Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry


# Asymmetric Michael Reactions Catalyzed by a Highly Efficient and Recyclable Quaternary Ammonium Ionic Liquid-Supported Organocatalyst in Aqueous Media

Subrata Ghosh, Yupu Qiao, Bukuo Ni* and Allan D. Headley*

Department of Chemistry, Texas A&M University-Commerce

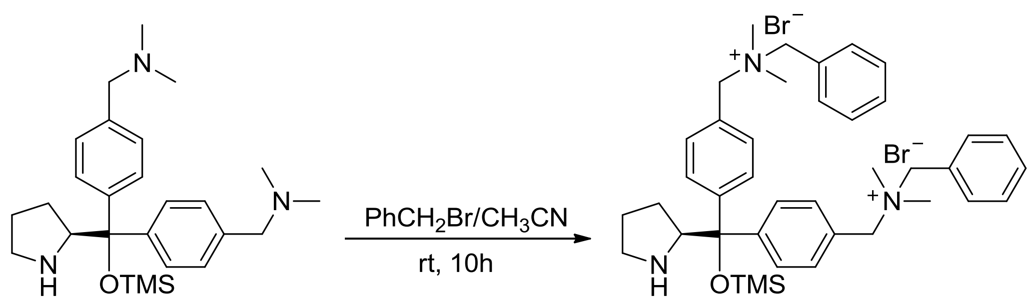
Commerce, TX 75429-3001, USA

E-Mail: allan.headley@tamuc.edu; bukuo.ni@tamuc.edu

Supporting Information

**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. $^{1}$H and $^{13}$C NMR spectra were recorded on the Bruker Avance 400. The high resolution mass spectra were analyzed by using ESI-TOF high-acc from the Scripps Research Institute. All the compounds synthesized (shown in Table 3) in the manuscript are known compounds.[1] Their relative and absolute configurations of the products were determined by comparison with the known $^{1}$H and $^{13}$C NMR, chiral HPLC analysis, and optical rotation values.

**Synthesis of the catalyst1:**



**Catalyst 1**

Benzyl bromide (521mg, 3 mmol) was added dropwise to the solution of diarylprolinol silyl ether (670 mg, 1.5 mmol) in $CH_3CN$ (10 mL). After addition, the reaction mixture was continued to stirring overnight. The reaction mixture was concentrated and the crude product was washed with diethyl ether (5x10 mL) to give the product **1** as a solid (1.13g, 95% yield). $[\alpha]_D^{25}$ = -4.8 (c = 0.5, MeOH). $^{1}$H NMR (400 MHz, MeOH) δ = 7.72-6.97 (m, 18H), 4.56-4.52 (dd, $J$ = 18Hz, 10Hz, 8H), 3.88-3.57 (m, 2H), 2.88-2.76 (m, 12H), 2.42-2.26 (m, 3H), 2.00-1.92 (m, 2H), 1.74-1.72 (m, 1H), 1.32-1.17 (m, 1H), 0.66 (s, 1H), -0.01--0.27 (m, 9H). $^{13}$C NMR (100 MHz, MeOH) δ = 135.5, 135.4, 135.3, 135.2, 135.2, 134.3, 134.2, 132.8, 132.6, 132.3, 131.3, 131.2, 130.1, 130.0, 129.6, 128.9, 86.9, 84.8, 84.4, 70.3, 69.8, 64.2, 56.8, 48.3, 31.1, 29.0, 26.5, 25.8, 3.2, 3.2, 1.8. HRMS (ESI-TOF high-acc) m/z calcd for $C_{40}H_{55}N_3OSi_2^+$ (M-2Br$^-$): 621.4103, found: 621.4102.

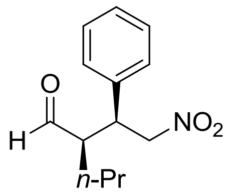
**The general procedure for the Michael addition reactions of aldehydes to nitroolefines**

In a 5 mL flask was added the catalyst **1** (0.02 mmol), acid (0.12mmol), nitroolefin (0.4 mmol) water (0.5 mL) and aldehyde (0.8 mmol). The reaction mixture was stirred for the listed hours and extracted with $Et_2O$:Hexane = 1:8 (v/v). The crude product was purified by flash column chromatography (eluent: hexane/ethyl acetate) to give the Michael Addition products shown in Table 2.

**Experimental procedure for catalyst 1 recycling on water**

*n*-Pentanal (0.0689g, 0.8 mmol) was added to a solution of catalyst **1** (15.6 mg, 0.02 mmol), *trans*-β-nitroolefins (59.7mg, 0.4 mmol) and IL-Benzoic acid (48.5 mg, 0.12mmol) on water (0.5 mL) at room temperature for 18 h. The reaction mixture was extracted with a solvent mixture of ethyl ether-hexane (1:8, 2 x 3 mL). The organic phase was combined and concentrated in vacuum to give the crude product, which was purified by flash column chromatography (silica gel, hexane/AcOEt = 5/1) to afford the Michael adduct **2a** (99%) with enantioselectivity (99% *ee*) and diastereoselectivity (*syn*/*anti* = 96/4). The recovered aqueous phase was used directly for the next cycle by addition of new reactants *n*-Pentanal (0.0689g, 0.8 mmol) and *trans*-β-nitroolefins (59.7mg, 0.4 mmol). The reaction mixture was stirred for the listed time in Table 3.

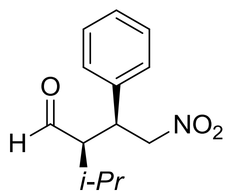
**(R)-2-((S)-2-nitro-1-phenylethyl) pentanal**



**2a**

Yield: 93.2mg, 99%. $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 9.70 (d, *J* = 2.8 Hz, 1H), 7.38-7.15 (m, 5H), 4.73-4.62 (m, 2H), 3.78 (dt, *J* = 7.2 and 5.2 Hz, 1H), 2.74-2.67 (m, 1H), 1.54-1.12 (m, 4H), 0.80 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl3) δ = 203.3, 136.7, 128.8, 127.8, 127.83, 78.3, 53.5, 42.9, 29.1, 19.5, 13.7. HPLC: Chiralcel OD-H column, 80:20 hexane:isopropanol, flow rate 1.0 mL/min, syn/anti= 96:4, 99% ee, Syn: $t_R$= 11.0 min (minor), $t_R$=14.6 min (major).

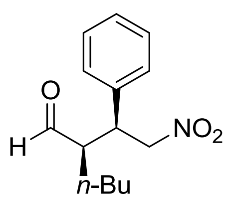
**(2R,3S)-2-isopropyl-4-nitro-3-phenylbutanal**



**2b**

Yield: 68.7mg, 73%. $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 9.93 (d, *J* = 2.0 Hz, 1H), 7.37-7.17 (m, 5H), 4.69-4.55 (m, 2H), 3.90 (dt, *J* = 10.4 and 4.4 Hz, 1H), 2.80-2.74 (m, 1H), 1.76-1.68 (m, 1H), 1.10 (d, *J* = 7.2 Hz, 3H), 0.89(d, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 204.3, 137.1, 129.1, 128.4, 128.1, 127.9, 79.0, 58.8, 41.9, 27.9, 21.6, 17.0. HPLC: Chiralcel IC column, 80:20 hexane:isopropanol, flow rate 0.8 mL/min, syn/anti= 98:2, 99% ee, Syn: $t_R$= 17.3 min (minor), $t_R$=18.2 min (major).

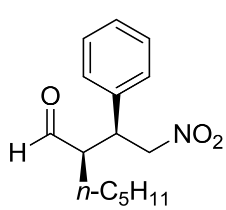
**(R)-2-((S)-2-nitro-1-phenylethyl)hexanal**



**2c**

Yield: 98.7mg, 99%. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.70 (d, *J* = 2.8 Hz, 1H), 7.37-7.15 (m, 5H), 4.73-4.61 (m, 2H), 3.77 (dt, *J* = 10.0 and 4.2 Hz, 1H), 2.73-2.66 (m, 1H), 1.68-1.06 (m, 6H), 0.78 (t, *J* = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl3) δ = 203.3, 136.8, 129.1, 128.1, 128.0, 78.4, 53.8, 43.1, 28.5, 27.0, 22.4, 13.6. HPLC: Chiralcel OD-H column, 80:20 hexane:isopropanol, flow rate 1.0 mL/min, syn/anti= 98:2, 99% ee, Syn: $t_R$= 10.2 min (minor), $t_R$=12.8 min (major).

