Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Synthesis of Enantioenriched Azo Compounds: Organocatalytic Michael Addition of Formaldehyde *N-tert*-butyl Hydrazone to Nitroalkenes

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Contents

General methods

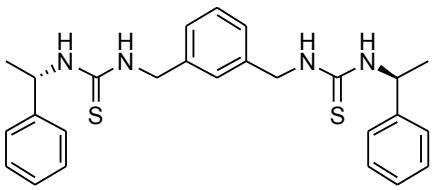
^{1}H NMR spectra were recorded at 300 MHz, 400 MHz or 500 MHz; ^{13}C NMR spectra were recorded at 75 MHz, 100 MHz or 125 MHz, with the solvent peak used as the internal standard. The following abbreviations are used to indicate the multiplicity in ^{1}H NMR spectra: s, singlet; d, doublet; t, triplet; q, quartet; dd, double doublet; m, multiplet; bs, broad signal. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel 60-F plates and visualized by ultraviolet irradiation and $KMnO_4$, anisaldehyde or phosphomolibdic acid stains. Optical rotations were measured on a Perkin-Elmer 341 MC polarimeter. The enantiomeric ratios (*er*) of the products were determined by HPLC on chiral stationary phases (Daicel Chiralpak AD-H, OD columns).

Materials. Unless otherwise noted, analytical grade solvents and commercially available reagents or catalysts were used without further purification. For flash chromatography (FC) silica gel (0.040-0.063 mm) was used. Formaldehyde monosubstituted hydrazones **1**,[1] not commercially available nitroalkenes **2**,[2] and catalysts **4d**,**e**,**f**,**k-p**[3] were synthesized according to literature procedures.

General procedure for the synthesis of catalysts 4g-i

A solution of 1,3-bis(isothiocyanatomethyl)benzene[4] (1 mmol) in THF (5 mL) was added dropwise to a stirred solution of the corresponding chiral amine (2.5 mmol) in THF (10 mL). The reaction was stirred at room temperature for 24-48 h, the solvent was evaporated under reduced pressure and the residue was purified by FC on silica gel (hexane/AcOEt). Yields and characterization data for **4g-i** are as follows:

1,1'-[1,3-Phenylenebis(methylene)]bis{3-[(*S*)-1-phenylethyl]thiourea} (4g)



White solid (91% yield); M.p.: 85-87 °C; $[\alpha]_D^{20}$ −43.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.23 (m, 10H), 7.08 (t, *J* = 7.6, 1H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.61 (s, 1H), 6.41 (s, 2H), 5.80 (s, 2H), 4.85 (bs, 2H), 4.55 (dd, *J* = 14.0 Hz, *J* = 3.9 Hz, 2H), 4.45 (dd, *J* = 14.0 Hz, *J* = 3.9 Hz, 2H), 1.46 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.2, 142.2, 137.8, 129.1, 129.0, 127.9, 126.6, 126.0, 125.9, 54.00, 48.6, 23.3; HRMS (FAB): calculated for $[C_{26}H_{30}N_4S_2Na]^+$ 485.1810; found: 485.1794.

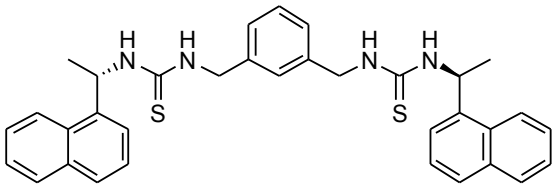
[1] (*a*) J-S. M. Lehn, S. Javed and D. M. Hoffman, *Inorg. Chem.* 2007, **46**, 993; (*b*) Y. Kamitori, M. Hojo, R. Masuda, T. Yoshida, S. Ohara, K. Yamada and N. Yoshikawa, *J. Org. Chem.* 1988, **53**, 129; (*c*) M. Barbero, S. Cadamuro, S. Dughera and G. Ghigo, *Eur. J. Org. Chem.* 2008, 862.

[2] (*a*) R. A. Kunetsky and A. D. Dilman, *Tetrahedron Lett.* 2005, **46**, 5203; (*b*) D. Lucet, S. Sabelle, *Eur. J. Org. Chem.* 1999, 2583; (*c*) E. Hata, T. Yamada and T. Mukaiyama, *Bull. Chem. Soc. Jpn*. 1995, **68**, 3629.

[3] For catalyst **4d**: (*a*) R.P. Herrera, V. Sgarzani, L. Bernardi and A. Ricci, *Angew. Chem. Int. Ed.* 2005, **44**, 6576; For Catalyst **4e**: (*b*) H. Jiang, M. W. Paixão, D. Monge and K.A. Jørgensen, *J. Am. Chem. Soc*. 2010, **132**, 2775. For catalyst **4f**: (*c*) Y. Sohtome, A. Tanatani, Y. Hashimoto and K. Nagasawa, *Tetrahedron Lett*. 2004, **45**, 5589; For catalyst **4k-p**: (*d*) X. G. Liu, J. J. Jiang and M. Shi, *Tetrahedron Lett.* 2007, **18**, 2773.

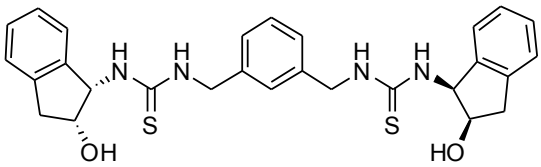
[4] J. M. Benito, M. Gómez-.García, J. L. Jiménez, C. Ortiz, J. M. García, *J. Org. Chem*. 2001, **66**, 1366.

1,1'-[1,3-Phenylenebis(methylene)]bis{3-[(*S*)-1-(naphthalen-1-yl)ethyl]thiourea} (4h)



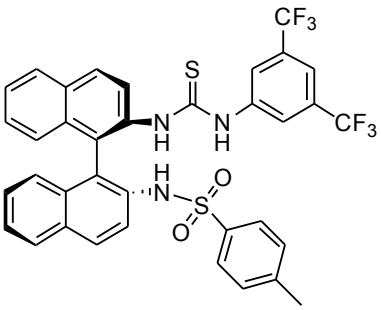
White solid (84% yield); MP: 93-95 °C; $[\alpha]_D^{20}$ −43.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.18 (m, 14H), 6.71-6.56 (m, 4H), 6.44 (s, 2H), 6.00 (s, 2H), 5.01 (bs, 2H), 4.15-4.25 (m, 4H), 1.40 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.0, 139.6, 137.5, 133.2, 132.8, 128.9, 128.7, 127.8, 127.6, 126.4 (2C), 126.1, 125.7, 124.5, 123.9, 53.9, 48.2, 23.0; HRMS (FAB): calculated for $[C_{34}H_{34}N_4S_2Na]^+$ 585.2123; found: 585.2125.

1,1'-[1,3-Phenylenebis(methylene)]bis{3-[(1*S*,2*R*)-2-hydroxy-2,3-dihydro-1H-inden-1-yl]thiourea} (4i)



White solid (73% yield); MP: 96-97 °C; $[\alpha]_D^{20}$ −86.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-6.93 (m, 12H), 6.44 (s, 2H), 5.82 (s, 2H), 4.65 (s, 2H), 4.45-4.23 (m, 2H), 3.03 (dd, *J* = 16.8, 4.7 Hz, 2H), 2.68 (d, *J* = 16.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 140.1, 139.9, 129.1, 128.3 (2C), 127.1, 126.6, 125.1 (2C), 124.5, 72.9, 62.4, 60.3, 39.5; HRMS (FAB): calculated for $[C_{28}H_{30}N_4O_2S_2Na]^+$ 541.1708; found: 541.1701.

***N*-{2'-[3-(3,5-Bis(trifluoromethyl)phenyl]thioureido}-(1,1'-binaphthalen)-2-yl-4-methylbenzenesulfonamide (4j)**



To a stirred solution of 1-[2'-amino-(1,1'-binaphthalen)-2-yl]-3-[3,5-bis(trifluoromethyl)phenyl]thiourea[5] (120.3 mg, 0.22 mmol) in dry pyridine (3 mL) under Argon, *p*-toluenesulfonyl chloride (61.9 mg, 0.32 mmol) was added. The reaction was stirred at room temperature for 3 hours and purified by FC on silica gel (Hexane/Et_2O, 3:1) affording **4j** (82.4 mg, 53%) as a white solid; MP: 148-150 °C; $[\alpha]_D^{20}$ −173.2 (*c* 0.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (s, 2H), 8.05-7.94 (m, 2H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.76-7.63 (m, 2H), 7.49-7.02 (m, 9H), 6.93 (d, *J* = 8.6 Hz, 1H), 6.35 (d, *J* = 8.1 Hz, 2H), 1.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 143.3, 142.9, 140.7, 138.7, 136.3, 133.6, 132.4, 132.0, 131.5, 131.1, 130.6, 130.5, 129.3, 128.8, 128.4, 128.1, 127.8 (2C), 126.9, 126.3, 125.8, 125.6, 125.4, 124.7, 123.4, 123.3 (q, $J_{C\text{-}F}$ = 272.5 Hz),

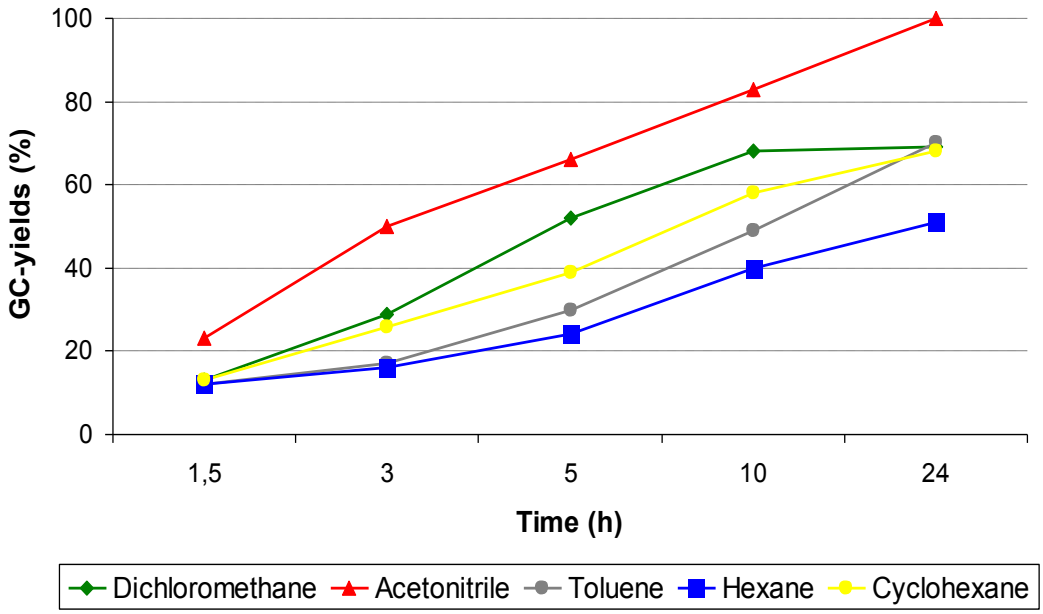
[5] P. Galzerano; G. Bencibenni; F. Pesciaioli; A. Mazzanti; B. Giannichi; L. Sambri; G. Bartoli, P. Melchiorre. *Chem. Eur. J.* 2009, **15**, 7846.

118.7 (2C), 116.2, 21.4; HRMS (FAB): calculated for $[C_{36}H_{25}F_6N_3O_2S_2Na]^+$ 732.2568; found: 732.1957.

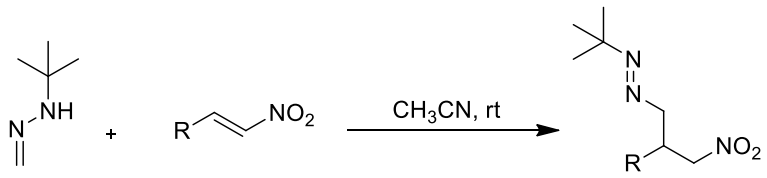
General procedure for reaction monitoring

Hydrazone **1a** (17.7 µL, 0.15 mmol) was added to a solution of nitroalkene **2a** (0.1 mmol) and mesytilene (0.1 mmol, as standard patron) in solvent (1 mL) at room temperature. The mixture was stirred and monitorized by GC [GC condition: TEKNOKROMA TRB-1, injector temp.= 300 ºC, detector temp.= 280 ºC, column temp.= 60 ºC (3 min), 80 ºC/min (until 270 ºC), 270 ºC (1 min), t_{2a} = 6.9 min, t_{3a} = 15.1 min, $t_{dodecane}$ = 7.8 min].

Reaction rates monitoring of non-catalyzed reactions in different solvents



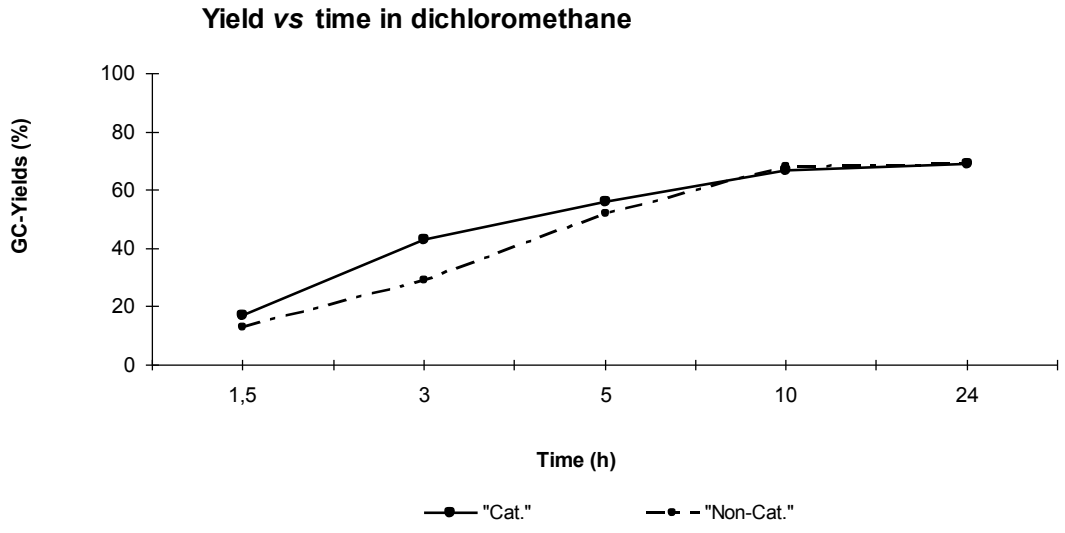
General procedure for the racemic 1,4-addition of formaldehyde *tert*-butyl hydrazone 1a to nitroalkenes 2

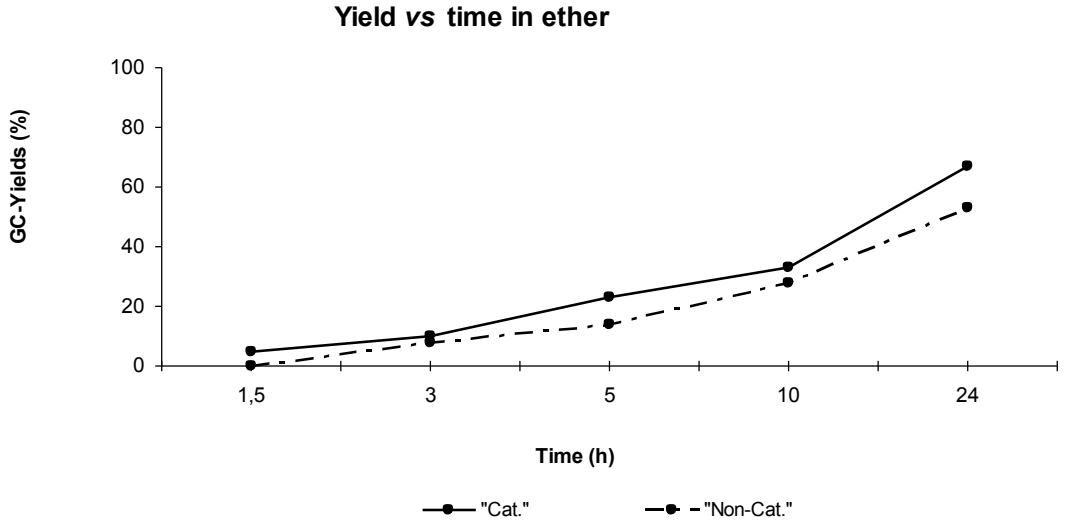


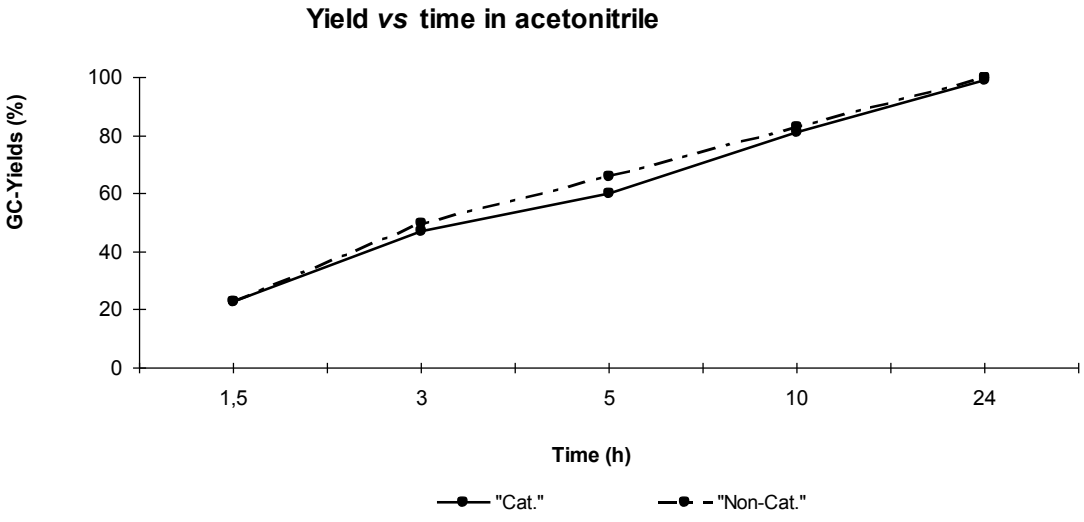
1a **2** **3**

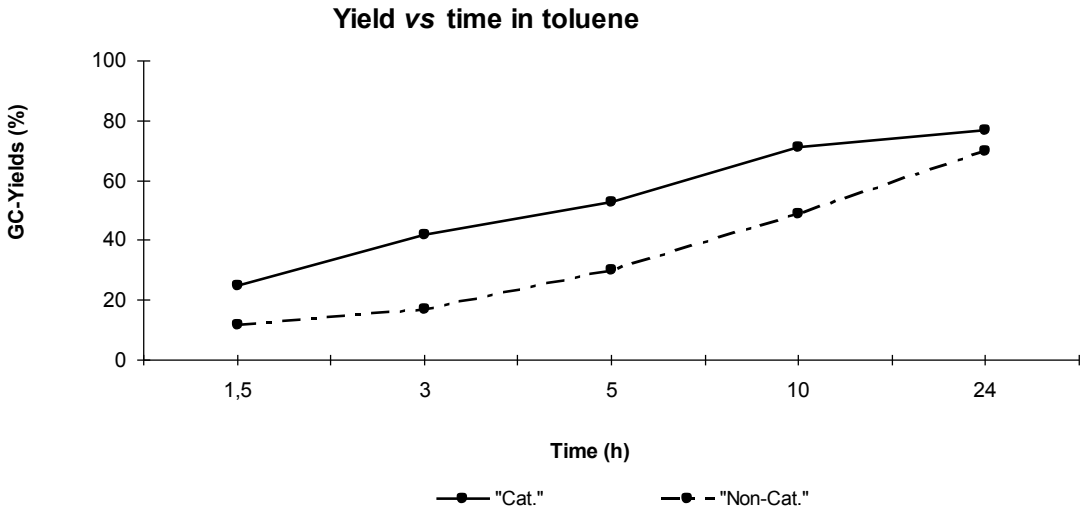
Hydrazone **1a** (35.4 µL, 0.3 mmol) was added to a solution of nitroalkene **2** (0.2 mmol) in CH_3CN (0.1 mL) and the mixture was stirred for ~24 h at room temperature. The racemic products **3** were isolated by FC on silica gel (pentane/CH_2Cl_2).

