Organocatalytic and Highly Enantioselective Direct α-Amination of Aromatic Ketones

Tian-Yu Liu,[†] Hai-Lei Cui,[†] Yan Zhang,[†] Kun Jiang,[†] Wei Du,[†] Zhao-Quan He,[†] and Ying-Chun Chen* [†,‡]

[†] *Key Laboratory of Drug-Targeting of Education Ministry and Department of Medicinal Chemistry, West China School of Pharmacy, Sichuan University, Chengdu 610041, China,* [‡] *State Key Laboratory of Biotherapy, West China Hospital, Sichuan University, Chengdu, China.*

E-mail: ycchenhuaxi@yahoo.com.cn

Supporting Information

1. General Methods:

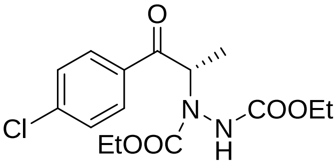
NMR spectra were recorded with tetramethylsilane as the internal standard. TLC was performed on glass-backed silica plates. Column chromatography was performed using silica gel (200-300 mesh) eluting with ethyl acetate and petroleum ether. ^{1}H NMR spectra were recorded at 300 MHz, and ^{13}C NMR spectra were recorded at 75 MHz (Bruker Avance). Chemical shifts (δ) are reported in ppm downfield from $CDCl_3$ (δ = 7.27 ppm) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.0 ppm) for ^{13}C NMR spectroscopy. Coupling constants (*J*) are given in Hz. ESI-HRMS spectrometer was measured with a Finnigan LCQ^{DECA} ion trap mass spectrometer. Optical rotations were measured at 589 nm at 20 °C. Enantiomeric excess was determined by HPLC analysis on chiral Chiralpak columns. Commercial grade solvents were dried and purified by standard procedures as specified in Purification of Laboratory Chemicals, 4th Ed (Armarego, W. L. F.; Perrin, D. D. Butterworth Heinemann: 1997). Primary aminocatalysts **1d**-**1e** were prepared according to literature procedures.[1]

2. General procedure for primary amine catalyzed asymmetric Direct α-Amination of Aromatic Ketones

A number of reaction conditions have been investigated in the synthesis of racemic α-amination products of aryl ketones. We could not obtain the desired products when various racemic α-amino acids were used. Moreover, the combination of simple primary amine (benzylamine) and *p*-TSA also could not give the expected α-amination products. Fortunately, we found that a strong organic base, tetramethylguanidine (TMG), could efficiently deproton aryl ketones and promote the α-amination reaction with azodicarboxylates in quite high yields.

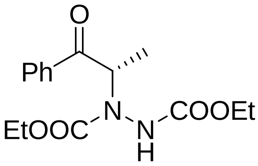
General procedure for TMG catalyzed direct α-amination of aromatic ketones: TMG (tetramethylguanidine) (0.02 mmol, 20 mol %), aromatic ketones **2** (0.2 mmol) and DEAD (diethyl azodicarboxylates) **3a** (0.1 mmol) were stirred in dry DCM (0.5 mL) at 40 °C for 48 h. Then the product was purified by flash chromatography on silica gel to give the racemic product **4**.

General procedure for primary amine catalyzed asymmetric reaction: Catalyst **1e** (0.02 mmol, 20 mol %), additive (0.04 mmol, 40 mol %), aromatic ketones **2** (0.2 mmol), azodicarboxylates **3** (0.1 mmol) and 4Å MS (20 mg) were stirred in dry 2-PrOH (0.3 mL) at 40 °C for 72h. Then the product **4** was purified by flash chromatography on silica gel eluting with petroleum ether/EtOAc. The enantiomeric excess was determined by HPLC analysis on chiral column.



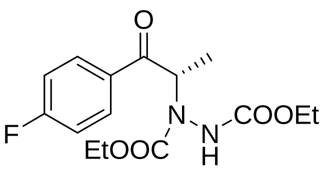
4a

R_f = 0.1 (petroleum ether/EtOAc = 9:1); 76% yield; colorless oil; $[\alpha]_D^{20}$ = -7.9 (*c* = 0.35 in EtOH); 98% ee, determined by HPLC analysis [Daicel chiralcel AS, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 6.93 min, t (minor) = 10.75 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 6.86 (s, 1H), 5.81-5.74 (m, 1H), 4.23-4.09 (m, 4H); 1.45 (d, *J* = 7.1 Hz, 3H), 1.28-1.21 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.1, 198.6, 156.9, 156.3, 155.9, 140.1, 132.9, 130.0, 129.7, 129.1, 77.2, 62.9, 61.9, 59.0, 57.8, 38.9, 38.7, 29.6, 29.4, 22.9, 22.6, 14.8, 14.3, 14.1, 14.0 ppm; ESI-HRMS: calcd. for $C_{15}H_{19}ClN_2O_5$+H 343.1055, found 343.1053.



4b

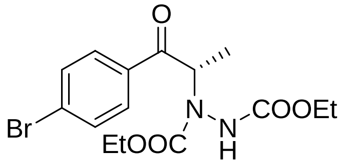
R_f = 0.1 (petroleum ether/EtOAc = 9:1); 65% yield; colorless oil; $[\alpha]_D^{20}$ = -5.6 (*c* = 0.36 in EtOH); $[\alpha]_D^{20}$ = +38.6 (*c* = 0.58 in $CHCl_3$) [lit.:[2] $[\alpha]_D^{24}$ = -31.2 (*c* = 2.795 in $CHCl_3$), 84% ee, *R*-isomer]; 94% ee, determined by HPLC analysis [Daicel chiralcel AS, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 7.14 min, t (minor) = 10.40 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 6.88 (s, 1H), 5.86-5.84 (m, 1H), 4.26-4.17 (m, 4H); 1.48 (d, *J* = 6.8 Hz, 3H), 1.33-1.20 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.6, 157.0, 156.5, 156.3, 156.1, 134.5, 133.7, 133.3, 130.0, 129.6, 128.8, 128.5, 128.4, 128.3, 77.2, 68.7, 67.9, 62.8, 62.0, 61.9, 59.1, 58.0, 25.6, 25.3, 14.9, 14.5, 14.4 ppm; ESI-HRMS: calcd. for $C_{15}H_{20}N_2O_5$+H 309.1445, found 309.1449.



4c

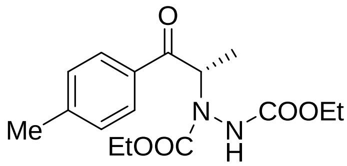
R_f = 0.1 (petroleum ether/EtOAc = 9:1); 52% yield; colorless oil; $[\alpha]_D^{20}$ = -10.8 (*c* = 0.33 in EtOH); 93% ee, determined by HPLC analysis [Daicel chiralcel AS, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 7.02 min, t (minor) = 11.33 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 5.4 Hz, 2H), 7.15 (t, *J* = 8.5 Hz, 2H), 6.85 (s, 1H), 5.81-5.76 (m, 1H), 4.25-4.10 (m, 4H); 1.47 (d, *J* = 6.9 Hz, 3H), 1.33-1.23 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.8, 166.0 (d, $^{1}J_{C,F}$ = 254.4 Hz), 156.9, 156.4, 132.3, 131.2 (d, $^{3}J_{C,F}$ = 9.2 Hz), 116.0 (d, $^{2}J_{C,F}$ = 21.8 Hz), 115.4, 77.2, 68.7, 62.9, 62.0, 58.9, 57.8, 29.7, 27.0, 25.3, 14.9, 14.4, 14.3 ppm; ESI-HRMS: calcd. for $C_{15}H_{19}FN_2O_5$+H 327.1351, found 327.1353.

R_f = 0.1 (petroleum ether/EtOAc = 10:1); 62% yield; colorless oil; $[\alpha]_D^{20}$ = 8.9 (*c* = 0.29 in EtOH); 97% ee, determined by HPLC analysis [Daicel chiralcel AS, *n*-hexane/*i*-PrOH = 70/30, 1.0



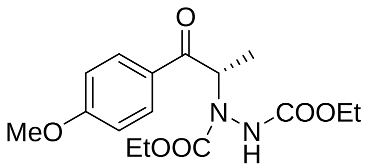
4d

mL/min, λ = 254 nm, t (major) = 7.38 min, t (minor) = 11.20 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 7.3 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 6.83 (s, 1H), 5.78-5.76 (m, 1H), 4.21-4.10 (m, 4H); 1.45 (d, *J* = 6.9 Hz, 3H), 1.29-1.16 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.4, 198.8, 156.9, 156.3, 133.3, 132.1, 131.8, 131.1, 130.0, 129.8, 128.9, 77.2, 62.9, 62.3, 62.0, 59.0, 57.8, 31.5, 29.7, 24.1, 22.6, 14.8, 14.4, 14.3, 14.2 ppm; ESI-HRMS: calcd. for $C_{15}H_{19}BrN_2O_5$+H 387.0550, found 387.0547.



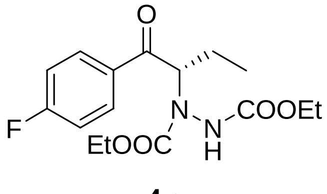
4e

R_f = 0.1 (petroleum ether/EtOAc = 9:1); 62% yield; colorless oil; $[\alpha]_D^{20}$ = 6.7 (*c* = 0.32 in EtOH); 94% ee, determined by HPLC analysis [Daicel chiralcel AS, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 6.49 min, t (minor) = 9.37 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 7.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.91 (s, 1H), 5.83-5.81 (m, 1H), 4.24-4.17 (m, 4H), 2.42 (s, 3H), 1.47 (d, *J* = 6.7 Hz, 3H), 1.30-1.23 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.2, 156.5, 144.7, 134.4, 132.0, 129.5, 129.2, 128.6, 62.8, 61.9, 59.0, 57.9, 29.7, 21.7, 15.1, 14.7, 14.4, 14.3 ppm; ESI-HRMS: calcd. for $C_{16}H_{22}N_2O_5$+H 323.1601, found 323.1605.



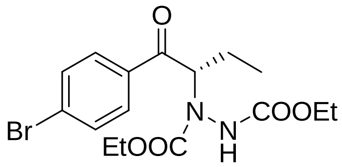
4f

R_f = 0.1 (petroleum ether/EtOAc = 7:1); 77% yield; colorless oil; $[\alpha]_D^{20}$ = 8.1 (*c* = 0.37 in EtOH); 94% ee, determined by HPLC analysis [Daicel chiralcel AS, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 8.67 min, t (minor) = 13.95 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 7.6 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.43 (s, 1H), 5.81-5.79 (m, 1H), 4.35-4.15 (m, 4H), 3.87 (s, 3H), 1.48 (d, *J* = 7.0 Hz, 3H), 1.35-1.25 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.1, 163.9, 156.5, 156.3, 130.9, 130.7, 127.3, 114.0, 113.7, 77.2, 62.8, 62.5, 62.3, 61.8, 58.7, 57.6, 55.5, 29.7, 15.2, 14.8, 14.4, 14.1 ppm; ESI-HRMS: calcd. for $C_{16}H_{22}N_2O_6$+H 339.1551, found 339.1549.



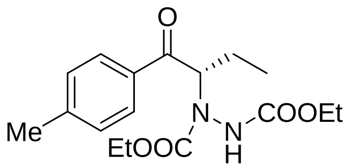
4g

R_f = 0.1 (petroleum ether/EtOAc = 9:1); 77% yield; colorless oil; $[\alpha]_D^{20}$ = 4.8 (*c* = 0.42 in EtOH); 96% ee, determined by HPLC analysis [Daicel chiralcel AS, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 5.39 min, t (minor) = 9.74 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (br.s, 2H), 7.14 (t, *J* = 8.5 Hz, 2H), 6.86 (br.s, 1H), 5.58-5.56 (m, 1H), 4.27-4.07 (m, 4H), 1.86-1.78 (m, 2H), 1.35-1.18 (m, 6H), 1.10 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ = 198.8, 165.9 (d, $^{1}J_{C,F}$ = 254.3 Hz), 156.6, 156.0, 131.6, 131.1 (d, $^{3}J_{C,F}$ = 9.2 Hz), 116.0 (d, $^{2}J_{C,F}$ = 21.8 Hz), 77.2, 64.5, 64.0, 63.4, 63.0, 61.9, 31.9, 29.6, 29.3, 22.5, 22.1, 14.3, 14.1, 11.3 ppm; ESI-HRMS: calcd. for $C_{16}H_{21}FN_2O_5$+H 341.1507, found 341.1503.



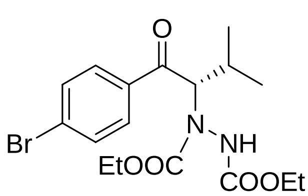
4h

R$_f$ = 0.1 (petroleum ether/EtOAc = 12:1); 54% yield; colorless oil; $[\alpha]_D^{20}$ = -14.0 (*c* = 0.37 in EtOH); 99% ee, determined by HPLC analysis [Daicel chiralcel AS, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 6.35 min, t (minor) = 11.02 min]; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.79 (br.s, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 6.80 (br.s, 1H), 5.56 (br.s, 1H), 4.20-4.17 (m, 4H), 1.86-1.82 (m, 2H), 1.29-1.23 (m, 6H), 1.10 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ = 199.3, 156.9, 156.0, 136.4, 134.0, 132.1, 131.8, 131.3, 130.4, 129.9, 128.9, 77.2, 67.9, 64.6, 64.0, 63.4, 63.0, 61.9, 29.7, 25.6, 22.4, 22.0, 14.4, 11.2 ppm; ESI-HRMS: calcd. for $C_{16}H_{21}BrN_2O_5$+Na 423.0526, found 423.0530.



4i

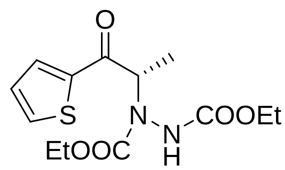
R$_f$ = 0.1 (petroleum ether/EtOAc = 12:1); 49% yield; colorless oil; $[\alpha]_D^{20}$ = 6.0 (*c* = 0.30 in EtOH); 98% ee, determined by HPLC analysis [Daicel chiralcel AS, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 6.18 min, t (minor) = 9.78 min]; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.81 (br.s, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 6.92 (s, 1H), 5.60-5.59 (m, 1H), 4.27-4.12 (m, 4H), 2.41 (s, 3H), 1.88-1.82 (m, 2H), 1.29-1.19 (m, 6H), 1.11 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ = 200.2, 157.0, 156.7, 156.1, 144.6, 134.4, 132.7, 130.0, 129.5, 129.2, 129.1, 128.5, 77.2, 64.8, 63.8, 62.9, 61.8, 31.6, 29.6, 29.5, 29.3, 22.6, 22.3, 22.0, 21.8, 21.7, 21.3, 14.3, 14.1, 11.4 ppm; ESI-HRMS: calcd. for $C_{17}H_{24}N_2O_5$+H 337.1758, found 337.1756.



4j

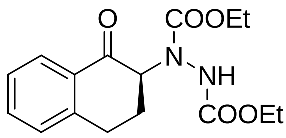
R$_f$ = 0.1 (petroleum ether/EtOAc = 15:1); 52% yield; colorless oil; $[\alpha]_D^{20}$ = -3.4 (*c* = 0.23 in EtOH); 97% ee, determined by HPLC analysis [Daicel chiralcel AS, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 8.28 min, t (minor) = 14.94 min]; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.89 (br.s, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 6.60 (br.s, 1H), 5.36 (br.s, 1H), 4.21-4.15 (m, 4H), 2.40 (br.s, 1H), 1.24 (t, *J* = 7.1 Hz, 6H), 1.06 (d, *J* = 6.3 Hz, 3H), 0.87 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ = 155.6, 135.7, 132.1, 130.1, 128.8, 77.2, 65.7, 64.5, 63.2, 62.0, 27.3, 19.6, 18.7, 14.4 ppm; ESI-HRMS: calcd. for

$C_{17}H_{23}BrN_2O_5$+H 415.0863, found 415.0846.



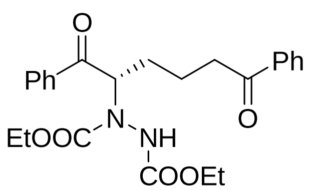
4k

R$_f$ = 0.1 (petroleum ether/EtOAc = 10:1); 63% yield; colorless oil; $[\alpha]_D^{20}$ = 3.1 (*c* = 0.23 in EtOH); 96% ee, determined by HPLC analysis [Daicel chiralcel AS, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 8.24 min, t (minor) = 12.58 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (br.s, 1H), 7.70 (d, *J* = 4.9 Hz, 1H), 7.17 (t, *J* = 4.3 Hz, 1H), 6.85 (s, 1H), 5.68-5.66 (m, 1H), 4.24-4.10 (m, 4H), 1.55 (d, *J* = 7.0 Hz, 3H), 1.36-1.18 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.9, 156.3, 134.6, 133.3, 133.0, 132.6, 128.7, 128.4, 77.2, 64.1, 62.9, 62.5, 62.3, 62.0, 59.9, 58.6, 31.6, 29.7, 25.2, 22.6, 15.1, 14.4, 14.3, 14.2, 14.1 ppm; ESI-HRMS: calcd. for $C_{13}H_{18}N_2O_5S$+H 315.1009, found 315.1012.



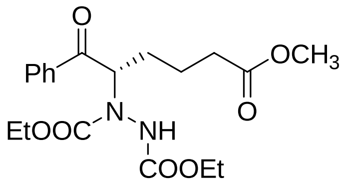
4l

R$_f$ = 0.1 (petroleum ether/EtOAc = 9:1); 74% yield; colorless oil; $[\alpha]_D^{20}$ = 4.1 (*c* = 0.25 in EtOH); 90% ee, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 14.82 min, t (major) = 15.66 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 6.7 Hz, 1H), 6.70 (s, 1H), 5.22-5.17 (m, 1H), 4.27-4.17 (m, 4H), 3.26-3.20 (m, 1H), 3.10-3.05 (m, 1H), 2.55-2.52 (m, 1H), 2.38-2.28 (m, 1H), 1.33-1.23 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.9, 157.0, 156.6, 156.3, 143.8, 134.1, 131.9, 128.8, 127.7, 126.8, 65.4, 64.4, 63.0, 62.9, 62.0, 29.7, 28.8, 27.7, 27.6, 21.9, 14.4 ppm; ESI-HRMS: calcd. for $C_{16}H_{20}N_2O_5$+H 321.1445, found 321.1439.



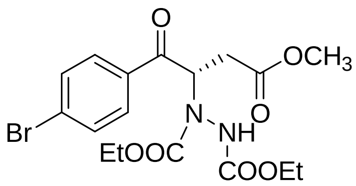
4m

R$_f$ = 0.1 (petroleum ether/EtOAc = 7:1); 51% yield; colorless oil; $[\alpha]_D^{20}$ = -8.4 (*c* = 0.36 in EtOH); 88% ee, determined by HPLC analysis [Daicel chiralcel AS, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 10.54 min, t (minor) = 13.90 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.4 Hz, 4H), 7.61-7.53 (m, 2H), 7.47-7.43 (m, 4H), 6.98 (s, 1H), 5.79-5.76 (m, 1H), 4.21-4.09 (m, 4H), 3.12-3.04 (m, 2H), 2.17-1.82 (m, 4H), 1.28-1.25 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.9, 156.6, 156.0, 136.8, 134.9, 133.7, 133.0, 129.3, 128.8, 128.6, 128.0, 77.2, 68.7, 63.4, 63.0, 61.9, 37.7, 31.9, 29.7, 29.3, 27.8, 22.7, 21.2, 14.4, 14.1 ppm; ESI-HRMS: calcd. for $C_{24}H_{28}N_2O_6$+H 441.2020, found 441.2022.



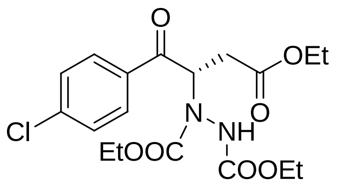
4n

R_f = 0.1 (petroleum ether/EtOAc = 7:1); 39% yield; colorless oil; $[\alpha]_D^{20}$ = -7.0 (c = 0.24 in EtOH); 96% ee, determined by HPLC analysis [Daicel chiralcel AS, n-hexane/i-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 8.70 min, t (minor) = 10.22 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 (br.s, 2H), 7.59 (t, J = 7.1 Hz, 1H), 7.48 (t, J = 7.4 Hz, 2H), 6.90 (br.s, 1H), 5.71 (br.s, 1H), 4.35-4.16 (m, 4H), 3.64 (s, 3H), 2.38-2.36 (m, 2H), 2.02 (br.s, 1H), 1.86 (br.s, 3H), 1.35-1.25 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.7, 173.6, 156.9, 156.0, 135.0, 133.7, 128.8, 128.5, 77.2, 64.1, 63.0, 62.5, 61.9, 51.5, 33.4, 32.7, 31.9, 30.0, 29.7, 29.3, 27.7, 27.1, 22.7, 21.8, 14.4, 14.1 ppm; ESI-HRMS: calcd. for $C_{19}H_{26}N_2O_7$+H 395.1813, found 395.1818.



