Electronic Supplementary Material for Chemical Communications

Supporting Information

Highly Enantio- and Diastereoselective Organocatalytic Cascade aza-Michael-Michael Reactions: A Direct Method for the Synthesis of Trisubstituted Chiral Pyrrolidines

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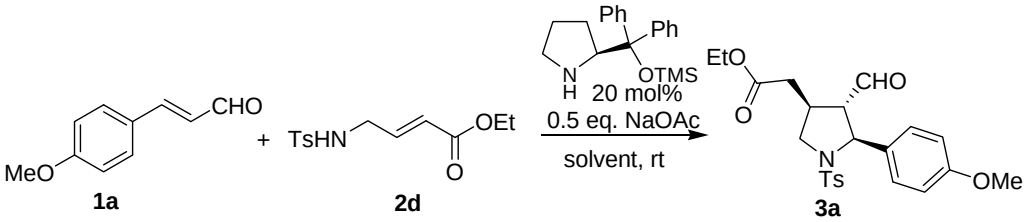
General Information: Commercial reagents were used as received, unless otherwise stated. Merck 60 silica gel was used for chromatography, and Whatman silica gel plates with fluorescence F_{254} were used for thin-layer chromatography (TLC) analysis. ^{1}H and ^{13}C NMR spectra were recorded on Broker Avance 500, and tetramethylsilane (TMS) was used as a reference. Data for ^{1}H are reported as follows: chemical shift (ppm), and multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Data for ^{13}C NMR are reported as ppm.

General Procedure for addition of 4-(4-methylphenylsulfonamido)but-2-enoic acid ethyl ester to unsaturated aldehydes: To a solution of *trans*-4-methoxycinnamaldehyde **1a** (32 mg, 0.2 mmol) in the presence of catalyst **(**10 mol %) and NaOAc (8.2 mg, 0.1 mmol) in $CHCl_3$ (0.5 mL) was added (*E*)-ethyl 4-(4-methylphenylsulfonamido)but-2-enoate **2d** (28 mg, 0.1 mmol) and the resulting solution was stirred for 4 d at rt. The reaction mixture was directly purified by silica gel chromatography (EtOAc/Hexane = 4:1) and fractions were collected and concentrated *in vacuo* to give a colorless oil (92% yield), >30:1 dr (determined by ^{1}H NMR analysis), (HPLC Daicel CHIRALCEL OD-H column, Hexane/*i*PrOH = 80:20 at 0.5 mL min^{-1}, λ = 235 nm); t_{major} = 41.61 min, ee = >99%.

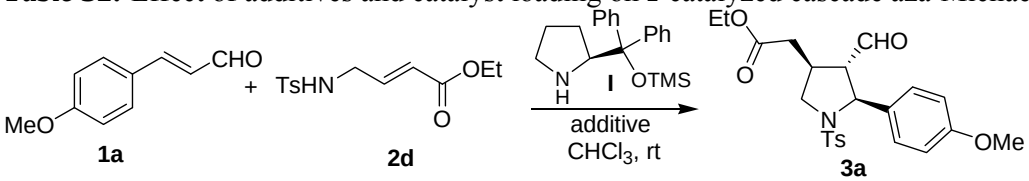
Table S1: Solvent effect on **I**-catalyzed cascade aza-Michael-Michael reactions.



1a **2d** **3a**

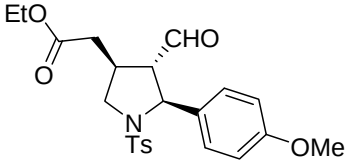
Entry	Solvent	t	Yield (%)	ee (%)	dr
1	CH_2Cl_2	3 d	83	93	15:1
2	$CHCl_3$	3 d	91	>99	>30:1
3	$ClCH_2CH_2Cl$	3 d	78	93	25:1
4	toluene	16 h	90	92	16:1
5	EtOH	1 d	72	93	20:1

Table S2: Effect of additives and catalyst loading on **I**-catalyzed cascade aza-Michael-Michael reactions.

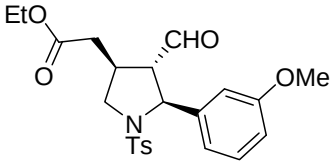


1a **2d** **3a**

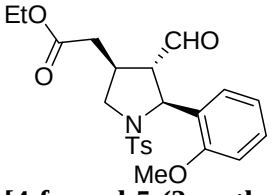
Entry	Catalyst loading	Additive	t	Yield (%)	ee (%)	dr
1	20 mol%	0.5 eq. NaOAc	3 d	91	>99	>30:1
2	20 mol%	0.5 eq. LiOAc	3 d	86	94	20:1
3	20 mol%	0.5 eq. K_2CO_3	3 d	75	>99	>30:1
4	20 mol%	0.5 eq. Cs_2CO_3	3 d	<10	nd	nd
5	20 mol%	0.5 eq. Na_2CO_3	2 d	86	>99	>30:1
6	20 mol%	none	3 d	85	94	20:1
7	20 mol%	0.2 eq. $PhCO_2H$	1 d	82	94	8:1
8	10 mol%	0.5 eq. NaOAc	4 d	85	>99	15:1
9	**10 mol%**	**1.0 eq. NaOAc**	**4 d**	**92**	**>99**	**>30:1**
10	5 mol%	0.5 eq. NaOAc	7 d	82	>99	12:1



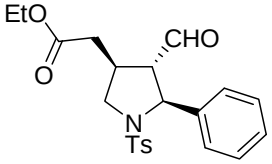
Ethyl 2-(4-formyl-5-(4-methoxyphenyl)-1-tosylpyrrolidin-3-yl)acetate (3a): Yield: 92%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.47 (s, 1H), 7.61 (d, 2H, *J* = 8.0 Hz), 7.28 (d, 2H, *J* = 8.0 Hz), 7.21 (d, 2H, *J* = 8.0 Hz), 6.83 (d, 2H, *J* = 8.0 Hz), 4.89 (d, 1H, *J* = 7.5 Hz), 4.10 (q, 2H, *J* = 7.0 Hz), 3.97 (dd, 1H, J_1 = 7.5 Hz, J_2 = 11.0 Hz), 3.79 (s, 3H), 3.34 (t, 1H, *J* = 9.0 Hz), 2.78 (t, 1H, *J* = 7.5 Hz), 2.41-2.48 (m, 6H), 1.23 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.2, 170.9, 159.2, 143.8, 134.7, 132.5, 129.7, 127.55, 127.50, 114.1, 65.8, 63.1, 60.9, 55.3, 54.0, 36.1, 35.9, 21.5, 14.1; HRMS: calcd for $[M+H^+]$ $C_{23}H_{27}NO_6S$ 446.1637, found 446.1634; $[\alpha]_D^{23}$ = - 111.5 (c = 2.0, $CHCl_3$); Converted to enone with PPh_3=CHCOPh for HPLC analysis (Daicel CHIRALPAK AD, Hexane/*i*PrOH = 70:30, flow rate 0.6 mL min^{-1}, λ = 254 nm): t_{major} = 20.10 min, ee = >99%.



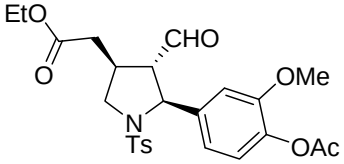
Ethyl 2-(4-formyl-5-(3-methoxyphenyl)-1-tosylpyrrolidin-3-yl)acetate (3b): Yield: 91%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.48 (s, 1H), 7.64 (d, 2H, *J* = 8.0 Hz), 7.28 (d, 2H, *J* = 8.0 Hz), 7.22 (t, 1H, *J* = 8.0 Hz), 6.87 (d, 1H, *J* = 7.5 Hz), 6.81 (s, 1H), 6.79 (d, 1H, *J* = 8.5 Hz), 4.96 (d, 1H, *J* = 7.0 Hz), 4.09 (q, 2H, *J* = 7.0 Hz), 3.99 (dd, 1H, J_1 = 6.0 Hz, J_2 = 11.0 Hz), 3.77 (s, 3H), 3.34 (dd, 1H, J_1 = 8.0 Hz, J_2 = 11.0 Hz), 2.78 (t, 1H, *J* = 7.5 Hz), 2.38-2.47 (m, 6H), 1.22 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.1, 170.9, 159.9, 143.9, 142.4, 134.7, 129.9, 129.7, 129.6, 127.5, 118.4, 113.1, 111.9, 65.7, 63.2, 60.9, 55.2, 54.1, 36.12, 36.09, 21.5, 14.1; HRMS: calcd for $[M+H^+]$ $C_{23}H_{27}NO_6S$ 446.1637, found 446.1633; $[\alpha]_D^{23}$ = - 111.5 (c = 2.0, $CHCl_3$); $[\alpha]_D^{23}$ = - 138.6 (*c* = 1.8, $CHCl_3$); Converted to enone with PPh_3=CHCOPh for HPLC analysis (Daicel CHIRALPAK AD, Hexane/*i*PrOH = 70:30, flow rate 0.6 mL min^{-1}, λ = 254 nm): t_{major} = 16.13 min, ee = >99%.



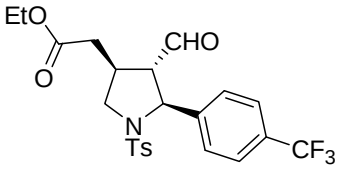
[4-formyl-5-(2-methoxy-phenyl)-1-(toluene-4-sulfonyl)-pyrrolidin-3-yl]-acetic acid ethyl ester (3c). The title compound was prepared according to the general procedure, as described above in 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$): 9.44 (d, 1H; *J* = 1.0 Hz), 6.83-7.69 (m, 8H; Ar), 5.25 (d, 1H; *J* = 6.5 Hz), 4.08 (m, 3H), 3.75 (s, 3H), 3.27 (m, 1H), 2.54 (m, 1H), 2.44 (s, 3H), 2.37 (m, 1H), 2.25 (m, 2H), 1.24 (t, 3H; *J* = 4.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.3, 170.9, 155.5, 143.8, 135.0, 129.8, 129.5, 128.5, 127.6, 127.5, 126.7, 120.9, 110.3, 64.0, 60.8, 60.0, 54.8, 54.1, 36.3, 35.7, 21.5, 14.1; HRMS: calcd for $[M+H^+]$ $C_{23}H_{27}NO_6S$ 446.1637, found 446.1629; $[\alpha]_D^{23}$ = - 111.5 (c = 2.0, $CHCl_3$); Reduced to the alcohol for HPLC analysis: Chiralpak OJ-H, *i*PrOH/hexanes = 30/70, flow rate = 0.7 mL min^{-1}, λ = 254 nm): t_{major} = 21.875 min, t_{minor} = 16.342 min, ee = 96%.



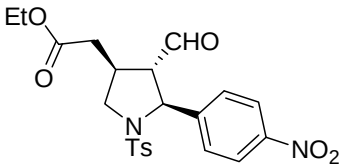
Ethyl 2-(4-formyl-5-phenyl-1-tosylpyrrolidin-3-yl)acetate (3d): Yield: 94%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.47 (s, 1H), 7.63 (d, 2H, J = 8.0 Hz), 7.26-7.30 (m, 7H), 4.98 (d, 1H, J = 7.5 Hz), 4.09 (q, 2H, J = 7.0 Hz), 3.98 (dd, 1H, J_1 = 6.0 Hz, J_2 = 11.0 Hz), 3.35 (dd, 1H, J_1 = 8.0 Hz, J_2 = 11.0 Hz), 2.79 (t, 1H, J = 7.0 Hz), 2.38-2.47 (m, 6H), 1.22 (t, 3H, J = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.1, 170.9, 143.9, 140.7, 134.6, 129.7, 128.7, 127.8, 127.5, 126.2, 65.8, 63.3, 60.9, 54.1, 36.1, 21.5, 14.1; HRMS: calcd for [M+H$^+$] $C_{22}H_{25}NO_5S$ 416.1531, found 416.1533; $[\alpha]_D^{23}$ = - 111.5 (c = 2.0, $CHCl_3$); $[\alpha]_D^{23}$ = - 180.8 (c = 0.4, $CHCl_3$); HPLC (Daicel CHIRALCEL OD-H), Hexane/*i*PrOH = 85:15, flow rate 0.6 mL min^{-1}, λ = 254 nm); t_{major} = 26.73 min, t_{minor} = 31.99 min, ee = >99%.



