

**Ionic Liquid-Supported (ILS) (S)-Pyrrolidine Sulfonamide, a Recyclable
Organocatalyst for the Highly Enantioselective Michael Addition to Nitroolefins**

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Supporting Information

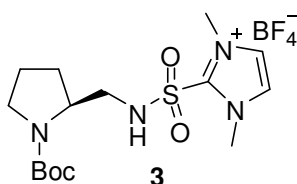
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General Information: Commercial reagents were used as received, unless otherwise stated. Merck 60 silica gel was used for chromatography, and Whatman silica gel plates with fluorescence UV₂₅₄ were used for thin-layer chromatography (TLC) analysis. ¹H and ¹³C NMR spectra were recorded on the Bruker Avance 400. The data of Elemental Analysis were obtained from Quantitative Technologies INC.

All the compounds synthesized (shown in Table 3) in the manuscript are known compounds.²⁻⁷ Their relative and absolute configurations of the products were determined by comparison with the known ¹H and ¹³C NMR, chiral HPLC analysis, and optical rotation values.

1. Synthesis of compound 3

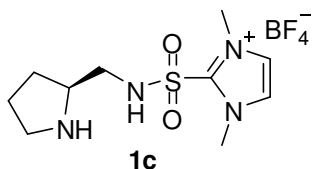


To a solution of (S)-2-amino-1-N-Boc-pyrrolidine (660 mg, 3.3 mmol) and Et₃N (364 mg, 3.6 mmol) in CH₂Cl₂ (5 mL) was added 1-methyl-2-sufonylchlorideimidazole¹ (596 mg, 3.3 mmol) in CH₂Cl₂ (2 mL) at 0°C. After addition, the reaction mixture was warmed up to room temperature and continued to stirring for 1 h. Then water was added and the reaction mixture was extracted with CH₂Cl₂, the organic phase was dried over Na₂SO₄. Filtration, removal of the solvent, and purification by falsh column chromatography (eluent: ethyl acetate) afforded the product **2** (1.1 g, 96%). This compound was used for the next step directly without further characterization.

To a solution of compound **2** (584 mg, 1.70 mmol) in AcOEt (5 mL) was added Me₃OBF₄ (251 mg, 1.70 mmol) at 0°C. After addition, the reaction mixture was warmed up to room temperature and continued to stirring for 2 h. The solid was precipitated, filtrated, and dried to give product **3** (679 mg, 90%) as a white solid. mp: 138-140°C; [α]_D²⁰ = -47.2° (c = 0.25, MeOH); ¹H NMR (400 MHz, CD₃OD) δ 7.75 (s, 2H), 4.11 (s, 6H), 3.90 and 3.70 (br, 1H), 3.40-3.10 (m, 4H), 2.05-1.78 (m, 4H), 1.43 (br, 9H); ¹³C NMR (100 MHz, CD₃OD) δ 156.7, 141.2, 140.1, 127.3, 126.9, 81.6, 81.1, 61.2, 58.5,

58.1, 47.0, 46.3, 45.9, 44.3, 39.0, 29.4, 29.1, 28.7, 27.2, 24.4, 23.7; anal calcd for C₁₅H₂₇BF₄N₄O₂S: C 40.37, H 6.10, N 12.55; Found: C 40.52, H 6.31, N 12.41.

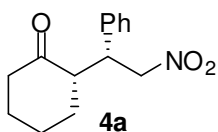
2. Synthesis of catalyst **1c**



The obtained product **3** (500 mg, 1.23 mmol) was added 4 M HCl dioxane solution (5 mL). The reaction was stirred at room temperature for 5 h and removed the solvent to give the hydrogen chloride salts, which was dissolved in methanol and neutralized with NaHCO₃ solid. Removal the solvent left a residue, which was further purified by short column chromatography on basic aluminum oxide (eluent: methanol) to remove the inorganic salt and give product **1c** (403 mg, 95%) as a white solid. mp: 147-148°C; [α]_D²⁰ = 4.5° (c = 0.31, MeOH); ¹H NMR (400 MHz, CD₃OD) δ 7.53 and 7.50 (s, 2H), 4.06 (s, 6H), 3.70-3.50 (m, 1H), 3.36-2.90 (m, 4H), 2.20-1.90 (m, 3H), 1.78-1.64 (m, 1H); ¹³C NMR (100 MHz, CD₃OD) δ 148.11, 124.7, 124.6, 113.2, 63.1, 46.9, 46.5, 38.1, 37.9, 30.7, 29.2, 28.4, 24.8, 24.4; anal calcd for C₁₀H₁₉BF₄N₄O₂S: C 34.70, H 5.53, N 16.19; Found: C 34.58, H 5.62, N 16.32.

The general procedure for the Michael addition reaction

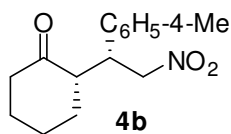
3. (*S*)-2-((*R*)-2-nitro-1-phenylethyl)cyclohexanone **4a**²



The catalyst **1c** (7 mg, 10 mol%) was added to a solution of cyclohexanone (98 mg, 1.0 mmol) in *i*-PrOH (0.5 mL) at room temperature. The reaction mixture was stirred for 20 min, and then *trans*- β -nitrostyrene (30 mg, 0.2 mmol) was added. After stirring at room temperature for 16 h, the reaction mixture was concentrated in vacuum and the residue was diluted with ethyl acetate (or ether) to precipitate the catalyst. The organic layer was separated and purified by flash silica gel column (eluent: hexane : ethyl acetate = 4 : 1) to give the Michael adduct **4a** (45 mg, 91%) as a white solid. The catalyst was recovered and reused for the next cycle. ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.23 (m, 3H), 7.20-7.14 (m, 2H), 4.94 (dd, *J* = 12.4 and 4.4 Hz, 1H), 6.43 (dd, *J* = 12.4 and 10.0 Hz, 1H), 3.76 (dt, *J* = 9.6 and 4.4 Hz, 1H), 2.74-2.64 (m, 1H), 2.52-2.34 (m, 2H), 2.13-2.03 (m, 1H), 1.83-1.50 (m, 4H), 1.30-1.18 (m, 1H); *syn/anti* =

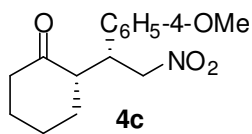
95/5; ee = 90%; HPLC (Chiralpak AS-H, i-Propanol/Hexane = 10/90, flow rate 0.7 mL/min, λ = 238 nm): t_{minor} = 18.2 min, t_{major} = 27.5 min.

4. (S)-2-((R)-1-(4-methylphenyl)-2-nitroethyl)cyclohexanone **4b**³



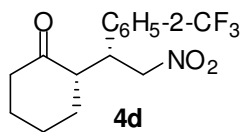
¹H NMR (400 MHz, CDCl₃) δ 7.12 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 4.91 (dd, J = 12.4 and 4.8 Hz, 1H), 4.62 (dd, J = 12.4 and 10.0 Hz, 1H), 3.72 (dt, J = 10.0 and 4.8 Hz, 1H), 2.71-2.62 (m, 1H), 2.51-2.32 (m, 2H), 2.31 (s, 3H), 2.12-2.02 (m, 1H), 1.82-1.50 (m, 4H), 1.30-1.18 (m, 1H); *syn/anti* = 99/1; ee = 99%; HPLC (Chiralpak AS-H, i-Propanol/Hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm): t_{minor} = 12.4 min, t_{major} = 20.6 min.

5. (S)-2-((R)-1-(4-methoxyphenyl)-2-nitroethyl)cyclohexanone **4c**²



¹H NMR (400 MHz, CDCl₃) δ 7.08 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 4.95 (dd, J = 12.4 and 4.4 Hz, 1H), 4.58 (dd, J = 12.4 and 10.0 Hz, 1H), 3.78 (s, 3H), 3.72 (dt, J = 10.0 and 4.4 Hz, 1H), 2.69-2.60 (m, 1H), 2.53-2.33 (m, 2H), 2.13-2.04 (m, 1H), 1.82-1.50 (m, 4H), 1.30-1.17 (m, 1H); *syn/anti* = 99/1; ee = 98%. HPLC (Chiralpak AD, i-Propanol/Hexane = 10/90, flow rate 0.5 mL/min, λ = 254 nm): t_{minor} = 26.9 min, t_{major} = 32.7 min.

