**= 6 min, **(*S*)-2g**= 6.64 min.

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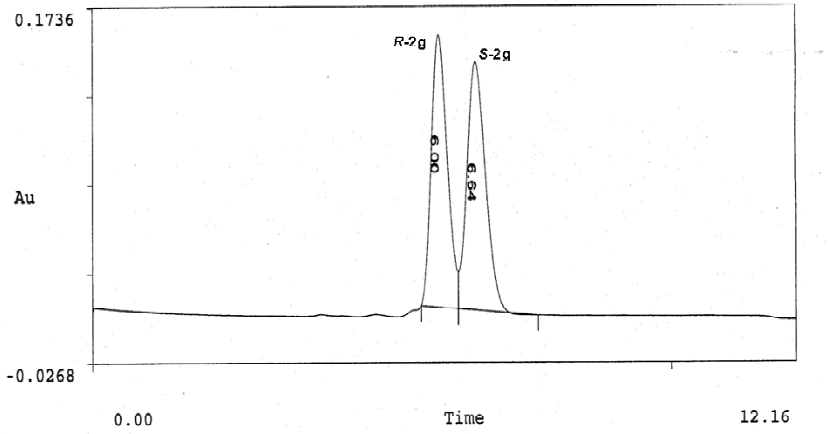
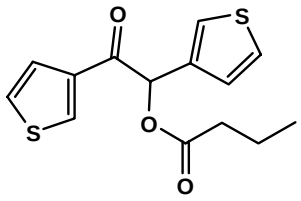
Retention	Height	Area	Start	End	% Height	% Ar
6.00	1739521	3327790	5.69	6.33	52.407	48.5
6.64	1579715	3521815	6.34	7.71	47.593	51.4



4. 4: 2-oxo-1,2-di(thiophen-3-yl)ethyl butyrate (*R*,*S*-2h) (89% yield)



^{1}H NMR (250 MHz, $CDCl_3$): 8.02 (1H, dd, *J*=2.9 Hz, *J*=1.3 Hz), 7.45 (1H, dd, *J*=5.1 Hz, *J*=1.3 Hz), 7.35 (1H, ddd, *J*=2.9 Hz, *J*=1.3 Hz, *J*=0.5 Hz), 7.25 (1H, dd, *J*=5 Hz, *J*=4 Hz), 7.21 (1H, dd, *J*=5, *J*=2.9 Hz), 7.06 (1H, dd, *J*=5 Hz, *J*=1.3 Hz), 6.9 (1H, s), 2.37 (1H, t, *J*=7.5 Hz), 2.36 (1H, t, *J*=7.3 Hz), 1.62 (2H, sex, *J*=7.4 Hz), 0.89 (3H, t, *J*=7.4 Hz). **^{13}C NMR** (63 MHz, $CDCl_3$) δ (ppm): 188.1, 173.4, 139.2, 134.8, 133.7, 127.7, 127.4, 127.3, 126.8, 126.0, 74.3, 36.2, 18.8, 14.0. Anal. Calcd. for $C_{14}H_{14}O_3S_2$: C, 57.12; H, 4.79; S, 21.78. Found: C, 56.09; H, 4.69; S, 21.43.

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8 mL/min): retention time: **(*R*)-2h**= 5.92 min, **(*S*)-2h**= 6.50 min.

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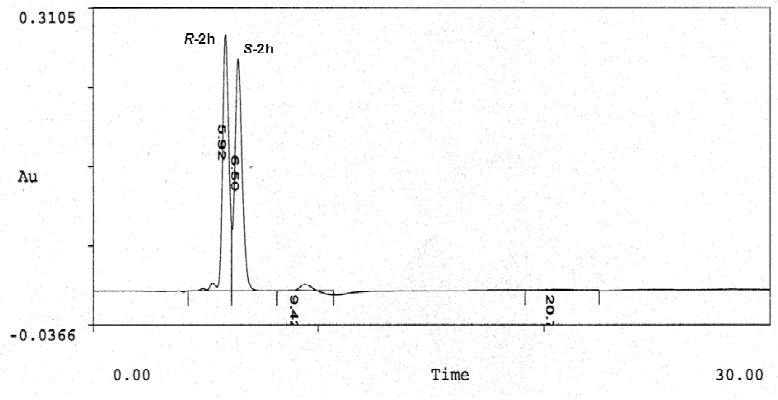
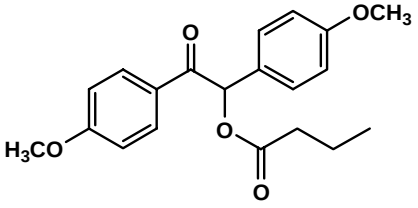
Retention	Height	Area	Start	End	% Height	% Ar
5.92	3095434	5936883	4.25	6.17	52.494	46.8
6.50	2719124	6412933	6.18	8.17	46.112	50.5
9.42	72473	238797	8.18	10.67	1.229	1.8
20.75	9708	93670	19.17	22.42	0.165	0.7

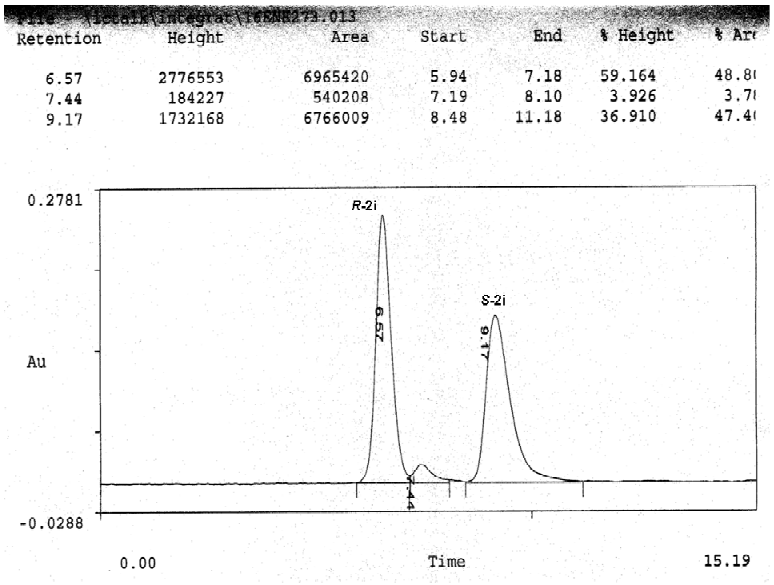


4. 5: 1,2-bis(4-methoxyphenyl)-2-oxoethyl butyrate (*R*,*S*-2i) (85% yield)

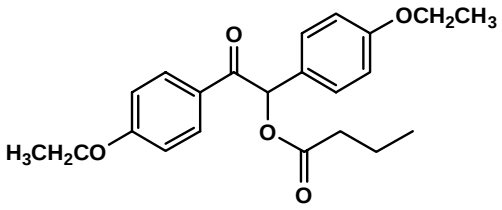


^{1}H NMR (250 MHz, $CDCl_3$): 7.85 (2H, d, *J*=9 Hz), 7.30 (2H, d, *J*=9 Hz), 6.80 (2H, d, *J*=8.8 Hz), 6.79 (2H, d, *J*=9.0 Hz), 6.73 (1H, s), 3.75 (3H, s), 3.70 (3H, s), 2.42 (1H, c, *J*=7.6 Hz), 2.30 (1H, c, *J*=7.6 Hz), 1.63 (2H, sex, *J*=7.4 Hz), 0.90 (3H, t, *J*=7.4 Hz). **^{13}C NMR** (63 MHz, $CDCl_3$) δ (ppm): 192.7, 174.4, 164.8, 160.3, 134.6, 130.1, 129.0, 127.7, 113.4, 112.8, 75.6, 54.4, 54.2, 34.8, 17.6, 13.1. Anal. Calcd. for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48. Found: C, 68.75; H, 6.28.

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8 mL/min): retention time: **(*R*)-2i**= 6.57 min, **(*S*)-2i**= 9.17 min.

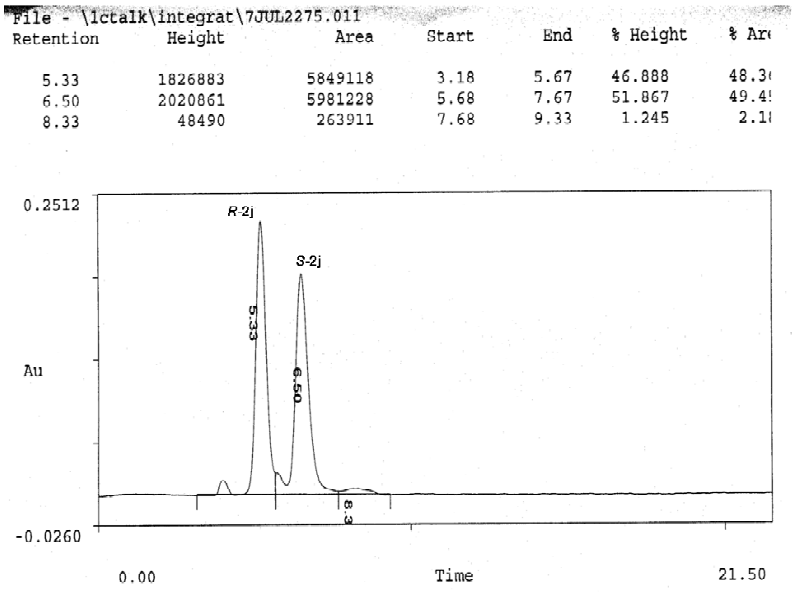


4. 6: 1,2-bis(4-ethoxyphenyl)-2-oxoethyl butyrate (*R*,*S*-2j) (83% yield)



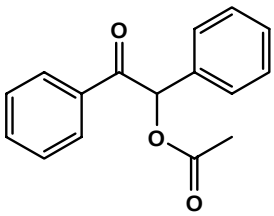
^{1}H NMR (250 MHz, $CDCl_3$): 7.83 (2H, d, *J*=9 Hz), 7.30 (2H, d, *J*=8.8 Hz), 6.8 (2H, d, *J*=8.8 Hz), 6.76 (2H, d, *J*=9.0 Hz), 6.72 (1H, s), 3.94 (4H, c, *J*=7Hz), 2.42 (1H, c, *J*=7.7 Hz), 2.30 (1H, c, *J*=7.6 Hz), 1.63 (2H, sex, *J*=7.4 Hz), 1.33(t, 3H, *J*=7Hz), 1.31(t, 3H, *J*=7Hz), 0.89 (3H, t, *J*=7.4 Hz). **^{13}C NMR** (63 MHz, $CDCl_3$) δ (ppm): 192.7, 173.7, 163.4, 160.0, 131.5, 130.4, 127.7, 126.4, 115.3, 114.6, 77.1, 64.1, 63.8, 36.3, 18.6, 15.1, 15.0, 13.1. Anal. Calcd. for $C_{22}H_{26}O_5$: C, 71.33; H, 7.07. Found: C, 70.11; H, 6.90.

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8 mL/min): retention time: **(*R*)-2j**= 5.33 min, **(*S*)-2j**= 6.50 min.