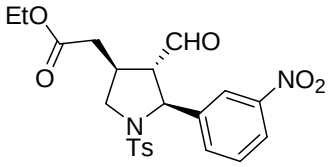
Ethyl 2-(4-formyl-5-(4-acetoxy-3-methoxyphenyl)-1-tosylpyrrolidin-3-yl)acetate (3e): Yield: 88%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.49 (s, 1H), 7.62 (d, 2H, J = 8.0 Hz), 7.29 (d, 2H, J = 8.0 Hz), 6.95 (d, 1H, J = 8.0 Hz), 6.87 (s, 1H), 6.84 (d, 1H, J = 8.0 Hz), 5.03 (d, 1H, J = 7.0 Hz), 4.10 (q, 2H, J = 7.0 Hz), 4.02 (dd, 1H, J_1 = 6.5 Hz, J_2 = 11.0 Hz), 3.77 (s, 3H), 3.32 (dd, 1H, J_1 = 9.0 Hz, J_2 = 10.5 Hz), 2.80 (t, 1H, J = 6.5 Hz), 2.39-2.49 (m, 6H), 2.30 (s, 3H), 1.23 (t, 3H, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.1, 170.9, 168.9, 151.2, 144.0, 139.6, 139.2, 134.8, 129.8, 127.5, 122.9, 118.2, 110.2, 65.5, 62.8, 61.0, 55.8, 54.0, 36.3, 36.0, 21.5, 20.6, 14.1; HRMS: calcd for [M+H$^+$] $C_{25}H_{29}NO_8S$ 504.1692, found 504.1678; $[\alpha]_D^{23}$ = - 84.2 (c = 2.0, $CHCl_3$); Converted to enone with PPh_3=CHCOPh for HPLC analysis (Daicel CHIRALPAK AD, Hexane/*i*PrOH = 70:30, flow rate 0.6 mL min^{-1}, λ = 254 nm): t_{major} = 13.32 min, t_{minor} = 28.53 min, ee = 96%.



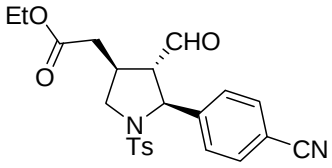
Ethyl 2-(4-formyl-1-tosyl-5-(4-(trifluoromethyl)phenyl)pyrrolidin-3-yl)acetate (3f): Yield: 92%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.49 (s, 1H), 7.63 (d, 2H, J = 8.0 Hz), 7.56 (d, 2H, J = 8.0 Hz), 7.43 (d, 2H, J = 8.0 Hz), 7.29 (d, 2H, J = 8.0 Hz), 5.05 (d, 1H, J = 7.0 Hz), 4.09 (q, 2H, J = 7.0 Hz), 3.96 (dd, 1H, J_1 = 5.5 Hz, J_2 = 12.0 Hz), 3.38 (t, 1H, J = 7.5 Hz), 2.78 (t, 1H), 2.35-2.48 (m, 6H), 1.22 (t, 3H, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.5, 170.8, 144.9, 144.3, 134.2, 129.8, 127.6, 126.6, 125.8, 65.6, 62.6, 61.0, 54.1, 36.2, 36.0, 21.5, 14.1; HRMS: calcd for [M+H$^+$] $C_{23}H_{24}F_3NO_5S$ 484.1405, found 484.1421; $[\alpha]_D^{23}$ = - 95.1 (c = 2.0, $CHCl_3$); HPLC (Daicel CHIRALCEL OD-H, Hexane/*i*PrOH = 85:15, flow rate 0.5 mL min^{-1}, λ = 235 nm); t_{major} = 36.82 min, ee = >99%.



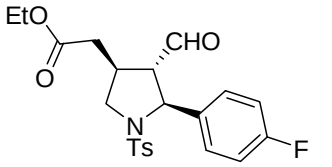
Ethyl 2-(4-formyl-5-(4-nitrophenyl)-1-tosylpyrrolidin-3-yl)acetate (3g): Yield: 85%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.50 (s, 1H), 8.17 (d, 2H, *J* = 8.5 Hz), 7.67 (d, 2H, *J* = 7.5 Hz), 7.52 (d, 2H, *J* = 8.5 Hz), 7.34 (d, 2H, *J* = 8.0 Hz), 5.09 (d, 1H, *J* = 7.0 Hz), 4.10 (q, 2H, *J* = 7.0 Hz), 3.92 (dd, 1H, J_1 = 7.0 Hz, J_2 = 11.5 Hz), 3.40 (dd, 1H, J_1 = 8.5 Hz, J_2 = 11.0 Hz), 2.79 (t, 1H, *J* = 7.0 Hz), 2.41-2.45 (m, 6H), 1.22 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.2, 170.7, 148.4, 147.4, 144.5, 133.8, 130.0, 129.8, 127.8, 127.6, 127.2, 124.0, 123.9, 65.3, 62.3, 61.1, 54.1, 36.3, 36.0, 29.7, 21.6, 14.1; HRMS: calcd for [M+H$^+$] $C_{22}H_{24}N_2O_7S$ 461.1382, found 461.1376; $[\alpha]_D^{23}$ = - 139.2 (*c* = 0.6, $CHCl_3$); HPLC (Daicel CHIRALCEL OD-H, Hexane/*i*PrOH = 85:15, flow rate 0.5 mL min^{-1}, λ = 254 nm); t_{major} = 66.56 min, ee = >99%.



Ethyl 2-(4-formyl-5-(3-nitrophenyl)-1-tosylpyrrolidin-3-yl)acetate (3h): Yield: 80%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.53 (s, 1H), 8.12 (d, 1H, *J* = 8.5 Hz), 8.09 (s, 1H), 7.70 (d, 1H, *J* = 7.5 Hz), 7.64 (d, 2H, *J* = 8.0 Hz), 7.52 (t, 1H, *J* = 8.0 Hz), 7.31 (d, 1H, *J* = 8.0 Hz), 5.08 (d, 1H, *J* = 7.5 Hz), 4.11 (q, 2H, *J* = 7.0 Hz), 3.99 (m, 1H), 3.42 (dd, 1H, J_1 = 8.0 Hz, J_2 = 11.0 Hz), 2.81 (t, 1H, *J* = 7.0 Hz), 2.42-2.49 (m, 6H), 1.23 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.2, 170.7, 148.5, 144.5, 143.1, 134.1, 132.7, 130.0, 129.8, 127.6, 122.9, 121.3, 65.5, 62.3, 61.1, 60.8, 54.1, 36.4, 36.0, 21.5, 14.1; HRMS: calcd for [M+H$^+$] $C_{22}H_{24}N_2O_7S$ 461.1382, found 461.1389; $[\alpha]_D^{23}$ = - 199.6 (*c* = 0.5, $CHCl_3$); HPLC (Daicel CHIRALCEL OD-H, Hexane/*i*PrOH = 85:15, flow rate 0.5 mL min^{-1}, λ = 254 nm); t_{major} = 52.15 min, ee = >99%.

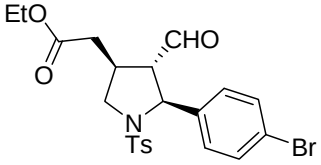


Ethyl 2-(5-(4-cyanophenyl)-4-formyl-1-tosylpyrrolidin-3-yl)acetate (3i): Yield: 89%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.48 (s, 1H), 7.65 (d, 2H, *J* = 8.0 Hz), 7.61 (d, 2H, *J* = 8.0 Hz), 7.45 (d, 2H, *J* = 8.0 Hz), 7.33 (d, 2H, *J* = 8.0 Hz), 5.04 (d, 1H, *J* = 7.0 Hz), 4.09 (q, 2H, *J* = 7.0 Hz), 3.91 (dd, 1H, J_1 = 6.0 Hz, J_2 = 11.0 Hz), 3.37 (dd, 1H, J_1 = 8.0 Hz, J_2 = 11.0 Hz), 2.76 (t, 1H, *J* = 6.5 Hz), 2.41-2.45 (m, 6H), 1.22 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.3, 170.7, 146.4, 144.4, 133.7, 132.5, 129.9, 127.5, 127.0, 118.4, 111.5, 65.2, 62.5, 61.0, 54.0, 36.3, 35.9, 21.5,14.0; HRMS: calcd for [M+H$^+$] $C_{23}H_{24}N_2O_5S$ 441.1484, found 441.1468; $[\alpha]_D^{23}$ = - 64.7 (*c* = 1.0, $CHCl_3$); HPLC (Daicel CHIRALPAC AD, Hexane/*i*PrOH = 60:40, flow rate 0.6 mL min^{-1}, λ = 254 nm); t_{major} = 15.94 min, ee = >99%.



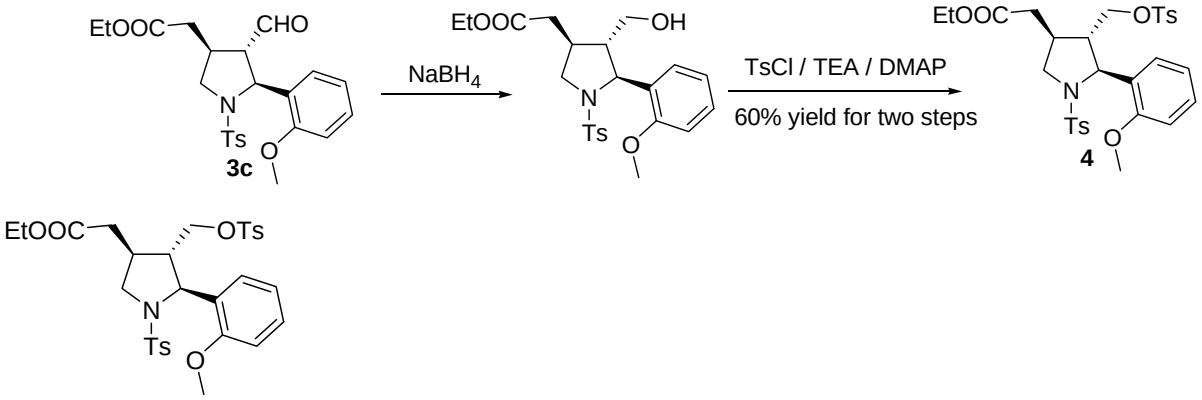
Ethyl 2-(5-(4-fluorophenyl)-4-formyl-1-tosylpyrrolidin-3-yl)acetate (3j): Yield: 85%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.47 (s, 1H), 7.73 (d, 2H, *J* = 7.5 Hz), 7.30 (d, 2H, *J* = 8.5 Hz), 7.27 (m, 2H), 6.99 (d, 2H, *J* = 8.0 Hz), 4.94 (d, 1H, *J* = 7.0 Hz), 4.09 (q, 2H, *J* = 7.0 Hz), 3.96 (dd, 1H, J_1 = 6.0 Hz, J_2 = 11.5 Hz), 3.35 (dd, 1H, J_1 = 8.0 Hz, J_2 = 11.0 Hz), 2.77 (t, 1H, *J* = 6.5 Hz), 2.40-2.48 (m, 6H), 1.22 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.9, 170.8, 163.2, 161.2, 144.1, 136.5, 134.4, 129.8, 128.02, 127.96, 127.5, 115.7, 115.5, 65.8, 62.7, 61.0, 54.0, 36.07, 36.03, 21.5, 14.1; HRMS: calcd for [M+H$^+$] $C_{22}H_{24}FNO_5S$ 434.1437, found 434.1442; $[\alpha]_D^{23}$ = - 114.0 (*c* = 2.0, $CHCl_3$); Converted to enone with

PPh_3=CHCOPh for HPLC analysis (Daicel CHIRALPAK AD, Hexane/*i*PrOH = 70:30, flow rate 0.6 mL min^{-1}, λ = 254 nm): t_{major} = 14.66 min, ee = >99%.



Ethyl 2-(5-(4-bromophenyl)-4-formyl-1-tosylpyrrolidin-3-yl)acetate (3k): Yield: 90%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.47 (s, 1H), 7.62 (d, 2H, *J* = 8.0 Hz), 7.42 (d, 2H, *J* = 8.0 Hz), 7.30 (d, 2H, *J* = 8.0 Hz), 7.18 (d, 2H, *J* = 8.0 Hz), 4.92 (d, 1H, *J* = 7.5 Hz), 4.09 (q, 2H, *J* = 7.0 Hz), 3.94 (dd, 1H, J_1 = 6.0 Hz, J_2 = 11.5 Hz), 3.34 (dd, 1H, J_1 = 8.0 Hz, J_2 = 11.0 Hz), 2.75 (t, 1H, *J* = 6.5 Hz), 2.40-2.47 (m, 6H), 1.22 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.7, 170.8, 144.1, 139.9, 134.3, 131.8, 129.8, 128.0, 127.5, 121.7, 65.6, 62.7, 61.0, 54.0, 36.1, 21.5, 14.1; HRMS: calcd for [M+H$^+$] $C_{22}H_{24}BrNO_5S$ 494.0637, found 494.0621; $[\alpha]_D^{23}$ = - 169.1 (*c* = 1.5, $CHCl_3$); HPLC (Daicel CHIRALPAC AD, Hexane/*i*PrOH = 75:25, flow rate 0.6 mL min^{-1}, λ = 235 nm); t_{major} = 25.48 min, ee = >99%.