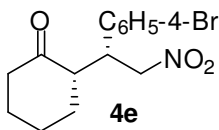
6. (S)-2-((R)-1-(2-trifluoromethanophenyl)-2-nitroethyl)cyclohexanone **4d**⁴



¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.39 (dd, J = 16.4 and 10.0 Hz, 2H), 5.02 (dd, J = 12.0 and 6.8 Hz, 1H), 4.76 (dd, J = 12.0 and 4.0 Hz, 1H), 4.13-4.05 (m, 1H), 3.06-2.96 (m, 1H), 2.54-2.40 (m, 3H), 2.18-2.08 (m, 1H), 1.84-1.52 (m, 4H), 1.38-1.24 (m, 1H); *syn/anti* 98/2; ee = 95%; HPLC

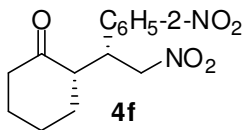
(Chiralpak AD, i-Propanol/Hexane = 10/90, flow rate 0.5 mL/min, λ = 254 nm): t_{minor} = 13.7 min, t_{major} = 18.6 min.

7. **(S)-2-((R)-1-(4-bromophenyl)-2-nitroethyl)cyclohexanone 4e**⁵



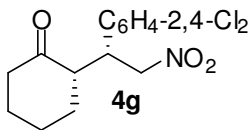
¹H NMR (400 MHz, CDCl₃) δ 7.45 (dd, J = 6.8 and 1.6 Hz, 2H), 7.06 (dd, J = 6.8 and 1.6 Hz, 2H), 4.92 (dd, J = 12.4 and 4.4 Hz, 1H), 4.60 (dd, J = 12.4 and 10.0 Hz, 1H), 3.74 (dt, J = 9.6 and 4.4 Hz, 1H), 2.70-2.60 (m, 1H), 2.52-2.32 (m, 2H), 2.14-2.04 (m, 1H), 1.84-1.52 (m, 4H), 1.30-1.18 (m, 1H); *syn/anti* = 93/7; ee = 94%; HPLC (Chiralpak AS-H, i-Propanol/Hexane = 10/90, flow rate 1 mL/min, λ = 254 nm): t_{minor} = 15.5 min, t_{major} = 27.1 min.

8. **(S)-2-((R)-2-nitro-(2-nitrophenyl)ethyl)cyclohexanone 4f**⁶



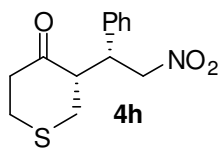
¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 8.0 Hz, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.48-7.42 (m, 2H), 4.98-4.87 (m, 2H), 4.32 (dt, J = 8.8 and 4.8 Hz, 1H), 2.99-2.91 (m, 1H), 2.52-2.32 (m, 2H), 2.16-2.08 (m, 1H), 1.88-1.78 (m, 2H), 1.72-1.40 (m, 4H); *syn/anti* = 97/3; ee = 90%; HPLC (Chiralpak AD, i-Propanol/Hexane = 5/95, flow rate 1 mL/min, λ = 238 nm): t_{minor} = 20.1 min, t_{major} = 29.3 min.

9. **(S)-2-((R)-1-(2,4-dichlorophenyl)-2-nitroethyl)cyclohexanone 4g**⁶



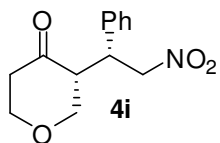
¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, J = 2.0 Hz, 1H), 7.28-7.14 (m, 2H), 4.95-4.80 (m, 2H), 4.25 (dt, J = 9.6 and 4.8 Hz, 1H), 2.93-2.82 (m, 1H), 2.52-2.32 (m, 2H), 2.16-2.07 (m, 1H), 1.87-1.50 (m, 4H), 1.40-1.25 (m, 1H); *syn/anti* = 99/1; ee = 99%; HPLC (Chiralpak AS-H, i-Propanol/Hexane = 5/95, flow rate 1 mL/min, λ = 238 nm): t_{minor} = 14.3 min, t_{major} = 25.5 min.

10. **(R)-Tetrahydro-3-((R)-2-nitro-1-phenylethyl)thiopyran-4-one 4h**⁵



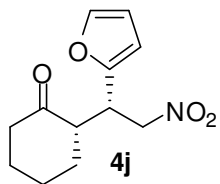
¹H NMR (400 MHz, CDCl₃) δ 7.37-7.26 (m, 3H), 7.21-7.16 (m, 2H), 4.96 (dd, J = 12.4 and 4.8 Hz, 1H), 4.64 (dd, J = 12.4 and 10.0 Hz, 1H), 4.20-4.10 (m, 1H), 3.87-3.68 (m, 2H), 3.70 (dd, J = 11.2 and 5.2 Hz, 1H), 3.27 (dd, J = 11.2 and 10.0 Hz, 1H), 2.93-2.83 (m, 1H), 2.73-2.61 (m, 1H), 2.60-2.53 (m, 1H); *syn/anti* = 96/4; ee = 92%; HPLC (Chiralpak AS-H, i-Propanol/Hexane = 40/60, flow rate 0.5 mL/min, λ = 254 nm): t_{minor} = 21.8 min, t_{major} = 27.7 min.

11. **(R)-Tetrahydro-3-((R)-2-nitro-1-phenylethyl)pyran-4-one 4i**⁵



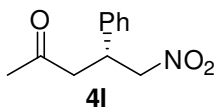
¹H NMR (400 MHz, CDCl₃) δ 7.37-7.26 (m, 3H), 7.21-7.16 (m, 2H), 4.96 (dd, J = 12.4 and 4.8 Hz, 1H), 4.64 (dd, J = 12.4 and 10.0 Hz, 1H), 4.20-4.10 (m, 1H), 3.87-3.68 (m, 2H), 3.70 (dd, J = 11.2 and 5.2 Hz, 1H), 3.27 (dd, J = 11.2 and 10.0 Hz, 1H), 2.93-2.83 (m, 1H), 2.73-2.61 (m, 1H), 2.60-2.53 (m, 1H); *syn/anti* 94/6; ee = 93%; HPLC (Chiralpak AS-H, i-Propanol/Hexane = 50/50, flow rate 0.5 mL/min, λ = 254 nm): t_{minor} = 18.7 min, t_{major} = 22.7 min.

12. **(S)-2-((S)-1-(furan-2-yl)-2-nitroethyl)cyclohexanone 4j**⁷



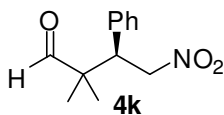
¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.34 (d, J = 1.2 Hz, 1H), 6.28 (dd, J = 2.8, 2.1 Hz, 1H), 6.17 (dd, 1H), 4.78 (dd, J = 12.5 and 4.8 Hz, 1H), 4.67 (dd, J = 12.5 and 9.2 Hz, 1H), 3.97 (dt, J = 9.1, 4.7 Hz, 1H), 2.78-2.71 (m, 1H), 2.49-2.44 (m, 1H), 2.40-2.32 (m, 1H), 2.13-2.07 (m, 1H), 1.86-1.82 (m, 1H), 1.79-1.73 (m, 1H), 1.71-1.61 (m, 2H), 1.33-1.23 (m, 1H). *syn/anti* 92/8; ee = 80%; HPLC (Chiralpak AS-H, i-Propanol/Hexane = 10/90, flow rate 0.7 mL/min, λ = 220 nm): t_{major} = 14.4 min, t_{major} = 17.6 min.

13. **(R)-5-nitro-4-phenylpentan-2-one 2l**⁸



¹H NMR (400 MHz, CDCl₃) δ 7.38-7.20 (m, 5H), 4.69 (dd, *J* = 12.4 and 6.8 Hz, 1H), 4.60 (dd, *J* = 12.4 and 7.6 Hz, 1H), 4.04-3.96 (m, 1H), 2.92 (d, *J* = 7.2 Hz, 2H), 2.12 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 205.3, 138.8, 129.1, 127.9, 127.4, 79.4, 46.1, 39.0, 30.4; ee = 14%; HPLC (Chiralpak AS-H, i-Propanol/Hexane = 20/80, flow rate 0.5 mL/min, λ = 254 nm): t_{minor} = 30.4 min, t_{major} = 41.2 min.

14. **(R)-2,2-dimethyl-4-nitro-3-phenylbutanal 4m**⁵



¹H NMR (400 MHz, CDCl₃): δ 9.50 (s, 1H), 7.40-7.15 (m, 5H), 4.83 (dd, *J* = 13.0 and 11.4 Hz, 1H), 4.67 (dd, *J* = 13.0 and 4.0 Hz, 1H), 3.76 (dd, *J* = 11.4 and 4.0 Hz, 1H), 1.11 (s, 3H), 0.98 (s, 3H). ee = 76%; HPLC (Chiralpak AS-H, i-Propanol/Hexane = 5/95, flow rate 0.5 mL/min, λ = 238 nm): t_{major} = 32.2 min, t_{major} = 33.5 min.

