Organocatalytic asymmetric addition of alcohols and thiols to activated electrophiles – efficient dynamic kinetic resolution and desymmetrization protocols

Aldo Peschiulli, Cormac Quigley, Seán Tallon, Yurii Gun'ko and Stephen J. Connon*

Centre for Synthesis and Chemical Biology, School of Chemistry, University of Dublin, Trinity College, Dublin 2, Ireland

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1.0 General

Proton Nuclear Magnetic Resonance spectra were recorded on a 400 MHz spectrometer in $CDCl_3$ and referenced relative to residual $CHCl_3$ (δ = 7.26 ppm). Chemical shifts are reported in ppm and coupling constants in Hertz. Carbon NMR spectra were recorded on the same instrument (100 MHz) with total proton decoupling. All melting points are uncorrected. Flash chromatography was carried out using silica gel, particle size 0.04-0.063 mm. TLC analysis was performed on precoated $60F_{254}$ slides, and visualised by UV irradiation and $KMnO_4$ staining. Optical rotation measurements are quoted in units of 10^{-1} deg cm^2 g^{-1}. Unless otherwise stated, all compounds were sourced commercially and used without purification. Racemic azlactones were obtained following literature procedures from the corresponding commercially available racemic aminoacids and used immediately after purification.[1] Toluene and methylene chloride were distilled from calcium hydride and stored under Argon. Tetrahydrofuran and diethyl ether were distilled over sodium-benzophenone ketyl radical and stored under argon. Commercially available anhydrous *t*-butyl methyl ether was used. All reactions were carried out under a protective argon atmosphere.

Analytical CSP-HPLC was performed on a Daicel CHIRALPAK AD or AS (4.6 mm x 25 cm) columns.

2.0 Dynamic kinetic resolution of racemic azlactones

Room temperature procedure (Table 2, entries 2, 5, 7)

A 5 mL reaction vial containing a stirring bar was charged with the appropriate azlactone (0.20 mmol) and **4a** (5.8 mg, 0.01 mmol). The reaction vial was flushed with argon and fitted with a septum. CH_2Cl_2 (1.0 mL) was added followed by allyl alcohol (27 μL, 0.4 mmol) in a dropwise manner *via* syringe and the resulting reaction was stirred at room temperature for the time indicated in Table 2. The solution was then poured directly onto a column of silica gel and the product purified by flash chromatography.

Low temperature procedure (Table 2, entries 1, 3-4, 6)

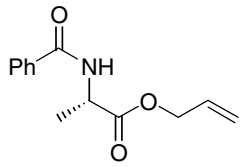
A 5 mL reaction vial containing a stirring bar was charged with the appropriate azlactone (0.20 mmol) and **4a** (11.6 mg, 0.02 mmol). The reaction vial was flushed with argon and fitted with a septum and the solution was cooled to -20 °C. Allyl alcohol (27 μL, 0.4 mmol) was added in a dropwise manner *via* syringe and the resulting reaction was stirred at -20 °C for the time indicated in Table 2. The solution was then poured directly onto a column of silica gel and the product purified by flash chromatography.

One pot procedure

A 5 mL reaction vial containing a stirring bar was charged with *N*-benzoylalanine (58.0 mg, 0.3 mmol), flushed with argon and fitted with a septum. CH_2Cl_2 (0.5 mL) was added followed by a solution of DCC (65.0 mg, 0.315 mmol) in CH_2Cl_2 (0.5 mL) *via* syringe and the mixture was stirred at room temperature for 2 h. **4a** (17.4 mg, 0.03 mmol) was added as a solution in CH_2Cl_2 (0.5 mL) and the resulting mixture was cooled to -20 °C. Allyl alcohol (41 μL, 0.6 mmol) was then added in a dropwise manner *via* syringe and the reaction was stirred at -20 °C for 24 h. After filtration of the white precipitate, the product was purified by flash chromatography and obtained as a white solid (66.0 mg, 94%, 88% *ee*).

3.0 Characterization data

***N*-Benzoylalanine, allyl ester** (**12**, Table 2, entry 1-2)



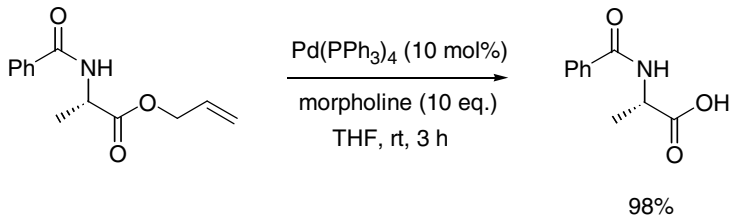
The desired product was obtained as a white solid (m.p. 56-57 °C) in 99% yield and 82% *ee* following the room temperature procedure.

Following the low temperature procedure the product could be obtained in 96% yield and 88% *ee*. $[\alpha]_D^{20}$ = +27.3 (c 0.62, $CHCl_3$).

CSP-HPLC analysis. Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm, retention times: 9.6 min (minor enantiomer) and 12.8 (major enantiomer).

^{1}H NMR ($CDCl_3$) δ 1.58 (d, J = 7.0, 3H), 4.67-4.77 (m, 2H), 4.86 (app. quintet, J = 7.0, 1H), 5.31 (dd, J = 10.5, 1.5, 1H), 5.39 (dd, J = 17.3, 1.5, 1H), 5.91-6.02 (m, 1H), 6.77 (br d, J = 7.0, -NH-), 7.48 (app. t, J = 7.0, 2H), 7.55 (t, J = 7.3, 1H), 7.84 (d, J = 7.0, 2H). ^{13}C NMR ($CDCl_3$) δ 18.8, 48.5, 66.14, 118.9, 127.0, 128.6, 131.5, 131.8, 133.9 (q), 166.8 (q), 172.9 (q). HRMS (ESI): Found 256.0949 ($M + Na^+$) $C_{13}H_{15}NO_3Na$ requires 256.0950.

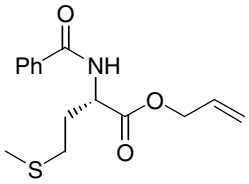
The absolute configuration of **12** was established by comparing the optical rotation of the corresponding *N*-benzoylalanine derivative with the literature data.[2]



Morpholine (260 μL, 3.0 mmol) was added to a solution of **12** (70.0 mg, 0.3 mmol) in dry THF (1 mL) under an argon atmosphere. $Pd(PPh_3)_4$ (33.5 mg, 0.03 mmol) was added as a solution in THF (1 mL) and the resulting mixture was stirred at room temperature for 3 h. The solvent was removed

in vacuo and the mixture was dissolved in AcOEt (5 mL). The organic phase was washed twice with 1 N HCl (5 mL) and then extracted with 2 N NaOH (3 x 5 mL). The combined aqueous layers were washed with AcOEt (5 mL), made acidic by addition of 2 N HCl and finally extracted with AcOEt (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was concentrated *in vacuo*. A short filtration on silica gel afforded the desired product in 98% yield as a white solid. $[\alpha]_D^{20}$ = +8.0 (c 0.70, EtOH).

***N*-Benzoylmethionine, allyl ester** (**13**, Table 2, entry 3)

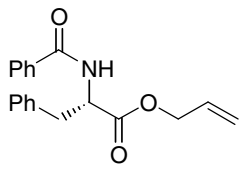


The desired product was obtained as a white solid (m.p. 82.5-83.5 °C) in 97% yield and 79% *ee* following the low temperature procedure. $[\alpha]_D^{20}$ = +20.2 (c 0.51, $CHCl_3$).

CSP-HPLC analysis. Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm, retention times: 16.9 min (minor enantiomer) and 22.0 (major enantiomer).

^{1}H NMR ($CDCl_3$) δ 2.09-2.22 (m, 4H), 2.28-2.40 (m, 1H), 2.53-2.70 (m, 2H), 4.72 (m, 2H), 4.95-5.04 (m, 1H), 5.32 (dd, J = 10.3, 1.1, 1H), 5.40 (dd, J = 17.3, 1.1, 1H), 5.90-6.03 (m, 1H), 6.98 (br d, J = 7.2, -NH-), 7.48 (app. t, J = 7.3, 2H), 7.55 (t, J = 7.3, 1H), 7.85 (d, J = 7.3, 2H). ^{13}C NMR ($CDCl_3$) 15.5, 30.0, 31.7, 52.2, 66.3, 119.3, 127.1, 128.7, 131.4, 131.9, 133.7 (q), 167.0 (q), 171.8 (q). HRMS (ESI): Found 316.0994 ($M + Na^+$) $C_{15}H_{19}NO_3NaS$ requires 316.0983.

***N*-Benzoylphenylalanine, allyl ester** (**14**, Table 2, entry 4)

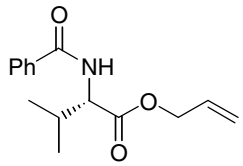


The desired product was obtained as a white solid (m.p. 89.5-90.5 °C) (lit. m.p. 90 °C)[3] in 98% yield and 78% *ee* following the low temperature procedure. $[\alpha]_D^{20}$ = +52.2 (c 0.54, $CHCl_3$).

CSP-HPLC analysis. Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm, retention times: 14.8 min (minor enantiomer) and 20.6 (major enantiomer).

^{1}H NMR ($CDCl_3$) δ 3.28 (dd, J = 13.8, 5.3, 1H), 3.34 (J = 13.8, 5.8, 1H), 4.62-4.76 (m, 2H), 5.11-5.18 (m, 1H), 5.32 (dd, J = 10.5, 1.25, 1H), 5.37 (dd, J = 17.1, 1.25, 1H), 5.88-5.99 (m, 1H), 6.62 (br d, J = 7.3, -NH-), 7.18 (dd, J = 7.5, 1.8, 2H), 7.25-7.35 (m, 3H), 7.46 (app. t, J = 7.0, 2H), 7.54 (t, J = 7.3, 1H), 7.76 (d, J = 7.0, 2H). ^{13}C NMR ($CDCl_3$) δ 37.9, 53.5, 66.2, 119.3, 127.0, 127.2, 128.6, 128.7, 129.4, 131.3, 131.8, 133.9 (q), 135.8 (q), 166.8 (q), 171.3 (q). HRMS (ESI): Found 332.1278 ($M + Na^+$) $C_{19}H_{19}NO_3Na$ requires 332.1263.