5. ***Synthesis of acetylated products: 2-oxo-1,2-diphenylethyl acetate (R,S-2a), 1,2-di(furan-2-yl)-2-oxoethyl acetate (R,S-2c)***

5. 1: 2-oxo-1,2-diphenyethyl acetate (*R,S*-2a)

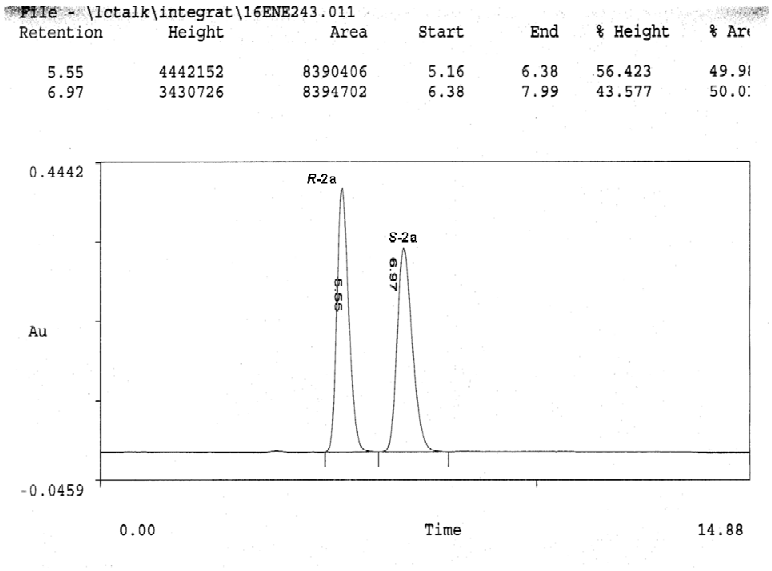


1a (4.2 g, 19.78 mmol) was solved in glacial acetic acid (4mL) and acetic anhydride (4 mL). 0.4 mL of H_2SO_4 were slowly added. The mixture was stirred in a 100ºC bath during 30 min and then was added over 50 mL of water. After 2 h the flask was introduced in an ice bath and the product started to precipitate. It was filtered and the yellow solid was recrystallized, producing white crystals of **2a** (3.97 g, 79% yield).

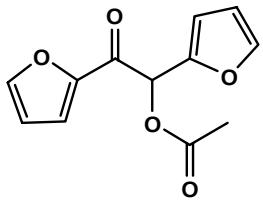
^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.96 (1H, m), 7.93 (1H, m), 7.53 (1H, t, J=2.3 Hz), 7.50 (1H, t, J=1.3 Hz), 7.48 (1H, d, J=1.9 Hz), 7.46 (1H, d, J=1.8 Hz), 7.43 (1H, c, J=2.4 Hz), 7.41 (1H, q, J=1.4 Hz), 7.38 (1H, d, J=2 Hz), 7.36 (1H, d, J=1.9 Hz),

6.87, 2.54. **^{13}C RMN** (63 MHz, $CDCl_3$) δ (ppm): 133.9, 129.7, 129.5, 129.1, 129.0, 129.0, 78.0, 21.2. Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 74.28; H, 5.45.

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8 mL/min): retention time: **(*R*)-2a**= 5.55 min, **(*S*)-2a**= 6.97 min.



5. 2: 1,2-di(furan-2-yl)-2-oxoethyl acetate (*R*,*S*-2c)

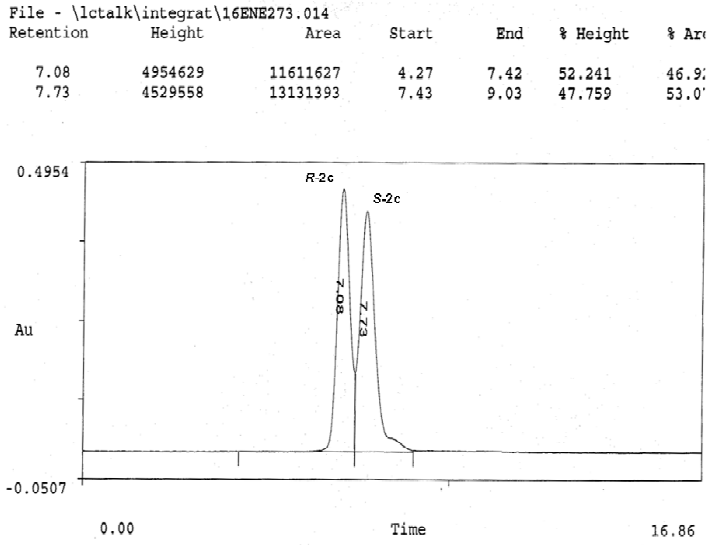


2-Furoin (200mg, 1.04mmol) was solved in 11mL of THF and 155 μL of DBU and 111.43 μL of acetyl chloride were added. After 24 h the product was purified by silica gel column chromatography (n-hexane/ethyl acetate, 7/2 (v/v)). The fractions were evaporated under vacuum, collecting a white solid (206 mg, 85% yield).

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.51 (1H, dd, J=1.6 Hz, J=0.7 Hz), 7.39 (1H, dd, J=1.8 Hz, J= 0.7Hz), 7.19 (1H, s), 6.69 (1H, s), 6.46 (1H, dd, J=3.6 Hz, J=1.7Hz), 6.44 (1H, dd, J=3.3 Hz, J=0.3 Hz), 6.32 (1H, dd, J= 3.3 Hz, J=1.8 Hz), 2.14

(3H, s). **^{13}C NMR** (63 MHz, $CDCl_3$) δ (ppm): 178.6, 169.1, 149.1 148.4, 146.1, 145.4, 143.2, 119.5, 110.7, 110.0, 69.3, 19.6. Anal. Calcd. for $C_{12}H_{10}O_5$: C, 61.54; H, 4.30. Found: C, 60.43; H, 4.21.

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8 mL/min): retention time: **(*R*)-2c**= 7.08 min, **(*S*)-2c**= 7.73 min.



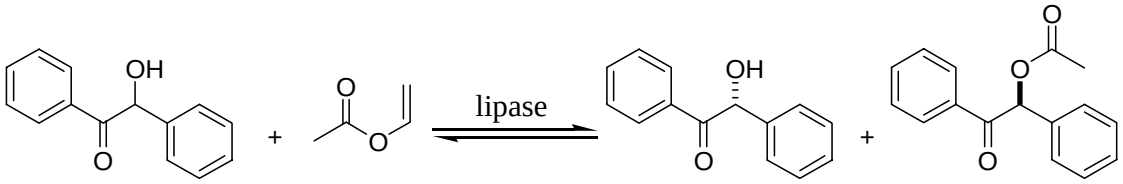
6. ***General methods for transesterification (Kinetic resolution)***

The reactions were generally performed in the following manner: 0,47 mmol of **1** were dissolved in 5 mL of organic solvent (dry THF) and 2.82 mmol of acyl donor were added. The reaction was started by the addition of 20 mg/mL of Lipase TL® (previously dried under vacuum overnight), and the mixture was stirred under argon atmosphere. The reactions were monitored by HPLC, taking 20 μL at different time intervals for analysis. As THF may damage the chiral column (Chiralcel OD®), each sample was evaporated under vacuum and the solid collected was re-solved n-hexane/2-propanol (50:50, v/v) before analyzing by HPLC (**1a**, λ_{max}=246 nm; **2a** and **2b,** λ_{max}=243 nm; **1b**, λ_{max}=273 nm; **2c** and **2d**, λ_{max}=273 nm; **1c**, λ_{max}=255 nm; **2e**, λ_{max}=252 nm, **1d**, λ_{max}=261 nm; **2f** and **2g**, λ_{max}=249 nm; **1e**, λ_{max}=250 nm; **2h**,

λ_{max}=247 nm; **1f**, λ_{max}=276 nm; **2i**, λ_{max}=274 nm; **1g**, λ_{max}=278 nm; **2j**, λ_{max}=275 nm). The conversions and ee values were determined by the HPLC data.

When the reaction was finished the product (**2**) was purified by silica gel column chromatography (n-hexane/ethyl acetate 5:1, v/v) and the optical rotation was measured. NMR spectra of optically pure acylated benzoins were similar to those ones of the racemic mixtures previously described on each case.

6.1. Transesterification of (*R*,*S*)-1a with vinyl acetate:



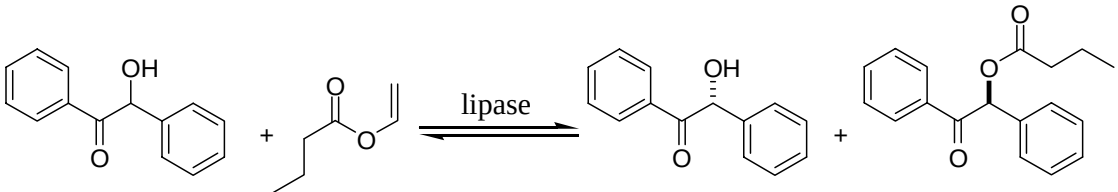
(*R*,*S*)-1a **R(-)-1a** ***S*(+)-2a**

The NMR data of ***S*(+)-2a** are similar to those of the racemic **(*R*,*S*)-2a**.

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8 mL/min): retention times: **(*R*)-1a**= 13.11 min, **(*S*)-1a**= 9.52 min., **(*S*)-2a**= 6.90 min. **1a**, λ_{max}=246 nm; **2a**, λ_{max}=243 nm. Conversions and e.e are shown in manuscript (Table 2).

(*S*)-2a: $[\alpha]^{20}_{D}$: +91.8 (*c* 0.2 $CHCl_3$)

6.2. Transesterification of (*R*,*S*)-1a with vinyl butyrate:



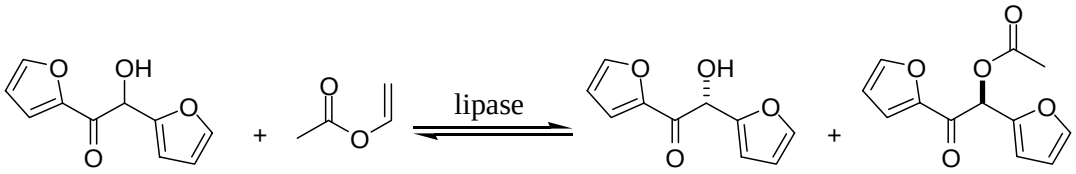
(*R*,*S*)-1a **R(-)-1a** ***S*(+)-2b**

The NMR data of ***S*(+)-2b** are similar to those of the racemic **(*R*,*S*)-2b**.

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8 mL/min): retention times: **(*R*)-1a**= 13.11 min, **(*S*)-1a**= 9.52 min., **(*S*)-2b**= 5.53 min. **1a** ; λ_{max}=246 nm; **2b**, λ_{max}=243 nm. Conversions and e.e are shown in manuscript (Table 2).

(*S*)-2b: $[\alpha]^{20}_{D}$: +117.8 (*c* 3.5 $CHCl_3$)

6.3. Transesterification of (*R,S*)-1b with vinyl acetate:



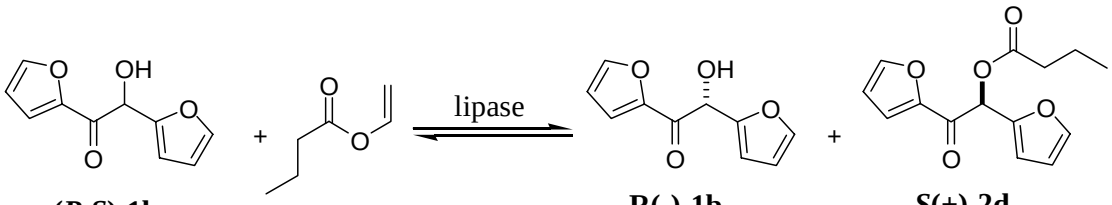
(*R,S*)-1b **R(-)-1b** ***S*(+)-2c**

The NMR data of ***S*(+)-2c** are similar to those of the racemic **(*R,S*)-2c**.

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8 mL/min): retention times: **(*R*)-1b**= 13.33 min, **(*S*)-1b**= 11.54 min., **(*S*)-2c**= 7.75 min. **1b** ; λ_{max}=273 nm; **2c**, λ_{max}=273 nm. Conversions and e.e are shown in manuscript (Table 2).