References:

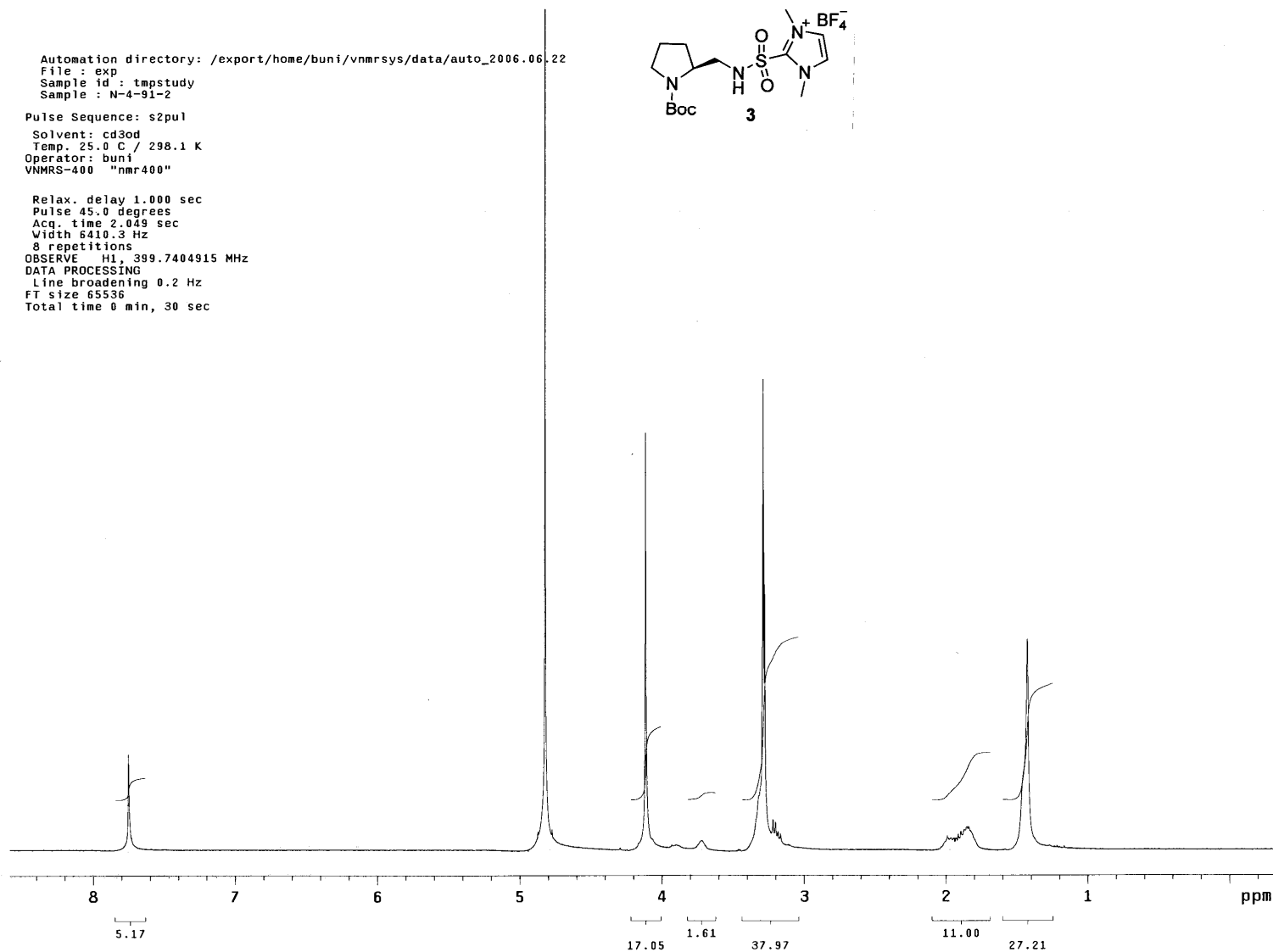
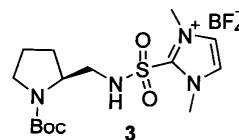
1. Diltz, S.; Aguirre, G.; Ortega, F.; Walsh, P. J. *Tetrahedron: Asymmetry* **1997**, 8, 3559
2. Ishii, T.; Fujioka, S.; Sekiguchi, Y.; Kotsuki, H. *J. Am. Chem. Soc.* **2004**, 126, 9558.
3. Saraswathy, V. G.; Sankararaman, S. *J. Org. Chem.* **1995**, 60, 5024.
4. Betancort, J. M.; Sakthivel, K.; Thayumanavan, R.; Tanaka, F.; Barbas III, C. F. *Synthesis* **2004**, 1509.
5. Wang, J.; Li, H.; Lou, B.; Zu, L.; Guo, H.; Wang, W. *Chem. Eur. J.* **2006**, 12, 4321.
6. Cao, C-L.; Ye, M-C.; Sun, X-L.; Tang, Y. *Org. Lett.* **2006**, 8, 2901.
7. Pansare, S. V.; Pandya, K. *J. Am. Chem. Soc.* **2006**, 128, 9624-9625.
8. Halland, N.; Hazell, R. G.; Jørgensen, K. A. *J. Org. Chem.* 2002, **67**, 8331.

