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Supporting information for

Hydrogen Bonding Phase-Transfer Catalysis with Potassium Fluoride: Enantioselective Synthesis of β-Fluoroamines

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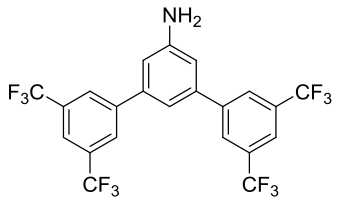
General Information

Unless otherwise stated, all reagents were purchased from commercial suppliers (Sigma-Aldrich, Alfa Aesar, Fluorochem and Apollo Scientific) and used without further purification. Unless otherwise stated, solvents were used without prior drying/degassing. Reactions requiring anhydrous conditions are clearly stated and were conducted after flame-drying of the appropriate reaction vessel (round-bottom two-neck flasks or Schlenk) and under an inert atmosphere of nitrogen. Dry solvents were purchased from commercial suppliers. The dry chloroform employed in the fluorination was purchased from Acros and passed on a column of basic alumina prior to use (to ensure absence of HCl impurities). KF (99.9% trace metal basis from Alfa Aesar) was used as provided by the supplier (fine powder) and used without pre-drying. CsF (99.9% trace metal basis from Sigma-Aldrich) was ground prior to the reaction and used without pre-drying. Reactions were monitored by thin layer chromatography (TLC) on silica gel pre-coated aluminium sheets (Merck Kieselgel 60 F_{254} plates). Visualization was accomplished by irradiation with UV light at 254 nm, and/or phosphomolybdic acid (PMA) stain, and/or cerium ammonium molybdate (CAM) stain, and/or permanganate stain. Flash column chromatography (FCC) was performed on Merck silica gel (60, particle size 0.040-0.063 mm). Optical rotations were measured on an Autopol L 2000 (Schmidt-Haensh) at 589 nm, 25 °C. Data are reported as: $[\alpha]_D^T$, concentration (c in g/100 mL), and solvent. The absolute configuration of the stilbene-derived products was determined by X-ray analysis of compound **2g** and further confirmed by comparing the optical rotation values of compound **8** (derived from compound **4**) to literature values. The configuration of the other stilbene-derived products was assigned by analogy to **2g**. The absolute configuration of **2t** was determined by comparing the optical rotation values of the corresponding β-fluoropicolinamide derivative to literature values. The configuration of the other cyclic products (**2u**–**2v**) was assigned by analogy to **2t**. All NMR spectra were recorded on Bruker AVIIIHD 400, AVIIIHD 500 or VII 500. ^{1}H and ^{13}C NMR spectral data are reported as chemical shifts (δ) in parts per million (ppm) relative to the solvent peak using the Bruker internal referencing procedure (edlock). ^{19}F NMR spectra are referenced relative to $CFCl_3$. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, pent = pentet, sept = septet, br = broad, m = multiplet), coupling constants (Hz) and integration. NMR spectra were processed with MestReNova 11.0 or Topsin 3.5. High resolution mass spectra (HRMS, *m/z*) were recorded on a Thermo Exactive mass spectrometer equipped with Waters Acquity liquid chromatography system using either the heated electrospray (HESI-II) probe for positive electrospray ionization (ESI^+) or the atmospheric pressure chemical ionization (APCI) probe. Infrared spectra were recorded as the neat compound or in solution using a Bruker tensor 27 FT-IR spectrometer. Absorptions are reported in wavenumber (cm^{-1}). Melting points of solids were measured on a Griffin apparatus and are uncorrected. The enantiomeric ratios were determined by HPLC analysis on a Shimadzu *i*-Prominence LC-2030 (PDA detector) employing a chiral stationary phase column specified in the individual experiment by comparing the samples with the appropriate racemic mixtures.

Catalyst Synthesis and Characterization

Catalysts **3a–d** were prepared according to literature procedures and their analytical data were in agreement with the literature values.[1] Catalysts **3e–g** and their precursor aniline **6** were unknown: their synthesis and characterization is therefore described herein.

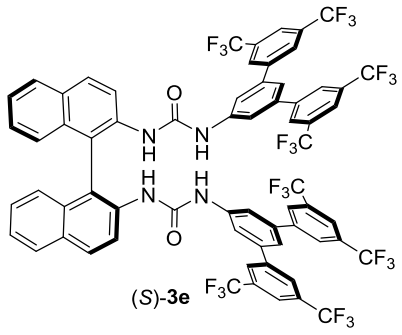
3,3'',5,5''-tetrakis(trifluoromethyl)-[1,1':3',1''-terphenyl]-5'-amine (6)



6

A two-neck round bottom flask equipped with a stirring bar and a condenser was charged with 3,5-dibromoaniline (2.79 g, 11.11 mmol, 1 equiv.), (3,5-bis(trifluoromethyl)phenyl)boronic acid (10.00 g, 38.91 mmol, 3.50 equiv.), S-Phos (455 mg, 1.11 mmol, 10 mol%) and K_2CO_3 (7.67 g , 55.55 mmol, 5 equiv.) under inert atmosphere. Degassed THF (110 mL) and degassed H_2O (27 mL) were added followed by $Pd(OAc)_2$ (124 mg, 0.55 mmol, 5 mol%). The reaction mixture was then stirred overnight under nitrogen at reflux. After cooling to r.t., the mixture was diluted with water and extracted three times with DCM. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated *in vacuo*. The crude product was purified by FCC (Pentane:DCM = 70:30) to afford a white solid (4.63 g, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.03 (s, 4H), 7.90 (s, 2H), 7.12 (br t, J = 1.7 Hz, 1H), 6.96 (d, J = 1.6 Hz, 2H), 4.03 (br s, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ = –62.82 (s, 12F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 148.1, 143.2, 140.9, 132.3 (q, $J_{C–F}$ = 33.3 Hz), 127.5, 123.5 (q, $J_{C–F}$ = 273.0), 121.5, 116.5, 114.1; **IR** (thin layer film) ν (cm^{-1}) = 3407, 1624, 1602, 1400, 1309, 1170, 1124, 899, 842, 753, 705; **MP** 123 – 124 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{22}H_{12}F_{12}N^+$ $[M+H]^+$ 518.07726, found 518.07727.

1,1'-([1,1'-binaphthalene]-2,2'-diyl)bis(3-(3,3'',5,5''-tetrakis(trifluoromethyl)-[1,1':3',1''-terphenyl]-5'-yl)urea) (3e)

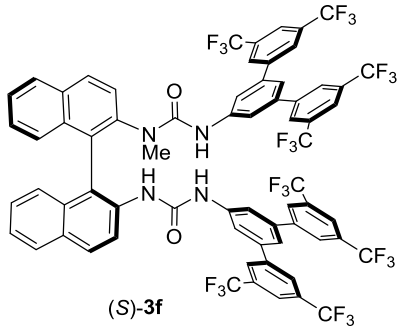


(*S*)-**3e**

In a flame-dried two-neck flask under inert atmosphere, triphosgene (874 mg, 2.95 mmol, 0.7 equiv.) was dissolved in DCM (5 mL). To this solution, a 0.2 M solution of aniline **6** (4.36 g, 8.45 mmol, 2 equiv.) in DCM (37 mL) was added at 0 °C. Then NEt_3 (2.35 mL, 16.88 mmol, 4 equiv.) was added dropwise at 0 °C and the reaction mixture was allowed to stir at r.t. for 2 h under a flow of nitrogen. (*S*)-(–)-1,1′-binaphthyl-2,2′-diamine (1.2 g, 4.22 mmol, 1 equiv.) was then added as a solid and the reaction stirred at r.t. for 24 h (until TLC showed no further conversion). The reaction was then quenched by addition of water and the aqueous phase was extracted with DCM three times. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated *in vacuo*. The crude mixture was then purified by FCC (Pentane:DCM = 80:20 to 0:100, gradient) to afford a white solid (4.23 g, 73% yield). **^{1}H NMR** (400 MHz, DMSO-d_6) δ = 9.33 (br s, 2H), 8.43 (d, J = 9.1 Hz, 2H), 8.14 (d, J = 9.1 Hz, 2H), 8.10 (s, 8H), 8.04 (d, J = 8.3 Hz, 2H), 7.99 (s, 4H), 7.64 (s, 4H), 7.61 (s, 2H), 7.52 (s, 2H), 7.44 (t, J = 7.4 Hz, 2H), 7.28 (t, J = 8.0 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H); **^{19}F NMR** (376

MHz, DMSO-d_6) δ = –61.4 (s, 24F); **^{13}C NMR** (101 MHz, DMSO-d_6) δ = 153.0, 142.2, 141.0, 138.2, 136.2, 132.9, 130.8 (q, $J_{C–F}$ = 33.0 Hz), 130.3, 128.9, 128.2, 127.3, 126.7, 124.8, 124.6, 123.1 (q, $J_{C–F}$ = 272.8 Hz), 122.8, 121.1, 119.6, 119.4, 117.2; **IR** (thin layer film) ν (cm^{-1}) = 3361, 1691, 1599, 1569, 1505, 1428, 1396, 1367, 1278, 1220, 1177, 1131, 1107, 900, 866, 844, 824, 747, 705, 682, 638; **MP** not determined (decomposition at T >200 °C); **HRMS** (APCI$^+$) *m/z* calculated for $C_{66}H_{35}O_2N_4F_{24}$ $[M+H]^+$ 1371.2371, found 1371.2368; **$[\alpha]_D^{25\,°C}$** = –96.7 ° (c = 0.5, $CHCl_3$).

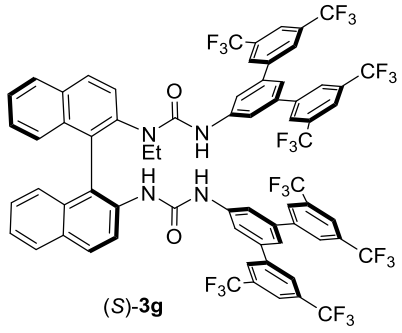
1-methyl-3-(3,3'',5,5''-tetrakis(trifluoromethyl)-[1,1':3',1''-terphenyl]-5'-yl)-1-(2'-(3-(3,3'',5,5''-tetrakis(trifluoromethyl)-[1,1':3',1''-terphenyl]-5'-yl)ureido)-[1,1'-binaphthalen]-2-yl)urea (3f)



(*S*)-**3f**

In a flame-dried two-neck flask under inert atmosphere, triphosgene (257 mg, 0.87 mmol, 0.7 equiv.) was dissolved in DCM (3 mL). To this solution, a solution of aniline **6** (1.28 g, 2.48 mmol, 2 equiv.) in DCM (9 mL) was added at 0 °C. Then NEt_3 (692 µL, 4.96 mmol, 4 equiv.) was added dropwise at 0 °C and the reaction mixture was allowed to stir at r.t. for 2 h under a flow of nitrogen. (*S*)-N^2-methyl-[1,1'-binaphthalene]-2,2'-diamine[1] (363.8 mg, 1.24 mmol, 1 equiv.) was then added as a solid and the reaction stirred at r.t. for 24 h (until TLC showed no further conversion). The reaction was then quenched by addition of water and the aqueous phase was extracted with DCM three times. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated *in vacuo*. The crude mixture was then purified by FCC (Pentane:Et_2O = 80:20) to afford a white solid (929.6 mg, 54% yield). **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 8.77 (br s, 1H), 8.73 (d, J = 7.9 Hz, 1H), 8.43 (d, J = 8.4 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.8 Hz, 1H), 8.00 (s, 5H), 7.90 – 7.71 (m, 10H), 7.69 (d, J = 7.4 Hz, 1H), 7.58 (s, 1H), 7.51 – 7.44 (m, 3H), 7.38 (br t, J = 6.5 Hz, 1H), 7.33 – 7.18 (m, 5H), 7.12 (d, J = 8.4 Hz, 1H), 6.69 (br d, J = 7.4 Hz, 1H), 2.60 (s, 3H); **^{19}F NMR** (470 MHz, DMSO-d_6) δ = –61.5 (two overlapped singlets, 24F); **^{13}C NMR** (126 MHz, DMSO-d_6) [overlapping signals] δ = 154.0, 152.3, 142.2, 141.8, 140.6, 140.0, 138.0, 137.4, 136.1, 133.7, 133.0, 132.7, 131.9, 131.4 130.6 (q, $J_{C–F}$ = 32.9 Hz), 130.5 (q, $J_{C–F}$ = 32.9 Hz), 129.5, 128.9, 128.2, 127.7, 127.4, 127.1, 126.9, 126.7, 125.8, 124.8, 124.3, 123.1 (q, $J_{C–F}$ = 273.2 Hz), 123.0 (q, $J_{C–F}$ = 272.9 Hz), 120.9 (m), 120.7, 120.5, 119.8 (overlapped), 119.3, 118.6, 116.4, 36.2; **IR** (thin layer film) ν (cm^{-1}) = 3330, 1599, 1551, 1507, 1468, 1428, 1397, 1367, 1279, 1180, 1132, 900, 865, 844, 825, 751, 705, 683, 639; **MP** not determined (decomposition at T >200 °C);; **HRMS** (APCI$^+$) *m/z* calculated for $C_{67}H_{37}O_2N_4F_{24}$ $[M+H]^+$ 1385.2578, found 1385.2525; **$[\alpha]_D^{25\,°C}$** = –106.9 ° (c = 0.5, $CHCl_3$).

1-ethyl-3-(3,3'',5,5''-tetrakis(trifluoromethyl)-[1,1':3',1''-terphenyl]-5'-yl)-1-(2'-(3-(3,3'',5,5''-tetrakis(trifluoromethyl)-[1,1':3',1''-terphenyl]-5'-yl)ureido)-[1,1'-binaphthalen]-2-yl)urea (3g)



(*S*)-**3g**

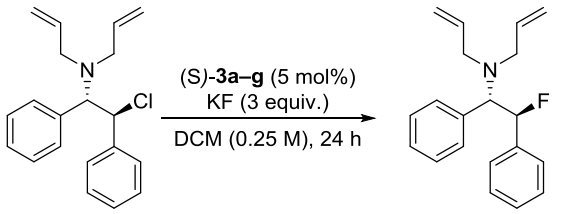
To a solution of **3e** (4.05 g, 2.95 mmol, 1 equiv.) in acetone (0.1 M, 29 mL) were added iodoethane (4.74 mL, 59 mmol, 20 equiv.) and K_2CO_3 (4.076 g, 29.5 mmol, 10 equiv.). The reaction mixture was stirred at r.t. for 72 h. After filtration on celite, the solvent was evaporated *in vacuo*. To the crude mixture were added DCM and H_2O. The aqueous phase was then extracted with DCM three times. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated *in vacuo*. The crude mixture was purified by FCC (Pentane:EtOAc = 100:0 to 80:20, gradient) to afford a white solid (2.10 g, 51% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.49 (br s, 1H), 8.15 (d, *J* = 8.9 Hz, 1H), 8.08 (d, *J* = 9.3 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.84 (s, 4H), 7.77 (s, 2H), 7.74 (s, 2H), 7.72 (s, 4H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.59 (s, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.1 Hz, 1H), 7.33 (t, *J* = 7.1 Hz, 1H), 7.30 (s, 3H), 7.21 (s, 3H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.05 (s, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.72 (s, 1H), 3.44 – 3.33 (m, 1H), 3.07 (br s, 1H), 1.05 (t, *J* = 7.0 Hz, 3H); **^{19}F NMR** (470 MHz, $CDCl_3$) δ = –62.9 (s, 12F), –63.0 (s, 12F); **^{13}C NMR** (126 MHz, $CDCl_3$) [overlapping signals] δ = 156.1, 152.7, 142.2, 141.6, 140.1, 139.9, 139.8, 139.7, 138.6, 135.3, 133.9, 133.4, 133.3, 132.3 (q, $J_{C–F}$ = 33.0 Hz), 132.0 (q, $J_{C–F}$ = 33.0 Hz), 131.9, 130.8, 130.3, 128.7, 128.5, 128.1, 127.8, 127.4, 127.1, 127.0, 126.7, 125.3, 123.2 (q, $J_{C–F}$ = 273.0 Hz), 123.1 (q, $J_{C–F}$ = 272.9 Hz), 121.6 (m), 121.5 (m), 121.3, 120.7, 120.3, 120.0 119.9, 118.2, 44.4, 13.6; **IR** (thin layer film) ν (cm^{-1}) = 3323, 2929, 1600, 1756, 1507, 1469, 1367, 1279, 1179, 1132, 901, 845, 706, 683; **MP** not determined (decomposition at T >200 °C); **HRMS** ($APCI^+$) *m/z* calculated for $C_{68}H_{39}O_2N_4F_{24}$ $[M+H]^+$ 1399.2684, found 1399.2690; **$[\alpha]_D^{25\,°C}$** = –116.1 ° (c = 0.5, $CHCl_3$).

N. B. When the same procedure used for the synthesis of catalyst **3f** was used to prepare **3g**, only very poor yields were obtained (<10% yield).

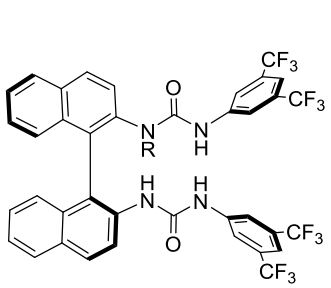
Optimization of Reaction Conditions

Despite our efforts, the isolation of alternative starting materials based on the stilbene backbone (bromides or mesylates) proved to be challenging due to their instability. We therefore focused our investigation on chlorides.

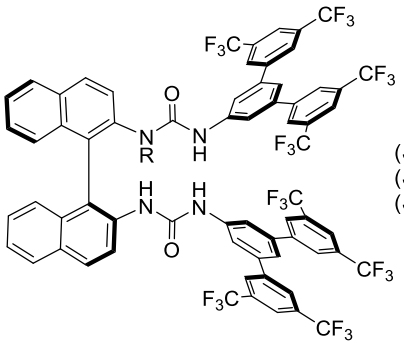
Table S1: Catalyst Screening



rac-**1a** (0.05 mmol) *(S,S)*-**2a**



(*S*)-**3a**:R=H
(*S*)-**3b**:R=Me
(*S*)-**3c**:R=Et
(*S*)-**3d**:R=^{i}Pr

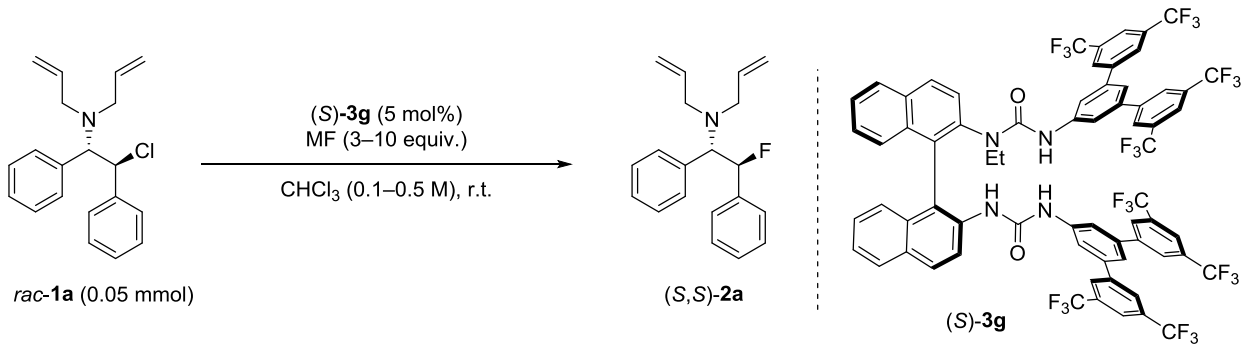


(*S*)-**3e**:R=H
(*S*)-**3f**:R=Me
(*S*)-**3g**:R=Et

Entry	Catalyst	Yield[a]	e.r.[b]
1	(*S*)-**3a**	>99%	55:45
2	(*S*)-**3b**	98%	85:15
3	(*S*)-**3c**	>99%	86:14
4	(*S*)-**3d**	83%	86:14
5	(*S*)-**3e**	77%	55:45
6	(*S*)-**3f**	72%	88:12
7	(*S*)-**3g**	80%	90.5:9.5

Reaction conditions: 0.05 mmol of *rac*-**1a**, KF (3 equiv.) and (*S*)-**3** (5 mol%) were stirred in DCM at 900 rpm at r.t. for 24h. [a] Determined by ^{19}F NMR using 4-fluoroanisole as internal standard; [b] e.r.= enantiomeric ratio, determined by HPLC using a chiral stationary phase.

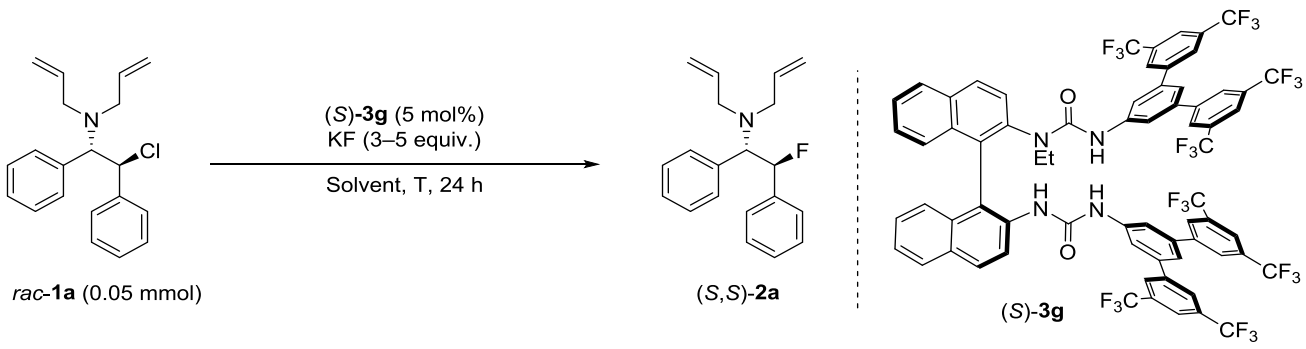
***Table S2*:** Concentration and Nucleophile Equivalents Screening



Entry	MF	MF (equiv.)	Concentration (M)	Time (h)	Yield[a]	e.r.[b]
1	KF	3	0.25	5	14%	89.5:10.5
2	KF	5	0.25	5	18%	90.5:9.5
3	KF	10	0.25	5	55%	90.5:9.5
4	KF	3	0.1	24	20%	90:10
5	KF	3	0.5	5	59%	90:10
6	KF	5	0.5	5	87%	90.5:9.5
7	KF	5	0.5	24	>99%	90.5:9.5
8	CsF	3	0.25	24	>99%	91:9

Reaction conditions: 0.05 mmol of *rac*-**1a**, MF, (*S*)-**3g** (5 mol%) in dry $CHCl_3$ (filtered on basic alumina to remove residual HCl), stirring at 900 rpm at r.t. for the indicated time. [a] Determined by ^{19}F NMR using 4-fluoroanisole as internal standard; [b] e.r.= enantiomeric ratio, determined by HPLC using a chiral stationary phase.

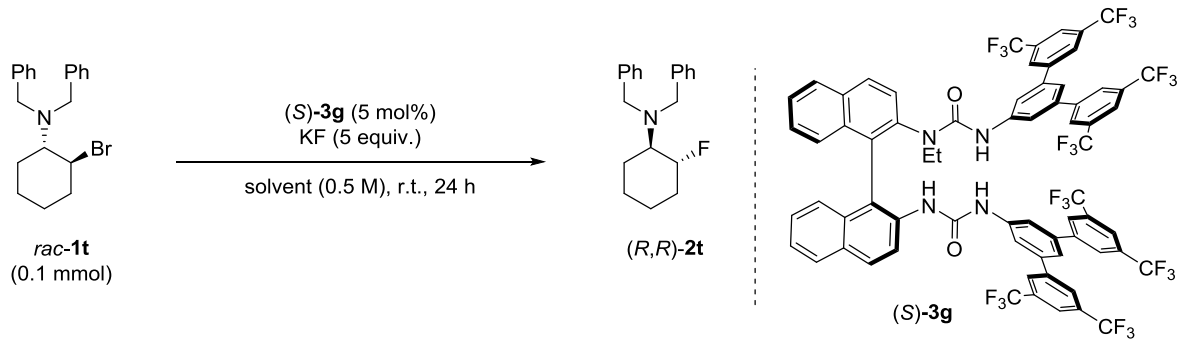
Table S3: Solvent and Temperature Screening



Entry	Solvent (Concentration/M)	KF (equiv.)	Temperature (°C)	Yield [a]	e.r. [b]
1	CH_3CN (0.25)	3	r.t.	9%	-
2	1,2-difluorobenzene(0.25)	3	r.t.	95%	93:7
3	α,α,α-trifluorotoluene (0.25)	3	r.t.	98%	93:7
4	DCM (0.25)	3	r.t.	80%	90.5:9.5
5	Chlorobenzene (0.25)	3	r.t.	17%	93:7
6	$CHCl_3$ (0.25)[c]	3	r.t.	80%	90.5:9.5
7	$CHCl_3$ (0.25)	3	r.t.	52%	85:15
8	Toluene (0.25)	3	r.t.	36%	93:7
9	1,2-difluorobenzene (0.5)	5	0	58%	94:6
10	α,α,α-trifluorotoluene (0.5)	5	0	77%	94:6
11	DCM (0.5)	5	0	80%	93:7
12	$CHCl_3$ (0.5) [c]	5	0	98%	93.5:6.5
13	$CHCl_3$ (0.5) [c,d]	5	-10	72%	94.5:5.5
14	$CHCl_3$ (0.5) [c,d]	5	-15	71%[e]	95:5

Reaction conditions: 0.05 mmol of *rac*-**1a**, KF (3-5 equiv., as reported), (*S*)-**3g** (5 mol%), stirring at 900 rpm at the indicated temperature for 24 h. [a] Determined by ^{19}F NMR using 4-fluoroanisole as internal standard; [b] e.r.= enantiomeric ratio, determined by HPLC using a chiral stationary phase; [c] Dry $CHCl_3$, filtered on basic alumina to remove residual HCl; [d] 10 mol% of (*S*)-**3g** were used; [e] isolated yield after 72 h.

***Table S4*:** Optimization of Reaction Conditions for Aliphatic Substrates

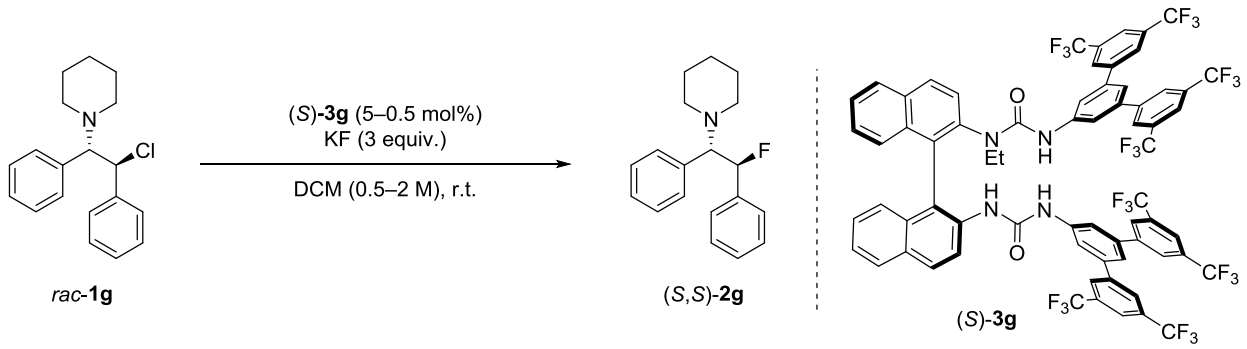


Entry	Solvent	Yield [a]	e.r. [b]
1	1,2-difluorobenzene	28%	83.5:16.5
2	α,α,α-trifluorotoluene	47%	85.5:14.5
3	DCM	25%	84.5:15.5
4	Chlorobenzene	12%	-
5	$CHCl_3$[c]	20%	83.5:16.5
6	Toluene	traces	-

Reaction conditions: 0.1 mmol of *rac*-**1t**, KF (5 equiv.), (*S*)-**3g** (5 mol%) stirring at 900 rpm at r.t. for 24 h. [a] Determined by ^{19}F NMR using 4-fluoroanisole as internal standard; [b] e.r.= enantiomeric ratio, determined by HPLC using a chiral stationary phase; [c] Dry $CHCl_3$, filtered on basic alumina to remove residual HCl.

N. B. Under similar conditions, the corresponding aliphatic chloride starting materials were unreactive. We therefore selected β-aminobromides as substrates.

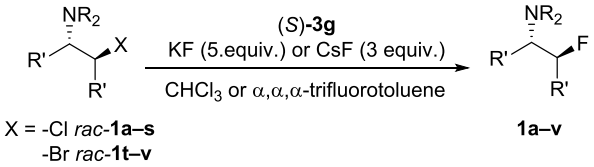
Table S5: Optimization of the Reaction Conditions for the Multi-Decagram Scale



Entry	Mass of 1g (mmol of 1g)	Concentration (M)	Catalyst Loading	Time (h)	Yield [a]	e.r. [b]
1	0.017 g (0.05)	0.25	5	48	>99%	92.5:7.5
2	0.017 g (0.05)	0.25	2	48	>99%	92:8
3	0.017 g (0.05)	0.25	1	48	>99%	92:8
4	0.017 g (0.05)	0.25	0.5	72	95%	91:9
6	0.167 g (0.5)	0.5	0.5	13	23%	91.5:8.5
7	0.167 g (0.5)	1	0.5	13	64%	92.5:7.5
8	0.167 g (0.5)	2	0.5	13	85%	92:8
9	1.0 g (3.34)	2	0.5	24	83%	91:9
10	5.5 g (18.3)	2	0.5	72	95%	92:8
11	50.0 g (167.2)	2	0.5	72	95% (66%)[c]	92:8 (97:3)[c]

Reaction conditions: *rac*-**1g**, KF (3 equiv.), (*S*)-**3g**, in DCM stirring at 900 rpm at r.t. for the indicated time. [a] Determined by ^{19}F NMR using 4-fluoroanisole as internal standard; [b] e.r.= enantiomeric ratio, determined by HPLC using a chiral stationary phase; [c] In parenthesis: yield and e.r. after a single recrystallization.

General Procedure for the Asymmetric Nucleophilic Fluorination of Aziridinium Ions



*Method A, fluorination with **KF:*** In a vial equipped with a magnetic stirring bar were sequentially added the substrate (1 equiv.), the catalyst, KF (5 equiv.) and dry $CHCl_3$ or α,α,α-trifluorotoluene (0.5 M, pre-cooled at the same temperature as the reaction). The vial was sealed and the reaction mixture was stirred at 900 rpm at the appropriate temperature for the indicated time. The crude mixture was then filtered through a small plug of silica (and eluted with cold DCM/EtOAc = 1:1), evaporated to dryness under reduced pressure and directly purified by FCC. For reaction optimization the crude mixture was analyzed by ^{1}H and ^{19}F NMR (4-fluoroanisole as internal standard) to determine the yield; an aliquot of the reaction mixture was purified by preparative TLC and analyzed by HPLC (chiral stationary phase) to determine the e.r.

*Method B, fluorination with **CsF:*** In a vial equipped with a magnetic stirring bar were sequentially added the substrate (1 equiv.), catalyst **3g**, CsF (3 equiv.) and dry $CHCl_3$ or α,α,α-trifluorotoluene (0.25 M, pre-cooled at the same temperature as the reaction). The vial was sealed and the reaction mixture was stirred at 900 rpm at the appropriate temperature for the indicated time. The crude mixture was then filtered through a small plug of silica (and eluted with cold DCM/EtOAc = 1:1), evaporated to dryness under reduced pressure and directly purified by FCC.

Note: KF (99.9% trace metal basis from Alfa Aesar) was used as provided (fine powder) by the supplier and used without pre-drying. CsF (99.9% trace metal basis from Sigma-Aldrich) was ground prior to the reaction and used without pre-drying. The dry chloroform was passed on a column of basic alumina prior to use to ensure absence of HCl impurities. α,α,α-trifluorotoluene was used as provided by the supplier without further drying/purification.

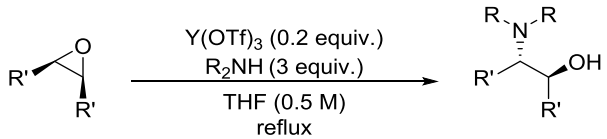
Racemate synthesis: The racemic reference products for HPLC analysis were obtained using the same procedure as above (KF or CsF, 3 equiv.) and Schreiner's urea catalyst (r.t.). Alternatively, the starting material was reacted with AgF (1.2 equiv.) in CH_3CN at 60 °C for 2 h.

Substrates Synthesis and Characterization

β-Aminoalcohols

β-Aminoalcohols **7a–v** were prepared by heating the corresponding *meso* epoxides[2] in the presence of the appropriate secondary amine either with a Lewis acid (**7a, l–q**, **s–v**) (*method A*) or neat (**7b–k, r**) (*method B*). For the synthesis of **7b** and **7i**, the hydrochloride salt of the amine was used and details for the release of the free amine are given in the single experiment.

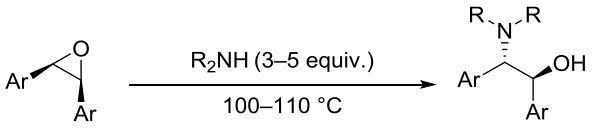
General Procedure for the Synthesis of β-Aminoalcohols: Method A



rac-**7a, l–p**, **s-v**

Following a slightly modified procedure from the one reported by Yamamoto,[3] in a flame-dried two-neck round bottom flask, the *cis*-epoxide (1 equiv.), the amine (3 equiv.) and $Y(OTf)_3$ (0.2 equiv.) were refluxed in anhydrous THF (0.5 M) under inert atmosphere until complete conversion of the epoxide (14–72 h, monitored by TLC). The reaction mixture was then cooled to r.t. and the solvent evaporated *in vacuo*. The residue was re-dissolved in EtOAc washed with a saturated solution of $NaHCO_3$. The layers were separated and the aqueous phase was extracted twice with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by FCC over silica gel.

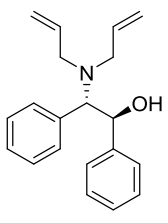
General Procedure for the Synthesis of β-Aminoalcohols: Method B



rac-**7b–k**, **r**

In a pressure tube, the *cis*-epoxide was dissolved in 3–5 equivalents of the amine and stirred at 100–110 °C until complete conversion of the starting material (14–48 h, monitored by TLC). The excess amine was then removed by evaporation under reduced pressure and the crude product was directly purified by FCC over silica gel.

***rac*-2-(diallylamino)-1,2-diphenylethan-1-ol (7a)**

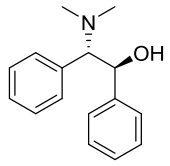


rac-**7a**

Alcohol **7a** was prepared following the general procedure (*method A*, 48 h), from *cis*-stilbene oxide (3.5 g, 17.8 mmol, 1 equiv.) and diallylamine (6.6 mL, 53.5 mmol, 3 equiv.). Purification by FCC(Pentane:Et_2O = 98:2) afforded the title compound as a pale yellow solid (3.26 g, 63% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.36 – 7.06 (m, 10H), 5.92 (tdd, J = 14.0, 8.6, 4.1 Hz, 2H), 5.25 (d, J = 13.7 Hz, 4H), 5.09 – 5.04 (m, 2H), 3.92 (d, J = 10.3 Hz, 1H), 3.54 (ddt, J =

13.9, 4.1, 2.0 Hz, 2H), 2.68 (dd, *J* = 14.0, 8.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 141.6, 136.3, 133.6, 130.2, 128.1, 128.0, 127.8, 127.5, 127.5, 118.3, 71.1, 69.8, 52.8; **IR** (thin layer film) ν (cm^{-1}) = 3356, 3064, 3030, 2824, 1642, 1493, 1451, 1400, 1335, 1081, 1053, 972, 757, 698, 607; **MP** 44 – 46 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{20}H_{24}NO^+$ $[M+H]^+$ 294.18524, found 294.18507.

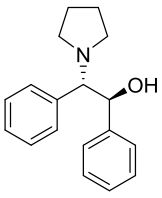
***rac*-2-(dimethylamino)-1,2-diphenylethan-1-ol (7b)**



rac-**7b**

In a pressure tube, dimethylamine hydrochloride (2.45 g, 30 mmol, 5 equiv.) and sodium hydroxide (2.4 g, 60 mmol, 10 equiv.) were dissolved in 30 mL of MeOH/Water (1:1) and stirred at 0 °C for 10 min before addition of *cis*-stilbene oxide (1.2 g, 6.0 mmol, 1 equiv.). The pressure tube was sealed, and the reaction stirred at 65 °C overnight. The reaction mixture was then allowed to cool to r.t. and extracted with EtOAc. The combined organic layers were washed with brine, dried on $MgSO_4$ and evaporated to dryness. Purification by FCC (Pentane:EtOAc = 90:10 to 80:20, gradient) afforded **7b** as a white solid (1.20 g, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.23 – 7.10 (m, 5H), 7.10 – 6.90 (m, 5H), 4.91 (d, *J* = 10.3 Hz, 1H), 3.47 (d, *J* = 10.3 Hz, 1H), 2.16 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 141.5, 132.4, 130.2, 128.0, 127.8, 127.8, 127.4, 127.4, 75.9, 71.1, 40.9; **IR** (thin layer film) ν (cm^{-1}) = 3291, 3030, 2941, 2903, 2869, 2835, 2789, 1602, 1493, 1474, 1079, 1051, 1036, 877, 700; **MP** 88 – 91 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{16}H_{20}NO^+$ $[M+H]^+$ 242.15394, found 242.15385.

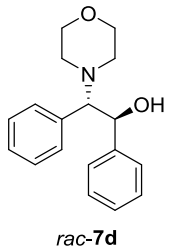
***rac*-1,2-diphenyl-2-(pyrrolidin-1-yl)ethan-1-ol (7c)**



rac-**7c**

Alcohol **7c** was prepared following the general procedure (*method B*, 14 h), from *cis*-stilbene oxide (2.0 g, 10.2 mmol, 1 equiv.) and pyrrolidine (4.0 mL, 51 mmol, 5 equiv.). Purification by FCC (DCM:MeOH = 98:2) afforded the title compound as a white solid (2.27 g, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.40 – 7.24 (m, 5H), 7.22 – 7.10 (m, 5H), 5.29 (br s, 1H), 5.02 (d, *J* = 9.9 Hz, 1H), 3.85 (d, *J* = 10.0 Hz, 1H), 2.72 – 2.62 (m, 2H), 2.57 – 2.44 (m, 2H), 1.79 – 1.64 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 141.9, 133.5, 130.4, 128.0, 127.9, 127.7, 127.4, 127.3, 72.1, 71.8, 48.1, 22.8; **IR** (thin layer film) ν (cm^{-1}) = 3370, 3027, 2954, 2925, 1620, 1452, 1261, 1081, 1056, 701; **MP** 80 – 81 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{18}H_{22}NO^+$ $[M+H]^+$ 268.16959, found 268.16949. Spectroscopic data were in agreement with the ones previously reported in literature.[4]

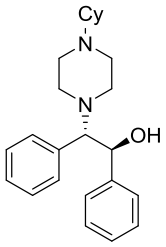
***rac*-2-morpholino-1,2-diphenylethan-1-ol (7d)**



rac-**7d**

Alcohol **7d** was prepared following the general procedure (*method B*, 24 h), from *cis*-stilbene oxide (1.00 g, 5.0 mmol, 1 equiv.) and morpholine (2.2 mL, 25 mmol, 5 equiv.). Purification by FCC (Hexane:EtOAc = 100:0 to 60:40, gradient) afforded the title compound as a white solid (1.22 g, 86% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.35 – 7.23 (m, 5H), 7.23 – 7.15 (m, 3H), 7.14 – 7.09 (m, 2H), 5.13 (br s, 1 H), 5.11 (d, J = 10.3 Hz, 1H), 3.84 (ddd, J = 9.8, 6.4, 3.0 Hz, 2H), 3.79 (ddd, J = 11.0, 6.4, 2.9 Hz, 2H), 3.61 (d, J = 10.3 Hz, 1H), 2.81 – 2.65 (m, 2H), 2.49 – 2.39 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) [overlapped signals] δ = 141.2, 132.7, 130.0, 128.0 (overlapped), 127.6, 127.4, 76.9, 70.4, 67.4, 49.3 (br); **IR** (thin layer film) ν (cm^{-1}) = 3352, 3030, 2912, 2851, 1452, 1402, 1115, 1028, 994, 912, 873, 700; **HRMS** (ESI^+) *m/z* calculated for $C_{18}H_{22}NO_2^+$ $[M+H]^+$ 284.16451, found 284.16437. Spectroscopic data were in agreement with the ones previously reported in literature.[5]

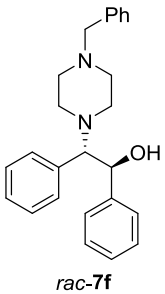
***rac*-2-(4-cyclohexylpiperazin-1-yl)-1,2-diphenylethan-1-ol (7e)**



rac-**7e**

Alcohol **7e** was prepared following the general procedure (*method B*, 14 h), dissolving *cis*-stilbene oxide (1.00 g, 5.0 mmol, 1 equiv.) and 1-cyclohexylpiperazine (2.50 g, 15 mmol, 3 equiv.) in 5 mL of EtOH. Purification by FCC (Pentane:EtOAc = 80:20 with 3% NEt_3) afforded the title compound as a white solid (1.57 g, 86% yield). **^{1}H NMR** (500 MHz, DMSO-d_6, 70 °C) δ = 7.48 – 7.27 (m, 10H), 5.29 (d, J = 9.9 Hz, 1H), 5.08 (br s, 1H), 3.87 (d, J = 9.9 Hz, 1H), 2.85 – 2.69 (m, 6H), 2.57 – 2.50 (m, 2H), 2.40 – 2.33 (m, 1H), 2.00 – 1.86 (m, 4H), 1.77 (dt, J = 12.8, 2.9 Hz, 1H), 1.48 – 1.23 (m, 5H); **^{13}C NMR** (126 MHz, DMSO-d_6, 70 °C) δ = 142.0, 133.7, 129.5, 127.2, 127.2, 127.0, 126.8, 126.5, 74.7, 69.6, 62.1, 48.8, 48.6, 28.2, 25.6, 24.8; **IR** (thin layer film) ν (cm^{-1}) = 3335, 2922, 2851, 1405, 1187, 1148, 1000, 977, 703; **MP** 153 – 157 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{24}H_{33}N_2O^+$ $[M+H]^+$ 365.25984, found 365.25830.

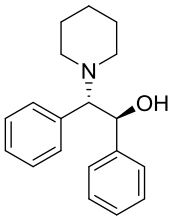
***rac*-2-(4-benzylpiperazin-1-yl)-1,2-diphenylethan-1-ol (7f)**



rac-**7f**

Alcohol **7f** was prepared following the general procedure (*method B*, 14 h), from *cis*-stilbene oxide (1.00 g, 5.0 mmol, 1 equiv.) and 1-benzylpiperazine (2.6 mL, 15 mmol, 3 equiv.). Purification by FCC (Pentane:EtOAc = 95:5 to 90:10, gradient) afforded the title compound as a pale yellow solid (1.40 g, 75% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.37 – 7.23 (m, 10H), 7.22 – 7.14 (m, 3H), 7.13 – 7.08 (m, 2H), 5.24 (br s, 1H), 5.09 (d, J = 10.3 Hz, 1H), 3.63 (d, J = 10.3 Hz, 1H), 3.57– 3.50 (m, 2H), 2.90 – 2.31 (m, 8H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 141.5, 138.0, 133.1, 130.0, 129.3, 128.3, 128.0, 128.0, 127.9, 127.5, 127.4, 127.2, 76.4, 70.5, 63.2, 53.6, 49.6 (br); **IR** (thin layer film) ν (cm^{-1}) = 3327, 3030, 2934, 2853, 1725, 1452, 1408, 1271, 1091, 1052, 1025, 700; **MP** 135 – 137 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{25}H_{29}N_2O^+$ $[M+H]^+$ 373.22744, found 373.22736.

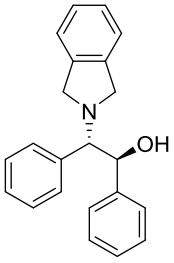
***rac*-1,2-diphenyl-2-(piperidin-1-yl)ethan-1-ol (7g)**



rac-**7g**

Alcohol **7g** was prepared following the general procedure (*method B*, 14 h), from *cis*-stilbene oxide (2.32 g, 11.8 mmol, 1 equiv.) and piperidine (6.0 mL, 59 mmol, 5 equiv.). Purification by FCC (Pentane:Et_2O = 100:0 to 90:10, gradient with 4% of NEt_3) afforded the title compound as a white solid (2.22 g, 67% yield). **For the multi-decagram scale reaction:** *cis*-stilbene (91.7 g, 0.47 mol, 1 equiv.) was dissolved in piperidine (184 mL, 1.4 mol, 4 equiv.) and refluxed for 24 h. The reaction was then cooled to r.t. and the excess amine was removed under vacuum. Hexane was added and after stirring for 15 min, the solution was filtered and the solid was washed with cold hexane. The brown solid was then dried overnight under vacuum and directly used for the successive step without any further purification (111.7 g, 0.40 mol, 85% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.32 – 7.22 (m, 5H), 7.20 – 7.09 (m, 5H), 5.36 (br s, 1H), 5.06 (d, J = 10.3 Hz, 1H), 3.56 (d, J = 10.3 Hz, 1H), 2.67 (br s, 2H), 2.31 (br s, 2H), 1.81 – 1.58 (m, 4H), 1.48 – 1.25 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 141.8, 133.5, 130.1, 128.0, 127.9, 127.7, 127.4, 127.4, 77.2, 70.5, 50.4, 26.7, 24.4; **IR** (thin layer film) ν (cm^{-1}) = 3320, 3030, 2933, 2852, 1452, 1407, 1217, 1195, 1156, 1088, 1052, 1025, 984, 875, 758, 745, 700; **MP** 96 – 97 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{19}H_{24}NO^+$ $[M+H]^+$ 282.18524, found 282.18495.

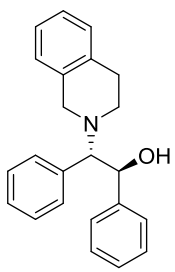
***rac*-2-(isoindolin-2-yl)-1,2-diphenylethan-1-ol (7h)**



rac-**7h**

In an extraction funnel, isoindoline hydrochloride (2.1 g, 13.5 mmol, 3 equiv.) was dissolved in Et_2O and washed with NaOH (1 M). Phases were separated and the aqueous phase was extracted twice with Et_2O. The combined organic phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was dissolved in 3 mL of EtOH and transferred into a pressure tube. *Cis*-stilbene oxide (785 mg, 4.0 mmol, 1 equiv.) was added and the pressure tube sealed. The reaction mixture was stirred at 100 °C overnight. Volatiles were evaporated *in vacuo* and the crude product was purified by FCC (Pentane:Et_2O = 100:0 to 90:10, gradient) to afford **7h** as a brown solid (1.18 g, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.25 – 7.14 (m, 4H), 7.14 – 7.03 (m, 10H), 5.05 (d, J = 9.5 Hz, 1H), 4.03 – 3.90 (m, 5H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 141.5, 139.2, 134.3, 130.2, 128.2, 128.0, 127.8, 127.4, 127.3, 126.8, 122.4, 72.4, 72.1, 54.0; **IR** (thin layer film) ν (cm^{-1}) = 3366, 3029, 2894, 2803, 1493, 1453, 1398, 1188, 1112, 1075, 909, 741, 700; **MP** 131 – 132 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{22}H_{22}NO^+$ $[M+H]^+$ 316.16959, found 316.16907.

***rac*-2-(3,4-dihydroisoquinolin-2(1H)-yl)-1,2-diphenylethan-1-ol (7i)**

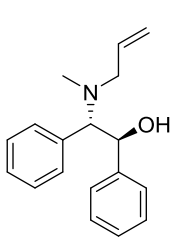


rac-**7i**

Alcohol **7i** was prepared following the general procedure (*method B*, 14 h), from *cis*-stilbene oxide (1.0 g, 5.0 mmol,1 equiv.) and tetrahydroisoquinoline (3.2 mL, 25 mmol, 5 equiv.). Purification by FCC (Pentane:EtOAc = 100:0 to 97:3, gradient) afforded the title compound as an ivory solid (1.55 g, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$); δ = 7.35 – 7.12 (m, 13H), 7.07 (dd, J = 6.4, 2.5 Hz, 1H), 5.24 (d, J = 10.3 Hz, 1H), 5.18 (br s, 1H), 4.00 – 3.80 (m, 2H), 3.70 (d, J = 14.5 Hz, 1H), 3.19 – 3.09 (m, 1H), 3.10 – 2.96 (m, 2H), 2.59 (ddd, J = 11.8, 7.3,

5.1 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) [overlapping signals] δ = 141.4, 134.7, 134.1, 133.0, 130.1, 128.8, 128.1, 128.0, 127.5 (overlapped), 126.7, 126.3, 125.8, 76.3, 70.9, 52.1, 46.6, 29.9; **IR** (thin layer film) ν (cm^{-1}) = 3350, 3028, 2916, 2832, 1495, 1453, 1403, 1193, 1127, 1086, 1048, 909, 760, 739, 700; **MP** 117 – 121 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{23}H_{24}NO^+$ $[M+H]^+$ 330.18634, found 330.18497 .

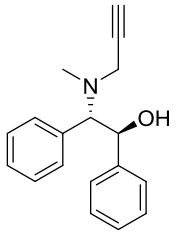
***rac*-2-(allyl(methyl)amino)-1,2-diphenylethan-1-ol (7j)**



rac-**7j**

Alcohol **7j** was prepared following the general procedure (*method B*, 48 h), from *cis*-stilbene oxide (1.0 g, 5.0 mmol, 1 equiv.) and *N*-Allylmethylamine (2.4 mL, 25 mmol, 5 equiv.). Purification by FCC (Pentane:EtOAc = 98:2 to 90:10, gradient) afforded the title compound as a white solid (1.16 g, 87% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.31 – 7.22 (m, 5H), 7.20 – 7.10 (m, 5H), 6.00 – 5.87 (m, 1H), 5.25 – 5.23 (m, 1H), 5.22 – 5.20 (m, 1H), 5.06 (d, *J* = 10.4 Hz, 1H), 3.75 (d, *J* = 10.4 Hz, 1H), 3.18 (dd, *J* = 13.5, 5.6, Hz, 1H), 2.95 (dd, *J* = 13.5, 7.3 Hz, 1H), 2.26 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 141.6, 136.1, 133.0, 130.2, 128.0, 128.0, 127.8, 127.5, 127.5, 118.1, 73.8, 71.0, 57.5, 37.0; **IR** (thin layer film) ν (cm^{-1}) = 3329, 3030, 2881, 1643, 1493, 1452, 1399, 1335, 1274, 1185, 1127, 1081, 1034, 1013, 921, 757, 699. **MP** 63 – 64 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{18}H_{22}NO^+$ $[M+H]^+$ 268.16959, found 268.16915.

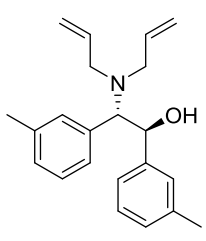
***rac*-2-(methyl(prop-2-yn-1-yl)amino)-1,2-diphenylethan-1-ol (7k)**



rac-**7k**

Alcohol **7k** was prepared following the general procedure (*method B*, 48 h), from *cis*-stilbene oxide (750 mg, 3.8 mmol, 1 equiv.) and *N*-Methylpropargylamine (1.3 mL, 15 mmol, 4 equiv.). Purification by FCC (Pentane:EtOAc = 98:2 to 90:10, gradient) afforded the title compound as a white solid (500 mg, 49% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 5H), 7.21 – 7.12 (m, 5H), 5.08 (d, *J* = 10.2 Hz, 1H), 4.88 (br s, 1H), 3.98 (d, *J* = 10.2 Hz, 1H), 3.34 (dd, *J* = 16.2, 2.5 Hz, 1H), 3.13 (dd, *J* = 16.2, 2.5 Hz, 1H), 2.35 (s, 3H), 2.32 (t, *J* = 2.4 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.4, 132.4, 130.2, 128.1 (overlapped), 128.0, 127.6, 127.5, 80.2, 73.1, 73.0, 71.2, 44.0, 34.0; **IR** (thin layer film) ν (cm^{-1}) = 3364, 3291, 3031, 2879,2803, 1423, 1357, 1302, 1186, 1016, 759, 670; **MP** 58 – 60 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{18}H_{20}NO^+$ $[M+H]^+$ 266.15394, found 266.15396.

***rac*-2-(diallylamino)-1,2-di-*m*-tolylethan-1-ol (7l)**

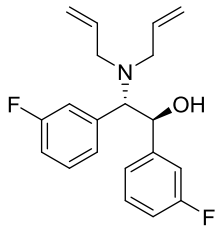


rac-**7l**

Alcohol **7l** was prepared following the general procedure (*method A*, 48 h), from *cis*-2,3-di-*m*-tolyloxirane (1.10 g, 4.5 mmol, 1 equiv.) and diallylamine (1.7 mL, 14 mmol 3 equiv.). Purification by FCC (Hexane:Et_2O = 100:0 to 98:2, gradient) afforded the title compound as a colorless oil (1.00 g, 70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$); δ = 7.15 (t, *J* = 7.5 Hz, 1H), 7.07 (s, 1H), 7.04 – 7.00 (m, 2H), 6.95 – 6.91 (m, 3H), 6.89 (s, 1H), 5.94 – 5.86 (m, 2H), 5.23 (d, *J* = 13.3 Hz, 4H), 5.07 (br s, 1H), 5.02 (d, *J* = 10.3 Hz, 1H), 3.87 (d, *J* = 10.3 Hz, 1H), 3.51 (d, *J* = 14.0 Hz, 2H), 2.67 (dd, *J* = 8.3, 14.0 Hz, 2H), 2.3 (s, 3H), 2.2 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 141.5, 137.5, 137.4, 136.4, 133.5, 131.0, 128.5, 128.2, 128.1, 127.9, 127.8, 127.1, 124.7, 118.2, 70.9, 69.4, 52.8, 21.7, 21.5; **IR** (thin layer film) ν (cm^{-1}) = 3356, 3025, 2977, 2921, 2826,

1642, 1607, 1489, 1448, 1398, 1318, 1245, 1153, 1093, 1055, 994, 972, 920, 885, 848, 782, 703; **HRMS** (ESI$^+$) *m/z* calculated for $C_{22}H_{28}NO^+$ $[M+H]^+$ 322.2165, found 322.2164.

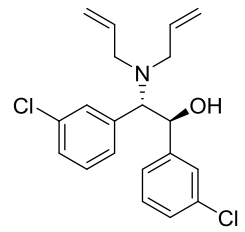
***rac*-2-(diallylamino)-1,2-bis(3-fluorophenyl)ethan-1-ol (7m)**



rac-**7m**

Alcohol **7m** was prepared following the general procedure (*method A*, 24 h), from *cis*-2,3-bis(3-fluorophenyl)oxirane (800 mg, 3.4 mmol, 1 equiv.) and diallylamine (1.2 mL, 10.3 mmol, 3 equiv.). Purification by FCC (Hexane:Et_2O = 100:0 to 95:5 gradient) afforded the title compound as a white solid (1.00 g, 88% yield). **^{1}H NMR** (500 MHz, $CDCl_3$); δ = 7.28 – 7.19 (m, 1H), 7.01 – 7.03 (m, 1H), 6.99 – 6.90 (m, 2H), 6.90 – 6.80 (m, 2H), 6.80 – 6.75 (m, 2H), 5.90 – 5.79 (m, 2H), 5.29 – 5.18 (m, 4H), 4.96 (d, *J* = 10.6 Hz, 1H), 4.95 (br s, 1H), 3.82 (d, *J* = 10.6 Hz, 1H), 3.49 (d, *J* = 14 Hz, 2H), 2.63 (dd, *J* = 9.3, 14 Hz, 2H); **^{19}F NMR** (470 MHz, $CDCl_3$); -112.6 (m, 1F), -113.4 (m, 1F); **^{13}C NMR** (126 MHz, $CDCl_3$); 162.78 (d, $J_{C–F}$ = 245 Hz), 162.6 (d, J_{C-F} = 245 Hz), 144.05 (d, $J_{C–F}$ = 8 Hz), 136.02 (d, $J_{C–F}$ = 8.0 Hz), 135.84, 129.75 (d, $J_{C–F}$ = 8.5 Hz), 129.54 (d, J_{C-F} = 8.5 Hz), 125.78 (d, $J_{C–F}$ = 2.8 Hz), 123.23 (d, $J_{C–F}$ = 2.8 Hz), 118.73, 116.81 (d, $J_{C–F}$ = 21.3 Hz), 115.04 (d, $J_{C–F}$ = 21.3 Hz), 114.6 (d, $J_{C–F}$ = 21.3 Hz), 114.11 (d, $J_{C–F}$ = 21.3 Hz), 70.60, 69.35, 52.84; **IR** (thin layer film) ν (cm^{-1}) = 3366, 3080, 2826, 1643, 1614, 1589, 1488, 1447, 1398, 1314, 1247, 1137, 1079, 1054, 995, 958, 923, 878, 782, 759, 705, 696; **MP** 60 – 63 °C; **HRMS** (ESI$^+$) *m/z* calculated for $C_{20}H_{22}F_2NO^+$ $[M+H]^+$ 330.1664, found 330.1663.

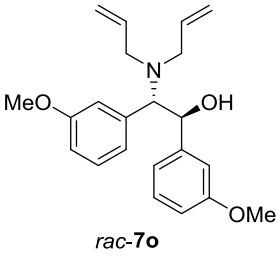
***rac*-1,2-bis(3-chlorophenyl)-2-(diallylamino)ethan-1-ol (7n)**



rac-**7n**

Alcohol **7n** was prepared following the general procedure (*method A*, 24 h), from *cis*-2,3-bis(3-chlorophenyl)oxirane (1.00 g, 3.7 mmol, 1 equiv.) and diallylamine (1.3 mL, 11 mmol, 3 equiv.). Purification by FCC (Hexane:Et_2O = 100:0 to 90:10 gradient) afforded the title compound as colorless oil (0.98 g, 70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$); δ = 7.27 – 7.18 (m, 3H), 7.13 – 7.03 (m, 3H), 7.00 – 6.93 (m, 2H), 5.90 – 5.80 (m, 2H), 5.28 – 5.21 (m, 4H), 4.95 (d, *J* = 10.5 Hz, 1H), 3.80 (d, *J* = 10.5 Hz, 1H), 3.49 (d, *J* = 14 Hz, 2H), 2.64 (dd, *J* = 8.7, 14 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 143.4, 135.8, 135.4, 134.3, 134.2, 130.0, 129.5, 129.4, 128.3, 128.6, 127.9, 127.4, 125.8, 118.8, 70.5, 69.4, 52.8; **IR** (thin layer film) ν (cm^{-1}) = 3358, 3077, 2825, 1643, 1596, 1572, 1477, 1431, 1127, 1394, 1311, 1259, 1191, 1096, 1081, 1058, 996, 973, 922, 885, 836, 785, 733; **HRMS** (ESI$^+$) *m/z* calculated for $C_{20}H_{22}NOCl_2^+$ $[M+H]^+$ 362.1073, found 362.1071.

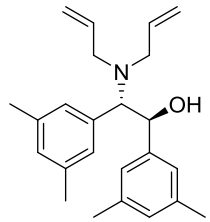
***rac*-2-(diallylamino)-1,2-bis(3-methoxyphenyl)ethan-1-ol (7o)**



rac-**7o**

Alcohol **7o** was prepared following the general procedure (*method A*, 24 h), from *cis*-2,3-bis(3-methoxyphenyl)oxirane (800 mg, 3.12 mmol, 1 equiv.) and diallylamine (1.16 mL, 9.37 mmol, 3 equiv.). Purification by FCC (Hexane:Et_2O = 90:10 to 80:20, gradient) afforded the title compound as a pale yellow oil (788 mg, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.19 (t, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.81 – 6.75 (m, 3H), 6.73 (d, *J* = 7.7 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 6.63 (s, 1H), 5.95 – 5.83 (m, 2H), 5.27 – 5.18 (m, 4H), 5.04 (br s, 1H), 5.00 (d, *J* = 10.4 Hz, 1H), 3.85 (d, *J* = 10.4 Hz, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 3.54 – 3.48 (m, 2H), 2.68 (dd, *J* = 14.1, 8.6 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 159.3 (overlapped), 143.3, 136.3, 135.2, 129.0, 129.0, 122.5, 120.0, 118.3, 116.6, 113.1, 112.9, 112.6, 70.9, 69.1, 55.3, 55.2, 52.9. **IR** (thin layer film) ν (cm^{-1}) = 3350, 2936, 2835, 1600, 1585, 1490, 1260, 1154, 1046, 877. **HRMS** could not be recorded as the compound did not ionize and/or decomposed under any standard technique.

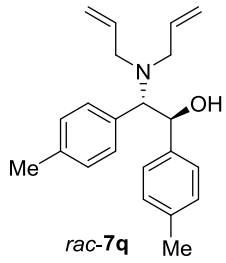
***rac*-2-(diallylamino)-1,2-bis(3,5-dimethylphenyl)ethan-1-ol (7p)**



rac-**7p**

Alcohol **7p** was prepared following the general procedure (*method A*, 24 h), *cis*-2,3-bis(3,5-dimethylphenyl)oxirane (1.00 g, 4 mmol, 1 equiv.) and diallylamine (1.5 mL, 12 mmol, 3 equiv.). Purification by FCC (Hexane:Et_2O = 100:0 to 98:2 gradient) afforded the title compound as a white solid (550 mg, 40% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 6.84 (s, 1H), 6.81 (s, 2H), 6.74 (s, 1H), 6.70 (s , 2H), 5.93 – 5.85 (m, 2H), 5.22 (d, *J* = 13.8 Hz, 4H), 4.95 (d, *J* = 10.3 Hz, 1H), 3.84 (d, *J* = 10.3 Hz, 1H), 3.50 – 3.43 (m, 2H), 2.65 (dd, *J* = 8.7, 14 Hz, 2H), 2.26 (s, 6H), 2.17 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 141.5, 137.3, 137.2, 136.6, 133.5, 129.3, 129.2, 128.0, 125.5, 118.1, 70.8, 69.0, 52.8, 21.6, 21.4; **IR** (thin layer film) ν (cm^{-1}) = 3363, 3078, 3008, 2976, 2918, 1642, 1605, 1448, 1416, 1399, 1377, 1311, 1291, 1158, 1114, 1064, 994, 974, 919, 860, 849, 748, 704; **MP** 99 – 102 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{24}H_{32}NO^+$ $[M+H]^+$ 350.2478, found 350.2479.

***rac*-2-(diallylamino)-1,2-di-*p*-tolylethan-1-ol (7q)**

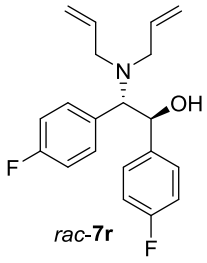


rac-**7q**

cis-2,3-di-p-tolyloxirane (900 mg, 4.02 mmol, 1 equiv.), diallylamine (1.48 mL, 12.0 mmol, 3 equiv.) and $ZnCl_2$ (1.1 g, 8.04 mmol, 2 equiv.) were stirred in DMF (8 mL, 0.5 M) at 70 °C for 24 h. The reaction mixture was then cooled to r.t., diluted with water and extracted three times with DCM. The combined organic layers were washed twice with LiCl (10% w/v solution), dried on $MgSO_4$ and evaporated *in vacuo*. Purification by FCC (Hexane:Et_2O = 100:0 to 95:5, gradient) afforded the title compound as a yellow oil (410 mg, 31% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.11 – 7.08 (m, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 7.02 – 6.97 (m, 2H), 6.96 (d, *J* = 7.9 Hz, 2H), 5.89 (dddd, *J* = 18.1, 9.8, 8.6, 4.1 Hz, 2H), 5.28 – 5.23 (m, 2H), 5.22– 5.20 (m, 2H), 5.07 (br s, 1H), 5.00 (d, *J* = 10.4 Hz, 1H), 3.87 (d, *J* = 10.3 Hz, 1H), 3.53 – 3.47 (m, 2H), 2.63 (dd, *J* = 14.0, 8.6 Hz, 2H), 2.29 (s, 3H), 2.22 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 138.6, 137.3,

136.9, 136.5, 130.5, 130.0, 128.8, 128.8, 127.4, 118.2, 70.8, 69.2, 52.8, 21.2 (overlapped). **IR** (thin layer film) ν (cm^{-1}) = 3364, 3008, 2978, 2922, 1643, 1448, 1396, 1327, 1057, 920, 814; **HRMS** (ESI^+) *m/z* calculated for $C_{22}H_{28}NO^+$ $[M+H]^+$ 322.21654, found 322.21658.

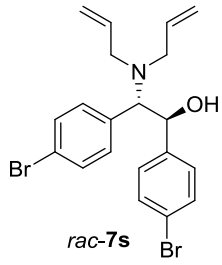
***rac*-2-(diallylamino)-1,2-bis(4-fluorophenyl)ethan-1-ol (7r)**



rac-**7r**

Alcohol **7r** was prepared following the general procedure (*method B*, 72 h), from *cis*-2,3-bis(4-fluorophenyl)oxirane (1.03 g, 4.44 mmol, 1equiv.) and diallylamine (13 mL, 13.3 mmol, 3 equiv.). Purification by FCC(Pentane:EtOAc = 100:0 to 90:10) afforded the title compound as a colorless oil (1.053 g, 73% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.16 – 7.11 (m, 2H), 7.07 – 7.02 (m, 2H), 6.99 – 6.93 (m, 2H), 6.87 – 6.81 (m, 2H), 5.88 (dddd, *J* = 16.9, 10.4, 8.6, 4.1 Hz, 2H), 5.28 – 5.18 (m, 4H), 4.99 (br s, 1H), 4.97 (d, *J* = 10.4 Hz, 1H), 3.83 (d, *J* = 10.3 Hz, 1H), 3.53 – 3.48 (m, 2H), 2.63 (dd, *J* = 13.9, 8.7 Hz, 2H); **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -114.00 – -114.09 (m, 1F), -115.02 – -115.16 (m,1F); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.4 (d, J_{C-F} = 246.0 Hz), 162.2 (d, J_{C-F} = 245.8 Hz), 137.1 (d, J_{C-F} = 3.4 Hz), 136.1, 131.5 (d, J_{C-F} = 7.9 Hz), 129.3 (d, J_{C-F} = 3.6 Hz), 129.0 (d, J_{C-F} = 8.1 Hz), 118.5, 115.2 (d, J_{C-F} = 21.1 Hz), 115.0 (d, J_{C-F} = 21.4 Hz), 70.8, 69.3, 52.8; **IR** (thin layer film) ν (cm^{-1}) = 3367, 3078, 2826, 1644, 1605, 1510, 1224, 924, 835; **HRMS** (ESI^+) *m/z* calcd. for $C_{20}H_{22}FNO^+$ $[M+H]^+$ 330.16640, found 330.16594.

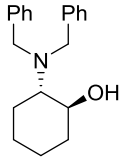
***rac*-1,2-bis(4-bromophenyl)-2-(diallylamino)ethan-1-ol (7s)**



rac-**7s**

Alcohol **7s** was prepared following the general procedure (*method A*, 24h), from *cis*-2,3-bis(4-bromophenyl)oxirane (540 mg, 1.5 mmol, 1 equiv.) and diallylamine (0.55 mL, 4.5 mmol, 3 equiv.). Purification by FCC(Hexane:Et_2O = 100:0 to 80:20, gradient) afforded the title compound as a white solid (450 mg, 67% yield). **^{1}H NMR** (500 MHz, $CDCl_3$); δ = 7.40 (d, *J* = 8.3, 2H), 7.26 (d, *J* = 8.3, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.93 (d, *J* = 8.3 Hz, 2H), 5.92 – 5.78 (m, 2H), 5.29 – 5.49 (m, 4H), 4.92 (d, *J* = 10.3 Hz, 1H), 3.76 (d, *J* = 10.3 Hz, 1H), 3.47 (d, *J* = 14.0 Hz, 2H), 2.59 (dd, *J* = 8.7, 14.0 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 140.5, 136.0, 132.4, 131.7, 131.6, 131.4, 129.2, 122.3, 121.6, 118.8, 70.6, 69.4, 52.9; **IR** (thin layer film) ν (cm^{-1}) = 3372, 3068, 3015, 2973, 2916, 2830, 2810, 1486, 1446, 1389, 1353, 1340, 1324, 1286, 1103, 1008, 998, 974, 87, 799, 727; **MP** 119 – 120 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{20}H_{22}NOBr_2^+$ $[M+H]^+$ 450.00736, found 450.00641.

***rac*-2-(dibenzylamino)cyclohexan-1-ol (7t)**

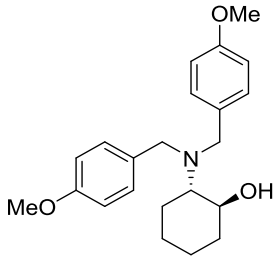


rac-**7t**

Alcohol **7t** was prepared following the general procedure (*method A*, overnight) from cyclohexene oxide (5 mL, 50 mmol, 1 equiv.) and dibenzylamine (18.5 mL, 100 mmol, 2 equiv.). Purification by FCC (Pentane: EtOAc = 95:5 to 80:20, gradient) afforded the title compound as a white solid (11.32 g, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.36 – 7.20 (m, 10H), 3.85 (d, *J* = 13.3 Hz, 2H), 3.77 (br s, 1H), 3.51 (td, *J* = 10.0, 4.4 Hz, 1H), 3.37 (d, *J* = 13.3 Hz, 2H), 2.36 (ddd, *J* = 11.9, 9.7, 3.4 Hz, 1H), 2.12 – 2.02 (m, 1H), 2.02 – 1.92 (m, 1H), 1.82 – 1.74 (m, 1H), 1.72 – 1.61 (m, 1H), 1.32 – 1.03 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 139.5, 129.0, 128.5, 127.2, 69.1, 64.2,

53.6, 33.3, 25.5, 24.2, 22.1; **IR** (thin layer film) ν (cm^{-1}) = 3449, 3061, 3027, 1494, 1452, 1129, 1093, 987, 751, 736, 699; **MP** 86 – 87 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{20}H_{26}NO^+$ $[M+H]^+$ 296.20089, found 296.20081. Spectroscopic data were in agreement with the ones previously reported in literature.[6]

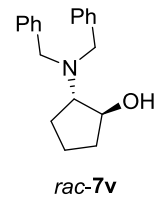
***rac*-2-(bis(4-methoxybenzyl)amino)cyclohexan-1-ol (7u)**



rac-**7u**

Alcohol **7u** was prepared following the general procedure (*method A*, overnight) from cyclopentene oxide (384 µl, 3.8 mmol, 1 equiv.) and bis(4-methoxybenzyl)amine[7] (2.00 g, 7.75 mmol, 2 equiv.). Purification by FCC (Pentane: EtOAc = 95:5 to 80:20, gradient) afforded the title compound as a pale-yellow oil (1.35 g, 99% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.17 (d, *J* = 8.5 Hz, 4H), 6.85 (d, *J* = 8.5 Hz, 4H), 3.82 – 3.74 (m, 9H), 3.49 (td, *J* = 10.0, 4.4 Hz, 1H), 3.29 (d, *J* = 13.2 Hz, 2H), 2.34 (ddd, *J* = 11.8, 9.7, 3.4 Hz, 1H), 2.13 – 2.02 (m, 1H), 1.98 – 1.90 (m, 1H), 1.82 – 1.74 (m, 1H), 1.72 – 1.62 (m, 1H), 1.34 – 1.03 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.8, 131.7, 130.1, 113.9, 69.0, 63.9, 55.3, 52.8, 33.3, 25.6, 24.2, 22.2; **IR** (thin layer film): ν (cm^{-1}) = 2918, 2850, 2361, 1736, 1612, 1512, 1463, 1302, 1248, 1174, 1089, 1036, 808, 617; **HRMS** (ESI^+) *m/z* calculated for $C_{22}H_{30}NO_3^+$ $[M+H]^+$ 356.22202, found 356.22178.

***rac*-2-(dibenzylamino)cyclopentan-1-ol (7v)**

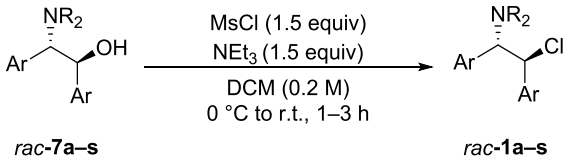


rac-**7v**

Alcohol **7v** was prepared following the general procedure (*method A*, overnight) from cyclopentene oxide (872 µl, 10 mmol, 1 equiv.) and dibenzylamine (3.8 mL, 20 mmol, 2 equiv.). Purification by FCC (Pentane: EtOAc = 95:5 to 80:20, gradient) afforded the title compound as a white solid (2.51 g, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.43 – 7.36 (m, 4H), 7.36 – 7.29 (m, 4H), 7.29 – 7.21 (m, 2H), 4.09 (q, *J* = 7.4 Hz, 1H), 3.79 (d, *J* = 13.8 Hz, 2H), 3.52 (d, *J* = 13.8 Hz, 2H), 2.99 – 2.92 (m, 1H), 1.98 (br s, 1H), 1.94-184 (m, 1H), 1.83 – 1.74 (m, 1H), 1.70 – 1.55 (m, 3H), 1.49 –1.39 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 140.2, 128.7, 128.4, 127.0, 73.8, 68.8, 55.1, 31.7, 22.1, 20.1; **IR** (thin layer film) ν (cm^{-1}) = 3391, 3061, 3027, 2954, 2872, 1493, 1453, 1362, 1248, 1105, 978, 737, 697; **MP** 47 – 50 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{19}H_{24}NO^+$ $[M+H]^+$ 282.18524 found 282.18514.

β-Chloro and β-Bromoamines

General Procedure for the Synthesis of β-Chloroamines:

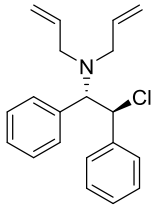


rac-**7a–s** *rac*-**1a–s**

Following the procedure reported by Nelson,[4] the appropriate aminoalcohol (1 equiv.) was dissolved in anhydrous DCM (0.2 M) and the solution was cooled to 0 °C. NEt_3 (1.5 equiv.) was added at once, followed by dropwise addition of MsCl (1.5 equiv.) at 0 °C. The reaction mixture was allowed to warm to r.t. and stirred for 1–3 h. After disappearance of both the starting material and the mesylate intermediate (monitored by ^{1}H NMR), the reaction mixture was washed with $NaHCO_3$ (sat.) and brine. The organic layers were dried over $MgSO_4$, filtered and evaporated *in vacuo*. The crude product was then purified with a short silica plug.

N.B. No degradation was observed when silica plugs were employed for purification, however extended contact with silica led to hydrolysis of these compounds.

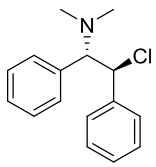
***rac*-*N*, *N*-diallyl-2-chloro-1,2-diphenylethan-1-amine (1a)**



rac-**1a**

Chloride **1a** was prepared according to the general procedure from **7a** (2.50 g, 8.5 mmol) followed by purification through a silica pad using toluene as eluent. White solid (2.40 g, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.24 – 7.06 (m, 8H), 7.01 – 6.96 (m, 2H), 5.97 (dddd, J = 17.3, 10.2, 8.1, 4.2 Hz, 2H), 5.41 (d, J = 11.0 Hz, 1H), 5.32 – 5.25 (m, 2H), 5.24 – 5.17 (m, 2H), 4.37 (d, J = 11.0 Hz, 1H), 3.56 – 3.48 (m, 2H), 2.73 (dd, J = 14.2, 8.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 140.2, 137.3, 135.2, 129.3, 128.4, 128.2, 128.0, 128.0, 127.3, 117.2, 68.8, 63.8, 53.1. **IR** (thin layer film) ν (cm^{-1}) = 3065, 3030, 2813, 1641, 1494, 1453, 1417, 1211, 1030, 920, 720, 696; **MP** 47 – 49 °C; **HRMS** ($APCI^+$) *m/z* calculated for $C_{20}H_{23}ClN^+$ $[M+H]^+$ 312.15135, found 312.15100.

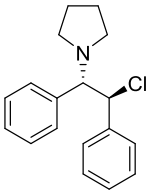
***rac*-1(-2-chloro-*N*,*N*-dimethyl-1,2-diphenylethan-1-amine (1b)**



rac-**1b**

Chloride **1b** was prepared according to the general procedure from **7b** (1.00 g, 4.0 mmol) followed by purification through a silica pad using DCM:EtOAc 1:1 as eluent. Ivory solid (710 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.27 – 7.09 (m, 8H), 7.02 – 6.97 (m, 2H), 5.39 (d, J = 10.8 Hz, 1H), 4.13 (d, J = 10.8 Hz, 1H), 2.35 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 139.8, 133.6, 129.5, 128.4, 128.2, 128.1, 127.8, 127.5, 74.8, 63.2, 41.1. **IR** (thin layer film) ν (cm^{-1}) = 3030, 2968, 2936, 2826, 2783, 1493, 1452, 1267, 1174, 1047, 784, 717, 704; **MP** 51 – 55 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{16}H_{19}ClN^+$ $[M+H]^+$ 260.12005, found 260.12015. Spectroscopic data were in agreement with the ones previously reported in literature.[8]

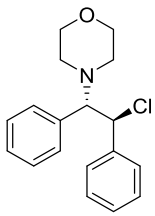
***rac*-1(-2-chloro-1,2-diphenylethyl)pyrrolidine (1c)**



rac-**1c**

Chloride **1c** was prepared according to the general procedure from **7c** (2.27 g, 8.5 mmol) followed by purification through a silica pad using Hexane:Et_2O (96:4 to 80:20, gradient) as eluent. Ivory solid (1.73 g, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.21 – 7.03 (m, 8H), 7.05 – 6.93 (m, 2H), 5.44 (d, *J* = 7.5 Hz, 1H), 4.08 (d, *J* = 7.4 Hz, 1H), 2.79 – 2.65 (m, 2H), 2.64 – 2.50 (m, 2H), 1.84 – 1.67 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 139.1, 136.4, 130.0, 128.5, 127.9, 127.9, 127.5, 127.4, 74.5, 64.4, 50.9, 23.4. **IR** (thin layer film) ν (cm^{-1}) = 3061, 2956, 2798, 1994, 1452, 1358, 1312, 1127, 1075, 1031, 702; **MP** 42 – 43 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{18}H_{21}ClN^+$ $[M+H]^+$ 286.13570, found 286.13539. Spectroscopic data were in agreement with the ones previously reported in literature.[4]

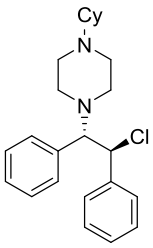
***rac*-4-(2-chloro-1,2-diphenylethyl)morpholine (1d)**



rac-**1d**

Chloride **1d** was prepared according to the general procedure from **7d** (600 mg, 2.12 mmol) followed by purification through a silica pad using Hexane:EtOAc (100:0 to 90:10, gradient) as eluent. Pale pink solid (562.6 mg, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.27 – 7.11 (m, 8H), 7.02 – 6.96 (m, 2H), 5.42 (d, *J* = 10.4 Hz, 1H), 4.09 (d, *J* = 10.4 Hz, 1H), 3.83 (ddd, *J* = 11.0, 6.3, 3.1 Hz, 2H), 3.76 (ddd, *J* = 11.0, 6.1, 3.1 Hz, 2H), 2.62 (ddd, *J* = 9.9, 6.4, 3.0 Hz, 2H), 2.52 (ddd, *J* = 10.7, 6.3, 3.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 139.6, 134.4, 129.3, 128.4, 128.2, 128.1, 128.0, 127.7, 75.3, 67.4, 62.4, 49.7; **IR** (thin layer film) ν (cm^{-1}) = 3030, 2957, 2855, 2818, 1494, 1451, 1114, 697; **MP** 142 – 145 °C; **HRMS** ($APCI^+$) *m/z* calculated for $C_{28}H_{21}ClNO^+$ $[M+H]^+$ 3012.13062, found 3012.13062.

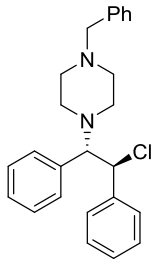
***rac*-1-(2-chloro-1,2-diphenylethyl)-4-cyclohexylpiperazine (1e)**



rac-**1e**

Chloride **1e** was prepared according to the general procedure from **7e** (750 mg, 2.00 mmol) followed by purification through a silica pad using DCM:EtOAc (100:0 to 80:20, gradient) as eluent. White solid (541 mg, 71% yield). **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 7.36 (d, *J* = 7.6 Hz, 2H), 7.16 – 7.04 (m, 8H), 5.88 (d, *J* = 11.3 Hz, 1H), 4.23 (d, *J* = 11.4 Hz, 1H), 2.65 – 2.06 (m, 9H), 1.73 – 1.61 (m, 4H), 1.57 – 1.47 (m, 1H), 1.23 – 0.94 (m, 5H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ = 140.3, 133.9, 129.3, 128.2, 128.1, 127.7, 127.3, 126.9, 72.5, 62.6, 62.0, 48.7, 48.3, 28.2, 25.9, 25.2; **IR** (thin layer film) ν (cm^{-1}) = 2928, 2853, 2817, 1494, 1452, 1376, 1287, 1145, 1005, 703; **MP** 103 – 105 °C; **HRMS** ($APCI^+$) *m/z* calculated for $C_{24}H_{32}ClN_2^+$ $[M+H]^+$ 383.22485, found 383.22513.

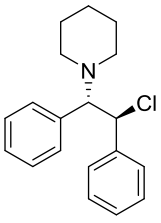
***rac*-1-benzyl-4-(-2-chloro-1,2-diphenylethyl)piperazine (1f)**



rac-**1f**

Chloride **1f** was prepared according to the general procedure from **7f** (660 mg, 1.77 mmol) followed by purification through a silica pad using Hexane:Et_2O (100:0 to 85:15, gradient) as eluent. White solid (458 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.30 – 7.18 (m, 7H), 7.16 – 7.06 (m, 6H), 6.96 – 6.91 (m, 2H), 5.37 (d, *J* = 10.6 Hz, 1H), 4.07 (d, *J* = 10.6 Hz, 1H), 3.48 (s, 2H), 2.64–2.42 (m, 8H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 139.9, 138.3, 134.6, 129.4, 129.3, 128.3, 128.3, 128.2, 128.0, 127.9, 127.5, 127.1, 74.8, 63.3, 62.7, 53.6, 49.1 (br); **IR** (thin layer film) ν (cm^{-1}) = 3062, 2934, 2813, 1494, 1453, 1137, 1007, 733, 698; **MP** 112 – 114 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{25}H_{28}ClN_2^+$ $[M+H]^+$ 391.19355, found 391.19302.

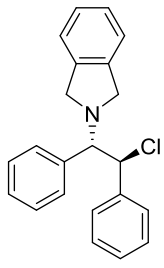
***rac*-1-(2-chloro-1,2-diphenylethyl)piperidine (1g)**



rac-**1g**

Chloride **1g** was prepared according to the general procedure from **7g** (2.22 g, 7.9 mmol) followed by purification through a silica pad using Pentane:EtOAc = 90:10 as eluent. White solid (1.45 g, 61% yield). **For the multi-decagram scale reaction:** The alcohol **7g** (111.7 g, 0.4 mol, 1 equiv.) was dissolved in DCM (0.5 M, 800 mL) and the solution was cooled to 0 °C. MsCl (46 mL, 0.6 mol, 1.5 equiv.) followed by dry NEt_3 (83 mL, 0.6 mol, 1.5 equiv.) were slowly added (dropping funnel) at 0 °C. The reaction mixture was then stirred at r.t. for 2 h. After quenching at 0 °C by addition of $NaHCO_3$ (sat.), the aqueous phase was extracted three times with Et_2O and the combined organic phases were washed with brine, dried over $MgSO_4$ and evaporated *in vacuo*. The crude product was quickly passed through a silica plug (Pentane:EtOAc = 70:30). Finally, the light brown solid was washed with small amounts of Et_2O to afford a white solid (85.3 g , 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.24 – 7.19 (m, 2H), 7.19 – 7.06 (m, 6H), 6.98 – 6.93 (m, 2H), 5.39 (d, *J* = 10.8 Hz, 1H), 4.04 (d, *J* = 10.8 Hz, 1H), 2.57 – 2.48 (m, 2H), 2.41 – 2.33 (m, 2H), 1.73 – 1.54 (m, 4H), 1.40 – 1.30 (m, 2H); **^{13}C NMR (**101 MHz, $CDCl_3$) δ = 140.0, 134.9, 129.2, 128.2, 128.1, 127.9, 127.6, 127.2, 75.4, 62.8, 50.4, 26.4, 24.6; **IR** (thin layer film) ν (cm^{-1}) = 3030, 2932, 2851, 2802, 1493, 1452, 1306, 1200, 1161, 1102, 990, 869, 718, 696, 658; **MP** 93 – 95 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{29}H_{23}ClN^+$ $[M+H]^+$ 300.15135, found 300.15118.

***rac*-2-(-2-chloro-1,2-diphenylethyl)isoindoline (1h)**

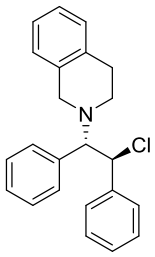


rac-**1h**

Chloride **1h** was prepared according to the general procedure from **7h** (530 mg, 1.68 mmol) followed by purification by FCC using Pentane:Et_2O (100:0 to 98:2, gradient) as eluent. Due to the limited stability of the compound, the solvent was evaporated under a flow of nitrogen without evaporation *in vacuo* (thus avoiding warm water baths). White solid (200 mg, 34% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.21 – 7.14 (m, 12H), 7.10 – 7.02 (m, 2H), 5.53 (d, *J* = 6.7 Hz, 1H), 4.36 (d, *J* = 6.8 Hz, 1H), 4.20 (d, *J* = 11.9 Hz, 2H), 4.09 (d, *J* = 11.9 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) [overlapping signals] δ = 139.4, 138.5, 136.5, 130.1, 128.5, 128.1, 127.9, 127.8, 126.9, 122.4, 74.9, 64.3, 57.1; **IR** (thin layer film) ν (cm^{-1}) = 3030, 2939, 2892, 2793,

1493, 1464, 1363, 1314, 1133, 1077, 909, 742, 702; **MP** 84 – 86 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{22}H_{21}ClN^+$ $[M+H]^+$ 334.13570, found 334.13528.

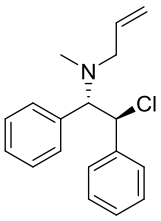
***rac*-2-(2-chloro-1,2-diphenylethyl)-1,2,3,4-tetrahydroisoquinoline (1i)**



rac-**1i**

Chloride **1i** was prepared according to the general procedure from **7i** (750 mg, 2.3 mmol) followed by purification through a silica pad using Pentane:Et_2O (100:0 to 95:5, gradient) as eluent. White solid (628 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.33 – 7.28 (m, 2H), 7.27 – 7.08 (m, 11H), 7.07 – 7.02 (m, 1H), 5.58 (d, *J* = 10.5 Hz, 1H), 4.34 (d, *J* = 10.5 Hz, 1H), 3.83 (d, *J* = 14.5 Hz, 1H), 3.73 (d, *J* = 14.6 Hz, 1H), 3.22 – 3.03 (m, 2H), 2.96 (dt, *J* = 16.0, 4.5 Hz, 1H), 2.68 (ddd, *J* = 10.4, 8.2, 4.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 139.8, 135.2, 134.8, 134.7, 129.3, 128.8, 128.4, 128.2, 128.1, 128.0, 127.6, 126.6, 126.0, 125.6, 74.7, 62.9, 52.7, 46.1, 30.0; **IR** (thin layer film) ν (cm^{-1}) = 3028, 2916, 2805, 1495, 1454, 1134, 1099, 1001, 936, 730, 697. **MP** 85 – 87 °C; **HRMS** ($APCI^+$) *m/z* calculated for $C_{23}H_{23}ClN^+$ $[M+H]^+$ 348.15135, found 348.15155. Spectroscopic data were in agreement with the ones previously reported in literature.[8]

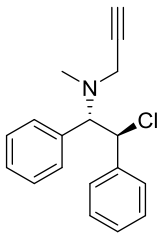
***rac*-*N*-(2-chloro-1,2-diphenylethyl)-*N*-methylprop-2-en-1-amine (1j)**



rac-**1j**

Chloride **1j** was prepared according to the general procedure from **7j** (700 mg, 2.6 mmol) followed by purification through a silica pad using Pentane:Et_2O (100:0 to 90:10, gradient) as eluent. White solid (581 mg, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.24 – 7.06 (m, 8H), 6.99 – 6.94 (m, 2H), 5.99 (dddd, *J* = 17.5, 10.2, 7.6, 5.1 Hz, 1H), 5.40 (d, *J* = 11.0 Hz, 1H), 5.28 – 5.18 (m, 2H), 4.24 (d, *J* = 10.9 Hz, 1H), 3.24 (ddt, *J* = 13.7, 5.2, 1.8 Hz, 1H), 2.89 (dd, *J* = 13.7, 7.6 Hz, 1H), 2.30 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 140.0, 136.8, 134.3, 129.4, 128.4, 128.2, 128.1, 127.9, 127.4, 117.5, 72.2, 63.4, 57.3, 37.6; **IR** (thin layer film) ν (cm^{-1}) = 3063, 3030, 2974, 2853, 2793, 1642, 1493, 1451, 1205, 1156, 1020, 998, 921, 758, 720, 697. **MP** 60 – 61 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{18}H_{21}ClN^+$ $[M+H]^+$ 286.13570, found 286.13580.

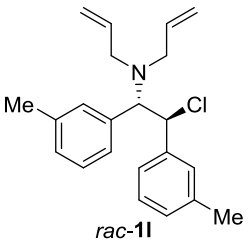
***rac*-*N*-(2-chloro-1,2-diphenylethyl)-*N*-methylprop-2-yn-1-amine (1k)**



rac-**1k**

Chloride **1k** was prepared according to the general procedure from **7k** (500 mg, 1.88 mmol) followed by purification through a silica pad using Pentane:Et_2O (100:0 to 90:10, gradient) as eluent. White solid (420 mg, 79% yield).**^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.27 – 7.23 (m, 2H), 7.23 – 7.13 (m, 6H), 7.08 – 7.03 (m, 2H), 5.45 (d, *J* = 9.8 Hz, 1H), 4.46 (d, *J* = 9.8 Hz, 1H), 3.44 (dd, *J* = 16.5, 2.5 Hz, 1H), 3.16 (dd, *J* = 16.6, 2.4 Hz, 1H), 2.44 (s, 3H), 2.32 (t, *J* = 2.5 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 139.5, 134.0, 129.7, 128.2 (overlapped), 128.1, 127.9, 127.8, 80.0, 73.2, 71.9, 62.9, 44.2, 37.8; **IR** (thin layer film) ν (cm^{-1}) = 3293, 3030, 2796, 1493, 1452, 1208, 1122, 1076, 1059, 1022, 757, 696; **MP** 45–46 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{18}H_{19}ClN^+$ $[M+H]^+$ 284.12005, found 284.11990.

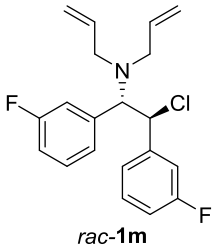
***rac*-*N*-allyl-*N*-(-2-chloro-1,2-di-m-tolylethyl)prop-2-en-1-amine (1l)**



rac-**1l**

Chloride **1l** was prepared according to the general procedure from **7l** (480 mg, 2.8 mmol) followed by purification through a silica pad using toluene as eluent. White solid (280 mg, 55% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.10 – 6.95 (m, 4H), 6.95 – 6.86 (m, 2H), 6.86 – 6.83 (m, 2H), 6.06 – 5.88 (m, 2H), 5.37 (d, J = 11.0 Hz, 1H), 5.27 (d, J = 17.0 Hz, 2H), 5.19 (d, J = 10.4 Hz, 2H), 4.30 (d, J = 11, 1H), 3.48 (d, J = 14.5, 2H), 2.71 (dd, J = 8.0, 14.5 Hz, 2H), 2.24 (s, 3H), 2.22 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 140.2, 137.9, 137.4, 137.3, 135.1, 130.1, 128.9, 128.8, 128.2, 128.0, 127.7, 126.3, 125.2, 117.1, 68.4, 64.0, 53.2, 21.6, 21.4; **IR** (thin layer film) ν (cm^{-1}) = 3022, 2920, 2813, 1641, 1605, 1489, 1445, 1417, 1378, 1344, 1262, 1155, 1123, 1093, 1042, 997, 973, 918, 883, 791, 775, 708; **MP** 54 – 56 °C **HRMS** ($APCI^+$) *m/z* calculated for $C_{22}H_{27}ClN^+$ $[M+H]^+$ 340.1826, found 340.1826.

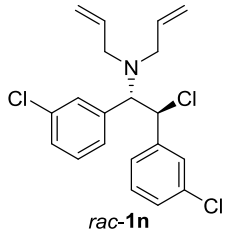
***rac*-*N*-allyl-*N*-2-chloro-1,2-bis(3-fluorophenyl)ethyl)prop-2-en-1-amine (1m)**



rac-**1m**

Chloride **1m** was prepared according to the general procedure from **7m** (500 mg, 1.5 mmol) followed by purification through a silica pad using toluene as eluent. White solid (350 mg, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.19 – 7.07 (m, 2H), 7.00 – 6.90 (m, 2H), 6.88 – 6.78 (m, 2H), 6.75 (d, J = 8.0 Hz, 1H), 6.68 (d, J = 9.5 Hz, 1H) 5.99 – 5.87 (m, 2H), 5.35 – 5.17 (m, 5H), 4.28 (d, J = 10.7 Hz, 1H), 3.49 (d, J = 14.6 Hz, 2H), 2.70 (dd, J = 14.2, 8.0 Hz, 2H); **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -112.6 (m, 1F), -112.7 (m, 1F); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.6 (d, J_{C-F} = 246.6 Hz), 162.5 (d, J_{C-F} = 246.6 Hz), 141.3 (d, J_{C-F} = 8 Hz), 139.6 (d, J_{C-F} = 8.0 Hz), 136.8, 130.0 (d, J_{C-F} = 8.5 Hz), 129.6 (d, J_{C-F} = 8.5 Hz), 124.9 (d, J_{C-F} = 2.8 Hz), 123.9 (d, J_{C-F} = 2.8 Hz), 178.6, 115.9 (d, J_{C-F} = 20.7 Hz), 115.3 (d, J_{C-F} = 20.7 Hz), 115.1 (d, J_{C-F} = 22.3 Hz), 114.5 (d, J_{C-F} = 21.3 Hz), 68.3, 62.4, 53.1; **IR** (thin layer film) ν (cm^{-1}) = 3078, 2926, 2814, 1641, 1612, 1590, 1488, 1446, 1418, 1344, 1258, 1140, 1077, 998, 976, 922, 878, 782, 767, 734, 703; **MP** 65 – 66 °C; **HRMS** ($APCI^+$) *m/z* calculated for $C_{20}H_{21}ClF_2N^+$ $[M+H]^+$ 348.1325, found 348.1323.

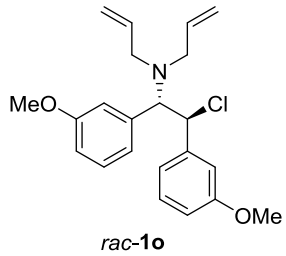
***rac*-*N*-allyl-*N*-2-chloro-1,2-bis(3-chlorophenyl)ethyl)prop-2-en-1-amine (1n)**



rac-**1n**

Chloride **1n** was prepared according to the general procedure from **7n** (540 mg, 1.5 mmol) followed by purification through a silica pad using toluene as eluent. White solid (540 mg, 90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.21 (s, 1H), 7.18 – 7.02 (m, 5H), 6.96 (s, 1H), 6.86 – 6.82 (s, 1H), 5.92 (dddd, J = 17.9, 10.1, 8.0, 4.3 Hz, 2H), 5.35 – 5.16 (m, 5H), 4.26 (d, J = 10.8 Hz, 1H), 3.53 – 3.42 (m, 2H), 2.71 (dd, J = 8.0, 14.6, 5.0 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 141.8, 137.0, 136.7, 134.3, 134.2, 129.8, 129.4, 129.1, 128.5, 128.3, 127.8, 127.3, 126.4, 117.7, 68.4, 62.3, 53.1; **IR** (thin layer film) ν (cm^{-1}) = 3076, 3008, 2977, 2925, 2814, 1641, 1593, 1573, 1476, 1430, 1344, 1265, 1210, 1195, 1155, 1124, 1096, 1080, 1049, 998, 975, 922, 883, 845; **MP** 67 – 68 °C; **HRMS** ($APCI^+$) *m/z* calculated for $C_{20}H_{21}Cl_3N^+$ $[M+H]^+$ 382.0705, found 382.0702.

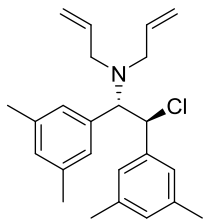
***rac*-*N*-allyl-*N*-(2-chloro-1,2-bis(3-methoxyphenyl)ethyl)prop-2-en-1-amine (1o)**



rac-**1o**

Chloride **1o** was prepared according to the general procedure from **7o** (750 mg, 2.12 mmol) followed by purification through a silica pad using Hexane:Et_2O 80:20 as eluent. White solid (592 mg, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.14 – 7.02 (m, 2H), 6.84 – 6.79 (m, 1H), 6.77 (t, *J* = 2.6 Hz, 1H), 6.69 – 6.63 (m, 2H), 6.60 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.53 – 6.50 (m, 1H), 5.95 (dddd, *J* = 17.2, 10.1, 8.1, 4.2 Hz, 2H), 5.35 (d, *J* = 10.9 Hz, 1H), 5.31 – 5.24 (m, 2H), 5.21 – 5.17 (m, 2H), 4.31 (d, *J* = 10.9 Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.50 (ddt, *J* = 14.3, 4.2, 2.0 Hz, 2H), 2.74 (ddt, *J* = 14.2, 8.1, 1.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.4, 159.2, 141.7, 137.3, 136.8, 129.4, 128.9, 121.6, 120.6, 117.2, 115.5, 114.1, 113.4, 112.3, 68.5, 63.6, 55.3, 55.2, 53.2. **IR** (thin layer film) ν (cm^{-1}) = 3076, 3004, 2936, 2834, 1600, 1585, 1491, 1436, 1261, 1154, 1046, 921, 730; **MP** 69 – 70 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{22}H_{27}ClNO_2^+$ $[M+H]^+$ 372.17248, found 372.17236.

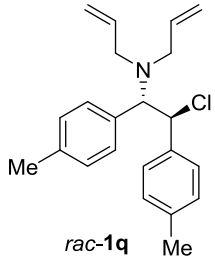
***rac*-*N*-allyl-*N*-2-chloro-1,2-bis(3,5-dimethylphenyl)ethyl)prop-2-en-1-amine (1p)**



rac-**1p**

Chloride **1p** was prepared according to the general procedure from **7p** (450 mg, 1.3 mmol) followed by purification through a silica pad using toluene as eluent. White solid (300 mg, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$); δ = 6.82 (s, 2H), 6.74 (d, *J* = 8.7 Hz, 2H), 6.59 (s, 2H), 6.03 – 5.90 (m, 2H), 5.35 (d, *J* = 10.6 Hz, 1H), 5.27 (d, *J* = 17.3 Hz, 2H), 5.19 (d, *J* = 10 Hz, 2H), 4.27 (d, *J* = 10.6 Hz, 1H), 3.50 – 3.42 (m, 2H), 2.70 (dd, *J* = 8.7, 1.4 Hz, 2H), 2.21 (s, 6H), 2.18 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 140.1, 137.7, 137.6, 137.0, 134.9, 129.8, 128.8, 127.2, 126.0, 117.2, 68.1, 64.1, 53.2, 21.5, 21.3; **IR** (thin layer film) ν (cm^{-1}) = 3075, 3010, 2918, 2812, 1640, 1604, 1446, 1416, 1376, 1344, 1288, 1265, 1206, 1123, 1038, 997, 975, 916, 850, 774, 727, 698, 689, 660; **MP** 109 – 110 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{24}H_{31}ClN^+$ $[M+H]^+$ 368.2139, found 368.2141.

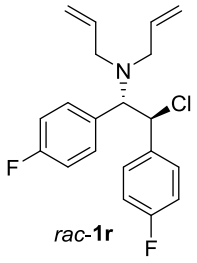
***rac*-*N*-allyl-*N*-(2-chloro-1,2-di-p-tolylethyl)prop-2-en-1-amine (1q)**



rac-**1q**

Chloride **1q** was prepared according to the general procedure from **7q** (380 mg, 1.18 mmol) followed by purification by FCC using Pentane:Et_2O (95:5 to 90:10, gradient) as eluent. White solid (346 mg, 86% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.10 (d, *J*= 7.6 Hz, 2H), 6.98 (d, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 7.5 Hz, 2H), 6.02 – 5.90 (m, 2H), 5.39 (d, *J* = 11.0 Hz, 1H), 5.27 (d, *J* = 17.3 Hz, 2H), 5.19 (d, *J*= 10.1 Hz, 2H), 4.33 (d, *J* = 11.0 Hz, 1H), 3.48 (ddd, *J* = 14.3, 4.3, 2.1 Hz, 2H), 2.68 (dd, *J* = 14.3, 8.1 Hz, 2H), 2.23 (s, 3H), 2.21 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 137.7, 137.5, 137.4, 136.8, 132.0, 129.2, 129.1, 128.7, 128.0, 117.1, 68.1, 63.8, 53.1, 21.2, 21.1; **IR** (thin layer film) ν (cm^{-1}) = 3008, 2977, 2922, 2812, 1641, 1513, 1344, 1263, 1042, 919, 811, 739; **MP** 55 – 56 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{22}H_{27}ClN^+$ $[M+H]^+$ 340.18265, found 340.18288.