***N*-Benzoylvaline, allyl ester** (**7a**, Table 2, entry 5-6)

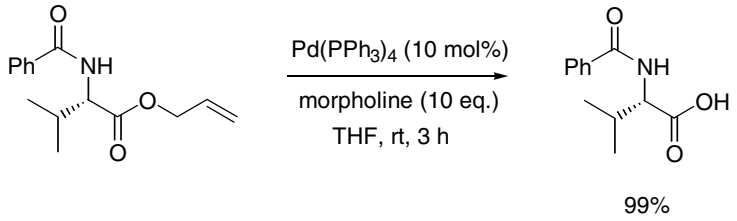


The desired product was obtained as a white solid (m.p. 43-45 °C) in 99% yield and 85% *ee* following the room temperature procedure. $[\alpha]_D^{20}$ = +26.5 (c 0.52, $CHCl_3$).

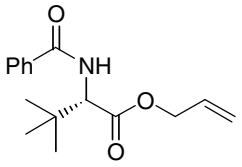
CSP-HPLC analysis. Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm, retention times: 8.4 min (minor enantiomer) and 11.7 (major enantiomer).

^{1}H NMR ($CDCl_3$) δ 1.02 (d, J = 6.8, 3H), 1.05 (d, J = 6.8, 3H), 2.28-2.40 (m, 1H), 4.65-4.76 (m, 2 H), 4.85 (dd, J = 8.5, 4.5, 1H), 5.31 (dd, J = 10.3, 1.3, 1H), 5.40 (dd, J = 17.0, 1.3), 5.91-6.02 (m, 1H), 6.67 (br d, J = 8.5, -NH-), 7.48 (app. t, J = 7.0, 2H), 7.55 (t, J = 7.3, 1H), 7.84 (d, J = 7.0, 2H). ^{13}C NMR ($CDCl_3$) δ 17.9, 19.0, 31.7, 57.4, 66.0, 119.2, 127.1, 128.6, 131.5, 131.7, 134.2 (q), 167.3 (q), 171.9 (q). HRMS (ESI): Found 284.1263 ($M + Na^+$) $C_{15}H_{19}NO_3Na$ requires 284.1263.

The absolute configuration of **15** was established by comparing the optical rotation of the corresponding *N*-benzoylvaline derivative with the literature data.[4] $[\alpha]_D^{20}$ = +14.7 (c 0.64, EtOH).



***N*-Benzoyl*tert*leucine, allyl ester** (**15**, Table 2, entry 7)



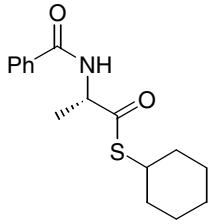
The desired product was obtained as a white solid (m.p. 3435 °C) in 93% yield and 85% *ee* following the room temperature procedure. $[\alpha]_D^{20}$ = +27.7 (c 0.45, $CHCl_3$).

CSP-HPLC analysis. Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm, retention times: 7.4 min (minor enantiomer) and 10.8 (major enantiomer).

^{1}H NMR ($CDCl_3$) δ 1.09 (s, 9H), 4.63-4.74 (m, 2H), 4.76 (d, J = 9.5, 1H), 5.30 (dd, J = 10.3, 1.5, 1H), 5.40 (d, J = 17.3, 1.5, 1H), 5.96-6.01 (m, 1H), 6.70 (br d, J = 9.5, -NH-), 7.48 (app. t, J = 7.0, 2H), 7.55 (t, J = 7.3, 1H), 7.83 (d, J = 7.0, 2H). ^{13}C NMR ($CDCl_3$) δ 26.7, 35.3 (q), 60.2, 65.8, 119.2, 127.0, 128.6, 131.5, 131.7, 134.2 (q), 167.1 (q), 171.5 (q). HRMS (ESI): Found 298.1424 (M + Na^+) $C_{16}H_{21}NO_3Na$ requires 298.1419.

4.0 Dynamic kinetic resolution using thiol nucleophiles: low temperature procedure

***N*-Benzoylalanine, cyclohexyl thioester** (**17**, Table 3, entry 4)



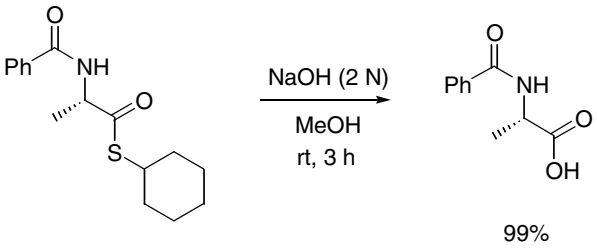
A 5 mL reaction vial containing a stirring bar was charged with **8** (52.5 mg, 0.30 mmol) and **4a** (17.4 mg, 0.03 mmol). The reaction vial was flushed with argon and fitted with a septum and the

solution was cooled to -30 °C. Cyclohexyl mercaptan (110 μL, 0.90 mmol) was added in a dropwise manner *via* syringe and the resulting reaction was stirred at -30 °C for 48 h. The solution was then poured directly onto a column of silica gel and the product, purified by flash chromatography, was obtained as a white solid (79 mg, 90% yield, 64% *ee*). M.p. 101-103 °C.
$[\alpha]_D^{20}$ = +9.0 (c 0.72, $CHCl_3$).

CSP-HPLC analysis. Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm, retention times: 9.4 min (minor enantiomer) and 11.7 (major enantiomer).

^{1}H NMR ($CDCl_3$) δ 1.24-1.36 (m, 1H), 1.38-1.51 (m, 4H), 1.53 (d, J = 7.3, 3H), 1.57-1.66 (m, 1H), 1.67-1.1.79 (m, 3H), 1.90-2.0 (m, 2H), 3.51-3.60 (m, 1H), 4.94 (app quintet, J = 7.0, 1H), 6.71 (br d, J = 7.3, -NH-), 7.45-7.51 (m, 2H), 7.52-7.58 (m, 1H), 7.82-7.86 (m, 2H).). ^{13}C NMR ($CDCl_3$) δ 19.4, 25.5, 25.9, 32.9, 33.0, 42.6, 55.4, 127.1, 128.6, 131.8, 133.9 (q), 166.8 (q), 200.7 (q).
HRMS (ESI): Found 292.1380 ($M + H^+$) $C_{16}H_{22}NO_2S$ requires 292.1371.

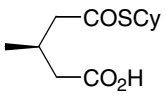
The absolute configuration of **17** was established by comparing the optical rotation of the corresponding N-benzoylalanine derivative with the literature data.[2]



99%

NaOH (2 N) (3 mL) was added to a solution of **17** (76 mg, 0.260 mmol) in MeOH (2 mL) and the resulting reaction mixture was stirred at room temperature for 3 h. The solvent was concentrated *in vacuo* and HCl (1 N) was added to acidify the solution. The product was extracted with AcOEt (3 x 10 mL) and purified by a short filtration on silica gel (50 mg, 99% yield). $[\alpha]_D^{20}$ = + 5.0 (c 0.50, EtOH).

5.0 Asymmetric thiolysis of 3-methyl-glutaric anhydride (**19**)

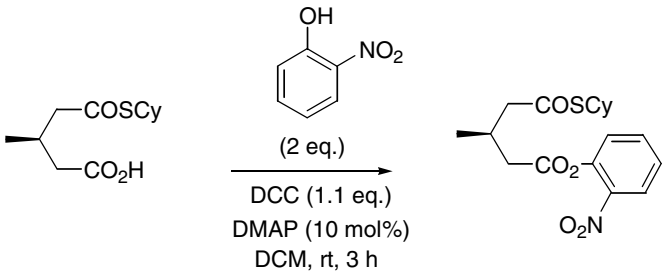


A 40 mL reaction vial containing a stirring bar was charged with 3-methyl-glutaric anhydride (**18**) (76.8 mg, 0.60 mmol) and **3b** (7.1 mg, 0.012 mmol). The vial was fitted with a septum and flushed with argon. MTBE (40 mL) was added followed by cyclohexyl mercaptan (368 μL, 3.00 mmol) in a dropwise manner *via* syringe. The solution was then stirred at room temperature for 48 h. The solvent was removed under reduced pressure and the crude product purified by a short filtration on silica gel to afford the desired hemi-thioester (**19**) (143 mg, 98% yield, 92% *ee*). $[\alpha]_D^{20}$ = - 2.3 (c 0.90, $CHCl_3$).

^{1}H NMR ($CDCl_3$) δ 1.06 (d, J = 6.3, 3H), 1.20-1.35 (m, 1H), 1.36-1.46 (m, 4H), 1.57-1.63 (m, 1H), 1.64-1.77 (m, 2H), 1.88-1.98 (m, 2H), 2.28 (dd, J = 7.3, 7.0, 1H), 2.42-2.65 (m, 4H), 3.49-3.59 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 19.6, 25.5, 25.9, 27.9, 33.0, 40.4, 42.4, 50.1, 178.4 (q), 198.2 (q). HRMS (ESI): Found 267.1024 (M + Na^+) $C_{12}H_{20}O_3NaS$ requires 267.1031.

Enantiomeric excess determination

The enantiomeric excess of **19** was determined by CSP-HPLC after conversion into the corresponding *o*-nitrophenoxy ester.



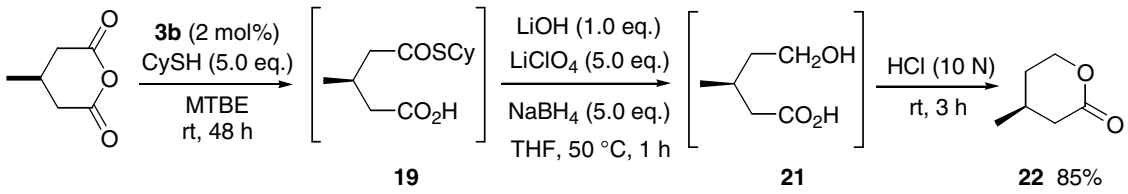
20 95%

A 5 mL reaction vial containing a stirring bar was charged with **19** (19.5 mg, 0.08 mmol), 2-nitrophenol (22.2 mg, 0.16 mmol) and DMAP (1.0 mg). The vial was flushed with argon and the resulting mixture was dissolved in dry CH_2Cl_2 (1 mL). A solution of DCC (18.5 mg, 0.09 mmol) in dry DCM (1 mL) was then added and the reaction mixture was stirred for 3 h at room temperature. After filtration of the resulting white precipitate, the filtrate was concentrated *in vacuo*. The residue was purified by chromatography on silica gel to afford the desired compound as a yellow clear oil. (27.7 mg, 95% yield).