**(R)-2-((S)-2-nitro-1-phenylethyl)heptanal**

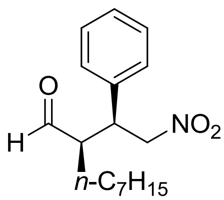


**2d**

Yield: 103.2mg, 98%. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.69 (d, *J* = 2.4 Hz, 1H), 7.36-7.15 (m, 5H), 4.73-4.60 (m, 2H), 3.78 (dt, *J* = 9.2 and 5.6 Hz, 1H), 2.74-

2.66 (m, 1H), 1.52-1.04 (m, 8H), 0.80 (t, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl3) δ = 203.2, 136.8, 128.9, 128.0, 127.9, 78.4, 53.8, 43.0, 31.4, 27.2, 25.9, 22.1, 13.7. HPLC: Chiralcel OD-H column, 85:15 hexane:isopropanol, flow rate 1.0 mL/min, syn/anti= 98:2, 99% ee, Syn: $t_R$= 11.4 min (minor), $t_R$=14.9 min (major).

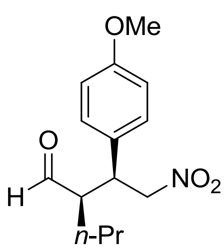
**(R)-2-((S)-2-nitro-1-phenylethyl)nonanal**



**2e**

Yield: 109.6mg, 94%. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, $J$ = 2.8 Hz, 1H), 7.37-7.14 (m, 5H), 4.74-4.55 (m, 2H), 3.78 (dt, $J$ = 9.6 and 5.2 Hz, 1H), 2.74-2.66 (m, 1H), 1.64-1.04 (m, 12H), 0.84 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl3) δ = 203.2, 136.7, 129.0, 128.0, 127.9, 78.4, 53.8, 43.0, 31.5, 29.2, 28.7, 27.2, 26.2, 22.4, 14.0. HPLC: Chiralcel OD-H column, 90:10 hexane:isopropanol, flow rate 1.0 mL/min, syn/anti= 98:2, 99% ee, Syn: $t_R$= 12.9 min (minor), $t_R$=17.7 min (major).

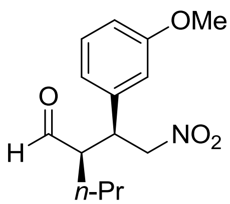
**(R)-2-((S)-1-(4-methoxyphenyl)-2-nitroethyl)pentanal**



**2f**

Yield: 92.3mg, 87%. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.70 (d, $J$ = 2.8 Hz, 1H), 7.08 (d, $J$ = 8.8 Hz, 2H), 6.87 (d, $J$ = 8.8 Hz, 2H), 4.69-4.56 (m, 2H), 3.79 (s, 3H), 3.75-2.62 (m, 1H), 2.68-2.62 (m, 1H), 1.53-1.14 (m, 4H), 0.81 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl3) δ= 203.4, 159.1, 129.2, 129.0, 128.5, 114.4, 78.6, 55.1, 53.9, 42.4, 29.3, 19.7, 13.9. HPLC: Chiralcel IC column, 80:20 hexane:isopropanol, flow rate 0.8 mL/min, syn/anti= 94:6, 99% ee, Syn: $t_R$= 24.2 min (minor), $t_R$=27.6 min (major).

**(R)-2-((S)-1-(3-methoxyphenyl)-2-nitroethyl)pentanal**

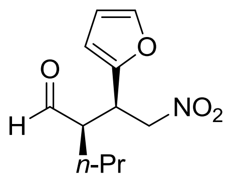


**2g**

Yield: 101.9mg, 96%. $^1$H NMR (400 MHz, $CDCl_3$) δ= 9.69 (d, J=2.8Hz, 1H), 7.28-7.23 (m, 1H), 6.84-6.71 (m, 3H), 4.71-4.60 (m, 2H), 3.79 (s, 3H), 3.80-3.70 (m, 1H), 2.72-2.65, (m, 1H), 1.56-1.10 (m, 4H), 0.81 (t, $J$ = 7.2Hz, 3H);

$^{13}$C NMR (100 MHz, $CDCl_3$) δ= 203.0, 159.9, 138.4, 130.1, 120.1, 114.2, 112.9, 78.2, 55.2, 53.7, 43.1, 29.4, 19.7, 13.9. HPLC: Chiralcel OD-H column, 90:10 hexane:isopropanol, flow rate 1.0 mL/min, syn/anti= 95:5, 99% ee, Syn: $t_R$= 21.4 min (minor), $t_R$=48.0 min (major).

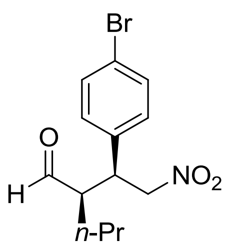
**(R)-2-((R)-1-(furan-2-yl)-2-nitroethyl)pentanal**



**2h**

Yield: 89.2mg, 99%. $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.69 (d, $J$ = 2.0Hz, 1H), 7.36 (d, $J$ = 2.4 Hz, 1H), 6.30 (d, $J$ = 3.6 and 2.4 Hz, 1H), 6.19 (d, $J$ = 3.2Hz, 1H), 4.75-4.63 (m, 2H), 4.01 (dt, $J$ = 8.8 and 5.2, 1H), 2.82-2.76 (m, 1H), 1.58-1.16 (m, 4H), 0.87 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl3) δ = 202.3, 150.1, 142.5, 110.3, 108.6, 76.0, 52.0, 36.9, 28.9, 19.8, 13.9. HPLC: Chiralcel OD-H column, 90:10 hexane:isopropanol, flow rate 0.8 mL/min, syn/anti= 99:1, 99% ee, Syn: $t_R$= 14.1 min (major), $t_R$=30.3 min (minor).

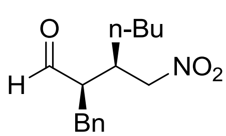
**(R)-2-((S)-1-(4-bromophenyl)-2-nitroethyl)pentanal**



**2i**

Yield: 118.1mg, 94%. $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.68 (d, $J$ = 2.4 Hz, 1H), 7.48 (d, $J$ = 8.0 Hz, 2H), 7.07 (d, $J$ = 8.0 Hz, 2H), 4.73-4.58 (m, 2H), 3.76 (dt, $J$ = 9.6 and 4.8 Hz, 1H), 2.72-2.65 (m, 1H), 1.52-1.12 (m, 4H), 0.81 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl3) δ = 202.8, 135.9, 132.2, 129.6, 122.0, 78.0, 53.4, 42.4, 29.4, 19.6, 13.8. HPLC: Chiralcel IC column, 80:20 hexane:isopropanol, flow rate 0.8 mL/min, syn/anti= 92:8, 99% ee, Syn: $t_R$= 19.1 min (minor), $t_R$=19.6 min (major).