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Total time 0 min, 30 sec



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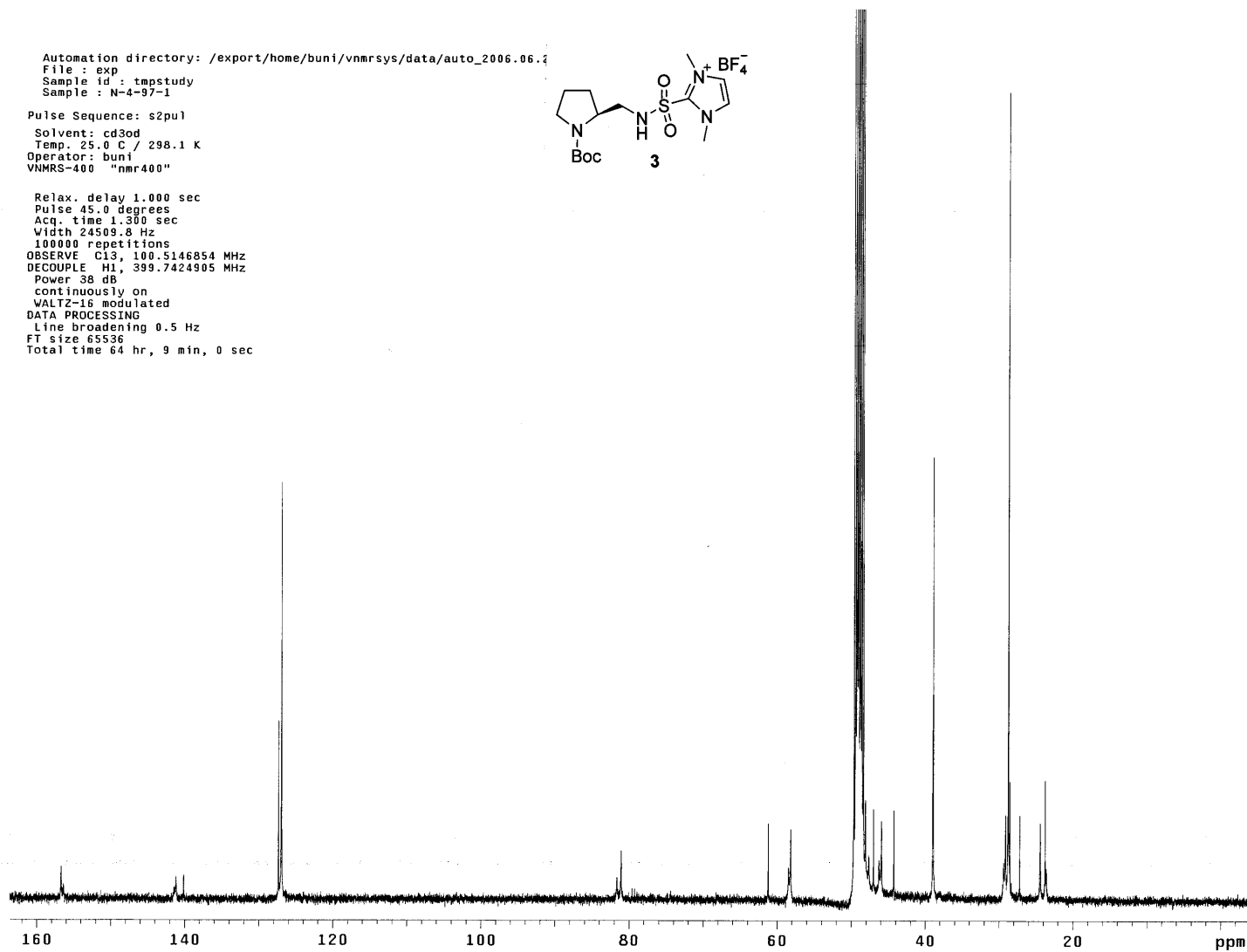
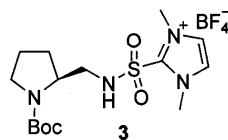
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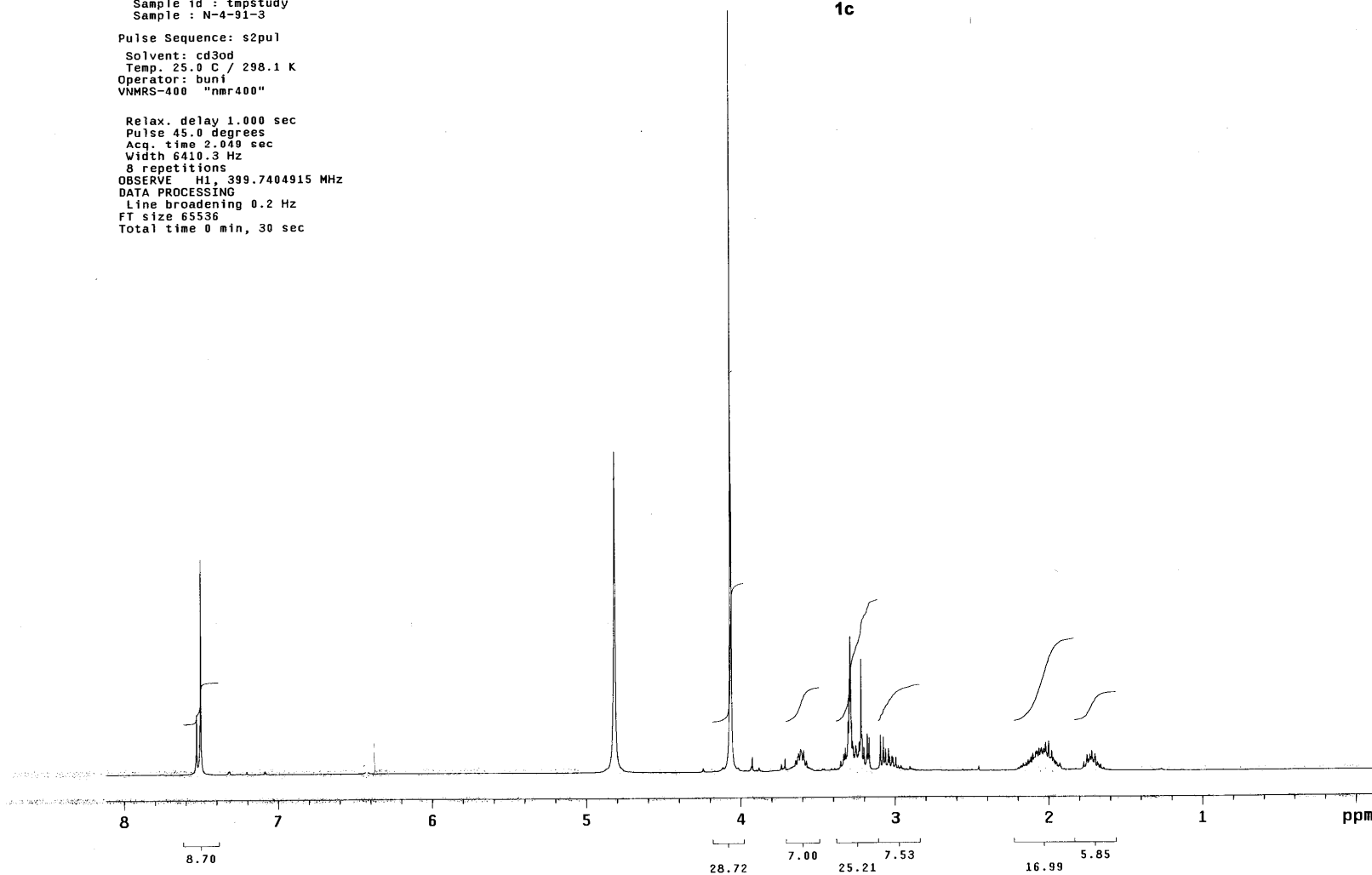
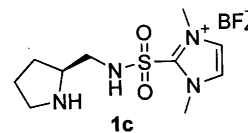
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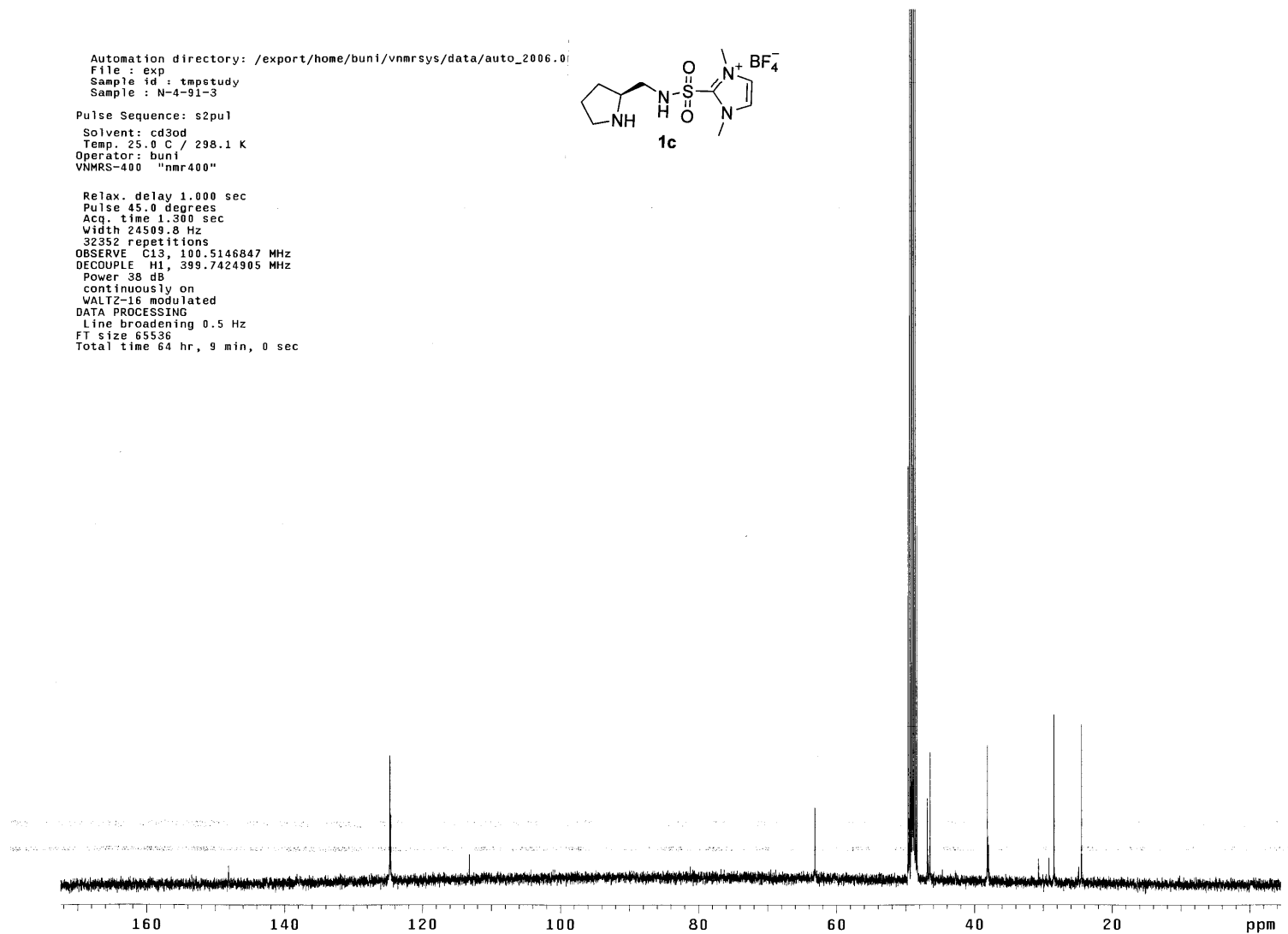
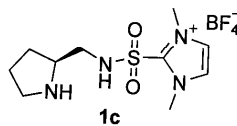
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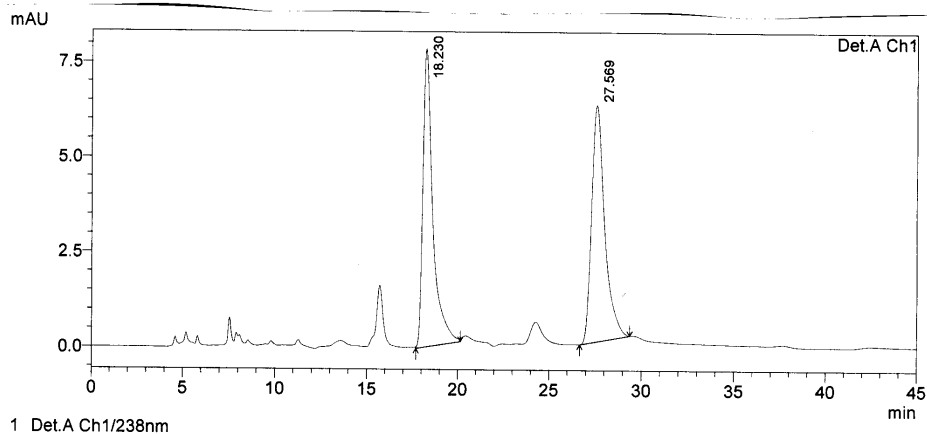
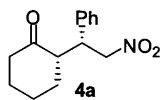