CSP-HPLC analysis. Chiralpak AS (4.6 mm x 25 cm), hexane/IPA: 9/1, 0.5 mL min^{-1}, RT, UV detection at 220 nm, retention times: 16.5 min (minor enantiomer) and 19.2 (major enantiomer).

Absolute configuration determination

The absolute configuration of **19** was determined by comparison of the optical rotation of the corresponding lactone derivative (**22**) with the literature data.[5]

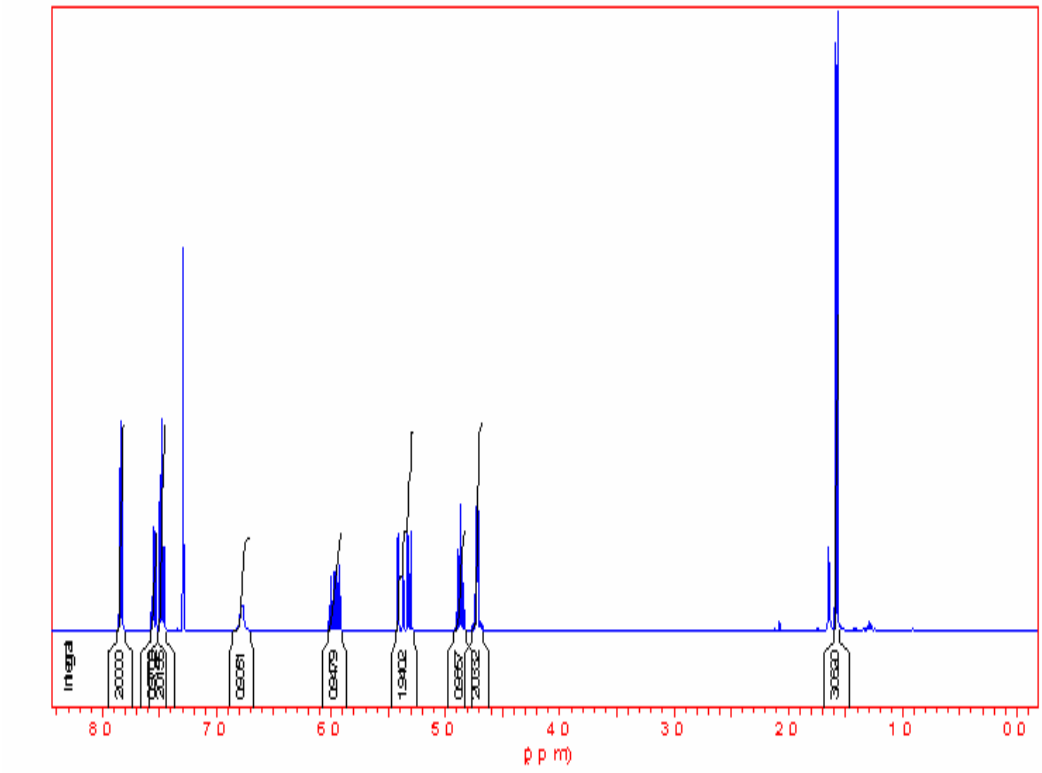


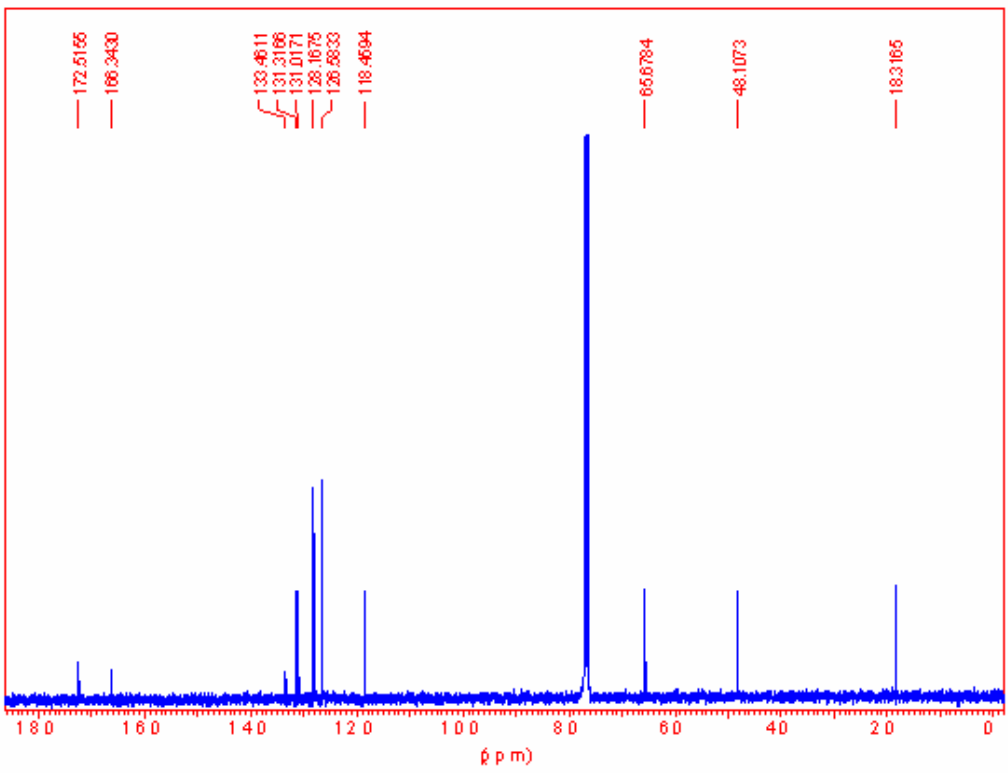
A 100 mL reaction vial containing a stirring bar was charged with 3-methyl-glutaric anhydride (**18**) (115.3 mg, 0.90 mmol) and **3b** (10.7 mg, 0.018 mmol). The vial was fitted with a septum and flushed with argon. MTBE (60 mL) was added followed by cyclohexyl mercaptan (552 μL, 4.50 mmol) in a dropwise manner *via* syringe. The solution was stirred at room temperature for 48 h and the solvent was then removed under reduced pressure. The mixture was dissolved in THF (10 mL) and LiOH (37.8 mg, 0.90 mmol) was added. The reaction was heated to 50 °C and stirred for 15 minutes. $LiClO_4$ (478.7 mg, 4.50 mmol) and $NaBH_4$ (170.2 mg, 4.50 mmol) were then added and the reaction mixture was stirred at 50 °C for 1 h. The solvent was concentrated *in vacuo*, HCl (10 N) (10 mL) was added and the mixture was stirred at room temperature for 3 h. The desired product, extracted with $CHCl_3$ (3 x 10 mL) and purified by flash-chromatography, was obtained as a colourless oil (87 mg, 85% yield). $[\alpha]_D^{20}$ = - 23.3 (c 0.72, $CHCl_3$).

^{1}H NMR ($CDCl_3$) δ 1.09 (d, J = 6.0, 3H), 1.49-1.61 (m, 1H), 1.90-2.00 (m, 1H), 2.08-2.18 (m, 2H), 2.65-2.76 (m, 1H), 4.28 (td, J = 10.5, 3.5, 1H), 4.41-4.49 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 21.3, 26.4, 30.5, 38.1, 68.4, 171.0 (q).

6.0 NMR spectra and CSP-HPLC Analysis

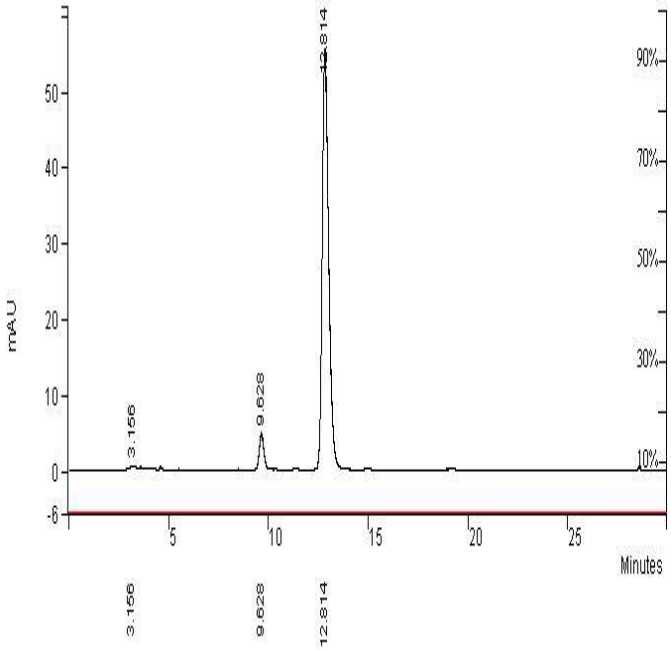
N-Benzoylalanine, allyl ester (**12**)