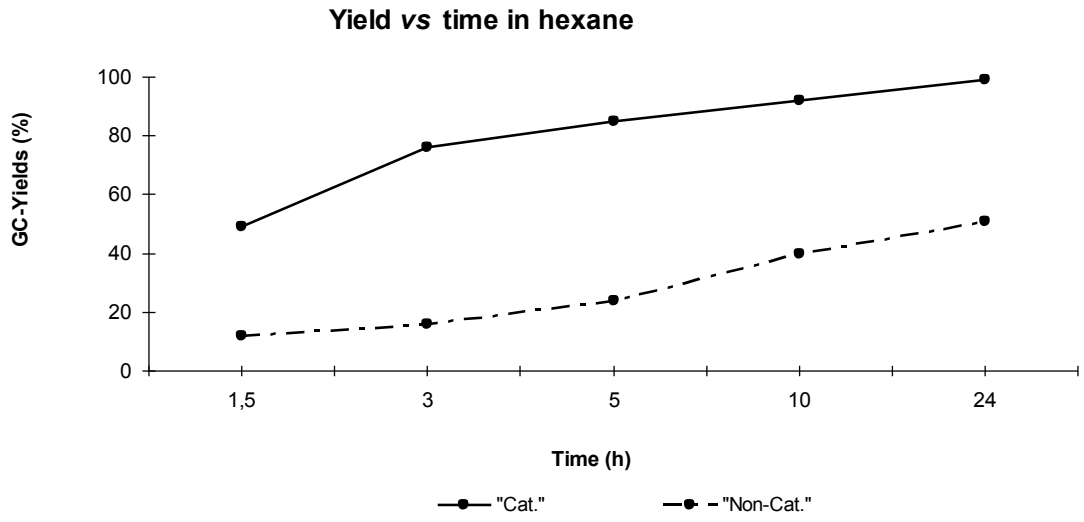
Comparative reaction rates of non-catalyzed *vs* organocatalytic reactions

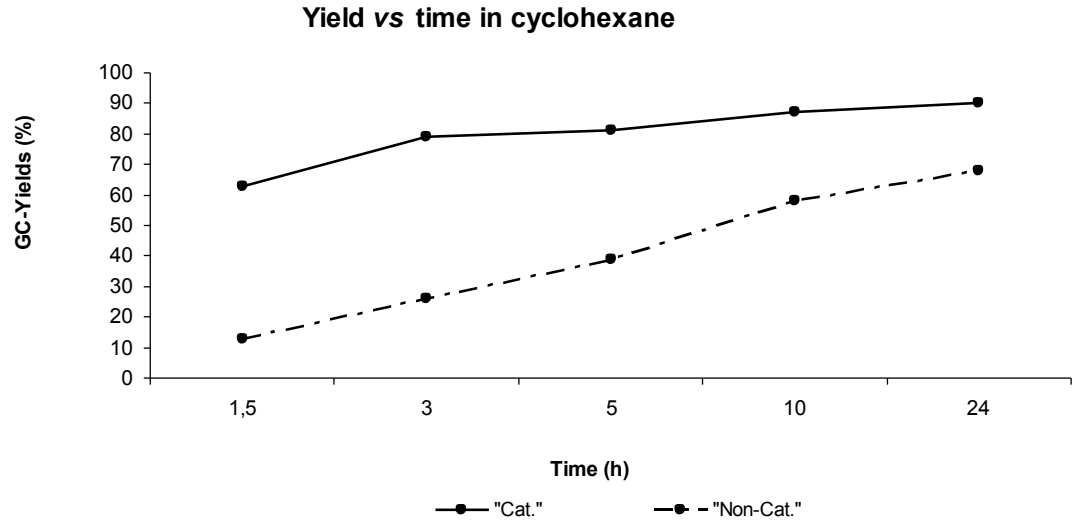




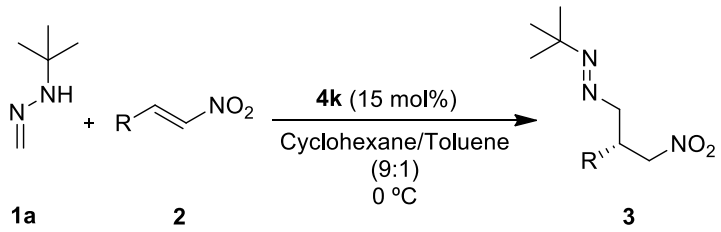








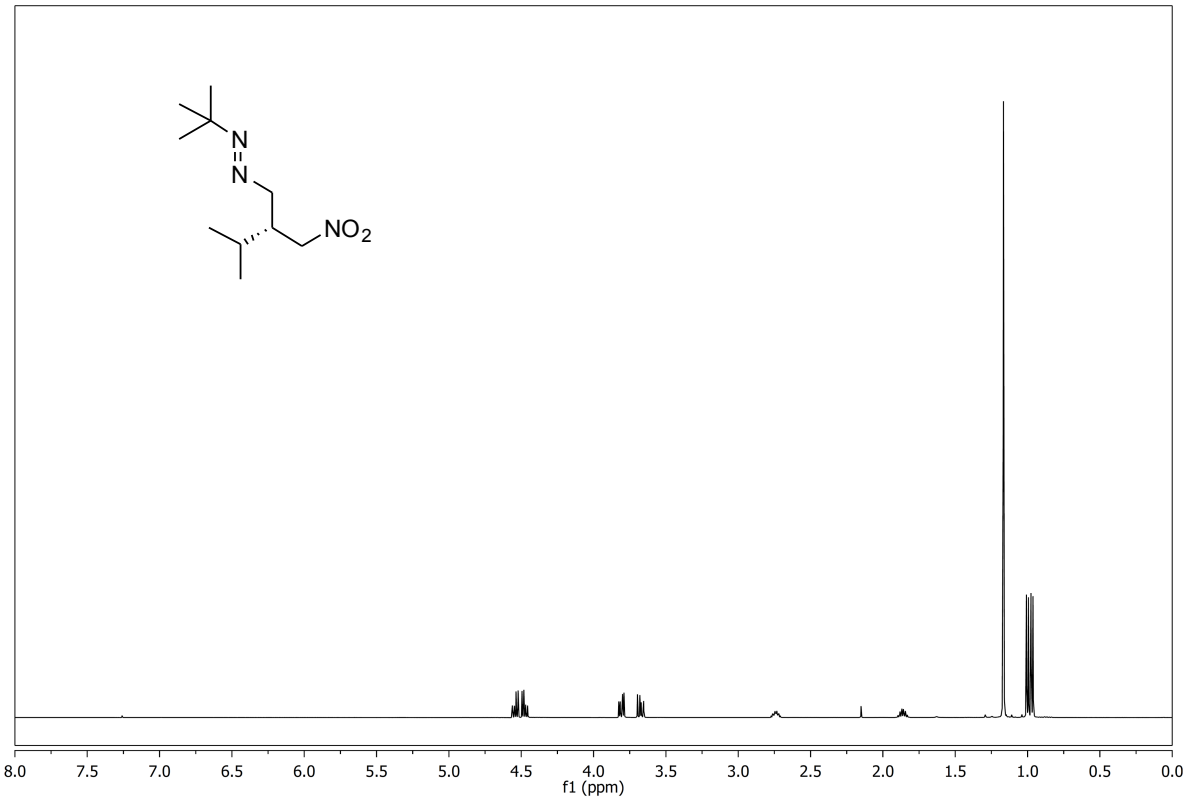
General procedure for the enantioselective 1,4-addition of formaldehyde *tert*-butyl hydrazone 1a to nitroalkenes 2



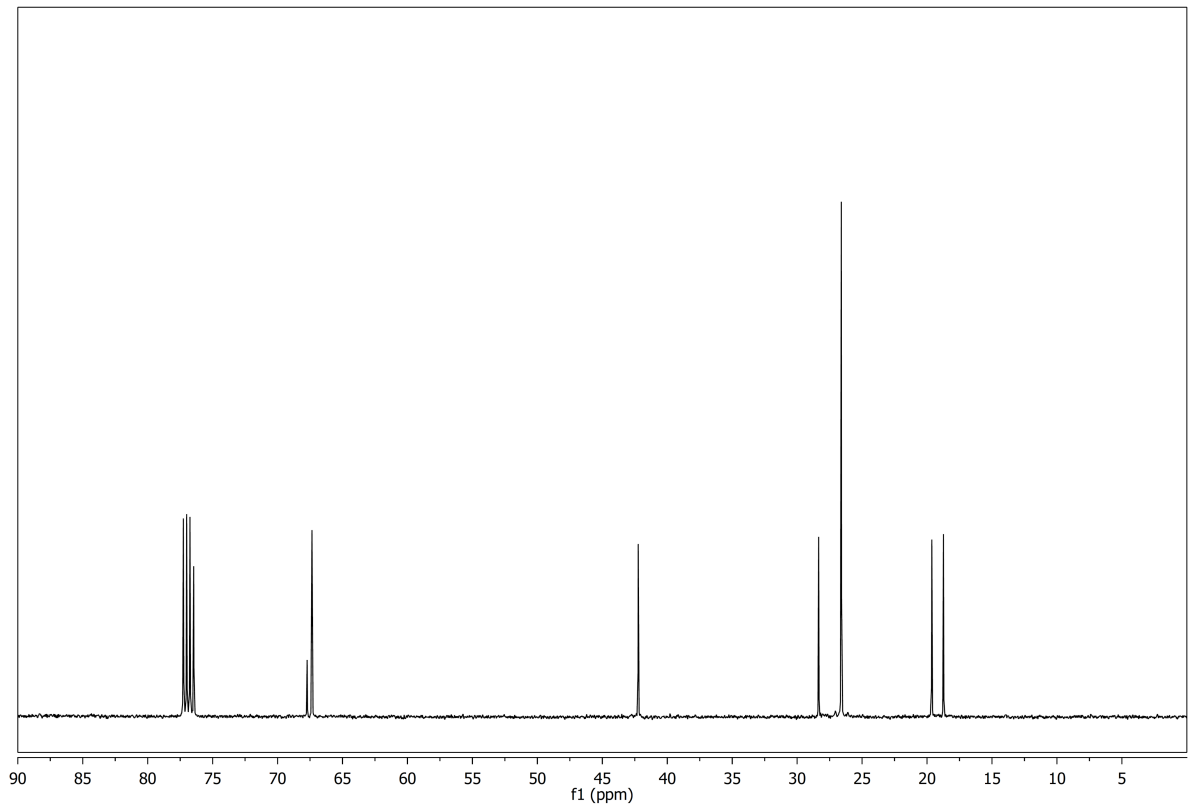
Hydrazone **1a** (17.7 µL, 0.15 mmol) was added to a solution of nitroalkene **2** (0.1 mmol) and catalyst **4k** (0.015 mmol) in (Cyclohexane/Toluene, 9:1, 1 mL) at 0 ºC. The mixture was stirred for ~48 h. The enantioenriched products **3** were isolated by FC (Pentane/CH_2Cl_2). Enantiomeric ratios were determined by HPLC analysis.

NMR spectra and HPLC traces for compounds 3, 5 and 6:

^{1}H NMR ($CDCl_3$, 300 MHz) of **3a**:

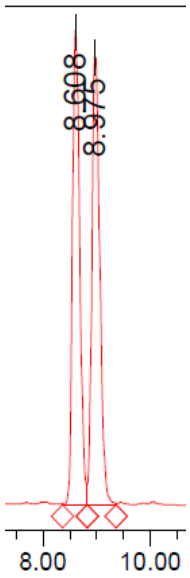


^{13}C NMR ($CDCl_3$, 125 MHz) of **3a**:

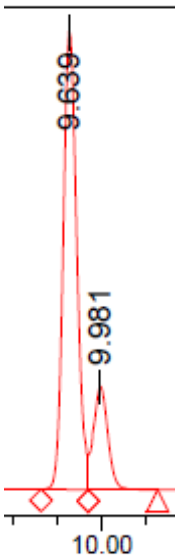


HPLC conditions for **3a**: Chiralpak AD-H column [heptane/*i*-PrOH (99.5:0.5) 0.5 mL/min]

Racemic



Non Racemic



Processed Channel: PDA 209.7 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
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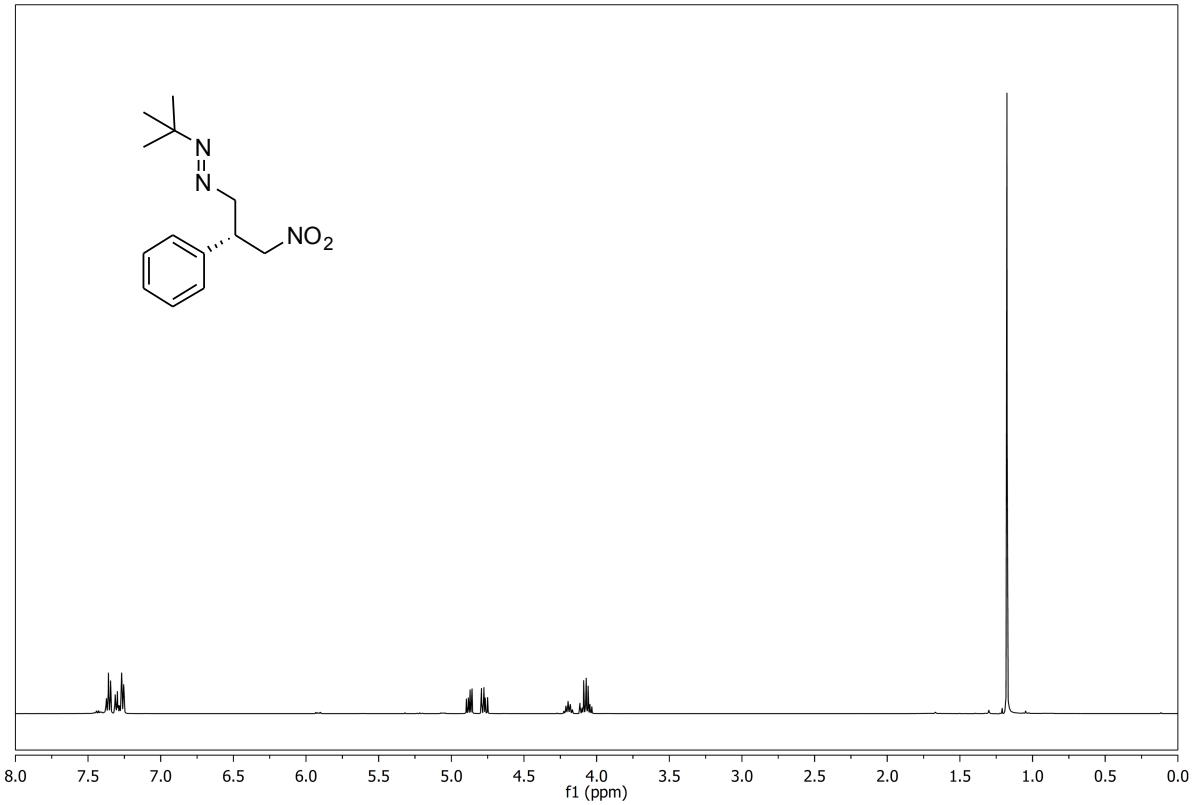
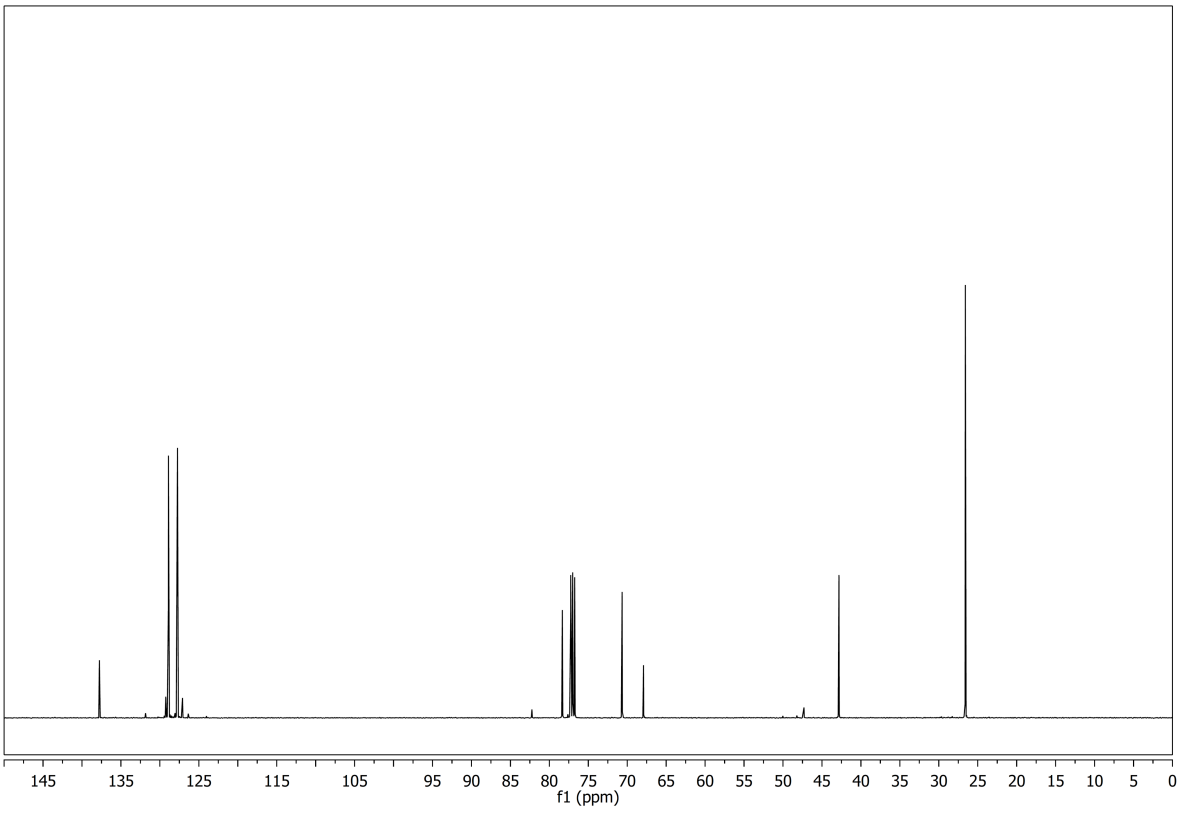
^{1}H NMR ($CDCl_3$, 300 MHz) of **3b**:

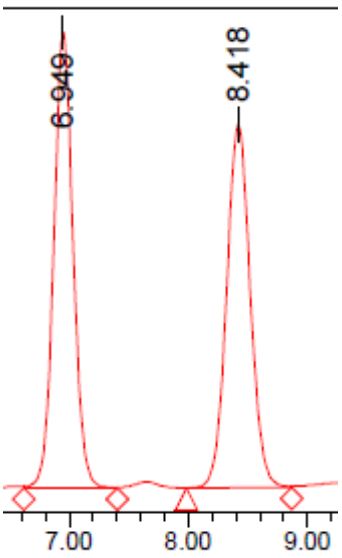


^{13}C NMR ($CDCl_3$, 125 MHz) of **3b**:

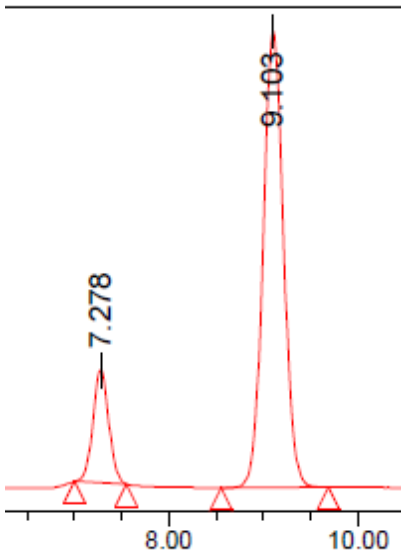


HPLC conditions for **3b**: Chiralpak OD column [hexane/*i*-PrOH (95:5) 1 mL/min]

Racemic



Non Racemic



Processed Channel: PDA 209.7 nm

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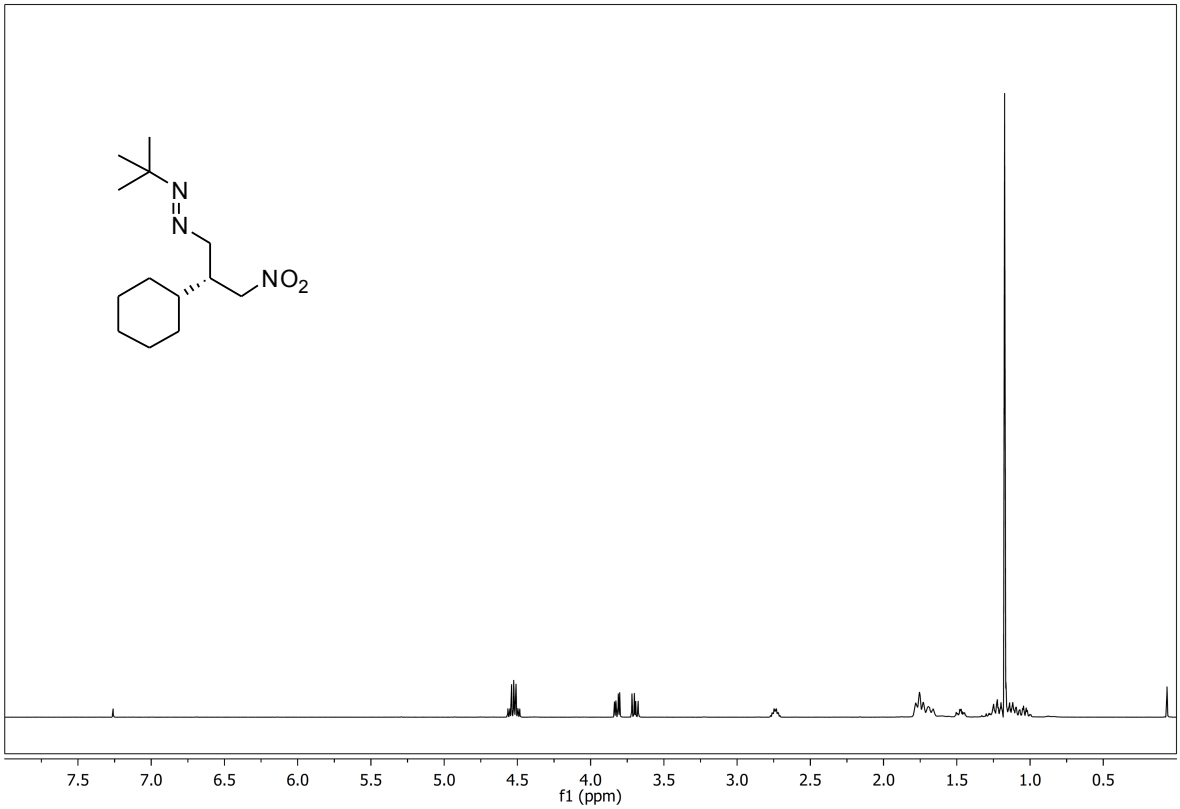
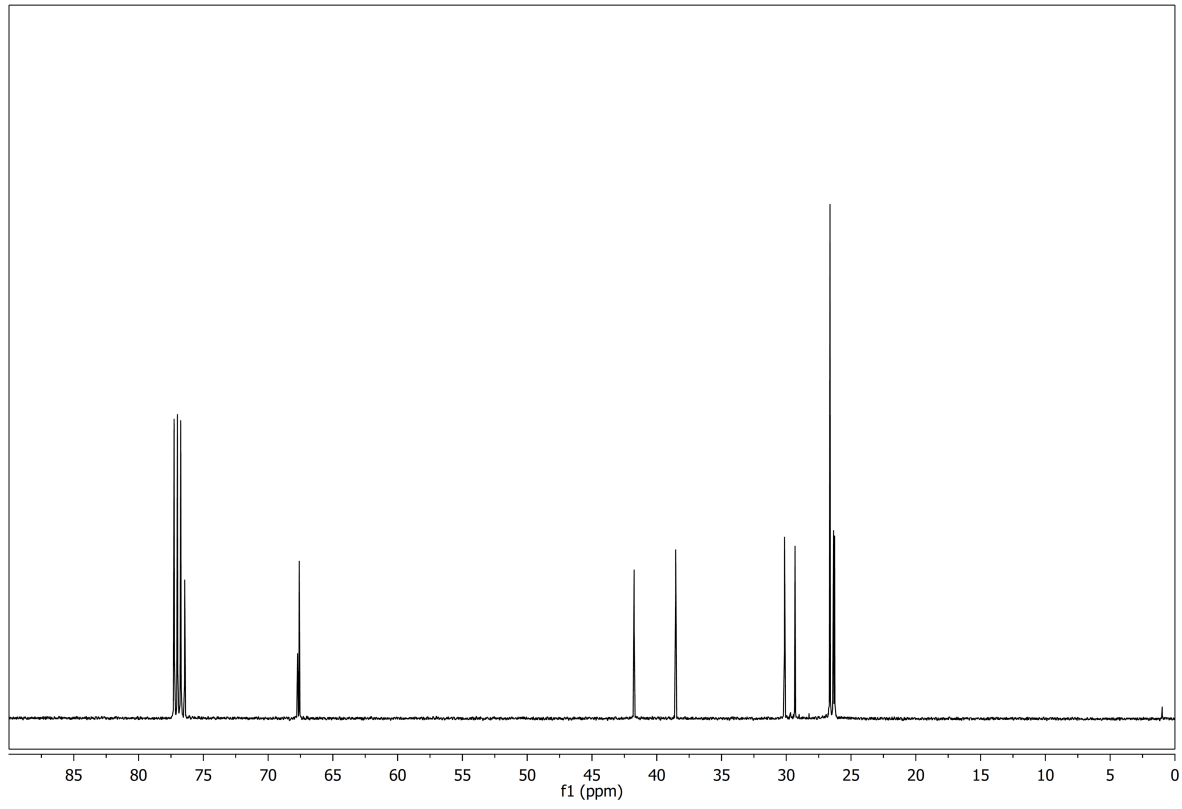
^{1}H NMR ($CDCl_3$, 300 MHz) of **3c**:

