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An Enantioselective Tandem Reduction/Nitro-Mannich Reaction of Nitroalkenes using a Simple Thiourea Organocatalyst

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Supplementary Information

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Copies of ^{1}H and ^{13}C NMR spectra for catalyst **5h** novel *β*-nitrotrifluoroacetamides:

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General experimental

Unless specified otherwise for all non-aqueous chemistry, glassware was flame-dried under an inert (N_2 or Ar) atmosphere. Cryogenic conditions (-78 ^oC) were achieved using solid carbon dioxide/acetone baths. Temperatures of -20 ^oC were achieved using a NESLAB CB-80 Cryobath. Temperatures of 0 ^oC were obtained by means of an ice bath. Room temperature indicates temperatures in the range of 20-25 ^oC. For the purposes of thin layer chromatography (tlc), Merck silica-aluminium plates were used, with *uv* light (254 nm) and potassium permanganate used for visualisation. For column chromatography, Apollo Scientific ZEOprep 60 or Merck Geduran® Si 60 silica gel was used. Removal of solvents (*in vacuo*) was achieved using a Vacuubrand diaphragm pump or house vacuum and Büchi rotary evaporators.

Purification of Solvents and Reagents

Commercial solvents and reagents were used as supplied or purified in accordance with standard procedures, as described below.

Tetrahydrofuran (THF) was pre-dried over sodium wire and distilled under an atmosphere of dry nitrogen from sodium benzophenone ketal or obtained from a solvent tower, where degassed THF was passed through two columns of activated alumina and a 7 micron filter under 4 bar pressure. Diethyl ether (Et_2O) was pre-dried over sodium wire and distilled under an atmosphere of dry nitrogen from sodium benzophenone ketal or obtained from a solvent tower, where degassed Et_2O was passed through two columns of activated alumina and a 7 micron filter under 4 bar pressure. Toluene was obtained from a solvent tower, where degassed toluene was passed through two columns of activated alumina and a 7 micron filter under 4 bar pressure. Dichloromethane was distilled from calcium hydride powder or purchased as an analytical grade and stored over 4Å molecular sieves. Anhydrous MeCN was used as supplied.

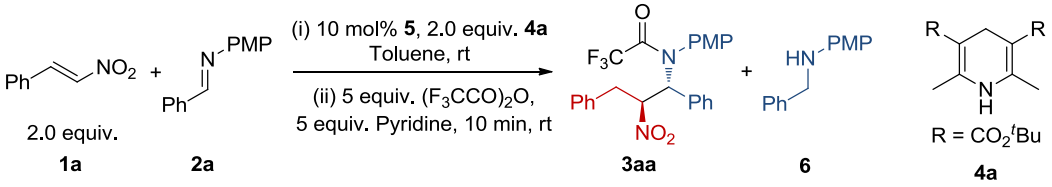
Characterisation

Melting points are uncorrected. All NMR data was collected using a Bruker AMX 300 MHz, Bruker AVANCE III 400 MHz, Bruker AVANCE 500 MHz or Bruker AVANCE III 600 MHz. Data was manipulated directly using Bruker XwinNMR (version 2.6) or TopSpin (version 2.1). Reference values for residual solvents were taken as δ = 7.27 ($CDCl_3$) and 2.51 ppm (DMSO-*d*6) for ^1H NMR; δ = 77.16 ppm ($CDCl_3$) for ^{13}C NMR. Multiplicities for coupled signals were denoted as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br. = broad, apt. = apparent and dd = double doublet *etc.* Coupling constants (*J*) are given in Hz and are uncorrected. Where appropriate, COSY, DEPT, HMBC, HMQC and NOE experiments were carried out to aid assignment. Mass spectroscopy data was collected on a Thermo Finnigan Mat900xp **(**EI/CI)

VG-70se (FAB) and Waters LCT Premier XE (ES) instruments. Infrared data was collected using a Perkin-Elmer 1600 FTIR machine as a thin film unless otherwise stated. Elemental analysis was performed on an Exeter Analytical Inc. EA440 horizontal load analyser. Melting points are uncorrected and were recorded on a Stuart Scientific SMP3 system. Optical rotations were obtained using a Jasco DIP370 digital polarimeter and are reported in deg cm^2 g^{-1}. Chiral HPLC was performed using either a Chiralcel AD 25 cm analytical column or an OD-H 15 cm analytical column. Samples were dissolved in solutions of MeCN/^{i}PrOH/^{n}hexane (5:15:80) to concentrations of 2.5 mg/mL.

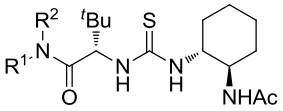
Full catalyst screening experiments

Table 1. Full catalyst screen

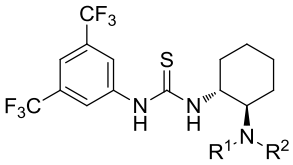


Entry	Catalyst	Rxn. Time	Yield of 6[a]	Yield of 3aa[b]	*dr* of 3aa[c]	% *ee* of 3aa[d]
1	**5a**	2 h	5	87	95:5	50
2	**5b**	2 h	<5	<5	n.d.	n.d.
3	**5c**	2 h	5	25	>95:5	86
4	**5d**	2 h	10	48	>95:5	90
5	**5d**	5 h	10	72	>95:5	88
6	**5e**	2 h	40	36	>95:5	-64
7	**5f**	2 h	25	37	>95:5	76
8	**5g**	2 h	5	72	>95:5	90
9	**5h**	2 h	5	75	90:10	90
10	**5i**	2 h	15	47	95:5	12
11	**5j**	2 h	15	45	>95:5	90
12	**5k**	2 h	10	67	>95:5	89
13	**5l**	2 h	<5	<5	n.d.	n.d.

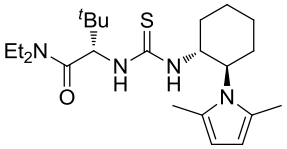
[a] Estimated yield of **6** determined using ^{1}H NMR data. [b] Isolated yield of **3aa**. [c] Calculated from ^{1}H data. [d] Determined by chiral HPLC.



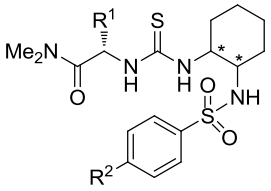
5a R^1,R^2 = Me
5i R^1 = H, R^2 = Me



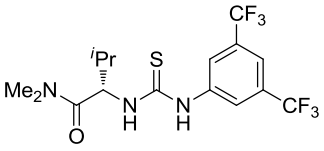
5b R^1,R^2 = Me
5e R^1 = H, R^2 = Ts



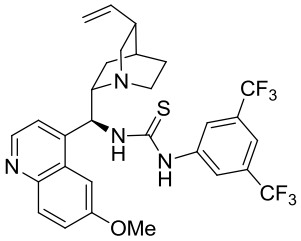
5c



5d R^1 = Me, R^2 = ^{t}Bu, (*R,R*)
5f R^1 = Me, R^2 = ^{t}Bu, (*S,S*)
5g R^1 = Me, R^2 = ^{i}Pr, (*R,R*)
5j R^1 = OMe, R^2 = ^{t}Bu, (*R,R*)
5k R^1 = NO_2, R^2 = ^{t}Bu, (*R,R*)



5h

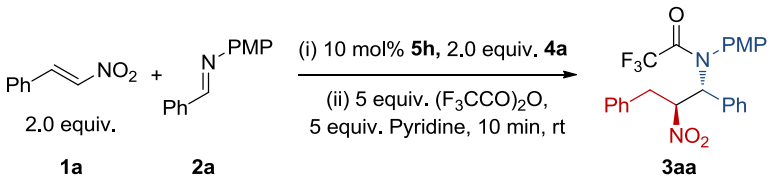


5l

For catalyst screening. To a flask containing *N*-PMP-phenyl imine **2** (0.20 mmol), *β*-nitrostyrene **1** (0.40 mmol), Hantzsch ester **4a** (0.40 mmol) and catalyst **5** (0.02 mmol) was added toluene (1.5 mL) and the reaction was stirred at room temperature for 2 h. After this time, a small aliquot (10 μL) was removed and analysed by ^{1}H NMR spectroscopy to measure reaction progress. Then trifluoroacetic anhydride (1.0 mmol), followed by pyridine (1.0 mmol) were added at -20 ^{o}C and the solution was allowed to warm to rt and stirred for 2 h. After this time, 2.0 M HCl (10 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (2 x 5 mL) and the combined organic phases were washed with sat. aq. $NaHCO_3$ 10 mL) and sat. brine (10 mL). The organic phase was then dried ($MgSO_4$) and the excess solvents were removed *in vacuo* to afford crude *β*-nitrotrifluoroacetamide **3**.

Solvent screen and further optimization

Table 2. Further optimization of reaction with catalyst 5h



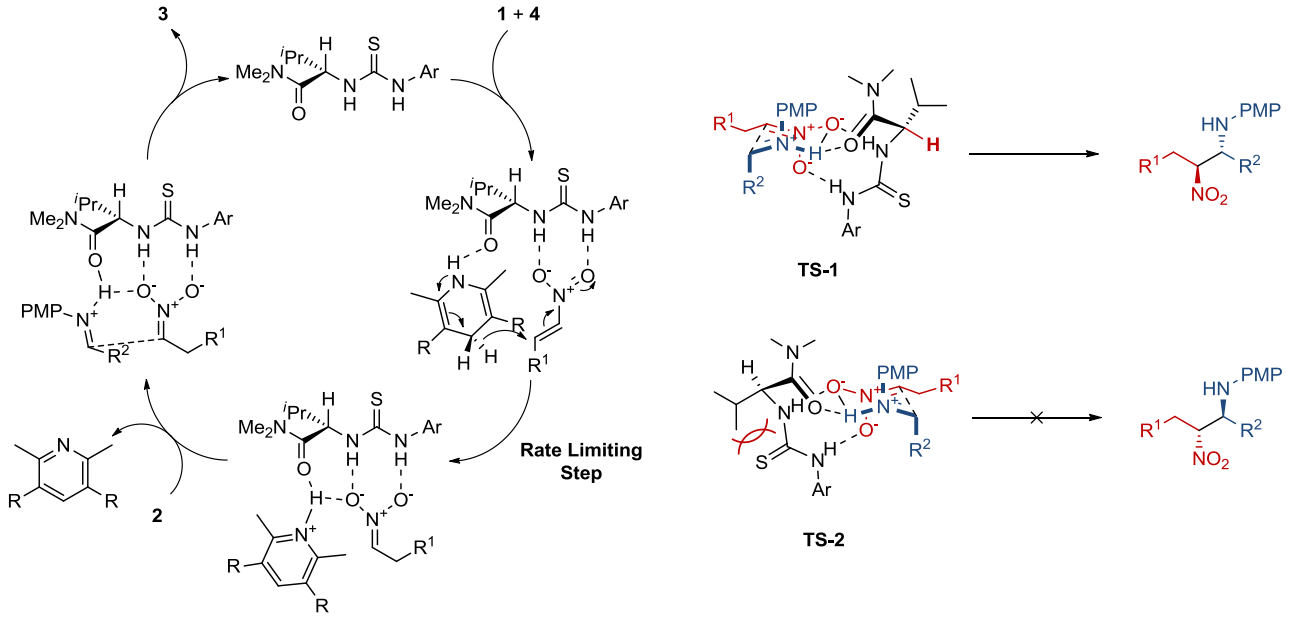
Entry	Solvent	Temp. (°C)	Time	Yield (%)	*dr* (anti:syn)[a]	*ee* (%)[b]
1	Et_2O	rt	2 h	70	90:10	16
2	THF	rt	2 h	13	90:10	94
3	MeCN	rt	2 h	<5	n/a	n/a
4	CH_2Cl_2	rt	2 h	70	90:10	90
5	Toluene	rt	2 h	75	90:10	90
6	Toluene	rt	30 min	74	90:10	94
7	Toluene	0	6 h	84	>95:5	95
8	Toluene	-20	20 h	81	>95:5	98
9	Toluene	-20	72 h	83	>95:5	98

[a] Determined by 1H NMR. [b] Determined by chiral HPLC.

Proposed mechanism

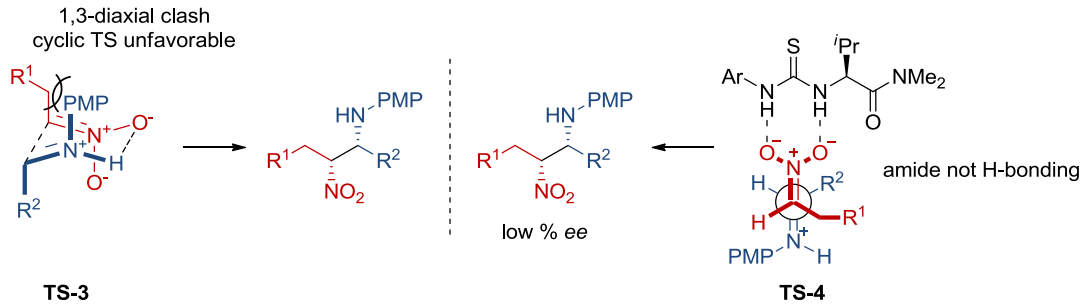
Our working mechanistic hypothesis (see Scheme below) requires initial H-bonding of the thiourea to the nitroalkene to activate it towards reduction. The more basic PMP-imine **2** then displaces the pyridine species, which activates the imine towards a nitro-Mannich reaction with the neighboring nitronate species through a six-membered transition state. As no nitroalkane is observed in the reaction until complete consumption of imine **2**, the kinetics of the nitro-Mannich reaction must be faster than protonation of the nitronate species. The six-membered transition state as depicted in Scheme 4 consists of two H-bonds between the thiourea and nitro group as well as an amide H-bond with the iminium species. If we assume from the detailed work of Jacobsen on a similar catalyst that the most stable conformation of catalyst **5h** is when the highlighted C-H bond is in the same plane as the large C=S bond,[1] the amide can freely H-bond to the iminium species in a *pseudo* equatorial position giving rise to the observed enantiomer (**TS-1**). Conversely, to obtain the opposite enantiomer the *iso*-propyl group would be required to be in the same plane as the C=S

bond (**TS-2**). Such a conformation would have a large steric penalty and would as such be unfavorable.



Proposed cause for low enantiomeric excess of *syn* diastereomers

When *N*-PMP imine **2** was substituted in the *ortho* position with a CF_3, Me or Br group the reactions were only moderately diastereoselective and the enantioselectivity was poor for the *syn* diastereomer (see main article, Table 2). This low enantioselectivity suggests that the *syn* diastereomer is formed *via* an alternative transition state. The *syn* diastereomer could be formed by a cyclic transition state where all substituents are in *pseudo* axial positions (see below, **TS-3**). Due to the 1,3-diaxial interactions, such a transition state may be unfavourable and an acyclic transition state may be in operation. In such a transition state it would be very difficult for the amide moiety of the catalyst to also H-bond to the imine, preventing the catalyst from implementing high levels of stereocontrol for the *syn* diastereomer (see below, **TS-4**).



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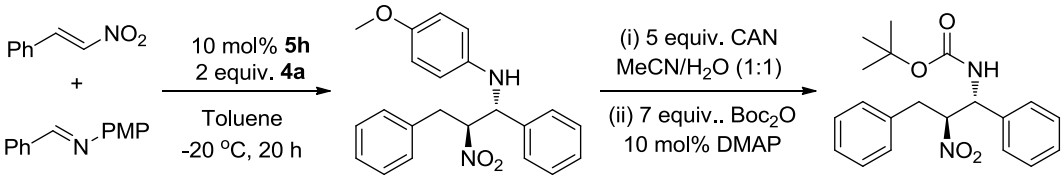
Synthesis of nitroalkene and imine starting materials

Nitroalkenes were prepared according to literature procedures,[2] and their data was in accord with that published.[3] Imines were prepared according to literature procedure.[4]

Determination of absolute stereochemistry

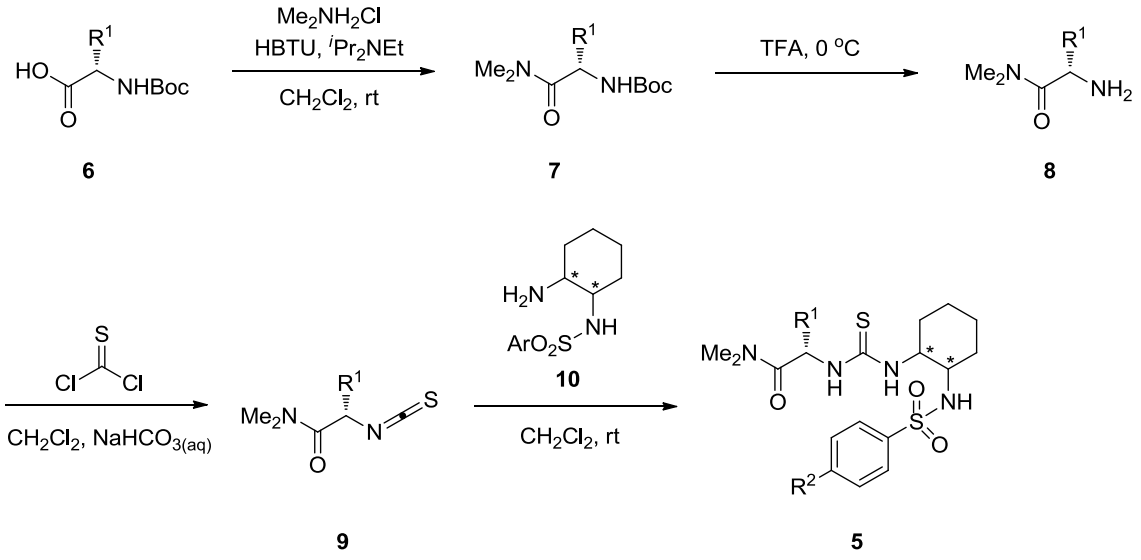
tert-Butyl ((1*R*,2*S*)-2-nitro-1,3-diphenylpropyl)carbamate



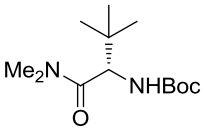
To a mixture containing imine **2a** (84 mg, 0.40 mmol), nitroalkene **1a** (120 mg, 0.80 mmol) and Hantzsch ester **4a** (248 mg, 0.80 mmol) in toluene (3 mL) cooled to -20 ^{o}C (Cryobath) was added a solution of catalyst **5h** (200 μL, 0.04 mmol, 0.2 M in toluene) and the reaction was stirred for 20 h. The excess solvent was removed *in vacuo* and the crude *β*-nitroamine was dissolved in MeCN (8 mL) and added to a pre-cooled solution of ceric ammonium nitrate (1.10 g, 2.00 mmol) in water (8 mL) at 0 ^{o}C. The reaction was stirred for 1 h at this temperature to give a black mixture and then di-*tert*-butyl dicarbonate (611 mg, 2.80 mmol) and 4-dimethylpyridine (5 mg, 0.04 mmol) were added and the reaction was allowed to warm to rt and stirred for 16 h. The excess solvent was then removed *in vacuo* and the resultant residue was diluted with EtOAc (40 mL). This mixture was then washed with sat. aq. $NaHCO_3$ 2 x 20 mL), dried ($MgSO_4$) and the excess solvent was removed *in vacuo* to give, after purification by column chromatography (20% EtOAc/pet. ether), the title compound (56 mg, 0.16 mmol, 39% yield) as a white solid; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 90:10, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 11.0 min, t_r (minor) = 12.7 min, shows 94% *ee*; mp 179-180 ^{o}C; $[\alpha]_D^{25}$ = -46.0 ^{o} (c = 0.90, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.47 (9H, s), 3.18 (1H, dd, *J* = 14.8, 3.52), 3.32 (1H, dd, *J* = 14.6, 10.56), 5.13 (1H, br. s), 5.26 (2H, br. s), 7.16 (2H, d, *J* = 6.8), 7.23-7.33 (5H, m), 7.36-7.43 (3H, m); ^{1}H NMR data and $[\alpha]_D$ are consistent with literature data.[5]

Synthesis of catalysts

Catalysts **5a** and **5i** were prepared according to literature procedure.[6] Catalysts **5b** and **5p** were purchased from commercial sources. Catalyst **5c** was prepared according to literature procedure.[7] Catalysts **5d**, **5f**, **5j**, **5k** and **5g** were prepared according to the general synthetic scheme below.

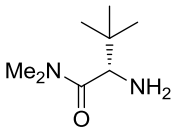


(*S*)-*tert*-butyl (1-(dimethylamino)-3,3-dimethyl-1-oxobutan-2-yl)carbamate (7a)



Prepared according to literature procedure.[8] *N*-Boc-*L*-*tert*-leucine (2.0 mmol) gave the title compound **7a** (410 mg, 1.6 mmol, 80% yield) as a colourless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.97 (9H, s), 1.42 (9H, s), 2.96 (3H, s), 3.13 (3H, s), 4.52 (1H, d, *J* = 9.8), 5.34 (1H, d, *J* = 9.8). ^{1}H NMR data are consistent with literature data.