(*S*)-2c: $[\alpha]^{20}_{D}$: +103.8 (*c* 3.0 $CHCl_3$)

6.4. Transesterification of (*R,S*)-1b with vinyl butyrate:

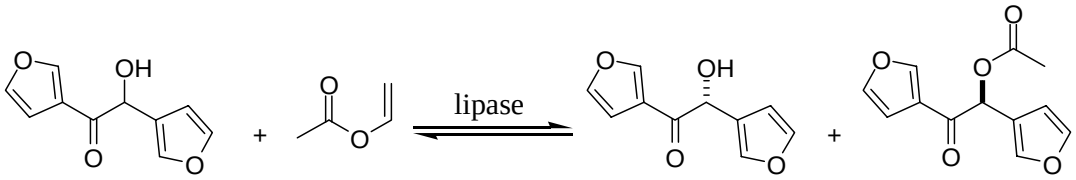


(*R,S*)-1b **R(-)-1b** ***S*(+)-2d**

The NMR data of ***S*(+)-2d** are similar to those of the racemic **(*R,S*)-2d**.

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8 mL/min): retention times: **(*R*)-1b**= 13.33 min, **(*S*)-1b**= 11.54 min., **(*S*)-2d**= 6.40 min. **1b** ; λ_{max}=273 nm; **2d**, λ_{max}=273 nm. Conversions and e.e are shown in manuscript (Table 2).

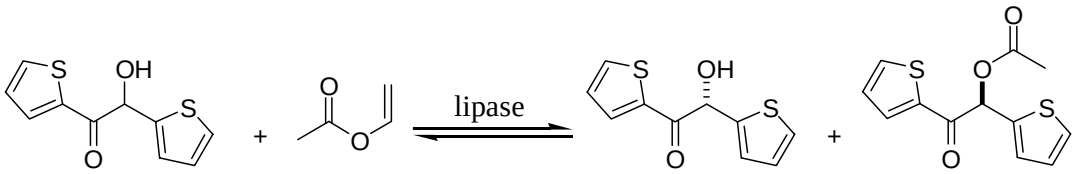
6.5. Transesterification of (*R,S*)-1c with vinyl acetate:



(*R,S*)-1c **R(-)-1c** ***S*(+)-2e**

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8 mL/min): retention times: **(*R*)-1c**= 12.88 min, **(*S*)-1c**= 11.91 min., (*S*)-2e= 7.52 min. **1c** ; λ_{max}=255 nm; **2e**, λ_{max}=252 nm. Conversions and e.e are shown in manuscript (Table 2).

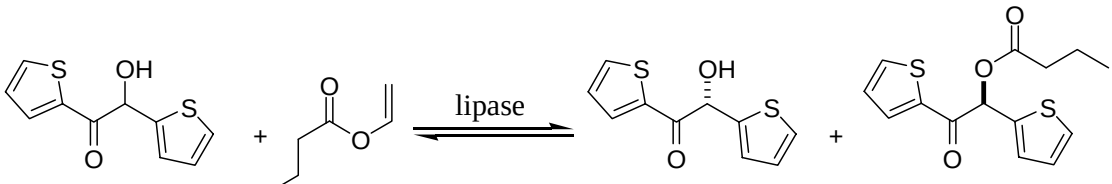
6.6. Transesterification of (*R,S*)-1d with vinyl acetate:



(*R,S*)-1d **R(-)-1d** ***S*(+)-2f**

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8mL/min): retention times: **(*R*)-1d**= 11.15 min, **(*S*)-1d**= 10.13 min., **(*S*)-2f**= 6.20 min. **1d** ; λ_{max}=261 nm; **2f**, λ_{max}=249 nm. Conversions and e.e are shown in manuscript (Table 2).

6.7. Transesterification of (*R,S*)-1d with vinyl butyrate:



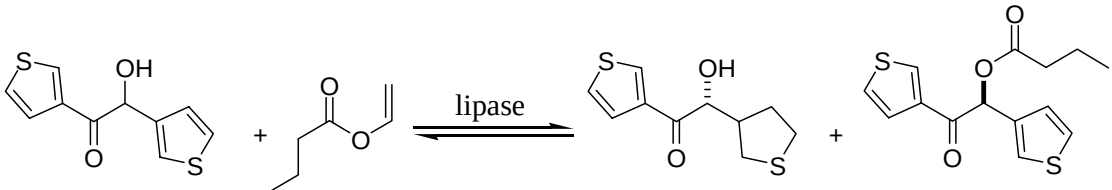
(*R,S*)-1d **R(-)-1d** ***S*(+)-2g**

The NMR data of ***S*(+)-2g** are similar to those of the racemic **(*R*,*S*)-2g**.

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8 mL/min): retention times: **(*R*)-1d**= 11.15 min, **(*S*)-1d**= 10.13 min., **(*S*)-2g**= 6.64 min. **1d** ; λ_{max}=261 nm; **2g**, λ_{max}=249 nm. Conversions and e.e are shown in manuscript (Table 2).

(*S*)-2g: $[\alpha]^{20}_{D}$: +95.9 (*c* 3.15 $CHCl_3$)

6.8. Transesterification of (*R*,*S*)-1e with vinyl butyrate:



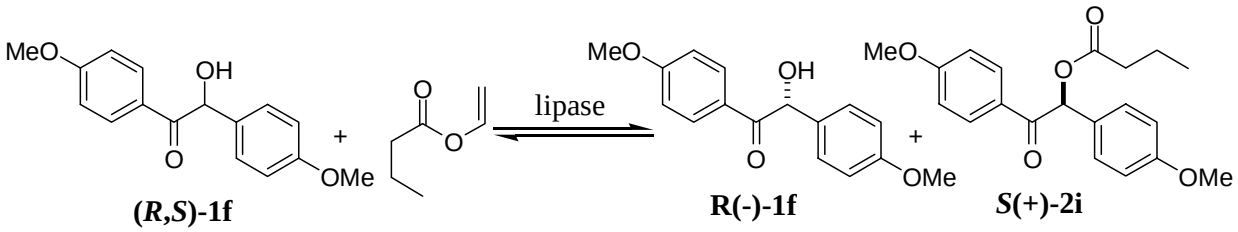
(*R*,*S*)-1e **R(-)-1e** ***S*(+)-2h**

The NMR data of ***S*(+)-2h** are similar to those of the racemic **(*R*,*S*)-2h**.

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8 mL/min): retention times: **(*R*)-1e**= 12.60 min, **(*S*)-1e**= 10.72 min., **(*S*)-2h**= 6.50 min. **1e** ; λ_{max}=250 nm; **2h**, λ_{max}=247 nm. Conversions and e.e are shown in manuscript (Table 2).

(*S*)-2h: $[\alpha]^{20}_{D}$: +92.1 (*c* 2.6 $CHCl_3$)

6.9. Transesterification of (*R*,*S*)-1f with vinyl butyrate:



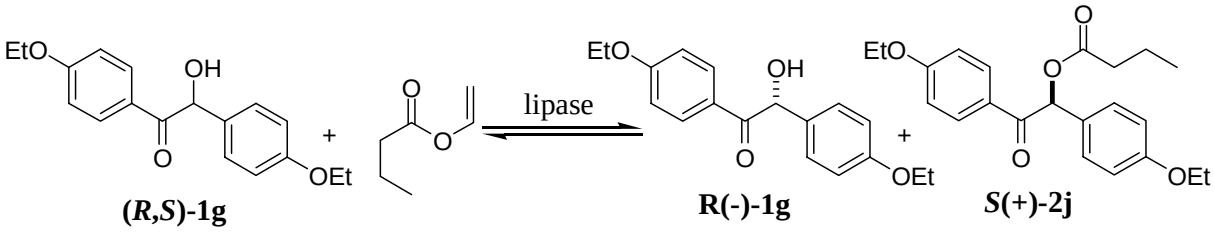
(*R*,*S*)-1f **R(-)-1f** ***S*(+)-2i**

The NMR data of ***S*(+)-2i** are similar to those of the racemic **(*R,S*)-2i**.

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8 mL/min): retention times: **(*R*)-1f**= 11.28 min, **(*S*)-1f**= 10.04 min., **(*S*)-2i**= 9.00 min. **1f** ; λ_{max}=276 nm; **2i**, λ_{max}=274 nm. Conversions and e.e are shown in manuscript (Table 2).

(*S*)-2i: $[\alpha]^{20}_{D}$: +104.0 (*c* 3.7 $CHCl_3$)

6.9. Transesterification of (*R,S*)-1g with vinyl butyrate:



(*R,S*)-1g **R(-)-1g** ***S*(+)-2j**

The NMR data of ***S*(+)-2j** are similar to those of the racemic **(*R,S*)-2j**.

HPLC analysis (n-hexane/2-propanol, 90/10; Flow 0.8mL/min): retention times: **(*R*)-1g**= 8.00 min, **(*S*)-1g**= 7.52 min., **(*S*)-2j**= 6.50 min. **1g** ; λ_{max}=278 nm; **2j**, λ_{max}=275 nm. Conversions and e.e are shown in manuscript (Table 2).

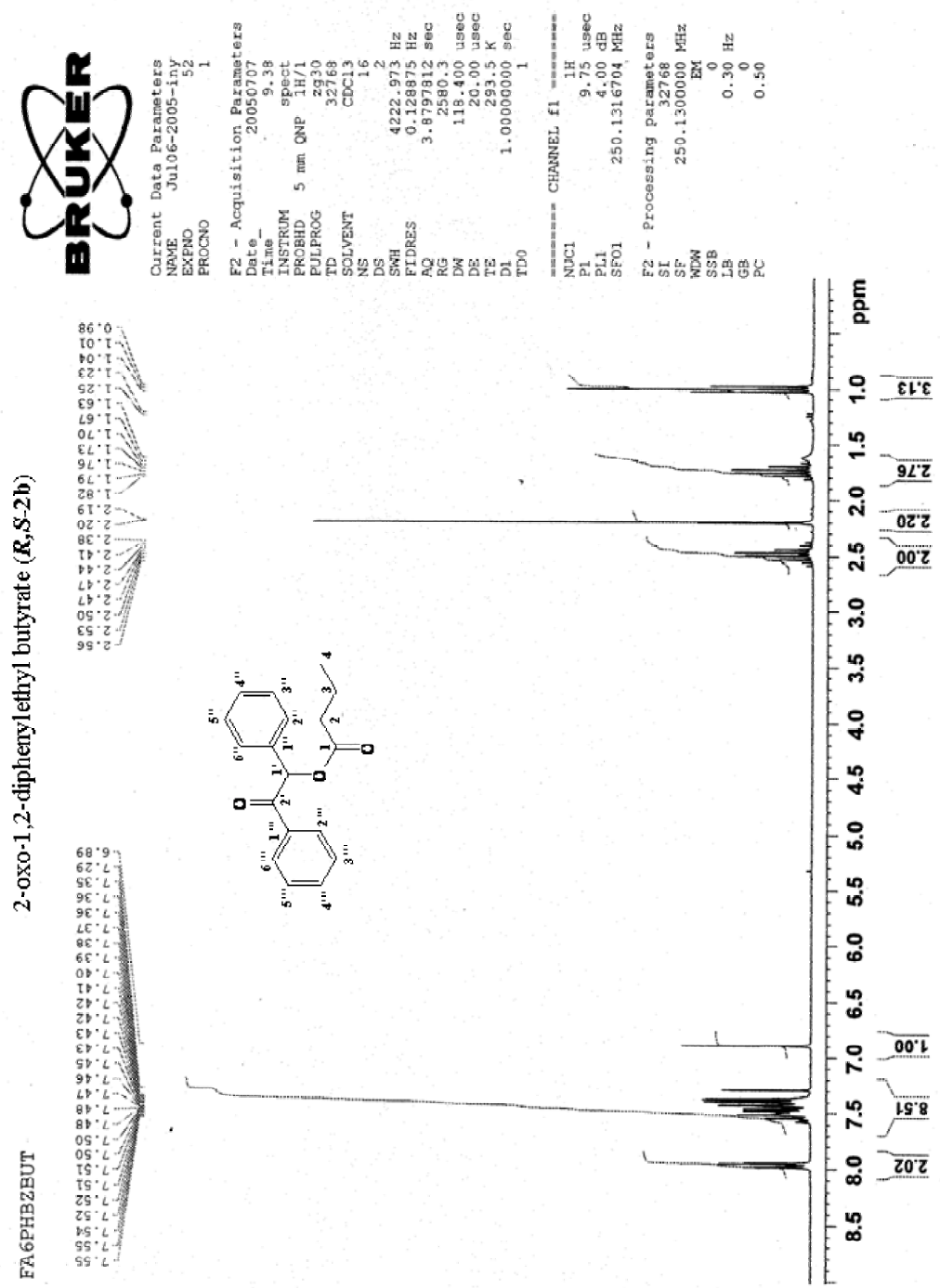
(*S*)-2j: $[\alpha]^{20}_{D}$: +94.6 (*c* 3.2 $CHCl_3$).