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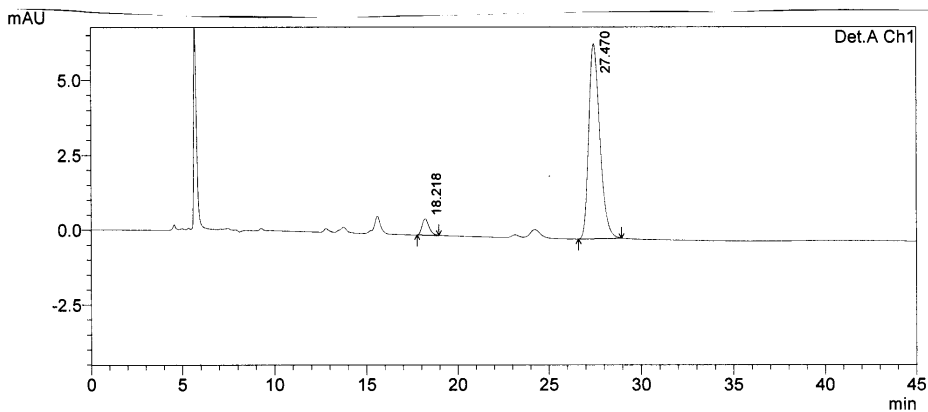
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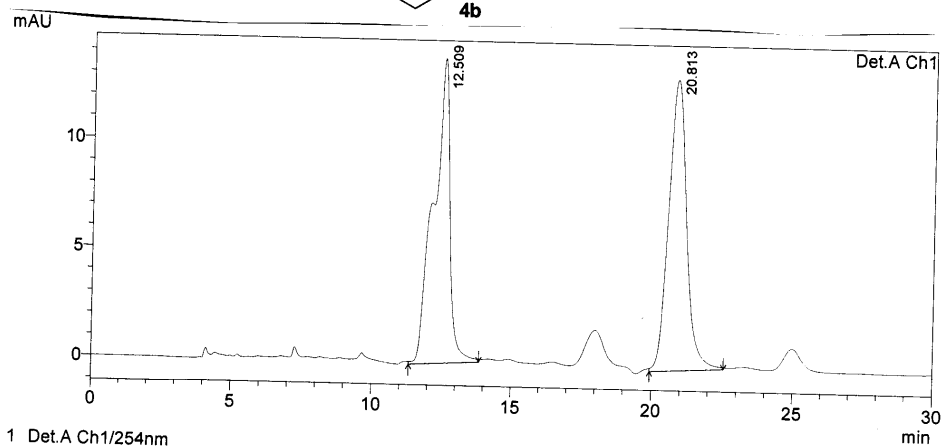
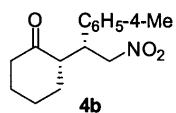
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Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.230	297529	7843	49.223	55.775
2	27.569	306918	6218	50.777	44.225
Total		604447	14061	100.000	100.000



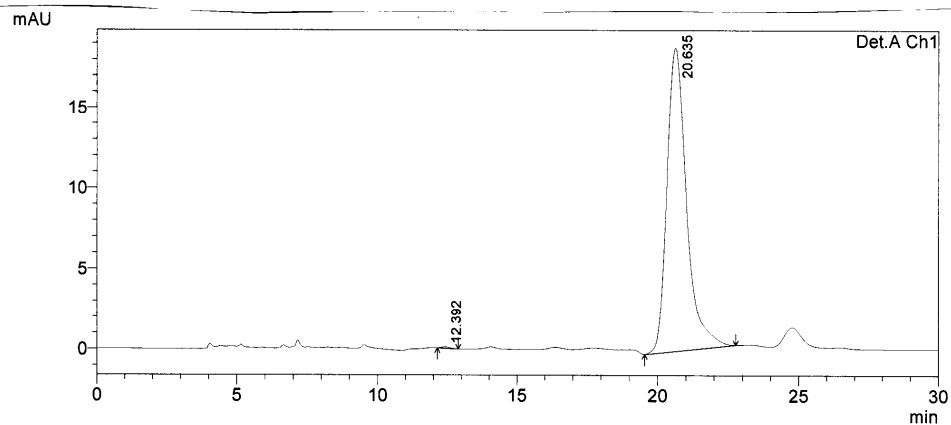
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.218	14410	543	5.035	7.704
2	27.470	271767	6502	94.965	92.296
Total		286177	7044	100.000	100.000



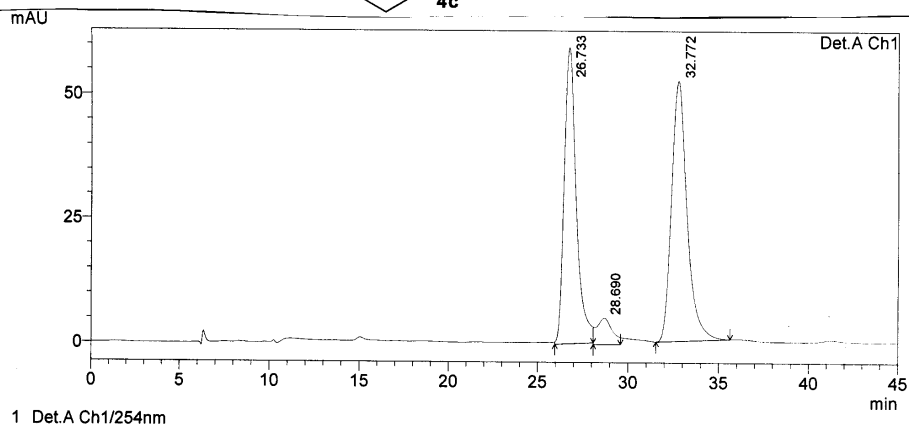
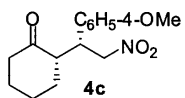
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.509	570295	13906	49.261	51.167
2	20.813	587399	13272	50.739	48.833
Total		1157694	27178	100.000	100.000



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.392	1589	82	0.174	0.435
2	20.635	910061	18852	99.826	99.565
Total		911651	18935	100.000	100.000

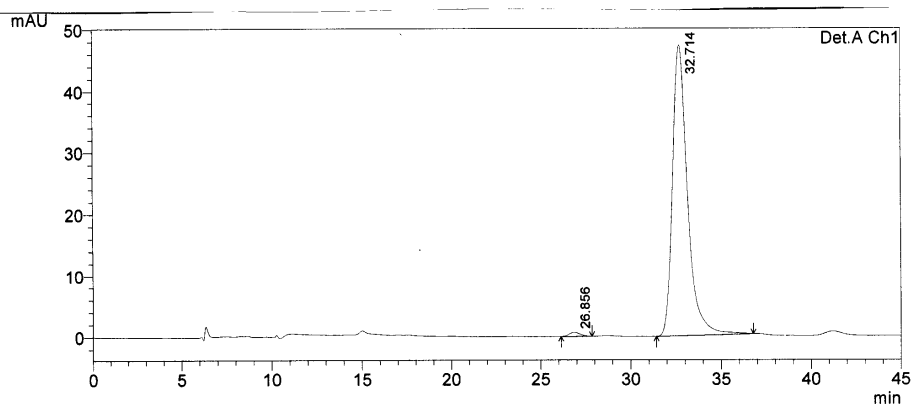


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.733	2761327	59448	44.584	50.786
2	28.690	315930	5264	5.101	4.497
3	32.772	3116277	52345	50.315	44.718
Total		6193534	117057	100.000	100.000