(*S*)-2-Amino-*N*,*N*,3,3-tetramethylbutanamide (8a)



A mixture of TFA (20 mL) and *N*-Boc amide (2.09 mmol) were stirred at 0 °C for 2 h. The excess solvent was then removed *in vacuo* and the concentrated residue was cooled to 0 °C. To this

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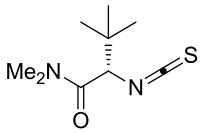
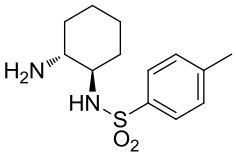
residue was added 2.0 M NaOH (40 mL) and 5% MeOH/CH_2Cl_2 (60 mL) and the mixture was stirred for 15 min. The biphasic mixture was then separated and the aqueous layer was re-extracted with more 5% MeOH/CH_2Cl_2 (2 x 60 mL). The combined organics were dried (Na_2SO_4) and the excess solvent was removed *in vacuo* to give the title compound **8a** (248 mg, 1.57 mmol, 75% yield) as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (9H, s), 2.84 (3H, s), 2.97 (3H, s), 3.42 (1H, s); ^{1}H NMR data are consistent with literature data.

(*S*)-2-Isothiocyanato-*N*,*N*,3,3-tetramethylbutanamide (9a)



Prepared using a modified literature procedure.[6] A solution of amine (1.57 mmol) in CH_2Cl_2 (15 mL) and sat. aq. $NaHCO_3$ (15 mL) was cooled to 3 ^{o}C (ice bath) and stirred for 15 min. Stirring was then stopped and thiophosgene (180 μL, 2.34 mmol) was syringed directly into the organic layer. The mixture was then vigorously stirred for 1 h at 3 ^{o}C. The reaction was extracted with CH_2Cl_2 (2 x 15 mL), dried ($MgSO_4$) and the excess solvent removed to give title compound **9a** (342 mg, 1.72 mmol, quantitative yield) as a colourless oil; IR υ_{max} 2970, 2037, 1641, 1496, 1473, 1398, 1137 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.09 (9H, s), 3.01 (3H, s), 3.08 (3H, s), 4.27 (1H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 26.6 (*C*H_3), 36.5 (*C*H_3), 37.7 (*C*), 38.4 (*C*H_3), 64.2 (*C*H), 135.6 (*C*), 166.5 (*C*); *m/z* (CI) 201 (72, M+H), 144 (100, M+H-^{t}Bu); HRMS $C_9H_{16}N_2OSH$ calcd. 201.1062, found 201.1053.

***N*-((1*R*,2*R*)-2-aminocyclohexyl)-4-methylbenzenesulfonamide (10a)**



Prepared by a modified of literature procedure.[9] To a solution of (*R*,*R*)-diaminocyclohexane *L*-tartrate (9.0 g, 34.1 mmol) in 2.0 M NaOH (45 mL) was added Et_3N (6.3 mL, 45.5 mmol) and CH_2Cl_2 (35 mL). The mixture was cooled to 0 ^{o}C and a solution of para-toluenesulfonyl chloride

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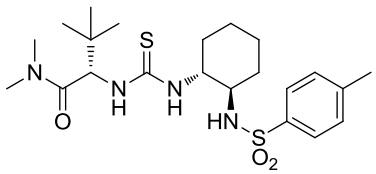
(4.3 g, 22.7 mmol) in CH_2Cl_2 (25 mL) was added dropwise over 30 min. After complete addition the reaction was allowed to warm to rt and stirred for 16 h. The reaction was then extracted with 2.0 M HCl (3 x 100 mL). The combined aqueous extracts were basified to pH 9 with NaOH pellets to give a cloudy white mixture which was then extracted with CH_2Cl_2 (3 x 100 mL). The combined organics were then dried ($MgSO_4$) and the excess solvent removed *in vacuo* to give title compound **10a** (5.18 g, 19.3 mmol, 85% yield) as a white solid; mp 97-99 ^oC (Lit.[10] 108-110 ^oC); ^1H NMR (600 MHz, $CDCl_3$) δ 1.01-1.23 (4H, m), 1.54-1.67 (2H, m), 1.74-1.84 (1H, m), 1.88-1.95 (1H, m), 2.36 (1H, apt. td, *J* = 10.4, 4.0), 2.42 (3H, s), 2.63 (1H, apt. td, *J* = 10.3, 4.2), 7.29 (2H, d, *J* = 7.9), 7.77 (2H, dm, *J* = 8.3). ^1H NMR data are consistent with literature data.[9]

(*S*)-*N*,*N*,3,3-Tetramethyl-2-(3-((1*R*,2*R*)-2-(4-methylphenylsulfonamido)cyclohexyl)thioureido)butanamide (5d)



A solution of isothiocyanate **9a** (160 mg, 0.80 mmol) and sulfonamide **10a** (258 mg, 0.96 mmol) in CH_2Cl_2 (5 mL) was stirred at rt for 3 d or until complete reaction as judged by tlc analysis. The excess solvent was then removed and the crude product was purified by column chromatography (5% MeOH/CH_2Cl_2) to give title compound **5d** (362 mg, 0.77 mmol, 96% yield) as a white solid; mp 84-86 ^oC; $[\alpha]_D^{25}$ = +63.8 ^{o} (c = 1.015, $CHCl_3$); IR υ_{max} 3311, 2934, 1622, 1528, 1318, 1156, 1091, 661 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.02 (9H, s), 1.05-1.16 (2H, m), 1.21-1.35 (2H, m), 1.56-1.70 (2H, m), 1.97 (1H, apt. d, *J* = 11.9), 2.07 (1H, apt. d, *J* = 11.7), 2.41 (3H, s), 2.84-2.93 (1H, m), 2.98 (3H, s), 3.28 (3H, s), 4.21-4.34 (1H, m), 5.69 (1H, br. d, *J* = 9.2), 6.11 (1H, br. d, *J* = 7.0), 6.63-6.82 (2H, br. m), 7.22-7.29 (2H, m), 7.69 (2H, d, *J* = 8.1); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.7 (*C*H_3), 24.5 (*C*H_2), 24.7 (*C*H_2), 26.8 (*C*H_3), 33.0 (*C*H_2), 34.0 (*C*H_2), 35.9 (*C*H_3), 36.6 (*C*), 38.9 (*C*H_3), 56.8 (*C*H), 59.0 (*C*H), 59.8 (*C*H), 127.1 (*C*H), 129.7 (*C*H), 138.4 (*C*), 143.1 (*C*), 172.2

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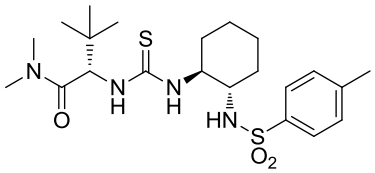
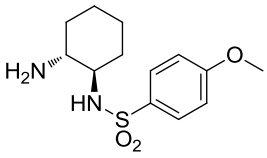
(*C*), 183.8 (*C*); *m/z* (ESI$^+$) 491 (100, M+Na), 424 (54, M–Me_2N); HRMS $C_{22}H_{36}N_4O_3S_2Na^+$ calcd. 491.2127, found 491.2119.

(*S*)-*N*,*N*,3,3-Tetramethyl-2-(3-((1*S*,2*S*)-2-(4-methylphenylsulfonamido)cyclohexyl)thioureido)butanamide (5f)



Synthesised in an analogous fashion to **5d** on 0.68 mmol scale to give title compound **5f** (273 mg, 0.58 mmol, 86% yield) as an off-white solid; mp 181-183 ^oC; $[\alpha]_D^{25}$ = -75.7 ^{o} (c = 1.01, $CHCl_3$); IR υ_{max} 3305, 2931, 1622, 1539, 1326, 1160, 1074, 900, 666 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.90-1.09 (2H, m), 1.04 (9H, m), 1.14-1.33 (2H, m), 1.54-1.70 (2H, m), 1.80-1.97 (2H, m), 2.41 (3H, s), 2.85-2.95 (4H, m), 3.26 (3H, s), 4.27 (1H, br. s), 5.60 (1H, br. s), 6.27-6.45 (1H, m), 6.47-6.64 (1H, m), 6.91-7.07 (1H, m), 7.22-7.29 (2H, m), 7.73 (2H, d, *J* = 8.3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.7 (*C*H_3), 24.6 (*C*H_2), 24.8 (*C*H_2), 26.9 (*C*H_3), 32.7 (*C*H_2), 33.9 (*C*H_2), 35.9 (*C*H_3), 36.1 (*C*) 38.8 (*C*H_3), 56.3 (*C*H), 59.8 (*C*H), 60.2 (*C*H), 127.1 (*C*H), 129.6 (*CH*), 138.6 (C), 142.9 (C), 173.0 (*C*), 183.9 (*C*); *m/z* (CI) 469 (4, M+H), 435 (100, M-H_2O); HRMS $C_{22}H_{36}N_4O_3S_2H^+$ calcd. 469.2307, found 469.2305.

***N*-((1*R*,2*R*)-2-aminocyclohexyl)-4-methoxybenzenesulfonamide (10b)**



Synthesised in an analogous fashion to **10a** on 3.8 mmol scale to give title compound **10b** (859 mg, 3.02 mmol, 80% yield) as a white solid; mp 90-92 ^oC (Lit.[11] 96-98 ^oC); ^1H NMR (600 MHz, $CDCl_3$) δ 1.01-1.25 (4H, m), 1.56-1.67 (2H, m), 1.78-1.86 (1H, m), 1.88-1.94 (1H, m), 2.30-2.37 (1H, m), 2.60 (1H, m), 3.87 (3H, s), 6.97 (2H, dm, *J* = 8.8), 7.82 (2H, dm, *J* = 8.8). ^1H NMR data are consistent with literature data.[11]

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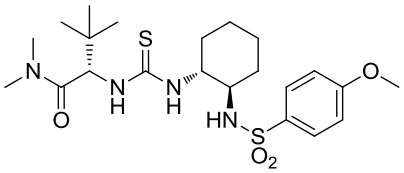
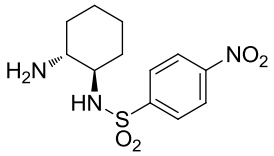
(*S*)-2-(3-((1*R*,2*R*)-2-(4-Methoxyphenylsulfonamido)cyclohexyl)thioureido)-*N*,*N*,3,3-tetramethylbutanamide (5j)



Synthesised in an analogous fashion to **5d** on 0.63 mmol scale to give title compound **5j** (273 mg, 0.56 mmol, 90% yield) as an off-white solid; mp 98-100 ^{o}C; $[\alpha]_D^{25}$ = +73.6 ^{o} (c = 0.990, $CHCl_3$); IR υ_{max} 3315, 2938, 1620, 1531, 1319, 1258, 1154, 731 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (9H, s), 1.04-1.13 (2H, m), 1.18-1.38 (2H, m), 1.63 (2H, t, *J* = 11.7), 1.95-2.13 (2H, m), 2.71-2.82 (1H, m), 2.85 (3H, s), 3.27 (3H, s), 3.85 (3H, s), 4.25-4.38 (1H, m), 5.76 (1H, d, *J* = 9.5), 6.73 (1H, d, *J* = 8.0), 6.90 (2H, dm, *J* = 9.0), 7.05 (2H, d, *J* = 9.3), 7.64 (2H, d, *J* = 8.8); ^{13}C NMR (151 MHz, $CDCl_3$) δ 24.5 (*C*H_2), 24.8 (*C*H_2), 26.8 (*C*H_3), 33.0 (*C*H_2), 34.0 (*C*H_2), 35.8 (*C*H_3), 36.6 (C), 38.9 (*C*H_3), 55.8 (*C*H_3), 56.8 (*C*H), 59.0 (*C*H), 59.9 (*C*H), 114.2 (*CH*), 129.2 (*CH*), 132.6 (C), 162.7 (*C*), 172.2 (*C*), 183.8 (*C*); *m/z* (ESI$^+$) 507 (88, M+Na), 440 (100, M-Me_2N); HRMS $C_{22}H_{36}N_4O_4S_2Na^+$ calcd. 507.2076, found 507.2066.

***N*-((1*R*,2*R*)-2-aminocyclohexyl)-4-nitrobenzenesulfonamide (10c)**



Synthesised in an analogous fashion to **10a** on 3.8 mmol scale to give title compound **10c** (860 mg, 2.87 mmol, 76% yield) as a yellow solid; mp 159-161 ^{o}C (Lit.[12] 177.5-178 ^{o}C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.05-1.27 (4H, m), 1.59-1.70 (2H, m), 1.86-1.96 (2H, m), 2.40 (1H, apt. td, *J* = 10.5, 4.0), 2.70 (1H, apt. td, *J* = 10.4, 4.1), 8.10 (2H, dm, *J* = 8.8), 8.36 (2H, dm, *J* = 8.8). ^{1}H NMR data are consistent with literature data.[12]

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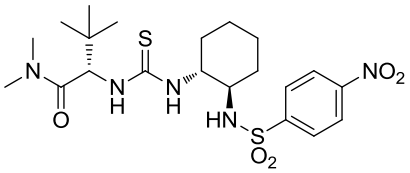
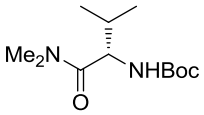
(*S*)-*N*,*N*,3,3-Tetramethyl-2-(3-((1*R*,2*R*)-2-(4-nitrophenylsulfonamido)cyclohexyl)thioureido)butanamide (5k)



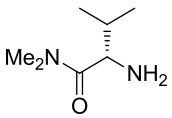
Synthesised in an analogous fashion to **5d** on 0.82 mmol scale to give title compound **5k** (403 mg, 0.81 mmol, 99% yield) as a yellow solid; mp 197-199 ^{o}C; $[\alpha]_D^{25}$ = +72.5 ^{o} (c = 1.00, $CHCl_3$); IR υ_{max} 3336, 3067, 2937, 2865, 1641, 1529, 1349, 1307, 1159 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.02 (9H, s), 1.09-1.17 (2H, m), 1.20-1.35 (2H, m), 1.62 (1H, br. d, *J* = 13.4), 1.68 (1H, br. d, *J* = 13.4), 1.90 (1H, br. d, *J* = 13.4), 2.08 (1H, br. d, *J* = 12.4), 2.98-3.04 (1H, m), 3.06 (3H, s), 3.28 (3H, s), 4.28-4.37 (1H, m), 5.68 (1H, br. d, *J* = 8.7), 6.31 (1H, br. s), 6.88 (1H, br. d, *J* = 9.2), 7.61 (1H, br. s), 8.04 (2H, d, *J* = 8.8), 8.32 (2H, d, *J* = 9.2); ^{13}C NMR (151 MHz, $CDCl_3$) δ 24.4 (*C*H_2), 24.7 (*C*H_2), 26.8 (*C*H_3), 32.8 (*C*H_2), 34.1 (*C*H_2), 36.0 (*C*H_3), 36.7 (*C*), 38.9 (*C*H_3), 56.6 (C*H*), 59.3 (C*H*), 60.0 (C*H*), 124.4 (*CH*), 128.2 (*CH*), 147.8 (C), 149.8 (*C*), 172.4 (*C*), 183.7 (*C*); *m/z* (ESI$^+$) 522 (79, M+Na), 455 (100, M-Me_2N); HRMS $C_{21}H_{33}N_5O_5S_2Na^+$ calcd. 522.1821, found 522.1813.

(*S*)-*tert*-Butyl (1-(dimethylamino)-3-methyl-1-oxobutan-2-yl)carbamate (7b)



Prepared according to literature procedure.[13] *N*-Boc-*L*-valine (19.2 mmol) gave title compound **7b** (4.60 g, 18.2 mmol, 95% yield) as a white solid. mp 54-55 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.89 (3H, d, *J* = 6.8), 0.94 (3H, d, *J* = 6.8), 1.42 (9H, s), 1.87-1.97 (1H, m), 2.96 (3H, s), 3.10 (3H, s), 4.46 (1H, dd, *J* = 9.2, 6.0), 5.37 (1H, d, *J* = 8.7). ^{1}H NMR data are consistent with literature data.[8]

(*S*)-2-Amino-*N*,*N*,3-trimethylbutanamide (8b)



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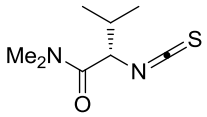
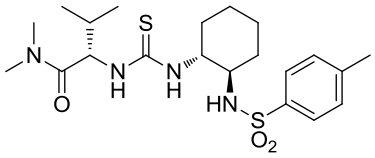
Synthesised in an analogous fashion to **8a** on 6.05 mmol scale to give title compound **8b** (820 mg, 5.70 mmol, 94% yield) as a white solid; mp 30-32 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.91 (2H, d, *J* = 6.8), 0.96 (2H, d, *J* = 7.0), 1.70 (2H, br. s_2), 1.85(1H, apt. oct, *J* = 6.6), 2.97 (3H, s), 3.03 (3H, s), 3.50 (1H, d, *J* = 5.3). ^{1}H NMR data are consistent with literature data.[8]

(*S*)-2-Isothiocyanato-*N*,*N*,3-trimethylbutanamide (9b)



Synthesised in an analogous fashion to **9a** on 0.63 mmol scale to give title compound **9b** (107 mg, 0.58 mmol, 92% yield) as a colourless oil; IR υ_{max} 2967, 2067, 1655, 1495, 1400 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (3H, d, *J* = 6.8), 1.06 (3H, d, *J* = 6.5), 2.18-2.30 (1H, m), 3.00 (3H, s), 3.06 (3H, s), 4.26 (1H, d, *J* = 5.8); ^{13}C NMR (151 MHz, $CDCl_3$) δ 17.8 (*C*H_3), 20.0 (*C*H_3), 32.2 (*C*H), 36.5 (*C*H_3), 37.4 (*C*H_3), 63.6 (*C*H), 136.6 (*C*), 166.9 (*C*); *m/z* (CI) 187 (75, M+H); HRMS $C_8H_{14}N_2OSH^+$ calcd. 187.0897, found 187.0950.

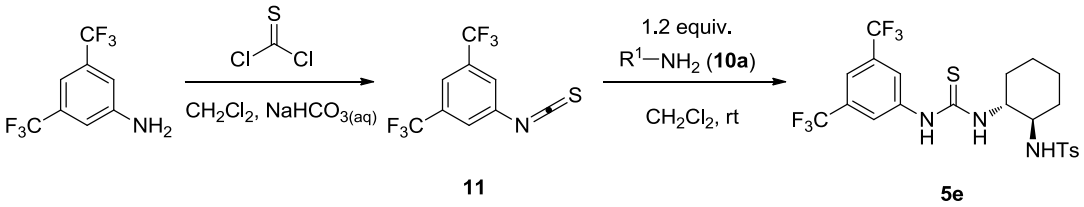
(*S*)-*N*,*N*,3-Trimethyl-2-(3-((1*R*,2*R*)-2-(4-methylphenylsulfonamido)cyclohexyl)thioureido)butanamide (5g)



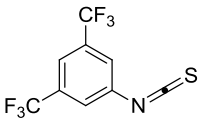
Synthesised in an analogous fashion to **5d** on 0.40 mmol scale to give title compound **5g** ((157 mg, 0.35 mmol, 86% yield) as an off-white solid; mp 75-77 ^{o}C; $[\alpha]_D^{25}$ = +39.8 ^{o} (c = 1.015, $CHCl_3$); IR υ_{max} 3303, 2934, 1625, 1540, 1324, 1159, 1091, 915, 730 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.91 (3H, dd, *J* = 6.8, 0.9), 0.99 (3H, d, *J* = 6.8), 1.02-1.16 (2H, m), 1.20-1.35 (2H, m), 1.56-1.70 (2H, m), 1.75-1.82 (1H, m), 1.95-2.09 (2H, m), 2.38 (3H, s), 2.86-2.93 (4H, m), 3.32 (3H, s), 4.31 (1H, m), 5.40-5.63 (1H, m), 6.72-7.03 (2H, br. m), 7.20 (2H, d, *J* = 7.3), 7.52-7.63 (1H, br. m), 7.65 (2H, d, *J* = 7.9); ^{13}C NMR (151 MHz, $CDCl_3$) δ 18.6 (*C*H_3), 18.9 (*C*H_3), 21.7 (*C*H_3), 24.4 (*C*H_2), 24.8 (*C*H_2), 33.0 (*C*H_2), 33.0 (*C*HMe_2), 33.8 (*C*H_2), 36.0 (*C*H_3), 38.5 (*C*H_3), 56.2 (*C*H), 58.9 (C*H*), 59.8

(*C*H), 126.9 (*CH*), 129.5 (*CH*), 138.5 (C), 143.1 (C), 173.1 (*C*), 183.7 (*C*); *m/z* (ESI^+) 477 (57, M+Na), 410 (100, M-Me_2N); HRMS $C_{21}H_{34}N_4O_3S_2Na^+$ calcd. 477.1970, found 477.1961.

Catalyst **5e** was prepared according to the general synthetic scheme below.