**(2*R*, 3*R*)-2-benzyl-3-(nitromethyl)heptanal**

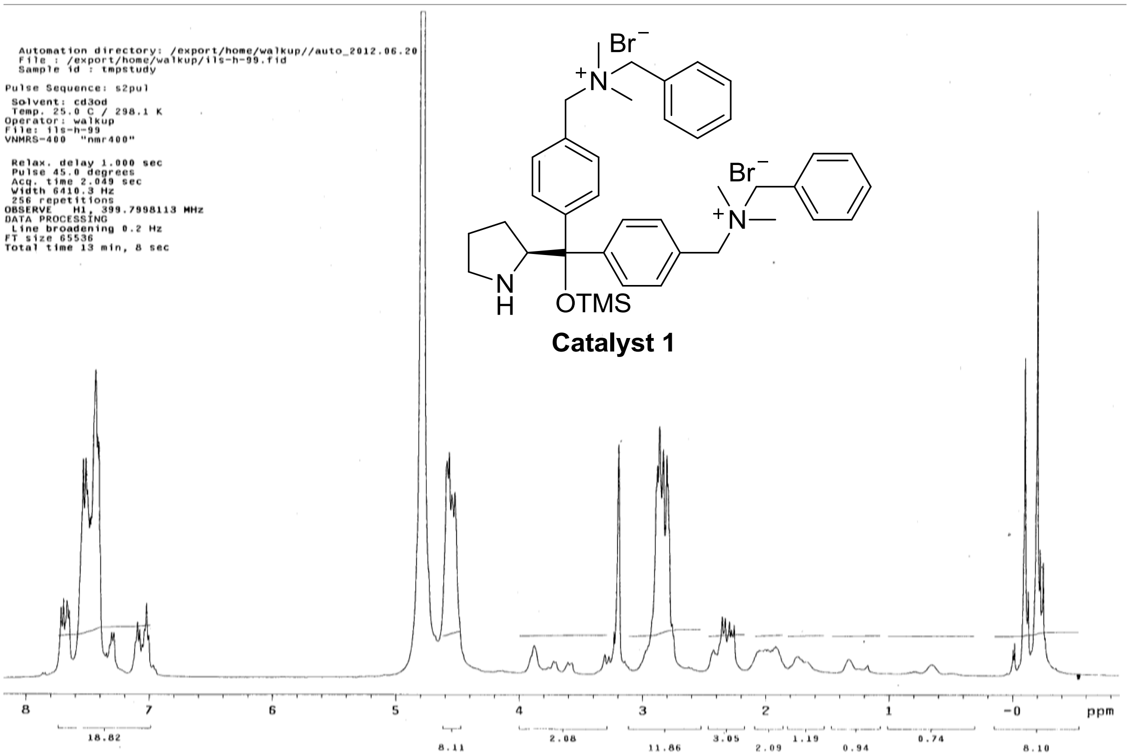


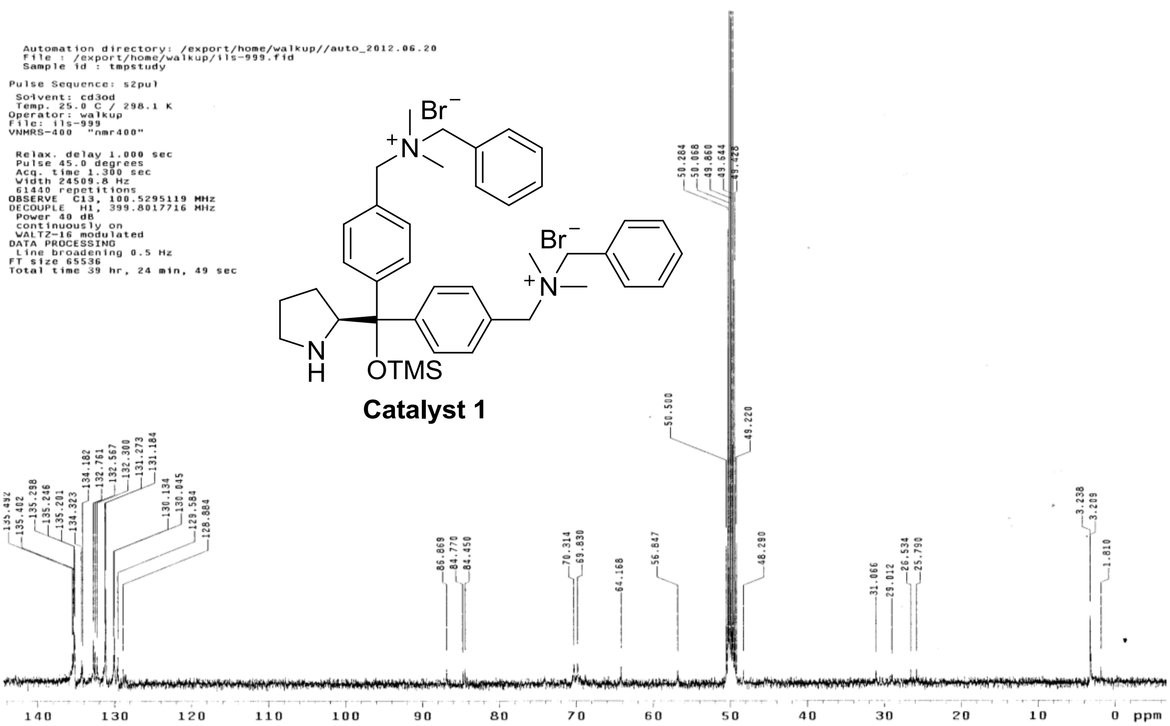
**2j**

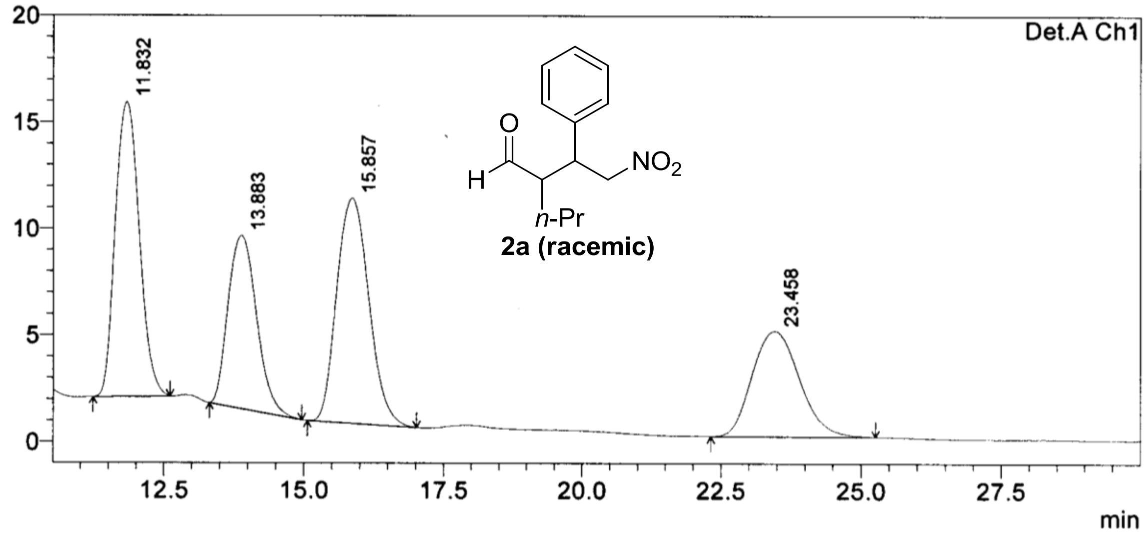
Yield: 79.0mg, 75%. $^1$H NMR (400 MHz, CDCl3) δ = 9.69 (d, $J$ = 0.8 Hz, 1H), 7.34-7.16 (m, 5H), 4.50-4.34 (m, 2H), 3.11-2.66 (m, 4H), 1.58-1.20 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H); $^{13}$C NMR (100MHz, CDCl3) δ = 202.4, 138.2, 128.9, 128.8, 126.8, 76.9, 54.1, 37.0, 31.5, 29.0, 28.9, 22.4, 13.8. HPLC: Chiralcel IC column, 90:10 hexane:isopropanol, flow rate 1.0 mL/min, syn/anti= 96:4, 99% ee, Syn: $t_R$= 11.5 min (minor), $t_R$=16.2 min (major).

**References:**

1. (a) A. Alexakis, O. Andrey, *Org. Lett.*, 2002, **4**, 3611. (b) J. M. Betancort, C. F. Barbas III, *Org. Lett.*, 2001, **3**, 3737. (c) W. Wang, J. Wang, H. Li, *Angew. Chem. Int. Ed.*, 2005, **44**, 1369. (d) L. Zu, J. Wang, H. Li, W. Wang, *Org. Lett.*, 2006, **8**, 3077. (e) B. Ni, Q. Zhang, A. D. Headley, *Green Chem.*, 2007, **9**, 737. (f) Q. Zhang, B. Ni, A. D. Headley, *etrahedron*, 2008, **64**, 5091. (g) J. Wu, B. Ni, A. D. Headley, *Org. Lett.*, 2009, **11**, 3354-3356. (h) S. Zhu, S. Yu, D. Ma, *Angew. Chem. Int. Ed.*, 2008, **47**, 545. (i) Z. Zheng, B. Perkins, B. Ni, *J. Am. Chem. Soc.*, 2010, **132**, 50.