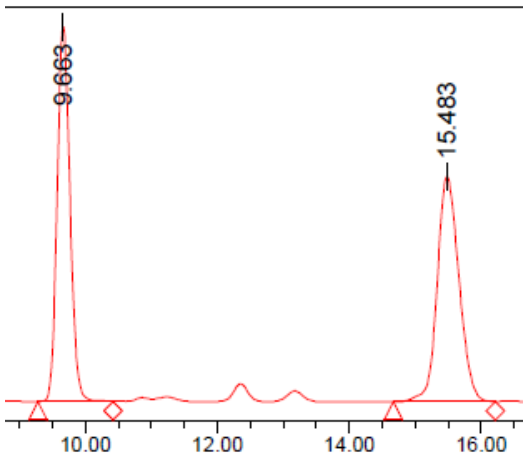


^{13}C NMR ($CDCl_3$, 75 MHz) of **3c**:

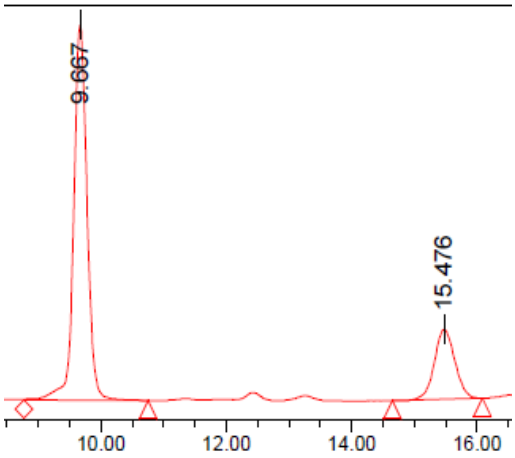


HPLC conditions for **3c**: Chiralpak AD-H column [hexane/*i*-PrOH (98:2) 0.5 mL/min]

Racemic



Non Racemic



Processed Channel: PDA 209.7 nm

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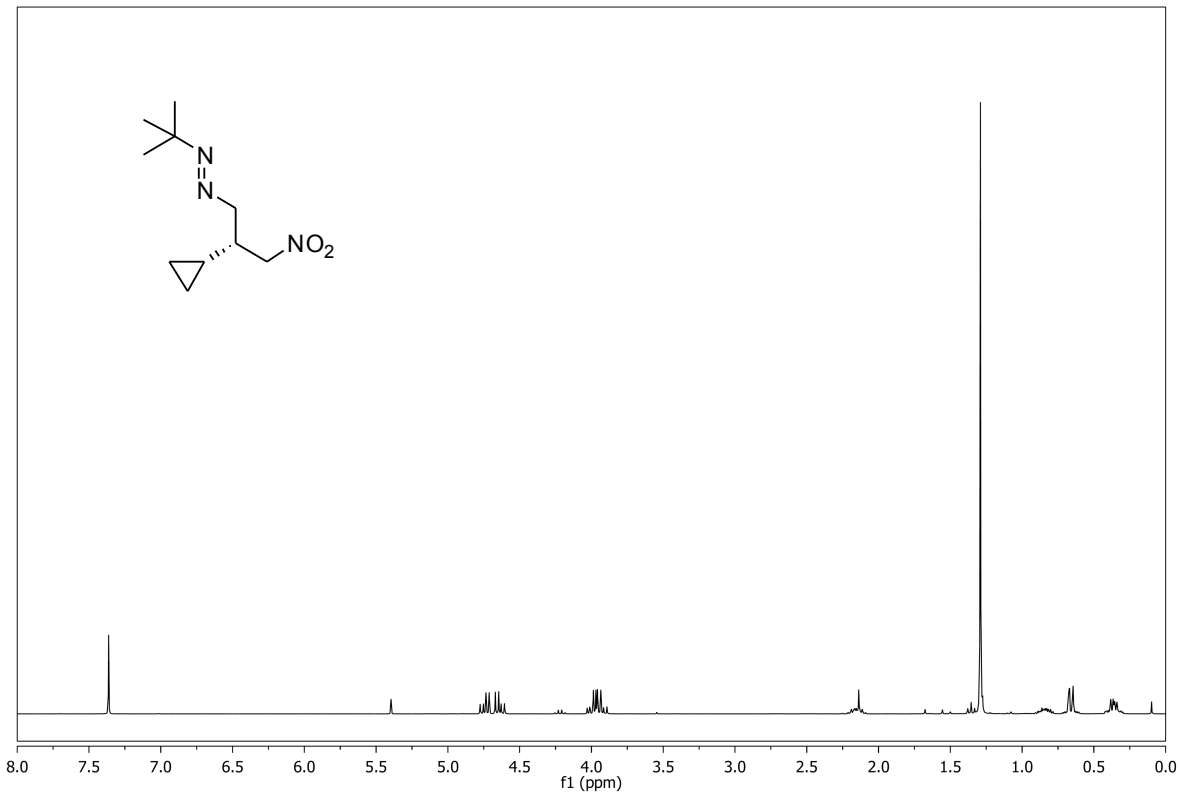
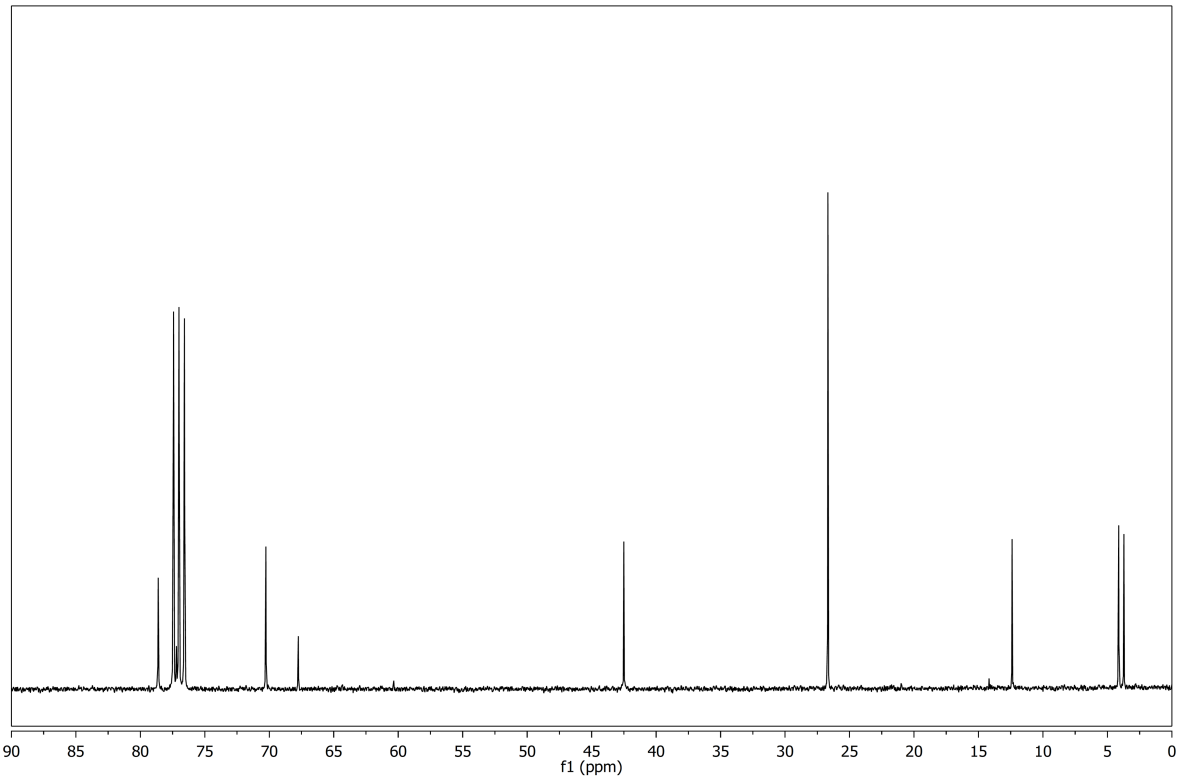
^{1}H NMR ($CDCl_3$, 300 MHz) of **3d**:

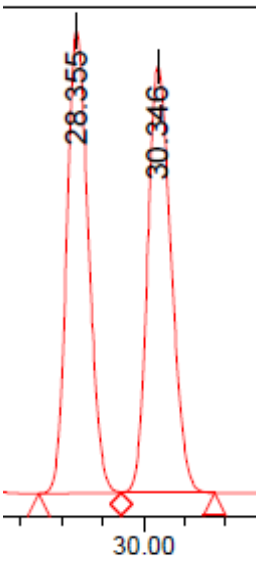


^{13}C NMR ($CDCl_3$, 75 MHz) of **3d**:

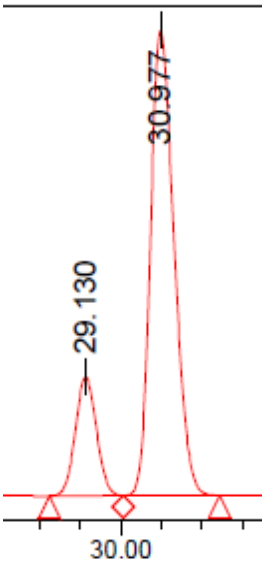


HPLC conditions for **3d**: Chiralpak OD column [hexane/*i*-PrOH (99.5:0.5) 0.25 mL/min]

Racemic



Non Racemic



Processed Channel: PDA 209.7 nm

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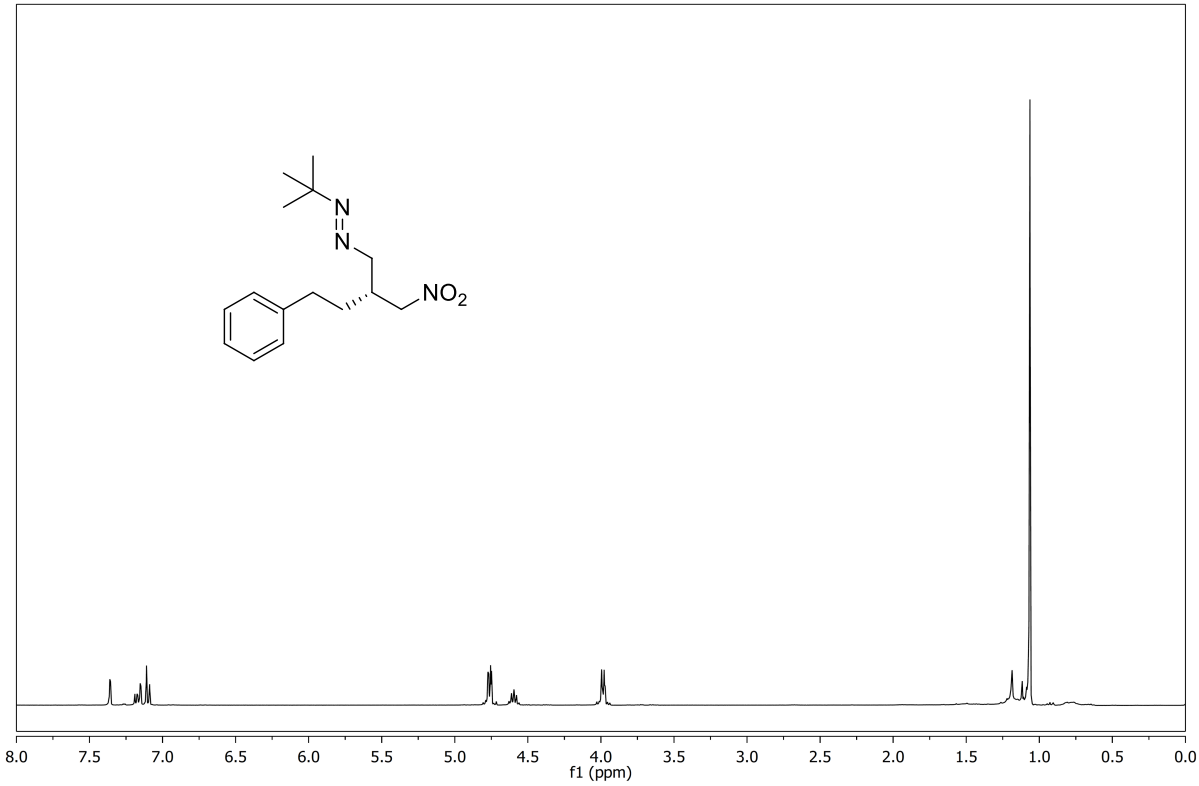
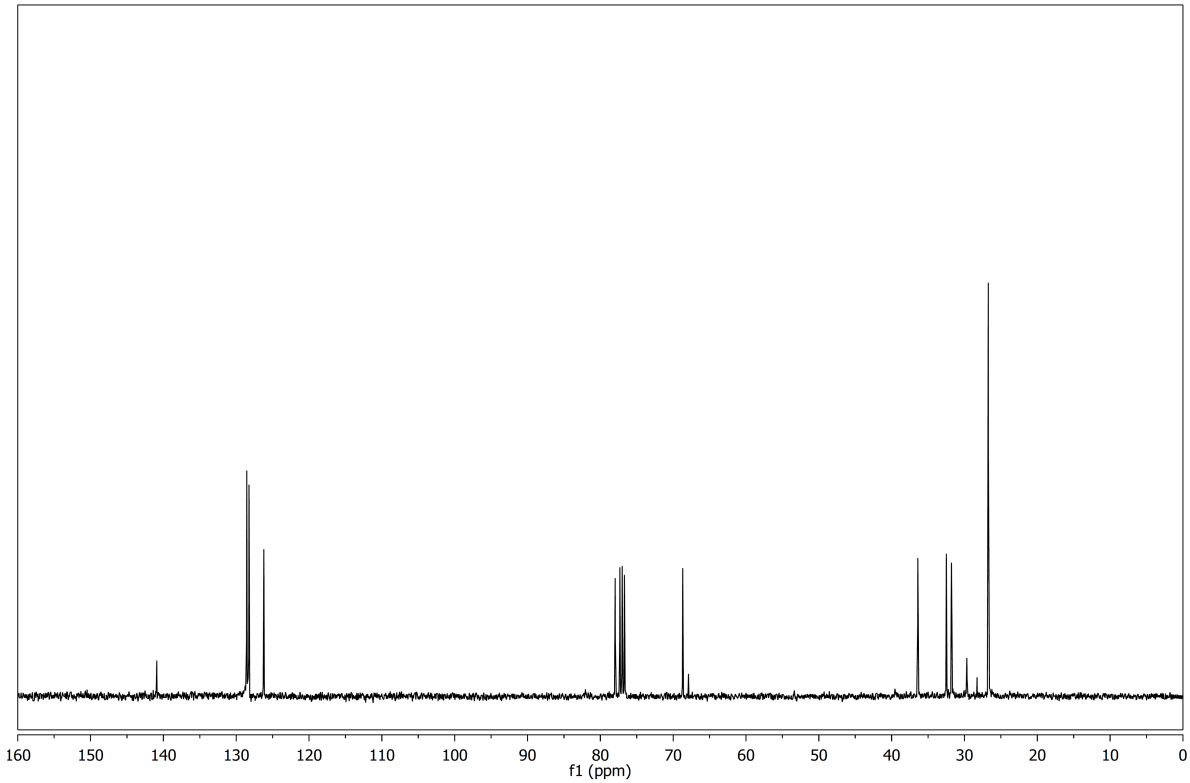
2	PDA 209.7 nm	30.977	37343278	81.38	924847

^{1}H NMR ($CDCl_3$, 400 MHz) of **3e**:



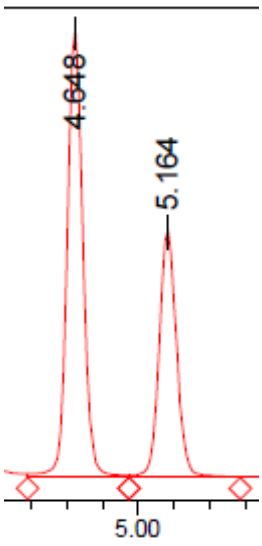
^{13}C NMR ($CDCl_3$, 100 MHz) of **3e**:



HPLC conditions for **3e**: Chiralpak AD-H column [hexane/*i*-PrOH (97:3) 1 mL/min]

Racemic

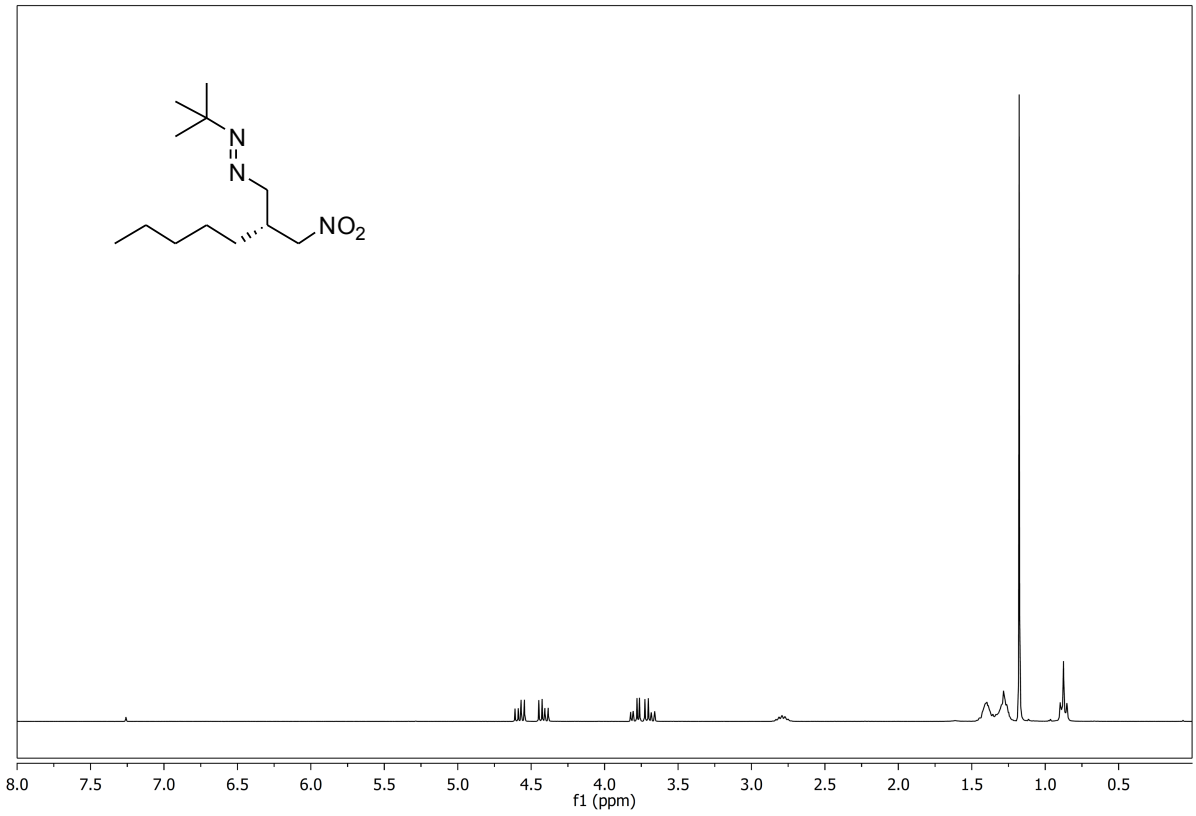
Non Racemic



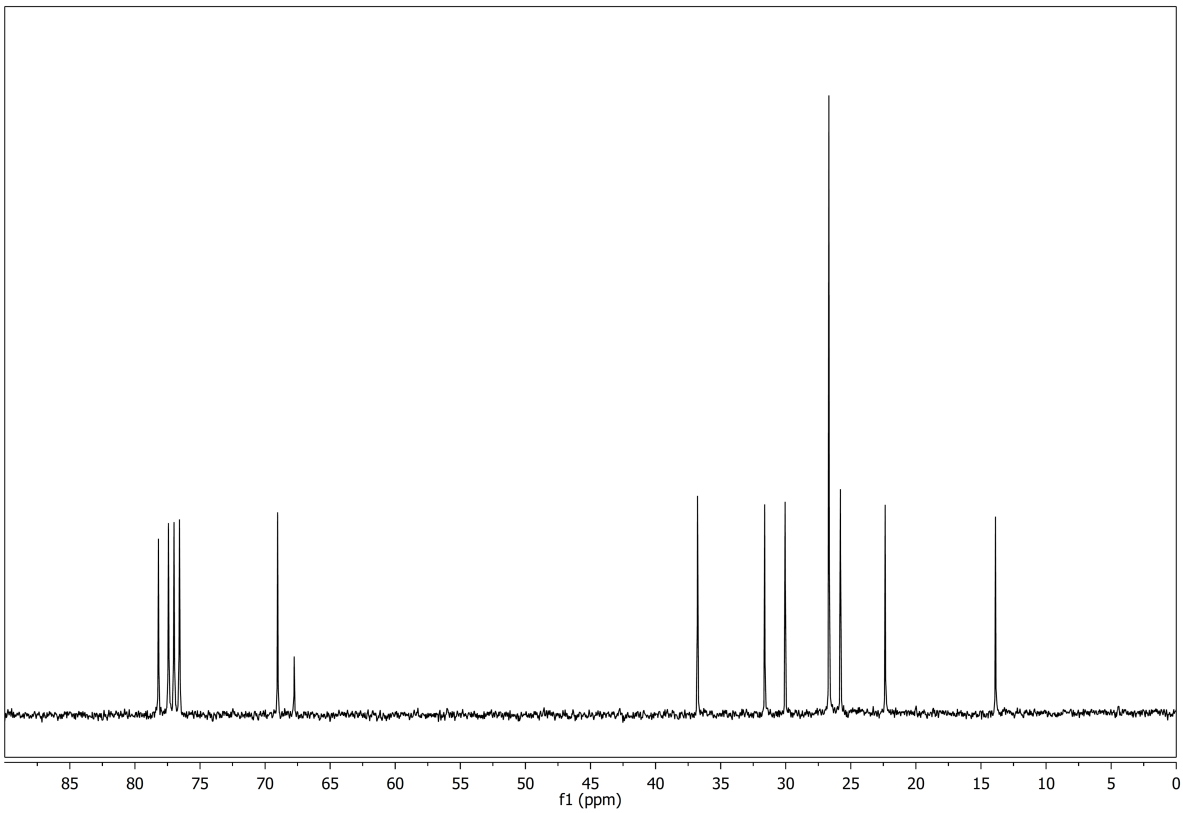
Processed Channel: PDA 209.7 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 209.7 nm	4.648	11325055	62.66	1827345
2	PDA 209.7 nm	5.164	6749155	37.34	1009255