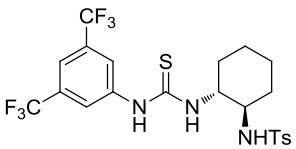


1-Isothiocyanato-3,5-bis(trifluoromethyl)benzene (11)



A solution of 3,5-Bis(trifluoromethyl)aniline (3.4 mL, 21.8 mmol) in CH_2Cl_2 (50 mL) and sat. aq. $NaHCO_3$ 50 mL) was cooled to 3 ^oC (ice bath) and stirred for 15 min. Stirring was then stopped and thiophosgene (2.5 mL, 32.7 mmol) was syringed directly into the organic layer. The mixture was then vigorously stirred for 1 h at 3 ^oC. The reaction was extracted with CH_2Cl_2 (2 x 30 mL), dried ($MgSO_4$) and the excess solvent removed to give title compound **11** (5.33 g, 19.7 mmol, 90% yield) as a pale yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.64 (2H, s), 7.76 (1H, s). ^1H NMR data are consistent with literature data.[14]

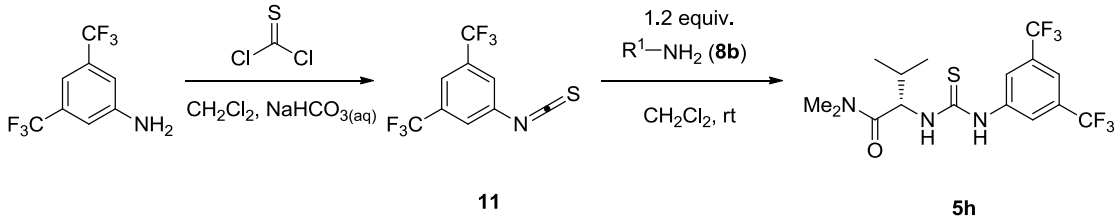
***N*-((1*R*,2*R*)-2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)cyclohexyl)-4-methylbenzenesulfonamide (5e)**



To a solution of *iso*thiocyanate **11** (271 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) at room temperature was added amine **10a** (322 mg, 1.2 mmol) and the reaction was stirred at rt for 3 days or until reaction complete, as judged by tlc analysis. The excess solvent was then removed *in vacuo* to give the crude product which was recrystallized (CH_2Cl_2/pet. ether) to give title compound **5e** (384 mg, 0.71 mmol, 71% yield) as a white solid; mp 180-182 ^oC; $[\alpha]_D^{25}$ = +37.0 ^{o} (c = 1.03, $CHCl_3$); IR υ_{max}

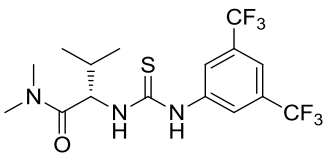
3353, 3088, 2935, 2862, 1538, 1387, 1305, 1270, 1113 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.13-1.23 (1H, m), 1.23-1.36 (3H, m), 1.64 (1H, apt. d, *J* = 13.4), 1.68-1.79 (2H, m), 2.13-2.22 (1H, m), 2.36 (3H, s), 3.23 (1H, apt. td, *J* = 11.1, 4.0), 4.37 (1H, br. s), 6.28 (1H, br. s), 6.88 (1H, d, *J* = 8.1), 7.20-7.30 (2H, m), 7.57 (1H, s), 7.73 (2H, d, *J* = 8.3), 7.91 (2H, s), 8.48 (1H, br. s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5 (*C*H_3), 24.5 (*C*H_2), 24.6 (*C*H_2), 32.1 (*C*H_2), 33.6 (*C*H_2), 57.4 (*C*H), 59.0 (*C*H), 118.7 (m, *C*H), 123.0 (2C, q, *J* = 272.9, *C*F_3), 123.7 (*C*H), 126.7 (*C*H), 129.9 (*C*H), 132.0 (2C, q, *J* = 33.0, *C*), 138.1 (*C*), 139.6 (*C*), 143.9 (*C*), 181.4 (*C*); *m/z* (ESI^+) 540 (100, M+H); HRMS $C_{22}H_{23}F_6N_3O_2S_2H^+$ calcd. 540.1214, found 540.1213.

Catalyst **5h** was prepared according to the general synthetic scheme below.



11 **5h**

(*S*)-2-(3-(3,5-Bis(trifluoromethyl)phenyl)thioureido)-*N*,*N*,3-trimethylbutanamide (5h)



To a solution of *iso*thiocyanate **11** (1.4 g, 5.18 mmol) in CH_2Cl_2 (20 mL) at room temperature was added amine **10a** (900 mg, 6.24 mmol) and the reaction was stirred at rt for 3 days or until reaction complete, as judged by tlc analysis. The excess solvent was then removed *in vacuo* to give the crude product which was recrystallized (40% TBME/pet. ether) to give title compound **5h** (1.62 g, 3.90 mmol, 75% yield) as a white solid; mp 135-136 °C; $[\alpha]_D^{25}$ = -45.9 ° (c = 1.015, $CHCl_3$); IR υ_{max} 3320, 2971, 1609, 1534, 1380, 1272, 1164, 1111 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.05 (3H, d, *J* = 6.8), 1.10 (3H, d, *J* = 6.8), 2.06 (1H, apt. oct, *J* = 7.0), 3.05 (3H, s), 3.39 (3H, s), 5.34 (1H, apt. t, *J* = 8.2), 7.51 (1H, s), 8.04 (2H, s), 8.30 (1H, d, *J* = 7.7), 9.43 (1H, br. s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 19.1 (*C*H_3), 19.2 (*C*H_3), 32.0 (*C*H), 36.3 (*C*H_3), 38.5 (*C*H_3), 59.3 (*C*H), 117.6 (1C, m, *C*), 122.6 (2C, m, *C*), 123.3 (2C, q, *J* = 272.9, *C*F_3), 131.5 (2C, q, *J* = 34.1, *C*), 140.7 (*C*), 174.6

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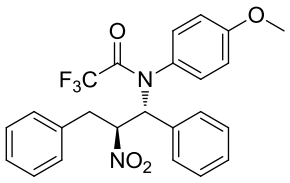
(*C*), 181.5 (*C*); *m/z* (CI) 416 (18, M+H), 396 (34, M-F), 371 (100, M–Me_2N); HRMS $C_{16}H_{19}F_6N_3OSH^+$ calcd. 416.12313, found 416.12264.

Synthesis of enantioenriched *β*-nitrotrifluoroacetamides

For asymmetric reactions at -20 ^oC. To a mixture containing imine **2** (0.20 mmol), nitroalkene **1** (0.40 mmol) and Hantzsch ester **4a** (0.40 mmol) in toluene (1.5 mL) cooled to -20 ^oC (Cryobath) was added a solution of catalyst **5h** (0.02 mmol, 0.2 M in toluene) and the reaction was stirred until reaction complete as monitored by ^1H NMR. Once reaction complete, trifluoroacetic anhydride (1.0 mmol), followed by pyridine (1.0 mmol) were added at -20 ^oC and the solution was allowed to warm to rt and stirred for 1 h. After this time, 2.0 M HCl (10 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (2 x 5 mL) and the combined organic phases were washed with sat. aq. $NaHCO_3$ 10 mL) and sat. brine (10 mL). The organic phase was then dried ($MgSO_4$) and the excess solvents were removed *in vacuo* to afford crude *β*-nitrotrifluoroacetamide **3**.

Copies of NMR spectra for literature compounds can be found in our previous work.[15]

2,2,2-Trifluoro-*N*-(4-methoxyphenyl)-*N*-((1*R*,2*S*)-2-nitro-1,3-diphenylpropyl)acetamide (3aa)



Imine **2a** (0.200 mmol) afforded, after purification by column chromatography (10% Me_2CO/pet. ether), pure **3aa** (74 mg, 0.162 mmol, 81% yield) as a yellow foam; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 95:5, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 7.8 min, t_r (minor) = 10.6 min, shows 98% *ee*; mp 70-72 ^oC; $[\alpha]_D^{25}$ = -61.5 ^{o} (c = 1.01, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 3.47 (1H, dd, *J* = 14.4, 10.8), 3.56 (1H, dd, *J* = 14.4, 3.0), 3.83 (3H, s), 5.61 (1H, br. s), 6.06 (1H, br. s), 6.39 (1H, br. s), 6.72 (1H, dd, *J* = 8.4, 2.4), 6.93 (1H, dd, *J* = 8.4, 2.4), 7.04 (1H, br. d, *J* = 7.8), 7.12 (2H, d, *J* = 7.2), 7.22-7.27 (3H, m), 7.29-7.38 (5H, m). ^1H NMR data are consistent with literature.[15]

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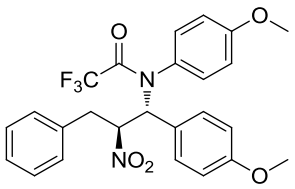
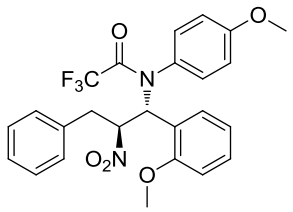
2,2,2-Trifluoro-*N*-(4-methoxyphenyl)-*N*-((1*S*,2*R*)-1-(4-methoxyphenyl)-2-nitro-3-phenylpropyl)acetamide (3ab)



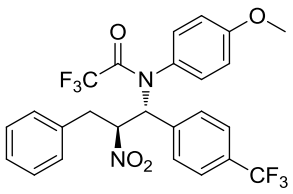
Imine **2b** (0.20 mmol) afforded, after purification by column chromatography (10% EtOAc/pet. ether and 50% CH_2Cl_2/pet. ether), pure **3ab** (73 mg, 0.150 mmol, 75% yield) as a yellow solid; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 90:10, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 8.6 min, t_r (minor) = 15.4 min, shows 97% *ee*; mp 59-61 ^oC; $[\alpha]_D^{25}$ = -58.7 ^{o} (c = 0.87, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 3.48 (1H, dd, *J* = 14.6, 10.9), 3.57 (1H, dd, *J* = 14.6, 3.2), 3.80 (3H, s), 3.86 (3H, s), 5.59 (1H, br. t, *J* = 9.5), 6.01 (1H, br. s), 6.47 (1H, br. d, *J* = 7.2), 6.70-6.80 (3H, m), 6.95 (1H, dd, *J* = 8.7, 2.8), 7.00-7.10 (3H, m), 7.20-7.30 (2H, m), 7.30-7.40 (3H, m). ^1H NMR data are consistent with literature.[15]

2,2,2-Trifluoro-*N*-(4-methoxyphenyl)-*N*-((1*S*,2*R*)-1-(2-methoxyphenyl)-2-nitro-3-phenylpropyl)acetamide (3ac)



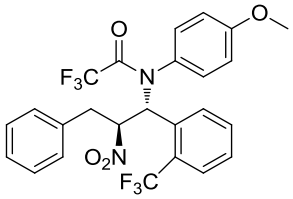
Imine **2a** (0.200 mmol) afforded, after purification by column chromatography (4% Me_2CO/pet. ether and 40% CH_2Cl_2/pet. ether), pure **3ac** (81 mg, 0.166 mmol, 83% yield) as a yellow foamy solid; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 97.5:2.5, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (minor) = 12.2 min, t_r (major) = 15.3 min, shows 99% *ee*; mp 49-51 ^oC; $[\alpha]_D^{25}$ = -69.1 ^{o} (c = 1.03, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 3.50-3.57 (2H, m), 3.77 (3H, s), 3.80 (3H, s), 5.48 (1H, m), 6.20 (1H, d, *J* = 7.8), 6.59 (1H, dd, *J* = 8.8, 2.8), 6.70 (1H, t, *J* = 7.5 CH), 6.79 (1H, br. d, *J* = 11.0), 6.83 (1H, br. d, *J* = 6.2), 6.86 (1H, d, *J* = 8.2), 6.92 (1H, dd, *J* = 8.7, 2.9), 7.08 (1H, dd, *J* = 8.6, 2.1), 7.23-7.28 (3H, m), 7.30 (1H, m), 7.36 (2H, t, *J* = 7.6). ^1H NMR data are consistent with literature.[15]

2,2,2-Trifluoro-*N*-(4-methoxyphenyl)-*N*-((1*S*,2*R*)-2-nitro-3-phenyl-1-(4-(trifluoromethyl)phenyl)propyl)acetamide (3ad)



Imine **2d** (0.200 mmol) afforded, after purification by column chromatography (10% EtOAc/pet. ether and 40% CH_2Cl_2/pet. ether), pure **3ad** (78 mg, 0.148 mmol, 74% yield) as a yellow foamy solid; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 97.5:2.5, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 8.2 min, t_r (minor) = 10.9 min, shows 94% *ee*; mp 48-50 ^oC; $[\alpha]_D^{25}$ = -55.7 ^{o} (c = 0.91, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 3.50 (1H, dd, *J* = 14.4, 11.4), 3.62 (1H, dd, *J* = 14.4, 2.4), 3.82 (3H, s), 5.70 (1H, br. s), 6.11 (1H, br. s), 6.49 (1H, br. s), 6.78 (1H, d, *J* = 6.6), 6.97 (1H, dd, *J* = 8.4, 2.4), 7.08 (1H, br. d, *J* = 7.2), 7.26 (2H, d, *J* = 7.2), 7.29-7.34 (3H, m), 7.37 (2H, t, *J* = 7.2), 7.55 (2H, d, *J* = 7.8). ^1H NMR data are consistent with literature.[15]

2,2,2-Trifluoro-*N*-(4-methoxyphenyl)-*N*-((1*S*,2*R*)-2-nitro-3-phenyl-1-(2-(trifluoromethyl)phenyl)propyl)acetamide (3ae)



Imine **2e** (0.200 mmol) afforded, after purification by column chromatography (10-20% EtOAc/pet. ether and 40-50% CH_2Cl_2/pet. ether), pure major diastereomer **3ae *anti*** (70 mg, 0.133 mmol, 67% yield) as a white solid; mp 128-130 ^oC; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 97.5:2.5, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 9.0 min, t_r (minor) = 11.0 min, shows 80% *ee*; $[\alpha]_D^{25}$ = -28.2 ^{o} (c = 1.06, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 3.53 (1H, dd, *J* = 15.0, 3.0), 3.64 (1H, dd, *J* = 15.0, 11.4), 3.80 (3H, s, O CH_3), 5.40 (1H, apt. td, *J* = 11.4, 3.0), 6.04 (1H, dd, *J* = 9.0, 1.8), 6.51 (1H, dd, *J* = 9.0, 3.0), 6.68 (1H, d, *J* = 5.4), 6.98 (1H, dd, *J* = 8.4, 3.0), 7.06 (1H, d, *J* = 10.9), 7.14-7.19 (2H, m), 7.23-7.26 (2H, m), 7.32 (1H, t, *J* = 7.2), 7.35-7.41 (3H, m), 7.74 (1H, d, *J* = 7.8). ^1H NMR data are consistent with literature.[15] And pure minor diastereomer **3ae *syn*** (16 mg, 0.030 mmol, 15% yield) as a white solid; mp 150-152 ^oC; HPLC analysis (Chiralcel OD-H 15 cm, hexane/*iso*-propanol 95:5, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 7.8 min, t_r (minor) = 9.0 min, shows 8% *ee*; IR υ_{max} 1706, 1561, 1511, 1313, 1207, 1156, 1120 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.60 (1H, dd, *J* = 15.1, 2.4), 3.26 (1H,

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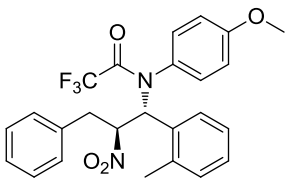
dd, *J* = 15.0, 11.4), 3.81 (3H, s), 5.63 (1H, br. s), 6.27 (1H, br. d, *J* = 6.6), 6.61 (1H, dd, *J* = 8.8, 2.8), 6.74 (1H, br. s), 6.80 (1H, br. s), 6.90 (1H, dd, *J* = 8.7, 2.8), 6.97-7.02 (2H, m), 7.19-7.29 (3H, m), 7.38 (1H, t, *J* = 7.6), 7.42 (1H, d, *J* = 5.5), 7.51 (1H, t, *J* = 7.6), 7.81 (1H, d, *J* = 7.7); ^{19}F NMR (300 MHz, $CDCl_3$) δ -67.5; ^{13}C NMR (151 MHz, $CDCl_3$) δ 37.0 (*C*H_2), 55.6 (*C*H_3), 59.8 (*C*H), 90.2 (*C*H), 114.0 (*CH*), 114.4 (*CH*), 116.1 (1C, q, *J* = 289.1, *C*F_3), 123.7 (1C, q, *J* = 274.2, *C*F_3), 127.1 (1C, q, *J* = 6.0), 127.4 (C), 127.8 (*CH*), 128.6 (*CH*), 129.1 (*CH*), 129.9 (*CH*), 130.6 (1C, q, *J* = 30.4, *C*), 130.9 (*CH*), 131.4 (C), 131.5 (*CH*), 132.0 (*CH*), 132.5 (*CH*), 134.7 (C), 157.2 (1C, q, *J* = 36.4, *C*), 160.5 (*C)*; *m/z* (CI) 527 (100, M+H); HRMS $C_{25}H_{20}F_6N_2O_4$ calcd. 527.1406, found 527.1407.

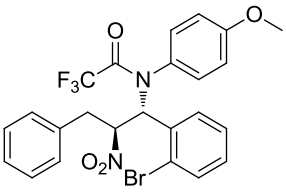
2,2,2-Trifluoro-*N*-(4-methoxyphenyl)-*N*-((1*S*,2*R*)-2-nitro-3-phenyl-1-(*o*-tolyl) propyl)acetamide (3af)



Imine **2f** (0.200 mmol) afforded, after purification by column chromatography (10% EtOAc/pet. ether and 50% CH_2Cl_2/pet. ether), pure major diastereomer **3af** ***anti*** (71 mg, 0.150 mmol, 75% yield) as a yellow foamy solid; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 99:1, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 10.5 min, t_r (minor) = 14.6 min, shows 90% *ee*; mp 60-61 ^{o}C; $[\alpha]_D^{25}$ = -67.2 ^{o} (c = 0.69, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.36 (3H, s), 3.56 (2H, m), 3.81 (3H, s), 5.47 (1H, br. s), 6.13 (1H, br. s), 6.59 (1H, dd, *J* = 8.4, 2.4), 6.66 (2H, br. s), 6.89 (1H, t, *J* = 7.2), 6.93 (1H, dd, *J* = 8.4, 3.0), 7.07 (1H, d, *J* = 7.8), 7.15-7.20 (2H, m), 7.25 (2H, d, *J* = 7.8), 7.32 (1H, t, *J* = 7.2), 7.37 (2H, t, *J* = 7.2). ^{1}H NMR data are consistent with literature.[15] And pure minor diastereomer **3af** ***syn*** (11 mg, 0.023 mmol, 12% yield) as an off-white solid; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 99:1, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 12.7 min, t_r (minor) = 16.0 min, shows 34% *ee*; mp 123-124 ^{o}C; IR υ_{max} 2925, 1700, 1557, 1511, 1254, 1206, 1156 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.44 (3H, s), 2.84 (1H, dd, *J* = 14.9, 2.3), 3.13 (1H, dd, *J* = 14.8, 11.2), 3.80 (3H, s), 5.53 (1H, br. t, *J* = 10.2), 6.13 (1H, br. d, *J* = 6.2), 6.55 (1H, br. s), 6.59 (1H, dd, *J* = 8.8, 2.9), 6.65 (1H, br. d, *J* = 9.2), 6.90 (1H, dd, *J* = 8.8, 2.9), 6.97-7.06 (3H, m), 7.21-7.28 (4H, m), 7.28-7.32 (1H, m), 7.36 (1H, d, *J* = 7.5); ^{19}F NMR (300 MHz, $CDCl_3$) δ -67.5; ^{13}C NMR (151 MHz, $CDCl_3$) δ 20.2 (*C*H_3), 37.4 (*C*H_2), 55.5 (*C*H_3), 59.8 (*C*H), 90.5 (*C*H), 113.8 (*CH*), 114.0 (*CH*), 116.2 (1C, q, *J* = 289.1), 126.2 (*CH*), 127.0 (C), 127.8 (*CH*), 128.7 (*CH*), 128.8 (*CH*), 129.1 (*CH*), 129.5 (*CH*), 131.2 (*CH*), 131.3 (C), 131.7 (*CH*), 132.9 (*CH*), 134.8 (C), 138.6 (C), 157.5 (1C, q, *J* = 35.8, *C*F_3), 160.3 (*C)*; *m/z* (ESI$^+$) 495 (17,

M+Na), 473 (3, M+H), 426 (30, M-NO_2); HRMS $C_{25}H_{23}F_3N_2O_4Na^+$ calcd. 495.1508, found 495.1489.