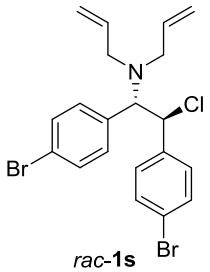
***rac*-*N*-allyl-*N*-(2-chloro-1,2-bis(4-fluorophenyl)ethyl)prop-2-en-1-amine (1r)**



rac-**1r**

Chloride **1r** was prepared according to the general procedure from **7r** (900 mg, 2.73 mmol) followed by purification by FCC using pentane:Et_2O (100:0 to 98:2, gradient) as eluent. White solid (776 mg, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.17 – 7.12 (m, 2H), 6.95 – 6.81 (m, 6H), 5.94 (dddd, J = 17.2, 10.2, 8.0, 4.2 Hz, 2H), 5.33 (d, J = 10.9 Hz, 1H), 5.26 (dtd, J = 17.3, 2.0, 1.0 Hz, 2H), 5.20 (dtd, J = 10.2, 1.9, 0.8 Hz, 2H), 4.29 (d, J = 10.9 Hz, 1H), 3.49 (ddt, J = 14.2, 4.1, 2.0 Hz, 2H), 2.77 – 2.63 (m, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -113.41– -113.49 (m, 1F), -114.52 – -114.62 (m, 1F); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.1 (d, $J_{C–F}$ = 247.6 Hz), 162.0 (d, $J_{C–F}$ = 245.6 Hz), 137.0, 136.0 (d, $J_{C–F}$ = 3.3 Hz), 131.0 (d, $J_{C–F}$ = 3.4 Hz), 130.7 (d, $J_{C–F}$ = 7.8 Hz), 129.8 (d, $J_{C–F}$ = 8.2 Hz), 117.5, 115.4 (d, $J_{C–F}$ = 21.6 Hz), 115.1 (d, $J_{C–F}$ = 21.1 Hz), 68.4, 62.8, 53.1; **IR** (thin layer film) ν (cm^{-1}) = 307, 278, 2814, 1604, 1509, 1230, 1159, 922, 833, 750; **MP** 81 – 83 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{20}H_{21}F_2ClN^+$ $[M+H]^+$ 348.13251, found 348.13226.

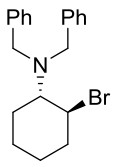
***rac*-*N*-allyl-*N*-2-chloro-1,2-bis(4-bromophenyl)ethyl)prop-2-en-1-amine (1s)**



rac-**1s**

Chloride **1s** was prepared according to the general procedure from **7s** (450 mg, 1.0 mmol) followed by purification through a silica pad using toluene as eluent. White solid (320 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$); δ = 7.37 – 7.24 (m, 4H), 7.10 – 7.02 (m, 2H), 6.86 – 6.79 (m, 2H), 6.01 – 5.84 (m, 2H), 5.34 – 5.16 (m, 5H) 4.26 (d, J = 10.9 Hz, 1H), 3.52 – 3.40 (m, 2H), 2.67 (dd, J = 8, 14.8 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 139.0, 136.8, 133.9, 131.7, 131.4, 130.7, 129.8, 122.2, 121.6, 117.6, 68.2, 62.4, 53.1; **IR** (thin layer film) ν (cm^{-1}) = 3077, 3007, 2976, 2924, 2814, 1641, 1590, 1521, 1488, 1447, 1416, 1405, 1183, 1125, 1106, 1074, 1010, 975, 921, 881, 834, 752, 726, 704; **MP** 83 – 86 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{20}H_{21}ClNBr_2^+$ $[M+H]^+$ 467.9724, found 467.9728.

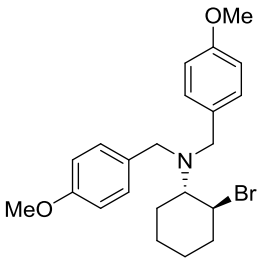
***rac*-*N*,*N*-dibenzyl-2-bromocyclohexan-1-amine (1t)**



rac-**1t**

Following the procedure reported by Chong,[9] alcohol **7t** (3.49 g, 12 mmol, 1 equiv.) and PPh_3 (3.78 g, 14.4 mmol, 1.2 equiv.) were dissolved in anhydrous $CHCl_3$ (60.0 mL, 0.2 M). The reaction mixture was cooled to 0 °C and NBS (2.56 g, 14.4 mmol, 1.2 mmol) was added portionwise. The reaction was stirred at r.t. until disappearance of the starting material (monitored by TLC). The solvent was removed *in vacuo* and the crude product was purified by FCC (Pentane:EtOAc = 100:0 to 95:5, gradient). White solid (1.96 g, 45%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.52 (d, J = 7.3 Hz, 4H), 7.36 – 7.28 (m, 4H), 7.27 – 7.20 (m, 2H), 4.16 (td, J = 11.4, 4.3 Hz, 1H), 3.88 (d, J = 13.7 Hz, 2H), 3.47 (d, J = 13.7 Hz, 2H), 2.67 (td, J = 11.3, 3.7 Hz, 1H), 2.47 – 2.36 (m, 1H), 2.17 – 2.06 (m, 1H), 1.86 – 1.71 (m, 2H), 1.69 – 1.61 (m, 1H), 1.39 – 1.06 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 140.0, 129.2, 128.2, 126.9, 63.3, 55.8, 53.7, 38.9, 27.7, 26.3, 25.3; **IR** (thin layer film): ν (cm^{-1}) = 3061, 3026, 2933, 2856, 2802, 1494, 1452, 1141, 745, 697; **MP** 93 – 95 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{20}H_{25}BrN^+$ $[M+H]^+$ 358.11649, found 358.11694.

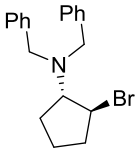
***rac*-2-bromo-*N*,*N*- bis(4-methoxybenzyl)cyclohexan-1-amine (1u)**



rac-**1u**

Alcohol **7u** (1.5 g, 4.2 mmol, 1 equiv.), CBr_4 (1.39 g, 4.2 mmol, 1 equiv.) and PPh_3 (1.10 g, 4.2 mmol, 1 equiv.) were stirred in anhydrous CH_3CN at r.t. for 24 h. Then Et_2O was added causing the precipitation of a white solid. The mixture was filtered and the solvent removed *in vacuo*. Purification by FCC (Pentane:EtOAc= 99:1 to 96:4, gradient) afforded the title compound as a white solid (662 mg, 38% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.40 (d, *J* = 8.6 Hz, 4H), 6.85 (d, *J* = 8.6 Hz, 4H), 4.14 (td, *J* = 11.3, 4.3 Hz, 1H), 3.84 – 3.76 (m, 8H), 3.38 (d, *J* = 13.5 Hz, 2H), 2.65 (td, *J* = 11.2, 3.6 Hz, 1H), 2.46 – 2.36 (m, 1H), 2.11 – 2.03 (m, 1H), 1.83 – 1.70 (m, 2H), 1.68- 1.60 (m, 1H), 1.37 – 1.07 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.6, 132.1, 130.2, 113.6, 63.0, 56.0, 55.4, 52.8, 38.9, 27.7, 26.2, 25.3; **IR** (thin layer film): ν (cm^{-1}) = 2932, 2856, 2833, 1611, 1509, 1245, 1170, 1035; **MP** 69 – 72 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{22}H_{29}BrNO_2^+$ $[M+H]^+$ 418.13762, found 418.13770.

***rac*-*N*,*N*-dibenzyl-2-bromocyclopentan-1-amine (1v)**

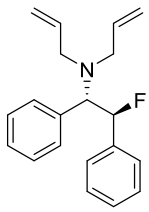


rac-**1v**

Alcohol **7v** (750 mg, 2.66 mmol, 1 equiv.) was dissolved in anhydrous DCM (6.7 mL, 0.2 M) and the solution was cooled to 0 °C. NEt_3 (403 µL, 3.99 mmol, 1.5 equiv.) was added at once, followed by dropwise addition of MsBr (634 µL, 3.99 mmol, 1.5 equiv.) at 0 °C. The reaction mixture was allowed to warm to r.t. and stirred for 6 h. After disappearance of both the starting material and the mesylate intermediate (monitored by ^{1}H NMR), the reaction mixture was washed with $NaHCO_3$ (sat.). The organic layer was dried over $MgSO_4$, filtered and evaporated *in vacuo*. The crude product was then purified with a short silica plug (Pentane:Et_2O = 98:2) to afford the title compound as a pale yellow solid (647 mg, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.44 – 7.39 (m, 4H), 7.33 – 7.28 (m, 4H), 7.25 – 7.20 (m, 2H), 4.33 (q, *J* = 6.9 Hz, 1H), 3.75 (d, *J* = 14.0, 2H), 3.60 (d, *J* = 14.0, 2H), 3.56 – 3.50 (m, 1H), 2.22 – 2.15 (m, 1H), 1.99 – 1.90 (m, 1H), 1.88 – 1.80 (m, 1H), 1.78 – 1.56 (m, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 138.9, 128.8, 128.3, 127.1, 69.6, 54.7, 51.5, 36.6, 25.4, 22.6; **IR** (thin layer film): ν (cm^{-1}) = 3027, 2961, 2801, 1493, 1453, 1363, 1028, 743, 698; **MP** 40 – 42 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{19}H_{23}BrN^+$ $[M+H]^+$ 344.10084, found 344.10092.

Product Characterization

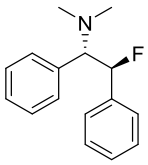
N-allyl-*N*-((1*S*,2*S*)-2-fluoro-1,2-diphenylethyl)prop-2-en-1-amine (2a)



(*S*,*S*)-**2a**

Fluoride **2a** was prepared from **1a** (62.4 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at –15 °C for 72 h. *Purification:* FCC, eluent = Hexane:Et_2O (100:0 to 99.6:0.4, gradient). Colorless oil, 42.0 mg, 71% yield, e.r. = 95:5. **Method B:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at –15 °C for 72 h. *Purification:* FCC, eluent = Hexane:Et_2O (100:0 to 99.6:0.4, gradient). Colorless oil, 56.3 mg, 95% yield, e.r. = 95:5. **Gram scale reaction:** In a round bottom flask, **1a** (1.1 g, 3.53 mmol, 1 equiv.), catalyst (*S*)-**3g** (148 mg, 0.105 mmol, 3 mol%) and KF (1.025 g, 17.6 mmol, 5 equiv.) were stirred at +5 °C in dry $CHCl_3$ at 900 rpm. After 96 h the reaction mixture was filtered through a silica plug eluting with DCM/EtOAc = 1:1. *Purification:* FCC, eluent = Hexane:Et_2O (100:0 to 99.6:0.4, gradient) to elute the pure product (colorless oil, 794 mg, 76% yield, e.r. = 93:7); then Hexane:EtOAc (95:5 to 80:20, gradient) to recover the catalyst (140 mg, 94% catalyst recovery). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.19 – 7.06 (m, 10H), 5.82 (dd, *J* = 47.2, 7.2 Hz, 1H), 5.69 (dddd, *J* = 17.5, 10.1, 7.6, 4.9 Hz, 2H), 5.11 – 4.99 (m, 4H), 4.15 (dd, *J* = 18.2, 7.2 Hz, 1H), 3.47 – 3.40 (m, 2H), 2.83 (dd, *J* = 14.3, 7.6 Hz, 2H); **^{19}F NMR** (377 MHz, CDCl3) δ = -179.25 (dd, *J* = 47.2, 18.2 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 138.7 (d, $J_{C\text{-}F}$ = 20.3 Hz), 137.1, 136.6 (d, $J_{C\text{-}F}$ = 4.5 Hz), 129.7 (d, $J_{C\text{-}F}$ = 1.2 Hz), 128.2 (d, $J_{C\text{-}F}$ = 2.0 Hz), 128.1, 128.0, 127.4, 127.0 (d, $J_{C\text{-}F}$ = 6.7 Hz), 117.1, 95.3 (d, $J_{C\text{-}F}$ = 178.6 Hz), 67.3 (d, $J_{C\text{-}F}$ = 20.9 Hz), 54.0 (d, $J_{C\text{-}F}$ = 2.1 Hz); **IR** (thin layer film) ν (cm^{-1}) = 3066, 3031, 2923, 2814, 1641, 1495, 1453, 1418, 1205, 1124, 1080, 1031, 918, 759, 698, 607; **HRMS** (APCI$^+$) *m/z* calculated for $C_{20}H_{23}FN^+$ $[M+H]^+$ 296.18090, found 296.18069; **$[\alpha]_D^{25\,°C}$** = +27.5 ° (c = 0.5, $CHCl_3$, e.r. = 95:5); **HPLC separation**: DAICEL CHIRALPAK® IA-3, Heptane:^{i}PrOH = 99.75:0.25, 1 mL/min; t_1 = 3.37 min (minor), t_2 = 3.61 min (major).

(1*S*,2*S*)-2-fluoro-*N*,*N*-dimethyl-1,2-diphenylethan-1-amine (2b)

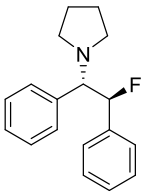


(*S*,*S*)-**2b**

Fluoride **2b** was prepared from **1b** (52.0 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at +5 °C for 72 h. *Purification:* FCC, eluent = Toluene:Et_2O (100:0 to 95:5, gradient +2% NEt_3). Colorless oil, 34.2 mg, 65% yield, e.r. = 95:5. **Method B:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at 0 °C for 72 h. *Purification:* FCC eluent = Toluene:Et_2O (100:0 to 95:5, gradient +2% NEt_3). Colorless oil, 41.3 mg, 85% yield, e.r. = 97:3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.14 – 7.02 (m, 8H), 6.95 (dd, *J* = 7.6, 2.0 Hz, 2H), 5.76 (dd, *J* = 47.5, 8.8 Hz, 1H), 3.80 (dd, *J* = 12.3, 8.8 Hz, 1H), 2.29 (s, 6H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -172.86 (dd, *J* = 47.6, 12.3 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 138.1 (d, $J_{C\text{-}F}$ = 20.1 Hz), 135.2 (d, $J_{C\text{-}F}$ = 6.8 Hz), 129.6, 128.3 (d, $J_{C\text{-}F}$ = 2.3 Hz), 128.1, 128.0, 127.6, 127.1 (d, $J_{C\text{-}F}$ = 6.2 Hz), 94.2 (d, $J_{C\text{-}F}$ = 177.3 Hz), 74.3 (d, $J_{C\text{-}F}$ = 22.1 Hz), 42.7 (d, $J_{C\text{-}F}$ = 1.8 Hz); **IR** (thin layer film) ν (cm^{-1}) = 3032, 2967, 2825, 2781, 1603, 1494, 1309, 992, 758, 697; **HRMS** (ESI$^+$) *m/z* calculated for $C_{16}H_{19}FN^+$ $[M+H]^+$ 244.14960, found 244.14951. **$[\alpha]_D^{25\,°C}$** = –22.7 ° (c = 0.9, $CHCl_3$, e.r. = 97:3); **HPLC separation**:

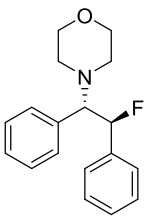
DAICEL CHIRALPAK® ID-3, Heptane: ^{i}PrOH = 99.6:0.4 + 0.1% Et_2NH, 1 mL/min; t_1 = 4.05 min (major), t_2 = 4.44 min (minor).

(1*S*,2*S*)-(2-fluoro-1,2-diphenylethyl)pyrrolidine (2c)


(*S*,*S*)-**2c**

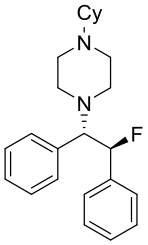
Fluoride **2c** was prepared from **1c** (57.2 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at 0 °C for 72 h. *Purification:* FCC, eluent = Pentane:Et_2O (98:2 to 95:5, gradient). White solid, 49.5 mg, 92% yield, e.r. = 94.5:5.5. **Method B:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at -20 °C for 36 h. *Purification:* FCC, eluent = Hexane:Et_2O (98:2 to 96:4, gradient). White solid, 48.5 mg, 90% yield, e.r. = 97:3. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.16 – 7.09 (m, 6H), 7.04-6.98 (m, 4H), 5.75 (dd, *J* = 46.8, 7.6 Hz, 1H), 3.70 (dd, *J* = 13.2, 7.6 Hz, 1H), 2.80 – 2.68 (m, 2H), 2.62 – 2.53 (m, 2H), 1.83 – 1.72 (m, 4H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -170.81 (dd, *J* = 47.3, 13.4 Hz, 1F); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 138.5 (d, $J_{C\text{-}F}$ = 7.5 Hz), 138.1 (d, $J_{C\text{-}F}$ = 20.7 Hz), 129.3, 128.0 (d, $J_{C\text{-}F}$ = 2.0 Hz), 127.9, 127.8, 127.4, 126.8 (d, $J_{C\text{-}F}$ = 6.6 Hz), 97.3 (d, $J_{C\text{-}F}$ = 177.6 Hz), 74.9 (d, $J_{C\text{-}F}$ = 23.0 Hz), 53.4 (d, $J_{C\text{-}F}$ = 3.4 Hz), 23.4; **IR** (thin layer film) ν (cm^{-1}) = 3032, 2966, 2793, 1493, 1454, 1131, 996, 763, 698; **MP** 58 – 60 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{18}H_{21}FN^+$ $[M+H]^+$ 270.16525, found 270.16513; **$[\alpha]_D^{25\,°C}$ =** –25.5 ° (c = 0.5, $CHCl_3$, e.r. = 97:3); **HPLC separation**: DAICEL CHIRALPAK® IC-3, Heptane:EtOH = 99.75:0.25 + 0.2% ^{n}$BuNH_2$, 1 mL/min; t_1 = 3.30 min (minor), t_2 = 3.49 min (major).

4-((1*S*,2*S*)-2-fluoro-1,2-diphenylethyl)morpholine (2d)


(*S*,*S*)-**2d**

Fluoride **2d** was prepared from **1d** (60.4 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 15 mol% of catalyst (*S*)-**3g**. The reaction was stirred at +10 °C for 72 h. *Purification:* FCC, eluent = DCM: Pentane = 95:5 to DCM:EtOAc = 97:3, gradient. White solid, 46.6 mg, 81% yield, e.r. = 94:6. **Method B**: 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at +5 °C for 72 h. **Purification**: FCC eluent = DCM:Pentane = 95:5 to DCM:EtOAc = 97:3, gradient. White solid, 43.0 mg, 75 % yield, e.r. = 94.5:5.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.19 – 7.13 (m, 6H), 7.13 – 7.09 (m, 2H), 7.07 – 7.03 (m, 2H), 5.83 (dd, *J* = 47.1, 7.9 Hz, 1H), 3.83 (dd, *J* = 14.9, 7.9 Hz, 1H), 3.73 (dd, *J* = 5.5, 3.9 Hz, 4H), 2.64 (dd, *J* = 6.0, 3.5 Hz, 4H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -171.87 (dd, *J* = 47.2, 15.0 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 138.0 (d, $J_{C\text{-}F}$ = 20.6 Hz), 136.2 (d, $J_{C\text{-}F}$ = 6.9 Hz), 129.4, 128.2 (d, $J_{C\text{-}F}$ = 2.1 Hz), 128.0, 127.9, 127.6, 126.8 (d, $J_{C\text{-}F}$ = 6.4 Hz), 95.0 (d, $J_{C\text{-}F}$ = 178.1 Hz), 74.6 (d, $J_{C\text{-}F}$ = 21.9 Hz), 67.3, 51.6 (d, $J_{C\text{-}F}$ = 2.9 Hz); **IR** (thin layer film) ν (cm^{-1}) = 3032, 2957, 2852, 2815, 1494, 1452, 1117, 993, 881, 760, 699; **MP** 59 – 62 °C; **HRMS** (APCI$^+$) *m/z* calculated for $C_{18}H_{21}FNO^+$ $[M+H]^+$ 286.16017, found 286.16010; **$[\alpha]_D^{25\,°C}$ =** –29.4 ° (c = 0.5, $CHCl_3$, e.r. = 94.5:5.5); **HPLC separation**: DAICEL CHIRALPAK® IC-3, Heptane:^{i}PrOH:^{n}$BuNH_2$ = 99.0: 0.9: 0.1, 1 mL/min; t_1 = 9.89 min (major), t_2 = 10.97 min (minor).

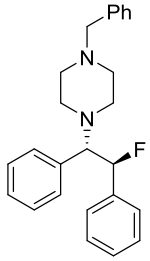
1-cyclohexyl-4-((1*S*,2*S*)-2-fluoro-1,2-diphenylethyl)piperazine (2e)



(*S*,*S*)-**2e**

Fluoride **2e** was prepared from **1e** (76.6 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at +5 °C for 72 h. *Purification:* FCC, eluent = DCM:Pentane = 95:5 to DCM:MeOH = 98:2, gradient. White solid, 66.6 mg, 90% yield, e.r. = 94:6. **Method B:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at 0 °C for 72 h. *Purification:* FCC eluent = DCM:Pentane = 95:5 to DCM:MeOH = 98:2, gradient. White solid, 67.4 mg, 94% yield, e.r. = 96:4. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.18 – 7.08 (m, 8H), 7.04 – 7.00 (m, 2H), 5.82 (dd, *J* = 47.3, 8.2 Hz, 1H), 3.89 (dd, *J* = 13.7, 8.2 Hz, 1H), 2.84 – 2.61 (m, 7H), 2.33 (br s, 1H), 1.95 (br s, 2H), 1.85 – 1.74 (m, 2H), 1.66 – 1.58 (m, 1H), 1.28 – 1.17 (m, 5H), 1.15 – 1.05 (m, 1H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -172.48 (d, *J* = 49.1 Hz, 1F); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 138.0 (d, $J_{C\text{-}F}$ = 20.4 Hz), 135.8 (d, $J_{C\text{-}F}$ = 6.7 Hz), 129.4, 128.2 (d, $J_{C\text{-}F}$ = 2.1 Hz), 128.0, 127.9, 127.5, 126.9 (d, $J_{C\text{-}F}$ = 6.3 Hz), 94.6 (d, $J_{C\text{-}F}$ = 178.0 Hz), 74.0 (d, $J_{C\text{-}F}$ = 21.8 Hz), 63.9, 50.3, 49.2, 28.6, 26.1, 25.7; **IR** (thin layer film) ν (cm^{-1}) = 3062, 3031, 2918, 2853, 2814, 1494, 1452, 1282, 1153, 994, 759, 699; **MP** 92 – 95 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{24}H_{32}FN_2^+$ $[M+H]^+$ 367.25440, found 367.25519 **$[\alpha]_D^{25\ °C}$ =** –21.1 ° (c = 0.5, $CHCl_3$, e.r. = 94:6); **HPLC separation**: DAICEL CHIRALPAK® IA-3, Heptane:EtOH = 99:1 +0.2% ^{n}BuNH$_2$, 1 mL/min; t_1 = 6.29 min (minor), t_2 = 7.19 min (major).

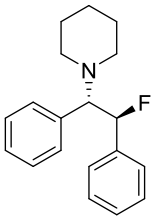
1-benzyl-4-((1*S*,2*S*)-2-fluoro-1,2-diphenylethyl)piperazine (2f)



(*S*,*S*)-**2f**

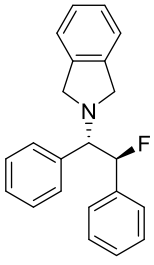
Fluoride **2f** was prepared from **1f** (78.0 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at 0 °C for 72 h. *Purification:* FCC, eluent = DCM:EtOAc (100:0 to 50:50, gradient). White solid, 51.8 mg, 69% yield, e.r. = 95:5. **Method B:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at 0 °C for 48 h. *Purification:* FCC eluent = DCM:EtOAc (100:0 to 50:50, gradient), white solid, 63.0 mg, 84% yield, e.r. = 95.5:4.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.32 – 7.20 (m, 5H), 7.19 – 7.11 (m, 8H), 7.06 – 7.02 (m, 2H), 5.84 (dd, *J* = 47.2, 8.2 Hz, 1H), 3.89 (dd, *J* = 14.1, 8.2 Hz, 1H), 3.50 (s, 2H), 2.76 – 2.60 (m, 4H), 2.57-2.45 (m, 4H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -173.21 (dd, *J* = 47.3, 14.1 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 138.2 (d, $J_{C\text{-}F}$ = 18.3 Hz), 138.1, 135.8 (d, $J_{C\text{-}F}$ = 6.3 Hz), 129.5, 129.3, 128.1, 128.1 (d, $J_{C\text{-}F}$ = 1.9 Hz), 127.9 (overlapped), 127.4, 127.0, 126.9 (d, $J_{C\text{-}F}$ = 6.5 Hz), 94.3 (d, $J_{C\text{-}F}$ = 178.1 Hz), 74.1 (d, $J_{C\text{-}F}$ = 21.8 Hz), 63.1, 53.5, 50.5. **IR** (thin layer film) ν (cm^{-1}) = 3030, 2932, 2811, 1494, 1454, 1289, 1137, 1006, 759, 698; **MP** 56 – 58 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{25}H_{28}FN_2^+$ $[M+H]^+$ 375.22310, found 375.22314. **$[\alpha]_D^{25\ °C}$ =** –22.7 ° (c = 0.5, $CHCl_3$, e.r. = 95.5:4.5); **HPLC separation**: DAICEL CHIRALPAK® IA-3, Heptane:EtOH = 99.5:0.5 +0.2% Et_2NH, 1 mL/min; t_1 = 6.40 min (major), t_2 = 8.55 min (minor).

1-((1*S*,2*S*)-2-fluoro-1,2-diphenylethyl)piperidine (2g)


(*S*,*S*)-**2g**

Fluoride **2g** was prepared from **1g** (60.0 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at -10 °C for 72 h. *Purification:* FCC, eluent = Pentane:Et_2O (100:0 to 97:3, gradient). White solid, 36.3 mg, 56% yield, e.r. = 96:4. **Method B:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at -10 °C for 24 h. *Purification:* FCC eluent = Pentane:Et_2O (100:0 to 94:6, gradient). White solid, 51.0 mg, 90% yield, e.r. = 95:5. **Multi-Decagram scale reaction**: A 250 mL round-bottom flask was charged with chloride **1g** (50.0 g, 300 mmol, 1 equiv.), catalyst (*S*)-**3g** (1.169 g, 0.836 mmol, 0.5 mol%) and KF (29.10 g, 501.7 mmol, 3 equiv.). DCM was added (84 mL, 2 M) and the mixture was stirred at r.t. for 72 h. After filtration on a celite pad (eluted with Et_2O), the solvent was removed *in vacuo* and the crude mixture was re-dissolved in Et_2O. A 1 M solution of HCl was added and the product was counter-extracted from the organic phase into the acqueous phase three times (as the HCl salt). The organic phase (containing the catalyst) was evaporated *in vacuo* and after purification by FCC (Pent:EtOAc 100:0 to 80:20, gradient), 1.157 g of catalyst were recovered (99% recovery). The pH of the combined aqueous phases was then raised to 8–9 with a 3 M NaOH solution. EtOAc was added and the acqueous phase was extracted with EtOAc three times. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated *in vacuo*. The crude product (45.1 g, e.r.= 92:8) was purified by recrystallization from warm MeOH (45.1 mL, reflux to r.t.) to afford **2g** as a white solid (31.1 g, 66% yield, e.r.= 97:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.19 – 7.15 (m, 8H), 7.08 – 7.03 (m, 2H), 5.88 (dd, *J* = 47.4, 8.5 Hz, 1H), 3.93 (dd, *J* = 13.4, 8.5 Hz, 1H), 2.61 (ddd, *J* = 11.1, 7.0, 3.7 Hz, 2H), 2.50 (ddd, *J* = 11.0, 7.0, 3.6 Hz, 2H), 1.72 – 1.53 (m, 4H), 1.42-1.34 (m, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -174.27 (dd, *J* = 47.3, 13.6 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 138.4 (d, $J_{C\text{-}F}$ = 20.2 Hz), 135.8 (d, $J_{C\text{-}F}$ = 6.4 Hz), 129.6, 128.1 (d, $J_{C\text{-}F}$ = 2.2 Hz), 127.9, 127.7, 127.3, 127.0 (d, $J_{C\text{-}F}$ = 6.4 Hz), 93.7 (d, $J_{C\text{-}F}$ = 177.9 Hz), 74.6 (d, $J_{C\text{-}F}$ = 21.8 Hz), 51.5, 26.2, 24.6; **IR** (thin layer film) ν (cm^{-1}) = 3031, 2932, 2802, 1494, 1452, 1160, 988, 758, 698; **MP** 63 – 65 °C; **HRMS** ($APCI^+$) *m/z* calculated for $C_{19}H_{23}FN^+$ $[M+H]^+$ 284.18090, found 284.18103. **$[\alpha]_D^{25\,°C}$** = –33.8 ° (c = 0.5, $CHCl_3$, e.r. = 95:5); **HPLC separation**: DAICEL CHIRALPAK® IC-3 Heptane:EtOH:^{n}BuNH$_2$ = 99.5:0.1:0.4, 1 mL/min: t_1 = 3.40 min (major), t_2 = 4.01 min (minor).

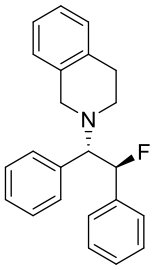
2-((1*S*,2*S*)-2-fluoro-1,2-diphenylethyl)isoindoline (2h)


(*S*,*S*)-**2h**

Fluoride **2h** was prepared from **1h** (68.0 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at 0 °C for 72 h. *Purification:* FCC, eluent = Pentane:Et_2O (100:0 to 97:3, gradient). White solid, 48.0 mg, 76% yield, e.r. = 92:8. **Method B:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at -10 °C for 72 h. *Purification:* FCC, eluent = Pentane:Et_2O (100:0 to 97.5:2.5, gradient). White solid, 39.0 mg, 61% yield, e.r. = 93:7. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.21 – 7.13 (m, 10H), 7.12 – 7.08 (m, 2H), 7.05 – 7.01 (m, 2H), 5.79 (dd, *J* = 47.0, 7.6 Hz, 1H), 4.17 – 4.11 (m, 2H), 4.10 – 4.00 (m, 3H); **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -170.50 (dd, *J* = 47.1, 13.2 Hz,

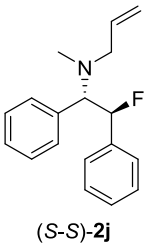
1F); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 139.9, 138.2 (d, $J_{C\text{-}F}$ = 7.8 Hz), 137.8 (d, $J_{C\text{-}F}$ = 20.8 Hz), 129.4, 128.3, 128.2 (d, $J_{C\text{-}F}$ = 2.1 Hz), 127.9, 127.7, 126.9, 126.8, 122.3, 98.1 (d, $J_{C\text{-}F}$ = 178.0 Hz), 74.6 (d, $J_{C\text{-}F}$ = 22.7 Hz), 59.0 (d, $J_{C\text{-}F}$ = 3.9 Hz); **IR** (thin layer film) ν (cm^{-1}) = 3031, 2940, 2790, 1490, 1454, 1337, 1264, 1137, 1075, 992, 764, 745, 700; **MP** 79 – 80 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{22}H_{21}FN^+$ $[M+H]^+$ 318.16525, found 318.16501. **$[\alpha]_D^{25\,°C}$ =** –16.8 ° (c = 0.5, $CHCl_3$, e.r. = 92:8); **HPLC separation**: DAICEL CHIRALPAK® IA-3, Heptane:^{i}PrOH = 99:1, 1 mL/min; t_1 = 4.52 min (minor), t_2 = 5.54 min (major).

2-((1*S*,2*S*)-2-fluoro-1,2-diphenylethyl)-1,2,3,4-tetrahydroisoquinoline (2i)


(*S*,*S*)-**2i**

Fluoride **2i** was prepared from **1i** (66.0 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at 0 °C for 72 h. *Purification:* FCC eluent = Pentane:Et_2O (100:0 to 98:2, gradient). Colorless oil, 60.5 mg, 91% yield, e.r. = 96:4. **Method B:** 5 mol% of catalyst (*S*)-**3g**. The reaction was stirred at 0 °C for 72 h. *Purification:* FCC, eluent = Pentane:Et_2O (100:0 to 98:2, gradient). Colorless oil, 63.6 mg, 96% yield, e.r. = 96:4. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.22 – 7.08 (m, 13H), 7.03 – 6.99 (m, 1H), 5.97 (dd, *J* = 47.1, 8.0 Hz, 1H), 4.10 (dd, *J* = 14.3, 8.0 Hz, 1H), 3.93 (d, *J* = 14.8 Hz, 1H), 3.84 (d, *J* = 14.8 Hz, 1H), 3.09 (dt, *J* = 10.8, 5.2 Hz, 1H), 2.97 (ddd, *J* = 16.2, 8.0, 5.0 Hz, 1H), 2.92 – 2.76 (m, 2H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -172.35 (dd, *J* = 47.4, 14.3 Hz, 1F); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 138.3 (d, $J_{C\text{-}F}$ = 20.5 Hz), 136.4 (d, $J_{C\text{-}F}$ = 6.5 Hz), 135.3, 134.7, 129.6, 128.8, 128.3 (d, $J_{C\text{-}F}$ = 2.1 Hz), 128.1, 128.1 , 127. 7, 127.0 (d, $J_{C\text{-}F}$ = 6.4 Hz), 126.8, 126.1, 125.6, 95.0 (d, $J_{C\text{-}F}$ = 178.1 Hz), 73.9 (d, $J_{C\text{-}F}$ = 22.0 Hz), 53. 9 (d, $J_{C\text{-}F}$ = 3.2 Hz), 48.2 (d, $J_{C\text{-}F}$ = 2.2 Hz), 29.7; **IR** (thin layer film) ν (cm^{-1}) = 3030, 2919, 2803, 1586, 1496, 1454, 1133, 1087, 995, 935, 742, 698; **HRMS** (ESI^+) *m/z* calculated for $C_{23}H_{23}FN^+$ $[M+H]^+$ 332.18090, found 332.18057. **$[\alpha]_D^{25\,°C}$** = –45.6 ° (c = 0.5, $CHCl_3$, e.r. = 96:4); **HPLC separation**: DAICEL CHIRALPAK® IF-3, Heptane:^{i}PrOH = 99:1, 1 mL/min; t_1 = 4.77 min (major), t_2 = 5.83 min (minor).

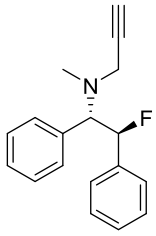
***N*-((1*S*,2*S*)-2-fluoro-1,2-diphenylethyl)-*N*-methylprop-2-en-1-amine (2j)**


(*S*-*S*)-**2j**

Fluoride **2j** was prepared from **1j** (53.9 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at -10 °C for 72 h. *Purification:* FCC, eluent = Pentane:Et_2O (100:0 to 95:5, gradient). Colorless oil, 48 mg, 89% yield, e.r. = 95.5:4.5. **Method B:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at -15 °C for 72 h. FCC, eluent = Pentane:Et_2O (100:0 to 95:5, gradient). Colorless oil, 38.5 mg, 72% yield, e.r. = 95.5:4.5. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.23 – 7.14 (m, 8H), 7.10 – 7.06 (m, 2H), 5.97 – 5.81 (m, 1H), 5.88 (dd, *J* = 47.5, 8.5 Hz, 1H), 5.23 – 5.09 (m, 2H), 4.10 (dd, *J* = 13.8, 8.5 Hz, 1H), 3.26 (dd, *J* = 13.7, 5.2 Hz, 1H), 2.99 (dd, *J* = 13.7, 7.3 Hz, 1H), 2.38 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -174.62 (dd, *J* = 47.5, 13.8 Hz, 1F); **^{13}C NMR** (126 MHz, $CDCl_3$) δ= 138.3 (d, $J_{C\text{-}F}$ = 20.1 Hz), 136.6, 135.5 (d, $J_{C\text{-}F}$ = 6.2 Hz), 129.7, 128.3 (d, $J_{C\text{-}F}$ = 2.3 Hz), 128.1 128.0, 127.6, 127.1 (d, $J_{C\text{-}F}$ = 6.5 Hz), 117.5, 94.4 (d, $J_{C\text{-}F}$ = 177.5 Hz), 71.4 (d, $J_{C\text{-}F}$ = 21.8 Hz), 58.4, 38.7 (d, $J_{C\text{-}F}$ = 2.1 Hz); **IR** (thin layer film) ν (cm^{-1}) = 3065, 3032, 2928, 2794, 1494, 1453, 1207, 996, 919, 759, 698; **HRMS** (ESI^+) *m/z* calculated for $C_{18}H_{21}NF^+$ $[M+H]^+$ 270.16525, found 270.16501. **$[\alpha]_D^{25\,°C}$ =** –5.0° (c = 0.5, $CHCl_3$, e.r. = 95.5:4.5); **HPLC separation**:

DAICEL CHIRALPAK® IA, Heptane:^{i}PrOH:^{n}BuNH$_2$ = 99.5:0.4:0.1, 1 mL/min; t_1 = 5.47 min (minor), t_2 = 6.00 min (major).

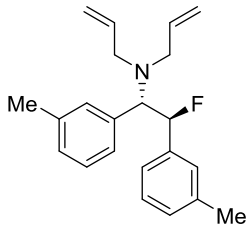
***N*-((1S,2S)-2-fluoro-1,2-diphenylethyl)-*N*-methylprop-2-yn-1-amine (2k)**



(*S*-*S*)-**2k**

Fluoride **2k** was prepared from **1k** (56.8 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at 0 °C for 72 h. *Purification:* FCC, eluent = Pentane:Et_2O (100:0 to 95:5, gradient). Colorless oil, 39.3 mg, 73% yield, e.r. = 94:6. **Method B:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at 0 °C for 72 h. *Purification:* FCC eluent = Pentane:Et_2O (100:0 to 95:5, gradient). Colorless oil, 36.9 mg, 69% yield, e.r. = 96:4. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = δ 7.17–7.13 (m, 6H), 7.11 – 7.05 (m, 4H), 5.81 (dd, *J* = 47.0, 7.9 Hz, 1H), 4.14 (dd, *J* = 14.1, 7.9 Hz, 1H), 3.52 (dd, *J* = 17.0, 2.4 Hz, 1H), 3.28 (dd, *J* = 17.0, 2.3 Hz, 1H), 2.53 (d, *J* = 1.9 Hz, 3H), 2.27 (t, *J* = 2.4 Hz, 1H); **^{19}F NMR** (471 MHz, $CDCl_3$ -170.82 (dd, *J* = 47.2, 14.2 Hz, 1F); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 138.11 (d, $J_{C\text{-}F}$ = 20.6 Hz), 136.67 (d, $J_{C\text{-}F}$ = 7.0 Hz), 129.54, 128.22 (d, $J_{C\text{-}F}$ = 2.2 Hz), 128.13, 127.96, 127.71, 126.95 (d, $J_{C\text{-}F}$ = 6.4 Hz), 95.77 (d, $J_{C\text{-}F}$ = 177.7 Hz), 79.42, 73.33, 71.26 (d, $J_{C\text{-}F}$ = 22.7 Hz), 45.16 (d, $J_{C\text{-}F}$ = 3.1 Hz), 40.23 (d, $J_{C\text{-}F}$ = 4.0 Hz); **IR** (thin layer film) ν (cm^{-1}) = 3296, 2924, 1454, 1019, 759, 699, 625; **HRMS** (ESI$^+$) *m/z* calculated for $C_{18}H_{19}FN^+$ $[M+H]^+$ 268.14960, found 268.14926. **$[\alpha]_D^{25\ °C}$** +48.5 ° (c = 0.5, $CHCl_3$, e.r. = 94:6); **HPLC separation**: DAICEL CHIRALPAK® IC-3, Heptane:^{i}PrOH = 99:1, 1 mL/min; t_1 = 4.15 min (major), t_2 = 4.63 min (minor).

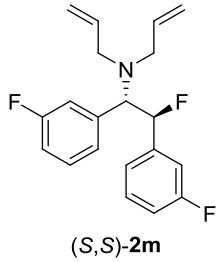
***N*-allyl-*N*-((1*S*,2*S*)-2-fluoro-1,2-di-m-tolylethyl)prop-2-en-1-amine (2l)**



(*S*,*S*)-**2l**

Fluoride **2l** was prepared from **1l** (68.0 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 5 mol% of catalyst (*S*)-**3g**. The reaction was stirred at 0 °C for 72 h. *Purification:* FCC, eluent = Pentane:Et_2O (100:0 to 99:1, gradient). Colorless oil, 56.3 mg, 87% yield, e.r. = 96:4. **Method B:** 5 mol% of catalyst (*S*)-**3g**. The reaction was stirred at 0 °C for 24 h. *Purification:* FCC eluent = Hexane:Et_2O (100:0 to 98.7:1.3, gradient). Colorless oil, 53.5 mg, 83% yield, e.r. = 96:4. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.16 – 7.10 (m, 2H), 7.07 – 6.96 (m, 6H), 5.86 (dd, *J* = 47.2, 7.1 Hz, 1H), 5.83–5.72 (m, 2H), 5.22 – 5.06 (m, 4H), 4.18 (dd, *J* = 18.5, 7.1 Hz, 1H), 3.50 (ddt, *J* = 14.3, 5.0, 1.8 Hz, 2H), 2.91 (dd, *J* = 14.3, 7.5 Hz, 2H), 2.30 (s, 3H), 2.29 (s, 3H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -179.33 (dd, *J* = 47.3, 18.6 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 138.7 (d, $J_{C\text{-}F}$ = 20.1 Hz), 137.6, 137.3, 136.6 (d, $J_{C\text{-}F}$ = 4.4 Hz), 130.5, 128.9, (d, $J_{C\text{-}F}$ = 2.0 Hz), 128.1, 127.9, 127.9, 127.7 (d, $J_{C\text{-}F}$ = 6.6 Hz), 126.7, 124.1, 124.0, 117.0, 95.5 (d, $J_{C\text{-}F}$ = 178.3 Hz), 67.1 (d, $J_{C\text{-}F}$ = 20.7 Hz), 54.1 (d, $J_{C\text{-}F}$ = 2.1 Hz), 21.7, 21.5; **IR** (thin layer film) ν (cm^{-1}) = 3009, 2921, 2813, 1641, 1607, 1489, 1447, 1417, 1159, 997, 917, 787, 703; **HRMS** (ESI$^+$) *m/z* calculated for $C_{22}H_{27}FN^+$ $[M+H]^+$ 324.21220, found 324.21282. **$[\alpha]_D^{25\ °C}$** = +24.0 ° (c = 0.5, $CHCl_3$, e.r. = 96:4); **HPLC separation**: DAICEL CHIRALPAK® IA-3, Heptane:^{i}PrOH = 99:1, 1 mL/min; t_1 = 2.51 min (minor), t_2 = 2.88 min (major).

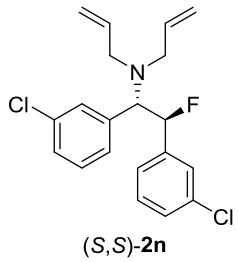
***N*-allyl-*N*-((1S,2S)-2-fluoro-1,2-bis(3-fluorophenyl)ethyl)prop-2-en-1-amine (2m)**



(*S*,*S*)-**2m**

Fluoride **2m** was prepared from **1m** (69.6 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at +10 °C for 72 h. *Purification:* FCC, eluent = Pentane:Et_2O (100:0 to 99.6:0.4, gradient). Colorless oil, 48.2 mg, 73% yield, e.r. = 94:6. **Method B:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at 0 °C for 72 h. *Purification:* FCC eluent = Pentane:Et_2O (100:0 to 99.5:0.5, gradient). Colorless oil, 46.5 mg, 70% yield, e.r. = 95.5:4.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.27 – 7.18 (m, 2H), 7.02 – 6.90 (m, 6H), 5.85 (dd, *J* = 46.8, 6.4 Hz, 1H), 5.71 (dddd, *J* = 17.5, 10.1, 7.6, 4.8 Hz, 2H), 5.19 – 5.06 (m, 4H), 4.16 (dd, *J* = 20.5, 6.5 Hz, 1H), 3.48 (ddt, *J* = 14.2, 4.8, 1.8 Hz, 2H), 2.96 – 2.85 (m, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -112.83 (td, *J* = 9.3, 6.0 Hz, 1F), -113.12 (td, *J* = 9.0, 5.6 Hz, 1F), -181.74 (dd, *J* = 46.8, 20.5 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) 162.8 (d, $J_{C\text{-}F}$ = 247.6 Hz), 162.7 (d, $J_{C\text{-}F}$ = 246.4 Hz), 140.1 (dd, $J_{C\text{-}F}$ = 21.0, 7.2 Hz), 139.1 (dd, $J_{C\text{-}F}$ = 6.4, 3.8 Hz), 136.6, 129.7 (dd, $J_{C\text{-}F}$ = 8.2, 2.7 Hz), 125.2 (dd, $J_{C\text{-}F}$ = 2.8, 1.3 Hz), 122.4 (dd, $J_{C\text{-}F}$ = 7.1, 2.9 Hz), 117.4, 116.4 (dd, $J_{C\text{-}F}$ = 21.5, 1.7 Hz), 115.2 (dd, $J_{C\text{-}F}$ = 21.1, 1.7 Hz), 114.6 (d, $J_{C\text{-}F}$ = 21.0 Hz), 113.9 (d, $J_{C\text{-}F}$ = 7.6 Hz), 113.7 (d, $J_{C\text{-}F}$ = 7.5 Hz), 94.7 (dd, $J_{C\text{-}F}$ = 180.8, 1.9 Hz), 66.6 (dd, $J_{C\text{-}F}$ = 20.7, 1.6 Hz), 54.1 (d, $J_{C\text{-}F}$ = 2.4 Hz); **IR** (thin layer film) ν (cm^{-1}) = 3077, 2816, 1642, 1591, 1489, 1449, 1251, 1243, 923, 788, 767, 700; **HRMS** (APCI$^+$) *m/z* calculated for $C_{20}H_{21}F_3N^+$ $[M+H]^+$ 332.16206, found 332.16168. **$[\alpha]_D^{25\,°C}$** = +23.8 ° (c = 0.5, $CHCl_3$, e.r. = 95.5:4.5); **HPLC separation**: DAICEL CHIRALPAK® IB-3, Heptane:^{i}PrOH = 99.5:0.5, 1 mL/min; t_1 = 3.23 min (minor), t_2 = 3.90 min (major).

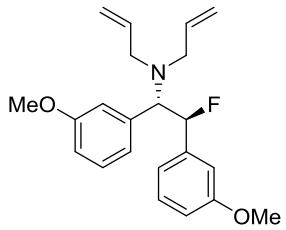
***N*-allyl-*N*-((1*S*,2*S*)-1,2-bis(3-chlorophenyl)-2-fluoroethyl)prop-2-en-1-amine (2n)**



(*S*,*S*)-**2n**

Fluoride **2n** was prepared from **1n** (76.0 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at +10 °C for 72 h. *Purification:* FCC, eluent = Pentane:Et_2O (100:0 to 99.68:0.32, gradient). Colorless oil, 55.8 mg, 77% yield, e.r. = 94:6. **Method B:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at 0 °C for 72 h. *Purification:* FCC eluent = Pentane:Et_2O (100:0 to 99.5:0.5, gradient). Colorless oil, 55.0 mg, 76% yield, e.r. = 97.5:2.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.29 – 7.18 (m, 6H), 7.08 (dt, *J* = 6.5, 1.8 Hz, 2H), 5.82 (dd, *J* = 46.7, 6.1 Hz, 1H), 5.68 (dddd, *J* = 17.6, 10.2, 7.6, 4.9 Hz, 2H), 5.18 – 5.08 (m, 4H), 4.12 (dd, *J* = 21.5, 6.1 Hz, 1H), 3.47 (ddt, *J* = 14.4, 4.9, 1.8 Hz, 2H), 2.87 (dd, *J* = 14.4, 7.6 Hz, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -182.86 (dd, *J* = 46.8, 21.5 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 140.4 (d, $J_{C\text{-}F}$ = 21.0 Hz), 138.6 (d, $J_{C\text{-}F}$ = 3.4 Hz), 136.5, 134.3, 134.1, 129.6 (d, $J_{C\text{-}F}$ = 1.8 Hz), 129.5, 129.4, 128.5 (d, $J_{C\text{-}F}$ = 1.7 Hz), 127.9, 127.7 (d, $J_{C\text{-}F}$ = 1.5 Hz), 126.9 (d, $J_{C\text{-}F}$ = 7.6 Hz), 124.8 (d, $J_{C\text{-}F}$ = 7.1 Hz), 117.5, 94.9 (d, $J_{C\text{-}F}$ = 181.1 Hz), 66.5 (d, $J_{C\text{-}F}$ = 20.6 Hz), 54.1 (d, $J_{C\text{-}F}$ = 2.4 Hz); **IR** (thin layer film) ν (cm^{-1}) = 3076, 2925, 2817, 1596, 1572, 1477, 1431, 1205, 1082, 999, 922, 787, 706; **HRMS** (APCI$^+$) *m/z* calculated for $C_{20}H_{21}Cl_2FN^+$ $[M+H]^+$ 364.10296, found 364.10324. **$[\alpha]_D^{25\,°C}$** = +15.8 ° (c = 0.5, $CHCl_3$, e.r. = 97.5:2.5); **HPLC separation**: DAICEL CHIRALPAK® IA-3, Heptane:^{i}PrOH = 99.5:0.5, 1 mL/min; t_1 = 3.04 min (minor), t_2 = 3.32 min (major).

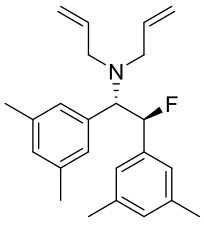
***N*-allyl-*N*-((1*S*,2*S*)-2-fluoro-1,2-bis(3-methoxyphenyl)ethyl)prop-2-en-1-amine (2o)**



(*S*,*S*)-**2o**

Fluoride **2o** was prepared from **1o** (74.4 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at +10 °C for 36 h. *Purification:* FCC, eluent = Hexane:Et_2O (96:4). Colorless oil, 61.3 mg, 86% yield, e.r. = 95.5. **Method B:** 5 mol% of catalyst (*S*)-**3g**. The reaction was stirred at 0 °C for 36 h. *Purification:* FCC eluent = Pentane:Et_2O (96:4). Colorless oil, 69.0 mg, 97% yield, e.r. = 97.5:2.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.21 – 7.11 (m, 2H), 6.87 – 6.67 (m, 6H), 5.96 – 5.73 (m, 3H), 5.22 – 5.05 (m, 4H), 4.19 (dd, *J* = 18.3, 7.1 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.51 (ddt, *J* = 14.2, 4.8, 1.8 Hz, 2H), 2.93 (dd, *J* = 14.3, 7.6 Hz, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -179.64 (dd, *J* = 47.2, 18.3 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.2, 159.2, 140.1 (d, $J_{C\text{-}F}$ = 20.3 Hz), 138.0 (d, $J_{C\text{-}F}$ = 4.4 Hz), 137.0, 129.0, 128.9, 121.9, 119.2 (d, $J_{C\text{-}F}$ = 6.8 Hz), 117.0, 115.5 (d, $J_{C\text{-}F}$ = 1.3 Hz), 113.8 (d, $J_{C\text{-}F}$ = 1.9 Hz), 112.5, 112.3 (d, $J_{C\text{-}F}$ = 7.2 Hz), 95.0 (d, $J_{C\text{-}F}$ = 179.3 Hz), 67.0 (d, $J_{C\text{-}F}$ = 20.7 Hz), 55.2, 55.1, 53.9 (d, $J_{C\text{-}F}$ = 2.1 Hz); **IR** (thin layer film) ν (cm^{-1}) = 3076, 3004, 2936, 2835, 1601, 1491, 1455, 1264, 1158, 1047, 997, 920, 788, 700; **HRMS** (APCI$^+$) *m/z* calculated for $C_{22}H_{27}FNO_2^+$ $[M+H]^+$ 356.20203, found 356.20133. **$[\alpha]_D^{25\,°C}$** = +13.0 ° (c = 0.5, $CHCl_3$, e.r. = 97.5:2.5); **HPLC separation**: DAICEL CHIRALPAK® IA-3, Heptane: ^{i}PrOH:Et_2NH = 99.2:0.7:0.1, 1 mL/min; t_1 = 3.74 min (minor), t_2 = 4.49 min (major).

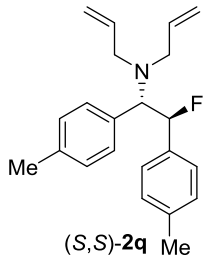
***N*-allyl-*N*-((1*S*,2*S*)-1,2-bis(3,5-dimethylphenyl)-2-fluoroethyl)prop-2-en-1-amine (2p)**



(*S*,*S*)-**2p**

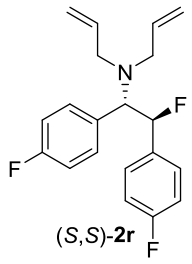
Fluoride **2p** was prepared from **1p** (73.6 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at -15 °C for 72 h. *Purification:* FCC, eluent = Pentane:Et_2O (100:0 to 99.55:0.45, gradient). Colorless oil, 40.9 mg, 58% yield, e.r. = 90:10. **Method B:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at -20 °C for 72 h. *Purification:* FCC eluent = Pentane:Et_2O (100:0 to 99.55:0.45, gradient). Colorless oil, 59.6 mg, 85% yield, e.r. = 91:9. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 6.87 (s, 4H), 6.82 (s, 2H), 5.91 – 5.71 (m, 3H), 5.16 (d, *J* = 17.3 Hz, 2H), 5.11 (d, *J* = 10.1 Hz, 2H), 4.14 (dd, *J* = 19.3, 6.9 Hz, 1H), 3.50 (ddd, *J* = 14.4, 4.8, 1.9 Hz, 2H), 2.92 (dd, *J* = 14.4, 7.5 Hz, 2H), 2.28 (s, 6H), 2.27 (s, 6H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -179.64 (dd, *J* = 47.6, 19.3 Hz, 1F); **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 138.7 (d, $J_{C\text{-}F}$ = 19.8 Hz), 137.5, 137.3, 137.3, 136.5 (d, $J_{C\text{-}F}$ = 4.0 Hz), 129.7 (d, $J_{C\text{-}F}$ = 2.1 Hz), 128.9, 127.6, 124.8 (d, $J_{C\text{-}F}$ = 6.7 Hz), 116.8, 95.7 (d, $J_{C\text{-}F}$ = 178.0 Hz), 66.8 (d, $J_{C\text{-}F}$ = 20.4 Hz), 54.1 (d, $J_{C\text{-}F}$ = 2.2 Hz), 21.6, 21.4; **IR** (thin layer film) ν (cm^{-1}) = 3076, 3009, 2919, 2813, 1641, 1607, 1448, 1417, 1163, 1125, 1037, 917, 851, 710; **HRMS** (ESI$^+$) *m/z* calculated for $C_{24}H_{31}FN^+$ $[M+H]^+$ 352.24350, found 352.24319. **$[\alpha]_D^{25\,°C}$** = +16.5 ° (c = 0.5, $CHCl_3$, e.r. = 90:10); **HPLC separation**: DAICEL CHIRALPAK® IA-3 Heptane:^{i}PrOH = 99:1, 1 mL/min; t_1 = 2.30 min (minor), t_2 = 2.69 min (major).

***N*-allyl-*N*-((1*S*,2*S*)-2-fluoro-1,2-di-p-tolylethyl)prop-2-en-1-amine (2q)**



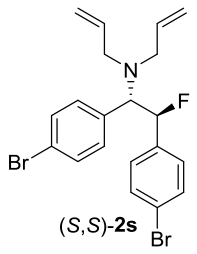
Fluoride **2q** was prepared from **1q** (68.0 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at -10 °C for 60 h. *Purification:* FCC, eluent = Hexane:Et_2O (100:0 to 99.4:0.6, gradient). Colorless oil, 50 mg, 71% yield, e.r. = 95:5. **Method B:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at -10 °C for 24 h. *Purification:* FCC eluent = Hexane:Et_2O (100:0 to 99.2:0.8, gradient). Colorless oil, 48.1 mg, 74% yield, e.r. = 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.13 (d, *J* = 8.0, Hz, 2H), 7.06-7.03 (m, 6H), 5.96 – 5.73 (m, 3H), 5.22 – 5.07 (m, 4H), 4.22 (dd, *J* = 16.6, 7.8 Hz, 1H), 3.51 (ddt, *J* = 14.3, 5.0, 1.8 Hz, 2H), 2.95 – 2.81 (m, 2H), 2.29 (s, 3H), 2.28 (s, 3H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -176.66 (dd, *J* = 47.3, 16.5 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 137.9 (d, $J_{C\text{-}F}$ = 2.3 Hz), 137.4, 136.9, 135.7 (d, $J_{C\text{-}F}$ = 20.3 Hz), 133.2 (d, $J_{C\text{-}F}$ = 4.9 Hz), 129.5, 128.8, 127.1 (overlapped), 116.9, 95.0 (d, $J_{C\text{-}F}$ = 177.5 Hz), 66.8 (d, $J_{C\text{-}F}$ = 21.1 Hz), 54.0 (d, $J_{C\text{-}F}$ = 2.0 Hz), 21.3, 21.2; **IR** (thin layer film) ν (cm^{-1}) = 3076, 3008, 2923, 2813, 1641, 1515, 1447, 1417, 1115, 997, 918, 814; **HRMS** ($APCI^+$) *m/z* calculated for $C_{22}H_{27}FN^+$ $[M+H]^+$ 324.21220, found 324.21213; **$[\alpha]_D^{25\ °C}$** = +21.0 ° (c = 0.5, $CHCl_3$, e.r. = 95:5); **HPLC separation**: DAICEL CHIRALPAK® OJ-H Heptane: ^{i}PrOH = 99.2:0.8, 1 mL/min; t_1 = 5.30 min (minor), t_2 = 6.12 min (major).

***N*-allyl-*N*-((1*S*,2*S*)-2-fluoro-1,2-bis(4-fluorophenyl)ethyl)prop-2-en-1-amine (2r)**



Fluoride **2r** was prepared from **1r** (69.6 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at -5 °C for 72 h. *Purification:* FCC eluent = Pentane:Et_2O (100:0 to 99.69:0.31, gradient). Colorless oil, 44.7 mg, 67% yield, e.r. = 95:5. **Method B:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at -10 °C for 72 h. *Purification:* FCC, eluent = Pentane:Et_2O (100:0 to 99.65:0.35, gradient). Colorless oil, 52.8 mg, 80% yield, e.r. = 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.21 – 7.16 (m, 2H), 7.15 – 7.09 (m, 2H), 6.98 – 6.90 (m, 4H), 5.93 – 5.68 (m, 3H), 5.21 – 5.08 (m, 4H), 4.17 (dd, *J* = 18.5, 7.0 Hz, 1H), 3.49 (ddt, *J* = 14.3, 4.9, 1.8 Hz, 2H), 2.89 (dd, *J* = 14.3, 7.6 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -113.54 – -113.66 (m, 1F), -114.59 – -114.72 (m, 1F), -177.78 (dd, *J* = 46.6, 18.5 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 162.6 (d, $J_{C\text{-}F}$ =247.5 Hz), 162.1 (d, $J_{C\text{-}F}$ = 246.4 Hz) 136.7, 134.4 (dd, $J_{C\text{-}F}$ = 21.0, 3.3 Hz), 132.3 (t, $J_{C\text{-}F}$ = 4.0 Hz), 131.1 (dd, $J_{C\text{-}F}$ =7.9, 1.3 Hz), 128.7 (dd, $J_{C\text{-}F}$ = 8.3, 6.5 Hz), 117.4, 115.1 (d, $J_{C\text{-}F}$ = 20.9 Hz), 115.0 (d, $J_{C\text{-}F}$ =21.2 Hz), 94.8 (d, $J_{C\text{-}F}$ = 179.1 Hz), 66.7 (d, $J_{C\text{-}F}$ = 21.4 Hz), 53.9 (d, $J_{C\text{-}F}$ = 2.2 Hz); **IR** (thin layer film) ν (cm^{-1}) = 3078, 2926, 2814, 1606, 1511, 1227, 1159, 921, 834; **HRMS** (ESI^+) *m/z* calculated for $C_{20}H_{21}F_3N^+$ $[M+H]^+$ 332.16206, found 332.16180. **$[\alpha]_D^{25\ °C}$** +23.7 ° (c = 0.5, $CHCl_3$, e.r. = 95:5); **HPLC separation**: DAICEL CHIRALPAK® OJ-H Heptane:^{i}PrOH = 99:1, 1 mL/min; t_1 = 6.16 min (minor), t_2 = 7.66 min (major).

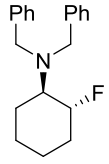
***N*-allyl-*N*-((1*S*,2*S*)-1,2-bis(4-bromophenyl)-2-fluoroethyl)prop-2-en-1-amine (2s)**



(*S*,*S*)-**2s**

Fluoride **2s** was prepared from **1s** (93.9 mg, 0.2 mmol) according to the general procedure using $CHCl_3$ as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at +5 °C for 72 h. *Purification:* FCC eluent = Pentane:Et_2O (100:0 to 99:1, gradient). Colorless oil, 64 mg, 71% yield, e.r. = 91:9. **Method B:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at -5 °C for 72 h. *Purification:* FCC, eluent = Pentane:Et_2O (100:0 to 99:1, gradient). Colorless oil, 68.0 mg, 73% yield, e.r. = 90.5:9.5. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.41–7.37 (m, 4H), 7.08 (d, J = 8.2 Hz, 2H), 7.04 (d, J = 8.3 Hz, 2H), 5.80 (dd, J = 47.0, 6.8 Hz, 1H) 5.88 – 5.65 (m, 2H), 5.18 – 5.08 (m, 4H), 4.12 (dd, J = 19.4, 6.8 Hz, 1H), 3.46 (ddd, J = 14.3, 4.6, 2.2 Hz, 2H), 2.85 (dd, J = 14.3, 7.6 Hz, 2H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -180.69 (dd, J = 47.0, 19.6 Hz, 1F); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 137.3 (d, $J_{C\text{-}F}$ = 20.9 Hz), 136.5, 135.2 (d, $J_{C\text{-}F}$ = 4.0 Hz), 131.3, 131.2, 131.1 (d, $J_{C\text{-}F}$ = 1.3 Hz), 128.4 (d, $J_{C\text{-}F}$ = 6.8 Hz), 122.7 (d, $J_{C\text{-}F}$ = 2.3 Hz), 121.6, 117.4, 94.5 (d, $J_{C\text{-}F}$ = 179.9 Hz), 66.4 (d, $J_{C\text{-}F}$ = 21.1 Hz), 53.8 (d, $J_{C\text{-}F}$ = 2.2 Hz); **IR** (thin layer film) ν (cm^{-1}) = 3077, 2977, 2924, 2814, 1164, 1594, 1488, 1405, 1073, 1010, 920, 819, 804; **HRMS** (ESI^+) *m/z* calculated for $C_{20}H_{21}Br_2FN^+$ $[M+H]^+$ 452.00193, found 452.00165; **$[\alpha]_D^{25\,°C}$** = –8.4 ° (c = 0.9, $CHCl_3$, e.r. = 90.5:9.5); **HPLC separation**: DAICEL CHIRALPAK® OJ-H, Heptane:EtOH:Et_2NH = 98.9:1.0:0.1, 1 mL/min; t_1 = 6.23 min (minor), t_2 = 10.97 min (major).

(*R*,*R*)-*N*,*N*-dibenzyl-2-fluorocyclohexan-1-amine (2t)



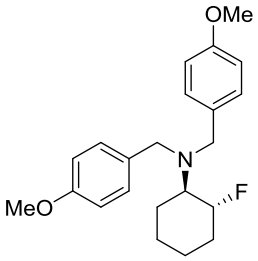
(*R*,*R*)-**2t**

Fluoride **2t** was prepared from **1t** (72 mg, 0.2 mmol) according to the general procedure using α,α,α-trifluorotoluene as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at r.t. for 72 h. *Purification:* FCC, eluent = Hexane:Et_2O (100:0 to 99.6:0.4, gradient). White solid, 40.7 mg, 68% yield, e.r. = 85.5:14.5. **Method B:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at r.t. for 72 h. *Purification:* FCC, eluent = Hexane:Et_2O (100:0 to 99.6:0.4, gradient). White solid, 35.5 mg, 60% yield, e.r. = 85:15. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.42 – 7.07 (m, 10H), 4.55 (dddd, J = 50.7, 10.4, 10.4, 4.8 Hz, 1H), 3.75 (d, J = 13.9 Hz, 2H), 3.67 (d, J = 14.0 Hz, 2H), 2.68 – 2.54 (m, 1H), 2.12 – 1.97 (m, 1H), 1.91 – 1.76 (m, 1H), 1.67 – 1.52 (m, 2H), 1.35 – 1.17 (m, 2H), 1.15 – 0.93 (m, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -174.71 (d, J = 50.6 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 140.7, 128.6, 128.1, 126.6, 93.3 (d, $J_{C\text{-}F}$ = 177.9 Hz), 61.2 (d, $J_{C\text{-}F}$ = 14.8 Hz), 54.4, 32.6 (d, $J_{C\text{-}F}$ = 17.5 Hz), 27.7 (d, $J_{C\text{-}F}$ = 8.8 Hz), 24.9 (d, $J_{C\text{-}F}$ = 2.2 Hz), 24.0 (d, $J_{C\text{-}F}$ = 11.4 Hz). **IR** (thin layer film) ν (cm^{-1}) = 3026, 2937, 2860, 1602, 1494, 1453, 1030, 989, 773, 746, 698; **MP** 69 – 71 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{20}H_{25}FN^+$ $[M+H]^+$ 298.19655, found 298.19650; **$[\alpha]_D^{25\,°C}$** = –9.0 ° (c = 0.2, $CHCl_3$, e.r. = 85.5:14.5); **HPLC separation**: DAICEL CHIRALPAK® IB-3, Heptane:^{i}PrOH = 99:1, 1 mL/min; t_1 = 3.02 min (minor), t_2 = 3.66 min (major). Spectroscopic data were in agreement with the ones previously reported in literature.[9]

The absolute configuration was assigned by derivatizing **2t** to its corresponding β-fluoropicolinamide (debenzylation with Pearlman's catalyst followed by amide formation). The reported value for *N*-((1*R*,2*R*)-2-fluorocyclohexyl)picolinamide was **$[\alpha]_D^{21\,°C}$ =** –36.5 ° (c = 0.7, $CHCl_3$, e.r. = 92:8).[12] Our measured value was

$[\alpha]_D^{25\,°C}$ = –13.5 ° (c = 0.5, $CHCl_3$, e.r. = 85.5:14.5) indicating (*R*,*R*) configuration for **2t**. The configuration of the other cyclic products was assigned by analogy.

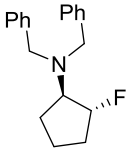
(1*R*,2*R*)-2-fluoro-*N*,*N*-bis(4-methoxybenzyl)cyclohexan-1-amine (2u)



(*R*,*R*)-**2u**

Fluoride **2u** was prepared from **1u** (83.6 mg, 0.2 mmol) according to the general procedure using α,α,α-trifluorotoluene as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at r.t. for 72 h. *Purification:* FCC, eluent = Hexane:Toluene (50:50 to 35:65, gradient). White solid, 45.3 mg, 63% yield, e.r. = 84:16. **Method B:** 15 mol% of catalyst (*S*)-**3g**. The reaction was stirred at r.t. for 72 h. *Purification:* FCC, eluent = Hexane:Toluene (50:50 to 35:65, gradient). White solid, 37.3 mg, 52% yield, e.r. = 85.5:14.5. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.38 – 7.32 (m, 4H), 6.93 – 6.81 (m, 4H), 4.64 (dddd, *J*= 50.7, 10.5, 10.5, 5.0 Hz, 1H), 3.82 (s, 6H), 3.77 (d, *J* = 13.6 Hz, 2H), 3.69 (d, *J* = 13.6 Hz, 2H), 2.75 – 66 (m, 1H), 2.20 – 2.12 (m, 1H), 1.95 – 1.86 (m,1H), 1.76 – 1.63 (m, 2H), 1.48 – 1.27 (m, 2H), 1.24 – 1.05 (m, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -174.75 (d, *J*= 50.7 Hz, 1F); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 158.4, 132.8, 129.6, 113.5, 93.3 (d, $J_{C\text{-}F}$ = 177.7 Hz), 60.9 (d, $J_{C\text{-}F}$ = 15.0 Hz), 55.2, 53.6, 32.7 (d, $J_{C\text{-}F}$ = 17.5 Hz), 27.6 (d, $J_{C\text{-}F}$ = 8.8 Hz), 24.9 (d, $J_{C\text{-}F}$ = 2.2 Hz), 24.0 (d, $J_{C\text{-}F}$ = 11.5 Hz); **IR** (thin layer film) ν (cm^{-1}) = 2936, 2834, 1611, 1510, 1245, 823; **MP** 50 – 53 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{22}H_{29}FNO_2^+$ $[M+H]^+$ 358.21768, found 358.21794; $[\alpha]_D^{25\,°C}$ = –11.9 ° (c = 0.44, $CHCl_3$, e.r. = 85.5:14.5); **HPLC separation**: DAICEL CHIRALPAK® IA-3, Heptane:^{i}PrOH = 99:1, 1 mL/min, t_1 = 6.04 min (major),t_2 = 7.01 min (minor).

(1*R*,2*R*)-*N*,*N*-dibenzyl-2-fluorocyclopentan-1-amine (2v)

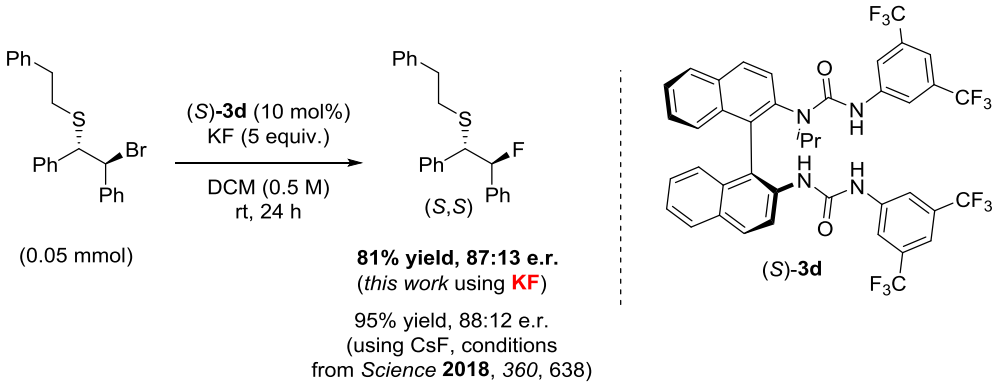


(*R*,*R*)-**2v**

Fluoride **2v** was prepared from **1v** (68.8 mg, 0.2 mmol) according to the general procedure using α,α,α-trifluorotoluene as solvent. **Method A:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at r.t. for 24 h. *Purification:* FCC, eluent = Pentane: Et_2O (100:0 to 99.4:06, gradient). Colorless oil, 40.0 mg, 70% yield, e.r. = 74.5:25.5. **Method B:** 10 mol% of catalyst (*S*)-**3g**. The reaction was stirred at r.t. for 24 h. *Purification:* FCC, eluent = Pentane: Et_2O (100:0 to 99.4:06, gradient). Colorless oil, 38.7 mg, 68% yield, e.r. = 75:25; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.41 – 7.36 (m, 4H), 7.34 – 7.28 (m, 4H), 7.27 – 7.19 (m, 2H), 5.15 (ddt, *J* = 54.0, 6.9, 3.6 Hz, 1H), 3.70 (d, *J* = 14.1 Hz, 2H), 3.63 (d, *J* = 14.1 Hz, 2H), 3.37 (dtd, *J* = 28.5, 8.5, 3.9 Hz, 1H), 2.01 – 1.72 (m, 3H), 1.72 – 1.48 (m, 3H); **^{19}F NMR** (376 MHz, , $CDCl_3$) δ = -172.99 (dtd, *J* = 53.5, 28.3, 23.5 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 139.9, 128.8, 128.3, 127.0, 97.1 (d, $J_{C\text{-}F}$ = 176.9 Hz), 68.1 (d, $J_{C\text{-}F}$ = 22.3 Hz), 55.5, 32.8 (d, $J_{C\text{-}F}$ = 22.8 Hz), 27.4 (d, $J_{C\text{-}F}$ = 5.8 Hz), 22.0 (d, $J_{C\text{-}F}$ = 2.1 Hz); **IR** (thin layer film) ν (cm^{-1}) = 3062, 3028, 2959, 2875, 1603, 1494, 1454, 1363, 1110, 1075, 1028, 956745, 698; **HRMS** (ESI^+) *m/z* calculated for $C_{19}H_{23}FN^+$ $[M+H]^+$ 284.18090, found 284.18088; $[\alpha]_D^{25\,°C}$ = –10.0 ° (c = 0.5, $CHCl_3$, e.r. = 74.5:25.5); **HPLC separation**: DAICEL CHIRALPAK® IF-3, Heptane:MTBE = 99:1, 1 mL/min; t_1 = 5.15 min (major), t_2 = 5.66 min (minor).

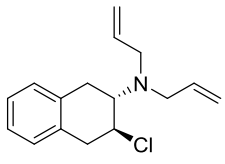
Additional substrates tested

Desymmetrization of episulfonium ions with KF

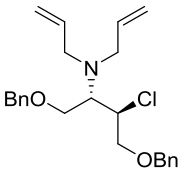


Additional aziridinium precursors

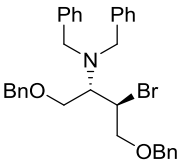
Aziridiniums precursors which were suitable substrates to fluorination but that didn't show high selectivity:



>99% NMR yield, 60:40 e.r.



85% NMR yield, 55:45 e.r.



42% NMR yield, 55:45 e.r.

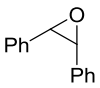
Conditions: 5 mol% of (*S*)-**3g**, α,α,α-trifluorotoluene, r.t., 24 h

Additional electrophiles tested for nucleophilic fluorination with KF

no reaction

no reaction

traces

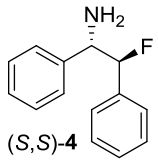


no reaction

Conditions: 10 mol% of Schreiner's urea, chlorinated or aromatic solvents, up to 100 °C, 24 h

Deprotection and Further Modifications

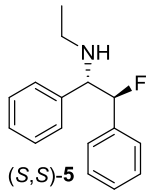
(1*S*,2*S*)-2-fluoro-1,2-diphenylethan-1-amine (4)



(*S*,*S*)-**4**

Fluoride **4** was synthesized *via* a slightly modified version of the deprotection protocol previously reported by Cossy *et al*..[10] In a flame-dried two-neck round bottom flask, $Pd(dba)_2$ (154 mg, 0.27 mmol, 0.1 equiv.) and 1,4-bis(diphenylphosphino)butane (dppb, 115 mg, 0.27 mmol, 0.1 equiv.) were stirred at r.t. in degassed THF (20 mL) for 15 min. Then (*S*,*S*)-**2a** (794 mg, 2.7 mmol, 1 equiv.; e.r. = 93:7) was added as a solution in THF (6 mL) followed by thiosalicylic acid (1.036 g, 6.75 mmol, 2.5 equiv.). The reaction mixture was stirred at 60 °C overnight, then it was diluted with Et_2O and acidified with HCl 1 M (checked with pH paper). The layers were separated and the aqueous one was washed 3 times with Et_2O prior of being neutralized with NaOH 2.5 M (checked with pH paper). The aqueous layer was extracted three times with EtOAc, dried on $MgSO_4$ and evaporated *in vacuo*. The crude product was purified by FCC (DCM:EtOAc = 100:0 to 80:20, gradient) to afford **4** as a white solid (489.2 mg, 84% yield, e.r. = 93:7). Recrystallization of 450 mg of the obtained compound from warm hexane (1 drop of $CHCl_3$) afforded **4** in > 99.8:0.2 e.r. (370.0 mg, 72% recrystallization yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.24 – 6.97 (m, 10H), 5.36 (dd, *J* = 47.3, 7.0 Hz, 1H), 4.21 (dd, *J* = 14.5, 7.0 Hz, 1H), 1.70 (s, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -182.68 (dd, *J* = 47.4, 14.6 Hz, 1F); **^{13}C NMR** (101 MHz, CDCl3) δ = 140.3 (d, $J_{C\text{-}F}$ = 6.1 Hz), 137.4 (d, $J_{C\text{-}F}$ = 20.3 Hz), 128.5 (d, $J_{C\text{-}F}$ = 1.7 Hz), 128.4, 128.2, 127.9, 127.8, 126.5 (d, $J_{C\text{-}F}$ = 7.0 Hz), 98.7 (d, $J_{C\text{-}F}$ = 177.6 Hz), 61.6 (d, $J_{C\text{-}F}$ = 23.1 Hz). **IR** (thin layer film) ν (cm^{-1}) = 3388, 3064, 3032, 2918, 2849, 1604, 1495, 1454, 1074, 1027, 1018, 834, 764, 698; **MP** 47 – 50 °C; **HRMS** (ESI^+) *m/z* calculated for $C_{14}H_{15}FN^+$ $[M+H]^+$ 216.11830, found 216.11813. **$[\alpha]_D^{25\,°C}$** = –96.2 ° (c = 0.5, $CHCl_3$, e.r. > 99.8:0.2); **HPLC separation**: DAICEL CHIRALPAK® IB-3, Heptane:^{i}PrOH:EtOH = 97:2:1 + 0.1% ethanol amine, 1 mL/min; t_1 = 5.28 min (major), t_2 = 6.94 min (minor). Spectroscopic data were in agreement with the ones previously reported in literature.[11]

(1*S*,2*S*)-N-ethyl-2-fluoro-1,2-diphenylethan-1-amine (5)



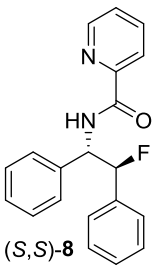
(*S*,*S*)-**5**

In a round bottom flask, CH_3CHO (294 µL, 5 mmol, 5 equiv.) was dissolved in MeOH (5 mL, 0.2 M). (*S*,*S*)-**4** (1 equiv, 1 mmol, 215 mg; e.r. > 99.8:0.2) and $NaBH(OAc)_3$ (635mg, 3 mmol, 3 equiv.) were subsequently added as solids. The reaction was stirred at r.t. for 3 h then quenched with $NaHCO_3$ (sat.) and extracted three times with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated *in vacuo*. The crude brown oil was purified by FCC (Pentane:Et_2O 100:0 to 90:10, gradient) to afford a pale yellow oil (137.1 mg, 56% yield, e.r. > 99.9:0.1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.25 – 7.14 (m, 6H), 7.13 – 7.05 (m, 2H), 7.05 – 6.96 (m, 2H), 5.40 (dd, *J* = 47.7, 8.2 Hz, 1H), 4.04 (dd, *J* = 10.6, 8.2 Hz, 1H), 2.59 – 2.40 (m, 2H), 1.91 (s br, 1H), 1.10 (t, *J* = 7.1 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -177.82 (dd, *J* = 47.7, 10.7 Hz)**;** **^{13}C NMR** (101 MHz, $CDCl_3$) δ= 138.5 (d, $J_{C\text{-}F}$ = 6.7 Hz), 137.2 (d, $J_{C\text{-}F}$ = 19.9 Hz), 128.7, 128.5 (d, $J_{C\text{-}F}$ = 1.9 Hz), 128.2, 128.0, 127.7, 126.8 (d, $J_{C\text{-}F}$ = 6.7 Hz), 98.2 (d, $J_{C\text{-}F}$ = 177.9 Hz), 69.0 (d, $J_{C\text{-}F}$ = 22.6 Hz), 41.8, 15.5; **IR** (thin layer film) ν (cm^{-1}) = 3032, 2967, 2818, 1454, 1340, 1208, 1151, 1062, 1032, 758, 698; **HRMS** (ESI^+) *m/z* calculated for $C_{16}H_{19}FN^+$

$[M+H]^+$ 244.14960, found 244.14954. **$[\alpha]_D^{25\,°C}$ =** –68.3 ° (c = 0.4, $CHCl_3$, e.r. > 99.9:0.1); **HPLC separation**: DAICEL CHIRALPAK® OJ-H Hept:EtOH = 96:4, 1 mL/min; t_1 = 5.09 min (major), t_2 = 6.22 min (minor).

N.B. Attempts to access this compound *via* asymmetric fluorination from the corresponding chloride were unsuccessful as the synthesis of the chloride precursor proved to be very challenging (mixture of products, poor yields).

***N*-((1S,2S)-2-fluoro-1,2-diphenylethyl)picolinamide (8)**



(*S*,*S*)-**8**

β-Fluoroamide **8** was synthesized according to the procedure reported by Doyle.[12] In a flame-dried Schlenk tube, β-fluoroamine **4** (80.0 mg, 0.37 mmol, 1 equiv., 78:22 e.r.) was dissolved in anhydrous DCM. Picolinic acid (45.8 mg, 0.37 mmol, 1 equiv.), DMAP (50.0 mg, 0.41 mmol, 1.1 equiv.) and *N*, *N'*-diisopropylcarbodiimide (63.5 mg, 0.41 mmol, 1 equiv.) were added and the reaction stirred overnight at r.t.. After disappearance of the starting material (monitored by TLC), hexane was added and the solid removed by filtration. The filtrate was evaporated *in vacuo* and the crude product purified by FCC (Pentane:EtOAc = 90:10 to 70:30, gradient). White solid (80 mg, 67% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.84 (d, *J* = 9.1 Hz, 1H), 8.56 (d, *J* = 4.9 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.78 (td, *J* = 7.7, 1.7 Hz, 1H), 7.40 (dd, *J* = 7.6, 4.8, 1.3 Hz, 1H), 7.36 – 7.20 (m, 10H), 5.81 (dd, *J* = 46.0, 4.4 Hz, 1H), 5.59 (ddd, *J* = 21.4, 9.1, 4.4 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -188.34 (dd, *J* = 45.9, 21.4 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 163.9, 149.6, 148.3, 138.4 (d, $J_{C\text{-}F}$ = 2.0 Hz), 137.4, 136.8 (d, $J_{C\text{-}F}$ = 20.7 Hz), 128.7 (overlapped), 128.4, 128.0, 127.6, 126.4, 126.1 (d, $J_{C\text{-}F}$ = 7.3 Hz), 122.5, 95.6 (d, $J_{C\text{-}F}$ = 180.9 Hz), 57.7 (d, $J_{C\text{-}F}$ = 21.6 Hz). Spectroscopic data were in agreement with the ones previously reported in literature.[12]

The reported value for the (*R*,*R*)-enantiomer was **$[\alpha]_D^{25\,°C}$ =** –4.5 ° (c = 1.0, $CHCl_3$, e.r. = 74:26).[12] Our measured value was **$[\alpha]_D^{25\,°C}$ =** +4.7 ° (c = 1.0, $CHCl_3$, e.r. = 77.5:22.5) indicating (*S*,*S*) configuration for **8** (and consequently for its precursors **4** and **2a**). The configuration of the other stilbene-derived products was assigned by analogy. Finally, this assignment was further confirmed by single crystal x-ray diffraction analysis of **2g**.

NMR studies

In order to gain insights into the anion binding interaction of the urea catalyst (*S*)-**3g** with alkali metal fluorides, a mixture of CsF (114 mg, 0.75 mmol) and (*S*)-**3g** (20 mg, 0.014 mmol) were stirred in DCM-d_2 (0.6 mL). After 2 h the mixture was filtered through a syringe filter (0.45 µm PTFE membrane) and analyzed by NMR. ^{1}H NMR spectrum suggests an interaction between catalyst and fluoride, indicated by significant line broadening and downfield shifting of NH protons (Fig. S1). We noted that F^- resonance does not appear in ^{19}F NMR, presumably due to extensive broadening of the signal.

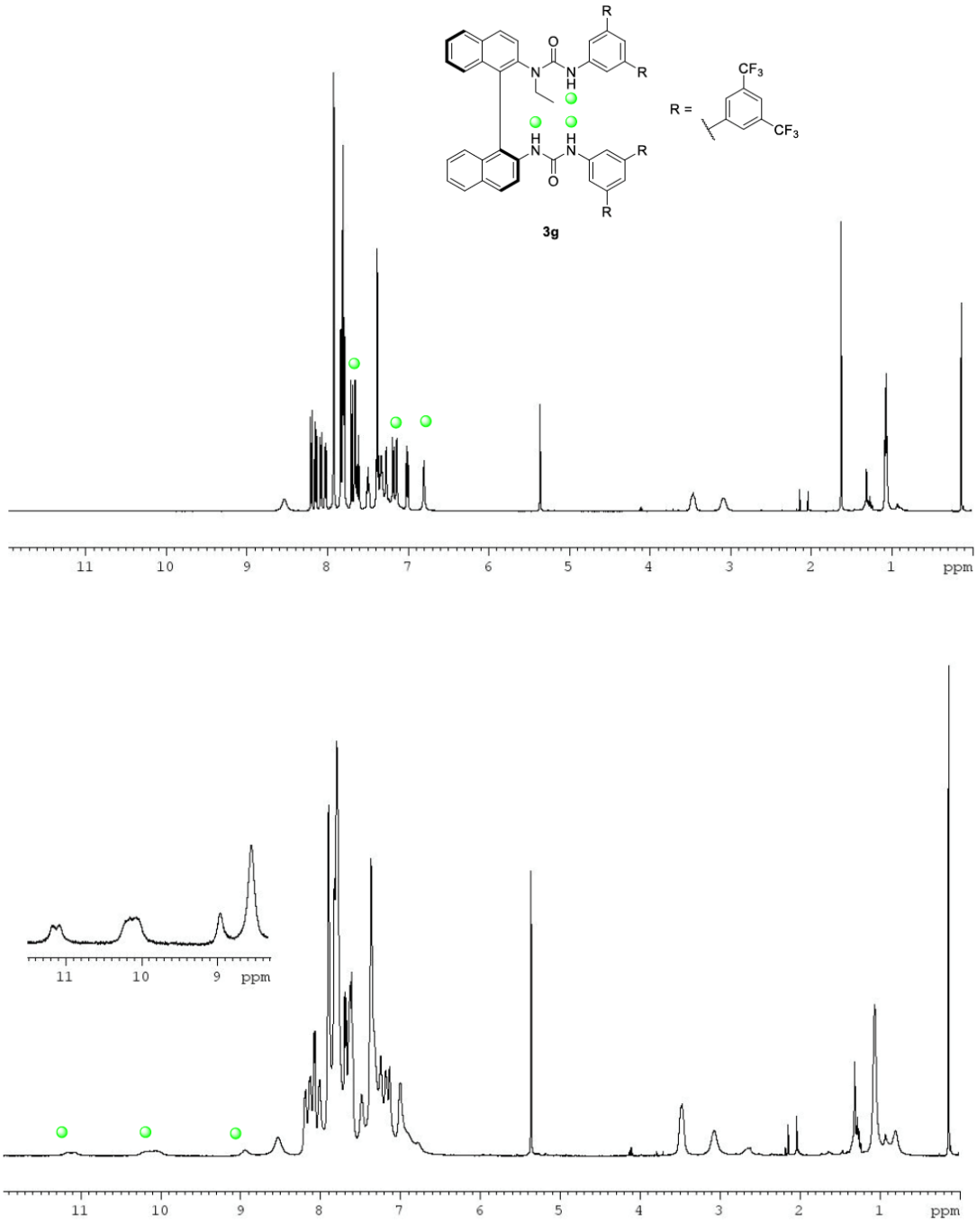


Figure S1: ^{1}H NMR of (*S*)-**3g** in DCM-d_2 (top); ^{1}H NMR of (*S*)-**3g** after stirring with CsF in DCM-d_2 (bottom); deshielded NH protons (bottom insert).

To overcome this problem we did the following experiments: after stirring (*S*)-**3g** and CsF in DCM-d_2 (2 h) and syringe filtration, the solution was evaporated to dryness, dissolved in 1 mL of CD_3OD and analyzed by NMR. ^{19}F NMR and ^{133}Cs NMR showed the corresponding signals for F^- (-150 ppm) and Cs^+ (-38 ppm) proving the presence of CsF in solution (Fig. S2), as the chemical shifts are identical to the ones of an independently prepared sample of CsF in CD_3OD. A control experiment, in which CsF was stirred in DCM in the absence of catalyst then filtered and re-dissolved in CD_3OD as described above, shows no trace of either Cs^+ or F^-, thus indicating that (*S*)-**3g** acts as a phase-transfer catalyst.

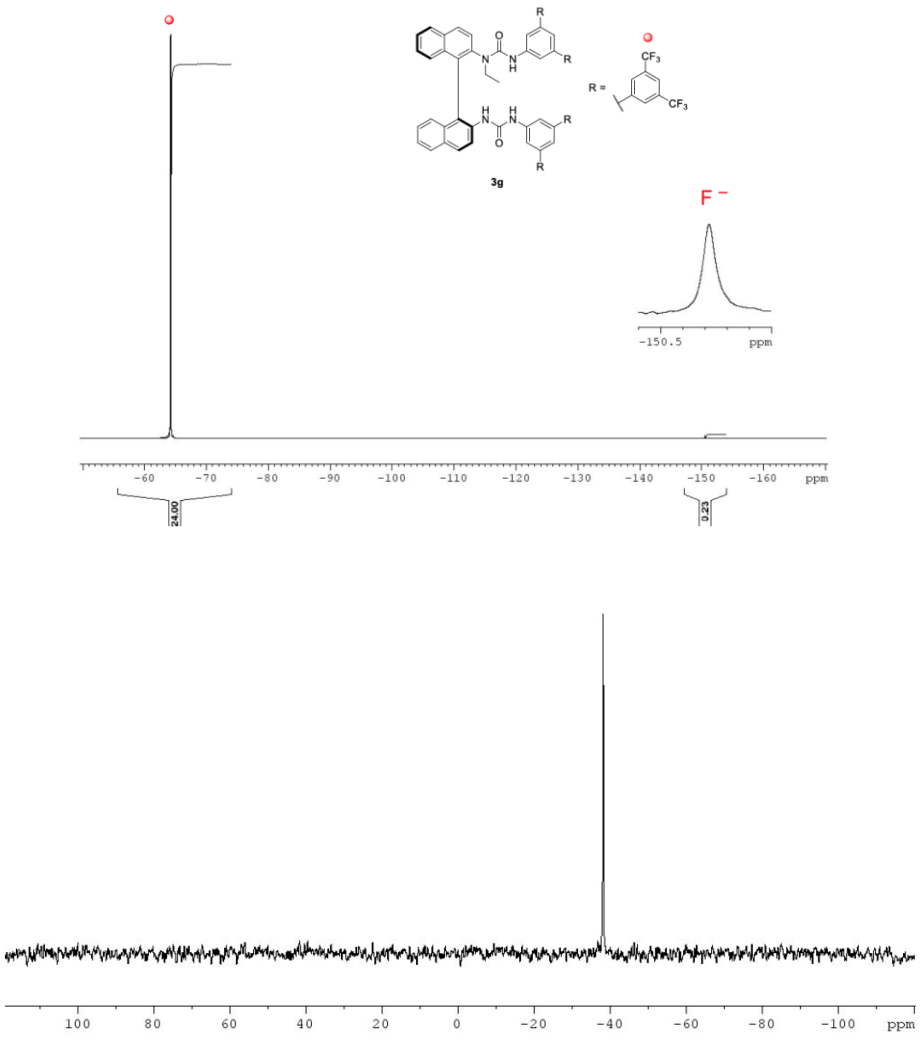


Figure S2: ^{19}F-NMR (top) and ^{133}Cs-NMR (bottom) in CD_3OD of (*S*)-**3g** after stirring with CsF in DCM.

Computational Methods

All calculations were performed using *N*,*N*-dimethyl compounds **1–2b**, catalyst **3g**, in chloroform solvent, with Gibbs free energies evaluated at 298.15 K and 1 M concentration unless otherwise stated. Molecular dynamics simulations were used for conformational sampling of ion pairs[13] in explicit chloroform. The methods used are based upon those in our previous work.[1] Structures were visualized using Pymol.[14]

Density Functional Theory (DFT)

Density functional theory (DFT) geometry optimizations and frequency calculations were performed in Gaussian 09, Revision D.01[15] using the M06-2X hybrid functional[16] and mixed basis set, referred to as def2-SVP(TZVPPD), comprising def2-TZVPPD on non-catalyst heteroatoms and def2-SVP otherwise.[17–20] The ultrafine (99,590) integration grid was used[21] and calculations were performed in chloroform solvent using the conductor like polarizable continuum model (CPCM).[22–24] Stationary points were classified by vibrational frequencies; those with no imaginary frequencies being classified as minima, and those with a single imaginary frequency, transition states (TS). Thermochemistry was evaluated using the *Goodvibes* python script, with free-rotor cutoff of 100 cm^{-1}.[25, 26] The non-covalent interaction index was used to visualize non-covalent interactions from the optimization density.[27, 28]

A single point energy correction was performed in ORCA 3.0.3[29] using the ωB97X-D3 hybrid functional[30, 31] and (ma)-def2-TZVPP basis set, referring to ma-def2-TZVPP[32] on heteroatoms and def2-TZVPP otherwise, with ECP on Cs. ωB97X-D3 incorporates Grimme's D3 dispersion correction.[33] The conductor-like screening model (COSMO)[34] was used to model solvation in chloroform.

Reference to the intrinsic reaction coordinate (IRC) refers to a projection of the IRC onto a new coordinate, defined as breaking C-N bond distance minus forming C-F distance.[35, 36]

Truncated models (fragmentation), used to rationalize the energy difference between major and minor transition states (TSs), were performed by deleting part of the TS structure in both major and minor TS, followed by a single point energy evaluation (i.e. no re-optimization). Any unsatisfied valance was satisfied by adding a hydrogen atom, in a consistent geometry. Comparison at the TSs, as opposed to over the IRC, introduces negligible error as the difference in TS position is small (TS energy changes by ~0.2 kJ/mol).

Molecular Dynamics (MD)

Molecular dynamics (MD) simulations were performed using the GROMACS 5.1.4 package,[37–42] with the optimized potential for liquid simulations (OPLA-AA 2005) forcefield[43, 44] and restrained electrostatic potential charges (RESP).[45, 46] Compatible parameters were generated using Schrödinger Maestro software (ffld_server utility, version 14)[47] and RESP charges fitted to HF/6-31G(d) potential using Ambertools.[48] Simulations were performed in explicit chloroform solvent with topology obtained from virtualchemistry.org.[49, 50]

The system for simulation was centered in a cubic box, with minimum distance to the boundary of 15 Å, and 3-dimensional periodic boundary conditions (PBC). The velocity rescaling method was used to maintain system temperature (time constant = 100 fs);[51] system pressure was maintained using the Parrinello-Rahman barostat (time constant = 2 ps, reference pressure = 1 bar, compressibility = 4.5 x 10^{-5} bar^{-1}).[52, 53] Van der Waals interactions and the particle mesh Ewald method used a 1 nm cut-off. Simulations used the linear constraint solver algorithm (LINCS).[54]

Each simulation was equilibrated by steepest-descents minimization of 5000 steps, followed by constant volume (NVT) simulation under heavy atom position restraints, with 1 fs timestep and velocities initiated according to a Maxwell-Boltzmann distribution at 173 K. Over the course of the 200 ps simulation, system temperature was raised to reaction temperature and allowed to equilibrate. After NVT equilibration, the system was equilibrated under constant pressure (NPT) for 400 ps, with 2 fs timestep and the stability of the system volume verified. Data was derived from a continuation of NPT simulation for a further 300 ns.

MD trajectories were clustered using the GROMOS algorithm,[55] accounting for molecular symmetry, with RMSD matrix calculated using an in-house python script. The framework used for calculating RMSD, and the cut-off used for clustering, are given in each case. Geometries were saved every 10 ps. Catalyst conformations and catalyst-cesium fluoride binding modes were investigated at elevated temperature of 373 K. Simulations of the reactive ion pair were performed at 298 K.

Naming and Definitions

The naming and numbering conventions for catalyst **3g** (Fig. S3) and aziridinium substrate (Fig. S4) are defined, along with dihedral angles of interest.

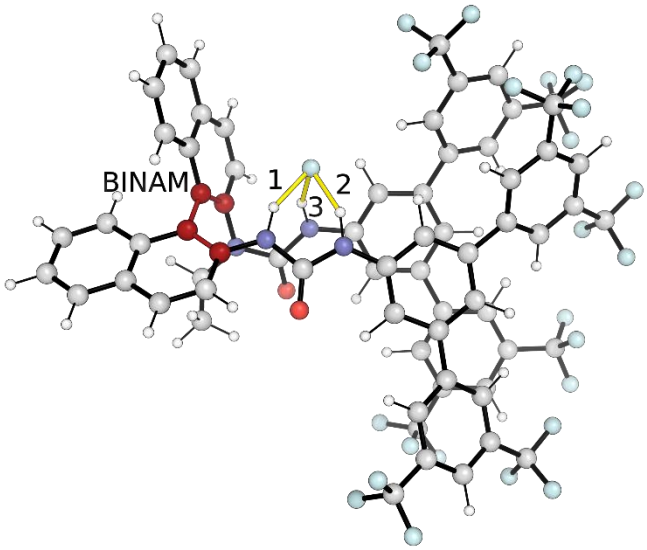


Figure S3 Conventions for catalyst **3g**. Numbering of hydrogen bonds (1–3) is shown. The atoms used to measure the BINAM dihedral angle are highlighted in dark red.

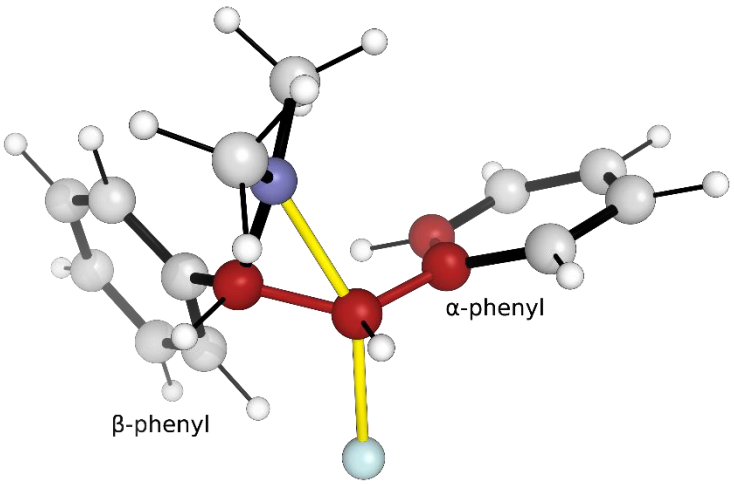


Figure S4 Conventions for aziridinium ion. The phenyl rings are identified by their positioning relative to the forming and breaking bonds. The atoms used to measure the dihedral of the α-phenyl ring (α-dihedral) are highlighted in dark red. The β-dihedral is defined analogously. Sign convention is used such that, as shown in the figure, clockwise rotation of the α-dihedral and counter-clockwise rotation of the β-dihedral corresponds to a more positive dihedral angle.

Computation – MF Solubilization

The relative thermodynamic favorability of solubilizing CsF and KF in dichloromethane was calculated by combining experimental thermodynamic data with computed values in a thermodynamic cycle. Data by Chase *et al.*[56] were obtained from the NIST Chemistry WebBook SRD 69.[57] "MF" refers to a giant ionic lattice in solid state and an ion paired formula unit in gas and solution phases (Tables S6-S8).

***Table S6*:** Standard enthalpy and entropy changes at 298.15 K

	Source	**ΔH (kJ/mol)**	**ΔS (J/K/mol)**
Δ_f ($CsF_{(s)}$)	Ref (56)	-554.7	-
Δ_f ($KF_{(s)}$)	Ref (56)	-568.6	-
Δ_f ($CsF_{(g)}$)	Ref (56)	-356.5	-
Δ_f ($KF_{(g)}$)	Ref (56)	-326.8	-
Δ_{solv} (CsF)	Computed	-122.8	-22.3
Δ_{solv} (KF)	Computed	-130.8	-23.1

Gas phase entropies evaluated at 1 bar pressure. Solution phase at 1 M concentration

***Table S7*:** Standard molar entropies at 298.15 K

	Source	**ΔS (J/K/mol)**
$CsF_{(s)}$	Ref (56)	88.3
$CsF_{(g)}$	Ref (56)	243.2
$KF_{(s)}$	Ref (56)	66.6
$KF_{(g)}$	Ref (56)	226.6

***Table S8*:** Derived Gibbs free energies at 298.15 K

Process	**ΔG (kJ/mol)**
$CsF_{(s)}$ -> $CsF_{(g)}$	152
$KF_{(s)}$ -> $KF_{(g)}$	194
$CsF_{(g)}$ -> $CsF_{(DCM)}$	-116
$KF_{(g)}$ -> $KF_{(DCM)}$	-124
$CsF_{(s)}$ -> $CsF_{(DCM)}$	35.8
$KF_{(s)}$ -> $KF_{(DCM)}$	70.2
3b$_{(DCM)}$ + $CsF_{(DCM)}$ -> **3b**$FCs_{(DCM)}$	-35.4
3b$_{(DCM)}$ + $KF_{(DCM)}$ -> **3b**$FK_{(DCM)}$	-37.2
3b$_{(DCM)}$ + $CsF_{(s)}$ -> **3b**$FCs_{(DCM)}$	0.4
3b$_{(DCM)}$ + $KF_{(s)}$ -> **3b**$FK_{(DCM)}$	33.0

Computation – Asymmetric Catalytic System

*Catalyst **3g***

Catalyst **3g** MD simulation was performed in chloroform for 300 ns. The framework used for RMSD calculation (Fig. S5) was chosen to prioritize urea conformation. All frames from the trajectory were used for clustering with RMSD cut-off of 0.7 Å. The 11 highest weighted clusters (> 0.5 % weight) were optimized using DFT (Fig. S6).