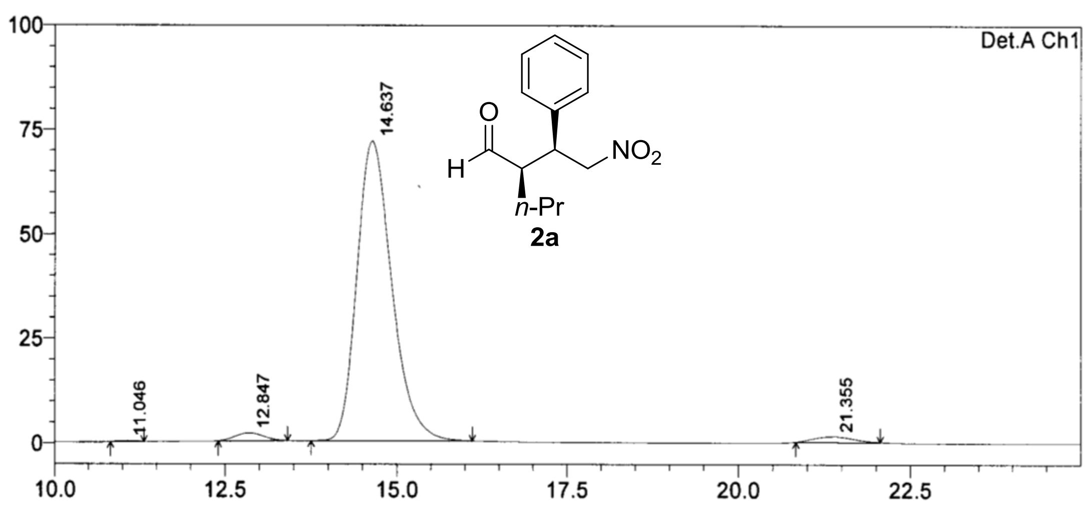

Br⁻
Br⁻
N
H
OTMS
Catalyst 1
ppm


Br⁻
Br⁻
N
H
OTMS
Catalyst 1
ppm



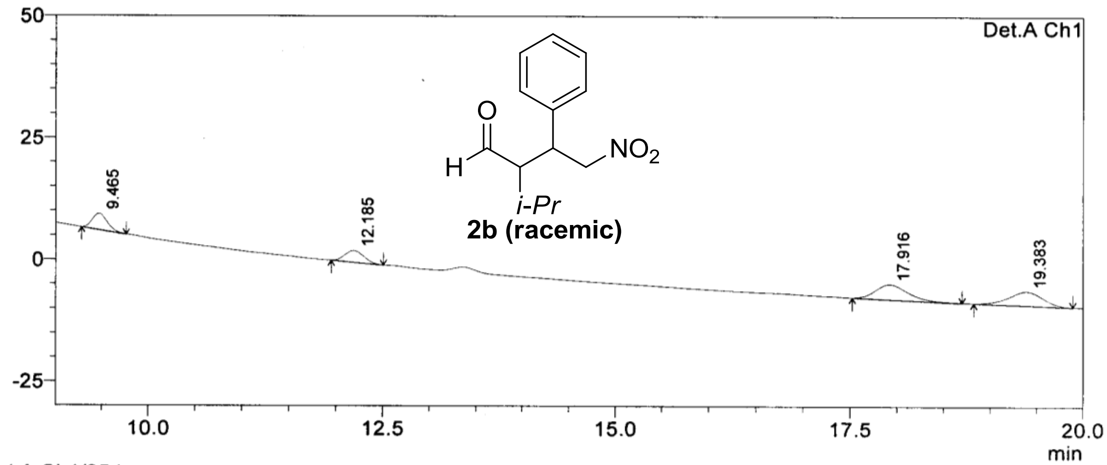

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 11.832 | 415953 | 13827 | 29.343 | 36.922 |
| 2 | 13.883 | 287066 | 8112 | 20.251 | 21.662 |
| 3 | 15.857 | 422564 | 10570 | 29.809 | 28.223 |
| 4 | 23.458 | 291982 | 4941 | 20.597 | 13.193 |
| Total | | 1417565 | 37450 | 100.000 | 100.000 |



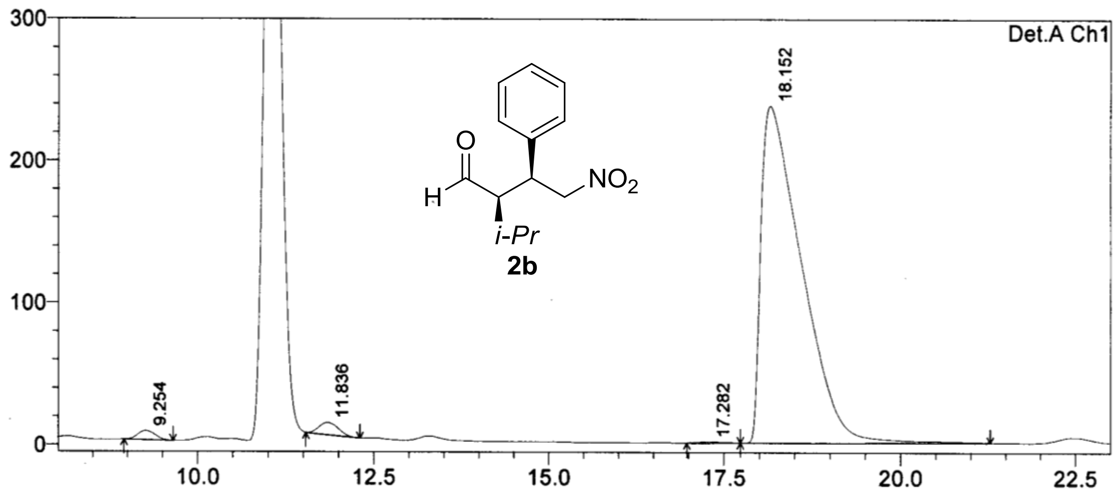

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 11.046 | 3448 | 196 | 0.130 | 0.261 |
| 2 | 12.847 | 53396 | 1863 | 2.012 | 2.480 |
| 3 | 14.637 | 2543949 | 71698 | 95.846 | 95.415 |
| 4 | 21.355 | 53406 | 1386 | 2.012 | 1.845 |
| Total | | 2654199 | 75143 | 100.000 | 100.000 |



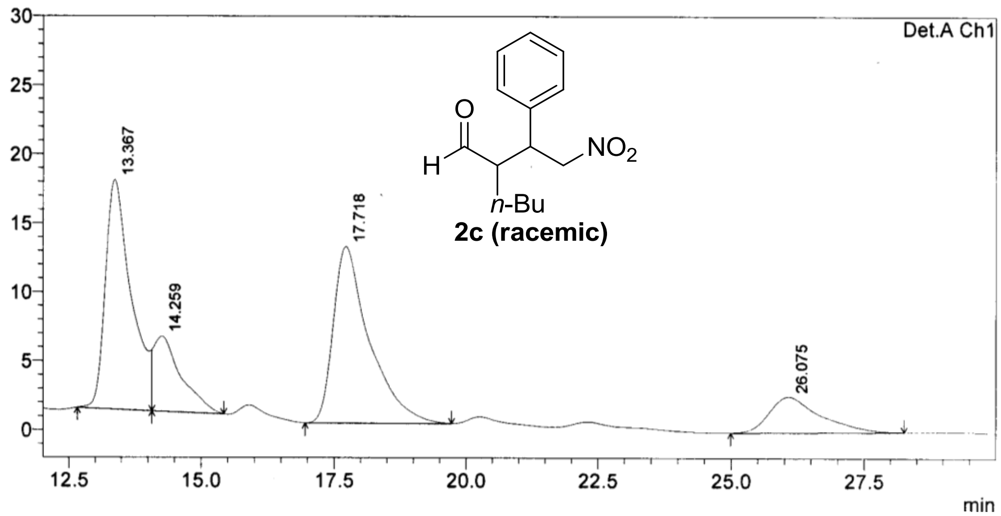

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 9.465 | 37139 | 3289 | 17.120 | 28.345 |
| 2 | 12.185 | 33406 | 2383 | 15.399 | 20.533 |
| 3 | 17.916 | 73195 | 3074 | 33.740 | 26.488 |
| 4 | 19.383 | 73199 | 2859 | 33.742 | 24.634 |
| Total | | 216939 | 11605 | 100.000 | 100.000 |