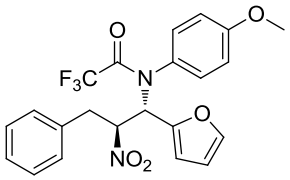
N-((1*R*,2*S*)-1-(2-Bromophenyl)-2-nitro-3-phenylpropyl)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)acetamide (3ag)



Imine **2g** (0.200 mmol) afforded, after purification by column chromatography (10% EtOAc/pet. ether and 50% CH_2Cl_2/pet. ether), pure major diastereomer **3ag** (75 mg, 0.140 mmol, 70% yield) as a white solid; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 97.5:2.5, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 12.6 min, t_r (minor) = 15.7 min, shows 92% *ee*; mp 158-160 ^oC; $[\alpha]_D^{25}$ = -61.4 ^{o} (c = 1.04, $CHCl_3$); IR υ_{max} 2935, 1702, 1556, 1510, 1256, 1208, 1181 cm^1; ^1H NMR (600 MHz, $CDCl_3$) δ 3.55 (1H, dd, *J* = 14.7, 2.8), 3.60 (1H, dd, *J* = 15.2, 10.7), 3.80 (3H, s), 5.48 (1H, apt. td, *J* = 10.7, 3.4), 6.27 (1H, br. d, *J* = 8.3), 6.58 (1H, dd, *J* = 8.8, 2.7), 6.80 (1H, br. d, *J* = 11.1), 6.83 (1H, br. d, *J* = 7.7), 6.92 (1H, dd, *J* = 8.8, 2.9), 7.02 (1H, t, *J* = 7.6), 7.05 (1H, dd, *J* = 8.7, 1.7), 7.15 (1H, td, *J* = 7.5, 1.1), 7.25 (2H, d, *J* = 7.2), 7.32 (1H, t, *J* = 7.3), 7.37 (2H, t, *J* = 7.3), 7.62 (1H, d, *J* = 8.1); ^{19}F NMR (300 MHz, $CDCl_3$) δ -67.6; ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.2 (*C*H_2), 55.6 (*C*H_3), 62.2 (*C*H), 89.7 (*C*H), 113.9 (*CH*), 114.5 (*CH*), 116.4 (1C, q, *J* = 288.5, *C*F_3), 126.1 (C), 127.2 (C), 127.4 (*CH*), 128.1 (*CH*), 128.7 (*CH*), 129.3 (*CH*), 129.8 (*CH*), 130.1 (*CH*), 131.0 (*CH*), 132.3 (*CH*), 132.4 (C), 133.8 (*CH*), 134.7 (C), 157.9 (1C, q, *J* = 35.8, *C*), 160.5 (*C)*; *m/z* (CI) 538 (17, ^{81}M), 536 (17, ^{79}M), 492 (26, ^{81} M-NO_2), 490 (25, ^{79}M-NO_2); HRMS $C_{24}H_{20}BrF_3N_2O_4$ calcd. 536.0559, found 536.0554. And pure minor diastereomer **3ag *syn*** (10 mg, 0.019 mmol, 9% yield) as a white solid; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 90:10, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 11.3 min, t_r (minor) = 17.4 min, shows 10% *ee*; mp 134-135 ^oC; IR υ_{max} 2843, 1706, 1559, 1511, 1206, 1183 cm^{-1} ^1H NMR (400 MHz, $CDCl_3$) δ 2.79 (1H, br. d, *J* = 13.6), 3.26 (1H, dd, *J* = 14.8, 11.3), 3.83 (3H, s), 5.84 (1H, br. t, *J* = 9.8), 6.56 (2H, br. d, *J* = 8.3), 6.72 (1 H, dd, *J* = 8.8, 3.0), 6.87 (1H, dd, *J* = 8.8, 3.0), 7.02-7.09 (2H, m), 7.10-7.28 (7H, m), 7.71 (1H, d, *J* = 7.5); ^{19}F NMR (300 MHz, $CDCl_3$) δ -67.7; ^{13}C NMR (151 MHz, $CDCl_3$) δ 37.3 (*C*H_2), 55.6 (*C*H_3), 65.2 (*C*H), 89.9 (*C*H), 113.9 (*CH*), 114.5 (*CH*), 116.1 (1C, q, *J* = 289.1, *C*F_3), 126.4 (C), 127.8 (*CH*), 128.0 (*CH*), 128.6 (*CH*), 129.1 (*CH*), 130.5 (*CH*), 131.0 (*CH*), 131.1 (*CH*), 131.6 (*CH*), 133.3 (C), 134.1 (*CH*), 134.7 (C), 157.5 (1C, q, *J* = 35.8,

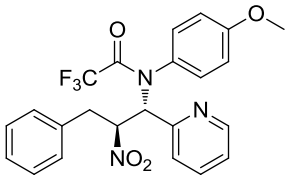
CF_3), 160.3 (*C*); *m/z* (ESI$^+$) 539 (5, ^{81}M+H), 537 (6, ^{79}M+H), 492 (100, ^{81}M-NO_2), 490 (98, ^{79}M-NO_2); HRMS $C_{24}H_{20}BrF_3N_2O_4$ calcd. 537.0637, found 537.0631.

2,2,2-Trifluoro-*N*-((1*R*,2*R*)-1-(furan-2-yl)-2-nitro-3-phenylpropyl)-*N*-(4-methoxyphenyl)acetamide (3ah)



Imine **2h** (0.200 mmol) afforded, after purification by column chromatography (4% Me_2CO/pet. ether and 40% CH_2Cl_2/pet. ether), pure **3ah** (69 mg, 0.154 mmol, 77% yield) as an orange foamy solid; mp 53-54 ^oC; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 97.5:2.5, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 11.6 min, t_r (minor) = 17.5 min, shows 97% *ee*; $[\alpha]_D^{25}$ = -104.3 ^{o} (c = 1.04, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.41 (1H, dd, *J* = 14.4, 10.8), 3.49 (1H, dd, *J* = 15.0, 3.6), 3.83 (3H, s), 5.35 (1H, apt. td, *J* = 11.4, 3.6), 6.27, (2H, dd, *J* = 0.6), 6.33 (1H, d, *J* = 10.8), 6.47 (1H, d, *J* = 8.4), 6.75 (1H, dd, *J* = 9.0, 2.4), 6.96 (1H, dd, *J* = 8.4, 6.0), 7.20 (3H, d, *J* = 7.2), 7.29-7.37 (4H, m). ^{1}H NMR data are consistent with literature.[15]

2,2,2-Trifluoro-*N*-(4-methoxyphenyl)-*N*-((1*R*,2*R*)-2-nitro-3-phenyl-1-(pyridin-2-yl)propyl)acetamide (3ai)



Imine **2i** (0.200 mmol) afforded, after purification by column chromatography (40% EtOAc/pet. ether and 25% Me_2CO/pet. ether), pure **3ai** (70 mg, 0.152 mmol, 76% yield) as a white solid; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 90:10, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 10.4 min, t_r (minor) = 18.3 min, shows 96% *ee*; mp 94-95 ^oC; $[\alpha]_D^{25}$ = -55.5 ^{o} (c = 0.99, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.41 (1H, dd, *J* = 14.4, 10.8), 3.60 (1H, dd, *J* = 14.4, 3.0), 3.80 (3H, s), 5.63 (1H, apt. td, *J* = 10.8, 3.0), 6.08 (1H, d, *J* = 7.2), 6.59 (2H, d, *J* = 10.8), 6.94 (1H, d, *J* = 7.2), 7.19-7.24 (4H, m), 7.28-7.32 (1H, m), 7.35 (2H, t, *J* = 6.6), 7.48 (1H, d, *J* = 7.8), 7.71 (1H, td, *J* = 7.8, 1.8), 8.31 (1H, d, *J* = 4.8). ^{1}H NMR data are consistent with literature.[15]

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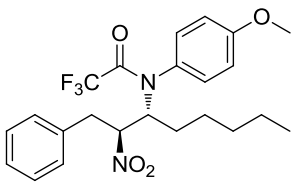
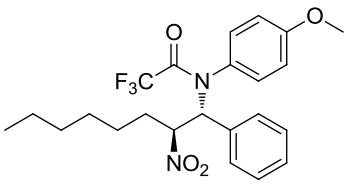
2,2,2-Trifluoro-*N*-(4-methoxyphenyl)-*N*-((2*R*,3*S*)-2-nitro-1-phenyloctan-3-yl) acetamide (3aj)



To a mixture containing Imine **2j** (0.200 mmol), nitroalkene **1a** (0.400 mmol) and Hantzsch ester **4a** (0.400 mmol) in toluene (1.5 mL) at room temperature was added a solution of catalyst 5h (0.020 mmol, 0.2 M in toluene) and the reaction was stirred until reaction complete as monitored by ^{1}H NMR (1 h). Once reaction complete, trifluoroacetic anhydride (1.0 mmol), followed by pyridine (1.0 mmol) were added and the solution was stirred for 1 h at rt. After this time, 2.0 M HCl (10 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic phases were then washed with sat. aq. $NaHCO_3$ 10 mL) and sat. brine (10 mL). The organic phase was then dried ($MgSO_4$) and the excess solvents were removed *in vacuo* to afford after purification by column chromatography (4% Me_2CO/pet. ether and 40% CH_2Cl_2/pet. ether) pure **3aj** (53 mg, 0.117 mmol, 59% yield) as a yellow oil; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 99:1, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 10.2 min, t_r (minor) = 15.9 min, shows 73% *ee*; $[\alpha]_D^{25}$ = -39.5 ^{o} (c = 1.10, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.89 (3H, t, *J* = 7.0), 1.20-1.35 (4H, m), 1.40-1.50 (3H, m), 1.65 (1H, br. s), 3.30-3.40 (2H, m), 3.88 (3H, s), 4.87 (1H, br s), 4.97 (1H, br. s), 6.96-7.01 (2H, m), 7.14 (2H, d, *J* = 7.0), 7.19 (2H, d, *J* = 7.0), 7.26-7.29 (1H, m), 7.30-7.33 (2H, m). ^{1}H NMR data are consistent with literature.[15]

2,2,2-Trifluoro-*N*-(4-methoxyphenyl)-*N*-((1*R*,2*S*)-2-nitro-1-phenyloctyl) acetamide (3ab)



Imine **2a** (0.200 mmol) afforded, after purification by column chromatography (7.5% Me_2CO/pet. ether and 40% CH_2Cl_2/pet. ether), pure **3ab** (64 mg, 0.142 mmol, 71% yield) as a yellow oil; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 99:1, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 7.9 min, t_r (minor) = 9.3 min, shows 97% *ee*; $[\alpha]_D^{25}$ = -12.9 ^{o} (c = 0.96, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.91 (3H, t, *J* = 6.6), 1.30-1.50 (8H, m), 2.14 (1H, m), 2.26 (1H, m), 3.80 (3H, s), 5.30 (1H, br. s), 6.03 (1H, br. s), 6.27 (1H, br. s), 6.66 (1H, d, *J* = 9.0), 6.88 (1H, dd, *J* = 9.0, 3.0), 6.92 (1H, d, *J* = 8.4), 7.07 (2H, d, *J* = 7.8), 7.24 (2H, d, *J* = 7.8), 7.31 (1H, t, *J* = 7.2). ^{1}H NMR data are consistent with literature.[15]

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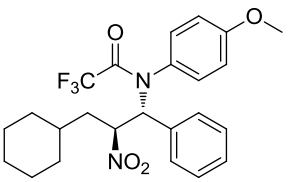
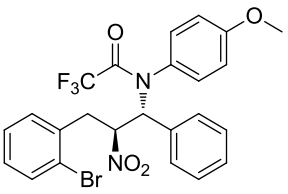
_N_-((1_R_,2_S_)-3-Cyclohexyl-2-nitro-1-phenylpropyl)-2,2,2-trifluoro-_N_-(4-methoxyphenyl)acetamide (3ca)



Imine **2a** (0.200 mmol) afforded, after purification by column chromatography (4% Me_2CO/pet. ether and 40% CH_2Cl_2/pet. ether), pure **3ca** (70 mg, 0.150 mmol, 75% yield) as a yellow foam; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 95:5, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 4.8 min, t_r (minor) = 6.2 min, shows 95% *ee*; mp 56-57 ^oC; $[\alpha]_D^{25}$ = -38.7 ^{o} (c = 1.00, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 1.01(1H, apt. qd, *J* = 12.0, 3.0), 1.08 (1H, apt qd, *J* = 12.0, 3.0), 1.25 (4H, m), 1.70 (3H, m), 1.80 (1H, br. d, *J* = 13.2), 1.90 (1H, m), 2.09 (1H, br. d, *J* = 12.0), 2.28 (1H, m), 3.82 (3H, s), 5.45 (1H, br. s), 6.03 (1H, br. s), 6.24 (1H, br. s), 6.66 (1H, br. d, *J* = 10.2), 6.89 (1H, dd, *J* = 9.0, 3.0), 6.96 (1H, br. d, *J* = 7.8), 7.06 (2H, d, *J* = 7.8), 7.24 (2H, t, *J* = 7.8), 7.31 (1H, t, *J* = 7.8). ^1H NMR data are consistent with literature.[15]

_N_-((1_R_,2_S_)-3-(2-Bromophenyl)-2-nitro-1-phenylpropyl)-2,2,2-trifluoro-_N_-(4-methoxyphenyl)acetamide (3da)



Imine **2a** (3.00 mmol) afforded, after purification by column chromatography (10% Me_2CO/pet. ether and 40% CH_2Cl_2/pet. ether), pure **3da** (1.27 g, 2.36 mmol, 79% yield, 98% *ee*) as a white solid; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 95:5, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 8.0 min, t_r (minor) = 16.1 min, shows 98% *ee*; which after recrystallisation (*iso*-propanol) gave enantiopure **3da** (990 mg, 1.84 mmol, 61% yield) as a white solid; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 95:5, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 8.0 min, t_r (minor) = 16.1 min, shows >99% *ee*; mp 128-130 ^oC; $[\alpha]_D^{25}$ = -114.7 (c = 0.97, $CHCl_3$, after recrystallisation (*iso*-propanol) to >99% *ee*); ^1H NMR (600 MHz, $CDCl_3$) δ 3.59 (1H, dd, *J* = 14.3, 11.5), 3.78 (1H, dd, *J* = 14.3, 3.8), 3.81 (3H, s), 5.74 (1H, br. t, *J* = 10.0), 6.25 (1H, br. s), 6.31 (1H, br. s), 6.62 (1H, dd, *J* = 8.7, 2.6), 6.91 (1H, dd, *J* = 8.8, 2.9), 7.06 (2H, d, *J* = 7.5), 7.15-7.20 (2H, m), 7.22 (2H, t, *J* = 7.7), 7.24-7.28 (1H, m), 7.28-7.32 (1H, m), 7.41 (1H, br. d, *J* = 7.9), 7.61 (1H, dd, *J* = 8.1, 1.1). ^1H NMR data are consistent with literature data.[15]

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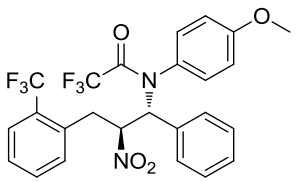
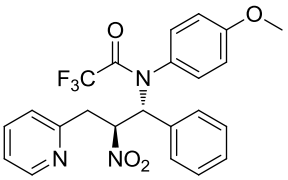
2,2,2-Trifluoro-*N*-(4-methoxyphenyl)-*N*-((1*S*,2*R*)-2-nitro-1-phenyl-3-(2-(trifluoromethyl)phenyl)propyl)acetamide (3ea)



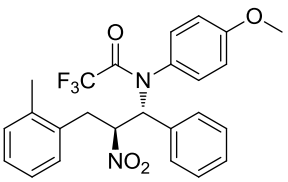
Imine **2a** (0.200 mmol) afforded, after purification by column chromatography (4% Me_2CO/pet. ether and 40% CH_2Cl_2/pet. ether), pure **3ea** (77 mg, 0.146 mmol, 73% yield) as a yellow solid; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 90:10, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 5.2 min, t_r (minor) = 9.6 min, shows 95% *ee*; mp 109-111 ^oC; $[\alpha]_D^{25}$ = -69.0 ^{o} (c = 1.00, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 3.65 (1H, dd, *J* = 14.4, 12.0), 3.82 (3H, s), 3.85 (1H, dd, *J* = 15.0, 3.0), 5.74 (1H, br. s), 6.17 (1H, br. s), 6.33 (1H, br. s), 6.65 (1H, d, *J* = 6.6), 6.92 (1H, dd, *J* = 9.0, 3.0), 7.10 (2H, d, *J* = 7.2), 7.15 (1H, d, *J* = 7.8), 7.24 (2H, t, *J* = 7.8), 7.29-7.33 (2H, m), 7.42 (1H, t, *J* = 7.8 CH), 7.51 (1H, t, *J* = 7.8), 7.71 (1H, d, *J* = 7.8). ^1H NMR data are consistent with literature data.[15]

2,2,2-Trifluoro-*N*-(4-methoxyphenyl)-*N*-((1*S*,2*R*)-2-nitro-1-phenyl-3-(pyridin-2-yl)propyl)acetamide (3fa)



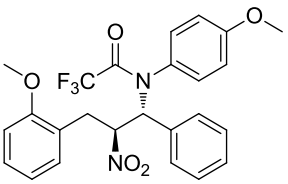
Imine **2a** (0.20 mmol) afforded, after purification by column chromatography (4% Me_2CO/pet. ether and 40% CH_2Cl_2/pet. ether), pure **3fa** (62 mg, 0.135 mmol, 68% yield) as a pink solid; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 80:20, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 6.9 min, t_r (minor) = 12.9 min, shows 98% *ee*; mp 100-102 ^oC; $[\alpha]_D^{25}$ = -25.6 ^{o} (c = 1.01, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 3.66 (1H, dd, *J* = 15.0, 10.5), 3.72 (1H, dd, *J* = 15.0, 3.5), 3.82 (3H, s), 5.94 (1H, apt. td, *J* = 11.0, 3.5), 6.13 (1H, d, *J* = 7.0), 6.50 (1H, d, *J* = 11.5), 6.60 (1H, dd, *J* = 8.5, 3.0), 7.01 (1H, dd, *J* = 9.0, 3.0), 7.04 (2H, d, *J* = 7.5), 7.15 (1H, d, *J* = 7.5), 7.20-7.23 (3H, m), 7.30 (1H, m), 7.52 (1H, dd, *J* = 8.5, 2.5), 7.63 (1H, td, *J* = 7.5, 2.0), 8.65 (1H, m). ^1H NMR data are consistent with literature data.[15]

2,2,2-Trifluoro-*N*-(4-methoxyphenyl)-*N*-((1*S*,2*R*)-2-nitro-1-phenyl-3-(*o*-tolyl)propyl)acetamide (3ga)



Imine **2a** (0.200 mmol) afforded, after purification by column chromatography (4% Me_2CO/pet. ether and 40% CH_2Cl_2/pet. ether), pure **3ga** (66 mg, 0.140 mmol, 70% yield) as a yellow foamy solid; mp 52-54 ^oC; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 99:1, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 10.0 min, t_r (minor) = 12.3 min, shows 98% *ee*; $[\alpha]_D^{25}$ = -74.9 ^{o} (c = 1.03, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.41 (3H, s), 3.54 (2H, m), 3.84 (3H, s), 5.82 (2H, m), 6.57 (1H, br. s), 6.77 (1H, d, *J* = 7.2), 6.89 (1H, dd, *J* = 8.4, 2.4), 6.98 (1H, d, *J* = 8.4), 7.14-7.21 (6H, m), 7.27 (2H, t, *J* = 7.8), 7.34 (1H, m). ^{1}H NMR data are consistent with literature data.[15]

2,2,2-Trifluoro-*N*-(4-methoxyphenyl)-*N*-((1*R*,2*S*)-3-(2-methoxyphenyl)-2-nitro-1-phenylpropyl)acetamide (3ha)



Imine **2a** (0.200 mmol) afforded, after purification by column chromatography (4% Me_2CO/pet. ether and 40% CH_2Cl_2/pet. ether), pure **3ha** (63 mg, 0.129 mmol, 64% yield) as a yellow foam; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 90:10, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 7.3 min, t_r (minor) = 15.6 min, shows 98% *ee*; $[\alpha]_D^{25}$ = -64.3 ^{o} (c = 0.98, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.31 (1H, dd, *J* = 14.4, 12.0), 3.78 (1H, dd, *J* = 14.4, 3), 3.82 (3H, s), 4.00 (3H, s), 5.54 (1H, br. t, *J* = 9.6), 6.08 (1H, br. d, *J* = 7.2), 6.52 (1H br. d, *J* = 8.4), 6.57 (1H, dd, *J* = 8.4, 2.4), 6.89 (1H, td, *J* = 7.8, 0.6), 6.93 (1H, d, *J* = 7.8), 6.96 (1H, dd, *J* = 8.4, 2.4), 6.99 (2H, d, *J* = 7.2), 7.03 (1H, dd, *J* = 7.8, 1.8), 7.19 (2H, t, *J* = 8.4), 7.26-7.30 (2H, m), 7.53 (1H, d, *J* = 7.2). ^{1}H NMR data are consistent with literature data.[15]

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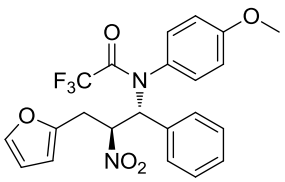
2,2,2-Trifluoro-*N*-((1*S*,2*R*)-3-(furan-2-yl)-2-nitro-1-phenylpropyl)-*N*-(4-methoxyphenyl)acetamide (3ia)



Imine **2a** (0.200 mmol) afforded, after purification by column chromatography (4% Me_2CO/pet. ether and 40% CH_2Cl_2/pet. ether), pure **3ia** (29 mg, 0.064 mmol, 32 % yield) as a yellow foam; HPLC analysis (Chiralcel AD, hexane/*iso*-propanol 95:5, flow rate = 1 mL/min, λ = 254 nm): retention time t_r (major) = 8.8 min, t_r (minor) = 14.8 min, shows 95% *ee*; $[\alpha]_D^{25}$ = -66.2 ^{o} (c = 0.75, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.57 (1H, dd, *J* = 16.2, 3.6), 3.63 (1H, dd, *J* = 16.2, 10.2), 3.83 (3H, s), 5.24, (1H, br. t, *J* = 10.2), 6.17 (1H, d, *J* = 7.8), 6.21 (1H, d, *J* = 3.0), 6.32 (1H, br. s), 6.34 (1H, dd, *J* = 3.0, 1.8), 6.64 (1H, dd, *J* = 9.0, 3.0), 6.97 (1H, dd, *J* = 8.4, 2.4), 7.04 (2H, d, *J* = 7.2), 7.15 (1H, dd, *J* = 8.4, 2.4), 7.24 (2H, t, *J* = 7.8), 7.33 (1H, m), 7.44 (1H, d, *J* = 1.2). ^{1}H NMR data are consistent with literature data.[15]

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[1] For computational investigations with a similar catalyst see Zuend, S. J.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2009**, *131*, 15358.

[2] (a) Fieser, L. F.; Gates, M. *J. Am. Chem. Soc.* **1946**, *68*, 2249. (b) Melton, J.; McMurry, J. E. *J. Org. Chem.* **1975**, *40*.

[3] (a) Kumaran, G.; Kulkarni, G.H. *Synthesis*, **1995**, 1545. (b) Enders, D.; Wiedemann, J. *Synthesis*, **1996**, 1443.

