Enantioselective Construction of Quaternary Carbon Centre Catalysed by Bifunctional Organocatalyst

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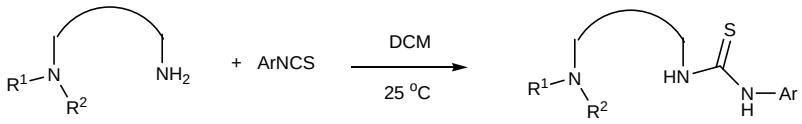
Supplementary Information

Table of Contents

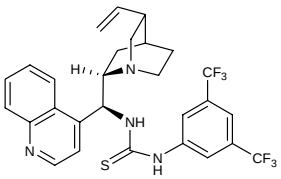
1. General Methods: TLC was performed on glass-backed silica plates. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H and ^{13}C NMR were recorded on Bruker 300 or 400 MHz spectrometers. Chemical shifts were reported in ppm down field from tetramethylsilane with the solvent resonance as the internal standard. ESI-HRMS spectra were recorded on BioTOF instrument of Bruker Daltonics Inc.. Enantiomeric excess was determined by HPLC analysis on Chiralpak AS and OD 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).

General procedure for the preparation of bifunctional catalysts[1]:

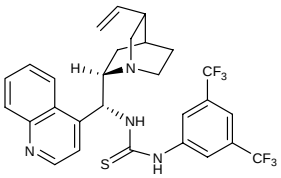


1a-f

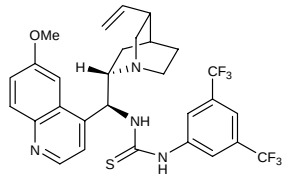
To the *N'*,*N*'-disubstituted primary amine (2 mmol) in dry DCM (10 mL) was added a solution of aryl isothiocyanate (2.5 mmol) in dry DCM (5 mL). After stirred at room temperature for 2 h, the reaction mixture was concentrated in vacuum. The residue was purified by column chromatography on silica gel (DCM/MeOH) to give the desired tertiary amine-thiourea **1a-1f**.



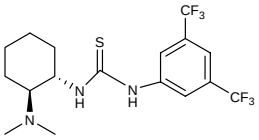
1a, 92% yield; $\alpha]_D^{20}$ = -78.6 (c 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.36 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 2H), 7.76 (t, *J* = 6.8 Hz, 1H), 7.70 (s, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.29 (s, 1H), 5.86-5.79 (m, 1H), 5.72-5.64 (m, 1H), 5.04-4.98 (m, 2H), 3.28-3.16 (m, 3H), 2.80 (br.s, 2H), 2.35 (br.s, 1H), 1.72-1.66 (m, 2H), 1.42-1.32 (m, 1H), 1.19-0.80 (m, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 180.8, 149.9, 148.5, 140.6, 132.9, 132.2, 130.4, 129.5, 127.1, 125.6, 123.5, 120.2, 118.9, 115.1, 78.2, 61.5, 54.8, 41.0, 39.1, 27.4, 27.1, 25.6, 24.9, 11.9 ppm; IR (CH_2Cl_2) ν 3423, 2927, 1509, 1473, 1384, 1278, 1178, 1135, 958 cm^{-1}; EI-HRMS: calcd. for $C_{28}H_{26}F_6N_4S$ 564.1782, found 564.1770.



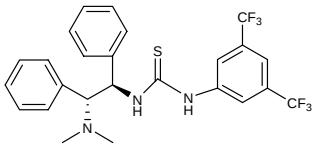
1b, 90% yield; $[\alpha]_D^{20}$ = +151.1 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.28 (s, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.86 (s, 2H), 7.76 (t, *J* = 6.4 Hz, 1H), 7.68 (s, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.36 (s, 1H), 5.81 (br.s, 2H), 5.16-5.11 (m, 2H), 3.16-2.92 (m, 5H), 2.38-2.38 (m, 1H), 1.66-1.41 (m, 2H), 1.29-1.22 (m, 1H), 0.97-0.83 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 149.8, 148.4, 139.3, 132.5, 132.2, 131.9, 130.2, 129.5, 127.0, 124.3, 123.4, 122.8, 121.6, 118.8, 118.6, 115.4, 61.5, 48.4, 47.0, 38.8, 27.2, 25.9, 25.5, 24.9, 11.8 ppm; IR (CH_2Cl_2) ν 3405, 3247, 2942, 2875, 1622, 1587, 1511, 1472, 1385, 1280, 1184, 1125 cm^{-1}; EI-HRMS: calcd. for $C_{28}H_{26}F_6N_4S$ 564.1782, found 564.1781.



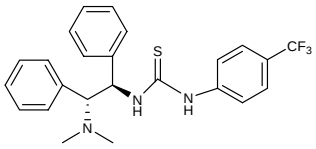
1c, 88% yield; $[\alpha]_D^{20}$ = -61.8 (c 0.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.5 Hz, 1H), 8.02 (d, *J* = 9.3 Hz, 1H), 7.88 (s, 2H), 7.68 (s, 1H), 7.40 (dd, *J* = 2.6, 9.2Hz, 1H), 7.29 (d, *J* = 4.4 Hz, 1H), 5.70-5.65 (m, 1H), 5.04 (d, *J* = 3.9 Hz, 1H), 4.99 (s, 1H), 3.97 (s, 3H), 3.44-3.42 (m, 2H), 3.23 (dd, *J* = 10.2, 13.5 Hz, 1H), 2.88-2.80 (m, 2H), 2.40-2.31 (m, 1H), 1.76 (br.s, 1H), 1.28-1.24 (m, 1H), 0.96 (br.s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.8, 158.3, 147.5, 144.8, 140.3, 139.9, 132.6, 132.1, 131.8, 124.9, 123.4, 122.2, 121.2, 118.5, 115.6, 102.3, 61.2, 55.9, 54.9, 41.6, 38.7, 30.9, 27.1, 25.5 ppm; IR (CH_2Cl_2) ν 3249, 2945, 1623, 1590, 1510, 1474, 1384, 1279, 1178, 1134 cm^{-1}; ESI-HRMS: calcd. for $C_{29}H_{28}F_6N_4OS$+H 595.1961, found 595.1939.



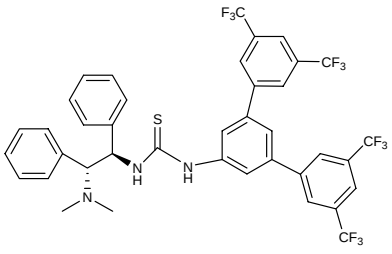
1d, 75% yield; $[\alpha]_D^{20}$ = -30.4 (c 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.61 (s, 1H), 4.13-4.11 (m, 1H), 2.56 (br.s, 1H), 2.38 (br.s, 7H), 1.97-1.93 (m, 1H), 1.88-1.85 (m, 1H), 1.77-1.75 (m, 1H), 1.34-1.19 (m, 4H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 178.5, 141.5, 132.5, 131.9, 131.1, 125.8, 123.1, 120.2, 118.1, 114.8, 67.3, 56.2, 40.1, 32.8, 24.6, 24.4, 21.8 ppm; IR (CH_2Cl_2) ν 3405, 3246, 2940, 2865, 1542, 1474, 1385, 1317, 1279, 1178, 1134, 993, 681 cm^{-1}; ESI-HRMS: calcd. for $C_{17}H_{21}F_6N_3S$+H, 414.1433, found 414.1443.



1e, 80% yield; $[\alpha]_D^{20}$ = +125.4 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.70 (s, 2H), 7.67 (s, 1H), 7.29-7.24 (m, 3H), 7.15(br.s, 5H), 7.08-7.06 (m, 2H), 5.33 (br.s, 1H), 3.82 (d, *J* = 10.8 Hz, 1H), 2.22 (s, 6H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 180.4, 139.6, 139.0, 132.8, 132.1, 131.2, 129.9, 128.5, 128.1, 127.9, 127.8, 125.6, 123.6, 120.2, 118.9, 73.9, 59.4, 40.5 ppm; IR (CH_2Cl_2) ν 3447, 2926, 2792,1624, 1509, 1473, 1383, 1279, 1178, 1135, 1043, 958, 886, 700 cm^{-1}; ESI-HRMS: calcd. for $C_{25}H_{23}F_6N_3S$+H, 512.1590, found 512.1589.



1f, 85% yield; $[\alpha]_D^{20}$ = +170.5 (c 0.4, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.30-7.24 (m, 3H), 7.15 (br.s, 5H), 7.08-7.05 (m, 2H), 5.36 (br.s, 1H), 3.76 (d, *J* = 10.8 Hz, 1H), 2.20 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.4, 141.1, 139.6, 131.8, 129.9, 125.5, 128.1, 128.0, 127.9, 127.6, 127.4, 126.6, 125.8, 123.6, 122.2, 74.1, 59.3, 40.7 ppm; IR (CH_2Cl_2) ν 3264, 2940, 2871, 2835, 2790, 1521, 1456, 1325, 1162, 1125; ESI-HRMS: calcd. for $C_{24}H_{24}F_3N_3S$+H 444.1716, found 444.1740.



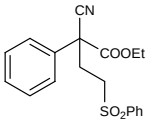
1g, 85% yield; $[\alpha]_D^{20}$ = +85.6 (c 0.27, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (s, 4H), 7.91 (s, 2H), 7.56 (s, 1H), 7.52 (s, 2H), 7.26-7.24 (m, 3H), 7.18 (br.s, 5H), 7.08-7.05 (m, 2H), 5.35 (br.s, 1H), 3.80 (d, *J* = 10.8 Hz, 1H), 2.19 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 180.8, 142.1, 140.5, 140.0, 139.2, 133.2, 132.8, 132.3, 131.9, 131.3, 129.9, 128.8, 128.2, 128.1, 128.0, 127.4, 125.1, 123.2, 121.9, 121.5, 74.1, 59.2, 40.6 ppm; IR (CH_2Cl_2) ν 3385, 2938, 2872, 2792, 1599, 1520, 1475, 1396, 1369, 1280, 1179, 1136 cm^{-1}; ESI-HRMS: calcd. for $C_{39}H_{29}F_{12}N_3S$+H 800.1963, found 800.1987.

(1) (*a*) T. Okino, Y. Hoashi and Y. Takemoto, *J. Am. Chem. Soc.*, 2003, **125**, 12672; (*b*) B.-J. Li, L.

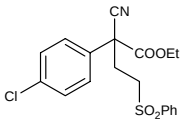
Jiang, M. Liu, Y.-C. Chen, L.-S. Ding and Y. Wu, *Synlett*, 2005, 603; (*c*) J. Ye, D. J. Dixon and P. S. Hynes, *Chem. Commun.,* 2005, 4481; (d) B. Vakulya, S. Varga, A. Csampai and T. Sóos, *Org. Lett.,* 2005, 7, 1967.

General procedure for asymmetric Michael addition

Catalyst **1e** (or **1d**) (0.02 mmol, 20 mol%), vinyl sulfone **3** (or **5**, for α-alkyl cyanoacetates) (0.1 mmol) and 4A MS (20 mg) were stirred in dry toluene (0.5 mL) and cooled to the desired temperature under argon. Then cyanoacetate **2** (0.2 mmol) in dry toluene (0.5 mL) was added. After the stated reaction time, the product was purified by flash chromatography on silica gel (*Previously saturated with cold petroleum ether*. *In general slightly lower enantioselectivity was obtained when the FC was conducted at room temperature, probably due to the rapid reaction of the unchanged starting materials in column*) to give the addition product **4**. The enantiomeric excess was determined by HPLC analysis on chiral column.

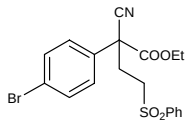


4a Purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10/1, R_f = 0.10); 83 % yield; $[\alpha]_D^{20}$ = + 28.5 (c 0.24, $CHCl_3$) [lit.[2] $[\alpha]_D^{25}$ = + 31.6 (c 1.13, $CHCl_3$), 95% ee]; 94 % ee, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ 220 nm, t (minor) = 15.31 min, t (major) = 16.55 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.2 Hz, 2H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 7.45-7.39 (m, 5H), 4.26-4.17 (m, 2H), 3.26 (td, *J* = 5.2, 13.2 Hz, 1H), 3.03 (td, *J* = 4.4, 12.8 Hz, 1H), 2.74-2.59 (m, 2H), 1.21 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 138.4, 134.1, 132.6, 129.6, 129.5, 128.0, 125.8, 117.1, 63.8, 52.4, 52.2, 30.9, 13.7 ppm; IR (film) ν 3064, 2984, 2935, 1746, 1449, 1321, 1237, 1087 cm^{-1}; ESI-MS: 380.1$[M + Na]^+$.

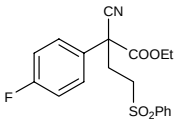


4d Purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 12/1, R_f = 0.10); 90 % yield; $[\alpha]_D^{20}$ = + 29.2 (c 0.39, $CHCl_3$) [lit.[2] $[\alpha]_D^{25}$ = + 31.9 (c 1.10, $CHCl_3$), 94% ee]; 94 % ee, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ 220 nm, t (minor) = 20.71 min, t (major) = 24.11 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7. 89 (d, *J* = 7.0 Hz, 2H), 7.70 (t, *J* = 7.4 Hz,, 1H), 7.59 (t, *J* = 7.8 Hz, 2H), 7.38 (br.s, 4H, ArH),

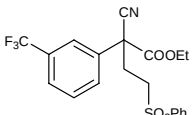
4.24-4.20 (m, 2H), 3.25 (td, *J* = 4.9, 12.8 Hz, 1H), 3.01 (td, *J* = 4.3, 12.9 Hz, 1H), 2.77-2.55 (m, 2H), 1.22 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 138.3, 135.8, 134.2, 131.1, 129.7, 129.5, 128.0, 127.3, 116.7, 64.0, 52.0, 51.9, 30.8, 13.7 ppm; IR (KBr) ν 3061, 2985, 1747, 1492, 1447, 1328, 1236, 1154 cm^{-1}; ESI-MS: 414.1[M + Na]$^+$.



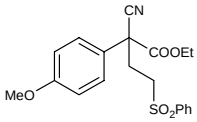
4e Purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 15/1, R_f = 0.12); 93 % yield; $[\alpha]_D^{20}$ = + 27.6 (c 0.64, $CHCl_3$) [lit.[2] $[\alpha]_D^{25}$ = + 28.8 (c 1.10, $CHCl_3$), 94% ee]; 96 % ee, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ 220 nm, t (minor) = 23.38 min, t (major) = 26.64 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.3 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.9 Hz, 2H), 7.55 (d, *J* = 6.7 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 4.27-4.20 (m, 2H), 3.25 (td, *J* = 4.5, 13.1 Hz, 1H), 3.01 (td, *J* = 4.2, 12.3 Hz, 1H), 2.75-2.58 (m, 2H), 1.22 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 138.3, 134.2, 132.7, 131.7, 129.5, 128.0, 127.5, 123.9, 116.7, 64.0, 52.0, 30.9, 30.7, 13.7ppm; IR (KBr) ν 2983, 1746, 1488, 1447, 1328, 1236, 1154 cm^{-1}; ESI-MS: 458.1[M + Na]$^+$.



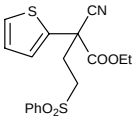
4f Purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10/1, R_f = 0.12); 92 % yield; $[\alpha]_D^{20}$ = + 25.1 (c 0.64, $CHCl_3$) [lit.[2] $[\alpha]_D^{25}$ = + 27.2 (c 1.13, $CHCl_3$), 94% ee]; 93 % ee, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ 220 nm, t (minor) = 19.06 min, t (major) = 21.39 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.0 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.2 Hz, 2H), 7.45-7.41 (m, 2H), 7.13-7.07 (m, 2H), 4.24-4.20 (m, 2H), 3.25 (td, *J* = 4.7, 13.4 Hz, 1H), 3.01 (td, *J* = 4.0, 12.2 Hz, 1H), 2.71 (td, *J* = 4.7, 13.8 Hz, 1H), 2.60 (td, *J* = 4.0, 13.9 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 163.1 (d, $^1J_{C,F}$ = 248.9 Hz), 138.5, 134.2, 129.6, 128.5, 128.0, 127.9 (d, $^3J_{C,F}$ = 8.5 Hz), 116.9, 116.6 (d, $^2J_{C,F}$ = 21.8 Hz), 63.9, 52.2, 51.9, 30.9, 13.7 ppm; IR (KBr) ν 2986, 2925, 1751, 1510, 1447, 1305, 1237, 1088 cm^{-1}; ESI-MS: 398.1 [M + Na]$^+$.



4g Purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10/1, R_f = 0.10); 92 % yield; $[\alpha]_D^{20}$ = +21.8 (c 0.16, $CHCl_3$); 91 % ee, determined by HPLC analysis [Daicel chiralcel OD, n-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ 220 nm, t (minor) = 16.48 min, t (major) = 18.21 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91-7.88 (m, 2H), 7.70-7.66 (m, 4H), 7.62-7.57 (m, 3H), 4.28-4.20 (m, 2H), 3.28 (td, *J* = 4.5, 12.9 Hz, 1H), 3.05 (td, *J* = 4.8, 13.2 Hz, 1H), 2.79 (td, *J* = 4.5, 12.9 Hz, 1H), 2.60 (td, *J* = 4.8, 13.2 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 138.3, 134.3, 134.0, 132.0 (q, $J_{C,F}$ = 32.6 Hz), 130.3, 129.6, 129.3, 128.0, 126.5 (d, $J_{C,F}$ = 3.2 Hz), 123.3 ((q, $J_{C,F}$ = 271.0 Hz), 122.8 (d, $J_{C,F}$ = 3.5 Hz), 116.4, 64.2, 52.2, 52.1, 31.0, 13.7 ppm; IR (film) ν 3068, 2924, 1747, 1446, 1328, 1237, 1147, 1083 cm^{-1}; ESI-HRMS: calcd. for $C_{20}H_{18}F_3NO_4S$+Na 448.0801, found 448.0807.

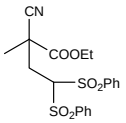


4h Purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 9/1, R_f = 0.10); 73 % yield; $[\alpha]_D^{20}$ = +29.0 (c 0.14, $CHCl_3$) [lit.[2] $[\alpha]_D^{25}$ = + 31.0 (c 1.10, $CHCl_3$), 93% ee]; 94 % ee, determined by HPLC analysis [Daicel chiralcel AS, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ 220 nm, t (major) = 22.35 min, t (minor) = 29.66 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.1 Hz, 2H), 7.69 (t, *J* = 7.3 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 4.23-4.18 (m, 2H), 3.81 (s, 3H), 3.23 (td, *J* = 5.2, 12.2 Hz, 1H), 3.03 (td, *J* = 4.7, 11.6 Hz, 1H), 2.67-2.60 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 160.3, 138.5, 134.1, 129.5, 128.0, 127.2, 124.4, 117.3, 114.9, 63.7, 55.4, 52.2, 51.8, 30.8, 13.7 ppm; IR (film) ν 2981, 1744, 1512, 1307, 1257, 1148 cm^{-1}; ESI-MS: 410.1[M + Na]$^+$.