4o

R_f = 0.1 (petroleum ether/EtOAc = 7:1); 65% yield; colorless oil; $[\alpha]_D^{20}$ = -5.8 (c = 0.36 in EtOH); 91% ee, determined by HPLC analysis [Daicel chiralcel AS, n-hexane/i-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 7.47 min, t (minor) = 11.84 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89-7.80 (m, 2H), 7.62 (d, J = 8.5 Hz, 2H), 6.48 (s, 1H), 6.10 (br.s, 1H), 4.29-4.10 (m, 4H), 3.67 (s, 3H), 2.96-2.92 (m, 2H), 1.33-1.16 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.0, 171.1, 156.0, 155.4, 133.6, 132.1, 130.2, 130.0, 128.9, 77.2, 63.3, 62.3, 59.7, 57.8, 52.1, 33.3, 32.7, 31.9, 29.7, 29.5, 29.3, 14.3, 14.1 ppm; ESI-HRMS: calcd. for $C_{17}H_{21}BrN_2O_7$+H 445.0610, found 445.0613.



4p

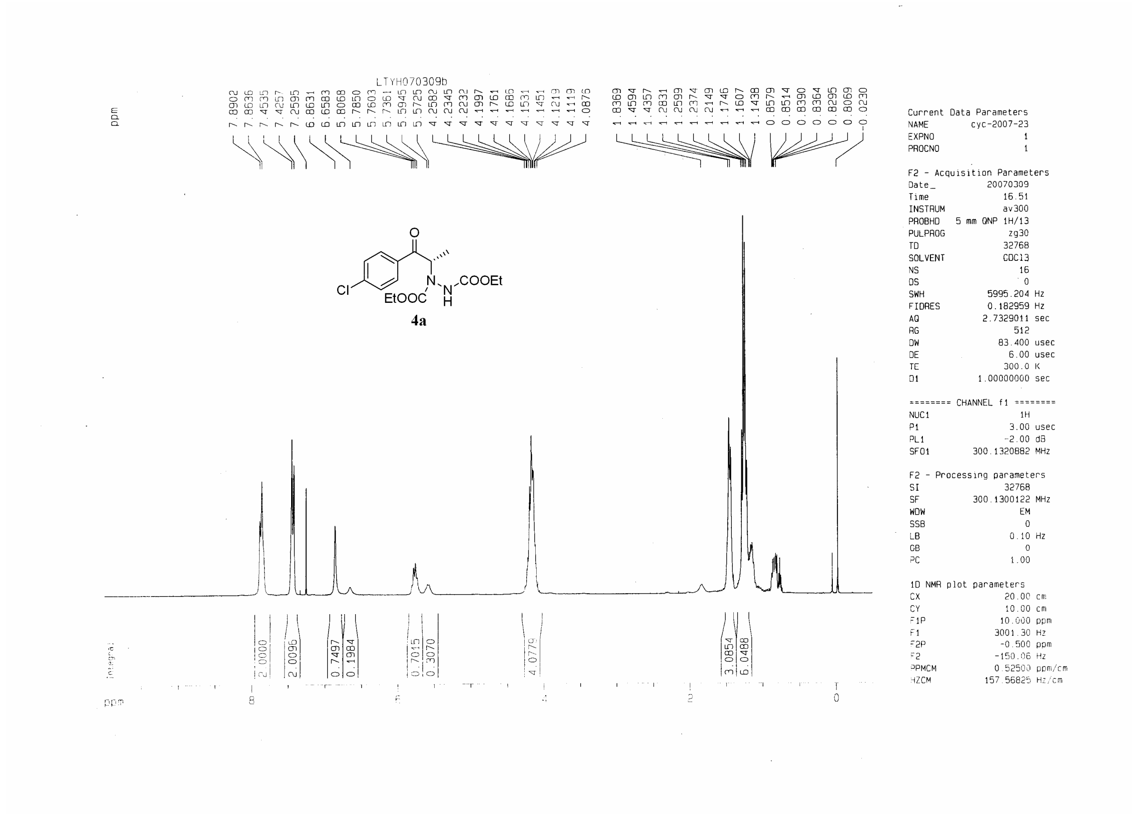
R_f = 0.1 (petroleum ether/EtOAc = 9:1); 63% yield; colorless oil; $[\alpha]_D^{20}$ = -20.0 (c = 0.31 in EtOH); 91% ee, determined by HPLC analysis [Daicel chiralcel AS, n-hexane/i-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 7.30 min, t (minor) = 10.93 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98-7.91 (m, 2H), 7.45 (d, J = 8.4 Hz, 2H), 6.49 (s, 1H), 6.11 (br.s, 1H), 4.15-4.09 (m, 6H), 2.95-2.93 (m, 2H), 1.22 (t, J = 6.9 Hz, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.8, 170.6, 156.0, 155.5, 140.1, 133.3, 130.1, 129.9, 129.1, 77.2, 63.5, 63.3, 62.2, 61.0, 59.6, 57.6, 33.6, 33.0, 29.7, 22.6, 14.3, 14.0 ppm; ESI-HRMS: calcd. for $C_{18}H_{23}ClN_2O_7$+H 415.1267, found 415.1271.

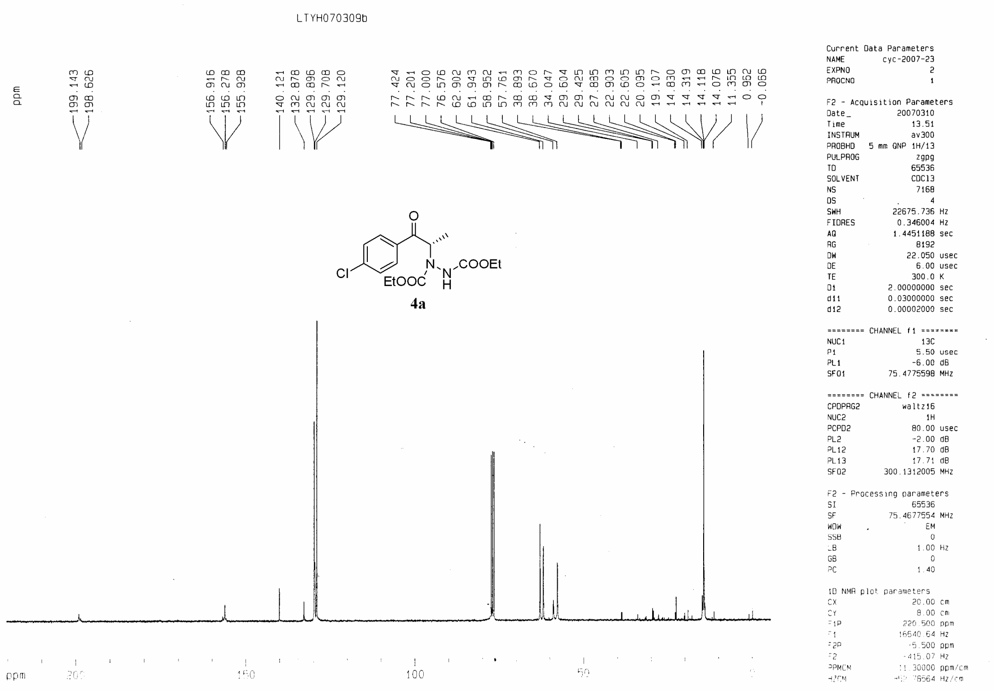
References

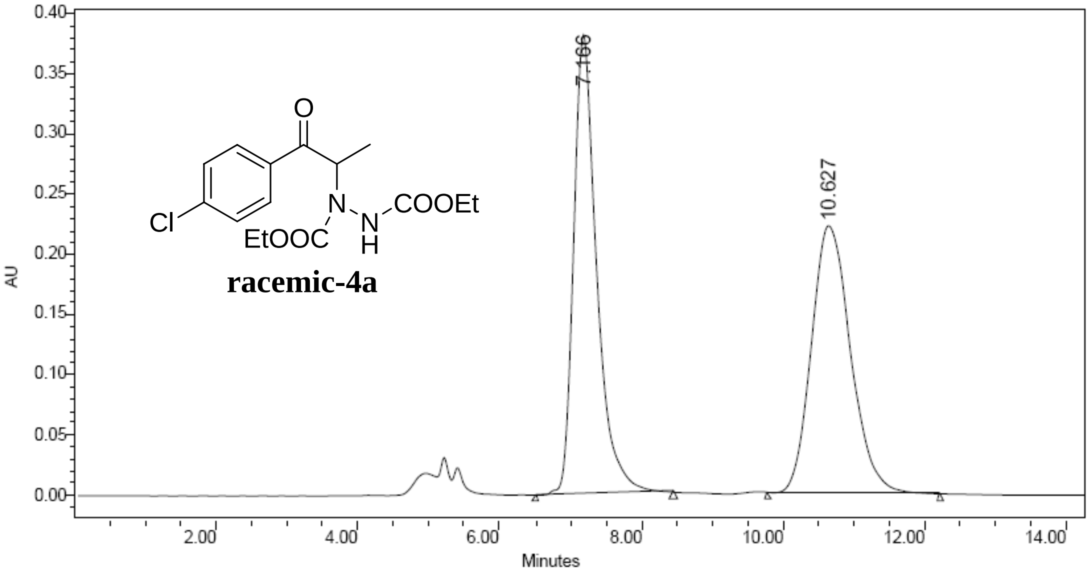
(1) Brunner, H.; Bügler, J.; Nuber, B. *Tetrahedron: Asymmetry* **1995**, *6*, 1699.

(2) Matsubara, R.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2006,** *45*, 7993.

NMR and HPLC spectra







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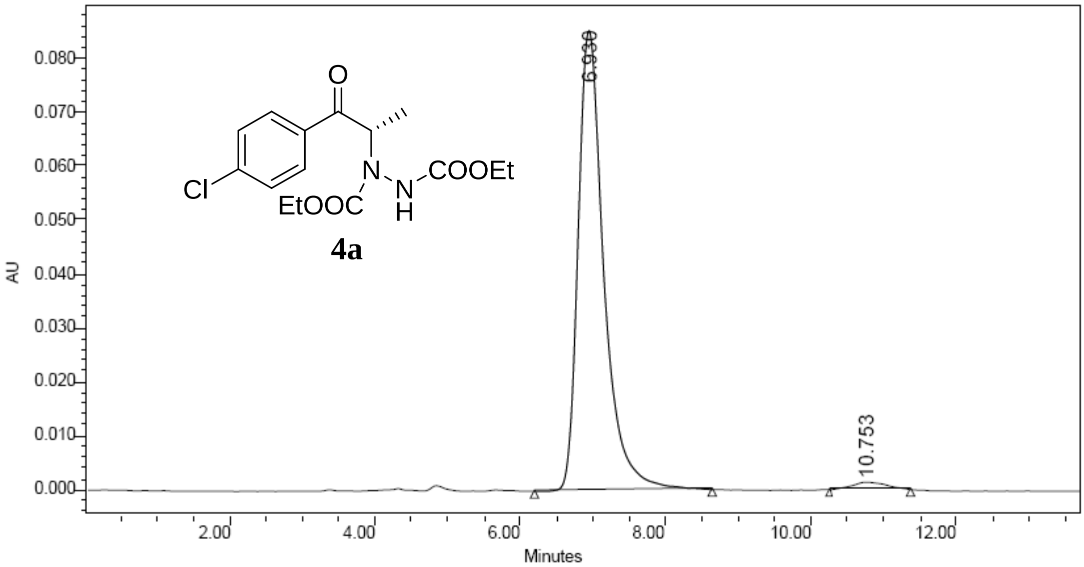

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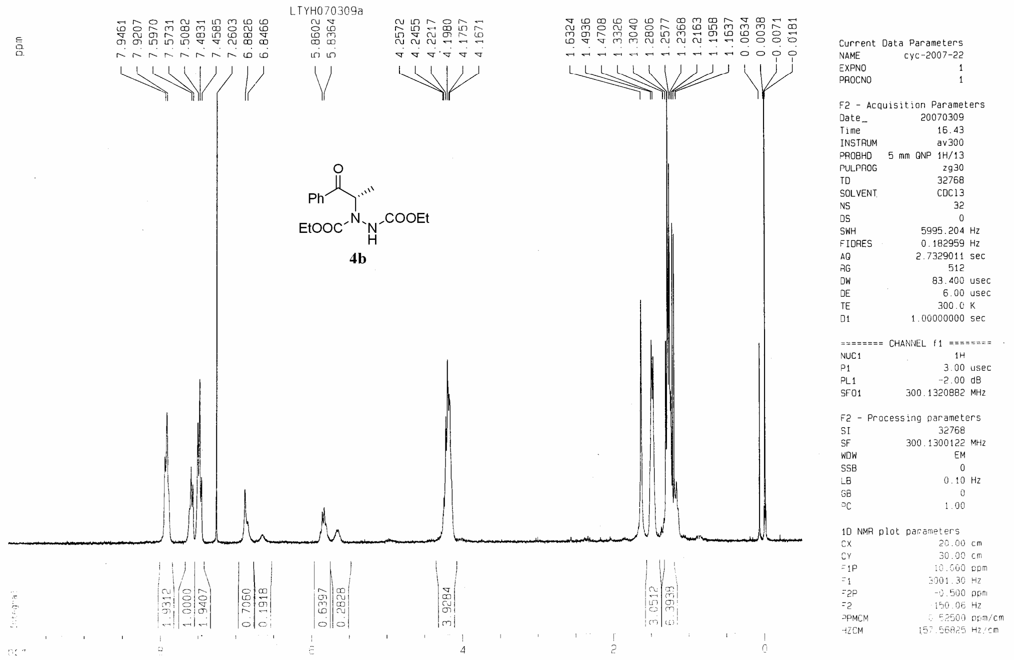
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4.2455
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1.3040
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COOEt
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LB 0.10 Hz
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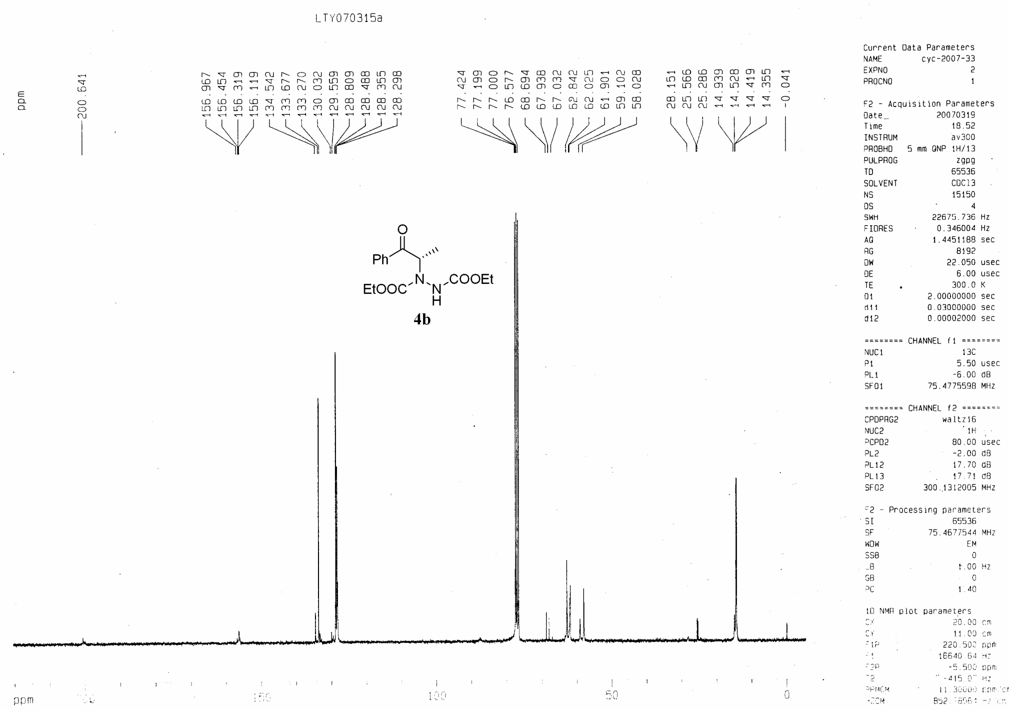
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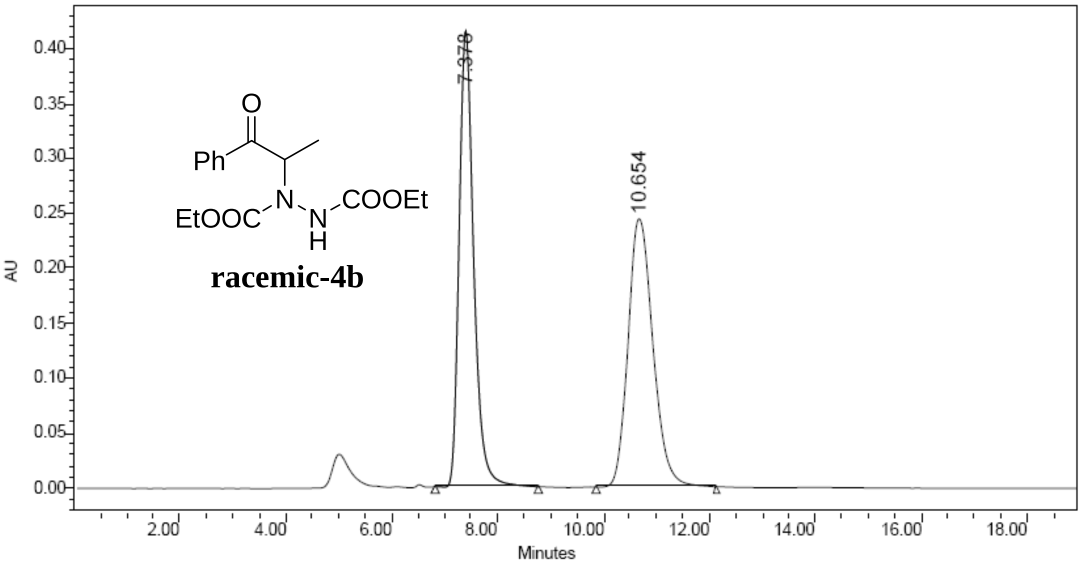

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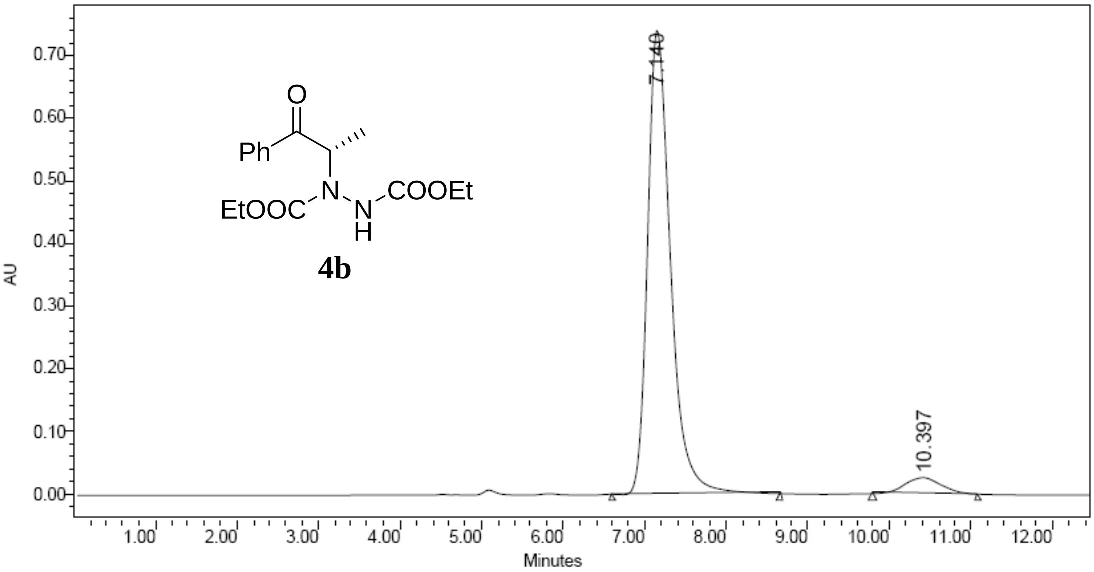

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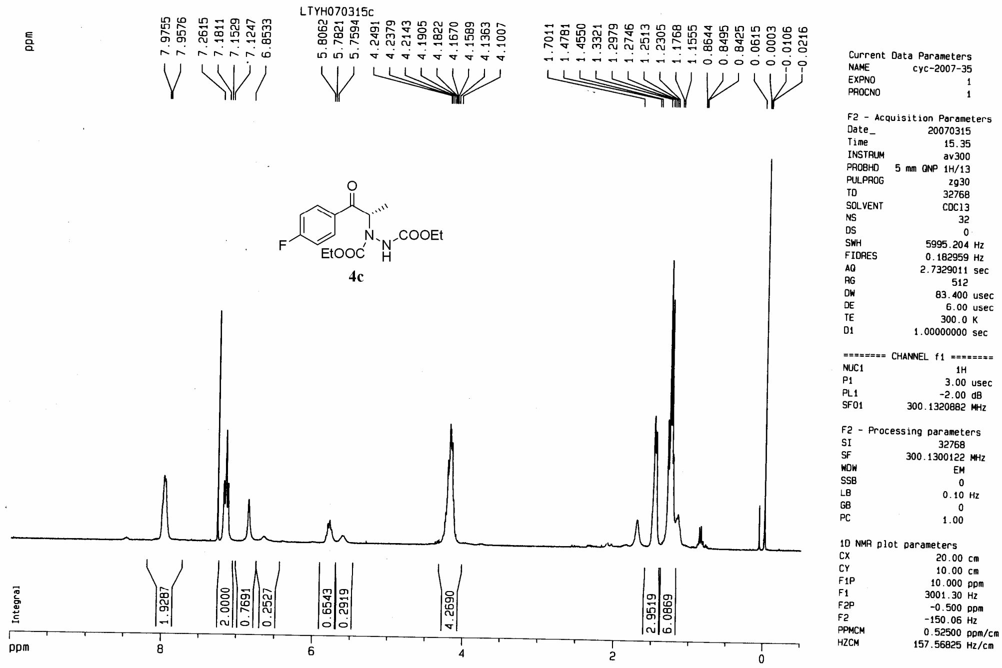