^{1}H NMR ($CDCl_3$, 300 MHz) of **3f**:

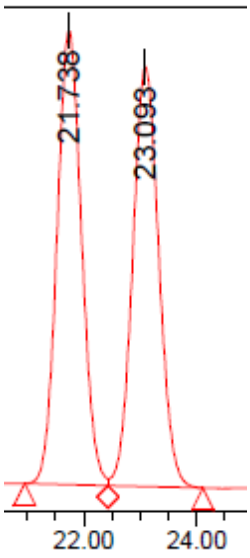


^{13}C NMR ($CDCl_3$, 75 MHz) of **3f**:

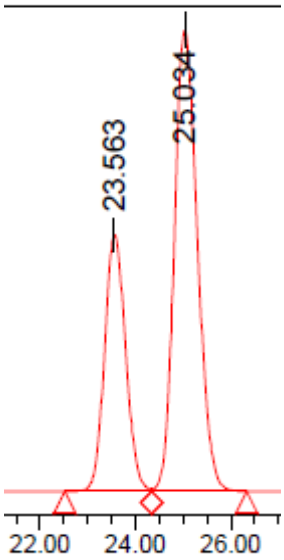


HPLC conditions for **3f**: Chiralpak OD column [hexane/*i*-PrOH (99.5:0.5) 0.25 mL/min]

Racemic



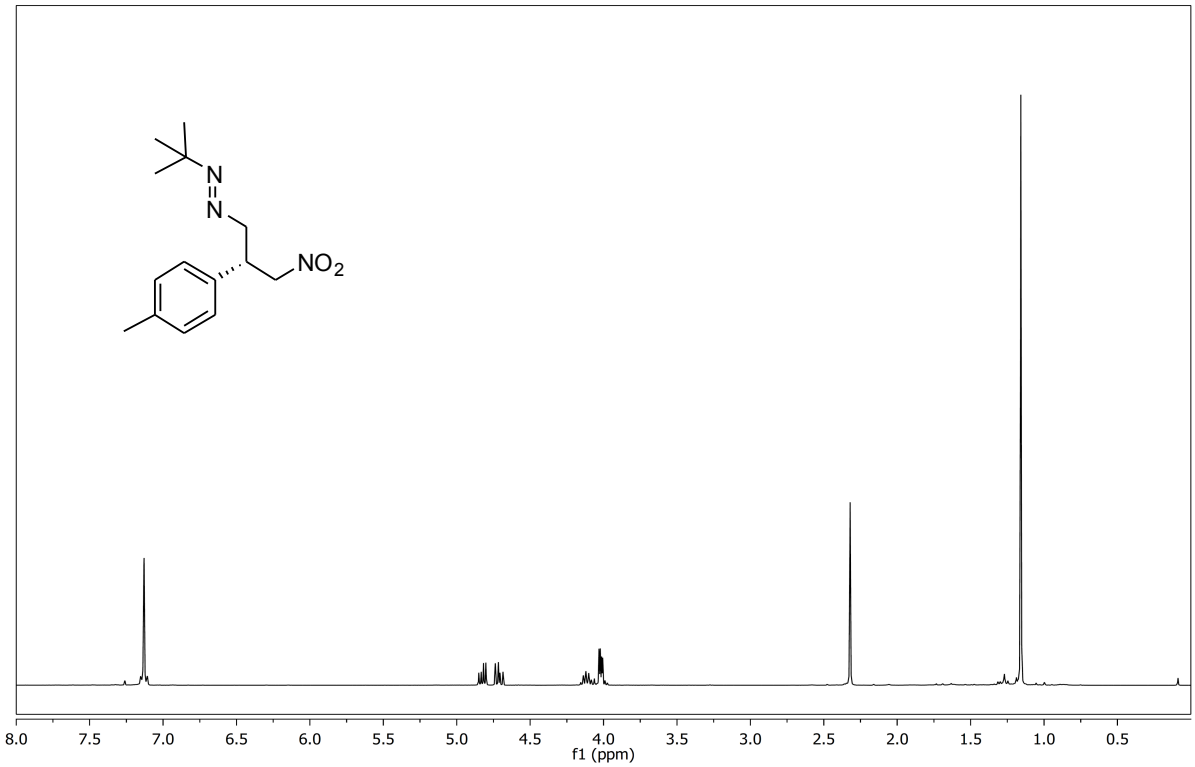
Non Racemic



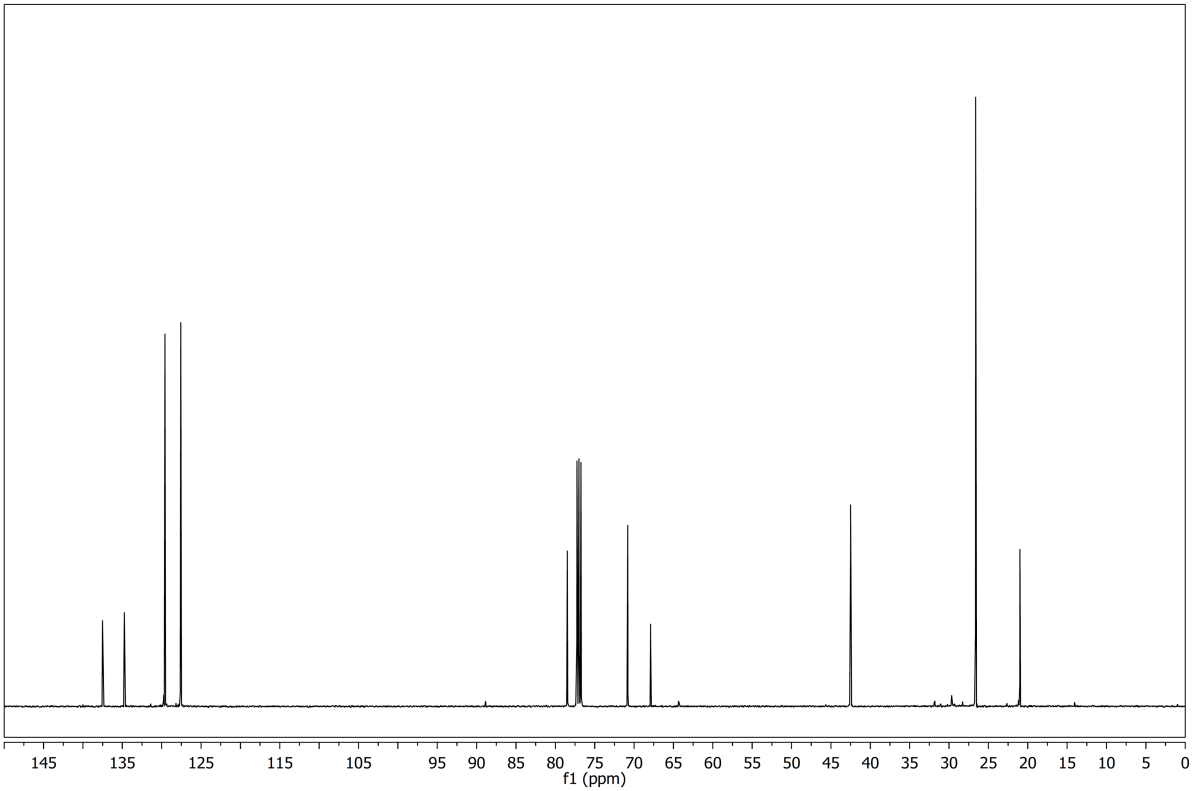
Processed Channel: PDA 209.7 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 209.7 nm	23.563	20257401	33.70	660031
2	PDA 209.7 nm	25.034	39845545	66.30	1187207

^{1}H NMR ($CDCl_3$, 400 MHz) of **3g**:

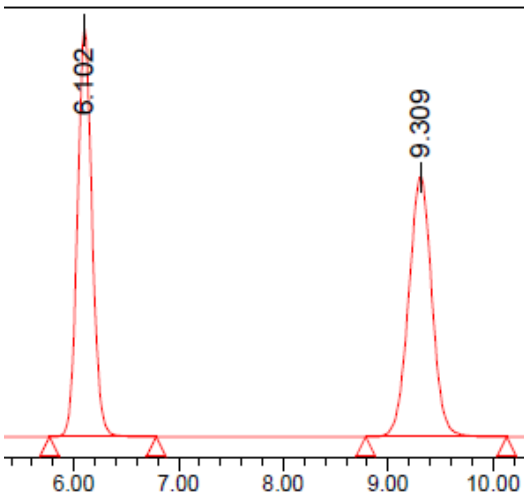


^{13}C NMR ($CDCl_3$, 125 MHz) of **3g**:

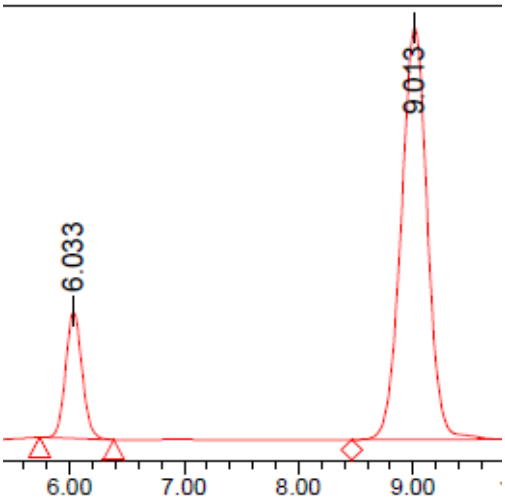


HPLC conditions for **3g**: Chiralpak OD column [hexane/*i*-PrOH (95:5) 1 mL/min]

Racemic



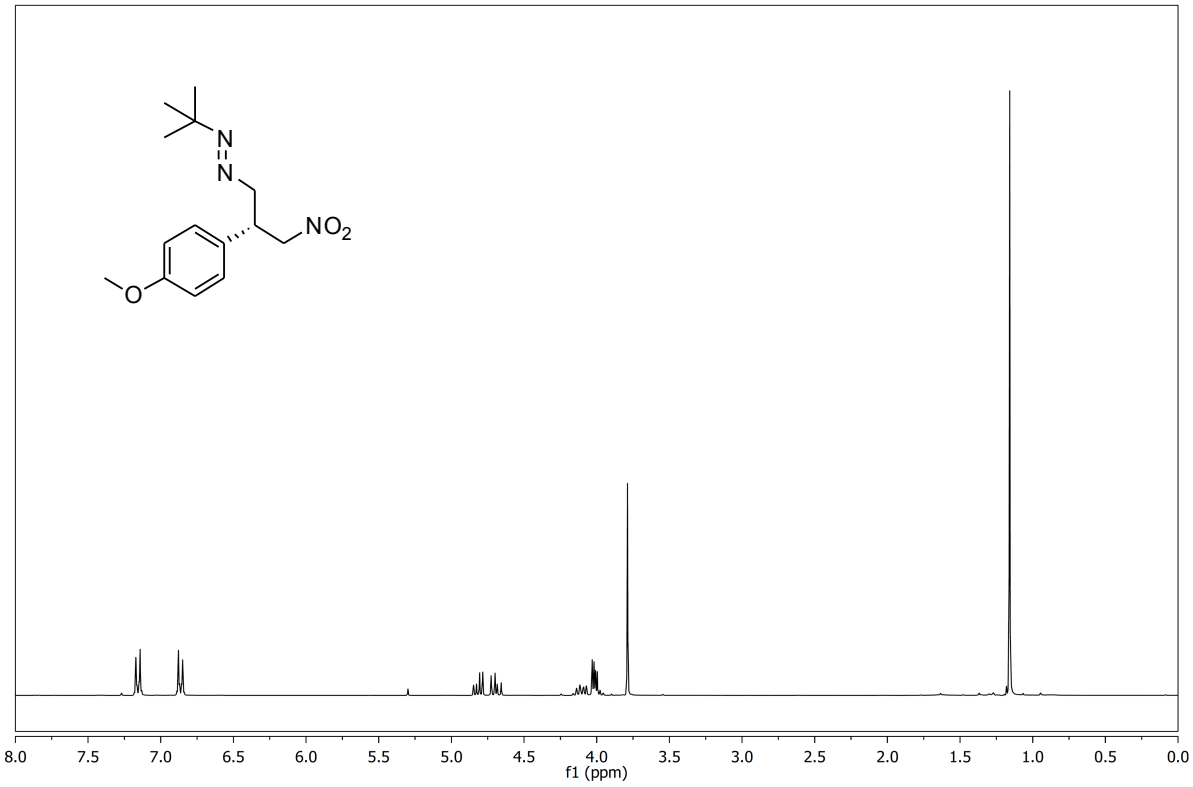
Non Racemic



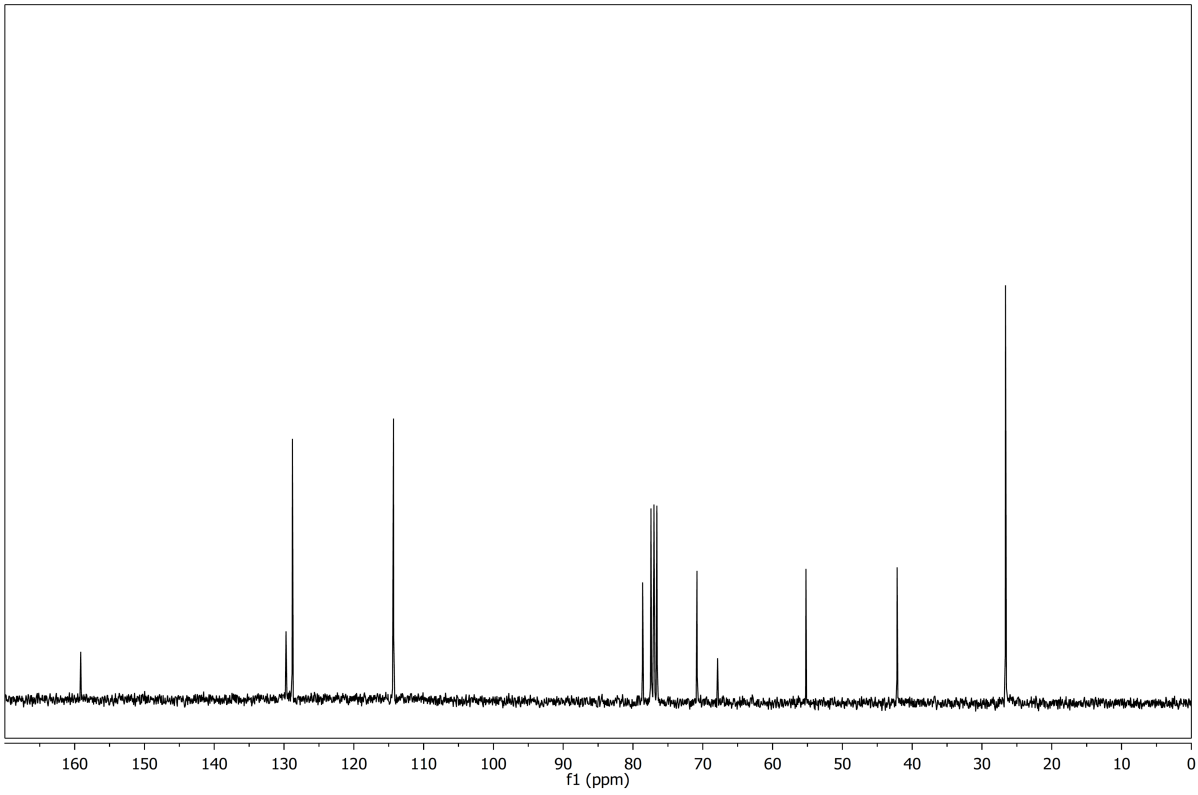
Processed Channel: PDA 209.7 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 209.7 nm	6.033	3115719	16.18	312295
2	PDA 209.7 nm	9.013	16146701	83.82	1017905

^{1}H NMR ($CDCl_3$, 300 MHz) of **3h**:

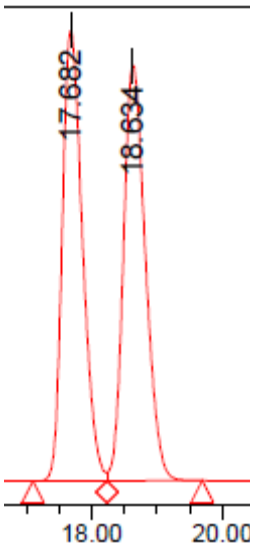


^{13}C NMR ($CDCl_3$, 75 MHz) of **3h**:

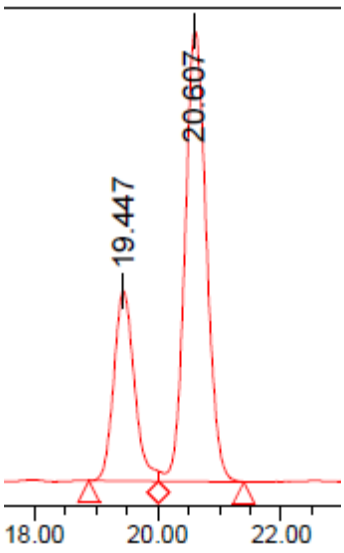


HPLC conditions for **3h**: Chiralpak AD-H column [hexane/*i*-PrOH (98:2) 0.5 mL/min]

Racemic



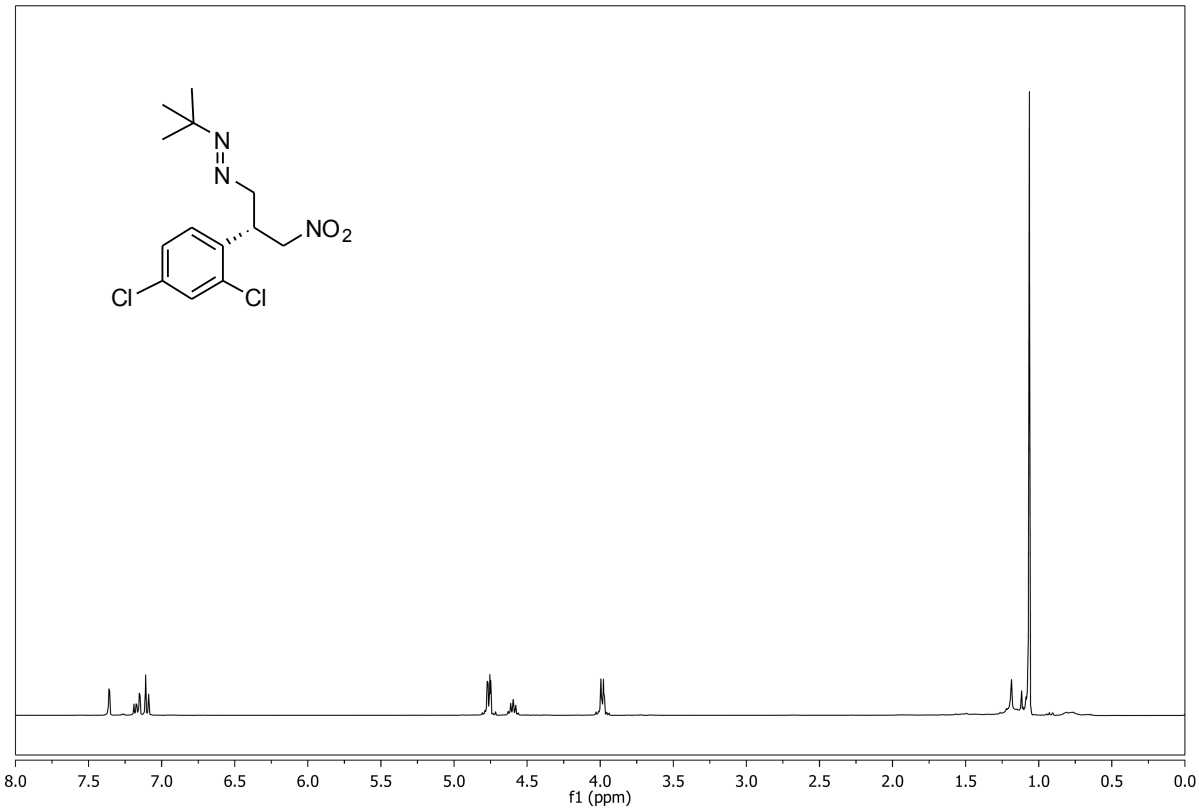
Non Racemic



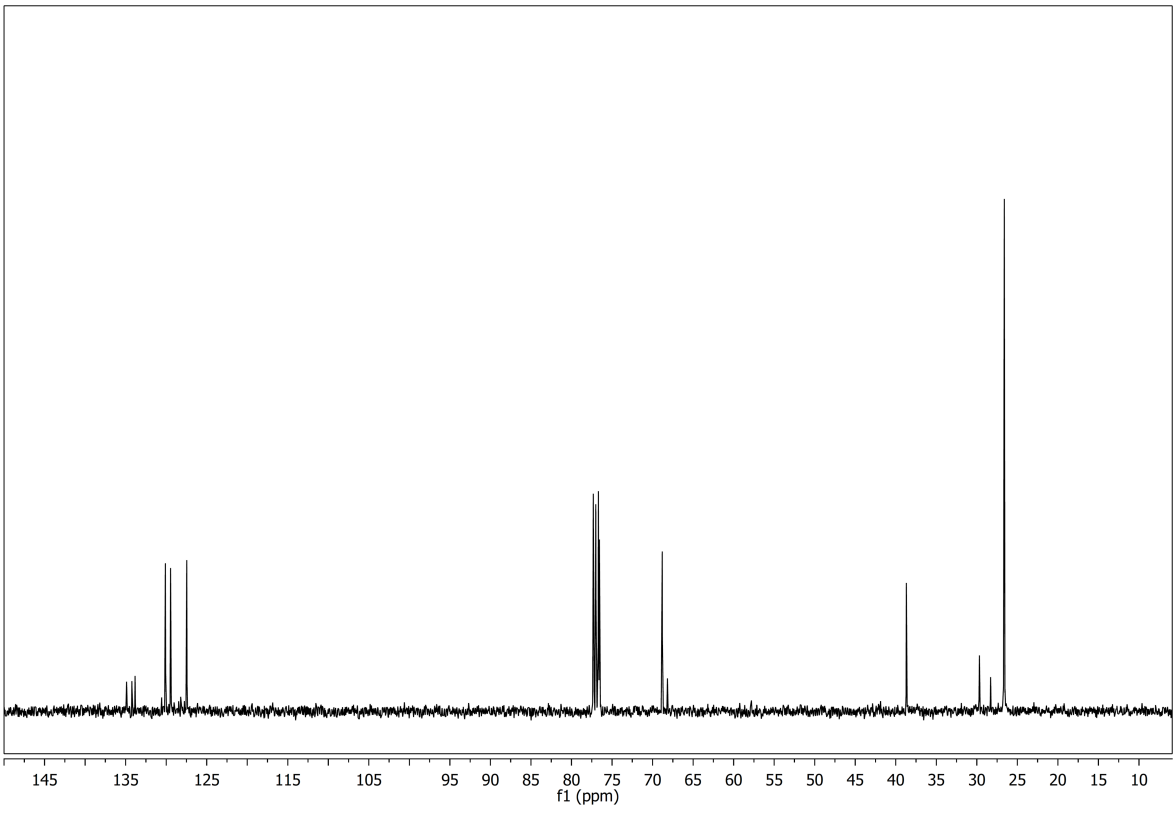
Processed Channel: PDA 209.7 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 209.7 nm	13.873	5950811	23.00	375710
2	PDA 209.7 nm	19.456	19925543	77.00	808920