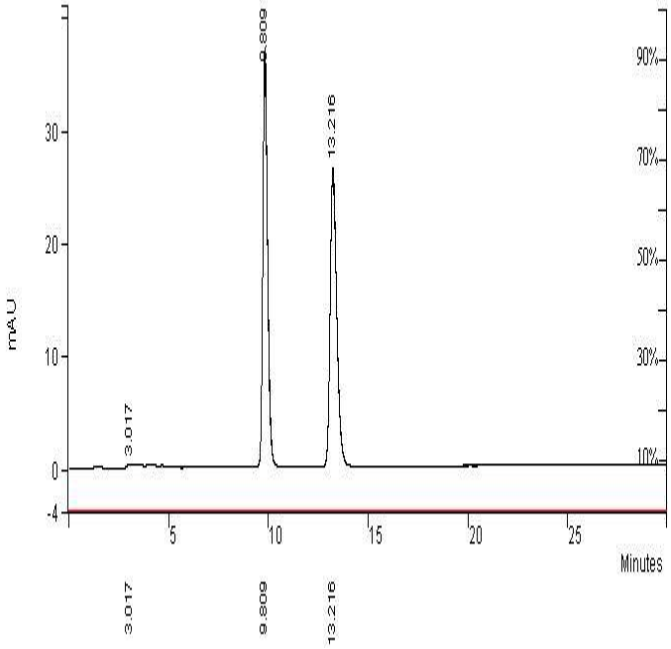


Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm

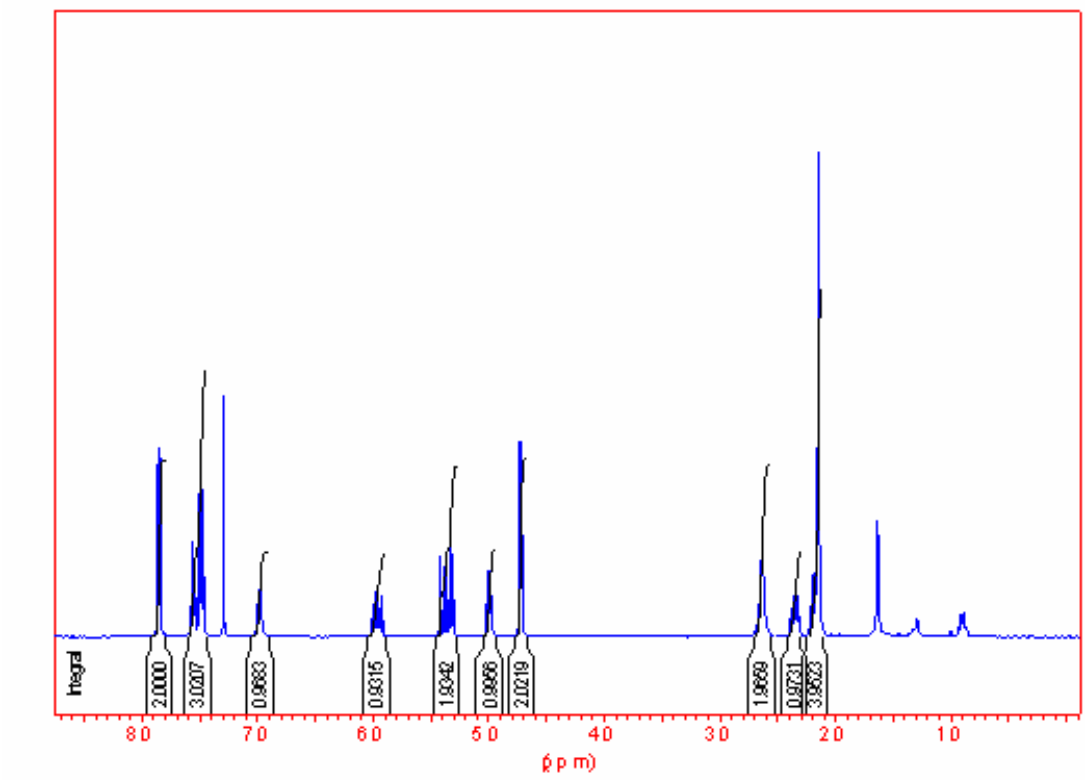
Peak No	Result	Ret. Time (min)	Area (counts)
1	5.8023	9.628	781418
2	93.8654	12.814	12641224

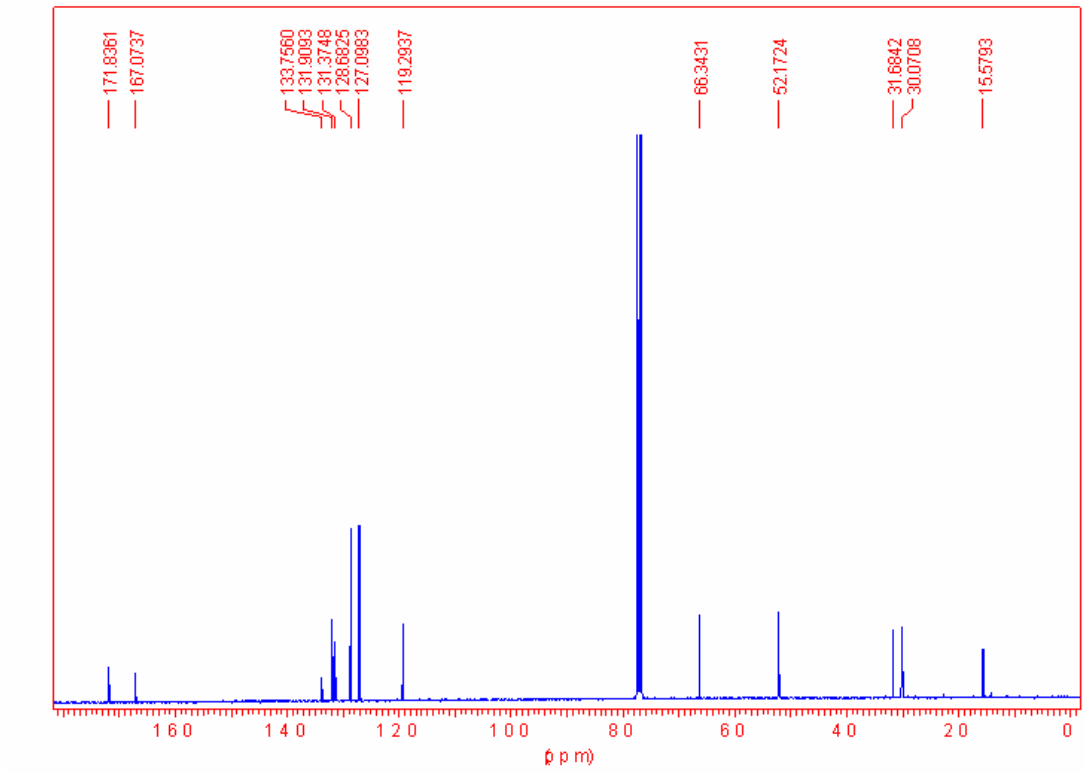


Peak No	Result	Ret. Time (min)	Area (counts)
1	49.5439	9.809	6338800
2	49.1453	13.216	6287802



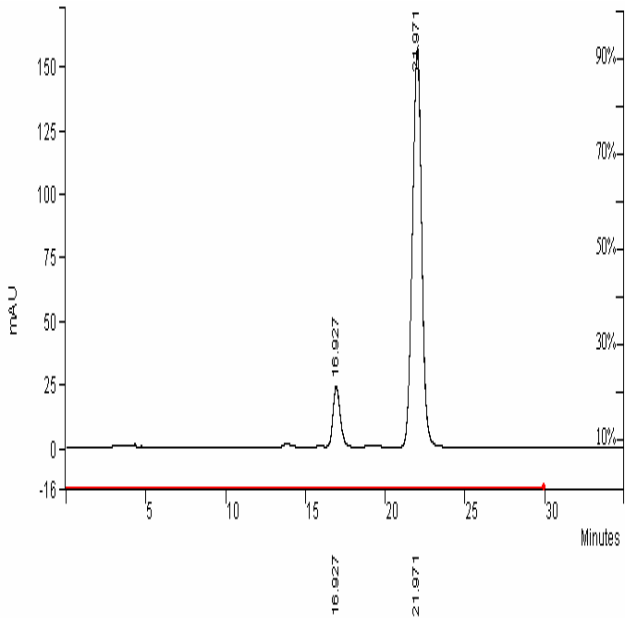
***N*-Benzoylmethionine, allyl ester (13)**



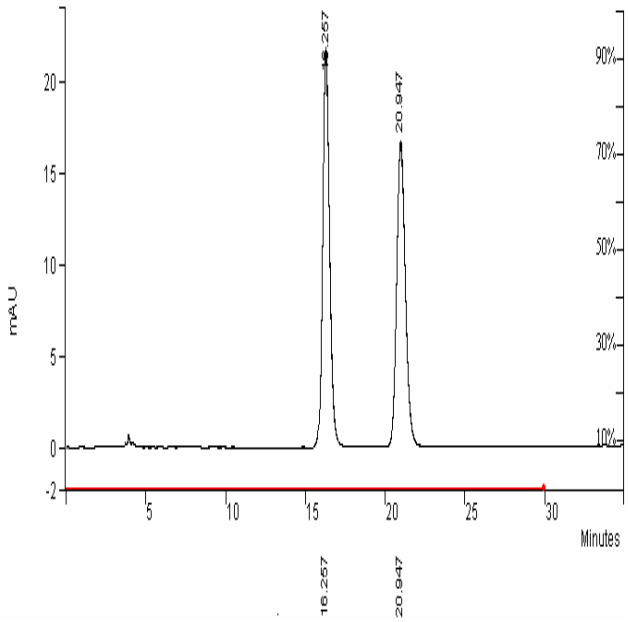


Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm

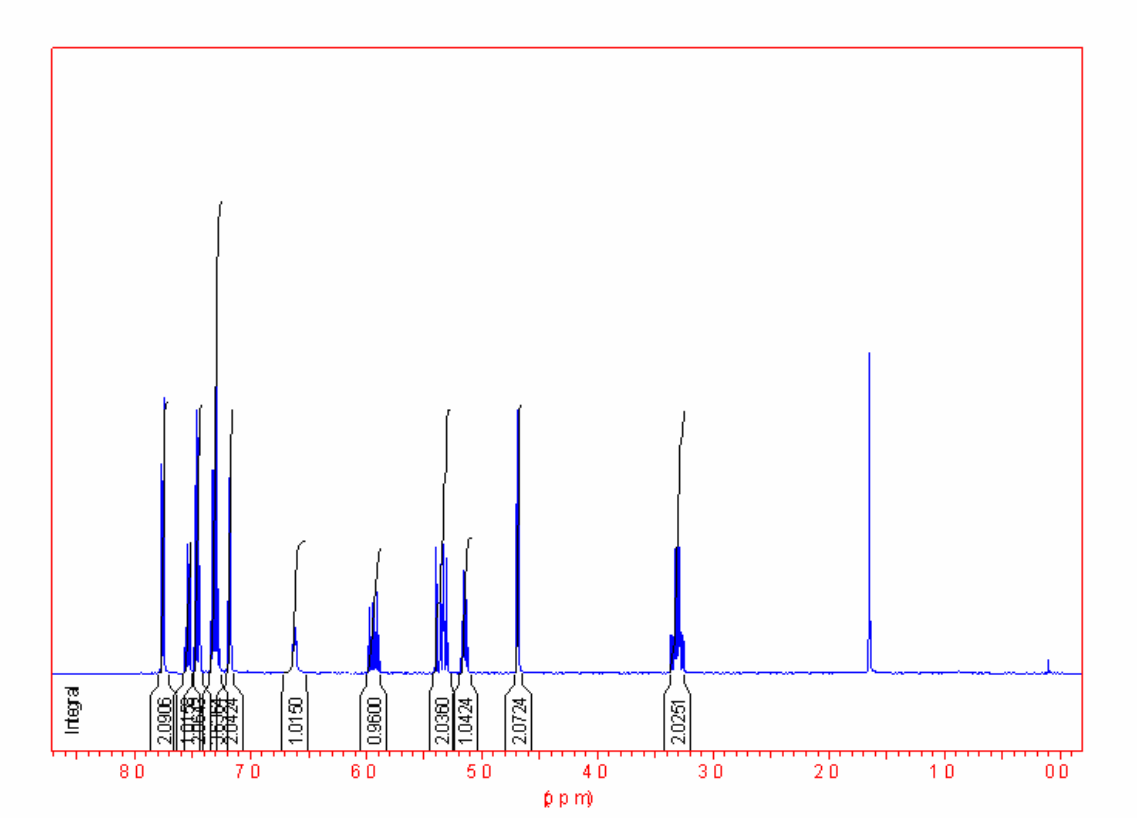
Peak No	Result	Ret. Time (min)	Area (counts)
1	10.6021	16.927	2457800
2	89.3979	21.971	20724402