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FIDRES 0.182959 Hz
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CY 10.00 cm
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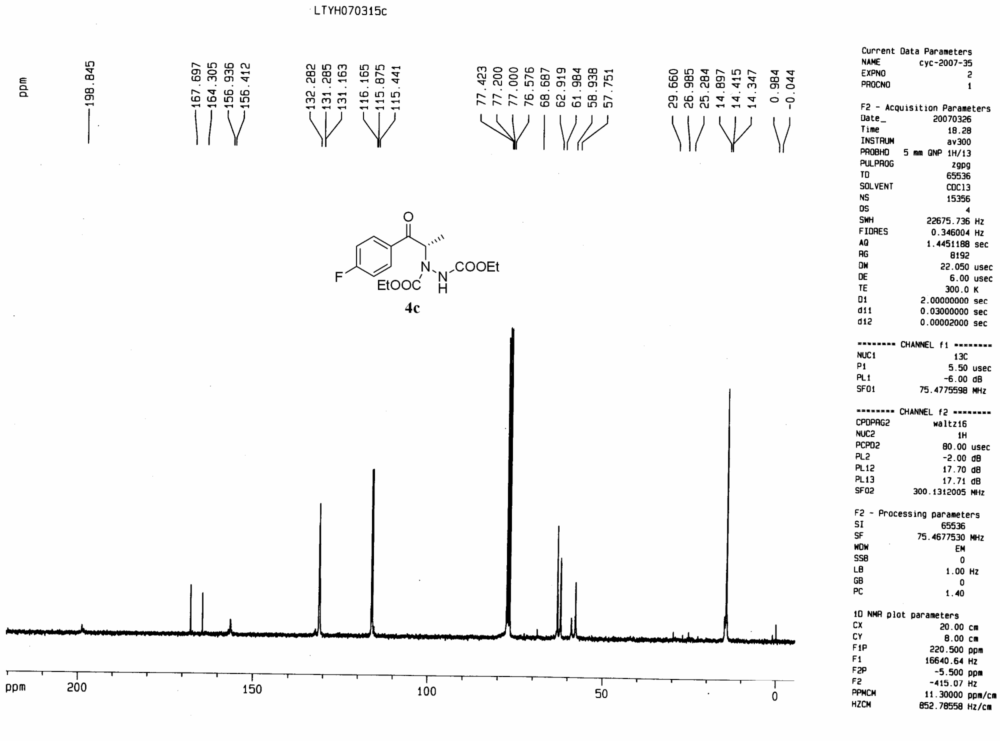
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm



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PROCNO 1
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F2P -5.500 ppm
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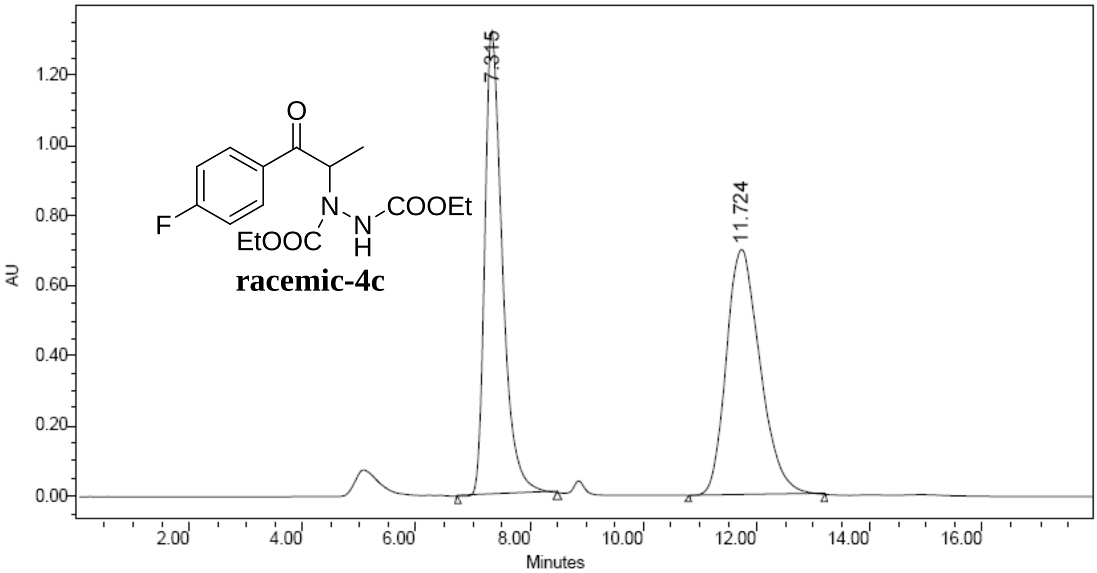
HZCM 852.78558 Hz/cm



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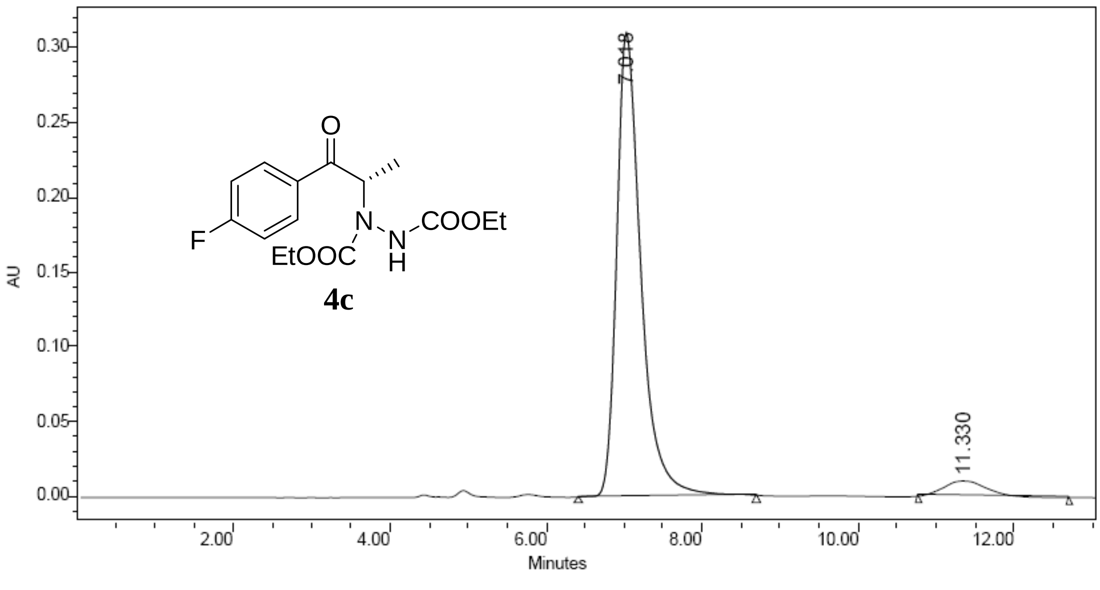

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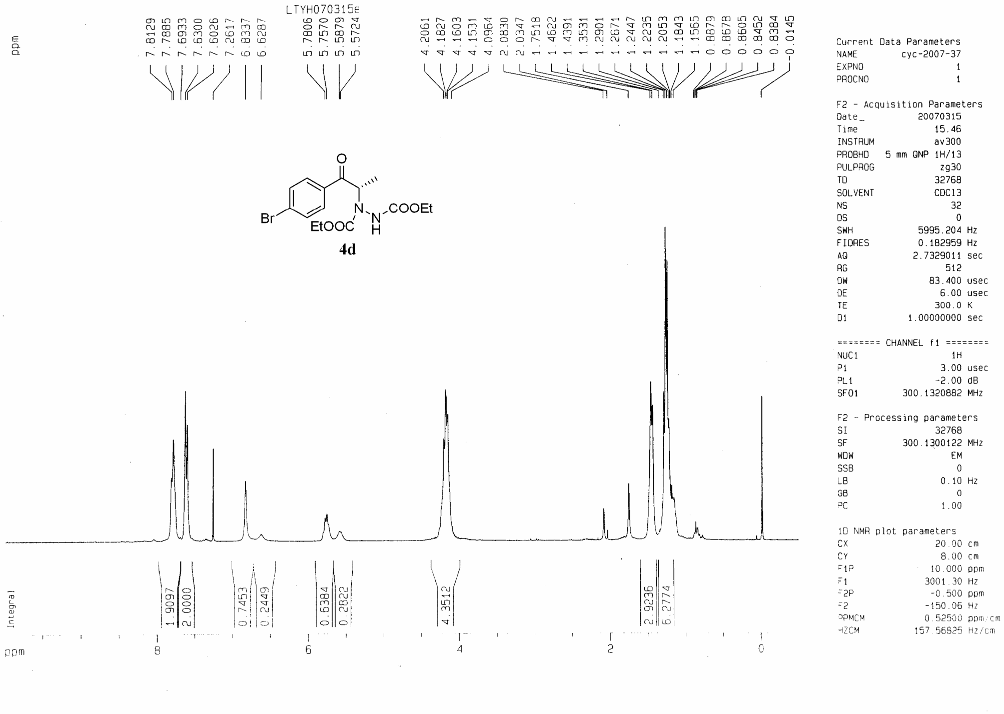

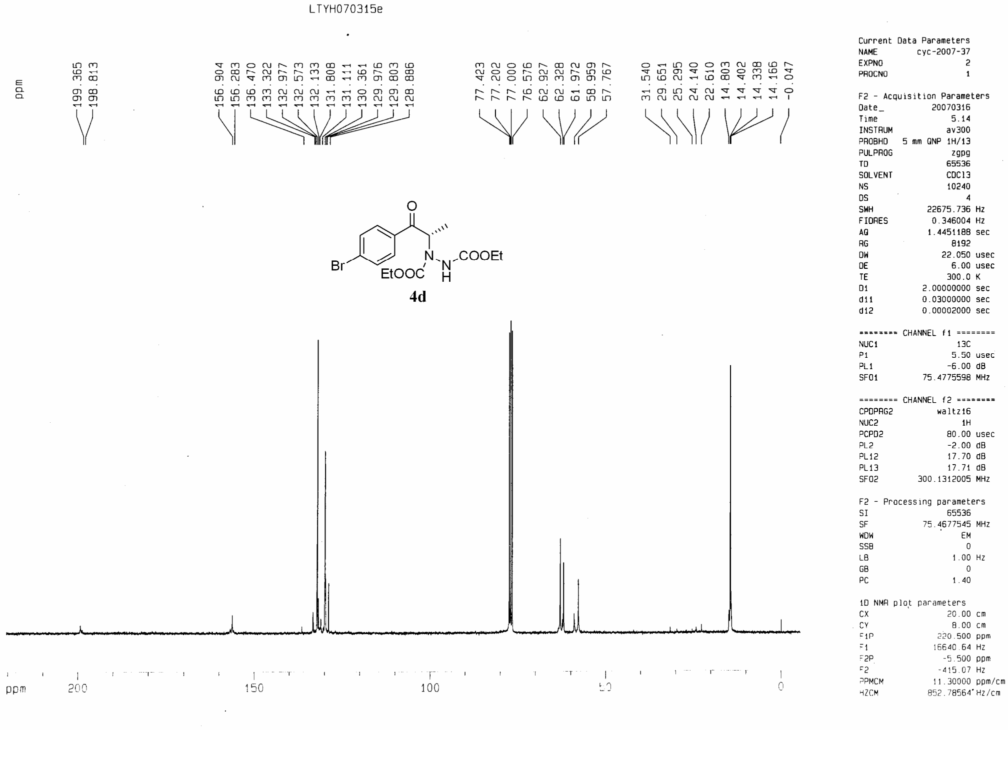

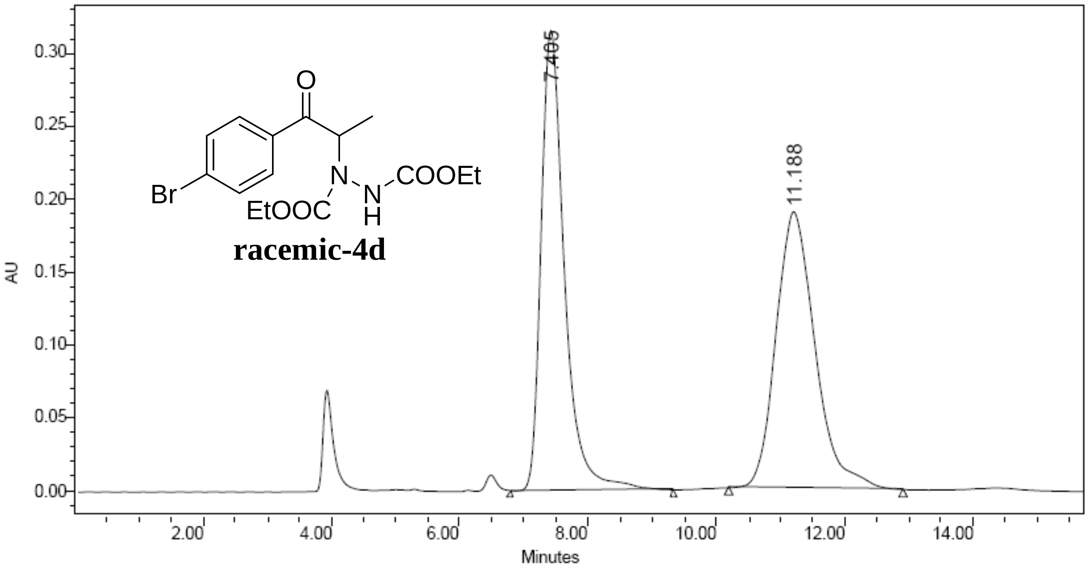

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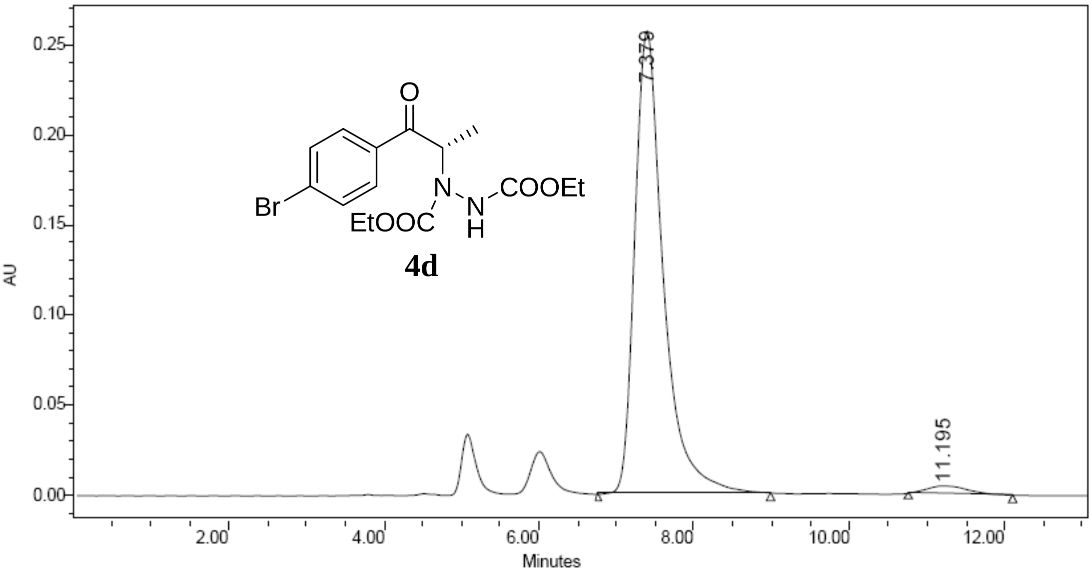

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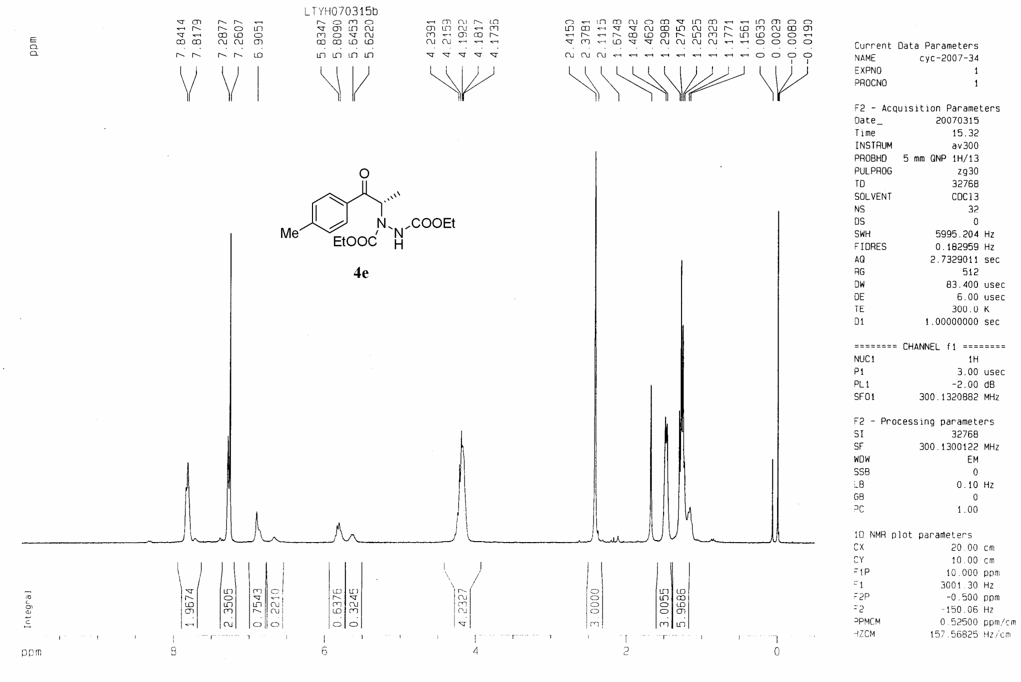
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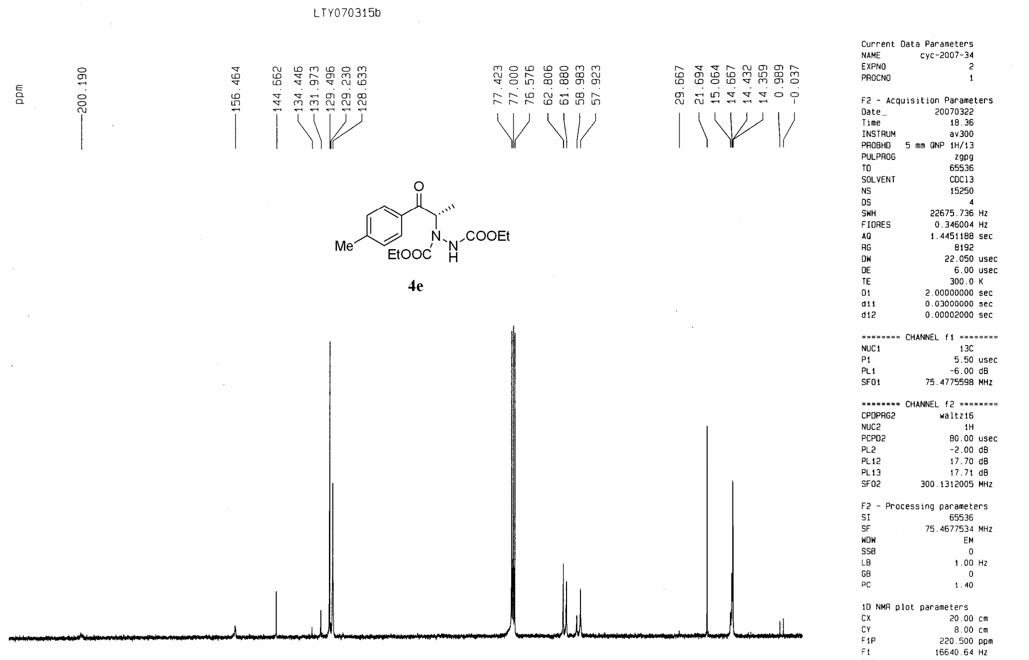
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RG 8192
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DE 6.00 usec
TE 300.0 K
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CY 8.00 cm
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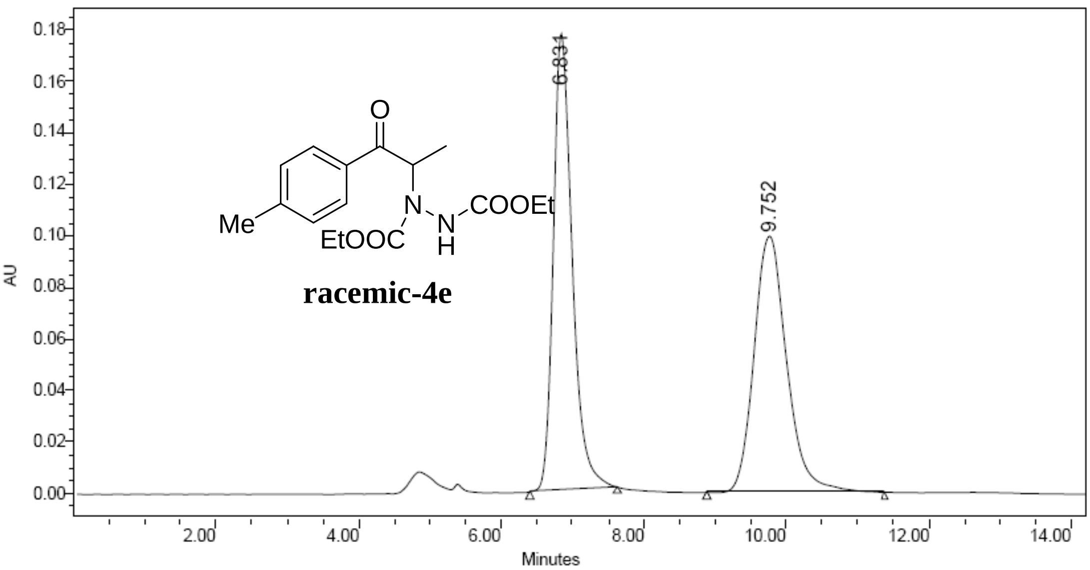