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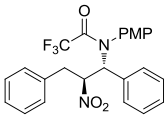
[13] Zuend, S. J.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2007**, *129*, 15872.

[14] Kotke, M.; Schreiner, P. R. *Synthesis* **2007**, 779.

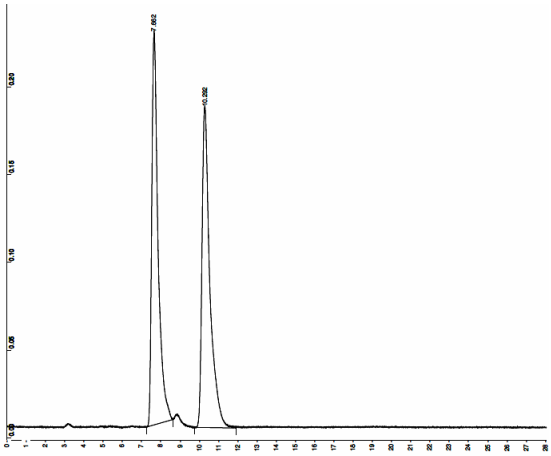
[15] Anderson, J. C.; Blake, A. J.; Koovits, P. J.; Stepney, G. J. *J. Org. Chem.* **2012**, *77*, 4711.

HPLC Data



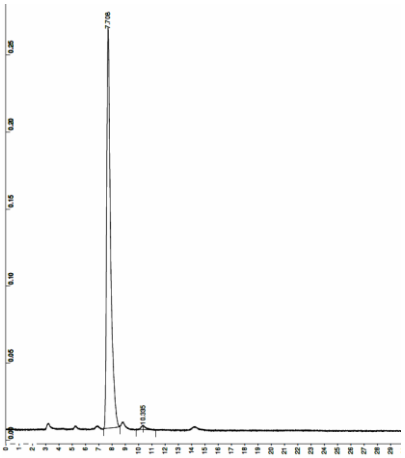
3aa *anti* Chiral HPLC : Chiracel AD, 5% isopropanol:hexanes, 1 mL/min

Racemate:



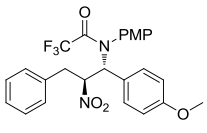
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.5310	7.662	0.000	5103706	BB	19.2	
2		50.4690	10.292	0.000	5200365	BB	23.1	
	Totals:	100.0000		0.000	10304071			

Enantioenriched:



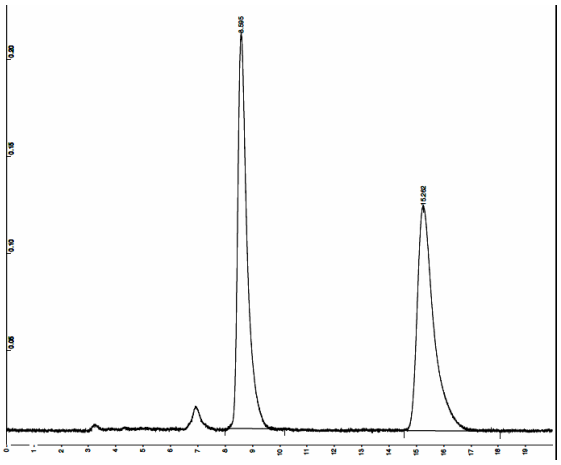
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		98.9171	7.708	0.000	5359530	BB	17.5	
2		1.0829	10.335	0.000	58673	BB	14.5	
	Totals:	100.0000		0.000	5418203			

98% *ee*



3ab *anti* Chiral HPLC : Chiracel AD, 10% isopropanol:hexanes, 1 mL/min

Racemate:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.8096	8.595	0.000	4844147	BB	20.3	
2		50.1904	15.262	0.000	4881180	BB	35.5	
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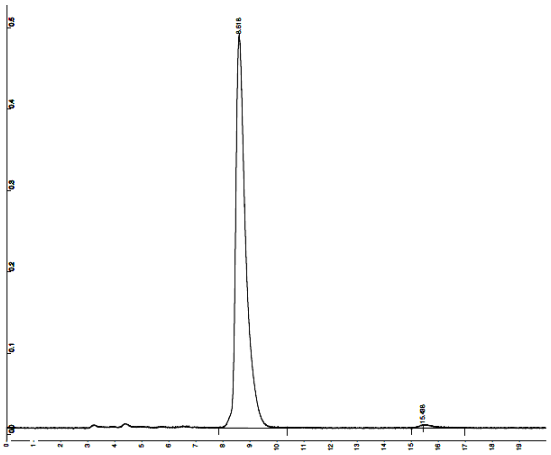
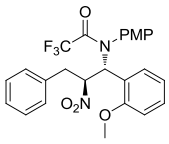
Enantioenriched:



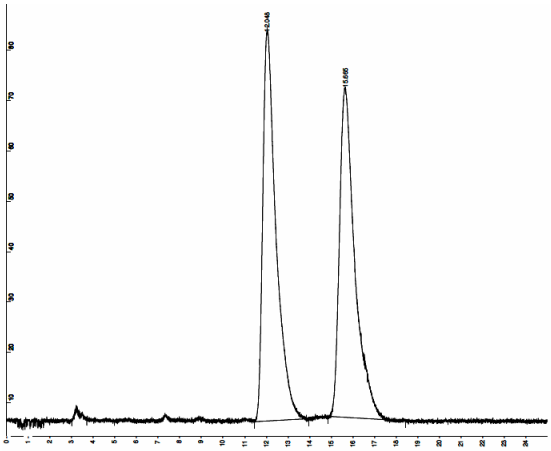
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		98.6961	8.618	0.000	12490266	BB	21.7	
2		1.3039	15.438	0.000	165014	BB	26.3	
	Totals:	100.0000		0.000	12655280			

97% *ee*



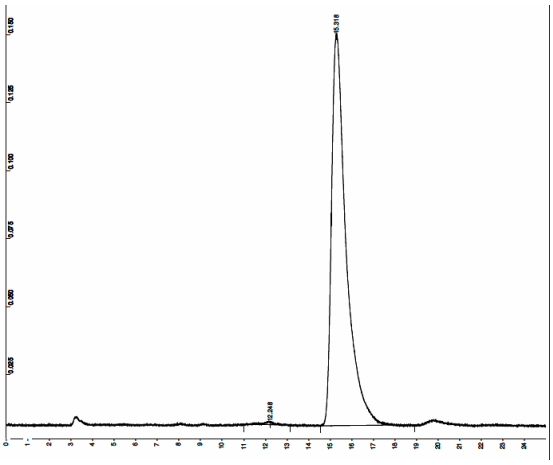
3ac *anti* Chiral HPLC : Chiracel AD, 2.5% isopropanol:hexanes, 1 mL/min

Racemate:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.6460	12.048	0.000	3286849	BB	36.2	
2		49.3540	15.665	0.000	3203001	BB	41.8	
	Totals:	100.0000		0.000	6489850			

Enantioenriched:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		0.5345	12.248	0.000	36205	BB	1.3	
2		99.4655	15.318	0.000	6736931	BB	39.0	
	Totals:	100.0000		0.000	6773136			

99% *ee*

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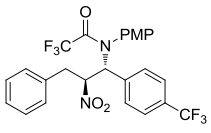
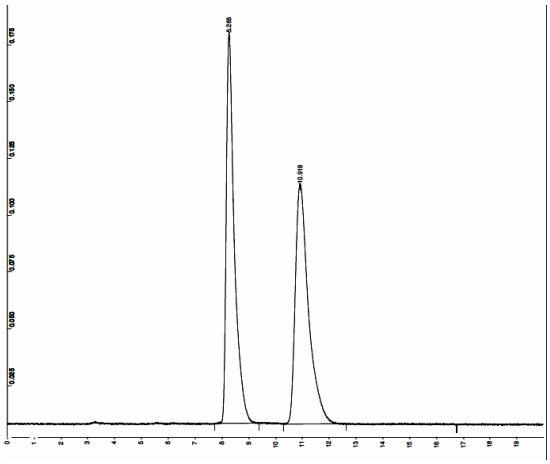


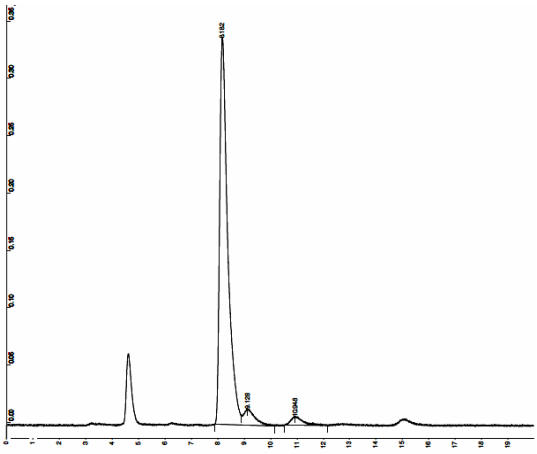
3ad *anti* Chiral HPLC : Chiracel AD, 2.5% isopropanol:hexanes, 1 mL/min

Racemate:



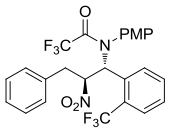
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.9364	8.268	0.000	3582515	BB	17.5	
2		50.0636	10.918	0.000	3591636	BB	29.3	
	Totals:	100.0000		0.000	7174151			

Enantioenriched:



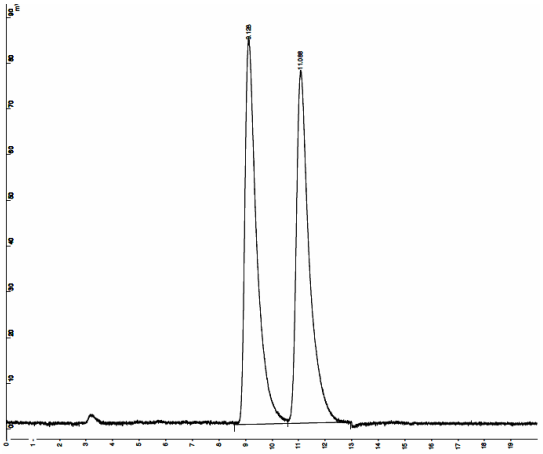
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		91.3840	8.182	0.000	7148503	BV	0.0	
2		5.5324	9.128	0.000	432767	VB	12.6	
3		3.0836	10.948	0.000	241215	BB	23.0	
	Totals:	100.0000		0.000	7822485			

94% *ee*



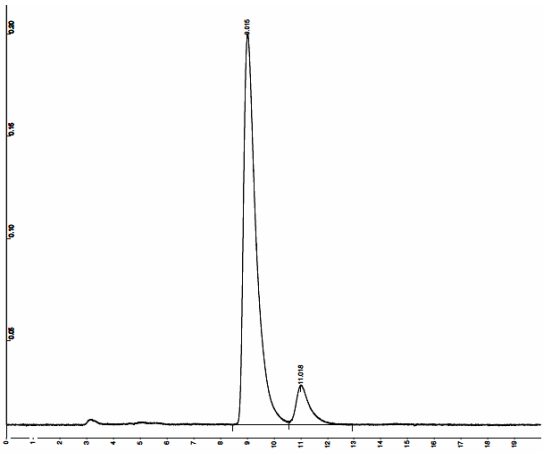
3ae *anti* **Chiral HPLC : Chiracel AD, 2.5% isopropanol:hexanes, 1 mL/min**

Racemate:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.2922	9.128	0.000	2634071	BV	0.0	
2		49.7078	11.088	0.000	2603468	VB	28.1	
	Totals:	100.0000		0.000	5237539			

Enantioenriched:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		90.2788	9.015	0.000	6250838	BV	0.0	
2		9.7212	11.018	0.000	673091	VB	28.0	
	Totals:	100.0000		0.000	6923929			

80% *ee*

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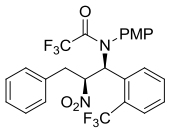
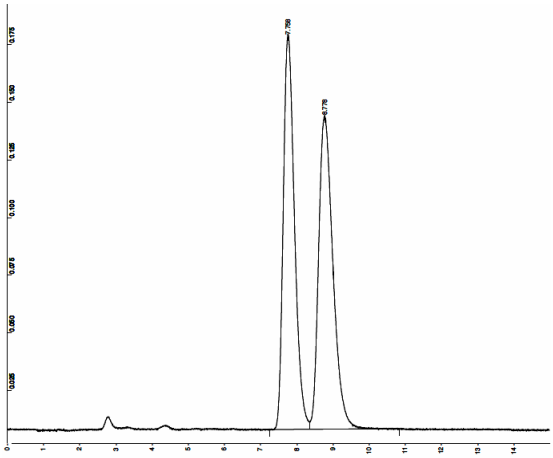


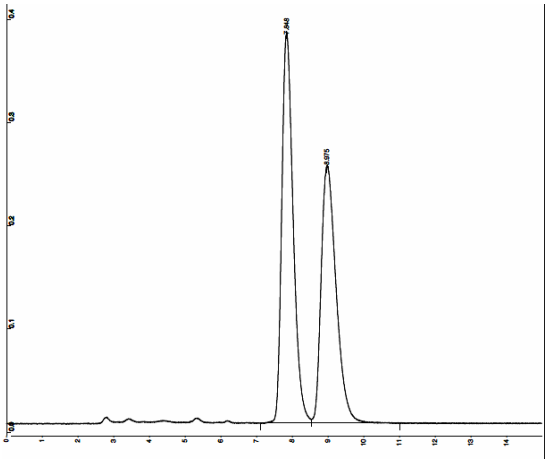
3ae *syn* **Chiral HPLC : Chiracel OD-H (15 cm), 5% isopropanol:hexanes, 1 mL/min**

Racemate:



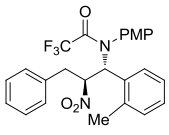
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.7168	7.758	0.000	3678466	BV	0.0	
2		50.2832	8.778	0.000	3720376	VB	24.7	
	Totals:	100.0000		0.000	7398842			

Enantioenriched:



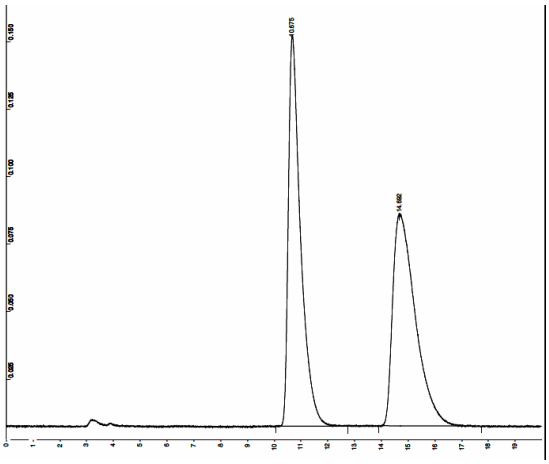
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		53.6388	7.848	0.000	8359446	BV	0.0	
2		46.3612	8.975	0.000	7225258	VB	26.5	
	Totals:	100.0000		0.000	15584704			

8% *ee*



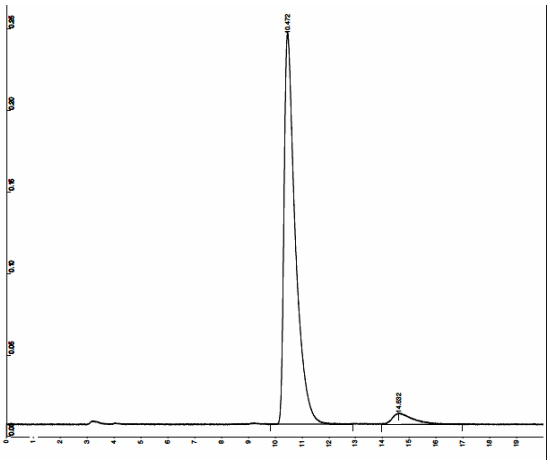
3af *anti* **Chiral HPLC : Chiracel AD, 1% isopropanol:hexanes, 1 mL/min**

Racemate:



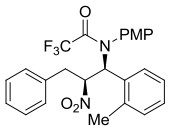
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.9431	10.675	0.000	4577781	BB	27.5	
2		50.0569	14.692	0.000	4588217	BB	53.3	
	Totals:	100.0000		0.000	9165998			

Enantioenriched:



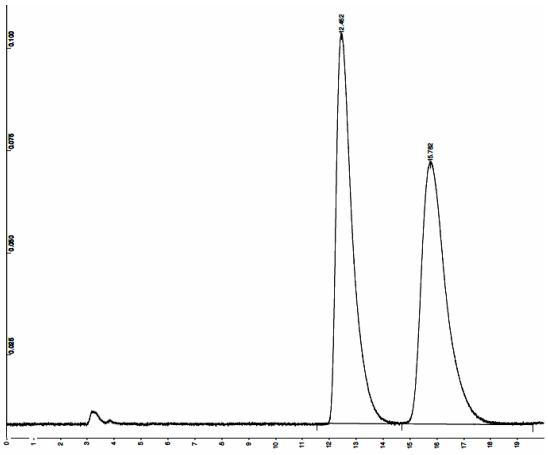
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		95.2128	10.472	0.000	7001089	BB	25.0	
2		4.7872	14.632	0.000	352006	BB	45.2	
	Totals:	100.0000		0.000	7353095			

90% *ee*



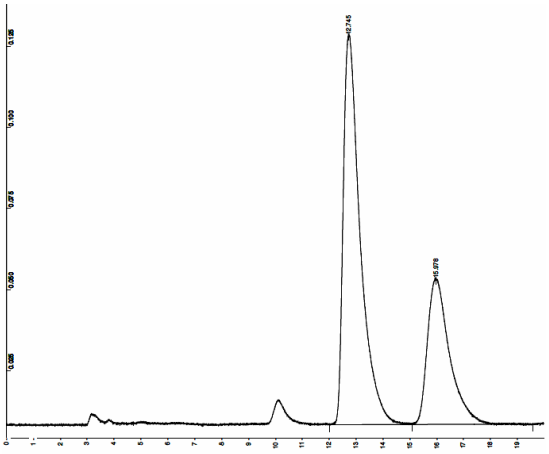
3af *syn* **Chiral HPLC : Chiracel AD, 1% isopropanol:hexanes, 1 mL/min**

Racemate:



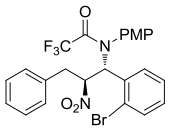
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.6289	12.462	0.000	4033338	BV	0.0	
2		50.3711	15.782	0.000	4093660	VB	56.2	
	Totals:	100.0000		0.000	8126998			

Enantioenriched:



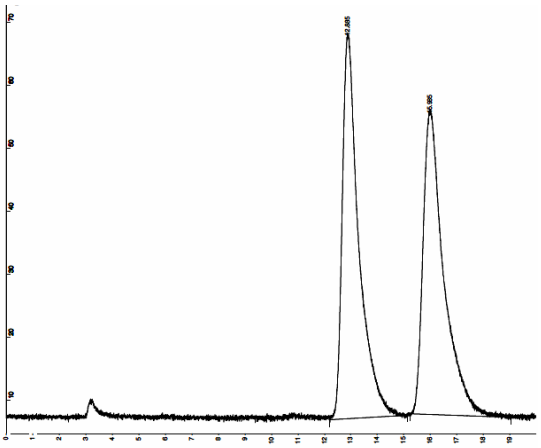
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		67.2529	12.745	0.000	5273381	BV	0.0	
2		32.7471	15.978	0.000	2567745	VB	49.8	
	Totals:	100.0000		0.000	7841126			

34% *ee*



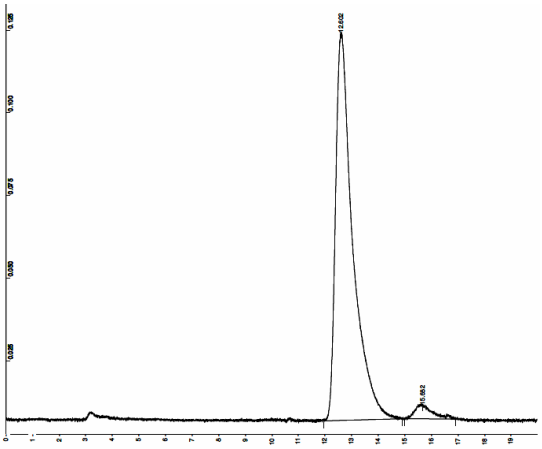
3ag *anti* **Chiral HPLC : Chiracel AD, 2.5% isopropanol:hexanes, 1 mL/min**

Racemate:



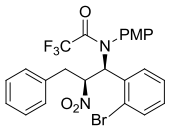
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.3627	12.885	0.000	2651789	BB	35.6	
2		49.6373	15.985	0.000	2613593	BB	44.7	
	Totals:	100.0000		0.000	5265382			

Enantioenriched:



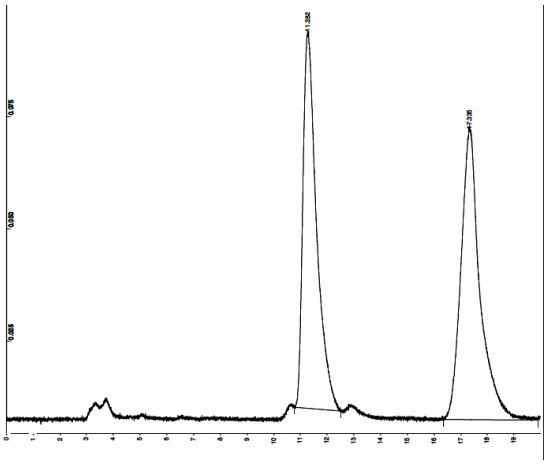
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		96.2917	12.602	0.000	5249251	BB	36.7	
2		3.7083	15.682	0.000	202154	BB	34.1	
	Totals:	100.0000		0.000	5451405			