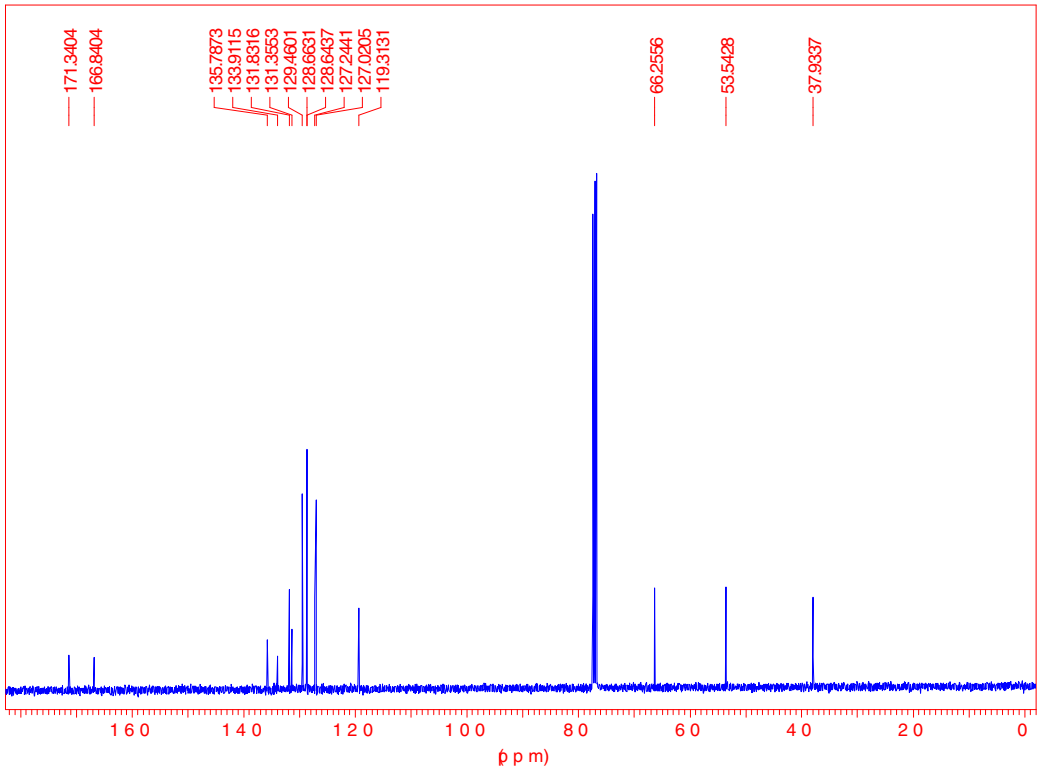


Peak No	Result	Ret. Time (min)	Area (counts)
1	49.8756	16.267	6507613
2	50.0238	20.947	6526950



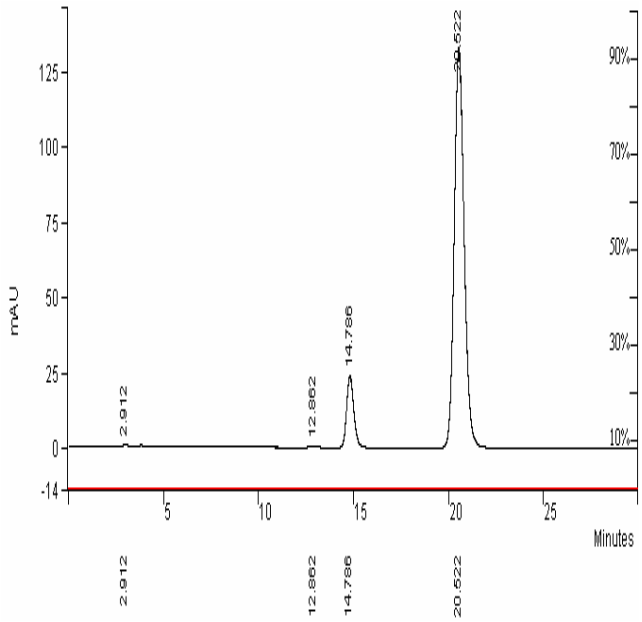
***N*-Benzoylphenylalanine, allyl ester (14)**



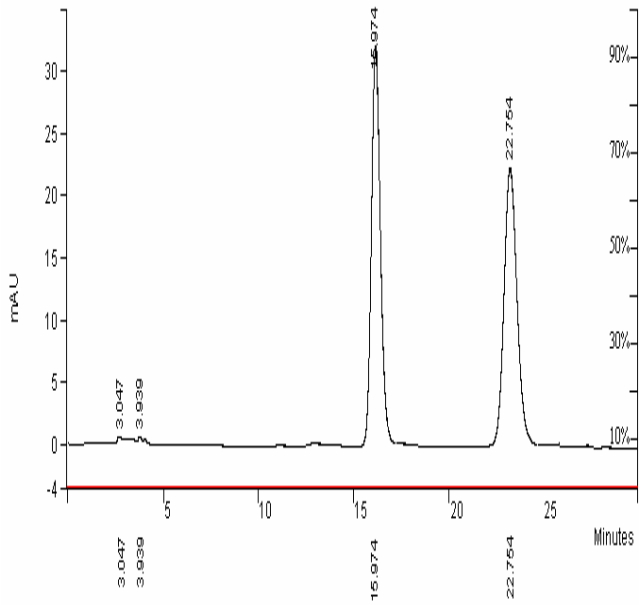


Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm

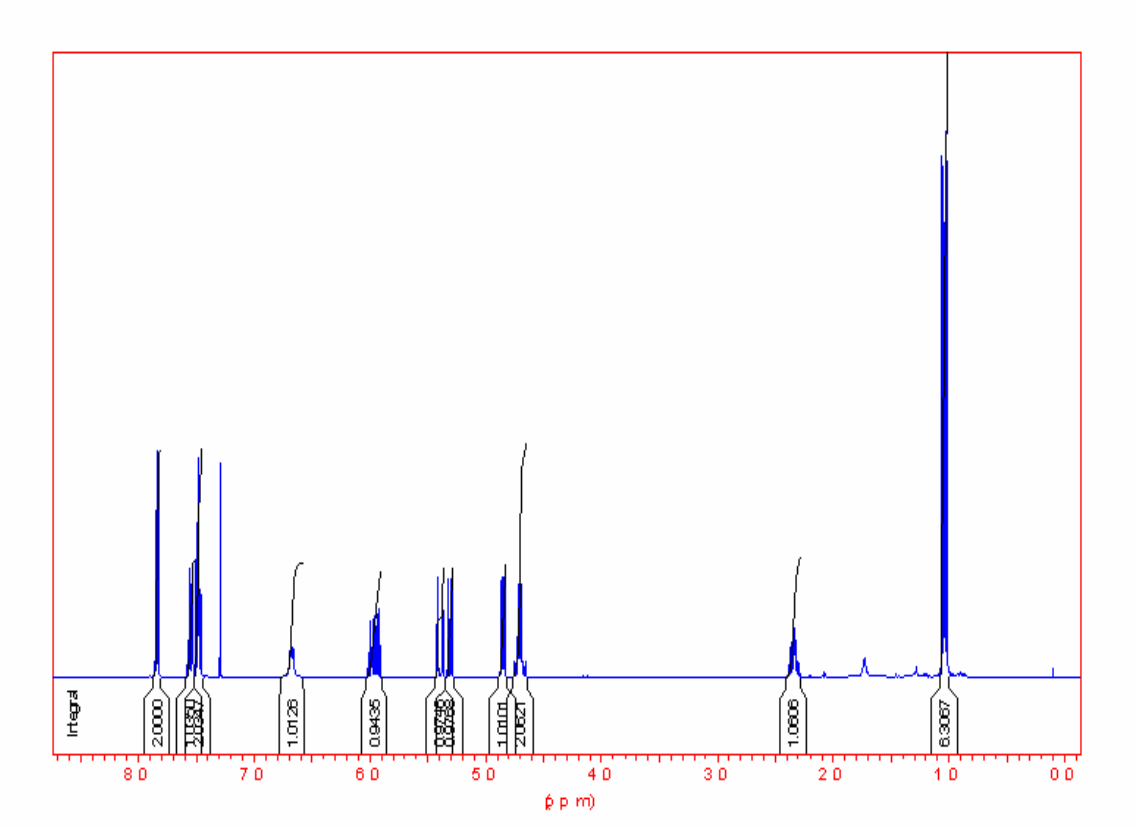
Peak No	Result	Ret. Time (min)	Area (counts)
1	11.1312	14.786	6061443
2	88.7005	20.622	48301448