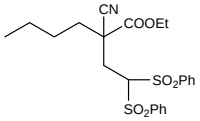


4i Purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 13/1, R_f = 0.12); 96% yield; $[\alpha]_D^{20}$ = + 19.0 (c 0.70, $CHCl_3$) [lit.[2] $[\alpha]_D^{25}$ = + 20.2 (c 1.00, $CHCl_3$), 93% ee]; 95 % ee, determined by HPLC analysis [Daicel chiralcel AS, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ 220 nm, t (minor) = 19.93 min, t (major) = 21.83 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.2 Hz, 2H), 7.70 (t, *J* = 7.3 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 6.8 Hz, 1H),

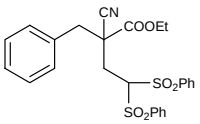
7.19 (d, *J* = 3.7 Hz, 1H), 6.99 (t, *J* = 4.4 Hz, 1H), 4.30-4.23 (m, 2H), 3.27 (td, *J* = 5.1, 12.5 Hz, 1H), 3.12 (td, *J* = 4.8, 13.0 Hz, 1H), 2.76 -2.59 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 138.2, 135.0, 134.2, 129.5, 128.0, 127.6, 127.5, 127.2, 116.4, 64.2, 52.0, 49.4, 32.2, 13.7 ppm; IR (film) ν 3068, 2984, 2928, 1749, 1447, 1305, 1233, 1087 cm^{-1}; ESI-MS: 386.2 $[M + Na]^+$.



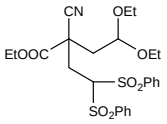
4j Purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 9/1, R_f = 0.12); 96% yield; $[\alpha]_D^{20}$ = + 12.1 (c 0.22 ,$CHCl_3$); 73 % ee, determined by HPLC analysis [Daicel chiralcel AS, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ 220 nm, t (major) = 20.67 min, t (minor) = 27.20 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.91 (m, 4H), 7.73-7.68 (m, 2H), 7.61-7.54 (m, 4H), 4.88 (dd, *J* = 3.6, 5.2 Hz, 1H), 4.35-4.29 (m, 2H), 2.91 (dd, *J* = 5.6, 16.2 Hz, 1H), 2.79 (dd, *J* = 3.6, 16.0 Hz, 1H), 1.66 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.0, 137.2, 136.8, 134.9, 134.8, 130.0, 129.6, 129.3, 129.2, 118.5, 79.8, 63.8, 43.3, 31.8, 24.2, 13.8 ppm; IR (film) ν 3067, 2925, 1744, 1449, 1334, 1252, 1160, 1080 cm^{-1}; ESI-HRMS: calcd. for $C_{20}H_{21}NO_6S_2$+Na 458.0702, found: 458.0703.



4k Purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 9/1, R_f = 0.15); 98% yield; $[\alpha]_D^{20}$ = + 10.1 (c 0.47, $CHCl_3$); 82 % ee, determined by HPLC analysis [Daicel chiralcel AS, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ 220 nm, t (major) = 12.88 min, t (minor) = 17.23 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.92 (m, 4H), 7.73-7.68 (m, 2H), 7.59-7.55 (m, 4H), 4.91 (dd, *J* = 3.2, 6.0 Hz, 1H), 4.36-4.30 (m, 2H), 2.86 (dd, *J* = 6.0, 16.2 Hz, 1H), 2.79 (dd, *J* = 3.6, 16.4 Hz, 1H), 1.96 (td, *J* = 4.0, 13.2 Hz, 1H), 1.68 (td, *J* = 4.0, 13.2 Hz, 1H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.32-1.22 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.7, 137.3, 136.8, 134.9, 134.8, 130.1, 129.5, 129.3, 129.1, 117.8, 80.1, 63.6, 49.1, 37.7, 30.7, 27.4, 22.2, 13.8, 13.6 ppm; IR (film) ν 3067, 2960, 1742, 1584, 1448, 1334, 1248, 1158, 1079 cm^{-1}; ESI-HRMS: calcd. for $C_{23}H_{27}NO_6S_2$+Na 500.1172, found 500.1157.



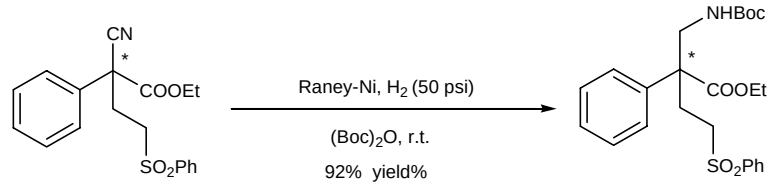
4l Purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 7/1, R_f = 0.10); 98% yield; $[\alpha]_D^{20}$ = +15.9 (c 0.26, $CHCl_3$); 72 % ee, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ 220 nm, t (minor) = 10.90 min, t (major) = 13.34 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.79 (d, *J* = 7.6 Hz, 2H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.35-7.34 (m, 3H), 7.28-7.26 (m, 2H), 4.92 (dd, *J* = 2.8, 6.8 Hz, 2H), 4.20 (q, *J* = 6.8 Hz, 2H), 3.26 (d, *J* = 14.0 Hz, 1H), 3.06 (d, *J* = 13.6 Hz, 1H), 2.98 (dd, *J* = 6.8, 16.2 Hz, 1H), 2.80 (dd, *J* = 3.2, 16.2 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.3, 137.2, 134.9, 134.8, 133.1, 130.2, 129.6, 129.4, 129.2, 128.7, 128.2, 117.4, 80.4, 63.6, 53.4, 50.6, 43.6, 30.9, 13.7 ppm; IR (KBr) ν 2923, 1752, 1448, 1332, 1080 cm^{-1}; ESI-HRMS: calcd. for $C_{26}H_{25}NO_6S_2$ +Na 534.1016, found 534.1025.



4m Purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 8/1, R_f = 0.10); 56% yield; $[\alpha]_D^{20}$ = + 23.5 (c 0.12, $CHCl_3$); 96 % ee, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ 220 nm, t (major) = 15.38 min, t (minor) = 17.54 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.90 (m, 4H), 7.73-7.67 (m, 2H), 7.62-7.54 (m, 4H), 4.92 (dd, *J* = 1.2, 4.8 Hz, 1H), 4.77 (dd, *J* = 2.4, 7.2 Hz, 1H), 4.34-4.24 (m, 2H), 3.75-3.64 (m, 2H), 3.62-3.51 (m, 2H), 2.98 (dd, *J* = 4.0, 16.2 Hz, 1H), 2.81 (dd, *J* = 5.2, 16.4 Hz, 1H), 2.46 (dd, *J* = 7.2, 14.0 Hz, 1H), 2.05-1.99 (m, 1H), 1.27-1.17 (m, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 140.3, 136.6, 134.9, 134.7, 130.2, 129.9, 129.6, 129.2, 128.4, 117.3, 100.2, 79.6, 63.6, 62.3, 45.8, 40.3, 31.2, 29.7, 15.2, 15.0, 13.7 ppm; IR (CH_2Cl_2) ν 3448, 3044, 2928, 1744, 1449, 1326, 1148, 1081 cm^{-1}; ESI-HRMS: calcd. for $C_{25}H_{31}NO_8S_2$+Na 560.1383, found 560.1388.

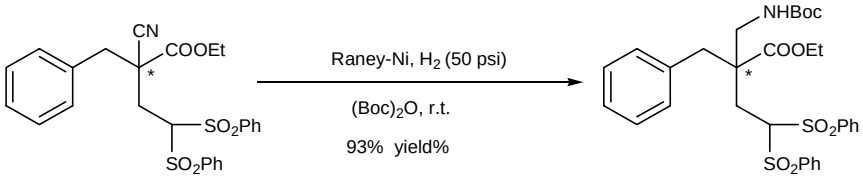
(2) H. Li, J. Song, X. Liu and L. Deng, *J. Am. Chem. Soc.,* 2005, **127**, 8948.

Synthesis of optically active $\beta^{2,2}$-amino acid 6a and 6b



4a 94% ee **6a** 94% ee

To a solution of **4a** (35.7 mg, 0.1mmol, 94% ee) in ethanol (10 mL) was added $(Boc)_2O$ 24.0 mg (0.11 mmol) and Raney-Ni 7.2 mg. The mixture was stirred under H_2 (50 psi) at room temperature for 24 h. Then the mixture was filtered through celite, washed with EtOAc (20 mL) and the resulting filtrate was concentrated in vacuum. The residue was subjected to flash chromatography (eluent: petroleum ether/EtOAc = 10/1, R_f = 0.10) to give the Boc-protected $\beta^{2,2}$-amino ester **6a** 42.4 mg (92% yield). $[\alpha]_D^{20}$ = -11.0 (c 0.15, $CHCl_3$); 94% ee, determined by HPLC analysis [Daicel chiralcel AS, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ 220 nm, t (major) = 14.58 min, t (minor) = 19.70 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.33-7.25 (m, 3H), 7.12 (d, *J* = 7.2 Hz, 2H), 4.70 (t, *J* = 6.4 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.73 (dd, *J* = 6.4, 14.0 Hz, 1H), 3.59 (dd, *J* = 6.8, 14.0 Hz, 1H), 3.21-3.11 (m, 2H), 2.47 (td, *J* = 6.0, 13.2 Hz, 1H), 2.36 (td, *J* = 5.2, 12.0 Hz, 1H), 1.38 (s, 9H), 1.21 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 155.9, 139.1, 138.1, 133.6, 129.3, 129.0, 128.1, 127.7, 126.3, 79.7, 61.6, 54.6, 52.1, 45.5, 28.3, 26.9, 14.0 ppm; IR (KBr) ν 3361, 2981, 1725, 1449, 1308, 1225, 1088 cm^{-1}; ESI-HRMS: calcd. for $C_{24}H_{31}NO_6S$+Na 484.1764, found 484.1752.

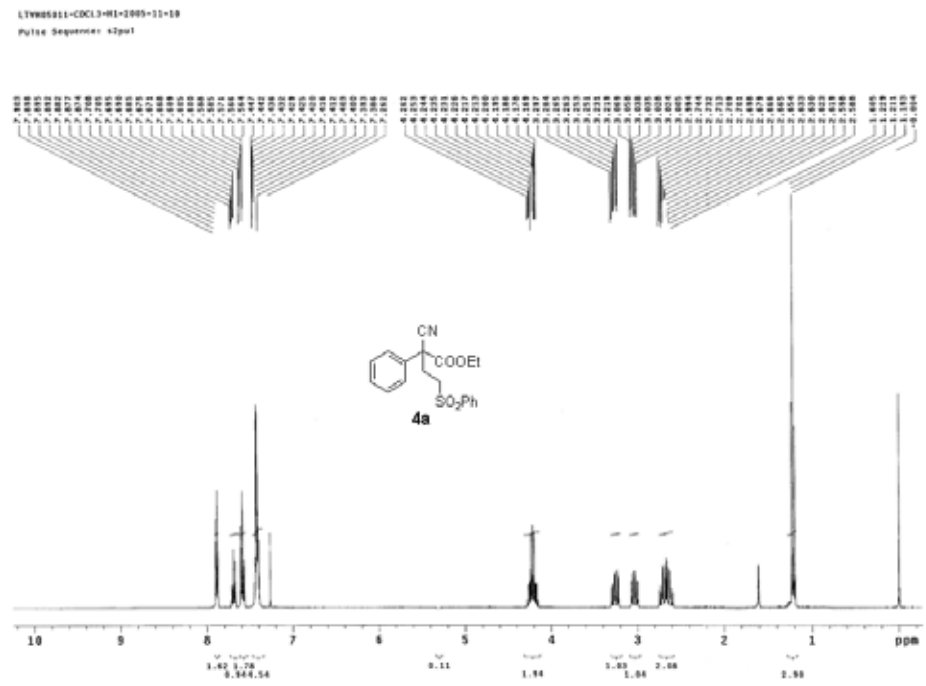


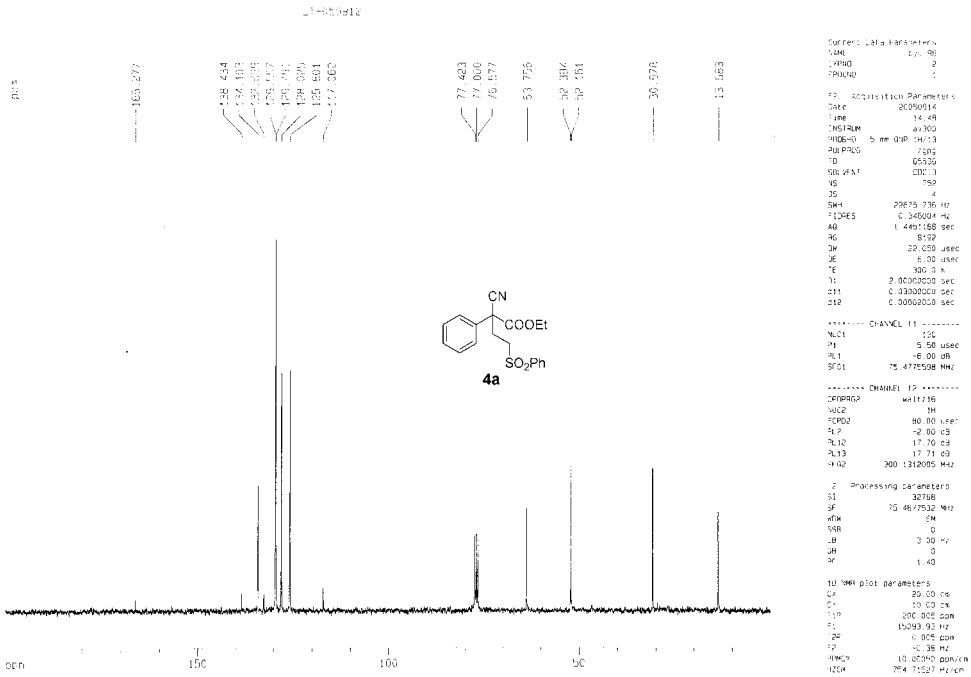
4l 99 ee% **6b** 95 ee%

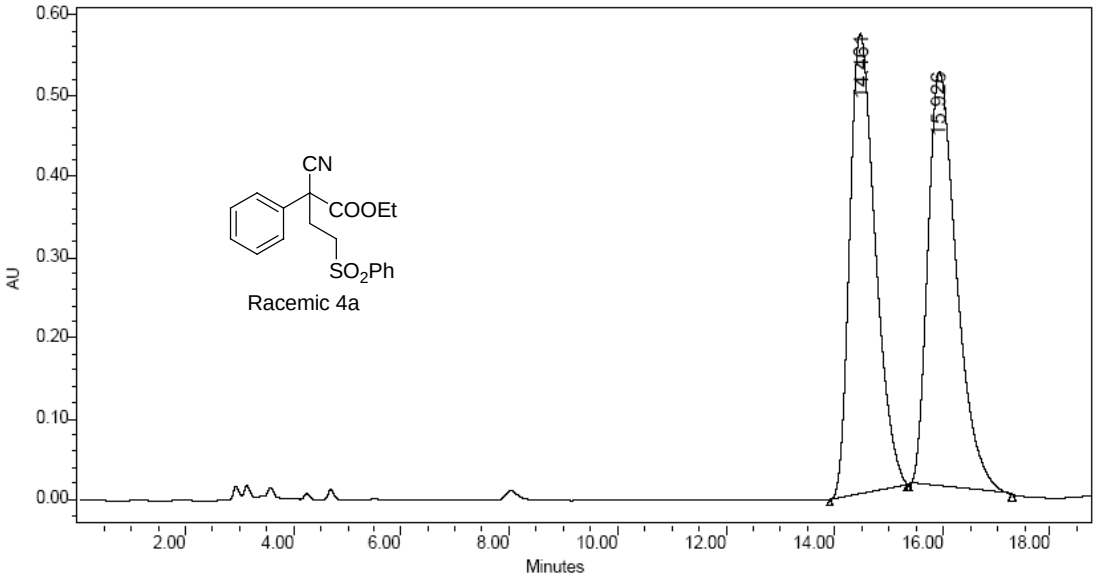
To a solution of **4l** 51.1 mg (0.1mmol, 99% ee) in ethanol (10 mL) was added $(Boc)_2O$ 24.0 mg (0.11 mmol) and Raney-Ni 10.2 mg. The mixture was stirred under H_2 (50 psi) at room temperature for 24 h. The reaction mixture was then filtered through celite, and the resulting filtrate was washed with EtOAc (20 mL) and the filtrate was concentrated in vacuum. The residue was subjected to flash chromatography (eluent: petroleum ether/EtOAc = 12/1 R_f = 0.12) to give the Boc-protected β-amino ester **6b** 57.4 mg (93% yield). $[\alpha]_D^{20}$ = -15.8 (c 0.12, $CHCl_3$); 95% ee, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ 220

nm, t (minor) = 13.25 min, t (major) = 16.54 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.90 (m, 4H), 7.67-7.64 (m, 2H), 7.56-7.51 (m, 4H), 7.27-7.23 (m, 3H), 7.01-6.98 (m, 2H), 5.40 (t, *J* = 4.8 Hz, 1H), 5.04 (br.s, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.33-3.27 (m, 2H), 3.13 (d, *J* = 13.6 Hz, 1H), 2.66-2.60 (m, 2H), 2.49 (dd, *J* = 4.4, 12.0 Hz, 1H), 1.44 (s, 9H), 1.25 (t, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.8, 156.3, 137.7, 137.4, 135.6, 134.5, 134.4, 130.3, 130.0, 129.8, 129.7, 129.0, 128.9, 128.4, 127.0, 78.9, 61.8, 61.2, 49.6, 43.8, 41.7, 29.9, 28.3, 13.9 ppm; IR (CH_2Cl_2) ν 3749, 2925, 1713, 1505, 1451, 1250, 1159, 1081 cm^{-1}; ESI-HRMS: calcd. for $C_{31}H_{37}NO_8S_2$+Na 638.1853, found 638.1824.