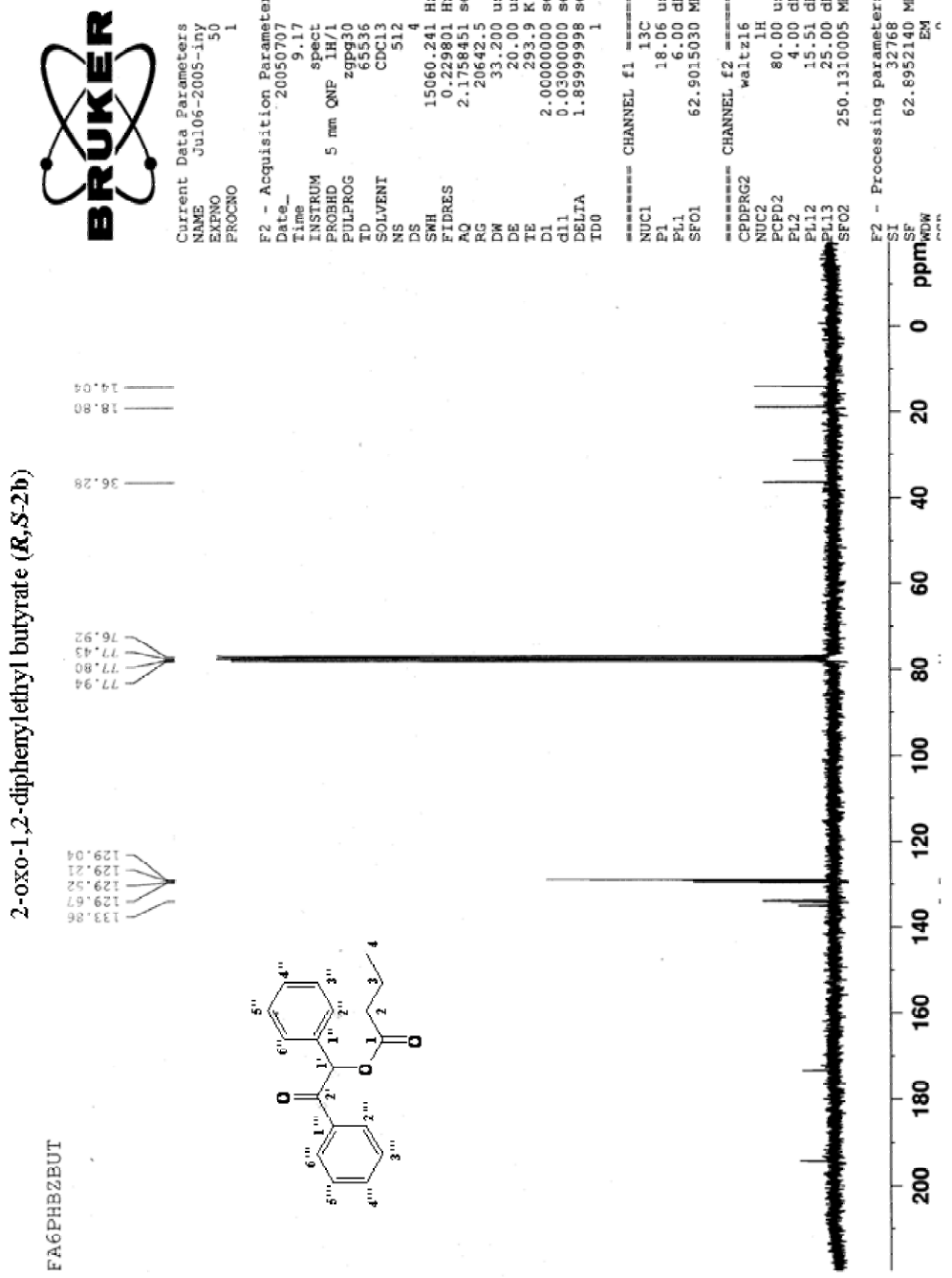
7. *General procedure for the Dynamic Kinetic Resolution.*

7. 1. One pot DKR: 12 mg of SHVO's catalyst (0.011 mmol) and 50mg of lipase TL® from *Pseudomonas stutzeri* were added to a 5 ml flask, and 2,5 mL of solution of **(*R,S*)-1a** 94.22 mM in anhydrous THF were added. The reaction was started adding the acylating agent trifluoroethyl butyrate (200 μL, 1.32 mmol). The mixture was stirred at 50ºC under argon. Each sample taken was evaporated under vacuum and

the solid collected was re-solved in n-hexane/2-propanol (50:50, v/v) before analyzing by HPLC.

7. 2. Sequential DKR: 25 mg of lipase TL® from *Pseudomonas stutzeri* were added to 2.5 mL of a solution 94.22 mM of **1a** in anhydrous THF. The reaction was started by addition of 300 μL of vinyl butyrate (2.36 mmol) and it was stirred at 50ºC under argon for 2.75 h, until 30% conversion was reached. Then, the mixture was filtered under vacuum and the THF and remnant vinyl butyrate were evaporated. The solid collected (70% substrate; 30% product) was re-solved in 2.5 mL of anhydrous THF, and 6 mg of SHVO´s catalyst (0.0055 mmol) and 200 μL of trifluoroethyl butyrate (1.32 mmol) were added. The reaction was stirred again at 50ºC. After 17 h, 25 mg of fresh enzyme were added, and the reaction was followed until almost no remnant substrate was detected by HPLC. 92% conversion and $e.e_p$>99.9% were reached.


2-oxo-1,2-diphenylethyl butyrate (R,S-2b)
FA6PHB2EUT
BRUKER
Current Data Parameters
NAME Ju106-2005-iny
EXPNO 52
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050707
Time 9.38
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG 2g30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 4222.973 Hz
FIDRES 0.128875 Hz
AQ 3.8797812 sec
RG 2580.3
DW 118.400 usec
DE 20.00 usec
TE 293.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.75 usec
PL1 4.00 dB
SFO1 250.1316704 MHz
F2 - Processing parameters
SI 32768
SF 250.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.50
ppm
3.13
2.76
2.20
2.00
1.00
8.51
2.02


2-oxo-1,2-diphenylethyl butyrate (R,S-2b)
FA6PHB2BUT
Current Data Parameters
NAME Jul06-2005-iny
EXPNO 50
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050707
Time 9.17
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 15060.241 Hz
FIDRES 0.229801 Hz
AQ 2.1758451 sec
RG 20642.5
DW 33.200 usec
DE 20.00 usec
TE 293.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 18.06 usec
PL1 6.00 dB
SFO1 62.9015030 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 15.51 dB
PL13 25.00 dB
SFO2 250.1310005 MHz
F2 - Processing parameters
SI 32768
SF 62.8952140 MHz
WDW EM
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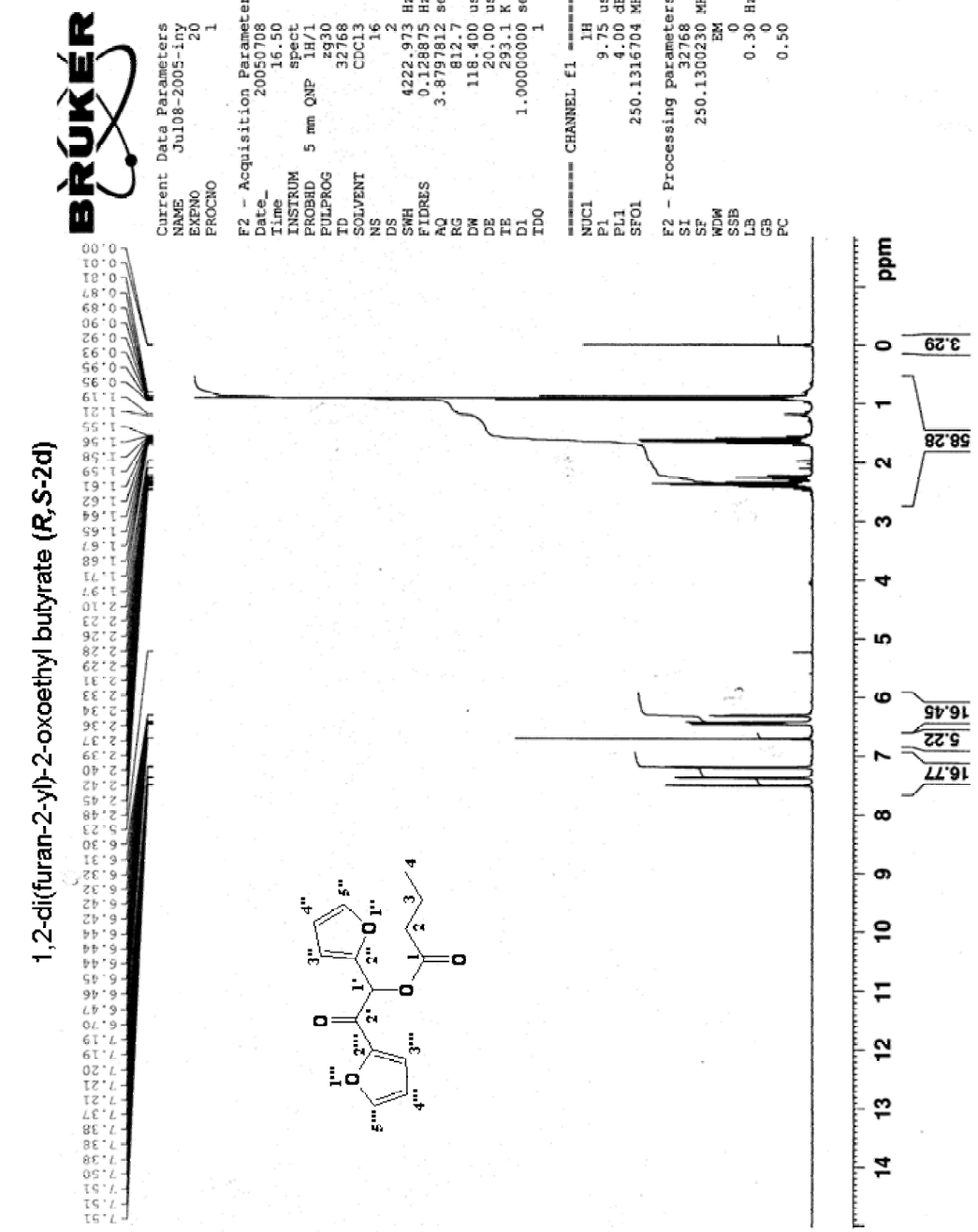
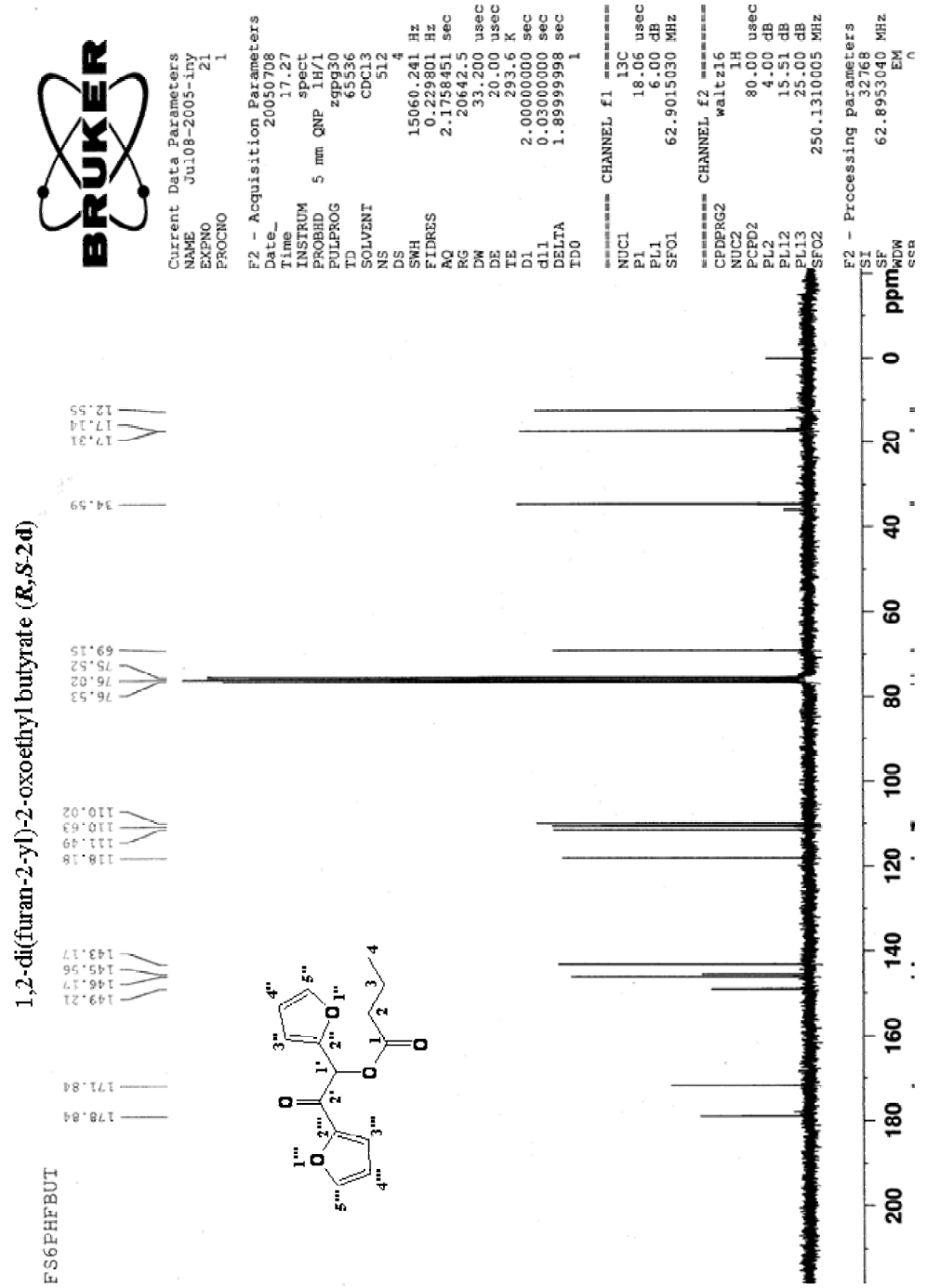
129.21
129.04
77.94
77.80
77.43
76.92
36.28
18.80
14.05
ppm