92% *ee*



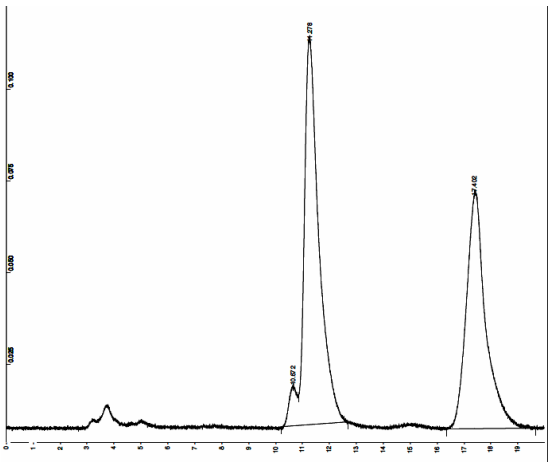
3ag *syn* **Chiral HPLC : Chiracel AD, 5% isopropanol:hexanes, 1 mL/min**

Racemate:



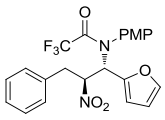
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		48.0375	11.282	0.000	2963964	BB	30.8	
2		51.9625	17.335	0.000	3206136	BB	39.6	
	Totals:	100.0000		0.000	6170100			

Enantioenriched:



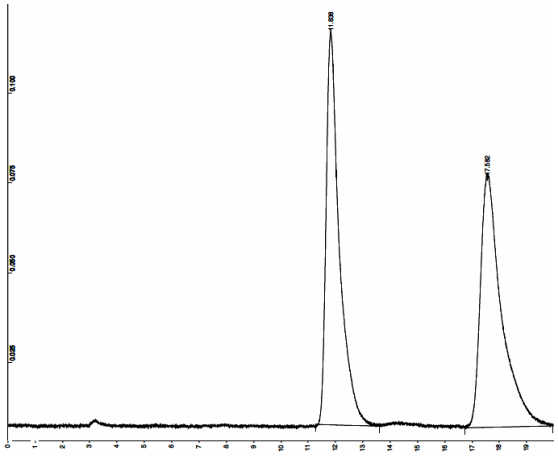
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		3.1117	10.672	0.000	228000	BV	0.0	
2		53.1856	11.278	0.000	3897014	VB	29.7	
3		43.7027	17.402	0.000	3202187	BB	40.5	
	Totals:	100.0000		0.000	7327201			

10% *ee*



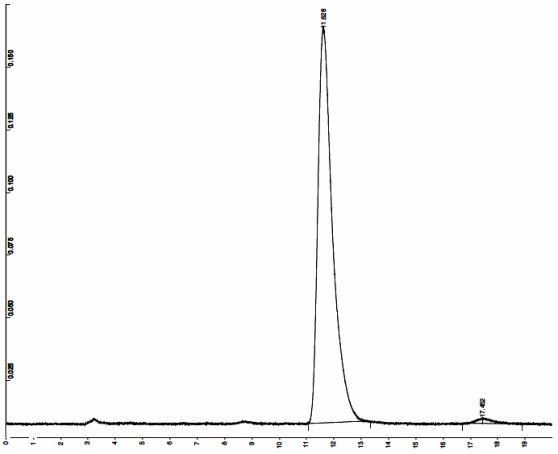
3ah *anti* Chiral HPLC : Chiracel AD, 2.5% isopropanol:hexanes, 1 mL/min

Racemate:



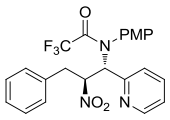
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.3837	11.838	0.000	3679937	BB	27.6	
2		50.6163	17.582	0.000	3771786	BB	43.8	
	Totals:	100.0000		0.000	7451723			

Enantioenriched:



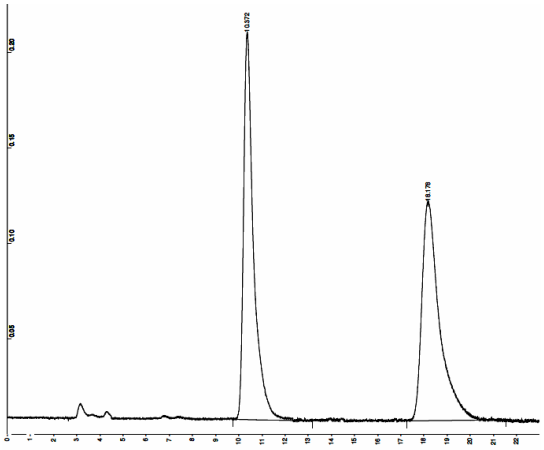
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		98.6506	11.628	0.000	5891534	BB	32.7	
2		1.3494	17.452	0.000	80591	BB	16.7	
	Totals:	100.0000		0.000	5972125			

97% *ee*



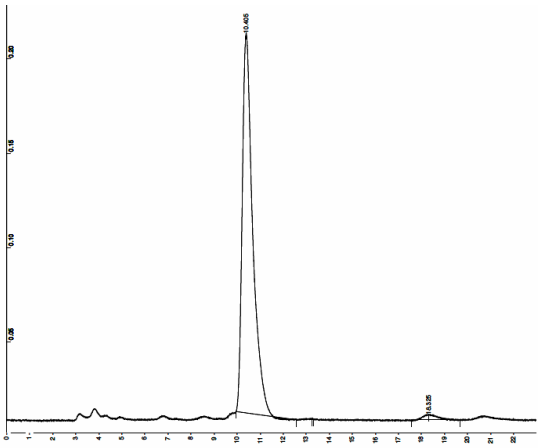
3ai *anti* Chiral HPLC : Chiracel AD, 10% isopropanol:hexanes, 1 mL/min

Racemate:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.1460	10.372	0.000	6078498	BB	24.2	
2		49.8540	18.178	0.000	6043106	BB	43.1	
	Totals:	100.0000		0.000	12121604			

Enantioenriched:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		98.1868	10.405	0.000	6309584	BB	27.1	
2		1.8132	18.325	0.000	116519	BB	34.4	
	Totals:	100.0000		0.000	6426103			

96% *ee*

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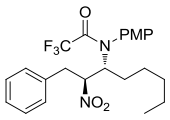
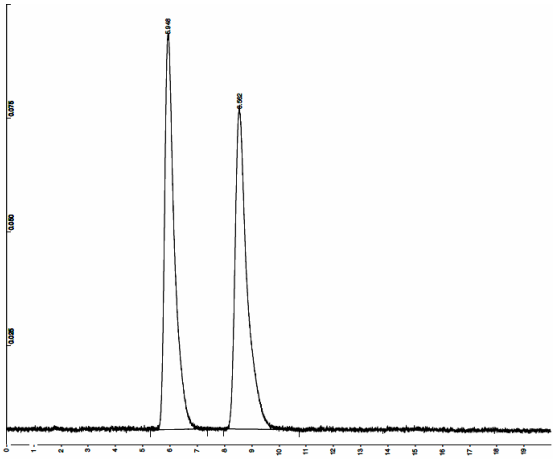


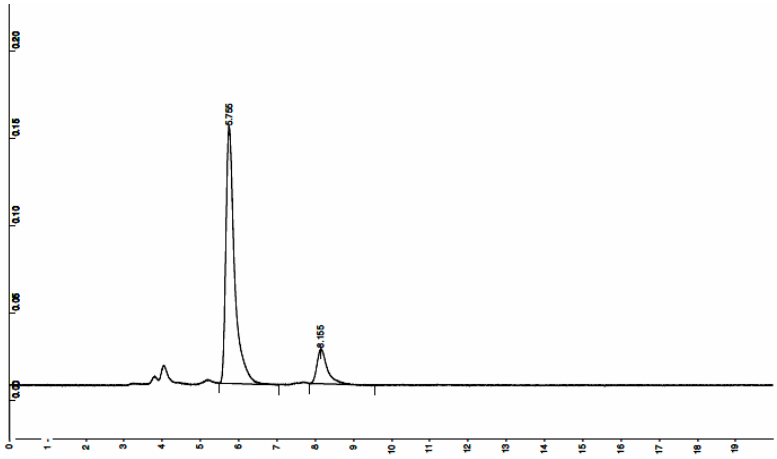
3aj *anti* Chiral HPLC : Chiracel AD, 5% isopropanol:hexanes, 1 mL/min

Racemate:



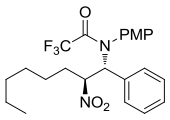
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.3164	5.948	0.000	2183279	BB	21.2	
2		49.6836	8.562	0.000	2155820	BB	24.8	
	Totals:	100.0000		0.000	4339099			

Enantioenriched:



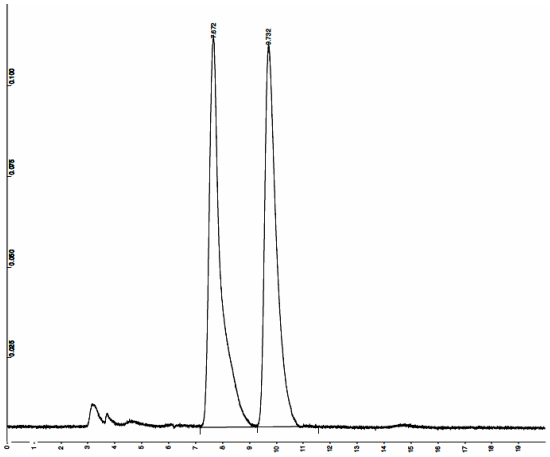
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		86.5599	5.755	0.000	2322230	BB	12.9	
2		13.4401	8.155	0.000	360570	BB	15.5	
	Totals:	100.0000		0.000	2682800			

73% *ee*



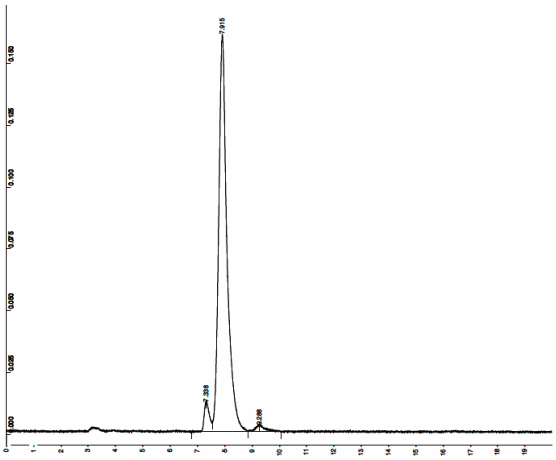
3ba *anti* Chiral HPLC : Chiracel AD, 1% isopropanol:hexanes, 1 mL/min

Racemate:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.5166	7.672	0.000	3236916	BV	0.0	
2		49.4834	9.732	0.000	3170712	VB	26.4	
	Totals:	100.0000		0.000	6407628			

Enantioenriched:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		4.2901	7.338	0.000	153853	BV	0.0	
2		94.1421	7.915	0.000	3376176	VV	0.0	
3		1.5678	9.288	0.000	56226	VB	13.7	
	Totals:	100.0000		0.000	3586255			

97% *ee*

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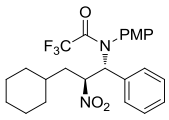
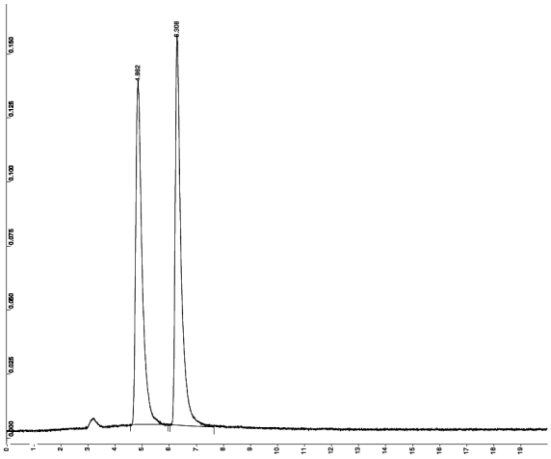


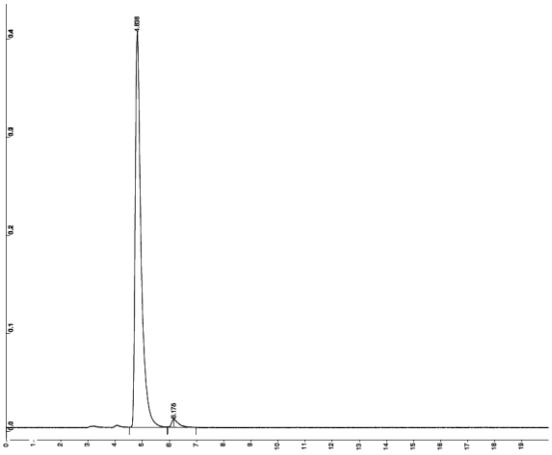
3ca *anti* Chiral HPLC : Chiracel AD, 5% isopropanol:hexanes, 1 mL/min

Racemate:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		48.9617	4.862	0.000	2202904	BB	14.1	
2		51.0383	6.308	0.000	2296331	BB	12.0	
	Totals:	100.0000		0.000	4499235			

Enantioenriched:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		97.7016	4.838	0.000	6089438	BB	12.7	
2		2.2984	6.178	0.000	143254	BB	13.9	
	Totals:	100.0000		0.000	6232692			

95% *ee*

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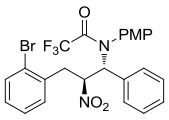
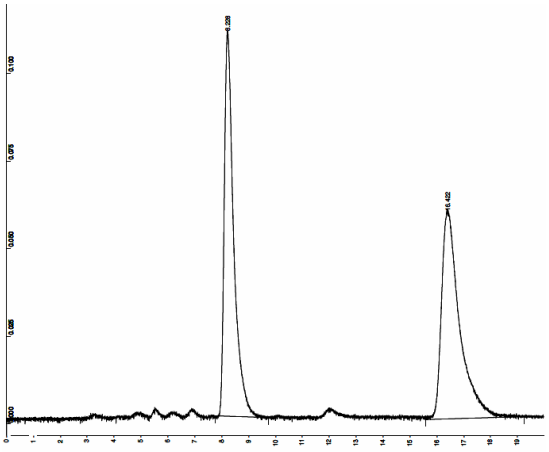


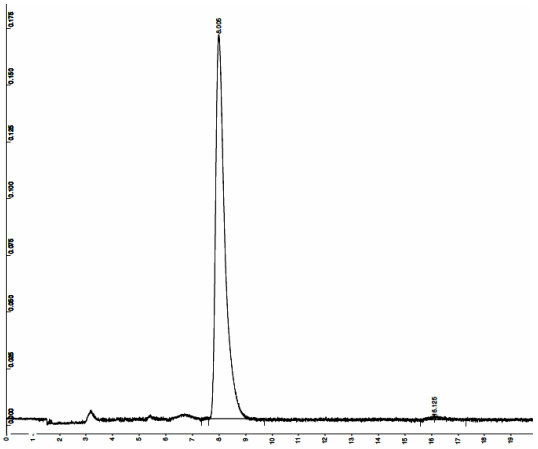
3da *anti* Chiral HPLC : Chiracel AD, 5% isopropanol:hexanes, 1 mL/min

Racemate:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		48.9869	8.228	0.000	2665063	BB	20.6	
2		51.0131	16.422	0.000	2775299	BB	38.5	
	Totals:	100.0000		0.000	5440362			

Enantioenriched:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		99.0110	8.005	0.000	4075258	BB	20.5	
2		0.9890	16.125	0.000	40706	BB	1.6	
	Totals:	100.0000		0.000	4115964			

98% *ee*

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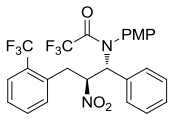
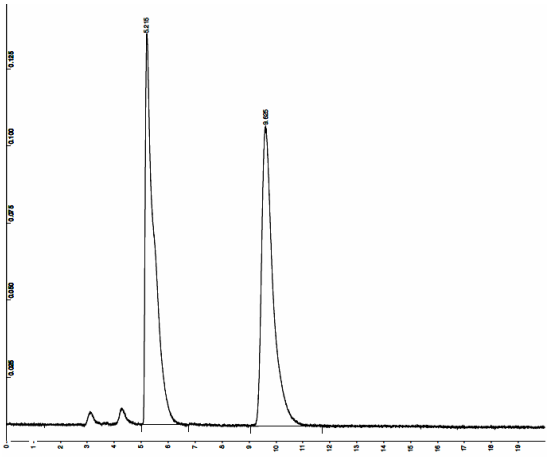


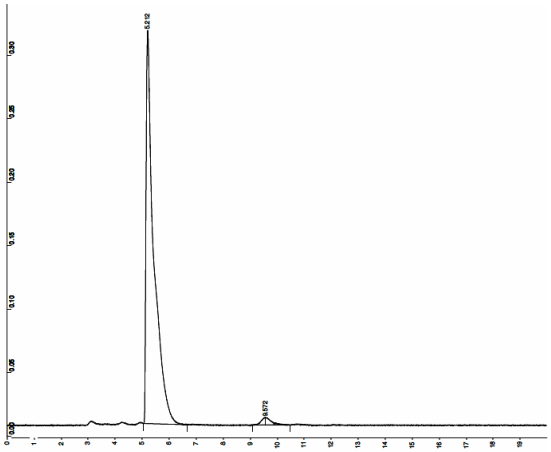
3ea *anti* Chiral HPLC : Chiracel AD, 10% isopropanol:hexanes, 1 mL/min

Racemate:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.8218	5.215	0.000	2853054	BB	18.8	
2		50.1782	9.625	0.000	2873463	BB	24.7	
	Totals:	100.0000		0.000	5726517			

Enantioenriched:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		97.7027	5.212	0.000	6183850	BB	14.2	
2		2.2973	9.572	0.000	145405	BB	22.0	
	Totals:	100.0000		0.000	6329255			

95% *ee*

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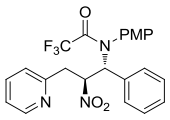
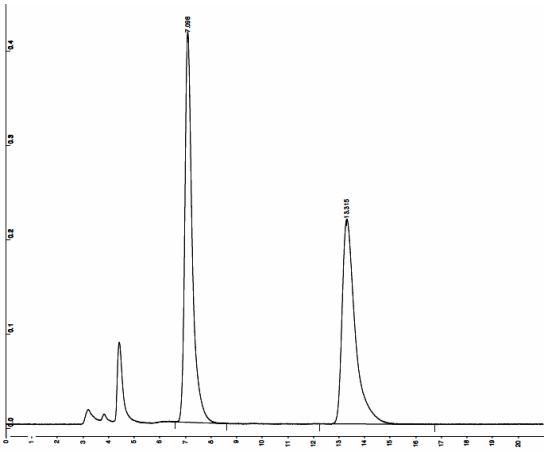


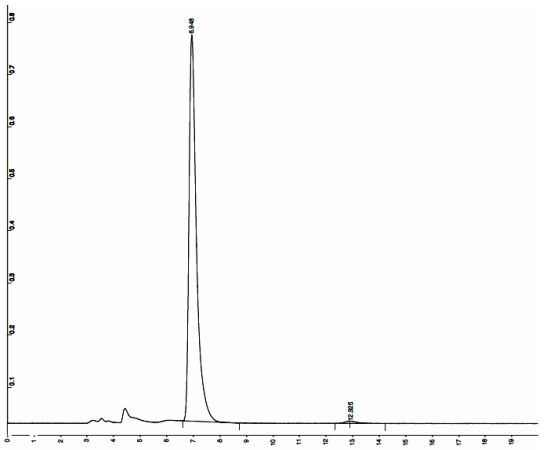
3fa *anti* Chiral HPLC : Chiracel AD, 20% isopropanol:hexanes, 1 mL/min

Racemate:



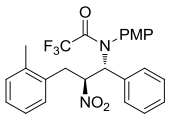
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		52.0856	7.098	0.000	8334772	BB	16.8	
2		47.9144	13.315	0.000	7667288	BB	29.8	
	Totals:	100.0000		0.000	16002060			

Enantioenriched:



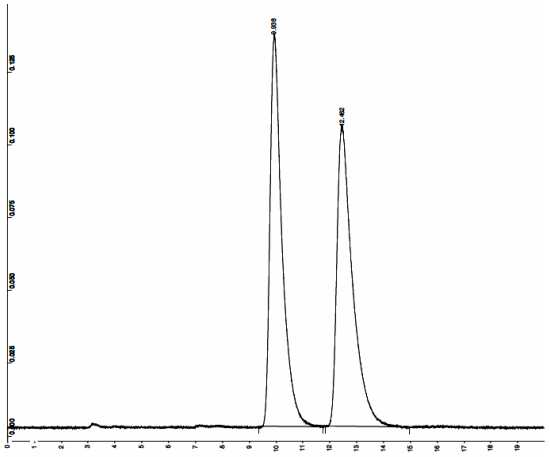
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		99.0203	6.948	0.000	14439710	BB	16.7	
2		0.9797	12.925	0.000	142863	BB	23.9	
	Totals:	100.0000		0.000	14582573			