Synthesis of compound 4 for X-ray analysis:



[5-(2-methoxy-phenyl)-1-(toluene-4-sulfonyl)-4-(toluene-4-sulfonyloxym ethyl)-pyrrolidin- 3-yl]-acetic acid ethyl ester (4). Aldehyde **3c** (35 mg) in 0.5 mL methanol, cooled to 0 °C, was added $NaBH_4$ (2 eq.). The resulting mixture was stirred from 0℃ to rt for 10 min. Methanol was removed in vacuo, and the residue was dissolved in CH_2Cl_2, washed with water, dried with $MgSO_4$. After removal of CH_2Cl_2, the residue was redissolved in 0.5 mL CH_2Cl_2, cooled to 0 °C, then TsCl (1.1 eq.), TEA (1.1 eq.) and DMAP (0.1 eq.) were added. The mixture was stirred from 0℃ to RT for over night. The reaction mixture was loaded on to silica gel column directly, and the designed product was isolated with 60% yield (2 steps). ^{1}H NMR (500 MHz, $CDCl_3$): 7.65 (d, 2H; *J* = 7.5 Hz), 7.53 (d, 2H; *J* = 4.0 Hz), 7.31 (d, 2H; *J* = 7.5 Hz), 7.19-7.26 (m, 4H), 6.90 (t, 1H; *J* = 7.0 Hz), 6.71 (d, 1H; *J* = 8.0 Hz), 4.63 (d, 1H; *J* = 6.5 Hz), 4.01 (m, 2H), 3.93 (m, 2H), 3.73 (m, 1H), 3.62 (s, 3H), 3.30 (m, 1H), 2. 45 (s, 3H), 2.42 (s, 3H), 2.31 (m, 1H), 2.16 (m, 3H), 1.24 (t, 3H; *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.2, 156.3, 144.9, 143.3, 135.0, 132.7, 129.9, 129.5, 128.9, 128.8, 128.5, 127.8, 127.3, 120.8, 110.6, 68.4, 61.5, 60.7, 55.0, 53.8, 51.4, 36.7, 36.4, 29.7, 21.6, 21.5, 14.2; HRMS: calcd for [M+H$^+$] $C_{30}H_{35}NO_8S_2$ 602.1882, found 602.1853.

Crystallography Report

*Experimental for compound **4***

Several colorless plates were examined and cut into suitable pieces. The nicest piece was approximately 0.092 x 0.346 x 0.506 mm in size. It was mounted on a standard Bruker X8 Apex2 CCD-based X-ray

diffractometer equipped with an Oxford Cryostream 700 low temperature device and normal focus Mo-target X-ray tube (λ = 0.71073 Å) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 228(2) K; the detector was placed at a distance 5.00 cm from the crystal. A full sphere of data consisting of 4662 frames was collected with a scan width of 0.5°in ω and phi with an exposure time of 10 s/frame. The frames were integrated with the Bruker SAINT software package with a narrow frame algorithm. The integration of the data yielded a total of 137938 reflections to a maximum 2θ value of 63.22° Of these 20125 were independent. The final cell constants follow; these were based on the xyz centroids of 9758 reflections above 10σ(I).

CELL 8.4976 12.1259 29.9079 98.9097 98.1925 90.2571 3012.357

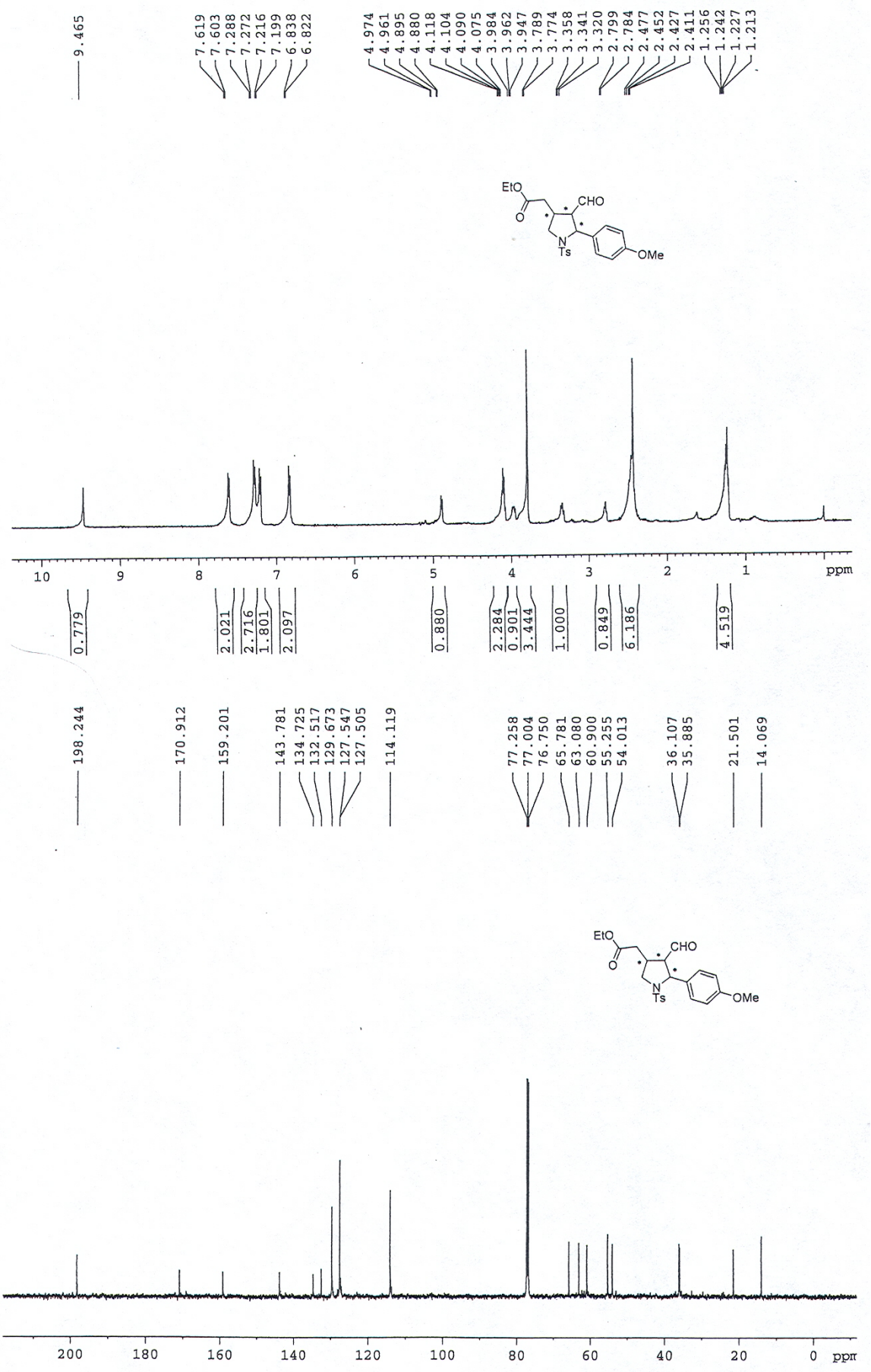
CELLSD 0.0006 0.0009 0.0022 0.0040 0.0038 0.0039 0.417

Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the chiral triclinic space group P1 with four independent molecules. There were refinement problems with one of the 4 unique molecules. The R-factors seemed higher than expected. A closer look at the data showed that an A lattice could be chosen instead of a P lattice with relatively small loss of data. This gave the cell as listed in Table 1. Refinement proceeds smoothly in this cell with two independent molecules in the unit cell. There are signs indicating unaccounted for twinning or missing atoms due to solvent disorder. These are seen in unusual U(eq) range, but mostly in the the large residual electron densities in final difference Fourier: the top 5 peaks are 2.50 e/Å^3 [1.97Å from H39], 2.45 [1.28 from H9], 2.06 [0.68 from C57],1.66 [0.63 from C27] and 0.95 [0.45 from H3]. Attempts to include twinning did not improve the R-factors. In fact the twin models gave higher R-factors. No reasonable solvent model could be found. The untreated data and model are presented here.

All non-hydrogen atoms were refined anisotropically. The carbon hydrogen atoms were included in ideal positions. Their isotropic U's were fixed, U=1.5Uequiv of parent atom for hydrogens on terminal groups and U=1.2Uequiv of parent atoms for others. The final model represents the absolute geometry of the molecule as determined by anomalous dispersion effects of S. The geometries of C1,C2,C3 of molecule 1 and C31,C32,C33 of molecule 2 are all S. The two independent molecules have the same basic geometric arrangement [see superpositioning of molecule 1 and 2]. There are close approaches of the type C-H—O,N. See possible hydrogen bonding table. There are also close approaches between O5—C28(x-1,y,z) at 2.991(4) Å and O13—C58(x-1,y,z) at 2.998(4) Å. The S-O(5,13)—C(28,58) angle averages to 119°, while the O(5,13)—C(28,58)-C(27,57) angle averages to 84.5° and the O(5,13)—C(28,58)-O(7,8/15,16) angles are almost 90°. Oxygen atoms O5 and O13 are sitting almost directly over the central C of the C-C(O)-O group of the molecules in the next cell along the a-axis. This may be an interaction as 3.0Å is less than the van der Waals radii of O and C [=3.22Å].

Table S1. Crystal data and structure refinement for compound 4.