^{1}H NMR ($CDCl_3$, 300 MHz) of **3i**:

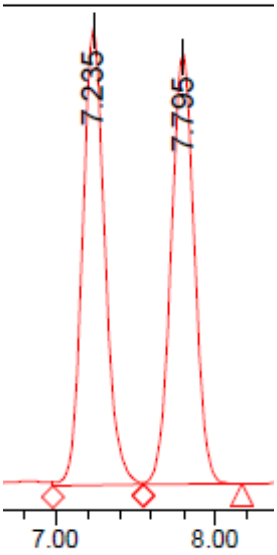


^{13}C NMR ($CDCl_3$, 100 MHz) of **3i**:

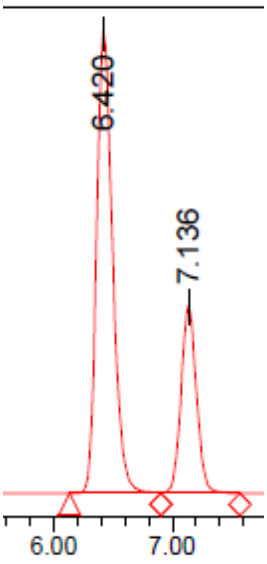


HPLC conditions for **3i**: Chiralpak AD-H column [hexane/*i*-PrOH (98:2) 1 mL/min]

Racemic



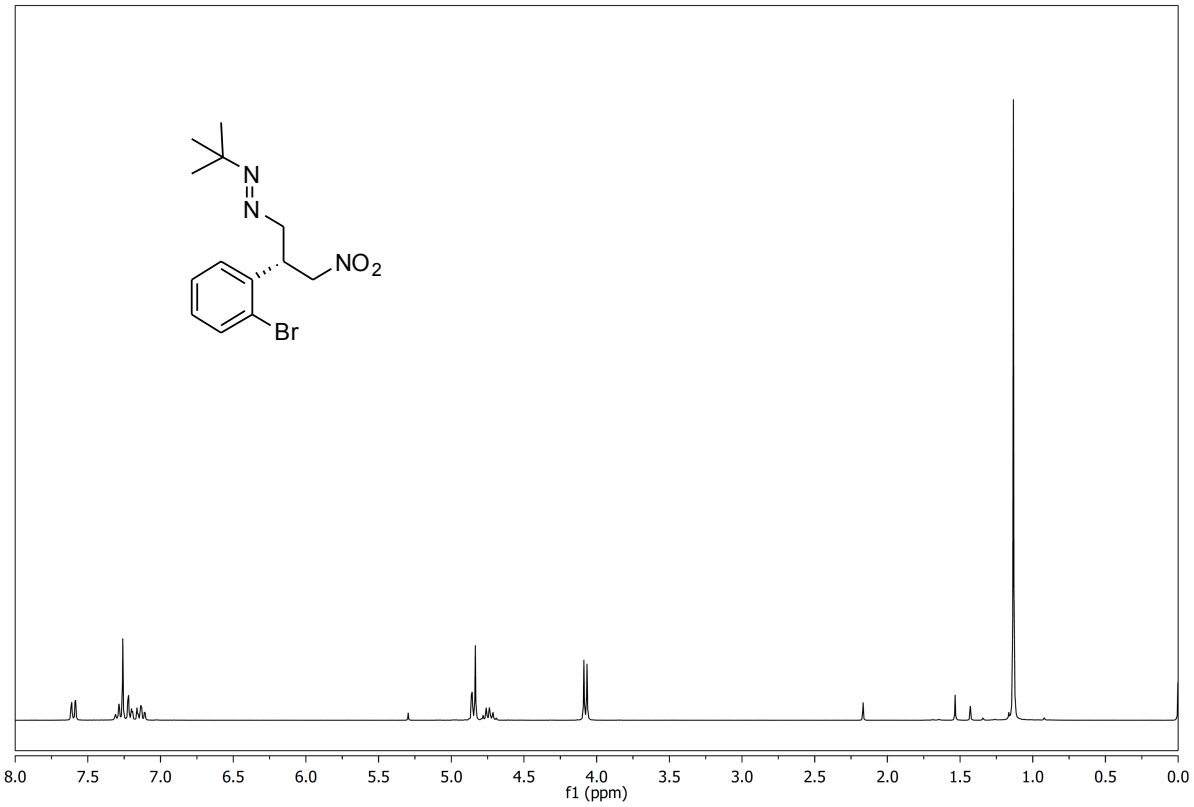
Non Racemic



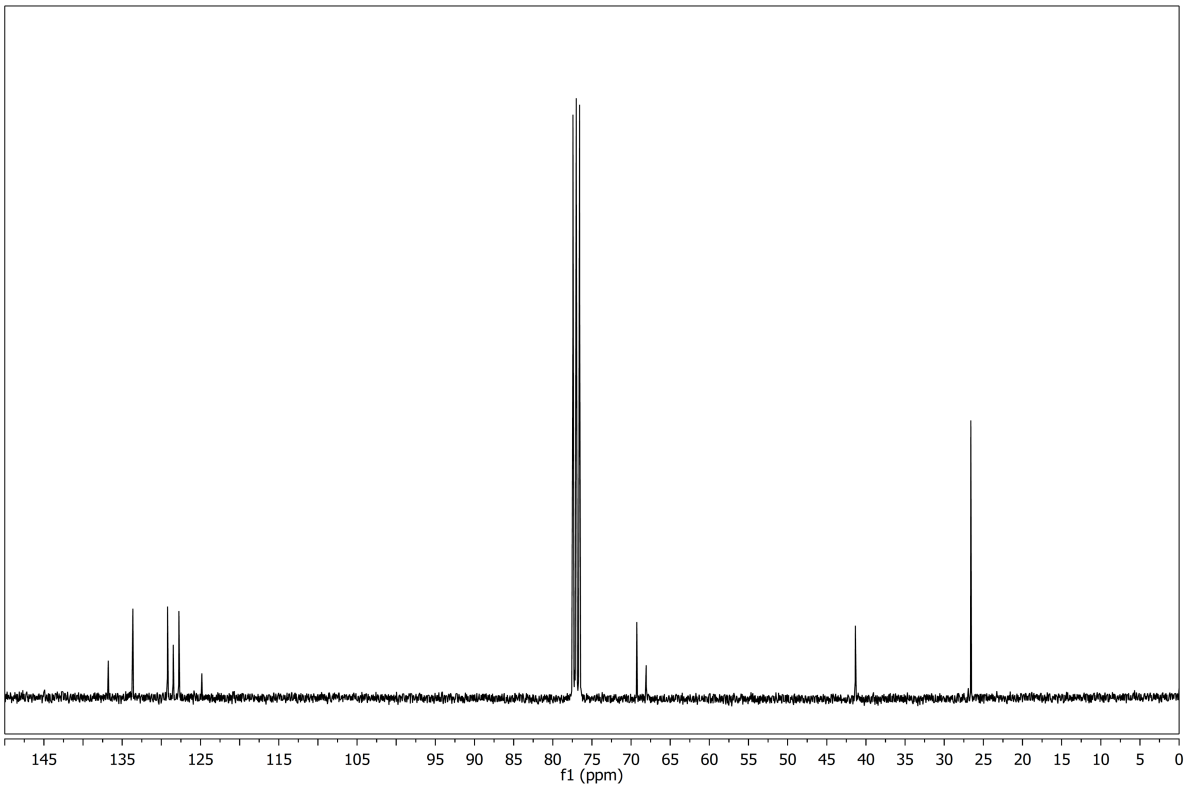
Processed Channel: PDA 209.7 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 209.7 nm	6.420	12353519	71.81	1315259
2	PDA 209.7 nm	7.136	4849023	28.19	531931

^{1}H NMR ($CDCl_3$, 300 MHz) of **3j**:

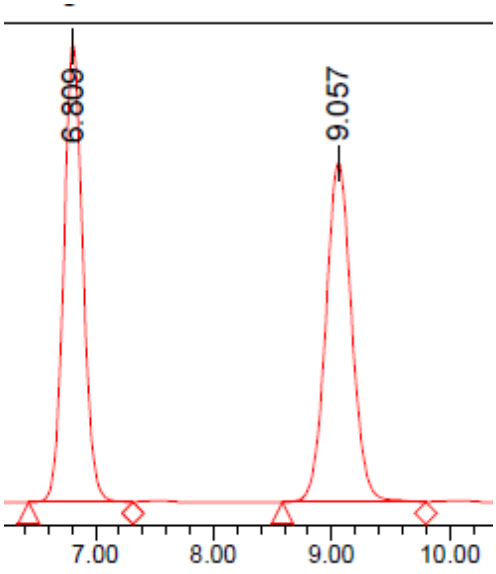


^{13}C NMR ($CDCl_3$, 75 MHz) of **3j**:

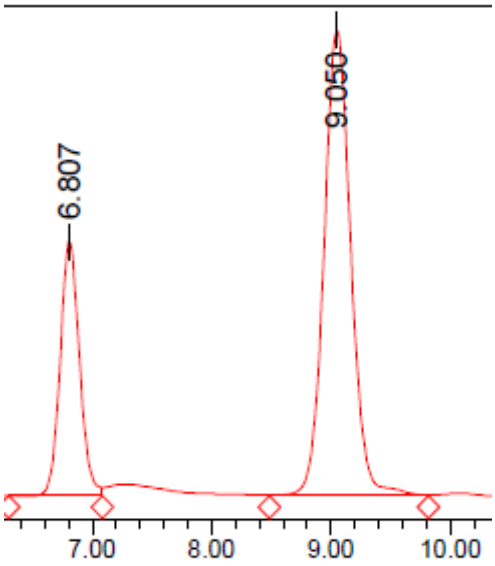


HPLC conditions for **3j**: Chiralpak OD column [hexane/*i*-PrOH (95:5) 1 mL/min]

Racemic



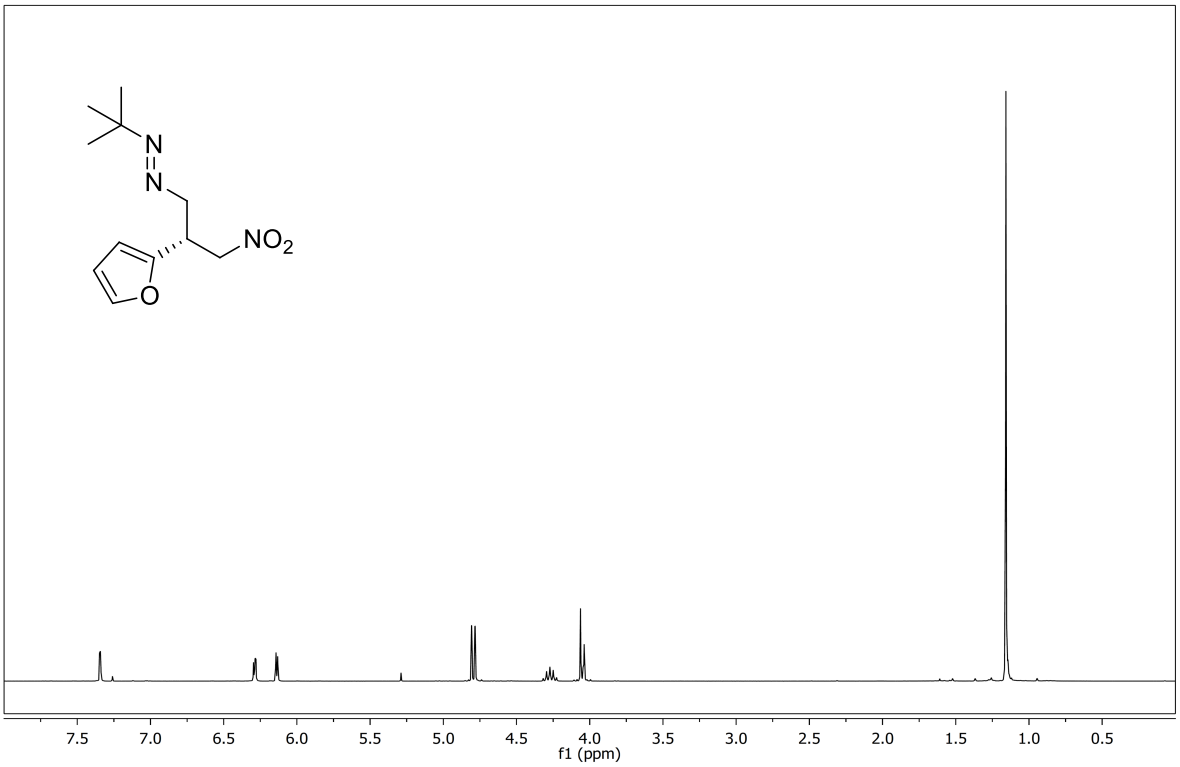
Non Racemic



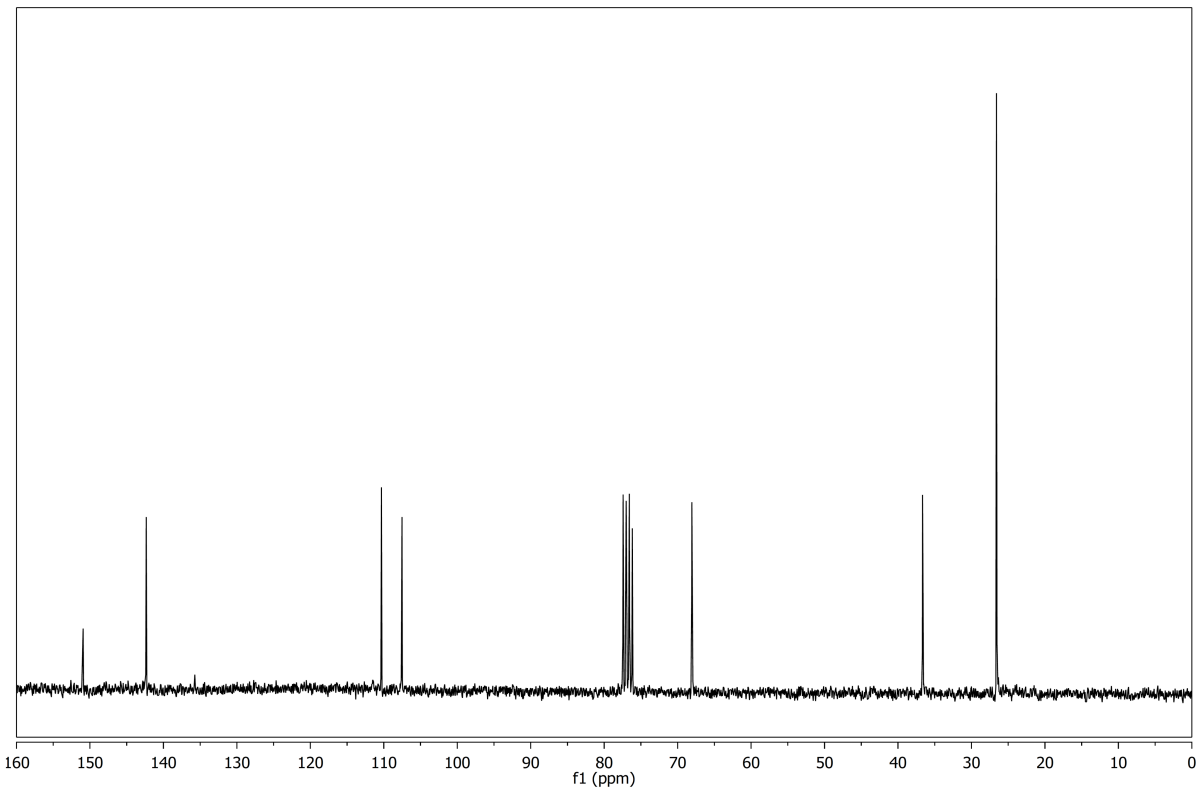
Processed Channel: PDA 209.7 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 209.7 nm	6.807	9621858	28.29	853901
2	PDA 209.7 nm	9.050	24395011	71.71	1557039

^{1}H NMR ($CDCl_3$, 300 MHz) of **3k**:

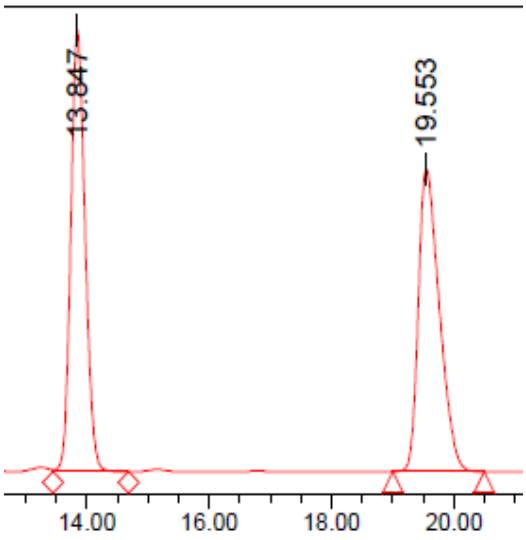


^{13}C NMR ($CDCl_3$, 100 MHz) of **3k**:

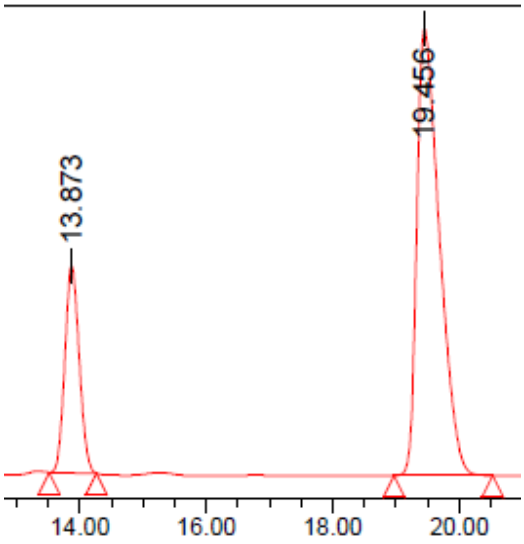


HPLC conditions for **3k**: Chiralpak AD-H column [hexane/*i*-PrOH (98:2) 0.5 mL/min]