NMR, HRMS and HPLC spectra of products







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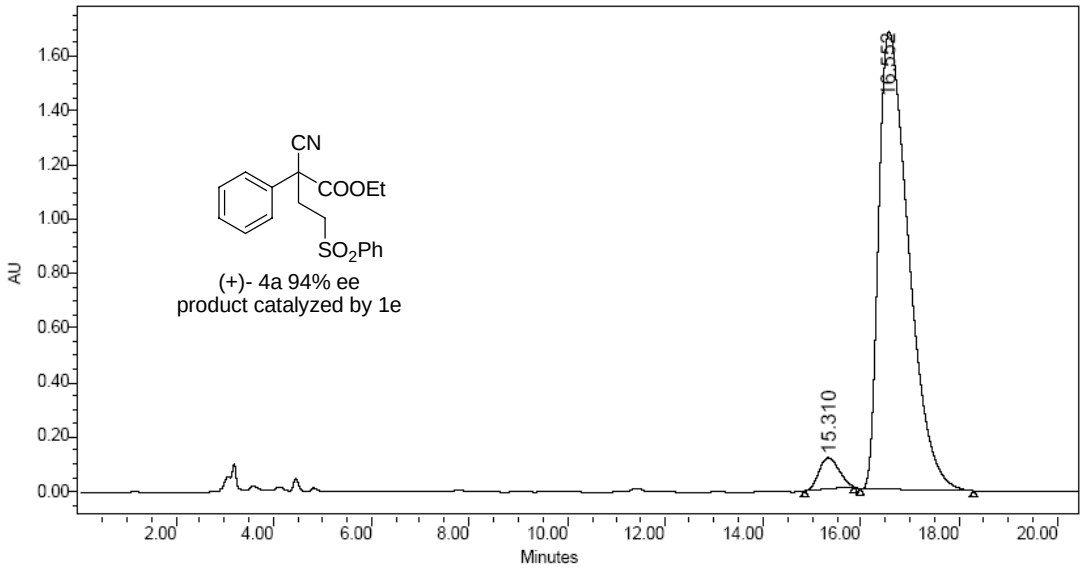

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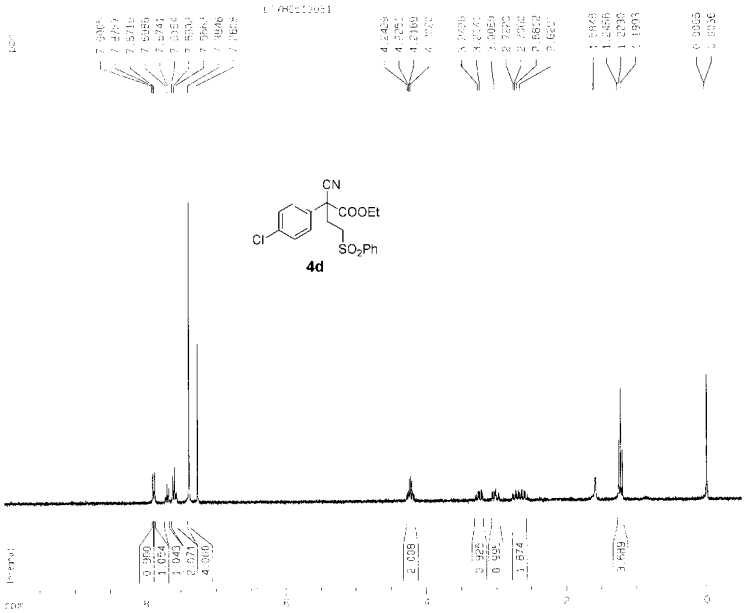
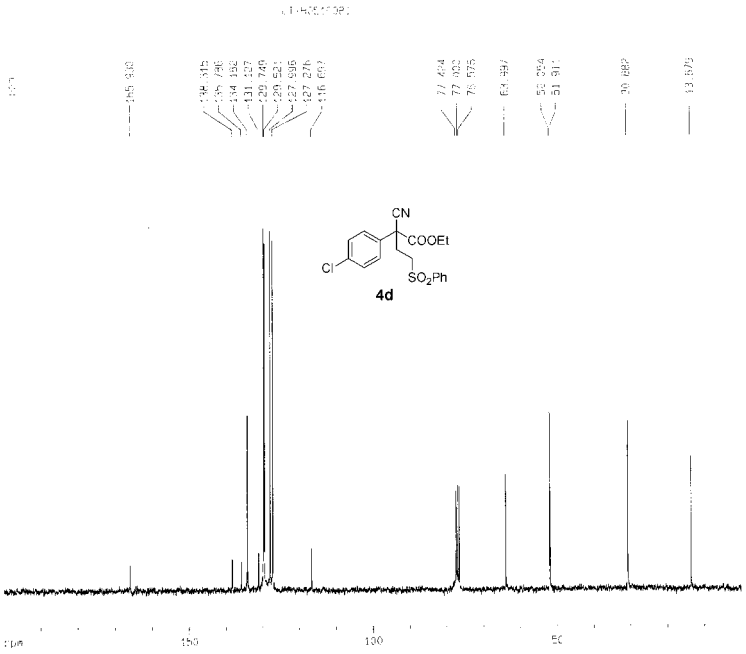
2	16.552	71187819	96.74	1683655	94.48


CN
COOEt
Cl
SO2Ph
4d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Cl
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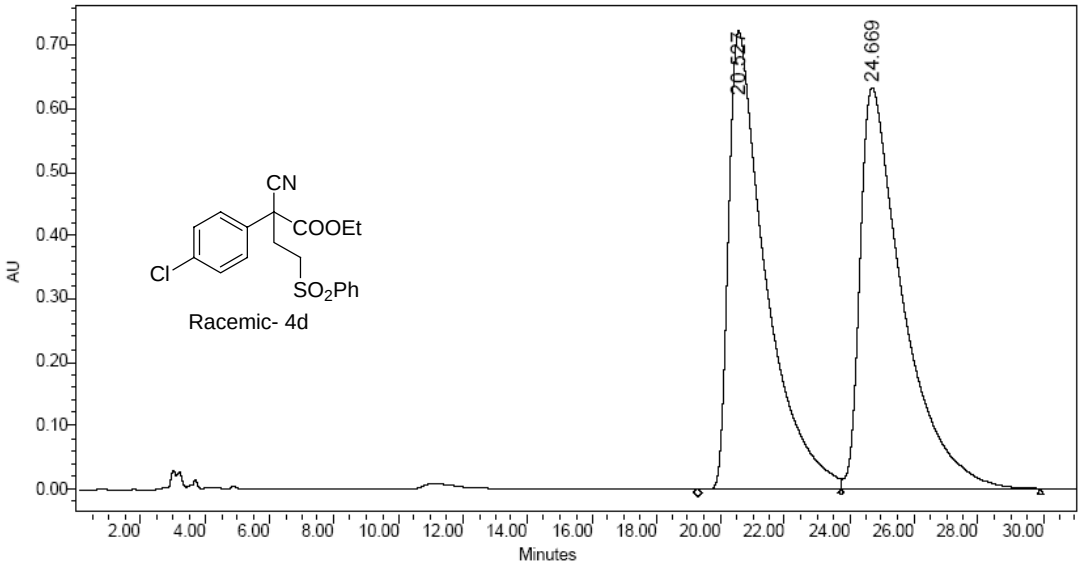
4d



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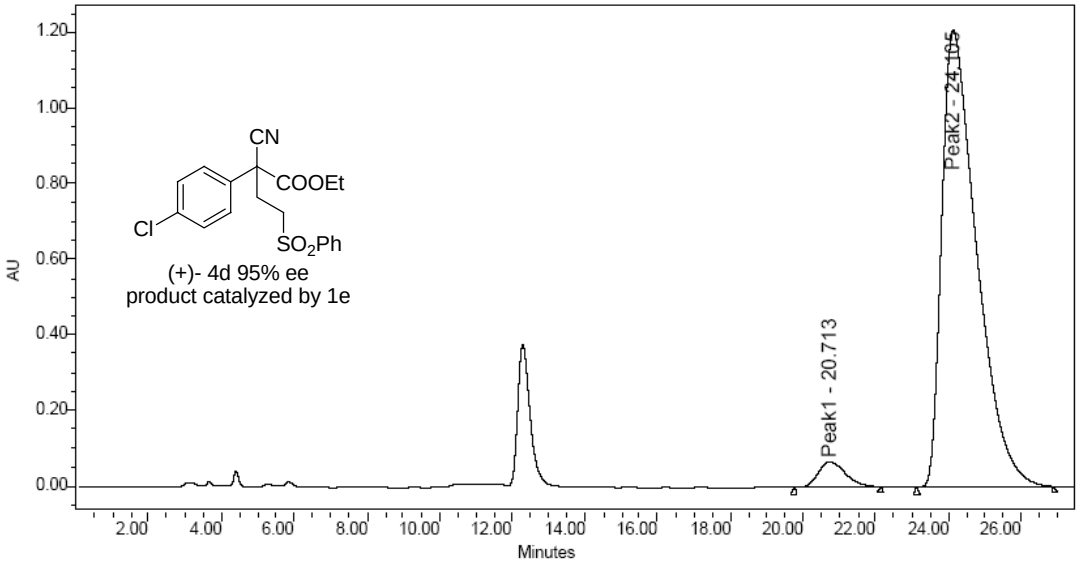

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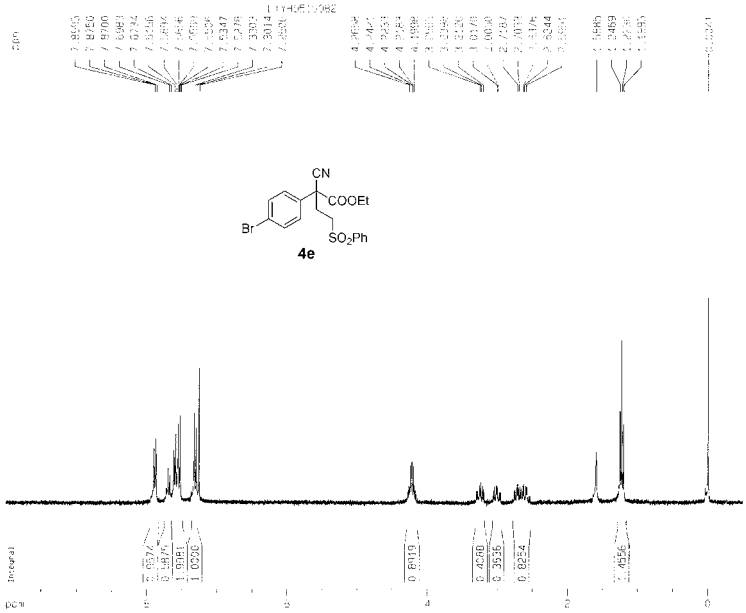
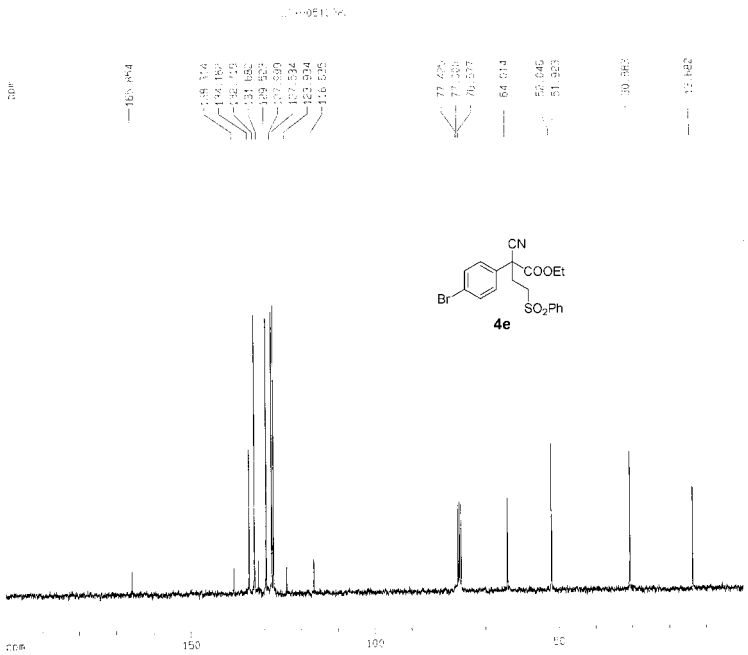

CN
COOEt
Br
SO2Ph
4e


CN
COOEt
Br
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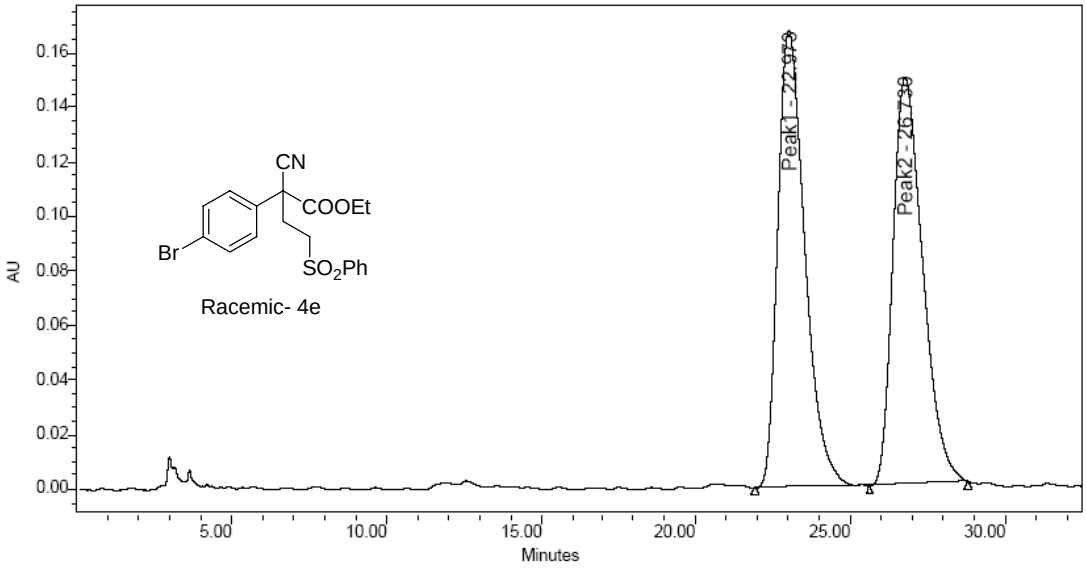
4e



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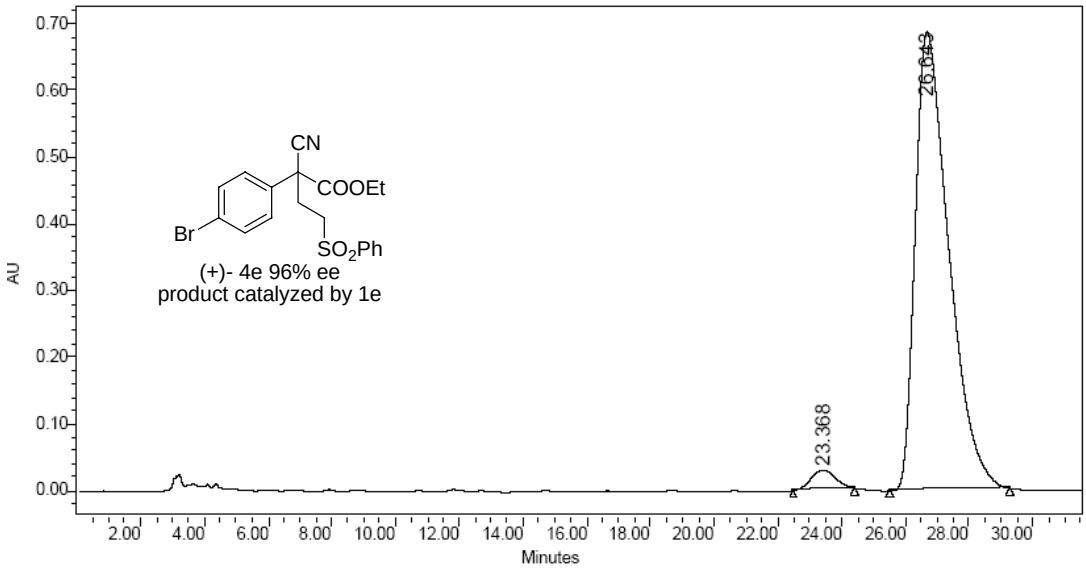
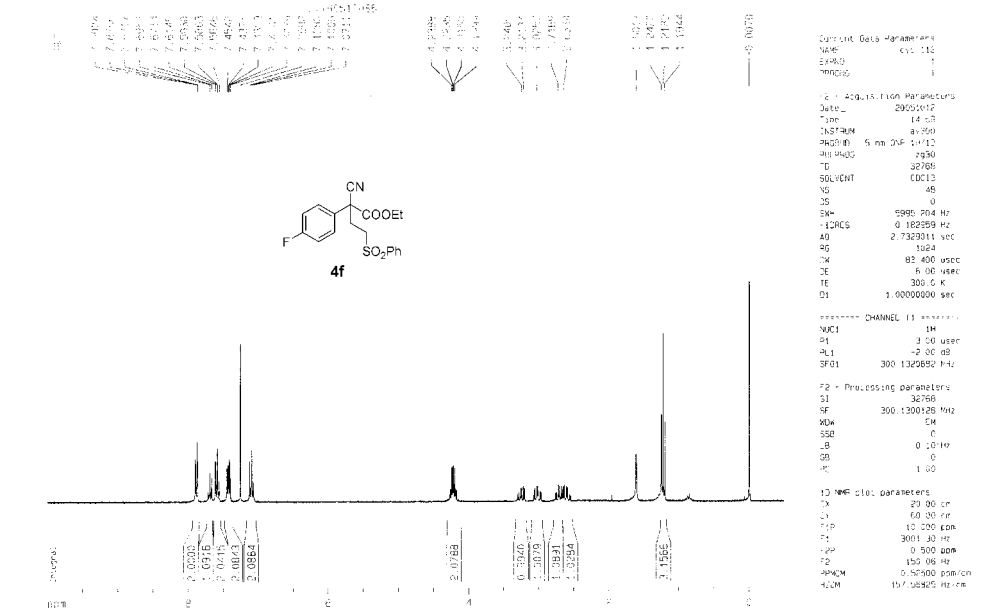
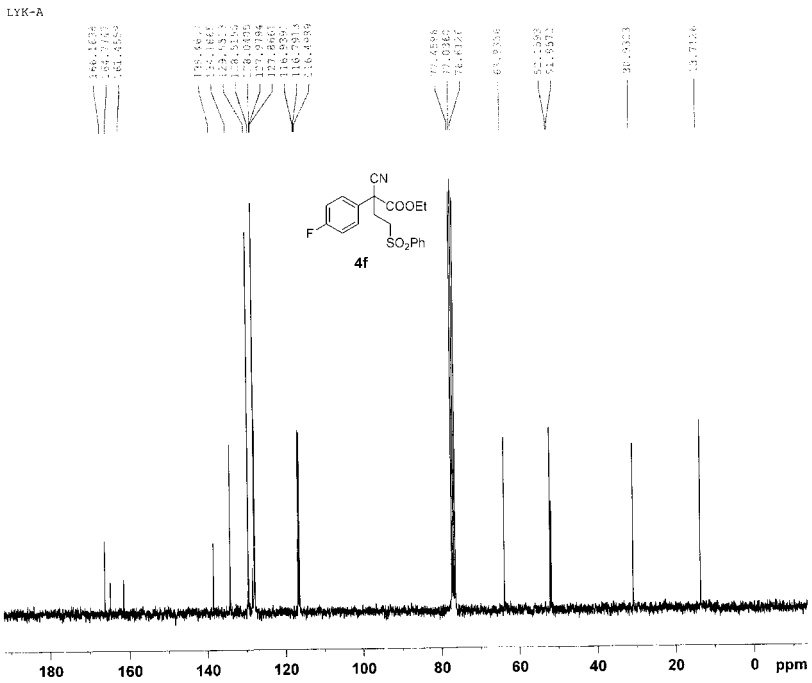
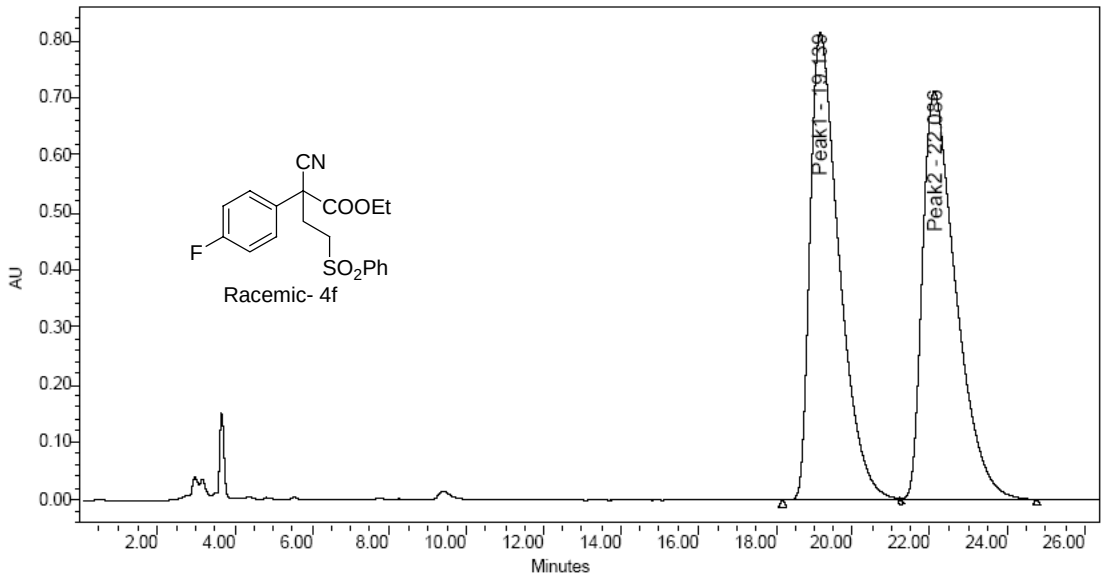