Empirical formula	$C_{30}H_{35}NO_8S_2$	
Formula weight	601.71	
Temperature	228(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 8.4976(6) Å	α= 75.768(3)°.
	b = 12.1259(9) Å	β= 81.860(4)°.
	c = 15.2413(12) Å	γ = 89.743(4)°.
Volume	1506.19(19) $Å^3$	
Z	2	
Density (calculated)	1.327 Mg/m^3	
Absorption coefficient	0.227 mm^{-1}	
F(000)	636	
Crystal size	0.51 x 0.35 x 0.09 mm^3	
Theta range for data collection	2.79 to 30.51°.	
Index ranges	-11<=h<=12, -17<=k<=17, -21<=l<=21	
Reflections collected	66367	
Independent reflections	18076 [R(int) = 0.0331]	
Completeness to theta = 30.51°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9794 and 0.8937	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18076 / 3 / 747	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2sigma(I)]	R1 = 0.0666, wR2 = 0.1679	
R indices (all data)	R1 = 0.0723, wR2 = 0.1742	
Absolute structure parameter	0.01(5)	
Largest diff. peak and hole	2.497 and -0.430 $e.Å^{-3}$	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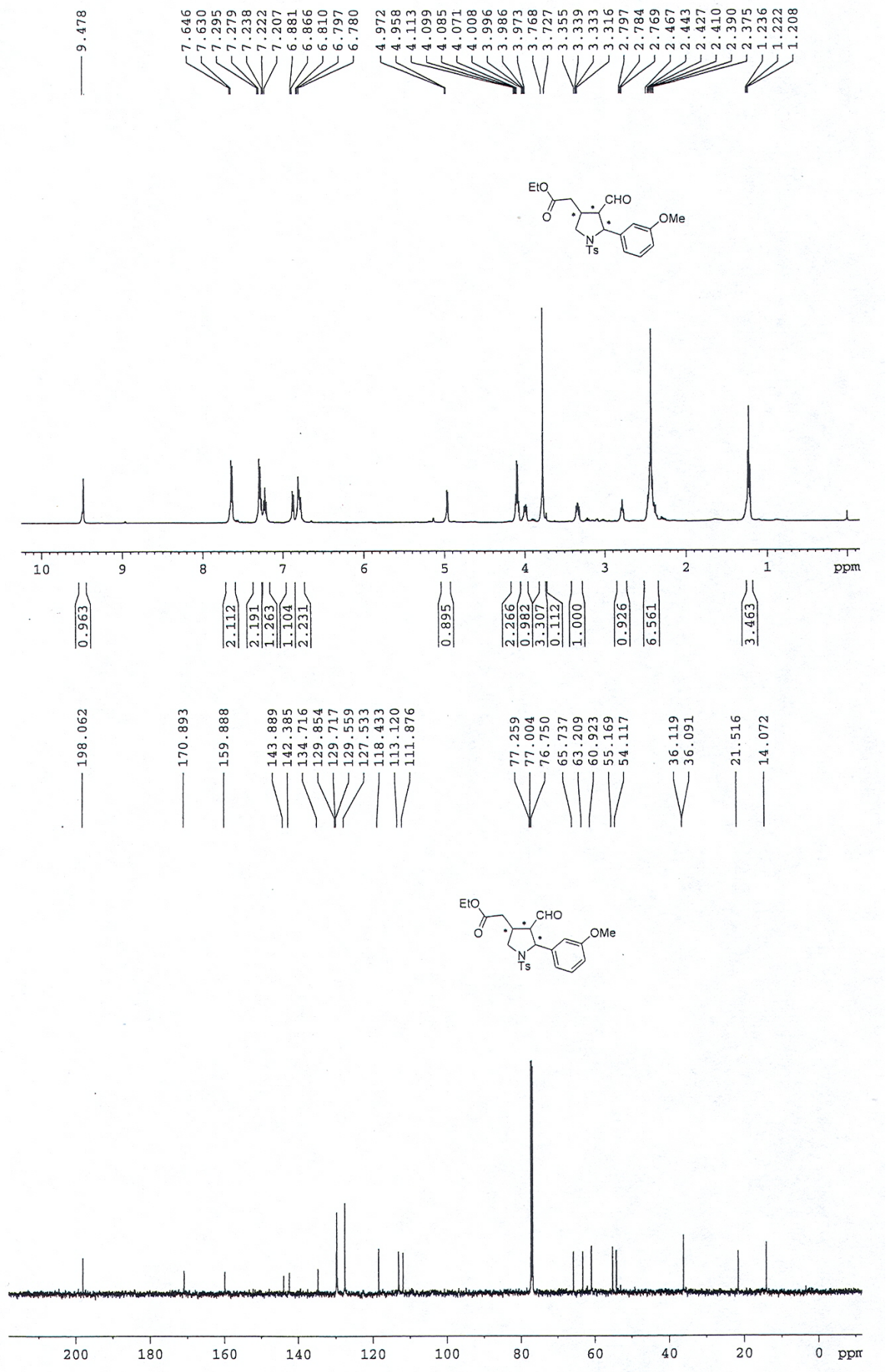
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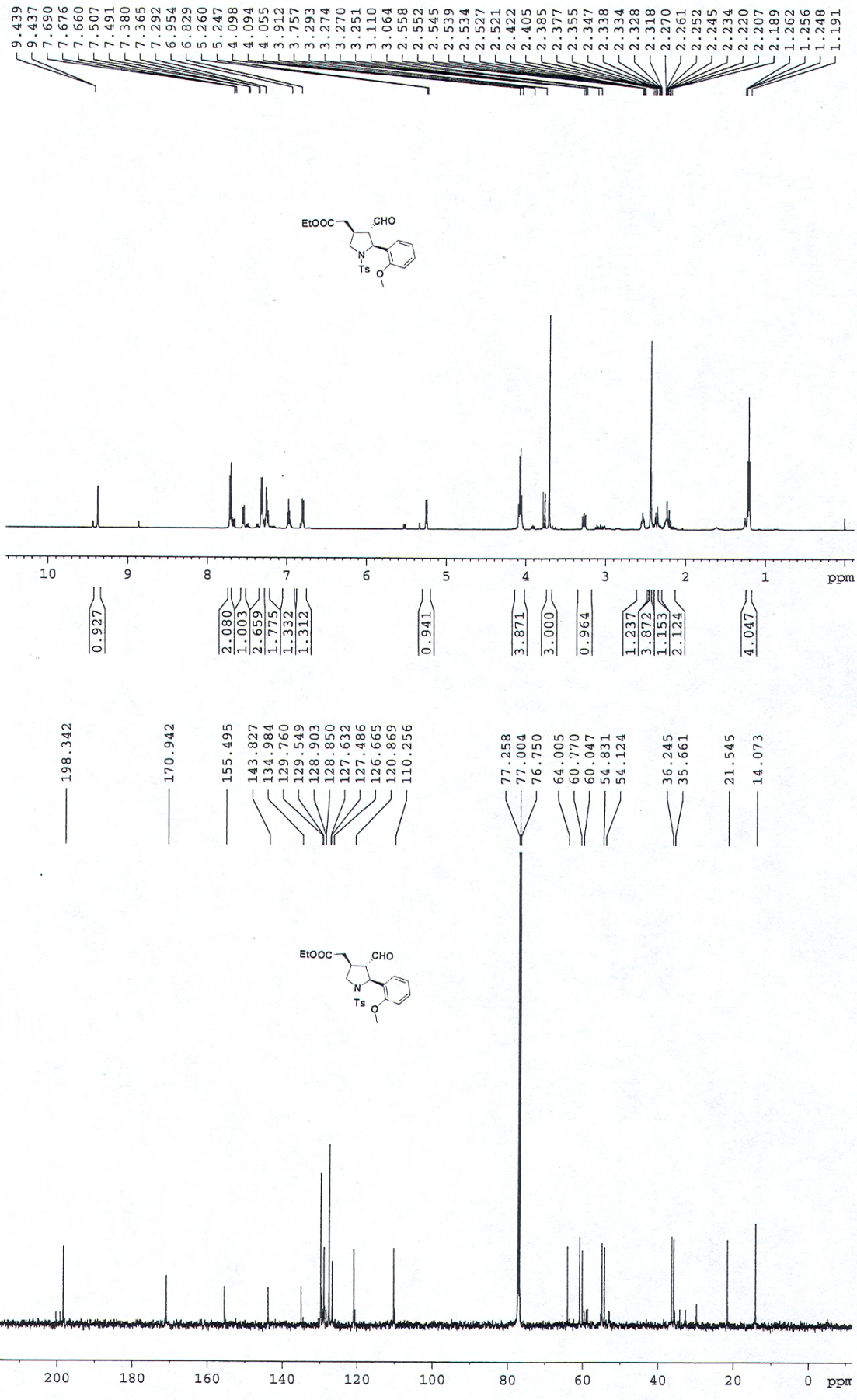
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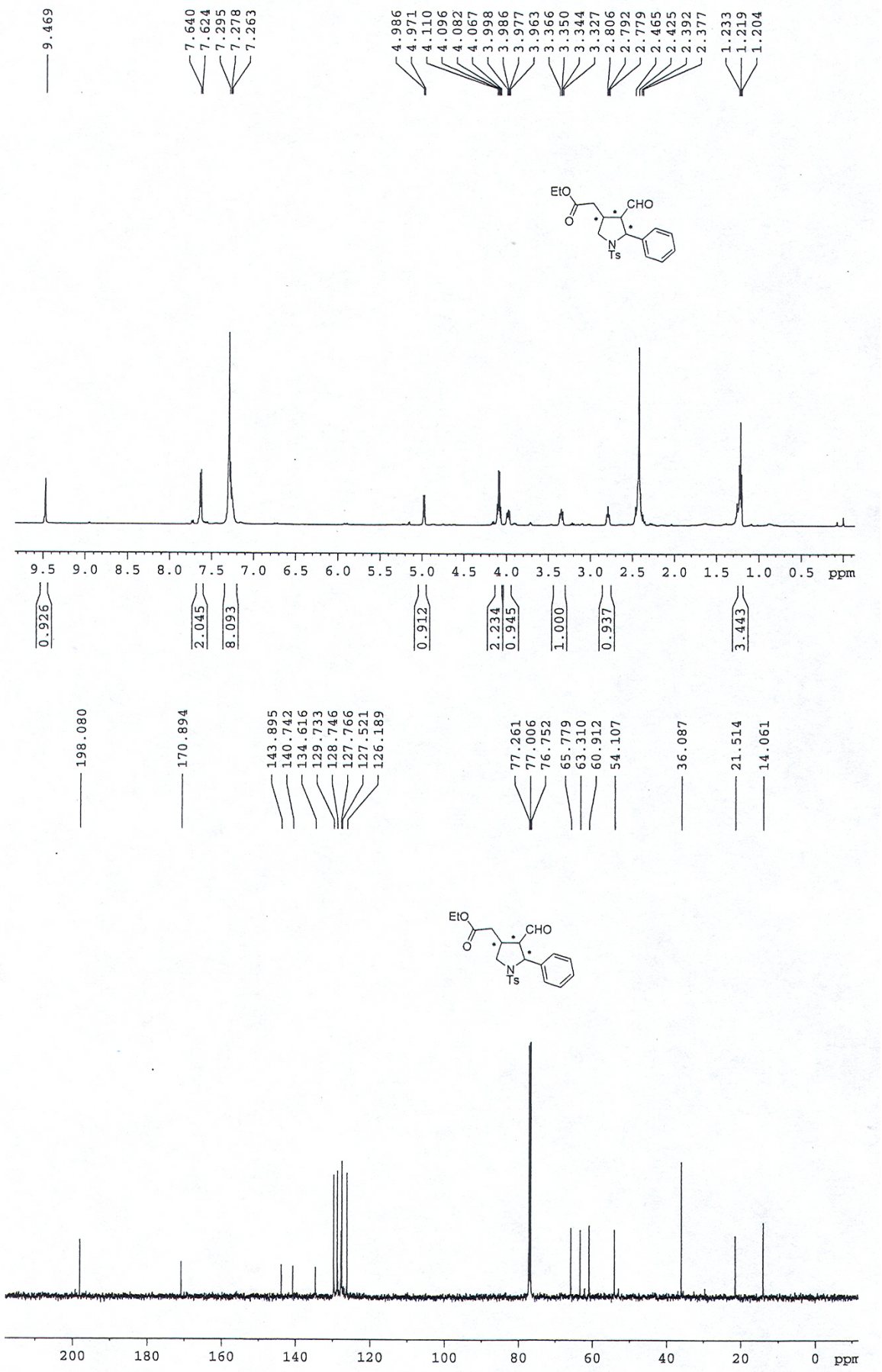
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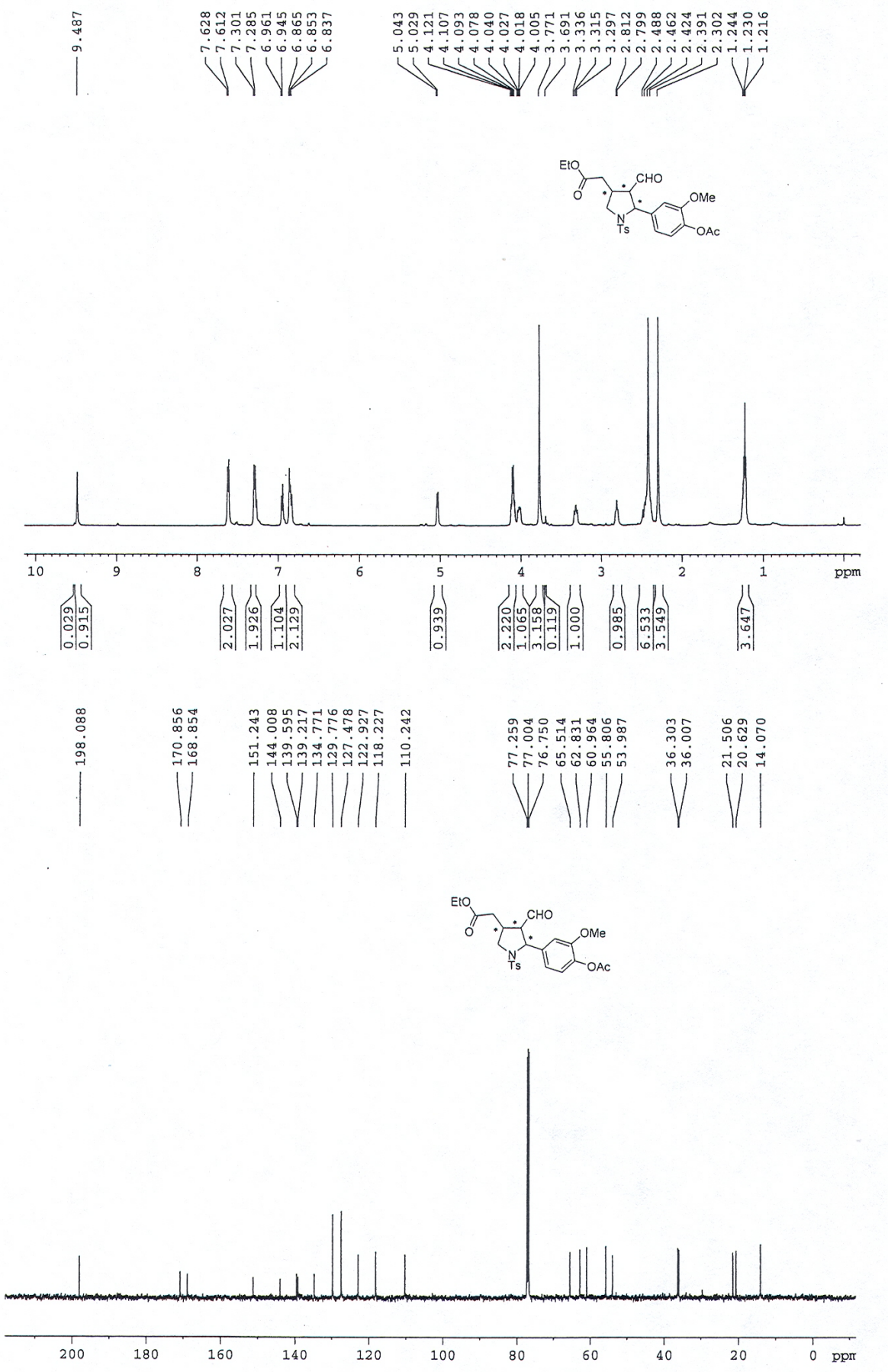
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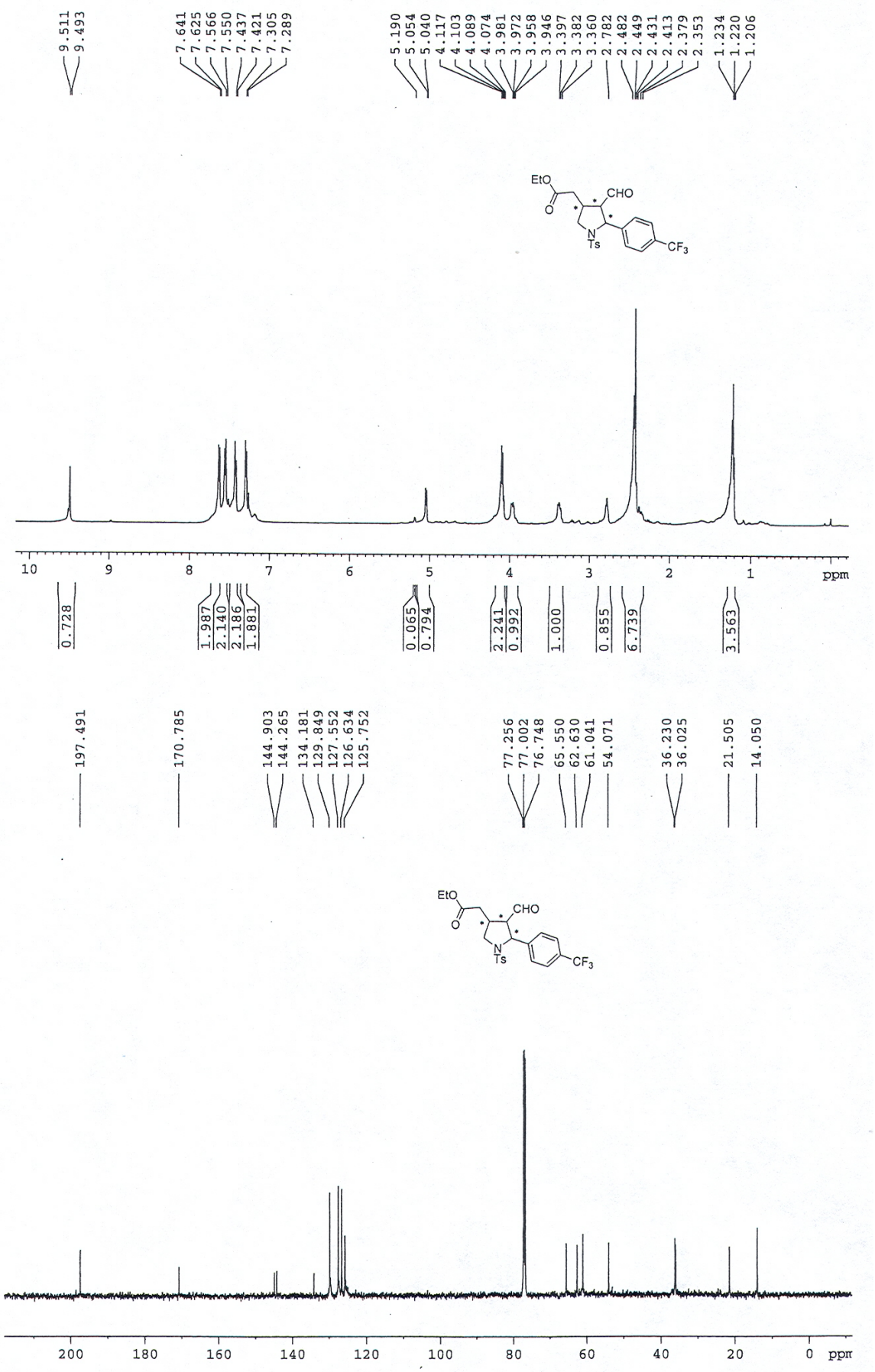
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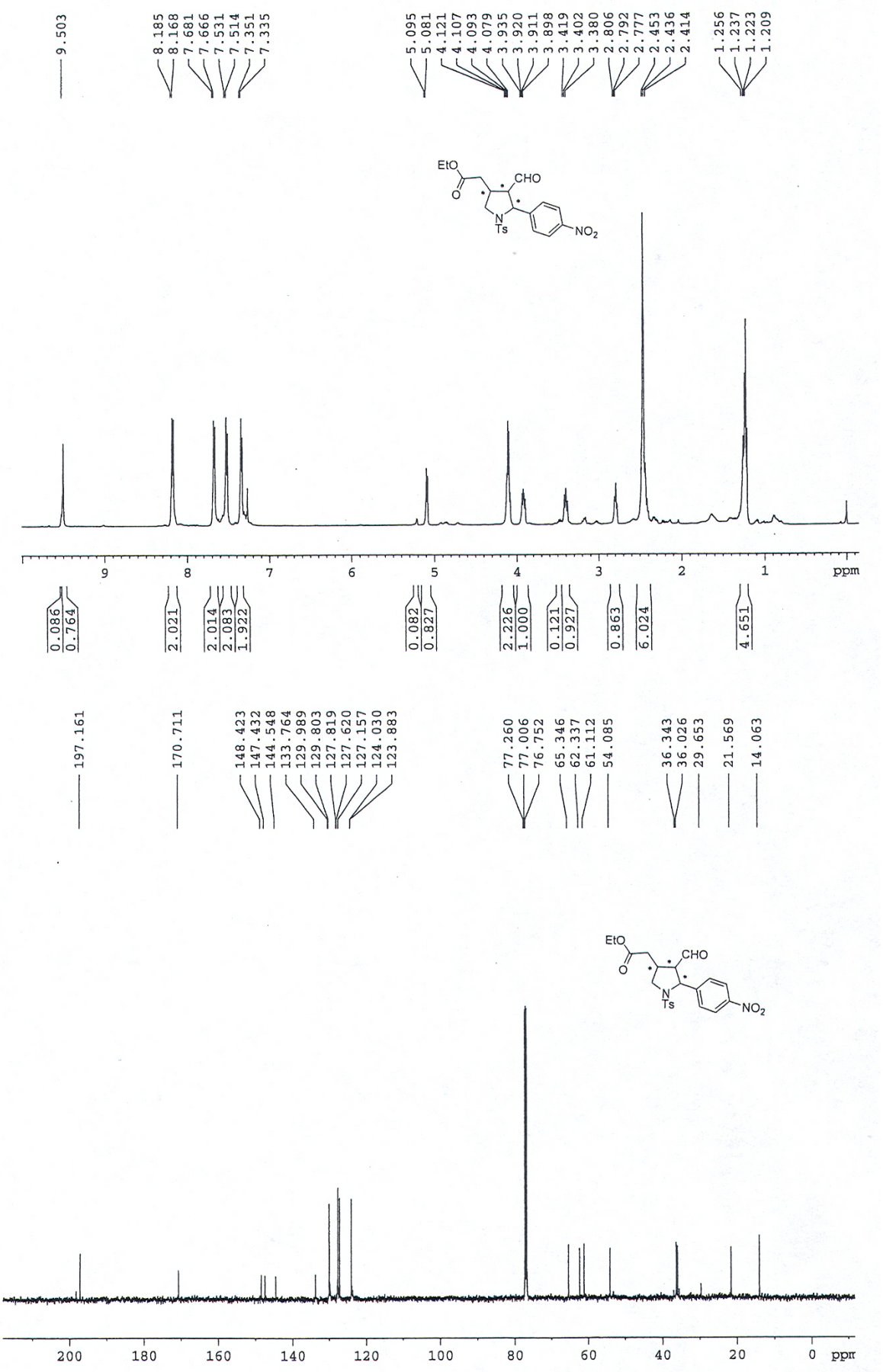
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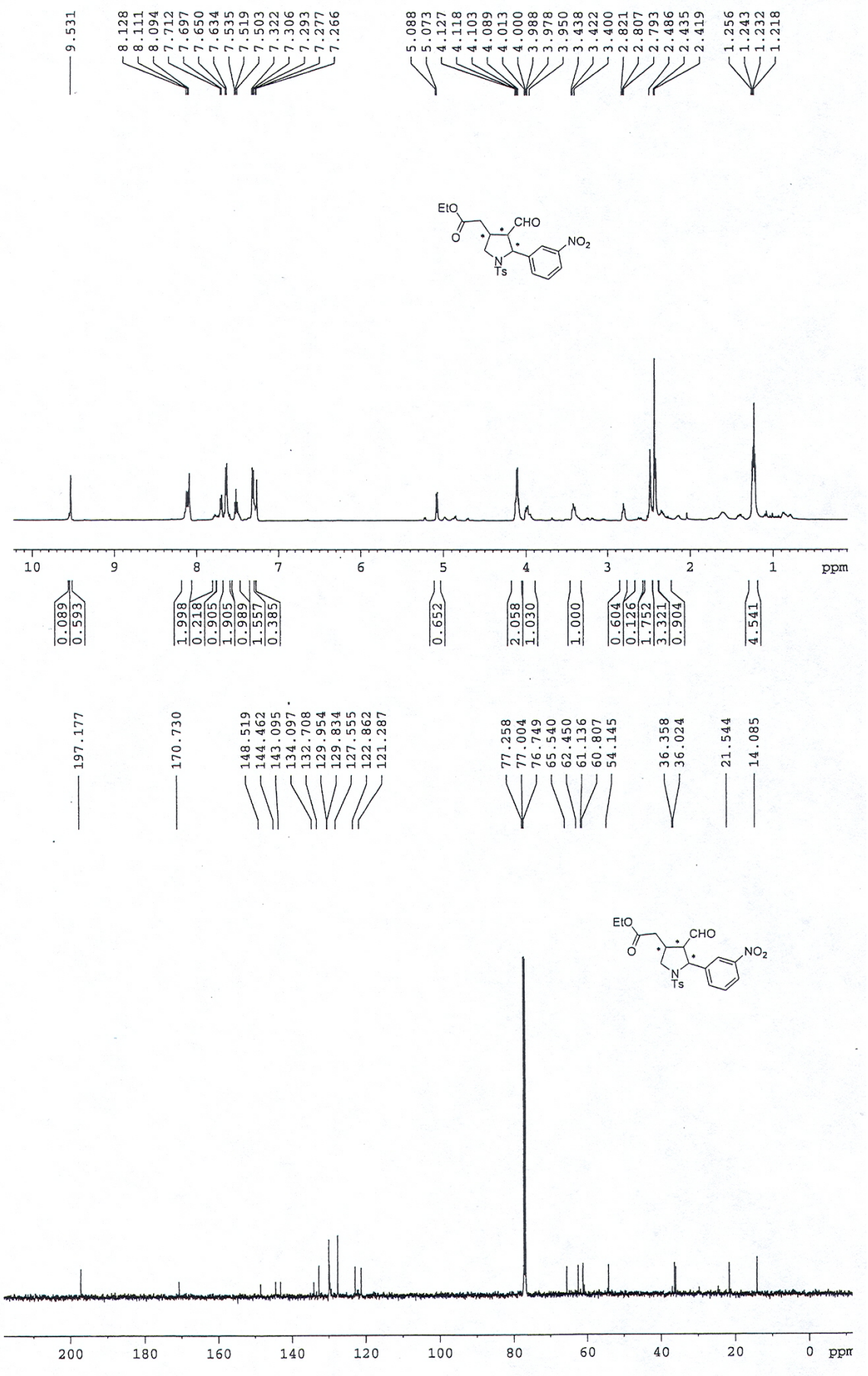
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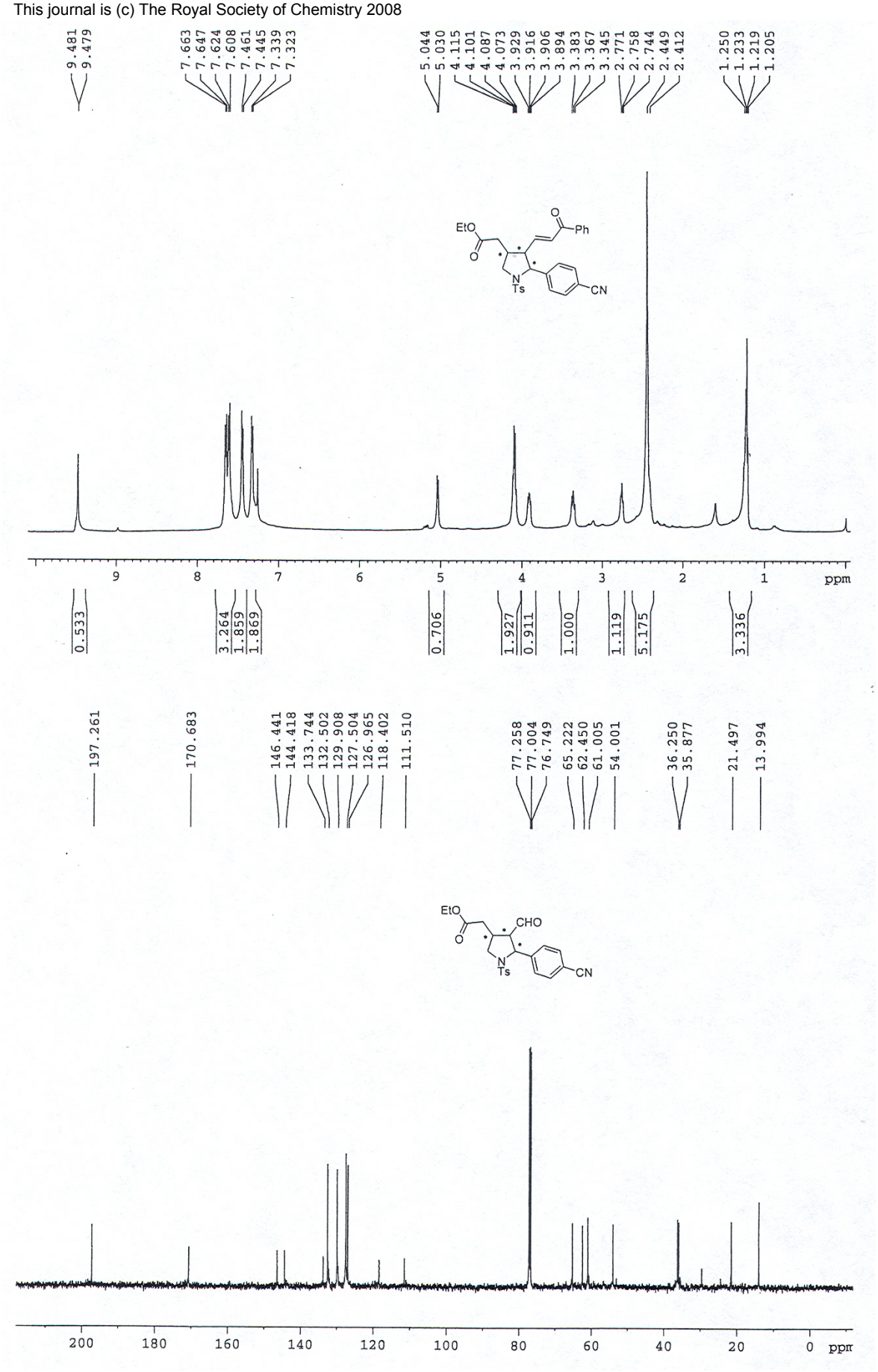