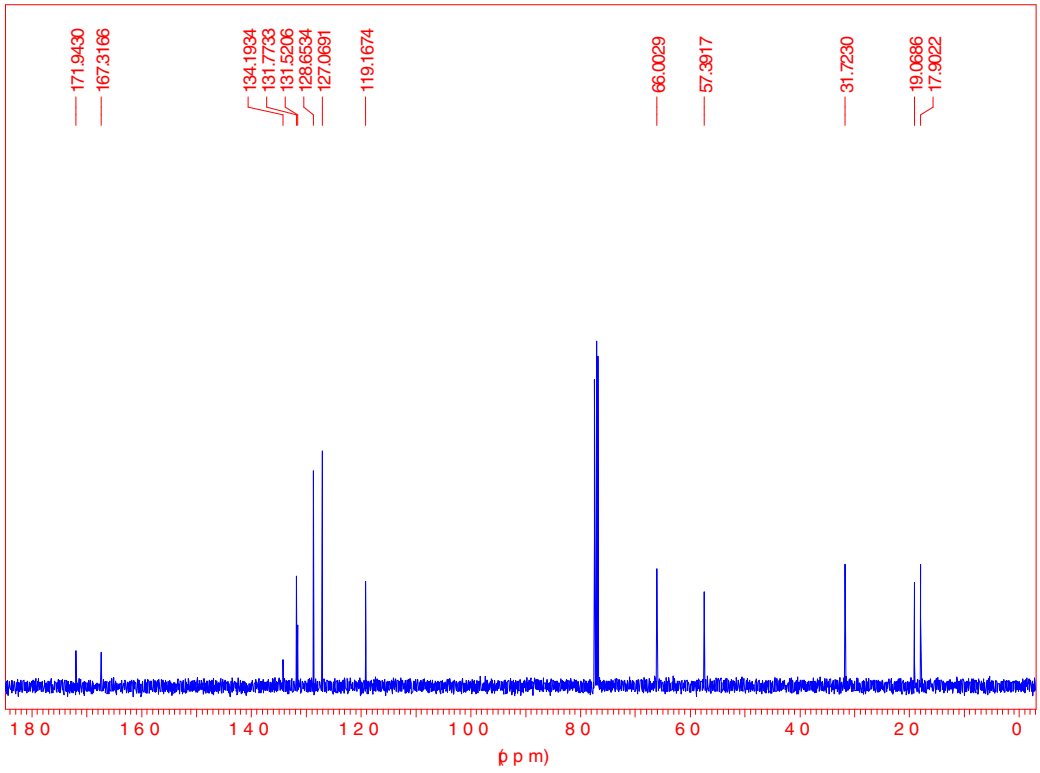


Peak No	Result	Ret. Time (min)	Area (counts)
1	49.3334	15.974	9174430
2	49.9869	22.754	9295960



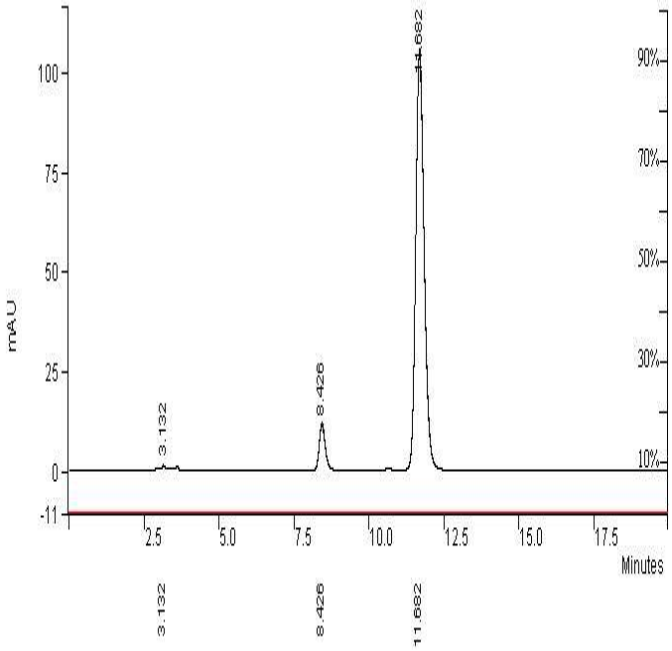
***N*-Benzoylvaline, allyl ester (7a)**



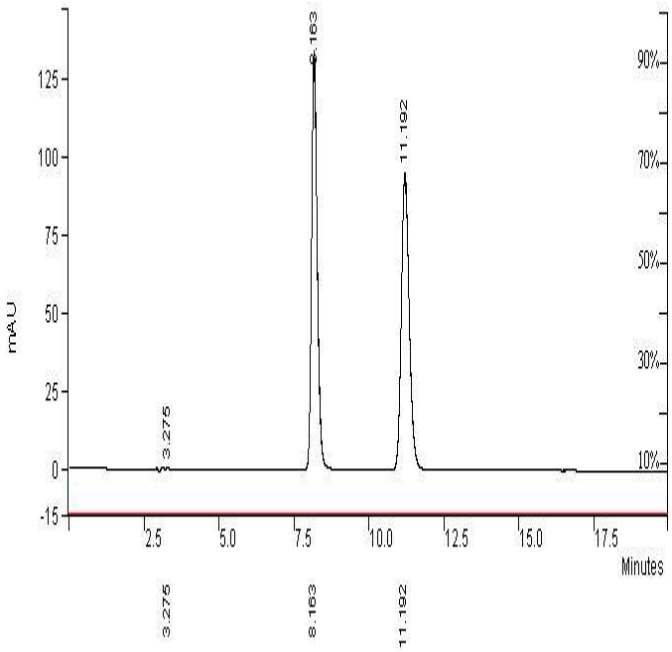


Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm

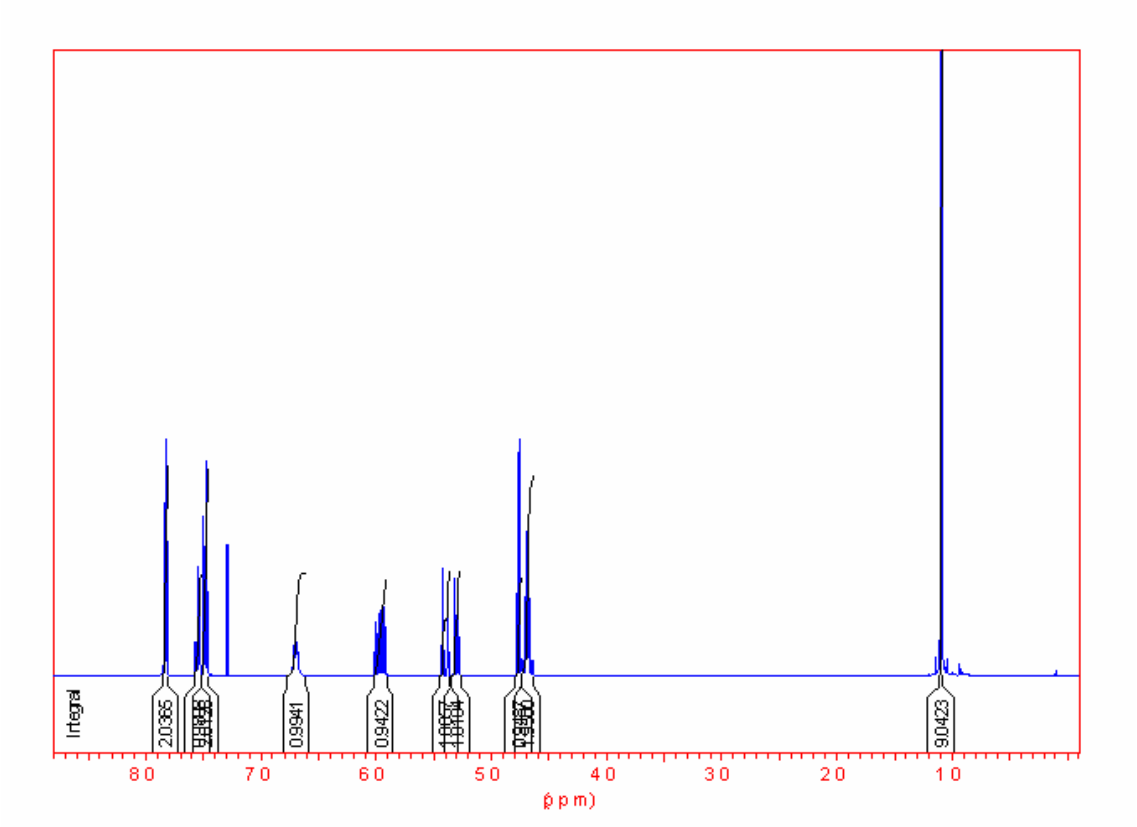
Peak No	Result	Ret. Time (min)	Area (counts)
1	7.6335	8.426	1720069
2	91.9729	11.682	20724402

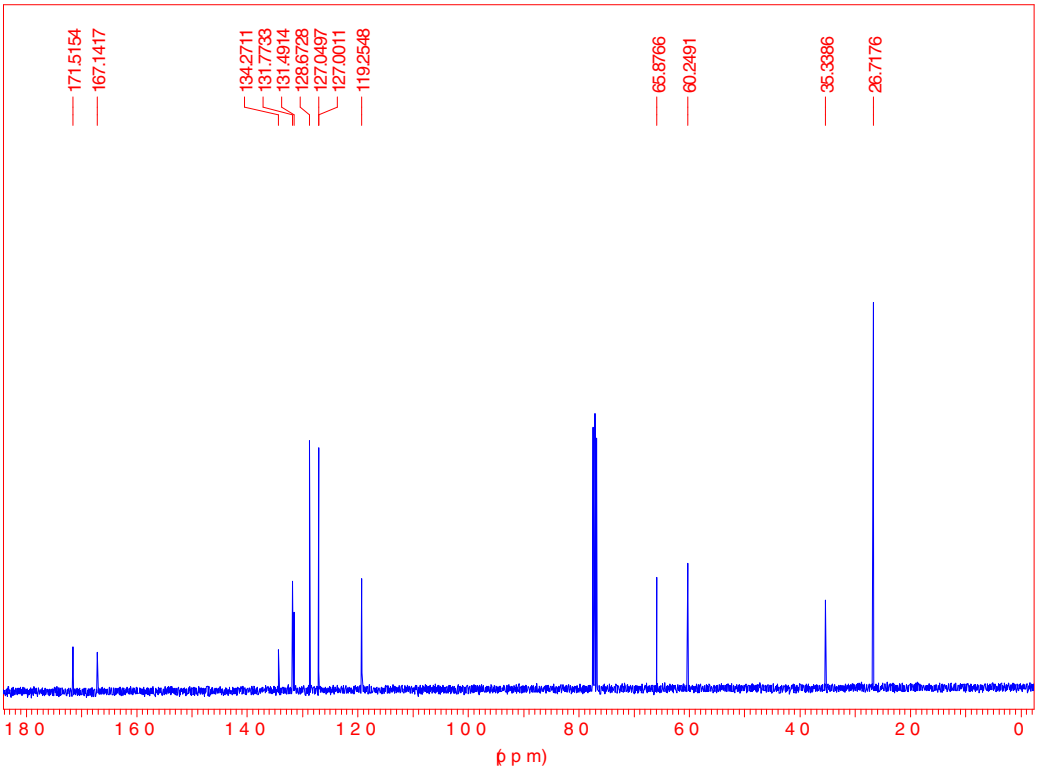


Peak No	Result	Ret. Time (min)	Area (counts)
1	49.8002	8.163	17369615
2	49.6356	11.192	17312205