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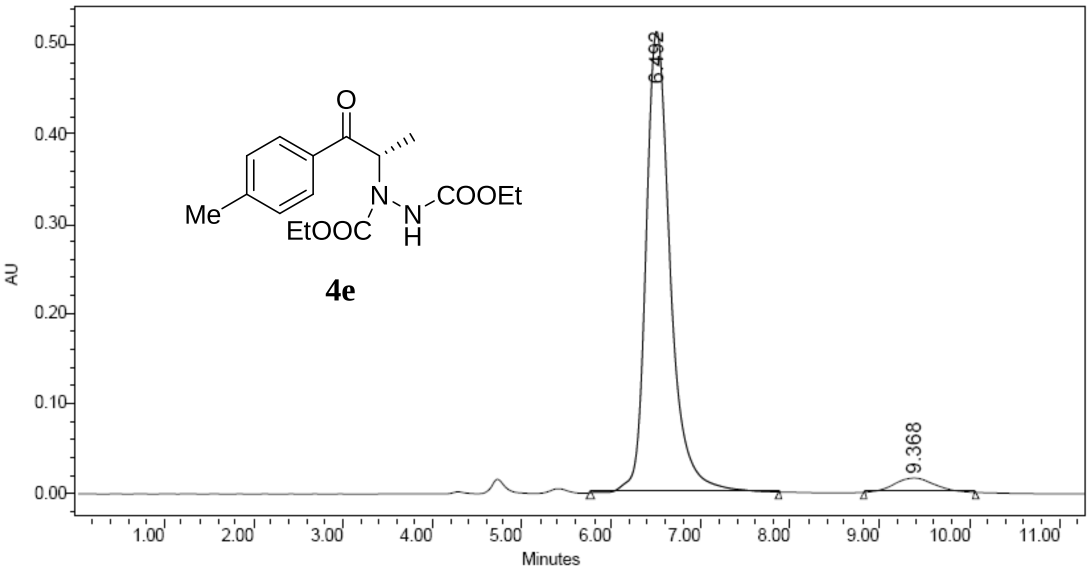

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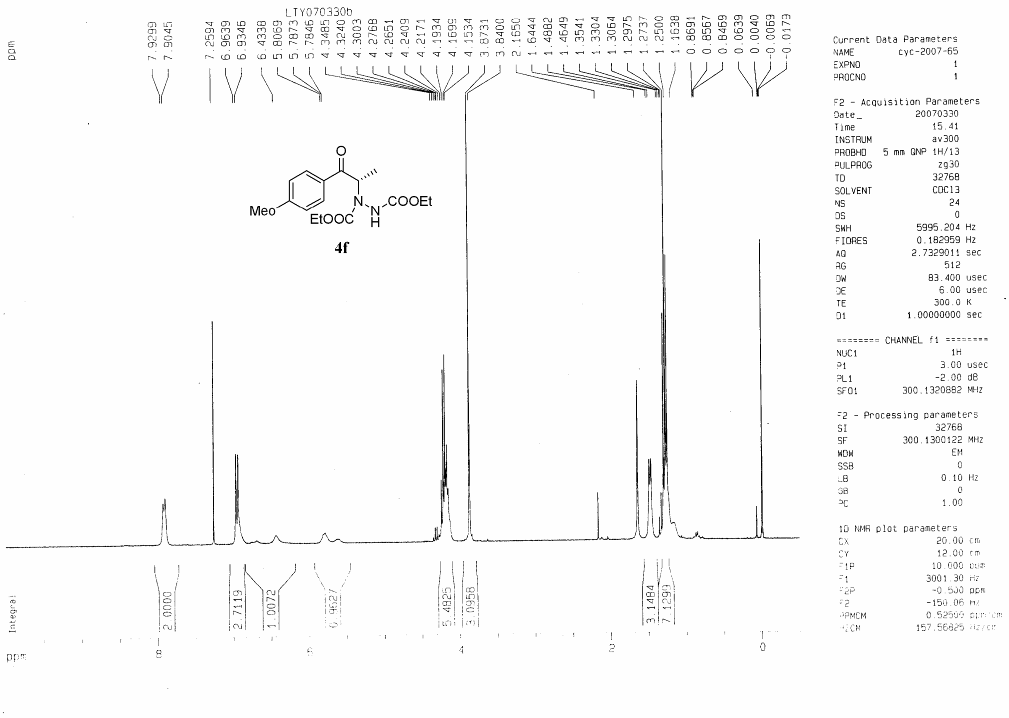
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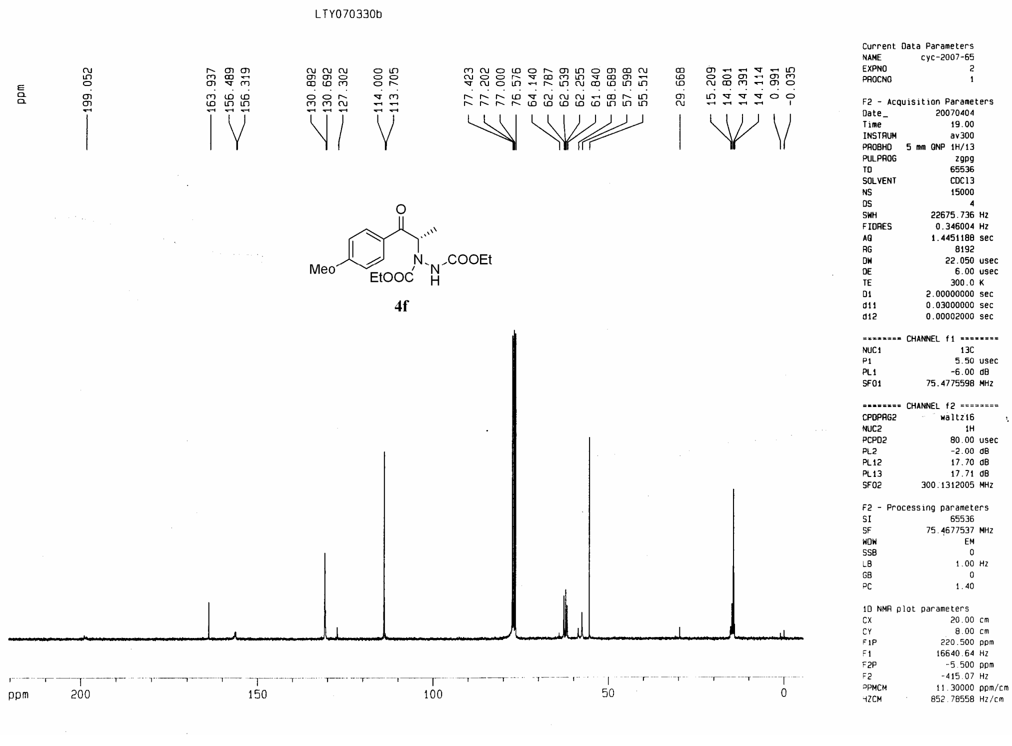
COOEt
O
4f
Integral 2.0000 2.7119 1.0072 0.9627 5.4825 3.0958 3.1484 7.1291
ppm 6 4 2 0
Current Data Parameters
NAME cyc-2007-65
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070330
Time 15.41
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 24
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 512
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz
F2 - Processing parameters
SI 32768
SF 300.1300122 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 12.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm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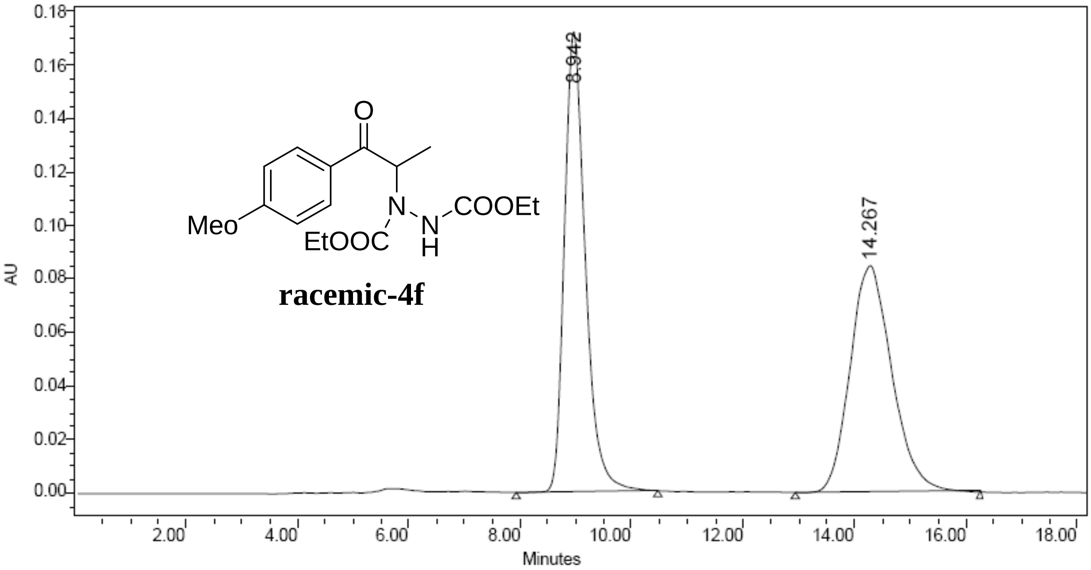
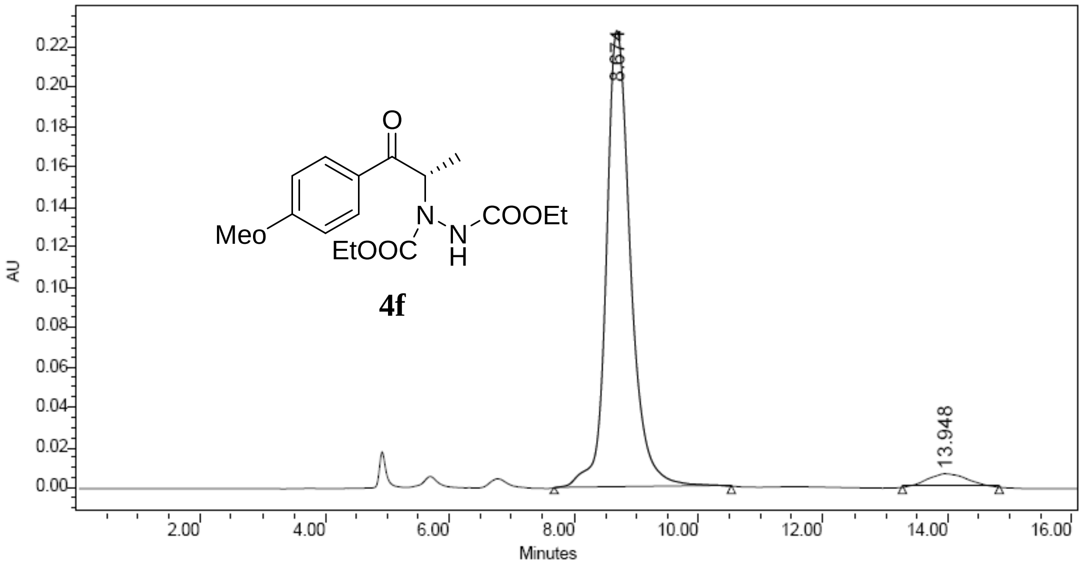
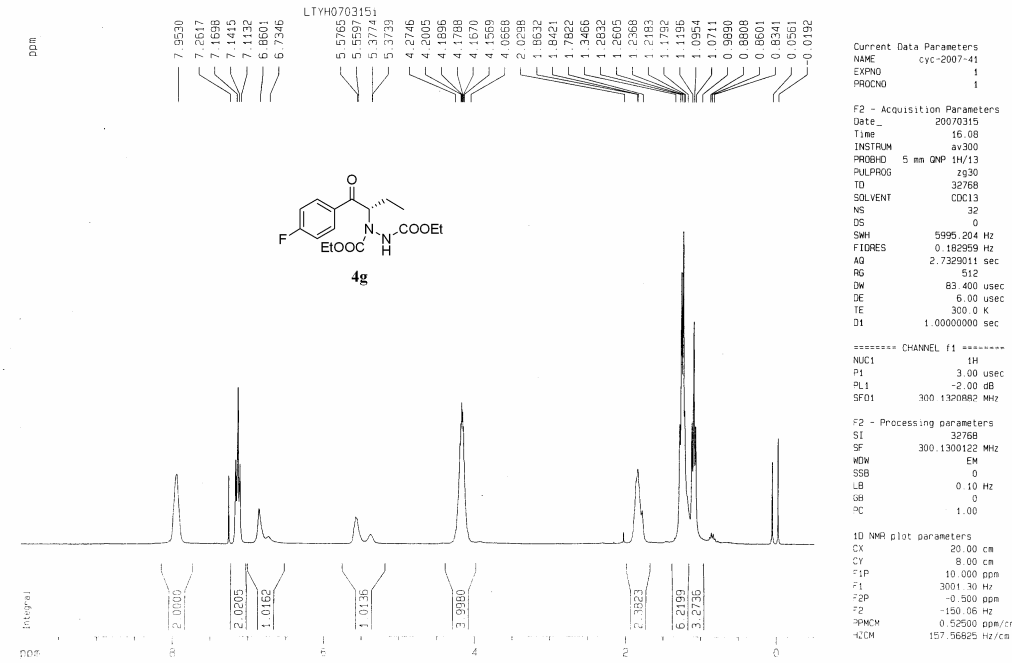
MeO
EtOOC
N
N
H
COOEt
O
4f
ppm 200 150 100 50 0
Current Data Parameters
NAME cyc-2007-65
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070404
Time 19.00
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 15000
DS 4
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SFO1 75.4775598 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 65536
SF 75.4677537 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
CY 8.00 cm
F1P 220.500 ppm
F1 16640.64 Hz
F2P -5.500 ppm
F2 -415.07 Hz
PPMCM 11.30000 ppm/cm
HZCM 852.78558 Hz/cm



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	8.942	4495742	50.31	172420	67.01
2	14.267	4440619	49.69	84880	32.99



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	8.674	6281791	96.88	228123	97.69
2	13.948	202047	3.12	5398	2.31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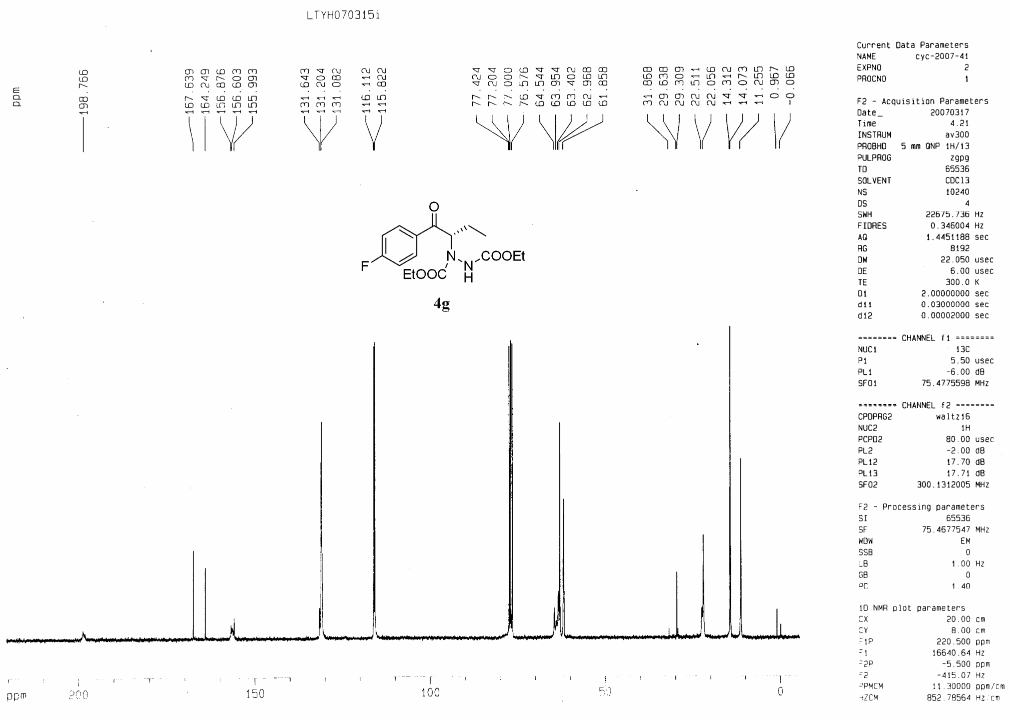
EtOOC
COOEt
F
4g
2.0000 2.0205 1.0162 1.0136 3.9980 2.3823 6.2199 3.2736
Integral
ppm 8 6 4 2 0
Current Data Parameters
NAME cyc-2007-41
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070315
Time 16.08
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 512
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz
F2 - Processing parameters
SI 32768
SF 300.1300122 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 8.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm


LTYH070315i
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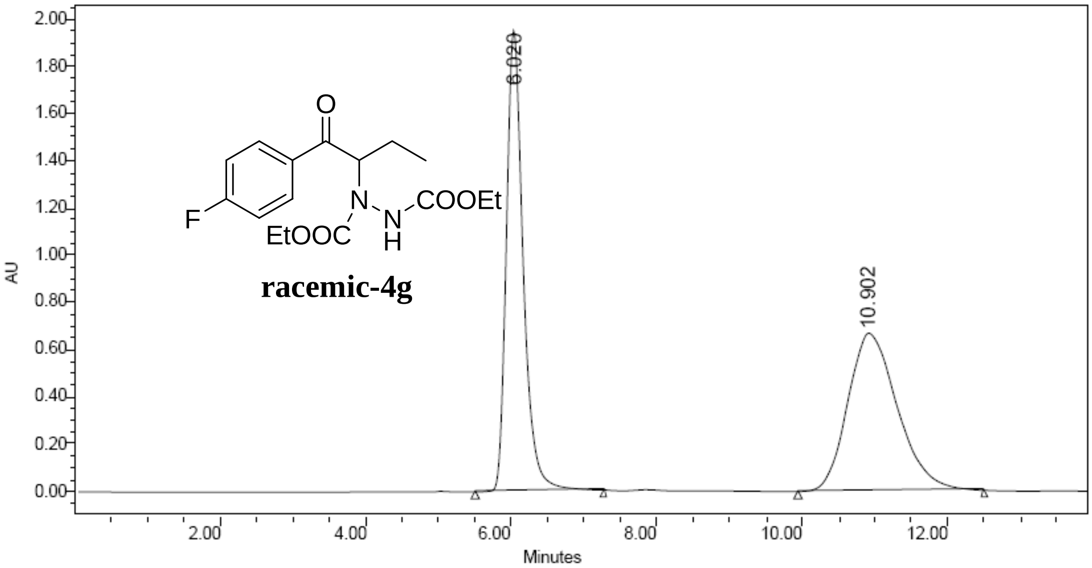
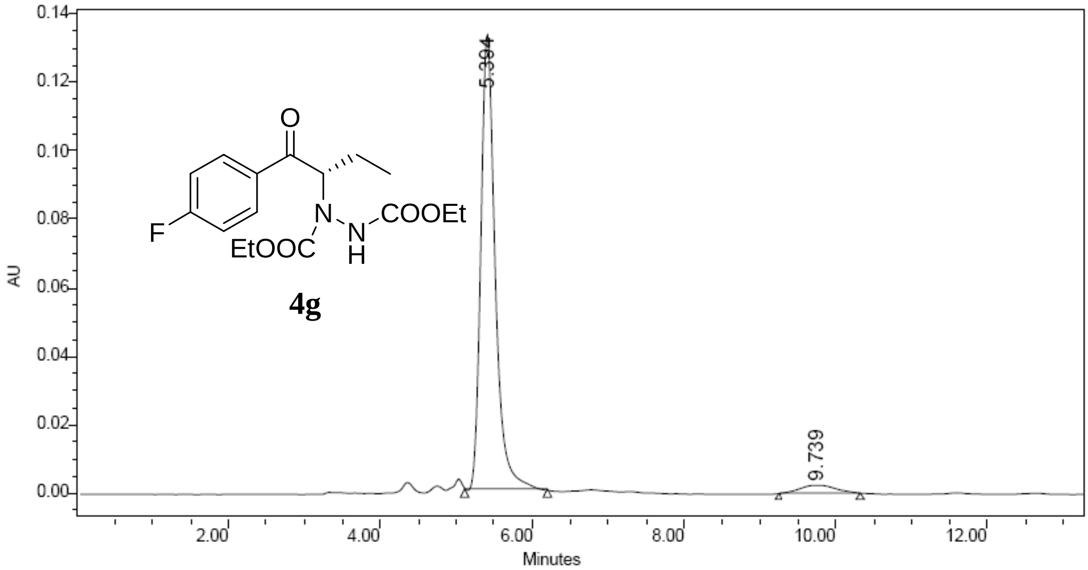
EtOOC
COOEt
F
4g
ppm 200 150 100 50 0
Current Data Parameters
NAME cyc-2007-41
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070317
Time 4.21
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 10240
DS 4
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SFO1 75.4775598 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 65536
SF 75.4677547 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
CY 8.00 cm
F1P 220.500 ppm
F1 16640.64 Hz
F2P -5.500 ppm
F2 -415.07 Hz
PPMCM 11.30000 ppm/cm
HZCM 852.78564 Hz/cm