	RT (min)	Area (μV *sec)	% Area	Height (μV)	% Height
1	23.376	1046805	2.02	23291	3.27
2	26.643	50787017	97.98	689097	96.73

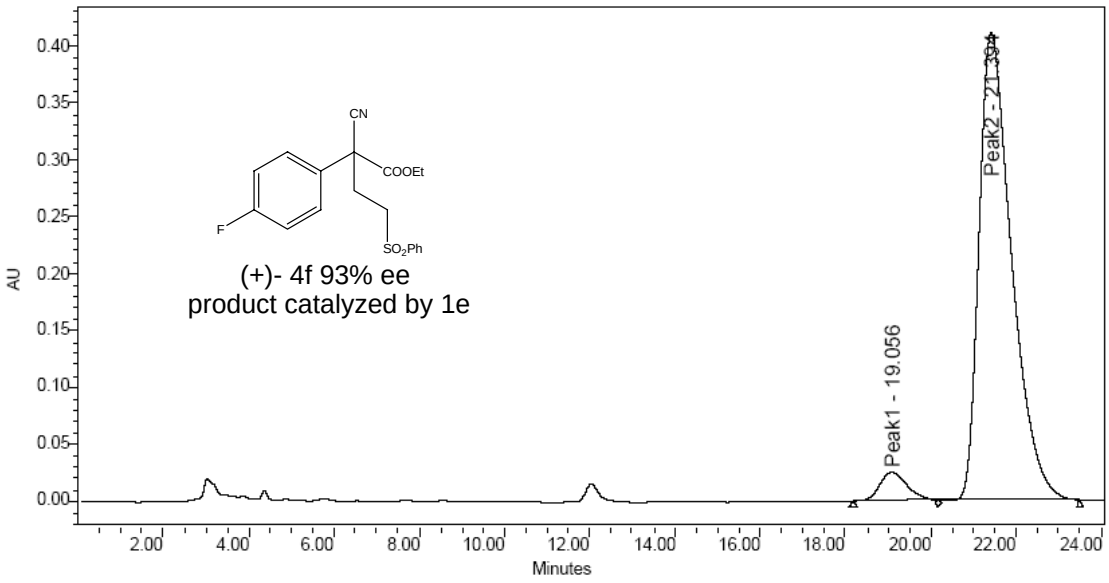

CN
COOEt
F
SO2Ph
4f

LYK-A

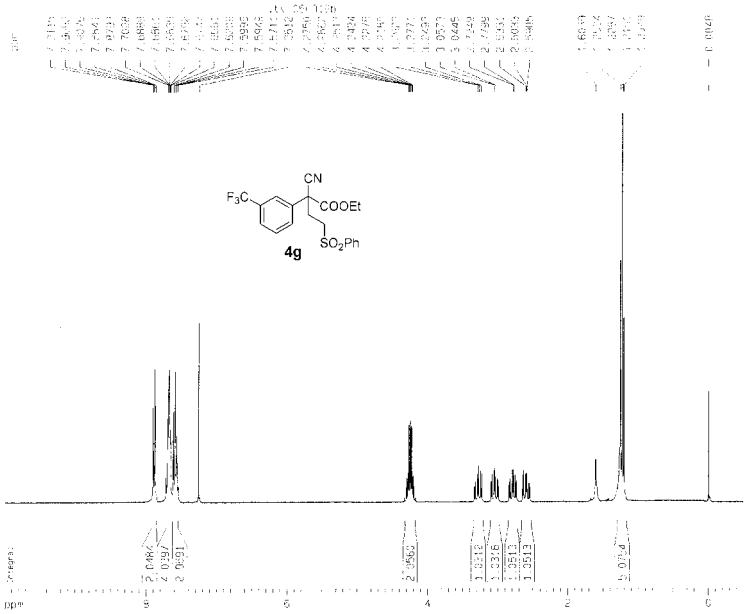

CN
COOEt
F
SO2Ph
4f
180
160
140
120
100
80
60
40
20
0
ppm

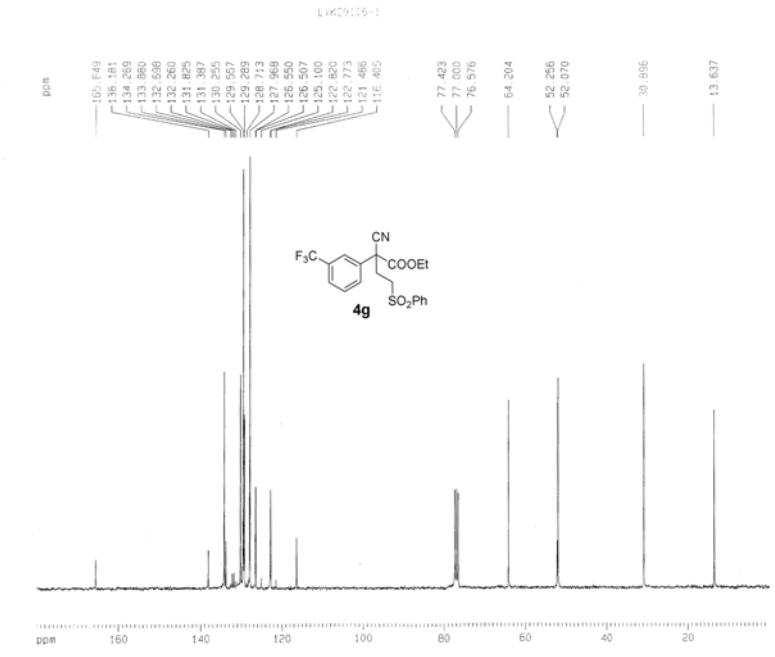


	Peak Name	RT (min)	Area (μV *sec)	% Area	Height (μV)	% Height
1	Peak1	19.139	42612464	49.95	813693	53.30
2	Peak2	22.086	42701158	50.05	713024	46.70



	RT (min)	Area (μV *sec)	% Area	Height (μV)	% Height
1	19.056	826974	3.65	22018	5.09
2	21.394	21806774	96.35	410655	94.91


CN
F3C
COOEt
SO2Ph
4g


CN
F3C
COOEt
SO2Ph
4g

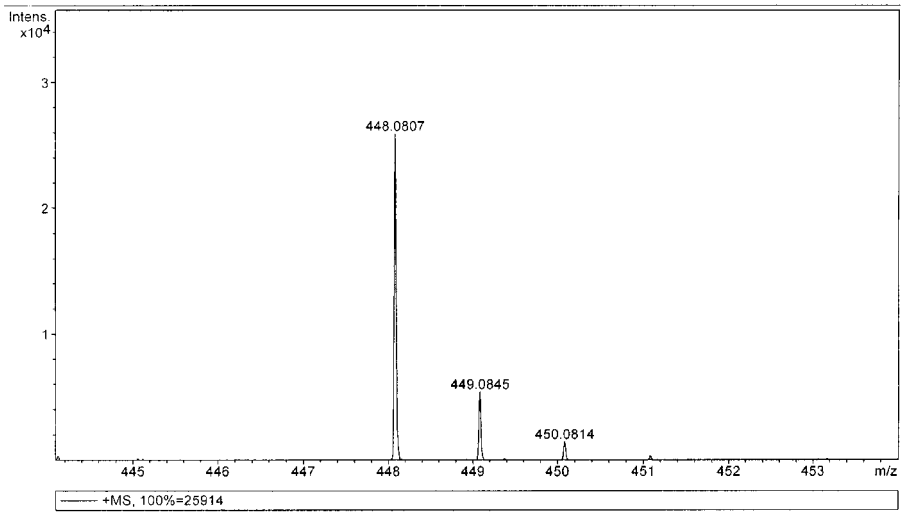
Mass Spectrum Molecular Formular Report

Analysis Info

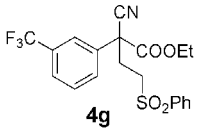
Analysis Name	D:\Bruker\data\msdata\LR0106-1\1.d	Acquisition Date	1/10/2006 10:50:12 AM
Method	1pass_pos_low.tofpar	Operator	operator name
Sample Name	LR0106-1	Instrument	BioTOF Q
Comment	ESI Source		

Acquisition Parameter

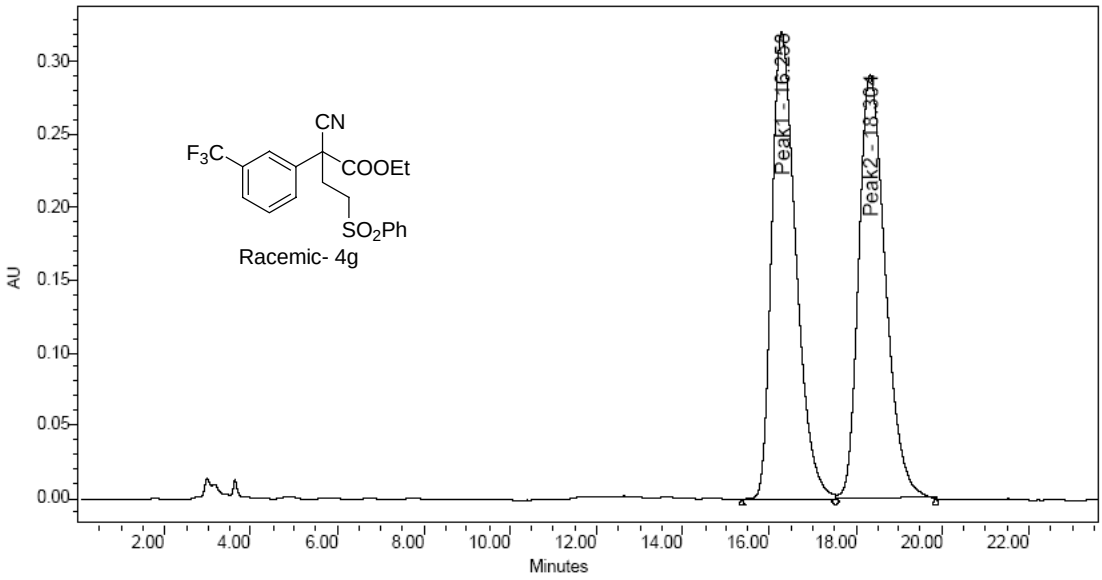
Capilary End Plate	-4500 V	Capilary Exit	120 V	detbias	2 V
EndP	-4000 V	Collision energy	0 eV	Number of Averages	100



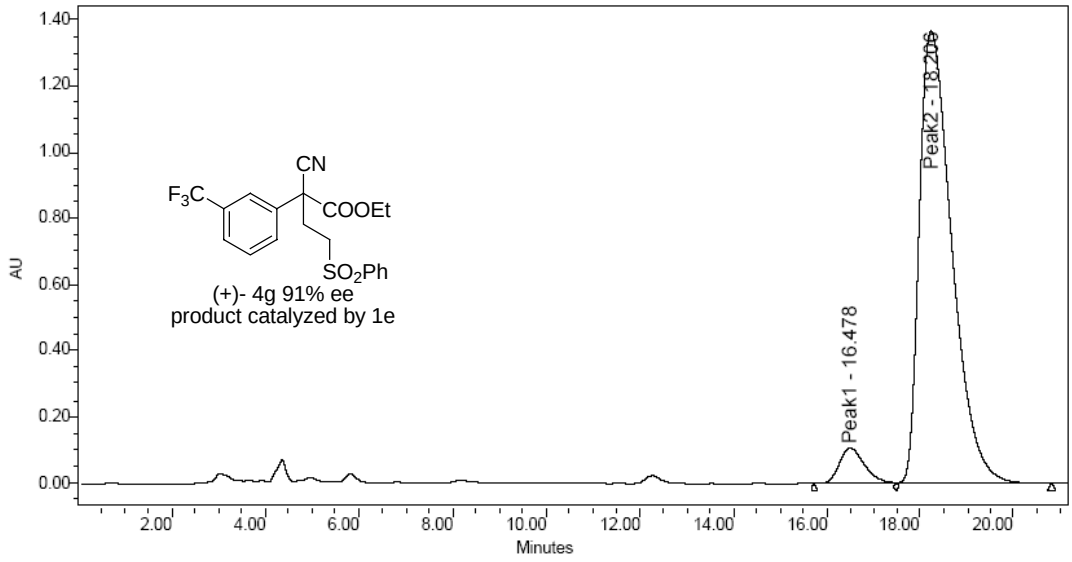
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdb	N Rule	e⁻
C 20 H 18 F 3 N 1 Na 1 O 4 S 1	0.02	448.0801	-1.41	-1.62	10.50	ok	even



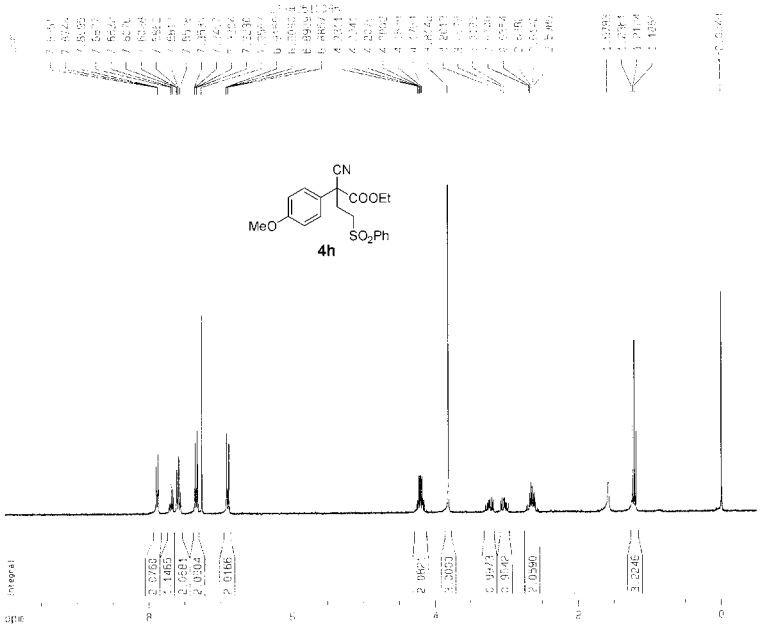
4g

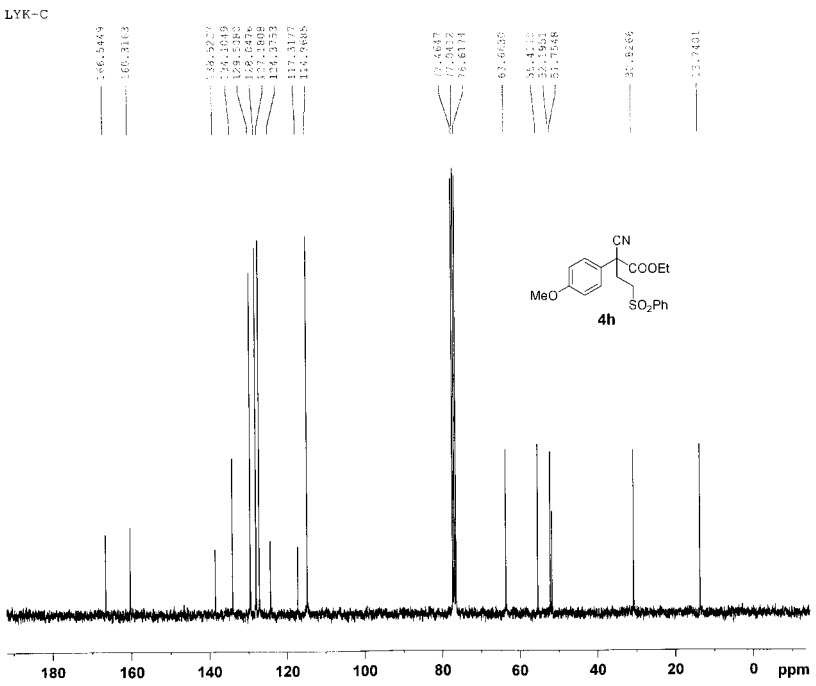


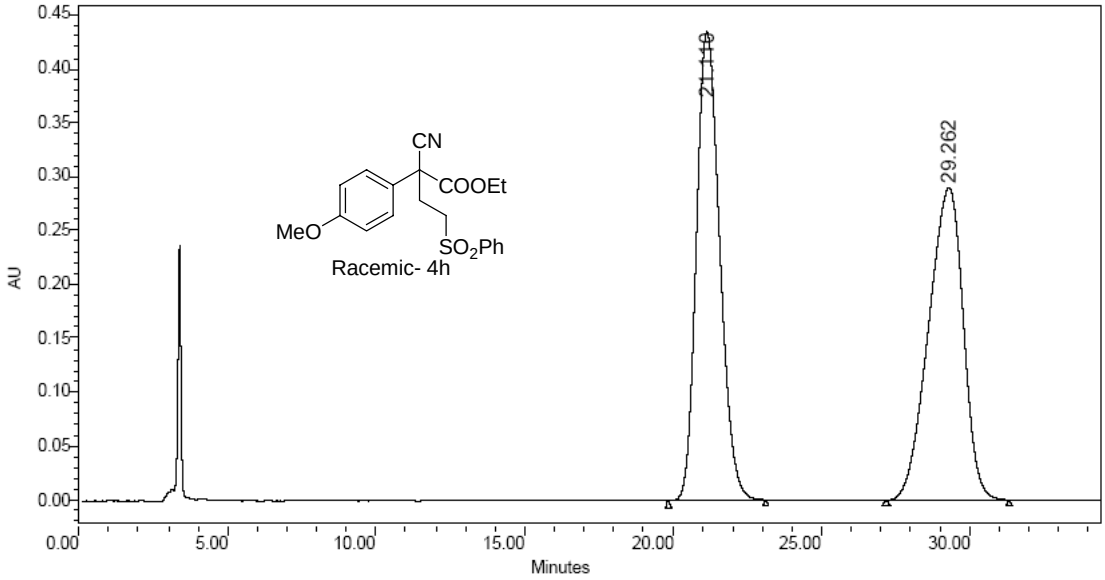
	Peak Name	RT (min)	Area (μV *sec)	% Area	Height (μV)	% Height
1	Peak1	16.258	12558626	49.97	321803	52.42
2	Peak2	18.304	12574205	50.03	292102	47.58