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Ts
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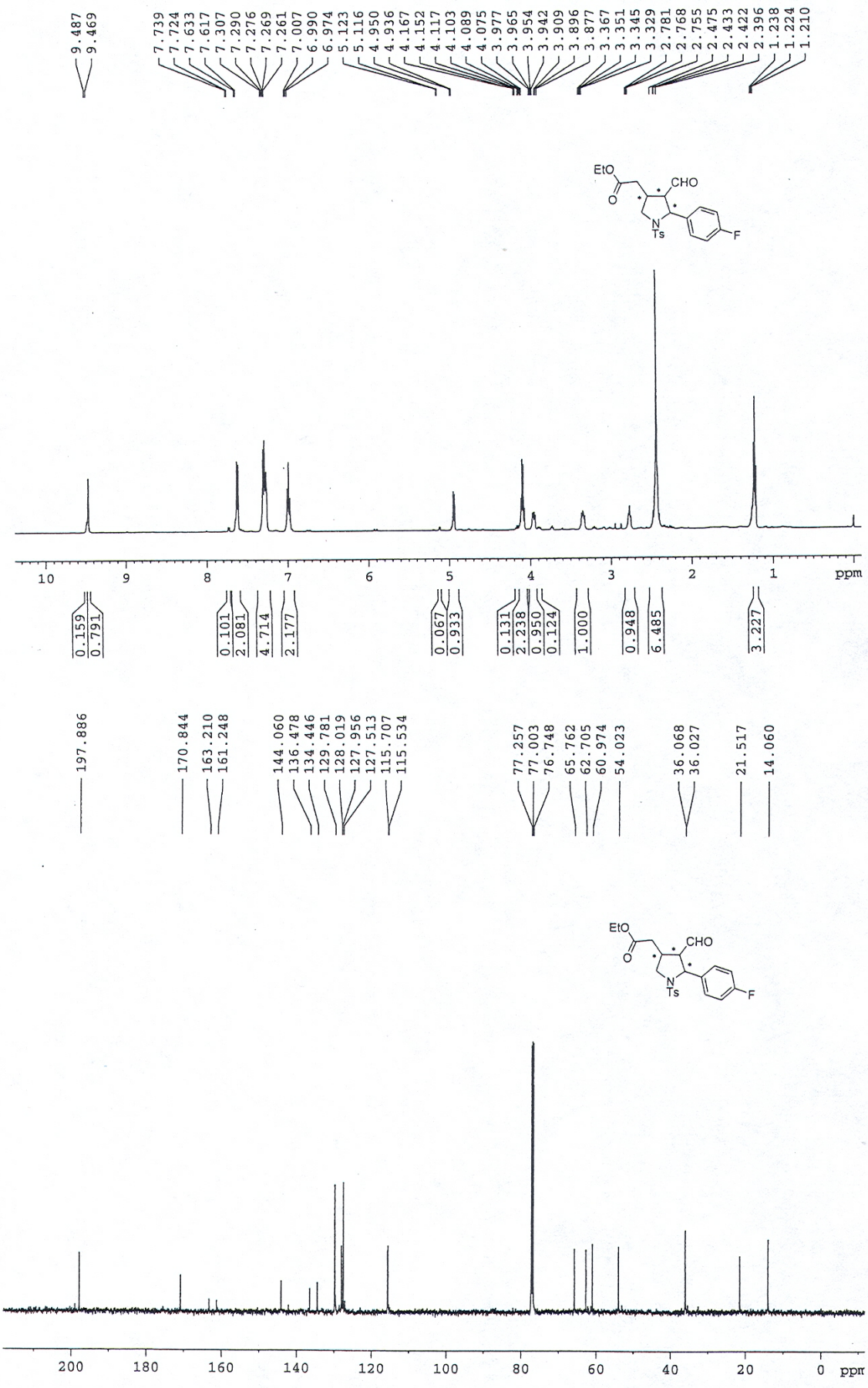
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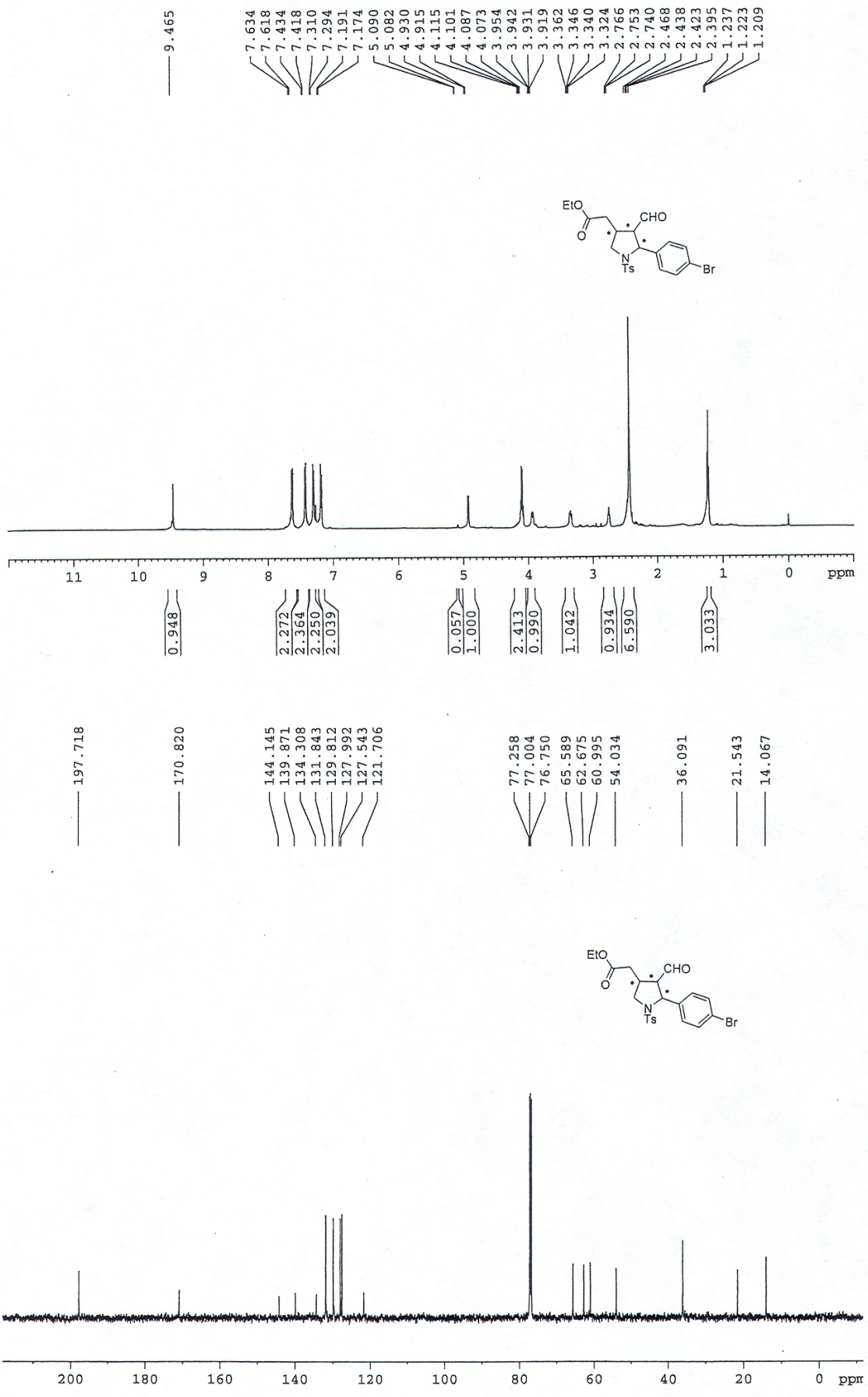
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2.438
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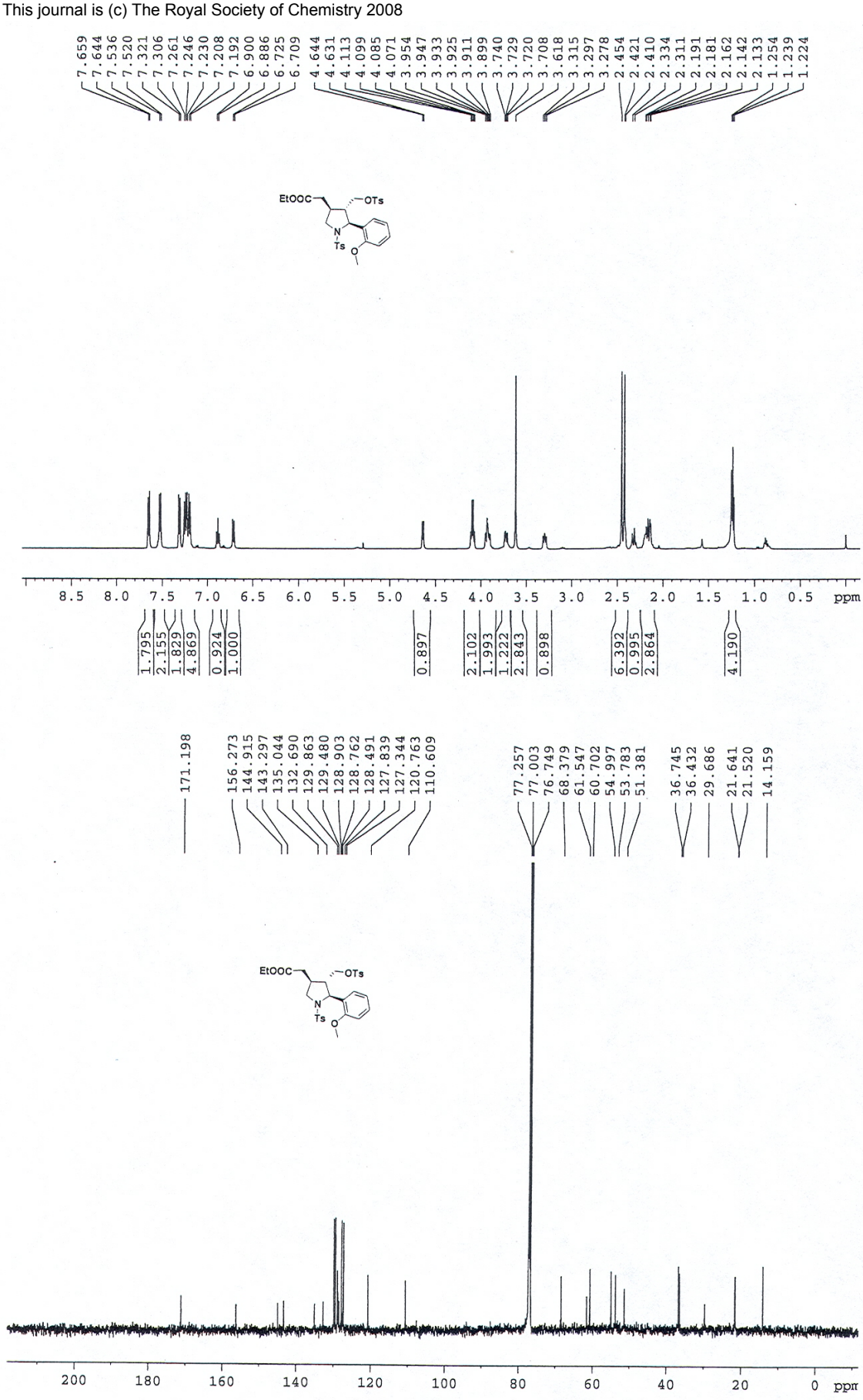
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OTs
N
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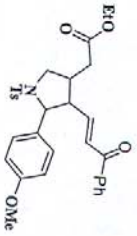
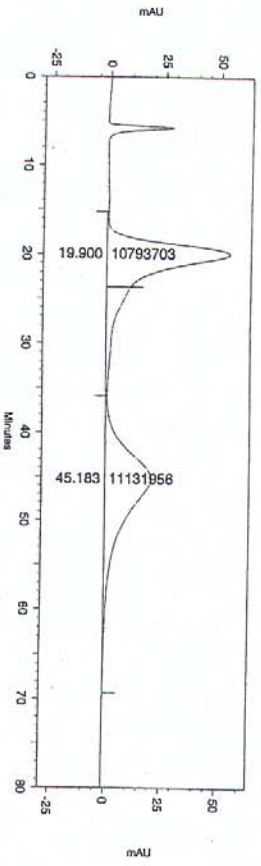
Method Name: C:\EZStart\Projects\Default\Method\zls1869.met
Data File: C:\EZStart\Projects\Default\Data\zls1938ad3.dat
Data Acquired: 8/19/2008 1:13:37 PM
Date Printed: 8/20/2008 12:51:28 AM
Sample ID: zls1938