Racemic



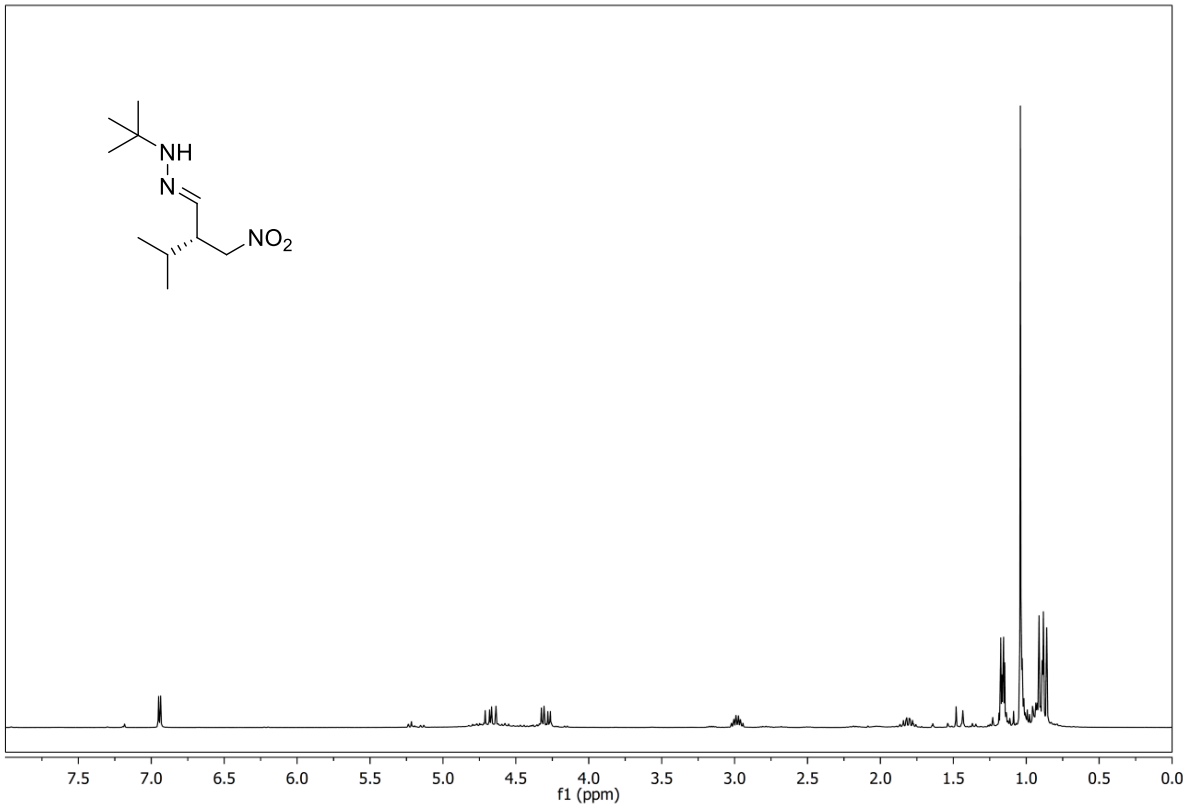
Non Racemic



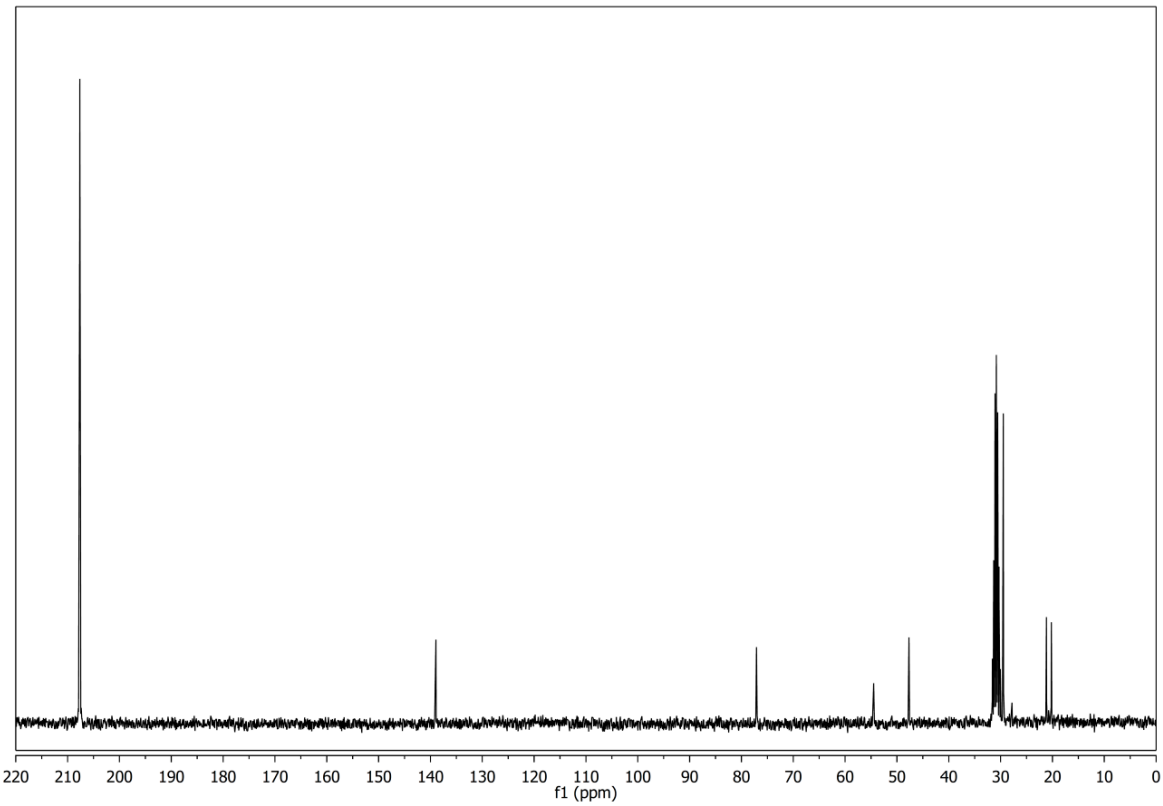
Processed Channel: PDA 209.7 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 209.7 nm	13.873	5950811	23.00	375710
2	PDA 209.7 nm	19.456	19925543	77.00	808920

^{1}H NMR ($CDCl_3$, 300 MHz) of **5a**:

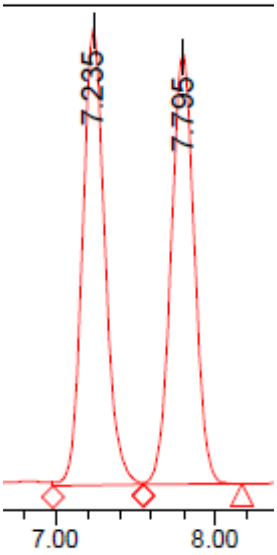


^{13}C NMR [$(CD_3)_2CO$, 75 MHz] of **5a**:

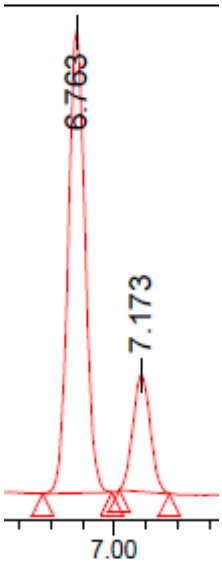


HPLC conditions for **5a**: Chiralpak AD-H column [hexane/*i*-PrOH (98:2) 1 mL/min]

Racemic



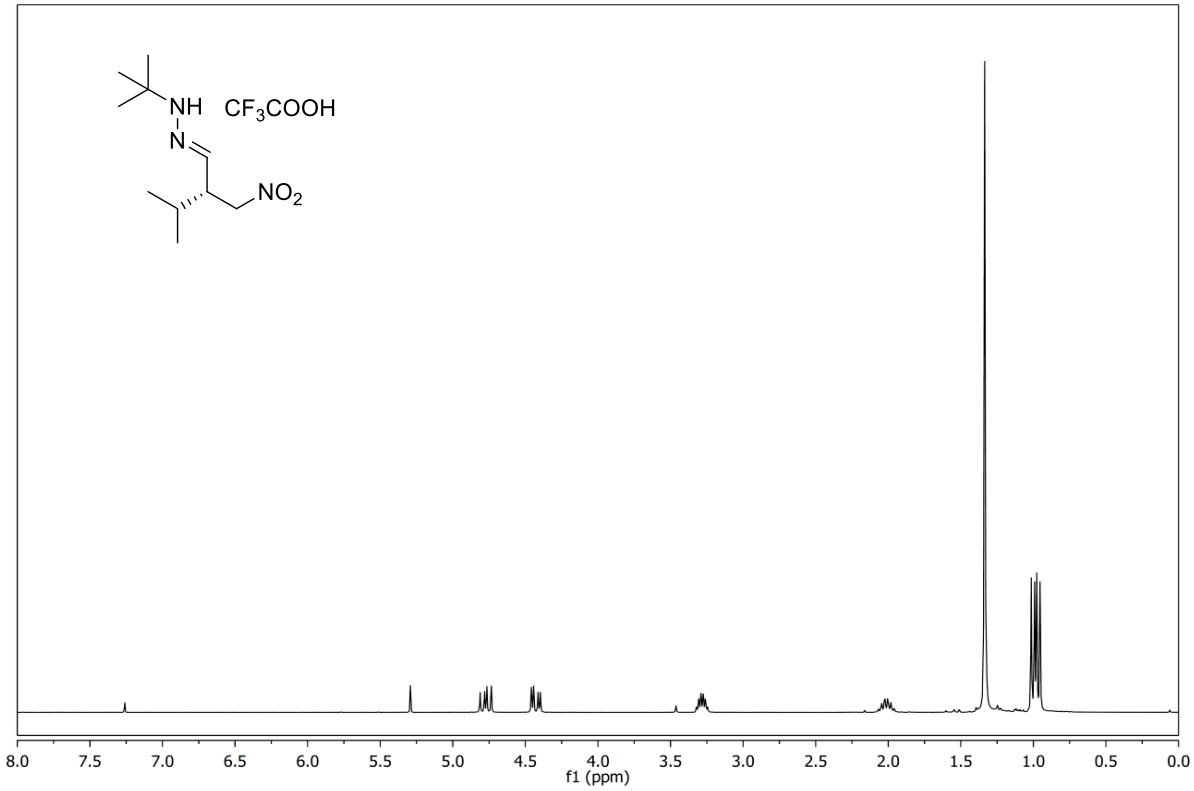
Non Racemic



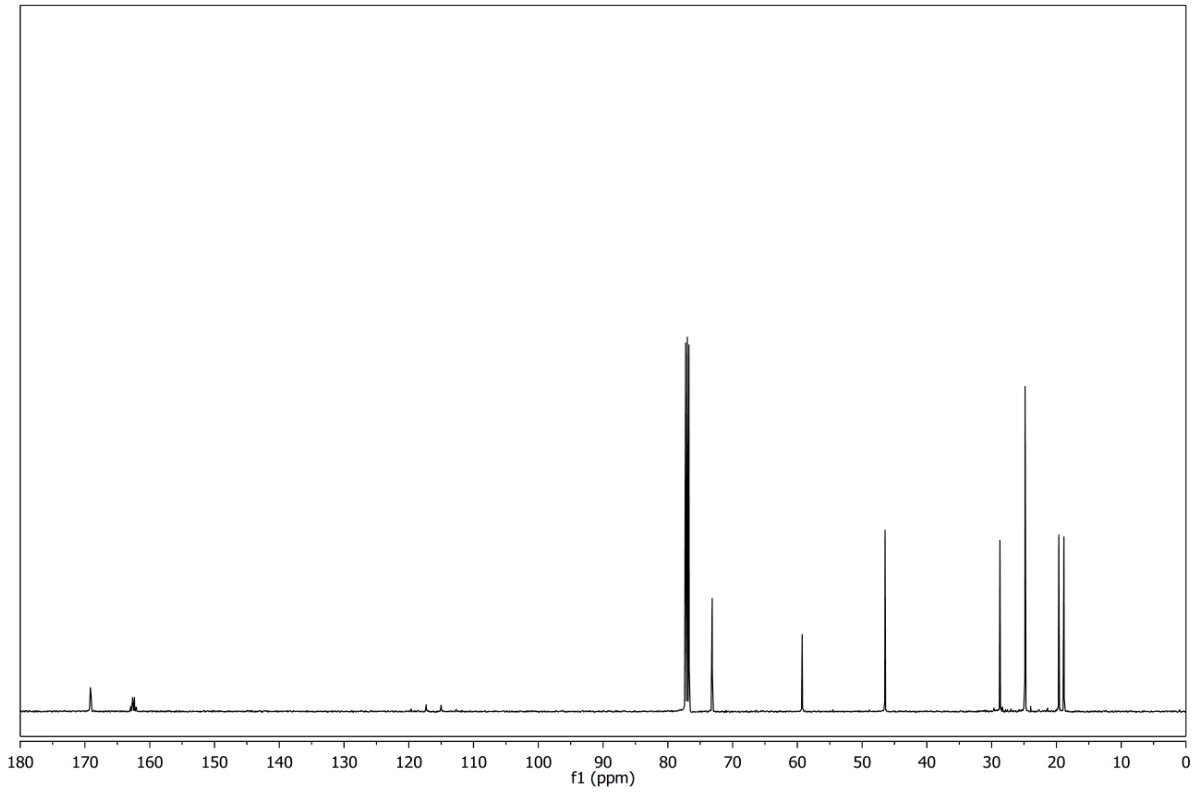
Processed Channel: PDA 245.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 245.0 nm	6.763	317275	79.50	42882
2	PDA 245.0 nm	7.173	81814	20.50	10841

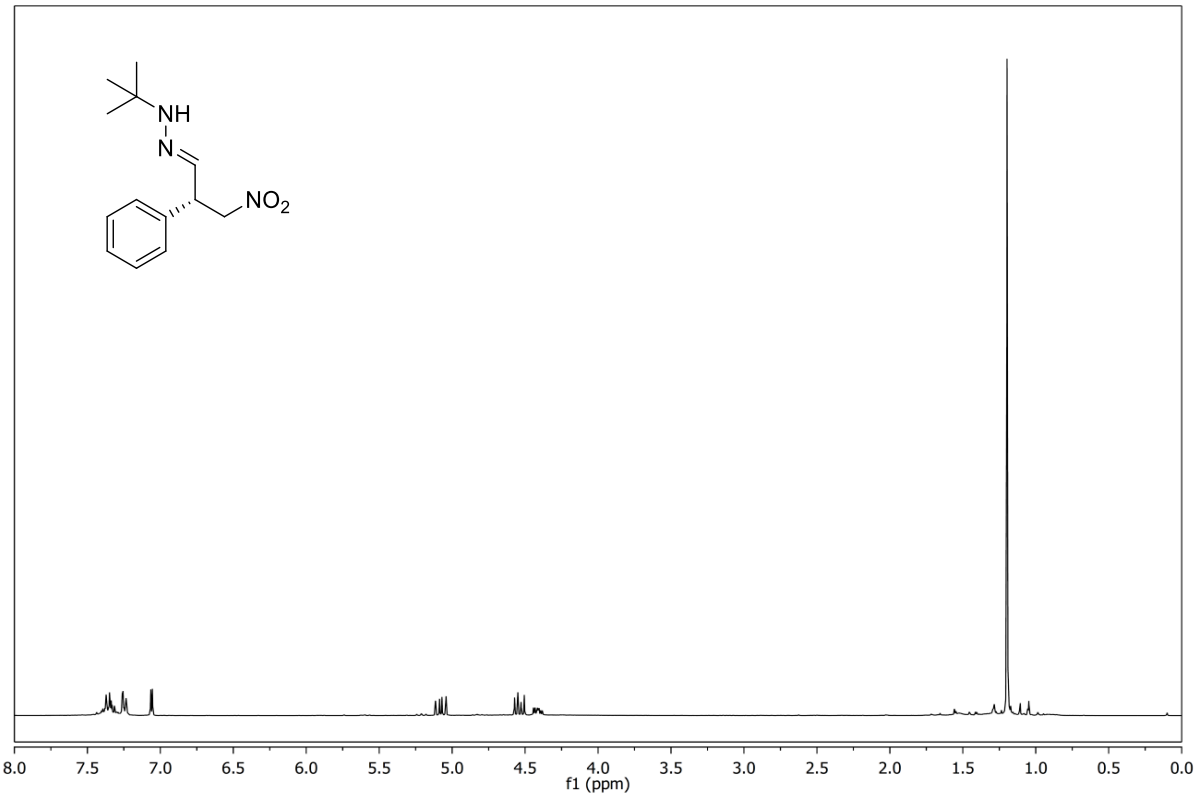
^{1}H NMR ($CDCl_3$, 300 MHz) of **5a-TFA**:



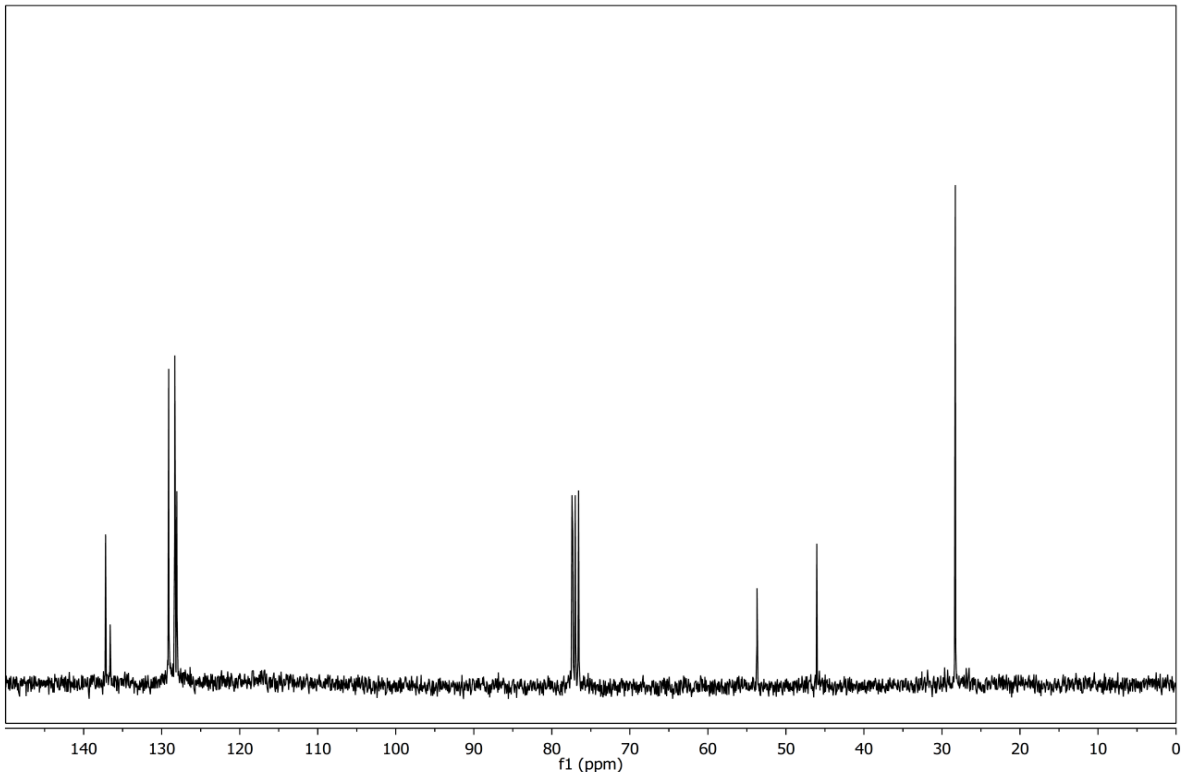
^{13}C NMR ($CDCl_3$, 100 MHz) of **5a-TFA**:



^{1}H NMR ($CDCl_3$, 300 MHz) of **5b**:

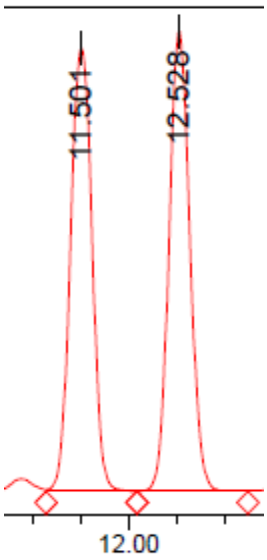


^{13}C NMR ($CDCl_3$, 75 MHz) of **5b**:

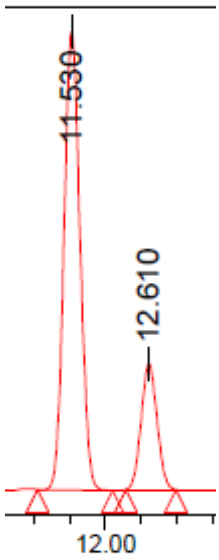


HPLC conditions for **5b**: Chiralpak AD-H column [hexane/*i*-PrOH (98:2) 1 mL/min]

Racemic



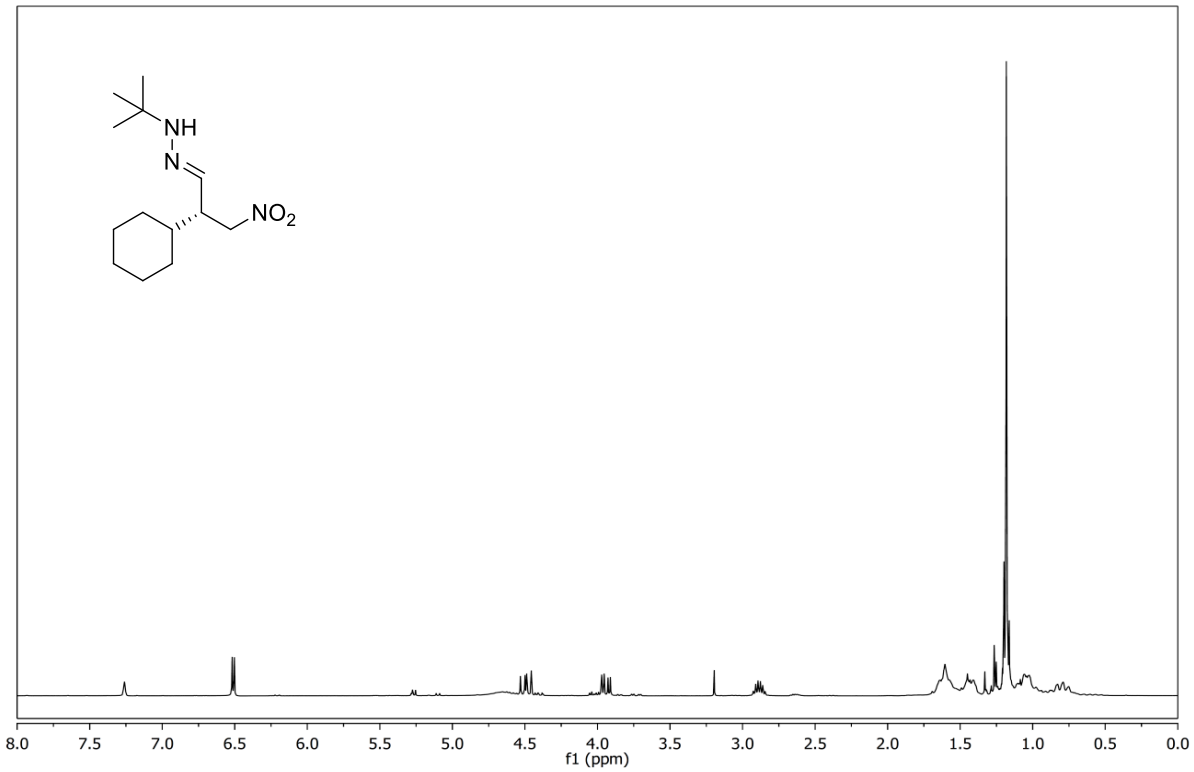
Non Racemic



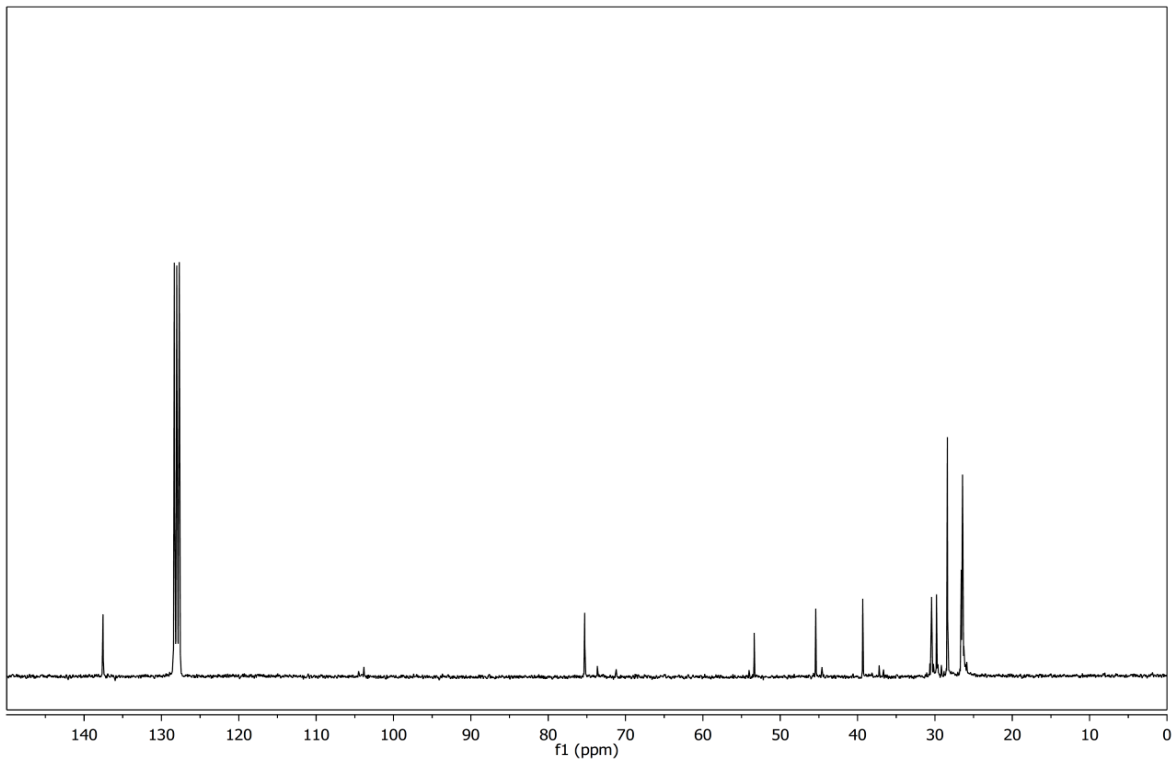
Processed Channel: PDA 246.2 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 246.2 nm	11.530	8881432	78.54	570873
2	PDA 246.2 nm	12.610	2427436	21.46	156422