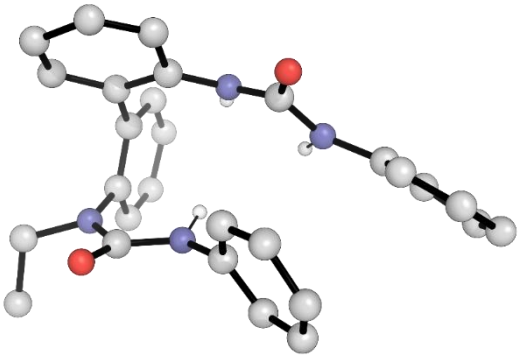
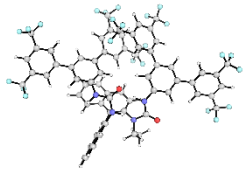
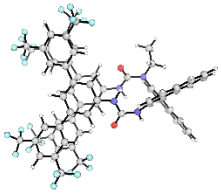


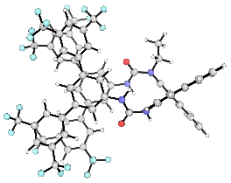
Figure S5 Molecular framework used for RMSD clustering of frames in trajectory of uncoordinated catalyst, **3g**.



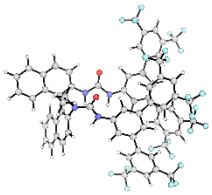
3g-1
0.0 kJ/mol



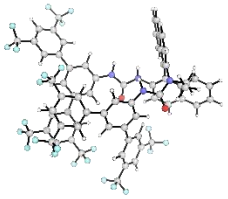
3g-2
+13.7 kJ/mol



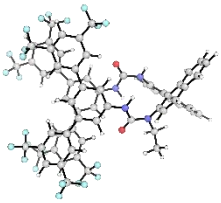
3g-3
+15.0 kJ/mol



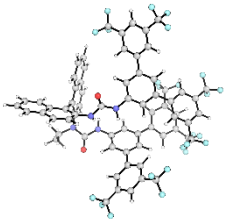
3g-4
+15.3 kJ/mol



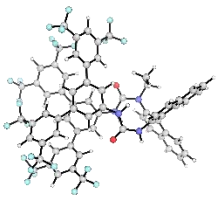
3g-5
+15.8 kJ/mol



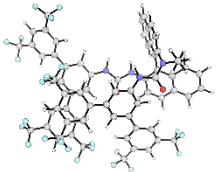
3g-6
+17.5 kJ/mol



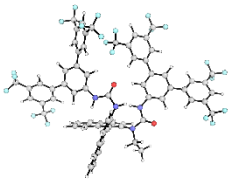
3g-7
+20.4 kJ/mol



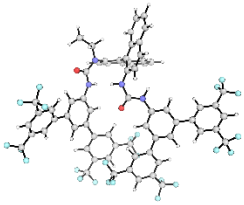
3g-8
+26.2 kJ/mol



3g-9
+26.2 kJ/mol



3g-10
+32.9 kJ/mol



3g-11
+36.3 kJ/mol

Figure S6 Conformers of **3g** with relative Gibbs free energies.

3g*-*Fluoride Complexes

Catalyst **3g** complexed with cesium fluoride was simulated using MD for 300 ns. The framework used for RMSD calculation is shown in Figure S7. All frames from the trajectory were used for clustering with RMSD cut-off of 0.6 Å. The 11 highest weighted clusters were optimized by DFT, with potassium cation (replacing cesium) and without cation.

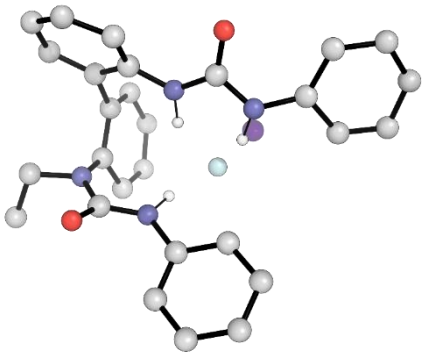
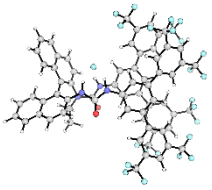
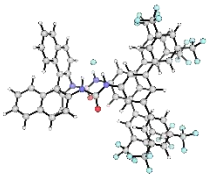


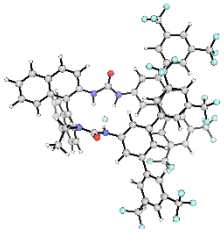
Figure S7 Molecular framework used for RMSD clustering of frames in trajectory of catalyst **3g** with CsF.



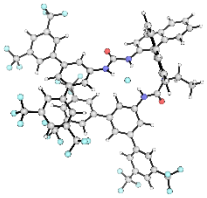
3gF-1
0.0 kJ/mol



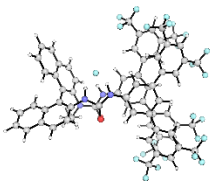
3gF-2
+1.5 kJ/mol



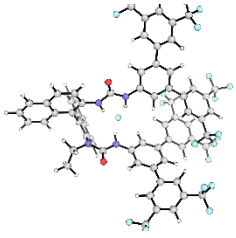
3gF-3
+1.7 kJ/mol



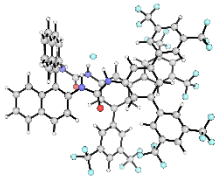
3gF-4
+4.3 kJ/mol



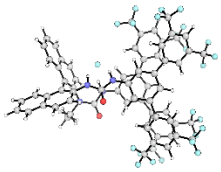
3gF-5
+5.5 kJ/mol



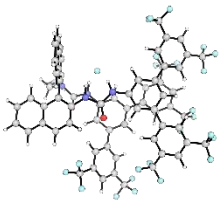
3gF-6
+6.1 kJ/mol



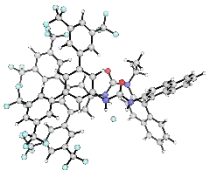
3gF-7
+6.8 kJ/mol



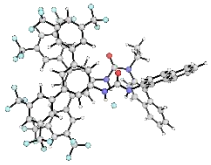
3gF-8
+8.8 kJ/mol



3gF-9
+9.0 kJ/mol

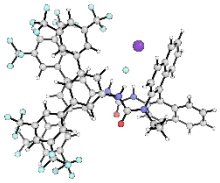


3gF-10
+9.5 kJ/mol

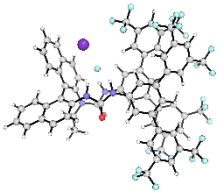


3gF-11
+17.1 kJ/mol

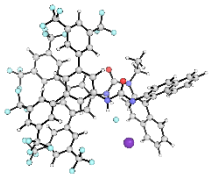
Figure S8 Conformers of **3g**F complex, with relative Gibbs free energies.



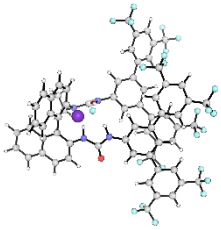
3gF•K-1
0.0 kJ/mol



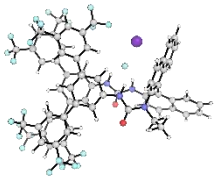
3gF•K-2
+1.0 kJ/mol



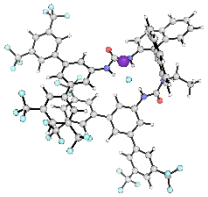
3gF•K-3
+5.5 kJ/mol



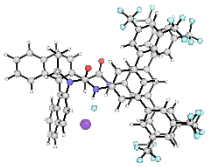
3gF•K-4
+6.1 kJ/mol



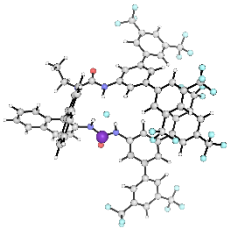
3gF•K-5
+6.2 kJ/mol



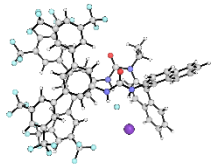
3gF•K-6
+7.4 kJ/mol



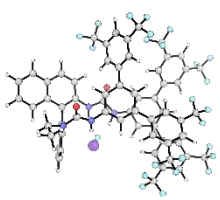
3gF•K-7
+7.8 kJ/mol



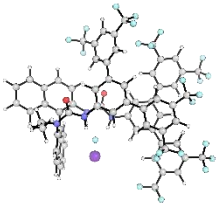
3gF•K-8
+9.8 kJ/mol



3gF•K-9
+13.6 kJ/mol



3gF•K-10
+22.6 kJ/mol



3gF•K-11
+23.2 kJ/mol

Figure S9 Conformers of **3g**F•K complex, with relative Gibbs free energies.

***Table S9*:** Key geometric parameters for complexes of **3g** with fluoride

	Key Distances (Å)				Key Angles (◦)	
	H-Bond 1	**H-Bond 2**	**H-Bond 3**	**M-F**	**H-Bond 3**	**Backbone**
3gF-1	1.719	1.693	1.733	-	153.8	71.5
3gF-2	1.812	1.576	1.709	-	156.7	73.2
3gF-3	1.862	1.514	1.589	-	168.9	79.2
3gF-4	1.785	1.544	1.619	-	164.8	86.4
3gF-5	1.740	1.670	1.712	-	155.0	70.4
3gF-6	1.792	1.603	1.597	-	164.7	79.9
3gF-7	1.874	1.539	1.698	-	155.3	105.1
3gF-8	1.696	1.699	1.798	-	155.7	72.6
3gF-9	1.852	1.566	1.708	-	155.4	108.6
3gF-10	1.714	1.748	1.670	-	161.7	71.6
3gF-11	1.714	1.757	1.691	-	160.7	67.7

***Table S10*:** Key geometric parameters for complexes of **3g** with potassium fluoride

	Key Distances (Å)				Key Angles (◦)	
	H-Bond 1	**H-Bond 2**	**H-Bond 3**	**M-F**	**H-Bond 3**	**Backbone**
3gF•K 1	1.744	1.794	1.872	2.427	153.0	72.6
3gF•K 2	1.729	1.811	1.895	2.427	151.4	74.4
3gF•K 3	1.732	1.858	1.804	2.433	160.8	74.7
3gF•K 4	1.845	1.650	1.696	2.442	168.0	77.5
3gF•K 5	1.743	1.785	1.939	2.424	153.6	74.4
3gF•K 6	1.808	1.637	1.714	2.461	166.1	85.4
3gF•K 7	1.801	1.698	1.827	2.429	153.9	74.8
3gF•K 8	1.803	1.731	1.715	2.444	162.3	83.7
3gF•K 9	1.734	1.878	1.810	2.429	159.9	69.5
3gF•K 10	1.837	1.643	1.851	2.449	150.3	107.7
3gF•K 11	1.820	1.662	1.870	2.447	151.2	110.0

__3g__-Aziridinium Ion Pairs

Catalyst complexed with fluoride and aziridinium ion ("reactive ion pair") was simulated using MD for 300 ns. The framework used for RMSD calculation is shown in Figure S10. All frames from the trajectory were used for clustering with RMSD cut-off of 0.8 Å. The 7 highest weighted clusters (> 1 % weighting) were optimized using DFT. Cluster weightings at half simulation time (150 ns) compare favorably with those at 300 ns;

additionally, a duplicate simulation was run with different starting point and was verified to produce comparable high-weighted clusters after 300 ns.

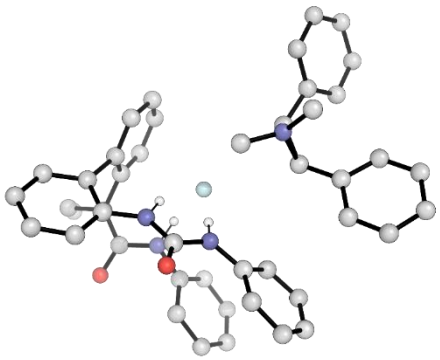
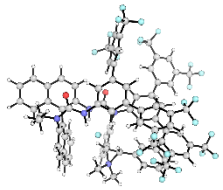
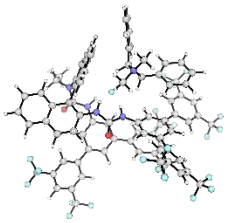


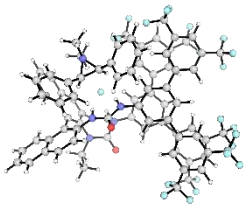
Figure S10 Molecular framework used for RMSD clustering of frames in trajectory of the reactive ion pair.



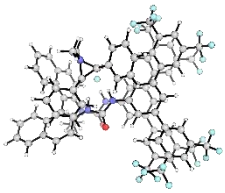
3gF-Azir-1
0.0 kJ/mol



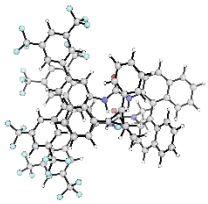
3gF-Azir-2
+0.8 kJ/mol



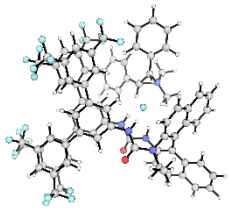
3gF-Azir-3
+7.4 kJ/mol



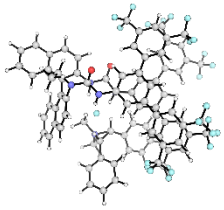
3gF-Azir-4
+7.9 kJ/mol



3gF-Azir-5
+8.4 kJ/mol



3gF-Azir-6
+14.0 kJ/mol



3gF-Azir-7
+24.8 kJ/mol

Figure S11 Conformers of **3g**-F aziridinium reactive ion pair, with relative Gibbs free energies.

Computation – Transition State Structures and Enantioselectivity

The reactive ion pairs were used to generate transition structure (TS) guesses by aligning the substrate C-N σ* with fluoride, resulting in an ensemble of 11 TSs (with (*S*) catalyst: 5 to (*S*,*S*) product and 6 to (*R*,*R*) product). Ethyl group rotation was checked for the 4 TSs within a 14 kJ/mol window, generating a further 3 conformers within the window. This ensemble of 7 low energy TSs is used for further analysis.

The TS ensemble indicates that (*S*)-catalyst affords (*S*,*S*) product in 95:5 e.r. in chloroform at 278.15 K. The major enantiomer is in agreement with experimental data, and the e.r. compares favorably with the experimental enantioselectivity of 95:5 e.r with potassium fluoride.

The Gibbs free energy distribution of the lowest energy TSs is shown in Figure S12. TS geometries and relative Gibbs free are given in Figure S13. Key geometric data are tabulated in Table S11. All TS Gibbs free energies are evaluated at 278.15 K.

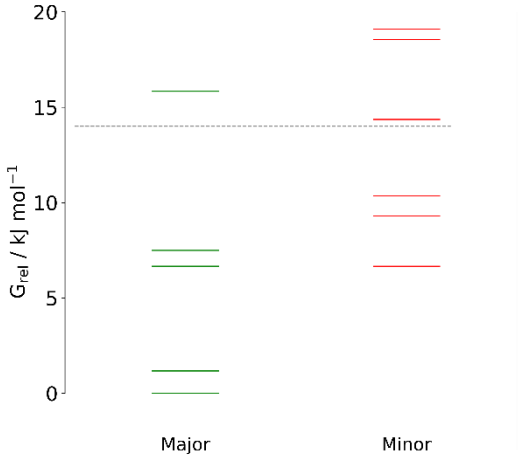
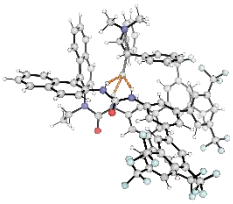
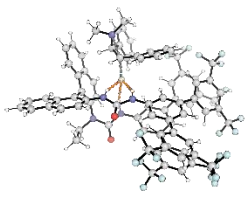


Figure S12 Distribution of TS Gibbs free energies at 278.15 K, to major and minor product.

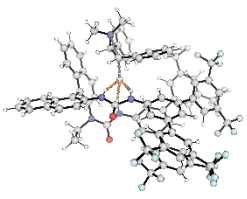
Transition structures to major enantiomer:



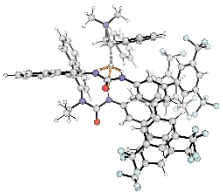
TS_3gF-Azir-major1
0.0 kJ/mol



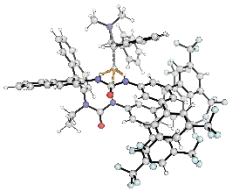
TS_3g-F-Azir-major2
+1.2 kJ/mol



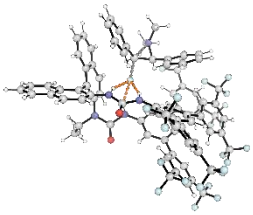
TS_3g-F-Azir-major3
+6.7 kJ/mol



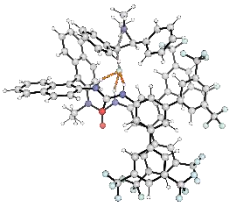
TS_3g-F-Azir-major4
+7.5 kJ/mol



TS_3g-F-Azir-major5
+15.8 kJ/mol

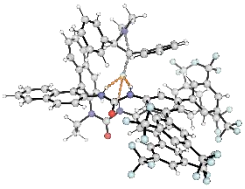


TS_3g-F-Azir-major6
+20.3 kJ/mol

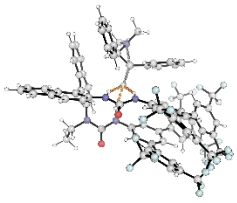


TS_3g-F-Azir-major7
+48.1 kJ/mol

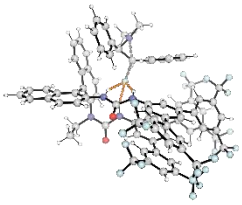
Transition structures to minor enantiomer:



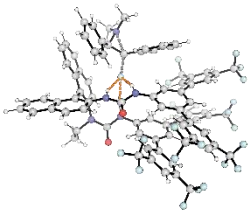
TS_3g-F-Azir-minor1
+6.7 kJ/mol



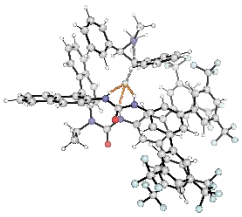
TS_3g-F-Azir-minor2
+9.3 kJ/mol



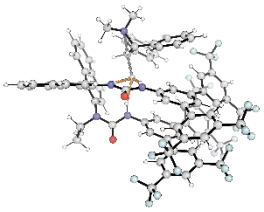
TS_3g-F-Azir-minor3
+10.4 kJ/mol



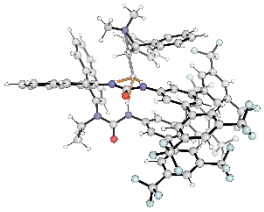
TS_3g-F-Azir-minor4
+14.4 kJ/mol



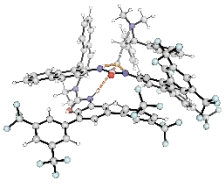
TS_3g-F-Azir-minor5
+18.6 kJ/mol



TS_3g-F-Azir-minor6
+19.2 kJ/mol



TS_3g-F-Azir-minor7
+20.5 kJ/mol



TS_3g-F-Azir-minor8
+46.4 kJ/mol

Figure S13 Transition state structures to major and minor product, with relative Gibbs free energies at 278.15 K.

***Table S11*:** Key geometric parameters for TSs

TS	Freq. imag.	Key Distances / Å					Key Angles / º			
		C-F	C-N	H bond 1	H bond 2	H bond 3	H bond 3	α-Dihedral†	β-Dihedral†	Backbone
TS_3gF-Azir-major1	-553.0	1.914	1.932	1.801	1.813	2.012	142.5	-34.5	-43.5	70.7
TS_3gF-Azir-major2	-553.0	1.912	1.935	1.790	1.823	1.987	145.3	-34.2	-44.1	71.3
TS_3gF-Azir-major3	-553.1	1.916	1.940	1.738	1.860	2.053	152.0	-27	-34.0	67.3
TS_3gF-Azir-major4	-553.1	1.915	1.940	1.737	1.867	2.045	154.7	-27.2	-34.1	68.5
TS_3gF-Azir-major5	-554.0	1.915	1.942	1.857	1.775	1.976	151.2	-21.2	-43.4	68.4
TS_3gF-Azir-major6	-580.6	1.896	1.876	1.857	1.810	1.875	144.5	-86.3	-21.8	70.9
TS_3gF-Azir-major7	-569.6	1.891	1.892	1.925	1.724	1.990	149.0	-72.5	-38.1	65.4
TS_3gF-Azir-minor1	-567.3	1.908	1.904	1.887	1.739	2.115	139.9	-54.2	-46.4	67.5
TS_3gF-Azir-minor2	-566.1	1.906	1.898	1.827	1.794	2.022	145.0	-49.8	-43.1	69.4
TS_3gF-Azir-minor3	-565.5	1.904	1.899	1.820	1.799	1.992	148.3	-50.7	-43.0	70.4
TS_3gF-Azir-minor4	-562.8	1.910	1.922	1.894	1.692	2.281	150.9	-42.6	-43.5	69.6
TS_3gF-Azir-minor5	-570.7	1.890	1.895	1.837	1.785	2.061	145.7	-65.6	-42.2	67.5
TS_3gF-Azir-minor6	-571.9	1.897	1.892	1.960	1.680	2.012	145.8	-71.8	37.4	68.7
TS_3gF-Azir-minor7	-571.9	1.897	1.892	1.959	1.679	2.014	145.8	-71.8	37.5	68.8
TS_3gF-Azir-minor8	-579.6	1.915	1.872	1.873	1.642	3.035	169.9	-78.3	26.0	112.3

†Phenyl ring dihedrals measured relative to C-C bond. See Fig. S4 for definition.

Origins of Enantioselectivity

The remainder of this analysis focuses on the two most important TSs, the lowest energy TS to major product (**TS_3gF-Azir-major1**, referred to as TS_{Major}), and the lowest energy TS to minor product (**TS_3gF-Azir-minor1**, referred to as TS_{Minor}), with $\Delta\Delta G^{\ddagger}$ = -6.7 kJ/mol and $\Delta\Delta E^{\ddagger}$ = -7.1 kJ/mol.

Catalyst Conformation

Catalyst **3g** forms extensive intramolecular sandwich π-π stacking, reducing conformational freedom. TS_{Major} and TS_{Minor} have the same catalyst conformation, eliminating this as a significant factor in determining enantioselectivity (Fig. S14).

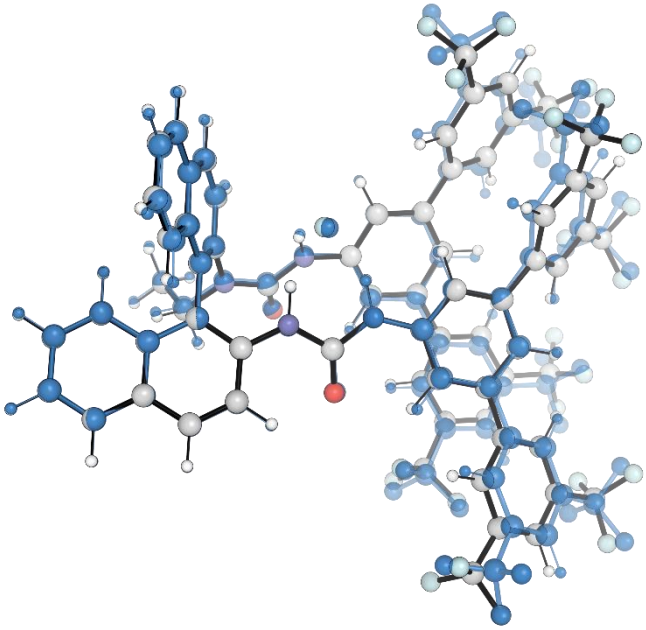


Figure S14 Superposition of TS_{Major} (conventional coloring) and TS_{Minor} (blue), showing close agreement of catalyst conformation. Substrate was removed for clarity.

Substrate Conformation

Substrate conformation favors conjugation of phenyl ring with the forming and breaking bonds, as typical for a benzylic substitution. In TS_{Major}, this ring has dihedral of -34.5°, whereas in TS_{Minor} it is further from conjugation at -54.2° . A dihedral scan of the α-phenyl ring in the fluoride delivery TS with achiral Schreiner's urea was used to estimate this contribution as ~4 kJ/mol (Fig. S15. See Fig. S4 for dihedral definition). Fitting of a quartic polynomial to the 9 points -65° < dihedral < 25° estimates that the minimum of the curve is at -27.6°, thus TS_{Major} is approximately 7° from optimum and TS_{Minor} 27° from optimum.

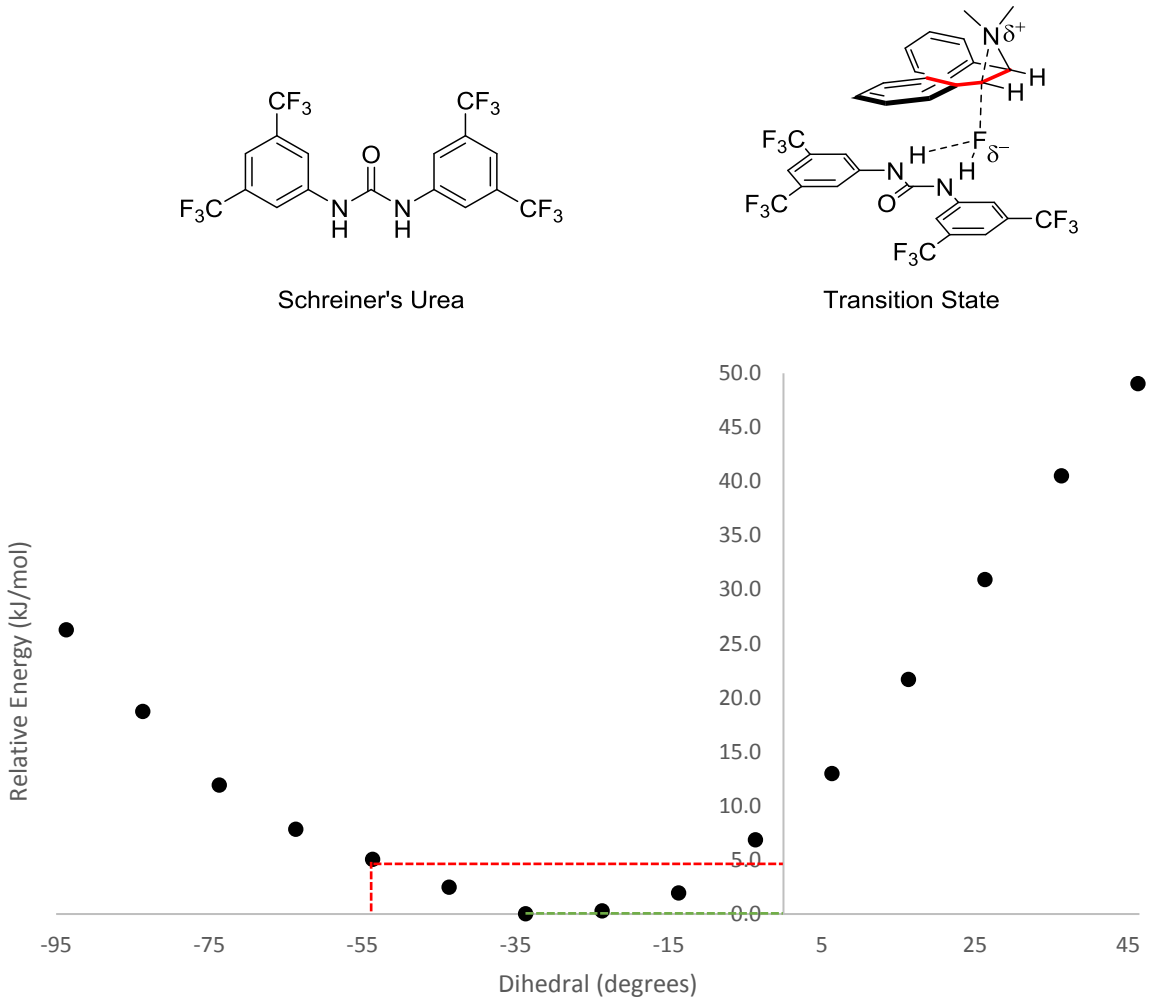


Figure S15 Dihedral scan of α-phenyl ring in TS with achiral Schreiner's urea. The dihedral angles of TS_{Major} (green) and TS_{Minor} (red) are indicated on the energy plot.

Single point energy evaluation of TS_{Major} and TS_{Minor} with catalyst removed (*i.e.* aziridinium + fluoride) favors TS_{Major} by 4.9 kJ/mol, consistent with α-phenyl conjugation as the main factor in substrate distortion. TS_{Major} is looser than TS_{Minor}, with both C–F and C–N bonds longer. If the α-phenyl ring of the aziridinium + fluoride TS units is replaced by methyl, the energetic preference for the major drops to 1.7 kJ/mol, further supporting that conjugation of the α-phenyl ring is key to stabilizing TS_{Major} (Fig. S16).

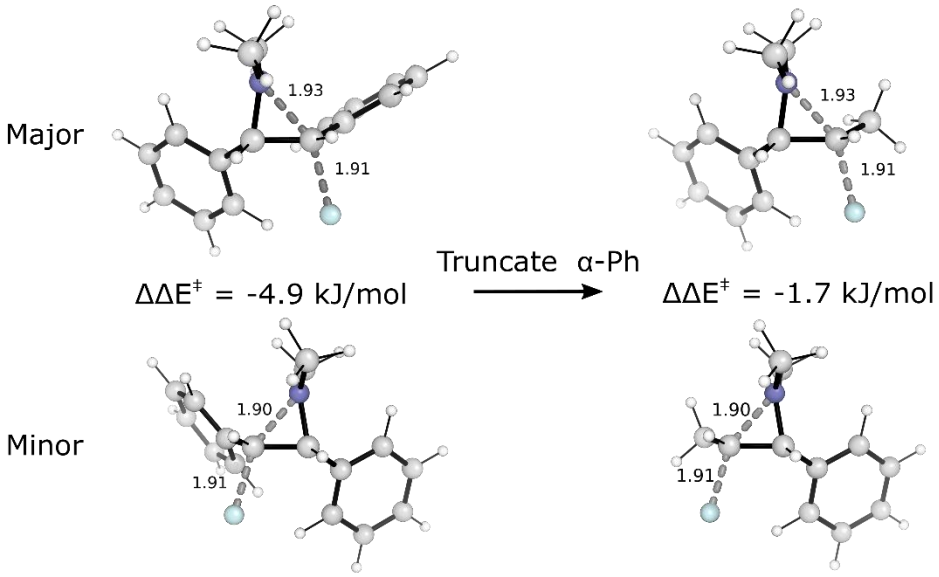


Figure S16 Truncated TS_{Major} and TS_{Minor}. LHS: TS geometries and energetic preference with catalyst removed. RHS: Energetic preference with conjugating α-phenyl truncated to methyl group. The drop in energetic preference for major over minor by 3.2 kJ/mol is consistent with a key role for α-phenyl conjugation is stabilizing the major.

Non-covalent Interactions

Aziridinium substrate docks into the catalyst, forming a cation-π interaction with one of the BINAM aromatic rings (TS_{Major}: 2.26 Å, TS_{Minor}: 2.41 Å). To estimate the difference in cation-π strength, the BINAM aromatic ring was truncated, suggesting a difference in strength of approximately 1.5 kJ/mol (Fig. S17).

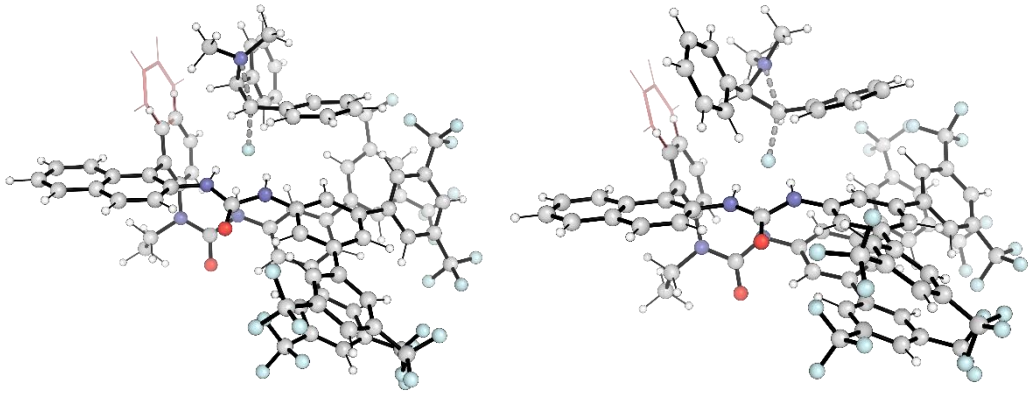


Figure S17 Truncated TS_{Major} (LHS) and TS_{Minor} (RHS), with key BINAM aromatic ring removed (red wireframe). $\Delta E^{‡}$ is reduced from -7.1 kJ/mol to -5.5 kJ/mol suggesting a stronger cation-π interaction in TS_{Major} by approximately 1.5 kJ/mol.

All low energy TSs feature 3 hydrogen bonds from catalyst to fluoride (though H Bond 3 is relatively elongated). Hydrogen bond lengths demonstrate that in TS_{Minor}, fluoride is bound further away from the

BINAM core (H bonds 1 and 3, longer; H bond 2, shorter). Analysis of the geometry of TS_{Minor} suggests that this is due to lack of room for the substrate, caused by the proximity of the BINAM backbone (Fig. S18, see also IRC analysis). Single point energy of catalyst binding fluoride in the TS geometries (*i.e.* aziridinium removed) favors TS_{Major} by 2.5 kJ/mol, consistent with slightly preferential fluoride binding in TS_{Major}.

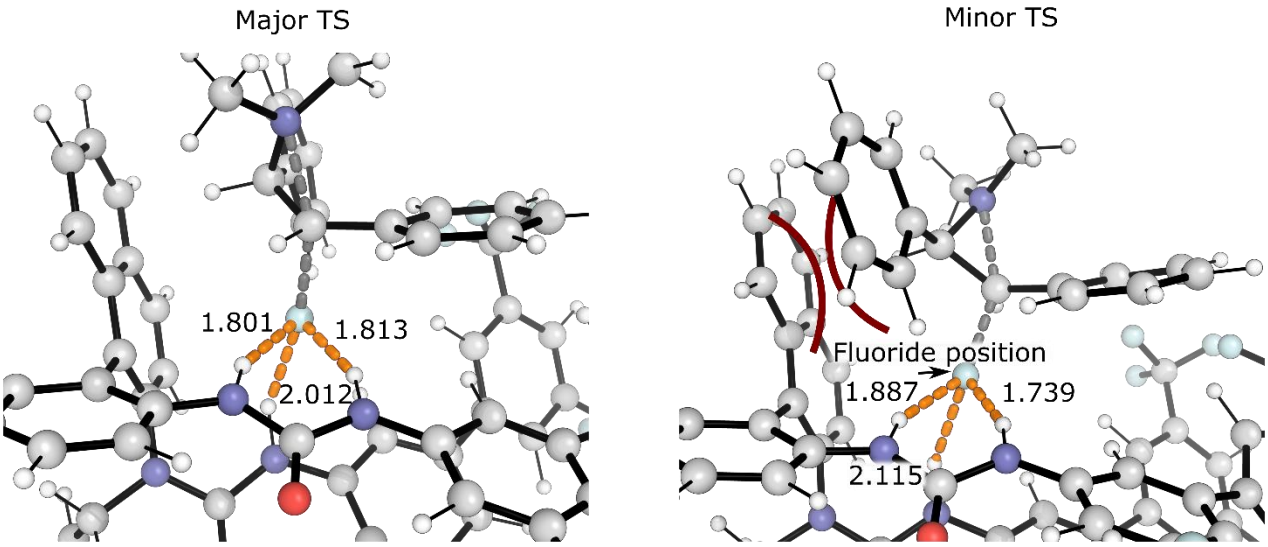


Figure S18 Comparison of fluoride binding environment in TS_{Major} and TS_{Minor}. Distances are consistent with steric congestion in TS_{Minor}.

Non-covalent interaction (NCI) plots were calculated for TS_{Major} and TS_{Minor} from the optimization density, highlighting the extensive non-covalent interactions in the TSs (Fig. S19).

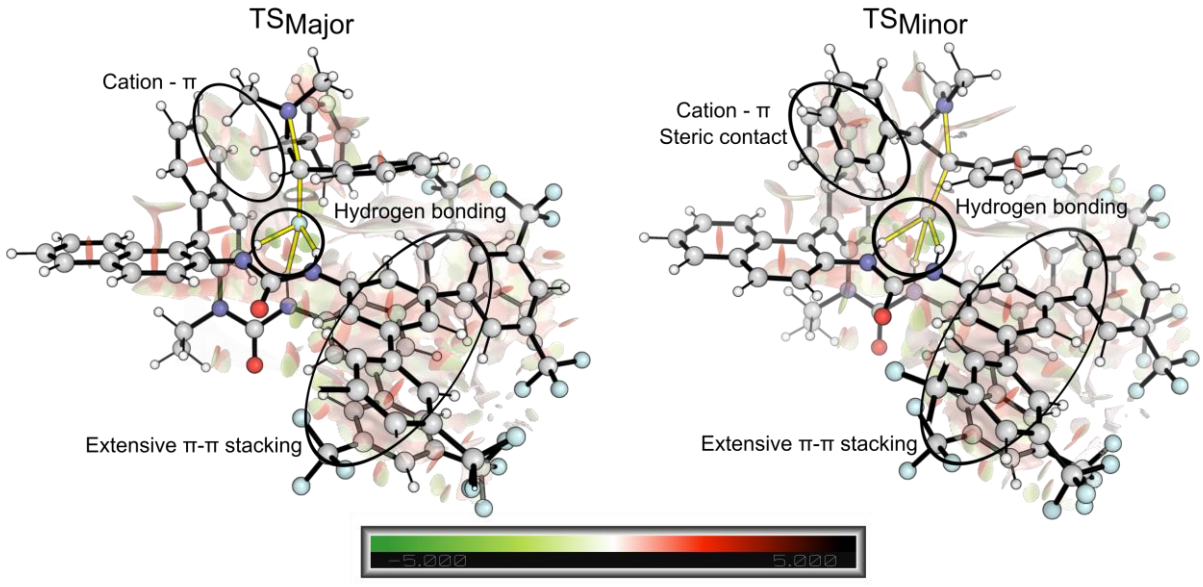


Figure S19 Visualization of non-covalent interactions in TS_{Major} and TS_{Minor} using the non-covalent interaction index. Key NCIs are highlighted.

Substituent Tolerance

Diverse substituents are tolerated on aziridinium nitrogen, without substantial change in enantioselectivity (11 examples (**2a**-**2k**) each with KF and CsF, ranging from 92:8 e.r. to 97:3 e.r.). Substrate **2h**, with isoindoline motif, suffers the lowest enantioselectivity at 92:8 e.r.; however, this corresponds to an energy change on the order of 1 kJ/mol, which is not easily attributable. Substituent tolerance on nitrogen is consistent with the computed TSs, as the nitrogen substituents point outward of the catalyst pocket in both TS_{Major} and TS_{Minor}.

Non Stilbene-derived Cyclic Substrates

Cyclic substrates not derived from stilbene are fluorinated with lower enantioselectivity and produce the opposite enantiomer (*R*,*R*) of product. The key substrate-catalyst cation-π interaction is retained, continuing to orient the substrate such that substituents on nitrogen point out of the catalyst pocket. However, the S_N2 is no longer benzylic; a factor that contributes approximately half of $\Delta\Delta G^{\ddagger}$ for stilbene-derived substrates. This factor, along with minor rearrangements of the catalyst pocket and substrate docking pose are the expected origin of reversal of enantioselectivity.

Intrinsic Reaction Coordinate (IRC) Analysis

The intrinsic reaction coordinate (IRC) pathway was followed for the two TSs, with the IRC pathway to major and minor products referred to as IRC_{Major} and IRC_{Minor} respectively. Geometries were monitored over the IRCs (Fig. S20). The main bond forming and breaking occurs in the region -0.9 < IRC < 0.9, after which substrate relaxation occurs. The IRC is plotted from a value of -1.2, where C–F distance is 1.3 Å longer than equilibrium, but fluoride is aligned with the C-N σ*. Geometric parameters of the optimized product complex are plotted as points.

Summary:

- IRC_{Major} is consistently looser in the main bond forming and breaking region than IRC_{Minor}, consistent with conjugation of the α-phenyl ring with the forming and breaking bonds.
- Both begin tridentate, however H-bond 3 is substantially elongated by the TSs, exceeding 2.11 Å in the case of IRC_{Minor}.
- At IRC = -1.2, all hydrogen bonds are similar lengths, both within each IRC pathway and between each pathway.
- In both IRC_{Major} and IRC_{Minor}, H-bond 3 elongates rapidly over the IRC. In IRC_{Minor}, H Bond 3 is consistently ~0.1 Å longer during main bond forming and bond breaking.
- In IRC_{Minor}, fluoride moves away from the BINAM backbone over the IRC (H Bond 1 elongates, H Bond 2 shortens). H Bond 1 is broken in the product complex.
- Both cation-π interactions lengthen as they transition to CH-π interactions, with the interaction in IRC_{Minor} consistently longer. As bond forming begins, both cation-π interactions shorten as the substrate is pulled towards the catalyst. In the minor product complex, the substrate moves significantly away from the aromatic ring, in contrast to the major where the CH-π remains at roughly consistent length.
- As bond forming begins, both BINAM dihedrals decrease, corresponding to an opening of the catalytic site. Once bond formation is complete, both dihedrals increase, however to a much greater degree in IRC_{Minor} (1.5° vs 3.5°).

The latter 3 points are consistent with steric clash of substrate and BINAM backbone over IRC_{Minor}, building up as the TS is approached and is relieved after the TS, into the product complex.

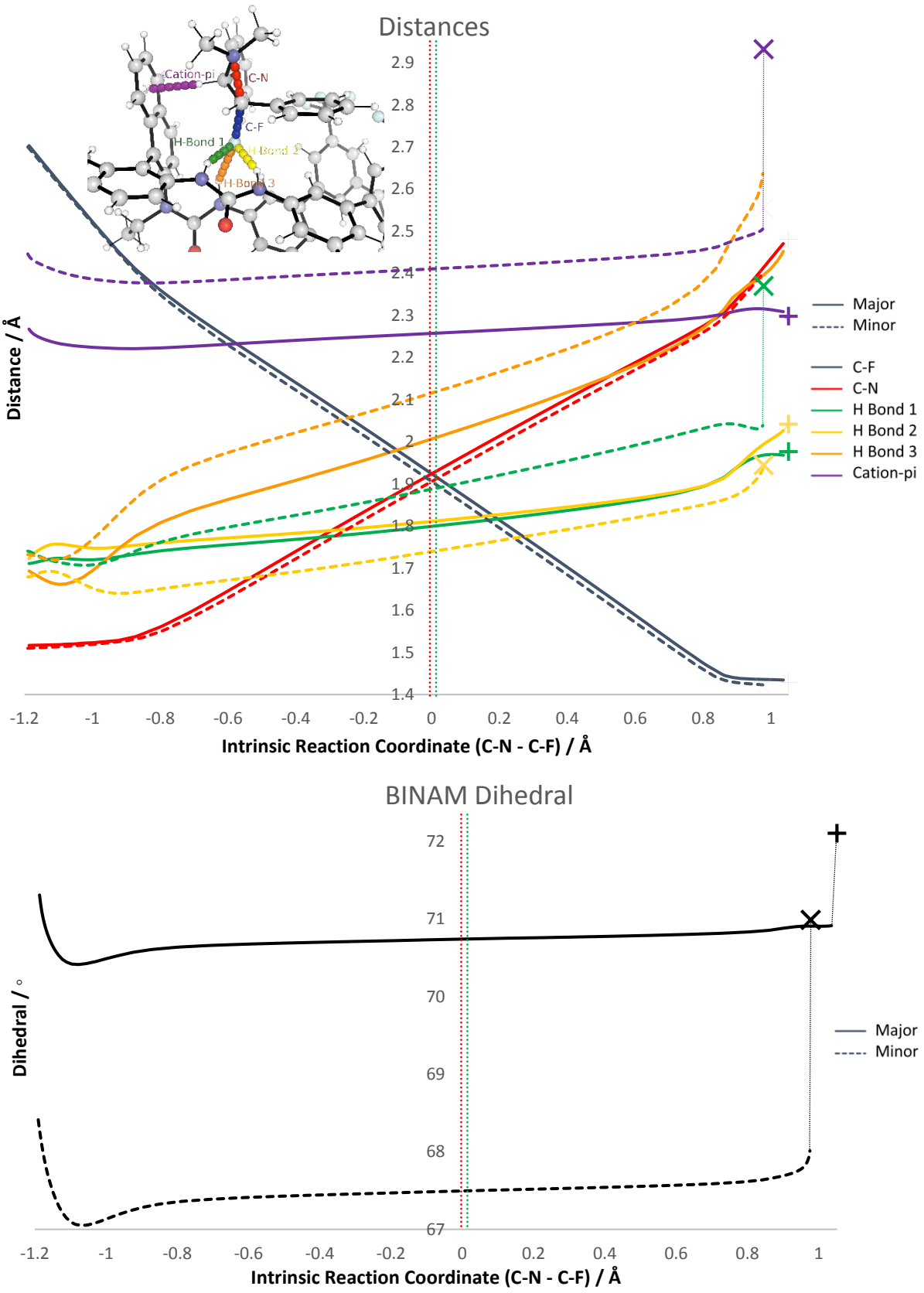


Figure S20 Plot of distances and BINAM backbone angle over the intrinsic reaction coordinate pathway to major (solid lines) and minor (dashed lines) product. Axes are drawn at the position of TS_{Major} (green) and TS_{Minor} (red). Relevant optimized product complex geometries are plotted (major: +, minor: **X**) – note that steep vertical displacement of these points should not be interpreted as rapid change.

Computation – Thermochemical Data

***Table S12*:** Catalyst **3b**

	Energies (Ha)				
	E (opt)	**G (opt)**	**G-qh (opt)**	**E (sp)**	**G-qh (sp)**
3b	-3064.986424	-3064.490460	-3064.476912	-3068.773763	-3068.264251
3bF•Cs	-3185.082340	-3184.585204	-3184.572779	-3188.943228	-3188.433667
3bF•K	-3764.904108	-3764.406820	-3764.394299	-3768.696028	-3768.186219

***Table S13*:** Uncoordinated **3g**

	Energies (Ha)				
	E (opt)	**G (opt)**	**G-qh (opt)**	**E (sp)**	**G-qh (sp)**
3g-1	-5374.209878	-5373.382114	-5373.356062	-5380.855333	-5380.001517
3g-2	-5374.228039	-5373.389687	-5373.369400	-5380.854932	-5379.996293
3g-3	-5374.230811	-5373.390093	-5373.370810	-5380.855792	-5379.995791
3g-4	-5374.212056	-5373.381566	-5373.357044	-5380.850705	-5379.995693
3g-5	-5374.214784	-5373.381662	-5373.358268	-5380.852000	-5379.995484
3g-6	-5374.223051	-5373.386103	-5373.364819	-5380.853067	-5379.994835
3g-7	-5374.201461	-5373.374535	-5373.348240	-5380.846975	-5379.993755
3g-8	-5374.227783	-5373.389910	-5373.368635	-5380.850705	-5379.991556
3g-9	-5374.213794	-5373.380408	-5373.357475	-5380.847852	-5379.991532
3g-10	-5374.193262	-5373.366071	-5373.339738	-5380.842507	-5379.988984
3g-11	-5374.190779	-5373.367488	-5373.339304	-5380.839176	-5379.987700

***Table S14*: 3g**-fluoride Complexes

	Energies (Ha)				
	E (opt)	**G (opt)**	**G-qh (opt)**	**E (sp)**	**G-qh (sp)**
3gF-1	-5474.244879	-5473.410096	-5473.387919	-5480.881541	-5480.024581
3gF-2	-5474.246598	-5473.409569	-5473.389287	-5480.881334	-5480.024023
3gF-3	-5474.228022	-5473.400973	-5473.374906	-5480.877042	-5480.023925
3gF-4	-5474.219531	-5473.392783	-5473.366686	-5480.875802	-5480.022957
3gF-5	-5474.247213	-5473.408169	-5473.388308	-5480.881400	-5480.022495
3gF-6	-5474.224673	-5473.399835	-5473.372668	-5480.874245	-5480.022240
3gF-7	-5474.236455	-5473.403109	-5473.380553	-5480.877899	-5480.021998
3gF-8	-5474.248257	-5473.409339	-5473.389425	-5480.880066	-5480.021234
3gF-9	-5474.238684	-5473.403568	-5473.381433	-5480.878410	-5480.021160
3gF-10	-5474.243694	-5473.405371	-5473.384767	-5480.879874	-5480.020947
3gF-11	-5474.248476	-5473.408220	-5473.388610	-5480.877945	-5480.018079
3gF•K-1	-6074.138225	-6073.302407	-6073.280984	-6080.776963	-6079.919723
3gF•K-2	-6074.136304	-6073.300721	-6073.278988	-6080.776652	-6079.919336
3gF•K-3	-6074.132760	-6073.298404	-6073.275528	-6080.774851	-6079.917620
3gF•K-4	-6074.115471	-6073.289652	-6073.262649	-6080.770231	-6079.917409
3gF•K-5	-6074.139953	-6073.303028	-6073.281797	-6080.775534	-6079.917379
3gF•K-6	-6074.106044	-6073.284670	-6073.255697	-6080.767244	-6079.916896
3gF•K-7	-6074.134805	-6073.298567	-6073.277711	-6080.773858	-6079.916764
3gF•K-8	-6074.114247	-6073.290510	-6073.262567	-6080.767683	-6079.916002
3gF•K-9	-6074.138144	-6073.300149	-6073.279590	-6080.773103	-6079.914550
3gF•K-10	-6074.123575	-6073.287110	-6073.265514	-6080.769170	-6079.911108
3gF•K-11	-6074.125895	-6073.291268	-6073.268698	-6080.768092	-6079.910894

***Table S15*: 3g**-F-Aziridinium Ion Pairs

	Energies (Ha)				
	E (opt)	**G (opt)**	**G-qh (opt)**	**E (sp)**	**G-qh (sp)**
3gF-Azir-1	-6148.639173	-6147.519998	-6147.491095	-6156.073614	-6154.925536
3gF-Azir-2	-6148.636685	-6147.520388	-6147.489509	-6156.072391	-6154.925215
3gF-Azir-3	-6148.658183	-6147.527920	-6147.504483	-6156.076418	-6154.922719
3gF-Azir-4	-6148.653838	-6147.524558	-6147.500643	-6156.075710	-6154.922515
3gF-Azir-5	-6148.646573	-6147.521140	-6147.495077	-6156.073840	-6154.922343
3gF-Azir-6	-6148.649583	-6147.524317	-6147.498962	-6156.070828	-6154.920208
3gF-Azir-7	-6148.644443	-6147.519600	-6147.493603	-6156.066932	-6154.916092

***Table S16*: 3g**-F-Aziridinium Transition State Structures (278.15 K)

	Energies (Ha)				
TS_3gF-Azir-	**E (opt)**	**G (opt)**	**G-qh (opt)**	**E (sp)**	**G-qh (sp)**
major1	-6148.620859	-6147.482565	-6147.459223	-6156.047669	-6154.886032
major2	-6148.621222	-6147.482462	-6147.459606	-6156.047206	-6154.885590
major3	-6148.620397	-6147.478730	-6147.457556	-6156.046317	-6154.883475
major4	-6148.621335	-6147.478758	-6147.458213	-6156.046283	-6154.883160
major5	-6148.615643	-6147.476561	-6147.454183	-6156.041464	-6154.880004
major6	-6148.608842	-6147.470890	-6147.447411	-6156.039741	-6154.878311
major7	-6148.614400	-6147.469990	-6147.449556	-6156.032544	-6154.867700
minor1	-6148.616610	-6147.478326	-6147.455128	-6156.044981	-6154.883498
minor2	-6148.617157	-6147.478132	-6147.455271	-6156.044371	-6154.882485
minor3	-6148.617085	-6147.477681	-6147.455286	-6156.043888	-6154.882090
minor4	-6148.620942	-6147.479131	-6147.458279	-6156.043213	-6154.880551
minor5	-6148.619145	-6147.478918	-6147.456607	-6156.041499	-6154.878961
minor6	-6148.618055	-6147.475814	-6147.454514	-6156.042275	-6154.878734
minor7	-6148.618091	-6147.475443	-6147.454226	-6156.042070	-6154.878205
minor8	-6148.592956	-6147.458077	-6147.432952	-6156.028361	-6154.868357

***Table S17*:** Miscellaneous

	Energies (Ha)				
	E (opt)	**G (opt)**	**G-qh (opt)**	**E (sp)**	**G-qh (sp)**
$CsF_{(g)}$	-120.001129	-120.021281	-120.021283	-120.088507	-120.108661
$CsF_{(DCM)}$	-120.040461	-120.061200	-120.061202	-120.135181	-120.155922
$KF_{(g)}$	-699.816535	-699.834673	-699.834674	-699.839431	-699.857570
$KF_{(DCM)}$	-699.866799	-699.885504	-699.885506	-699.889109	-699.907816

Computation – Coordinates and MD Input Files

Coordinates for DFT stationary points (in .xyz format) are provided and uploaded separately. MD topology and input files are also provided.

Determination of the Absolute Configuration (Single Crystal X-ray Diffraction Studies)

The absolute configuration was determined both by comparison of the optical rotation of compound **8** (see characterization section) to known literature values[12] and by single crystal X-ray diffraction.

Four attempts were made to grow single crystals of **2g** and its **2g·HCl** salt from 1) heptane/THF (vial 1), 2) heptane/THF (vial 2), 3) EtOH (vial 3) and 4) Heptane/EtOAc (vial 4).

Single crystal X-ray diffraction data were collected using a (Rigaku) Oxford Diffraction Supernova diffractometer (λ_{Cu} = 1.54184 Å; λ_{Mo} = 0.71073 Å) fitted with an Oxford CryoSystems 700 Series CryoStream.[58] In general, a suitable crystal was chosen and was mounted on a 200 μm MiTeGen loop using perfluoropolyether oil. The CrysAlisPro software was used for data collection, as well as peak hunting, indexing reflections in reciprocal space, integration of the raw frames and application of corrections including interframe scaling, Lorentz, flood field and dark current corrections. The CrysAlisPro suite was also used to examine raw images, study harvested peaks in reciprocal space and produce reconstructions of reciprocal lattice layers. All structures were solved *ab initio* from the integrated intensities using ShelXS,[59] and refined using full-matrix least-squares refinement with CRYSTALS.[60, 61] For ease of comparison, for isomorphous structures, the results reported here were based on the same starting model which was modified and refined as appropriate. In some cases, the displacement ellipsoids were found to be prolate, so these structures were modelled as disordered with a split-site and competitive occupancy refinement. Hydrogen atoms were usually clearly visible in the difference Fourier map. The hydrogen atoms were positioned at geometrically sensible positions and refined using soft restraints prior to inclusion in the refinement using a riding model.[62] While most hydrogen aqueous atoms were visible in the difference Fourier maps, some were not, in particular those for data collected at room temperature; these were positioned based on hydrogen bonding interactions. It is highly possible that some of these are dynamic which may explain the unusual contacts.

Initial studies at 150 K indicated the presence of two distinct compounds, both monoclinic: 13.50 Å, 18.04 Å, 15.82 Å, β = 107.1°, V = 3683 Å^3, and 8.47 Å, 11.66 Å, 16.09 Å, β = 100.5°, V = 1562 Å^3. Preliminary structure determination showed these to be the HCl salt (**2g·HCl**) and the neutral molecule respectively. The data collected on the **2g·HCl** solved in the space group $P2_1$ with an approximate *c*-glide plane and giving a structure with four formula units in the asymmetric unit. Significant systematic absence violations in the *h*0*l* class suggested this was a pseudo-glide as well as the high degree of enantiopurity (the crystals came from a 95:5 e.r. mixture). The neutral species also solved in the space group $P2_1$, this time with two molecules in the asymmetric unit partially related by an approximate inversion centre.

Crystals were tested at 300 K from the four different crystallisations. Multiple crystals from samples 1, 3 & 4 were found to contain the neutral species with no indication of a phase change. Crystals from sample 2 were also tested at 300 K and found to exhibit a different cell, 8.85 Å, 17.94 Å, 12.01 Å, β = 99.7°, V = 1880 Å^3, which corresponds to a B-centred cell in the original setting seen for **2g·HCl**. The structure solved in the space group $P2_1$ with two molecules in the asymmetric unit. In order to confirm the relationship between the two

phases, a variable temperature data collection was carried out with full data collections at 300 K and 150 K and unit cells recorded at 25 K intervals. The unit cell parameters were determined (based on the original cell) and plotted as a function of temperature (Fig. S21). There was a clear discontinuity between 200 K and 175 K indicative of a phase transition. This was also visible when following the 6 1 7 reflection (Fig. S22) which was clearly absent at 200 K (and above), and present at 175 K (and below).

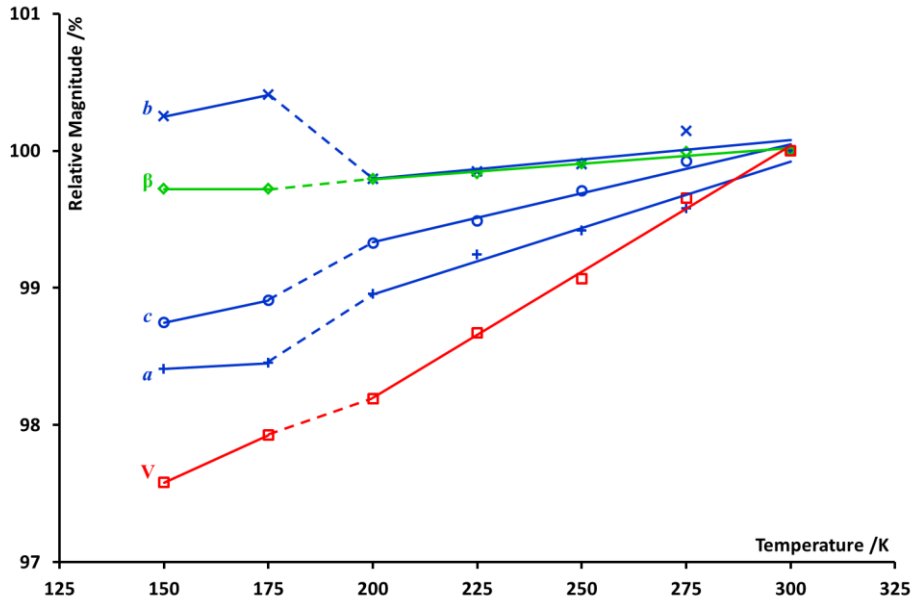


Figure S21. Unit cell parameters relative to the values at 300 K plotted as a function of temperature. Trend-lines are shown above and below the transition with a broken line in between to guide the eye.

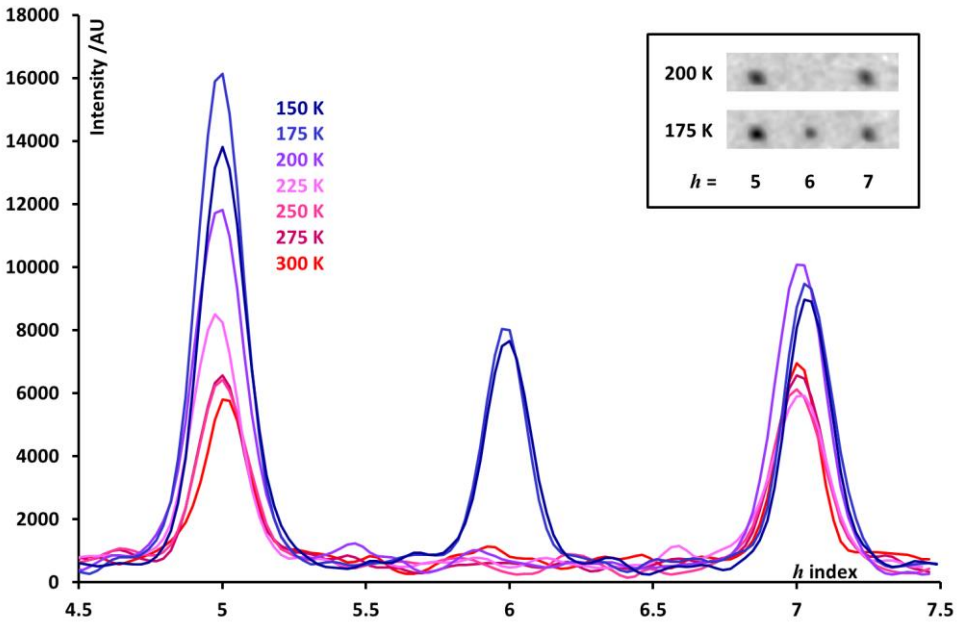


Figure S22. Intensity for the *h* 1 7 region where 4.5 < *h* < 7.5 as a function of temperature showing the appearance of the 6 1 7 reflection between 200 K and 175 K on cooling and a reconstruction of the relevant part of the *h* 1 *l* layer is shown inset.

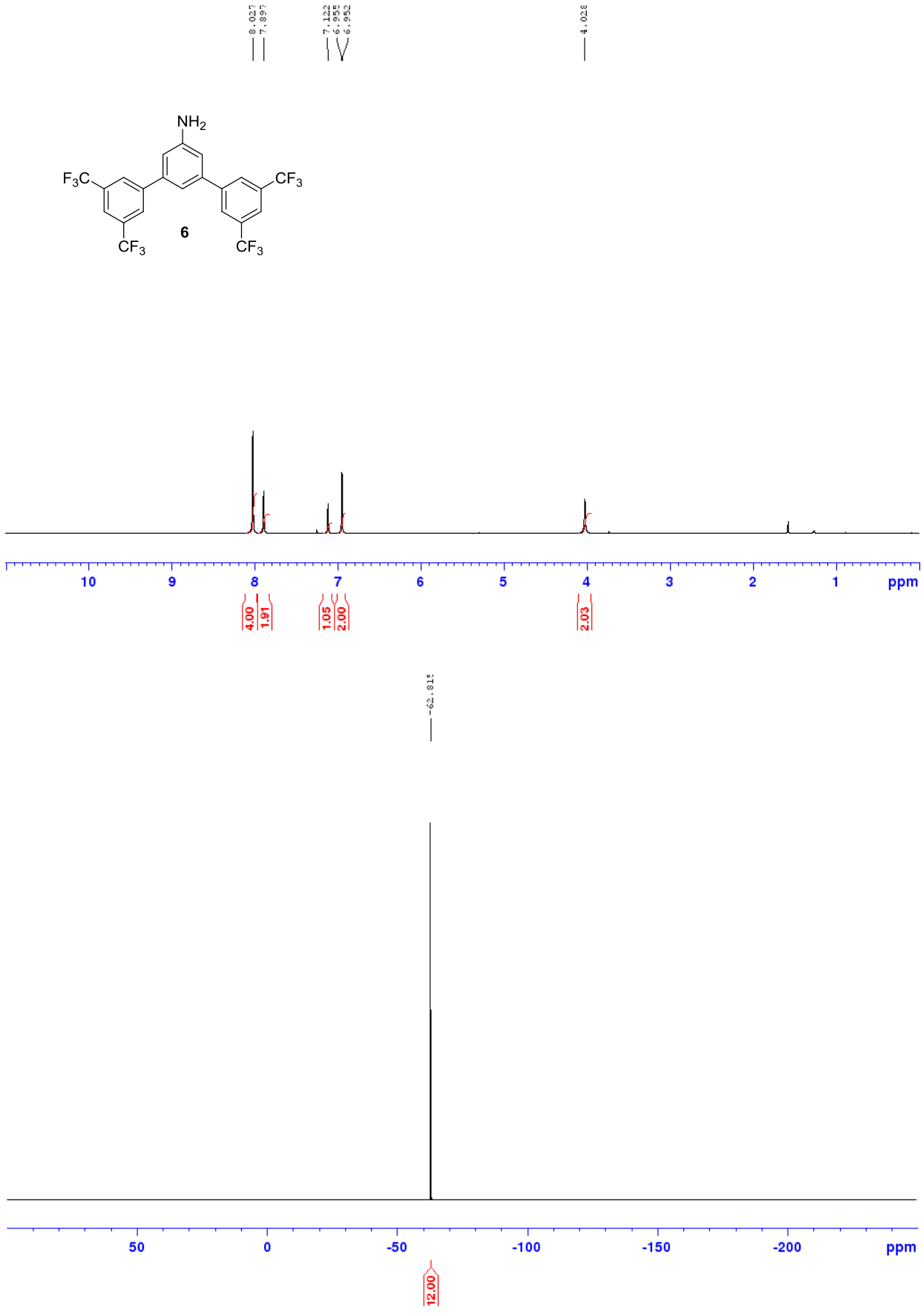
Table S18. Values for the absolute structure determination for **2g** and **2g·HCl**. P2 probability that the configuration as refined is correct given the binary condition that the crystal is enantiopure, while P3 is the probability allowing for the additional racemic possibility. The configuration determination is poor for the VT experiment particularly after the crystal has undergone the phase transition which visibly degraded the data quality.

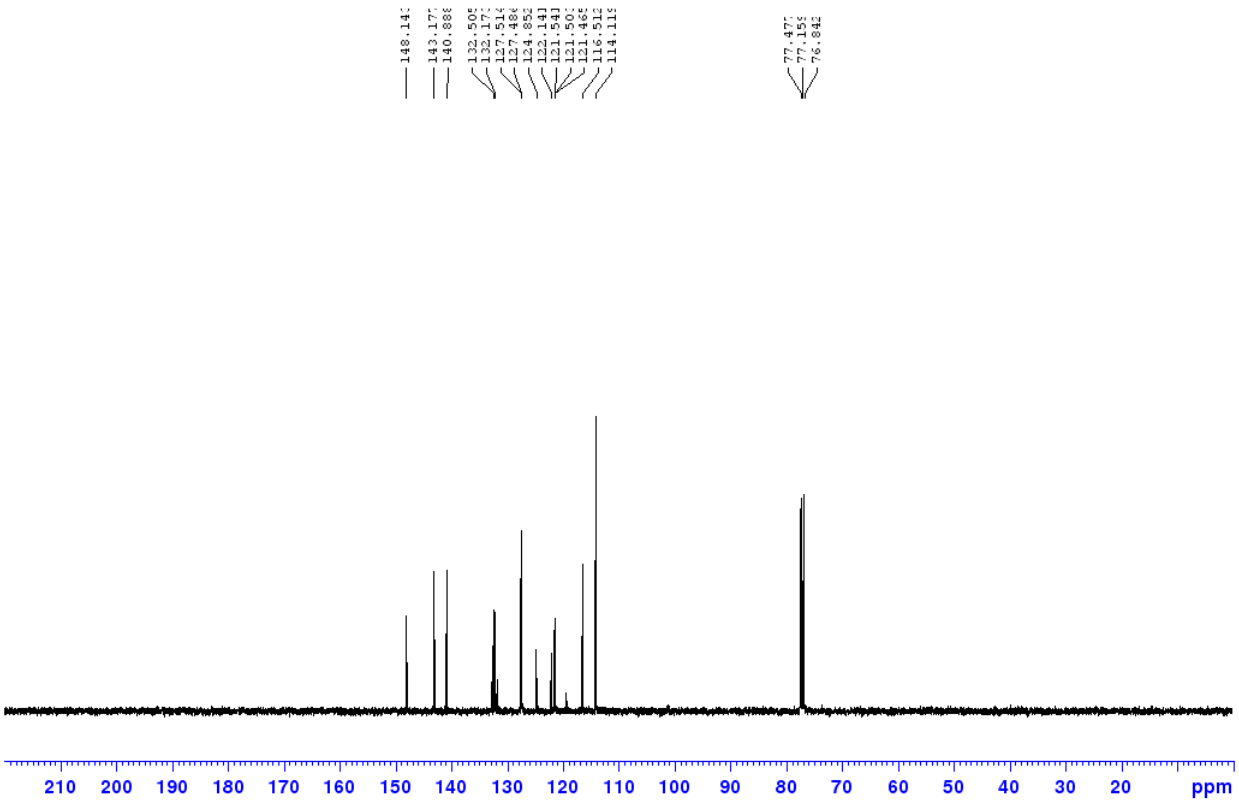
Form (vial)	Temp./K	Flack *x*	P2 (correct)	P3 (correct)	P3 (racemic)	Configuration
2g (3)	150 K	-0.02(11)	>0.999999	>0.999999	$<0.38 \times 10^{-11}$	100% "SS"
2g·HCl (2)	150 K-Q	0.03(3)	>0.999999	>0.999999	$< 0.01 \times 10^{-12}$	~75% "SS"
2g·HCl (2)	300 K-VT	0.16(13)	>0.999999	0.999694	$<0.31 \times 10^{-3}$	~75% "SS"
2g·HCl (2)	150 K-VT	0.29(10)	-	$>0.56 \times 10^{-4}$	>0.999943	>50% "SS"

Single crystal diffraction data collected with copper data on the neutral species and on **2g·HCl** quench-cooled to 150 K were examined in detail, as were data for **2g·HCl** collected at 300 K and 150 K as part of the variable temperature study using molybdenum radiation. In the case of the neutral species, both molecules in the asymmetric unit exhibited the same conformation and the Flack *x* parameter[63–65] was found to be -0.02(11). In the case of **2g·HCl** the situation was more complex with half of the molecules (two at 300 K and four at 150 K) exhibiting prolate ellipsoids. The most affected carbon atoms were the stereo centres, but the two adjacent phenyl rings were also affected though to a lesser extent. Modelling this as disorder led to an inversion at both centres. Competitively refining the occupancy the disordered components indicated the disorder was approximately 50% in each case, leading to an overall 3:1 ratio of the two configurations, "SS" and "RR". Flack *x* parameters were refined in each case and Bayesian analysis[66] of the probabilities carried out. The Friedel differences were smaller for the molybdenum data leading to a marked loss of precision, and the data suggested that crystals suffer damage when cooled slowly through the transition. Nevertheless, these values were in keeping with the major configuration agreeing with that seen for the neutral species (Table S18).

For further details see the full crystallographic data (in CIF format) which are available as associated content and have been deposited with Cambridge Crystallographic Data Centre (reference codes CCDC 1880527-1880530); these data can also be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

Copies of NMR Spectra

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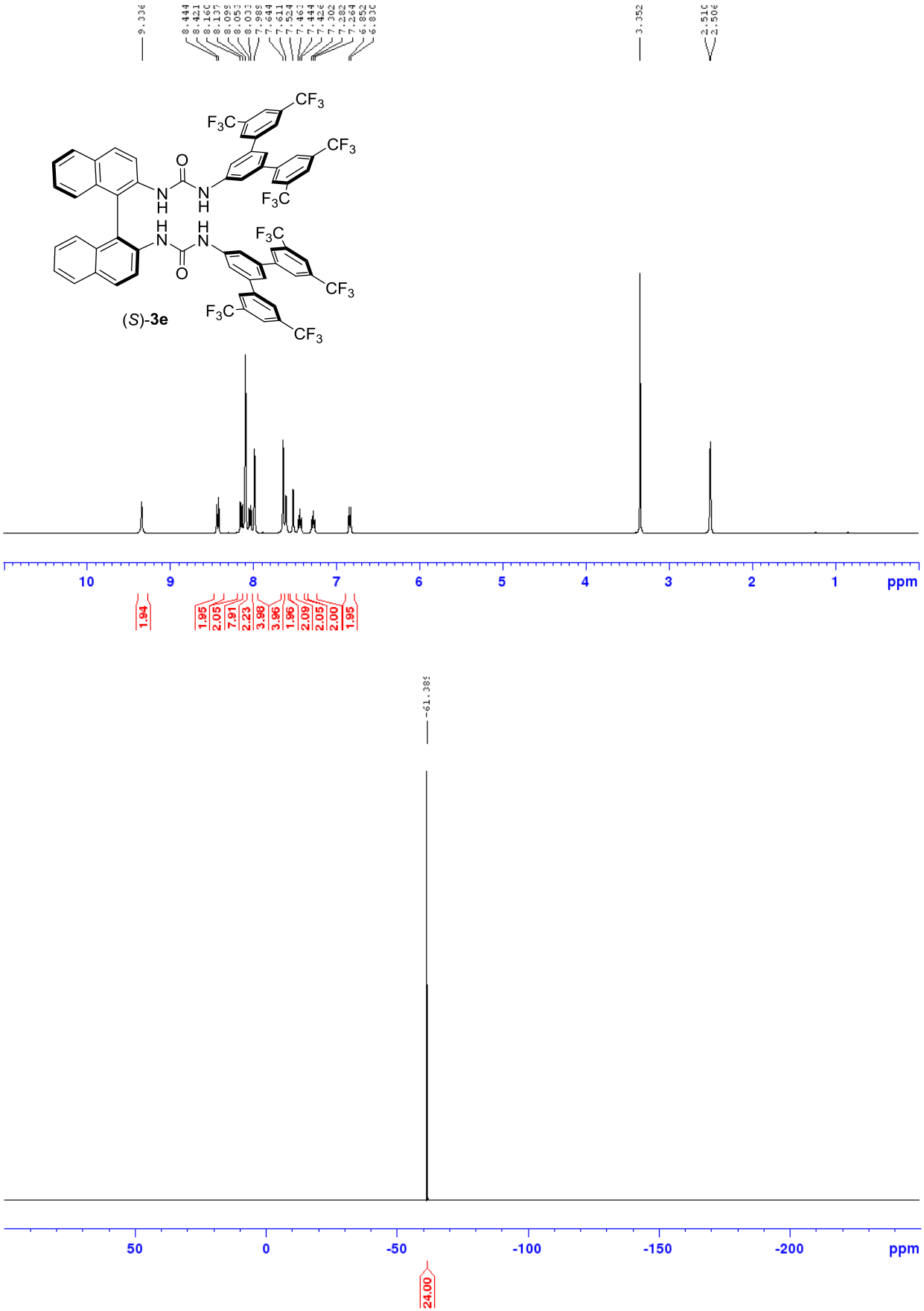
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5
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2.23
3.98
3.96
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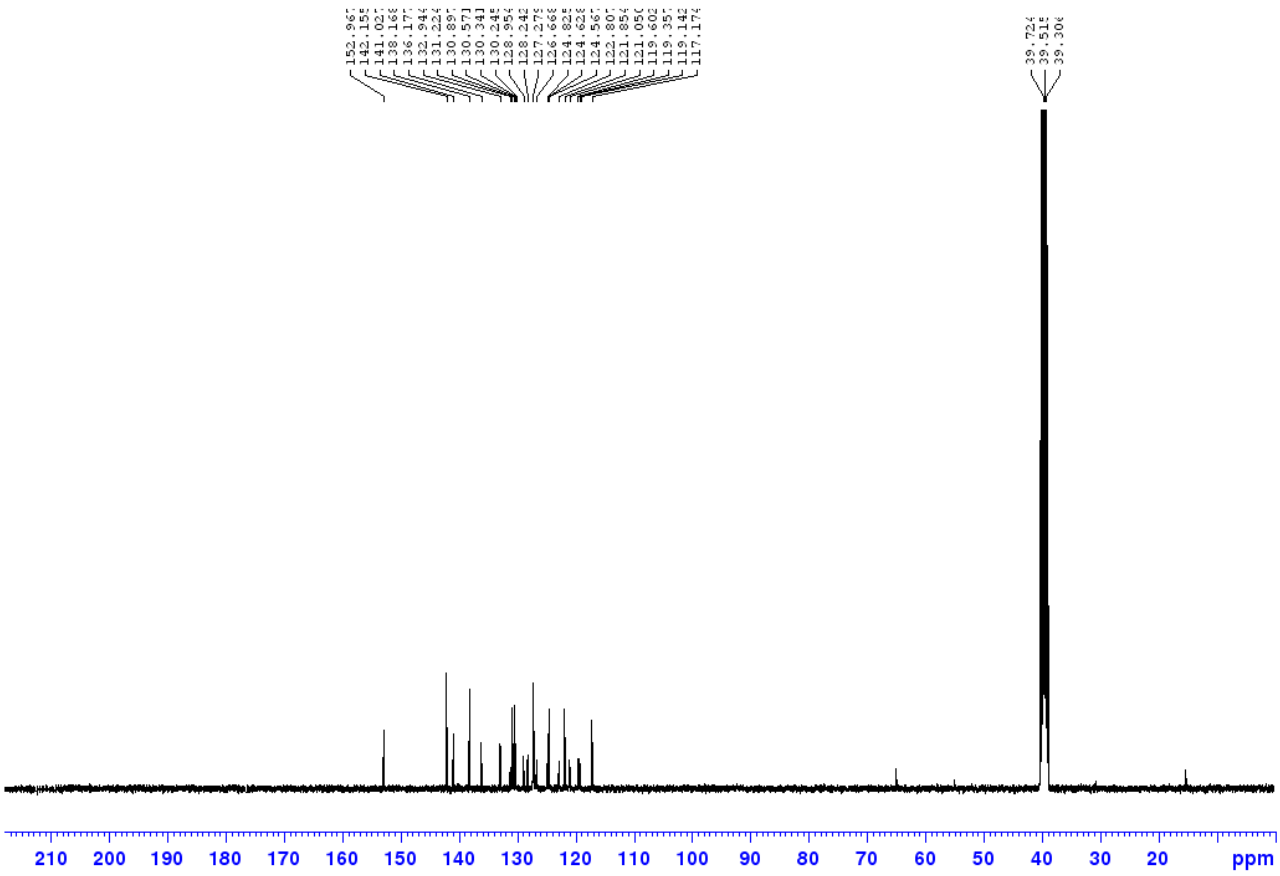
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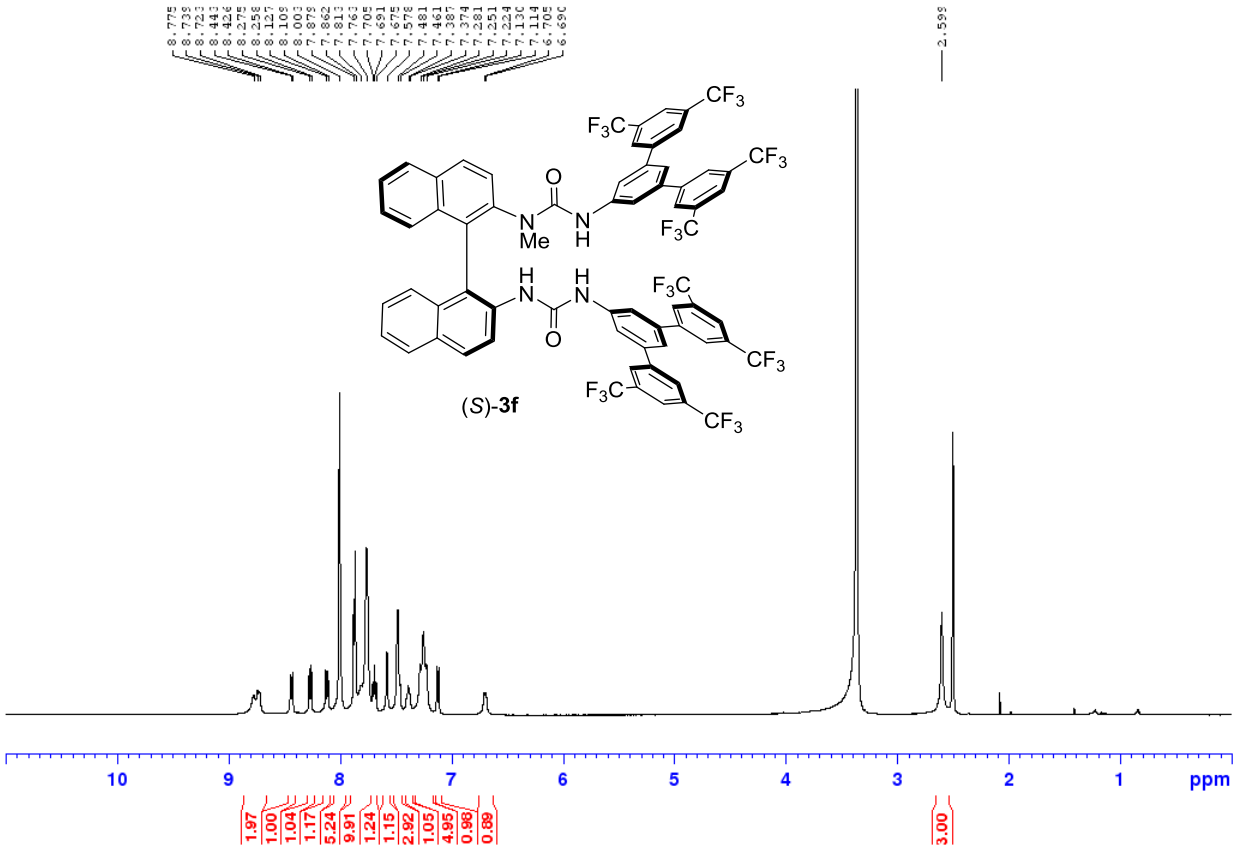
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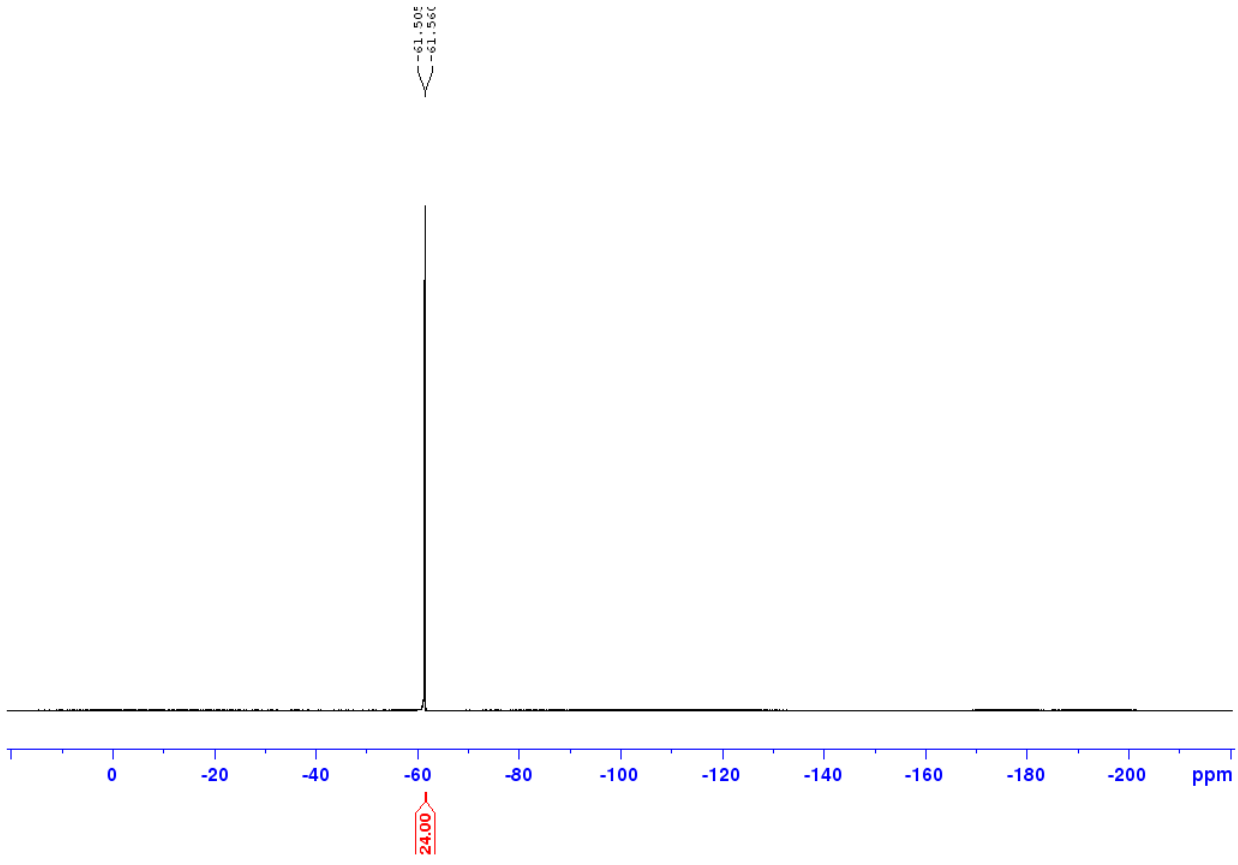
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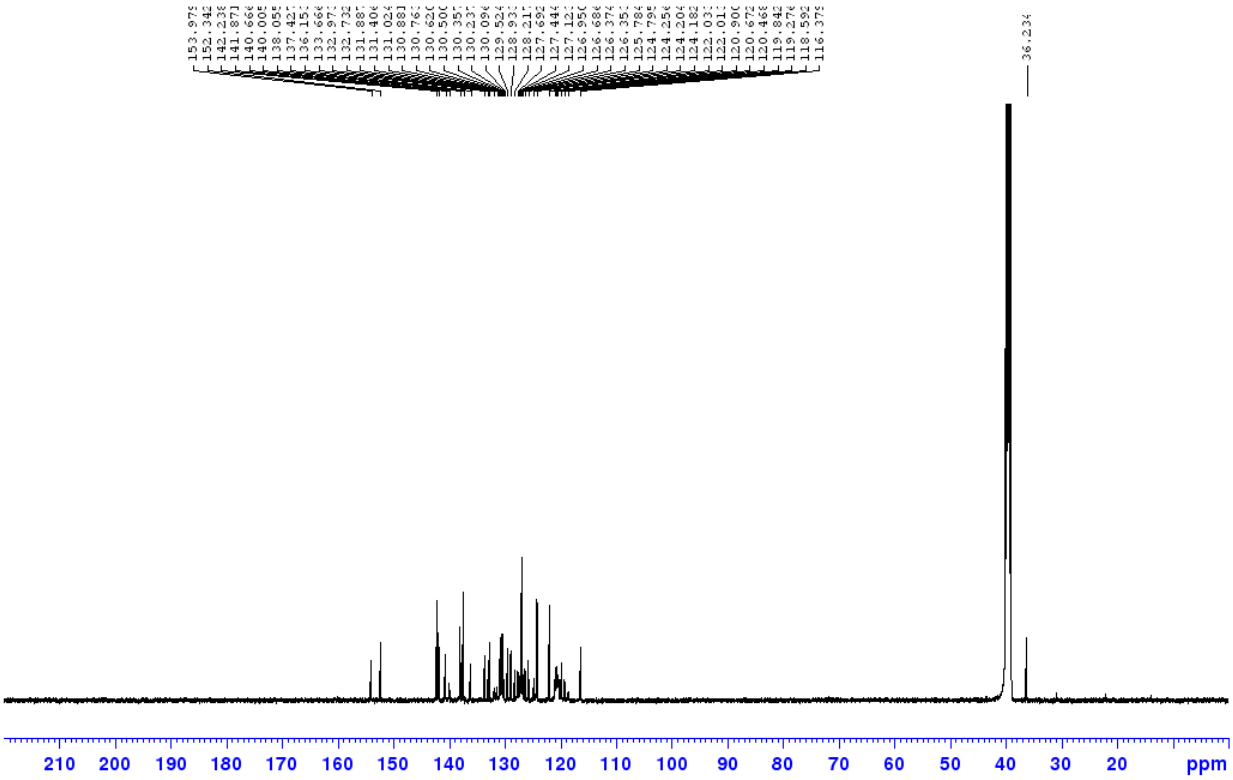
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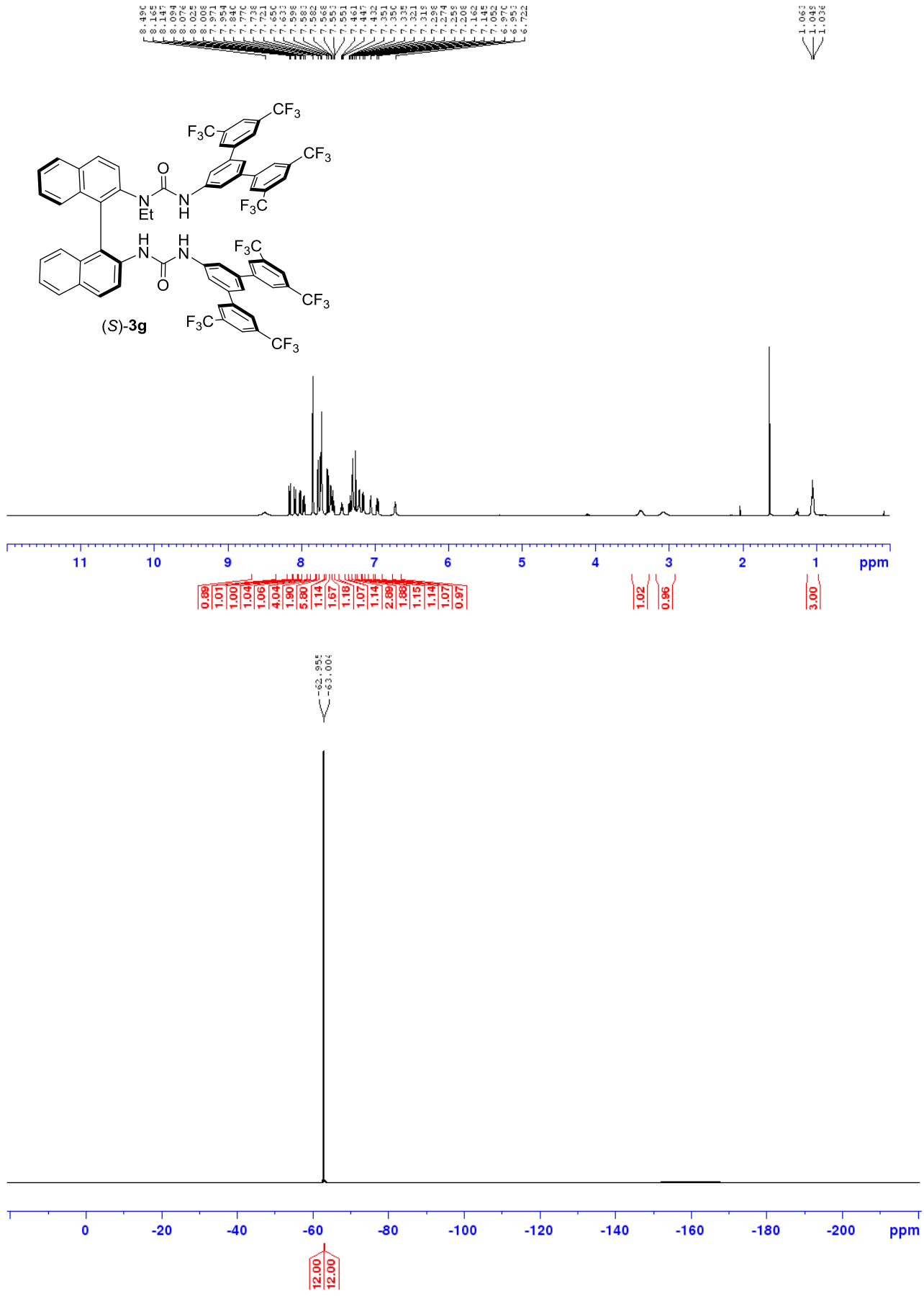
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ppm
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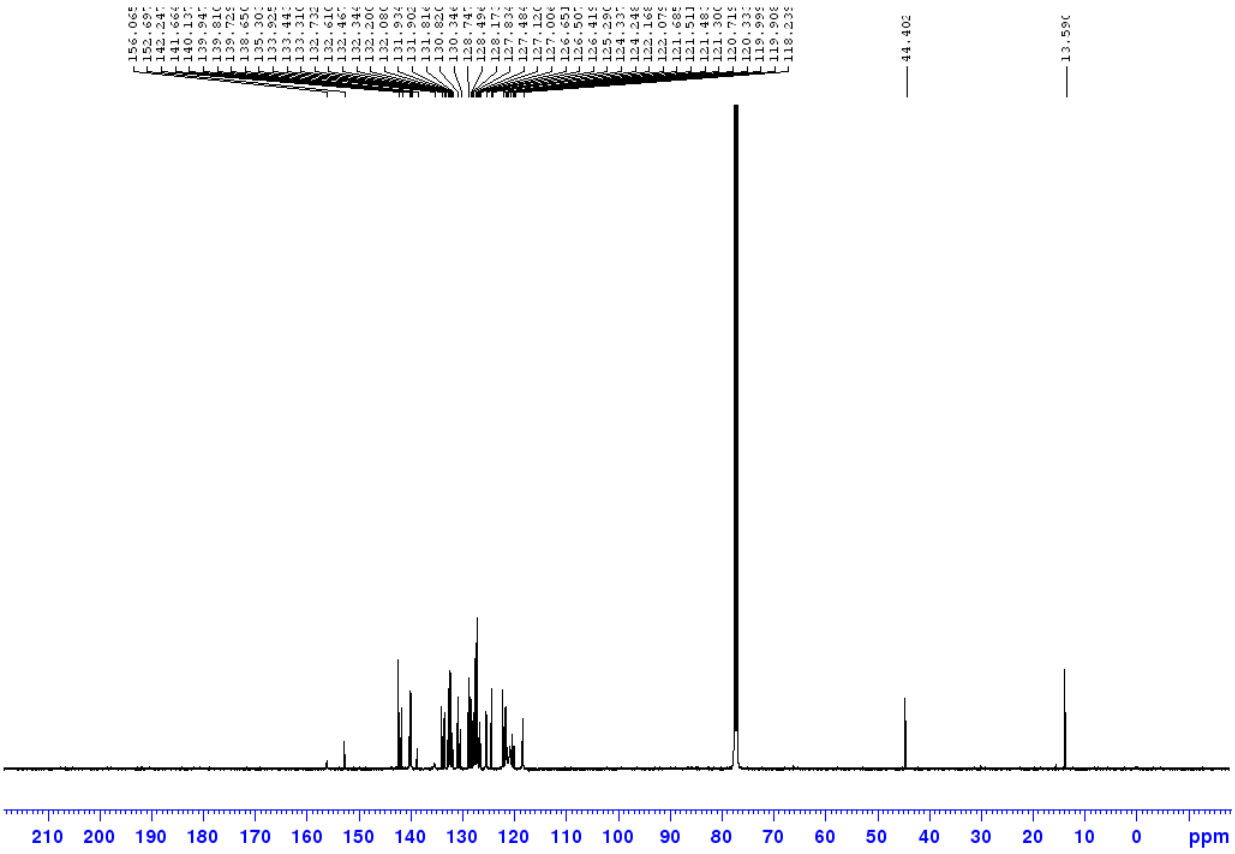
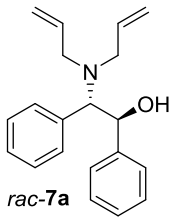
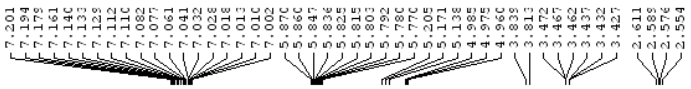
-160
-180
-200
ppm

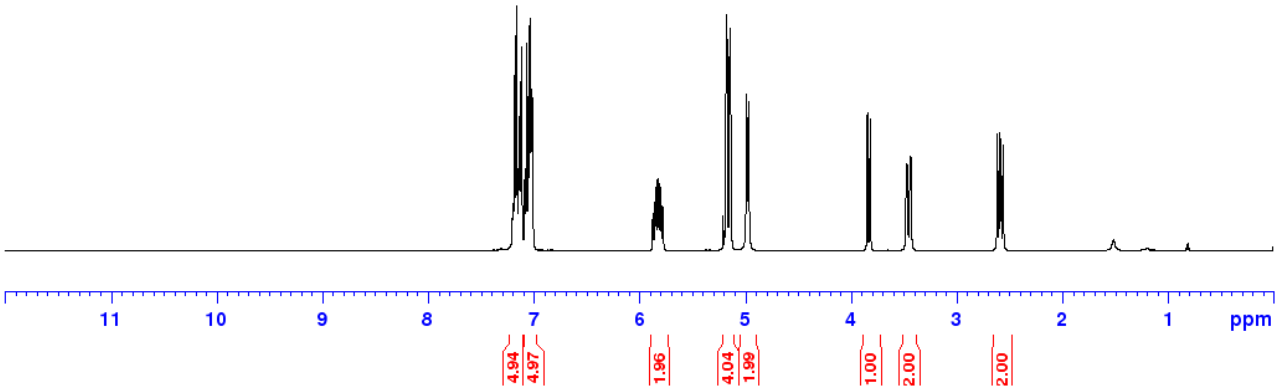

44.402
13.590
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

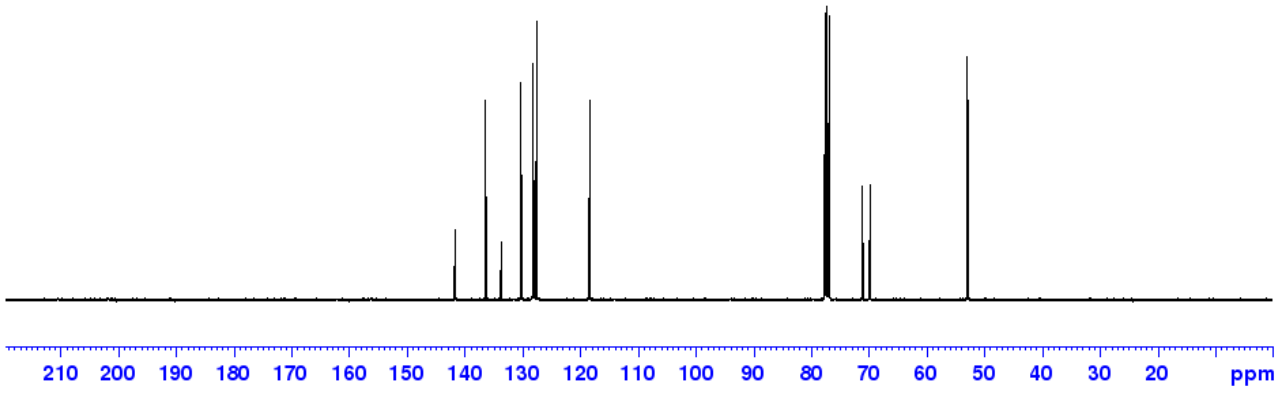
Substrate Precursors (alcohols)

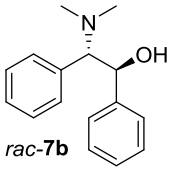


rac-**7a**



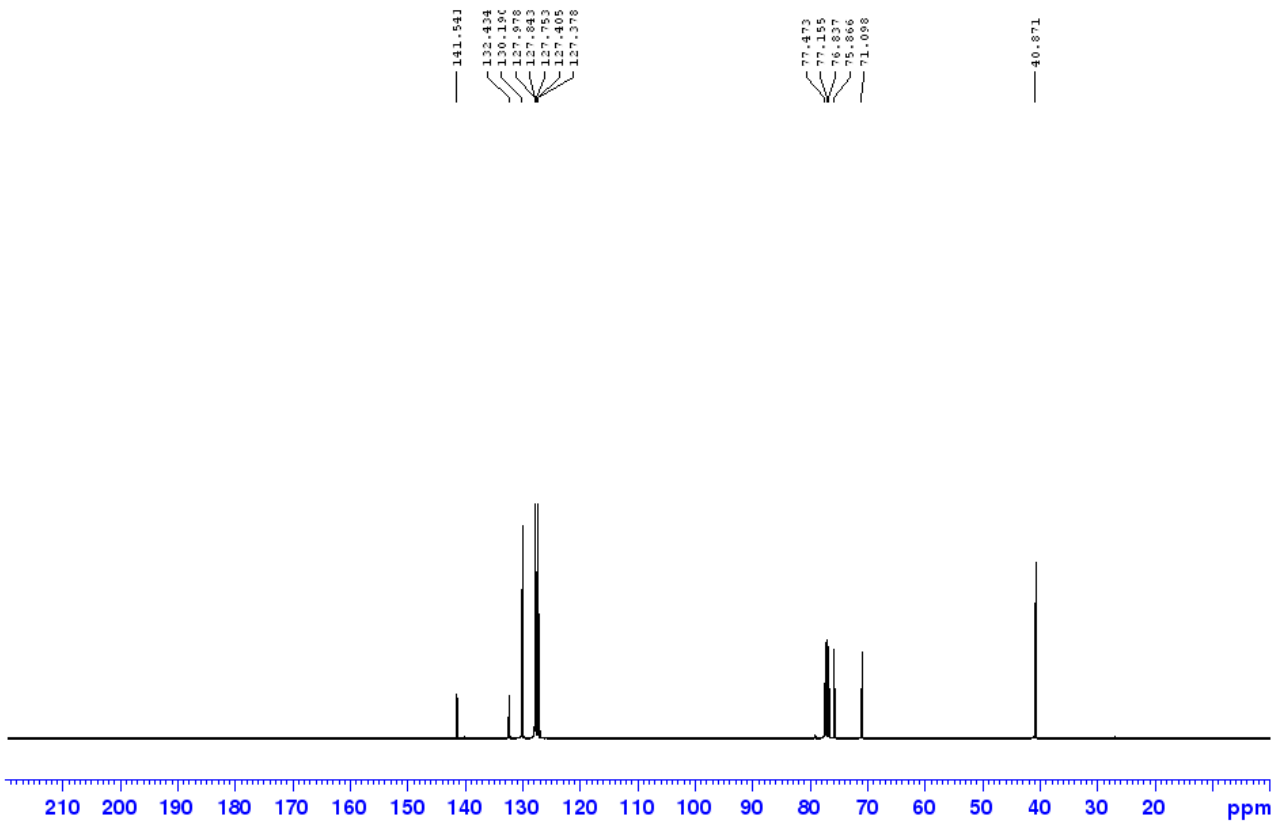


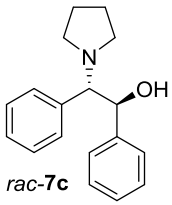



N
OH

rac-**7b**

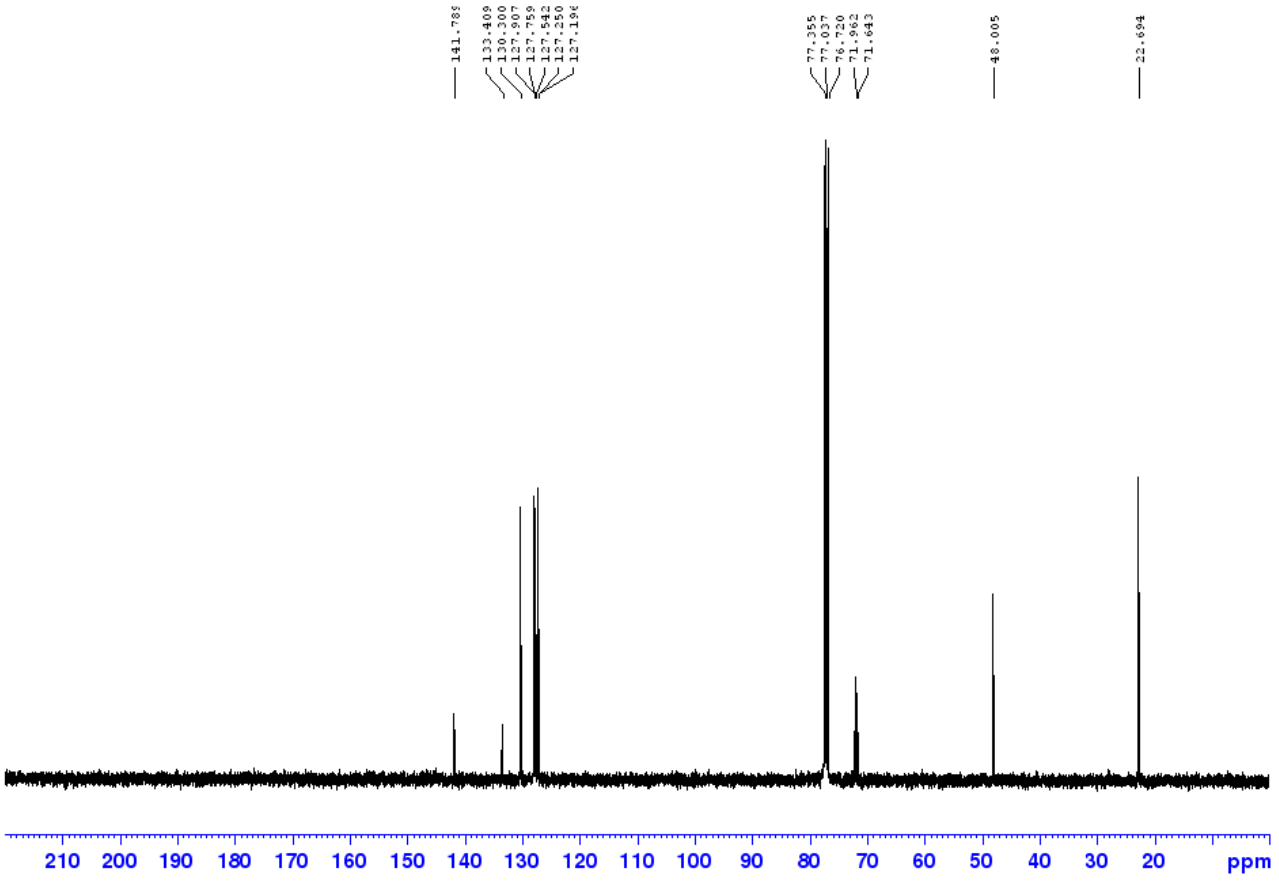
7.171
7.153
7.148
7.142
7.138
7.079
7.075
7.058
7.039
7.033
7.029
7.010
7.005
6.990
4.926
4.900
3.483
3.457
2.164
11
10
9
8
7
6
5
4
3
2
1
ppm
5.17
5.04
1.03
1.00
6.04