Detector A Ch1 254nm

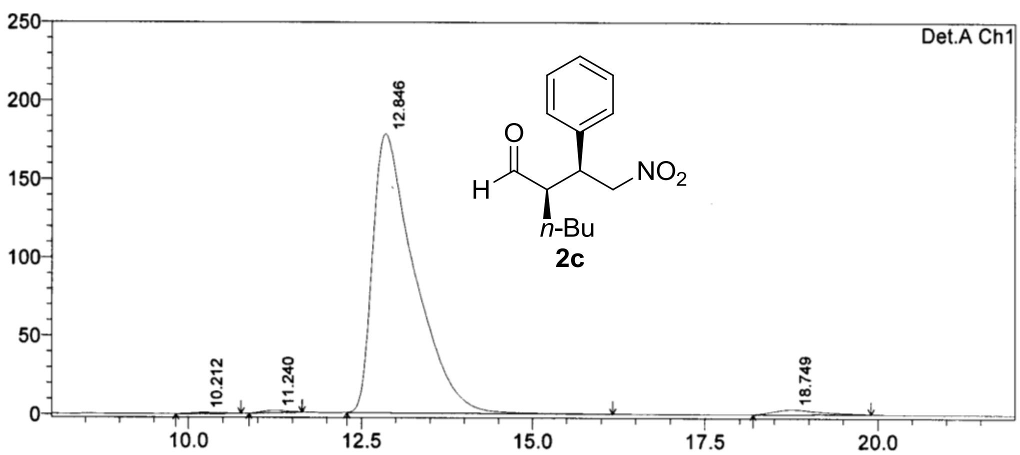
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 9.254 | 108400 | 6374 | 1.110 | 2.519 |
| 2 | 11.836 | 160657 | 8543 | 1.645 | 3.376 |
| 3 | 17.282 | 19361 | 873 | 0.198 | 0.345 |
| 4 | 18.152 | 9478535 | 237251 | 97.047 | 93.760 |
| Total | | 9766953 | 253042 | 100.000 | 100.000 |




PeakTable

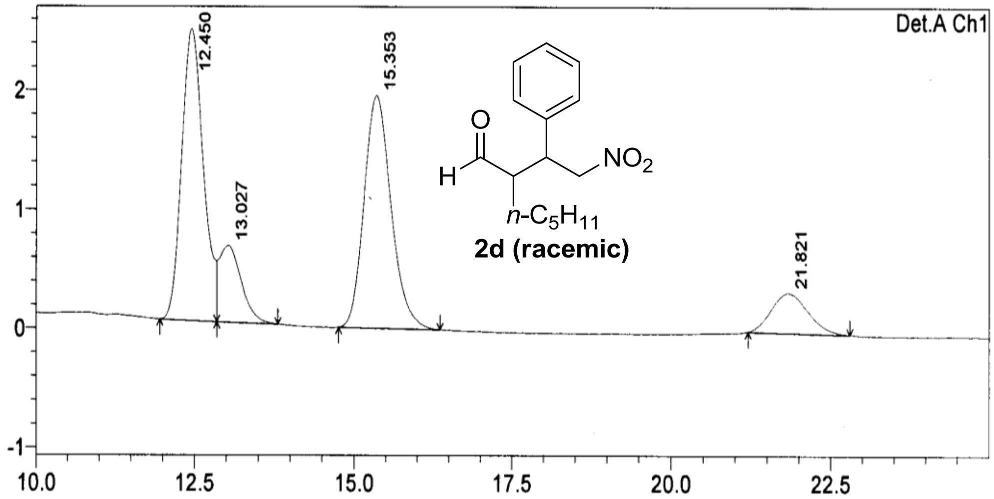
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 13.367 | 573094 | 16647 | 37.013 | 44.406 |
| 2 | 14.259 | 193508 | 5427 | 12.498 | 14.476 |
| 3 | 17.718 | 608990 | 12819 | 39.331 | 34.195 |
| 4 | 26.075 | 172781 | 2595 | 11.159 | 6.923 |
| Total | | 1548373 | 37489 | 100.000 | 100.000 |



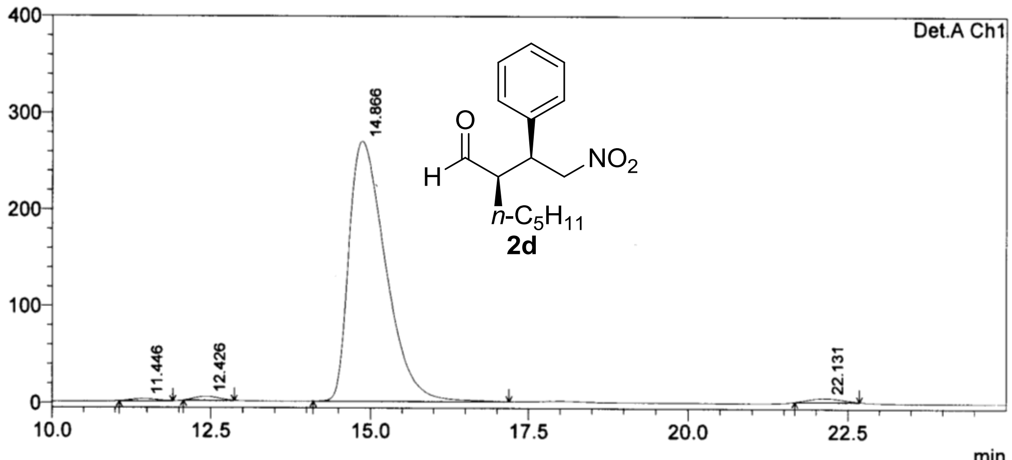

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 10.212 | 16706 | 675 | 0.215 | 0.369 |
| 2 | 11.240 | 35306 | 1493 | 0.454 | 0.817 |
| 3 | 12.846 | 7583479 | 177511 | 97.478 | 97.131 |
| 4 | 18.749 | 144166 | 3074 | 1.853 | 1.682 |
| Total | | 7779657 | 182754 | 100.000 | 100.000 |



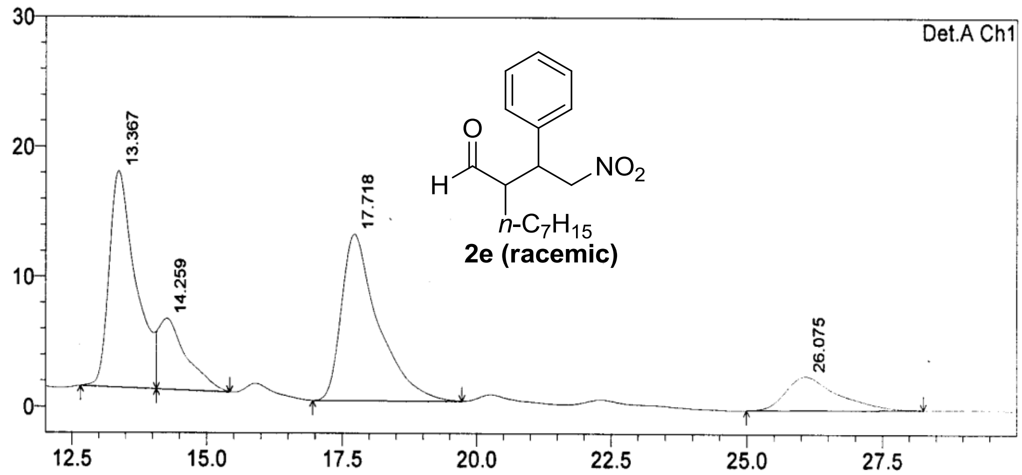

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 12.450 | 57988 | 2451 | 39.950 | 45.467 |
| 2 | 13.027 | 15523 | 645 | 10.694 | 11.967 |
| 3 | 15.353 | 58178 | 1958 | 40.081 | 36.318 |
| 4 | 21.821 | 13461 | 337 | 9.274 | 6.247 |
| Total | | 145150 | 5391 | 100.000 | 100.000 |