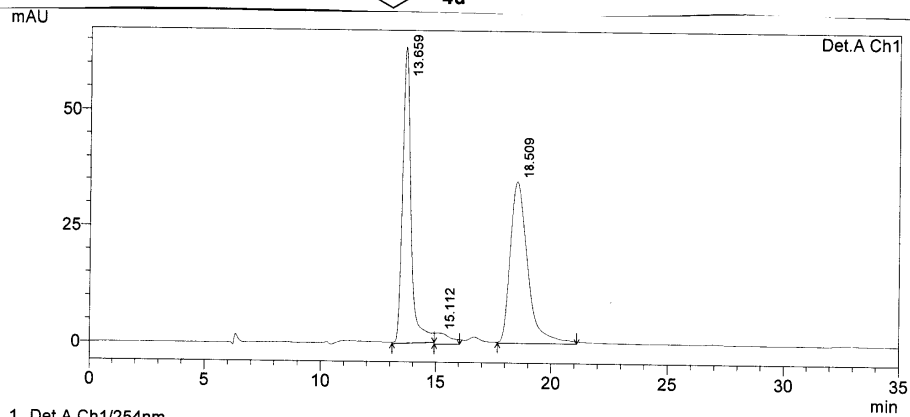
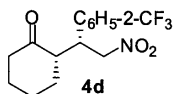


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

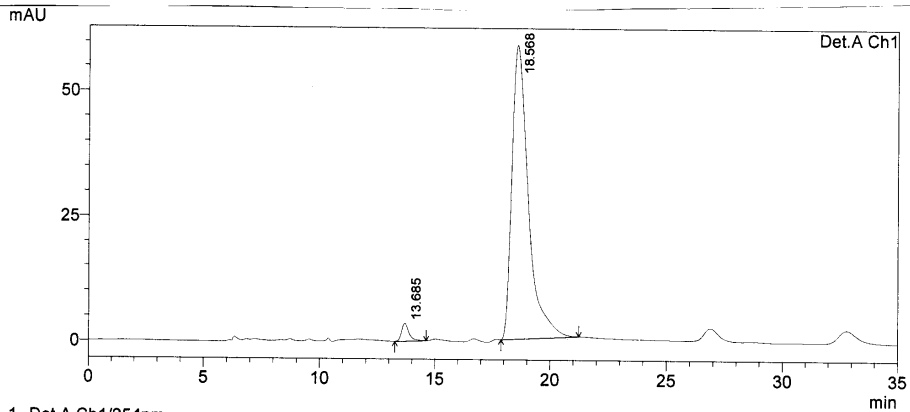
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.856	27003	649	0.985	1.355
2	32.714	2713152	47264	99.015	98.645
Total		2740155	47913	100.000	100.000



1 Det.A Ch1/254nm

Detector A Ch1 254nm

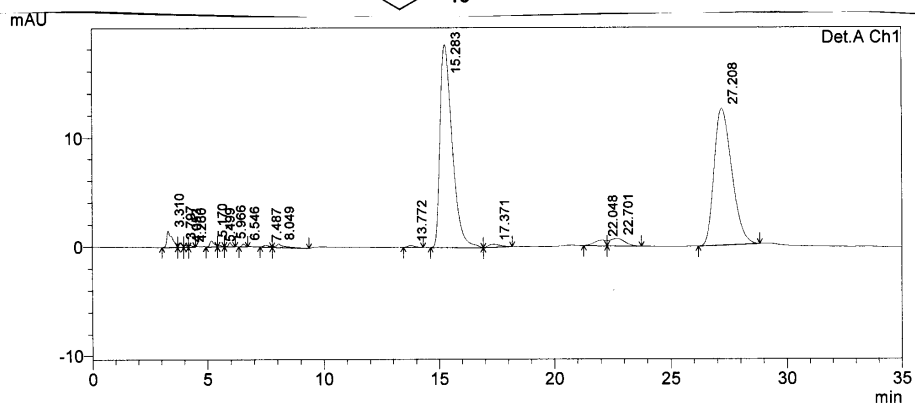
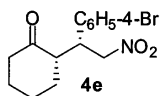
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.659	1637430	63585	45.840	63.250
2	15.112	113248	2331	3.170	2.319
3	18.509	1821380	34613	50.990	34.431
Total		3572059	100529	100.000	100.000



1 Det.A Ch1/254nm

Detector A Ch1 254nm

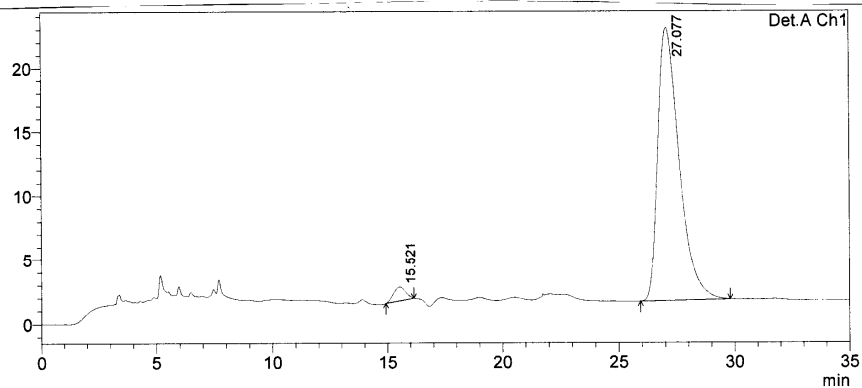
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.685	78532	3533	2.632	5.660
2	18.568	2905428	58898	97.368	94.340
Total		2983960	62432	100.000	100.000



1 Det.A Ch1/254nm

PeakTable

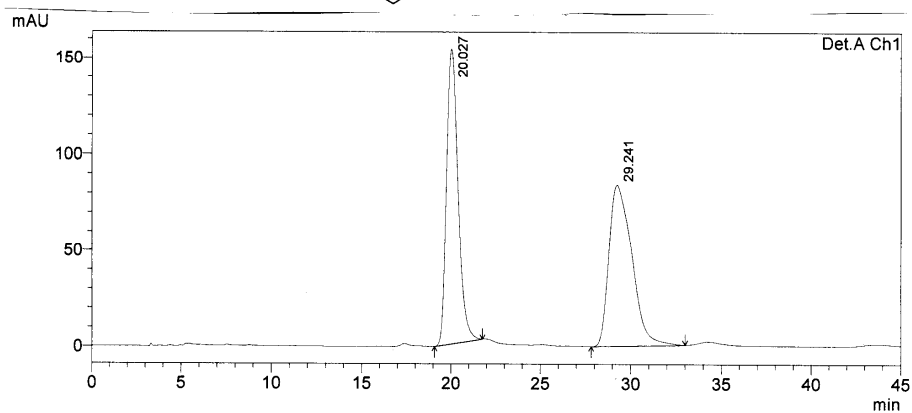
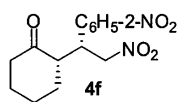
Peak#	Ret. Time	Area	Height	Area %	Height %
12	15.283	681347	18507	46.543	50.489
13	17.371	10238	287	0.699	0.783
14	22.048	17882	499	1.221	1.361
15	22.701	30042	667	2.052	1.821
16	27.208	664036	12538	45.360	34.205



1 Det.A Ch1/254nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.521	39403	1083	2.813	4.831
2	27.077	1361455	21332	97.187	95.169
Total		1400857	22415	100.000	100.000

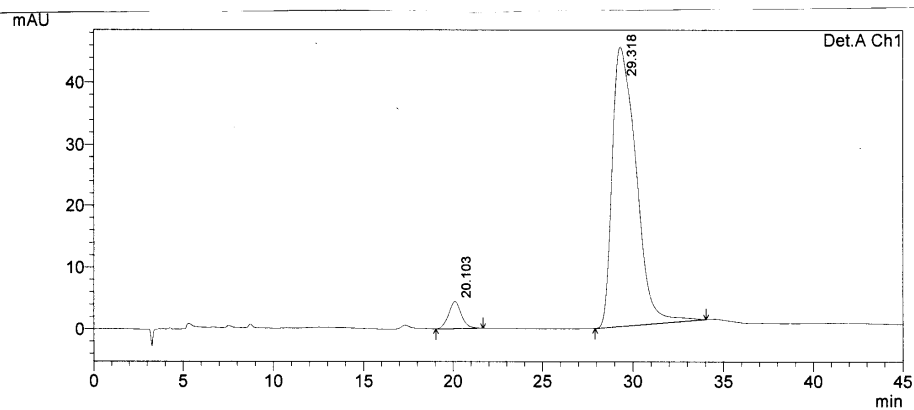


1 Det. A Ch1/238nm

PeakTable

Detector A Ch1 238nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.027	6905169	153658	48.240	64.635
2	29.241	7409114	84073	51.760	35.365
Total		14314284	237731	100.000	100.000