^{1}H NMR (C_6D_6, 300 MHz) of **5c**:

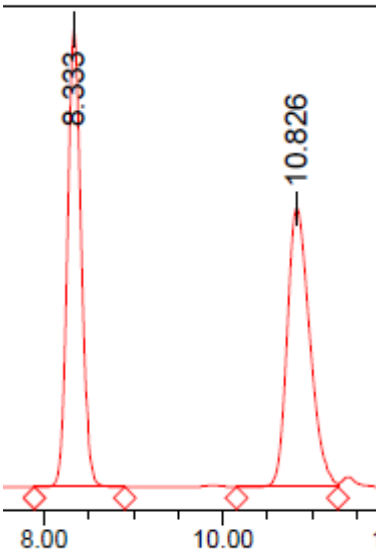


^{13}C NMR (C_6D_6, 75 MHz) of **5c**:

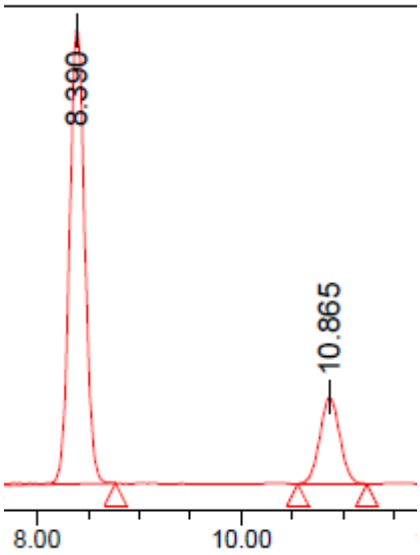


HPLC conditions for **5c**: Chiralpak AD-H column [hexane/*i*-PrOH (98:2) 1 mL/min]

Racemic



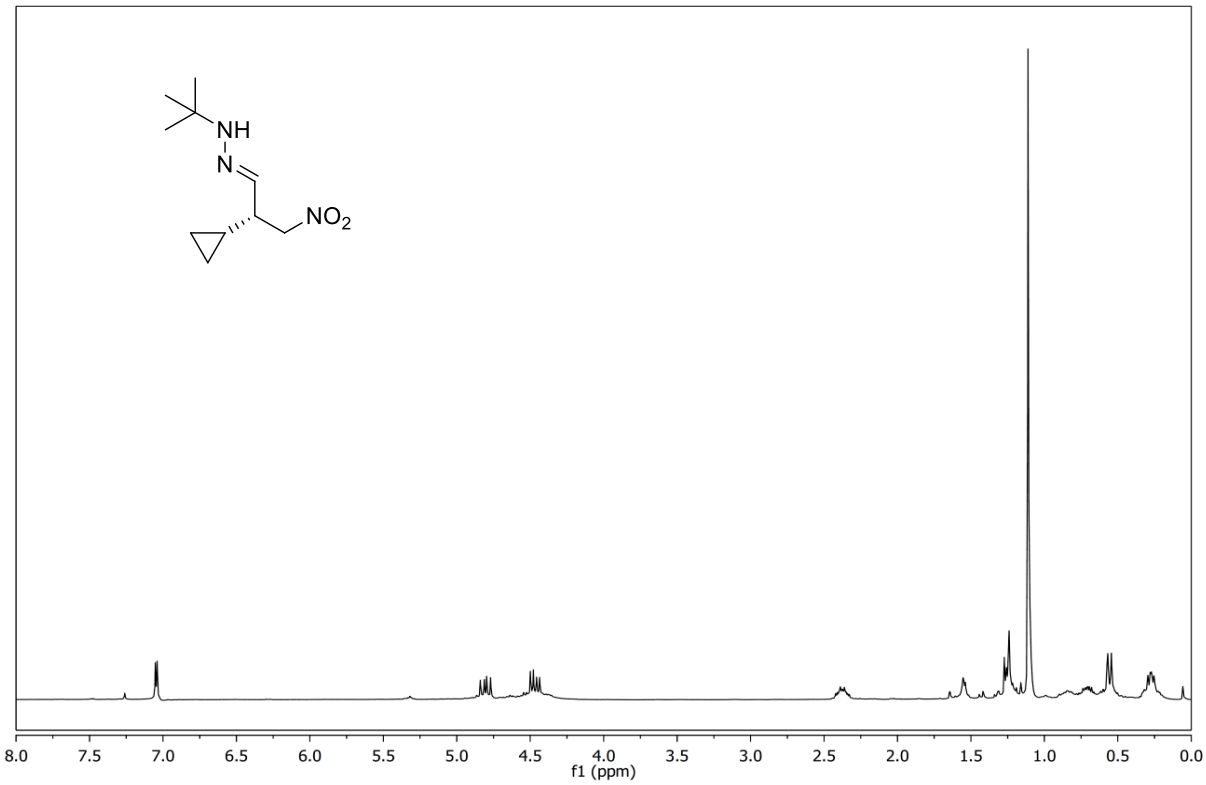
Non Racemic



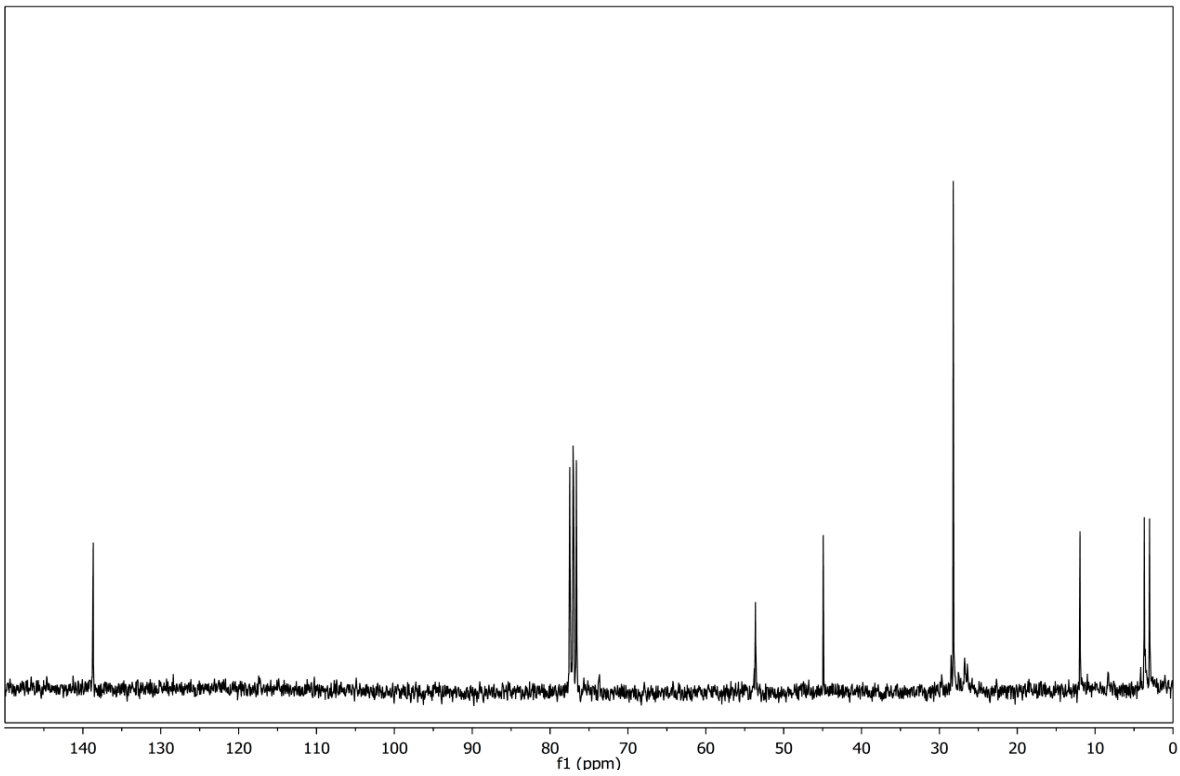
Processed Channel: PDA 245.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 245.0 nm	8.390	1055962	80.18	101840
2	PDA 245.0 nm	10.865	260992	19.82	19290

^{1}H NMR ($CDCl_3$, 300 MHz) of **5d**:

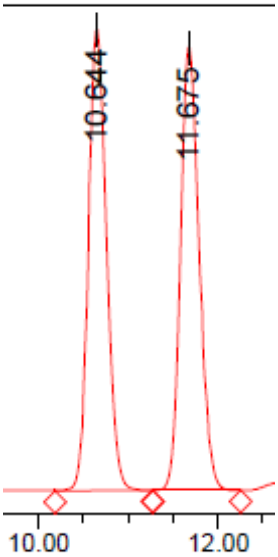


^{13}C NMR ($CDCl_3$, 75 MHz) of **5d**:

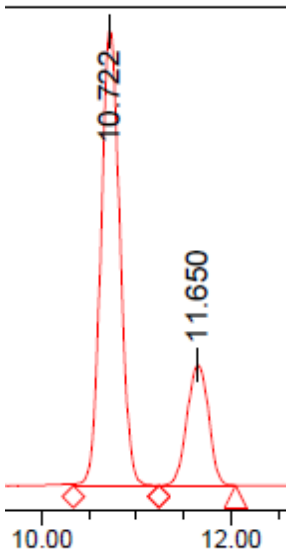


HPLC conditions for **5d**: Chiralpak AD-H column [hexane/*i*-PrOH (98:2) 1 mL/min]

Racemic



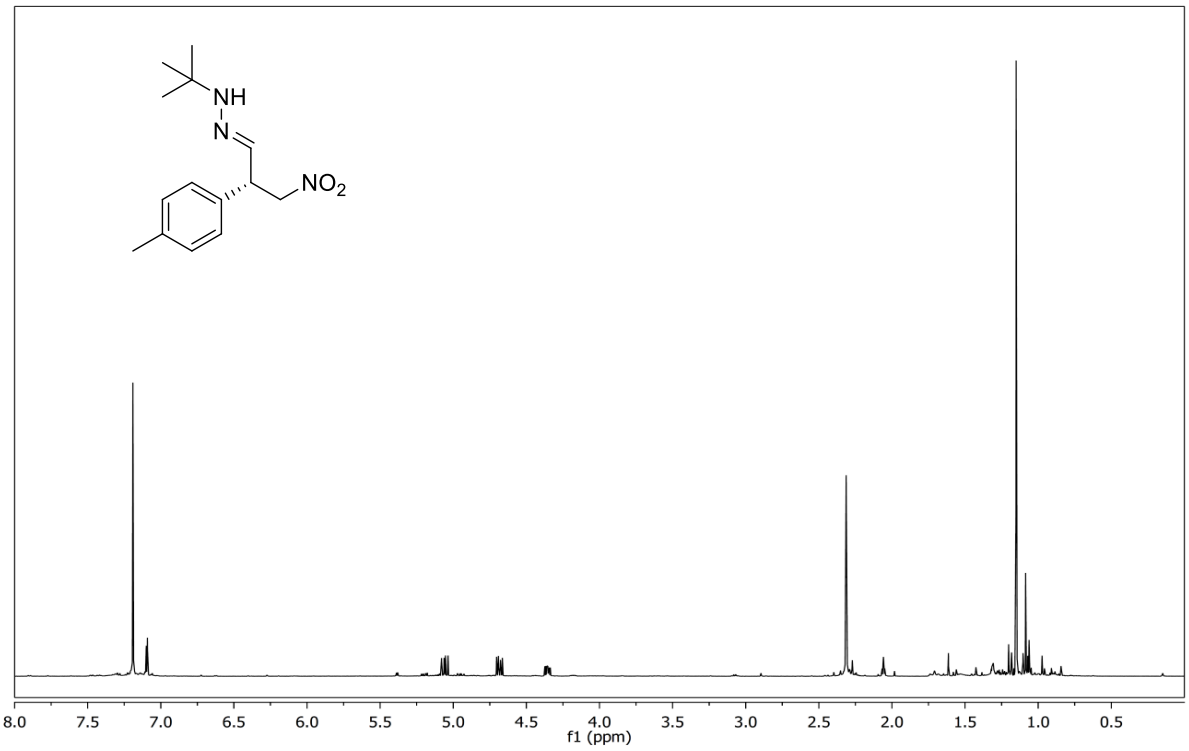
Non Racemic



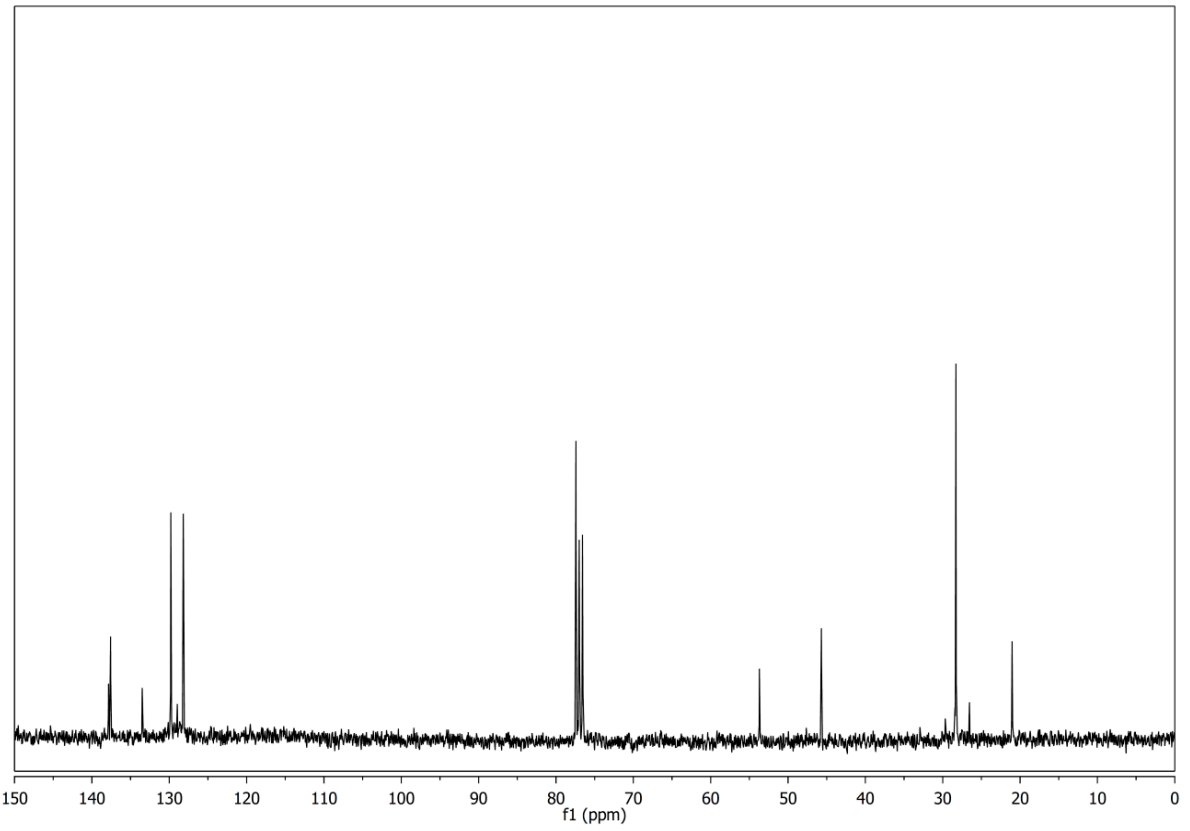
Processed Channel: PDA 245.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 245.0 nm	10.722	5974289	76.85	430776
2	PDA 245.0 nm	11.650	1799245	23.15	113563

^{1}H NMR [$(CD_3)_2CO$, 500 MHz] of **5e**:

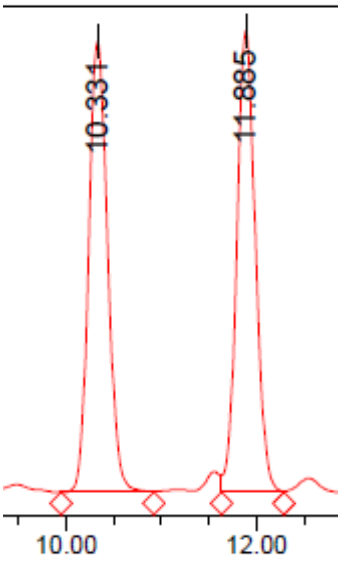


^{13}C NMR ($CDCl_3$, 75 MHz) of **5e**:

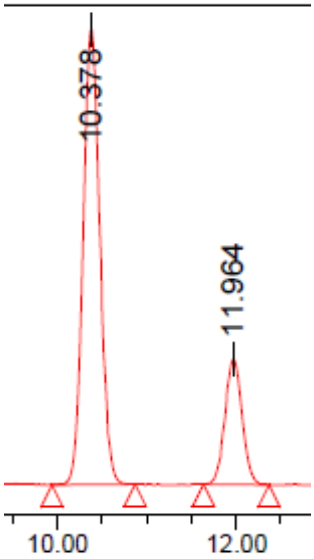


HPLC conditions for **5e**: Chiralpak AD-H column [hexane/*i*-PrOH (98:2) 1 mL/min]