1,2-di(furan-2-yl)-2-oxoethyl butyrate (R,S-2d)
BRÜKER
Current Data Parameters
NAME Jul08-2005-iny
EXPNO 20
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050708
Time 16.50
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 4222.973 Hz
FIDRES 0.128875 Hz
AQ 3.8797812 sec
RG 812.7
DW 118.400 usec
DE 20.00 usec
TE 293.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.75 usec
PL1 4.00 dB
SFO1 250.1316704 MHz
F2 - Processing parameters
SI 32768
SF 250.1300230 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.50
3.29
58.28
16.45
5.22
16.77
ppm


1,2-di(furan-2-yl)-2-oxoethyl butyrate (R,S-2d)
FS6PHFBUT
BRUKER
Current Data Parameters
NAME Jul08-2005-iny
EXPNO 21
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050708
Time 17.27
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 15060.241 Hz
FIDRES 0.229801 Hz
AQ 2.1758451 sec
RG 20642.5
DW 33.200 usec
DE 20.00 usec
TE 293.6 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 18.06 usec
PL1 6.00 dB
SFO1 62.9015030 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 15.51 dB
PL13 25.00 dB
SFO2 250.1310005 MHz
F2 - Processing parameters
SI 32768
SF 62.8953040 MHz
WDW EM
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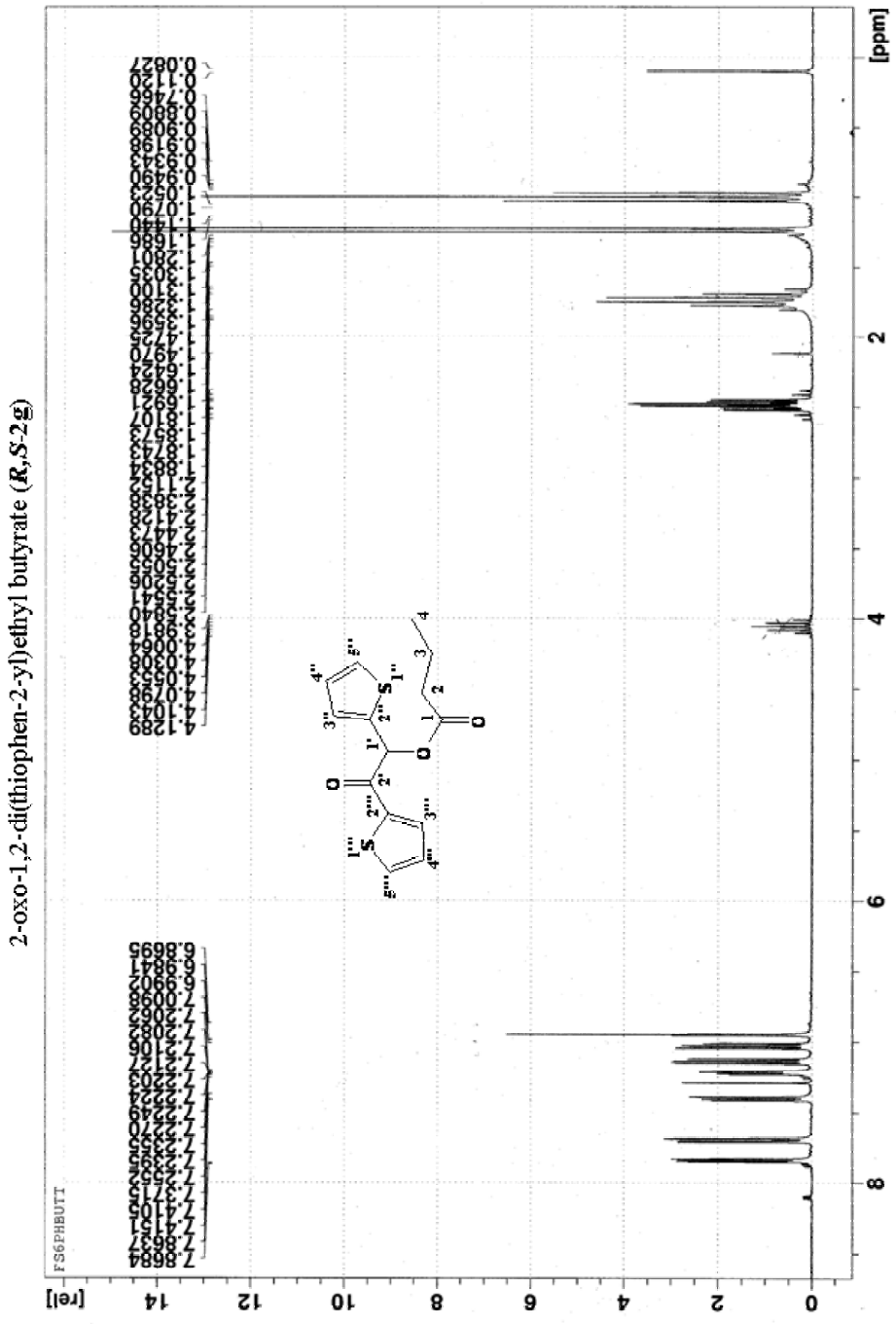
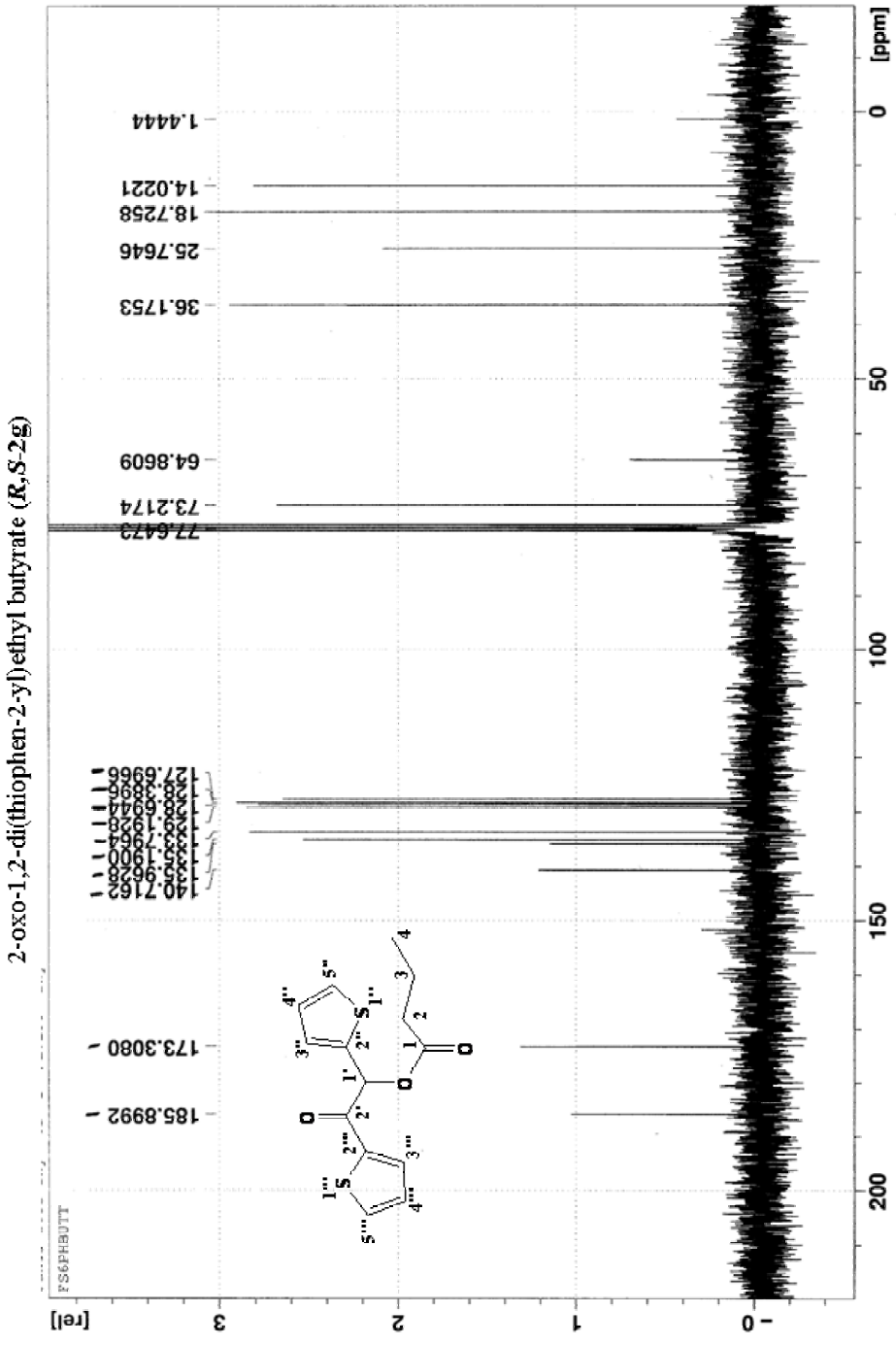
171.84
149.21
146.17
145.56
143.17
118.18
111.49
110.63
110.02
76.53
76.02
75.52
69.15
34.59
17.31
17.14
12.55
ppm
200
180
160
140
120
100
80
60
40
20
0