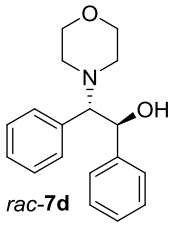

141.541
132.434
130.196
127.978
127.843
127.753
127.405
127.378
77.473
77.155
76.837
75.866
71.098
40.871
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


N
OH

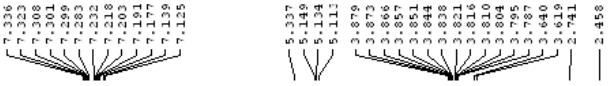
rac-**7c**

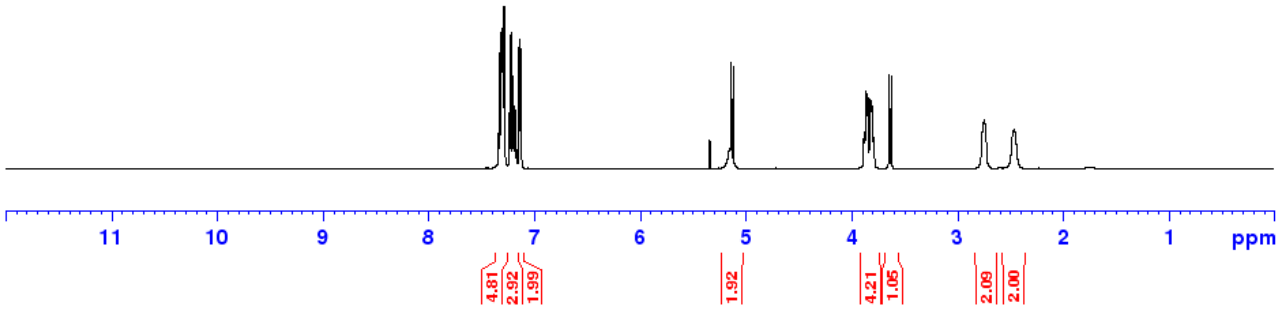
7.284
7.267
7.250
7.237
7.197
7.179
7.161
7.137
5.292
5.034
5.009
3.862
3.837
2.673
2.653
2.516
2.496
1.750
1.735
1.718
1.702
11
10
9
8
7
6
5
4
3
2
1
ppm
5.13
4.84
0.83
1.03
1.00
2.00
2.02
4.37


141.785
133.409
130.300
127.907
127.759
127.542
127.250
77.355
77.037
76.720
71.962
71.643
48.005
22.694
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

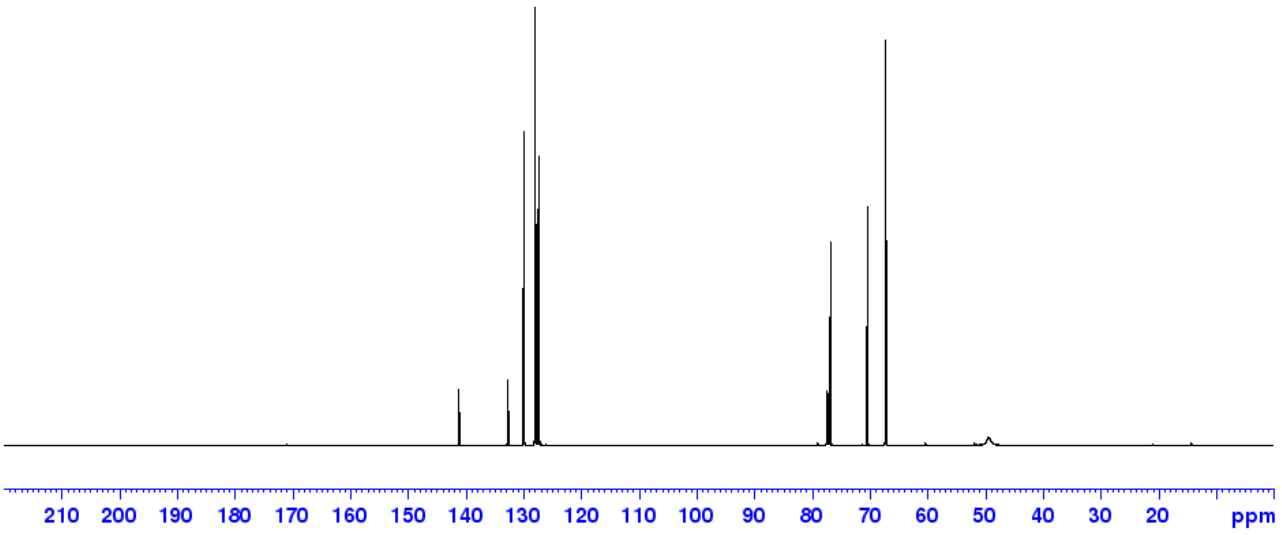

O
N
OH

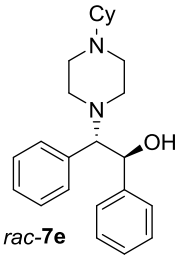
rac-**7d**


7.336
7.323
7.308
7.301
7.299
7.283
7.232
7.218
7.203
7.191
7.177
7.139
7.125
5.137
5.149
5.134
3.879
3.873
3.866
3.857
3.851
3.844
3.838
3.821
3.816
3.810
3.804
3.795
3.787
3.640
3.619
2.741
2.458


11
10
9
8
7
6
5
4
3
2
1
ppm
4.81
2.92
1.99
1.92
4.21
1.05
2.09
2.00

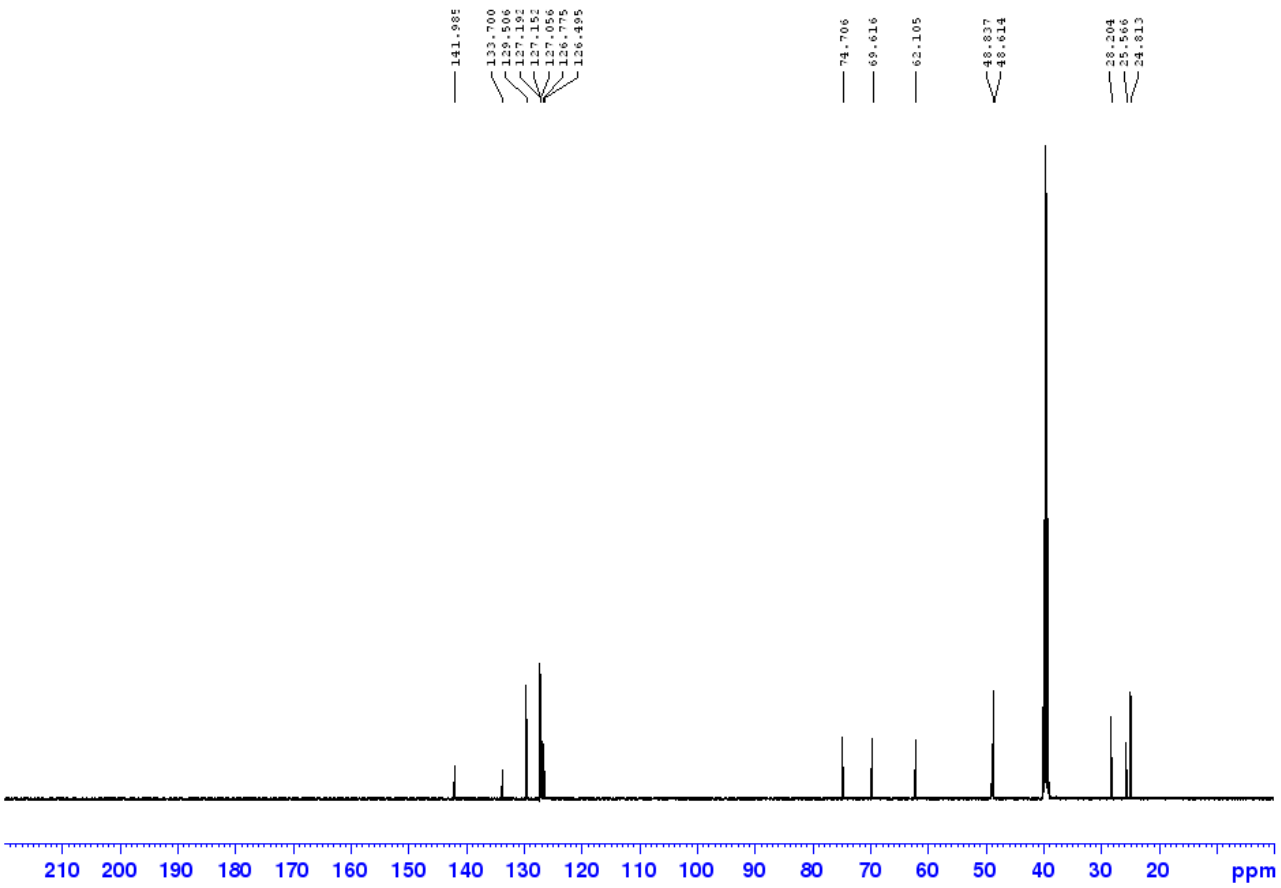

141.111
132.611
129.886
127.934
127.425
127.281
77.410
77.156
76.901
76.720
70.302
67.216
49.323

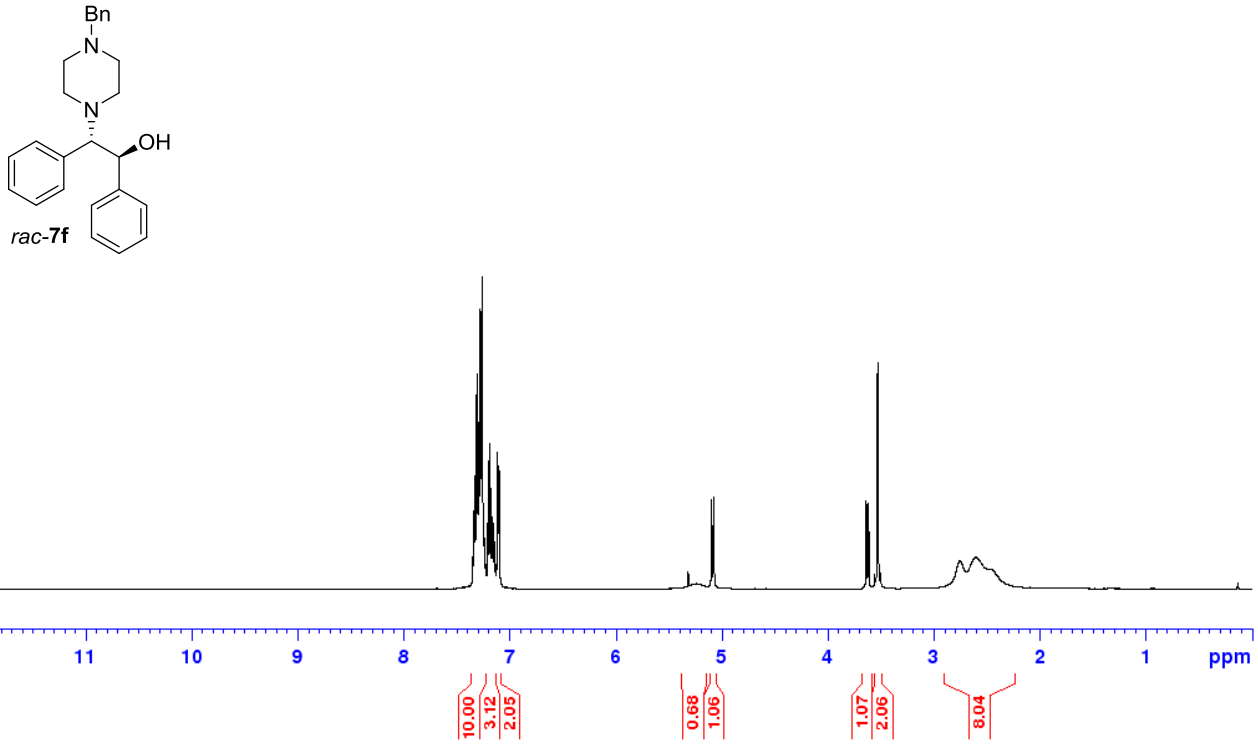

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

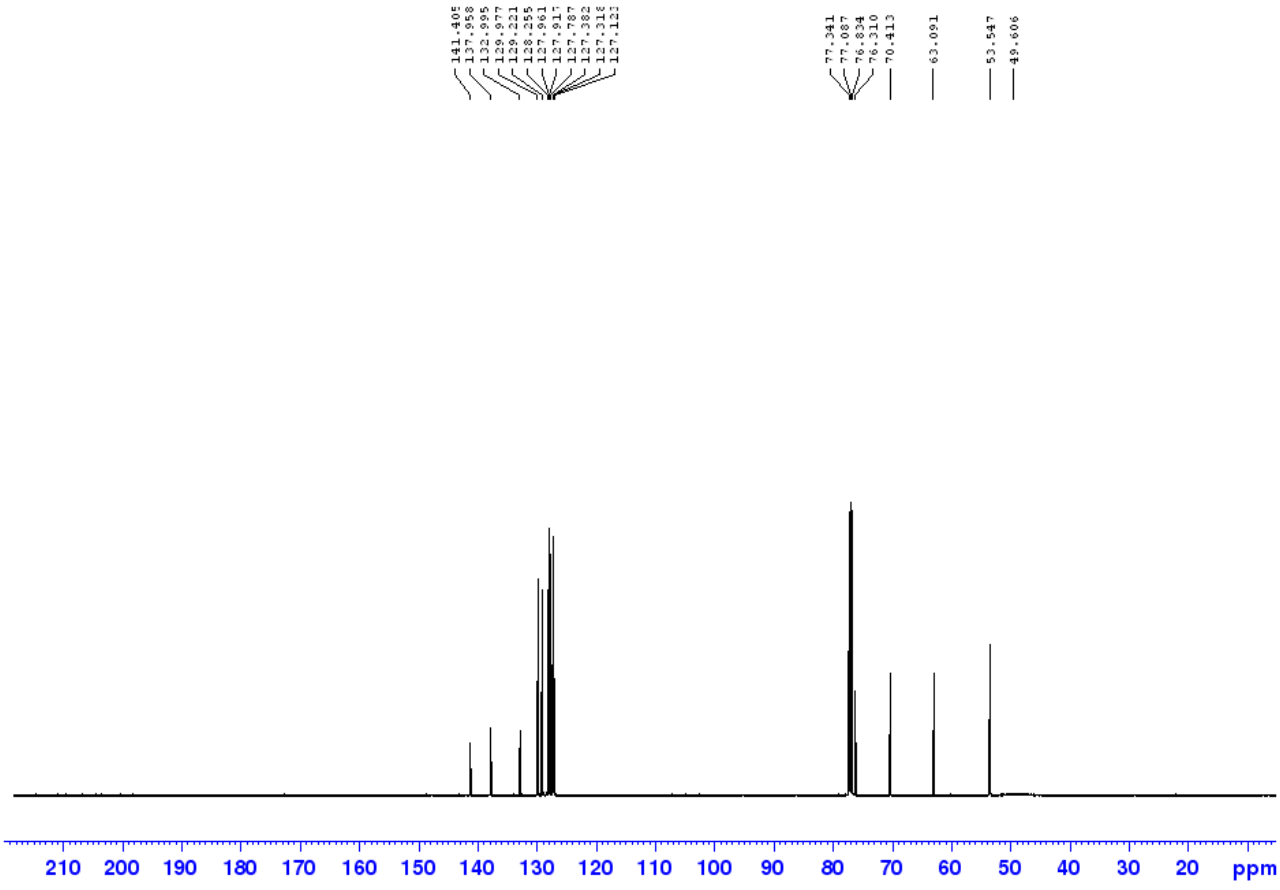


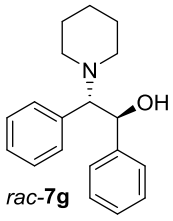
rac-**7e**

NMR spectra at 70° C



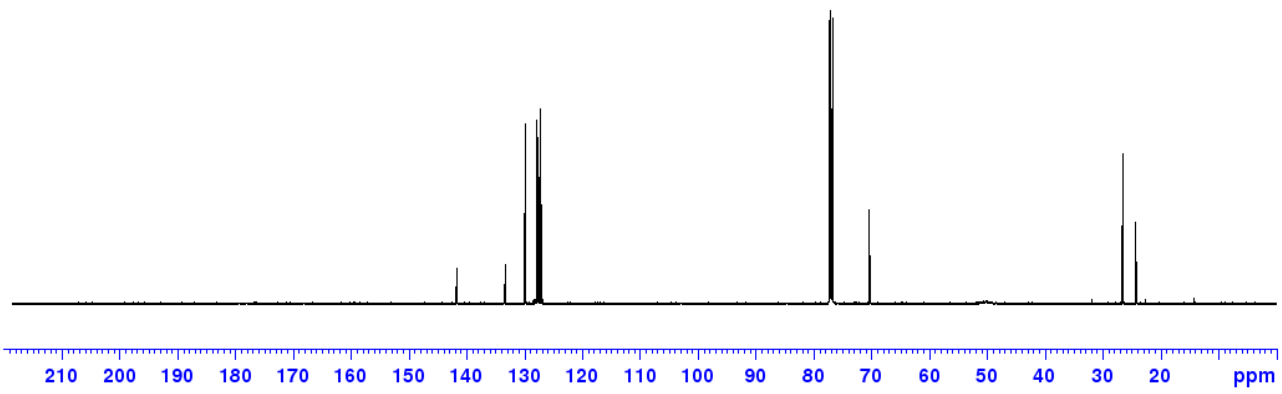

7.348
7.334
7.326
7.310
7.296
7.280
7.266
7.246
7.238
7.232
7.210
7.196
7.181
7.168
7.158
7.154
7.138
7.118
7.105
5.241
3.641
3.626
3.532
2.757
2.608
2.472
Bn
N
N
OH
rac-7f
11
10
9
8
7
6
5
4
3
2
1
ppm
10.00
3.12
2.05
0.68
1.06
1.07
2.06
8.04

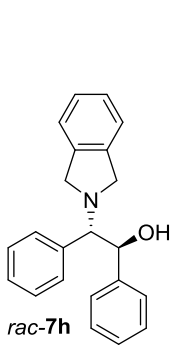

141.405
137.958
132.995
129.977
129.221
128.255
127.961
127.911
127.787
127.382
127.318
127.123
77.341
77.087
76.834
76.310
70.413
63.091
53.547
49.606
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


N
OH

rac-**7g**

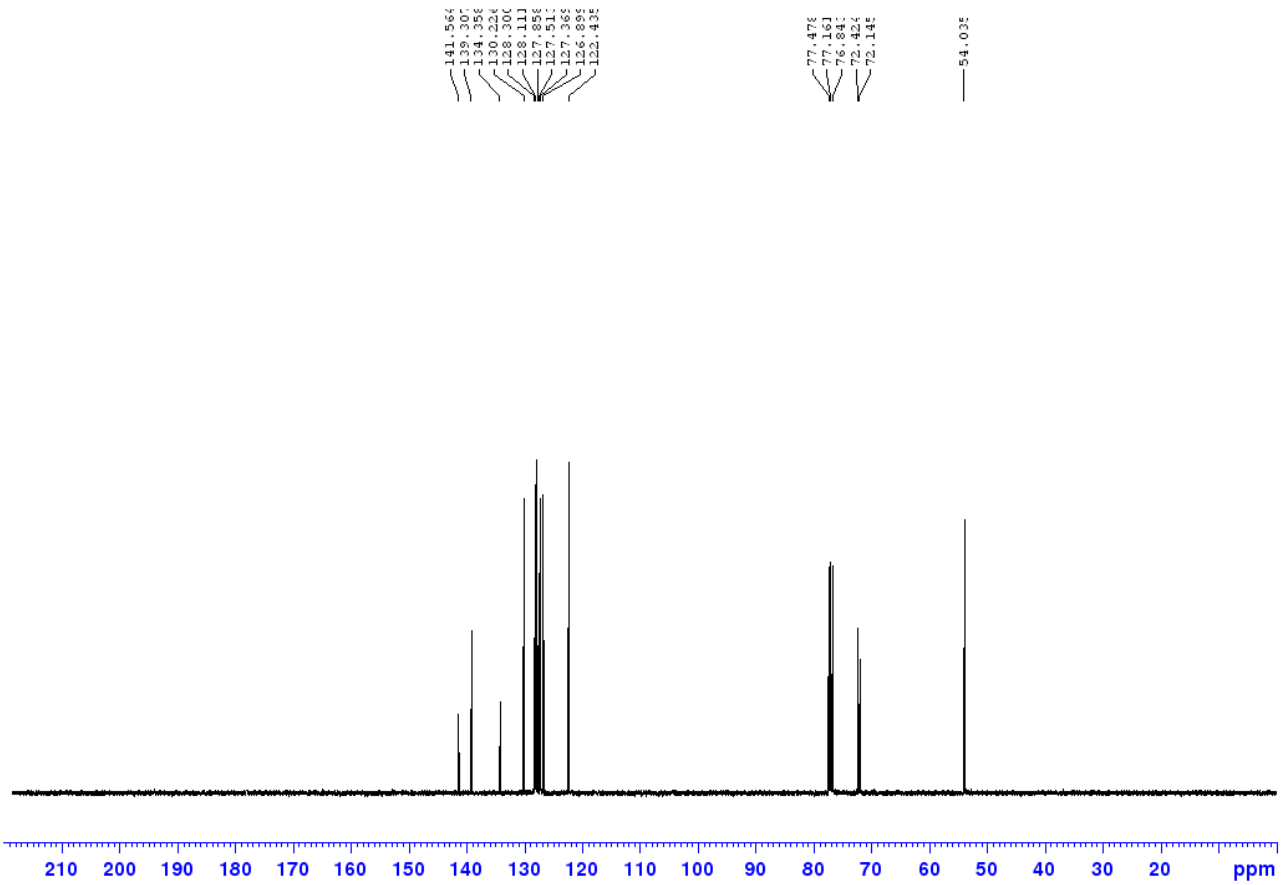
7.296
7.291
7.284
7.279
7.263
7.259
7.257
7.243
7.222
7.213
7.187
7.173
7.158
7.144
7.135
7.130
7.123
7.120
7.108
5.396
5.072
5.051
3.569
3.548
2.667
2.317
1.748
1.723
1.709
1.701
1.692
1.677
1.653
1.645
1.631
1.606
1.385
1.324
1.298
1.290
11
10
9
8
7
6
5
4
3
2
1
ppm
5.00
5.06
0.69
1.09
1.05
2.02
2.02
4.49
2.43
141.81
133.48
130.04
127.99
127.83
127.71
127.37
127.35
77.39
77.21
77.13
76.88
70.46
50.38
26.66
24.37

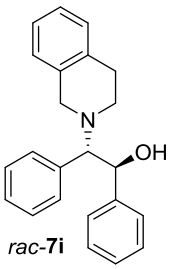

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


N
OH

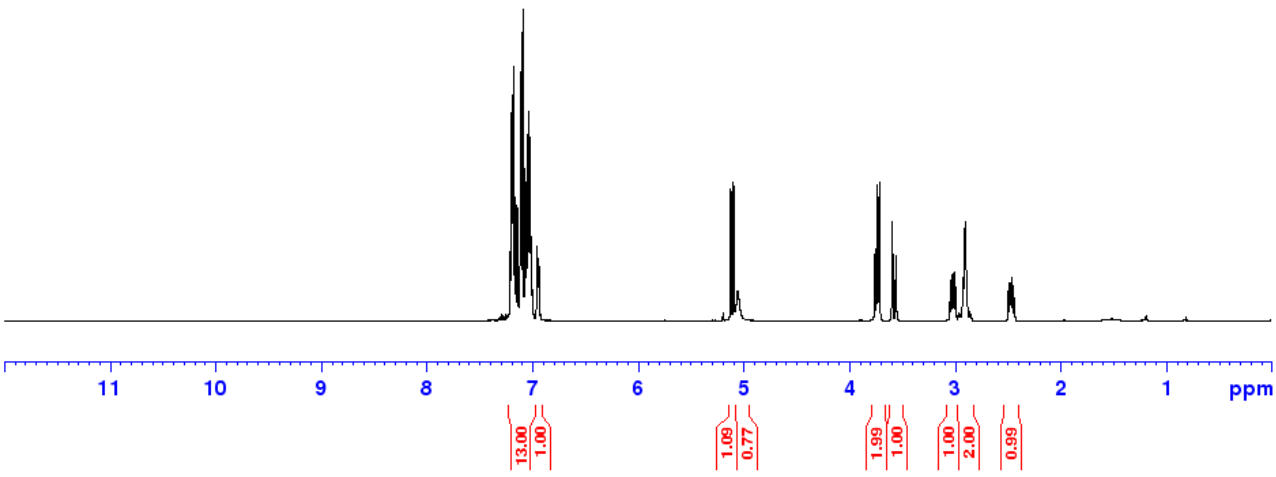
rac-**7h**

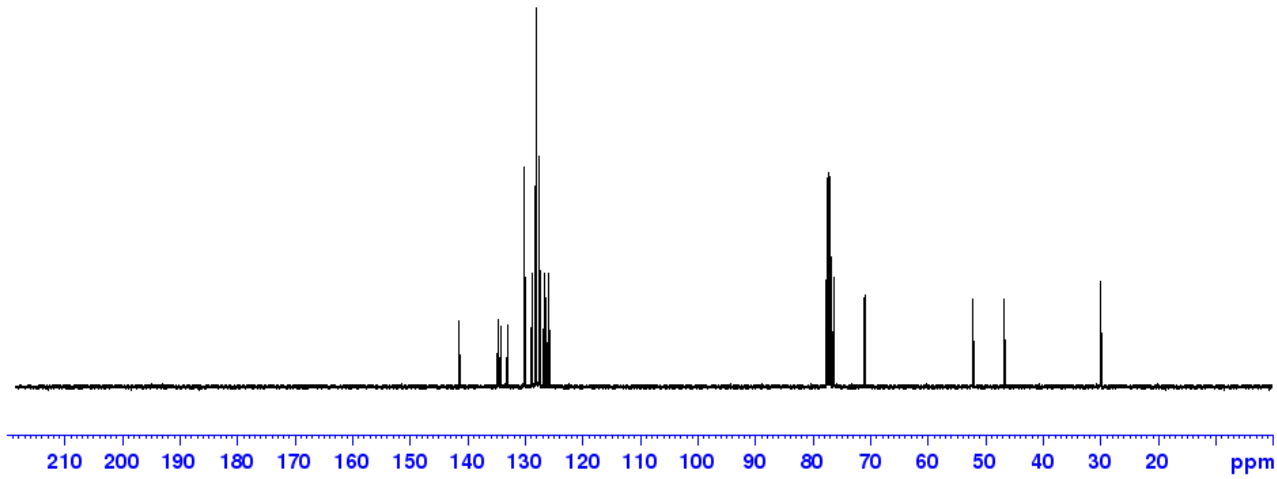
7.357
7.353
7.335
7.328
7.308
7.299
7.291
7.271
7.247
7.236
7.230
7.224
7.217
7.209
7.194
7.190
7.187
7.172
5.182
5.158
4.134
4.106
4.099
4.091
4.063
4.039
11
10
9
8
7
6
5
4
3
2
1
ppm
4.13
9.60
1.00
3.72
1.23

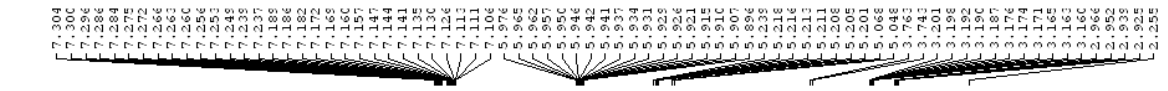

141.564
139.307
134.358
130.226
128.300
128.111
127.858
127.513
127.369
126.899
122.435
77.478
77.161
76.841
72.426
72.145
54.035
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

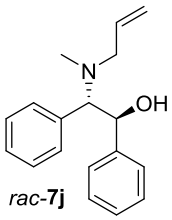

N
OH

rac-**7i**

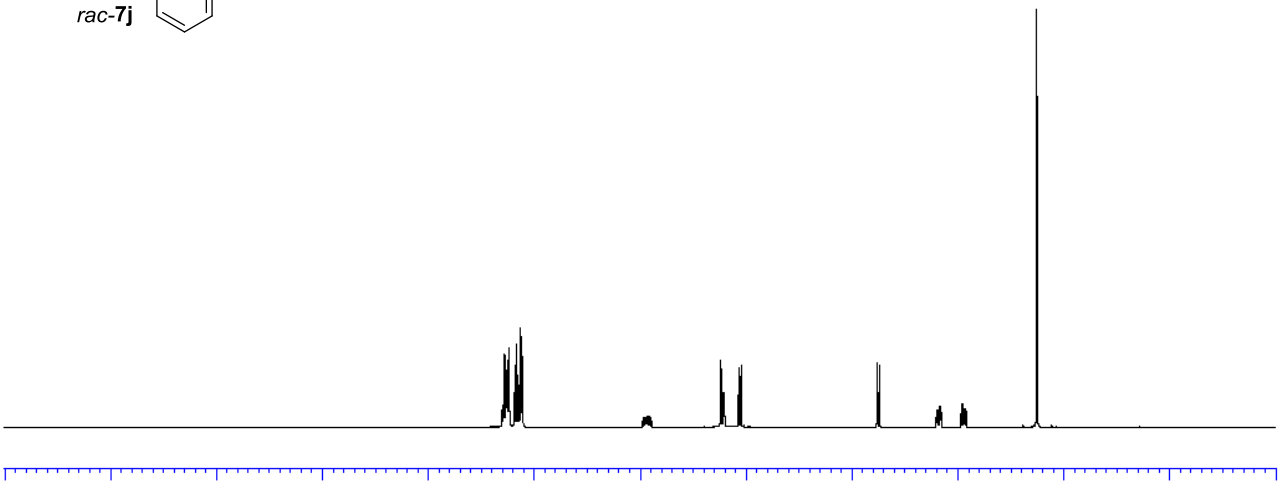

11
10
9
8
7
6
5
4
3
2
1
ppm
13.00
1.00
1.09
0.77
1.99
1.00
1.00
2.00
0.99

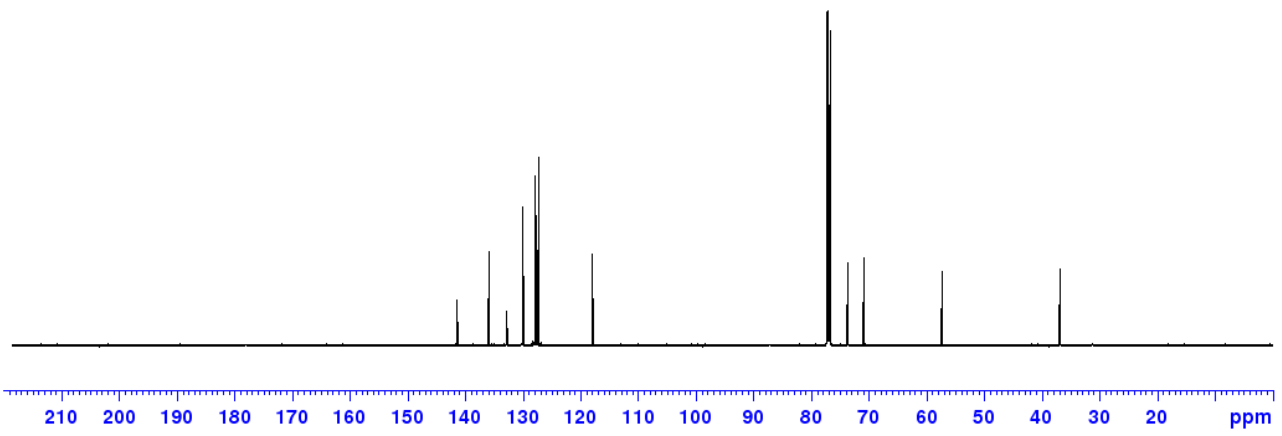

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

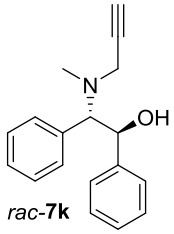



N
OH

rac-**7j**

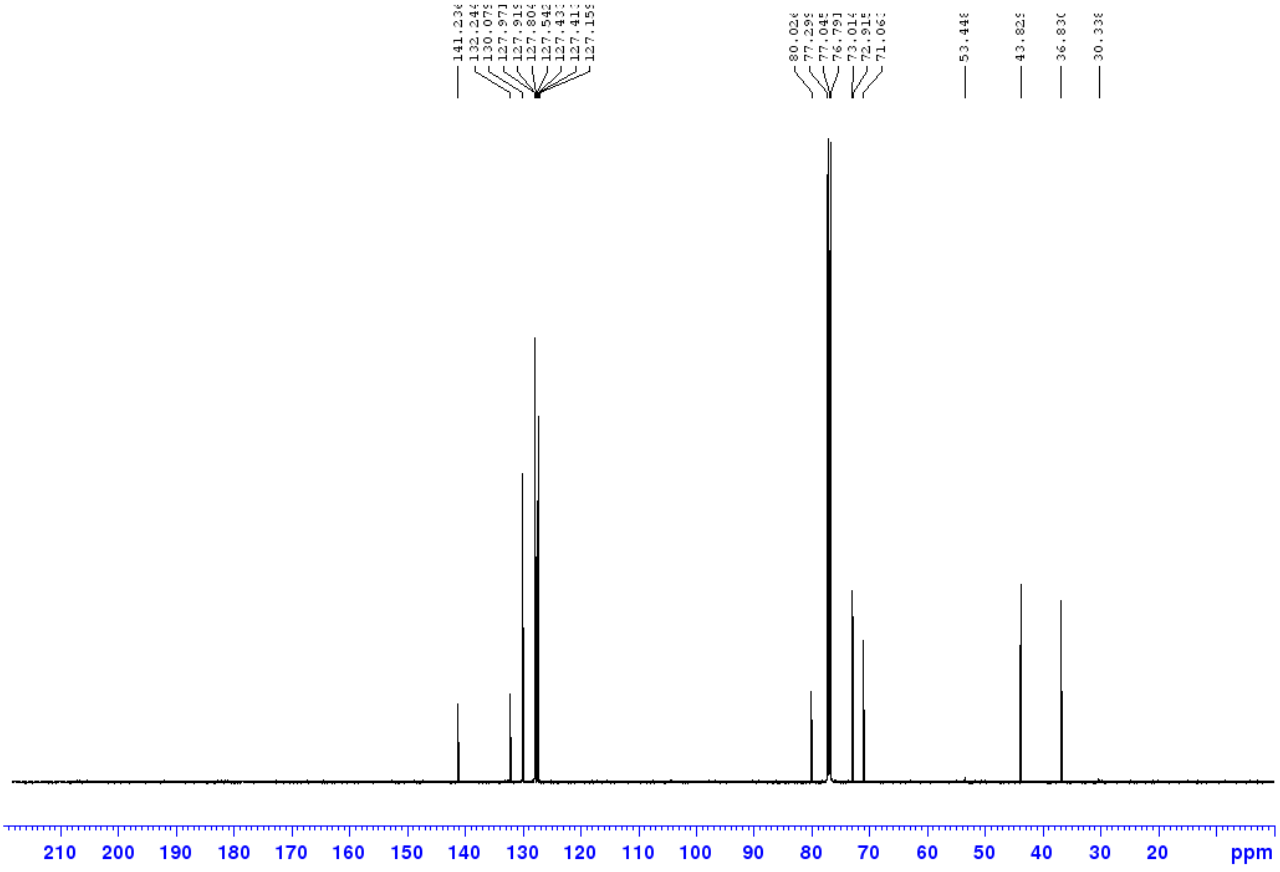

11
10
9
8
7
6
5
4
3
2
1
ppm
4.80
4.70
0.91
1.04
1.05
1.14
1.02
1.06
1.04
3.12

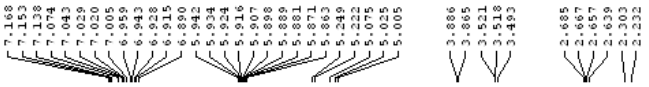

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

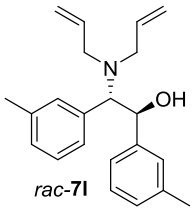

N
OH

rac-**7k**

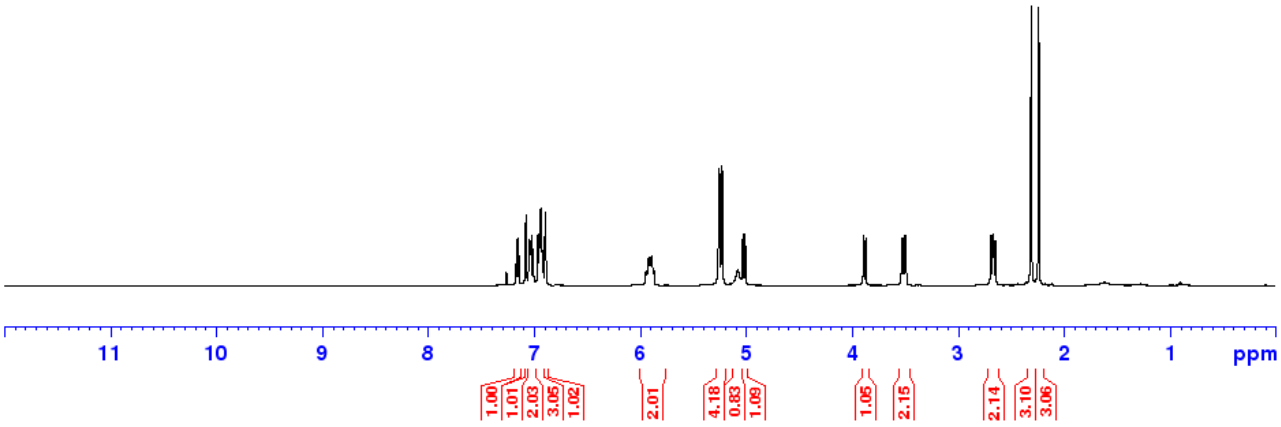
11
10
9
8
7
6
5
4
3
2
1
ppm
4.73
4.65
1.00
0.75
1.00
1.03
1.03
3.02
0.81

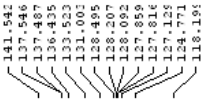

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

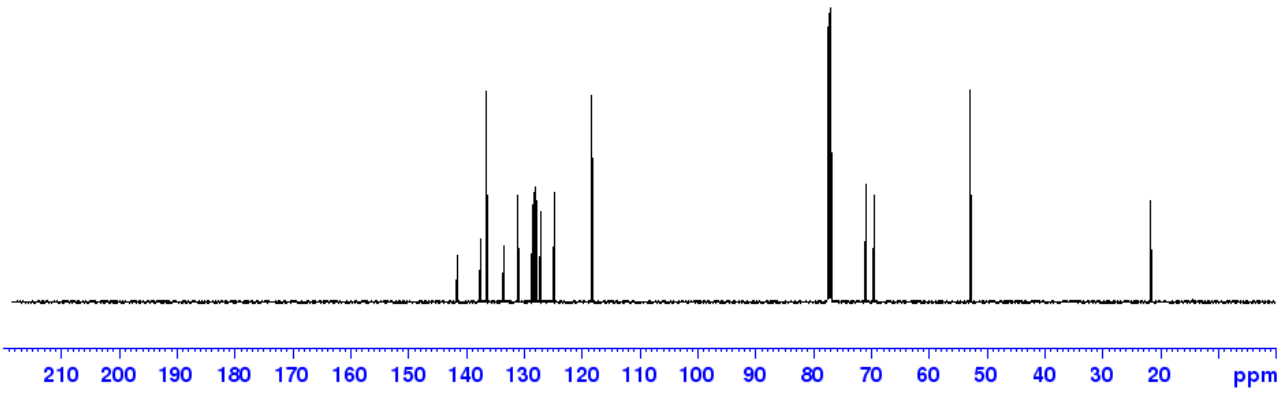


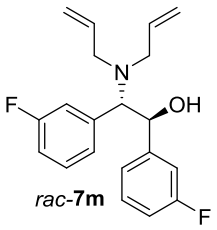

N
OH

rac-**7l**


11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
2.03
3.05
1.02
2.01
4.18
0.83
1.09
1.05
2.15
2.14
3.10
3.06

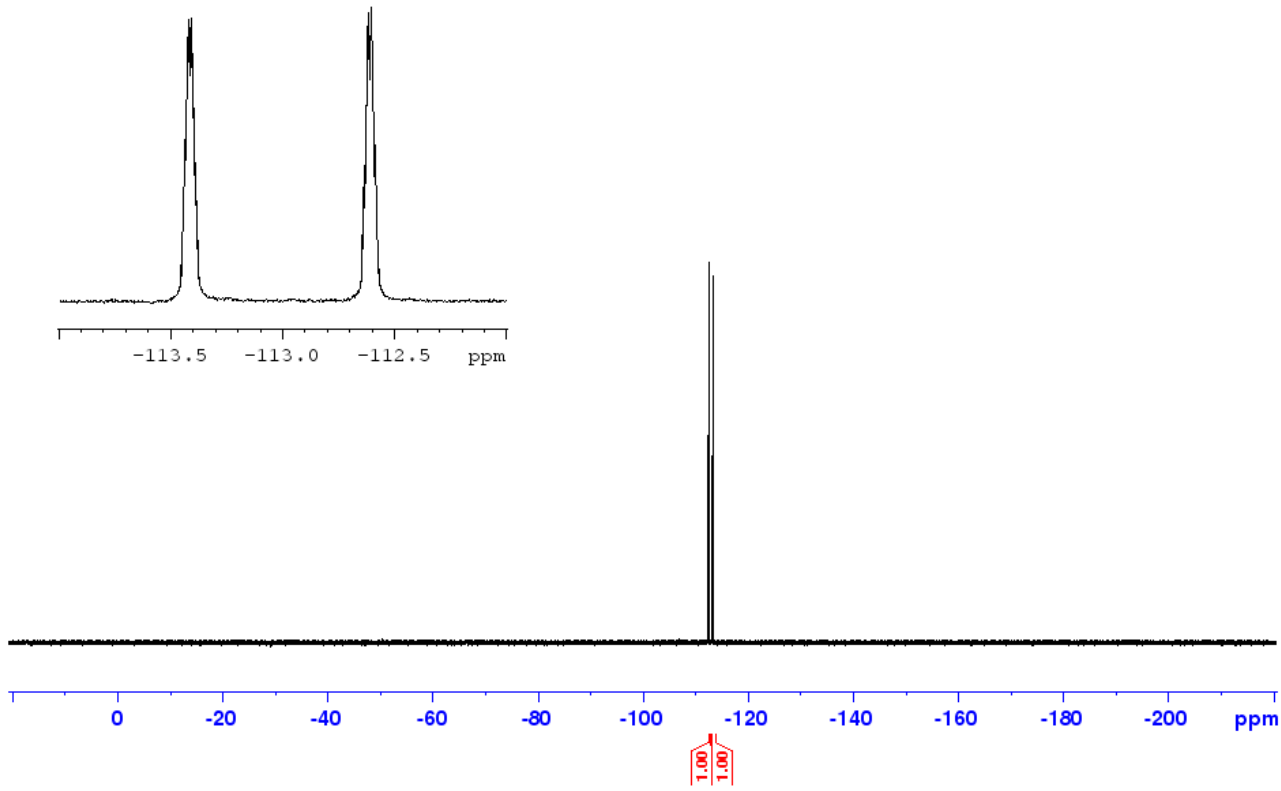

70.884
69.411
52.806
21.672
21.541

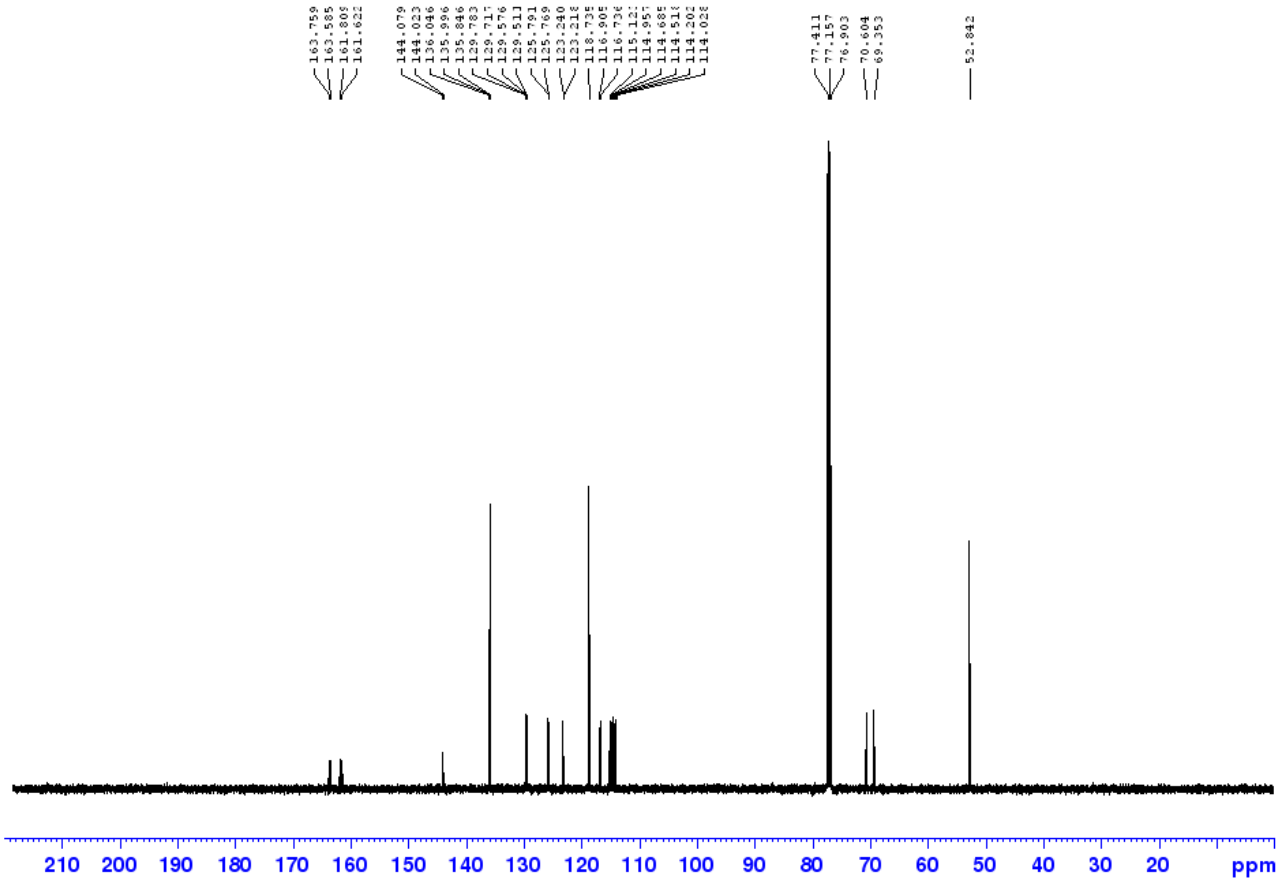

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

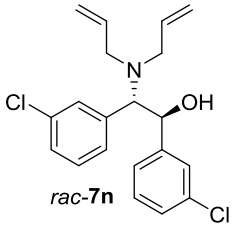

N
F
OH
F

rac-**7m**

7.236
7.219
7.205
7.089
7.077
7.063
7.050
6.952
6.934
6.883
6.867
6.855
6.840
6.799
6.782
5.888
5.867
5.853
5.838
5.818
5.244
5.227
5.207
4.972
4.952
3.829
3.809
3.510
3.482
2.663
2.644
2.636
2.618
11
10
9
8
7
6
5
4
3
2
1
ppm
1.11
0.95
1.84
1.94
1.83
1.84
3.94
1.82
1.00
2.03
2.02

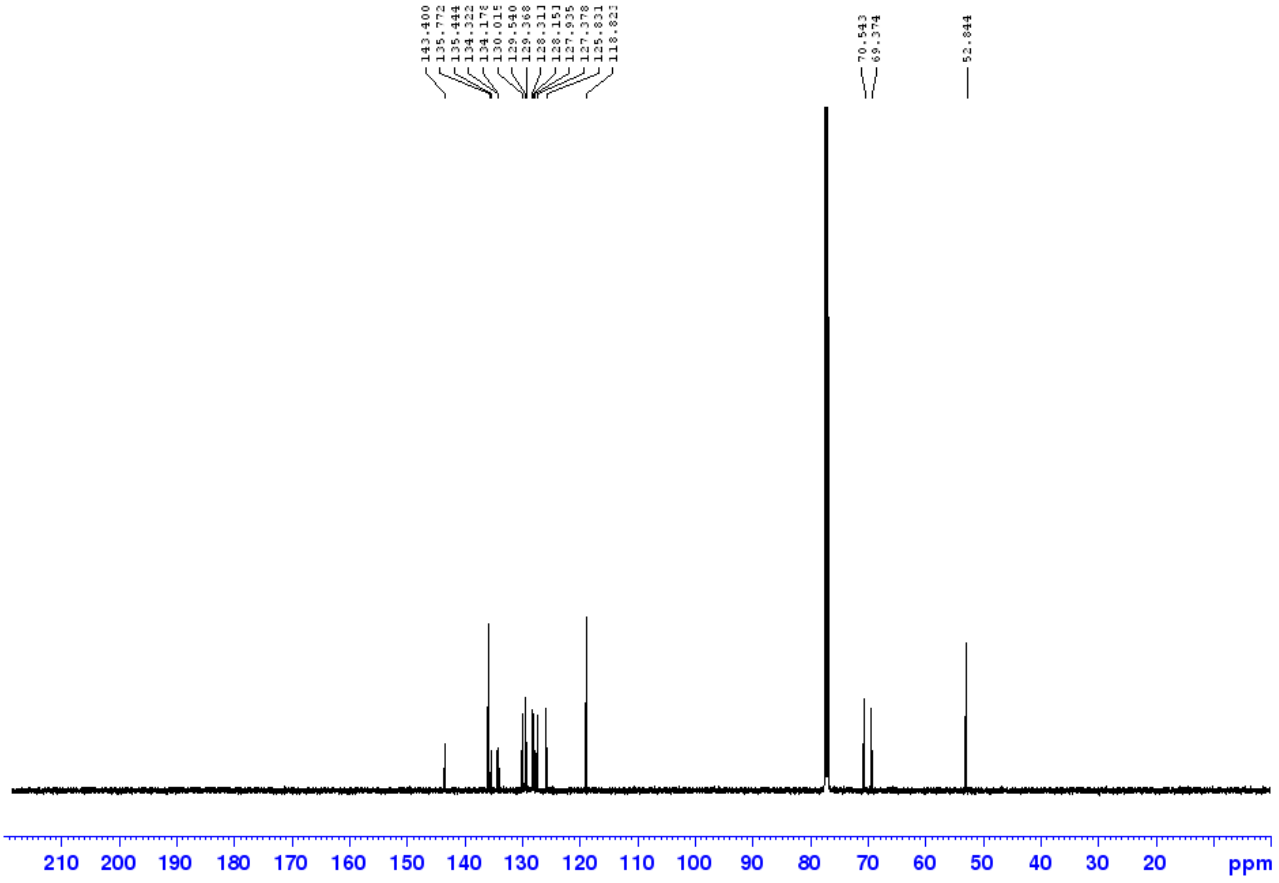

-113.5
-113.0
-112.5
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00
1.00

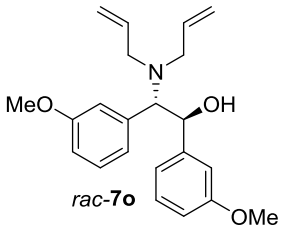

163.759
163.585
161.805
161.622
144.079
144.023
136.046
135.996
135.846
128.783
128.717
128.576
128.511
125.791
125.769
123.240
123.218
118.735
116.905
116.736
115.12
114.95
114.685
114.518
114.202
114.028
77.411
77.157
76.903
70.604
69.353
52.842
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


N
Cl
OH
Cl

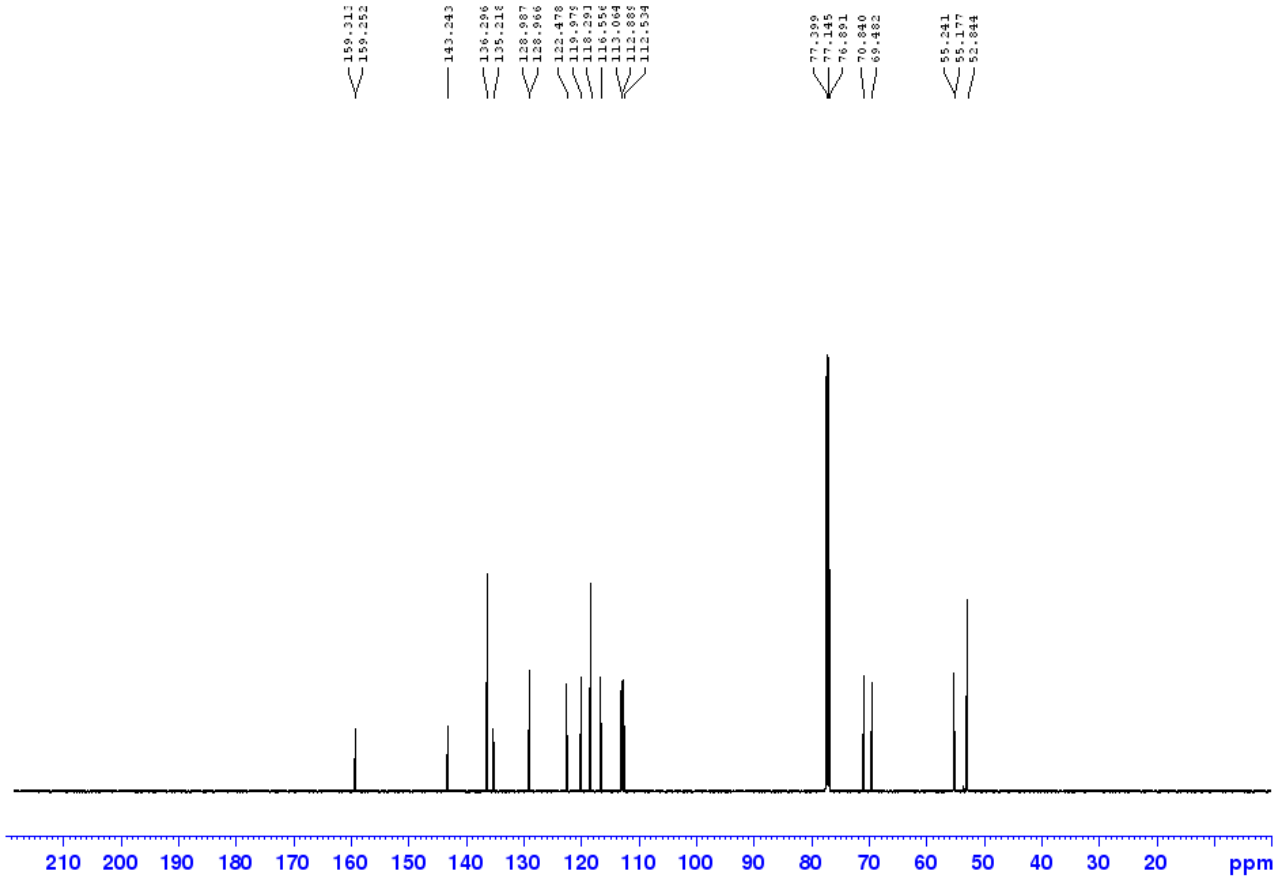
rac-**7n**

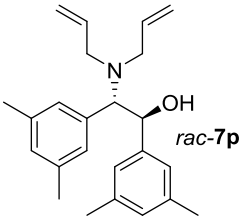
7.252
7.226
7.214
7.139
7.116
7.094
7.067
7.052
7.036
6.983
6.967
6.951
5.900
5.893
5.881
5.874
5.861
5.847
5.830
5.822
5.262
5.245
5.222
4.966
4.945
3.811
3.791
3.508
3.481
2.667
2.648
2.638
2.622
11
10
9
8
7
6
5
4
3
2
1
ppm
3.27
2.86
2.00
1.95
4.13
0.66
1.14
1.05
2.13
2.11


143.400
135.772
135.444
134.322
134.178
130.015
129.540
129.368
128.311
128.151
127.936
127.378
125.831
118.823
70.543
69.374
52.844
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

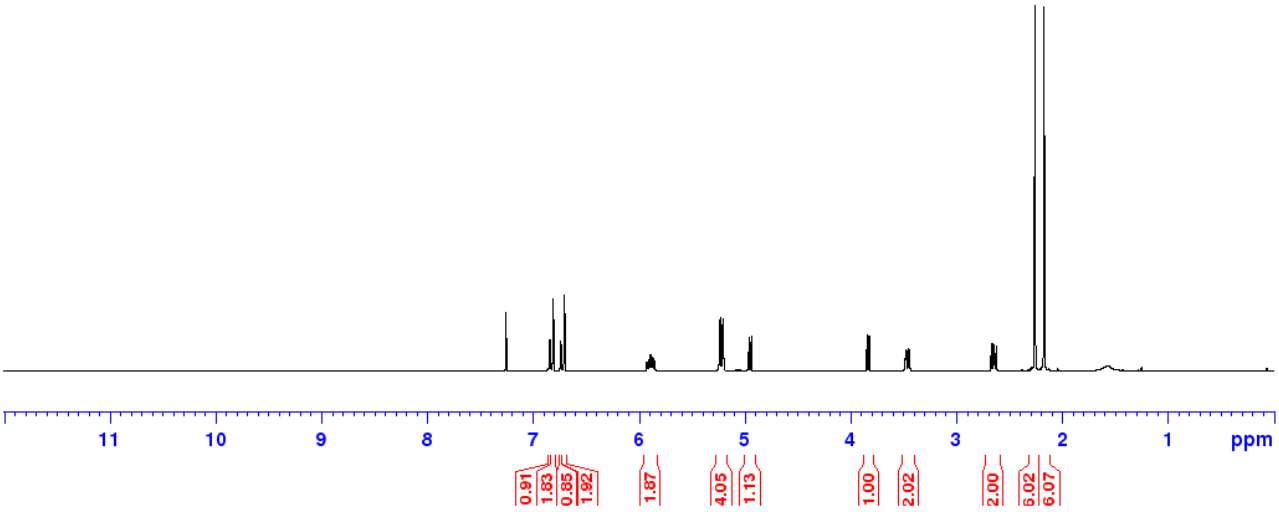


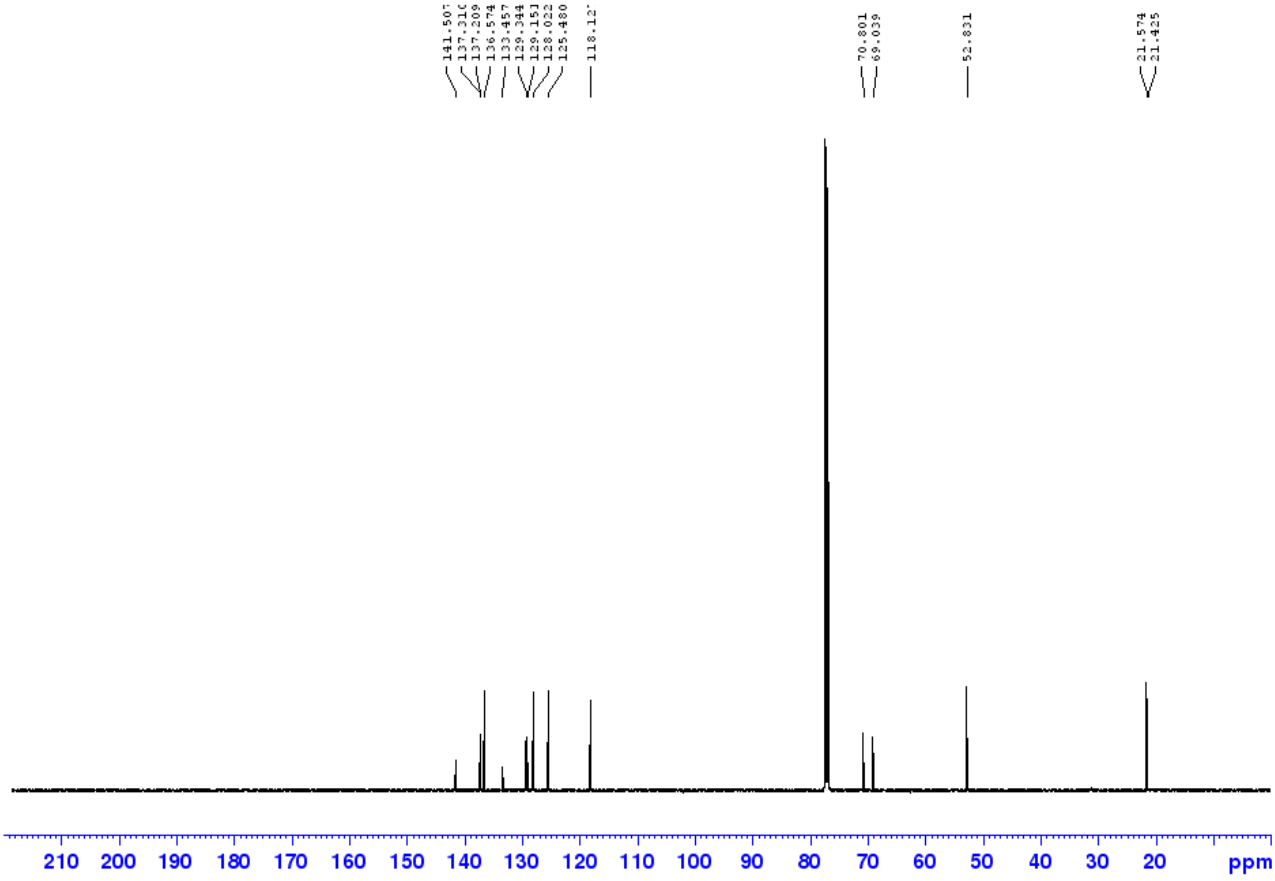
rac-**7o**

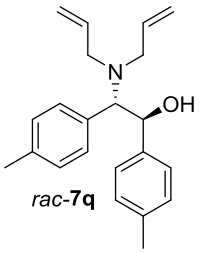



N
OH

rac-**7p**

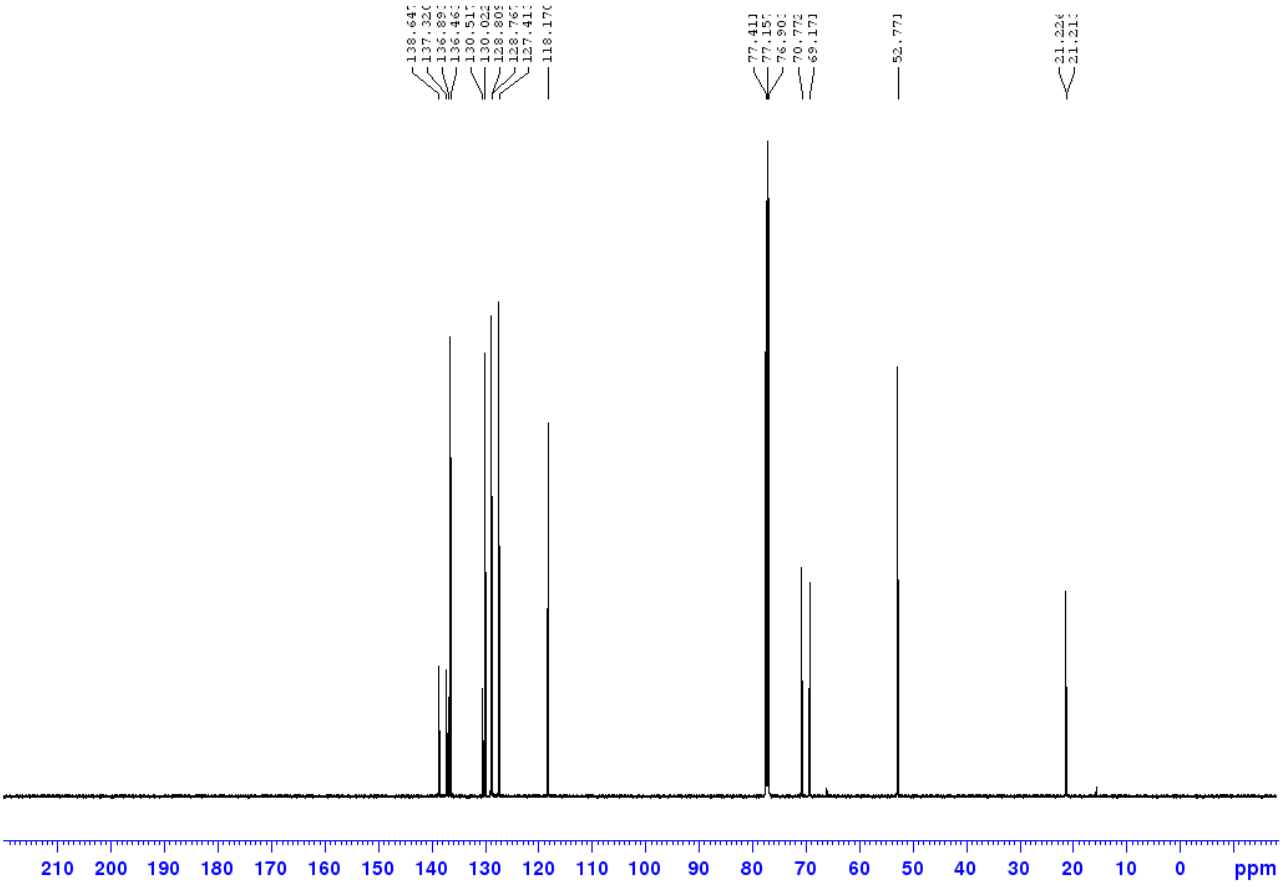

11
10
9
8
7
6
5
4
3
2
1
ppm
0.91
1.83
0.85
1.92
1.87
4.05
1.13
1.00
2.02
2.00
6.02
6.07

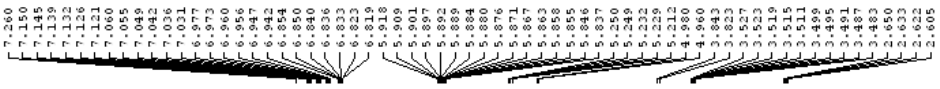

70.801
69.039
52.831
21.574
21.425
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

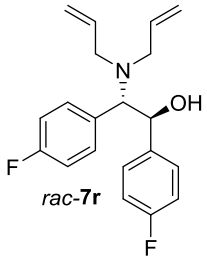

N
OH

rac-**7q**

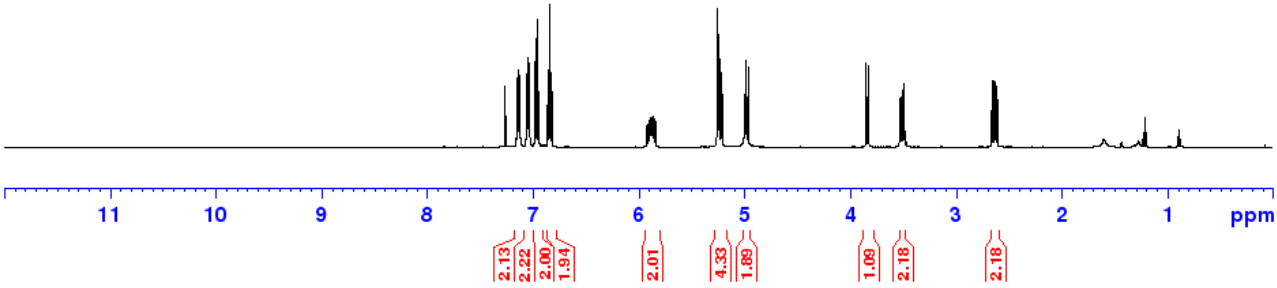
7.260
7.104
7.088
7.070
7.054
6.999
6.983
6.963
6.947
5.926
5.917
5.915
5.909
5.907
5.898
5.890
5.881
5.879
5.873
5.871
5.862
5.854
5.242
5.240
5.235
5.232
5.212
5.210
5.014
4.993
3.885
3.864
3.516
3.512
3.508
3.488
3.484
3.480
2.657
2.640
2.629
2.612
2.291
2.216
11
10
9
8
7
6
5
4
3
2
1
ppm
4.00
4.04
2.02
4.10
0.89
1.09
1.06
2.14
2.09
3.01
3.01

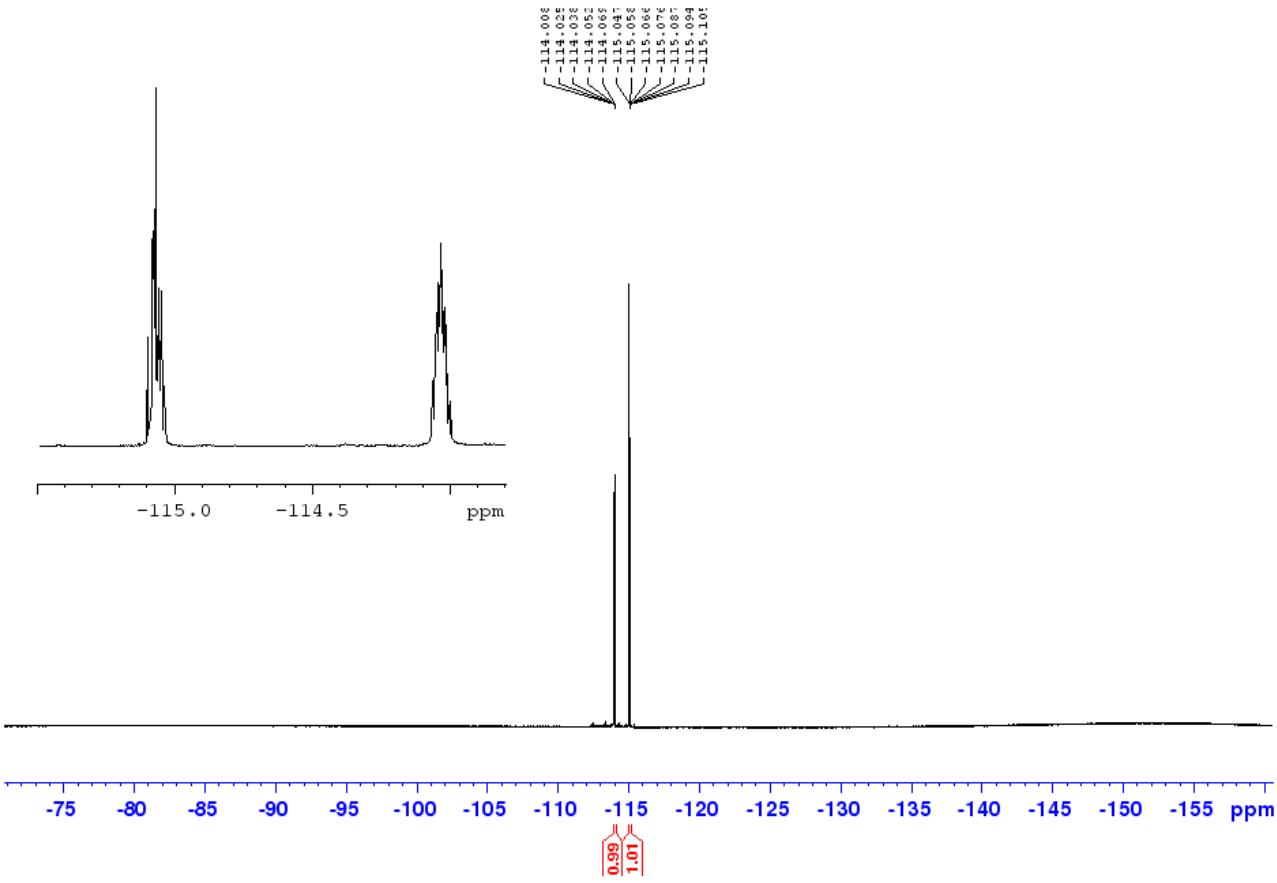

138.64
137.32
136.89
136.46
130.51
130.02
128.80
128.76
127.41
118.17
77.41
77.15
76.90
70.77
69.17
52.77
21.22
21.21
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

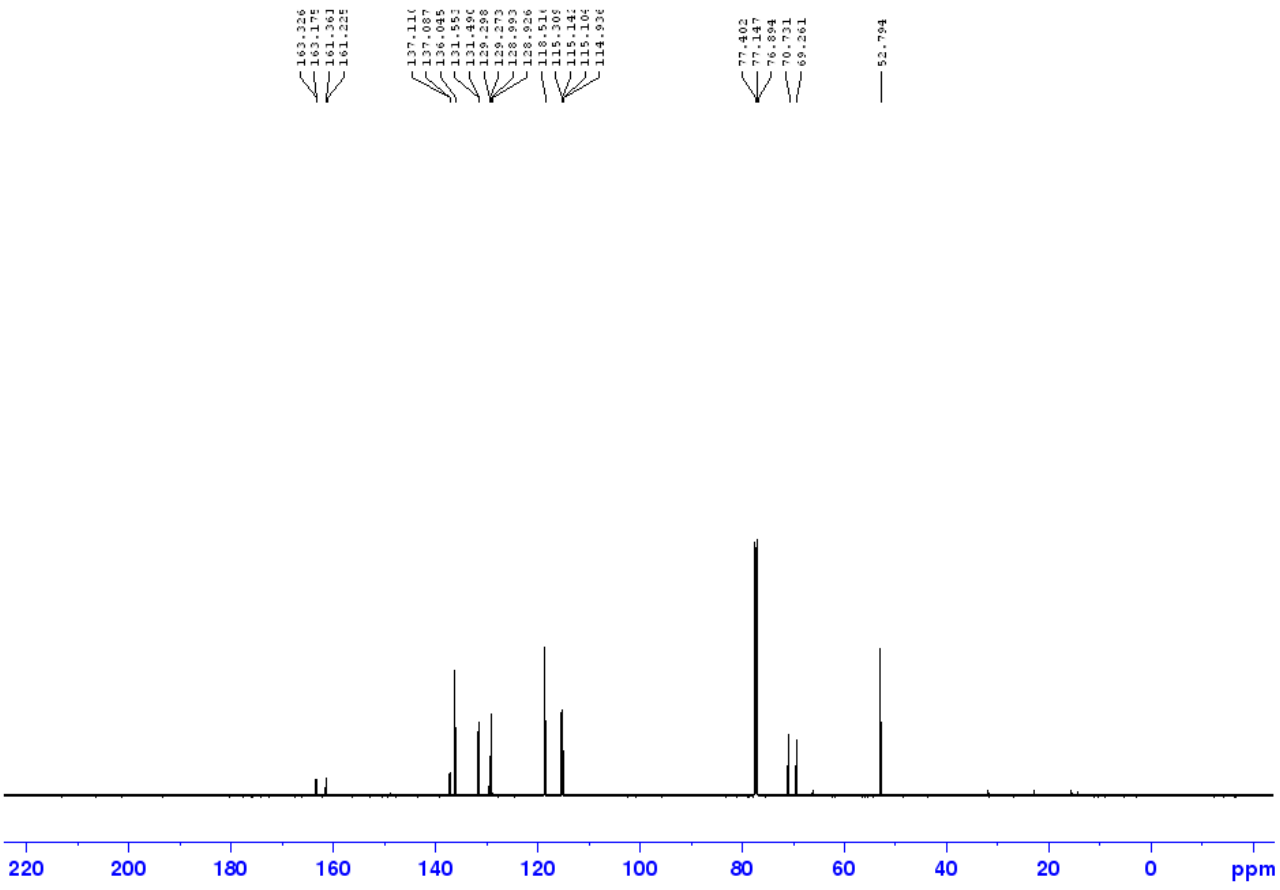


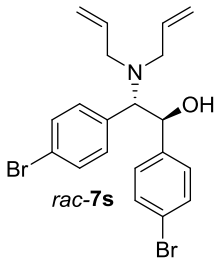

N
OH
F
F

rac-**7r**

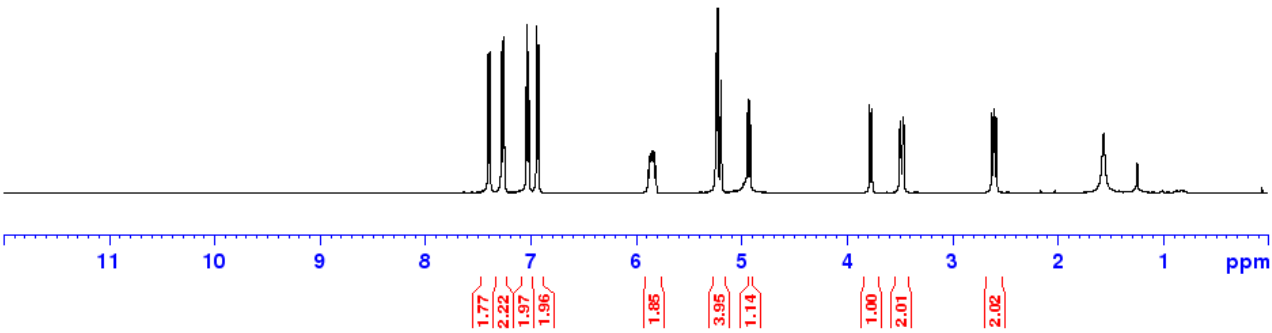

11
10
9
8
7
6
5
4
3
2
1
ppm
2.13
2.22
2.00
1.94
2.01
4.33
1.89
1.08
2.18
2.18

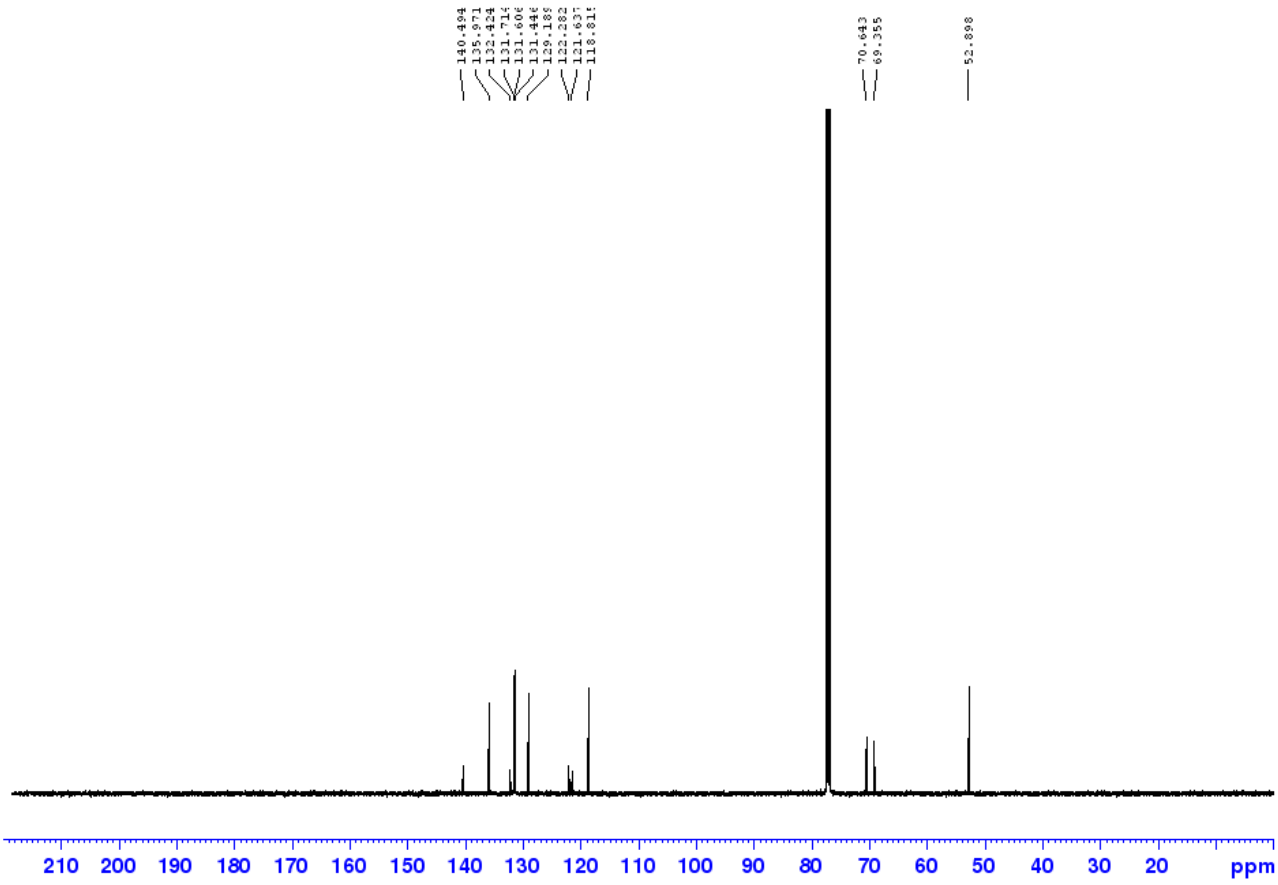

-115.0
-114.5
ppm
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
ppm
0.99
1.01

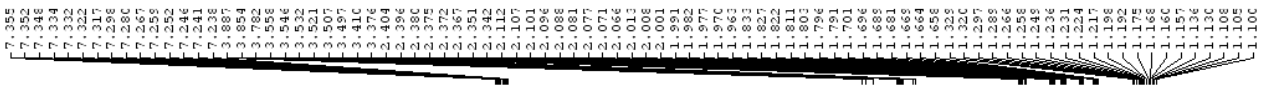

163.326
163.175
161.361
161.225
137.110
137.087
136.045
131.555
131.490
129.298
129.273
128.993
128.926
118.516
115.309
115.142
115.104
114.936
77.402
77.147
76.894
70.731
69.261
52.794
220
200
180
160
140
120
100
80
60
40
20
0
ppm

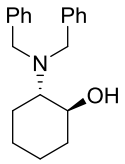

N
OH
Br
Br

rac-**7s**

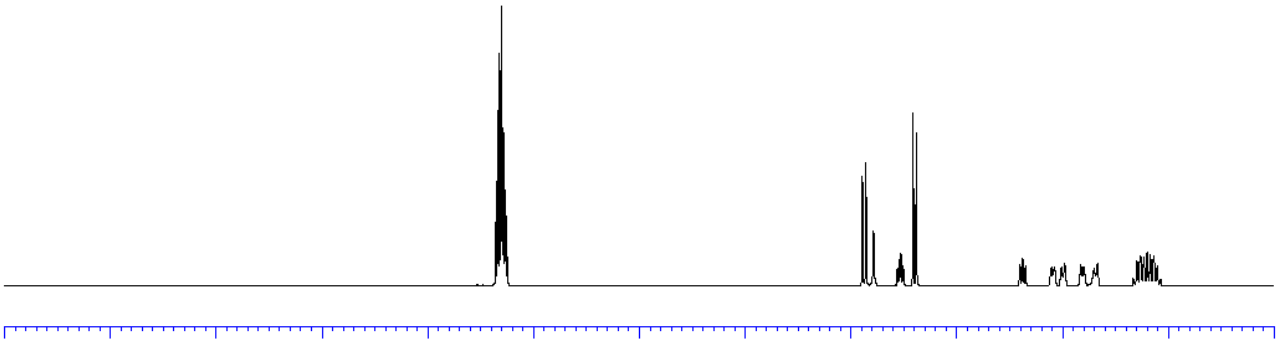

11
10
9
8
7
6
5
4
3
2
1
ppm
1.77
2.22
1.97
1.96
1.85
3.95
1.14
1.00
2.01
2.02

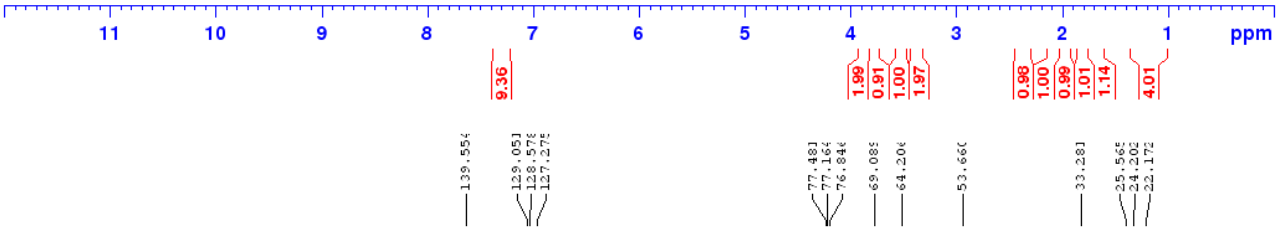

70.643
69.355
52.898
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

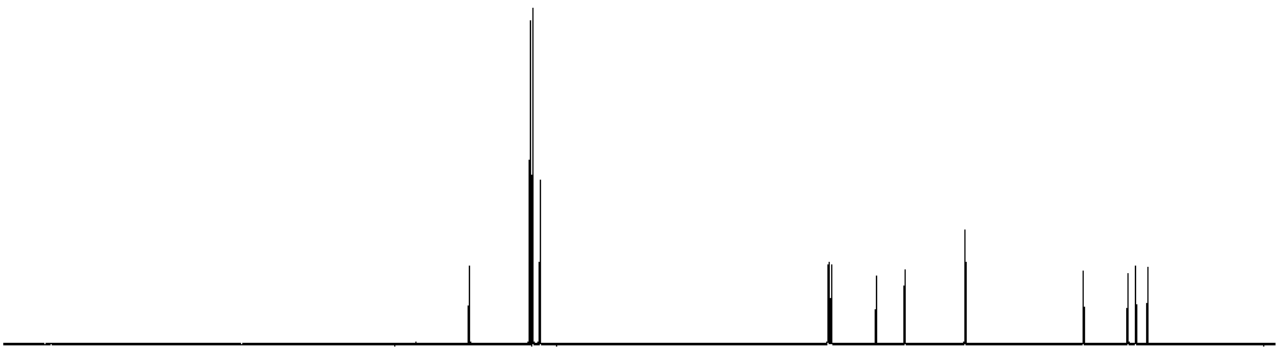



Ph
Ph
N
OH

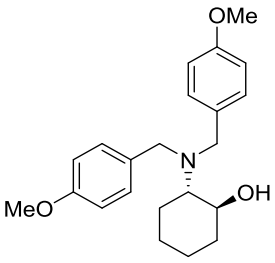
rac-**7t**



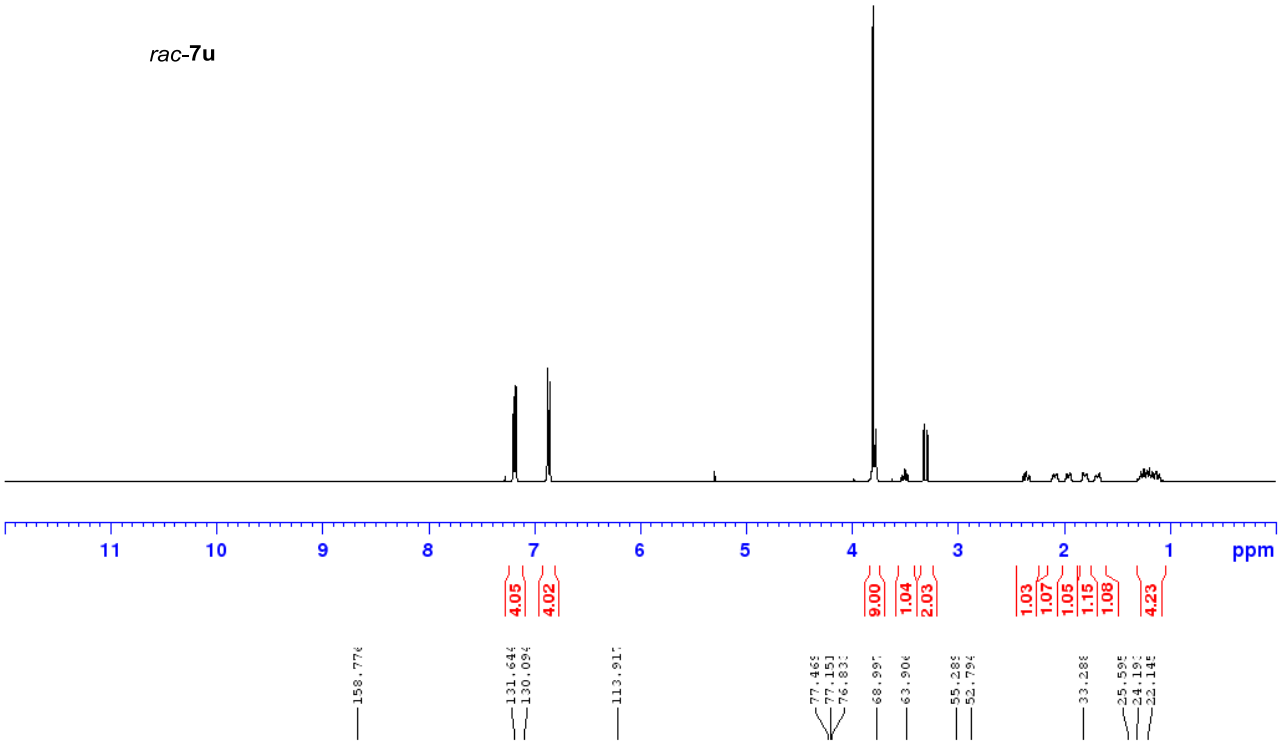

11
10
9
8
7
6
5
4
3
2
1
ppm
9.36
1.99
0.91
1.00
1.97
0.98
1.00
0.99
1.01
1.14
4.01

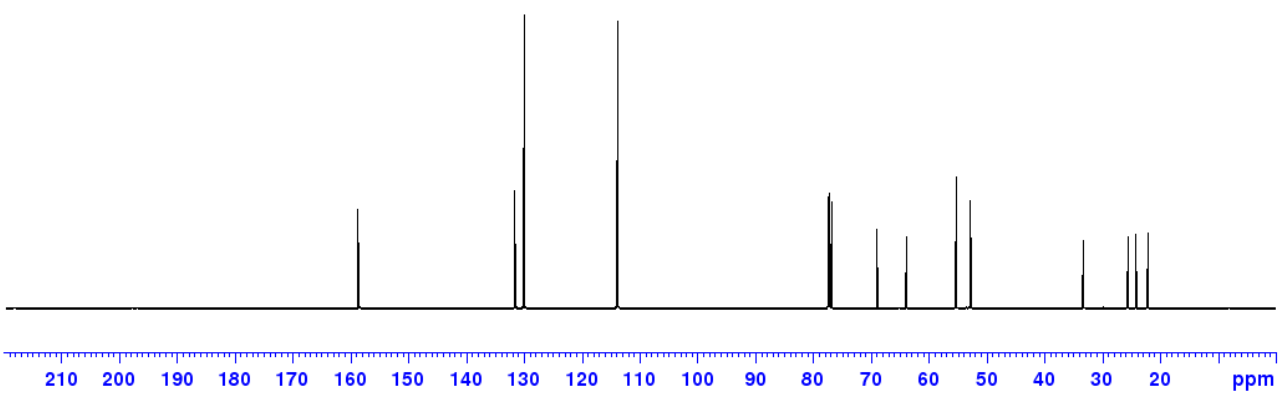


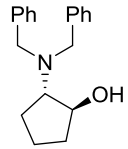

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


OMe
N
OH
MeO

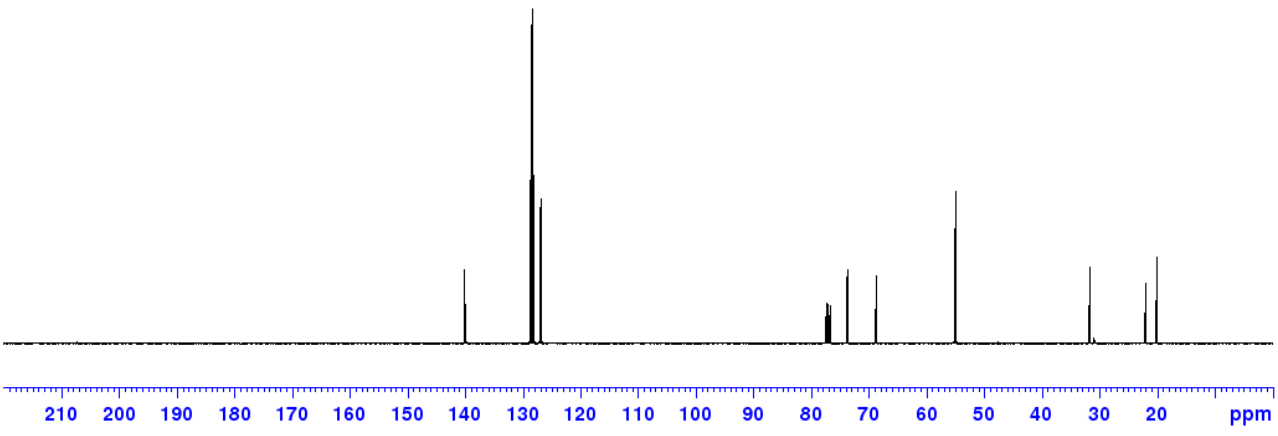
rac-**7u**


11
10
9
8
7
6
5
4
3
2
1
ppm
4.05
4.02
9.00
1.04
2.03
1.03
1.07
1.05
1.15
1.08
4.23

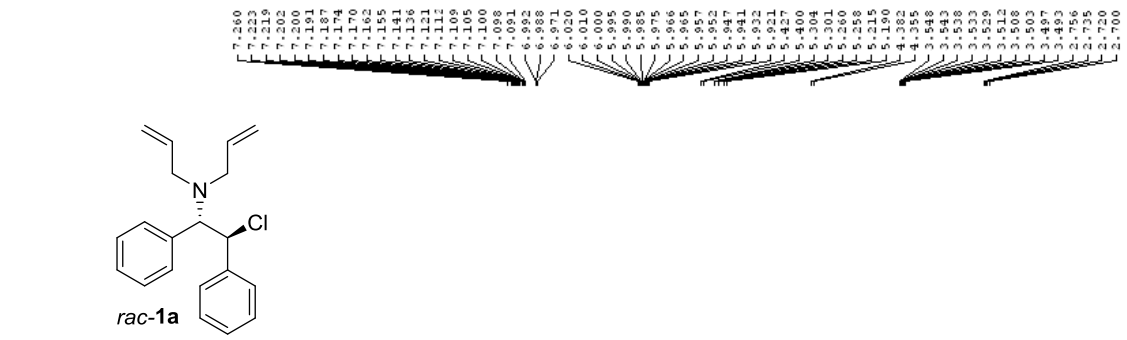

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



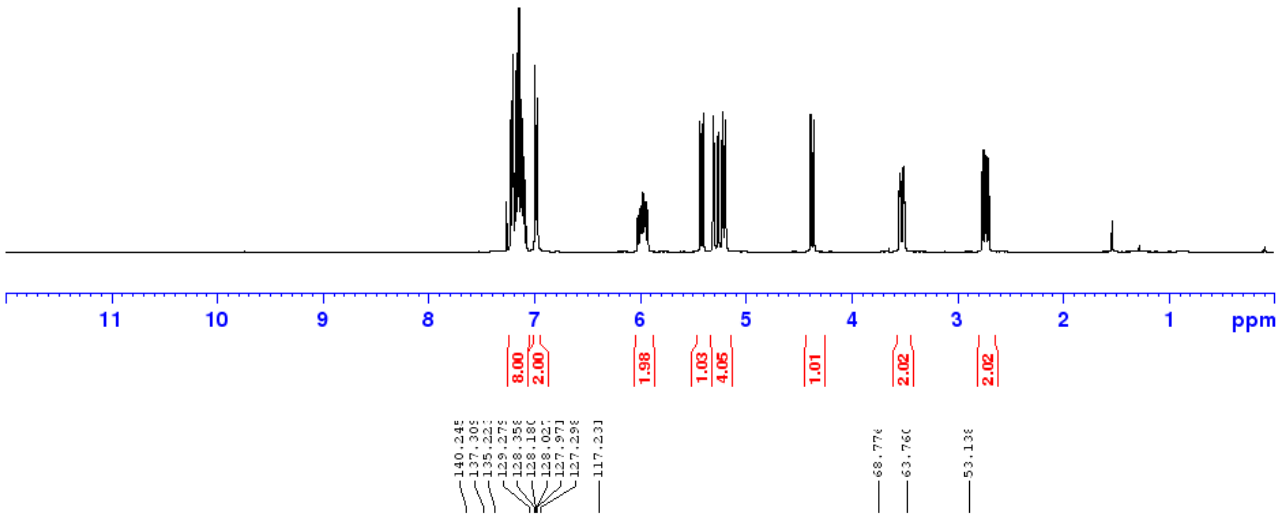
rac-**7v**

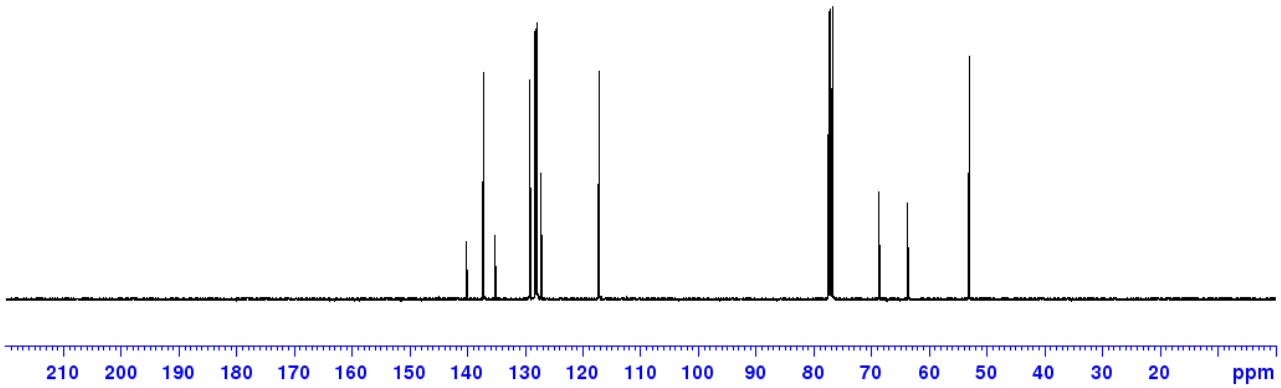


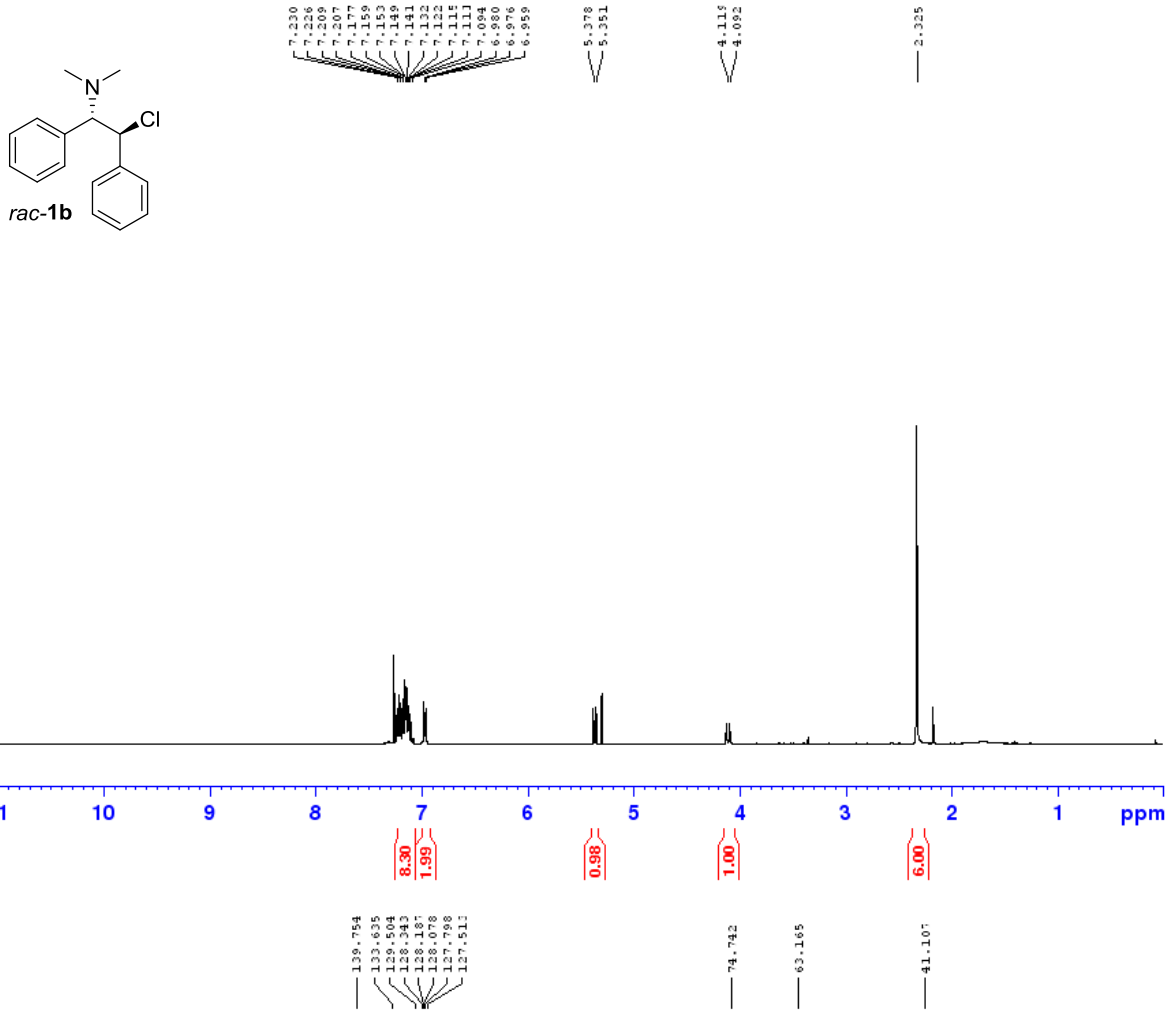
Substrates (chlorides and bromides)