Racemic



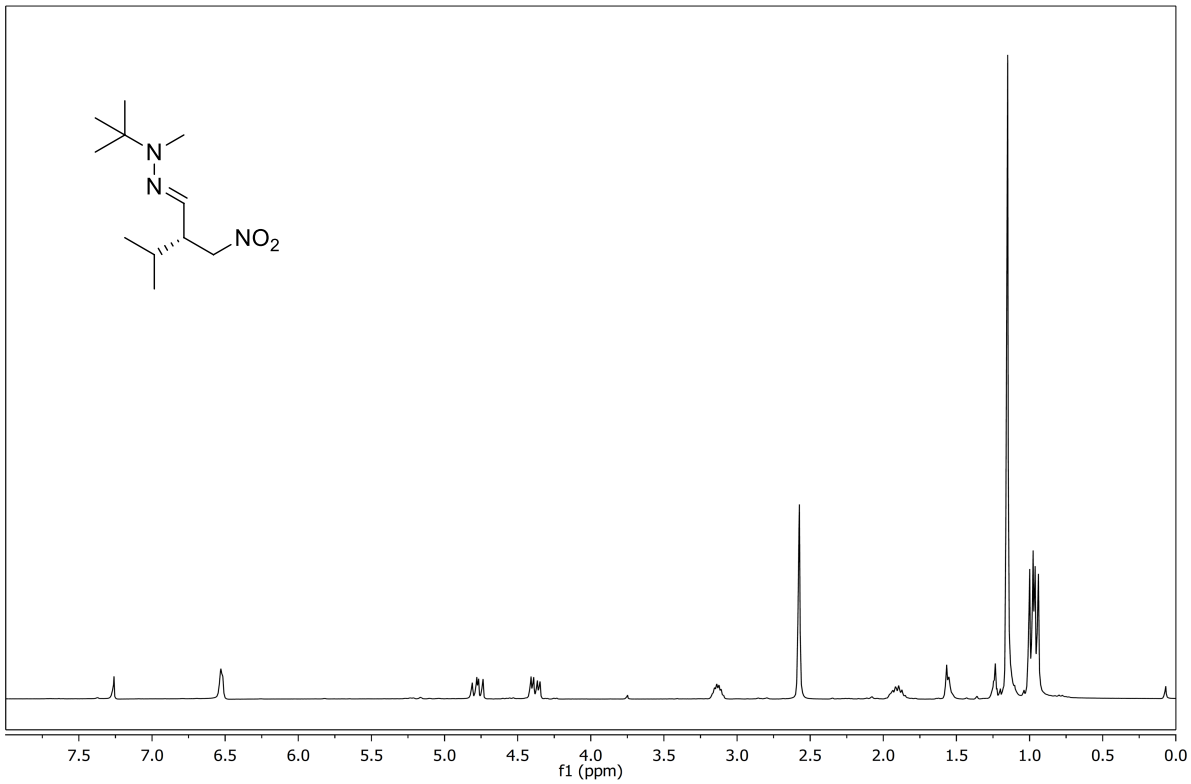
Non Racemic



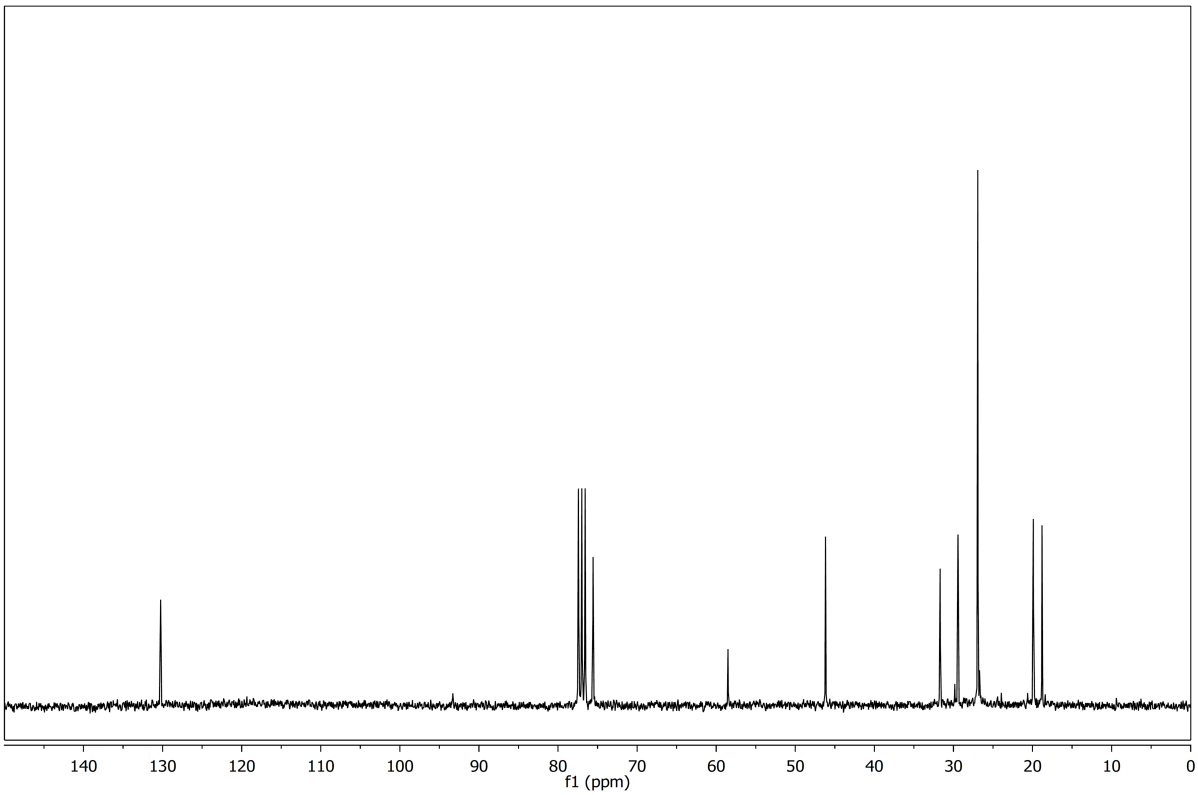
Processed Channel: PDA 246.2 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 246.2 nm	10.378	899709	77.99	69330
2	PDA 246.2 nm	11.964	253878	22.01	19119

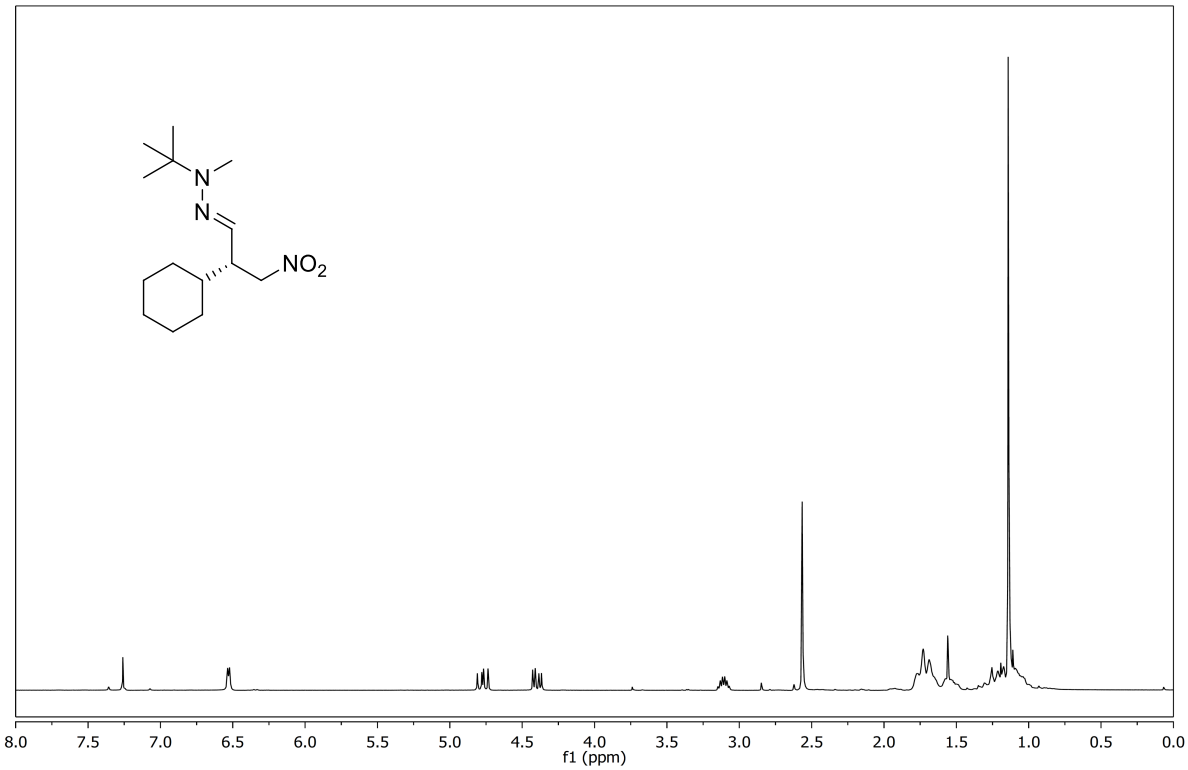
^{1}H NMR ($CDCl_3$, 300 MHz) of **6a**:



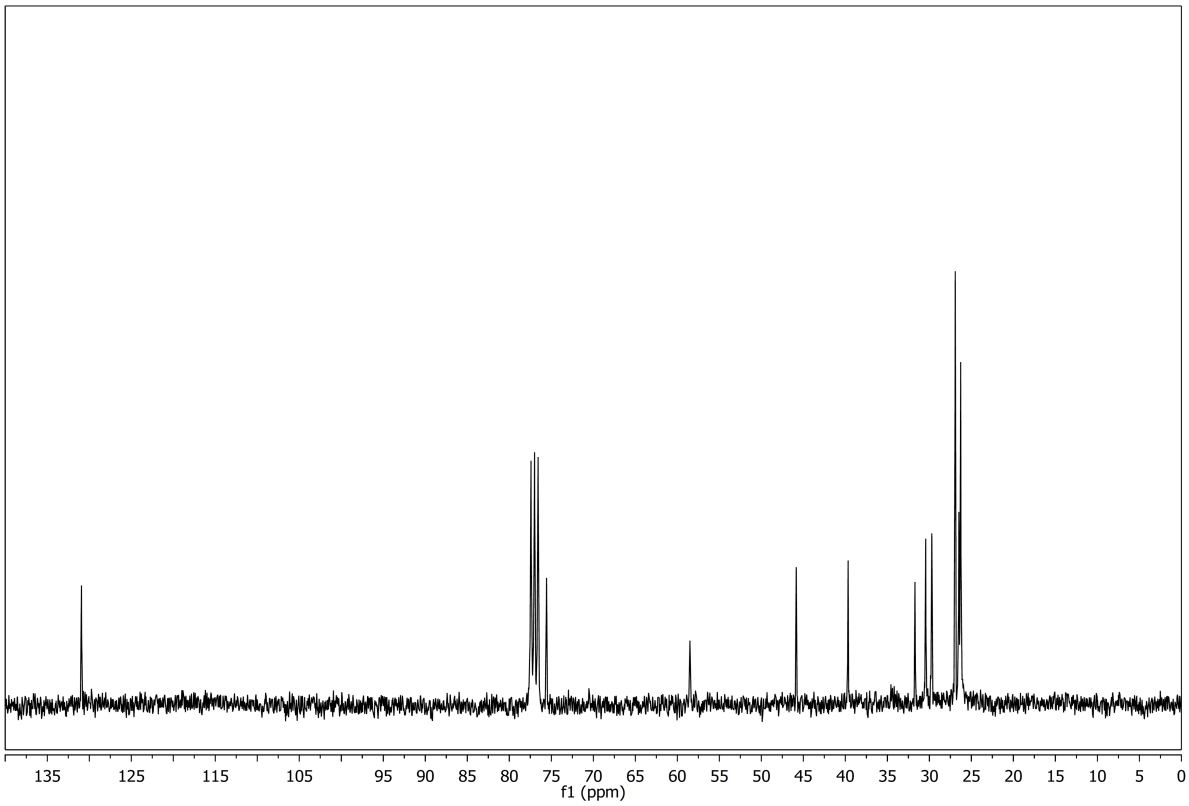
^{13}C NMR ($CDCl_3$, 75 MHz) of **6a**:



^{1}H NMR ($CDCl_3$, 300 MHz) of **6b**:



^{13}C NMR ($CDCl_3$, 75 MHz) of **6b**:

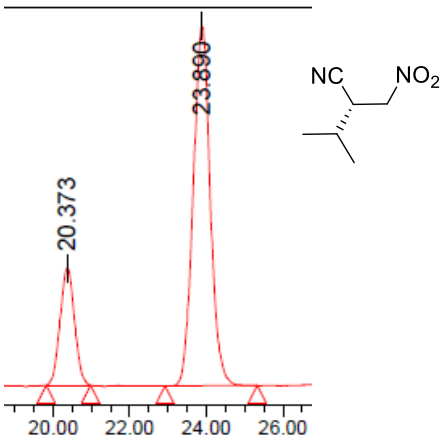


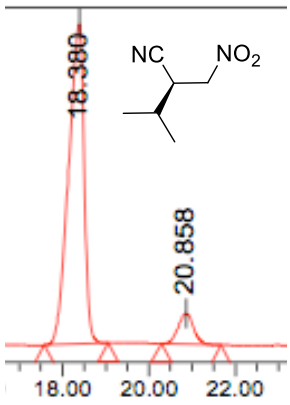
Absolute configuration determination

The absolute configurations of **7a,b** were assigned to be *S* by comparison of their HPLC retention times with those of *ent*-**7a,b** previously described in our group.[6]

(*S*)-3-Methyl-2-(nitromethyl)butanenitrile (7a)

HPLC using a Chiralpak AD-H column [hexane/*i*-PrOH (98:2)]; flow rate 1.0 mL/min





Previously reported

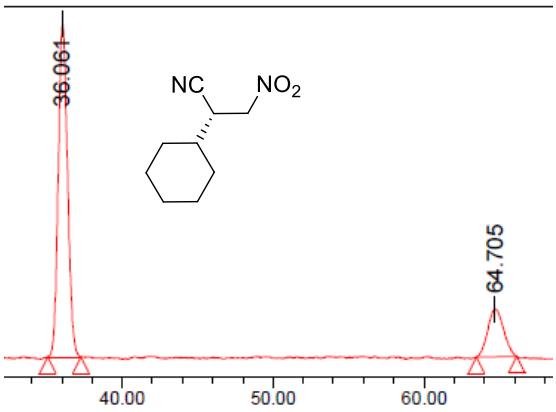
Processed Channel: PDA 209.7 nm

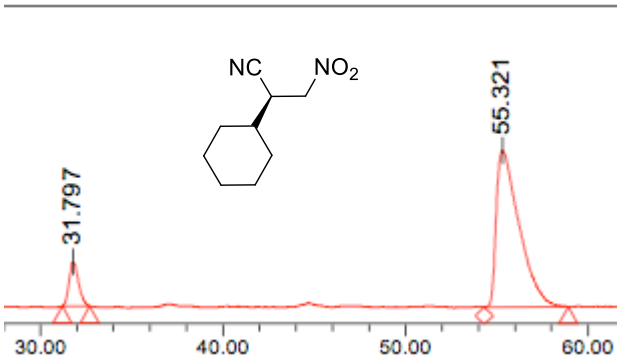
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 209.7 nm	20.373	1999199	21.62	76049
2	PDA 209.7 nm	23.890	7246211	78.38	234075

[6] P. Bernal, R. Fernández, J. M. Lassaletta, *Chem. Eur. J.* 2010, **16**, 7714.

(*S*)-2-Cyclohexyl-3-nitropropanenitrile (7b)

HPLC using a Chiralpak AD-H column [hexane/*i*-PrOH (98:2)]; flow rate 1.0 mL/min





Previously reported

Processed Channel: PDA 209.7 nm

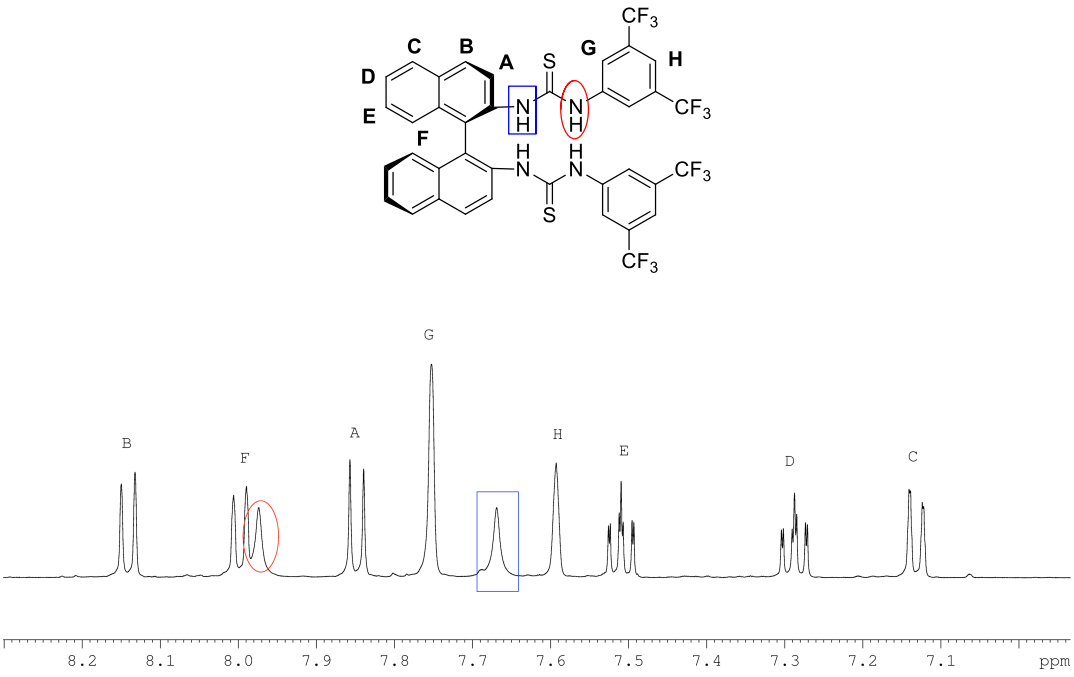
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 209.7 nm	36.061	3687030	80.18	86441
2	PDA 209.7 nm	64.705	911355	19.82	12395

NMR data collection and processing

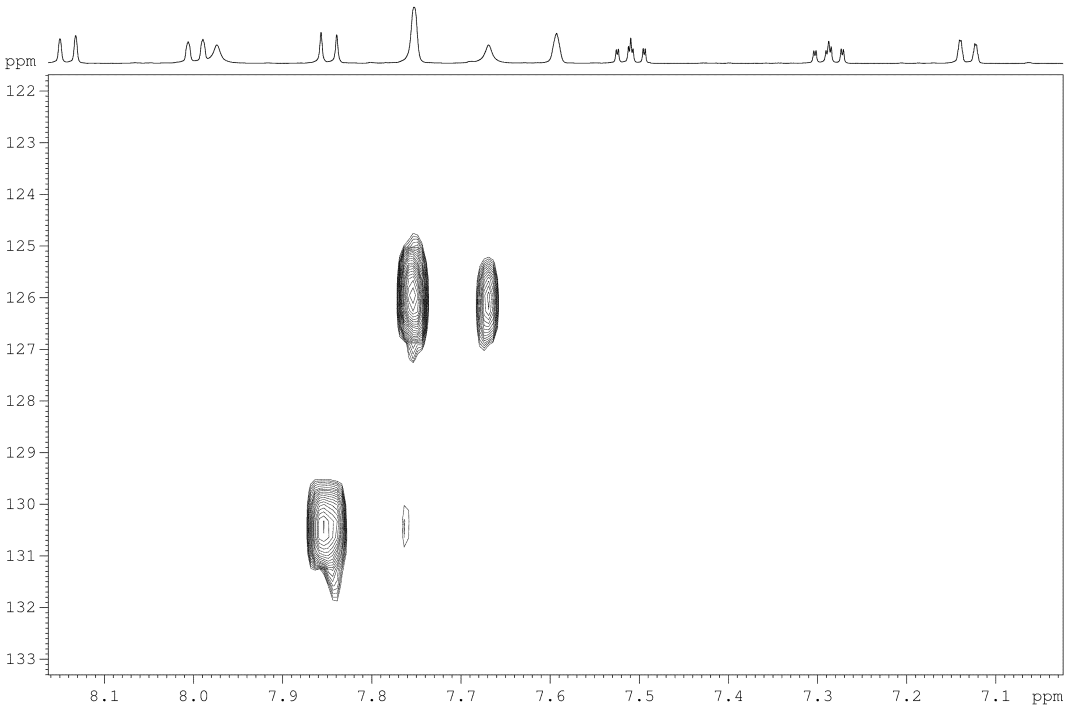
The NMR spectra were recorded on a 500 MHz spectrometer equipped with a 5 mm broadband Z-gradient probe (maximum gradient strength 53.5 G/cm). The ^{1}H, ^{15}N HMBC spectra were acquired with pulsed field gradients (ppm from external liquid NH_3).

All diffusion experiments were performed with a convection-suppressing double STE pulse sequence (dstegp3s)*4 in pseudo-2D mode. The temperature was set and controlled at 303 K with an air flow of 535 l h^{-1}. For each experiment, 16 acquisition scans and 24 scans were used, with a relaxation delay of 2 s and a diffusion delay of 100 ms. The shape of the gradients was sinusoidal, with a length of 1 ms, and the strength was varied in 32 increments (2-95%) in a linear ramp.

^{1}H NMR and ^{1}H, ^{15}N HMBC of the *bis*-thiourea 4k

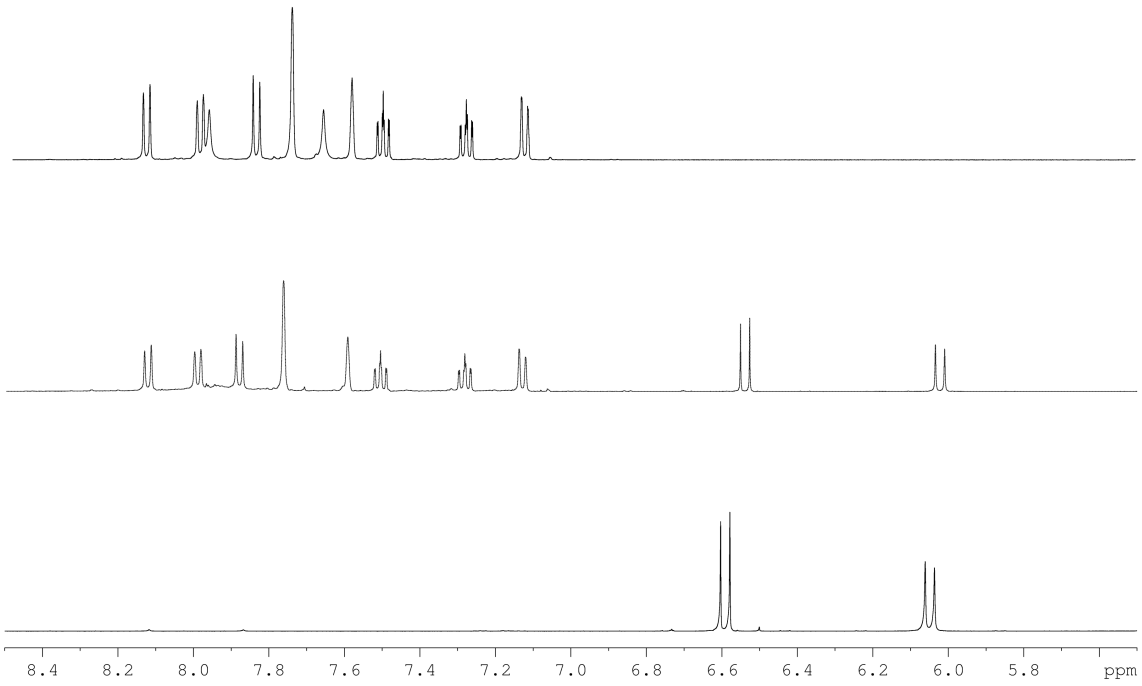


Section of the ^{1}H NMR (500 MHz, CD_2Cl_2, 0.03M) spectra for *bis*-thiourea catalyst **4k**



Section of the ^{1}H, ^{15}N HMBC (500 MHz, CD_2Cl_2, 0.03M) spectra for *bis*-thiourea catalyst **4k**

^{1}H NMR of the binary bifunctional thiourea 4k/ hydrazone 1a complex



Section of the ^{1}H NMR (500 MHz, CD_2Cl_2, 0.03M) spectra for *bis*-thiourea catalyst **4k** (up) (0.02 mmol), mixture (1:1 at 0.02 mmol) of **4k** and **1a** (middle) and hydrazone **1a** (down) (0.02 mmol).