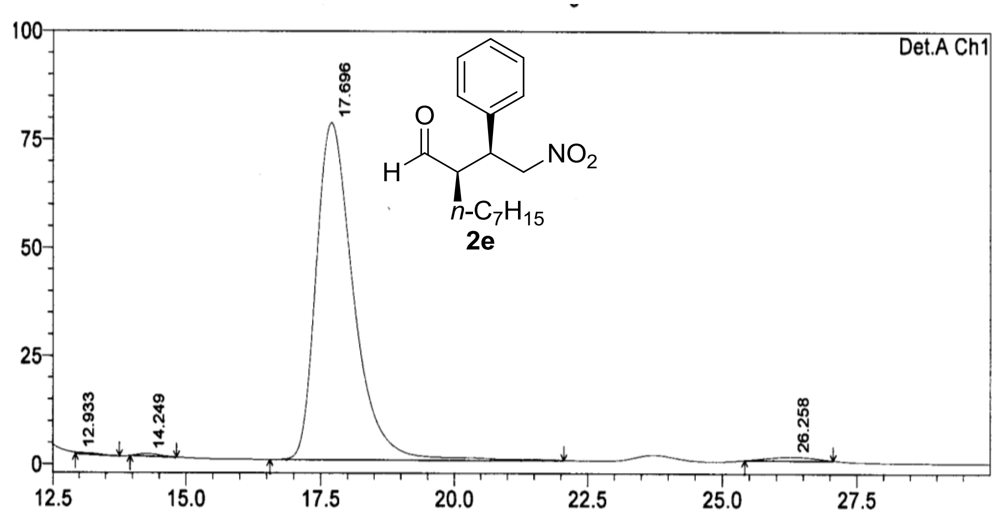

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 11.446 | 59772 | 2266 | 0.537 | 0.812 |
| 2 | 12.426 | 105783 | 4067 | 0.951 | 1.457 |
| 3 | 14.866 | 10814643 | 268834 | 97.244 | 96.288 |
| 4 | 22.131 | 140951 | 4032 | 1.267 | 1.444 |
| Total | | 11121149 | 279198 | 100.000 | 100.000 |



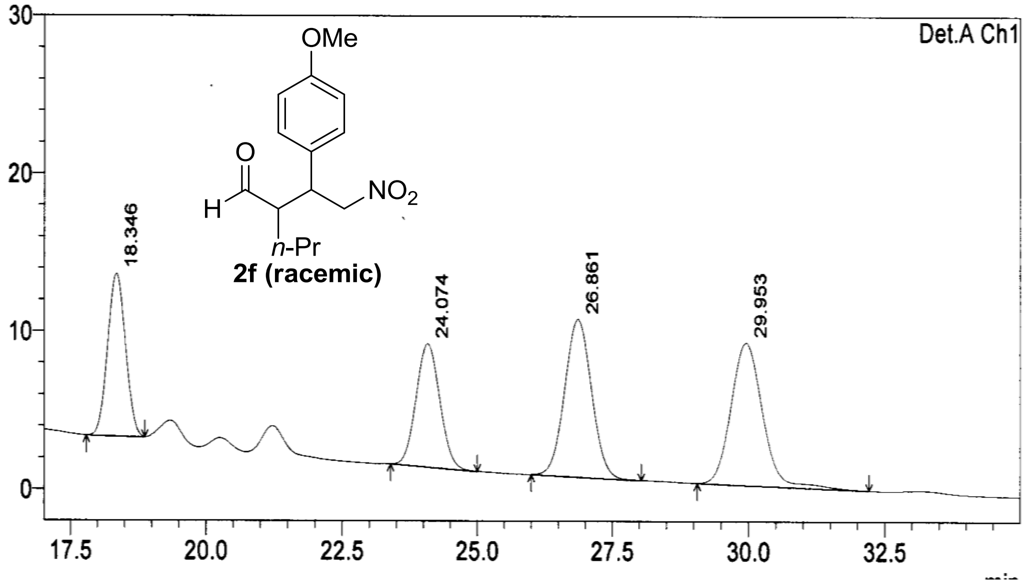

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 13.367 | 573094 | 16647 | 37.013 | 44.406 |
| 2 | 14.259 | 193508 | 5427 | 12.498 | 14.476 |
| 3 | 17.718 | 608990 | 12819 | 39.331 | 34.195 |
| 4 | 26.075 | 172781 | 2595 | 11.159 | 6.923 |
| Total | | 1548373 | 37489 | 100.000 | 100.000 |



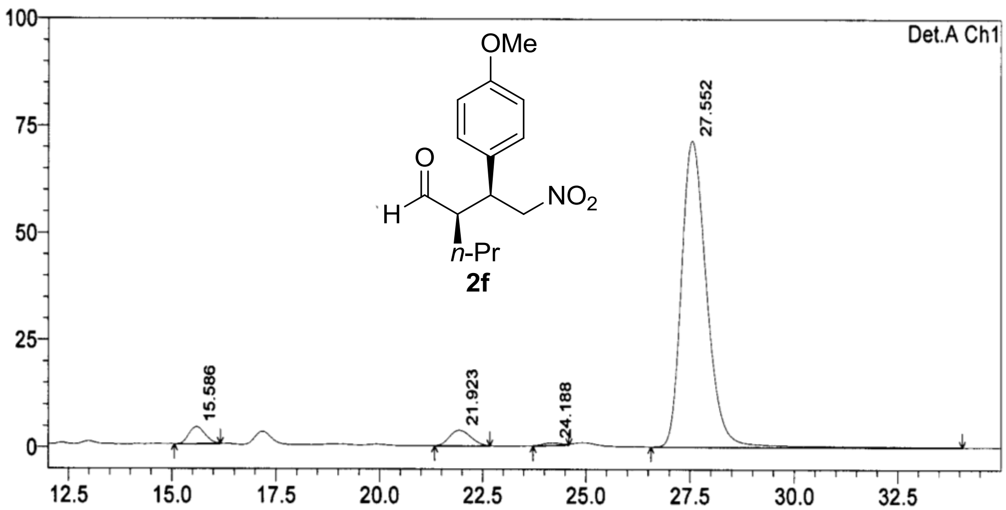

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 12.933 | 7658 | 275 | 0.199 | 0.346 |
| 2 | 14.249 | 15725 | 584 | 0.409 | 0.735 |
| 3 | 17.696 | 3772050 | 77836 | 98.080 | 97.834 |
| 4 | 26.258 | 50455 | 864 | 1.312 | 1.086 |
| Total | | 3845889 | 79560 | 100.000 | 100.000 |