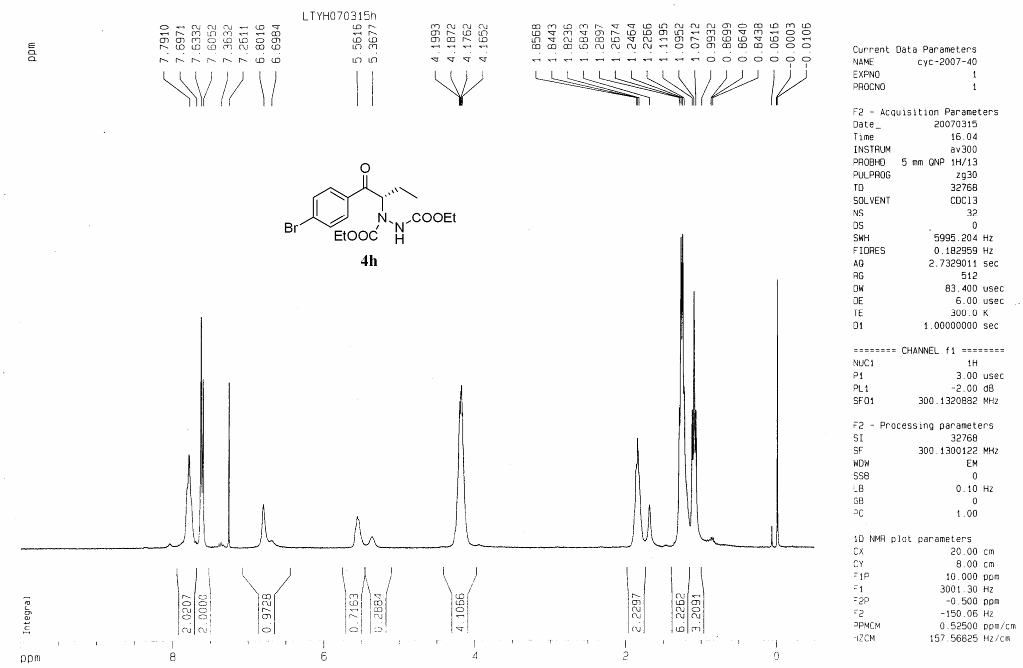
racemic-4g

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.020	31467918	49.72	1953225	74.47
2	10.902	31826290	50.28	669546	25.53



4g

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.394	1757264	98.05	133179	98.91
2	9.739	34960	1.95	1465	1.09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7.6052
7.3632
7.2611
6.8016
6.6984
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4.1993
4.1872
4.1762
4.1652
1.8568
1.8443
1.8236
1.6843
1.2897
1.2674
1.2464
1.2266
1.1195
1.0952
1.0712
0.9932
0.8699
0.8640
0.8438
0.0616
-0.0003
-0.0106
Br
EtOOC
N
N
H
COOEt
O
4h
Current Data Parameters
NAME cyc-2007-40
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070315
Time 16.04
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 512
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz
F2 - Processing parameters
SI 32768
SF 300.1300122 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 8.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56625 Hz/cm
2.0207
2.0000
0.9728
0.7163
0.2884
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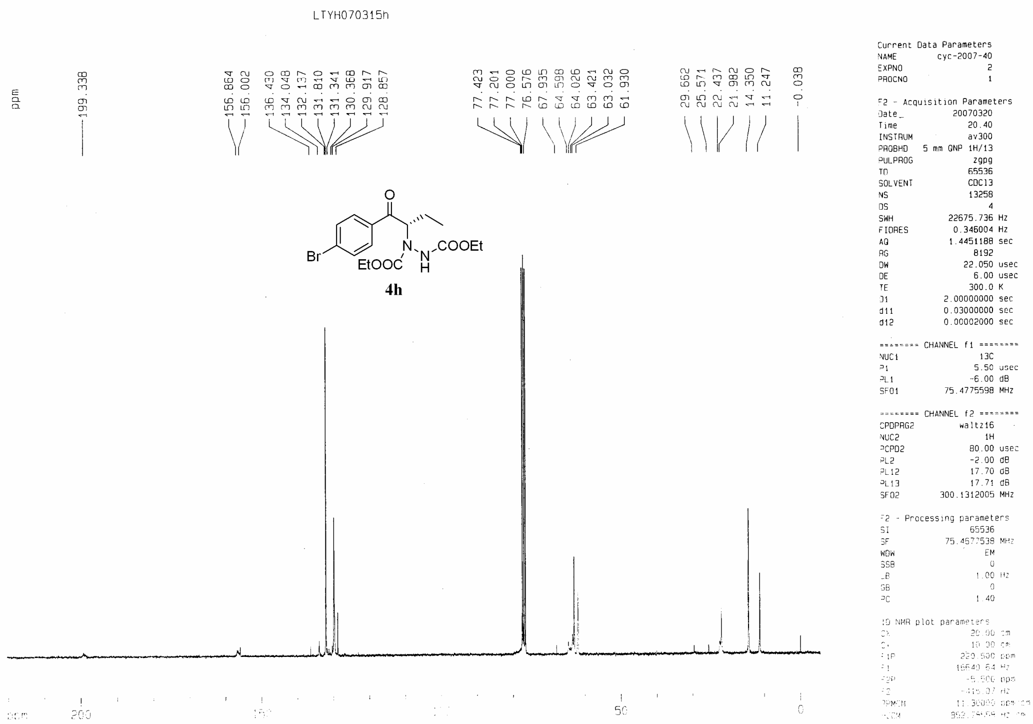
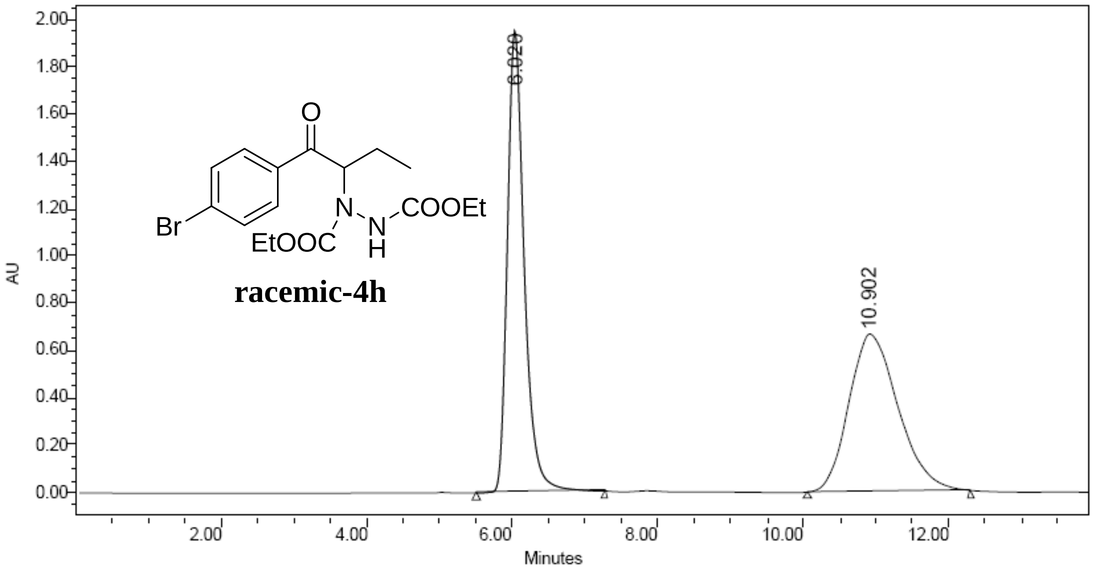
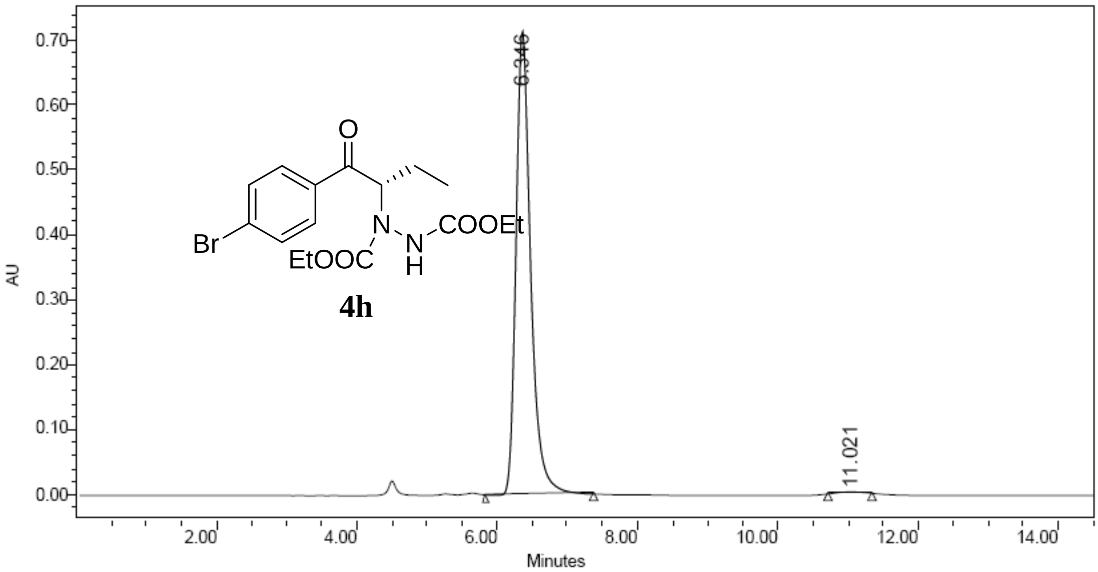
8
6
4
2
0

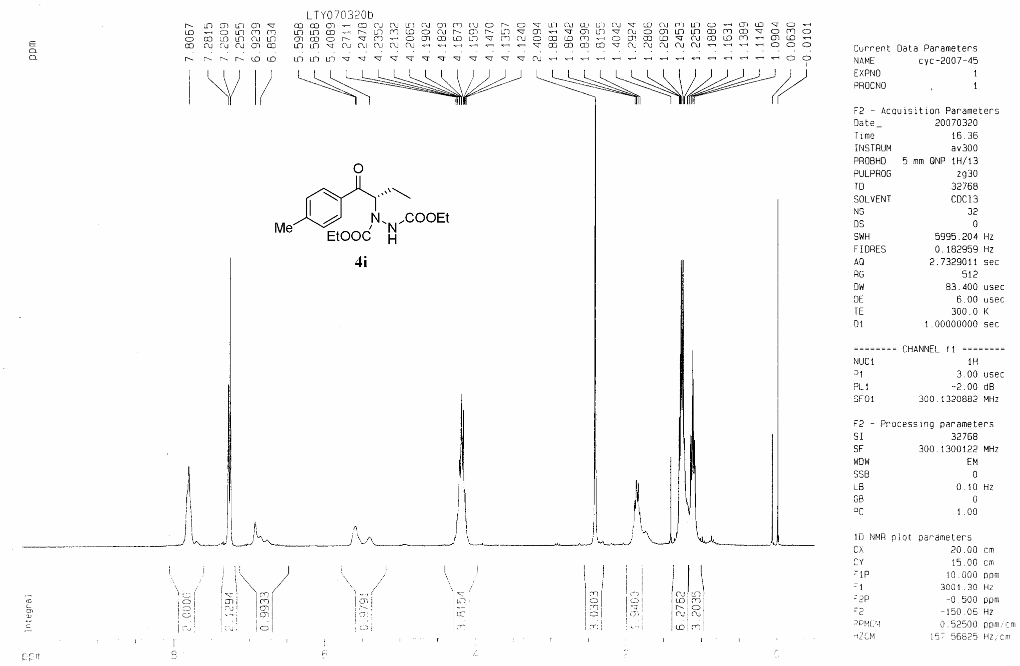

LTYH070315h
199.338
156.864
156.002
136.430
134.048
132.137
131.810
131.341
130.368
129.917
128.857
77.423
77.201
77.000
76.576
67.935
64.598
64.026
63.421
63.032
61.930
29.662
25.571
22.437
21.982
14.350
11.247
-0.038
Br
EtOOC
N
N
H
COOEt
O
4h
Current Data Parameters
NAME cyc-2007-40
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070320
Time 20.40
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 13258
DS 4
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SFO1 75.4775598 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 65536
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
ppm
200
50
0



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.020	31467918	50.07	1953225	74.55
2	10.902	31373957	49.93	666670	25.45



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.346	10408808	99.39	714110	99.62
2	11.021	63632	0.61	2742	0.38


LTY070320b
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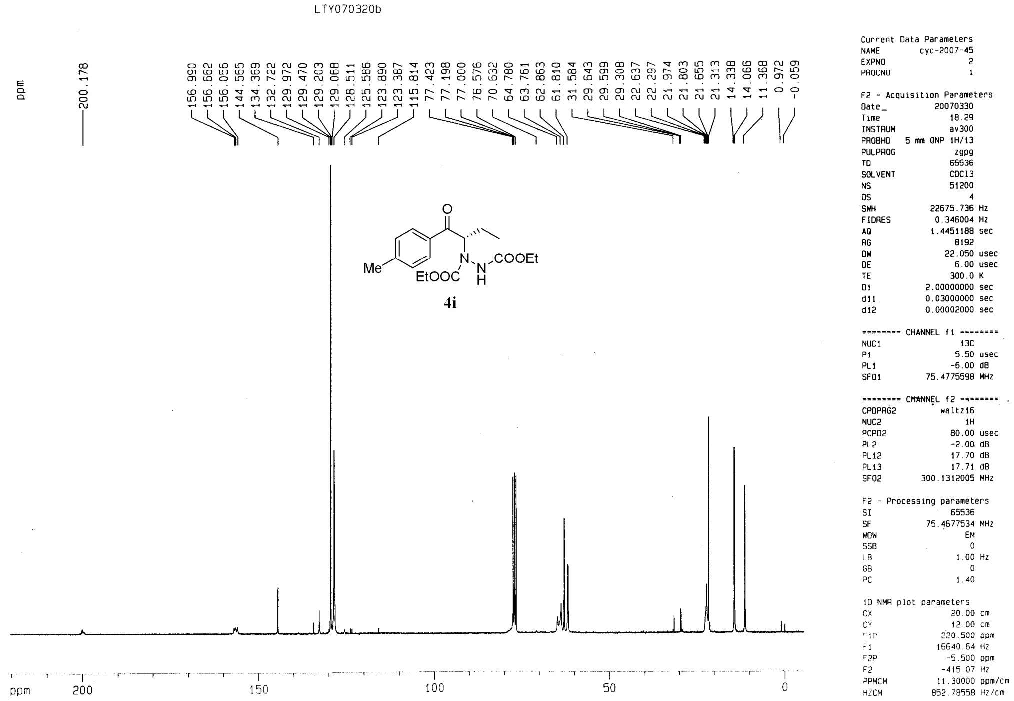
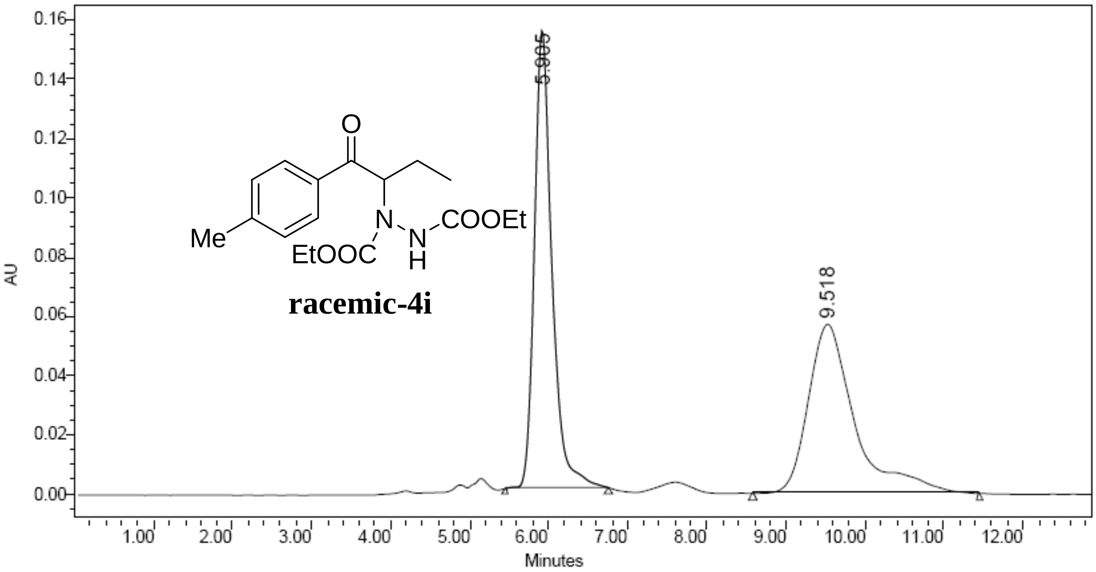
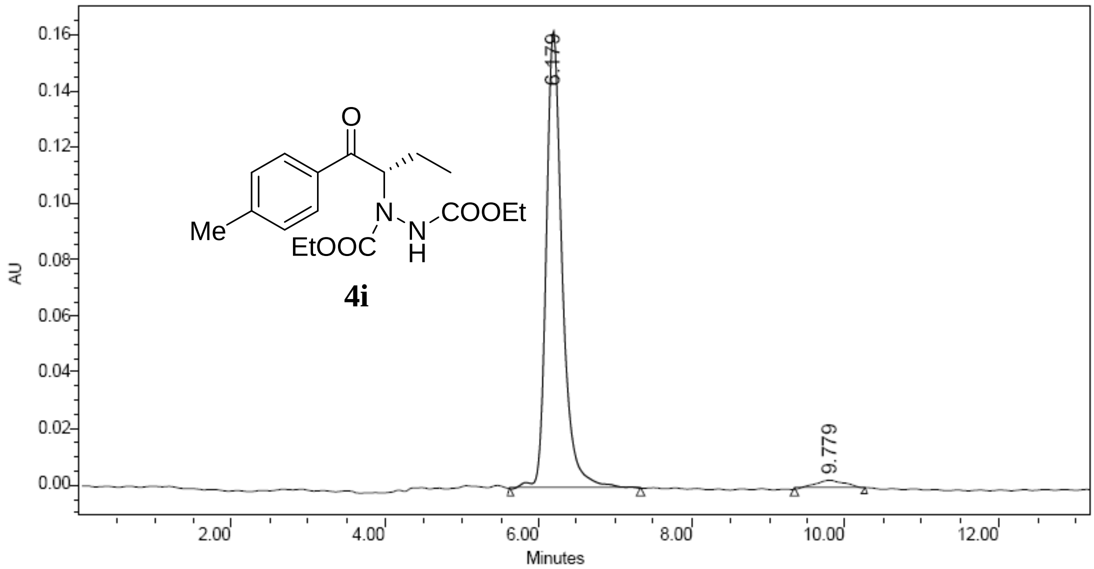
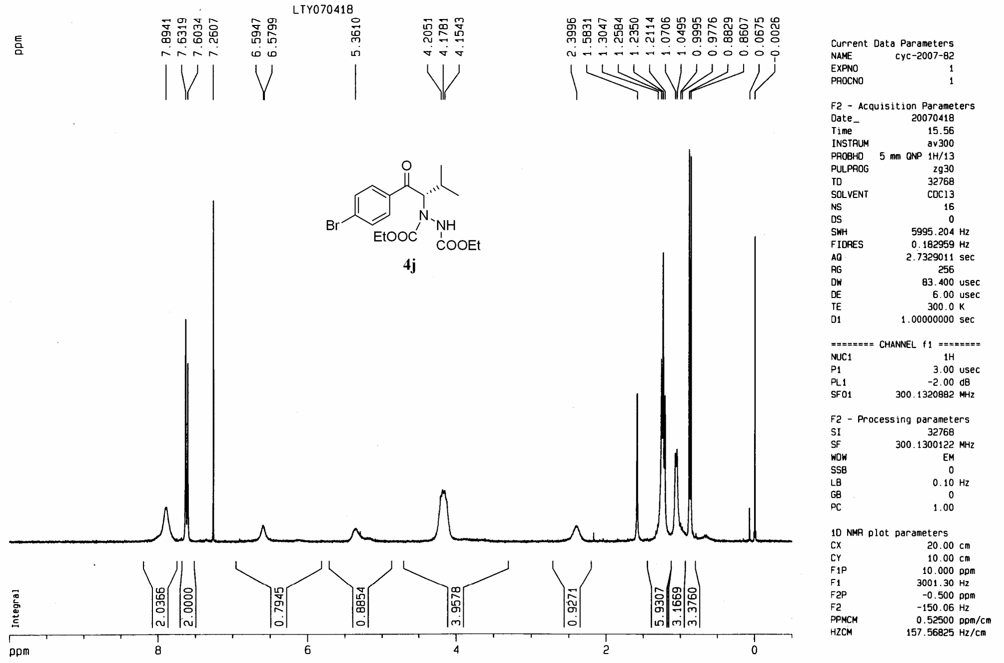