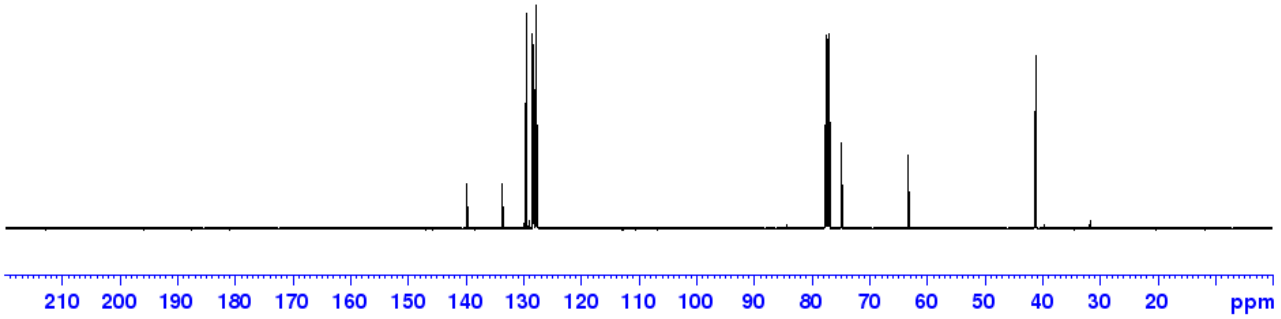


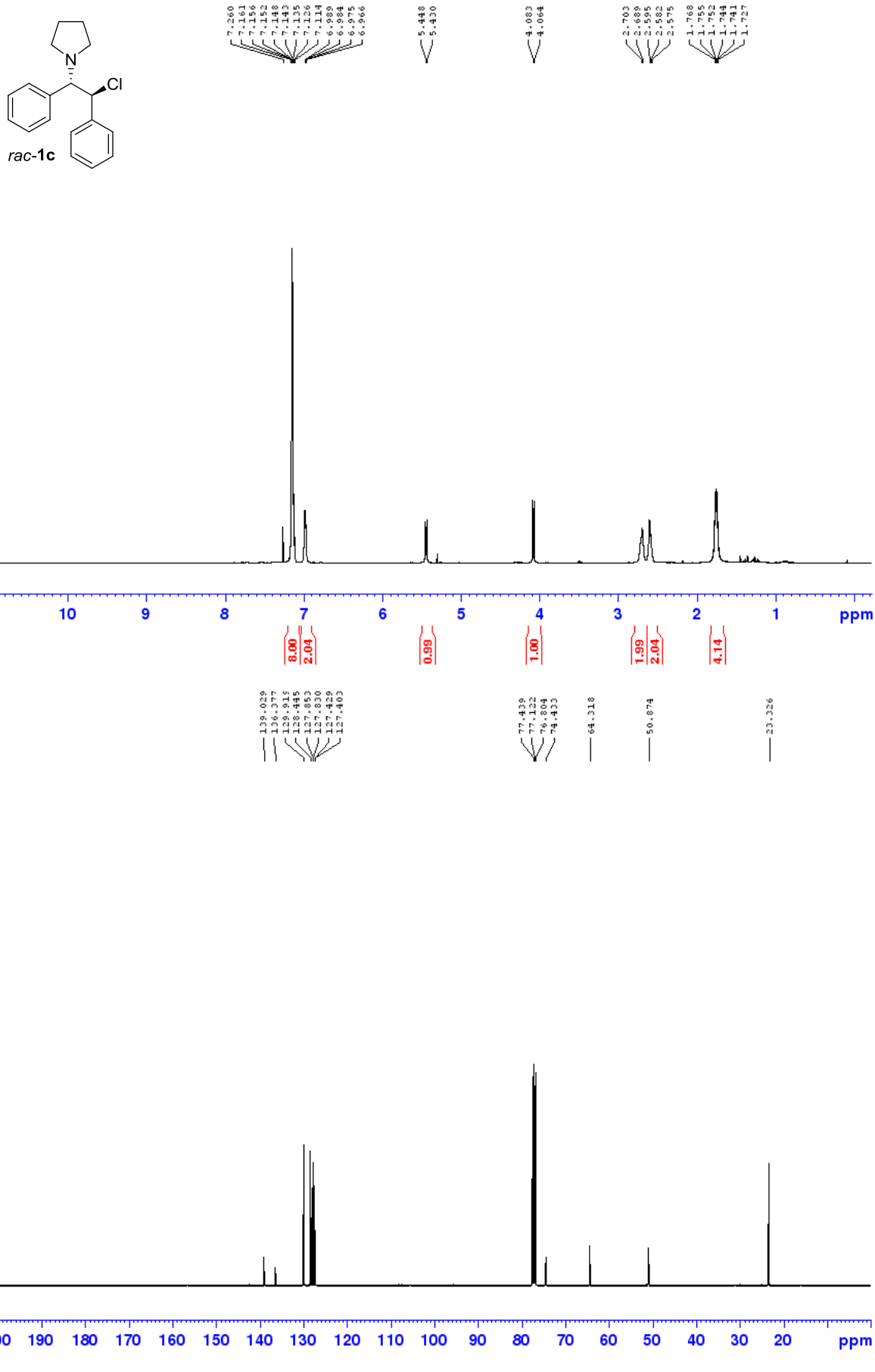
rac-**1a**






rac-1b
Cl
N
ppm
8.30
1.99
0.98
1.00
6.00


ppm


rac-1c
Cl
N
7.260
7.161
7.156
7.152
7.148
7.143
7.135
7.126
7.114
6.989
6.984
6.975
6.966
5.448
5.430
4.083
4.064
2.703
2.689
2.595
2.582
2.575
1.768
1.755
1.752
1.744
1.741
1.727
11
10
9
8
7
6
5
4
3
2
1
ppm
8.00
2.04
0.99
1.00
1.99
2.04
4.14
139.029
136.377
129.915
128.445
127.853
127.830
127.429
127.403
77.439
77.122
76.804
74.433
64.318
50.874
23.326
210
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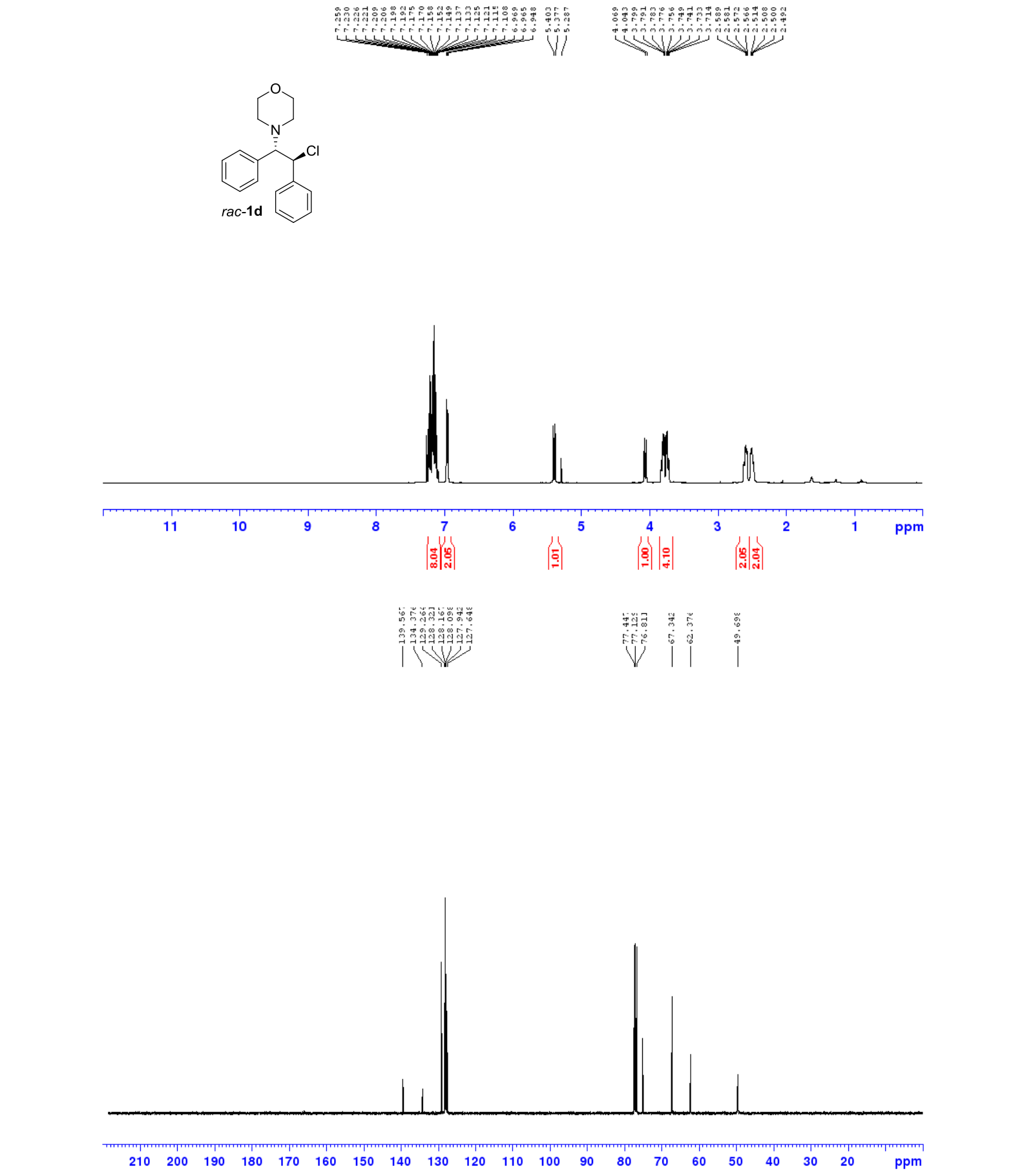
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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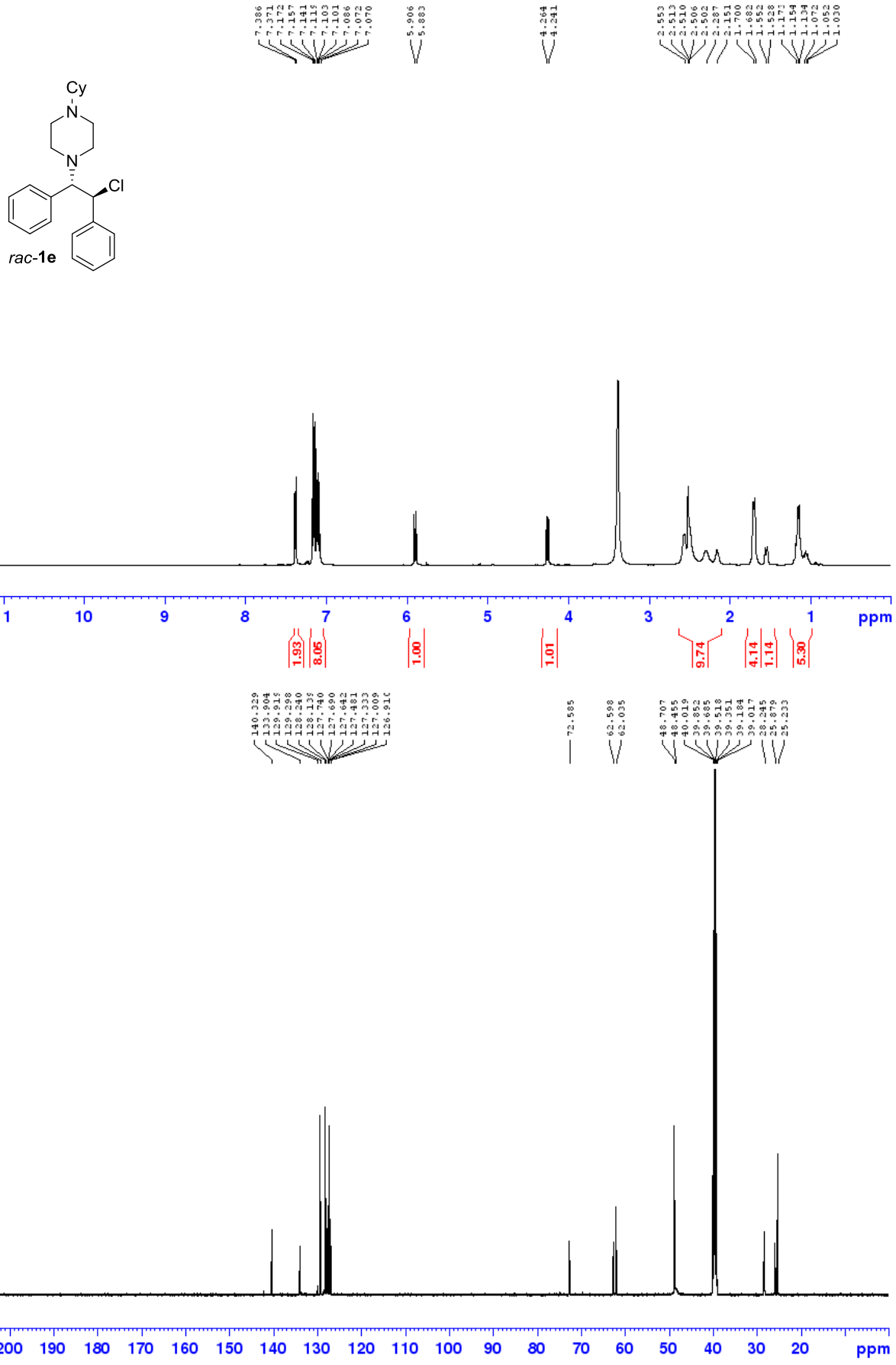
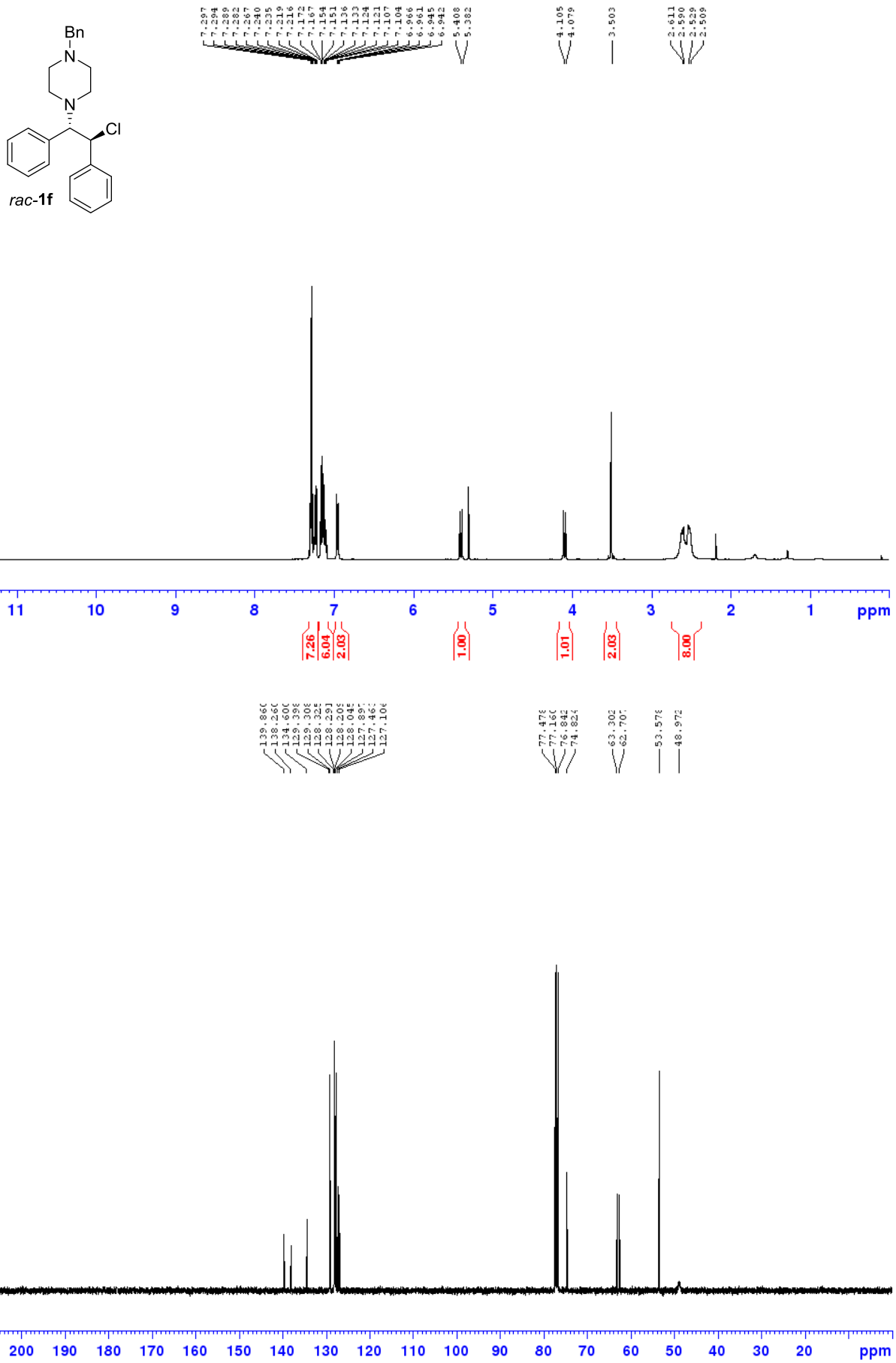
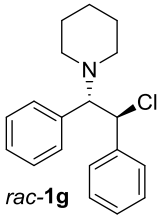
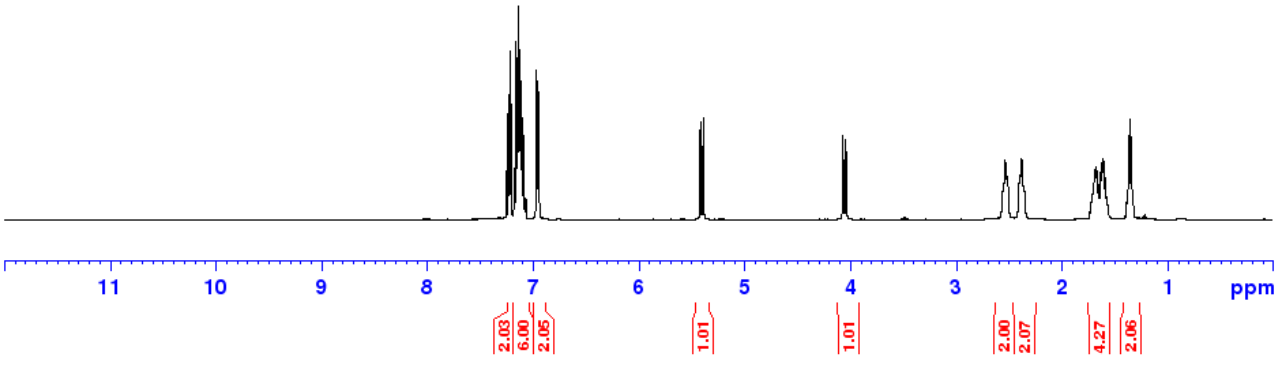
7.230
7.226
7.221
7.209
7.206
7.198
7.192
7.175
7.170
7.158
7.152
7.149
7.137
7.133
7.125
7.121
7.115
7.108
6.969
6.965
6.948
5.403
5.377
5.287
4.069
4.043
3.799
3.791
3.783
3.776
3.756
3.749
3.741
3.733
3.714
2.589
2.581
2.572
2.566
2.514
2.508
2.500
2.492
O
N
Cl
rac-1d
11
10
9
8
7
6
5
4
3
2
1
ppm
8.04
2.05
1.01
1.00
4.10
2.05
2.04
139.567
134.376
129.264
128.321
128.167
128.098
127.942
127.648
77.447
77.125
76.811
67.342
62.376
49.698
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

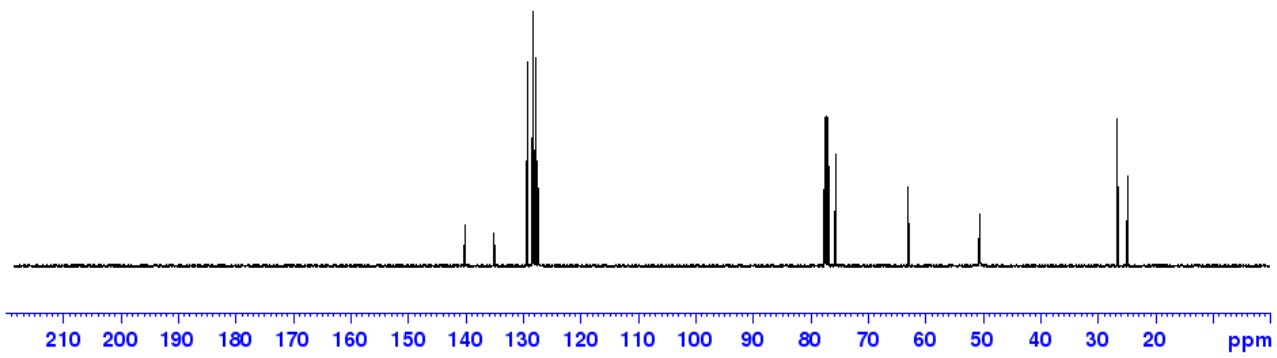

Cy
N
N
Cl
rac-1e
7.386
7.371
7.172
7.157
7.141
7.115
7.103
7.101
7.086
7.072
7.070
5.906
5.883
4.264
4.241
2.553
2.513
2.510
2.506
2.502
2.287
2.151
1.700
1.682
1.552
1.528
1.171
1.154
1.134
1.072
1.052
1.030
11
10
9
8
7
6
5
4
3
2
1
ppm
1.93
8.05
1.00
1.01
9.74
4.14
1.14
5.30
140.329
133.904
129.915
129.298
128.240
128.135
127.740
127.690
127.642
127.481
127.333
127.009
126.910
72.585
62.598
62.035
48.707
48.455
40.019
39.852
39.685
39.518
39.351
39.184
39.017
28.245
25.879
25.233
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

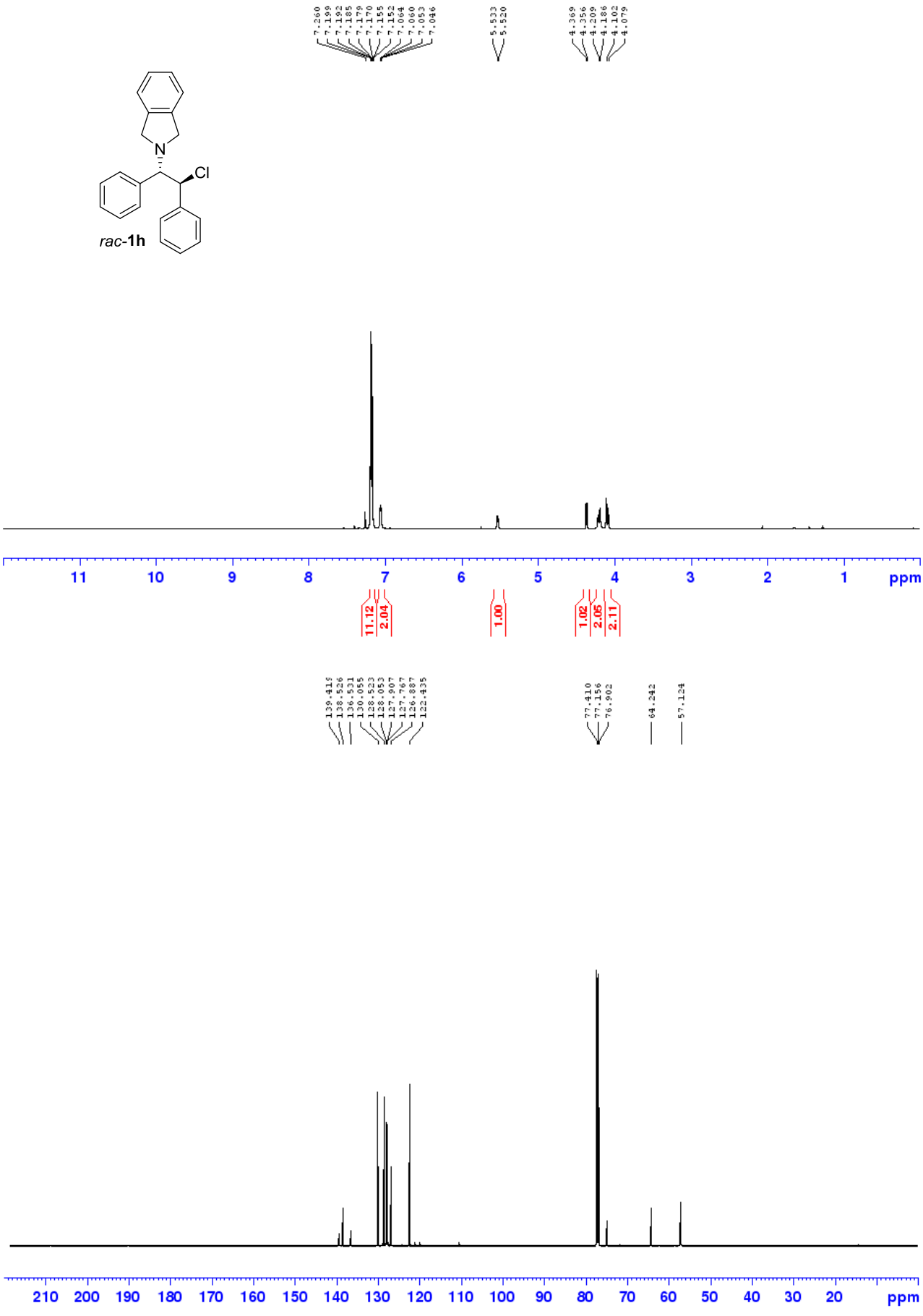

Bn
N
N
Cl
rac-1f
7.297
7.294
7.289
7.282
7.267
7.240
7.235
7.219
7.216
7.172
7.167
7.154
7.151
7.136
7.133
7.124
7.121
7.107
7.104
6.966
6.961
6.945
6.942
5.408
5.382
4.105
4.079
3.503
2.611
2.590
2.529
2.509
11
10
9
8
7
6
5
4
3
2
1
ppm
7.26
6.04
2.03
1.00
1.01
2.03
8.00
139.860
138.260
134.600
129.398
129.308
128.325
128.291
128.205
128.045
127.897
127.466
127.104
77.478
77.166
76.842
74.824
63.302
62.707
53.578
48.972
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

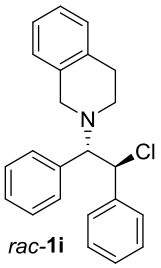

N
Cl

rac-**1g**

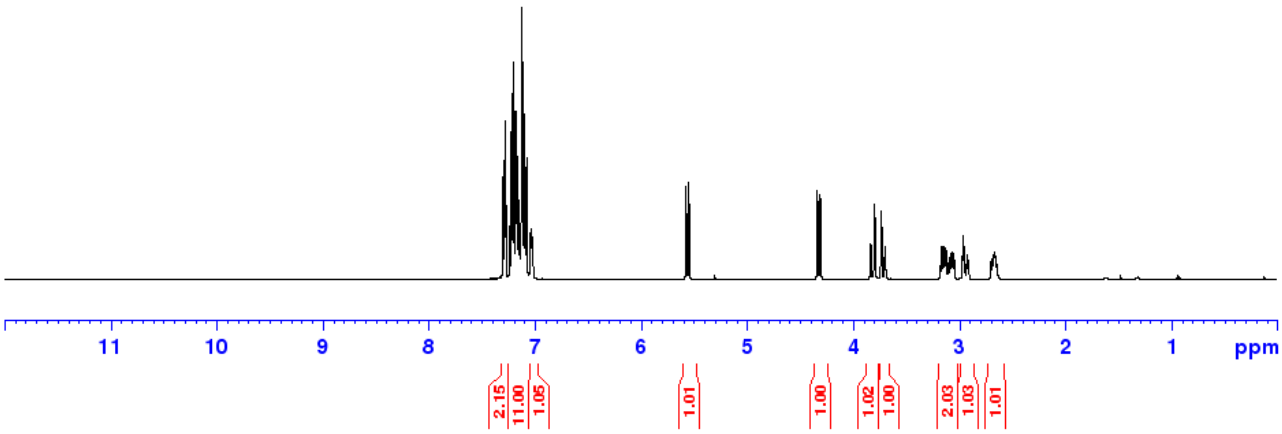

11
10
9
8
7
6
5
4
3
2
1
ppm
2.03
6.00
2.05
1.01
1.01
2.00
2.07
4.27
2.06

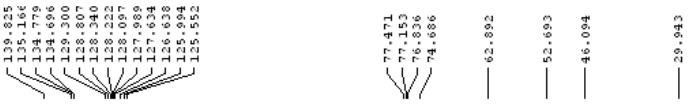

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

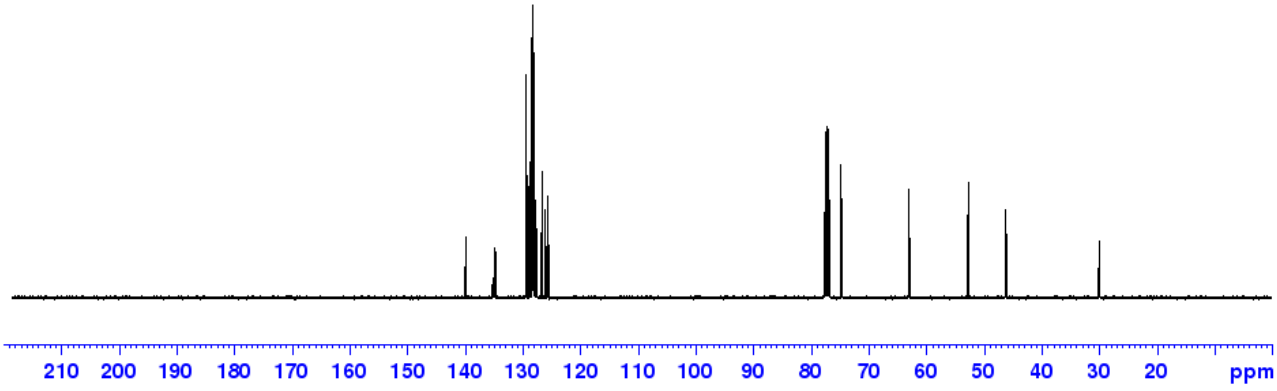

7.260
7.199
7.192
7.185
7.179
7.170
7.155
7.152
7.064
7.060
7.053
7.046
5.533
5.520
4.369
4.356
4.209
4.186
4.102
4.079
N
Cl
rac-1h
11
10
9
8
7
6
5
4
3
2
1
ppm
11.12
2.04
1.00
1.02
2.05
2.11
139.415
138.526
136.531
130.055
128.523
128.053
127.907
127.767
126.887
122.435
77.410
77.156
76.902
64.242
57.134
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

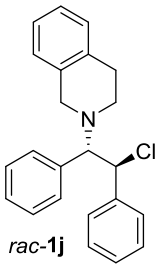

N
Cl

rac-**1i**

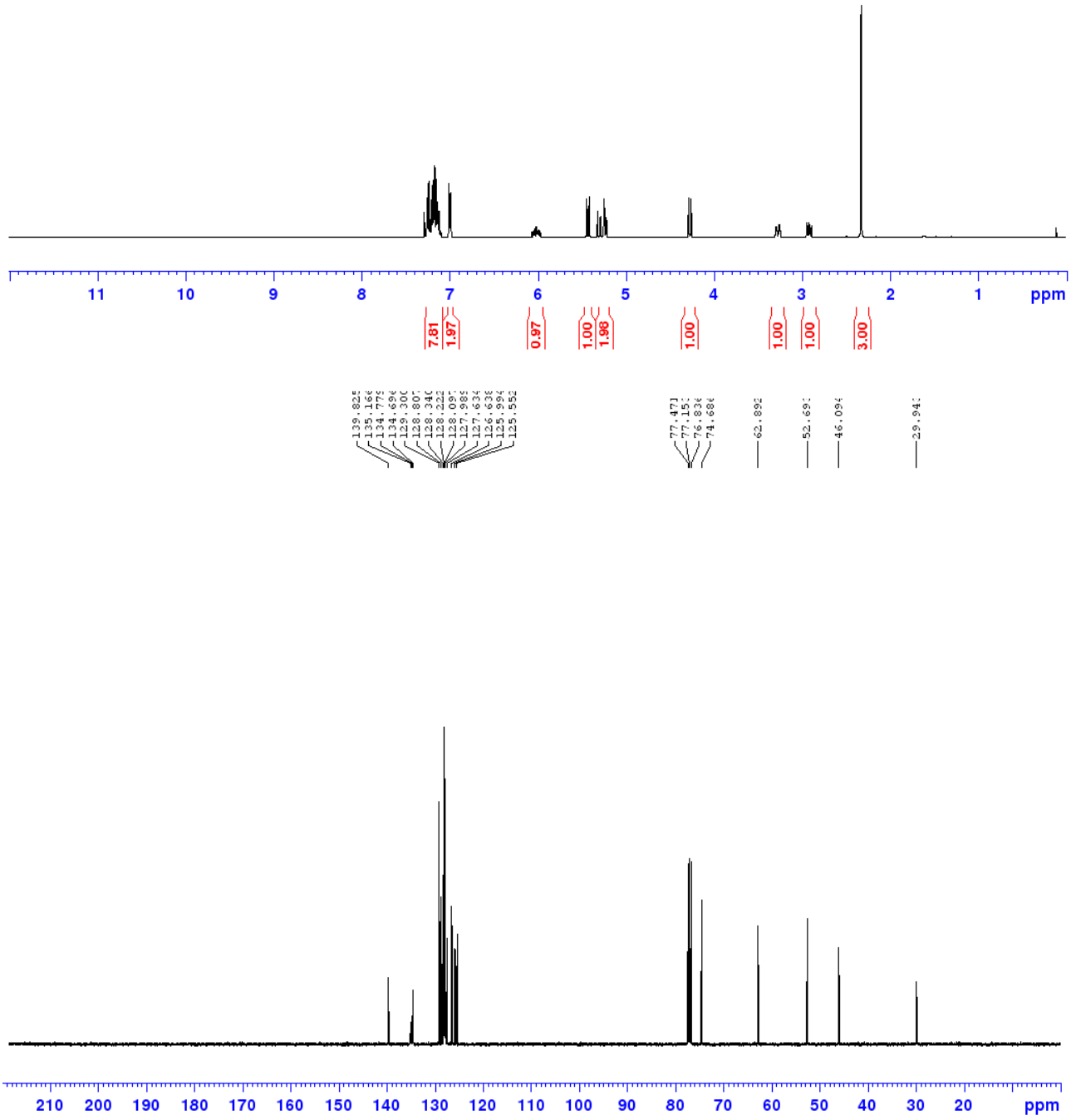

11
10
9
8
7
6
5
4
3
2
1
ppm
2.15
11.00
1.05
1.01
1.00
1.02
1.00
2.03
1.03
1.01

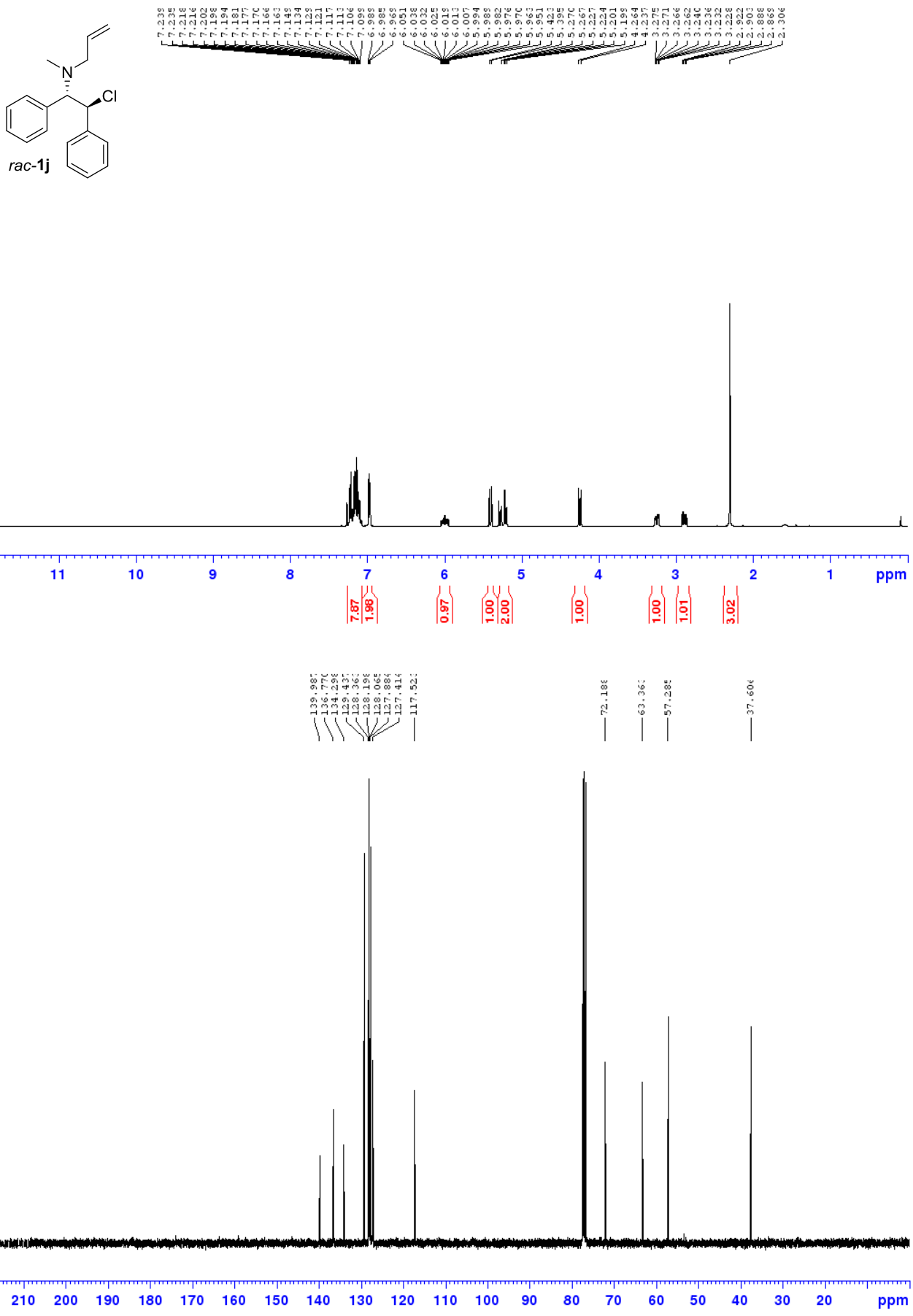


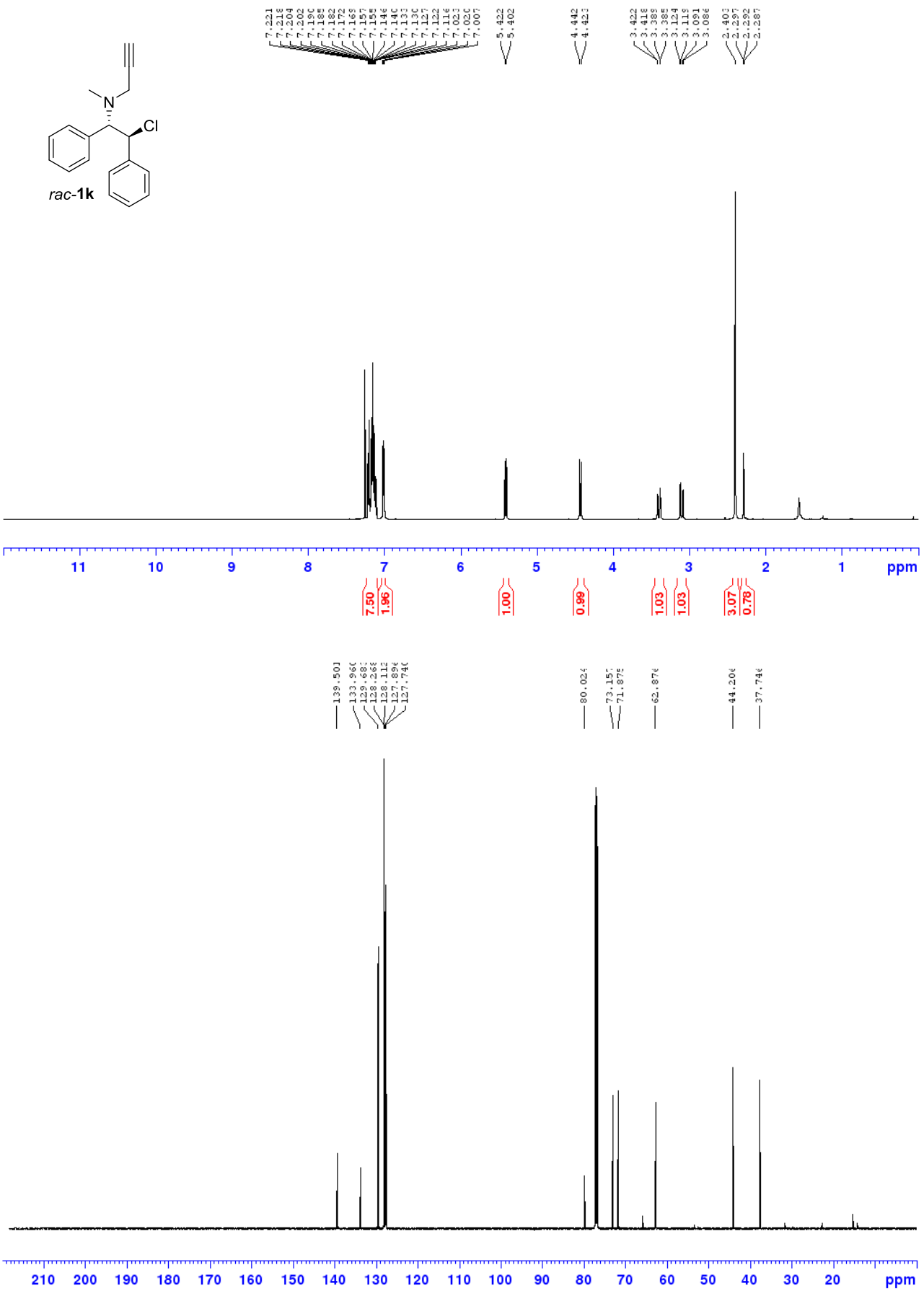

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

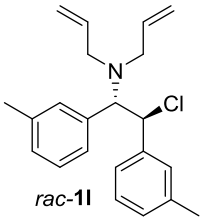

N
Cl

rac-**1j**

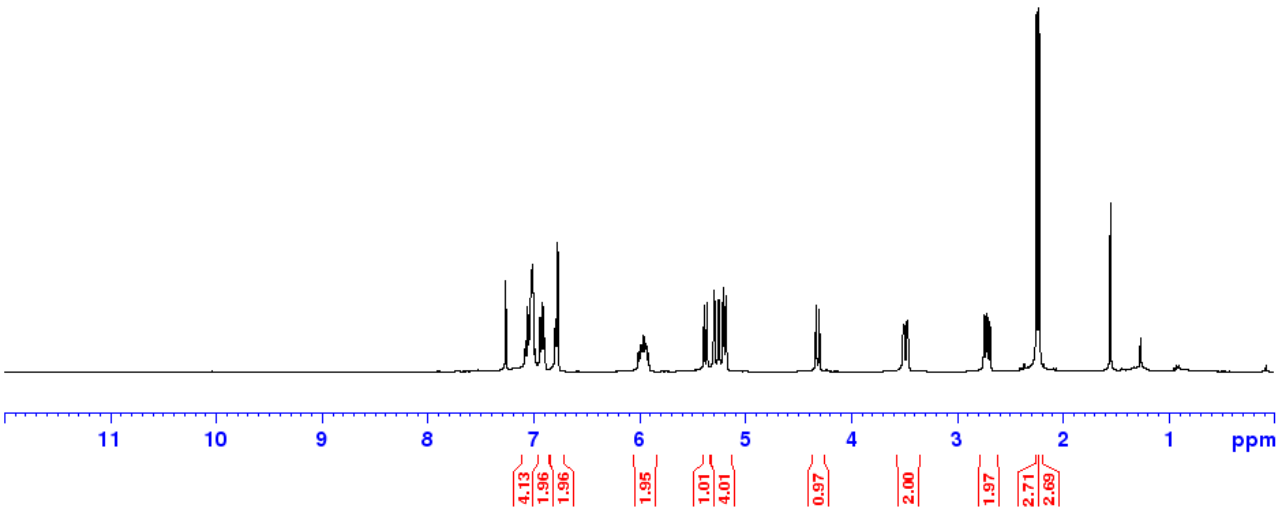

11
10
9
8
7
6
5
4
3
2
1
ppm
7.81
1.97
0.97
1.00
1.98
1.00
1.00
1.00
3.00
62.892
52.691
46.094
29.941
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

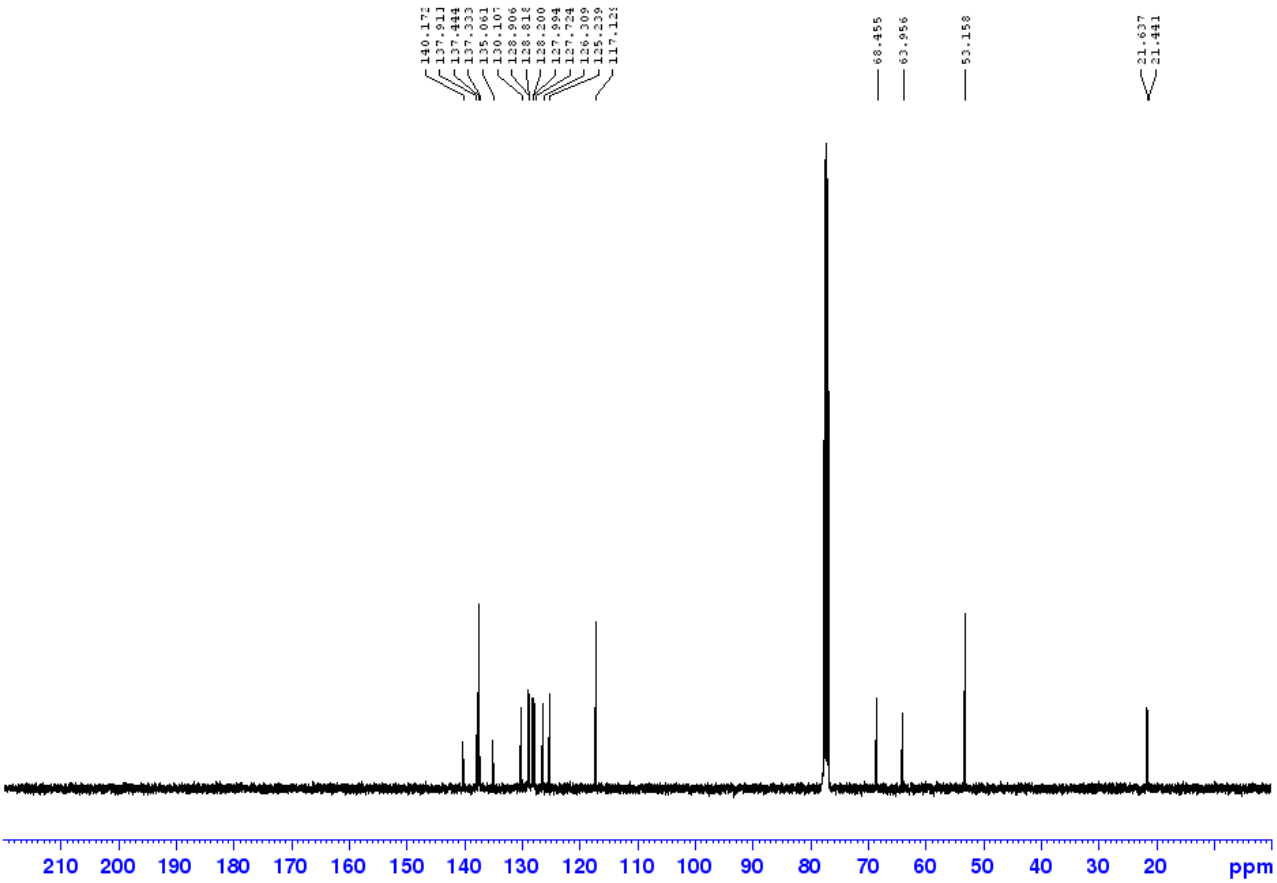

N
Cl
rac-1j
11
10
9
8
7
6
5
4
3
2
1
ppm
7.87
1.98
0.97
1.00
2.00
1.00
1.00
1.01
3.02
139.98
136.77
134.29
129.43
128.36
128.19
128.06
127.88
127.41
117.52
72.18
63.36
57.28
37.60
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

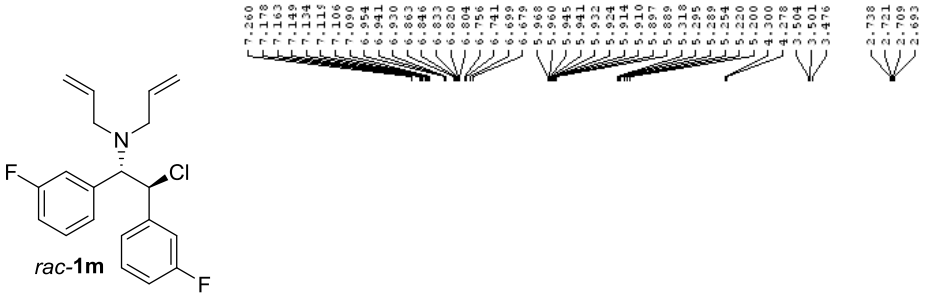

rac-1k
N
Cl
ppm
ppm


N
Cl

rac-**1l**

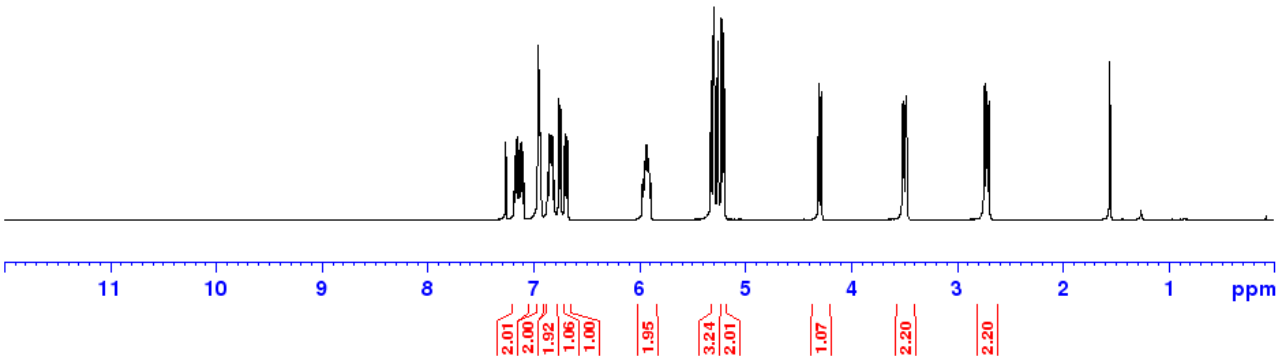

11
10
9
8
7
6
5
4
3
2
1
ppm
4.13
1.96
1.96
1.95
1.01
4.01
0.97
2.00
1.97
2.71
2.69

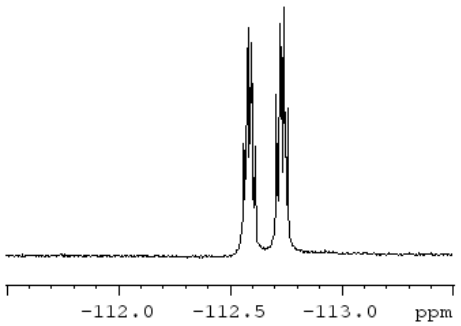

68.455
63.956
53.158
21.637
21.441
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

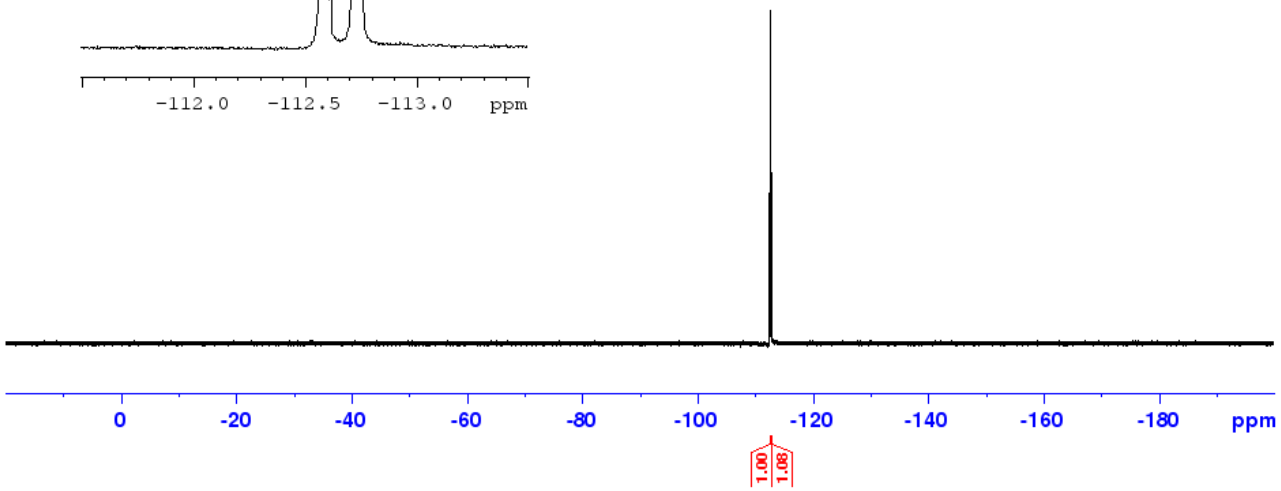

7.260
7.178
7.163
7.149
7.134
7.115
7.106
7.090
6.954
6.941
6.930
6.863
6.846
6.833
6.820
6.804
6.756
6.741
6.699
6.679
5.968
5.960
5.945
5.941
5.932
5.924
5.914
5.910
5.897
5.889
5.318
5.295
5.289
5.254
5.220
5.200
4.300
4.278
3.504
3.501
3.476
2.738
2.721
2.709
2.693

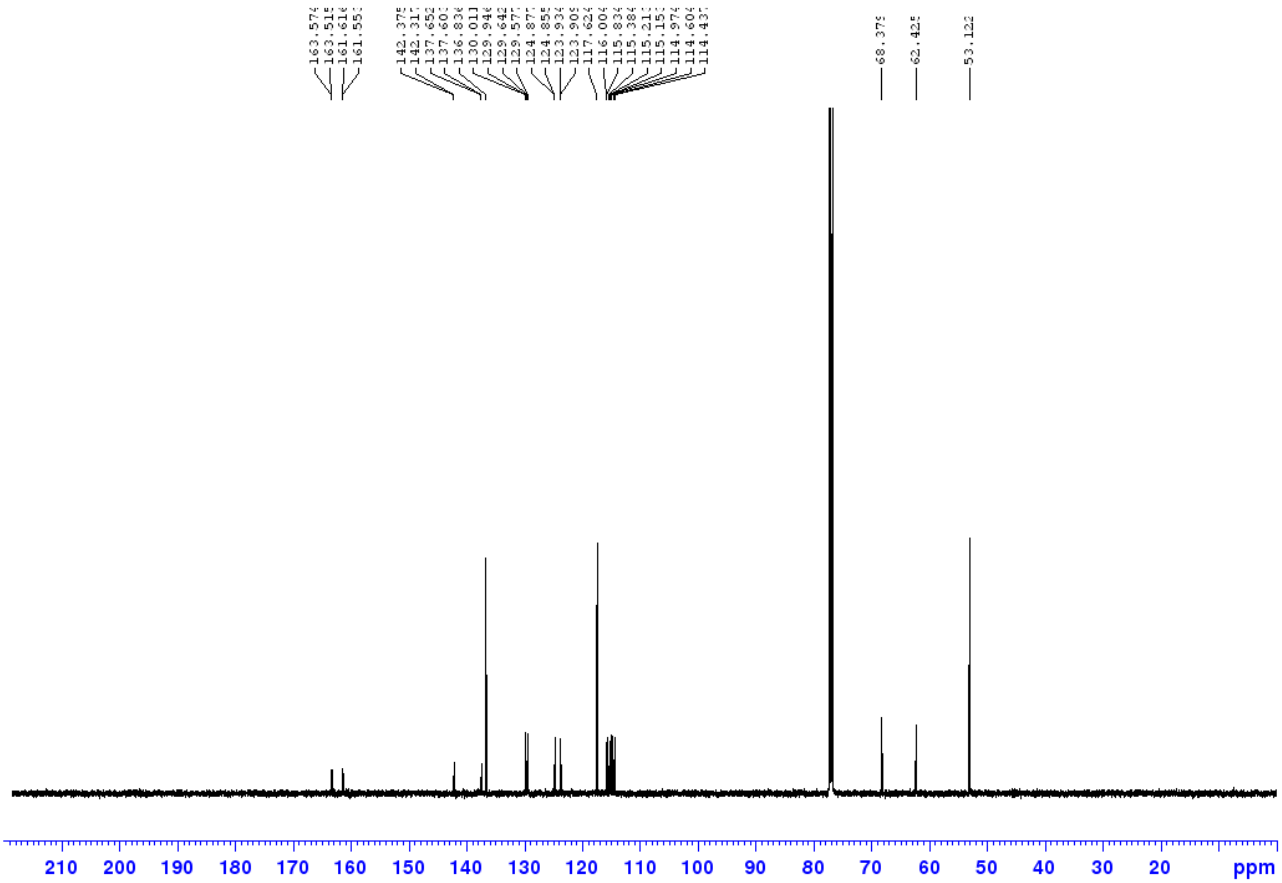
F
Cl
N
F

rac-**1m**


11
10
9
8
7
6
5
4
3
2
1
ppm
2.01
2.00
1.92
1.06
1.00
1.95
3.24
2.01
1.07
2.20
2.20


-112.0
-112.5
-113.0
ppm


0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
1.00
1.08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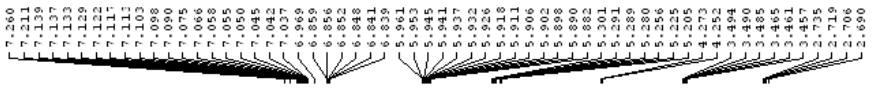
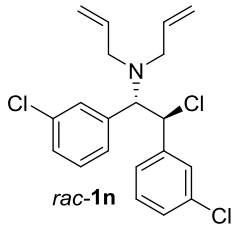
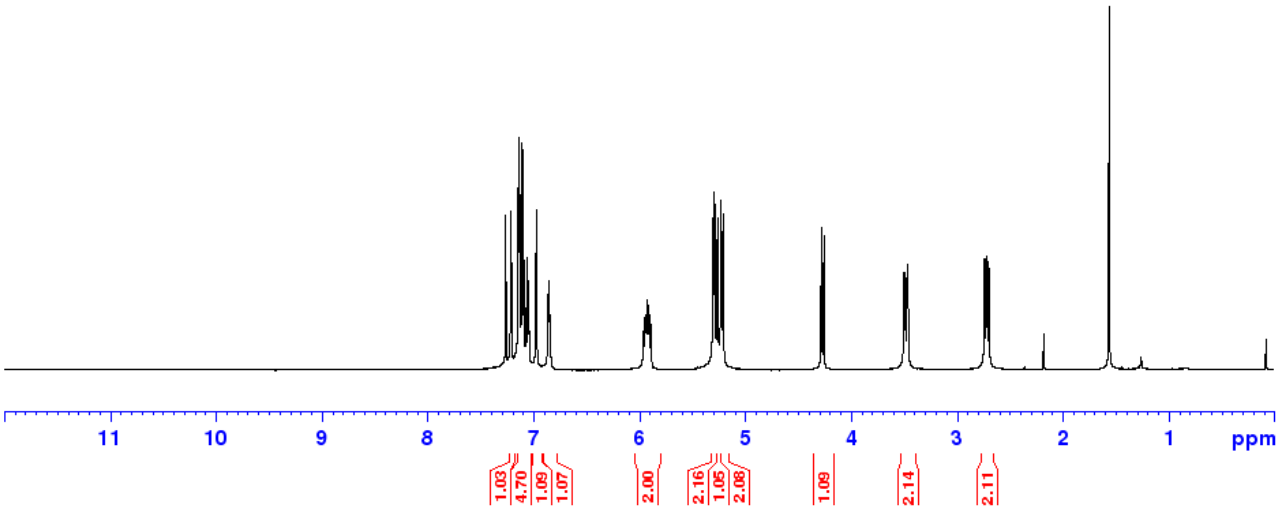
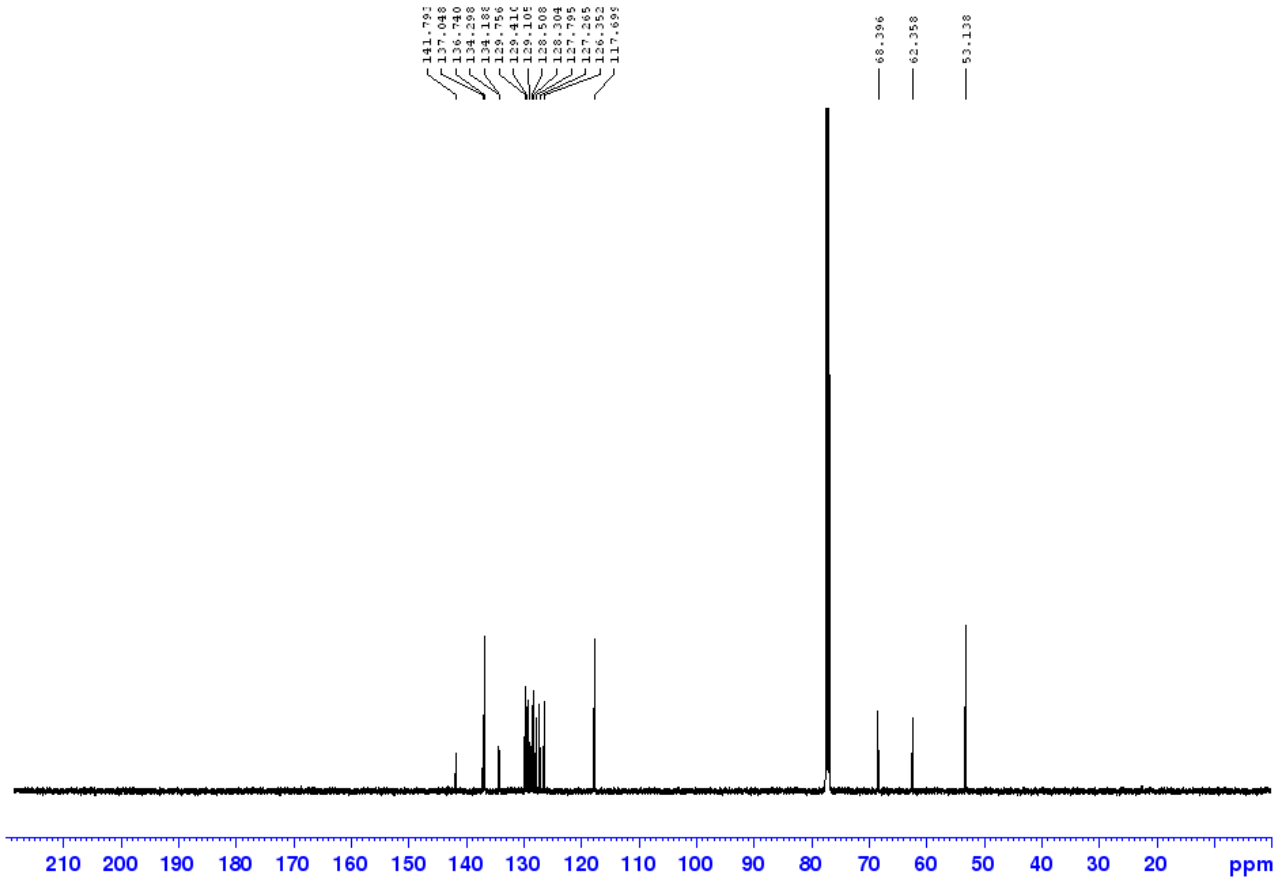
62.425
53.122
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm




N
Cl
Cl
Cl

rac-**1n**


11
10
9
8
7
6
5
4
3
2
1
ppm
1.03
4.70
1.09
1.07
2.00
2.16
1.05
2.08
1.09
2.14
2.11


68.396
62.358
53.138
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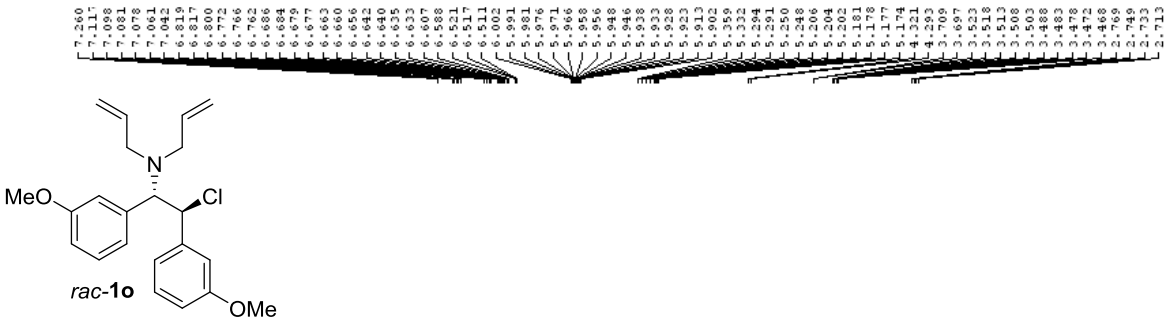
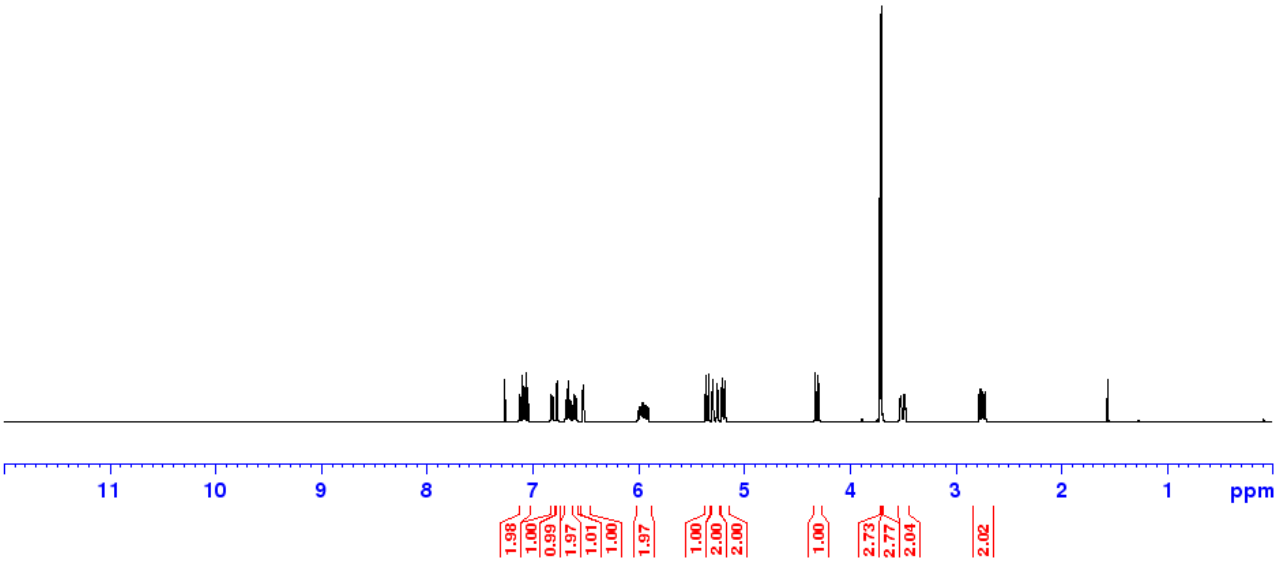
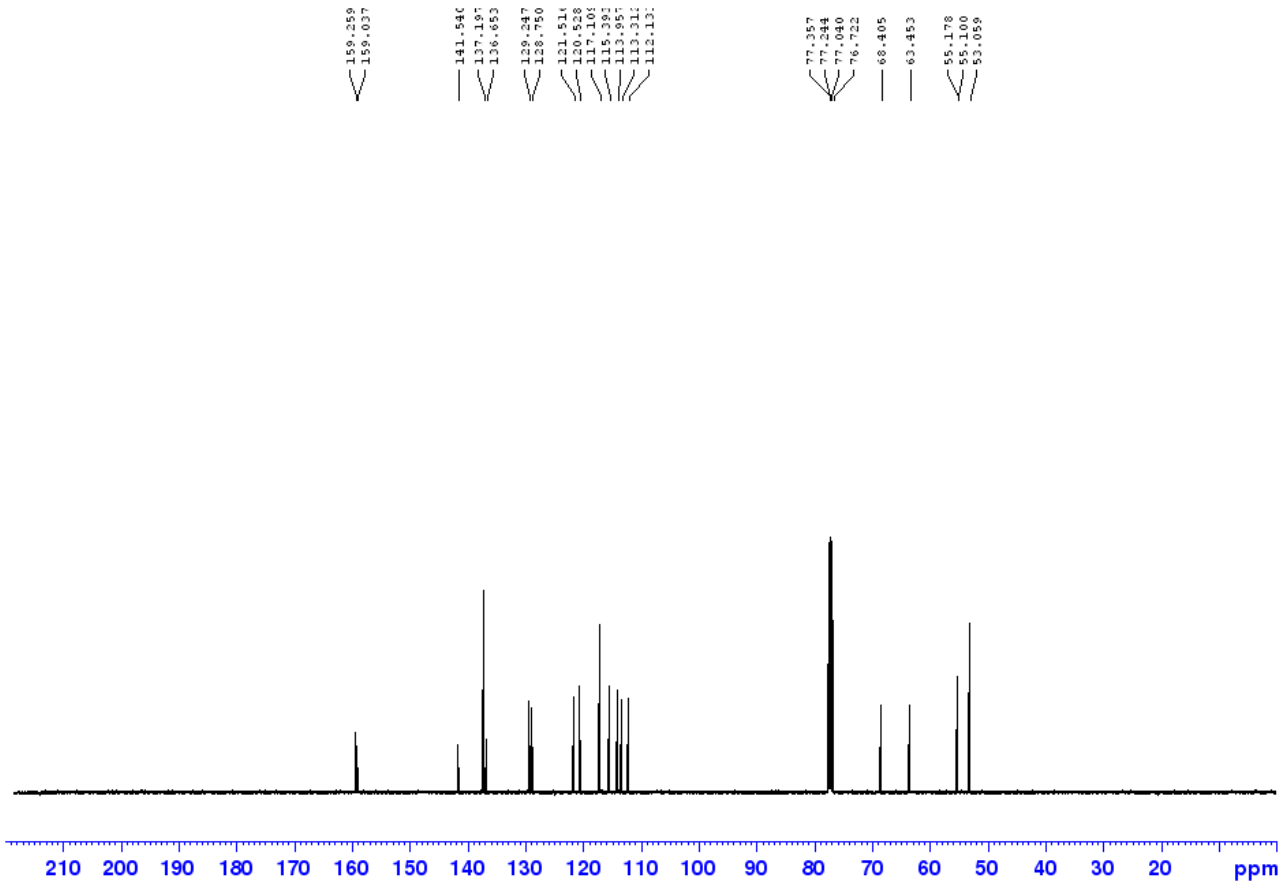
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

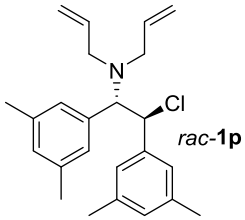


N
MeO
Cl
OMe

rac-**1o**

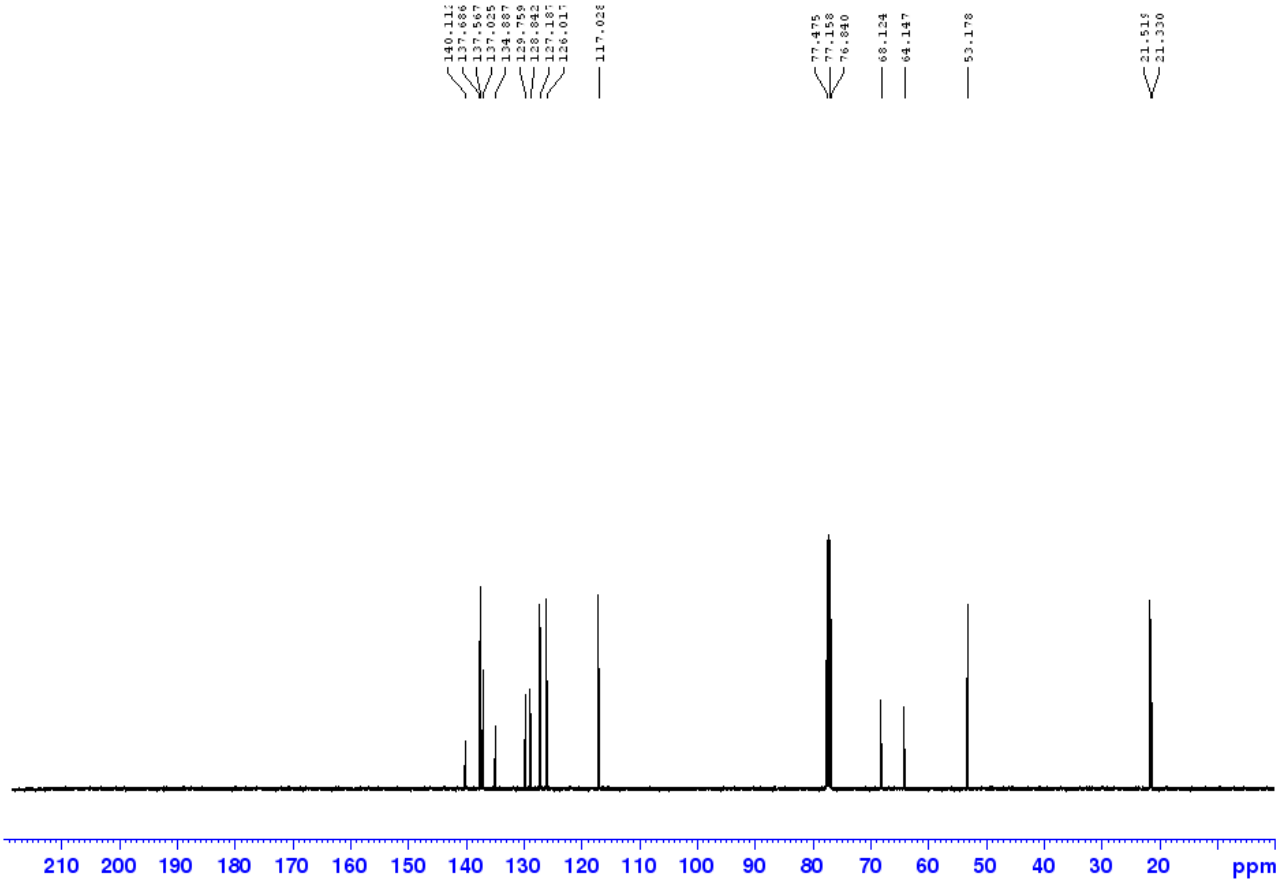

11
10
9
8
7
6
5
4
3
2
1
ppm
1.98
1.00
0.99
1.97
1.01
1.00
1.97
1.00
2.00
2.00
1.00
2.73
2.77
2.04
2.02

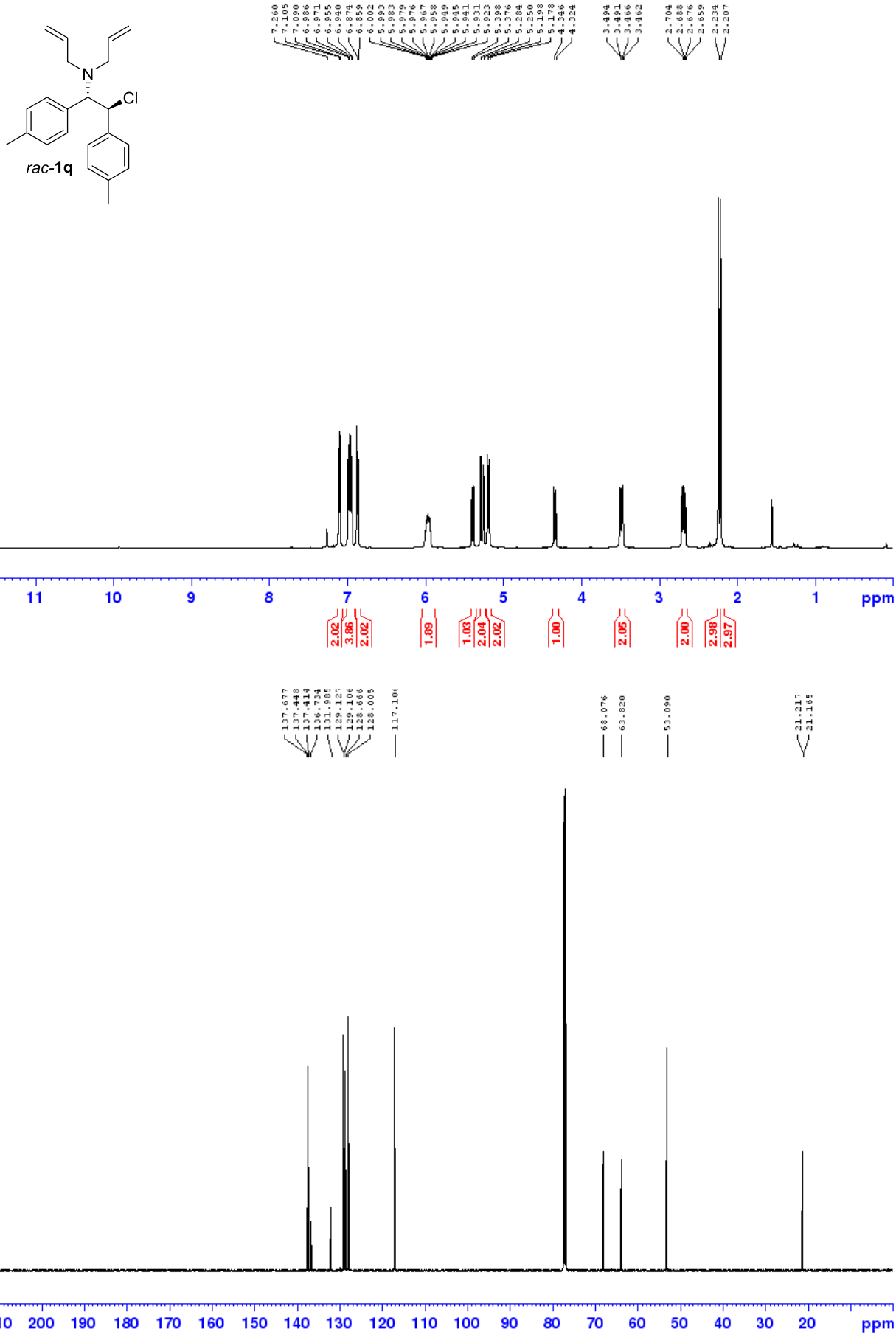

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

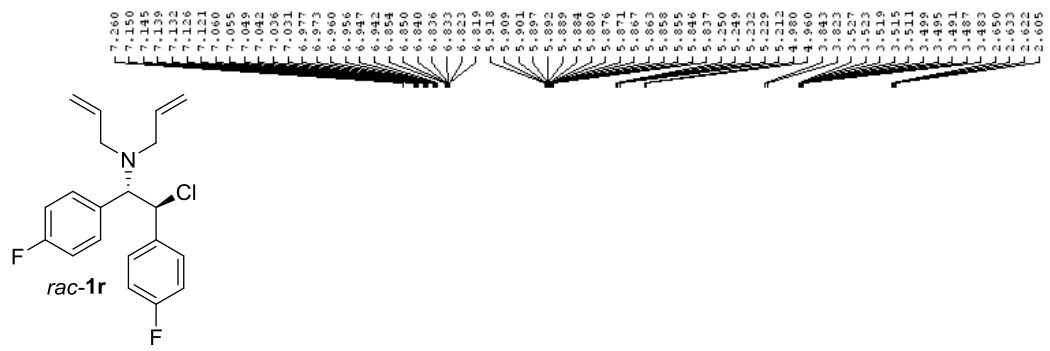

N
Cl

rac-**1p**

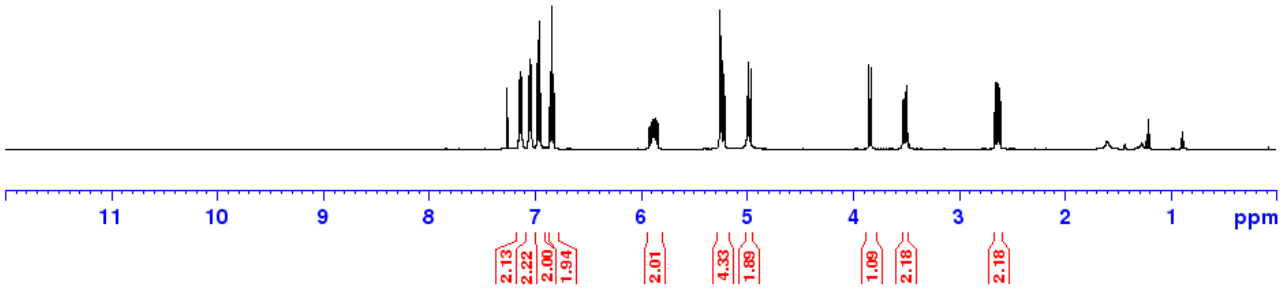
7.260
6.828
6.754
6.731
6.594
6.016
6.005
5.996
5.990
5.985
5.980
5.971
5.962
5.953
5.947
5.942
5.937
5.927
5.917
5.362
5.335
5.298
5.296
5.255
5.253
5.209
5.208
5.184
4.291
4.264
3.492
3.487
3.482
3.476
3.472
3.456
3.451
3.446
3.441
3.436
2.744
2.724
2.708
2.688
2.214
2.185
11
10
9
8
7
6
5
4
3
2
1
ppm
2.03
2.00
2.01
2.01
1.03
2.11
2.05
1.01
2.04
2.03
6.06
6.06

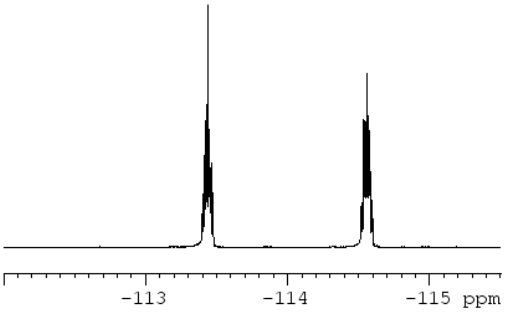

140.11
137.686
137.567
137.025
134.887
129.759
128.842
127.187
126.017
117.028
77.475
77.158
76.840
68.124
64.147
53.178
21.516
21.330
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

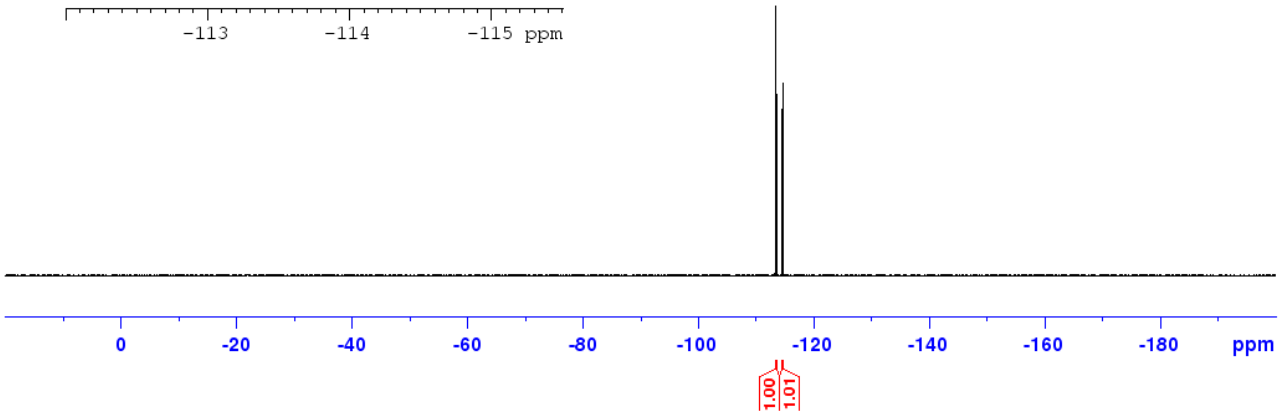

rac-1q
Cl
N
ppm
ppm

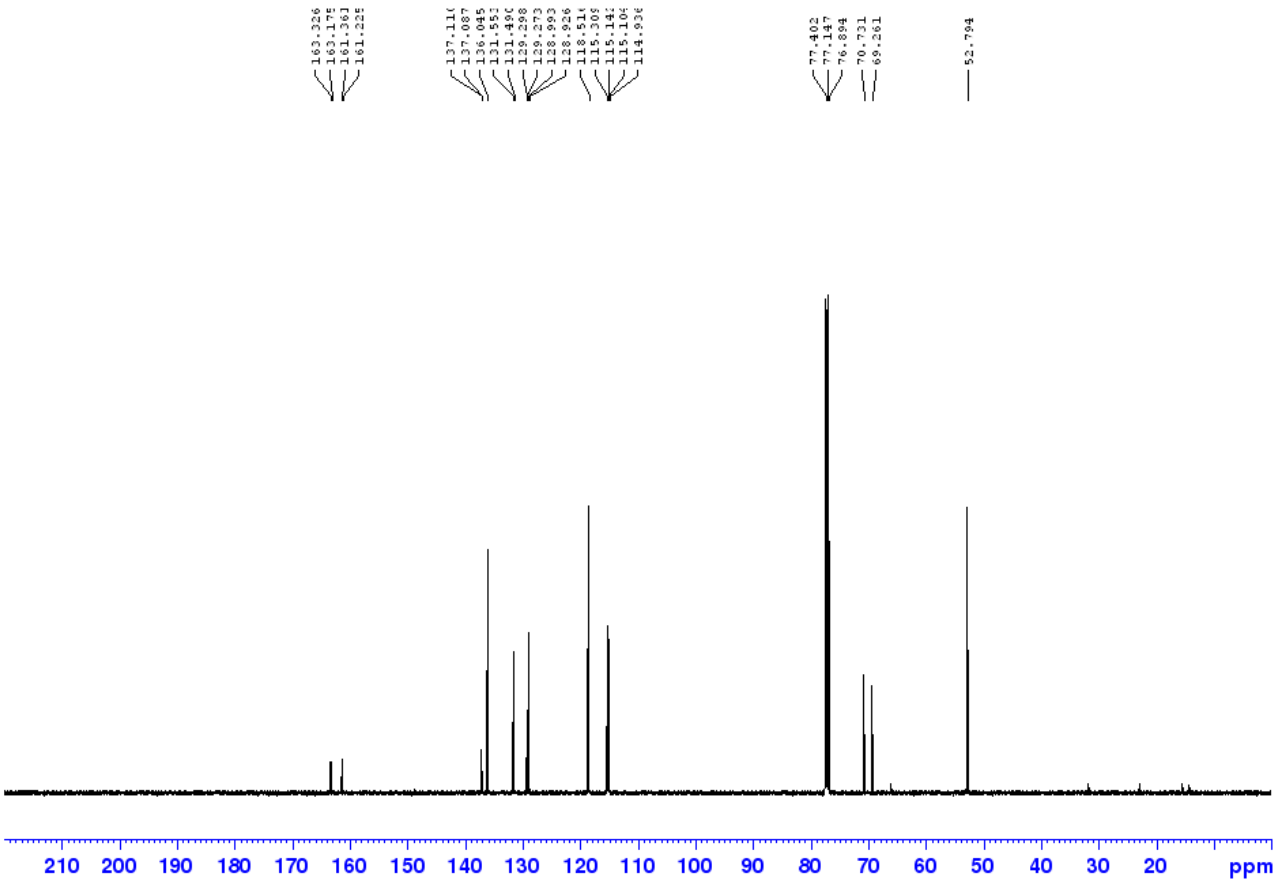

N
Cl
F
F

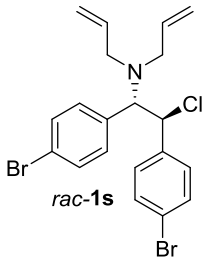
rac-**1r**


11
10
9
8
7
6
5
4
3
2
1
ppm
2.13
2.22
2.00
1.94
2.01
4.33
1.89
1.09
2.18
2.18

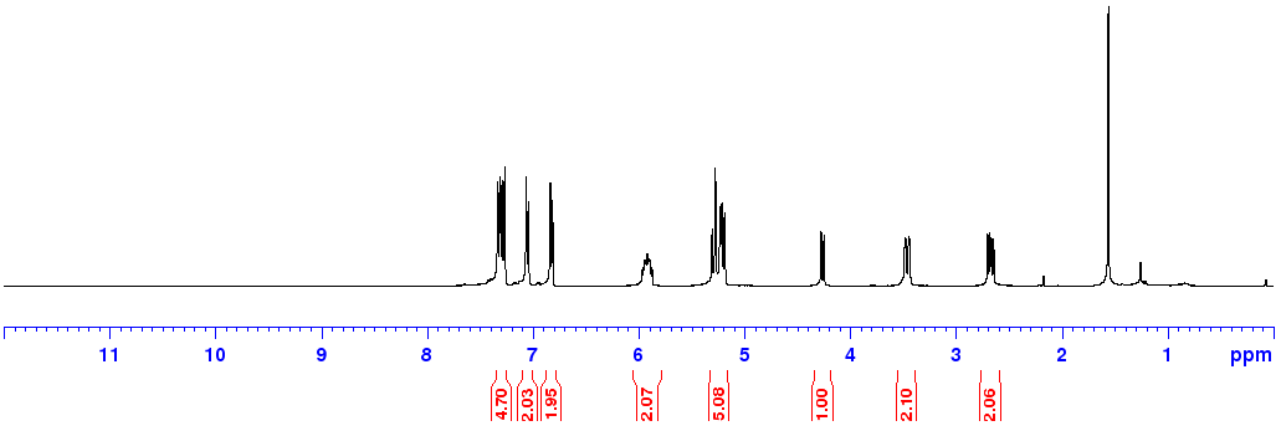

-113
-114
-115 ppm

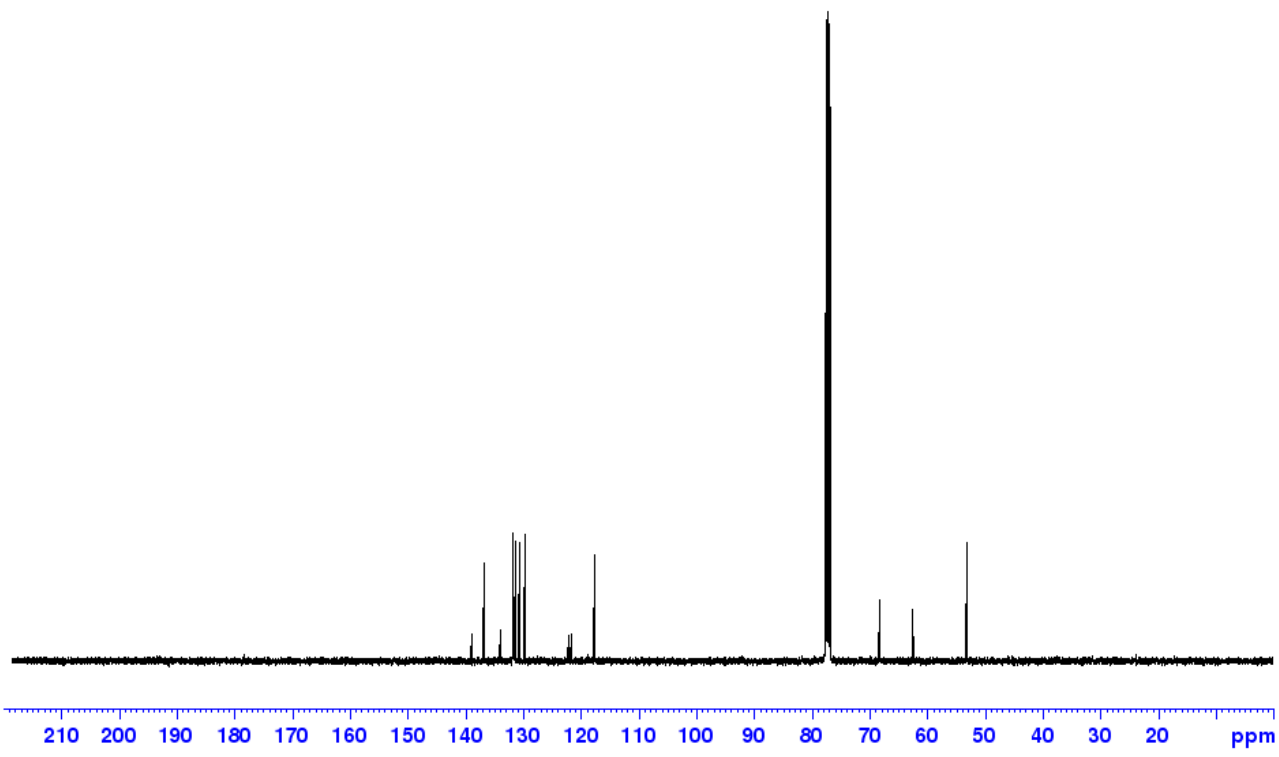

0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
1.00
1.01

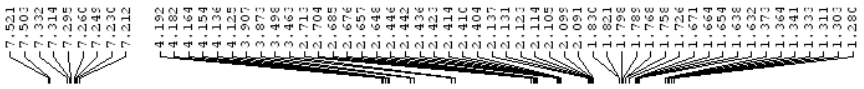

163.326
163.175
161.361
161.225
137.110
137.087
136.045
131.551
131.490
129.298
129.273
128.993
128.926
118.514
115.309
115.143
115.104
114.936
77.402
77.147
76.894
70.731
69.261
52.794
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