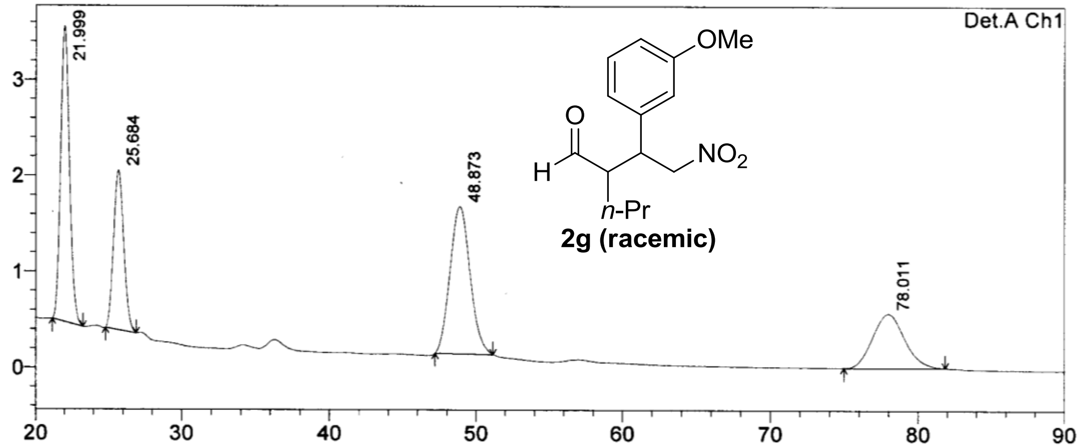

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 18.346 | 237332 | 10321 | 20.006 | 27.791 |
| 2 | 24.074 | 238039 | 7805 | 20.066 | 21.017 |
| 3 | 26.861 | 346063 | 9981 | 29.172 | 26.875 |
| 4 | 29.953 | 364852 | 9031 | 30.756 | 24.318 |
| Total | | 1186286 | 37138 | 100.000 | 100.000 |



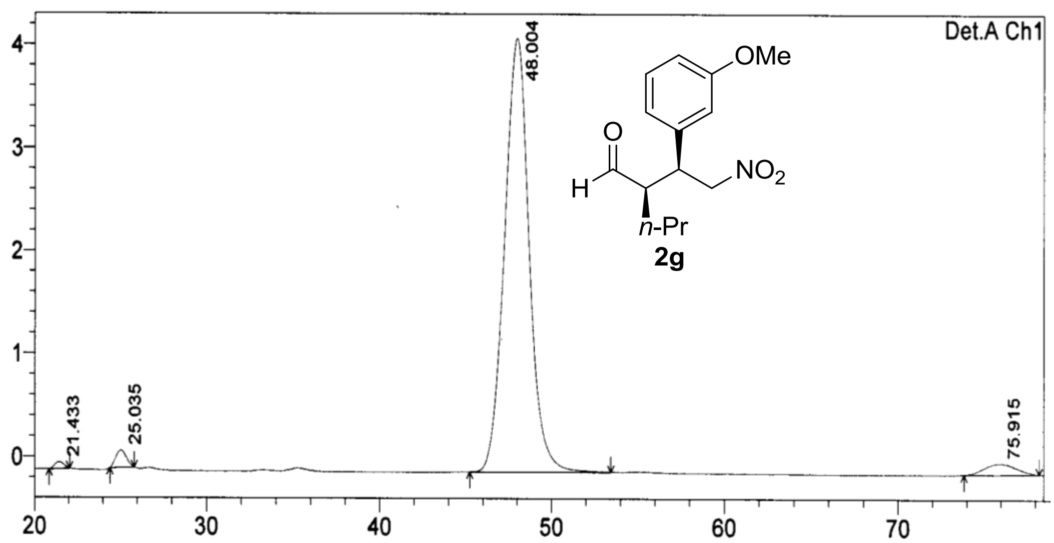

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 15.586 | 106474 | 3963 | 3.272 | 4.983 |
| 2 | 21.923 | 127994 | 3598 | 3.934 | 4.523 |
| 3 | 24.188 | 17763 | 585 | 0.546 | 0.735 |
| 4 | 27.552 | 3001509 | 71400 | 92.248 | 89.759 |
| Total | | 3253740 | 79546 | 100.000 | 100.000 |



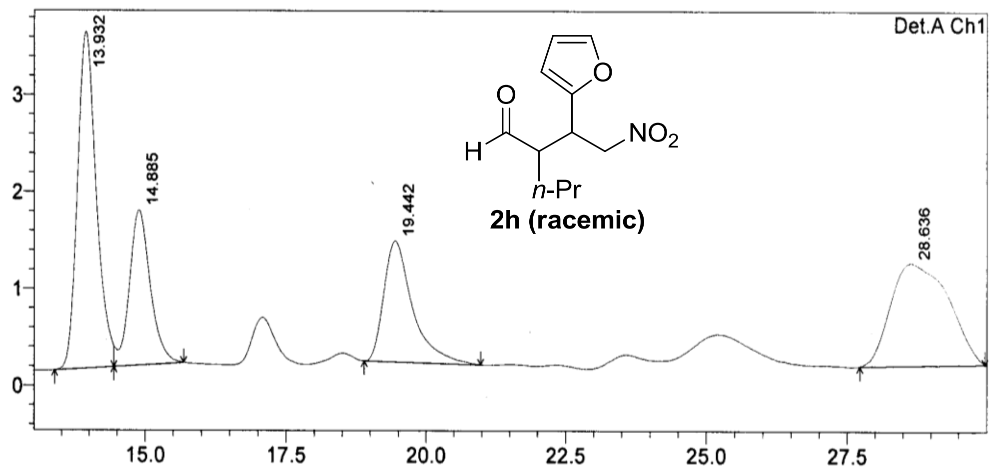

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 21.999 | 131718 | 3086 | 29.685 | 45.075 |
| 2 | 25.684 | 80163 | 1662 | 18.066 | 24.270 |
| 3 | 48.873 | 146378 | 1535 | 32.989 | 22.422 |
| 4 | 78.011 | 85458 | 564 | 19.260 | 8.232 |
| Total | | 443717 | 6847 | 100.000 | 100.000 |



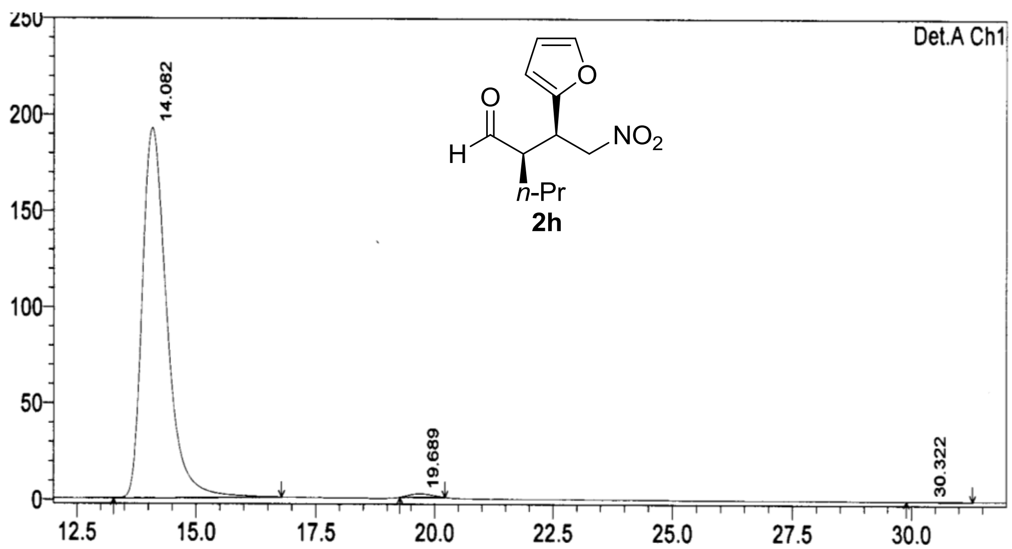

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 21.433 | 2318 | 65 | 0.525 | 1.424 |
| 2 | 25.035 | 7075 | 168 | 1.601 | 3.696 |
| 3 | 48.004 | 418829 | 4207 | 94.794 | 92.503 |
| 4 | 75.915 | 13609 | 108 | 3.080 | 2.377 |
| Total | | 441832 | 4548 | 100.000 | 100.000 |