LTY070320b
4i

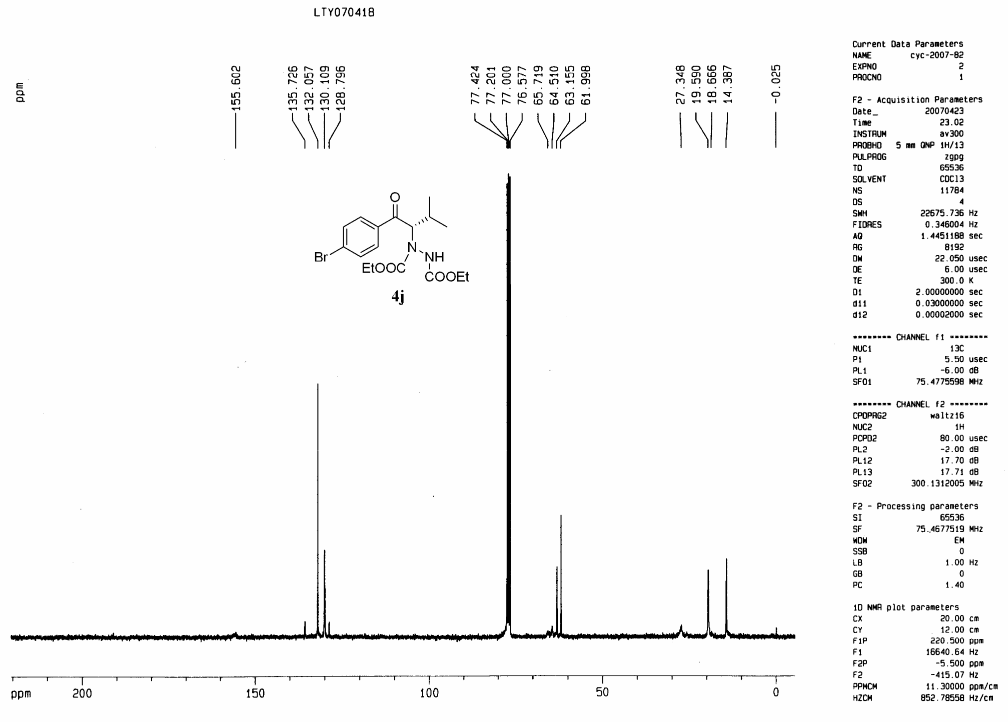


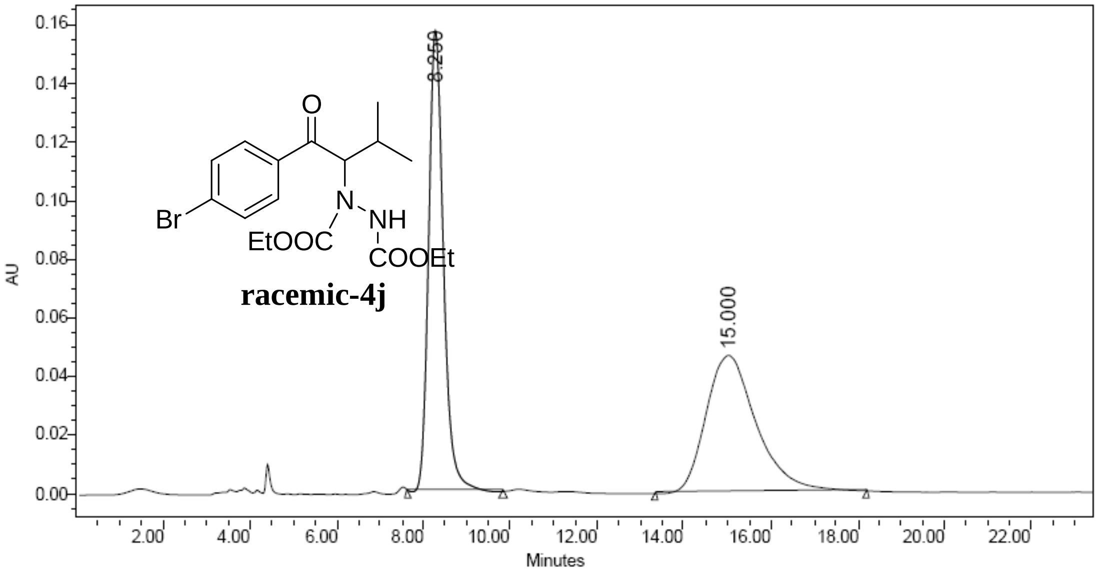
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.905	2385442	50.44	154666	73.01
2	9.518	2343500	49.56	57184	26.99



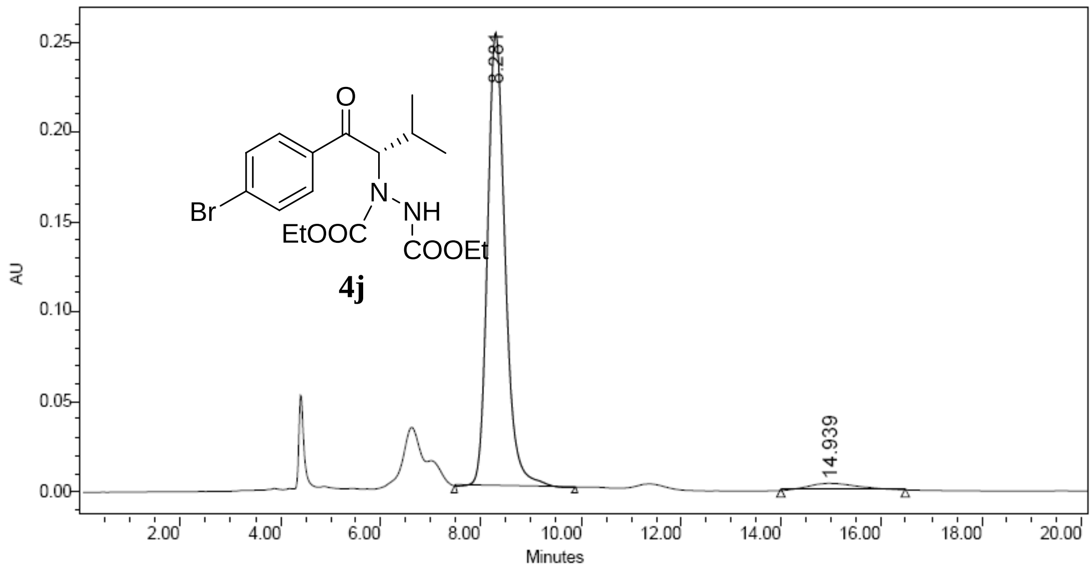
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.179	2363984	98.85	162528	99.01
2	9.779	27474	1.15	1626	0.99



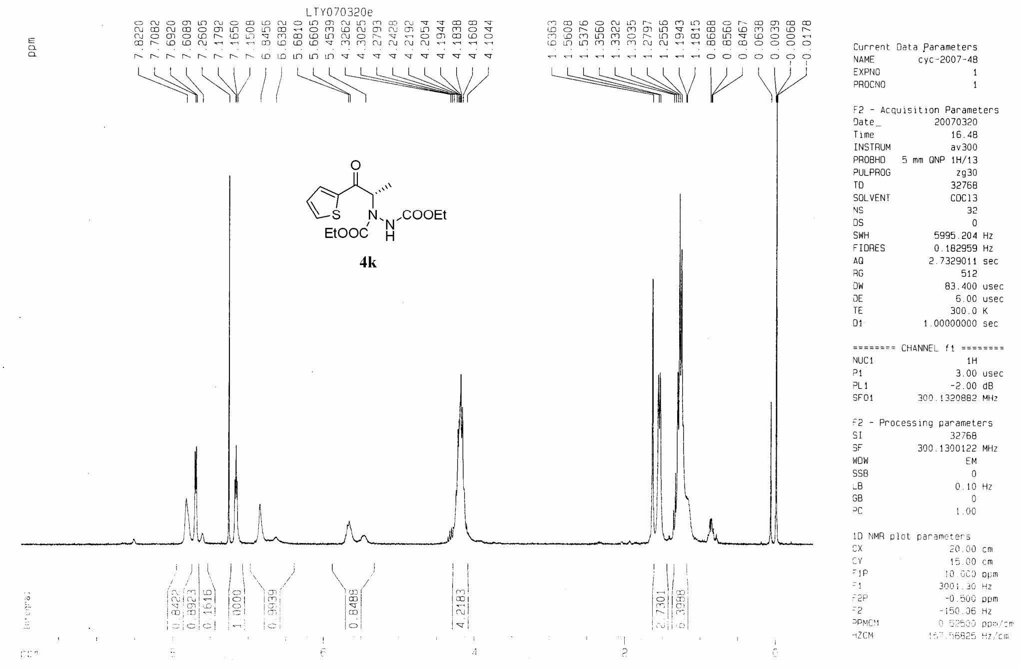


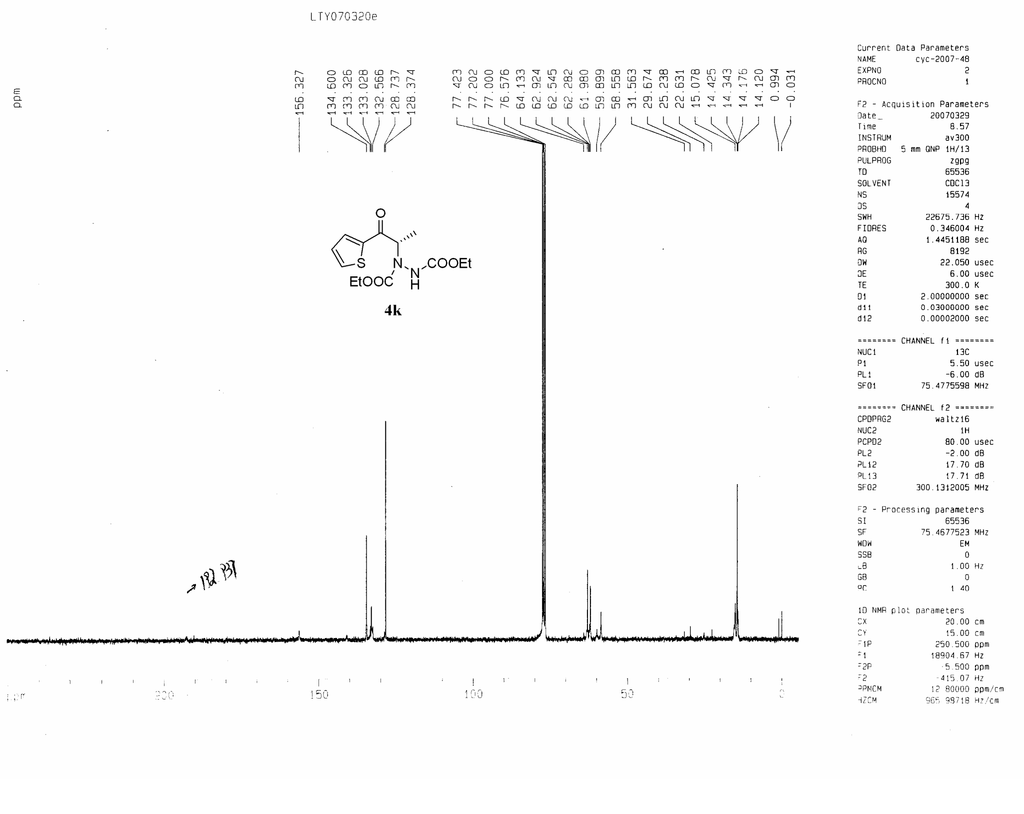


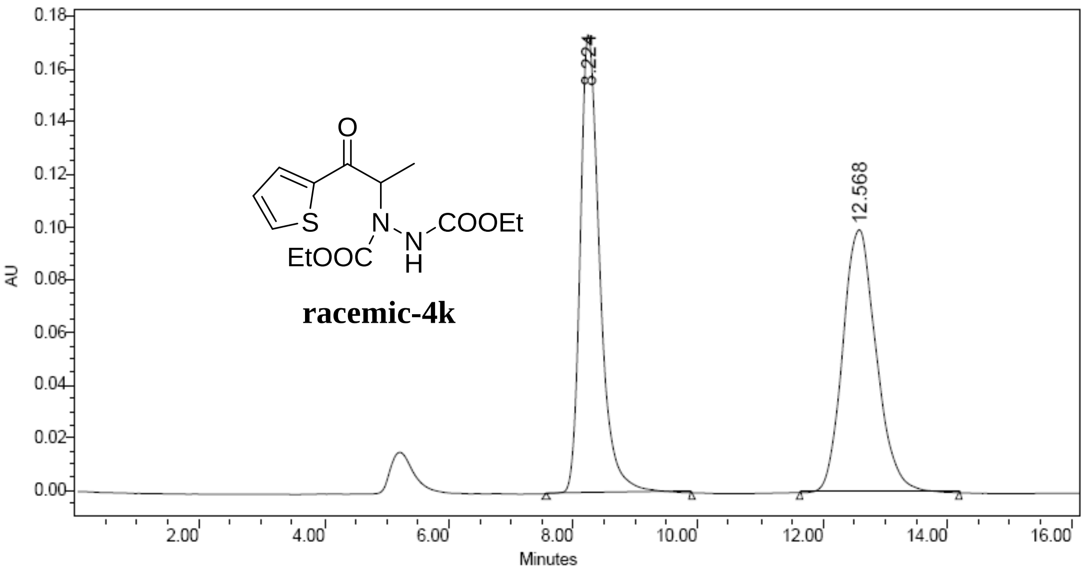
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	8.250	3726191	49.53	156802	77.00
2	15.000	3797236	50.47	46833	23.00



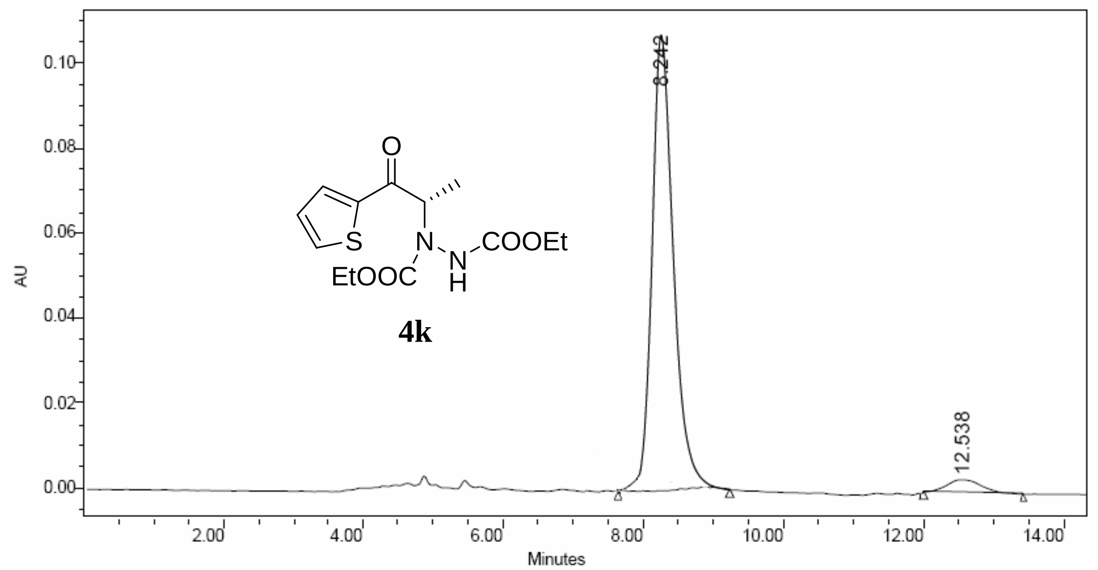
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	8.281	6193192	98.40	252512	99.12
2	14.939	100970	1.60	2241	0.88



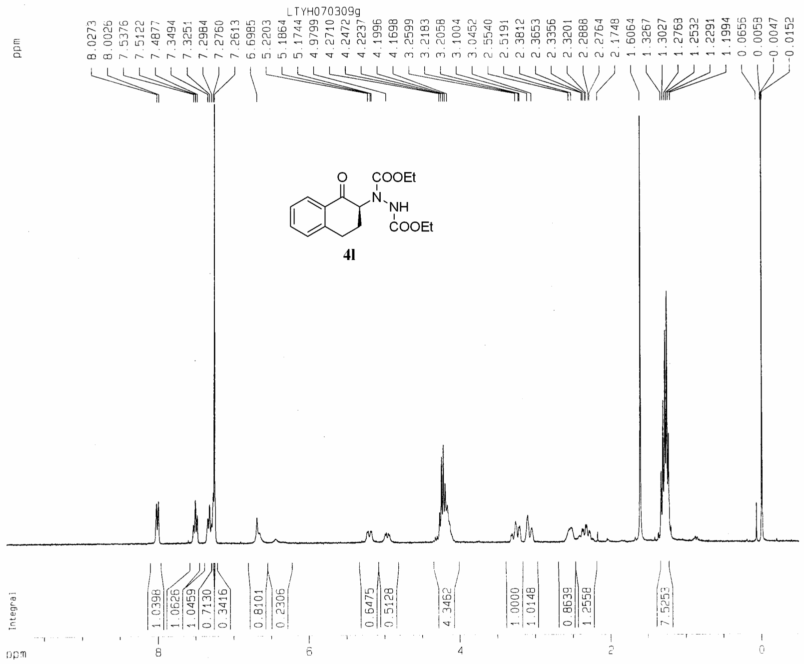




	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	8.224	3812947	50.35	174296	63.58
2	12.568	3759901	49.65	99845	36.42



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	8.242	2173054	97.84	105343	98.17
2	12.538	48030	2.16	1960	1.83



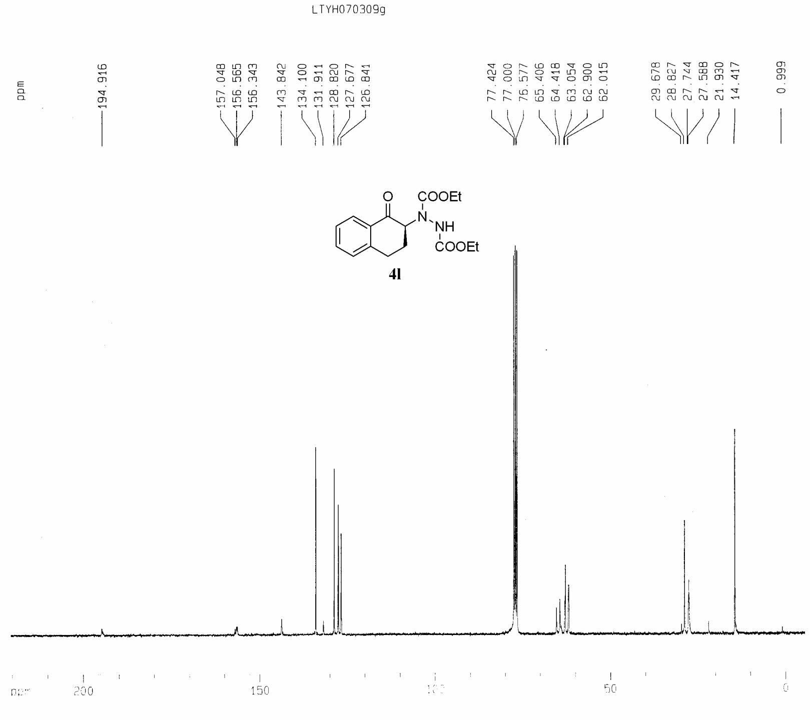
Current Data Parameters
NAME cyc-2007-27
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070309
Time 17.38
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 512
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz

F2 - Processing parameters
SI 32768
SF 300.1300122 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 15.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm



Current Data Parameters
NAME cyc-2007-27
EXPNO 2
PROCNO 1

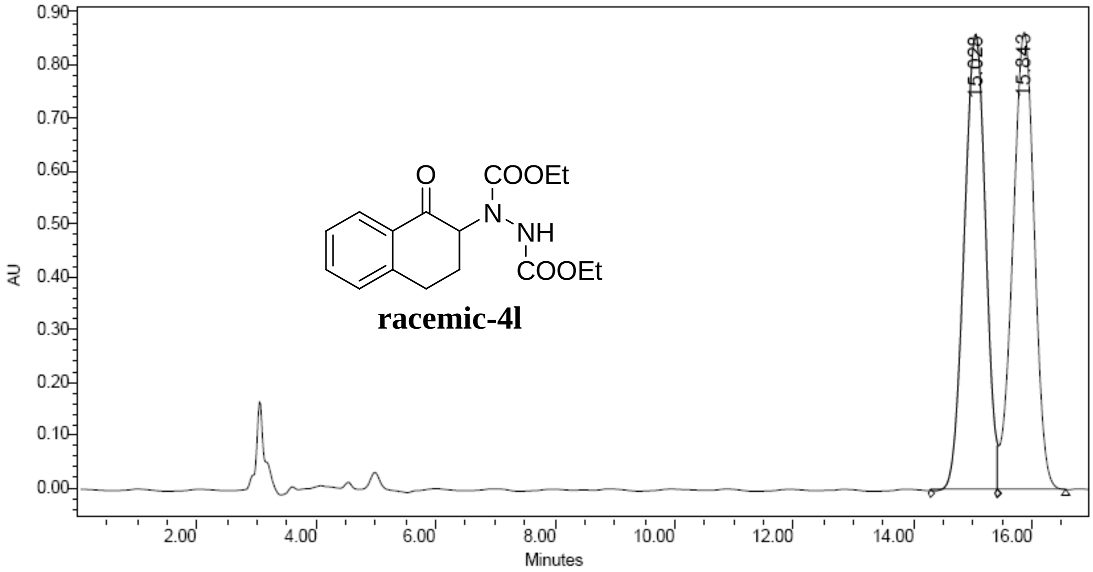
F2 - Acquisition Parameters
Date_ 20070323
Time 19.27
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 40960
DS 4
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SFO1 75.4775598 MHz