98% *ee*



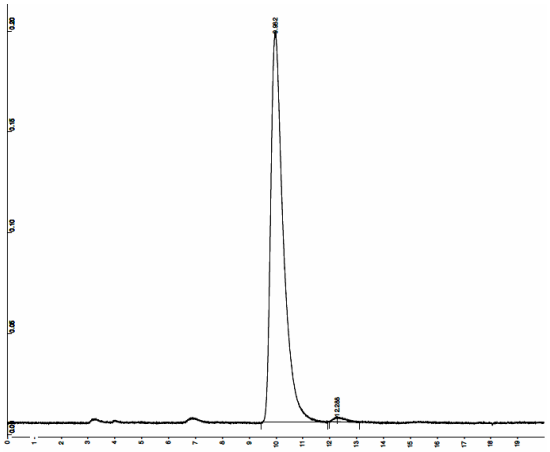
3ga *anti* Chiral HPLC : Chiracel AD, 10% isopropanol:hexanes, 1 mL/min

Racemate:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.0707	9.938	0.000	4164641	BB	26.5	
2		49.9293	12.462	0.000	4152875	BB	34.8	
	Totals:	100.0000		0.000	8317516			

Enantioenriched:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		98.9199	9.982	0.000	6259481	BB	28.2	
2		1.0801	12.288	0.000	68350	BB	14.9	
	Totals:	100.0000		0.000	6327831			

98% *ee*

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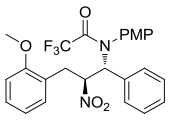
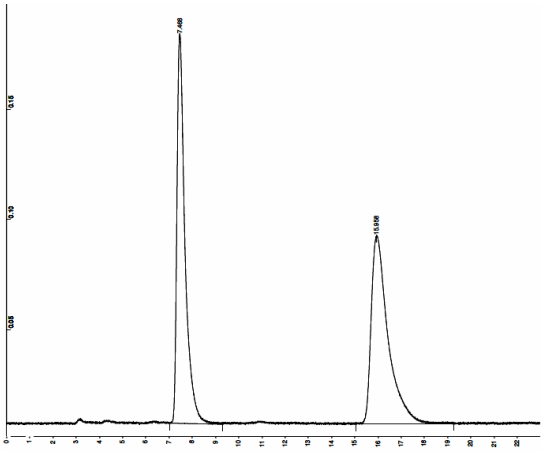


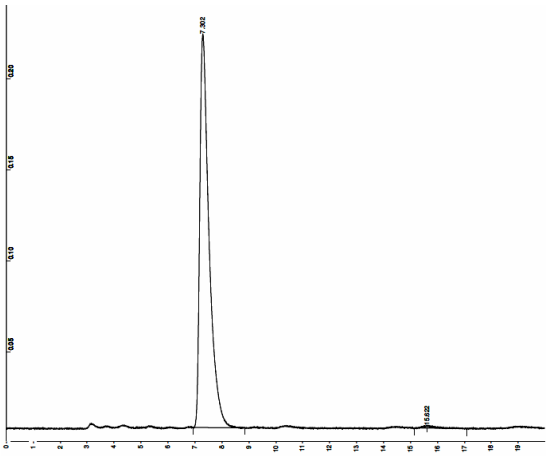
3ha *anti* Chiral HPLC : Chiracel AD, 10% isopropanol:hexanes, 1 mL/min

Racemate:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.6896	7.468	0.000	4265070	BB	20.2	
2		50.3104	15.958	0.000	4318357	BB	42.3	
	Totals:	100.0000		0.000	8583427			

Enantioenriched:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		99.1031	7.302	0.000	5156256	BB	20.7	
2		0.8969	15.622	0.000	46665	BB	3.3	
	Totals:	100.0000		0.000	5202921			

98% *ee*

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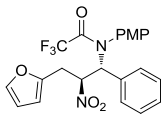
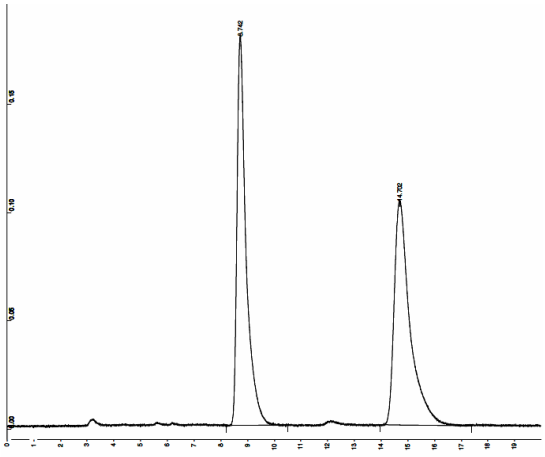


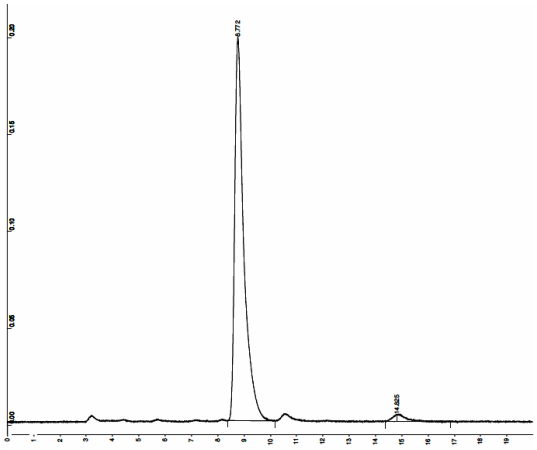
3ia *anti* Chiral HPLC : Chiracel AD, 5% isopropanol:hexanes, 1 mL/min

Racemate:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.1123	8.742	0.000	4230819	BB	19.3	
2		49.8877	14.702	0.000	4211857	BB	33.3	
	Totals:	100.0000		0.000	8442676			

Enantioenriched:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		97.6341	8.772	0.000	4770962	BB	19.8	
2		2.3659	14.825	0.000	115613	BB	25.2	
	Totals:	100.0000		0.000	4886575			

95% *ee*

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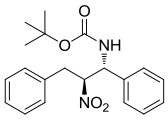
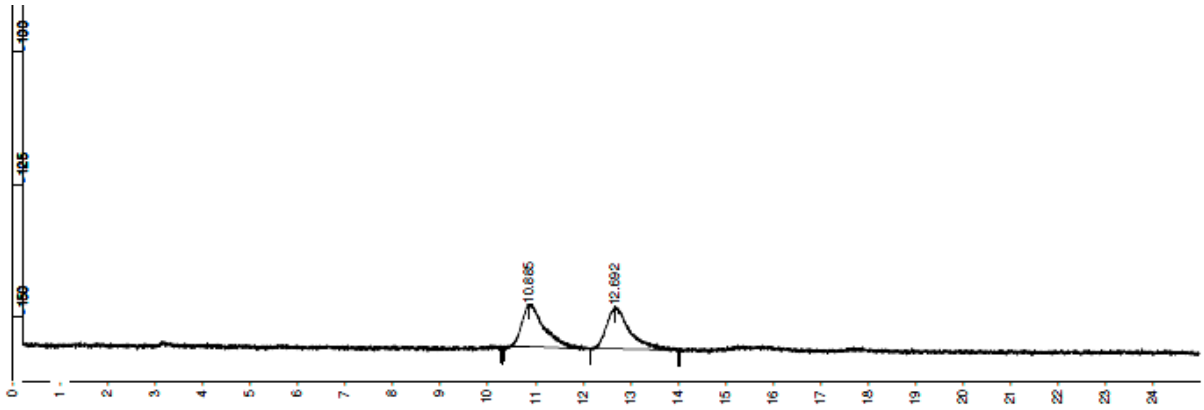


tert-Butyl ((1*R*,2*S*)-2-nitro-1,3-diphenylpropyl)carbamate

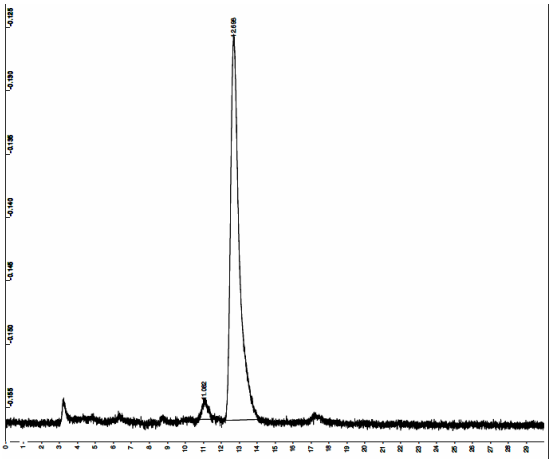
Chiral HPLC : Chiracel AD, 10% isopropanol:hexanes, 1 mL/min

Racemate:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.3389	10.885	0.000	254587	BP	0.0	
2		50.6611	12.692	0.000	261410	PB	26.3	
	Totals:	100.0000		0.000	515997			

Enantioenriched:



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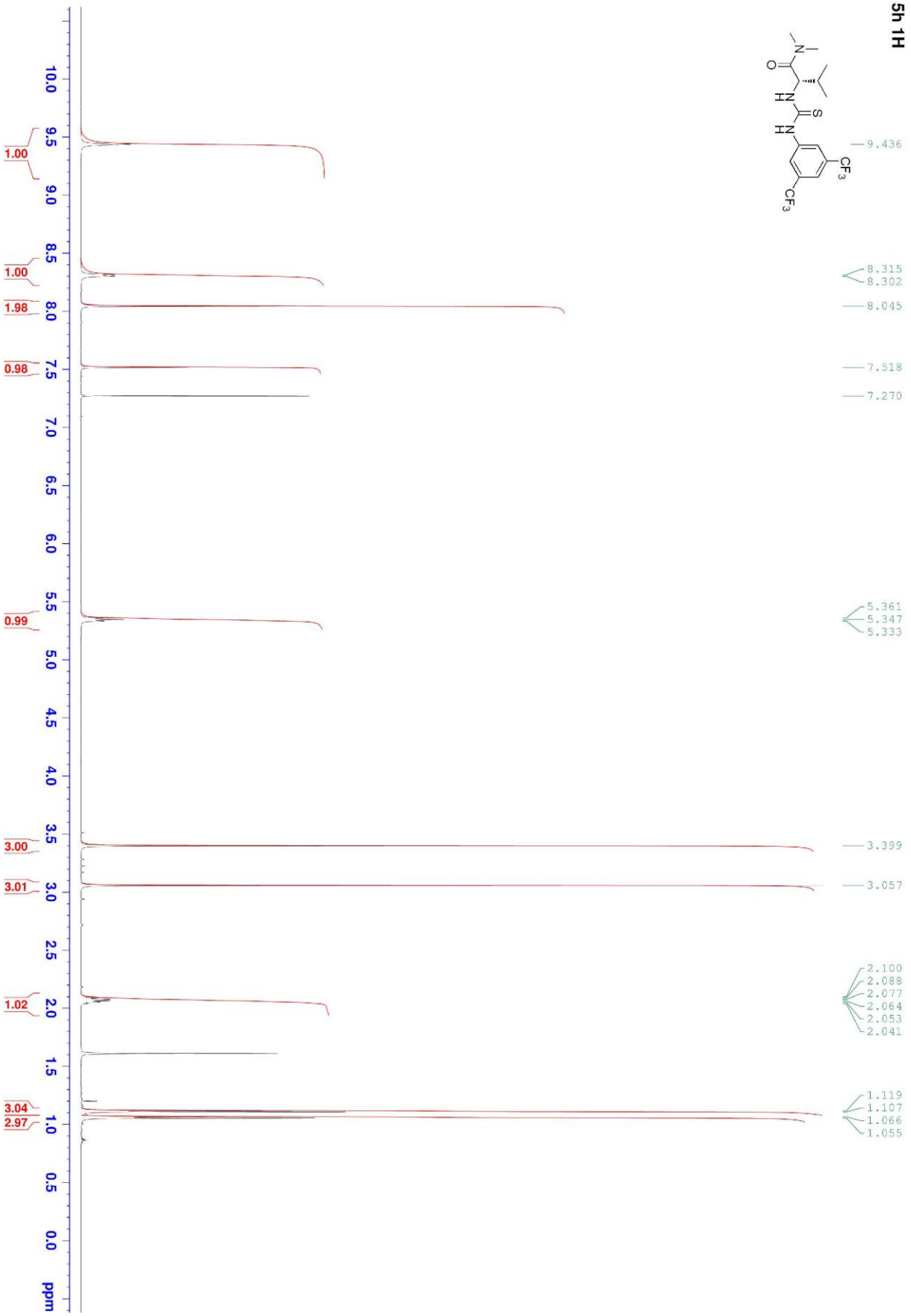
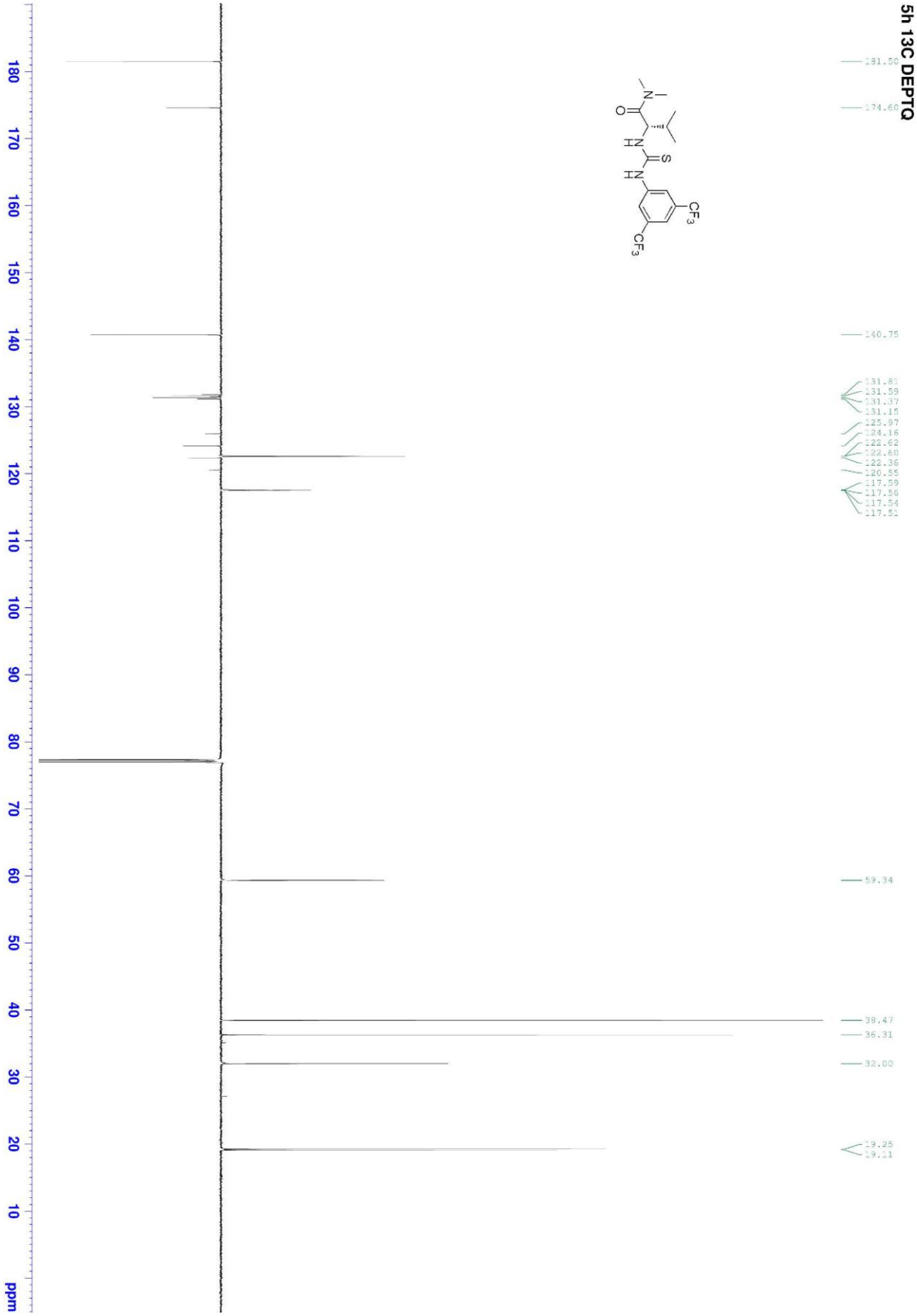
1		3.1504	11.082	0.000	33190	BB	13.2	
2		96.8496	12.698	0.000	1020339	BB	27.8	
	Totals:	100.0000		0.000	1053529			

94% *ee*

Copies of NMR spectra for novel *β*-nitrotrifluoroacetamides 3ae, 3af, 3ag and catalyst 5h

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140.75
131.81
131.59
131.37
131.15
125.97
124.16
122.62
122.60
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117.56
117.54
117.51
59.34
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36.31
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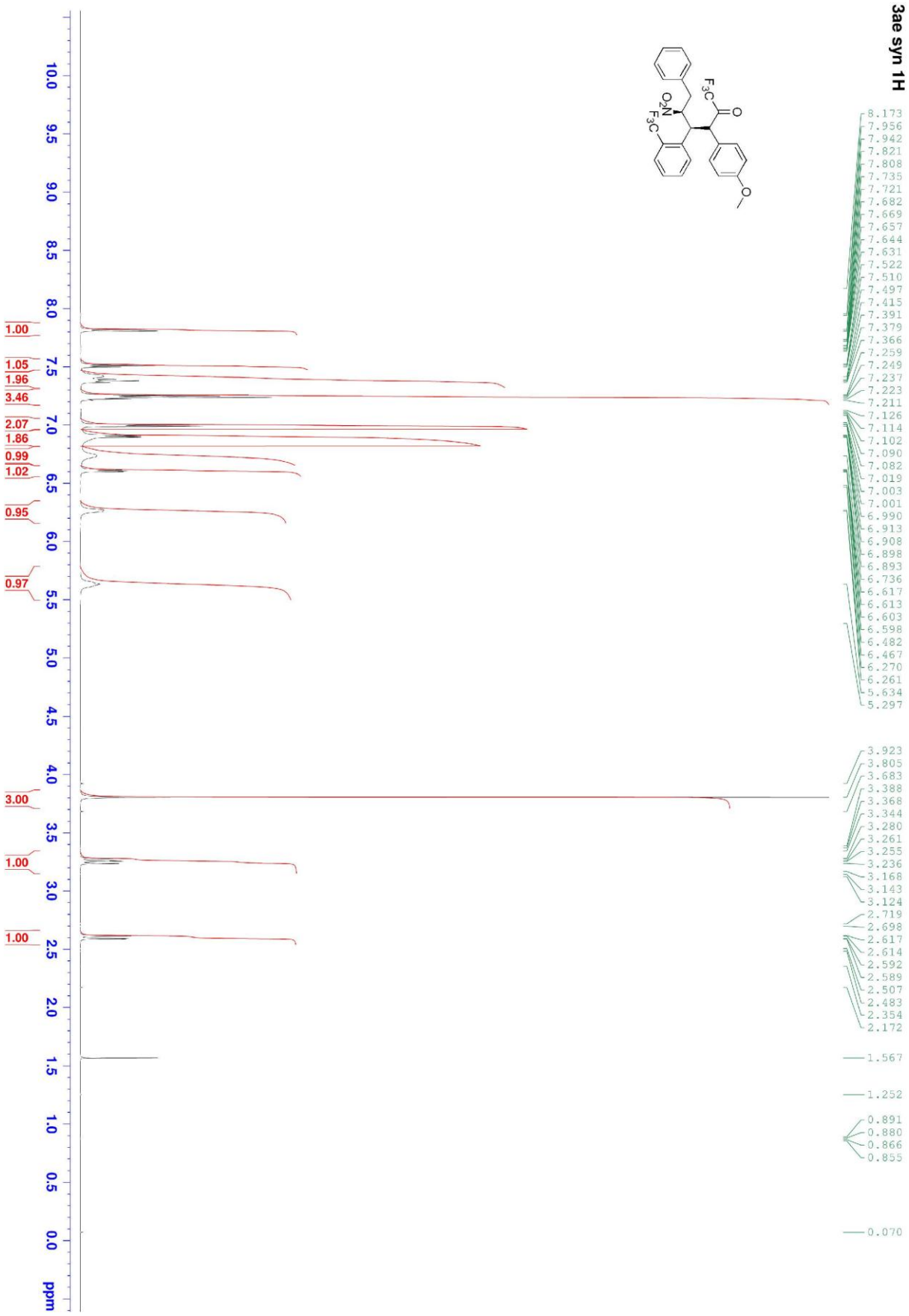
19.25
19.11
ppm