2-oxo-1,2-di(thiophen-2-yl)ethyl butyrate (R,S-2g)
FS6PHBUTT
[rel]
[ppm]


2-oxo-1,2-di(thiophen-2-yl)ethyl butyrate (R,S-2g)
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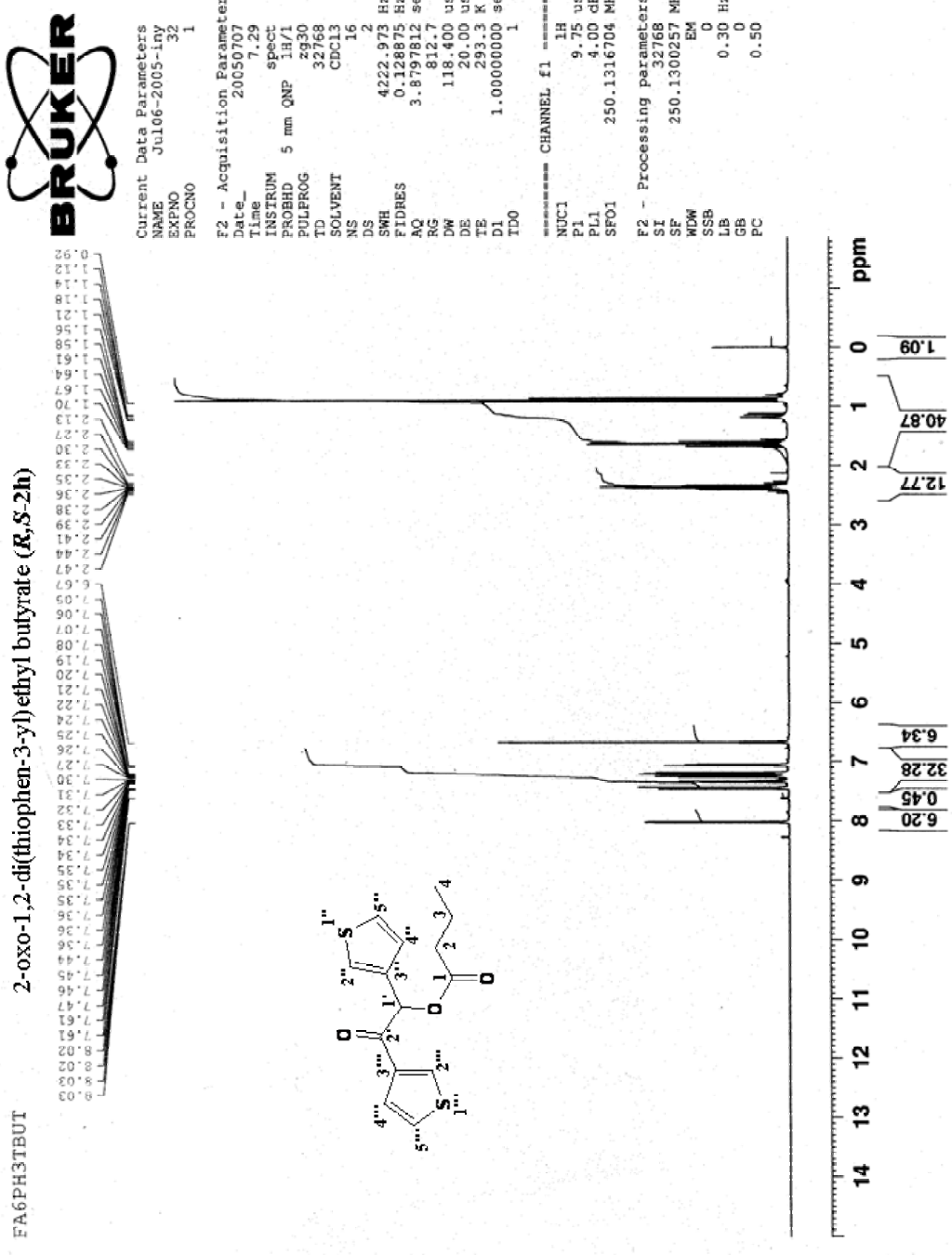
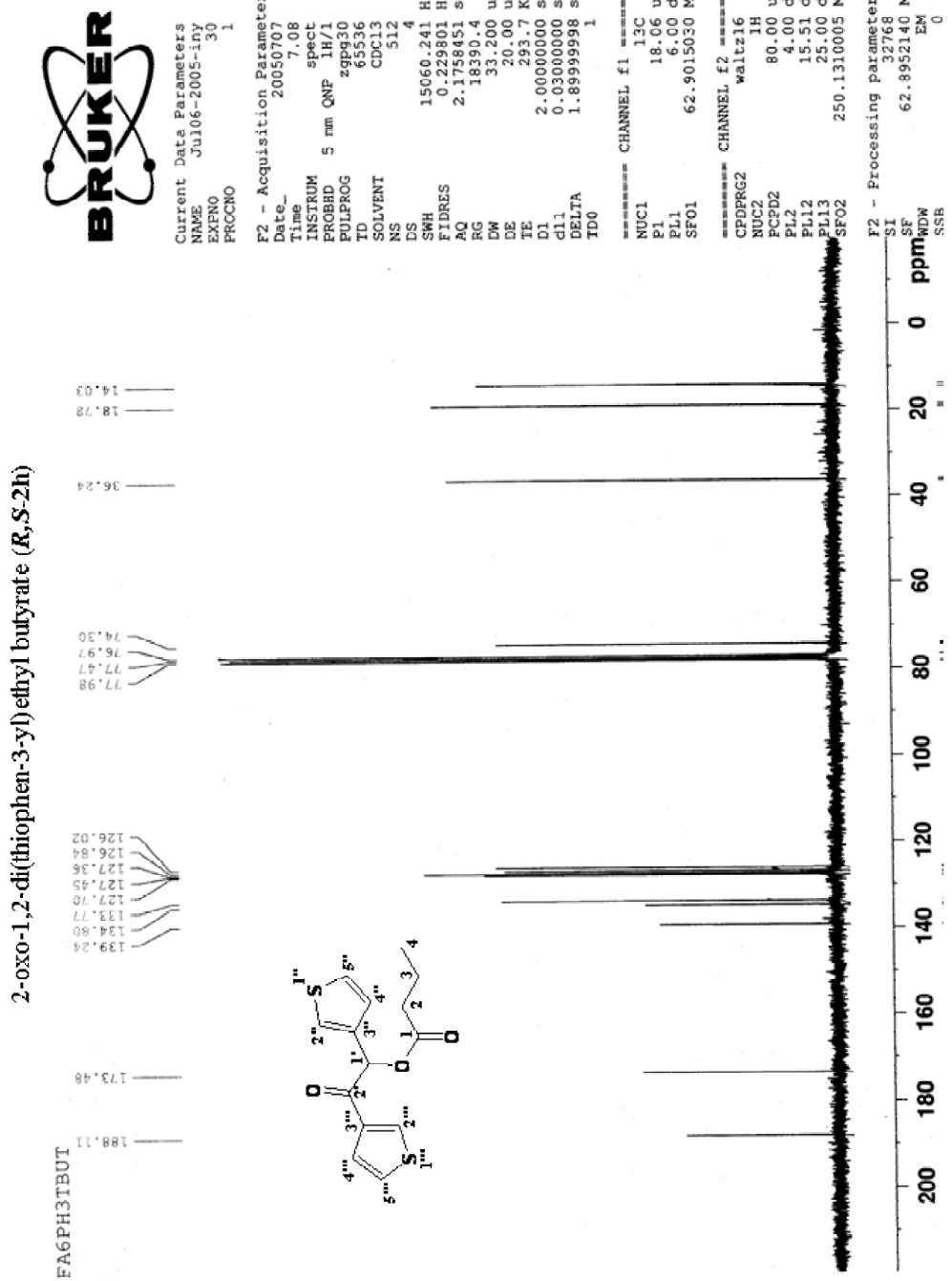
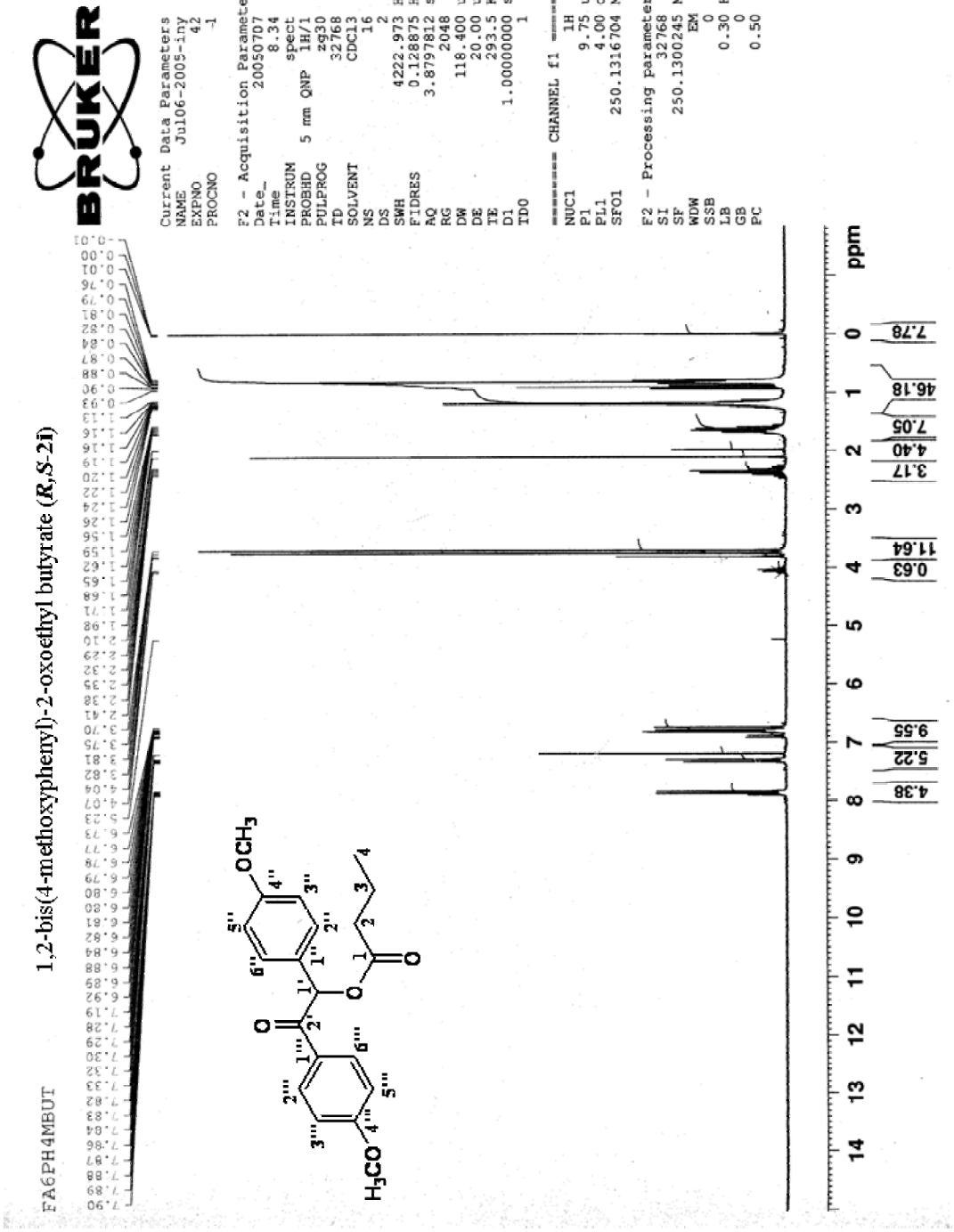
140.7162
135.9628
135.1900
133.7964
129.1928
128.6944
128.3896
127.6966
77.6473
73.2174
64.8609
36.1753
25.7646
18.7258
14.0221
1.4444
[rel]
[ppm]
PS6PBUTT