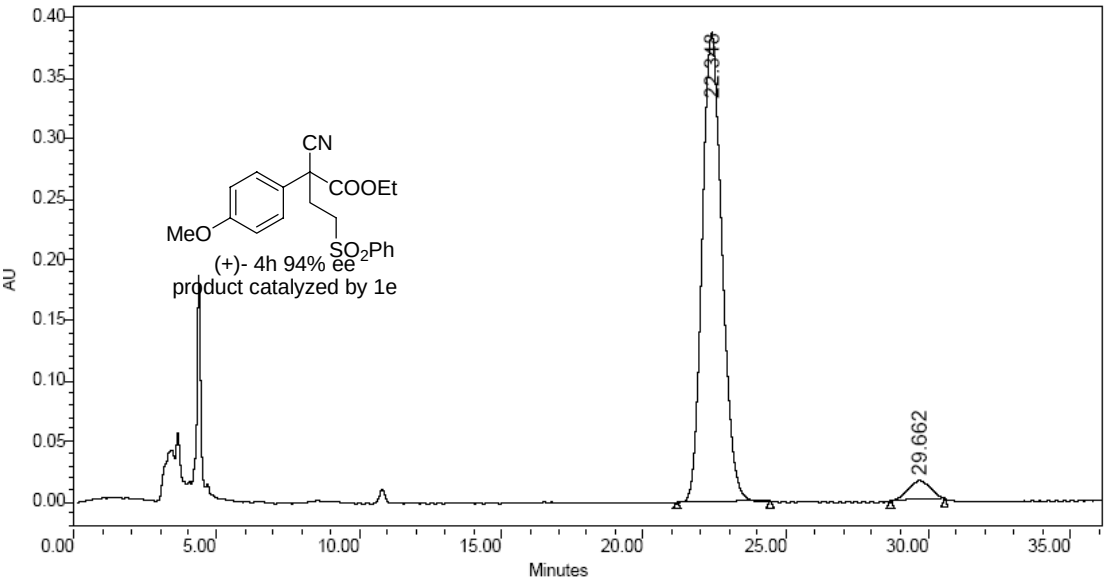
	RT (min)	Area (μV *sec)	% Area	Height (μV)	% Height
1	16.478	3232717	4.70	98606	6.74
2	18.206	65494007	95.30	1364339	93.26


CN
COOEt
MeO
SO2Ph
4h

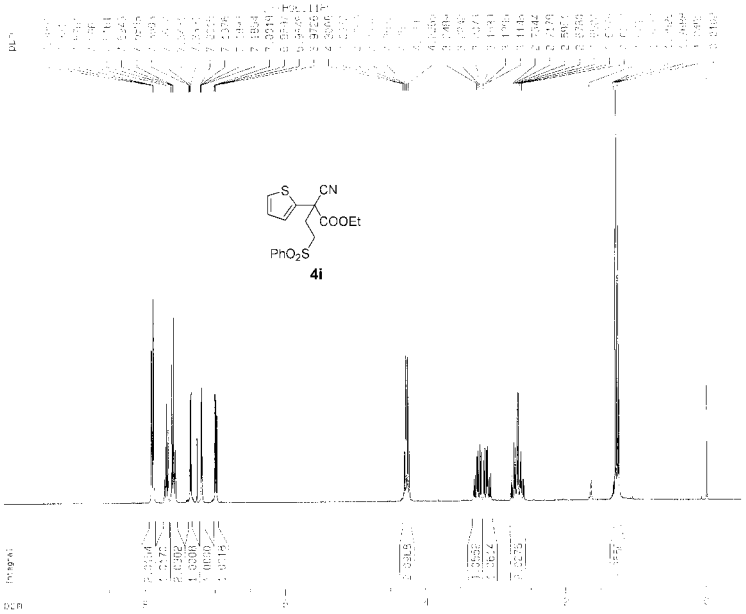

LYK-C
CN
COOEt
MeO
SO2Ph
4h
180
160
140
120
100
80
60
40
20
0
ppm

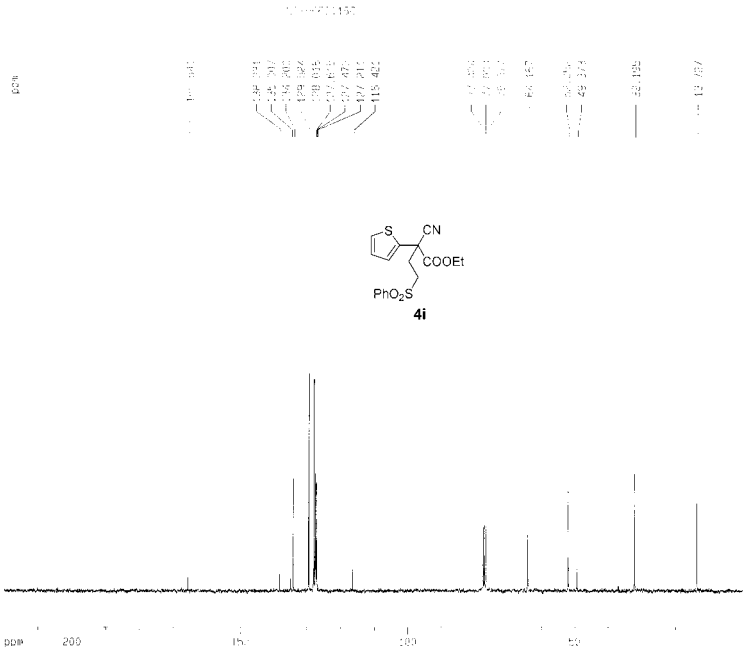


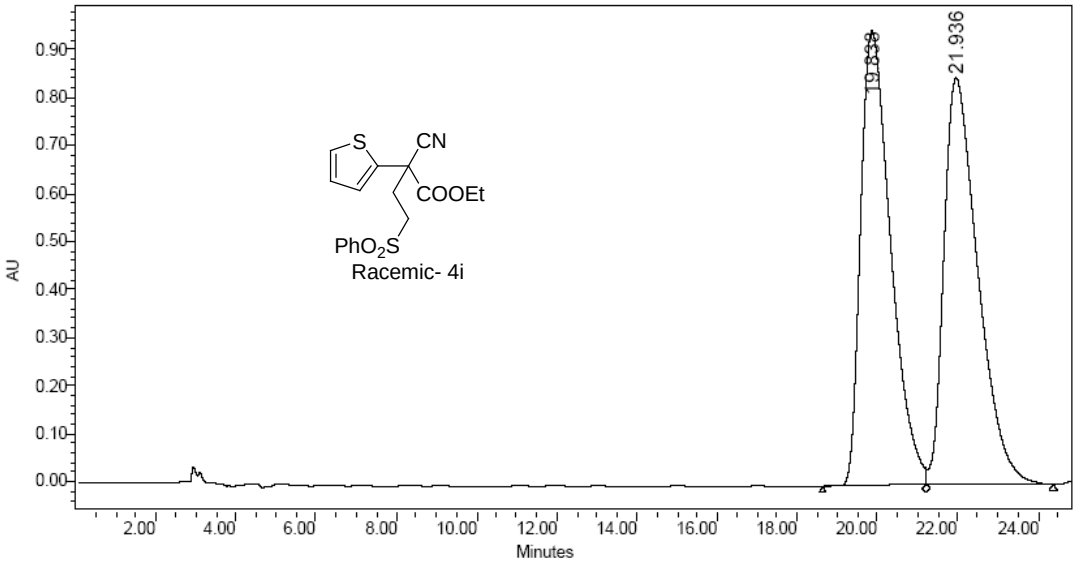
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	21.110	23710710	50.08	434965	60.01
2	29.262	23633929	49.92	289912	39.99



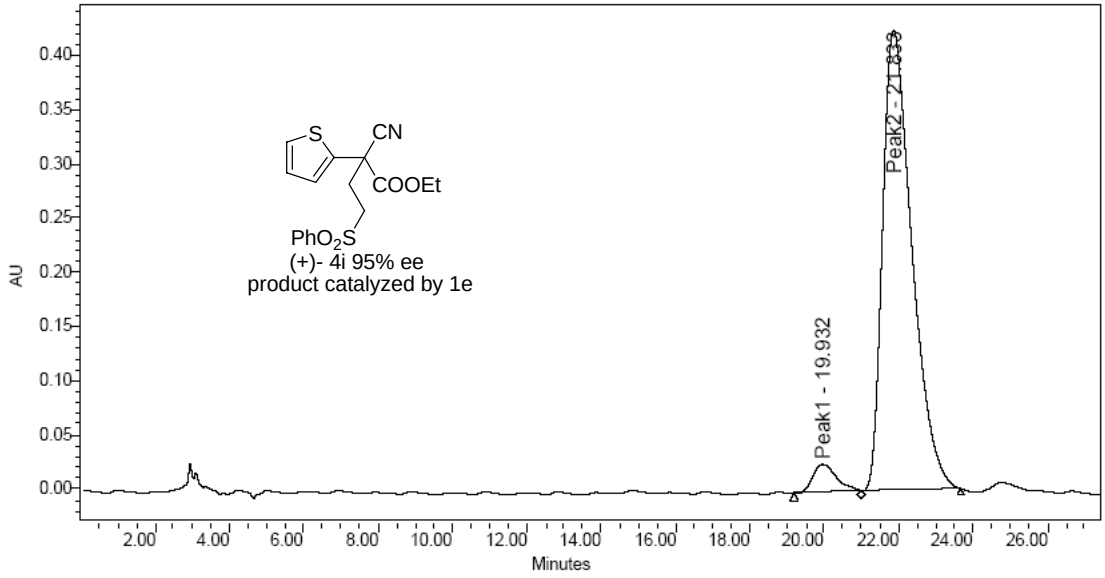
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	22.348	18792229	96.73	388037	96.67
2	29.662	634334	3.27	13371	3.33


S
CN
COOEt
PhO2S
4i

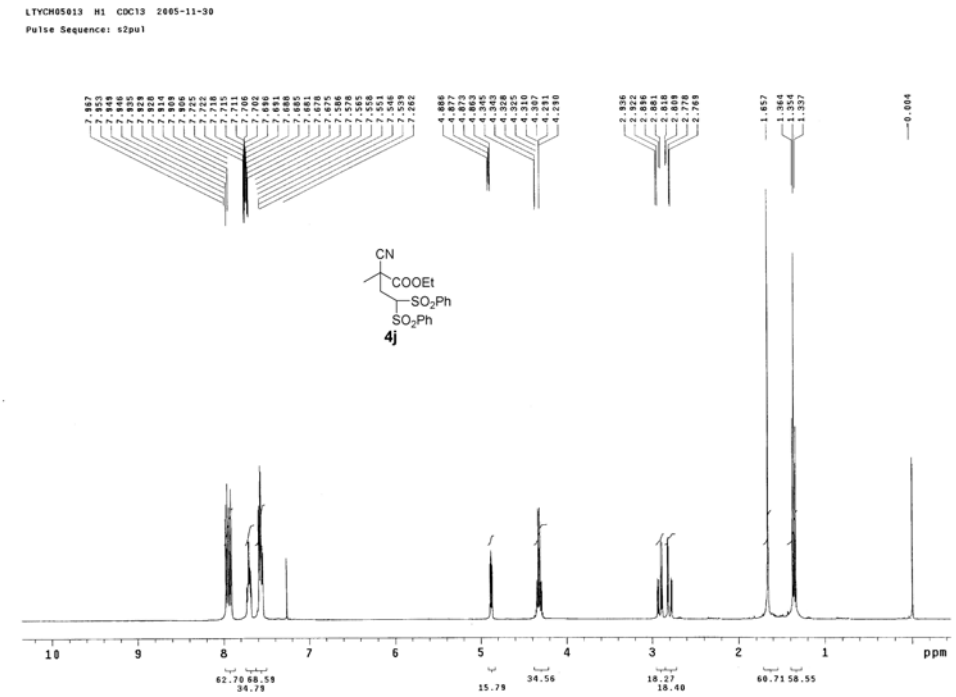

S
CN
COOEt
PhO2S
4i

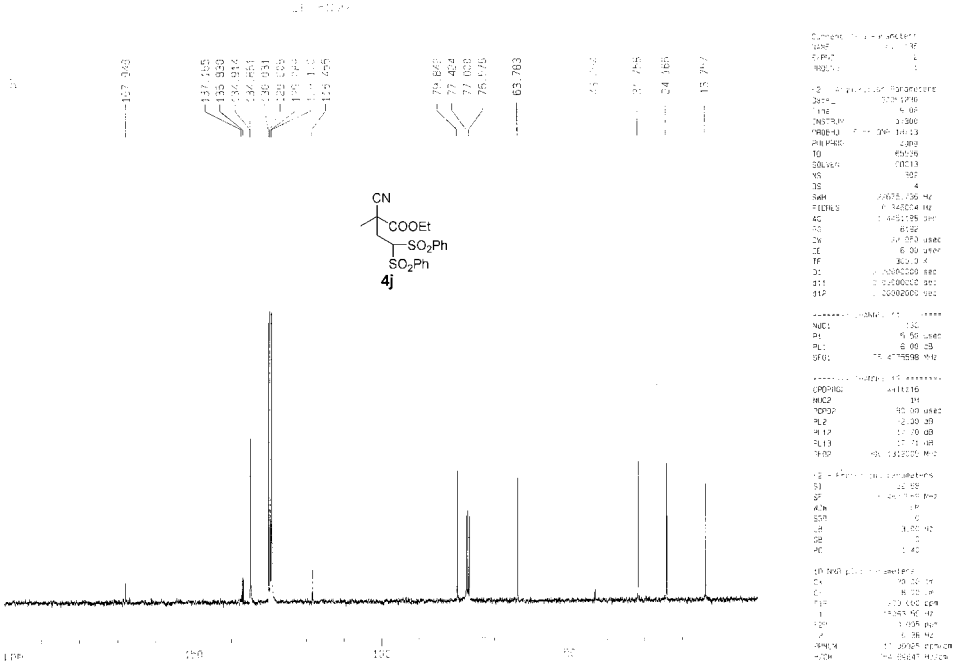


	RT (min)	Area (μV *sec)	% Area	Height (μV)	% Height
1	19.838	49545245	49.76	947873	52.77
2	21.936	50022053	50.24	848330	47.23



	RT (min)	Area (μV *sec)	% Area	Height (μV)	% Height
1	19.932	620006	2.57	18777	4.23
2	21.833	23509303	97.43	424988	95.77


LTYCH05013 H1 CDCl3 2005-11-30
Pulse Sequence: s2pul
CN
COOEt
SO2Ph
SO2Ph
4j
ppm


CN
COOEt
SO2Ph
SO2Ph
4j

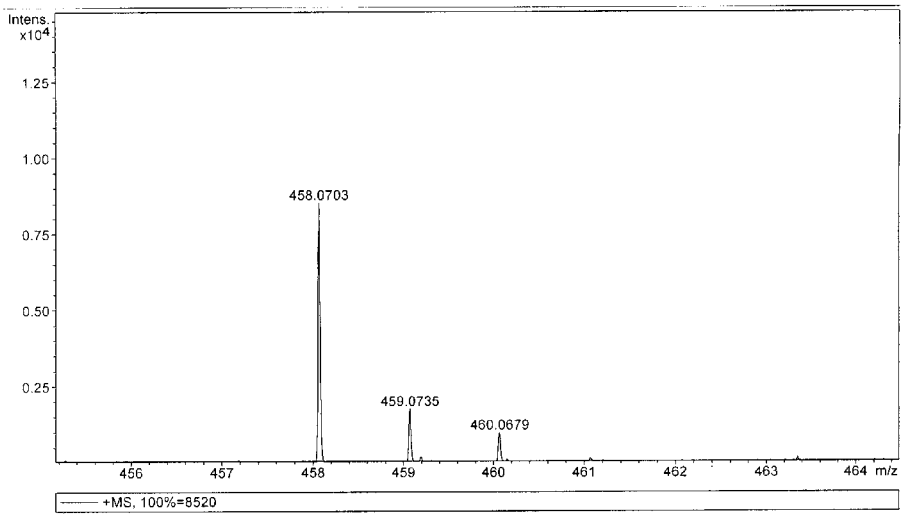
Mass Spectrum Molecular Formular Report

Analysis Info

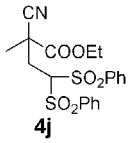
Analysis Name	D:\Bruker\data\msdata\LR060113\1.d	Acquisition Date	1/13/2006 2:11:40 PM
Method	1pass_pos_mid.tofpar	Operator	operator name
Sample Name	LR060113	Instrument	BioTOF Q
Comment	ESI Source		

Acquisition Parameter

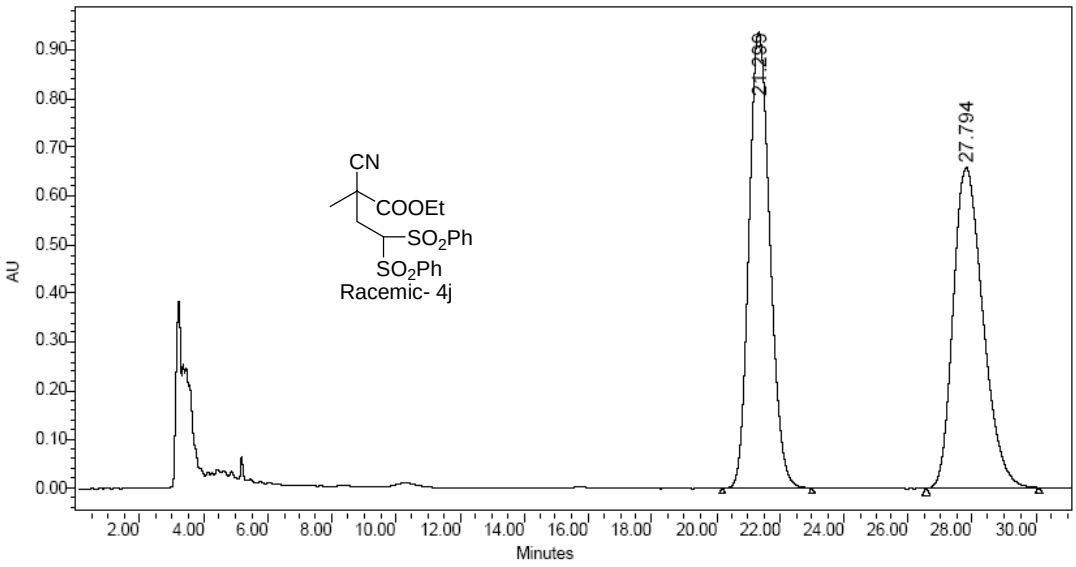
Capilary End Plate	-4500 V	Capilary Exit	120 V	detbias	2 V
EndP	-4000 V	Collision energy	0 eV	Number of Averages	100