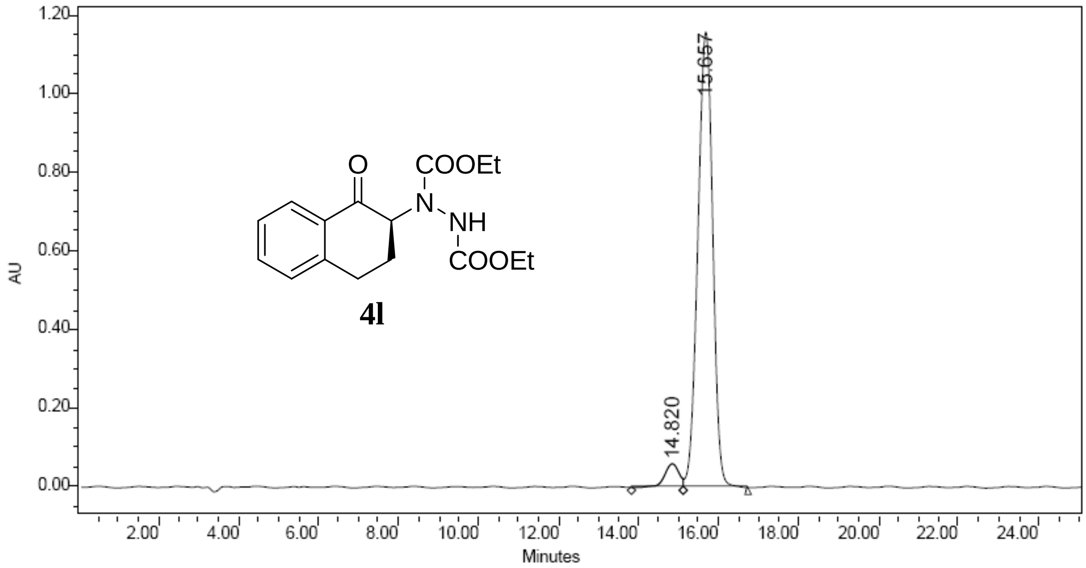
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 65536
SF 75.4677525 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

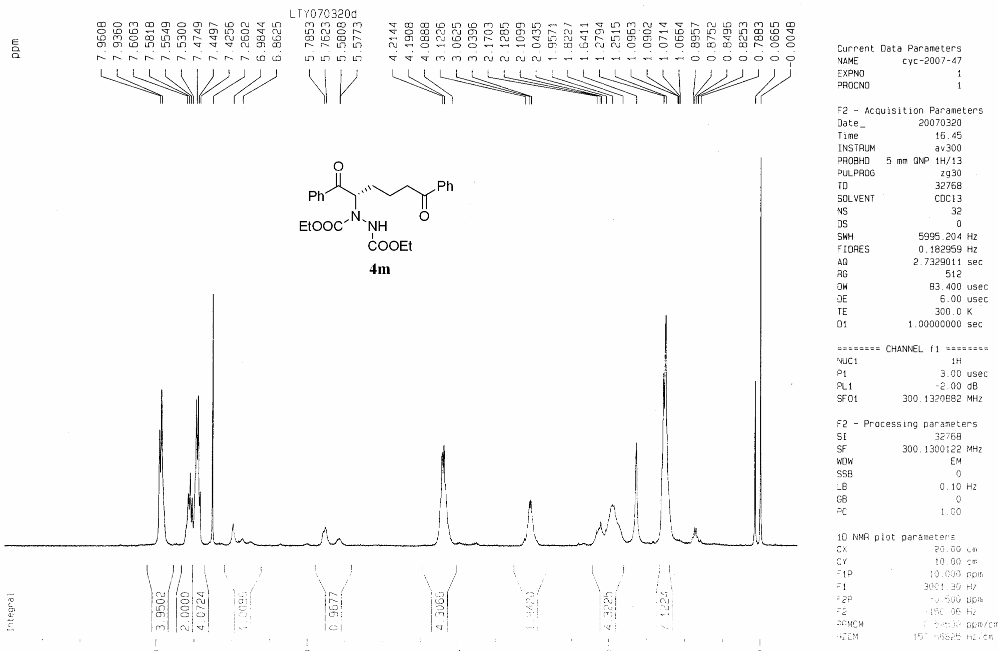
1D NMR plot parameters
CX 20.00 cm
CY 12.00 cm
F1P 220.500 ppm
F1 16640.64 Hz
F2P -5.500 ppm
F2 -415.07 Hz
PPMCM 11.30000 ppm/cm
HZCM 852.78558 Hz/cm



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	15.028	21519177	49.84	863374	49.92
2	15.843	21661043	50.16	866244	50.08



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	14.820	1539657	4.88	60559	4.96
2	15.657	30027615	95.12	1161141	95.04


LTY070320d
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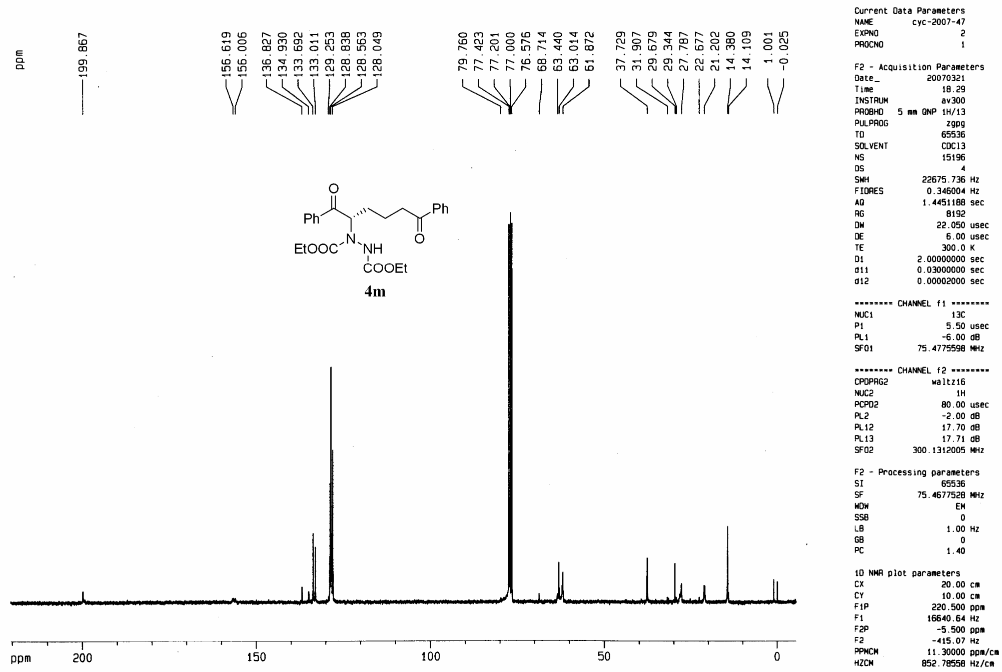
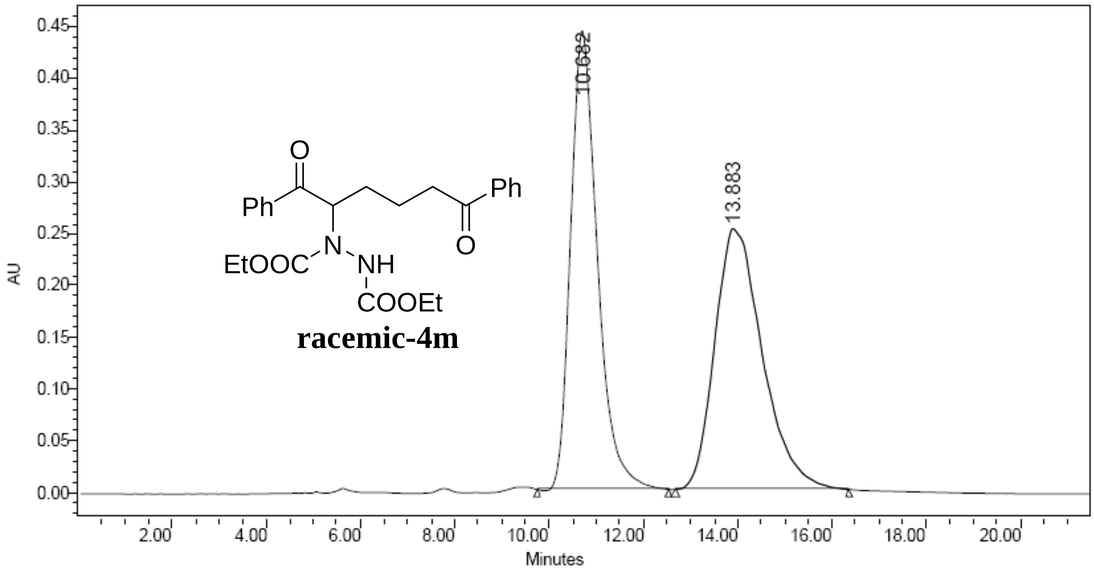
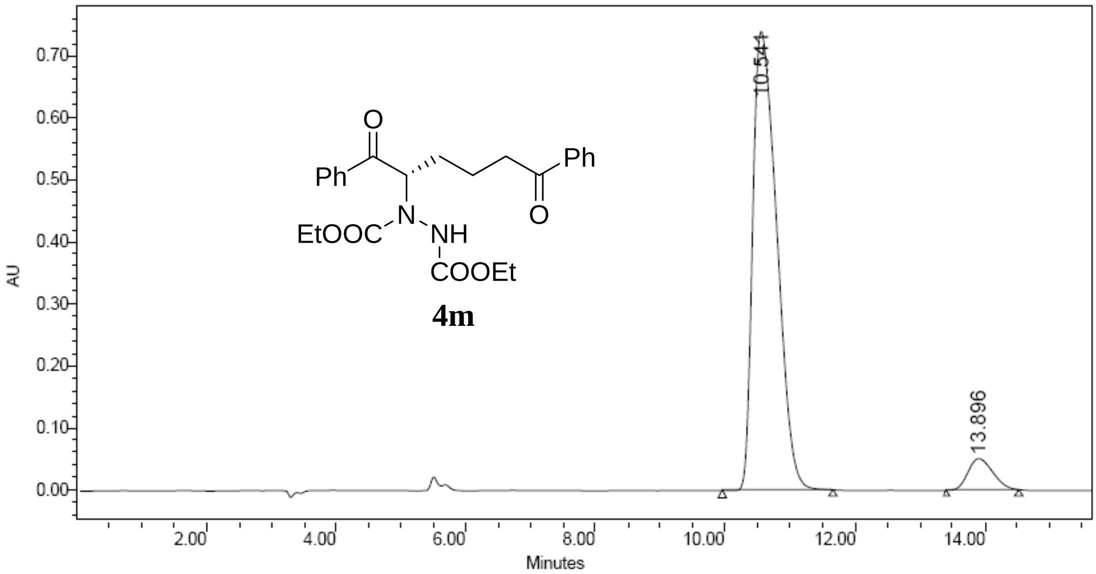
4m
3.9502 2.0000 4.0724 0.9677 4.3065 4.3225
Current Data Parameters
NAME cyc-2007-47
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070320
Time 16.45
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 512
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz
F2 - Processing parameters
SI 32768
SF 300.1300122 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 10.000 ppm
F2P -0.500 ppm
ppm
Integral

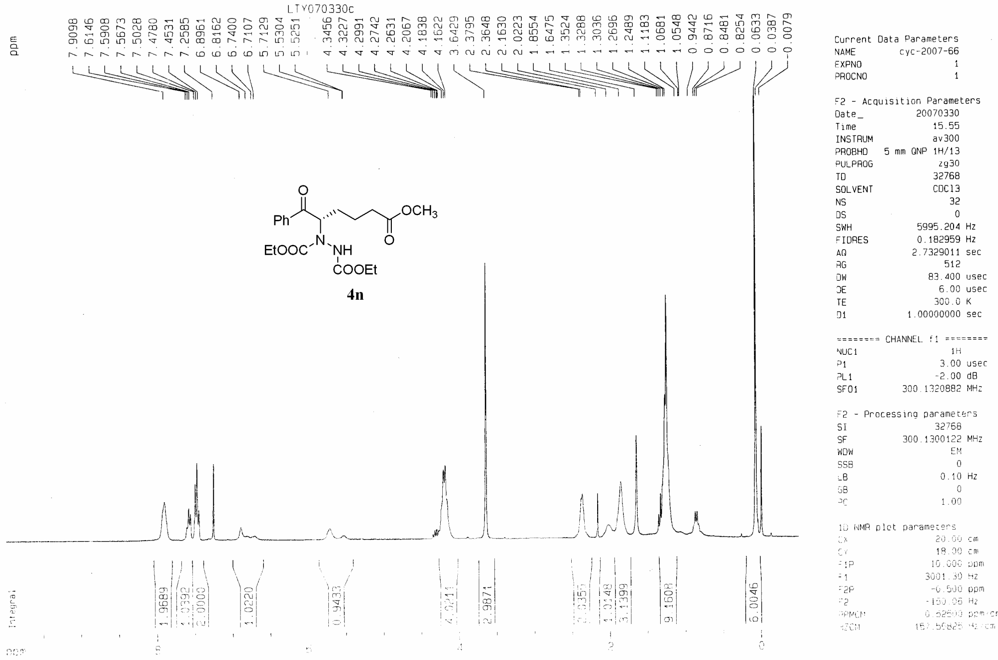

LTY070320d
199.867 156.619 156.006 136.827 134.930 133.692 133.011 129.253 128.838 128.563 128.049 79.760 77.423 77.201 77.000 76.576 68.714 63.440 63.014 61.872 37.729 31.907 29.679 29.344 27.787 22.677 21.202 14.380 14.109 1.001 -0.025
4m
Current Data Parameters
NAME cyc-2007-47
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070321
Time 18.29
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 15196
DS 4
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SFO1 75.4775598 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 65536
SF 75.4677528 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 220.500 ppm
F1 16640.64 Hz
F2P -5.500 ppm
F2 -415.07 Hz
PPMCM 11.30000 ppm/cm
HZCM 852.78558 Hz/cm
ppm 200 150 100 50 0



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	10.682	17460261	49.69	442360	63.75
2	13.883	17680757	50.31	251514	36.25



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	10.541	18963758	93.80	739957	93.78
2	13.896	1252773	6.20	49104	6.22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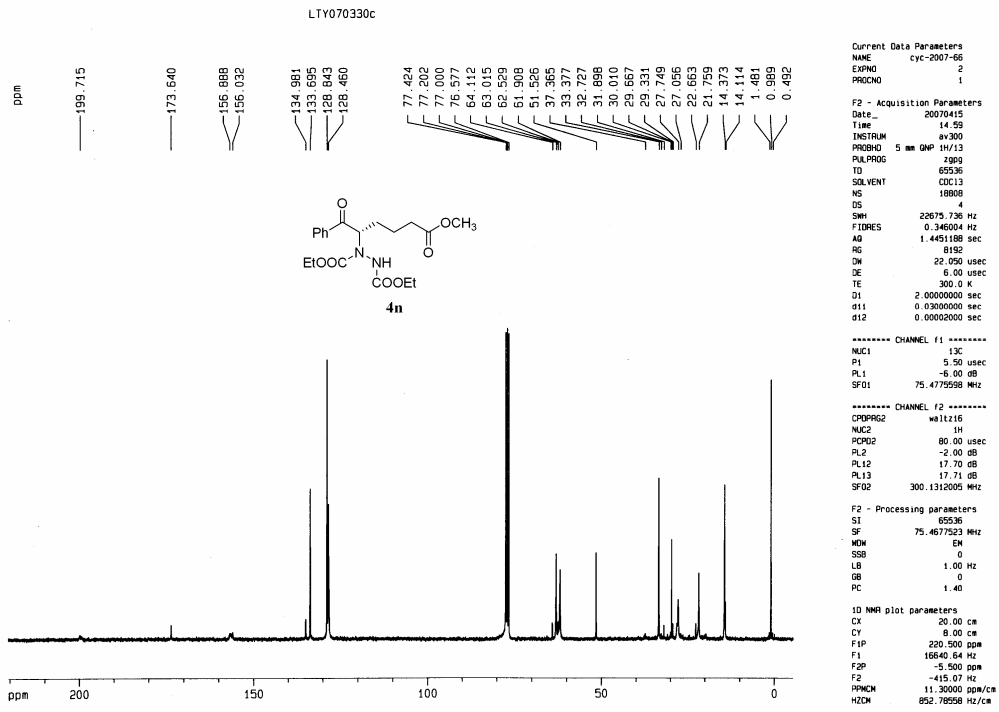
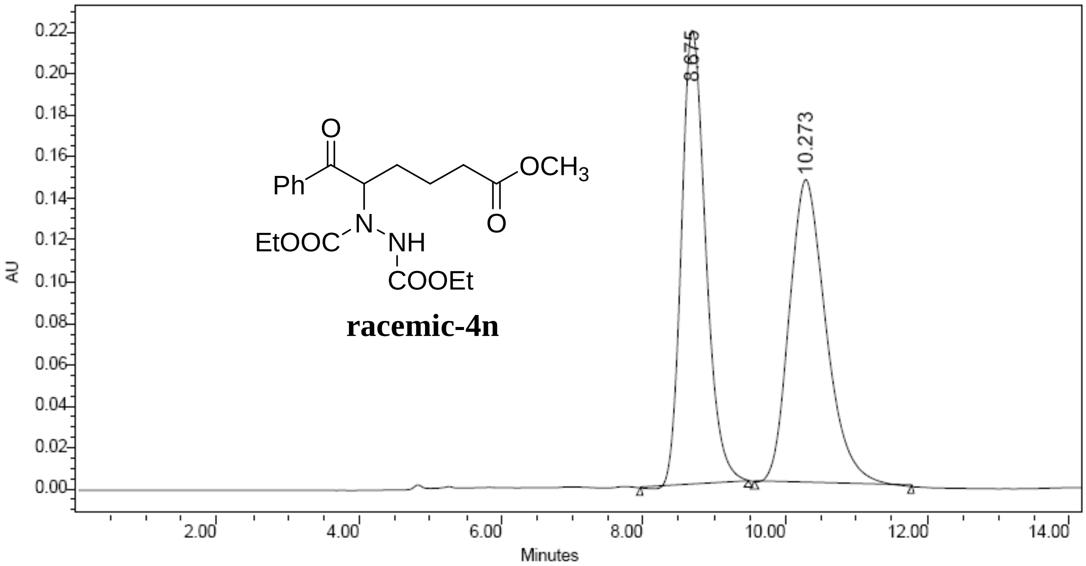
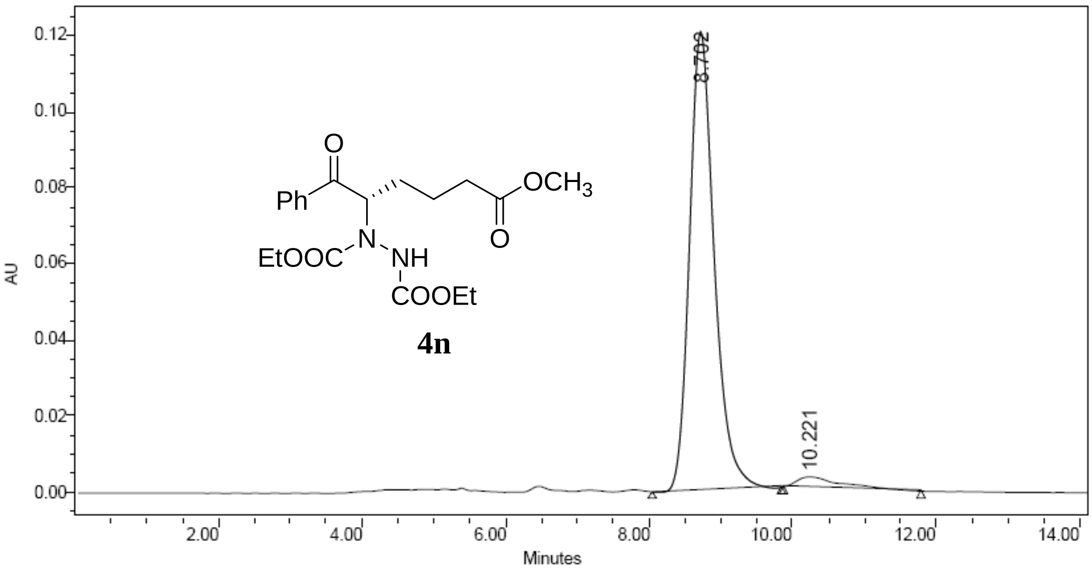
7.6146
7.5908
7.5673
7.5028
7.4780
7.4531
7.2585
6.8961
6.8162
6.7400
6.7107
5.7129
5.5304
5.5251
4.3456
4.3227
4.2991
4.2742
4.2631
4.2067
4.1838
4.1622
3.6429
2.3795
2.3648
2.1630
2.0223
1.8554
1.6475
1.3524
1.3288
1.3036
1.2696
1.2489
1.1183
1.0681
1.0548
0.9442
0.8716
0.8481
0.8254
0.0633
0.0387
-0.0079
Ph
EtOOC
N
NH
COOEt
OCH3
4n
Current Data Parameters
NAME cyc-2007-66
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070330
Time 15.55
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 512
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz
F2 - Processing parameters
SI 32768
SF 300.1300122 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 19.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
1.9689
1.0392
2.0000
1.0220
0.9433
4.0241
2.9871
9.1608
6.0046
Integral
ppm