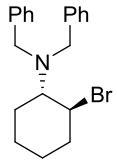

N
Cl
Br
Br

rac-**1s**

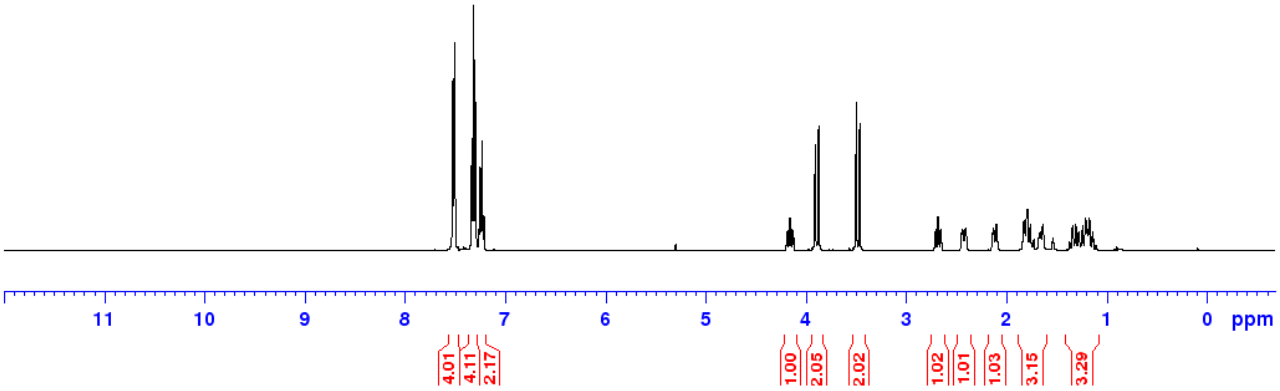

11
10
9
8
7
6
5
4
3
2
1
ppm
4.70
2.03
1.95
2.07
5.08
1.00
2.10
2.06

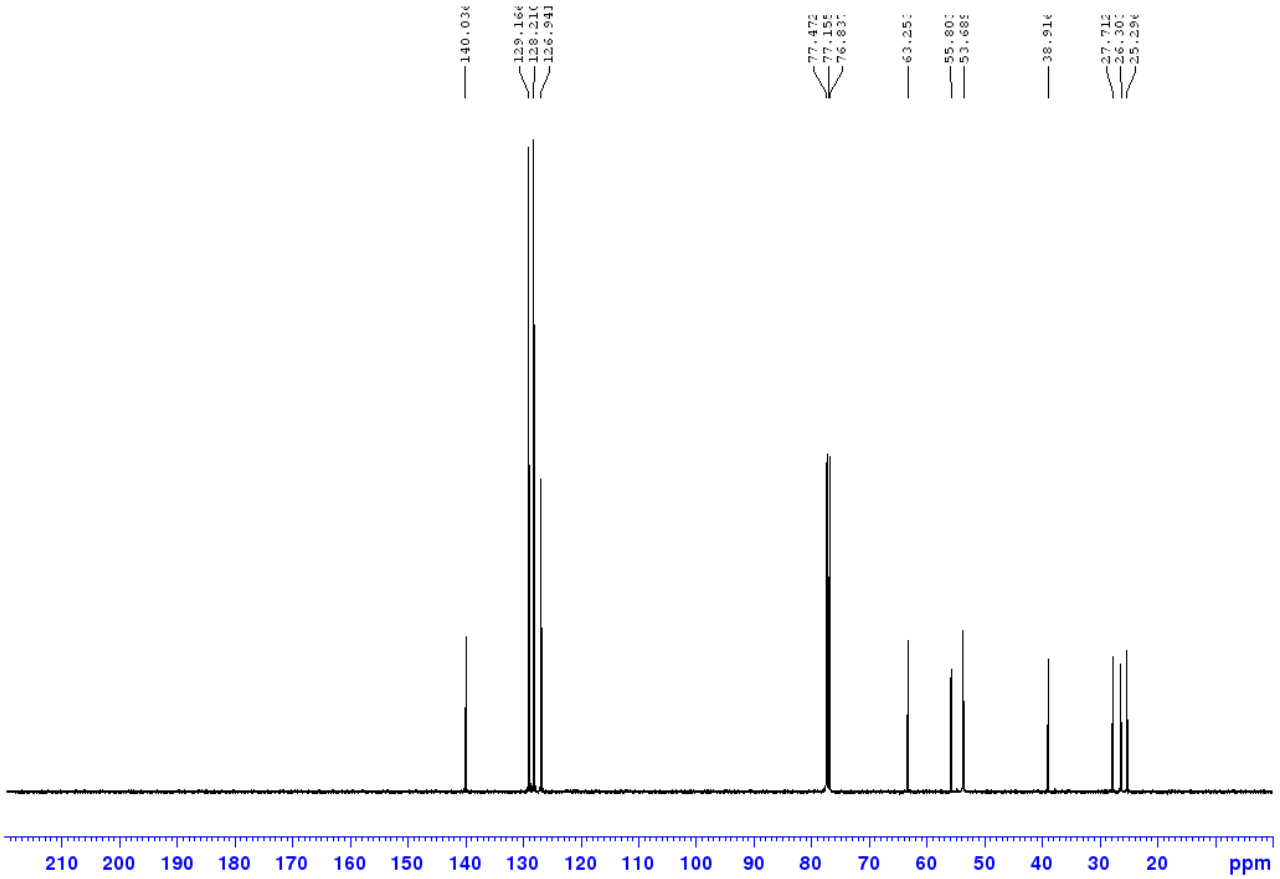

68.214
62.457
53.085
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

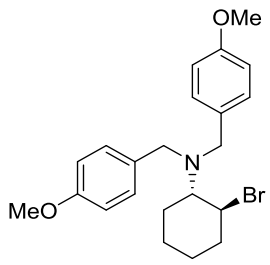



Ph
Ph
N
Br

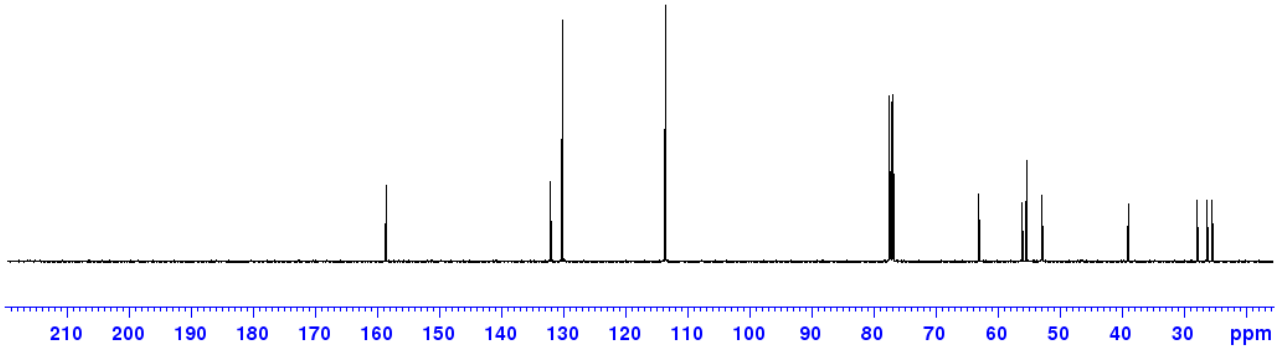
rac-**1t**

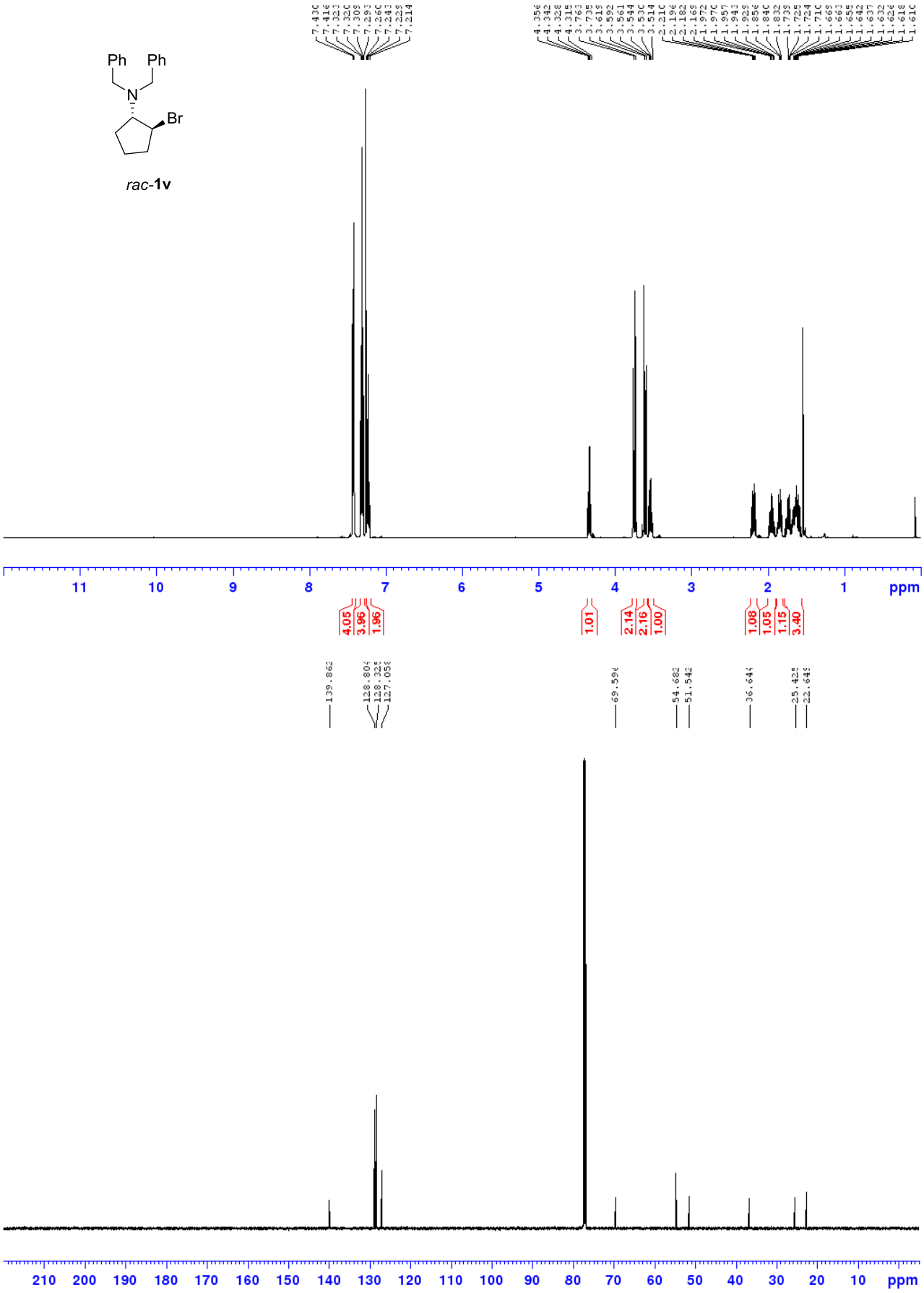

11
10
9
8
7
6
5
4
3
2
1
0
ppm
4.01
4.11
2.17
1.00
2.05
2.02
1.02
1.01
1.03
3.15
3.29


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

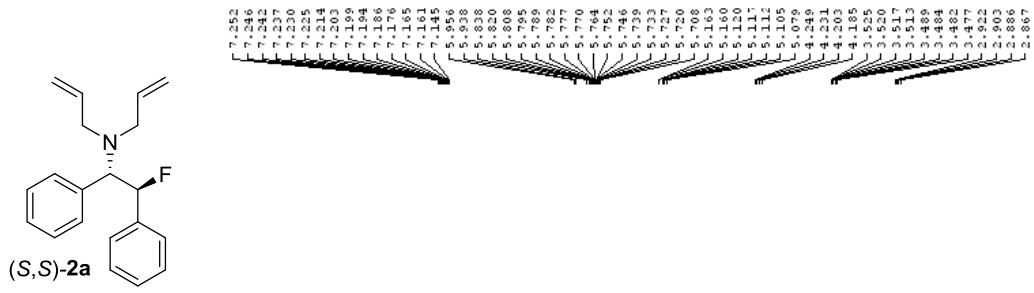


rac-**1u**

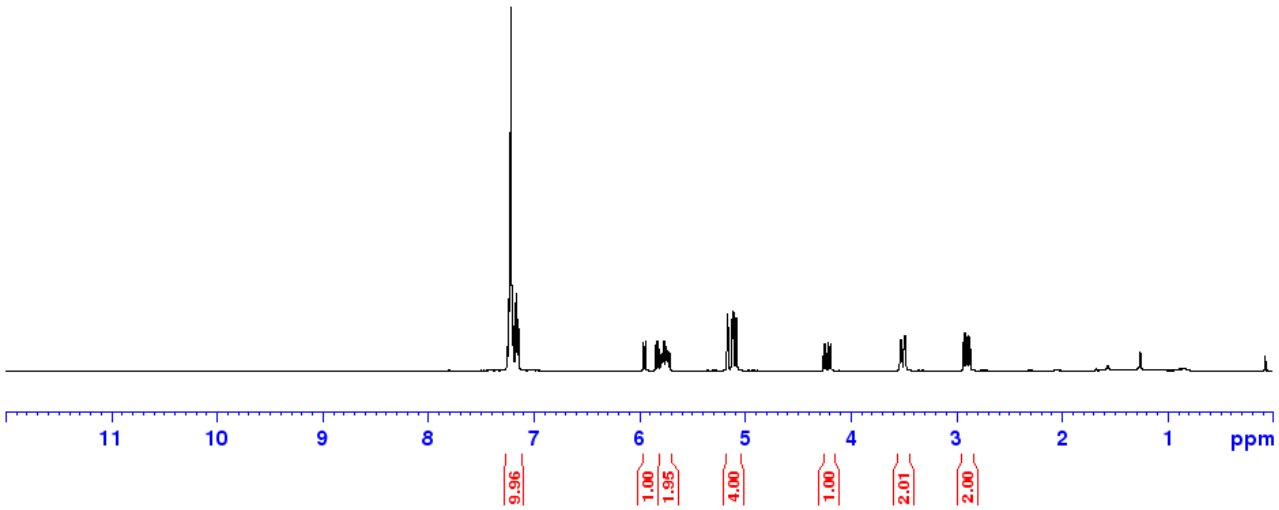


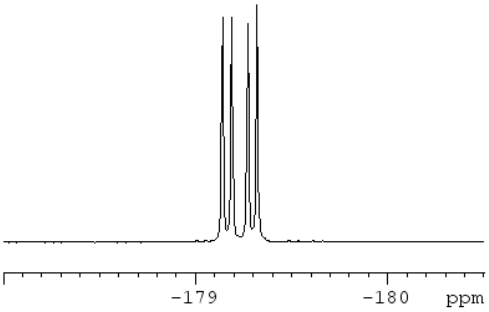

Ph
Ph
N
Br
rac-1v
ppm
ppm

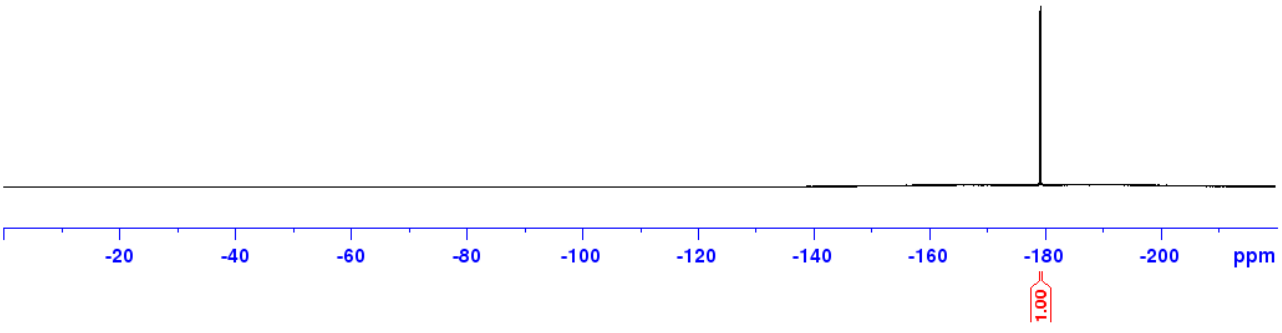
Products (fluorides)

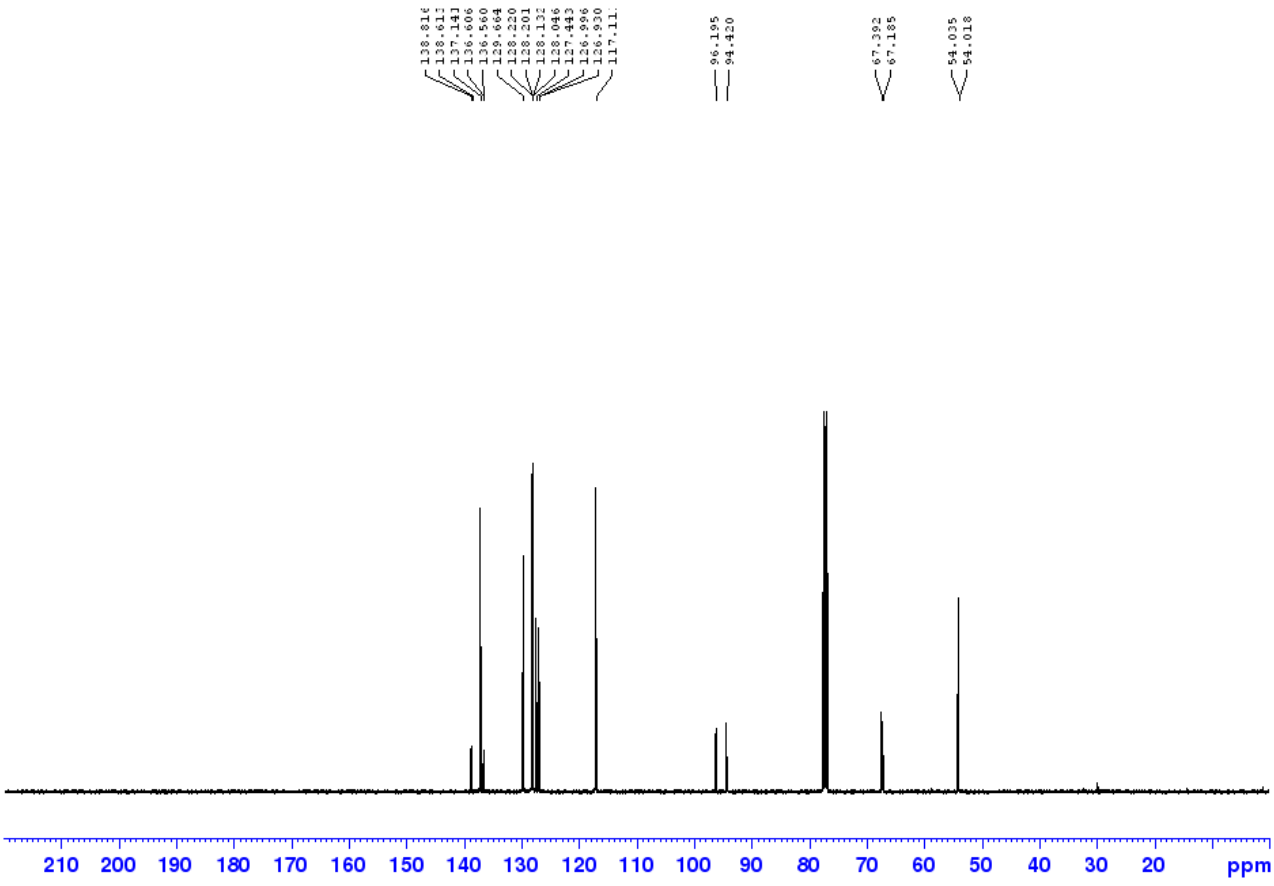


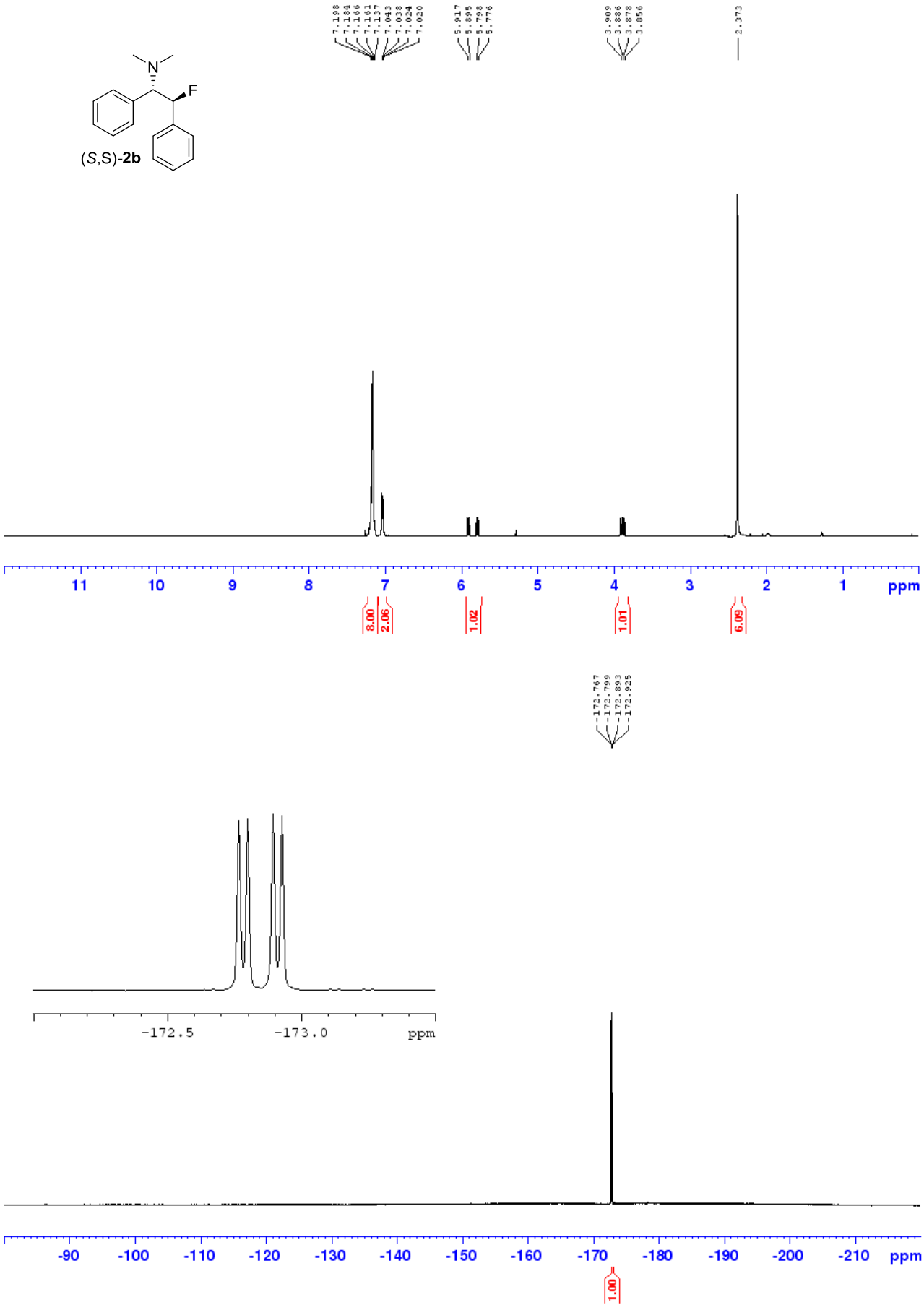
(*S*,*S*)-**2a**

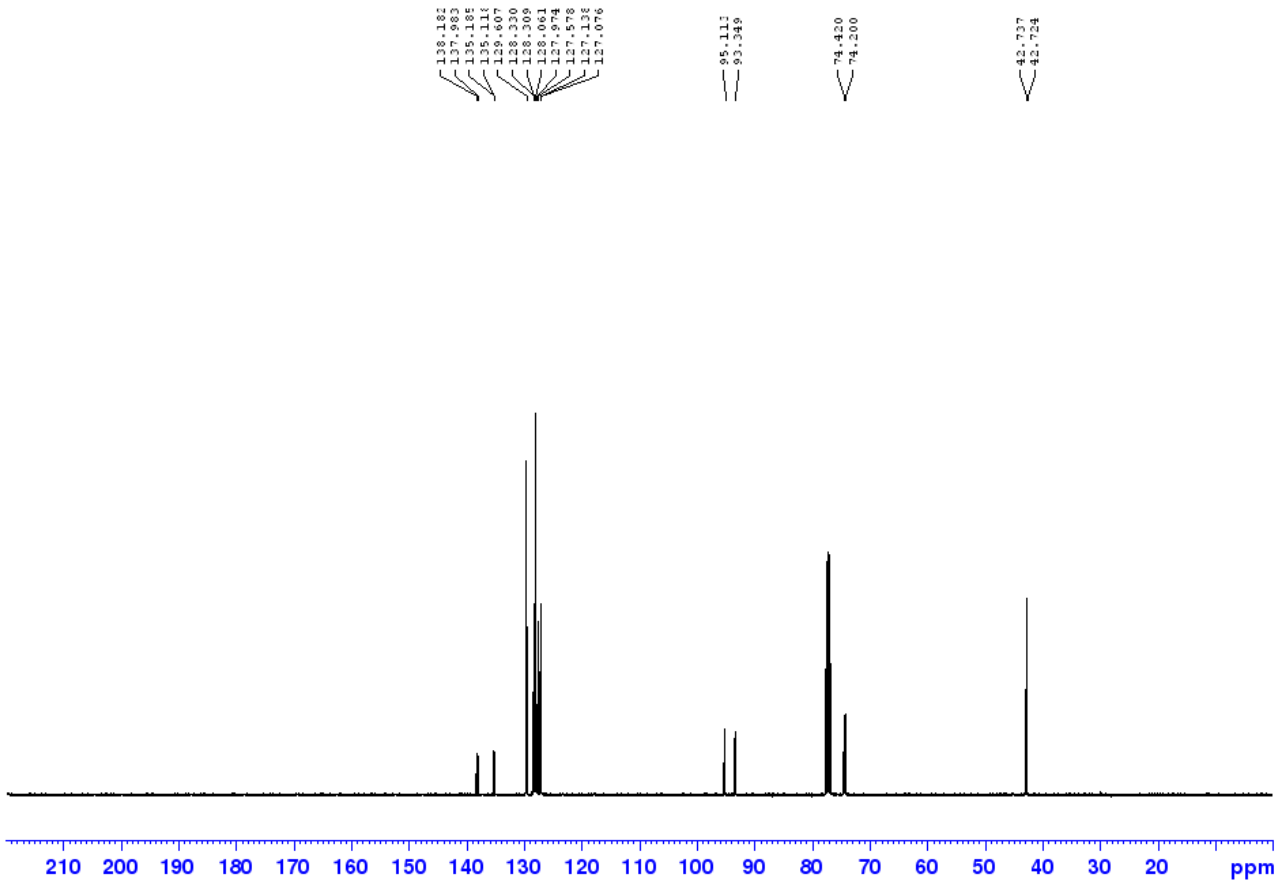


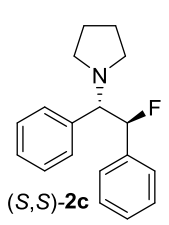





138.816
138.611
137.141
136.606
136.560
129.664
128.220
128.201
128.132
128.046
127.443
126.996
126.930
117.11
96.195
94.420
67.392
67.185
54.035
54.018
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

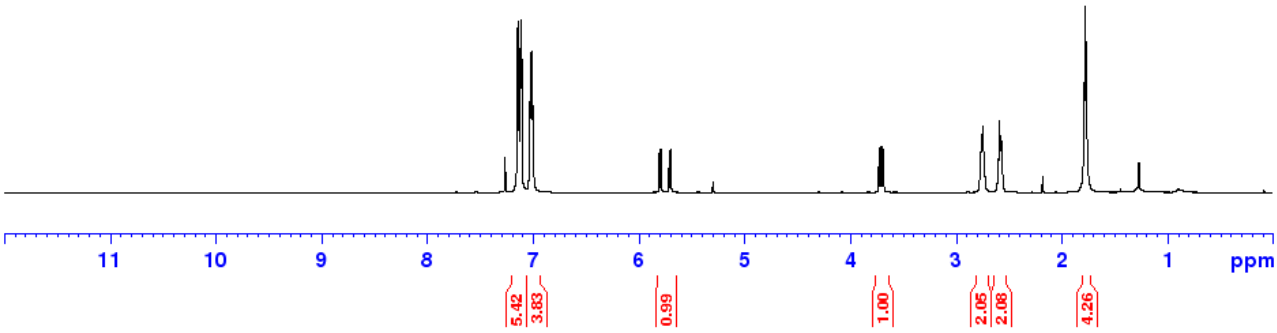

(S,S)-2b
7.198
7.184
7.166
7.161
7.137
7.043
7.038
7.024
7.020
5.917
5.895
5.798
5.776
3.909
3.886
3.878
3.856
2.373
11
10
9
8
7
6
5
4
3
2
1
ppm
8.00
2.06
1.02
1.01
6.08
-172.767
-172.799
-172.893
-172.925
-172.5
-173.0
ppm
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm
1.00


138.182
137.983
135.185
135.116
129.607
128.330
128.309
128.061
127.974
127.578
127.138
127.076
95.111
93.349
74.420
74.200
42.737
42.724
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

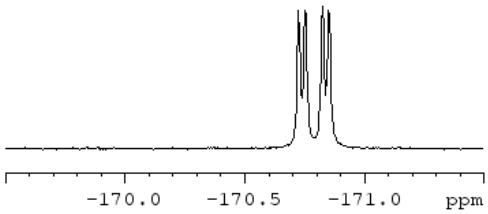

N
F

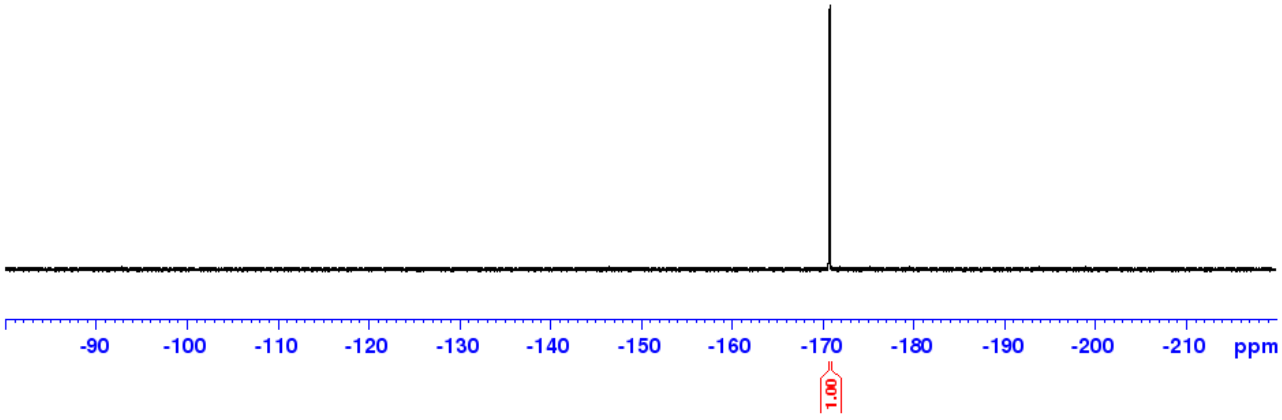
(*S*,*S*)-**2c**

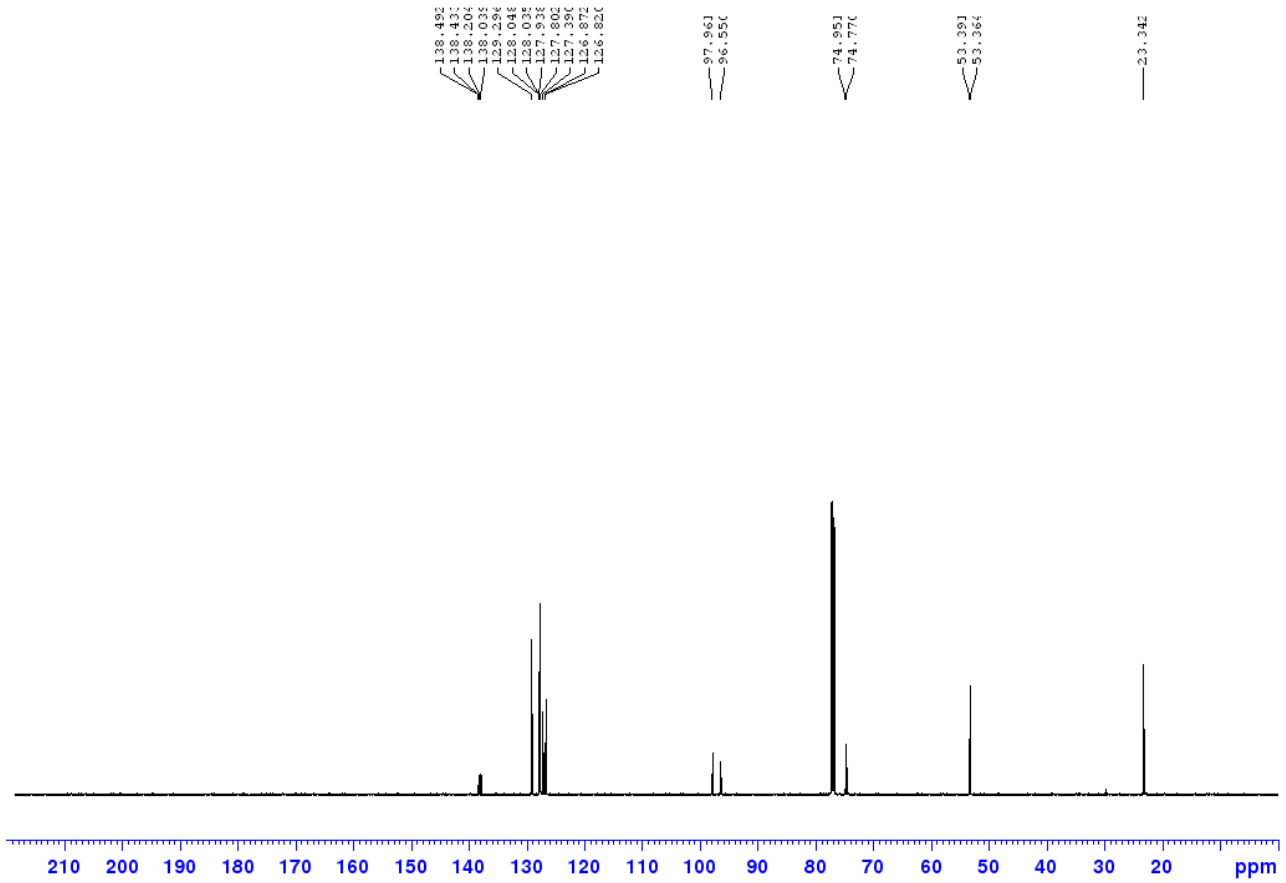

7.259
7.144
7.140
7.134
7.130
7.117
7.116
7.104
7.026
7.020
7.018
7.012
7.010
7.007
7.000
6.994
5.800
5.784
5.706
5.691
3.721
3.705
3.694
3.679
2.753
2.739
2.593
2.583
2.572
2.566
1.782
1.776
1.770
1.763
1.757

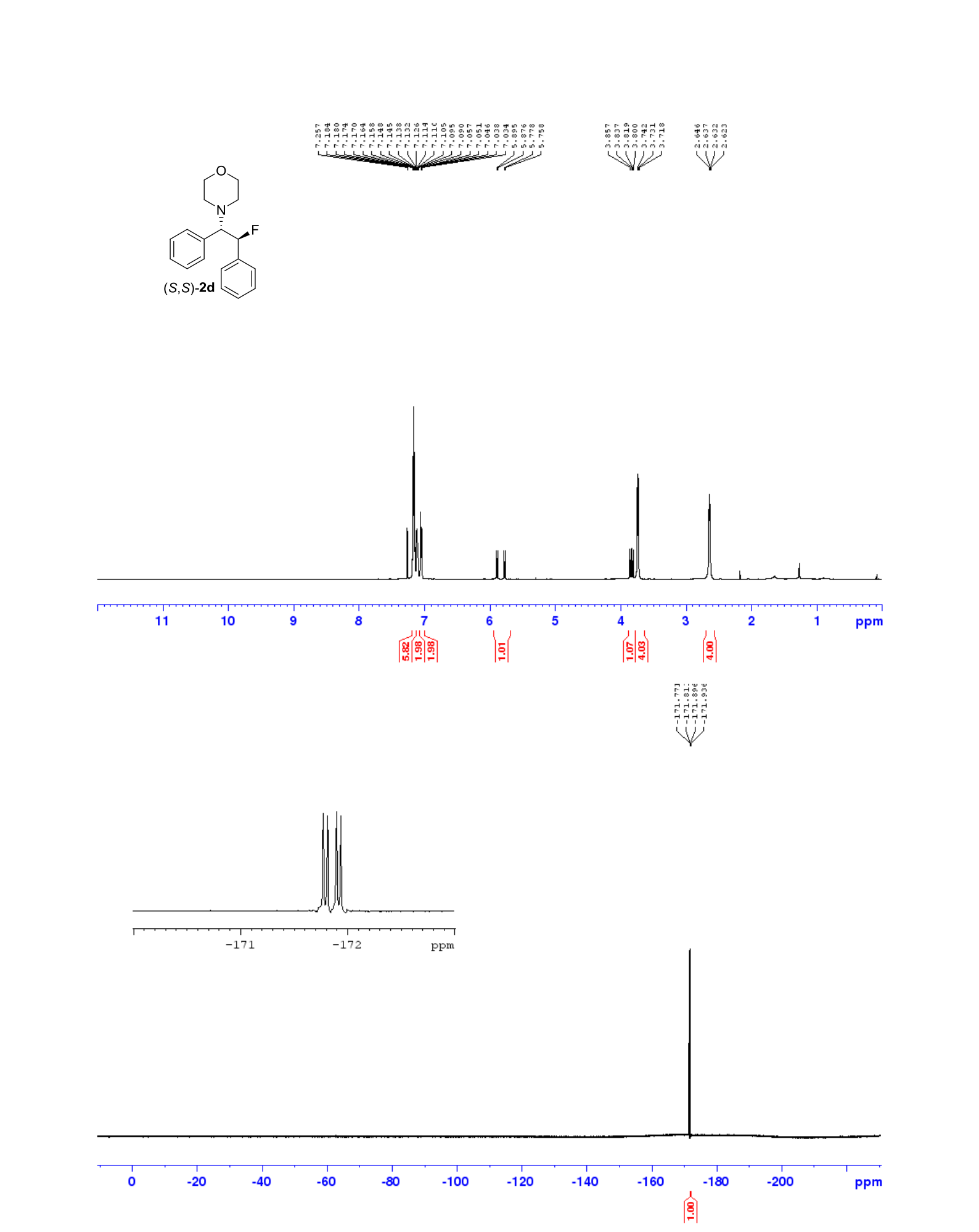

11
10
9
8
7
6
5
4
3
2
1
ppm
5.42
3.83
0.99
1.00
2.05
2.08
4.26

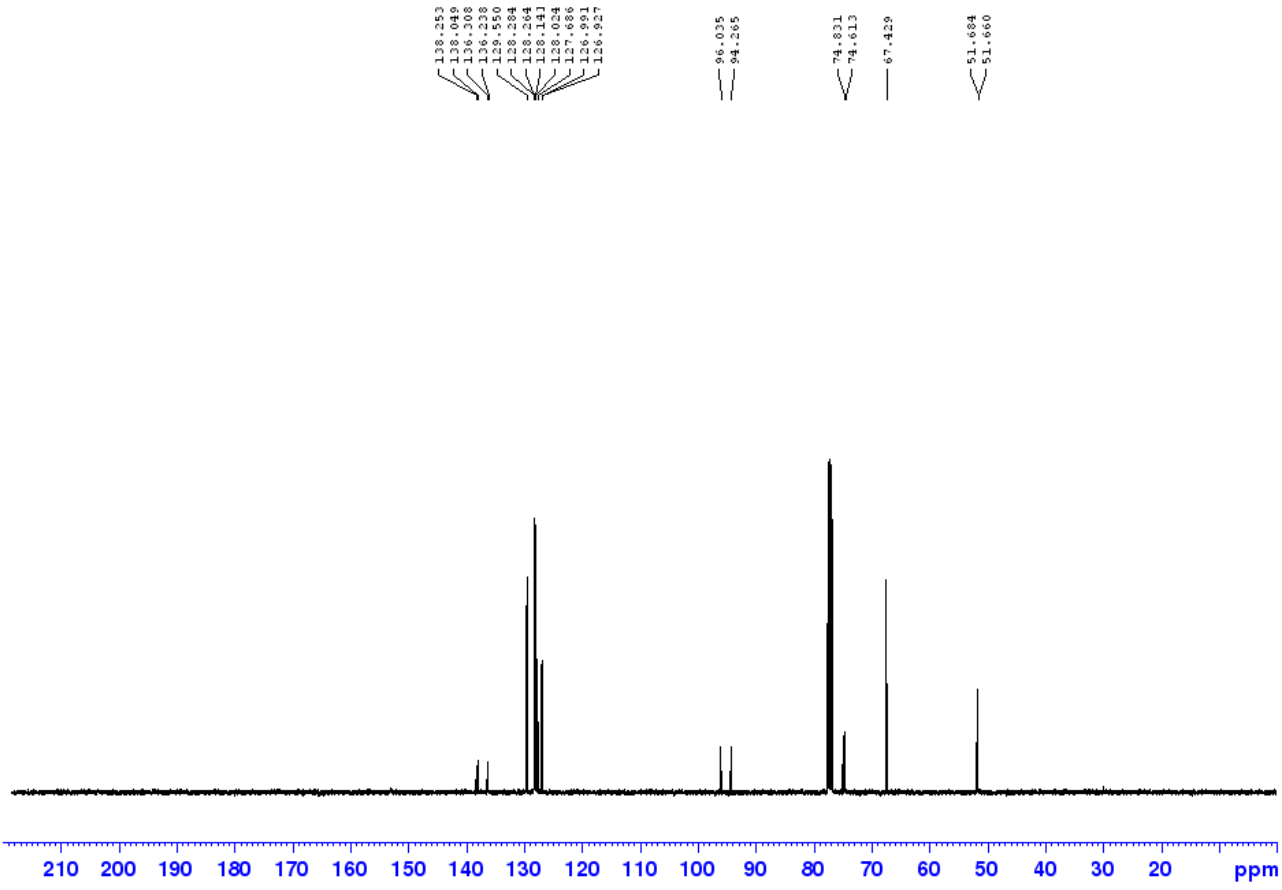

-170.728
-170.755
-170.827
-170.855

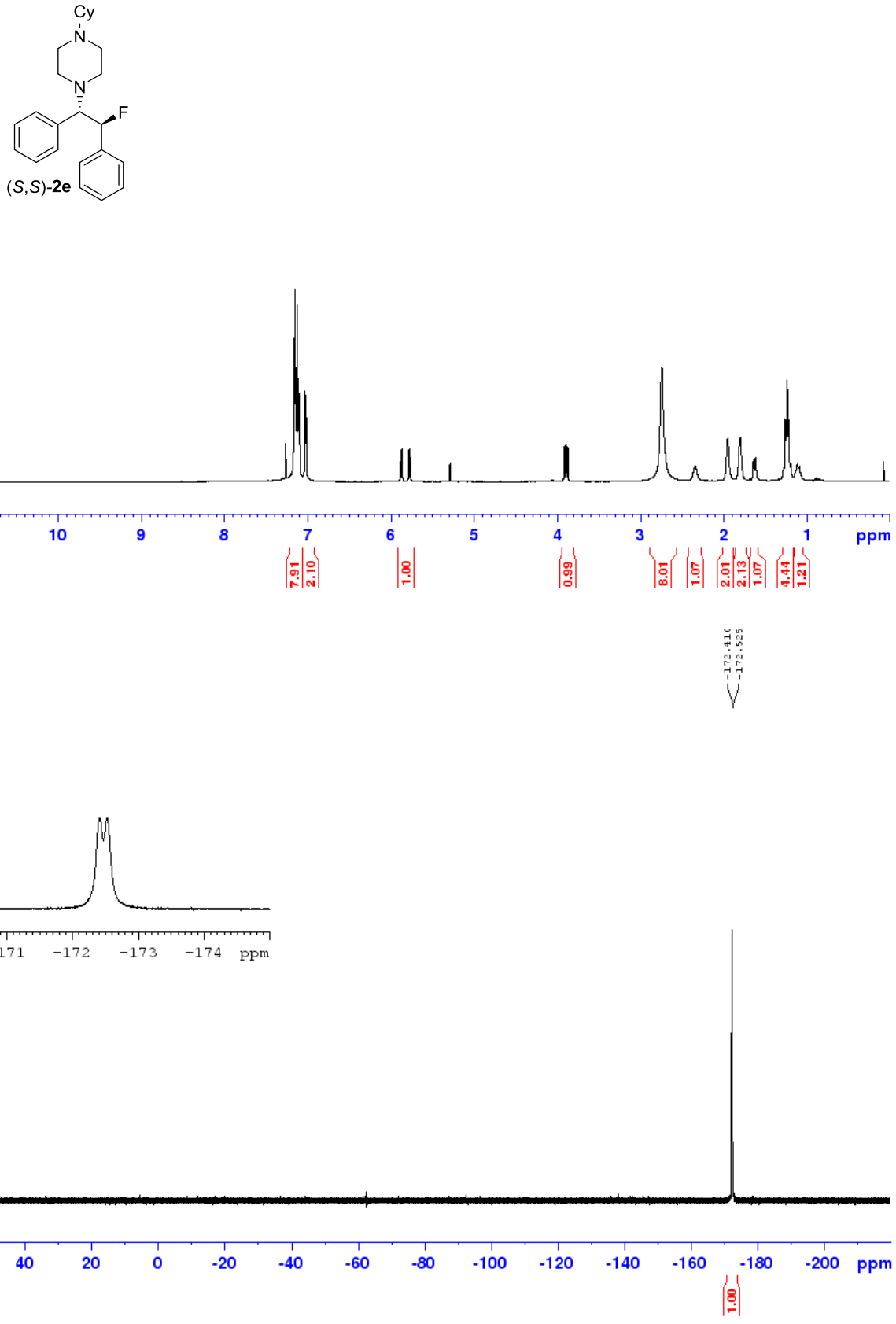

-170.0
-170.5
-171.0
ppm

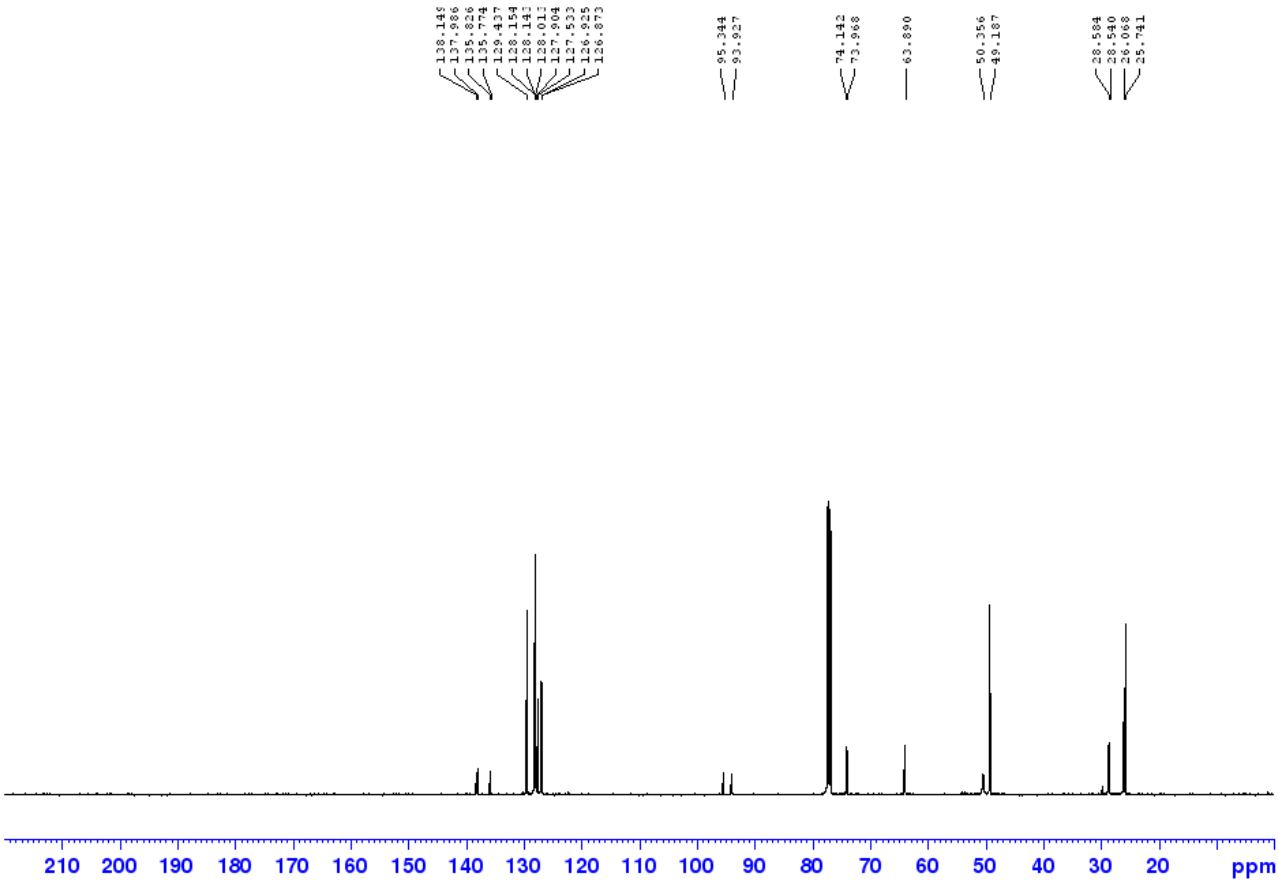

-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm
1.00

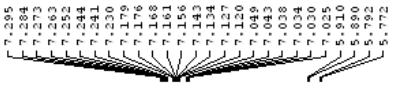

138.492
138.43
138.204
138.035
129.29
128.04
128.03
127.93
127.80
127.39
126.87
126.82
97.961
96.55
74.951
74.77
53.391
53.364
23.342
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

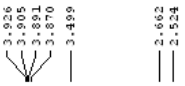

(S,S)-2d
ppm
-171
-172
ppm

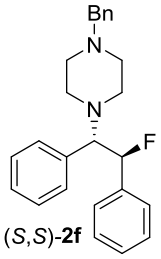

138.253
138.049
136.308
136.238
129.550
128.284
128.264
128.141
128.024
127.686
126.991
126.927
96.035
94.265
74.831
74.613
67.429
51.684
51.660
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


Cy
N
N
F
(S,S)-2e
ppm
-171
-172
-173
-174
ppm

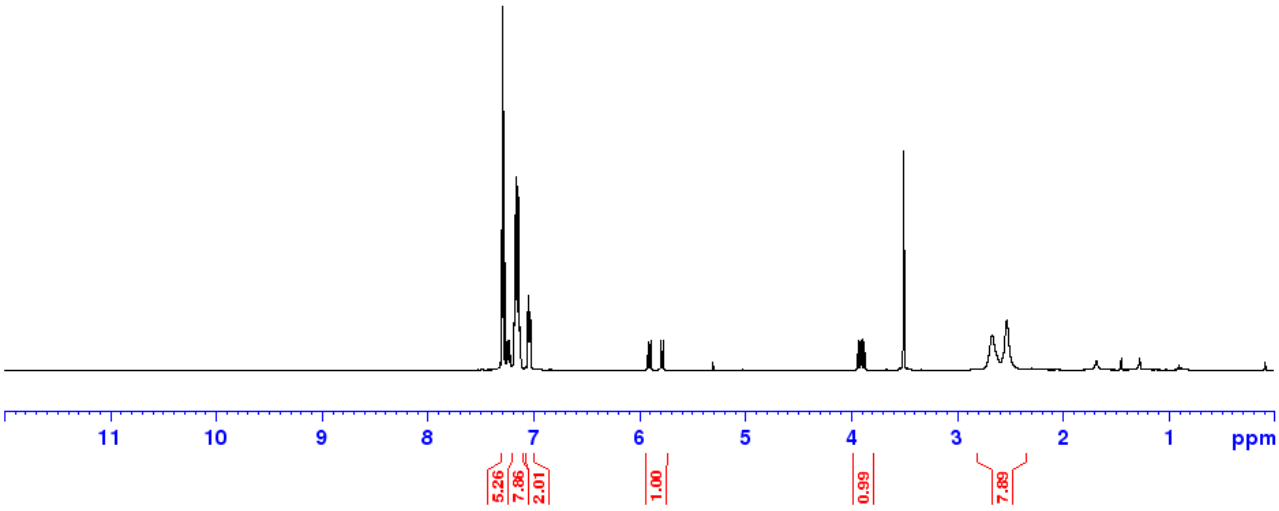

138.145
137.986
135.826
135.774
129.437
128.159
128.143
128.011
127.904
127.533
126.935
126.873
95.344
93.927
74.142
73.968
63.890
50.356
49.187
28.584
28.540
26.068
25.741
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.295
7.284
7.273
7.263
7.252
7.244
7.241
7.230
7.179
7.176
7.168
7.161
7.156
7.143
7.134
7.127
7.120
7.049
7.043
7.038
7.034
7.030
7.025
5.910
5.890
5.792
5.772

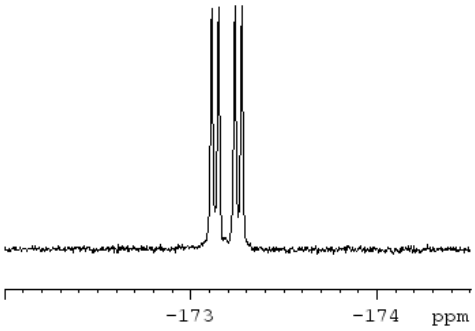

3.926
3.905
3.891
3.870
3.499
2.662
2.524

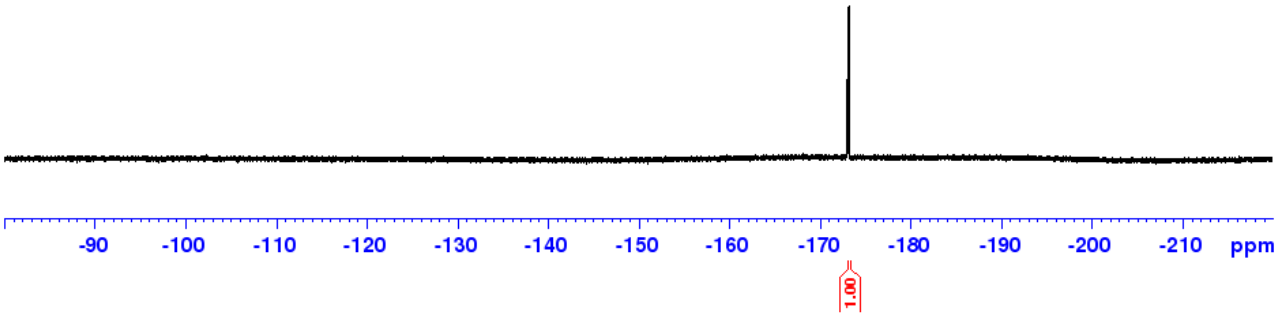

Bn
N
N
F

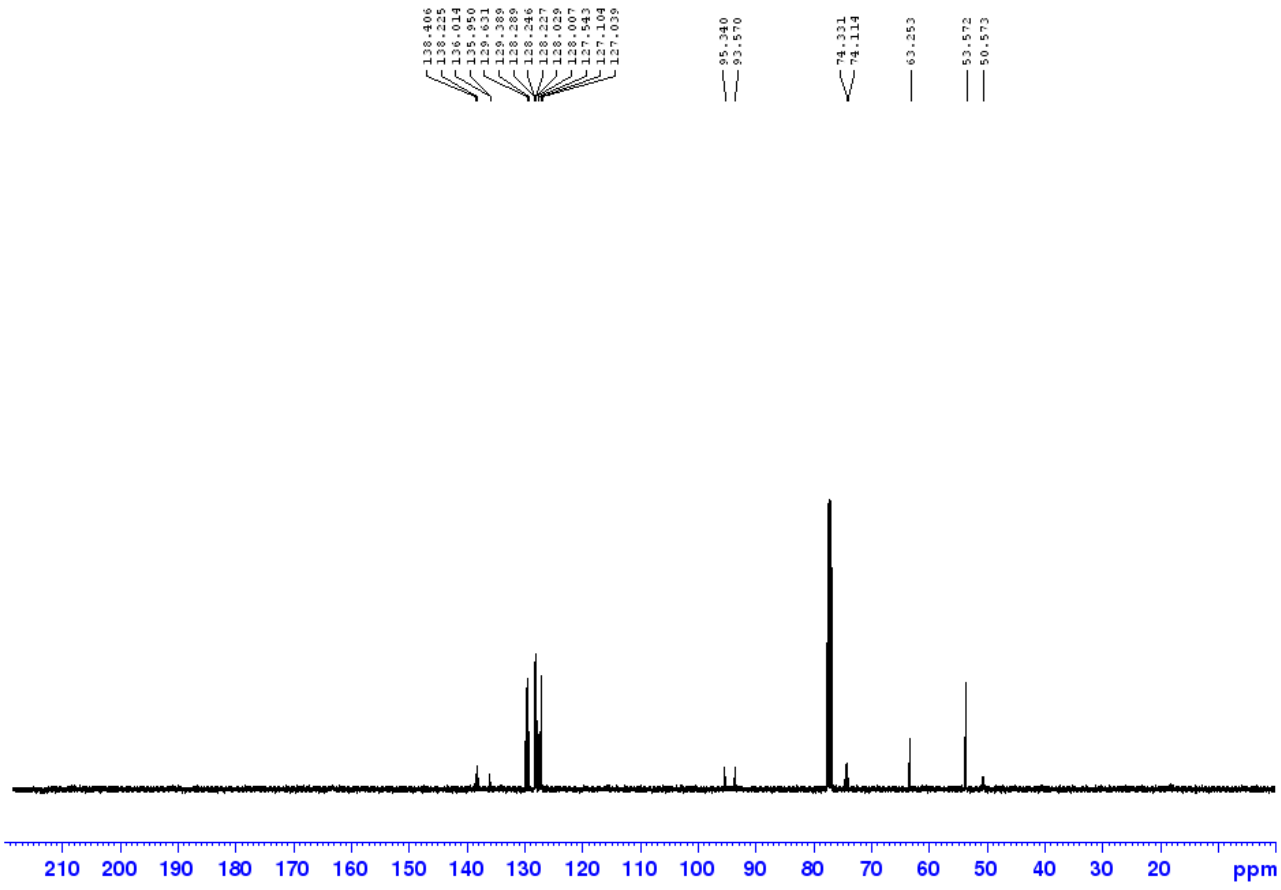
(*S*,*S*)-**2f**

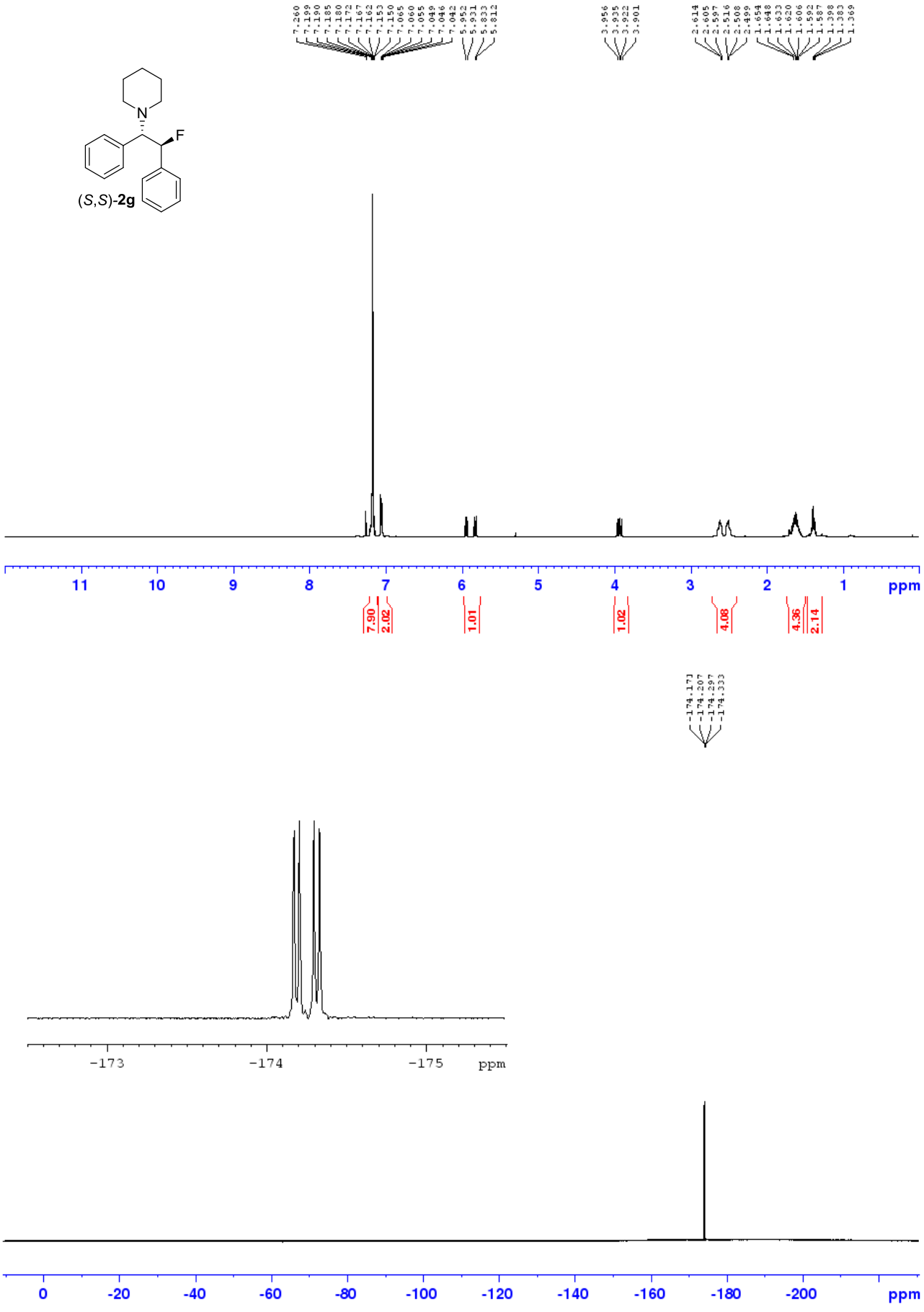

11
10
9
8
7
6
5
4
3
2
1
ppm
5.26
7.86
2.01
1.00
0.99
7.89

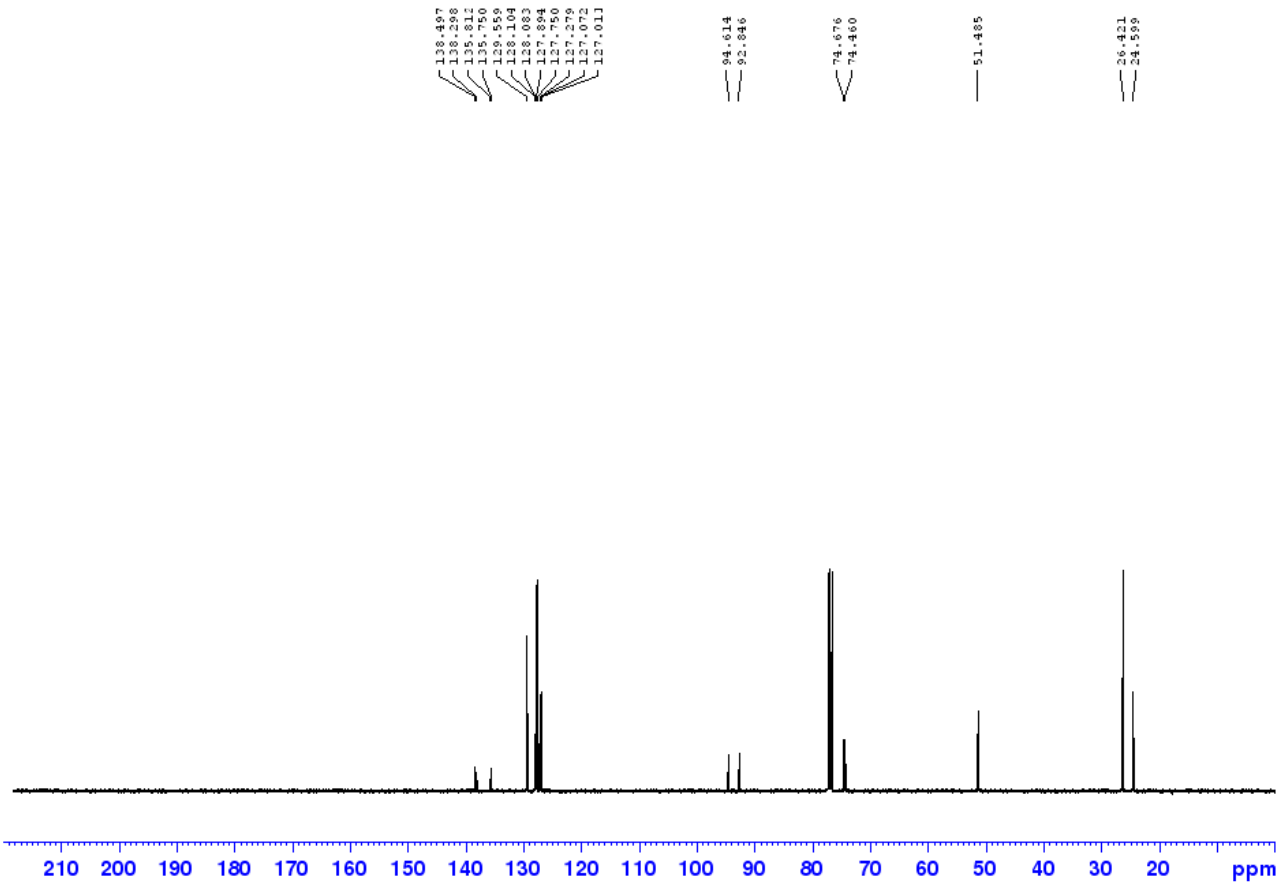

-173.111
-173.148
-173.236
-173.273

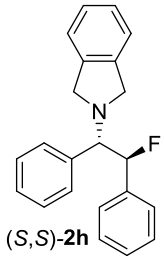

-173
-174
ppm


-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm
1.00


138.406
138.225
136.014
135.950
129.631
129.389
128.289
128.246
128.227
128.029
128.007
127.543
127.104
127.039
95.340
93.570
74.331
74.114
63.253
53.572
50.573
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

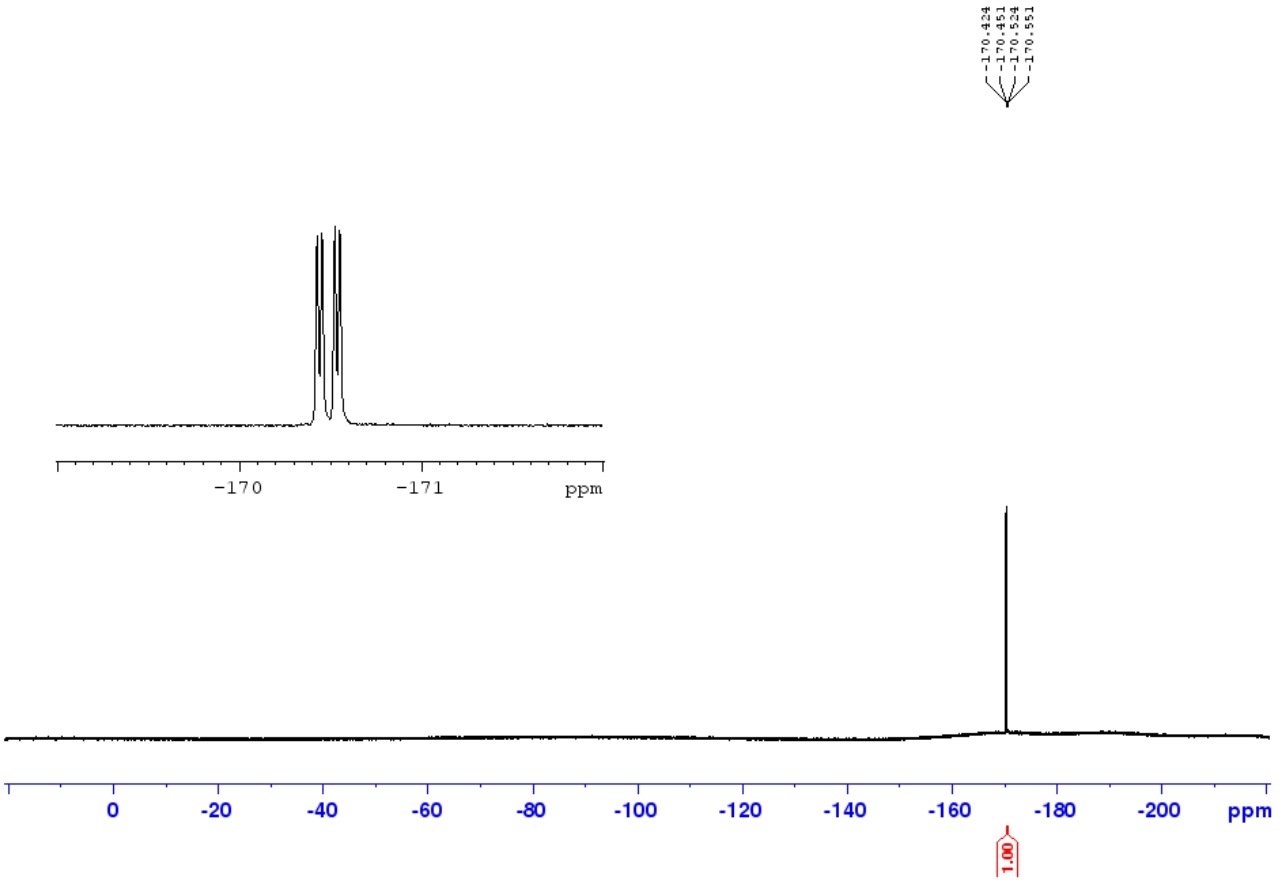

(S,S)-2g
F
N
ppm
-173
-174
-175
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

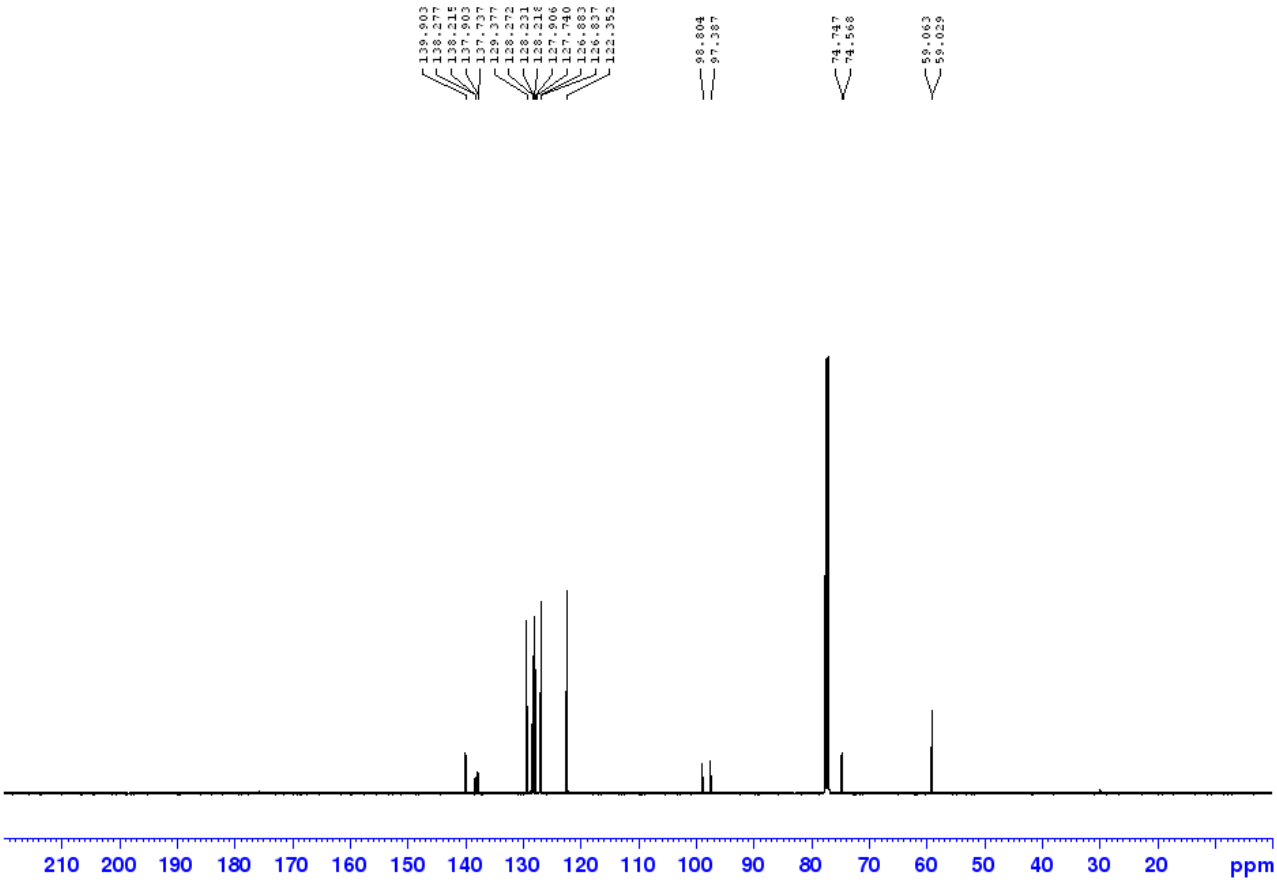

138.497
138.298
135.811
135.750
129.559
128.104
128.083
127.894
127.750
127.279
127.072
127.011
94.614
92.846
74.676
74.460
51.485
26.421
24.599
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

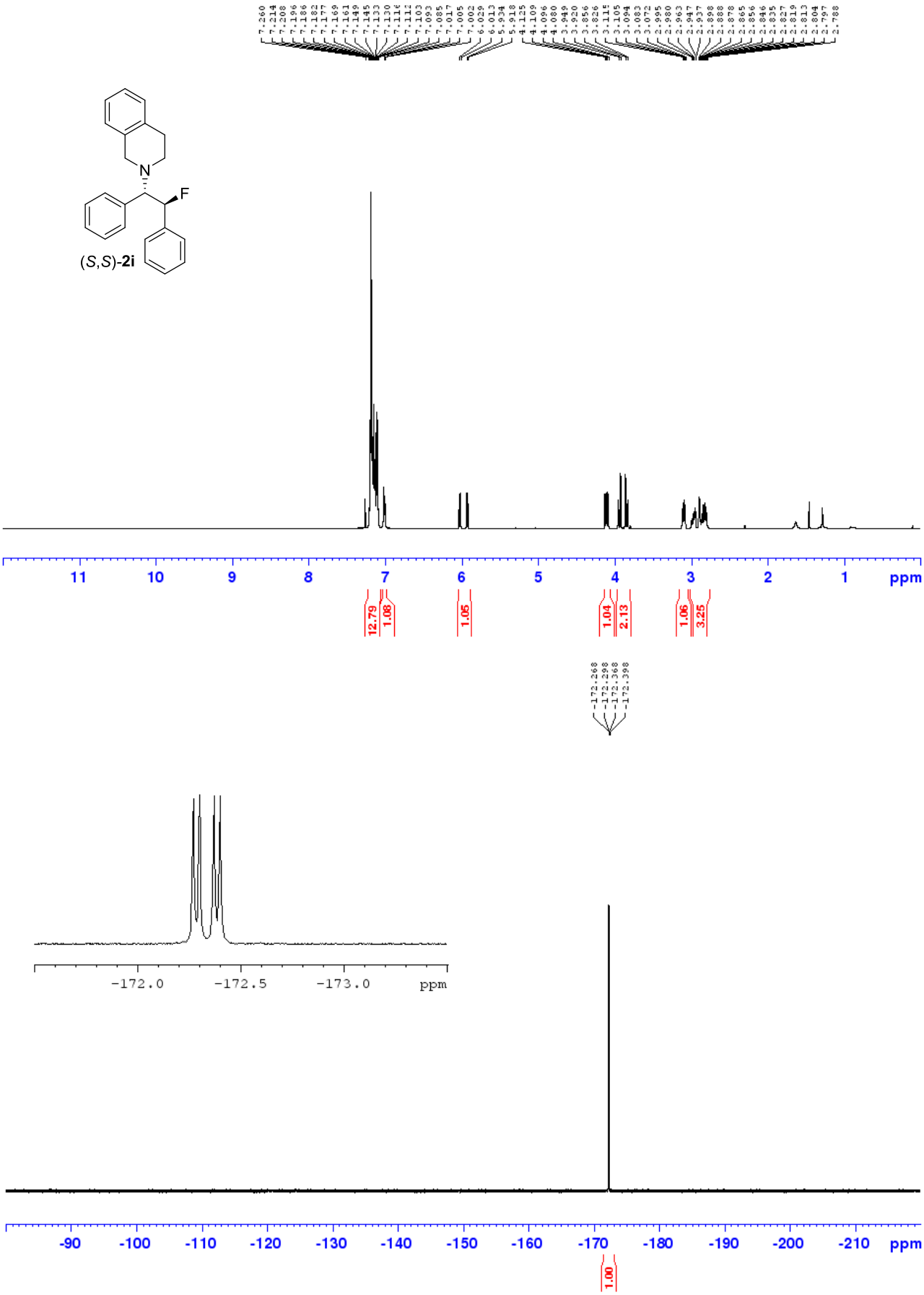

N
F

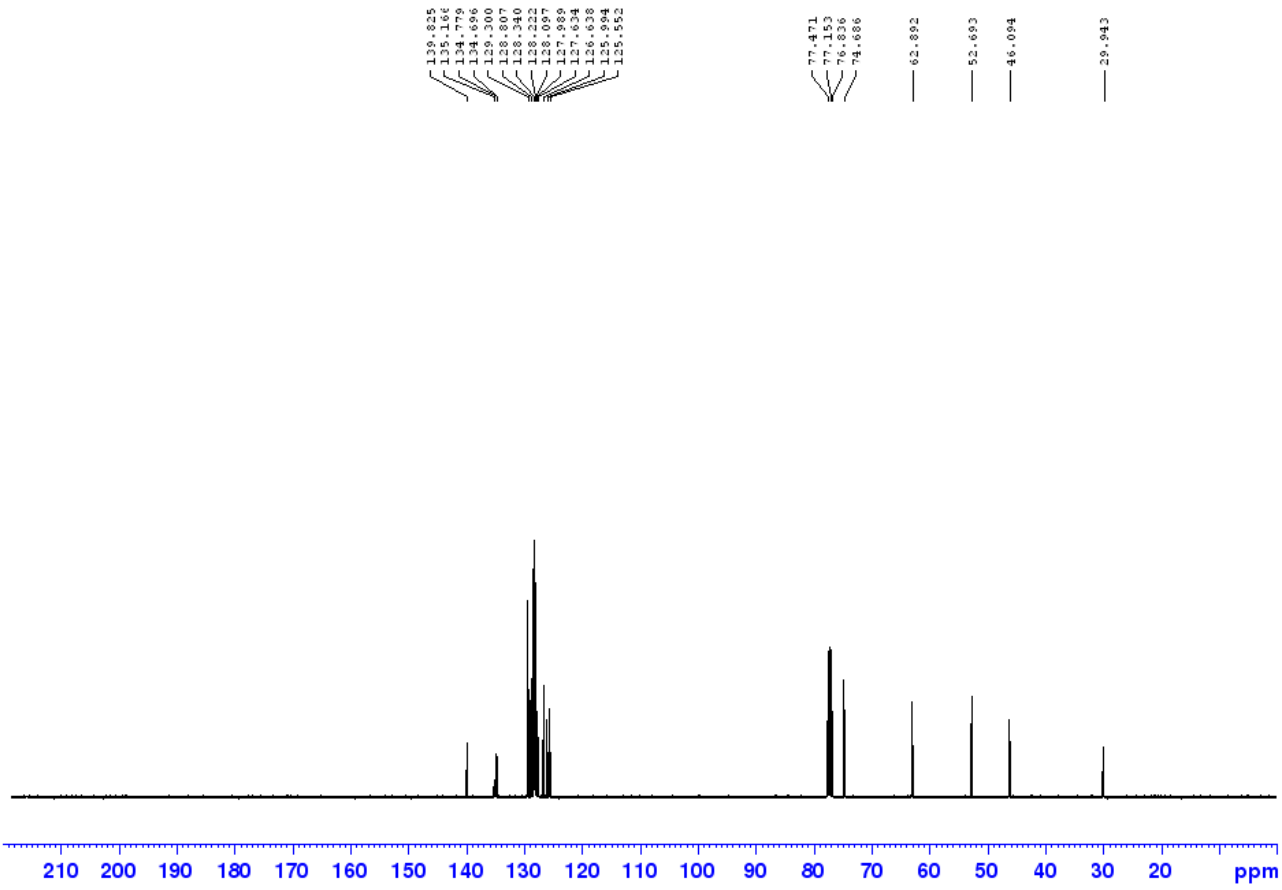
(*S*,*S*)-**2h**

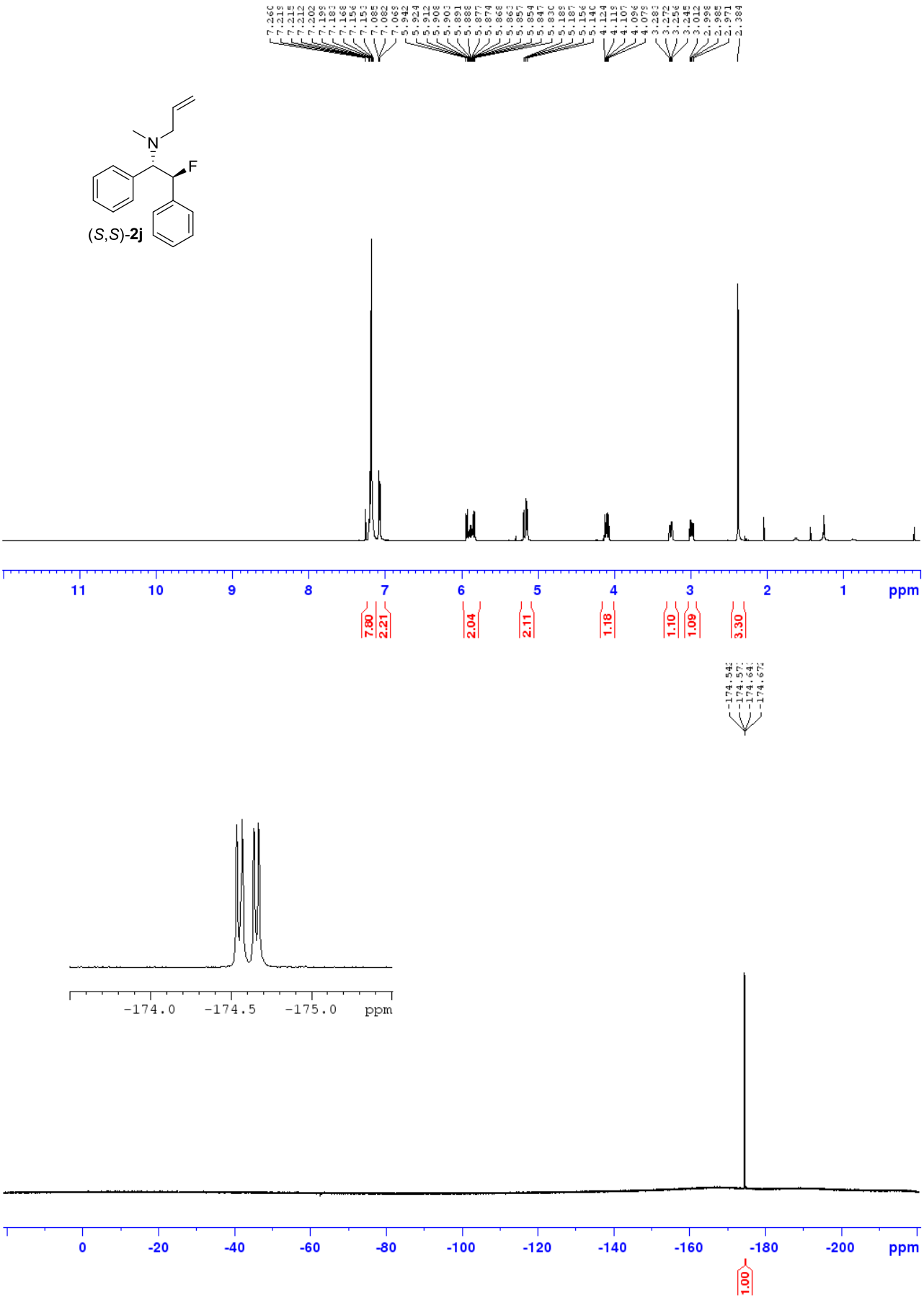
7.190
7.176
7.173
7.165
7.162
7.160
7.152
7.102
7.098
7.091
7.083
7.036
7.023
7.019
5.843
5.828
5.749
5.734
4.154
4.150
4.131
4.127
4.088
4.073
4.062
4.046
4.040
4.015
11
10
9
8
7
6
5
4
3
2
1
ppm
9.14
1.93
1.94
1.00
2.01
3.05

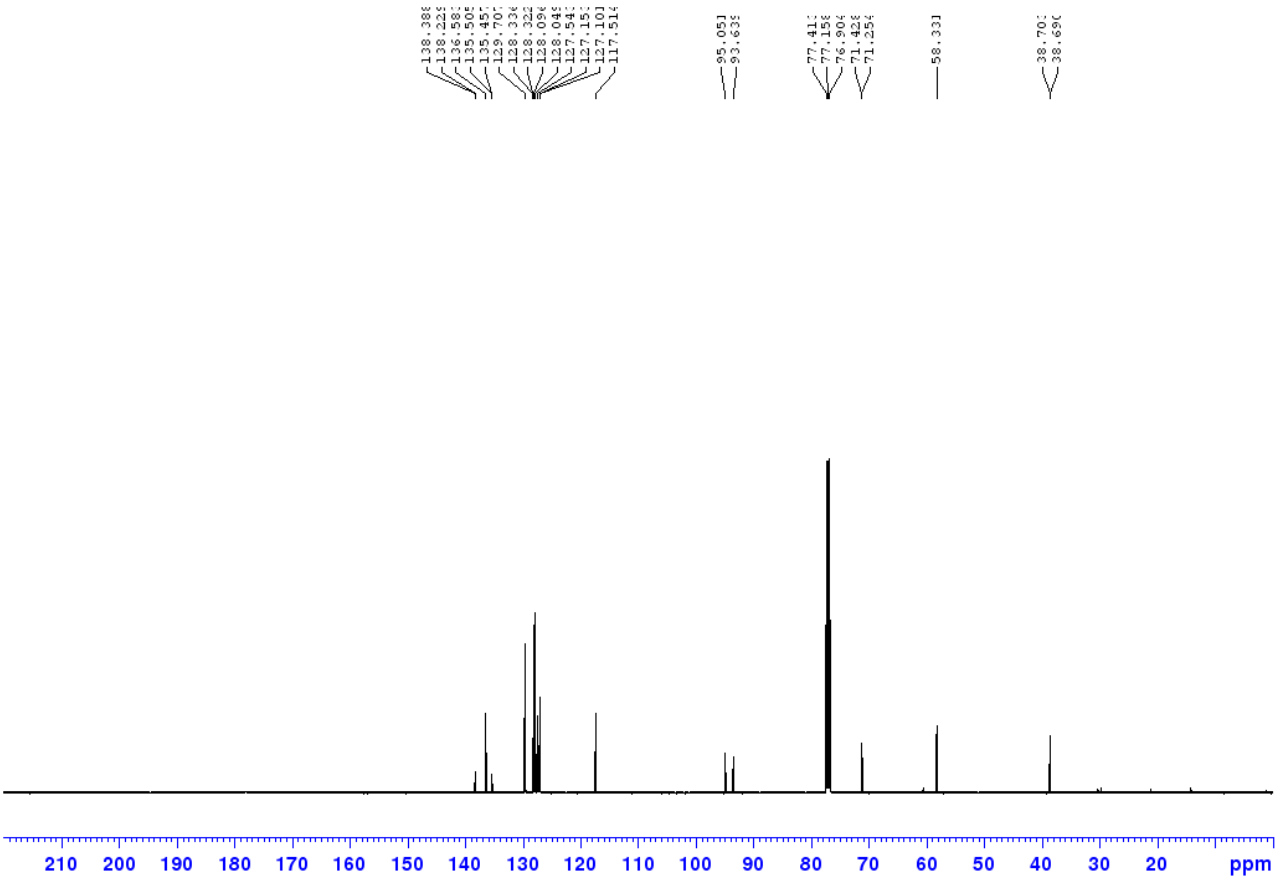

-170.424
-170.451
-170.524
-170.551
-170
-171
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00

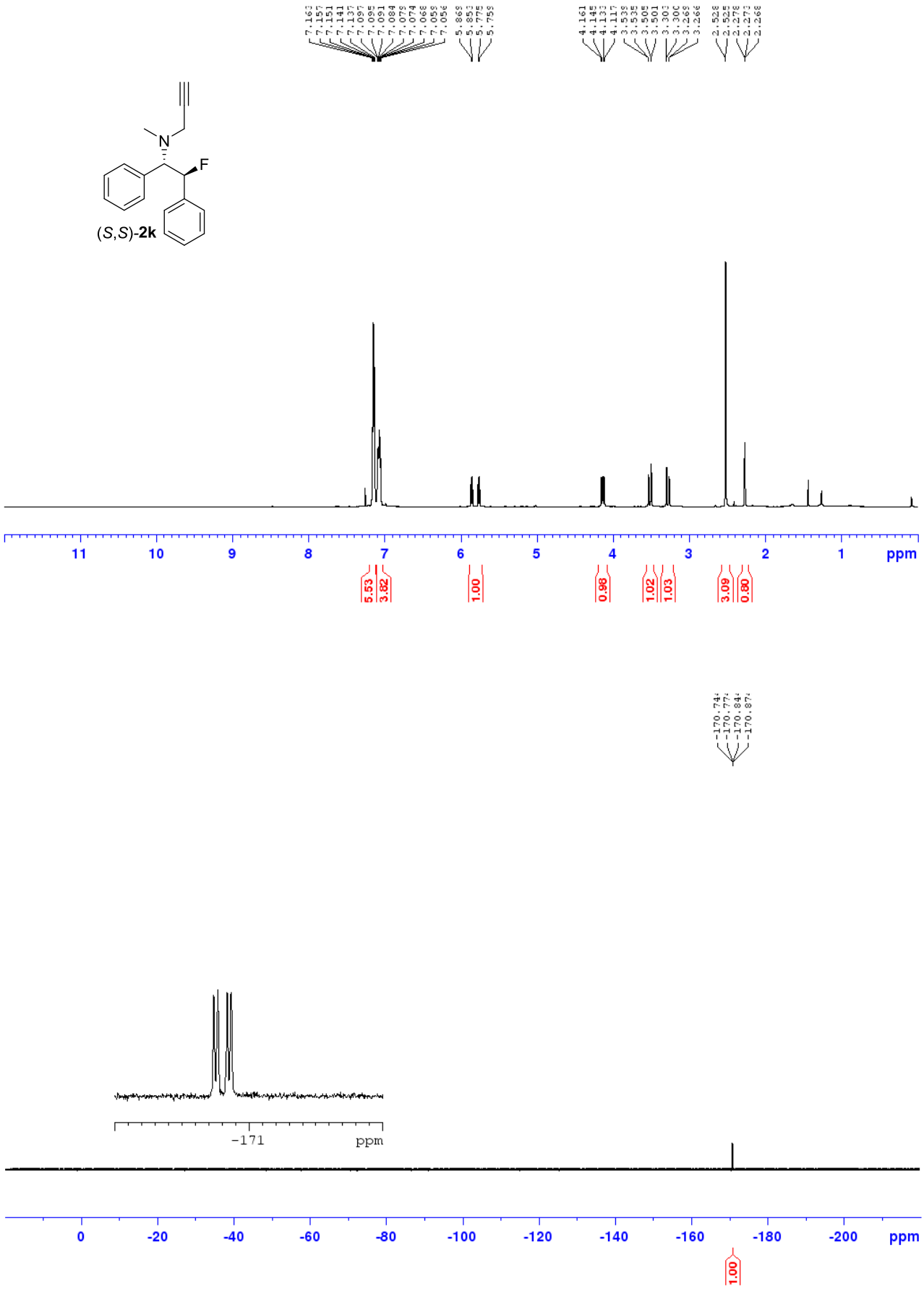

139.903
138.277
138.215
137.903
137.737
129.377
128.272
128.231
128.218
127.906
127.740
126.883
126.837
122.352
98.804
97.387
74.747
74.568
59.063
59.029
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

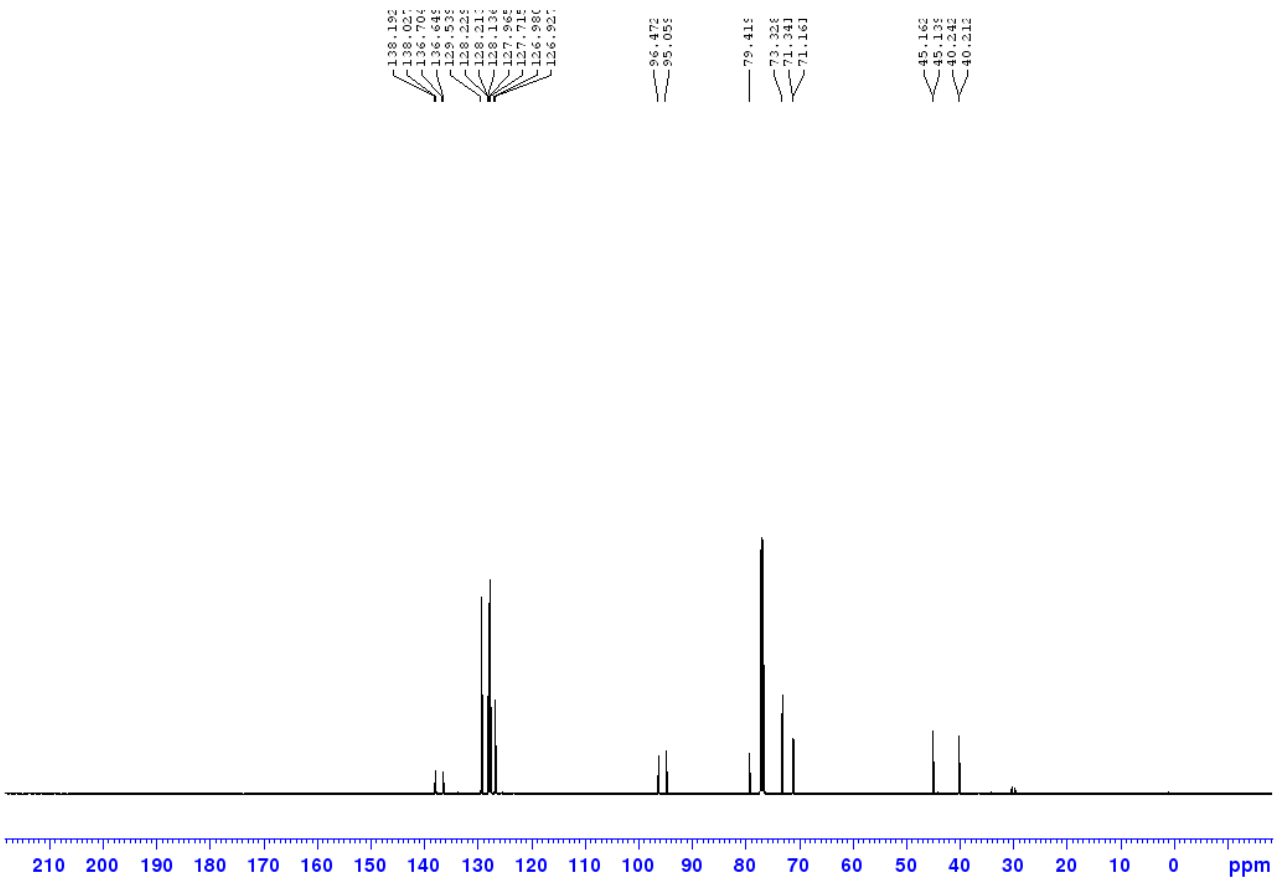

(S,S)-2i
N
F
ppm
-172.0
-172.5
-173.0
ppm

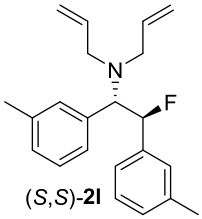

139.825
135.166
134.779
134.696
129.300
128.807
128.340
128.222
128.097
127.989
127.634
126.638
125.994
125.552
77.471
77.153
76.836
74.686
62.892
52.693
46.094
29.943
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


(S,S)-2j
11
10
9
8
7
6
5
4
3
2
1
ppm
7.80
2.21
2.04
2.11
1.18
1.10
1.09
3.30
-174.0
-174.5
-175.0
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00

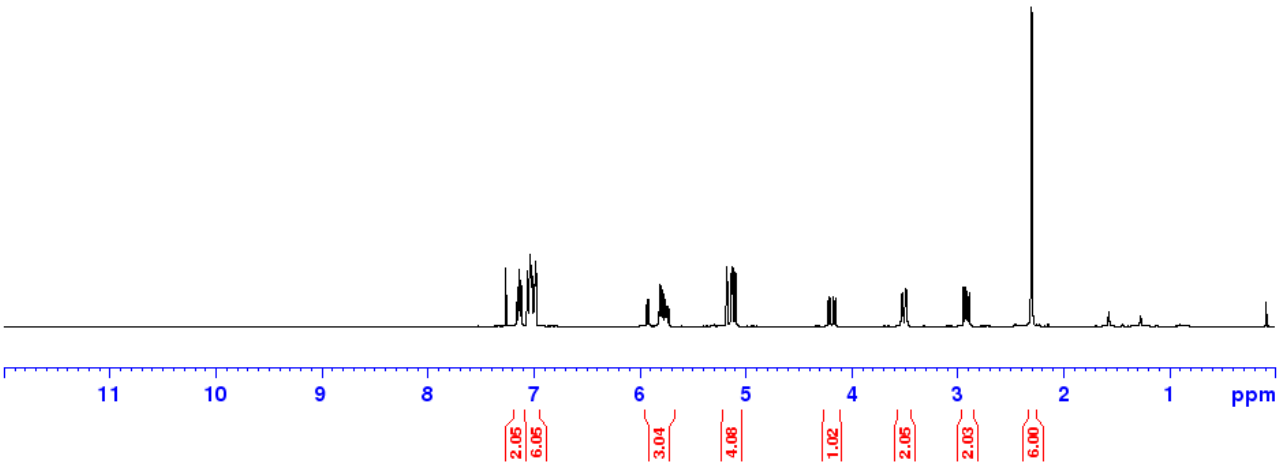

138.388
138.225
136.583
135.505
135.457
129.707
128.336
128.322
128.059
128.043
127.541
127.153
127.101
117.514
95.053
93.638
77.411
77.158
76.904
71.428
71.254
58.333
38.703
38.690
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

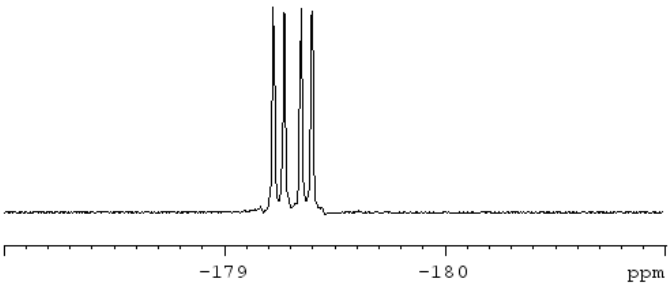

(S,S)-2k
11
10
9
8
7
6
5
4
3
2
1
ppm
5.53
3.82
1.00
0.98
1.02
1.03
3.09
0.80
-171
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00

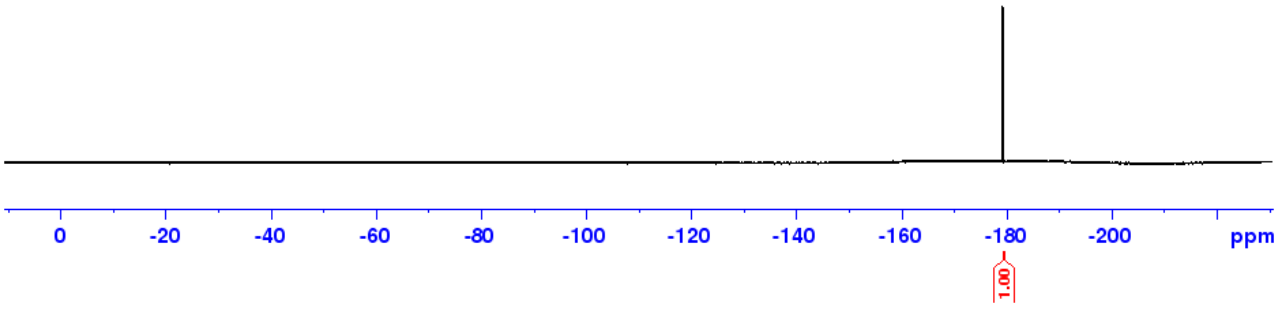

138.192
138.027
136.704
136.644
129.535
128.225
128.211
128.136
127.965
127.715
126.980
126.927
96.472
95.055
79.415
73.328
71.343
71.163
45.162
45.135
40.242
40.212
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