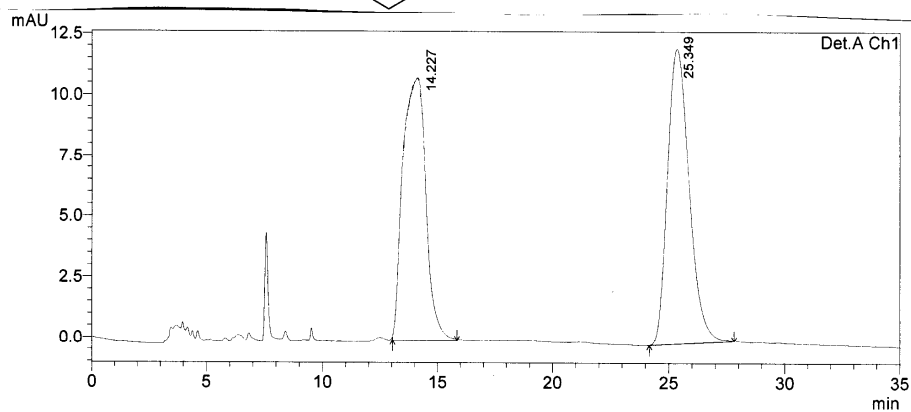
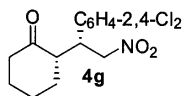


1 Det. A Ch1/238nm

PeakTable

Detector A Ch1 238nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.103	219080	4400	5.010	8.853
2	29.318	4153882	45301	94.990	91.147
Total		4372961	49701	100.000	100.000

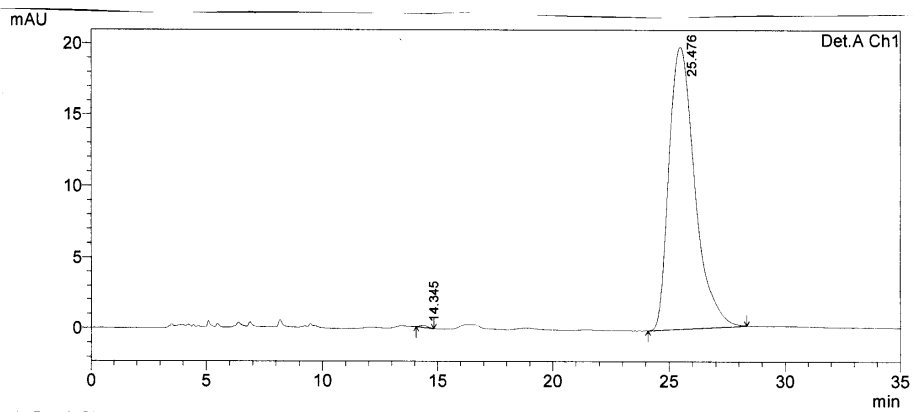


1 Det.A Ch1/238nm

PeakTable

Detector A Ch1 238nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.227	681543	10129	46.319	45.446
2	25.349	789869	12159	53.681	54.554
Total		1471412	22288	100.000	100.000

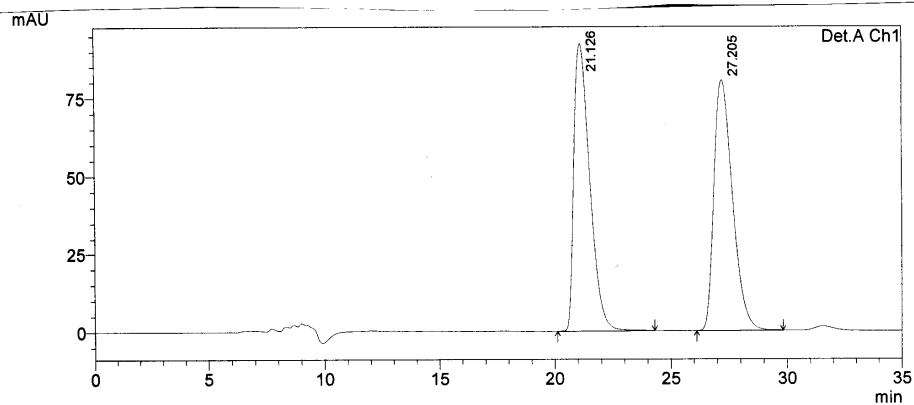
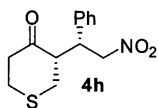


1 Det.A Ch1/238nm

PeakTable

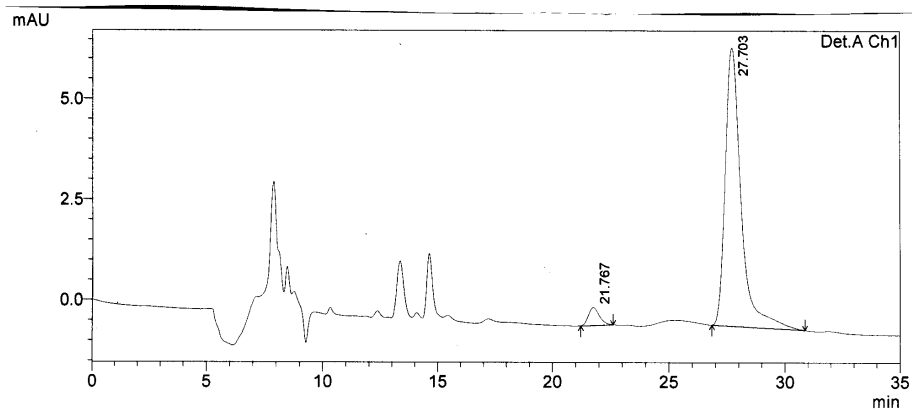
Detector A Ch1 238nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.345	2966	132	0.193	0.661
2	25.476	1531692	19808	99.807	99.339
Total		1534658	19940	100.000	100.000



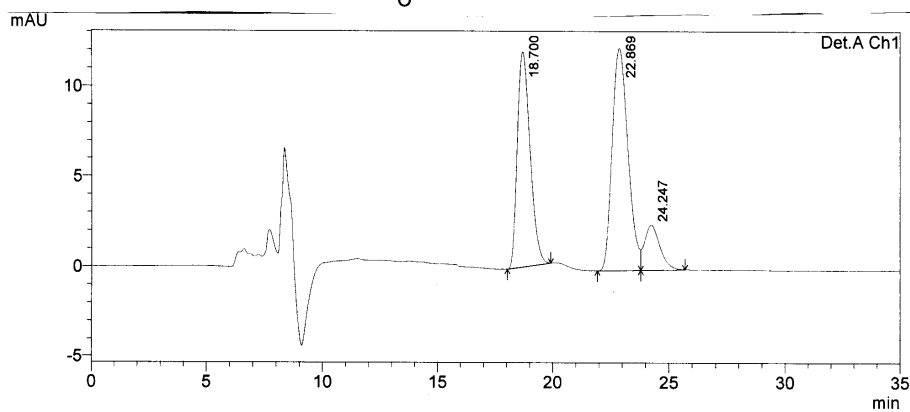
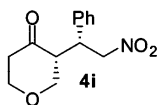
1 Det.A Ch1/254nm

PeakTable					
Detector A Ch1 254nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.126	4390428	92368	49.640	53.502
2	27.205	4454104	80275	50.360	46.498
Total		8844531	172643	100.000	100.000



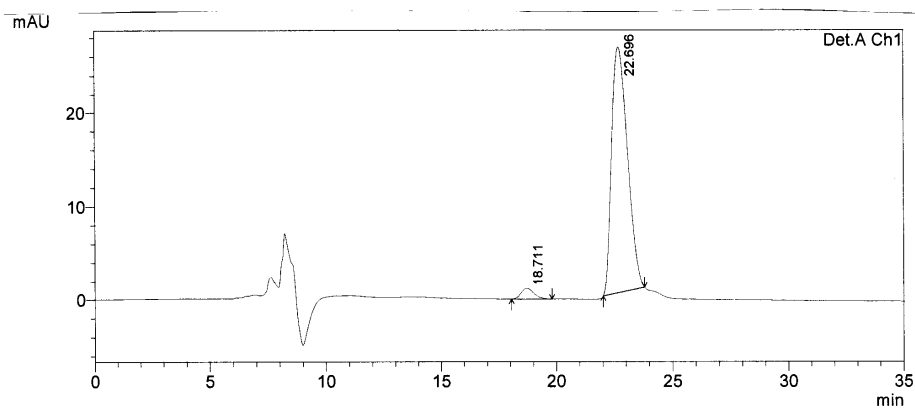
1 Det.A Ch1/254nm

PeakTable					
Detector A Ch1 254nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.767	14504	443	4.214	6.005
2	27.703	329677	6937	95.786	93.995
Total		344180	7381	100.000	100.000