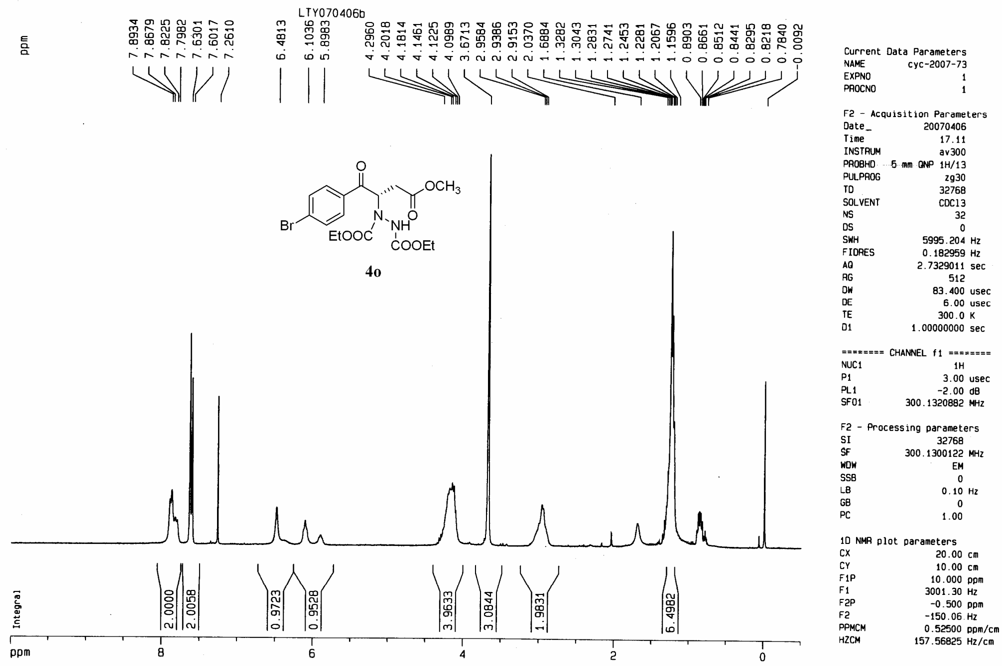

LTY070330c
199.715
173.640
156.888
156.032
134.981
133.695
128.843
128.460
77.424
77.202
77.000
76.577
64.112
63.015
62.529
61.908
51.526
37.365
33.377
32.727
31.898
30.010
29.667
29.331
27.749
27.056
22.663
21.759
14.373
14.114
1.481
0.989
0.492
Ph
EtOOC
N
NH
COOEt
OCH3
4n
Current Data Parameters
NAME cyc-2007-66
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070415
Time 14.59
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 18808
DS 4
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SFO1 75.4775598 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 65536
SF 75.4677523 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
CY 8.00 cm
F1P 220.500 ppm
F1 16640.64 Hz
F2P -5.500 ppm
F2 -415.07 Hz
PPMCM 11.30000 ppm/cm
HZCM 852.78558 Hz/cm
ppm
200
150
100
50
0



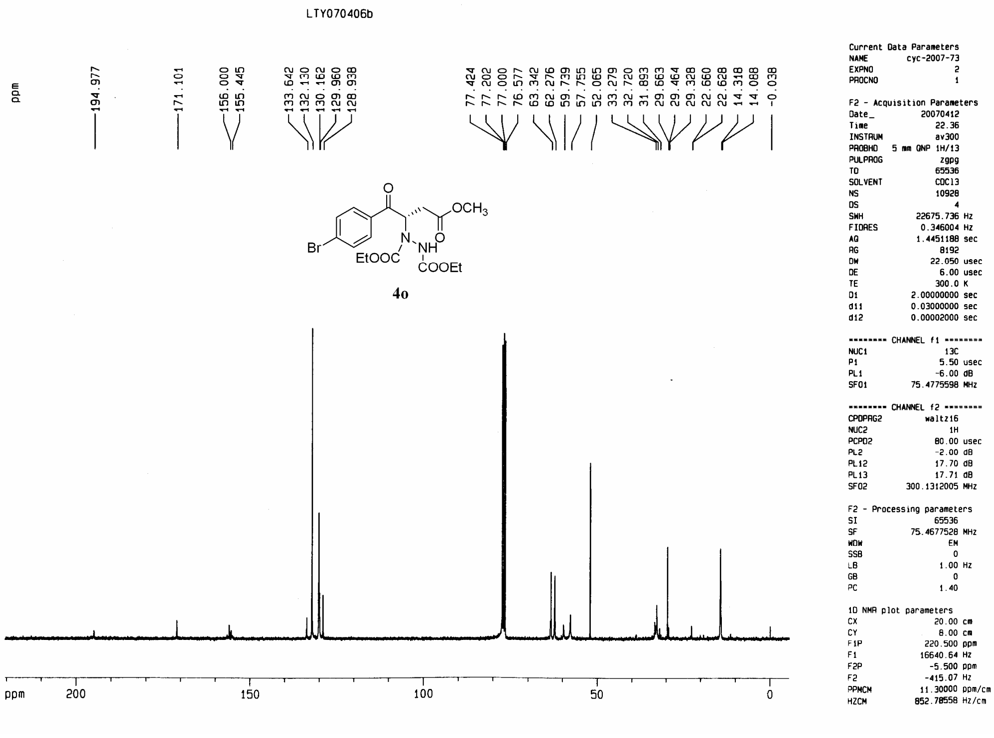
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	8.675	5196785	49.67	218775	59.93
2	10.273	5265730	50.33	146257	40.07



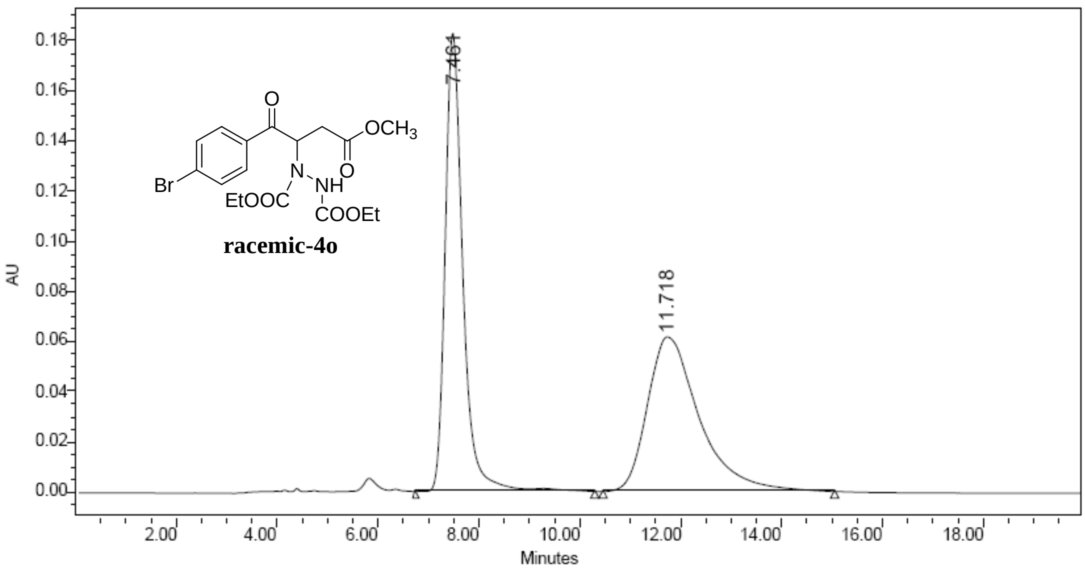
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	8.702	2884352	97.84	120541	98.33
2	10.221	63605	2.16	2047	1.67



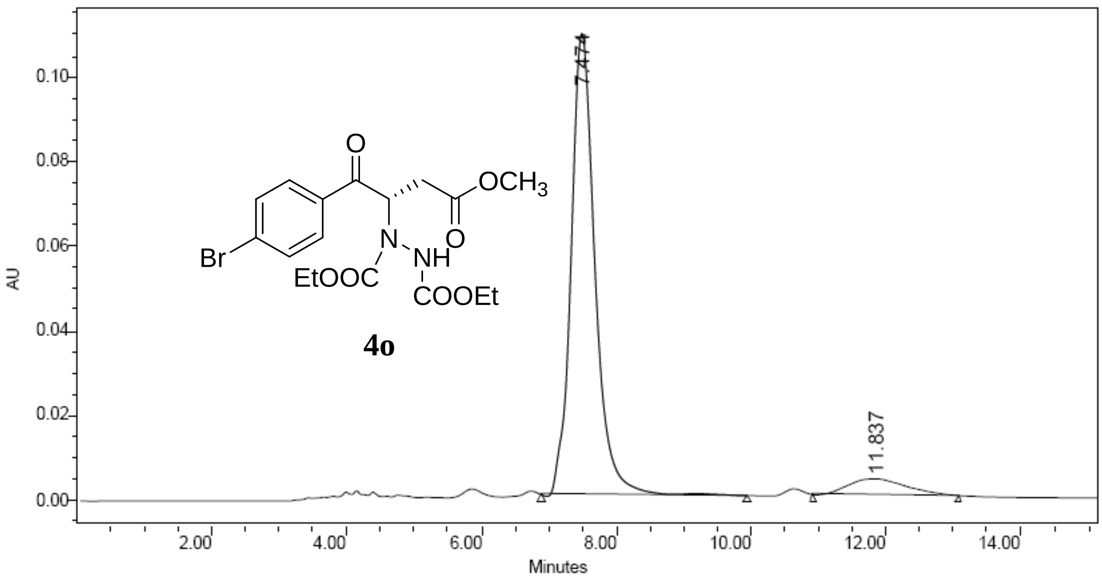
LTY070406b
ppm
7.8934 7.8679 7.8225 7.7982 7.6301 7.6017 7.2610
6.4813
6.1036 5.8983
4.2960 4.2018 4.1814 4.1461 4.1225 4.0989 3.6713 2.9584 2.9386 2.9153 2.0370 1.6884 1.3282 1.3043 1.2831 1.2741 1.2453 1.2281 1.2067 1.1596 0.8903 0.8661 0.8512 0.8441 0.8295 0.8218 0.7840 -0.0092
O
OCH3
Br
EtOOC
N
NH
O
COOEt
4o
Integral
2.0000 2.0058 0.9723 0.9528 3.9633 3.0844 1.9831 6.4982
ppm 8 6 4 2 0
Current Data Parameters
NAME cyc-2007-73
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070406
Time 17.11
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 512
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz
F2 - Processing parameters
SI 32768
SF 300.1300122 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm



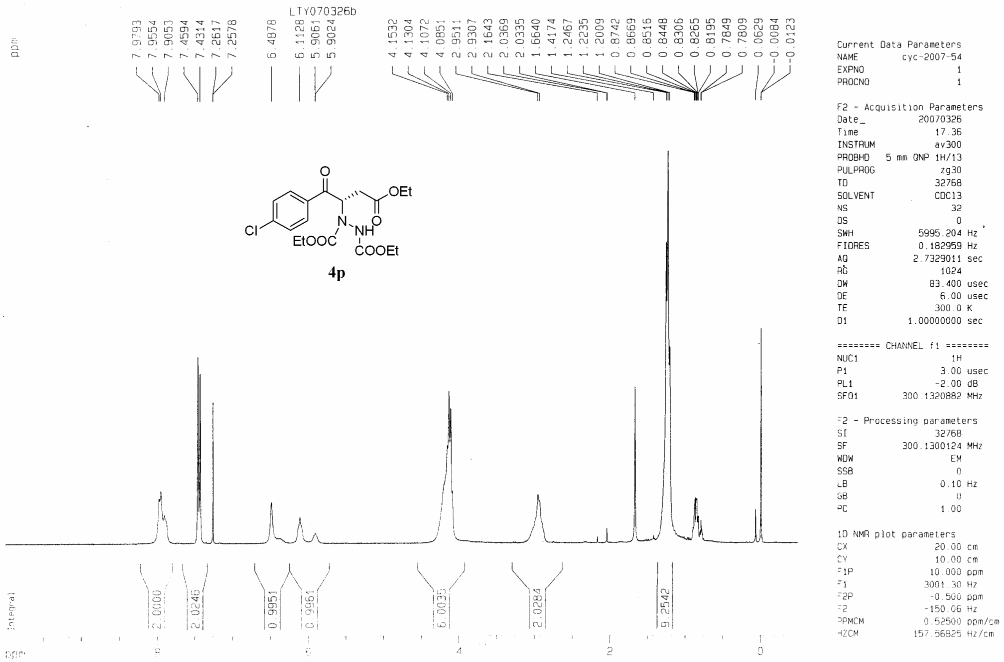
LTY070406b
ppm
194.977
171.101
156.000 155.445
133.642 132.130 130.162 129.960 128.938
77.424 77.202 77.000 76.577 63.342 62.276 59.739 57.755 52.065 33.279 32.720 31.893 29.663 29.464 29.328 22.660 22.628 14.318 14.088 -0.038
O
OCH3
Br
EtOOC
N
NH
O
COOEt
4o
ppm 200 150 100 50 0
Current Data Parameters
NAME cyc-2007-73
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070412
Time 22.36
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 10928
DS 4
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SFO1 75.4775598 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 65536
SF 75.4677528 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
CY 8.00 cm
F1P 220.500 ppm
F1 16640.64 Hz
F2P -5.500 ppm
F2 -415.07 Hz
PPMCM 11.30000 ppm/cm
HZCM 852.78558 Hz/cm



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	7.461	4473622	50.24	182745	74.75
2	11.718	4431529	49.76	61720	25.25



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	7.474	2701703	95.25	109157	97.49
2	11.837	134644	4.75	2815	2.51


LTY070326b
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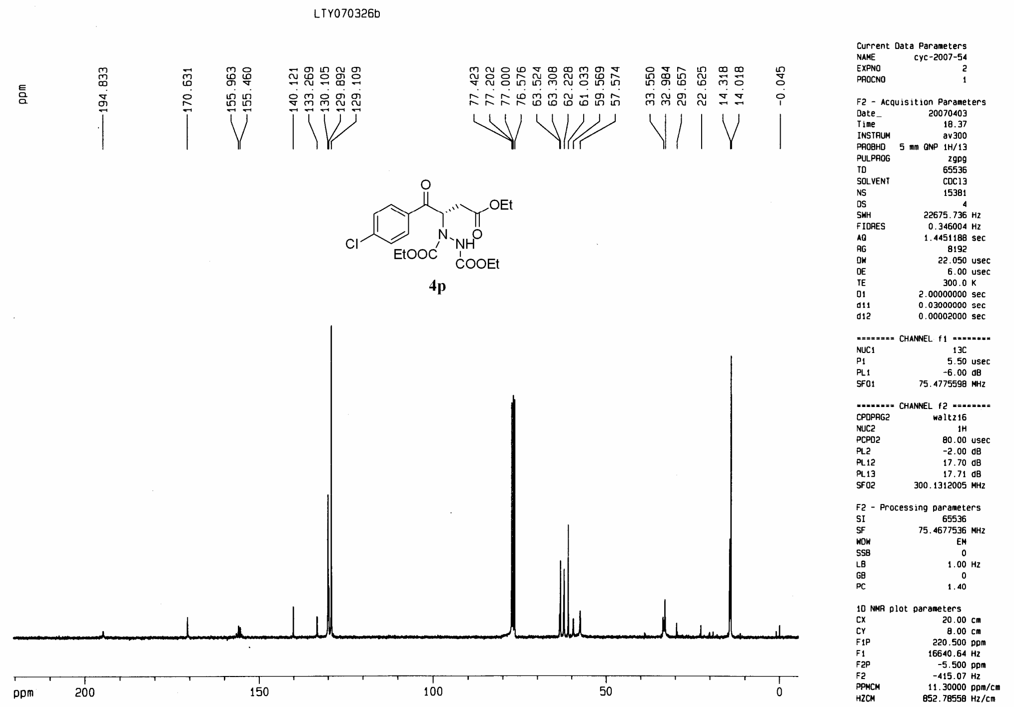
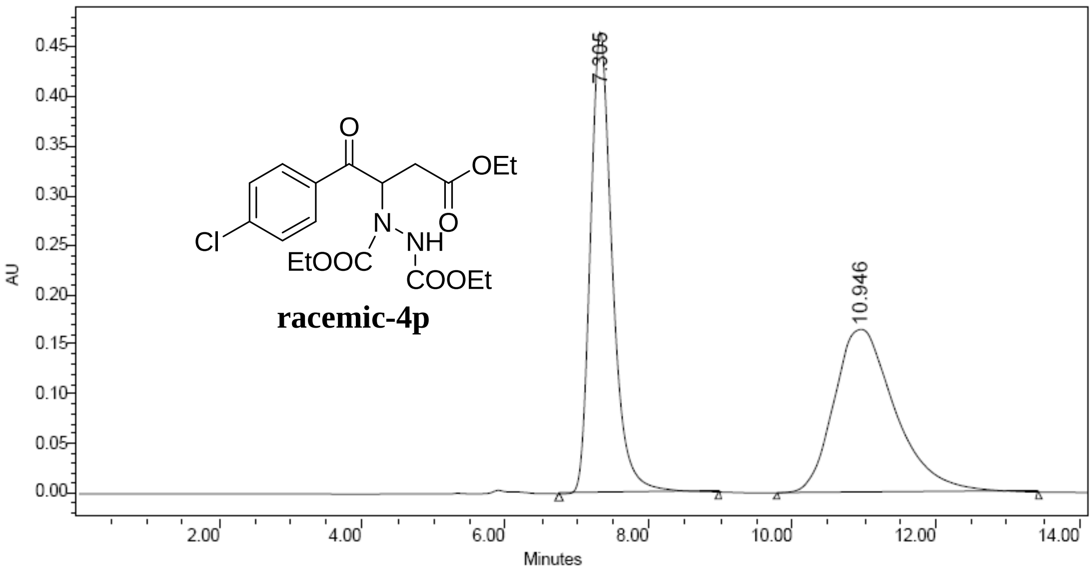
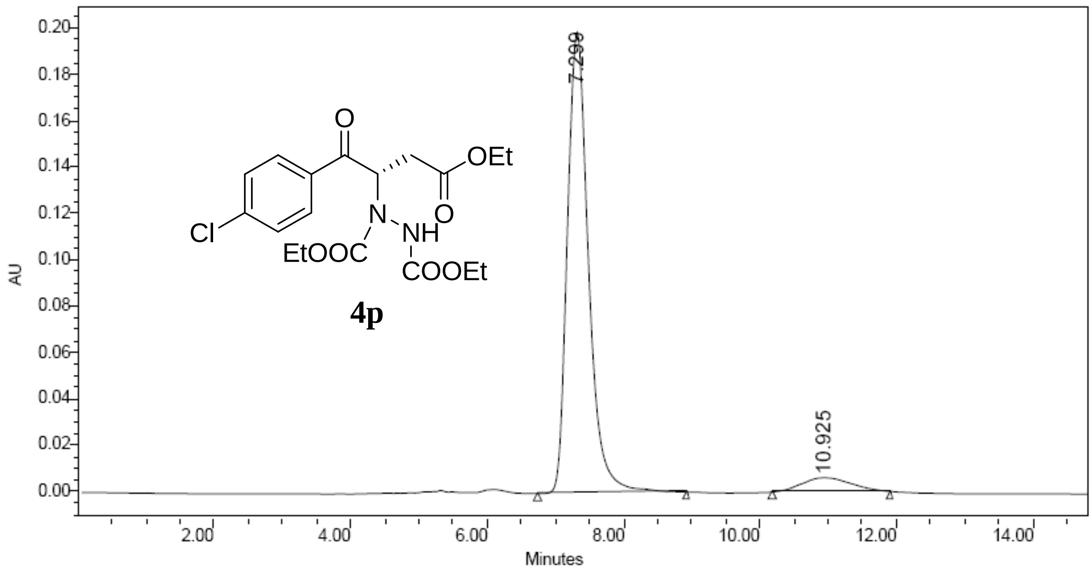
6.4878 6.1128 5.9061 5.9024
4.1532 4.1304 4.1072 4.0851 2.9511 2.9307 2.1643 2.0369 2.0335 1.6640 1.4174 1.2467 1.2235 1.2009 0.8742 0.8669 0.8516 0.8448 0.8306 0.8265 0.8195 0.7849 0.7809 0.0629 -0.0084 -0.0123
Cl
O
OEt
N
NH
EtOOC
COOEt
4p
Integral
2.0000 2.0246 0.9951 0.9961 6.0035 2.0284 9.2542
ppm 4 2 0
Current Data Parameters
NAME cyc-2007-54
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070326
Time 17.36
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 1024
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz
F2 - Processing parameters
SI 32768
SF 300.1300124 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm


LTY070326b
ppm
194.833 170.631 155.963 155.460 140.121 133.269 130.105 129.892 129.109
77.423 77.202 77.000 76.576 63.524 63.308 62.228 61.033 59.569 57.574
33.550 32.984 29.657 22.625 14.318 14.018 -0.045
Cl
O
OEt
N
NH
EtOOC
COOEt
4p
ppm 200 150 100 50 0
Current Data Parameters
NAME cyc-2007-54
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070403
Time 18.37
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 15381
DS 4
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SFO1 75.4775598 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 65536
SF 75.4677536 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
CY 8.00 cm
F1P 220.500 ppm
F1 16640.64 Hz
F2P -5.500 ppm
F2 -415.07 Hz
PPMCM 11.30000 ppm/cm
HZCM 852.78558 Hz/cm



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	7.305	9931671	50.22	465514	73.85
2	10.946	9845115	49.78	164820	26.15



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	7.299	4294486	95.60	198801	97.68
2	10.925	197481	4.40	4732	2.32