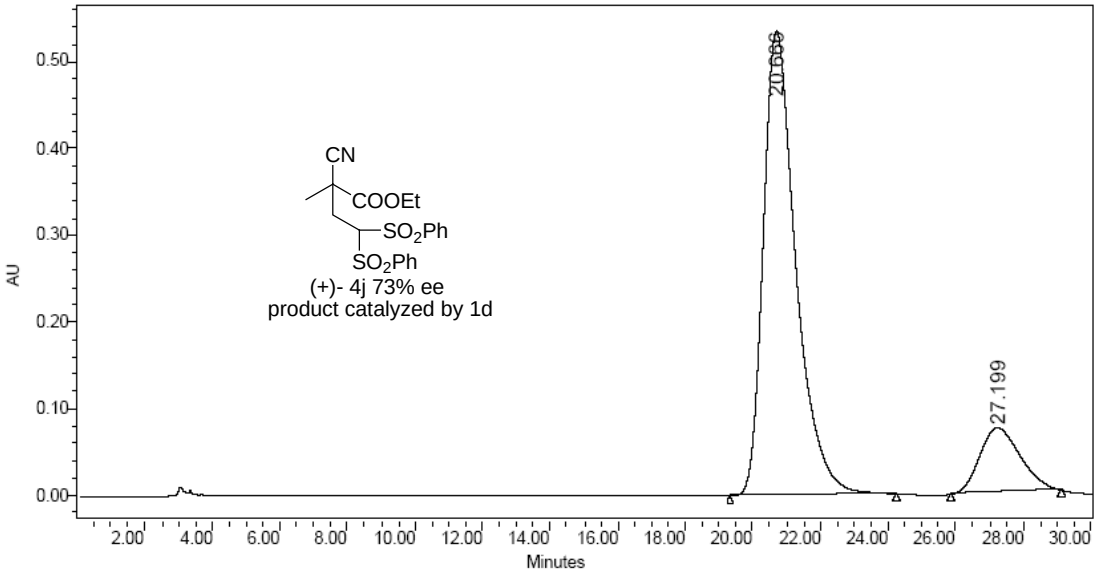
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdb	N Rule	e⁻
C 20 H 21 N 1 Na 1 O 6 S 2	0.02	458.0702	-0.16	-0.35	10.50	ok	even



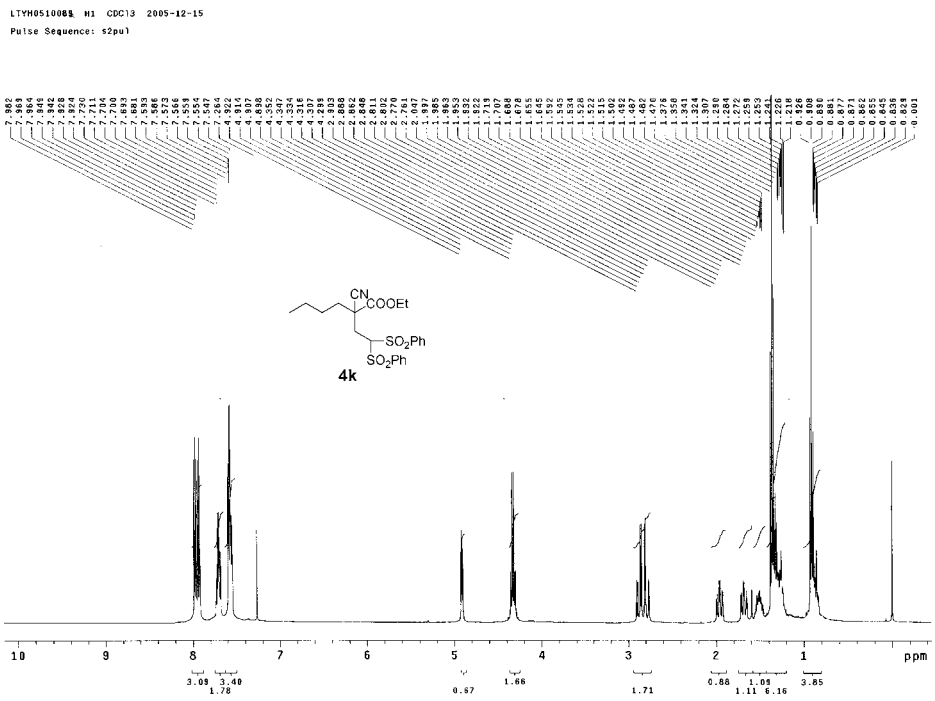
4j

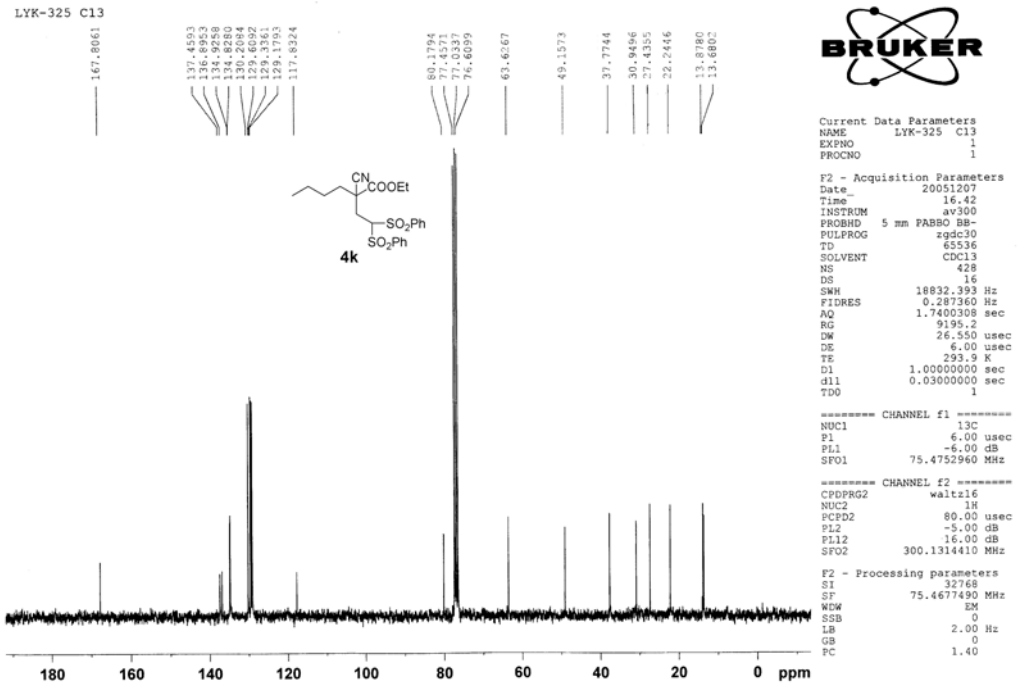


	RT (min)	Area (μV *sec)	% Area	Height (μV)	% Height
1	21.299	42625091	49.99	937547	58.72
2	27.794	42640550	50.01	659009	41.28



	RT (min)	Area (μV *sec)	% Area	Height (μV)	% Height
1	20.666	35978598	86.71	536244	88.40
2	27.198	5515030	13.29	70384	11.60


LTYH051008% H1 CDCl3 2005-12-15
Pulse Sequence: s2pul
CN
COOEt
SO2Ph
SO2Ph
4k
10
9
8
7
6
5
4
3
2
1
ppm
3.09
3.40
1.78
0.87
1.66
1.71
0.88
1.09
1.11
6.16
3.85


LYK-325 C13
167.8061
137.4593
136.8953
134.9258
134.8280
130.2084
129.6022
129.3361
129.1793
117.8324
80.1794
77.4571
77.0337
76.6099
63.6267
49.1573
37.7744
30.9496
27.4355
22.2446
13.8780
13.6802
CN
COOEt
SO2Ph
SO2Ph
4k
180
160
140
120
100
80
60
40
20
0
ppm
BRUKER
Current Data Parameters
NAME LYK-325 C13
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20051207
Time 16.42
INSTRUM av300
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 428
DS 16
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 9195.2
DW 26.550 usec
DE 6.00 usec
TE 293.9 K
D1 1.00000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 6.00 usec
PL1 -6.00 dB
SFO1 75.4752960 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 16.00 dB
SFO2 300.1314410 MHz
F2 - Processing parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

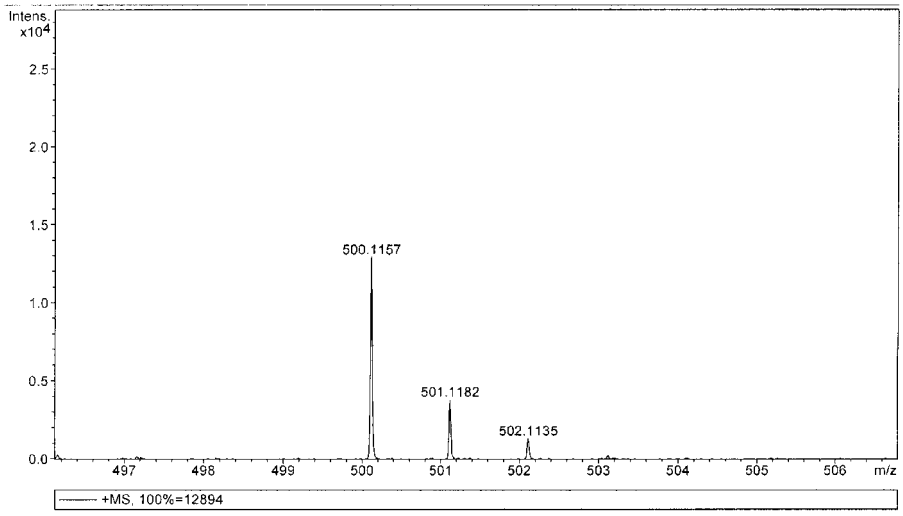
Mass Spectrum Molecular Formular Report

Analysis Info

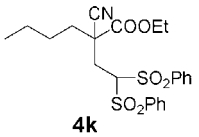
Analysis Name	D:\Bruker\data\msdata\PD\LR0510089\1.d	Acquisition Date	12/15/2005 2:29:54 PM
Method	1pass_pos_low.tofpar	Operator	operator name
Sample Name	LR0510089	Instrument	BioTOF Q
Comment	ESI Source		

Acquisition Parameter

Capilary End Plate	-4500 V	Capilary Exit	120 V	detbias	2 V
EndP	-4000 V	Collision energy	0 eV	Number of Averages	100

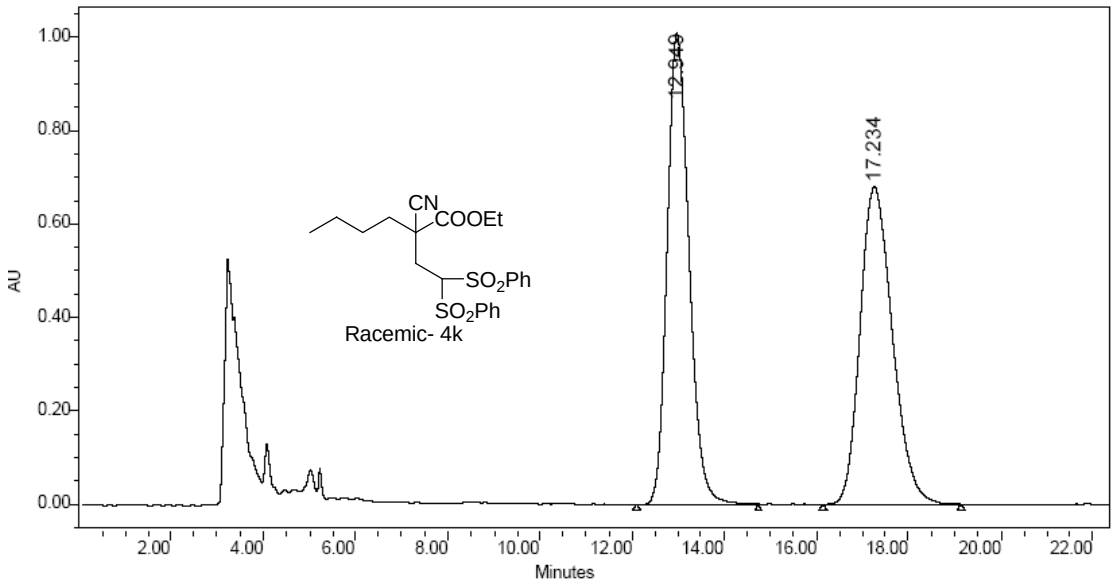


Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdb	N Rule	e⁻
C 23 H 27 N 1 Na 1 O 6 S 2	0.02	500.1172	2.98	3.06	10.50	ok	even

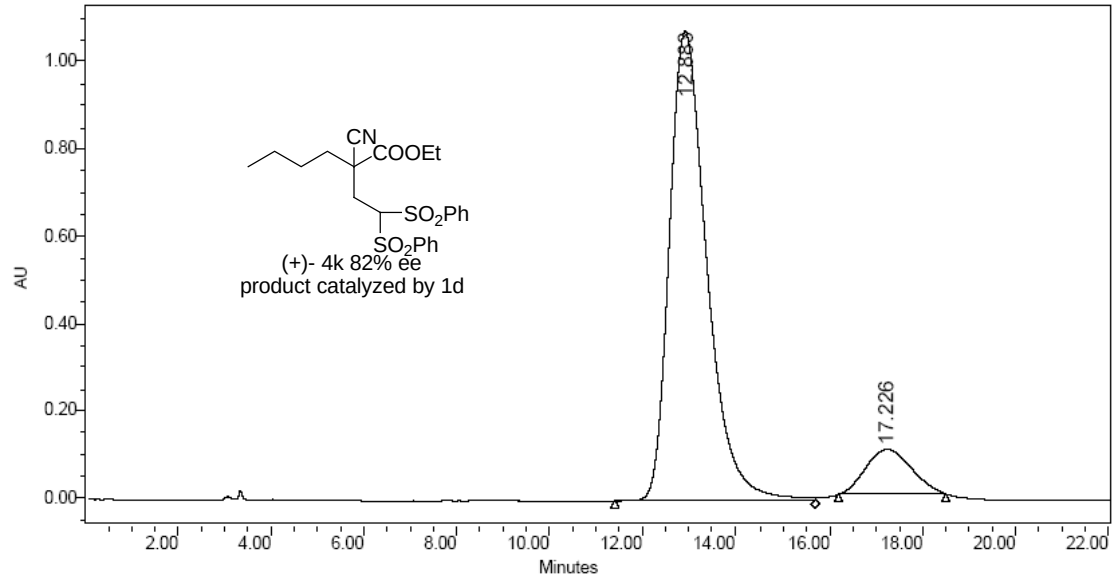


4k

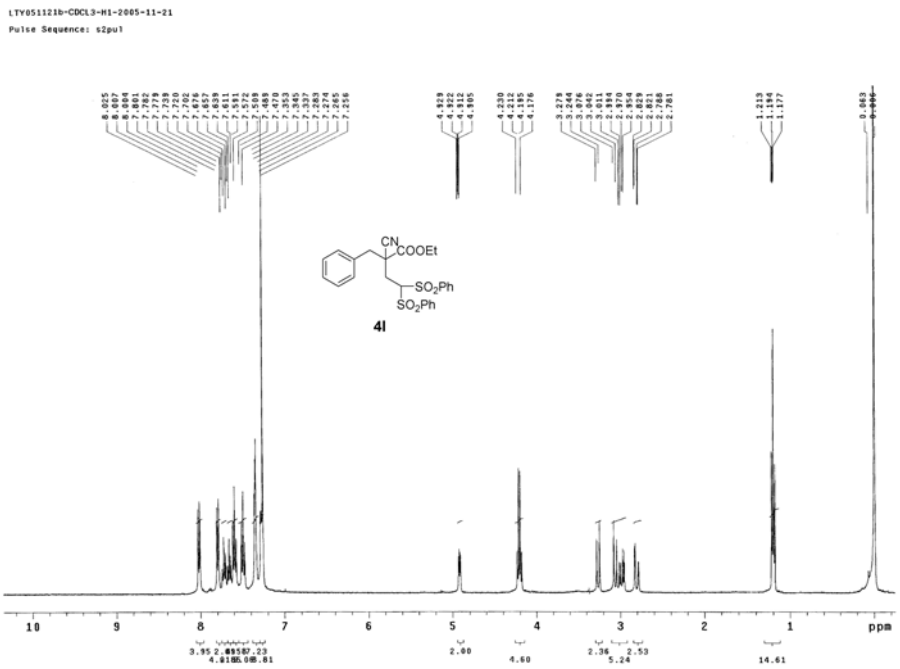
Bruker Daltonics DataAnalysis 3.2 printed: 12/15/2005 02:33:05 PM Page 1 of 1

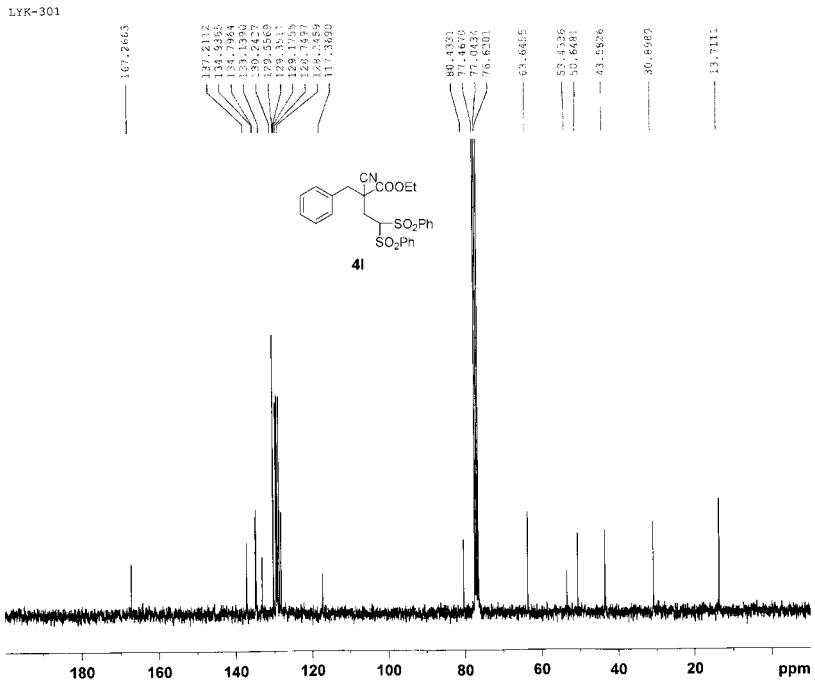


	RT (min)	Area (μV *sec)	% Area	Height (μV)	% Height
1	12.949	33238118	50.02	1009110	59.72
2	17.234	33211408	49.98	680737	40.28



	RT (min)	Area (μV *sec)	% Area	Height (μV)	% Height
1	12.883	58907565	90.73	1070845	91.88
2	17.226	6018713	9.27	94638	8.12





BRUKER

Current Data Parameters
NAME LYK-301
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20051122
Time 13.59
INSTRUM av300
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 460
DS 16
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 4096
DW 26.550 usec
DE 6.00 usec
TE 299.1 K
D1 1.00000000 sec
d11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 6.00 usec
PL1 -6.00 dB
SFO1 75.4752960 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 16.00 dB
SFO2 300.1314410 MHz

F2 - Processing parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

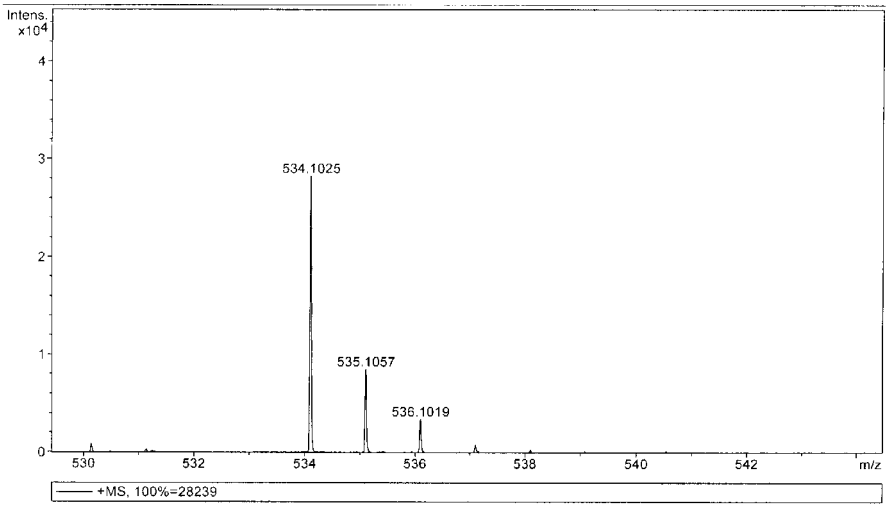
Mass Spectrum Molecular Formular Report

Analysis Info

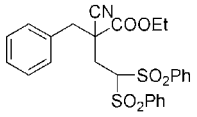
Analysis Name	D:\Bruker\data\msdata\LR05012\1.d	Acquisition Date	11/21/2005 4:07:49 PM
Method	1pass_pos_low.tofpar	Operator	operator name
Sample Name	LR05012	Instrument	BioTOF Q
Comment	ESI Source		