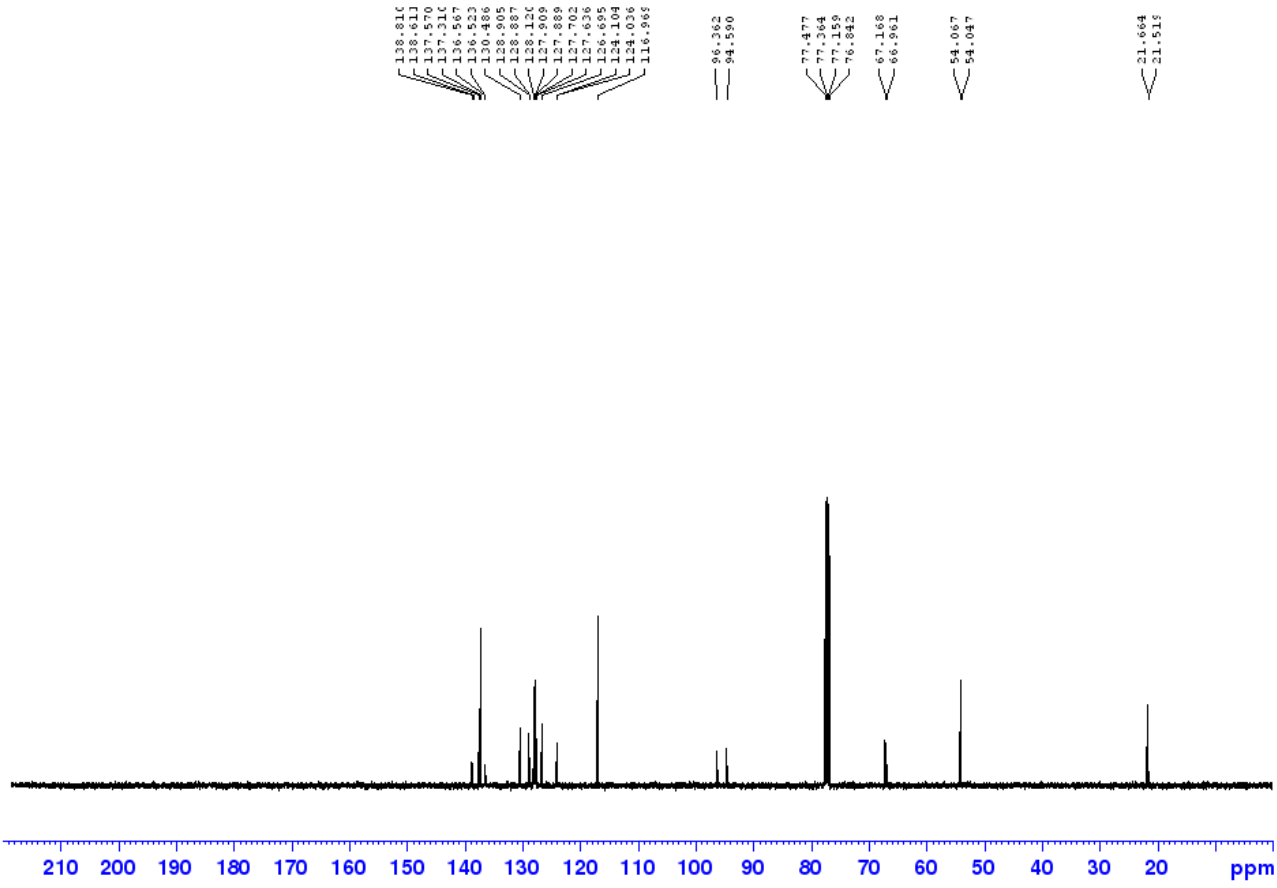

N
F

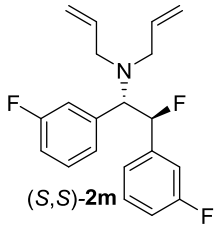
(*S*,*S*)-**2l**

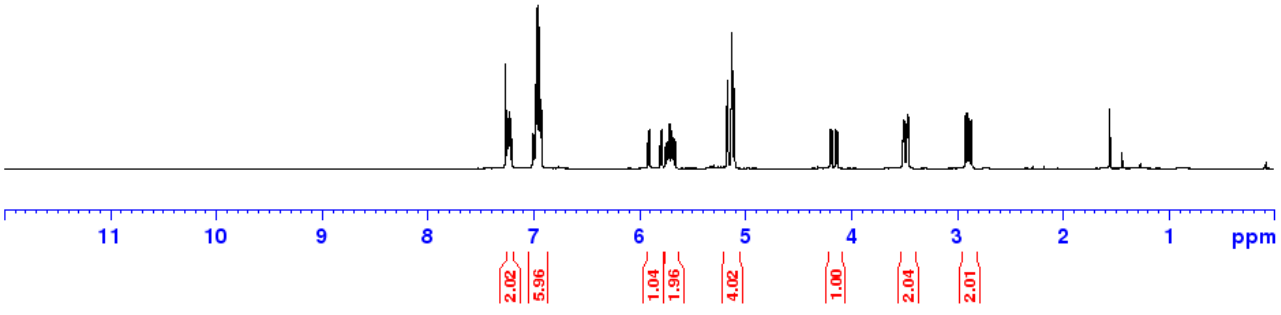

11
10
9
8
7
6
5
4
3
2
1
ppm
2.05
6.05
3.04
4.08
1.02
2.05
2.03
6.00

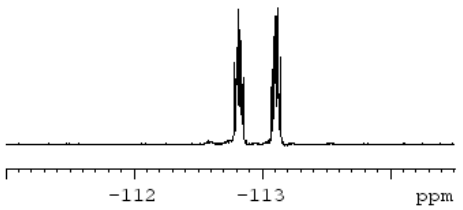

-179
-180
ppm

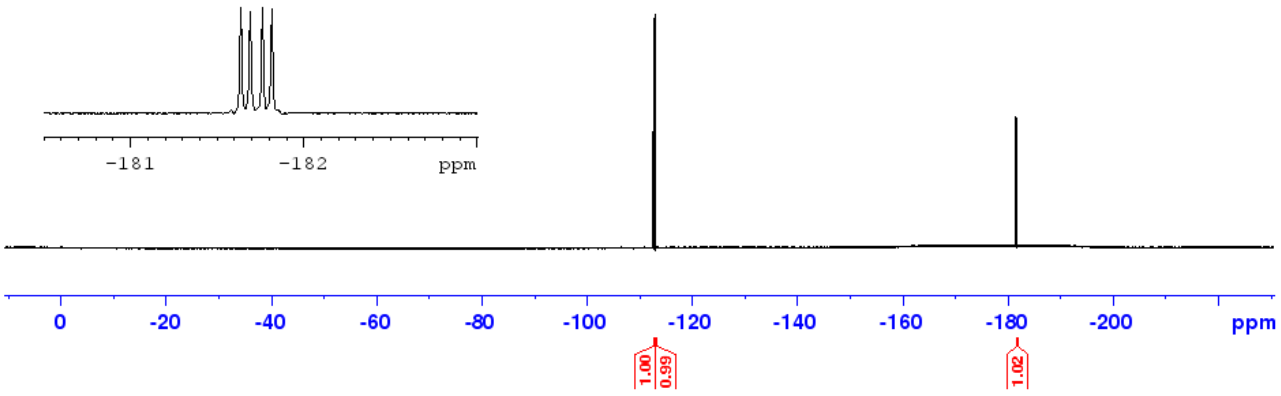

0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00

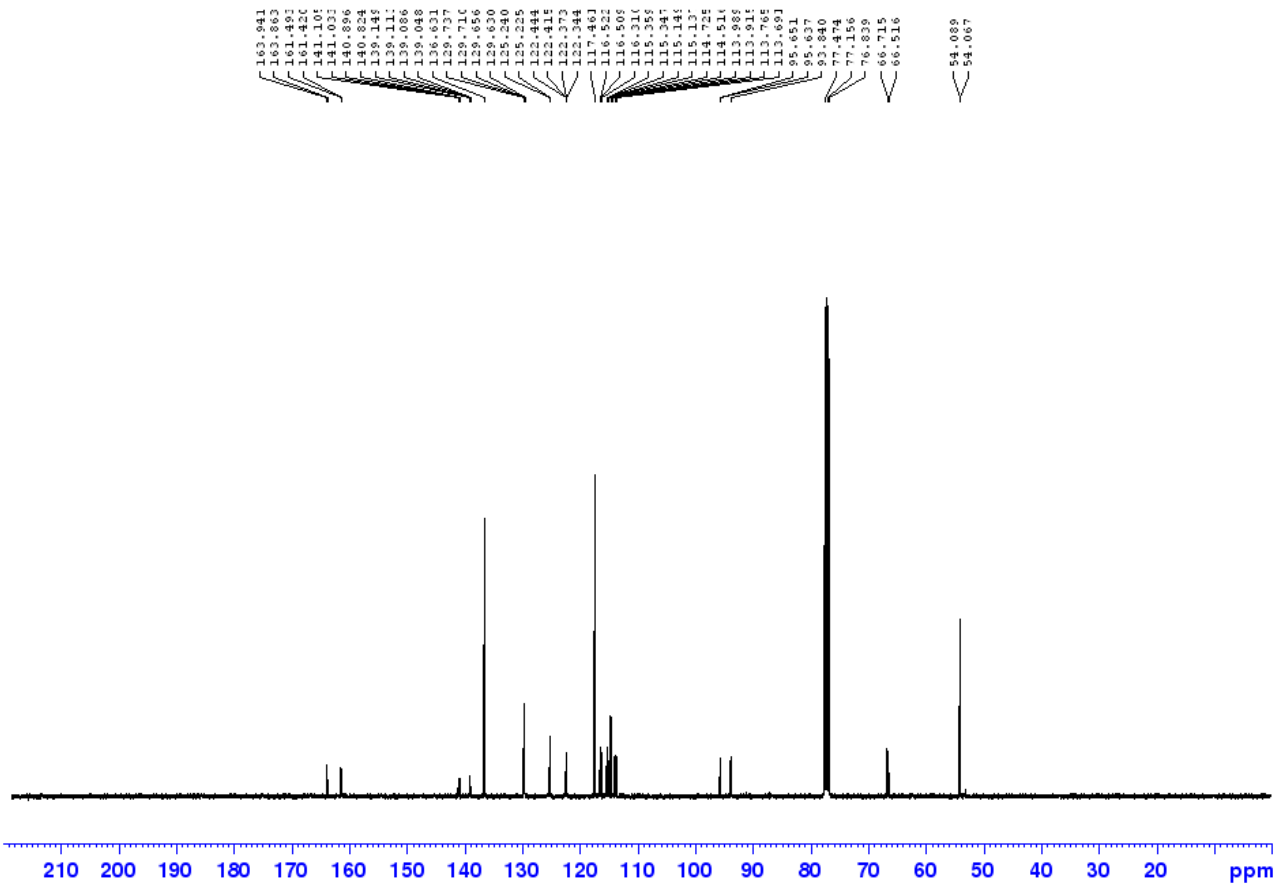

138.810
138.611
137.570
137.310
136.567
136.523
130.486
128.905
128.887
128.120
127.909
127.889
127.702
127.636
126.695
124.104
124.036
116.965
96.362
94.590
77.477
77.364
77.159
76.842
67.168
66.961
54.067
54.047
21.664
21.515
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

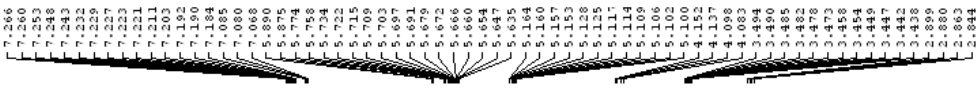

N
F
F
F
(S,S)-2m

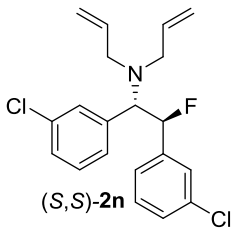

11
10
9
8
7
6
5
4
3
2
1
ppm
2.02
5.96
1.04
1.96
4.02
1.00
2.04
2.01


−112
−113
ppm

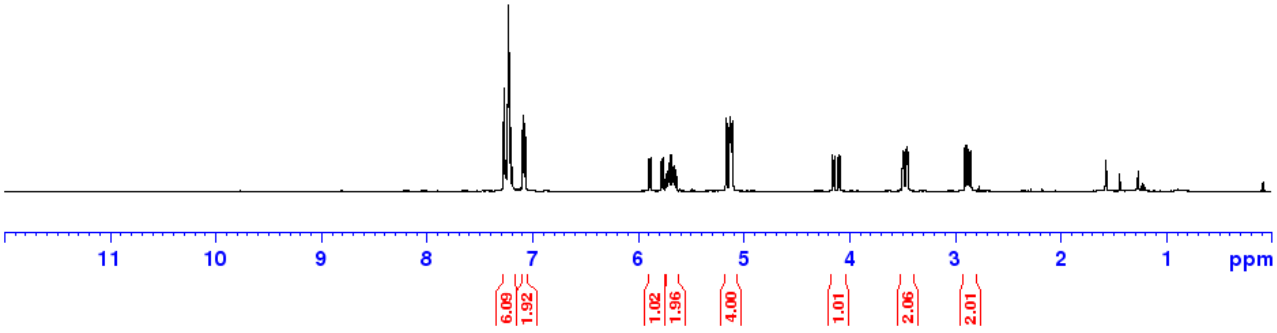

−181
−182
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00
0.99
1.02

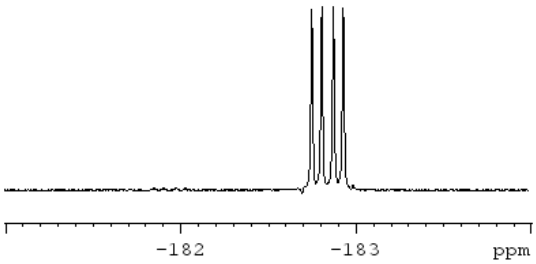

163.941
163.863
161.493
161.426
141.105
141.031
140.896
140.824
139.145
139.117
139.086
139.048
136.631
129.737
129.716
129.656
129.630
125.240
125.225
122.444
122.415
122.373
122.344
117.461
116.522
116.505
116.316
115.358
115.345
115.145
115.137
114.725
114.514
113.988
113.916
113.765
113.693
95.651
95.637
93.840
77.474
77.156
76.839
66.715
66.516
54.089
54.067
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

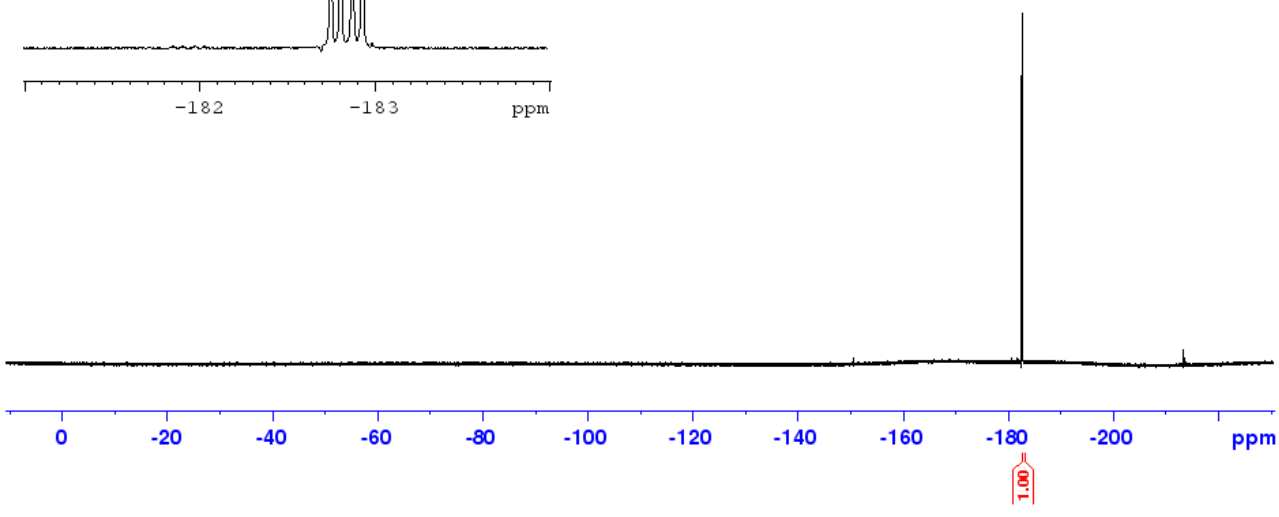


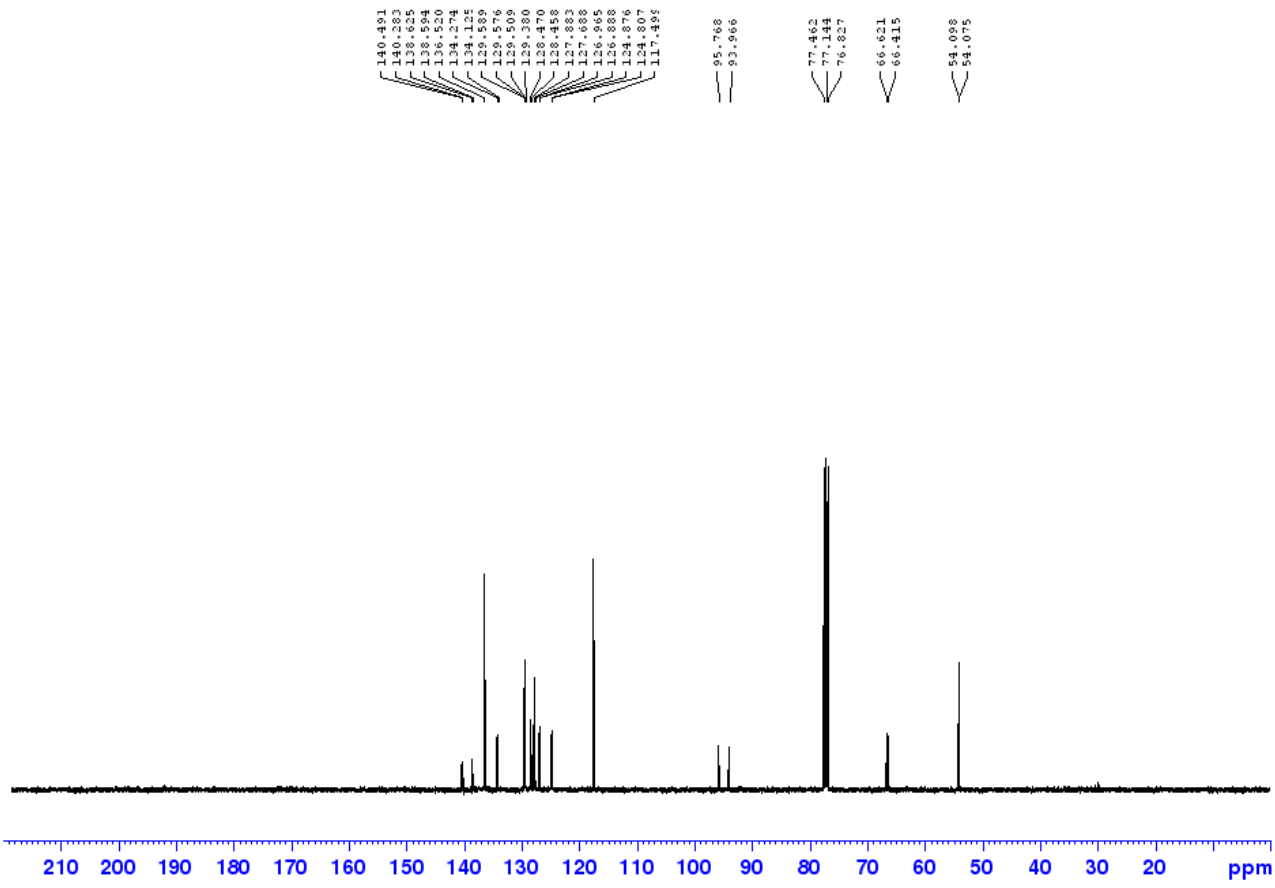

N
Cl
F
Cl

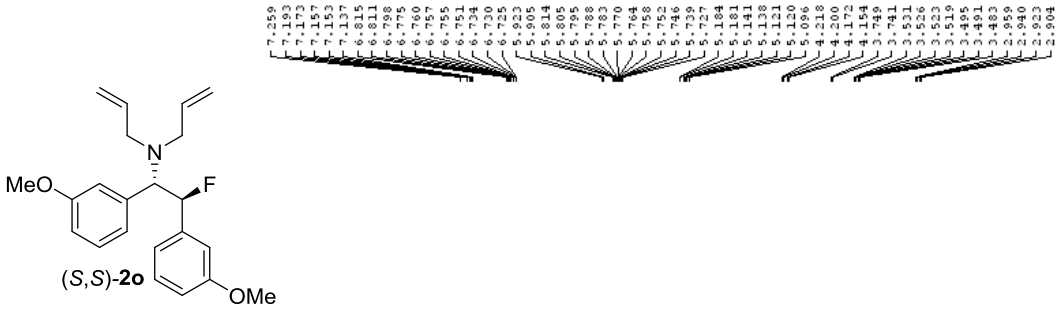
(*S*,*S*)-**2n**


11
10
9
8
7
6
5
4
3
2
1
ppm
6.09
1.92
1.02
1.96
4.00
1.01
2.06
2.01

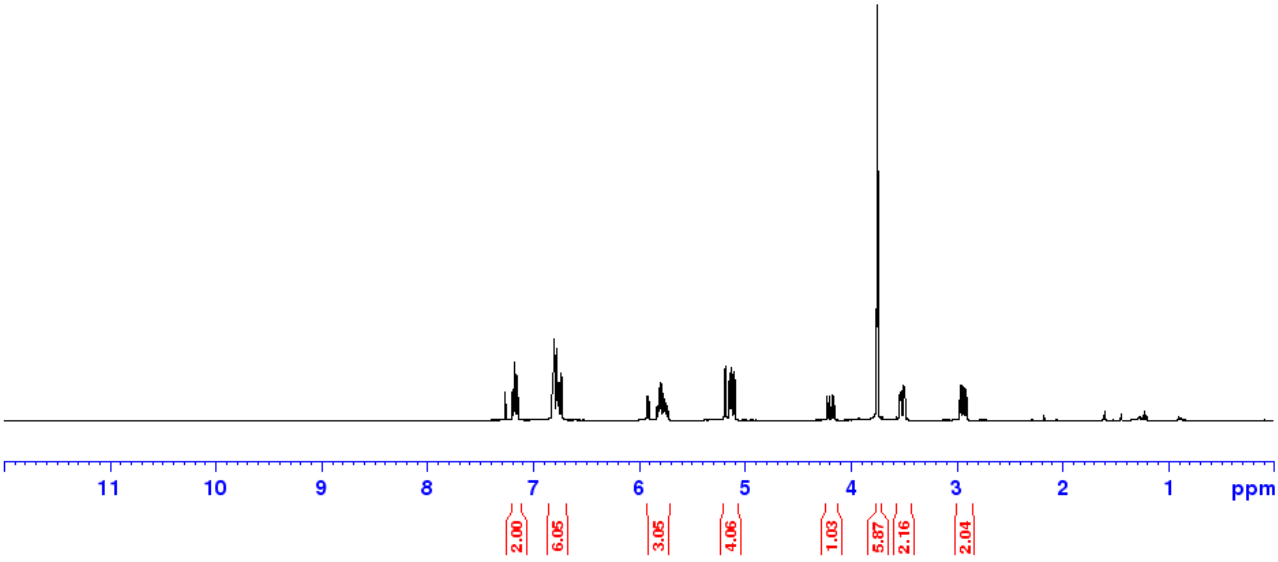

-182
-183
ppm

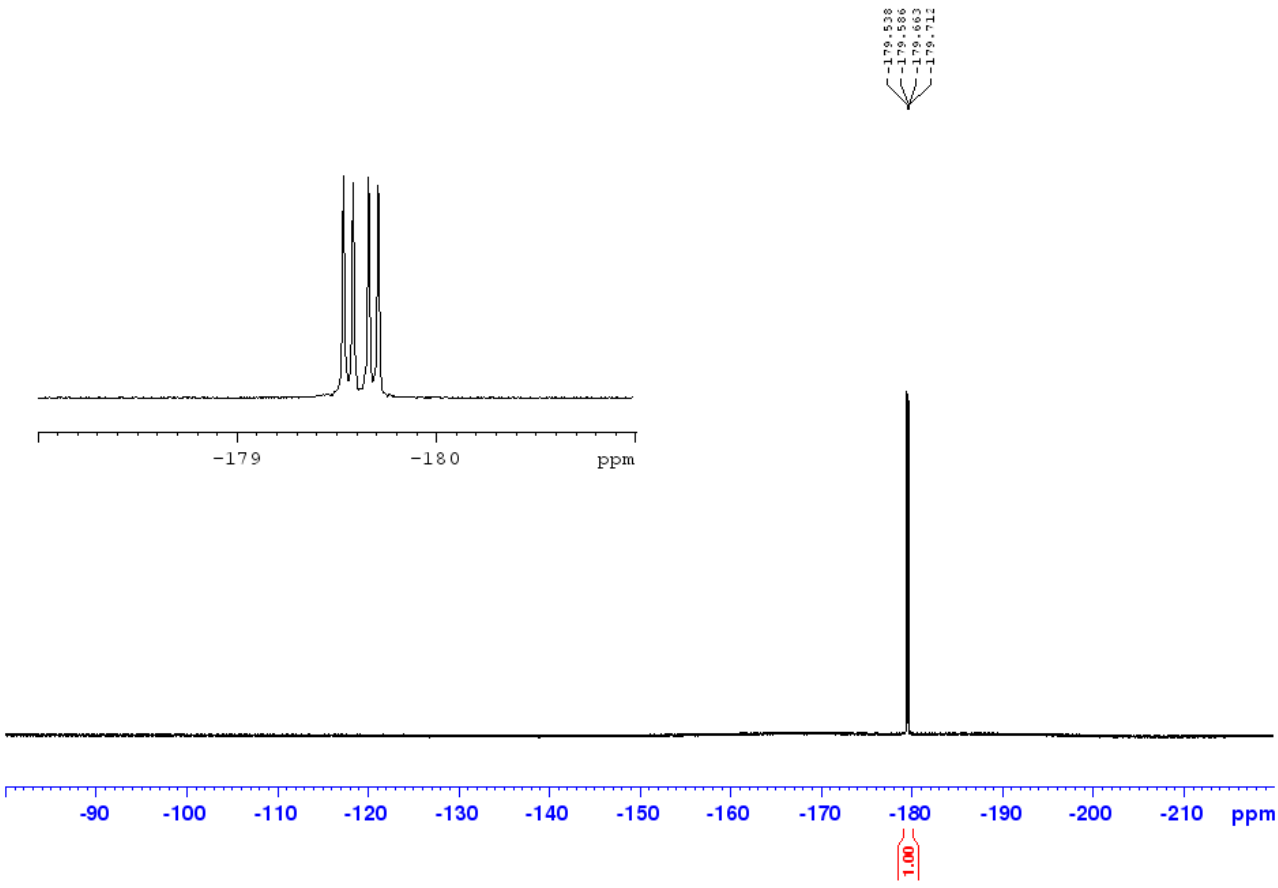

0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00

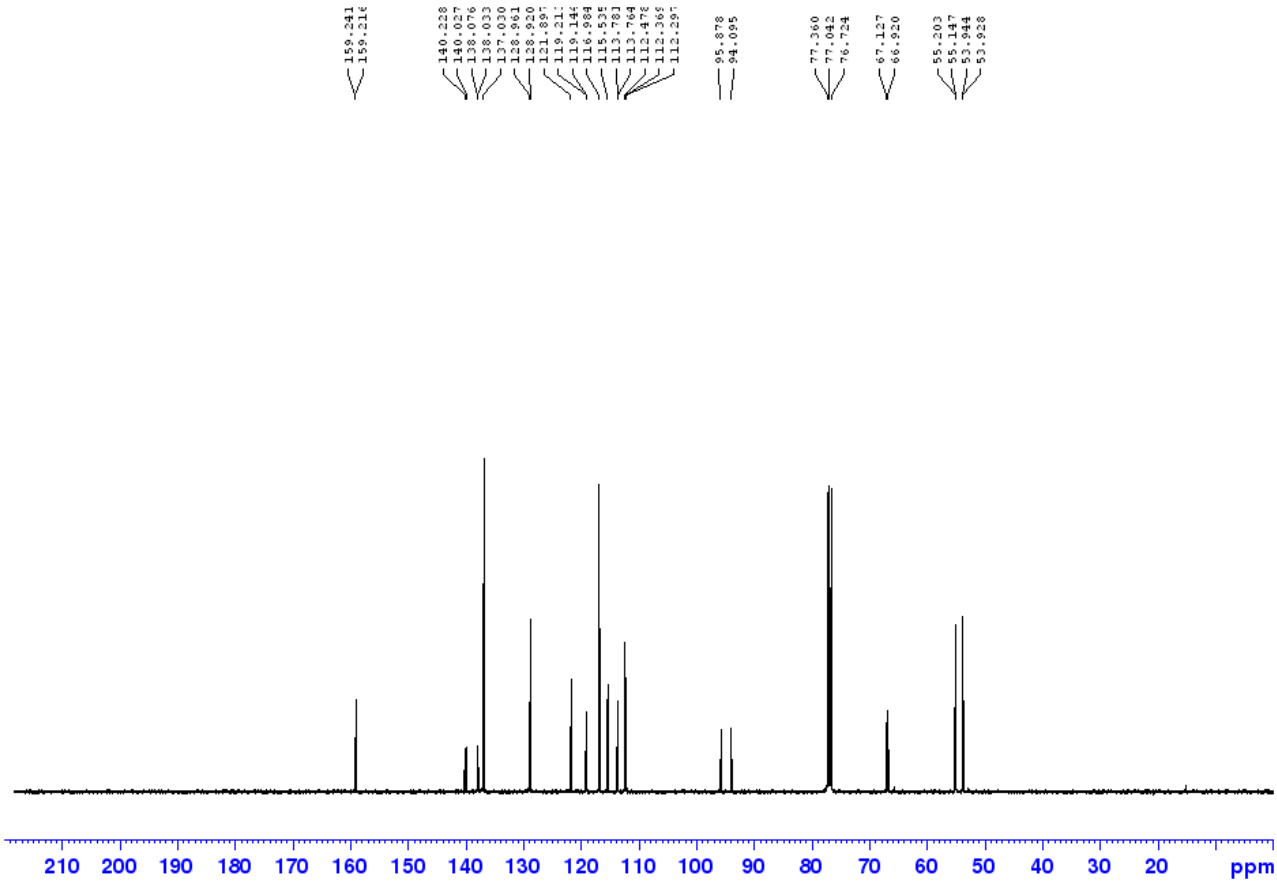

140.491
140.283
138.625
138.594
136.520
134.274
134.125
129.589
129.576
129.509
129.380
128.470
128.458
127.883
127.688
126.965
126.888
124.876
124.807
117.499
95.768
93.966
77.462
77.144
76.827
66.621
66.415
54.098
54.075
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

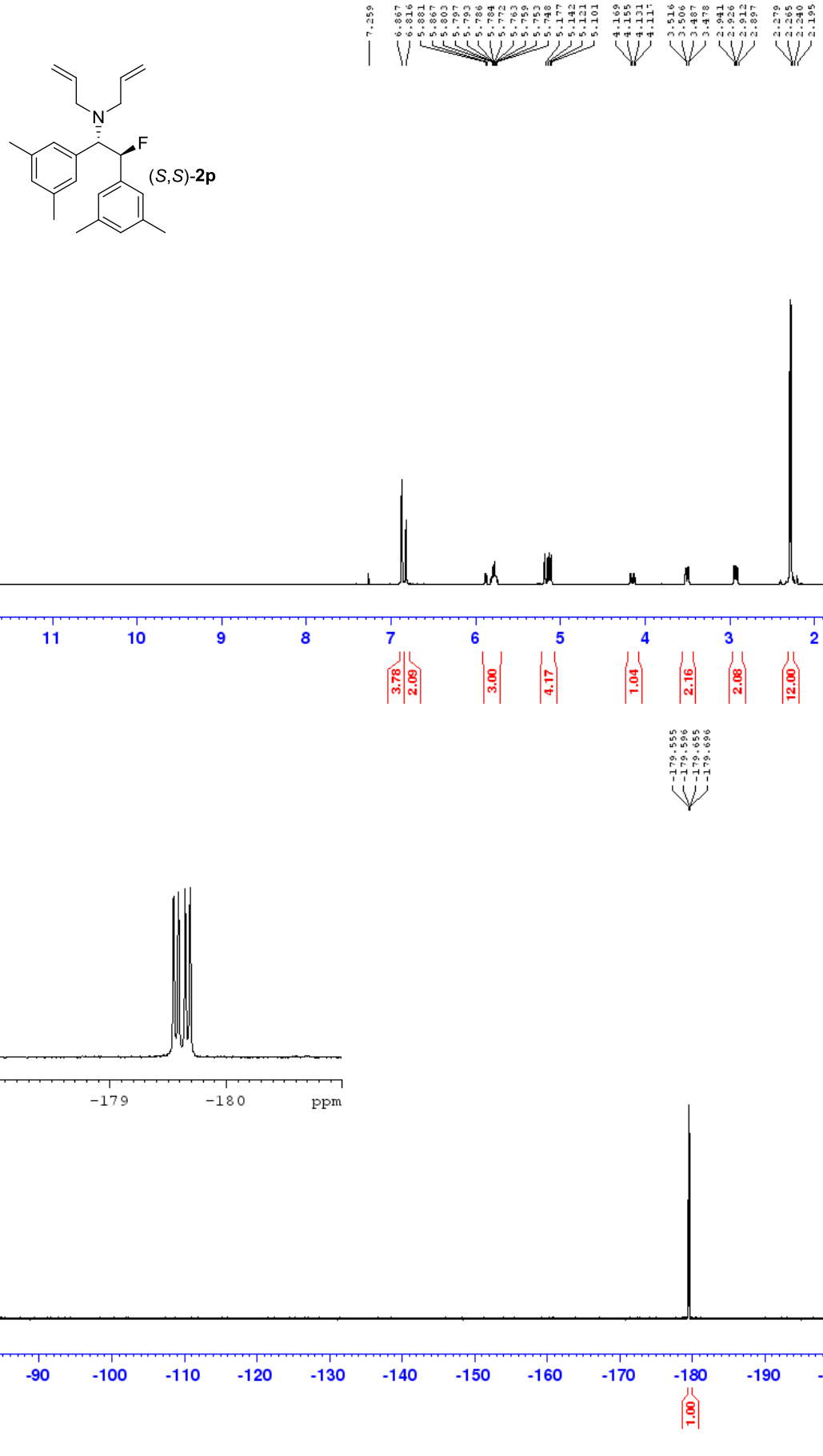

7.259
7.193
7.173
7.157
7.153
7.137
6.815
6.811
6.798
6.775
6.760
6.757
6.755
6.751
6.734
6.730
6.725
5.923
5.905
5.814
5.805
5.795
5.788
5.783
5.770
5.764
5.758
5.752
5.746
5.739
5.727
5.184
5.181
5.141
5.138
5.121
5.120
5.096
4.218
4.200
4.172
4.154
3.749
3.741
3.531
3.526
3.523
3.519
3.495
3.491
3.483
2.959
2.940
2.923
2.904

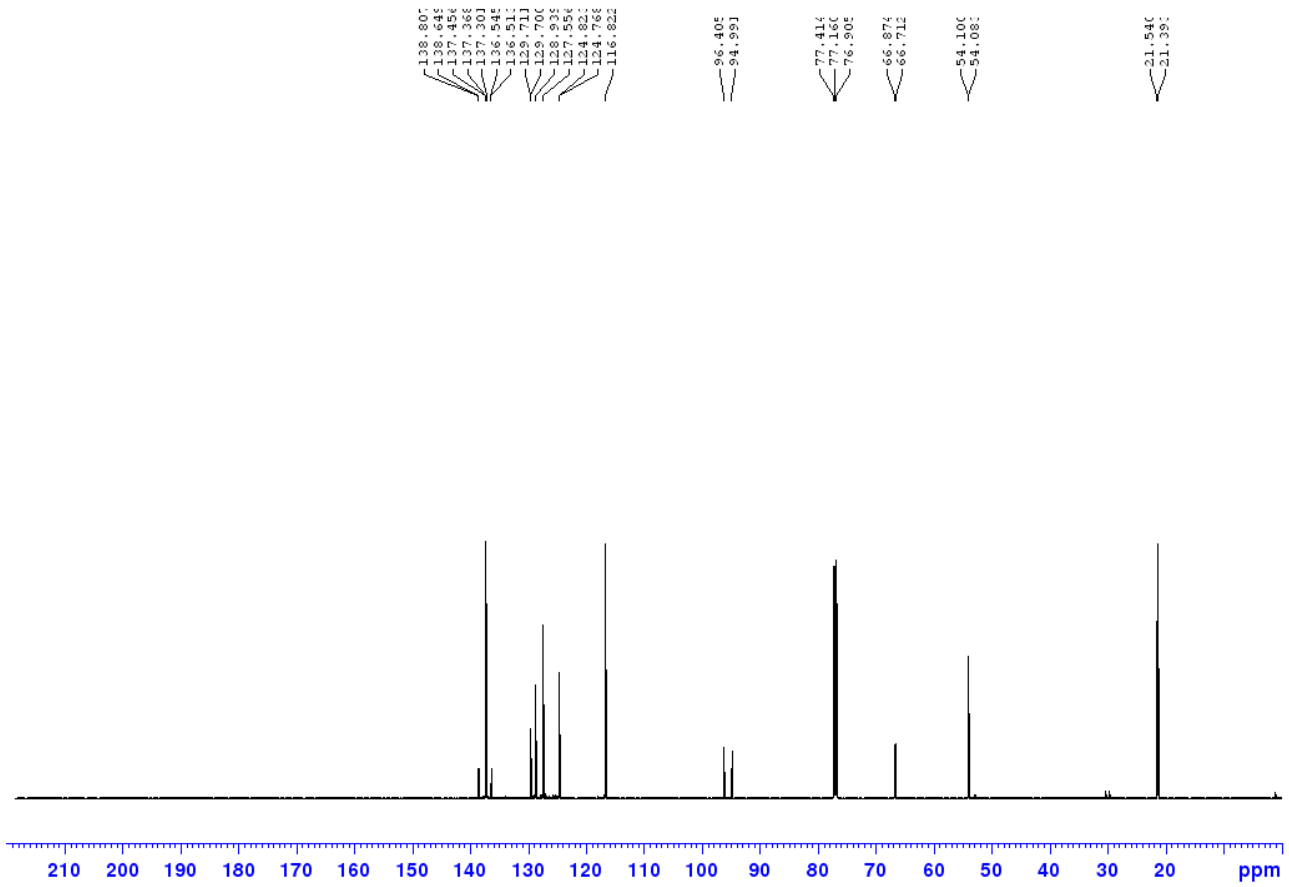
MeO
F
OMe
(S,S)-2o

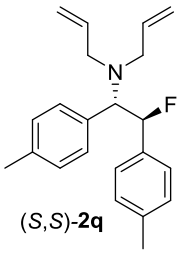

11
10
9
8
7
6
5
4
3
2
1
ppm
2.00
6.05
3.05
4.06
1.03
5.87
2.16
2.04


-179.538
-179.586
-179.663
-179.712
-179
-180
ppm
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm
1.00


159.241
140.228
140.027
138.076
138.033
137.030
128.961
128.920
95.878
94.095
77.360
77.042
76.724
67.127
66.920
55.203
55.147
53.944
53.928
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

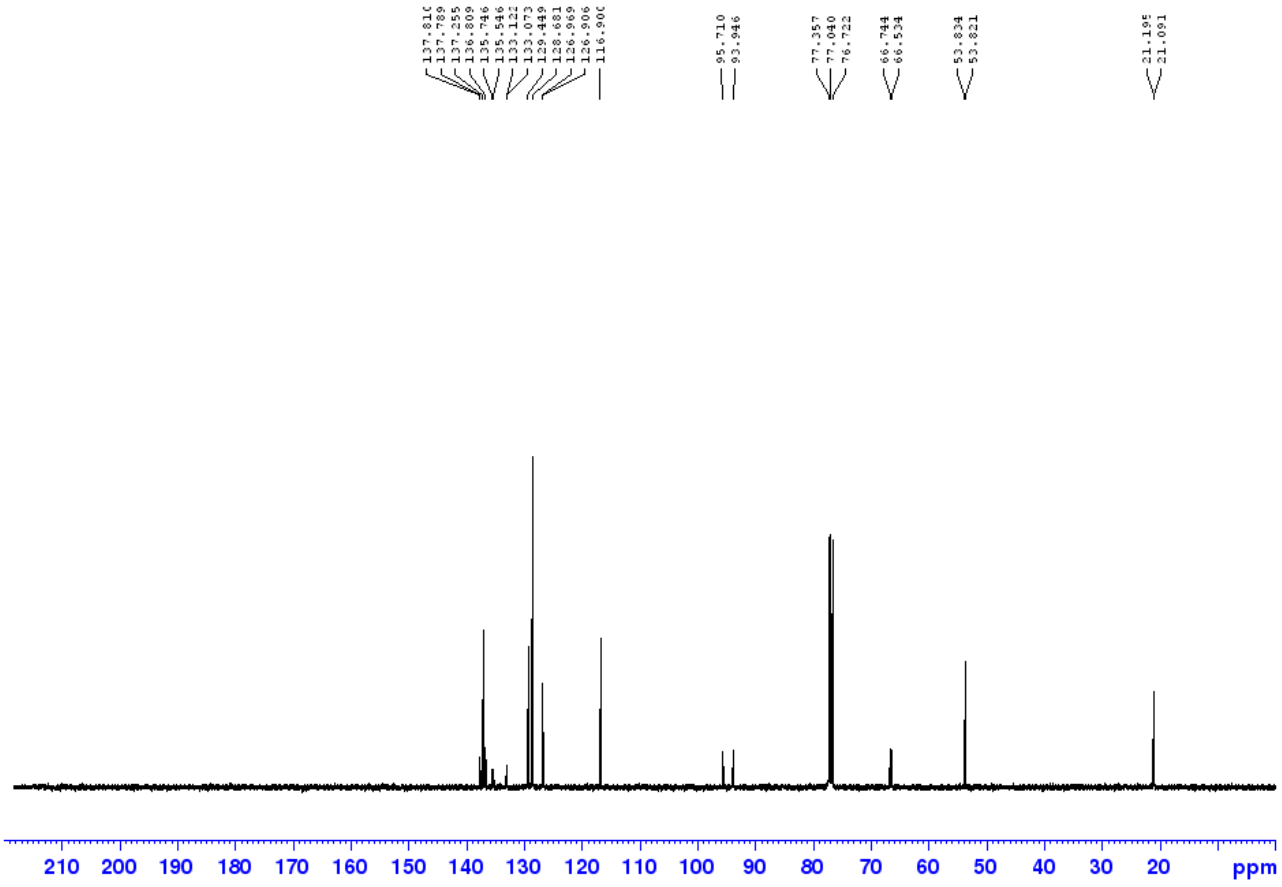

(S,S)-2p
F
N
7.259
6.867
6.816
5.881
5.867
5.803
5.797
5.793
5.786
5.784
5.772
5.763
5.759
5.753
5.748
5.177
5.142
5.121
5.101
4.169
4.155
4.131
4.117
3.516
3.506
3.487
3.478
2.941
2.926
2.912
2.897
2.279
2.265
2.240
2.195
11
10
9
8
7
6
5
4
3
2
1
ppm
3.78
2.09
3.00
4.17
1.04
2.16
2.08
12.00
-179.555
-179.596
-179.655
-179.696
-179
-180
ppm
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm
1.00

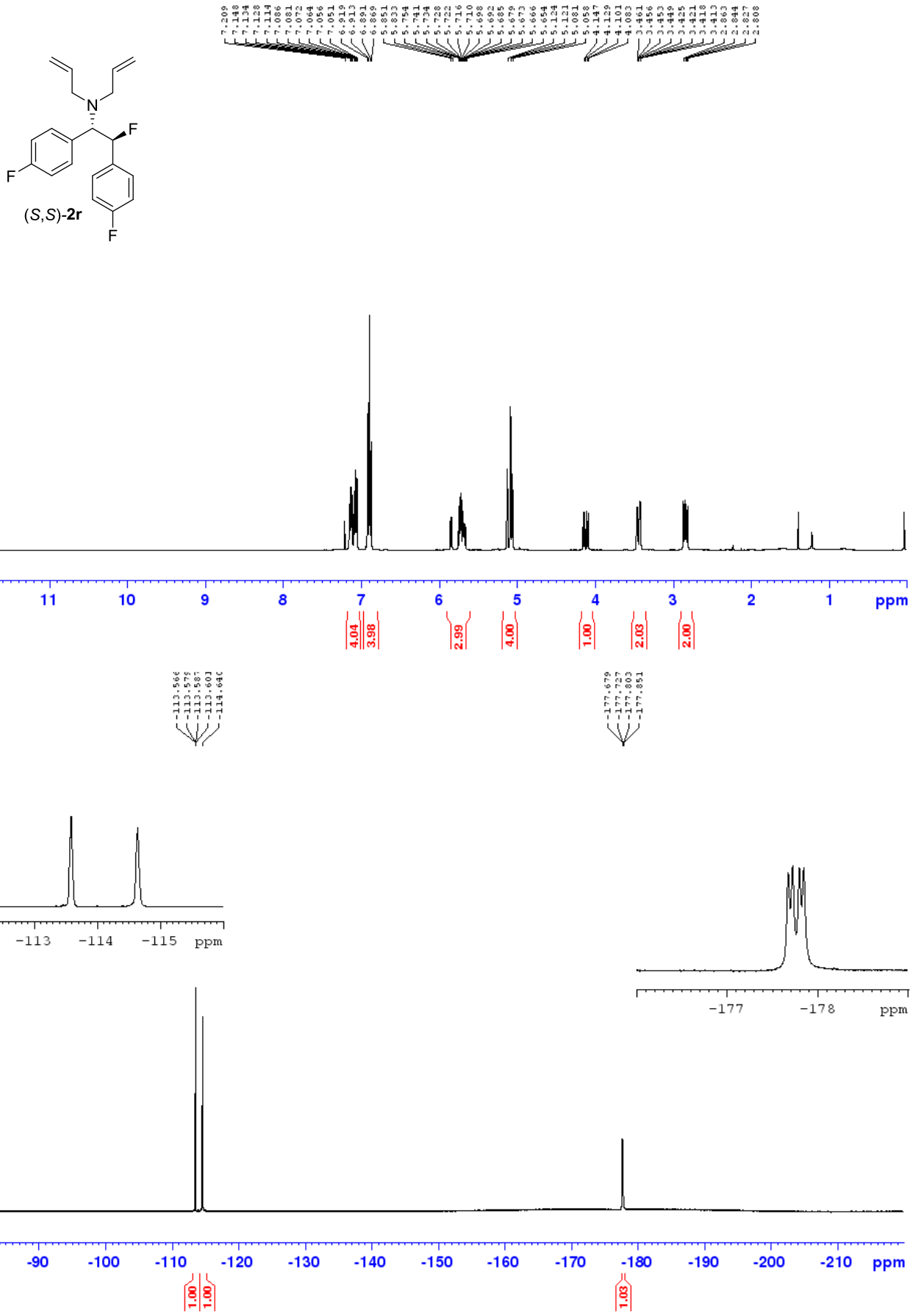

138.80
138.64
137.45
137.36
137.30
136.54
136.51
129.71
129.70
128.93
127.55
124.82
124.76
116.82
96.40
94.99
77.41
77.16
76.90
66.87
66.71
54.10
54.08
21.54
21.39
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

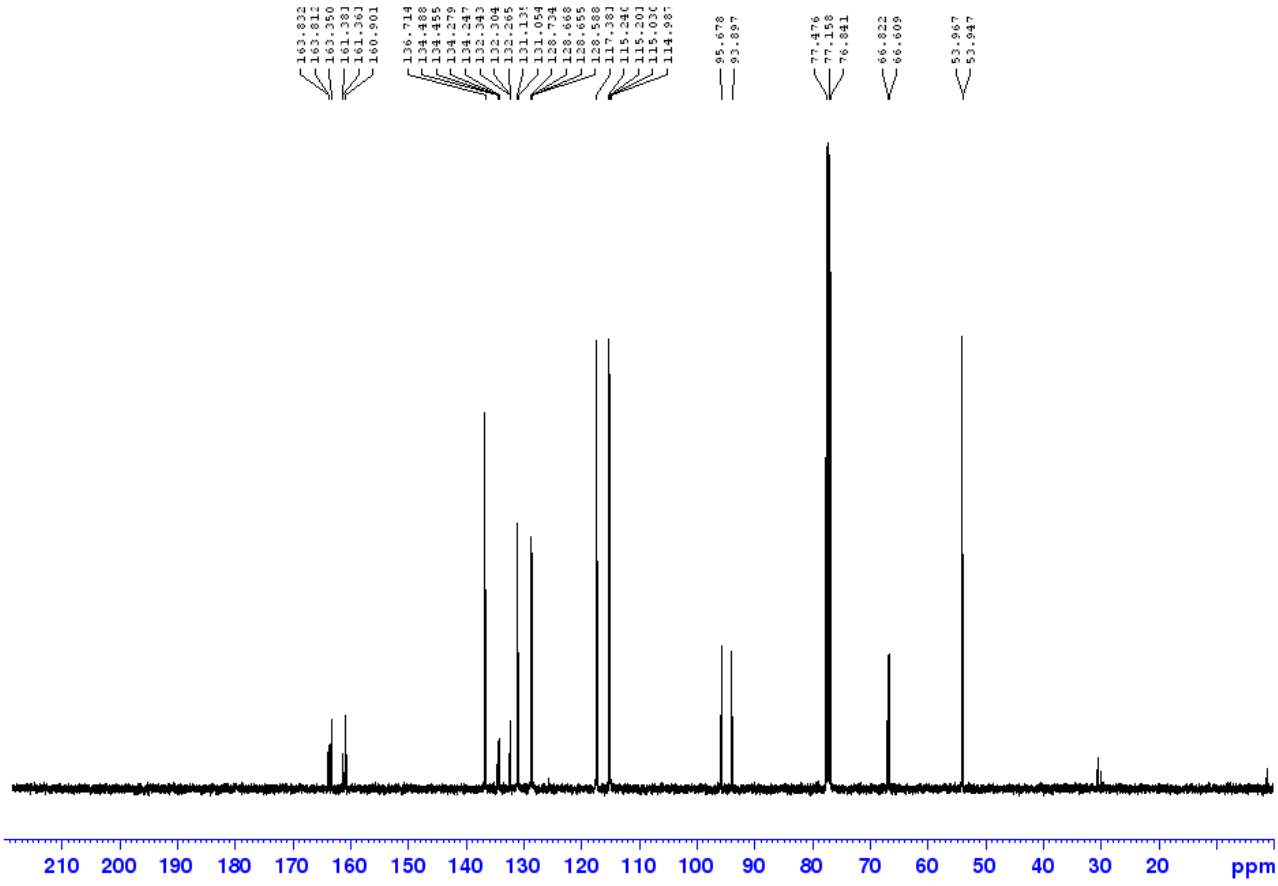

N
F

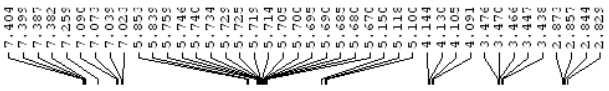
(*S*,*S*)-**2q**

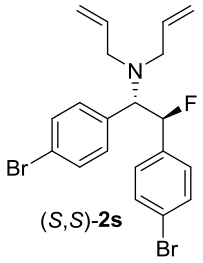
7.174
7.051
7.033
6.967
6.959
6.948
6.840
5.830
5.733
5.727
5.722
5.715
5.709
5.702
5.697
5.690
5.106
5.103
5.063
5.060
5.042
5.040
5.016
4.169
4.149
4.137
4.108
3.445
3.440
3.437
3.433
3.409
3.404
3.402
3.397
2.829
2.810
2.793
2.774
2.204
2.196
11
10
9
8
7
6
5
4
3
2
1
ppm
2.26
6.00
3.07
4.13
1.02
2.06
2.04
6.12
-176.555
-176.598
-176.680
-176.724
-177
-176
ppm
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm
1.00


137.816
137.789
137.255
136.809
135.746
135.546
133.122
133.073
129.449
128.681
126.969
126.906
116.900
95.710
93.946
77.357
77.040
76.722
66.744
66.534
53.834
53.821
21.195
21.091
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

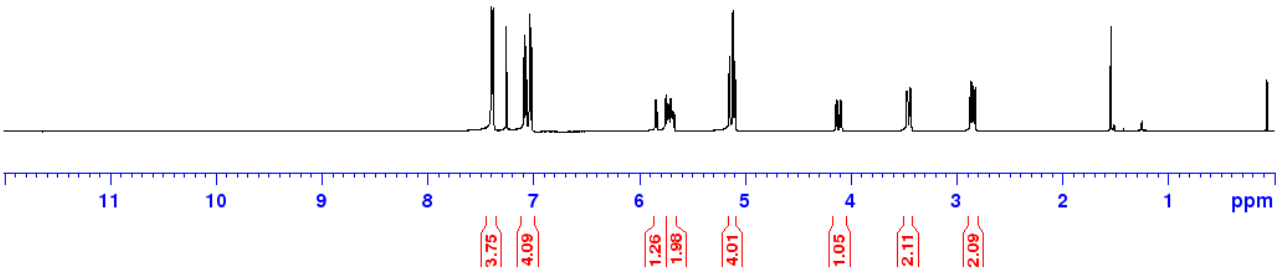

(S,S)-2r
F
F
F
N
7.209
7.148
7.134
7.128
7.114
7.086
7.081
7.072
7.064
7.056
7.051
6.919
6.913
6.891
6.869
5.851
5.833
5.754
5.741
5.734
5.728
5.722
5.716
5.710
5.698
5.692
5.685
5.679
5.673
5.666
5.654
5.124
5.121
5.081
5.058
4.147
4.129
4.101
4.083
3.461
3.456
3.453
3.449
3.425
3.421
3.418
3.413
2.863
2.844
2.827
2.808
11
10
9
8
7
6
5
4
3
2
1
ppm
4.04
3.98
2.99
4.00
1.00
2.03
2.00
-113.566
-113.575
-113.587
-113.603
-114.640
-177.679
-177.727
-177.803
-177.851
-113
-114
-115
ppm
-177
-178
ppm
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm
1.00
1.00
1.03

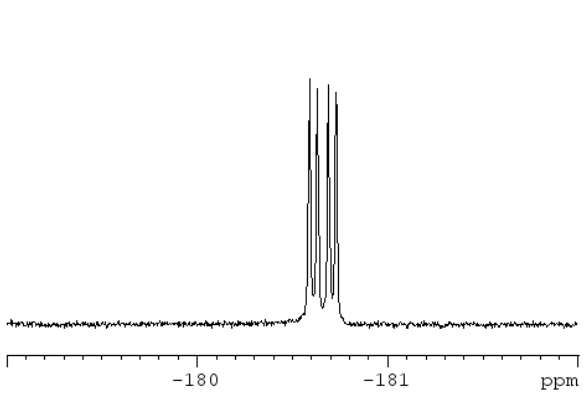

163.832
163.812
163.350
161.381
161.361
160.901
136.714
134.488
134.455
134.279
134.247
132.343
132.304
132.265
131.135
131.054
128.734
128.668
128.655
128.588
117.381
115.246
115.201
115.030
114.987
95.678
93.897
77.476
77.158
76.841
66.822
66.609
53.967
53.947
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

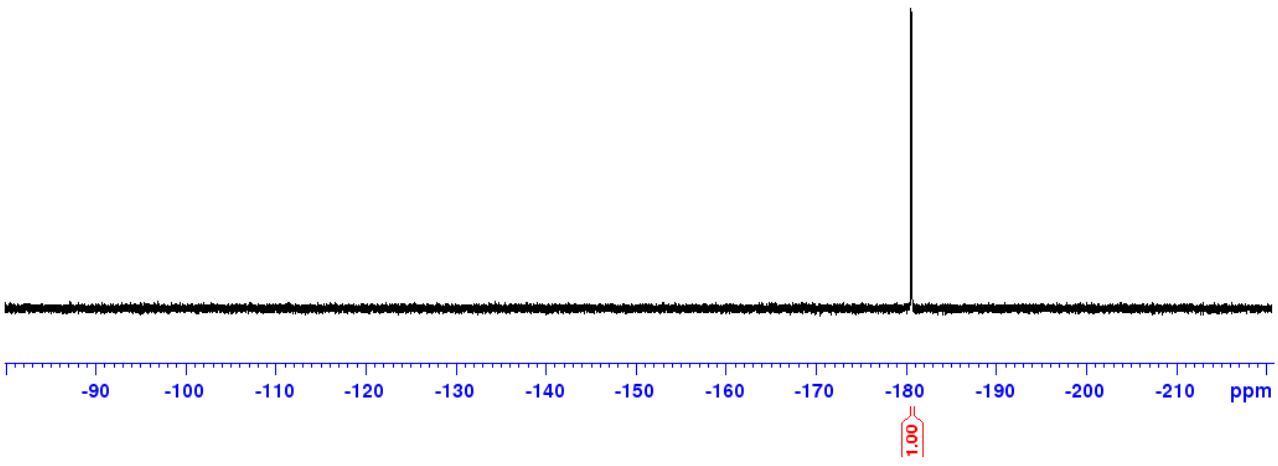


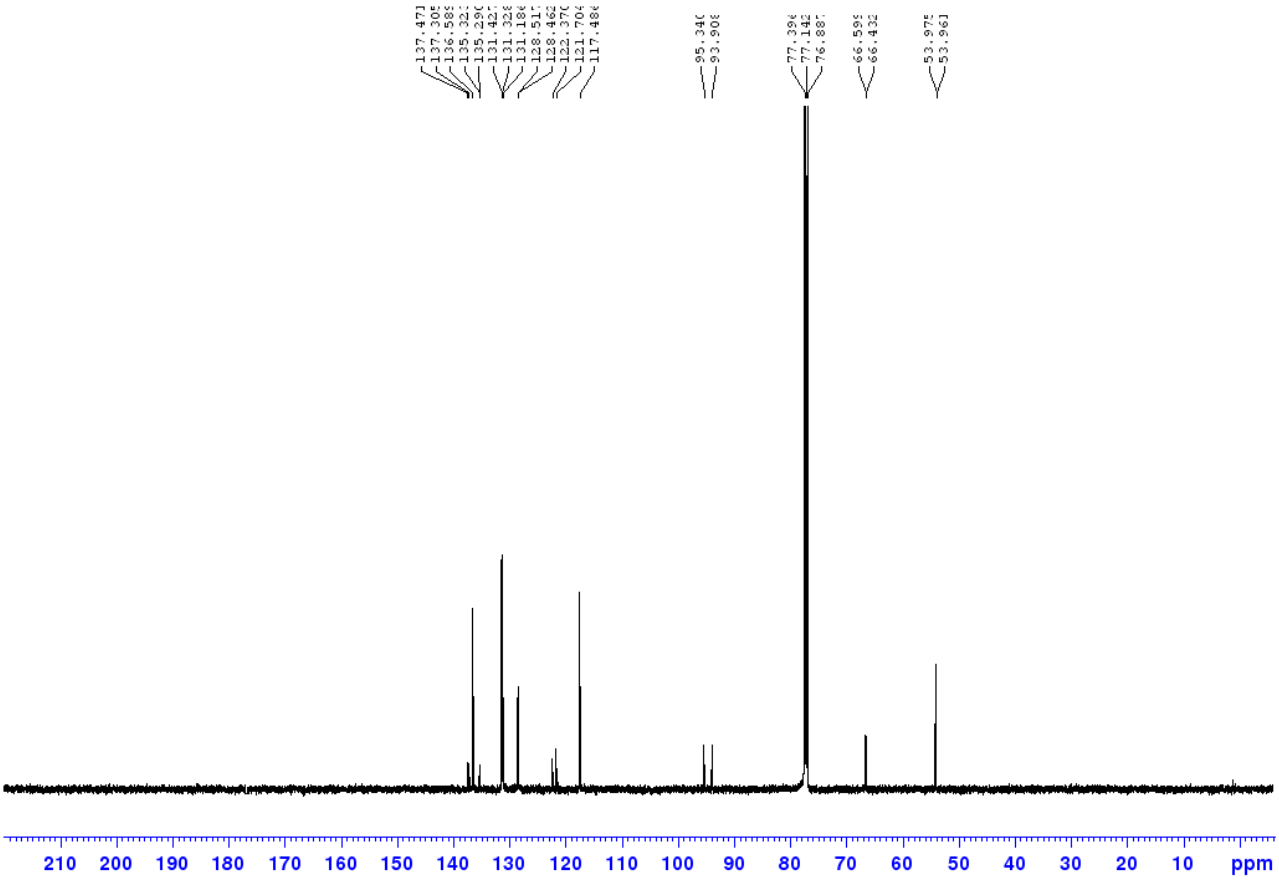

N
F
Br
Br

(*S*,*S*)-**2s**


11
10
9
8
7
6
5
4
3
2
1
ppm
3.75
4.09
1.26
1.98
4.01
1.05
2.11
2.09


-180
-181
ppm

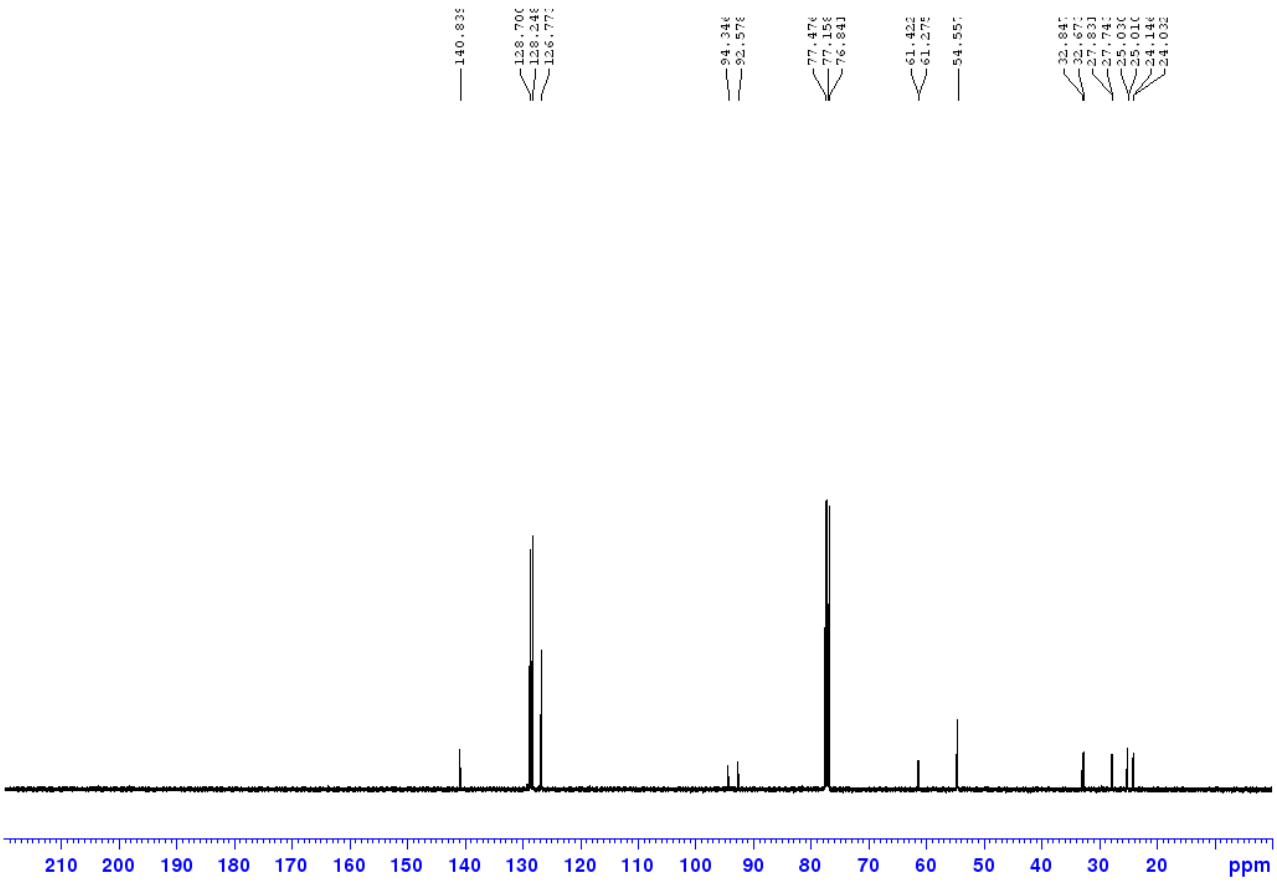

-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm
1.00

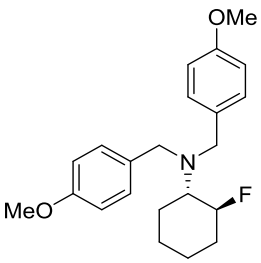

137.471
137.305
136.588
135.321
135.290
131.427
131.328
131.184
128.511
128.462
122.370
121.704
117.484
95.346
93.908
77.394
77.142
76.887
66.595
66.432
53.975
53.961
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Ph
Ph
N
F

(*S*,*S*)-**2t**

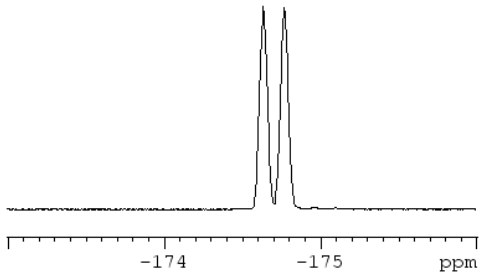
11
10
9
8
7
6
5
4
3
2
1
ppm
3.75
4.00
1.96
1.02
3.93
1.04
1.08
0.98
2.26
2.11
2.16
-174
-175
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

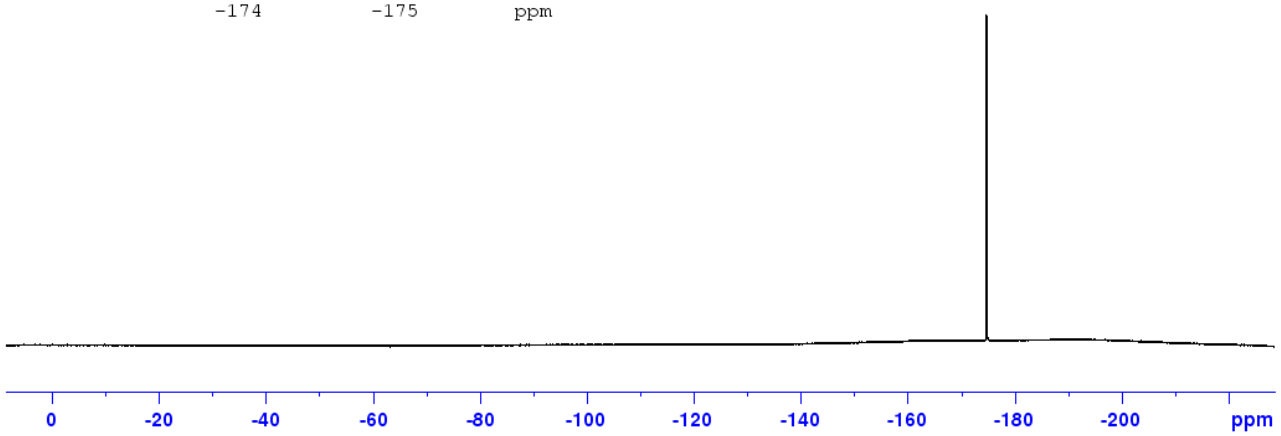

140.83
128.70
128.24
126.77
94.34
92.57
77.47
77.15
76.84
61.42
61.27
54.55
32.84
32.67
27.83
27.74
25.03
25.01
24.14
24.03
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

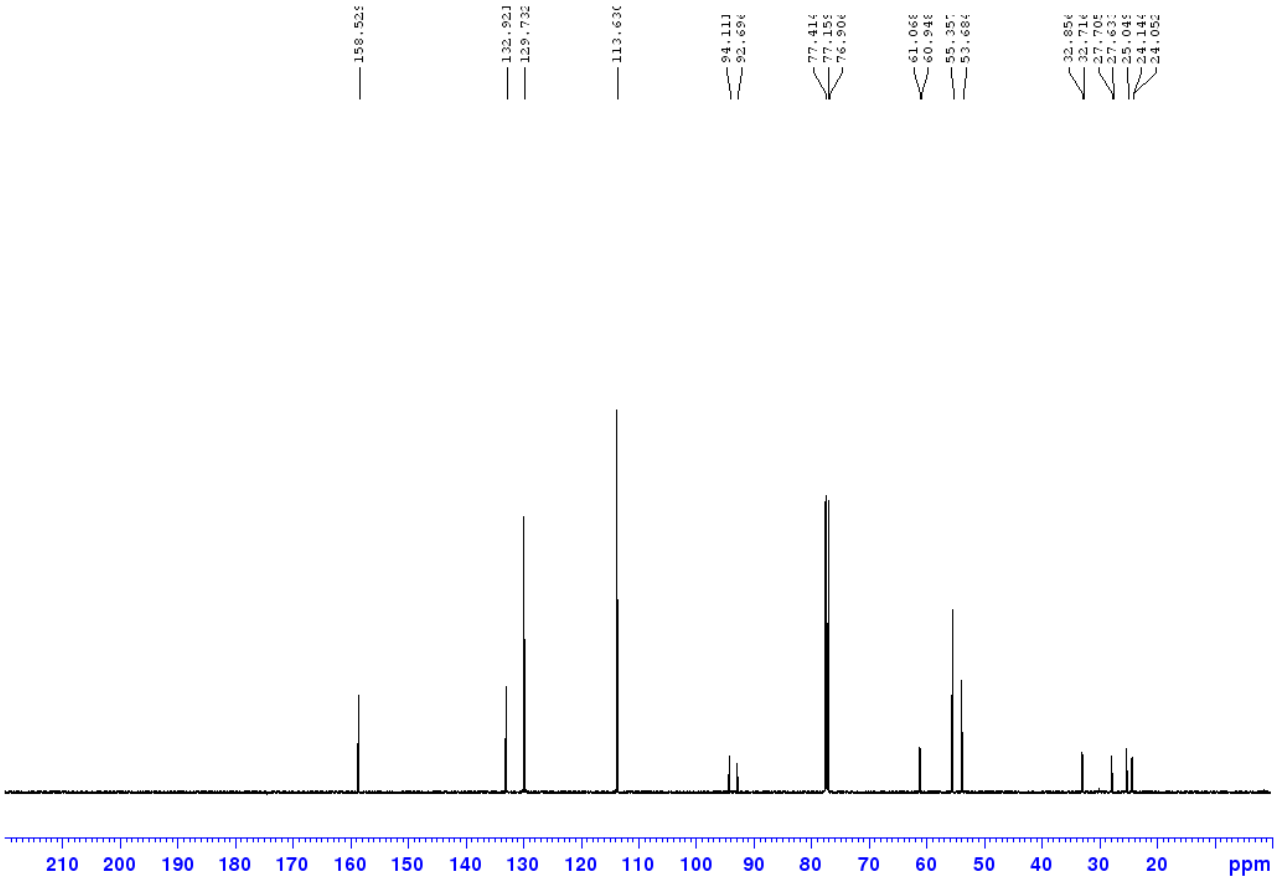

OMe
MeO
N
F

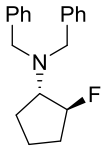
(*S*,*S*)-**2u**

11
10
9
8
7
6
5
4
3
2
1
ppm
3.88
3.75
1.00
5.84
2.01
2.01
0.99
1.01
1.01
2.06
2.38
2.12


-174
-175
ppm

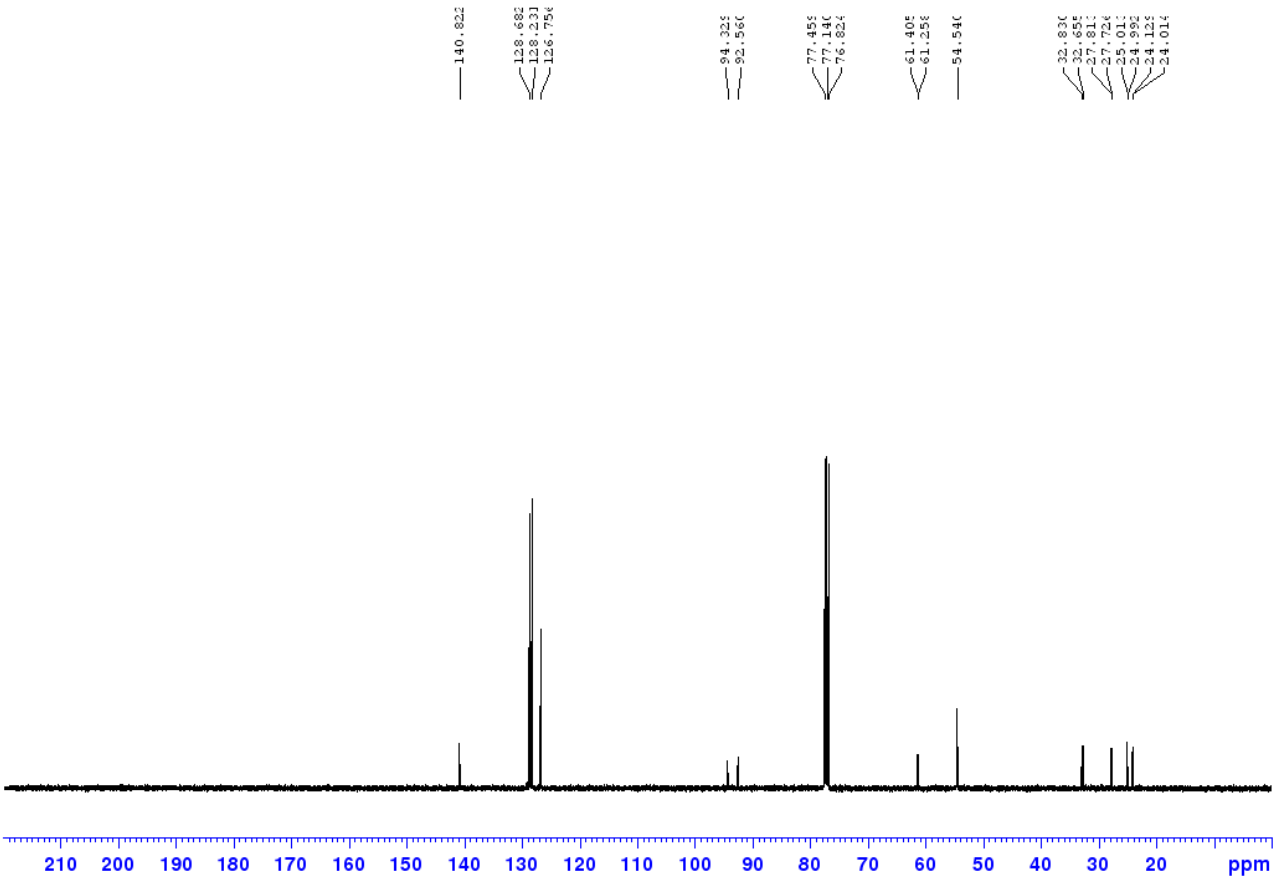

0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

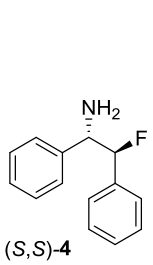

158.525
132.921
129.732
113.630
94.111
92.694
77.414
77.155
76.900
61.068
60.948
55.357
53.684
32.856
32.716
27.705
27.633
25.045
24.144
24.052
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


Ph
Ph
N
F

(*S*,*S*)-**2v**

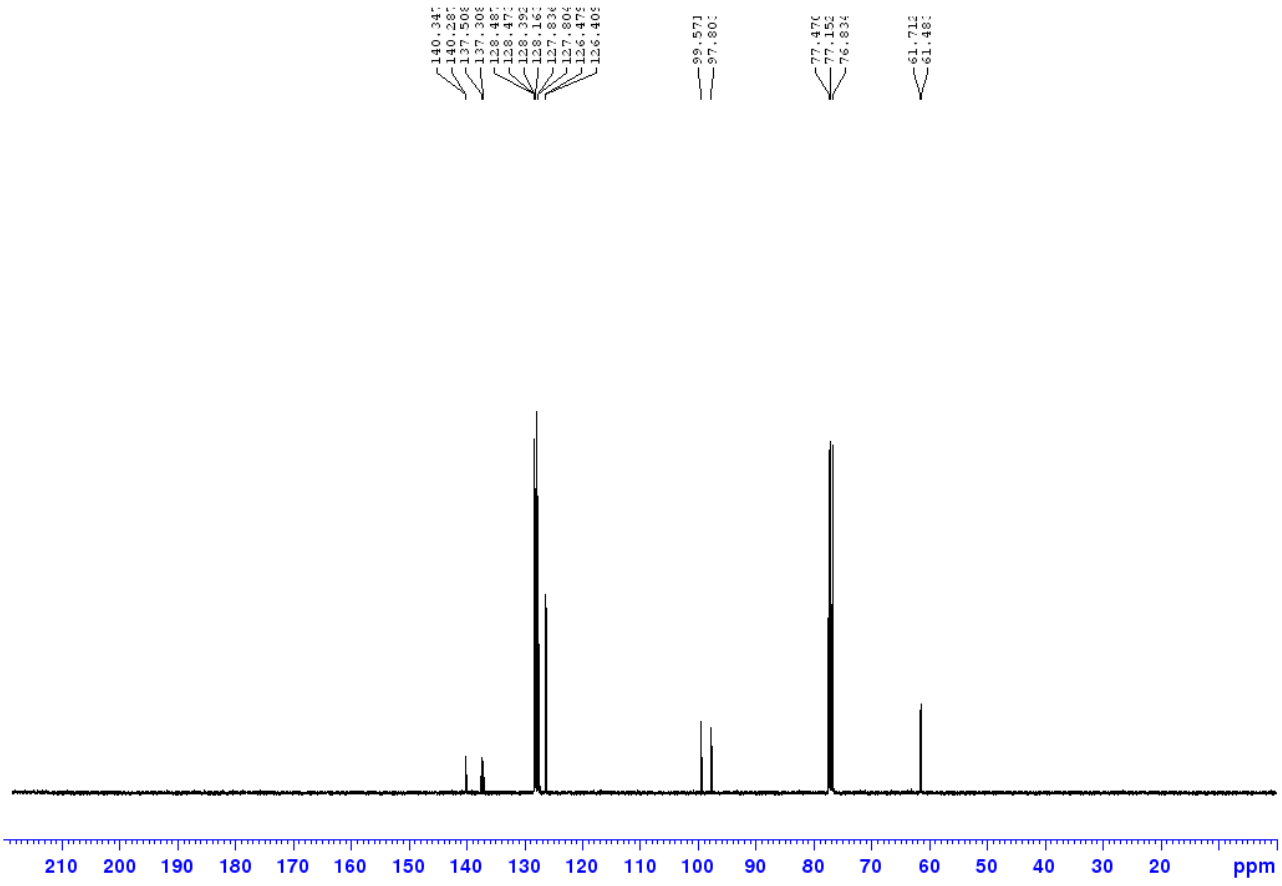
11
10
9
8
7
6
5
4
3
2
1
ppm
4.03
4.00
1.95
1.01
4.11
1.02
3.12
3.56
-173
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

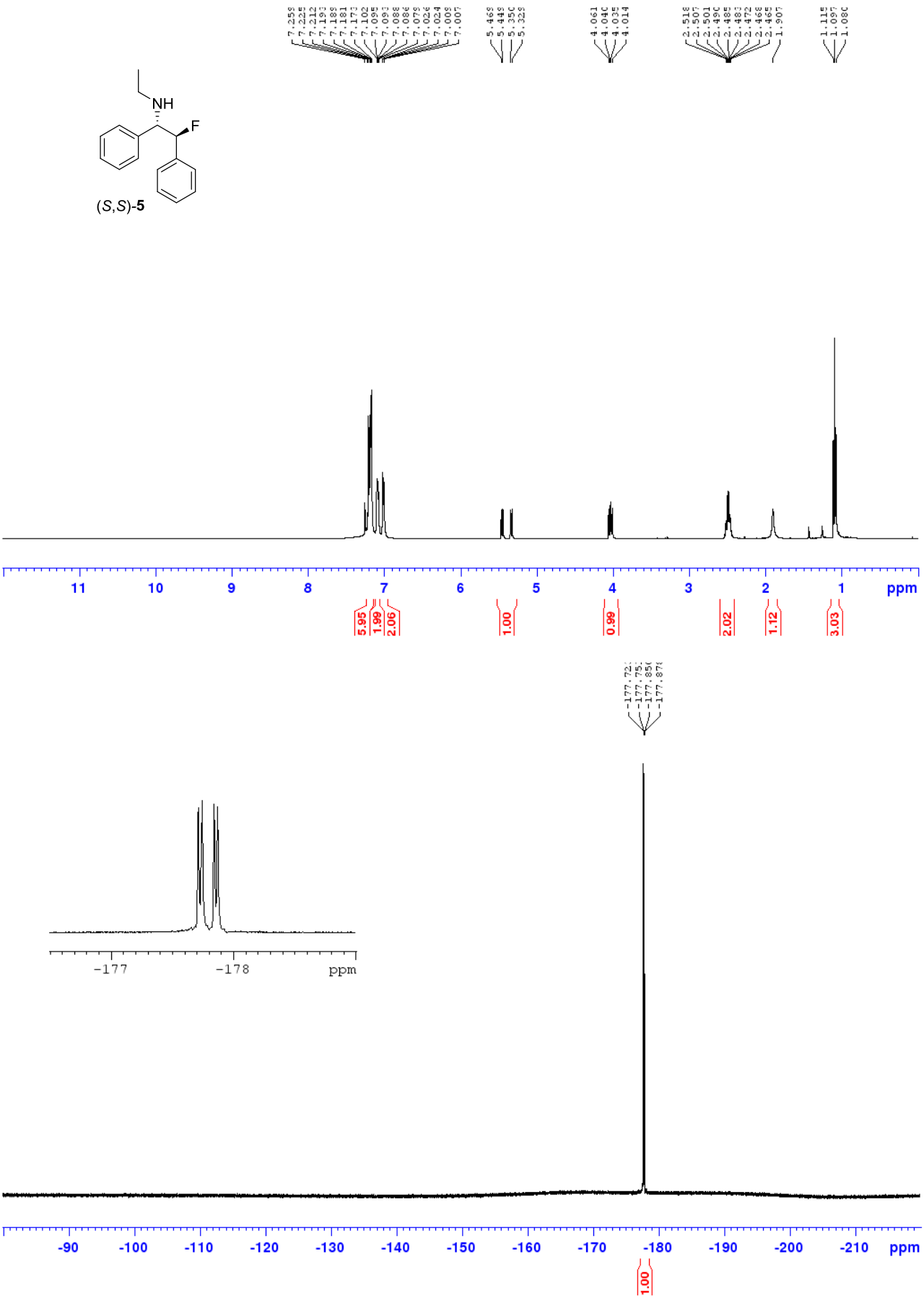

140.822
128.682
128.231
126.756
94.325
92.560
77.455
77.140
76.824
61.405
61.258
54.540
32.830
32.655
27.811
27.726
25.011
24.992
24.125
24.014
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

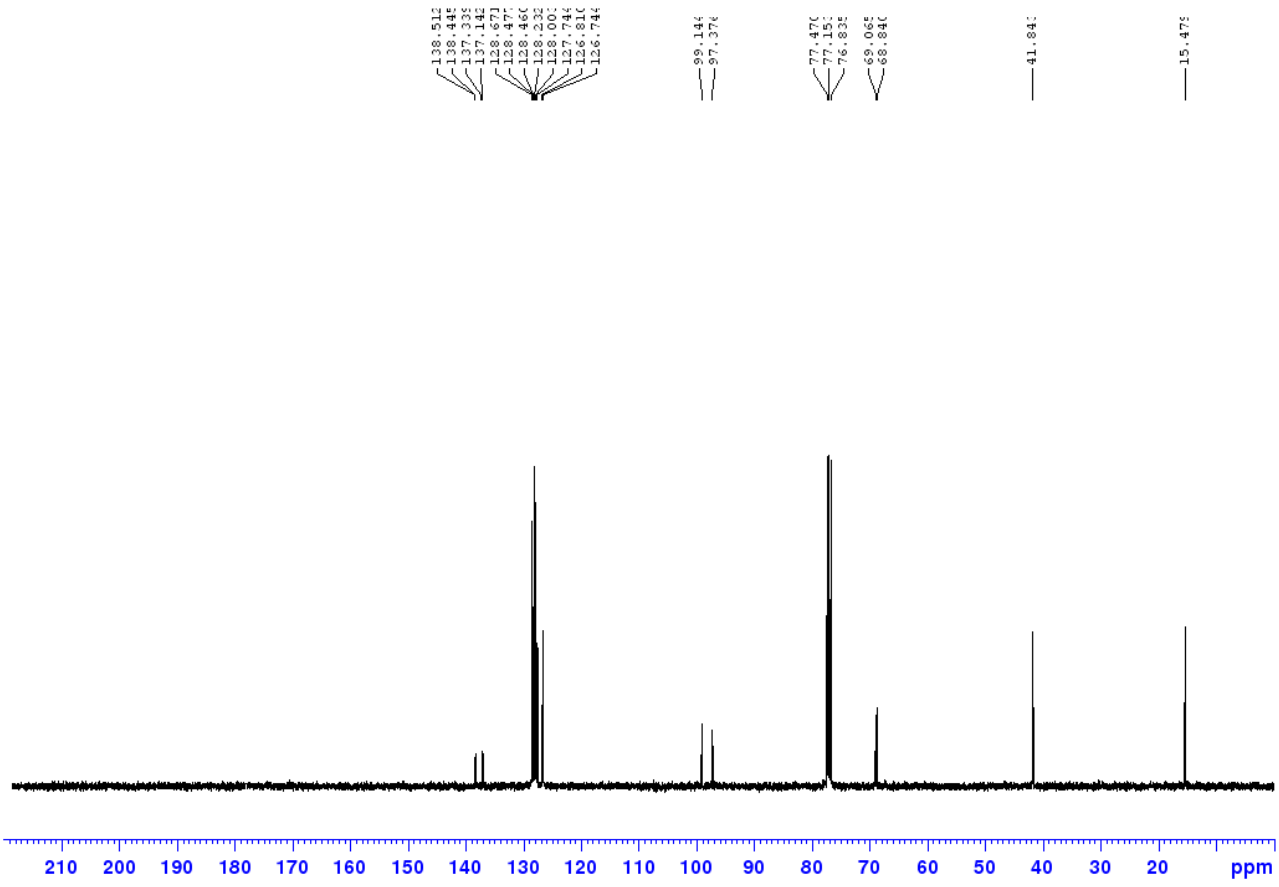

NH2
F

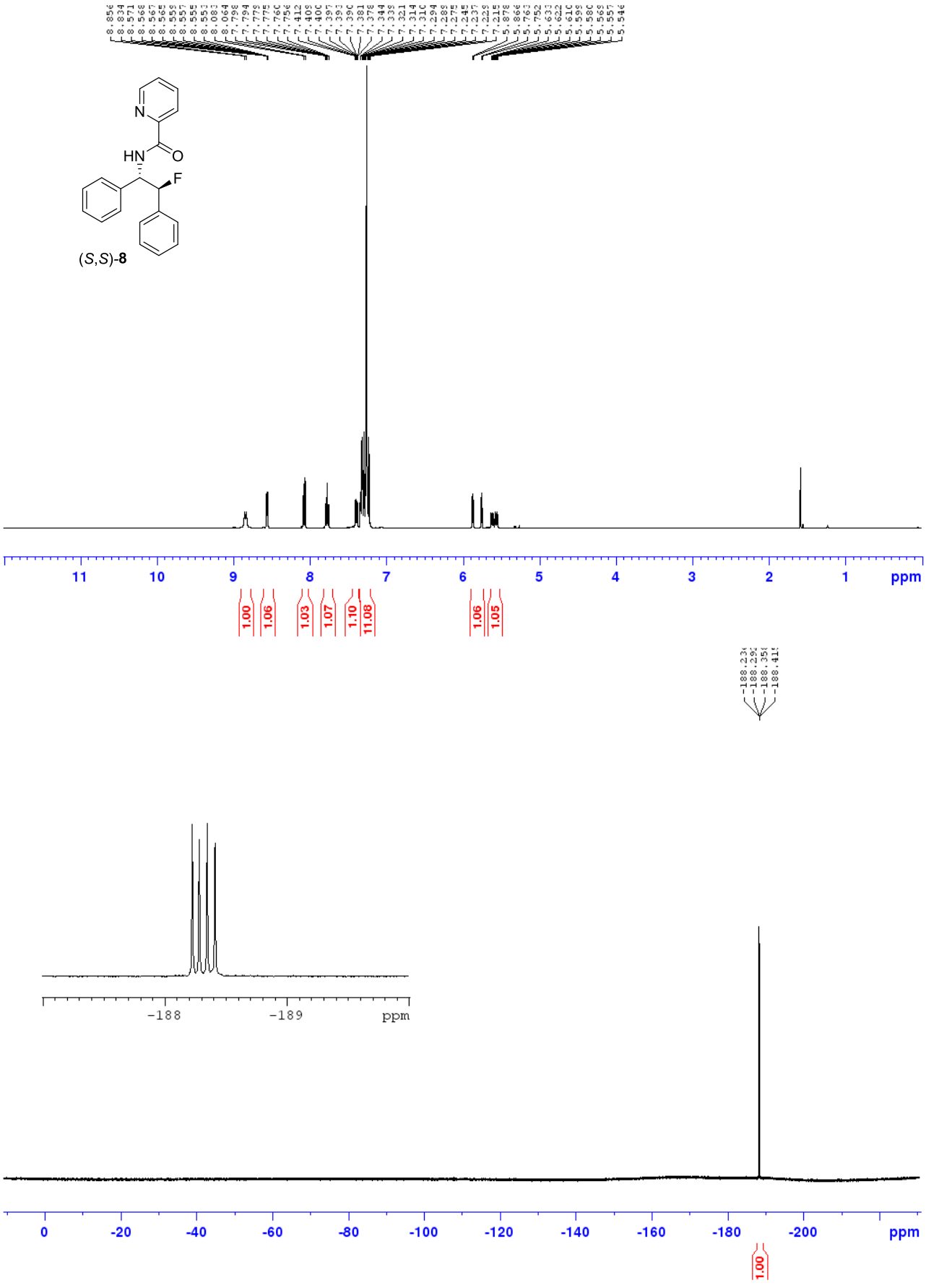
(*S*,*S*)-**4**

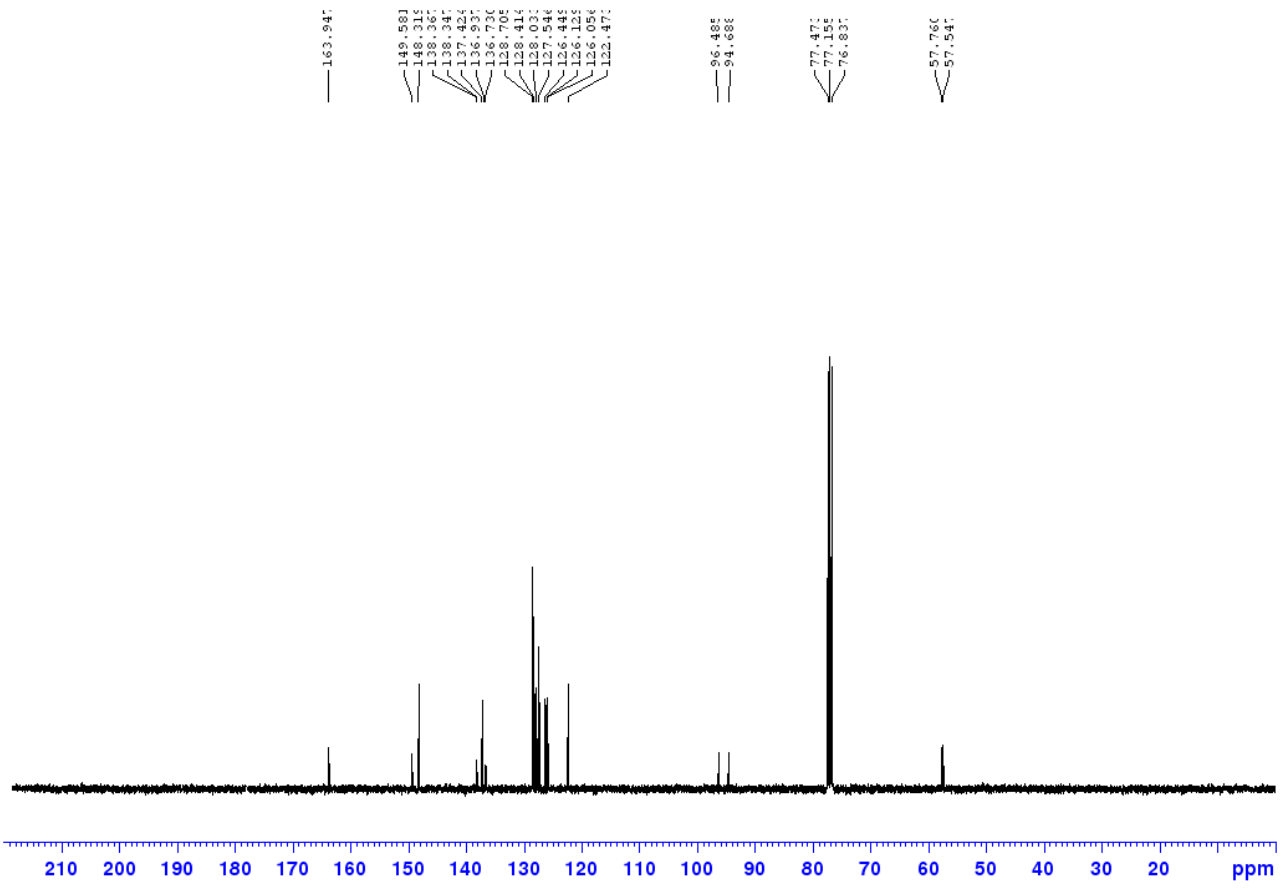
7.270
7.260
7.254
7.246
7.244
7.241
7.238
7.235
7.227
7.222
7.216
7.211
7.188
7.181
7.176
7.169
7.164
7.108
7.103
7.095
7.093
7.084
5.498
5.480
5.380
5.362
4.309
4.292
4.273
4.255
1.775
11
10
9
8
7
6
5
4
3
2
1
ppm
6.34
2.03
2.00
1.05
1.06
2.57
-182.554
-182.592
-182.679
-182.718
-182
-183
ppm
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm
1.00


140.34
140.28
137.50
137.30
128.48
128.47
128.39
128.16
127.83
127.80
126.47
126.40
99.57
97.80
77.47
77.15
76.83
61.71
61.48
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

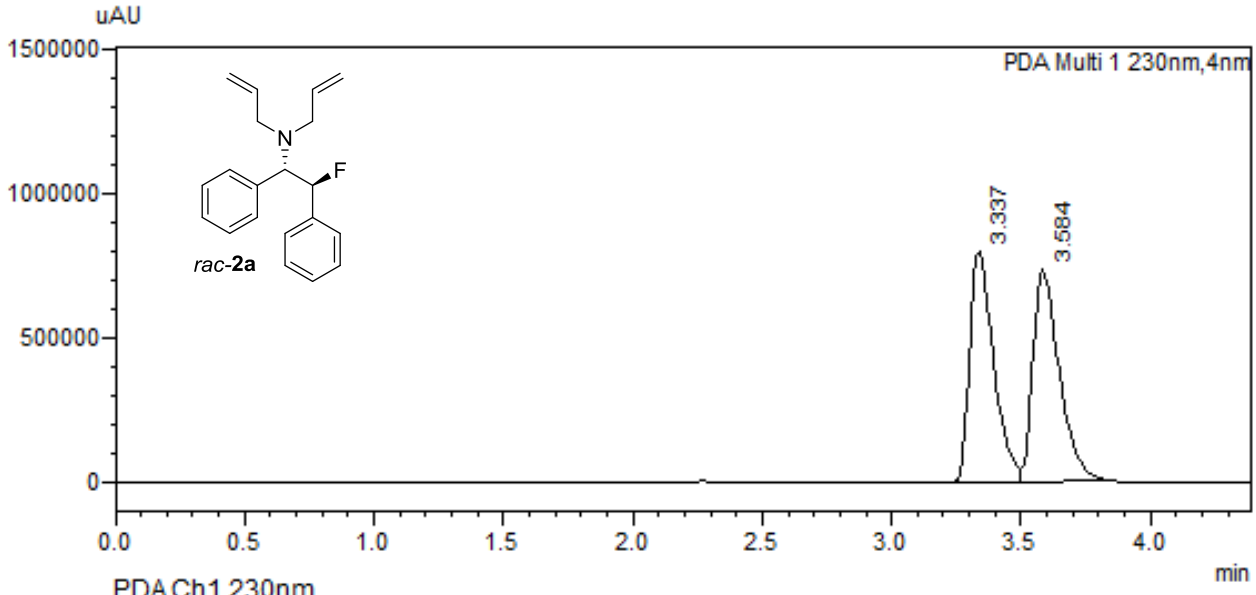

NH
F
(S,S)-5
ppm
-177
-178
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210


138.512
138.448
137.335
137.142
128.673
128.477
128.460
128.232
128.000
127.744
126.810
126.744
99.144
97.376
77.476
77.155
76.838
69.065
68.840
41.841
15.475
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


(S,S)-8
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.06
1.03
1.07
1.10
11.08
1.06
1.05
-188
-189
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00

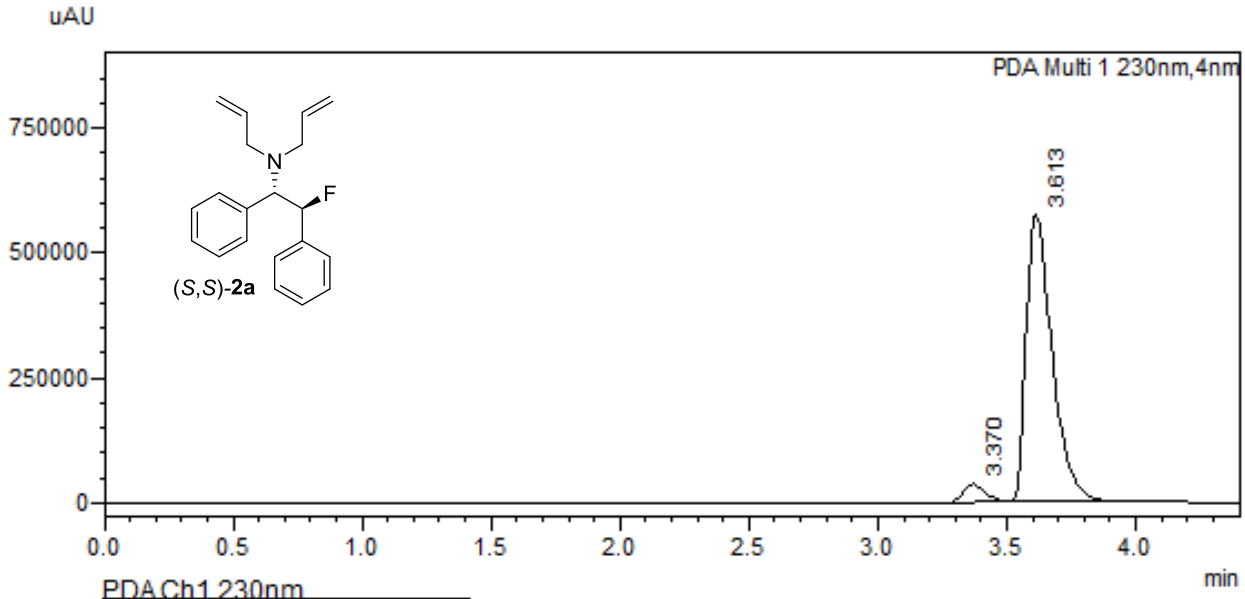

163.94
149.58
148.31
138.36
138.34
137.42
137.37
136.73
136.70
128.41
128.03
127.54
126.44
126.12
126.05
122.47
96.48
94.68
77.47
77.15
76.83
57.76
57.54
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

Copies of HPLC traces



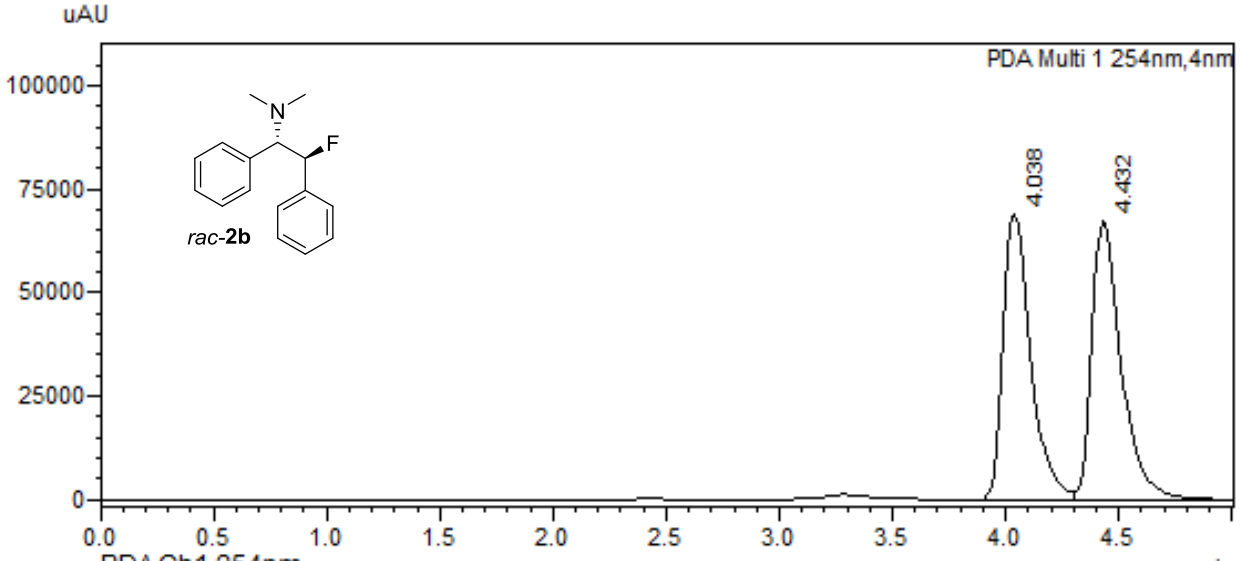
PDA Ch1 230nm

Peak#	Ret. Time	Area%
1	3.337	49.552
2	3.584	50.448



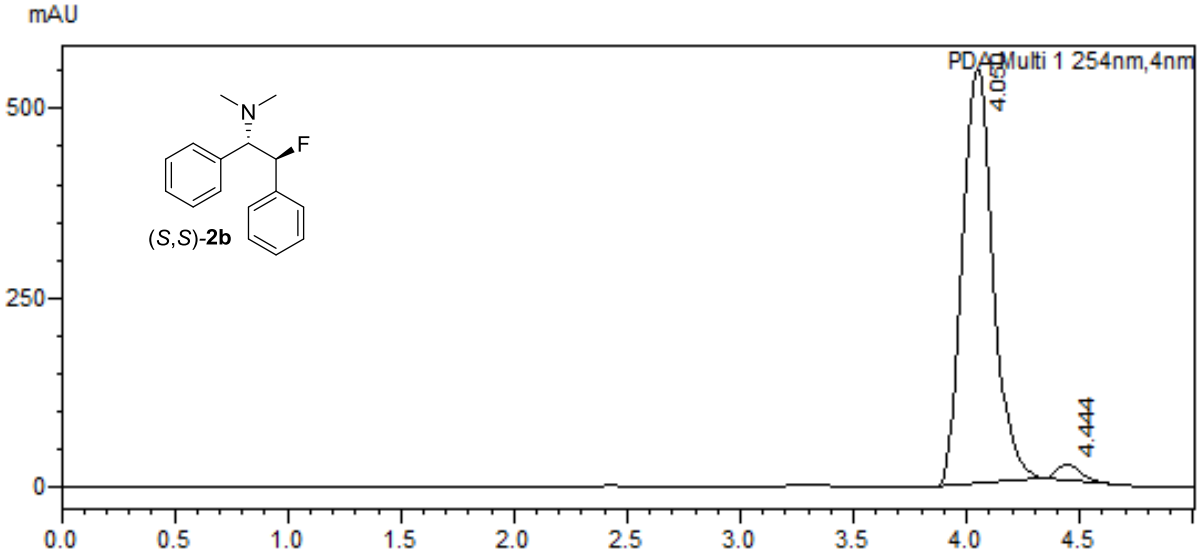
PDA Ch1 230nm

Peak#	Ret. Time	Area%
1	3.370	4.976
2	3.613	95.024



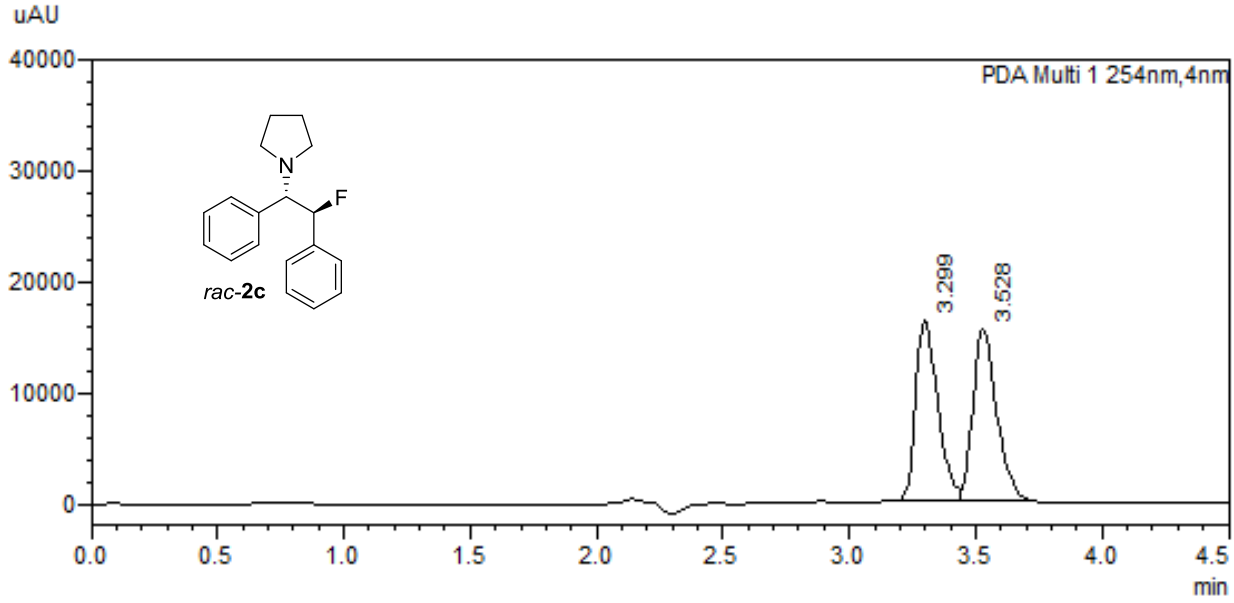
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	4.038	49.303
2	4.432	50.697