3ae syn 1H
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7.249
7.237
7.223
7.211
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7.114
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7.001
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6.736
6.617
6.613
6.603
6.598
6.482
6.467
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5.634
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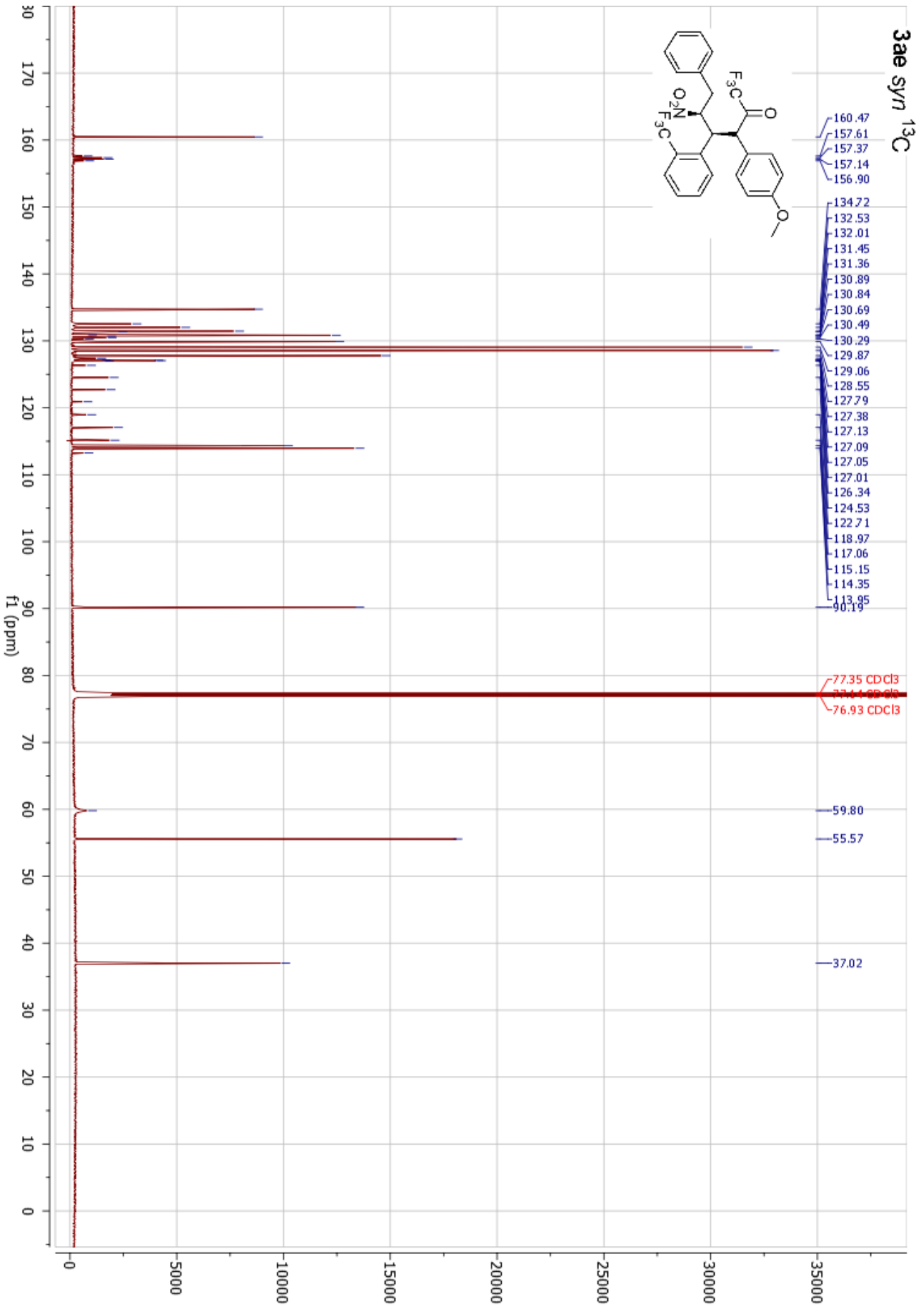

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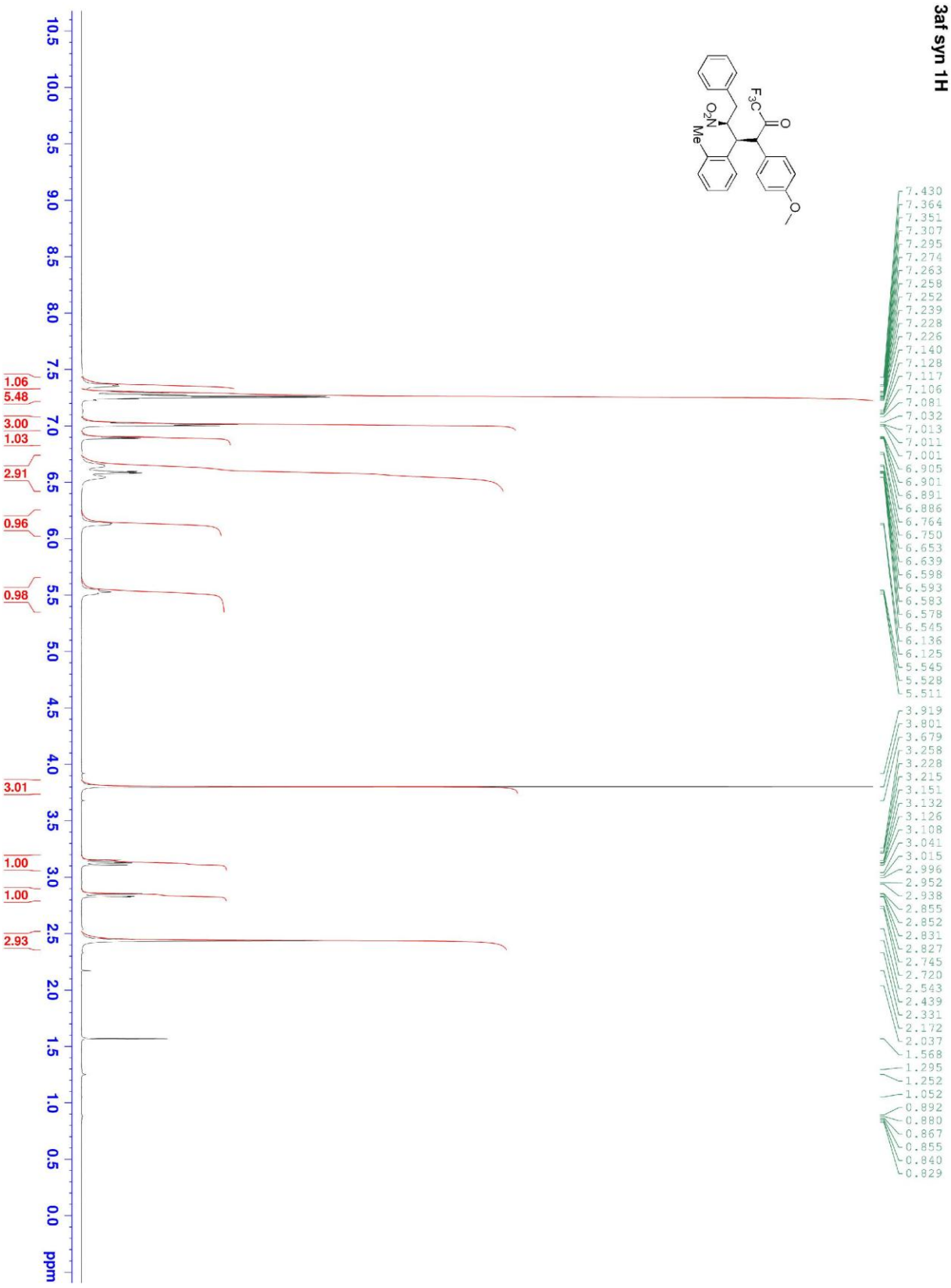

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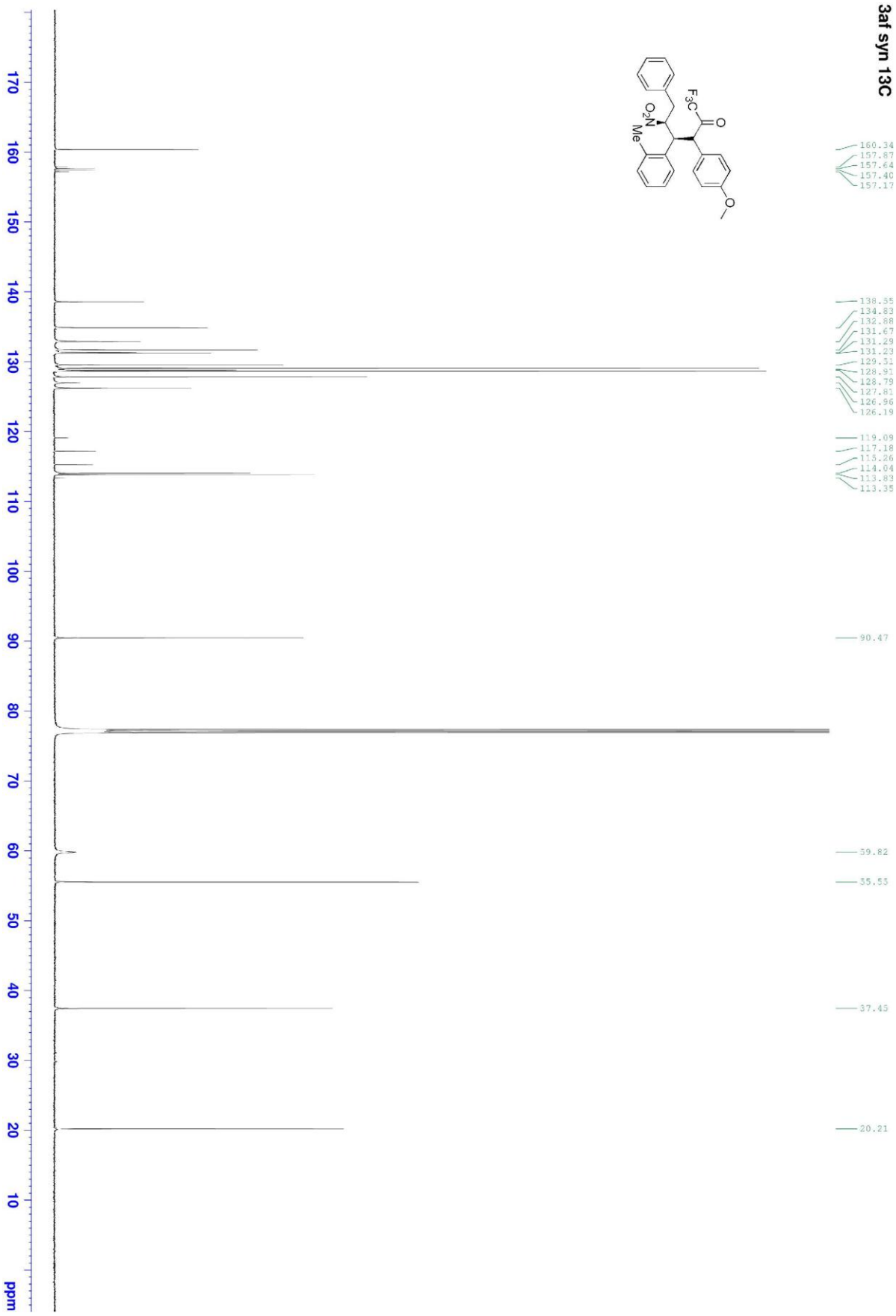

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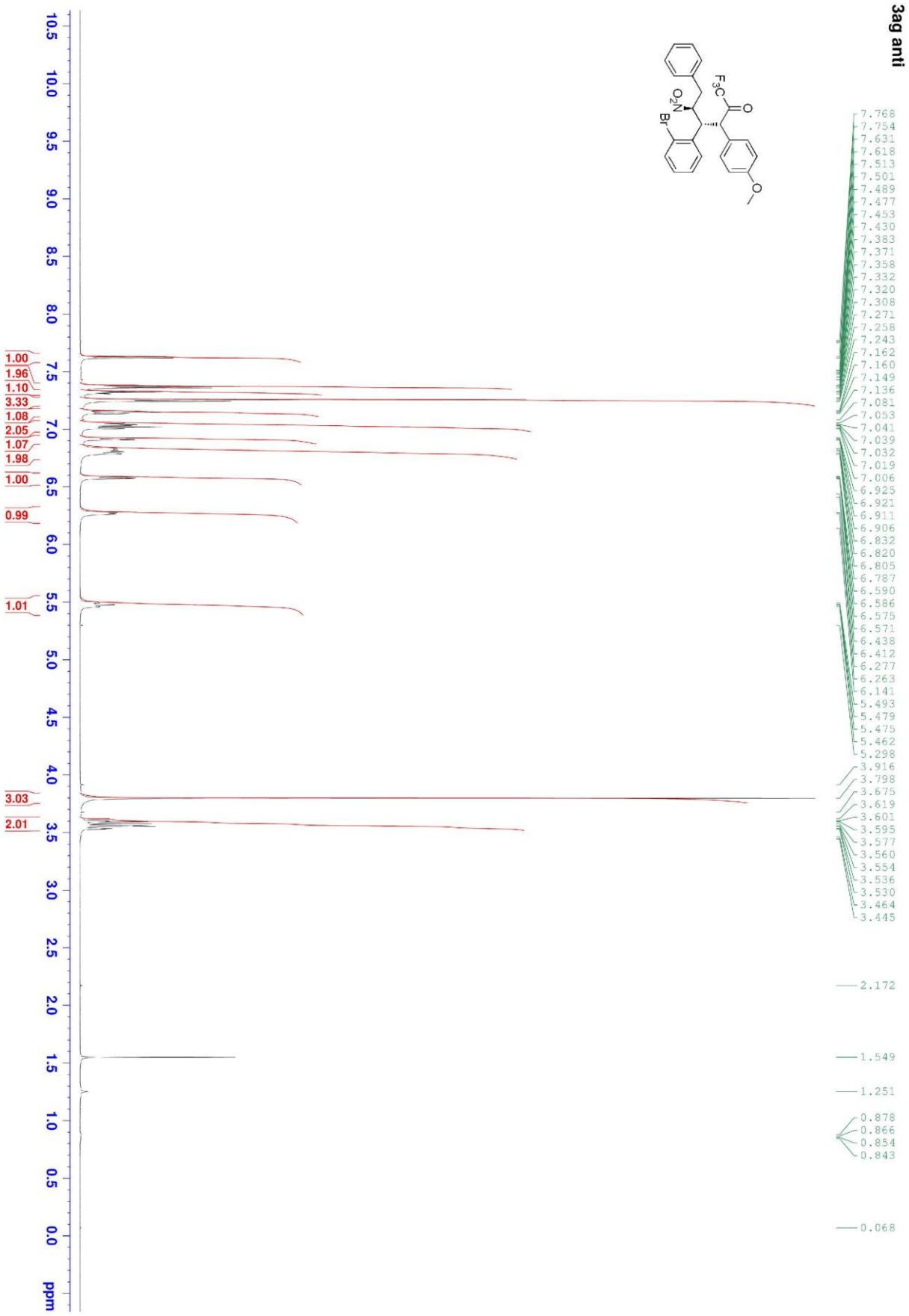

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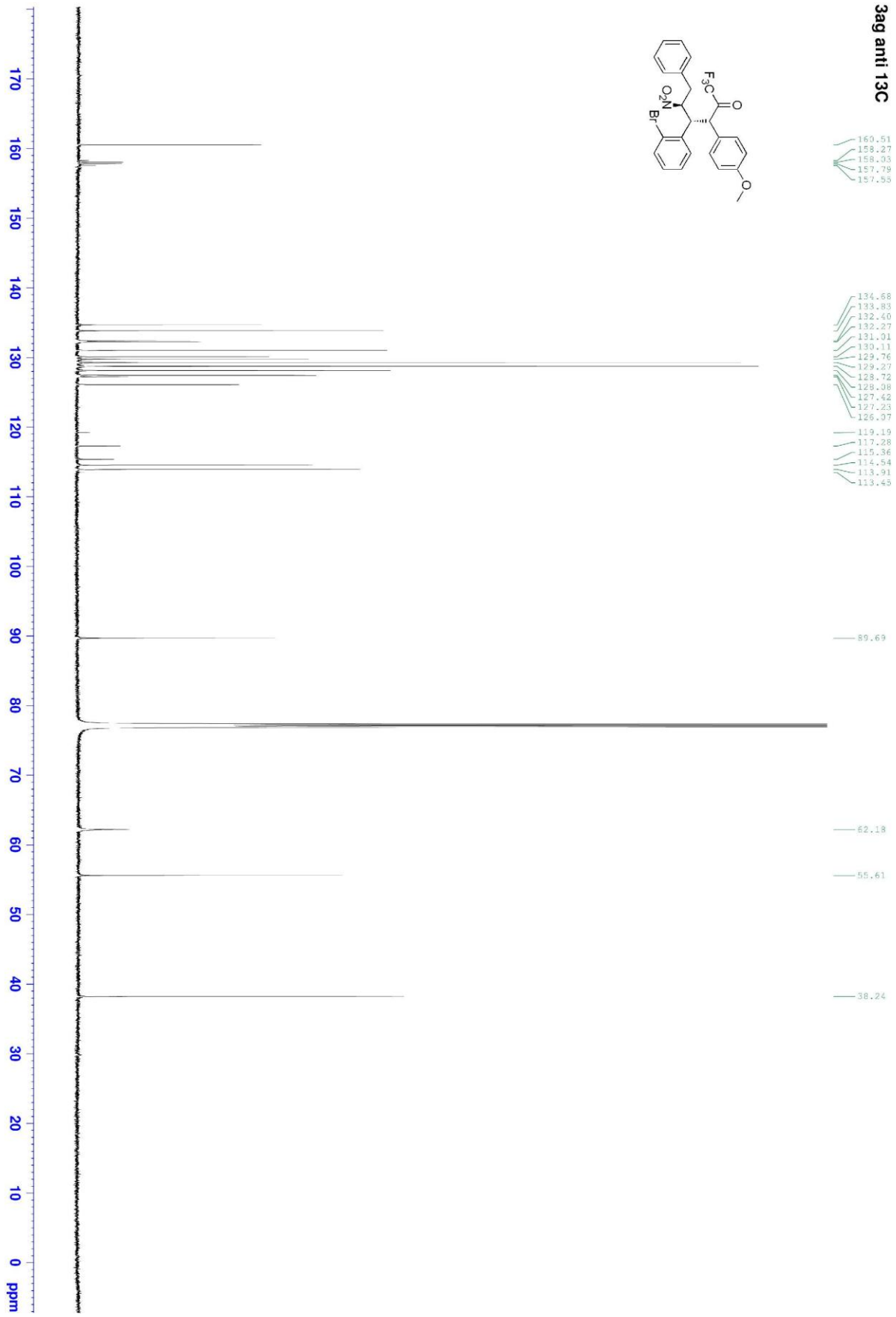

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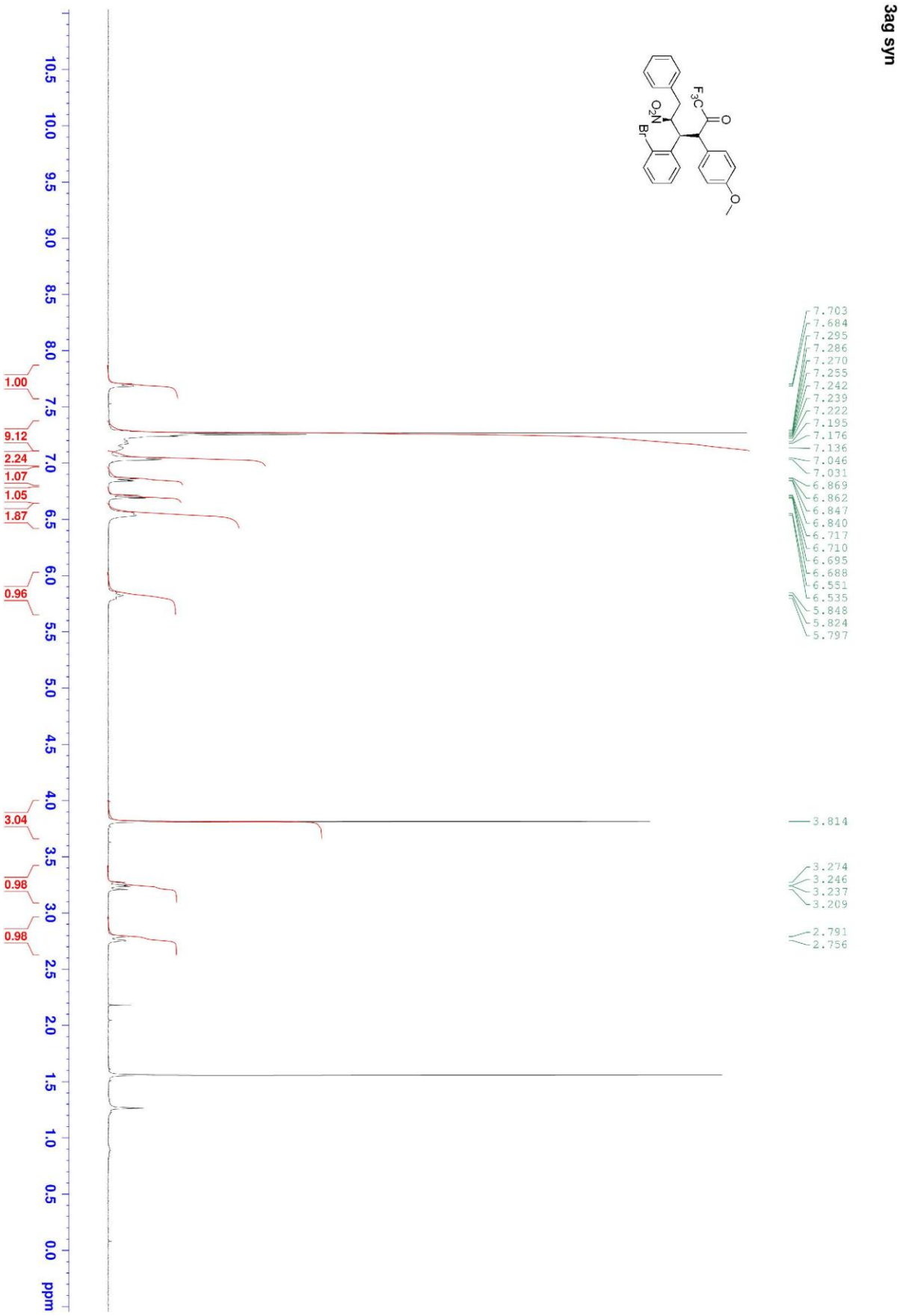

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