SPD-20A
Ch1-254nm Results

Pk #	Retention Time	Area	Area Percent
1	19.900	10793703	49.229
2	45.183	11131956	50.771
Totals		21925659	100.000

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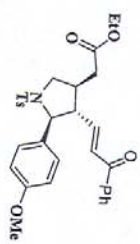
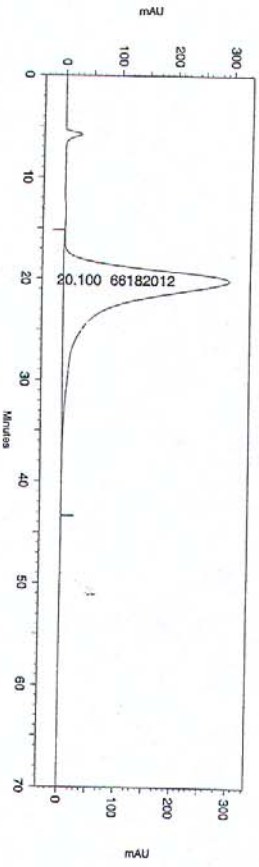
Method Name: C:\EZStart\Projects\Default\Method\zls1869.met
Data File: C:\EZStart\Projects\Default\Data\zls1942ad.dat
Data Acquired: 8/19/2008 4:14:04 PM
Date Printed: 8/20/2008 12:52:07 AM
Sample ID: zls1942





SPD-20A
Ch1-254nm Results

Pk #	Retention Time	Area	Area Percent
1	20.100	66182012	100.000
Totals		66182012	100.000

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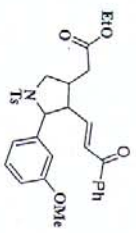
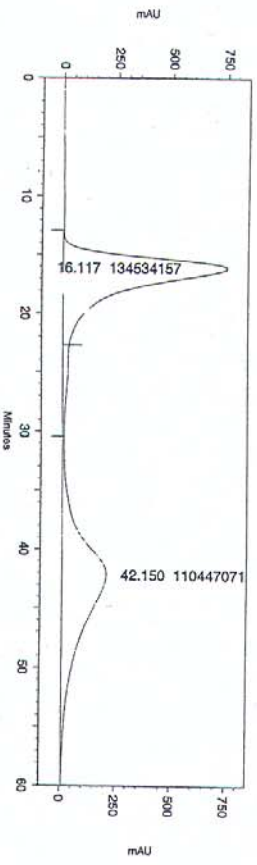
Method Name: C:\EZStart\Projects\Default\Method\zls1869.met
Data File: C:\EZStart\Projects\Default\Data\zls1935ad2.dat
Data Acquired: 8/18/2008 11:40:45 PM
Date Printed: 8/20/2008 12:47:45 AM
Sample ID: zls1935





SPD-20A
Chl-254nm Results

Pk #	Retention Time	Area	Area Percent
1	16.117	134534157	54.916
2	42.150	110447071	45.084
Totals		244981228	100.000

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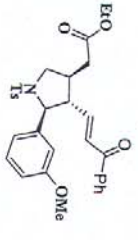
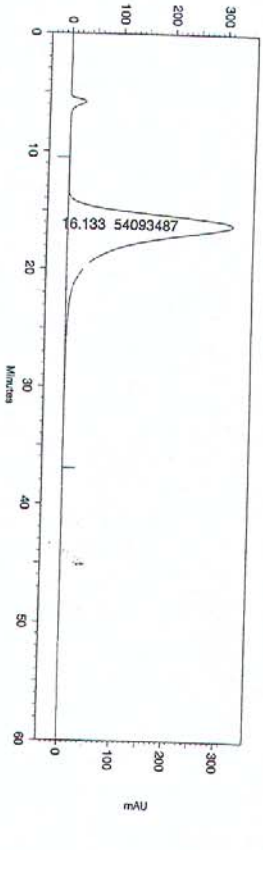
Method Name: C:\EZStart\Projects\Default\Method\zls1869.met
Data File: C:\EZStart\Projects\Default\Data\zls1940ad.dat
Data Acquired: 8/19/2008 6:15:22 PM
Date Printed: 8/20/2008 12:45:42 AM
Sample ID: zls1940



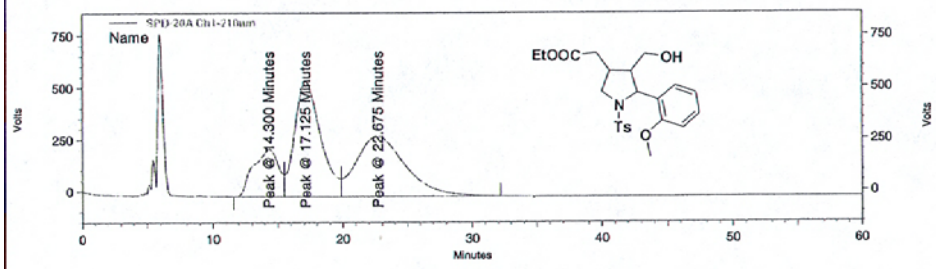


SPD-20A
Chl-254nm Results

Pk #	Retention Time	Area	Area Percent
1	16.133	54093487	100.000
Totals		54093487	100.000

Normalization Report

Method Name: C:\EZStart\Projects\Default\Method\zls1680.met
Data: C:\EZStart\Projects\Default\Data\zls1680-oj.dat
User: System
Acquired: 2/19/2008 11:33:40 PM
Printed: 3/28/2008 12:15:54 AM



SPD-20A
Ch1-210nm
Results

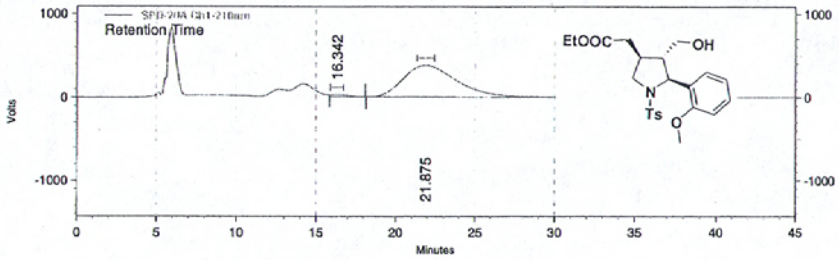
Pk #	*Name*	*Retention Time*	*Area*	*Concentration*
1	Peak @ 14.300 Minutes	14.300	30807677	0.000
2	Peak @ 17.125 Minutes	17.125	77836090	0.000
3	Peak @ 22.675 Minutes	22.675	77083453	0.000
Totals			185727220	0.000

SPD-20A
Ch2-254nm
Results

Pk #	*Name*	*Retention Time*	*Area*	*Concentration*

Area % Report

Data File: C:\EZStart\Projects\Default\Data\zls1710-1.dat
Method: C:\EZStart\Projects\Default\Method\zls1680.met
Acquired: 2/27/2008 4:56:39 PM
Printed: 3/28/2008 12:13:21 AM



SPD-20A
Ch1-210nm
Results

Retention Time	Area	Area %	Height	Height %
16.342	1954993	2.13	24748	6.17
21.875	89680452	97.87	376583	93.83
Totals	91635445	100.00	401331	100.00

SPD-20A
Ch2-254nm
Results

Retention Time	Area	Area %	Height	Height %
5.150	21800	0.23	1435	1.84
5.958	51526	0.54	1533	1.97
12.675	809515	8.56	12643	16.22
14.192	1813748	19.18	21330	27.36
16.350	214119	2.26	2816	3.61
21.883	6545685	69.22	38197	48.99
33.700	84	0.00	12	0.02
Totals	9456477	100.00	77966	100.00

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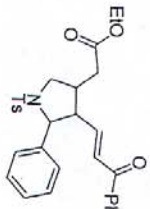
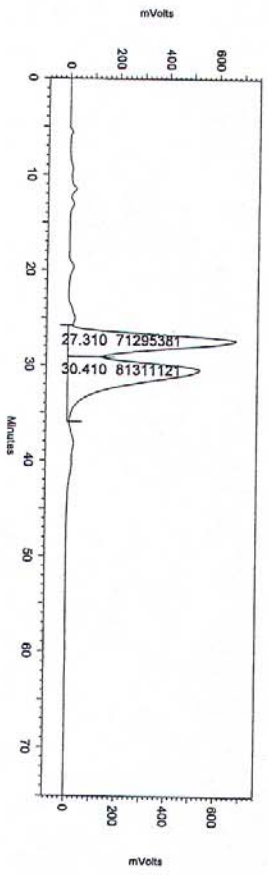
Method Name: C:\EZStart\projects\WeiWang\aa07.met
Data File: C:\EZStart\projects\WeiWang\hlx4c4.dat
Date Acquired: 12/4/2007 10:38:03 AM Date Printed: 01/17/2008 12:54:21 PM
Sample ID: hlx4c





SPD-10Avp
Ch1-254nm Results

Pk #	RT	Area	Area %
1	27.310	71295381	46.718
2	30.410	81311121	53.282
Totals		152606502	100.000

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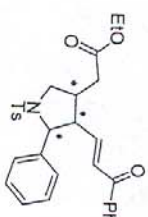
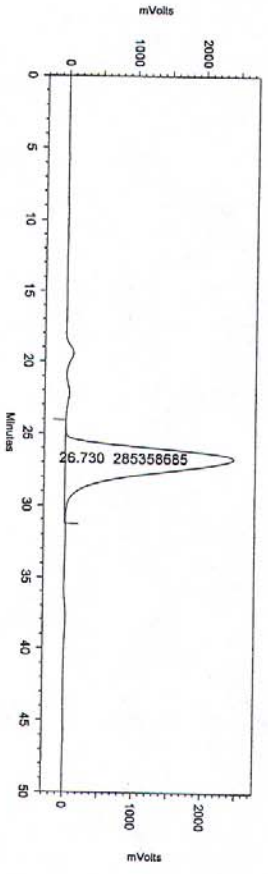
Method Name: C:\EZStart\projects\WeiWang\zls1558.met
Data File: C:\EZStart\projects\WeiWang\hlx18c2.dat
Date Acquired: 12/16/2007 2:32:25 PM Date Printed: 01/17/2008 12:55:23 PM
Sample ID: hlx18c





SPD-10Avp
Ch1-254nm Results

Pk #	RT	Area	Area %
1	26.730	285358685	100.000
Totals		285358685	100.000

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Method Name: C:\EZStart\Projects\Default\Method\zls1869.met
Data File: C:\EZStart\Projects\Default\Data\zls1939ad.dat
Data Acquired: 8/18/2008 10:09:21 PM
Date Printed: 8/20/2008 12:53:45 AM
Sample ID: zls1939

SPD-20A
Ch1-254nm Results

Pk #	Retention Time	Area	Area Percent
1	13.275	9869265	48.397
2	24.192	10522874	51.603
Totals		20392139	100.000

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Method Name: C:\EZStart\Projects\Default\Method\zls1869.met
Data File: C:\EZStart\Projects\Default\Data\zls1943ad.dat
Data Acquired: 8/19/2008 5:26:02 PM
Date Printed: 8/20/2008 12:56:14 AM
Sample ID: zls1943

SPD-20A
Ch1-254nm Results

Pk #	Retention Time	Area	Area Percent
1	13.317	27582766	98.240
2	28.525	494119	1.760
Totals		28076885	100.000

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Method Name: C:\EZStart\Projects\WeiWang\ff3.met
Data File: C:\EZStart\Projects\WeiWang\hlw48e2.dat
Date Acquired: 11/13/2007 4:23:06 PM Date Printed: 01/17/2008 12:51:19 PM
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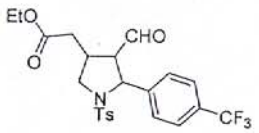

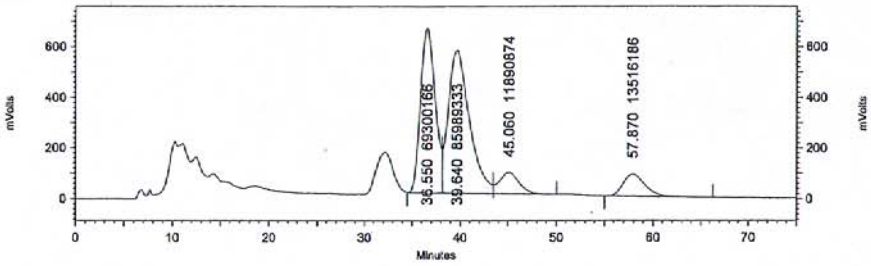

SPD-10Avp
Ch1-235nm Results

Pk #	RT	Area	Area %
1	36.550	69300166	38.352
2	39.640	85989333	47.588
3	45.060	11890874	6.581
4	57.870	13516186	7.480
Totals		180696559	100.000

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Method Name: C:\EZStart\Projects\WeiWang\11.met
Data File: C:\EZStart\Projects\WeiWang\hlx5e1.dat
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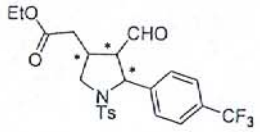