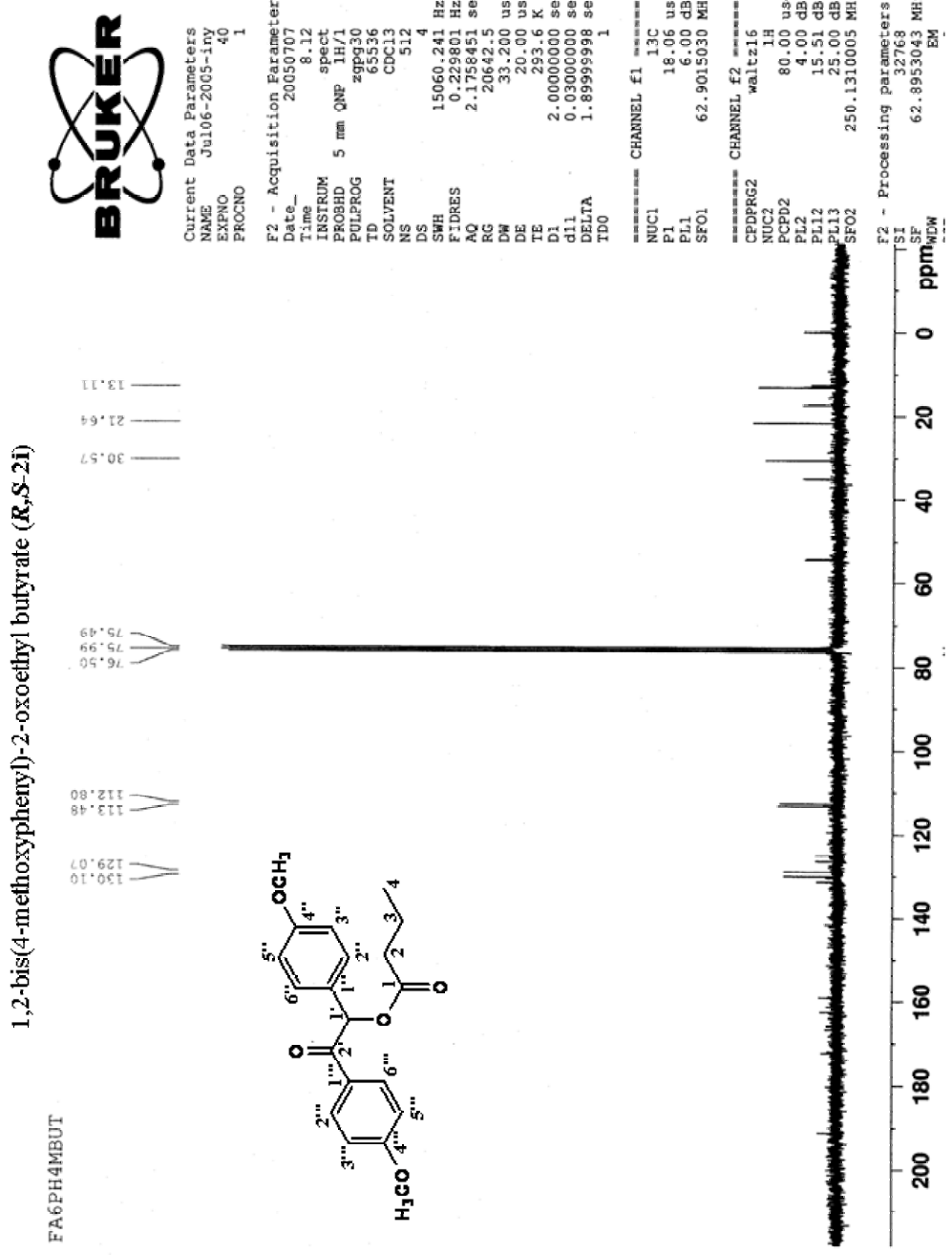

FA6PH3TBUT
2-oxo-1,2-di(thiophen-3-yl)ethyl butyrate (R,S-2h)
BRUKER
Current Data Parameters
NAME Ju106-2005-iny
EXPNO 32
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050707
Time 7.29
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 4222.973 Hz
FIDRES 0.128875 Hz
AQ 3.8797812 sec
RG 812.7
DW 118.400 usec
DE 20.00 usec
TE 293.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.75 usec
PL1 4.00 dB
SFO1 250.1316704 MHz
F2 - Processing parameters
SI 32768
SF 250.1300257 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.50
1.09
40.87
12.77
6.34
32.28
0.45
6.20
ppm

2-oxo-1,2-di(thiophen-3-yl)ethyl butyrate (*R,S*-2h)