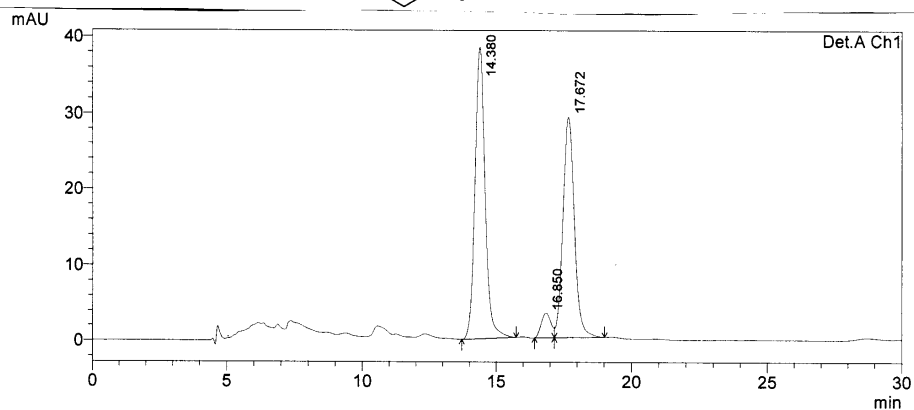
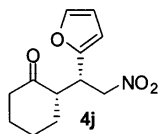
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.700	460289	11901	39.765	44.590
2	22.869	582657	12298	50.337	46.078
3	24.247	114563	2491	9.897	9.332
Total		1157509	26689	100.000	100.000



PeakTable

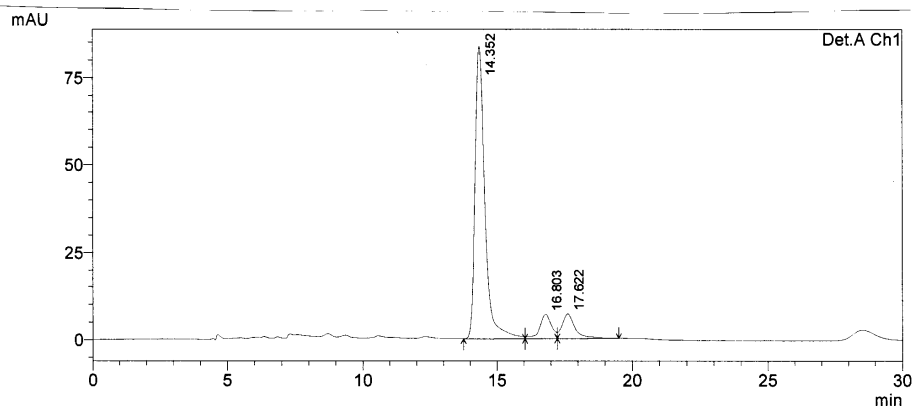
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.711	43172	1136	3.331	4.133
2	22.696	1252943	26347	96.669	95.867
Total		1296115	27483	100.000	100.000



1 Det.A Ch1/220nm

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.380	1009006	38356	51.804	54.217
2	16.850	80865	3270	4.152	4.623
3	17.672	857855	29119	44.044	41.160
Total		1947727	70746	100.000	100.000

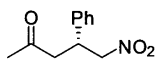


1 Det.A Ch1/220nm

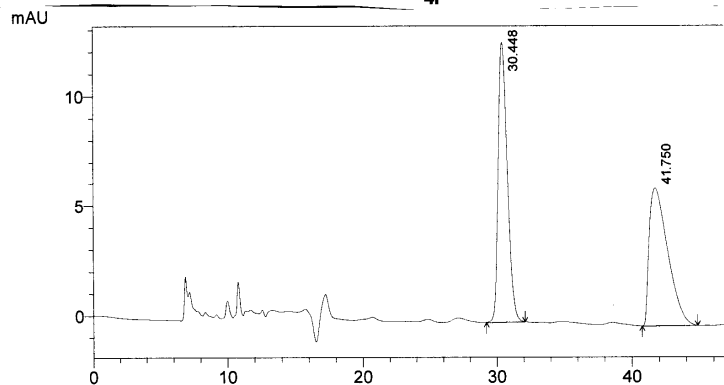
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.352	2127030	83677	82.889	85.833
2	16.803	206996	6833	8.066	7.009
3	17.622	232091	6978	9.044	7.158
Total		2566117	97489	100.000	100.000



4l

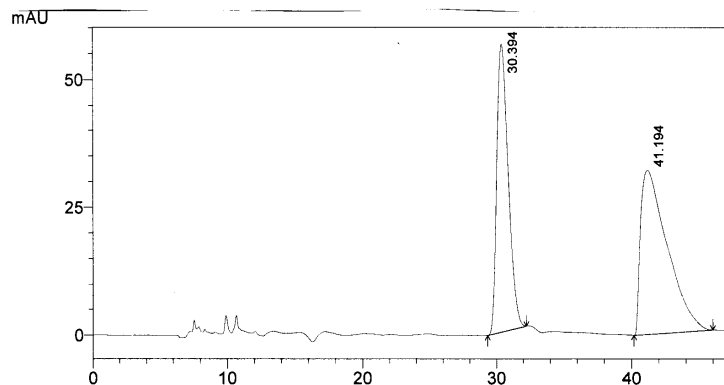


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.448	604929	12729	50.402	67.063
2	41.750	595282	6252	49.598	32.937
Total		1200210	18981	100.000	100.000

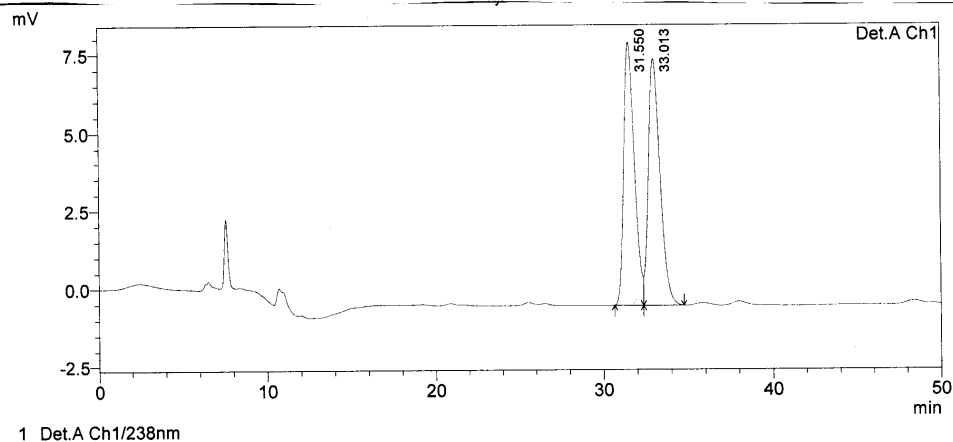
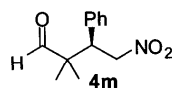


1 Det.A Ch1/254nm

PeakTable

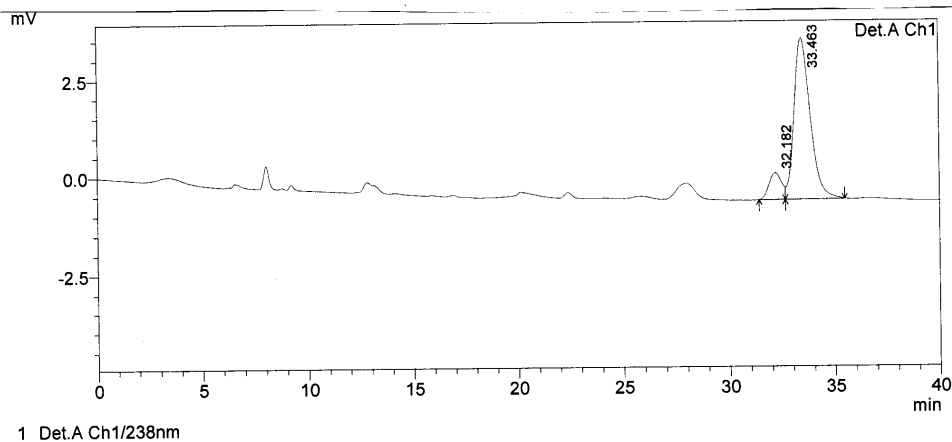
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.394	3345902	56251	43.237	63.719
2	41.194	4392597	32028	56.763	36.281
Total		7738499	88279	100.000	100.000



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.550	366765	8420	49.202	51.618
2	33.013	378665	7892	50.798	48.382
Total		745430	16311	100.000	100.000



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.182	28291	682	11.390	14.192
2	33.463	220104	4123	88.610	85.808
Total		248395	4805	100.000	100.000