PDA Ch1 254nm

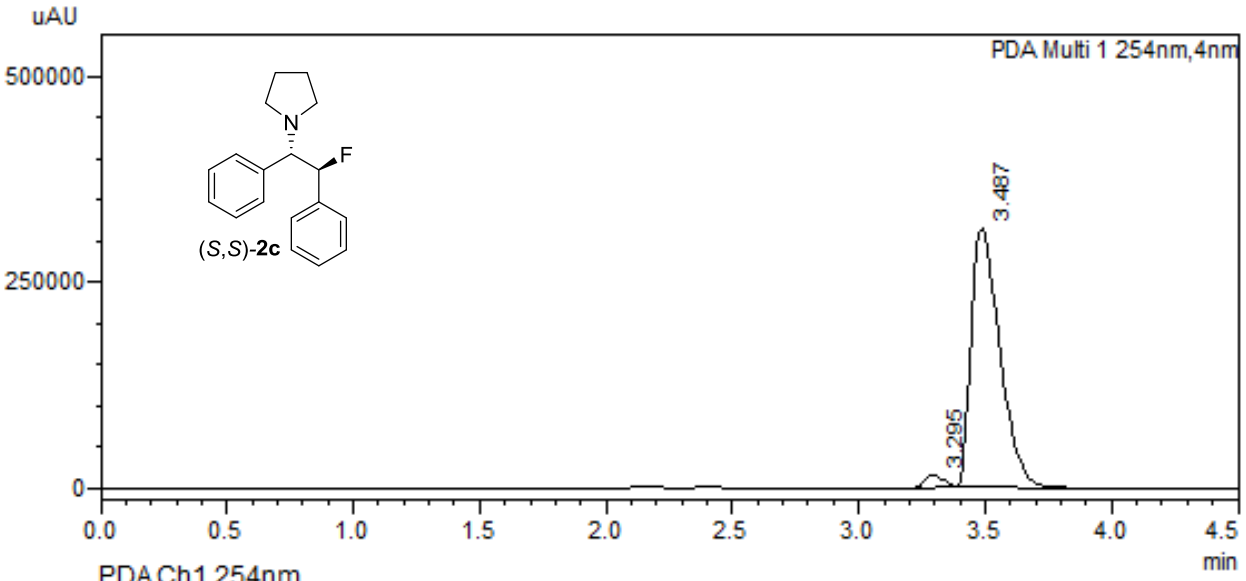
Peak#	Ret. Time	Area%
1	4.050	97.099
2	4.444	2.901



rac-**2c**

PDA Ch1 254nm

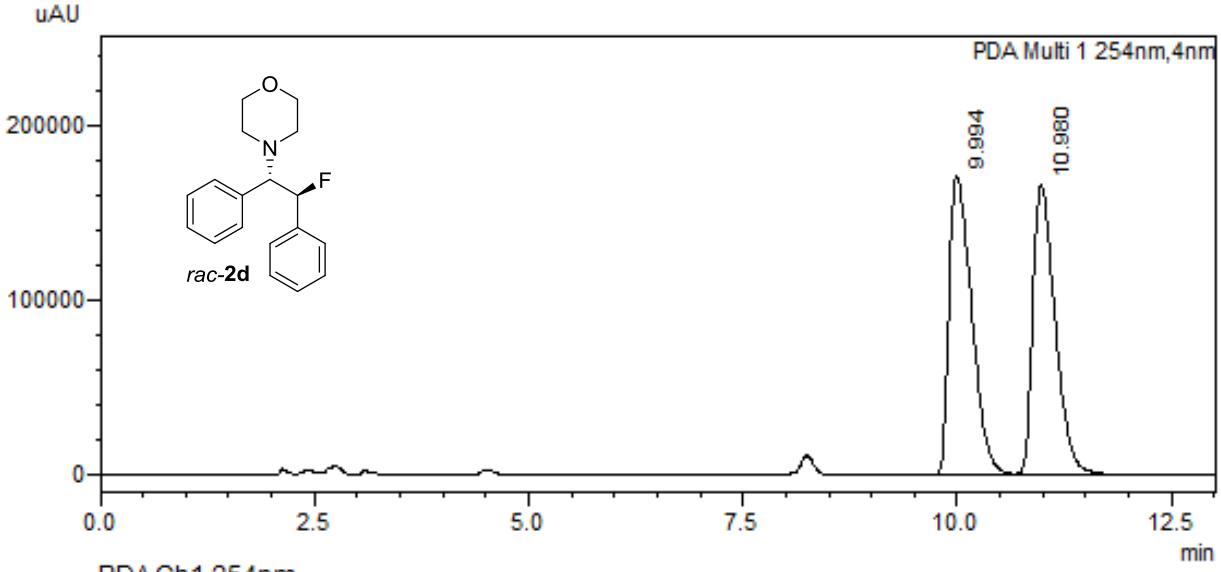
Peak#	Ret. Time	Area%
1	3.299	49.292
2	3.528	50.708



(*S*,*S*)-**2c**

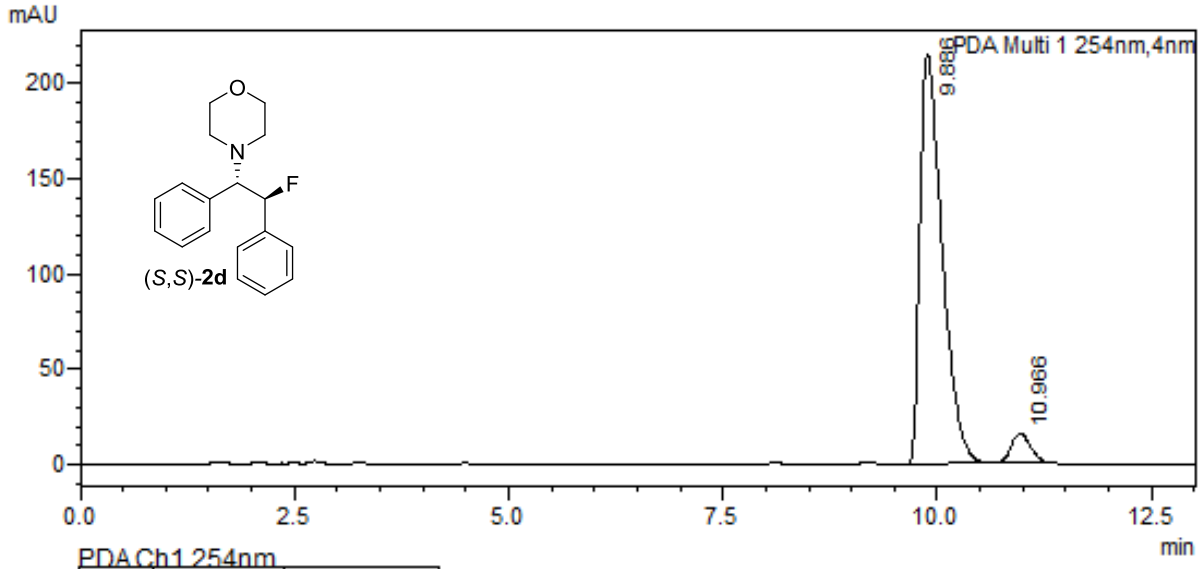
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	3.295	2.841
2	3.487	97.159



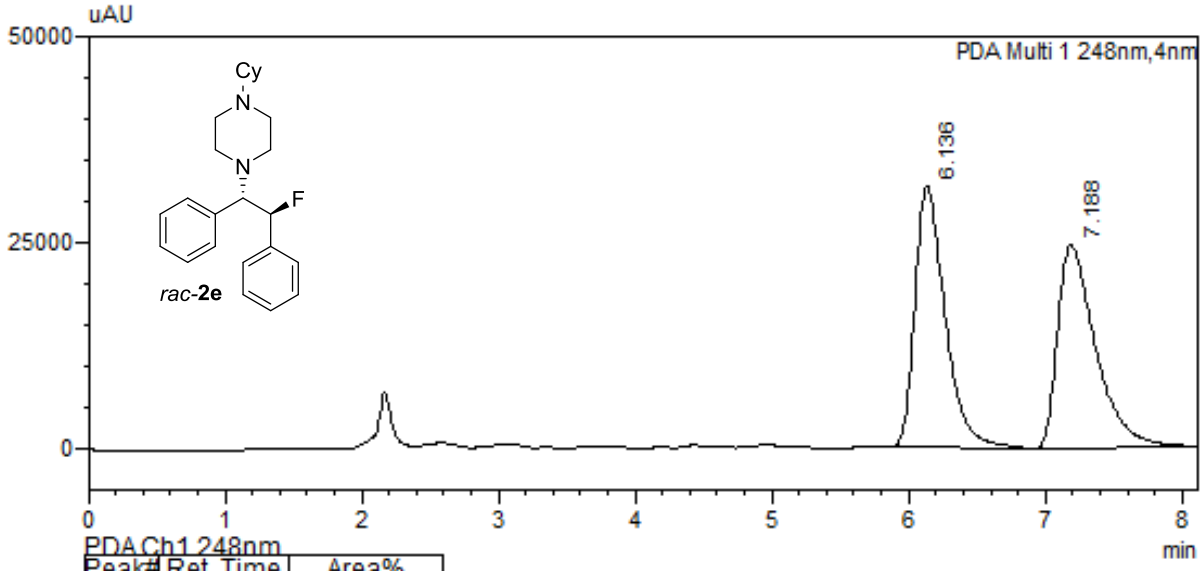
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	9.994	51.167
2	10.980	48.833



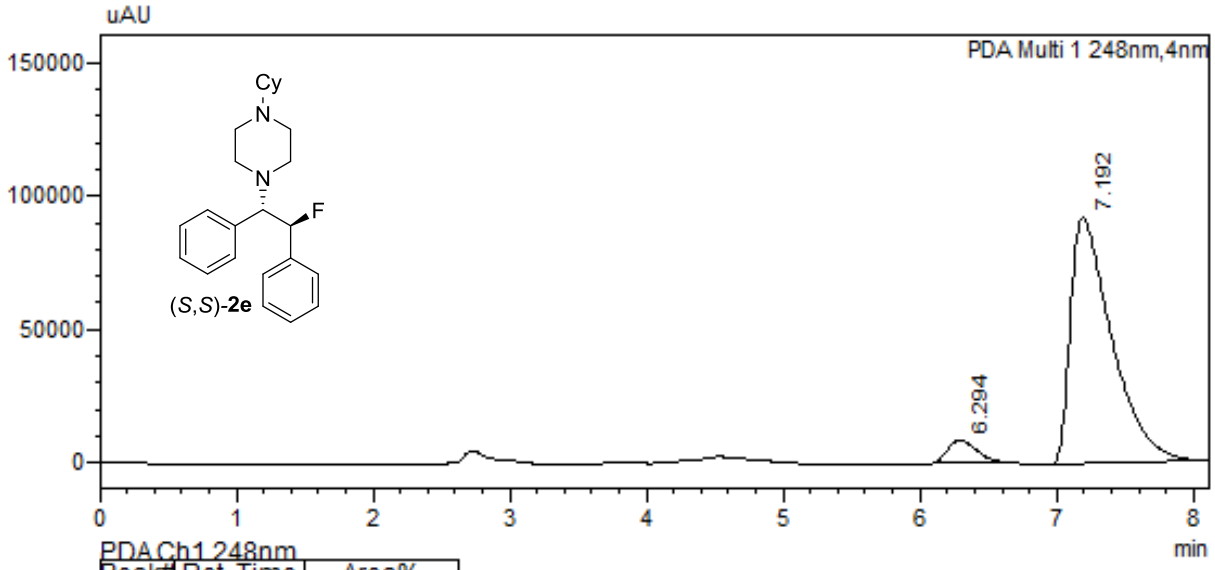
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	9.886	94.310
2	10.966	5.690



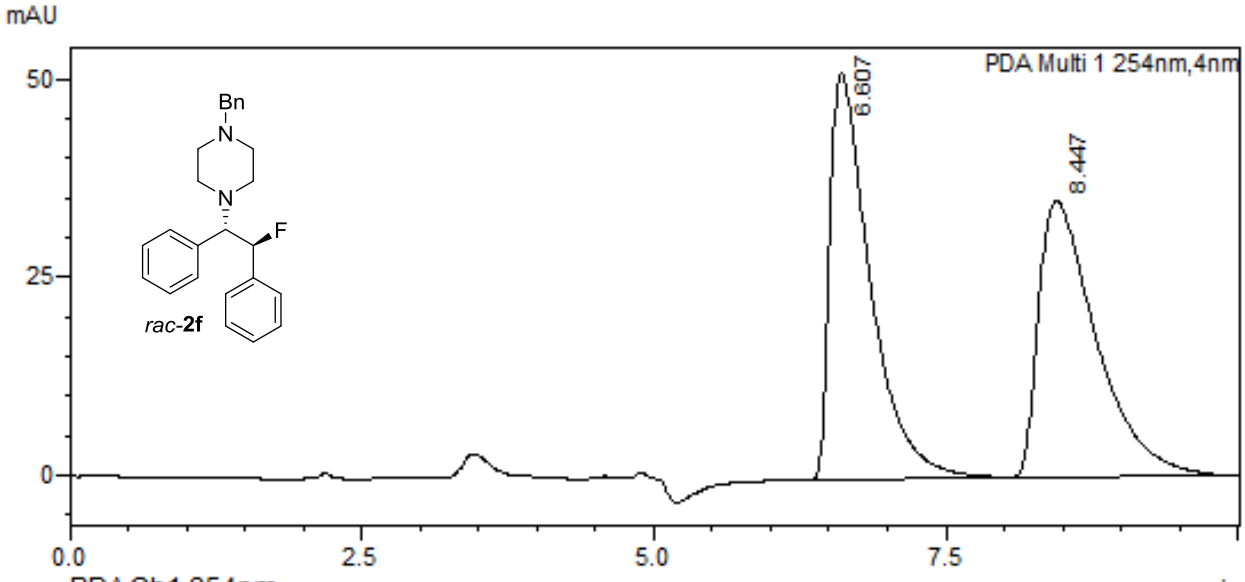
PDA Ch1 248nm

Peak#	Ret. Time	Area%
1	6.136	50.389
2	7.188	49.611



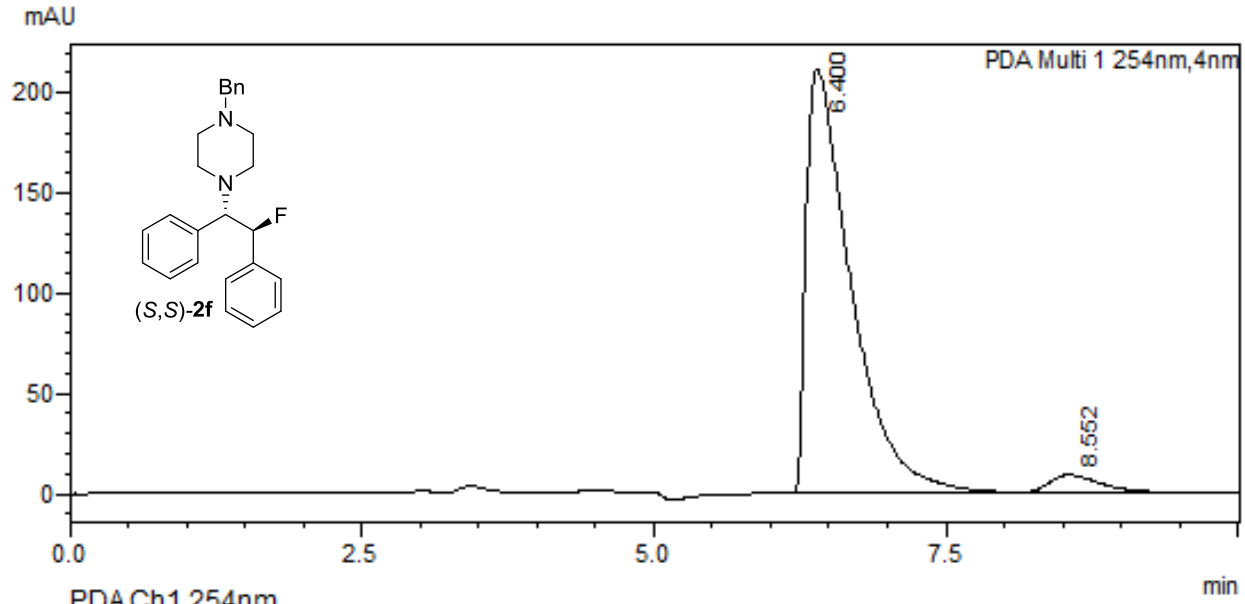
PDA Ch1 248nm

Peak#	Ret. Time	Area%
1	6.294	5.850
2	7.192	94.150



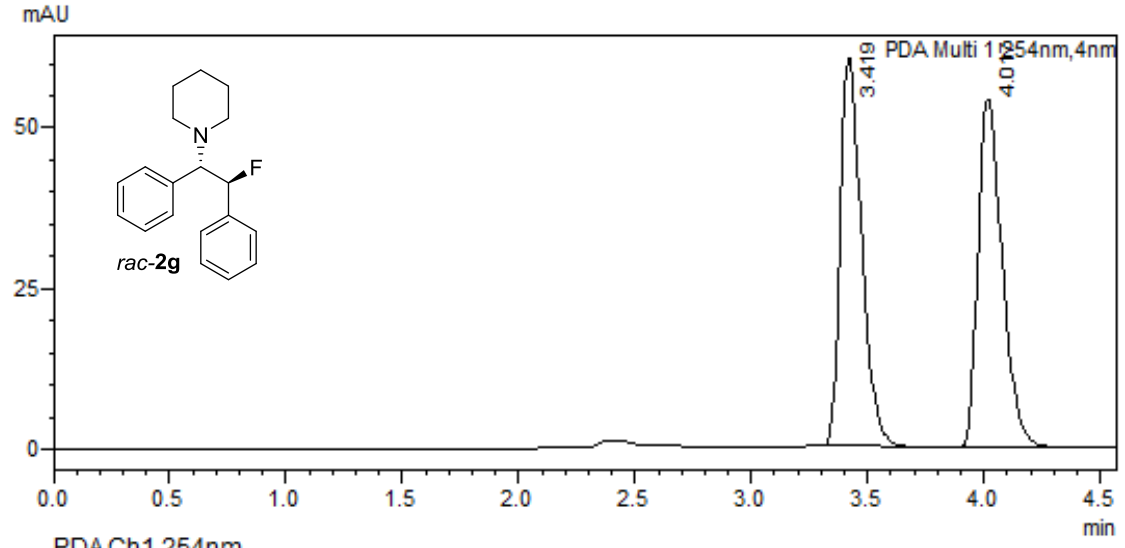
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	6.607	50.657
2	8.447	49.343



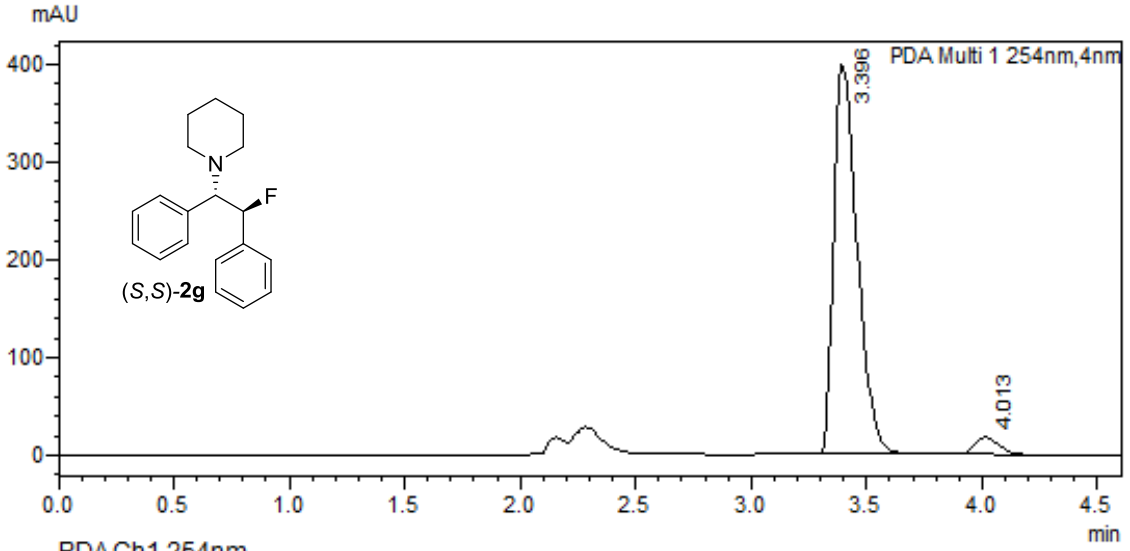
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	6.400	95.545
2	8.552	4.455



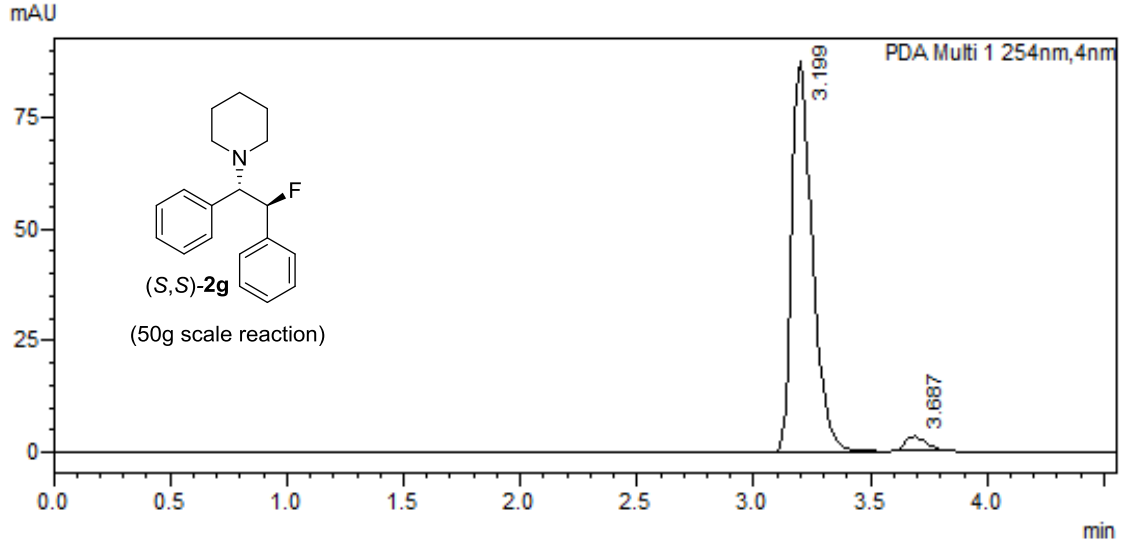
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	3.419	49.742
2	4.017	50.258



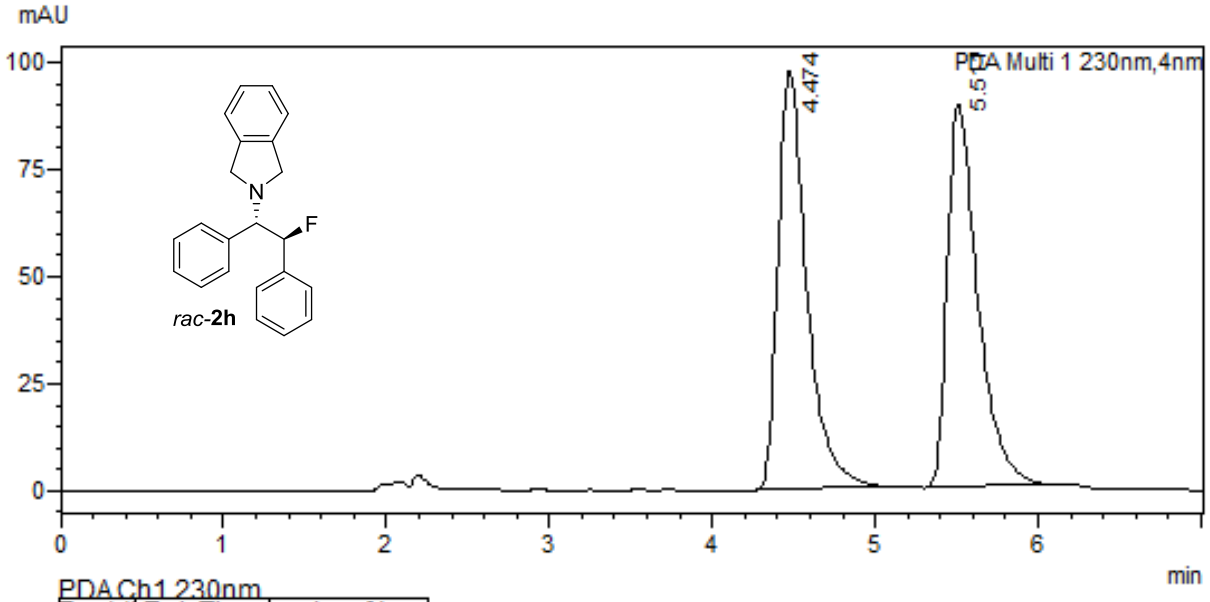
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	3.396	96.123
2	4.013	3.877



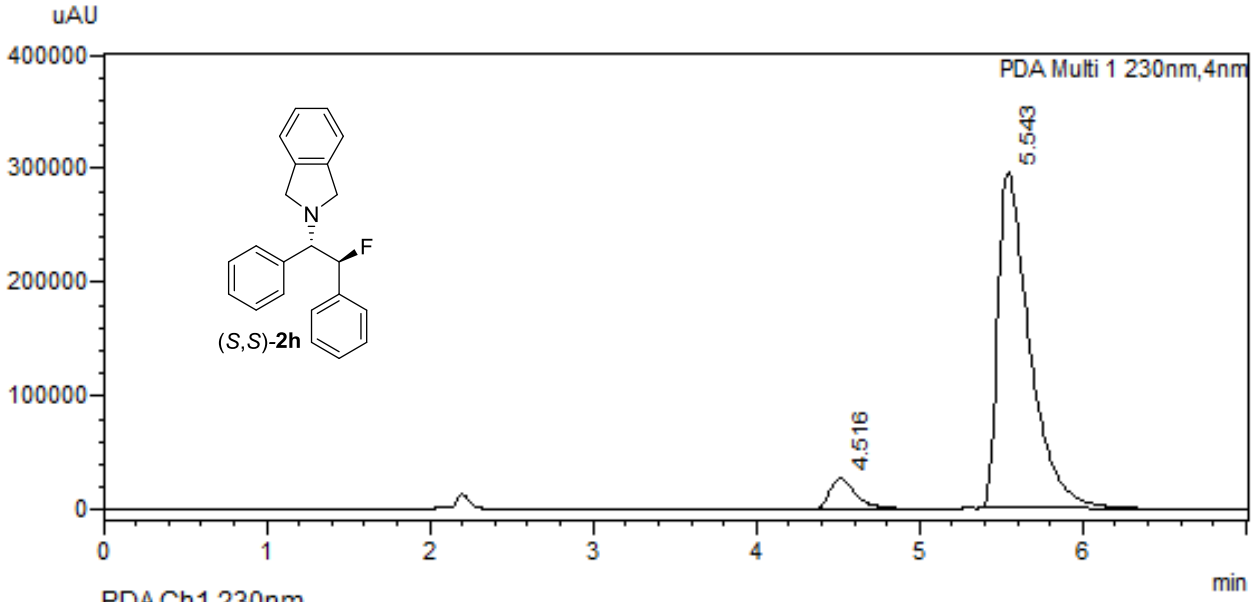
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	3.199	96.958
2	3.687	3.042



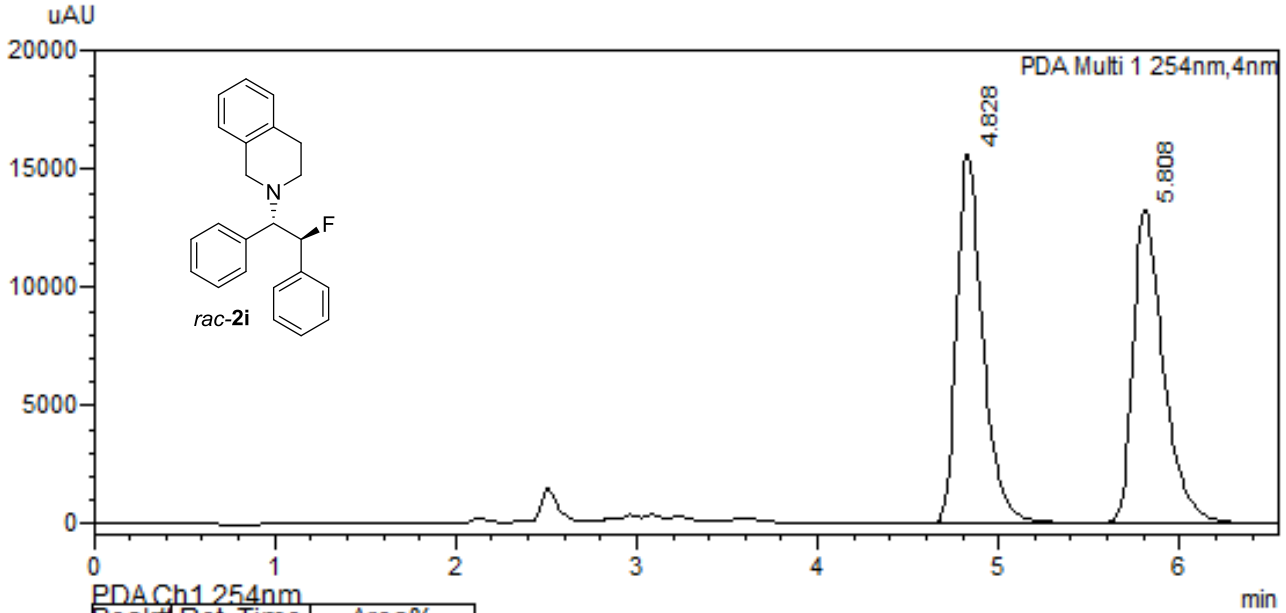
PDA Ch1 230nm

Peak#	Ret. Time	Area%
1	4.474	50.996
2	5.511	49.004



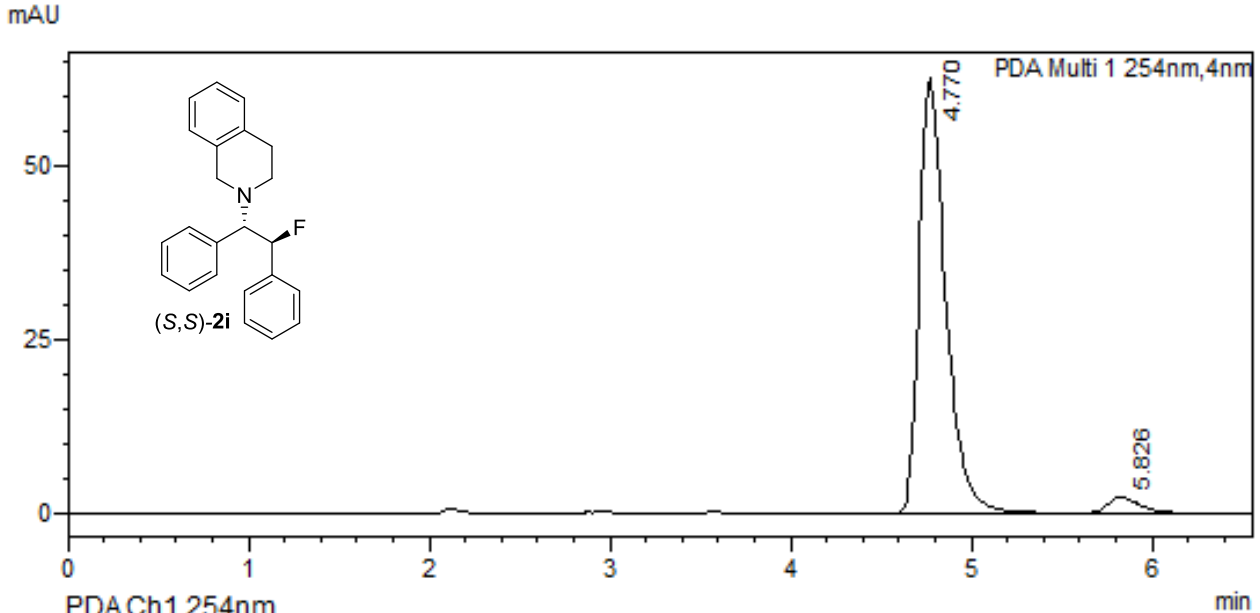
PDA Ch1 230nm

Peak#	Ret. Time	Area%
1	4.516	6.827
2	5.543	93.173



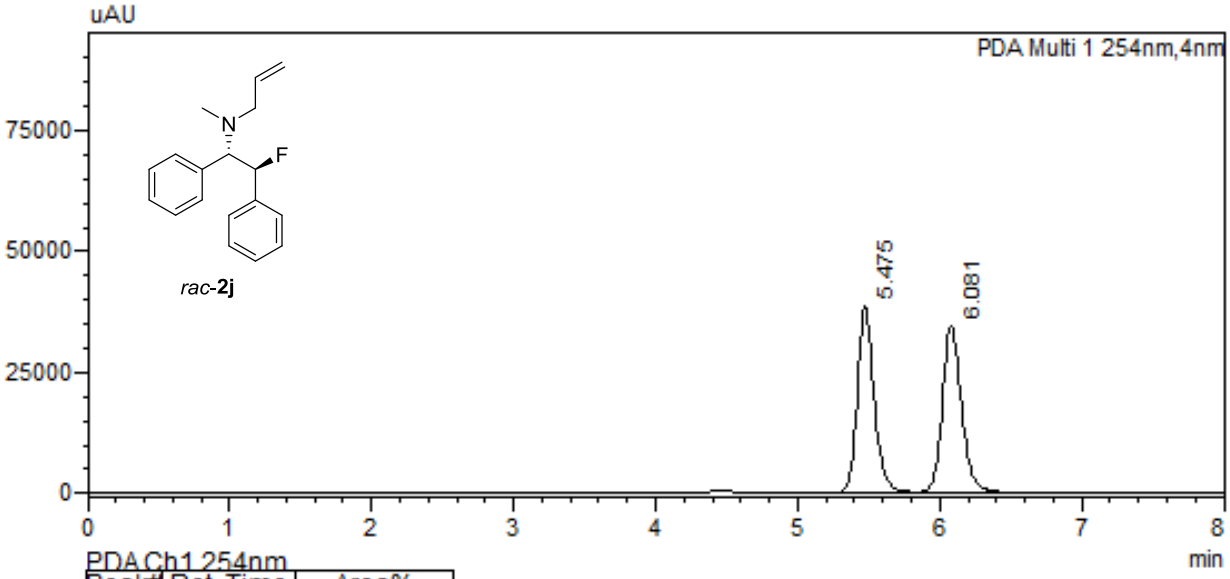
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	4.828	50.192
2	5.808	49.808



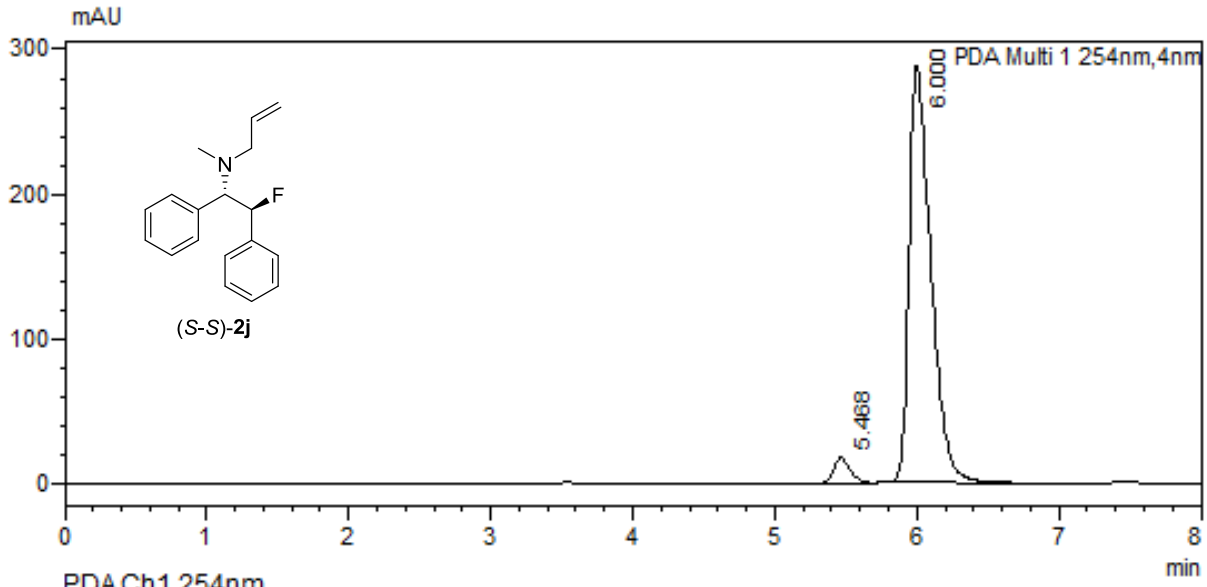
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	4.770	95.945
2	5.826	4.055



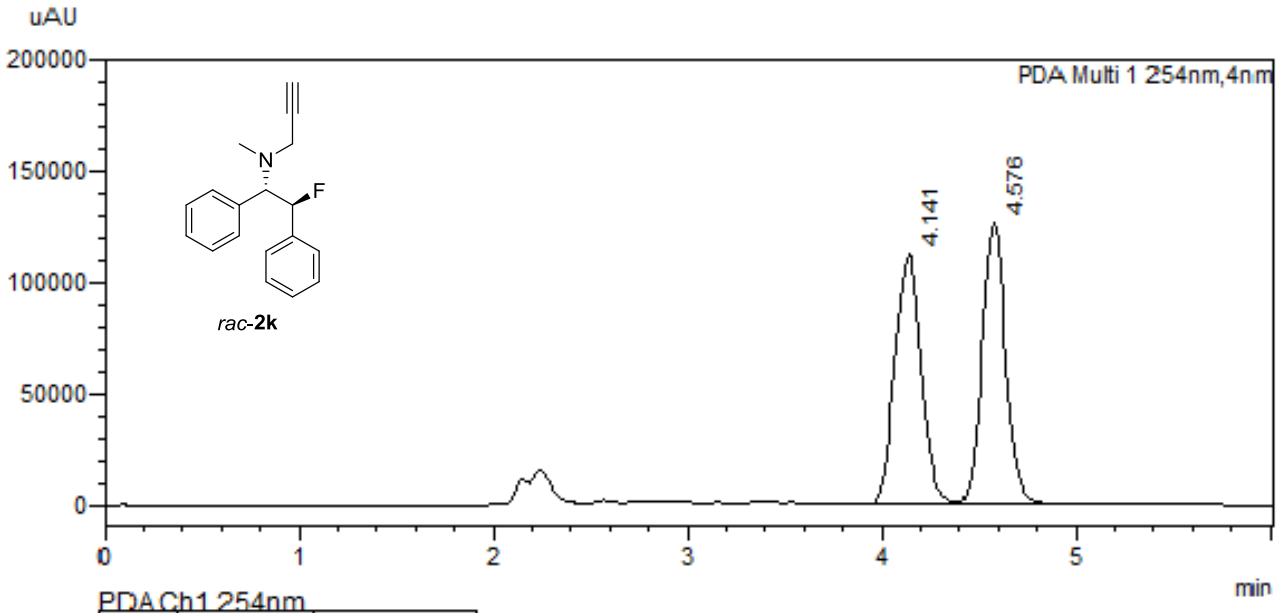
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	5.475	49.808
2	6.081	50.192



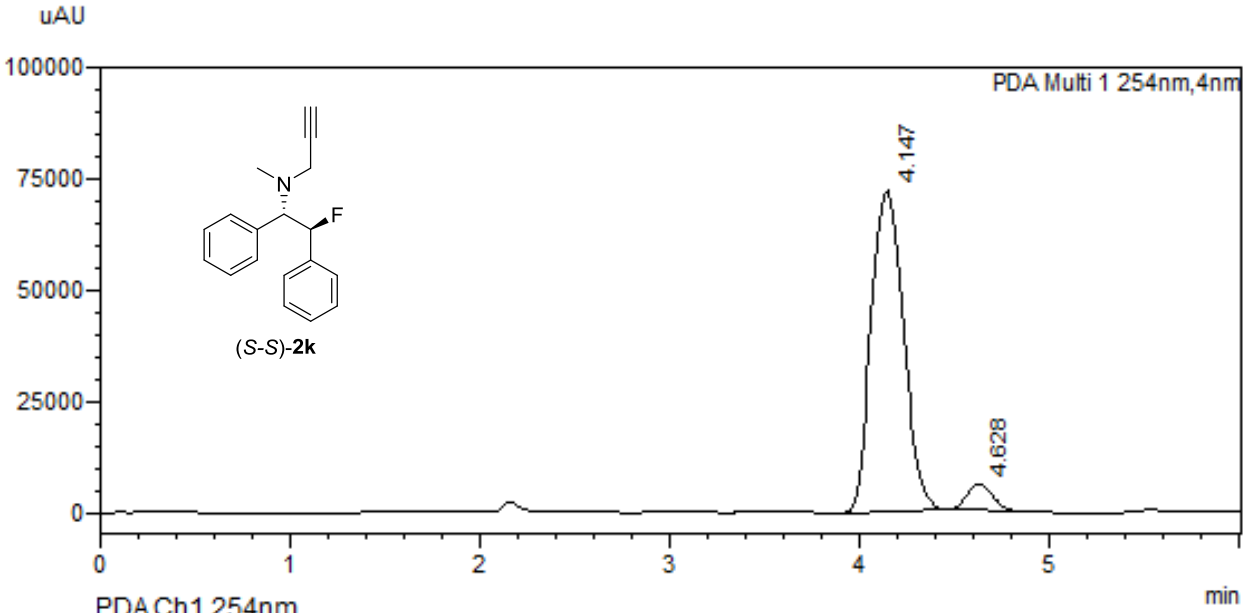
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	5.468	4.442
2	6.000	95.558



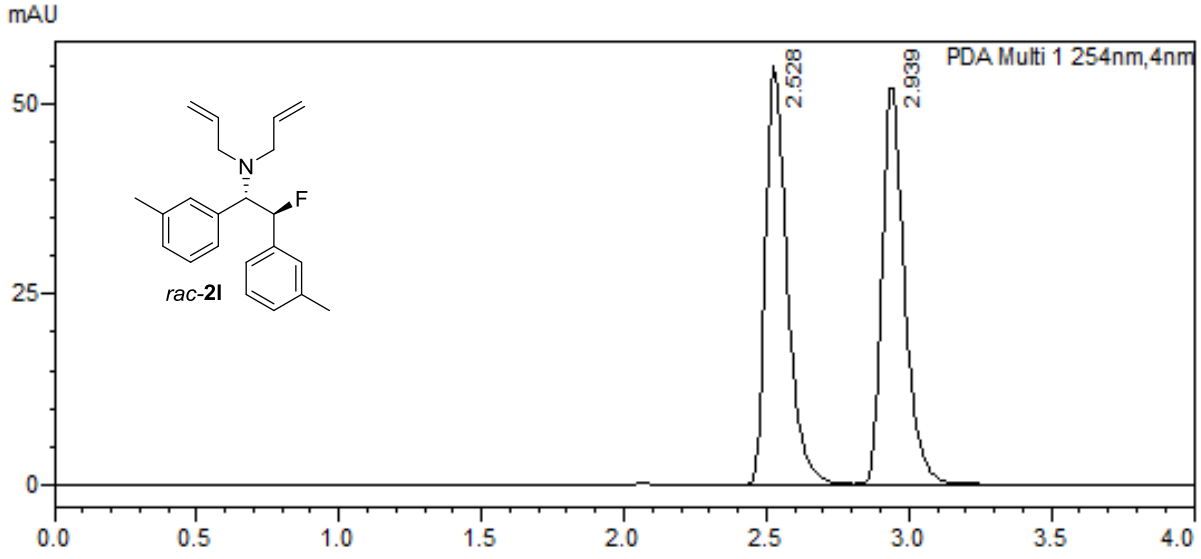
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	4.141	49.913
2	4.576	50.087



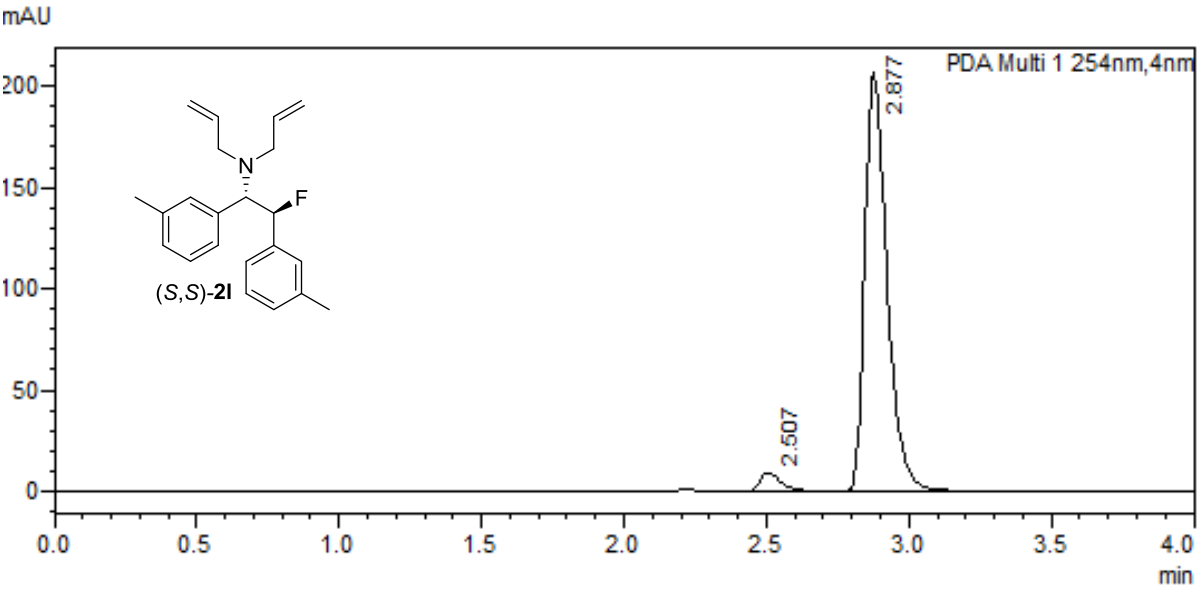
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	4.147	93.899
2	4.628	6.101



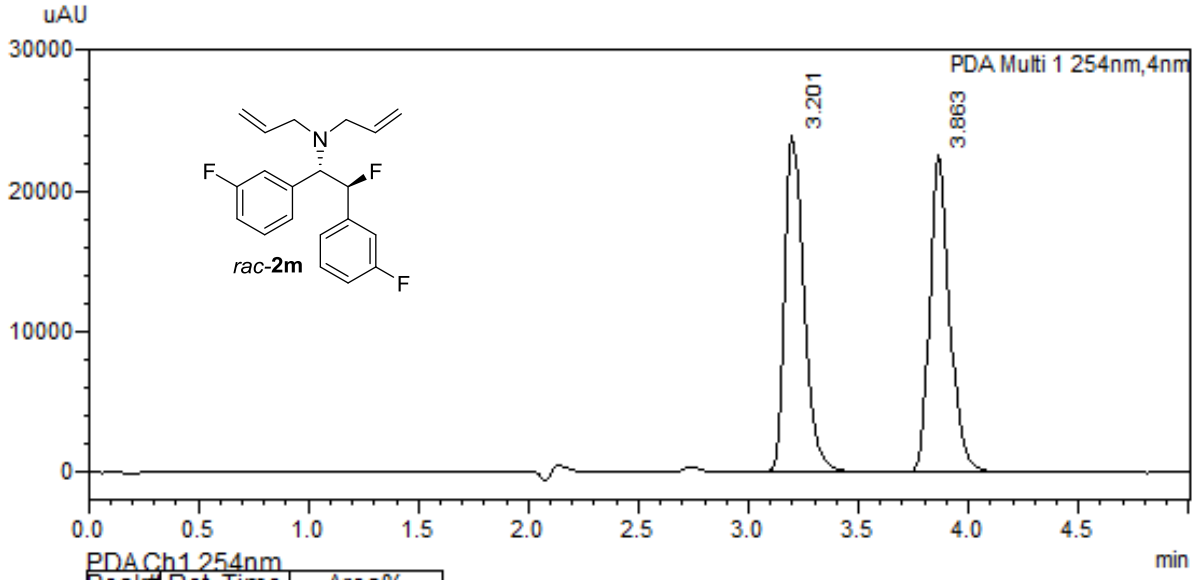
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	2.528	49.907
2	2.939	50.093



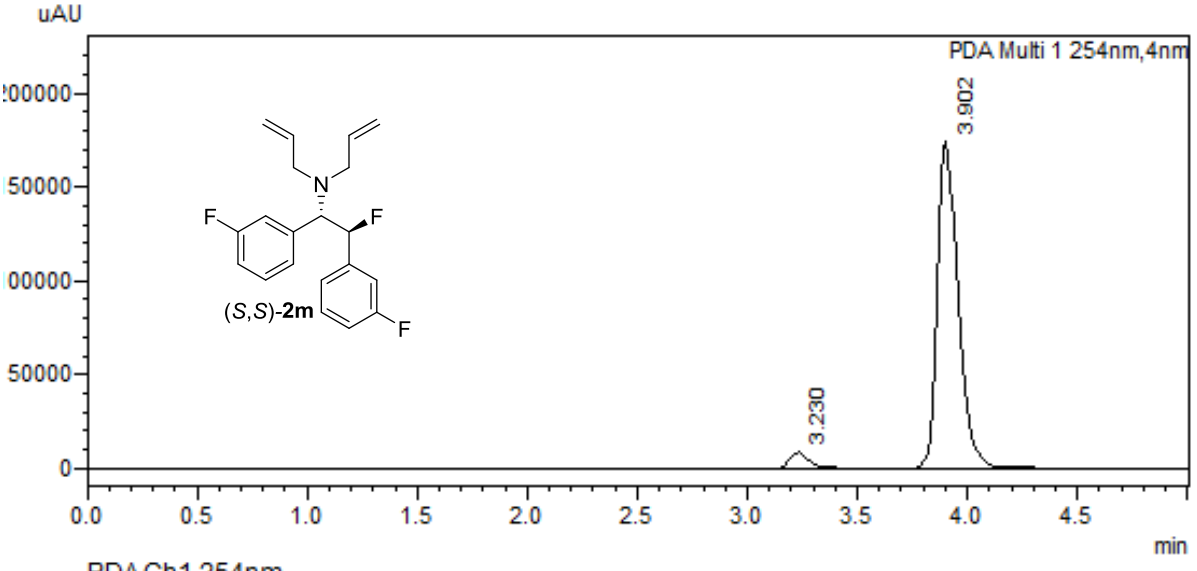
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	2.507	3.916
2	2.877	96.084



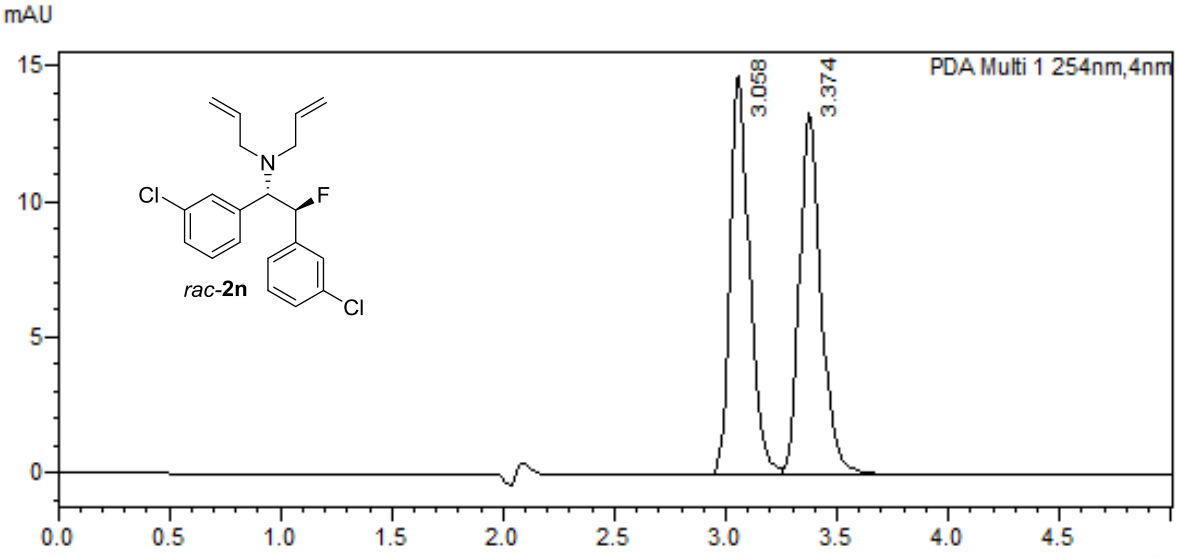
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	3.201	50.440
2	3.863	49.560



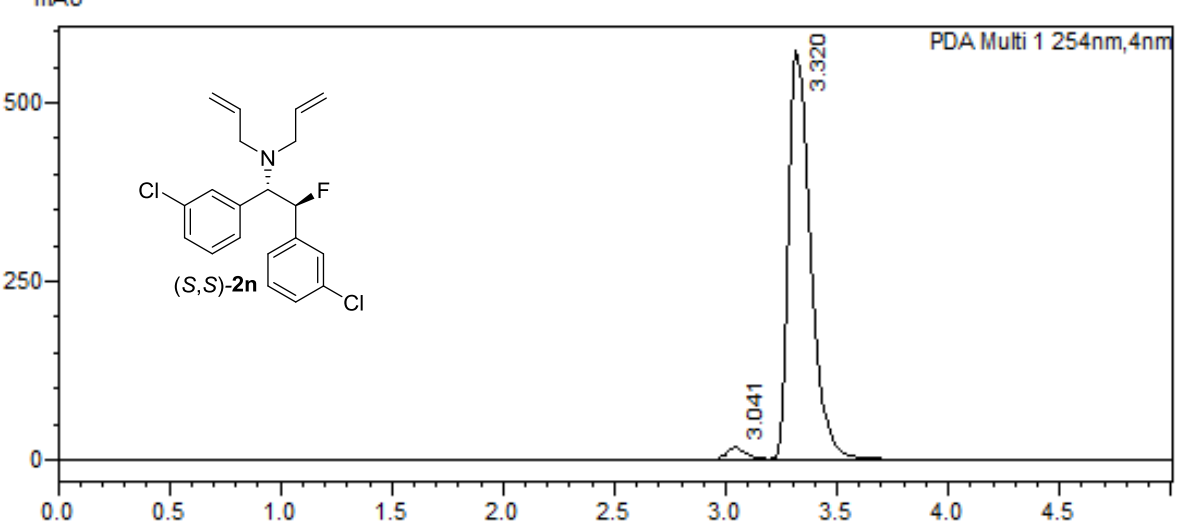
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	3.230	4.323
2	3.902	95.677



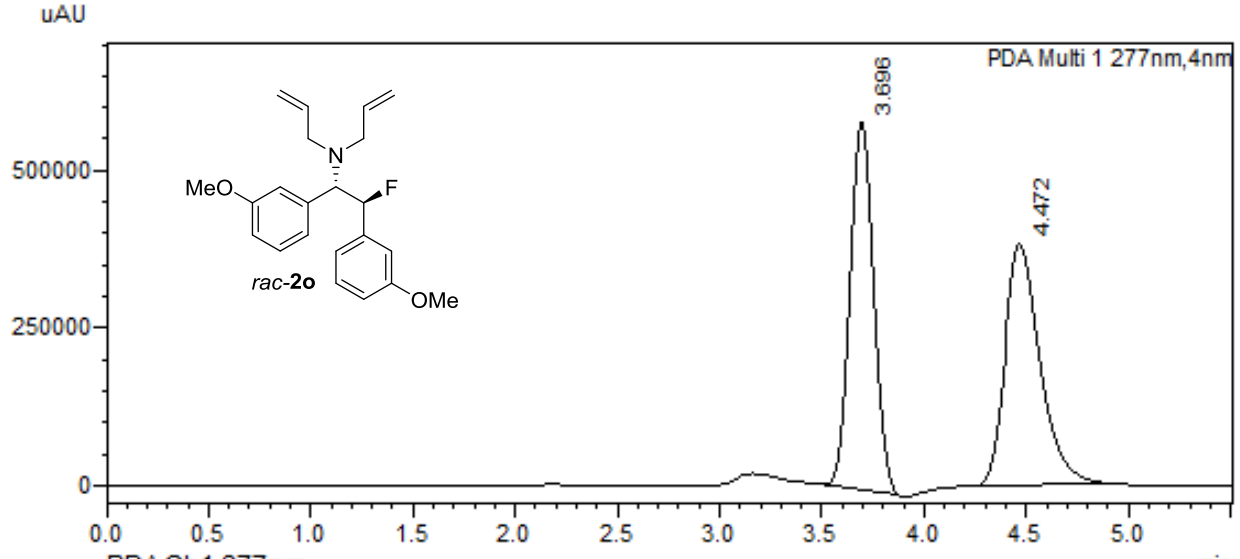
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	3.058	50.151
2	3.374	49.849



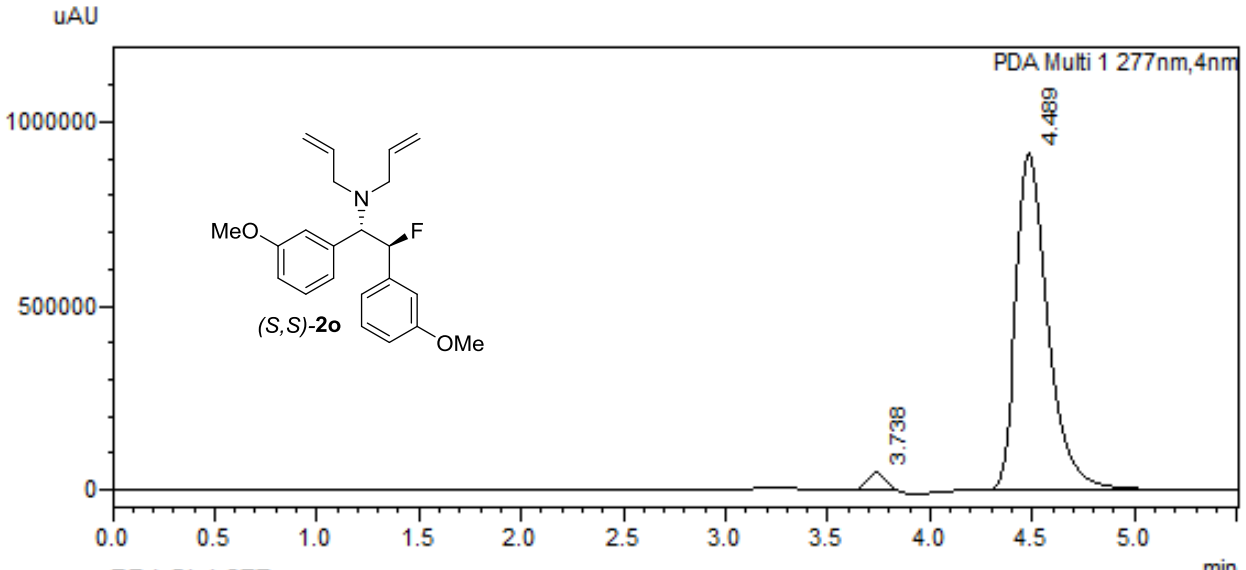
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	3.041	2.488
2	3.320	97.512



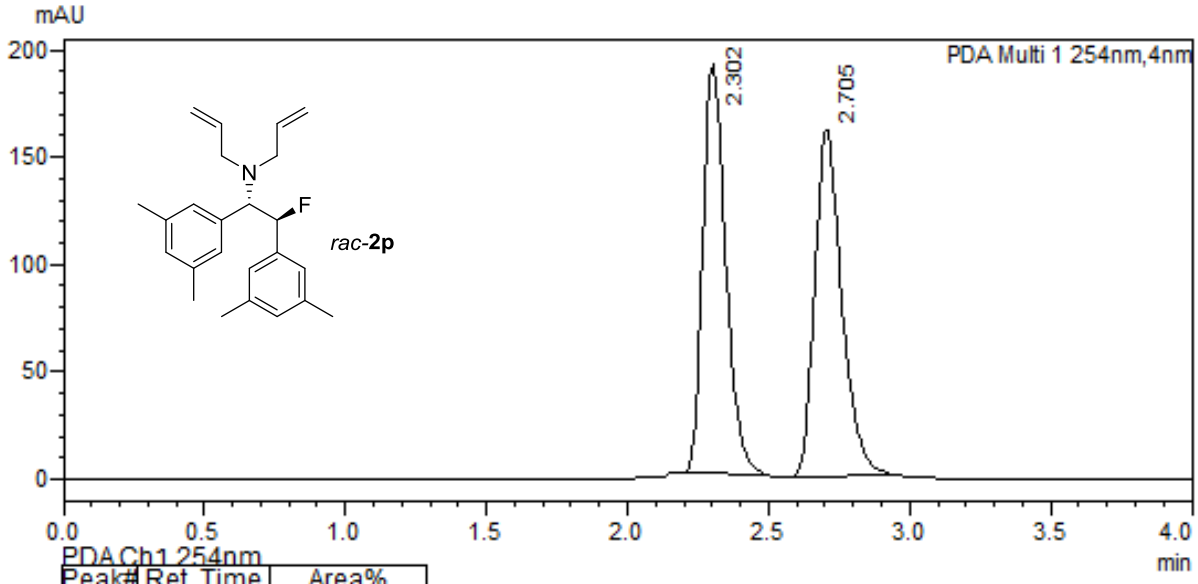
PDA Ch1 277nm

Peak#	Ret. Time	Area%
1	3.696	49.769
2	4.472	50.231



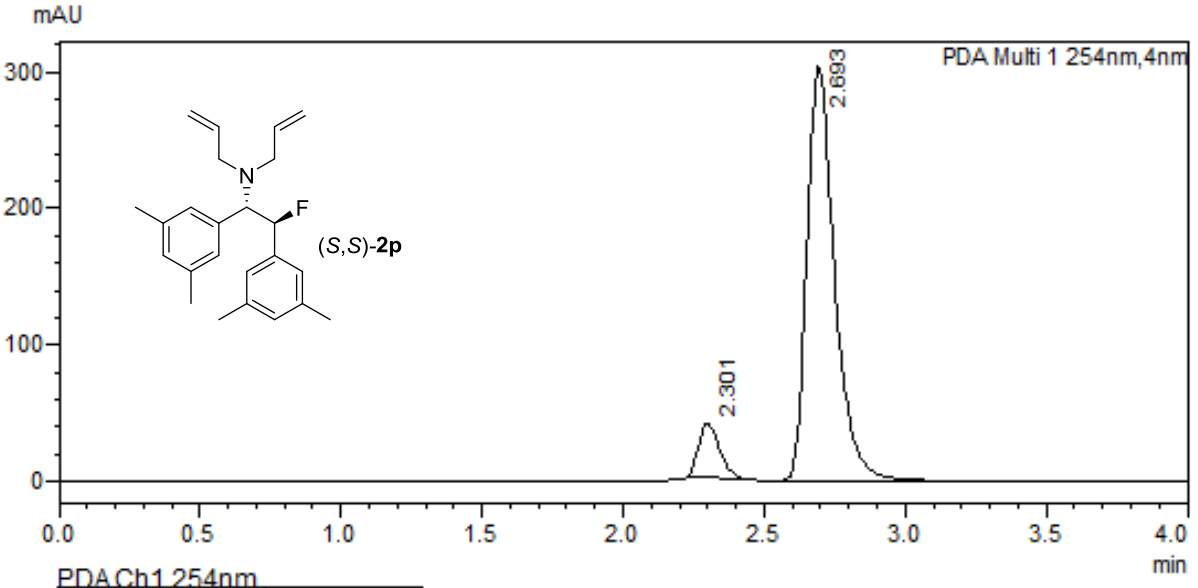
PDA Ch1 277nm

Peak#	Ret. Time	Area%
1	3.738	2.348
2	4.489	97.652



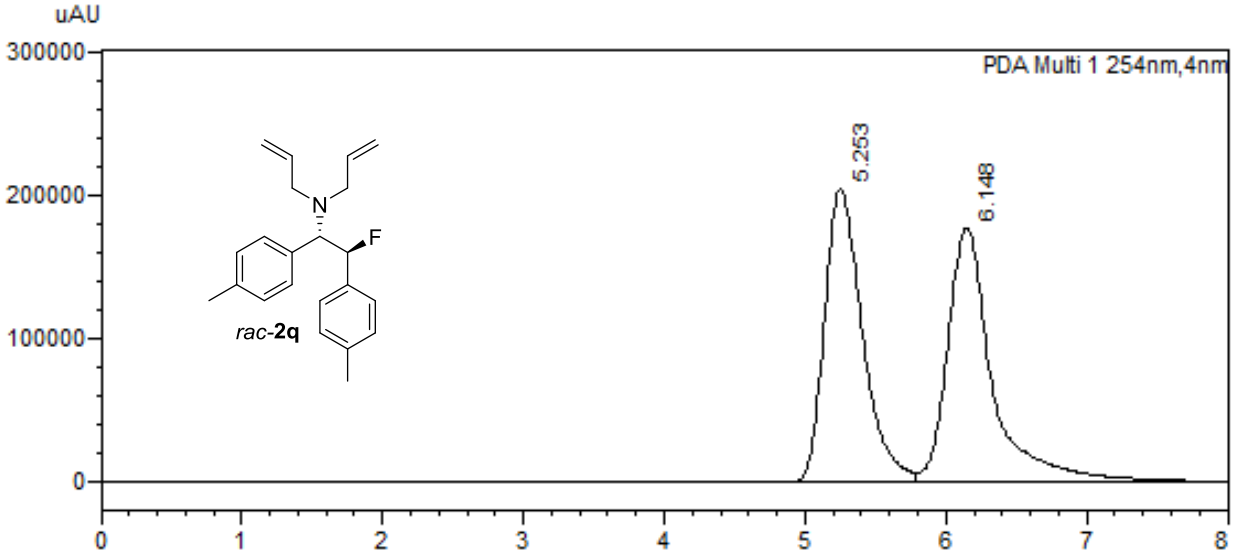
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	2.302	49.679
2	2.705	50.321



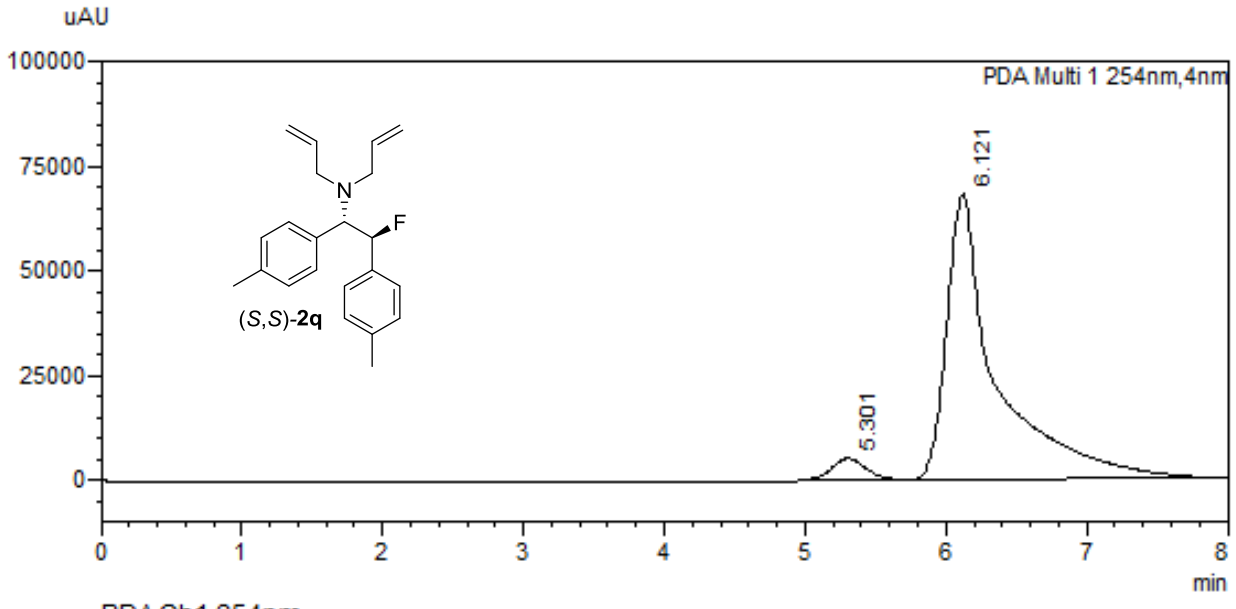
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	2.301	9.079
2	2.693	90.921



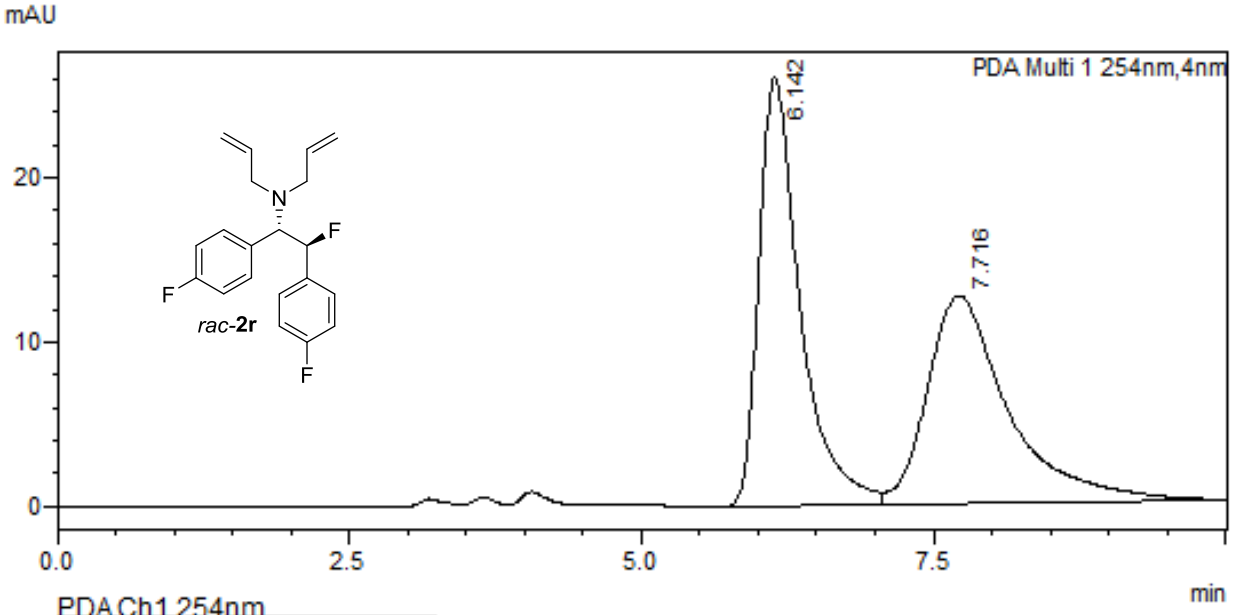
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	5.253	49.547
2	6.148	50.453



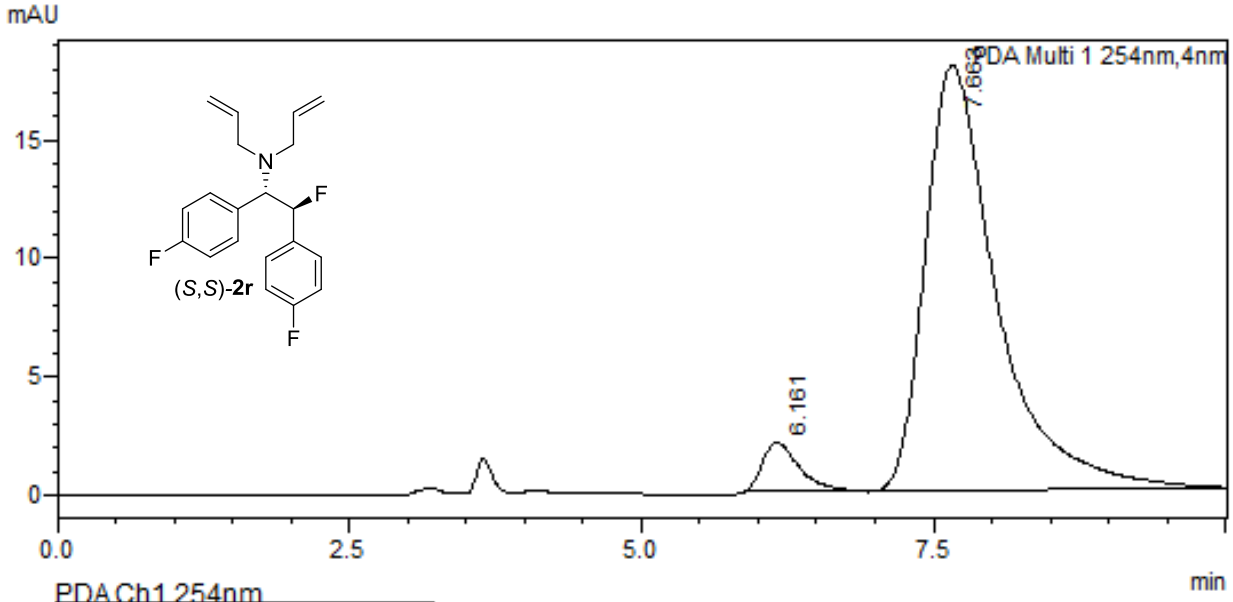
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	5.301	4.872
2	6.121	95.128



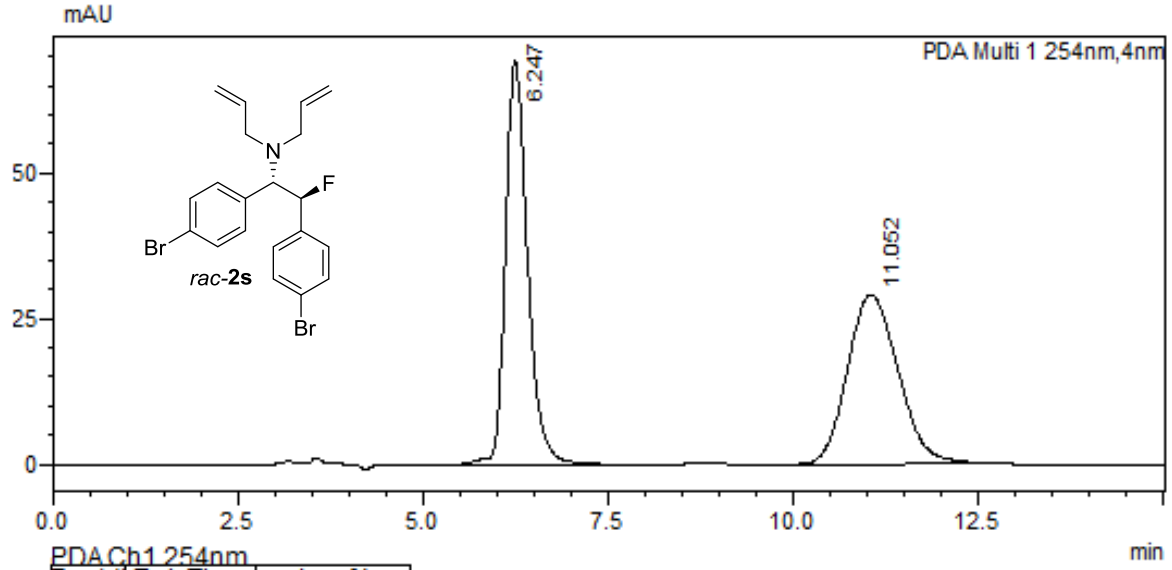
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	6.142	51.021
2	7.716	48.979



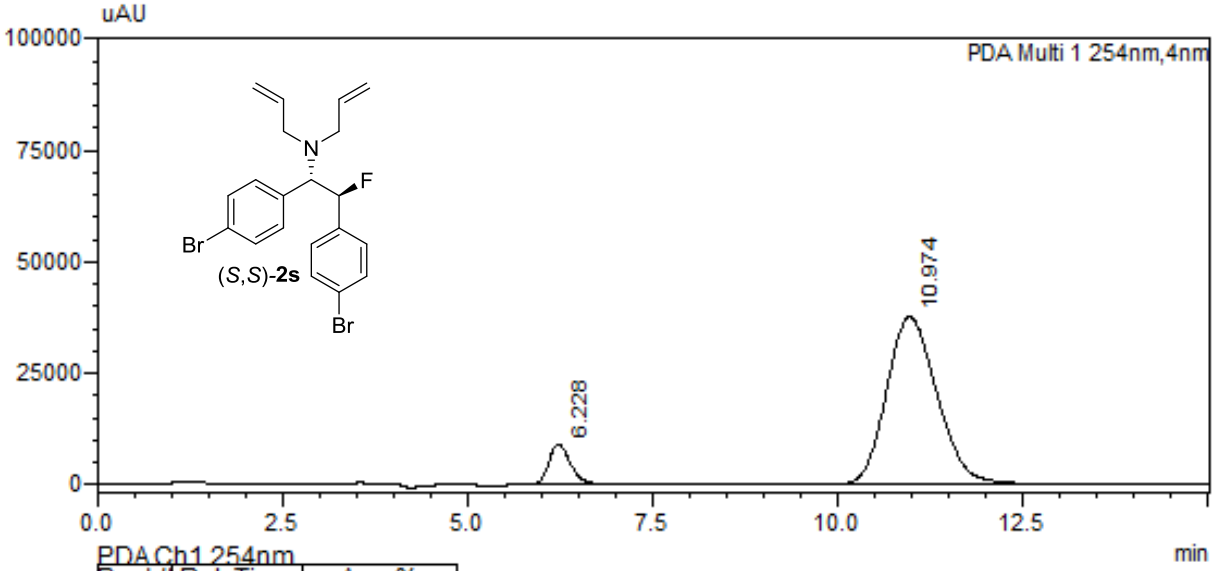
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	6.161	5.120
2	7.663	94.880



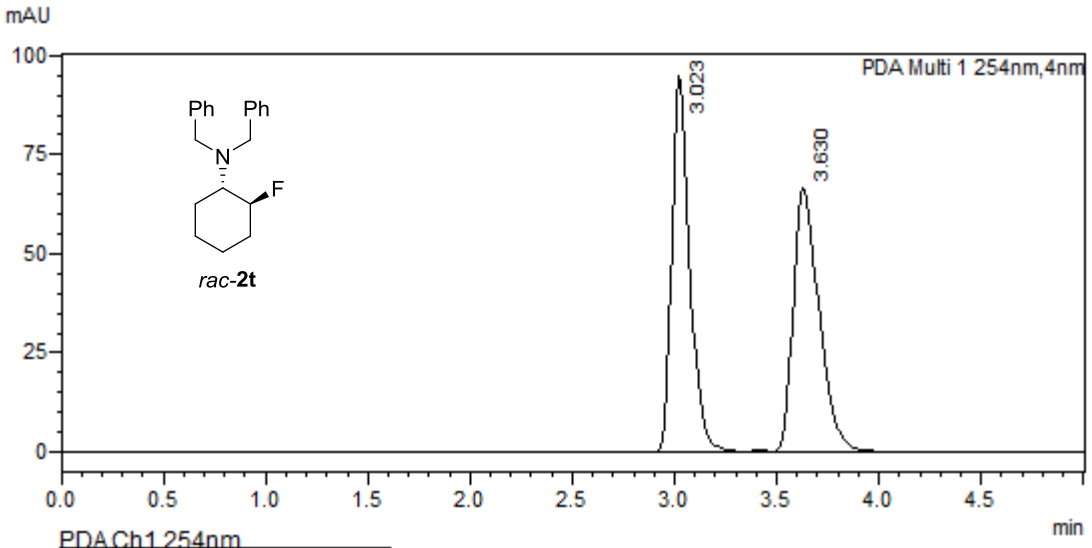
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	6.247	50.796
2	11.052	49.204



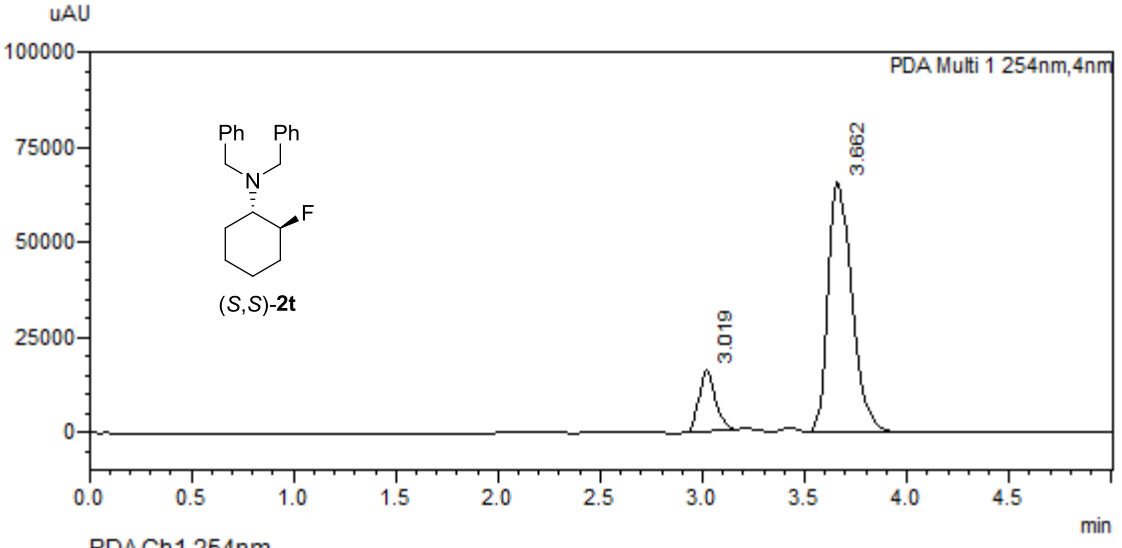
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	6.228	8.855
2	10.974	91.145



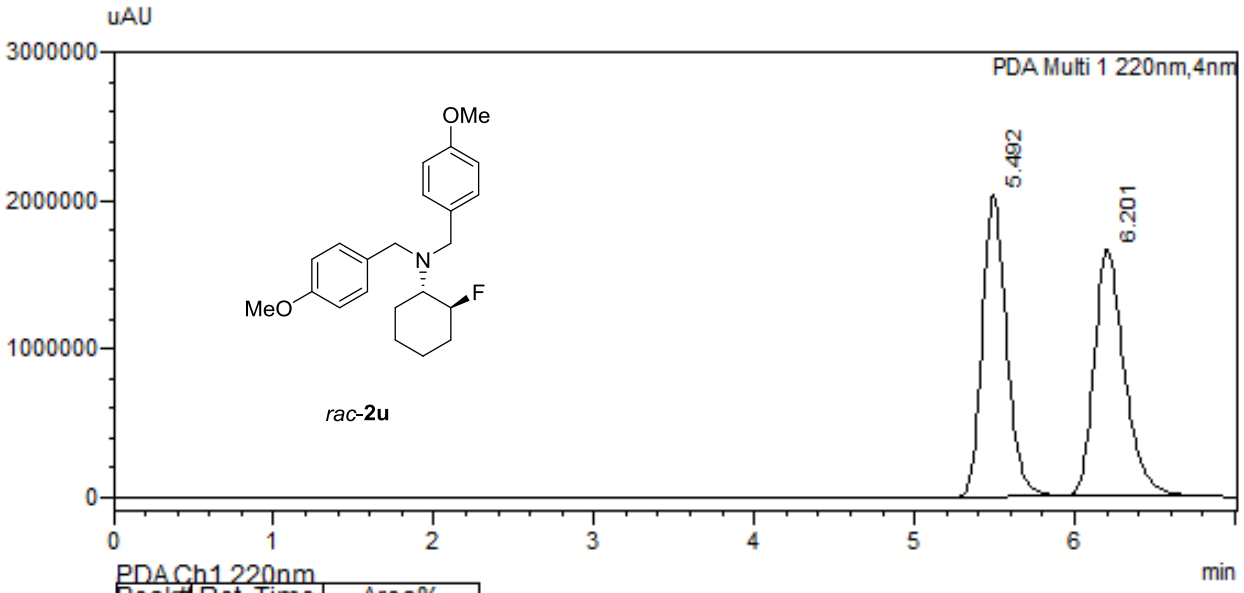
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	3.023	49.580
2	3.630	50.420



PDA Ch1 254nm

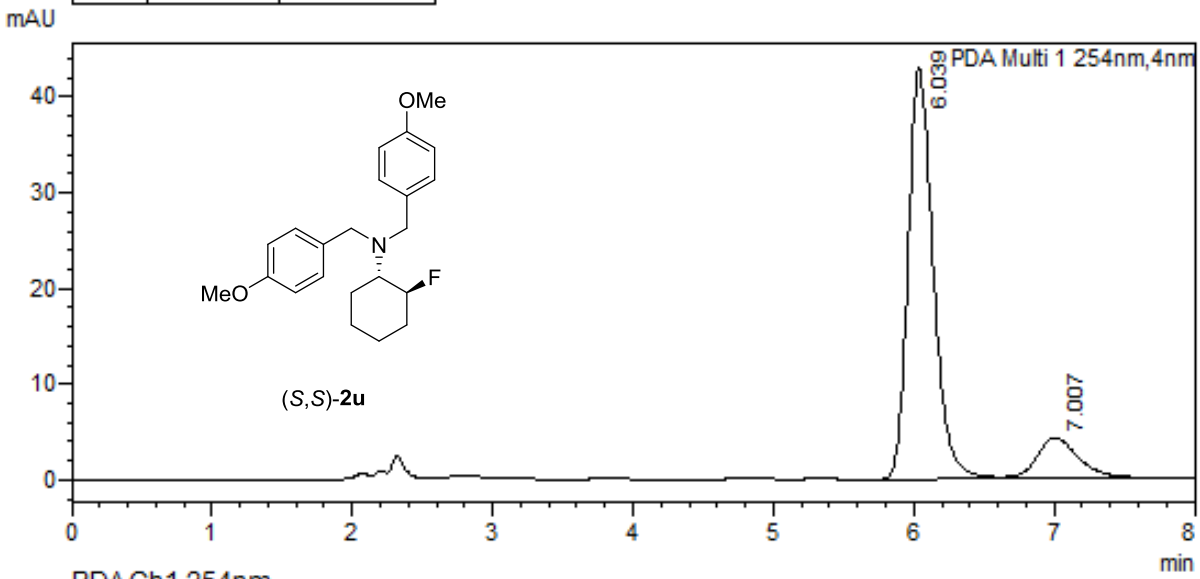
Peak#	Ret. Time	Area%
1	3.019	14.356
2	3.662	85.644



rac-**2u**

PDA Ch1 220nm

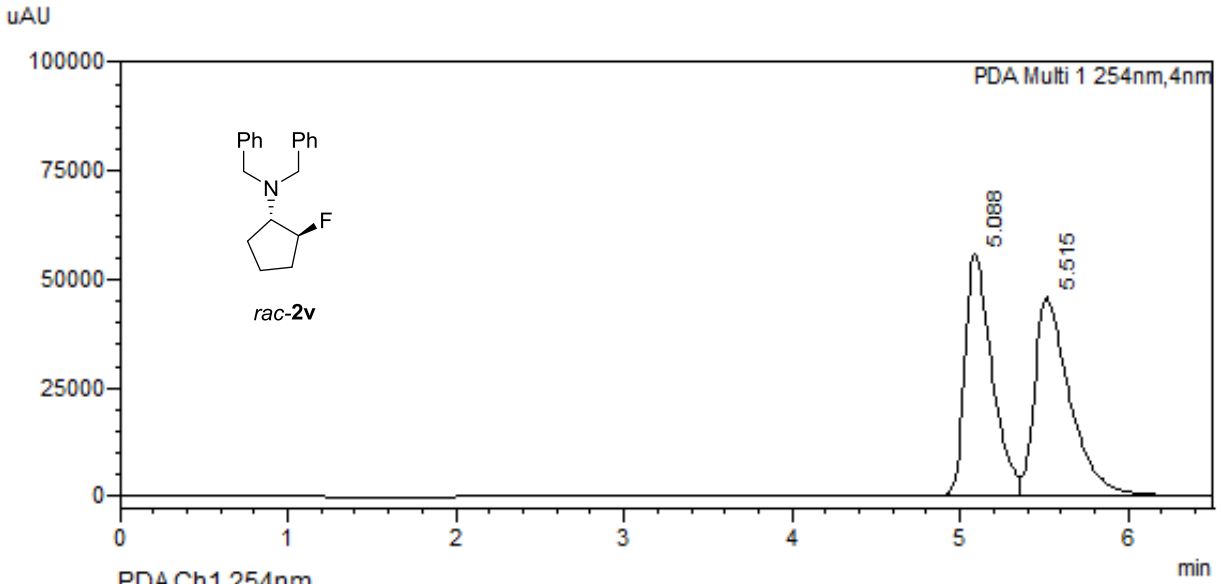
Peak#	Ret. Time	Area%
1	5.492	49.533
2	6.201	50.467



(*S*,*S*)-**2u**

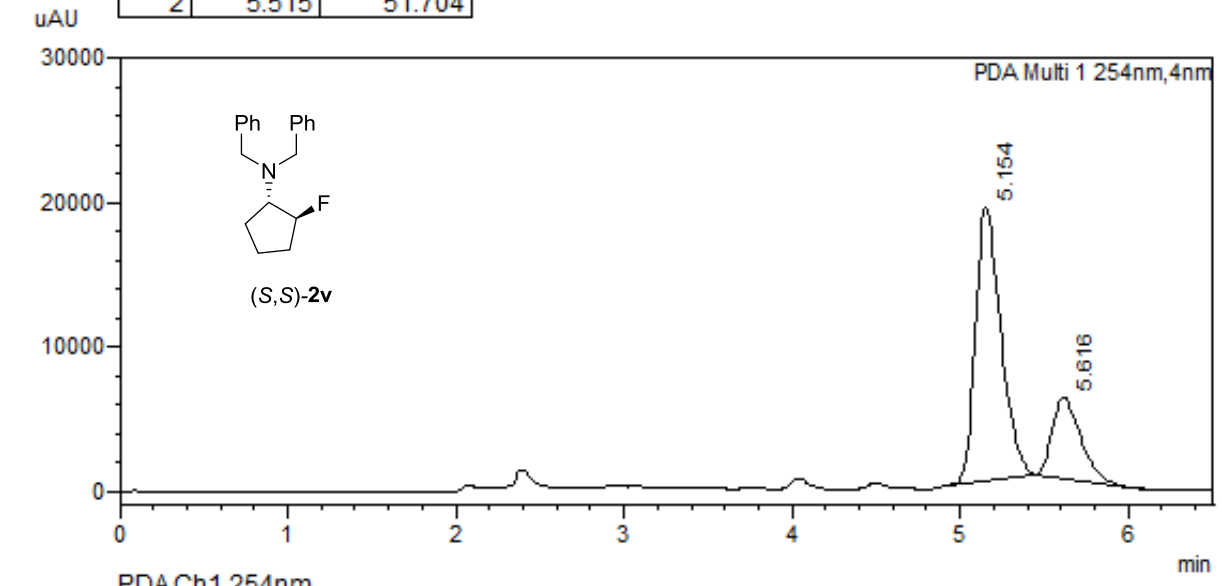
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	6.039	85.292
2	7.007	14.708



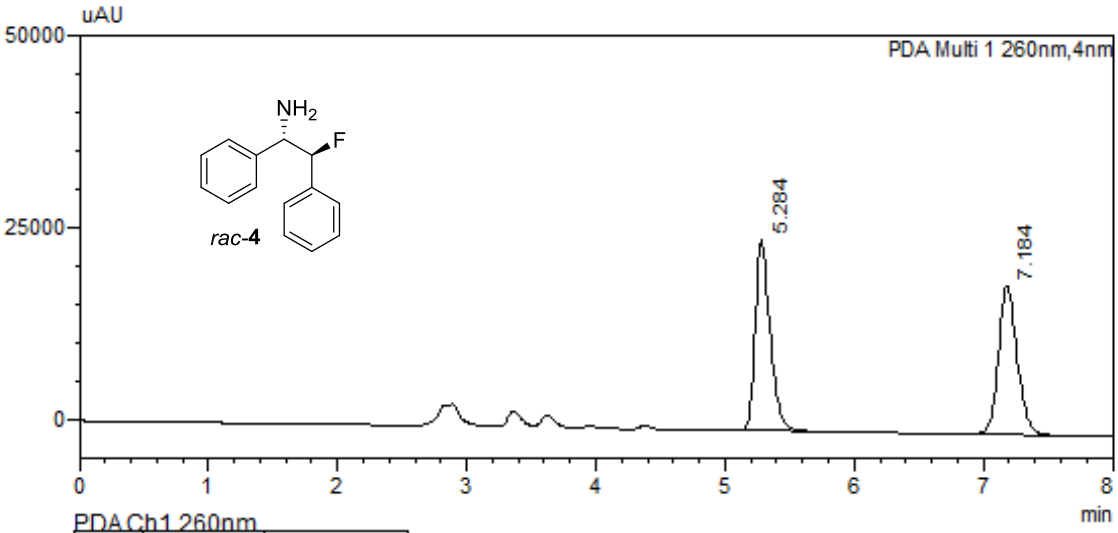
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	5.088	48.296
2	5.515	51.704



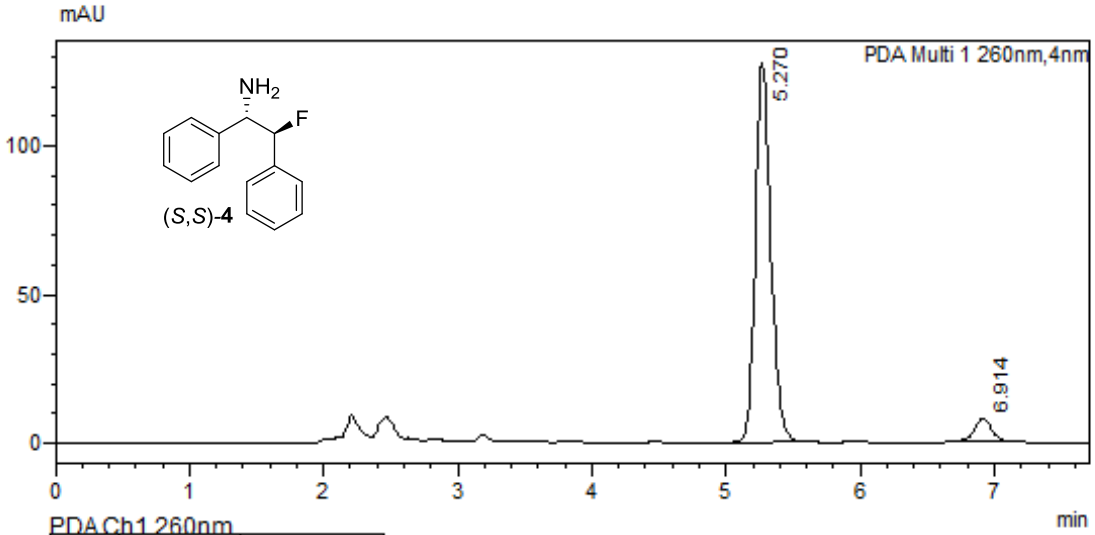
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	5.154	75.322
2	5.616	24.678



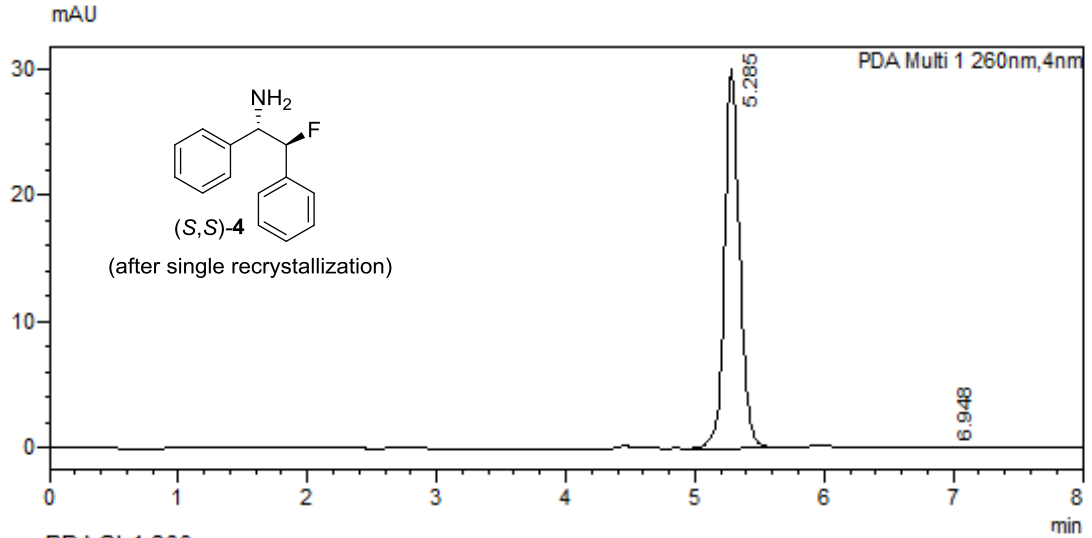
PDA Ch1 260nm

Peak#	Ret. Time	Area%
1	5.284	50.668
2	7.184	49.332



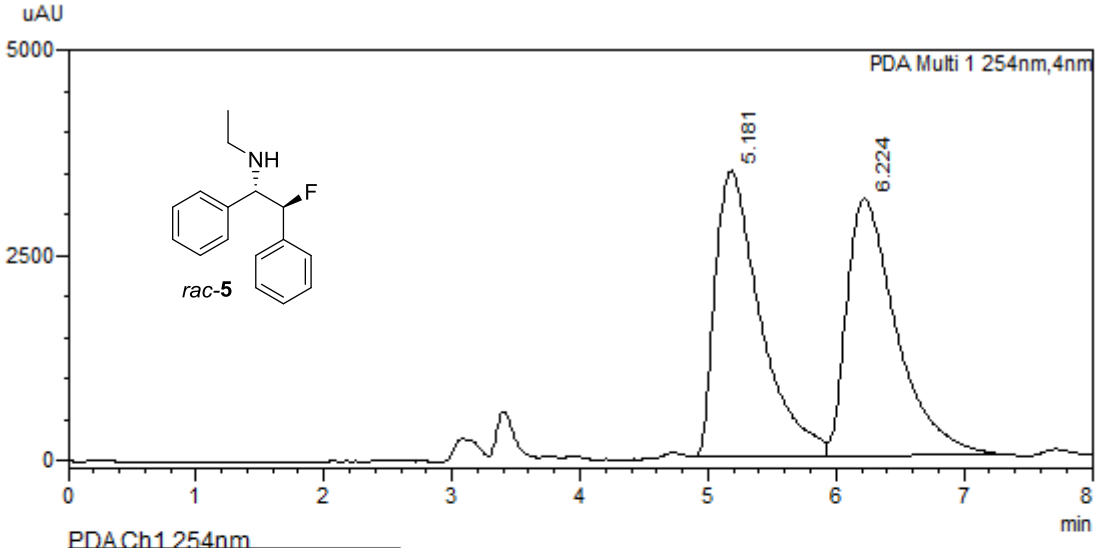
PDA Ch1 260nm

Peak#	Ret. Time	Area%
1	5.270	93.950
2	6.914	6.050



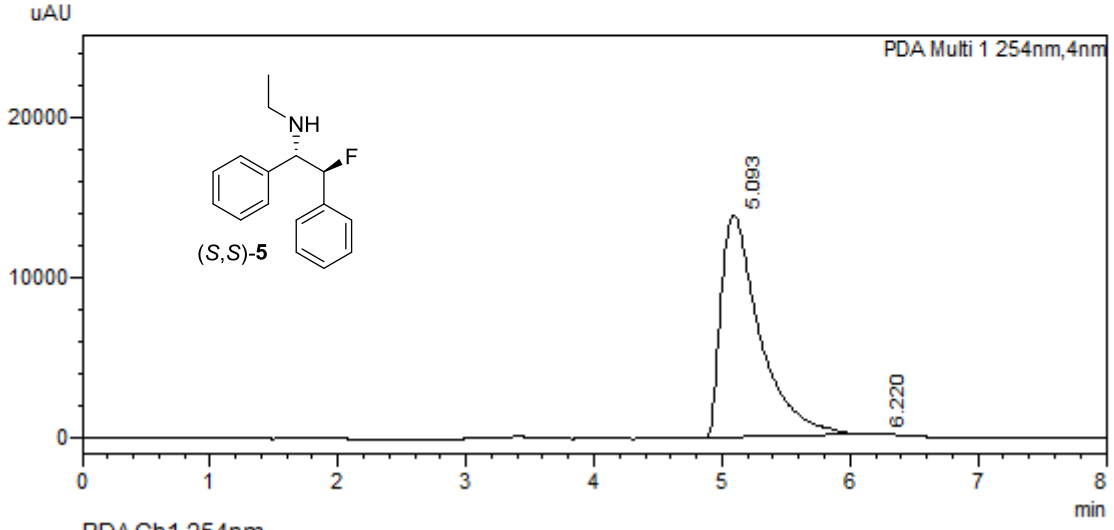
PDA Ch1 260nm

Peak#	Ret. Time	Area%
1	5.285	99.814
2	6.948	0.186



PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	5.181	50.332
2	6.224	49.668



PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	5.093	99.957
2	6.220	0.043

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