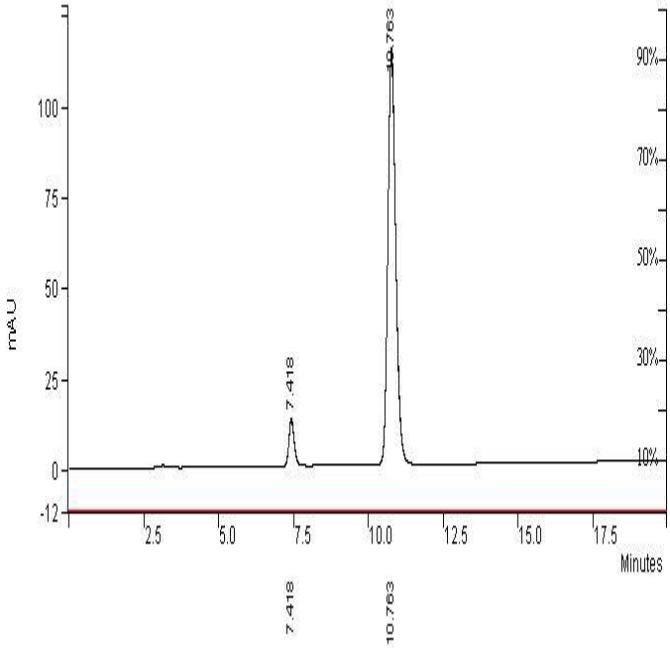
***N*-Benzoyl*tert*leucine, allyl ester (15)**



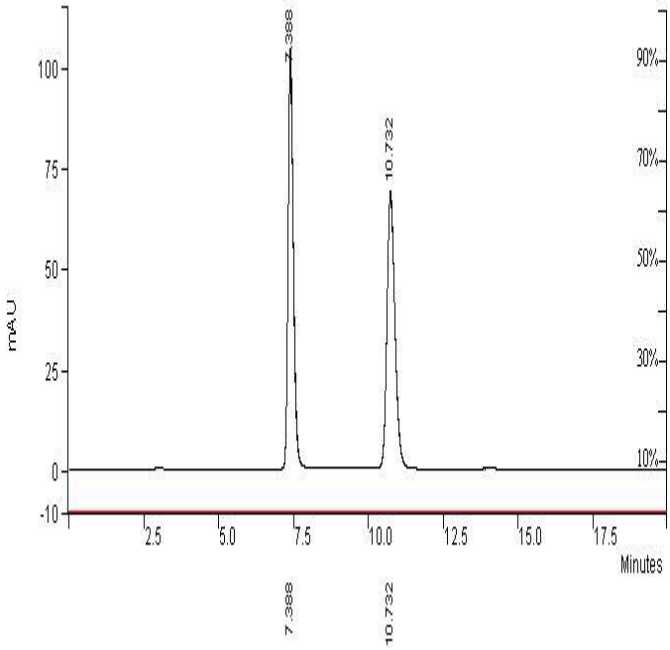


Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm

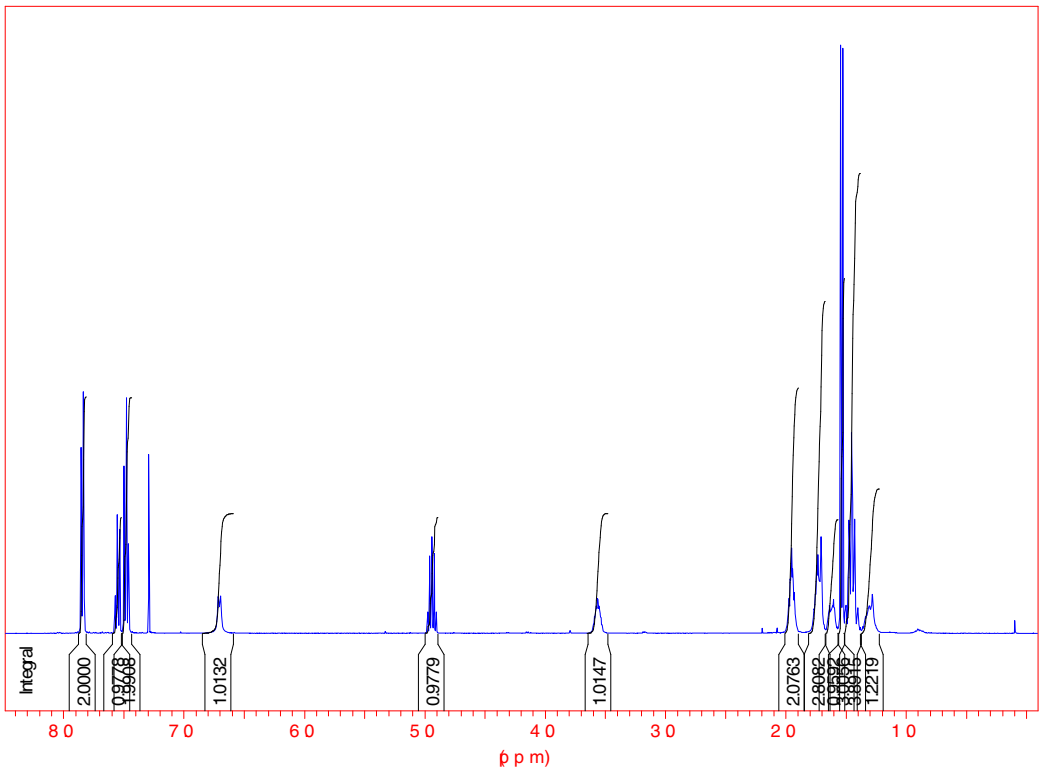
Peak No	Result	Ret. Time (min)	Area (counts)
1	7.6589	7.418	1771046
2	91.8662	10.763	21243168

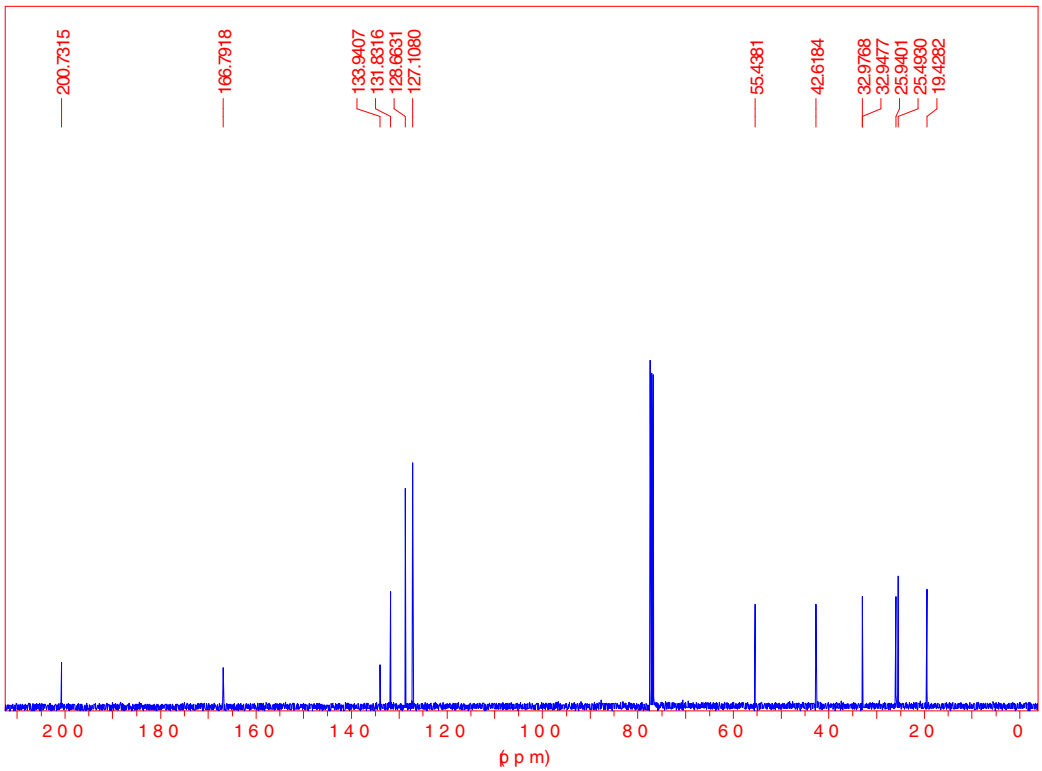


Peak No	Result	Ret. Time (min)	Area (counts)
1	50.0345	7.388	13462334
2	49.8802	10.732	13420813



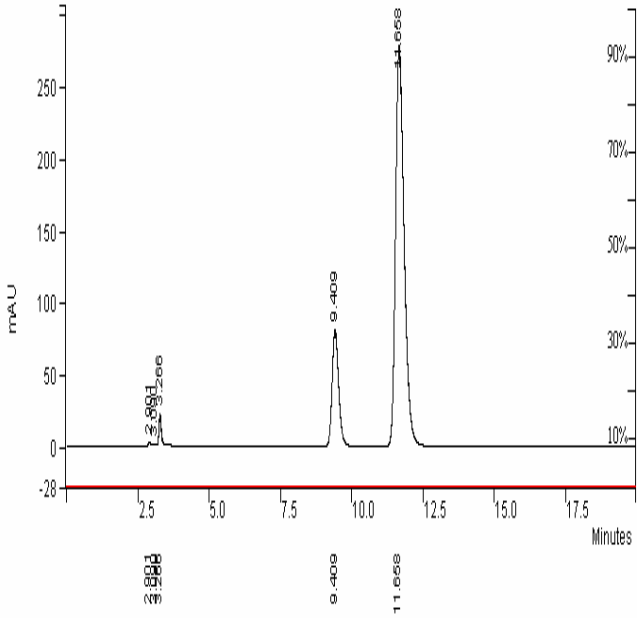
***N*-Benzoylalanine, cyclohexyl thioester (17)**