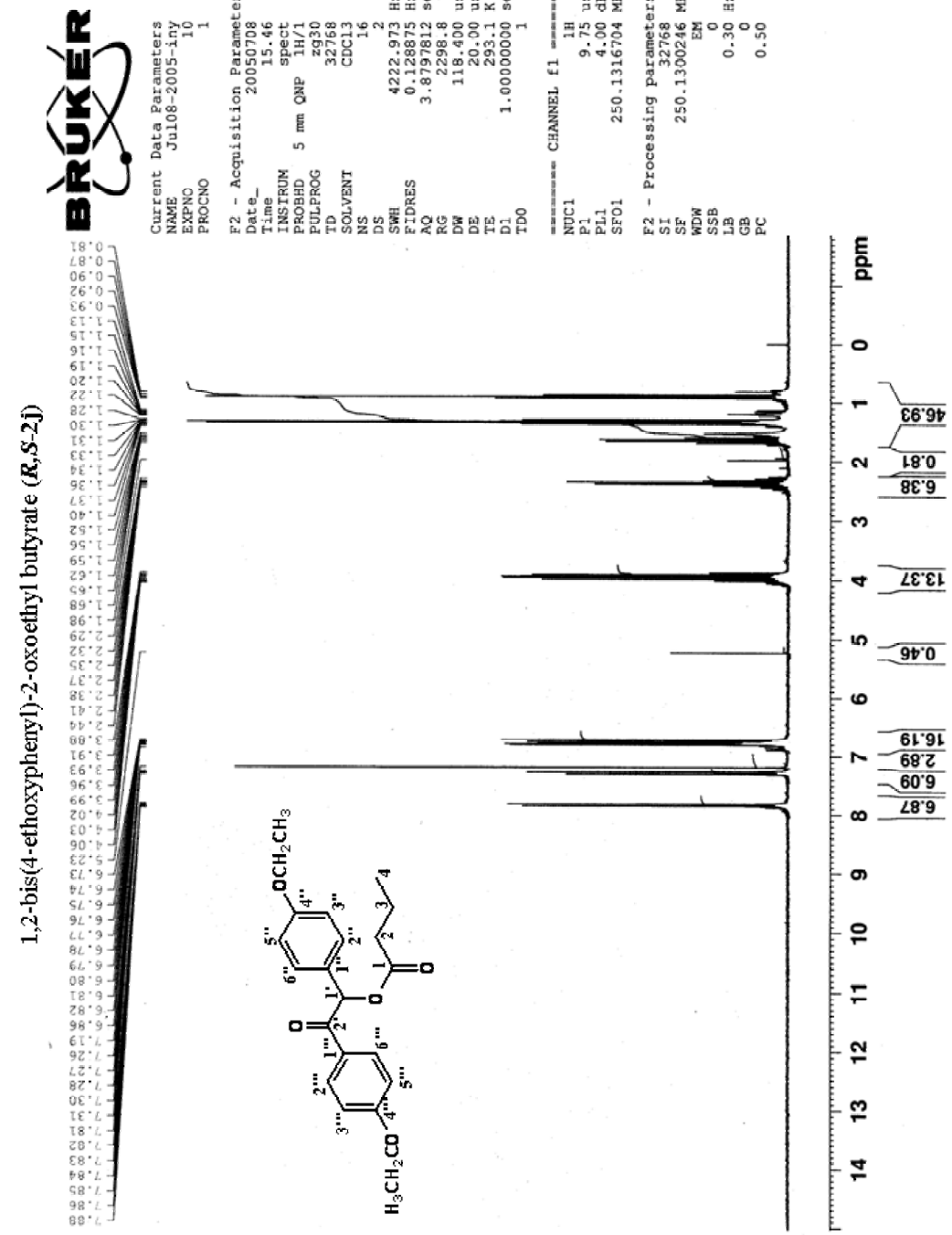


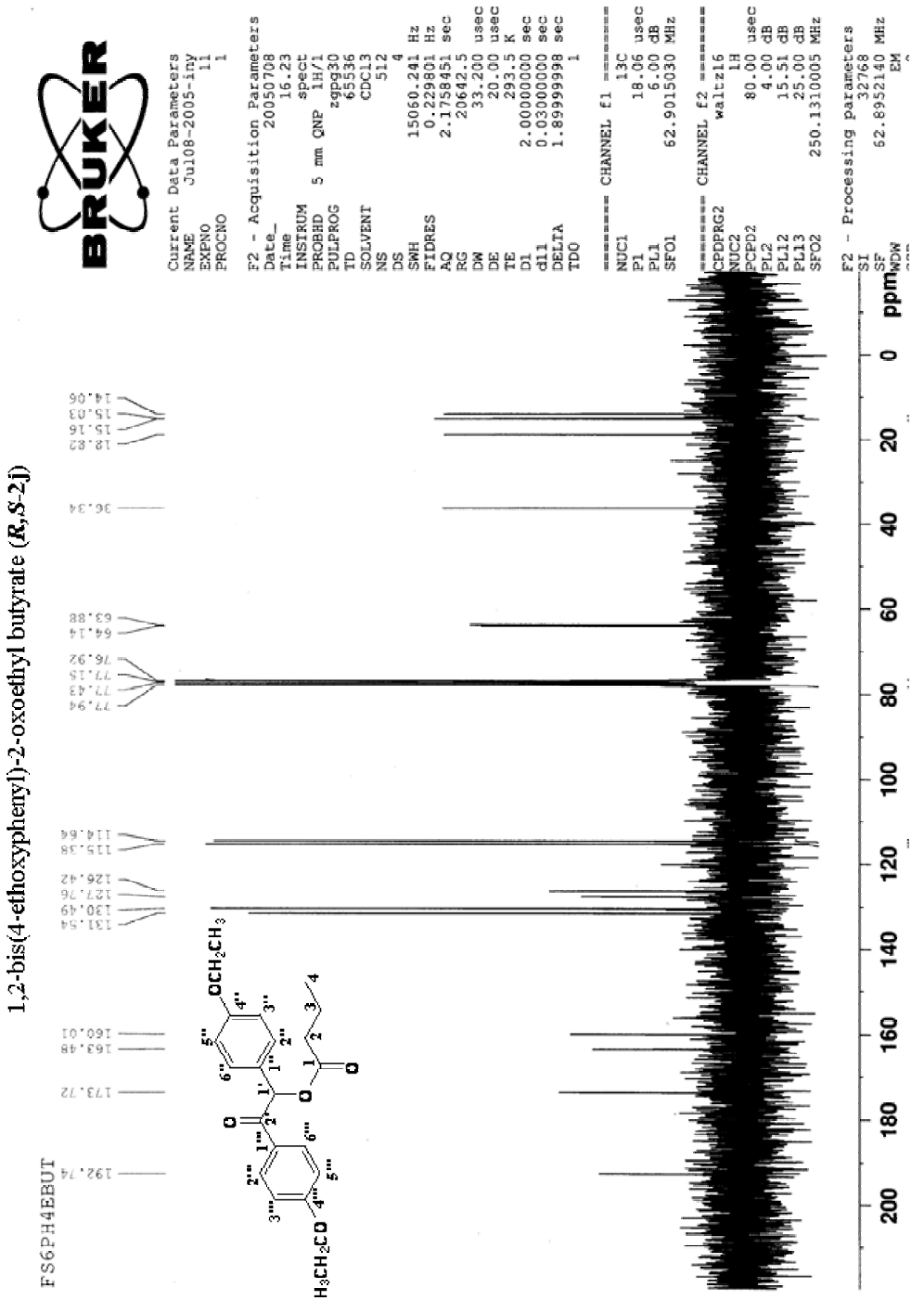

FA6PH4MBUT
1,2-bis(4-methoxyphenyl)-2-oxoethyl butyrate (R,S-2i)
BRUKER
Current Data Parameters
NAME Ju106-2005-iny
EXPNO 42
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050707
Time 8.34
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 4222.973 Hz
FIDRES 0.128875 Hz
AQ 3.8797812 sec
RG 2048
DW 118.400 usec
DE 20.00 usec
TE 293.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.75 usec
PL1 4.00 dB
SFO1 250.1316704 MHz
F2 - Processing parameters
SI 32768
SF 250.1300245 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.50
OCH3
H3CO
ppm
7.78
46.18
7.05
4.40
3.17
0.63
11.64
9.55
5.22
4.38

1,2-bis(4-methoxyphenyl)-2-oxoethyl butyrate (*R,S*-2i)

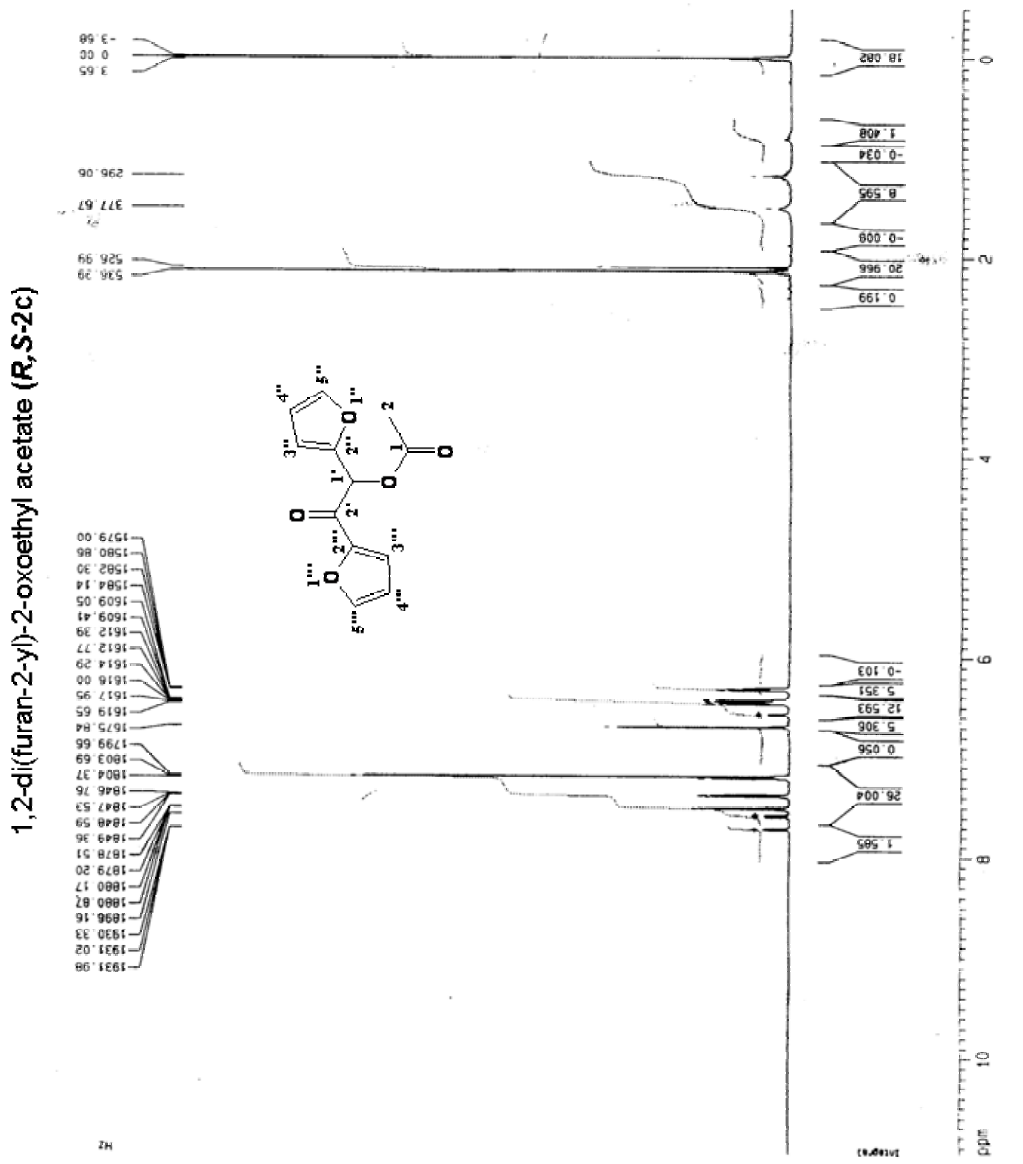


1,2-bis(4-ethoxyphenyl)-2-oxoethyl butyrate (*R*,*S*-2j)

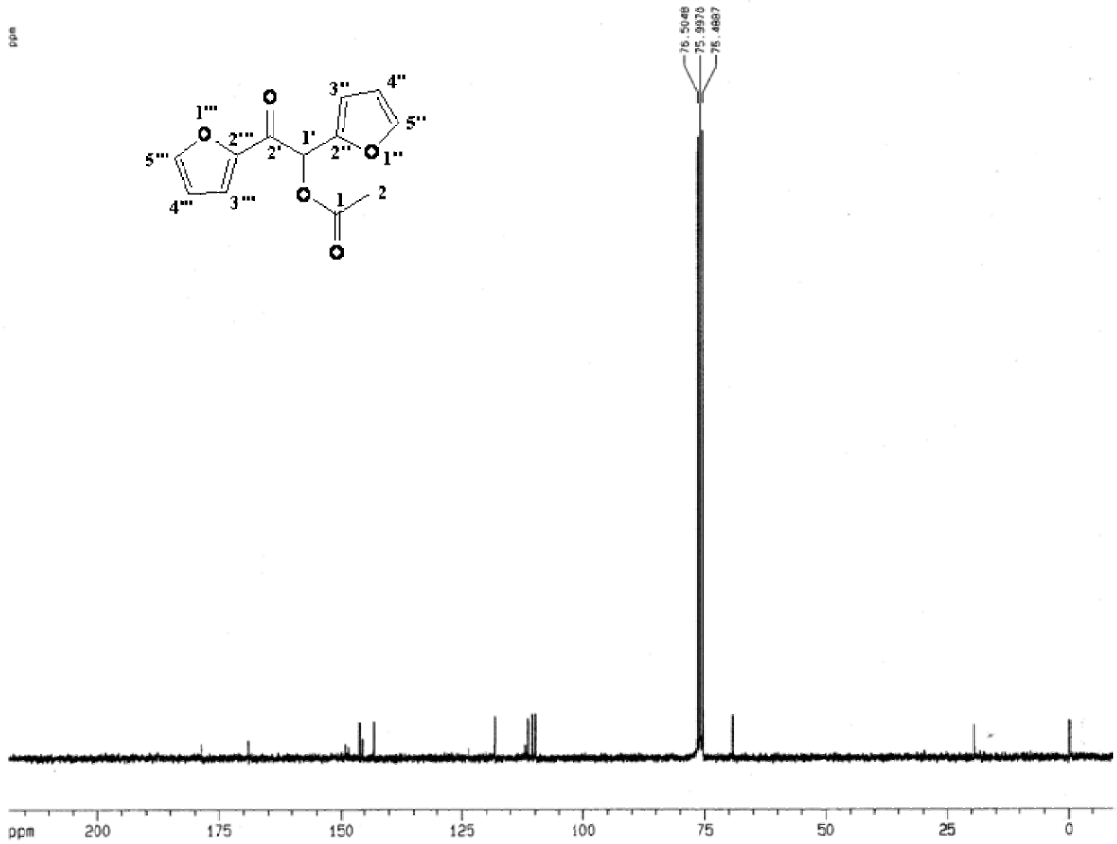



1,2-bis(4-ethoxyphenyl)-2-oxoethyl butyrate (R,S-2j)
FS6PH4EBUT
BRUKER
Current Data Parameters
NAME Jul08-2005-iny
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050708
Time 16.23
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 15060.241 Hz
FIDRES 0.229801 Hz
AQ 2.1758451 sec
RG 20642.5
DW 33.200 usec
DE 20.00 usec
TE 293.5 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 18.06 usec
PL1 6.00 dB
SFO1 62.9015030 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 15.51 dB
PL13 25.00 dB
SFO2 250.1310005 MHz
F2 - Processing parameters
SI 32768
SF 62.8952140 MHz
WDW EM
192.74
173.72
163.48
160.01
131.54
130.49
127.76
126.42
119.38
114.64
77.94
77.43
77.15
76.92
64.14
63.88
36.34
18.82
15.16
15.03
14.06
200
180
160
140
120
100
80
60
40
20
0
ppm

1,2-di(furan-2-yl)-2-oxoethyl acetate (*R,S*-2c)



1,2-di(furan-2-yl)-2-oxoethyl acetate (***R,S*-2c**)

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Current Data Parameters
NAME      Jul02-2004-iny
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20040702
Time               20.54
INSTRUM            spect
PROBHD   5 mm QNP  1H/1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2000
DS                    4
SWH           15060.241 Hz
FIDRES        0.229801 Hz
AQ            2.1758451 sec
RG               20642.5
DW               33.200 usec
DE               20.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                15.25 usec
PL1                6.00 dB
SFO1          62.9015030 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2             80.00 usec
PL2                4.00 dB
PL12              18.50 dB
PL13              25.00 dB
SFO2         250.1310005 MHz

F2 - Processing parameters
SI                 32768
SF            62.8953022 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                  1.30

1D NMR plot parameters
CX                22.00 cm
CY                12.50 cm
F1P              219.372 ppm
F1               13797.47 Hz
F2P              -9.037 ppm
F2               -568.37 Hz
PPMCM            10.38222 ppm/cm
HZCM            652.99274 Hz/cm
```