Acquisition Parameter

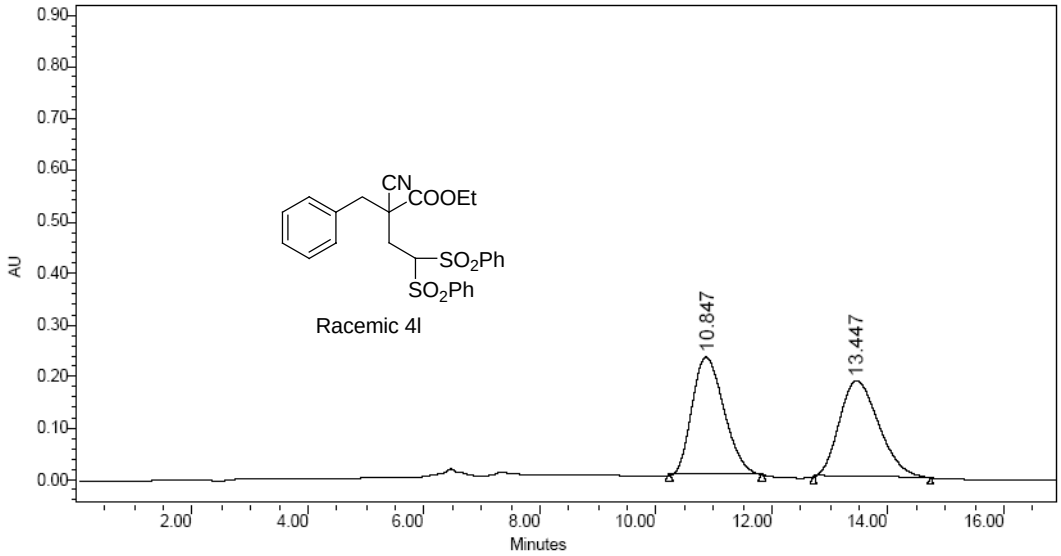
Capilary End Plate	-4500 V	Capilary Exit	120 V	detbias	2 V
EndP	-4000 V	Collision energy	0 eV	Number of Averages	100



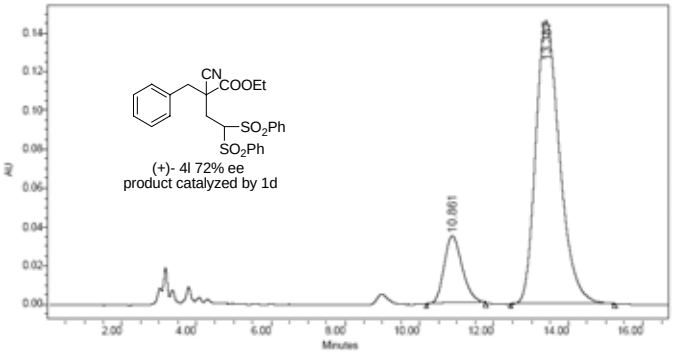
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdb	N Rule	e⁻
C 26 H 25 N 1 Na 1 O 6 S 2	0.01	534.1016	-1.72	-1.34	14.50	ok	even



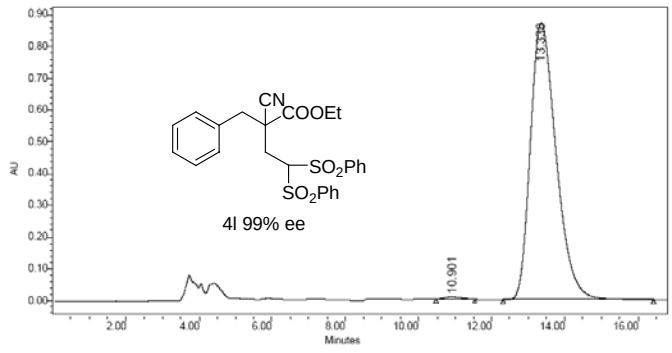
4l



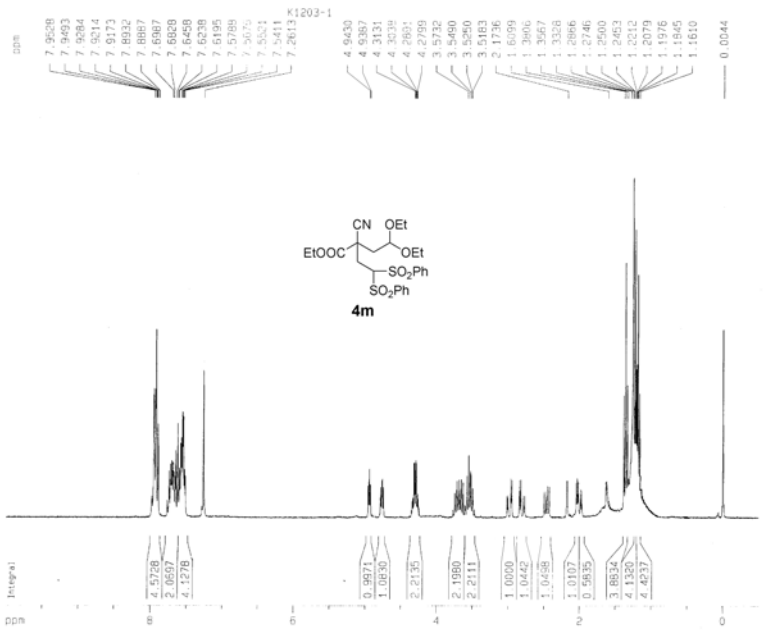
	RT (min)	Area (μV *sec)	% Area	Height (μV)	% Height
1	10.847	8854765	50.00	228995	55.15
2	13.447	8854782	50.00	186251	44.85

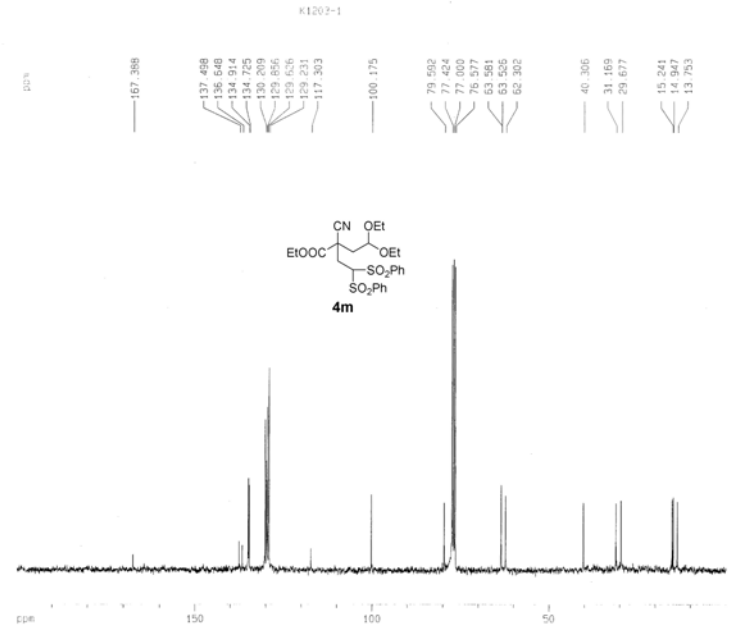


	RT (min)	Area (μV *sec)	% Area	Height (μV)	% Height
1	10.861	1064955	13.91	33469	18.61
2	13.387	6592160	86.09	146407	81.39



	RT (min)	Area (μV *sec)	% Area	Height (μV)	% Height
1	10.901	52516	0.12	2929	0.33
2	13.338	42843418	99.88	874669	99.67


K1203-1
CN OEt
EtOOC OEt
SO2Ph
SO2Ph
4m


K1203-1
CN OEt
EtOOC OEt
SO2Ph
SO2Ph
4m

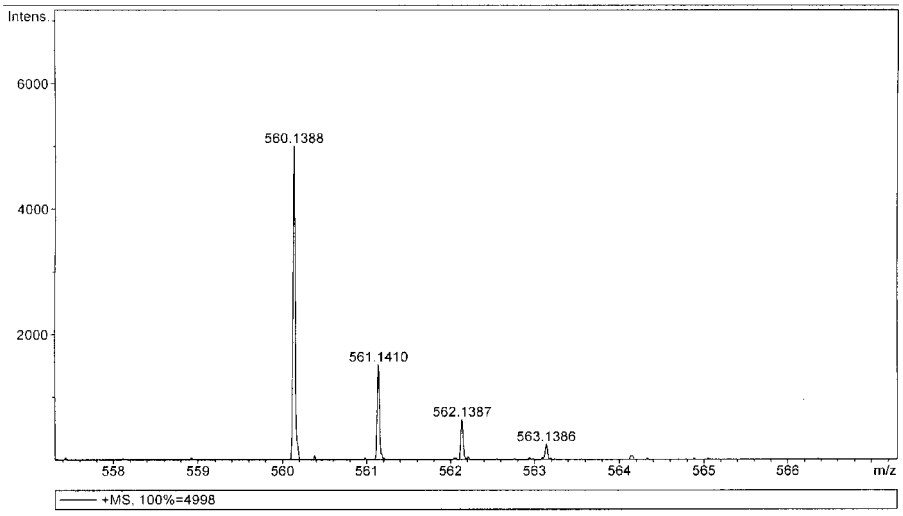
Mass Spectrum Molecular Formular Report

Analysis Info

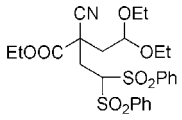
Analysis Name	D:\Bruker\data\msdata\LRM05018n\1.d	Acquisition Date	1/5/2006 5:09:37 PM
Method	1pass_pos_low.tofpar	Operator	operator name
Sample Name	LRM05018n	Instrument	BioTOF Q
Comment	ESI Source		

Acquisition Parameter

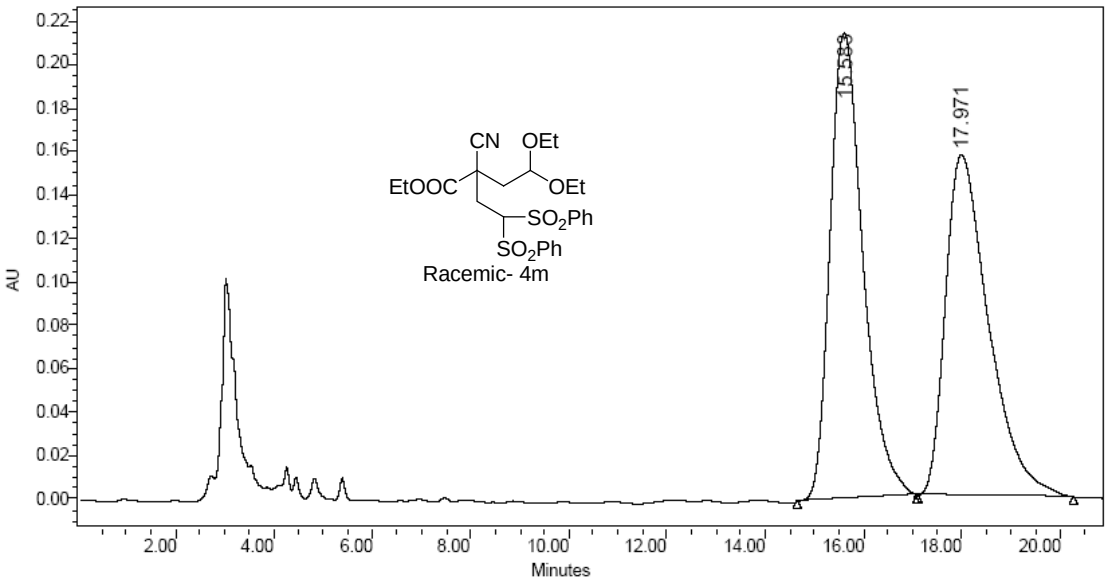
Capilary End Plate	-4500 V	Capilary Exit	120 V	detbias	2 V
EndP	-4000 V	Collision energy	0 eV	Number of Averages	100



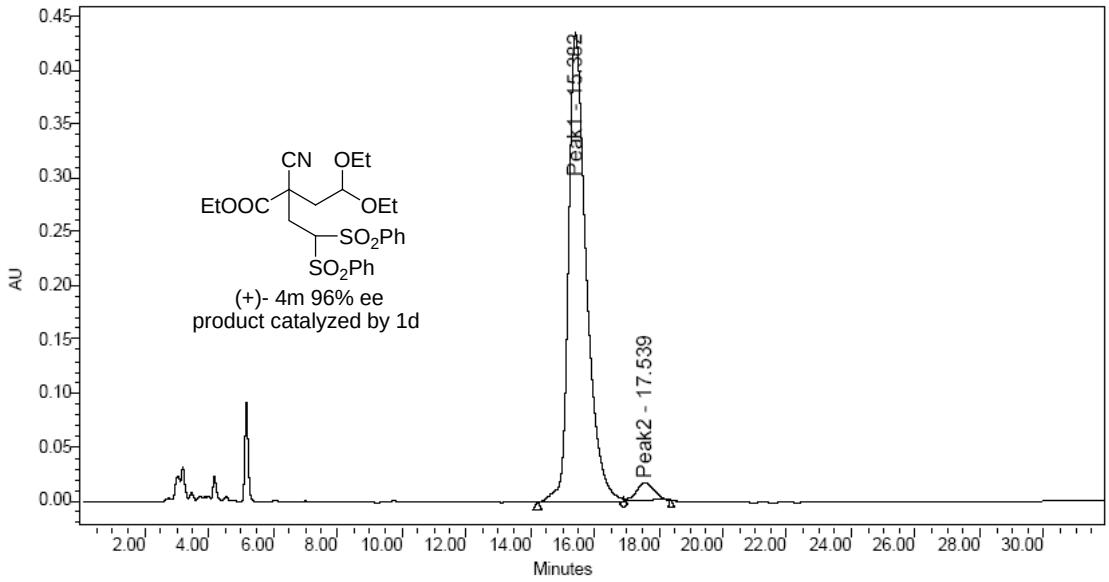
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdb	N Rule	e⁻
C 25 H 31 N 1 Na 1 O 8 S 2	0.01	560.1383	-0.76	-0.40	10.50	ok	even



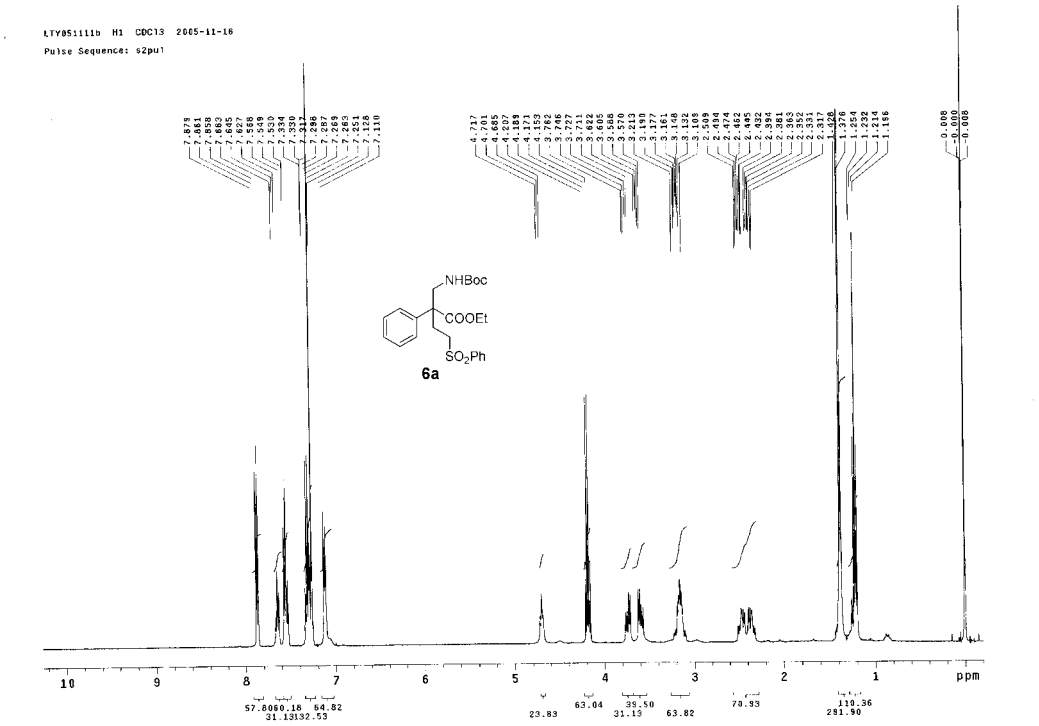
4m

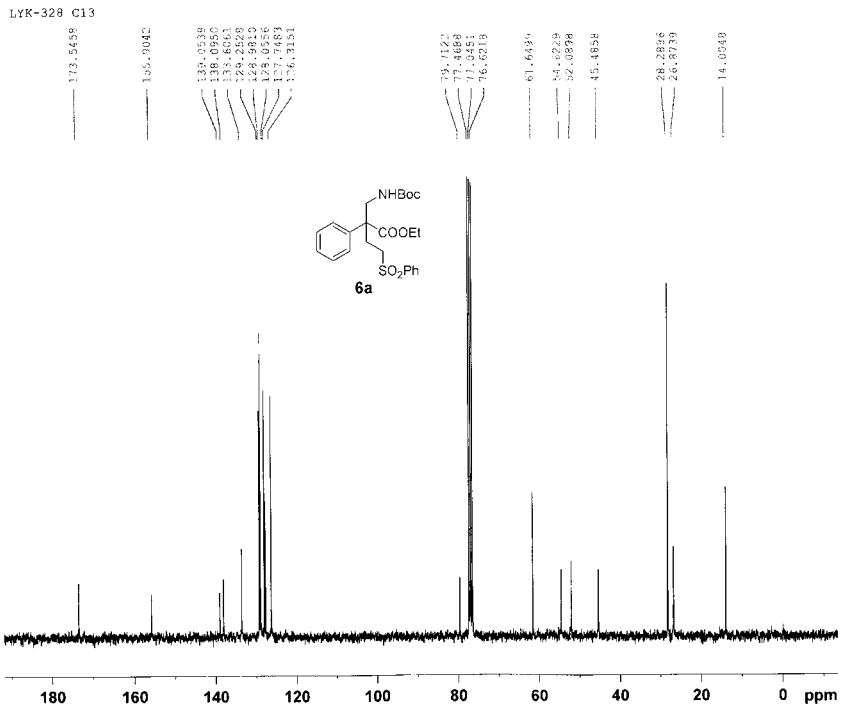


	RT (min)	Area (μV *sec)	% Area	Height (μV)	% Height
1	15.583	9651553	50.11	212196	57.45
2	17.971	9607703	49.89	157192	42.55