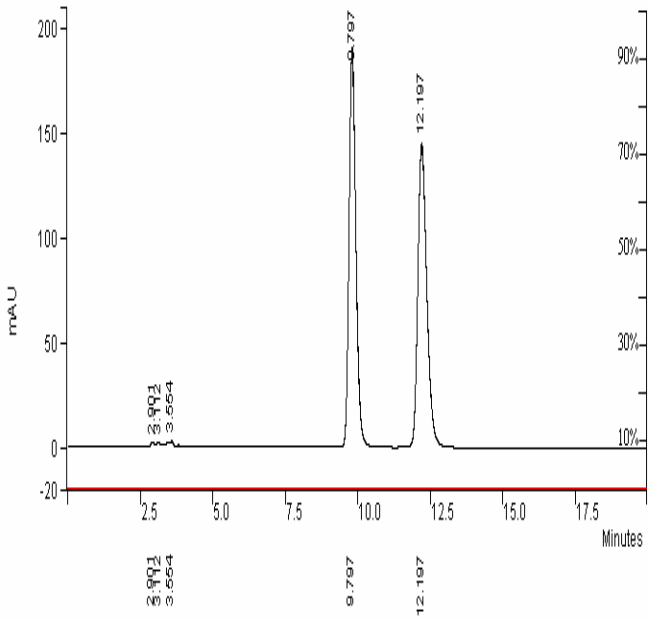


Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 9/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm

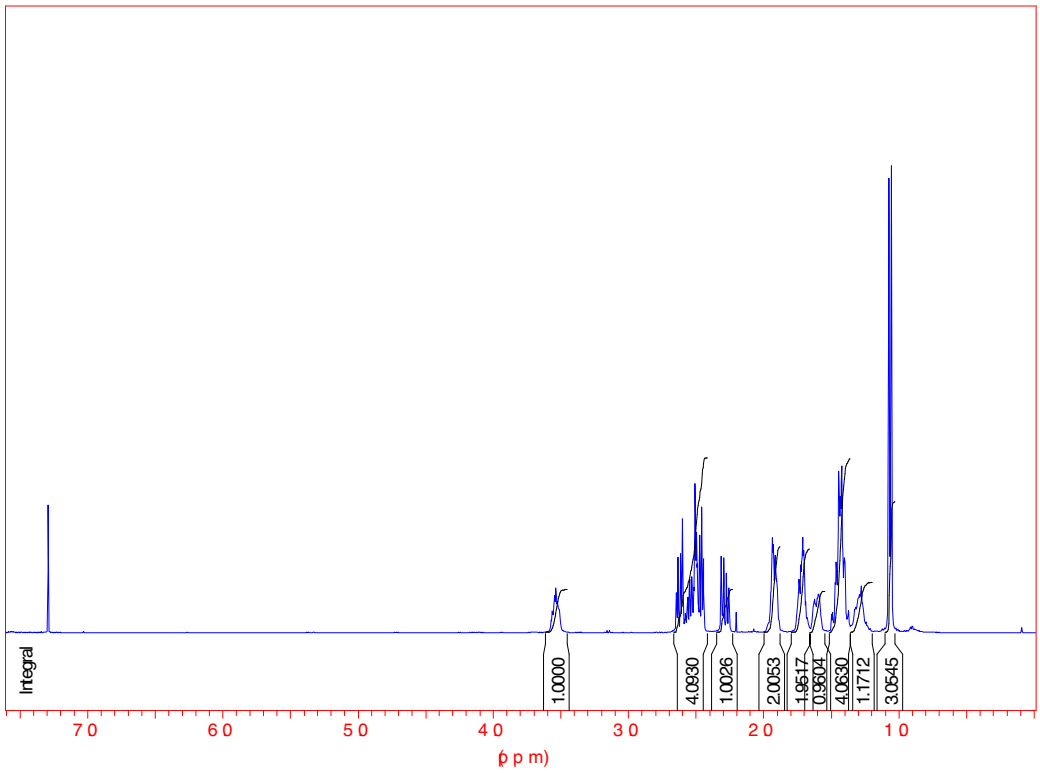
Peak No	Result	Ret. Time (min)	Area (counts)
1	17.4567	9.409	12991982
2	80.3413	11.658	59793244

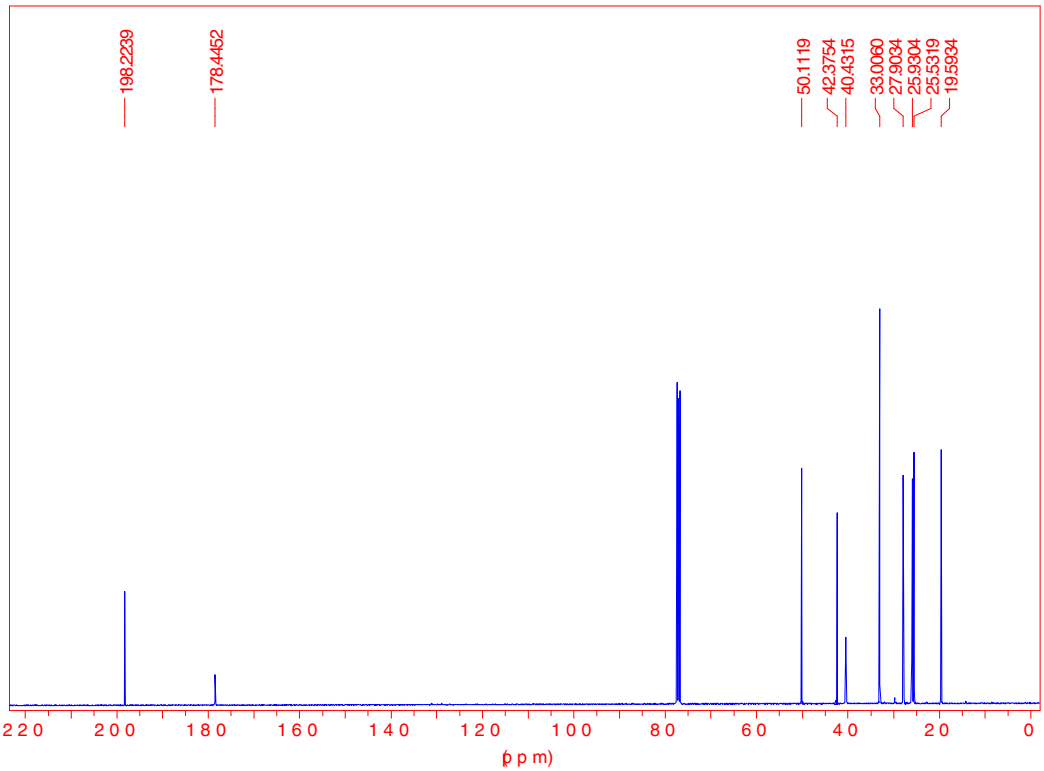


Peak No	Result	Ret. Time (min)	Area (counts)
1	49.3792	9.797	17420788
2	49.5691	12.197	17487784



4-Cyclohexylsulfanylcarbonyl-3-methyl-butyric acid (19)

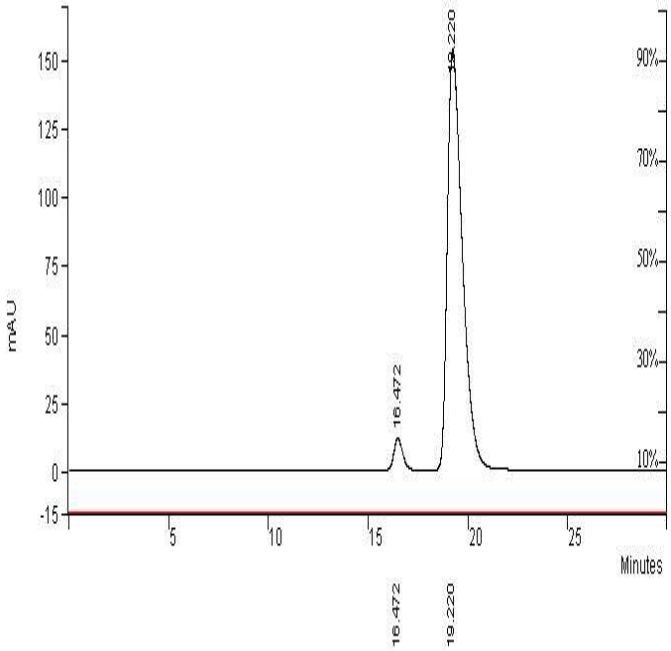




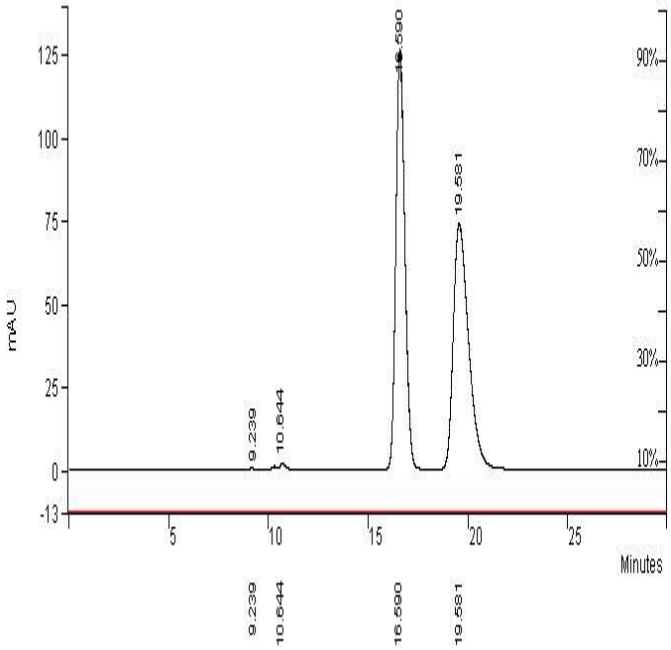
4-Cyclohexylsulfanylcarbonyl-3-methyl-butyric acid 2-nitro-phenyl ester (**20**)

Chiralpak AS (4.6 mm x 25 cm), hexane/IPA: 9/1, 0.5 mL min^{-1}, RT, UV detection at 220 nm

Peak No	Result	Ret. Time (min)	Area (counts)
1	4.1219	16.472	3600372
2	95.8045	19.220	83682729



Peak No	Result	Ret. Time (min)	Area (counts)
1	49.2198	16.590	39680180
2	49.3689	19.581	39800382



7.0 References

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[2] Pope, W. J.; Gibson, C. S. *J. Chem. Soc., Transactions*. **1912**, *101*, 939.

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[4] Karrer, P.; Van der Sluys Veer, F. C. *Helv. Chim. Acta*. **1932**, *15*, 746.

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