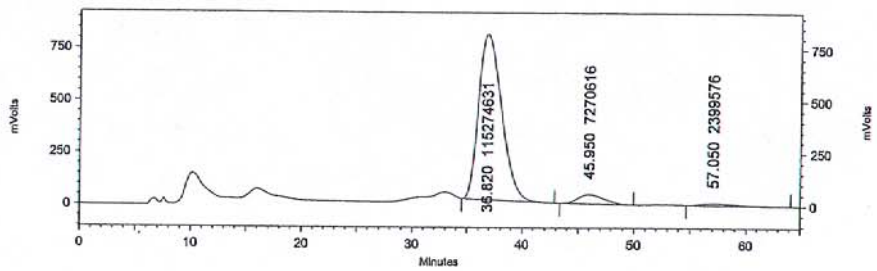

SPD-10Avp
Ch1-235nm Results

Pk #	RT	Area	Area %
1	36.820	115274631	92.260
2	45.950	7270616	5.819
3	57.050	2399576	1.921
Totals		124944823	100.000

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Method Name: C:\EZStart\Projects\WeiWang\aa04.met
Data File: C:\EZStart\Projects\WeiWang\hlw80c3.dat
Date Acquired: 11/14/2007 4:40:13 PM Date Printed: 01/17/2008 12:48:14 PM
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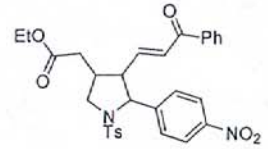

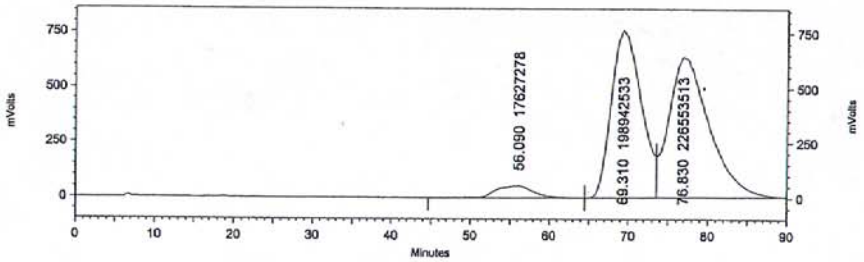

SPD-10Avp
Ch1-254nm Results

Pk #	RT	Area	Area %
2	69.310	198942533	44.896
3	76.830	226553513	51.127
Totals		425496046	96.022

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Method Name: C:\EZStart\Projects\WeiWang\zls1558.met
Data File: C:\EZStart\Projects\WeiWang\hlx16c2.dat
Date Acquired: 12/16/2007 11:24:55 AM Date Printed: 01/17/2008 12:49:04 PM
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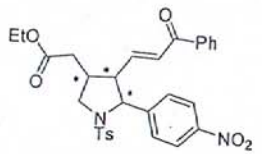

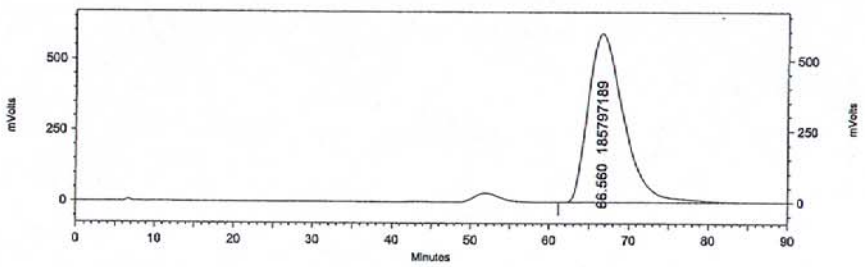

SPD-10Avp
Ch1-254nm Results

Pk #	RT	Area	Area %
1	66.560	185797189	100.000
Totals		185797189	100.000

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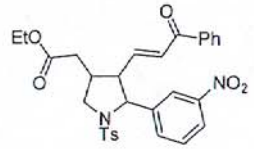
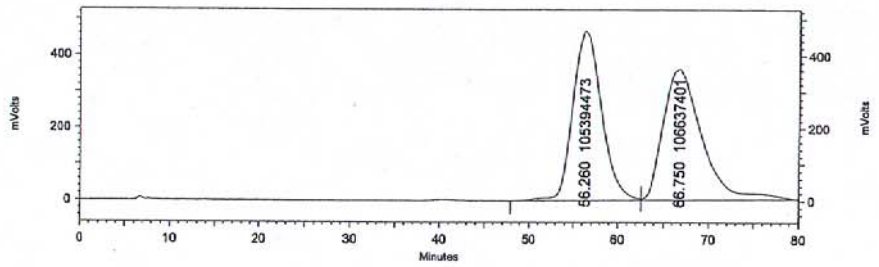
Method Name: C:\EZStart\Projects\WeiWang\zls1376.met
Data File: C:\EZStart\Projects\WeiWang\hlw18c2.dat
Date Acquired: 10/2/2007 1:37:01 PM Date Printed: 01/17/2008 12:44:17 PM
Sample ID: hlw18c





SPD-10Avp
Ch1-254nm Results

Pk #	RT	Area	Area %
1	56.260	105394473	49.707
2	66.750	106637401	50.293
Totals		212031874	100.000

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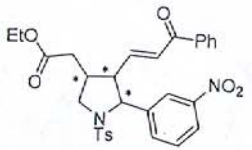
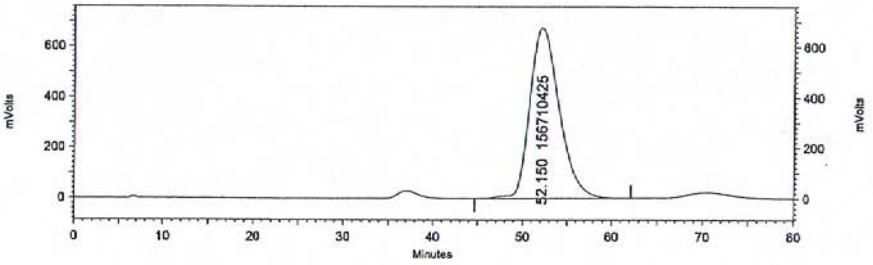
Method Name: C:\EZStart\Projects\WeiWang\zls1558.met
Data File: C:\EZStart\Projects\WeiWang\hlx17c2.dat
Date Acquired: 12/16/2007 12:58:03 PM Date Printed: 01/17/2008 12:46:04 PM
Sample ID: hlx17c





SPD-10Avp
Ch1-254nm Results

Pk #	RT	Area	Area %
1	52.150	156710425	100.000
Totals		156710425	100.000

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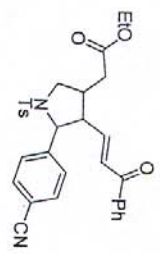
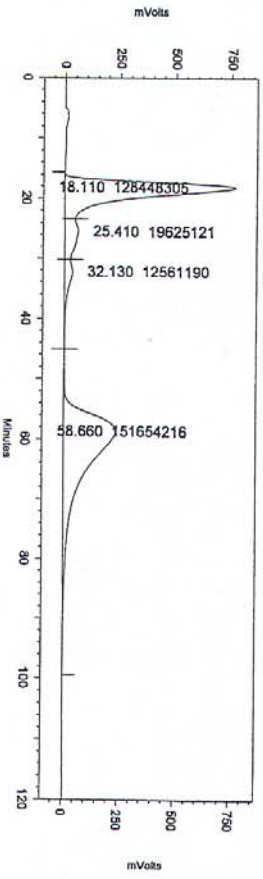
Method Name: C:\EZStart\Projects\WeiWang\aa06.met
Data File: C:\EZStart\Projects\WeiWang\hlw85e9.dat
Date Acquired: 11/28/2007 3:47:03 PM Date Printed: 01/17/2008 01:07:39 PM
Sample ID: hlw85e





SPD-10Avp
Ch1-254nm Results

Pk #	RT	Area	Area %
1	18.110	128448305	41.132
2	25.410	19625121	6.284
3	32.130	12561190	4.022
4	58.660	151654216	48.562
Totals		312288832	100.000

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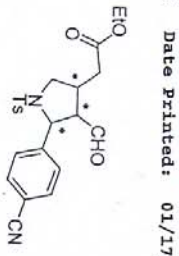
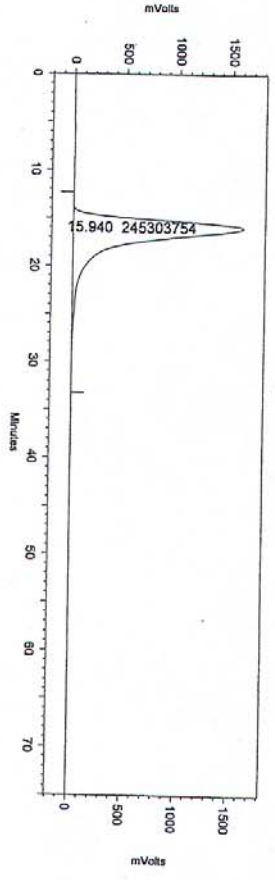
Method Name: C:\EZStart\Projects\WeiWang\aa09.met
Data File: C:\EZStart\Projects\WeiWang\hlx15e1.dat
Date Acquired: 12/7/2007 12:30:29 PM Date Printed: 01/17/2008 01:08:15 PM
Sample ID: hlx15e





SPD-10Avp
Ch1-254nm Results

Pk #	RT	Area	Area %
1	15.940	245303754	100.000
Totals		245303754	100.000

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Method Name: C:\EZStart\Projects\Default\Method\zls1869.met
Data File: C:\EZStart\Projects\Default\Data\zls1936ad.dat
Data Acquired: 8/19/2008 12:53:19 AM
Date Printed: 8/20/2008 12:49:24 AM
Sample ID: zls1936

SPD-20A
Ch1-254nm Results

Pk #	Retention Time	Area	Area Percent
1	14.617	55255692	49.176
2	47.792	57108274	50.824
Totals		112363966	100.000

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Method Name: C:\EZStart\Projects\Default\Method\zls1869.met
Data File: C:\EZStart\Projects\Default\Data\zls1941ad.dat
Data Acquired: 8/19/2008 2:38:08 PM
Date Printed: 8/20/2008 12:49:43 AM
Sample ID: zls1941

SPD-20A
Ch1-254nm Results

Pk #	Retention Time	Area	Area Percent
1	14.658	42335537	100.000
Totals		42335537	100.000

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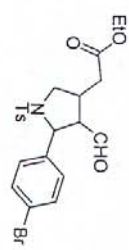
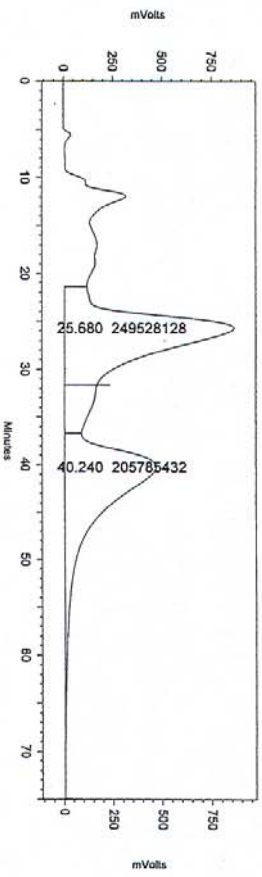
Method Name: C:\EZStart\projects\WeiWang\aa07.met
Data File: C:\EZStart\projects\WeiWang\hlxle4.dat
Date Acquired: 11/30/2007 9:29:55 AM Date Printed: 01/17/2008 12:37:04 PM
Sample ID: hlxle





SPD-10Avp
Ch1-235nm Results

Pk #	RT	Area	Area %
1	25.680	249528128	54.804
2	40.240	205785432	45.196
Totals		455313560	100.000

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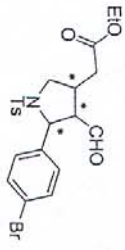
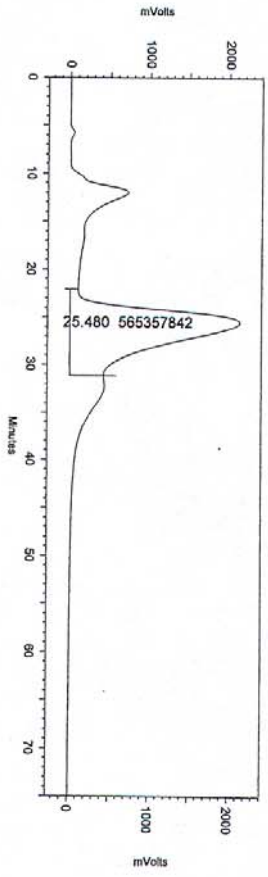
Method Name: C:\EZStart\Projects\WeiWang\xxx3.met
Data File: C:\EZStart\Projects\WeiWang\hlx13e1.dat
Date Acquired: 12/6/2007 8:47:39 PM Date Printed: 01/17/2008 12:38:19 PM
Sample ID: hlx13e





SPD-10Avp
Ch1-235nm Results

Pk #	RT	Area	Area %
1	25.480	565357842	100.000
Totals		565357842	100.000