	RT (min)	Area (μV *sec)	% Area	Height (μV)	% Height
1	15.382	16558104	97.74	434325	97.11
2	17.539	382075	2.26	12941	2.89





BRUKER

```
Current Data Parameters
NAME        LYK-328  C13
EXPNO               1
PROCNO              1

F2 - Acquisition Parameters
Date_          20051207
Time              15.35
INSTRUM           av300
PROBHD  5 mm PABBO BB-
PULPROG        zgdc30
TD              65536
SOLVENT          CDCl3
NS                 424
DS                  16
SWH         18832.393 Hz
FIDRES       0.287360 Hz
AQ           1.7400308 sec
RG              9195.2
DW             26.550 usec
DE              6.00 usec
TE             293.9 K
D1          1.00000000 sec
d11         0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1              13C
P1               6.00 usec
PL1             -6.00 dB
SFO1      75.4752960 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2              1H
PCPD2           80.00 usec
PL2             -5.00 dB
PL12            16.00 dB
SFO2     300.1314410 MHz

F2 - Processing parameters
SI                32768
SF        75.4677490 MHz
WDW               EM
SSB                0
LB              2.00 Hz
GB                 0
PC              1.40
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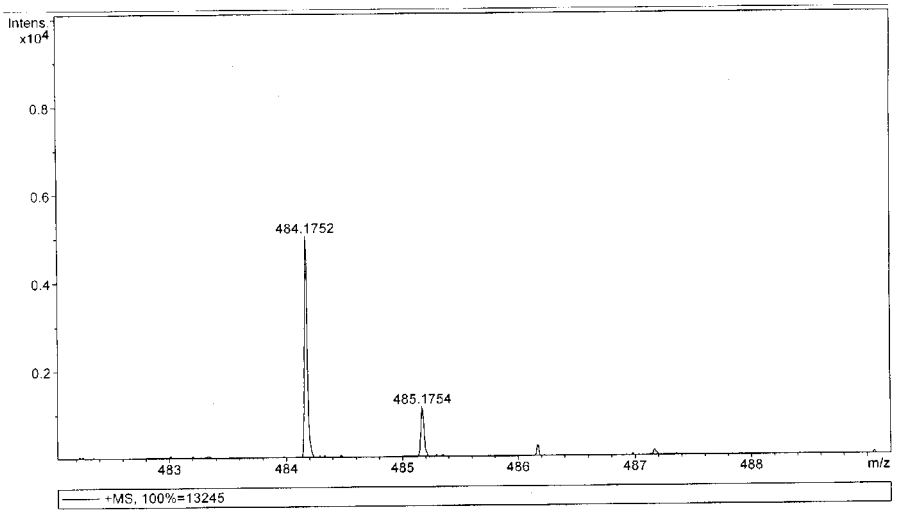
Mass Spectrum Molecular Formular Report

Analysis Info

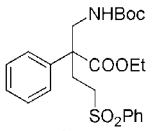
Analysis Name	D:\Bruker\data\msdata\LRM05014\1.d	Acquisition Date	12/9/2005 2:28:36 PM
Method	1pass_pos_low.tofpar	Operator	operator name
Sample Name	LRM05014	Instrument	BioTOF Q
Comment	ESI Source		

Acquisition Parameter

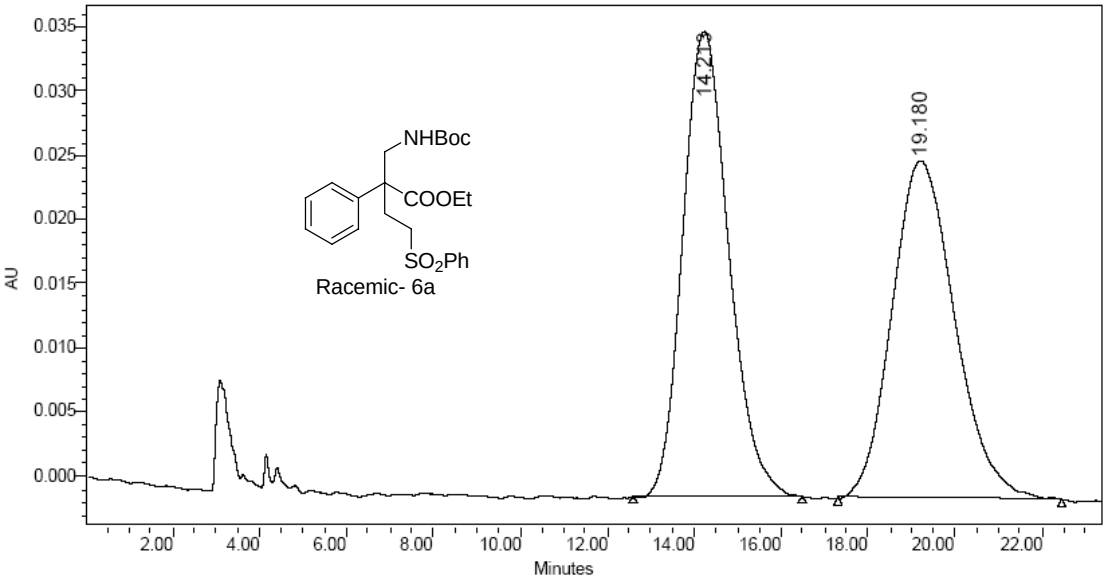
Capilary End Plate	-4500 V	Capilary Exit	120 V	detbias	2 V
EndP	-4000 V	Collision energy	0 eV	Number of Averages	100



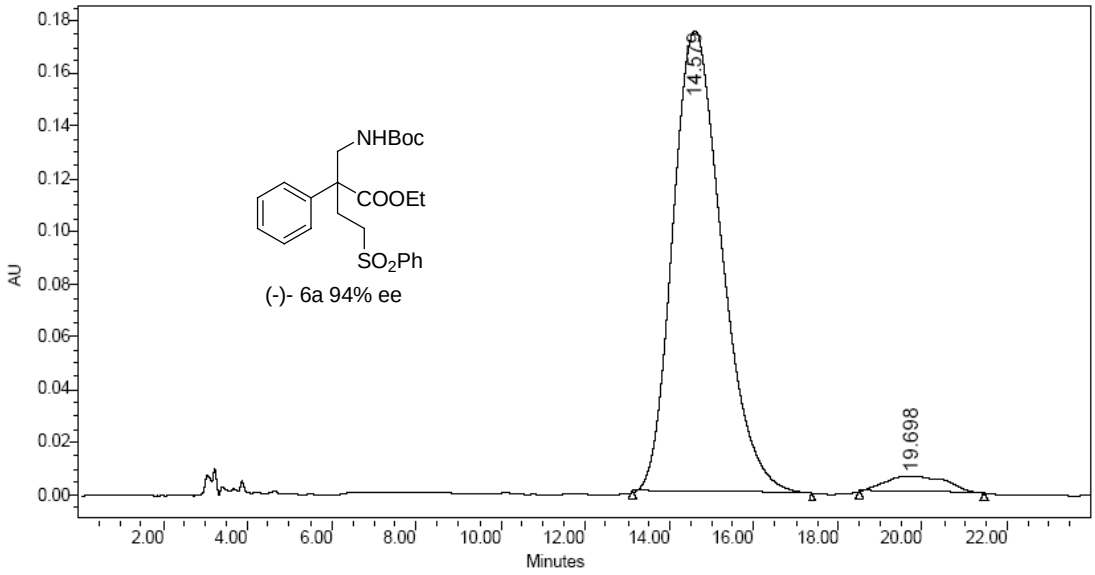
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdb	N Rule	e⁻
C 24 H 31 N 1 Na 1 O 6 S 1	0.05	484.1764	2.50	3.43	9.50	ok	even



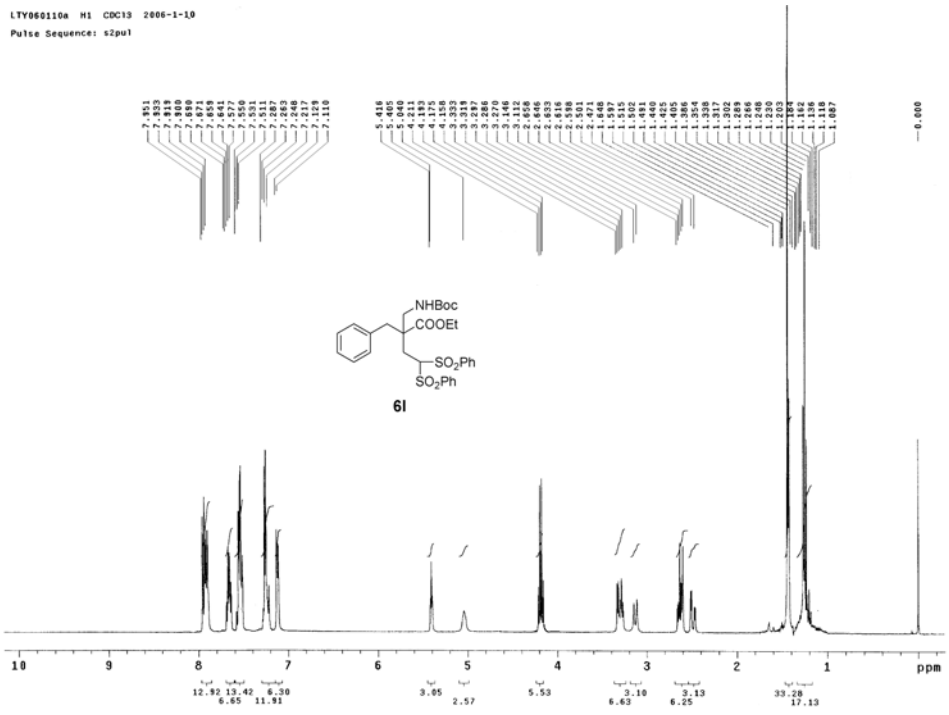
6a

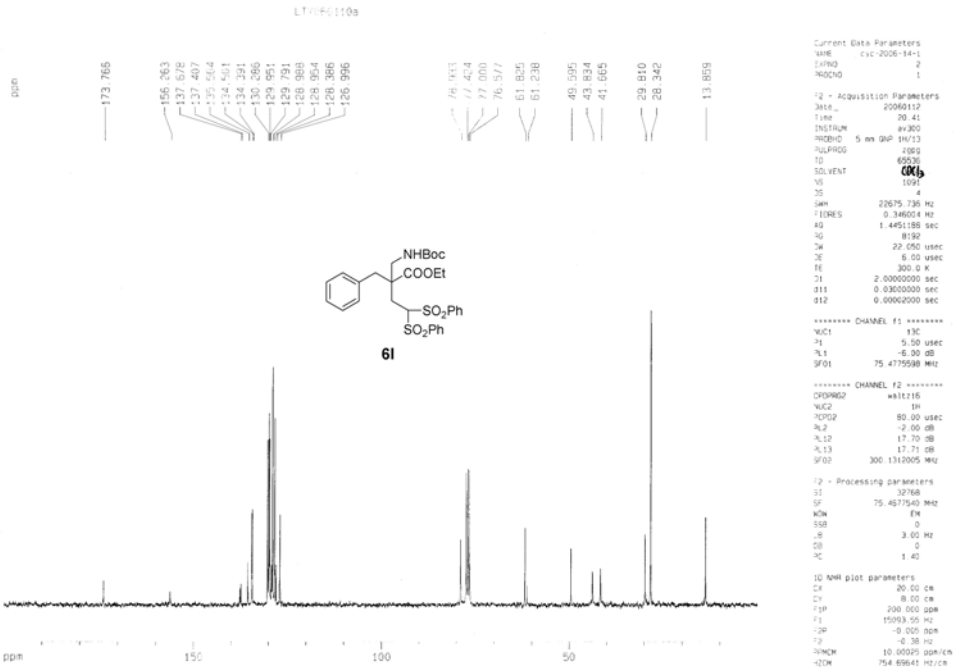


	RT (min)	Area (µV *sec)	% Area	Height (µV)	% Height
1	14.213	2673278	50.24	36286	57.95
2	19.180	2647313	49.76	26331	42.05



	RT (min)	Area (µV *sec)	% Area	Height (µV)	% Height
1	14.579	14375280	97.09	175685	97.36
2	19.698	430480	2.91	4757	2.64


LTY060110a H1 CDCl3 2006-1-10
Pulse Sequence: s2pul
NHBoc
COOEt
SO2Ph
SO2Ph
6l
ppm


NHBoc
COOEt
SO2Ph
SO2Ph
6l
ppm

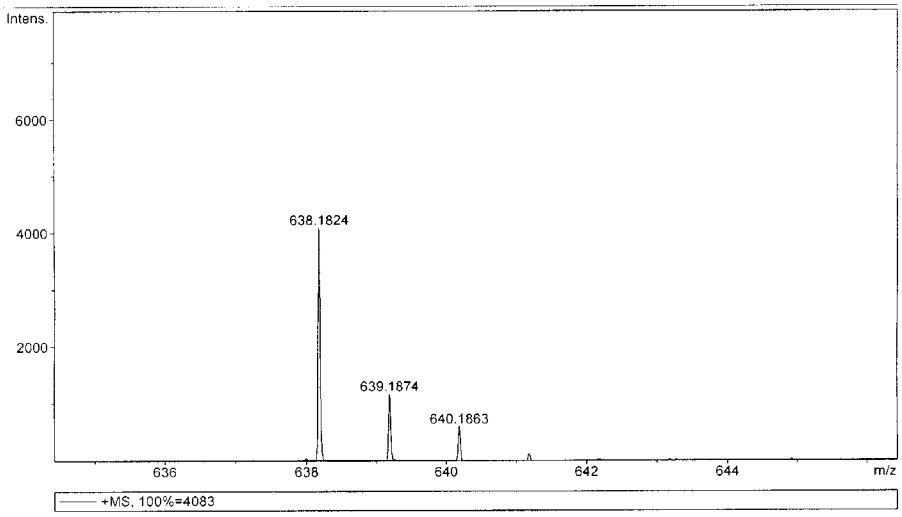
Mass Spectrum Molecular Formular Report

Analysis Info

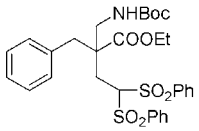
Analysis Name	D:\Bruker\data\msdata\LRM05017n\2.d	Acquisition Date	1/5/2006 5:20:27 PM
Method	1pass_pos_low.tofpar	Operator	operator name
Sample Name	LRM05017n	Instrument	BioTOF Q
Comment	ESI Source		

Acquisition Parameter

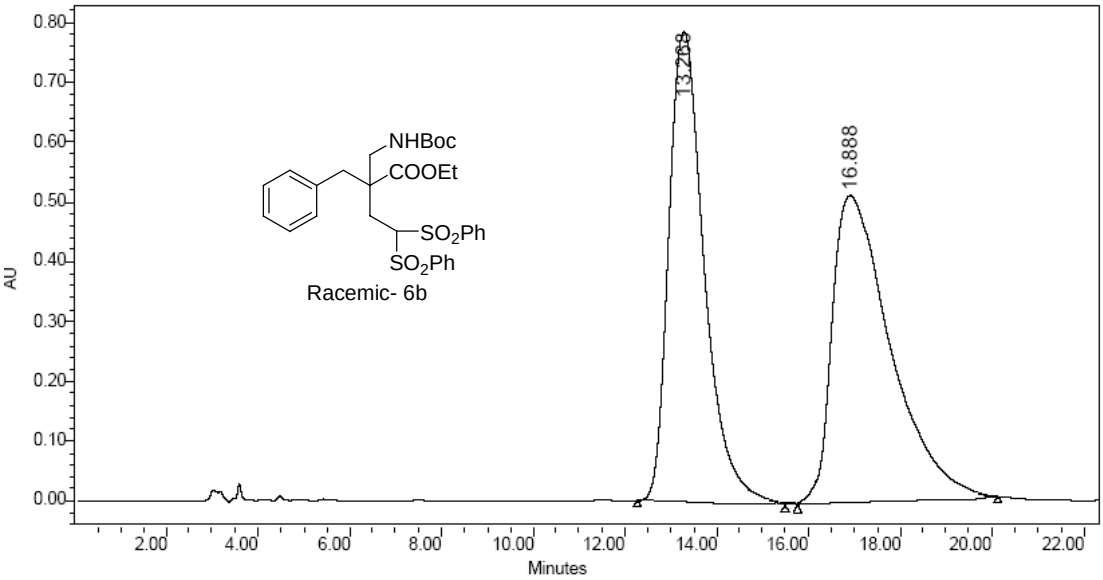
Capilary End Plate	-4500 V	Capilary Exit	120 V	detbias	2 V
EndP	-4000 V	Collision energy	0 eV	Number of Averages	100



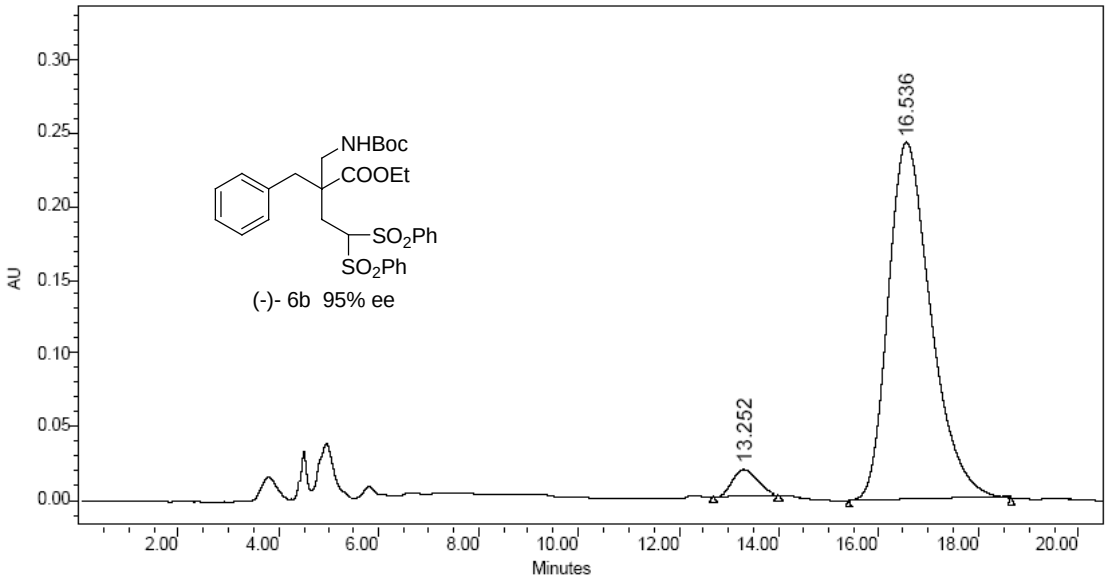
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdb	N Rule	e⁻
C 31 H 37 N 1 Na 1 O 8 S 2	0.04	638.1853	4.58	3.34	13.50	ok	even



6l



	RT (min)	Area (□V *sec)	% Area	Height (□V)	% Height
1	13.268	40722761	49.88	779946	61.66
2	16.888	40916406	50.12	485057	38.34



	RT (min)	Area (□V *sec)	% Area	Height (□V)	% Height
1	13.252	416978	2.79	14742	5.70
2	16.536	14525376	97.21	243814	94.30