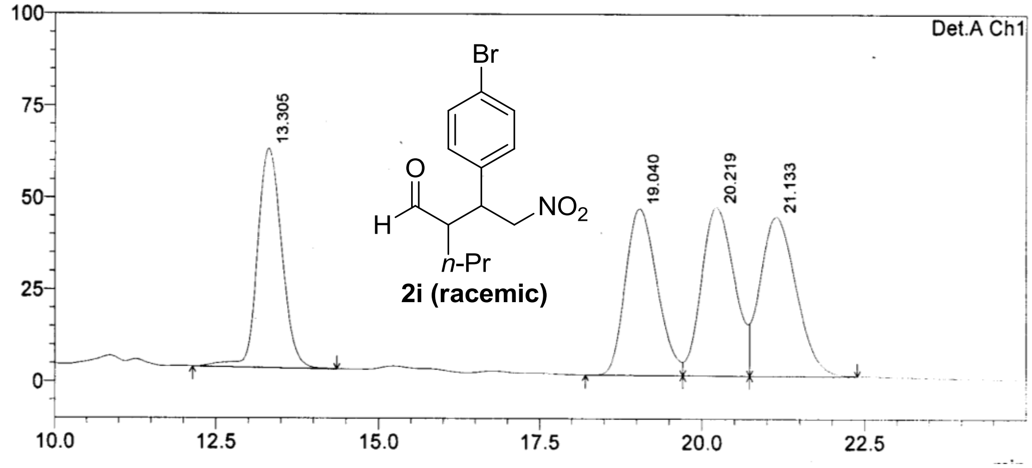

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 13.932 | 82195 | 3478 | 33.516 | 47.082 |
| 2 | 14.885 | 41720 | 1603 | 17.012 | 21.693 |
| 3 | 19.442 | 44926 | 1250 | 18.320 | 16.925 |
| 4 | 28.636 | 76396 | 1056 | 31.152 | 14.300 |
| Total | | 245237 | 7388 | 100.000 | 100.000 |



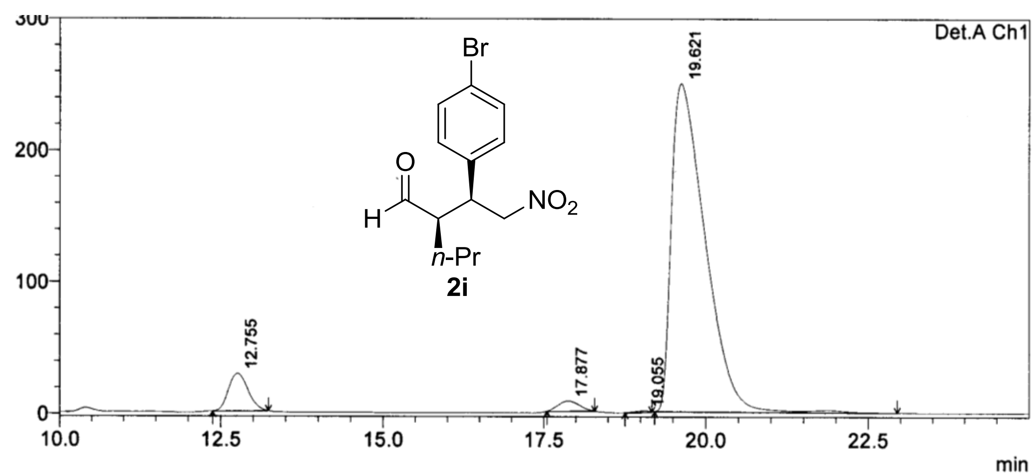

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 14.082 | 6869590 | 192299 | 99.054 | 99.021 |
| 2 | 19.689 | 59114 | 1775 | 0.852 | 0.914 |
| 3 | 30.322 | 6505 | 127 | 0.094 | 0.065 |
| Total | | 6935209 | 194201 | 100.000 | 100.000 |



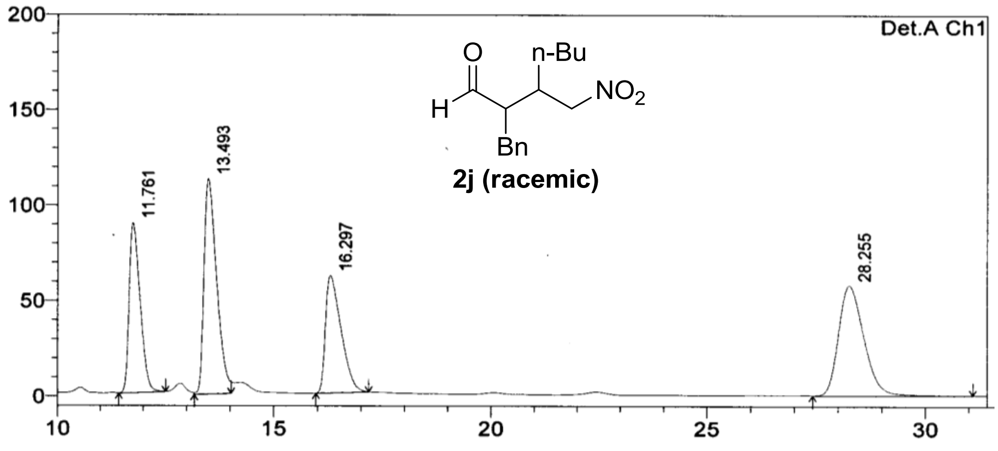

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 13.305 | 1545430 | 59580 | 24.246 | 30.679 |
| 2 | 19.040 | 1545332 | 45366 | 24.244 | 23.360 |
| 3 | 20.219 | 1619043 | 45912 | 25.401 | 23.641 |
| 4 | 21.133 | 1664185 | 43346 | 26.109 | 22.320 |
| Total | | 6373990 | 194204 | 100.000 | 100.000 |



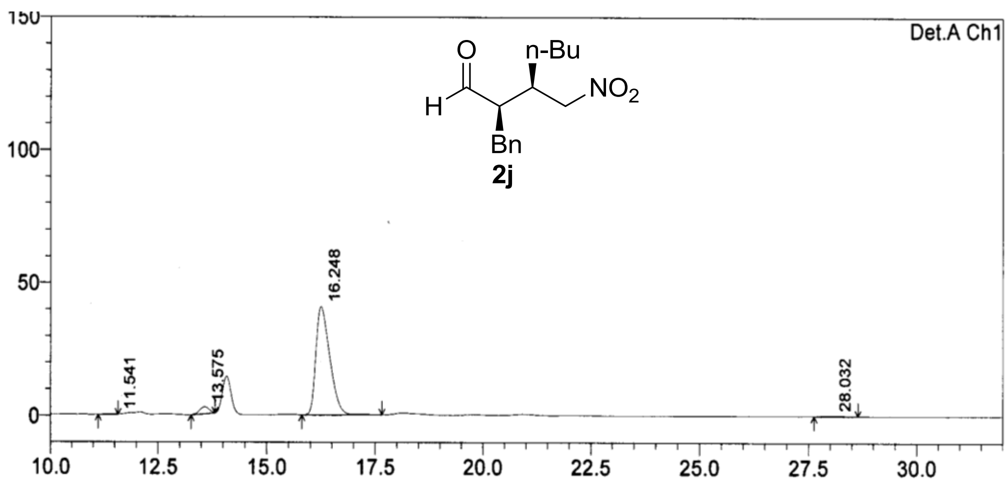

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 12.755 | 594958 | 28623 | 6.092 | 10.001 |
| 2 | 17.877 | 179237 | 7774 | 1.835 | 2.716 |
| 3 | 19.055 | 20139 | 1068 | 0.206 | 0.373 |
| 4 | 19.621 | 8972277 | 248741 | 91.867 | 86.910 |
| Total | | 9766611 | 286205 | 100.000 | 100.000 |




Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 11.761 | 1572664 | 89134 | 20.362 | 27.755 |
| 2 | 13.493 | 2282012 | 112892 | 29.546 | 35.153 |
| 3 | 16.297 | 1532655 | 61533 | 19.844 | 19.161 |
| 4 | 28.255 | 2336276 | 57585 | 30.249 | 17.931 |
| Total | | 7723606 | 321145 | 100.000 | 100.000 |




| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 11.541 | 4201 | 228 | 0.438 | 0.519 |
| 2 | 13.575 | 38349 | 2595 | 3.997 | 5.915 |
| 3 | 16.248 | 908316 | 40773 | 94.678 | 92.946 |
| 4 | 28.032 | 8510 | 272 | 0.887 | 0.620 |
| Total | | 959376 | 43868 | 100.000 | 100.000 |